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Article

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N-Arylation of Carbamates through Photosensitized Nickel Catalysis.

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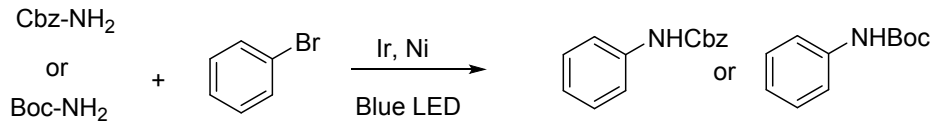


- ***room temperature***
- ***broad FG tolerance***
- ***user friendly and scalable***
- ***inexpensive and ready available Cbz-amine or Boc-amine***
- ***easily removable protecting groups***

Abstract

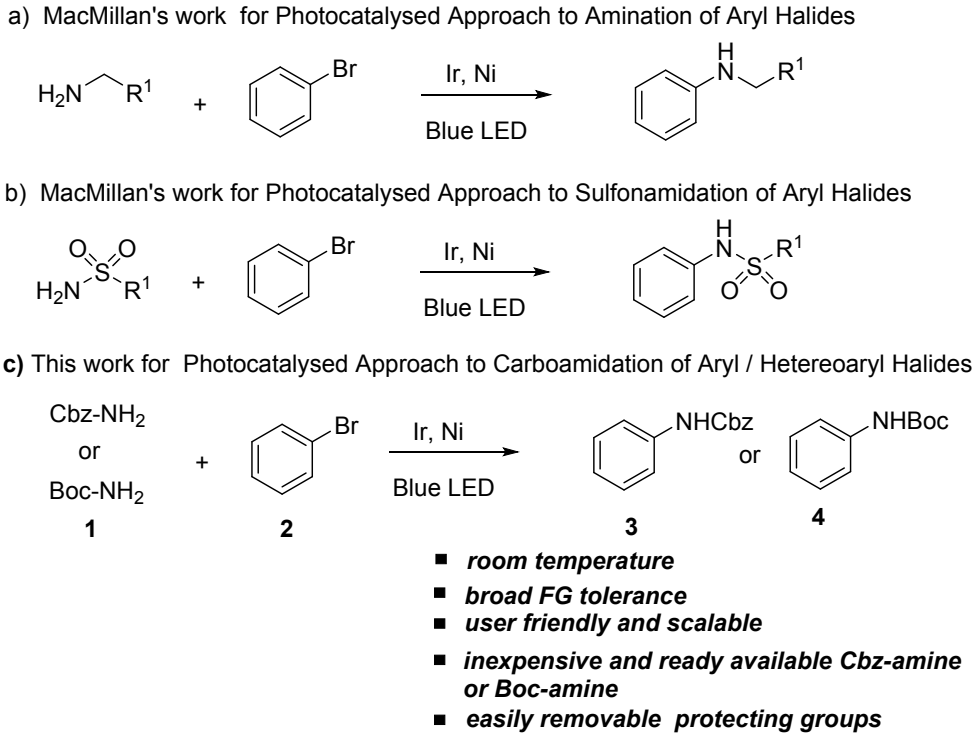
A highly efficient method of visible light mediated Ni (II) catalyzed photoredox *N*-arylation of Cbz-amines / Boc-amines with aryl electrophiles at room temperature is reported. The methodology provides a common access to a wide variety of *N*-aromatic and *N*-heteroaromatic carbamate products that find use in the synthesis of several biologically active molecules and provides a distinct advantage over traditional palladium catalysed Buchwald reaction.

Introduction

Visible light mediated photoredox catalysis has recently emerged as a powerful activation strategy for the discovery and invention of new organic transformations affording valuable molecules in a safe, inexpensive, non-polluting, and thus potentially sustainable manner.[1] Professor Deronzier,[2] reported the first synthetic application of ruthenium photocatalysted Pschorr-type transformation

via single electron transfer (SET) process. In recently, several groups started reporting the direct photoexcitation of transition-metal catalyzed synthetic transformation to demonstrate this paradigm.[3] In particularly, Professor MacMillan's sophisticated report on C-N bond formation of aryl bromide with amines using Ni(II) salts and photoredox catalysis is the best alternative for Buchwald–Hartwig reaction.[4] Later, Professor MacMillan also published the *N*-arylation of sulfonamides with aryl electrophiles via photosensitized Ni (II) catalysis.[5] Inspired by the work of Professor MacMillan, we reasoned that *N*-arylation / heteroarylation of carbamates through photosensitized nickel catalysis could be a viable alternative for Buchwald-Hartwig *N*-arylation of carbamates cross-coupling reaction (Scheme 1).[6] Herein, we disclose the *N*-arylation / heteroarylation of carbamates under Ni (II) catalyzed photoredox conditions.

Scheme 1. Nickel-catalyzed of *N*-arylation of carbamates.

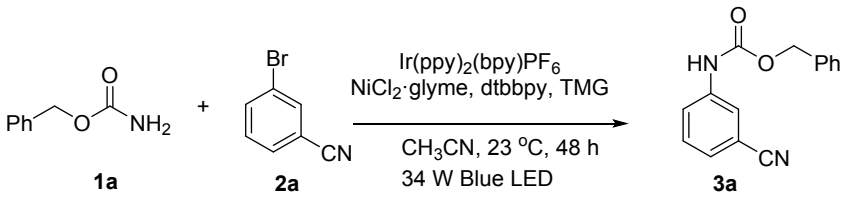


Results and discussion

At the outset of our investigation, we chose the 3-bromobenzonitrile (**2a**) and Cbz-amine (**1a**) as

our model substrates. We began studying the proposed C-N bond formation reaction of 3-bromobenzonitrile (**2a**) with Cbz-amine (**1a**) with emphasis on the development of a user-friendly and scalable method. Fortunately, we found that the commercial bench-stable precatalyst systems $Ir(ppy)_2(bpy)PF_6$ and $NiCl_2 \cdot$glyme with 4,4'-di-*t*-butyl-2,2'-bipyridine ligand (dtbbpy) combined with two equivalents of base (tetramethylguanidine, TMG) in CH_3CN under irradiation with blue LED (34 W) enabled the aryl amine (**3a**) in 93% yield (Table 1, entry 1). Based on the control experiments, it has been found that both nickel and blue light presence were vital for the product formation (Table 1). It has been also noticed that in the absence of photocatalyst, trace quantity (<5%) of product was formed under direct irradiation of blue LED light. We observed that $Ir(ppy)_2(bpy)PF_6$ gives better results compared to $Ir[dF(CF_3)ppy]_2$-$(dtbbpy)PF_6$ and $Ru(bpy)_3(PF_6)_2$ (Table-2, entries 1, 3 and 4). In a similar manner $NiCl_2$.glyme gives superior results compared to $Ni(cod)_2$ (Table 1, entries 1 and 2). While it could be advantageous to employ aryl iodides or chlorides as substrates in these transformations, we observed that aryl bromide is providing the better yield compare to the aryl chloride and aryl iodide (Table 2, entries 3 to 5).

Table 1 Controlled experiments for *N*-arylation of Cbz-amine.

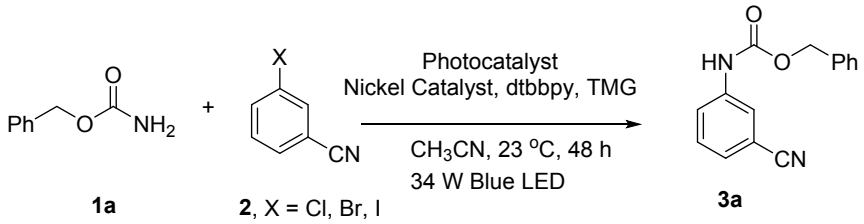


Entry	Conditions[b]	Yield (%)[a]
1	As mentioned above conditions	93
2	without light	No product
3	without Nickel catalyst	No product
4	without photocatalyst	<5
5	without photocatalyst and light	No product

[a] Isolated yield. [b]Conducted with 0.05 mol% of $Ir(ppy)_2(bpy)PF_6$, 5.0 mol % of $NiCl_2 \cdot$glyme, 1.0 equiv of aryl bromide, 1.5 equiv of Cbz-amine and 1.5 equiv of tetramethylguanidine.

With optimal reaction conditions for C–N bond formation in hand, we then examined the flexibility of the substrate scope of the photocatalytic reaction. Interestingly several electron-neutral aryl halides and electron-rich halides delivered excellent yields (75–93%) (Table-3). We obtained excellent yields (90–94%) with a variety of electron-deficient aryl electrophiles such as *p*-cyano, *p*-methyl ester and *p*-trifluoromethyl derivatives with Cbz-amine (Table 3). Furthermore, a wide range of heteroaromatic halides such as pyrimidine, pyridine and benzothiophene derivatives were successfully coupled with Cbz-amine with good yields (73–80%).

Table 2 Optimization of *N*-arylation reaction conditions**.**



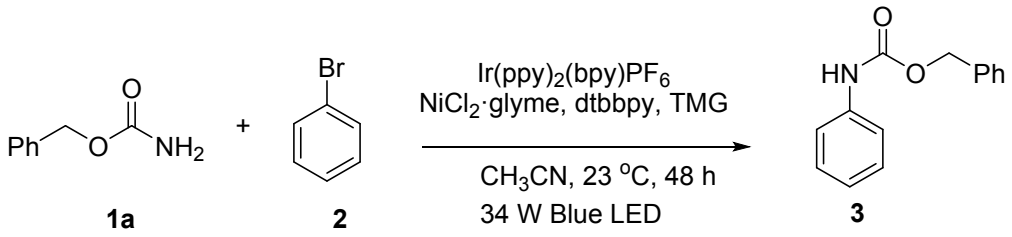
1a **2**, X = Cl, Br, I **3a**

Entry	**2**	Photocatalyst[b]	Ni catalyst	Yield (%)[a]
1	X = Br	$Ir(ppy)_2(bpy)PF_6$	$NiCl_2 \cdot glyme$	93
2	X = Br	$Ir(ppy)_2(bpy)PF_6$	$Ni(cod)_2$	70
3	X = Br	$Ir[dF(CF_3)ppy]_2$-$(dtbbpy)PF_6$	$NiCl_2 \cdot glyme$	68
4	X = Br	$Ru(bpy)_3(PF_6)_2$	$NiCl_2 \cdot glyme$	13
5	X = I	$Ir(ppy)_2(bpy)PF_6$	$NiCl_2 \cdot glyme$	45
6	X = Cl	$Ir(ppy)_2(bpy)PF_6$	$NiCl_2 \cdot glyme$	28

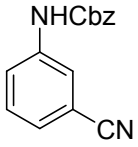
[a]Isolated yield. [b]Conducted with 0.05 mol% of $Ir(ppy)_2(bpy)PF_6$, 5.0 mol % of $NiCl_2 \cdot glyme$, 1.0 equiv of aryl bromide, 1.5 equiv of Cbz-amine and 1.5 equiv of tetramethylguanidine.

Encouraged by these results, we turned our attention to the Boc-amine. Under optimal conditions the Boc-amine was reacted with a large number of aryl halide electrophiles such as an electron-neutral, electron-rich, electron-deficient and heteroaryl halides to obtain the Boc protected arylamines **4** in good to excellent yields (Table 4). Finally, we have also checked reaction of the benzamide (**1c**) with 4-bromobenzonitrile (**2g)** under optimal conditions and obtained benzoyl protected **4r** in excellent yield (92%) (Scheme 2).

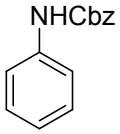
Table 3. Scope of *N*-arylation / heteroarylation of Cbz-amine.[a,b]



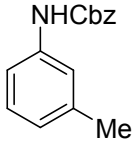
1a **2** **3**



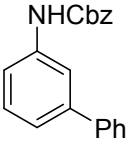
3a
Yield : 93 %



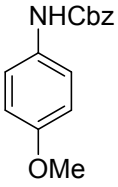
3b
Yield : 79 %



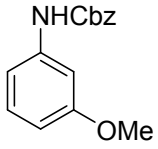
3c
Yield : 82 %



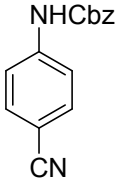
3d
Yield : 85 %



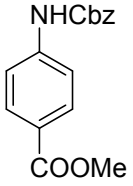
3e
Yield : 79 %



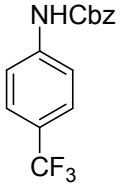
3f
Yield : 75%



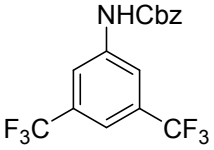
3g
Yield : 94 %



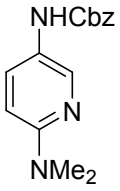
3h
Yield : 92%



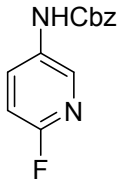
3i
Yield : 90 %



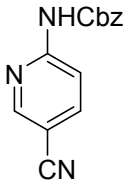
3j
Yield : 91 %



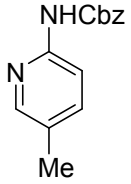
3k
Yield : 75 %



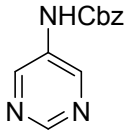
3l
Yield : 77 %



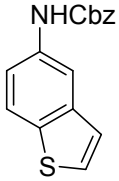
3m
Yield : 74 %



3n
Yield : 76 %



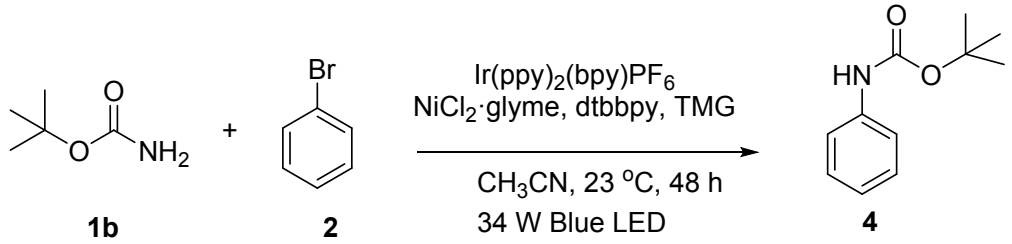
3o
Yield : 73 %



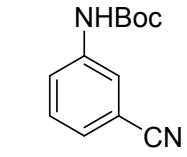
3p
Yield : 78 %

[a]Isolated yield. [b]Conducted with 0.05 mol% of $Ir(ppy)_2(bpy)PF_6$, 5.0 mol % of $NiCl_2$·glyme, 1.0 equiv of aryl bromide, 1.5 equiv of Cbz-amine and 1.5 equiv of tetramethylguanidine.

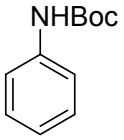
Table 4 Scope of *N*-arylation / heteroarylation of Boc-amine.



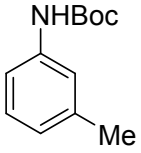
1b **2** **4**



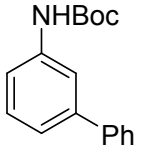
4a
Yield : 90 %



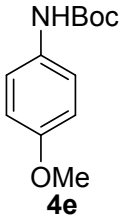
4b
Yield : 74 %



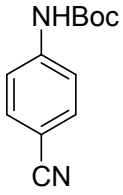
4c
Yield : 79 %



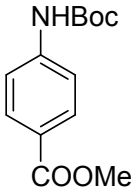
4d
Yield : 81 %



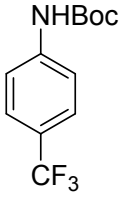
4e
Yield : 75 %



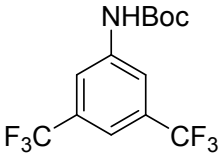
4g
Yield : 91 %



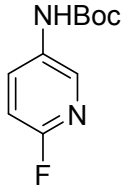
4h
Yield : 90%



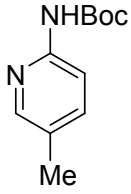
4i
Yield : 89 %



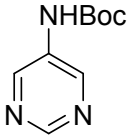
4j
Yield : 92 %



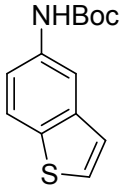
4l
Yield : 75 %



4n
Yield : 74 %



4o
Yield : 71 %



4p
Yield : 82 %

[a]Isolated yield. [b]Conducted with 0.05 mol% of $Ir(ppy)_2(bpy)PF_6$, 5.0 mol % of $NiCl_2$·glyme, 1.0 equiv of aryl bromide, 1.5 equiv of Cbz-amine and 1.5 equiv of tetramethylguanidine.

Based on previous reports[4,5,7] of the mechanism of photoredox catalysis, we envisioned that visible light mediated Ni (II) catalyzed *N*-arylation of carbamate (**1**) with aryl electrophiles (**2**) is shown in Figure 1. The catalysis process starts with oxidative addition of Ni^0 complex **5** into aromatic halide **2** to from Ni^{II}-aryl complex **6**. The ligand exchange of Ni^{II}-aryl complex **6** with Cbz-amine (**1**) might generates Ni^{II}-aromatic amido complex **7**. Simultaneously, blue light irradiation of Ir^{III} photocatalyst **8** would generate triplet excited $*Ir^{III}$ (**9**). The Ni^{II}-aryl complex **6** and excited-state Ir system **9** might go through triplet–triplet energy transfer to procedure excited nickel species **10**. The formed triplet-excited-state complex **10** would readily go through a reductive elimination step to deliver ***N***-aryl carbamate product **3** and restore Ni^0 catalyst **5**.

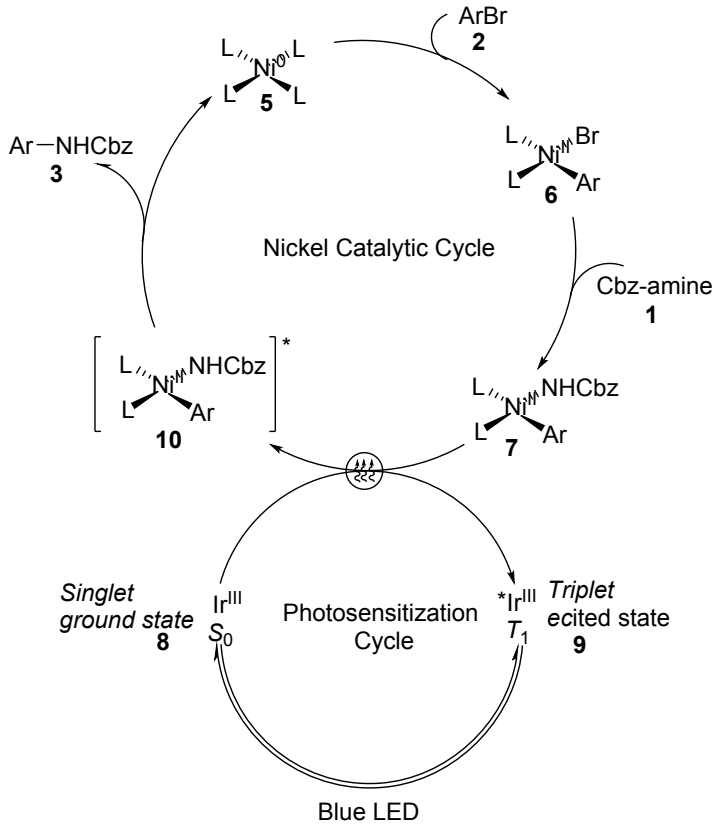
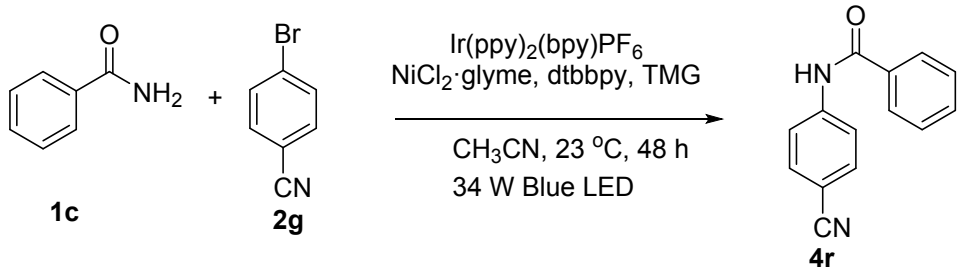


Figure 1. Proposed catalytic cycle.

Scheme 2. Reaction of benzamide with 4-bromobenzonitrile.



Conclusions

In conclusion, we have demonstrated a photoredox catalysis of *N*-arylation of Cbz-amine/ Boc-amine with aromatic bromides / hetero aromatic bromides under exceptionally mild conditions. The methodology provides a distinct advantage over traditional palladium catalysed Buchwald reaction.

Experimental Section

General Information. All the reactions were performed under nitrogen gas in glasswares that was flame-dried and equipped with a magnetic stirring bar. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated plates (0.25 mm). All the reactions monitored by the TLC analysis (single spot/ two solvent systems) using a UV lamp or PMA for detection purposes. Flash chromatography was performed using silica gel (40 μm particle size). ^{1}H and ^{13}C NMR spectra were recorded on a FT-NMR spectrometer at 400 and 100 MHz, respectively. The aryl bromides/heteroaryl bromides, Boc amine/Cbz amine, $Ir[dF(CF_3)ppy]_2$-$(dtbbpy)PF_6$, $Ru(bpy)_3(PF_6)_2$, $Ir(ppy)_2(bpy)PF_6$, $NiCl_2$.glyme, $Ni(cod)_2$, 4,4'-di-t-butyl-2,2'-bipyridine (dtbbpy) and tetramethylguanadine (TMG) were purchased from commercial source and used as received. All solvents were purchased from Aldrich and used without further purification. All the products

(**3a-q** and **4a-r**) were characterized by comparing with literature known data or commercially available reference standards.

General procedure (GP):

To an oven dried 10 mL vial, aryl bromide (1.0 mol, 1.0 equiv.), carbamate (1.5 mol, 1.5 equiv.) and acetonitrile were added. The reaction mixture was degassed with Argon (for 15 minutes) then TMG (1.5 mol, 1.50 equiv.), dtbbpy (0.1 mol, 0.1 equiv.) $NiCl_2$·glyme (0.05 mol, 0.05 equiv.) and $Ir(ppy)_2(dtbbpy)PF_6$ (0.005 mol, 0.005 equiv.) were added. The vial was irradiated with 32 W blue LED for 48 h at room temperature. After completion of the reaction, the reaction mixture was concentrated to dry ness and crude material was purified by column chromatography (silica gel, 10% Ethyl acetate in Hexanes) to afford the pure compound **3** and **4**.

Benzyl (3-cyanophenyl)carbamate **(3a):** Following the general procedure (GP), the reaction of 3-bromobenzonitrile **2a** (182 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3a** as white solid (234 mg, 93%). The compound data was matched with commercially available compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.61-7.55 (m, 1H), 7.49-7.28 (m, 7H), 6.99 (bs, 1H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.0, 138.7, 135.5, 129.9, 128.7, 128.6, 128.4, 126.9, 122.6, 121.5, 118.5, 113.0, 67.5.

Benzyl phenylcarbamate **(3b):** Following the general procedure (GP), the reaction of bromobenzene **2b** (157 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3b** as white solid (179 mg, 79%). The compound matched previously reported characterization data.[8a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.28 (m, 9H), 7.12-7.06 (m, 1H), 6.76

(bs, 1H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.3, 137.7, 136.0, 129.1, 128.6, 128.4, 128.3, 123.5,118.6, 67.0.

Benzyl m-tolylcarbamate **(3c):** Following the general procedure (GP), the reaction of 1-bromo-3-methylbenzene **2c** (171 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3c** as white solid (197 mg, 82%). The compound matched previously reported characterization data.[8b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.30 (m, 5H), 7.28-7.14 (m, 3H), 6.94-6.88 (m, 1H), 6.68 (bs, 1H), 5.22 (s, 2H), 2.35 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.3, 139.0, 137.6, 136.0, 128.9, 128.6, 128.3, 128.3,124.3, 119.3, 115.7, 66.9, 21.5.

Benzyl [1,1'-biphenyl]-3-ylcarbamate **(3d):** Following the general procedure (GP), the reaction of 3-bromo-1,1'-biphenyl **2d** (233 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3d** as white solid (257 mg, 85%). The compound matched previously reported characterization data.[8c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.56 (m, 3H), 7.48-7.19 (m, 11H), 6.83 (s, 1H), 5.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.3, 142.2, 140.7, 138.2, 136.0, 129.4, 128.7, 128.6, 128.4, 128.3, 127.5, 127.2, 122.4, 117.5, 67.1.

Benzyl (4-methoxyphenyl)carbamate **(3e):** Following the general procedure (GP), the reaction of 1-bromo-4-methoxybenzene **2e** (187 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), NiCl2.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3e** as white solid (203 mg, 79%). The compound matched previously reported characterization data.[8d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.28 (m, 7H), 6.92-6.86 (m, 2H), 6.67 (bs, 1H), 5.23 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.0, 153.7, 136.2, 130.8, 128.6, 128.3, 120.7, 114.3, 66.9, 55.5.

Benzyl (3-methoxyphenyl)carbamate **(3f):** Following the general procedure (GP), the reaction of 1-bromo-3-methoxybenzene **2f** (187 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3f** as white solid (192 mg, 75%). The compound matched previously reported characterization data.[8e] ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.34 (m, 5H), 7.28-7.15 (m, 2H), 6.95-6.85 (m, 1H), 6.84-6.71 (m, 1H), 6.7-6.56 (m, 1H), 5.22 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.2, 153.4, 139.0, 135.9, 129.7, 128.6, 128.4, 128.3, 110.8, 109.3, 104.3, 67.0, 55.2.

Benzyl (4-cyanophenyl)carbamate **(3g):** Following the general procedure (GP), the reaction of 4-Bromo benzonitrile **2g** (182 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3g** as white solid (236 mg, 94%). The compound matched previously reported characterization data.[8f] ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.48-7.40 (m, 5H), 6.93 (bs, 1H), 5.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm, 152.7, 142.0, 135.4, 133.4, 128.7, 128.7, 128.4, 118.3, 106.4, 67.6.

Methyl 4-(((benzyloxy)carbonyl)amino)benzoate **(3h):** Following the general procedure (GP), the reaction of Methyl 4-bromobenzoate **2h** (215 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3h** as white solid (262 mg, 92%). The compound matched previously reported characterization data.[8g] ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.58-7.37 (m, 7H), 6.99 (bs, 1H), 5.25 (s, 2H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.6,152.9, 142.1, 135.7, 130.9, 128.7, 128.5, 128.4, 124.9, 117.6, 67.4, 52.0.

Benzyl (4-(trifluoromethyl)phenyl)carbamate **(3i):** Following the general procedure (GP), the reaction of 1-bromo-4-(trifluoromethyl)benzene **2i** (225 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3i** as white solid (265 mg, 90%). The compound matched previously reported characterization data.[8h] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.49 (m, 4H), 7.46-7.36 (m, 5H), 6.89 (bs, 1H), 5.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.9, 140.9, 135.6, 128.7, 128.5, 128.4, 126.4, 126.4, 126.3, 125.4, 125.1, 122.7, 118.0, 67.4.

Benzyl (3,5-bis(trifluoromethyl)phenyl)carbamate **(3j):** Following the general procedure (GP), the reaction of 1-bromo-3,5-bis(trifluoromethyl)benzene **2j** (293 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3j** as white solid (330 mg, 91%). The compound data was matched with commercially available compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.58 (s, 1H), 7.43-7.37 (m, 5H), 7.03 (bs, 1H), 5.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.8, 139.3, 135.3, 132.9, 132.6, 132.3, 131.9, 128.7, 128.7, 128.4, 124.4, 121.7, 118.2, 116.8, 67.7.

Benzyl (6-(dimethylamino)pyridin-3-yl)carbamate **(3k):** Following the general procedure (GP), the reaction of 5-bromo-N,N-dimethylpyridin-2-carbamide **2k** (201 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3k** as white solid (203 mg, 75%). The compound data was matched with commercially available compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.30 (m, 6H), 7.30-7.25 (m, 1H), 7.22-7.16 (m, 1H), 6.22 (d, J =8 Hz, 1H), 5.22 (s, 2H), 3.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.2, 152.9, 149.5, 139.3, 136.0, 128.5, 128.4, 128.2, 128.2, 100.7, 98.7, 66.8, 37.7.

Benzyl (6-fluoropyridin-3-yl)carbamate **(3l):** Following the general procedure (GP), the reaction of 5-bromo-2-fluoropyridine **2l** (175 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3l** as white solid (189 mg, 77%). The compound data was matched with commercially available compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.44-7.35 (m, 5H), 6.96-6.89 (m, 2H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.8, 158.4, 153.4, 137.3, 135.5, 132.6, 132.5, 132.0, 131.9, 128.7, 128.6, 128.4, 109.7, 109.3, 67.5.

Benzyl (5-cyanopyridin-2-yl)carbamate **(3m):** Following the general procedure (GP), the reaction of 6-bromonicotinonitrile **2m** (183 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3m** as white solid (187 mg, 74%). The compound data was matched with commercially available compound. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.95 (bs, 1H), 8.75 (s 1H), 8.26-8.21 (m, 1H), 8.02-7.98 (m, 1H), 7.48-7.34 (m, 5H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d6) δ ppm 155.4, 153.6, 152.6, 142.2, 136.5, 128.9, 128.6, 128.5, 117.8, 112.1, 103.1, 66.8.

Benzyl (5-methylpyridin-2-yl)carbamate **(3n):** Following the general procedure (GP), the reaction of 2-bromo-5-methylpyridine **2n** (172 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3n** as white solid (183 mg, 76%). The compound data was matched with commercially available compound. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.21 (bs, 1H), 8.08 (s, 1H), 7.74 (d, J =8.4 Hz, 1H), 7.58 (d, J =8.4 Hz, 1H), 7.46-7.30 (m, 5H), 5.17 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ ppm 153.9, 150.3, 148.0, 139.0, 137.0, 128.8, 128.4, 128.3, 127.9, 112.3, 66.1, 17.6.

Benzyl pyrimidin-5-ylcarbamate **(3o):** Following the general procedure (GP), the reaction of 5-bromopyrimidine **2o** (158 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3o** as white solid (167 mg, 73%). The compound matched previously reported characterization data.[8i] ^1H NMR (400 MHz, DMSO-d6) δ 9.88 (s, 1H), 8.85-8.83 (m, 3H), 7.47-7.32 (m, 5H), 5.22 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d6) δ ppm 153.8, 152.9, 146.6, 136.5, 135.0, 128.9, 128.7, 66.9.

Benzyl benzo[b]thiophen-5-ylcarbamate **(3p):** Following the general procedure (GP), the reaction of 5-bromobenzo[b]thiophene **2p** (213 mg, 1.0 mol) with benzyl carbamate (226 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **3p** as white solid (220 mg, 78%). The compound data was matched with commercially available compound. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (bs, 1H), 7.81 (d, *J* =8.4 Hz, 1H), 7.52-7.36 (m, 6H), 7.32-7.26 (m, 2H), 6.87 (s, 1H), 5.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.6, 140.3, 136.1, 134.9, 134.6, 128.6, 128.4, 128.4, 127.6, 123.8, 122.8, 116.8, 113.2, 67.1.

tert-Butyl (3-cyanophenyl)carbamate **(4a):** Following the general procedure (GP), the reaction of 3-bromobenzonitrile **2a** (182 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4a** as white solid (196 mg, 90%). The compound matched previously reported characterization data.[8j] ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.56-7.50 (m, 1H), 7.43-7.26 (m, 2H), 6.67 (bs, 1H), 1.54 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 147.5, 134.5, 125.0, 121.7, 117.6, 116.6, 113.8, 108.2, 76.7, 23.5.

tert-Butyl phenylcarbamate **(4b):** Following the general procedure (GP), the reaction of bromobenzene **2b** (157 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4b** as white solid (142 mg, 74%). The compound matched previously reported characterization data.[8k] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.24 (m, 4H), 7.09-7.01 (m, 1H), 6.54 (bs, 1H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.7, 138.3, 128.9, 123.0, 118.5, 80.5, 28.3.

tert-Butyl m-tolylcarbamate **(4c):** Following the general procedure (GP), the reaction of 1-bromo-3-methylbenzene **2c** (171 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4c** as white solid (163 mg, 79%). The compound matched previously reported characterization data.[8b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 1H), 7.24-7.08 (m, 2H), 6.89 (d, J = 7.2 Hz, 1H), 6.49 (bs, 1H), 2.37 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.8, 138.9, 138.2, 128.7, 123.8, 119.1, 115.5, 80.4, 28.3, 21.5.

tert-Butyl [1,1'-biphenyl]-3-ylcarbamate **(4d):** Following the general procedure (GP), the reaction of 3-bromo-1,1'-biphenyl **2d** (233 mg, 1.0 mol) with tert-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4d** as white solid (217 mg, 81%). The compound matched previously reported characterization data.[8l] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.60 (m, 3H), 7.51-7.43 (m, 2H), 7.41-7.35 (m, 3H), 7.33-7.29 (m, 1H), 6.61 (bs, 1H), 1.58 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.7, 142.1, 140.8, 138.7, 129.3, 128.7, 127.4, 127.2, 121.9, 117.3, 117.3, 80.6, 28.3.

tert-Butyl (4-methoxyphenyl)carbamate **(4e):** Following the general procedure (GP), the reaction of 1-bromo-4-methoxybenzene **2e** (187 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4e** as white solid (167 mg, 75%). The compound matched previously reported characterization data.[8k] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.43 (bs, 1H), 3.81 (s, 3H), 1.55 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.6, 153.1, 131.4, 120.6, 114.1, 80.2, 55.5, 28.3.

tert-butyl (4-cyanophenyl)carbamate **(4g):** Following the general procedure (GP), the reaction of 4-Bromo benzonitrile **2g** (182 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4g** as white solid (198 mg, 91%). The compound matched previously reported characterization data.[8m] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 6.72 (bs, 1H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.0, 142.6, 133.3, 119.1, 118.1, 105.7, 81.7, 28.2.

Methyl 4-((tert-butoxycarbonyl)amino)benzoate **(4h):** Following the general procedure (GP), the reaction of methyl 4-bromobenzoate **2h** (215 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4h** as white solid (225 mg, 90%). The compound matched previously reported characterization data.[8n] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.71 (bs, 1H), 3.93 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.7,152.2, 142.7, 130.9, 124.3, 117.3, 81.2, 51.9, 28.2.

tert-Butyl (4-(trifluoromethyl)phenyl)carbamate **(4i):** Following the general procedure (GP), the reaction of 1-bromo-4-(trifluoromethyl)benzene **2i** (225 mg, 1.0 mol) with *tert*-butyl carbamate

(175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4i** as white solid (232 mg, 89%). The compound matched previously reported characterization data.[8j] ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 6.71 (bs, 1H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.3, 141.5, 128.3, 126.3, 126.3, 126.2, 126.2, 125.6, 125.3, 124.9, 124.6, 124.3, 122.9, 120.2, 117.9, 81.3, 28.2.

tert-butyl (3,5-bis(trifluoromethyl)phenyl)carbamate **(4j):** Following the general procedure (GP), the reaction of 1-bromo-3,5-bis(trifluoromethyl)benzene **2j** (293 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4j** as white solid (302 mg, 92%). The compound matched previously reported characterization data.[8o] ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.54 (s, 1H), 6.86 (bs, 1H), 1.55 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.1, 139.8, 132.8, 132.4, 132.1, 131.8, 127.2, 124.5, 121.7, 119.0, 117.9, 116.2, 116.2, 116.1, 81.9, 28.1.

tert-butyl (6-fluoropyridin-3-yl)carbamate **(4l):** Following the general procedure (GP), the reaction of 5-bromo-2-fluoropyridine **2l** (175 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4l** as white solid (159 mg, 75%). The compound data was matched with commercially available compound. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19-8.01 (m, 2H), 6.95-6.88 (m, 1H), 6.78 (bs, 1H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.5, 158.2, 152.7, 137.3, 133.1, 131.8, 109.5, 109.1, 81.4, 28.2.

tert-butyl (5-methylpyridin-2-yl)carbamate **(4n):** Following the general procedure (GP), the reaction of 2-bromo-5-methylpyridine **2n** (172 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg,

1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4n** as white solid (153 mg, 74%). The compound matched previously reported characterization data.[8p] ^1H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.22 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.55-7.49 (m, 1H), 2.3 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.9, 150.4, 147.4, 138.9, 127.2, 112.0, 80.5, 28.4, 17.6.

tert-Butyl pyrimidin-5-ylcarbamate **(4o):** Following the general procedure (GP), the reaction of 5-bromopyrimidine **2o** (158 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4o** as white solid (138 mg, 71%). The compound matched previously reported characterization data.[8q] ^1H NMR (400 MHz, $CDCl_3$) δ 8.96-8.87 (m, 3H), 7.12 (bs, 1H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.9, 152.2, 146.5, 134.0, 82.1, 28.2.

tert-Butyl benzo[b]thiophen-5-ylcarbamate **(4p):** Following the general procedure (GP), the reaction of 5-bromobenzo[b]thiophene **2p** (213 mg, 1.0 mol) with *tert*-butyl carbamate (175 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4p** as white solid (204 mg, 82%). The compound matched previously reported characterization data.[8r] ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 5.6 Hz, 1H), 7.32-7.27 (m, 1H), 7.26-7.21 (m, 1H), 6.64 (bs, 1H), 1.58 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.0, 140.3, 135.2, 134.4, 127.4, 123.8, 122.6, 116.7, 112.9, 80.6, 28.4.

N-(4-cyanophenyl)benzamide **(4r):** Following the general procedure (GP), the reaction of 4-bromo benzonitrile **2g** (182 mg, 1.0 mol) with benzamide (182 mg, 1.5 mol), tetramethyl guanidine (172 mg, 1.5 mol), $NiCl_2$.glyme (11 mg, 0.05 mol) and $Ir(ppy)_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mol) afforded **4r** as white solid (200 mg, 90%). The compound matched previously reported

characterization data.[8s] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.02 (bs, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.80 (m, 2H), 7.66 (d, J=8.4 Hz, 2H), 7.60 (m, 1H), 7.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 166.2, 143.5, 134.4, 133.1, 132.1, 128.5, 127.9, 120.2, 119.1, 105.3.

Supporting Information Available: Copies of NMR spectra of all the compounds, This material is available free of charge via the Internet at http://pubs.acs.org**.**

Dedication

Dedicated to Professor E. J. Corey (Sheldon Emory Professor Emeritus, Harvard University, USA) on the occasion of his 90th birthday.

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Conflicts of interest

There are no conflicts to declare.

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