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DEVELOPMENT OF FLUORESCENT 2-PYRONE DERIVATIVES USING KETENE DITHIOACETALS FOR ORGANIC EL DEVICES

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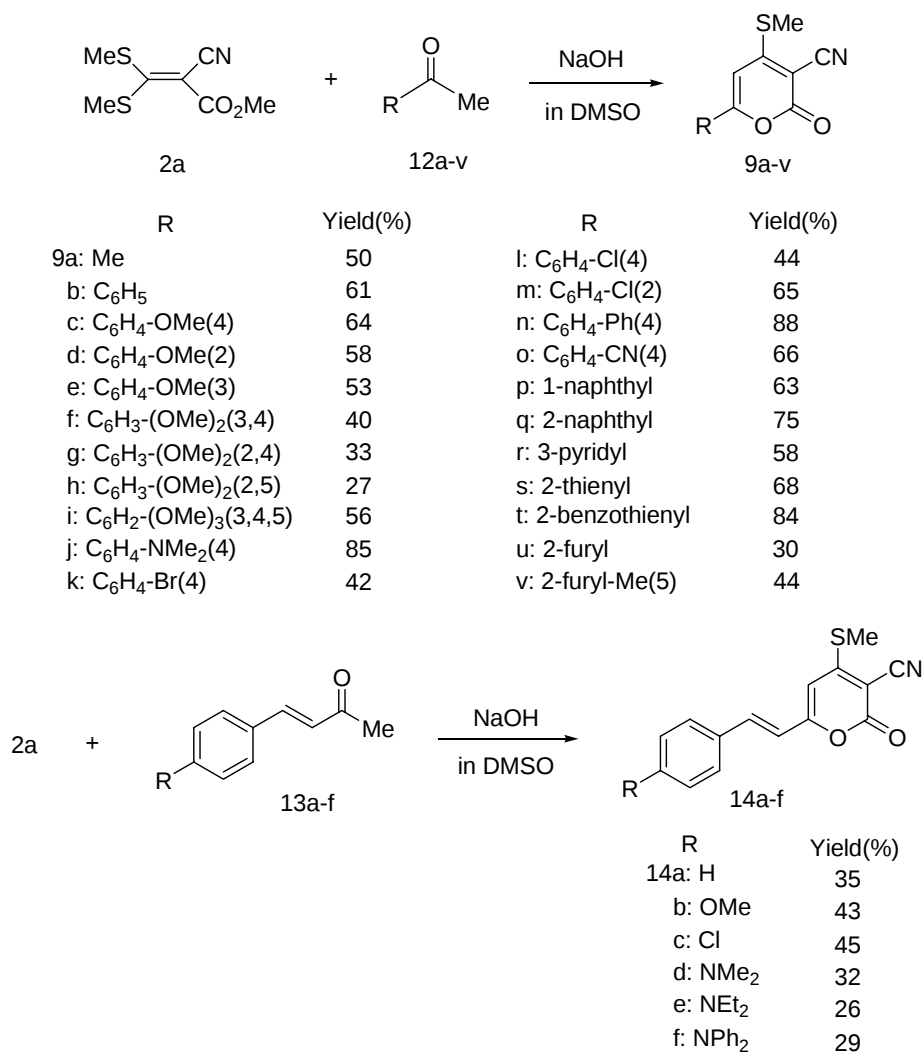
Abstract – In recent years, organic electro luminescent (EL) materials have received considerable attention due to their potential application in next-generation display devices with high brightness levels, wide color ranges, and wide viewing angles. Fluorescent 2-pyrone derivatives have been synthesized using a convenient method involving ketene dithioacetals, which emit fluorescence (red, green, and blue) in both solution (dichloromethane and ethanol) and solid state. The structure-activity relationships of various 2-pyrone derivatives have been clarified.

1. INTRODUCTION

Pigment chemistry such as that of mauveine pigments from the United Kingdom and indigo pigments from Germany has contributed to modern chemistry.¹⁻⁴ Many heterocycles are examples of pigment compounds. The design of pigment compounds has become easier with the development of computational chemistry; however, not all compounds can be designed theoretically since practical and experimental pigment compounds possess large molecules.^{5,6} Since pigment chemistry obviously involves the π electron system, it is important that the chemical structure should include a functional group such as a chromophore or auxochrome. In particular, utilizing the properties of hetero atoms such as nitrogen, oxygen, and sulfur is critical in the design of pigments with various functionalities.²

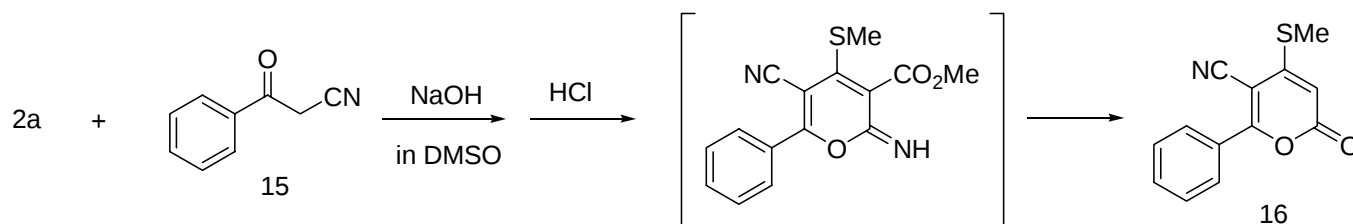
Since 1962, research on the use of this reagent in the synthesis of heterocyclic compounds has been greatly advanced by R. Gompper *et al.* in Germany and our group. As shown in Figure 1, these reactions proceed *via* an addition-elimination mechanism, which is initiated by a nucleophilic addition at the sp^2 sulfur-substituted carbon atom of ketene dithioacetal, followed by an elimination of the methylsulfanyl group to complete the substitution reaction. Further, the same substitution reaction occurs at the other methylsulfanyl group and produces various derivatives. Therefore, ketene dithioacetals enable the introduction of various functional groups. In particular, chromophores and auxochromes can be introduced into the pigment molecules.^{13–19}

