Supporting Information

An Improved Method for the Synthesis of *F*-BODIPYs from Dipyrrins and Bis(dipyrrin)s

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1.1 General Experimental Section

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 77.16 ppm); MeOD-*d4* (^{1}H 3.31 ppm, ^{13}C 49.00 ppm)] as an internal reference for ^{1}H and ^{13}C, and BF_3•OEt_2 as an external reference for ^{11}B at 0 ppm. 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. Column chromatography, as indicated, was performed using 230-400 mesh ultra pure silica. Dipyrrins **2**,[1] **3**,[2] **5**,[3] **7**[4] and **8**[5] were prepared using literature procedures. The free-bases were obtained by adding concentrated ammonium hydroxide (28%) to a suspension of the HBr salt in diethyl ether. Within 15 minutes, the formation of a yellow precipitate (NH_4Br) was observed. Distilled water was used to extract the by-products. The resulting organic fraction was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the title compound. Compounds were dried under vacuum before use. Compounds **3BF$_2$-5BF$_2$**[6] and **8BF$_2$**[7] have been previously reported.

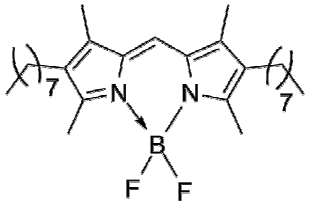
General Procedure for the Synthesis of *F*-BODIPYs (GP1)

Each dipyrrin was used as the free-base. The dipyrrin (50 mg) was dissolved in anhydrous dichloromethane (20 mL) and a solution of LiHMDS [1.1 eq.; 2.2 eq. for the bis(dipyrrin)s] in anhydrous tetrahydrofuran was added drop-wise. The reaction was stirred for two hours. A solution of BF_3•OEt_2 [1 eq.; 2 eq. for bis(dipyrrin)s] in anhydrous dichloromethane was then added to the reaction mixture drop-wise, and stirring was

continued for another three hours. Upon completion of the reaction, the mixture was filtered over a pad of Celite, and silica if necessary, in both cases flushing with dichloromethane. The solutions were then concentrated *in vacuo* to obtain the *F*-BODIPY product.

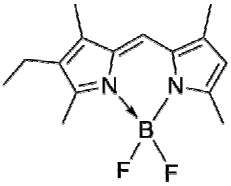
1.2 Experimental Procedures and Characterization Data

1,3,5,7-Tetramethyl-2-octyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($1BF_2$)

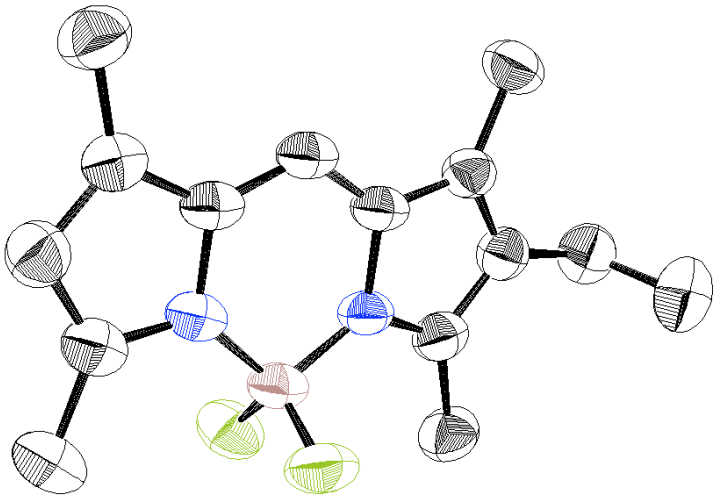


Using **GP1**, compound **$1BF_2$** was synthesized from the corresponding free-base dipyrrin. Bright orange solid (55 mg, 98 %). δ_H (500 MHz, $CDCl_3$) 6.94 (s, 1H), 2.49 (s, 6H), 2.34 (t, J = 7.6, 4H), 2.15 (s, 6H), 1.43-1.39 (m, 4H), 1.30-1.27 (m, 20H), 0.89 (t, J = 6.8, 6H); δ_C (125 MHz, $CDCl_3$) 155.0, 137.1, 132.5, 130.4, 118.6, 32.0, 30.3, 29.7, 29.6, 29.4, 24.2, 22.8, 14.2, 12.8, 9.7; δ_B (160 MHz, $CDCl_3$) 0.90 (t, $J_{B\text{-}F}$ = 34); LRMS-ESI (*m/z*): 495.4 $[M + Na]^+$; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{29}H_{47}BF_2N_2Na$ 495.3693; found 495.3709.

1,3,5,7-Tetramethyl-2-ethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($2BF_2$)

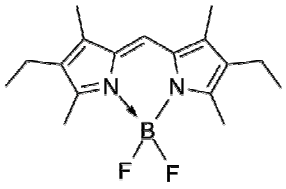


Using **GP1**, compound **2BF$_2$** was synthesized from the corresponding free-base dipyrrins.[1] Bright orange solid (55 mg, 91 %). δ_H (500 MHz, $CDCl_3$) 6.99 (s, 1H), 6.00 (s, 1H), 2.51 (s, 6H), 2.39 (q, J = 7.5, 2H), 2.23 (s, 3H), 2.17 (s, 3H), 1.07 (t, J = 7.6, 3H); δ_C (125 MHz, $CDCl_3$) 156.6, 155.2, 140.0, 137.8, 133.2, 132.9, 132.6, 119.4, 118.4, 17.4, 14.7, 14.6, 12.8, 11.4, 9.6; δ_B (160 MHz, $CDCl_3$) 0.89 (t, $J_{B\text{-}F}$ = 33); LRMS-ESI (*m/z*): 299.2 $[M + Na]^+$; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{15}H_{19}BF_2N_2Na$ 299.1502; found 299.1514.

