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Pd/C-Catalyzed Aminocarbonylation of Aryl Iodides via Oxidative C−N Bond Activation of Tertiary Amines to Tertiary Amides

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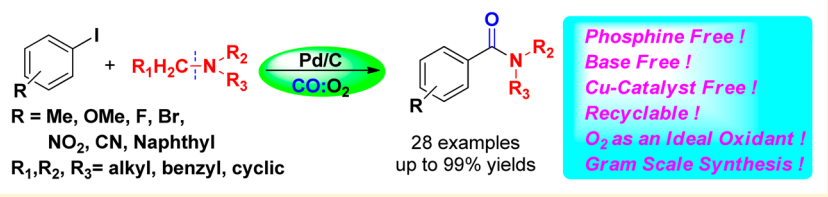
Supporting Information



ABSTRACT: This work reports oxidative *N*-dealkylation/carbonylation of tertiary amines to tertiary amides by using molecular oxygen as a sole oxidant using a Pd/C catalyst. This protocol is free from ligands, additives, bases, and cocatalysts. Different tertiary amines as well as aryl iodides have been examined for this transformation, providing desired products in good to excellent yield.

Amide structural motifs are important functional groups because of their wide applications in pharmaceuticals, natural products, agrochemicals, and biologically active molecules.[1,2] Traditionally, amides are synthesized by the reaction of acyl chloride or carboxylic acid derivatives with amines.[3] Several named reactions, such as Beckmann,[4] Staudinger,[5] Ugi,[6] and Ritter,[7] are also known. Direct oxidative amidation of aldehydes (or alcohols),[8] hydroamination of alkynes,[9] and transamidation[10] with amines are also widely studied. Ours and other groups have disclosed DMF as a coupling reagent for the synthesis of tertiary amides.[11] However, despite their potential utility, these methods have limitations due to their poor atom economy, the use of highly hazardous reagents, and the expensive and toxic nature of many of the coupling reagents.

The synthesis of secondary as well as tertiary amides through carbonylation of aryl halides with primary and secondary amines is studied.[12] They have limitations due to the use of excess base, additives, and moisture-sensitive phosphine ligands along with non-recyclable Pd precursors. The C−N bond activation of highly stable tertiary amine is a challenging task.[13] The literature reveals that there are very few reports on the carbonylation reactions.[14] Recently, Deng et al. reported carbonylative synthesis of amides via C−N bond activation of tertiary amines.[15] This protocol is disadvantageous as it requires 3.0 equiv of CuO as an oxidant for the cleavage of the C−N bond as well as limits in their poor substrate scope and non-recyclability with harsh reaction conditions. The use of Pd/C catalysts has gained attention in green and sustainable chemistry as it is inexpensive, easily available, and can be recycled, thus making it an interesting catalytic system. Molecular oxygen is considered as an ideal oxidant due to its natural, inexpensive, and eco-friendly character.[17]

In continuation of our ongoing work on Pd/C-catalyzed carbonylation reactions,[16] we describe herein a simple approach for the direct synthesis of a wide range of tertiary amides under mild conditions. Pd/C was found to be a highly efficient catalyst for the carbonylation of aryl iodides via oxidative *N*-dealkylation/carbonylation of tertiary amines using O_2 as a sole oxidant (Scheme 1).

Our studies began with the carbonylation of iodobenzene **1a** and triethyl amine **2a** as an aminal source under the pressure of CO/O_2 (9:1) in MeCN using 10% Pd/C as a catalyst. Initially, we examined various palladium precursors including $PdCl_2$, $Pd(OAc)_2$, $PdCl_2(PPh_3)_2$ with PPh_3 as a ligand, and Pd/C (Table 1). The results revealed that 10% Pd/C was the optimal

Scheme 1. Overview of the Synthetic Approach for the Tertiary Amides

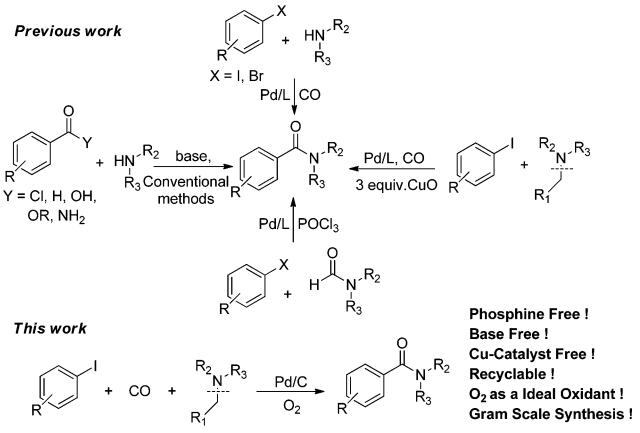


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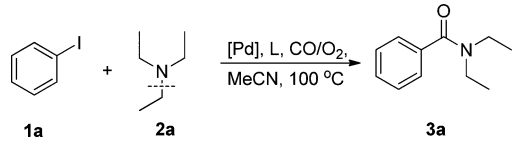
Table 1. Summary of Screening of Catalyst, Loading of Catalyst, and Ligands[a]



