DOI: 10.1002/ejoc.200((will be filled in by the editorial staff))

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

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Keywords: 4*H*-quinolizine derivatives / sulfonyl ketene dithioacetal / desulfurization / fluorescence / organic light-emitting diode

In the synthesis of fluorescent 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. The reaction of 3,3-bis(methylsulfanyl)-2-phenylsulfonyl-acrylonitriles (**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**) without desulfurization using metallic reagents. In addition, fluorescent properties of these compounds were investigated.

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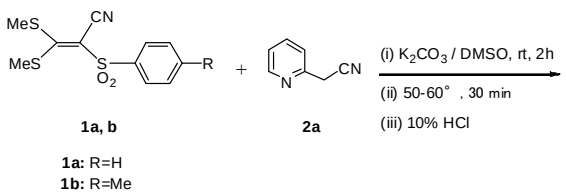
Introduction

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.[3] In general, one methylsulfanyl group in ketene dithioacetals having two methylsulfanyl groups is eliminated in the reaction, and consequently, the corresponding heterocycles in which one more methylsulfanyl group remains are obtained. 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 in mild conditions. 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.

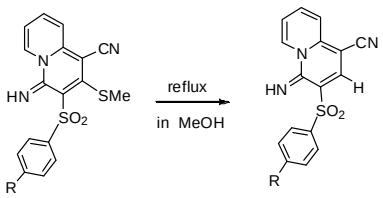
Results and Discussion

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 to 4-imino-3-phenylsulfonyl-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, 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.[4] 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.



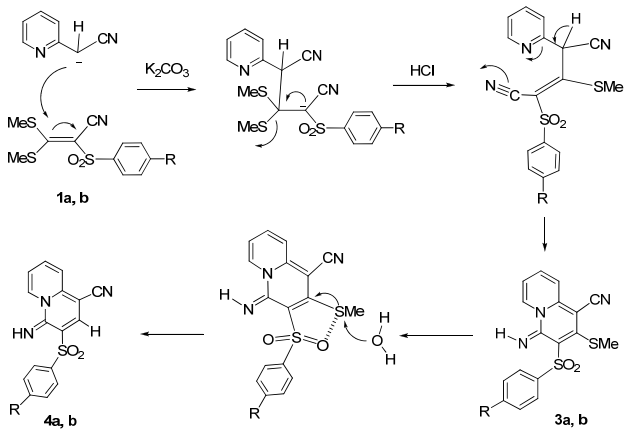
1a, b **2a**

1a: R=H
1b: R=Me



3a, b **4a, b**

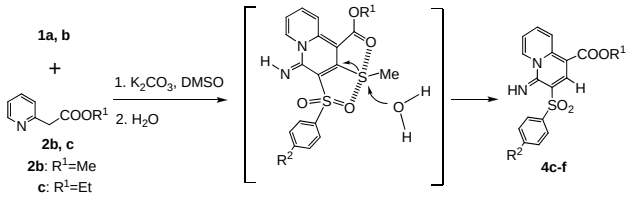
Scheme 1. Synthesis of **3a, b** and **4a, b**



Scheme 2. Presumed reaction pathway for synthesis of **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 cm^{-1} 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 ^{1}H NMR spectra, a signal for the proton could be assigned to the C-2 proton at 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.



4	R^1	R^2	mp	Yield %
c	Me	H	203-205°	47
d	Me	Me	216-218°	41
e	Et	H	152-155°	46
f	Et	Me	177-178°	48

The vital part of this reaction is 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.[5] The calculation of atomic partial charges by 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.[6] S–O interaction and the electron-deficient effect in the pyridine ring enables nucleophilic attack of water or methanol anions on the sulfur atom in the methylsulfanyl group. The "de-methylsulfanyl reaction" is easily initiated if the cyano group at the 1-position on the quinolizine ring is changed to a methyl or an ethyl ester group. In this case, when the reaction mixture was poured into water, the de-methylsulfanyl 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 the hydrogen bonding between the NH group and an ester carbonyl group at 14.20 ppm and methyl protons of the methylsulfanyl group at 2.14 ppm and methyl protons of the tolyl group at 3.39 and 3.51 ppm (ratio 1:1). The ^{1}H-NMR measurement revealed that the products were a mixture of the non-closed compounds **5a** and **6a**. After the purification of crude products, this product was identified as 2Z, 3E methyl 4-cyano-3-methylsulfanyl-4-phenylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate on the basis of spectral (IR, UV, NMR, mass) and elemental analysis. Compounds **5b–d** or **6b–d** were also synthesized from **1a, b** and **2b, c** in a similar manner to **5a**, **6a** (Table 2). The x-ray analysis of **5b** conclusively established that the structure of this compound is as shown in Figure 1. These products were not converted to quinolizine derivatives under basic or acidic reaction conditions in DMSO.