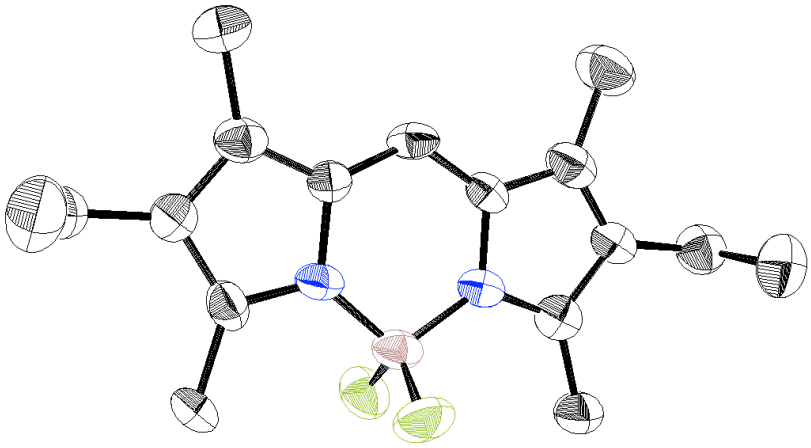


Crystal data for compound **2BF2**: $C_{15}H_{19}BF_2N_2$, MM = 276.14 g/mol, colourless prism crystal 0.26 x 0.23 x 0.17 mm; triclinic, space group P_{-1} (#2), a = 8.6184(9) Å, b = 9.2516(10) Å, c = 10.4144(10) Å, V = 730.81(13) Å^3, Z = 2, ρ = 1.255 g/cm^3, μ(MoKα) = 0.71070 cm^{-1}, 2721 reflections (1612 unique, R_{int} = 0.040), R = 0.0476, R_w = 0.0548, GOF = 1.077.

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($3BF_2$)

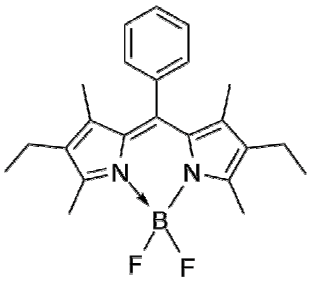


Using **GP1**, compound **$3BF_2$** was synthesized from the corresponding free-base dipyrrin.[2] Bright red solid (56 mg, 94 %). δ_H (500 MHz, $CDCl_3$) 6.93 (s, 1H), 2.49 (s, 6H), 2.36 (q, J = 7.6, 4H), 2.14 (s, 6H), 1.05 (t, J = 7.6, 6H); δ_C (125 MHz, $CDCl_3$) 154.7, 136.7, 132.5, 131.7, 118.7, 17.4, 14.7, 12.6, 9.4; δ_B (160 MHz, $CDCl_3$) 0.76 (t, $J_{B\text{-}F}$ = 32). NMR data matches that previously reported.[6]



Crystal data for compound **3BF2**: $C_{17}H_{23}BF_2N_2$, MM = 304.19 g/mol, colourless needle crystal 0.34 x 0.11 x 0.08 mm; triclinic, space group P_{-1} (#2), a = 9.3694(16) Å, b = 12.210(2) Å, c = 8.6351(16) Å, V = 833.1(3) $Å^3$, Z = 2, ρ = 1.213 g/cm^3, μ(MoKα) = 0.71070 cm^{-1}, 3365 reflections (1947 unique, R_{int} = 0.090), R = 0.0693, R_w = 0.0775, GOF = 0.944.

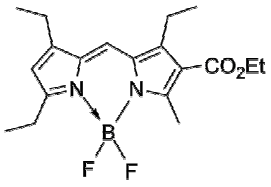
1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene ($5BF_2$)



Method 1: Using **GP1**, compound **$5BF_2$** was synthesized from the corresponding free-base dipyrrin.[3] Bright orange solid (50 mg, 88 %).

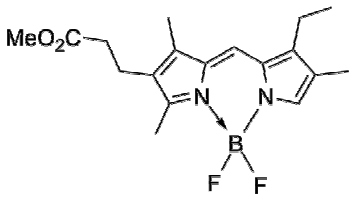
Method 2: To a solution of 5,5'-(phenylmethylene)bis(3-ethyl-2,4-dimethyl-1*H*-pyrrole) (800 mg, 2.39 mmol) in anhydrous DCM (80 mL) under nitrogen was added DDQ (543 mg, 2.39 mmol). The reaction mixture was stirred at room temperature for an hour before LiHMDS in anhydrous hexane (1.0 M, 7.9 mL) was added. The reaction mixture was stirred for another hour before the addition of neat BF_3•OEt_2 (0.30 mL, 2.39 mmol). After three hours the reaction mixture was filtered over Celite, flushing with dichloromethane. The filtrate was washed with 0.1 M NaOH (25 mL), 1 M HCl (25 mL) and brine (25 mL). The organic fraction was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting solid was purified via filtration over a pad of silica eluting with DCM. Removal of the solvent *in vacuo* afforded a bright orange solid (470 mg, 52%). δ_H (500 MHz, $CDCl_3$) 7.37-7.40 (m, 3H), 7.17-7.21 (m, 2H), 2.45 (s, 6H), 2.21 (q, J = 7.5, 4H), 1.20 (s, 6H), 0.90 (t, J = 7.6, 6H); δ_C (125 MHz, $CDCl_3$) 150.3, 138.9, 137.8, 136.0, 135.0, 131.4, 129.8, 128.5, 128.2, 17.7, 15.0, 14.5, 11.9; δ_B (160 MHz, $CDCl_3$) 0.65 (t, $J_{B\text{-}F}$ = 32). NMR data matches that previously reported.[6]

1-Methyl-3,5,7-triethyl-2-ethylcarboxylato-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($6BF_2$)



