

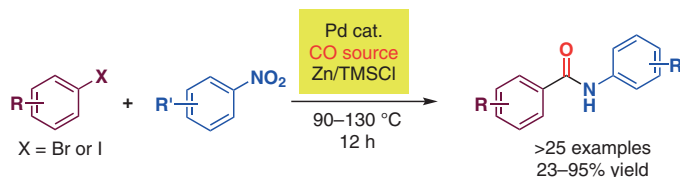
# Palladium-Catalysed Reductive Aminocarbonylation of Aryl Bromides and Iodides with Nitroarenes

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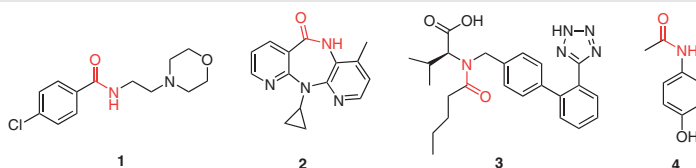
**Abstract** Amide functional groups are a structural feature in a vast array of beneficial organic molecules. This has resulted in a surge in new methodologies developed to enable access to this functional group using a broad range of coupling partners. Herein, we report a palladium-catalysed reductive aminocarbonylation of aryl bromides and iodides with nitroarenes to afford the respective amide products. The developed protocol employs Mo(CO)<sub>6</sub> as a carbonyl source and a combination of Zn and TMSCl as co-reducing agents. For most substrates, the anticipated amide products were obtained in modest to high amide product yields.

**Key words** amides, reductive aminocarbonylation, palladium, nitroarenes, C–N bond formation

The amide functional group is present in several interesting compounds, including natural products, peptides and agrochemicals.<sup>1–3</sup> Furthermore, this functional group is found to be present in two-thirds of drug candidates and in over 25% of commercially available drugs.<sup>4,5</sup> Some of the drugs are highlighted in Figure 1 and these include mo-

globemide (**1**), used for the treatment of depression, nevirapine (**2**), an antiretroviral drug for HIV, valsartan (**3**), which is known as a treatment for hypertension and cardiovascular diseases, and paracetamol (**4**), which is a commonly used analgesic.<sup>6–9</sup>

Thus, research and development of new amide synthesis procedures has become a key research area due to the prevalence of amide functional groups in beneficial organic molecules.<sup>10,11</sup> Traditionally, amides are synthesised from the condensation of carboxylic acids and amines. However, some of these methods are associated with drawbacks, such as using stoichiometric amounts of carboxylic acid activators. These usually generate undesired products in high quantities.<sup>12,13</sup> Furthermore, one of the commonly used activators, 1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxide hexafluorophosphate (hexafluorophosphate azabenzotriazole tetramethyl uronium, HATU), has been reported to cause allergies, raising health concerns.<sup>14</sup> Protocols using alternative functional groups instead of carboxylic acids have been established to try to overcome some of these challenges and these include reactions that utilise catalytic activators, esters, aldehydes, alcohols and amides as amine coupling partners.<sup>15–18</sup> The direct use of nitroarenes as arylamine surrogates has also gained momentum in the amidation reactions as they offer step-economic access to amides.<sup>19,20</sup> Nitroarenes are cheaper and more stable than their amine analogues and are ideal for



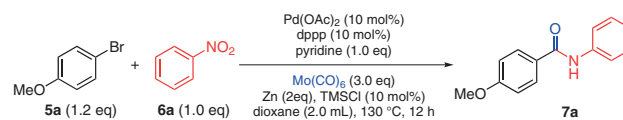
**Figure 1** Commercially available amide-containing drugs

late-stage transformation in multistep syntheses due to their 'chemical inertness'. They have been successfully coupled to various functional groups such as esters, carboxylic acids, amides, aldehydes, aryl iodides and alcohols to afford the respective amide products.<sup>21–26</sup> In addition, amides have been obtained from reactions between nitroarenes and aryl halides (or equivalent) in the presence of a carbonyl source, and in most cases, nickel was employed as the catalyst of choice.<sup>27–29</sup> Although nickel offers a more sustainable option, the general superior robustness of palladium catalysts in cross-coupling reactions prompted us to explore herein an optimisation study for a palladium-catalysed reductive aminocarbonylation of aryl halides with nitroarenes and a subsequent application of the protocol in the synthesis of a variety of amides.<sup>30</sup>

Our optimal reaction conditions revealed that palladium(II) acetate [Pd(OAc)<sub>2</sub>] catalyst, 1,3-bis(diphenylphosphino)propane (dppp) as a supporting ligand for the metal, molybdenum hexacarbonyl [Mo(CO)<sub>6</sub>] as a carbonyl source, pyridine as a base and Zn/TMSCl as additives were essential for the successful coupling of the model substrates, 4-bromoanisole (**5a**) and nitrobenzene (**6a**), to afford the amide product **7a** in 95% yield at 130 °C (Table 1, entry 1). Alternative inorganic and organic bases did not afford better yields in comparison to pyridine (entries 2–7). For example, the use of NaOH, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> resulted in lowered product yields (entries 2–4). In comparison to the inorganic bases, Et<sub>3</sub>N, quinoline and 2-quinolone afforded slightly improved yields of 50%, 63% and 55%, respectively (entries 5–7). The stronger basicity of pyridine in comparison to its derivatives quinoline and 2-quinolone could be the reason for the observed reactivity trend.<sup>31,32</sup> Although pyridine has been reported as a suitable ligand in other studies, such as the C–H activation reaction, phosphine-free reactions in our case afforded poor yields (entry 8).<sup>33</sup> Monodentate ligand 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (SPhos) and bidentate ligand 1,2-bis(diphenylphosphino)ethane (dppe) were also investigated as suitable alternative ligands. However, these did not outperform dppp as lower amide product yields of 54% and 60% for dppe and SPhos, respectively, were obtained (entries 9 and 10).

