

One-Pot Synthesis and Fluorescence Properties of 2-Arylquinolines

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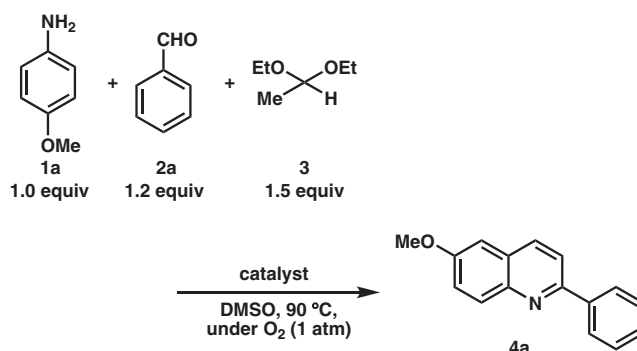
The one-pot synthesis of 2-arylquinoline with arylamines, arylaldehyde, and 1,1-diethoxyethane were studied using a catalytic amount ytterbium triflate. Various 2-arylquinolines showed fluorescence properties and the fluorescence was quenched by introducing the nitro group into aryl moiety of 2-arylquinolines.

Creation of new materials and development of their synthetic processes are fundamental problems in organic synthesis. Various multi-component coupling reactions (MCRs) forming carbon–carbon and carbon–heteroatom bonds in one-pot have been developed as useful tools to achieve with ease a chemical diversity of products, which are concerned with discovery of functional molecules with efficient acquisition and fine tuning of their chemical properties. Quinolines and their derivatives are a very important class of compounds and are widely used from medicines to functional materials. So far a variety of synthetic methods such as Skraup,¹ Doebner–von Miller,² Friedländer,³ Combes,⁴ Povarov,⁵ and Pfitzinger⁶ reactions have been reported.⁷ However, most synthetic methods proceed under strong acid or basic conditions, therefore the methods cannot be applied to molecules having acid-sensitive functional groups. We are interested in transition or rare earth metal catalyzed carbon–carbon bond forming reactions which proceed under mild conditions in an environmentally benign way.⁸ In recent years we have found that iridium- and ytterbium complexes catalyze one-pot three-component coupling reactions to give multi-substituted quinolines⁹ and 2-arylquinolines without substituents at the 3-position with strong fluorescence properties. In this paper we describe a facile synthetic method for 2-arylquinolines and the relationship between structure and fluorescent properties.

Results and Discussion

One-Pot Synthesis of 2-Arylquinolines in the Presence of Various Catalysts. At first we optimized the one-pot three-component coupling reaction with various metal or acid catalysts and results of the reactions of *p*-anisidine (**1a**), benzaldehyde (**2a**), and 1,1-diethoxyethane (**3**) are shown in Table 1. When the reaction was carried out using Yb(OTf)₃ in DMSO under oxygen at 90 °C, 6-methoxy-2-phenylquinoline (**4a**) was obtained in 55% yield (Entry 1). 1,1-Diethoxyethane (**3**) was effective as a precursor of enolizable acetaldehyde equivalent. However, in the reaction using acetaldehyde and ethyl vinyl ether the yields were decreased to 27% and 42% respectively (Entries 2 and 3). The reaction with trivalent