On the basis of the initial research on ketene dithioacetals, it has been suggested that their skeletons are significant in the construction of dye molecules such as merocyanine dyes and the styryl series. We began our studies on the synthesis of materials for information storage with absorption in the near infrared and luminol type chemical luminescence reagents as high-sensitive analytical reagents of enzymes and reactive oxygen. This research finding triggered the development of fluorescence 2*H*-pyrone derivatives.^{20–26}



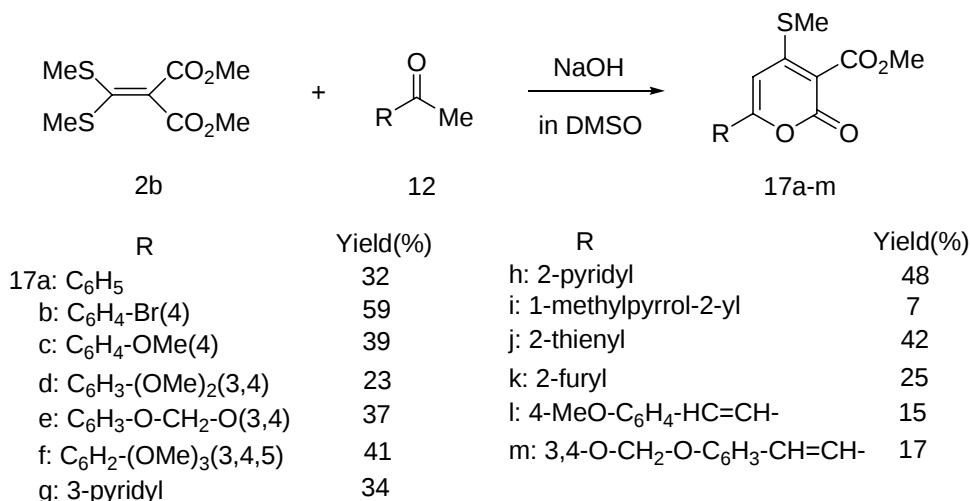
Scheme 1

The arrangement of suitable chromophores and auxochromes within the molecules both in the solution and solid states is necessary to confer fluorescent properties to a compound. In this respect, heterocycles synthesized using ketene dithioacetals have good substituents show fluorescence, due to ketene dithioacetals having strong electro-donating groups such as a methylsulfanyl group and strong electro-withdrawing groups such as cyano and ester groups. Therefore, many fluorescent materials are expected to be included under the category of heterocycles that we have previously synthesized. While in search of a solid fluorescent material, we found that 2*H*-pyrone derivatives exhibit strong fluorescence; this was first reported in 1977.²⁷ A variety of pyrone derivatives were obtained *via* the reactions of various active methylene compounds with ketene dithioacetals; however, not all these derivatives were found to be fluorescent compounds. Our research suggests that the substitution of an aryl group without electro-withdrawing group such as a phenyl group at position 6 and not position 5 of the pyrone ring was important for fluorescence to occur. For example, 6-methyl- (**9a**), 6-(4-cyanophenyl)- (**9o**), 5-cyano- (**16**), and 6-pyrid-3-yl-2*H*-pyrone (**9r**) do not show fluorescence (Schemes 1 and 2).

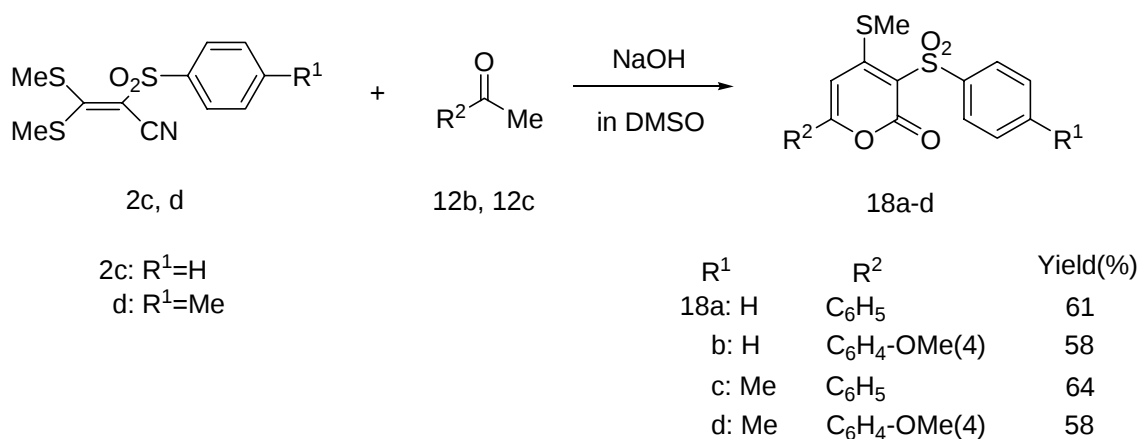


Scheme 2

In a similar manner to **9** and **14**, methyl ester compounds (**17a–m**) were synthesized *via* the reactions between arylacetyl compounds and ketene dithioacetal (**2b**), which was prepared from methyl malonate (**12**) (Scheme 3). In addition, reactions of methyl ketones with sulfonyl ketene dithioacetal (**2c, d**) afforded 3-phenylsulfonyl derivatives (**18a–d**) (Scheme 4).²⁸

