Electronic Supplementary Information


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1. General methods:

$^1$H NMR and $^{13}$C NMR spectra were recorded at Bruker Avance 400. Chemical shifts are reported in ppm downfield from CDCl$_3$ ($\delta = 7.26$ ppm) for $^1$H NMR and relative to the central CDCl$_3$ resonance ($\delta = 77.0$ ppm) for $^{13}$C NMR spectroscopy. Coupling constants are given in Hz. ESI-MS analysis was performed using a Finnigan LCQ$^{DECA}$ ion trap mass spectrometer.

All reagents and solvents were obtained from commercial sources and used without further purification. 3,4-Dihydroisoquinoline imines 1 and MBH carbonates 2 were prepared according to reported procedure.$^{1,2}$

2. General procedure for the synthesis of compounds 3:

A mixture of 3,4-dihydro-isoquinoline imine 1 (0.2 mmol), MBH carbonate 2 (0.3 mmol) and CHCl$_3$ (1 mL) was stirred at room temperature without exclusion of air. Upon the consumption of imine 1 (monitored by TLC), the mixture was purified directly by a silica gel flash chromatography (PE/EtOAc) to afford compound 3.

**Compound 3a:** White solid, 61.7 mg, 96% yield; m.p. 159-161 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32-7.24 (m, 5H), 7.19-7.16 (m, 3H), 7.05 (d, $J = 7.6$ Hz, 1H), 4.88 (d, $J = 2.8$ Hz, 1H), 4.32 (d, $J = 3.6$ Hz, 1H), 3.74 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.51 (s, 3H), 3.37 (td, $J = 13.6$, 3.6 Hz, 1H), 3.08-3.00 (m, 1H), 2.69 (dd, $J = 16.0$, 3.2 Hz, 1H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.8, 150.4, 142.1, 138.6, 136.2, 133.4, 129.4, 128.9, 127.2, 127.0, 126.7, 125.7, 108.7, 71.2, 56.0, 50.4, 44.9, 29.3, 21.1; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1677, 1595, 1574, 1511, 1492, 1257, 1154; ESI-HRMS: calcd. for C$_{21}$H$_{22}$NO$_2$ $^+$(M+H)$^+$ 320.1645, found 320.1645.

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**Compound 3b:** White solid, 57.1 mg, 85% yield; $^1$H NMR (400 MHz, CDCl₃) δ 7.34 (d, $J = 8.4$ Hz, 2H), 7.28-7.26 (m, 3H), 7.20-7.16 (m, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 2H), 4.87 (d, $J = 2.4$ Hz, 1H), 4.31 (d, $J = 3.2$ Hz, 1H), 3.81 (s, 3H), 3.74 (dd, $J = 14.0$, 6.0 Hz, 1H), 3.52 (s, 3H), 3.38 (td, $J = 12.8$, 4.0 Hz, 1H), 3.09-2.97 (m, 1H), 2.70 (dd, $J = 16.0$, 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 165.8, 158.4, 150.3, 138.5, 137.3, 133.4, 128.9, 128.1, 127.2, 126.7, 125.7, 114.1, 108.9, 71.2, 55.6, 55.3, 50.4, 44.9, 29.3; IR (CH₂Cl₂, cm⁻¹) 1677, 1595, 1574, 1508, 1492, 1439, 1243, 1157; ESI-HRMS: calcd. for C₂₁H₂₂NO₃⁺ (M+H)⁺ 336.1594, found 336.1595.

**Compound 3c:** White solid, 61.0 mg, 84% yield; m.p. 108-110°C; $^1$H NMR (400 MHz, CDCl₃) δ 7.42 (d, $J = 7.2$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.30 (s, 1H), 7.28-7.24 (m, 1H), 6.71 (s, 1H), 6.53 (s, 1H), 4.85 (s, 1H), 4.30 (d, $J = 3.2$ Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.74 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.52 (s, 3H), 3.35 (td, $J = 12.8$, 3.6 Hz, 1H), 3.03-2.92 (m, 1H), 2.63-2.59 (m, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 165.8, 150.5, 148.4, 147.9, 145.1, 130.0, 128.8, 127.1, 126.8, 125.5, 111.4, 108.4, 108.2, 70.9, 56.4, 56.0, 55.9, 50.4, 44.9, 28.8; IR (CH₂Cl₂, cm⁻¹) 1675, 1598, 1512, 1494, 1463, 1453, 1254, 1155; ESI-HRMS: calcd. for C₂₂H₂₄NO₄⁺ (M+H)⁺ 366.1700, found 366.1700.