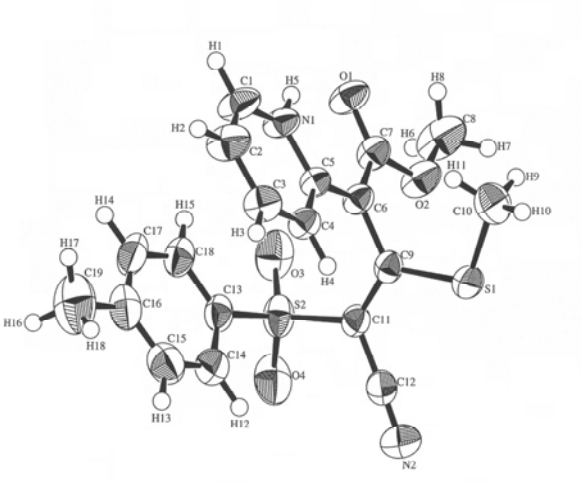
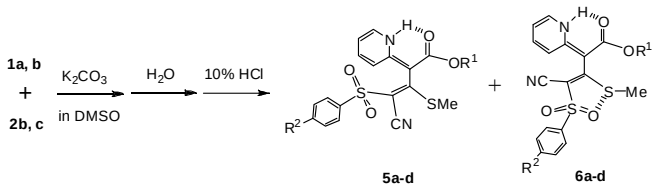


Figure 1. ORTEP drawing of **5b**

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



5, 6	R^1	R^2	mp	Yield % (5 : 6)
a	Me	H	203-205°	47 (1 : 1)
b	Me	Me	165-168°	19 (1 : 1)
c	Et	H	143-146°	44 (1 : 1)
d	Et	Me	132-135°	44 (1 : 1)

Schwarz et al. carried out detailed research on the UV–visible spectra of quinolizine derivatives.[7] Other authors have carried out research on the synthesis of 4*H*-quinolizines in studies of [3.3.3]cyclazine derivatives,[8] 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 used in devices et al.[9] 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 solid states, respectively, at room temperature (Table 3). The spectroscopic properties—absorption maxima (λmax), molar absorptivities (ε), fluorescence maxima (Em max), and relative fluorescent intensities (RI)—are listed in Table 3. The Em max of **3a, b** and **4a**–**f** were in the range 507–522 nm in dichloromethane and 528–564 nm in the solid states. With regard to Em max, the obvious substitution effects at the 1- or 2-position of the 4*H*-quinolizine ring were not observed. On the other hand, the RIs of **4a, b** were slightly stronger than those of **3a, b** in dichloromethane and solid states, indicating that desulfurization 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 Em values in the solid and solution states, varied from 17 nm to 44 nm in all compounds. The crystal structure of compounds **4a, 4c** were determined by X-ray crystallographic analysis. Single crystals of **4a, 4c** were obtained by the recrystallized from MeOH and acetonitrile. The crystal analysis of **4a, 4c** as shown in Figure 2 and 3 suggests that the π–π stacking interactions of aromatic rings is not existence. In these 4*H*-quinolizine derivatives, the packing sturcture dose not affect the solid state fluorescence.

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

No.	max (log e)[a] nm	Ex(nm) CH_2Cl_2	Em(nm) CH_2Cl_2	SS[b]	RI[c]	Ex(nm) Solid	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]Measurement in ethanol.
[b]Stokes' Shift, Em – Ex (in solution).
[c]Relative intensity of fluorescence in solution, determined using DCM as the standard compound.
[d]Stokes' Shift, Em – Ex (in solid states).
[e]Relative intensity of fluorescence in solid states, determined using Alq_3 as the standard compound.
[f]ΔF = Em (solid) – Em (solution).

