Supporting Information

Bu₄NI/ıBuOOH Catalyzed, α-Regioselective Cross-Dehydrogenative Coupling of BODIPY with Allylic Alkenes and Ethers

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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. Melting points reported were not corrected.

2. Synthesis and characterization

BODIPYs 2 were synthesized according to literature (Eur J. Org. Chem. 2011, 28, 5460).

**Figure S1.** Chemical structure of BODIPYs 2a-i, allylic alkenes and (poly)ethers.
General procedure for the synthesis of BODIPYs 1a-r

To BODIPY 2 (0.50 mmol) and Bu₄NI (0.10 mmol, 37 mg) in a Schlenk tube was added solvent (3.0 mL) and TBHP (70% aqueous solution, 0.36 mL, 2.5 mmol) via a syringe. The reaction mixture was stirred at 90 °C in an oil bath for 12 h. The organic solvent was removed under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1→9:1, v/v) as eluent to provide the corresponding product.

1a was obtained as orange oil in 63% yield (109 mg) from 2a (134 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 70-73 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.80 (s, 1H), 7.62-7.48 (m, 5H), 6.89 (d, J = 4.2 Hz, 1H), 6.78 (s, 1H), 6.48 (s, 1H), 6.45 (s, 1H), 5.93 (d, J = 9.7 Hz, 1H), 5.71 (d, J = 9.9 Hz, 1H), 4.18 (s, 1H), 2.29-2.22 (m, 1H), 2.12 (s, 2H), 1.87-1.67 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.9, 143.6, 139.5, 134.2, 132.8, 132.6, 131.7, 129.2, 129.1, 128.1, 127.5, 127.1, 125.7, 118.0, 115.9, 34.6, 28.4, 23.6, 19.8. HRMS calcd. for C₂₁H₁₉BF₂N₂ [M-F]⁺: 329.1620, found 329.1606.

1b was obtained as orange oil in 60% yield (113 mg) from 2b (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 75-77 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (s, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 4.4 Hz, 1H), 6.82 (d, J = 3.9 Hz, 1H), 6.49 (s, 1H), 6.44 (d, J = 4.4 Hz, 1H), 5.93 (d, J = 7.6 Hz, 1H), 5.72 (d, J = 10.1 Hz, 1H), 4.17 (s, 1H), 3.91 (s, 3H), 2.31-2.19 (m, 1H), 2.12 (s, 2H), 1.90-1.78 (m, 1H), 1.77-1.66 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 168.5, 161.7, 145.0, 140.3, 135.4, 133.9, 132.8, 132.3, 129.3, 128.6, 127.1, 126.1, 119.0, 117.0, 114.0, 55.6, 35.9, 29.6, 24.9, 21.1. HRMS calcd. for C₂₂H₂₁BF₂N₂O [M-F]⁺: 359.1725, found 359.1710.

1c was obtained as red oil in 54% yield (106 mg) from 2c (156 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 87-90 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, J = 8.6 Hz, 2H), 7.84 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 4.5 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 6.49 (d, J = 4.5 Hz, 1H), 5.95 (d, J = 7.6 Hz, 1H), 5.69 (d, J = 10.0 Hz, 1H), 4.17 (s, 1H), 2.35-2.19 (m, 1H), 2.13 (s, 2H), 1.87-1.78 (m, 1H), 1.77-1.66 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 171.3, 149.3,
142.2, 141.6, 140.6, 135.5, 133.6, 132.8, 131.6, 130.1, 128.6, 126.7, 124.0, 120.6, 118.2, 36.4, 29.7, 25.1, 21.3. HRMS calcd. for C_{21}H_{18}BF_{2}N_{3}O_{2} [M-F]^+: 374.1471, found 374.1463.

1d was obtained as yellow oil in 56% yield (116 mg) from 2d (168 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 72-74 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.78 (s, 1H), 7.55-7.43 (m, 2H), 7.42-7.37 (m, 1H), 6.64 (d, \(J = 4.5\) Hz, 1H), 6.54 (d, \(J = 3.9\) Hz, 1H), 6.44 (d, \(J = 2.3\) Hz, 1H), 6.41 (d, \(J = 4.4\) Hz, 1H), 5.94 (d, \(J = 7.6\) Hz, 1H), 5.73 (d, \(J = 10.0\) Hz, 1H), 4.17 (s, 1H), 2.31-2.24 (m, 1H), 2.11 (s, 2H), 1.90-1.77 (m, 1H), 1.76-1.68 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 171.1, 141.9, 138.4, 135.8, 133.6, 132.0, 131.6, 131.4, 130.0, 128.6, 127.2, 127.0, 120.3, 117.8, 36.4, 29.7, 25.2, 21.4. HRMS calcd. for C_{21}H_{17}BCl_{2}F_{2}N_{2} [M-F]^+: 397.0840, found 397.0828.

