Supporting Information for

Copper-Catalyzed α–Benzylation of BODIPYs via Radical-Triggered Oxidative Cross-Coupling of Two C–H Bonds

Fan Lv, a Yang Yu, a Erhong Hao, a* Changjiang Yu, a Hua Wang, a Lijuan Jiao a* and Noël Boens b* 

a The Key Laboratory of Functional Molecular Solids, Ministry of Education; School of Chemistry and Materials Science, Anhui Normal University, Wuhu, China 241000. 
b Department of Chemistry, KU Leuven (Katholieke Universiteit Leuven), Celestijnenlaan 200f, 3001 Leuven, Belgium. 

* Correspondence authors. E-mail: jiao421@ahnu.edu.cn, haoehong@ahnu.edu.cn, Noel.Boens@kuleuven.be

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1. General information

Reagents and solvents were used as received from commercial suppliers (Energy Chemicals, Shanghai, China) unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless stated otherwise and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). $^1$H and $^{13}$C NMR spectra were recorded on a 300 or 500 MHz NMR spectrometer at room temperature. Chemical shifts ($\delta$) are given in ppm relative to CDCl$_3$ (7.26 ppm for $^1$H and 77 ppm for $^{13}$C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI-TOF in positive mode.

UV-vis absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh FS5 spectrometers). All measurements were made at 25 ºC, using 5×10 mm cuvettes. Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various organic solvents with fluorescein ($\Phi_r = 0.90$ in 0.1 N NaOH aqueous solution).$^1$ Non-degassed, spectroscopic grade solvents and 10 mm optical path length quartz cuvettes were used. Dilute solutions (0.01 < $A(\lambda_{ex})$ < 0.05) were used to minimize the inner-filter effects. Quantum yields $\Phi_x$ were determined according to equation (S1):$^2$

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1 - 10^{-A_r(\lambda_{ex})}}{1 - 10^{-A_x(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2}$$

(S1)

where the subscripts $x$ and $r$ refer respectively to the BODIPY sample $x$ and reference (standard) fluorophore $r$ with known quantum yield $\Phi_r$ in a specific solvent; $F$ stands for the spectrally corrected, integrated fluorescence spectra; $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength $\lambda_{ex}$ and $n$ represents the refractive index of the solvent (in principle at the average emission wavelength).

Crystals of compounds 3p, 3r and 4f suitable for X-ray analysis were obtained via the slow diffusion of petroleum ether into their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using
grease. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART\textsuperscript{5} software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo K\(\alpha\) radiation (\(\lambda\)) at 0.71073 Å. Data reduction was performed using the SAINT software, which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-974 program and refined by least squares method on \(F^2\), SHELXL-97,\textsuperscript{7} incorporated in SHELXTL V5.10.\textsuperscript{8} CCDC-1588356 (3p), CCDC-1588396 (3r), CCDC-1588355 (4f), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre \textit{via} www.ccdc.cam.ac.uk/data_request/cif.
Figure S1. Chemical structure of BODIPYs 1a-h and toluene derivatives 2a-j.
3. Synthesis and characterization

General radical C–H monofunctionalization procedure: BODIPY 1a (1 equiv, 0.2 mmol), Cu(OAc)$_2$ (0.02 mmol, 10 mol%), the oxidant t-BuOOH (tert-butyl hydroperoxide (TBHP), 4 equiv, 0.8 mmol) were dissolved in solvent (4 mL). The reaction mixture was heated at 100 °C and stirred for the indicated time. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na$_2$SO$_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 100:1-50:1 v/v).

3a Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h, providing an orange solid (46 mg, 65%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.84 (s, 1H), 7.56-7.49 (m, 5H), 7.35-7.28 (m, 5H), 6.83 (d, $J = 7.4$ Hz, 2H), 6.81(d, $J = 4.3$ Hz, 1H), 6.15 (d, $J = 4.3$ Hz, 1H), 4.42 (s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.83, 145.70, 141.68, 137.50, 135.88, 134.41, 134.32, 133.09, 130.80, 130.77, 129.92, 129.61, 129.15, 128.74, 127.29, 120.53, 117.82, 35.74; HRMS calcd. for C$_{22}$H$_{17}$BF$_2$N$_2$, [M–F]$^+$: 339.1463, found: 339.1474.

