Supporting Information for

Metal-free Tandem Cyclization/Hydrosilylation to Construct Tetrahydroquinolines

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1. General information:

Unless otherwise noted, all experiments were carried out in air, and all commercially available chemicals including organic solvents 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 100.6 MHz, respectively). Chemical shifts ($\delta$) are given in ppm and are referenced to residual solvent peaks. 4,5-Dibromobenzene-1,2-diamine (1m), 4,5-dimethoxybenzene-1,2-diamine (1n), $\alpha$-ketoesters $^{3a}$, chiral diene ligands $^{4b}$ and HB(C$_6$F$_5$)$_2$ $^{4b}$ were prepared according to the previous reports.

2. Determination of the optimal reaction conditions

<table>
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<tr>
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$^a$ Reaction conditions: 1a (0.25 mmol), 2a (0.275 mmol), B(C$_6$F$_5$)$_3$ (5.0 mol%), THF (1.5 mL), hydrosilane (1.0 mmol) at 110 °C for 16 h. $^b$ Yield determined by $^1$H NMR with CH$_2$Br$_2$ as an internal standard.
Table S2. Screening of catalysts.\textsuperscript{a}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Entry & Catalyst & 3aa (\%)\textsuperscript{b} & 4aa (\%)\textsuperscript{b} & 5aa (\%)\textsuperscript{b} \\
\hline
1 & B(C6F5)3 & 80 & 13 & 2 \\
2 & BF3·OEt2 & 12 & 18 & 68 \\
3 & BEt3 & 3 & 20 & 73 \\
4 & BPh3 & <1 & <1 & 95 \\
5 & InCl3 & 60 & 25 & 12 \\
6 & Fe(CO)12 & 45 & 35 & 16 \\
7 & Zn(OAc)2 & 10 & 15 & 73 \\
8 & Cu(OTf)2 & 12 & 15 & 62 \\
9 & Co(acac)3 & 3 & 11 & 82 \\
10 & Co(acac)2 & 2 & 25 & 67 \\
11 & Co2(CO)8 & 23 & 36 & 37 \\
12 & Ni(acac)2 & 3 & 22 & 71 \\
13 & & 4 & 12 & 82 \\
14 & & 3 & 15 & 77 \\
15 & & 4 & 18 & 75 \\
16 & & 7 & 41 & 50 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Reaction conditions: 1a (0.25 mmol), 2a (0.275 mmol), catalyst (5.0 mol%), THF (1.5 mL), PMHS (1.0 mmol) at 110 °C for 16 h. \textsuperscript{b} Yield determined by \textsuperscript{1}H NMR with CH$_3$Br$_2$ as an internal standard.
Table S3. Screening of solvents.$^a$

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$^a$Reaction conditions: 1a (0.25 mmol), 2a (0.275 mmol), B(C$_6$F$_5$)$_3$ (5.0 mol%), solvent (1.5 mL), PMHS (0.06 mL, 1.0 mmol) at 110 °C for 16 h. $^b$Yield determined by $^1$H NMR with CH$_2$Br$_2$ as an internal standard.
Table S4. Screening of catalyst loadings.\(^a\)

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<th>Entry</th>
<th>X (mol%)</th>
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\(^a\) Reaction conditions: 1a (0.25 mmol), 2a (0.275 mmol), B(C\(_6\)F\(_5\))\(_3\), toluene (1.5 mL), PMHS (0.06 mL, 1.0 mmol) at 110 °C for 16 h. \(^b\) Yield determined by \(^1\)H NMR with CH\(_2\)Br\(_2\) as an internal standard.

Table S5. Screening of reaction temperature.\(^a\)

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<th>Entry</th>
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\(^a\) Reaction conditions: 1a (0.25 mmol), 2a (0.275 mmol), B(C\(_6\)F\(_5\))\(_3\) (5.0 mol%), PMHS (0.06 mL, 1.0 mmol), toluene (1.5 mL) at 110 °C for 16 h. \(^b\) Yield determined by \(^1\)H NMR with CH\(_2\)Br\(_2\) as an internal standard.
Table S6. Variation of the amount of PMHS.\(^a\)

![Chemical structures](image)

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\(^a\)Reaction conditions: 1a (0.25 mmol), 2a (0.275 mmol), B(C\(_6\)F\(_5\))\(_3\) (5.0 mol%), toluene (1.5 mL), PMHS (0.06 mL, 1.0 mmol) at 110 °C for 16 h. \(^b\)Yield determined by \(^1\)H NMR with CH\(_2\)Br\(_2\) as an internal standard.
**Table S7.** Preliminary optimization studies for asymmetric synthesis of 3aa.  

![Chemical reaction image](image)

<table>
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</table>
3. General procedure for the synthesis of tetrahydroquinoxalines

(1) General procedure for the synthesis of 2-substituted tetrahydroquinoxalines

To an oven-dried screw-capped pressure tube were sequentially added 1,2-diaminobenzene 1 (0.25 mmol), α-ketoester 2 (0.275 mmol), B(C₆F₅)₃ (6.4 mg, 5.0 mol%), PMHS (0.06 mL, 1.0 mmol) and toluene (1.5 mL). Then the reaction mixture was stirred at 110 °C for 16 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (5.0 mL). Then water (5.0 mL) was added to the reaction mixture, which was extracted with EtOAc three times (5.0 mL each). The combined organic phases were dried over Na₂SO₄, then filtered and evaporated under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by silica gel column chromatography using a mixture of EtOAc and hexane to give the corresponding pure product.

(2) General procedure for the synthesis of 3,4-dihydroquinoxalin-2(1H)-ones

To an oven-dried screw-capped pressure tube were sequentially added 1,2-diaminobenzene 1 (0.25 mmol), α-ketoester 2 (0.275 mmol), B(C₆F₅)₃ (6.4 mg, 5.0 mol%), PMHS (22.5 μL, 0.375 mmol) and toluene (1.5 mL). Then the reaction mixture was stirred at 110 °C for 3 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (5.0 mL). Then water (5.0 mL) was added to the reaction mixture, which was then extracted with EtOAc three times (5.0 mL each). The combined organic phases were dried over Na₂SO₄, then filtered and evaporated under reduced pressure.
After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by silica gel column chromatography using a mixture of EtOAc and hexane to give the corresponding pure product.

(3) **General procedure for grammar-scale transformation reaction**

To an oven-dried screw-capped pressure tube were sequentially added 1,2-diaminobenzene **1a** (1.08 g, 10.0 mmol), ethyl 2-oxopropanoate **2a** (1.28 g, 11.0 mmol), B(C$_6$F$_5$)$_3$ (250.0 mg, 5.0 mol%), PMHS (2.4 mL, 40.0 mmol) and toluene (60.0 mL). Then the reaction mixture was stirred at 110 °C for 16 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (120.0 mL). Then water (100.0 mL) was added to the reaction mixture, which was extracted with EtOAc five times (30.0 mL each). The combined organic phases were dried over Na$_2$SO$_4$, then filtered and evaporated under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by silica gel column chromatography using a mixture of EtOAc and hexane to give pure **3aa** (yellow solid, 1.3 g, 90%).

