Supporting Information

Direct palladium-catalysed C–H arylation of BODIPY dyes at the 3- and 3,5-positions

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Experimental procedures and characterisation data

Chemicals were purchased from Acros Organics and Sigma Aldrich, and used as received. All reactions were carried out in flame dried glassware, but no special precautions were taken for the exclusion of moisture. Solvents were not dried prior to use, except o-xylene which was dried over molecular sieves. All reactions were carried out under a nitrogen atmosphere.

$^1$H and $^{13}$C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for $^1$H and 75 MHz for $^{13}$C. In the case of ambiguous assignments, spectra were run on a Bruker 400 or Bruker 600. $^1$H NMR spectra in CDCl$_3$ were referenced to tetramethylsilane (0.00 ppm) as an internal standard. $^{13}$C NMR spectra in CDCl$_3$ were referenced to the CDCl$_3$ (77.16 ppm) signal. Mass spectra were recorded on a Hewlett-Packard 5989A mass spectrometer (EI mode and CI mode). High-resolution mass data were obtained with a Kratos MS 50TC instrument. Melting points were taken on a Reichert Thermovar and are uncorrected.

The electronic absorption spectra and absorbances were measured at 20 °C on a Perkin-Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state excitation and emission spectra were recorded on a Spex Fluorolog instrument with temperature-controlled cell holder. Freshly prepared samples in 1 cm quartz cells were used to perform all UV–vis absorption and fluorescence measurements.

8-Arylated BODIPY dyes were prepared according to published literature procedures, through a water based dipyrromethane synthesis followed by oxidation and condensation.$^5$

Optimisation of reaction protocol

Table S1 Optimisation of the reaction protocol for the direct C–H arylation of 8-(2,6-dichlorophenyl)-BODIPY

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<th>Solvent</th>
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<th>Time</th>
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13 Pd(OAc)$_2$ PCy$_3$HBF$_4$ / CsOPIv toluene PhBr-d$_5$ 110 °C 24 h 69 23 6
14 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ $\alpha$-xylene PhBr-d$_5$ 110 °C 24 h 28 45 22
15 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ $\alpha$-xylene PhBr-d$_5$ 144 °C 24 h 22 41 26
16 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ 1,4-dioxane PhBr-d$_5$ 101 °C 24 h 56 30 9
17 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ DMF PhBr-d$_5$ 110 °C 3.5 h 20 0 0
18 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ DMF PhBr-d$_5$ 110 °C 24 h 0 0 0
19 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ toluene PhCl$^\dagger$ 110 °C 4 d 94 2 0
20 Pd(OAc)$_2$ PCy$_3$HBF$_4$ PivOH K$_2$CO$_3$ toluene PhF$^\dagger$ 110 °C 4 d 90 4 0

$^a$ Experimental condition: 5 mol% catalyst, 10 mol% ligand, 30 mol% additive, 3 eq base, 1.1 eq arylhalide, solvent (0.1 M solution). $^b$ R is 2,6-dichlorophenyl. $^c$ All yields were determined via NMR-spectroscopy using pentadeuterated phenylhalides to avoid overlapping peaks. $^d$ Highest yielding condition. $^e$ No deuterated phenylhalide was used.

General C–H arylation procedure

BODIPY 1 (one equivalent) was weighed together with K$_2$CO$_3$ (3 equivalents), Pd(OAc)$_2$ (5 mol%), PCy$_3$HBF$_4$ (10 mol%), pivalic acid (30 mol%, IUPAC name 2,2-dimethylpropanoic acid) and, if a solid, the bromoarene (1.1 equivalents). This was placed in a Schlenk flask with a magnetic stirring bar and dissolved in toluene (or $\alpha$-xylene) to form a 0.1 M solution. Next, the reaction vessel was thrice evacuated and backfilled with nitrogen. If the bromoarene (1.1 equivalents) was a liquid it was added next, using a syringe. This reaction mixture was heated to 110 °C for the indicated time. Upon completion, the reaction mixture was cooled to room temperature. Subsequently, the solution was poured in diethyl ether (100 ml), washed three times with water (100 ml), dried over MgSO$_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

3-Phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2a

The compound was prepared following the general procedure using 0.4 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in $\alpha$-xylene for 24 h. Bromobenzene was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH$_2$Cl$_2$; 2:1 v/v) providing the desired product 2a in 44% (73 mg) and the diarylated product 3a in 17% (34 mg) yield.

