Activation and Deprotection of F-BODIPYs using Boron Trihalides

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1.1 General Experimental Procedures and Information

All $^1$H NMR (500 MHz), $^{13}$C NMR (125 MHz) and $^{11}$B NMR (160 MHz) spectra were recorded using a 500 MHz spectrometer. Chemical shifts are expressed in parts per million (ppm) using the solvent signal [CDCl$_3$ ($^1$H 7.26 ppm; $^{13}$C 71.16 ppm)] as an internal reference for $^1$H and $^{13}$C and BF$_3$·OEt$_2$ as an external reference for $^{11}$B. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants ($J$) are reported in Hertz (Hz). Mass spectra were obtained using ion trap (ESI) instruments operating in positive mode.

**General Procedure for the Synthesis of HX Salts, X = Cl, Br (GP1)**

The $F$-BODIPY (50 mg) was dissolved in anhydrous dichloromethane (10 mL) and 1 eq of BCl$_3$ (or BBr$_3$) was added drop-wise from a 1.0 M solution in anhydrous hexanes. The reaction mixture was stirred for an hour to allow in situ formation of the $Cl$-BODIPY. The reaction mixture was then concentrated in vacuo. The residue was dissolved in a mixture of acetone:water (10:1) and the solution was stirred for 10 min. The reaction mixture was extracted into dichloromethane and the organic layer was dried over Na$_2$SO$_4$. The solution was then concentrated in vacuo to obtain the HX salt of the dipyrrin.

**General Procedure for the Synthesis of HBF$_4$ Salts (GP2)**

The $F$-BODIPY (50 mg) was dissolved in anhydrous dichloromethane (10 mL) and 1 eq of BF$_3$·OEt$_2$ was added drop-wise. The reaction mixture was stirred for 10 minutes and then 3 eq of water was added and the mixture was further stirred for 3 hours. The reaction
mixture was washed with water and the organic layer dried over Na$_2$SO$_4$. The solution was concentrated in vacuo. The resulting solid was washed with diethyl ether to remove any unreacted F-BODIPY, leaving an orange powder corresponding to the HBF$_4$ salt of the dipyrrin.

1.2 Procedures and characterization Data

*(Z)-3-Ethyl-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1H-pyrrole hydrochloride (2a)*

Using GP1, compound 2a was synthesized from the corresponding F-BODIPY. Bright orange solid (48 mg, 99%). $\delta_H$ (500 MHz, CDCl$_3$) 13.36 (2H, br s), 7.00 (1H, s), 2.59 (6H, s), 2.40 (4H, q, $J = 7.5$), 2.24 (6H, s), 1.05 (6H, t, $J = 7.5$). Data matches that previously reported for this compound.

*(Z)-2-((4-Ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-3,5-dimethyl-1H-pyrrole hydrochloride (2b)*

Using GP1, compound 2b was synthesized from the corresponding F-BODIPY. Bright orange solid (48 mg, 99%). $\delta_H$ (500 MHz, CDCl$_3$) 13.71 (2H, br s), 7.02 (1H, s), 6.11 (1H, s), 2.63 (3H, s), 2.62 (3H, s), 2.42 (2H, q, $J = 7.5$), 2.33 (3H, s), 2.26 (3H, s), 1.07 (3H, t, $J = 7.5$); $\delta_C$ (125 MHz, CDCl$_3$) 155.4, 148.8, 141.9, 139.1, 131.0, 126.84, 126.82, 119.4, 116.8, 17.4, 14.53, 14.51, 13.0, 12.2, 10.1. LRMS-ESI (m/z): 229.2 [M + H]$^+$
HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{13}$H$_{21}$N$_2$ 229.1699; found, 229.1691.

(Z)-2-((3,5-Dimethyl-2H-pyrrol-2-ylidene)methyl)-3,5-dimethyl-1H-pyrrole hydrochloride (2c)

\[
\text{HCl}
\]

Using GP1, compound 2c was synthesized from the corresponding F-BODIPY. Bright orange solid (48 mg, 99%). $\delta_H$ (500 MHz, CDCl$_3$) 13.72 (2H, br s), 7.03 (1H, s), 6.13 (2H, s), 2.62 (6H, s), 2.32 (6H, s). Data matches that previously reported for this compound.$^5$

(Z)-1-(2-((4-Heptanoyl-3,5-dimethyl-1H-pyrrol-2-yl)methylene)-3,5-dimethyl-2H-pyrrol-4-yl)heptan-1-one hydrochloride (2d)

\[
\text{HCl}
\]