1a 2a 3a

entry	catalyst	mol %	L	yield (%)[b]
1	$PdCl_2$	5	PPh_3	77
2	$Pd(OAc)_2$	5	PPh_3	73
3	$PdCl_2(PPh_3)_2$	5	PPh_3	75
4	$PdCl_2$	5		82
5	$Pd(OAc)_2$	5		78
6	10% Pd/C	5		94
7	5% Pd/C	5		81
8	10% Pd/C	3		95
9	10% Pd/C	7		96
10[c]	10% Pd/C	3		73

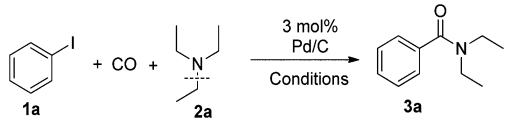
[a]Reaction conditions: **1a** (1.0 mmol), Et_3N (2.0 mmol), Pd catalyst, Pd/P = 1/4, MeCN (10 mL) under 10 atm of CO/O_2 (9:1) at 100 °C for 8 h. [b]GC and GCMS. [c]With 2 equiv of CuO.

catalyst for this transformation (Table 1, entry 6). The Pd/C catalyst works at a loading of 3 mol %, and **3a** was obtained in excellent yield (Table 1, entry 8). In the absence of Pd/C, the reaction does not provide the desired product. It is noteworthy that the reaction can also be performed in the presence of CuO as an oxidant, regrettably, the yield of **3a** decreased to 73% (Table 1, entry 10).

Furthermore, we have investigated various reaction parameters for optimizing the yield of **3a**, the results are summarized in Table 2. First, we investigated the choice of solvent, including acetonitrile, toluene, THF, and DMF. It was found that the acetonitrile was the best solvent for this transformation, which gave an excellent yield (Table 2, entry 1). When the reaction temperature was lowered to 80 °C, the yield of **3a** decreased, whereas increasing it had no significant effect on the yield of **3a** (Table 2, entries 5−7). Conversely, when the reaction time was reduced to 4 h, the yield of **3a** was decreased to 61%, and increasing the reaction time to 24 h had no significant effect on yield (Table 2, entries 8−11). Under a 9:1 ratio of CO/O_2 pressure, the reaction proceeded faster within 8 h to give **3a** in 95% yield. We found that the corresponding tertiary amide product was obtained in an excellent yield under CO/O_2 (5:1) pressure (Table 2, entry 13). When air was used as the oxidant instead of O_2, the obtained yield of **3a** decreased (Table 2, entry 15).[18] In contrast, under an inert atmosphere, the reaction did not proceed (Table 2, entry 16). Thus, this indicates that molecular oxygen plays an important role in the oxidative cleavage of tertiary amines to secondary amines. Notably, the reaction was successfully performed with 1.5 mmol Et_3N to afford **3a** in 95% yield (Table 2, entry 17).

We examined the substrate scope of aryl iodides with Et_3N **2a** as an amine source, allowing the desired amides in high yields at optimized reaction conditions (Scheme 2). Both electron-rich and -deficient aryl iodides could be employed efficiently under mild conditions (**3a**−**3n**). Aryl iodides bearing methyl, methoxy, bromo, fluoro, nitro, and cyano substituents on the phenyl ring were compatible with the developed catalytic system, providing desired amides in good to excellent yields. 1-Iodo and 2-iodonaphthalene were afforded excellent yields of the corresponding amides (**3f** and **3g**). Gratifyingly,

Table 2. Screening of Optimized Reaction Parameters for Aminocarbonylation Reactions[a]

