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Photocatalytic Approach for Construction of 5,6-Dihydroimidazo[2,1-*a*]isoquinolines and Their Luminescent Properties

Zaibin Wang, Hanjie Li, Zhichao Wang, Muhammad Suleman, Yanguang Wang,* and Ping Lu*

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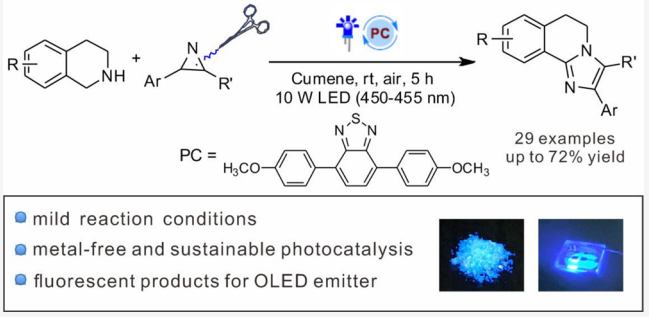
ABSTRACT: A visible-light-driven photoredox reaction of tetrahydroisoquinoline with 2*H*-azirines is described. 4,7-Bis(4-methoxyphenyl)benzo[*c*][1,2,5]thiadiazole, a benzothiadiazole (BTD) derived fluorophore, is used as an organic photoredox catalyst, and the reaction offers an efficient access to 5,6-dihydroimidazo[2,1-*a*]isoquinolines with a broad range of functional groups. The resulting 5,6-dihydroimidazo[2,1-*a*]-isoquinolines present strong photoluminecence in solutions and powders and could be applied in the fabrication of blue OLED devices.



INTRODUCTION

Because of the additional double bond in 2*H*-azirines in comparison with aziridines, 2*H*-azirines present much higher reactivity and are valuable precursors in modern organic synthesis.[1] In general, the ring of 2*H*-azirines could be isomerized and opened in two manners under heat, light, or transition metal catalysts. One leads to the formation of vinyl nitrenes via C−N cleavage,[2] while another forms nitrile ylides via C−C cleavage[3] as illustrated in Scheme 1A. In contrast to C−N and C−C cleavage of 2*H*-azirines, the C═N bond cleavage presents fewer examples. As one of the examples, transition-metal catalyzed formal [2 + 2] cycloadditions could selectively break the C═N bond, thanks to the highly reactive intermediate of 1-azabicyclo[2.1.0]pent-2-ene generated from the formal [2 + 2] cycloaddition between the C═N of 2*H*-azirines and electron-deficient triple bond of alkynes.[4] Based on these three strategies, various heterocycles, especially five-membered rings, have been effectively prepared. Recently, photoinduced reactions have been widely investigated due to being transition metal free and the environmental benign which fit the basic requirements of green chemistry. In the presence of a photosensitizer and UV or visible light, highly active species, 2*H*-azirines radical cation **A**, could be generated from 2*H*-azirines through single electron transfer and further isomerized into radical cation **B**[5] or radical cation **C**[6] depending on the substituents on the 2*H*-azirine ring (Scheme 1B). In this report, we tried the visible-light-driven reaction between tetrahydroisoquinolines and 2*H*-azirines using benzothiadiazole derivatives as organic photocatalysts. To our delight, the reaction furnished 5,6-dihydroimidazo[2,1-*a*]-isoquinolines with high efficiency. In our case, the C═N cleavage of 2*H*-azirines was observed (Scheme 1C).

RESULTS AND DISCUSSION

The initial trial was carried out between 1,2,3,4-tetrahydroisoquinoline (**1a**) and 2,3-diphenyl-2*H*-azirine (**2a**) in the presence of $Ru(bpy)_3Cl_2·6H_2O$ in air. After the cumene mixture was irradiated at 450−455 nm at room temperature for 10 h, 5,6-dihydroimidazo[2,1-*a*]isoquinoline **3a** was isolated in 59% yield (Table 1, entry 1). The structure of **3a** was determined by ^1H NMR, ^{13}C NMR, and HRMS and further established by the single crystal analysis of its analogs (**3l** and **3u**) (CCDC 2016722, 2050830). By altering the catalyst to other transition metal complexes, such as $Ru(bpy)_3(PF_6)_2$, $Ir(bpy)_3$, and $Ir(ppy)_2(bpy)PF_6$,[7] **3a** was afforded in similar yields (Table 1, entries 2−4). As the transition-metal-free photocatalysts such as Eosin Y[8] and 4CzIPN[9] were used, **3a** was isolated in lower yields of 43% and 40%, respectively (Table 1, entries 5 and 6). Benzothiadiazole (BTD) derived fluorophores **PC-1**[10] and **PC-2**[11] (Scheme 2) are seldom reported as photocatalysts. They present the maximum absorption wavelengths at 440 and 405 nm with a molar absorptivity of 2.26×10^4 and 1.21×10^4 L mol^{-1} cm^{-1}, respectively (Scheme 2, Figure S1). We then screened their

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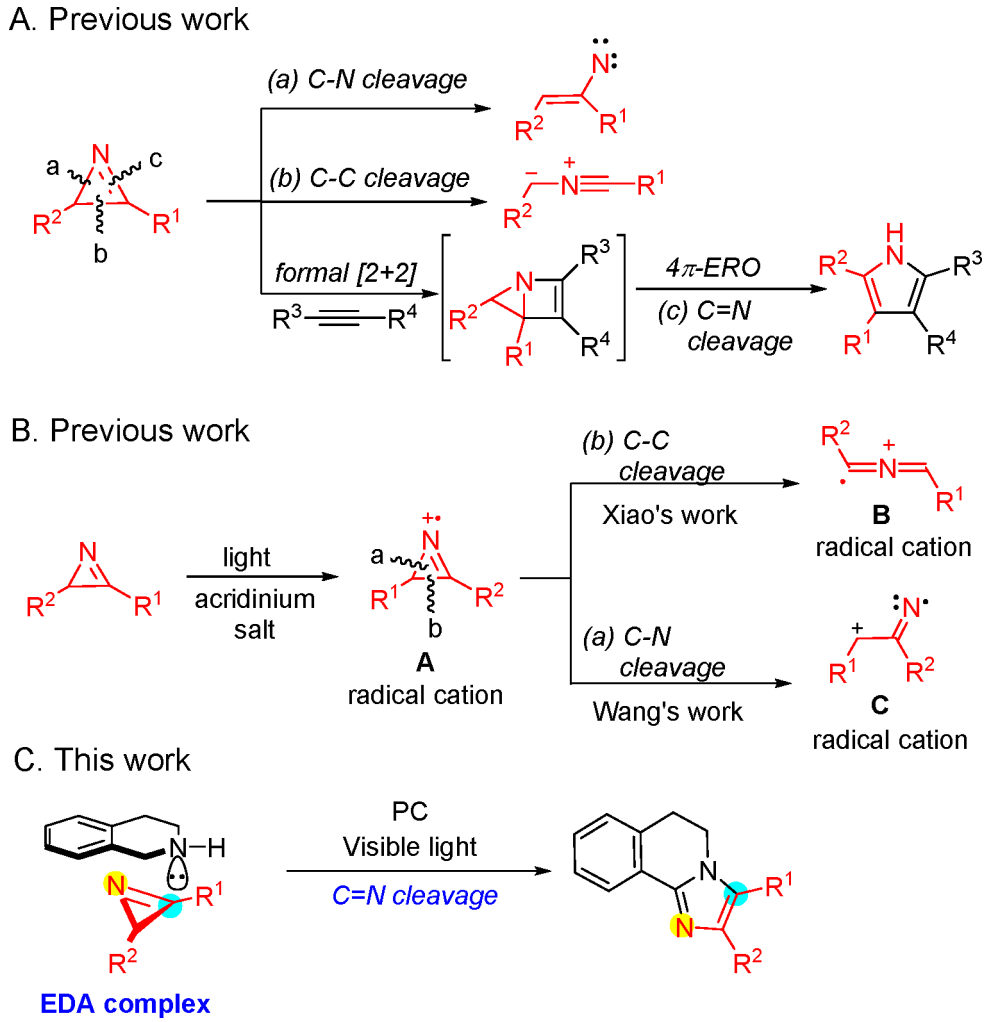
Scheme 1. Representative Bond Cleavage of 2*H*-Azirines and This Work



catalytic efficiency for this transformation. When **PC-1** was tested, **3a** was obtained in 56% yield under visible light irradiation at 435−445 nm (Table 1, entry 7). The optimal photocatalyst was determined to be **PC-2** which provided **3a** in an improved yield (63%). Finally, the optimal wavelength (Table 1, entries 8−12), solvent (Table 1, entries 13−17), and reaction time (Table 1, entries 18−20) were also screened and determined to be 450−455 nm, cumene, and 5 h, respectively. Without the photocatalyst, **3a** could be obtained but in much lower yields either with or without the light irradiation (Table 1, entries 21 and 22). When the reaction was carried out in oxygen or nitrogen, **3a** was afforded in 13% and 45% yields, respectively (Table 1, entries 23 and 24). When 2 equiv of TEMPO were added into the reaction mixture under the standard reaction conditions, only a trace amount of **3a** was detected by TLC tracking (Table 1, entry 25).

