Supporting Information

Nickel-catalyzed decarbonylative silylation, borylation, and amination of arylamides via a deamidative reaction pathway

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I. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and freshly distilled prior to use. Ni(COD)$_2$ and tri-n-butylphosphine ligand were purchased from Sigma-Aldrich, and CuF$_2$ was purchased from Fluorochem. Toluene used in reactions was analytical grade and distilled from benzophenone/Na. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel (Macherey Nagel, particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume. $^1$H-NMR and $^{13}$C-NMR were recorded on a Varian AV400 or AV600 spectrometer in CDCl$_3$ and are reported relative to the solvents residual $^1$H-signal (CHCl$_3$, δ(H) 7.26). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), br s (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants ($J$) are in Hertz (Hz). Melting points were measured using open glass capillaries in a Buchi SMP-20 apparatus. IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$). Mass spectra (EI-MS, 70 eV) were conducted on a Finnigan SSQ 7000 spectrometer.
II. Synthesis of the Starting Materials

Table S1. Structures of amide substrates

Amides in Table S1 were prepared by following method A.

Method A

Thionyl chloride (9 mL) was added to the carboxylic acid (1.0 equiv, 10.0 mmol) and the mixture was refluxed for 2 h. The solution was then concentrated in vacuo. An oven-dried round-bottomed flask (100 mL) equipped with a stir bar was charged with glutarimide (909.4 mg, 0.91 equiv, 8.04 mmol), acyl chloride (1.0 equiv, 8.84 mmol), 4-dimethylaminopyridine (DMAP, 280.4 mg, 0.25 equiv, 2.5 mmol) and dichloromethane (50 mL). Triethylamine (typically, 2.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred overnight at room temperature. After the indicated time, the reaction mixture was diluted with Et₂O (20 mL) and filtered. The organic layer was washed with HCl (1.0 N, 30 mL), brine (30 mL), dried, and concentrated. The residue was purified by recrystallization or chromatography on silica gel to afford the corresponding amide.
1-([1,1'-biphenyl]-4-carbonyl)piperidine-2,6-dione (6b)

Following method A, the product was isolated as a white solid after chromatography on silica gel. **Mp**: 194-195 °C; **1H NMR** (600 MHz, CDCl₃): δ = 7.93 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.61-7.59 (m, 2H), 7.50-7.46 (m, 2H), 7.44-7.40 (m, 1H), 2.80 (t, J = 6.6 Hz, 4H), 2.20-2.14 (m, 2H); **13C NMR** (150 MHz, CDCl₃): δ = 171.9, 170.4, 147.8, 139.4, 130.7, 130.4, 129.0, 128.6, 127.8, 127.4, 17.5; **IR (ATR)**: ν = 3732, 3391, 2913, 2327, 2077, 1745, 1682, 1598, 1463, 1409, 1336, 1247, 1173, 1062, 1002, 927, 849, 744, 697 cm⁻¹; **MS (EI)**: m/z (%) = 293.0 (M⁺, 91), 180.9 (100), 151.9 (34).

1-(4-(tert-butyl)benzoyl)piperidine-2,6-dione (6c)

Following method A, the product was isolated as a white solid after chromatography on silica gel. **Mp**: 142-143 °C; **1H NMR** (400 MHz, CDCl₃): δ = 7.79 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 2.77 (t, J = 6.6 Hz, 4H), 2.19-2.10 (m, 2H), 1.33 (s, 9H); **13C NMR** (100 MHz, CDCl₃): δ = 171.9, 170.4, 147.8, 139.4, 130.7, 130.4, 129.0, 126.2, 35.4, 32.4, 31.0, 17.5; **IR (ATR)**: ν = 3412, 3391, 2913, 2328, 2085, 1746, 1682, 1601, 1466, 1411, 1339, 1250, 1180, 1140, 1063, 1006, 932, 849, 805, 729, 688 cm⁻¹; **MS (EI)**: m/z (%) = 273.0 (M⁺, 71), 257.9 (62), 230.0 (54), 161.0 (100).

1-([1,1'-biphenyl]-2-carbonyl)piperidine-2,5-dione (6g)

Following method A, the product was isolated as a light yellow solid after chromatography on silica gel. **Mp**: 141-142 °C; **1H NMR** (600 MHz, CDCl₃): δ = 8.00-7.98 (m, 1H), 7.59-56 (m, 1H), 7.50-7.48 (m, 1H), 7.42-7.39 (m, 3H), 7.34-7.32 (m, 2H), 7.26-7.24 (m, 1H), 2.20 (t, J = 6.6 Hz, 4H), 1.49-1.44 (m, 2H); **13C NMR** (150 MHz, CDCl₃): δ = 171.4, 170.6, 142.4, 140.5, 132.9, 132.1, 131.8, 131.6, 128.9, 128.3, 128.0, 127.7, 32.4, 16.1; **IR (ATR)**: ν = 3056, 2962, 2317, 2093, 1928, 1710, 1599, 1446, 1235, 1124, 996, 921, 745, 704 cm⁻¹; **MS (EI)**: m/z (%) = 293.9 (M⁺, 52), 292.9 (88), 264.9 (59), 180.8 (100), 151.9 (65).

1-(benzofuran-2-carbonyl)piperidine-2,6-dione (6k)

Following method A, the product was isolated as a light yellow solid after
1-(benzo[b]thiophene-2-carbonyl)piperidine-2,6-dione (6l)

Following method A, the product was isolated as brown solid after chromatography on silica gel. **Mp**: 115-116 °C; **^1H NMR** (600 MHz, CDCl₃): δ = 7.72-7.65 (m, 2H), 7.54-7.48 (m, 2H), 7.33-7.29 (m, 1H), 2.78 (t, J = 6.6 Hz, 4H), 2.17-2.09 (m, 2H); **^13C NMR** (150 MHz, CDCl₃): δ = 171.7, 161.3, 156.2, 147.5, 129.4, 126.9, 124.3, 123.6, 117.7, 112.5, 32.3, 17.3; **IR (ATR)**: ν = 3842, 3388, 2914, 2323, 2045, 1974, 1744, 1688, 1553, 1331, 1249, 1166, 1139, 1078, 1002, 901, 817, 745, 680 cm⁻¹; **MS (EI)**: m/z (%) = 256.9 (M⁺, 100), 144.9 (72), 133.9 (35).

1-(2-phenylquinoline-3-carbonyl)piperidine-2,6-dione (6m)

Following method A, the product was isolated as white solid after chromatography on silica gel. **Mp**: 200-201 °C; **^1H NMR** (600 MHz, CDCl₃): δ = 8.67 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 7.4 Hz, 2H), 7.94 (s, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 7.9 Hz, 1H), 7.56-7.49 (m, 3H), 2.78 (t, J = 6.5 Hz, 4H), 2.17-2.08 (m, 2H); **^13C NMR** (150 MHz, CDCl₃): δ = 172.1, 170.8, 156.8, 149.3, 138.7, 137.8, 130.5, 130.3, 129.8, 129.0, 128.8, 127.4, 125.0, 123.0, 119.1, 32.5, 17.3; **IR (ATR)**: ν = 3746, 3060, 2954, 2322, 2059, 1958, 1766, 1679, 1592, 1546, 1331, 1241, 1175, 1129, 1073, 997, 923, 769, 674 cm⁻¹; **MS (EI)**: m/z (%) = 343.9 (M⁺, 100), 259.9 (27.8), 203.9 (46.0).
III. Optimization Tables

Borylation

\[
\begin{align*}
\text{6a} + \text{B}_2\text{pin}_2 & \xrightarrow{\text{Ni(cod)}_2 (10 \text{ mol\%})} \text{10a} \\
\text{Reagents and conditions: 6a (53.5 mg, 0.20 mmol), 9 (76.2 mg, 0.30 mmol), Ni(cod)}_2 (5.5 \text{ mg, 10 mol\%}), \text{ligand, base (1.5 equiv.), solvent (1 mL, 0.2 M), 160 °C, 36 h.} \quad & \text{Yield for isolated product.}
\end{align*}
\]

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<th>Base</th>
<th>Solvent</th>
<th>Yield (%)</th>
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<td>2</td>
<td>Pcy$_3$ (40%)</td>
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<td>P&quot;Bu$_3$ (40%)</td>
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</table>

Amination

\[
\begin{align*}
\text{6a} + \text{PhNH} & \xrightarrow{1. \text{Ni(cod)}_2 (10 \text{ mol\%})} \xrightarrow{2. \text{Imine cleavage}} \text{12a} \\
\text{Reagents and conditions: 6a (53.5 mg, 0.20 mmol), 11 (72.5 mg, 0.40 mmol), Ni(cod)}_2 (5.5 \text{ mg, 10 mol\%}), \text{ligand (10 mol\%), base (1.5 equiv.), solvent (1 mL, 0.2 M), 170 °C, 24 h.} \quad & \text{Yields for isolated products.}
\end{align*}
\]

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</table>
IV. Typical Procedures for the Decarbonylative Reactions

**Procedure I:**

\[
\text{amide 6 (0.20 mmol, 1.0 equiv), yellow Ni(COD)\textsubscript{2} (5.5 mg, 10 mol\%), copper fluoride (II) (6.1 mg, 30 mol\%) and potassium fluoride (34.9 mg, 0.60 mmol, 3.0 equiv). Subsequently, freshly distilled toluene (1.0 mL) was added, and then triethylsilylborane 7 (96.9 mg, 0.40 mmol, 2.0 equiv) and tri-n-butylphosphine ligand (20 μL, 40 mol\%) were added respectively via microsyringe. The tube with the mixture was sealed and removed from the glovebox. After stirring at 160 °C for 36 h, the mixture was allowed to cool to room temperature, diluted with EtOAc (5 mL) and filtered through a celite plug, eluting with additional EtOAc (10 mL). The filtrate was concentrated and purified by column chromatography on silica gel to yield the title product 8.}
\]

**Procedure II:**

\[
\text{amide 6 (0.20 mmol, 1.0 equiv), yellow Ni(COD)\textsubscript{2} (5.5 mg, 10 mol\%) and lithium carbonate (22.2 mg, 0.30 mmol, 1.5 equiv). Subsequently, freshly distilled toluene (1.0 mL) was added, and then bis(pinacolato)diboron 9 (76.2 mg, 0.30 mmol, 1.5 equiv) and tri-n-butylphosphine ligand (20 μL, 40 mol\%) were added respectively via microsyringe. The tube with the mixture was sealed and removed from the glovebox. After stirring at 160 °C for 36 h, the mixture was then allowed to cool to room temperature, diluted with EtOAc (5 mL) and filtered through a celite plug, eluting with additional EtOAc (10 mL). The filtrate was concentrated and purified by column chromatography on silica gel to yield the title product 10.}
\]
**Procedure III:**

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R=\text{NH}_{2}
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**First step:** In a nitrogen-filled glovebox, an oven-dried sealed tube containing a stirring bar was charged with amide \(6\) (0.20 mmol), yellow \(\text{Ni(cod)}_2\) (5.5 mg, 0.02 mmol, 10 mol%), dppf ligand (11.0 mg, 0.02 mmol, 10 mol%), benzophenone imine \(11\) (72.5 mg, 0.40 mmol), tripotassium phosphate (127.0 mg, 0.60 mmol) and lithium chloride (17.0 mg, 0.40 mmol) with freshly distilled toluene (1.0 mL). The reaction mixture was stirred at 170 °C for 48 h. The reaction mixture was cooled to room temperature, diluted with 10 mL diethyl ether, filtered through a pad of Celite, and concentrated in *vacuo* to give the crude ketimine.

**Second Step (Ketimine Cleavage):** The crude ketimine was suspended in a 1:1 (v/v) ratio of 1N HCl:THF (5 mL) solution and stirred at room temperature for 3-5 h. Upon consumption of the ketimine as determined by TLC, THF was removed by rotary evaporation and the aqueous residue was basified using 1N KOH to a pH range of 10 - 14. The aqueous layer was then extracted three times with ethyl acetate (30 mL). The organic layer was dried with anhydrous \(\text{Na}_2\text{SO}_4\), filtered and concentrated in *vacuo* to give the crude aniline. Upon purification via column chromatography the pure product was obtained after solvent removal.
V. Spectroscopic Data of the Products

Triethyl(naphthalen-2-yl)silane (8a)

As for general procedure I, starting from 1-(2-naphthoyl)piperidine-2,6-dione (53.5 mg, 0.20 mmol), the title product was isolated as colorless oil after flash chromatography on silica gel, 38.3 mg (79%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.98 (s, 1H), 7.85-7.81 (m, 3H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.49-7.46 (m, 2H), 1.00 (t, $J = 7.8$ Hz, 9H), 0.91-0.85 (m, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta =$ 135.0, 134.8, 133.6, 132.9, 130.6, 128.0, 127.7, 126.7, 126.1, 125.7, 7.5, 3.4; Data in accordance with the literature.¹

[1,1'-Biphenyl]-4-yltriethylsilane (8b)

As for general procedure I, starting from 1-[[1,1'-biphenyl]-4-carbonyl]piperidine-2,6-dione (58.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 40.3 mg (75%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.65-7.55 (m, 6H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H), 1.01 (t, $J = 8.0$ Hz, 9H), 0.84 (q, $J = 7.9$ Hz, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta =$ 141.4, 141.1, 136.2, 134.7, 128.7, 127.2, 127.1, 126.4, 7.4, 3.4; Data in accordance with the literature.¹

(4-(Tert-butyl)phenyl)triethylsilane (8c)

As for general procedure I, starting from 1-(4-(tert-butyl)benzoyl)piperidine-2,6-dione (54.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 25.8 mg (52%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.43 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 7.8$ Hz, 2H), 1.32 (s, 9H), 0.97 (t, $J = 7.9$ Hz, 9H), 0.78 (q, $J = 7.9$ Hz, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta =$ 151.5, 134.0, 133.8, 124.6, 34.6, 31.2, 7.5, 3.4; Data in accordance with the literature.²

Methyl 4-(triethylsilyl)benzoate (8d)

As for general procedure I, starting from methyl 4-(2,6-dioxopiperidine-1-carbonyl)benzoate (58.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 33.1 mg (66%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.99 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H), 3.91 (s, 3H), 0.96 (t,
\[ J = 7.7 \text{ Hz, 9H}, 0.81 (q, J = 7.0 \text{ Hz, 6H}); \] \text{\textsuperscript{13}C NMR (150 MHz, CDCl}_3): \delta = 167.3, 144.0, 134.1, 130.2, 128.4, 52.0, 7.3, 3.2; Data in accordance with the literature.\textsuperscript{1}

\textit{(4-methoxyphenyl)triethylsilane (8e)}

As for general procedure I, starting from 1-(4-methoxybenzoyl)piperidine-2,6-dione (49.5 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 30.3 mg (68\%). \textit{\textsuperscript{1}H NMR (600 MHz, CDCl}_3): \delta = 7.46-7.38 (m, 2H), 6.93-6.91 (m, 2H), 3.82 (s, 3H), 0.96 (t, \textit{J} = 7.9 \text{ Hz, 9H}), 0.77 (q, \textit{J} = 7.9 \text{ Hz, 6H}); \textit{\textsuperscript{13}C NMR (150 MHz, CDCl}_3): \delta = 160.1, 135.5, 128.1, 113.4, 54.9, 7.4, 3.5; Data in accordance with the literature.\textsuperscript{1}

\textit{Benzo[d][1,3]dioxol-5-yltriethylsilane (8f)}

As for general procedure I, starting from 1-(benzo[d][1,3]dioxole-5-carbonyl)piperidine-2,6-dione (52.3 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 44.9 mg (95\%). \textit{\textsuperscript{1}H NMR (600 MHz, CDCl}_3): \delta = 7.01-6.87 (m, 2H), 6.84 (d, \textit{J} = 7.5 \text{ Hz, 1H}), 5.93 (s, 2H), 0.95 (t, \textit{J} = 7.9 \text{ Hz, 9H}), 0.75 (q, \textit{J} = 7.9 \text{ Hz, 6H}); \textit{\textsuperscript{13}C NMR (150 MHz, CDCl}_3): \delta = 148.1, 147.2, 130.3, 128.0, 113.4, 108.5, 100.4, 7.4, 3.5; Data in accordance with the literature.\textsuperscript{2}

\textit{[1,1'-Biphenyl]-2-ytriethylsilane (8g)}

As for general procedure I, starting from 1-([1,1'-bibphenyl]-2-carbonyl)piperidine-2,6-dione (58.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 40.3 mg (75\%). \textit{\textsuperscript{1}H NMR (600 MHz, CDCl}_3): \delta = 7.57 (d, \textit{J} = 7.3 \text{ Hz, 1H}), 7.41-7.32 (m, 5H), 7.31-7.27 (m, 2H), 7.22 (d, \textit{J} = 7.4 \text{ Hz, 1H}), 0.81 (t, \textit{J} = 7.9 \text{ Hz, 9H}), 0.47 (q, \textit{J} = 7.9 \text{ Hz, 6H}); \textit{\textsuperscript{13}C NMR (150 MHz, CDCl}_3): \delta = 149.6, 144.6, 135.8, 135.1, 129.6, 129.1, 128.3, 127.5 127.0, 126.0, 7.5, 4.2; Data in accordance with the literature.\textsuperscript{2}

\textit{Triethyl(p-tolyl)silane (8h)}

As for general procedure I, starting from 1-(4-methylbenzoyl)piperidine-2,6-dione (46.3 mg, 0.20 mmol), the title product was isolated after
chromatography on silica gel, 25.2 mg (61%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.41 (d, $J$ = 7.9 Hz, 2H), 7.19 (d, $J$ = 7.5 Hz, 2H), 2.36 (s, 3H), 0.97 (t, $J$ = 7.9 Hz, 9H), 0.83-0.75 (m, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 138.5, 134.2, 133.7, 128.5, 21.5, 7.4, 3.4; Data in accordance with the literature.$^1$

**Triethyl(4-fluorophenyl)silane (8i)**

As for general procedure I, starting from 1-(4-fluorobenzoyl)piperidine-2,6-dione (47.0 mg, 0.20 mmol), the title product was isolated as colorless oil after flash chromatography on silica gel, 18.5 mg (44%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.48-7.43 (m, 2H), 7.08-7.01 (m, 2H), 0.95 (t, $J$ = 7.8 Hz, 9H), 0.8-0.76 (m, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 164.3, 162.7, 136.0, 135.9, 132.7, 132.7, 114.9, 114.7, 7.3, 3.4; $^{19}$F NMR (564 MHz, CDCl$_3$): $\delta$ = -112.69; IR (ATR): $\nu$ = 3031, 2951, 2882, 2327, 2102, 1898, 1586, 1498, 1459, 1231, 1161, 1100, 1007, 818, 721 cm$^{-1}$; MS (ESI): m/z (%) = 210.0 (M$^+$, 38), 182.1 (28), 181.0 (47), 153.0 (20).

**Triethyl(3-methoxyphenyl)silane (8j)**

As for general procedure I, starting from 1-(3-methoxybenzoyl)piperidine-2,6-dione (49.5 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 42.3 mg (95%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.31-7.29 (m, 1H), 7.09-7.08 (m, 1H), 7.04 (d, $J$ = 2.6 Hz, 1H), 6.91-6.89 (m, 1H), 3.82 (s, 3H), 0.97 (t, $J$ = 7.9 Hz, 9H), 0.83-0.77 (m, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 158.8, 139.1, 128.8, 126.5, 119.9, 113.6, 55.0, 7.4, 3.3. Data in accordance with the literature.$^2$

**Benzofuran-2-yltriethylsilane (8k)**

As for general procedure I, starting from 1-(benzofuran-2-carbonyl)piperidine-2,6-dione (51.5 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 28.4 mg (61%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.58 (d, $J$ = 7.6 Hz, 1H), 7.51 (d, $J$ = 8.2 Hz, 1H), 7.29-7.19 (m, 2H), 6.99 (s, 1H), 1.04 (t, $J$ = 7.9 Hz, 9H), 0.86 (q, $J$ = 7.9 Hz, 6H); $^{13}$C NMR (600 MHz, CDCl$_3$): $\delta$ = 161.6, 158.0, 127.9, 124.1, 122.2, 120.8, 117.1, 111.2, 7.3, 3.1; Data in accordance with the literature.$^1$
Benzo[b]thiophen-2-yltriethylsilane (8l)

As for general procedure I, starting from 1-(benzo[b]thiophene-2-carbonyl)piperidine-2,6-dione (54.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 28.3 mg (57%). \(^{1}H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.89 (d, J = 8.1 \text{ Hz}, 1H), 7.83 (d, J = 7.3 \text{ Hz}, 1H), 7.48 (s, 1H), 7.37-7.29 (m, 2H), 1.04 (t, J = 7.9 \text{ Hz}, 9H), 0.88 (q, J = 7.9 \text{ Hz}, 6H);\(^{13}C\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 143.5, 141.0, 139.0, 131.5, 124.0, 123.9, 123.3, 122.1, 7.4, 4.2;\) Data in accordance with the literature.\(^{1}\)

2-Phenyl-4-(triethylsilyl)quinoline (8m)

As for general procedure I, starting from 1-(2-phenylquinoline-4-carbonyl)piperidine-2,6-dione (68.9 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 44.1 mg (69%). \(^{1}H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.21 (d, J = 8.4 \text{ Hz}, 1H), 8.15 (d, J = 8.0 \text{ Hz}, 2H), 8.06 (d, J = 8.3 \text{ Hz}, 1H), 8.00 (s, 1H), 7.71 (t, J = 7.6 \text{ Hz}, 1H), 7.57-7.50 (m, 3H), 7.47 (t, J = 7.3 \text{ Hz}, 1H), 1.08 (q, J = 7.5 \text{ Hz}, 6H), 1.01 (t, J = 7.4 \text{ Hz}, 9H);\(^{13}C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 155.8, 147.6, 146.8, 140.1, 131.2, 130.8, 129.1, 128.9, 128.8, 127.6, 127.4, 126.7, 125.9, 7.6, 4.2;\) Data in accordance with the literature.\(^{1}\)

4,4,5,5-tetramethyl-2-(naphthalene-2-yl)-1,3,2-dioxaborolane (10a)

As for general procedure II, starting from 1-(2-naphthoyl)piperidine-2,6-dione (53.5 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 32.0 mg (63%). \(^{1}H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.38 (s, 1H), 7.89 (d, J = 8.0 \text{ Hz}, 1H), 7.86-7.76 (m, 3H), 7.49 (dt, J = 14.7, 7.0 \text{ Hz}, 2H), 1.40 (s, 12H);\(^{13}C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 136.2, 135.0, 132.8, 130.4, 128.6, 127.7, 127.0, 125.8, 83.9, 24.9.\) Data in accordance with the literature.\(^{4}\)

2-[[1,1'-Biphenyl]-4-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10b)

As for general procedure II, starting from 1-([1,1'-biphenyl]-4-carbonyl)piperidine-2,6-dione (58.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 34.2 mg (61%). \(^{1}H\) NMR (600 MHz,
CDCl₃): δ = 7.89 (d, J = 7.9 Hz, 2H), 7.66-7.58 (m, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 1.37 (s, 12H); ¹³C NMR (150 MHz, CDCl₃): δ = 144.0, 141.1, 135.3, 128.8, 127.6, 127.3, 126.5, 83.9, 25.0; Data in accordance with the literature.

2-[4-(diethoxymethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10c)

As for general procedure II, starting from 1-(4-(tert-butyl)benzoyl)piperidine-2,6-dione (54.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 26.0 mg (50%). ¹H NMR (600 MHz, CDCl₃): δ = 7.77 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 1.34 (s, 12H), 1.33 (s, 9H). ¹³C NMR (150 MHz, CDCl₃): δ =154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8. Data in accordance with the literature.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (10d)

As for general procedure II, starting from methyl 4-(2,6-dioxopiperidine-1-carbonyl)benzoate (58.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 27.3 mg (52%). ¹H NMR (400 MHz, CDCl₃): δ = 8.02 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 136.5, 113.3, 83.5, 55.1, 24.9. Data in accordance with the literature.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10e)

As for general procedure II, starting from 1-(4-methoxybenzoyl)piperidine-2,6-dione (49.5 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 25.3 mg (54%). ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz): δ = 162.1, 136.5, 113.3, 83.5, 55.1, 24.9; Data in accordance with the literature.
2-(benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10f)

As for general procedure II, starting from 1-(benzo[d][1,3]dioxole-5-carbonyl)piperidine-2,6-dione (52.3 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 27.8 mg (56%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.36 (d, $J$ = 7.7 Hz, 1H), 7.24 (s, 1H), 6.83 (d, $J$ = 7.8 Hz, 1H), 5.95 (s, 2H), 1.32 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.1, 147.2, 129.7, 113.9, 108.3, 100.7, 83.7, 24.8; Data in accordance with the literature.$^5$

2-Aminonaphthalene (12a)

As for general procedure III, starting from 1-(2-naphthoyl)piperidine-2,6-dione (53.5 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 16.0 mg (56%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.69 (d, $J$ = 8.2 Hz, 1H), 7.66 (d, $J$ = 8.6 Hz, 1H), 7.59 (d, $J$ = 8.3 Hz, 1H), 7.38-7.35 (m, 1H), 7.24-7.21 (m, 1H), 6.99 (d, $J$ = 1.8 Hz, 1H), 6.95 (dd, $J$ = 8.6, 2.2 Hz, 1H), 3.85 (br s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 144.0, 134.9, 129.2, 127.9, 126.3, 125.8, 122.5, 118.2, 108.6; Data in accordance with the literature.$^6$

4-phenylaniline (12b)

As for general procedure III, starting from 1-([1,1'-biphenyl]-2-carbonyl)piperidine-2,6-dione (58.7 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 16.9 mg (50%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.54-7.53 (m, 2H), 7.45-7.37 (m, 4H), 7.28-7.26 (m, 1H), 6.77-6.76 (m, 2H), 3.75 (br s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 145.8, 141.1, 131.6, 128.6, 128.0, 126.4, 126.2, 115.4; Data in accordance with the literature.$^7$

2-Phenylquinolin-4-amine (12c)

As for general procedure III, starting from 1-(2-phenylquinoline-4-carbonyl)piperidine-2,6-dione (68.9 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 23.4 mg (53%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 8.10-8.06 (m, 3H), 7.76 (d, $J$ = 8.3 Hz, 1H), 7.67 (t, $J$ = 7.6 Hz, 1H), 7.50-7.37 (m, 4H), 7.07 (s, 1H), 4.76 (br s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 158.1, 150.0, 149.1,
140.3, 130.2, 129.6, 129.0, 128.6, 127.4, 124.7, 119.9, 117.9, 101.6; Data in accordance with the literature.  

**1,3-Benzodioxol-5-amine (12d)**

As for general procedure III, starting from 1-(benzo[d][1,3]dioxole-5-carbonyl)piperidine-2,6-dione (52.3 mg, 0.20 mmol), the title product was isolated after chromatography on silica gel, 15.1 mg (55%). $^1$H NMR (CDCl$_3$): δ = 6.62 (d, $J = 8.1$ Hz, 1H), 6.29 (d, $J = 2.3$ Hz, 1H), 6.13 (dd, $J = 8.2$, 2.3 Hz, 1H), 5.86 (s, 2H), 3.46 (br s, 2H); $^{13}$C NMR (CDCl$_3$): δ = 148.2, 141.4, 140.3, 108.6, 106.9, 100.6, 98.1; Data in accordance with the literature.  

**References**

V. Copies of $^1$H and $^{13}$C NMR Spectra
12d

[chemical structure diagram]

12d

[chemical structure diagram]

[spectroscopic data]