Palladium-Catalyzed Insertion of \( \alpha \)-Diazocarbonyl Compounds for the Synthesis of Cyclic Amino Esters

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1. General remarks.

For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90°C) are used. ^1H NMR spectra were recorded on 400 MHz in CDCl₃ and ^13C NMR spectra were recorded on 100 MHz in CDCl₃ using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm⁻¹. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^1H NMR and ^13C NMR spectra were provided.

2. General procedure for the preparation of 1a-c and 1g.

2-Iodoaniline derivative⁵-⁶ (1.0 equiv) was added slowly to a mixture of benzaldehyde (1.2 equiv) and MgSO₄ (4.0 equiv) in DCM under argon over two minutes and stirred at room temperature. After 36 h, the reaction mixture was filtered, concentrated under reduced pressure. Methanol was added to the crude oil, the solution was cooled to 0°C and NaBH₄ (4.0 equiv) was added slowly, the reaction mixture was stirred at room temperature for 12 h. After cooling, water was added to the mixture, and the whole was extracted with EtOAc. The extract was washed with water, brine and dried over MgSO₄. The organic layer was concentrated under reduced pressure to leave a residue, which was purified by column chromatography over silica gel.

N-benzyl-2-iodoaniline 1a: oil; ^1H NMR (400 MHz, CDCl₃) δ: 7.64-7.62 (m, 1H), 7.30 (d, J = 4.4 Hz, 4H), 7.24-7.21 (m, 1H), 7.11-7.07 (m, 1H), 6.47 (dd, J = 8.0 Hz, 1.2 Hz, 1.0H), 6.41-6.37 (m, 1H), 4.58 (s, 1H), 4.30 (d, J = 4.0 Hz, 2H); ^13C NMR (100 MHz, CDCl₃) δ: 146.9, 138.8, 138.5, 129.3, 128.6, 127.2, 127.1, 118.8, 110.9, 85.3, 48.2.
**N-benzyl-4-chloro-2-iodoaniline 1b:** oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.63-7.60 (m, 1H), 7.31-7.29 (m, 5H), 7.06 (t, $J = 8.0$ Hz, 1H), 6.37-6.34 (m, 1H), 4.59 (s, 1H), 4.29 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 145.7, 138.0, 137.7, 129.1, 128.6, 127.3, 127.0, 122.0, 111.1, 84.6, 48.2.

**N-benzyl-2-iodo-4-methylaniline 1c:** oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.50 (s, 1H), 7.33-7.29 (m, 4H), 7.25-7.23 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.41 (d, $J = 8.4$ Hz, 1H), 4.53 (s, 1H), 4.34 (d, $J = 5.6$ Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 144.8, 139.2, 138.8, 129.9, 128.6, 128.2, 127.2, 127.1, 110.8, 85.3, 48.5, 19.7.

**N-(2-iodophenyl)-4-methylbenzenesulfonamide 1e:** solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.64-7.62 (m, 3H), 7.31 (d, $J = 0.8$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.84-6.80 (m, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 144.2, 139.1, 137.4, 135.9, 129.6, 129.4, 127.4, 126.8, 122.4, 92.3, 21.5.

**2-iodo-N-methylaniline 1f:** oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.63-7.61 (m, 1H), 7.22-7.18 (m, 1H), 6.51 (d, $J = 8.0$ Hz, 1H), 6.43-6.40 (m, 1H), 4.16 (s, 1H), 2.82 (d, $J = 5.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 148.0, 138.7, 129.4, 118.3, 109.9, 85.1, 30.9.
N-benzyl-2-iodo-4,6-dimethylaniline 1g: oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.44(d, $J = 9.2$ Hz, 3H), 7.38-7.34(m, 2H), 7.29(t, $J = 7.2$ Hz, 1H), 6.94(s, 1H), 4.07(s, 2H), 3.49(s, 1H), 2.36(s, 3H), 2.22(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 145.3, 139.6, 137.2, 134.3, 132.5, 131.6, 128.5, 128.2, 127.3, 96.3, 52.8, 20.0, 19.5.


Methyl 2-diazo-2-phenylacetate 2a: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.49-7.47(m, 2H), 7.39-7.36(m, 2H), 7.18(t, $J = 7.2$ Hz, 1H), 3.86(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.5, 128.9, 125.8, 125.4, 123.9, 51.9.

Methyl 2-(4-chlorophenyl)-2-diazoacetate 2b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.40 (d, $J = 8.0$ Hz, 2H), 7.33(d, $J = 8.0$ Hz, 2H), 3.85(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.2, 131.4, 129.0, 124.9, 124.1, 52.0.

Methyl 2-(4-bromophenyl)-2-diazoacetate 2c: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.51-7.49(m, 2H), 7.38-7.36(m, 2H), 3.87(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.2, 132.0, 125.3, 124.7, 119.3, 52.1.
Methyl 2-diazo-2-(p-tolyl) acetate 2d: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.33(d, $J = 8.0$ Hz, 2H), 7.21-7.09(m, 2H), 3.82(s, 3H), 2.30(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.6, 135.5, 129.5, 123.9, 121.9, 51.7, 20.8.

Methyl 2-(3-chlorophenyl)-2-diazoacetate 2e: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.52(d, $J = 1.2$ Hz, 1H), 7.29-7.27(m, 2H), 7.13-7.10(m, 1H), 3.85(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 164.8, 134.9, 129.9, 127.6, 125.6, 123.5, 121.4, 52.0.

Methyl 2-(3-bromophenyl)-2-diazoacetate 2f: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.68-7.67(m, 1H), 7.38-7.35(m, 1H), 7.30-7.27(m, 1H), 7.23(d, $J = 8.0$ Hz, 1H), 3.86(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 164.9, 130.2, 128.6, 127.9, 126.4, 123.1, 122.0, 52.1.

