Supporting Information


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Experimental Section

**General Consideration.** Acetonitrile (CH\(_2\)CN) was dried with CaH\(_2\) and distilled. Dichloromethane (CH\(_2\)Cl\(_2\)) was dried with CaH\(_2\) and distilled. Toluene was dried with Na and distilled. All other commercial reagents were used as received without additional purification. Melting point was uncorrected. Mass spectra and HPLC data was recorded on a LC/MS system with ELSD. The \(^1\)H and \(^13\)C NMR data were obtained on a 300 MHz NMR spectrometer with TMS as the internal standard and CDCl\(_3\) as solvent unless otherwise stated. Multiplicities are indicated as the following: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doubled doublet; br, broad. Coupling constants (J values) where noted are quoted in Hertz.

**Table S1** Synthesis of substrates 4–10

![Chemical Structure](image)

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<th>(3/) (%)</th>
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**General procedure for the synthesis of compounds 2a-d.**
The solution of one of various substituted N-methylallylamines (28.2 mmol) and Et₃N (4.07 mL, 28.2 mmol) in CHCl₃ (20 mL) was added dropwise to a stirred solution of 4,6-dichloro-5-formylpyrimidine 1 (5.0 g, 28.2 mmol) in CHCl₃ (40 mL). The resulting solution was stirred for 0.5 h at 0–5 °C, then washed with H₂O (30 mL) and saturated aqueous NaHCO₃ (30 mL), dried over MgSO₄, and concentrated in vacuo. Purification by flash chromatography (Petroleum ether/EtOAc = 20:1 to 5:1, v/v) afforded the desired product 2a-d.

4-( Allyl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2a: 94%; mp: 55–56 °C; ¹H NMR δ 10.38 (s, 1H), 8.35 (s, 1H), 5.92–5.75 (m, 1H), 5.29–5.19 (m, 2H), 4.31 (d, 2H, J = 5.1), 2.88 (s, 3H); MS (ESI): m/z 211.8 [M + H⁺].

(E)-4-(But-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b: 72%; mp: 30–31 °C; ¹H NMR δ 10.36 (s, 1H), 8.34 (s, 1H), 5.77–5.64 (m, 1H), 5.55–5.44 (m, 1H), 4.20 (d, 2H, J = 6.3), 2.86 (s, 3H), 1.73 (m, 3H); ¹³C NMR δ 187.4, 164.5, 160.9, 157.3, 130.7, 124.6, 109.7, 54.1, 39.7, 17.8; MS (ESI): m/z 225.9 [M + H⁺].

4-Chloro-6-(cinnamyl(methyl)amino)pyrimidine-5-carbaldehyde 2c: 53%; mp: 84–85 °C; ¹H NMR δ 10.40 (s, 1H), 8.40 (s, 1H), 7.41–7.27 (m, 5H), 6.59 (d, 1H, J = 15.9), 6.28–6.18 (m, 1H), 4.45 (dd, 2H, J = 6.9, 1.2), 2.93 (s, 3H); ¹³C NMR δ 187.5, 164.7, 161.0, 157.5, 136.1, 134.2, 128.7, 128.1, 126.5, 123.1, 109.9, 54.2, 40.0; MS (ESI): m/z 287.9 [M + H⁺].

(E)-Methyl-2-(((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenyl acrylate 2d: 99%; oil; ¹H NMR δ 10.29 (s, 1H), 8.30 (s, 1H), 7.98 (s, 1H), 7.39–7.27 (m, 5H), 4.71 (s, 2H), 3.74 (s, 3H), 2.81 (s, 3H); ¹³C NMR δ 186.8, 167.0, 164.2, 161.3, 156.9, 144.1, 134.1, 128.9, 128.8, 128.4, 127.2, 109.9, 52.0, 48.0, 39.0; MS (ESI): m/z 346.0 [M + H⁺].

General procedure for the synthesis of compounds 3a-d.
To a stirred solution of compound 2 (6.6 mmol) in EtOH (13 mL) was added NaBH₄CN (13.2 mmol) followed by AcOH (0.7 mL). The mixture was stirred for the corresponding time (1–3.5 h) at room temperature. The volatiles were removed \textit{in vacuo} before saturated aqueous NaHCO₃ (20 mL) was added. The reaction mixture was extracted with extracted with EtOAc (3 × 20 mL). The combined EtOAc layer was dried over MgSO₄ and concentrated \textit{in vacuo}. Purification by flash column chromatography (Petroleum ether/EtOAc = 5:1 to 3:1, v/v) afforded the desired product 3a-d.

\textbf{(4-(Allyl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3a: 99%; mp: 57–58 °C; ¹H NMR δ 8.31 (s, 1H), 6.00–5.87 (m, 1H), 5.30–5.23 (m, 2H), 4.67 (s, 2H), 4.23 (d, 2H, J = 5.1), 3.19 (s, 3H), 2.35 (br, 1H); ¹³C NMR δ 164.6, 161.7, 155.5, 133.1, 117.0, 113.6, 58.1, 55.1, 38.0; MS (ESI): m/z 213.8 [M + H⁺].}

\textbf{(E)-(4-(But-2-en-1-yl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3b: 93%; mp: 55–56 °C; ¹H NMR δ 8.31 (s, 1H), 5.76–5.64 (m, 1H), 5.60–5.51 (m, 1H), 4.67 (s, 2H), 4.14 (d, 2H, J = 5.4), 3.16 (s, 3H), 2.36 (br, 1H), 1.76–1.22 (m, 3H); ¹³C NMR δ 162.0, 155.9, 129.1, 126.1, 113.9, 58.7, 54.8, 37.9, 17.9; MS (ESI): m/z 227.9 [M + H⁺].}

\textbf{(E)-(4-Chloro-6-(cinnamyl(methyl)amino)pyrimidin-5-yl)methanol 3c: 94%; oil; ¹H NMR δ 8.34 (s, 1H), 7.42–7.22 (m, 5H), 6.58 (d, 1H, J = 15.9), 6.35–6.25 (m, 1H), 4.70 (s, 2H), 4.38 (dd, 2H, J = 6.0, 1.2), 3.24 (s, 3H), 2.27 (br, 1H); ¹³C NMR δ 164.9, 162.1, 155.9, 136.5, 132.6, 128.7, 127.8, 126.5, 124.8, 114.0, 58.5, 54.9, 38.2; MS (ESI): m/z 290.0 [M + H⁺].}

\textbf{(E)-Methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d: 76%; mp: 67–68 °C; ¹H NMR δ 8.24 (s, 1H), 7.91 (s, 1H), 7.35–7.25 (m, 5H), 4.82 (s, 2H), 4.44 (s, 2H), 3.76 (s, 3H), 2.98 (s, 3H), 2.31 (br, 1H); ¹³C NMR δ 167.9, 165.5, 161.9, 155.5, 143.2, 134.7, 129.0, 128.9, 128.4, 128.3, 114.8, 58.1, 55.1, 38.0; MS (ESI): m/z 290.0 [M + H⁺].}
Preparation of (E)-methyl-2-((methylamino)methyl)-3-phenylacrylate.

The solution of methyl 2-(acetoxy(phenyl)methyl)acrylate (4.0 g, 15.6 mmol) in THF (20 mL) was added dropwise to a stirred solution of methyamine alcohol solution (30%, 20 mL) in THF (80 mL) at 0 °C. The resulting solution was stirred for 30 min at 0 °C. The volatiles were removed in vacuo before saturated aqueous NaHCO₃ (20 mL) was added. The reaction mixture was extracted with extracted with EtOAc (3 x 20 mL).

