Facile deprotection of F-BODIPYs using methylboronic acid†

Craig D. Smith and Alison Thompson 

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacenes (F-BODIPYs) are deprotected through removal of the –BF₂ moiety upon treatment with methylboronic acid. The tolerance of various substitution patterns about the dipyrrinato core is demonstrated via the deprotection of thirteen F-BODIPYs and an F-aza-BODIPY. Work-up with aq. HBr affords the desired dipyrrin HBr salt in quantitative yield without need for purification.

Results and discussion

Upon treating an F-BODIPY with methyl boronic acid, with anticipation that an appended boronic ester would be hydrolysed, a dipyrrin was isolated as a result of removal of the –BF₂ unit. Cognisant that these conditions represent a mild alternative to existing methods for the deprotection of F-BODIPYs, and in light of the fact that the volatility of methylboronic acid renders work-up facile, we investigated the scope of the reaction conditions. Treatment of 4,4-difluoro-8-phenyl-4-bora-3a,4a-diaza-s-indacene (1a) with 5 equiv. methylboronic acid at room temperature (Table 1) gave clean conversion, after 24 hours, to provide the corresponding dipyrrin 2a in quantitative yield (entry 1). The incorporation of alkyl groups about the pyrrolic units was well tolerated, as was a methyl substituent in the meso-position (entries 2 and 3, respectively). Work-up using aqueous HBr provided the corresponding dipyrrin salts which are known to be more stable and more crystalline than their HX counterparts, an observation of significant value when storing meso-unsubstituted dipyrrins.† Using these reaction conditions provided the meso-unsubstituted dipyrrin salts 2d and 2e in quantitative yield (entries 4 and 5, respectively). The preparation of the HBr salt of 2d was equally successful on a one-gram scale (entry 4). Furthermore, the corresponding free-base was isolated in quantitative yield, again on a one-gram scale, upon implementation of a basic work-up procedure. The removal of the –BF₂ unit using methylboronic acid was effective for F-BODIPYs bearing unsubstituted positions about the pyrrolic core (entry 6), as well as for unsymmetrical variants (entry 7).

Introduction

The dipyrrinato framework is a useful ligand for complexation to metals, the most common featuring first-row transition metals and boron. The photophysical characteristics of –BF₂ complexes of dipyrins, known widely as 4,4-di-boro-3a,4a-diaza-s-indacenes (F-BODIPYs), have enabled applications across many of the chemical sciences. For example, F-BODIPYs have been used as dyes to label proteins, DNA and functional materials. Furthermore, the potential of F-BODIPYs for use in photo-assisted rechargeable batteries has been investigated. Recently, efforts have focused on substituting the boron centre of BODIPYs with alkyl, alkynyl and chloro substituents in order to tune spectroscopic properties and thus potentially extend the performance of these conjugated chemical species.

Parallel to the photophysical and spectroscopic advances that have involved BODIPYs, dipyrins have emerged as capable of providing a useful structural framework for incorporation into catalysts, supramolecular assemblies, and polypyrroles with desirable biological activity. As such, there is a desire to substitute, functionalise and manipulate dipyrins, in route to accessing the dipyrrinato ligand. Given the broad range of strategies by which to functionalise F-BODIPYs, as well as the facile manner by which to purify them using chromatography, the use of the –BF₂ moiety has emerged as a useful approach to the protection of dipyrins. Reported methods for the removal of the –BF₂ moiety from F-BODIPYs, i.e. deprotection to yield the parent dipyrin, have involved the use of alkoxides and strong Bronstead and Lewis acids. Herein, we report using methylboronic acid to deprotect thirteen F-BODIPYs and an F-aza-BODIPY to generate the corresponding dipyrins and aza-dipyrin in quantitative yield.