Using GP1, compound 2d was synthesized from the corresponding F-BODIPY.$^3$ Bright orange solid (49 mg, 99%). $\delta_H$ (500 MHz, CDCl$_3$) 7.44 (1H, s), 3.00 (6H, s), 2.76 (4H, t, $J = 7.2$), 2.51 (6H, s), 1.74-1.66 (4H, m), 1.39-1.28 (12H, m), 0.90 (6H, t, $J = 6.6$); $\delta_C$ (125 MHz, CDCl$_3$) 198.4, 165.7, 142.1, 136.8, 132.0, 123.1, 43.8, 31.9, 29.9, 24.2, 22.7, 17.5, 14.2, 12.4. LRMS-ESI (m/z): 425.3 [M + H]$^+$; HRMS-ESI (m/z): [M + H]$^+$ calcd for C$_{27}$H$_{41}$N$_2$O$_2$ 425.3163; found, 425.3147.
(Z)-1-(2-((4-Acetyl-3,5-dimethyl-1H-pyrrol-2-yl)(phenyl)methylene)-3,5-dimethyl-2H-pyrrol-4-yl)ethanone hydrochloride (2e)

Using GP1, compound 2e was synthesized from the corresponding F-BODIPY. Bright orange solid (49 mg, 99%). δ_H (500 MHz, CDCl₃) 13.93 (2H, brs), 7.50-7.46 (3H, m), 7.30-7.28 (2H, m), 2.58 (6H, s), 2.39 (6H, s), 1.53 (6H, s); δ_C (125 MHz, CDCl₃) 196.7, 154.5, 143.7, 143.6, 137.2, 137.1, 131.0, 129.4, 129.3, 129.2, 31.8, 18.1, 14.5. LRMS-ESI (m/z): 361.2 [M + H]^+; HRMS-ESI (m/z): [M + H]^+ calcd for C_{23}H_{25}N_{2}O_{3} 361.1916; found, 361.1913.

(Z)-3-Ethyl-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)(phenyl)methyl)-2,4-dimethyl-1H-pyrrole hydrochloride (2f)

Using GP1, compound 2f was synthesized from the corresponding F-BODIPY. Bright orange solid (48 mg, 99%). δ_H (500 MHz, CDCl₃) 11.46 (2H, brs), 7.55-7.41 (3H, m), 7.26-7.25 (2H, m), 2.58 (6H, s), 2.33 (4H, q, J = 7.5), 1.31 (6H, s), 0.99 (6H, t, J = 7.5). Data matches that previously reported for this compound.
Using **GP1**, compound **2g** was synthesized from the corresponding *F*-BODIPY. Bright orange solid (55 mg, 99%). \( \delta _H (500 \text{ MHz, CDCl}_3) 13.73 \) (1H, br s), \( 13.35 \) (1H, br s), \( 7.76 \) (1H, d, \( J = 3.5 \)), \( 7.34 \) (1H, s), \( 4.36 \) (2H, q, \( J = 7.0 \)), \( 3.07 \) (2H, q, \( J = 7.5 \)), \( 2.96 \) (3H, s), \( 2.33 \) (3H, s), \( 2.10 \) (3H, s), \( 1.40 \) (3H, t, \( J = 7.0 \)), \( 1.27 \) (3H, t, \( J = 7.5 \)); \( \delta _C (125 \text{ MHz, CDCl}_3) 163.2, 158.6, 155.6, 144.7, 144.5, 128.9, 126.6, 125.3, 122.9, 118.2, 60.7, 19.6, 16.9, 15.6, 14.4, 10.5, 10.2. LRMS-ESI (m/z): 287.2 \([\text{M} + \text{H}]^+\); HRMS-ESI (m/z): \([\text{M} + \text{H}]^+\) calcd for C\(_{17}\)H\(_{23}\)N\(_2\)O\(_2\) 287.1754; found, 287.1752.

**1,3,5,7-Tetramethyl-2,6-diethyl-8-\(H\)-4,4\(^{\prime}\)-dibromo-bora-3a,4a-diaza-s-indacene (3a)**

![Diagram](image-url)

The analogous *F*-BODIPY (50 mg) was dissolved in anhydrous CCl\(_4\) (10 mL) and treated with 1 eq of BBr\(_3\). The bright orange solution became dark red/purple in colour. The solution was concentrated *in vacuo* and compound **3a** was isolated as a dark red solid (70 mg, 99%). \( \delta _H (500 \text{ MHz, CDCl}_3) 7.02 \) (1H, s), \( 2.80 \) (6H, s), \( 2.40 \) (4H, q, \( J = 7.5 \)), \( 2.21 \) (6H, s), \( 1.08 \) (6H, t, \( J = 7.5 \)); \( \delta _C (125 \text{ MHz, CDCl}_3) 154.2, 139.6, 134.1, 131.6, 119.4, 17.4, 14.7, 14.4, 10.2; \( \delta _B (160 \text{ MHz, CDCl}_3) -5.89 \) (s).

