Direct Synthesis of 8-Aryl Tetrahydroquinolines via Pd-catalyzed ortho-Arylation of Aryl Ureas in Water

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1. General information:

Unless otherwise noted, all experiments were carried out in air, and all commercially available chemicals were used as received from Aldrich, Acros or Strem without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer ($^1$H 400 MHz and $^{13}$C 106 MHz, respectively). Chemical shifts ($\delta$) are given in ppm and are referenced to residual solvent peaks. Et$_2$O was dried by distillation from Na/Ph$_2$CO. Tetrahydroquinolines were prepared according to the previous reports.$^1$, $^2$

2. The general procedure for the synthesis of N-urea tetrahydroquinolines

To a solution of 1,2,3,4-tetrahydroquinoline (5.0 mmol) in anhydrous Et$_2$O was added dropwise a solution of n-BuLi in hexane ($2.6$ mL, 6.5 mmol) in an ice bath. The resulting mixture was stirred at room temperature under N$_2$ for 1 h. Then the mixture was cooled to 0 $^\circ$C, and dimethylcarbamic chloride (6.0 mmol, 646 mg) was added dropwise. After being stirred at room temperature for 12 h, the reaction was quenched with saturated aqueous NH$_4$Cl, and extracted with CH$_2$Cl$_2$ ($3 \times 20$ ml). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), filtered, and concentrated in vacuo. The residue was then purified via flash chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

$N,N$-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1a), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.97 (m, 2H), 2.75 (t, $J$ = 6.64 Hz, 2H), 2.82 (s, 6H), 3.56 (t, $J$ = 6.16 Hz, 2H), 6.87 (d, $J$ = 6.08 Hz, 2H), 7.06 (d, $J$ = 6.88 Hz, 2H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 23.5, 26.9, 37.8, 45.4, 119.3, 121.6, 126.4, 127.6, 129.0, 140.9, 160.9; IR (neat, cm$^{-1}$): 1645; HRMS (ESI) calcd. for C$_{12}$H$_{16}$N$_2$NaO [M+H]$^+$: 227.1155, found: 227.1152.

$N,N,2$-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1b), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.18 (d, $J$ = 6.52 Hz, 3H), 1.73 (m, 1H), 2.03 (m, 1H), 2.71 (m, 2H), 2.78 (s, 6H), 4.73 (m, 1H), 6.77 (d, $J$ = 8.2 Hz, 1H), 6.85 (t, $J$ = 7.36 Hz, 1H), 7.07 (m, 2H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 19.0, 24.2, 29.7, 37.7, 49.5, 119.5, 121.3, 126.6, 127.4, 128.7, 139.5, 160.6; IR (neat, cm$^{-1}$): 1645; HRMS (ESI) calcd. for C$_{13}$H$_{18}$N$_2$NaO [M+H]$^+$: 241.1311, found: 241.1309.

6-methoxy-$N,N,2$-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1c), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.15 (d, $J$ = 6.52 Hz, 3H), 1.63 (m, 1H), 2.07 (m, 1H), 2.65 (m, 2H), 2.73 (s, 6H), 4.23 (m, 1H), 6.66 (m, 2H), 6.79 (d, $J$ = 8.44 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 18.9, 24.7, 30.2, 37.8, 49.4, 55.4, 112.4, 113.4, 121.7, 139.7, 132.7, 154.6, 160.9; IR (neat, cm$^{-1}$): 1645; HRMS (ESI) calcd. for C$_{14}$H$_{20}$N$_2$NaO$_2$ [M+H]$^+$: 271.1417, found: 271.1414.

2-ethyl-$N,N$-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (1d), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.85 (t, $J$ = 7.52 Hz, 3H), 1.59 (m, 1H), 1.65 (m, 1H), 1.81 (m, 1H), 1.91 (m, 1H), 2.61 (m, 2H), 2.68 (s, 6H), 3.96 (m, 1H), 6.77 (m, 2H), 6.98 (m, 2H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 10.5, 23.9, 25.2, 26.4, 37.8, 54.9, 119.9, 121.5, 126.5, 127.5, 128.8, 139.6, 160.5; IR (neat, cm$^{-1}$): 1645; HRMS (ESI)
calcd. for C\textsubscript{14}H\textsubscript{20}N\textsubscript{2}NaO [M+H]\textsuperscript{+}: 255.1468, found: 255.1464.

\textit{N,N}-dimethyl-2-propyl-3,4-dihydroquinoline-1(2H)-carboxamide (1e), yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 0.91 (t, \(J = 7.2\) Hz, 3H), 1.38 (m, 3H), 1.68 (m, 1H), 1.86 (m, 1H), 2.01 (m, 1H), 2.75 (m, 2H), 2.81 (s, 6H), 4.14 (m, 1H), 6.87 (m, 2H), 7.08 (m, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 14.1, 19.4, 23.9, 26.9, 34.5, 37.9, 53.5, 120.2, 121.5, 126.5, 127.5, 128.9, 139.6, 160.6; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{15}H\textsubscript{22}N\textsubscript{2}NaO [M+H]\textsuperscript{+}: 269.1624, found: 269.1621.

\textit{N,N}-dimethyl-2-butyl-3,4-dihydroquinoline-1(2H)-carboxamide (1f), yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 0.86 (t, \(J = 7.08\) Hz, 3H), 1.31 (m, 6H), 1.69 (m, 1H), 1.84 (m, 1H), 1.93 (m, 1H), 2.70 (m, 1H), 2.74 (s, 6H), 4.09 (m, 1H), 6.84 (m, 2H), 7.06 (m, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 14.1, 22.7, 23.9, 26.8, 28.3, 31.9, 37.9, 53.7, 120.2, 121.5, 126.5, 127.5, 128.8, 139.6, 160.6; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{16}H\textsubscript{24}N\textsubscript{2}NaO [M+H]\textsuperscript{+}: 283.1781, found: 283.1777.

