Supporting Information

A Facile Access to Substituted Cationic 12-Azapyrene Salts by Rhodium(III)-Catalyzed C–H Annulation of N-Arylpyridinium Salts

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I. General remarks

Unless otherwise noted, all reagents were prepared from commercial suppliers and used without further purification. Alkynes\(^1\) and \([\text{Cp}^*\text{RhCl}]_2\)\(^2\) were prepared according to the literature procedure. DCE, MeCN, DMF, DMSO were dried by refluxing over Ca\(\text{H}_2\) and freshly distilled prior to use. Toluene and 1,4-dioxane were dried by refluxing over sodium and freshly distilled prior to use. NMR spectra were recorded on a Bruker AV II-400 MHz or Agilent 400-MR DD2 spectrometer (\(^1\)H NMR at 400 MHz, \(^{13}\)C NMR at 100 MHz and \(^{19}\)F at 376 MHz). The \(^1\)H NMR (400 MHz) chemical shifts and the \(^{13}\)C NMR (100 MHz) chemical shifts were measured relative to CDCl\(_3\) or DMSO-\(d_6\) as the internal reference (CDCl\(_3\): \(\delta_H = 7.26\) ppm, \(\delta_C = 77.16\) ppm; DMSO-\(d_6\): \(\delta_H = 2.50\) ppm, \(\delta_C = 39.52\) ppm). High resolution mass spectra (HRMS) were recorded on a Waters-Q-TOF-Premier (ESI) or a Shimadzu LCMS-IT-TOF (ESI). UV/vis spectra were measured on a HITACHI U-2910. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system.

II. General procedure for the synthesis of \(N\)-arylpyridinium salts

\[
\begin{align*}
\text{R}^1_N^+ & + \text{R}^2_{i}^{+\text{BF}_4} & \xrightarrow{\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}} & \text{Cu(OAc)\text{BF}_4} \\
\text{DMF, 8 h, 100 °C} & & & \text{DMF, 8 h, 100 °C}
\end{align*}
\]

The \(N\)-arylpyridinium salts were synthesized from a modified procedure of our previous report.\(^3\) To a 25 mL round bottom flask, a substituted pyridine (2 mmol), a diaryliodonium tetrafluoroborate (3 mmol, 1.5 equiv), copper acetate monohydrate (10 mol\%, 0.2 mmol) and DMF (8 ml) were added. The reaction mixture was then heated at 100 °C for 8 hours. After cooled down to room temperature, DMF was removed under vacuum. The mixture was dissolved in methanol and precipitated using ethyl ether to give the pure product suitable for analysis.
III. Optimization of the reaction conditions

Table S1 Optimization of the reaction conditions.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (5 mol %)</th>
<th>Oxidant (equiv)</th>
<th>Base (equiv)</th>
<th>Solvent</th>
<th>Yield \textsuperscript{b} of 3a</th>
<th>Yield \textsuperscript{b} of 4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Cp*RhCl\textsubscript{2}]\textsubscript{2}</td>
<td>AgBF\textsubscript{4}(2)</td>
<td>NaOAc(2)</td>
<td>DCE</td>
<td>Trace</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>[Cp*Rh(MeCN)\textsubscript{2}(SbF\textsubscript{6})\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>n.d.</td>
<td>88 %</td>
</tr>
<tr>
<td>3</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(acac)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>CuO(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>–</td>
<td>DCE</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>–</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DMF</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DMSO</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>10</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>Toluene</td>
<td>28%</td>
<td>21%</td>
</tr>
<tr>
<td>11</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>MeCN</td>
<td>24%</td>
<td>45%</td>
</tr>
<tr>
<td>12</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>Dioxane</td>
<td>42%</td>
<td>Trace</td>
</tr>
<tr>
<td>13</td>
<td>[Cp*RhCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>20%</td>
<td>36%</td>
</tr>
<tr>
<td>14</td>
<td>[Cp*IrCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>40%</td>
<td>Trace</td>
</tr>
<tr>
<td>15</td>
<td>[Cp*CoCl\textsubscript{2}]</td>
<td>Cu(OAc)\textsubscript{2}(4)</td>
<td>NaOAc(4)</td>
<td>DCE</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: 1a(0.1 mmol, 1 equiv), 2a(0.4 mmol, 4 equiv), catalyst, base, oxidants in solvent (2 mL) under N\textsubscript{2} at 140 °C for 16 h. \textsuperscript{b} Isolated yields.