Other palladium catalysts were also explored and, in our case, Pd(acac)<sub>2</sub>, PdCl<sub>2</sub> and PdCl<sub>2</sub>(cod) afforded low yields to no product (entries 11–13). A different choice of a metal catalyst, NiCl<sub>2</sub>, showed no reactivity as no amide product was formed (entry 14). Furthermore, different solvents were investigated and these included CH<sub>3</sub>CN, DMF and THF which all gave diminished product yields of 23%, 32% and 43%, respectively (entries 15–17). The use of NMP afforded no amide product at all while DMSO only gave trace amounts of the amide product (entries 18 and 19). Lastly, reducing the reaction temperature to below 130 °C afforded trace amounts of the amide product.

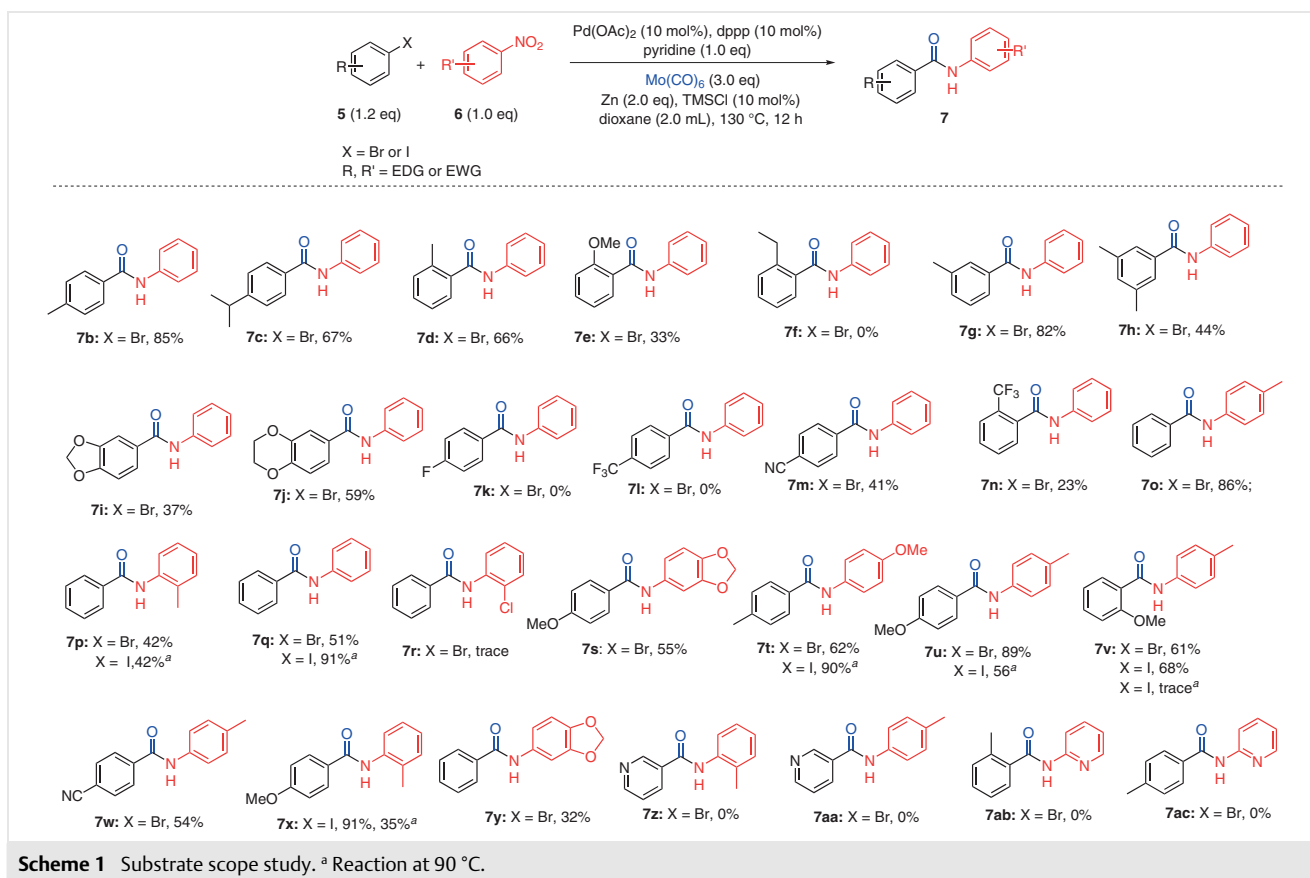
**Table 1** Optimisation Study for the Reductive Aminocarbonylation Reaction