† Electronic supplementary information (ESI) available: Images of NMR spectra. See DOI: 10.1039/d0ra05151a

Fig. 1 Bromo-substituted F-BODIPY.
Given the previously documented sternutatory properties of the free base of 2f, an alternative work-up procedure was implemented so as to ensure successful formation of the corresponding HBr salt. Dipyrrin 2g was also isolated in quantitative yield upon treatment of 4,4-difluoro-1,3-dimethyl-2-ethyl-6-pinacolatoboron-8-H-4-bora-3a,4a-diaza-s-indacene with 5 equiv. methylboronic acid, thereby effecting both deborylation (of the BPin moiety) as well as removal of the –BF₂ unit. The new method for the deprotection of F-BODIPYS proceeded in the presence of bromo-substituents, as exemplified by the isolation of quantitative yields of the dipyrrins 2h and 2i (entries 8 and 9). Similarly, the dipyrrin 2j was isolated in quantitative yield upon

| Entry | Product dipyrrin salt yield (%) | Entry | Product dipyrrin salt yield (%) |
|-------|--------------------------------|-------|--------------------------------|
| 1     | ![image](2a.png) 2a, >99%°     | 8     | ![image](2h.png) 2h, >99%°     |
| 2     | ![image](2b.png) 2b, >99%°     | 9     | ![image](2i.png) 2i, >99%°     |
| 3     | ![image](2c.png) 2c, >99%°     | 10    | ![image](2j.png) 2j, >99%°     |
| 4     | ![image](2d.png) 2d, >99%°,d,e  | 11    | ![image](2k.png) 2k, >99%°     |
| 5     | ![image](2e.png) 2e, >99%°     | 12    | ![image](2l.png) 2l, >99%°     |
treatment of the corresponding F-BODIPY with methylboronic acid, thereby demonstrating tolerance of the hydroxy and trifluoromethyl functionalities within these electron-poor constructs. Further demonstration of the ability of methylboronic acid to deprotect F-BODIPYs bearing aryl substituents involved isolation of the two triphenyl-substituted dipyrrins 2k and 2l in quantitative yields (entries 11 and 12, respectively), with 2l being isolated as its free-base on account of the rather poor solubility of the corresponding HBr salt. Expanding the scope further, an aza-F-BODIPY i.e. a bridging nitrogen between the two pyrrolic sub-units, was successfully deprotected to provide the aza-dipyrrin 2m in quantitative yield (entry 13).

Attempts to reduce the equivalencies of the Lewis acid were briefly explored, resulting in the observation that 2d could be generated in quantitative yield upon treatment of the corresponding F-BODIPY with just 1 equiv. methylboronic acid. However, this achievement did not extend to the deprotection of F-BODIPYs appended with meso-aryl substituents. Despite the successful deprotection of thirteen F-BODIPYs and one F-aza-BODIPY using 5 equiv. methylboronic acid, the bromo-substituted F-BODIPY 3 (Fig. 1) reacted sluggishly to result in decomposition. Equally unsuccessful were attempts to use methylboronic acid to remove the –BF2 unit from F-BODIPYs bearing carboxylate- or azido- functionality around the dipyrrolic core.

Conclusion

In conclusion, we have developed a high yielding and mild method for the deprotection of F-BODIPYs through the use of volatile methylboronic acid using 5% TFA and CH2Cl2 as solvent. The reaction is performed at room temperature, tolerates substrates bearing a range of substituents around the F-BODIPY framework, and requires only a facile work-up procedure in order to isolate quantitative yields of the dipyrrin as either an HBr salt or a free-base.

Experimental section

General information

Reactions involving air-sensitive reagents and dry solvents were performed using glassware that had been oven-dried (150 °C) or flame-dried prior to use. NMR spectra were recorded using a 500 MHz spectrometer. 1H chemical shifts are reported in ppm relative to tetramethylsilane using the solvent residual as an internal standard (δ = 7.26 for CDCl3; 5.32 for CD2Cl2; 2.05 for acetone-d6; 2.50 for DMSO-d6). 13C NMR chemical shifts are reported in ppm using the residual solvent as an internal standard (δ = 77.2 for CDCl3; 53.8 for CD2Cl2; 29.8 for acetone-d6; 39.5 for DMSO-d6). Signals in NMR spectra are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br.), apparent (app.) or a combination of these, referring
to the observed spin–spin coupling pattern. Spin–spin coupling constants are reported in hertz (Hz), and are uncorrected. Mass spectrometry was performed using a TOF spectrometer operating in ESI⁺ or APCI mode, as indicated. Flash chromatography was performed using forced air flow of the indicated solvent system using silica gel 60 as solid support. Reactions were monitored by thin layer chromatography (TLC) on silica gel 60-covered aluminium sheets. TLC plates were developed under UV-light and/or with an acidic Ethanolic anisaldehyde solution, vanillin or a KMnO₄-solution upon heating. All reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. F-BODIPYs 1a, 1b, 1c, 1d, 1f, 1g, 2h, 2j, 2k were prepared according to literature procedures, as was F-aza-BODIPY 1m.