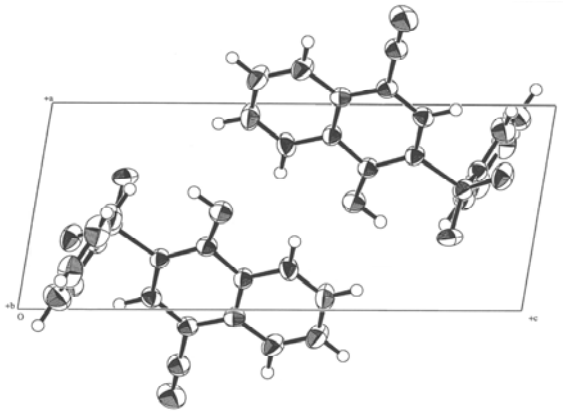


Figure 2. X-ray crystallography of **4a**

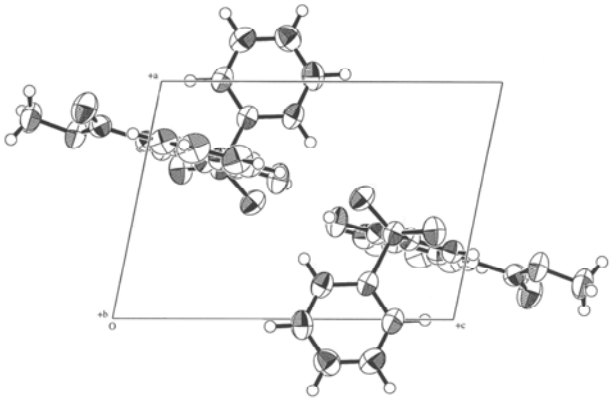


Figure 3. X-ray crystallography of **4c**

Conclusions

The reaction of 3,3-bis(methylsulfanyl)-2-phenylsulfonyl-acrylonitriles (**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 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**), without carrying out desulfurization involving the use of any metallic reagents. The synthesized 4-imino-3-phenylsulfonyl-4*H*-quinolizine derivatives exhibited strong fluorescence in solid states, 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.
a) In the solid state: A powder sample of subject compound is heaped in a tray. After covering the sample with a quartz plate, this part was fixed in fluorescence spectrometer. After fixing the fluorescent wavelength, the excitation spectrum was determined by the scanning with the fluorescent wavelength. Similarly, Fluorescent spectrum was obtained after scanning with the excitation wavelength. After obtaining these results, the excitation wavelength was decided and the fluorescence spectrum measured. The fluorescent relative intensity was determined using Alq_3 as the standard.[10] Fluorescence of Alq_3 and test compounds was measured at an excitation wavelength of 345 nm. b) In solution: The fluorescence spectra in solution were obtained in a manner similar to that described for the measurement in the solid states. Relative intensity of fluorescence in solution was determined by using DCM: [4-(dicyanomehylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran] as a standard compound.[11] Fluorescence of standard sample and all subject compounds were measured in CH_2Cl_2 solution ($1.0x10^{-5}$M) on 480 nm excitation.