IV. General procedure for the synthesis of 12-azapyrene derivatives

A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with an
arylpyridinium salt 1 (0.1 mmol), an alkyne 2 (0.4 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol), Cu(OAc)₂ (73 mg, 0.4 mmol) and NaOAc (32.8 mg, 0.4 mmol) under N₂. Dry DCE (2.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 °C for 16 h. After cooled to ambient temperature, 4.0 mL of saturated NaBF₄ (aq.) was added and the mixture was stirred at room temperature for another 0.5 h under air. The organic layer was then separated and the water layer was extracted with CH₂Cl₂ (5.0 mL x 3). The combined organic phase was concentrated under vacuum and the residue was purified by column chromatography on Al₂O₃ (neutral, 200-300 mesh) with MeCN/CH₂Cl₂ (1/10 to 1/3) to provide the desired product.

V. H/D Exchange experiments

a) A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with 1a (0.1 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol), Cu(OAc)₂ (73 mg, 0.4 mmol) and NaOAc (32.8 mg, 0.4 mmol) under N₂. Dry DCE (2.0 mL) and D₂O (1.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the ¹H NMR analysis. The ¹H NMR spectrum shows the incorporation
of deuterium into the labeled protons of the substrate 1a.

b) A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with 1a (0.1 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol) and Cu(OAc)₂ (73 mg, 0.4 mmol) under N₂. Dry DCE (2.0 mL) and D₂O (1.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the ¹H NMR analysis. The ¹H NMR spectrum shows the incorporation of deuterium into the labeled protons of the substrate 1a.
c) A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with 1a (0.1 mmol), diphenylacetylene (0.4 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol), Cu(OAc)$_2$ (73 mg, 0.4 mmol) and NaOAc (32.8 mg, 0.4 mmol) under N$_2$. Dry DCE (2.0 mL) and D$_2$O (1.0 mL) was then added and the tube was sealed with a teflon-coated screw cap. The reaction solution was heated at 140 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the $^1$H NMR analysis. The $^1$H NMR spectrum shows the incorporation of deuterium into the labeled protons of the single annulated product 3a.
VI. Experimental data for the described substances

4-(tert-Butyl)-1-phenylpyridin-1-ium tetrafluoroborate (1a): A white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.43$ (s, 9H), 7.61 – 7.68 (m, 5H), 8.21 (d, $J = 5.6$ Hz, 2H), 8.88 (d, $J = 5.6$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 30.0, 37.0, 124.0, 126.3, 130.9, 131.7, 142.3, 143.4, 172.8$ ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -151.92$ (s) ppm. HRMS (ESI) calcd for [C$_{15}$H$_{18}$N]$^+$ [M-BF$_4$]$^+$ 212.1434, found 212.1431.

4-(tert-butyl)-1-phenylpyridin-1-ium trifluoromethanesulfonate (4a'): A white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.45$ (s, 9H), 7.63 – 7.64 (m, 3H), 7.72 – 7.74 (m, 2H), 8.21 (d, $J = 6.8$ Hz, 2H), 8.93 (dd, $J = 6.4$ Hz, 1.2 Hz 2H) ppm. $^{13}$C NMR (100
MHz, CDCl$_3$): $\delta$ = 30.1, 37.1, 124.1, 126.3, 131.0, 131.8, 142.2, 143.6, 172.9 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -78.27 (s) ppm. HRMS (ESI) calcd for [C$_{15}$H$_{18}$N]$^+$ [M-BF$_4$]$^+$ 212.1434, found 212.1430.

1-Phenylpyridin-1-ium tetrafluoroborate (1b): An off-white solid. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 7.70 – 7.80 (m, 3H), 7.88 – 7.90 (m, 2H), 8.29 – 8.33 (m, 2H), 8.79 (tt, $J$ = 8.0 Hz, 1.2 Hz, 1H), 9.34 – 9.35 (m, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 124.8, 128.1, 130.2, 131.2, 142.8, 145.0, 146.6 ppm. $^{19}$F NMR (376 MHz, DMSO-d$_6$): $\delta$ = -148.25 (s) ppm. HRMS (ESI) calcd for [C$_{11}$H$_{10}$N]$^+$ [M-BF$_4$]$^+$ 156.0808, found 156.0808.

4-Methoxy-1-phenylpyridinium tetrafluoroborate (1c): An off-white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 4.19 (s, 3H), 7.61 – 7.64 (m, 7H), 8.67 – 8.70 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 58.6, 114.6, 123.9, 131.0, 131.4, 142.0, 145.3, 172.4 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -152.15 (s) ppm. HRMS (ESI) calcd for [C$_{12}$H$_{12}$NO]$^+$ [M-BF$_4$]$^+$ 186.0913, found 186.0913.