With the optimized reaction conditions (Table 1, entry 19), various substrates were tested and the results are summarized in Scheme 3. When the 6-position of tetrahydroisoquinoline was occupied by an electron-donating (CH_3O) and electron-withdrawing (Cl) substituent, **3b** and **3c** were obtained in lower yields (62% and 55%) in comparison to the yield of the unsubstituted **3a**. 7-Methyl tetrahydroisoquinoline afforded **3d** in 48% yield. By moving bromo from the 5-, 6-, and 7-position to the 8-position of tetrahydroisoquinolines, **3e**, **3f**, **3g**, and **3h** were afforded in yields of 61%, 62%, 49%, and 59%, respectively. Aryl at the 3-position of 2*H*-azirine could be 4-fluorophenyl, 4-chlorophenyl, 4-bromophenyl, 4-methoxyphenyl, 4-*tert*-butylphenyl, and 4-trifluoromethylphenyl. Thus, **3i**−**3n** were obtained in yields ranging from 39% to 69%. **3o** could be prepared in 52% yield when 3-chlorophenyl was substituted at the 3-position of 2*H*-azirine. Furthermore, the aryl at the 3-position of 2*H*-azirine could be changed to 2-naphthlenyl, 1-naphthlenyl, and 9-phenanthrenyl. Thus, **3p**, **3q**, and **3r** were prepared in yields of 55%, 47%, and 57%, respectively. The aryl at the 2-position of 2*H*-azirine could be 4-fluorophenyl, 4-chlorophenyl, 4-bromophenyl, 4-methylphenyl and 4-trifluoromethylphenyl. In this way, **3s**−**3w** were obtained in yields ranging from 47% to 63%. **3x** and **3y** were afforded in yields of 58% and 45% by moving chloro from the para to meta position. 2,3-Bis(4-chlorophenyl)-2*H*-azirine and 2,3-bis(4-bromophenyl)-2*H*-azirine furnished **3z** and **3A** in 43% and 52% yields, respectively. 3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-2*H*-azirine provided the desired product **3B** in 71% yield. A relatively lower yield (28%) was observed when 3-benzyl-2-phenyl-2*H*-azirine was used as the substrate. Limited to the volume of the photoirradiate reactor, the maximum amounts of **1a** and **2a** in one batch were loaded as 1 and 1.5 mmol. Based on this, 152 mg of **3a** were obtained in 47% yield.

In order to gain insights into the mechanism, we recorded the absorptive spectra of the cumene solutions of **1a**, **2a**, **PC-2**,

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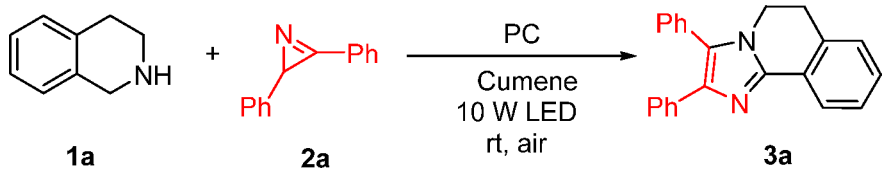
J. Org. Chem. 2021, 86, 8101−8111

Table 1. Optimization of the Reaction Conditions[a]

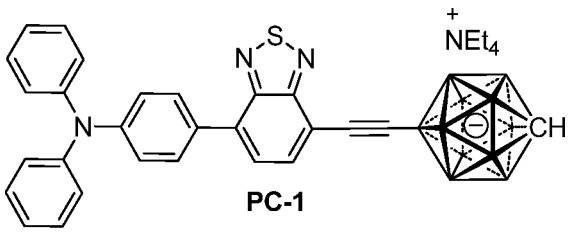


1a 2a 3a

entry	PC	wavelength (nm)	solvent	time (h)	yield (%)[b]
1	$Ru(bpy)_3Cl_2·6H_2O$	450−455	Cumene	10	59
2	$Ru(bpy)_3(PF_6)_2$	450−455	Cumene	10	57
3	$Ir(bpy)_3$	450−455	Cumene	10	50
4	Ir(ppy)2(bpy)PF6	450−455	Cumene	10	56
5	Eosin Y	530−535	Cumene	10	43
6	4CzIPN	530−535	Cumene	10	40
7	**PC-1**	435−445	Cumene	10	56
8	**PC-2**	410−415	Cumene	10	63
9	**PC-2**	390−395	Cumene	10	58
10	**PC-2**	430−435	Cumene	10	67
11	**PC-2**	450−455	Cumene	10	68
12	**PC-2**	470−475	Cumene	10	62
13	**PC-2**	450−455	*p*-Cymene	10	44
14	**PC-2**	450−455	toluene	10	43
15	**PC-2**	450−455	MeCN	10	35
16	**PC-2**	450−455	1,4-dioxane	10	38
17	**PC-2**	450−455	DCE	10	40
18	**PC-2**	450−455	Cumene	7	69
19	**PC-2**	450−455	Cumene	5	72
20	**PC-2**	450−455	Cumene	3	55
21	–	450−455	Cumene	5	30
22	–	–	Cumene	5	15
23	**PC-2**	450−455	Cumene	5	13[c]
24	**PC-2**	450−455	Cumene	5	45[d]
25	**PC-2**	450−455	Cumene	5	trace[e]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (3 mol %), solvent (2 mL). [b]Isolated yield. [c]Under an O_2 atmosphere. [d]Under an N_2 atmosphere. [e]2 equiv of TEMPO was added.

Scheme 2. Structure of Photocatalysts PC-1 and PC-2 and Their Major Photophysical Properties



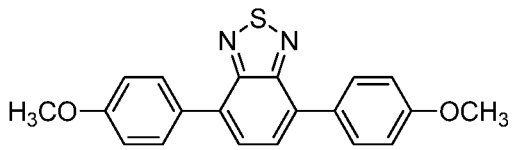
PC-1

In MeCN: λ = 440 nm

ε = 2.26*10^4 L mol^{-1} cm^{-1}

$E_{1/2}(P^*/P^-)$ = 0.67 V

$E_{1/2}(P^+/P^*)$ = -1.12 V



PC-2

In MeCN: λ = 405 nm

ε = 1.21*10^4 L mol^{-1} cm^{-1}

$E_{1/2}(P^*/P^-)$ = 0.80 V

$E_{1/2}(P^+/P^*)$ = -1.10 V

[**1a** + **2a**] and [**1a** + **2a** + **PC-2**] in a concentration in line with standard reaction conditions, respectively (Figure 1a). Initially, both **1a** and **2a** are nonabsorptive as the wavelength started from 375 nm to a longer wavelength. By combination of the equivalents **1a** and **2a**, a shift of the intense absorption band far from the individual absorbances was apparently observed which indicated the formation of an electron-donor−acceptor (EDA) complex between **1a** and **2a**.[12] Further coupled interaction between **PC-2** and the EDA complex was evidenced by the intense and red-shifted absorption of the mixture of **PC-2** and the EDA complex. Upon addition of TEMPO, the synthesis was effectively inhibited (Table 1, entry 25). Stern−Volmer experiments indicated that [**1a** + **2a**] could efficiently quench **PC-2** (Figure 2, Figure S2). These results imply that a single electron transfer may be involved during the reaction process. When TEMP was added to the mixture [**1a** + **2a** + **PC-2**], an amplified ESR signal of TEMPO was observed by irradiation of the mixture with blue LED for 15 min (Figure