4-Imino-2-methylsulfanyl-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitrile (3a) A mixture of 2.53 g (10.0 mmoles) of **1a**, 1.77 g (10.0 mmoles) of 2-pyridylacetonitrile (**2a**), and 3.44 g (20.0 mmoles) of potassium carbonate in 30 mL of DMSO was stirred for 2 h at rt. This mixture was stirred and heated for 30 min at 50-60°C. The reaction mixture was poured into 200 mL of ice-water and acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from a mixture of MeOH and toluene (ratio 1:5) to give 2.91 g (8.20 mmoles, 82% yield) of yellow crystals, mp 203-204°. IR (KBr, cm^{-1}): 3329 (NH), 2209 (CN), 1610, 1140, 768 cm^{-1}. UV (EtOH) λ nm (log ε): 399.0 (2.66), 309.0 (2.29), 282.5 (3.26). Fluoresence (solid): Ex, 344 nm; Em, 564 nm; RI=0.07. Fluoresence (CH_2Cl_2): Ex, 262 nm; Em, 520 nm; RI=0.25. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.26 (3H, s, SMe), 7.20-7.26 (1H, m, 7-H), 7.44-7.56 (3H, m, phenyl-H), 7.60 (1H, m, 8-H), 7.82 (2H, m, phenyl-H), 7.99 (1H, d, *J*=7.8 Hz, 6-H), 9.77 (1H, d, *J*=7.8 Hz, 9-H), 10.11 (1H, s, N-H). ^{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. Ms: m/z 356 (M^++1, 6), 355 (M^+, 28), 309 (29), 229 (27), 290 (100), 244 (81), 214 (38), 167 (95), 78 (26). *Anal*. Calcd for $C_{17}H_{13}N_3O_2S_2$=355.434: 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 mmoles) was prepared in 81% yield from 1.44 g (5.0 mmoles) of **1b** and 0.62 g (5.0 mmoles) of **2a** in a manner similar to that described for the synthesis of **3a**. An analytical sample was recrystallized from DMF to give orange needles, mp 178-182°. IR (KBr, cm^{-1}): 3326 (NH), 2208 (CN), 1607, 1554, 1505 1452 cm^{-1}. UV (EtOH) λ nm (log ε): 384.5 (3.84), 279.0 (3.97). Fluoresence (solid): Ex, 333 nm; Em, 552 nm; RI=0.09. Fluoresence (CH_2Cl_2): Ex, 262 nm; Em, 522 nm; RI=0.36. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.29 (3H, s, SMe), 2.42 (3H, s, Me), 7.17-7.23 (1H, m, 7-H), 7.30 (2H, m, phenyl-H), 7.81 (1H, m, 8-H), 7.82-7.88 (2H, m, phenyl-H), 7.88 (1H, d, *J*=8.3 Hz, 6-H), 9.64 (1H, d, *J*=7.4 Hz, 9-H), 10.11 (1H, s, N-H). ^{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. Ms: m/z 370 (M^++1, 4), 369 (M^+, 69), 368 (15), 305 (28), 304 (100), 214 (26), 167 (51), 127 (33). *Anal*. Calcd for $C_{18}H_{15}N_3O_2S_2$=369.0606: 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 0.36 g (1.0 mmol) of **3a** in 100 mL of MeOH was refluxed for 5 h. After removal of the solvent, the residue was washed with 10 mL of MeOH to give 0.31 g of orange crystals in 100% yield. An analytical sample was recrystallized from a mixture of MeOH and toluene (ratio 5:1) to give orange leaflets, mp 208-209°. IR (KBr, cm^{-1}): 3337 (C=NH), 2210 (CN), 1608, 1500, 1298, 1099, 583 cm^{-1}. UV (EtOH) λ nm (log ε): 385.5 (3.35), 315.5 (3.09), 282.0 (3.41). Fluoresence (solid): Ex, 339 nm; Em, 546 nm; RI=0.09. Fluoresence (CH_2Cl_2): Ex, 262 nm; Em, 520 nm; RI=0.31. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54 (1H, m, 7-H), 7.54-7.62 (2H, m, phenyl-H), 7.85 (1H, m, 8-H), 7.87-7.95 (2H, m, phenyl-H), 7.93 (1H, d, *J*=7.0 Hz, 6-H), 8.27 (1H, s, 2-H), 8.81 (1H, brs, N-H), 9.62 (1H, d, *J*=7.7 Hz, 9-H). ^{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. Ms: m/z 310 (M^++1,5), 309 (M^+, 23), 245 (20), 244 (100), 168 (37), 167 (42), 141 (16), 114 (13). *Anal*. Calcd for $C_{16}H_{11}N_3O_2S$=309.3436: 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 mmoles) was prepared in 100% yield from 0.37 g (1.0 mmoles) of **3b** in a manner similar to that described for the synthesis of **4a**. An analytical sample was recrystallized from DMF to give orange needles, mp 180-184°. IR (KBr, cm^{-1}): 3347 (C=NH), 2208 (CN), 1614, 1490, 1292, 1095, 570 cm^{-1}. UV (EtOH) λ nm (log ε): 451.5 (3.67), 383.0 (3.65), 328.5 (3.41), 278.5 (3.85). Fluoresence (solid): Ex, 344 nm; Em, 556 nm; RI=0.20. Fluoresence (CH_2Cl_2): Ex, 271 nm; Em, 513 nm; RI=0.42. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.41 (3H, s, Me), 7.21 (1H, m, 7-H), 7.32 (2H, m, phenyl-H), 7.81 (1H, m, 8-H), 7.83 (2H, m, phenyl-H), 7.86 (1H, *J*=6.6 Hz, 6-H), 8.26 (1H, s, 2-H), 8.78 (1H, brs, NH), 9.61 (1H, d, *J*=7.8 Hz, 9-H). ^{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. Ms: m/z 324 (M^++1, 5), 323 (M^+, 23), 259 (21), 258 (100), 168 (25), 167 (33), 114 (13). *Anal*. Calcd. for $C_{17}H_{13}N_3O_2S$=323.3701: 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 2.53 g (10.0 mmoles) of **1a**, 1.77 g (10.0 mmoles) of methyl 2-pyridylacetate (**2b**), and 3.44 g (20.0 mmoles) of potassium carbonate in 30 mL of DMSO was stirred for 2 h at rt. This mixture was stirred and heated for 30 min at 50-60°. The reaction mixture was poured into 200 mL of ice-water. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from a mixture of MeOH and toluene (ratio 5:1) to give 1.61 g (4.7 mmoles, 47% yield) of yellow crystals (**4c**). This filtrate was acidified with 10% hydrochloric chloride solution to give the red brown caramel oil which was crystallized by treatment with MeOH. The crystallized products were collected by filtration to give 1.71 g (4.4 mmoles, 44% yield) of red crystals (**5a, 6a**).
Methyl 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carboxylate (**4c**): mp 203-205°C. IR (KBr, cm^{-1}): 3336 (C=NH), 1702 (CO), 1617, 1492, 1295, 1140, 579. UV (EtOH) λ nm (log ε): 437.0 (3.39), 364.0 (3.44), 272.0 (3.55). Fluoresence (solid): Ex, 342 nm; Em, 540 nm; RI=1.46. Fluoresence (CH_2Cl_2): Ex, 283 nm; Em, 507 nm; RI=0.40. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.89 (3H, s, OMe), 7.19 (1H, m, 7-H), 7.48-7.60 (3H, m, phenyl-H), 7.80 (1H, m, 8-H), 7.98 (2H, m, phenyl-H), 8.64 (1H, brs, NH), 8.86 (1H, s, 2-H), 9.31 (1H, d, *J*=10.0 Hz, 6-H), 9.68 (1H, d, *J*=7.8 Hz, 9-H). ^{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. Ms: m/z 343 (M^++1, 10), 342 (M^+, 50), 277 (100), 201 (22), 169 (25), 142 (11), 141(12). *Anal.* Calcd. for $C_{17}H_{14}N_20_4S$=342.3691: C, 59.64; H, 4.12; N, 8.18. Found: C, 59.77: H, 4.04; N, 8.22.
2Z,3E Methyl 4-cyano-3-methylsulfanyl-4-phenylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (**5a, 6a**): mp 125-128°C. IR (KBr, cm^{-1}): 2202 (CN), 1637 (CO), 1591, 1509. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.14 (3H, s, SMe), 3.39 (3H/2, s, OMe_2), 3.51 (3H/2, s. OMe_2), 6.42-6.61 (2H, m, pyridyl-H), 7.15-7.78 (6H, m, phenyl-H, pyridyl-H), 8.09 (1H, m, pyridyl-H), 14.20 (1H, brs, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.18,4 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. HRMS:

