

**Supporting Information**  
**for**  
**The first example of the Fischer–Hepp type rearrangement**  
**in pyrimidines**

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**Detailed data of all new materials, photos of rearrangement process, copies of NMR spectra of final compounds 6 and 8.**

Data for compounds **1a,b** [1], **1c** [2], **2a,b** [3], **2c** [4], **2d** [4], **4aa** [3], **4ba** [3], **4bb** [3], **4bc** [4], **4bd** [4], **5aa** [4], **5ba** [4], **5bb** [4], **5bc** [4], **5bd** [4] have been published previously.

***N*-Benzyl-6-chloro-2-methylpyrimidin-4-amine (1d)**: yellowish wax; yield 94%. IR (KBr):  $\nu_{\max} = 3324$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.51$  (3H, s,  $\text{CH}_3$ ), 4.45 – 4.60 (2H, m,  $\text{NHCH}_2\text{Ph}$ ), 5.42 (1H, br. s, NH), 6.21 (1H, s, C(5)-H), 7.26 – 7.50 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (75 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 26.02$  ( $\text{CH}_3$ ), 45.81 ( $\text{NHCH}_2\text{Ph}$ ), 98.84 (C-5), 127.58, 128.09, 129.16, 131.03 (Ar-C), 160.06, 163.68 (C-4 and C-6), 168.57 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{Na}^+$ , found 256.0620.  $\text{C}_{12}\text{H}_{12}^{35}\text{ClN}_3\text{Na}$  requires 256.0617.

***N*-Benzyl-6-chloro-2-methylthiopyrimidin-4-amine (1e)**: white solid; yield 96%, mp 72–74 °C. IR (KBr):  $\nu_{\max} = 3253$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.48$  (3H, s,  $\text{SCH}_3$ ), 4.56 (2H, br. s,  $\text{NHCH}_2\text{Ph}$ ), 5.77 (1H, br. s, NH), 6.07 (1H, s, C(5)-H), 7.29 – 7.38 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 14.14$  ( $\text{SCH}_3$ ), 45.27 ( $\text{NHCH}_2\text{Bn}$ ), 98.58 (broad, C-5), 127.25, 127.56, 128.67, 137.42 (Ar-C), 158.79, 162.54 (C-4 and C-6), 172.08 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{Na}^+$ , found 288.0334.  $\text{C}_{12}\text{H}_{12}^{35}\text{ClN}_3\text{NaS}$  requires 288,0338.

***6*-Chloro-*N*-(4-methoxybenzyl)-2-methylthiopyrimidin-4-amine (1f)**: white solid; yield 96%, mp 85–87 °C (decomp). IR (KBr):  $\nu_{\max} = 3252$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.48$  (3H, s,  $\text{SCH}_3$ ), 3.80 (3H, s,  $\text{OCH}_3$ ), 4.44 (2H, br. s,  $\text{NHCH}_2\text{Ar}$ ), 4.98 (1H, br. s, NH), 6.03 (1H, s, C(5)-H), 6.87 (2H, d,  $J = 9.0$  Hz, ArH), 7.21 (2H, d,  $J = 9.0$  Hz, ArH) ppm.  $^{13}\text{C}$  NMR (75 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 14.05$  ( $\text{SCH}_3$ ), 44.96 ( $\text{NHCH}_2\text{Ar}$ ), 55.27 ( $\text{OCH}_3$ ), 97.71 (broad, C-5), 114.18, 128.78, 137.42, 139.00 (Ar-C), 159.16, 161.54 (C-4 and C-6), 171.92 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{Na}^+$ , found 318.0448.  $\text{C}_{13}\text{H}_{14}^{35}\text{ClN}_3\text{NaOS}$  requires 318.0444.

**6-Chloro-N-(4-methoxyphenethyl)-2-methylthiopyrimidin-4-amine (1g):** white solid; yield 79%, mp 89–91 °C. IR (KBr):  $\nu_{\max} = 3250$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.50$  (3H, s,  $\text{SCH}_3$ ), 2.84 (3H, t,  $J = 6.0$  Hz,  $\text{CH}_2\text{Ar}$ ), 3.55 (2H, br. s,  $\text{NHCH}_2$ ), 3.79 (3H, s,  $\text{OCH}_3$ ), 5.28 (1H, br. s, NH), 6.00 (1H, s, C(5)-H), 6.85 (2H, d,  $J = 9.0$  Hz, ArH), 7.11 (2H, d,  $J = 9.0$  Hz, ArH) ppm.  $^{13}\text{C}$  NMR (75 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 14.07$  ( $\text{SCH}_3$ ), 34.36 ( $\text{CH}_2\text{Ar}$ ), 45.78 ( $\text{NHCH}_2$ ), 55.26 ( $\text{OCH}_3$ ), 98.44 (broad, C-5), 114.16, 129.66, 137.41, 139.05 (Ar-C), 158.63, 162.30 (C-4 and C-6), 172.00 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{Na}^+$ , found 332.0609.  $\text{C}_{14}\text{H}_{16}^{35}\text{ClN}_3\text{NaOS}$  requires 332.0600.

**N-Butyl-6-chloro-2-methylthiopyrimidin-4-amine (1h):** white solid; yield 99%, mp 63–64 °C (petroleum). IR (KBr):  $\nu_{\max} = 3255$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 0.95$  (3H, t,  $J = 7.6$  Hz,  $\text{CH}_3$ ), 1.35 – 1.44 (2H, m,  $\text{CH}_2$ ), 1.55 – 1.62 (2H, m,  $\text{CH}_2$ ), 2.49 (3H, s,  $\text{SCH}_3$ ), 3.29 (2H, br. s,  $\text{NHCH}_2$ ), 5.28 (1H, br. s, NH), 6.04 (1H, s, C(5)-H) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 13.63$  ( $\text{CH}_3$ ), 13.95 ( $\text{SCH}_3$ ), 19.92 ( $\text{CH}_2$ ), 31.10 ( $\text{CH}_2$ ), 41.20 ( $\text{NHCH}_2$ ), 99.89 (broad, C-5), 156.68, 162.62 (C-4 and C-6), 171.91 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{Na}^+$ , found 254.0487.  $\text{C}_9\text{H}_{14}^{35}\text{ClN}_3\text{NaS}$  requires 254.0489.

**6-Chloro-2-methylthio-N-phenylpyrimidin-4-amine (1i):** yellow solid; yield 88%, mp 97–98 °C (2-propanol). IR (KBr):  $\nu_{\max} = 3276$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.51$  (3H, s,  $\text{SCH}_3$ ), 6.37 (1H, s, C(5)-H), 7.04 – 7.24 (2H, m, ArH), 7.28 – 7.42 (4H, m and br. s, ArH, NH) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 14.22$  ( $\text{SCH}_3$ ), 98.37 (broad, C-5), 122.83, 125.52, 129.54, 137.37 (Ar-C), 159.87, 161.42 (C-4 and C-6), 172.79 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{Na}^+$ , found 274.0188.  $\text{C}_{11}\text{H}_{10}^{35}\text{ClN}_3\text{NaS}$  requires 274.0182.

