Synthesis of Unsymmetrical 2-Pyridyl Ureas via Selenium-Catalyzed Oxidative Carbonylation of 2-Aminopyridine with Aromatic Amines

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Abstract: A simple, one-pot, phosgene-free approach to a series of unsymmetrical 2-pyridyl ureas starting from 2-aminopyridine and various aromatic amines is reported for the first time. The procedure employs inexpensive selenium as the catalyst, and carbon monoxide (instead of phosgene) as the carbonyl reagent. The products are obtained in moderate to good yields via selenium-catalyzed oxidative cross-carbonylation of the substrate amines in the presence of oxygen. The selenium functions as a phase-transfer catalyst and can be recovered easily and reused without any significant degradation of its catalytic activity.

Key words: carbonylation, selenium, carbon monoxide, 2-pyridyl ureas, 2-aminopyridine

Pyridyl ureas are an important class of compounds which possess a nitrogen-containing heterocycle and a peptide linkage. Many of them possess biological activities,[1] and they are frequently employed as insecticides, agrochemical fungicides, herbicides and plant growth regulators.[2] In addition, pyridyl ureas have found important applications in supramolecular chemistry for anion recognition, and in crystal engineering for the organized self-assembly of co-crystals.[3] The conventional procedure for the synthesis of urea derivatives employs phosgene as a carbonyl reagent, but this method suffers from drawbacks which include the toxic and corrosive nature of phosgene, the formation of corrosive hydrogen chloride as a by-product, and multi-step syntheses.[4] Phosgene-free procedures have been developed for the synthesis of pyridyl ureas (Scheme 1).[1a,5–7] The isocyanate method has been employed frequently for this purpose.[5] However, harmful, expensive and difficult to obtain isocyanates limit the utility of this approach. In the presence of a base (e.g. NaOH, K_3PO_4, *t*-BuOK) and a metal catalyst (such as a Cu or Pd complex), pyridyl halides can be coupled effectively to aromatic ureas to produce pyridyl ureas.[6] Honma and co-workers have reported a two-step synthetic approach to pyridyl ureas via a 2-pyridinecarbonyl azide intermediate.[1a] A one-pot catalytic carbonylation approach to pyridyl ureas is of particular importance from both synthetic and environmental standpoints. Various transition metals or their complexes, including rhodium,[8] ruthenium,[9] tungsten,[10] palladium,[11] thallium[12] and cobalt,[13] are commonly used as catalysts for this purpose. However, the high cost and limited availability of transition-metal catalyst systems, together with the complex and energy-consuming separation processes, renders these methods uneconomical. The inexpensive and readily available non-metal, selenium or its oxide, have proved to be efficient and economical catalysts for the carbonylation approach to urea derivatives,[14] including pyridyl ureas.[7] Unfortunately, the pyridyl ureas obtained by this approach were restricted to the redox carbonylation of nitro compounds with amines catalyzed by selenium or its oxide, in which only one third of the carbon monoxide consumed was transferred to the urea product. To the best of our knowledge, the direct employment of two different amines as substrates in a one-pot catalytic carbonylation approach to unsymmetrical pyridyl ureas has not been disclosed previously. Herein, we report a simple, phosgene-free approach toward unsymmetrical 2-pyridyl ureas via the selenium-catalyzed oxidative carbonylation of 2-aminopyridine with various aromatic amines in the presence of carbon monoxide and oxygen.

Initially, the reaction conditions were optimized using the selenium-catalyzed oxidative carbonylation of 2-aminopyridine with aniline as a model reaction (Table 1). All reagents were used directly without further purification. The carbonylation reaction did not proceed at all in the absence of selenium, indicating that the selenium catalyst was essential for this reaction (Table 1, entry 1). Higher product yields were afforded on increasing the amount of the selenium catalyst, with an acceptable yield (82%) being obtained when the selenium loading was 0.25 mmol (Table 1, entries 2, 3 and 15). A further increase in the amount of the selenium catalyst (0.35 mmol) led to no obvious increase in the product yield (Table 1, entry 4). The carbonylation reaction proceeded poorly in the absence of a base (Table 1, entry 5), and in the presence of common bases such as sodium hydroxide, anhydrous sodium acetate and pyridine (Table 1, entries 6–8). When triethylamine was used as the base a satisfactory yield was obtained (Table 1, entry 15), and thus was the base of choice for this carbonylation reaction. It is believed that triethylamine has appropriate alkalinity to be involved in the generation of an active carbonyl selenide (SeCO) complex. The choice of solvent for this reaction also proved to be important. Weakly polar toluene appeared to be the most suitable (Table 1, entry 15); the product yield decreased dramatically when polar solvents such as tetrahydrofuran, ethyl acetate and acetone were used as the