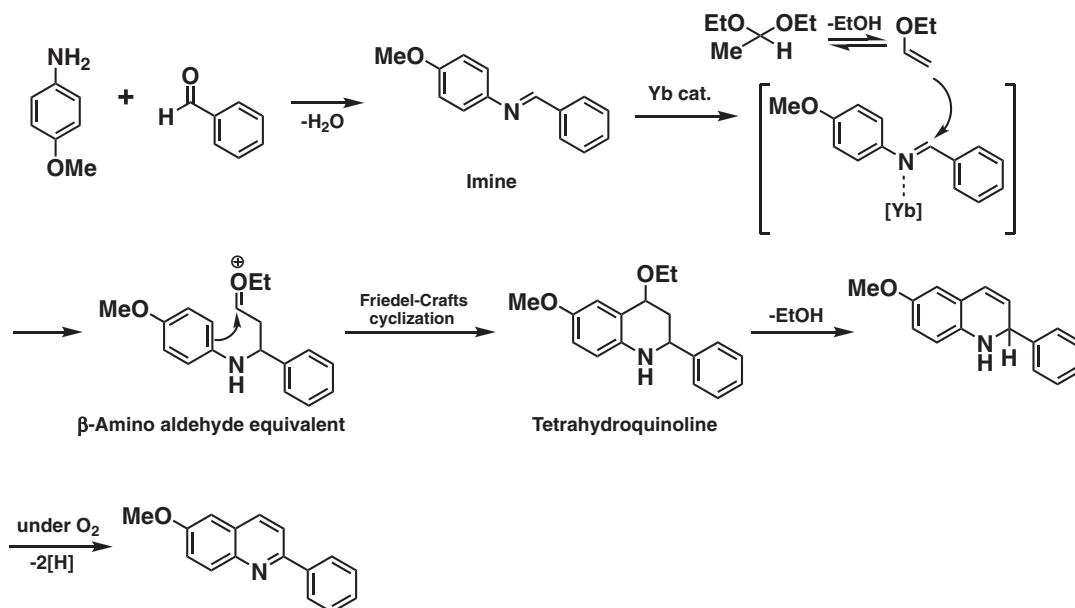
Table 1. One-Pot Synthesis of 2-Phenylquinolines with Various Catalysts



Entry	Catalyst (mol %)	Yield ^{a),b)}
1	Yb(OTf) ₃ (5)	55
2		27 ^{c)}
3		42 ^{d)}
4	[IrCl ₂ (H)(cod)] ₂ (5)	37
5	Ir(acac) ₃ (5)	49
6	[RhCl(cod)] ₂ (5)	29
7	Ru(acac) ₃ (5)	37
8	ZnCl ₂ (5)	54
9	SnCl ₂ (5)	30
10	TiCl ₄ (5)	33
11	HCl in 1,4-dioxane (5)	46

a) The yields were determined by GC. b) 1,2,4-Trimethylbenzene was used as an internal standard. c) Acetaldehyde was used instead of **3**. d) Ethyl vinyl ether was used instead of **3**.

iridium complexes [IrCl₂(H)(cod)]₂ and Ir(acac)₃ gave **4a** in 37% and 49% yields respectively (Entries 4 and 5). Reactions with late transition metal complexes [Rh(cod)Cl]₂ and Ru(acac)₃ did not give satisfactory results to afford **4a** in 29% and 37% yields respectively (Entries 6 and 7). Other Lewis acids such as SnCl₂ and TiCl₄ did not give satisfactory results, i.e., **4a** was obtained in 30% and 33% yields (Entries 9 and 10). ZnCl₂ is an efficient catalyst to give **4a** (54% yield,



Scheme 1. Plausible reaction mechanism of formation of 6-methoxy-2-phenylquinoline.

Entry 8), however, it is considerably hygroscopic. Recently, Baba et al. reported that a small amount of HCl catalyzed quinoline synthesis.¹⁰ When a catalytic amount of HCl in 1,4-dioxane was used, **4a** was obtained in 46% yield (Entry 11). Although Ir(acac)₃ and ZnCl₂ have enough Lewis acidity for activation of the imine moiety to give **4a** in similar yields, Yb(OTf)₃ is more convenient to handle because of its stability and tolerance to air and moisture. Therefore synthesis of other quinolines were carried out with Yb(OTf)₃.

A plausible reaction mechanism of 6-methoxy-2-phenylquinoline synthesis is shown in Scheme 1. At first, dehydration of *p*-anisidine and benzaldehyde proceeds to give the imine. The vinyl ether formed by elimination of ethanol from the acetal attacks the Yb-activated imine, and subsequent Friedel–Crafts cyclization of corresponding β -amino aldehyde equivalent proceeds to give tetrahydroquinoline. Finally auto-oxidation proceeds to give 6-methoxy-2-phenylquinoline. The atmospheric oxygen plays a role as an oxidant for dehydrogenation in this reaction mechanism. As shown in the mechanism the reaction requires Yb(OTf)₃ catalyst and oxygen as a “green” oxidant and ethanol is generated as sole by-product.

Ytterbium-Catalyzed One-Pot Synthesis of 2-Arylquinolines. The reactions of *p*-anisidine (**1a**), various arylaldehyde **2**, and 1,1-diethoxyethane (**3**) in the presence of a catalytic amount of Yb(OTf)₃ at 90 °C under oxygen atmosphere were carried out to afford the corresponding 6-methoxy-2-arylquinolines **4** in satisfactory yields. The results are summarized in Table 2 and various substituted quinolines were obtained.

