Supporting Information

Facile One-Pot Synthesis of Indolizinium Derivatives by Rhodium(III)-
Catalyzed Intramolecular Oxidative Annulation via C–H Activation:
Application to Ficuseptine Synthesis

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General. All reactions were conducted under a nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use.\textsuperscript{1} [Cp*RhCl\textsubscript{2}], [Cp*Rh(CH\textsubscript{3}CN)\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} and [Cp*Rh(CH\textsubscript{3}CN)\textsubscript{3}](SbF\textsubscript{6})\textsubscript{2} were prepared from RhCl\textsubscript{3}·xH\textsubscript{2}O following a literature procedure.\textsuperscript{2} Other reagents were commercially available and used as purchased.

General procedure for the synthesis of alkyne-amine\textsuperscript{3,4}

To a single-neck round bottom flask (100 mL) containing 5-chloropent-1-yne (5.0 g, 49.0 mmol, 1.0 equiv), potassium pthalimide (8.6 g, 59.0 mmol, 1.2 equiv), K\textsubscript{2}CO\textsubscript{3} (5.0 g, 59.0 mmol, 1.2 equiv) and KI (0.88 g, 4.93 mmol, 0.12 equiv) in 50 mL anhydrous DMF under argon atmosphere was added. The resulting reaction mixture was stirred at 100 °C for 12 h and after cooling, the solution was poured into 250 mL ice water, washed and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 100 mL). The combined organic extracts were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and the solvent was removed under reduced pressure to afford intermediate 6 in quantitative yield. The crude product was pure enough for the next step.

Intermediate 6 (2.6 g 12.0 mmol, 1.0 equiv), aryl iodide (2.6 g 13.0 mmol, 1.1 equiv), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (171 mg, 0.24 mmol, 0.02 equiv), CuI (91 mg, 0.48 mmol, 0.04 equiv), PPh\textsubscript{3} (126 mg, 0.48 mmol, 0.04 equiv), and \textsuperscript{t}Pr\textsubscript{2}NH (15 mL) were placed in a round-bottomed flask. After stirring the resulting reaction mixture at 25 to 40 °C for overnight, saturated aqueous NH\textsubscript{4}Cl solution was added. Then, the mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 50 mL). The combined organic layers were dried over MgSO\textsubscript{4} and concentrated under vacuum. After purifying by flash chromatography (EtOAc/hexane, 20:80), compound 7 in 90% overall yield was isolated as a brown solid.
Compound 7 (1.0 equiv) were placed in a round-bottomed flask containing methanol and hydrazine hydrate (1.5 equiv) were added drop wise then the reaction mixture was stirred for 4 h at 40 °C and was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried over MgSO₄ and concentrated under vacuum to give the desired alkyne-amine 2 in 80% yield. No further purification was required and 2 was stored at 5-10 °C.

**General procedure for the synthesis of isoquinolinium salts (3)**

A sealed tube containing [RhCp*Cl₂]₂ (2.0 mol %), Cu(BF₄)₂·6H₂O (0.45 mmol) and aryl aldehyde 1 (0.48 mmol), amine alkyne-amine 2 (0.40 mmol) was evacuated and filled with oxygen (O₂, 1 atm), then t-butyl alcohol (2.5 mL) was added to the system via syringe and the reaction mixture was allowed to stir at 90 °C for 6 h. When the reaction was complete, the mixture was cooled and diluted with CH₂Cl₂ (10 mL).
The mixture was filtered through a Celite pad which was further washed with CH$_2$Cl$_2$ (30 mL) and MeOH (20 mL). The combined filtrate was concentrated in vacuo and the residue was purified on a silica gel column using DCM/MeOH (95:5) as eluent to afford the desired pure product 3. All products 3 were made according to the above procedure. The spectral data and a copy of $^1$H and $^{13}$C NMR spectra of all compounds 3 are listed below (p. S21).
Spectral data of starting material

5-Phenylpent-4-yn-1-amine (2a)

Brown liquid; \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.38-7.36 (m, 2 H), 7.35-7.23 (m, 3 H), 2.91 (s, NH\(_2\)), 3.07 (t, \( J = 7.6 \) Hz, 2 H), 2.49 (t, \( J = 7.6 \) Hz, 2 H), 1.97-1.93 (m, 2 H); \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 131.5 (2 CH), 128.2 (2 CH), 127.5 (CH), 123.8 (C), 89.6 (C), 80.8 (C), 41.2 (CH\(_2\)), 32.36 (CH\(_2\)), 16.80 (CH\(_2\)).

6-Phenylhex-5-yn-1-amine (2b)

Brown liquid; \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.37-7.35 (m, 2 H), 7.27-7.22 (m, 3 H), 2.72 (t, \( J = 7.6 \) Hz, 2 H), 2.40 (t, \( J = 7.6 \) Hz, 2 H), 1.65-1.59 (m, 4 H), 1.58 (bs, NH\(_2\)); \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 131.2 (2 CH), 127.9 (2 CH), 127.2 (CH), 123.6 (C), 89.7 (C), 80.5 (C), 41.4 (CH\(_2\)), 32.7 (CH\(_2\)), 25.8 (CH\(_2\)), 19.0 (CH\(_2\)).