\textit{N,N}-dimethyl-2-pentyl-3,4-dihydroquinoline-1(2H)-carboxamide (1g), yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 0.85 (t, \(J = 7.04\) Hz, 3H), 1.33 (m, 8H), 1.71 (m, 1H), 1.87 (m, 1H), 1.96 (m, 1H), 2.70 (m, 1H), 2.76 (s, 6H), 4.11 (m, 1H), 6.86 (m, 2H), 7.08 (m, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 14.0, 22.6, 23.9, 25.7, 26.7, 31.8, 32.2, 53.7, 120.2, 121.5, 126.5, 127.5, 128.8, 139.6, 160.6; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{17}H\textsubscript{26}N\textsubscript{2}NaO [M+H]\textsuperscript{+}: 297.1937, found: 297.1932.

\textit{N,N}-dimethyl-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (1h), yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.27 (m, 2H), 2.68 (m, 2H), 2.85 (s, 6H), 5.24 (t, \(J = 5.04\) Hz, 1H), 6.92 (t, \(J = 7.32\) Hz, 1H), 7.00 (d, \(J = 8.12\) Hz, 1H), 7.07 (d, \(J = 7.32\) Hz, 1H), 7.19 (m, 2H), 7.28 (m, 4H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 24.3, 30.4, 37.9, 58.0, 119.9, 121.5, 126.4, 126.6, 126.9, 127.7, 128.4, 128.9, 140.3, 143.1, 160.9; IR (neat, cm\textsuperscript{-1}): 1651; HRMS (ESI) calcd. for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}NaO [M+H]\textsuperscript{+}: 303.1468, found: 303.1473.

\textit{N,N}-dimethyl-2H-benzo[b][1,4]oxazine-4(3H)-carboxamide (1k), yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.93 (s, 6H), 3.68 (t, \(J = 4.52\) Hz, 2H), 4.32 (t, \(J = 4.68\) Hz, 2H), 6.85 (m, 3H), 6.94 (m, 1H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 38.1, 43.4, 66.3, 117.1, 119.3, 120.6, 122.9, 128.1, 144.8, 159.2; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}NaO [M+H]\textsuperscript{+}: 309.1397, found: 309.1394.
calcd. for C_{11}H_{14}N_{2}NaO_{2} [M+H]^+: 229.0948, found: 229.0945.

\textit{N,N}-dimethylindoline-1-carboxamide (1l), red oil; \textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.93 (s, 6H), 3.02 (t, \(J = 8.20\) Hz, 2H), 3.90 (t, \(J = 8.20\) Hz, 2H), 6.87 (td, \(J = 7.41, 0.84\) Hz, 1H), 6.95 (d, \(J = 7.93\) Hz, 1H), 7.14 (q, \(J = 7.64\) Hz, 2H); \textit{^{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 28.1, 38.1, 50.3, 113.3, 121.3, 124.8, 126.9, 131.3, 144.3, 160.2; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C_{11}H_{14}N_{2}NaO [M+Na]^+: 213.0998, found: 213.0995.

1,1,3-Trimethyl-3-phenyl-urea (1m), brown liquid; \textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.57 ( s, 6H), 3.09 ( s, 3H), 6.96 (m, 3H), 7.20 (t, \(J = 8.08\) Hz, 2H); \textit{^{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 37.8, 39.4, 123.4, 124.0, 129.3, 146.8, 161.7; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C_{10}H_{14}N_{2}NaO [M+Na]^+: 201.0998, found: 201.0997.

3. The general procedure for the arylation of \textit{N}-urea tetrahydroquinolines

\textit{N}-urea tetrahydroquinoline (0.5 mmol), Pd(MeCN)\textsubscript{2}(Tos)\textsubscript{2} (25 mg, 10 mmol%), AgOAc (167 mg, 1.0 mmol), TsOH (285 mg, 1.5 mmol) and 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol) were sequentially added in air to a reaction tube. Then H\textsubscript{2}O (3.0 mL) was added and the resulting mixture was vigorously stirred for 16 h at 80 °C. After cooling to room temperature, the reaction mixture was neutralized by adding aqueous NaHCO\textsubscript{3} solution and extracted with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic phases were dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. The residue was then purified by flash chromatography (hexane/ethylacetate = 10/1) to give the pure product.

\textit{N,N}-dimethyl-8-p-tolyl-3,4-dihydroquinoline-1(2H)-carboxamide (3aa) yellow solid, mp: 123. °C; \textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.29 (m, 2H), 2.10 (s, 6H), 2.37 (s, 3H), 2.70 (s, 2H), 7.11 (m, 2H), 7.18 (m, 2H), 7.22 (m, 3H); \textit{^{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 21.1, 25.1, 27.6, 36.8, 45.0, 124.1, 126.9, 127.3, 129.0, 129.1, 134.6, 135.2, 136.4, 136.6, 138.7, 159.8; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C_{19}H_{22}N_{2}NaO [M+Na]^+: 317.1624, found: 317.1621.

\textit{N,N}-dimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ab), yellow solid, mp: 119 °C; \textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.27 (m, 2H), 2.08 (s, 6H), 2.69 (s, 2H), 3.70 (bs, 2H), 7.14 (m, 3H), 7.28 (m, 3H), 7.34 (m, 2H); \textit{^{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 25.0, 27.6, 36.7, 45.1, 124.1, 127.0, 127.2, 128.4, 129.2, 134.5, 135.2, 138.7, 139.3, 159.8; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C_{18}H_{20}N_{2}NaO [M+Na]^+: 303.1468, found: 303.1465.

