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Novel Synthesis of 4*H*-Quinolizine Derivatives Using Sulfonyl Ketene Dithioacetals

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In the synthesis of 4*H*-quinolizine derivatives involving the use of a sulfonyl ketene dithioacetal, we found a novel reaction in which the remaining methylsulfanyl group was replaced with a proton after the ring-closure reaction in the quinolizine skeleton under mild conditions, without the use of any metallic reagent. The reaction of 3,3-bis(methylsulfanyl)-2-phenylsulfonylacrylonitriles (**1a**,**b**) with 2-pyridylacetonitrile (**2a**) in the presence of potassium carbonate as a base in DMSO afforded 4-imino-2-methylsulfanyl-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitriles (**3a**,**b**). The methylsulfanyl group at the 2-position of **3a**,**b** was readily removed under methanol reflux conditions to afford 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitriles (**4a**,**b**) in good yields. Alkyl 3-phenylsulfonyl-4*H*-quinolizine-1-carboxylates (**4c**–**f**) were directly synthesized from sulfonyl ketene dithioacetal (**1a**,**b**) with alkyl 2-pyridylacetates (**2b**,**c**) and involved desulfanylation by simple hydrolysis. In addition, the fluorescent properties of these compounds were investigated.

Introduction

Appropriately functionalized ketene dithioacetals (cyano, methoxycarbonyl, sulfonyl, nitro, acyl) are versatile reagents that have been extensively utilized as building blocks in heterocyclic synthesis.[1] The sulfonyl ketene dithioacetals 3,3-bis(methylsulfanyl)-2-phenylsulfonyl acrylonitriles (**1a**,**b**) are used as two- or three-carbon fragments for the synthesis of heterocyclic compounds having sulfonyl or cyano groups. These ketene dithioacetals are readily prepared by the condensation of phenylsulfonyl acetonitriles with carbon disulfide in the presence of sodium hydroxide, followed by methylation with dimethyl sulfate.[2] It has been reported that 4-imino-2-methylsulfanyl-4*H*-quinolizine derivatives are synthesized from the corresponding 2-pyridylacetonitrile and ketene dithioacetals under basic conditions. Some of these 4*H*-quinolizine derivatives exhibit fluorescence, and as such, these compounds have attracted significant attention owing to their possible applications as photographic materials and dyes.[3] In general, in ketene dithioacetals having two methylsulfanyl groups, one of the methylsulfanyl groups is eliminated in the reaction, and consequently, the corresponding heterocycles contain one methylsulfanyl group. In the synthesis of 4*H*-quinolizine derivatives, we found a novel reaction in which the remaining methylsulfanyl group of the quinolizine skeleton was replaced with a proton after the ring-closure reaction under mild conditions, without the use of any metallic reagent.[4] In this paper, we report the synthesis of 4-imino-4*H*-quinolizine derivatives by a novel synthesis method involving the use of a ketene dithioacetal, and the fluorescent properties of these derivatives is discussed.

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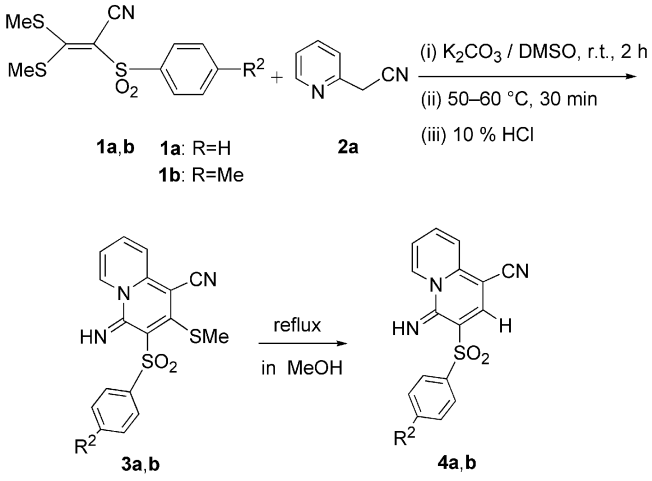
Results and Discussion

The reaction of 3,3-bis(methylsulfanyl)-2-(phenylsulfonyl)acrylonitrile (**1a**)[2] with 2-pyridylacetonitrile (**2a**) in the presence of potassium carbonate (base) in dimethyl sulfoxide (DMSO) at room temperature for 4 h afforded the expected product, 4-imino-2-methylsulfanyl-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitrile (**3a**), in 82% yield (Scheme 1). Compound **3a** was presumed to be formed by the addition of a nucleophile to a ketene dithioacetal, elimination of a methylsufanyl group, and subsequent cyclization; further, **3a** was readily converted into 4-imino-3-phenylsulfoyl-4*H*-quinolizine-1-carbonitrile (**4a**) by the elimination of a methylsulfanyl group in quantitative yield under reflux for 5 h in methanol (Scheme 2). When ammonia or aqueous NaOH solution was substituted for methanol, the desired product was not obtained. Compounds **3b** and **4b** were also prepared from **1b** and **2a**, respectively, in a manner similar to that described for the preparation of **3a** and **4a**. In the methylsulfanyl group in compounds **3a**,**b**, there

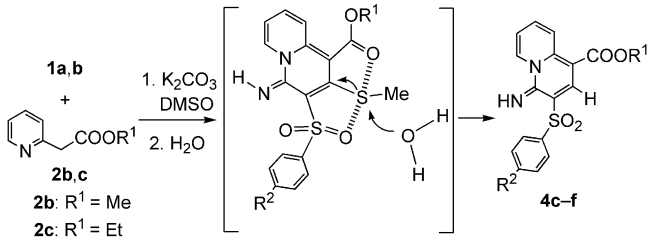
is a strong interaction between the sulfur of the methylsulfanyl group and an oxygen in the sulfonyl group.[5] The methylsulfanyl groups in compounds **3a**,**b** are readily attacked by nucleophilic molecules such as water or methanol, and protonation at the 2-position of compound **3** occurred to produce **4a**,**b** in good yields.



Scheme 1. Synthesis of **3a**,**b** and **4a**,**b**.