3-Methyl-1-phenylpyridinium tetrafluoroborate (1d): A reddish-brown solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.71 (s, 3H), 7.60 – 7.69 (m, 5H), 8.01 (d, $J$ = 6.4 Hz, 2H), 8.77 – 8.79 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 22.5, 124.07, 124.09, 129.7, 130.97, 130.99, 131.8, 142.4, 143.2, 161.2 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -151.93 (s) ppm. HRMS (ESI) calcd for [C$_{12}$H$_{12}$N]$^+$ [M-BF$_4$]$^+$ 170.0964, found
4-Cyano-1-phenylpyridinium-1-ium tetrafluoroborate (1e): A light-brown solid. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta = 7.77 - 7.79$ (m, 3H), $7.87 - 7.91$ (m, 2H), $8.90$ (d, $J = 6.0$ Hz, 2H), 9.67 (d, $J = 7.2$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta =$ 114.8, 124.8, 127.6, 130.3, 131.0, 131.9, 142.5, 146.4 ppm. $^{19}$F NMR (376 MHz, DMSO-d$_6$): $\delta = -148.26$ (s) ppm. HRMS (ESI) calcd for [C$_{12}$H$_9$N]$^+ [M-BF$_4$]$^+ 181.0760$, found 181.0758.

4-(tert-Butyl)-1-(4-methoxyphenyl)pyridinium-1-ium tetrafluoroborate (1f): A yellowish solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.44$ (s, 9H), 3.86 (s, 9H), 7.08 (d, $J = 8.8$ Hz, 2H), 7.62 (d, $J = 8.8$ Hz, 2H), 8.15 (d, $J = 6.4$ Hz, 2H), 8.81 (d, $J = 6.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 30.1, 36.9, 56.0, 110.2, 116.0, 125.3, 126.1, 143.2, 161.9, 172.1 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -152.11$ (s) ppm. HRMS (ESI) calcd for [C$_{16}$H$_{20}$NO]$^+ [M-BF$_4$]$^+ 242.1539$, found 242.1541.

4-tert-Butyl-1-(4-(methoxycarbonyl)phenyl)pyridinium tetrafluoroborate (1g): A white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.44$ (s, 9H), 3.96 (s, 3H), 7.82 (d, $J = 8.4$ Hz, 2H), 8.20 (d, $J = 6.8$ Hz, 2H), 8.25 (d, $J = 8.4$ Hz, 2H), 8.90 (d, $J = 6.8$ Hz, 2H)
ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 29.99, 37.2, 52.9, 124.4, 126.4, 132.2, 133.2, 143.3, 145.2, 165.3, 173.6$ ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -151.70$ (s) ppm. HRMS (ESI) calcd for [C$_{17}$H$_{20}$NO$_2$]$^+$ [M-BF$_4$]$^+$ 270.1489, found 270.1487.

![Chemical Structure of 3-(tert-Butyl)-5,6-bis(4-chlorophenyl)pyrido[1,2-a]quinolin-11-ium tetrafluoroborate (3a)](image)

**3-(tert-Butyl)-5,6-bis(4-chlorophenyl)pyrido[1,2-a]quinolin-11-ium tetrafluoroborate (3a):** Product 3a was prepared according to the general procedure as a white solid (39.3 mg, 83 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.32$ (s, 9H), 7.16 – 7.20 (m, 4H), 7.32 – 7.37 (m, 6H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 7.2$ Hz, 1H), 7.83 (s, 1H), 8.15 (t, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 6.8$ Hz, 1H), 9.19 (d, $J = 8.8$ Hz, 1H), 10.41 (d, $J = 7.2$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 29.9, 36.5, 118.5, 122.7, 123.9, 126.9, 128.6, 128.9, 129.09, 129.11, 129.12, 129.8, 130.5, 130.6, 133.1, 133.8, 133.9, 134.0, 134.6, 134.9, 143.3, 147.3, 166.0 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -152.78$ (s) ppm. HRMS (ESI) calcd for [C$_{29}$H$_{26}$N]$^+$ [M-BF$_4$]$^+$ 388.2060, found 388.2051.

