Supporting Information

BODIPY Catalyzed Amide Synthesis Promoted by BHT and Air under Visible Light

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1. Optimization of reaction conditions

1.1 Screening of the amount of substrates, photocatalyst and reaction time

Table S1 Screening of the equivalents

<table>
<thead>
<tr>
<th>Entry</th>
<th>SM1 (1a)</th>
<th>SM2 (2a)</th>
<th>Catalyst</th>
<th>Time</th>
<th>Yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 eq.</td>
<td>1 eq.</td>
<td>P2 (2 mol%)</td>
<td>16 h</td>
<td>12%</td>
</tr>
<tr>
<td>2</td>
<td>1 eq.</td>
<td>2 eq.</td>
<td>P2 (2 mol%)</td>
<td>16 h</td>
<td>30%</td>
</tr>
<tr>
<td>3</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>16 h</td>
<td>60%</td>
</tr>
<tr>
<td>4</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (1 mol%)</td>
<td>16 h</td>
<td>55%</td>
</tr>
<tr>
<td>5</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (3 mol%)</td>
<td>16 h</td>
<td>45%</td>
</tr>
<tr>
<td>6</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>6 h/25 °C</td>
<td>36%</td>
</tr>
<tr>
<td>7</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>12 h/25 °C</td>
<td>60%</td>
</tr>
<tr>
<td>8</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>24 h/25 °C</td>
<td>59%</td>
</tr>
<tr>
<td>9</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>6 h/30 °C</td>
<td>48%</td>
</tr>
<tr>
<td>10</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>12 h/30 °C</td>
<td>58%</td>
</tr>
</tbody>
</table>

a 4-Bromobenzaldehyde 1a (1 eq., 0.2 mmol), pyrrolidine, under air, 3 W Blue LEDs irradiation, MeCN (2 mL) as solvent. b Yield determined by 1H NMR, 1,3,5-trimethoxylbenzene as internal standard.

1.2 Screening of solvents and additives

Table S2-1 Screening of solvents and additives

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light source</th>
<th>Solvent</th>
<th>Additive</th>
<th>Yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Household bulb</td>
<td>MeCN</td>
<td>-</td>
<td>50%</td>
</tr>
<tr>
<td>2</td>
<td>Green LEDs</td>
<td>MeCN</td>
<td>-</td>
<td>37%</td>
</tr>
<tr>
<td>3</td>
<td>Blue LEDs</td>
<td>MeCN</td>
<td>-</td>
<td>60%</td>
</tr>
<tr>
<td>4</td>
<td>Blue LEDs</td>
<td>MeOH</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Blue LEDs</td>
<td>DCM</td>
<td>-</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>Blue LEDs</td>
<td>H2O</td>
<td>-</td>
<td>11%</td>
</tr>
<tr>
<td>7</td>
<td>Blue LEDs</td>
<td>DMSO</td>
<td>-</td>
<td>30%</td>
</tr>
<tr>
<td>8</td>
<td>Blue LEDs</td>
<td>THF</td>
<td>-</td>
<td>65%</td>
</tr>
<tr>
<td>Entry</td>
<td>SM1 (1a)</td>
<td>SM2 (2a)</td>
<td>Catalyst</td>
<td>Time</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>1 eq.</td>
<td></td>
<td></td>
<td>12 h</td>
</tr>
<tr>
<td>2</td>
<td>2 eq.</td>
<td></td>
<td></td>
<td>12 h</td>
</tr>
<tr>
<td>3</td>
<td>1 eq.</td>
<td>3 eq.</td>
<td>P2 (2 mol%)</td>
<td>12 h</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>4 eq.</td>
<td></td>
<td>12 h</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>5 eq.</td>
<td></td>
<td>12 h</td>
</tr>
</tbody>
</table>

Table S2-2 Screening of the equivalents

The set-up of oxidation amidation using solar light or 3 W Blue LEDs irradiation and BODIPY catalyst

2. Oxidative amidation under sunlight

The set-up of oxidation amidation using solar light or 3 W Blue LEDs irradiation and BODIPY catalyst

The gram-scale reaction: A sealed tube was equipped with a magnetic stir bar and was charged
with P2 (54 mg, 2 mol%), BHT (2.38 g, 10.82 mmol, 2 equiv.), 4-bromobenzaldehyde 1a (1.00 g, 5.41 mmol, 1 equiv.), pyrrolidine 2a (1.15 g, 16.23 mmol, 3 equiv.) and dioxane (50 mL) under air and stirred for 48 hours. The reaction tube was placed outside the laboratory under the irradiation of solar light or placed at a distance of 5 cm from 3 W Blue LEDs. After the reaction was completed, the reaction mixture was quenched with saturated aqueous Na$_2$SO$_3$ solution and extracted with EA. The organic phase was dried over Na$_2$SO$_4$ and concentrated on a rotary evaporator. The crude product was further purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to give the product 3a.

3. The effect of BHT derivatives to aerobic oxidative amidation

3.1 The reaction of BHT derivatives with oxygen activated by photocatalyst under the irradiation of visible light

A sealed tube was equipped with a magnetic stir bar and was charged with P2 (2.4 mg, 1 mol %), BHT derivatives (0.5 mmol, 1 equiv.) and dioxane (2 mL) under air at room temperature. The reaction mixture was placed at a distance of 5 cm from 3 W Blue LEDs and stirred for 6 hours (Scheme S1). After the reaction was completed, the solvent was evaporated under vacuo. The crude mixture was purified by flash column chromatography eluting with a mixture of petroleum ether/ethyl acetate.

3.2 The reactivity of BHT-OOH

The reaction was carried out in a sealed tube, BHT-OOH (126 mg, 0.5 mmol, 1 eq.), PPh$_3$ (131 mg, 0.5 mmol, 1 eq.), dioxane (2 mL) and a magnetic stir bar were added to the tube. The reaction mixture was stirred at the room temperature for 6 hours (Scheme S2) under the condition of the Argon, and the solvent was evaporated under vacuo. The compound structure determined by $^{31}$P NMR.

The BHT-OOH compound (100.8 mg, 0.4 mmol, 2 eq.) was added to a solution of 4-bromobenzaldehyde 1a (37.0 mg, 0.2 mmol, 1 eq.) and pyrrolidine 2a (42.6 mg, 0.6 mmol, 3 eq.) in 2 mL of dioxane under air at room temperature for 2-12 hours in the dark (Scheme S2). After the definite reaction time finished, the solvent was evaporated under vacuo, the yield of 3a was determined by NMR (1, 3, 5-trimethoxylbenzene as internal standard).
Scheme S1 The effect of BHT to aerobic oxidative amidation

Figure S1 The effect of BHT-OOH ($^{31}$P NMR of the PPh$_3$ and Ph$_3$PO)

Figure S2 The effect of BHT-OOH to aerobic oxidative amidation

3.3 Comparison of 30% H$_2$O$_2$ and BHT-OOHs

Table S3 Comparison of 30% H$_2$O$_2$ and BHT-OOHs
3.4 The reaction of pentane-2,4-dione with aniline promoted by BHT-OOH under solvent-free condition

A sealed reaction tube was charged with pentane-2, 4-dione (60.0 mg, 0.6 mmol, 1.2 eq.), aniline (46.5 mg, 0.5 mmol, 1 eq.), a magnetic stir bar and BHT-OOH (126 mg, 0.5 mmol, 1eq.). After the reaction was carried out under air at room temperature for 12 hours (Scheme S3), the reaction mixture was quenched with saturated aqueous Na₂SO₃ solution (20 mL) and extracted with EA (3×10 mL). The organic layers were dried over Na₂SO₄, and concentrated to yield the crude product, which was further purified by column chromatography (petroleum ether/ethyl acetate = 2:1) to give the 63% pure product 4a.

4. The study of reaction mechanism

4.1 The effect of H₂O₂ in the reaction

Table S4 The effect of H₂O₂ in the reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>H₂O₂ (30% aq.)</th>
<th>P2</th>
<th>BHT</th>
<th>Light</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 eq.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>49%</td>
</tr>
<tr>
<td>2</td>
<td>2 eq.</td>
<td>-</td>
<td>1 eq.</td>
<td>-</td>
<td>47%</td>
</tr>
<tr>
<td>3</td>
<td>2 eq.</td>
<td>2 mol%</td>
<td>-</td>
<td>Blue LEDs</td>
<td>66%</td>
</tr>
<tr>
<td>4</td>
<td>2 eq.</td>
<td>2 mol%</td>
<td>1 eq.</td>
<td>Blue LEDs</td>
<td>63%</td>
</tr>
<tr>
<td></td>
<td>eq.</td>
<td>mol%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>Blue LEDs</td>
<td>44</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>Blue LEDs</td>
<td>61</td>
</tr>
</tbody>
</table>

*The reaction conditions were as follows: 4-bromobenzaldehyde 1a (1 eq., 0.2 mmol), pyrrolidine 2a (3 equiv.), under air, dioxane (2 mL), 4 h. Yield determined by $^1$H NMR, 1,3,5-trimethoxybenzene as internal standard.

### 4.2 The determination of the O$_2^•$ in the reaction system

#### 4.2.1
A sealed tube was equipped with a magnetic stir bar and was charged with P2 (2.4 mg, 1 mol%), PPh$_3$ (131 mg, 0.5 mmol, 1 equiv.) and dioxane (2 mL) under air at room temperature. The reaction mixture was placed at a distance of 5 cm from 3 W Blue LEDs and stirred for 6 hours (Scheme S4). After the reaction was completed, the solvent was evaporated under vacuo. The crude mixture was purified by flash column chromatography eluting with a mixture of petroleum ether/ethyl acetate.

#### 4.2.2
The determination of the H$_2$O$_2$ in the reaction system

A sealed tube was equipped with a magnetic stir bar and was charged with P2 (2 mg, 2
mol %), 4-bromobenzaldehyde (0.2 mmol, 1 equiv.), pyrrolidine (0.6 mmol, 3 equiv.) and dioxane (2 mL) under air at room temperature. The reaction tube was placed at a distance of 5 cm from 3 W Blue LEDs and stirred for 4 hours. PPh₃ (131 mg, 0.5 mmol, 1 equiv.) was added. The reaction mixture was stirred for another 6 hours in dark. The solvent was evaporated under vacuo. Ph₃PO was determined by ³¹P NMR.

**Figure S3** ³¹P NMR of PPh₃ and Ph₃PO

**Figure S4** ³¹P NMR of the PPh₃ in the reaction end of the main reaction

### 4.4 The product 3a, BHT-OH and BHT conversions over the time

A sealed tube was equipped with a magnetic stir bar and was charged with P2 (2 mg, 2 mol %), BHT (88 mg, 0.4 mmol, 2 equiv.), 4-bromobenzaldehyde 1a (37.0 mg, 0.2 mmol, 1 equiv.), pyrrolidine 2a (42.6 mg, 0.6 mmol, 3 equiv.) and dioxane (2 mL) under air at room temperature. The reaction mixture was placed at a distance of 5 cm from 3 W Blue LEDs and stirred for 2, 4, 6, 8, 10, 12 hours respectively. After the reaction time was finished, the reaction mixture was quenched with saturated aqueous Na₂SO₃ solution (20 mL) and extracted with EA (3 × 10 mL).
The organic phase was dried over Na$_2$SO$_4$, and concentrated on a rotary evaporator. The product 3a, BHT-OH and BHT were determined by NMR.

![Conversion Graph](image)

Figure S5 The product 3a, BHT-OH and BHT conversions over the time
5. Spectral copies of $^1$H and $^{13}$C NMR data obtained in this study
5,5-Difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-dipyrrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide(I):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,8-Dichloro-5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-iium-5-uide (P1):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,8-Dibromo-5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-iium-5-uide(P2):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5,5-Difluoro-2,8-diiodo-1,3,7,9-tetramethyl-10-phenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide(P3):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,8-Dibromo-5,5-difluoro-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide(P4):

**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100 MHz, CDCl₃)**
2,8-Dibromo-5,5-difluoro-1,3,7,9-tetramethyl-10-(4-(trifluoromethyl)phenyl)-5H-dipyrrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (P5):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,8-Dibromo-10-(4-bromophenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-dipyrrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide(P6):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(4-bromophenyl)(pyrrolidin-1-yl)methanone (3a):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(4-chlorophenyl)(pyrrolidin-1-yl) methanone (3b):

$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(4-fluorophenyl)(pyrrolidin-1-yl)methanone(3c):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyridin-4-yl(pyrrolidin-1-yl)methanone (3d):

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))
(4-nitrophenyl)(pyrrolidin-1-yl)methanone(3e):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(pyrrolidine-1-carbonyl)benzonitrile(3f):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyrrolidin-1-yl(4-(trifluoromethyl)phenyl)methanone(3g):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
methyl 4-(pyrrolidine-1-carbonyl)benzoate (3h): 

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyrrolidin-1-yl(p-tolyl)methanone(3i):

$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
(4-methoxyphenyl)(pyrrolidin-1-yl)methanone(3j):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(3-nitrophenyl)(pyrrolidin-1-yl) methanone (3k):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
(3-bromophenyl)(pyrrolidin-1-yl)methanone (3l):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
naphthalen-2-yl(pyrrolidin-1-yl)methanone(3m):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyren-1-yl(pyrrrolidin-1-yl)methanone(3n):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-(pyrrolidine-1-carbonyl)benzaldehyde(3o):

$^1$H NMR (400 MHz, CDCl$_3$)

$^13$C NMR (100 MHz, CDCl$_3$)
pyrrolidin-1-yl(thiophen-2-yl)methanone(3p):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyridin-4-yl(pyrrolidin-1-yl)methanone (3q):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyridin-2-yl(pyrrolidin-1-yl)methanone(3r):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
methyl-1H-indol-2-yl)(pyrrolidin-1-yl)methanone(3s):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
pyrrolidin-1-yl(quinolin-2-yl)methanone(3t):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(piperidine-1-carbonyl)benzonitrile (3fb):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(1,2,3,4-tetrahydroisoquinoline-2-carbonyl)benzonitrile (3fc):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(morpholine-4-carbonyl)benzonitrile(3fd):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(4-methylpiperidine-1-carbonyl)benzonitrile (3fe):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(4-benzylpiperidine-1-carbonyl)benzonitrile(3ff):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
ethyl 1-(4-cyanobenzoyl)piperidine-3-carboxylate(3fg):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(4-ethylpiperazine-1-carbonyl)benzonitrile(3fh):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(isoindoline-2-carbonyl)benzonitrile(3fi):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-(azepane-1-carbonyl)benzonitrile (3f):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
N-phenylacetamide (4a):

$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
2,6-Di-tert-butyl-4-hydroperoxy-4-methylcyclohexa-2,5-dienone:

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,6-Di-tert-butyl-4-ethyl-4-hydroperoxycyclohexa-2,5-dienone:

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,4,6-Tri-tert-butyl-4-hydroperoxycyclohexa-2,5-dienone:

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2,6-Di-tert-butyl-4-hydroxy-4-methylcyclohexa-2,5-dienone:

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^1\)C NMR (100 MHz, CDCl\(_3\))