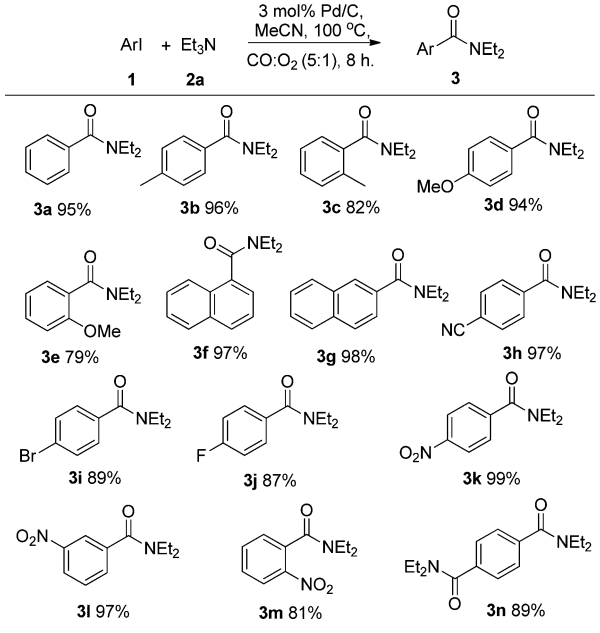


1a 2a 3a

entry	solvent	temp (°C)	t (h)	P_{CO/O_2} (bar)	yield (%)[b]
1	MeCN	100	8	10	95
2	toluene	100	8	10	79
3	THF	100	8	10	65
4	DMF	100	8	10	58
5	MeCN	120	8	10	93
6	MeCN	90	8	10	83
7	MeCN	80	8	10	74
8	MeCN	100	24	10	94
9	MeCN	100	12	10	95
10	MeCN	100	6	10	84
11	MeCN	100	4	10	61
12	MeCN	100	8	7	94
13	MeCN	100	8	6	95
14	MeCN	100	8	5	92
15[c]	MeCN	100	8	6	63
16[d]	MeCN	100	8	6	0
17[e]	MeCN	100	8	6	95

[a]Reaction conditions: **1a** (1 mmol), **2a** (2.0 mmol), 10% Pd/C (3 mol %), solvent (10 mL) under CO atm, 1 atm of O_2. [b]GC and GCMS. [c]One atm of air. [d]Under inert conditions, CO/O_2 = 6/0 atm. [e]Et3N (1.5 mmol).

Scheme 2. Scope of Carbonylation of Aryl Iodides with Triethyl Amine as Amine Source[a]



[a]Reaction conditions: ArI (1.0 mmol), Et_3N (1.5 mmol), Pd/C (3 mol %), MeCN (10 mL) under 6 atm CO/O_2 (5:1) at 100 °C for 8 h. [b]Isolated yield.

the double carbonylation of 1,4-diiodobenzene proceeded smoothly and afforded desired amide **3n** in 89% yield. The phenyl tosylate and phenyl mesylate were also tested under the optimized reaction conditions; unfortunately, the reaction did not proceed. The carbonylation of heteroaryl iodides does not

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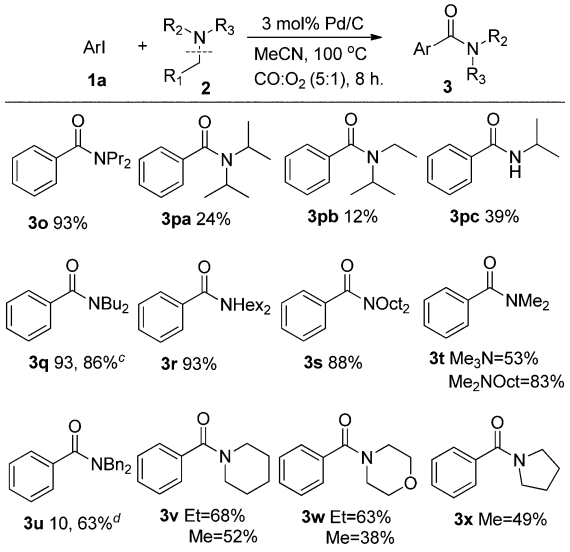
proceed, which could be because of the formation of stable metal chelates with nitrogen of the heteroaryl iodides.

Subsequently, the scope of oxidative *N*-dealkylation/carbonylation of a wide range of tertiary amines with **1a** was also investigated (Scheme 3). Both symmetrical as well as

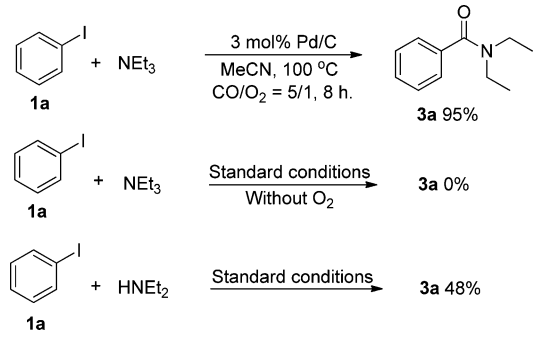
Scheme 3. Scope of Carbonylation of Aryl Iodides with C−N Bond Cleavage of Various Tertiary Amines[a]