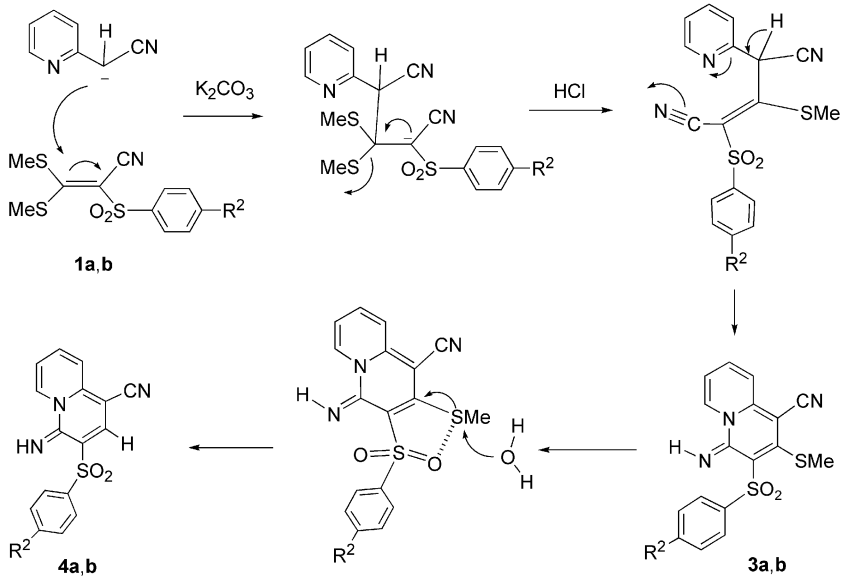
When compound **1a** was allowed to react with methyl 2-pyridylacetate (**2b**) under reaction conditions identical to those in the preparation of **3a**, methyl 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carboxlate (**4c**) was obtained from the basic solution. Compound **4c** exhibited absorption bands in the infrared spectrum at 3336 and 1702 cm^{-1} due to the imino and carbonyl groups, respectively, and no absorption band due to the cyano group. In this case, 4-imino-2-methylsulfonyl-4*H*-quinolizine derivatives such as **3a**,**b** were not obtained in any reaction mixture. In the ^1H NMR spectra, a signal for the proton could be assigned to the C-2 proton at δ = 8.86 ppm rather than to the methylsulfanyl group. We synthesized **4d**–**f** in a similar manner from the corresponding sulfonyl ketene dithioacetals (**1a**,**b**) and 2-pyridylacetates (**2b**,**c**; Table 1).

Table 1. Reaction of 2-pyridylacetates **2b**,**c** with sulfonyl ketene dithioacetals **1a**,**b** in the presence of a base.



Starting material	Product	R^1	R^2	M.p.[°C]	Yield [%]
1a + **2b**	**4c**	Me	H	203–205	47
1b + **2b**	**4d**	Me	Me	216–218	41
1a + **2c**	**4e**	Et	H	152–155	46
1b + **2c**	**4f**	Et	Me	177–178	48

The key step of this reaction was the displacement of the methylsulfanyl group at the 2-position by a proton after the ring-closure reaction in the quinolizine skeleton. A part of the pyridine ring in the quinolizine skeleton becomes electron deficient due to electron-withdrawing groups (e.g., cyano, sulfonyl, and imino groups), and a sulfur atom of the methylsulfanyl group becomes electron deficient due to strong interaction between the sulfur atom of the methylsulfanyl group and an oxygen atom of the sulfonyl group.[6] Calculation of atomic partial charges by the AM1 method of MOPAC supported the hypothesis that the intramolecular interaction between the sulfur atom of the methylsulfanyl group and an oxygen atom of the neighboring sulfonyl group causes the electron deficiency of the sulfur atom.[7] S–O interaction and the electron-deficient effect in the pyridine ring enables nucleophilic attack of water or methanol

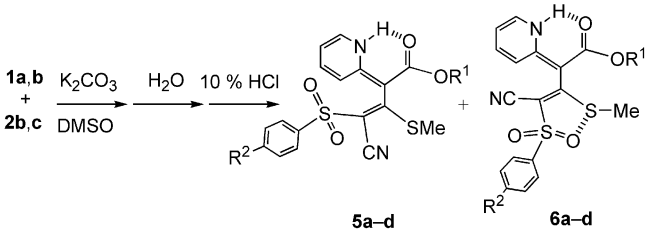


Scheme 2. Presumed reaction pathway for the synthesis of **4a**,**b**.

anions on the sulfur atom in the methylsulfanyl group. The "desulfanylation reaction" is easily initiated if the cyano group at the 1-position on the quinolizine ring is changed into a methyl or an ethyl ester group. In this case, when the reaction mixture was poured into water, the desulfanylated products were directly obtained from the alkali solution. An interaction effect between the oxygen atom of the carbonyl group of an ester and a sulfur atom of the methylsulfanyl group was produced in these reactions, but the reaction yield did not exceed 50%.

After removing pure product **4c**, the filtrate was acidified with 10% hydrogen chloride solution to afford red crystals in 48% yield. The ^{1}H NMR spectrum of this product exhibited signals corresponding to hydrogen bonding between the NH group and an ester carbonyl group at δ = 14.20 ppm and methyl protons of the methylsulfanyl group at δ = 2.14 ppm and methyl protons of the tolyl group at δ = 3.39 and 3.51 ppm (ratio 1:1). The ^{1}H NMR signals revealed that the ring-closure reaction did not take place in this case. After purification, the isolated product was identified (on the basis of IR, UV, and NMR spectroscopy, mass spectrometry, and elemental analysis) as a mixture of **5a** and **6a** (ratio 1:1), which are *E* and *Z* isomers of the methyl (2*Z*,3*E*)-4-cyano-3-methylsulfanyl-4-phenylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate. Compounds **5b**–**d** and **6b**–**d** were also synthesized from **1a**,**b** and **2b**,**c** in a similar manner to **5a** and **6a** (Table 2). The X-ray analysis of **5b** conclusively established that the structure of this compound is that shown in Figure 1. These products were not converted into quinolizine derivatives under basic or acidic reaction conditions in DMSO.

Table 2. Synthesis of **5a**–**d** and **6a**–**d**.