Calcd:$C_{18}H_{16}N_2O_4S_2$=388.0551. Found: 388.0559. *Anal*. Calcd for $C_{18}H_{16}N_2O_4S_2$=388.4627: 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 mmoles) was synthesized in 41% yield from **2b** (1.51 g, 10.0 mmoles) and **1b** (1.98 g, 5.0 mmoles) in a manner similar to that described for the preparation of **4c**. An analytical sample was recrystallized from MeOH to give yellow needles. **5b, 6b** (0.39 g, 1.0 mmoles) was synthesized in 19% yield in manner similar to that described for the preparation of **5a**, **6a**. An analytical sample was recrystallized from MeOH to give red crystals.

Methyl 4-imino-3-tolylsulfonyl-4*H*-quinolizine-1-carboxylate (**4d**): mp 216-218°. IR (KBr, cm^{-1}): 3343 (NH), 1691 (CO), 1618, 1492, 1141, 781. UV (EtOH) λ nm (log ε): 436.0 (3.99), 365.0 (4.03), 270.5 (4.19). Fluoresence (solid): Ex, 340 nm; Em, 533 nm, RI=1.17. Fluoresence (CH_2Cl_2): Ex, 280 nm; Em, 511 nm; RI=0.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.39 (3H, s, Me), 3.89 (3H, s, OMe), 7.18 (1H, m, 7-H), 7.30 (2H, *J*=8.4 Hz, phenyl-H), 7.80 (1H, m, 8-H), 7.84 (2H, d, *J*=8.4 Hz, phenyl-H), 8.60 (1H, brs, NH), 8.85 (1H, s, 2-H), 9.30 (1H, d, *J*=9.0 Hz, 6-H), 9.67 (1H, d, *J*=7.8 Hz, 9-H). ^{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. Ms: m/z 357 (M^++1, 11), 356 (M^+, 51), 291 (100), 201 (32), 169 (46). *Anal*. Calcd for $C_{18}H_{16}N_2O_4S_2$=356.3967: C, 60.66; H, 4.53; N, 7.86. Found: C, 60.75; H, 4.35; N, 7.88.

2Z,3E Methyl 4-cyano-3-methylsulfanyl-4-tolylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (**5b, 6b**): mp 165-168°. IR (KBr, cm^{-1}): 2201 (CN), 1618, 1590, 1283 1151, 584. UV (EtOH) λ nm (log ε): 393.0 (3.59), 302.5 (4.09). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.14 (3H, s, Me), 2.38 (3H/2, s, SMe), 2.48 (3H/2, s, SMe), 3.41 (3H/2, s OMe), 3.56 (3H/2, s, OMe), 6.40-6.60 (1H, m, pyridyl-H), 7.19 (1H, m, pyridyl-H), 7.38 (2H, m, phenyl-H), 7.48 (2H, m, phenyl-H), 7.61 (1H, d, *J*=7.8 Hz, pyridyl-H), 7.97 (1H, d, *J*=8.1 Hz, pyridyl-H), 14.00 (1H, brs, NH). ^{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. Ms: m/z 403 (M^++1, 5), 402 (M^+, 21), 247 (100), 215 (32), 200 (83), 168 (25), 91 (26). *Anal*. Calcd for $C_{19}H_{18}N_2O_4S_2$=402.4893: 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 mmoles) was synthesized in 46% yield from **2c** (0.33 g, 2.0 mmoles) and **1a** (0.86 g, 3.0 mmoles) in a manner similar to that described for the preparation of **4c**. An analytical sample was recrystallized from EtOH to give yellow needles. **5c, 6c** (0.35 g, 0.9 mmoles) was synthesized in 44% yield in manner similar to that described for the preparation of **5a**, **6a**. An analytical sample was recrystallized from MeOH to give red crystals.

Ethyl 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carboxylate (**4e**): mp 152-155°. IR (KBr, cm^{-1}): 3356 (NH), 1694 (CO), 1639, 1618, 1489, 578. UV (EtOH) λ nm (log ε): 437.0 (4.03), 364.5 (4.06), 272.0 (4.19). Fluoresence (solid): Ex, 339 nm; Em, 528 nm; RI=1.44. Fluoresence (CH_2Cl_2): Ex, 284 nm; Em, 511 nm; RI=0.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.43 (3H, t, *J*=7.1 Hz, O-CH_2-$\underline{CH_3}$), 4.36 (2H, q, *J*=7.1 Hz, O-CH_2-) , 7.17 (1H m, 7-H), 7.45-7.62 (3H, m, phenyl-H), 7.79 (1H, m, 8-H), 7.96 (2H, m, phenyl-H), 8.61 (1H, brs, NH), 8.86 (1H, s, 2-H), 9.32 (1H, d, *J*=9.0 Hz, 6-H), 9.67 (1H, d, *J*=6.9 Hz, 9-H). ^{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. Ms: m/z 357 (M^++1, 14), 356 (M^+, 65), 292 (20), 291 (95), 133 (100), 105 (45). *Anal*. Calcd for $C_{18}H_{16}N_2O_4S$=356.3967: C, 60.66; H, 4.53; N, 7.86. Found: C, 60.54; H, 4.38; N, 7.89.