Compound **$6BF_2$** was synthesized, from its corresponding free-base dipyrrin. Bright orange solid (49 mg, 85 %). δ_H (500 MHz, $CDCl_3$) 7.19 (s, 1H), 6.28 (s, 1H), 4.31 (q, J = 7.1, 2H), 3.00 (q, J = 7.6, 2H), 2.91 (q, J = 7.5, 2H), 2.79 (s, 3H), 2.69 (q, J = 7.5, 2H), 1.37 (t, J = 7.1, 3H), 1.32 (t, J = 7.6, 3H), 1.28 (t, J = 7.6, 3H), 1.21 (t, J = 7.5, 3H); δ_C (125 MHz, $CDCl_3$) 167.4, 164.6, 157.7, 151.2, 148.6, 134.6, 130.4, 121.2, 117.38, 117.35, 60.0, 22.4, 19.5, 19.4, 16.8, 14.8, 14.5, 12.6 (1C missing); δ_B (160 MHz, $CDCl_3$) 0.86 (t, $J_{B\text{-}F}$ = 32); LRMS-ESI (*m/z*): 385.2 $[M + Na]^+$; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{25}BF_2N_2NaO_2$ 385.1869; found 385.1855.

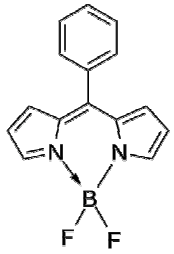
3-Ethyl-6-methylpropanocarboxylato-2,5,7-trimethyl-2-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($7BF_2$)



Using **GP1**, compound **$7BF_2$** was synthesized from the corresponding free-base dipyrrin.[4] Bright orange solid (47 mg, 81 %). δ_H (500 MHz, $CDCl_3$) 7.42 (s, 1H), 7.08 (s, 1H), 3.69 (t, J = 6.8, 2H), 2.66 (t, J = 6.8, 2H), 2.61 (q, J = 7.6, 2H), 2.53 (s, 3H), 2.23 (s, 3H), 2.04 (s, 6H), 1.17 (t, J = 7.6, 3H); δ_C (125 MHz, $CDCl_3$) 178.9, 158.9, 143.5, 141.0, 140.2,

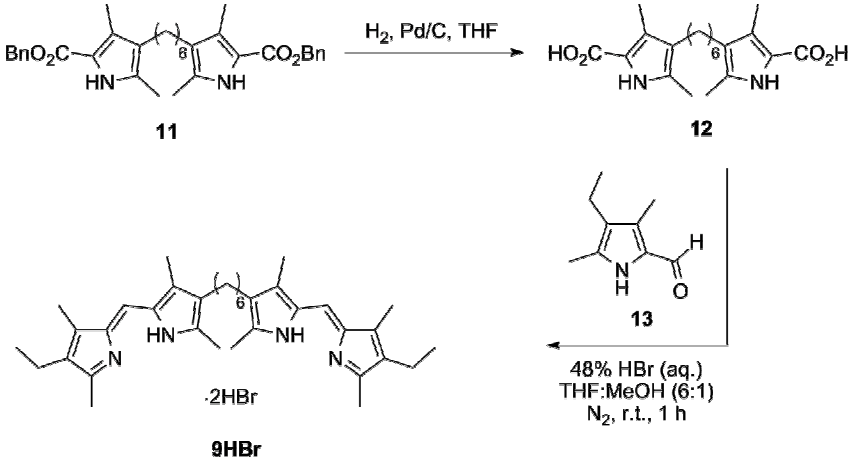
134.2, 132.02, 132.00, 125.3, 120.9, 62.2, 27.7, 18.1, 16.1, 13.2, 10.0, 9.9 (1C missing); δ_B (160 MHz, $CDCl_3$) 0.44 (t, $J_{B\text{-}F}$ = 32).

8-Phenyl-4-bora-3a,4a-diaza-*s*-indacene ($8BF_2$)



Using **GP1**, compound **$8BF_2$** was synthesized from the corresponding free-base dipyrrin.[5] Red-orange solid (37 mg, 60%). δ_H (500 MHz, $CDCl_3$) 7.93-7.97 (m, 2H), 7.51-7.60 (m, 5H), 6.94 (d, J = 3.6, 2H), 6.55 (d, J = 3.6, 2H); δ_C (125 MHz, $CDCl_3$) 147.3, 144.0, 134.9, 133.7, 131.6, 130.7, 130.4, 128.4, 118.5; δ_B (160 MHz, $CDCl_3$) 0.28 (t, $J_{B\text{-}F}$ = 29); NMR data matches that previously reported.[7]

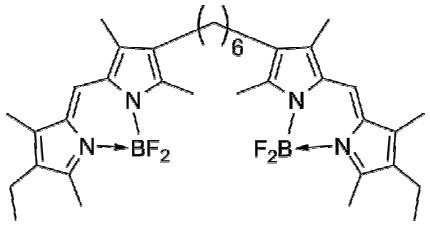
1,7-Bis(5-((*Z*)-(4-ethyl-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)hexane dihydrobromide (9HBr)



Dibenzyl 4,4'-(hexane-1,7-diyl)bis(3,5-dimethyl-1*H*-pyrrole-2-carboxylate) (**11**, 1.5 g, 2.8 mmol) was dissolved in THF (30 mL) and a drop of triethylamine. 10% Pd/C (300