1e was obtained as yellow oil in 39% yield (76 mg) from 2e (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 90-93 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.80 (s, 1H), 7.40 (t, \(J = 8.1\) Hz, 1H), 7.13-7.06 (m, 3H), 6.93 (d, \(J = 4.0\) Hz, 1H), 6.81 (d, \(J = 2.7\) Hz, 1H), 5.93 (d, \(J = 7.8\) Hz, 1H), 5.71 (d, \(J = 10.0\) Hz, 1H), 4.17 (s, 1H), 3.86 (s, 3H), 2.31-2.25 (m, 1H), 2.12 (s, 2H), 1.90-1.78 (m, 1H), 1.78-1.67 (m, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 169.6, 159.7, 144.9, 141.1, 135.8, 135.7, 134.1, 133.6, 133.3, 129.7, 129.0, 127.3, 123.3, 119.6, 117.5, 116.3, 116.2, 55.83, 36.22, 29.82, 25.17, 21.35. HRMS calcd. for C_{22}H_{21}BF_{2}N_{2}O [M-F]^+: 359.1725, found 359.1719.

1f was obtained as yellow oil in 52% yield (94 mg) from 2f (141 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 76-78 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.78 (s, 1H), 7.44 (d, \(J = 7.8\) Hz, 2H), 7.31 (d, \(J = 7.8\) Hz, 2H), 6.91 (d, \(J = 3.9\) Hz, 1H), 6.79 (d, \(J = 2.8\) Hz, 1H), 6.47 (s, 1H), 6.43 (d, \(J = 4.2\) Hz, 1H), 5.92 (d, \(J = 8.1\) Hz, 1H), 5.71 (d, \(J = 10.0\) Hz, 1H), 4.17 (s, 1H), 2.46 (s, 3H), 2.33-2.23 (m, 1H), 2.11 (s, 2H), 1.85-1.76 (m, 1H), 1.76-1.68 (m, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 169.1, 145.5, 141.1, 140.8, 135.8, 134.2, 133.2, 131.7, 130.9, 129.6, 129.4, 128.9, 127.3, 119.4, 117.4, 36.2, 29.9, 25.2, 21.8, 21.4. HRMS calcd. for C_{22}H_{21}BF_{2}N_{2} [M-F]^+: 343.1782, found 343.1799.
**1g** was obtained as yellow oil in 43% yield (94 mg) from **2g** (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 121-123 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H), 7.73-7.29 (m, 5H), 6.86 (d, $J = 4.1$ Hz, 1H), 6.74 (d, $J = 3.0$ Hz, 1H), 6.48 (s, 1H), 6.45 (d, $J = 4.3$ Hz, 1H), 5.94 (d, $J = 8.4$ Hz, 1H), 5.70 (d, $J = 10.0$ Hz, 1H), 4.16 (s, 1H), 2.34-2.26 (m, 1H), 2.11 (s, 2H), 1.85-1.75 (m, 1H), 1.76-1.66 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.1, 143.6, 141.5, 137.0, 133.9, 132.9, 132.8, 131.9, 129.8, 129.1, 128.7, 127.1, 125.8, 119.9, 117.7, 36.3, 29.8, 25.2, 21.3. HRMS calcd. for C$_{21}$H$_{18}$BClF$_2$N$_2$ [M-F]$^+$: 363.1266, found 363.1269.

**1h** was obtained as yellow oil in 45% yield (74 mg) from **2e** (125 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 56-58 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.02 (s, 1H), 6.84 (d, $J = 4.0$ Hz, 1H), 6.26 (d, $J = 3.9$ Hz, 1H), 5.85 (d, $J = 9.9$ Hz, 1H), 5.72 (d, $J = 10.0$ Hz, 1H), 4.03 (s, 1H), 2.54 (s, 3H), 2.40 (q, $J = 7.6$ Hz, 2H), 2.17 (s, 4H), 2.08 (s, 2H), 1.84-1.74 (m, 1H), 1.74-1.62 (m, 2H), 1.07 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.7, 159.6, 139.4, 134.8, 133.8, 133.2, 128.7, 128.6, 127.5, 123.1, 116.1, 35.8, 30.2, 25.3, 21.4, 17.7, 14.7, 13.3, 9.8. HRMS calcd. for C$_{19}$H$_{23}$BF$_2$N$_2$ [M-F]$^+$: 309.1933, found 309.1914.

**1i** was obtained as orange oil in 60% yield (101 mg) from **2a** (134 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 90-92 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H), 7.62-7.48 (m, 5H), 6.88 (d, $J = 4.4$ Hz, 1H), 6.77 (d, $J = 3.9$ Hz, 1H), 6.48 (d, $J = 3.7$ Hz, 1H), 6.36 (d, $J = 4.4$ Hz, 1H), 6.01 (d, $J = 3.0$ Hz, 1H), 5.80 (d, $J = 3.3$ Hz, 1H), 4.60 (s, 1H), 2.62-2.55 (m, 1H), 2.55-2.45 (m, 2H), 2.01-1.89 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.5, 145.1, 141.0, 135.9, 134.4, 134.3, 133.6, 131.6, 130.8, 130.7, 129.9, 129.0, 128.7, 118.6, 117.5, 45.3, 32.9, 32.2. HRMS calcd. for C$_{20}$H$_{17}$BF$_2$N$_2$ [M-F]$^+$: 315.1463, found 315.1441.

**1j** was obtained as orange oil in 57% yield (104 mg) from **2b** (150 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 93-95 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.78 (s, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 4.1$ Hz, 1H), 6.81 (d, $J = 2.9$ Hz, 1H), 6.48 (d, $J = 1.3$ Hz, 1H), 6.36 (d, $J = 4.1$ Hz, 1H), 6.00 (d, $J = 2.9$ Hz, 1H), 5.80 (d, $J = 3.2$ Hz, 1H), 4.59 (s, 1H), 3.90 (s, 3H), 2.64-2.56(m, 1H), 2.56-2.39 (m, 2H), 2.15-1.84 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.7, 162.0,
145.2, 140.5, 135.8, 134.1, 133.4, 132.6, 131.8, 130.0, 128.8, 126.9, 118.2, 117.3, 114.3, 55.9, 45.2, 32.9, 32.3. HRMS calcd. for C_{21}H_{19}BF_{2}N_{2}O [M-F]^+: 345.1569, found 345.1554.

1k was obtained as red oil in 40% yield (76 mg) from 2c (156 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 126-128 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.38 (d, J = 8.4 Hz, 2H), 7.84 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 3.6 Hz, 1H), 6.67 (s, 1H), 6.51 (s, 1H), 6.41 (d, J = 3.8 Hz, 1H), 6.03 (s, 1H), 5.79 (d, J = 2.8 Hz, 1H), 4.60 (s, 1H), 2.78-2.44 (m, 3H), 2.04-1.85 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 171.2, 149.3, 142.2, 141.5, 140.6, 135.6, 134.7, 133.6, 133.0, 131.6, 131.2, 128.5, 124.0, 119.6, 118.2, 45.4, 32.9, 32.2. HRMS calcd. for C_{20}H_{16}BF_{2}N_{3}O_{2} [M-F]^+: 360.1319, found 360.1319.

1l was obtained as yellow oil in 52% yield (105 mg) from 2d (168 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 85-87 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.55-7.41 (m, 2H), 7.40-7.37 (m, 1H), 6.64 (d, J = 4.5 Hz, 1H), 6.54 (d, J = 3.4 Hz, 1H), 6.44 (d, J = 3.7 Hz, 1H), 6.34 (d, J = 4.6 Hz, 1H), 6.02 (d, J = 3.1 Hz, 1H), 5.81 (d, J = 2.5 Hz, 1H), 4.60 (s, 1H), 2.63-2.54 (m, 1H), 2.54-2.46 (m, 1H), 2.05-1.91 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 171.0, 141.9, 138.5, 138.4, 135.8, 134.5, 133.6, 132.0, 131.4, 128.9, 128.6, 127.3, 119.5, 117.8, 45.5, 32.9, 32.1. HRMS calcd. for C_{20}H_{15}BCl_{2}F_{2}N_{2} [M-F]^+: 383.0684, found 383.0667.

1m was obtained as yellow oil in 40% yield (63 mg) from 2e (125 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 56-58 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.02 (s, 1H), 6.83 (d, J = 3.9 Hz, 1H), 6.18 (d, J = 3.9 Hz, 1H), 5.94 (d, J = 5.5 Hz, 1H), 5.80 (d, J = 5.5 Hz, 1H), 4.46 (s, 1H), 2.55 (s, 3H), 2.51-2.47 (m, 1H), 2.39 (t, J = 7.6 Hz, 2H), 2.17 (s, 3H), 1.91-1.85 (m, 1H), 1.25 (s, 2H), 1.07 (t, J = 7.6 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.7, 159.5, 139.5, 134.8, 133.9, 133.3, 131.3, 127.8, 123.1, 114.9, 44.9, 32.7, 30.1, 17.7, 14.8, 13.3, 9.8. HRMS calcd. for C_{18}H_{21}BF_{2}N_{2} [M-F]^+: 295.1776, found 295.1777.

1n was obtained as orange oil in 50% yield (88 mg) from 2a (134 mg, 0.5 mmol) and 2,3-dimethyl-2-butene (3.0 mL). Melting point: 108-109 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.57-7.49 (m, 5H), 6.86 (d, J = 4.3 Hz, 1H), 6.76 (d, J = 3.9 Hz,
1H), 6.47 (s, 1H), 6.27 (d, J = 4.3 Hz, 1H), 3.84 (s, 2H), 1.75 (s, 3H), 1.74 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 165.7, 144.7, 140.9, 136.2, 134.4, 134.2, 133.3, 130.8, 130.6, 128.9, 128.8, 128.7, 123.5, 120.1, 117.4, 34.5, 21.1, 21.0, 19.7. HRMS calcd. for C₂₁H₂₁BF₂N₂ [M-F]⁺: 331.1776, found 331.1757.

1o was obtained as yellow oil in 53% yield (114 mg) from 2a (134 mg, 0.5 mmol) and norbornene (3.0 mL). Melting point: 65-67 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.75 (s, 1H), 7.63-7.39 (m, 5H), 6.87 (s, 1H), 6.74 (s, 1H), 6.53 (d, J = 2.8 Hz, 1H), 6.45 (s, 1H), 4.40 (d, J = 5.6 Hz, 1H), 3.69 (s, 1H), 3.20 (d, J = 1.1 Hz, 1H), 2.72 (s, 1H), 2.38 (s, 1H), 2.02 (d, J = 8.1 Hz, 1H), 1.40 (s, 2H), 1.26 (s, 2H), 1.07(s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 164.9, 144.2, 140.2, 135.4, 134.6, 133.9, 132.6, 130.8, 130.6, 128.7, 128.2, 121.3, 117.0, 88.6, 80.7, 47.5, 42.4, 40.1, 35.2, 30.4, 26.7, 23.6. HRMS calcd. for C₂₆H₂₉BF₂N₂O [M-2F]⁺: 395.2404, found 395.2404.

General procedure for the synthesis of BODIPYs 3a-e

To BODIPY 2 (0.50 mmol) and Bu₄NI (0.10 mmol, 37 mg) in a Schlenk tube was added solvent (3.0 mL) and TBHP (70% aqueous solution, 0.36 mL, 2.5 mmol) via a syringe. The reaction mixture was stirred at 90 °C in an oil bath for 24 h. The organic solvent was removed under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1→9:1, v/v) as eluent to provide the corresponding product.

3a was obtained as yellow oil in 35% yield (75 mg) from 2a (134 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 72-74 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.49 (s, 5H), 6.74 (d, J = 4.1 Hz, 2H), 6.36 (d, J = 4.2 Hz, 2H), 5.89 (d, J = 9.9 Hz, 2H), 5.71 (d, J = 9.6 Hz, 2H), 4.15 (s, 2H), 2.29-2.18 (m, 2H), 2.10 (s, 4H), 1.89-1.75 (m, 2H), 1.74-1.63 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 166.0, 143.5, 134.7, 134.5, 130.8, 130.3, 129.2, 128.6, 128.0, 127.9, 118.0, 36.0, 30.1, 25.2, 21.4. HRMS calcd. for C₂₇H₂₇BF₂N₂ [M-F]⁺: 409.2246, found 409.2259.

3b was obtained as yellow oil in 35% yield (80 mg) from 2b (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 76-78 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 3.9 Hz, 2H), 6.35 (d, J = 4.1 Hz, 2H), 5.88 (d, J = 10.0 Hz, 2H), 5.71 (d, J = 9.9 Hz, 2H), 4.14 (s, 2H), 3.89 (s, 3H), 3.69 (s, 1H), 3.20 (d, J = 1.1 Hz, 1H), 2.72 (s, 1H), 2.38 (s, 1H), 2.02 (d, J = 8.1 Hz, 1H), 1.40 (s, 2H), 1.26 (s, 2H), 1.07(s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 164.9, 144.2, 140.2, 135.4, 134.6, 133.9, 132.6, 130.8, 130.6, 128.7, 128.2, 121.3, 117.0, 88.6, 80.7, 47.5, 42.4, 40.1, 35.2, 30.4, 26.7, 23.6. HRMS calcd. for C₂₇H₂₇BF₂N₂ [M-F]⁺: 409.2246, found 409.2259.
2.30-2.18 (m, 2H), 2.09 (s, 4H), 1.89-1.75 (m, 2H), 1.74-1.65 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.0, 161.1, 143.1, 134.0, 132.0, 130.1, 128.6, 127.7, 126.7, 117.4, 113.6, 55.4, 35.5, 29.7, 24.8, 21.0. HRMS calcd. for C$_{28}$H$_{29}$BF$_2$N$_2$O [M-F]$^+$: 439.2351, found 439.2359.

3c was obtained as red oil in 33% yield (78 mg) from 2c (156 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 106-108 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.36 (d, $J$ = 8.7 Hz, 1H), 7.69 (d, $J$ = 8.7 Hz, 1H), 6.64 (d, $J$ = 4.2 Hz, 1H), 6.40 (d, $J$ = 4.2 Hz, 1H), 5.91 (d, $J$ = 10.1 Hz, 1H), 5.70 (d, $J$ = 9.9 Hz, 1H), 4.15 (s, 1H), 2.28-2.17 (m, 1H), 2.11 (s, 2H), 1.86-1.77 (m, 1H), 1.78-1.63 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.4, 149.1, 141.0, 139.9, 134.0, 131.6, 130.2, 129.6, 127.5, 123.9, 118.9, 36.1, 30.0, 25.2, 21.4. HRMS calcd. for C$_{27}$H$_{26}$BF$_2$N$_3$O$_2$ [M-F]$^+$: 454.2097, found 454.2076.

3d was obtained as red oil in 35% yield (78 mg) from 2c (156 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 109-111 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J$ = 8.7 Hz, 2H), 7.68 (d, $J$ = 8.6 Hz, 2H), 6.63 (d, $J$ = 4.0 Hz, 2H), 6.32 (d, $J$ = 4.2 Hz, 2H), 5.99 (d, $J$ = 5.5 Hz, 2H), 5.80 (d, $J$ = 5.5 Hz, 2H), 4.58 (s, 2H), 2.68-2.54 (m, 2H), 2.53-2.43 (m, 4H), 1.99-1.89 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.3, 149.1, 141.0, 139.8, 134.0, 131.9, 131.8, 131.6, 130.4, 123.9, 117.8, 45.2, 32.9, 32.5. HRMS calcd. for C$_{25}$H$_{22}$BF$_2$N$_3$O$_2$ [M-F]$^+$: 426.1784, found 426.1760.

3e was obtained as yellow oil in 40% yield (86 mg) from 2a (134 mg, 0.5 mmol) and 2,3-dimethyl-2-butene (3.0 mL). Melting point: 121-123 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54-7.43 (m, 5H), 6.69 (d, $J$ = 4.2 Hz, 2H), 6.18 (d, $J$ = 4.2 Hz, 2H), 3.83 (s, 4H), 1.75 (s, 12H), 1.73 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.8, 142.7, 135.0, 134.6, 130.8, 130.6, 130.2, 128.5, 128.2, 124.0, 118.3, 34.2, 21.1, 21.0, 19.7. HRMS calcd. for C$_{28}$H$_{31}$BF$_2$N$_2$ [M-F]$^+$: 413.2559, found 413.2553.

**General procedure for the synthesis of BODIPYs 5a-g**

To BODIPY 2a (0.50 mmol) and Bu$_4$NI (0.10 mmol, 37 mg) in a Schlenk tube was added solvent (3.0 mL) and TBHP (70% aqueous solution, 0.36 mL, 2.5 mmol) via a syringe. The reaction mixture was stirred at 90 °C (except for diethyl ether, reflux
temperature) in an oil bath for 12 h. The organic solvent was removed under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1 → 9:1, v/v) as eluent to provide the corresponding product.

5a was obtained as yellow oil in 50% yield (73 mg) from 2a (134 mg, 0.5 mmol) and diethyl ether (3.0 mL) at refluxing temperature (40 °C oil bath). Melting point: 52-53 °C. \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.82 (s, 1H), 7.68-7.38 (m, 5H), 6.94 (d, \( J = 4.3 \) Hz, 1H), 6.82 (d, \( J = 3.4 \) Hz, 1H), 6.65 (d, \( J = 4.4 \) Hz, 1H), 6.50 (d, \( J = 2.1 \) Hz, 1H), 5.15-5.06 (m, 1H), 3.61-3.43 (m, 2H), 1.56 (d, \( J = 6.5 \) Hz, 3H), 1.33-1.12 (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 167.0, 145.7, 141.6, 135.0, 135.9, 133.8, 132.8, 130.4, 130.3, 129.6, 128.3, 117.6, 116.9, 71.2, 65.1, 22.2, 15.3. HRMS calcd. for C\(_{19}\)H\(_{19}\)BF\(_2\)N\(_2\)O [M-OC\(_2\)H\(_5\)]\(^+\): 295.1213, found 295.1229.

5b was obtained as yellow oil in 52% yield (102 mg) from 2a (134 mg, 0.5 mmol) and dibutyl ether (3.0 mL). Melting point: 56-59 °C. \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.81 (s, 1H), 7.62-7.49 (m, 5H), 6.93 (d, \( J = 4.3 \) Hz, 1H), 6.81 (d, \( J = 3.8 \) Hz, 1H), 6.63 (d, \( J = 4.4 \) Hz, 1H), 6.49 (d, \( J = 2.1 \) Hz, 1H), 4.95 (t, \( J = 5.3 \) Hz, 1H), 3.49-3.44 (m, 2H), 1.93-1.73 (m, 2H), 1.75-1.63 (m, 2H), 1.57-1.50 (m, 2H), 1.43-1.37 (m, 2H), 0.97 (t, \( J = 7.3 \) Hz, 3H), 0.89 (t, \( J = 7.3 \) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 166.9, 145.5, 141.3, 135.1, 133.9, 133.8, 132.7, 130.4, 129.4, 128.7, 128.3, 117.7, 117.4, 75.1, 69.7, 38.4, 31.9, 29.6, 19.3, 18.9, 13.8. HRMS calcd. for C\(_{23}\)H\(_{27}\)BF\(_2\)N\(_2\)O [M-OC\(_4\)H\(_9\)]\(^+\): 323.1526, found 323.1554.

5c was obtained as yellow solid in 55% yield (93 mg) from 2a (134 mg, 0.5 mmol) and tetrahydrofuran (3.0 mL). Melting point: 90-93 °C. \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.81 (s, 1H), 7.68-7.41 (m, 5H), 6.91 (d, \( J = 3.6 \) Hz, 1H), 6.82 (d, \( J = 3.0 \) Hz, 1H), 6.60 (d, \( J = 3.9 \) Hz, 1H), 6.49 (s, 1H), 5.49 (t, \( J = 6.4 \) Hz, 1H), 4.22-4.07 (m, 1H), 4.03-3.88 (m, 1H), 2.72-2.51 (m, 1H), 2.18-1.91 (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 165.9, 145.7, 141.6, 135.6, 133.9, 133.8, 132.7, 130.4, 129.5, 129.3, 128.3, 117.5, 117.1, 74.9, 69.3, 33.9, 26.3. HRMS calcd. for C\(_{19}\)H\(_{17}\)BF\(_2\)N\(_2\)O [M-BF\(_2\)]\(^+\): 289.1335, found 289.1336.

5d was obtained as yellow solid in 42% yield (74 mg) from 2a (134 mg, 0.5 mmol)
and 1,4-dioxane (3.0 mL). Melting point: 131-134 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.89 (s, 1H), 7.73-7.43 (m, 5H), 6.92 (d, \(J = 3.9\) Hz, 1H), 6.88 (d, \(J = 3.3\) Hz, 1H), 6.67 (d, \(J = 3.9\) Hz, 1H), 6.53 (s, 1H), 5.29 (d, \(J = 5.7\) Hz, 1H), 4.25 (d, \(J = 11.4\) Hz, 1H), 4.04-3.87 (m, 2H), 3.84-3.65 (m, 2H), 3.48 (t, \(J = 10.8\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 157.9, 146.7, 143.3, 135.1, 134.4, 133.7, 132.1, 130.8, 130.6, 130.4, 128.4, 118.4, 117.6, 72.5, 70.7, 66.7, 66.3. HRMS calcd. for C\(_{19}\)H\(_{17}\)BF\(_2\)N\(_2\)O\(_2\) [M-BF\(_2\)]\(^+\): 305.1285, found 305.1297; [M-BF\(_2\)+2H]\(^+\): 307.1447, found 307.1449.

5e was obtained as yellow oil in 43% yield (114 mg) from 2a (134 mg, 0.5 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (3.0 mL). Melting point: 56-59 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.78 (s, 1H), 7.65-7.31 (m, 5H), 6.85 (d, \(J = 2.6\) Hz, 1H), 6.78 (d, \(J = 4.2\) Hz, 1H), 6.70 (d, \(J = 10.0\) Hz, 1H), 6.45 (d, \(J = 4.3\) Hz, 1H), 5.24 (s, 1H), 3.93-3.79 (m, 2H), 4.05-3.23 (m, 20H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 161.44, 146.08, 142.34, 135.29, 134.22, 133.74, 132.26, 130.47, 130.35, 130.15, 128.30, 119.02, 117.88, 75.34, 73.25, 70.86, 70.76, 70.74, 70.67, 70.62, 70.57, 70.40, 70.05, 69.51, 69.50. HRMS calcd. for C\(_{27}\)H\(_{33}\)BF\(_2\)N\(_2\)O\(_6\) [M-2HF+H]\(^+\): 491.2353, found 491.2365.
3. **Scheme S1.** Proposed reaction mechanism for the formation of BODIPY 1o.
4. NMR and HRMS spectra for all new compounds

$^1$H NMR spectrum of 1a in CDCl$_3$
HRMS for 1a
$^1$H NMR spectrum of 1b in CDCl$_3$

$^{13}$C NMR spectrum of 1b in CDCl$_3$
HRMS for 1b

+APCI Scan (#3) Frag=175.0V 0009.d

Counts (%) vs. Mass-to-Charge (m/z)

- 283.1303
- 371.1904
- 359.1710
$^1$H NMR spectrum of $1c$ in CDCl$_3$

$^{13}$C NMR spectrum of $1c$ in CDCl$_3$
HRMS for 1c
\(^1\)H NMR spectrum of 1d in CDCl₃

\(^{13}\)C NMR spectrum of 1d in CDCl₃
HRMS for 1d
$^1$H NMR spectrum of 1e in CDCl$_3$

$^{13}$C NMR spectrum of 1e in CDCl$_3$
HRMS for 1e
$^1$H NMR spectrum of 1f in CDCl$_3$

$^{13}$C NMR spectrum of 1f in CDCl$_3$
$^1$H NMR spectrum of 1g in CDCl$_3$

$^{13}$C NMR spectrum of 1g in CDCl$_3$
HRMS for 1g
$^1$H NMR spectrum of $1h$ in CDCl$_3$

$^{13}$C NMR spectrum of $1h$ in CDCl$_3$
HRMS for 1h

+APCI Scan (#7) Frag=175.0V 0012.d

Counts (%) vs. Mass-to-Charge (m/z)

-4 0 4 8 12 16 20 24 28 32 36 40

0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5 5.5 6 6.5 7 7.5 8 8.5 9 9.5

-10

329.1974

279.0914

309.1914

229.1293
$^1$H NMR spectrum of 1i in CDCl$_3$

$^{13}$C NMR spectrum of 1i in CDCl$_3$
HRMS for 1i

![HRMS graph for 1i with masses at 237.1010, 256.2602, 274.2709, 299.1155, 315.1441, 285.1361, and 327.1636.](image)
$^1$H NMR spectrum of \textbf{1j} in CDCl$_3$

$^{13}$C NMR spectrum of \textbf{1j} in CDCl$_3$
HRMS for 1j
$^1$H NMR spectrum of 1k in CDCl$_3$

$^{13}$C NMR spectrum of 1k in CDCl$_3$
HRMS for 1k

![HRMS Graph](image)
$^1$H NMR spectrum of II in CDCl$_3$

$^{13}$C NMR spectrum of II in CDCl$_3$
HRMS for 11
$^1$H NMR spectrum of 1m in CDCl$_3$

$^{13}$C NMR spectrum of 1m in CDCl$_3$
HRMS for 1m
$^1$H NMR spectrum of 1n in CDCl$_3$