7-Phenylhept-6-yn-1-amine (2d)

Brown liquid; \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.38-7.37 (m, 2 H), 7.27-7.24 (m, 3 H), 2.73 (t, \( J = 7.6 \) Hz, 2 H), 2.39 (t, \( J = 7.6 \) Hz, 2 H), 2.38 (bs, 2 H), 1.62-1.58 (m, 2 H), 1.49-1.47 (m, 4 H); \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 131.5 (2 CH), 128.1 (2 CH), 127.4 (CH), 123.9 (C), 90.0 (C), 80.7 (C), 41.8 (CH\(_2\)), 32.7 (CH\(_2\)), 28.5 (CH\(_2\)), 26.1 (CH\(_2\)), 19.3 (CH\(_2\)).

S5
4-Phenylbut-3-yn-1-amine (2e)

Brown liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.37 (m, 2 H), 7.28-7.24 (m, 3 H), 2.91 (t, $J = 7.6$ Hz, 2 H), 2.55 (t, $J = 7.6$ Hz, 2 H), 2.30 (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 131.5 (2 CH), 128.2 (2 CH), 127.7 (CH), 123.5 (C), 87.4 (C), 82.1 (C), 40.8 (CH$_2$), 24.0 (CH$_2$).

5-(4-Methoxyphenyl)pent-4-yn-1-amine (2g)

Brown liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29-7.24 (m, 2 H), 6.79-6.74 (m, 2 H), 3.76 (s, 2 H), 3.06 (t, $J = 7.6$ Hz, 2 H), 2.46 (s, 2 H), 1.90 (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.5 (C), 132.3 (2 CH), 129.3 (C), 115.0 (C), 113.2 (2 CH), 85.8 (C), 80.9 (C), 54.6 (CH$_3$), 38.6 (CH$_2$), 26.0 (CH$_2$), 16.3 (CH$_2$).
Spectral data of product 3

10-Phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3aa)

Brown solid; m.p. 196-198 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.95 (s, 1 H), 8.45 (d, $J = 8.0$ Hz, 2 H), 7.95-7.93 (m, 1 H), 7.91-7.85 (m, 1 H), 7.83-7.81 (m, 1 H), 7.74-7.72 (m, 3 H), 7.59-7.37 (m, 2 H), 5.20 (t, $J = 7.6$ Hz, 2 H), 3.31 (t, $J = 7.6$ Hz, 2 H), 2.54-2.51 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.4 (C), 145.9 (CH), 137.9 (C), 136.5 (CH), 134.7 (C), 133.0 (C), 131.2 (CH), 130.3 (CH), 129.8 (CH), 129.6 (2 CH), 129.5 (2 CH), 127.8 (C), 125.5 (CH), 59.6 (CH$_2$), 31.3 (CH$_2$), 22.7 (CH$_2$); $^{11}$B NMR (160 MHz, CDCl$_3$): $\delta$ -3.48; $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -151.152, -151.205 and secondary isotopic shift ($^{10}$B, $^{11}$B) of 0.054 ppm; HRMS (FAB$^+$) calcd for C$_{22}$H$_{18}$N$_2$ 246.1277, found 246.1278; IR (KBr): 3070, 1619, 1473, 1056 (ν$_{B-F}$), 771 and 547 cm$^{-1}$

8-Bromo-10-phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ba)

Brown solid; m.p. 135-137 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.84 (s, 1 H), 8.25 (d, $J = 9.6$ Hz, 1 H), 7.83-7.80 (m, 2 H), 7.58-7.55 (m, 2 H), 7.40-7.37 (m, 2 H), 5.11 (t, $J = 7.6$ Hz, 2 H), 3.29 (t, $J = 7.6$ Hz, 2 H), 2.51-2.47 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.7 (C), 145.5 (CH), 138.3 (C), 133.5 (CH),
133.2 (C), 132.4 (CH), 132.2 (C), 132.0 (C), 129.6 (CH), 129.4 (CH), 129.3 (2 CH),
127.5 (CH), 126.0 (C), 59.4 (CH2), 31.1 (CH2), 22.2 (CH2); **HRMS (FAB+)** calcd for
C_{18}H_{15}BrN+ 324.0382, found 324.0380; IR (KBr): 3085, 1635, 1581, 1056 (ν_{B-F}), 771
and 501 cm^{-1}

**8,10-Diphenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate**
(3ca)

![Image](image_url)