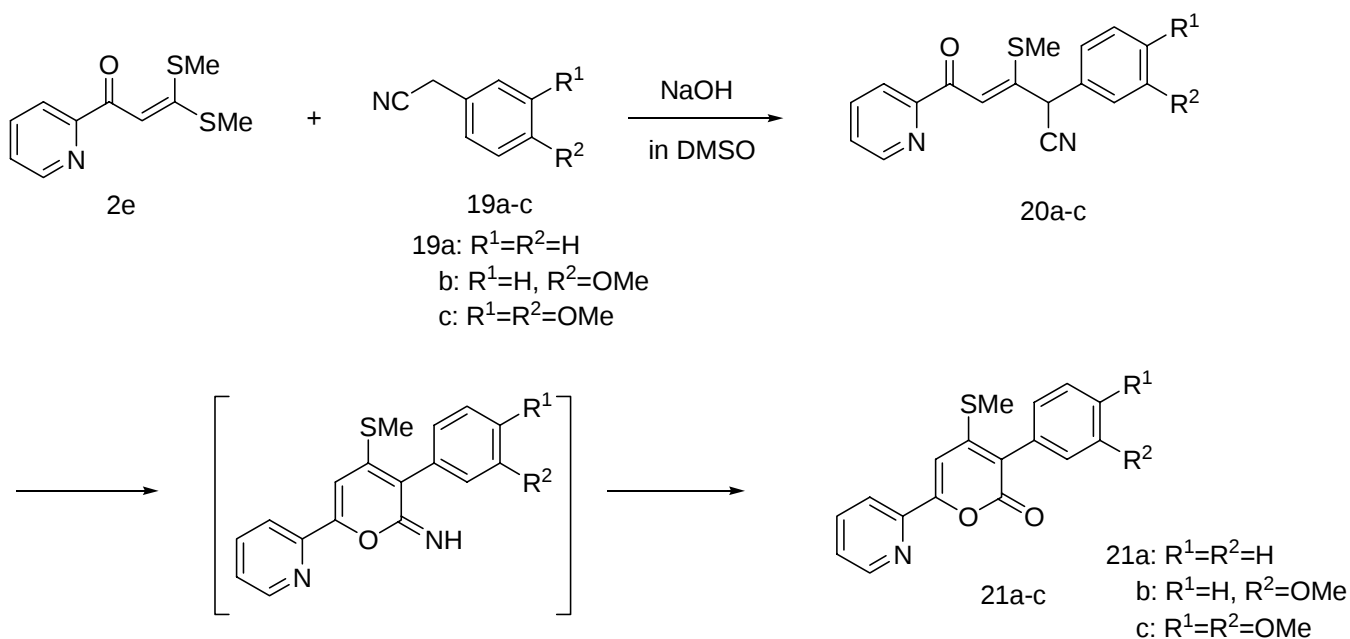


Scheme 3



Scheme 4

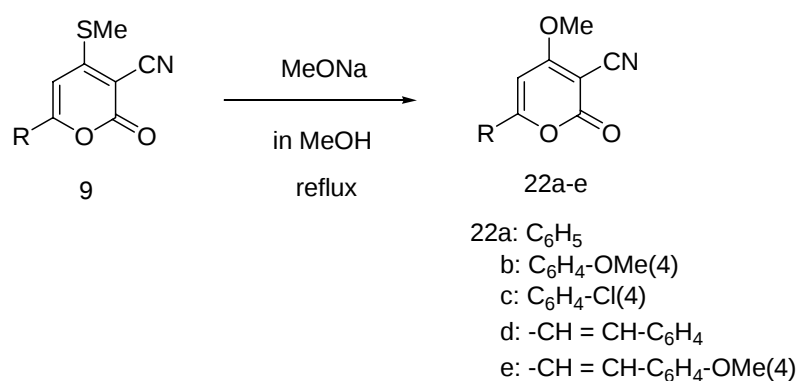
The introduction of electro-withdrawing groups such as cyano, ester, and sulfonyl groups at position 3 of the pyrone ring was necessary for fluorescence to occur in 2-pyrone derivatives. The introduction of electron-rich aromatic compounds at position 6 of the pyrone ring increased the intensity of fluorescence. In the case of derivatives in which electron-poor compounds were introduced, such as pyridine or 4-cyanophenyl derivative (**9o**), no fluorescence emission was observed.²⁹ However, 6-pyridyl-3-phenyl-4-sulfanyl-2-pyrone derivatives (**21a–c**), especially 3',4'-dimethoxyphenyl derivative (**21c**), exhibit strong fluorescence (Scheme 5).³⁰ These results suggest that derivatives with an electron-rich group and an electron-poor group at either position 3 or 6 of the pyrone ring, respectively, exhibit fluorescence. Compounds **21a–c** were obtained *via* the reactions of phenylacetonitrile (**19a–c**) with the ketene dithioacetal (**2e**) in the presence of sodium hydroxide as a base in DMSO followed by neutralization with hydrochloric acid.