Methyl 2-diazo-2-(m-tolyl) acetate 2g: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.27(s, 1H), 7.24-7.23(m, 2H), 6.96-6.95(m, 1H), 3.81(s, 3H), 2.32(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.4, 138.4, 128.6, 126.5, 125.1, 124.3, 120.9, 51.7, 21.3.

Methyl 2-diazo-2-(3-methoxyphenyl) acetate 2h: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 
7.25-7.21(m, 1H), 7.13(s, 1H), 6.92(d, \( J = 8.0 \) Hz, 1H), 6.67(d, \( J = 8.4 \) Hz, 1H), 3.80(s, 3H), 3.75(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.0, 159.8, 129.5, 126.6, 115.5, 111.0, 109.3, 54.8, 51.6.

\begin{center}
\textbf{Methyl 2-(2-bromophenyl)-2-diazoacetate 2i:} \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.57(dd, \( J = 8.0 \) Hz, 1.2 Hz, 1H), 7.49(dd, \( J = 7.6 \) Hz, 1.6 Hz, 1H), 7.35-7.31(m, 1H), 7.18-7.14(m, 1H), 3.80(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.5, 133.0, 132.7, 129.8, 127.4, 125.4, 124.1, 124.1, 52.0.
\end{center}

\begin{center}
\textbf{Methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate 2j:} \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.19(s, 1H), 6.88-6.86(m, 2H), 3.89(s, 3H), 3.87(s, 3H), 3.85(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.9, 149.3, 147.2, 117.2, 116.2, 111.5, 108.1, 55.8, 55.7, 51.7.
\end{center}

\begin{center}
\textbf{(E)-methyl 2-diazo-4-phenylbut-3-enoate 4a:} \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.34-7.31(m, 3H), 7.28(d, \( J = 8.0 \) Hz, 1H), 7.19-7.16(m, 1H), 6.46(d, \( J = 16.4 \) Hz, 1H), 6.17(d, \( J = 16.4 \) Hz, 1H), 3.83(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.5, 136.7, 128.6, 127.0, 125.8, 123.0, 111.2, 52.2.
\end{center}

\begin{center}
\textbf{(E)-methyl 4-(4-chlorophenyl)-2-diazo3-enoate 4b:} \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.26(s, 4H), 6.44(d, \( J = 16.4 \) Hz, 1H), 6.14(d, \( J = 16.4 \) Hz, 1H), 3.85(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.3, 135.3, 132.6, 128.8, 126.9, 121.7, 112.0, 52.3.
\end{center}
(E)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate 4c: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.41 (d, $J = 8.8$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.46 (d, $J = 16.4$ Hz, 1H), 6.12 (d, $J = 16.4$ Hz, 1H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.3, 135.7, 131.7, 127.2, 121.6, 120.7, 112.2, 52.3.

(E)-methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate 4d: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.27 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 6.28 (d, $J = 16.4$ Hz, 1H), 6.13 (d, $J = 16.4$ Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.8, 158.8, 129.6, 127.0, 122.8, 114.1, 108.6, 55.2, 52.2.

(E)-methyl 2-diazo-4-(3-methoxyphenyl)but-3-enoate 4e: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.23-7.20 (m, 1H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 2.0$ Hz, 1H), 6.75 (dd, $J = 8.0$ Hz, 2.4 Hz, 1H), 6.47 (d, $J = 16.0$ Hz, 1H), 6.16 (d, $J = 16.4$ Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.5, 159.8, 138.1, 129.7, 127.7, 122.8, 118.5, 112.8, 111.5, 110.9, 55.1, 52.3.

(E)-methyl 2-diazo-4-(2-methoxyphenyl)but-3-enoate 4f: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.42 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.20-7.16 (m, 1H), 6.92 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 6.51 (d, $J = 1.6$ Hz, 2H), 3.84 (d, $J = 1.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.7, 156.0, 128.1, 126.4, 125.8, 120.7, 118.0, 111.6, 110.8, 55.4, 52.2.
(E)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate 4g: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.74 (d, $J = 8.4$ Hz, 3H), 7.64 (s, 1H), 7.55 (dd, $J = 8.8$ Hz, 1.2 Hz, 1H), 7.44-7.37 (m, 2H), 6.56 (d, $J = 16.4$ Hz, 1H), 6.31 (d, $J = 16.4$ Hz, 1H), 3.83 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.6, 134.3, 133.7, 132.7, 128.4, 127.9, 127.7, 126.4, 125.8, 125.5, 123.2, 111.6, 52.4.

(E)-methyl 2-diazo-4-(furan-2-yl)but-3-enoate 4h: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.35 (d, $J = 1.6$ Hz, 1H), 6.41-6.37 (m, 2H), 6.19-6.12 (m, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.4, 152.7, 141.9, 111.7, 111.4, 109.7, 106.9, 52.2.

(E)-methyl 4-(benzo[d][1,3]dioxol-5-yl)-2-diazobut-3-enoate 4i: $^1$H NMR (400 MHz, CDCl$_3$) δ: 6.90 (d, $J = 4.0$ Hz, 1H), 6.77-6.73 (m, 2H), 6.25 (d, $J = 16.4$ Hz, 1H), 6.10 (d, $J = 16.0$ Hz, 1H), 5.94 (s, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.6, 148.1, 146.8, 131.3, 122.9, 120.4, 109.2, 108.3, 105.1, 101.0, 52.2.

To an oven-dried Schlenk tube were added N-substituted-2-iodoanilines (1a-d) (0.20 mmol, 1.0 eq), diazo ester (2a-j) (0.80 mmol, 4.0 eq), iPr2NEt (0.40 mmol, 2.0 eq), and Pd(OAc)2 (0.01 mmol, 5 mol %) under CO atmosphere, and then anhydrous DMAC (2.0 mL) was introduced by syringe. The mixture was stirred at 64°C. When the reaction was considered complete, as determined by TLC analysis, the reaction mixture was cooled to room temperature. Water was added to the mixture, followed by extraction with EtOAc. After washing with water and brine, the combined organic extracts were dried over MgSO4 and concentrated by rotary evaporation. The residue was purified by flash chromatography to afford 3a-m.