Brown solid; m.p. 196-198 °C; **¹H NMR** (400 MHz, CDCl₃): δ 9.87 (s, 1 H), 8.44 (d, J = 8.0 Hz, 1 H), 7.98-
7.96 (m, 1 H), 7.81 (s, 1 H), 7.60-7.54 (m, 3 H), 7.51-7.48 (m, 2 H), 7.44-7.40 (m, 4
H), 5.17 (t, J = 7.6 Hz, 2 H), 3.30 (t, J = 7.6 Hz, 2 H), 2.53-2.49 (m, 2 H); **¹³C NMR**
(100 MHz, CDCl₃): δ 148.7 (C), 146.6 (C), 145.0 (CH), 138.5 (C), 138.0 (C), 134.1
(C), 132.8 (C), 131.3 (CH), 129.6 (CH), 129.5 (CH), 129.4 (2 CH), 129.3 (2 CH),
129.2 (3 CH), 127.7 (2 CH), 126.5 (C), 122.3 (CH), 59.1 (CH₂), 31.0 (CH₂), 22.4
(CH₂); **HRMS (FAB+)** calcd for C_{24}H_{20}N+ 322.1590, found 322.1590; IR (KBr):
3062, 1635, 1465, 1056 (ν_{B-F}), 725 and 586 cm⁻¹

**8-Ethyl-10-phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium**
tetrafluoroborate (3da)

![Image](image_url)

Brown solid; m.p. 172-174°C; **¹H NMR** (400 MHz, CDCl₃):
δ 9.79 (s, 1 H), 8.33 (d, J = 8.0 Hz, 2 H), 7.66 (d, J = 8.0 Hz,
1 H), 7.59-7.53 (m, 3 H), 7.44 (s, 1 H), 7.37-7.36 (m, 2 H), 5.12 (t, J = 7.6 Hz, 2 H),
3.25 (t, J = 7.6 Hz, 2 H), 2.81-2.75 (m, 2 H), 2.48 (t, J = 7.6 Hz, 2 H), 1.21 (t, J =
7.6 Hz, 3 H); \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): \delta 154.2 (C), 146.1 (C), 144.7 (CH),
138.0 (C), 133.6 (C), 132.9 (C), 131.2 (CH), 130.7 (CH), 129.3 (3 CH), 129.2 (2 CH),
126.1 (C), 122.8 (CH), 59.0 (CH\textsubscript{2}), 30.9 (CH\textsubscript{2}), 29.8 (CH\textsubscript{2}), 22.4 (CH\textsubscript{2}), 14.6 (CH\textsubscript{3});
\textbf{HRMS} (FAB\textsuperscript{+}) calcd for C\textsubscript{20}H\textsubscript{20}N\textsuperscript{+} 274.1590, found 274.1588; IR (KBr): 3494, 2992,
2275, 817, 1056 (\nu_{\text{B-F}}), 740 and 509 cm\textsuperscript{-1}

\textit{8-Methoxy-10-phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium}
tetrafluoroborate (3ea)

\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}

Yellow solid; m.p. 220-222 °C; \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}):
\delta 9.63 (s, 1 H), 8.27 (d, J = 9.2 Hz, 1 H), 7.58-7.52 (m, 3 H), 7.39-7.34 (m, 3 H),
6.86-6.85 (m, 1 H), 5.04 (t, J = 7.6 Hz, 2 H), 3.78 (s, 3 H), 3.22 (t, J = 7.6 Hz, 2 H),
2.48-2.44 (m, 2 H); \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): \delta 165.7 (C), 146.3 (C), 143.5 (CH),
140.5 (C), 133.0 (C), 132.5 (C), 132.1 (C), 129.3 (CH), 129.3 (2 CH), 129.1 (2 CH),
123.0 (C), 122.8 (CH), 103.4 (CH), 58.4 (CH\textsubscript{3}), 55.9 (CH\textsubscript{2}), 30.9 (CH\textsubscript{2}), 22.3 (CH\textsubscript{2});
\textbf{HRMS} (FAB\textsuperscript{+}) calcd for C\textsubscript{19}H\textsubscript{18}NO\textsuperscript{+} 276.1383, found 276.1382; IR (KBr): 3779,
3070, 1619, 1473, 1056 (\nu_{\text{B-F}}), 771 and 547 cm\textsuperscript{-1}

\textit{8-Nitro-10-phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium}
tetrafluoroborate (3fa)

S9
Orange solid; m.p. 175-177 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.06 (s, 1 H), 8.65 (d, \( J = 8.4 \) Hz, 1 H), 8.52 (s, 1 H), 8.43 (d, \( J = 8.4 \) Hz, 1 H), 7.60-7.43 (m, 5 H), 5.21 (t, \( J = 7.6 \) Hz, 2 H), 3.36 (t, \( J = 7.6 \) Hz, 2 H), 2.54 (t, \( J = 7.6 \) Hz, 2 H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 151.4 (C), 148.9 (C), 146.1 (C), 137.6 (C), 136.5 (C), 133.4 (CH), 131.7 (C), 130.1 (CH), 129.5 (3 CH), 129.4 (2 CH), 122.9 (CH), 121.1 (CH), 60.1 (CH\(_2\)), 31.3 (CH\(_2\)), 22.2 (CH\(_2\)); HRMS (FAB\(^+\)) calcd for C\(_{18}\)H\(_{15}\)O\(_2\)N\(_2\)\(^+\) 291.1128, found 291.1130; IR (KBr): 3070, 1727, 1601, 1532, 1056 (\( \nu_{\text{B-F}} \)), 755 and 546 cm\(^{-1}\)