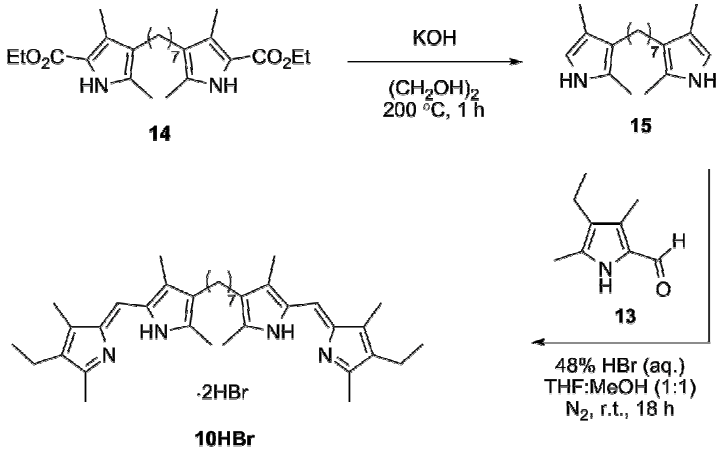
mg) was added to the solution, the flask was evacuated and refilled with H_2 (1 atm) and the reaction mixture then stirred overnight. The Pd/C was removed via filtration over Celite and another 300 mg of Pd/C was added to the solution. The flask was evacuated and refilled with H_2 (1 atm) once more and again stirred overnight. The Pd/C was removed via filtration over Celite and the solution was concentrated *in vacuo* to give **12** which was used in the next step without further purification. 2,4-Dimethyl-3-ethyl pyrrole-5-carboxaldehyde[8] (**13**, 848 mg, 5.61 mmol) was added to a solution of the preceeding bis(pyrrole) **12** in methanol:THF (1:6, 35 mL) and the solution was degassed by bubbling with nitrogen for 10 minutes. 48% aq. HBr (1 mL, 12 mmol) was then added dropwise, over 5 minutes, and the reaction mixture was stirred at room temperature under nitrogen for 1 hour. The reaction mixture was then concentrated *in vacuo* until little solvent remained. Diethyl ether was then added until a copious precipitate was evident. The precipitate was collected using filtration, dissolved in dichloromethane and the solution dried over Na_2SO_4. The solution was then concentrated *in vacuo* to give **9HBr** as a bright orange solid (1.67 g, 92% over 2 steps). δ_H (500 MHz, $CDCl_3$) 9.22 (s, 2H), 6.64 (s, 2H), 2.37 (q, J = 7.5, 4H), 2.32 (t, J = 8, 4H), 2.31 (s, 6H), 2.29 (s, 6H), 2.14 (s, 6H), 2.12 (s, 6H), 1.44-1.41 (m, 4H), 1.34-1.31 (m, 4H), 1.06 (t, J = 7.5, 6H); δ_C (125 MHz, $CDCl_3$) 151.5, 151.4, 136.8, 136.6, 133.8, 133.5, 130.1, 128.4, 115.4, 30.5, 29.5, 24.6, 17.9, 15.0, 14.6, 14.5, 9.8, 9.6; LRMS-ESI (*m/z*): 539.4 $[M + Na]^+$; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{36}H_{51}N_4$ 539.4108; found 539.4099.

1,7-Bis(1,3,5,7-tetramethyl-2-ethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene)hexane ($9BF_2$)



Compound **$9BF_2$** was synthesized, from its corresponding free-base dipyrrin, and purified using **GP1** to give a bright red solid (32 mg, 54 %). δ_H (500 MHz, $CDCl_3$) 6.94 (s, 2H), 2.49 (s, 6H), 2.47 (s, 6H), 2.36 (q, J = 7.3, 8H), 2.16 (s, 6H), 2.14 (s, 6H), 1.40 (m, 8H), 1.06 (t, J = 7.6, 6H); δ_C (125 MHz, $CDCl_3$) 154.9, 154.8, 137.1, 136.8, 132.5, 131.8, 130.2, 128.9, 118.7, 30.3, 29.5, 24.2, 17.4, 14.7, 12.8, 12.7, 9.7, 9.5; δ_B (160 MHz, $CDCl_3$) 0.86 (t, $J_{B\text{-}F}$ = 32); LRMS-ESI (*m/z*): 657.4 $[M + Na]^+$; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{36}H_{48}B_2F_4N_4Na$ 657.3983; found 657.3884.

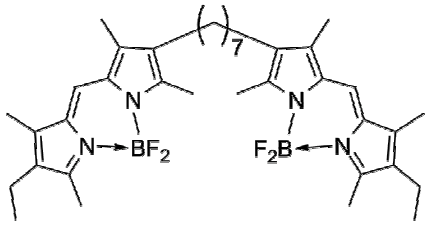
1,7-Bis(5-((Z)-(4-ethyl-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)heptane dihydrobromide (10HBr)



Diethyl 4,4'-(heptane-1,7-diyl)bis(3,5-dimethyl-1H-pyrrole-2-carboxylate)[9] (**14**, 410 mg, 0.952 mmol) was added to a suspension of potassium hydroxide (481 mg, 8.57 mmol) in ethylene glycol (10 mL) and the reaction mixture was heated at 200 °C, by means of a

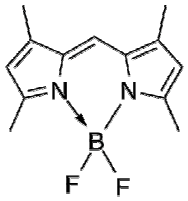
sand bath, for one hour.[8] After cooling to room temperature, the reaction mixture was separated between ethyl acetate (30 mL) and water (30 mL). The aqueous phase was extracted with ethyl acetate (3 x 20 mL) and combined organic extracts were washed with water (50 mL) and brine (50 mL), dried over anhydrous magnesium sulfate and concentrated *in vacuo* to give 1,7-bis(2,4-dimethyl-1H-pyrrol-3-yl)heptane (**15**), which was used in the next step without further purification. 2,4-Dimethyl-3-ethyl pyrrole-5-carboxaldehyde[8] (**13**, 288 mg, 1.90 mmol) was added to a solution of the preceding bis(pyrrole) **15** in methanol:THF (1:1, 12 mL) and the solution was degassed by bubbling with nitrogen for 10 minutes.[10,11] 48% aq. HBr (0.4 mL, 4.60 mmol) was then added drop-wise, over 5 minutes, and the reaction mixture was stirred at room temperature under nitrogen for 18 hours. The reaction mixture was then concentrated *in vacuo* until little solvent remained. Diethyl ether was then added until a copious precipitate was evident. The precipitate was collected using filtration, washed with 10% ethyl acetate in hexanes (10 mL) followed by diethyl ether (10 mL), and then dried using a vacuum oven to give the title compound (**10HBr**) as a brown solid (454 mg, 67% over 2 steps). δ_H (500 MHz, $CDCl_3$) 12.89 (brs, 4H), 7.03 (s, 2H), 2.66 (s, 6H), 2.64 (s, 6H), 2.44-2.37 (m, 8H), 2.26 (s, 6H), 2.25 (s, 6H), 1.45-1.39 (m, 4H), 1.31-1.25 (m, 6H), 1.07 (t, J = 7.5, 6H); δ_C (125 MHz, $CDCl_3$) 153.9, 153.8, 141.6, 141.4, 130.7, 129.0, 126.2, 126.1, 118.7, 30.0, 29.5, 29.4, 24.0, 17.3, 14.6, 13.1, 12.9, 10.3, 10.1; LRMS-ESI (*m/z*): 553.3 $[M + H]^+$; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{37}H_{54}N_4$ 277.2169; found 277.2161.

