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N-Acylbenzotriazoles as Proficient Substrates for an Easy Access to Ureas, Acylureas, Carbamates, and Thiocarbamates *via* Curtius Rearrangement Using Diphenylphosphoryl Azide (DPPA) as Azide Donor

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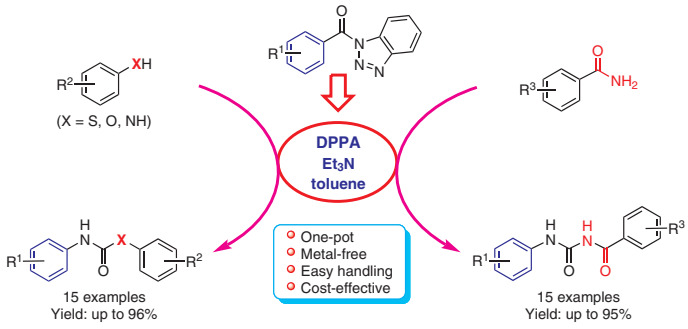
This manuscript is dedicated to the late Prof. Alan R. Katritzky for his notable contributions to benzotriazole chemistry.



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Abstract A diverse range of ureas, *N*-acylureas, carbamates, and thiocarbamates has been synthesized in good to excellent yields by reacting *N*-acylbenzotriazoles individually with amines or amides or phenols or thiols in the presence of diphenylphosphoryl azide (DPPA) as a suitable azide donor in anhydrous toluene at 110 °C for 3–4 hours. In this route, DPPA was found to be a good alternative to trimethylsilyl azide and sodium azide for the azide donor in Curtius degradation. The high reaction yields, one-pot and metal-free conditions, straightforward nature, easy handling, use of readily available reagents, and in many cases avoidance of column chromatography are the notable features of the devised protocol.

Key words *N*-acylbenzotriazoles, *N*-acylureas, benzotriazoles, Curtius rearrangement, diphenylphosphoryl azide, carbamates, thiocarbamates, ureas

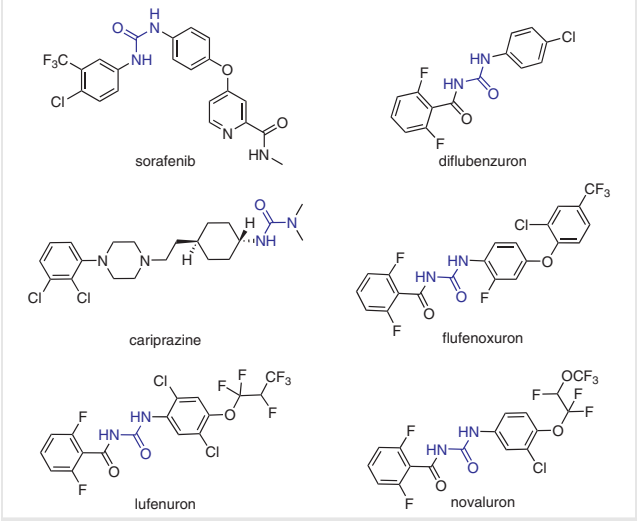
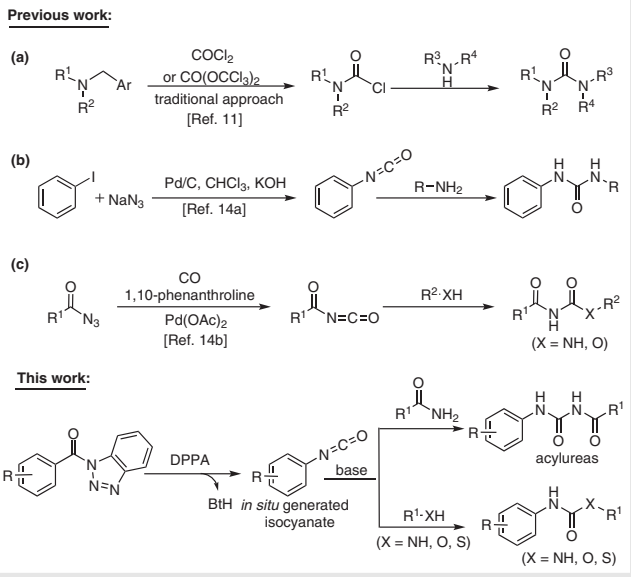


Figure 1 Structures of some biologically potent ureas and acylureas

Urea and its derivatives are fascinating candidates for drug design in medicinal chemistry due to their unique characteristics, i.e. H-bonding capability with biomolecular targets.[1,2] Many approved drugs to cure various frontline diseases contain urea as the core moiety,[2] including sorafenib (antineoplastic agent),[3] Hetrazan (antihelminthic),[4] and cariprazine (anti-psychotic)[5] (Figure 1). Acylureas, the close derivatives of urea, are depicted in a plethora of applications in the agrochemical field, including the insect growth regulators diflubenzuron,[6] flufenoxuron,[7] lufenuron,[8] and Novaluron[9] (Figure 1). Moreover, a number of *N*-acylureas are well-known human liver glycogen phosphorylase inhibitors and some of them can be used for the successful treatment of type 2 diabetes.[10]

