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A Synthetic Approach to *N*-Aryl Carbamates via Copper-Catalyzed Chan–Lam Coupling at Room Temperature

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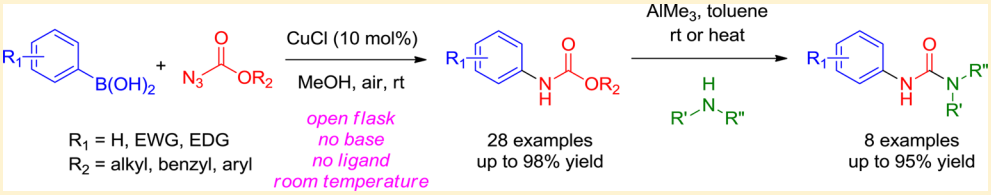
Supporting Information



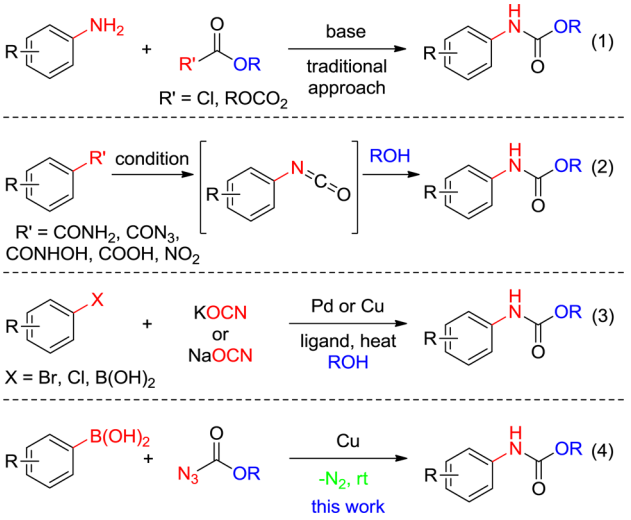
ABSTRACT: A mild and efficient synthesis of *N*-arylcarbamates was achieved by reacting azidoformates with boronic acids in the presence of 10 mol % of copper chloride catalyst. The reaction proceeds readily in an open flask at room temperature without additional base, ligand, or additive. Rapid access to urea analogues via a two-step one-pot procedure is enabled by reacting *N*-arylcarbamates with aluminum–amine complexes. In addition, among several boronic acid derivatives prepared, dimethylphenyl boronate was found to react rapidly in its reaction with benzyl azidoformate, invoking *in situ* generation of this species in the catalytic cycle.

INTRODUCTION

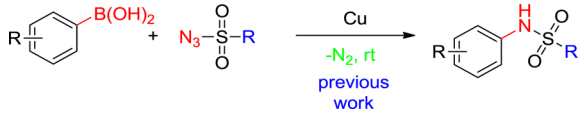
Carbamates are an important class of compounds found in pharmaceuticals[1] and agrochemicals,[2] such as pesticides, herbicides, insecticides, and fungicides. They serve as chemical intermediates in organic synthesis, protecting groups for amino functionalities, and linkers in combinatorial chemistry.[3] Thus, considerable synthetic attention has been paid to the formation of the carbamate linkage, which traditionally involved either the amination of phosgene and phosgene derivatives such as acid anhydrides and chloroformates (Scheme 1, eq 1),[4] the use of alcohols with isocyanates generated *in situ* via Hofmann,[5] Curtius,[6] Lossen,[7] and Schmidt[8] rearrangement reactions, or the reductive carbonylation of nitroaromatics (Scheme 1, eq 2).[9] Even though these approaches are generally employed, the *in situ* generation of aryl isocyanates via the copper- or palladium-catalyzed cross-coupling of aryl boronic acids or aryl halides with potassium and sodium cyanates under elevated temperatures has been investigated in order to avoid the use of toxic reagents and the generation of byproducts (Scheme 1, eq 3).[10]

Recently, we have successfully demonstrated a Cu-catalyzed Chan–Lam coupling reaction between sulfonyl azides and boronic acids in our efforts to improve methods for *N*-arylsulfonamide synthesis (Scheme 2).[11]

Scheme 1. Synthesis of *N*-Arylcarbamates



Scheme 2. Previously Reported Chan–Lam Coupling between Sulfonyl Azides and Boronic Acids



Seeking to expand upon this work, we envisioned an alternative approach to contribute to the existing methods of carbamate synthesis. We were hopeful that our reaction, unlike previously reported methods, would proceed under neutral and mild conditions at room temperature without the need for any acid, base, or ligand additive and would not require an exotic or expensive catalyst (Scheme 1, eq 4). The *N*-arylcarbamates produced by our method can be further functionalized with

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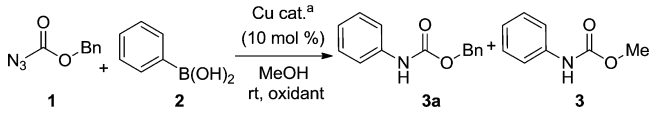
Table 1. Optimization of the *N*-Arylation Reaction of Benzyl Azidoformate 1 with Phenylboronic Acid 2[a]



entry	Cu cat.	equiv of **2**	oxidant	solvent	time (h)	yield **3a** (%)[b]	yield **3** (%)[b]
1	CuCl	1.0[c]	air	MeOH	4	70	4
2	CuCl	1.2	air	MeOH	4	84	4
3	CuCl	1.5	air	MeOH	4	88	4
4	CuCl	1.8	air	MeOH	2	91	4
5	CuCl	2.0	air	MeOH	1	94	4
6	CuCl[d]	2.0	air	MeOH	2	78	4
7	$CuBr{\cdot}S(Me)_2$	2.0	air	MeOH	1	85	3
8	CuBr	2.0	air	MeOH	3	87	3
9	$Cu(OAc)_2$	2.0	air	MeOH	2	79	4
10	$CuS0_4$	2.0	air	MeOH	24	20	3
11	$CuCI_2$	2.0	air	MeOH	12	84	5
12	$CuBr_2$	2.0	air	MeOH	24	0	0
13	CuCI	2.0	Ag_2CO_3	MeOH	24	20	4
14	CuCI	2.0	$K_2S_2O_8$	MeOH	24	83	4
15	CuCI	2.0	O_2	MeOH	1	90	3
16	CuCI	2.0		MeOH	2	92	4
17	none	2.0	air	MeOH	24	0	0
18	CuCI	2.0	air	EtOH	24	13	0
19	CuCI	2.0	air	^{i}PrOH	24	0	0
20	CuCI	2.0	O_2	CH_2CI_2	24	0	0
21	CuCI	2.0	air	BnOH	24	>5	0

[a]Reaction conditions: 1.0 mmol of benzyl azidoformate, MeOH (0.5 M), rt. [b]Isolated yield. [c]1.0 mmol of phenylboronic acid, 1.2 mmol of benzyl azidoformate. [d]5 mol % of CuCl.

aluminum−amine complexes to urea analogues in a single flask. Furthermore, to the best of our knowledge, the Cu-catalyzed Chan−Lam coupling reaction of azidoformates or acyclic carbamates with boronic acids at room temperature has not yet been reported, and while organic azides are widely used as an amine source in general organic synthesis, special precautions are still required.[12] With these considerations in mind, we herein report a mild and efficient synthesis of *N*-arylcarbamates using boronic acids and azidoformates.

RESULTS AND DISCUSSION

Optimization of the Cu-catalyzed Chan−Lam coupling was initiated at room temperature employing benzyl azidoformate **1** and phenylboronic acid **2** (Table 1). When phenylboronic acid **2** was utilized as a limiting reagent in the presence of 10 mol % of CuCl, desired *N*-arylcarbamate **3a** was isolated in moderate yield, along with trace amounts of methyl *N*-arylcarbamate **3** derived from the transesterification of **3a** with MeOH (Table 1, entry 1). However, when an excess of boronic acid was used, the coupled product **3a** was obtained in 84, 88, and 91% yield (Table 1, entries 2−4). Finally, the use of 2.0 equiv of boronic acid furnished **3** in 94% yield in 1 h (Table 1, entry 5). In addition, a lower catalyst loading of 5 mol % CuCl afforded the desired carbamate in a lower 78% yield (Table 1, entry 6). When various copper(I) catalysts, such as $CuBr{\cdot}S(Me)_2$ and CuBr, and copper(II) catalysts, such as $Cu(OAc)_2$, $CuSO_4$, $CuCl_2$, and $CuBr_2$, were investigated in MeOH, all proved inferior to CuCl in terms of yield and reaction time (Table 1, entries 7−12). Although performing the reaction in an open flask proved suitable for this transformation, different oxidants were nevertheless screened under Schlenk conditions. Thus, when Ag_2CO_3, $K_2S_2O_8$, and pure oxygen in the place of air were employed, lower yields were obtained (Table 1, entries 13−15). Additionally, under an argon atmosphere, the reaction afforded the desired product in a slightly lower 92% yield in 2 h (Table 1, entry 16), and in the absence of a copper catalyst, the reaction failed to take place at all (Table 1, entry 17). In addition, running the reaction in ethanol afforded the desired product **3a** in poor 13% yield in 24 h (Table 1, entry 18), and the use of isopropanol, dichloromethane, and benzyl alcohol as solvent afforded product either in trace amounts or not at all (Table 1, entries 19−21).