Entry	Change in reaction conditions	Product yield (%) <sup>a</sup>
1	none	95
2	NaOH instead of pyridine	25
3	K <sub>2</sub> CO <sub>3</sub> instead of pyridine	11
4	Cs <sub>2</sub> CO <sub>3</sub> instead of pyridine	15
5	Et <sub>3</sub> N instead of pyridine	50
6	quinoline instead of pyridine	63
7	2-quinolone instead of pyridine	55
8	no ligand	12
9	dppe instead of dppp	54
10	SPhos instead of dppp	60
11	Pd(acac) <sub>2</sub> instead of Pd(OAc) <sub>2</sub>	–
12	PdCl <sub>2</sub> instead of Pd(OAc) <sub>2</sub>	14
13	PdCl <sub>2</sub> (cod) instead of Pd(OAc) <sub>2</sub>	16
14	NiCl <sub>2</sub> instead of Pd(OAc) <sub>2</sub>	–
15	CH <sub>3</sub> CN instead of dioxane	23
16	THF instead of dioxane	43
17	DMF instead of dioxane	32
18	NMP instead of dioxane	–
19	DMSO instead of dioxane	trace

<sup>a</sup> Dash (–) indicates no amide product formed.

The substrate scope and limitations of our protocol were then explored by varying the aryl halide and nitroarene (Scheme 1). Firstly, we investigated the reactivities of variously substituted aryl bromides with nitrobenzene (**6a**). Substituted aryl bromides containing an electron-donating group (EDG) afforded products **7b–7d** and **7g** in good to excellent yields. However, product **7e** was obtained in a lower product yield and the anticipated product **7f** was not formed due to the possible steric hindrance presented by the *ortho*-substituted aryl bromide utilised. Aryl bromides with a methylene- or ethylenedioxy substituent afforded products **7i** and **7j** in 37% and 59% yield, respectively. Aryl bromides possessing an electron-withdrawing group (EWG) were less reactive than those with an EDG, and in some cases completely inactive. This could be due to a reduced inductive stabilisation of the intermediate complexes formed between the metal, carbonyl, halide, ligand and phenyl ring. This further results in reduced rates of carbonylation and thus, the observed poor reactivities.<sup>34,35</sup> This trend was prominent in *para*-substituted aryl bromides which did not react to afford the anticipated products **7k**



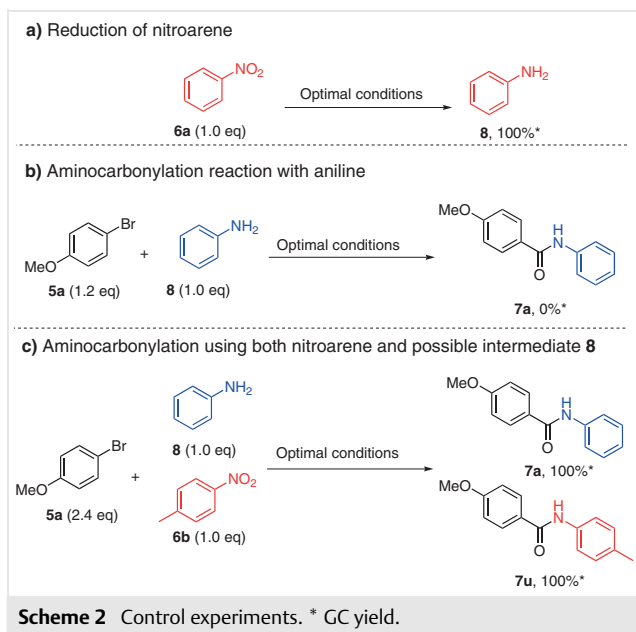
and **7l**. Amides **7m** and **7n** bearing an EWG on the *para* and *ortho* positions were obtained in 41% and 23% yield, respectively. Reactions between both substituted bromoarenes and nitroarenes afforded products **7s–7w** in average to excellent yields. The reactivities of electron-rich nitroarenes and an *ortho*-substituted bromobenzene resulted in higher product yields compared to yields obtained with neutral nitroarenes (product **7v** vs **7e**). The product yields of **7w** and **7m** also revealed a similar trend, whereby the reactivities of an aryl bromide possessing an EWG at the *para* position were improved when reacted with an electron-rich nitroarene.

Aryl iodides also reacted using the established reaction conditions and, in most cases, were found to be reactive at a lower reaction temperature of 90 °C (Scheme 1). Product **7q** was obtained in 91% yield using iodobenzene as the coupling partner compared to the 51% yield obtained with bromobenzene at 130 °C. A similar trend was observed with the yields of product **7t**. However, the use of aryl iodides for the synthesis of products **7p** and **7u** resulted in unimproved yields. Increasing the reaction temperature from 90 °C to 130 °C resulted in an improved product yield from 35% to 91% for product **7x**.

Heterocyclic aryl halides and nitropyridines were also investigated; however, reactions using these substrates did not afford the desired products (Scheme 1). 3-Bromopyridine was reacted with various nitroarenes resulting in no formation of anticipated products **7z** and **7aa**. Similarly, coupling reactions with 2-nitropyridine did not afford the anticipated amide products **7ab** and **7ac**. We also went on to investigate the reductive aminocarbonylation of aryl chlorides and aryl triflates and, unfortunately, these substrates did not afford the anticipated amide products. Increasing the catalyst loading (20 mol%), carbonyl source moles (5 eq) and reaction time (24 h), as well as the reaction temperature (150 °C), did not afford the anticipated product.