In addition to the widespread applications in drug discovery and development, the urea functionality has been well explored as an interesting synthetic auxiliary in organic synthesis for various other purposes.[1] Therefore, there is an increased demand for urea and its derivatives for their complete chemical, biochemical, and pharmacological investigation. A variety of synthetic approaches have been put forward for the facile synthesis of urea derivatives, mostly by the use of toxic phosgene or triphosgene (Scheme 1a)[11] or an iodine–DMSO reagent system.[12] To circumvent the toxicity issue, several alternate methods using carbonates[13] or Pd/C-catalyzed reaction of an aryl halide with sodium azide have also been illustrated to synthesize

ureas and their derivatives (Scheme 1b).[14a] Alternatively, the synthesis of *N*-acylureas can be achieved in good yields by using carbon monoxide (as carbonyl source)/palladium acetate (Scheme 1c)[14b] or the carbon monoxide involved reaction of aryl halide with substituted urea in the presence of a transition-metal catalyst.[15] Previously, our group has devised a synthetic method for carbamates, thiocarbamates, and symmetric ureas from *N*-acylbenzotriazoles *via* Curtius rearrangement.[16a] Although, this method has an issue, particularly for the synthesis of unsymmetrical ureas. Thus, we further extended the protocol by reacting *N*-acylbenzotriazoles with amine and $TMSN_3$ in the presence of Et_3N as base in anhydrous toluene at 110 °C to furnish high yields of required unsymmetrical ureas and their derivatives.[16b,c]

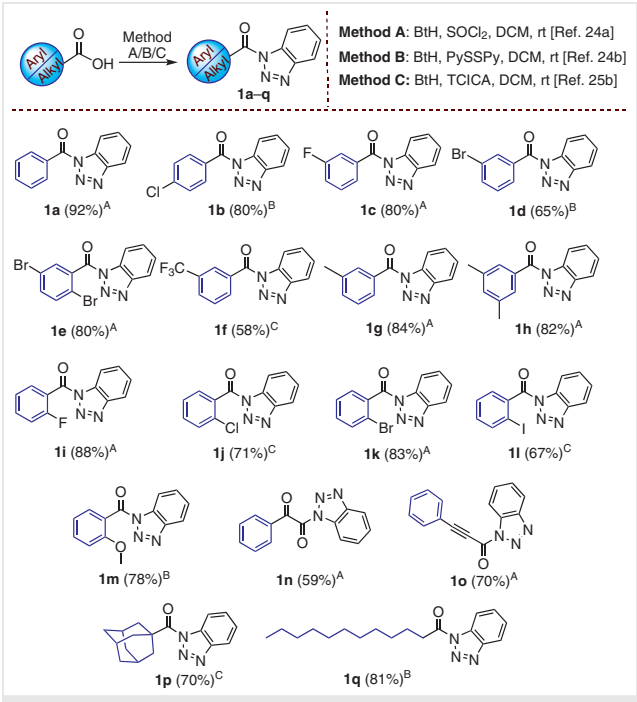


Scheme 1 Common approaches for the synthesis of urea and *N*-acylurea derivatives

In addition to this, thiocarbamates are biologically relevant compounds, particularly known for their antiviral, bactericidal, pesticidal, and herbicidal activities.[17] Thus, different approaches have been developed for their practical synthesis. The common methods include the reaction of amines with phosgene[18] or the reaction of gaseous carbonyl sulfide with amines followed by alkylation,[19] or iodine-catalyzed reaction with sodium sulfinates,[20] or with sulfonyl chlorides,[21a] and finally, selenium-based synthesis with the use of carbon monoxide as carbonyl source.[21b] However, all above-mentioned procedures still have some limitations, particularly in terms of sensitivity, toxicity, high cost, use of transition-metal-based catalysts, and highly explosive nature of reagents involved.

To overcome these major issues, we have devised a novel one-pot route for the synthesis of a series of symmetric urea, unsymmetric urea, acylurea, carbamate, and thiocarbamate derivatives using *N*-acylbenzotriazoles as model substrates and diphenylphosphoryl azide (DPPA) as azide donor, which we envisage to report herein. The reaction proceeds through *in situ* generation of *N*-acyl azide, which on heating is subsequently converted into an isocyanate intermediate *via* Curtius rearrangement and finally trapped with various nucleophiles like amines, amides, phenols, and thiophenols to afford the respective ureas, *N*-acylureas, carbamates, and thiocarbamates as sole products (Scheme 1).

Our synthesis commenced with the construction of *N*-acylbenzotriazoles **1a–q**, which were obtained from the respective carboxylic acids under a standard known protocol. *N*-Acylbenzotriazoles are generally solid, stable to moisture at room temperature, excellent substitutes for acid chlorides, and the most relevant substrate extensively used as an acylating agent in acylation reactions.[22] It is evident from the literature that a wide variety of devised protocols are available to synthesize *N*-acylbenzotriazoles, which mainly include the reaction of carboxylic acid with I_2/PPh_3 or $SOCl_2$ or NBS/PPh_3 or PySSPy and 1*H*-benzotriazole in anhydrous dichloromethane (Scheme 2).[23–25]



Scheme 2 *N*-Acylbenzotriazoles **1a–q** required for the synthesis of diverse ureas, acylureas, carbamates, and thiocarbamates

Apart from this, benzotriazoles have several advantages, as they act as a cation stabilizer and anion generator; further, they are found to be sufficiently stable during the

course of a reaction and, at the end, can be easily eliminated as well due to their good leaving group tendency. Owing to these notable features, acylbenzotriazoles have been widely explored for their diverse applications in chemistry and biology.[26]

In this investigation, (1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methanone (**1a**) with DPPA was chosen as the model substrate which was refluxed at 110 °C to generate the corresponding isocyanate as functional intermediate. Furthermore, this intermediate was trapped *in situ* by selective nucleophiles like amine, amide, thiol, and phenol derivatives to give the corresponding ureas, acylureas, thiocarbamates, and carbamates.

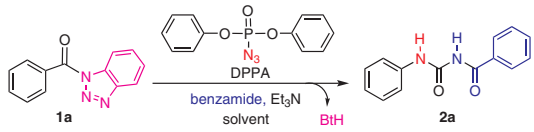
Initially, we took 1.0 equivalent of substrate **1a**, DPPA (1.0 equiv.), benzamide (1.0 equiv.), and Et_3N (1.0 equiv.) in anhydrous toluene at 110 °C; then, the reaction mixture was stirred for 2 hours which afforded compound **2a** in 71% yield (Table 1, entry 2). After achieving the target compound, the reaction was further optimized by varying other parameters, like solvent, equivalents of reactants, temperature, and amount of base used. Primarily, we optimized the reaction in different solvents like DMF, DMSO, THF, toluene, and chloroform; among them, toluene was found to be the most appropriate solvent for the reaction (Table 1, entry 11). Further, the reaction was carried out in the absence of solvent by increasing the equivalents of base (4.0 equiv.); the yield of compound **2a** was drastically reduced to only 24% (Table 1, entry 4), which inferred that the solvent was necessary for the reaction to proceed. In this continuation, we also checked the reaction without base and observed that there was a substantial decrease in the yield (only 15%) of compound **2a** (Table 1, entry 5).

After that, we investigated the effect of temperature on reaction yield; in this regard, when the temperature was raised to 140 °C, a slight decrease in yield was observed (Table 1, entry 17), while upon lowering the temperature, a substantial decrease in yield was noticed (Table 1, entries 15 and 16). Towards this optimization, the best result was obtained when compound **1a** (1.0 equiv.) was treated with DPPA (1.1 equiv.), Et_3N (2.0 equiv.), and benzamide (1.0 equiv.) at 110 °C in anhydrous toluene for 3 hours (Table 1, entry 11).

After the optimization, the set protocol was put forward to construct libraries of *N*-acylurea derivatives **2a–m** through incorporating different substitution on the aromatic ring of *N*-acylbenzotriazoles and benzamides (Scheme 3). The structures of the developed compounds were well elucidated by extensive spectral analysis, including ^1H NMR, ^{13}C NMR, and mass spectroscopy.

Furthermore, the optimized protocol was checked with aliphatic *N*-acylbenzotriazole **1p** having an adamantyl group which resulted in the formation of compound **2n** in 80% yield, whereas a similar reaction of 1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)dodecan-1-one (**1q**) having a long-chain aliphatic group furnished compound **2o** in 67% yield (Scheme 4). Unfortunately, 1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-phenylethane-1,2-dione (**1n**) and 1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-phenylprop-2-yn-1-one (**1o**) under the similar optimized conditions could not give the desired products. Although, by adopting the set protocol, there was not much fluctuation in the yield of targeted products **2**.

Table 1 Reaction Optimization Study for *N*-Acylurea Synthesis *via* the Curtius Rearrangement

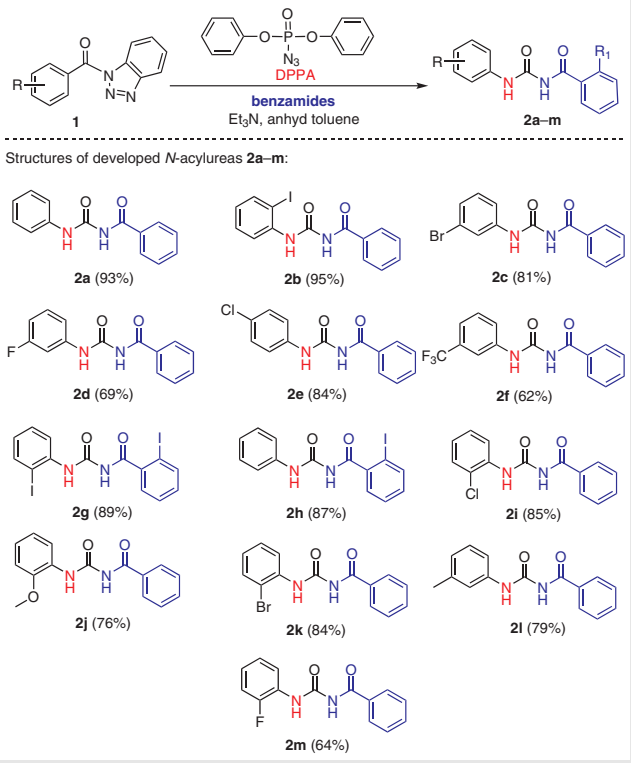


Entry[a]	DPPA (equiv.)	Et_3N (equiv.)	Solvent[b]	Time (h)	Temp (°C)	Yield (%)[c]
1	1.0	2.0	toluene	1.0	110	85
2	1.0	1.0	toluene	2.0	110	71
3	1.0	0	toluene	2.0	110	10
4	1.0	4.0	–	2.0	110	24
5	1.1	0	toluene	2.0	110	15
6	1.1	2.0	DCM	3.0	110	65
7	1.1	2.0	DMSO	3.0	110	55
8	1.1	2.0	$CHCl_3$	3.0	110	54
9	1.1	2.0	THF	3.0	110	40
10	1.1	2.0	DMF	2–3	110	trace
11	**1.1**	**2.0**	**toluene**	**3.0**	**110**	**93**
12	1.2	2.0	toluene	3.0	110	92
13	1.1	2.0	toluene	0.5	110	80
14	1.1	2.0	toluene	0.2	110	30
15	1.1	2.0	toluene	3.0	50	trace
16	1.1	2.0	toluene	3.0	80	30
17	1.1	2.0	toluene	3.0	140	82

[a] Reactions were carried out in a sealed tube at 110 °C, unless otherwise noted.
[b] Anhydrous solvents were used.
[c] Yields after column chromatography (silica gel).

To prove the effectiveness and usefulness of this methodology further, we applied the above-optimized reaction conditions for the synthesis of symmetric and asymmetric urea derivatives **3a–j**. Thus, the reaction of *N*-acylbenzotriazoles **1** with diverse amines (1.0 equiv.) in the presence of DPPA (1.1 equiv.) and Et_3N (2.0 equiv.) in refluxing toluene for 30 minutes to 5 hours resulted in moderate to good yields of the target ureas **3a–j** (Scheme 5).

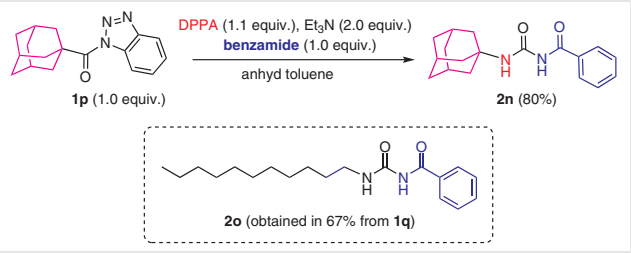
Moreover, this methodology was further exploited for the synthesis of thiocarbamate derivatives. The reaction of *N*-acylbenzotriazole derivatives, when carried out with thiophenols under the optimized conditions, afforded



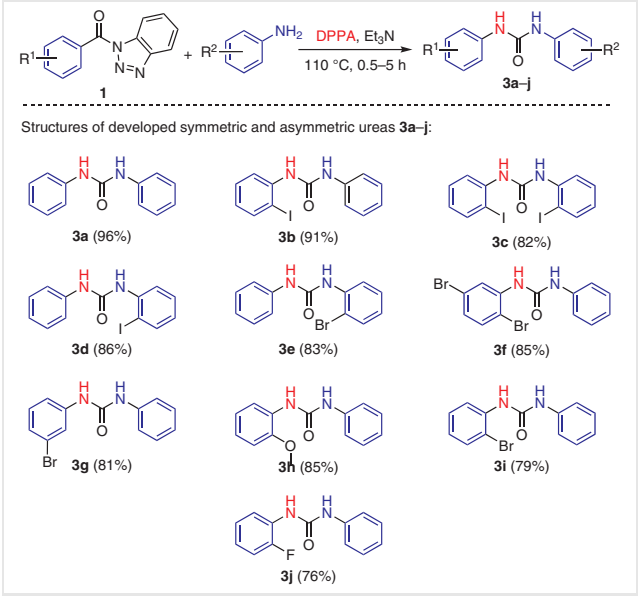
Scheme 3 Synthesis of *N*-acylurea derivatives **2a–m** from aromatic acids. *Reagents and conditions*: *N*-acylbenzotriazole **1** (1.0 equiv.), DPPA (1.1 equiv.), Et_3N (2.0 equiv.), benzamide (1.0 equiv.); yields after column chromatography (silica gel).

moderate to excellent yields of compounds **4a–c** (Scheme 6). The structures of the developed compounds were characterized by ^1H NMR and ^{13}C NMR spectroscopy, and mass spectrometry.

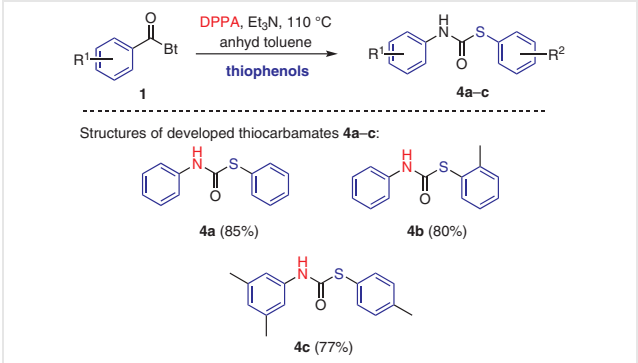
At the end, the established methodology was also investigated with some weak nucleophiles like phenols in order to furnish carbamate derivatives *via* isocyanate intermediates under Curtius rearrangement. The reaction of (1*H*-benzo[*d*][1,2,3]triazol-1-yl)(*m*-tolyl)methanone (**1g**) was carried out separately with phenol and *p*-bromophenol in the presence of DPPA and Et_3N under the optimized conditions, and as a result the respective carbamate derivatives **5a** and **5b** were obtained in moderate yields (Scheme 7).



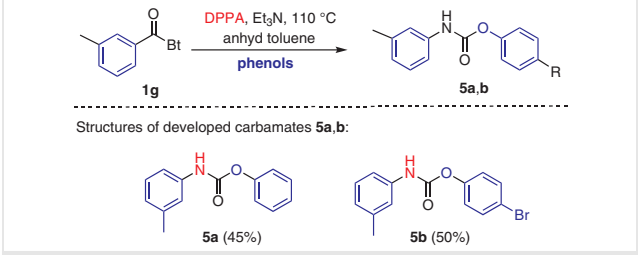
Scheme 4 Synthesis of *N*-acylurea derivatives **2n**,**o** from aliphatic acids



Scheme 5 Synthesis of symmetric and asymmetric urea derivatives **3a–j**. *Reagents and conditions*: *N*-acylbenzotriazole **1** (1.0 equiv.), DPPA (1.1 equiv.), Et_3N (2.0 equiv.), aniline (1.0 equiv.); yields after column chromatography (silica gel).

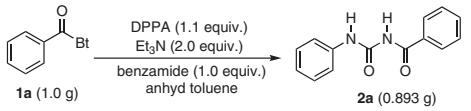


Scheme 6 Synthesis of thiocarbamate derivatives **4a–c**. *Reagents and conditions*: *N*-acylbenzotriazole **1** (1.0 equiv.), DPPA (1.1 equiv.), Et_3N (2.0 equiv.), thiophenol (1.0 equiv.); yields after column chromatography (silica gel).



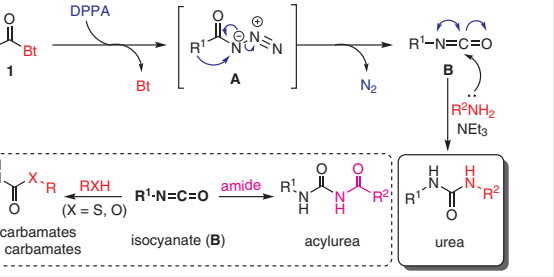
Scheme 7 Synthesis of carbamate derivatives **5a**,**b**. *Reagents and conditions*: *N*-acylbenzotriazole **1g** (1.0 equiv.), DPPA (1.1 equiv.), Et_3N (2.0 equiv.), phenol (1.0 equiv.); yields after column chromatography (silica gel).

For the quantitative feasibility of this method, the optimized reaction conditions were finally implemented using 1.0 g of (1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methanone (**1a**). The reaction went well and the final product *N*-acylurea **2a** was isolated in 83% yield, which indicates its importance in scale-up synthesis (Scheme 8).



Scheme 8 Reaction performed on gram scale

A possible mechanism for the formation of the ureas and their derivatives like acylureas and thiocarbamates is depicted in Scheme 9. First of all, reaction of *N*-acylbenzotriazole **1** with the azide donor DPPA furnishes the corresponding acyl azide **A** *via* nucleophilic substitution reaction. This acyl azide intermediate undergoes Curtius rearrangement to furnish the corresponding isocyanate intermediate **B** by the subsequent elimination of molecular N_2. Further, the isocyanate intermediate is trapped by a variety of nucleophiles to give the targeted ureas, carbamates, and thiocarbamates.



Scheme 9 Plausible mechanism involving the Curtius rearrangement

In conclusion, a practical and straightforward tool has been developed for the high-yielding synthesis of a diverse range of ureas, acylureas, carbamates, and thiocarbamates by utilizing *N*-acylbenzotriazoles as suitable precursors and readily available DPPA as azide source under one-pot conditions. 1*H*-Benzotriazole is the byproduct which is nontoxic and water soluble, and moreover can be easily removed from the reaction mixture.[27] Most of the developed ureas and *N*-acylureas were purified by simple filtration followed by washing with appropriate solvents and thus a column chromatography step was avoided. Therefore, the devised methodology demonstrates a practical applicability in academia and industry.

All chemicals and solvents were of pure analytical category. TLC was executed on silica gel 60 F254, precoated on aluminum plates, and seen under a UV lamp (λ_{max} = 254 nm). Solvents were condensed under low pressure at temperature <55 °C. Column chromatography was performed on silica gel (230–400 mesh, 100–200 mesh, E. Merck). EtOAc, *n*-hexane, and DCM were distilled for the column chromatography. Melting points were measured on a digital melting point apparatus (EI 934). ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, on a JEOL DELTA 2 spectrometer. Chemical shifts are provided in ppm downfield from internal TMS; *J* values in Hz. High-resolution mass spectra were taken using a SCIEX X500r Q-TOF system.

Ureas, Acylureas, Carbamates, and Thiocarbamates; General Procedure

N-Acylbenzotriazole **1** (1.0 equiv.) and diphenylphosphoryl azide (DPPA, 1.1 equiv.) in anhydrous toluene (3 mL) was taken into a sealed tube, and shaken for 5 min. Then, the required nucleophile (e.g., amine, benzamide, phenol, or thiol; 1.0 equiv.) was added, followed by addition of Et_3N (2.0 equiv.) as base. Further, the resulting reaction mixture was stirred for 3–4 h at 110 °C in a sealed tube. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (*n*-hexane/EtOAc) to afford the corresponding urea, *N*-acylurea, carbamate, or thiocarbamate as the desired product.

N-(Phenylcarbamoyl)benzamide (2a)[16b,28]

White crystals; yield: 0.200 g (93%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 210–212 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.02 (s, 1 H), 10.82 (s, 1 H), 8.01 (d, *J* = 7.5 Hz, 2 H), 7.64 (d, *J* = 7.0 Hz, 1 H), 7.58–7.51 (m, 4 H), 7.36–7.33 (m, 2 H), 7.11–7.08 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.7, 151.0, 137.6, 133.0, 132.2, 128.9, 128.5, 128.2, 123.7, 119.8.

N-((2-Iodophenyl)carbamoyl)benzamide (2b)

White solid; yield: 0.199 g (95%); R_f = 0.4 (20% EtOAc/*n*-hexane); mp 224–225 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.19 (s, 1 H), 11.03 (s, 1 H), 8.08–8.03 (m, 3 H), 7.90 (d, *J* = 7.5 Hz, 1 H), 7.67–7.64 (m, 1 H), 7.55–7.52 (m, 2 H), 7.42–7.39 (m, 1 H), 6.93–6.90 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.7, 151.3, 139.1, 138.9, 133.1, 132.0, 128.7, 128.5, 128.4, 126.0, 122.7, 90.9.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{12}IN_2O_2$: 366.9943; found: 366.9942.

N-((3-Bromophenyl)carbamoyl)benzamide (2c)

White crystals; yield: 0.171 g (81%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 203–204 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.08 (s, 1 H), 10.87 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.96 (s, 1 H), 7.66–7.63 (m, 1 H), 7.55–7.48 (m, 3 H), 7.30 (d, *J* = 6.5 Hz, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 151.1, 139.2, 133.0, 132.1, 130.8, 128.5, 128.2, 126.3, 122.1, 121.6, 118.8.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{12}BrN_2O_2$: 319.0082; found: 319.0073.

***N*-((3-Fluorophenyl)carbamoyl)benzamide (2d)**

White solid; yield: 0.147 g (69%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 178–180 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.09 (s, 1 H), 10.92 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.66–7.52 (m, 4 H), 7.38–7.31 (m, 2 H), 6.93 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 163.2, 161.2, 151.1, 139.4, 139.3, 133.1, 132.1, 130.6, 130.5, 129.0, 128.6, 128.3, 123.9, 119.8, 115.6, 110.3, 110.1, 106.8, 106.6.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{12}FN_2O_2$: 259.0883; found: 259.0867.

***N*-((4-Chlorophenyl)carbamoyl)benzamide (2e)**[14b]

White solid; yield: 0.179 g (84%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 194–196 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.08 (s, 1 H), 10.85 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.66–7.61 (m, 3 H), 7.54–7.51 (m, 2 H), 7.41–7.38 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 151.1, 136.6, 133.0, 132.2, 128.8, 128.5, 128.2, 127.4, 121.4.

***N*-((3-(Trifluoromethyl)phenyl)carbamoyl)benzamide (2f)**

White solid; yield: 0.131 g (62%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 162–164 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.13 (s, 1 H), 11.00 (s, 1 H), 8.10 (s, 1 H), 8.02 (d, *J* = 7.5 Hz, 2 H), 7.80 (d, *J* = 7.5 Hz, 1 H), 7.67–7.64 (m, 1 H), 7.59–7.52 (m, 3 H), 7.45 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 151.3, 138.5, 133.1, 132.1, 130.1, 129.7, 128.5, 128.3, 123.7, 120.1, 119.8, 116.0.

^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.15.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{15}H_{12}F_3N_2O_2$: 309.0851; found: 309.0847.

2-Iodo-*N*-((2-iodophenyl)carbamoyl)benzamide (2g)

White solid; yield: 0.250 g (89%); R_f = 0.4 (20% EtOAc/*n*-hexane); mp 198–199 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.34 (s, 1 H), 10.65 (s, 1 H), 8.06 (d, *J* = 8.5 Hz, 1 H), 7.93–7.89 (m, 2 H), 7.53–7.47 (m, 2 H), 7.42–7.39 (m, 1 H), 7.26–7.23 (m, 1 H), 6.94–6.91 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 171.1, 150.7, 140.6, 139.2, 139.1, 138.8, 131.8, 128.8, 128.3, 128.0, 126.1, 122.5, 93.1, 90.8.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{11}I_2N_2O_2$: 492.8910; found: 492.8897.

2-Iodo-*N*-(phenylcarbamoyl)benzamide (2h)

White solid; yield: 0.285 g (87%); R_f = 0.4 (20% EtOAc/*n*-hexane); mp 224–225 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.14 (s, 1 H), 10.44 (s, 1 H), 7.92 (d, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.50–7.47 (m, 2 H), 7.36–7.33 (m, 2 H), 7.26–7.18 (m, 1 H), 7.12–7.09 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 171.9, 151.3, 139.8, 137.6, 132.7, 129.89, 129.85, 128.9, 128.7, 125.0, 120.6, 93.0.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{12}IN_2O_2$: 366.9943; found: 366.9934.

***N*-((2-Chlorophenyl)carbamoyl)benzamide (2i)**[14b]

White solid; yield: 0.181 g (85%); R_f = 0.6 (20% EtOAc/*n*-hexane); mp 220–221 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.42 (s, 1 H), 11.25 (s, 1 H), 8.31 (d, *J* = 8.5 Hz, 1 H), 8.03 (d, *J* = 7.5 Hz, 2 H), 7.67–7.64 (m, 1 H), 7.55–7.52 (m, 3 H), 7.38–7.36 (m, 1 H), 7.15–7.12 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.1, 151.1, 134.7, 133.2, 132.0, 129.3, 128.6, 128.4, 127.9, 124.7, 122.4, 121.5.

***N*-((2-Methoxyphenyl)carbamoyl)benzamide (2j)**[29]

White solid; yield: 0.162 g (76%); R_f = 0.4 (20% EtOAc/*n*-hexane); mp 222–223 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.20 (s, 1 H), 11.02 (s, 1 H), 8.20 (d, *J* = 7.5 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.65–7.62 (m, 1 H), 7.54–7.51 (m, 2 H), 7.07–7.06 (m, 2 H), 6.96–6.93 (m, 1 H), 3.88 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.7, 151.0, 148.2, 133.1, 132.3, 128.6, 128.3, 127.1, 123.7, 120.7, 119.3, 110.9, 56.0.

***N*-((2-Bromophenyl)carbamoyl)benzamide (2k)**[30]

White solid; yield: 0.177 g (84%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 216–218 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.31 (s, 1 H), 11.22 (s, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 2 H), 7.69–7.64 (m, 2 H), 7.53 (t, *J* = 7.5 Hz, 2 H), 7.42–7.39 (m, 1 H), 7.09–7.06 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.0, 151.2, 136.0, 133.2, 132.6, 132.0, 128.6, 128.46, 128.42, 125.4, 122.1, 113.2.

***N*-(*m*-Tolylcarbamoyl)benzamide (2l)**[14b]

White solid; yield: 0.169 g (79%); R_f = 0.45 (20% EtOAc/*n*-hexane); mp 167–168 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.01 (s, 1 H), 10.79 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.66–7.63 (m, 1 H), 7.53 (t, *J* = 8.0 Hz, 2 H), 7.39–7.37 (m, 2 H), 7.24–7.21 (m, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 2.30 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.7, 151.0, 138.3, 137.5, 133.0, 132.2, 128.8, 128.5, 128.2, 124.4, 120.2, 116.9, 21.0.

***N*-((2-Fluorophenyl)carbamoyl)benzamide (2m)**

White solid; yield: 0.137 g (64%); R_f = 0.55 (20% EtOAc/*n*-hexane); mp 220–221 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.23 (s, 1 H), 11.16 (s, 1 H), 8.20 (t, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 2 H), 7.66–7.64 (m, 1 H), 7.55–7.52 (m, 2 H), 7.33–7.30 (m, 1 H), 7.22–7.20 (m, 1 H), 7.15–7.13 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.0, 151.3, 151.0, 137.4, 133.1, 132.0, 128.5, 128.3, 125.8, 124.7, 124.37, 124.32, 121.4, 115.2, 115.1.

^{19}F NMR (471 MHz, DMSO-d_6): δ = –124.87.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{12}FN_2O_2$: 259.0883; found: 259.0880.

***N*-((3*S*,5*S*,7*S*)-Adamantan-1-ylcarbamoyl)benzamide (2n)**

White crystals; yield: 0.169 g (80%); R_f = 0.55 (20% EtOAc/*n*-hexane); mp 203–204 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 10.46 (s, 1 H), 8.64 (s, 1 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 7.60–7.58 (m, 1 H), 7.49–7.46 (m, 2 H), 2.04 (s, 3 H), 1.98 (s, 6 H), 1.64 (s, 6 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 151.6, 132.6, 128.4, 128.0, 50.4, 41.2, 35.8, 28.8.

HRMS (ESI$^+$): m/z [M + H] calcd for $C_{18}H_{23}N_2O_2$: 299.1760; found: 299.1732.

***N*-(Undecylcarbamoyl)benzamide (2o)**

Off-white solid; yield: 0.141 g (67%); R_f = 0.45 (20% EtOAc/*n*-hexane); mp 85–87 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 10.62 (s, 1 H), 8.65 (s, 1 H), 7.94 (d, *J* = 7.5 Hz, 2 H), 7.59 (d, *J* = 7.0 Hz, 1 H), 7.49–7.46 (m, 2 H), 3.22–3.15 (m, 2 H), 1.26–1.21 (m, 18 H), 0.83–0.81 (m, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.2, 153.5, 132.7, 132.6, 128.4, 128.1, 67.0, 54.8, 31.3, 29.1, 29.0, 28.74, 28.72, 26.3, 25.1, 22.1, 13.9.

HRMS (ESI$^+$): m/z [M + H] calcd for $C_{19}H_{31}N_2O_2$: 319.2386; found: 319.2362.

1,3-Diphenylurea (3a)[16b]

White crystals; yield: 0.182 g (96%); R_f = 0.35 (20% EtOAc/*n*-hexane); mp 192–193 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.61 (s, 2 H), 7.45 (d, *J* = 8.5 Hz, 4 H), 7.28–7.25 (m, 4 H), 6.97–6.94 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.4, 139.6, 128.7, 121.7, 118.1.

1-(2-Iodophenyl)-3-phenylurea (3b)[31]

White solid; yield: 0.176 g (91%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 182–183 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.39 (s, 1 H), 7.86 (s, 1 H), 7.83–7.80 (m, 2 H), 7.45 (d, *J* = 7.5 Hz, 2 H), 7.34–7.26 (m, 3 H), 6.98–6.95 (m, 1 H), 6.84–6.81 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.3, 139.8, 139.5, 138.9, 128.8, 128.5, 125.0, 123.0, 122.0, 118.1, 91.3.

1,3-Bis(2-iodophenyl)urea (3c)[32]

White solid; yield: 0.217 g (82%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp >220 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.54 (s, 2 H), 7.84 (d, *J* = 7.5 Hz, 2 H), 7.70 (d, *J* = 7.5 Hz, 2 H), 7.33 (t, *J* = 7.5 Hz, 2 H), 6.87–6.84 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.8, 139.8, 138.9, 128.5, 125.6, 124.4, 92.5.

HRMS (ESI$^+$): m/z [M + H] calcd for $C_{13}H_{11}I_2N_2O$: 464.8961; found: 464.8936.

1-(2-Iodophenyl)-3-phenylurea (3d)[31]

White solid; yield: 0.260 g (86%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 182–183 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.40 (s, 1 H), 7.86 (s, 1 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.35–7.26 (m, 3 H), 6.98–6.95 (m, 1 H), 6.82 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.3, 139.8, 139.5, 138.9, 128.8, 128.5, 125.0, 123.0, 121.9, 118.1, 91.3.

1-(2-Bromophenyl)-3-phenylurea (3e)[33]

White solid; yield: 0.216 g (83%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 171–173 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.44 (s, 1 H), 8.11 (s, 1 H), 8.06–8.04 (m, 1 H), 7.61–7.59 (m, 1 H), 7.45 (d, *J* = 7.5 Hz, 2 H), 7.34–7.27 (m, 3 H), 6.99–6.94 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.1, 139.4, 137.0, 132.4, 128.8, 128.0, 124.0, 122.2, 122.1, 118.2, 113.0.

1-(2,5-Dibromophenyl)-3-phenylurea (3f)

White solid; yield: 0.166 g (85%); R_f = 0.45 (20% EtOAc/*n*-hexane); mp 205–206 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.59 (s, 1 H), 8.35 (d, *J* = 1.5 Hz, 1 H), 8.25 (s, 1 H), 7.56 (d, *J* = 9.0 Hz, 1 H), 7.46 (d, *J* = 8.5 Hz, 2 H), 7.29 (t, *J* = 7.5 Hz, 2 H), 7.15–7.12 (m, 1 H), 7.01 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 151.9, 139.1, 138.6, 134.0, 128.9, 126.2, 123.5, 122.3, 120.7, 118.3, 111.2.

HRMS (ESI$^+$): m/z [M + H] calcd for $C_{13}H_{11}Br_2N_2O$: 370.9218; found: 370.9190.

1-(3-Bromophenyl)-3-phenylurea (3g)[34]

White crystals; yield: 0.156 g (81%); R_f = 0.3 (20% EtOAc/*n*-hexane); mp 172–173 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.84 (s, 1 H), 8.71 (s, 1 H), 7.86 (s, 1 H), 7.45 (d, *J* = 7.5 Hz, 2 H), 7.30–7.25 (m, 3 H), 7.23–7.20 (m, 1 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 6.98–6.95 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.3, 141.3, 139.3, 130.6, 128.7, 124.2, 122.0, 121.6, 120.3, 118.3, 116.9.

1-(2-Methoxyphenyl)-3-phenylurea (3h)[16b]

White crystals; yield: 0.162 g (85%); R_f = 0.35 (20% EtOAc/*n*-hexane); mp 144–148 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.30 (s, 1 H), 8.22 (s, 1 H), 8.14 (d, *J* = 7.5 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 7.5 Hz, 2 H), 6.99–6.87 (m, 4 H), 3.85 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.4, 147.6, 139.8, 128.8, 128.7, 121.8, 121.7, 120.5, 118.3, 117.9, 110.7, 55.7.

1-(2-Bromophenyl)-3-phenylurea (3i)[33]

White crystals; yield: 0.152 g (79%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 171–173 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.44 (s, 1 H), 8.12 (s, 1 H), 8.06–8.05 (m, 1 H), 7.61–7.59 (m, 1 H), 7.46–7.44 (m, 2 H), 7.34–7.27 (m, 3 H), 6.99–6.94 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.1, 139.4, 137.0, 132.4, 128.8, 128.0, 124.0, 122.1, 122.0, 118.1, 112.9.

1-(2-Fluorophenyl)-3-phenylurea (3j)[35]

White crystals; yield: 0.145 g (76%); R_f = 0.5 (20% EtOAc/*n*-hexane); mp 176–177 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.06 (s, 1 H), 8.53 (s, 1 H), 8.15–8.12 (m, 1 H), 7.44 (d, *J* = 7.5 Hz, 2 H), 7.29–7.20 (m, 3 H), 7.14–7.11 (m, 1 H), 6.99–6.97 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 152.9, 152.1, 150.9, 139.4, 128.8, 127.59, 127.51, 124.4, 122.3, 122.0, 120.4, 118.0, 115.0, 114.8.

^{19}F NMR (471 MHz, DMSO-d_6): δ = –125.22.

***S*-Phenyl Phenylcarbamothioate (4a)**[36]

Off-white solid; yield: 0.174 g (85%); R_f = 0.8 (20% EtOAc/*n*-hexane); mp 105–106 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.60 (m, 2 H), 7.46–7.45 (m, 3 H), 7.37–7.36 (m, 2 H), 7.31–7.28 (m, 2 H), 7.12–7.09 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.3, 137.4, 135.5, 129.9, 129.5, 129.1, 127.9, 124.6, 119.5.

S-o-Tolyl Phenylcarbamothioate (4b)[37]

White solid; yield: 0.174 g (80%); R_f = 0.8 (20% EtOAc/*n*-hexane); mp 137–138 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.5 Hz, 1 H), 7.31–7.27 (m, 3 H), 7.22–7.17 (m, 4 H), 7.03–6.98 (m, 2 H), 2.42 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.0, 143.0, 137.5, 137.0, 131.1, 130.7, 129.1, 127.5, 127.0, 124.5, 119.4, 20.8.

S-p-Tolyl 3,5-Dimethylphenylcarbamothioate (4c)

White solid; yield: 0.166 g (77%); R_f = 0.85 (20% EtOAc/*n*-hexane); mp 112–114 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.46 (m, 2 H), 7.25–7.24 (m, 2 H), 6.98 (s, 3 H), 6.72 (s, 1 H), 2.39 (s, 3 H), 2.24 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.6, 140.3, 138.8, 137.3, 135.5, 130.3, 126.2, 124.6, 117.1, 21.3, 21.2.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{16}H_{18}NOS$: 272.1109; found: 272.1066.

Phenyl m-Tolylcarbamate (5a)

White solid; yield: 0.086 g (45%); R_f = 0.7 (20% EtOAc/*n*-hexane); mp 103–106 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 8.0 Hz, 2 H), 7.24–7.11 (m, 6 H), 6.85 (s, 2 H), 2.27 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.4, 150.5, 139.1, 137.2, 129.3, 128.9, 125.6, 124.7, 121.6, 119.3, 115.8, 21.4.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{14}NO_2$: 228.1020; found: 228.1024.

4-Bromophenyl m-Tolylcarbamate (5b)

White solid; yield: 0.129 g (50%); R_f = 0.7 (20% EtOAc/*n*-hexane); mp 110–112 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 2 H), 7.28 (s, 1 H), 7.24–7.21 (m, 2 H), 7.09–7.07 (m, 2 H), 6.94–6.89 (m, 2 H), 2.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.0, 149.6, 139.1, 136.9, 132.3, 129.0, 124.9, 123.4, 119.4, 118.6, 115.8, 21.4.

HRMS (ESI$^+$): *m*/*z* [M + H] calcd for $C_{14}H_{13}BrNO_2$: 306.0125; found: 306.0118.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1399-3823. Included are copies of ^{1}H and ^{13}C NMR spectra for all developed ureas and their derivatives, carbamates, and thiocarbamates.

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