With optimized conditions in hand, we began to examine the scope of the Cu-catalyzed Chan−Lam coupling with respect to various boronic acids (Table 2). Most of the reactions utilizing the optimized conditions furnished good to excellent yields in an open flask at room temperature. In general, arylboronic acids with electron-neutral and electron-donating alkyl, alkoxy, and alkenyl groups afforded the desired products **3a**−**3f** in high yields ranging from 87 to 95%. Naphthalene and methylenedioxy substituted arylboronic acids also displayed good reactivity, affording good yields, with the latter requiring a slightly longer reaction time to afford **3i** and **3j**. On the other hand, the *ortho*-substituted methoxy and methyl arylboronic acids furnished the desired products **3g** and **3h** in 23% and 42% yield with 41% and 58% conversion, respectively. It is hypothesized here that the low yield is due to either the chelation of the metal catalyst to the methoxy group or the moderate steric crowding provided by the *ortho*-methyl group slowing down the rate of the desired coupling. Consequently, undesired and competing homocoupling of the boronic acid can take place with complete consumption of the boronic acid.[13] When arylboronic acids containing electron-withdrawing groups were used as coupling partners, they showed less

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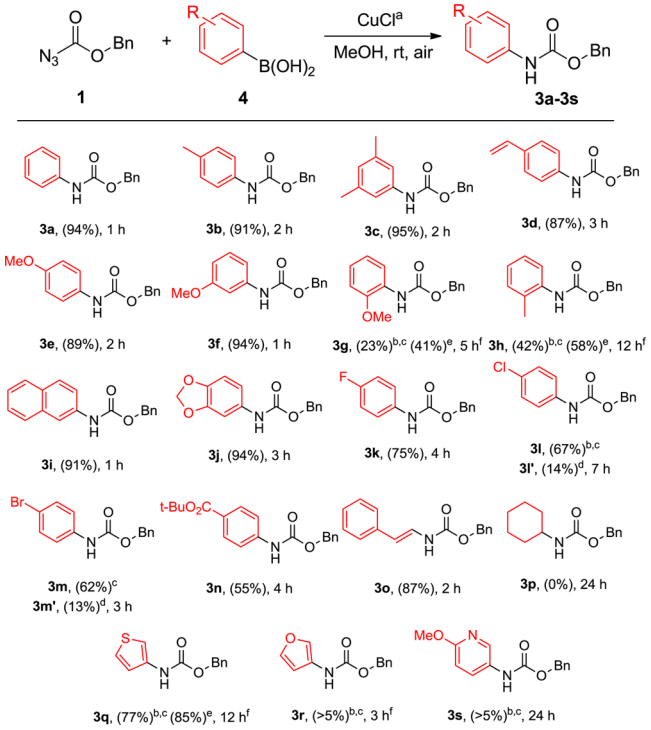
Table 2. Cu-Catalyzed *N*-Arylation of Benzyl Azidoformate 1 with Boronic Acids 4[a,b,c,d,e,f]

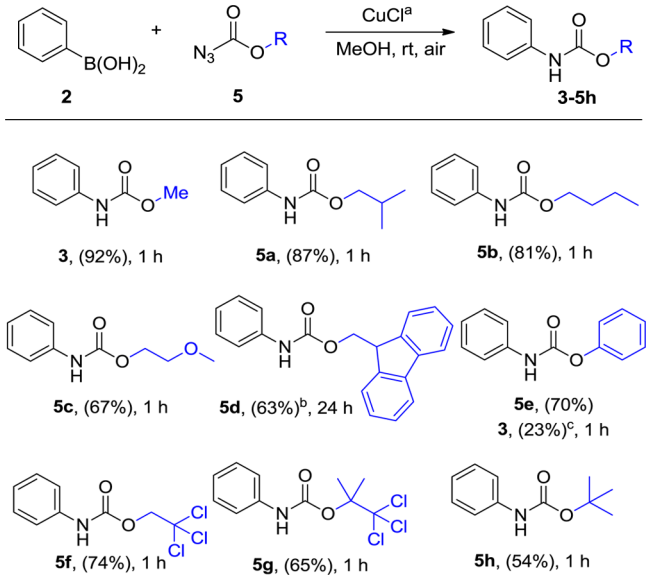


[a]Reaction conditions: 1.0 mmol of benzyl azidoformate, 2.0 mmol boronic acid, 10 mol % of CuCl, MeOH (0.5 M), air, rt. [b]2.5 mmol of boronic acid. [c]20 mol % of CuCl. [d]Trace amounts of methyl *N*-arylcarbamate was observed unless otherwise noted. [e]Conversion. [f]Reaction time based on complete consumption of boronic acid as determined by TLC analysis.

reactivity and provided lower yields of **3k**, **3l**, and **3m**. Particularly, when arylboronic acids bearing a chloro or bromo group were used, the reaction did not go to completion due to competitive homocoupling of the arylboronic acid. The use of 2.5 equiv of the arylboronic acid with CuCl (20 mol %), however, furnished full conversion and gave the desired carbamates **3l** and **3m**, along with a significant amount of methyl *N*-arylcarbamate **3l′** and **3m′**, respectively. The tolerance of halo groups under the optimized conditions is especially meaningful due to their potential for use in sequential catalytic cross-coupling reactions. Non-aryl boronic acids such as (*E*)-styrylboronic acid tolerated the reaction conditions, furnishing the desired product **3o** in 87% yield after 2 h. Cyclohexylboronic acid, however, was unsuitable; the desired product **3p** was not formed even after 24 h. In the reaction between benzyl azidoformate **1** and 3-thienylboronic acid, a good yield of 77% was obtained in 12 h with 85% conversion using 20 mol % of CuCl to furnish **3q**. Use of furan-3-ylboronic acid and 2-methoxy-5-pyridineboronic acid afforded less than 5% of the desired carbamates **3r** and **3s**.

Next, we turned our attention to the *N*-arylation of phenylboronic acid **2** with a variety of azidoformates **5** for the preparation of various carbamate protecting groups such as the Fmoc, Troc, and Boc group. As shown in Table 3, most of

Table 3. Cu-Catalyzed *N*-Arylation of Phenylboronic Acid 2 with Various Azidoformates 5[a,b,c]



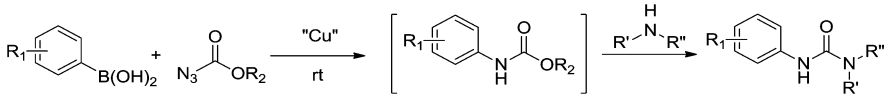
[a]Reaction conditions: 1.0 mmol of benzyl azidoformate, 2.0 mmol of phenylboronic acid, 10 mol % of CuCl, MeOH (0.5 M), air, rt. [b]MeOH:CH_2Cl_2 = 1:1. [c]Trace amounts of methyl *N*-arylcarbamate was observed unless otherwise noted.

the reactions readily proceeded at room temperature to yield the desired carbamate product in moderate to excellent yields within 1 h except for Fmoc azidoformate, which required a considerably longer reaction time to reach completion due to its poor solubility in MeOH. However, addition of CH_2Cl_2 to the reaction solvent afforded the corresponding Fmoc carbamate **5d** in 63% yield in 24 h. Interestingly, when phenyl azidoformate was used as a coupling partner, a considerable amount of methyl *N*-arylcarbamate **3** was isolated in 23% yield alongside **5e** (70%), presumably due to the good leaving group ability of the phenol moiety. Use of *tert*-butyl azidoformate under the optimized reaction conditions afforded Boc carbamate **5h** in a moderate yield of 54%.

Encouraged by the viability of the Cu-catalyzed Chan–Lam reaction for the synthesis of *N*-arylcarbamates, we next turned our attention to the preparation of the *N*,*N*′-unsymmetrical substituted ureas[14] present in many biologically active compounds in a two-step one-pot process (Scheme 3). This would allow synthesis of *N*,*N*′-unsymmetrical ureas directly from boronic acids. We, therefore, decided to modify the established method, demonstrated by Clapham, Janda, and co-workers, for the preparation of ureas from *N*-arylcarbamates.[15]

Pleasingly, addition of an aluminum–amine complex, prepared from amines and trimethylaluminum, to the aforementioned *N*-arylcarbamates obtained via the Cu-catalyzed Cham–Lam coupling furnished multicomponent

Scheme 3. Synthesis of *N*-Aryl *N*′-Ureas from Boronic Acids and Azidoformates



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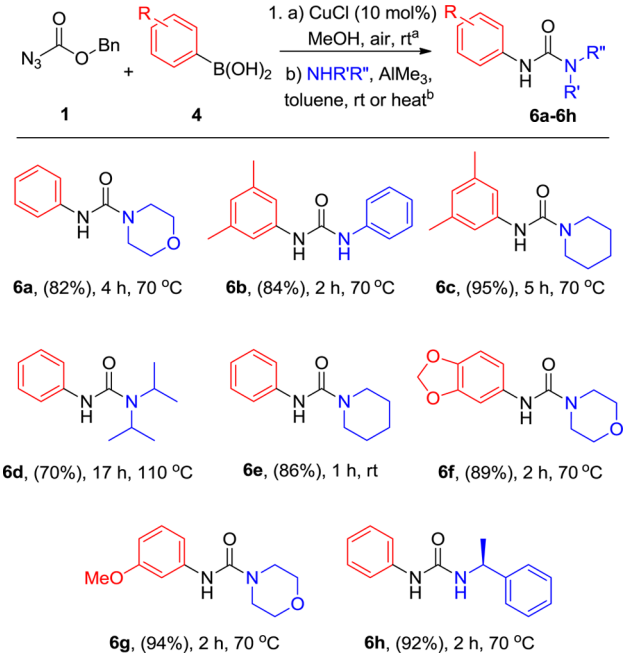
adducts **6a**–**6h** in yields ranging from 70 to 94% (Table 4).[16] In most instances, when heated at 70 °C, the benzyl carbamate (Cbz) intermediate directly proceeded into the corresponding urea in the presence of primary and secondary amines within 1–5 h. Even milder reaction conditions proved optimal in the reaction between the crude benzyl carbamate (Cbz) intermediate and piperidine, affording the desired urea **6e** in 86% yield in 1 h at room temperature. However, in the case of diisopropylamine, the reaction went to completion, affording **6d** only when heated at 110 °C for 17 h, presumably due to the low nucleophilicity. In addition, a chiral primary amine could form the corresponding urea **6h** with some epimerization (11% loss of ee down to 87% ee).

Table 4. Two-Step One-Pot Synthesis of Urea Derivatives from Boronic Acids[a,b]

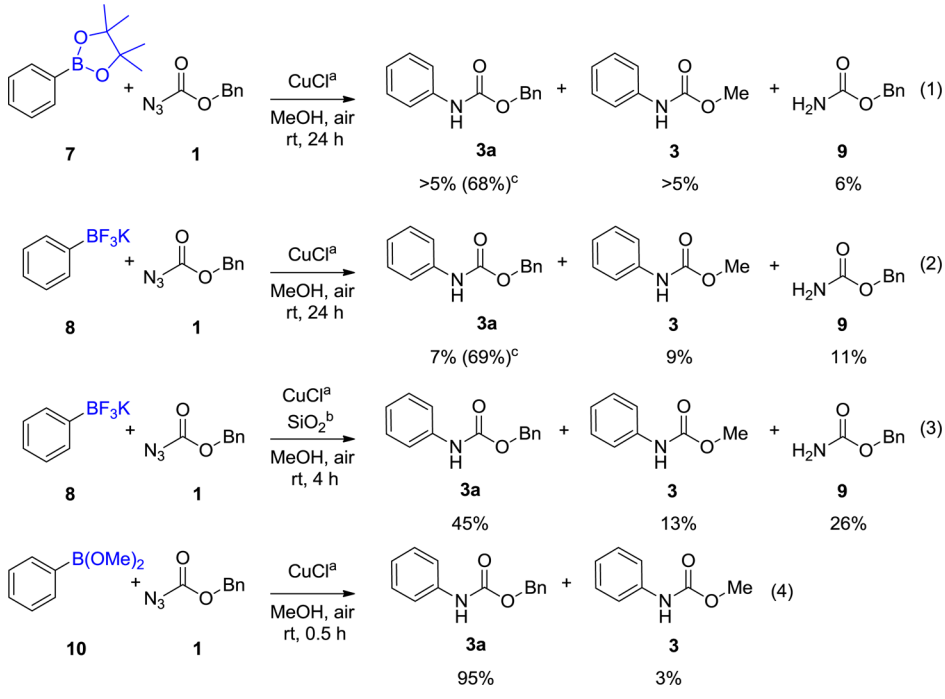


[a]Reaction conditions: 1.0 mmol of benzyl azidoformate, 2.0 mmol of phenylboronic acid, 10 mol % of CuCl, MeOH (0.5 M), air, rt. [b]Reaction conditions: 3.0 mmol of amine, 2.5 mmol of $AlMe_3$ in toluene (2.0 M), toluene (0.5 M), argon.

To further investigate the scope of this Cu-catalyzed Chan–Lam coupling utilizing azidoformate, various phenylboronic acid derivatives were used as a coupling partner under the optimized conditions (Scheme 4). When either pinacol phenylboronate **7** or potassium phenyltrifluoroborate **8** was used, reaction times were longer and the desired *N*-arylcarbamate **3a** and **3** were obtained in 6% and 11% yield, respectively; benzyl carbamate **9** derived from reduction of the azide was also formed (Scheme 4, eqs 1 and 2). Addition of a catalytic amount of silica gel to the reaction with trifluoroborate **8** accelerated the reaction significantly, affording carbamate **3a** and **3** in 45% and 13% yield along with the significant amount of benzyl carbamate **9** in 4 h (Scheme 4, eq 3). Finally, when dimethyl phenylboronate **10** was reacted with benzyl azidoformate **1**, the desired carbamate **3a** was furnished in 95% yield in 0.5 h (Scheme 4, eq 4).

From the outset of this work, it was recognized that the use of azides as an amine source for a Chan–Lam type reaction with boronic acids could be anticipated. With this in mind, a control experiment where benzyl carbamate **9** and phenylboronic acid **2** were reacted under traditional Chan–Lam coupling conditions[17] was designed, to highlight the unique necessity of the azidoformate functionality in preparation of *N*-

Scheme 4. Cu-Catalyzed *N*-Arylation of Benzyl Azidoformate 1 with Boronic Acid Derivatives[a,b,c]



[a]Reaction conditions: 1.0 mmol of benzyl azidoformate, 2.0 mmol of boronic acid derivative, 10 mol % of CuCl, MeOH (0.5 M), air, rt. [b]20 mol % of SiO_2 was used as an additive. [c]Conversion.

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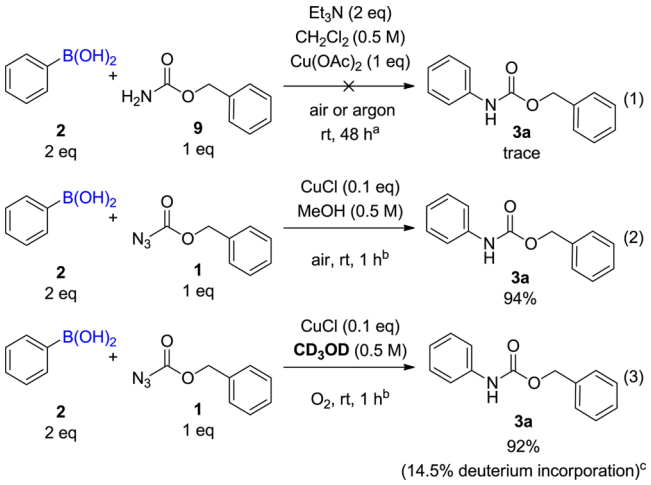
aryl carbamates. Under these reaction conditions and despite the prolonged reaction time of 48 h, the desired carbamate was found only in trace amounts (Scheme 5, eq 1). On the other hand, under the optimized conditions employing benzyl azidoformate **1** and phenylboronic acid **2**, the desired carbamate **3a** was afforded in 94% in only 1 h (Scheme 5, eq 2). Next, to investigate the proton source required for the azide reduction, we repeated the reaction using methanol-d_4 as a solvent and oxygen gas as the reaction atmosphere. (Scheme 5, eq 3). To our surprise, although the desired product **3a** was isolated in 92% yield after a reaction time of 1 h, we found only 14.5% deuterium incorporation in the final product. In consideration of this result, it can be hypothesized that both the solvent and the boronic acid can act as a proton source.

Scheme 5. Control Experiments[a,b,c]

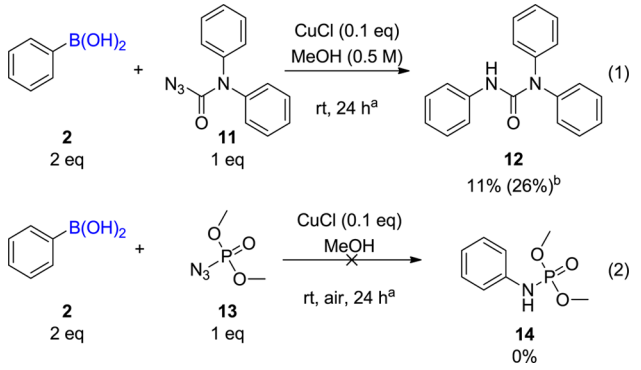


[a]Reaction conditions: 1.0 mmol of benzyl carbamate, 2.0 mmol of phenylboronic acid, 1.0 mmol of $Cu(OAc)_2$, 2.0 mmol of Et_3N, MeOH (0.5 M), air or Ar, rt. [b]Reaction conditions: 1.0 mmol of benzyl azidoformate, 2.0 mmol of phenylboronic acid, 10 mol % of CuCl, MeOH or MeOD (0.5 M), air, rt. [c]Deuterium incorporation was determined by Mass-Spec analysis. For details, see the Supporting Information.

Encouraged by the feasibility of Cu-catalyzed Chan–Lam reactions using azidoformates as coupling partners for boronic acids, we investigated the use of organic azides for the direct preparation of ureas. Thus, in the reaction of diphenylcarbamoyl azide **11** with phenylboronic acid **2**, urea **12** was furnished in 11% yield after 24 h, with 26% conversion (Scheme 6, eq 1). Despite this poor result, we next investigated the feasibility of direct phosphoramide synthesis from its azide. In the reaction between phenylboronic acid **2** and dimethyl phosphorazidate **13**, no phosphoramide **14** was formed, suggesting that the reaction conditions optimized in this report may be limited to reactions with azidoformates.

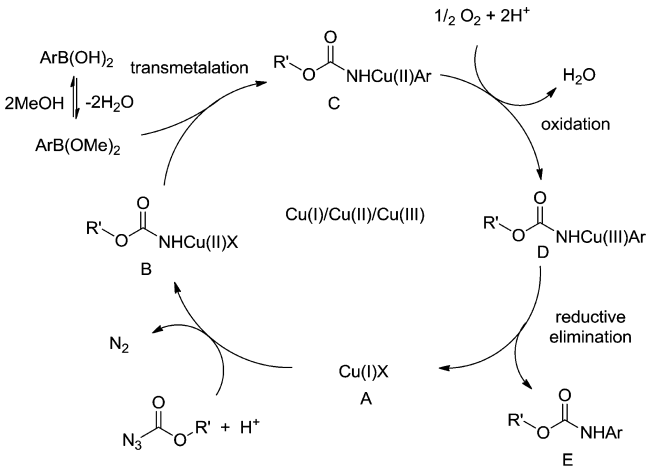
We propose the following mechanism for the coupling reaction between azidoformates and boronic acids (Scheme 7).[18] Reaction of Cu(I) salt **A** and an azidoformate yields Cu(II) complex **B** via copper nitrene formation.[19] The aryl boronic acid, meanwhile, is in equilibrium with the methyl boronate ester,[20] which can undergo transmetalation with **B** to afford Cu(II) complex **C**. Oxidation of **C** can in turn afford Cu(III) complex **D**, and final reductive elimination would furnish the coupled product carbamate **E** regenerating Cu(I) catalyst **A** in the process.

Scheme 6. Direct Synthesis of Urea and Phosphoramide from Organic Azides[a,b]



[a]Reaction conditions: 1.0 mmol of azide, 2.0 mmol of phenylboronic acid, 10 mol % of CuCl, MeOH (0.5 M), air, rt. [b]Conversion.

Scheme 7. Plausible Mechanism



CONCLUSION

In conclusion, we have described a new synthetic method for the preparation of *N*-arylcarbamates via Cu-catalyzed Chan–Lam C–N cross-coupling reactions under neutral conditions. The reaction requires 10 mol % of CuCl catalyst in an open flask at room temperature, without the need for any additional additives. The scope of this method has been explored employing different azidoformates and boronic acids. Furthermore, it was found that *N*-arylcarbamates prepared in this manner from boronic acids can be converted into *N*-aryl *N*′-ureas via a two-step one-pot reaction by treatment with aluminum–amine complexes. The rapid reaction of dimethylphenyl boronate with azidoformate under the optimized conditions has been demonstrated, presumably indicating the reactive species for the transmetalation step in the catalytic cycle. Direct synthesis of *N*-aryl *N*′-ureas and phosphoramides from their corresponding azides remains a challenge, and research into this matter is ongoing in our laboratory.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise indicated, all chemical reagents were purchased from commercial suppliers and were used without further purification. All reactions were carried out in oven-dried glassware equipped with a magnetic stir bar. Reactions were monitored by thin-layer chromatography (TLC) with 0.25 mm precoated silica gel plates (Kieselgel $60F_{254}$). Products were detected

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by viewing under a UV light, by staining with an anisaldehyde solution composed of acetic acid, sulfuric acid, and MeOH, or by staining with a $KMnO_4$ solution composed of potassium carbonate, sodium hydroxide, and water. Flash column chromatography was performed on silica gel (70−230 mesh). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. ^{1}H and ^{13}C spectra were recorded on a 300 or 500 MHz NMR spectrometer. Chemical shifts are reported as δ values relative to internal $SiMe_4$ or chloroform (δ 0.00 for ^{1}H and δ 77.0 for ^{13}C) or DMSO-d_6 (δ 2.50 for ^{1}H and δ 39.5 for ^{13}C). IR spectra were measured as neat oils and solids on an FT-IR spectrometer. HRMS data were obtained by electron ionization with a double-focusing high-resolution magnetic sector mass analyzer and electrospray ionization with a time-of-flight mass analyzer.

Preparation of Azidoformate Precursors. Benzyl azidoformate,[21] methyl azidoformate,[22] 2-methoxyethyl azidoformate,[23] (9*H*-fluoren-9-yl)methyl azidoformate,[24] phenyl azidoformate,[25] 2,2,2-trichloroethyl azidoformate,[26] 1,1,1-trichloro-2-methylpropan-2-yl azidoformate,[26] and *tert*-butyl azidoformate[27] were prepared as according to cited literature procedures. Synthesis of *iso*-butyl azidoformate and butyl azidoformate is as follows:

iso-Butyl Azidoformate. To a solution of *iso*-butyl chloroformate (1.37 g, 10.0 mmol) in acetone was added sodium azide (0.759 g, 11.7 mmol), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was then filtered and washed with acetone, and solvent was removed *in vacuo* to afford *iso*-butyl azidoformate (1.40 g, 9.8 mmol, 98%) as a colorless oil. R_f 0.67 (hexane/ethyl acetate = 4:1); IR (neat) 2967, 2878, 2415, 2139, 1732, 1470, 1380, 1247, 995, 754, 562 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (d, J = 6.69 Hz, 2H), 2.09−1.92 (m, 1H), 0.95 (d, J = 6.77 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 74.5, 27.7, 18.8; HRMS-EI: m/z 143.0689 [M^+; calcd for $C_5H_9O_2N_3^+$: 143.0695].

Butyl Azidoformate. To a solution of butyl chloroformate (1.37 g, 10.0 mmol) in acetone was added sodium azide (0.759 g, 11.7 mmol), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was then filtered and washed with acetone, and solvent was removed *in vacuo* to afford butyl azidoformate (1.42 g, 9.9 mmol, 99%) as a colorless oil. R_f 0.68 (hexane/ethyl acetate = 4:1); IR (neat) 2965, 2186, 2137, 1730, 1249, 1060, 1021, 948, 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (t, J = 6.66 Hz, 2H), 1.71−1.59 (m, 2H), 1.45−1.31 (m, 2H), 0.94 (t, J = 7.34 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 68.5, 30.4, 18.8, 13.6; HRMS-EI: m/z 143.0689 [M^+; calcd for $C_5H_9O_2N_3^+$: 143.0695].

General Procedure I for Synthesis of *N*-Arylcarbamates. A 10 mL round-bottom flask was charged with arylboronic acid (2.0 mmol), CuCl (10 mol %) and the corresponding azidoformate (1.0 mmol). MeOH (2 mL) was then added to the flask. The reaction mixture was stirred at room temperature in an open flask. After completion of the reaction as monitored by TLC analysis, the solvent was removed *in vacuo* and the residue was purified by flash column chromatography on silica gel to obtain the desired product.

*Benzyl Phenylcarbamate (**3a**).* General procedure **I** was used employing phenylboronic acid (0.245 g, 2.02 mmol) and benzyl azidoformate (0.179 g, 1.01 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3a** (0.216 g, 0.95 mmol, 94%) as a pale yellow solid. R_f 0.55 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.28 (m, 9H), 7.07 (t, J = 7.2 Hz, 1H), 6.68 (br, 1H), 5.21 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 137.7, 135.9, 128.9, 128.5, 128.2, 128.17, 123.4, 118.7, 66.9; Data are consistent with those reported in the literature.[28]

*Benzyl p-Tolylcarbamate (**3b**).* General procedure **I** was used employing *p*-tolylboronic acid (0.283 g, 2.08 mmol) and benzyl azidoformate (0.184 g, 1.04 mmol), and the reaction was complete in 2 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3b** (0.229 g, 0.95 mmol, 91%) as a white solid. R_f 0.49 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.33 (m, 5H), 7.26 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.61 (br, 1H), 5.19 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 136.1, 135.1, 133.1, 129.5, 128.6, 128.3, 128.28, 118.8, 66.9, 20.7; Data are consistent with those reported in the literature.[28]

*Benzyl (3,5-Dimethylphenyl)carbamate (**3c**).* General procedure **I** was used employing (3,5-dimethylphenyl)boronic acid (0.303 g, 2.02 mmol) and benzyl azidoformate (0.179 g, 1.01 mmol), and the reaction was complete in 2 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3c** (0.245 g, 0.96 mmol, 95%) as a pale yellow solid. R_f 0.54 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.31 (m, 5H), 7.01 (s, 2H), 6.71 (d, J = 0.6 Hz, 1H), 6.57 (br, 1H), 5.19 (s, 2H), 2.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 138.6, 137.5, 136.1, 128.5, 128.2, 128.19, 125.17, 116.4, 66.8, 21.3; Data are consistent with those reported in the literature.[29]

*Benzyl (4-Vinylphenyl)carbamate (**3d**).* General procedure **I** was used employing 4-vinylphenylboronic acid (0.311 g, 2.10 mmol) and benzyl azidoformate (0.186 g, 1.05 mmol), and the reaction was complete in 3 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3d** (0.231 g, 0.91 mmol, 87%) as a white solid. R_f 0.55 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.31 (m, 9H), 6.85 (br, 1H), 6.64 (dd, J = 17.7 and 11.1 Hz, 1H), 5.64 (d, J = 17.4 Hz, 1H), 5.19−5.13 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 137.3, 136.0, 135.9, 132.9, 128.5, 128.3, 128.2, 126.8, 118.6, 112.6, 67.0; Data are consistent with those reported in the literature.[30]

*Benzyl (4-Methoxyphenyl)carbamate (**3e**).* General procedure **I** was used employing 4-methoxyphenylboronic acid (0.304 g, 2.00 mmol) and benzyl azidoformate (0.177 g, 1.00 mmol), and the reaction was complete in 2 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3e** (0.229 g, 0.89 mmol, 89%) as a pale yellow solid. R_f 0.20 (hexane/ethyl acetate = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.27 (m, 7H), 6.84 (d, J = 9.0 Hz, 2H), 6.58 (br, 1H), 5.18 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 153.9, 136.2, 130.9, 128.6, 128.5, 128.3, 120.8, 114.3, 66.9, 55.5; Data are consistent with those reported in the literature.[28]

*Benzyl (3-Methoxyphenyl)carbamate (**3f**).* General procedure **I** was used employing 3-methoxyphenylboronic acid (0.322 g, 2.12 mmol) and benzyl azidoformate (0.188 g, 1.06 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3f** (0.257 g, 1.00 mmol, 94%) as a yellow oil. R_f 0.36 (hexane/diethyl ether = 2:1); IR (neat) 3326, 3953, 1611, 1538, 1456, 1221, 1045, 913, 768, 735, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.33 (m, 5H), 7.19 (t, J = 8.1 Hz, 1H), 7.12 (s, 1H), 6.86 (dd, J = 8.0 and 1.4 Hz, 1H), 6.68 (br, 1H), 6.62 (ddd, J = 8.2, 2.5 and 0.8, 1H), 5.19 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 153.2, 139.0, 135.9, 129.7, 128.6, 128.3, 128.2, 110.8, 109.2, 104.3, 66.9, 55.2; HRMS-ESI-TOF: m/z 280.0945 [$(M + Na)^+$; calcd for $C_{15}H_{15}NNaO_3^+$: 280.0944].

*Benzyl (2-Methoxyphenyl)carbamate (**3g**).* General procedure **I** was used employing 2-methoxyphenylboronic acid (0.403 g, 2.65 mmol) and benzyl azidoformate (0.187 g, 1.06 mmol), and the reaction was complete in 5 h. Flash chromatography on silica gel using hexane/diethyl ether (20:1) provided pure **3g** (0.062 g, 0.24 mmol, 23%) as a yellow oil. R_f 0.39 (hexane/dichloromethane = 1:1); IR (neat) 3424, 2925, 1728, 1601, 1459, 1332, 1212, 1037, 847, 744, 581 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20−8.09 (m, 1H), 7.50−7.33 (m, 6H), 7.08−6.95 (m, 2H), 6.91−6.84 (m, 1H), 5.24 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 147.5, 136.2, 128.6, 128.3, 127.5, 122.8, 121.1, 118.1, 112.5, 109.9, 66.9, 55.6; HRMS-ESI-TOF: m/z 280.0945 [$(M + Na)^+$; calcd for $C_{15}H_{15}NNaO_3^+$: 280.0944].

*Benzyl o-Tolylcarbamate (**3h**).* General procedure **I** was used employing *o*-tolylboronic acid (0.343 g, 2.52 mmol) and benzyl azidoformate (0.179 g, 1.01 mmol), and the reaction was complete in 12 h. Flash chromatography on silica gel using hexane/ethyl acetate (10:1) provided pure **3h** (0.102 g, 0.42 mmol, 42%) as a white solid. R_f 0.63 (hexane/ethyl acetate = 3:1); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.00 (br, 1H), 7.48−7.32 (m, 6H), 7.23−7.13 (m, 2H), 7.11−7.02 (m, 1H), 5.15 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6, 350 K) δ 153.9, 136.6, 136.1, 131.4, 129.9, 128.0, 127.4, 127.38, 125.6,

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124.5, 124.3, 65.4, 17.2; Data are consistent with those reported in the literature.[28]

*Benzyl Naphthalen-2-ylcarbamate (**3i**).* General procedure **I** was used employing naphthalene-2-ylboronic acid (0.355 g, 2.06 mmol) and benzyl azidoformate (0.183 g, 1.03 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3i** (0.261 g, 0.94 mmol, 91%) as a pale yellow solid. R_f 0.50 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.76 (d, J = 8.6 Hz, 3H), 7.47−7.34 (m, 8H), 6.86 (br, 1H), 5.23 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 135.9, 135.2, 133.8, 130.1, 128.8, 128.6, 128.3, 128.26, 127.5, 127.3, 126.4, 124.6, 119.1, 114.9, 67.0; Data are consistent with those reported in the literature.[29]

*Benzyl Benzo[d][1,3]dioxol-5-ylcarbamate (**3j**).* General procedure **I** was used employing 3,4-(methylenedioxy)phenylboronic acid (0.332 g, 2.00 mmol) and benzyl azidoformate (0.177 g, 1.00 mmol), and the reaction was complete in 3 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3j** (0.255 g, 0.94 mmol, 94%) as a white solid. mp: 97−99 °C; R_f 0.33 (hexane/diethyl ether = 2:1); IR (neat) 3407, 3328, 1699, 1545, 1255, 1055, 837, 776, 735, 696, 620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.34 (m, 5H), 7.09 (s, 1H), 6.74−6.65 (m, 2H), 6.52 (br, 1H), 5.94 (s, 2H), 5.19 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 147.9, 143.8, 136.0, 132.0, 128.6, 128.3, 128.27, 111.9, 108.0, 101.8, 101.2, 67.0; HRMS-ESI-TOF: m/z 294.0735 [(M + Na)$^+$; calcd for $C_{15}H_{13}NNaO_4^+$: 294.0737].

*Benzyl (4-Fluorophenyl)carbamate (**3k**).* General procedure **I** was used employing 4-fluorophenylboronic acid (0.283 g, 2.02 mmol) and benzyl azidoformate (0.179 g, 1.01 mmol), and the reaction was complete in 4 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3k** (0.186 g, 0.76 mmol, 75%) as a pale yellow solid. mp: 69−70 °C; R_f 0.38 (hexane/diethyl ether = 2:1); IR (neat) 3323, 3072, 1884, 1697, 1522, 1219, 1068, 832, 737, 693, 519 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.31 (m, 7H), 7.01 (t, J = 8.4 Hz, 2H), 6.61 (br, 1H), 5.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9 (d, J = 240.9 Hz), 153.6, 135.9, 133.7, 128.5, 128.3, 128.2, 120.5, 115.5 (d, J = 22.4 Hz), 67.0; HRMS-ESI-TOF: m/z 268.0745 [(M + Na)$^+$; calcd for $C_{14}H_{12}FNNaO_2^+$: 268.0744].

*Benzyl (4-Chlorophenyl)carbamate (**3l**) and Methyl (4-Chlorophenyl)carbamate (**3l′**).* General procedure **I** was used employing 4-chlorophenylboronic acid (0.391 g, 2.50 mmol) and benzyl azidoformate (0.177 g, 1.00 mmol), and the reaction was complete in 7 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3l** (0.175 g, 0.67 mmol, 67%) as a pale yellow solid. R_f 0.45 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.32 (m, 7H), 7.28−7.24 (m, 2H), 6.67 (br, 1H), 5.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 136.3, 135.7, 128.9, 128.7, 128.5, 128.3, 128.2, 120.0, 67.1; Data are consistent with those reported in the literature;[28] and **3l′** (0.026 g, 0.14 mmol, 14%) as a pale yellow solid. R_f 0.39 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.23 (m, 4H), 6.64 (br, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 136.4, 129.0, 128.5, 119.9, 52.5; Data are consistent with those reported in the literature.[31]

*Benzyl (4-Bromophenyl)carbamate (**3m**) and Methyl (4-Bromophenyl)carbamate (**3m′**).* General procedure **I** was used employing 4-bromophenylboronic acid (0.418 g, 2.08 mmol) and benzyl azidoformate (0.185 g, 1.04 mmol), and the reaction was complete in 3 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3m** (0.196 g, 0.64 mmol, 62%) as a pale yellow solid. R_f 0.67 (hexane/ethyl acetate = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.32 (m, 7H), 7.24 (d, J = 8.8 Hz, 2H), 6.87 (br, 1H), 5.16 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 136.8, 135.7, 131.9, 128.6, 128.4, 128.2, 120.2, 115.9, 67.1; Data are consistent with those reported in the literature;[32] and **3m′** (0.032 g, 0.14 mmol, 13%) as a pale yellow solid. R_f 0.50 (hexane/ethyl acetate = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 6.78 (br, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 136.9, 131.9, 120.2, 115.9, 52.4; Data are consistent with those reported in the literature.[33]

*tert-Butyl 4-(((Benzyloxy)carbonyl)amino)benzoate (**3n**).* General procedure **I** was used employing 4-(*tert*-butoxycarbonyl) phenylboronic acid (0.443 g, 1.90 mmol) and benzyl azidoformate (0.168 g, 0.95 mmol), and the reaction was complete in 4 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3n** (0.170 g, 0.52 mmol, 55%) a pale yellow solid. mp: 123−124 °C; R_f 0.75 (hexane/ethyl acetate = 2:1); IR (neat) 3323, 2980, 1716, 1599, 1301, 1221, 1168, 1048, 857, 773, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.33 (m, 6H), 5.17 (s, 2H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 153.0, 141.8, 135.7, 130.6, 128.5, 128.3, 128.2, 126.5, 117.4, 80.7, 67.1, 28.1; HRMS-ESI-TOF: m/z 350.1362 [(M + Na)$^+$; calcd for $C_{19}H_{21}NNaO_4^+$: 350.1363].

*(E)-Benzyl Styrylcarbamate (**3o**).* General procedure **I** was used employing (*E*)-styrylboronic acid (0.296 g, 2.00 mmol) and benzyl azidoformate (0.177 g, 1.00 mmol), and the reaction was complete in 2 h. Flash chromatography on silica gel using hexane/ethyl acetate (10:1) provided pure **3o** (0.220 g, 0.87 mmol, 87%) as a white solid. R_f 0.57 (hexane/ethyl acetate = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (br, 1H), 7.44−7.12 (m, 11H), 6.61 (d, J = 10.5 Hz, 1H), 5.96 (d, J = 14.5 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 136.1, 135.7, 128.6, 128.55, 128.4, 128.2, 126.3, 125.2, 123.9, 110.9, 67.3; Data are consistent with those reported in the literature.[34]

*Benzyl Thiophen-3-ylcarbamate (**3q**).* General procedure **I** was used employing 3-thiopheneboronic acid (0.354 g, 2.77 mmol) and benzyl azidoformate (0.196 g, 1.10 mmol), and the reaction was complete in 12 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3q** (0.198 g, 0.85 mmol, 77%) as a pale brown solid. mp: 60−61 °C; R_f 0.53 (hexane/ethyl acetate = 5:1); IR (neat) 3404, 3336, 2957, 2332, 1700, 1250, 1219, 1052, 839, 695, 621 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.30 (m, 5H), 7.28−7.14 (m, 2H), 6.99−6.83 (m, 2H), 5.19 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 135.9, 135.5, 128.5, 128.2, 128.1, 124.7, 120.7, 108.0, 67.0; HRMS-ESI-TOF: m/z 256.0402 [(M + Na)$^+$; calcd for $C_{12}H_{11}NNaO_2S^+$: 256.0403].

*Methyl Phenylcarbamate (**3**).* General procedure **I** was used employing phenylboronic acid (0.245 g, 2.02 mmol) and methyl azidoformate (0.102 g, 1.01 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/dichloromethane (2:1−1:1) provided pure **3** (0.141 g, 0.93 mmol, 92%) as a white solid. R_f 0.40 (hexane/diethyl ether = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.33 (m, 2H), 7.25−7.33 (m, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.86 (br, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 137.8, 128.9, 123.4, 118.7, 52.2; Data are consistent with those reported in the literature.[35]

*iso-Butyl Phenylcarbamate (**5a**).* General procedure **I** was used employing phenylboronic acid (0.244 g, 2.00 mmol) and *iso*-butyl azidoformate (0.143 g, 1.00 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (20:1) provided pure **5a** (0.168 g, 0.87 mmol, 87%) as a white solid. R_f 0.60 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.34 (m, 2H), 7.34−7.26 (m, 2H), 7.10−7.01 (m, 1H), 6.68 (br, 1H), 3.95 (d, J = 6.67 Hz, 2H), 2.07−1.87 (m, 1H), 0.97 (d, J = 6.76 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 138.1, 129.2, 123.5, 118.8, 71.5, 28.1, 19.2; Data are consistent with those reported in the literature.[36]

*Butyl Phenylcarbamate (**5b**).* General procedure **I** was used employing phenylboronic acid (0.244 g, 2.00 mmol) and butyl azidoformate (0.143 g, 1.00 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (20:1) provided pure **5b** (0.156 g, 0.81 mmol, 81%) as a white solid. R_f 0.58 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.23 (m, 4H), 7.00−7.11 (m, 1H), 6.16 (br, 1H), 4.17 (t, J = 6.72 Hz, 2H), 1.72−1.57 (m, 2H), 1.50−1.34 (m, 2H), 0.95 (t, J = 7.36 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 138.1, 129.2, 123.5, 118.8, 65.3, 31.1, 19.2, 13.9; Data are consistent with those reported in the literature.[37]

*2-Methoxyethyl Phenylcarbamate (**5c**).* General procedure **I** was used employing phenylboronic acid (0.244 g, 2.00 mmol) and 2-methoxyethyl azidoformate (0.145 g, 1.00 mmol), and the reaction was

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complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (10:1−4:1) provided pure **5c** (0.130 g, 0.67 mmol, 67%) as a colorless oil. R_f 0.30 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.33 (m, 2H), 7.36−7.24 (m, 2H), 7.09−7.01 (m, 1H), 6.99 (br, 1H), 4.32 (t, J = 4.54 Hz, 2H), 3.63 (t, J = 4.54 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 137.9, 129.1, 123.5, 118.8, 70.8, 64.1, 59.0; Data are consistent with those reported in the literature.[38]

*(9H-Fluoren-9-yl)methyl Phenylcarbamate (**5d**).* General procedure **I** was used employing phenylboronic acid (0.257 g, 2.10 mmol) and (9*H*-fluoren-9-yl)methyl azidoformate (0.280 g, 1.10 mmol) in MeOH/dichloromethane (1:1), and the reaction was complete in 24 h. Flash chromatography on silica gel using hexane/ethyl acetate (20:1−2:1) provided pure **5d** (0.212 g, 0.69 mmol, 63%) as an off-white solid. R_f 0.64 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86−7.75 (m, 2H), 7.71−7.58 (m, 2H), 7.50−7.22 (m, 8H), 7.16−7.03 (m, 1H), 6.65 (br, 1H), 4.57 (d, J = 6.52 Hz, 2H), 4.31 (t, J = 6.52 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 143.8, 141.4, 137.7, 129.1, 127.8, 127.1, 124.9, 123.6, 120.1, 118.8, 66.8, 47.1; Data are consistent with those reported in the literature.[39]

*Phenyl Phenylcarbamate (**5e**).* General procedure **I** was used employing phenylboronic acid (0.284 g, 2.33 mmol) and phenyl azidoformate (0.190 g, 1.16 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (10:1) provided pure **5e** (0.172 g, 0.81 mmol, 70%) as an off-white solid. R_f 0.45 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.15 (m, 9H), 7.15−7.06 (m, 1H), 6.94 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 137.4, 129.4, 129.2, 125.7, 123.9, 121.7, 120.9, 118.7; Data are consistent with those reported in the literature.[40]

*2,2,2-Trichloroethyl Phenylcarbamate (**5f**).* General procedure **I** was used employing phenylboronic acid (0.244 g, 2.00 mmol) and 2,2,2-trichloroethyl azidoformate (0.218 g, 1.00 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (20:1−2:1) provided pure **5f** (0.213 g, 0.74 mmol, 74%) as a white solid. R_f 0.63 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.36 (m, 2H), 7.36−7.25 (m, 2H), 7.15−6.98 (m, 2H), 4.81 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 137.1, 129.3, 124.3, 119.1, 95.4, 74.6; Data are consistent with those reported in the literature.[41]

*1,1,1-Trichloro-2-methylpropan-2-yl phenylcarbamate (**5g**).* General procedure **I** was used employing phenylboronic acid (0.244 g, 2.00 mmol) and 1,1,1-trichloro-2-methylpropan-2-yl azidoformate (0.247 g, 1.00 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (40:1−10:1) provided pure **5g** (0.194 g, 0.65 mmol, 65%) as a white solid. mp: 112−114 °C; R_f 0.72 (hexane/ethyl acetate = 4:1); IR (neat) 3318, 31 32, 2359, 1701, 1598, 1540, 1445, 1371, 1243, 1049, 800 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26−7.46 (m, 4H), 7.15−7.02 (m,1H), 6.72 (br, 1H), 1.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 137.6, 129.2, 123.9, 118.9, 106.4, 89.0, 21.8; HRMS-ESI-TOF: m/z 317.9825 [(M + Na)$^+$; calcd for $C_{11}H_{12}Cl_3NNaO_2^+$: 317.9826].

*tert-Butyl Phenylcarbamate (**5h**).* General procedure **I** was used employing phenylboronic acid (0.283 g, 2.32 mmol) and *tert*-butyl azidoformate (0.167 g, 1.17 mmol), and the reaction was complete in 1 h. Flash chromatography on silica gel using hexane/ethyl acetate (20:1) provided pure **5h** (0.122 g, 0.63 mmol, 54%) as a white solid. R_f 0.63 (hexane/ethyl acetate = 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.43 (m, 4H), 6.96−7.10 (m, 1H), 6.48 (br, 1H), 1.52 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 138.3, 128.9, 123.0, 118.5, 80.5, 28.3; Data are consistent with those reported in the literature.[42]

General Procedure II for Synthesis of *N*-Aryl *N*′-Ureas. To a solution of amine (3.0 mmol) in toluene (5 mL) at 0 °C was added dropwise a solution of $AlMe_3$ (2.0 M in toluene, 2.5 mmol), and the solution was stirred at 0 °C for 10 min. The reaction mixture was then warmed to r.t. and stirred for 1 h. In another flask, general procedure **I** for the synthesis of the carbamate was followed, and the MeOH was removed *in vacuo* to afford the crude carbamate. Without purification, toluene (3 mL) was added under argon and the solution cooled to 0 °C. The prepared aluminum amide solution was then cannulated into the flask containing crude carbamate solution, and the reaction mixture was stirred at a specified temperature. Upon completion of the reaction, water was added, followed by excess potassium sodium tartrate (Rochelle's salt) and EtOAc. The reaction mixture was extracted with EtOAc (×3), and the organic layer was washed once with brine. The combined organic extracts were dried over $MgSO_4$ and filtered, and the solvent was removed *in vacuo*. The crude product was purified via flash column chromatography to afford the desired urea.

*N-Phenylmorpholine-4-carboxamide (**6a**).* General procedure **II** was used employing phenylboronic acid (0.292 g, 2.40 mmol), benzyl azidoformate (0.188 g, 1.06 mmol), morpholine (0.21 mL, 3.50 mmol), and 2.0 M $AlMe_3$ in toluene (1.45 mL, 2.90 mmol), and the reaction was complete in 4 h at 70 °C. Flash chromatography on silica gel using hexane/ethyl acetate (3:1) provided pure **6a** (0.179 g, 0.87 mmol, 82%) as a white solid. mp: 150−152 °C; R_f 0.13 (hexane/ethyl acetate = 1:1); IR (neat) 3275, 2858, 1594, 1445, 1250, 1116, 748, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.21 (m, 4H), 7.09−6.99 (m, 1H), 6.63 (br, 1H), 3.73−3.62 (m, 4H), 3.49−3.38 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 138.9, 129.0, 123.5, 120.4, 66.6, 44.3; HRMS-ESI-TOF: m/z 229.0947 [(M + Na)$^+$; calcd for $C_{11}H_{14}N_2NaO_2^+$: 229.0947].

*1-(3,5-Dimethylphenyl)-3-phenylurea (**6b**).* General procedure **II** was used employing (3,5-dimethylphenyl)boronic acid (0.325 g, 2.20 mmol), benzyl azidoformate (0.195 g, 1.10 mmol), aniline (0.32 mL, 3.50 mmol), and 2.0 M $AlMe_3$ in toluene (1.45 mL, 2.90 mmol), and the reaction was complete in 2 h at 70 °C. Flash chromatography on silica gel using hexane/ethyl acetate (3:1) provided pure **6b** (0.271 g, 0.92 mmol, 84%) as a white solid. R_f 0.24 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.27 (m, 4H), 7.15−7.03 (m, 1H), 6.94 (s, 2H), 6.76 (s, 2H), 6.62 (s, 1H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 139.3, 138.2, 137.7, 129.4, 126.5, 124.3, 121.1, 119.5, 21.5; Data are consistent with those reported in the literature.[43]

*N-(3,5-Dimethylphenyl)piperidine-1-carboxamide (**6c**).* General procedure **II** was used employing (3,5-dimethylphenyl)boronic acid (0.318 g, 2.12 mmol), benzyl azidoformate (0.188 g, 1.06 mmol), piperidine (0.20 mL, 3.04 mmol), and 2.0 M $AlMe_3$ in toluene (1.25 mL, 2.50 mmol), and the reaction was complete in 5 h at 70 °C. Flash chromatography on silica gel using hexane/ethyl acetate (3:1) provided pure **6c** (0.260 g, 1.01 mmol, 95%) as a white solid. mp: 236−240 °C; R_f 0.12 (hexane/ethyl acetate = 4:1); IR (neat) 3322, 2935, 2855, 1616, 1554, 1271, 1233, 1028, 838 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.66 (s, 1H), 6.28 (br, 1H), 3.61−3.35 (m, 4H), 2.27 (s, 6H), 1.70−1.52 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 139.2, 138.6, 124.7, 117.7, 45.4, 25.8, 24.5, 21.5; HRMS-ESI-TOF: m/z 255.1467 [(M + Na)$^+$; calcd for $C_{14}H_{20}N_2NaO^+$: 255.1468].

*1,1-Diisopropyl-3-phenylurea (**6d**).* General procedure **II** was used employing phenylboronic acid (0.283 g, 2.32 mmol), benzyl azidoformate (0.206 g, 1.16 mmol), diisopropylamine (0.50 mL, 3.50 mmol), and 2.0 M $AlMe_3$ in toluene (1.45 mL, 2.90 mmol), and the reaction was complete in 17 h at 110 °C. Flash chromatography on silica gel using hexane/ethyl acetate (5:1) provided pure **6d** (0.179 g, 0.81 mmol, 70%) as a white solid. R_f 0.30 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.33 (m, 2H), 7.32−7.23 (m, 2H), 7.05−6.95 (m, 1H), 6.18 (br, 1H), 4.07−3.90 (m, 2H), 1.33 (d, J = 6.85 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 139.5, 128.9, 122.7, 119.8, 45.6, 21.6; Data are consistent with those reported in the literature.[44]

*N-Phenylpiperidine-1-carboxamide (**6e**).* General procedure **II** was used employing phenylboronic acid (0.259 g, 2.12 mmol), benzyl azidoformate (0.188 g, 1.06 mmol), piperidine (0.30 mL, 3.03 mmol), and 2.0 M $AlMe_3$ in toluene (1.25 mL, 2.50 mmol), and the reaction was complete in 1 h at rt. Flash chromatography on silica gel using hexane/ethyl acetate (10:1) provided pure **6e** (0.185 g, 0.91 mmol, 86%) as a white solid. R_f 0.12 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.31 (m, 2H), 7.31−7.23 (m, 2H), 7.07−6.96 (m, 1H), 6.34 (br, 1H), 3.54−3.33 (m, 4H), 1.74−1.50 (m 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 139.4, 129.0, 123.0, 119.9, 45.4, 25.8, 24.5; Data are consistent with those reported in the literature.[45]

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*N-(Benzo[d][1,3]dioxol-5-yl)morpholine-4-carboxamide (**6f**).* General procedure **II** was used employing 3,4-(methylenedioxy)-phenylboronic acid (0.330 g, 1.99 mmol), benzyl azidoformate (0.176 g, 0.99 mmol), morpholine (0.26 mL, 3.00 mmol), and 2.0 M $AlMe_3$ in toluene (1.25 mL, 2.50 mmol), and the reaction was complete in 2 h at 70 °C. Flash chromatography on silica gel using dichloromethane/ethyl acetate (1:0−3:1) provided pure **6f** (0.220 g, 0.88 mmol, 89%) as a white solid. R_f 0.11 (dichloromethane/ethyl acetate = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, J = 2.1 Hz, 1H), 6.71 (dd, J = 8.3 and 0.3 Hz, 1H), 6.62 (dd, J = 8.4 and 2.1 Hz, 1H), 6.30 (br, 1H), 5.93 (s, 2H), 3.72 (t, J = 5.0 Hz, 4H), 3.45 (t, J = 5.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 147.6, 143.8, 132.8, 114.0, 107.8, 104.0, 101.1, 66.4, 44.1; Data are consistent with those reported in the literature.[46]

*N-(3-Methoxyphenyl)morpholine-4-carboxamide (**6g**).* General procedure **II** was used employing 3-methoxyphenylboronic acid (0.348 g, 2.29 mmol), benzyl azidoformate (0.203 g, 1.14 mmol), piperidine (0.30 mL, 3.42 mmol), and 2.0 M $AlMe_3$ in toluene (1.43 mL, 2.85 mmol), and the reaction was complete in 2 h at 70 °C. Flash chromatography on silica gel using dichloromethane/ethyl acetate (1:0−3:1) provided pure **6g** (0.253 g, 1.07 mmol, 94%) as a pale orange solid. mp: 106−107 °C; R_f 0.11 (dichloromethane/ethyl acetate = 10:1); IR (neat) 3302, 2850, 2363, 1635, 1463, 1251, 1038, 783, 576 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.18 (t, J = 8.1 Hz, 1H), 7.12 (t, J = 2.2 Hz, 1H), 6.83 (ddd, J = 8.0, 2.0, and 0.8 Hz, 1H), 6.61 (ddd, J = 8.3, 2.5, and 0.8 Hz, 1H), 6.38 (br, 1H), 3.79 (s, 3H), 3.74 (t, J = 4.7 Hz, 4H), 3.47 (t, J = 4.7 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 155.1, 140.0, 129.5, 112.2, 109.1, 105.8, 66.4, 55.2, 44.2; HRMS-ESI-TOF: m/z 259.1053 [(M + Na)$^+$; calcd for $C_{12}H_{16}N_2NaO_3^+$: 259.1053].

*(S)-1-Phenyl-3-(1-phenylethyl)urea (**6h**).* General procedure **II** was used employing phenylboronic acid (0.259 g, 2.13 mmol), benzyl azidoformate (0.188 g, 1.06 mmol), (*S*)-(−)-α-methylbenzylamine (0.39 mL, 3.00 mmol, 98% ee), and 2.0 M $AlMe_3$ in toluene (1.25 mL, 2.50 mmol), and the reaction was complete in 2 h at 70 °C. Flash chromatography on silica gel using dichloromethane/ethyl acetate (1:0−3:1) provided pure **6h** (0.235 g, 0.98 mmol, 92%, 87% ee) as a pale yellow solid. mp: 148−150 °C; $[\alpha]_D^{20}$ −8.03 (*c* 1.00, $CHCl_3$); R_f 0.50 (hexane/ethyl acetate = 2:1); IR (neat) 3316, 2986, 2971, 2363, 2337, 1635, 1558, 1231, 1038, 668, 501 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.18 (m, 10H), 7.00−6.94 (m, 1H), 5.80 (d, J = 7.4 Hz, 1H), 4.88 (m, 1H), 1.32 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 144.1, 138.8, 129.0, 128.6, 127.1, 125.8, 123.1, 120.1, 49.8, 22.9; HRMS-ESI-TOF: m/z 263.1156 [(M + Na)$^+$; calcd for $C_{15}H_{16}N_2NaO^+$: 263.1155].

Preparation of Azide Precursors (Scheme 6). Diphenylcarbamoyl azide (**12**) was prepared as according to the cited literature procedure.[47] Synthesis of dimethyl phosphorazidate is as follows:

*Dimethyl Phosphorazidate (**13**).* To a solution of dimethylchloro phosphate (2.68 g, 18.5 mmol) in acetone (50 mL) was added sodium azide (2.59 g, 37.0 mmol), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was then filtered, and solvent was removed *in vacuo*. Flash chromatography on silica gel using hexane/ethyl acetate (10:1) provided pure **13** (1.79 g, 11.9 mmol, 64%) as a colorless liquid. R_f 0.50 (hexane/ethyl acetate = 3:1); IR (neat) 3423, 3011, 2962, 2859, 2170, 1453, 1273, 1188, 1047, 802, 602, 445 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (d, J = 12.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.9; ^{31}P NMR (120 MHz, $CDCl_3$) δ 1.62; HRMS-EI: m/z 151.0141 [M$^+$; calcd for $C_2H_6N_3O_3P^+$: 151.0141].

Direct Synthesis of Urea (Scheme 5). *1,1,3-Triphenylurea (**12**).* To a solution of diphenylcarbamoyl azide (0.55 g, 2.30 mmol) in MeOH (4.6 mL) was added phenylboronic acid (0.56 g, 4.59 mmol) and copper(I) chloride (22.7 mg, 0.23 mmol), and reaction mixture was stirred at rt for 24 h. Solvent was then removed *in vacuo*. Flash chromatography on silica gel using hexane/ethyl acetate (6:1) provided pure **12** (0.76 g, 0.26 mmol, 11%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.19−7.45 (m, 14H), 6.98−7.07 (m, 1H), 6.45 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.4, 138.5, 129.6, 128.9, 127.5, 126.7, 123.3, 119.3; Data are consistent with those reported in the literature.[15]

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C spectra and HRMS data for all novel compounds prepared and chiral HPLC trace for **6h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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