**Compound 3d:** White solid, 68.7 mg, 87% yield; m.p. 82-84°C; $^1$H NMR (400 MHz, CDCl₃) δ 7.33 (d, $J = 8.4$ Hz, 2H), 7.27 (s, 1H), 6.90 (d, $J = 8.4$ Hz, 2H), 6.70 (s, 1H), 6.53 (s, 1H), 4.81 (d, $J = 2.4$ Hz, 1H), 4.26 (d, $J = 3.6$ Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.73 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.52 (s, 3H), 3.34 (td, $J = 12.8$, 4.0 Hz, 1H), 3.01-2.91 (m, 1H), 2.60 (dd, $J = 16.0$, 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 165.8, 158.5, 150.3, 148.4, 147.9, 137.4, 130.1, 128.1, 125.4, 114.2, 111.4, 108.6, 108.2, 70.9, 56.0, 55.9, 55.6, 55.3, 50.4, 44.9, 28.8; IR (CH₂Cl₂, cm⁻¹) 1676, 1598, 1508, 1462, 1440, 1245, 1154; ESI-HRMS: calcd. for C₂₃H₂₆NO₅⁺ (M+H)⁺ 396.1806, found 396.1805.
Compound 3e: White solid, 62.6 mg, 82% yield; m.p. 110-113 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, $J = 8.0$ Hz, 2H), 7.28 (s, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.71 (s, 1H), 6.53 (s, 1H), 4.83 (s, 1H), 4.27 (d, $J = 3.6$ Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.73 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.52 (s, 3H), 3.34 (td, $J = 12.8$, 4.0 Hz, 1H), 3.01-2.93 (m, 1H), 2.60 (dd, $J = 16.0$, 3.6 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 150.3, 148.4, 147.9, 136.3, 130.1, 129.5, 127.0, 125.4, 111.4, 108.5, 108.2, 70.9, 56.0, 56.0, 50.4, 28.8, 21.1; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1676, 1599, 1510, 1463, 1439, 1254, 1154; ESI-HRMS: calcd. for C$_{38}$H$_{38}$NO$_4$+ (M+H)$^+$ 380.1856, found 380.1856.

Compound 3f: Pale yellow solid, 61.3 mg, 77% yield; m.p. 139-142 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.31 (m, 4H), 7.28 (s, 1H), 6.64 (s, 1H), 6.53 (s, 1H), 4.80 (d, $J = 2.4$ Hz, 1H), 4.27 (d, $J = 3.6$ Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.74 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.52 (s, 3H), 3.35 (td, $J = 13.6$, 3.6 Hz, 1H), 3.01-2.92 (m, 1H), 2.61 (dd, $J = 15.6$, 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.6, 150.5, 148.5, 148.0, 143.7, 132.5, 129.7, 128.9, 128.5, 125.5, 111.5, 108.2, 108.1, 70.7, 56.0, 56.0, 55.8, 50.5, 44.9, 28.8; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1677, 1598, 1514, 1488, 1463, 1439, 1254, 1155; ESI-HRMS: calcd. for C$_{22}$H$_{26}$ClNO$_4$+ (M+H)$^+$ 400.1310, found 400.1313.

