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Bis(trifluoroacetoxy)iodo benzene (PIFA)-promoted transamidation of carboxamides and carboxylic acids with amines

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Abstract

A simple and efficient method has been developed for the synthesis of amides promoted by PIFA [(bis(trifluoroacetoxy)iodo)benzene]. In this method, PIFA [(bis(trifluoroacetoxy)iodo)benzene] has been used as a useful promoter for the transamidation of dimethylformamide (DMF) with the amines. Besides, this hypervalent iodine smoothly promoted the N-formylation of various aromatic amines with formic acid. Notably, the small quantity of PIFA is found to be efficient for both strategies and large-scale synthesis can also be achieved. The present protocol involves a metal and solvent-free, mild, eco-friendly condition with a high yield of the amide products and moreover, the reactions are not air or moisture sensitive.

- Hypervalent iodine
- Metal and Solvent-free
- Easily accessible reagents
- High yields
- Gram scale synthesis

Keywords: Amide synthesis, PIFA [(bis(trifluoroacetoxy)iodo)benzene], carboxamides, carboxylic acids, metal-free

Introduction

In biological and pharmaceutical relevant compounds, the amide analogues are considered as an important structural unit and most the natural products and pharmaceutical compounds are associated with amide functionality.[1] It is noteworthy that nearly 25% of pharmaceutical substances contain an amide group.[2] Several natural products like penicillin-G, capsaicin, nacetyl, piperine, anthranilic acid, and taxol and clinical drugs such as paracetamol, lacosamide, formoterol, mepivacaine, lidocaine, articaine, amoxicillin, acetazolamide, valsartan, atorvastatin, protirelin, captopril, enalapril, chloramphenicol, methyprylon, benzipram, zolpidem and many more contain the eminent amide functional unit (Figure 1).[3-4] In particular, N-formyl amides are commonly applied as a useful synthetic intermediate to synthesize many important compounds such as amines,[5] N-methyl amines,[6] isonitriles,[7] thioamides,[8] isoselenocyanates.[9] Furthermore, in organic chemistry, the amides have a vast application in form of dyes, polymers, and agrochemicals substances. Significantly, the amides are known as potential functionalities of peptides and proteins and N-formyl deprotection can be accomplished without touching the peptide bond.[10-11] Eventually, the fatty acid amides can show anti-inflammatory, antimicrobial, antitubercular, and antiproliferative activities.[3]

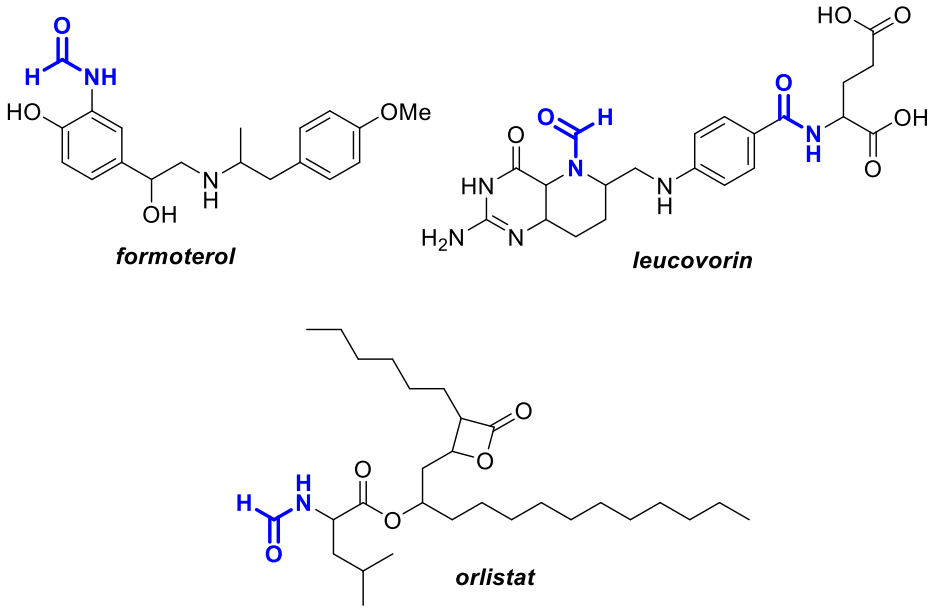
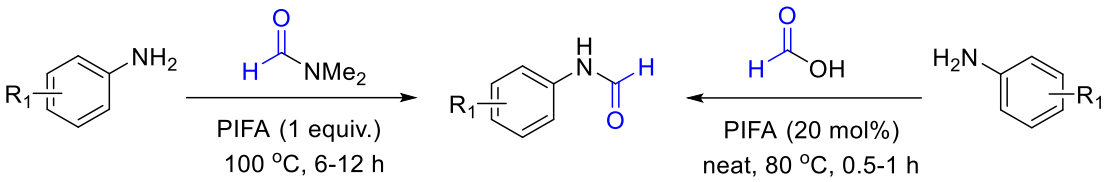


Figure 1. The representative drug molecules containing amide unit.