(Z)-4-Bromo-2-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidine) methyl)-1H-pyrole hydrobromide

Following a modified literature procedure,¹⁰ to a round-bottom flask was added 3-ethyl-2,4-dimethyl-pyrrole (1.73 g, 14.1 mmol) and 4-bromo-pyrrole-2-carbaldehyde (2.44 g, 14.1 mmol). The pyroles were dissolved in THF: MeOH (1:1; 85 mL), and the resulting solution was purged with nitrogen before 48% aq. HBr (3.2 mL, 28 mmol) was added drop-wise to the solution. The reaction mixture was stirred at 70 °C for 2 hours, monitoring by TLC analysis until complete consumption of starting material was observed. The reaction mixture was then poured into a mixture of diethyl ether (60 mL) to induce precipitation. The resulting solid was collected by suction filtration, and dried to a purified via column chromatography on silica (hexanes/CH₂Cl₂; 1:1) to afford the title compound as a red solid (3.60 g, 71%).¹¹ H NMR (500 MHz; CDCl₃) δ (ppm): 164.9, 146.4, 135.6, 134.7, 130.7, 130.7, 130.3, 127.0, 118.9, 118.3, 108.6, 7.41 (s, 1H), 7.04 (s, 1H), 2.75 (s, 3H), 2.45 (q, J = 7.6 Hz, 2H), 2.30 (s, 3H), 1.09 (t, J = 7.6 Hz, 3H);¹²¹³C NMR (125 MHz; CDCl₃) δ (ppm): 166.2, 142.3, 137.2, 136.1, 136.0, 130.1, 124.4, 122.6, 102.7, 17.4, 14.2, 13.7, 9.7;¹³¹⁴B NMR (160 MHz; CDCl₃) δ (ppm): 0.3 (t, J = 31 Hz);¹⁴¹⁵F NMR (470 MHz; CDCl₃) δ (ppm): −146.1 (q, J = 31 Hz); HRMS-APCI (m/z): [M + H]⁺ calcd for C₁₈H₁₈FBr₂N₂O₂, 375.0474; found, 375.0476.

4,4-Difluoro-1,3-dimethyl-2-ethyl-6-picolinatoboron-8-H-4-bora-3a,4a-diaza-s-indacene

A 4 mL screw-top vial was charged with 4,4-difluoro-1,3-dimethyl-2-ethyl-6-bromo-8-H-4-bora-3a,4a-diaza-s-indacene (163 mg, 0.5 mmol), Pd₂dba₂ (5 mg, 5 μmol), XPhos (9 mg, 20 μmol), bis-picolinato)diboron (380 mg, 1.50 mmol) and oven dried KOAc (147 mg, 1.50 mmol). The vial was capped with a septum and then evacuated and backfilled with N₂ (this sequence was carried out two times). 1,4-Dioxane (3 mL) was added via syringe through the septum. Under a flow of nitrogen, the septum was replaced with a screw cap. The reaction mixture was stirred at 110 °C in a preheated aluminium block until consumption of the F-BODIPY starting material was complete, as judged by TLC analysis (approximately 20 minutes). The reaction mixture was allowed to cool to room temperature and then filtered through a thin pad of Celite, eluting with CH₂Cl₂. The crude material was purified via rapid chromatography on silica (hexanes: EtOAc; 8:2), with minimal residence time ensured in order to minimise decomposition over the solid phase. The product was crystallised from hexanes to give the title compound as a bench- and air-stable brown solid (113 mg, 60%).¹⁵ H NMR (500 MHz; CDCl₃) δ (ppm): 7.96 (s, 1H), 7.22 (s, 1H), 7.17 (s, 1H), 2.61 (s, 3H), 2.45 (q, J = 7.6 Hz, 2H), 2.30 (s, 3H), 1.09 (t, J = 7.6 Hz, 3H);¹⁶¹⁷¹³C NMR (125 MHz; CDCl₃) δ (ppm): 164.2, 145.2, 141.4, 136.9, 135.6, 134.7, 130.7, 130.3, 127.0, 101.8, 17.4, 14.1, 13.8, 10.4; HRMS-ESI (m/z): [M + H]⁺ calcd for C₁₈H₂₃B₂F₂N₂O₂, 327.0474; found, 327.0475.