5a–d **6a–d**

Starting material	Product	R^1	R^2	M.p.[°C]	Yield [%] (**5**: **6**)
1a + **2b**	**5a**, **6a**	Me	H	203–205	47 (1:1)
1b + **2b**	**5b**, **6b**	Me	Me	165–168	19 (1:1)
1a + **2c**	**5c**, **6c**	Et	H	143–146	44 (1:1)
1b + **2c**	**5d**, **6d**	Et	Me	132–135	44 (1:1)

Schwarz et al. carried out detailed research on the UV/Vis spectra of quinolizine derivatives.[8] Other authors carried out research on the synthesis of 4*H*-quinolizines in studies of [3.3.3]cyclazine derivatives,[9] but fluorescence was not investigated. An organic light-emitting diode (OLED) that emits light in the solid state was recently investigated. The fused 2-pyrone derivative, namely, the pyrano[3,4-*d*]quinolizine derivative, exhibits red fluorescence in the solid state; however, previously synthesized fluorescent materials were not able to show sufficient fluorescence when

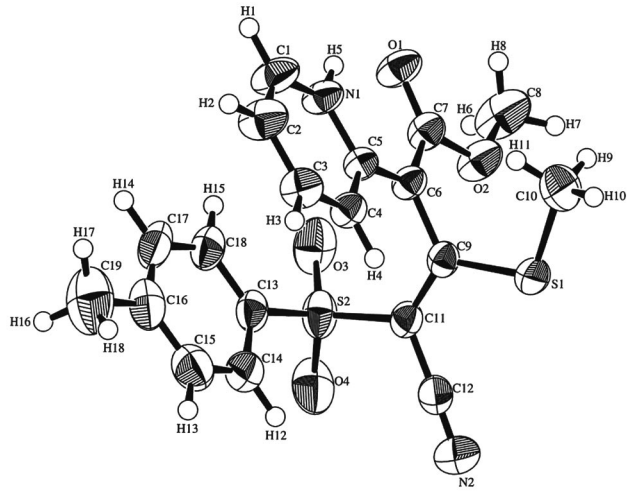


Figure 1. ORTEP drawing of **5b**.

used in devices and elsewhere.[10] There remains an interest in the fluorescence of compounds with a quinolizine skeleton. The fluorescence of synthesized 4-imino-3-phenylsulfonyl-4*H*-quinolizine derivatives in the solid state is of great interest to our research group.

The UV/Vis absorption and fluorescence emission data of **3a**,**b** and **4a**–**f** were analyzed in solution (dichloromethane) and in the solid state, respectively, at room temperature (Table 3). The spectroscopic properties − absorption maxima (λ_{max}), molar absorptivities (ε), fluorescence maxima ($\lambda_{Em\text{-}max}$), and relative fluorescent intensities (RI) − are listed in Table 3. The $\lambda_{Em\text{-}max}$ of **3a**,**b** and **4a**–**f** were in the range 507–522 nm in dichloromethane and 528–564 nm in the solid state. With regard to $\lambda_{Em\text{-}max}$, the obvious substitution effects at the 1- or 2-position of the 4*H*-quinolizine ring were not observed. In contrast, the RIs of **4a**,**b** were slightly stronger than those of **3a**,**b** in dichloromethane and in the solid state, indicating that desulfanylation at the 2-position of the 4*H*-quinolizine influenced the RI. Compounds **4c**–**f** exhibited strong fluorescence in the solid states; in particular, **4c**–**e** emitted stronger fluorescence than Alq_3. This suggests that the ester groups at the 1-position have a significant effect on the fluorescent intensity. In dichloromethane solutions of **4c**–**f**, the obvious substitution effects on the RI were not observed. Compounds **3a**,**b** and **4a**–**f** exhibited significantly larger Stokes' shifts (SS) in dichloromethane, indicating that the S_1 states of these compounds were stabilized by a solvent polarization field. The *F* value, which is the difference between the λ_{Em} values in the solid and solution states, varied from 17 to 44 nm in all compounds. The crystal structures of compounds **4a**,**c** were determined by X-ray crystallographic analysis. Single crystals of **4a**,**c** were obtained by recrystallized from MeOH and acetonitrile. The crystal analysis of **4a**,**c** as shown in Figures 2 and 3 suggests that π–π stacking interactions of the aromatic rings do not exist. In these 4*H*-quinolizine derivatives, the packing structure does not affect the solid-state fluorescence.

Table 3. UV and fluorescence data for 4*H*-quinolizine derivatives in dichloromethane and in the solid state.

	λ_{max} (log e)[a] [nm]	λ_{Ex} [nm] CH_2Cl_2	λ_{Em} [nm] CH_2Cl_2	SS[b]	RI[c]	λ_{Ex} [nm] Solid	λ_{Em} [nm] Solid	SS[d]	RI[e]	ΔF[f]
3a	283 (3.26)	262	520	258	0.25	344	564	220	0.07	44
3b	279 (3.97)	262	522	260	0.36	333	552	219	0.09	30
4a	282 (3.41)	262	520	258	0.31	339	546	207	0.09	26
4b	279 (3.85)	271	513	242	0.42	344	556	212	0.20	43
4c	272 (3.55)	283	507	224	0.40	342	540	198	1.46	33
4d	271 (4.19)	280	511	231	0.47	340	533	193	1.17	22
4e	272 (4.19)	284	511	227	0.47	339	528	189	1.44	17
4f	272 (3.34)	284	519	235	0.25	332	536	204	0.62	17

[a] Measured in ethanol. [b] Stokes' Shift, $\lambda_{Em} - \lambda_{Ex}$ (in solution). [c] Relative intensity of fluorescence in solution, determined by using DCM as the standard compound. [d] Stokes' shift, $\lambda_{Em} - \lambda_{Ex}$ (in the solid state). [e] Relative intensity of fluorescence in the solid state determined by using Alq_3 as the standard compound. [f] $\Delta F = \lambda_{Em}$ (solid) – λ_{Em} (solution).