2a: Red crystals with a green lustre; Mp 278 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.06-7.95 (m, 2H), 7.85 (s, 1H), 7.56-7.39 (m, 6H), 6.75 (d, $J$ = 3.96 Hz), 6.68 (d, $J$ = 3.96 Hz), 6.62 (d, $J$ = 3.00 Hz), 6.49 (s, 1H) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 161.8, 143.4, 135.6, 135.0, 132.0, 131.8, 131.3, 131.1, 130.5, 129.8, 129.7, 129.6, 129.0, 128.5, 128.4, 128.1, 121.8, 118.6 ppm; MS (EI): 412; HRMS: Calculated for C$_{21}$H$_{13}$BCl$_2$F$_2$N$_2$: 412.05169, found 412.05171.

3a: Purple crystals with a copper lustre; Mp 140 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 7.96-7.86 (m, 4H), 7.54-7.37 (m, 9H), 6.66 (d, $J$ = 4.14 Hz), 6.61 (d, $J$ = 4.14 Hz) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 159.9, 135.8, 132.5, 132.2, 131.2, 129.9, 129.7, 129.7, 129.6,
129.2, 128.4, 128.3, 121.6 ppm; MS (EI): 488; HRMS: Calculated for C$_{27}$H$_{17}$BCl$_2$F$_2$N$_2$: 488.08299, found 488.08194.

3-\textit{p}-Anisyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2b

The compound was prepared following the general procedure using 0.4 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in toluene for 43 h. 4-Bromoanisole was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/diethyl ether; 2:1 v/v) providing the desired product 2b in 42% (74 mg) and the diarylated product 3b in 10% (21 mg) yield.

2b: Dark red crystals with a copper lustre; Mp 70 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.04 (d, 2H, $J = 8.85$ Hz), 7.80 (s, 1H), 7.52-7.37 (m, 3H), 7.02 (d, 2H, $J = 8.85$ Hz), 6.76-6.69 (m, 2H), 6.56 (s, 1H), 6.46 (s, 1H), 3.89 (s, 3H) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 162.1, 161.8, 141.9, 137.5, 135.7, 132.0, 131.8, 131.7, 131.7, 131.4, 131.2, 128.3, 126.8, 124.2, 121.9, 118.0, 114.2, 55.5 ppm; MS (EI): 442; HRMS: Calculated for C$_{22}$H$_{15}$BCl$_2$F$_2$N$_2$: 442.06226, found 442.06248.

3b: Purple crystals with a green lustre; Mp 63 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 7.93 (d, 4H, $J = 8.85$ Hz), 7.52-7.38 (m, 3H), 6.97 (d, 4H, $J = 8.85$ Hz), 6.60 (s, 4H), 3.86 (s, 6H) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 160.9, 159.1, 135.8, 132.2, 131.3, 131.3, 131.2, 130.9, 128.5, 128.2, 125.0, 120.9, 113.8, 55.3 ppm; MS (EI): 548; HRMS: Calculated for C$_{29}$H$_{21}$BCl$_2$F$_2$N$_2$O$_2$: 548.10412, found 548.10536.

3-Thien-3-yl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2d

The compound was prepared following the general procedure using 0.1 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in toluene for 27 h. 3-Bromoanisole was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH$_2$Cl$_2$; 2:1 v/v) providing the desired product 2d in 55% (23 mg) and the diarylated product 3d in 10% (5 mg) yield.