4,4-Difluoro-1,3,5,7-tetramethyl-2-ethyl-6-bromo-8-H-4-bora-3a,4a-diaza-s-indacene (i)

To a 100 mL round-bottom flask, charged with a magnetic stirrer bar, was added 4,4-difluoro-1,3,5,7-tetramethyl-2-ethyl-8-H-4-bora-3a,4a-diaza-s-indacene¹⁷ (730 mg, 2.64 mmol) and CH₂Cl₂ (37 mL). To the solution was added N-bromosuccinimide (469 mg, 2.64 mmol). The reaction mixture was stirred at room temperature for 1 hour, then quenched with H₂O (30 mL) and extracted with CH₂Cl₂ (3× 50 mL). The combined organic fractions were dried over Na₂SO₄, filtered and concentrated in vacuo. The crude material was purified via column chromatography on silica (hexanes/CH₂Cl₂; 8:2) to afford the title compound as a red solid (906 mg, 97%).¹⁸ H NMR (500 MHz; CDCl₃) δ (ppm): 7.29 (s, 1H), 7.15 (s, 1H), 7.13 (d, J = 8 Hz, 2H), 2.75 (s, 3H), 1.12 (t, J = 7.6 Hz, 3H);¹⁹¹³C NMR (125 MHz; CDCl₃) δ (ppm): 164.2, 145.2, 141.4, 136.9, 135.6, 133.5, 131.8, 126.3, 83.5, 25.0, 17.5, 14.3, 13.5, 9.7, 1.7× Ar C signal missing;¹⁰¹⁵B NMR (160 MHz; CDCl₃) δ (ppm): 30.4 (br. s); 0.6 (t, J = 32 Hz);¹⁰¹⁷¹⁵F NMR (470 MHz; CDCl₃) δ (ppm): −146.0 (q, J = 31 Hz); HRMS-APCI (m/z): [M + H]⁺ calcd for C₁₉H₂₁B₂F₂N₂O₂, 375.2221; found, 375.2234.
NMR (125 MHz; CDCl₃) δ (ppm): 159.5, 150.8, 139.3, 136.3, 134.1, 133.7, 130.6, 119.5, 107.6, 17.4, 14.5, 13.3, 13.1, 11.0, 9.6; ¹³B NMR (160 MHz; CDCl₃) δ (ppm): 0.7 (t, J = 33 Hz); ¹⁹F NMR (470 MHz; CDCl₃) δ (ppm): −146.4 (q, J = 33 Hz); HRMS-APCI (m/z): [M + H]⁺ calcd for C₁₃H₁₅BrBF₄N₂, 355.0787; found, 355.0781.

General procedure (GP) for the deprotection of F-BODIPYs using MeB(OH)₂
A 4 mL screw-top vial was charged with F-BODIPY (0.2 mmol) and MeB(OH)₂ (1.0 mmol). To this was added CH₂Cl₂ (1.90 mL) and trifluoroacetic acid (0.10 mL). The vial was capped with a screw cap and the mixture was stirred until F-BODIPY had been completely consumed as judged by analysis using TLC (typically stirred for 24 hours).

Work-up A. The reaction mixture was transferred to a separatory funnel using CH₂Cl₂, quenched with 2 M aq. hydrobromic acid (40 mL) and the aqueous phase then extracted with CH₂Cl₂ (3 × 40 mL). The combined organic extracts were dried over Na₂SO₄ and volatiles were then removed in vacuo to afford the dipyrrin HBr salt.