![Chemical Structure of 2-(tert-Butyl)-4,5,9,10-tetraphenylquinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4a)](image)

**2-(tert-Butyl)-4,5,9,10-tetraphenylquinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4a):** Product 4a was prepared according to the general procedure as a yellow-green solid (58.5 mg, 90 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.12$ (s, 9H), 7.34 – 7.36 (m, 4H), 7.39 – 7.51 (m, 16H), 7.83 (s, 2H), 7.86 (d, $J = 8.0$ Hz, 2H), 8.19 (t, $J = 8.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 29.4, 35.5, 120.3, 126.8, 127.4, 128.6, 128.80, 128.83, 128.9, 129.2, 129.8, 130.3, 131.4, 134.5, 134.7, 134.9, 141.9, 144.8, 159.9 ppm. $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta = -148.34$ (s) ppm. HRMS (ESI) calcd for [C$_{43}$H$_{34}$N]$^+$ [M-BF$_4$]$^+$ 564.2686, found 564.2682.
2-(tert-Butyl)-4,5,9,10-tetraphenylquinolizino[3,4,5,6-ija]quinolin-11-ium
tetrafluoroborate (4a’): Product 4a’ was prepared according to the general procedure as a yellow solid (48.4 mg, 68 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.12$ (s, 9H), 7.32 – 7.36 (m, 4H), 7.39 – 7.51 (m, 16H), 7.83 (s, 2H), 7.876 (d, $J = 8.0$ Hz, 2H), 8.19 (t, $J = 8.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 29.4, 35.5, 120.3, 126.8, 127.4, 128.6, 128.80, 128.83, 128.9, 129.2, 129.8, 130.3, 131.4, 134.5, 134.7, 134.9, 141.9, 144.8, 159.9 ppm. $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta = -77.77$ (s) ppm. HRMS (ESI) calcd for [C$_{43}$H$_{34}$N]$^+$ [M-BF$_4$]$^+$ 564.2686, found 564.2684.

2-(tert-Butyl)-4,5,9,10-tetra-o-tolylquinolizino[3,4,5,6-ija]quinolin-11-ium
tetrafluoroborate (4b): Product 4b was prepared according to the general procedure as a green solid (58.1 mg, 82 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.1 – 1.13$ (m, 9H), 2.03 – 2.30 (m, 12H), 7.10 – 7.44 (m, 16H), 7.65 – 7.67 (m, 4H), 8.14 – 8.20 (m, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 19.2, 19.3, 29.4, 35.3, 109.6, 112.4, 119.6, 125.8, 126.0, 126.4, 126.5, 127.0, 128.9, 129.2, 129.3, 130.46, 130.47, 130.54, 130.6, 131.9, 133.5, 133.8, 133.9, 134.09, 134.13, 135.5, 135.6, 136.4, 141.36, 141.38, 144.9, 145.0, 160.3, 160.4 ppm. HRMS (ESI) calcd for [C$_{47}$H$_{42}$N]$^+$ [M-BF$_4$]$^+$ 620.3312, found 620.3307.

2-tert-Butyl-5,6,10,11-tetram-tolylquinolizino[3,4,5,6-ija]quinolinium
**tetrafluoroborate (4c):** Product 4c was prepared according to the general procedure as a yellow-green solid (60.1 mg, 85 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.13$ (s, 9H), 2.30 (s, 6H), 2.31 (s, 6H), 7.11–7.26 (m, 12H), 7.32–7.40 (m, 4H), 7.84–7.86 (m, 4H), 8.17 (t, $J = 8.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta =$20.9, 20.9, 20.98, 21.01, 29.4, 35.5, 120.3, 126.3, 126.4, 126.8, 127.3, 127.37, 127.39, 128.61, 128.63, 128.7, 129.2, 129.25, 129.34, 129.4, 129.5, 129.7, 130.7, 130.8, 131.2, 134.39, 134.44, 134.66, 134.69, 134.8, 134.85, 137.91, 137.93, 138.1, 141.86, 141.88, 144.66, 144.72, 159.7 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}N]^+ [M-BF_4]^+$ 620.3312, found 620.3311.

![Structure of 4c](image1.png)

**2-(tert-Butyl)-4,5,9,10-tetra-$p$-tolyquinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4d):** Product 4d was prepared according to the general procedure as a yellow-green solid (61.4 mg, 87 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.12$ (s, 9H), 2.34 (s, 6H), 2.35 (s, 6H), 7.21 – 7.23 (m, 4H), 7.27 – 7.32 (m, 12H), 7.81 – 7.82 (m, 4H), 8.13 (t, $J = 8.2$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta =$20.90, 20.93, 29.5, 35.5, 120.2, 126.7, 127.6, 129.1, 129.4, 129.5, 129.6, 130.2, 131.3, 132.0, 132.1, 134.5, 137.9, 138.0, 142.1, 144.8, 159.7 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}N]^+ [M-BF_4]^+$ 620.3312, found 620.3308.