6-Methyl-10-phenyl-2,3-dihydro-1\(H\)-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ga)

Yellow solid; m.p. 114-116 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.91 (s, 1 H), 7.78-7.74 (m, 1 H), 7.59-7.51 (m, 5 H), 7.36-7.34 (m, 2 H), 5.21 (t, \( J = 7.6 \) Hz, 2 H), 3.26 (t, \( J = 7.6 \) Hz, 2 H), 2.88 (s, 3 H), 2.53-2.47 (m, 2 H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 145.8 (C), 142.6 (CH), 139.6 (C), 138.3 (C), 135.9 (CH), 134.5 (C), 133.0 (C), 130.5 (CH), 129.3 (3 CH), 129.1 (2 CH), 127.1 (C), 123.3 (CH), 59.5 (CH\(_2\)), 31.0 (CH\(_2\)), 22.3 (CH\(_2\)), 18.5 (CH\(_3\)); HRMS (FAB\(^+\)) calcd for C\(_{19}\)H\(_{18}\)N\(^+\) 260.1434, found 260.1436; IR (KBr): 3694, 2946, 1712, 1504, 1056 (\( \nu_{\text{B-F}} \)), 771 and 593 cm\(^{-1}\)
6-Nitro-10-phenyl-2,3-dihydro-1\textit{H}-pyrrolo[1,2-b]isoquinolin-4-ium

tetrafluoroborate (3ha)

Brown solid; m.p. 186-188 °C; \textit{\textsuperscript{1}H NMR} (400 MHz, C\textsubscript{2}D\textsubscript{6}CO): δ 9.85 (s, 1 H), 8.71 (d, \(J = 5.6\) Hz, 1 H), 7.68-7.60 (m, 6 H), 7.52 (d, \(J = 8.0\) Hz, 1 H), 5.20 (t, \(J = 7.6\) Hz, 2 H), 3.53 (t, \(J = 7.6\) Hz, 2 H), 2.69-2.61 (m, 2 H);

\textit{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): δ 149.4 (C), 142.0 (C), 138.8 (C), 135.8 (C), 133.9 (CH), 132.4 (CH), 132.1 (C), 131.3 (CH), 130.0 (CH), 129.5 (2 CH), 129.5 (2 CH), 128.2 (CH), 125.1 (C), 61.2 (CH\textsubscript{2}), 31.6 (CH\textsubscript{2}), 22.0 (CH\textsubscript{2}); \textit{HRMS} (FAB\textsuperscript{+}) calcd for C\textsubscript{18}H\textsubscript{15}N\textsubscript{2}O\textsubscript{2}+ 291.1128 found 291.1130; IR (KBr): 3040, 1727, 1571, 1056 (\(\nu_{B-F}\)), 701 and 556 cm\textsuperscript{-1}

9-Methoxy-10-phenyl-2,3-dihydro-1\textit{H}-pyrrolo[1,2-b]isoquinolin-4-ium
tetrafluoroborate (3ia) and 7-methoxy-10-phenyl-2,3-dihydro-1\textit{H}-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ia’)

Brown solid; m.p. 180-182 °C; \textit{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): δ 9.77 (s, 1 H), 9.74 (s, 1 H), 7.32 (d, \(J = 8.4\) Hz, 1 H), 7.72-7.68 (m, 2 H), 7.61-7.47 (m, 5 H), 7.44-7.41 (m, 4 H), 7.38-7.36 (m, 2 H), 7.25-7.19 (m, 4 H), 5.12 (q, \(J = 7.6\) Hz, 4 H), 3.93 (s, 3 H), 3.46 (s, 3 H), 3.27 (t, \(J = 7.6\) Hz, 2 H), 3.13 (t, \(J = 7.6\) Hz, 2 H), 2.51-2.42 (m, 2 H);
**13C NMR** (100 MHz, CDCl₃): δ 160.3 (C), 155.6 (C), 146.9 (C), 145.0 (C), 144.2 (C), 143.1 (CH), 137.3 (C), 134.3 (C), 133.6 (C), 133.4 (C), 132.9 (C), 130.9 (CH), 129.9 (CH), 129.6 (C), 129.4 (CH), 129.3 (3 CH), 129.2 (C), 128.8 (C), 127.9 (3 CH), 127.7 (2 CH), 126.5 (CH), 122.6 (2 CH), 115.1 (CH), 106.9 (CH), 59.4 (OCH₃), 59.3 (OCH₃), 56.2 (CH₂), 55.7 (CH₂), 31.4 (CH₂), 30.8 (CH₂), 22.4 (CH₂), 22.1 (CH₂); **HRMS** (FAB⁺) calcd for C₁₉H₁₈ON⁺ 276.1383, found 276.1382; IR (KBr): 3070, 1617, 1481, 1241, 1056 (νB-F), 771 and 547 cm⁻¹

