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Synthesis of Axially Chiral Cationic Benzo[*c*]phenanthridinium Derivatives

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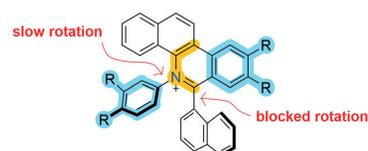
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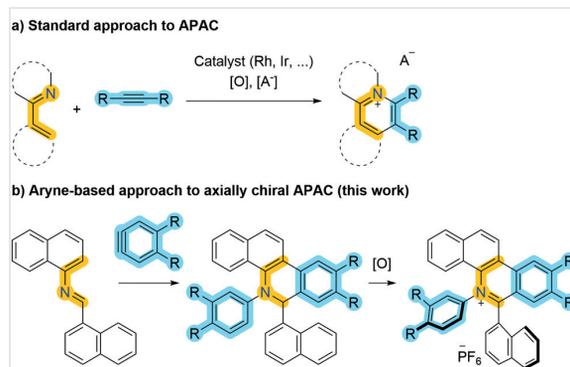


Abstract Cationic polycyclic aromatic compounds containing one or more nitrogen atom(s), also known as azonia polycyclic aromatic compounds, form a valuable class of molecules because of their fluorescent and/or medicinal properties. *N*-Arylated hydroisoquinoline derivatives were synthesized through an aryne aza-Diels–Alder cycloaddition/*N*-arylation sequence. A subsequent two-electron oxidation allowed the synthesis of some axially chiral cationic benzo[*c*]phenanthridinium derivatives. The structural and optical properties of some of these molecules were determined. Their chirality was evidenced experimentally by single-crystal X-ray diffraction and ¹H NMR spectroscopy, and their conformational behavior was examined by computational DFT methods.

Key words arynes, axial chirality, azadienes, azonia compounds, crystallography, DFT, fluorescence, rotamers

Polycyclic aromatic compounds (PAC) are molecules of high interest because of the electronic properties of their π -systems that allow for applications in innovative organic materials for technological developments.¹ The properties of the extended π -systems in PAC can be tuned by varying their size, their composition, their architecture, their charges, and their symmetry. Much is to be discovered in this area. For instance, positively charged *N*-containing PAC, so-called azonia polycyclic aromatic compounds or simply APAC, have recently attracted attention for their luminescence properties.² APAC are most conveniently synthesized from 1-azadienes and alkynes by transition-metal-catalyzed annulative reactions through C–H bond activation (Scheme 1, a).³ This approach has allowed for the synthesis of structurally diverse π -elongated APAC. However, chiral APAC have been scarcely described,⁴ and methods for their synthesis are desirable. Herein, we describe how the aryne

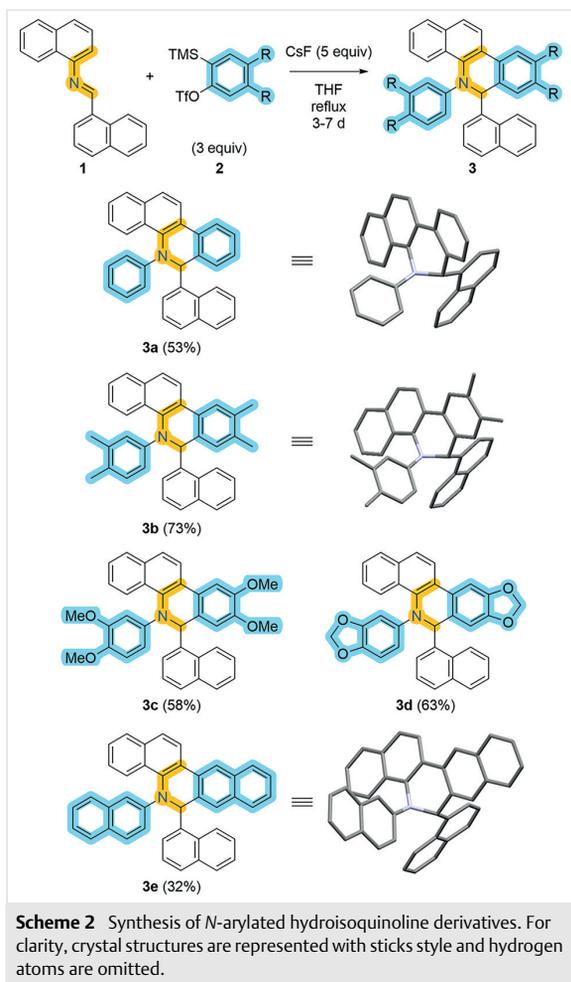
aza-Diels–Alder reaction of 2-azadienes⁵ was used for the synthesis of axially chiral APAC exhibiting a blocked C(*sp*²)-C(*sp*²) stereogenic axis and a vicinal conformationally labile N(*sp*²)-C(*sp*²) stereogenic axis⁶ (Scheme 1, b).



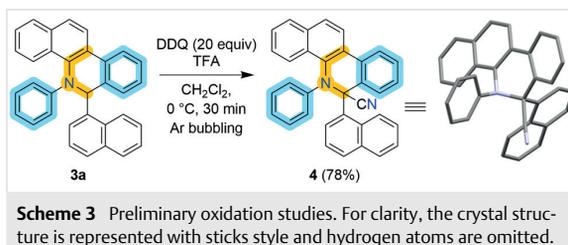
Scheme 1 Background and scope of the work

Aryne cycloadditions were demonstrated as useful for the synthesis of benzo[*c*]phenanthridine derivatives more than 30 years ago.⁷ It was hypothesized that 2-azadiene **1**, easily derived from 1-naphthaldehyde and 1-aminonaphthalene, could undergo a pseudo-multicomponent aza-Diels–Alder/*N*-arylation cascade reaction,^{5b} followed by an oxidative aromatization to afford the corresponding cationic benzo[*c*]phenanthridinium derivatives (Scheme 2). Using the previously described conditions^{5b} with an excess of *o*-(trimethylsilyl)phenyl triflate (**2a**)⁸ and KF/18-crown-6 as the fluoride anion source, the expected 1,2-dihydroisoquinoline derivative **3a** was obtained in 29% yield. Under optimized conditions with CsF as the fluoride anion source, **3a**

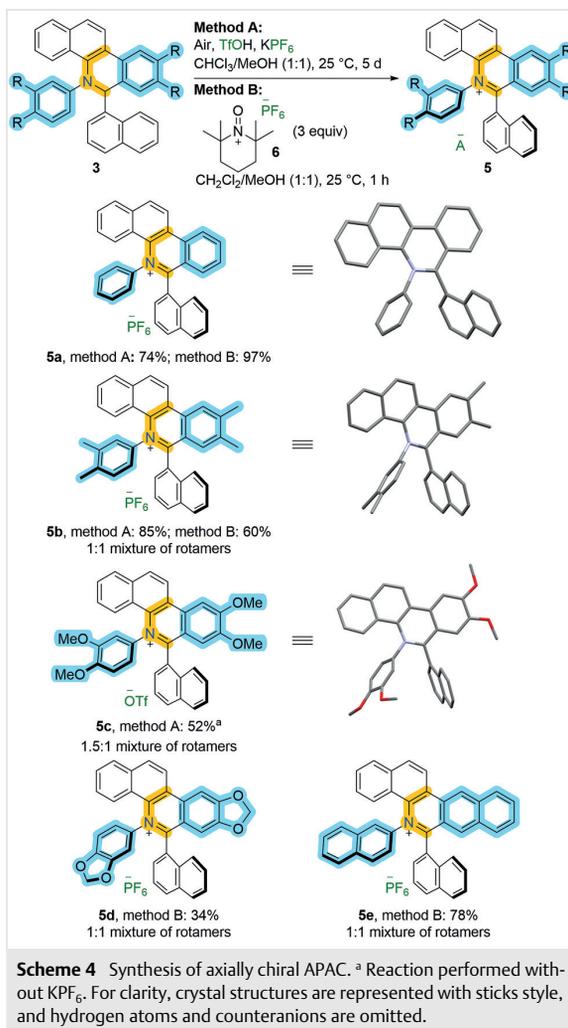
was obtained in 53% yield. Using similar conditions with various aryne precursors, the 1,2-dihydroisoquinoline derivatives **3b–e** were obtained in comparable yields. The crystallographic structures of products **3a** (CCDC 2163406), **3b** (CCDC 2163412), and **3e** (CCDC 2163407) were resolved by single-crystal X-ray diffraction analyses, which ascertained their identity.⁹



An attempt for the dehydrogenation of 1,2-dihydroisoquinoline derivative **3a** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the presence of trifluoroacetic acid afforded the cyanide adduct **4** in 78% yield, the structure of which was secured by single-crystal X-ray diffraction analysis (CCDC 2163410, Scheme 3).⁹ From this experiment, it was concluded that dehydrogenation occurred to produce the corresponding cation, which underwent addition of a cyanide anion derived from the decomposition of DDQ.



After some optimization, two suitable reaction conditions were identified for the oxidative dehydrogenation of 1,2-dihydroisoquinoline derivatives **3a–e** (Scheme 4). Method A relies on aerobic conditions, requiring prolonged reaction times, and method B uses the oxoammonium hexafluorophosphate salt **6** as the oxidant, allowing for faster reactions. The crystallographic structures of APAC **5a**



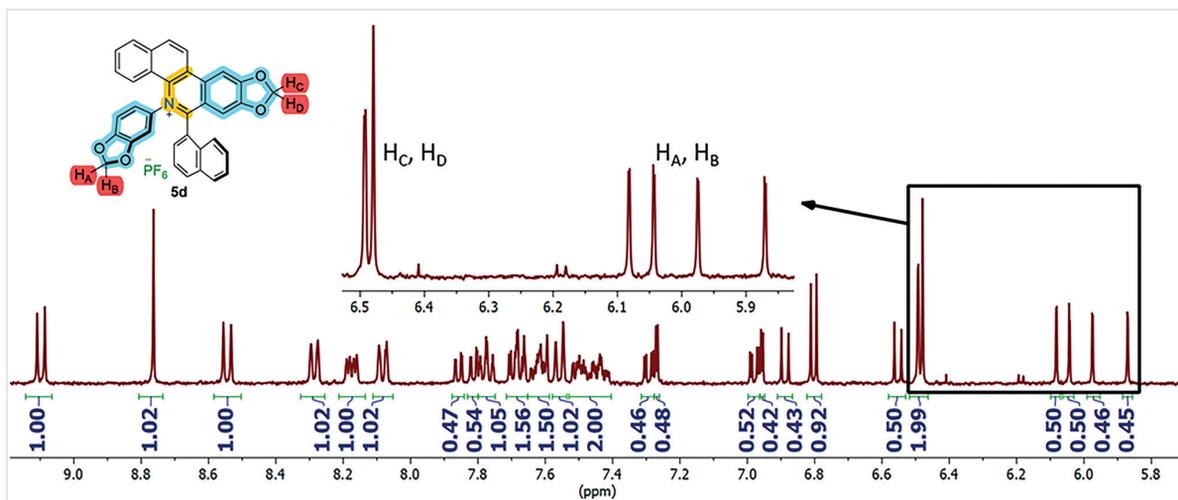


Figure 1 ^1H NMR spectrum of compound **5d** in acetone- d_6 (400 MHz) at 25 $^\circ\text{C}$

(PF_6^- salt, CCDC 2163408), **5b** (PF_6^- salt, 3:1 mixture of rotamers, CCDC 2163411), and **5c** (OTf^- salt, CCDC 2163409) were resolved by single-crystal X-ray diffraction analyses.⁹

A remarkable feature of APAC **5a–e** is they are chiral and **5b–e** exist as pairs of rotamers at 25 $^\circ\text{C}$ (1:1 to 1:1.5 mixtures). This was unambiguously demonstrated by the structural analysis of APAC **5b** with both rotamers (3:1) co-existing in the analyzed crystalline material (CCDC 2163411).⁹ This was further evidenced in the ^1H NMR analysis of APAC **5d**, with pairs of resonances accounting for the pairs of diastereotopic H atoms at the 1,3-dioxole moieties in APAC **5d** (Figure 1). APAC **5b–e** embed a conformationally stable stereogenic axis around their $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond and a configurationally labile but slowly rotating stereogenic axis around their $\text{N}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond. A conformational study using DFT calculations allowed us to capture the full picture of the conformational behavior of **5a** and **5d** (Figure 2, see details in the Supporting Information). It was calculated that rotation around the $\text{N}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond is occurring slowly at 25 $^\circ\text{C}$ with $\Delta G_{\text{rot}}^\ddagger = 89.8 \text{ kJ}\cdot\text{mol}^{-1}$ for **5a** and $\Delta G_{\text{rot}}^\ddagger = 92.0 \text{ kJ}\cdot\text{mol}^{-1}$ for **5d**, corresponding to $t_{1/2} = 10 \text{ min}$ and 24 min , respectively, leading ultimately to the



Figure 2 Conformational study of APAC **5a** and **5d** using DFT calculations [B3LYP-D3/6-31G(d) in the gas phase]; relative Gibbs free energies. Details are available in the Supporting Information.

thermodynamic mixture of rotamers over time. Contrastingly, the stereogenic axis around the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond was identified as conformationally stable at 25 $^\circ\text{C}$, with a barrier to rotation (enantiomerization) calculated at $\Delta G_{\text{rot}}^\ddagger = 164.6 \text{ kJ}\cdot\text{mol}^{-1}$ ($t_{1/2} \approx 0.25$ billion years) for **5a** and $\Delta G_{\text{rot}}^\ddagger = 170.8 \text{ kJ}\cdot\text{mol}^{-1}$ ($t_{1/2} \approx 3$ billion years) for **5d**.

The photophysical properties of APAC **5a** (PF_6^- salt) were examined in solution and in the solid state (Figure 3). The UV/vis absorption spectrum of a dichloromethane solution of **5a** showed absorption bands around 300 and 410 nm. The fluorescence spectrum showed an emission maximum at 536 nm with a broad bandwidth, and the quantum yield was measured at 3%. Measurements of emission in the solid state revealed a green fluorescence ($\lambda_{\text{FL,max}} = 504 \text{ nm}$) and a quantum yield of 7%.

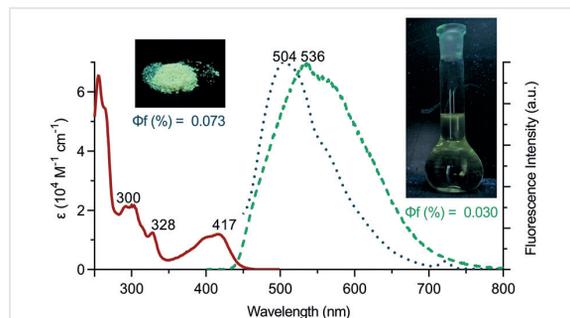


Figure 3 UV/Vis absorption (solid line) (ca. $1.6 \times 10^{-5} \text{ M}$) and fluorescence (dashed line) spectra of **5a** in CH_2Cl_2 ($\lambda_{\text{EX}} = 360 \text{ nm}$), plus fluorescence spectrum (dotted line) of **5a** under amorphous solid state ($\lambda_{\text{EX}} = 360 \text{ nm}$). Solution fluorescence quantum yield determined relative to that for 9,10-diphenylanthracene as an actinometer. Photographs of **5a** in solution (CH_2Cl_2) and solid state under 365 nm UV light.

In summary, the synthesis of an original class of axially chiral APAC is described from 2-azadiene **1** using an aryne aza-Diels-Alder cycloaddition/*N*-arylation sequence followed by two-electron oxidation. Chirality in these APAC, as well as the existence of rotamers in some cases, was probed experimentally by X-ray diffraction and NMR methods. A conformational analysis using DFT calculations confirmed the existence of a slowly rotating N(sp²)-C(sp²) single bond axis and of a blocked C(sp²)-C(sp²) single bond axis in these molecules at 25 °C. The prototype of this class of APAC **5a** exhibited some green fluorescence properties. The determination of the chiroptical properties of these molecules must await the resolution of their enantiomers.

Reactions were generally carried out under an argon atmosphere using syringes, cannula, oven-dried glassware, and dry solvents obtained from a MBRAUN solvent purification system MB SPS-800. Anhydrous solvents were all purchased from Sigma-Aldrich. All reagents were weighed and handled in air at room temperature unless otherwise mentioned, and all commercially available reagents were used as received unless otherwise mentioned. Reactions were monitored by TLC on Merck Kieselgel 60 F254 0.2 mm plates. Visualization was accomplished using UV light (254 and/or 365 nm) and/or using an acidic *p*-anisaldehyde ethanolic stain. Purifications were routinely performed using flash chromatography columns packed with 40–63 μm silica gel, generally eluted with pentane, CH₂Cl₂, toluene, EtOAc, and MeOH. Melting points were recorded using a Büchi Melting Point B-540 apparatus. NMR data were generally recorded in deuterated chloroform at 298 ± 3 K at 300, 400, or 500 MHz using the residual nondeuterated solvent as an internal standard for ¹H NMR (δ = 7.26 ppm) and the deuterated solvent signal for ¹³C NMR (δ = 77.16 ppm). In some cases, acetone-*d*₆ was used to record the NMR data, using as an internal standard the residual acetone signal for ¹H NMR (δ = 2.05 ppm) and the deuterated acetone signal for ¹³C NMR (δ = 206.26 and 29.84 ppm). Chemical shifts (δ) are in ppm, coupling constants (*J*) are in hertz (Hz), and the classical abbreviations are used to describe the signal multiplicities. High-resolution mass spectra (HRMS) were recorded in triplicate at the Spectropole (<http://fr-chimie.univ-amu.fr/spectropole/>) on a Waters Synapt G2 HRMS apparatus using a positive electrospray ionization (ESI) source.

Aryne precursors **2a**, **2c**, and **2e** were purchased from commercial sources; aryne precursors **2b** and **2d** were synthesized according to literature procedures.¹⁰ Oxoammonium hexafluorophosphate salt **6** was prepared according to a literature procedure.¹¹

N,1-Di(naphthalen-1-yl)methanimine (1)

In a dedicated microwave tubular reaction vessel, 1-naphthylamine (102 mg, 0.69 mmol) and 1-naphthaldehyde (95 μL, 0.70 mmol) were charged without solvent. The mixture was subjected to microwave irradiation at 120 °C for 30 min, after which the reaction was cooled to 55 °C with an air flow. The resulting solid was triturated in cold EtOH (5 mL) to afford **1** (177 mg, 90%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 9.30 (d, *J* = 8.6 Hz, 1 H), 9.18 (s, 1 H), 8.46–8.38 (m, 1 H), 8.20 (dd, *J* = 7.2, 1.3 Hz, 1 H), 8.03 (d, *J* = 8.2 Hz, 1 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 7.94–7.85 (m, 1 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.72–7.47 (m, 6 H), 7.14 (dd, *J* = 7.2, 1.1 Hz, 1 H).

HRMS (ESI+): *m/z* [M + H]⁺ calcd for C₂₁H₁₆N⁺: 282.1277; found: 282.1272.

These data are in accordance with previously reported data for this compound.¹²

6-(Naphthalen-1-yl)-5-phenyl-5,6-dihydrobenzo[c]phenanthridine (3a); Typical Procedure

A sealable oven-dried tubular flask was charged with azadiene **1** (106 mg, 0.38 mmol), aryne precursor **2a** (340 mg, 1.13 mmol), and CsF (286 mg, 1.91 mmol). The mixture was placed under an argon atmosphere, and anhydrous THF (3.0 mL) was added. The solution was stirred at 70 °C for 3 d. The final reaction mixture was diluted with CH₂Cl₂ and water. The organic layer was separated, and the aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude product was recrystallized (MeOH) to afford **3a** (86.8 mg, 53%) as colorless prisms.

Mp 267 °C (MeOH); *R*_f = 0.56 (toluene/petroleum ether, 1:3).

¹H NMR (300 MHz, CDCl₃): δ = 9.11 (d, *J* = 8.6 Hz, 1 H), 8.02 (d, *J* = 8.6 Hz, 2 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 7.72–7.64 (m, 4 H), 7.55–7.45 (m, 3 H), 7.39–7.30 (m, 2 H), 7.24–7.13 (m, 3 H), 7.11–7.02 (m, 4 H), 6.95 (t, *J* = 7.7 Hz, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 6.56 (d, *J* = 7.3 Hz, 1 H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 148.7, 136.2, 135.8, 135.4, 133.9, 132.8, 131.9, 130.7, 129.2, 128.9, 128.4, 128.3, 128.2, 128.0, 127.8, 126.8, 126.1, 125.8, 125.7, 125.4, 125.2, 124.7, 124.1, 123.7, 121.8, 120.5, 117.8, 62.7.

The structure of **3a** was ascertained by single-crystal X-ray diffraction analysis.⁹

5-(3,4-Dimethylphenyl)-8,9-dimethyl-6-(naphthalen-1-yl)-5,6-dihydrobenzo[c]phenanthridine (3b)

Following the typical procedure with azadiene **1** (107 mg, 0.38 mmol), aryne precursor **2b** (377 mg, 1.16 mmol), CsF (287 mg, 1.88 mmol), and anhydrous THF (3.0 mL), the mixture was stirred for 3 d. The crude product was recrystallized (MeOH) to afford **3b** (136 mg, 73%) as an off-white solid.

Mp 251 °C (MeOH); *R*_f = 0.56 (toluene/petroleum ether, 1:3).

¹H NMR (400 MHz, CDCl₃): δ = 9.03 (dd, *J* = 8.7, 4.6 Hz, 1 H), 7.89 (dd, *J* = 8.6, 2.7 Hz, 1 H), 7.70–7.62 (m, 2 H), 7.60–7.51 (m, 4 H), 7.42–7.35 (m, 2 H), 7.08 (dd, *J* = 8.1, 6.6 Hz, 1 H), 6.99–6.91 (m, 2 H), 6.86–6.82 (m, 2 H), 6.79 (dd, *J* = 8.1, 3.0 Hz, 2 H), 6.61 (tt, *J* = 5.3, 2.7 Hz, 1 H), 6.48 (dd, *J* = 7.4, 4.3 Hz, 1 H), 2.27 (d, *J* = 1.9 Hz, 3 H), 2.15 (d, *J* = 1.4 Hz, 3 H), 2.02 (s, 6 H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 147.1, 137.2, 136.5, 136.4, 136.3, 136.2, 133.9, 133.6, 132.9, 131.9, 130.9, 130.5, 130.2, 128.9, 128.5, 128.3, 128.2, 127.7, 126.7, 125.9, 125.4, 125.3, 125.3, 125.2, 124.8, 124.7, 124.3, 121.8, 119.1, 115.5, 62.5, 20.4, 19.9, 19.7, 18.8.

The structure of **3b** was ascertained by single-crystal X-ray diffraction analysis.⁹

5-(3,4-Dimethoxyphenyl)-8,9-dimethoxy-6-(naphthalen-1-yl)-5,6-dihydrobenzo[c]phenanthridine (3c)

Following the typical procedure with azadiene **1** (110 mg, 0.39 mmol), aryne precursor **2c** (421 mg, 1.17 mmol), CsF (295 mg, 1.98 mmol), and anhydrous THF (3.0 mL), the mixture was stirred for 3 d. The crude product was recrystallized (MeOH) to afford **3c** (125 mg, 58%) as an off-white solid.

Mp 296 °C (MeOH); *R*_f = 0.56 (toluene/petroleum ether, 1:3).

¹H NMR (400 MHz, CDCl₃): δ = 9.04 (d, *J* = 8.6 Hz, 1 H), 7.87 (d, *J* = 8.7 Hz, 1 H), 7.69 (dd, *J* = 8.2, 1.3 Hz, 1 H), 7.62 (dt, *J* = 8.8, 1.4 Hz, 2 H), 7.60–7.55 (m, 2 H), 7.50–7.38 (m, 3 H), 7.12 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1 H), 6.99 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H), 6.90 (t, *J* = 7.7 Hz, 1 H), 6.71 (d, *J* = 12.8 Hz, 2 H), 6.64–6.55 (m, 3 H), 6.52 (dd, *J* = 8.7, 2.7 Hz, 1 H), 3.97 (s, 3 H), 3.74 (s, 3 H), 3.69 (s, 3 H), 3.52 (s, 3 H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 149.4, 149.3, 149.0, 143.9, 143.9, 136.4, 135.9, 134.0, 133.6, 131.7, 130.6, 129.1, 128.3, 127.9, 127.7, 127.6, 126.6, 126.0, 125.9, 125.3, 125.0, 125.0, 123.9, 121.3, 112.1, 110.8, 110.5, 106.8, 104.5, 63.4, 56.2, 56.1, 55.9, 55.7.

HRMS (ESI+): *m/z* [M + H]⁺ calcd for C₃₇H₃₂NO₄⁺: 554.2326; found: 554.2329.

5-(Benzo[d][1,3]dioxol-5-yl)-6-(naphthalen-1-yl)-5,6-dihydrobenzo[c][1,3]dioxolo[4,5-*j*]phenanthridine (3d)

Following the typical procedure with azadiene **1** (101 mg, 0.36 mmol), aryne precursor **2d** (430 mg, 1.26 mmol), CsF (273 mg, 1.80 mmol), and anhydrous THF (3.0 mL), the mixture was stirred for 3 d. Some amount of aryne precursor (50 mg, 0.15 mmol) was then added to the reaction mixture, which was stirred for a total of 5 d. The crude product was purified by column chromatography and then recrystallized (MeOH) to increase purity and afford **3d** (118 mg, 63%) as an off-white solid.

Mp 283 °C (MeOH); *R*_f = 0.37 (EtOAc/pentane, 1:4) (blue fluorescence under 365 nm UV light).

¹H NMR (300 MHz, CDCl₃): δ = 9.08 (d, *J* = 8.6 Hz, 1 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.77–7.61 (m, 5 H), 7.56–7.44 (m, 3 H), 7.20 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1 H), 7.08 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 7.01–6.94 (m, 1 H), 6.73 (d, *J* = 10.3 Hz, 2 H), 6.63 (d, *J* = 8.3 Hz, 2 H), 6.60 (d, *J* = 2.3 Hz, 1 H), 6.51 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.01 (dd, *J* = 7.5, 1.4 Hz, 2 H), 5.85 (s, 2 H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 148.2, 148.0, 147.7, 144.6, 142.1, 135.9, 135.6, 133.9, 133.6, 131.8, 130.6, 129.1, 129.0, 128.2, 127.9, 127.7, 127.0, 126.6, 126.1, 125.7, 125.5, 125.4, 125.3, 124.9, 124.8, 124.0, 121.5, 111.6, 108.4, 107.9, 104.2, 101.4, 101.3, 101.0, 64.3.

HRMS (ESI+): *m/z* [M + H]⁺ calcd for C₃₅H₂₄NO₄⁺: 522.1700; found: 522.1704.

6-(Naphthalen-1-yl)-5-(naphthalen-2-yl)-5,6-dihydrodibenzo[c,j]phenanthridine (3e)

Following the typical procedure with azadiene **1** (101 mg, 0.36 mmol), aryne precursor **2e** (400 mg, 1.15 mmol), CsF (273 mg, 1.80 mmol), and anhydrous THF (3.0 mL), the mixture was stirred for 3 d. Some amount of aryne precursor (50 mg, 0.14 mmol) was then added to the reaction mixture, which was stirred for a total of 7 d. The crude product was purified by column chromatography and then recrystallized (MeOH) to increase purity and afford **3e** (65 mg, 32%) as an off-white solid.

Mp 273 °C (MeOH); *R*_f = 0.36 (toluene/pentane, 4:6) (blue fluorescence under 365 nm UV light).

¹H NMR (400 MHz, CDCl₃): δ = 9.26 (dd, *J* = 8.7, 1.1 Hz, 1 H), 8.47 (s, 1 H), 8.21 (d, *J* = 8.7 Hz, 1 H), 7.98 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.83 (s, 1 H), 7.81–7.68 (m, 6 H), 7.65 (d, *J* = 8.8 Hz, 2 H), 7.56–7.38 (m, 7 H), 7.36–7.27 (m, 2 H), 7.27–7.18 (m, 2 H), 7.05 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H), 6.92 (dd, *J* = 8.2, 7.3 Hz, 1 H), 6.58 (dt, *J* = 7.4, 1.1 Hz, 1 H).

¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 146.5, 136.8, 135.9, 134.4, 134.1, 134.0, 133.9, 133.6, 133.0, 132.0, 131.2, 130.9, 129.0, 128.9, 128.8, 128.7, 128.4, 128.2, 127.8, 127.7, 127.3, 127.1, 126.9, 126.3, 126.2, 126.2, 126.1, 126.0, 125.5, 125.0, 124.6, 124.3, 123.6, 123.0, 122.3, 119.1, 113.2, 63.3.

The structure of **3e** was ascertained by single-crystal X-ray diffraction analysis.⁹

6-(Naphthalen-1-yl)-5-phenyl-5,6-dihydrobenzo[c]phenanthridine-6-carbonitrile (4)

In a round-bottom flask, **3a** (51 mg, 0.12 mmol) was reacted with DDQ (534 mg, 2.35 mmol), in triflic acid (3 mL) and CH₂Cl₂ (5 mL) at 0 °C (ice bath) with constant bubbling of argon for 30 min. Then, the reaction mixture was poured into saturated sodium carbonate. The resulting mixture was filtered to isolate a raw brown solid that was resolubilized in boiling MeOH and recrystallized to afford **4** (42 mg, 78%) as pale pink microcrystals.

Mp >350 °C (dec) (MeOH); *R*_f = 0.35 (CH₂Cl₂/MeOH, 10:1).

¹H NMR (300 MHz, CDCl₃): δ = 10.00 (dq, *J* = 8.8, 0.9 Hz, 1 H), 8.12–8.02 (m, 2 H), 7.87 (d, *J* = 8.7 Hz, 1 H), 7.83–7.74 (m, 2 H), 7.74–7.65 (m, 2 H), 7.56 (td, *J* = 7.4, 1.3 Hz, 4 H), 7.46 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1 H), 7.43–7.37 (m, 2 H), 7.25–7.07 (m, 5 H), 6.95 (dd, *J* = 8.2, 7.5 Hz, 1 H), 6.55 (dd, *J* = 7.5, 1.2 Hz, 1 H).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 145.8, 137.3, 134.6, 134.5, 133.1, 132.8, 131.1, 130.8, 129.9, 129.6, 129.0, 128.9, 128.9, 127.9, 127.7, 127.7, 127.5, 127.1, 126.4, 126.3, 126.3, 126.1, 126.1, 125.8, 125.5, 124.8, 124.2, 124.0, 120.5, 118.9, 69.3.

The structure of **4** was ascertained by single-crystal X-ray diffraction analysis.⁹

6-(Naphthalen-1-yl)-5-phenylbenzo[c]phenanthridin-5-ium Hexafluorophosphate (5a); Method A Typical Procedure

Hydroisoquinoline derivative **3a** (72 mg, 0.16 mmol) was added to a 10-mL round-bottom flask, dissolved in a mixture of MeOH/CHCl₃ (1:1) (5.0 mL), and triflic acid (1 mL) was added. The mixture was stirred in open atmosphere for 5 d, then a saturated solution of potassium hexafluorophosphate in EtOH (5 mL) was added. The mixture was filtered and washed with MeOH to afford **5a** (70 mg, 74%) as yellow bright prisms.

Mp >350 °C (dec) (EtOH); *R*_f = 0.42 (CH₂Cl₂/MeOH, 3:1) (yellow fluorescence under 365 nm UV light).

Following Method B typical procedure (see below) with **3a** (192 mg, 0.44 mmol) afforded **5a** (250 mg, 97%) as a yellow solid.

¹H NMR (400 MHz, acetone-*d*₆): δ = 9.48 (d, *J* = 8.7 Hz, 1 H), 9.32 (d, *J* = 9.1 Hz, 1 H), 8.68 (d, *J* = 9.0 Hz, 1 H), 8.54 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1 H), 8.34 (d, *J* = 8.1 Hz, 1 H), 8.16 (d, *J* = 8.3 Hz, 1 H), 8.07 (d, *J* = 8.3 Hz, 1 H), 8.01 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1 H), 7.89–7.75 (m, 4 H), 7.69–7.58 (m, 3 H), 7.56–7.40 (m, 4 H), 7.37–7.30 (m, 2 H), 7.16 (td, *J* = 7.7, 1.4 Hz, 1 H).

¹³C{¹H} NMR (101 MHz, acetone-*d*₆): δ = 164.8, 144.7, 139.6, 137.2, 136.9, 135.8, 134.5, 134.0, 133.5, 132.8, 132.4, 132.4, 132.0, 131.2, 130.9, 130.8, 130.7, 130.0, 129.9, 129.8, 129.0, 128.9, 128.5, 128.1, 128.0, 127.5, 127.4, 126.8, 126.1, 125.8, 125.2, 121.2.

The structure of **5a** was ascertained by single-crystal X-ray diffraction analysis.⁹

5-(3,4-Dimethylphenyl)-8,9-dimethyl-6-(naphthalen-1-yl)benzo[c]phenanthridin-5-ium Hexafluorophosphate (5b)

Following Method A typical procedure with **3b** (88 mg, 0.18 mmol), triflic acid (1 mL), and a mixture of MeOH/CHCl₃ (1:1) (5.0 mL) afforded **5b** (97 mg, 85%) as yellow bright prisms.

Mp 295 °C (MeOH/CHCl₃, 1:1); *R*_f = 0.64 (CH₂Cl₂/pentane, 1:9) (yellow fluorescence under 365 nm UV light).

Following Method B typical procedure (see below) with **3b** (45 mg, 0.092 mmol) afforded **5b** (35 mg, 60%) as a yellow solid.