Work-up B. The reaction mixture was transferred into a 100 mL round-bottomed flask using CH₂Cl₂ and all volatiles removed in vacuo. To the 100 mL round-bottomed flask was added 1 M aq. hydrobromic acid (40 mL) which was then removed under reduced pressure, followed by the addition of CH₂Cl₂. After filtration of the resulting mixture, volatiles were removed in vacuo to afford the dipyrrin HBr salt.

Work-up C. The reaction mixture was transferred to a separatory funnel using CH₂Cl₂ and to the resulting solution was added sat. aq. NaHCO₃ (40 mL). The mixture was extracted with CH₂Cl₂ (3 × 40 mL), the combined organic extracts dried over Na₂SO₄ and volatiles removed in vacuo to afford the dipyrrin as a free base.

(Z)-3-Ethyl-5-(1-(4-ethyl-3,5-dimethyl-2H-pyrryl-2-ylidene)ethyl)-2,4-dimethyl-1H-pyryro hydrobromide (2e)
Following the GP and work-up A, using 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-8-bora-3a,4a-diaza-s-indacene (1e),¹ provided the title compound as a brown solid (70 mg, > 99%). ¹H NMR (500 MHz; CDCl₃) δ (ppm): 11.82 (br. s, 2H), 2.87 (s, 3H), 2.54 (s, 6H), 2.39 (q, J = 7.4 Hz, 4H), 2.05 (s, 6H), 1.05 (t, J = 7.4 Hz, 6H); ¹³C NMR (125 MHz; CDCl₃) δ (ppm): 194.2, 146.7, 137.1, 132.2, 131.5, 25.0, 17.6, 14.5, 12.7, 12.4. Data correspond to literature values.¹²

(Z)-3-Ethyl-5-(1-(4-ethyl-3,5-dimethyl-2H-pyrryl-2-ylidene)ethyl)-2,4-dimethyl-1H-pyryro hydrobromide (2d)
Following the GP and work-up A, using 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (1d),¹ provided the title compound as a brown solid (67 mg, > 99%). ¹H NMR (500 MHz; CDCl₃) δ (ppm): 12.87 (br. s, 2H), 7.01 (s, 1H), 2.64 (s, 6H), 2.40 (q, J = 7.6 Hz, 4H), 2.25 (s, 6H), 1.05 (t, J = 7.6 Hz, 6H); ¹³C NMR (125 MHz; CDCl₃) δ (ppm): 153.7, 141.3, 130.6, 126.1, 118.7, 17.3, 14.5, 12.8, 10.1. Data correspond to literature values.¹³

(Z)-3-(3,3-Dimethylbutyl)-5-(4-(3,3-dimethylbutyl)-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1H-pyryro hydrobromide (2c)
Following the GP and work-up A, using 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (1e), provided the title compound as a red solid (90 mg, > 99%). ¹H NMR (500 MHz; CDCl₃) δ (ppm): 13.42 (br. s, 2H), 7.64 (s, 1H), 7.51–7.45 (m, 4H), 6.81 (s, 2H), 6.63 (s, 2H); ¹³C NMR (125 MHz; CDCl₃) δ (ppm): 149.9, 143.9, 136.7, 133.9, 132.1, 131.6, 131.3, 128.2, 117.5; HRMS-ESI (m/z): [M + H]⁺ calcd for C₂₅H₃₇N₂, 369.3264; found, 369.3278.

(Z)-2-(3,5-Dimethyl-2H-pyrrol-2-ylidene)methyl)-3,5-dimethyl-1H-pyryro hydrobromide (2f)
Following the GP and work-up B, using 4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1f),² provided the title compound as a red solid (56 mg, > 99%). ¹H NMR (500 MHz; CDCl₃) δ (ppm): 13.06 (br. s, 2H), 7.07 (s, 1H), 6.14 (s, 2H), 2.66 (s, 6H), 2.34 (s, 6H); ¹³C NMR (125 MHz; CDCl₃) δ (ppm): 155.6, 146.1, 126.8, 120.1, 117.6, 14.6, 12.3. Data correspond to literature values.⁴ Caution: the free-base of 2f has been reported to exhibit stenuratory properties.⁷