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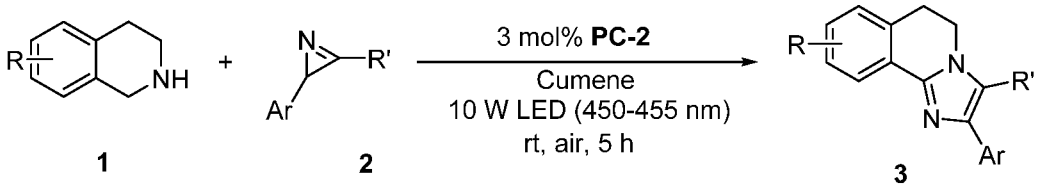
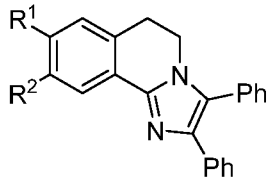
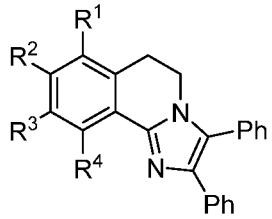
J. Org. Chem. 2021, 86, 8101−8111

Scheme 3. Preparation of Compounds 3a−3C

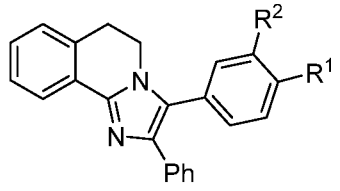




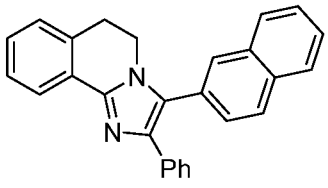
3a, $R^1 = R^2 = H$, 72%
3b, $R^1 = CH_3O$, $R^2 = H$, 62%
3c, $R^1 = Cl$, $R^2 = H$, 55%
3d, $R^1 = H$, $R^2 = CH_3$, 48%



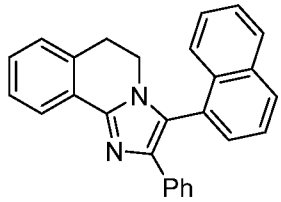
3e, $R^1 = Br$, $R^2 = R^3 = R^4 = H$, 61%
3f, $R^2 = Br$, $R^1 = R^3 = R^4 = H$, 62%
3g, $R^3 = Br$, $R^1 = R^2 = R^4 = H$, 49%
3h, $R^4 = Br$, $R^1 = R^2 = R^3 = H$, 59%



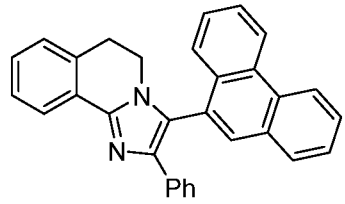
3i, $R^1 = F$, $R^2 = H$, 64%
3j, $R^1 = Cl$, $R^2 = H$, 50%
3k, $R^1 = Br$, $R^2 = H$, 69%
3l, $R^1 = CH_3O$, $R^2 = H$, 61%
3m, R^1 = Bu-*t*, $R^2 = H$, 68%
3n, $R^1 = CF_3$, $R^2 = H$, 39%
3o, $R^1 = H$, $R^2 = Cl$, 52%



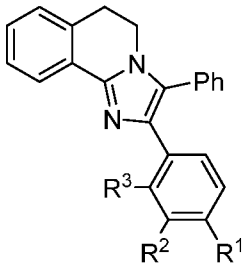
3p, 55%



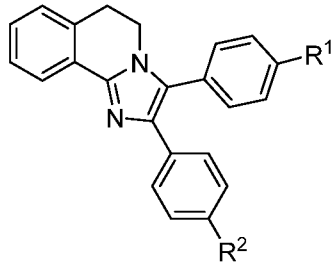
3q, 47%



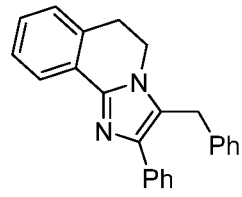
3r, 57%



3s, $R^1 = F$, $R^2 = R^3 = H$, 63%
3t, $R^1 = Cl$, $R^2 = R^3 = H$, 56%
3u, $R^1 = Br$, $R^2 = R^3 = H$, 58%
3v, $R^1 = CH_3$, $R^2 = R^3 = H$, 52%
3w, $R^1 = CF_3$, $R^2 = R^3 = H$, 47%
3x, $R^2 = Cl$, $R^1 = R^3 = H$, 58%
3y, $R^1 = R^2 = H$, $R^3 = Cl$, 45%



3z, $R^1 = R^2 = Cl$, 43%
3A, $R^1 = R^2 = Br$, 52%
3B, $R^1 = CH_3O$, $R^2 = CF_3$, 71%



3C, 28%

1b). This result indicated that the singlet oxygen ($^1O_2$) might be the reactive species appearing during the process.

Combining the above observations, we postulated a cascade mechanism as illustrated in Scheme 4. First, the EDA complex between **1a** and **2a** is in situ generated and equilibrates with adduct **A** through the nucleophilic addition of **1a** to the C═N double bond of 2*H*-azirine **2a**. Under light, the excited state of PC abstracts an electron from adduct **A** via the single electron transfer (SET) process and forms radical cation **B** and radical anion $PC^{-\bullet}$. On the other hand, in the presence of light and photocatalyst, singlet oxygen ($^1O_2$) is produced and reduces PC^- to the ground state of PC. A subsequent hydrogen atom transfer (HAT) from radical cation **B** to reduced oxygen ($O_2^{-\bullet}$) generates iminium intermediate **C** and HOO^-.[13] Intramolecular trapping of iminium with aziridine leads to the formation of the active 1,7-diazatricycle **D**. Followed by deprotonation and partial aromatization, 5,6-dihydroimidazo-[2,1-*a*]isoquinoline **3a** is finally produced.

During the preparation, we observed that the synthesized 2,3-diaryl-5,6-dihydroimidazo[2,1-*a*]isoquinolines (**3a−3B**) are highly emissive in solids and the emissive color could be tuned by the substitutents (Figure 3, Table S1, and Figure S3)

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J. Org. Chem. 2021, 86, 8101−8111

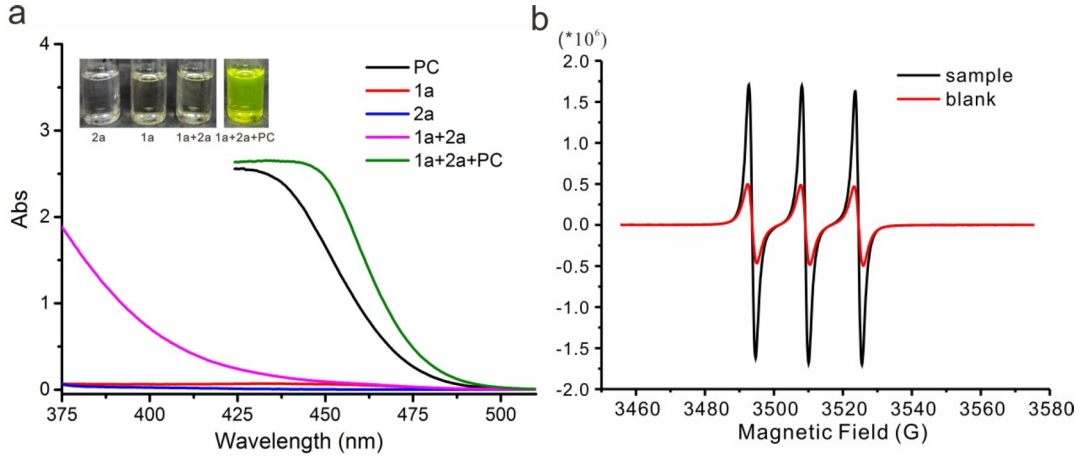

Figure 1. (a) Absorption spectra recorded in cumene solutions in 1 cm quartz cell. [**1a**] = 0.1 M, [**2a**] = 0.15 M. (b) Electron spin resonance (ESR) spectra with blue LED irradiation for 15 min (sample), without blue LED irradiation (blank).

