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ARTICLE

Energy transfer-driven regioselective synthesis of functionalized phenanthridines by visible-light Ir photocatalysis

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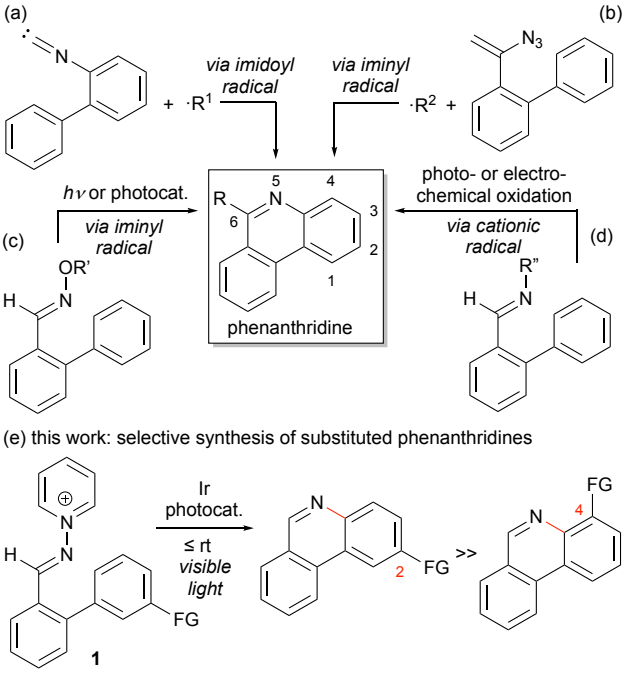
A photocatalytic strategy for regioselective synthesis of phenanthridine derivatives from *N*-(2-arylbenzylidenamino)pyridinium salts has been developed. Utilization of an Ir photocatalyst, [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (dF(CF$_3$)ppy = 3,5-difluoro-2-(5-(trifluoromethyl)-2-pyridyl)phenyl, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine), is a key to successful reactions. The excited Ir catalyst does not serve as a 1e-redox reagent but as an energy donor toward the pyridinium salts. The present system can be also applied to one-pot synthesis of Trisphaeridine, an *anti*-cancer drug.

Introduction

Phenanthridine scaffolds are frequently observed in natural alkaloids and therapeutically active compounds. Thus, a variety of synthetic strategies have been developed so far and new methodologies for selective synthesis are still in demand.[1] Recently, radical-mediated protocols from several precursors have been reported as depicted in Scheme 1. Radical addition to biaryl isonitrile (Scheme 1a)[1b,2] and vinyl azide (Scheme 1b)[3] followed by cyclization is an attractive method for synthesis of phenanthridines, with which selective introduction of various functional groups at the 6-position is viable. In addition, 1e-redox reactions of oxime or imine precursors (Scheme 1c and d),[4,5,6d] which are easily accessible and less hazardous and toxic than the above-mentioned chemicals, also have become useful methods for construction of nitrogen-containing polyaromatics including phenanthridines. Interestingly, according to the seminal works by the groups of Yu and Xu, the *O*-acyl oxime and imine precursors derived from *meta*-MeO-substituted 1,1'-biphenyl-2-carbaldehyde (*vide infra*, see Scheme 3a) afforded the corresponding phenanthridines with the completely opposite regioselectivity (2-:4-substituted product = 1:3 (Scheme 1c), >20:1 (Scheme 1d)).[4b,5b] The selectivity should be strongly influenced by the involved radical intermediate, *i.e.*, iminyl radical[6] *vs.* cationic radical of oxime or imine precursors. However, there were only limited studies on the control of the selectivity at the 2- and 4-positions in the radical-mediated synthesis of phenanthridines.

Recently, synthetic methods through redox reaction of designed pyridinium salts have been well studied because the system can be applied to generation of the corresponding various *C*-, *O*-, and *N*-centered radicals.[7] We developed aroyloxylation and amidation with the corresponding *N*-aroyloxy- and amidyl-pyridinium salts by visible-light photoredox catalysis.[8] In this context, we designed *N*-(2-arylbenzylidenamino)pyridinium salts **1** as the precursors for photocatalytic synthesis of phenanthridines (Scheme 1e). Herein we will describe photocatalytic reaction of **1**, leading to regioselective synthesis of functionalized phenanthridines, especially, 2-substituted products. It is notable that the reaction turned out to be initiated by energy transfer from the photoexcited catalyst rather than electron transfer.



Scheme 1. Radical-mediated synthesis of phenanthridines.