(Z)-2-(1-(4-Ethyl-3,5-dimethyl-2H-pyrryl-2-ylidene)phenyl)methyl)-2,4-dimethyl-1H-pyryro hydrobromide (2b)
Following the GP and work-up A, using 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-8-bora-3a,4a-diaza-s-indacene (1b),² provided the title compound as a red solid (82 mg, > 99%). ¹H NMR (500 MHz; CDCl₃) δ (ppm): 11.01 (br. s, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 7.30 (d, J = 7.4 Hz, 2H), 2.70 (br. s, 6H), 2.41–2.35 (m, 4H), 1.36 (br. s, 6H), 1.06–1.03 (m, 6H); ¹³C NMR (125 MHz; CDCl₃) δ (ppm): 152.4, 144.2, 140.1, 137.1, 133.7, 131.8, 128.7, 129.0, 17.5, 14.5, 13.7, 12.3, 1× aryl signal missing; HRMS-ESI (m/z): [M + H]⁺ calcd for C₃₂H₃₀N₂, 333.2325; found, 333.2323.
Following the GP and work-up A, using 4,4-difluoro-1,3-dimethyl-2-ethyl-6-pinacolatoborono-8-H-4-bora-3a,4a-diaza-5-indacene provided the title compound as a red solid (56 mg, > 99%). Data as above.

(Z)-2-((4-Bromophenyl)(2H-pyrrol-2-ylidene)methyl)-1H-pyrrole hydrobromide (2h)

Following the GP and work-up A, using 4,4-difluoro-8-(phenyl(4-bromo)-4-bora-3a,4a-diaza-5-indacene (1h),7 provided the title compound as a red solid (76 mg, > 99%).1H NMR (500 MHz; CDCl3) δ (ppm): 13.48 (br. s, 2H), 8.10 (br. s, 2H), 7.66 (d, J = 6.3 Hz, 2H), 7.29 (br. s, 2H), 6.81 (br. s, 2H), 6.65 (s, 2H); 13C NMR (125 MHz; CDCl3) δ (ppm): 148.2, 144.4, 136.3, 135.3, 133.5, 131.6, 131.0, 126.6, 117.8.

(Z)-3-Bromo-5-((4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1H-pyrrole hydrobromide (2i)

Following the GP and work-up B, using 4,4-difluoro-1,3,5,7-tetramethyl-2-ethyl-6-bromo-8-H-4-bora-3a,4a-diaza-5-indacene (1i),7 provided the title compound as a red solid (78 mg, > 99%).1H NMR (500 MHz; CDCl3) δ (ppm): 13.20 (br. s, 2H), 7.08 (s, 1H), 2.67 (s, 3H), 2.64 (s, 3H), 2.42 (q, J = 7.6 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 1.07 (t, J = 7.6 Hz, 3H); 13C NMR (125 MHz; CDCl3) δ 158.2, 150.3, 143.7, 141.1, 132.3, 127.4, 124.8, 119.8, 106.6, 17.4, 14.3, 13.4, 13.2, 11.9, 10.3; HRMS-ESI (m/z): [M + H]+ calcd for C13H20BrN3, 307.0804; found, 307.0803.

(Z)-1-(2-(4-(Ethyl-3,5-dimethyl-1H-pyrrol-2-yl)methylene)-3,5-dimethyl-2H-pyrrol-4-yl)-2,2,2-trifluoroethanol hydrobromide (2j)

Following the GP and work-up B, using 4,4-difluoro-1,3,5,7-tetramethyl-2-trifluoroethanol-6-ethyl-4-bora-3a,4a-diaza-5-indacene (1j),7 provided the title compound as a red solid (81 mg, > 99%).1H NMR (500 MHz; acetone-d6) δ (ppm): 13.75 (br. s, 1H), 13.53 (br. s, 1H), 7.44 (s, 1H), 5.86 (d, J = 5.0 Hz, 1H), 5.39–5.33 (m, 1H), 2.72 (s, 3H), 2.69 (s, 3H), 2.51 (q, J = 7.5 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H), 1.11 (t, J = 7.5 Hz, 3H); 13C NMR (125 MHz; acetone-d6) δ (ppm): 158.5, 152.5, 145.0, 144.0, 132.8, 128.1, 126.4 (q, J = 281 Hz), 125.9, 121.4, 110.8, 66.8 (q, J = 33 Hz), 17.6, 14.5, 13.3, 12.8, 10.6, 10.1; 19F NMR (470 MHz; acetone-d6) δ (ppm): −78.4 (d, J = 7.6 Hz). Data correspond to literature values.16