![Structure of 4d](image2.png)

**2-(tert-Butyl)-4,5,9,10-tetrakis(4-(tert-butyl)phenyl)quinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4e):** Product 4e was prepared according to the general procedure as a yellow solid (78.8 mg, 90 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.13$ (s, 9H), 1.27 (s, 36H), 7.22 (d, $J = 8.0$ Hz, 4H), 7.28 (d, $J = 8.0$ Hz, 4H), 7.43...
– 7.47 (m, 8H), 7.87 (s, 2H), 7.92 (d, J = 8.0 Hz, 2H), 8.20 (t, J = 8.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 29.4, 30.92, 30.93, 34.41, 34.44, 35.4, 120.1, 125.3, 125.4, 126.67, 126.68, 127.4, 129.0, 130.1, 131.3, 131.9, 132.1, 134.7, 141.9, 145.0, 150.9, 151.1, 159.7 ppm. HRMS (ESI) calcd for $[C_{59}H_{66}N]^+[M-BF_4]^+$ 788.5190, found 788.5184.

2-(tert-Buty)-4,5,9,10-tetrakis(4-methoxyphenyl)quinolizino[3,4,5,6-ija]quinolin-11-iium tetrafluoroborate (4f): Product 4f was prepared according to the general procedure as a green solid (71 mg, 92 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.16$ (s, 9H), 3.79 (s, 6H), 3.80 (s, 6H), 7.02 – 7.06 (m, 8H), 7.25 (d, J = 8.8 Hz, 4H), 7.31 (d, J = 8.8 Hz, 4H), 7.87 (s, 3H), 7.89 (s, 1H), 8.15 (t, J = 8.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 29.5, 35.5, 55.16, 55.18, 114.25, 114.31, 120.1, 126.7, 126.9, 127.1, 127.8, 129.6, 130.7, 131.3, 131.7, 134.5, 142.3, 144.9, 159.0, 159.1, 159.7 ppm. HRMS (ESI) calcd for $[C_{47}H_{42}NO_4]^+[M-BF_4]^+$ 684.3108, found 684.3099.

2-(tert-Buty)-4,5,9,10-tetrakis(4-chlorophenyl)quinolizino[3,4,5,6-ija]quinolin-11-iium tetrafluoroborate (4g): Product 4g was prepared according to the general procedure as a yellow solid (78.8 mg, 90 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.18$ (s, 9H), 7.38 (d, J = 8.0 Hz, 4H), 7.46 (d, J = 8.4 Hz, 4H), 7.59 (t, J = 8.0 Hz, 8H), 7.84 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 8.19 (t, J = 8.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 29.5, 35.7, 120.5, 127.0, 127.2, 129.1, 129.2, 130.1, 131.2, 131.4, 132.3, 133.3, 133.5, 133.59, 133.61, 133.8, 141.6, 144.1, 160.6 ppm. HRMS (ESI) calcd for $[C_{47}H_{30}Cl_4N]^+[M-BF_4]^+$ 700.1127, found 700.1134.
2-tert-Butyl-5,6,10,11-tetrakis(4-(trifluoromethyl)phenyl)quinolizino[3,4,5,6-
ija]quinolinium tetrafluoroborate (4h): Product 4h was prepared according to the
general procedure as a green solid (85.8 mg, 93%). \(^1H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 1.16 \text{ (s, 9H), 7.62 \text{ (d, } J = 8.0 \text{ Hz, 4H), 7.70 \text{ (d, } J = 7.6 \text{ Hz, 4H), 7.80 \text{ (s, 2H), 7.87} - 7.91 \text{ (m, 10H), 8.22 \text{ (t, } J = 8.0 \text{ Hz, 1H) ppm.} \)
\(^{13}C\) NMR (100 MHz, DMSO-\(d_6\)): \(\delta = 29.35, 35.71, 120.67, 123.89 \text{ (q, } J_{C-F} = 272.1 \text{ Hz), 123.92 \text{ (q, } J_{C-F} = 272.4 \text{ Hz), 125.90} \text{ (q, } J_{C-F} = 3.8 \text{ Hz), 125.98 \text{ (q, } J_{C-F} = 3.5 \text{ Hz), 126.75, 127.43, 129.28 \text{ (q, } J_{C-F} = 32.1 \text{ Hz), 129.45} \text{ (q, } J_{C-F} = 32.1 \text{ Hz), 130.40, 131.49, 131.53, 133.44, 138.72, 141.31, 143.90, 160.89 \text{ ppm.} \)
\(^{19}F\) NMR (376 MHz, DMSO-\(d_6\)): \(\delta = -61.24 \text{ (d, } J = 4.0 \text{ Hz, 4H), -148.34} \text{ (s) ppm.} \)
HRMS (ESI) calcd for \([C_{47}H_{30}NF_{12}]^{+} [M-BF_4]^{+}\) 836.2181, found 836.2179.