8-(4-methoxyphenyl)-\textit{N,N}-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ac), yellow solid, mp: 149 °C; \textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.04 (s, 2H), 2.13 (s, 6H), 2.68 (s, 2H), 3.69 (bs, 2H), 3.81 (s, 3H), 6.95 (d, \(J = 8.72\) Hz, 2H), 7.08 (m, 1H), 7.13 (m, 2H), 7.23 (d, \(J = 8.68\) Hz, 2H); \textit{^{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 25.1, 27.6, 36.8, 45.0, 55.3, 113.8, 123.9, 126.7, 128.6, 129.1, 132.0, 134.5, 134.9, 138.8, 158.7, 159.6; IR (neat, cm\textsuperscript{-1}): 1651; HRMS (ESI) calcd. for C_{19}H_{22}N_{2}O_{2} [M+Na]^+: 333.1574, found: 333.1571.

8-(4-isopropylphenyl)-\textit{N,N}-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ad), yellow, mp: 117 °C; \textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.04 (d, \(J = 6.92\) Hz, 6H), 2.68 (s, 2H), 2.93 (s, 3H), 3.71 (bs, 2H), 7.10 (t, \(J = 7.36\) Hz, 2H), 7.62 (t, \(J = 7.36\) Hz, 2H), 7.68 (m, 3H), 8.03 (d, \(J = 7.36\) Hz, 2H), 8.12 (m, 2H); \textit{^{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 25.1, 27.6, 36.8, 45.0, 55.3, 113.8, 123.9, 126.7, 128.6, 129.1, 132.0, 134.5, 134.9, 138.8, 158.7, 159.6; IR (neat, cm\textsuperscript{-1}): 1651; HRMS (ESI) calcd. for C_{19}H_{22}N_{2}O_{2} [M+Na]^+: 333.1574, found: 333.1571.
Hz, 1H), 7.15 (d, J = 5.92 Hz, 1H), 7.20 (dd, J = 7.36, 1.48 Hz, 1H), 7.24 (d, J = 8.16 Hz, 2H), 7.29 (d, J = 8.24 Hz, 2H); 13C NMR (100.6 MHz, CDCl3) δ 24.0, 25.1, 27.6, 33.9, 36.6, 45.0, 123.9, 126.9, 127.4, 129.1, 134.4, 135.2, 136.9, 138.9, 147.7, 159.6; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C21H26N2NaO [M+Na]⁺: 345.1937, found: 345.1933.

8-(3,5-dimethylphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ae), yellow, mp: 116 °C; 1H NMR (400 MHz, CDCl3) δ 2.07 (s, 2H), 2.11 (s, 6H), 2.37 (s, 6H), 2.70 (s, 2H), 3.70 (bs, 2H), 6.91 (s, 2H), 6.95 (d, J = 8.36 Hz, 1H), 7.09 (t, J = 7.41 Hz, 1H), 7.15 (dd, J = 7.28, 1.64 Hz, 1H), 7.20 (dd, J = 7.44, 1.66 Hz, 1H); 13C NMR (100.6 MHz, CDCl3) δ 21.5, 25.1, 27.7, 36.7, 45.1, 123.8, 125.3, 126.9, 128.5, 129.1, 134.5, 135.4, 137.7, 138.9, 139.2, 159.8; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C20H24N2NaO [M+Na]⁺: 331.1781, found: 331.1779.

8-(3,4-dimethylphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3af), yellow solid, mp: 121 °C; 1H NMR (400 MHz, CDCl3) δ 1.28 (s, 2H), 2.10 (s, 6H), 2.29 (s, 3H), 2.32 (s, 3H), 2.69 (s, 2H), 3.71 (bs, 2H), 7.05 (m, 2H), 7.12 (m, 2H), 7.19 (m, 2H); 13C NMR (100.6 MHz, CDCl3) δ 19.4, 19.9, 25.1, 27.6, 29.7, 36.7, 45.0, 124.0, 124.9, 126.8, 126.5, 129.1, 129.6, 134.6, 135.2, 135.3, 136.4, 136.8, 136.7, 159.8; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C20H24N2NaO [M+Na]⁺: 331.1781, found: 331.1776.

8-(3-methoxyphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ag), yellow oil; 1H NMR (400 MHz, CDCl3) δ 2.06 (bs, 2H), 2.13 (s, 6H), 2.70 (s, 2H), 3.71 (s, 2H), 3.87 (s, 3H), 6.82 (m, 2H), 6.90 (d, J = 7.61 Hz, 1H), 7.02 (m, 1H), 7.17 (d, J = 6.42 Hz, 1H), 7.22 (dd, J = 7.48, 1.36 Hz, 1H), 7.32 (m, 1H); 13C NMR (100.6 MHz, CDCl3) δ 25.1, 27.6, 36.7, 45.1, 55.3, 112.8, 112.9, 120.0, 124.0, 127.2, 129.1, 129.3, 134.6, 138.9, 140.7, 159.5, 159.7; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C19H22N2NaO2 [M+Na]⁺: 333.1574, found: 333.1570.

8-(4-fluorophenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ah), yellow soild, mp: 126 °C; 1H NMR (400 MHz, CDCl3) δ 2.03 (s, 2H), 2.16 (s, 6H), 2.69 (m, 2H), 3.66 (m, 2H), 3.67 (m, 2H), 7.11 (t, J = 7.41 Hz, 1H), 7.16 (d, J = 5.40 Hz, 2H), 7.35 (d, J = 8.36 Hz, 2H); 13C NMR (100.6 MHz, CDCl3) δ 24.9, 27.5, 36.8, 45.2, 115.0, 115.3, 124.0, 127.4, 129.1(t, J = 14.86 Hz), 134.3, 135.6, 138.9, 159.7, 160.7, 163.2; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C18H19FN2NaO [M+Na]⁺: 321.1371, found: 321.1374.