$^{13}$C NMR spectrum of 1n in CDCl$_3$
HRMS for 1n
$^1$H NMR spectrum of $1\text{a}$ in CDCl$_3$

$^{13}$C NMR spectrum of $1\text{a}$ in CDCl$_3$
HRMS for 10
$^1$H NMR spectrum of 3a in CDCl$_3$

$^{13}$C NMR spectrum of 3a in CDCl$_3$
HRMS for 3a
$^1$H NMR spectrum of 3b in CDCl$_3$

$^{13}$C NMR spectrum of 3b in CDCl$_3$
HRMS for 3b
$^1$H NMR spectrum of 3c in CDCl$_3$

$^{13}$C NMR spectrum of 3c in CDCl$_3$
HRMS for 3c

![HRMS Spectrum for 3c](image)
$^1$H NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
HRMS for 3d

+APCI Scan (# 2-3, 2 scans) Frag=175.0V 0019.d

Counts (%) vs. Mass-to-Charge (m/z)

- 223.0624
- 283.1306
- 338.3384
- 426.1760
- 446.1812
$^1$H NMR spectrum of 3e in CDCl$_3$

$^{13}$C NMR spectrum of 3e in CDCl$_3$
HRMS for 3e

Counts (%) vs. Mass-to-Charge (m/z)
\( ^1H \) NMR spectrum of 5a in CDCl₃

\( ^{13}C \) NMR spectrum of 5a in CDCl₃
HRMS for 5a
$^1$H NMR spectrum of 5b in CDCl$_3$

$^{13}$C NMR spectrum of 5b in CDCl$_3$
HRMS for 5b
$^1$H NMR spectrum of 5c in CDCl$_3$

$^{13}$C NMR spectrum of 5c in CDCl$_3$
$^1$H NMR spectrum of 5d in CDCl$_3$

$^{13}$C NMR spectrum of 5d in CDCl$_3$
HRMS for 5d
$^1$H NMR spectrum of 5e in CDCl$_3$

$^{13}$C NMR spectrum of 5e in CDCl$_3$
HRMS for 5e
5. Photophysical properties of selected BODIPYs

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 °C, 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 (Φᵣ = 0.90 in 0.1 N NaOH aqueous solution). Non-degassed, spectroscopic grade solvents and 10 mm optical path length quartz cuvettes were used. Dilute solutions (0.01 < A(λₑₓ) < 0.05) were used to minimize the inner-filter effects. Quantum yields Φₓ were determined according to equation (S1):

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1 - 10^{-A_x(\lambda_{ex})}}{1 - 10^{-A_r(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2}$$  \hspace{1cm} (S1)

where the subscripts x and r refer respectively to the BODIPY sample x and reference (standard) fluorophore r with known quantum yield Φᵣ in a specific solvent; F stands for the spectrally corrected, integrated fluorescence spectra; A(λₑₓ) denotes the absorbance at the used excitation wavelength λₑₓ and n represents the refractive index of the solvent (in principle at the average emission wavelength).
Table S1: Photophysical properties of selected BODIPYs in different solvents at room temperature

<table>
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<tr>
<th>dyes</th>
<th>solvent</th>
<th>$\lambda_{\text{abs}}$(max) [nm]</th>
<th>log $\varepsilon^a$</th>
<th>$\lambda_{\text{em}}$(max) [nm]</th>
<th>$\Phi^b$</th>
<th>Stokes-shift [cm$^{-1}$]</th>
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<tr>
<td>2a</td>
<td>CH$_2$Cl$_2$</td>
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<td>4.52</td>
<td>527</td>
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<td>718</td>
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<tr>
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<td>toluene</td>
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<td>527</td>
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<tr>
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<tr>
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<tr>
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<td>4.63</td>
<td>522</td>
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</table>

$^a$ Molar absorption coefficient at $\lambda_{\text{abs}}$(max). $^b$ Fluorescence quantum yield was calculated using fluorescein ($\Phi = 0.90$ in 0.1 N NaOH aqueous solution) as standard. $^c$ Data from ref (Eur J. Org. Chem. 2011, 28, 5460–5468).

Figure S2. Absorption (left) and fluorescence emission (right) spectra of 1a recorded in different solvents (excitation at 470 nm).
Figure S3. Absorption (left) and fluorescence emission (right) spectra of 3a recorded in different solvents (excitation at 470 nm).

Figure S4. Absorption (left) and fluorescence emission (right) spectra of 5c recorded in different solvents (excitation at 470 nm).