The reaction with 4-(methoxymethoxy)benzaldehyde (**2b**) gave the corresponding MOM-protected 2-arylquinoline **4p** in 14% yield, and a deprotected 2-arylquinoline **4q** in 25% yield, which was caused by acid hydrolysis of **4p** with Yb(OTf)₃ or trace amount of trifluoromethanesulfonic acid from the catalyst (Scheme 2).

For comparison of fluorescence properties of 2-arylquinolines, several 2-arylquinoline derivatives were also synthesized.

The reduction of the nitro group in **4c** using Pd/C–H₂ gave the quinoline amine **4r** in 76% yield (Scheme 3).

The reaction with 2,4-dimethoxyaniline (**1b**) and *N,N*-dimethyl-*p*-phenylenediamine (**1c**), instead of *p*-anisidine, gave the corresponding 2-phenylquinoline derivatives **4s** and **4t** in 52% and 27% yields (Table 3).

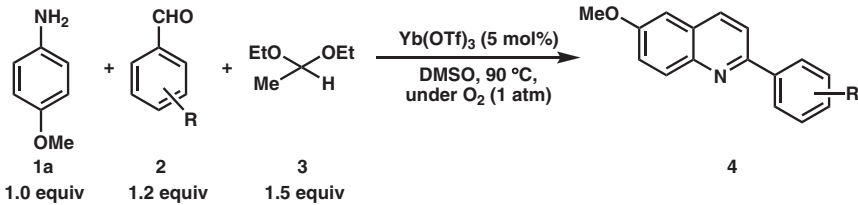
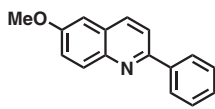
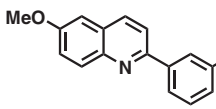
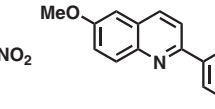
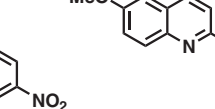
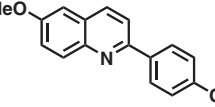
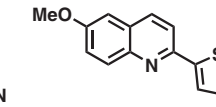
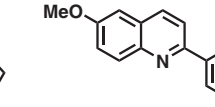
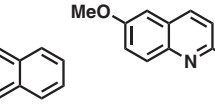
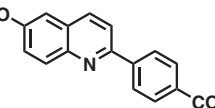
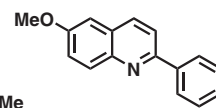
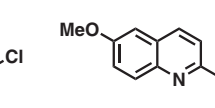
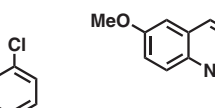
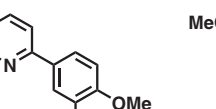
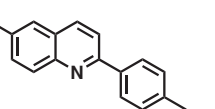
Synthesis of 2-Aryl-*N*-methylquinolinium and 2-Arylquinoline *N*-Oxide Derivatives. For the comparison of fluorescent properties 2-arylquinoline derivatives, **5a** and **5b**, were prepared. As shown in Scheme 3, *N*-methylation of 6-methoxy-2-phenylquinoline (**4a**) with methyl trifluoromethanesulfonate gave the corresponding 2-aryl-*N*-methylquinolinium triflate salt **5a** in 80% yield.¹¹ On the other hand, 6-methoxy-2-phenylquinoline *N*-oxide (**5b**) was obtained via the treatment of **4a** with mCPBA in 56% yield¹² (Scheme 4).