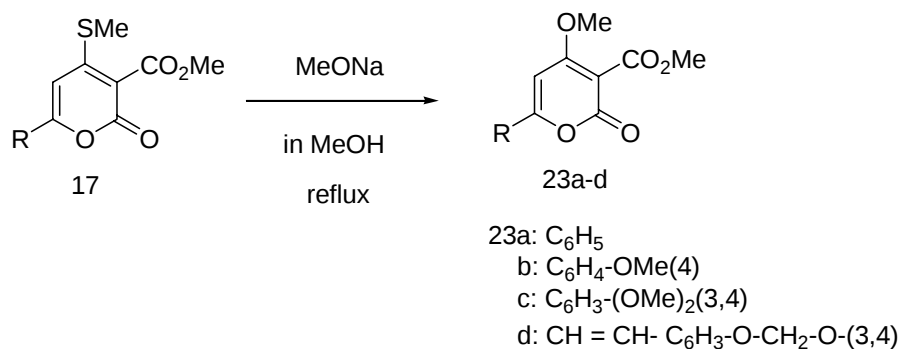
Scheme 5

3. SYNTHESIS OF 2-PYRONE DERIVATIVES VIA THE NUCLEOPHILIC-SUBSTITUTION REACTION OF 4-METHYLSULFANYL-2-PYRONES

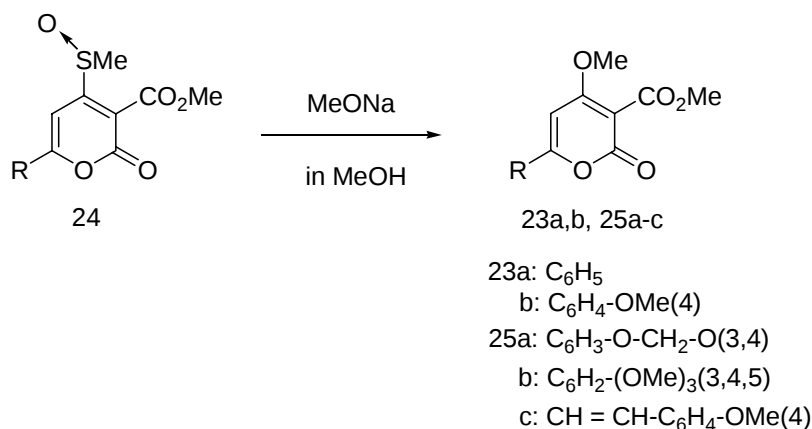
When 2-pyrone derivatives are synthesized using ketene dithioacetals, they have a methylsulfanyl group at position 4 of the pyrone ring, which can be easily substituted by other functional groups. The reactions of **9a–e** with methyl alkoxide afford 4-methoxy-2-pyrone derivatives (**22a–e**) (Scheme 6), and the reactions of ester compounds (**17a–d**) with methyl alkoxide produce 2-pyrone derivatives such as methoxyphenylcoumarin (**23a**)³¹ and methoxyparakotoin (**23d**)³² that are found in natural products, albeit



Scheme 6



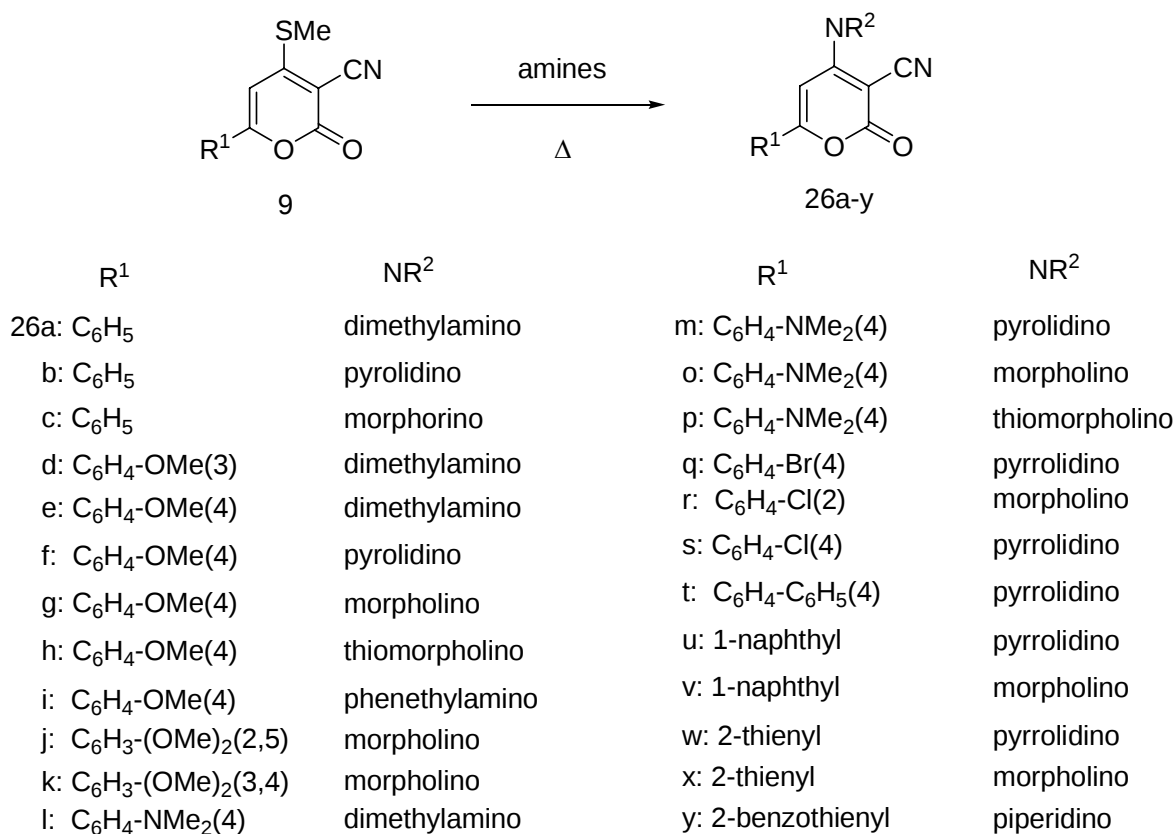
Scheme 7



Scheme 8

very weak intensities (Scheme 7). In order to avoid altering the ester group, the above reaction was performed and was then followed by conversion of the methylsulfonyl group to a sulfonyl group; this reaction was found to be effective (Scheme 8).³³

4-Amino-2-pyrone derivatives (**26a–y**, **27a–f**) were synthesized by reacting methylsulfonyl and methylsulfonyl derivatives (**9**, **24**) with amines (Schemes 9 and 10). Although only aliphatic amine derivatives are examined in this section, aromatic amine derivatives are of more interest from the viewpoint of fluorescence. These derivatives will be examined in the future. Amine derivatives are easily synthesized using an excess of amines in methanol; however, the reactions are slow. Without the presence of a solvent, **9** directly reacts with amines; however, this reaction is accompanied by the ring-opening reaction of the pyrone ring.³⁴ The resulting amine derivatives, in which the sulfur atom at position 4 of the pyrone ring is replaced by an oxygen or nitrogen atom, show relatively strong fluorescence, and the emitting regions showed an approximately 30–50 nm blue shift.