2Z,3E Ethyl 4-cyano-3-methylsulfanyl-4-phenylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (**5c, 6c**): mp 143-146°. IR (KBr, cm^{-1}): 2204 (CN), 1638 (CO), 1582, 1277. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90-1.17 (3H, m, *J*=7.1 Hz, O-CH_2-$\underline{CH_3}$), 2.15 (3H, s, SMe), 3.60-4.16 (2H, m, O-CH_2-), 6.40-6.70 (1H, m, pyridyl-H), 7.20-7.80 (7H, m, phenyl-H, pyridyl-H), 8.12 (1H, d, *J*=10.2 Hz, pyridyl-H), 14.02 (1H, brs, NH). ^{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. Ms: m/z 403 (M^++1, 5), 402 (M^+, 19), 261 (100), 260 (55), 215 (63), 77 (34). *Anal*. Calcd for $C_{19}H_{18}N_2O_4S_2$=402.4893: 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 mmoles) was synthesized in 48% yield from **2c** (1.65 g, 10.0 mmoles) 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. **5d, 6d** (0.92 g, 2.2 mmoles) was synthesized in 44% yield in manner similar to that described for the preparation of **5a**, **6a**. An analytical sample was recrystallized from MeOH to give red crystals.

Ethyl 4-imino-3-tolylsulfonyl-4*H*-quinolizine-1-carboxylate (**4f**): mp 177-178°. IR (KBr, cm^{-1}): 3302 (NH), 1761 (CO), 1704 (CO), 1615, 1513. UV (EtOH) λ nm (log ε): 435.5 (3.12), 364.5 (3.17), 271.5 (3.34). Fluoresence (solid): Ex, 332 nm; Em, 536 nm, RI=0.62. Fluoresence (CH_2Cl_2): Ex, 284 nm; Em, 519 nm; RI=0.25. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.42 (3H, t, *J*=7.1 Hz, O-CH_2-$\underline{CH_3}$), 2.39 (3H, s, Me), 4.36 (2H, q, *J*=7.1 Hz, O-CH_2-), 7.17 (1H, m, 7-H), 7.30 (2H, d, *J*=7.9 Hz, phenyl-H), 7.77 (1H, m, 8-H), 7.84 (2H, d, *J*=7.9 Hz, phenyl-H), 8.56 (1H, brs, NH), 8.84 (1H, s, 2-H), 9.31 (1H, d, *J*=9.0 Hz, 6-H), 9.66 (1H, d, *J*=6.6 Hz, 9-H). ^{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. Ms: m/z 371 (M^++1, 9), 370 (M^+, 40), 306 (23), 305 (100), 277 (28), 225 (25). *Anal*. Calcd for $C_{19}H_{18}N_2O_4S_2$=370.4233: C, 61.61; H, 4.90; N, 7.56. Found: C, 61.63; H, 4.93; N, 7.42.

2Z,3E Ethyl 4-cyano-3-methylsulfanyl-4-tolylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (**5d, 6d**): mp 132-135°. IR (KBr, cm^{-1}): 2207 (CN), 1650 (CO), 1615, 1585, 1267, 1150, 588. UV (EtOH) λ nm (log ε): 392.0 (3.69), 304.0 (4.19). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.98 (3H/2, t, *J*=7.1 Hz, O-CH_2-$\underline{CH_3}$), 1.10 (3H/2, t, *J*=7.1 Hz, O-CH_2-$\underline{CH_3}$), 2.15 (3H, s, Me), 2.39 (3H, s, Me), 3.70 (2H/2, m, O-CH_2-), 4.0 (2H/2, m, O-CH_2-), 6.43-6.65 (1H, m, pyridyl-H), 7.20 (1H, m, pyridyl-H), 7.37 (2H, m, phenyl-H), 7.46 (2H, m, phenyl-H), 7.62 (1H, m, pyridyl-H), 7.97 (1H, m, pyridyl-H), 14.00 (1H, brs, NH). ^{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. Ms: m/z 416 (M^+, 3), 260 (100), 215 (72), 214 (38), 188 (20), 139 (30), 91 (27). *Anal*. Calcd for $C_{20}H_{20}N_2O_4S_2$=416.5159: C, 57.67; H, 4.84; N, 6.73. Found: C, 57.34; H, 4.82; N, 6.59.