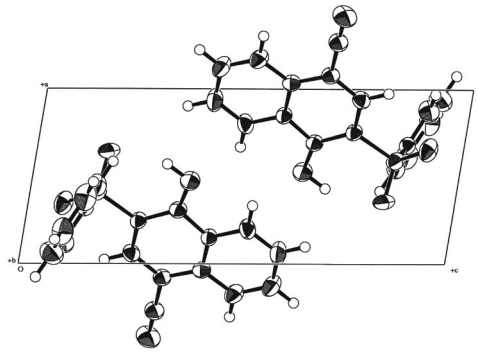


Figure 2. X-ray crystal structure of **4a**.

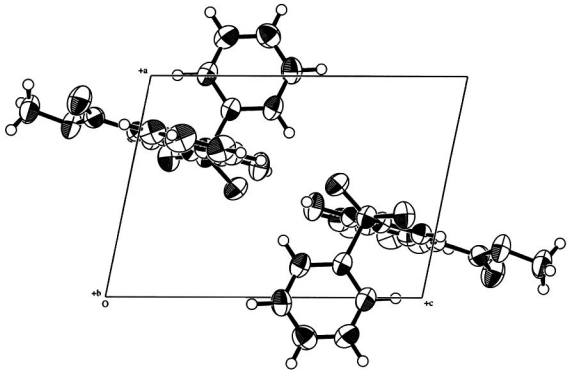


Figure 3. X-ray crystal structure of **4c**.

Conclusions

The reaction of 3,3-bis(methylsulfanyl)-2-phenylsulfonylacrylonitriles (**1a**,**b**) with 2-pyridiylacetonitrile (**2a**) in the presence of potassium carbonate as a base in DMSO afforded 4-imino-2-methylsulfanyl-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitriles (**3a**,**b**). A methylsulfanyl group at the 2-position on the 4*H*-quinolizine-1-carbonitriles was readily removed under methanol reflux conditions to afford 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitriles (**4a**,**b**) in good yields. Alkyl 3-phenylsulfonyl-4*H*-quinolizine-1-carboxylates (**4c**–**f**) were directly synthesized from sulfonyl ketene dithioacetal (**1a**,**b**) with alkyl 2-pyridylacetates (**2b**,**c**), under mild conditions (methanolysis or hydrolysis), without the use of any metallic reagents. The synthesized 4-imino-3-phenylsulfonyl-4*H*-quinolizine derivatives exhibited strong fluorescence in the solid state, suggesting that it is possible to obtain a design for enhancing fluorescence intensity without changing their fluorescence wavelength.

Experimental Section

General Procedures: Identifications of compounds and measurements of properties were carried out by general procedures using the following equipment. Melting points were determined in a capillary tube and were uncorrected. IR spectra were recorded in potassium bromide pellets on a JASCO 810 or Shimazu IR-460 spectrometer. UV absorption spectra were determined in 95% ethanol on a Hitachi 323 spectrometer. Fluorescence spectra were determined on Shimazu RF-5300pc. NMR spectra were obtained on Gemini 300NMR (300 MHz) and Varian Unityplus 500NMR (500 MHz) spectrometers using tetramethylsilane as the internal standard. Mass spectra (MS) were recorded on JEOL-DX-303 mass spectrometers. Microanalyses were performed by K. Yoshida on a Perkin–Elmer at Nagasaki University. All compounds were reagent grade and used without further purification unless otherwise specified.

Method of Measurement of Fluorescence

In the Solid State: A powder sample of the subject compound was heaped in a tray. After covering the sample with a quartz plate, this part was fixed in a fluorescence spectrometer. After fixing the fluorescent wavelength, the excitation spectrum was determined by scanning with the fluorescent wavelength. Similarly, the fluorescent spectrum was obtained after scanning with the excitation wavelength. After obtaining these results, the excitation wavelength was decided and the fluorescence spectrum was measured. The fluorescent relative intensity was determined by using Alq_3 as the standard.[11] The fluorescence of Alq_3 and test compounds was measured at an excitation wavelength of 345 nm.

In Solution: The fluorescence spectra in solution were obtained in a manner similar to that described for the measurement in the solid state. The relative intensity of fluorescence in solution was determined by using DCM and [4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran] as a standard compound.[12] Fluorescence spectra of a standard sample and all subject compounds were measured in CH_2Cl_2 solution (1.0×10^{-5} M) at 480 nm excitation.

4-Imino-2-methylsulfanyl-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitrile (3a): A mixture of **1a** (2.53 g, 10.0 mmol), 2-pyridylacetonitrile (**2a**; 1.77 g, 10.0 mmol), and potassium carbonate (3.44 g, 20.0 mmol) in DMSO (30 mL) was stirred for 2 h at room temperature. This mixture was stirred and heated for 30 min at 50–60 °C. The reaction mixture was poured into ice water (200 mL) and acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from MeOH/toluene (1:5) to give yellow crystals (2.91 g, 8.20 mmol, 82% yield). M.p. 203–204 °C. IR (KBr): $\tilde{\nu}$ = 3329 (NH), 2209 (CN), 1610, 1140, 768 cm^{-1}. UV (EtOH): λ ($\log\varepsilon$) = 399.0 (2.66), 309.0 (2.29), 282.5 (3.26) nm. Fluorescence (solid): λ_{Ex} = 344 nm; λ_{Em} = 564 nm; RI = 0.07. Fluorescence (CH_2Cl_2): λ_{Ex} = 262 nm; λ_{Em} = 520 nm; RI = 0.25. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, SMe), 7.20–7.26 (m, 1 H, 7-H), 7.44–7.56 (m, 3 H, phenyl-H), 7.60 (m, 1 H, 8-H), 7.82 (m, 2 H, phenyl-H), 7.99 (d, *J* = 7.8 Hz, 1 H, 6-H), 9.77 (d, *J* = 7.8 Hz, 1 H, 9-H), 10.11 (s, 1 H, N-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.63, 85.74, 115.74, 116.58, 117.36, 122.50, 127.06, 128.66, 131.99, 133.09, 138.94, 143.13, 147.53, 150.53, 151.67 ppm. MS: *m*/*z* (%) = 356 (6) [M + 1]$^+$, 355 (28) [M]$^+$, 309 (29), 229 (27), 290 (100), 244 (81), 214 (38), 167 (95), 78 (26). $C_{17}H_{13}N_3O_2S_2$ (355.434): calcd. C 57.45, H 3.69, N 11.82; found C 57.44, H 3.68, N 11.51.