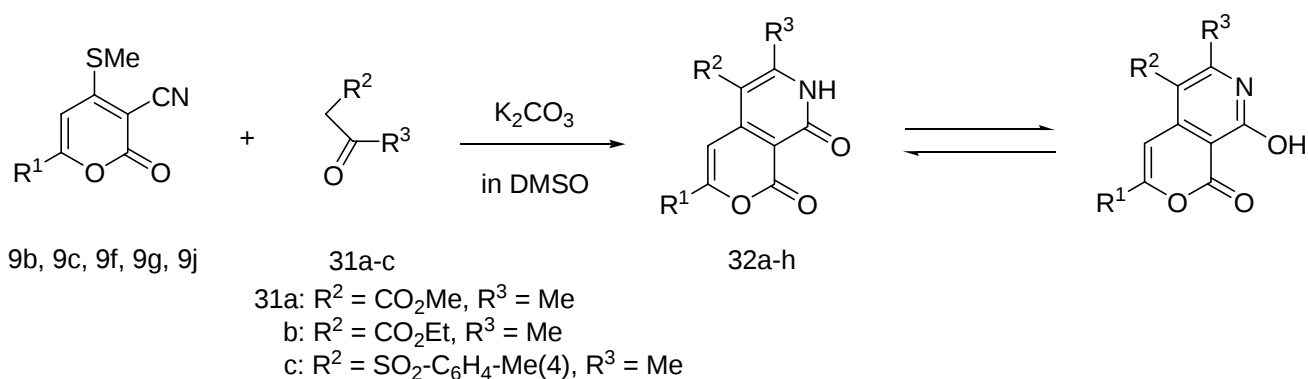
Scheme 9

H-bonded structure resulting between the proton of the hydroxyl group and the carbonyl group, which leads to a molecular flatness arising from electron delocalization.³⁵

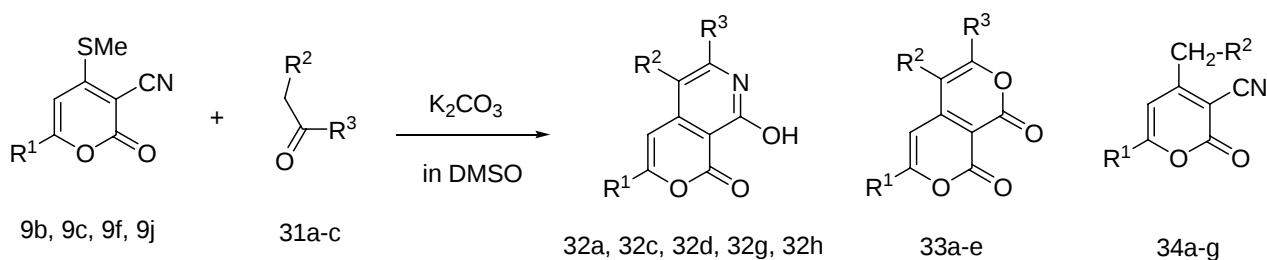
Table 2. Synthesis of dialkyl 3-methoxycarbonyl-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates

	17a, c, e	28a, b			30a-e
No.	R ¹	R ²	Yield(%)	mp(°C)	Appearance
30a	C ₆ H ₅	Me	88	120-121	yellow needles
b	C ₆ H ₅	Et	80	80-90	yellow needles
c	C ₆ H ₄ -OMe(4)	Me	90	120-121	yellow needles
d	C ₆ H ₄ -OMe(4)	Et	79	89-92	yellow needles
e	C ₆ H ₃ -O-CH ₂ -O(3,4)	Me	53	143-146	yellow needles

