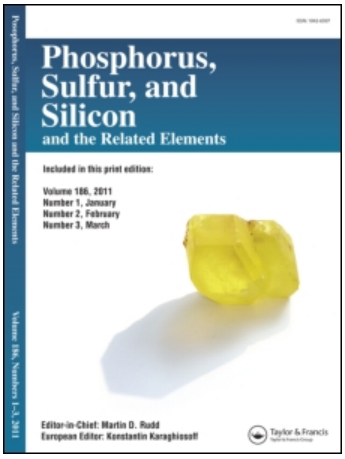

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Microwave Promoted Environmentally Benign Synthesis of 2-Aminobenzothiazoles and Their Urea Derivatives

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2-Aminobenzothiazoles were efficiently synthesized using stable, crystalline tetrabutylammonium tribromide instead of toxic, corrosive liquid bromine under solvent-free and microwave irradiation condition. Furthermore, benzothiazol-2-ylureas were synthesized in good to high yield by reactions of 2-aminobenzothiazoles with N-trichloroacetanilides, which were used as a substitute for toxic, unstable isocyanates, under microwave irradiation condition. This protocol has advantages of no utilization of hazardous chemicals, rapid reaction rate, high yield, and easy work-up procedure.

Keywords 2-Aminobenzothiazole; microwave irradiation; N-trichloroacetanilide; tetrabutylammonium tribromide; urea

INTRODUCTION

2-Aminobenzothiazoles are important intermediates, which have been used in the synthesis of dithiocarbamates,[1] heterocyclic compounds,[2] phosphorus complexes,[3] etc. 2-Aminobenzothiazoles are prepared by many methods which include i) the cyclization of arylthioureas with liquid bromine,[4] benzyltrimethylammonium tribromide,[5] thionyl chloride,[6] or sulfuryl chloride;[7] ii) the reactions of arylamines with liquid bromine and potassium thiocyanate;[8–9] iii) the reactions of 1,2-aminoiodoarenes with thiourea in the presence of nickel(0)

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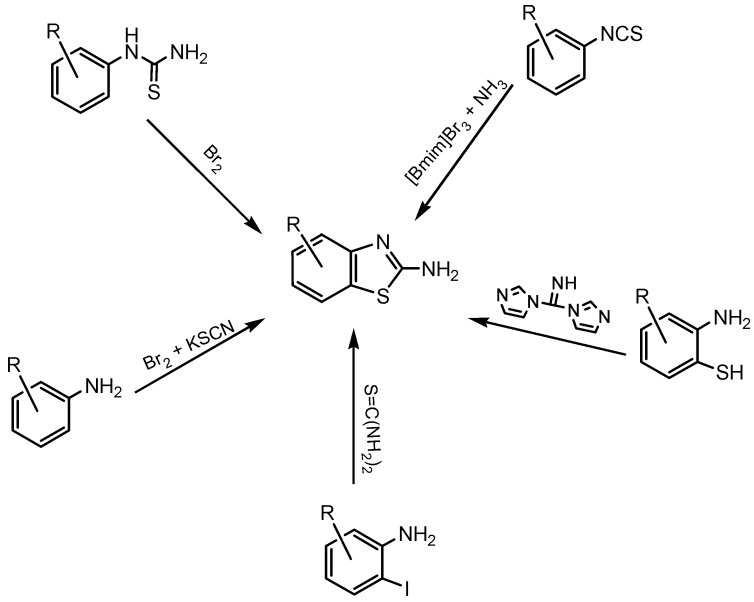
complex;[10] iv) the reactions of 2-aminobenzenethiols with di(imidazole-1-yl)methanimine;[11] and v) the reactions of phenyl isothiocyanate with amines and [Bmin]Br_3 in ionic liquid[12] (Scheme 1). However, the generally used reagent, liquid bromine, is a toxic and corrosive reagent, and can be difficult to manipulate on small scale. Meanwhile, the volatile organic solvents and other hazardous reagents are also used, which can result in environmental pollution.



SCHEME 1 The reported synthetic methods for 2-aminobenzothiazoles.