3b Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2b (4 mL). This reaction was completed after 12 h, providing an orange solid (51 mg, 70%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.85 (s, 1H), 7.55-7.49 (m, 5H), 7.24-7.21 (m, 4H), 6.81 (d, $J = 3.8$ Hz, 2H), 6.51 (d, $J = 2.0$ Hz, 1H), 5.93 (d, $J = 4.3$ Hz, 1H), 4.43 (s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.46, 145.11, 141.24, 137.03, 135.88, 134.40, 133.32, 133.09, 130.80, 130.77, 129.52, 129.16, 128.27, 127.22, 126.19, 119.70, 117.36, 33.10, 19.34; HRMS calcd. for C$_{23}$H$_{19}$BF$_2$N$_2$, [M–F]$^+$: 353.1625, found: 353.1615.

3c Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2c (4 mL). This reaction was completed after 12 h, providing an oily compound (50 mg, 68%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ...
7.84 (s, 1H), 7.55-7.46 (m, 5H), 7.22 (d, J = 7.4 Hz, 1H), 7.15 (d, J = 10.8 Hz, 2H), 7.08 (d, J = 7.3 Hz, 1H), 6.81 (d, J = 3.9 Hz, 2H), 6.50 (d, J = 4.2 Hz, 1H), 6.15 (d, J = 4.3 Hz, 1H), 4.38 (s, 2H), 2.34 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 163.70, 145.14, 141.08, 138.35, 136.91, 135.44, 133.91, 132.62, 130.34, 130.28, 130.27, 130.23, 129.00, 128.56, 128.26, 127.58, 126.49, 120.18, 117.27, 35.22, 21.35; HRMS calcd. for C\(_{23}\)H\(_{19}\)BF\(_2\)N\(_2\), [M–F]+: 353.1625, found: 353.1618.

3d Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2d (4 mL). This reaction was completed after 12 h, providing an oily compound (51 mg, 69%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.83 (s, 1H), 7.55-7.49 (m, 5H), 7.22 (s, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 8.4 Hz, 1H), 6.79 (d, J = 4.1 Hz, 1H), 6.49 (d, J = 4.3 Hz, 1H), 6.15 (d, J = 4.4 Hz, 1H), 4.37 (s, 2H), 2.33 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 164.04, 145.11, 141.05, 136.41, 135.46, 133.92, 133.90, 132.64, 130.34, 130.27, 129.38, 129.34, 128.98, 128.44, 128.26, 120.13, 117.25, 34.96, 20.60; HRMS calcd. for C\(_{24}\)H\(_{21}\)BF\(_2\)N\(_2\), [M–F]+: 366.1813, 367.1776, found: 366.1810, 367.1752.

3e Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2e (4 mL). This reaction was completed after 12 h, providing an oily compound (50 mg, 65%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.84 (s, 1H), 7.52 (s, 5H), 6.96 (s, 2H), 6.90 (s, 1H), 6.81 (d, J = 3.0 Hz, 1H), 6.80 (s, 1H), 6.50 (s, 1H), 6.17 (d, J = 3.7 Hz, 1H), 4.34 (s, 2H), 2.30 (s, 6H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 162.06, 145.09, 140.98, 138.27, 136.90, 136.84, 135.50, 133.98, 132.69, 130.40, 130.31, 128.93, 128.53, 128.31, 127.34, 120.33, 117.25, 35.20, 21.28; HRMS calcd. for C\(_{23}\)H\(_{20}\)BBrF\(_2\)N\(_2\), [M–F]+: 432.0803, found: 432.0796.
3g Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2g (4 mL). This reaction was completed after 12 h, providing an oily compound (44 mg, 60%). 1H NMR (300 MHz, CDCl₃) δ 7.83 (s, 1H), 7.55-7.49 (m, 5H), 7.50 (d, J = 7.3 Hz, 2H), 7.36-7.23 (m, 3H), 6.85 (d, J = 4.3 Hz, 1H), 6.78 (d, J = 3.5 Hz, 1H), 6.49 (s, 1H), 6.36 (d, J = 4.4 Hz, 1H), 4.94 (q, J = 14.0 Hz, 1H), 1.74 (d, J = 7.1 Hz, 3H); 13C NMR (126 MHz, CDCl₃) δ 168.56, 145.19, 142.59, 140.90, 134.86, 133.94, 133.83, 132.87, 130.29, 130.21, 128.81, 128.54, 128.23, 127.56, 126.75, 118.38, 117.19, 38.10, 19.95; HRMS calcd. for C₂₃H₁₉BF₂N₂, [M–F]+: 353.1625, found: 353.1642.