1,7-Bis(1,3,5,7-tetramethyl-2-ethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene)heptane ($10BF_2$)

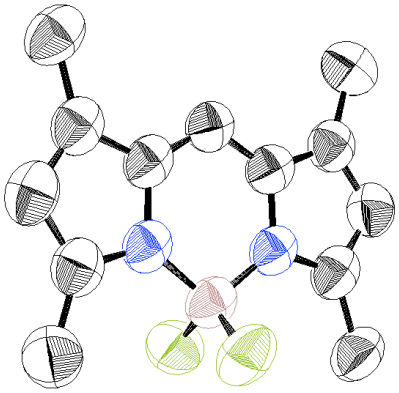


Using **GP1**, compound $\mathbf{10BF_2}$ was synthesized from corresponding free-base dipyrrin. Red solid (26 mg, 45 %). δ_H (500 MHz, $CDCl_3$) 6.94 (s, 2H), 2.49 (s, 6H), 2.47 (s, 6H), 2.36 (td, J = 7.3, 15.4, 8H), 2.15 (s, 6H), 2.14 (s, 6H), 1.44-1.39 (m, 4H), 1.32-1.23 (m, 6H), 1.05 (t, J = 7.6, 6H); δ_C (125 MHz, $CDCl_3$) 155.0, 154.7, 137.1, 136.8, 132.5, 131.7, 130.3, 128.3, 118.7, 30.3, 29.6, 29.5, 24.2, 17.4, 14.7, 12.8, 12.7, 9.7, 9.5; δ_B (160 MHz, $CDCl_3$) 0.89 (t, $J_{B\text{-}F}$ = 33); LRMS-ESI (*m/z*): 671.4 $[M + Na]^+$; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{37}H_{50}B_2F_4N_4Na$ 671.4050; found 671.4047.

1,3,5,7-Tetramethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($4BF_2$)



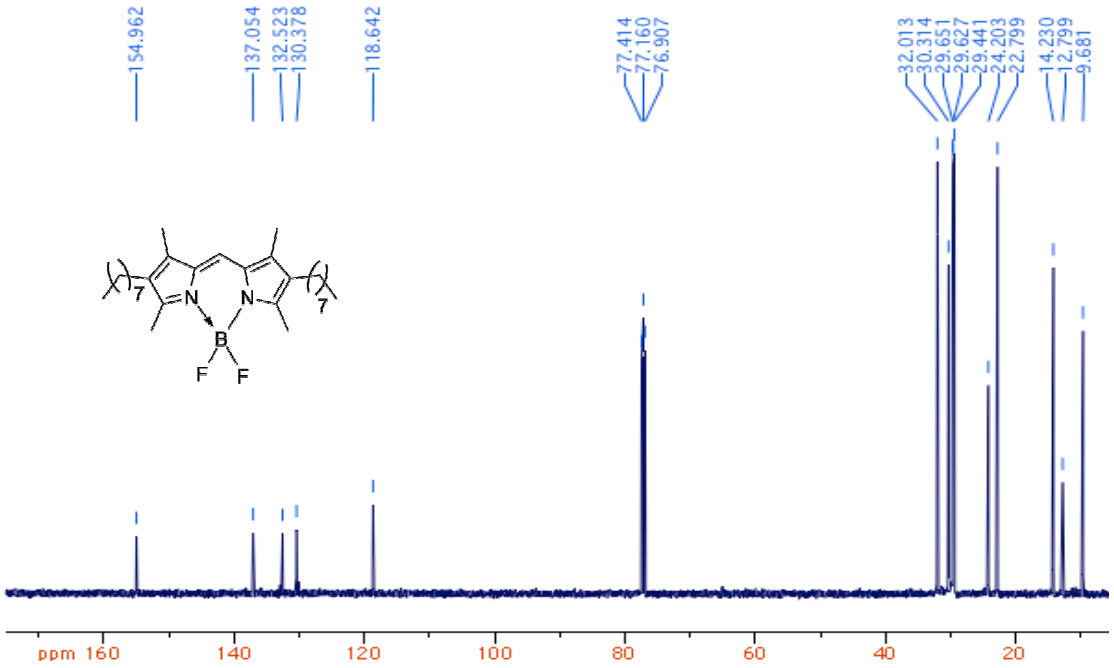
Compound $\mathbf{4BF_2}$ was obtained as a by-product in the formation of $\mathbf{2BF_2}$ using the traditional method involving excess BF_3•OEt_2 and NEt_3. δ_H (500 MHz, $CDCl_3$) 7.04 (s, 1H), 6.05 (s, 2H), 2.53 (s, 6H), 2.25 (s, 6H); δ_C (125 MHz, $CDCl_3$) 156.9, 141.3, 133.5, 120.2, 119.2, 14.8, 11.4; δ_B (160 MHz, $CDCl_3$) 0.76 (t, $J_{B\text{-}F}$ = 32). NMR data matches that previously reported.[6]



