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Selenium-catalyzed carbonylation of substituted nitrobenzenes with aminomethylpyrimidines as co-reagents to synthesize *N*-phenyl-*N*′-methylpyrimidylurea derivatives

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Abstract

A series of *N*-phenyl-*N*′-methylpyrimidylurea derivatives have been synthesized via selenium-catalyzed reductive carbonylation of substituted nitrobenzenes with aminopyrimidine derivatives as co-reagents and carbon monoxide as carbonyl reagent instead of phosgene in one-pot reaction.

Keywords: Reduction; Carbonylation; Methylpyrimidylurea; Selenium

1. Introduction

Pyrimidylurea derivatives used as immunosuppresants and anti-viral agents were found about 30 years ago [1,2]. These pyrimidylurea derivatives provide a method of treatment of autoimmune diseases and viral infection in mammals, excluding man.

Traditionally, pyrimidylureas have been obtained by reacting aminopyrimidines with isocyanates; however, such process has several disadvantages such as the use of toxic phosgene, the formation of large quantities of corrosive hydrogen chloride as a secondary product and furthermore, the presence of difficult-to-remove hydrolyzable chlorine compounds. Accordingly, there are numerous attempts to produce urea derivatives by using non-phosgene methods. Since aromatic amines are generally obtained by the reduction of aromatic nitro compounds, one of the promising approaches is the reductive carbonylation of aromatic nitro compounds with carbon monoxide in the presence of an appropriate catalyst to give urea derivatives in one-pot reaction. A few of effective catalyst systems have been reported for preparing urea derivatives via reductive carbonylation of aromatic nitro compounds. The VIII group transition metals, such as rhodium, ruthenium and palladium are commonly used as catalysts for this purpose [3].

Recently, non-transition elements usually and sulfur have also been found to catalyze the synthesis of urea derivatives. Franz et al. reported sulfur mediated reactions to give symmetrical ureas by oxidative carbonylation of amines [4,5], in these cases, the active species may be carbonyl sulfide (SCO) derived from carbon monoxide and sulfur. Sonoda et al. developed a series of selenium-catalyzed reactions [6,7]. Yang et al. synthesized a series of unsymmetrical

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phenylurea in one-pot reaction by first combining selenium-catalyzed oxidative carbonylation of amines with reductive carbonylation of aromatic nitro compounds under relatively mild conditions [8]. Xue et al. found that nitrobenzene reacted with aminopyridine to give phenylpyridylureas [9].

In this paper, selenium-catalyzed reductive carbonylation of substituted nitrobenzenes with aminomethylpyrimidine derivatives as co-reagents was studied, and a series of substituted *N*-phenyl-*N*′-methylpyrimidylurea derivatives were synthesized.

2. Experimental

Melting points were determined on a Taike X-4 apparatus (Beijing, China) and were uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (δ-units), and dimethylsulfoxide-d_6 G.R. as solvent. Solvent toluene was reagent grade and used without further purification. Elemental selenium (99.999%), carbon monoxide (99.9%), nitro compounds, aminopyrimidines and triethylamine were used as purchased.

Typical procedure for synthesis of *N*-phenyl-*N*′-3-(2,6-dimethyl-4-pyrimidyl)urea: Selenium (39.5 mg, 0.5 mmol), 4-amino-2,6-dimethylpyrimidine (1.30 g, 10 mmol), nitrobenzene (1.23 g, 10 mmol), triethylamine (2.02 g, 20 mmol) and toluene (10 ml) were placed in a 100ml stainless-steel autoclave. The reactor was sealed, carbon monoxide (3.0 MPa) was introduced to the system, and the reaction vessel was placed in the oil bath preheated to 150 °C, with stirring. After 4 h, the apparatus was cooled to room temperature, and the remaining carbon monoxide was evacuated. The reaction mixture was then evaporated, and the *N*-phenyl-*N*′-3-(2,6-dimethyl-4-pyrimidyl)urea was obtained in 82.6% (2.0 g) as a pure by a flash chromatography (silica gel, hexane: AcOEt = 10:3).