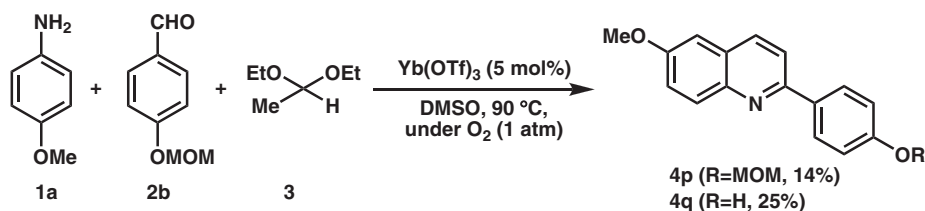
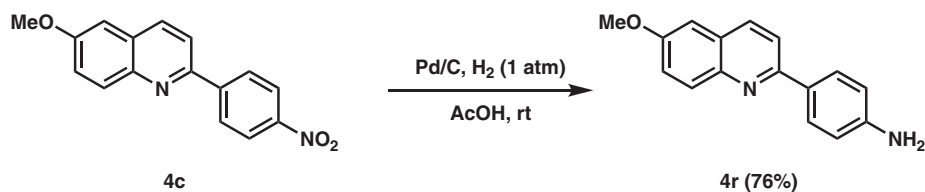
Fluorescent Properties of 2-Arylquinolines. Fluorescence of synthesized 2-arylquinolines was measured in CHCl₃ or DMSO solutions (The details of the measurement conditions can be found in Supporting Information). Most of the 2-arylquinolines were excited at 320 nm. All fluorescence quantum efficiencies were obtained with the following equation (F denotes the area under the fluorescence band ($F = \sum I_{\text{ex}}(\lambda)$), where $I_{\text{ex}}(\lambda)$ is the fluorescence intensity at each emission wavelength), A denotes the absorbance at the excitation wavelength, and n denotes the refractive index of the solvent).¹³

$$\Phi_{\text{X}} = \Phi_{\text{st}} \cdot \left(\frac{F_{\text{X}}}{F_{\text{st}}} \right) \cdot \left(\frac{A_{\text{st}}}{A_{\text{X}}} \right) \cdot \left(\frac{n_{\text{X}}^2}{n_{\text{st}}^2} \right) \quad (1)$$

As shown in Table 4, 2-phenylquinoline (**6**) had a large Stokes shift and does not show fluorescence, however by introducing a methoxy group in the 6-position of the quinoline ring, Φ of **4a** is increased because of the increase of electron density of the quinoline rings (Entries 1 and 2). More electron-rich quinolines **4s** and **4t** also showed good Φ s and **4t** showed a large Stokes shift (Entries 3 and 4). From these results, the electron density of the quinoline ring may cause the high fluorescence intensity. Surprisingly, 3-ethyl-6-methoxy-2-phenyl-

Table 2. Yb-Catalyzed One-Pot Synthesis of 6-Methoxy-2-arylquinolines with Various Arylaldehydes

			
Product (Yield ^{a)})			
			
4a (50%)	4b (39%)	4c (49%)	4d (11%)
			
4e (50%)	4f (46%)	4g (50%)	4h (48%)
			
4i (24%)	4j (54%)	4k (55%)	4l (52%)
			
4m (43%)	4n (43%)	4o (40%)	

a) Isolated yields based on **1a**.**Scheme 2.** Synthesis of 4-(6-methoxyquinolin-2-yl)phenol.**Scheme 3.** Hydrogenation reduction of **4c**.

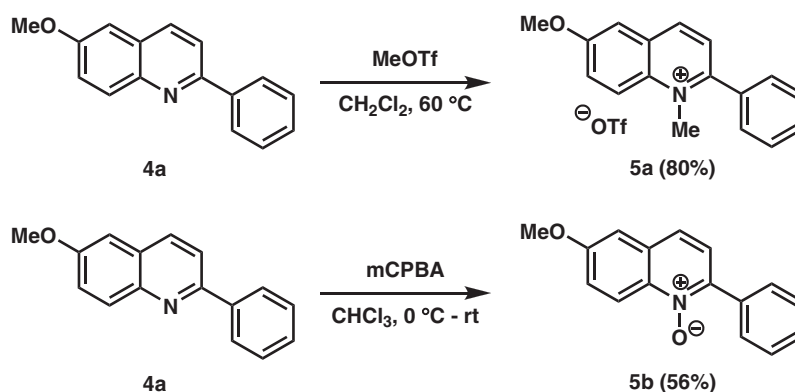
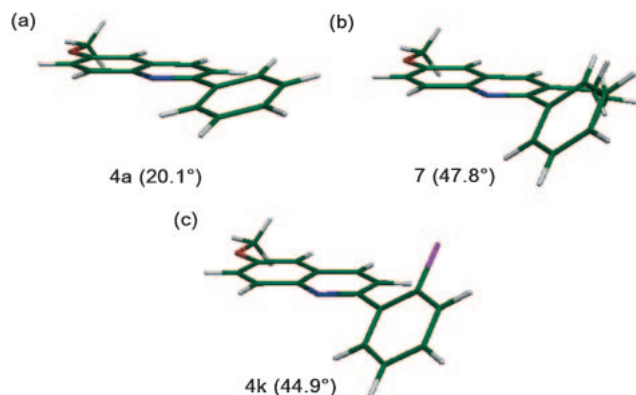
quinoline¹⁴ (**7**) and 2-(2-chlorophenyl)-6-methoxyquinoline (**4k**) showed low fluorescence (Entries 5 and 6). The dihedral angle of the quinoline scaffold and aryl moiety had a possibility of correlation with fluorescence. Then the dihedral angles were calculated with 6-31G**/B3LYP by Gaussian 98.¹⁵ From