**7-Bromo-8-methoxy-10-phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ja)**

Brown solid; m.p. 130-132 °C; **¹H NMR** (400 MHz, CDCl₃): δ 9.70 (s, 1 H), 8.54 (s, 1 H), 7.61-7.55 (m, 3 H), 7.41-7.38 (m, 2 H), 6.86 (s, 1 H), 5.11 (t, J = 7.6 Hz, 2 H), 3.84 (s, 3 H), 3.24 (t, J = 7.6 Hz, 2 H), 2.51-2.47 (m, 2 H); **¹³C NMR** (100 MHz, CDCl₃): δ 161.7 (C), 146.8 (C), 143.2 (CH), 139.4 (C), 134.7 (CH), 132.8 (C), 132.5 (C), 129.7 (CH), 129.6 (2 CH), 129.1 (2 CH), 123.5 (C), 118.9 (C), 103.4 (CH), 58.4 (OCH₃), 56.8 (CH₂), 31.1 (CH₂), 22.4 (CH₂); **HRMS** (FAB⁺) calcd for C₁₉H₁₇BrNO⁺ 354.0488, found 354.0497; IR (KBr): 3062, 1635, 1419, 1056 (νB-F), 740 and 632 cm⁻¹

**7,8-Dimethoxy-10-phenyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3ka)**
Brown solid; m.p. 229-230 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.59 (s, 1 H), 7.71 (s, 1 H), 7.68-7.64 (m, 3 H), 7.57-7.56 (m, 2 H), 6.84 (S, 1 H), 5.04 (t, $J = 7.6$ Hz, 2 H), 4.02 (t, $J = 7.6$ Hz, 3 H), 3.82 (t, $J = 7.6$ Hz, 3 H), 3.24-3.20 (m, 2 H), 2.49-2.45 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 157.8 (C), 152.3 (C), 144.5 (CH), 141.3 (C), 135.6 (C), 133.3 (C), 131.9 (C), 129.4 (2 CH), 129.1 (2 CH), 128.1 (CH), 124.4 (C), 107.6 (CH), 102.9(CH), 58.7 (CH$_2$), 56.7 (OCH$_3$), 56.4 (OCH$_3$), 31.0 (CH$_2$), 22.4 (CH$_2$); HRMS (FAB$^+$) calcd for C$_{20}$H$_{20}$NO$_2^+$ 306.1489, found 306.1486; IR (KBr): 3072, 1465, 1056 (ν$_{B-F}$), 1041, 724 and 571 cm$^{-1}$

11-Phenyl-9,10-dihydro-8H-[1,3]dioxolo[4,5-f]pyrrolo[1,2-b]isoquinolin-7-ium tetrafluoroborate (3la)

Orange solid; m.p. 209-211 °C; $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 9.65 (s, 1 H), 8.15 (d, $J = 8.4$ Hz, 1 H), 7.57 (d, $J = 8.4$ Hz, 1 H), 7.82-7.49 (m, 3 H), 7.38-7.36 (m, 2 H), 6.06 (s, 2 H), 5.00 (t, $J = 7.6$ Hz, 2 H), 3.18 (t, $J = 7.6$ Hz, 2 H), 2.51-2.45 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.4 (C), 146.0 (CH), 145.8 (C), 141.2 (C), 134.0 (C), 129.1 (2 CH), 129.0 (C), 128.9 (CH), 128.8 (CH), 128.2 (2 CH), 123.5 (C), 122.2 (C), 114.7(CH), 103.1 (CH$_2$), 58.6 (CH$_2$), 30.6 (CH$_2$), 22.3 (CH$_2$); HRMS (FAB$^+$) for C$_{19}$H$_{16}$NO$_2$+ 290.1176, found 290.1178; IR (KBr): 3062, 1465, 1303, 1056 (ν$_{B-F}$), 1041, 763 and 593 cm$^{-1}$

4-Phenyl-6,7-dihydro-5H-furo[2,3-f]indolizin-8-ium tetrafluoroborate (3ma)
Brown solid; m.p. 192-194 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.28 (s, 1 H), 8.20-8.19 (m, 1 H), 7.59-7.53 (m, 3 H), 7.49-7.46 (m, 2 H), 6.94-6.93 (m, 1 H), 5.14 (t, \(J = 7.6\) Hz, 2 H), 3.44 (t, \(J = 7.6\) Hz, 2 H), 2.60-2.52 (m, 2 H); \(^13\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 157.1 (CH), 151.1 (C), 149.5 (C), 141.8 (C), 132.7 (C), 130.6 (C), 130.3 (C), 129.8 (2 CH), 129.1 (2 CH), 125.9 (CH), 107.4 (CH), 60.2 (CH\(_2\)), 31.6 (CH\(_2\)), 23.3 (CH\(_2\)); HRMS (FAB\(^+\)) calcd for C\(_{16}\)H\(_{14}\)NO\(^+\) 236.1070, found 236.1072; IR (KBr): 3112, 1617, 1441, 1056 (\(\nu_{\text{B-F}}\)), 717 and 476 cm\(^{-1}\)

4-Phenyl-6,7-dihydro-5\(H\)-thieno[2,3-f]indolizin-8-ium tetrafluoroborate (3na)