4,5,9,10-Tetrakis(4-acetylphenyl)-2-(tert-butyl)quinolizino[3,4,5,6-ija]quinoline-
11-ium tetrafluoroborate (4i): Product 4i was prepared according to the general
procedure as a yellow solid (68.8 mg, 84%). \(^1H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 1.13 \text{ (s, 9H), 2.60 \text{ (s, 6H), 2.61 \text{ (s, 6H), 7.55 \text{ (d, } J = 8.4 \text{ Hz, 4H), 7.62 \text{ (d, } J = 8.4 \text{ Hz, 4H), 7.79 \text{ (s, 2H), 7.82 \text{ (d, } J = 8.0 \text{ Hz, 2H), 8.05} - 8.08 \text{ (m, 8H), 8.18 \text{ (t, } J = 8.0 \text{ Hz, 1H) ppm.} \)
\(^{13}C\) NMR (100 MHz, DMSO-\(d_6\)): \(\delta = 26.85, 26.88, 29.4, 35.7, 120.6, 126.9, 127.2, 128.8, 128.9, 129.8, 130.2, 130.9, 131.4, 133.6, 136.7, 136.8, 139.0, 139.2, 141.4, 144.1, 160.6, 197.5, 197.6 \text{ ppm.} \)
HRMS (ESI) calcd for \([C_{51}H_{42}NO_4]^{+} [M-BF_4]^{+}\) 732.3108, found 732.3093.
2-(tert-Butyl)-4,5,9,10-tetrakis(3-cyanophenyl)quinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4j): Product 4j was prepared according to the general procedure as a yellow solid (61.6 mg, 82 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.19$ (s, 9H), 7.61 – 7.82 (m, 11H), 7.91 – 8.06 (m, 9H), 8.22 (t, $J = 8.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 29.4, 35.9, 112.06, 112.14, 118.2, 121.0, 126.7, 127.7, 130.4, 130.47, 130.53, 131.5, 132.9, 133.1, 133.2, 133.95, 133.98, 134.2, 135.1, 135.2, 135.3, 135.4, 135.6, 141.2, 143.6 ppm. HRMS (ESI) calcld for [C$_{47}$H$_{30}$N$_5$]$^+$ [M-BF$_4$]$^+$ 664.2496, found 664.2499.

2-(tert-Butyl)-4,5,9,10-tetra(naphthalen-1-yl)quinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4k): Product 4k was prepared according to the general procedure as a yellow solid (63.8 mg, 75 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 0.68$ (s, 9H), 7.14 – 7.30 (m, 8H), 7.50 – 7.74 (m, 11H), 7.80 – 8.02 (m, 14H) ppm. HRMS (ESI) calcld for [C$_{59}$H$_{42}$N]$^+$ [M-BF$_4$]$^+$ 764.3312, found 764.3302.

2-(tert-butyl)-4,5,9,10-tetrapropylquinolizino[3,4,5,6-ija]quinolin-11-ium (4l): Product 4l was prepared according to the general procedure as a yellow solid (39.6 mg, 77 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.236 – 1.244$ (m, 12H), 1.62 (s, 9H), 1.78 –
1.84 (m, 8H), 3.23 – 3.29 (m, 8H), 8.31 (t, \( J = 8.0 \) Hz, 1H), 8.43 – 8.47 (m, 4H), ppm. 

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 14.7, 14.8, 22.7, 23.0, 30.6, 31.8, 32.0, 36.5, 117.8, 124.3, 126.8, 129.9, 130.4, 132.1, 140.9, 144.6, 160.8 \) ppm. HRMS (ESI) calcd for \([\text{C}_{31}\text{H}_{42}\text{N}]^+ [\text{M-BF}_4]^+\) 428.3312, found 428.3310.

4,5,9,10-Tetraphenylquinolizino[3,4,5,6-\text{i\text{ja}}]quinolin-11-ium tetrafluoroborate (4m): Product 4m was prepared according to the general procedure as a yellow solid (48.2 mg, 81 %). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 7.32 – 7.34 \) (m, 4H), 7.39 – 7.46 (m, 16H), 7.88 (d, \( J = 8.0 \) Hz, 2H), 8.02 (d, \( J = 8.0 \) Hz, 2H), 8.21 (t, \( J = 8.0 \) Hz, 1H), 8.55 (t, \( J = 8.0 \) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \( \delta = 124.0, 126.6, 127.7, 128.6, 128.7, 128.8, 128.9, 129.2, 129.9, 130.3, 131.3, 131.8, 134.8, 134.9, 137.7, 141.9, 144.8 \) ppm. HRMS (ESI) calcd for \([\text{C}_{43}\text{H}_{34}\text{N}]^+ [\text{M-BF}_4]^+\) 564.2686, found 564.2682.