3. Results and discussion

3.1. Carbonylation of substituted nitrobenzenes with 4-amino-2,6-dimethylpyrimidine

Substituted nitrobenzenes reacted with 4-amino-2,6-dimethylpyrimidine in the presence of selenium and carbon monoxide according to following equation, and the results were summarized in Table 1 (Scheme 1).

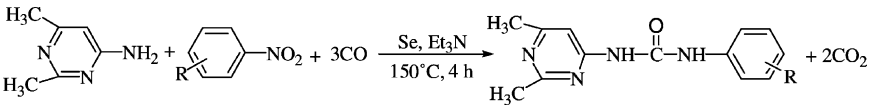
Conditions: substrate, 10 mmol; 4-amino-2,6-dimethylpyrimidine, 10 mmol; Se, 0.5 mmol; Et_3N, 20 mmol; CO, 3.0 MPa; PhMe, 10 ml; 150 °C; 4.0 h.

3.2. Carbonylation of substituted nitrobenzenes with 2-amino-4,6-dimethylpyrimidine

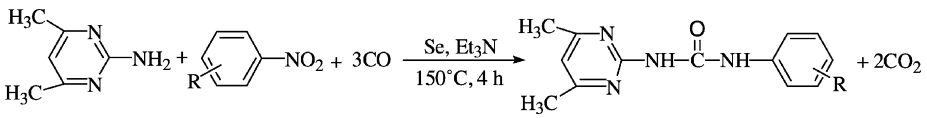
Substituted nitrobenzenes reacted with 2-amino-4,6-dimethylpyrimidine in the presence of selenium and carbon monoxide according to following equation, and the results were summarized in Table 2 (Scheme 2).

Conditions: substrate, 10 mmol; 2-amino-4,6-dimethylpyrimidine, 10 mmol; Se, 0.5 mmol; Et_3N, 20 mmol; CO, 3.0 MPa; PhMe, 10 ml; 150 °C; 4.0 h.

In the tables, it is found that the catalytic system is very efficient and the yields of products are moderate to good.



Scheme 1.



Scheme 2.

Table 1
Carbonylation of substituted nitrobenzenes with 4-amino-2,6-dimethylpyrimidine

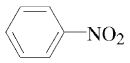
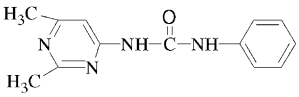
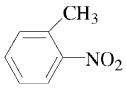
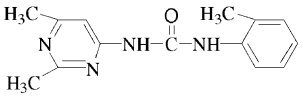
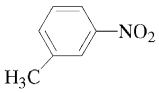
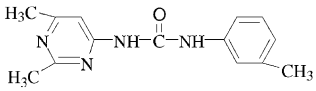
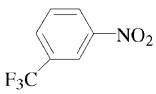
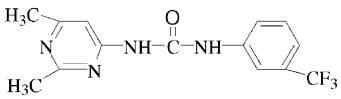
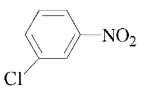
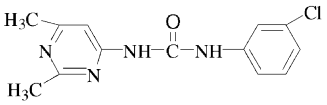
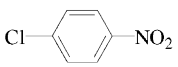
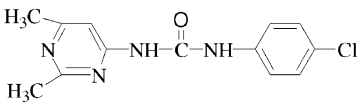
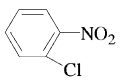
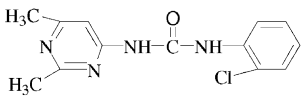
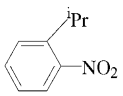
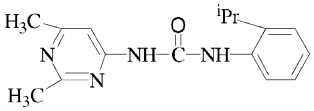
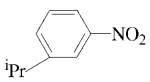
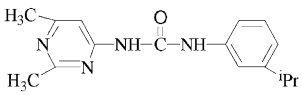
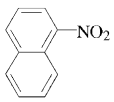
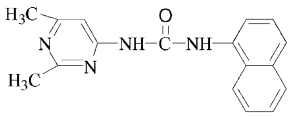
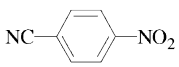
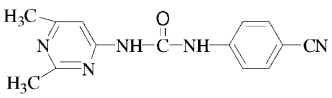
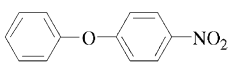
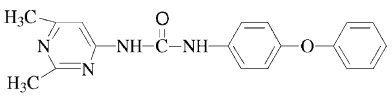
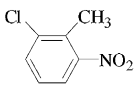
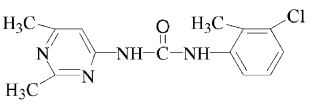
Entry	Substrates	Products	mp (°C) (lit.)	Yield (%)
1			229–231 (226) [10]	82.6
2			203–204 (205) [10]	70.3
3			194–196	55.4
4			229–230 (232) [10]	83.0
5			221–222 (225) [9]	83.0
6			222 (215) [10]	57.8
7			209–211	41.5
8			182–183	73.9
9			187–189	73.9
10			210–212	93.0
11			269–272	86.1
12			195–198	71.8
13			240	89.3