Results and discussion

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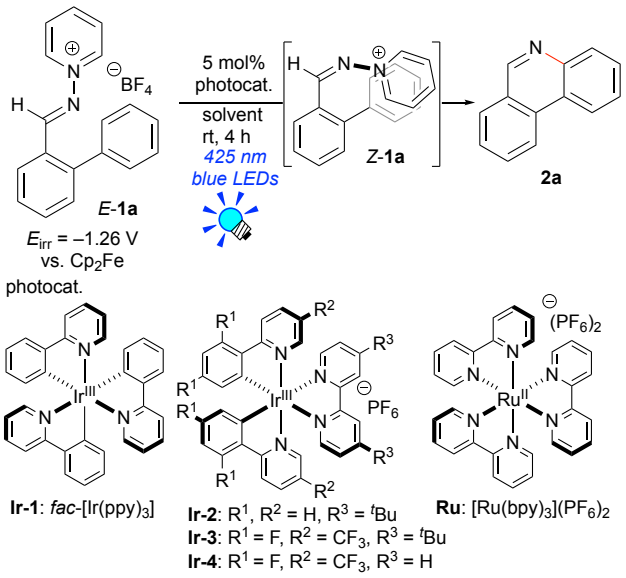
Table 1. Examination of the reaction conditions.[a)]

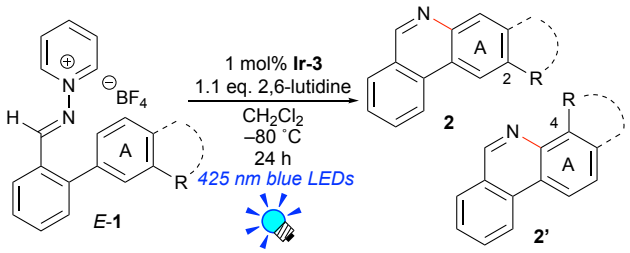


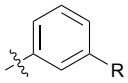
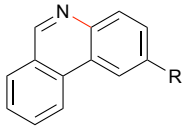
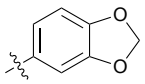
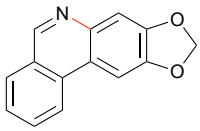
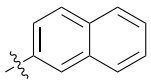
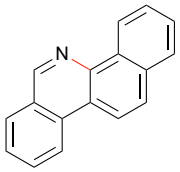
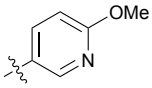
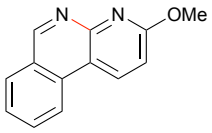
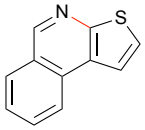
Entry	Photocat.	Solvent	E^*_{ox}[b)]	E_T[c)]	Yield of **2a**/%
1	**Ir-1**	CD_2Cl_2	–2.14	232	0
2	**Ir-2**	CD_2Cl_2	–1.37	209	0
3	**Ir-3**	CD_2Cl_2	–1.30	254	85 (76[e)], 41[f)])
4	**Ir-4**	CD_2Cl_2	–1.26	253	78
5	**Ru**	CD_2Cl_2	–1.22	196	0
6	**Ir-3**	CD_3CN			76
7	**Ir-3**	acetone-d_6			54
8	**Ir-3**	dmso-d_6			45
9[g)]	**Ir-3**	CD_2Cl_2			0
10	–	CD_2Cl_2			10

[a)] Reaction conditions: A mixture of photocatalyst (2.5 μmol, 5 mol%) and **1a** (50 μmol) dissolved in a deuterated solvent (0.50 mL) was irradiated by 3 W blue LEDs (λ = 425 ± 15 nm) at rt for 4 h. [b)] Reported reducing power in the excited state (E^*_{ox} V vs. Cp_2Fe). E^*_{ox} (vs. Cp_2Fe) = E^*_{ox} (vs. SCE) – 0.41.[9] [c)] Triplet energy (E_T [kJ mol^{-1}]) was estimated by the emission spectra ($\lambda_{em\ max}$). [d)] Yields were determined by ^{1}H NMR spectroscopy using Me_2SO_2 as an internal standard. [e)] Isolated yield, reaction time = 8 h. [f)] A large-scale reaction (2.5 mmol of **1a**), reaction time = 48 h. [g)] In the dark.

We initially examined photocatalysts for the reaction of (*E*)-*N*-(2-phenylbenzylidenamino)pyridinium salt (*E*-**1a**)[10] at room temperature under visible-light irradiation with blue LEDs (λ = 425 nm). Taking account of the redox potential of **1a** (E_{irr} = –1.26 V vs. Cp_2Fe), Ir photocatalysts with high reducing power (E^*_{ox}) in the excited state, **Ir-1** (E^*_{ox} = –2.14 V)[9d] and **Ir-2** (E^*_{ox} = –1.37 V),[9b] were tested in CD_2Cl_2. But, to our surprise, the reactions did not proceed at all (entries 1 and 2 in Table 1). In contrast, **Ir-3** (E^*_{ox} = –1.30 V)[9c,f] and **Ir-4** (E^*_{ox} = –1.26 V)[9e] efficiently gave the desired phenanthridine product **2a** in 85 and 78% NMR yields, respectively (entries 3 and 4). A preparative-scale experiment afforded **2a** in 76% isolated yield (entry 3). It is noteworthy that monitoring the reaction in the presence of **Ir-3** and **Ir-4** by NMR spectroscopy revealed formation of an intermediate, which is assigned to *Z*-**1a**. Efficient isomerization from *E*-**1a** to *Z*-**1a** was observed prior to formation of **2a** (see the Supporting Information). In addition, photocatalysts with a larger triplet energy (E_T = 254 kJ mol^{-1} (**Ir-3**), 253 kJ mol^{-1} (**Ir-4**), 232 kJ mol^{-1} (**Ir-1**), and 209 kJ mol^{-1} (**Ir-2**) promoted the present reaction smoothly (entries 1–4).

Table 2. The scope of the present photocatalytic reaction.[a)]

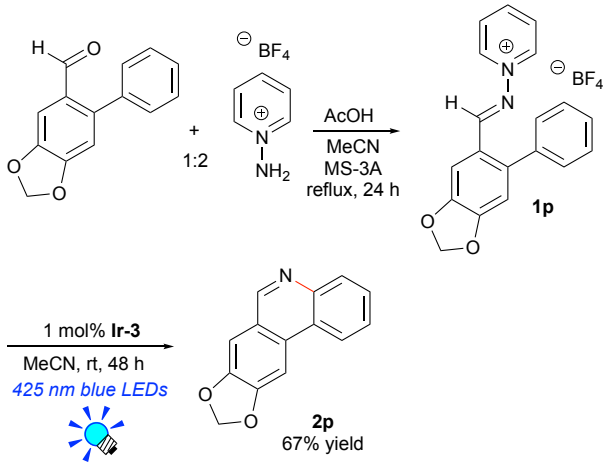


Entry	Aromatic A	**2** (major product)	Yield/% (**2**:**2'**)[b)]
1			
	1b (R = OMe)	**2b** (R = OMe)	63 (6:1)
2	**1c** (R = NHAc)	**2c** (R = NHAc)	57[c,d,e)] (5:1)
3	**1d** (R = Me)	**2d** (R = Me)[10]	66[f)], single isomer
4	**1e** (R = ^{i}Pr)	**2e** (R = ^{i}Pr)	82, single isomer
5	**1f** (R = Ph)	**2f** (R = Ph)	36[d)] (3:1)
6	**1g** (R = F)	**2g** (R = F)	74[h,g)], single isomer
7	**1h** (R = Cl)	**2h** (R = Cl)	73[d,e)] (2:1)
8	**1i** (R = Br)	**2i** (R = Br)	48[d,e)] (3:1)
9	**1j** (R = CF_3)	**2j** (R = CF_3)	30[e,h,i)] (3:1)
10	**1k** (R = NO_2)	**2k** (R = NO_2)	0[f)]
11			
	1l	**2l**	70, single isomer
12			
	1m	**2m**	74, single isomer
13			
	1n	**2n**	50[f,j)]
14			
	1o	**2o**	62, single isomer

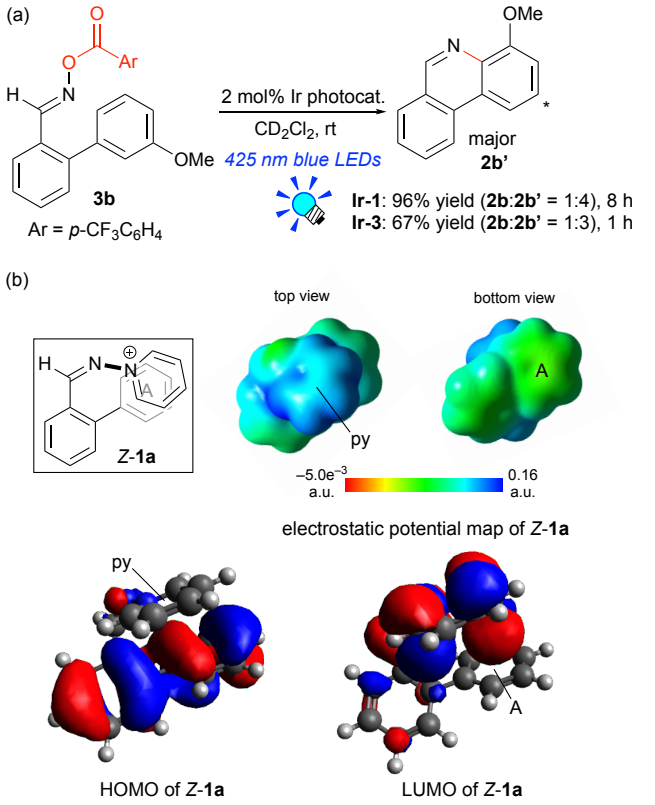
[a)] For the details of the conditions, see the Supporting Information. [b)] Yield was obtained after purification. Isomer ratios were determined by ^{1}H NMR spectroscopy for crude reaction mixtures. [c)] MeCN was used as a solvent. [d)] Reaction time = 48 h. [e)] Reaction temperature = 0 °C. [f)] Reaction temperature = rt, [g)] NMR scale. [h)] Reaction time = 96 h, [i)] Isolated yield of the major isomer. [j)] The crude mixture contained a trace amount of an unidentified product.

A Ru photocatalyt, $[Ru(bpy)_3](PF_6)_2$, with lower reducing power (E^*_{ox} = –1.22 V)[9a] and triplet energy (E_T = 196 KJ mol^{-1}) did not induce the reaction at all (entry 5). Examination of solvent revealed that dichloromethane was the best (entries 6–8). Irradiation with visible light and the presence of the photocatalyst are vital for efficient reaction (entries 9 and 10).

Next, we explored the reaction scope, especially reactions of precursors bearing one substituent at the *meta*-position of the aromatic ring A, which would cyclize at the two different positions, thus creating regioisomers (2- (**2**) or 4-substituted phenanthridines (**2'**)). First, the reaction of the precursor bearing MeO group (**1b**) at room temperature afforded the phenanthridine resulting from the favorable cyclization at the *para*-position with respect to the MeO group (93% NMR yield, **2b**:**2b'** = 1.4:1.0). The selectivity was improved by carrying out the reaction at lower temperature. The preparative-scale reaction at –80 ˚C afforded the corresponding phenanthridine (**2b** and **2b'**) in 63% yield with better regioselectivity (6:1, entry 1 in Table 2). The present reaction system preferentially afforded 2-substituted phenanthridines **2** with good to excellent regioselectivity regardless of the electronic nature of the substituent (entries 1–9 in Table 2). On the other hand, reactivity of **1** was significantly dependent on the substituent. In particular, electron-withdrawing groups required higher temperature than –80 ˚C and longer reaction time for production of the phenanthridines, (entries 6–9) and NO_2 derivative (**1k**) did not yield the product even at room temperature (entry 10). Noticeably, all precursors underwent the *E*-to-*Z* isomerization. The acetamido (**1c**), methyl (**1d**), ^{i}Pr (**1e**), Ph (**1f**), F (**1g**), Cl (**1h**), Br (**1i**), and CF_3 (**1j**) substituted derivatives regioselectively gave the corresponding phenanthridines (30–82% yields, 2:1 to a single isomer). (entries 2–9). It should be noted that this selectivity was in contrast to the simple iminyl radical cyclization under photochemical conditions[4a,b] but was similar to those obtained from the reaction *via* cationic radicals.[5]



Scheme 2. Application to one-pot synthesis of Trisphaeridine (**2p**).

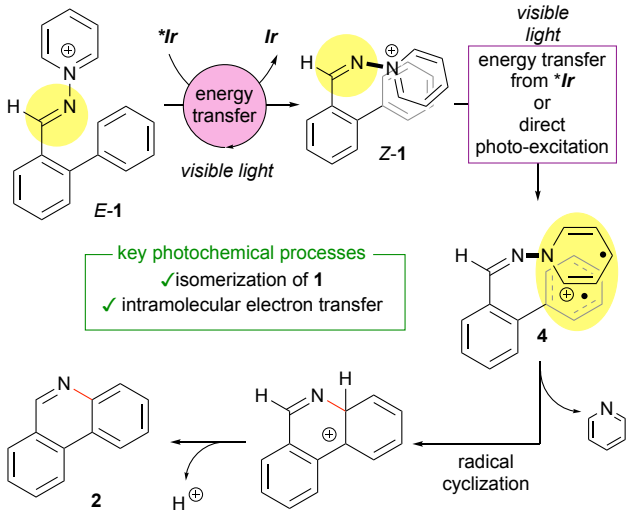


Scheme 3. Control experiments (a) photocatalytic reaction of *O*-acyl oxime using Ir catalysts and (b) computational analysis for *Z*-**1a** (only cationic part).

Then, we also applied the present reaction to precursors linked at the *meta*- and *para*-position of the aromatic ring A. The 2,3-substituted phenanthridine **2l** was obtained in 70% yield as a single regioisomer from the reaction of methylenedioxybenzene derivative **1l** (entry 11). To our delight, selective synthesis of benzo-fuzed and heteroatom-doped phenanthridines was also viable. Benzo[c]phenanthridine (**2m**), benzo[c][1,8]naphthyridine derivatives **2n** and thieno[2,3-c]isoquinoline **2o** were obtained in 74, 50, and 62% yields, respectively (entries 12–14). These results show that the present photocatalytic system is highly compatible with various functionalities such as ether, amide, halogen, acetal, and heteroaromatic groups.[11]

To demonstrate utility of the present reaction system, one-pot synthesis of Trisphaeridine (**2p**) from the corresponding aldehyde was studied (Scheme 2). As a result, **2p** was obtained in 67% isolated yield from the corresponding aldehyde without purification at the stage of intermediate **1p**.

The triplet energy (E_T) of *E*-**1a** was estimated by DFT calculation (UB3LYP/6-311G+(2d,p)/CH_2Cl_2)[12] to be 234 kJ mol^{-1}, which was lower in energy than E_T of the photoexcited catalysts ***Ir-3** and ***Ir-4**, indicating that, taking into account of the irrelevance to the E^*_{ox} values discussed above, photoisomerization of *E*-**1a** was triggered by energy transfer from ****Ir*** rather than electron transfer, as was also supported by the emission quenching experiment (see the Supporting Information). Simple cyclization of the iminyl radical intermediate can be excluded, because the photocatalytic



Scheme 4. A possible reaction mechanism.

reaction of *O*-acyl oxime **3b** reported by Yu and co-workers under our reaction conditions produced the 4-substituted isomer **2b'** as a major product (**2b**:**2b'** = 1:3) in contrast to our photocatalytic system preferentially giving the other isomer **2b** (entry 1 in Table 2 and Scheme 3a).[13] It should be noted that **3b** did not undergo the *E*-to-*Z* photoisomerization under those reaction conditions. In addition, an electron-rich aromatic ring A significantly enhanced the present cyclization (Table 2). In one conformer obtained by DFT calculation of *Z*-**1a** (B3LYP/6-311G+(2d,p)/CH_2Cl_2)[12] shown in Scheme 3b, the distance between the nitrogen atom in the pyridinium ring and the *ipso* carbon atom in the aromatic ring A is 3.2 Å, suggesting possible cation-π interaction,[14] which was also supported by a 2D NOESY NMR spectrum of *Z*-**1a** (see the Supporting Information). In addition, the electrostatic potential map and frontier orbitals indicate that the aromatic ring A and the pyridinium unit would serve as an electron donor and an acceptor, respectively, as in electron donor-acceptor complex (EDA). [15]

Based on the obtained data and the previous reports,[4,5,8] a plausible reaction mechanism is illustrated in Scheme 4. First, energy transfer from the excited Ir photocatalyst (***Ir***) to precursor *E*-**1** causes isomerization to *Z*-**1**. One conformer of *Z*-**1** with the cation-π interaction is excited by energy transfer from the photoexcited catalyst ***Ir*** or direct excitation of *Z*-**1** to form radical intermediate **4**, which follows the homolytic N–N bond cleavage, leading to dissociation of pyridine and radical cyclization. It is considered that electronic properties of aromatic ring A significantly influence the above-mentioned intramolecular interaction and electron transfer. Thus, the mechanisms with respect to N–N bond cleavage and C–N bond formation might be different for electron-rich and -deficient aromatic rings. Finally, deprotonation produces phenanthridine **2**. The radical intermediate **4** plays an important role in the present regioselective cyclization, which resembles the *para*-selective S_NAr-type reactions *via* cationic aryl radical intermediates.[16]

Conclusions

We have developed a synthetic method for selectively substituted phenanthridines from *N*-(2-arylbenzylidenamino)pyridinium salts, in which the pyridinium moiety in the photoexcited *Z*-**1** accepts an electron from the terminal aryl group of the biaryl skeleton to generate the key radical intermediate. The Ir photocatalyst with higher triplet energy plays vital roles in the sensitization of the precursors through energy transfer. Further studies on photocatalytic synthesis of nitrogen-containing polyaromatics are underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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