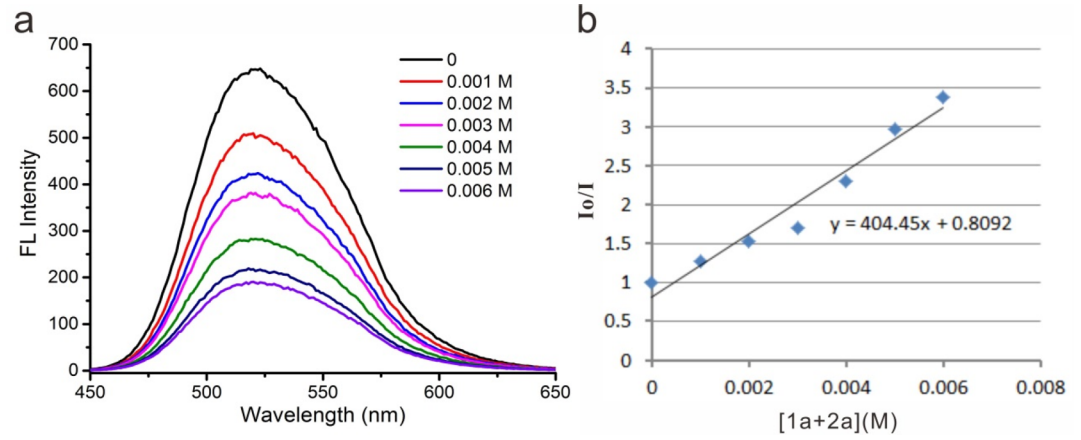

Figure 2. Stern−Volmer quenching experiment.

which indicated that these compounds might exhibit potential application as emitters in OLED. In order to know the effect of structure on the photophysical property, we selected five respective compounds (**3a**, **3l**, **3n**, **3w**, and **3B**) and the data are shown in Table 2. Absorption of these five compounds are almost identical with the maximum absorption wavelength set around 314 nm and molar absorptivity ranging from 2.04×10^4 to 4.08×10^4. The values of Stokes shift rely on the 3-aryl of 5,6-dihydroimidazo[2,1-*a*]isoquinoline. The one with an electron-withdrawing group (**3n**, 4-$CF_3C_6H_4$) presents a larger Stokes shift than the one with the electron-donating group (**3l**, 4-$CH_3OC_6H_4$), indicating a better intramolecular charge transfer (ICT) in **3n** from the imidazole ring to 4-trifluoromethylphenyl. When 4-$CF_3C_6H_4$ was substituted at the 2-position of 5,6-dihydroimidazo[2,1-*a*]isoquinoline, **3w** presented a smaller Stokes shift, but the highest quantum yield (14.1%) in CH_2Cl_2 solution among these five compounds.[14] When both electron-withdrawing and electron-donating groups exist on the molecule, **3B** absorbs light at 316 nm with the largest molar absorptivity. The direction of the molecular dipole moment, from imidazole to 3-aryl, is consistent with the solvent-dependence emissive spectra of these five compounds (Figure S4). Moreover, the larger the dipole moment changes are from the ground state to excited state, the larger the solvatofluorochromic effect is.[15] Among these five compounds, the largest dipole moment change is observed for **3n**.

Three compounds (**3d**, **3i**, and **3w**) were selected to be the emitters for fabrication of blue OLED because they provided the good quantum yields in solids. As listed in Table S2, the quantum yields for **3d**, **3i**, and **3w** in solids are 61.0%, 41.4%, and 35.0%, respectively. When the OLED devices with the sandwich structure of ITO/PEDOT:PSS (40 nm)/compound (65 nm)/TBPI (40 nm)/LiF (1.5 nm)/Al (100 nm) were fabricated by respectively applying **3d**, **3i**, and **3w** as emitters, Devices A, B, and C were manufactured. Electrolumenicent spectra and the current−density−voltage characteristics were shown in Figures S5−S7, and data were summarized in Table S3. Device **3w** emitted light at 407 nm at a voltage of 8.1 V. At a brightness of 100 cd m^{-2}, the external quantum yield (0.54%), the luminous efficiency (0.19 cd A^{-1}), and the power efficiency (0.06 lm W^{1-}) were approached.

■ CONCLUSIONS

In conclusion, we have developed a visible-light-driven (3 + 2) annulation of 2*H*-azirines with tetrahydroisoquinolines using benzothiadiazole (BTD) derived 4,7-bis(4-methoxyphenyl)-benzo[*c*][1,2,5]thiadiazole as an organic photoredox catalyst. The reaction furnished a series of 5,6-dihydroimidazo[2,1-*a*]isoquinolines through a novel and photoactive EDA complex. This approach features a metal-free organic photo-

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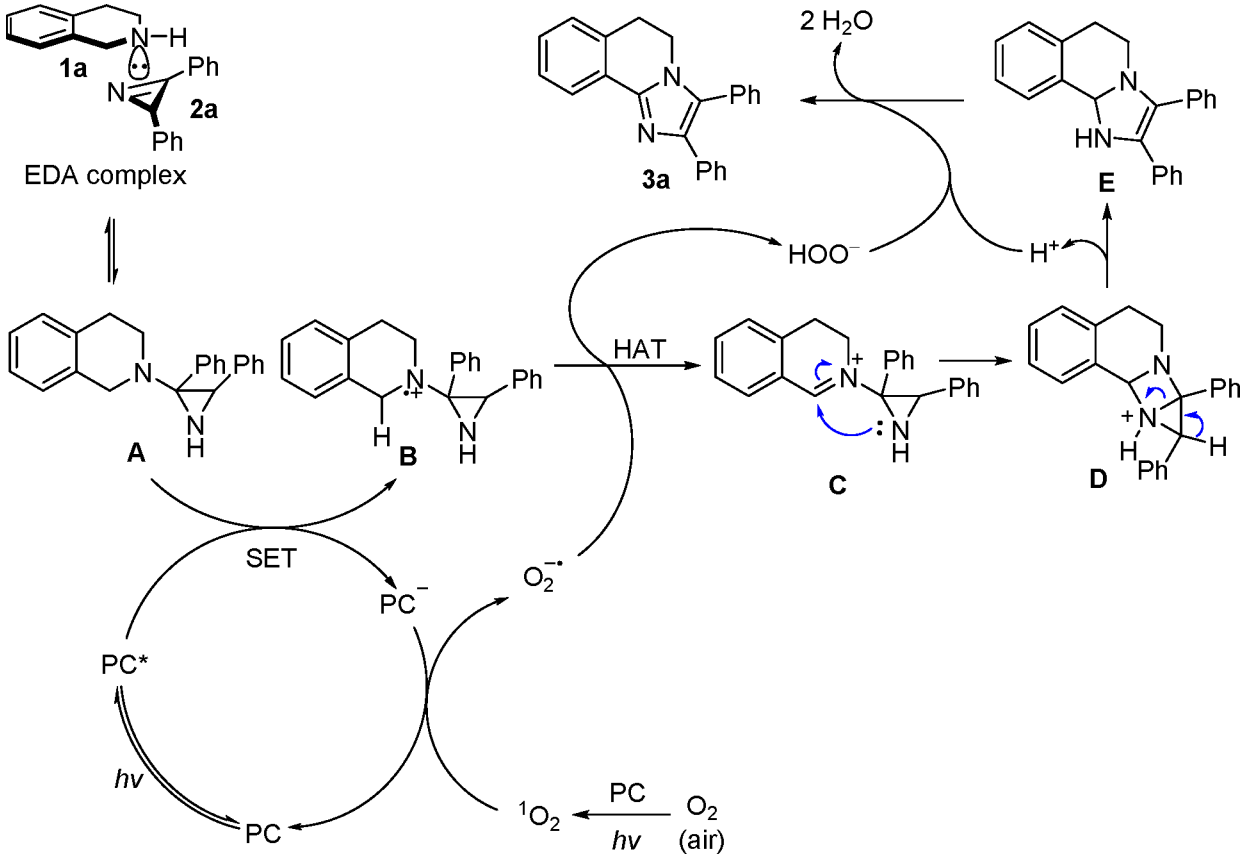
Scheme 4. Proposed Reaction Mechanism