**\((Z)-3\)-Ethyl-5-(4-ethyl-3,5-dimethyl-2\(H\)-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1\(H\)-pyrrole tetrafluoroborate (4a)**

![Diagram](image-url)
Using GP2, compound 4a was synthesized from the corresponding F-BODIPY.\textsuperscript{1} Bright orange solid (56 mg, 99%). \(\delta_H\) (500 MHz, CDCl\(_3\)) 10.78 (2H, brs), 7.06 (1H, s), 2.55 (6H, s), 2.44 (4H, q, \(J = 7.5\)), 2.28 (6H, s), 1.09 (6H, t, \(J = 7.5\)); \(\delta_C\) (125 MHz, CDCl\(_3\)) 154.3, 142.6, 131.1, 126.9, 118.9, 17.4, 14.5, 12.8, 10.2; \(\delta_B\) (160 MHz, CDCl\(_3\)) -0.65 (s); \(\delta_F\) (282 MHz, CDCl\(_3\)) -155.0 (s). LRMS-ESI (m/z): 87.0 [M].

\((Z)-2-((4\text{-Ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl}-3,5\text{-dimethyl-1H-pyrrole tetrafluoroborate (4b)}}\)

\begin{center}
\includegraphics[width=0.2\textwidth]{image1.png}
\end{center}

Using GP2, compound 4b was synthesized from the corresponding F-BODIPY.\textsuperscript{1} Bright orange solid (52 mg, 91%). \(\delta_H\) (500 MHz, CDCl\(_3\)) 10.83 (1H, br s), 10.73 (1H, brs), 7.09 (1H, s), 6.19 (1H, s), 2.57 (6H, s, 2 x CH\(_3\)), 2.45 (2H, q, \(J = 7.5\)), 2.35 (3H, s), 2.29 (3H, s), 1.09 (3H, t, \(J = 7.5\)); \(\delta_C\) (125 MHz, CDCl\(_3\)) 156.1, 154.8, 146.2, 143.5, 131.7, 127.30, 127.28, 119.5, 117.4, 17.5, 14.4, 12.9, 12.3, 10.2 (1C signal missing); \(\delta_B\) (160 MHz, CDCl\(_3\)) -0.65 (s); \(\delta_F\) (282 MHz, CDCl\(_3\)) -155.0 (s). LRMS-ESI (m/z): 87.0 [M].

\((Z)-2-((3,5\text{-Dimethyl-2H-pyrrol-2-ylidene)methyl}-3,5\text{-dimethyl-1H-pyrrole tetrafluoroborate (4c)}}\)

\begin{center}
\includegraphics[width=0.2\textwidth]{image2.png}
\end{center}

Using GP2, compound 4c was synthesized from the corresponding F-BODIPY.\textsuperscript{2} Bright orange solid (46 mg, 80%). \(\delta_H\) (500 MHz, CDCl\(_3\)) 10.84 (2H, brs), 7.09 (1H, s), 6.21 (2H, s), 2.58 (6H, s), 2.34 (6H, s); \(\delta_C\) (125 MHz, CDCl\(_3\)) 156.2, 147.4, 133.5, 127.6, 120.3,
14.5, 12.2; $\delta_B$ (160 MHz, CDCl$_3$) -0.65 (s); $\delta_F$ (282 MHz, CDCl$_3$) -154.9 (s). LRMS-ESI (m/z): 87.0 [M$^-$].

(Z)-3-Ethyl-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)(phenyl)methyl)-2,4-dimethyl-1H-pyrrole tetrafluoroborate (4e)

![Chemical structure of 4e]

Using GP2, compound 4d was synthesized from the corresponding F-BODIPY. Bright orange solid (25 mg, 45%). $\delta_H$ (500 MHz, CDCl$_3$) 9.89 (2H, br s), 7.53-7.45 (3H, m), 7.35-7.31 (2H, m), 2.52 (6H, s), 2.41 (4H, q, $J=7.5$), 1.45 (6H, s), 1.06 (6H, t, $J=7.5$); $\delta_C$ (125 MHz, CDCl$_3$) 153.7, 138.5, 136.6, 135.9, 133.8, 132.2, 129.3, 129.1, 128.3, 17.5, 14.3, 12.7, 12.1; $\delta_B$ (160 MHz, CDCl$_3$) -1.01 (s); $\delta_F$ (282 MHz, CDCl$_3$) -157.4 (s). LRMS-ESI (m/z): 87.0 [M$^-$].

(Z)-2-(Phenyl(2H-pyrrol-2-ylidene)methyl)-1H-pyrrole tetrafluoroborate (4h)

![Chemical structure of 4h]

Using GP2, compound 4e was synthesized from the corresponding F-BODIPY. Bright orange solid (3 mg, 5%). $\delta_H$ (500 MHz, CDCl$_3$) 8.46 (2H, brs), 7.68 (2H, t, $J=1.2$), 7.52-7.42 (5H, m), 6.62 (2H, dd, $J=4.2$, 1.2), 6.41 (2H, dd, $J=4.2$, 1.5); $\delta_C$ (125 MHz, CDCl$_3$) 143.8, 142.7, 140.3, 137.4, 131.0, 129.5, 129.2, 127.7, 117.7; $\delta_B$ (160 MHz, CDCl$_3$) -1.00 (s); $\delta_F$ (282 MHz, CDCl$_3$) -157.0 (s). LRMS-ESI (m/z): 87.0 [M$^-$].
(Z)-3-Ethyl-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1H-pyrrole hydrobromide (4a-HBr)

Compound 4a-HBF4 (50 mg) was dissolved in anhydrous dichloromethane (10 mL) and treated with excess (0.1 mL) aqueous HBr (48%). The resulting solution was stirred for 15 min and then washed with water. The organic layer was dried over Na₂SO₄ and concentrated in vacuo to give 4a-HBr as a bright orange solid (49 mg, 99%). δ_H (500 MHz, CDCl₃) 12.87 (2H, br s), 7.02 (1H, s), 2.66 (6H, s), 2.41 (4H, q, J = 7.5), 2.26 (6H, s), 1.06 (6H, t, J = 7.5). Data matches that previously reported for this compound.⁷

1,3,5,7-Tetramethyl-2,6-diethyl-8-H-4,4′-diethyl-bora-3a,4a-diaza-s-indacene (5a)

F-BODIPY 1a (50 mg) was dissolved in anhydrous dichloromethane (10 mL) and treated with 1 eq of BF₃·OEt₂, followed by the addition of 2 eq of EtMgBr (3.0 M in THF) added drop-wise. The solution was then washed with water and the organic layer was dried over Na₂SO₄ and concentrated in vacuo to give 5a as a bright orange solid (53 mg, 99%). δ_H (500 MHz, CDCl₃) 6.99 (1H, s), 2.44-2.39 (10H, m, 2x(CH₃+CH₂)), 2.18 (6H, s), 1.06 (6H, t, J = 7.6), 0.82 (4H, q, J=7.6), 0.31 (6H, t, J=7.6). Compound has been previously characterized.⁶
1.3 References


1.4 $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

(Z)-2-((4-Ethyl-3,5-dimethyl-2$H$-pyrrol-2-ylidene)methyl)-3,5-dimethyl-1$H$-pyrrole hydrochloride (2b)

$^1\text{H}$ NMR Spectrum in CDCl$_3$

$^{13}\text{C}$ NMR Spectrum in CDCl$_3$
(Z)-1-(2-((4-Heptanoyl-3,5-dimethyl-1H-pyrrol-2-yl)methylene)-3,5-dimethyl-2H-pyrrol-4-yl)heptan-1-one hydrochloride (2d)

\(^1\)H NMR Spectrum in CDCl₃

\(^13\)C NMR Spectrum in CDCl₃
(Z)-1-(2-((4-Acetyl-3,5-dimethyl-1H-pyrrol-2-yl)(phenyl)methylene)-3,5-dimethyl-2H-pyrrol-4-yl)ethanone hydrochloride (2e)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$CNMR Spectrum in CDCl$_3$
(Z)-Ethyl 2-((3,4-dimethyl-1H-pyrrol-2-yl)methylene)-3-ethyl-5-methyl-2H-pyrrole-4-carboxylate hydrobromide (2g)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$
1,3,5,7-Tetramethyl-2,6-diethyl-8-H,4,4’-dibromo-bora-3a,4a-diaza-s-indacene (3a)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$
(Z)-3-Ethyl-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1H-pyrrole tetrafluoroborate (4a)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$
(Z)-2-((4-Ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-3,5-dimethyl-1H-pyrrole tetrafluoroborate (4b)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$
(Z)-2-((3,5-Dimethyl-2H-pyrrol-2-ylidene)methyl)-3,5-dimethyl-1H-pyrrole tetrafluoroborate (4c)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$
(Z)-3-Ethyl-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)(phenyl)methyl)-2,4-dimethyl-1H-pyrrole tetrafluoroborate (4e)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$
(Z)-2-(Phenyl(2H-pyrrol-2-ylidene)methyl)-1H-pyrrole tetrafluoroborate (4h)

$^1$H NMR Spectrum in CDCl$_3$

$^{13}$C NMR Spectrum in CDCl$_3$