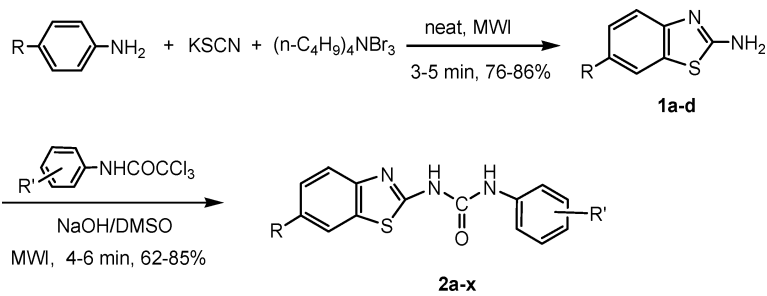
Meanwhile *N*, *N*′-disubstituted ureas are important subunits present in a number of naturally occurring compounds and have found numerous applications as dyes, antioxidants, pesticides, corrosion inhibitors, intermediates for the preparation of pharmaceuticals, and agricultural chemicals.[13] The most commonly used synthetic method for substituted ureas is by reactions of isocyanates with amines.[14] This method has several disadvantages: i) the synthesis of isocyanates usually involves the use of highly toxic phosgene; ii) most of the isocyanates are toxic, unstable, and their storage is inconvenient.

In this paper, we report an expeditious and environmentally benign method to prepare the 2-aminobenzothiazoles using nontoxic, easy to handle tetrabutylammonium tribromide (TBATB) as the substitute for hazardous liquid bromine under solvent-free and microwave conditions, and further to prepare benzothiazolylureas via non-phosgene approach

using eco-friendly N-trichloroacetanilides as substitutes for toxic and unstable isocyanates under microwave irradiation condition.

RESULTS AND DISCUSSION

In our investigation, we chose one-pot method to synthesize 2-aminobenzothiazoles (**1a–d**) using commercially available aromatic amines and potassium thiocyanate as starting materials and TBATB as substitute reagent for liquid bromine. TBATB can be prepared by no use of liquid bromine via environmentally benign methods, such as by the reaction of tetrabutylammonium bromide with V_2O_5 and aqueous H_2O_2[15] or the reaction of tetrabutylammonium bromide with sodium bromate and hydrobromic acid in aqueous media.[16] TBATB is a high molecular weight, stable, crystalline organic ammonium tribromide, and can deliver a stoichiometric amount of bromine where small amounts are necessary for microscale reactions, and can be readily utilized as an alternative electrophilic bromine source. The reactions were performed under solvent-free and microwave irradiation conditions to readily afford the 2-aminobenzothiazoles (**1a–d**) in high yield. The amines bearing electron-donating groups were easier to give products than bearing electron-withdrawing groups.



SCHEME 2 Synthesis of 2-aminobenzothiazoles and their urea derivatives.

Furthermore, the resulting 2-aminobenzothiazoles (**1a–d**) reacted with N-trichloroacetanilides, which were easily prepared by reactions of aromatic amines with trichloroacetic acid,[17] in the presence of sodium hydroxide in DMSO under microwave irradiation to afford N-aryl-N'-(benzothiazol-2-yl)ureas (**2a–x**) in good to high yield (Scheme 2, Table I). All reactions were complete in a 4–6 min time period under 130 W of microwave power. In these reactions, N-trichloroacetanilides acted as in situ isocyanate generating reagents for the synthesis of disubstituted ureas.[17] This protocol effectively avoided the preparation, separation, and storage of the unstable and hazardous isocyanates. The