**N-(4-(Benzylamino)-6-chloropyrimidin-2-yl)acetamide (1j):** white solid; yield 97%, mp 152–154 °C. IR (KBr):  $\nu_{\max} = 3341$ , 3250 (NH), 1676 (CO)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz, DMSO, 25 °C):  $\delta = 2.19$  (3H, s,  $\text{COCH}_3$ ), 4.53 (2H, br. s,  $\text{NHCH}_2\text{Ph}$ ), 6.22 (1H, s, C(5)-H), 7.20 – 7.29 (5H, m, ArH), 7.99 (1H, t,  $J = 6.0$  Hz,  $\text{NHCH}_2$ ), 9.85 (1H, br. s, NH), ppm.  $^{13}\text{C}$  NMR (75 Hz, DMSO, 25 °C):  $\delta = 24.96$  ( $\text{CH}_3$ ), 43.91 ( $\text{NHCH}_2\text{Ph}$ ), 98.57 (C-5), 126.88, 127.33, 128.24, 138.84 (Ar-C), 157.02, 157.41, 163.71 (C-4, C-6 and C-2), 170.27 (CO) ppm. HRMS (ESI):  $\text{M}+\text{H}^+$ , found 277.0851.  $\text{C}_{13}\text{H}_{14}^{35}\text{ClN}_4\text{O}$  requires 277.0852.

**N-(4-(Butylamino)-6-chloropyrimidin-2-yl)acetamide (1k):** white solid; yield 81%, mp 118–119 °C. IR (KBr):  $\nu_{\max} = 3343$ , 3255 (NH), 1675 (CO)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 0.94$  (3H, t,  $J = 6.0$  Hz,  $\text{CH}_3$ ), 1.35 – 1.43 (2H, m,  $\text{CH}_2$ ), 1.56 – 1.66 (2H, m,  $\text{CH}_2$ ), 2.54 (3H, s,  $\text{COCH}_3$ ), 3.15 (2H, br. s,  $\text{NHCH}_2$ ), 6.05 (1H, s, C(5)-H), 7.53 (1H, br. s, NH), 9.68 (1H, br. s, NH) ppm.  $^{13}\text{C}$  NMR (75 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 13.69$  ( $\text{CH}_3$ ), 20.07 ( $\text{CH}_2$ ), 25.46 ( $\text{CH}_3\text{CO}$ ), 30.79 ( $\text{CH}_2$ ), 41.72 ( $\text{NHCH}_2$ ), 95.45 (C-5), 164.13, 164.27, 166.36 (C-4, C-6 and C-2), 173.96 (CO) ppm. HRMS (ESI):  $\text{M}+\text{H}^+$ , found 243.1007.  $\text{C}_{10}\text{H}_{16}^{35}\text{ClN}_4\text{O}$  requires 243.1012.

**N-Benzyl-6-chloro-2-morpholin-4-ylpyrimidin-4-amine (1l):** white solid; yield 85%; mp 154–156 °C. IR (KBr):  $\nu_{\max} = 3321$  (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 3.71$  – 3.76 (m, 8H,  $\text{N}(\text{CH}_2)_4\text{O}$ ), 4.53 (2H, s,  $\text{NHCH}_2\text{Ph}$ ), 5.08 (1H, br. s, NH), 5.75 (1H, s, C(5)-H), 7.30 – 7.39 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 44.30$  ( $\text{NCH}_2$ ), 45.41 ( $\text{NCH}_2$ ), 66.82 ( $\text{OCH}_2$ ), 92.13 (C-5), 127.52, 127.65, 128.81, 138.35 (Ar-C), 159.90, 161.10 (C-4 and C-6), 163.58 (C-2) ppm. HRMS (ESI):  $\text{M}+\text{H}^+$ , found 305.1168.  $\text{C}_{15}\text{H}_{18}\text{ClN}_4\text{O}$  requires 305.1164.

**N-Benzyl-6-chloro-2-methylthio-N-nitrosopyrimidin-4-amine (2e):** yellow solid; yield 99%, mp 89–90 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.58$  (3H, s,  $\text{SCH}_3$ ), 5.33 (2H, br. s,  $\text{NCH}_2\text{Ph}$ ), 7.19 – 7.36 (5H, m, ArH), 7.72 (1H, s, C(5)-H) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 14.46$  ( $\text{SCH}_3$ ), 43.57 ( $\text{NCH}_2\text{Ph}$ ), 102.54 (C-5), 127.90, 128.15, 128.67, 134.32 (Ar-

C), 161.57, 161.70 (C-4 and C-6), 173.61 (C-2) ppm. HRMS (ESI): M+H<sup>+</sup>, found 295.0422. C<sub>12</sub>H<sub>12</sub><sup>35</sup>ClN<sub>4</sub>OS requires 295.0420.

**6-Chloro-N-(4-methoxybenzyl)-2-methylthio-N-nitrosopyrimidin-4-amine (2f):** yellowish solid; yield 81%, mp 88–89 °C. <sup>1</sup>H NMR (300 MHz, DMSO, 25 °C): δ = 2.57 (3H, s, SCH<sub>3</sub>), 3.71 (3H, s, OCH<sub>3</sub>), 5.22 (2H, s, NCH<sub>2</sub>Ar), 6.86 (2H, d, *J* = 9.0 Hz, ArH), 7.14 (2H, d, *J* = 9.0 Hz, ArH), 7.88 (1H, s, C(5)-H), ppm. <sup>13</sup>C NMR (75 Hz, DMSO, 25 °C): δ = 13.91 (SCH<sub>3</sub>), 43.24 (NCH<sub>2</sub>Ar), 55.04 (OCH<sub>3</sub>), 102.92 (C-5), 113.92, 126.40, 129.00 (2C) (Ar-C), 158.59, 160.71 (C-4 and C-6), 172.61 (C-2) ppm. HRMS (ESI): M+Na<sup>+</sup>, found 347.0348. C<sub>13</sub>H<sub>13</sub><sup>35</sup>ClN<sub>4</sub>NaO<sub>2</sub>S requires 347.0345.

**6-Chloro-N-(4-methoxyphenethyl)-2-methylthio-N-nitrosopyrimidin-4-amine (2g):** yellowish solid; yield 89%, mp 92–93 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.60 (3H, s, SCH<sub>3</sub>), 2.67–2.72 (3H, m, CH<sub>2</sub>Ar), 3.78 (3H, s, OCH<sub>3</sub>), 4.26–4.31 (2H, m, NCH<sub>2</sub>), 6.82 (2H, d, *J* = 9.0 Hz, ArH), 7.10 (2H, d, *J* = 9.0 Hz, ArH), 7.62 (1H, s, C(5)-H), ppm. <sup>13</sup>C NMR (75 Hz, CDCl<sub>3</sub>, 25 °C): δ = 14.38 (SCH<sub>3</sub>), 31.76 (CH<sub>2</sub>Ar), 41.84 (NCH<sub>2</sub>), 55.24 (OCH<sub>3</sub>), 102.24 (C-5), 114.00, 129.41, 129.68, 129.69 (Ar-C), 158.46, 161.49 (C-4 and C-6), 173.49 (C-2) ppm. HRMS (ESI): M+Na<sup>+</sup>, found 361.0506. C<sub>14</sub>H<sub>15</sub><sup>35</sup>ClN<sub>4</sub>NaO<sub>2</sub>S requires 361.0502.