The combined EtOAc layer was dried over MgSO₄ and concentrated in vacuo. Purification by flash column chromatography (Petroleum ether/EtOAc = 1:1, v/v) afforded 3.16 g (99%) of (E)-methyl-2-((methylamino)methyl)-3-phenylacrylate. oil; ¹H NMR δ 7.83 (s, 1H), 7.48–7.37 (m, 5H), 3.84 (s, 3H), 3.57 (s, 2H), 2.44 (s, 3H), 1.93 (s, 1H); ¹³C NMR δ 168.5, 142.0, 135.1, 130.6, 129.6, 128.6, 128.9, 52.1, 47.8, 36.2; MS (ESI): m/z 206.0 [M + H⁺].

General procedure for the synthesis of compounds 4, 6 and 7.

To a stirred solution of 3a (641 mg, 3 mmol) in CH₂Cl₂ (10 mL) was added SOCl₂ (0.85 mL, 12 mmol) at room temperature. After complete consumption of the starting material 3a, as indicated by TLC, the volatiles were removed in vacuo to give crude chlorinated product. The crude chlorinated product was dissolved in CH₃CN (15 mL). To the resulting solution was added R¹NH₂ (6 mmol) and followed by Et₃N (3 mmol) at room temperature. The mixture was stirred for the corresponding time (2–4 h) at reflux. The volatiles were removed in vacuo before saturated aqueous NaHCO₃ (20 mL) was added. The reaction mixture was extracted with EtOAc (3 x 20 mL). The
combined EtOAc layer was dried over MgSO₄ and concentrated in vacuo. Purification by flash column chromatography (Petroleum ether/EtOAc = 10:1 to 5:1, v/v) afforded the desired products 4, 6 or 7.

\textbf{N-\textit{Allyl}-5-((butylamino)methyl)-6-chloro-\textit{N}-methylpyrimidin-4-amine 4:} 69\%, oil; \textsuperscript{1}H NMR \(\delta\) 8.29 (s, 1H), 5.97–5.88 (m, 1H), 5.28–5.21 (m, 2H), 4.33 (d, 2H, \(J = 4.8\)), 3.61 (s, 2H), 3.15 (s, 3H), 2.65 (t, 2H, \(J = 6.6\)), 1.52–1.31 (m, 4H), 0.90 (t, 3H, \(J = 7.5\)); \textsuperscript{13}C NMR \(\delta\) 165.2, 161.2, 155.1, 133.9, 116.4, 114.2, 55.1, 49.7, 47.3, 37.5, 31.8, 20.3, 13.7; MS (ESI): \textit{m/z}\ 268.8 [M + H\textsuperscript{+}].

\textbf{N-\textit{Allyl}-6-chloro-5-((isopropylamino)methyl)-\textit{N}-methylpyrimidin-4-amine 6:} 72\%; oil; \textsuperscript{1}H NMR \(\delta\) 8.29 (s, 1H), 5.96–5.86 (m, 1H), 5.27 (t, 1H, \(J = 1.8\)), 5.24–5.21 (m, 1H), 4.35 (d, 2H, \(J = 4.5\)), 3.62 (s, 2H), 3.16 (s, 3H), 2.88–2.83 (m, 1H), 1.48 (br, 1H), 1.11 (s, 3H), 1.08 (s, 3H); \textsuperscript{13}C NMR \(\delta\) 165.3, 161.6, 155.4, 134.2, 116.6, 114.4, 55.4, 49.6, 45.6, 37.9, 22.9; MS (ESI): \textit{m/z}\ 255.0 [M + H\textsuperscript{+}].

\textbf{N-\textit{Allyl}-6-chloro-\textit{N}-methyl-5-((phenylamino)methyl)pyrimidin-4-amine 7:} 63\%; mp: 85–86 °C; \textsuperscript{1}H NMR \(\delta\) 8.34 (s, 1H), 7.26–7.21 (m, 2H), 6.84–6.79 (m, 1H), 6.71–6.68 (m, 2H), 5.95–5.85 (m, 1H), 5.29–5.21 (m, 2H), 4.23–4.20 (m, 2H), 4.18 (s, 2H), 3.15 (s, 3H); \textsuperscript{13}C NMR \(\delta\) 164.9, 162.0, 155.6, 147.3, 133.4, 129.1, 118.5, 116.8, 113.4, 112.0, 55.0, 42.6, 37.7; MS (ESI): \textit{m/z}\ 289.0 [M + H\textsuperscript{+}].

\textbf{General procedure for the synthesis of compounds 5, 8-10.}

![Chemical diagram](image)

To a stirred solution of 3 (3 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) was added SOCl\textsubscript{2} (0.85 mL, 12 mmol) at room temperature. After complete consumption of the starting material 3, as indicated by TLC, the volatiles were removed in vacuo to give crude chlorinated product. The crude chlorinated product was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The above solution was added to the methylamine alcohol solution (30\%, 5 mL) at room temperature. The mixture was stirred for the corresponding time (1–5 h). The volatiles were removed in vacuo before saturated aqueous NaHCO\textsubscript{3} (20 mL) was added. The
reaction mixture was extracted with EtOAc (3 x 20 mL). The combined EtOAc layer was dried over MgSO$_4$ and concentrated in vacuo. Purification by flash column chromatography (Petroleum ether/EtOAc = 3:1 to 2:1, v/v) afforded the desired products 5, 8-10.

**$N$-Allyl-6-chloro-$N$-methyl-5-((methylamino)methyl)pyrimidin-4-amine 5**: 73%; mp: 46–48 $^0$C; $^1$H NMR $\delta$ 8.30 (s, 1H), 5.98–5.88 (m, 1H), 5.29–5.22 (m, 2H), 4.33–4.29 (m, 2H), 3.59 (s, 2H), 3.15 (s, 3H), 2.47 (s, 3H), 1.71 (br, 1H); $^{13}$C NMR $\delta$ 165.5, 161.5, 155.4, 134.1, 116.8, 114.3, 55.4, 49.4, 37.8, 36.7; MS (ESI): $m/z$ 227.0 [M + H$^+$].

**(E)-$N$-(But-2-en-1-yl)-6-chloro-$N$-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8**: 63%; oil; $^1$H NMR $\delta$ 8.28 (s, 1H), 5.74–5.63 (m, 1H), 5.59–5.50 (m, 1H), 4.18 (d, 2H, $J$ = 5.7), 3.61 (s, 2H), 3.13 (s, 3H), 2.48 (s, 3H), 1.93 (br, 1H), 1.76–1.73 (m, 3H); $^{13}$C NMR $\delta$ 165.3, 161.5, 155.4, 128.6, 126.6, 114.3, 54.7, 49.6, 37.5, 36.8, 17.9; MS (ESI): m/z 241.0 [M + H$^+$].

$6$-Chloro-$N$-cinnamyl-$N$-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9: 61%; mp: 60–61 $^0$C; $^1$H NMR $\delta$ 8.32 (s, 1H), 7.42–7.22 (m, 5H), 6.60 (d, 1H, $J$ = 16.2), 6.35–6.26 (m, 1H), 4.46 (dd, 2H, $J$ = 5.4, 1.2), 3.62 (s, 2H), 3.21 (s, 3H), 2.48 (s, 3H), 1.68 (br, 1H); $^{13}$C NMR $\delta$ 165.4, 161.6, 155.5, 136.6, 132.1, 128.7, 127.8, 126.4, 125.5, 114.4, 55.0, 49.5, 37.8, 36.8; MS (ESI): m/z 303.0 [M + H$^+$].

**(E)-Methyl-2-(((6-chloro-5-((methylamino)methyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10**: 67%; oil; $^1$H NMR $\delta$ 8.21 (s, 1H), 7.90 (s, 1H), 7.35–7.25 (m, 5H), 4.86 (s, 2H), 3.76 (s, 3H), 3.44 (s, 2H), 3.01 (s, 3H), 2.43 (s, 3H), 1.64 (br, 1H); $^{13}$C NMR $\delta$ 168.1, 166.0, 161.4, 155.1, 143.0, 134.8, 129.1, 128.9, 128.8, 128.4, 115.2, 52.3, 49.7, 47.7, 38.2, 36.8; MS (ESI): m/z 361.0 [M + H$^+$].

**General procedure for the synthesis of compound 11.**
To a stirred solution of compound 4-10 (0.5 mmol) in toluene (2 mL) was added aldehyde (0.6 mmol). The resulting solution was heated in an azeotropic distillation apparatus for the corresponding time under N\textsubscript{2}. The volatiles were removed \textit{in vacuo}.

Purification by flash column chromatography (Petroleum ether/EtOAc = 3:1, v/v) afforded the desired product 11.

(2\textit{R*},3\textit{aR*},9\textit{bR*})-1-Butyl-9-chloro-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1\textit{H}\-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11\textit{a}: 89%; mp: 120–121 °C; \textsuperscript{1}H NMR δ 8.30 (s, 1H), 7.38–7.23 (m, 5H), 4.67 (d, 1H, J = 3.6), 4.32 (t, 1H, J = 7.5), 3.45 (t, 1H, J = 12), 3.25–3.18 (m, 4H), 2.47 (t, 2H, J = 6.9), 2.35–2.30 (m, 1H), 2.26–2.07 (m, 2H), 1.08–0.93 (m, 4H), 0.62 (t, 3H, J = 6.6); \textsuperscript{13}C NMR δ 160.3, 159.5, 156.7, 144.8, 128.4, 127.8, 126.8, 109.3, 61.7, 58.4, 51.0, 46.4, 38.8, 36.6, 33.2, 30.7, 20.0, 13.7; MS (ESI): m/z 357.1 [M + H\textsuperscript{+}].

(2\textit{R*},3\textit{aR*},9\textit{bR*})-1-Butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1\textit{H}-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11\textit{b}: 95%; mp: 116–117 °C; \textsuperscript{1}H NMR δ 8.33 (s, 1H), 8.23 (d, 2H, J = 8.4), 7.53 (d, 2H, J = 8.4), 4.69 (d, 1H, J = 3.3), 4.39 (t, 1H, J = 8.1), 3.34–3.28 (m, 2H), 3.24 (s, 3H), 2.50–2.47 (m, 2H), 2.42–2.36 (m, 1H), 2.32–2.02 (m, 1H), 2.10–1.90 (m, 1H), 1.23–0.84 (m, 4H), 0.63 (t, 3H, J = 6.6); \textsuperscript{13}C NMR δ 160.2, 159.7, 156.9, 153.6, 146.9, 127.9, 123.8, 108.6, 62.6, 59.1, 50.7, 48.4, 39.0, 36.6, 33.9, 31.3, 19.9, 13.7; MS (ESI): m/z 402.0 [M + H\textsuperscript{+}].

(2\textit{R*},3\textit{aR*},9\textit{bR*})-1-Butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1\textit{H}-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11\textit{c}: 86%; mp: 111–112 °C; \textsuperscript{1}H NMR δ 8.30 (s, 1H), 7.34–7.25 (m, 4H), 4.63 (d, 1H, J = 3.9), 4.26 (t, 1H, J = 7.8), 3.40 (t, 1H, J = 12.3), 3.25–3.19 (m, 4H), 2.46 (t, 2H, J = 6.3), 2.36–2.25 (m, 1H), 2.20–2.02 (m, 2H), 1.08–0.97 (m, 4H), 0.63 (t, 3H, J = 7.2); \textsuperscript{13}C NMR δ 160.2, 159.5, 156.7, 143.4, 132.3, 128.7, 128.5, 108.9, 61.5, 58.4, 50.8, 46.9, 38.7, 36.4, 33.3, 30.7, 19.8, 13.5; MS (ESI): m/z 391.1 [M + H\textsuperscript{+}].

(2\textit{R*},3\textit{aR*},9\textit{bR*})-1-Butyl-9-chloro-2-(3-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1\textit{H}-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11\textit{d}: 93%; oil; \textsuperscript{1}H NMR δ 8.33 (s, 1H), 7.68 (dd, 1H, J = 7.8, 1.8), 7.34–7.27 (m, 2H), 7.17 (t, 1H, J = 7.8), 4.70
(d, 1H, \(J = 4.5\)), 4.67 (d, 1H, \(J = 8.4\)), 3.31–3.27 (m, 2H), 3.24 (s, 3H), 2.70–2.54 (m, 1H), 2.51–2.38 (m, 2H), 2.37–2.28 (m, 1H), 1.90–1.81 (m, 1H), 1.21–0.95 (m, 4H), 0.75–0.55 (m, 3H); \(^{13}\)C NMR \(\delta\) 160.2, 159.6, 156.8, 143.0, 132.3, 129.5, 128.1, 127.6, 127.0, 108.8, 60.2, 59.2, 50.8, 49.6, 37.6, 36.5, 34.3, 31.6, 19.9, 13.6; MS (ESI): \(m/z\) 390.9 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-1-Butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11e: 97%; mp: 86–87 °C; \(^1\)H NMR \(\delta\) 8.33 (s, 1H), 7.67 (d, 1H, \(J = 6.6\)), 7.67–7.27 (m, 2H), 7.20–7.16 (m, 1H), 4.70–4.65 (m, 2H), 3.31–3.27 (m, 2H), 3.22 (s, 3H), 2.61–2.28 (m, 4H), 1.87–1.80 (m, 1H), 1.23–0.85 (m, 4H), 0.70–0.59 (m, 3H); \(^{13}\)C NMR \(\delta\) 160.2, 159.5, 156.8, 143.0, 132.3, 129.4, 128.1, 127.6, 127.0, 108.0, 60.2, 59.2, 50.8, 49.6, 37.6, 36.5, 34.3, 31.6, 19.9, 13.7; MS (ESI): \(m/z\) 391.1 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-1-Butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11f: 85%; mp: 113–114 °C; \(^1\)H NMR \(\delta\) 8.29 (s, 1H), 7.23–7.14 (m, 4H), 4.64 (d, 1H, \(J = 3.6\)), 4.30 (t, 1H, \(J = 7.8\)), 3.46 (t, 1H, \(J = 12.0\)), 3.23–3.17 (m, 4H), 2.51–2.40 (m, 2H), 2.37–2.25 (m, 4H), 2.16–2.05 (m, 2H), 1.21–0.85 (m, 4H), 0.62 (t, 3H, \(J = 6.9\)); \(^{13}\)C NMR \(\delta\) 160.3, 159.5, 156.7, 141.7, 136.4, 129.1, 127.8, 109.4, 61.2, 58.2, 51.1, 46.0, 38.7, 36.6, 33.1, 30.6, 21.2, 20.0, 13.7; MS (ESI): \(m/z\) 371.1 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-1-Butyl-9-chloro-5-methyl-2-(m-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11g: 97%; mp: 66–67 °C; \(^1\)H NMR \(\delta\) 8.29 (s, 1H), 7.23 (d, 1H, \(J = 7.8\)), 7.14–7.12 (m, 2H), 7.06 (d, 1H, \(J = 7.5\)), 4.66 (d, 1H, \(J = 3.6\)), 4.29 (t, 1H, \(J = 7.8\)), 3.44 (t, 1H, \(J = 12.0\)), 3.24–3.18 (m, 4H), 2.48 (t, 2H, \(J = 6.0\)), 2.37 (s, 3H), 2.36–2.25 (m, 1H), 2.23–2.08 (m, 2H), 1.09–0.97 (m, 4H), 0.62 (t, 3H, \(J = 6.9\)); \(^{13}\)C NMR \(\delta\) 160.4, 159.5, 156.7, 144.9, 138.0, 128.5, 128.4, 127.6, 124.8, 109.4, 61.7, 58.4, 51.1, 46.3, 38.8, 36.8, 33.3, 30.7, 21.7, 20.0, 13.7; MS (ESI): \(m/z\) 371.0 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-1-Butyl-9-chloro-5-methyl-2-(o-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11h: 97%; mp: 75–76 °C; \(^1\)H NMR \(\delta\)
8.32 (s, 1H), 7.52 (d, 1H, J = 7.2), 7.25–7.21 (m, 1H), 7.12 (d, 2H, J = 4.2), 4.74 (d, 1H, J = 3.6), 4.51 (t, 1H, J = 7.8), 3.39–3.27 (m, 1H), 3.26–3.23 (m, 1H), 3.23 (s, 3H), 2.65–2.59 (m, 1H), 2.55–2.47 (m, 1H), 2.34 (s, 3H), 2.32–2.22 (m, 2H), 1.94–1.84 (m, 1H), 1.04–0.96 (m, 4H), 0.71–0.50 (m, 3H); 13C NMR δ 160.3, 159.5, 156.7, 134.5, 130.5, 126.5, 126.2, 126.1, 109.3, 59.0, 58.8, 50.9, 48.5, 37.9, 36.5, 34.0, 31.4, 19.9, 19.5, 13.7; MS (ESI): m/z 371.0 [M + H]+.

(2R*,3aR*,9bR*)-1-Butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2’,3’;4,5]pyrido[2,3-d]pyrimidine 11i: 83%; mp: 119–120 °C; 1H NMR δ 8.29 (s, 1H), 7.25 (d, 2H, J = 8.4), 6.89 (d, 2H, J = 8.4), 4.61 (d, 1H, J = 3.9), 4.30 (t, 1H, J = 7.2), 3.82 (s, 3H), 3.46 (t, 1H, J = 12.0), 3.36–3.17 (m, 4H), 2.53–2.35 (m, 2H), 2.34–2.25 (m, 1H), 2.18–2.04 (m, 2H), 1.23–0.85 (m, 4H), 0.63 (t, 3H, J = 6.6); 13C NMR δ 160.4, 159.5, 158.5, 156.7, 136.7, 128.9, 113.8, 109.4, 60.9, 58.1, 55.3, 51.1, 46.0, 38.7, 36.7, 33.1, 30.6, 20.0, 13.8; MS (ESI): m/z 387.1 [M + H]+.

(2R*,3aR*,9bR*)-1-Butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2’,3’;4,5]pyrido[2,3-d]pyrimidine 11j: 66%; mp: 107–109 °C; 1H NMR δ 8.29 (s, 1H), 7.41 (d, 1H, J = 7.2), 7.23 (d, 1H, J = 6.6), 6.98–6.88 (m, 2H), 4.68 (d, 1H, J = 3.3), 4.60 (t, 1H, J = 7.8), 3.84 (s, 3H), 3.37–3.11 (m, 4H), 2.51–2.35 (m, 2H), 2.29–2.24 (m, 1H), 2.21–2.13 (m, 1H), 2.06–2.01 (m, 1H), 1.22–0.65 (m, 4H), 0.61 (t, 3H, J = 6.6); 13C NMR δ 160.4, 159.4, 156.9, 156.6, 132.5, 129.0, 127.9, 120.6, 110.5, 109.8, 58.3, 58.2, 55.3, 51.1, 47.6, 36.7, 36.6, 33.8, 31.4, 20.0, 13.8; MS (ESI): m/z 387.1 [M + H]+.

(2R*,3aR*,9bR*)-1-Butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2’,3’;4,5]pyrido[2,3-d]pyrimidine 11k: 88%; mp: 102–103 °C; 1H NMR δ 8.27 (s, 1H), 7.43 (d, 1H, J = 1.5), 6.33 (dd, 1H, J = 3.0, 1.8), 6.20 (d, 1H, J = 2.4), 4.43–4.38 (m, 1H), 4.37 (d, 1H, J = 3.6), 3.51 (t, 1H, J = 11.7), 3.21 (s, 3H), 3.15 (dd, 1H, J = 12.6, 6.0), 2.45–2.40 (m, 1H), 2.33–2.25 (m, 2H), 2.23–2.09 (m, 1H), 1.97–1.82 (m, 1H), 1.30–1.22 (m, 2H), 1.20–1.00 (m, 2H), 0.72 (t, 3H, J = 7.2); 13C NMR δ 160.5, 159.5, 156.6, 142.1, 109.8, 109.2, 108.1, 56.8, 53.5, 51.4, 45.8, 36.6,
33.2, 31.8, 30.4, 20.2, 13.7; MS (ESI) m/z 347.1 [M + H⁺].

(2R*,3aR*,9bR*)-1-Butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11l: 83% mp: 131–132 ⁰C; ¹H NMR δ 8.29 (s, 1H), 7.25–7.24 (m, 1H), 6.97 (dd, 1H, J = 5.1, 3.6), 6.93 (dd, 1H, J = 3.3, 1.2), 4.70 (dd, 1H, J = 8.7, 5.1), 4.43 (d, 1H, J = 3.3), 3.48 (t, 1H, J = 11.7), 3.21 (s, 3H), 3.17 (dd, 1H, J = 12.0, 5.1), 2.44–2.32 (m, 2H), 2.30–2.14 (m, 3H), 1.30–0.99 (m, 4H), 0.69 (t, 3H, J = 7.2); ¹³C NMR δ 160.3, 159.5, 156.5, 146.8, 126.1, 125.8, 124.4, 108.7, 56.4, 55.9, 51.2, 45.1, 37.9, 36.4, 31.8, 30.3, 19.9, 13.6; MS (ESI): m/z 363.1 [M + H⁺].

(2R*,3aR*,9bR*)-1-Butyl-9-chloro-5-methyl-2-(E-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11m: 95%; mp: 114–115 ⁰C; ¹H NMR δ 8.28 (s, 1H), 7.42–7.24 (m, 5H), 6.48 (d, 1H, J = 15.6), 6.52–6.36 (m, 1H), 4.21 (d, 1H, J = 2.1), 4.00–3.80 (m, 1H), 3.46 (t, 1H, J = 8.4), 3.20 (s, 3H), 3.25–3.07 (m, 1H), 2.80–2.66 (m, 1H), 2.59–2.38 (m, 1H), 2.29–2.10 (m, 1H), 1.99–1.78 (m, 2H), 1.31–1.09 (m, 4H), 0.73 (t, 3H, J = 7.5); ¹³C NMR δ 160.4, 159.4, 156.6, 137.0, 131.2, 130.9, 128.7, 127.6, 126.4, 109.2, 59.0, 56.7, 51.4, 45.5, 36.6, 34.9, 32.2, 30.0, 20.3, 13.9; MS (ESI): m/z 383.2 [M + H⁺].

(2R*,3aR*,9bR*)-1-Butyl-9-chloro-2-cyclohexyl-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11p: 51%; mp: 93–94 ⁰C; ¹H NMR δ 8.27 (s, 1H), 4.19 (d, 1H, J = 3.9), 3.40–3.11 (m, 6H), 2.70–2.60 (m, 1H), 2.43–2.34 (m, 1H), 2.19–2.09 (m, 1H), 1.97–1.87 (m, 1H), 1.78–1.67 (m, 6H), 1.66–1.54(m, 2H), 1.29–1.09 (m, 8H), 0.74 (t, 3H, J = 7.2); ¹³C NMR δ 160.5, 159.5, 156.7, 156.6, 58.1, 51.6, 47.6, 40.8, 36.7, 33.6, 31.9, 30.0, 29.3, 27.7, 26.9, 26.8, 26.3, 20.1, 13.9; MS (ESI): m/z 363.1 [M + H⁺].

(2R*,3aR*,9bR*)-9-Chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q: 75%; mp: 102–103 ⁰C; ¹H NMR δ 8.28 (s, 1H), 7.40–7.27 (m, 5H), 4.53 (d, 1H, J = 4.5), 4.26 (t, 1H, J = 7.8), 3.46 (t, 1H, J = 12.3), 3.27 (dd, 1H, J = 12.3, 6.0), 3.22 (s, 3H), 2.47–2.41 (m, 1H), 2.26–2.11 (m, 2H), 2.11 (s, 3H); ¹³C NMR δ 160.5, 159.3, 156.7, 143.2, 128.5, 128.3, 127.4, 64.9, 58.4,
51.1, 38.0, 36.8, 35.7, 33.2; MS (ESI): m/z 315.1 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-9-Chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydropyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r: 59%; mp: 122–123 °C; \(^1\)H NMR  δ 8.31 (s, 1H), 7.42 (d, 2H, J = 6.9), 7.30 (t, 2H, J = 6.9), 7.21 (t, 1H, J = 7.5), 4.93 (d, 1H, J = 3.9), 4.42 (t, 1H, J = 8.1), 3.23 (s, 3H), 3.23–3.12 (m, 3H), 2.36–2.25 (m, 1H), 2.18–2.10 (m, 1H), 1.99–1.95 (m, 1H), 0.77 (d, 3H, J = 6.3), 0.68 (d, 3H, J = 6.9); \(^1^3\)C NMR δ 160.7, 156.9, 149.5, 128.4, 126.7, 126.6, 59.7, 57.9, 50.0, 46.8, 40.7, 36.7, 34.2, 24.8, 19.1; MS (ESI): m/z 343.0 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-9-Chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydropyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s: 32%; mp: 164–165 °C; \(^1\)H NMR  δ 8.24 (s, 1H), 7.30–7.28 (m, 4H), 7.21–7.18 (m, 1H), 6.96 (t, 2H, J = 7.5), 6.70 (d, 2H, J = 7.2), 6.62 (t, 1H, J = 7.2), 5.33 (d, 1H, J = 3.0), 5.11 (t, 1H, J = 7.2), 3.38–3.34 (m, 2H), 3.18 (s, 3H), 2.59–2.49 (m, 1H), 2.42–2.34 (m, 1H), 2.23–2.11 (m, 1H); \(^1^3\)C NMR δ 160.1, 160.0, 156.8, 146.0, 144.2, 128.8, 128.6, 126.9, 126.3, 119.0, 118.3, 108.6, 61.8, 58.5, 50.5, 39.3, 36.5, 34.9; MS (ESI): m/z 377.1 [M + H\(^+\)].

\((2R^*,3aR^*,9bR^*)\)-9-Chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydropyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u: 46%; mp: 192–193 °C; \(^1\)H NMR  δ 8.35 (s, 1H), 7.15–7.05 (m, 5H), 7.00–6.92 (m, 5H), 5.01 (d, 1H, J = 7.5), 4.44 (d, 1H, J = 7.5), 3.76 (t, 1H, J = 6.0), 3.36 (dd, 1H, J = 12.3, 4.8), 3.21–3.09 (m, 5H), 2.38 (s, 3H); \(^1^3\)C NMR δ 163.2, 158.9, 156.1, 139.4, 139.2, 129.0, 128.5, 128.0, 127.8, 126.7, 126.5, 111.9, 72.7, 58.1, 53.2, 52.3, 43.9, 37.3, 37.1; MS (ESI): m/z 391.0 [M + H\(^+\)].

\((2R^*,3aS^*,9bR^*)\)-Methyl-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydropyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine-3a-carboxylate 11v: 41%; mp: 173–174 °C; \(^1\)H NMR  δ 8.29 (s, 1H), 7.40–7.19 (m, 10H), 5.18 (s, 1H), 4.68 (d, 1H, J = 8.7), 4.15 (d, 1H, J = 8.7), 3.79–3.70 (m, 4H), 3.22–3.14 (m, 4H), 2.20 (s, 3H); \(^1^3\)C NMR δ 172.1, 159.7, 157.3, 141.3, 134.7, 130.3, 130.1, 128.8, 128.7, 128.6, 128.4, 128.0, 127.8, 68.9, 63.0, 60.5, 52.9, 51.8, 48.8, 36.8, 35.9; MS (ESI): m/z 449.1 [M + H\(^+\)].
ORTEP Diagrams:

11a

11q

11v
Figure Legends:
Fig. S-1: LC-MS-ELSD of 4-(allyl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2a
Fig. S-2: $^1$H Spectra of 4-(allyl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2a
Fig. S-3: LC-MS-ELSD of (E)-4-(but-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b
Fig. S-4: $^1$H Spectra of (E)-4-(but-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b
Fig. S-5: $^{13}$C Spectra of (E)-4-(but-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b
Fig. S-6: LC-MS-ELSD of 4-chloro-6-(cinnamyl(methyl)amino)pyrimidine-5-carbaldehyde 2c
Fig. S-7: $^1$H Spectra of 4-chloro-6-(cinnamyl(methyl)amino)pyrimidine-5-carbaldehyde 2c
Fig. S-8: $^{13}$C Spectra of 4-chloro-6-(cinnamyl(methyl)amino)pyrimidine-5-carbaldehyde 2c
Fig. S-9: LC-MS-ELSD of (E)-methyl-2-(((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 2d
Fig. S-10: $^1$H Spectra of (E)-methyl-2-(((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 2d
Fig. S-11: $^{13}$C Spectra of (E)-methyl-2-(((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 2d
Fig. S-12: LC-MS-ELSD of (4-(allyl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3a
Fig. S-13: $^1$H Spectra of (4-(allyl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3a
Fig. S-14: $^{13}$C Spectra of (4-(allyl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3a
Fig. S-15: LC-MS-ELSD of (E)-(4-(but-2-en-1-yl)(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3b
Fig. S-16: $^1$H Spectra of (E)-(4-(but-2-en-1-yl)(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3b
Fig. S-17: $^{13}$C Spectra of (E)-(4-(but-2-en-1-yl)(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3b
Fig. S-18: LC-MS-ELSD of (E)-(4-chloro-6-(cinnamyl)(methyl)amino)pyrimidin-5-yl)methanol 3c
Fig. S-19: $^1$H Spectra of (E)-(4-chloro-6-(cinnamyl)(methyl)amino)pyrimidin-5-yl)methanol 3c
Fig. S-20: $^{13}$C Spectra of (E)-(4-chloro-6-(cinnamyl)(methyl)amino)pyrimidin-5-yl)methanol 3c
Fig. S-21: LC-MS-ELSD of (E)-methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d
Fig. S-22: $^1$H Spectra of (E)-methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d
Fig. S-23: $^{13}$C Spectra of (E)-methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d
Fig. S-24: LC-MS-ELSD of (E)-methyl-2-(((methylamino)(methyl))-3-phenylacrylate
Fig. S-25: $^1$H Spectra of (E)-methyl-2-(((methylamino)(methyl))-3-phenylacrylate
Fig. S-26: $^{13}$C Spectra of (E)-methyl-2-(((methylamino)(methyl))-3-phenylacrylate
Fig. S-27: LC-MS-ELSD of N-allyl-5-(((butylamino)(methyl))-6-chloro-N-methylpyrimidin-4-amine 4
Fig. S-28: $^1$H Spectra of N-allyl-5-(((butylamino)(methyl))-6-chloro-N-methylpyrimidin-4-amine 4
Fig. S-29: $^{13}$C Spectra of N-allyl-5-(((butylamino)(methyl))-6-chloro-N-methylpyrimidin-4-amine 4
Fig. S-30: LC-MS-ELSD of N-allyl-6-chloro-N-methyl-5-(((methylamino)(methyl))pyrimidin-4-amine 5
Fig. S-31: $^1$H Spectra of N-allyl-6-chloro-N-methyl-5-((methylamino)methyl) pyrimidin-4-amine 5
Fig. S-32: $^{13}$C Spectra of N-allyl-6-chloro-N-methyl-5-((methylamino)methyl) pyrimidin-4-amine 5
Fig. S-33: LC-MS-ELSD of N-allyl-6-chloro-5-((isopropylamino)methyl)-N-methyl pyrimidin-4-amine 6
Fig. S-34: $^1$H Spectra of N-allyl-6-chloro-5-((isopropylamino)methyl)-N-methyl pyrimidin-4-amine 6
Fig. S-35: $^{13}$C Spectra of N-allyl-6-chloro-5-((isopropylamino)methyl)-N-methyl pyrimidin-4-amine 6
Fig. S-36: LC-MS-ELSD of N-allyl-6-chloro-N-methyl-5-((phenylamino)methyl) pyrimidin-4-amine 7
Fig. S-37: $^1$H Spectra of N-allyl-6-chloro-N-methyl-5-((phenylamino)methyl) pyrimidin-4-amine 7
Fig. S-38: $^{13}$C Spectra of N-allyl-6-chloro-N-methyl-5-((phenylamino)methyl) pyrimidin-4-amine 7
Fig. S-39: LC-MS-ELSD of (E)-N-(but-2-en-1-yl)-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8
Fig. S-40: $^1$H Spectra of (E)-N-(but-2-en-1-yl)-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8
Fig. S-41: $^{13}$C Spectra of (E)-N-(but-2-en-1-yl)-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8
Fig. S-42: LC-MS-ELSD of 6-chloro-N-cinnamyl-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9
Fig. S-43: $^1$H Spectra of 6-chloro-N-cinnamyl-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9
Fig. S-44: $^{13}$C Spectra of 6-chloro-N-cinnamyl-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9
Fig. S-45: LC-MS-ELSD of (E)-methyl-2-(((6-chloro-5-((methylamino)methyl)
pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10

Fig. S-46: $^1$H Spectra of (E)-methyl-2-(((6-chloro-5-((methylamino)methyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10

Fig. S-47: $^{13}$C Spectra of (E)-methyl-2-(((6-chloro-5-((methylamino)methyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10

Fig. S-48: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11a

Fig. S-49: $^1$H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11a

Fig. S-50: $^{13}$C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11a

Fig. S-51: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11b

Fig. S-52: $^1$H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11b

Fig. S-53: $^{13}$C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11b

Fig. S-54: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11c

Fig. S-55: $^1$H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11c

Fig. S-56: $^{13}$C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11c

Fig. S-57: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(3-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine

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Fig. S-58: $^1$H Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-2-(3-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-59: $^{13}$C Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-2-(3-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-60: LC-MS-ELSD of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-61: $^1$H Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-62: $^{13}$C Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-63: LC-MS-ELSD of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-64: $^1$H Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-65: $^{13}$C Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-66: LC-MS-ELSD of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(m-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-67: $^1$H Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(m-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-68: $^{13}$C Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(m-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-69: LC-MS-ELSD of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(o-tolyl)-2,3,3a,4,5,9b-hexahydro-$1^H$-pyrrolo[2',3':4,5]pyrido[2,3-$d$]pyrimidine

Fig. S-70: $^1$H Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-(o-tolyl)
-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11h

Fig. S-71: $^{13}$C Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-5-methyl-2-(o-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11h

Fig. S-72: LC-MS-ELSD of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11i

Fig. S-73: $^1$H Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11i

Fig. S-74: $^{13}$C Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11i

Fig. S-75: LC-MS-ELSD of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11j

Fig. S-76: $^1$H Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11j

Fig. S-77: $^{13}$C Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11j

Fig. S-78: LC-MS-ELSD of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11k

Fig. S-79: $^1$H Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11k

Fig. S-80: $^{13}$C Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11k

Fig. S-81: LC-MS-ELSD of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11l

Fig. S-82: $^1$H Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11l

Fig. S-83: $^{13}$C Spectra of $(2R^*,3aR^*,9bR^*)$-1-butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11l
Fig. S-84: LC-MS-ELSD of *(2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-((E)-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11m

Fig. S-85: ¹H Spectra of *(2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-((E)-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11m

Fig. S-86: ¹³C Spectra of *(2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-((E)-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11m

Fig. S-87: LC-MS-ELSD of *(2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11n

Fig. S-88: ¹H Spectra of *(2R*,3aR*,9bR*)-1-butyl-9-chloro-2-cyclohexyl-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11n

Fig. S-89: ¹³C Spectra of *(2R*,3aR*,9bR*)-1-butyl-9-chloro-2-cyclohexyl-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11n

Fig. S-90: LC-MS-ELSD of *(2R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q

Fig. S-91: ¹H Spectra of *(2R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q

Fig. S-92: ¹³C Spectra of *(2R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q

Fig. S-93: LC-MS-ELSD of *(2R*,3aR*,9bR*)-9-chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r

Fig. S-94: ¹H Spectra of *(2R*,3aR*,9bR*)-9-chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r

Fig. S-95: ¹³C Spectra of *(2R*,3aR*,9bR*)-9-chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r

Fig. S-96: LC-MS-ELSD of *(2R*,3aR*,9bR*)-9-chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s
Fig. S-97: $^1$H Spectra of (2$^{R*}$,3$^{aR*}$,9b$^{R*}$)-9-chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s

Fig. S-98: $^{13}$C Spectra of (2$^{R*}$,3$^{aR*}$,9b$^{R*}$)-9-chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s

Fig. S-99: LC-MS-ELSD of (2$^{R*}$,3$^{R*}$,3a$^{R*}$,9b$^{R*}$)-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u

Fig. S-100: $^1$H Spectra of (2$^{R*}$,3$^{R*}$,3a$^{R*}$,9b$^{R*}$)-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u

Fig. S-101: $^{13}$C Spectra of (2$^{R*}$,3$^{R*}$,3a$^{R*}$,9b$^{R*}$)-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u

Fig. S-102: LC-MS-ELSD of (2$^{R*}$,3$^{R*}$,3a$^{S*}$,9b$^{R*}$)-methyl-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine-3$^{a}$-carboxylate 11v

Fig. S-103: $^1$H Spectra of (2$^{R*}$,3$^{R*}$,3a$^{S*}$,9b$^{R*}$)-methyl-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine-3$^{a}$-carboxylate 11v

Fig. S-104: $^{13}$C Spectra of (2$^{R*}$,3$^{R*}$,3a$^{S*}$,9b$^{R*}$)-methyl-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine-3$^{a}$-carboxylate 11v
Fig. S-1: LC-MS-ELSD of 4-(allyl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2a
Fig. S-2: $^1$H Spectra of 4-(allyl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2a
Fig. S-3: LC-MS-ELSD of (E)-4-(but-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b
Fig. S-4: $^1$H Spectra of (E)-4-(but-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b

Fig. S-5: $^{13}$C Spectra of (E)-4-(but-2-en-1-yl(methyl)amino)-6-chloropyrimidine-5-carbaldehyde 2b
Fig. S-6: LC-MS-ELSD of 4-chloro-6-(cinnamyl(methyl)amino)pyrimidine-5-carbaldehyde 2c
Fig. S-7: $^1$H Spectra of 4-chloro-6-(cinnamyl(methyl)amino)pyrimidine -5-carbaldehyde 2c

Fig. S-8: $^{13}$C Spectra of 4-chloro-6-(cinnamyl(methyl)amino)pyrimidine -5-carbaldehyde 2c
Fig. S-9: LC-MS-ELSD of (E)-methyl-2-((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 2d
Fig. S-10: $^1$H Spectra of (E)-methyl-2-(((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 2d

Fig. S-11: $^{13}$C Spectra of (E)-methyl-2-(((6-chloro-5-formylpyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 2d
Fig. S-12: LC-MS-ELSD of (4-(allyl(methyl)amino)-6-chloropyrimidin-5-yl) methanol 3a
Fig. S-13: $^1$H Spectra of (4-(allyl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3a

Fig. S-14: $^{13}$C Spectra of (4-(allyl(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3a
Fig. S-15: LC-MS-ELSD of \((E)-(4-(\text{but-2-en-1-yl})(\text{methyl})\text{amino})-6\text{-chloropyrimidin-5-yl})\text{methanol} \; 3b
Fig. S-16: $^1$H Spectra of (E)-(4-(but-2-en-1-yl)(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3b

Fig. S-17: $^{13}$C Spectra of (E)-(4-(but-2-en-1-yl)(methyl)amino)-6-chloropyrimidin-5-yl)methanol 3b
Fig. S-18: LC-MS-ELSD of (E)-(4-chloro-6-(cinnamyl(methyl)amino)pyrimidin-5-yl) methanol 3c
Fig. S-19: $^1$H Spectra of (E)-(4-chloro-6-(cinnamyl(methyl)amino)pyrimidin-5-yl)methanol 3c

Fig. S-20: $^{13}$C Spectra of (E)-(4-chloro-6-(cinnamyl(methyl)amino)pyrimidin-5-yl)methanol 3c
Fig. S-21: LC-MS-ELSD of (E)-methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d
Fig. S-22: $^1$H Spectra of (E)-methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d

Fig. S-23: $^{13}$C Spectra of (E)-methyl-2-(((6-chloro-5-(hydroxymethyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 3d
Fig. S-24: LC-MS-ELSD of (E)-methyl-2-((methylamino)methyl)-3-phenylacrylate
Fig. S-25: $^1$H Spectra of (E)-methyl-2-(((methylamino)methyl)-3-phenylacrylate

Fig. S-26: $^{13}$C Spectra of (E)-methyl-2-(((methylamino)methyl)-3-phenylacrylate
Chemical Formula: $C_{13}H_{21}ClN_4$
Exact Mass: 268.1
Molecular Weight: 268.8

Fig. S-27: LC-MS-ELSD of $N$-allyl-5-((butylamino)methyl)-6-chloro-$N$-methyl pyrimidin-4-amine 4
Fig. S-28: $^1$H Spectra of $N$-allyl-5-((butylamino)methyl)-6-chloro-$N$-methyl pyrimidin-4-amine 4

Fig. S-29: $^{13}$C Spectra of $N$-allyl-5-((butylamino)methyl)-6-chloro-$N$-methyl pyrimidin-4-amine 4
Fig. S-30: LC-MS-ELSD of N-allyl-6-chloro-N-methyl-5-((methylamino)methyl) pyrimidin-4-amine 5
Fig. S-31: $^1$H Spectra of N-allyl-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 5

Fig. S-32: $^{13}$C Spectra of N-allyl-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 5
Fig. S-33: LC-MS-ELSD of N-allyl-6-chloro-5-((isopropylamino)methyl)-N-methyl pyrimidin-4-amine 6
Fig. S-34: $^1$H Spectra of N-allyl-6-chloro-5-((isopropylamino)methyl)-N-methyl pyrimidin-4-amine 6

Fig. S-35: $^{13}$C Spectra of N-allyl-6-chloro-5-((isopropylamino)methyl)-N-methyl pyrimidin-4-amine 6
Fig. S-36: LC-MS-ELSD of N-allyl-6-chloro-N-methyl-5-((phenylamino)methyl) pyrimidin-4-amine 7
Fig. S-37: $^1$H Spectra of N-allyl-6-chloro-N-methyl-5-((phenylamino)methyl) pyrimidin-4-amine 7

Fig. S-38: $^{13}$C Spectra of N-allyl-6-chloro-N-methyl-5-((phenylamino)methyl) pyrimidin-4-amine 7
Fig. S-39: LC-MS-ELSD of (E)-N-(but-2-en-1-yl)-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8
Fig. S-40: $^1$H Spectra of (E)-N-(but-2-en-1-yl)-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8

Fig. S-41: $^{13}$C Spectra of (E)-N-(but-2-en-1-yl)-6-chloro-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 8
Fig. S-42: LC-MS-ELSD of 6-chloro-N-cinnamyl-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9
Fig. S-43: $^1$H Spectra of 6-chloro-N-cinnamyl-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9

Fig. S-44: $^{13}$C Spectra of 6-chloro-N-cinnamyl-N-methyl-5-((methylamino)methyl)pyrimidin-4-amine 9
Fig. S-45: LC-MS-ELSD of (E)-methyl-2-(((6-chloro-5-((methylamino)methyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10
Fig. S-46: $^1$H Spectra of (E)-methyl-2-(((6-chloro-5-((methylamino)methyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10

Fig. S-47: $^{13}$C Spectra of (E)-methyl-2-(((6-chloro-5-((methylamino)methyl)pyrimidin-4-yl)(methyl)amino)methyl)-3-phenylacrylate 10
Fig. S-48: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrindo[2,3-d]pyrimidine 11a
Fig. S-49: $^1$H Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-phenyl-
-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11a

Fig. S-50: $^{13}$C Spectra of ($2R^*,3aR^*,9bR^*$)-1-butyl-9-chloro-5-methyl-2-phenyl-
-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11a
Fig. S-51: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11b
Fig. S-52: $^1$H Spectra of (2$^R$,3a$^R$,9b$^R$)-1-butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11b

Fig. S-53: $^{13}$C Spectra of (2$^R$,3a$^R$,9b$^R$)-1-butyl-9-chloro-5-methyl-2-(4-nitrophenyl)-2,3,3a,4,5,9b-hexahydro-1$^H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11b
Fig. S-54: LC-MS-ELSD of \((2R^*,3aR^*,9bR^*)-1\text{-butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11c}
Fig. S-55: $^1$H Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11c

Fig. S-56: $^{13}$C Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-2-(4-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11c
Fig. S-57: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(3-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11d
Fig. S-58: $^1$H Spectra of (2$R^*$,3$aR^*$,9$bR^*$)-1-butyl-9-chloro-2-(3-chloro phenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11d

Fig. S-59: $^{13}$C Spectra of (2$R^*$,3$aR^*$,9$bR^*$)-1-butyl-9-chloro-2-(3-chloro phenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11d
Fig. S-60: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11e
Fig. S-61: $^1$H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2′,3′:4,5]pyrido[2,3-d]pyrimidine 11e

Fig. S-62: $^{13}$C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(2-chlorophenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2′,3′:4,5]pyrido[2,3-d]pyrimidine 11e
Fig. S-63: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11f
Fig. S-64: $^1$H Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-$^1$H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11f

Fig. S-65: $^{13}$C Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-5-methyl-2-(p-tolyl)-2,3,3a,4,5,9b-hexahydro-$^1$H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11f
Fig. S-66: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(m-tolyl) -2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11g
Fig. S-67: $^1$H Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-5-methyl-2-(m-tolyl)-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11g

Fig. S-68: $^{13}$C Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-5-methyl-2-(m-tolyl)-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11g
Fig. S-69: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-(o-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11h
Fig. S-70: $^1$H Spectra of (2R*, 3aR*, 9bR*)-1-butyl-9-chloro-5-methyl-2-(o-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11h

Fig. S-71: $^{13}$C Spectra of (2R*, 3aR*, 9bR*)-1-butyl-9-chloro-5-methyl-2-(o-tolyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11h
Fig. S-72: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11i
Fig. S-73: ^1^H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11i

Fig. S-74: ^13^C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(4-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11i
Fig. S-75: LC-MS-ELSD of \((2R^*,3aR^*,9bR^*)\)-1-butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11j
Fig. S-76: $^1$H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11j

Fig. S-77: $^{13}$C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(2-methoxyphenyl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11j
Fig. S-78: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11k
Fig. S-79: $^1$H Spectra of (2$R^*$,3$aR^*$,9$bR^*$)-1-butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11k

Fig. S-80: $^{13}$C Spectra of (2$R^*$,3$aR^*$,9$bR^*$)-1-butyl-9-chloro-2-(furan-2-yl)-5-methyl-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11k
Fig. S-81: LC-MS-ELSD of \((2R*,3aR*,9bR*)-1\)-butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3';4,5]pyrido[2,3-d]pyrimidine \(\text{11l}\)
Fig. S-82: $^1$H Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11l

Fig. S-83: $^{13}$C Spectra of (2$R^*$,3a$R^*$,9b$R^*$)-1-butyl-9-chloro-5-methyl-2-(thiophen-2-yl)-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11l
Fig. S-84: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-5-methyl-2-((E)-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2′,3′:4,5]pyrido[2,3-d]pyrimidine 11m
Fig. S-85: \(^1\)H Spectra of (2R*,3aR*,9bR*)-1-buty1-9-chloro-5-methyl-2-((E)-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11m

Fig. S-86: \(^{13}\)C Spectra of (2R*,3aR*,9bR*)-1-buty1-9-chloro-5-methyl-2-((E)-styryl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11m
Fig. S-87: LC-MS-ELSD of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-cyclohexyl-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3'-4,5]pyrido[2,3-d]pyrimidine

11p
Fig. S-88: ^1^H Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-cyclohexyl-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine

Fig. S-89: ^1^C Spectra of (2R*,3aR*,9bR*)-1-butyl-9-chloro-2-cyclohexyl-5-methyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine
Fig. S-90: LC-MS-ELSD of (2R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q
Fig. S-91: $^1$H Spectra of (2R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q

Fig. S-92: $^{13}$C Spectra of (2R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11q
Chemical Formula: $C_{19}H_{23}ClN_4$

Exact Mass: 342.2

Molecular Weight: 342.9

**Fig. S-93:** LC-MS-ELSD of (2R*,3aR*,9bR*)-9-chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r
Fig. S-94: $^1$H Spectra of (2$R^*$,3$aR^*$,9$bR^*$)-9-chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r

Fig. S-95: $^{13}$C Spectra of (2$R^*$,3$aR^*$,9$bR^*$)-9-chloro-1-isopropyl-5-methyl-2-phenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11r
**Chemical Formula:** $C_{22}H_{21}ClN_4$

**Exact Mass:** 376.1

**Molecular Weight:** 376.9

**11s**

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**Fig. S-96:** LC-MS-ELSD of $(2R^*,3aR^*,9bR^*)$-9-chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s
Fig. S-97: $^1$H Spectra of (2R*,3aR*,9bR*)-9-chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s

Fig. S-98: $^{13}$C Spectra of (2R*,3aR*,9bR*)-9-chloro-5-methyl-1,2-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11s
Fig. S-99: LC-MS-ELSD of (2R*,3R*,3aR*,9bR*)-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u
Fig. S-100: $^1$H Spectra of (2R*, 3R*, 3aR*, 9bR*)-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u

Fig. S-101: $^{13}$C Spectra of (2R*, 3R*, 3aR*, 9bR*)-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine 11u
Fig. S-102: LC-MS-ELSD of (2R*,3R*,3aS*,9bR*)-methyl-9-chloro-1,5-dimethyl-2,3-diphenyl-2,3a,4,5,9b-hexahydro-1H-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine-3a-carboxylate 11v
Fig. S-103: $^1$H Spectra of (2$R^*$,3$R^*$,3a$S^*$,9b$R^*$)-methyl-9-chloro-1,5-dimethyl
-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine
3a-carboxylate 11v

Fig. S-104: $^{13}$C Spectra of (2$R^*$,3$R^*$,3a$S^*$,9b$R^*$)-methyl-9-chloro-1,5-dimethyl
-2,3-diphenyl-2,3,3a,4,5,9b-hexahydro-1$H$-pyrrolo[2',3':4,5]pyrido[2,3-d]pyrimidine
3a-carboxylate 11v