(4) **General procedure for asymmetric synthesis of 2-substituted tetrahydroquinoxalines**

To an oven-dried screw-capped pressure tube were sequentially added 1,2-diaminobenzene **1** (0.25 mmol), α-ketoester **2** (0.275 mmol), HB(C$_6$F$_5$)$_2$ (8.67 mg, 10.0 mol%), chiral diene **6** (7.88 mg, 5.0 mol%), Ph$_2$H$_2$Si (0.185 mL, 1.0 mmol) and THF (1.5 mL). Then the reaction mixture was stirred at 70 °C for 16 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (5.0 mL). Then water (5.0 mL) was added to the reaction mixture, which was extracted with EtOAc three times (5.0 mL each). The combined organic phases were dried over Na$_2$SO$_4$, then filtered and evaporated under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by silica gel column chromatography using a mixture of EtOAc and hexane to give the pure product.

(5) **General procedure for asymmetric synthesis of 3,4-dihydroquinoxalin-2(1H)-ones**

To an oven-dried screw-capped pressure tube were sequentially added 1,2-diaminobenzene **1** (0.25 mmol), α-ketoester **2** (0.275 mmol), HB(C$_6$F$_5$)$_2$ (8.67 mg, 10.0 mol%), chiral diene **6** (7.88 mg, 5.0 mol%), Ph$_2$H$_2$Si (0.069 mL, 0.375 mmol) and THF (1.5 mL). Then the reaction mixture was stirred at 45 °C for 16 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (5.0 mL). Then water (5.0
mL) was added to the reaction mixture, which was extracted with EtOAc five times (5.0 mL each). The combined organic phases were dried over Na₂SO₄, then filtered and evaporated under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by silica gel column chromatography using a mixture of EtOAc and hexane to give the pure product.

4. Characterization of the products

2-Methyl-1,2,3,4-tetrahydroquinoxaline (3aa)⁵

Yellow solid, mp: 71-72 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.99-6.13 (m, 4H), 4.05 (s, 2H), 3.60-3.40 (m, 2H), 3.12-2.89 (m, 1H), 1.15 (dd, J = 17.4, 6.5 Hz, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 134.37, 133.58, 133.15, 118.81, 118.76, 114.57, 48.23, 45.73, 19.90; HRMS (ESI) calcd. for C₉H₁₃N₂ [M+H]⁺: 149.1073, found: 149.1075.

2-Ethyl-1,2,3,4-tetrahydroquinoxaline (3ab)⁵

Yellow solid, mp: 67-69 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.59-6.48 (m, 4H), 3.41-3.36 (m, 1H), 3.32 (ddd, J = 14.1, 6.7, 2.9 Hz, 1H), 3.08-3.04 (m, 1H), 1.55-1.48 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 133.41, 133.15, 118.97, 118.72, 114.60, 51.71, 46.21, 27.06, 10.03; HRMS (ESI) calcd. for C₁₀H₁₅N₂ [M+H]⁺: 163.1230, found: 163.1227.

2-Propyl-1,2,3,4-tetrahydroquinoxaline (3ac)⁶

Brown-yellow solid, mp: 66-67 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.60-6.58 (m, 2H), 6.50 (dd, J = 8.4, 4.1 Hz, 2H), 3.36-3.34 (m, 2H), 3.08-3.03 (m, 1H), 1.47-1.44 (m, 4H), 0.97 (td, J = 6.8, 3.9 Hz, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 133.53, 133.41, 118.76, 118.61, 114.49, 114.44, 53.45, 49.99, 36.44, 18.86, 14.16; HRMS (ESI) calcd. for C₁₁H₁₇N₂ [M+H]⁺: 177.1386, found: 177.1388.

2-Isopropyl-1,2,3,4-tetrahydroquinoxaline (3ad)⁷

Brown solid, mp: 73-75 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.59-6.48 (m, 4H), 3.37-3.34 (m, 1H), 3.11 (dt, J = 14.0, 6.7 Hz, 1H), 1.76-1.67 (m, 1H), 0.98 (ddd, J = 21.7, 14.8, 6.9 Hz, 6H); ¹³C NMR (100.6 MHz, CDCl₃) δ 133.87, 133.36, 118.84, 118.39, 114.37, 114.32, 56.00, 53.44, 31.03, 18.73; HRMS (ESI) calcd. for C₁₁H₁₇N₂ [M+H]⁺: 177.1386, found: 177.1395.
2-Butyl-1,2,3,4-tetrahydroquinoxaline (3ae)\(^7\)

Brown solid; mp: 58-59\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.59-6.53 (m, 2H), 6.52-6.51 (m, 2H), 3.38 (d, \(J = 8.5\) Hz, 2H), 3.07 (dd, \(J = 17.8, 6.9\) Hz, 1H), 1.51-1.36 (m, 6H), 0.95 (dd, \(J = 9.1, 5.0\) Hz, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 134.37, 133.58, 133.15, 118.79, 118.62, 114.47, 50.24, 46.66, 33.98, 31.68, 27.82, 21.05, 14.20; HRMS (ESI) calcd. for C\(_{12}\)H\(_{19}\)N\(_2\) [M+H]\(^+\): 191.1543, found: 191.1548.

2-Isobutyl-1,2,3,4-tetrahydroquinoxaline (3af)\(^8\)

Yellow solid, mp: 69-70\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.65-6.40 (m, 4H), 3.62 (s, 2H), 3.43 (qd, \(J = 7.8, 2.8\) Hz, 1H), 3.33 (dd, \(J = 10.7, 2.8\) Hz, 1H), 3.14-2.85 (m, 1H), 1.74 (dp, \(J = 13.3, 6.7\) Hz, 1H), 1.44-1.24 (m, 3H), 0.99-0.90 (m, 6H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 133.57, 133.52, 118.77, 118.69, 114.60, 114.49, 48.18, 47.09, 43.41, 24.53, 23.24, 22.59; HRMS (ESI) calcd. for C\(_{12}\)H\(_{19}\)N\(_2\) [M+H]\(^+\): 191.1543, found: 191.1550.

2-(Tert-butyl)-1,2,3,4-tetrahydroquinoxaline (3ag)\(^8\)

Yellow solid, mp: 82-83\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.56 (dq, \(J = 29.5, 4.6\) Hz, 4H), 3.80-3.47 (m, 1H), 3.45-3.23 (m, 1H), 3.23-2.88 (m, 2H), 0.98 (s, 9H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 134.57, 133.36, 118.85, 118.24, 114.32, 114.25, 59.02, 42.52, 32.79, 26.05; HRMS (ESI) calcd. for C\(_{12}\)H\(_{19}\)N\(_2\) [M+H]\(^+\): 191.1543, found: 191.1546.