¹H NMR (400 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1:1 ratio) = 9.32–9.21 (m, 2 H), 8.59 (d, *J* = 9.0 Hz, 1 H), 8.30–8.27 (m, 1 H), 8.13 (ddt, *J* = 8.3, 2.1, 1.1 Hz, 1 H), 8.09–8.00 (m, 1 H), 7.83 (td, *J* = 7.1, 1.2 Hz, 1 H), 7.77–7.68 (m, 1 H), 7.69–7.61 (m, 1 H), 7.62–7.56 (m, 2.5 H), 7.55–7.50 (m, 1 H), 7.49–7.37 (m, 2 H), 7.36 (dq, *J* = 9.1, 0.9 Hz, 0.5 H), 7.28 (dddd, *J* = 9.2, 6.8, 1.5, 0.9 Hz, 1 H), 7.22–7.15 (m, 1 H), 7.13 (dd, *J* = 8.1, 2.4 Hz, 0.5 H), 6.87 (d, *J* = 8.1 Hz, 0.5 H), 2.82–2.79 (m, 3 H), 2.36 (dd, *J* = 6.3, 1.0 Hz, 3 H), 2.16 (s, 3 H), 2.14 (s, 1.5 H), 1.77 (s, 1.5 H).

¹³C{¹H} NMR (101 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1:1 ratio; some resonances are overlapping, some are not and appear as half-intensity signals) = 163.4, 163.3, 152.3, 152.2, 143.1, 143.1, 142.2, 142.1, 140.6, 140.5, 139.6, 139.2, 136.5, 135.6, 135.3, 135.2, 133.9, 133.8, 133.8, 132.7, 132.6, 132.0, 131.9, 131.3, 131.1, 131.0, 130.9, 130.6, 130.5, 130.1, 130.0, 129.6, 129.6, 128.8, 128.7, 128.5, 128.2, 128.0, 128.0, 127.9, 127.8, 127.3, 127.3, 127.0, 126.8, 126.7, 126.1, 126.1, 126.1, 126.1, 125.6, 125.6, 125.1, 124.9, 121.1, 21.7, 20.2, 19.6, 19.5, 19.4, 19.1.

The structure of **5b** was ascertained by single-crystal X-ray diffraction analysis.⁹ Note that the crystal selected for the analysis contained a 3:1 mixture of the two rotamers.

5-(3,4-Dimethoxyphenyl)-8,9-dimethoxy-6-(naphthalen-1-yl)benzo[c]phenanthridin-5-ium Trifluoromethanesulfonate (5c)

Following Method A typical procedure with **3c** (82 mg, 0.15 mmol), triflic acid (1 mL), and MeOH/CHCl₃ (5 mL), without adding the saturated solution of potassium hexafluorophosphate, afforded **5c** (54 mg, 52%) as yellow bright prisms.

Mp >350 °C (dec) (EtOH); *R*_f = 0.35 (CH₂Cl₂/MeOH, 1:1) (yellow fluorescence under 365 nm UV light).

¹H NMR (500 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1.5:1 ratio) = 9.25 (d, *J* = 9.1 Hz, 1 H), 8.75 (s, 1 H), 8.53 (d, *J* = 9.1 Hz, 1 H), 8.27 (d, *J* = 7.9 Hz, 1 H), 8.18–8.08 (m, 1.6 H), 8.03 (t, *J* = 7.1 Hz, 0.8 H), 7.87 (d, *J* = 8.3 Hz, 0.6 H), 7.73 (t, *J* = 7.2 Hz, 1.4 H), 7.70–7.63 (m, 1.2 H), 7.62–7.52 (m, 2 H), 7.50–7.40 (m, 1.8 H), 7.37–7.31 (m, 1 H), 7.14 (dd, *J* = 8.6, 2.6 Hz, 0.6 H), 7.10 (d, *J* = 2.5 Hz, 0.6 H), 6.96 (d, *J* = 8.6 Hz, 0.6 H), 6.92 (dd, *J* = 8.6, 2.6 Hz, 0.4 H), 6.88 (s, 0.6 H), 6.85 (s, 0.4 H), 6.62 (d, *J* = 8.7 Hz, 0.4 H), 4.40 (d, *J* = 2.5 Hz, 3 H), 3.77 (s, 1.8 H), 3.68 (s, 1.2 H), 3.66 (s, 1.2 H), 3.52 (d, *J* = 3.1 Hz, 3 H), 3.03 (s, 1.8 H).

¹³C{¹H} NMR (126 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1.5:1 ratio; some resonances are overlapping, some are not and appear as 0.6 or 0.4 intensity signals) = 160.7, 160.4, 160.1, 153.7, 153.7, 151.7, 151.7, 150.9, 150.5, 137.2, 137.1, 136.5, 135.4, 135.3, 134.1, 134.0, 133.1, 133.0, 132.3, 132.1, 131.9, 130.9, 130.8, 130.8, 130.6, 130.5, 129.9, 129.7, 129.6, 129.0, 128.7, 128.3, 128.2, 128.0, 127.9, 127.6, 127.4, 127.1, 127.1, 126.9, 126.7, 126.2, 126.1, 125.8, 123.2, 122.1, 121.6, 121.0, 114.3, 112.5, 112.3, 112.0, 110.0, 104.7, 58.2, 56.7, 56.5, 55.8.

The structure of **5c** was ascertained by single-crystal X-ray diffraction analysis.⁹

5-(Benzo[d][1,3]dioxol-5-yl)-6-(naphthalen-1-yl)benzo[c][1,3]dioxolo[4,5-*j*]phenanthridin-5-ium Hexafluorophosphate (5d)

Method B Typical Procedure

Hydroisoquinoline derivative **3d** (95 mg, 0.18 mmol) was added to a 10-mL round-bottom flask, dissolved in a mixture of MeOH/CH₂Cl₂ (1:1) (4.0 mL), and 2,2,6,6-tetramethyl-1-oxopiperidin-1-ium hexafluorophosphate (**6**; 150 mg, 0.50 mmol) was added. The mixture was stirred in open atmosphere for 1 h, filtered, and washed with MeOH to afford **5d** (41 mg, 34%) as a bright brown solid.