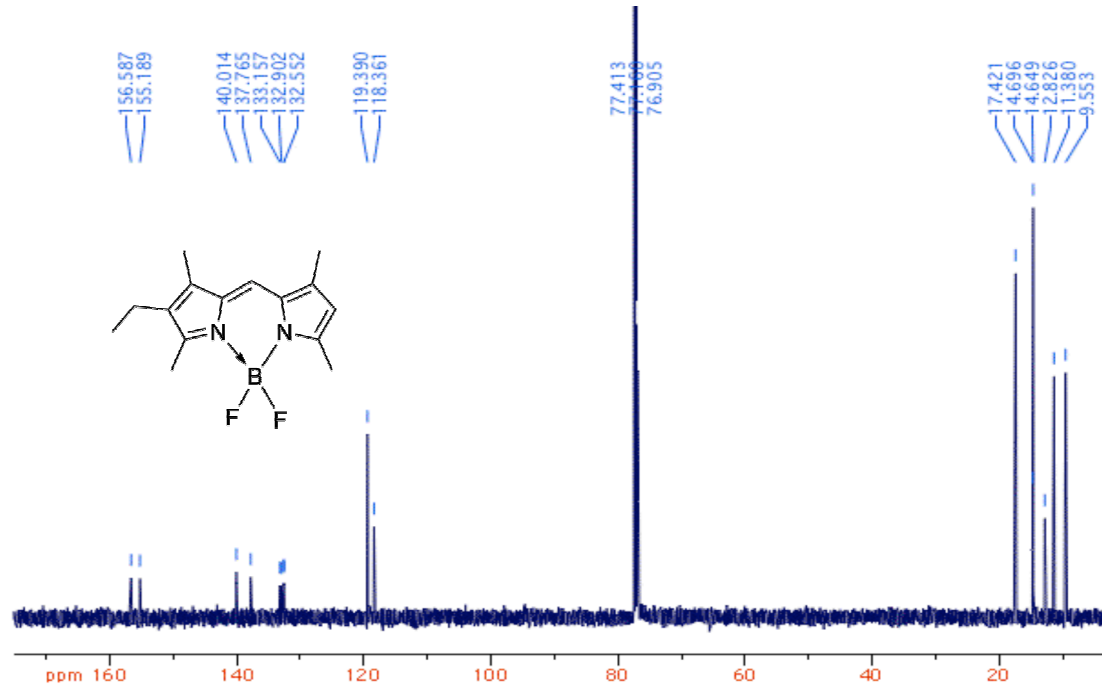
Crystal data for compound **4BF$_2$**: $C_{13}H_{15}BF_2N_2$, MM = 248.08 g/mol, colourless needle crystal 0.29 x 0.22 x 0.12 mm; monoclinic, space group $P2_{1/c}$ (#14), a = 11.700(6) Å, b = 14.423(2) Å, c = 11.934(3) Å, V = 1255.3(7) Å^3, Z = 4, ρ = 1.313 g/cm^3, μ(MoKα) = 1.54178 cm^{-1}, 2075 reflections (1162 unique, R_{int} = 0.067), R = 0.0554, R_w = 0.2073, GOF = 1.035.

1.4 NMR Spectra

1,3,5,7-Tetramethyl-2-octyl-8-*H*-4,4'-dichloro-bora-3a,4a-diaza-*s*-indacene ($1BF_2$)
^{13}C NMR Spectrum in $CDCl_3$

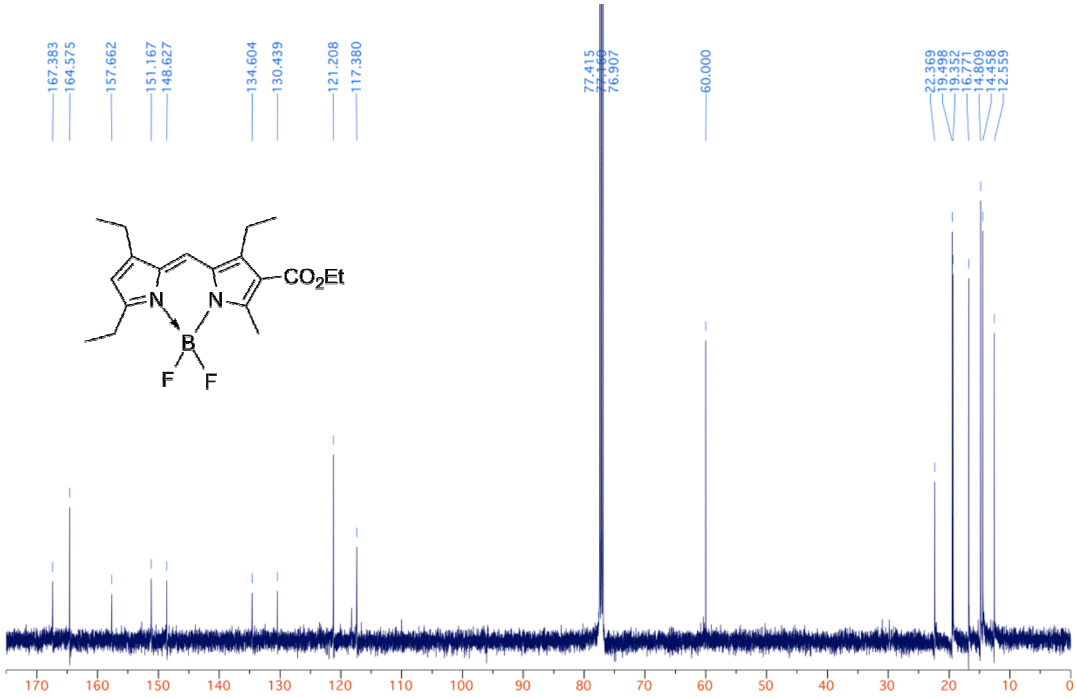


1,3,5,7-Tetramethyl-2-ethyl-8-*H*-4,4'-dichloro-bora-3a,4a-diaza-*s*-indacene ($2BF_2$)
^{13}C NMR Spectrum in $CDCl_3$