8-(4-chlorophenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ai), yellow solid, mp: 124 °C; 1H NMR (400 MHz, CDCl3) δ 2.03 (m, 2H), 2.15 (s, 6H), 2.70 (m, 2H), 3.67 (m, 2H), 3.68 (bs, 2H), 3.90 (s, 3H), 7.10 (t, J = 7.41 Hz, 1H), 7.16 (d, J = 5.40 Hz, 2H), 7.35 (d, J = 8.04 Hz, 2H), 8.06 (m, 2H); 13C NMR (100.6 MHz, CDCl3) δ 20.9, 24.8, 27.5, 36.7, 45.3, 52.1, 124.1, 127.5, 128.0, 128.6, 129.0, 129.7, 134.0, 134.3, 138.7, 144.2, 159.9, 166.7, 174.5; IR (neat, cm⁻¹): 1645, 1720; HRMS (ESI) calcd. for C18H19ClN2NaO [M+Na]⁺: 337.1079, found: 337.1074.

Methyl 4-(1-(dimethylcarbamoyl)-1,2,3,4-tetrahydroquinolin-8-yl)- benzoate (3aj), orange solid, mp: 148 °C; 1H NMR (400 MHz, CDCl3) δ 2.05 (s, 2H), 2.08 (s, 6H), 2.70 (s,2H), 3.68 (bs, 2H), 3.90 (s, 3H), 7.10 (t, J = 7.41 Hz, 1H), 7.16 (d, J = 5.40 Hz, 2H), 7.35 (d, J = 8.04 Hz, 2H), 8.06 (m, 2H); 13C NMR (100.6 MHz, CDCl3) δ 20.9, 24.8, 27.5, 36.7, 45.3, 52.1, 124.1, 127.5, 128.0, 128.6, 129.0, 129.7, 134.0, 134.3, 138.7, 144.2, 159.9, 166.7, 174.5; IR (neat, cm⁻¹): 1645, 1720; HRMS (ESI) calcd. for C18H19ClN2NaO [M+Na]⁺: 337.1079, found: 337.1074.
calcd. for HRMS (ESI) calcd. for C_{20}H_{22}N_{2}NaO_{3} [M+Na]^+: 361.1523, found: 361.1518.

8-(4-acetylphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ak), yellow solid, mp: 146 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.03 (s, 1H), 2.08 (s, 6H), 2.12 (d, J = 3.32 Hz, 1H), 2.60 (s, 3H), 2.72 (s, 2H), 3.69 (bs, 2H), 7.11 (t, J = 7.32 Hz, 1H), 7.17 (t, J = 7.02 Hz, 2H), 7.38 (d, J = 8.16 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 24.8, 26.7, 27.6, 36.7, 45.2, 124.0, 127.6, 128.1, 128.5, 128.6, 129.0, 133.9, 134.2, 135.5, 138.9, 144.5, 159.7, 197.7; IR (neat, cm⁻¹): 1645, 1680; HRMS (ESI) calcd. for C_{20}H_{23}N_{2}O_{2} [M+H]^+: 323.1754, found: 323.1751.

N,N-dimethyl-8-(4-nitrophenyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3al), yellow solid, mp: 156 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.04 (m, 2H), 2.16 (s, 6H), 2.77 (s, 2H), 3.69 (s, 2H), 7.16 (t, J = 6.24 Hz, 2H), 7.24 (m, 1H), 7.25 (d, J = 8.68 Hz, 2H), 8.28 (d, J = 8.72 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 24.6, 27.5, 36.8, 45.4, 123.6, 124.2, 126.9, 128.4, 128.8, 132.9, 134.0, 138.9, 146.5, 146.6, 159.8; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C_{18}H_{19}N_{3}NaO_{3} [M+Na]^+: 348.1319, found: 348.1317.

N,N-dimethyl-8-(3-(trifluoromethyl)phenyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3am), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 2.07 (s, 2H), 2.15 (s, 6H), 2.76 (s, 2H), 3.69 (s, 2H), 7.17 (m, 2H), 7.21 (dd, J = 6.76, 2.16 Hz, 1H), 7.47 (d, J = 6.88 Hz, 1H), 7.56 (m, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 24.7, 27.5, 36.7, 45.4, 123.6, 124.1, 126.5, 128.1, 128.8, 128.9, 129.1, 131.3, 133.9, 134.0, 139.5, 159.8; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C_{19}H_{19}F_{3}N_{2}NaO [M+Na]^+: 371.1342, found: 371.1342.

N,N-dimethyl-8-(3-nitrophenyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3an), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 2.04 (s, 2H), 2.19 (s, 6H), 2.77 (s, 2H), 3.67 (s, 2H), 7.15 (m, 2H), 7.22 (dd, J = 6.14, 2.84 Hz, 1H), 7.57 (t, J = 7.78 Hz, 1H), 7.62 (d, J = 7.92 Hz, 1H), 8.13 (t, J = 3.28 Hz, 1H), 7.12 (m, 2H), 7.18 (dd, J = 8.84, 1.72 Hz, 1H), 7.22 (d, J = 9.72 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 24.4, 27.5, 36.8, 45.7, 121.7, 122.5, 124.2, 128.7, 128.9, 132.3, 133.0, 133.8, 134.3, 138.8, 141.6, 148.2, 160.0; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C_{18}H_{19}N_{3}NaO_{3} [M+Na]^+: 348.1319, found: 348.1314.

N,N,2-trimethyl-8-(p-tolyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3ba), yellow solid, mp: 121 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.46 (d, J = 6.44 Hz, 3H), 1.55 (m, 1H), 2.06 (s, 6H), 2.37 (s, 3H), 2.43 (m, 1H), 2.54 (m, 1H), 2.75 (m, 1H), 4.33 (t, J = 6.68 Hz, 1H), 7.12 (m, 2H), 7.18 (dd, J = 8.84, 1.72 Hz, 1H), 7.22 (d, J = 7.92 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 21.1, 22.7, 26.8, 29.7, 36.7, 51.2, 124.0, 125.4, 126.7, 127.4, 128.9, 129.4, 135.9, 136.5, 136.8, 137.1, 159.9; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C_{20}H_{24}N_{2}NaO [M+Na]^+: 331.1781, found: 331.1778.

N,N,2-trimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bb), yellow solid, mp: 118 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.55 (m, 1H), 2.07 (s, 6H), 2.42 (d, J = 5.02 Hz, 1H), 2.57 (m, 1H), 2.76 (m, 1H), 4.33 (t, J = 3.28 Hz, 1H), 7.12 (t, J = 7.32 Hz, 1H), 7.17 (m, 2H), 7.29 (m, 1H), 7.39 (m, 4H); ¹³C NMR (100.6 MHz, CDCl₃) δ 21.2, 26.7, 33.1, 36.6, 51.2, 124.0, 126.9, 127.0, 127.6, 128.2, 129.4, 134.4, 135.9, 137.1, 139.7, 159.8; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for
C_{19}H_{22}N_{2}NaO [M+Na]^+ : 317.1624, found: 317.1621.

8-(4-methoxyphenyl)-N,N,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bc), yellow solid, mp: 157 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.44 (d, \(J = 6.44\) Hz, 3H), 1.53 (m, 1H), 2.10 (s, 6H), 2.42 (d, \(J = 5.64\) Hz, 1H), 2.54 (m, 1H), 2.74 (m, 1H), 3.83 (s, 3H), 4.33 (t, \(J = 6.56\) Hz, 1H), 6.95 (d, \(J = 8.68\) Hz, 2H), 7.12 (m, 3H), 7.31 (d, \(J = 8.62\) Hz, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 21.1, 22.7, 26.8, 29.7, 36.7, 51.2, 124.0, 126.7, 127.4, 128.9, 135.9, 136.5, 136.8, 137.1, 159.9; IR (neat, cm\textsuperscript{-1}): 1651; HRMS (ESI) calcd. for C\textsubscript{20}H\textsubscript{24}N\textsubscript{2}NaO\textsubscript{2} [M+Na]^+ : 347.1730, found: 347.1725.

8-(4-fluorophenyl)-N,N,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bh), yellow solid, mp: 128 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.43 (d, \(J = 6.48\) Hz, 3H), 1.55 (m, 1H), 2.13 (s, 6H), 2.39 (m, 1H), 2.57 (m, 1H), 2.76 (m, 1H), 4.30 (m, 1H), 7.13 (m, 5H), 7.34 (m, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 21.0, 26.5, 32.7, 36.7, 51.2, 114.9, 115.2, 124.1, 127.2, 129.3, 135.0, 135.8, 137.1, 159.9, 160.7, 163.1; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{19}H\textsubscript{21}FN\textsubscript{2}NaO [M+Na]^+ : 335.1530, found: 335.1528.

8-(4-chlorophenyl)-N,N,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3bi), yellow solid, mp: 124 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.43 (d, \(J = 6.48\) Hz, 3H), 1.55 (m, 1H), 2.12 (s, 6H), 2.39 (m, 1H), 2.56 (m, 1H), 2.76 (m, 1H), 4.30 (m, 1H), 7.14 (m, 3H), 7.30 (d, \(J = 8.52\) Hz, 2H), 7.38 (d, \(J = 8.52\) Hz, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 21.0, 26.5, 32.6, 36.7, 51.3, 124.1, 127.5, 128.0, 128.4, 128.9, 129.2, 132.7, 134.7, 137.0, 138.3, 159.9; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{19}H\textsubscript{21}ClN\textsubscript{2}NaO [M+Na]^+ : 351.1235, found: 351.1234.

6-methoxy-8-(4-methoxyphenyl)-N,N,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3cc), brown oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.42 (d, \(J = 6.44\) Hz, 3H), 1.49 (m, 1H), 2.10 (s, 6H), 2.38 (m, 1H), 2.49 (m, 1H), 2.68 (m, 1H), 3.82 (s, 3H), 3.83 (s, 3H), 4.31 (m, 1H), 6.71 (s, 2H), 6.91 (d, \(J = 8.64\) Hz, 2H), 7.31 (d, \(J = 8.64\) Hz, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 21.2, 27.2, 29.7, 36.8, 51.1, 55.3, 55.4, 112.1, 113.7, 114.1, 128.6, 130.1, 132.1, 136.1, 136.8, 156.1, 158.8, 160.0; IR (neat, cm\textsuperscript{-1}): 1649; HRMS (ESI) calcd. for C\textsubscript{21}H\textsubscript{26}N\textsubscript{2}NaO\textsubscript{3} [M+Na]^+ : 377.1836, found: 377.1834.

2-ethyl-N,N-dimethyl-8-(p-tolyl)-3,4-dihydroquinoline-1(2H)-carboxamide (3da), brown solid, mp: 127 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.01 (t, \(J = 7.40\) Hz, 3H), 1.49 (m, 1H), 1.64 (m, 1H), 2.07 (s, 6H), 2.36 (s, 3H), 2.39 (d, \(J = 6.96\) Hz, 2H), 2.55 (m, 1H), 2.76 (m, 1H), 4.03 (m, 1H), 7.09 (t, \(J = 7.32\) Hz, 1H), 7.15 (m, 2H), 7.22 (d, \(J = 8.00\) Hz, 2H), 7.27 (d, \(J = 8.44\) Hz, 2H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 21.1, 26.6, 28.3, 30.1, 36.7, 57.0, 123.9, 126.8, 127.5, 128.8, 129.4, 134.2, 135.7, 136.5, 136.9, 137.5, 159.9; IR (neat, cm\textsuperscript{-1}): 1645; HRMS (ESI) calcd. for C\textsubscript{21}H\textsubscript{26}N\textsubscript{2}NaO [M+Na]^+ : 345.1937, found: 345.1933.

2-ethyl-N,N-dimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide (3db), yellow solid, mp: 120 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.02 (t, \(J = 7.44\) Hz, 3H), 1.47 (m, 1H), 1.65 (m, 1H), 2.07 (s, 6H), 2.36 (t, \(J = 5.92\) Hz, 2H), 2.56 (m, 1H), 2.76 (m, 1H), 4.04 (m, 1H), 7.10 (t, \(J = 7.36\) Hz, 1H), 7.17 (t, \(J = 7.64\) Hz, 2H), 7.29 (m, 1H), 7.39 (m, 4H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) \(\delta\) 10.7, 26.4, 28.1, 29.7, 36.7, 57.0,
123.9, 126.9, 127.1, 127.6, 128.2, 129.4, 134.1, 135.7, 137.5, 139.8, 160.0; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C₂₀H₂₄N₂NaO [M+Na]⁺: 331.1781, found: 331.1781.

2-ethyl-8-(4-methoxyphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3dc), brown solid, mp: 158 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, J = 7.44 Hz, 3H), 1.44 (m, 1H), 1.63 (m, 1H), 2.10 (s, 6H), 2.36 (t, J = 6.26 Hz, 2H), 2.53 (m, 1H), 2.75 (m, 1H), 3.83 (s, 3H), 4.03 (t, J = 7.94 Hz, 1H), 6.95 (d, J = 8.68 Hz, 2H), 7.08 (t, J = 7.24 Hz, 1H), 7.13 (m, 2H), 7.30 (t, J = 7.96 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 10.7, 26.6, 28.3, 29.7, 36.8, 55.3, 57.0, 113.6, 123.9, 126.6, 128.7, 129.4, 132.4, 134.2, 135.4, 137.5, 158.6, 159.9; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C₂₁H₂₆N₂NaO₂ [M+Na]⁺: 361.1887, found: 361.1883.

8-(4-methoxyphenyl)-N,N-dimethyl-2-propyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ec), brown solid, mp: 154 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, J = 7.02 Hz, 3H), 1.45 (m, 3H), 1.64 (m, 1H), 2.11 (s, 6H), 2.24 (s, 1H), 2.35 (m, 1H), 2.55 (m, 1H), 2.77 (m, 1H), 3.84 (s, 3H), 4.15 (s, 1H), 6.96 (d, J = 8.56 Hz, 2H), 7.08 (t, J = 7.24 Hz, 1H), 7.14 (m, 2H), 7.31 (d, J = 8.56 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.1, 19.6, 26.5, 29.7, 36.8, 37.2, 55.2, 55.3, 113.7, 123.9, 126.7, 128.8, 129.4, 132.4, 134.0, 135.5, 137.5, 158.7, 160.0; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C₂₂H₂₈N₂NaO₂ [M+Na]⁺: 375.2043, found: 375.2041.

2-butyl-8-(4-methoxyphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3fc), brown solid, mp: 157 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, J = 3.70 Hz, 3H), 1.04 (d, J = 6.56 Hz, 2H), 1.43 (m, 2H), 1.68 (m, 1H), 2.11 (s, 6H), 2.36 (m, 1H), 2.56 (m, 1H), 2.76 (m, 1H), 3.84 (s, 3H), 4.26 (bs, 1H), 6.97 (d, J = 8.72 Hz, 2H), 7.09 (t, J = 7.31 Hz, 1H), 7.14 (m, 2H), 7.31 (d, J = 8.72 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 19.2, 21.2, 24.1, 25.1, 26.5, 29.7, 36.8, 37.2, 55.2, 55.3, 113.7, 124.0, 126.7, 128.7, 129.4, 130.9, 132.4, 135.6, 137.4, 158.6, 160.1; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C₂₃H₃₀N₂NaO₂ [M+Na]⁺: 389.2200, found: 389.2197.

8-(4-methoxyphenyl)-N,N-dimethyl-2-pentyl-3,4-dihydroquinoline-1(2H)-carboxamide (3gc), brown solid, mp: 159 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, J = 3.40 Hz, 3H), 0.99 (m, 1H), 1.45 (m, 4H), 1.63 (m, 3H), 2.11 (s, 6H), 2.27 (s, 1H), 2.36 (m, 1H), 2.56 (m, 1H), 2.76 (m, 1H), 3.84 (s, 3H), 4.17 (bs, 1H), 6.95 (d, J = 8.68 Hz, 2H), 7.05 (t, J = 7.31 Hz, 1H), 7.14 (m, 2H), 7.29 (d, J = 8.72 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.0, 22.7, 25.9, 26.5, 29.7, 31.9, 35.1, 37.0, 55.2, 55.5, 113.8, 124.0, 126.7, 128.8, 129.4, 130.9, 132.4, 135.6, 137.4, 158.6, 160.1; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C₂₄H₃₂N₂NaO₂ [M+Na]⁺: 403.2356, found: 403.2356.

2-isopentyl-8-(4-methoxyphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3hc), brown solid, mp: 159 °C; ¹H NMR (400 MHz, CDCl₃)  δ 0.95 (t, J = 6.56 Hz, 2H), 0.99 (m, 1H), 1.45 (s, 6H), 2.11 (s, 6H), 2.33 (m, 2H), 2.56 (m, 1H), 2.75 (m, 1H), 3.84 (s, 3H), 4.12 (bs, 1H), 6.96 (d, J = 8.60 Hz, 2H), 7.08 (t, J = 7.28 Hz, 1H), 7.14 (m, 2H), 7.31 (d, J = 8.60 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.2, 22.7, 25.9, 26.5, 29.7, 34.8, 36.8, 55.3, 55.5, 113.6, 123.9, 126.7, 128.8, 129.4, 132.4, 134.0, 135.5, 137.5, 158.6, 159.9; IR (neat, cm⁻¹): 1645; HRMS (ESI) calcd. for C₂₄H₃₂N₂NaO₂ [M+Na]⁺: 403.2356, found: 403.2354.
2-cyclohexyl-8-(4-methoxyphenyl)-N,N-dimethyl-3,4-dihydroquinoline-1(2H)-carboxamide (3ic), brown oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.90 (t, \(J = 6.62\) Hz, 1H), 1.01 (m, 4H), 1.29 (m, 3H), 1.45 (m, 1H), 1.59 (d, \(J = 4.12\) Hz, 1H), 1.73 (m, 4H), 1.91 (m, 1H), 2.08 (m, 1H), 2.70 (s, 6H), 2.76 (m, 1H), 3.88 (s, 1H), 3.97 (m, 1H), 6.83 (m, 1H), 6.98 (m, 3H), 7.12 (t, \(J = 7.16\) Hz, 2H), 7.55 (m, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 23.8, 24.9, 26.1, 26.3, 26.4, 29.4, 30.2, 37.8, 38.3, 55.4, 58.1, 114.1, 121.7, 122.1, 126.5, 127.8, 129.1, 131.0, 131.1, 132.3, 139.8, 160.8; IR (neat, cm\(^{-1}\)): 1645; HRMS (ESI) calcd. for C\(_{25}\)H\(_{32}\)N\(_2\)NaO\(_2\) [M+Na\(^+\)]: 415.2356, found: 415.2352.

5-(4-methoxyphenyl)-N,N-dimethyl-2,3-dihydrobenzo[b][1,4]oxazine-4-carboxamide (3kc), yellow solid, mp: 154°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.35 (s, 6H), 3.83 (s, 3H), 3.82 (m, 2H), 4.36 (t, \(J = 4.76\) Hz, 2H), 6.83 (d, \(J = 8.08\) Hz, 1H), 6.95 (d, \(J = 8.64\) Hz, 2H), 7.04 (t, \(J = 7.84\) Hz, 1H), 7.28 (d, \(J = 8.64\) Hz, 2H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 37.1, 44.0, 55.3, 66.8, 113.6, 116.0, 123.0, 124.6, 126.3, 128.8, 130.6, 132.0, 135.2, 147.2, 158.7; IR (neat, cm\(^{-1}\)): 1645; HRMS (ESI) calcd. for C\(_{18}\)H\(_{20}\)N\(_2\)NaO\(_3\) [M+Na\(^+\)]: 335.1366, found: 335.1361.

5-(3,5-dimethylphenyl)-N,N-dimethyl-2,3-dihydrobenzo[b][1,4]oxazine-4-carboxamide (3ke), yellow solid, mp: 129°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.32 (s, 6H), 2.36 (s, 6H), 3.80 (brs, 2H), 4.34 (t, \(J = 4.80\) Hz, 2H), 6.85 (dd, \(J = 7.52, 1.44\) Hz, 1H), 6.89 (dd, \(J = 8.12, 1.48\) Hz, 1H), 6.94 (m, 3H), 7.04 (t, \(J = 7.80\) Hz, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 21.4, 36.9, 44.0, 66.8, 116.1, 123.1, 124.4, 125.4, 126.4, 128.6, 135.6, 137.6, 139.2, 147.1, 158.8; IR (neat, cm\(^{-1}\)): 1645; HRMS (ESI) calcd. for C\(_{19}\)H\(_{22}\)N\(_2\)NaO\(_2\) [M+Na\(^+\)]: 333.1574, found: 333.1572.

5-(3,4-dimethylphenyl)-N,N-dimethyl-2,3-dihydrobenzo[b][1,4]oxazine-4-carboxamide (3kf), yellow solid, mp: 133°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.29 (s, 3H), 2.32 (m, 9H), 3.83 (bs, 2H), 3.50 (t, \(J = 4.80\) Hz, 2H), 6.89 (dd, \(J = 8.08\) Hz, 1H), 7.12 (s, 1H), 7.17 (d, \(J = 7.72\) Hz, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 19.4, 19.8, 37.0, 43.9, 66.9, 116.0, 123.1, 124.5, 125.1, 126.4, 128.7, 129.4, 135.2, 135.5, 136.2, 136.9, 147.1, 158.7; IR (neat, cm\(^{-1}\)): 1645; HRMS (ESI) calcd. for C\(_{19}\)H\(_{22}\)N\(_2\)NaO\(_2\) [M+Na\(^+\)]: 333.1574, found: 333.1573.

\(N,N\)-dimethyl-7-p-tolylindoline-1-carboxamide (3la), white solid, mp: 103°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.38 (s, 3H), 2.61 (s, 6H), 3.12 (t, \(J = 8.0\) Hz, 2H), 3.99 (t, \(J = 8.0\) Hz, 2H), 7.04 (t, \(J = 7.40\) Hz, 1H), 7.18 (dd, \(J = 10.4, 8.0\) Hz, 4H), 7.35 (d, \(J = 8.0\) Hz, 2H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 21.1, 29.7, 36.8, 51.8, 122.9, 123.3, 126.6, 126.7, 128.8, 129.1, 133.6, 136.2, 137.4, 142.2, 159.7; IR (neat, cm\(^{-1}\)): 1645; HRMS (ESI) calcd. for C\(_{18}\)H\(_{20}\)N\(_2\)NaO [M+Na\(^+\)]: 303.1468, found: 303.1467.

7-(4-methoxyphenyl)-N,N-dimethylindoline-1-carboxamide (3lb), orange oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.63 (s, 6H), 3.12 (t, \(J = 8.0\) Hz, 2H), 3.84 (s, 3H), 3.98 (t, \(J = 8.0\) Hz, 2H), 6.93 (dt, \(J = 9.63, 2.91\) Hz, 2H), 7.04 (t, \(J = 7.40\) Hz, 1H), 7.16 (m, 2H), 7.39 (dt, \(J = 9.63, 2.91\) Hz, 2H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 29.8, 37.0, 51.9, 55.2, 113.7, 123.1, 123.3, 128.1, 128.8, 129.0, 132.9, 133.8, 142.3, 158.5, 159.8; IR (neat, cm\(^{-1}\)): 1645; HRMS (ESI) calcd. for C\(_{18}\)H\(_{20}\)N\(_2\)NaO\(_2\) [M+Na\(^+\)]: 319.1417, found: 319.1414.

1-(biphenyl-2-yl)-1,3,3-trimethylurea (3mb), white solid, mp: 62.4°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.34 (s, 6H), 3.20 (s, 3H), 7.26 (m, 2H), 7.35 (m, 5H), 7.43 (m,
2H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 37.5, 40.1, 125.7, 126.8, 127.3, 128.0, 128.4, 128.7, 131.6, 137.6, 139.2, 143.9, 160.6; IR (neat, cm$^{-1}$): 1645; HRMS (ESI) calcd. for C$_{16}$H$_{18}$N$_{2}$NaO$^{[M+Na]}$: 277.1311, found: 277.1308.

1-(4'-methoxybiphenyl-2-yl)-1,3,3-trimethylurea (3mc), red solid, mp: 72.5°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.38(s, 6H), 3.16(s, 3H), 3.83(s, 3H), 6.95(d, $J=6.72$, 2H), 7.19–7.24(m, 2H), 7.28(s, 1H), 7.30–7.34(m, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 37.62, 39.93, 55.26, 113.80, 125.78, 126.81, 128.25, 129.13, 131.51, 131.64, 137.08, 143.75, 158.91, 160.72; IR (neat, cm$^{-1}$): 1645; HRMS (ESI) calcd. for C$_{17}$H$_{20}$N$_{2}$NaO$_2^{[M+Na]}$: 307.1417, found: 307.1417.

(R)-N,N,2-trimethyl-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxamide ((R)-3bb), yellow solid, mp: 118 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.46 (m, 3H), 1.55(m, 1H), 2.07 (s, 6H), 2.42 (d, $J=5.02$ Hz, 1H), 2.57 (m, 1H), 2.76 (m, 1H), 4.33 ( t, $J=3.28$ Hz, 1H), 7.12 (t, $J=7.32$ Hz, 1H), 7.17 (m, 2H), 7.29 (m, 1H), 7.39 (m, 4H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 21.2, 26.7, 33.1, 36.6, 51.2, 124.0, 126.9, 127.0, 127.6, 128.2, 129.4, 134.4, 135.9, 137.1, 139.7, 159.8; $[\alpha]^{22}_D = -100.5$ (c = 1.0, CHCl$_3$); HPLC (AD-H, elute: Hexanes / i-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5ml/min), (R) $t_1$= 15.1 min, (S) $t_2$ = 10.3 min.

(R)-8-(4-methoxyphenyl)-N,N,2-trimethyl-3,4-dihydroquinoline-1(2H)-carboxamide ((R)-3bc), yellow solid, mp: 157 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.44 (d, $J=6.44$ Hz, 3H), 1.53 (m, 1H), 2.10 (s, 6H), 2.42 (d, $J=5.64$ Hz, 1H), 2.54 (m, 1H), 2.74 (m, 1H), 3.83 (s, 3H), 4.33 (t, $J=6.56$ Hz, 1H), 6.95 (d, $J=8.68$ Hz, 2H), 7.12 (m, 3H), 7.31(d, $J=8.62$ Hz, 2H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 21.1, 22.7, 26.8, 29.7, 36.7, 51.2, 124.0, 125.4, 126.7, 127.4, 128.9, 129.4, 135.9, 136.5, 136.8, 137.1, 159.9; $[\alpha]^{22}_D = -108.7$ (c = 1.0, CHCl$_3$); HPLC (AD-H, elute: Hexanes / i-PrOH = 90 / 10, detector: 254 nm, flow rate: 0.5ml/min), (R) $t_1$= 12.4 min, (S) $t_2$ = 33.3 min.

4. References:
5. $^1$H and $^{13}$C NMR spectra of the ureas and arylated ureas
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3ec

CONMe₂

nC₃H₇

CONMe₂

OMe

OMe

nC₃H₇

1H NMR

13C NMR
3kc

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5. HPLC spectra of the chiral aryalted ureas

![HPLC spectra of the chiral aryalted ureas]

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