4-Imino-2-methylsulfanyl-3-tolylsulfonyl-4*H*-quinolizine-1-carbonitrile (3b): This compound (1.31 g, 4.1 mmol) was prepared in 81% yield from **1b** (1.44 g, 5.0 mmol) and **2a** (0.62 g, 5.0 mmol) in a manner similar to that described for the synthesis of **3a**. An analytical sample was recrystallized from DMF to give orange needles. M.p. 178–182 °C. IR (KBr): $\tilde{\nu}$ = 3326 (NH), 2208 (CN), 1607, 1554, 1505 1452 cm^{-1}. UV (EtOH): λ ($\log\varepsilon$) = 384.5 (3.84), 279.0 (3.97) nm. Fluorescence (solid): λ_{Ex} = 333 nm; λ_{Em} = 552 nm; RI = 0.09. Fluorescence (CH_2Cl_2): λ_{Ex} = 262 nm; λ_{Em} = 522 nm; RI = 0.36. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, SMe), 2.42 (s, 3 H, Me), 7.17–7.23 (m, 1 H, 7-H), 7.30 (m, 2 H, phenyl-H), 7.81 (m, 1 H, 8-H), 7.82–7.88 (m, 2 H, phenyl-H), 7.88 (d, *J* = 8.3 Hz, 1 H, 6-H), 9.64 (d, *J* = 7.4 Hz, 1 H, 9-H), 10.11 (s, 1 H, N-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.75, 21.60, 85.64, 116.11, 116.63, 117.27, 122.44, 127.11, 129.23, 131.92, 138.84, 140.10, 144.07, 147.43, 150.53, 151.46 ppm. MS: *m*/*z* (%) = 370 (4) [M + 1]$^+$, 369 (69) [M]$^+$, 368 (15), 305 (28), 304 (100), 214 (26), 167 (51), 127 (33). $C_{18}H_{15}N_3O_2S_2$ (369.0606): calcd. C 58.52, H 4.09, N 11.37; found C 58.51, H 4.05, N 11.45.

4-Imino-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitrile (4a): A solution of **3a** (0.36 g, 1.0 mmol) in MeOH (100 mL) was heated at reflux for 5 h. After removal of the solvent, the residue was washed with MeOH (10 mL) to give orange crystals (0.31 g, 100% yield). An analytical sample was recrystallized from MeOH/toluene (5:1) to give orange leaflets. M.p. 208–209 °C. IR (KBr): $\tilde{\nu}$ = 3337 (C=NH), 2210 (CN), 1608, 1500, 1298, 1099, 583 cm^{-1}. UV (EtOH): λ ($\log\varepsilon$) = 385.5 (3.35), 315.5 (3.09), 282.0 (3.41) nm. Fluorescence (solid): λ_{Ex} = 339 nm; λ_{Em} = 546 nm; RI = 0.09. Fluorescence (CH_2Cl_2): λ_{Ex} = 262 nm; λ_{Em} = 520 nm; RI = 0.31. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (m, 1 H, 7-H), 7.54–7.62 (m, 2 H, phenyl-H), 7.85 (m, 1 H, 8-H), 7.87–7.95 (m, 2 H, phenyl-H), 7.93 (d, *J* = 7.0 Hz, 1 H, 6-H), 8.27 (s, 1 H, 2-H), 8.81 (br. s, 1 H, N-H), 9.62 (d, *J* = 7.7 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 80.17, 114.71, 116.73, 117.58, 123.18, 127.02, 127.14, 129.39, 131.35, 133.67, 139.16, 140.17, 148.16, 150.41 ppm. MS: *m*/*z* (%) = 310 (5) [M + 1]$^+$, 309 (23) [M]$^+$, 245 (20), 244 (100), 168 (37), 167 (42), 141 (16), 114 (13). $C_{16}H_{11}N_3O_2S$ (309.3436): calcd. C 62.12, H 3.58, N 13.58; found C 62.13, H 3.55, N 13.56.

4-Imino-3-tolylsulfonyl-4*H*-quinolizine-1-carbonitrile (4b): This compound (0.32 g, 1.0 mmol) was prepared in 100% yield from **3b** (0.37 g, 1.0 mmol) in a manner similar to that described for the synthesis of **4a**. An analytical sample was recrystallized from DMF to give orange needles. M.p. 180–184 °C. IR (KBr): $\tilde{\nu}$ = 3347 (C=NH), 2208 (CN), 1614, 1490, 1292, 1095, 570 cm^{-1}. UV (EtOH): λ ($\log\varepsilon$) = 451.5 (3.67), 383.0 (3.65), 328.5 (3.41), 278.5 (3.85) nm. Fluorescence (solid): λ_{Ex} = 344 nm; λ_{Em} = 556 nm; RI = 0.20. Fluorescence (CH_2Cl_2): λ_{Ex} = 271 nm; λ_{Em} = 513 nm; RI = 0.42. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, Me), 7.21 (m, 1 H, 7-H), 7.32 (m, 2 H, phenyl-H), 7.81 (m, 1 H, 8-H), 7.83 (m, 2 H, phenyl-H), 7.86 (d, *J* = 6.6 Hz, 1 H, 6-H), 8.26 (s, 1 H, 2-H), 8.78 (br. s, 1 H, NH), 9.61 (d, *J* = 7.8 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.57, 80.04, 115.18, 116.62, 117.28, 122.43, 127.10, 127.22, 129.22, 131.27, 138.82, 144.07, 147.41, 150.41, 151.45 ppm. MS: *m*/*z* (%) = 324 (5) [M + 1]$^+$, 323 (23) [M]$^+$, 259 (21), 258 (100), 168 (25), 167 (33), 114 (13). $C_{17}H_{13}N_3O_2S$ (323.37): calcd. C 63.14, H 4.05, N 12.99; found C 62.98, H 3.83, N 13.00.