[a]Reaction conditions: **1a** (1.0 mmol), amines (1.5 mmol), Pd/C (3 mol %), MeCN (10 mL), and 6 bar CO/O_2 (5:1) at 100 °C for 8 h. [b]Isolated yield. [c]With 5.0 mmol of **1a**. [d]With 2.0 equiv of CuO.

unsymmetrical tertiary amines reacted smoothly to afford the corresponding amides in good yields. For symmetrical tertiary amines, the selectivity of *N*-dealkylation independent of alkyl chain lengths and oxidative *N*-dealkylation/carbonylation of different aliphatic amines with **1a**, afforded the corresponding amides in high yields (**3o** and **3q**−**3u**). In unsymmetrical tertiary amines, *N*,*N*-diisopropylethyl amine, we observed three kinds of *N*-dealkylation that potentially results in the formation of three types of products (**3pa**, **3pb**, and **3pc**). *N*,*N*-Dimethyloctyl amine also gave good yield selectively (**3t**). Remarkably, trimethyl amine also proceeded smoothly and gave the corresponding amides (**3t**). These results indicate that the C−N bond cleavage of tertiary amines was selective at the less-steric sides. When tribenzyl amines were used, the obtained yield was very low (**3u**). For increasing the yield of **3u**, the reaction was carried out in the presence of 2 equiv of CuO, which afforded **3u** in 63% yield. When triphenyl amine (NPh_3) was used under the optimized conditions, the desired product was not observed. In the case of cyclic tertiary amines, *N*-ethyl and *N*-methyl derivatives of cyclic amines were also proven to be good substrates (**3v**, **3w**, and **3x**). To further demonstrate the robustness of developed catalytic system, we performed the reaction on the gram scale under optimal reaction conditions. It is noteworthy that the reaction of 5.0 mmol of **1a** with Bu_3N as an amine source proceeded smoothly to give **3q** in 86% yield. Some control experiments were also carried out for the confirmation of tertiary amines as an aminal source via C−N bond activation. When $HNEt_2$ was used as the amine source under standard conditions, only 48% yield of **3a** was obtained (Scheme 4).

Scheme 4. Control Experiments



The recyclability of Pd/C catalyst was investigated by the reaction of **1a** with **2a** under the optimal reaction conditions (Table 3). The recovered catalyst could be reused up to five

Table 3. Reusability of Pd/C Catalyst

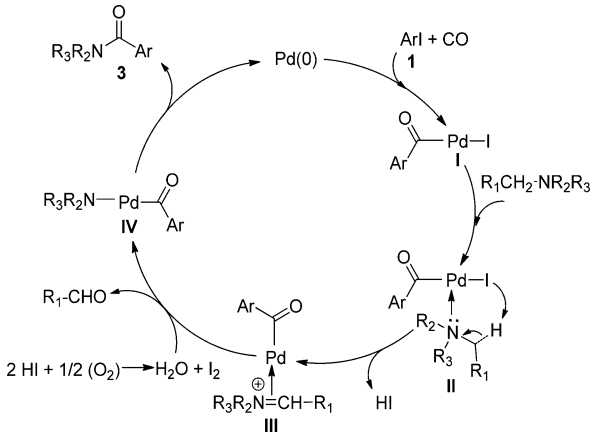
run	1st	2nd	3rd	4th	5th
yield (%)[b]	95	94	92	89	88

[a]Standard conditions: **1a** (1 mmol), **2a** (1.5 mmol), Pd/C (3 mol %), CO/O_2 = 5/1 in 10 mL of MeCN, 100 °C, 8 h. [b]GC Yield.

times with a slight decrease in its catalytic activity. The leaching of palladium metal was also explored and first and fifth recycle samples subjected to the inductively coupled plasma atomic emission spectrometry (ICP−AES) technique. No detectable amount of palladium (below 0.1 ppm) was present in these samples, indicating a negligible catalyst leaching.

On the basis of experimental results and previous literature,[13d,f,g] we proposed here a plausible reaction mechanism for the palladium-catalyzed oxidative *N*-dealkylation/carbonylation of tertiary amines with aryl iodides (Scheme 5). Initially, oxidative addition of ArI to Pd^0 was

Scheme 5. Plausible Reaction Mechanism



followed by insertion of CO to form acylpalladium complex **I**. The nitrogen of tertiary amines coordinates with complex **I** to form complex **II** followed by elimination of HI to give a Pd-imminium type intermediate (**III**).[13f,g,19] Notably, the HI liberated in situ are oxidized by oxygen to form water and iodine.[18] Furthermore, hydrolysis of **III** eliminates aldehyde and forms complex **IV**. Finally, desired amide **3** was provided by reductive elimination of complex **IV** with formation of Pd^0 species and completion of the catalytic cycle.