**Methyl 1-benzyl-3-oxo-2-phenylindoline-2-carboxylate 3a**: solid; m.p. 122-124°C; 1H NMR (400 MHz, CDCl3) δ: 7.63(d, J = 7.6 Hz, 1H), 7.44-7.40(m, 2H), 7.36-7.34(m, 3H), 7.31-7.29(m, 2H), 7.24-7.22(m, 2H), 7.09(d, J = 6.8 Hz, 2H), 6.83-6.80(m, 1H), 6.70(d, J = 8.4 Hz, 1H), 4.77(d, J = 17.2 Hz, 1H), 4.63(d, J = 16.8 Hz, 1H), 3.54(s, 3H); 13C NMR (100 MHz, CDCl3) δ: 194.4, 168.1, 160.8, 137.9, 136.9, 134.0, 128.8, 128.7, 128.6, 128.5, 127.5, 127.2, 126.4, 125.8, 118.7, 109.5, 79.9, 52.8, 48.2; IR(neat) 3029, 2922, 1742, 1710, 1608, 1483, 1243, 1011, 750, 696; HRMS (ESI) m/z: calcd for C23H19NO3: M+H=358.1438; found: 358.1440.

**Methyl 1-benzyl-5-chloro-3-oxo-2-phenylindoline-2-carboxylate 3b**: solid; m.p. 136-138°C; 1H NMR (400 MHz, CDCl3) δ: 7.59(d, J = 2.0 Hz, 1H), 7.39-7.35(m, 4H), 7.28-7.26(m, 3H), 7.24-7.22(m, 2H), 7.10-7.07(m, 2H), 6.64(d, J = 8.8 Hz, 1H), 4.75(d, J = 16.8 Hz, 1H), 4.63(d, J = 17.2 Hz, 1H), 3.58(s, 3H); 13C NMR (100 MHz, CDCl3) δ: 193.3, 167.7, 159.2, 137.8, 136.5, 133.6, 129.0, 128.9, 128.7, 127.5, 127.4, 126.4, 125.1, 124.1, 119.7, 110.8, 80.5, 53.0, 48.3; IR(neat) 3027, 2923, 1745, 1715, 1611, 1478, 1248, 1010, 758, 698; HRMS (ESI) m/z: calcd for C23H18ClNO3:
M+H=392.1048; found: 392.1051.

**Methyl 1-benzyl-5-methyl-3-oxo-2-phenylindoline-2-carboxylate 3c:** solid; m.p. 126-128°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.43(s, 1H), 7.36-7.33(m, 3H), 7.31-7.29(m, 2H), 7.25(d, $J = 5.6$ Hz, 2H), 7.22-7.20(m, 2H), 7.10(d, $J = 7.2$ Hz, 2H), 6.62(d, $J = 8.4$ Hz, 1H), 4.75(d, $J = 17.2$ Hz, 1H), 4.60(d, $J = 16.8$ Hz, 1H), 3.54(s, 3H), 2.27(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.4, 168.2, 159.4, 139.3, 137.2, 134.2, 128.8, 128.6, 128.5, 128.2, 127.5, 127.1, 126.4, 125.2, 118.7, 109.3, 80.2, 52.8, 48.3, 20.3; IR(neat) 3030, 2923, 1743, 1708, 1623, 1497, 1244, 1015, 770, 699; HRMS (ESI) m/z: calcd for C$_{24}$H$_{21}$NO$_3$: M+H=392.1594; found: 392.1598.

**Methyl 1-benzyl-2-(4-chlorophenyl)-3-oxoindoline-2-carboxylate 3d:** solid; m.p. 121-123°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.64(d, $J = 7.6$ Hz, 1H), 7.49-7.45(m, 1H), 7.34(d, $J = 8.8$ Hz, 2H), 7.28-7.25(m, 5H), 7.12(d, $J = 6.4$ Hz, 2H), 6.87-6.83(m, 1H), 6.75(d, $J = 8.4$ Hz, 1H), 4.78(d, $J = 17.2$ Hz, 1H), 4.59(d, $J = 17.2$ Hz, 1H), 3.52(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.4, 167.9, 160.9, 138.1, 136.6, 134.8, 132.4, 129.1, 129.0, 128.6, 127.4, 126.5, 126.0, 119.0, 118.5, 109.6, 79.2, 53.0, 48.2; IR(neat) 3027, 2922, 1744, 1711, 1609, 1485, 1244, 1093, 1010, 757; HRMS (ESI) m/z: calcd for C$_{23}$H$_{18}$ClNO$_3$: M+H=392.1048; found: 392.1054.

**Methyl 1-benzyl-2-(4-bromophenyl)-3-oxoindoline-2-carboxylate 3e:** solid; m.p. 126-128°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.65-7.63(m, 1H), 7.51-7.45(m, 3H), 7.30-7.24(m, 3H), 7.23-7.19(m, 2H), 7.12(d, $J = 6.4$ Hz, 2H), 6.87-6.84(m, 1H), 6.76(d, $J = 8.4$ Hz, 1H), 4.79(d, $J = 16.8$ Hz, 1H), 4.58(d, $J = 17.2$ Hz, 1H), 3.51(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.1, 167.8, 160.9, 138.2, 136.5, 132.8, 132.0, 129.2, 128.6, 127.4, 126.5, 126.0, 123.0, 119.0, 118.4, 109.6, 79.2, 53.0, 48.1; IR(neat) 3432, 2921, 1743, 1711, 1609, 1483, 1244, 1011, 770; HRMS (ESI) m/z: calcd for C$_{23}$H$_{18}$BrNO$_3$: M+H=436.0543; found: 436.0550.
Methyl 1-benzyl-3-oxo-2-(p-tolyl)indoline-2-carboxylate 3f: solid; m.p. 133-135°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.65-7.63(m, 1H), 7.45-7.41(m, 1H), 7.27-7.21(m, 3H), 7.18(s, 4H), 7.11(d, \(J = 6.8\) Hz, 2H), 6.84-6.80(m, 1H), 6.69(d, \(J = 8.4\) Hz, 1H), 4.76(d, \(J = 17.2\) Hz, 1H), 4.63(d, \(J = 17.2\) Hz, 1H), 3.54(s, 3H), 2.33(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 194.7, 168.3, 160.8, 138.7, 137.9, 137.0, 130.9, 129.6, 128.5, 127.4, 127.2, 126.4, 125.9, 118.7, 118.6, 109.5, 79.8, 52.9, 48.2, 21.1; IR(neat) 3027, 2951, 1744, 1711, 1609, 1482, 1242, 1097, 1016, 771; HRMS (ESI) m/z: calcd for C\(_{24}\)H\(_{21}\)NO\(_3\): M+H=372.1594; found: 372.1602.

Methyl 1-benzyl-2-(3-chlorophenyl)-3-oxoindoline-2-carboxylate 3g: solid; m.p. 141-143°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.64(d, \(J = 8.0\) Hz, 1H), 7.50-7.46(m, 1H), 7.32-7.21(m, 7H), 7.13(d, \(J = 6.8\) Hz, 2H), 6.87-6.84(m, 1H), 6.77(d, \(J = 8.0\) Hz, 1H), 4.81(d, \(J = 16.8\) Hz, 1H), 4.61(d, \(J = 17.2\) Hz, 1H), 3.52(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 193.9, 167.7, 160.9, 138.2, 136.6, 135.9, 134.7, 130.1, 128.9, 128.6, 127.6, 127.4, 126.5, 126.1, 125.9, 119.0, 118.4, 109.6, 79.2, 53.0, 48.2; IR(neat) 3027, 2922, 1744, 1712, 1480, 1245, 1017, 769, 697; HRMS (ESI) m/z: calcd for C\(_{23}\)H\(_{18}\)ClNO\(_3\): M+H=392.1048; found: 392.1044.

Methyl 1-benzyl-2-(3-bromophenyl)-3-oxoindoline-2-carboxylate 3h: solid; m.p. 127-129°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.64(d, \(J = 7.6\) Hz, 1H), 7.50-7.46(m, 2H), 7.44-7.43(m, 1H), 7.29-7.22(m, 5H), 7.12(d, \(J = 6.8\) Hz, 2H), 6.87-6.84(m, 1H), 6.77(d, \(J = 8.4\) Hz, 1H), 4.80(d, \(J = 17.2\) Hz, 1H), 4.60(d, \(J = 17.2\) Hz, 1H), 3.51(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 193.8, 167.7, 160.9, 138.2, 136.5, 136.1, 131.8, 130.3, 130.0, 128.6, 127.4, 126.5, 126.4, 126.0, 122.7, 119.0, 118.4, 109.6, 79.1, 53.0, 48.1; IR(neat) 3026, 2951, 1743, 1711, 1609, 1479, 1244, 1007, 753, 696; HRMS (ESI) m/z: calcd for C\(_{23}\)H\(_{18}\)BrNO\(_3\): M+H=436.0543; found: 436.0543.
Methyl 1-benzyl-3-oxo-2-(m-tolyl)indoline-2-carboxylate 3i: solid; m.p. 103-105°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.64(d, \(J = 7.6\) Hz, 1H), 7.46-7.42(m, 1H), 7.27-7.25(m, 2H), 7.23-7.21(m, 2H), 7.15(d, \(J = 7.6\) Hz, 1H), 7.10(d, \(J = 6.4\) Hz, 3H), 7.06(d, \(J = 7.6\) Hz, 1H), 6.84-6.81(m, 1H), 6.70(d, \(J = 8.4\) Hz, 1H), 4.76(d, \(J = 17.2\) Hz, 1H), 4.64(d, \(J = 17.2\) Hz, 1H), 3.56(s, 3H), 2.33(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 194.6, 168.2, 160.8, 138.7, 138.0, 137.1, 133.9, 129.6, 128.8, 128.5, 128.2, 127.2, 125.9, 124.4, 118.7, 118.6, 109.5, 80.0, 52.9, 48.2, 21.6; IR(neat) 3027, 2921, 1744, 1712, 1609, 1483, 1234, 1021, 752, 699; HRMS (ESI) m/z: calcd for C\(_{24}\)H\(_{21}\)NO\(_3\): M+H=372.1594; found: 372.1602.

Methyl 1-benzyl-2-(3-methoxyphenyl)-3-oxoindoline-2-carboxylate 3j: solid; m.p. 130-132°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.64(dd, \(J = 7.6\) Hz, 0.8 Hz, 1H), 7.46-7.42(m, 1H), 7.31-7.21(m, 4H), 7.13-7.11(m, 2H), 6.90-6.87(m, 2H), 6.85-6.81(m, 2H), 6.70(d, \(J = 8.4\) Hz, 1H), 4.78(d, \(J = 17.2\) Hz, 1H), 4.64(d, \(J = 17.2\) Hz, 1H), 3.76(s, 3H), 3.54(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 194.3, 168.0, 160.8, 159.9, 138.0, 137.0, 135.4, 129.9, 128.6, 127.2, 126.5, 125.9, 119.8, 118.7, 118.6, 113.9, 113.7, 109.5, 79.8, 55.3, 52.9, 48.3; IR(neat) 3021, 2952, 1742, 1704, 1618, 1508, 1491, 1415, 1354, 1285, 1195, 1184, 1158, 753, 698; HRMS (ESI) m/z: calcd for C\(_{24}\)H\(_{21}\)NO\(_4\): M+H=388.1543; found: 388.1547.

Methyl 1-benzyl-5,7-dimethyl-3-oxo-2-phenylindoline-2-carboxylate 3l: solid; m.p. 134-136°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.36-7.32(m, 6H), 7.25-7.22(m, 2H), 7.18(d, \(J = 7.2\) Hz, 1H), 7.10(d, \(J = 8.0\) Hz, 3H), 5.32(d, \(J = 18.4\) Hz, 1H), 4.65(d, \(J = 18.4\) Hz, 1H), 3.30(s, 3H), 2.37(s, 3H), 2.25(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 195.2, 168.6, 157.7, 142.8, 139.5, 133.8, 128.7, 128.5, 128.4, 127.4, 126.9, 125.4, 123.4, 119.7, 119.6, 79.8, 52.5, 48.9, 20.0, 19.2; IR(neat) 3027, 2924, 1742, 1704, 1618, 1491, 1243, 1013, 910, 733; HRMS (ESI) m/z: calcd for C\(_{25}\)H\(_{23}\)NO\(_3\): M+H=386.1751; found: 386.1747.
Methyl 1-benzyl-2-(3,4-dimethoxyphenyl)-3-oxoindoline-2-carboxylate 3m: solid; m.p. 188-190°C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.65(d, \(J = 7.6\) Hz, 1H), 7.47-7.43(m, 1H), 7.26-7.22(m, 3H), 7.13(d, \(J = 6.8\) Hz, 2H), 6.85-6.82(m, 4H), 6.72(d, \(J = 8.4\) Hz, 1H), 4.76(d, \(J = 17.2\) Hz, 1H), 4.64(d, \(J = 17.2\) Hz, 1H), 3.86(s, 3H), 3.80(s, 3H), 3.56(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 194.7, 168.3, 160.8, 149.5, 149.2, 138.0, 137.0, 128.6, 127.2, 126.6, 126.1, 125.9, 120.0, 118.7, 118.6, 111.1, 111.0, 109.5, 79.8, 56.0, 55.9, 52.9, 48.3; IR(neat) 3434, 2923, 1744, 1709, 1609, 1477, 1245, 1023, 763; HRMS (ESI) m/z: calcd for C\(_{25}\)H\(_{23}\)NO\(_5\): M+H=418.1649; found: 418.1654.

Methyl 3-(2-(benzylamino)phenyl)-3-oxo-2-phenylpropanoate 3': oil; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 9.27(s, 1H), 7.54(d, \(J = 8.0\) Hz, 1H), 7.41-7.38(m, 3H), 7.36(s, 1H), 7.33-7.32(m, 4H), 7.28-7.24(m, 3H), 6.65(d, \(J = 8.8\) Hz, 1H), 6.55-6.51(m, 1H), 5.70(s, 1H), 4.44(d, \(J = 6.4\) Hz, 2H), 3.76(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 195.2, 169.8, 152.0, 138.2, 135.5, 134.0, 132.0, 129.4, 128.7, 128.0, 127.3, 127.1, 116.0, 114.7, 112.6, 60.6, 52.7, 46.9.

5. General procedure for the preparation of the products 5.

To an oven-dried Schlenk tube were charged with \(N\)-substituted-2-iodoanilines (1a-f) (0.20 mmol, 1.0 eq), \(t\)Pr\(_2\)NEt (0.40 mmol, 2.0 eq), Pd(OAc)\(_2\) (0.02 mmol, 10 mol%), and TFP (0.04 mmol, 20 mol%) under an argon atmosphere, and then anhydrous THF (1.0 mL) was introduced by syringe. The mixture was heated at 60°C and diazoesters (4a-i) (0.80 mmol, 4.0 eq) were added slowly about 1h and stirred for another 2h. When the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure. The corresponding products 5 were purified by chromatography on silica gel.
**Methyl 1-benzyl-2-phenyl-1,2-dihydroquinoline-4-carboxylate 5a:** oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.83(d, $J = 7.6$ Hz, 1H), 7.28-7.25(m, 7H), 7.22-7.20(m, 3H), 7.04(t, $J = 7.6$ Hz, 1H), 6.68(t, $J = 7.6$ Hz, 1H), 6.62(d, $J = 6.0$ Hz, 1H), 6.50(d, $J = 8.0$ Hz, 1H), 5.22(d, $J = 5.6$ Hz, 1H), 4.54(d, $J = 16.4$ Hz, 1H), 4.08(d, $J = 16.0$ Hz, 1H), 3.80(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.6, 144.3, 141.0, 137.1, 133.5, 129.8, 128.9, 128.6, 128.2, 127.1, 126.8, 126.7, 126.5, 117.9, 117.0, 111.5, 62.5, 51.9, 51.6; IR(neat) 3028, 2923, 1720, 1595, 1492, 1446, 1250, 1192, 742, 700; HRMS (ESI) m/z: calcd for C$_{24}$H$_{20}$NO$_2$: M+H=356.1645; found: 356.1649.

**Methyl 1-benzyl-6-chloro-2-phenyl-1,2-dihydroquinoline-4-carboxylate 5b:** oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.93(d, $J = 2.0$ Hz, 1H), 7.29-7.27(m, 5H), 7.25-7.21(m, 3H), 7.20-7.18(m, 2H), 6.96(dd, $J = 8.8$ Hz, 2.4 Hz, 1H), 6.71(d, $J = 6.0$ Hz, 1H), 6.38(d, $J = 8.8$ Hz, 1H), 5.22(d, $J = 6.0$ Hz, 1H), 4.47(d, $J = 16.4$ Hz, 1H), 4.09(d, $J = 16.4$ Hz, 1H), 3.80(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.9, 142.8, 140.4, 136.5, 135.1, 129.3, 129.0, 128.7, 128.5, 127.3, 127.0, 126.6, 126.4, 125.7, 122.1, 119.2, 112.7, 62.7, 52.0, 51.8; IR(neat) 3431, 3028, 2923, 1720, 1492, 1446, 1250, 1192, 742, 699; HRMS (ESI) m/z: calcd for C$_{24}$H$_{20}$ClNO$_2$: M+H=390.1255; found: 390.1258.

**Methyl 1-benzyl-6-methyl-2-phenyl-1,2-dihydroquinoline-4-carboxylate 5c:** solid; m.p. 106-108°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.66(s, 1H), 7.28-7.25(m, 7H), 7.23-7.20(m, 3H), 6.86(d, $J = 8.4$ Hz, 1H), 6.62(d, $J = 5.6$ Hz, 1H), 6.41(d, $J = 8.4$ Hz, 1H), 5.18(d, $J = 6.0$ Hz, 1H), 4.51(d, $J = 16.0$ Hz, 1H), 4.06(d, $J = 16.4$ Hz, 1H), 3.81(s, 3H), 2.23(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.7, 142.1 140.9, 137.3, 133.7, 130.2, 128.8, 128.6, 128.2, 127.2, 127.0, 126.9, 126.7, 126.0, 118.0, 111.6, 62.4, 51.8, 51.7, 20.5; IR(neat) 3027, 2920, 1720, 1496, 1445, 1251, 1148, 1033, 732, 700; HRMS (ESI) m/z: calcd for C$_{25}$H$_{23}$NO$_2$: M+H=370.1802; found: 370.1818.
Methyl 2-phenyl-1-tosyl-1,2-dihydroquinoline-4-carboxylate 5e: solid; m.p. 167-169°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.76-7.74 (m, 1H), 7.64-7.62 (m, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.26-7.20 (m, 6H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.80 (d, $J = 6.4$ Hz, 1H), 6.09 (d, $J = 6.8$ Hz, 1H), 3.72 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 164.8, 143.7, 136.3, 135.8, 135.5, 133.2, 129.3, 129.0, 128.6, 128.5, 128.2, 128.1, 127.4, 127.2, 126.9, 126.2, 56.5, 51.9, 21.4; IR (neat) 3432, 2922, 1720, 1352, 1255, 1162, 1065, 1032, 771; HRMS (ESI) m/z: calcd for C$_{24}$H$_{21}$NO$_4$S: M+H=420.1264; found: 420.1263.

Methyl 1-methyl-2-phenyl-1,2-dihydroquinoline-4-carboxylate 5f: oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.81 (d, $J = 7.6$ Hz, 1H), 7.28-7.25 (m, 3H), 7.24-7.21 (m, 2H), 7.17-7.13 (m, 1H), 6.72-6.68 (m, 1H), 6.61 (d, $J = 6.0$ Hz, 1H), 6.48 (d, $J = 8.4$ Hz, 1H), 5.15 (d, $J = 6.0$ Hz, 1H), 3.80 (s, 3H), 2.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.5, 144.9, 140.5, 133.5, 129.9, 128.8, 128.2, 126.8, 126.5, 126.3, 117.6, 116.8, 110.6, 64.9, 51.8, 36.3; IR (neat) 3389, 3153, 2923, 1719, 1595, 1490, 1249, 1103, 1029, 770; HRMS (ESI) m/z: calcd for C$_{18}$H$_{17}$NO$_2$: M+H=280.1332; found: 280.1337.

Methyl 1-benzyl-2-(4-chlorophenyl)-1,2-dihydroquinoline-4-carboxylate 5g: oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.82 (d, $J = 7.2$ Hz, 1H), 7.31-7.28 (m, 2H), 7.26-7.22 (m, 5H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.09-7.05 (m, 1H), 6.71 (t, $J = 7.6$ Hz, 1H), 6.58 (d, $J = 6.0$ Hz, 1H), 6.52 (d, $J = 8.4$ Hz, 1H), 5.18 (d, $J = 6.0$ Hz, 1H), 4.55 (d, $J = 16.0$ Hz, 1H), 4.05 (d, $J = 16.0$ Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.4, 144.1, 139.2, 136.8, 134.1, 132.8, 129.9, 129.0, 128.7, 128.0, 127.3, 127.2, 127.2, 126.6, 117.9, 117.3, 111.7, 61.5, 52.0, 51.7; IR (neat) 3432, 2922, 1721, 1595, 1490, 1249, 1063, 1020, 771; HRMS (ESI) m/z: calcd for C$_{24}$H$_{20}$ClNO$_2$: M+H=390.1255; found: 390.1274.
Methyl 1-benzyl-2-(4-bromophenyl)-1,2-dihydroquinoline-4-carboxylate 5h: oil; 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.82(d, $J = 8.0$ Hz, 1H), 7.39(d, $J = 8.0$ Hz, 2H), 7.29(d, $J = 6.0$ Hz, 2H), 7.25(d, $J = 6.4$ Hz, 3H), 7.07(d, $J = 8.4$ Hz, 3H), 6.71(t, $J = 7.6$ Hz, 1H), 6.57(d, $J = 6.0$ Hz, 1H), 6.53(d, $J = 8.4$ Hz, 1H), 5.17(d, $J = 6.0$ Hz, 1H), 4.56(d, $J = 16.0$ Hz, 1H), 4.05(d, $J = 16.0$ Hz, 1H), 3.82(s, 3H); 
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.5, 144.1, 139.7, 136.8, 132.7, 132.0, 130.0, 128.7, 128.4, 127.3, 127.2, 126.6, 122.2, 117.9, 117.4, 111.7, 61.6, 51.9, 51.7; IR(neat) 3425, 2946, 1720, 1594, 1488, 1249, 1191, 1066, 1013, 741; HRMS (ESI) m/z: calcd for C$_{24}$H$_{20}$BrNO$_2$: M+H=434.0750; found: 434.0755.

Methyl 1-benzyl-2-(4-methoxyphenyl)-1,2-dihydroquinoline-4-carboxylate 5i: solid; m.p. 127-129°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.84(d, $J = 7.6$ Hz, 1H), 7.29-7.22(m, 5H), 7.11(d, $J = 8.4$ Hz, 2H), 7.05-7.01(m, 1H), 6.78(d, $J = 8.4$ Hz, 2H), 6.68(t, $J = 7.6$ Hz, 1H), 6.61(d, $J = 6.0$ Hz, 1H), 6.48(d, $J = 8.4$ Hz, 1H), 5.15(d, $J = 6.0$ Hz, 1H), 4.51(d, $J = 16.4$ Hz, 1H), 4.08(d, $J = 16.4$ Hz, 1H), 3.80(s, 3H), 3.74(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.6, 159.6, 144.3, 137.1, 133.8, 133.0, 129.7, 128.6, 128.0, 127.1, 126.6, 126.4, 118.0, 117.0, 114.1, 111.6, 61.7, 51.9, 51.8, 51.4; IR(neat) 3431, 2923, 1719, 1600, 1499, 1445, 1249, 1172, 1029, 771; HRMS (ESI) m/z: calcd for C$_{25}$H$_{23}$NO$_3$: M+H=386.1751; found: 386.1765.

Methyl 1-benzyl-2-(3-methoxyphenyl)-1,2-dihydroquinoline-4-carboxylate 5j: oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.83-7.81(m, 1H), 7.33(d, $J = 8.0$ Hz, 1H), 7.29-7.25(m, 4H), 7.21-7.17(m, 1H), 7.06-7.02(m, 1H), 6.82-6.78(m, 2H), 6.76-6.75(m, 1H), 6.70-6.66(m, 1H), 6.61(d, $J = 6.0$ Hz, 1H), 6.51(d, $J = 8.0$ Hz, 1H), 5.21(d, $J = 6.0$ Hz, 1H), 4.56(d, $J = 16.0$ Hz, 1H), 4.10(d, $J = 15.2$ Hz, 1H), 3.80(s, 3H), 3.69(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.5, 160.0, 144.4, 142.6, 137.1, 133.4, 129.9, 129.8, 128.6, 127.8, 127.1, 127.1, 126.5, 119.0, 117.9, 117.1, 113.4, 112.3, 111.5, 62.5, 55.1, 51.8, 51.7; IR(neat) 3398, 2921, 1720, 1598, 1442, 1381,
1252, 1062, 772; HRMS (ESI) m/z: calcd for C_{25}H_{23}NO_3: M+H=386.1751; found: 386.1756.

**Methyl 1-benzyl-2-(2-methoxyphenyl)-1,2-dihydroquinoline-4-carboxylate 5k:** oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.78(dd, \(J = 7.6\) Hz, 1.6 Hz, 1H), 7.30-7.20(m, 7H), 7.05-7.01(m, 1H), 6.86-6.82(m, 2H), 6.71(d, \(J = 6.0\) Hz, 1H), 6.67-6.63(m, 1H), 6.50(d, \(J = 8.0\) Hz, 1H), 5.79(d, \(J = 6.0\) Hz, 1H), 4.58(d, \(J = 16.4\) Hz, 1H), 4.17(d, \(J = 16.4\) Hz, 1H), 3.80(s, 3H), 3.75(s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 166.8, 144.7, 137.6, 133.2, 129.7, 128.9, 128.5, 128.0, 126.9, 126.9, 126.8, 126.5, 121.1, 117.8, 116.7, 111.3, 110.5, 56.5, 55.3, 52.4, 51.8; IR(neat) 3396, 2923, 1721, 1625, 1443, 1382, 1220, 1046, 1023, 771; HRMS (ESI) m/z: calcd for C_{25}H_{23}NO_3: M+H=386.1751; found: 386.1761.

**Methyl 1-benzyl-2-(naphthalen-2-yl)-1,2-dihydroquinoline-4-carboxylate 5l:** oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.86(d, \(J = 8.0\) Hz, 1H), 7.80-7.74(m, 3H), 7.58(s, 1H), 7.46-7.41(m, 3H), 7.31-7.23(m, 5H), 7.09-7.05(m, 1H), 6.71(t, \(J = 7.6\) Hz, 1H), 6.65(d, \(J = 6.0\) Hz, 1H), 6.52(d, \(J = 8.4\) Hz, 1H), 5.43(d, \(J = 5.6\) Hz, 1H), 4.56(d, \(J = 16.4\) Hz, 1H), 4.12(d, \(J = 16.4\) Hz, 1H), 3.80(s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 166.6, 144.4, 138.4, 137.0, 133.3, 133.2, 129.9, 129.1, 128.7, 128.1, 127.7, 127.1, 126.6, 126.3, 126.1, 125.1, 124.9, 117.8, 117.1, 111.5, 62.9, 51.9, 51.5; IR(neat) 3426, 2922, 1720, 1597, 1489, 1447, 1219, 1124, 1063, 771; HRMS (ESI) m/z: calcd for C_{28}H_{23}NO_2: M+H=406.1802; found: 406.1819.

**Methyl 1-benzyl-2-(furan-2-yl)-1,2-dihydroquinoline-4-carboxylate 5m:** oil; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.84(dd, \(J = 7.6\) Hz, 1.2 Hz, 1H), 7.32-7.30(m, 5H), 7.25(s, 1H), 7.10-7.06(m, 1H), 6.77-6.73(m, 1H), 6.68(d, \(J = 6.4\) Hz, 1H), 6.56(d, \(J = 8.4\) Hz, 1H), 6.21(q, \(J = 1.6\) Hz, 1H), 6.05(d, \(J = 3.2\) Hz, 1H), 5.14(d, \(J = 6.4\) Hz, 1H), 4.62(d, \(J = 15.6\) Hz, 1H), 4.30(d, \(J = 15.2\) Hz, 1H), 3.86(s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 166.5, 152.5, 143.9, 142.5, 137.2, 130.2, 129.5, 128.9, 128.6, 127.5, 127.2,
126.6, 119.0, 117.7, 112.6, 110.2, 108.2, 54.2, 52.4, 52.0; IR(neat) 3395, 2923, 1722, 1444, 1382, 1219, 1065, 1023, 771; HRMS (ESI) m/z: calcd for C22H19NO3: M+H=346.1438; found: 346.1450.

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-1,2-dihydroquinoline-4-carboxylate 5n: oil; 1H NMR (400 MHz, CDCl3) δ: 7.83-7.78(m, 2H), 7.33(d, J = 8.4 Hz, 1H), 7.30-7.25(m, 3H), 7.06-7.02(m, 1H), 6.73(d, J = 1.6 Hz, 1H), 6.69(d, J = 7.6 Hz, 2H), 6.62(dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.58(d, J = 6.0 Hz, 1H), 6.49(d, J = 8.0 Hz, 1H), 5.90(s, 2H), 5.12(d, J = 6.0 Hz, 1H), 4.54(d, J = 16.0 Hz, 1H), 4.11(d, J = 16.0 Hz, 1H), 3.82(s, 3H); 13C NMR (100 MHz, CDCl3) δ: 166.6, 148.1, 147.6, 144.1, 137.0, 134.9, 133.4, 129.8, 128.6, 127.8, 127.1, 126.8, 126.5, 119.9, 117.7, 117.1, 111.6, 108.2, 107.3, 101.1, 62.1, 51.8, 51.4; IR(neat) 3430, 2918, 1721, 1597, 1490, 1245, 1216, 1036, 772; HRMS (ESI) m/z: calcd for C25H21NO4: M+H=400.1543; found: 400.1559.

Methyl 1-benzyl-6-chloro-2-(4-methoxyphenyl)-1,2-dihydroquinoline-4-carboxylate 5o: oil; 1H NMR (400 MHz, CDCl3) δ: 7.93(d, J = 1.6 Hz, 1H), 7.28(d, J = 6.8 Hz, 2H), 7.25-7.22(m, 3H), 7.10(d, J = 8.0 Hz, 2H), 6.95(q, J = 2.4 Hz, 1H), 6.80(d, J = 8.4 Hz, 2H), 6.70(d, J = 6.0 Hz, 1H), 6.37(d, J = 8.8 Hz, 1H), 5.15(d, J = 5.6 Hz, 1H), 4.44(d, J = 16.0 Hz, 1H), 4.09(d, J = 16.0 Hz, 1H), 3.81(s, 3H), 3.75(s, 3H); 13C NMR (100 MHz, CDCl3) δ: 166.0, 159.7, 142.8, 136.6, 135.4, 132.4, 129.1, 128.7, 128.0, 127.3, 127.0, 126.3, 125.4, 122.0, 119.3, 114.2, 112.8, 61.9, 55.2, 52.0, 51.6; IR(neat) 3046, 2923, 1719, 1604, 1488, 1249, 1220, 1029, 771; HRMS (ESI) m/z: calcd for C25H22ClNO3: M+H=420.1361; found: 420.1372.
2-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-6-chloro-1,2-dihydroquinoline-4-carboxylate 5p: oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.91 (d, $J$ = 2.4 Hz, 1H), 7.30-7.22 (m, 5H), 6.96 (dd, $J$ = 8.8 Hz, 2.4 Hz, 1H), 6.71-6.66 (m, 3H), 6.61 (dd, $J$ = 8.0 Hz, 1.2 Hz, 1H), 6.38 (d, $J$ = 9.2 Hz, 1H), 5.90 (s, 2H), 5.13 (d, $J$ = 6.0 Hz, 1H), 4.47 (d, $J$ = 16.0, 1H), 4.11 (d, $J$ = 16.0 Hz, 1H), 3.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.0, 148.2, 147.8, 142.6, 136.5, 134.9, 129.3, 128.7, 127.3, 127.0, 126.3, 125.6, 122.1, 119.9, 119.1, 112.8, 108.3, 107.2, 101.1, 62.3, 51.9, 51.6; IR(neat) 3395, 2921, 1720, 1487, 1441, 1360, 1221, 119.9, 119.1, 119.1, 112.8, 108.3, 107.2, 101.1, 62.3, 51.9, 51.6; HRMS (ESI) m/z: calcd for C$_{25}$H$_{20}$ClNO$_4$: M+H=434.1154; found: 434.1164.

6. References.


7. The tables for optimizing reaction conditions.

7.1 Table 1: Optimization of the palladium-catalyzed reaction of CO with 1a and 2a.$^{[a]}$

<table>
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<tr>
<th>Entry</th>
<th>Cat. (mol %)</th>
<th>Base</th>
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<th>Yield (%)$^{[b]}$</th>
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Unless otherwise noted, reaction conditions are as follows: 1a (0.2 mmol, 1.0 equiv), 2a (0.8 mmol, 4.0 equiv), base (0.4 mmol, 2.0 equiv), Pd (5 mol%), ligand (10 mol%).

[b] Yield of isolated product.

c] The reaction was carried out with 2.0 equiv of 2a. TFP = tris(2-furyl)phosphine, Xphos = 2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl, DMF = N,N-dimethylformamide, DMAC = N,N-dimethylacetamide, NMP = N-methyl-2-pyrrolidinone.

### Table 2: Selected conditions of palladium-catalyzed reaction of 1a with 4a.
8. The crystal structure of product 3m and 5i.

![Crystal structure of 3m and 5i](image)

**Datablock: p21c**

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<th>Wavelength=0.71073 Å</th>
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Datablock: p21c

Bond precision: C–C = 0.0077 Å

Wavelength = 0.71073 Å

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- b = 9.614(9) Å
- c = 20.75(2) Å
- α = 90°
- β = 101.745(11)°
- γ = 90°

Temperature: 296 K

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Correction method: MULTI–SCAN

Data completeness = 0.988

θ(max) = 25.500°

R(reflections) = 0.0901(2285)

wR2(reflections) = 0.3272(3723)

S = 1.139

Npar = 265
9. $^1$H and $^{13}$C NMR spectra for new compounds.