Insights into the reductive aminocarbonylation reaction mechanism have been sought.<sup>35</sup> A variety of possible reactive nitroarene intermediates have also been identified. To establish the reaction mechanism, we also undertook a brief study to identify the possible reactive intermediates that are formed under the current protocol. GC analysis of products obtained from the reaction of nitrobenzene (**6a**) under the optimal conditions, as highlighted in Scheme 2 a, revealed aniline (**8**) as the reduction intermediate. However, and similarly to reports by Wu and co-workers, the direct use of aniline as a coupling partner under these reaction

conditions did not afford the desired product (Scheme 2, b).<sup>36</sup> Interestingly, when the reaction was repeated in the presence of nitrobenzene **6b**, the amide products **7a** and **7u** were successfully formed in 100% GC yield (Scheme 2, c). Although specific mechanistic studies are yet to be established, this indicates that the presence of the nitro group plays a vital role in the reductive aminocarbonylation reaction.



In addition, coupling aryl bromides with other possible intermediates, such as azobenzene (**9a**), azoxybenzene (**9b**), 1,2-diphenylhydrazine (**9c**) and nitrosobenzene (**9d**), did not afford the anticipated amide products. However, these intermediates apart from **9d** were also successfully coupled to in the presence of nitroarene **6b** and afforded the anticipated amide products (Table 2, entries 2–4). This further demonstrates the possible role of the nitro functional group in activating the coupling of the proposed intermediates.

Scheme 3 outlines a general proposed mechanism of the reductive aminocarbonylation reaction. Initially, the Pd(II) species is converted into Pd(0) by the ligand. This is then followed by the oxidative addition of the aryl halide to give the aryl–Pd–halide intermediate **ii**. CO liberated from Mo(CO)<sub>6</sub> then coordinates to Pd affording the aryl–Pd–CO intermediate **iii** that undergoes a rearrangement and carbonylation to form the phenacyl–Pd–halide complex **iv**. Zn or Mo and TMSCl reduce nitroarene **v** to the possible intermediates of type **8** and **9a–9c**. These undergo amidation followed by a base-promoted reductive elimination to afford the target amide product **vi** and regeneration of the active Pd(0) catalyst.

**Table 2** Reductive Aminocarbonylation between Nitroarene **6b**, Intermediates and Aryl Bromide **5a**

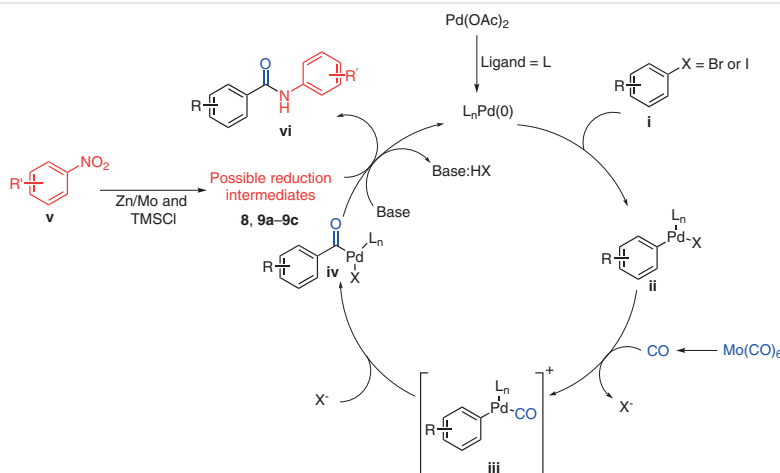
Entry	Intermediate	Yield (%) <sup>a</sup> <b>7a</b>	Yield (%) <sup>a</sup> <b>7u</b>
1		100	100
2		100	100
3		100	100
4		100	100
5		0	0

<sup>a</sup> GC yield.

In conclusion, we have demonstrated the potential applicability of Pd as a metal catalyst in reductive aminocarbonylation of nitroarenes with aryl bromides and iodides. Overall, products were obtained in modest to excellent yields. Aryl iodides showed better reactivities at lower reaction temperatures. Detailed mechanistic studies to establish the role of nitroarenes in activating the possible reduction intermediates are underway and these will be reported in the future. We will also focus on the development of more active catalysts that will promote the reductive coupling of a broader substrate scope.

#### Amides **7**; General Procedure

Pd(OAc)<sub>2</sub> (18 mg, 10 mol%), dppp (34 mg, 10 mol%) and pyridine (66 μL, 1.0 eq) were added in a pressure tube (10 mL) with dioxane (2.0 mL) as a solvent, followed by the addition of the reacting starting materials, nitroarene (e.g., nitrobenzene, 100 mg, 1.0 eq) and aryl halide (e.g., 4-bromoanisole, 0.12 mL, 1.2 eq). The additives TMSCl (0.011 mL, 10 mol%) and Zn (106 mg, 2.0 eq) were added to the reaction vessel, followed by Mo(CO)<sub>6</sub> (643 mg, 3.0 eq). The reaction was sealed and stirred at 130 °C for 12 h. After the reaction was stopped, water



**Scheme 3** Proposed reductive amidation mechanism

(20 mL) was added and the mixture was extracted with EtOAc ( $3 \times 10$  mL). The extracts were combined and dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated using a rotary evaporator. The concentrated crude material was then purified using silica gel column chromatography (30% EtOAc/hexane) to afford the desired amide product **7**. The following notes apply to the yields below: <sup>a</sup> Aryl halide used was Br. <sup>b</sup> Aryl halide used was I. \* Reaction temperature was 90 °C.