2-Hexyl-1,2,3,4-tetrahydroquinoxaline (3ah)\(^8\)

Yellow solid, mp: 74-76\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.54 (dq, \(J = 29.5, 4.6\) Hz, 4H), 3.62 (s, 1H), 3.40-3.25 (m, 1H), 3.04 (dd, \(J = 11.1, 8.4\) Hz, 1H), 1.59-1.16 (m, 10H), 0.89 (t, \(J = 6.5\) Hz, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 133.58, 133.47, 118.72, 118.59, 114.47, 114.42, 50.27, 46.72, 34.34, 31.81, 29.41, 25.64, 22.65, 14.13; HRMS (ESI) calcd. for C\(_{14}\)H\(_{23}\)N\(_2\) [M+H]\(^+\): 219.1856, found: 219.1866.
2-Cyclohexyl-1,2,3,4-tetrahydroquinoxaline (3ai)<sup>8</sup>

Yellow solid, mp: 105-106°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.63-6.53 (m, 2H), 6.52-6.42 (m, 2H), 3.67 (s, 2H), 3.36 (dd, J = 10.4, 2.3 Hz, 1H), 3.24-3.03 (m, 2H), 1.92-1.63 (m, 5H), 1.54-1.36 (m, 1H), 1.33-0.95 (m, 6H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 133.77, 133.42, 118.69, 118.28, 114.26, 55.12, 43.90, 40.65, 29.11, 28.88, 26.39, 26.12, 26.07; HRMS (ESI) calcd. for C<sub>14</sub>H<sub>21</sub>N<sub>2</sub>[M+H]<sup>+</sup>: 217.1699, found: 217.1705.

2-Benzyl-1,2,3,4-tetrahydroquinoxaline (3aj)<sup>6</sup>

Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.17 (m, 5H), 6.62-6.35 (m, 4H), 3.65-3.53 (m, 1H), 3.37 (dd, J = 10.8, 2.8 Hz, 1H), 3.15 (dd, J = 10.7, 7.1 Hz, 1H), 2.89-2.75 (m, 1H), 2.75-2.59 (m, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 138.05, 133.29, 133.07, 129.33, 128.72, 126.67, 118.87, 118.79, 114.64, 114.49, 51.29, 46.29, 40.58, 29.76; HRMS (ESI) calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>[M+H]<sup>+</sup>: 225.1386, found: 225.1379.

2-(Trifluoromethyl)-1,2,3,4-tetrahydroquinoxaline (3ak)

Pale-yellow oil; <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.92 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.9 Hz, 2H), 4.38 (t, J = 4.8 Hz, 1H), 3.44 (tt, J = 17.0, 8.5 Hz, 2H); <sup>13</sup>C NMR (100.6 MHz, DMSO) δ 152.17, 134.20, 133.96, 130.34, 124.63, 116.33, 56.48, 55.38, 19.02; HRMS (ESI) calcd. for C<sub>9</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>[M+H]<sup>+</sup>: 203.0791, found: 203.0793.

2-Phenyl-1,2,3,4-tetrahydroquinoxaline (3ai)<sup>9</sup>

Yellow solid, mp: 121-123 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43-7.28 (m, 5H), 6.70-6.53 (m, 4H), 4.48 (dd, J = 8.2, 3.1 Hz, 1H), 3.46 (dd, J = 11.0, 3.1 Hz, 1H), 3.32 (dd, J = 11.0, 8.2 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 134.13, 132.82, 128.65, 127.91, 127.01, 118.90, 118.78, 114.70, 114.43, 53.46, 49.15; HRMS (ESI) calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>[M+H]<sup>+</sup>: 211.1230, found: 211.1233.
2-(p-Tolyl)-1,2,3,4-tetrahydroquinoxaline (3am)\(^9\)

Yellow solid, mp: 120-121°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35-7.17 (m, 4H), 6.69-6.55 (m, 4H), 4.48 (dd, \(J = 8.2, 3.0\) Hz, 1H), 3.88 (t, \(J = 18.3\) Hz, 2H), 3.46 (dd, \(J = 11.0, 3.1\) Hz, 1H), 3.34 (dd, \(J = 11.0, 8.2\) Hz, 1H), 2.38 (s, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 137.63, 129.32, 126.89, 118.88, 118.72, 114.68, 114.39, 54.44, 49.20, 21.15; HRMS (ESI) calcd for C\(_{15}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 225.1386, found 225.1384.

2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline (3an)\(^9\)

Yellow solid, mp: 63-65 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34-7.28 (m, 2H), 6.94-6.91 (m, 2H), 6.67-6.57 (m, 4H), 4.45 (ddd, \(J = 11.3, 8.2, 3.0\) Hz, 1H), 3.84 (s, 3H), 3.45-3.42 (m, 1H), 3.34-3.29 (m, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 159.29, 134.22, 133.92, 132.85, 128.12, 118.84, 118.75, 114.65, 114.41, 114.01, 55.34, 54.09, 49.29; HRMS (ESI) calcd for C\(_{15}\)H\(_{17}\)ON\(_2\) [M+H]\(^+\): 241.1335, found 242.1339.

2-[[1,1'-Biphenyl]-4-yl]-1,2,3,4-tetrahydroquinoxaline (3ao)\(^10\)

White solid, mp: 118-120 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (ddd, \(J = 5.8, 5.1, 4.3\) Hz, 4H), 7.46-7.43 (m, 4H), 6.67-6.58 (m, 5H), 4.54 (dd, \(J = 8.0, 3.0\) Hz, 1H), 3.51 (dd, \(J = 11.0, 3.1\) Hz, 1H), 3.37 (dd, \(J = 11.0, 8.1\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 140.92, 132.83, 128.82, 127.40, 127.12, 118.98, 118.84, 114.76, 114.47, 54.45, 49.09; HRMS (ESI) calcd for C\(_{20}\)H\(_{19}\)N\(_2\) [M+H]\(^+\): 287.1543 found: 287.1547.

2-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoxaline (3ap)\(^9\)

Yellow solid, mp: 103-104°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.02 (m, 4H), 6.65-6.57 (m, 4H), 4.47 (dd, \(J = 8.1, 3.0\) Hz, 1H), 3.42 (dd, \(J = 11.0, 3.1\) Hz, 1H), 3.28 (dd, \(J = 11.0, 8.1\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 150.80, 142.98, 130.47, 129.65, 129.17, 128.62, 128.54, 118.95, 116.39, 115.59, 114.71, 54.02, 49.18; HRMS (ESI) calcd for C\(_{14}\)H\(_{14}\)FN\(_2\) [M+H]\(^+\): 229.1136, found: 229.1131.
2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinoxaline (3a)\(^9\)

Yellow solid, mp 104-105°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.29 (m, 4H), 6.65-6.55 (m, 4H), 4.45 (dd, \(J = 8.0, 3.1\) Hz, 1H), 3.42 (dd, \(J = 11.1, 3.1\) Hz, 1H), 3.26 (dd, \(J = 11.1, 8.0\) Hz, 1H); \(^1^3\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 140.45, 133.79, 132.75, 128.81, 128.36, 119.03, 118.99, 114.77, 114.53, 54.09, 49.00; HRMS (ESI) calcd for C\(_{14}\)H\(_{14}\)ClN\(_2\) [M+H]*: 245.0840, found: 245.0833.

2-(4-Bromophenyl)-1,2,3,4-tetrahydroquinoxaline (3ar)\(^9\)

Yellow solid, mp: 144-146°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53-7.50 (m, 2H), 7.29-7.27 (m, 2H), 6.68-6.58 (m, 4H), 4.48 (dd, \(J = 8.0, 3.0\) Hz, 1H), 3.46 (dt, \(J = 4.8, 2.4\) Hz, 1H), 3.31 (ddd, \(J = 11.1, 8.0, 5.6\) Hz, 1H); \(^1^3\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 140.99, 133.77, 132.75, 131.76, 128.73, 121.68, 119.04, 119.00, 114.78, 114.55, 54.15, 48.93; HRMS (ESI) calcd for C\(_{14}\)H\(_{14}\)BrN\(_2\) [M+H]*: 289.0335, found: 285.0329.