2-Methoxy-4,5,9,10-tetraphenylquinolizino[3,4,5,6-\text{i\text{ja}}]quinolin-11-ium tetrafluoroborate (4n): Product 4n was prepared according to the general procedure as a grey solid (48.1 mg, 77 %). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 3.34 – 4.32 \) (m, 3H), 7.21 – 7.27 (m, 3H), 7.32 – 7.33 (m, 4H), 7.38 – 7.45 (m, 15H), 7.77 (d, \( J = 8.0 \) Hz, 2H), 8.09 (t, \( J = 8.0 \) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \( \delta = 56.9, 109.0, 126.5, 127.17, 127.18, 128.5, 128.7, 128.8, 128.9, 129.2, 130.3, 131.2, 133.8, 134.6, 134.9, 144.4, 144.5, 163.6 \) ppm. HRMS (ESI) calcd for \([\text{C}_{40}\text{H}_{28}\text{NO}]^+ [\text{M-BF}_4]^+\) 548.2165, found 548.2169.
2-(\textit{tert}-Butyl)-7-methoxy-4,5,9,10-tetraphenylquinolizino[3,4,5,6-\textit{ija}]quinolin-11-ium tetrafluoroborate (4o): Product 4o was prepared according to the general procedure as a yellow solid (50.4 mg, 74 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.17$ (s, 9 H), 3.70 (s, 3H), 7.28 – 7.37 (m, 22H), 7.93 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 30.1$, 35.9, 55.9, 112.6, 121.7, 128.65, 128.74, 128.9, 129.0, 129.6, 130.0, 130.7, 131.8, 135.2, 135.3, 135.5, 141.3, 144.9, 159.2, 159.5 ppm. HRMS (ESI) calcd for [C$_{44}$H$_{36}$NO]$^+$ [M-BF$_4$]$^+$ 594.2791, found 594.2794.

1-Methyl-4,5,9,10-tetraphenylquinolizino[3,4,5,6-\textit{ija}]quinolin-11-ium tetrafluoroborate (4p): Product 4p was prepared according to the general procedure as a green solid (36.6 mg, 70 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 2.56$ (s, 3H), 7.30 – 7.47 (m, 20H), 7.76 (s, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 8.16 (t, $J = 8.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 21.6$, 124.1, 126.7, 127.3, 128.5, 128.69, 128.72, 128.8, 129.2, 129.6, 130.4, 131.5, 134.3, 134.7, 135.0, 141.5, 144.8, 149.7 ppm. HRMS (ESI) calcd for [C$_{44}$H$_{36}$N]$^+$ [M-BF$_4$]$^+$ 522.2216, found 522.2208.

2-Cyano-4,5,9,10-tetraphenylquinolizino[3,4,5,6-\textit{ija}]quinolin-11-ium tetrafluoroborate (4q): Product 4q was prepared according to the general procedure as a reddish-brown solid (37.9 mg, 61 %). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.32 –
7.33 (m, 4H), 7.37 – 7.46 (m, 16H), 8.02 (d, J = 7.6 Hz, 2H), 8.33-8.39 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 115.4, 118.9, 125.5, 127.6, 128.0, 128.8, 128.98, 129.03, 129.1, 130.5, 131.2, 131.84, 133.84, 134.5, 135.0, 142.2, 146.8 ppm. HRMS (ESI) calcd for [C$_{40}$H$_{25}$N$_2^+$] [M-BF$_4^+$] 533.2012, found 533.2007.

2-(tert-Butyl)-7-(methoxycarbonyl)-4,5,9,10-tetra-ortho-tolylquinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4r): Product 4r was prepared according to the general procedure as a greenwish solid (49.9 mg, 64%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 1.13 (s, 9H), 2.03 – 2.31 (m, 12H), 3.79 (s, 3H), 7.26 – 7.43 (m, 16H), 7.72 (s, 2H), 8.13 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 19.2, 19.3, 29.4, 53.2, 109.6, 112.4, 120.1, 125.8, 126.0, 126.1, 127.5, 129.2, 129.4, 130.6, 130.7, 131.8, 133.2, 133.4, 135.1, 135.47, 135.51, 136.3, 141.8, 144.9, 164.6, 192.5 ppm. HRMS (ESI) calcd for [C$_{49}$H$_{44}$NO$_2^+$] [M-BF$_4^+$] 678.3367, found 678.3360.