#### 4-Methoxy-N-phenylbenzamide (**7a**)

Isolated yield: 175 mg (95%); mp 173 °C.

IR (neat): 3336 (N-H), 1652  $\text{cm}^{-1}$  (C=O).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.83 (d,  $J$  = 8.50 Hz, 2 H, Ar), 7.75 (br, 1 H, -NH), 7.62 (d,  $J$  = 8.00 Hz, 2 H, Ar), 7.40–7.30 (m, 2 H, Ar), 7.15–7.10 (m, 1 H, Ar), 6.96 (d,  $J$  = 8.50 Hz, 2 H, Ar), 3.85 (s, 3 H, -OCH<sub>3</sub>).

<sup>13</sup>C NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.20 (-C=O), 162.51 (-Ar), 138.14 (-Ar), 129.04 (-Ar), 128.88 (-Ar), 127.22 (-Ar), 124.32 (-Ar), 120.17 (-Ar), 113.99 (-Ar), 55.45 (-OCH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 228.1026; found: 228.1025.

Data in agreement with literature.<sup>37</sup>

#### 4-Methyl-N-phenylbenzamide (**7b**)<sup>37</sup>

Isolated yield: 145 mg (85%)<sup>a</sup>; mp 148 °C.

IR (neat): 3350 (N-H), 1648  $\text{cm}^{-1}$  (C=O).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.94 (br, 1 H, -NH), 7.75 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.63 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.39–7.20 (m, 4 H, -Ar), 7.14–7.10 (m, 1 H, -Ar), 2.39 (s, 3 H, -CH<sub>3</sub>).

<sup>13</sup>C NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.70 (-C=O), 142.27 (-Ar), 138.06 (-Ar), 132.10 (-Ar), 129.41 (-Ar), 129.35 (-Ar), 128.99 (-Ar), 124.36 (-Ar), 120.20 (-Ar), 21.42 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 212.0997; found: 212.1078.

#### 4-Isopropyl-N-phenylbenzamide (**7c**)<sup>38</sup>

Isolated yield: 130 mg (67%)<sup>a</sup>; mp 168 °C.

IR (neat): 3368 (N-H), 1630  $\text{cm}^{-1}$  (C=O).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.79 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.63 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.40–7.30 (m, 4 H, -Ar), 7.15–7.11 (m, 1 H, -Ar), 3.00–2.90 (m, 1 H, -CH), 1.27 (d,  $J$  = 7.00 Hz, 6 H, -CH<sub>3</sub>).

<sup>13</sup>C NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.63 (-C=O), 153.20 (-Ar), 138.04 (-Ar), 132.52 (-Ar), 129.08 (-Ar), 127.12 (-Ar), 126.87 (-Ar), 124.41 (-Ar), 120.09 (-Ar), 34.12 (-CH), 23.75 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 240.1390; found: 240.1380.

#### 2-Methyl-N-phenylbenzamide (**7d**)<sup>38</sup>

Isolated yield: 113 mg (66%)<sup>a</sup>; mp 124 °C.

IR (neat): 3307 (N-H), 1643  $\text{cm}^{-1}$  (C=O).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.61 (d,  $J$  = 7.50 Hz, 2 H, -Ar), 7.51 (br, 1 H, -NH), 7.48–7.32 (m, 1 H, -Ar), 7.32–7.30 (m, 2 H, -Ar), 7.28–7.20 (m, 3 H, -Ar), 7.16–7.10 (m, 1 H, -Ar), 2.48 (s, 3 H, -CH<sub>3</sub>).

<sup>13</sup>C NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.02 (-C=O), 154.79 (-Ar), 137.99 (-Ar), 136.44 (-Ar), 131.27 (-Ar), 130.27 (-Ar), 129.19 (-Ar), 126.58 (-Ar), 125.90 (-Ar), 124.54 (-Ar), 119.88 (-Ar), 18.78 (-CH<sub>3</sub>).

#### 2-Methoxy-N-phenylbenzamide (**7e**)<sup>39</sup>

Isolated yield: 61 mg (33%)<sup>a</sup>; mp 147 °C.

IR (neat): 3336 (N-H), 1728  $\text{cm}^{-1}$  (C=O).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.78 (br, 1 H, -NH), 8.29 (dd,  $J$  = 2.00, 8.00 Hz, 1 H, -Ar), 7.67 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.50–7.45 (m, 1 H, -Ar), 7.36 (t,  $J$  = 7.50 Hz, 2 H, -Ar), 7.16–7.09 (m, 2 H, -Ar), 7.02 (d,  $J$  = 8.00 Hz, 1 H, -Ar), 4.04 (s, 3 H, -OCH<sub>3</sub>).

<sup>13</sup>C NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.19 (-C=O), 157.19 (-Ar), 138.38 (-Ar), 133.20 (-Ar), 132.52 (-Ar), 128.95 (-Ar), 124.12 (-Ar), 121.76 (d,  $J$  = 19.2 Hz, -Ar), 120.43 (-Ar), 111.53 (-Ar), 56.21 (-OCH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 228.1026; found: 228.1028.

#### 3-Methyl-N-phenylbenzamide (**7g**)<sup>38</sup>

Isolated yield: 140 mg (82%)<sup>a</sup>; mp 126 °C.

IR (neat): 3350 (N-H), 1647  $\text{cm}^{-1}$  (C=O).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92 (br, 1 H, -NH), 7.69–7.71 (m, 4 H, -Ar), 7.37–7.30 (m, 4 H, -Ar), 7.13–7.10 (m, 1 H, -Ar), 2.39 (s, 3 H, -CH<sub>3</sub>).