Table 3. Synthesis of 1*H*-pyrano[3,4-*c*]pyridines

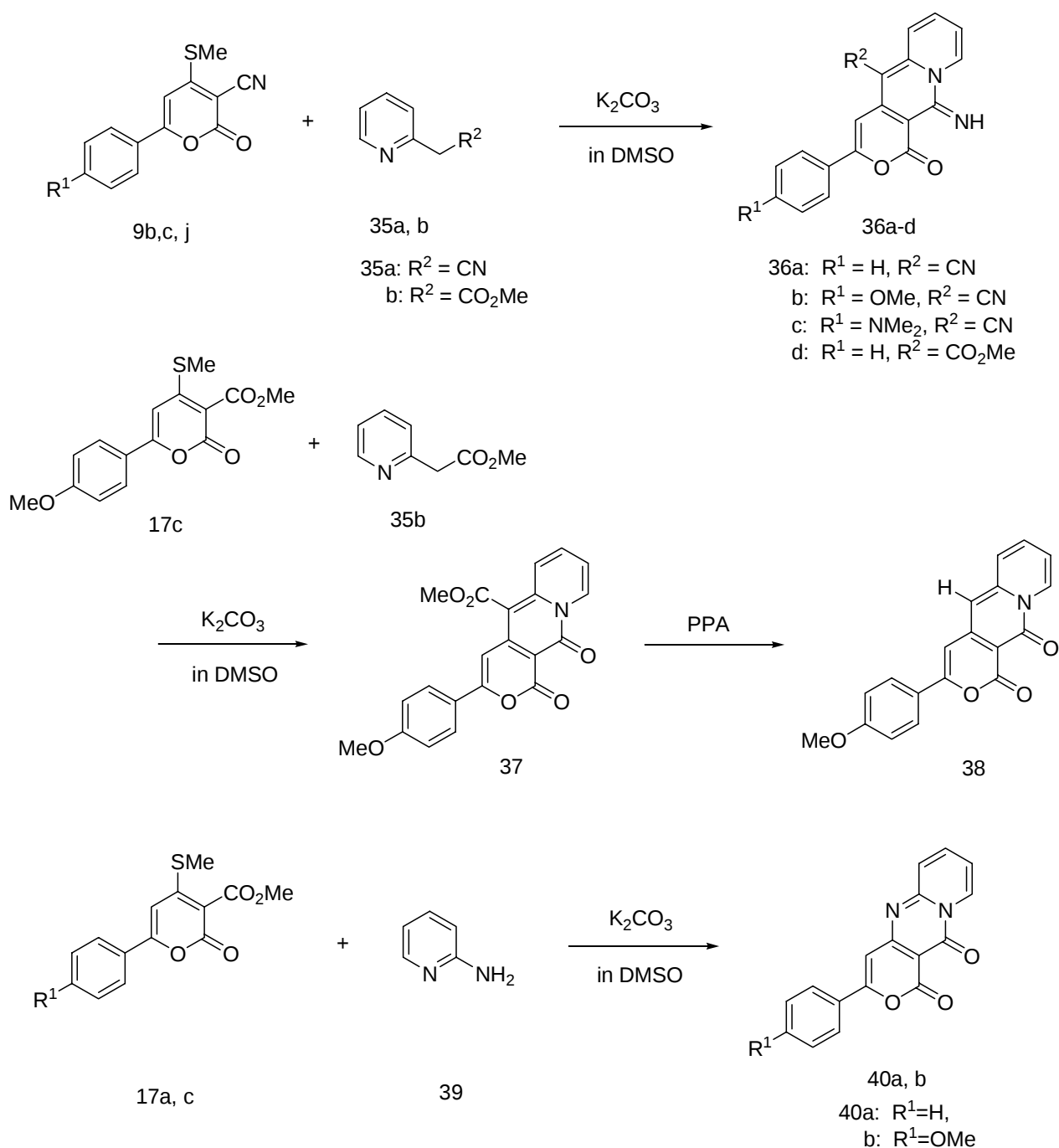


No.	R ¹	R ²	R ³	Yield(%)	Mp(°C)
32a	C ₆ H ₅	CO ₂ Me	Me	52	>300
b	C ₆ H ₄ -OMe(4)	CO ₂ Me	Me	30	296-297
c	C ₆ H ₅	CO ₂ Et	Me	70	295-297
d	C ₆ H ₄ -OMe(4)	CO ₂ Et	Me	31	287-288
e	C ₆ H ₃ -OMe ₂ (2,4)	CO ₂ Et	Me	30	298-299
f	C ₆ H ₃ -OMe ₂ (3,4)	CO ₂ Et	Me	28	303-304
g	C ₆ H ₄ -NMe ₂ (4)	CO ₂ Et	Me	9	298-299
h	C ₆ H ₄ -OMe(4)	SO ₂ -C ₆ H ₄ -Me(4)	Me	22	260-270

Table 4. Synthesis of 1*H*-pyrano[3,4-*c*]pyridines

Entry	R ¹	R ²	R ³	32 Yield(%)	33 Yield(%)	34 Yield(%)
1	C ₆ H ₅	CO ₂ Me	Me	32a 10	-- --	34a 60
2	C ₆ H ₅	CO ₂ Et	Me	32c 12	33a 11	34b 36
3	C ₆ H ₄ -OMe(4)	CO ₂ Et	Me	32d 30	33b 21	34c 22
4	C ₆ H ₃ -(OMe) ₂ (3,4)	CO ₂ Et	Me	-- --	33c 14	34d 45
5	C ₆ H ₄ -NMe ₂ (4)	CO ₂ Et	Me	32g 9	-- --	34e 2
6	C ₆ H ₅	CO ₂ Et	Ph	-- --	33d 11	34b 69
7	C ₆ H ₄ -OMe(4)	CO ₂ Et	Ph	-- --	33e 14	34c 43
8	C ₆ H ₅	SO ₂ -C ₆ H ₄ -Me(4)	Me	-- --	-- --	34f 66
9	C ₆ H ₄ -OMe(4)	SO ₂ -C ₆ H ₄ -Me(4)	Me	32h 22	-- --	34g 18

Coumarin derivatives, which are fused pyrone derivatives, are essential intramolecular excimer-forming fluorescence derivatization reagents required for high-sensitivity analysis. The fused pyrone derivatives (**33a–e**) obtained from ketene dithioacetal show weak or no fluorescence; however, the pyrano[4,3-*b*]quinolizine derivatives (**36a–d**) shown in Scheme 11 exhibit strong fluorescence. These derivatives are easily synthesized *via* the reactions of pyridine-2-acetonitriles (**35a, b**) (an active methylene compound) with 2-pyrone derivatives (**9b, c, j**) in the presence of potassium carbonate as the base in DMSO. The reaction of these compounds results in the formation of an intramolecular hydrogen bond as shown in **32a–h**. However, although the pyrano[4,3-*b*]quinolizine derivative (**37**) does not possess a hydrogen bond, it exhibits fluorescence when synthesized *via* the reaction of **35b** with **17c**. Moreover, its decarboxylated derivative (**38**) is easily obtained by treating **37** with polyphosphoric acid (PPA). This derivative shows fluorescence although it does not contain an electro-withdrawing group. These results suggest that fluorescence is determined by the presence of a quinolizine ring. For similar reasons, **40a** and **b** synthesized *via* the reaction of 2-aminopyridine (**39**) with **17a** and **c** exhibited yellow fluorescence. Thus, stretching the conjugated structures of 2-pyrone derivatives affords near-infrared fluorescent dyes.³⁸

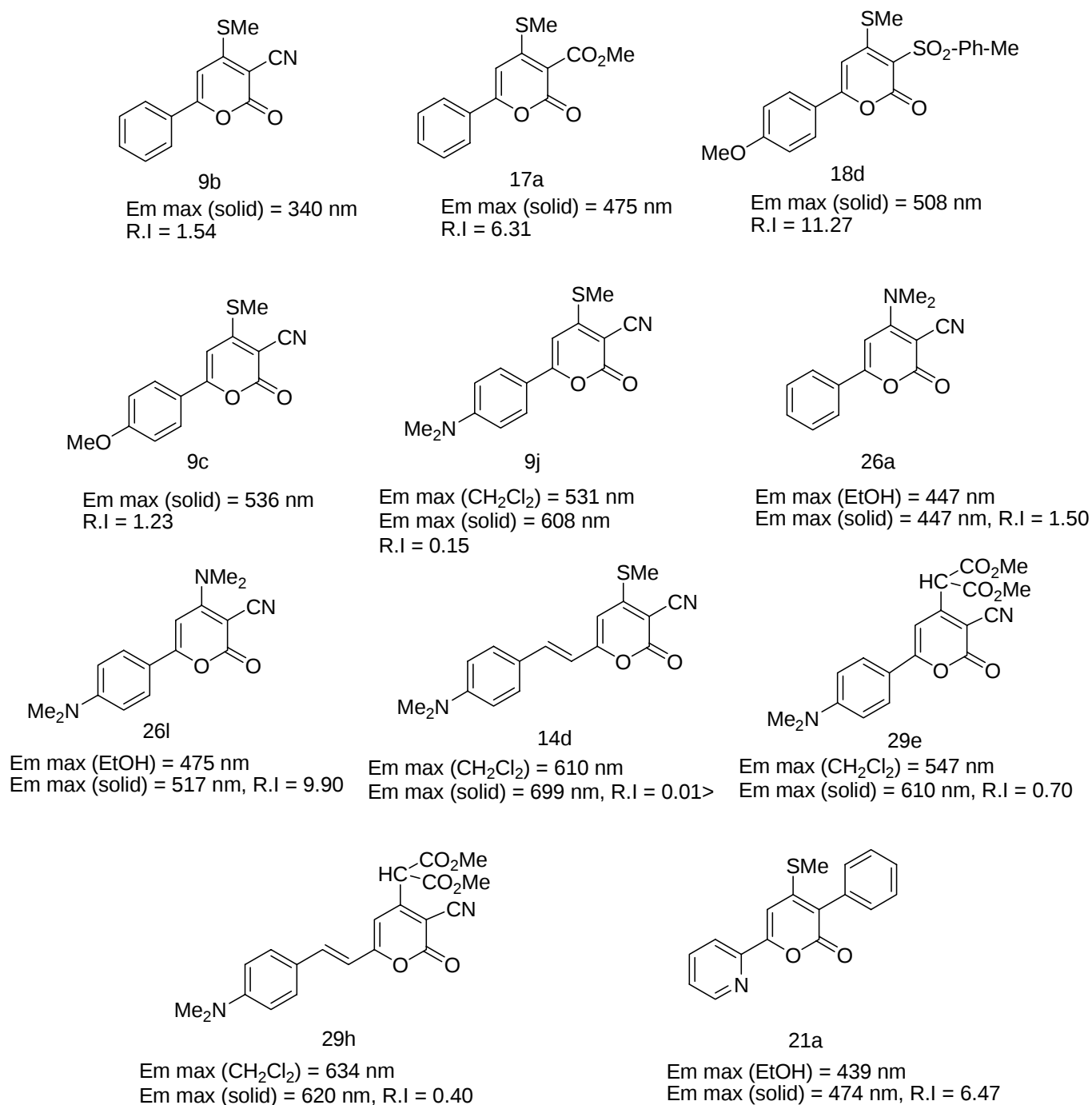


Scheme 11

3. FLUORESCENCE PROPERTY

In 2-pyrone derivatives, the arrangement of the substitution groups in the pyrone ring is very important for fluorescence. In particular, aryl groups such as the phenyl group at position 6 have a significant effect on the fluorescent properties. Compounds possessing alkyl groups such as the methyl group at position 6 exhibit no fluorescence. Figure 2 shows representative fluorescent 2*H*-pyrone derivatives. An aryl group such as the phenyl group is absolutely necessary at position 6 in order for it to emit fluorescence. Further, electro-donating groups such as an amino or alkoxy group on the aryl group influence the fluorescence

emission and bathochromic shifts. The dimethylamino derivative (**9j**) emits at 608 nm and the 6-(4-dimethylamino)styryl derivative (**14d**) emits at 610 nm in dichloromethane; both these are red fluorescent compounds (Figure 3). Electro-withdrawing groups such as the cyano group are necessary at position 3 of the pyrone ring. Moreover, ester derivatives (**17a**, **18d**) exhibit stronger fluorescence than cyano derivatives. Detailed structural analysis using X-ray crystallography has revealed that the intramolecular nonbonded S...O (SMe...CO₂Me) distance is 2.735 Å, which is shorter than the sum of



RI = relative intensity

Figure 2

the van der Waals distance for O and S (3.25 Å). This result suggests the presence of strong molecular stacking because of the planar nature of molecules, and this strong molecular stacking strongly influences the fluorescence properties. The same phenomenon is observed when compounds **32** and **33** are compared. Although compound **33** does not exhibit fluorescence in the solid state, compound **32**, which has an intramolecular H-bonded structure due to the C=O---H-O-C system, exhibits strong fluorescence. The reaction of 4-methylsulfanyl-2-pyrone derivatives with various nucleophilic reagents, as shown in Scheme 6–11 and Table 1–4, produces various derivatives by displacing the methylsulfanyl group at position 4 of the pyrone ring. Amino derivatives such as compounds **26a** and **26l** show stronger fluorescence; however, they also exhibit hypsochromic shifts. The malonate derivative (**29e**) exhibits a slight bathochromic shift and stronger fluorescence. In particular, the 6-(4-dimethylamino)styryl derivative (**29h**) emits at 620 nm, which is close to the ideal wavelength for red-fluorescent compounds used in EL devices. The derivatives not substituted at positions 5 have much greater fluorescence than compounds with an electro-withdrawing or electro-donating group at that position. This fact suggests that derivatives bridged at positions 5 and 6 exhibit no fluorescence. Our findings show that an electron-rich aryl group is necessary at position 6 of the pyrone ring for the emission of fluorescence, and derivatives containing electron-poor heterocycles such as the pyridyl group exhibit no fluorescence. However, the introduction of a phenyl group at position 3 of the 6-pyridyl-2-pyrone ring in **21a** affects the fluorescence expression. Consequently, in 2-pyrone derivatives, the introduction of various substituents at each position enables the control of the light-emission region and intensity, and also allows us to design pigments with various functionalities.³⁹