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In summary, this work reports an efficient and novel Pd/C−O_2 catalytic system for the aminocarbonylation of aryl iodides via C−N bond cleavage of tertiary amines as an amine source. The present approach is simple to perform, scalable, recyclable, ligand-free, additive-free, cocatalyst-free, and uses molecular oxygen as an ideal and greener oxidant. Remarkably, a wide range of substrates of aryl iodides as well as tertiary amines are well-tolerated.

EXPERIMENTAL SECTION

General. The Pd/C was purchased from Sigma-Aldrich (10 wt % loading; matrix: activated carbon support; product number: 205699; brand: Aldrich). Solvents were purchased with high purity and used without further purification. All of the reactions were monitored by using TLC, GC, and GC-MS techniques. Products were purified by column chromatography on silica (100−200 mesh). The ^{1}H NMR spectra were recorded on a 400 and 500 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectra were recorded on a 101 and 126 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to TMS as the internal standard. The J (coupling constant) values are described in Hz. Splitting patterns of proton are depicted as s (singlet), d (doublet), t (triplet), and m (multiplet). The products were confirmed by the comparison of their GC-MS and ^{1}H and ^{13}C NMR spectra with those of authentic data.

General Experimental Procedure for Oxidative *N*-Dealkylation/Carbonylation of Tertiary Amines with Aryl Iodides. To a 100 mL stainless steel autoclave were added aryl iodide (1 mmol), tertiary amine (1.5 mmol), and 10% Pd/C (3 mol %) in 10 mL of MeCN. The autoclave was closed and pressurized with oxygen (1 atm) and CO (5 atm) without flushing. The reaction mixture was stirred with a mechanical stirrer (550 rpm) and heated at 100 °C for 8 h. The reactor was then cooled to room temperature and degassed carefully, and the reactor was opened. The reactor vessel was washed with ethyl acetate (3 × 5 mL) to remove traces of product and catalyst if present. The reaction mixture was filtered; filtrates were dried over Na_2SO_4, and the solvent was evaporated under vacuum. Products were purified using column chromatography (Silica gel 100−200 mesh, petroleum ether/ethyl acetate) to afford the corresponding products in good to excellent yields. The purities of compounds were confirmed by GC and GCMS analysis. The structures of products were confirmed by GC-MS and ^{1}H and ^{13}C NMR spectroscopic techniques (***Caution!*** *CO and O_2 may form an explosive mixture under certain conditions*).[19]

Procedure for Recycling of Catalyst. After completion of the reaction, the recovered catalyst was washed with distilled water (3 × 5 mL) and finally with methanol (3 × 5 mL) to remove trace amounts of organic material. Then, the catalyst was dried in an oven at 80 °C for 5 h and after washing and drying, and the catalyst was reused for the next run.

N,N-Diethylbenzamide (***3a***).[8h] Colorless oil; 168.2 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 5H), 3.48 (s, 2H), 3.19 (s, 2H), 1.18 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 137.1, 129.0, 128.3, 126.2, 43.2, 39.2, 14.1, 12.8. GC-MS (EI, 70 eV) m/z (%): 177 (12) $[M]^+$, 176 (33), 148 (4), 134 (3), 105 (100), 77 (52), 51 (17).

N,N-Diethyl-4-methylbenzamide (***3b***).[12g] Colorless oil; 183.4 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.20 (dd, 8 Hz, 2H), 7.14 (dd, J = 7.9 Hz, 2H), 3.49 (s, 2H), 3.22 (s, 2H), 2.32 (s, 3H), 1.18 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.5, 139.0, 134.2, 128.9, 126.2, 43.2, 39.2, 21.3, 14.1, 12.8. GC-MS (EI, 70 eV) m/z (%): 191 (14) $[M]^+$, 190 (36), 162 (3), 148 (2.5), 119 (100), 91 (41), 65 (19.5), 42 (4.5).

N,N-Diethyl-2-methylbenzamide (***3c***).[12g] Colorless oil; 156.7 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−6.62 (m, 4H), 3.52 (d, 2H), 3.06 (d, 2H), 2.23 (s, 3H), 1.21 (t, 3H), 0.97 (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8, 137.0, 133.7, 130.2, 128.4, 125.7, 125.3, 42.5, 38.6, 18.7, 13.9, 12.8. GC-MS (EI, 70 eV) m/z (%): 227 (29) $[M]^+$, 226 (41), 198 (2), 155 (100), 127 (71), 101 (5), 77(6), 51(2).