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.95 (-C=O), 138.64 (-Ar), 138.00 (-Ar), 134.98 (-Ar), 132.51 (-Ar), 129.02 (-Ar), 128.58 (-Ar), 127.77 (-Ar), 124.45 (-Ar), 123.94 (-Ar), 120.19 (s), 21.33 (- $\text{CH}_3$ ).

HRMS:  $m/z$  [M + H] $^+$  calcd: 212.1071; found: 212.1073.

### 3,5-Dimethyl-N-phenylbenzamide (7h)

Isolated yield: 81 mg (44%)<sup>a</sup>; mp 135 °C.

IR (neat): 3367 (N-H), 1650  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.83 (br, 1 H, -NH), 7.64 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.44 (s, 2 H, -Ar), 7.40–7.30 (m, 2 H, -Ar), 7.18–7.09 (m, 2 H, -Ar), 2.36 (s, 6 H, - $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.09 (-C=O), 138.48 (-Ar), 138.05 (-Ar), 135.01 (-Ar), 133.39 (-Ar), 129.02 (-Ar), 124.76 (-Ar), 124.38 (-Ar), 120.12 (-Ar), 21.23 (- $\text{CH}_3$ ).

### N-Phenylbenzo[d][1,3]dioxole-5-carboxamide (7i)<sup>38</sup>

Isolated yield: 72 mg (37%)<sup>a</sup>; mp 139 °C.

IR (neat): 3347 (N-H), 1655  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77 (br, 1 H, -NH), 7.60 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.49–7.40 (m, 4 H, -Ar), 7.15–7.10 (m, 1 H, -Ar), 6.84 (d,  $J$  = 8.00 Hz, 1 H, -Ar), 6.03 (s, 2 H, - $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.96 (-C=O), 150.66 (-Ar), 148.19 (-Ar), 137.99 (-Ar), 129.19 (-Ar), 129.05 (-Ar), 124.43 (-Ar), 121.64 (-Ar), 120.18 (-Ar), 108.10 (-Ar), 107.74 (-Ar), 101.80 (- $\text{CH}_2$ ).

### N-Phenyl-2,3-dihydrobenzo[b][1,4]dioxine-6-carboxamide (7j)

Isolated yield: 122 mg (59%)<sup>a</sup>; mp 140 °C.

IR (neat): 3336 (N-H), 1646  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.76 (br, 1 H, -NH), 7.60 (d,  $J$  = 7.00 Hz, 2 H, -Ar), 7.40 (d,  $J$  = 2.0 Hz, 1 H, -Ar), 7.38–7.33 (m, 3 H, -Ar), 7.13–7.08 (m, 1 H, -Ar), 6.91 (d,  $J$  = 8.50 Hz, 1 H, -Ar), 4.29 (dd,  $J$  = 5.0, 10.5 Hz, 4 H, - $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.97 (-C=O), 146.78 (-Ar), 143.53 (-Ar), 138.05 (-Ar), 129.02 (-Ar), 128.95 (-Ar), 128.20 (-Ar), 124.35 (-Ar), 120.44 (-Ar), 120.14 (-Ar), 120.08 (-Ar), 117.42 (-Ar), 116.61 (-Ar), 64.55 (- $\text{CH}_2$ ), 64.20 (- $\text{CH}_2$ ).

HRMS:  $m/z$  [M + H] $^+$  calcd: 256.0975; found: 256.0968.

### 4-Cyano-N-phenylbenzamide (7m)<sup>40</sup>

Isolated yield: 74 mg (41%)<sup>a</sup>; mp 180 °C.

IR (neat): 3353 (N-H), 1655  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.96 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.85 (br, 1 H, -NH), 7.77 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.62 (d,  $J$  = 7.50 Hz, 2 H, -Ar), 7.39 (t,  $J$  = 8.00 Hz, 2 H, -Ar), 7.19–7.15 (m, 1 H, -Ar).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.89 (-C=O), 138.89 (-Ar), 137.28 (-Ar), 132.61 (-Ar), 129.22 (-Ar), 127.77 (-Ar), 125.25 (-Ar), 120.87 (-Ar), 120.41 (-Ar), 115.43 (-CN).

HRMS:  $m/z$  [M + H] $^+$  calcd: 223.0873; found: 223.0872.

### N-Phenyl-2-(trifluoromethyl)benzamide (7n)

Isolated yield: 50 mg (23%)<sup>a</sup>; mp 158 °C.

IR (neat): 3327 (N-H), 1652  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.74 (d,  $J$  = 8.00 Hz, 1 H, -NH), 7.64 (d,  $J$  = 6.00 Hz, 2 H, -Ar), 7.58 (d,  $J$  = 8.00 Hz, 3 H, -Ar), 7.46 (br, 1 H, -Ar), 7.38–7.31 (m, 1 H, -Ar), 7.18–7.11 (m, 2 H, -Ar).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.63 (-C=O), 137.42 (-Ar), 132.22 (-Ar), 130.20 (-Ar), 129.16 (-Ar), 128.64 (-Ar), 126.54 (-Ar), 126.50 (-Ar), 125.08 (-Ar), 120.27 (- $\text{CF}_3$ ).