Compound 3g: White solid, 78.6 mg, 90% yield; m.p. 79-82 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 2.0$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.29 (s, 1H), 7.26-7.24 (m, 1H), 6.60 (s, 1H), 6.53 (s, 1H), 4.79 (s, 1H), 4.23 (d, $J = 3.6$ Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.74 (dd, $J = 13.6$, 5.6 Hz, 1H), 3.52 (s, 3H), 3.35 (td, $J = 13.2$, 4.0 Hz, 1H), 3.00-2.91 (m, 1H), 2.61 (dd, $J = 15.6$, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.5, 150.8, 148.5, 148.1, 145.4, 132.8, 130.7, 130.7, 129.2, 129.1, 126.7, 125.6, 111.5, 108.0, 107.7, 70.6, 56.1, 56.0, 55.6, 50.6, 45.0, 28.8; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1676, 1597, 1514, 1466, 1440, 1255, 1158; ESI-HRMS: calcd. for C$_{22}$H$_{22}$Cl$_2$NO$_4$+ (M+H)$^+$ 434.0920, found 434.0920.
**Compound 3h:** White solid, 50.8 mg, 57% yield; m.p. 162-165 °C; $^1$H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.09 (s, 1H), 6.52 (s, 1H), 4.87 (d, J = 2.4 Hz, 1H), 4.76 (s, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.75 (dd, J = 13.6, 5.6 Hz, 1H), 3.51 (s, 3H), 3.35 (td, J = 12.8, 3.6 Hz, 1H), 3.03-2.95 (m, 1H), 2.62 (dd, J = 16.0, 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 128.9, 128.3, 125.2, 123.2, 116.4, 112.4, 112.0, 109.4, 65.4, 56.0, 54.3, 50.6, 45.0, 28.9; IR (CH₂Cl₂, cm⁻¹) 1678, 1598, 1514, 1463, 1438, 1256, 1154; ESI-HRMS: calcd. for C₂₂H₂₃BrNO₄ (M+H)+ 444.0805, found 444.0805.

**Compound 3i:** White solid, 58.3 mg, 83% yield; m.p. 146-148 °C; $^1$H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H), 6.65-6.64 (m, 2H), 6.52 (s, 1H), 6.42 (d, J = 1.2 Hz, 1H), 4.82 (s, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.81-3.75 (m, 4H), 3.55 (d, J = 5.2 Hz, 1H), 3.47 (dt, J = 12, 4.4 Hz, 1H), 3.17-3.11 (m, 1H), 2.91-2.84 (m, 1H), 2.74 (dt, J = 15.2, 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 169.8, 153.6, 148.3, 147.3, 144.4, 143.3, 127.0, 124.1, 112.4, 111.0, 104.9, 97.0, 96.4, 65.4, 56.1, 56.0, 54.3, 51.5, 28.2; IR (CH₂Cl₂, cm⁻¹) 1678, 1598, 1511, 1463, 1440, 1254, 1156; ESI-HRMS: calcd. for C₂₀H₂₂NO₅⁺ (M+H)+ 356.1493, found 356.1493.

**Compound 3j:** White solid, 49.8 mg, 71% yield; m.p. 58-60 °C; $^1$H NMR (400 MHz, CDCl₃) δ 7.31-7.28 (m, 3H), 7.20 (d, J = 8.8 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 6.84 (dd, J = 8.8, 2.4 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 4.84 (d, J = 2.4 Hz, 1H), 4.28 (d, J = 3.6 Hz, 1H), 3.79 (s, 3H), 3.72 (dd, J = 13.6, 6.0 Hz, 1H), 3.52 (s, 3H), 3.39-3.32 (m, 1H), 3.06-2.97 (m, 1H), 2.66 (dd, J = 16.0, 2.8 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 165.9, 158.2, 150.4, 142.1, 136.1, 134.7, 130.6, 129.4, 127.0, 126.8, 113.7, 113.4, 108.7, 70.9, 56.0, 55.3, 50.4, 44.8, 29.6, 21.1; IR (CH₂Cl₂, cm⁻¹) 1680, 1597, 1500, 1428, 1261, 1159; ESI-HRMS: calcd. for C₂₂H₂₄NO₅⁺ (M+H)+ 350.1751, found 350.1751.
**Compound 3m:** White solid, 29.7 mg, 41% yield; m.p. 151-153 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 1.6$ Hz, 1H), 8.04 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.27-7.23 (m, 2H), 7.20 (d, $J = 7.6$ Hz, 2H), 4.90 (s, 1H), 4.32 (d, $J = 3.2$ Hz, 1H), 3.80 (dd, $J = 13.6, 5.6$ Hz, 1H), 3.52 (s, 3H), 3.43-3.39 (m, 1H), 3.14-3.05 (m, 1H), 2.82 (dd, $J = 16.4, 3.2$ Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 149.9, 147.2, 141.1, 140.9, 140.2, 136.8, 130.0, 129.7, 126.9, 121.6, 121.2, 109.9, 70.8, 56.1, 50.6, 44.2, 29.2, 21.1; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1680, 1603, 1511, 1495, 1464, 1452, 1437, 1261, 1150; ESI-HRMS: calcd. for $C_{21}H_{21}N_2O_4^+$ (M+H)$^+$ 365.1496, found 365.1496.

**Compound 3n:** White solid, 40.5 mg, 90% yield (0.1 mmol scale); m.p. 156-158 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.50 (m, 1H), 7.22-7.21 (m, 3H), 7.13-7.11 (m, 4H), 7.10-7.08 (m, 4H), 6.80-6.79 (m, 2H), 5.28 (d, $J = 17.2$ Hz, 1H), 5.21 (d, $J = 17.2$ Hz, 1H), 5.08 (s, 1H), 4.28 (d, $J = 3.2$ Hz, 1H), 3.82 (dd, $J = 13.2, 4.8$ Hz, 1H), 3.47 (s, 3H), 3.33-3.25 (m, 1H), 3.01-2.93 (m, 1H), 2.85 (dd, $J = 15.2, 4.0$ Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.4, 150.6, 141.4, 137.5, 137.0, 136.4, 134.2, 129.3, 128.7, 127.4, 127.2, 126.9, 126.0, 122.0, 119.7, 118.3, 111.0, 110.1, 108.5, 52.7, 50.4, 47.6, 45.7, 22.5, 21.1; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1680, 1603, 1511, 1495, 1464, 1452, 1437, 1261, 1150; ESI-HRMS: calcd. for $C_{30}H_{29}N_2O_2^+$ (M+H)$^+$ 449.2224, found 449.2223.

**3. General procedure for the synthesis of compounds 4:**

![General procedure](image)

To a mixture of 3 (0.1 mmol) in PhCl (1.0 mL) was added DDQ (0.12 mmol) at room temperature. The resulting reaction mixture was stirred at rt. After compound 3 was consumed (monitored by TLC), the reaction was then washed with aq NaOH and
brine. The organic layer was concentrated and the residue was purified directly by a silica gel flash chromatography (PE/EtOAc) to give compound 4.

**Compound 4a:** White solid, 25.9 mg, 82% yield; m.p. 159-161 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17-7.15 (m, 2H), 7.14-7.11 (m, 2H), 7.09-7.04 (m, 1H), 6.96-6.92 (m, 1H), 6.85-6.82 (m, 2H), 3.99 (t, $J = 6.4$ Hz, 2H), 3.55 (s, 3H), 2.98 (t, $J = 6.4$ Hz, 2H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.8, 136.4, 132.6, 131.7, 130.3, 129.0, 128.9, 128.0, 126.9, 126.1, 125.9, 124.4, 123.2, 114.4, 50.7, 45.0, 29.9, 21.4; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1711, 1604, 1578, 1552, 1522, 1461, 1441, 1228, 1182; ESI-HRMS: calcd. for C$_{21}$H$_{19}$NO$_2$ (M+H)$^+$ 340.1313, found 340.1312.

**Compound 4b:** White solid, 27.7 mg, 90% yield; m.p. 113-115 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (s, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 7.2$ Hz, 1H), 7.06 (t, $J = 6.8$ Hz, 1H), 6.96-6.93 (m, 4H), 4.11 (t, $J = 6.4$ Hz, 2H), 3.87 (s, 3H), 3.67 (s, 3H), 3.09 (t, $J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.9, 158.7, 131.7, 131.5, 129.0, 128.0, 127.8, 127.0, 126.9, 126.1, 125.9, 124.3, 122.8, 114.4, 113.6, 55.2, 50.7, 45.0, 29.9; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1709, 1604, 1575, 1552, 1522, 1461, 1441, 1228, 1180; ESI-HRMS: calcd. for C$_{21}$H$_{20}$NO$_3$ (M+H)$^+$ 334.1438, found 334.1437.