2-(4-(Trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoxaline (3as)\(^11\)

White solid, mp: 143-144 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68-7.49 (m, 4H), 6.77-6.50 (m, 4H), 4.58 (dd, \(J = 7.7, 3.0\) Hz, 1H), 3.96 (d, \(J = 8.7\) Hz, 2H), 3.50 (dd, \(J = 11.1, 3.1\) Hz, 1H), 3.33 (dd, \(J = 11.1, 7.7\) Hz, 1H); \(^1^3\)C NMR (CDCl\(_3\), 100.6 MHz): \(\delta\) 146.08, 133.60, 132.74, 127.88, 127.35, 126.09, 125.60, 119.15, 119.10, 114.67, 114.60, 54.36, 48.77; HRMS (ESI) calcd for C\(_{15}\)H\(_{14}\)F\(_3\)N\(_2\) [M+H]*: 279.1104, found: 279.1108.

2-(o-Tolyl)-1,2,3,4-tetrahydroquinoxaline (3at)\(^9\)

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55-7.45 (m, 1H), 7.33-7.16 (m, 3H), 6.76-6.52 (m, 4H), 4.75 (dd, \(J = 8.2, 2.9\) Hz, 1H), 3.84 (d, \(J = 7.3\) Hz, 1H), 3.48 (dd, \(J = 11.1, 3.0\) Hz, 1H), 3.29 (dt, \(J = 21.6, 10.8\) Hz, 1H), 2.45 (s, 3H); \(^1^3\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 139.55, 135.28, 134.47, 132.84, 130.47, 127.50, 126.66, 126.54, 118.91, 118.79, 114.72, 114.54, 77.42, 77.10, 76.78, 50.57, 47.81, 19.27; HRMS (ESI) calcd for C\(_{15}\)H\(_{17}\)N\(_2\) [M+H]*: 225.1386, found 225.1381.
2-(m-Tolyl)-1,2,3,4-tetrahydroquinoxaline (3au)\(^9\)

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26-7.10 (m, 4H), 6.63-6.54 (m, 4H), 4.42 (dd, J = 8.3, 3.0 Hz, 1H), 3.90-3.79 (m, 2H), 3.42 (dd, J = 11.0, 3.1 Hz, 1H), 3.30 (dd, J = 11.0, 8.3 Hz, 1H), 2.27-2.35 (s, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 141.75, 138.36, 134.20, 132.86, 128.67, 128.57, 127.69, 124.10, 118.90, 118.78, 114.72, 114.45, 54.72, 49.23, 21.49; HRMS (ESI) calcd. for C\(_{15}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 225.1386, found 225.1396.

2-(Naphthalen-1-yl)-1,2,3,4-tetrahydroquinoxaline (3av)\(^11\)

White solid, mp: 108-110 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01-7.96 (m, 1H), 7.89-7.78 (m, 1H), 7.54-7.53 (m, 1H), 7.51-7.44 (m, 4H), 6.67-6.58 (m, 4H), 5.30 (dd, J = 7.9, 2.9 Hz, 1H), 4.05-3.75 (m, 2H), 3.65 (dd, J = 11.2, 3.0 Hz, 1H), 3.44-3.39 (m, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 137.17, 134.37, 134.06, 132.97, 130.49, 130.20, 129.71, 129.14, 128.21, 126.36, 125.74, 125.67, 124.12, 122.62, 119.06, 118.89, 114.89, 114.67, 50.71, 48.14; HRMS (ESI) calcd. for C\(_{18}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 261.1386, found 261.1379.

(E)-2-Styryl-1,2,3,4-tetrahydroquinoxaline (3aw)\(^10\)

Red solid, mp: 104-105 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43-7.23 (m, 6H), 6.67-6.49 (m, 6H), 4.50 (dt, J = 11.5, 5.8 Hz, 1H), 3.48 (dd, J = 11.0, 3.1 Hz, 1H), 3.35 (dd, J = 11.0, 8.2 Hz, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 134.14, 132.83, 128.65, 128.55, 128.36, 127.91, 127.01, 118.89, 118.77, 114.70, 114.43, 114.32, 53.47, 49.15; HRMS (ESI) calcd. for C\(_{16}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 237.1386, found: 233.1379.

2-Methyl-2,3,4,5-tetrahydro-1H-benzo[b] [1, 4] diazepine (3ax)\(^12\)

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.76-6.69 (m, 2H), 6.44-6.37 (m, 2H), 3.51-3.45 (m, 1H), 3.31-3.27 (m, 1H), 3.04-2.99 (m, 1H), 1.83-1.79 (m, 1H), 1.64-1.57 (m, 1H), 1.17 (d, J = 3.5 Hz, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 121.64, 120.69, 120.13, 114.97, 52.67, 45.91, 39.48, 19.74; HRMS (ESI) calcd. for C\(_{10}\)H\(_{15}\)N\(_2\) [M+H]\(^+\): 163.1230, found: 163.1234.
2-Methyl-1,2,3,4,5,6-hexahydrobenzo[b][1, 4]diazocine (3ay)

White solid, mp: 112-114 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.71\) (dd, \(J = 5.7, 3.3\) Hz, 2H), \(7.53\) (dd, \(J = 5.7, 3.3\) Hz, 2H), \(4.22\) (qd, \(J = 10.9, 6.0\) Hz, 3H), \(1.72-1.65\) (m, 2H), \(1.46-1.39\) (m, 2H), \(1.31\) (d, \(J = 3.0\) Hz, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta 119.64, 118.13, 117.68, 111.96, 53.67, 46.91, 31.48, 29.48, 22.75; HRMS (ESI) calcd. for C\(_{11}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 177.1386, found: 177.1397.

2,6-Dimethyl-1,2,3,4-tetrahydroquinoxaline (3ba1)

Yellow solid, mp: 77-79 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.39\) (ddd, \(J = 27.3, 13.5, 4.7\) Hz, 3H), \(3.50\) (ddd, \(J = 12.0, 6.0, 2.8\) Hz, 1H), \(3.29\) (dt, \(J = 10.7, 3.3\) Hz, 1H), \(3.07-2.93\) (m, 1H), \(2.17\) (s, 3H), \(1.17\) (d, \(J = 6.3\) Hz, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta 131.06, 130.64, 119.05, 115.20, 114.73, 48.42, 45.94, 45.87, 20.68, 19.94; HRMS (ESI) calcd. for C\(_{10}\)H\(_{15}\)N\(_2\) [M+H]\(^+\): 163.1230, found: 163.1233.

2,7-Dimethyl-1,2,3,4-tetrahydroquinoxaline (3ba2)

Yellow solid, mp: 75-76 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.44\) (m, 3H), \(3.91\) (s, 3H), \(3.56-3.42\) (m, 2H), \(3.29\) (dt, \(J = 10.7, 3.3\) Hz, 1H), \(3.05-2.96\) (m, 1H), \(1.17\) (d, \(J = 6.3\) Hz, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta 130.61, 127.92, 118.65, 114.82, 48.08, 45.51, 20.32, 19.58; HRMS (ESI) calcd. for C\(_{10}\)H\(_{15}\)N\(_2\) [M+H]\(^+\): 163.1230, found: 163.1238.

6-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ca1)

White solid, mp: 90-91 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.39\) (ddd, \(J = 27.3, 13.5, 4.7\) Hz, 3H), \(3.91\) (s, 3H), \(3.56-3.42\) (m, 2H), \(3.29\) (dt, \(J = 10.7, 3.3\) Hz, 1H), \(3.05-2.96\) (m, 1H), \(1.17\) (d, \(J = 6.3\) Hz, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta 153.17, 134.64, 127.88, 114.76, 102.90, 100.74, 55.62, 48.01, 45.53, 19.64; HRMS (ESI) calcd. for C\(_{10}\)H\(_{15}\)N\(_2\)O [M+H]\(^+\): 179.1179, found: 179.1185.

7-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ca2)

White solid, mp: 94-96 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.39\) (ddd, \(J = 27.3, 13.5, 4.7\) Hz, 3H), \(3.91\) (s, 3H), \(3.56-3.42\) (m, 2H), \(3.29\) (dt, \(J = 10.7, 3.3\) Hz, 1H), \(3.05-2.96\) (m, 1H), \(1.17\) (d, \(J = 6.3\) Hz, 3H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta 153.17, 134.64, 127.88, 114.76, 102.90, 100.74, 55.62, 48.01, 45.53, 19.64; HRMS (ESI) calcd. for C\(_{10}\)H\(_{15}\)N\(_2\)O
2-Methyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoxaline (3da)\textsuperscript{13}

Brown solid, mp: 112-113 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.84 (d, J = 8.1 Hz, 1H), 6.71 (s, 1H), 6.49 (dd, J = 8.1, 2.7 Hz, 1H), 3.83 (s, 1H), 3.62-3.45 (m, 1H), 3.36 (ddd, J = 10.8, 7.8, 3.0 Hz, 1H), 3.06 (ddd, J = 16.2, 10.8, 8.0 Hz, 1H), 1.22 (d, J = 6.3 Hz, 3H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) δ 136.38, 132.60, 123.60, 115.81, 112.94, 110.54, 47.57, 45.54, 19.70; HRMS (ESI) calcd. for C\textsubscript{10}H\textsubscript{12}F\textsubscript{3}N\textsubscript{2}[M+H]\textsuperscript{+}: 217.0947, found: 217.0953.

2-Methyl-7-(trifluoromethyl)-1,2,3,4-tetrahydroquinoxaline (3da\textsubscript{2})

White solid, mp: 101-103 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.95 (d, J = 8.3 Hz, 1H), 6.95 (s, 1H), 6.59 (dd, J = 8.1, 2.4 Hz, 1H), 3.69-3.60 (m, 1H), 3.50 (ddd, J = 11.2, 7.3, 3.3 Hz, 1H), 3.15 (ddd, J = 16.2, 11.8, 8.1 Hz, 1H), 1.34 (d, J = 6.3 Hz, 3H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) δ 136.86, 133.08, 124.08, 120.53, 116.29, 113.42, 111.03, 48.06, 45.67, 21.53; HRMS (ESI) calcd. for C\textsubscript{10}H\textsubscript{12}F\textsubscript{3}N\textsubscript{2}[M+H]\textsuperscript{+}: 217.0947, found: 217.0945.

6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ea\textsubscript{1})

White solid, mp: 84-85 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.48-6.11 (m, 3H), 3.63-3.18 (m, 3H), 3.11-2.90 (m, 1H), 1.18 (d, J = 6.2 Hz, 3H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) δ 114.84, 103.94, 103.72, 101.15, 100.89, 48.11, 45.81, 45.51, 19.77; HRMS (ESI) calcd. for C\textsubscript{9}H\textsubscript{12}FN\textsubscript{2}[M+H]\textsuperscript{+}: 167.0979, found: 167.0977.

7-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ea\textsubscript{2})

Yellow solid, mp: 92-93 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.45-6.22 (m, 3H), 3.56-3.51 (m, 1H), 3.32-2.97 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) δ 128.99, 115.11, 104.21, 103.99, 101.42, 101.16, 48.38, 46.08, 20.04; HRMS (ESI) calcd. for C\textsubscript{9}H\textsubscript{12}FN\textsubscript{2}[M+H]\textsuperscript{+}: 167.0985, found: 167.0979.

6-Chloro-2-methyl-1,2,3,4-tetrahydroquinoxaline (3fa\textsubscript{1})\textsuperscript{6}

Yellow solid, mp: 86-87 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.52-6.38 (m, 3H), 3.52-3.45 (m, 1H), 3.33-3.30 (m, 1H), 3.04-2.96 (m, 1H), 1.17 (d, J = 6.2 Hz, 3H); \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}) δ 131.53, 130.00, 117.92, 114.94, 113.76, 47.91, 45.55, 19.78; HRMS (ESI) calcd. for
C<sub>9</sub>H<sub>12</sub>ClN<sub>2</sub> [M+H]<sup>+</sup>: 183.0684, found: 183.0681.

7-Chloro-2-methyl-1,2,3,4-tetrahydroquinoxaline (3fa)<

White solid, mp: 77-78 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.45-6.22 (m, 3H), 3.55-3.44(m, 1H), 3.35-3.29 (m, 1H), 3.07-2.99 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 134.36, 131.65, 130.12, 118.03, 115.05, 113.87, 48.02, 45.67, 19.90; HRMS (ESI) calcd. for C<sub>9</sub>H<sub>12</sub>ClN<sub>2</sub> [M+H]<sup>+</sup>: 183.0684, found: 183.0681.

6-Bromo-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ga)<

Dark brown solid, mp: 88-90 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.67-6.23 (m, 3H), 3.54-3.33 (m, 1H), 3.30 (dd, J = 10.8, 2.7 Hz, 1H), 3.08-2.88 (m, 1H), 1.17 (d, J = 6.3 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 134.98, 132.46, 120.76, 116.45, 115.34, 110.09, 47.83, 45.48, 19.73; HRMS (ESI) calcd. for C<sub>9</sub>H<sub>12</sub>BrN<sub>2</sub> [M+H]<sup>+</sup>: 227.0178, found: 227.0171.

7-Bromo-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ga)<

Brown solid, mp: 77-80 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.60-6.29 (m, 3H), 3.46-3.40 (m, 2H), 3.27 (dd, J = 9.8, 2.5 Hz, 1H), 2.99-2.92 (m, 1H), 1.14 (d, J = 6.6 Hz, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 134.98, 132.46, 120.76, 116.45, 115.34, 110.09, 47.83, 45.48, 19.73; HRMS (ESI) calcd. for C<sub>9</sub>H<sub>12</sub>BrN<sub>2</sub> [M+H]<sup>+</sup>: 227.0178, found: 227.0185.

2-Methyl-1,2,3,4-tetrahydroquinoxaline-6-carbonitrile (3ha)<

Grey solid, mp: 100-101°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.47-6.33 (m, 3H), 3.53-3.44 (m, 1H), 3.33-3.24 (m, 1H), 3.04-2.94 (m, 1H), 1.17 (d, J = 6.3 Hz, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 131.06, 123.84, 119.08, 116.30, 115.17, 114.74, 112.99, 48.42, 45.87, 19.87; HRMS (ESI) calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 174.1026, found: 174.1037.

2-Methyl-1,2,3,4-tetrahydroquinoxaline-7-carbonitrile (3ha)<

White solid, mp: 95-96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.44-6.37 (m, 3H), 3.51-3.44 (m, 3H), 3.32-3.27 (m, 1H), 3.04-2.99 (m, 1H), 1.17 (d, J = 6.2 Hz, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 130.86, 123.64, 118.88, 116.20, 114.96, 114.53, 112.79, 48.22, 45.67, 20.48; HRMS (ESI) calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 174.1026, found: 174.1029.
Methyl 2-methyl-1,2,3,4-tetrahydroquinoxaline-6-carboxylate (3ia)

Yellow oil; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.19 (m, 2H), 6.43 (d, \(J = 8.2\) Hz, 1H), 3.83 (s, 3H), 3.62-3.57 (m, 2H), 3.47-3.06 (m, 1H), 1.23-1.16 (m, 3H); \(^{13}\text{C} \text{NMR}\) (100.6 MHz, CDCl\(_3\)) \(\delta\) 167.54, 138.32, 131.91, 121.69, 119.05, 115.18, 112.52, 51.51, 47.44, 45.86, 44.90, 19.83; HRMS (ESI) calcd. for C\(_{11}\)H\(_{15}\)N\(_2\)O\(_2\) [M+H]\(^+\): 207.1128, found: 207.1131.

Methyl 2-methyl-1,2,3,4-tetrahydroquinoxaline-7-carboxylate (3ia2)

Colourless oil; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.19 (m, 2H), 6.43 (d, \(J = 7.8\) Hz, 1H), 3.82 (s, 3H), 3.62-3.57 (m, 2H), 3.47-3.06 (m, 1H), 1.23-1.16 (m, 3H); \(^{13}\text{C} \text{NMR}\) (100.6 MHz, CDCl\(_3\)) \(\delta\) 167.54, 138.32, 131.91, 121.69, 119.05, 115.18, 112.52, 51.51, 47.44, 45.86, 44.90, 19.83; HRMS (ESI) calcd. for C\(_{11}\)H\(_{15}\)N\(_2\)O\(_2\) [M+H]\(^+\): 207.1128, found: 207.1133.

2,6,7-Trimethyl-1,2,3,4-tetrahydroquinoxaline (3ja)

White solid, mp: 105-106 °C; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 6.33 (d, \(J = 4.9\) Hz, 2H), 3.27 (m, 2H), 3.07-2.89 (m, 1H), 2.04 (s, 6H), 1.14 (dd, \(J = 21.9, 8.0\) Hz, 3H); \(^{13}\text{C} \text{NMR}\) (100.6 MHz, CDCl\(_3\)) \(\delta\) 131.43, 130.97, 126.42, 116.37, 48.61, 46.07, 21.04, 19.88, 18.87; HRMS (ESI) calcd. for C\(_{11}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 177.1386, found: 177.1381.

6,7-Dichloro-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ka)

White solid, mp: 101-102 °C; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 6.52 (t, \(J = 3.7\) Hz, 2H), 3.53-3.37 (m, 1H), 3.36 (dd, \(J = 10.8, 3.0\) Hz, 1H), 2.99 (dd, \(J = 10.7, 8.1\) Hz, 1H), 1.18 (d, \(J = 6.3\) Hz, 3H); \(^{13}\text{C} \text{NMR}\) (100.6 MHz, CDCl\(_3\)) \(\delta\) 133.15, 132.84, 120.27, 114.68, 114.57, 47.57, 45.35, 19.68; HRMS (ESI) calcd. for C\(_{9}\)H\(_{11}\)Cl\(_2\)N\(_2\) [M+H]\(^+\): 217.0294, found: 217.0299.

6,7-Dibromo-2-methyl-1,2,3,4-tetrahydroquinoxaline (3la)

Brown solid, mp: 112-114 °C; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 6.56 (d, \(J = 3.7\) Hz, 2H), 3.53-3.49 (m, 1H), 3.36 (dd, \(J = 10.8, 3.0\) Hz, 1H), 3.01 (dd, \(J = 10.7, 8.1\) Hz, 1H), 1.23 (d, \(J = 6.3\) Hz, 3H); \(^{13}\text{C} \text{NMR}\) (100.6 MHz, CDCl\(_3\)) \(\delta\) 133.14, 132.86, 118.28, 114.69, 1114.57, 47.57, 45.33, 19.77; HRMS (ESI) calcd. for C\(_{9}\)H\(_{11}\)Br\(_2\)N\(_2\) [M+H]\(^+\): 304.9283, found: 304.9291.
6,7-Dimethoxy-2-methyl-1,2,3,4-tetrahydroquinoxaline (3ma)

White solid, mp: 131-132 °C; 1H NMR (400 MHz, CDCl₃) δ 6.25 (d, J = 4.9 Hz, 2H), 4.04 (d, J = 7.1 Hz, 6H), 3.38 (s, 2H), 3.20 (d, J = 8.8 Hz, 1H), 2.89 (d, J = 14.6 Hz, 1H), 1.09 (d, J = 6.3 Hz, 3H); 13C NMR (100.6 MHz, CDCl₃) δ 139.55, 139.09, 125.53, 100.48, 59.50, 47.72, 45.19, 17.99; HRMS (ESI) calcd. for C₁₁H₁₇O₂N₂ [M+H]+: 209.1285, found: 209.1277.

2-Methyl-1,2,3,4-tetrahydrobenzo[g]quinoxaline (3na)

White solid, mp: 173-175 °C; 1H NMR (400 MHz, CDCl₃) δ 7.47 (dd, J = 5.9, 3.3 Hz, 2H), 7.14 (dd, J = 6.2, 3.3 Hz, 2H), 6.82 (s, 2H), 3.72-3.55 (m, 1H), 3.39 (d, J = 3.1 Hz, 1H), 3.16 (d, J = 8.5 Hz, 1H), 1.26 (d, J = 3.8 Hz, 3H); 13C NMR (100.6 MHz, CDCl₃) δ 134.80, 134.46, 129.08, 125.20, 125.12, 122.57, 122.49, 107.96, 107.73, 47.87, 45.76, 19.75; HRMS (ESI) calcd. for C₁₃H₁₅N₂ [M+H]+: 199.1230, found: 199.1226.

1,3-Dimethyl-1,2,3,4-tetrahydroquinoxaline (3oa)

Yellow oil; 1H NMR (400 MHz, CDCl₃) δ 6.69-6.65 (m, 1H), 6.58-6.55 (m, 2H), 6.48 (dd, J = 7.5, 1.4 Hz, 1H), 3.62 (s, 1H), 3.15 (dd, J = 10.6, 2.4 Hz, 1H), 2.94 (t, J = 8.8 Hz, 1H), 2.85 (s, 3H), 1.17 (d, J = 6.3 Hz, 3H); 13C NMR (100.6 MHz, CDCl₃) δ 129.33, 126.91, 118.19, 114.42, 113.47, 111.56, 56.97, 45.67, 39.11, 20.08; HRMS (ESI) calcd. for C₁₀H₁₅N₂ [M+H]+: 163.1230, found: 163.1238.

1-Allyl-3-methyl-1,2,3,4-tetrahydroquinoxaline (3pa)

Pale-yellow oil; 1H NMR (400 MHz, CDCl₃) δ 6.72-6.48 (m, 4H), 5.93-5.83 (m, 1H), 5.28-5.17 (m, 2H), 3.86 (dt, J = 20.8, 16.7, 8.7 Hz, 2H), 3.57 (d, J = 6.2 Hz, 1H), 3.22 (dd, J = 10.7, 2.6 Hz, 1H), 3.04 (dd, J = 13.1, 6.0 Hz, 1H); 13C NMR (100.6 MHz, CDCl₃) δ 135.79, 134.48, 133.65, 119.15, 118.15, 117.55, 113.97, 111.53, 59.71, 55.15, 45.27, 19.91; HRMS (ESI) calcd. for C₁₂H₁₇N₂ [M+H]+: 189.1286, found: 189.1282.
1-Benzyl-3-methyl-1,2,3,4-tetrahydroquinoxaline (3qa)

Colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.28 (m, 5H), 6.60-6.51 (m, 4H), 4.72 (s, 1H), 4.43 (s, 1H), 3.58-3.55 (m, 1H), 3.26-3.23 (m, 1H), 3.11-3.07 (m, 1H), 1.17 (d, $J$ = 6.3 Hz, 2H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 138.77, 134.93, 133.70, 128.57, 126.99, 126.87, 119.15, 117.59, 113.97, 111.51, 55.28, 55.16, 45.31, 19.91; HRMS (ESI) calcd. for C$_{16}$H$_{19}$N$_2$ [M+H]$^+$: 239.1543, found: 239.1547.

5-Methyl-1,4,5,6-tetrahydropyrazine-2,3-dicarbonitrile (3ra)

White solid, mp: 101-102 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 3.348-3.44 (m, 1H), 3.31-3.28 (m, 1H), 3.00-2.96 (m, 1H), 1.18 (d, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 120.34, 120.27, 114.70, 114.58, 47.56, 45.35, 19.65; HRMS (ESI) calcd. for C$_7$H$_9$N$_4$ [M+H]$^+$: 149.0822, found: 149.0826.

3-Methyl-3,4-dihydro-2H-benzo[b][1,4]oxazine (3sa)$^8$

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.76-6.48 (m, 4H), 4.28 (m, 1H), 3.69-3.62 (m, 1H), 3.50-3.45 (m, 1H), 1.27 (dd, $J$ = 17.4, 6.3 Hz, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 143.75, 132.14, 121.20, 118.87, 116.20, 113.53, 45.87, 19.88; HRMS (ESI) calcd. for C$_9$H$_{12}$NO [M+H]$^+$: 150.0913, found: 150.0921.

3-Methyl-3,4-dihydroquinoxalin-2(1H)-one (4aa)$^8$

White solid, mp:136-136 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.47(s, 1H), 6.94-6.70 (m, 4H), 4.06(m, 1H), 1.49 (d, $J$ = 10.6 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 170.25, 133.92, 123.94, 121.52, 119.66, 115.43, 114.15, 51.92, 17.827; HRMS (ESI) calcd. for C$_9$H$_{11}$N$_2$O [M+H]$^+$: 163.0866, found: 163.0869.

3-Ethyl-3,4-dihydroquinoxalin-2(1H)-one (4ab)$^8$

Yellow solid, mp: 77-78 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86-7.24 (m, 4H), 2.95(m, 2H), 1.89(m, 2H), 1.09 (t, $J$ = 10.6 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 169.41, 133.41, 125.17, 122.15, 118.97, 116.71, 114.60, 51.71, 27.06, 10.03; HRMS (ESI) calcd. for C$_{10}$H$_{13}$N$_2$O [M+H]$^+$: 177.1022, found: 177.1029.
3-Isopropyl-3,4-dihydroquinoxalin-2(1H)-one (4ad)\(^8\)

Yellow solid, mp: 121-123\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.76(s, 1H), 7.29-6.67 (m, 4H), 4.09(s, 1H), 3.81(s, 1H), 2.28 (d, \(J = 10.6\) Hz, 1H), 1.08-1.01(dd, \(J = 17.4, 16.3\) Hz, 6H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 168.83, 133.31, 124.89, 123.91, 118.79, 115.51, 113.39, 81.77, 30.83, 20.23, 19.04, 17.508; HRMS (ESI) calcd. for C\(_{11}\)H\(_{15}\)N\(_2\)O [M+H]\(^+\): 191.1179, found: 191.1181.

3-Benzyl-3,4-dihydroquinoxalin-2(1H)-one (4aj)\(^9\)

Yellow solid, mp: 188-189 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.04(s, 1H), 7.40-7.25 (m, 5H), 6.93-6.61(m, 4H), 4.12 (d, \(J = 10.6\) Hz, 1H), 3.95(s, 1H), 3.32(m, 1H), 2.93 (m, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 169.28, 136.91, 132.43, 129.49, 128.99, 127.09, 125.56, 124.12, 119.60, 115.82, 114.59, 57.82, 37.57; HRMS (ESI) calcd. for C\(_{15}\)H\(_{15}\)N\(_2\)O [M+H]\(^+\): 239.1179, found: 239.1177.

3-Phenyl-3,4-dihydroquinoxalin-2(1H)-one (4al)\(^10\)

White solid, mp: 79-81 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39-7.25 (m, 5H), 6.84 (m, 1H), 6.63-6.56(m, 3H), 5.09 (s, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 177.13, 139.13, 132.82, 129.91, 127.00, 122.90, 118.78, 115.70,114.42, 53.46; HRMS (ESI) calcd. for C\(_{14}\)H\(_{13}\)N\(_2\)O [M+H]\(^+\): 225.1022, found: 225.1017.

(E)-3-styryl-3,4-dihydroquinoxalin-2(1H)-one (4aw)\(^11\)

White solid, mp: 134-136\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.24-8.20 (m, 1H), 7.92-7.74 (m, 4H), 7.52-7.41(m, 6H), 4.42 (d, \(J = 6.3\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 169.78, 140.77, 133.06, 131.76, 127.58, 126.83, 125.93, 117.82, 117.70, 117.27, 113.62, 113.35, 113.25, 61.14; HRMS (ESI) calcd. for C\(_{16}\)H\(_{15}\)N\(_2\)O [M+H]\(^+\): 251.1022, found: 251.1017.

3,6,7-Trimethyl-3,4-dihydroquinoxalin-2(1H)-one (4ja)\(^12\)

Yellow solid, mp: 125-127\(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.33-6.32 (m, 2H), 3.99 (s, 1H), 3.79 (s, 1H), 2.14 (s, 6H), 1.32 (d, \(J = 6.3\) Hz, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 170.43, 133.97, 126.47, 123.42, 117.79, 116.38, 51.62, 19.89, 18.87; HRMS (ESI) calcd. for C\(_{16}\)H\(_{15}\)N\(_2\)O [M+H]\(^+\): 191.1179, found: 191.1183.
4-Methyl-1,3,4,5-tetrahydro-2H-benzo[b][1,4]diazepin-2-one (4ax)

Yellow solid, mp: 110-113°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.07 (m, 4H), 3.26 (m, 1H), 2.66 (m, 1H), 2.28 (m, 1H), 1.24 (d, \(J = 6.3\) Hz, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 170.43, 138.99, 133.98, 126.47, 123.42, 117.79, 116.38, 51.62, 41.38, 23.89; HRMS (ESI) calcd. for C\(_{10}\)H\(_{13}\)N\(_2\)O \([\text{M+H}]^+: 177.1022\), found: 177.1028.

5-Methyl-6-oxo-1,4,5,6-tetrahydropyrazine-2,3-dicarbonitrile (4ua)

White solid, mp: 239-240 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.55 (m, 1H), 1.60 (d, \(J = 6.3\) Hz, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 151.56, 116.02, 115.70, 111.74, 100.41, 55.34, 14.35; HRMS (ESI) calcd. for C\(_7\)H\(_7\)N\(_4\)O \([\text{M+H}]^+: 163.0614\), found: 163.0621.

3-Methyl-3,4-dihydro-2H-benzo[b] [1,4] oxazin-2-one (4ya)

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.03-6.76 (m, 4H), 3.99 (m, 1H), 1.55 (d, \(J = 6.3\) Hz, 3H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 166.14, 144.55, 137.11, 123.60, 120.44, 116.38, 114.38, 50.85, 21.31; HRMS (ESI) Calcd for C\(_9\)H\(_{10}\)NO \([\text{M+H}]^+: 164.0706\), found: 164.0710.

5. The mechanistic study

1) ESI-MS Study

\[
\text{Chemical Formula: } C_9H_9N_2^+ \\
\text{Exact Mass: } 149.1073
\]

\[
\text{Chemical Formula: } C_8H_7N_2O^+ \\
\text{Exact Mass: } 163.0666
\]

\[
\text{Chemical Formula: } C_8H_7N_2O^+ \\
\text{Exact Mass: } 161.0709
\]
2) General procedure for the reaction of 1a with 2a

A mixture of o-phenylenediamine 1a (27.5 mg, 0.25 mmol), ethyl 2-oxopropanoate 2a (31.93 mg, 0.275 mmol) and toluene (1.5 mL) with or without B(C₆F₅)₃ (6.4 mg, 5.0 mol%) in an oven-dried screw-capped pressure tube was stirred at 110 °C for 1 h. After cooling to ambient temperature, the volatiles were removed under reduced pressure, and the reaction mixture was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the target compound 5aa as a light solid.

3) General procedure for the synthesis 3aa from 5aa

A mixture of 3-methylquinoxalin-2(1H)-one 5aa (40.04 mg, 0.25 mmol), B(C₆F₅)₃ (6.4 mg, 5.0 mol%) and PMHS (0.06 mL, 1.0 mmol) in toluene (1.5 mL) in an oven-dried screw-capped pressure tube was stirred at 110 °C for 16 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (5.0 mL). Then water (5.0 mL) was added to the reaction mixture, which was extracted with EtOAc three times (5.0 mL each). The combined organic phases were dried over Na₂SO₄, filtered and evaporated
under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the target compound 3aa as a light yellow oil.

4) General procedure for the synthesis 3aa from 4aa

\[
\begin{align*}
\text{4aa} & \underset{\text{B(C₁₀F₁₆)₃ (5.0 mol%)}}{\text{PMHS, toluene, 110 °C, 16 h}} \rightarrow \text{3aa, 95%}
\end{align*}
\]

A mixture of 4aa (40.55 mg, 0.25 mmol), B(C₁₀F₁₆)₃ (6.4 mg, 5.0 mol%) and PMHS (0.06 mL, 1.0 mmol) in toluene (1.5 mL) in an oven-dried screw-capped pressure tube was stirred at 110 °C for 16 h. After cooling to ambient temperature, the mixture was diluted with EtOAc (5.0 mL). Then water (5.0 mL) was added to the reaction mixture, which was extracted with EtOAc three times (5.0 mL each). The combined organic phases were dried over Na₂SO₄, filtered and evaporated under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the target compound 3aa as a light yellow oil.

6. References:

7. $^1$H and $^{13}$C NMR spectra of the products
8. HPLC CHART

(S)-2-methyl-1,2,3,4-tetrahydroquinoxaline
Chiralcel OD-H
Hexane / i-PrOH = 95/5 0.5 ml/min, 230 nm
tr = 12.207 (S) and 15.687 (R)
\( ee = 47.76 [\alpha]D^{25} = -15.8 \) (c 1.06, EtOH)
(S)-2-ethyl-1,2,3,4-tetrahydroquinoxaline
Chiralcel OD-H
Hexane / i-PrOH = 95/5 1ml/min, 230 nm
t_r = 6.483 (S) and 7.890 (R)
ee = 52.56 [α]_D^{25} = -13.1 (c 1.00, EtOH)
(S)-2-isopropyl-1,2,3,4-tetrahydroquinoxaline
Chiralcel OD-H
Hexane / i-PrOH = 95/5  0.5ml/min, 230 nm
t_r = 15.009 (S) and 18.503 (R)
\text{ee} = 51.74 \text{[\alpha]_D}^{25} = -13.8 \text{ (c 1.06, EtOH)}
(S)-2-benzyl-1,2,3,4-tetrahydroquinoxaline
Chiralcel OD-H
Hexane / i-PrOH = 95/5 0.5 ml/min, 230 nm
t_r = 16.512 (S) and 21.259 (R)
ee = 58.72 [α]_D^{25} = -14.7 (c 1.06, EtOH)
(S)-2-phenyl-1,2,3,4-tetrahydroquinoxaline
Chiralcel OD-H
Hexane / i-PrOH = 99/1 1 ml/min, 230 nm
t_r = 4.660 (S) and 6.127 (R)
ee = 76.28 [α]_D^{25} = +75.8 (c 1.06, EtOH)
(S)-3-methyl-3,4-dihydroquinoxalin-2(1H)-one
Chiralcel  OD-H
Hexane / i-PrOH = 99/1  1 ml/min, 230 nm
t_{r} = 30.480 (S) and 37.352 (R)
ee = 57.38 [α]_{D}^{25} = -18.7 (c 1.06, EtOH)

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(S)-3-ethyl-3,4-dihydroquinazolin-2(1H)-one
Chiralcel OD-H
Hexane / i-PrOH = 97/3 1 ml/min, 230 nm
t_r = 20.048 (S) and 24.951 (R)
ee = 61.88 [α]_D^{25} = -13.2 (c 1.06, EtOH)
(S)-3-isopropyl-3,4-dihydroquinoxalin-2(1H)-one
Chiralcel OD-H
Hexane / i-PrOH = 99/1 0.5 ml/min, 230 nm
t<sub>r</sub> = 57.695 (S) and 65.833 (R)
ee = 60.96 [α]<sub>D</sub><sup>25</sup> = -18.4 (c 1.06, EtOH)

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(S)-3-benzyl-3,4-dihydroquinoxalin-2(1H)-one
Chiralcel OD-H
Hexane / i-PrOH = 98/2 1 ml/min, 230 nm
t_r = 17.717(S) and 26.785 (R)
ee = 71.00 \left[ \alpha \right]_D^{25} = -20.7 \ (c \ 1.06, \ EtOH)
(S)-3-phenyl-3,4-dihydroquinoxalin-2(1H)-one
Chiralcel OD-H
Hexane / i-PrOH = 99/1 1 ml/min, 230 nm
t_r = 29.800 (R) and 34.011 (S)
ee = 82.24 [α]_D^25 = +73.8 (c 1.06, EtOH)