**N-Butyl-6-chloro-2-methylthio-N-nitrosopyrimidin-4-amine (2h):** yellow powder; yield 96%, mp 45–46 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.89 (3H, t, *J* = 7.3 Hz, CH<sub>3</sub>), 1.21–1.30 (2H, m, CH<sub>2</sub>), 1.40–1.47 (2H, m, CH<sub>2</sub>), 2.56 (3H, s, SCH<sub>3</sub>), 4.08 (2H, t, *J* = 7.3 Hz, NCH<sub>2</sub>), 7.62 (1H, s, C(5)-H) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C): δ = 13.61 (CH<sub>3</sub>), 14.39 (SCH<sub>3</sub>), 20.23 (CH<sub>2</sub>), 28.64 (CH<sub>2</sub>), 40.35 (NHCH<sub>2</sub>), 102.31 (C-5), 161.50, 161.81 (C-4 and C-6), 173.52 (C-2) ppm. HRMS (ESI): M+Na<sup>+</sup>, found 283.0386. C<sub>9</sub>H<sub>13</sub><sup>35</sup>ClN<sub>4</sub>NaOS requires 283.0391.

**6-Chloro-2-methylthio-N-phenyl-N-nitrosopyrimidin-4-amine (2i):** yellow solid; yield 66%, mp 104–106 °C (2-propanol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.27 (3H, s, SCH<sub>3</sub>), 6.95–7.05 (2H, m, ArH), 7.49–7.58 (3H, m, ArH), 7.64 (1H, s, C(5)-H) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C): δ = 14.12 (SCH<sub>3</sub>), 102.37 (C-5), 128.18, 129.52, 130.05, 133.43 (Ar-C), 161.58, 162.14 (C-4 and C-6), 173.66 (C-2) ppm. HRMS (ESI): M+Na<sup>+</sup>, found 303.0087. C<sub>11</sub>H<sub>9</sub><sup>35</sup>ClN<sub>4</sub>NaOS requires 303.0083.

**N-(4-(Benzyl(nitroso)amino)-6-chloropyrimidin-2-yl)acetamide (2j):** white solid; yield 60%, mp 129–130 °C. IR (KBr): ν<sub>max</sub> = 3050 (NH), 1659 (CO) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO, 25 °C): δ = 2.50 (3H, s, COCH<sub>3</sub>), 5.32 (2H, s, NCH<sub>2</sub>Ph), 7.21–7.28 (5H, m, ArH), 7.75 (1H, s, C(5)-H), 8.30 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (75 Hz, DMSO, 25 °C): δ = 25.31 (CH<sub>3</sub>), 43.60 (NCH<sub>2</sub>Ph), 102.08 (C-5), 127.84, 127.88, 128.66, 133.91 (Ar-C), 156.49, 162.41, 163.02 (C-4, C-6 and C-2), 170.52 (CO) ppm. HRMS (ESI): M+H<sup>+</sup>, found 328.0579. C<sub>13</sub>H<sub>12</sub><sup>35</sup>ClN<sub>5</sub>O<sub>2</sub> requires 328.0577.

**N-(4-(Butyl(nitroso)amino)-6-chloropyrimidin-2-yl)acetamide (2k):** white solid; yield 77%, mp 111–113 °C. IR (KBr): ν<sub>max</sub> = 3062 (NH), 1651 (CO) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.94 (3H, t, *J* = 7.2 Hz, CH<sub>3</sub>), 1.24–1.37 (2H, m, CH<sub>2</sub>), 1.43–1.53 (2H, m, CH<sub>2</sub>), 2.59 (3H, s, COCH<sub>3</sub>), 4.10 (2H, t, *J* = 7.8 Hz, NCH<sub>2</sub>), 7.70 (1H, s, C(5)-H), 8.21 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (75 Hz, CDCl<sub>3</sub>, 25 °C): δ = 13.57 (CH<sub>3</sub>), 20.21 (CH<sub>2</sub>), 25.30 (CH<sub>3</sub>CO), 28.57 (CH<sub>2</sub>), 40.49 (NCH<sub>2</sub>), 101.84 (C-5), 156.58, 162.27, 163.28 (C-4, C-6 and C-2), 170.85 (CO) ppm. HRMS (ESI): M+Na<sup>+</sup>, found 294.0728. C<sub>10</sub>H<sub>14</sub><sup>35</sup>ClN<sub>5</sub>NaO<sub>2</sub> requires 294.0722.

**N-Benzyl-6-chloro-2-morpholin-4-yl-N-nitrosopyrimidin-4-amine (2l):** yellowish solid; yield 37%; mp 130–132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.73–3.78 (4H, m, N(CH<sub>2</sub>)<sub>2</sub>), 3.81–3.87 (4H, m, O(CH<sub>2</sub>)<sub>2</sub>), 5.28 (2H, s, NHCH<sub>2</sub>Ph), 7.16–7.20 (2H, s and m,

C(5)-H, ArH), 7.25 – 7.32 (4H, m, ArH) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 43.51 (NCH<sub>2</sub>), 44.40 (NCH<sub>2</sub>), 66.62 (OCH<sub>2</sub>), 96.03 (C-5), 127.68, 127.71, 128.62, 134.80 (Ar-C), 160.42, 162.34 (C-4 and C-6), 162.44 (C-2) ppm. HRMS (ESI):  $[\text{M} + \text{Na}]^+$ , found 356.0880.  $\text{C}_{15}\text{H}_{16}\text{ClN}_5\text{NaO}_2$  requires 356.0885.

***N*-Benzyl-6-chloro-2-morpholin-4-yl-5-nitrosopyrimidin-4-amine (3)**: blue solid; yield 35%; mp 139–141 °C (decomp.). IR (KBr):  $\nu_{\text{max}}$  = 3237 (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ , 25 °C):  $\delta$  = 3.70 – 3.73 (2H, m, NCH<sub>2</sub>), 3.75 – 3.78 (2H, m, NCH<sub>2</sub>), 3.95 – 3.98 (2H, m, OCH<sub>2</sub>), 4.02 – 4.05 (2H, m, OCH<sub>2</sub>), 4.73 – 4.75 (2H, m,  $\text{NHCH}_2\text{Ph}$ ), 7.16 – 7.20 (2H, m, C(5)-H, ArH), 7.26 – 7.40 (4H, m, ArH), 11.03 (1H, br. s, NH) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 43.30 (NCH<sub>2</sub>), 45.24 (NCH<sub>2</sub>), 66.03 (OCH<sub>2</sub>), 66.32 (OCH<sub>2</sub>), 127.31, 127.84, 128.53, 138.04 (Ar-C), 144.06 (C-5), 149.03, 157.80 (C-4 and C-6), 172.32 (C-2) ppm. HRMS (ES):  $[\text{M} + \text{Na}]^+$ , found 356.0889.  $\text{C}_{15}\text{H}_{16}\text{ClN}_5\text{NaO}_2$  requires 356.0885.

***N*-Benzyl-*N*-(6-diethylamino-2-methylpyrimidin-4-yl)nitrous amide (4db)**: yellowish wax; yield 69%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 1.19 (6H, t,  $J$  = 7.1 Hz,  $(\text{CH}_2\text{CH}_3)_2$ ), 2.53 (3H, s, CH<sub>3</sub>), 3.39 – 3.70 (4H, m,  $(\text{CH}_2\text{CH}_3)_2$ ), 5.38 (2H, s, NCH<sub>2</sub>), 6.82 (1H, s, C(5)-H), 7.17 – 7.34 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 12.0 (CH<sub>3</sub>), 26.35 (CH<sub>3</sub>), 42.34 (NCH<sub>2</sub>), 43.66 (NCH<sub>2</sub>), 85.67 (C-5), 127.38, 128.37, 128.60, 135.48 (Ar-C), 160.05, 162.20 (C-4 and C-6), 167.16 (C-2) ppm. HRMS (ES):  $\text{M} + \text{Na}^+$ , found 322.1639.  $\text{C}_{16}\text{H}_{21}\text{N}_5\text{NaO}$  requires 322.1644.

***N*-Benzyl-*N*-(2-methylthio-6-(piperidin-1-yl)pyrimidin-4-yl)nitrous amide (4ea)**: yellowish solid; yield 95%, mp 127–128 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 1.61 – 1.69 (4H, m, 2CH<sub>2</sub>), 1.69 – 1.77 (2H, m, CH<sub>2</sub>), 2.53 (3H, s, SCH<sub>3</sub>), 3.60 – 3.75 (4H, m,  $\text{N}(\text{CH}_2)_2$ ), 5.37 (2H, s, NCH<sub>2</sub>Ph), 6.86 (1H, s, C(5)-H), 7.21 – 7.32 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 14.24 (SCH<sub>3</sub>), 24.63 (CH<sub>2</sub>), 25.58 (CH<sub>2</sub>), 43.75 (NCH<sub>2</sub>), 45.47 (NCH<sub>2</sub>), 83.65 (C-5), 127.44, 128.35, 128.42, 135.27 (Ar-C), 160.08, 162.28 (C-4 and C-6), 171.03 (C-2) ppm. HRMS (ES):  $\text{M} + \text{Na}^+$ , found 366.1361.  $\text{C}_{17}\text{H}_{21}\text{N}_5\text{NaOS}$  requires 366.1359.

***N*-Benzyl-*N*-6-diethylamino-2-methylpyrimidin-4-amine (5db)**: white solid; yield 36%, mp 121–123 °C (hexane). IR (KBr):  $\nu_{\text{max}}$  = 3234 (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 1.23 (6H, t,  $J$  = 7.9 Hz,  $(\text{CH}_2\text{CH}_3)_2$ ), 2.57 (3H, s, CH<sub>3</sub>), 3.58 (4H, br. s,  $(\text{NCH}_2)_2$ ), 5.44 (2H, s, NCH<sub>2</sub>), 6.85 (1H, s, C(5)-H), 7.24 – 7.35 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (75 Hz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 13.08 (CH<sub>3</sub>), 26.30 (CH<sub>3</sub>), 42.05 (NCH<sub>2</sub>), 46.35 (NCH<sub>2</sub>), 80.06 (C-5), 127.42, 128.90, 138.88, 141.16 (Ar-C), 162.04, 163.17 (C-4 and C-6), 166.46 (C-2) ppm. HRMS (ES):  $\text{M} + \text{H}^+$ , found 271.1928.  $\text{C}_{16}\text{H}_{23}\text{N}_4$  requires 271.1923.

***N*-Benzyl-2-methylthio-6-(piperidin-1-yl)pyrimidin-4-amine (5ea)**: white solid; yield 96%, mp 134–136 °C (ethanol). IR (KBr):  $\nu_{\text{max}}$  = 3257 (NH)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO, 25 °C):  $\delta$  = 1.37 – 1.50 (4H, m, 2CH<sub>2</sub>), 1.51 – 1.61 (2H, m, CH<sub>2</sub>), 2.32 (3H, s, SCH<sub>3</sub>), 3.40 – 3.44 (4H, m,  $\text{N}(\text{CH}_2)_2$ ), 4.41 (2H, d,  $J$  = 5.4 Hz,  $\text{NHCH}_2\text{Ph}$ ), 5.36 (1H, s, C(5)-H), 7.16 – 7.35 (5H, m, ArH) ppm.  $^{13}\text{C}$  NMR (100 Hz, DMSO, 25 °C):  $\delta$  = 13.64 (SCH<sub>3</sub>), 21.68 (CH<sub>2</sub>), 25.41 (CH<sub>2</sub>), 44.19 (NCH<sub>2</sub>), 45.05 (NCH<sub>2</sub>), 78.01 (C-5), 127.08, 127.66, 128.67, 140.67 (Ar-C), 161.96, 163.36 (C-4 and C-6), 168.98 (C-2) ppm. HRMS (ES):  $\text{M} + \text{H}^+$ , found 315.1642.  $\text{C}_{17}\text{H}_{23}\text{N}_4\text{S}$  requires 315.1643.

***N*<sup>4</sup>-Benzyl-*N*<sup>6</sup>-cyclohexyl-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6ef)**: blue solid; yield 87%; mp 128–130 °C. IR (KBr):  $\nu_{\text{max}}$  = 3318 (NH)  $\text{cm}^{-1}$ . NMR spectra contain signals of two rotamers.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  = 1.27 – 1.47 (6H, m,  $(\text{CH}_2)_3$ ), 1.60 – 1.65, 1.75 – 1.82, 1.94 – 1.98 and 2.06 – 2.11 (4H, 4m,  $\text{CH}(\text{CH}_2)_2$ ), 2.54 (3H, s, SCH<sub>3</sub>), 2.06 – 2.11 (4H, 4m,  $\text{CH}(\text{CH}_2)_2$ ), 4.16 – 4.26 (1H, m,  $\text{CH}(\text{CH}_2)_2$ ), 4.73 (2H, d,  $J$  = 6 Hz, NCH<sub>2</sub>Bn), 4.85 (2H, d,  $J$  = 6 Hz, NCH<sub>2</sub>Bn), 7.28 – 7.40 (5H, m, ArH), 7.82 and 11.68 (1H, 2d,  $J$  = 8 Hz,  $\text{NHCH}$ ), 8.13 and 11.94 (1H, 2 t,  $J$  = 6 Hz,  $\text{NHCH}_2$ ) ppm.  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  = 14.60, 14.63 (SCH<sub>3</sub>), 24.30, 24.61, 25.34, 32.22, 32.71 ((CH<sub>2</sub>)<sub>3</sub>), 43.50, 44.82 (CH(CH<sub>2</sub>)<sub>2</sub>), 48.47, 49.76 (NCH<sub>2</sub>Bn), 127.59, 127.65, 127.70, 127.83, 128.65, 128.67, 126.84, 137.18, (Ar-C), 137.21, 137.32 (C-5), 145.28, 146.23, 160.14, 161.12 (C-4 and C-6), 180.86, 181.12 (C-2) ppm. HRMS (ES): M+Na<sup>+</sup>, found 346.1672. C<sub>18</sub>H<sub>23</sub>N<sub>5</sub>NaOS requires 346.1672.

**N<sup>4</sup>-Benzyl-N<sup>6</sup>-methyl-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6eg)**: blue solid; yield 97%; mp 152–154 °C. IR (KBr):  $\nu_{\max}$  = 3284 (NH) cm<sup>-1</sup>. NMR spectra contain signals of two rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.56 and 2.57 (3H, 2s, SCH<sub>3</sub>), 3.08 and 3.22 (3H, 2d,  $J$  = 5.2 Hz, NCH<sub>3</sub>), 4.76 and 4.87 (2H, 2d,  $J$  = 6 Hz, NCH<sub>2</sub>Bn), 7.28 – 7.41 (5H, m, ArH), 7.96 and 8.170 (1H, 2 br. s, NH), 11.50 and 11.83 (1H, 2 br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.79 (SCH<sub>3</sub>), 26.48, 27.98 (NCH<sub>3</sub>), 43.80, 45.05 (NCH<sub>2</sub>Bn), 127.82, 127.85, 127.95, 128.81, 128.83, 136.77 137.26, (Ar-C), 137.32, 137.39 (C-5), 146.28, 147.30, 160.96, 161.58 (C-4 and C-6), 181.45, 181.59 (C-2) ppm. HRMS (ES): M+Na<sup>+</sup>, found 312.0893. C<sub>13</sub>H<sub>15</sub>N<sub>5</sub>NaOS requires 312.0890.

**N<sup>4</sup>-Benzyl-N<sup>6</sup>-cyclopropyl-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6eh)**: blue solid; yield 36%; mp 142–144 °C. IR (KBr):  $\nu_{\max}$  = 3320 (NH) cm<sup>-1</sup>. NMR spectra contain signals of two rotamers. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.70 – 0.76 and 0.90 – 0.99 (4H, 2m, CH(CH<sub>2</sub>)<sub>2</sub>), 2.58, 2.59 (3H, 2s, SCH<sub>3</sub>), 3.71 – 3.79 (1H, m, CH(CH<sub>2</sub>)<sub>2</sub>), 4.76 and 4.87 (2H, 2d,  $J$  = 6 Hz, NCH<sub>2</sub>Bn), 7.32 – 7.40 (5H, m, ArH), 7.84 and 8.11 (1H, 2 br. s, NH), 11.61 and 11.85 (1H, 2 br. s, NH) ppm. <sup>13</sup>C NMR (75 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.31, 7.52 (CH<sub>2</sub>)<sub>2</sub>, 15.05 (SCH<sub>3</sub>), 23.26, 24.47 (CH(CH<sub>2</sub>)<sub>2</sub>), 43.86, 45.20 (NCH<sub>2</sub>Bn), 127.96, 128.05, 128.18, 129.02, 129.04, 137.12, (Ar-C), 137.58, 137.74 (C-5), 146.21, 147.28, 161.32, 162.75 (C-4 and C-6), 181.48, 181.65 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 316.1239. C<sub>15</sub>H<sub>18</sub>N<sub>5</sub>OS requires 316.1227.

**N<sup>4</sup>-Benzyl-2-methylthio-5-nitroso-N<sup>6</sup>-phenethylpyrimidine-4,6-diamine (6ei)**: blue solid; yield 89%; mp 84–86 °C. IR (KBr):  $\nu_{\max}$  = 3326 (NH) cm<sup>-1</sup>. NMR spectra contains signals of two rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.57 (3H, s, SCH<sub>3</sub>), 2.93 and 3.03 (2H, 2t,  $J$  = 7.2 Hz, CH<sub>2</sub>), 3.79 and 3.95 (2H, 2m, NCH<sub>2</sub>), 4.75 and 4.86 (2H, 2d,  $J$  = 6 Hz and  $J$  = 5.6 Hz NCH<sub>2</sub>Bn), 7.24 – 7.39 (10H, m, ArH), 7.97 and 8.19 (1H, 2 br. s, NH), 11.64 and 11.88 (1H, 2 br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.69 (SCH<sub>3</sub>), 35.25, 35.54 (CH<sub>2</sub>), 41.27, 42.27 (NCH<sub>2</sub>), 43.51, 44.92 (NCH<sub>2</sub>Bn), 126.59, 126.54, 127.61, 127.66, 127.70, 127.82, 128.60, 128.63, 128.66, 128.71, 136.77, 137.27, 137.35 (Ar-C), 138.20, 138.25 (C-5), 146.04, 146.16, 160.99, 161.09 (C-4 and C-6), 180.97, 181.10 (C-2) ppm. HRMS (ES): M+Na<sup>+</sup>, found 402.1354. C<sub>20</sub>H<sub>21</sub>N<sub>5</sub>NaOS requires 402.1359.

**N-(4-Methoxybenzyl)-2-methylthio-5-nitroso-6-(piperidin-1-yl)pyrimidin-4-amine (6fa)**: blue wax; yield 65%. IR (KBr):  $\nu_{\max}$  = 3321 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.76 (6H, br. s (CH<sub>2</sub>)<sub>3</sub>), 2.51 (3H, s, SCH<sub>3</sub>), 3.79 (3H, s, OCH<sub>3</sub>), 4.15 (4H, br. s, N(CH<sub>2</sub>)<sub>2</sub>), 4.65 (2H, d,  $J$  = 6 Hz, NHCH<sub>2</sub>), 6.86 (2H, d,  $J$  = 8.4 Hz, ArH), 7.24 (2H, d,  $J$  = 8.4 Hz, ArH), 12.25 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.46 (SCH<sub>3</sub>), 24.51 (CH<sub>2</sub>), 26.70 (CH<sub>2</sub>), 43.25 (NCH<sub>2</sub>Bn), 49.70 (broad, N(CH<sub>2</sub>)<sub>2</sub>), 55.14 (OCH<sub>3</sub>), 113.90, 129.03, 129.26, 141.23 (Ar-C), 147.38 (C-5), 158.88, 159.85 (C-4 and C-6), 176.99 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 374.1645. C<sub>18</sub>H<sub>24</sub>N<sub>5</sub>O<sub>2</sub>S requires 374.1638.

**N<sup>4</sup>-Isopropyl-N<sup>6</sup>-(4-methoxybenzyl)-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6fb)**: blue solid; yield 65%, mp 86–88 °C. IR (KBr):  $\nu_{\max}$  = 3322 (NH) cm<sup>-1</sup>. NMR spectra contain signals of two rotamers. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.28 and 1.35 (6H, 2d,  $J$  = 6.6 Hz, (CH<sub>3</sub>)<sub>2</sub>), 2.56 and 2.57 (3H, 2s, SCH<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 4.43 – 4.64 (1H, m, NHCH), 4.68 and 4.78 (2H, 2d,  $J$  = 6 Hz, NHCH<sub>2</sub>), 6.87 - 6.91 (2H, m, ArH), 7.24 and 7.32 (2H, 2d,  $J$  = 9 Hz, ArH), 7.76 and 8.11 (1H, 2br. s, NH), 11.50 and 11.80 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (75 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.14, 14.67 (SCH<sub>3</sub>), 22.29, 22.54 (CH<sub>3</sub>), 42.09,

43.14, 43.15, 44.44 (NCH, NCH<sub>2</sub>), 55.24 (OCH<sub>3</sub>), 114.10, 128.78, 129.18, 129.32, 136.86 (Ar-C), 145.45, 146.16 (C-5), 159.13, 159.18, 160.05, 160.77 (C-4 and C-6), 181.14, 181.72 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 348.1489. C<sub>16</sub>H<sub>22</sub>N<sub>5</sub>O<sub>2</sub>S requires 348.1483.

**N<sup>4</sup>-Benzyl-N<sup>6</sup>-(4-methoxybenzyl)-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6fc)**: blue solid; yield 66%; mp 113–114 °C. IR (KBr):  $\nu_{\max}$  = 3302 (NH) cm<sup>-1</sup>. NMR spectra contain signals of two rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.56 and 2.57 (3H, 2s, SCH<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 4.68, 4.75, 4.80 and 4.87 (4H, 4d, *J* = 5.6; 6; 5.6; 6 Hz, 2NHCH<sub>2</sub>), 6.88 - 6.91 (2H, m, ArH), 7.25 (1H, d, *J* = 8.8 Hz, ArH), 7.32 - 7.39 (6H, m, ArH), 8.10 and 8.16 (1H, 2t, *J* = 5.6 Hz, NH), 11.80 and 11.88 (1H, 2t, *J* = 6 Hz, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.73 (SCH<sub>3</sub>), 43.07, 43.56, 44.44, 44.90 (NCH<sub>2</sub>), 55.25 (OCH<sub>3</sub>), 114.11, 127.65, 127.73, 127.85, 128.70, 128.72, 128.83, 129.16, 129.27, 129.30, 136.81, 137.28 (Ar-C), 145.83, 146.01 (C-5), 159.12, 159.18, 160.93, 161.13 (C-4 and C-6), 181.13, 181.16 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 396.1489. C<sub>20</sub>H<sub>22</sub>N<sub>5</sub>O<sub>2</sub>S requires 396.1484.

**N-(4-Methoxyphenethyl)-2-methylthio-6-morpholino-5-nitrosopyrimidin-4-amine (6ga)**: blue solid; yield 80%; mp 109–110 °C (2-PrOH). IR (KBr):  $\nu_{\max}$  = 3109 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.51 (3H, s, SCH<sub>3</sub>), 2.86 (2H, t, *J* = 7.2 Hz, CH<sub>2</sub>), 3.71 - 3.77 (2H, m, CH<sub>2</sub>), 3.79 (3H, s, OCH<sub>3</sub>), 3.83 (4H, t, *J* = 4.5 Hz, N(CH<sub>2</sub>)<sub>2</sub>), 4.27 (4H, t, *J* = 4.5 Hz, O(CH<sub>2</sub>)<sub>2</sub>), 6.90 (2H, d, *J* = 8.5 Hz, ArH), 7.14 (2H, d, *J* = 8.5 Hz, ArH), 11.90 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (75 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.38 (SCH<sub>3</sub>), 34.03(CH<sub>2</sub>), 41.89 (CH<sub>2</sub>), 48.00 (broad, N(CH<sub>2</sub>)<sub>2</sub>), 54.97 (OCH<sub>3</sub>), 67.00 (O(CH<sub>2</sub>)<sub>2</sub>), 113.81, 129.40, 130.04, 140.50 (Ar-C), 147.39 (C-5), 158.11, 159.59 (C-4 and C-6), 177.68 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 390.1594. C<sub>18</sub>H<sub>24</sub>N<sub>5</sub>O<sub>3</sub>S requires 390.1596.

**N-Butyl-2-methylthio-5-nitroso-6-(piperidin-1-yl)pyrimidin-4-amine (6ha)**: blue solid; yield 96%; mp 54–56 °C. IR (KBr):  $\nu_{\max}$  = 3150 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.93 (3H, t, *J* = 7.3 Hz, CH<sub>3</sub>), 1.33 - 1.42 (2H, m, CH<sub>2</sub>), 1.55 - 1.62 (2H, m, CH<sub>2</sub>), 1.70 (6H, br. s (CH<sub>2</sub>)<sub>3</sub>), 2.48 (3H, s, SCH<sub>3</sub>), 3.47 - 3.52 (2H, m, NHCH<sub>2</sub>), 4.13 (4H, br. s, N(CH<sub>2</sub>)<sub>2</sub>), 12.05 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 13.77, 14.57 (SCH<sub>3</sub> and CH<sub>3</sub>) 20.21, 24.68, 26.84, 31.04 (CH<sub>2</sub>, CH), 39.77 (NCH<sub>2</sub>Bn), 50.31 (broad, N(CH<sub>2</sub>)<sub>2</sub>), 141.25 (C-5), 148.01, 160.01 (C-4 and C-6), 177.11 (C-2) ppm. HRMS (ES): M+Na<sup>+</sup>, found 332.1509. C<sub>14</sub>H<sub>23</sub>N<sub>5</sub>NaOS requires 332.1516.

**N-Butyl-2-methylthio-5-nitroso-6-morpholinopyrimidin-4-amine (6hb)**: blue solid; yield 82%; mp 60–62 °C. IR (KBr):  $\nu_{\max}$  = 3443 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.93 (3H, t, *J* = 7.2 Hz, CH<sub>3</sub>), 1.34 - 1.43 (2H, m, CH<sub>2</sub>), 1.55 - 1.63 (2H, m, CH<sub>2</sub>), 2.48 (3H, s, SCH<sub>3</sub>), 3.48 - 3.53 (2H, m, NHCH<sub>2</sub>), 3.81 - 3.83 (4H, m, N(CH<sub>2</sub>)<sub>2</sub>), 4.24 - 4.27 (4H, m, O(CH<sub>2</sub>)<sub>2</sub>), 12.00 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 13.73, 14.57 (SCH<sub>3</sub> and CH<sub>3</sub>) 20.19 (CH<sub>2</sub>), 31.00 (CH<sub>2</sub>), 39.82 (CH<sub>2</sub>), 49.44 (broad, N(CH<sub>2</sub>)<sub>2</sub>), 67.32 (O(CH<sub>2</sub>)<sub>2</sub>), 141.45 (C-5), 147.69, 160.19 (C-4 and C-6), 177.53 (C-2) ppm. HRMS (ES): M+Na<sup>+</sup>, found 334.1309. C<sub>13</sub>H<sub>21</sub>N<sub>5</sub>NaO<sub>2</sub>S requires 334.1308.

**N<sup>4</sup>-Butyl-N<sup>6</sup>,N<sup>6</sup>-diethyl-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6hc)**: blue wax; yield 90%. IR (KBr):  $\nu_{\max}$  = 3325 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.91 (3H, td, *J* = 7.3, 1.9 Hz, CH<sub>3</sub>), 1.28 (3H, br. t, CH<sub>3</sub>), 1.34 - 1.40 (2H, m, CH<sub>2</sub>), 1.53 - 1.61 (2H, m, CH<sub>2</sub>), 2.48 (3H, s, SCH<sub>3</sub>), 3.45 - 3.50 (2H, m, NHCH<sub>2</sub>), 3.82 - 3.87 (4H, m., N(CH<sub>2</sub>)<sub>2</sub>), 12.29 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 13.75, 14.41 (SCH<sub>3</sub> and CH<sub>3</sub>) 20.20 (CH<sub>3</sub>), 31.03, 39.64, (CH<sub>2</sub>), 46.07 and 47.76 (broad, N(CH<sub>2</sub>)<sub>2</sub>), 141.57 (C-5), 148.12, 159.49 (C-4 and C-6), 176.75 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 298.1700. C<sub>13</sub>H<sub>24</sub>N<sub>5</sub>OS requires 298.1696.

***N*<sup>4</sup>,*N*<sup>6</sup>-Dibutyl-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6hd)**: blue solid; yield 96%, mp 57–59 °C. IR (KBr):  $\nu_{\max}$  = 3330 (NH)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.89 – 0.96 (6H, m, 2CH<sub>3</sub>), 1.33 – 1.41 (4H, m, CH<sub>2</sub>), 1.52 – 1.57 and 1.62 – 1.68 (4H, 2m, CH<sub>2</sub>), 2.49 (3H, br. s, SCH<sub>3</sub>), 3.46 – 3.52 and 3.59 – 3.64 (4H, 2m, NHCH<sub>2</sub>), 7.84 (1H, br. s, NH), 11.67 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 13.70, 13.75, 14.65 (SCH<sub>3</sub> and 2CH<sub>3</sub>) 20.05, 20.13, 31.03, 31.39 (CH<sub>2</sub>), 39.38 and 40.72 (2NCH<sub>2</sub>), 137.34 (C-5), 146.54, 161.14 (C-4 and C-6), 180.89 (C-2) ppm. HRMS (ES): M+Na+, found 320.1514. C<sub>13</sub>H<sub>23</sub>N<sub>5</sub>NaOS requires 320.1516.

***N*<sup>4</sup>-Butyl-*N*<sup>6</sup>-cyclohexyl-2-methylthio-5-nitrosopyrimidine-4,6-diamine (6he)**: blue solid; yield 91%, mp 67–68 °C. IR (KBr):  $\nu_{\max}$  = 3239 (NH)  $\text{cm}^{-1}$ . NMR spectra contain signals of two rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.94 and 0.96 (3H, 2t, *J* = 7.2 Hz, CH<sub>3</sub>), 1.23 – 1.46 (7H, m, CH<sub>2</sub>), 1.55 – 1.68 (3H, m, CH<sub>2</sub>), 1.73 – 1.81 (2H, m, CH<sub>2</sub>), 1.92 – 1.95 and 2.05 – 2.09 (4H, 2m, CH<sub>2</sub>), 2.53 (3H, s, SCH<sub>3</sub>) 3.50 – 3.55 and 3.62 – 3.67 (2H, 2m, CH<sub>2</sub>), 4.14 – 4.26 (1H, m, NHCH), 7.76 and 7.84 (1H, d and t, *J* = 8 Hz; 4.8 Hz, NH), 11.71 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 13.60, 13.65, 14.55 (SCH<sub>3</sub> and 2CH<sub>3</sub>), 19.96, 20.04, 24.31, 24.62, 25.35, 25.37 (CH, CH<sub>2</sub>), 39.30, 40.62, 48.45 and 49.64 (NCH<sub>2</sub>, NHCH), 137.05, 137.07 (C-5), 145.43, 146.61, 160.11, 161.12 (C-4 and C-6), 180.84, 180.89 (C-2) ppm. HRMS (ES): M+Na+, found 346.1672. C<sub>15</sub>H<sub>25</sub>N<sub>5</sub>NaS requires 346.1672.

***N*<sup>4</sup>-Butyl-2-methylthio-5-nitroso-*N*<sup>6</sup>-phenethylpyrimidine-4,6-diamine (6hf)**: blue solid; yield 92%, mp 65–66 °C. IR (KBr):  $\nu_{\max}$  = 3321 (NH)  $\text{cm}^{-1}$ . NMR spectra contain signals of two rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.94 – 1.00 (3H, m, CH<sub>3</sub>), 1.36 – 1.48 (2H, m, CH<sub>2</sub>), 1.57 – 1.50 (2H, m, CH<sub>2</sub>), 2.56 (3H, s, SCH<sub>3</sub>) 2.92 and 3.01 (2H, 2t, *J* = 7.2 Hz, CH<sub>2</sub>), 3.53 and 3.66 (2H, 2q, *J* = 6 and 6.4 Hz, NHCH<sub>2</sub>), 3.77 and 3.92 (2H, 2q, *J* = 6.4 Hz, NHCH<sub>2</sub>), 7.22 – 7.36 (5H, m, ArH), 7.88 and 7.94 (1H, 2t, *J* = 5.6 Hz, NH), 11.68 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 13.76, 13.81, 14.76 (SCH<sub>3</sub> and 2CH<sub>3</sub>), 20.09, 20.18, 31.07, 31.43, 35.40, 35.67 (CH<sub>2</sub>), 39.47, 40.79, 41.38 and 42.36 (2NCH<sub>2</sub>), 126.63, 126.69, 126.74, 128.72, 128.74, 128.76, 137.37, 137.40 (Ar-C), 138.38, 138.44 (C-5), 146.46, 146.57, 161.20, 161.22 (C-4 and C-6), 181.00 (C-2) ppm. HRMS (ES): MH+, found 346.1700. C<sub>17</sub>H<sub>24</sub>N<sub>5</sub>OS requires 346.1696.

***N*-Phenyl-2-methylthio-6-morpholino-5-nitrosopyrimidin-4-amine (6ia)**: blue solid; yield 42%; mp 122–124 °C. IR (KBr):  $\nu_{\max}$  = 3443 (NH)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.54 (3H, s, SCH<sub>3</sub>), 3.88 (4H, t, *J* = 4.4 Hz, N(CH<sub>2</sub>)<sub>2</sub>), 4.32 (4H, t, *J* = 4.4 Hz, O(CH<sub>2</sub>)<sub>2</sub>), 7.20 (1H, tt, *J* = 7.2, 1.2 Hz, ArH), 7.36 – 7.40 (2H, m, ArH), 7.76 (2H, dd, *J* = 7.2, 1.2 Hz, ArH), 14.10 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.72 (SCH<sub>3</sub>), 49.10 (broad, NCH<sub>2</sub>), 67.29 (OCH<sub>2</sub>), 123.80, 125.58, 128.79, 136.68 (Ar-C), 140.94 (C-5), 144.43 160.12 (C-4 and C-6), 178.42 (C-2) ppm. HRMS (ES): M+Na+, found 354.1000. C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>NaO<sub>2</sub>S requires 354.0995.

**2-Acetamido-*N*-benzyl--6-morpholino-5-nitrosopyrimidin-4-amine (6ja)**: blue solid; yield 78%; mp 148–150 °C. IR (KBr):  $\nu_{\max}$  = 3278 (NH), 1679 (C=O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.48 (3H, s, COCH<sub>3</sub>), 3.75 – 3.83 (4H, m, N(CH<sub>2</sub>)<sub>2</sub>), 4.17 – 4.23 (4H, m, O(CH<sub>2</sub>)<sub>2</sub>), 4.63 (2H, d, *J* = 6 Hz, CH<sub>2</sub>), 7.22 – 7.32 (5H, m, ArH), 8.12 (1H, br. s, NH), 12.31 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 25.89 (COCH<sub>3</sub>), 44.22 (NCH<sub>2</sub>Bn), 49.15 (broad, NCH<sub>2</sub>), 67.26 (OCH<sub>2</sub>), 127.44, 127.72, 128.80, 136.77 (Ar-C), 141.25 (C-5), 150.31, 158.02, 162.76 (C-4, C-6 and NHCOCH<sub>3</sub>), 172.00 (C-2) ppm. HRMS (ES): MH+, found 357.1673. C<sub>17</sub>H<sub>21</sub>N<sub>6</sub>O<sub>3</sub> requires 357.1670.

**2-Acetamido-*N*-benzyl--6-(piperidin-1-yl)-5-nitrosopyrimidin-4-amine (6jb)**: blue wax; yield 69%. IR (KBr):  $\nu_{\max}$  = 3206 (NH), 1689 (C=O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.74 (6H, br. s, (CH<sub>2</sub>)<sub>3</sub>), 2.50 (3H, s, COCH<sub>3</sub>), 4.09 (4H, br. s, N(CH<sub>2</sub>)<sub>2</sub>), 4.63 (2H, d, *J* = 5.6

Hz, CH<sub>2</sub>), 7.23 – 7.30 (5H, m, ArH), 8.22 (1H, br. s, NH), 12.37 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C): δ = 24.59, 25.84, 26.86 (COCH<sub>3</sub>, (CH<sub>2</sub>)<sub>3</sub>), 44.14 (NCH<sub>2</sub>Bn), 49.08 and 52.80 (broad, NCH<sub>2</sub>), 127.49, 127.60, 128.73, 137.00 (Ar-C), 140.98 (C-5), 150.53, 158.00, 162.34 (C-4, C-6 and NHCOCH<sub>3</sub>), 172.35 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 355.1877. C<sub>18</sub>H<sub>23</sub>N<sub>6</sub>O<sub>2</sub> requires 355.1877.

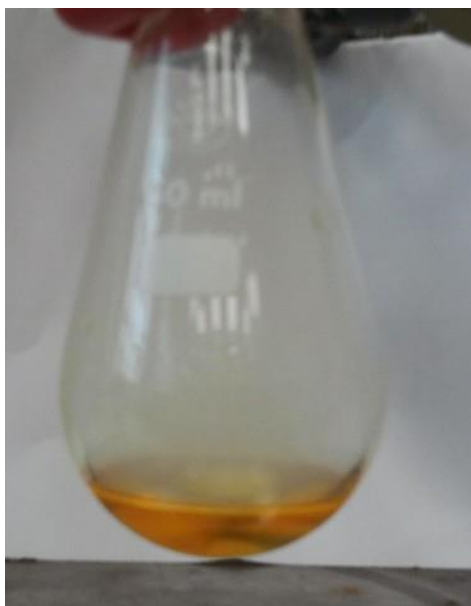
**2-Acetamido-N-butyl-6-morpholino-5-nitrosopyrimidin-4-amine (6ka)**: blue solid; yield 79%; mp 82–84 °C. IR (KBr): ν<sub>max</sub> = 3190 (NH), 1674 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.92 (3H, t, J = 7.2 Hz, CH<sub>3</sub>), 1.38 (2H, sext., J = 7.2 Hz, CH<sub>2</sub>), 1.58 (2H, pent., J = 7.2 Hz, CH<sub>2</sub>), 1.73 – 1.81 (2H, m, CH<sub>2</sub>), 2.55 (3H, s, COCH<sub>3</sub>), 3.40 – 3.45 (2H, m, NHCH<sub>2</sub>), 3.76 – 3.82 (4H, m, N(CH<sub>2</sub>)<sub>2</sub>), 4.22 (4H, br. s, O(CH<sub>2</sub>)<sub>2</sub>), 8.13 (1H, br. s, NH), 12.08 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>, 25 °C): δ = 13.72 (CH<sub>3</sub>), 20.22 (CH<sub>2</sub>), 25.85 (COCH<sub>3</sub>), 30.92, 40.19 (NCH<sub>2</sub>Bn), 49.54 (broad, NCH<sub>2</sub>), 67.25 (OCH<sub>2</sub>), 141.18 (C-5), 150.45, 157.98, 162.79 (C-4, C-6 and NHCOCH<sub>3</sub>), 172.09 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 323.1826. C<sub>14</sub>H<sub>23</sub>N<sub>6</sub>O<sub>3</sub> requires 323.1824.

**N-Benzyl-2,6-dimorpholino-5-nitrosopyrimidin-4-amine (6la)**: blue solid; yield 72%; mp 162–164 °C. IR (KBr): ν<sub>max</sub> = 3153, 3088 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.69 – 3.91 (12H, m, O(CH<sub>2</sub>)<sub>2</sub>, N(CH<sub>2</sub>)<sub>4</sub>), 4.21 (4H, s, O(CH<sub>2</sub>)<sub>2</sub>), 4.67 (2H, d, J = 5.6 Hz, PhCH<sub>2</sub>), 7.28 – 7.36 (5H, m, ArH), 12.14 (1H, br. s, NH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 44.0, 44.7, 49.3 (NCH<sub>2</sub>), 66.7, 67.2 (OCH<sub>2</sub>), 127.4, 127.6, 128.6, 137.7 (Ar-C), 139.8 (C-5), 159.5, 151.7 (C-4 and C-6), 162.3 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 385.1980. C<sub>19</sub>H<sub>25</sub>N<sub>6</sub>O<sub>3</sub> requires 385.1983.

**N-Benzyl-4-chloro-6-morpholino-N-nitrosopyrimidin-2-amine (7)**: white solid; yield 91%; mp 123–125 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.67 (4H, br. s, N(CH<sub>2</sub>)<sub>2</sub>), 3.76 – 3.79 (4H, m, O(CH<sub>2</sub>)<sub>2</sub>), 5.31 (2H, s, NCH<sub>2</sub>Ph), 6.45 (1H, s, C(5)-H), 7.20 – 7.34 (5H, m, ArH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 45.30, 44.58, (NCH<sub>2</sub>), 66.28 (OCH<sub>2</sub>), 98.89 (C-5), 127.45, 127.85, 128.47, 135.24 (Ar-C), 158.27, 160.97 (C-4 and C-6), 163.07 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 334.1071. C<sub>15</sub>H<sub>17</sub>ClN<sub>5</sub>O<sub>2</sub> requires 334.1071.

**2-Benzyl-4,6-dimorpholino-5-nitrosopyrimidin-2-amine (8)**: violet solid; yield 92%; mp 80–82 °C. IR (KBr): ν<sub>max</sub> = 3277 (NH) cm<sup>-1</sup>. NMR spectra contain signals of two tautomers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.11 (2H, br. s, N(CH<sub>2</sub>)<sub>2</sub>), 3.69 – 3.83 (10H, m, O(CH<sub>2</sub>)<sub>2</sub>, N(CH<sub>2</sub>)<sub>4</sub>), 4.00 – 4.09 (4H, m, O(CH<sub>2</sub>)<sub>2</sub>), 4.54 – 4.61 (2H, m, PhCH<sub>2</sub>), 6.18 (1H, br. s, NH), 7.26 – 7.28 (5H, m, ArH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 45.14, 45.53, 51.64, 51.62 (NCH<sub>2</sub>), 66.36, 67.11 (OCH<sub>2</sub>), 125.08, 127.31, 128.01, 128.43, 128.81, 138.14 (Ar-C), 140.42 (C-5), 150.74, 150.89, 160.48, 160.48 (C-4 and C-6), 165.26, 165.50 (C-2) ppm. HRMS (ES): MH<sup>+</sup>, found 385.1988. C<sub>19</sub>H<sub>25</sub>N<sub>6</sub>O<sub>3</sub> requires 385.1983.





**Figure S1a:** Typical one-pot nucleophilic substitution – rearrangement procedure. Stirring in 50% H<sub>2</sub>SO<sub>4</sub> step.



**Figure S1b:** Typical one-pot nucleophilic substitution – rearrangement procedure. Extraction of final product after the quenching of reaction mixture (Figure. S1a) with sodium bicarbonate.

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