2d: Dark purple crystals with a green lustre; Mp 214 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.44 (d, 1H, $J = 1.53$ Hz), 7.84 (s, 1H), 7.72 (d, 1H, $J = 4.71$ Hz), 7.53-7.35 (m, 4H), 6.80 (d, 1H, $J = 4.32$ Hz), 6.72 (d, 1H, $J = 4.32$ Hz), 6.58 (d, 1H, $J = 3.39$ Hz), 6.49 (s, 1H) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 155.7, 142.4, 137.2, 135.6, 133.6, 132.1, 131.9, 131.3, 131.2,
130.6, 130.5, 128.9, 128.4, 127.1, 125.9, 121.8, 118.3 ppm; MS (EI): 418; HRMS: Calculated for C_{19}H_{11}BCl_{2}F_{2}N_{2}: 418.00811, found 418.00869.

3d: Blue solid; Mp 205 °C; ¹H-NMR (CDCl₃, 300 MHz): δ 8.37 (s, 2H), 7.69 (d, 2H, J = 4.71 Hz), 7.52-7.33 (m, 5H), 6.75 (d, 2H, J = 3.78 Hz), 6.59 (d, 2H, J = 3.78 Hz) ppm; ¹³C-NMR (CDCl₃, 75 MHz): δ 153.2, 136.0, 135.9, 132.7, 131.1, 129.3, 129.2, 129.0, 128.6, 128.3, 125.6, 121.1 ppm; MS (EI): 500; HRMS: Calculated for C_{23}H_{13}BCl_{2}F_{2}N_{2}: 499.99583, found 499.99666.

3-Mesityl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2e

![Chemical Structure of 3-Mesityl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2e]

The compound was prepared following the general procedure using 0.1 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in toluene for 43 h. 2-Bromo-1,3,5-trimethylbenzene was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH₂Cl₂; 1:1 v/v) providing the desired product 2e in 35% (16 mg) yield. Orange solid with a green lustre; Mp 152 °C; ¹H-NMR (CDCl₃, 300 MHz): δ 7.72 (s, 1H), 7.55-7.39 (m, 3H), 6.96 (s, 2H), 6.79 (d, 1H, J = 4.14 Hz), 6.62 (d, 1H, J = 4.14 Hz), 6.44 (d, 1H, J = 3.75 Hz), 6.37 (d, 1H, J = 4.14 Hz), 2.34 (s, 3H), 2.17 (s, 6H) ppm; ¹³C-NMR (CDCl₃, 75 MHz): δ 162.3, 143.6, 139.2, 139.1, 137.4, 135.7, 135.5, 131.8, 131.3, 131.1, 130.8, 129.1, 129.0, 128.4, 127.8, 121.7, 118.4, 21.4, 20.1 ppm; MS (EI): 454 (M), 434 (M-HF); HRMS: Calculated for C_{24}H_{19}BCl_{2}F_{2}N_{2}: 454.09864, found 454.09852.

3-(1-Naphthyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2f

![Chemical Structure of 3-(1-Naphthyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2f]

The compound was prepared following the general procedure using 0.4 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in o-xylene for 24 h. 1-Bromonaphthalene was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH₂Cl₂; 2:1 v/v) providing the diarylated product 3f in 16% (37 mg) yield and impure 2f. Analytically pure 2f was obtained through HPLC purification (silica; toluene/CH₂Cl₂; 2:1 v/v), providing the desired product 2f in 20% (37 mg) yield. 

2f: Red crystals with a green lustre; Mp 282 °C; ¹H-NMR (CDCl₃, 300 MHz): δ 8.03-7.95 (m, 2H), 7.94-7.84 (m, 2H), 7.77 (s, 1H), 7.62 (t, 1H, J = 7.73 Hz), 7.55-7.43 (m, 5H), 6.83 (d, 1H, J = 4.14 Hz), 6.65 (m, 2H), 6.46 (d, 1H, J = 3.03 Hz) ppm; ¹³C-NMR (CDCl₃, 75 MHz): δ 160.1, 144.0, 139.3, 136.1, 135.6, 134.2, 133.6, 131.9, 131.8, 131.3, 130.3, 130.0,
129.8, 128.6, 128.4, 126.7, 126.2, 126.1, 125.0, 123.4, 118.8 ppm; MS (EI): 462; HRMS: Calculated for C\textsubscript{25}H\textsubscript{15}BCl\textsubscript{2}F\textsubscript{2}N\textsubscript{2}: 462.06734, found 462.06839.