Fundamentally, the amides have immensely surrounded many chemical strategies that have enriched the synthetic organic chemistry zone. Due to such valuable contribution of amide compound, many strategic methods have been developed for years. In this regard, some common effective solvents like dimethylformamide (DMF) have exhibited reactivity in the case of N-formylation reaction with various amines. In the reported literature, the transamidation of amines has been completed using DMF as carbonyl sources using various metal catalysts such as iron, palladium, nickel, cerium, manganese,[12] NH_4I,[13] sulfated polyborate,[14] hydroxylamine hydrochloride ($NH_2OH.Cl$),[15] H_2SO_4–SiO_2,[16] $K_2S_2O_8$,[17] graphene oxide (GO),[18] boric acid,[19] ionic liquids.[20] On the other hand, several carboxylic acids and their derivatives like acid chloride or anhydrates have taken part in N-formylation process.[21-25] Different types of formylating reagents have been brought in for the amidation process by employing various catalytic systems such as Brønsted acids, Lewis acids, nano-oxides and

many others.[26] However, the previous methods still have some strategic deficiencies in terms of the condition and reagents used.

In recent advanced chemistry, iodine-containing compounds have attracted considerable attention in synthetic organic chemistry. Especially, hypervalent iodine has been raised as a useful and efficient alternative reagent for many important organic transformations.[27-28] Remarkably, these novel substances show promising activity in oxidation or catalytic reactions.[29] However, PIFA has been considered to be an active and elegant reagent to promote several important organic reactions such as amination, sulfenylation, oxidative coupling, amidation, carboxylation, ring-rearrangement, cascade reaction, alkylarylation, and many others.[30-33] Particularly, hypervalent iodine (III) has been involved in the direct C-N bond formation and metal-free functionalization.[34] For the last five years, we have immensely engaged in the development of green and sustainable methodologies.[35-41] In this account, we have utilized the catalytic activity of PIFA[42] for the facile and collective transamidation of dimethylformamide, and formic acid.



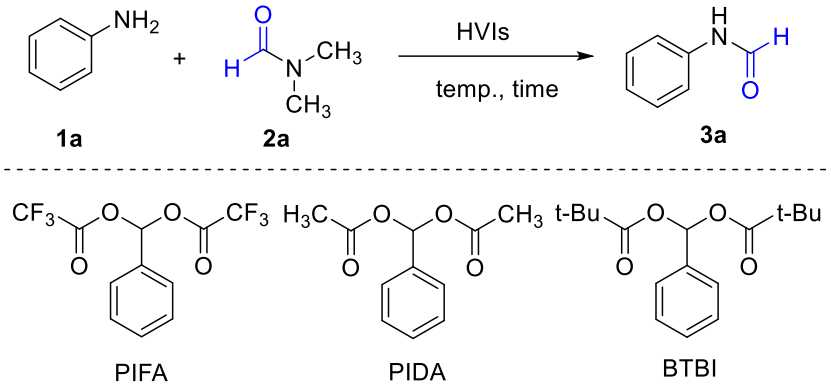
Scheme 1. Transamidation of carboxamides and carboxylic acids.

Results and Discussion

At the initial point, at 100 °C we have conducted the transamidation reaction of aniline, **1a** with 2 ml of formamide, **2a** in the presence of a useful hypervalent iodine reagent phenyliodine(III) diacetate (PIDA) (20 mol%) and as a result of 75% of the N-phenylformamide, **3a** was produced (Table 1, entry 1). Interestingly, in the next observation, the reaction was carried out with (bis(trifluoroacetoxy)iodo)benzene (PIFA) which provided a better yield of the desired product (82%) (Table 1, entry 2). After that, the reactions were thoroughly investigated with varying amounts of the catalyst. The use of 50 mol% of the catalyst did not improve much to form the targeted product, **3a** (Table 1, entry 3). On the other hand, when the quantity of the PIFA was decreased to 10 mol% and 5 mol% there was a certain decline in the product formation (Table 1, entry 4-5). Certainly, bis(tert-butylcarbonyloxy)iodobenzene (BTBI) was not found to be a suitable hypervalent iodine catalyst for this purpose (Table 1, entry 6). Next, the reaction was checked taking 1 equiv. of PIFA and surprisingly, we got 86% of N-phenylformamide (Table 1, enty 7). Thereafter, the heating process at 140 °C did not show a considerable change in the yield while a less amount of product was generated at the lower temperature, 50 °C (Table 1, entry 8 & 9). Next, we also investigated the addition of solvent to the reaction. In this regard, the presence of DMSO was not effective for this reaction (Table 1, entry 10). Interestingly, the solvent mixture with an equal ratio of DMF and other solvents (1:1) gave an unsatisfactory yield. In addition, the other solvent medium pairing DMF with DMSO, toluene and acetonitrile were found inappropriate to get a better result (Table 1, entry 11-13). Eventually, the product was formed with 66% of yield by the use of ½ ml of DMF (Table 1, entry 14). Moreover, we examined the reaction for a prolonged time of 12 hours and the formation of the desired product was not changed (Table 1, entry 15). So, the optimized condition of the present reaction was 1 equiv. of PIFA and 2 ml of DMF upon treatment with anile at 100 °C temperature to produce the

N-phenylformamide with the best yield. The reaction was also investigated in the absence of catalyst and under nitrogen atmosphere, but both conditions were not suitable (Table 1, entry 16 & 17).

Table 1. Optimization of reaction conditions for N-formylation of aniline[a]



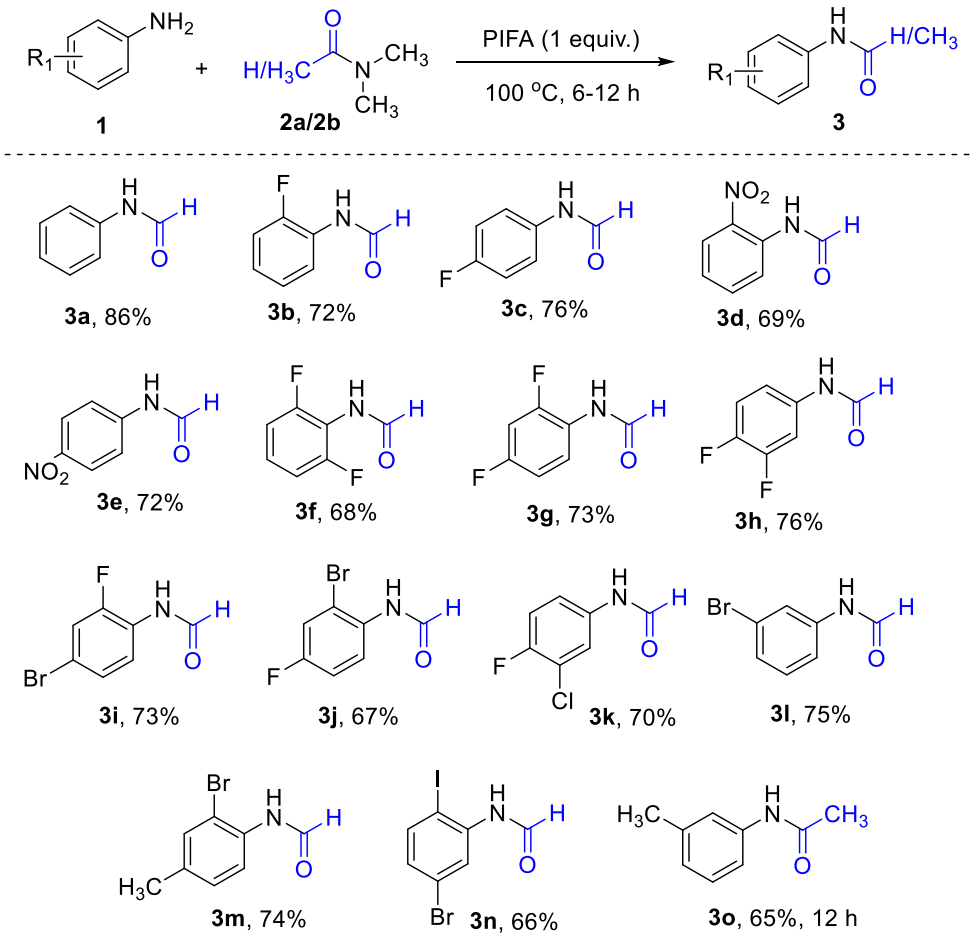
Entry	Promoter	Solvents	Temp. (°C)	Yield[b] (%)
1	PIDA (20 mol%)	DMF	100	75
2	PIFA (20 mol%)	DMF	100	82
3	PIFA (50 mol%)	DMF	100	83
4	PIFA (10 mol%)	DMF	100	56
5	PIFA (5 mol%)	DMF	100	33
6	BTBI (20 mol%)	DMF	100	47
7	PIFA (1 equiv.)	DMF	100	86
8	PIFA (1 equiv.)	DMF	140	84
9	PIFA (1 equiv.)	DMF	50	62
10	PIFA (1 equiv.)	DMSO	100	55
11	PIFA (1 equiv.)	DMF/DMSO (1:1)	100	46
12	PIFA (1 equiv.)	DMF/toluene (1:1)	100	38
13	PIFA (1 equiv.)	DMF/CH_3CN (1:1)	100	53
14	PIFA (1 equiv.)	DMF	100	66[c]
15	PIFA (1 equiv.)	DMF	100	86[d]
16	-	DMF	100	nr
17	PIFA (1 equiv.)	DMF	100	24[e]

[a]Reaction conditions: aniline (**1a**, 1 mmol), DMF (**2a**, 2 ml), HVIs (5 mol%-1 equiv.); 100 °C; 6 h. [b]Isolated yield. [c]DMF (0.5 mL) was used. [d]Reaction carried out for 12 h. [e]The reaction was performed under a nitrogen atmosphere.

After getting the optimized reaction condition we then engaged to increase the substrate scope (Table 2). To check the tolerance of the electron-withdrawing groups in the nucleophile, we have used 2-F and 4-F aniline and notably, both the anilines smoothly converted to the corresponding formamide products **3b** and **3c** in excellent yields. Even, 2-nitroaniline and 4-nitroaniline easily underwent the reaction to give the desired formamides **3d** and **3e** in 69% and 72% yields respectively. Importantly, sterically hindered 2,6-difluoroaniline easily underwent the reaction to produce the desired product **3f** in good yield. Other difluoro substituted anilines such as 2,4-F, 3,4-F also afforded the respective compounds **3g** and **3h** in high yields. Interestingly, other

halogen-containing anilines like 2-fluoro-4-bromoaniline, 2-bromo-4-fluoroaniline, 3-chloro-4-fluoroaniline, 3-bromoaniline, 2-bromo-4-methylaniline, 2-iodo-3-bromoaniline were also equally effective for the N-formylation reaction and the corresponding formamide compounds (**3i**-**3n**) were obtained in good yields. In addition, DMA was also found to be an effective agent for the N-acylation of aniline and the N-(m-tolyl)acetamide, **3o** was obtained in 65% yield.

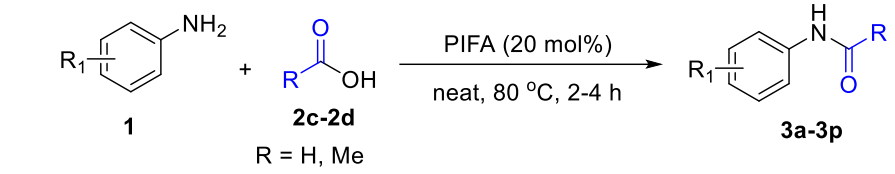
Table 2. Synthesis of amides using DMF and DMA[a]

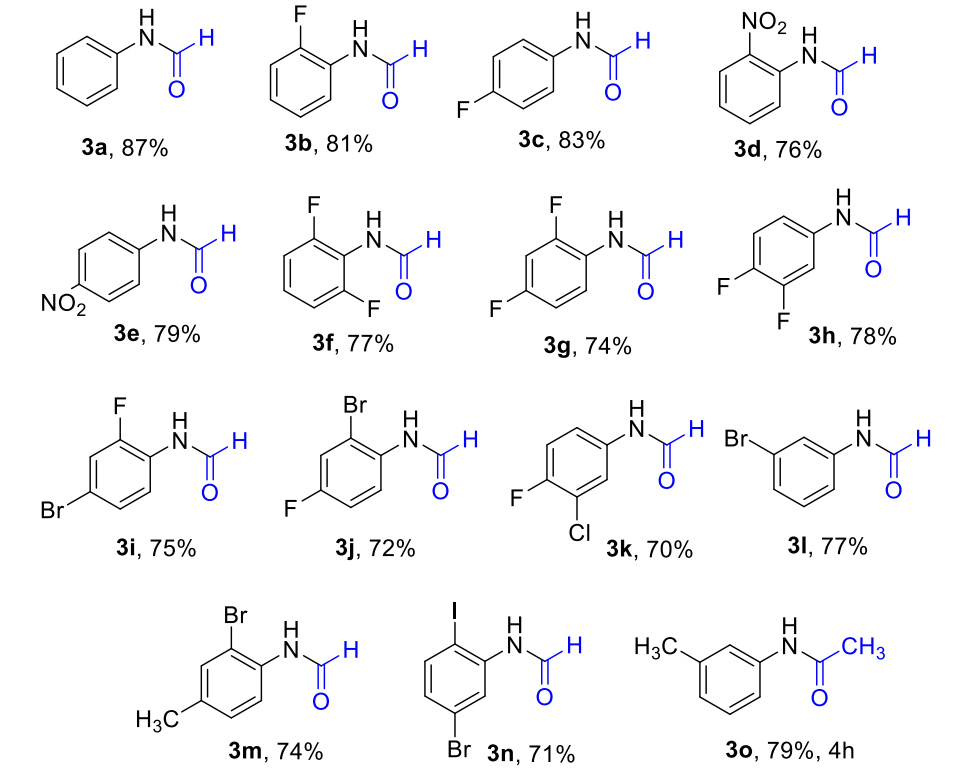


[a]Reaction conditions: aniline (**1a**, 1 mmol), DMF (**2a/2b**, 2 ml); PIFA (1 equiv.); 100 °C. [b]Isolated yield.

To our delight, we have applied our present method for the transamidation of various carboxylic acids namely, HCO_2H, and CH_3CO_2H (Table 3). Notably, these carboxylic acids were easily converted to the corresponding amides under solvent-free conditions and 80 °C heating. At first, we successfully prepared the N-formylated product by the reaction of aniline with formic acid. The N-phenylformamide **3a** was resulted in an excellent yield of 87%. Later on, we investigated the reaction with a few electron-withdrawing halogen and nitro-substituted anilines to get the desired products **3b**-**3h** in high yields. It is noteworthy that formic acid also reacted with halogen-containing anilines to afford the expected compounds **3i**-**3n** in very high yields. In addition, upon reaction with substituted anilines with acetic acid, the respective acetamide product was formed in 79% yield.

Table 3. Synthesis of amides using carboxylic acids[a]





[a]Reaction conditions: aniline (**1a**, 1 mmol), carboxylic acids (**2c**-**2d**, 4 mmol); PIFA (20 mol%); 80 °C. [b]Isolated yield.

The structure of the product was further supported by X-ray crystallographic analysis. The crystal structure of *N*-(2,6-difluorophenyl)formamide **3f** has been shown in figure 2. CCDC No. **2167435**

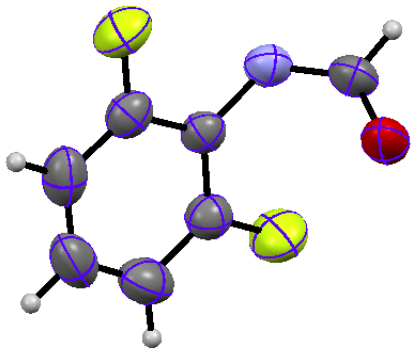
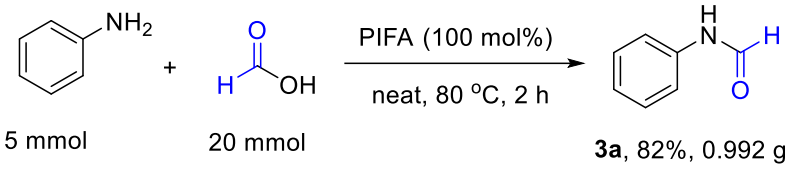


Figure 2. X-ray crystallographic structure of compound **3f**.

Being motivated by the excellent yield formation of the corresponding products, we then performed the reaction with a large number of reactants. Under the standard reaction condition, the mixture of 5 mmol of aniline, and 20 mmol of formic acid in the presence of PIFA (100 mol%) was successfully converted to the expected N-formamide, **3a** in 81% yield.



Scheme 2. Gram-scale synthesis of *N*-phenylformamide.

Based on the above results, we have established a probable mechanism for transamidation in the presence of PIFA which is known as an efficient promoter for several reactions.[31] Initially, formamide coordinate with (bis(trifluoroacetoxy)iodo)benzene and the nucleophilic attack of amines is facilitated to form the intermediate A. Then, in the next step of the easy proton transfer process, the second intermediate B was generated and finally, the deamination led to the desired amide product **3**.

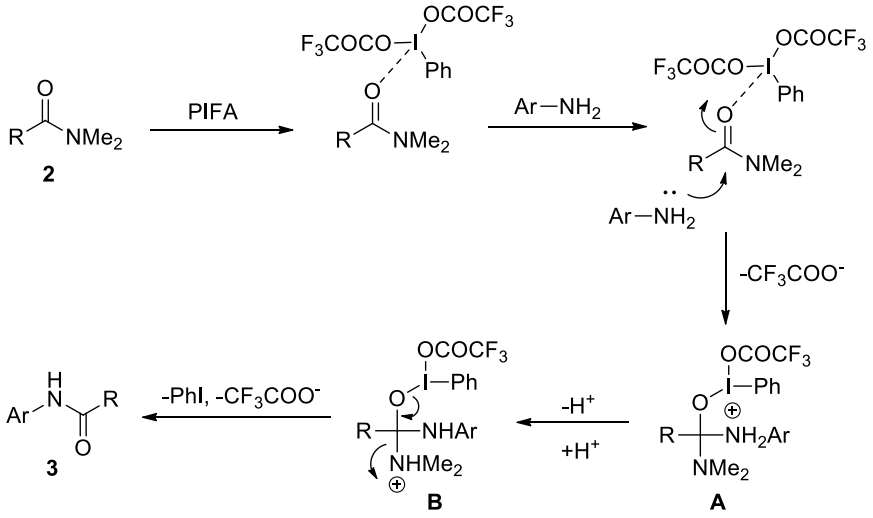


Figure 2. Plausible mechanism of PIFA promoted transamidation.

Conclusions

In summary, a very simple and useful environment benign method has been developed using PIFA as a catalyst for the transamidation of DMF and formic acid. Different types of aromatic amines, mostly bearing fluoro substituents gave the corresponding amide derivatives in high yields. Notably, DMF solvent and formic acid have been successfully utilized as N-formylating agents. The readily available reagents, hypervalent iodine promoter, short reaction time, simple, aerobic and mild reaction conditions are the advantageous features of the present protocol.

Experimental Section

General. All starting materials and commercial reagent were purchased from Alfa Aesar, Sigma Aldrich, Avra, Spectrochem, TCI. Chemicals like anilines (95-99%), DMF (anhydrous, 99.5%), DMA (98%), formic acid (85%), acetic acid (glacial, 99.5%) have been used for the reactions. Thin Layer Chromatography plates were visualized by exposure to ultraviolet light (UV) with 254 nm of wavelength and then further analyzed by using iodine chamber. Thin-layer chromatography was performed using pre-coated plates. Column chromatography was performed in 120 to 200 mesh size silica gel. The reactions were carried out in round bottom flask and sealed tube. All NMR spectra were recorded by Bruker Avance 400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts for ^{1}H NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Similarly, ^{13}C NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.16 ppm). The ^{1}H NMR and ^{13}C NMR of the known products were compared with literature reports.

General procedure for N-formylation of amines using DMF. Aniline (1.0 mmol), DMF (2 mL) and PIFA (430 mg, 1 equiv.) were added to a round-bottomed flask. The mixture was carefully stirred at 100 °C for 6 h and the progress of the reaction was monitored by TLC visualized with UV short wavelengths. Upon completion, the mixture was kept at room temperature and then diluted with EtOAc (20 mL) and water (10 mL). The EtOAc layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to obtain crude product. After performing column purification with n-hexane/ethyl acetate N-formamide product was obtained.

General procedure for N-formylation of amines using formic acid. Alternatively, aniline (1.0 mmol), HCOOH (184.1 mg, 4.0 mmol) and PIFA (86 mg, 0.2 mmol) were added. The mixture was stirred at 80 °C for 2 h and the progress of the reaction was checked by TLC and UV short wavelength. After completion, the reaction mixture was diluted with EtOAc (20 mL) and water (10-15 mL). The EtOAc layer was dried over anhydrous Na_2SO_4 and the crude was obtained after evaporation of the solvent. Later, by the column chromatography, the pure N-formamide compound was separated.

***N*-Phenylformamide (3a)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.69 (d, *J* 11.4 Hz, 1H), 8.35 (s, 1H), 7.96 (s, 1H), 7.55 (d, *J* 7.9 Hz, 2H), 7.19 (d, *J* 10.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.10 (s), 159.47 (s), 136.88 (d, *J* 19.5 Hz), 129.77 (s), 129.34 (s), 129.11 (s), 125.33 (s), 124.83 (s), 120.10 (s), 118.83 (s), 115.25 (s)

***N*-(2-Fluorophenyl)formamide (3b)**[13]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.49 (s, 1H), 8.32 (d, *J* 27.3 Hz, 1H), 8.19 (dd, *J* 14.3, 7.5 Hz, 1H), 7.25 (dd, *J* 10.9, 3.6 Hz, 1H), 7.04 (td, *J* 26.4, 13.0 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.90 (d, *J* 20.1 Hz), 160.78 (s), 160.43 – 160.23 (m), 154.74 (s), 153.86 (s), 152.30 (s), 151.37 (s), 126.63 (s), 125.21 (d, *J* 38.5 Hz), 124.79 (d, *J* 39.7 Hz), 124.50 – 124.42 (m), 122.62 (s), 120.64 (s), 116.47 (d, *J* 19.2 Hz), 115.06 (d, *J* 19.0 Hz)

***N*-(4-Fluorophenyl)formamide (3c)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* 11.4 Hz, 1H), 8.30 (s, 1H), 8.08 (s, 1H), 7.44 (dd, *J* 9.0, 4.7 Hz, 2H), 7.01 (d, *J* 6.3 Hz, 3H), 6.95 (d, *J* 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.90 (d, *J*= 213 Hz), 157.92 (s), 131.66, 120.77 (d, *J*= 8 Hz), 120.37 (d, *J*= 9 Hz), 115.61 (d, *J*= 23 Hz), 114.81 (d, *J*= 22 Hz)

***N*-(2-Nitrophenyl)formamide (3d)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.34 (t, *J* 2.1 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.47 (dd, *J* 16.8, 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.95 (s), 129. 84 (s), 129.08 (s), 124.53 (s), 118.82 (s), 118.44 (s), 113.56 (s)

***N*-(4-Nitrophenyl)formamide (3e)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* 10.9 Hz, 1H), 8.41 (s, 1H), 8.18 (d, *J* 9.1 Hz, 2H), 7.67 (d, *J* 9.1 Hz, 2H), 7.34 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.18 (s), 160.91 (s), 142.35 (s), 142.05 (s), 133.68 (s), 133.37 (s), 130.73 (s), 129.00 (s), 118.88 (s), 113.37 (s)

***N*-(2,6-Difluorophenyl)formamide (3f)**[13]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* 10.8 Hz, 1H), 8.41 (s, 1H), 7.70 (s, 1H), 7.32 (s, 1H), 7.22 (dd, *J* 14.4, 6.5 Hz, 1H), 7.18 – 7.09 (m, 1H), 6.99 (dt, *J* 16.4, 8.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.54 (t, *J* 4.9 Hz), 159.09 (s), 156.38 (d, *J* 4 Hz), 153.90 (d, *J* 5 Hz), 128.08 (t, *J* 20 Hz), 125.64 (t, *J* 19 Hz), 114.53 (s), 112.24 (dd, *J* 17.8 Hz, 5.6 Hz), 111.91 (s), 111.68 (s)

***N*-(2,4-Difluorophenyl)formamide (3g)**[44]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* 11.3 Hz, 1H), 8.45 (s, 7H), 8.30 (dd, *J* 14.8, 8.8 Hz, 1H), 7.33 (s, 1H), 7.21 (d, *J* 5.5 Hz, 1H), 6.93 – 6.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ) ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.89 (s), 160.01 (s), 158.60 (s), 123.11 (dd, *J* 10.2, 1.0 Hz), 111.52 (d, *J* 3 Hz), 111.31 (d, *J* 3 Hz), 103.96 (d, *J* 2.2 Hz), 103.72 (dd, *J* 26.8, 23.2 Hz), 103.72 (d, *J* 3.7 Hz)

***N*-(3,4-Difluorophenyl)formamide (3h)**[45]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* 6.7 Hz, 1H), 8.47 (s, 1H), 7.60 (s, 1H), 7.24 – 7.15 (m, 1H), 6.99 (d, *J* 19.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.58 (s), 158.82 (s), 152.35 (s), 149.92 (s), 128.66 (d, *J* 7.3 Hz), 127.62 (d, *J* 7.7 Hz), 126.61 (d, *J* 11.6 Hz), 124.76 (s), 122.19 (s), 118.02 (s), 117.82 (s), 117.14 (d, *J* 3.5 Hz), 116.41 (s), 116.20 (s)

***N*-(5-Bromo-2-fluorophenyl)formamide (3i)**[46]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* 11.2 Hz, 1H), 8.58 (d, *J* 7.0 Hz, 3H), 8.47 (s, 3H), 7.41 (s, 4H), 7.21 (dd, *J* 9.8, 5.7 Hz, 3H), 7.03 – 6.93 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.09 (s), 161.65 (s), 158.57 (s), 151.95 (s), 127.65 (s), 127.57 (s), 126.66 (s), 126.55 (s), 124.71 (s), 117.18 (s), 116.38 (s), 116.18 (s)

***N*-(2-Bromo-4-fluorophenyl)formamide (3j)**[47]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* 11.2 Hz, 1H), 8.41 (s, 1H), 8.30 (dd, *J* 9.2, 5.5 Hz, 1H), 7.46 (s, 1H), 7.25 (dd, *J* 7.8, 2.9 Hz, 1H), 7.01 (dd, *J* 7.0, 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.67 (s), 158.92 (s), 157.62 (s), 130.21 (s), 122.24 (d, *J* 8.1 Hz), 118.60 (s), 118.34 (s), 114.45 (s), 114.23 (s)

***N*-(3-Chloro-4-fluorophenyl)formamide (3k)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.58 (d, *J* 11.2 Hz, 1H), 8.37 (s, 1H), 7.74 (dd, *J* 6.5, 2.5 Hz, 1H), 7.56 (s, 1H), 7.43 – 7.33 (m, 1H), 7.21 – 7.06 (m, 2H), 7.00 (dt, *J* 8.7, 3.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.95 (s), 163.01 (s), 159.12 (s), 157.20 (s), 156.32 (s), 154.74 (s), 153.87 (s), 133.46 – 133.18 (m), 122.31 (s), 121.54 (s), 119.67 (d, *J* 6.8 Hz), 119.03 (d, *J* 7.1 Hz), 117.73 (s), 117.51 (s), 116.92 (s), 116.70 (s)

***N*-(3-Bromophenyl)formamide (3l)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* 10.5 Hz, 1H), 8.37 (s, 1H), 7.81 (s, 1H), 7.46 (d, *J* 8.0 Hz, 1H), 7.36 – 7.15 (m, 4H), 7.04 (d, *J* 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.92 (s), 159.15 (s), 134.84 (s), 133.51 (s), 132.48 (s), 128.88 (s), 128.59 (s), 126.52 (s), 125.81 (s), 122.53 (s), 119.45(s), 114.72 (s), 113.42 (s)

***N*-(2-Bromo-4-methylphenyl)formamide (3m)**[43]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.61 (s, 1H), 7.49 (d, *J* 8.6 Hz, 1H), 6.97 (d, *J* 8.6 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98 (m), 132.88 (s), 132.17, 131.99 (s), 121.42 (s), 121.29 (s), 120.55 (s), 22.81 (s)

***N*-(5-Bromo-2-iodophenyl)formamide (3n)**[48]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.49 (s, 1H), 7.63 (d, *J* 8.5 Hz, 1H), 7.45 (s, 1H), 7.03 (d, *J* 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99 (s), 139.71 (s), 129.38 (s), 124.73 (s),123.32 (s), 121.81 (s), 86.48 (s)

***N*-(*m*-Tolyl)acetamide (3o)**[49]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* 11.2 Hz, 1H), 8.44 (s, 1H), 7.82 (d, *J* 8.2 Hz, 1H), 7.39 (s, 1H), 7.01 (d, *J* 8.4 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.01 (s), 134.03 (s), 133.27 (s), 130.12 (s), 129.85 (s), 124.33 (s), 122.04 (s), 17.62 (s), 17.57 (s)

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Supplementary Material

^{1}H and ^{13}C NMR spectra of compounds **3a**-**3o** and X-ray crystallographic data of compound **3f** are available in the Supplementary material file associated with this paper.

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