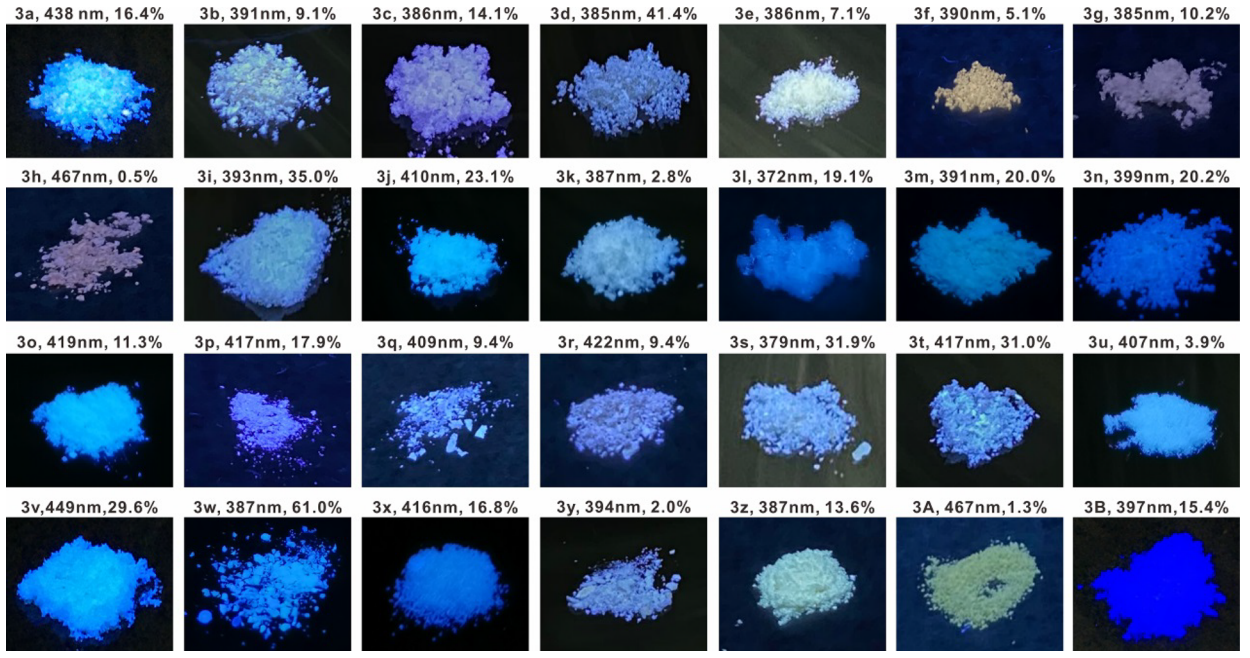


Figure 3. Photos of compounds **3a**–**3B** under UV lamp.

redox catalyst, mild conditions, a broad substrate scope, good functional group compatibility, and high yields. More importantly, the synthesized 5,6-dihydroimidazo[2,1-*a*]-isoquinolines products showed strong photoluminescence in solutions and powders and could be applied as blue OLED device emitters.

EXPERIMENTAL SECTION

General Information. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. ^{1}H NMR spectra were obtained on a 400 MHz spectrometer at room temperature. The chemical shifts were reported relative to internal TMS (0 ppm) in $CDCl_3$. The following abbreviations were used to describe peak patterns when appropriate: s = singlet, d =

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J. Org. Chem. 2021, 86, 8101−8111

Table 2. Photophysical Properties of Five Compounds

	λ_{max}^{abs} ($\varepsilon/10^4$)[a]	λ_{max}^{em}[a]	fwhm	Stokes	Φ (%)[b]	λ_{powder}^{em}	fwhm	QY (%)[c]	CIE(x,y)$_{powder}$
3a	313 (2.85)	384	51	71	13.7	438	72	16.4	(0.1389, 0.0939)
3l	314 (2.49)	387	54	73	13.8	372	48	19.1	(0.1579, 0.0186)
3n	312 (2.04)	416	71	104	10.5	399	50	20.2	(0.1598, 0.016)
3w	315 (2.79)	394	63	79	14.1	387	46	61.0	(0.167, 0.0088)
3B	316 (4.08)	406	72	90	10.9	397	61	15.4	(0.1532, 0.0289)

[a]Measured in CH_2Cl_2 solution, $c = 2 \times 10^{-5}$ M. [b]Quantum yields (Φ) in CH_2Cl_2 solution were calculated based on Anthracene (Φ = 0.27 in Ethanol). [c]Powder quantum yields were obtained from an integrating sphere.

doublet, t = triplet, q = quartet, m = multiplet. *J* values were reported in Hz. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer, and the chemical shifts were referenced to the central line of the triplet of $CDCl_3$ (77.00 ppm). Infrared spectra were obtained on an FTIR spectrometer. All high-resolution mass spectra (HRMS) data were obtained by using EI ionization on a time-of-flight (TOF) mass spectrometer or ESI ionization on an LCMS-IT-TOF mass spectrometer. Melting points were measured with a micro melting point apparatus. Flash column chromatography was performed employing 300−400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254. FL spectra were recorded on a fluorospectro photometer with a xenon lamp excitation source. Cyclic voltammetry measurements were performed on an electrochemical analyzer in solution at room temperature. EPR spectra were recorded at room temperature on a Bruker BioSpin GmbH spectrometer operating at 9.852 GHz with the cavity equipped with a Bruker Aquax liquid sample cell. Typical spectrometer parameters were as follows: scan range, 120 G; field set, 3455.6 G; time constant, 81.92 ms; scan time, 40 s; modulation amplitude 1 G; modulation frequency 100 kHz; receiver gain 3.17; microwave power, 20.46 mW. 2,2,6,6-Tetramethylpiperidine (TEMP) was used to capture $^1O_2$, by mixing PC (3 mol %), **1a** (0.2 mmol), and **1b** (0.3 mmol) in cumene under blue LED irradiation (λ = 450−455 nm) for 15 min (sample), without blue LED irradiation (blank).

The starting materials of **1** were supplied by commercial vendors without further purification. 2*H*-Azirines **2** were known compounds except for 3-(phenanthren-9-yl)-2-phenyl-2*H*-azirine (**2k**) and prepared according to the published methods.[5a,16] The ketones were supplied by commercial vendors without further purification or prepared according to the published methods.[17] **PC-1** and **PC-2** were prepared according to the published methods.[10,11]

Typical Procedure for the Synthesis of 3-(Phenanthren-9-yl)-2-phenyl-2*H*-azirine (2k)..[5a,16] The mixture of 1-(phenanthren-9-yl)-2-phenylethan-1-one (894 mg, 3.02 mmol), $NH_2OH{\cdot}HCl$ (315 mg, 4.53 mmol, 1.5 equiv), and sodium acetate was dissolved in MeOH/H_2O (20:1, v/v, 105 mL) at room temperature and monitored by TLC. After the reaction completed, the mixture was concentrated under vacuum to remove most of the solvent. The solution was sequentially washed with saturated $NaHCO_3$ and brine. The aqueous layer was extracted with DCM, and the organic layer was dried over Na_2SO_4. Removal of the solvent gave 1-(phenanthren-9-yl)-2-phenylethan-1-one oxime. The crude product was directly used for the next step without purification.

Triethylamine (455 mg, 4.5 mmol, 1.5 equiv) and methanesulfonyl chloride (516 mg, 4.5 mmol, 1.5 equiv) were added sequentially to a solution of 1-(phenanthren-9-yl)-2-phenylethan-1-one oxime (933 mg, 3.0 mmol) in dry THF (30 mL) at 0 °C. The solution became cloudy after the addition of methanesulfonyl chloride. Then, the resulting mixture was stirred for 30 min, and DBU (685 mg, 4.5 mmol, 1.5 equiv) was added slowly. After stirring for additional 30 min, the reaction mixture was passed through a pad of silica gel and washed with petroleum ether (PE). The mixture was concentrated in vacuo, and the resulting residue was purified by column chromatography on silica gel (PE/EtOAc = 15:1, v/v) to give pure **2k** as a white solid; yield: 299 mg, 34%; ^1H NMR (400 MHz, $CDCl_3$) δ 9.19−9.21 (m, 1H), 8.75−8.78 (m, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 8.17 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.78−7.83 (m, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.25−7.32 (m, 5H), 3.38 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7, 141.0, 135.8, 132.3, 130.6, 130.4, 130.1, 129.6, 129.3, 128.3, 128.1, 127.8, 127.3, 127.0, 126.2, 125.9, 123.0, 122.9, 118.6, 31.5; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}N$ 294.1277; found 294.1278; IR: 3028, 1732, 1603, 1527, 1495, 1452, 1264, 1181, 1143, 1076, 905, 765, 725 cm^{-1}.

General Procedure for the Synthesis of Products 3. To a 20 mL reaction tube equipped with a magnetic stir bar were added **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), photocatalyst (3 mol %), and cumene (2 mL). The solution was stirred irradiated with blue LEDs (450−455 nm) at room temperature for 5 h under air. Upon completion of the reaction monitored by TLC, the crude product was purified by flash chromatography on silica gel to provide pure product **3**.

Preparation of 3a in 1 mmol Scale. To a 20 mL reaction tube equipped with a magnetic stir bar were added **1a** (1 mmol, 133.1 mg), **2a** (1.5 mmol, 289.7 mg), PC (3 mol %, 10.4 mg), and cumene (5 mL). The solution was stirred irradiated with 10 W blue LED light (450−455 nm) at room temperature for 5 h under air. Upon completion of the reaction monitored by TLC, the crude product was purified by flash chromatography on silica gel to provide product **3a** (152 mg, 47%).