Reaction of 1a with 2b: A mixture of **1a** (2.53 g, 10.0 mmol), methyl 2-pyridylacetate (**2b**; 1.77 g, 10.0 mmol), and potassium carbonate (3.44 g, 20.0 mmol) in DMSO (30 mL) was stirred for 2 h at room temperature. This mixture was stirred and heated for 30 min at 50–60 °C. The reaction mixture was poured into ice water (200 mL). The precipitate that appeared was collected by filtration, washed with water, and recrystallized from MeOH/toluene (5:1) to give yellow crystals of **4c** (1.61 g, 4.7 mmol, 47% yield). This filtrate was acidified with 10% hydrochloric chloride solution to give a red brown caramel oil, which was crystallized by treatment with MeOH. The crystallized products were collected by filtration to give **5a** and **6a** (1.71 g, 4.4 mmol, 44% yield) as red crystals.

Methyl 4-Imino-3-phenylsulfonyl-4*H*-quinolizine-1-carboxylate (4c): M.p. 203–205 °C. IR (KBr): $\tilde{\nu}$ = 3336 (C=NH), 1702 (CO), 1617, 1492, 1295, 1140, 579 cm^{-1}. UV (EtOH): λ ($\log\varepsilon$) = 437.0 (3.39), 364.0 (3.44), 272.0 (3.55) nm. Fluorescence (solid): λ_{Ex} = 342 nm; λ_{Em} = 540 nm; RI = 1.46. Fluorescence (CH_2Cl_2): λ_{Ex} = 283 nm; λ_{Em} = 507 nm; RI = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 3 H, OMe), 7.19 (m, 1 H, 7-H), 7.48–7.60 (m, 3 H, phenyl-H), 7.80 (m, 1 H, 8-H), 7.98 (m, 2 H, phenyl-H), 8.64 (br. s, 1 H, NH), 8.86 (s, 1 H, 2-H), 9.31 (d, *J* = 10.0 Hz, 1 H, 6-H), 9.68 (d, *J* = 7.8 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.83, 97.24, 112.69, 117.10, 123.98, 127.09, 129.24, 131.05, 133.30, 137.68, 139.50, 140.78, 147.90, 151.62, 165.12 ppm. MS: *m*/*z* (%) = 343 (10) [M + 1]$^+$, 342 (50) [M]$^+$, 277 (100), 201 (22), 169 (25), 142 (11), 141(12). $C_{17}H_{14}N_2O_4S$ (342.37): calcd. C 59.64, H 4.12, N 8.18; found C 59.77: H 4.04, N 8.22.

Methyl (2*Z*,3*E*)-4-Cyano-3-methylsulfanyl-4-phenylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (5a and 6a): M.p. 125–128 °C. IR (KBr): $\tilde{\nu}$ = 2202 (CN), 1637 (CO), 1591, 1509 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, SMe), 3.39 (s, 3H/2, OMe_2), 3.51 (s. 3H/2, OMe_2), 6.42–6.61 (m, 2 H, pyridyl-H), 7.15–7.78 (m, 6 H, phenyl-H, pyridyl-H), 8.09 (m, 1 H, pyridyl-H), 14.20 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.18, 16.32, 50.75, 51.06, 81.34, 110.78, 110.97, 111.50, 114.07, 114.71, 117.72, 118.60, 127.64, 127.95, 128.76, 128.95, 129.22, 133.15, 133.41, 133.93, 138.16, 139.16, 139.85, 140.78, 150.79, 150.95, 166.48, 166.89, 173.75, 175.65 ppm. HRMS: calcd. for $C_{18}H_{16}N_2O_4S_2$ 388.0551; found 388.0559. $C_{18}H_{16}N_2O_4S_2$ (388.4627): calcd. C 55.65, H 4.15, N 7.21; found C 55.70, H 4.04, N 6.96.

Reaction of 1b with 2b: Compound **4d** (0.83 g, 2.1 mmol) was synthesized in 41% yield from **2b** (1.51 g, 10.0 mmol) and **1b** (1.98 g, 5.0 mmol) in a manner similar to that described for the preparation of **4c**. An analytical sample was recrystallized from MeOH to give yellow needles. Compounds **5b** and **6b** (0.39 g, 1.0 mmol) were syn-

thesized in 19% yield in a manner similar to that described for the preparation of **5a** and **6a**. An analytical sample was recrystallized from MeOH to give red crystals.

Methyl 4-Imino-3-tolylsulfonyl-4*H*-quinolizine-1-carboxylate (4d): M.p. 216–218 °C. IR (KBr): $\tilde{\nu}$ = 3343 (NH), 1691 (CO), 1618, 1492, 1141, 781 cm^{-1}. UV (EtOH): λ (logε) = 436.0 (3.99), 365.0 (4.03), 270.5 (4.19) nm. Fluorescence (solid): λ_{Ex} = 340 nm; λ_{Em} = 533 nm, RI = 1.17. Fluorescence (CH_2Cl_2): λ_{Ex} = 280 nm; λ_{Em} = 511 nm; RI = 0.47. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, Me), 3.89 (s, 3 H, OMe), 7.18 (m, 1 H, 7-H), 7.30 (d, J = 8.4 Hz, 2 H, phenyl-H), 7.80 (m, 1 H, 8-H), 7.84 (d, J = 8.4 Hz, 2 H, phenyl-H), 8.60 (br. s, 1 H, NH), 8.85 (s, 1 H, 2-H), 9.30 (d, J = 9.0 Hz, 1 H, 6-H), 9.67 (d, J = 7.8 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.55, 51.79, 97.15, 113.19, 116.98, 123.94, 127.17, 129.85, 130.94, 137.51, 137.74, 139.21, 144.29, 147.81, 151.62, 165.15 ppm. MS: *m*/*z* (%) = 357 (11) $[M + 1]^+$, 356 (51) $[M]^+$, 291 (100), 201 (32), 169 (46). $C_{18}H_{16}N_2O_4S_2$ (388.46): calcd. C 60.66, H 4.53, N 7.86; found C 60.75, H 4.35, N 7.88.