**Compound 4c:** White solid, 23.0 mg, 63% yield; m.p. 139-140 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.41-7.40 (m, 4H), 7.36 (s, 1H), 7.33-7.30 (m, 1H), 6.66 (s, 1H), 6.40 (s, 1H), 4.09 (t, $J = 6.6$ Hz, 2H), 3.84 (s, 3H), 3.66 (s, 3H), 3.28 (s, 3H), 3.03 (t, $J = 6.6$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.0, 147.5, 147.3, 136.2, 130.8, 128.2, 127.2, 127.0, 125.5, 124.0, 121.6, 121.5, 114.1, 111.1, 107.6, 56.0, 55.1, 50.8, 45.1, 29.3; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1709, 1606, 1550, 1508, 1484, 1463, 1443, 1227, 1186; ESI-HRMS: calcd. for C$_{22}$H$_{21}$NO$_4$ (M+Na)$^+$ 386.1368, found 386.1371.
**Compound 4d:** White solid, 33.5 mg, 85% yield; m.p. 161-163 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, $J = 2.8$ Hz, 2H), 7.31 (s, 1H), 6.96 (d, $J = 8.4$ Hz, 2H), 6.66 (s, 1H), 6.48 (s, 1H), 4.08 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.67 (s, 3H), 3.35 (s, 3H), 3.02 (t, $J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.0, 158.7, 147.6, 147.3, 131.8, 128.2, 127.2, 125.4, 124.0, 121.7, 121.2, 114.2, 113.7, 111.1, 107.7, 55.9, 55.3, 55.1, 50.7, 45.1, 29.2; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1710, 1608, 1577, 1550, 1503, 1481, 1462, 1440, 1215, 1184; ESI-HRMS: calcd. for C$_{23}$H$_{24}$NO$_5$ $^+$ (M+H)$^+$ 394.1649, found 394.1649.

**Compound 4e:** White solid, 19.4 mg, 61% yield; m.p. 160-163 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (s, 1H), 7.28 (d, $J = 7.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.66 (s, 1H), 6.44 (s, 1H), 4.09 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 3.66 (s, 3H), 3.30 (s, 3H), 3.02 (t, $J = 6.4$ Hz, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.9, 147.5, 147.3, 136.4, 133.0, 130.6, 128.8, 127.1, 125.3, 123.9, 121.6, 114.1, 111.1, 107.8, 55.9, 54.9, 50.7, 45.1, 29.2, 21.2; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1710, 1608, 1554, 1519, 1489, 1443, 1226, 1186; ESI-HRMS: calcd. for C$_{23}$H$_{24}$NO$_4^+$ (M+H)$^+$ 378.1700, found 378.1700.

**Compound 4f:** White solid, 30.0 mg, 75% yield; m.p. 154-157 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40-7.34 (m, 5H), 6.68 (s, 1H), 6.37 (s, 1H), 4.09 (t, $J = 6.4$ Hz, 2H), 3.85 (s, 3H), 3.67 (s, 3H), 3.36 (s, 3H), 3.03 (t, $J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.8, 147.6, 147.5, 134.6, 132.9, 132.3, 128.3, 127.3, 125.6, 124.2, 121.2, 120.1, 114.0, 111.2, 107.6, 56.0, 55.1, 50.8, 45.1, 29.2; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1706, 1610, 1550, 1504, 1482, 1453, 1442, 1226, 1184; ESI-HRMS: calcd. for C$_{22}$H$_{21}$ClNO$_4^+$ (M+H)$^+$ 398.1154, found 398.1154.
**Compound 4g:** White solid, 33.5 mg, 77% yield; m.p. 153-156 °C; "H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 1.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.28 (dd, J = 8.4, 2.0 Hz, 1H), 6.69 (s, 1H), 6.39 (s, 1H), 4.09 (t, J = 6.8 Hz, 2H), 3.86 (s, 3H), 3.68 (s, 3H), 3.39 (s, 3H), 3.03 (t, J = 6.4 Hz, 2H); "C NMR (100 MHz, CDCl₃) δ 164.6, 147.8, 147.7, 136.3, 132.7, 132.0, 130.9, 130.6, 130.0, 127.5, 125.8, 124.5, 120.9, 118.7, 114.0, 111.3, 107.5, 56.0, 55.2, 50.8, 45.1, 29.2; IR (CH₂Cl₂, cm⁻¹) 1707, 1611, 1544, 1524, 1501, 1473, 1441, 1228, 1187; ESI-HRMS: calcd. for C₂₂H₂₀Cl₂NO₄ (M+H)⁺ 432.0764, found 432.0764.