Device Fabrication. Before device fabrication, the ITO glass substrates were precleaned carefully. Then hole transporting material PEDOT:PSS was made with 4000 r/s for 45 s and annealing for 25 min at 150 °C. The emission layer was prepared by spin coating the chlorobenzene solution of compounds. Then it was made with 3000 r/s for 45 s and annealing for 25 min at 50 °C. After the organic film deposition, 40 nm of TPBi, 1.5 nm of LiF, and 100 nm of aluminum were thermally evaporated onto the organic surface.

*2,3-Diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3a**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 46 mg, 72%; mp 163.1−163.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.35−7.47 (m, 6H), 7.22−7.31 (m, 4H), 7.15−7.19 (m, 1H), 3.98 (t, *J* = 6.8 Hz, 2H), 3.10 (t, *J* = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.6, 138.7, 134.7, 132.7, 130.5, 130.5, 128.9, 128.4, 128.4, 128.1, 127.6, 127.6, 127.2, 126.4, 124.0, 41.5, 28.6; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{23}H_{18}N_2$ 322.1470; found 322.1469; IR: 3058, 2925, 1602, 1580, 1533, 1503, 1475, 1457, 1444, 1347, 1121, 1029, 962, 774, 700 cm^{-1}.

*8-Methoxy-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3b**).* Light yellow solid; column chromatography (PE/EtOAc = 9:1); yield: 43 mg, 62%; mp 168.2−168.9 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8 Hz, 2H), 7.35−7.45 (m, 5H), 7.15−7.26 (m, 3H), 6.90−6.93 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 6.78 (s, 1H), 3.97 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 3.08 (t, *J* = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 143.9, 138.2, 134.6, 130.5, 128.9, 128.3, 128.1, 127.8, 127.2, 126.4, 125.7, 120.2, 113.3, 112.8, 55.3, 41.4, 28.9; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{24}H_{20}N_2O$ 352.1576; found 352.1577; IR: 2999, 2946, 1612, 1546, 1480, 1464, 1348, 1242, 1174, 1030, 838, 778 cm^{-1}.

*8-Chloro-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3c**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 39 mg, 55%; mp 217.2−218.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.41−7.48 (m, 3H), 7.34−7.37 (m, 3H), 7.16−7.26 (m, 4H), 3.99 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.8, 138.8, 134.4, 134.3, 133.9, 130.5, 130.2, 129.0, 128.6, 128.2, 127.9, 127.8, 127.2, 126.7, 126.6, 125.8, 125.4, 41.3, 28.4; HRMS

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J. Org. Chem. 2021, 86, 8101−8111

(ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}ClN_2$ 357.1153; found 357.1153; IR: 3062, 2951, 1637, 1599, 1501, 1487, 1428, 1346, 1111, 1085, 962, 828, 779 cm^{-1}.

*9-Methyl-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3d**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 32 mg, 48%; mp 187.7−188.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.42−7.48 (m, 3H), 7.36−7.38 (m, 2H), 7.09−7.26 (m, 5H), 3.97 (t, J = 6.8 Hz, 2H), 3.06 (t, J = 6.8 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.8, 137.3, 134.6, 130.5, 130.5, 129.7, 129.2, 129.0, 128.9, 128.4, 128.3, 128.1, 127.5, 127.3, 126.9, 126.4, 124.5, 41.7, 28.2, 21.1; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{21}N_2$ 337.1699; found 337.1699; IR: 2955, 2924, 2854, 1602, 1496, 1453, 1378, 1339, 1158, 1107, 965, 775, 699 cm^{-1}.

*7-Bromo-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3e**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 49 mg, 61%; mp 194.7−195.3 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.2 Hz, 1H), 7.52−7.57 (m, 3H), 7.44−7.49 (m, 3H), 7.36−7.38 (m, 2H), 7.16−7.26 (m, 4H), 4.00 (t, J = 6.8 Hz, 2H), 3.25 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.7, 139.2, 134.4, 132.3, 132.1, 130.4, 130.1, 129.1, 129.0, 128.8, 128.6, 128.2, 127.2, 126.6, 123.5, 123.2, 41.0, 28.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{17}N_2Br$ 400.0575; found 400.0573; IR: 3060, 2956, 2925, 2834, 1601, 1474, 1457, 1378, 1346, 1129, 964, 913, 776, 697 cm^{-1}.

*8-Bromo-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3f**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 50 mg, 62%; mp 229.8−230.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.49−7.52 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.41−7.46 (m, 4H), 7.35−7.37 (m, 2H), 7.16−7.24 (m, 3H), 3.98 (t, J = 6.8 Hz, 2H), 3.09 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.8, 138.9, 134.5, 134.3, 130.8, 130.6, 130.5, 130.2, 129.0, 128.6, 128.6, 128.2, 127.2, 126.6, 126.1, 125.6, 122.1, 41.3, 28.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{17}N_2Br$ 400.0575; found 400.0574; IR: 3050, 2958, 1654, 1599, 1500, 1478, 1442, 1427, 1343, 1075, 962, 826, 779 cm^{-1}.

*9-Bromo-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3g**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 39 mg, 49%; mp 219.6−220.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.35−7.48 (m, 6H), 7.17−7.26 (m, 4H), 7.11(d, J = 8.4 Hz, 1H), 3.98 (t, J = 6.8 Hz, 2H), 3.06 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.3, 139.0, 134.3, 131.3, 131.1, 130.5, 130.1, 129.2, 129.0, 128.8, 128.6, 128.2, 127.2, 126.7, 126.6, 121.5, 41.4, 28.1; HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{17}N_2Br$ 400.0575; found 400.0575; IR: 3049, 2951, 1654, 1599, 1501, 1481, 1452, 1342, 1248, 1070, 961, 776, 699 cm^{-1}.

*10-Bromo-2,3-diphenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3h**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 47 mg, 59%; mp 178.1−178.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63−7.67 (m, 3H), 7.45−7.51 (m, 3H), 7.37−7.40 (m, 2H), 7.14−7.24 (m, 4H), 7.08 (t, J = 7.6 Hz, 1H), 3.91 (t, J = 6.8 Hz, 2H), 3.08 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.2, 138.0, 136.3, 134.6, 134.2, 130.6, 130.5, 129.0, 128.7, 128.5, 128.2, 128.1, 126.9, 126.7, 126.4, 124.3, 119.5, 40.9, 30.1; HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{17}N_2Br$ 400.0575; found 400.0573. IR: 3059, 2955, 2925, 2853, 1602, 1559, 1473, 1456, 1343, 1189, 1027, 966, 774, 696 cm^{-1}.

*3-(4-Fluorophenyl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3i**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 44 mg, 64%; mp 193.8−194.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.6 Hz, 1H), 7.54−7.56 (m, 2H), 7.24−7.40 (m, 7H), 7.13−7.21 (m, 3H); 3.96 (t, J = 6.8 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 247.2 Hz), 143.7, 138.8, 134.4, 132.6, 132.4(d, J = 8.1 Hz), 128.5, 128.2, 127.6, 127.2, 127.2, 127.0, 126.6, 126.4 (d, J = 3.0 Hz), 124.1, 116.1 (d, J = 21.5 Hz), 41.5, 28.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −112.58; HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{17}N_2F$ 340.1376; found 340.1377; IR: 3062, 2956, 2925, 1600, 1558, 1509, 1480, 1378, 1225, 1157, 963, 843, 774,718 cm^{-1}.

*3-(4-Chlorophenyl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3j**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 35 mg, 50%; mp 175.0−175.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.36−7.44 (m, 3H), 7.18−7.32 (m, 7H), 3.98 (t, J = 6.8 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.9, 139.0, 134.5, 134.2, 132.6, 131.8, 129.3, 128.8, 128.6, 128.3, 127.7, 127.6, 127.3, 127.0, 126.9, 126.7, 124.2, 41.6, 28.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}ClN_2$ 357.1153; found 357.1154; IR: 3058, 2955, 2925, 1734, 1601, 1500, 1474, 1445, 1348, 1122, 1091, 1015, 962, 838, 753, 715 cm^{-1}.