Brown solid; m.p. 182-184 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.68 (s, 1 H), 8.23 (d, \(J = 5.6\) Hz, 1 H), 7.57-7.53 (m, 3 H), 7.45-7.42 (m, 2 H), 7.34 (d, \(J = 5.6\) Hz, 1 H), 5.13 (t, \(J = 7.6\) Hz, 2 H), 3.36 (t, \(J = 7.6\) Hz, 2 H), 2.57-2.50 (m, 2 H); \(^13\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 149.7 (C), 148.3 (C), 143.1 (CH), 136.6 (C), 136.5 (C), 133.1 (C), 131.9 (CH), 129.8 (CH), 129.3 (2 CH), 128.8 (2 CH), 123.0 (CH), 59.3 (CH\(_2\)), 31.0 (CH\(_2\)), 22.9 (CH\(_2\)); HRMS (FAB\(^+\)) calcd for C\(_{16}\)H\(_{14}\)NS\(^+\) Exact Mass: 252.0841, found 252.0841; IR (KBr): 3694, 1619, 1442, 1056 (\(\nu_{\text{B-F}}\)), 779 and 593 cm\(^{-1}\)

9-Chloro-11-phenyl-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate (3ob)
Brown solid; m.p. 127-128 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.79 (s, 1 H), 8.37 (d, $J = 8.8$ Hz, 1 H), 7.65 (d, $J = 8.8$ Hz, 1 H), 7.57-7.56 (m, 3 H), 7.41 (s, 1 H), 7.31-7.29 (m, 2 H) 4.84 (t, $J = 7.6$ Hz, 2 H), 2.91 (t, $J = 7.6$ Hz, 2 H), 2.19-2.16 (m, 2 H), 1.91-1.83 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.2 (CH), 144.8 (C), 143.4 (C), 138.5 (C), 136.0 (C), 132.5 (C), 132.4 (CH), 131.2 (CH), 129.5 (5 CH), 124.7 (C), 124.4 (CH), 56.4 (CH$_2$), 25.9 (CH$_2$), 20.6 (CH$_2$), 17.8 (CH$_2$); HRMS (FAB$^+$) calcd for C$_{19}$H$_{17}$ClN$^+$ 294.1044, found 294.1043; IR (KBr): 3085, 1635, 1465, 1056 (ν$_{B-F}$), 779 and 593 cm$^{-1}$

9-Methyl-11-phenyl-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate (3pb)

![Diagram of 9-Methyl-11-phenyl-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate]

Brown solid; m.p. 215-217 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.70 (s, 1 H), 8.30 (d, $J = 8.4$ Hz, 1 H), 7.60-7.55 (m, 3 H), 7.28-7.20 (m, 3 H), 4.82 (t, $J = 7.6$ Hz, 2 H), 2.90-2.86 (m, 2 H), 2.45 (s, 3 H), 2.18-2.15 (m, 2 H), 1.91-1.82 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.7 (C), 148.6 (CH), 143.6 (C), 138.3 (C), 136.3 (CH), 133.4 (C), 132.6 (C), 130.6 (CH), 129.8 (2 CH), 129.6 (2 CH), 129.5 (CH), 125.1 (C), 124.5 (CH), 56.3 (CH$_2$), 26.0 (CH$_2$), 23.2 (CH$_2$), 21.0 (CH$_2$), 18.2 (CH$_3$); HRMS (FAB$^+$) calcd for C$_{20}$H$_{20}$N$^+$ 274.1590, found 274.1590; IR (KBr): 3494, 1712, 1504, 1056 (ν$_{B-F}$), 771 and 593 cm$^{-1}$

11-(p-Tolyl)-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate (3ac)

![Diagram of 11-(p-Tolyl)-1,2,3,4-tetrahydropyrido[1,2-b]isoquinolin-5-ium tetrafluoroborate]
Brown sticky solid; \textit{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.86 (s, 1 H), 8.45 (d, 1 H), 7.88-7.84 (m, 1 H), 7.80-7.76 (m, 1 H), 7.53 (d, \(J = 8.4\) Hz, 1 H), 7.38-7.36 (m, 2 H) 7.18-7.16 (m, 2 H), 4.89 (t, \(J = 7.6\) Hz, 2 H), 2.94 (t, \(J = 7.6\) Hz, 2 H), 2.46 (s, 3 H), 2.21-2.16 (m, 2 H), 1.93-1.83 (m, 2 H); \textit{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): \(\delta\) 148.7 (C), 143.5 (C), 139.2 (C), 137.9 (C), 137.0 (C), 136.1 (CH), 130.4 (CH), 129.9 (4 CH), 129.3 (2 CH), 126.3 (C), 125.4 (CH), 55.2 (CH\textsubscript{2}), 25.6 (CH\textsubscript{2}), 21.2 (CH\textsubscript{2}), 20.6 (CH\textsubscript{2}), 17.8 (CH\textsubscript{3}); \textbf{HRMS} (FAB\textsuperscript{+}) calcd for C\textsubscript{20}H\textsubscript{10}N\textsuperscript{+} 274.1590, found 274.1589; IR (KBr): 3077, 1612, 1511, 1058 (\nu\textsubscript{B-F}), 760 and 546 cm\textsuperscript{-1}