3\textsubscript{f}: Purple solid with a copper lustre; Mp: decomposition at 310 °C; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta\) 7.91-7.77 (m, 8H), 7.60-7.54 (m, 2H), 7.52-7.37 (m, 7H), 6.79 (d, 2H, \(J = 3.21\) Hz), 6.59 (d, 2H, \(J = 3.39\) Hz) ppm; \textsuperscript{13}C-NMR: product is too insoluble to obtain a fully resolved spectrum; MS (EI): 588; HRMS: Calculated for C\textsubscript{35}H\textsubscript{21}BCl\textsubscript{2}F\textsubscript{2}N\textsubscript{2}: 588.11429, found 588.11553.

3,8-Diphenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2\textsubscript{i}

The compound was prepared following the general procedure using 0.2 mmol 8-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in o-xylene for 28 h. Bromobenzene was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH\textsubscript{2}Cl\textsubscript{2}; 2:1 v/v) providing the desired product 2\textsubscript{i} in 31% (21 mg) and the diarylated product 3\textsubscript{i} in 32% (27 mg) yield.

2\textsubscript{i}: Red solid with a green lustre; Mp 58 °C; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta\) 8.00-7.92 (m, 2H), 7.85 (s, 1H), 7.63-7.45 (m, 8H), 6.99 (d, 1H, \(J = 4.17\) Hz), 6.86 (d, 1H, \(J = 3.60\) Hz), 6.69 (d, 1H, \(J = 4.35\) Hz), 6.52 (d, 1H, \(J = 2.46\) Hz) ppm; \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 160.6, 145.8, 142.5, 137.3, 134.3, 132.9, 132.3, 130.7, 130.6, 130.1, 129.8, 129.6, 128.5, 125.9, 121.1, 118.2 ppm; MS (EI): 344; HRMS: Calculated for C\textsubscript{21}H\textsubscript{15}BF\textsubscript{2}N\textsubscript{2}: 344.12964, found 344.13011.

3\textsubscript{i}: Dark purple solid; Mp 191 °C; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta\) 7.91-7.83 (m, 4H), 7.63-7.50 (m, 5H), 7.47-7.37 (m, 6H), 6.90 (d, 2H, \(J = 4.35\) Hz), 6.63 (d, 2H, \(J = 4.17\) Hz) ppm; \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 75 MHz): \(\delta\) 159.0, 144.2, 136.5, 134.4, 132.7, 131.0, 130.7, 130.2, 129.6, 128.4, 128.3, 121.0 ppm (one carbon overlap); MS (EI): 420; HRMS: Calculated for C\textsubscript{27}H\textsubscript{19}BF\textsubscript{2}N\textsubscript{2}: 420.16094, found 420.16196.

3-Phenyl-8-(\(p\)-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2\textsubscript{j}

The compound was prepared following the general procedure using 0.2 mmol 8-(\(p\)-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in o-xylene for 46 h. Bromobenzene was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH\textsubscript{2}Cl\textsubscript{2}; 1:1 v/v) providing the desired product 2\textsubscript{j} in 28% (22 mg) and the diarylated product 3\textsubscript{j} in 18% (17 mg) yield.
2j: Purple crystals with a green lustre; Mp 193 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.41 (d, 2H, $J$ = 8.85 Hz), 8.00-7.93 (m, 2H), 7.79 (s, 1H), 7.77 (d, 2H, 8.67 Hz), 7.55-7.47 (m, 3H), 6.89 (d, 1H, $J$ = 4.53 Hz), 6.79-6.70 (m, 2H), 6.55 (d, 1H, $J$ = 3.21 Hz) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 149.1, 143.5, 140.4, 136.9, 133.7, 132.4, 131.8, 131.5, 130.6, 129.7, 129.6, 129.6, 129.2, 128.6, 123.8, 122.1, 118.9 ppm; MS (EI): 389; HRMS: Calculated for C$_{21}$H$_{14}$BF$_2$N$_3$O$_2$: 389.11471, found 389.11459.