(Z)-2-Phenyl-5-(phenyl(5-phenyl-2H-pyrrol-2-ylidene)methyl)-1H-pyrrole hydrobromide (2k)

Following the GP and work-up C, using 4,4-difluoro-2,5,8-triphenyl-4-bora-3a,4a-diaza-5-indacene (1k),6 provided the title compound as a red solid (90 mg, > 99%).1H NMR (500 MHz; acetone-d6) δ (ppm): 13.05 (br. s, 2H), 8.36–8.29 (m, 4H), 9.74 (t, J = 7.2 Hz, 1H), 7.62 (t, J = 7.6 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.53–7.50 (m, 6H), 7.33 (s, 2H), 7.20–6.90 (m, 2H); 13C NMR (125 MHz; acetone-d6) δ (ppm): 134.6, 147.2, 137.8, 135.8, 135.1, 134.8, 133.5, 131.7, 130.0, 129.8, 129.5, 129.2, 117.9; HRMS-ESI (m/z): [M + H]+ calcd for C27H23N3, 373.1699; found, 373.1702.

(Z)-4-Phenyl-2-(phenyl(4-phenyl-2H-pyrrol-2-ylidene)methyl)-1H-pyrrole (2l)

Following the GP and work-up C, using 4,4-difluoro-3,6,8-triphenyl-4-bora-3a,4a-diaza-5-indacene (1l), provided the title compound as a dark blue solid (74 mg, >99%).1H NMR (500 MHz; DMSO-d6) δ (ppm): 8.28 (s, 2H), 7.62–7.57 (m, 9H), 7.36–7.33 (m, 4H), 7.23–7.20 (m, 2H), 6.76 (s, 2H); HRMS-ESI (m/z): [M + H]+ calcd for C27H24N4, 373.1699; found, 373.1699. The title compound was insufficiently soluble to enable the acquisition of 13C NMR data.

(Z)-N-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine (2m)

Following the GP and work-up C, using 4,4-difluoro-1,3,5,7-tetratriphenyl-4-bora-3a,4a,8-triaza-5-indacene (1m),9 provided the title compound as a dark blue solid (90 mg, > 99%).1H NMR (500 MHz; CDCl3) δ (ppm): 8.07 (d, J = 7.3 Hz, 4H), 7.96 (d, J = 7.4 Hz, 4H), 7.54 (t, J = 7.5 Hz, 4H), 7.48 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.5 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H), 7.21 (s, 2H); 13C NMR (125 MHz; CDCl3) δ (ppm): 155.3, 149.8, 142.8, 139.9, 133.4, 130.2, 129.3, 129.2, 128.4, 128.2, 126.7, 115.1. Data correspond to literature values.17

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

Financial support for this work was provided by NSERC of Canada via a Discovery Grant and the CREATE Training Program in BioActives (510963). Dr Mike Lumsden and Mr Xiao Feng (both at Dalhousie University) are thanked for sharing their expertise in NMR spectroscopy and mass spectrometry, respectively.

References

1 R. M. Diaz-Rodriguez, K. N. Robertson and A. Thompson, Chem. Commun., 2018, 54, 13139–13142.
2 R. M. Diaz-Rodriguez, K. N. Robertson and A. Thompson, Dalton Trans., 2019, 48, 7546–7550.
3 G. Ulrich, R. Ziessel and A. Harriman, Angew. Chem., Int. Ed., 2008, 47, 1184–1201.
4 T. E. Wood and A. Thompson, Chem. Rev., 2007, 107, 1831–1861.
5 M. Benstead, G. H. Mehl and R. W. Boyle, Tetrahedron, 2011, 67, 3573–3601.
6 A. Loudet and K. Burgess, Chem. Rev., 2007, 107, 4891–4932.