3h Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1b (41 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h providing an orange solid (29 mg, 50%). 1H NMR (300 MHz, CDCl₃) δ 7.75 (s, 1H), 7.34-7.17 (m, 5H), 7.20 (d, J = 3.0 Hz, 1H), 7.18 (d, J = 3.0 Hz, 1H), 6.51 (s, 1H), 6.14 (d, J = 4.2 Hz, 1H), 4.37 (s, 2H), 2.56 (s, 3H); 13C NMR (126 MHz, CDCl₃) δ 162.58, 143.24, 140.44, 137.13, 135.92, 134.44, 129.42, 129.11, 128.64, 126.76, 125.51, 119.45, 116.69, 35.13, 15.66; HRMS calcd. for C₁₇H₁₅BF₂N₂, [M–F]+: 277.1307, found: 277.1323.

3i Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h, providing a green solid (51 mg, 64%). 1H NMR (300 MHz, CDCl₃) δ 7.81 (s, 1H), 7.36-7.29 (m, 5H), 6.93 (s, 2H), 6.57-6.55 (m, 2H), 6.42 (s, 1H), 6.05 (d, J = 4.1 Hz, 1H), 4.41 (s, 2H), 2.33 (s, 3H), 2.09 (s, 6H); 13C NMR (126 MHz, CDCl₃) δ 163.43, 145.29, 141.21, 138.55, 136.91, 136.41, 135.84, 134.19, 131.15, 129.78, 129.55, 128.68, 128.03, 127.69, 126.83, 119.93, 117.29, 35.34, 21.04, 19.92; HRMS calcd. for C₂₅H₂₃BF₂N₂, [M–F]+: 381.1933, found: 381.1923.

3j Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2b (4 mL). This reaction was completed after 12 h, providing an oily compound (56 mg, 68%). 1H NMR (300 MHz, CDCl₃) δ 7.80 (s, 1H), 7.24-7.17 (m, 4H), 6.93 (s, 2H), 6.55 (s, 2H), 6.43 (s, 1H), 5.85 (d, J = 4.2 Hz, 1H), 4.42 (s, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 2.10 (s, 6H); 13C NMR (126 MHz, CDCl₃) δ 163.54, 145.20, 141.27, 138.62, 137.09, 136.47, 136.07, 135.36, 134.29, 131.17, 130.51, 130.45, 129.85, 128.10, 127.75, 127.28, 126.26, 119.69,

3k Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2h (4 mL). This reaction was completed after 12 h, providing a green solid (47 mg, 50%). ^1H NMR (300 MHz, CDCl_3) δ 7.82 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 6.8 Hz, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.93 (s, 2H), 6.57 (d, J = 3.6 Hz, 2H), 6.43 (s, 1H), 6.00 (d, J = 4.0 Hz, 1H), 4.59 (s, 2H), 2.35 (s, 3H), 2.11 (s, 6H); HRMS calcd. for C_{25}H_{22}BF_2N_2, [M–F]^+: 395.2089, found: 395.2091.

3l Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2e (4 mL). This reaction was completed after 12 h, providing a green solid (57 mg, 67%). ^1H NMR (300 MHz, CDCl_3) δ 7.80 (s, 1H), 6.98 (s, 2H), 6.92 (d, J = 5.1 Hz, 3H), 6.56 (d, J = 6.0 Hz, 2H), 6.42 (s, 1H), 6.07 (d, J = 4.0 Hz, 1H), 4.33 (s, 2H), 2.35 (s, 3H), 2.31 (s, 6H), 2.10 (s, 6H); ^13C NMR (126 MHz, CDCl_3) δ 164.11, 145.41, 141.55, 138.64, 136.90, 136.47, 135.94, 134.37, 133.04, 131.79, 131.17, 129.81, 128.76, 128.10, 128.00, 127.81, 124.94, 119.76, 117.50, 35.63, 21.12, 20.02; HRMS calcd. for C_{27}H_{27}BF_2N_2, [M–F]^+: 409.2246, found: 409.2242.

3m Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2i (4 mL). This reaction was completed after 12 h, providing a green solid (57 mg, 60%). ^1H NMR (500 MHz, CDCl_3) δ 7.77 (s, 1H), 7.34-7.31 (m, 4H), 7.27–7.23 (m, 6H), 6.93 (s, 2H), 6.62 (d, J = 4.3 Hz, 1H), 6.55 (d, J = 3.9 Hz, 1H), 6.39 (d, J = 2.2 Hz, 1H), 6.25 (d, J = 4.3 Hz, 1H), 6.23 (s, 1H), 2.35 (s, 3H), 2.10 (s, 6H); ^13C NMR (126 MHz, CDCl_3) δ 164.46, 145.94, 141.91, 141.43, 138.66, 136.51, 135.44, 134.45, 130.77, 129.86, 129.09, 128.55, 128.11, 126.89, 120.42, 120.40, 117.59, 50.32, 21.13, 20.10; HRMS calcd. for C_{31}H_{27}BF_2N_2, [M–F]^+: 457.2246, found: 457.2255.

