Supporting Information

Decarboxylative Formylation of Aryl Halides with Glyoxylic Acid by Merging Organophotoredox with Palladium Catalysis

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1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity ≥ 99.999%) unless otherwise mentioned. Commercial reagents were purchased from Adamas-beta, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

$^1$H-NMR, $^{19}$F-NMR and $^{13}$C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for $^1$H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity ($s =$ singlet, $d =$ doublet, $t =$ triplet, $q =$ quartet, $m =$ multiplet and/or multiplet resonances, $br =$ broad), coupling constant (Hz), and integration. Data for $^{13}$C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software.

2. Preparation of Photocatalyst (4CzIPN)

\[
\text{4,4 equiv} \quad \text{NaHMDS (4.2 equiv)} \quad \text{THF, 0 °C to r.t. 45 min} \quad \text{4CzIPN}
\]

2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN)

A 100 mL Schlenk tube containing a stirring bar was charged with carbazole (6.43 g, 38.5 mmol, 4.4 equiv). The tube was then evacuated and back-filled with argon three times. Anhydrous Tetrahydrofuran (THF, 77 mL) was added subsequently,
and the solution was cooled to 0 °C. The flask was then charged with NaHMDS in THF (2 M, 18.4 mL, 36.7 mmol, 4.2 equiv) by syringe, resulting in an orange-brown solution. After 5 min, the solution was warmed to room temperature and stirred for 30 min. The flask was then charged with tetrafluoroisophthalonitrile (1.75 g, 8.75 mmol, 1.0 equiv) and equipped with a reflux condenser. The solution was heated at 65 °C under the Ar atmosphere and allowed to stir at this temperature for 72 h. During this time, the solution became a very dark brown with a voluminous yellow precipitate. After the 72 h, the flask was cooled to the room temperature and the contents of the flask were poured into a medium porosity fritted glass funnel. After the solids and liquid were separated, the solids were washed with Et₂O (350 mL) to remove the residual carbazole. The filtrate was discarded, and the solid was then washed with CHCl₃ (600 mL), to which 4CzIPN has partial solubility. The bright yellow filtrate was collected and the solvent was removed in vacuo by rotary evaporation. The compound (6.37 g, 92%) was obtained as a bright yellow solid. The compound data was in agreement with the literature (Nature 2012, 492, 234–238).

$^1$H NMR (400 MHz, CDCl₃) δ 8.22 (d, $J = 7.7$ Hz, 2H), 7.77 – 7.64 (m, 8H), 7.48 (t, $J = 7.0$ Hz, 2H), 7.32 (d, $J = 7.5$ Hz, 2H), 7.25 – 7.18 (m, 4H), 7.13 – 7.02 (m, 8H), 6.82 (t, $J = 8.1$ Hz, 4H), 6.62 (t, $J = 7.5$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl₃) δ 145.2, 144.62, 134.0, 138.2, 137.0, 134.8, 127.0, 125.8, 125.0, 124.8, 124.5, 123.9, 122.4, 121.9, 121.4, 121.0, 120.4, 119.7, 116.4, 111.6, 110.0, 109.5, 109.4.

3. Investigation of the Key Reaction Parameters

3.1 Control experiment

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation</th>
<th>Conv.$^a$ (%)</th>
<th>Yield.$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>&gt;99</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>without 4CzIPN</td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>without Pd(Xantphos)Cl₂</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>

S4
Reaction condition: 4-iodotoluene (0.2 mmol), Glyoxylic acid monohydrate (0.3 mmol) (Glyoxylic acid monohydrate was lyophilized in a lyophilizer for 24 hours), 4CzIPN (5 mol %), Pd(Xantphos)Cl$_2$ (5 mol %), CsOAc (150 mol %), DMF (2 mL), irradiation by 36W Blue-LEDS at room temperature for 10 h under Ar atomphere. *GC yields using diphenyl as an internal standard.

3.2 Optimize the reaction conditions

3.2.1 Screening of Photoredox Catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photoredox catalyst</th>
<th>Conv.$^a$ (%)</th>
<th>Yield$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><a href="PF$_6$">Ir(df(CF$_3$)ppy)$_2$(dtbbpy)</a></td>
<td>86</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>Ir(ppy)$_2$(dtbbpy)PF$_6$</td>
<td>&gt;99</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>4CzIPN</td>
<td>&gt;99</td>
<td>71</td>
</tr>
<tr>
<td>4$^b$</td>
<td><a href="PF$_6$">Ir(df(CF$_3$)ppy)$_2$(dtbbpy)</a></td>
<td>80</td>
<td>7</td>
</tr>
</tbody>
</table>

*GC yields using diphenyl as an internal standard. $^b$ Using Pd(PPh$_3$)$_2$Cl$_2$ (5 mol %) and Xantphos (6 mol %) instead of Pd(xantphos)Cl$_2$ (5 mol %).

3.2.2 Screening of Solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variations from above conditions</th>
<th>Conv.$^a$ (%)</th>
<th>Yield$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>&gt;99</td>
<td>71</td>
</tr>
</tbody>
</table>

S5
2. THF instead of DMF >90 trace
3. Dioxane instead of DMF >90 trace
4. MeCN instead of DMF >90 trace
5. EtOAc instead of DMF >90 trace
6. DCM instead of DMF >90 trace
7. Toluene instead of DMF >90 trace
8. Acetone instead of DMF >90 trace
9. DMSO instead of DMF 98 22
10. NMP instead of DMF >99 61
11. DMA instead of DMF >99 60
12. Add to 1 equiv H₂O 99 61
13. Add to 5 equiv H₂O 68 5

*GC yields using diphenyl as an internal standard.

### 3.2.3 Screening of Ligand

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variations from above conditions</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>&gt;99</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PhCN)₂Cl₂/Xantphos (1:1) instead of Pd(Xantphos)Cl₂</td>
<td>97</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PhCN)₂Cl₂/1,10-Phen (1:1) instead of Pd(Xantphos)Cl₂</td>
<td>35</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PhCN)₂Cl₂/dCype (1:1) instead of Pd(Xantphos)Cl₂</td>
<td>30</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PhCN)₂Cl₂/dppp (1:1) instead of Pd(Xantphos)Cl₂</td>
<td>58</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>Pd(PhCN)₂Cl₂/PPh₃ (1:2) instead of Pd(Xantphos)Cl₂</td>
<td>54</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Pd(PhCN)₂Cl₂/PCy₃ (1:2) instead of Pd(Xantphos)Cl₂</td>
<td>49</td>
<td>trace</td>
</tr>
</tbody>
</table>

*GC yields using diphenyl as an internal standard. Xantphos = 4,5-Bis(diphenylphosphino)-9,9-diMethylxanthene, 1,10-Phen = 1,10-Phenanthroline, dCype = 1,2-Bis(dicyclohexylphosphino)ethane, dppp = 1,3-Bis(diphenylphosphino)propane, PPh₃ = Triphenylphosphine, PCy₃ = Tricyclohexyl phosphine.

### 3.2.4 Screening of Base

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variations from above conditions</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>&gt;99</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>Cs₂CO₃ instead of CsOAc</td>
<td>75</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>K₂HPO₄ instead of CsOAc</td>
<td>38</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>KOAC instead of CsOAc</td>
<td>70</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>KHCO₃ instead of CsOAc</td>
<td>74</td>
<td>35</td>
</tr>
</tbody>
</table>
6  $\text{K}_2\text{CO}_3$ instead of CsOAc  71  29
7  Et$_3$N instead of CsOAc  62  16

*GC yields using diphenyl as an internal standard.

3.2.5 Screening of Solution Concentration

\[ \text{Reactor condition: 4-iodotoluene (0.2 mmol), Glyoxylic acid monohydrate (0.3 mmol), 4CzIPN (5 mol %), Pd(Xantphos)Cl$_2$ (5 mol %), CsOAc (150 mol %), DMF (2 mL), irradiation by 36W Blue-LEDs at room temperature for 10 h under Ar atomphere.} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variations from standard conditions</th>
<th>Conv.$^a$ (%)</th>
<th>Yield$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>&gt;99</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>DMF (1 mL)</td>
<td>65</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>DMF (3 mL)</td>
<td>89</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>Glyoxylic acid (0.2 mmol)</td>
<td>96</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>Glyoxylic acid (0.4 mmol)</td>
<td>&gt;99</td>
<td>71</td>
</tr>
<tr>
<td>6</td>
<td>Glyoxylic acid (0.5 mmol)</td>
<td>&gt;99</td>
<td>63</td>
</tr>
<tr>
<td>7</td>
<td>CsOAc (0.2 mmol)</td>
<td>86</td>
<td>46</td>
</tr>
<tr>
<td>8</td>
<td>CsOAc (0.4 mmol)</td>
<td>&gt;99</td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>CsOAc (0.5 mmol)</td>
<td>&gt;99</td>
<td>65</td>
</tr>
</tbody>
</table>

4. Experimental Procedures and Spectral Data

4.1 Experimental procedures

General Procedure for Decarboxylative Formylation

A 10 mL Schlenk tube containing a stirring bar was charged with aryl halide (1.0 equiv, 0.2 mmol), Glyoxylic acid monohydrate (1.5 equiv, 0.3 mmol, 27.6 mg), 4CzIPN (5 mol %, 7.9 mg), Pd(Xantphos)Cl$_2$ (5 mol %, 7.6 mg) and CsOAc (1.5 equiv, 0.3 mmol, 57.6 mg). The tube was then evacuated and back-filled with argon three times. Anhydrous N,N-Dimethylformamide (DMF, 2.0 mL) was added subsequently. The reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 1.0 cm from the bulb) at 30-35 °C for 10 h. After reaction
completed, the mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel with petroleum ether / ethyl acetate.

4.2 Spectral Data

4-methylbenzaldehyde (1): Following the general procedure, obtained in 78% yield as colorless liquid after silica gel chromatography. (18.7 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.96 (s, 1H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 7.8$ Hz, 2H), 2.44 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.0, 145.6, 134.2, 129.9, 129.7, 21.9.

3,5-dimethylbenzaldehyde (2): Following the general procedure, obtained in 75% yield as colorless liquid after silica gel chromatography. (20.1 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Org. Lett., 2014, 16, 3492–3495).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.95 (s, 1H), 7.49 (s, 2H), 7.26 (s, 1H), 2.39 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.8, 138.8, 136.6, 136.2, 127.6, 21.1.

4-(tert-butyl)benzaldehyde (3): Following the general procedure, obtained in 80% yield as colorless liquid after silica gel chromatography. (25.9 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature
4-fluorobenzaldehyde (4): Following the general procedure, obtained in 61% yield as colorless liquid after silica gel chromatography. (15.1 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.97 (s, 1H), 7.98 – 7.85 (m, 2H), 7.26 – 7.16 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.5, 166.5 (d, $J = 256.7$ Hz), 132.8 (d, $J = 9.5$ Hz), 132.2 (d, $J = 9.7$ Hz), 116.4 (d, $J = 22.3$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -102.4.

4-chlorobenzaldehyde (5): Following the general procedure, obtained in 62% yield as colorless liquid after silica gel chromatography. (17.4 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.99 (s, 1H), 7.83 (d, $J = 8.1$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.9, 141.0, 134.7, 130.9, 129.5.

4-bromobenzaldehyde (6): Following the general procedure, obtained in 64% yield as white solid after silica gel chromatography. (23.6 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Org. Lett., 2014, 16, 390–393.)
$^1$H NMR (400 MHz, CDCl$_3$) δ 9.98 (s, 1H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.69 (d, $J = 8.1$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.1, 135.1, 132.5, 131.0, 129.8.

**4-methoxybenzaldehyde (7):** Following the general procedure, obtained in 60% yield as light yellow liquid after silica gel chromatography. (16.3 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (*Chem. Commun.*, 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.89 (s, 1H), 7.84 (d, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 7.6$ Hz, 2H), 3.89 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.9, 164.6, 132.0, 129.9, 114.3, 55.6.

**3-chlorobenzaldehyde (8):** Following the general procedure, obtained in 65% yield as colorless liquid after silica gel chromatography. (18.2 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (*Org. Lett.*, 2017, 19, 1646–1649).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.98 (s, 1H), 7.86 (s, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.9, 137.8, 135.5, 134.4, 130.4, 129.3, 128.0.

**3-formylbenzonitrile (9):** Following the general procedure, obtained in 87% yield as light yellow solid after silica gel chromatography. (22.8 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (*Org. Lett.*, 2014, 16, 390–393).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.06 (s, 1H), 8.18 (s, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 7.92 (d, $J = 7.7$ Hz, 1H), 7.71 (t, $J = 7.7$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.0, 137.3, 136.8, 133.4, 133.2, 130.2, 117.6, 113.7.
4-formylbenzonitrile (10): Following the general procedure, obtained in 67% yield as white solid after silica gel chromatography. (17.6 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.10 (s, 1H), 8.01 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.6, 138.7, 132.9, 129.9, 117.7, 117.6.

4-formylbenzonitrile (11): Following the general procedure, obtained in 68% yield as white solid after silica gel chromatography. (17.8 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.10 (s, 1H), 8.01 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.6, 138.7, 132.9, 129.9, 117.7, 117.6.

4-(trifluoromethyl)benzaldehyde (12): Following the general procedure, obtained in 73% yield as colorless liquid after silica gel chromatography. (25.4 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Angew. Chem. Int. Ed., 2014, 53, 10090–10094).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.11 (s, 1H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.1, 138.6, 135.6 (q, $J = 32.8$ Hz), 129.9, 126.1 (q, $J = 3.8$ Hz), 123.4 (q, $J = 272.9$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.2.
4-(methylsulfonyl)benzaldehyde (13): Following the general procedure, obtained in 62% yield as white solid after silica gel chromatography. (22.8 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with the literature (Angew. Chem. Int. Ed., 2017, 56, 1500–1505).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.11 (s, 1H), 8.11 (d, $J$ = 8.1 Hz, 2H), 7.99 (d, $J$ = 8.1 Hz, 2H), 2.67 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.4, 191.6, 141.2, 139.1, 129.8, 128.8, 27.0.

[1,1'-biphenyl]-4-carbaldehyde (14): Following the general procedure, obtained in 81% yield as white solid after silica gel chromatography. (29.5 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.06 (s, 1H), 8.02 – 7.91 (m, 2H), 7.78 – 7.72 (m, 2H), 7.67 – 7.61 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.0, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.4.

Terephthalaldehyde (15): Following the general procedure, obtained in 83% yield as white solid after silica gel chromatography. (22.2 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.14 (s, 2H), 8.06 (s, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.5, 140.0, 130.1.
4-acetylbenzaldehyde (16): Following the general procedure, obtained in 84% yield as white solid after silica gel chromatography. (24.5 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Org. Lett., 2014, 16, 3492–3495).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.12 (s, 1H), 8.11 (d, $J$ = 8.0 Hz, 2H), 7.99 (d, $J$ = 8.0 Hz, 2H), 2.67 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.4, 191.7, 141.2, 139.0, 129.8, 128.8, 27.0.

4-acetylbenzaldehyde (17): Following the general procedure, obtained in 63% yield as white solid after silica gel chromatography. (18.6 mg, eluent: petroleum ether/ethyl acetate = 25/1). The compound data was in agreement with the literature (Org. Lett., 2014, 16, 3492–3495).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.12 (s, 1H), 8.11 (d, $J$ = 8.0 Hz, 2H), 7.99 (d, $J$ = 8.0 Hz, 2H), 2.67 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.4, 191.7, 141.2, 139.0, 129.8, 128.8, 27.0.

4-nitrobenzaldehyde (18): Following the general procedure, obtained in 62% yield as colorless liquid after silica gel chromatography. (18.7 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.17 (s, 1H), 8.41 (d, $J$ = 8.3 Hz, 2H), 8.09 (d, $J$ = 8.3 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.3, 151.2, 140.1, 130.5, 124.3.
4-nitrobenzaldehyde (19): Following the general procedure, obtained in 61% yield as colorless liquid after silica gel chromatography. (18.4 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \delta 10.17 (s, 1H), 8.41 (d, \textit{J} = 8.3 \text{ Hz}, 2H), 8.09 (d, \textit{J} = 8.3 \text{ Hz}, 2H). \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})} \delta 190.3, 151.2, 140.1, 130.5, 124.3. \]

4-formylbenzoic acid (20): Following the general procedure, obtained in 54% yield as white solid after silica gel chromatography. (16.2 mg, eluent: petroleum methanol/ethyl Acetate = 10/1). The compound data was in agreement with the literature (Angew. Chem. Int. Ed., 2017, 129, 8313–8317).

\[ \text{\textsuperscript{1}H NMR (400 MHz, DMSO)} \delta 13.42 (s, 1H), 10.11 (s, 1H), 8.14 (d, \textit{J} = 7.9 \text{ Hz}, 2H), 8.02 (d, \textit{J} = 7.9 \text{ Hz}, 2H). \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, DMSO)} \delta 193.5, 167.0, 139.4, 136.1, 130.4, 130.0. \]

ethyl 4-formylbenzoate (21): Following the general procedure, obtained in 62% yield as white solid after silica gel chromatography. (22.1 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Org. Lett., 2017, 19, 1646–1649).

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \delta 10.11 (s, 1H), 8.21 (d, \textit{J} = 8.0 \text{ Hz}, 2H), 7.96 (d, \textit{J} = 8.0 \text{ Hz}, 2H), 4.42 (q, \textit{J} = 7.1 \text{ Hz}, 2H), 1.43 (t, \textit{J} = 7.1 \text{ Hz}, 3H). \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})} \delta 191.8, 165.6, 139.1, 135.5, 130.2, 129.5, 61.6, 14.3. \]

1-naphthaldehyde (22): Following the general procedure, obtained in 60% yield as a yellow oil after silica gel chromatography. (18.7 mg, eluent: petroleum ether/ethyl ether/ethyl acetate = 15/1).
acetate = 25/1). The compound data was in agreement with the literature (Org. Lett., 2014, 16, 3492–3495).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.41 (s, 1H), 9.26 (d, \(J = 8.7\) Hz, 1H), 8.11 (d, \(J = 8.2\) Hz, 1H), 8.00 (d, \(J = 7.0\) Hz, 1H), 7.93 (d, \(J = 8.1\) Hz, 1H), 7.70 (t, \(J = 7.6\) Hz, 1H), 7.67 – 7.57 (m, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 193.6, 136.7, 135.3, 133.8, 131.4, 130.6, 129.1, 128.5, 127.0, 124.9.

2-naphthaldehyde (23): Following the general procedure, obtained in 76% yield as white solid after silica gel chromatography. (23.7 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Angew. Chem. Int. Ed., 2014, 53, 10090–10094).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.16 (s, 1H), 8.34 (s, 1H), 8.08 – 7.86 (m, 4H), 7.69 – 7.54 (m, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 192.3, 136.5, 134.6, 134.1, 132.7, 129.5, 129.1, 128.1, 127.1, 122.8.

2-(furan-2-ylmethoxy)benzaldehyde (24): Following the general procedure, obtained in 68% yield as white solid after silica gel chromatography. (27.5 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature. (Chem. Ber., 1981, 114, 384–388)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.46 (s, 1H), 7.88 – 7.81 (m, 1H), 7.60 – 7.53 (m, 1H), 7.47 – 7.46 (m, 1H), 7.13 (d, \(J = 8.4\) Hz, 1H), 7.09 – 7.04 (m, 1H), 6.46 (d, \(J = 3.2\) Hz, 1H), 6.42 – 6.39 (m, 1H), 5.13 (s, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 189.8, 160.8, 149.4, 143.4, 135.8, 128.4, 125.5, 121.4, 113.4, 110.6, 110.5, 63.1.
4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzaldehyde (25): Following the general procedure, obtained in 65% yield as white solid after silica gel chromatography. (28.3 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Adv. Synth. Catal., 2014, 356, 1527–1532)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 10.04 (s, 1H), 7.96 (d, J = 8.1 \text{ Hz}, 2H), 7.85 (d, J = 8.1 \text{ Hz}, 2H), 3.80 (s, 4H), 1.04 (s, 6H). \\
\text{C NMR (101 MHz, CDCl}_3\text{)} & \delta 193.0, 137.8, 134.3, 128.7, 72.4, 31.9, 21.9. \text{ The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.}
\end{align*}
\]

tert-butyl (4-formylphenyl)carbamate (26): Following the general procedure, obtained in 63% yield as white solid after silica gel chromatography. (27.9 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Org. Lett., 2013, 15, 1394–1397).

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 9.89 (s, 1H), 7.82 (d, J = 8.4 \text{ Hz}, 2H), 7.57 (d, J = 8.4 \text{ Hz}, 2H), 7.19 (s, 1H), 1.53 (s, 9H). \\
\text{C NMR (101 MHz, CDCl}_3\text{)} & \delta 191.1, 152.2, 144.4, 131.3, 131.2, 117.8, 81.4, 28.3.
\end{align*}
\]

methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-formylphenyl)propanoate (27):
Following the general procedure, obtained in 68% yield as a yellow oil after silica gel chromatography. (41.8 mg, eluent: petroleum ether/ethyl acetate = 8/1). The compound data was in agreement with the literature (Synthetic Communications, 1998, 28, 4279–4285).
$^1$H NMR (400 MHz, CDCl$_3$) δ 10.00 (s, 1H), 7.83 (d, $J = 7.7$ Hz, 2H), 7.32 (d, $J = 7.7$ Hz, 2H), 5.05 (d, $J = 7.0$ Hz, 1H), 4.64 (d, $J = 6.3$ Hz, 1H), 3.74 (s, 3H), 3.36 – 3.02 (m, 2H), 1.42 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.8, 171.9, 154.9, 143.4, 135.3, 130.0, 129.9, 80.2, 77.2, 54.2, 52.4, 38.7, 29.7, 28.3.

(8S,9R,13R,14R,17R)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-2-carbaldehyde (28): Following the general procedure, obtained in 66% yield as white solid after silica gel chromatography. (43.3 mg, eluent: petroleum ether/ethyl acetate = 5/1). (mp 168.6 – 170.8 °C)

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.39 (s, 1H), 7.75 (s, 1H), 6.67 (s, 1H), 3.89 (s, 3H), 3.38 (s, 3H), 3.32 (t, $J = 8.3$ Hz, 1H), 2.96 – 2.87 (m, 2H), 2.44 – 2.33 (m, 1H), 2.22 – 2.12 (m, 1H), 2.12 – 2.01 (m, 2H), 1.96 – 1.86 (m, 1H), 1.74 – 1.64 (m, 1H), 1.62 – 1.16 (m, 7H), 0.79 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 189.7, 159.7, 146.3, 133.2, 125.7, 122.7, 111.7, 90.7, 58.0, 55.6, 50.2, 43.6, 43.2, 38.4, 37.9, 30.5, 27.8, 26.9, 26.3, 23.0, 11.5.


thiophene-2-carbaldehyde (29): Following the general procedure, obtained in 72% yield as yellow liquid after silica gel chromatography. (16.1 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Chem. Commun., 2014, 50, 2330–2333).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.95 (s, 1H), 7.81 – 7.75 (m, 2H), 7.24 – 7.21 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 183.1, 144.0, 136.4, 135.2, 128.3.
quinoline-3-carbaldehyde (30): Following the general procedure, obtained in 72% yield as brown liquid after silica gel chromatography. (16.1 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Chem. Commun., 2015, 51, 6572–6575).

\[
\begin{array}{c}
\text{CHO} \\
\text{OH} \\
\text{CHO}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.94 (s, 1H), 8.13 (dd, $J = 2.8, 1.0$ Hz, 1H), 7.56 (dd, $J = 5.1, 0.8$ Hz, 1H), 7.39 (dd, $J = 5.0, 2.9$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 185.0, 143.0, 136.8, 127.4, 125.3.

furan-2,5-dicarbaldehyde (31): Following the general procedure, obtained in 81% yield as white solid after silica gel chromatography. (20.0 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with the literature (J. Am. Chem. Soc., 2016, 138, 8344–8347).

\[
\begin{array}{c}
\text{CHO} \\
\text{OHC} \\
\text{CHO}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.87 (s, 2H), 7.35 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.2, 154.2, 119.3.

6-fluoronicotinaldehyde (32): Following the general procedure, obtained in 65% yield as colorless liquid after silica gel chromatography. (16.3 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Biochemistry, 2010, 49, 10421–10439).

\[
\begin{array}{c}
\text{CHO} \\
\text{CHO} \\
\text{F}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.09 (s, 1H), 8.76 (d, $J = 2.0$ Hz, 1H), 8.42 – 8.25 (m, 1H), 7.11 (dd, $J = 8.5, 2.6$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.7, 166.3 (d, $J = 248.5$ Hz), 152.1 (d, $J = 16.7$ Hz), 141.0 (d, $J = 9.9$ Hz), 130.3 (d, $J = 4.2$ Hz), 110.8 (d, $J = 37.6$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.7.
**benzo[b]thiophene-2-carbaldehyde (33):** Following the general procedure, obtained in 77% yield as yellow solid after silica gel chromatography. (24.9 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Org. Lett., 2014, 16, 3492–3495).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.11 (s, 1H), 8.03 (s, 1H), 7.99 – 7.84 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 184.7, 143.3, 142.7, 138.5, 134.5, 128.2, 126.3, 125.3, 123.3.

![benzo[b]thiophene-2-carbaldehyde](image)

**1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (34):** Following the general procedure, obtained in 70% yield as brown solid after silica gel chromatography. (39.9 mg, eluent: petroleum ether/ethyl acetate = 4/1). The compound data was in agreement with the literature (Eur. J. Med. Chem., 2012, 53, 283–291).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.10 (s, 1H), 8.28 – 8.21 (m, 2H), 8.01 – 7.95 (m, 3H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.56 – 7.49 (m, 2H), 7.45 – 7.33 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 185.4, 137.4, 136.2, 135.3, 134.8, 129.7, 127.2, 126.4, 126.3, 125.2, 122.7, 122.5, 113.3.

![1-(phenylsulfonyl)-1H-indole-3-carbaldehyde](image)

**6-chloronicotinaldehyde (35):** Following the general procedure, obtained in 53% yield as colorless liquid after silica gel chromatography. (14.9 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Org. Lett., 2005, 7, 2965–2967).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.10 (s, 1H), 8.87 (s, 1H), 8.14 (d, $J = 8.2$ Hz, 1H), 7.52 (d, $J = 8.3$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 189.2, 157.0, 152.4, 138.0, 130.4, 125.2.
quinoline-3-carbaldehyde (36): Following the general procedure, obtained in 57% yield as light yellow solid after silica gel chromatography. (17.9 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Angew. Chem. Int. Ed., 2017, 56, 1500–1505).

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.26 (s, 1H), 9.37 (s, 1H), 8.64 (s, 1H), 8.20 (d, $J = 8.5$ Hz, 1H), 8.00 (d, $J = 8.2$ Hz, 1H), 7.90 (t, $J = 7.7$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.8, 150.5, 149.1, 140.2, 132.7, 129.7, 129.5, 128.6, 127.9, 127.1.
5. NMR Spectra

$^1$H NMR spectrum of 4CzIPN

$^{13}$C NMR spectrum of 4CzIPN
$^1$H NMR spectrum of 4-methylbenzaldehyde (I)

$^{13}$C NMR spectrum of 4-methylbenzaldehyde (I)
$^1$H NMR spectrum of 3,5-dimethylbenzaldehyde (2)

$^{13}$C NMR spectrum of 3,5-dimethylbenzaldehyde (2)
$^{1}$H NMR spectrum of 4-(tert-butyl)benzaldehyde (3)

$^{13}$C NMR spectrum of 4-(tert-butyl)benzaldehyde (3)
$^1$H NMR spectrum of 4-fluorobenzaldehyde (4)

$^{13}$C NMR spectrum of 4-fluorobenzaldehyde (4)
$^{19}$F NMR spectrum of 4-fluorobenzaldehyde (4)

$^1$H NMR spectrum of 4-chlorobenzaldehyde (5)
$^{13}$C NMR spectrum of \textbf{4-chlorobenzaldehyde (5)}

\[\text{Diagram of 4-chlorobenzaldehyde (5)}\]

$^1$H NMR spectrum of \textbf{4-bromobenzaldehyde (6)}

\[\text{Diagram of 4-bromobenzaldehyde (6)}\]
$^{13}$C NMR spectrum of 4-bromobenzaldehyde (6)

$^1$H NMR spectrum of 4-methoxybenzaldehyde (7)
$^{13}$C NMR spectrum of 4-methoxybenzaldehyde (7)

$^1$H NMR spectrum of 3-chlorobenzaldehyde (8)
$^{13}$C NMR spectrum of 3-chlorobenzaldehyde (8)

$^1$H NMR spectrum of 3-formylbenzonitrile (9)
$^{13}$C NMR spectrum of 3-formylbenzonitrile (9)

$^1$H NMR spectrum of 4-formylbenzonitrile (10, 11)
$^{13}$C NMR spectrum of 4-formylbenzonitrile (10, 11)

$^1$H NMR spectrum of 4-(trifluoromethyl)benzaldehyde (12)
$^{13}$C NMR spectrum of 4-(trifluoromethyl)benzaldehyde (12)

$^{19}$F NMR spectrum of 4-(trifluoromethyl)benzaldehyde (12)
$^1$H NMR spectrum of 4-(methylsulfonyl)benzaldehyde (13)

$^{13}$C NMR spectrum of 4-(methylsulfonyl)benzaldehyde (13)
$^1$H NMR spectrum of [1,1'-biphenyl]-4-carbaldehyde (14)

$^{13}$C NMR spectrum of [1,1'-biphenyl]-4-carbaldehyde (14)
$^1$H NMR spectrum of Terephthalaldehyde (15)

$^{13}$C NMR spectrum of Terephthalaldehyde (15)
$^1$H NMR spectrum of 4-acetylbenzaldehyde (16, 17)

$^{13}$C NMR spectrum of 4-acetylbenzaldehyde (16, 17)
$^1$H NMR spectrum of 4-nitrobenzaldehyde (18, 19)

$^{13}$C NMR spectrum of 4-nitrobenzaldehyde (18, 19)
$^1$H NMR spectrum of 4-formylbenzoic acid (20)

$^{13}$C NMR spectrum of 4-formylbenzoic acid (20)
$^1$H NMR spectrum of ethyl 4-formylbenzoate (21)

$^{13}$C NMR spectrum of ethyl 4-formylbenzoate (21)
$^1$H NMR spectrum of 1-naphthaldehyde (22)

$^{13}$C NMR spectrum of 1-naphthaldehyde (22)
$^1$H NMR spectrum of 2-naphthaldehyde (23)

$^{13}$C NMR spectrum of 2-naphthaldehyde (23)
$^1$H NMR spectrum of 2-(furan-2-ylmethoxy)benzaldehyde (24)

$^{13}$C NMR spectrum of 2-(furan-2-ylmethoxy)benzaldehyde (24)
$^1$H NMR spectrum of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzaldehyde (25)

$^{13}$C NMR spectrum of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzaldehyde (25)
$^1$H NMR spectrum of tert-butyl (4-formylphenyl)carbamate (26)

$^{13}$C NMR spectrum of tert-butyl (4-formylphenyl)carbamate (26)
$^1$H NMR spectrum of methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-formylphenyl)propanoate (27)

$^{13}$C NMR spectrum of methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-formylphenyl)propanoate (27)
$^{1}$H NMR spectrum of (8S,9R,13R,14R,17R)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-2-carbaldehyde (28)

$^{13}$C NMR spectrum of (8S,9R,13R,14R,17R)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-2-carbaldehyde (28)
$^1$H NMR spectrum of thiophene-2-carbaldehyde (29)

$^{13}$C NMR spectrum of thiophene-2-carbaldehyde (29)
$^1$H NMR spectrum of quinoline-3-carbaldehyde (30)

$^{13}$C NMR spectrum of quinoline-3-carbaldehyde (30)
$^1$H NMR spectrum of furan-2,5-dicarbaldehyde (31)

$^{13}$C NMR spectrum of furan-2,5-dicarbaldehyde (31)
$^1$H NMR spectrum of 6-fluoronicotinaldehyde (32)

$^{13}$C NMR spectrum of 6-fluoronicotinaldehyde (32)
$^{19}$F NMR spectrum of 6-fluoronicotinaldehyde (32)

$^1$H NMR spectrum of benzo[b]thiophene-2-carbaldehyde (33)
$^{13}$C NMR spectrum of benzo[b]thiophene-2-carbaldehyde (33)

$^1$H NMR spectrum of 1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (34)
$^{13}$C NMR spectrum of 1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (34)

$^1$H NMR spectrum of 6-chloronicotinaldehyde (35)
$^{13}$C NMR spectrum of 6-chloronicotinaldehyde (35)

$^1$H NMR spectrum of quinoline-3-carbaldehyde (36)
$^{13}$C NMR spectrum of quinoline-3-carbaldehyde (36)