N,N-Diethyl-4-methoxybenzamide (***3d***).[3i] Colorless oil; 194.7 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.31 (s, 4H), 1.11 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 160.2, 129.3, 128.1, 113.6, 55.2, 43.3, 39.3, 14.1, 9.3. GC-MS (EI, 70 eV) m/z (%): 207 (13) $[M]^+$, 206 (29.5), 135 (100), 107 (13), 92 (14), 77 (21), 42 (3.5).

N,N-Diethyl-2-methoxybenzamide (***3e***).[3i] Colorless oil; 163.6 mg, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (dd, J = 8.3, 7.5 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 6.95−6.87 (m, 2H), 3.78 (s, 3H), 3.57−3.51 (m, 2H), 3.14−3.10 (q, 2H), 1.22 (t, 3H), 1.00 (t, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.8, 155.1, 129.9, 127.4, 126.8, 120.7, 110.9, 55.46, 42.8, 38.8, 13.9, 12.9. GC-MS (EI, 70 eV) m/z (%): 207 (9) $[M]^+$, 206 (29), 135 (100), 92 (11), 77 (23), 42 (3).

N,N-Diethyl-1-naphthamide (***3f***).[12i] Colorless oil; 220.3 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93−7.69 (m, 2H), 7.54−7.44 (m, 2H), 7.39 (dd, 1H), 3.82 (s, 1H), 3.50 (s, 1H), 3.00−3.04 (t, 1H), 1.34 (t, 3H), 0.95 (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 135.1, 133.4, 129.5, 128.7, 128.3, 126.8, 126.3, 125.1, 124.7, 123.1, 43.1, 39.0, 14.2, 13.0. GC-MS (EI, 70 eV) m/z (%): 227 (38) $[M]^+$, 226 (44), 198 (3), 155 (100), 127 (84), 101 (5), 77 (8), 51(2).

N,N-Diethyl-2-naphthamide (***3g***).[8e] Colorless oil; 222.5 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, J = 6.4 Hz, 4H), 7.55−7.41 (m, 3H), 3.58 (s, 2H), 3.29 (s, 2H), 1.26 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 134.4, 133.3, 132.7, 128.3, 128.2, 127.7, 126.7, 126.6, 125.7, 123.8, 43.4, 39.4, 14.2, 12.9. GC-MS (EI, 70 eV) m/z (%): 227 (29) $[M]^+$, 226 (41), 198 (2), 155 (100), 127 (71), 101 (5), 77(6), 51(2).

4-Cyano-N,N-diethylbenzamide (***3h***).[3i] White solid; 196 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0, 2 Hz, 2H), 3.51 (d, J = 6.6 Hz, 2H), 3.16 (d, J = 6.7 Hz, 2H), 1.15 (dd, J = 56.9, 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.1, 141.5, 132.3, 127.0, 118.2, 112.9, 43.2, 39.4, 14.8, 12.8. GC-MS (EI, 70 eV) m/z (%): 202 (10) $[M]^+$, 201 (27), 159 (3), 130 (100), 102 (37), 75 (8), 51(6).

4-Bromo-N,N-diethylbenzamide (***3i***).[8g] Colorless oil; 227 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.44 (m, 2H), 7.23−7.17 (m, 2H), 3.47 (s, 2H), 3.18 (s, 2H), 1.18 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 135.9, 131.6, 128.0, 123.3, 43.3, 39.3, 14.2, 12.8. GC-MS (EI, 70 eV) m/z (%): 255 (62) $[M]^+$, 254 (62), 184 (90), 182 (100), 156 (30), 154 (31.3), 104 (18.4), 76 (39), 75 (27), 50 (16.5), 42 (16.5).

4-Fluoro-N,N-diethyl-benzamide (***3j***).[3j] Colorless oil; 169.7 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.09 (dd, 2H), 7.02 (dd, 2H), 3.47 (s, 2H), 3.20 (s, 2H), 1.12 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 164.2, 161.7, 133.2, 133.2, 128.4, 128.4, 115.5, 115.3, 43.3, 39.4, 14.1, 12.8. GC-MS (EI, 70 eV) m/z (%): 195 (10.5) $[M]^+$, 194 (28), 166 (2), 123 (100), 95 (33), 75 (10), 42 (10).

N,N-Diethyl-4-nitrobenzamide (***3k***).[3i] Yellow oil; 219.9 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43−8.12 (d, 2H), 7.58−7.34 (d, 2H), 3.51 (s, 2H), 3.15 (q, 2H), 1.13 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 147.9, 143.3, 127.3, 123.8, 43.2, 39.4, 14.1, 12.8. GC-MS (EI, 70 eV) m/z (%): 222 (16) $[M]^+$, 221 (36.5), 205 (7), 175 (5), 150 (100), 120 (14), 134 (34.5), 92 (14.2), 76 (26), 32 (17).

N,N-Diethyl-3-nitrobenzamide (***3l***).[3i] Yellow oil; 215.4 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43−7.94 (m, 2H), 7.68 (dd, J = 7.6, 1H), 7.57 (dd, 1H), 3.53 (d, 2H), 3.21 (d, 2H), 1.23 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.6, 147.9, 138.6, 132.4, 129.7, 124.0, 121.5, 43.4, 39.6, 14.2, 12.9. GC-MS (EI, 70 eV) m/z (%): 222 (10) $[M]^+$, 221 (20), 204 (9), 150 (100), 134 (5.4), 104 (32), 76 (24.8), 50 (5).

N,N-Diethyl-2-nitrobenzamide (***3m***). Yellow oil; 179.9 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.2 Hz, 1H), 7.66 (td, J = 7.5, 1H), 7.51 (td, J = 8.3, 1H), 7.38−7.32 (m, 1H), 3.55 (s, 2H), 3.08 (q, 2H), 1.27−1.20 (m, 3H), 1.04−0.98 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 144.9, 134.3, 133.5, 129.5, 127.9, 124.7, 42.7, 38.9, 13.5, 11.9. GC-MS (EI, 70 eV) m/z (%): 222 (2) $[M]^+$, 161 (3), 151 (72), 150 (79), 134 (12.5), 121 (18.5), 104 (15), 72 (100), 51 (33.6), 44 (13), 39 (55).

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*N_1,N_1,N_4,N_4-Tetraethylterephthalamide (**3n**).*[3h] White solid; 245.8 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 4H), 3.50 (s, 4H), 3.19 (s, 4H), 1.20−1.04 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 137.9, 126.4, 43.2, 39.2, 14.2, 12.8. GC-MS (EI, 70 eV) m/z (%): 276 (33) $[M]^+$, 275 (56), 247 (10), 233 (2), 205 (21), 204 (100), 176 (7), 132 (8), 105 (28), 105 (28), 76 (12), 44 (5).

*N,N-Dipropylbenzamide (**3o**).*[12g] Colorless oil; 190.8 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.28 (m, 5H), 3.41 (s, 2H), 3.11 (s, 2H), 1.65 (d, J = 6.8 Hz, 2H), 1.47 (d, J = 6.7 Hz, 2H), 0.95−0.69 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 137.3, 128.9, 128.3, 126.3, 50.6, 46.2, 21.8, 20.6, 11.4, 11.0. GC-MS (EI, 70 eV) m/z (%): 205(10) $[M]^+$, 204 (14), 176 (7), 134 (8), 105 (100), 77 (35), 51 (7).

*N,N-Diisopropylbenzamide (**3pa**).*[12g] White solid; 49.2 mg, 24% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.24 (m, 5H), 3.80 (s, 1H), 3.49 (s, 1H), 1.50−1.11 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1, 138.8, 132.6, 129.8, 128.6, 128.4, 128.1, 125.5, 50.9, 45.8, 20.7. GC-MS (EI, 70 eV) m/z (%): 205 (3) $[M]^+$, 190 (7), 162 (11), 105 (100), 77 (32.5), 51(8), 40 (27.8).

*N-Ethyl-N-isopropylbenzamide (**3pb**).* GC-MS (EI, 70 eV) m/z (%): 191 (3) $[M]^+$, 190 (5), 163 (10), 162 (8), 148 (7), 122 (5), 105 (100), 77 (43), 51(15), 32 (29).

*N-Isopropylbenzamide (**3pc**).*[8f] White solid; 63.6 mg, 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.71 (m, 2H), 7.46−7.37 (m, 3H), 5.97 (s, 1H), 4.26 (m, 1H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 13.9, 131.2, 130.0, 128.5, 128.3, 126.8, 41.9, 22.8. GC-MS (EI, 70 eV) m/z (%): 163 (23) $[M]^+$, 162 (8.5), 148 (10), 106 (8), 105 (100), 77 (35), 51 (11).