\textbf{2-Chloro-12-phenyl-8,9,10,11-tetrahydro-7H-azepino[1,2-b]isoquinolin-6-ium tetrafluoroborate (3od)}

Yellow solid; m.p. 201-203 °C; \textit{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 10.05 (s, 1 H), 8.50 (d, \(J = 8.8\) Hz, 1 H), 7.74-7.72 (m, 1 H), 7.61-7.58 (m, 3 H), 7.36 (s, 1 H), 7.27-7.25 (m, 2 H), 5.05 (t, \(J = 7.6\) Hz, 2 H), 3.05 (t, \(J = 7.6\) Hz, 2 H), 2.14-2.12 (m, 2 H), 1.80-1.86 (m, 2 H), 1.76-1.71 (m, 2 H); \textit{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): \(\delta\) 150.6 (C), 148.2 (C), 144.1 (C), 138.8 (C), 136.6 (C), 133.4 (C), 132.9 (CH), 131.4 (CH), 129.5 (3 CH), 129.3 (2 CH), 125.0 (CH), 62.4 (CH\textsubscript{2}), 30.3 (CH\textsubscript{2}), 28.2 (CH\textsubscript{2}), 27.9 (CH\textsubscript{2}), 25.9 (CH\textsubscript{2}); \textbf{HRMS} (FAB\textsuperscript{+}) calcd for C\textsubscript{20}H\textsubscript{19}ClN\textsuperscript{+} 308.1201, found 308.1200; IR (KBr): 3200, 1672, 1590, 1056 (\nu\textsubscript{B-F}), 775 and 601 cm\textsuperscript{-1}
10-Methyl-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium tetrafluoroborate (3af)

![Chemical Structure]

Brown solid; m.p. 131-132 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.63 (s, 1 H), 8.38-8.35 (m, 1 H), 8.20-8.18 (m, 1 H), 8.15-8.10 (m, 1 H), 7.92-7.88 (m, 1 H), 5.05 (t, $J$ = 7.6 Hz, 2 H), 3.54 (t, $J$ = 7.6 Hz, 2 H), 2.27 (s, 3 H), 2.63-2.57 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.0 (C), 144.3 (CH), 138.3 (C), 136.7 (CH), 131.2 (CH), 130.6 (C), 130.6 (CH), 127.3 (C), 123.9 (CH), 59.6 (CH$_2$), 30.7 (CH$_2$), 22.4 (CH$_2$), 15.0 (CH$_3$); HRMS (FAB$^+$) calcld for C$_{13}$H$_{14}$N$^+$ 184.1121, found 184.1120; IR (KBr): 3070, 1427, 1581, 1056 (ν$_{\text{B-F}}$), 755 and 486 cm$^{-1}$

8-Phenyl-2,3-dihydro-1H-indolizin-4-ium tetrafluoroborate (3qa)

![Chemical Structure]

Brown solid; m.p. 150-151 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.81 (d, $J$ = 8.0 Hz, 1 H), 8.20 (d, $J$ = 8.0 Hz, 1 H), 7.89-7.85 (m, 1 H), 7.50-7.42 (m, 5 H), 5.01 (t, $J$ = 7.6 Hz, 2 H), 3.51 (t, $J$ = 7.6 Hz, 2 H), 2.50-2.47 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.8 (C), 144.1 (CH), 140.0 (CH), 138.9 (C), 134.2 (C), 129.7 (CH), 129.2 (2 CH), 128.4 (2 CH), 126.0 (CH), 59.8 (CH$_2$), 32.4 (CH$_2$), 21.6 (CH$_2$); HRMS (FAB$^+$) calcld for C$_{14}$H$_{14}$N$^+$ 196.1121, found 196.1120; IR (KBr): 3060, 1627, 1256, 1058 (ν$_{\text{B-F}}$), 755 and 590 cm$^{-1}$
7-Methyl-6,8-diphenyl-2,3-dihydro-1H-indolizin-4-ium tetrafluoroborate (3ra)

Brown solid; m.p. 161-163 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\)
8.75 (s, 1 H), 7.23-7.19 (m, 6 H), 7.06-7.04 (m, 2 H), 6.99-6.97 (m, 2 H), 5.03 (t, \(J = 7.6\) Hz, 2 H), 3.24 (t, \(J = 7.6\) Hz, 2 H), 2.50-2.43 (m, 2 H), 2.25 (t, \(J = 7.6\) Hz, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\)
157.4 (C), 154.8 (C), 139.6 (CH), 137.6 (C), 136.1 (C), 134.1 (C), 133.7 (C), 129.1 (2 CH), 128.5 (2 CH), 128.4 (3 CH), 128.3 (2 CH), 128.2 (2 CH), 59.4 (CH\textsubscript{2}), 32.5 (CH\textsubscript{2}), 21.3 (CH\textsubscript{2}), 18.0 (CH\textsubscript{3}); HRMS (FAB\textsuperscript{+}) calcd for C\textsubscript{21}H\textsubscript{20}N\textsuperscript{+} 286.1590, found 286.1591; IR (KBr): 3062, 1673, 1442, 1058 (\(\nu\)B-F), 755 and 593 cm\textsuperscript{-1}