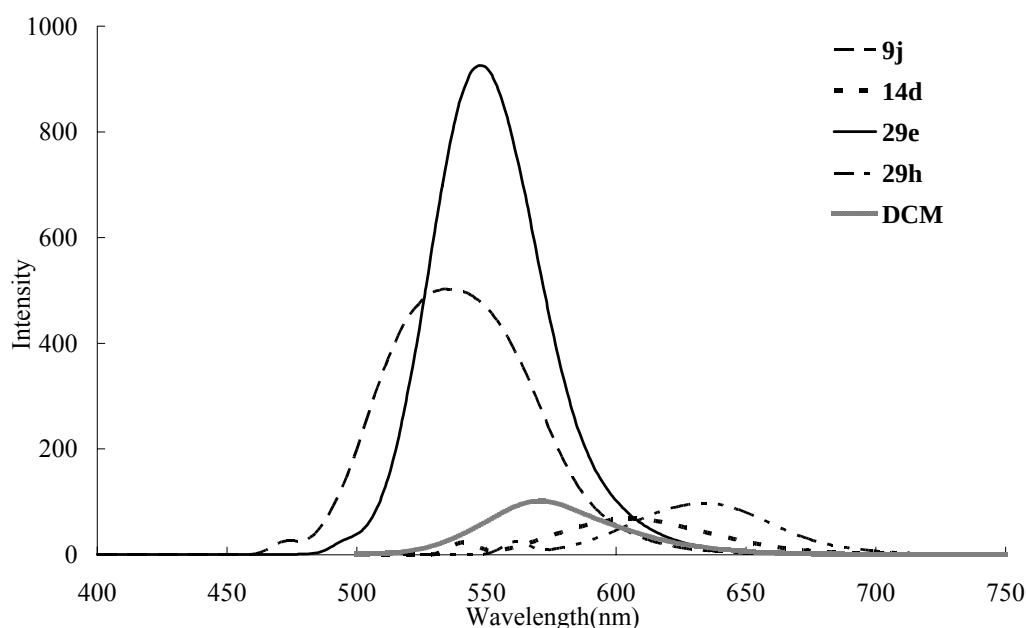


Figure 3. Comparison of fluorescent intensity of 2-pyrone derivatives **9j**, **14d**, **29e**, **29h** and DCM in dichloromethane.

4. CONCLUSION

Display devices using organic EL materials are making rapid progress in terms of practical use. Studies on novel organic EL compounds are underway, with particular focus on aromatic compounds. Heterocycles, in which a carbon atom in the aromatic ring is replaced by an oxygen or nitrogen atom, have also received considerable attention due to their diversity. In fact, many fluorescent heterocycles have been reported as diagnostic reagents or intramolecular excimer-forming fluorescence derivatization reagents for use in biological samples and pharmaceuticals. These findings will contribute to the development of organic EL materials. In addition, fluorescent heterocycles will be applicable not only to the synthesis of optimal organic EL materials but also to the synthesis of exotic materials that support the progress in technology, such as laser dyes and chemical luminous materials. We expect that ketene dithioacetals will be the best starting materials for the synthesis of various useful dyes. For almost 5 decades, there has been research on these reagents; however, their application to the synthesis of merocyanine dyes and chemical luminescence reagents is only a recent development. Therefore, these reagents will be applied in the development of useful fluorescent dyes.

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Masayori Hagimori was born in 1976, and obtained his M.Sc. degree in pharmaceutical science from Kyoto University, Japan. After working on drug metabolism at Takeda Research Institute of Banyu pharmaceutical CO., Ltd., he moved to Nagasaki International University, Japan, where he is now a research associate in pharmaceutical science, and then joined the group of Prof. Yoshinori Tominaga (Nagasaki University, Japan) in 2006. His current research interests include synthesis and characterization of functional heterocyclic molecules.



Naoko Mizuyama graduated from Nagasaki University, Japan, in pharmaceutical science, where she obtained her Ph.D. degree in environmental science in 2007 under the supervision of Prof. Yoshinori Tominaga in synthetic study of fluorescent heterocycles. She spent some years as a pharmacist at University of Occupational and Environmental Health, Japan, and then she moved to the department of hospital pharmacy of Saga University, Japan. Her research focuses on synthesis of fluorescent heterocycles from ketene-dithioacetals and chemical luminescence.



Yasuhiro Shigemitsu earned his B.Sc. in Industrial Chemistry and M.Sc. in Synthetic Chemistry from Tokyo University in 1989 and 1991, respectively. After doctoral research on quantum chemistry at Kyushu Institute of Technology, Japan, he moved Industrial Technology Center of Nagasaki (ITCN) where he is engaged in computational molecular design of functional dyes from 1996 up to present. From 1998 to 1999, he visited the Department of Chemistry, Odense University, Denmark, as a research fellow, in order to study polarization propagator methods under the supervision of Prof. J. Oddershede. He received the Ph.D. degree in Physical Chemistry in 2004 from Tokyo University under the supervision of Prof. K. Araki on theoretical molecular design of photo-functional compounds which was jointly conducted with Prof. Y. Tominaga of Nagasaki University. He currently works as a senior Research Scientist at ITCN and as an Associate Professor of Graduate school of Science and Engineering, Nagasaki University.



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Yoshinori Tominaga was born at Saga prefecture in Kyushu Island on October 25, 1945. He received his bachelor's degree at Faculty of Pharmaceutical Sciences, Nagasaki University in 1969 and then received his Ph.D. degree at Kyushu University in 1974, working with the late Professor Goro Kobayashi. His thesis dealt with the reaction of indole derivatives with carbon disulfide, which involved the new Diels-Alder reaction of dithiocarboxylates with dienophiles. In 1971-1975 he was a Special Fellow of Japan Society for the Promotion of Science. In 1975 he joined the faculty of Nagasaki University in Nagasaki. In 1981-1982 and 1991-1992 he was postdoctoral fellow under late Professor Raymon N. Castle at Brigham Young University and South Florida University. Dr. Yoshinori Tominaga's research interests have been in developing new synthetic reactions, use of ketene dithioacetals and carbon disulfide in heterocyclic chemistry, and synthesis of fluorescent materials. He has published over 200 papers, a number of reviews, and the author of books.