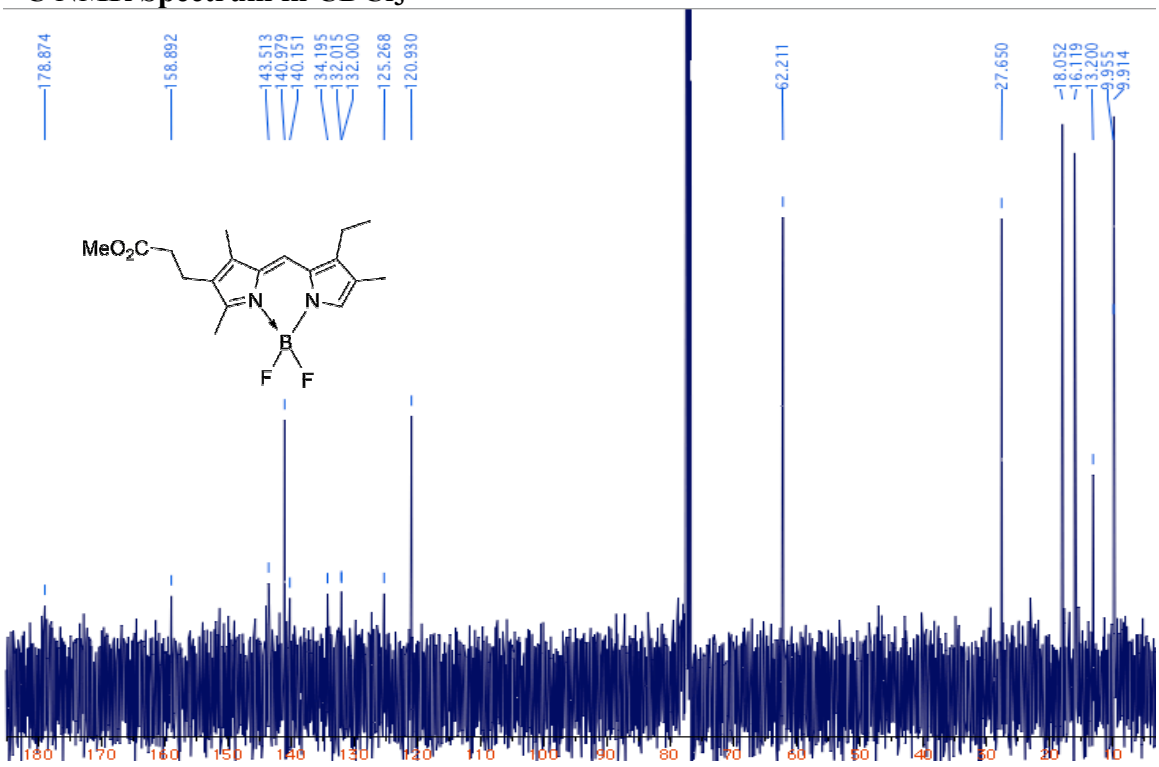
3-Methyl-1,5,7-triethyl-2-ethylcarboxylato-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($6BF_2$)

^{13}C NMR Spectrum in $CDCl_3$



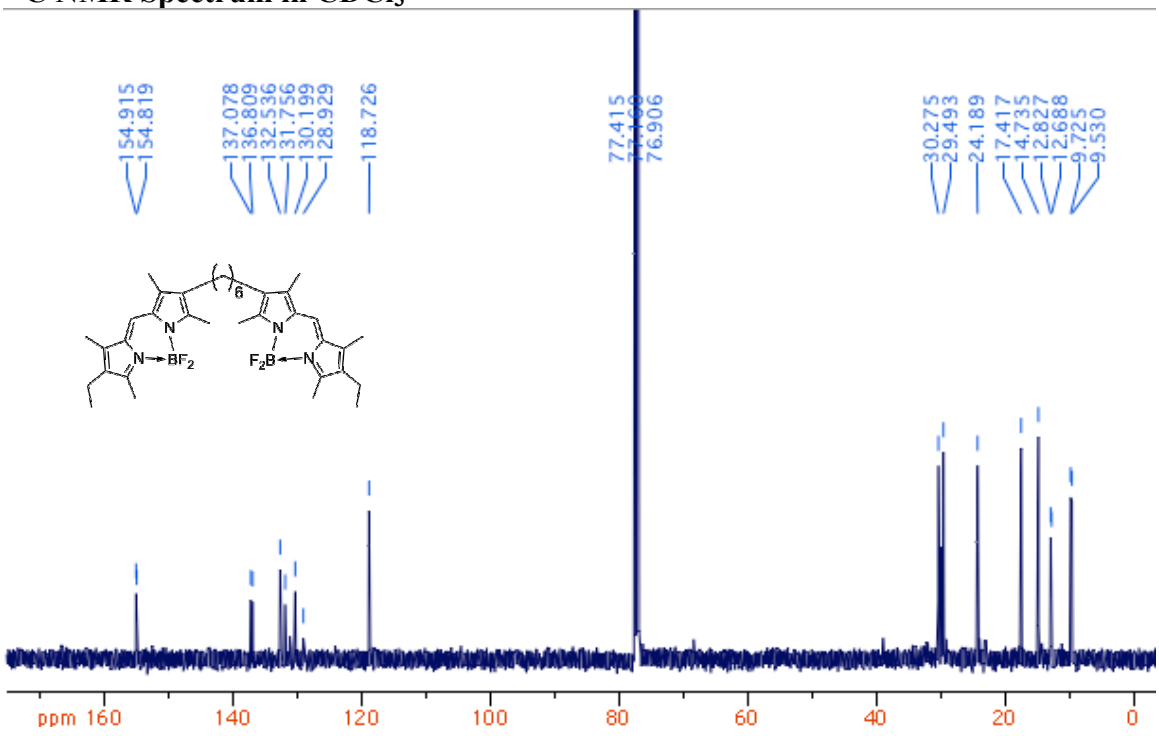
1,3,6-Trimethyl-7-ethyl-2-8-*H*-4-bora-3a,4a-diaza-*s*-indacene ($7BF_2$)