3n Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2j (4 mL). This reaction was completed after 12 h, providing an oily compound (45 mg, 48%). ^1H NMR (300 MHz, CDCl_3) δ
8.02 (d, $J = 8.0$ Hz, 2H), 7.82 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 2H), 6.93 (s, 2H), 6.72 (s, 2H), 6.61 (d, $J = 4.3$ Hz, 1H), 6.39 (s, 1H), 6.45 (t, $J = 3.8$ Hz, 1H), 2.31 (s, 3H), 2.10 (s, 6H), 1.39 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.83, 162.10, 146.19, 142.61, 142.28, 139.09, 136.83, 136.21, 134.86, 131.52, 130.41, 130.13, 129.95, 129.65, 128.68, 128.51, 120.02, 118.07, 61.31, 35.69, 21.49, 20.37, 14.72; HRMS calcd. for C$_{28}$H$_{27}$BF$_2$N$_2$O$_2$, [M+H]$^+$: 473.2212, found: 473.2208.

3o Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1d (62 mg, 0.2 mmol) and 2b (6 mL). This reaction was completed after 12 h, providing a green solid (55 mg, 65%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.83 (s, 1H), 7.46-7.36 (m, 3H), 7.20 (s, 4H), 6.56 (s, 2H), 6.47 (s, 1H), 5.91 (d, $J = 3.9$ Hz, 1H), 4.43 (s, 2H), 2.30 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.13, 142.20, 138.39, 137.11, 135.65, 135.33, 135.07, 133.52, 131.51, 131.06, 130.94, 130.54, 130.47, 128.18, 127.43, 127.37, 126.30, 120.44, 117.80, 33.52, 19.59; HRMS calcd. for C$_{23}$H$_{17}$BF$_2$N$_2$, [M–F]$^+$: 421.0846, found: 421.0839.

3p Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1e (60 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h, providing a red solid (38 mg, 48%). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.38 (d, $J = 8.0$ Hz, 2H), 7.89 (s, 1H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.34 (s, 5H), 6.72 (s, 2H), 6.54 (s, 1H), 6.19 (s, 1H), 4.42 (s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.54, 149.33, 142.86, 142.08, 140.46, 137.01, 135.52, 133.82, 132.54, 131.59, 129.90, 129.25, 129.13, 127.48, 123.99, 121.53, 118.55, 35.84; HRMS calcd. for C$_{22}$H$_{16}$BF$_2$N$_3$O, [M–F]$^+$: 384.1314, found: 384.1334.

3q Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1f (60 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h providing an orange solid (49 mg, 64%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.49 (d, $J = 8.7$ Hz, 2H), 7.35-7.28 (m, 5H), 7.02 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 4.3$ Hz, 1H), 6.84 (d, $J = 3.8$ Hz, 1H), 6.51 (d, $J = 2.1$ Hz, 1H), 6.14 (d, $J = 4.3$ Hz, 1H), 4.41 (s, 2H), 3.89 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 162.63, 161.63, 145.30, 140.69, 137.20, 135.31, 133.91, 132.39, 132.13, 129.46, 128.93, 128.65, 126.76, 126.36, 119.77, 117.15, 113.86, 55.42, 35.23; HRMS calcd. for C$_{23}$H$_{19}$BF$_2$N$_2$O, [M–F]$^+$: 369.1569, found: 369.1563.
3r Prepared according to the general radical C–H monofunctionalization procedure using BODIPY 1g (50 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h, providing an orange solid (31 mg, 46%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.32-7.22 (m, 5H), 6.99 (d, $J$ = 3.8 Hz, 1H), 6.07 (d, $J$ = 3.8 Hz, 1H), 4.19 (s, 2H), 2.49 (s, 3H), 2.40 (q, $J$ = 7.5 Hz, 2H), 2.20 (s, 3H), 1.04 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, DMSO) $\delta$ 160.29, 156.15, 141.14, 139.05, 134.97, 134.34, 133.26, 129.86, 129.30, 128.44, 127.25, 125.39, 117.44, 34.82, 14.98, 13.57, 9.92; HRMS calcd. for C$_{31}$H$_{27}$BF$_2$N$_2$, [M+H]$^+$: 339.1844, found: 339.1838.