3j: Dark purple solid; Mp 99 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.42 (d, 2H, $J$ = 8.67 Hz), 7.92-7.83 (m, 4H), 7.79 (d, 2H, $J$ = 8.46 Hz), 7.49-7.39 (m, 6H), 6.79 (d, 2H, $J$ = 4.14 Hz), 6.67 (d, 2H, $J$ = 3.96 Hz) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 160.3, 140.8, 136.0, 132.3, 131.6, 130.4, 130.1, 129.7, 129.6, 129.6, 128.5, 123.7, 121.8 ppm; MS (EI): 465; HRMS: Calculated for C$_{27}$H$_{18}$BF$_2$N$_3$O$_2$: 465.14601, found 465.14769.

3-Phenyl-5-thien-3-yl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 4

![Image](https://via.placeholder.com/150)

The compound was prepared following the general procedure using 0.2 mmol 3-phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2a in o-xylene for 48 h. 3-Bromothiophene was the bromoarene used. The crude product was purified via column chromatography (silica; petroleum ether/CH$_2$Cl$_2$; 3:1 v/v) providing the desired product in 62% (61 mg) yield. Dark purple solid; Mp 197 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.32 (s, 1H), 7.97 (d, 2H, $J$ = 6.03 Hz), 7.65 (d, 1H, $J$ = 4.71 Hz), 7.54-7.39 (m, 6H), 7.38-7.31 (m, 1H), 6.75 (d, 1H, $J$ = 3.93 Hz), 6.68-6.58 (m, 3H) ppm; $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 159.0, 154.0, 136.2, 135.9, 132.8, 132.4, 132.2, 131.1, 129.7, 129.4, 129.7, 129.0, 128.4, 128.3, 125.6, 121.4, 121.2 ppm; MS (EI): 494; HRMS: Calculated for C$_{25}$H$_{15}$BCl$_2$F$_2$N$_2$: 494.03941, found 494.04022.

1,4-Di(3-phenyl-5-yl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene)benzene 5

![Image](https://via.placeholder.com/150)
The compound was prepared following the general C–H arylation procedure using 0.36 mmol 3-phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2a in toluene for 53 h. 1,4-Dibromobenzene (0.15 mmol, 0.42 equivalents) was used as bromoarene. The crude product was purified via column chromatography (silica; petroleum ether/diethyl ether; 1:1 v/v) providing the desired product 5 in 23% (31 mg) yield. Dark crystals; Mp: decomposition at 290 °C; $^1$H-NMR (CDCl$_3$, 300 MHz): δ 8.02 (s, 4H), 7.93 (d, 4H, $J = 5.85$ Hz), 7.55-7.38 (m, 12 H), 6.71 (s, 2H), 6.67 (s, 4H), 6.63 (s, 2H) ppm; $^{13}$C-NMR (CDCl$_3$, 150 MHz): δ 160.2, 158.9, 137.1, 136.5, 136.3, 135.9, 133.4, 132.5, 132.1, 131.2, 129.9, 129.7, 129.2, 129.2, 128.4, 128.3, 121.9, 121.7 ppm (two carbons overlap); MS (ESI): 923 (M$^+$ + Na$^+$), 1823 (M$^+$ + M$^+$ + Na$^+$).
NMR-spectra of new compounds