^{13}C NMR Spectrum in $CDCl_3$



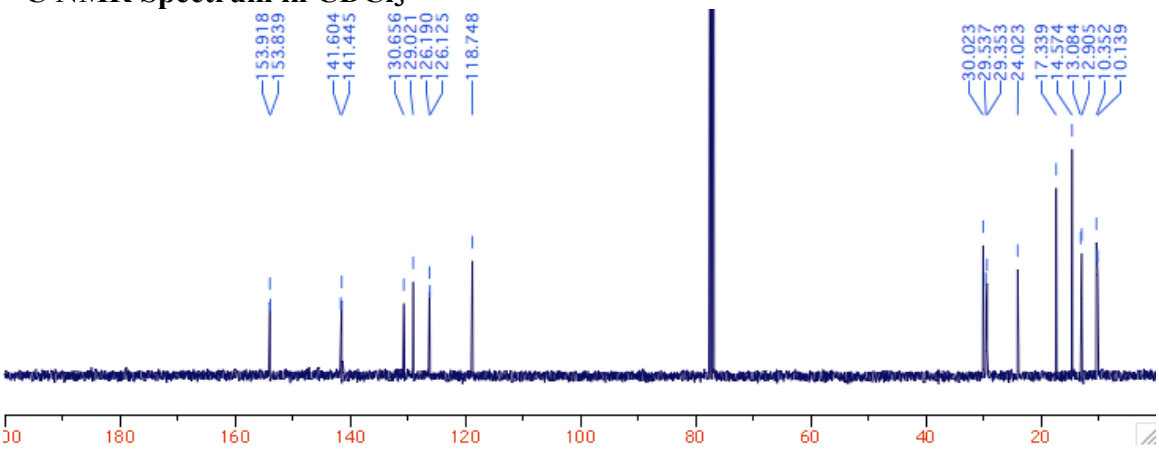
1,7-Bis(1,3,5,7-tetramethyl-2-ethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene)hexane ($9BF_2$)

^{13}C NMR Spectrum in $CDCl_3$



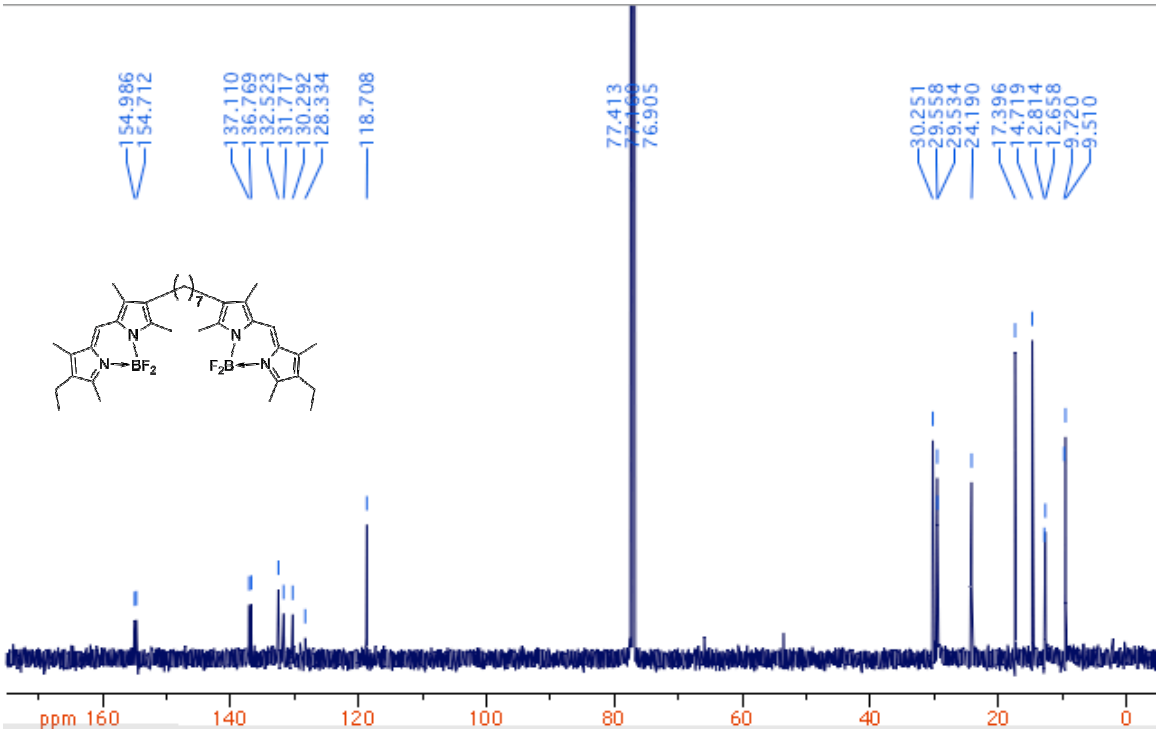
1,7-Bis(5-((Z)-(4-ethyl-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)heptane dihydrobromide (10HBr)

^{13}C NMR Spectrum in $CDCl_3$



1,7-Bis(1,3,5,7-tetramethyl-2-ethyl-8-*H*-4-bora-3a,4a-diaza-*s*-indacene)heptane ($10BF_2$)

^{13}C NMR Spectrum in $CDCl_3$



1.4 References

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