General radical C–H difunctionalization procedure: BODIPY 1a (1 equiv, 0.2 mmol), Cu(OAc)$_2$ (0.02 mmol, 10 mol%), the oxidant TBHP (6 equiv, 1.2 mmol) were dissolved in solvent (4 mL). The reaction mixture was heated at 100 °C and stirred for the indicated time. Upon completion, the reaction mixture was cooled to room temperature. Subsequently, the crude mixture was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na$_2$SO$_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 100:1-50:1 v/v).

4a Prepared according to the general radical C–H difunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2b (4 mL). This reaction was completed after 12 h, providing an orange solid (38 mg, 40%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52-7.46 (m, 2.5H), 7.26-7.19 (m, 4H), 6.67 (d, $J$ = 3.9 Hz, 1H), 5.86 (d, $J$ = 3.9 Hz, 1H), 4.45 (s, 2H), 2.31 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.61, 143.62, 137.08, 135.94, 135.79, 134.06, 133.75, 130.45, 130.38, 130.03, 128.54, 128.22, 127.13, 126.20, 118.58, 33.22, 19.54; HRMS calcd. for C$_{31}$H$_{27}$BF$_2$N$_2$, [M+H]$^+$: 477.2314, found: 477.2315.

4b Prepared according to the general radical C–H difunctionalization procedure using BODIPY 1a (54 mg, 0.2 mmol) and 2g (4 mL). This reaction was completed after 12 h, providing a green solid (37 mg, 32%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.46-7.44 (m, 5H), 7.36-7.20 (m, 2.5H), 6.69 (s, 1H), 6.26 (d, $J$ = 14.7 Hz, 1H), 4.96 (q, $J$ = 12.3 Hz,
$^{1}H$, 1.75 (d, $J = 7.1$ Hz, 3H); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 165.72, 143.78, 143.38, 134.10, 133.70, 130.52, 130.29, 129.88, 128.52, 128.14, 127.60, 126.61, 117.09, 38.30, 20.84; HRMS calcd. for C$_{31}$H$_{27}$BF$_2$N$_2$ [M–F]$^+$: 457.2282, found: 457.2285.

4c Prepared according to the general radical C–H difunctionalization procedure using BODIPY 1h (60 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h, providing an orange solid (34 mg, 36%). $^1H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.47–7.42 (m, 2H), 7.35–7.33 (m, 4H), 7.29–7.28 (m, 1H), 6.67 (d, $J = 4.2$ Hz, 1H), 6.09 (d, $J = 4.2$ Hz, 1H), 4.43 (s, 2H); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 160.98, 142.18, 137.55, 136.38, 134.26, 132.41, 131.52, 130.19, 129.47, 128.69, 128.62, 126.76, 119.16, 35.15. HRMS calcd. for C$_{29}$H$_{22}$BClF$_2$N$_2$ [M+H]$^+$: 483.1611 found: 483.1610.

4d Prepared according to the general radical C–H difunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2a (4 mL). This reaction was completed after 12 h, providing an orange solid (34 mg, 35%). $^1H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J = 6.7$ Hz, 1H), 6.91 (s, 1H), 6.45 (d, $J = 3.9$ Hz, 1H), 5.98 (d, $J = 4.0$ Hz, 1H), 4.43 (s, 2H), 2.33 (s, 1.5H), 2.10 (s, 3H); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 160.51, 143.69, 138.41, 137.59, 136.60, 134.73, 132.49, 129.97, 129.60, 129.05, 128.66, 128.02, 126.73, 118.73, 35.21, 21.10, 20.02; HRMS calcd. for C$_{32}$H$_{29}$BF$_2$N$_2$ [M+H]$^+$: 491.2470 found: 491.2458.

4e Prepared according to the general radical C–H difunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2b (4 mL). This reaction was completed after 12 h, providing an orange solid (39 mg, 38%). $^1H$ NMR (300 MHz, CDCl$_3$) $\delta$ 7.24–7.15 (m, 4H), 6.91 (s, 1H), 6.42 (d, $J = 4.1$ Hz, 1H), 5.78 (d, $J = 4.1$ Hz, 1H), 4.44 (s, 2H), 2.32 (s, 4.5H), 2.12 (s, 3H); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 162.05, 144.42, 141.96, 138.47, 136.70, 134.31, 130.05, 129.16, 128.90, 128.44, 128.04, 126.69, 119.57, 35.19, 21.12, 20.03, 19.59; HRMS calcd. for C$_{35}$H$_{34}$BF$_2$N$_2$ [M+H]$^+$: 519.2783 found: 519.2788.