6,8-Bis(4-methoxyphenyl)-2,3-dihydro-1H-indolizin-4-ium tetrafluoroborate (4)
or (ficuseptine)

Yellow solid; m.p. 201-203 °C (ref. m.p 186-187 °C); \textsuperscript{5}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\)
9.02 (s, 1 H), 8.16 (s, 1 H), 7.61 (d, \(J = 8.0\) Hz, 2 H), 7.42 (d, \(J = 8.0\) Hz, 2 H), 7.02 (d, \(J = 6.0\) Hz, 2 H), 6.93 (d, \(J = 6.0\) Hz, 2 H),
5.06 (t, \(J = 7.6\) Hz, 2 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 3.48 (t, \(J = 7.6\) Hz, 2 H), 2.48-
2.43 (m, 2 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\)
161.1 (C), 160.8 (C), 153.5 (C), 140.6 (CH), 139.2 (C), 138.4 (C), 136.7 (CH), 129.8 (2 CH), 128.7 (2 CH), 126.5 (C), 125.2
(C), 115.0 (2 CH), 114.7 (2 CH), 60.0 (CH
2
), 55.4 (CH
3
), 55.4 (CH
3
), 32.2 (CH
2
), 21.9
(CH
2
); HRMS (FAB+) calcd for C
22
H
22
N
+ O
2
 332.1651, found 332.1652; IR (KBr):
3077, 1612, 1180, 1056 (ν
B-F
), 717 and 601 cm
-1

References:

$^1$H and $^{13}$C NMR spectra of compound 2a
$^1$H and $^{13}$C NMR spectra of compound 2b
$^1$H and $^{13}$C NMR spectra of compound 2d
$^1$H and $^{13}$C NMR spectra of compound 2e
$^1$H and $^{13}$C NMR spectra of compound 2g
$^1$H and $^{13}$C NMR spectra of compound 3aa.
$^1$H and $^{13}$C NMR spectra of compound 3ba.
$^1$H and $^{13}$C NMR spectra of compound 3ca.
$^1$H and $^{13}$C NMR spectra of compound 3da.
$^1$H and $^{13}$C NMR spectra of compound 3ea.
$^1$H and $^{13}$C NMR spectra of compound 3fa.
$^1$H and $^{13}$C NMR spectra of compound 3ga.
$^1$H and $^{13}$C NMR spectra of compound 3ha.
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compound 3ia.
$^1$H and $^{13}$C NMR spectra of compound 3ka.
$^1$H and $^{13}$C NMR spectra of compound 3ja.
$^1$H and $^{13}$C NMR spectra of compound 31a.
$^1$H and $^{13}$C NMR spectra of compound 3ma.
$^1$H and $^{13}$C NMR spectra of compound 3na.
$^1$H and $^{13}$C NMR spectra of compound 3ob.
$^1$H and $^{13}$C NMR spectra of compound 3pb.
$^1$H and $^{13}$C NMR spectra of compound $3\text{ac}$.
$^1$H and $^{13}$C NMR spectra of compound 3od
$^1$H and $^{13}$C NMR spectra of compound 3af
$^1$H and $^{13}$C NMR spectra of compound 3qa
$^1$H and $^{13}$C NMR spectra of compound 3ra
$^1$H and $^{13}$C NMR spectra of compound (ficuseptine) 4
$^{11}$B & $^{19}$F NMR spectra of compound 3aa
ORTEP diagram of compound 3aa

Table 1. Crystal data and structure refinement for 3aa (140501LT_a).
Identification code: 140501LT_a
Empirical formula: C18 H16 B F4 N
Formula weight: 333.13
Temperature: 296(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: P n a 21
Unit cell dimensions: a = 20.2206(11) Å \( \alpha = 90^\circ \)
b = 9.2842(5) Å        α = 90°.
c = 8.5994(5) Å        β = 90°.
Volume               1614.38(16) Å³
Z                    4
Density (calculated) 1.371 Mg/m³
Absorption coefficient 0.111 mm⁻¹
F(000)               688
Crystal size         0.20 x 0.15 x 0.15 mm³
Theta range for data collection 2.014 to 26.436°.
Index ranges        -25<=h<=24, -11<=k<=11, -10<=l<=10
Reflections collected 12010
Independent reflections 3276 [R(int) = 0.0317]
Completeness to theta = 25.242° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9485 and 0.8438
Refinement method    Full-matrix least-squares on F²
Data / restraints / parameters 3276 / 187 / 264
Goodness-of-fit on F² 1.037
Final R indices [I>2sigma(I)] R1 = 0.0511, wR2 = 0.1324
R indices (all data)   R1 = 0.0769, wR2 = 0.1486
Absolute structure parameter 0.0(19)
Extinction coefficient n/a
Largest diff. peak and hole 0.265 and -0.236 e.Å⁻³