*3-(4-Bromophenyl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3k**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 55 mg, 69%; mp 168.7−169.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 1H), 7.54−7.59 (m, 4H), 7.37 (t, J = 7.6 Hz, 1H), 7.18−7.32 (m, 7H), 3.98 (t, J = 6.8 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 139.1, 134.3, 132.6, 132.2, 132.1, 129.3, 128.6, 128.3, 127.6, 127.3, 127.0, 127.0, 126.7, 124.1, 122.7, 41.6, 28.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}BrN_2$ 401.0648; found 401.0651; IR: 3060, 2955, 2925, 1601, 1497, 1340, 1299, 1122, 1071, 1011, 962, 835, 774, 697 cm^{-1}.

*3-(4-Methoxyphenyl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3l**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 43 mg, 61%; mp 185.1−185.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.23−7.30 (m, 6H), 7.15−7.18 (m, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.87 (s, 3H), 3.10 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.7, 143.4, 138.4, 134.8, 132.6, 131.8, 128.3, 128.2, 128.1, 127.6, 127.5, 127.3, 127.1, 126.3, 124.0, 122.6, 114.4, 55.3, 41.3, 28.6; HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{20}N_2O$ 352.1576; found 352.1576; IR: 2956, 2925, 2853, 1610, 1558, 1510, 1481, 1378, 1287, 1249, 1178, 1031, 963, 838, 774 cm^{-1}.

*3-(4-(Tert-butyl)phenyl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3m**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 52 mg, 68%; mp 153.5−154.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.21−7.29 (m, 6H), 7.15−7.18 (m, 1H), 3.97 (t, J = 6.8 Hz, 2H), 3.08 (t, J = 6.8 Hz, 2H), 1.37 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.4, 143.4, 138.4, 134.7, 132.7, 130.1, 128.4, 128.4, 128.1, 127.6, 127.5, 127.2, 127.2, 126.4, 125.8, 124.0, 41.5, 34.7, 31.3, 28.6; HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{26}N_2$ 378.2096; found 378.2095; IR: 3049, 2960, 2895, 1600, 1508, 1481, 1458, 1348, 1267, 1116, 1028, 962, 853, 774 cm^{-1}.

*2-Phenyl-3-(4-(trifluoromethyl)phenyl)-5,6-dihydroimidazo[2,1-a]isoquinoline (**3n**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 30 mg, 39%; mp 166.2−167−3 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.47−7.54 (m, 4H), 7.38 (t, J = 7.6 Hz, 1H), 7.19−7.33 (m, 5H), 4.01 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 139.7, 134.2, 134.1, 132.6, 130.8, 130.2 (q, J = 32.7 Hz), 128.8, 128.3, 127.7 (q, J = 4.0 Hz), 127.5, 126.9, 126.8, 126.7, 125.9 (q, J = 3.7 Hz), 124.2, 124.0 (q, J = 270.6 Hz), 41.7, 28.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ − 62.60; HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{17}N_2F_3$ 390.1344; found 390.1346; IR: 3047, 2920, 1620, 1595, 1481, 1325, 1169, 1123, 1067, 962, 852, 777, 698 cm^{-1}.

*3-(3-Chlorophenyl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3o**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 37 mg, 52%; mp 125.6−126.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.36−7.41 (m, 4H), 7.20−7.33 (m, 6H), 3.99 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 139.2, 134.7, 134.2, 132.6, 132.3, 130.3, 130.2, 129.0, 128.9, 128.8, 128.6, 128.6, 128.3, 127.6, 127.3, 127.0, 126.8, 124.2, 41.6, 28.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}ClN_2$ 357.1153; found 357.1157; IR: 3058, 2955, 2925, 1599, 1566, 1485, 1465, 1341, 1078, 1029, 970, 771, 737, 697 cm^{-1}.

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J. Org. Chem. 2021, 86, 8101−8111

*3-(Naphthalen-2-yl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3p**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 41 mg, 55%; mp 190.2−190.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 6.0 Hz, 1H), 7.84−7.92 (m, 4H), 7.53−7.61 (m, 4H), 7.43−7.45 (dd, J_1 = 0.6 Hz, J_2 = 6.8 Hz, 1H), 7.39 (t, J = 6.0 Hz, 1H), 7.31 (t, J = 6.0 Hz, 1H), 7.20−7.25 (m, 3H), 7.15−7.18 (m, 1H), 4.04 (t, J = 5.6 Hz, 2H), 3.13 (t, J = 5.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.77, 138.9, 134.4, 134.4, 133.4, 132.9, 132.7, 129.6, 128.6, 128.7, 128.5, 128.3, 128.2, 128.1, 128.1, 127.8, 127.6, 127.3, 127.1, 126.7, 126.6, 41.6, 28.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{21}N_2$ 373.1699; found 373.1701; IR: 3054, 2956, 2925, 1602, 1486, 1463, 1349, 1269, 1157, 1029, 974, 824, 775, 739 cm^{-1}.

*3-(Naphthalen-1-yl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3q**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 35 mg, 47%; mp 223.4−224.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.6 Hz, 1H), 7.95−8.01 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.50−7.57 (m, 5H), 7.39−7.45 (m, 2H), 7.28−7.32 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.06−7.15 (m, 3H), 3.70 (t, J = 6.8 Hz, 2H), 3.04 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 139.4, 134.4, 133.8, 132.9, 132.7, 129.7, 129.6, 128.6, 128.5, 128.1, 127.7, 127.6, 127.1, 127.1, 126.4, 126.4, 126.3, 126.3, 125.7, 125.3, 124.0, 41.4, 28.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{21}N_2$ 373.1699; found 373.1701; IR: 3055, 2923, 2856, 1603, 1507, 1485, 1459, 1324, 1120, 944, 809, 775, 738 cm^{-1}.

*3-(Phenanthren-9-yl)-2-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3r**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 48 mg, 57%; mp 238.5−239.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77−8.82 (q, J_1 = 8.4 Hz, J_2 = 3.6 Hz, 2H), 8.29 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.85 (s, 1H), 7.60−7.77 (m, 6H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.04−7.13 (m, 3H), 3.66−3.78 (m, 2H), 3.02 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.0, 139.6, 134.4, 132.6, 131.4, 131.3, 130.9, 130.8, 130.7, 129.1, 128.5, 128.2, 127.7, 127.6, 127.4, 127.2, 127.0, 126.3, 126.1, 126.1, 124.0, 123.2, 122.7, 41.3, 28.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{23}N_2$ 423.1856; found 423.1857; IR: 3057, 2929, 1602, 1533, 1483, 1449, 1416, 1349, 1299, 1081, 903, 774, 744, 696 cm^{-1}.

*2-(4-Fluorophenyl)-3-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3s**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 43 mg, 63%; mp 173.1−173.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.6 Hz, 1H), 7.51−7.54 (m, 2H), 7.43−7.49 (m, 3H), 7.23−7.40(m, 5H), 6.93 (t, J = 8.8 Hz, 2H), 3.99 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J = 243.7 Hz), 143.6, 137.8, 132.7, 130.7, 130.7, 130.5, 130.2, 129.0, 128.8 (d, J = 7.9 Hz), 128.5, 128.1, 127.6 (d, J = 2.7 Hz), 127.0, 124.0, 115.0 (d, J = 21.2 Hz), 41.5, 28.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ − 116.21; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}FN_2$ 341.1449; found 341.1448; IR: 2956, 2925, 2853, 1603, 1539, 1509, 1476, 1378, 1345, 1221, 1156, 963, 840, 793 cm^{-1}.

*2-(4-Chlorophenyl)-3-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3t**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 40 mg, 56%; mp 167.6−168.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 1H), 7.66 (s, 1H), 7.45−7.50 (m, 3H), 7.24−7.41 (m, 6H), 7.10−7.14 (m, 2H), 3.99 (t, J = 6.4 Hz, 2H), 3.12 (t, J = 6.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.7, 137.0, 136.2, 134.1, 132.7, 130.4, 129.8, 129.3, 129.1, 129.0, 128.8, 128.8, 127.7, 127.1, 126.8, 126.5, 125.1, 124.2, 41.5, 28.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}ClN_2$ 357.1153; found 357.1152; IR: 3057, 2954, 2925, 1597, 1568, 1496, 1465, 1341, 1299, 1128, 1075, 970, 816, 771 cm^{-1}.