4f Prepared according to the general radical C–H difunctionalization procedure using BODIPY 1c (60 mg, 0.2 mmol) and 2i (4 mL). This reaction was completed after 12 h, providing an orange solid (43 mg, 34%). $^1H$ NMR (300 MHz, CDCl$_3$) $\delta$ 7.32–7.22 (m, 10H), 6.91 (s, 1H), 6.51 (d, $J = 3.9$ Hz, 1H), 6.25 (s, 2H), 6.22 (d, $J = 3.4$ Hz, 1H), 2.33 (s, 1.5H), 2.10 (s, 3H); $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 162.05, 144.42, 141.96, 138.47, 136.70, 134.31, 130.05, 129.16, 128.90, 128.44, 128.04, 126.69, 119.57,
49.93, 21.11, 20.20; HRMS calcd. for C_{44}H_{37}BF_2N_2, [M–F]^+: 623.3028, found: 623.3026.

4g Prepared according to the general radical C–H difunctionalization procedure using 4 BODIPY 1d (62 mg, 0.2 mmol) and 2h (4 mL). This reaction was completed after 12 h, providing a red solid (36 mg, 35%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 – 7.42 (m, 1H), 7.38–7.34 (m, 0.5H), 7.25 (s,1H), 7.23 – 7.18 (m, 3H), 6.44 (d, $J$ = 4.2 Hz, 1H), 5.83 (d, $J$ = 4.2 Hz, 1H), 4.45 (s, 2H), 2.32 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.79, 144.96, 137.11, 136.78, 135.67, 135.50, 134.37, 131.70, 130.88, 130.46, 128.69, 128.11, 127.19, 126.22, 119.04, 33.31, 29.71, 19.61; HRMS calcd. for C_{31}H_{25}BCl_2F_2N_2, [M–F]^+: 525.1581, found: 525.1570.
4. Crystal data

Table S1. Selected Geometrical Parameters of 3p, 3r, and 4f obtained from crystallography

<table>
<thead>
<tr>
<th></th>
<th>3p</th>
<th>3r</th>
<th>4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-N bond distances (Å)</td>
<td>1.5455(24)</td>
<td>1.5514(24)</td>
<td>1.5525(24)</td>
</tr>
<tr>
<td></td>
<td>1.5613(26)</td>
<td>1.5437(22)</td>
<td>1.5524(27)</td>
</tr>
<tr>
<td>dihedral angles between dippyrin core and phenyl ring at 3- and/or 5- positions (deg)</td>
<td>72.960(64)</td>
<td>84.384(88)</td>
<td>87.373(83) (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80.386(61) (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>79.063(69) (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>79.894(54) (4)</td>
</tr>
<tr>
<td>dihedral angles between meso-mesityl group and dippyrin core (deg)</td>
<td>59.457(58)</td>
<td>/</td>
<td>77.573(39)</td>
</tr>
<tr>
<td>dihedral angles of two pyrrole rings in dippyrin core (deg)</td>
<td>4.200(71)</td>
<td>4.758(55)</td>
<td>4.514(81)</td>
</tr>
</tbody>
</table>
**Figure S2.** Crystal-packing pattern of BOPPY 3r between the adjacent interlayered crystals. Dihedral angle between the adjacent molecules is 0.0°. The interlayer distance is 3.67 Å
Figure S3. Crystal-packing pattern of BOPPY 4f between the adjacent interlayered crystals. Dihedral angle between the adjacent molecules is 46.5°.
5. Table S2: Spectroscopic and photophysical properties of BODIPYs in CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>dyes</th>
<th>$\lambda_{\text{abs}}^{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{abs}}^{\text{max}}$</th>
<th>$\lambda_{\text{em}}^{\text{max}}$ (nm)</th>
<th>$\Phi$</th>
<th>Stokes shift (cm$^{-1}$)</th>
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</thead>
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<tr>
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<td>49900</td>
<td>527</td>
<td>0.10</td>
<td>750</td>
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<tr>
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<td>506</td>
<td>44500</td>
<td>526</td>
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<td>750</td>
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<tr>
<td>3c</td>
<td>507</td>
<td>48400</td>
<td>525</td>
<td>0.10</td>
<td>680</td>
</tr>
<tr>
<td>3d</td>
<td>506</td>
<td>54900</td>
<td>523</td>
<td>0.10</td>
<td>640</td>
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<tr>
<td>3e</td>
<td>507</td>
<td>48900</td>
<td>525</td>
<td>0.10</td>
<td>680</td>
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<tr>
<td>3f</td>
<td>507</td>
<td>50800</td>
<td>517</td>
<td>0.11</td>
<td>380</td>
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<tr>
<td>3g</td>
<td>507</td>
<td>49400</td>
<td>527</td>
<td>0.11</td>
<td>750</td>
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<tr>
<td>3h</td>
<td>501</td>
<td>43200</td>
<td>514</td>
<td>0.71</td>
<td>510</td>
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<tr>
<td>3i</td>
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<td>546</td>
<td>0.01</td>
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<td>0.13</td>
<td>650</td>
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<td>534</td>
<td>0.55</td>
<td>620</td>
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<tr>
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<td>517</td>
<td>86400</td>
<td>535</td>
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<td>650</td>
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<td>518</td>
<td>68200</td>
<td>535</td>
<td>0.32</td>
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<tr>
<td>4d</td>
<td>516</td>
<td>60600</td>
<td>528</td>
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<td>4f</td>
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<td>96400</td>
<td>543</td>
<td>0.93</td>
<td>490</td>
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$^a$ Fluorescence quantum yield was calculated using fluorescein ($\Phi = 0.90$ in 0.1 N NaOH aqueous solution) as reference at room temperature. Standard uncertainties on $\Phi$ are less than 10%. $^b$ Standard uncertainties on $\varepsilon_{\text{abs}}^{\text{max}}$ are less than 1000 M$^{-1}$ cm$^{-1}$. $^c$ The Stokes shift values of are rounded to the nearest 10 cm$^{-1}$. 
6. UV-Vis absorption and fluorescence emission spectra in CH$_2$Cl$_2$.