Methyl (2*Z*,3*E*)-4-Cyano-3-methylsulfanyl-4-tolylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (5b and 6b): M.p. 165–168 °C. IR (KBr): $\tilde{\nu}$ = 2201 (CN), 1618, 1590, 1283 1151, 584 cm^{-1}. UV (EtOH): λ (logε) = 393.0 (3.59), 302.5 (4.09) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, Me), 2.38 (s, 3H/2, SMe), 2.48 (s, 3H/2, SMe), 3.41 (s 3H/2, OMe), 3.56 (s, 3H/2, OMe), 6.40–6.60 (m, 1 H, pyridyl-H), 7.19 (m, 1 H, pyridyl-H), 7.38 (m, 2 H, phenyl-H), 7.48 (m, 2 H, phenyl-H), 7.61 (d, J = 7.8 Hz, 1 H, pyridyl-H), 7.97 (d, J = 8.1 Hz, 1 H, pyridyl-H), 14.00 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.14, 16.27, 21.54, 21.73, 50.72, 51.10, 81.40, 110.57, 110.85, 111.94, 114.12, 114.73, 117.80, 118.77, 127.77, 128.10, 129.35, 129.58, 133.36, 133.93, 136.95, 137.82, 137.97, 139.06, 144.22, 145.01, 150.86, 151.00, 166.59, 166.97, 173.04, 174.86 ppm. MS: *m*/*z* (%) = 403 (5) $[M + 1]^+$, 402 (21) $[M]^+$, 247 (100), 215 (32), 200 (83), 168 (25), 91 (26). $C_{19}H_{18}N_2O_4S_2$ (402.4893): calcd. C 56.70, H 4.51, N 6.96; found C 56.71, H 4.48, N 6.79.

Reaction of 1a with 2c: Compound **4e** (0.33 g, 0.9 mmol) was synthesized in 46% yield from **2c** (0.33 g, 2.0 mmol) and **1a** (0.86 g, 3.0 mmol) in a manner similar to that described for the preparation of **4c**. An analytical sample was recrystallized from EtOH to give yellow needles. Compounds **5c** and **6c** (0.35 g, 0.9 mmol) were synthesized in 44% yield in a manner similar to that described for the preparation of **5a** and **6a**. An analytical sample was recrystallized from MeOH to give red crystals.

Ethyl 4-Imino-3-phenylsulfonyl-4*H*-quinolizine-1-carboxylate (4e): M.p. 152–155 °C. IR (KBr): $\tilde{\nu}$ = 3356 (NH), 1694 (CO), 1639, 1618, 1489, 578 cm^{-1}. UV (EtOH): λ (logε) = 437.0 (4.03), 364.5 (4.06), 272.0 (4.19) nm. Fluorescence (solid): λ_{Ex} = 339 nm; λ_{Em} = 528 nm; RI = 1.44. Fluorescence (CH_2Cl_2): λ_{Ex} = 284 nm; λ_{Em} = 511 nm; RI = 0.47. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.1 Hz, 3 H, O-CH_2-CH_3), 4.36 (q, J = 7.1 Hz, 2 H, O-CH_2-), 7.17 (m, 1 H, 7-H), 7.45–7.62 (m, 3 H, phenyl-H), 7.79 (m, 1 H, 8-H), 7.96 (m, 2 H, phenyl-H), 8.61 (br. s, 1 H, NH), 8.86 (s, 1 H, 2-H), 9.32 (d, J = 9.0 Hz, 1 H, 6-H), 9.67 (d, J = 6.9 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.47, 60.76, 97.60, 112.60, 117.04, 124.03, 127.08, 129.21, 130.99, 133.27, 137.54, 139.43, 140.75, 147.88, 151.64, 164.70 ppm. MS: *m*/*z* (%) = 357 (14) $[M + 1]^+$, 356 (65) $[M]^+$, 292 (20), 291 (95), 133 (100), 105 (45). $C_{18}H_{16}N_2O_4S$ (356.3967): calcd. C 60.66, H 4.53, N 7.86; found C 60.54, H 4.38, N 7.89.

Ethyl (2*Z*,3*E*)-4-Cyano-3-methylsulfanyl-4-phenylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (5c and 6c): M.p. 143–146 °C. IR (KBr): $\tilde{\nu}$ = 2204 (CN), 1638 (CO), 1582, 1277 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90–1.17 (m, J = 7.1 Hz, 3 H, O-CH_2-CH_3), 2.15 (s, 3 H, SMe), 3.60–4.16 (m, 2 H, O-CH_2-), 6.40–6.70 (m, 1 H, pyridyl-H), 7.20–7.80 (m, 7 H, phenyl-H, pyridyl-H), 8.12 (d, J = 10.2 Hz, 1 H, pyridyl-H), 14.02 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.24, 15.14, 16.28, 59.66, 81.43, 110.62, 110.78, 111.77, 114.15, 114.62, 117.81, 118.76, 127.69, 127.97, 128.74, 129.01, 133.16, 133.31, 133.92, 137.97, 139.94, 140.85, 150.92, 166.24, 145.00, 166.51, 173.84, 175.86 ppm. MS: *m*/*z* (%) = 403 (5) $[M + 1]^+$, 402 (19) $[M]^+$, 261 (100), 260 (55), 215 (63), 77 (34). $C_{19}H_{18}N_2O_4S_2$ (402.4893): calcd. C 56.70, H 4.51, N 6.96; found C 56.69, H 4.54, N 6.86.

Reaction of 1b with 2c: Compound **4f** (0.89 g, 2.4 mmol) was synthesized in 48% yield from **2c** (1.65 g, 10.0 mmol) and **1b** (1.44 g, 5.0 mmol) in a manner similar to that described for the preparation of **4c**. An analytical sample was recrystallized from EtOH to give yellow needles. Compounds **5d** and **6d** (0.92 g, 2.2 mmol) was synthesized in 44% yield in manner similar to that described for the preparation of **5a** and **6a**. An analytical sample was recrystallized from MeOH to give red crystals.