the results of calculations, deconjugation between quinoline scaffold and aryl moiety occurred with the increase of dihedral angle, which may cause low fluorescence (Figure 1). In recent years, Nagano et al. reported notable fluorescein–xanthene fluorescence probes. In these probes, benzene moiety and

Table 3. Yb-Catalyzed One-Pot Synthesis of 2-Phenylquinolines with Various Arylamines

4a (50%)	4s (52%)
4t (27%)	

a) Isolated yields based on arylamine 1.

**Scheme 4.** Synthesis of 2-aryl-*N*-methylquinolinium and 2-arylquinoline *N*-oxide derivatives.**Figure 1.** Structures of 3-alkyl-2-arylquinoline and 2-arylquinolines and its dihedral angles; (a) 6-methoxy-2-phenylquinoline (**4a**) (Entry 2 in Table 4), (b) 3-ethyl-6-methoxy-2-phenylquinoline (**7**) (Entry 5 in Table 4), and (c) 2-(2-chlorophenyl)-6-methoxyquinoline (**4k**) (Entry 6 in Table 4) (Green: C, White: H, Red: O, Blue: N, Purple: Cl, dihedral angle is shown in the parenthesis).

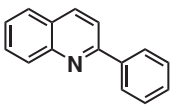
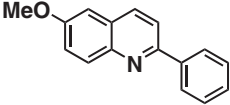
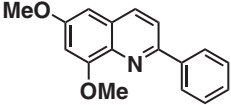
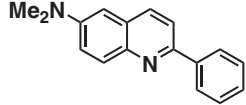
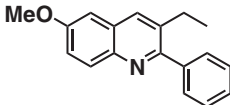
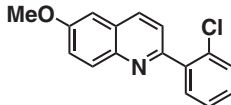
fluorophore were orthogonal to each other and played an important role to photoinduced electron transfer (PeT).¹⁶

Next, 6-methoxy-2-arylquinolines **4** were ordered in LUMO energies levels (calculated with 6-31G**/B3LYP by Gaussian 98¹⁵). As shown in Table 5, **4r** showed a large Stokes shift

in this series. The synthesized 6-methoxy-2-arylquinolines **4r**, **4o**, and **4q** having electron-donating groups of the aryl moiety (Entries 1, 2, and 4) showed good Φ_s (0.57, 0.61, and 0.54) relatively, and 2-arylquinolines **4f**, **4j**, **4l**, and **4h** having electron-withdrawing group of the aryl moiety (Entries 5, 6, 7, and 8) showed Φ_s in 0.23, 0.44, 0.48, and 0.41, however other quinolines **4g**, **4i**, and **4e** showed good Φ_s (0.77, 0.60, and 0.64) (Entries 9, 10, and 11). These differences were caused by steric hindrance or electron repulsion of the aryl moiety. Furthermore, quenching of fluorescence was observed by introducing nitro group(s) in the 2-aryl moiety (Entries 12, 13, 14, and 15).

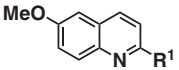
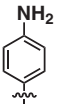
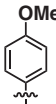
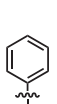
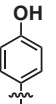
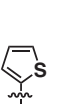
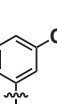
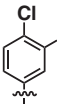
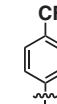
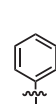
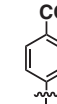
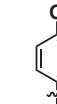
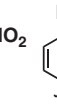
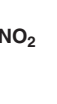
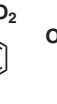
Furthermore, 2-aryl-*N*-methylquinolinium and 2-arylquinoline *N*-oxide derivatives **5a** and **5b** showed lower fluorescence than the corresponding quinoline **4a** (Table 6). As shown above, 2-arylquinolines including a nitro group in aryl moiety had no fluorescence in spite of energy absorption. In recent years, Albini et al. reported intramolecular electron transfer in the photochemistry of some nitrophenyldihydropyridines.¹⁷ We supposed that the photochemical reaction with the nitro group might occur in 2-arylquinoline and the fluorescence would be quenched by generation of nitro radical species. Nagano et al. succeeded to observe radical species of fluorescein under UV irradiation with ESR.¹⁸ To confirm the radical species, we also tried to measure ESR spectra, but in this case no mean signals were observed.