**Compound 4h:** White solid, 33.0 mg, 75% yield; m.p. 176-179 °C; "H NMR (600 MHz, CDCl₃) δ 7.70 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 7.37-7.34 (m, 2H), 7.23-7.20 (m, 1H), 6.67 (s, 1H), 6.30 (s, 1H), 4.13 (dd, J = 8.4, 6.0 Hz, 2H), 3.84 (s, 3H), 3.65 (s, 3H), 3.31 (s, 3H), 3.11-3.06 (m, 1H), 3.00 (td, J = 11.4, 5.6 Hz, 1H); "C NMR (150 MHz, CDCl₃) δ 164.7, 147.8, 147.5, 137.8, 132.6, 132.5, 128.8, 127.4, 127.2, 126.0, 125.3, 123.9, 121.4, 120.0, 114.3, 111.1, 106.9, 56.0, 55.2, 50.9, 45.1, 29.2; IR (CH₂Cl₂, cm⁻¹) 1708, 1611, 1553, 1524, 1501, 1473, 1441, 1228, 1187; ESI-HRMS: calcd. for C₂₂H₂₀BrNO₄ (M+Na)⁺ 464.0473, found 464.0479.

### 4. General Procedure for the one pot synthesis of compounds 4:

A mixture of 3,4-dihydro-isoquinoline imine 1 (0.2 mmol), MBH carbonate 2 (0.3 mmol) and CHCl₃ (1 mL) was stirred at room temperature without exclusion of air. Upon the consumption of imine 1 (monitored by TLC), DDQ (0.24 mmol) was added at room temperature. The resulting reaction mixture was stirred at rt. After compound 3 was consumed (monitored by TLC), the reaction was then washed with aq NaOH and brine. The organic layer was concentrated and the residue was purified directly by a silica gel flash chromatography (PE/EtOAc) to give compound 4.
Compound 4o: Pale yellow solid, 45.0 mg, 68% yield; m.p. 130-133 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50-7.48 (m, 2H), 7.45-7.41 (m, 2H), 7.35 (d, \(J = 7.2\) Hz, 1H), 7.21 (s, 1H), 6.70 (s, 1H), 6.69 (s, 1H), 4.09 (t, \(J = 6.4\) Hz, 2H), 3.87 (s, 3H), 3.38 (s, 3H), 3.05 (t, \(J = 6.4\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.1, 147.8, 133.5, 129.9, 128.7, 126.7, 126.4, 124.4, 122.7, 120.6, 116.4, 111.2, 107.8, 94.0, 56.0, 55.3, 45.3, 29.1; IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)) 2219, 1604, 1554, 1508, 1485, 1464, 1443, 1217, 1170; ESI-HRMS: calcd. for C\(_{21}\)H\(_{19}\)N\(_2\)O\(_2\)\(^+\)(M+H)\(^+\) 331.1441, found 331.1441.

5. Gram-scale reaction:

A mixture of 3,4-dihydro-isoquinoline imine 1b (0.96 g, 5.0 mmol, 1 equiv), MBH carbonate 2 (1.77 g, 5.5 mmol, 1.1 equiv) and CHCl\(_3\) (15 mL) was stirred at room temperature without exclusion of air. After imine 1 was consumed (monitored by TLC), the mixture was concentrated and the residue was purified directly by a silica gel flash chromatography (PE/EtOAc = 3/2) to afford compound 3d as white solid (1.57 g, 79% yield).

To a mixture of compound 3d (1.0 g, 2.53 mmol, 1 equiv) in PhCl (22 mL) was added DDQ (0.689 g, 3.04 mmol, 1.2 equiv) and the mixture was stirred at room temperature for 2.5 h. The reaction mixture was then diluted with DCM, washed with aq NaOH and brine, and dried with Na\(_2\)SO\(_4\). After concentrated, the residue was purified by a silica gel flash chromatography (PE/EtOAc = 7/3) to afford compound 4b as pale yellow solid (0.82 g, 82% yield).
A mixture of 3,4-dihydro-isouquinoline imine 1b (0.98 g, 5.1 mmol, 1 equiv), MBH carbonate 2 (1.82 g, 5.6 mmol, 1.1 equiv) and CHCl₃ (10 mL) was stirred at room temperature without exclusion of air. Upon the consumption of imine 1 (monitored by TLC), DDQ (1.42 g, 6.2 mmol, 1.2 equiv) was added. The resulting reaction mixture was stirred at room temperature for 2.5 h (monitored by TLC). The reaction mixture was then diluted with DCM, washed with aq NaOH and brine, and dried with Na₂SO₄. After concentrated, the residue was purified by a silica gel flash chromatography (PE/EtOAc = 7/3) to afford compound 4b as pale yellow solid (1.12 g, 56% yield).

6. Synthesis of compound 5:

To a solution of 4b (1 eq, 0.1 mmol, 39.3 mg) in DCM (1 mL) was added NBS (1.1 eq, 0.11 mmol, 19.6 mg). The resulting mixture was stirred at rt for 7 h. Then the mixture was purified by a silica gel flash chromatography (Hexane/EtOAc = 3/1 to 2/1) to give compound 5 as white amorphous solid (40.5 mg, 95% yield); m.p. 142-144°C; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.66 (s, 1H), 6.38 (s, 1H), 4.14 (t, J = 6.4 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.64 (s, 3H), 3.31 (s, 3H), 3.01 (t, J = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 158.8, 147.6, 147.5, 131.8, 128.3, 128.3, 124.1, 122.1, 121.2, 114.3, 113.7, 110.8, 108.1, 107.6, 55.9, 55.3, 55.1, 50.9, 43.4, 28.8; IR (CH₂Cl₂, cm⁻¹) 1704, 1611, 1571, 1554, 1497, 1475, 1459, 1451, 1227, 1189; ESI-HRMS: calcd. for C₂₃H₂₃BrNO₅⁺ (M+H)⁺ 472.0754, found 472.0754.

7. Synthesis of compound 6
A mixture of compound 5 (1 eq, 0.05 mmol, 21.4 mg), Pd(PPh$_3$)$_4$ (0.1 eq, 0.005 mmol, 5.8 mg), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (2 eq, 0.1 mmol, 20.5 mg) and Na$_2$CO$_3$ (2 eq, 0.1 mmol, 10.6 mg) in DMF (0.4 mL) and H$_2$O (0.1 mL) was stirred at 120 °C for 3 h. Then the reaction mixture was cooled to rt, diluted with EtOAc, washed with sat Na$_2$CO$_3$ and brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. The residue was purified by a silica gel flash chromatography (Hexane/EtOAc/Et$_3$N = 30/30/1) to give compound 6 as white amorphous solid (20.8 mg, 88% yield); m.p. 192-193 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67-8.65 (m, 2H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.41 (dd, $J = 4.8$, 7.6 Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 8.4$ Hz, 2H), 6.67 (s, 1H), 6.49 (s, 1H), 3.88 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 3.84 (s, 3H), 3.43 (s, 3H), 3.35 (s, 3H), 2.95 (t, $J = 6.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.1, 158.7, 151.1, 149.2, 147.5, 147.5, 138.3, 132.7, 131.8, 128.5, 128.1, 127.5, 124.5, 122.8, 121.7, 121.5, 114.2, 113.8, 110.9, 108.1, 55.9, 55.3, 55.1, 50.6, 42.6, 29.2; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1703, 1612, 1555, 1517, 1488, 1463, 1441, 1224, 1167; ESI-HRMS: calcd. for C$_{28}$H$_{27}$N$_2$O$_5$ $^+$ (M+H)$^+$ 471.1915, found 471.1914.

Reference:


8. Crystal data of Compound 3b:
### Crystal data of Compound 3n:

![Crystal structure of Compound 3n](image.png)

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**Wavelength:** 0.71073 Å

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**S** = 1.080  
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### Notes:
- No syntax errors found.
- CIF dictionary.
- Interpreting this report.

This report is for guidance only. If used as part of a review procedure for publication, it should not replace the expertise of an experienced crystallographic referee.
Bond precision:  C-C = 0.0040 Å  Wavelength=0.71073

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