*2-(4-Bromophenyl)-3-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3u**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 46 mg, 58%; mp 231.2−231.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.6 Hz, 1H), 7.43−7.47 (m, 5H), 7.23−7.39 (m, 7H), 3.97 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 137.5, 133.6, 132.7, 131.2, 130.4, 130.1, 129.1, 128.7, 128.6, 128.6, 127.7, 127.6, 127.0, 124.0, 120.3, 41.5, 28.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}BrN_2$ 401.0648; found 401.0648; IR: 3030, 2956, 2922, 1608, 1592, 1498, 1474, 1351, 1339, 1122, 1298, 1010, 963, 841, 766, 742 cm^{-1}.

*3-Phenyl-2-(p-tolyl)-5,6-dihydroimidazo[2,1-a]isoquinoline (**3v**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 35 mg, 52%; mp 189.6−190.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 1H), 7.35−7.47 (m, 8H), 7.22−7.30 (m, 2H), 7.05 (d, J = 8 Hz, 2H), 3.98 (t, J = 6.8 Hz, 2H), 3.10 (t, J = 6.8 Hz, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.5, 138.7, 136.1, 132.7, 131.7, 130.5, 128.9, 128.3, 128.3, 128.0, 127.6, 127.5, 127.2, 127.1, 124.0, 41.5, 28.6, 21.2; HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{20}N_2$ 336.1626; found 336.1627; IR: 2955, 2924, 2854, 1606, 1511, 1487, 1457, 1378, 1341, 1182, 1120,963, 824, 772 cm^{-1}.

*3-Phenyl-2-(4-(trifluoromethyl)phenyl)-5,6-dihydroimidazo[2,1-a]isoquinoline (**3w**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 37 mg, 47%; mp 190−1−191.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.6 Hz, 1H), 8.67 (d, J = 8 Hz, 2H), 7.46−7.49 (m, 5H), 7.31−7.38 (m, 4H), 7.24−7.25 (m, 1H), 3.98 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 144.0, 138.2, 137.2, 132.7, 130.4, 130.0, 129.5, 129.2, 128.9, 128.7, 128.1 (q, J = 32.1 Hz), 127.7 (q, J = 3.4 Hz), 127.0, 126.9, 125.1 (q, J = 3.8 Hz), 124.1, 124.4 (q, J = 270.0 Hz), 41.5, 28.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.32; HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{17}N_2F_3$ 390.1344; found 390.1345; IR: 3053, 2924, 1617, 1486, 1458, 1417, 1324, 1164, 1120, 1066, 963, 849, 771, 718 cm^{-1}.

*2-(3-Chlorophenyl)-3-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3x**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 41 mg, 58%; mp 161.0−161.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.6 Hz, 1H), 7.66 (s, 1H), 7.44−7.48 (m, 3H), 7.22−7.39 (m, 6H), 7.09−7.13 (m, 2H), 3.97 (t, J = 6.8 Hz, 2H), 3.10 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.77, 137.21, 136.52, 134.08, 133.35, 132.67, 130.41, 129.94, 129.28, 129.04, 128.95, 128.72, 128.58, 127.65, 127.61, 126.98, 126.37, 125.05, 123.99, 41.49, 28.53; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}ClN_2$ 357.1153; found 357.1154; IR: 3059, 2955, 2925, 1597, 1568, 1496, 1465, 1341, 1128, 1075, 970, 816, 771, 701 cm^{-1}.

*2-(2-Chlorophenyl)-3-phenyl-5,6-dihydroimidazo[2,1-a]-isoquinoline (**3y**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 32 mg, 45%; mp 164.8−165.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17(d, J = 6.0 Hz, 1H), 7.48−7.50(m, 1H), 7.30−7.37(m, 6H), 7.20−7.28(m, 5H), 4.18(t, J = 5.6 Hz, 2H), 3.17(t, J = 5.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.6, 137.2, 134.0, 133.9, 132.7, 132.7, 130.0, 129.9, 129.7, 129.4, 128.9, 128.8, 128.6, 128.5, 127.8, 127.6, 127.1, 126.6, 124.2, 41.9, 28.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}ClN_2$ 357.1153; found 357.1156; IR: 3056, 2955, 2925, 1598, 1497, 1469, 1341, 1265, 1125, 1055, 965, 814, 772, 741 cm^{-1}.

*2,3-Bis(4-chlorophenyl)-5,6-dihydroimidazo[2,1-a]isoquinoline (**3z**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 34 mg, 43%; mp 202.1−202.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 1H), 7.43−7.49 (m, 4H), 7.35−7.39 (m, 1H), 7.21−7.33 (m, 6H), 3.96 (t, J = 6.8 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 138.0, 134.7, 132.9, 132.6, 132.4, 131.7, 129.4, 128.7, 128.6, 128.4, 128.4, 127.7, 127.2, 126.9, 124.0, 41.5, 28.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{17}Cl_2N_2$ 391.0763; found 391.0763; IR: 2938, 1638, 1618, 1497, 1473, 1384, 1341, 1120, 1091, 1015, 962, 839, 769 cm^{-1}.

*2,3-Bis(4-bromophenyl)-5,6-dihydroimidazo[2,1-a]isoquinoline (**3A**).* White solid; column chromatography (PE/EtOAc = 15:1); yield: 50 mg, 52%; mp 220.5−221.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.2 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.36−7.43 (m, 5H), 7.29−7.33 (m, 1H), 7.21−7.26 (m, 3H), 3.96 (t, J = 6.8 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 137.8, 133.1, 132.6, 132.4, 132.0, 131.4, 128.9, 128.8, 128.8, 127.7, 127.7, 127.3, 126.7, 124.2, 123.0, 120.7, 41.6, 28.5; HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{16}N_2Br_2$ 477.9680; found 477.9681; IR: 3049, 2942, 1654, 11495, 1468, 1415, 1344, 1119, 1071, 1012, 961, 836, 770 cm^{-1}.

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J. Org. Chem. 2021, 86, 8101−8111

*3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-5,6-dihydroimidazo[2,1-a]isoquinoline (**3B**).* Beige solid; column chromatography (PE/EtOAc = 15:1); yield: 60 mg, 71%; mp 196.5−197.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 6.8 Hz, 1H), 7.24−7.33 (m, 4H), 7.02(d, J = 8.4 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.89 (s, 3H), 3.12 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 143.7, 138.3, 136.9, 132.7, 131.7, 129.4, 128.7, 127.9 (q, J = 31.8 Hz), 127.7 (q, J = 3.4 Hz), 126.9, 126.8, 125.0 (q, J = 3.8 Hz), 124.0, 121.9, 124.4 (q, J = 270.0 Hz), 114.6, 55.3, 41.4, 28.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ − 62.29; HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{19}N_2OF_3$ 420.1449; found 420.1448; IR: 2956, 2924, 1616, 1521, 1492, 1460, 1324, 1251, 1163, 1121, 1066, 839, 771,717 cm^{-1}.

*3-Benzyl-2-phenyl-5,6-dihydroimidazo[2,1-a]isoquinoline (**3C**).* Yellow oil; column chromatography (PE/EtOAc = 15:1); yield: 19 mg, 28%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.27−7.40 (m, 7H), 7.22−7.24 (m, 1H), 7.18 (t, J = 6.8 Hz, 3H), 4.25(s, 2H), 3.82 (t, J = 6.8 Hz, 2H), 3.03 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.6, 140.0, 138.2, 134.9, 132.2, 128.9, 128.5, 128.3, 127.8, 127.6, 127.6, 127.3, 127.1, 126.7, 126.6, 125.0, 123.8, 41.0, 29.8, 28.3; HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{20}N_2$ 336.1626; found 336.1626; IR: 3060, 2923, 1639, 1603, 1533, 1458, 1453, 1417, 1262, 1085, 1029, 970, 772, 740 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00590.

Experimental procedures and spectral for all new compounds (^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS) (PDF)

Accession Codes

CCDC 2016722 and 2050830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Ping Lu − *Department of Chemistry, Zhejiang University, Hangzhou, P. R. China;* orcid.org/0000-0002-3221-3647; Email: pinglu@zju.edu.cn

Yanguang Wang − *Department of Chemistry, Zhejiang University, Hangzhou, P. R. China;* orcid.org/0000-0002-5096-7450; Email: orgwyg@zju.edu.cn

Authors

Zaibin Wang − *Department of Chemistry, Zhejiang University, Hangzhou, P. R. China*

Hanjie Li − *Department of Chemistry, Zhejiang University, Hangzhou, P. R. China*

Zhichao Wang − *Department of Chemistry, Zhejiang University, Hangzhou, P. R. China*

Muhammad Suleman − *Department of Chemistry, Zhejiang University, Hangzhou, P. R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00590

Notes

The authors declare no competing financial interest.

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