Table 4. Fluorescence Properties of 2-Arylquinoline Derivatives

						
	6	4a	4s	4t	7	4k
Entry	1	2	3	4	5	6
$\lambda_{\text{abs,max}}/\text{nm}$	258	264	272	276	242	256
$\lambda_{\text{em,max}}/\text{nm}^{\text{a)}$	443.5	370	400	433, 443	360	369
$\varepsilon/\text{M}^{-1} \text{cm}^{-1}$	36299	39616	44462	32364	32393	28475
$\Phi^{\text{b)}$	0.002	0.39	0.74	0.76	0.04	0.12

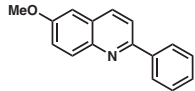
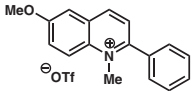
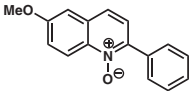
a) Excited at 320 nm. b) Obtained by calculation, based on the quinine sulfate as the standard ($\Phi_{\text{q}} = 0.55$).

Table 5. Fluorescence Properties of 6-Methoxy-2-arylquinolines

															
															
	4r	4o	4a	4q	4f	4j	4l	4h	4g	4i	4e	4m	4n	4c	4d
Entry	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\lambda_{\text{abs,max}}/\text{nm}$	240, 296	276	264	280	284	264	270	264	264	276	276	270	264	242	240
$\lambda_{\text{em,max}}/\text{nm}^{\text{a)}$	425	382	370	396	388	369	372	370	378	379	380	—	—	—	—
$\varepsilon/\text{M}^{-1} \text{cm}^{-1}$	21372	28647	39616	30676	21307	38239	38263	36808	55529	33751	36240	38437	42409	30110	14449
$\Phi^{\text{b)}$	0.57	0.61	0.39	0.54	0.23	0.44	0.48	0.41	0.77	0.60	0.64	0.003	0.000	0.004	0.000
LUMO energy /hartrees ^{c)}	0.01287	0.00404	0.00263	0.00051	-0.00840	-0.01343	-0.0248	-0.02712	-0.03598	-0.04372	-0.05242	-0.07604	-0.08568	-0.0895	-0.11535

a) Excited at 320 nm. b) Obtained by calculation, based on the quinine sulfate as the standard ($\Phi_{\text{q}} = 0.55$). c) LUMO energy levels were calculated with 6-31G**/B3LYP by Gaussian 98.

Table 6. Fluorescence Properties of 2-Aryl-*N*-methylquinolinium and 2-Arylquinoline *N*-Oxide Derivatives

			
	4a	5a	5b
Entry	1	2	3
$\lambda_{\text{abs,max}}/\text{nm}$	264	260	242, 268
$\lambda_{\text{em,max}}/\text{nm}^{\text{a)}$	370	459	371.5
$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	39616	30288	23740
$\Phi^{\text{b)}$	0.39	0.15	0.01

a) Excited at 320 nm. b) Obtained by calculation, based on the quinine sulfate as the standard ($\Phi_{\text{q}} = 0.55$).

Conclusion

In conclusion, we have found Yb(III)-catalyzed one-pot synthesis of 2-arylquinolines in satisfactory yields and also synthesized 2-aryl-*N*-methylquinolinium and 2-arylquinoline *N*-oxide derivatives. Most synthetic 2-arylquinolines had fluorescence properties, although the 2-arylquinolines which have a nitro group in 2-aryl moiety showed no fluorescence. Further application for the fluorescent probe is undergoing.

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Supporting Information

Typical synthesis procedure for Yb-catalyzed 2-arylquinoline synthesis, other synthesis procedures for 2-arylquinoline derivatives, spectral data, fluorescent properties, and parameters of the coordinates of optimized structures of **4a**, **7**, and **4k**. This material is available free of charge on the web at: <http://www.csj.jp/journals/bcsj/>.

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