### N-(p-Tolyl)benzamide (7o)<sup>39</sup>

Isolated yield: 132 mg (86%)<sup>a</sup>; mp 158 °C.

IR (neat): 3336 (N-H), 1650  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.95 (br, 1 H, -NH), 7.84 (d,  $J$  = 7.50 Hz, 2 H, -Ar), 7.52–7.39 (m, 5 H, -Ar), 7.14 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 2.32 (s, 3 H, - $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.72 (-C=O), 135.39 (-Ar), 135.07 (-Ar), 134.16 (-Ar), 131.61 (-Ar), 129.49 (-Ar), 128.64 (-Ar), 127.00 (-Ar), 120.40 (-Ar), 20.84 (- $\text{CH}_3$ ).

HRMS:  $m/z$  [M + H] $^+$  calcd: 212.1077; found: 212.1075.

### N-(o-Tolyl)benzamide (7p)<sup>39</sup>

Isolated yield: 65 mg (42%)<sup>a</sup>, 65 mg (42%)<sup>b</sup>; mp 146 °C.

IR (neat): 3255 (N-H), 1650  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92–7.85 (m, 3 H, Ar), 7.72 (br, -NH), 7.56–7.45 (m, 3 H, -Ar), 7.25–7.20 (m, 2 H, -Ar), 7.12–7.08 (m, 1 H, -Ar), 2.32 (s, 3 H, - $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.62 (-C=O), 135.77 (-Ar), 135.01 (-Ar), 131.78 (-Ar), 130.52 (-Ar), 129.32 (-Ar), 128.78 (-Ar), 127.03 (-Ar), 126.85 (-Ar), 125.35 (-Ar), 123.19 (-Ar), 17.77 (- $\text{CH}_3$ ).

HRMS:  $m/z$  [M + H] $^+$  calcd: 212.1077; found: 212.1071.

### N-Phenylbenzamide (7q)<sup>39</sup>

Isolated yield: 82 mg (51%)<sup>a</sup>, 146 mg (91%)<sup>b</sup>; mp 160 °C.

IR (neat): 3344 (N-H), 1655  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.90–7.82 (m, 3 H, NH and -Ar), 7.64 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.50–7.45 (m, 2 H, -Ar), 7.38–7.33 (m, 3 H, -Ar), 7.16–7.10 (m, 1 H, -Ar).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.69 (-C=O), 154.78 (-Ar), 137.93 (-Ar), 137.36 (-Ar), 135.02 (-Ar), 131.82 (-Ar), 129.09 (-Ar), 128.78 (-Ar), 126.99 (-Ar), 124.95 (-Ar), 124.55 (-Ar), 120.19 (-Ar).

HRMS:  $m/z$  [M + H] $^+$  calcd: 198.0921; found: 198.0917.

### N-(Benzo[d][1,3]dioxol-5-yl)-4-methoxybenzamide (7s)<sup>41</sup>

Isolated yield: 89 mg (55%)<sup>a</sup>; mp 172 °C.

IR (neat): 3304 (N-H), 1606  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81 (d,  $J$  = 8.50 Hz, 2 H, -Ar), 7.60 (br, 1 H, -NH), 7.33 (d,  $J$  = 1.0 Hz, 1 H, -Ar), 6.96 (d,  $J$  = 8.50 Hz, 2 H, -Ar), 6.89–6.83 (m, 1 H, -Ar), 6.77 (d,  $J$  = 8.00 Hz, 1 H, -Ar), 5.95 (s, 2 H, - $\text{CH}_2$ ), 3.85 (s, 3 H, - $\text{OCH}_3$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.48 (C=O), 147.93 (-Ar), 144.40 (-Ar), 132.36 (-Ar), 128.81 (-Ar), 127.09 (-Ar), 113.99 (-Ar), 113.39 (-Ar), 108.10 (-Ar), 103.17 (-Ar), 101.30 (- $\text{CH}_2$ ), 55.47 (- $\text{OCH}_3$ ).

HRMS:  $m/z$  [M + H] $^+$  calcd: 272.0925; found: 272.0921.

### N-(4-Methoxyphenyl)-4-methylbenzamide (7t)

Isolated yield: 104 mg (62%)<sup>a</sup>, 151 mg (90%)<sup>b</sup>.

IR (neat): 3336 (N-H), 1657  $\text{cm}^{-1}$  (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77 (br, 1 H, -NH), 7.74 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.52 (d,  $J$  = 9.00 Hz, 2 H, -Ar), 7.38–7.32 (m, 2 H, -Ar), 6.88 (d,  $J$  = 9.00 Hz, 2 H, -Ar), 3.79 (s, 3 H, - $\text{OCH}_3$ ), 2.39 (s, 3 H, - $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.55 (-C=O), 156.55 (-Ar), 142.13 (-Ar), 132.17 (-Ar), 131.15 (-Ar), 129.35 (-Ar), 126.97 (-Ar), 122.08 (-Ar), 114.22 (-Ar), 55.48 (-OCH<sub>3</sub>), 21.43 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 242.1183; found: 242.1178.

#### 4-Methoxy-*N*-(*p*-tolyl)benzamide (7u)

Isolated yield: 157 mg (89%)<sup>a</sup>, 99 mg (56%)<sup>b\*</sup>; mp 165 °C.