TABLE I Synthesis of Compounds 1a-d and 2a-x under Microwave Irradiation

Compound	R	R′	Microwave power (W)	Time (min)	M.p. (°C)	Yield (%)[a]
1a	CH_3	—	195	3	138–139 (132.5–133.5)[18]	86
1b	Cl	—	195	4	199–200 (199–201)[21]	80
1c	NO_2	—	195	5	247–248 (247–249)[20]	76
1d	OCH_3	—	195	4	164–166 (165–167)[19]	84
2a	CH_3	H	130	6	244–246	64
2b	Cl	H	130	6	299–301	66
2c	NO_2	H	130	4	324–326	78
2d	CH_3	4-CH_3	130	6	252–254	60
2e	Cl	4-CH_3	130	6	296–298	68
2f	NO_2	4-CH_3	130	4	305–306 (dec.)	80
2g	CH_3	4-Cl	130	6	249–251	69
2h	Cl	4-Cl	130	6	295–297	67
2i	NO_2	4-Cl	130	4	323–325 (dec.)	79
2j	CH_3	4-CH_3O	130	6	253–255	69
2k	Cl	4-CH_3O	130	6	298–300	62
2l	NO_2	4-CH_3O	130	4	312–314 (dec.)	77
2m	CH_3	4-NO_2	130	6	260–262	64
2n	Cl	4-NO_2	130	6	291–293	63
2o	NO_2	4-NO_2	130	4	324–325 (dec.)	85
2p	CH_3	2-CH_3	130	6	263–265	65
2q	Cl	2-CH_3	130	6	281–283	70
2r	NO_2	2-CH_3	130	4	342–344	78
2s	CH_3	2-CH_3-4-Br	130	6	238–250	64
2t	Cl	2-CH_3-4-Br	130	6	298–300	62
2u	NO_2	2-CH_3-4-Br	130	4	315–317 (dec.)	75
2v	CH_3	3-Br	130	6	266–268	67
2w	Cl	3-Br	130	6	318–320	62
2x	NO_2	3-Br	130	4	318–320 (dec.)	82

[a]Yields refer to the isolated products.

various substitutes on the aromatic ring have no obvious effect on the reaction rate and product yield.

The chemical structures of compounds **2a–x** were confirmed by IR, ^{1}H NMR spectra and elemental analyses. ^{1}H NMR analyses show the proton peaks at 11.18–11.68, 8.96–9.93 ppm for NH. IR spectra show the characteristic absorption at 3321–3368 cm^{-1} for NH and 1680–1722 cm^{-1} for C=O.[22]

In conclusion, we have developed an expeditious and convenient synthetic route for the preparation of 2-aminobenzothiazoles and their urea derivatives under microwaves irradiation. The use of TBATB as substitute for hazardous liquid bromine, and avoiding the use of highly toxic

phosgene and isocyanates make this protocol more environmentally benign, and a good alternative to synthesis of corresponding compounds over the current existing methods.

EXPERIMENTAL

IR spectra were recorded using KBr pellets on a Digilab FTS 3000 FTIR spectrophotometer and ^{1}H NMR spectra on a Mercury-400BB instrument using $(CD_3)_2SO$ as solvent and Me_4Si as internal standard. Elemental analyses were performed on a Vario E1 Elemental Analysis instrument. Melting points were observed in an electrothermal melting point apparatus. Microwave reactions were conducted in a modified microwave oven fitted with a condenser (LG-WP650, China). TBATB[15–16] and N-trichloroacetanilides[17] were prepared according to literature procedures.

General Procedure for Preparation of 2-Aminobenzothiazoles (1a–d)

The mixture of aromatic amine (1.0 mmol), potassium thiocyanate (1.0 mmol), and TBATB (1.0 mmol) was ground in a mortar with a pestle until a homogeneous powder was given. Then the mixture was transferred to a round-bottomed flask and subjected to microwave irradiation at power of 195 W for appropriate time indicated in Table I. The progress of reaction was monitored by TLC using petroleum ether, ethyl acetate and acetone (4:2:1) as eluent. The resulting solid was dissolved in water, and the solution was neutralized with ammonia. Then the precipitate was collected by filtration and recrystallized from ethanol and water to give the product. The analytical data for represent compounds are given below:

2-Amino-6-chlorobenzothiazole (1b)

IR (KBr): ν = 3455, 3087, 1632, 1532, 1445, 1304, 1105. ^{1}H NMR (DMSO-d_6, 400 MHz):δ 7.77 (s, 1H, Ar-H), 7.62 (s, 2H, NH_2), 7.30 (d, J = 9.2 Hz, 1H, Ar-H), 7.21 (d, J = 9.2 Hz, 1H, Ar-H). Anal. Calcd. for $C_7H_5ClN_2S$: C, 45.53; H, 2.73; N, 15.17. Found: C, 45.67; H, 2.69; N, 15.31.