2a, $^1$H, 300 MHz, CDCl$_3$

$^1$C, 75 MHz, CDCl$_3$
3a, $^1$H, 300 MHz, CDCl$_3$

3a, $^{13}$C, 75 MHz, CDCl$_3$
2b, $^1$H, 300 MHz, CDCl$_3$

2b, $^{13}$C, 75 MHz, CDCl$_3$
3b, $^1$H, 300 MHz, CDCl$_3$

3b, $^{13}$C, 75 MHz, CDCl$_3$
2d, $^1$H, 300 MHz, CDCl$_3$

2d, $^{13}$C, 75 MHz, CDCl$_3$
3d, $^1$H, 300 MHz, CDCl$_3$

3d, $^{13}$C, 75 MHz, CDCl$_3$
2e, $^1$H, 300 MHz, CDCl$_3$

$^13$C, 75 MHz, CDCl$_3$
$2f$, $^1$H, 300 MHz, CDCl$_3$
$3f$, $^1H$, 300 MHz, CDCl$_3$
2i, $^1$H, 300 MHz, CDCl$_3$

2i, $^{13}$C, 100 MHz, CDCl$_3$
3i, $^1$H, 300 MHz, CDCl$_3$

3i, $^{13}$C, 75 MHz, CDCl$_3$
2j, $^1$H, 300 MHz, CDCl$_3$

2j, $^{13}$C, 75 MHz, CDCl$_3$
3j, $^1$H, 300 MHz, CDCl$_3$

\[
\begin{array}{cccccccccccc}
\end{array}
\]

3j, $^{13}$C, 75 MHz, CDCl$_3$

\[
\begin{array}{ccccccccccccccc}
\text{Integral} & 160.2650 & 140.8352 & 135.9986 & 132.3476 & 131.5584 & 130.4202 & 130.0566 & 129.6711 & 129.6166 & 129.5656 & 128.4820 & 123.7072 & 121.8417
\end{array}
\]
**4. **$^1$H, 300 MHz, CDCl$_3$

![NMR spectrum 1H](image)

**4. **$^{13}$C, 75 MHz, CDCl$_3$

![NMR spectrum 13C](image)
5, $^1$H, 300 MHz, CDCl$_3$

$^1$H NMR spectrum of compound 5 in CDCl$_3$.

5, $^{13}$C, 150 MHz, CDCl$_3$

$^{13}$C NMR spectrum of compound 5 in CDCl$_3$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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Spectroscopic data

Figure S1  (a) Normalized, visible absorption spectra of a selection of meso-(2,6-dichlorophenyl) substituted BODIPY dyes (1, 2d, 2f, 3d, 4) in THF. (b) Corresponding normalized fluorescence emission spectra. Note that merging figures (a) and (b) produces the ‘congested’ Figure 1.
Table S2  Spectroscopic and fluorescence quantum yield data of bis-BODIPY 5 as a function of solvent. The solvents are listed from top to bottom according to increasing refractive index $n$.

<table>
<thead>
<tr>
<th>Product</th>
<th>Solvent</th>
<th>$\lambda_{\text{abs (max)}}^a$ / nm</th>
<th>$\lambda_{\text{em (max)}}^b$ / nm</th>
<th>$\Delta \nu^c$ / cm$^{-1}$</th>
<th>$\Phi^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH</td>
<td>621</td>
<td>707</td>
<td>1959</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>612</td>
<td>707</td>
<td>2196</td>
<td>$^e$</td>
</tr>
<tr>
<td></td>
<td>Ethyl acetate</td>
<td>625</td>
<td>708</td>
<td>1876</td>
<td>$^e$</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>636</td>
<td>717</td>
<td>1776</td>
<td>0.524 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>638</td>
<td>718</td>
<td>1746</td>
<td>0.634 ± 0.004</td>
</tr>
</tbody>
</table>

$a$ Absorption maximum.

$b$ Fluorescence emission maximum.

$^c$ Stokes shift ($=1/\lambda_{\text{abs (max)}} - 1/\lambda_{\text{em (max)}}$).

$d$ Fluorescence quantum yield ± one standard uncertainty. $\Phi$ determined vs. cresyl violet in methanol ($\Phi_r = 0.55$) as reference.

$^e$ Not possible to obtain reliable $\Phi$ values due to very limited solubility in the solvents indicated.