Ethyl 4-Imino-3-tolylsulfonyl-4*H*-quinolizine-1-carboxylate (4f): M.p. 177–178 °C. IR (KBr): $\tilde{\nu}$ = 3302 (NH), 1761 (CO), 1704 (CO), 1615, 1513 cm^{-1}. UV (EtOH): λ (logε) = 435.5 (3.12), 364.5 (3.17), 271.5 (3.34) nm. Fluorescence (solid): λ_{Ex} = 332 nm; λ_{Em} = 536 nm, RI = 0.62. Fluorescence (CH_2Cl_2): λ_{Ex} = 284 nm; λ_{Em} = 519 nm; RI = 0.25. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, J = 7.1 Hz, 3 H, O-CH_2-CH_3), 2.39 (s, 3 H, Me), 4.36 (q, J = 7.1 Hz, 2 H, O-CH_2-), 7.17 (m, 1 H, 7-H), 7.30 (d, J = 7.9 Hz, 2 H, phenyl-H), 7.77 (m, 1 H, 8-H), 7.84 (d, J = 7.9 Hz, 2 H, phenyl-H), 8.56 (br. s, 1 H, NH), 8.84 (s, 1 H, 2-H), 9.31 (d, J = 9.0 Hz, 1 H, 6-H), 9.66 (d, J = 6.6 Hz, 1 H, 9-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.48, 21.56, 60.73, 97.52, 113.09, 116.91, 124.00, 127.19, 129.85, 130.94, 137.38, 137.73, 139.16, 144.28, 147.82, 151.66, 164.76 ppm. MS: *m*/*z* (%) = 371 (9) $[M + 1]^+$, 370 (40) $[M]^+$, 306 (23), 305 (100), 277 (28), 225 (25). $C_{19}H_{18}N_2O_4S$ (370.4233): calcd. C 61.61, H 4.90, N 7.56; found C 61.63, H 4.93, N 7.42.

Ethyl (2*Z*,3*E*)-4-Cyano-3-methylsulfanyl-4-tolylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (5d and 6d): M.p. 132–135 °C. IR (KBr): $\tilde{\nu}$ = 2207 (CN), 1650 (CO), 1615, 1585, 1267, 1150, 588 cm^{-1}. UV (EtOH): λ (logε) = 392.0 (3.69), 304.0 (4.19) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.1 Hz, 3H/2, O-CH_2-CH_3), 1.10 (t, J = 7.1 Hz, 3H/2, O-CH_2-CH_3), 2.15 (s, 3 H, Me), 2.39 (s, 3 H, Me), 3.70 (m, 2H/2, O-CH_2-), 4.0 (m, 2H/2, O-CH_2-), 6.43–6.65 (m, 1 H, pyridyl-H), 7.20 (m, 1 H, pyridyl-H), 7.37 (m, 2 H, phenyl-H), 7.46 (m, 2 H, phenyl-H), 7.62 (m, 1 H, pyridyl-H), 7.97 (m, 1 H, pyridyl-H), 14.00 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.91, 14.12, 15.04, 16.20, 21.45, 21.60, 59.54, 61.83, 81.32, 110.46, 110.75, 111.94, 114.12, 114.67, 117.70, 118.62, 126.82, 127.67, 127.98, 129.29, 129.56, 133.40, 133.95, 136.42, 136.94, 137.84, 138.96, 144.18, 145.00, 150.85, 166.22, 166.45, 173.29, 174.31 ppm. MS: *m*/*z* (%) = 416 (3) $[M]^+$, 260 (100), 215 (72), 214 (38), 188 (20), 139 (30), 91 (27). $C_{20}H_{20}N_2O_4S_2$ (416.5159): calcd. C 57.67, H 4.84, N 6.73; found C 57.34, H 4.82, N 6.59.

X-ray Crystallographic Studies: The reflection data were collected at 23 ± 1 °C with a Rigaku Mercury area detector with graphite monochromated Mo-K_α radiation. All calculations were performed by using the CrystalStructure crystallographic software package.[13] CCDC-736921 (for **4a**), -736922 (for **4c**), and -725724 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.au.uk/data_request/cif.

Crystal Data for 4a: This crystal was obtained by recrystallization from MeOH/acetonitrile (1:1) to give orange prisms of formula $C_{16}H_{11}N_3O_2S$ and having approximate dimensions of $0.50 \times 0.40 \times 0.15$ mm. This crystal was mounted on a glass fiber. Crystal data formula weight: 309.34; crystal color, habit: orange, prisms; crystal system: triclinic; lattice type: primitive; lattice parameters: a = 5.9847(10) Å, b = 8.3812(14) Å, c = 14.2469(15) Å, β = 80.363(15)°, V = 703.50(18) Å^3; space group: $P\bar{1}$ (#2); Z value: 2; $D_{calcd.}$: 1.460 g cm^{-3}; $F(000)$ = 320.00; μ(Mo-K_α) = 2.406 cm^{-1}.

Crystal Data for 4c: This crystal was obtained by recrystallization from MeOH/acetonitrile (1:1) to give yellow prisms of formula $C_{17}H_{14}N_2O_4S$ and having approximate dimensions of $0.40 \times 0.30 \times 0.20$ mm. This crystal was mounted on a glass fiber. Crystal data formula weight: 342.37; crystal color, habit: yellow, prisms; crystal system: triclinic; lattice type: primitive; lattice parameters: a = 7.4827(10) Å, b = 10.6167(10) Å, c = 11.1355(10) Å, β = 74.953(8)°, V = 781.977(13) Å^3; space group: $P\bar{1}$ (#2); Z value: 2; $D_{calcd.}$: 1.454 g cm^{-3}; $F(000)$ = 356.00; μ(Mo-K_α) = 2.314 cm^{-1}.

Crystal Data 5b: This crystal was obtained by recrystallization from MeOH to give orange prisms of formula $C_{19}H_{18}N_2O_4S_2$ and having approximate dimensions of $0.40 \times 0.20 \times 0.20$ mm. This crystal was mounted on a glass fiber. Crystal data formula weight: 402.48; crystal color, habit: orange, prisms; crystal system: monoclinic; lattice type: primitive; lattice parameter: a = 10.3450(5) Å, b = 11.8475(5) Å, c = 16.1782(10) Å, β = 101.7174(10)°, V = 1941.52(17) Å^3; space group: $P2_1/n$ (#14); Z value: 4; $D_{calcd.}$: 1.377 g cm^{-3}; $F(000)$ = 840.00; μ(Mo-K_α) = 3.012 cm^{-1}.

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