Crystal Data of 4-Imino-3-phenylsulfonyl-4*H*-quinolizine-1-carbonitrile (4a) This crystal was obtained by the recrystallized from MeOH and acetonitrile (ratio 1:1) to give an orange prisms crystal of $C_{16}H_{11}N_3O_2S$ having approximate dimension of 0.50x0.40x0.15 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercuryarea detector with graphite monochromated Mo-Kα radiation. A crystal data formula weight: 309.34; Crystal color habit: orange, prisms; Crystal system: triclinic; Lattice type: primitive; Lattice parameter: 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-1 (#2); Z value: 2; Dcalc : 1.460 g/cm^3; F_{000}=320.00; μ(MoKα)=2.406 cm^{-1}.

Crystal Data of Methyl 4-imino-3-phenylsulfonyl-4*H*-quinolizine-1-carboxylate (4c) This crystal was obtained by the recrystallized from MeOH and acetonitrile (ratio 1:1) to give an yellow prisms crystal of $C_{17}H_{14}N_2O_4S$ having approximate dimension of 0.40x0.30x0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercuryarea detector with graphite monochromated Mo-Kα radiation. A crystal data formula weight: 342.37; Crystal color habit: yellow, prisms; Crystal system: triclinic; Lattice type: primitive; Lattice parameter: 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-1 (#2); Z value: 2; Dcalc : 1.454 g/cm^3; F_{000}=356.00; μ(MoKα)=2.314 cm^{-1}.

Crystal Data of 2Z,3E Methyl 4-cyano-3-methylsulfanyl-4-tolylsulfonyl-2-(1*H*-pyrid-2-ylidene)butenoate (5b) This crystal was obtained by the recrystallized from MeOH to give an orange prisms crystal of $C_{19}H_{18}N_2O_4S_2$ having approximate dimension of 0.40x0.20x0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercuryarea detector with graphite monochromated Mo-Kα radiation. A 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; Dcalc : 1.377 g/cm^3; F_{000}=840.00; μ(MoKα)=3.012 cm^{-1}.

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Layout 2:

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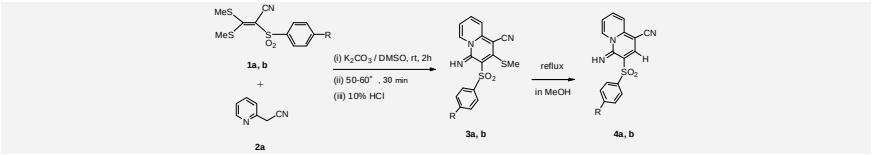

In the synthesis of 4*H*-quinolizine derivatives involving the use of a sulfonyl ketene dithioacetal, we found a novel reaction in which the remaining methylsulfanyl group is replaced with a proton after the ring closure reaction in the quinolizine skeleton. A methylsulfanyl group at the 2-position on 4*H*-quinolizin-4-one was readily removed under methanol reflux conditions to afford 3-phenylsulfonyl 4*H*-quinolizin-4-ones (**5a, b**) in good yields. Alkyl 3-phenylsulfonyl-4*H*-quinolizine-1-carboxylates (**5c**–**f**) were directly synthesized from sulfonyl ketene dithioacetal (**1a, b**) with alkyl 2-pyridylacetates (**2b**, **c**), without carrying out desulfurization involving the use of any metallic reagents. We presumed that S–O interaction and the electron-deficient effect in the pyridine ring enables nucleophilic attack of water or methanol anions on the sulfur atom in the methylsulfanyl group.

The synthesized 4-imino-3-phenylsulfonyl-4*H*-quinolizine derivatives exhibited strong fluorescence in solid states. An organic light-emitting diode (OLED) that emits light in the solid state have recently received considerable attention due to their potential application in next-generation display devices. Our findings will contribute to the development of OLED materials.

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

Keywords: 4*H*-quinolizine derivatives / sulfonyl ketene dithioacetal / desulfurization / fluorescence / organic light-emitting diode