![Structure of 4r](image)

2-(tert-Butyl)-4,5,9,10-tetrakis(4-(diphenylamino)phenyl)quinolizino[3,4,5,6-ija]quinolin-11-ium tetrafluoroborate (4s): Product 4s was prepared according to the general procedure as a crimson solid (121.2 mg, 92%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 1.28 (s, 9H), 7.05 – 7.12 (m, 32H), 7.21 – 7.25 (m, 8H), 7.32 – 7.36 (m, 16H), 8.07 (s, 2H), 8.17 (d, J = 8 Hz, 2H), 8.29 (t, J = 8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 29.5, 35.6, 120.16, 122.58, 123.22, 123.23, 123.5, 123.6, 124.0, 124.2, 126.9, 127.3, 128.6, 128.8, 129.69, 129.70, 130.8, 131.5, 131.8, 134.5, 141.9, 144.8, 146.8, 146.9, 147.35, 147.38, 159.85 ppm. HRMS (ESI) calcd for [C$_{91}$H$_{77}$N$_3^+$] [M-BF$_4^+$+H]$^+$ 1233.5704, found 1233.5708.
VII. Photophysical spectra of 12-azapyrene derivatives in CH$_2$Cl$_2$

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Table S2 Photophysical data of 12-azapyrene derivatives in CH$_2$Cl$_2$
VIII. Single crystal X-Ray structure

![Figure S1 X-Ray single crystal structure of 4s](image)

XI. References


IX. Copies of NMR Spectra for Compounds

$^1$H NMR spectra of 1a:

$^{13}$C NMR spectra of 1a:
$^{19}$F NMR spectra of 1a:

$^1$H NMR spectra of 1a':
$^{13}$C NMR spectra of 1a$^\prime$:

$^{19}$F NMR spectra of 1a$^\prime$:
$^1$H NMR spectra of 1b:

$^{13}$C NMR spectra of 1b:
$^{19}$F NMR spectra of 1b:

$^1$H NMR spectra of 1c:
$^{13}$C NMR spectra of 1c:

$^{19}$F NMR spectra of 1c:
$^1$H NMR spectra of 1d:

$^{13}$C NMR spectra of 1d:
$^{19}$F NMR spectra of 1d:

$^1$H NMR spectra of 1e:
$^{13}$C NMR spectra of 1e:

$^{19}$F NMR spectra of 1e:
$^1$H NMR spectra of 1f:

$^{13}$C NMR spectra of 1f:
$^{19}$F NMR spectra of 1f:

$^1$H NMR spectra of 1g:
$^{13}$C NMR spectra of 1g:

![C NMR spectrum](image)

$^{19}$F NMR spectra of 1g:

![F NMR spectrum](image)
$^1$H NMR spectra of 3a:

$^{13}$C NMR spectra of 3a:
$^{19}$F NMR spectra of 3a:

$^1$H NMR spectra of 4a:
$^{13}$C NMR spectra of 4a:

$^{19}$F NMR spectra of 4a:
$^1$H NMR spectra of $4a'$:

$^{13}$C NMR spectra of $4a'$:
$^{19}$F NMR spectra of 4a:

$^1$H NMR spectra of 4b:
$^{13}$C NMR spectra of 4b:

$^1$H NMR spectra of 4c:
$^{13}$C NMR spectra of 4c:

$^1$H NMR spectra of 4d:
$^{13}$C NMR spectra of 4d:

$^1$H NMR spectra of 4e:
$^{13}$C NMR spectra of 4e:

$^1$H NMR spectra of 4f:
$^{13}$C NMR spectra of 4f:

$^1$H NMR spectra of 4g:
$^{13}$C NMR spectra of 4g:

$^1$H NMR spectra of 4h:
$^{13}$C NMR spectra of 4h:

$^{19}$F NMR spectra of 4h:
$^1$H NMR spectra of 4i:

$^{13}$C NMR spectra of 4i:
$^1$H NMR spectra of 4j:

$^{13}$C NMR spectra of 4j:
$^1$H NMR spectra of 4k:

$^{13}$C NMR spectra of 4k:
$^1$H NMR spectra of 4:\n
$^{13}$C NMR spectra of 4:\n
S49
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$^{13}$C NMR spectra of 4m:
$^1$H NMR spectra of $4n$:

$^{13}$C NMR spectra of $4n$:
$^1$H NMR spectra of 40:

$^{13}$C NMR spectra of 40:
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\(^1\)H NMR spectra of 4q:

\(^{13}\)C NMR spectra of 4q:
$^1$H NMR spectra of 4r:

$^{13}$C NMR spectra of 4r:
$^1$H NMR spectra of 4s:

$^{13}$C NMR spectra of 4s: