JOC The Journal of Organic Chemistry

Article

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b03175 • Publication Date (Web): 06 Feb 2018

Just Accepted

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Synthesis of *N*-(Hetero)Aryl Carbamates *via* CuI/MNAO Catalyzed Cross-Coupling of (Hetero)Aryl Halides with Potassium Cyanate in Alcohols

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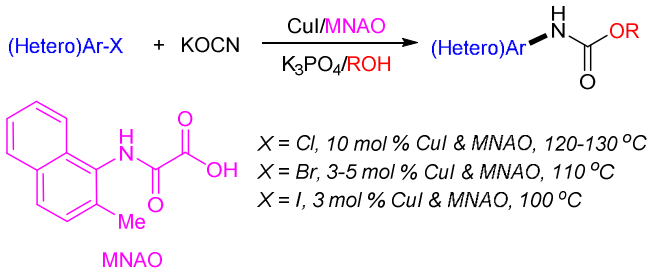
Abstract



An efficient route to *N*-(hetero)aryl carbamates has been developed through CuI/MNAO [2-((2-methylnaphthalen-1-yl)amino)-2-oxoacetic acid] catalyzed cross-coupling of (hetero)aryl chlorides with potassium cyanate in alcohols at 120-130 °C. This method utilizes broadly available substrates to afford various *N*-(hetero)aryl carbamates in good to excellent yields. Moreover, (hetero)aryl bromides and (hetero)aryl iodides were also reacted at low catalyst loadings and relatively low temperatures to provide *N*-(hetero)aryl carbamates.

Introduction

Carbamate-containing molecules play an important role in medicinal chemistry and the pharmaceutical industry, where they exhibit important biological activities such as anticancer,[1] antitubercolosis,[2] and HIV-1 protease.[3] Carbamate derivatives are widely represented in agrochemicals[4] such as pesticides, herbicides, insecticides and fungicides. They are often used in the chemical and paint industry as starting materials, intermediates, and solvents.[5] Carbamates serve as protecting groups in organic synthesis, especially in peptide chemistry due to their chemical stability toward acids, bases, and hydrogenation[6] and also as linkers in combinatorial chemistry.[7] As a result, there is continuing interest in the development of efficient methods for the synthesis of carbamates. The most important classical approaches to carbamates are based on condensation of anilines with phosgene and its derivatives[8] or reaction of alcohols with isocyanates generated *in situ* via Hofmann,[9] Curtius,[10] Lossen,[11] and Schmidt[12] rearrangement reactions. These reactions are limited by the availability of starting materials, as well as the highly reactive nature of the compounds. The other well known methods to synthesize carbamates are the reaction of amide with lead tetra-acetate,[13] from isonitriles,[14] and reductive carbonylation of aromatic nitro compounds.[15]

Transition metal catalyzed C−N bond formation reactions have recently enabled the development of alternative methodologies for carbamate synthesis. In this context, palladium-catalyzed reductive carbonylation of nitroarenes[16] as well as Pd-catalyzed cross-coupling of aryl chlorides or aryl triflates with sodium cyanate[18] have been reported for the synthesis of carbamates. Due to the less toxic and lower cost of copper catalysts, several new efficient routes to carbamate synthesis have also been developed via copper-catalyzed reactions. This includes $CuBr_2$-catalyzed coupling of

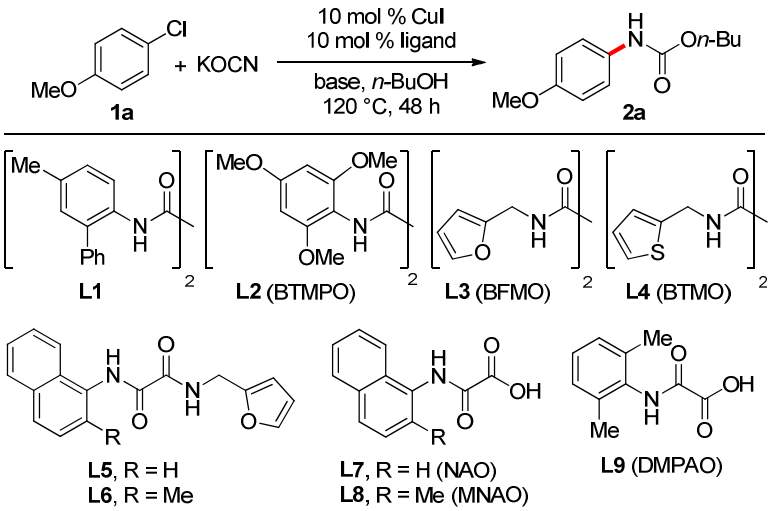
arylboronic acids with potassium cyanates[17] and CuCl-catalyzed Chan-Lam coupling of azidoformates with boronic acids at room temperature.[19] We have recently reported CuI/DMPAO-catalyzed cross-coupling reaction for the synthesis of aryl carbamates from aryl halides (Br, I) and potassium cyanate in alcohols.[20] The problem for this reaction is the requirement of 20 mol % CuI and DMPAO for complete conversion. Additionally, (hetero)aryl chlorides are difficult substrates under these conditions. Encouraged by our success in coupling of (hetero)aryl chlorides with nucleophiles using copper salt/oxalic diamide catalyst systems,[21] we reinvestigated the Cu-catalyzed coupling reaction of (hetero)aryl halides with potassium cyanate in alcohols using newly developed ligands, and identified that 2-[(2-methylnaphthalen-1-yl)amino]-2-oxoacetic acid (MNAO) is a more powerful ligand for this reaction. Under the assistance of this ligand, Cu-catalyzed coupling between (hetero)aryl chlorides and potassium cyanate in alcohols proceeded smoothly at 120-130 $^{\circ}$C, while only 3-5 mol % CuI and MNAO are needed for complete conversion in case of (hetero)aryl bromides and iodides as the coupling partners. Herein, we wish to disclose these results.

Results and Discussion

The copper catalyzed coupling of 4-chloroanisole **1a** with potassium cyanate in *n*-butanol was first examined using 10 mol % CuI and various ligands to optimize the reaction conditions for the synthesis of *N*-aryl carbamate **2a**. Initially, several bis(*N*-aryl/alkyl)-substituted oxalamides (**L1-L4**) that led to excellent yields in the amination/amidation of (hetero)aryl halides were examined.[21] However, none of them led to the formation of **2a** at 120 ^{o}C after 48 h (Table 1, entries 1-4). Interestingly, when two naphthalene-containing ligands (**L5** and **L6**) were used, the desired product could be isolated in 62-68% yields under the same conditions. These results clearly

indicate that the naphthalene group might have a dramatic influence on this coupling reaction. This speculation was further corroborated by the observation that 2-[(2-methylnaphthalen-1-yl)amino]-2-oxoacetic acid (**L8**, MNAO) gave the best yield, while **L9** (DMPAO) gave a poor conversion. Noteworthy is that when **L8** was replaced with 2-[(naphthalen-1-yl)amino]-2-oxoacetic acid (**L7**, NAO), only a slight decrease in yield was observed. Considering that (naphthalen-1-yl)amine is much cheaper than (2-methylnaphthalen-1-yl)amine, **L7** should be also considered as an alternative practical ligand in large-scale synthesis.

Table 1. Cu-Catalyzed Coupling of 4-Chloroanisole with Potassium Cyanate in *n*-Butanol in the Presence of Various Ligands[a]



entry	catalyst	ligand	base	yield (%)[b]
1	CuI	**L1**	K_3PO_4	0
2	CuI	**L2**	K_3PO_4	0
3	CuI	**L3**	K_3PO_4	0
4	CuI	**L4**	K_3PO_4	0
5	CuI	**L5**	K_3PO_4	62
6	CuI	**L6**	K_3PO_4	68

7	CuI	**L7**	K_3PO_4	78
8	CuI	**L8**	K_3PO_4	85
9	CuI	**L9**	K_3PO_4	16
10	CuBr	**L8**	K_3PO_4	76
11	CuCl	**L8**	K_3PO_4	57
12	Cu_2O	**L8**	K_3PO_4	20
13	CuI	**L8**	Cs_2CO_3	15
14	CuI	**L8**	K_2CO_3	8
15	CuI	**L8**	Na_2CO_3	5
16	CuI	**L8**	KOH	82
17[c]	CuI	**L8**	K_3PO_4	42

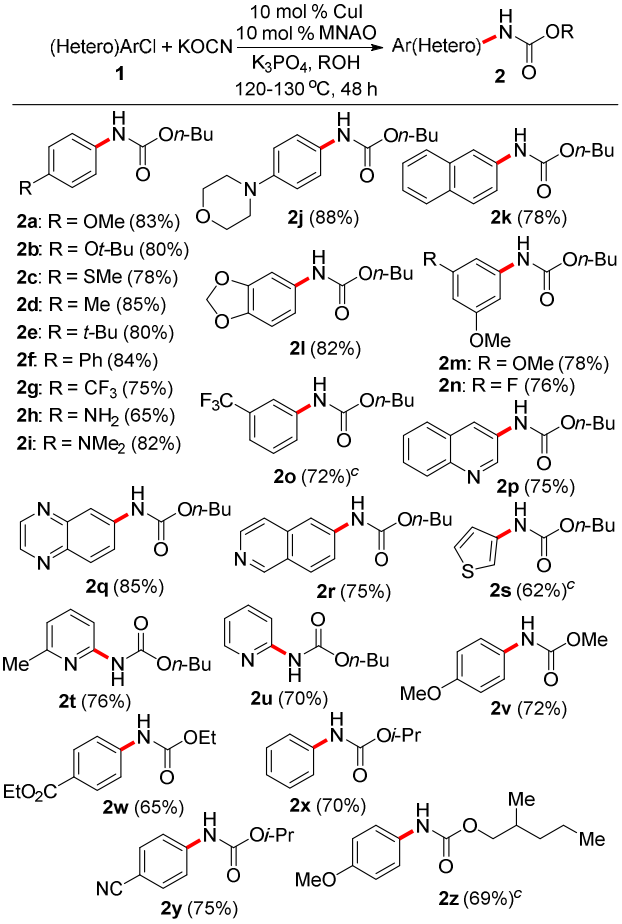
[a]Reaction conditions: **1a** (2.0 mmol), KOCN (4.0 mmol), CuI (0.2 mmol), ligand (0.2 mmol), base (0.2 mmol), *n*-BuOH (3 mL), 120 °C, 48 h. [b]Yield was determined by ^{1}H NMR of crude reaction mixture using CH_2Br_2 as the internal standard. [c]5 mol % CuI and **L8** were used, 72 h.

After identifying **L8** as the best ligand, we examined other copper catalysts and bases. When CuBr and CuCl were used, reaction yields were decreased (entries 10-11). However, a much lower yield was observed in case of Cu_2O as the catalyst (entry 12). Further screening revealed that although Cs_2CO_3, K_2CO_3, and Na_2CO_3 gave very poor yields, a comparable yield was observed in case of KOH as the base (entries 13-16). Attempt to reduce the catalyst loadings failed to give complete conversion even after prolonging reaction time (entry 17). Therefore, we concluded that optimal conditions are using 10 mol % CuI and **L8** as the catalytic system and K_3PO_4 (0.1 equiv) as the base.

We next explored the scope of the present protocol using the established optimized conditions, and the results are summarized in Table 2. As expected, a number of aryl chlorides bearing a functional group at the *para*-position worked well, providing carbamates **2a**-**2j** in 65-88% yields. Some *meta*-substituted aryl chlorides

were also applicable, leading to the formation of **2l**-**2o** in good yields. However, no conversion was observed in case of *ortho*-substituted substrates as the coupling partners. Additionally, coupling reaction with some heteroaryl chlorides proceeded smoothly to deliver quinolone-, quinoxaline-, isoquinoline-, thiophene- and pyridine-containing carbamates **2p**-**2u**. Changing the solvent to other alcohols such as methanol, ethanol, isopropanol and 2-methylpentanol could afford the corresponding carbamates **2v**-**2z**.

Table 2. CuI/MNAO-Catalyzed Coupling of (Hetero)Aryl Chlorides with Potassium Cyanate in Alcohols[a,b]

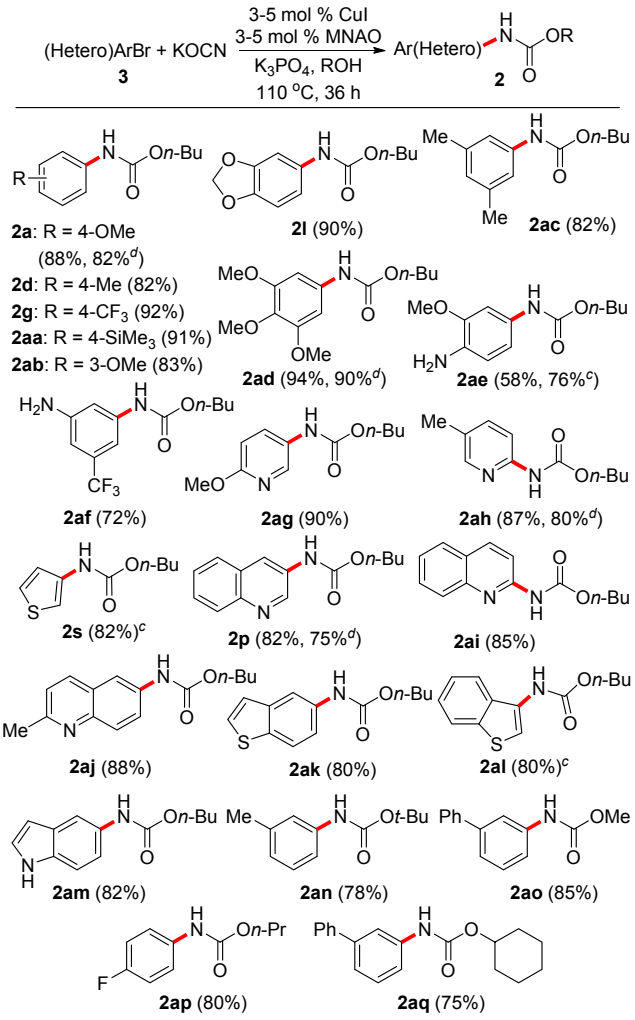


[a]Reaction conditions: **1** (2.0 mmol), KOCN (4.0 mmol), CuI (0.2 mmol), MNAO (0.2 mmol), K_3PO_4 (0.2 mmol), ROH (3 mL), 120 °C, 48 h. [b]Isolated yield. [c]The reaction was carried out at 130 °C.

In our previous report, more than 20 mol % CuI and DMPAO were required for catalysing the coupling reaction of (hetero)aryl bromides with KOCN. This problem prompted us to check if MNAO can give a better result. After a quick optimization, we found that using 3 mol % of CuI and MNAO catalytic system was sufficient for the coupling of 4-bromoanisole with KOCN in *n*-butanol to give *n*-butyl (4-methoxyphenyl)carbamate **2a** in 88% yield (Table 3, entry 1), and the reaction was applicable to a broad range of substituted aryl bromides (**2d**, **2g**, **2l** and **2aa-2af**). Notably, highly electron-rich 3,4,5-trimethoxybromobenzene also reacted smoothly with KOCN in *n*-butanol to afford **2ad** in 94% yield. Additionally, the (hetero)aryl bromides such as substituted pyridines (**2ag** and **2ah**), thiophene (**2s**), quinolines (**2p**, **2ai** and **2aj**), benzo[*b*]thiophenes (**2ak** and **2al**) and indole (**2am**) worked under these conditions, giving the corresponding *N*-(hetero)aryl carbamates in good yields. In case of coupling with 4-bromo-2-methoxyaniline, 3-bromothiophene, and 3-bromobenzo[*b*]thiophene, the reactions were relatively sluggish, and an increase in catalyst loading to 5 mol % was required to get a complete conversion (**2ae**, **2s** and **2al**). In addition, by using other alcohols as the solvents, carbamates **2an-2aq** were obtained in 75-85% yields. It is notable that **2aq**, known as URB602, is a selective monoacylglycerol lipase (MGL) inhibitor that can selectively block 2-arachidonoylglycerol degradation.[22] Considering that **L7** was derived from a relatively cheap aniline, we tried to replace **L8** with **L7** in the formation of **2a**, **2ad**, **2ah** and **2p**,

and were pleased that the complete conversion was still observed, although the yields were slightly decreased.

Table 3. CuI/MNAO-Catalyzed Coupling of (Hetero)Aryl Bromides with Potassium Cyanate in Alcohols[a,b]

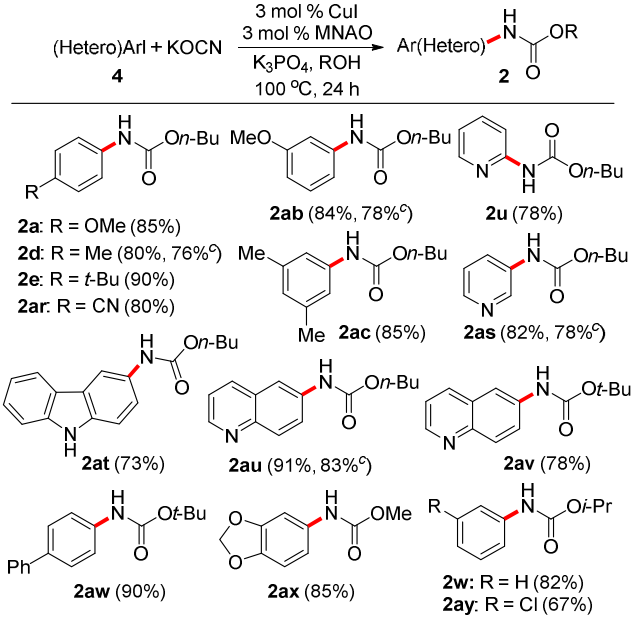


[a]Reaction conditions: **3** (4 mmol), KOCN (8 mmol), CuI (0.12 mmol), MNAO (0.12 mmol), K_3PO_4 (0.12 mmol), ROH (5 mL), 110 °C, 36 h. [b]Isolated yield. [c]5 mol % CuI, MNAO and K_3PO_4 were used. [d]Using **L7** as the ligand.

When more reactive (hetero)aryl iodides were employed as the coupling partners, both the reaction temperature and time could be further reduced (Table 4). The reaction proceeded smoothly with the catalysis of 3 mol % CuI and MNAO at 100 °C to give the corresponding carbamates in good to excellent yields. Using

inexpensive **L7** also gave satisfactory results (**2d**, **2ab**, **2as** and **2au**). When 6-iodoquinoline and 4-iodobiphenyl were coupled with KOCN in *t*-butanol, the corresponding carbamates **2av** and **2aw** were obtained in 78-90% yields. By changing solvent to *i*-PrOH, we could synthesize two herbicides, propham (**2w**), an effective pre-and postemergent herbicide used for the control of annual grasses,[23] and chlorpropham (**2ay**), a plant growth regulator and herbicide used as sprouting inhibitor for stored potatoes.[24]

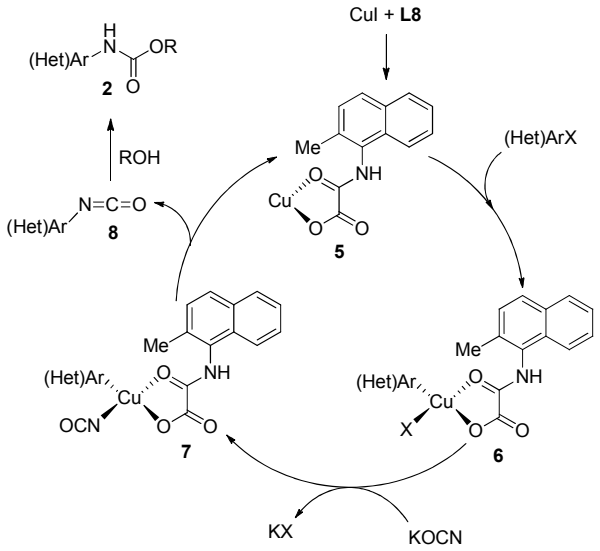
Table 4. CuI/MNAO-Catalyzed Coupling of (Hetero)Aryl Iodides with Potassium Cyanate in Alcohols[a,b]



[a]Reaction conditions: (Hetero)ArI (4 mmol), KOCN (8 mmol), CuI (0.12 mmol), **L8** (0.12 mmol), K_3PO_4 (0.12 mmol), ROH (5 mL), 100 °C, 24 h. [b]Isolated yield. [c]Using **L7** as the ligand.

A plausible reaction mechanism for this transformation is illustrated in Scheme 1. The Cu(I) complex **5** formed from CuI and ligand, undergoes oxidative addition with

(hetero)aryl halides to give Cu(III) complex **6**, followed by ligand exchange with KOCN gives Cu(III) complex **7**, which would undergo reductive elimination to produce (hetero)aryl isocyanide **8** and regenerates the Cu(I) complex **5**. Subsequent condensation of **8** with alcohol gives the (hetero)aryl carbamate **2**.



Scheme 1. Proposed reaction mechanism for the synthesis of (hetero)aryl carbamates

Conclusion

In summary, we have developed an efficient and practical route for preparing *N*-(hetero)aryl carbamates by CuI/MNAO-catalyzed coupling of (hetero)aryl halides and potassium cyanate in alcohols. The new methodology allows direct access to a broad range of *N*-(hetero)aryl carbamates from less reactive and less expensive (hetero)aryl chlorides. In addition, (hetero)aryl bromides and (hetero)aryl iodides were reactive at relatively low catalyst loadings and reaction temperatures. The usage of the methodology was further illustrated with the synthesis of URB602 (**2aq**, a selective MGL inhibitor) and few herbicides such as propham (**2w**) and chlorpropham (**2ay**) in good yields. The easy availability of starting materials along with the

efficiency of the present protocol should make it useful complement to the existing methods for the synthesis of *N*-(hetero)aryl carbamates.

Experimental Section

General Information. All the Cu-catalyzed coupling reactions were set up on the benchtop in the open air and carried out in re-sealable test tubes with Teflon septa under an argon atmosphere. Unless otherwise noted, the solvents and the solutions of reagents/reactants were transferred via micro syringe or plastic syringe (fitted with metal needle) into the reaction test tubes under a positive argon pressure. Commercially available dry solvents such as tetrahydrofuran (THF), *n*-butanol (*n*-BuOH), ethanol (EtOH), isopropanol (*i*-PrOH), tert-butanol (*t*-BuOH) and *n*-propanol (*n*-PrOH) were used for reaction. Other solvents such as ethyl acetate (EtOAc) and n-hexane were used as received. The reagents such as various amines, oxalyl chloride, KOCN, (hetero)aryl halides (Cl, Br, I) and potassium phosphate (Sigma-Aldrich) etc. were used as received, unless otherwise noted. Thin layer chromatography was performed using silicagel 60 F-254 precoated glass plates (0.25 mm) and visualized by UV irradiation. Flash chromatography was performed using 230-400 mesh SiliaFlash® P60. Melting points were recorded on a digital melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 400 MHz, 500 MHz, 125 MHz, 101 MHz, 376 MHz spectrometer (400 or 500 MHz for ^{1}H-NMR ; 101 or 125 MHz for ^{13}C-NMR; 376 MHz for ^{19}F-NMR). Chemical shifts were reported in δ ppm (parts per million) with residual solvent protons as internal standard (δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6, in ^{1}H NMR; δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-d_6 in ^{13}C NMR). Coupling constant (*J*) values are given in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd

(double doublet), m (multiplet), and br (broad). High resolution mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument and a Thermo Fisher Scientific LTQ FT Ultra instrument (Ion Trap based Fourier Transform ICR Mass Spectrometer).

The commercially available copper(I) iodide was purified according to a slightly modified literature procedure.[25] In a round-bottom flask, saturated aqueous solution of NaI (50 mL) was taken and approximately 25 g of copper iodide (from Acros Organics) was added to it and then heated at 100 °C for 30 min until the dark brown cleared solution formed. After that the clear solution was cooled and diluted with water. The white solid precipitate was then filtered and washed sequentially with H_2O, EtOH, EtOAc, ether, and *n*-hexane and dried in vacuo for 24 h. All the ligands (**L1-L9**) were prepared according to the earlier reported procedures from our group.[21] The known ligands were characterized by comparison of their spectral and analytical data with the reported data,[20-21] whereas the spectral and analytical data for the unknown ligands **L7** and **L8** are given below.

*2-(Naphthalen-1-ylamino)-2-oxoacetic acid (**L7**).* White solid (4.20 g, 95%); mp 195-197 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.24 (br s, 1H), 10.85 (s, 1H), 8.05-7.90 (m, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.67-7.48 (m, 4H); ^{13}C NMR (101 MHz, DMSO) δ 162.5, 158.3, 133.8, 132.4, 128.5, 128.2, 126.9, 126.4, 126.3, 125.6, 123.3, 123.0; HRMS (DART): *m/z* calculated for $C_{12}H_{10}NO_3$ $[M + H]^+$ 216.0654, found 216.0655.

*2-((2-Methylnaphthalen-1-yl)amino)-2-oxoacetic acid (**L8**).* Off-white solid (4.01 g, 92%); mp 210-212 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.21 (br s, 1H), 10.69 (s, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.85-7.81 (m, 2H), 7.55-7.45 (m, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 162.3, 158.0, 132.7, 132.3, 130.10, 130.09, 128.7, 127.9,

127.2, 126.5, 125.4, 122.9, 18.1; HRMS (DART): *m/z* calculated for $C_{13}H_{11}NNaO_3$ $[M + Na]^+$ 252.0637, found 252.0632.

General Procedure for the Synthesis of *N*-(Hetero)Aryl Carbamates from (Hetero)Aryl Chlorides. The (hetero)aryl chloride (2.0 mmol), KOCN (4.0 mmol), CuI (0.2 mmol, 38 mg), **L8** (0.2 mmol, 46 mg) and K_3PO_4 (0.2 mmol, 42.4 mg) were placed into a Schlenk flask (10 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and alcohol (3 mL) was added afterwards (Note: for liquid substrates, they were added after the tube was backfilled with argon). The mixture was sealed and stirred vigorously at 120 °C for 48 h before being diluted with 20 mL of ethyl acetate and filtered through celite pad and washed it two times with ethyl acetate. The filtrate was concentrated and residue was purified by flash chromatography (EtOAc:*n*-hexane = 1:33 to 1:1.5) on silica gel to afford the corresponding *N*-(hetero)aryl carbamates.

General Procedure for the Synthesis of *N*-(Hetero)Aryl Carbamates from (Hetero)Aryl Bromides. The (hetero)aryl bromide (4.0 mmol), KOCN (8.0 mmol), CuI (0.12 mmol, 22.8 mg), **L8** (0.12 mmol, 27.5 mg) or **L7** (0.12 mmol, 25.8 mg) and K_3PO_4 (0.12 mmol, 25.5 mg) were placed into a Schlenk flask (20 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and alcohol (5 mL) was added afterwards (Note: for liquid substrates, they were added after the tube was backfilled with argon). The mixture was sealed and stirred vigorously at 110 °C for 36 h before being diluted with 40 mL of ethyl acetate and filtered through celite pad and washed it two times with ethyl acetate. The filtrate was concentrated and residue was purified by flash chromatography (EtOAc:*n*-hexane = 1:33 to 1:2.3) on silica gel to afford the corresponding *N*-(hetero)aryl carbamates.

General Procedure for the Synthesis of *N*-(Hetero)Aryl Carbamates from (Hetero)Aryl Iodides. The (hetero)aryl iodide (4.0 mmol), KOCN (8.0 mmol), CuI (0.12 mmol, 22.8 mg), **L8** (0.12 mmol, 27.5 mg) or **L7** (0.12 mmol, 25.8 mg) and K_3PO_4 (0.12 mmol, 25.5 mg) were placed into a Schlenk flask (20 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and alcohol (5 mL) was added afterwards (Note: for liquid substrates, they were added after the tube was backfilled with argon). The mixture was sealed and stirred vigorously at 100 °C for 24 h before being diluted with 40 mL of ethyl acetate and filtered through celite pad and washed it two times with ethyl acetate. The filtrate was concentrated and residue was purified by flash chromatography (EtOAc:*n*-hexane = 1:33 to 1:4) on silica gel to afford the corresponding *N*-(hetero)aryl carbamates.

*Butyl (4-methoxyphenyl)carbamate (**2a**).*[20] Off-white solid (370 mg, 83% from 4-chloroanisole; 785 mg, 88% from 4-bromoanisole; 758 mg, 85% from 4-iodoanisole); mp 63-65 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.38 (br s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 4.04 (t, J = 8.0 Hz, 1H), 3.69 (s, 3H), 1.62-1.55 (m, 2H), 1.41–1.32 (m, 1H), 0.91 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.7, 153.8, 132.3, 119.7, 113.9, 63.7, 55.1, 30.7, 18.6, 13.6.

*Butyl (4-(t-butoxy)phenyl)carbamate (**2b**)*. Brown liquid (424 mg, 80%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.49 (br s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 1.62–1.55 (m, 2H), 1.41–1.32 (m, 2H), 1.23 (s, 9H), 0.90 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.8, 149.8, 134.8, 124.2, 118.9, 77.6, 63.8, 30.7, 28.5, 18.7, 13.6; HRMS (DART): *m/z* calculated for $C_{15}H_{24}NO_3$ $[M + H]^+$ 266.1751, found 266.1750.

*Butyl (4-(methylthio)phenyl)carbamate (**2c**)*. Off-white solid (372 mg, 78%); mp 73–75 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.61 (s, 1H), 7.42 (d, J = 8.3 Hz, 2H),

7.20 (d, J = 8.5 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.69–1.47 (m, 2H), 1.45–1.25 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.7, 136.9, 130.6, 127.6, 118.9, 63.9, 30.6, 18.7, 15.8, 13.6; HRMS (DART): *m/z* calculated for $C_{12}H_{18}NO_2S$ $[M + H]^+$ 240.1053, found 240.1052.

*Butyl p-tolylcarbamate (**2d**)*. Off-white solid (352 mg, 85% from 4-chlorotoluene; 679 mg, 82% from 4-bromotoluene; 662 mg, 80% from 4-iodotoluene); mp 63-65 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.54 (br s, 1H), 4.16 (t, J = 6.0 Hz, 2H), 2.30 (s, 1H), 1.69–1.62 (m, 2H), 1.47-1.37 (m, 2H), 0.96 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 135.5, 132.9, 129.6, 118.9, 65.1, 31.1, 20.8, 19.2, 13.8; HRMS (DART): *m/z* calculated for $C_{12}H_{18}NO_2$ $[M + H]^+$ 208.1332, found 208.1331.

*Butyl [4-(tert-butyl)phenyl]carbamate (**2e**)*. Pale yellow liquid (398 mg, 80% from 1-*tert*-butyl-4-chlorobenzene; 896 mg, 90% from 1-*tert*-butyl-4-iodobenzene); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 4H), 6.60 (br s, 1H), 4.17 (t, J = 6.0 Hz, 2H), 1.67–1.64 (m, 2H), 1.45–1.39 (m, 2H), 1.30 (s, 9H), 0.95 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 146.4, 135.5, 126.0, 118.6, 65.2, 34.4, 31.5, 31.1, 19.2, 13.9; HRMS (DART): *m/z* calculated for $C_{15}H_{24}NO_2$ $[M + H]^+$ 250.1802, found 250.1801.

*Butyl [1,1'-biphenyl]-4-ylcarbamate (**2f**)*.[20] White solid (452 mg, 84%); mp 110-112 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 (br s, 1H), 7.63–7.58 (m, 6H), 7.42 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 4.09 (t, J = 6.0 Hz, 2H), 1.64–1.57 (m, 2H), 1.43–1.34 (m, 2H), 0.92 (t, J = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.7, 139.8, 138.8, 134.1, 128.9, 127.0, 126.9, 126.2, 118.5, 64.0, 30.6, 18.7, 13.6; HRMS (DART): *m/z* calculated for $C_{17}H_{20}NO_2$ $[M + H]^+$ 270.1494, found 270.1488.

*Butyl (4-(trifluoromethyl)phenyl)carbamate (**2g**)*. White solid (391 mg, 75% from 1-chloro-4-(trifluoromethyl)benzene; 960 mg, 92% from 1-bromo-4-(trifluoromethyl) benzene); mp 88–90 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.04 (br s, 1H), 7.68-7.61 (m, 4H), 4.10 (t, J = 8.0 Hz, 2H), 1.64–1.57 (m, 2H), 1.42–1.33 (m, 2H), 0.90 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.5, 143.0, 126.0 (q, J = 3.0 Hz), 124.5 (q, J = 272.0 Hz), 122.4 (q, J = 32.3 Hz), 117.8, 64.2, 30.5, 18.6, 13.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ –64.5; HRMS (DART): *m/z* calculated for $C_{12}H_{13}F_3NO_2$ $[M - H]^+$ 260.0898, found 260.0898.

*Butyl (4-aminophenyl)carbamate (**2h**)*.[20] Brown semisolid (270 mg, 65%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 0H), 7.08 (d, J = 4.0 Hz, 2H), 6.48 (d, J = 8.0 Hz, 2H), 4.77 (br s, 2H), 4.01 (t, J = 8.0 Hz, 2H), 1.60–1.53 (m, 2H), 1.40–1.31 (m, 2H), 0.90 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.0, 144.2, 128.3, 120.3, 114.1, 63.5, 30.8, 18.7, 13.7; HRMS (DART): *m/z* calculated for $C_{11}H_{17}N_2O_2$ $[M + H]^+$ 209.1290, found 209.1285.

*Butyl (4-(dimethylamino)phenyl)carbamate (**2i**)*. Off-white solid (386 mg, 82%); mp 68–69 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (br s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 12.0 Hz, 2H), 4.03 (t, J = 6.0 Hz, 2H), 2.81 (s, 6H), 1.61–1.54 (m, 2H), 1.41–1.32 (m, 2H), 0.91 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.8, 146.6, 129.1, 119.7, 113.0, 63.5, 40.6, 30.7, 18.7, 13.6; HRMS (DART): *m/z* calculated for $C_{13}H_{21}N_2O_2$ $[M + H]^+$ 237.1598, found 237.1597.

*Butyl (4-morpholinophenyl)carbamate (**2j**)*. Off-white solid (489 mg, 88%); mp 122-124 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (br s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 4.04 (t, J = 6.0 Hz, 2H), 3.71 (t, J = 6.0 Hz, 4H), 3.0 (m, J = 4.0 Hz, 4H), 1.61–1.54 (m, 2H), 1.41–1.32 (m, 2H), 0.90 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.8, 146.7, 131.6, 119.3, 115.8, 66.2, 63.7, 49.2,

30.7, 18.7, 13.7; HRMS (DART): *m/z* calculated for $C_{15}H_{23}N_2O_3$ $[M + H]^+$ 279.1709, found 279.1703.

*Butyl naphthalen-2-ylcarbamate (**2k**)*. Off-white solid (379 mg, 78%); mp 68-69 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.78-7.76 (m, 3H), 7.47–7.37 (m, 3H), 6.93 (s, 1H), 4.23 (t, J = 8.0 Hz, 2H), 1.73–1.66 (m, 2H), 1.50–1.41 (m, 2H), 0.98 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 135.6, 134.0, 130.2, 128.9, 127.6, 127.5, 126.6, 124.7, 119.3, 114.9, 65.3, 31.1, 19.2, 13.9; HRMS (DART): *m/z* calculated for $C_{15}H_{18}NO_2$ $[M + H]^+$ 244.1332, found 244.1332.

*Butyl benzo[d][1,3]dioxol-5-ylcarbamate (**2l**)*. Off-white solid (388 mg, 82% from 5-chlorobenzo[*d*][1,3]dioxole; 853 mg, 90% from 5-bromobenzo[*d*][1,3]dioxole); mp 58-59 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (br s, 1H), 6.72–6.61 (m, 3H), 5.92 (s, 2H), 4.14 (t, J = 6.0 Hz, 2H), 1.67–1.62 (m, 2H), 1.42–1.37 (m, 2H), 0.94 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 148.0, 143.8, 132.4, 111.9, 108.2, 101.9, 101.3, 65.2, 31.1, 19.2, 13.8; HRMS (DART): *m/z* calculated for $C_{12}H_{16}NO_4$ $[M + H]^+$ 238.1074, found 238.1073.

*Butyl (3,5-dimethoxyphenyl)carbamate (**2m**)*. Pale yellow liquid (394 mg, 78%); ^1H NMR (400 MHz, DMSO-d_6) δ 9.55 (s, 1H), 6.72 (d, J = 4.0 Hz, 2H), 6.15 (t, J = 4.0 Hz, 1H), 4.06 (t, J = 8.0 Hz, 2H), 3.69 (s, 6H), 1.62–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.91 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.6, 153.5, 141.0, 96.6, 94.2, 63.9, 55.0, 30.6, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{13}H_{20}NO_4$ $[M + H]^+$ 254.1387, found 254.1386.

Butyl (3-fluoro-5-methoxyphenyl)carbamate (***2n***). Colourless liquid (366 mg, 76%); ^1H NMR (400 MHz, DMSO-d_6) δ 9.80 (br s, 1H), 6.96–6.91 (m, 2H), 6.43 (d, J = 12.0 Hz, 0H), 4.07 (t, J = 8.0 Hz, 2H), 3.71 (s, 3H), 1.562–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.90 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.3, 162.0,

160.8 (d, J = 13.1 Hz,), 153.5, 141.5 (d, J = 14.1 Hz), 99.9, 97.2 (d, J = 26.3 Hz), 95.2 (d, J = 26.3 Hz), 64.1, 55.4, 30.5, 18.6, 13.6; ^{19}F NMR (376 MHz, CDCl3) δ –116.0; HRMS (DART): *m/z* calculated for $C_{12}H_{17}FNO_3$ $[M + H]^+$ 242.1192, found 242.1187.

*Butyl (3-(trifluoromethyl)phenyl)carbamate (**2o**)*. Pale yellow liquid (376 mg, 72%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.94 (s, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.28 (d, J = 7.0 Hz, 1H), 4.09 (t, J = 7.0 Hz, 2H), 1.62–1.56 (m, 2H), 1.39–1.32 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.6, 140.2, 129.8, 129.7 (q, J = 31.3 Hz), 124.2 (q, J = 271.3 Hz), 121.6, 118.4 (q, J = 3.8 Hz), 114.1, 64.2, 30.6, 18.6, 13.4; ^{19}F NMR (376 MHz, DMSO-d_6) δ –66.1; HRMS (DART): *m/z* calculated for $C_{12}H_{15}F_3NO_2$ $[M + H]^+$ 262.1055, found 262.1048.

*Butyl quinolin-3-ylcarbamate (**2p**)*. Off-white solid (366 mg, 75% from 3-chloroquinoline; 800 mg, 82% from 3-bromoquinoline); mp 115-117 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 0H), 8.87 (s, 1H), 8.46 (s, 0H), 7.91 (dd, J = 19.3, 8.0 Hz, 1H), 7.57 (dd, J = 17.0, 7.6 Hz, 1H), 4.15 (t, J = 6.4 Hz, 2H), 1.63 (dd, J = 13.9, 6.7 Hz, 2H), 1.40 (dd, J = 14.6, 7.3 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.9, 144.0, 143.8, 133.1, 128. 6, 127.9, 127.5, 127.4, 127.0, 120.4, 64.4, 30.5, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{14}H_{17}N_2O_2$ $[M + H]^+$ 245.1285, found 245.1284.

*Butyl quinoxalin-6-ylcarbamate (**2q**)*. Off-white solid (416 mg, 85%); mp 91-93 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.21 (s, 1H), 8.80 (d, J = 28.0 Hz, 1H), 8.28 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 4.14 (t, J = 6.0 Hz, 2H), 1.64–1.61 (m, 2H), 1.42–1.36 (m, 2H), 0.91 (t, J = 8.0Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.6, 145.9, 143.6, 143.2, 140.7, 138.8, 129.6, 123.1, 113.8, 64.4, 30.5,

18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{13}H_{16}N_3O_2$ $[M + H]^+$ 246.1237, found 246.1236.

*Butyl isoquinolin-6-ylcarbamate (**2r**)*. Off-white solid (366 mg, 75%); mp 130-132 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.14 (br s, 1H), 8.47 (s, 1H), 8.05 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 0H), 7.48 (dd, J = 8.0, 4.0 Hz, 1H), 7.21 (s, 1H), 4.23 (t, J = 6.0 Hz, 2H), 1.73–1.65 (m, 2H), 1.48–1.39 (m, 2H), 0.96 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 151.9, 143.6, 139.9, 137.1, 129.0, 120.3, 112.5, 65.6, 31.1, 19.2, 13.8; HRMS (DART): *m/z* calculated for $C_{14}H_{17}N_2O_2$ $[M + H]^+$ 245.1285, found 245.1284.

*Butyl thiophen-2-ylcarbamate (**2s**)*. Yellow liquid (246 mg, 62% from 3-chlorothiophene; 652 mg, 82% from 3-bromothiophene); ^1H NMR (400 MHz, DMSO-d_6) δ 9.88 (br s, 1H), 7.40 (dd, J = 8.0, 4.0 Hz, 1H), 7.19 (s, 1H), 7.01 (d, J = 8.0 Hz, 1H), 4.07 (t, J = 6.0 Hz, 2H), 1.62–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.91 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.7, 137.1, 124.8, 121.0, 106.1, 63.9, 30.6, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_9H_{14}NO_2S$ $[M + H]^+$ 200.0740, found 200.0739.

*Butyl (6-methylpyridin-2-yl)carbamate (**2t**)*. Colourless liquid (316 mg, 76%); ^1H NMR (400 MHz, DMSO-d_6) δ 9.95 (s, 1H), 7.62–7.61 (m, 2H), 6.88 (m, 1H), 4.06 (t, J = 6.0 Hz, 2H), 2.36 (s, 3H), 1.60–1.53 (m, 2H), 1.39–1.30 (m, 2H), 0.89 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.43, 153.77, 151.68, 138.39, 117.75, 109.20, 64.04, 30.60, 23.64, 18.58, 13.64; HRMS (DART): *m/z* calculated for $C_{11}H_{17}N_2O_2$ $[M + H]^+$ 209.1285, found 209.1284.

*Butyl pyridin-2-ylcarbamate (**2u**)*.[20] White solid (272 mg, 70% from 2-chloropyridine; 605 mg, 78% from 2-iodopyridine); mp 60-62 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.35 (s, 1H), 8.05 (d, J = 12.0 Hz, 1H), 7.69 (t, J = 8.0

Hz, 1H), 6.97 (s, 1H), 4.21 (t, J = 6.0 Hz, 2H), 1.72–1.69 (m, 2H), 1.46-1.40 (m, 2H), 0.96 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 152.7, 147.7, 138.6, 118.5, 112.7, 65.3, 31.1, 19.2, 13.9; HRMS (DART): *m/z* calculated for $C_{10}H_{15}N_2O_2$ $[M + H]^+$ 195.1128, found 195.1127.

*Methyl (4-methoxyphenyl)carbamate (**2v**).* Off-white solid (260 mg, 72%); mp 90-92 $^{\circ}$C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 5.0 Hz, 2H), 6.84 (d, J = 10.0 Hz, 2H), 6.62 (br s, 1H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 154.6, 131.1, 120.8, 114.2, 55.5, 52.3; HRMS (DART): *m/z* calculated for $C_9H_{12}NO_3$ $[M + H]^+$ 182.0813, found 182.0817.

*Ethyl 4-((ethoxycarbonyl)amino)benzoate (**2w**).* White solid (308 mg, 65%); mp 137-139 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 6.88 (s, 1H), 4.35 (q, J = 8.0 Hz, 2H), 4.24 (q, J = 8.0 Hz, 2H), 1.38 (t, J = 8.0 Hz, 3H), 1.31 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 153.3, 142.3, 131.0, 125.2, 117.6, 61.7, 60.9, 14.6, 14.5; HRMS (DART): *m/z* calculated for $C_{12}H_{16}NO_4$ $[M + H]^+$ 238.1074, found 238.1073.

*Isopropyl phenylcarbamate (**2x**).* White solid (250 mg, 70% from chlorobenzene; 587 mg, 82% from iodobenzene); mp 86-88 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 4H), 6.98 (t, J = 8.0 Hz, 1H), 6.50 (br s, 1H), 4.98-4.91 (m, 1H), 1.23 (d, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 138.2, 129.2, 123.4, 118.7, 68.9, 22.2; HRMS (DART): *m/z* calculated for $C_{10}H_{14}NO_2$ $[M + H]^+$ 180.1025, found 180.1019.

*Isopropyl (4-cyanophenyl)carbamate (**2y**).* White solid (306 mg, 75%); mp 140-142 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (br s, 1H), 7.72 (d, J = 8.0 Hz, 0H), 7.63 (d, J = 8.0 Hz, 0H), 4.94-4.88 (m, 1H), 1.25 (d, J = 4.0 Hz, 6H); ^{13}C NMR (101 MHz,

DMSO-d_6) δ 152.9, 143.8, 133.3, 119.2, 118.0, 103.9, 68.2, 21.9; HRMS (DART): *m/z* calculated for $C_{11}H_{13}N_2O_2$ $[M + H]^+$ 205.0977, found 205.0972.

*2-methylpentyl (4-methoxyphenyl)carbamate (**2z**)*. Off-white solid (346 mg, 69%); mp 60-62 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.50 (br s, 1H), 4.06–3.91 (m, 2H), 3.78 (s, 3H), 1.86–1.78 (m, 1H), 1.39–1.25 (m, 3H), 1.17-1.12 (m, 1H), 0.95-0.89 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 154.3, 131.2, 120.7, 114.4, 70.3, 55.6, 35.7, 32.7, 20.1, 17.0, 14.4; HRMS (DART): *m/z* calculated for $C_{14}H_{22}NO_3$ $[M + H]^+$ 252.1600, found 252.1594.

*Butyl (4-(trimethylsilyl)phenyl)carbamate (**2aa**)*. Colourless liquid (241 mg, 91%), ^1H NMR (400 MHz, DMSO-d_6) δ 9.41 (s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 3.87 (t, J = 8.0 Hz, 2H), 1.40–1.36 (m, 2H), 1.22–1.13 (m, 2H), 0.71 (t, J = 8.0 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.6, 140.0, 133.7, 132.5, 117.5, 63.8, 30.6, 18.6, 13.59, -1.0; HRMS (DART): *m/z* calculated for $C_{14}H_{24}NO_2Si$ $[M + H]^+$ 266.1571, found 266.1569.

*Butyl (3-methoxyphenyl)carbamate (**2ab**)*. Pale yellow liquid (740 mg, 83% from 1-bromo-3-methoxybenzene; 749 mg, 84% from 1-iodo-3-methoxybenzene); ^1H NMR (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 7.18–7.14 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 6.56 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 4.06 (t, J = 6.0 Hz, 2H), 3.70 (s, 3H), 1.63–1.56 (m, 2H), 1.42–1.33 (m, 2H), 0.91 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.6, 153.6, 140.5, 129.5, 110.5, 107.6, 104.0, 63.8, 54.9, 30.6, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{12}H_{18}NO_3$ $[M + H]^+$ 224.1281, found 224.1281.

*Butyl (3,5-dimethylphenyl)carbamate (**2ac**)*. Pale yellow solid (724 mg, 82% from 1-bromo-3,5-dimethylbenzene; 751 mg, 85% from 1-iodo-3,5-dimethylbenzene); mp 61-63 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 9.44 (s, 1H), 7.09 (s, 2H), 6.61 (s, 1H), 4.05 (t, J = 6.0 Hz, 2H), 2.20 (s, 3H), 1.62–1.55 (m, 1H), 1.41-1.32 (m, 2H), 0.91 (t, J

= 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.6, 139.1, 137.6, 123.9, 116.0, 63.7, 30.7, 21.1, 18.7, 13.6; HRMS (DART): *m/z* calculated for $C_{13}H_{20}NO_2$ $[M + H]^+$ 222.1489, found 222.1487.

*Butyl (3,4,5-trimethoxyphenyl)carbamate (**2ad**)*. White solid (1.06 g, 94%); mp 95-96 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 6.85 (s, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.72 (s, 6H), 3.60 (s, 3H), 1.65–1.53 (m, 2H), 1.37 (dq, J = 14.8, 7.4 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.6, 152.9, 135.4, 132.8, 96.0, 63.8, 60.1, 55.6, 30.6, 18.7, 13.6; HRMS (DART): *m/z* calculated for $C_{14}H_{22}NO_5$ $[M + H]^+$ 284.1498, found 284.1492.

*Butyl (4-amino-3-methoxyphenyl)carbamate (**2ae**)*. Brown solid (723 mg, 76%); mp 91-93 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.13 (s, 1H), 7.02 (s, 1H), 6.71 (s, 1H), 6.52 (d, J = 8.0 Hz, 1H), 4.41 (br s, 2H), 4.02 (t, J = 6.0 Hz, 2H), 3.71 (s, 3H), 1.59-1.56 (m, 2H), 1.39–1.35 (m, 2H), 0.91 (t, J = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.8, 146.2, 132.9, 129.0, 113.6, 111.4, 103.0, 63.5, 55.1, 30.7, 18.7, 13.6. HRMS (DART): *m/z* calculated for $C_{12}H_{19}N_2O_3$ $[M + H]^+$ 239.1396, found 239.1390.

*Butyl (3-amino-5-(trifluoromethyl)phenyl)carbamate (**2af**)*. Brown liquid (792 mg, 72%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 6.96 (d, J = 12.0 Hz, 2H), 6.49 (s, 1H), 5.57 (s, 2H), 4.06 (t, J = 8.0 Hz, 2H), 1.62–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.90 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.6, 150.0, 140.7, 130.0 (q, J = 31.3 Hz), 124.5 (q, J = 272.7 Hz), 106.1, 104.1 (q, J = 4.3 Hz), 101.8 (q, J = 4.0 Hz), 63.9, 30.6, 18.6, 13.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ –66.2; HRMS (DART): *m/z* calculated for $C_{12}H_{16}F_3N_2O_2$ $[M + H]^+$ 277.1158, found 277.1157.

*Butyl (6-methoxypyridin-3-yl)carbamate (**2ag**)*. Pale yellow oily liquid (804 mg, 90%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.37 (d,

J = 8.0 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 4.08 (t, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 1.62–1.55 (m, 2H), 1.42–1.32 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.4, 153.5, 150.3, 140.8, 104.0, 103.8, 64.0, 53.0, 30.5, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{11}H_{17}N_2O_3$ $[M + H]^+$ 225.1234, found 225.1233.

*butyl (5-methylpyridin-2-yl)carbamate (**2ah**)*. Off-white solid (724 mg, 87%); mp 114-116 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 8.08 (s, 1H), 7.71 (d, *J* = 4.0 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.07 (t, *J* = 6.0 Hz, 2H), 2.22 (s, 3H), 1.61–1056 (m, 2H), 1.40–1.33 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.7, 150.1, 147.5, 138.5, 127.3, 111.9, 64.0, 30.6, 18.6, 17.2, 13.6; HRMS (DART): *m/z* calculated for $C_{11}H_{17}N_2O_2$ $[M + H]^+$ 209.1285, found 209.1284.

*Butyl quinolin-2-ylcarbamate (**2ai**)*. White solid (829 mg, 85%); mp 78–80 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.45 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 4.12 (t, *J* = 6.0 Hz, 2H), 1.63–1.56 (m, 2H), 1.39–1.32 (m, 2H), 0.89 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.0, 151.8, 146.4, 138.2, 129.9, 127.7, 126.8, 125.2, 124.6, 113.3, 64.3, 30.5, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{14}H_{17}N_2O_2$ $[M + H]^+$ 245.1290, found 245.1284.

*Butyl (2-methylquinolin-6-yl)carbamate (**2aj**)*. White solid (908 mg, 88%); mp 183-185 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.92 (s, 1H), 8.11-8.09 (m, 2H), 7.83 (d, *J* = 12.0 Hz, 1H), 7.70 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 4.12 (t, *J* = 6.0 Hz, 2H), 2.59 (s, 3H), 1.65–1.58 (m, 2H), 1.41–1.33 (m, 2H), 0.91 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.7, 153.8, 143.9, 136.5, 135.4, 128.7, 126.6, 122.5, 122.4, 113.3, 64.0, 30.6, 24.6, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{15}H_{19}N_2O_2$ $[M + H]^+$ 259.1447, found 259.1440.

*Butyl benzo[b]thiophen-5-ylcarbamate (**2ak**)*. Off-white solid (796 mg, 80%); mp 65-66 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 8.08 (s, 1H), 7.87 (d, J = 12.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.43–7.38 (m, 2H), 4.10 (t, J = 8.0 Hz, 2H), 1.65-1.58 (m, 2H), 1.43–1.34 (m, 2H), 0.91 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.8, 140.0, 136.3, 133.1, 128.1, 124.0, 122.6, 116.7, 112.2, 63.9, 30.7, 18.7, 13.6; HRMS (DART): *m/z* calculated for $C_{13}H_{16}NO_2S$ $[M + H]^+$ 250.0896, found 250.0896.

*Butyl benzo[b]thiophen-3-ylcarbamate (**2al**)*. Pale yellow solid (796 mg, 80%); mp 70–72 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.86 (s, 1H), 8.13 (d, J = 4.0 Hz, 1H), 7.93–7.92 (m, 1H), 7.63 (s, 1H), 7.41–7.36 (m, 2H), 4.15 (t, J = 4.0 Hz, 2H), 1.67–1.62 (m, 2H), 1.44–1.37 (m, 2H), 0.93 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.5, 137.3, 132.9, 130.3, 124.7, 123.8, 122.9, 121.2, 109.4, 64.3, 30.6, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{13}H_{16}NO_2S$ $[M + H]^+$ 250.0902, found 250.0896.

*Butyl 1H-indol-5-ylcarbamate (**2am**)*.[20] White solid (760 mg, 82%); mp 78–79 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.95 (s, 1H), 9.32 (s, 1H), 7.70 (s, 1H), 7.31–7.29 (m, 2H), 7.17 (d, J = 12.0 Hz, 1H), 6.36 (s, 1H), 4.08 (t, J = 8.0 Hz, 2H), 1.64–1.57 (m, 2H), 1.44–1.35 (m, 2H), 0.93 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.1, 132.4, 131.1, 127.6, 125.8, 114.4, 111.2, 109.7, 100.9, 63.6, 30.8, 18.7, 13.7; HRMS (DART): *m/z* calculated for $C_{13}H_{17}N_2O_2$ $[M + H]^+$ 233.1285, found 233.1284.

*Tert-butyl m-tolylcarbamate (**2an**)*. White solid (645 mg, 78%); mp 60–62 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 7.34 (s, 1H), 7.23 (t, J = 8.0 Hz, 1H); 7.11 (t, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 2.24 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.8, 139.5, 137.7, 128.4, 122.7, 118.6, 115.4, 78.8, 28.1,

21.3; HRMS (DART): *m/z* calculated for $C_{12}H_{18}NO_2$ $[M + H]^+$ 208.1332, found 208.1334.

*Methyl [1,1'-biphenyl]-3-ylcarbamate (**2ao**).* White solid (772 mg, 85%); mp 106-108 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (s, 1H), 7.78 (s, 1H), 7.60-7.58 (m, 2H), 7.48-7.44 (m, 3H), 7.39-7.35 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.1, 140.9, 140.3, 139.8, 129.4, 129.0, 127.6, 126.7, 120.9, 117.3, 116.5, 51.7; HRMS (DART): *m/z* calculated for $C_{14}H_{14}NO_2$ $[M + H]^+$ 228.1019, found 228.1021.

*Propyl (4-fluorophenyl)carbamate (**2ap**)*. Off-white solid (632 mg, 80%); mp 50-52 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.47 (dd, J = 8.0 Hz, 4.0 Hz, 2H), 7.10 (t, J = 8.0 Hz, 2H), 4.02 (t, J = 8.0 Hz, 2H), 1.67–1.58 (m, 2H), 0.92 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.6 (d, J = 239.4 Hz), 153.8, 135.6 (d, J = 2.0 Hz), 119.8, 115.2 (d, J = 22.2 Hz), 65.7, 21.9, 10.2; ^{19}F NMR (376 MHz, DMSO-d_6) δ –125.4; HRMS (DART): *m/z* calculated for $C_{10}H_{13}FNO_2$ $[M + H]^+$ 198.0930, found 198.0925.

*Cyclohexyl [1,1'-biphenyl]-3-ylcarbamate (**2aq**)*. White solid (885 mg, 75%); mp 129–131 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (br s, 1H), 7.80 (s, 1H), 7.60–7.57 (m, 2H), 7.48–7.44 (m, 3H), 7.38–7.33 (m, 2H), 7.26 (d, J = 8.0 Hz, 1H), 4.67–4.61 (m, 1H), 1.92–1.89 (2H), 1.73–1.70 (m, 2H), 1.54–1.51 (m, 1H), 1.43–1.22 (m, 5H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.1, 140.8, 140.3, 139.9, 129.3, 129.0, 127.5, 126.6, 120.7, 117.2, 116.4, 72.4, 31.7, 24.9, 23.5; HRMS (DART): *m/z* calculated for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1651, found 296.1645.

*Butyl (4-cyanophenyl)carbamate (**2ar**)*. White solid (697 mg, 80%); mp 80-82 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 4.09 (t, J = 6.0 Hz, 2H), 1.63-1.56 (m, 2H), 1.41-1.31 (m, 2H), 0.89 (t, J

= 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.3, 143.7, 133.2, 119.2, 118.0, 104.0, 64.4, 30.5, 18.6, 13.5; HRMS (DART): *m/z* calculated for $C_{12}H_{15}N_2O_2$ [M + H]$^+$ 219.1134, found 219.1128.

*Butyl pyridin-3-ylcarbamate (**2as**)*.[20] White solid (636 mg, 82%); mp 78–80 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.84 (s, 1H), 8.64 (s, 1H), 8.20 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.31 (dd, J = 8.0, 4.0 Hz, 1H), 4.09 (t, J = 6.0 Hz, 2H), 1.64–1.57 (m, 2H), 1.4–1.33 (m, 2H), 0.91 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.7, 143.3, 140.0, 136.0, 124.9, 123.6, 64.2, 30.5, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{10}H_{15}N_2O_2$ [M + H]$^+$ 195.1134, found 195.1128.

*Butyl 9H-carbazol-3-ylcarbamate (**2at**)*. Off-white solid (820 mg, 73%); mp 158-160 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 9.49 (s, 1H), 8.22 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.46–7.34 (m, 4H), 7.12 (t, J = 8.0 Hz, 1H), 4.10 (t, J = 6.0 Hz, 2H), 1.64–1.61 (m, 2H), 1.43–1.38 (m, 2H), 0.93 (t, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.2, 140.3, 136.0, 130.9, 125.5, 122.3, 122.3, 120.0, 118.5, 118.3, 111.0, 110.8, 110.2, 63.7, 30.8, 18.7, 13.7; HRMS (DART): *m/z* calculated for $C_{17}H_{19}N_2O_2$ [M + H]$^+$ 283.1441, found 283.1439.

*Butyl quinolin-6-ylcarbamate (**2au**)*. White solid (888 mg, 91%); mp 122-124 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.74 (d, J = 4 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.15 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.78–7.76 (m, 1H), 7.43 (dd, J = 8.0, 4.0 Hz, 1H), 4.12 (t, J = 6.0 Hz, 2H), 1.65–1.58 (m, 2H), 1.43–1.33 (m, 2H), 0.90 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.8, 148.6, 144.36, 137.3, 135.2, 129.5, 128.4, 122.7, 121.7, 113.2, 64.1, 30.6, 18.6, 13.6; HRMS (DART): *m/z* calculated for $C_{14}H_{17}N_2O_2$ [M + H]$^+$ 245.1285, found 245.1284.

*Tert-butyl quinolin-6-ylcarbamate (**2av**)*. Off-white solid (760 mg, 78%); mp 140-142 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.73 (s, 1H), 8.73 (d, J = 4.0 Hz, 1H), 8.22

(d, J = 4.0 Hz, 1H), 8.18 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 8.0 Hz, 4.0 Hz, 0H), 7.43 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.8, 148.4, 144.2, 137.5, 135.1, 129.4, 128.4, 122.8, 121.6, 113.0, 79.4, 28.1; HRMS (DART): *m/z* calculated for $C_{14}H_{17}N_2O_2$ $[M + H]^+$ 245.1285, found 245.1284.

*Tert-butyl [1,1'-biphenyl]-4-ylcarbamate (**2aw**).* White solid (968 mg, 90%); mp 152-154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 4H), 7.46-7.42 (m, 4H), 7.36-7.32 (m, 1H), 6.65 (br s, 1H), 1.56 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 140.7, 137.8, 136.0, 128.8, 127.7, 127.0, 126.9, 118.9, 80.7, 28.5; HRMS (DART): *m/z* calculated for $C_{17}H_{20}NO_2$ $[M + H]^+$ 270.1489, found 270.1491

*Methyl benzo[d][1,3]dioxol-5-ylcarbamate (**2ax**).* Off-white solid (663 mg, 85%); mp 83-85 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.06 (br s, 1H), 6.76 (s, 1H), 6.71-6.66 (m, 2H), 5.92 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.5, 148.0, 143.9, 132.2, 112.1, 108.1, 102.0, 101.3, 52.4; HRMS (DART): *m/z* calculated for $C_9H_{10}NO_4$ $[M + H]^+$ 196.0604, found 196.0605.

*Isopropyl (3-chlorophenyl)carbamate (**2ay**).*[20] Colourless liquid (568 mg, 67%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (s, 1H), 7.62 (s, 1H), 7.39–7.37 (m, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.01 (dd, J = 8.0, 1.2 Hz, 1H), 4.89 (hept, J = 6.6 Hz, 1H), 1.25 (d, J = 4.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.0, 140.9, 133.2, 130.3, 121.9, 117.4, 116.5, 67.8, 21.9; HRMS (DART): *m/z* calculated for $C_{10}H_{13}ClNO_2$ $[M + H]^+$ 214.0635, found 214.0629.

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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