Synthesis of 2-aminoBODIPYs by palladium catalysed amination

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Materials

(3,5-Dimethyl-1H-pyrrol-2-yl)(p-tolyl)methanone 4. Zinc oxide (0.30 g, 3.72 mmol) was taken in a flame-dried Schlenk tube. 2,4-Dimethyl pyrrole (1.00 g, 14.9 mmol) and p-toluoyl chloride (2.30 g, 14.9 mmol) were then added and the mixture was stirred at room temperature for 5 minutes. The solid crude was dissolved in CH₂Cl₂ (60 mL) and washed with an aqueous solution of sodium bicarbonate (100 mL × 2). The aqueous layer was back extracted with CH₂Cl₂ (2 × 30 mL). The combined organic layers were dried (MgSO₄) and the solvent was removed under pressure. The resulting orange crude product was purified by column chromatography (CH₂Cl₂) to give the title compound 4 as a sand coloured solid (1.75 g, 55%). The spectroscopic data obtained for this compound were consistent with those reported in the literature.⁵¹

Fluorescence titration

Separate solutions of triphosgene (20 µg mL⁻¹) and the BODIPY 6-ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-(2-aminophenyl)amino)-4-bora-3a,4a-diaza-s-indacene 9 (25 µg mL⁻¹) dissolved in MeCN containing Et₃N (3% v/v) were prepared by dilution. Aliquots of the triphosgene solution were added to a series of mixtures of 2 mL of the BODIPY solution and an additional volume of 3% (v/v) Et₃N in MeCN calculated such that the final total volume was 5 mL in each case and the final concentrations of the BODIPY = 21 µM and of triphosgene = 0, 0.40, 0.67, 1.21, 1.62, 2.02, 2.43, 2.70, 3.37 µM. The fluorescence emission spectrum (λex = 490 nm) was recorded directly after mixing. It was confirmed that the emission spectrum was unchanged after 60 min.

Figure S1. Overlay of the two independent molecules in the asymmetric unit of the X-ray structure of compound 6d.
Figure S2. Absorption spectra in terms of the molar absorption coefficient (ε) for 6a in the solvents indicated.
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
\(^1\text{H NMR (300 MHz, CDCl}_3\text{)}\)

\(^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}\)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{11}B$ NMR (96 MHz, CDCl$_3$)

$^{19}F$ NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{11}\text{B NMR (96 MHz, CDCl}_3\text{)}$

$^{19}\text{F NMR (282 MHz, CDCl}_3\text{)}$
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{11}$B NMR (96 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)