*N,N-Dibutylbenzamide (**3q**).*[15] Colorless oil; 200.5 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.24 (m, 5H), 3.42 (q, 2H), 3.15 (q, 2H), 1.44−1.36 (m, 4H), 1.22−1.09 (m, 2H), 0.94−0−0.74 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 137.2, 129.88, 129.0, 128.3, 128.2, 126.4, 48.7, 44.4, 30.7, 29.6, 20.2, 19.7, 13.9, 13.5. GC-MS (EI, 70 eV) m/z (%): 233 (8) $[M]^+$, 232 (7), 190 (12), 148 (5), 134 (4), 105 (100), 77 (25.9), 51(4), 40 (11).

*N,N-Dihexylbenzamide (**3r**).*[8j] Colorless oil; 269 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33−7.24 (m, 5H), 3.40 (d, 2H), 3.16 (d, 2H), 1.61−1.07 (t, 16H), 0.84 (s, 6H). ^{13}C NMR (126 MHz, CDC_3): δ 171.6, 162.7, 137.2, 128.9, 128.3, 126.3, 48.9, 47.4, 44.7, 42.1, 31.6, 31.3, 31.2, 29.6, 28.5, 27.4, 27.2, 26.7, 26.1, 22.5, 14.0. GC-MS (EI, 70 eV) m/z (%): 289 (8) $[M]^+$, 288 (9), 218 (17), 162 (2), 148 (7), 134 (3), 105 (100), 77 (22), 55 (3), 43 (8).

*N,N-Dioctylbenzamide (**3s**).*[3k] Colorless oil; 303.8 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.24 (m, 5H), 3.45 (s, 2H), 3.15 (s, 2H), 1.63−0.84 (m, 34H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 137.3, 128.9, 128.3, 126.4, 49.00, 44.7, 31.8, 29.0, 27.5, 27.0, 26.4, 22.6, 14.0. GC-MS (EI, 70 eV) m/z (%): 345 (5) $[M]^+$, 344 (7), 246 (15.6), 148 (7), 105 (100), 77 (2), 76 (14), 39 (44).

*N,N-Dimethylbenzamide (**3t**).*[8g] Colorless oil; 79 and 123.7 mg, 53 and 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43−7.26 (m, 5H), 3.01 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 136.2, 129.4, 128.2, 126.9, 39.5, 35.2. GC-MS (EI, 70 eV) m/z (%): 149 (18) $[M]^+$, 148 (56), 105 (100), 77 (66), 51 (18).

*N,N-Dibenzylbenzamide (**3u**).*[8i] White solid; 30 and 189.6 mg, 10 and 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.49 (m, 2H), 7.39−7.28 (m, 11H), 7.14 (s, 2H), 4.70 (s, 2H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 136.1, 129.6, 128.7, 128.5, 128.4, 127.6, 127.0, 126.7, 51.5, 46.8. GC-MS (EI, 70 eV) m/z (%): 301 (2) $[M]^+$, 211 (5.2), 210 (32.4), 105 (100), 91 (17), 77(30.4), 50 (4), 39 (17).

*Phenyl(piperidin-1-yl)methanone (**3v**).*[8i] Colorless oil; 128.5 and 98.3 mg, 68 and 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 5H), 3.66 (s, 2H), 3.29 (s, 2H), 1.62 (s, 4H), 1.46 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 136.4, 129.3, 128.3, 126.7, 48.7, 43.1, 26.50, 25.6, 24.5. GC-MS (EI, 70 eV) m/z (%): 188 $[M^+]$ (73.80), 160 (2.19), 105 (100), 84(10), 77 (67.40), 51 (19.09).

*Morpholino(phenyl)methanone (**3w**).*[8i] White solid; 129.9 and 72.6 mg, 63 and 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78−7.12 (m, 5H), 3.71−3.39 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 135.2, 129.8, 128.5, 127.0, 66.8, 48.8, 42.5, 20.6. GC-MS (EI, 70 eV) m/z (%): 191 $[M^+]$ (9), 190 (24.68), 176 (7), 105 (100), 84(10), 77 (42.31), 56 (12).

*Phenyl(pyrrolidin-1-yl)methanone (**3x**).*[8i] Colorless oil; 85.7 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.41 (m, 2H), 7.41−7.37 (m, 3H), 3.64 (t, 2H), 3.42 (t, 2H), 2.04−1.93 (p, 2H), 1.90−1.83 (p, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 137.1, 129.8, 128.2, 127.0, 77.4, 77.1, 76.8, 49.6, 46.8, 26.3, 24.4. GC-MS (EI, 70 eV) m/z (%): 175 $[M^+]$ (30), 146 (13), 122 (8), 105 (100), 77 (72), 51 (25), 32 (10).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02385.

^{1}H and ^{13}C NMR spectra and analysis by GC-MS (PDF)

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Notes

The authors declare no competing financial interest.

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