Mp >350 °C (amorphous); *R*_f = 0.05 (CH₂Cl₂) (orange fluorescence under 365 nm UV light).

¹H NMR (400 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1:1 ratio) = 9.10 (d, *J* = 9.2 Hz, 1 H), 8.76 (s, 1 H), 8.54 (d, *J* = 9.1 Hz, 1 H), 8.29 (d, *J* = 8.0 Hz, 1 H), 8.17 (dd, *J* = 8.3, 3.7 Hz, 1 H), 8.08 (d, *J* = 8.6 Hz, 1 H), 7.86 (dd, *J* = 7.2, 1.2 Hz, 0.5 H), 7.81 (dd, *J* = 7.1, 1.2 Hz, 0.5 H), 7.77 (ddt, *J* = 8.0, 6.8, 1.2 Hz, 1 H), 7.69 (ddd, *J* = 8.5, 7.2, 2.5 Hz, 1.5 H), 7.66–7.57 (m, 1.5 H), 7.56 (dd, *J* = 9.1, 0.9 Hz, 1 H), 7.54–7.46 (m, 1 H), 7.47–7.39 (m, 1 H), 7.29 (dd, *J* = 8.4, 2.3 Hz, 0.5 H), 7.27 (d, *J* = 2.3 Hz, 0.5 H), 6.98 (dd, *J* = 8.3, 2.2 Hz, 0.5 H), 6.96 (d, *J* = 2.3 Hz, 0.5 H), 6.89 (d, *J* = 8.4 Hz, 0.5 H), 6.80 (d, *J* = 6.7 Hz, 1 H), 6.55 (d, *J* = 8.4 Hz, 0.5 H), 6.52–6.46 (m, 2 H), 6.08 (d, *J* = 0.8 Hz, 0.5 H), 6.04 (d, *J* = 0.8 Hz, 0.5 H), 5.97 (d, *J* = 0.8 Hz, 0.5 H), 5.87 (d, *J* = 0.8 Hz, 0.5 H).

¹³C{¹H} NMR (101 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1:1 ratio; some resonances are overlapping, some are not and appear as half-intensity signals) = 159.5, 152.6, 150.2, 150.2, 149.8, 149.4, 138.0, 137.9, 137.9, 137.9, 136.7, 135.6, 134.1, 133.4, 132.6, 132.4, 132.1, 131.3, 130.7, 130.7, 130.7, 130.5, 130.4, 129.9, 129.9, 129.8, 128.9, 128.9, 128.5, 128.5, 128.0, 127.7, 127.5, 127.5, 126.7, 126.5, 125.9, 125.9, 124.9, 124.9, 124.6, 122.4, 121.4, 121.4, 110.8, 109.3, 109.3, 109.0, 107.3, 106.0, 103.8, 103.7, 102.2.

HRMS (ESI⁺): *m/z* [M⁺A]⁺ calcd for C₇₀H₄₄N₂O₈PF₆⁺: 1185.2734; found: 1185.2748.

6-(Naphthalen-1-yl)-5-(naphthalen-2-yl)dibenzo[c,j]phenanthridin-5-ium Hexafluorophosphate (5e)

Following Method B typical procedure with **3e** (30 mg, 0.056 mmol), 2,2,6,6-tetramethyl-1-oxopiperidin-1-ium hexafluorophosphate (**6**; 60 mg, 0.17 mmol), and a mixture of MeOH/CH₂Cl₂ (1:1) (4.0 mL) afforded **5e** (30 mg, 78%) as an orange solid.

Mp 237 °C (amorphous); *R*_f = 0.15 (CH₂Cl₂) (orange fluorescence under 365 nm UV light).

¹H NMR (400 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1:1 ratio) = 10.10 (d, *J* = 3.8 Hz, 1 H), 9.50 (dd, *J* = 9.1, 3.0 Hz, 1 H), 8.78 (s, 0.5 H), 8.72 (d, *J* = 9.6 Hz, 1.5 H), 8.59 (ddd, *J* = 8.6, 2.0, 1.0 Hz, 1 H), 8.34–8.26 (m, 1.5 H), 8.21–8.00 (m, 5.5 H), 7.96 (d, *J* = 8.8 Hz, 0.5 H), 7.93–7.74 (m, 4 H), 7.74–7.48 (m, 5.5 H), 7.48–7.36 (m, 3 H), 7.10 (dddd, *J* = 9.1, 6.8, 6.1, 1.5 Hz, 1 H).

¹³C{¹H} NMR (101 MHz, acetone-*d*₆): δ (mixture of two rotamers in a 1:1 ratio; some resonances are overlapping, some are not and appear as half-intensity signals) = 168.6, 168.3, 142.2, 142.0, 139.2, 139.2, 137.3, 137.2, 136.4, 136.4, 134.4, 134.4, 134.3, 134.0, 134.0, 133.9, 133.9, 133.9, 133.9, 133.4, 133.1, 133.1, 132.5, 132.3, 132.3, 131.4, 131.0, 131.0, 131.0, 130.8, 130.7, 130.6, 130.4, 130.2, 130.0, 129.9, 129.9, 129.9, 129.9, 129.8, 129.7, 129.6, 129.5, 129.5, 129.4, 129.1, 129.1, 129.1, 129.1, 129.1, 129.0, 129.0, 129.0, 128.9, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 127.9, 127.6, 126.9, 126.9, 126.8, 126.7, 126.5, 126.3, 125.8, 125.6, 125.1, 125.0, 124.9, 124.8, 121.5, 121.4.

HRMS (ESI⁺): *m/z* [M]⁺ calcd for C₄₁H₂₆N⁺: 532.2060; found: 532.2059.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/a-1845-3128>.

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