Table 1 (*Continued*)

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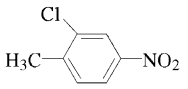
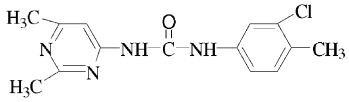
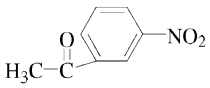
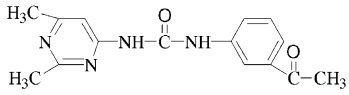
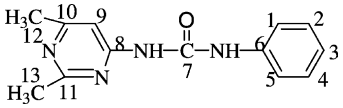
14			221–223	85.9
15			217–218	50.2

From a synthetic point of view, mild reaction conditions, good yields, one step to synthesize products and no use of toxic phosgene make the present reaction an useful method for the synthesis of *N*-phenyl-*N*′-methylpyrimidylurea derivatives. Further work related to the mechanism of the reaction is currently under way.

3.3. Analytical data

1-Phenyl-3-(2,6-dimethyl-4-pyrimidyl)urea: ^{1}H NMR: δ 2.58 (s, 3H, -C$\underline{H}_3$(13)); 2.39 (s, 3H, -C$\underline{H}_3$(12)); 7.02 (s, 1H, pyrimidyl 9); 7.50 (d, 2H, phenyl 1, 5); 7.30 (t, 2H, phenyl 2, 4); 7.04 (t, 1H, phenyl 3); 10.73 (s, 1H, pyrimidyl-N$\underline{H}$-); 9.67 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 25.2 (-$\underline{C}$H$_3$(13)); 23.6 (-$\underline{C}$H$_3$(12)); 118.6 (phenyl 1); 128.2 (phenyl 2); 122.4 (phenyl 3); 138.0 (phenyl 6); 151.5 (C=O 7); 158.1 (pyrimidyl 8); 103.5 (pyrimidyl 9); 164.9 (pyrimidyl 10); 166.2 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 242 (M^+, 100%). Microanalytical results (calc.): C: 64.14% (64.45%); H: 5.80% (5.82%); N: 22.92% (23.13%) (Scheme 3).

1-(3-Trifluoromethyl-phenyl)-3-(2,6 - dimethyl - 4 - pyrimidyl)urea: ^{1}H NMR: δ 2.52 (s, 3H, -C$\underline{H}_3$(13)); 2.37 (s, 3H, -C$\underline{H}_3$(12)); 7.26 (s, 1H, pyrimidyl 9); 7.60 (d, 1H, phenyl 1); 7.28 (t, 1H, phenyl 2); 7.38 (d, 1H, phenyl 3); 8.08 (s, 1H, phenyl 5); 10.43 (s, 1H, pyrimidyl-N$\underline{H}$-); 9.77 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 25.3 (-$\underline{C}$H$_3$(13)); 23.8 (-$\underline{C}$H$_3$(12)); 125.4 (phenyl 1); 129.8 (phenyl 2); 129.7 (phenyl 3); 130.1 (phenyl 4); 114.5 (phenyl 5); 139.3 (phenyl 6); 151.7 (C=O 7); 158.1 (pyrimidyl 8); 103.8 (pyrimidyl 9); 165.9 (pyrimidyl 10); 167.3 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 310 (M^+, 100%). Microanalytical results (calc.): C: 53.93% (54.19%); H: 4.09% (4.22%); N: 17.84% (18.06%).



Scheme 3.

1-(3-Chloro-2-methyl-phenyl)-3-(2,6 - dimethyl - 4-pyrimidyl)urea: ^{1}H NMR: δ 2.49 (s, 3H, -C$\underline{H}_3$(13)); 2.38 (s, 3H, -C$\underline{H}_3$(12)); 7.04 (s, 1H, pyrimidyl 9); 7.91 (d, 1H, phenyl 1); 7.20 (t, 1H, phenyl 2); 7.16 (d, 1H, phenyl 3); 2.34 (s, 3H, 5-C$\underline{H}_3$); 10.27 (s, 1H, pyrimidyl-N$\underline{H}$-); 9.80 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 24.8 (-$\underline{C}$H$_3$(13)); 23.3 (-$\underline{C}$H$_3$(12)); 120.1 (phenyl 1); 125.7 (phenyl 2); 123.7 (phenyl 3); 133.2 (phenyl 4); 126.5 (phenyl 5); 138.0 (phenyl 6); 14.3 (5-$\underline{C}$H$_3$); 151.4 (C=O 7); 158.1 (pyrimidyl 8); 103.4 (pyrimidyl 9); 165.2 (pyrimidyl 10); 166.6 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 290 (M^+, 100%). Microanalytical results (calc.): C: 57.76% (57.83%); H: 5.12% (5.20%); N: 18.40% (19.27%).

1-(3-Chloro-4-methyl-phenyl)-3-(2,6- dimethyl - 4 - pyrimidyl)urea: ^{1}H NMR: δ 2.49 (s, 3H, -C$\underline{H}_3$(13)); 2.34 (s, 3H, -C$\underline{H}_3$(12)); 7.19 (s, 1H, pyrimidyl 9); 7.28 (d, 1H, phenyl 1); 7.21 (d, 1H, phenyl 2); 7.32 (s, 1H, phenyl 5); 2.27 (s, 3H, 3-C$\underline{H}_3$); 10.26 (s, 1H, pyrimidyl-N$\underline{H}$-); 9.68 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 25.3 (-$\underline{C}$H$_3$(13)); 23.8 (-$\underline{C}$H$_3$(12)); 117.5 (phenyl 1); 129.4 (phenyl 2); 133.2 (phenyl 3); 137.5 (phenyl 4); 118.6 (phenyl 5); 137.6 (phenyl 6); 18.8 (3-$\underline{C}$H$_3$); 151.5 (C=O 7); 158.2 (pyrimidyl 8); 103.7 (pyrimidyl 9); 165.7 (pyrimidyl 10); 167.1 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 290 (M^+, 100%).

Table 2
Carbonylation of substituted nitrobenzenes with 2-amino-4,6-dimethylpyrimidine

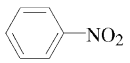
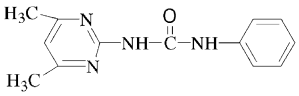
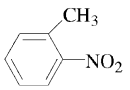
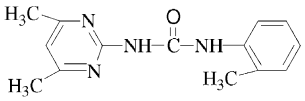
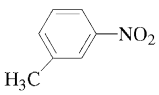
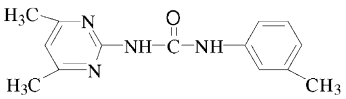
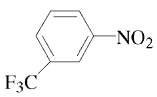
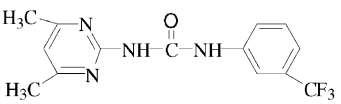
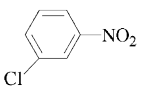
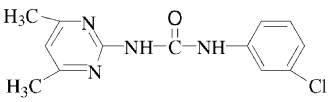
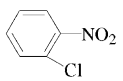
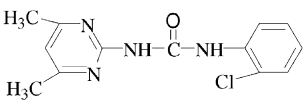
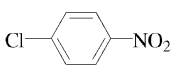
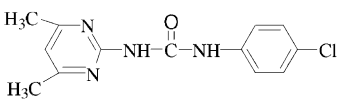
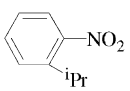
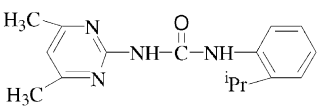
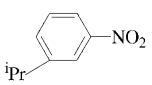
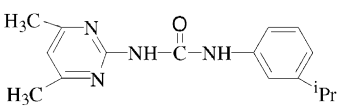
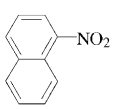
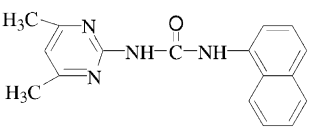
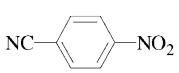
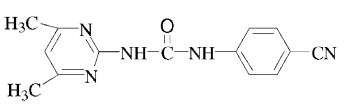
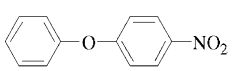
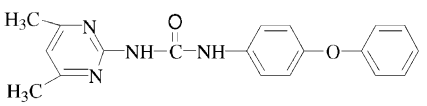
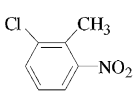
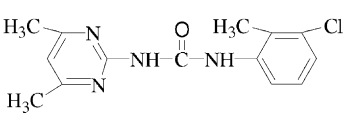
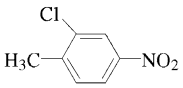
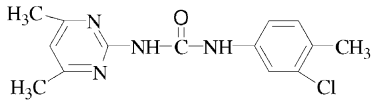
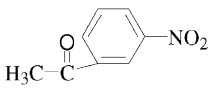
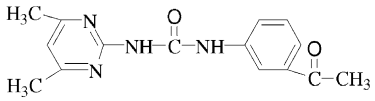
Entry	Substrates	Products	mp (°C) (lit.)	Yield (%)
1			200–202	78.5
2			196–198	78.1
3			188–190	47.2
4			210–211	64.5
5			195–196	75.8
6			209–210	32.3
7			207–208 (216) [11], (211–212) [12]	44.5
8			180–182	70.4
9			150–153	45.8
10			207–209	81.0
11			241–243	74.9
12			184–185	74.8
13			211–212	65.0

Table 2 (*Continued*)

Entry	Substrates	Products	mp (°C) (lit.)	Yield (%)
14			189–191	82.5
15			220–223	47.3

Microanalytical results (calc.): C: 57.06% (57.83%); H: 5.41% (5.20%); N: 18.65% (19.27%).

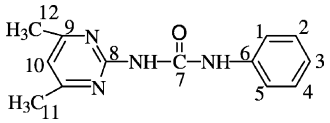
1-(2-Chloro-phenyl)-3-(2,6-dimethyl-4-pyrimidyl)-urea: ^{1}H NMR: δ 2.48 (s, 3H, -C$\underline{H}_3$(13)); 2.37 (s, 3H, -C$\underline{H}_3$(12)); 6.87 (s, 1H, pyrimidyl 9); 8.33 (d, 1H, phenyl 1); 7.34 (t, 1H, phenyl 2); 7.10 (t, 1H, phenyl 3); 7.49 (d, phenyl 4); 11.33 (s, 1H, pyrimidyl-N$\underline{H}$-); 10.27 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 25.2 (-$\underline{C}$H$_3$(13)); 23.7 (-$\underline{C}$H$_3$(12)); 121.1 (phenyl 1); 127.4 (phenyl 2); 121.9 (phenyl 3); 129.0 (phenyl 4); 123.7 (phenyl 5); 135.4 (phenyl 6); 151.4 (C=O 7); 158.1 (pyrimidyl 8); 103.6 (pyrimidyl 9); 165.0 (pyrimidyl 10); 166.6 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 276 (M^+, 100%). Microanalytical results (calc.): C: 56.91% (56.42%); H: 5.05% (4.74%); N: 20.06% (20.25%).

1-O-tolyl-3-(2, 6-dimethyl-4-pyrimidyl)urea: ^{1}H NMR: δ 2.48 (s, 3H, -C$\underline{H}_3$(13)); 2.33 (s, 3H, -C$\underline{H}_3$(12)); 6.97 (s, 1H, pyrimidyl 9); 8.04 (d, 1H, phenyl 1); 7.19 (t, 1H, phenyl 2); 6.97 (t, 1H, phenyl 3); 7.15 (d, phenyl 4); 2.33 (s, 3H, 5-C$\underline{H}_3$); 10.44 (s, 1H, pyrimidyl-N$\underline{H}$-); 10.03 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 25.2 (-$\underline{C}$H$_3$(13)); 23.7 (-$\underline{C}$H$_3$(12)); 120.2 (phenyl 1); 126.0 (phenyl 2); 122.8 (phenyl 3); 126.6 (phenyl 4); 129.9 (phenyl 5); 136.7 (phenyl 6); 18.3 (5-$\underline{C}$H$_3$); 151.4 (C=O 7); 158.4 (pyrimidyl 8); 103.5 (pyrimidyl 9); 165.1 (pyrimidyl 10); 166.4 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 256 (M^+, 100%). Microanalytical results (calc.): C: 65.68% (65.61%); H: 7.17% (6.29%); N: 21.99% (21.86%).

1-(3-Isopropyl-phenyl)-3-(2,6-dimethyl-4 - pyrimidyl)urea: ^{1}H NMR: δ 2.49 (s, 3H, -C$\underline{H}_3$(13)); 2.34 (s, 3H, -C$\underline{H}_3$(12)); 6.93 (s, 1H, pyrimidyl 9); 7.27 (d, 1H, phenyl 1); 7.23 (t, 1H, phenyl 2); 7.21 (d, 1H, phenyl 3); 7.29 (s, phenyl 5); 2.87 (m, 1H, 4-C$\underline{H}$); 1.20 (d, 6H, $^{\text{i}}$Pr-C$\underline{H}_3$); 10.44 (s, 1H, pyrimidyl-N$\underline{H}$-); 10.03 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 25.3 (-$\underline{C}$H$_3$(13)); 23.8 (-$\underline{C}$H$_3$(12)); 116.2 (phenyl 1); 128.6 (phenyl 2); 120.7 (phenyl 3); 149.0 (phenyl 4); 116.6 (phenyl 5); 138.3 (phenyl 6); 25.3 ($^{\text{i}}$Pr-$\underline{C}$H$_3$); 33.5 (4-$\underline{C}$H); 151.4 (C=O 7); 158.3 (pyrimidyl 8); 103.5 (pyrimidyl 9); 165.5 (pyrimidyl 10); 166.8 (pyrimidyl 11). MS (E.I., 70 eV): *m*/*z*: 284 (M^+, 100%). Microanalytical results (calc.): C: 68.15% (67.58%); H: 7.23% (7.09%); N: 19.22% (19.70%) (Scheme 4).

1-Phenyl-3-(4, 6-dimethyl-2-pyrimidyl)urea: ^{1}H NMR: δ 2.41 (s, 6H, -C$\underline{H}_3$(11, 12)); 6.84 (s, 1H, pyrimidyl 10); 7.56 (d, 2H, phenyl 1, 5); 7.33 (t, 2H, phenyl 2, 4); 7.04 (t, 1H, phenyl 3); 11.51 (s, 1H, pyrimidyl-N$\underline{H}$-); 9.18 (s, 1H, phenyl-N$\underline{H}$-); ^{13}C NMR: δ 22.7 (-$\underline{C}$H$_3$(11,12)); 118.8 (phenyl 1); 128.3 (phenyl 2); 122.4 (phenyl 3); 138.2 (phenyl 6); 150.9 (C=O 7); 167.0 (pyrimidyl 8); 157.0 (pyrimidyl 9); 113.1 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 242 (M^+, 100%). Microanalytical results (calc.): C: 64.21% (64.45%); H: 5.57% (5.82%); N: 22.73% (23.13%).

1-O-tolyl-3-(4, 6-dimethyl-2-pyrimidyl)urea: ^{1}H NMR: δ 2.40 (s, 6H, -C$\underline{H}_3$(11, 12)); 6.90 (s, 1H, pyrimidyl 10); 8.13 (d, 1H, phenyl 1); 7.22 (t, 1H, phenyl 2); 6.98 (t, 1H, phenyl 3); 7.17 (d, 1H, phenyl 4); 2.27 (s, 3H, 5-C$\underline{H}_3$); 11.41 (s, 1H, pyrimidyl-N$\underline{H}$-); 9.96 (s,



Scheme 4.

1H, phenyl-NH-); ^{13}C NMR: δ 23.3 (-CH$_3$(11, 12)); 120.0 (phenyl 1); 122.6 (phenyl 2); 126.1 (phenyl 3); 126.6 (phenyl 4); 130.1 (phenyl 5);138.3 (phenyl 6); 18.0 (5-CH$_3$); 151.5 (C=O 7); 167.5 (pyrimidyl 8); 151.5 (pyrimidyl 9); 113.8 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 256 (M^+, 100%). Microanalytical results (calc.): C: 65.65% (65.61%); H: 5.78% (6.29%); N: 21.70% (21.86%).

1-(3-Trifluoromethyl-phenyl)-3-(4, 6-dimethyl-2-pyrimidyl)urea: ^{1}H NMR: δ 2.43 (s, 6H, -CH$_3$(11, 12)); 6.89 (s, 1H, pyrimidyl 10); 7.67 (d, 1H, phenyl 1); 7.35 (t, 1H, phenyl 2); 7.53 (d, 1H, phenyl 3); 8.06 (s, 1H, phenyl 5); 11.85 (s, 1H, pyrimidyl-NH-); 9.53 (s, 1H, phenyl-NH-); ^{13}C NMR: δ 23.3 (-CH$_3$(11, 12)); 125.5 (phenyl 1); 129.8 (phenyl 2); 122.7 (phenyl 3); 130.1 (phenyl 4); 114.9 (phenyl 5);139.4 (phenyl 6); 119.2 (-CF$_3$); 151.6 (C=O 7); 167.6 (pyrimidyl 8); 157.2 (pyrimidyl 9); 113.9 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 310 (M^+, 100%). Microanalytical results (calc.): C: 54.01% (54.19%); H: 3.98% (4.22%); N: 17.93% (18.06%).

1-(4-Chloro-phenyl)-3-(4, 6-dimethyl-2-pyrimidyl)urea: ^{1}H NMR: δ 2.42 (s, 6H, -CH$_3$(11, 12)); 6.90 (s, 1H, pyrimidyl 10); 7.62 (d, 2H, phenyl 1, 5); 7.39 (d, 2H, phenyl 2, 4); 11.96 (s, 1H, pyrimidyl-NH-); 10.03 (s, 1H, phenyl-NH-); ^{13}C NMR: δ 23.3 (-CH$_3$(11, 12)); 120.5 (phenyl 1, 5); 126.4 (phenyl 2, 4); 128.8 (phenyl 3); 137.6 (phenyl 6); 151.5 (C=O 7); 167.5 (pyrimidyl 8); 157.2 (pyrimidyl 9); 113.8 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 276 (M^+, 100%). Microanalytical results (calc.): C: 57.11% (56.42%); H: 4.83% (4.74%); N: 20.01% (20.25%).

1-(4-Cyano-phenyl)-3-(4, 6-dimethyl-2-pyrimidyl)-urea: ^{1}H NMR: δ 2.42 (s, 6H, -CH$_3$(11, 12)); 6.93 (s, 1H, pyrimidyl 10); 7.78 (d, 2H, phenyl 1, 5); 7.74 (d, 2H, phenyl 2, 4); 12.27 (s, 1H, pyrimidyl-NH-); 112.27 (s, 1H, phenyl-NH-); ^{13}C NMR: δ 23.3 (-CH$_3$(11, 12)); 119.0 (phenyl 1, 5); 133.4 (phenyl 2, 4); 104.5 (phenyl 3); 143.0 (phenyl 6); 119.0 (-CN); 151.4 (C=O 7); 167.6 (pyrimidyl 8); 157.0 (pyrimidyl 9); 114.1 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 267 (M^+, 100%). Microanalytical results (calc.): C: 62.83% (62.91%); H: 5.14% (4.90%); N: 26.11% (26.20%).

1-(3-Chloro-phenyl)-3-(4, 6-dimethyl-2-pyrimidyl)-urea: ^{1}H NMR: δ 2.41 (s, 6H, -CH$_3$(11, 12)); 6.85 (s, 1H, pyrimidyl 10); 7.38 (d, 1H, phenyl 1); 7.06 (t, 1H, phenyl 2); 7.05 (d, 1H, phenyl 3); 7.78 (s, 1H, phenyl 5); 11.82 (s, 1H, pyrimidyl-NH-); 9.59 (s, 1H, phenyl-NH-); ^{13}C NMR: δ 22.9 (-CH$_3$(11, 12)); 117.1 (phenyl 1); 129.7 (phenyl 2); 121.9 (phenyl 3); 132.9 (phenyl 4); 118.0 (phenyl 5);139.7 (phenyl 6); 150.9 (C=O 7); 166.9 (pyrimidyl 8); 156.8 (pyrimidyl 9); 113.3 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 276 (M^+, 100%). Microanalytical results (calc.): C: 56.14% (56.42%); H: 4.89% (4.74%); N: 19.96% (20.25%).

1-(3-Chloro-2-methyl-phenyl)-3-(4, 6-dimethyl-2-pyrimidyl)urea: ^{1}H NMR: δ 2.50 (s, 6H, -CH$_3$(11, 12)); 6.89 (s, 1H, pyrimidyl 10); 8.07 (d, 1H, phenyl 1); 7.17 (t, 1H, phenyl 2); 7.13 (d, 1H, phenyl 3); 2.40 (s, 3H, 5-CH$_3$); 11.58 (s, 1H, pyrimidyl-NH-); 10.02 (s, 1H, phenyl-NH-); ^{13}C NMR: δ 23.3 (-CH$_3$(11, 12)); 119.3 (phenyl 1); 124.8 (phenyl 2); 123.4 (phenyl 3); 133.2 (phenyl 4); 126.9 (phenyl 5);138.6 (phenyl 6); 15.1 (5-CH$_3$); 151.4 (C=O 7); 167.2 (pyrimidyl 8); 157.2 (pyrimidyl 9); 113.7 (pyrimidyl 10). MS (E.I., 70 eV): *m*/*z*: 290 (M^+, 100%). Microanalytical results (calc.): C: 58.11% (57.83%); H: 5.33% (5.20%); N: 18.86% (19.27%).

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