IR (neat): 3339 (N-H), 1650 cm<sup>-1</sup> (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.86 (br, 1 H, -NH), 7.81 (d,  $J$  = 9.00 Hz, 2 H, -Ar), 7.50 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.13 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 6.91 (d,  $J$  = 8.50 Hz, 2 H, -Ar), 3.83 (s, 3 H, -OCH<sub>3</sub>), 2.31 (s, 3 H, -CH<sub>3</sub>).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.19 (-C=O), 162.33 (-Ar), 135.56 (-Ar), 133.89 (-Ar), 132.18 (-Ar), 129.47 (-Ar), 128.85 (-Ar), 127.23 (-Ar), 120.29 (-Ar), 113.85 (-Ar), 113.43 (-Ar), 55.39 (-OCH<sub>3</sub>), 20.83 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 242.1183; found: 242.1175.

#### 2-Methoxy-*N*-(*p*-tolyl)benzamide (7v)

Isolated yield: 107 mg (61%)<sup>a</sup>, 120 mg (68%)<sup>b</sup>, less than 10 mg (trace)<sup>b\*</sup>; mp 174 °C.

IR (neat): 3356 (N-H), 1652 cm<sup>-1</sup> (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.71 (br, 1 H, -NH), 8.28 (d,  $J$  = 7.00 Hz, 1 H, -Ar), 7.55 (d,  $J$  = 8.50 Hz, 2 H, -Ar), 7.48–7.40 (m, 1 H, -Ar), 7.15–7.05 (m, 3 H, -Ar), 7.01 (d,  $J$  = 8.50 Hz, 1 H, -Ar), 4.02 (s, 3 H, -OCH<sub>3</sub>), 2.32 (s, 3 H, -CH<sub>3</sub>).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.05 (-C=O), 157.18 (-Ar), 135.86 (-Ar), 133.66 (-Ar), 133.03 (-Ar), 132.47 (-Ar), 129.42 (-Ar), 121.98 (-Ar), 121.61 (-Ar), 120.42 (-Ar), 111.53 (-Ar), 56.18 (-OCH<sub>3</sub>), 20.84 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 242.1183; found: 242.1184.

#### 4-Cyano-*N*-(*p*-tolyl)benzamide (7w)

Isolated yield: 86 mg (54%)<sup>a</sup>; mp 178 °C.

IR (neat): 3339 (N-H), 1649 cm<sup>-1</sup> (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.94 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.87 (s, 1 H, -NH), 7.75 (d,  $J$  = 8.50 Hz, 2 H, -Ar), 7.49 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 7.17 (d,  $J$  = 8.00 Hz, 2 H, -Ar), 2.33 (s, 3 H, -CH<sub>3</sub>).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.80 (-C=O), 138.97 (-Ar), 135.02 (-Ar), 134.70 (-Ar), 132.55 (-Ar), 129.70 (-Ar), 127.74 (-Ar), 120.49 (-Ar), 117.89 (-CN), 115.29 (-Ar), 20.91 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 237.1030; found: 237.1028.

#### 4-Methoxy-*N*-(*o*-tolyl)benzamide (7x)

Isolated yield: 62 mg (91%)<sup>b</sup>, (35%)<sup>b\*</sup>; mp 160 °C.

IR (neat): 3279 (N-H), 1641 cm<sup>-1</sup> (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92 (d,  $J$  = 8.00 Hz, 1 H, -Ar), 7.84 (d,  $J$  = 8.50 Hz, 2 H, -Ar), 7.61 (br, 1 H, -NH), 7.26–7.18 (m, 2 H, -Ar), 7.11–7.04 (m, 1 H, -Ar), 6.97 (d,  $J$  = 9.00 Hz, 2 H, -Ar), 3.86 (s, 3 H, -OCH<sub>3</sub>), 2.31 (s, 3 H, -CH<sub>3</sub>).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.12 (-C=O), 162.48 (-Ar), 135.98 (-Ar), 130.49 (-Ar), 129.11 (-Ar), 128.99 (-Ar), 127.22 (-Ar), 126.85 (-Ar), 125.11 (-Ar), 123.09 (-Ar), 114.00 (-Ar), 55.45 (-OCH<sub>3</sub>), 17.80 (-CH<sub>3</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 242.1183; found: 242.1174.

#### *N*-(Benzo[*d*][1,3]dioxol-5-yl)benzamide (7y)

Isolated yield: 47 mg (32%)<sup>a</sup>; mp 135 °C.

IR (neat): 3329 (N-H), 1648 cm<sup>-1</sup> (C=O).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.84 (br, 1 H, -NH), 7.82 (d,  $J$  = 9.00 Hz, 2 H, -Ar), 7.55–7.40 (m, 3 H, -Ar), 7.32 (s, 1 H, -Ar), 6.88 (d,  $J$  = 8.00 Hz, 1 H, -Ar), 6.74 (d,  $J$  = 8.00 Hz, 1 H, -Ar), 5.94 (s, 2 H, -CH<sub>2</sub>).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.67 (-C=O), 147.87 (-Ar), 144.52 (-Ar), 134.87 (-Ar), 132.13 (-Ar), 131.73 (-Ar), 128.71 (-Ar), 126.96 (-Ar), 113.60 (-Ar), 108.07 (-Ar), 103.32 (-Ar), 101.30 (-CH<sub>2</sub>).

HRMS:  $m/z$  [M + H]<sup>+</sup> calcd: 242.0739; found: 242.0815.

## Conflict of Interest

The authors declare no conflict of interest.

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## Supporting Information

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