2-Amino-6-nitrobenzothiazole (1c)

IR (KBr): ν = 3457, 3063, 1653, 1531, 1494, 1327, 1296. ^{1}H NMR (DMSO-d_6, 400 MHz):δ 8.69 (s, 1H, Ar-H), 8.26 (s, 2H, NH_2), 8.10 (d, J = 8.4 Hz, 1H, Ar-H), 7.42 (d, J = 8.4 Hz, 1H, Ar-H). Anal. Calcd. for

$C_7H_5N_3O_2S$: C, 43.07; H, 2.58; N, 21.53. Found: C, 42.96; H, 2.65; N, 21.44.

General Procedure for Preparation of N-aryl-N′-(benzothiazol-2-yl)ureas (2a–x)

To the solution of 2-aminobenzothiazole (0.30 mmol) in 2 mL of DMSO, N-trichloroacetanilide (0.33 mmol) and NaOH (0.60 mmol) were added. Then the mixture was subjected to microwave irradiation under the power of 130 W for appropriate time indicated in Table I. The completion of reaction was monitored by TLC using petroleum ether, ethyl acetate and acetone (4:2:1) as eluent. The resulting mixture was poured into ice, and the solution was neutralized with 1M HCl to pH = 2–3. The precipitate was collected by filtration and recrystallized from DMF-H_2O to give the product. The analytical data for compounds **2a**–**x** are given below.

N-phenyl-N′-(6-methylbenzothiazol-2-yl)urea (2a)

IR (KBr): ν = 3330 (N—H), 1689 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.20 (s, 1H, NH), 9.74 (s, 1H, NH), 7.01–8.29 (m, 8H, Ar-H), 2.35 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{13}N_3OS$: C, 63.58; H, 4.62; N, 14.83. Found: C, 63.69; H, 4.52; N, 14.74.

N-phenyl-N′-(6-chlorobenzothiazol-2-yl)urea (2b)

IR (KBr): ν = 3332 (N—H), 1690 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.24 (s, 1H, NH), 9.77 (s, 1H, NH), 7.09–8.31 (m, 8H, Ar-H). Anal. Calcd. for $C_{14}H_{10}ClN_3OS$: C, 55.35; H, 3.32; N, 13.83. Found: C, 55.44; H, 2.28; N, 13.95.

N-phenyl-N′-(6-nitrobenzothiazol-2-yl)urea (2c)

IR (KBr): ν = 3348 (N—H), 1717 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.35 (s, 1H, NH), 9.66 (s, 1H, NH), 7.18–8.44 (m, 8H, Ar-H). Anal. Calcd. for $C_{14}H_{10}N_4O_3S$: C, 53.50; H, 3.21; N, 17.82. Found: C, 53.38; H, 3.30; N, 17.71.

N-(4-methylphenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2d)

IR (KBr): ν = 3325 (N—H), 1680 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.18 (s, 1H, NH), 9.70 (s, 1H, NH), 7.01–8.22 (m, 7H, Ar-H), 2.33 (s, 3H, CH_3), 2.25 (s, 3H, CH_3). Anal. Calcd. for $C_{16}H_{15}N_3OS$: C, 64.62; H, 5.08; N, 14.13. Found: C, 64.75; H, 5.11; N, 14.20.

N-(4-methylphenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2e)

IR (KBr): ν = 3330 (N—H), 1711 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.43 (s, 1H, NH), 9.08 (s, 1H, NH), 7.24–8.20 (m, 7H, Ar-H),

2.30 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}ClN_3OS$: C, 56.69; H, 3.81; N, 13.22. Found: C, 56.75; H, 2.74; N, 13.17.

N-(4-methylphenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2f)

IR (KBr): ν = 3349 (N—H), 1712 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.41 (s, 1H, NH), 9.49 (s, 1H, NH), 7.31–8.58 (m, 7H, Ar-H), 2.34 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}N_4O_3S$: C, 54.87; H, 3.68; N, 17.06. Found: C, 54.96; H, 3.60; N, 16.95.

N-(4-chlorophenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2g)

IR (KBr): ν = 3328 (N—H), 1712 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.33 (s, 1H, NH), 9.46 (s, 1H, NH), 7.11–8.18 (m, 7H, Ar-H), 2.26 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}ClN_3OS$: C, 56.69; H, 3.81; N, 13.22. Found: C, 56.54; H, 3.89; N, 13.30.

N-(4-chlorophenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2h)

IR (KBr): ν = 3330 (N—H), 1714 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.38 (s, 1H, NH), 9.50 (s, 1H, NH), 7.26–8.30 (m, 7H, Ar-H). Anal. Calcd. for $C_{14}H_9Cl_2N_3OS$: C, 49.72; H, 2.68; N, 12.42. Found: C, 49.61; H, 2.75; N, 12.33.

N-(4-chlorophenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2i)

IR (KBr): ν = 3334 (N—H), 1714 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.45 (s, 1H, NH), 9.38 (s, 1H, NH), 7.39–8.26 (m, 7H, Ar-H). Anal. Calcd. for $C_{14}H_9ClN_4O_3S$: C, 48.21; H, 2.60; N, 16.06. Found: C, 48.06; H, 2.52; N, 15.94.

N-(4-methoxyphenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2j)

IR (KBr): ν = 3326 (N—H), 1710 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.31 (s, 1H, NH), 9.42 (s, 1H, NH), 7.08–8.15 (m, 7H, Ar-H), 3.84 (s, 3H, CH_3), 2.25 (s, 3H, CH_3). Anal. Calcd. for $C_{16}H_{15}N_3O_2S$: C, 61.32; H, 4.82; N, 13.41. Found: C, 61.45; H, 4.77; N, 13.33.

N-(4-methoxyphenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2k)

IR (KBr): ν = 3329 (N—H), 1711 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.37 (s, 1H, NH), 9.49 (s, 1H, NH), 7.15–8.20 (m, 7H, Ar-H), 3.86 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}ClN_3O_2S$: C, 53.97; H, 3.62; N, 12.59. Found: C, 54.10; H, 3.55; N, 12.64.

N-(4-methoxyphenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2l)

IR (KBr): ν = 3347 (N—H), 1717 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.54 (s, 1H, NH), 9.23 (s, 1H, NH), 7.31–8.62 (m, 7H, Ar—H),

3.88 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}N_4O_4S$: C, 52.32; H, 3.51; N, 16.27. Found: C, 52.22; H, 3.42; N, 16.38.

N-(4-nitrophenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2m)

IR (KBr): ν = 3351 (N—H), 1714 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.56 (s, 1H, NH), 9.00 (s, 1H, NH), 7.05–8.57 (m, 7H, Ar-H), 2.27 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}N_4O_3S$: C, 54.87; H, 3.68; N, 17.06. Found: C, 54.98; H, 2.73; N, 16.92.

N-(4-nitrophenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2n)

IR (KBr): ν = 3357 (N—H), 1718 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.59 (s, 1H, NH), 9.08 (s, 1H, NH), 7.11–8.62 (m, 7H, Ar-H). Anal. Calcd. for $C_{14}H_9ClN_4O_3S$: C, 48.21; H, 2.60; N, 16.06. Found: C, 48.10; H, 2.53; N, 16.12.

N-(4-nitrophenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2o)

IR (KBr): ν = 3368 (N—H), 1722 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.68 (s, 1H, NH), 9.35 (s, 1H, NH), 7.22–8.69 (m, 7H, Ar-H). Anal. Calcd. for $C_{14}H_9N_5O_5S$: C, 46.80; H, 2.52; N, 19.49. Found: C, 46.71; H, 2.46; N, 19.55.

N-(2-methylphenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2p)

IR (KBr): ν = 3321 (N—H), 1685 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.21 (s, 1H, NH), 8.97 (s, 1H, NH), 7.00–8.19 (m, 7H, Ar-H), 2.26 (s, 3H, CH_3), 2.22 (s, 3H, CH_3). Anal. Calcd. for $C_{16}H_{15}N_3OS$: C, 64.62; H, 5.08; N, 14.13. Found: C, 64.50; H, 5.13; N, 14.19.

N-(2-methylphenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2q)

IR (KBr): ν = 3337 (N—H), 1707 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.52 (s, 1H, NH), 8.99 (s, 1H, NH), 7.01–8.53 (m, 7H, Ar-H), 2.25 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}ClN_3OS$: C, 56.69; H, 3.81; N, 13.22. Found: C, 56.77; H, 3.73; N, 13.15.

N-(2-methylphenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2r)

IR (KBr): ν = 3351 (N—H), 1714 (C═O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.28 (s, 1H, NH), 9.93 (s, 1H, NH), 7.21–8.32 (m, 7H, Ar-H), 2.36 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}N_4O_3S$: C, 54.87; H, 3.68; N, 17.06. Found: C, 54.73; H, 2.61; N, 17.12.

N-(2-methyl-4-bromophenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2s)

IR (KBr): ν = 3340 (N—H), 1706 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.57 (s, 1H, NH), 8.96 (s, 1H, NH), 7.32–8.60 (m, 6H, Ar—H), 2.28 (s, 3H, CH_3), 2.21 (s, 3H, CH_3). Anal. Calcd. for $C_{16}H_{14}BrN_3OS$: C, 51.07; H, 3.75; N, 11.17. Found: C, 49.95; H, 3.66; N, 11.26.

N-(2-methyl-4-bromophenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2t)

IR (KBr): ν = 3343 (N—H), 1709 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.59 (s, 1H, NH), 8.98 (s, 1H, NH), 7.34–8.61 (m, 6H, Ar—H), 2.22 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{11}BrClN_3OS$: C, 45.42; H, 2.79; N, 10.59. Found: C, 45.35; H, 2.88; N, 10.67.

N-(2-methyl-4-bromophenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2u)

IR (KBr): ν = 3350 (N—H), 1716 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ11.61 (s, 1H, NH), 9.01 (s, 1H, NH), 7.39–8.63 (m, 6H, Ar—H), 2.23 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{11}BrN_4O_3S$: C, 44.24; H, 2.72; N, 13.76. Found: C, 44.11; H, 2.65; N, 13.83.

N-(3-bromophenyl)-N′-(6-methylbenzothiazol-2-yl)urea (2v)

IR (KBr): ν = 3329 (N—H), 1713 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.35 (s, 1H, NH), 9.47 (s, 1H, NH), 7.13–8.20 (m, 7H, Ar—H), 2.26 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{12}BrN_3OS$: C, 49.73; H, 3.34; N, 11.60. Found: C, 49.88; H, 3.26; N, 11.53.

N-(3-bromophenyl)-N′-(6-chlorobenzothiazol-2-yl)urea (2w)

IR (KBr): ν = 3331 (N—H), 1715 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.39 (s, 1H, NH), 9.52 (s, 1H, NH), 7.28–8.32 (m, 7H, Ar—H). Anal. Calcd. for $C_{14}H_9BrClN_3OS$: C, 43.94; H, 2.37; N, 10.98. Found: C, 44.06; H, 2.44; N, 11.07.

N-(3-bromophenyl)-N′-(6-nitrobenzothiazol-2-yl)urea (2x)

IR (KBr): ν = 3335 (N—H), 1716 (C=O). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.47 (s, 1H, NH), 9.41 (s, 1H, NH), 7.40–8.28 (m, 7H, Ar—H). Anal. Calcd. for $C_{14}H_9BrN_4O_3S$: C, 42.76; H, 2.31; N, 14.25. Found: C, 42.63; H, 2.25; N, 14.34.

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