Figure S4. Absorption (a) and fluorescence emission (b) spectra of 3a recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S5. Absorption (a) and fluorescence emission (b) spectra of 3b recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S6. Absorption (a) and fluorescence emission (b) spectra of 3c recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S7. Absorption (a) and fluorescence emission (b) spectra of 3d recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S8. Absorption (a) and fluorescence emission (b) spectra of 3e recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S9. Absorption (a) and fluorescence emission (b) spectra of 3f recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S10. Absorption (a) and fluorescence emission (b) spectra of 3g recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S11. Absorption (a) and fluorescence emission (b) spectra of 3h recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S12. Absorption (a) and fluorescence emission (b) spectra of 3i recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S13. Absorption (a) and fluorescence emission (b) spectra of 3j recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S14. Absorption (a) and fluorescence emission (b) spectra of 3k recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S15. Absorption (a) and fluorescence emission (b) spectra of 3l recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S16. Absorption (a) and fluorescence emission (b) spectra of 3m recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S17. Absorption (a) and fluorescence emission (b) spectra of 3n recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S18. Absorption (a) and fluorescence emission (b) spectra of 3o recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S19. Absorption (a) and fluorescence emission (b) spectra of 3p recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S20. Absorption (a) and fluorescence emission (b) spectra of 3q recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S21. Absorption (a) and fluorescence emission (b) spectra of 3r recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S22. Absorption (a) and fluorescence emission (b) spectra of 4a recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S23. Absorption (a) and fluorescence emission (b) spectra of 4b recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S24. Absorption (a) and fluorescence emission (b) spectra of 4c recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S25. Absorption (a) and fluorescence emission (b) spectra of 4d recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S26. Absorption (a) and fluorescence emission (b) spectra of 4e recorded in CH$_2$Cl$_2$ (excitation at 480 nm).

Figure S27. Absorption (a) and fluorescence emission (b) spectra of 4f recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
Figure S28. Absorption (a) and fluorescence emission (b) spectra of 4g recorded in CH$_2$Cl$_2$ (excitation at 480 nm).
7. Solid-state fluorescence of selected dyes

Absolute fluorescence quantum yields $\Phi$ of these dyes in powdered solid state were measured using Edinburgh FLS 920 fluorescence spectrometer with an integrating sphere according to the definition of fluorescence efficiency.

Table S3: Solid-state fluorescence emission maxima and fluorescence quantum yields $\Phi$ of selected BODIPYs in powdered solid state.