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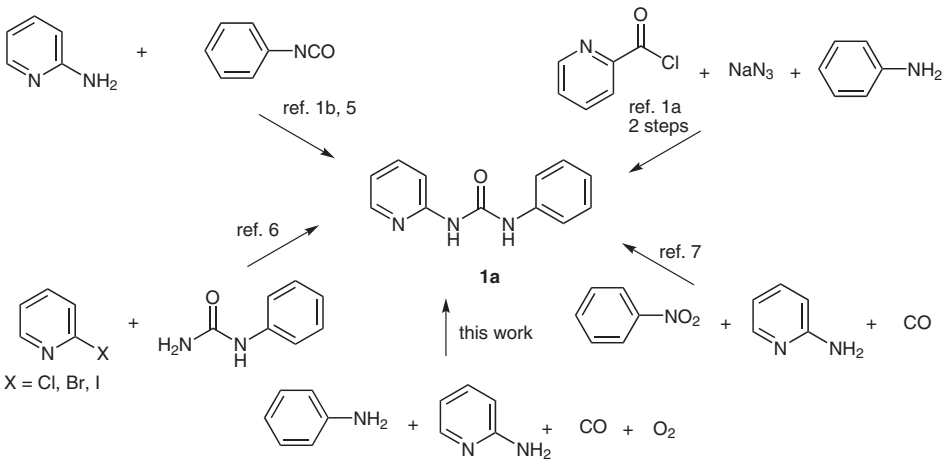


Scheme 1 Phosgene-free methods for preparing 2-pyridyl ureas

solvent (Table 1, entries 9–11), and especially so in the case of strongly polar *N*,*N*-dimethylformamide (Table 1, entry 12). The carbonylation reaction was very sensitive to the temperature employed. When the reaction was conducted at 120 °C for three hours, the expected product, *N*-phenyl-*N*′-(2-pyridyl)urea was obtained in only 51% yield, along with *N*,*N*′-diphenylurea (16%) as a result of the competitive carbonylation reaction of two molecules of aniline (Table 1, entry 13). None of the symmetrical urea, *N*,*N*′-di(pyridin-2-yl)urea was detected in any of

Table 1 Optimization of the Reaction Conditions[a]

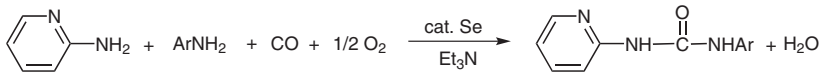
Entry	Temp (°C)	CO (MPa)	O_2 (MPa)	Se (mmol)	Base	Solvent	Yield (%)[b]
1	140	2	0.4	0	Et_3N	toluene	0
2	140	2	0.4	0.05	Et_3N	toluene	21
3	140	2	0.4	0.15	Et_3N	toluene	57
4	140	2	0.4	0.35	Et_3N	toluene	82
5	140	2	0.4	0.25	–	toluene	18
6	140	2	0.4	0.25	NaOH	toluene	21
7	140	2	0.4	0.25	NaOAc	toluene	40
8	140	2	0.4	0.25	py	toluene	20
9	140	2	0.4	0.25	Et_3N	THF	57
10	140	2	0.4	0.25	Et_3N	EtOAc	69
11	140	2	0.4	0.25	Et_3N	acetone	51
12	140	2	0.4	0.25	Et_3N	DMF	30
13	120	2	0.4	0.25	Et_3N	toluene	51 (16)[c]
14	130	2	0.4	0.25	Et_3N	toluene	74 (6)[c]
15	140	2	0.4	0.25	Et_3N	toluene	82 (trace)[c]
16	150	2	0.4	0.25	Et_3N	toluene	82 (trace)[c]
17	140	1	0.4	0.25	Et_3N	toluene	69
18	140	3	0.4	0.25	Et_3N	toluene	83
19	140	2	0.2	0.25	Et_3N	toluene	65

[a] Reaction conditions: 2-aminopyridine (5 mmol), aniline (5 mmol), base (5 mmol), solvent (5 mL), 3 h.
[b] Yield of isolated product.
[c] Yield of *N*,*N*′-diphenylurea in parentheses.

these carbonylation reactions at 120 °C, probably due to the weak reactivity of 2-aminopyridine. At lower temperatures, the amines themselves were apt to form symmetrical ureas, while the reactivity of 2-aminopyridine appeared to increase on raising the temperature. Thus, the cross-carbonylation reaction between 2-aminopyridine and the aromatic amine substrates possibly becomes easier. Hence, the yield of the unsymmetrical pyridyl urea increased on changing the temperature from 120 °C to 140 °C (Table 1, entries 13–15). When the reaction was conducted at 140 °C for three hours, a very good yield of the desired product was obtained (Table 1, entry 15); no further improvement in the yield was achieved when the reaction was conducted at a higher temperature (Table 1, entry 16). The amounts of carbon monoxide (CO) and oxygen employed also affected the reaction markedly. When the oxygen pressure was maintained at 0.4 MPa, the yield was improved significantly on increasing the carbon monoxide pressure (from 1.0 MPa to 2.0 MPa, Table 1, entries 15 and 17). A further increase in the carbon monoxide pressure to 3.0 MPa did not lead to an appreciable rise in the yield (Table 1, entry 18). Decreasing the oxygen pressure (from 0.4 MPa to 0.2 MPa) resulted in a drop in the yield of the pyridyl urea (Table 1, entry 19), which indicated that the optimum ratio of carbon monoxide to oxygen was 2:0.4 (Table 1, entry 15).

With optimized reaction conditions in hand, we next examined the scope of this selenium-catalyzed oxidative carbonylation reaction of 2-aminopyridine with a series of amines (Table 2). The selenium-catalyzed oxidative carbonylation of 2-aminopyridine proceeded smoothly with different substituted anilines and 1-naphthylamine, to afford the corresponding unsymmetrical pyridyl ureas in moderate to good yields. Along with the target unsymmetrical pyridyl ureas, water, as expected, and varying quantities of the corresponding symmetrical *N*,*N*′-diarylureas were formed, indicating that competitive carbonylation of the substituted anilines also occurred. Typically, *ortho*-substituted anilines gave lower yields of the expected products (Table 2, entries 2 and 6) compared to their *para*-substituted analogues (Table 2, entries 4 and 8), suggesting that the reaction was sensitive to steric factors. Thus, it was not surprising that *N*-(2,6-dimethylphenyl)-*N*′-(2-pyridyl)urea (**1e**) was obtained in only 27% yield via the selenium-catalyzed oxidative carbonylation of 2-aminopyridine with 2,6-dimethylaniline, most probably due to high steric hindrance (Table 2, entry 5). The reaction also appeared to be extremely sensitive to electronic factors. Thus, anilines with electron-donating groups (Table 2, entries 2–4 and 10) were more reactive than those with electron-withdrawing groups (Table 2, entries 6–9), leading to higher product yields. When this reaction was attempted with aliphatic amines and benzenesulfonamide, the desired products were not obtained. The use of benzylamine resulted in a very high yield of the corresponding symmetric *N*,*N*′-dibenzylurea, most probably due to its high reactivity. In contrast, the low reactivities of *n*-butylamine, piperidine (almost certainly due to steric hindrance) and benzenesulfonamide prevented the desired cross-carbonylation reactions taking place (Table 2, entries 12–15).

Table 2 Selenium-Catalyzed Oxidative Carbonylations of 2-Aminopyridine with Amines[a]



1a–k

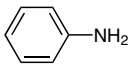
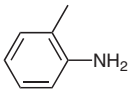
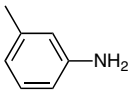
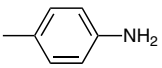
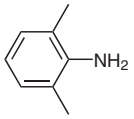
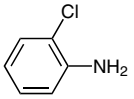
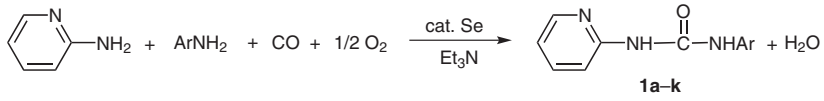
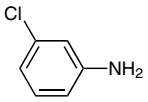
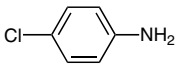
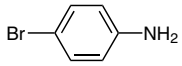
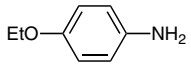
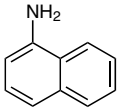
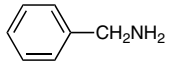
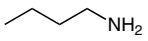
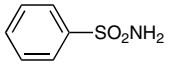
Entry	Substrate	Product	Yield (%)[b]
1		**1a**	82 (–)[c] (trace)[d]
2		**1b**	47 (10)[c] (15)[d]
3		**1c**	67 (6)[c] (9)[d]
4		**1d**	84 (–)[c] (trace)[d]
5		**1e**	27 (31)[c] (trace)[d]
6		**1f**	24 (33)[c] (trace)[d]

Table 2 Selenium-Catalyzed Oxidative Carbonylations of 2-Aminopyridine with Amines[a] (continued)



1a–k

Entry	Substrate	Product	Yield (%)[b]
7		**1g**	55 (12)[c] (10)[d]
8		**1h**	40 (20)[c] (7)[d]
9		**1i**	55 (11)[c] (9)[d]
10		**1j**	90 (–)[c] (trace)[d]
11		**1k**	81 (–)[c] (trace)[d]
12		–	– (7)[c] (84)[d]
13		–	– (56)[c] (16)[d]
14		–	– (57)[c] (trace)[d]
15		–	– (12)[c] (trace)[d]

[a] Reaction conditions: 2-aminopyridine (5 mmol), amine (5 mmol), Se (0.25 mmol), Et_3N (5 mmol), CO (2.0 MPa), O_2 (0.4 MPa), toluene (5 mL), 140 °C, 3 h.
[b] Isolated yield of the unsymmetrical 2-pyridyl urea.
[c] Isolated yield of *N*,*N*′-di(pyridin-2-yl)urea.
[d] Isolated yield of the symmetrical urea formed from the substrate amine.

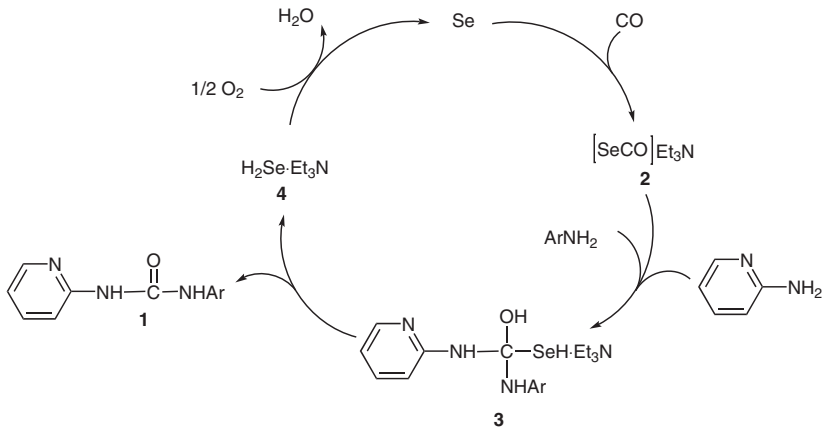
Generally, it is difficult to separate catalysts from a homogeneous system for further use. However, the present catalytic system does not suffer this disadvantage due to its role as a phase-transfer catalyst in the reaction. Selenium powder is insoluble in the organic solvent prior to the oxidative carbonylation reaction; it then reacts with carbon monoxide to form carbonyl selenide (SeCO) in situ, which is soluble in the reaction mixture, and is able to promote the homogeneous catalytic carbonylation reaction efficiently. After completion of the reaction, selenium powder can be precipitated conveniently from the reaction medium after oxidation. Thus, the selenium powder can be recovered easily by filtration and drying, and can be used directly in subsequent reactions. This recycling protocol was repeated four times and the percentage of the catalyst recovery was always greater than 95%. An examination of the reusability of the selenium catalyst using aniline as a model substrate was undertaken (Table 3). Successive recycling of the recovered catalyst gave the desired product in yields almost as high as those obtained using fresh selenium.

A plausible route to the unsymmetrical 2-pyridyl ureas is presented in Scheme 2. The reaction is initiated by formation of carbonyl selenide **2**,[14b,15] which is generated in situ from the reaction of carbon monoxide with selenium in the presence of triethylamine. Next, nucleophilic attack of 2-aminopyridine and the amine on complex **2** leads to for-

Table 3 Recycling of the Selenium Catalyst[a]

Entry	Cycle	Yield (%)[b]
1	0	82
2	1	81
3	2	81
4	3	80
5	4	80

[a] Reaction conditions: 2-aminopyridine (5 mmol), aniline (5 mmol), Se (0.25 mmol), Et_3N (5 mmol), CO (2.0 MPa), O_2 (0.4 MPa), toluene (5 mL), 140 °C, 3 h.
[b] Yield of isolated product.



Scheme 2 Proposed reaction pathway

mation of the intermediate **3**.[14a,b] Subsequently, species **3** undergoes elimination to afford the target unsymmetrical 2-pyridyl urea product **1**, accompanied by the formation of hydrogen selenide **4**, which is then oxidized in the presence of oxygen to give selenium for the ensuing catalytic cycle.

In summary, a simple, one-pot, phosgene-free approach to unsymmetrical 2-pyridyl ureas has been developed. The procedure employs the inexpensive, readily available and recyclable non-metal, selenium as the catalyst, triethylamine as the cocatalyst, and carbon monoxide (instead of phosgene) as the carbonylation reagent. The carbonylation reaction of 2-aminopyridine proceeds smoothly with a range of common aromatic amines to afford the corresponding unsymmetrical 2-pyridyl ureas in moderate to good yields. The low-cost, high atom economy and one-pot, phosgene-free conditions should make this approach very promising toward this class of compounds.

Carbon monoxide (99.95%) and selenium (99.95%) were used as purchased. All other chemicals were AR grade and were used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Column chromatography was accomplished on silica gel (200–300 mesh). Melting points were determined using a Keyi XT4 apparatus (Beijing, China) and are uncorrected. IR spectra were obtained using a Perkin-Elmer Avatar 360 E. S. P. FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. High-resolution mass spectrometry (HRMS) was performed using a Bruker micrOTOF instrument.

Unsymmetrical 2-Pyridyl Ureas; General Procedure

The Se-catalyzed oxidative carbonylation reactions were carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer, using a thermostatic oil bath. 2-Aminopyridine (5 mmol), the appropriate amine (5 mmol), Se (0.25 mmol), Et_3N (5 mmol) and toluene (5 mL) were added to the autoclave. The autoclave was sealed and flushed three times with a mixed gas combination of CO and O_2 (5:1). Next, the autoclave was pressurized with the mixed gas to the desired pressure, placed into an oil bath preheated to the required temperature and the contents stirred. Upon completion of the reaction, the reactor was cooled to r.t. and the residual gas released. The mixture was stirred for 30 min to precipitate Se, which was collected by suction filtration. The filtrate was concentrated and the residue purified either by column chromatography (silica gel, EtOAc–PE, 1:5–1:10), or by crystallization from EtOH, to give the desired unsymmetrical 2-pyridyl urea.

***N*-Phenyl-*N*′-(2-pyridyl)urea (1a)**

Yield: 874 mg (82%); colorless needles; mp 191–192 °C (Lit.[16] 190–193 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.49 (s, 1 H), 9.42 (s, 1 H), 8.26 (d, *J* = 4.8 Hz, 1 H), 7.73 (t, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 7.02–6.98 (m, 2 H).

***N*-(2-Methylphenyl)-*N*′-(2-pyridyl)urea (1b)**

Yield: 534 mg (47%); colorless needles; mp 209–219 °C (Lit.[7b] 208–220 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.91 (s, 1 H), 9.76 (s, 1 H), 8.26 (d, *J* = 4.0 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.74 (t, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 7.20 (d, *J* = 7.6 Hz, 1 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 6.99 (t, *J* = 5.2 Hz, 1 H), 6.95 (t, *J* = 7.2 Hz, 1 H), 2.30 (s, 3 H).

***N*-(3-Methylphenyl)-*N*′-(2-pyridyl)urea (1c)**

Yield: 761 mg (67%); colorless needles; mp 161–163 °C (Lit.[7b] 160–162 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.70 (s, 1 H), 8.90 (s, 1 H), 8.28 (d, *J* = 4.4 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.45 (s, 1 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 6.97–6.92 (m, 3 H), 2.31 (s, 3 H).

***N*-(4-Methylphenyl)-*N*′-(2-pyridyl)urea (1d)**

Yield: 954 mg (84%); colorless needles; mp 178–179 °C (Lit.[7b] 179–180 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.68 (s, 1 H), 8.27 (d, *J* = 4.8 Hz, 1 H), 7.65 (t, *J* = 6.8 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 6.95 (t, *J* = 6.0 Hz, 1 H), 6.89 (d, *J* = 7.6 Hz, 1 H), 2.35 (s, 3 H).

***N*-(2,6-Dimethylphenyl)-*N*′-(2-pyridyl)urea (1e)**

Yield: 326 mg (27%); colorless solid; mp >300 °C.

IR (KBr): 3373, 3204, 3112, 3057, 2984, 1700, 1591, 1554, 1509, 1481, 1445, 1420, 1313, 1297, 1239, 1150, 1061, 1037, 780, 748, 730, 670, 554 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.98 (s, 1 H), 9.54 (s, 1 H), 8.23 (d, *J* = 4.4 Hz, 1 H), 7.72 (t, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 8.4 Hz, 1 H), 7.08 (s, 3 H), 6.97 (t, *J* = 6.0 Hz, 1 H), 2.20 (s, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.8, 153.1, 147.1, 138.9, 135.5, 135.4, 128.2, 126.5, 117.5, 112.2, 18.8.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{14}H_{16}N_3O$: 242.1293; found: 242.1300.

***N*-(2-Chlorophenyl)-*N′*-(2-pyridyl)urea (1f)**
Yield: 297 mg (24%); colorless needles; mp 204–205 °C (Lit.[17] 200–201 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.82 (s, 1 H), 10.01 (s, 1 H), 8.34 (d, *J* = 8.4 Hz, 1 H), 8.30 (d, *J* = 4.4 Hz, 1 H), 7.78 (t, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.32 (t, *J* = 6.0 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 7.07 (t, *J* = 4.0 Hz, 1 H), 7.04 (t, *J* = 6.0 Hz, 1 H).

***N*-(3-Chlorophenyl)-*N′*-(2-pyridyl)urea (1g)**
Yield: 681 mg (55%); colorless needles; mp 169–172 °C (Lit.[18] 170–171 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.73 (s, 1 H), 9.52 (s, 1 H), 8.28 (d, *J* = 5.2 Hz, 1 H), 7.77 (s, 1 H), 7.74 (t, *J* = 7.8 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 6.0 Hz, 1 H), 7.06 (d, *J* = 7.2 Hz, 1 H), 7.01 (t, *J* = 6.0 Hz, 1 H).

***N*-(4-Chlorophenyl)-*N′*-(2-pyridyl)urea (1h)**
Yield: 495 mg (40%); colorless needles; mp 202–204 °C (Lit.[19] 203–204 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.94 (s, 1 H), 8.75 (s, 1 H), 8.26 (s, 1 H), 7.66 (d, *J* = 6.0 Hz, 1 H), 7.58 (d, *J* = 5.6 Hz, 2 H), 7.32 (d, *J* = 5.6 Hz, 2 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 6.89 (d, *J* = 7.8 Hz, 1 H).

***N*-(4-Bromophenyl)-*N′*-(2-pyridyl)urea (1i)**
Yield: 803 mg (55%); colorless needles; mp 209–210 °C.

IR (KBr): 3215, 3115, 3087, 3061, 2978, 1695, 1600, 1582, 1555, 1509, 1488, 1479, 1420, 1400, 1319, 1239, 1154, 1074, 1005, 820, 776, 503 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.96 (s, 1 H), 8.92 (s, 1 H), 8.27 (d, *J* = 4.8 Hz, 1 H), 7.68 (t, *J* = 6.0 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 6.97 (t, *J* = 6.4 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.1, 152.5, 147.3, 139.0, 138.9, 132.0, 121.2, 118.0, 114.4, 112.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{11}BrN_3O$: 292.0085; found: 292.0078.

***N*-(4-Ethoxyphenyl)-*N′*-(2-pyridyl)urea (1j)**
Yield: 1158 mg (90%); colorless needles; mp 190–191 °C (Lit.[7b] 180–181 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.53 (s, 1 H), 8.26 (d, *J* = 4.8 Hz, 1 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 8.8 Hz, 1 H), 6.95 (t, *J* = 6.0 Hz, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 4.07–4.01 (m, 2 H), 1.43 (t, *J* = 6.4 Hz, 3 H).

***N*-Naphthalen-1-yl-*N′*-(2-pyridyl)urea (1k)**
Yield: 1066 mg (81%); colorless needles; mp 197–199 °C (Lit.[20] 197–199 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.41 (s, 1 H), 9.87 (s, 1 H), 8.40 (d, *J* = 4.8 Hz, 1 H), 8.18–8.15 (m, 2 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.81–7.77 (m, 1 H), 7.67–7.62 (m, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.05 (t, *J* = 6.0 Hz, 1 H).

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