<table>
<thead>
<tr>
<th>dyes</th>
<th>3a</th>
<th>3b</th>
<th>3i</th>
<th>3m</th>
<th>3o</th>
<th>4a</th>
<th>4d</th>
<th>4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{em}}^{\text{max}}$ (nm)</td>
<td>626</td>
<td>602</td>
<td>628</td>
<td>610</td>
<td>625</td>
<td>648</td>
<td>600</td>
<td>622</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>0.12</td>
<td>0.10</td>
<td>0.11</td>
<td>0.17</td>
<td>0.14</td>
<td>0.13</td>
<td>0.12</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure S29. Photo of solid fluorescence of BODIPYs in powdered solid state under 365 nm handhold UV-light irradiation.

Figure S30. Normalized fluorescence emission spectra of selected BODIPYs in powdered solid state.
8. NMR-spectra of all new compounds

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

3a, $^{13}$C, 126 MHz, CDCl$_3$
$3b$, $^1$H, 300 MHz, CDCl$_3$

$3b$, $^{13}$C, 126 MHz, CDCl$_3$
$3c$, $^1H$, 300 MHz, CDCl$_3$

$3c$, $^{13}C$, 126 MHz, CDCl$_3$
$3d, ^1H, 300 MHz, CDCl_3$

$3d, ^{13}C, 126 MHz, CDCl_3$
$3e$, $^1H$, 300 MHz, CDCl$_3$

$3e$, $^{13}C$, 126 MHz, CDCl$_3$
$3f$, $^1$H, 300 MHz, CDCl$_3$

$3f$, $^{13}$C, 126 MHz, CDCl$_3$
$^{3}$g, $^1$H, 300 MHz, CDCl$_3$

$^{3}$g, $^{13}$C, 126 MHz, CDCl$_3$
$3h$, $^1H$, 300 MHz, CDCl$_3$
3i, $^1$H, 300 MHz, CDCl$_3$

3i, $^{13}$C, 126 MHz, CDCl$_3$
$3j$, $^1$H, 300 MHz, CDCl$_3$

$3j$, $^{13}$C, 126 MHz, CDCl$_3$
$3k$, $^1H$, 300 MHz, CDCl$_3$

$3k$, $^{13}C$, 126 MHz, CDCl$_3$
$^{31}$, $^1$H, 300 MHz, CDCl$_3$
3m, $^1$H, 300 MHz, CDCl$_3$
$3n, ^{1}H, 300 \text{ MHz, CDCl}_3$

$3n, ^{13}C, 126 \text{ MHz, CDCl}_3$
3o, \textsuperscript{1}H, 300 MHz, CDCl$_3$

![NMR spectrum of 3o, 1H, 300 MHz, CDCl$_3$](image1)

3o, \textsuperscript{13}C, 126 MHz, CDCl$_3$

![NMR spectrum of 3o, 13C, 126 MHz, CDCl$_3$](image2)
$3p, ^1H, 300\text{ MHz}, \text{CDCl}_3$

$3p, ^13C, 126\text{ MHz}, \text{CDCl}_3$
$3q$, $^1H$, 300 MHz, CDCl$_3$

$3q$, $^{13}C$, 126 MHz, CDCl$_3$
$3r$, $^1H$, 300 MHz, CDCl$_3$

$3r$, $^{13}C$, 126 MHz, DMSO
4a, $^1$H, 300 MHz, CDCl$_3$

4a, $^{13}$C, 126 MHz, CDCl$_3$
4b, $^1$H, 300 MHz, CDCl$_3$

4b, $^{13}$C, 126 MHz, CDCl$_3$
4c, $^1$H, 300 MHz, CDCl$_3$

4c, $^{13}$C, 126 MHz, CDCl$_3$
4d, $^1$H, 300 MHz, CDCl$_3$

4d, $^{13}$C, 126 MHz, CDCl$_3$
4e, $^1$H, 300 MHz, CDCl$_3$

4e, $^{13}$C, 126 MHz, CDCl$_3$
4f, $^1$H, 300 MHz, CDCl$_3$

4f, $^{13}$C, 126 MHz, CDCl$_3$
**4g, $^1$H, 300 MHz, CDCl$_3$**

![NMR spectrum](image)

**4g, $^{13}$C, 126 MHz, CDCl$_3$**

![NMR spectrum](image)
HRMS for 3a

HRMS for 3b
HRMS for 3c

![HRMS for 3c](image)

HRMS for 3d

![HRMS for 3d](image)
HRMS for 3i

HRMS for 3j
HRMS for 3n

[Graph showing mass spectra for 3m and 3n]
HRMS for 3o

HRMS for 3p
HRMS for 3q

HRMS for 3r
HRMS for 4a

HRMS for 4b
HRMS for 4e

HRMS for 4f
HRMS for $4^g$
References: