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A one-step strategy for synthesizing *N*-formanilide via benzamide activation and oxalic acid-driven reduction†

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A one-step synthetic strategy for directly converting benzamides into *N*-formanilide derivatives has been developed using oxalic acid as a hydride source. This strategy involves the selective cleavage of the amide C–N bond through a reaction with sodium azide, generating a benzyl azide intermediate. This intermediate subsequently undergoes Curtius rearrangement to form an isocyanate species, which is then reduced by thermally decomposed oxalic acid, yielding the final *N*-formylated product. This strategy demonstrates a broad substrate scope, including various substituted benzamides and heterocyclic amides, achieving yields of up to 95%.

*N*-Formylaniline stands out as a pivotal structural motif in medicinal chemistry because of its potential to exhibit anti-inflammatory, antibacterial, anti-osteoporotic, and central nervous system activities when modified with suitable substituents (Fig. 1).<sup>1</sup> Consequently, the development of efficient synthetic methods and modification strategies for *N*-formylaniline remains vital for producing novel bioactive agents and enhancing existing drugs.

Traditionally, *N*-formanilide has been synthesized by directly formylating aniline with formic acid or its derivatives. However, these reagents often raise concerns regarding stability and environmental impact (Scheme 1a).<sup>2</sup> Consequently, alternative strategies that bypass the use of classical formylating agents have been developed by employing carbon monoxide (CO), carbon dioxide, or methanol as one-carbon (C1) sources—sometimes in tandem with the oxidation of C2 or C3 substrates (Scheme 1b).<sup>3</sup> Although these strategies are both versatile and innovative, they often require highly specialized catalysts or have limitations in terms of broad applicability.

Another valuable method for preparing *N*-formanilide involves the Curtius rearrangement of acyl azides, which are

frequently derived from a wide array of precursors (Scheme 1c).<sup>4</sup> In this method, conventional organic hydrogen donors, including formaldehyde and formic acid, are routinely employed to facilitate the rearrangement and subsequent formation of *N*-formylated products.

In our laboratory, we recently developed an aminocarbonylation pathway that harnesses oxalic acid as both a CO source and a hydrogen donor under palladium catalysis, enabling the synthesis of *N*-formanilide in excellent yields (Scheme 1d).<sup>5</sup> This pathway proceeds under comparatively mild reaction conditions, and its operational simplicity and scalability make it highly attractive for practical synthetic applications.

In recent years, numerous research groups have advanced methodologies that enable the selective cleavage of amide C–N bonds, thereby creating opportunities for introducing new functionalities or inducing rearrangements.<sup>6</sup> Our laboratory has also contributed to this field by developing a range of acyl-substitution protocols for both activated and non-activated amides using various nitrogen-, carbon-, or oxygen-based nucleophiles.<sup>7</sup> Additionally, we have demonstrated a route whereby amides react with NaN<sub>3</sub> to generate acyl azides.<sup>8</sup>

Building on these findings, we now present a one-step procedure for synthesizing *N*-formanilide from amides via an acyl azide intermediate, with oxalic acid serving as an effective

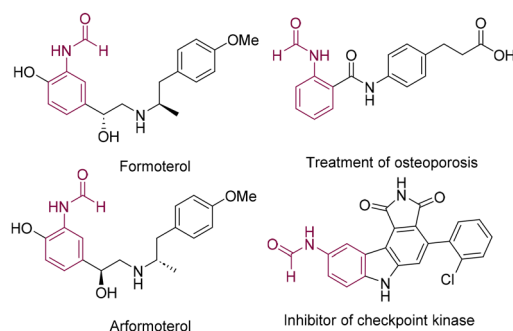
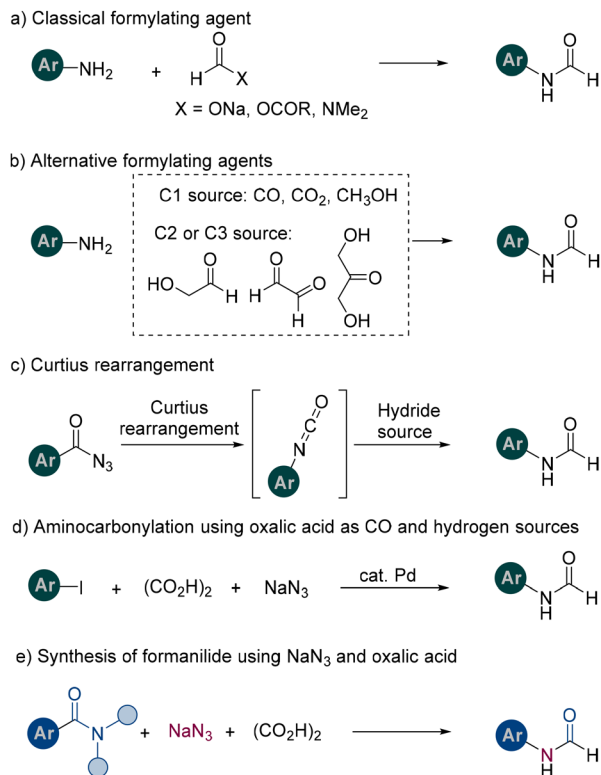


Fig. 1 Bioactive molecules containing an *N*-formanilide moiety.

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Scheme 1 Synthesis of *N*-formanilide.

hydrogen donor. Although benzoyl chlorides are widely utilized and offer straightforward access to acyl derivatives, their handling can sometimes present challenges due to their sensitivity toward moisture and potential functional group compatibility issues. In contrast, our method employing activated amides offers a complementary synthetic route that addresses these concerns. Moreover, to the best of our knowledge, the direct transformation of activated amides into *N*-formanilide groups using oxalic acid has not been previously reported. We believe that this strategy not only broadens the synthetic toolbox but also provides organic chemists with a practical and versatile alternative for formyl group installation.

The reaction conditions were optimized to maximize the yield of **2a** from the reaction of **1a**, NaN<sub>3</sub>, and oxalic acid (Table 1). The optimal conditions were identified as using 2.0 equiv. of NaN<sub>3</sub> and 6.0 equiv. of oxalic acid in NMP at 130 °C for 16 h, which afforded **2a** in 89% yield (entry 1). Subsequently, the effect of varying reaction parameters was examined. Decreasing the NaN<sub>3</sub> loading to 1.0 equiv. significantly lowered the yield to 32%, whereas increasing it to 1.5 equiv. provided an intermediate yield of 66% (entries 2 and 3). Further increasing the NaN<sub>3</sub> loading to 2.5 equiv. did not significantly improve the yield, which remained at 81% (entry 4). Next, the influence of (CO<sub>2</sub>H)<sub>2</sub> equivalents was studied. Reducing the (CO<sub>2</sub>H)<sub>2</sub> loading to 2.0 equiv. completely suppressed product formation (entry 5). Using 4.0 equiv. led to a modest yield of 32%, and increasing the loading to 5.0 equiv. improved the yield to 64% (entries 6 and 7). Further increasing the loading to 7.0 equiv. afforded an 80% yield, which is com-

Table 1 Optimization of reaction conditions for the synthesis of *N*-formanilide<sup>a</sup>

Entry	x equiv.	y equiv.	Solvent	Temperature (°C)	Time (h)	Yield <sup>b</sup> (%)
1	2.0	6.0	NMP	130	16	89
2	1.0	6.0	NMP	130	16	32
3	1.5	6.0	NMP	130	16	66
4	2.5	6.0	NMP	130	16	81
5	2.0	2.0	NMP	130	16	0
6	2.0	4.0	NMP	130	16	32
7	2.0	5.0	NMP	130	16	64
8	2.0	7.0	NMP	130	16	80
9	2.0	6.0	DMF	130	16	61
10	2.0	6.0	DMAc	130	16	4
11	2.0	6.0	DMSO	130	16	15
12	2.0	6.0	Toluene	130	16	0
13	2.0	6.0	Diglyme	130	16	0
14	2.0	6.0	Monoglyme	130	16	0
15	2.0	6.0	NMP	110	16	42
16	2.0	6.0	NMP	90	16	0
17	2.0	6.0	NMP	130	12	71
18	2.0	6.0	NMP	130	24	75

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), NaN<sub>3</sub> (x equiv.), and (CO<sub>2</sub>H)<sub>2</sub> (y equiv.) reacted in NMP. <sup>b</sup> Determined using gas chromatography with an internal standard (2-methoxynaphthalene).

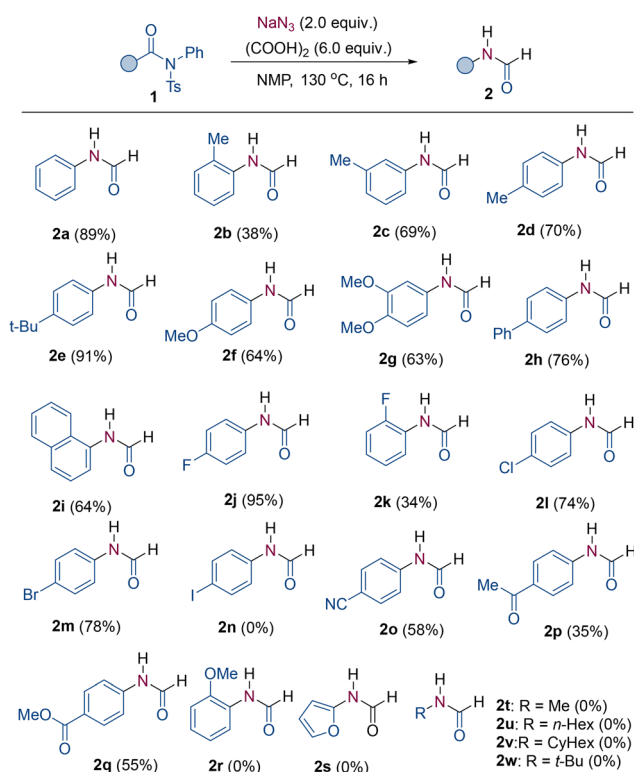
parable to the 89% yield obtained with 6.0 equiv. (entry 8). Solvent screening was then conducted. DMF provided a moderate yield of 61%, while DMAc and DMSO afforded significantly lower yields of 4% and 15%, respectively (entries 9–11). The use of toluene, diglyme, and monoglyme failed to produce any detectable product (entries 12–14). Lowering the reaction temperature to 110 °C reduced the yield to 42%, and further decreasing it to 90 °C resulted in no product formation (entries 15 and 16). Shortening the reaction time to 12 h resulted in a slightly reduced yield of 71%, whereas extending it to 24 h provided a 75% yield (entries 17 and 18).

Under the optimized reaction conditions, various substituted *N*-phenyl-*N*-tosylbenzamide derivatives were investigated for their reactivity with NaN<sub>3</sub> and oxalic acid (Scheme 2). As expected, *N*-phenyl-*N*-tosylbenzamide underwent the transformation smoothly, affording the desired product **2a** in an isolated yield of 89%. The introduction of methyl substituents influenced the reaction efficiency, with the *ortho*-, *meta*-, and *para*-methyl derivatives producing **2b**, **2c**, and **2d** in 38%, 69%, and 70% yields, respectively. Among the alkylated substrates, the *para*-*tert*-butyl-substituted derivative exhibited the highest efficiency, affording **2e** in 91% yield. The presence of methoxy groups also affected the transformation, with the mono- and dimethoxy-substituted derivatives leading to the formation of **2f** and **2g** in 64% and 63% yields, respectively. The reaction was further extended to larger aromatic systems, such as biphenyl- and 1-naphthyl-based amides, which delivered **2h** and **2i** in 76% and 64% yields, respectively. Interestingly, fluorine substitution had a position-dependent effect on the reaction outcome. While the *para*-fluoro-substituted derivative efficiently produced **2j** in an excellent 95% yield, its *ortho*-fluoro counterpart exhibited a significantly lower efficiency, producing **2k** in only 34% yield. A similar trend was observed for halogen-substituted derivatives, where the *para*-chloro and *para*-bromo analogs provided **2l** and **2m** in 74% and 78% yields, respectively. However, the *para*-iodo derivative did not afford the expected product **2n**; instead, the deiodinated compound **2a** was isolated in 40% yield, indicating a competing reaction pathway. Electron-withdrawing groups exhibited varying effects on the transformation. The cyano-substituted amide resulted in the formation of **2o** in 58% yield, while the acetyl and methyl ester derivatives afforded **2p** and **2q** in 35% and 55% yields, respectively. In contrast, in the case of the *ortho*-methoxy-substituted substrate, the desired product **2r** was not obtained. Analysis of the reaction mixture revealed that 2-methoxy-*N*-phenylbenzamide, formed *via* detosylation of the starting material, was the major product. Additionally, attempts to generate the desired products from 2-furanyl (**2s**) and alkyl amide derivatives (**2t–2w**) were unsuccessful. However, despite multiple attempts, heterocyclic substrates such as thiophene-, benzofuran-, pyrrole-, pyridine-, and quinoline-derived amides did not furnish the desired products. Optimization of reaction parameters, including temperature and concentration, did not lead to successful conversion in these cases.

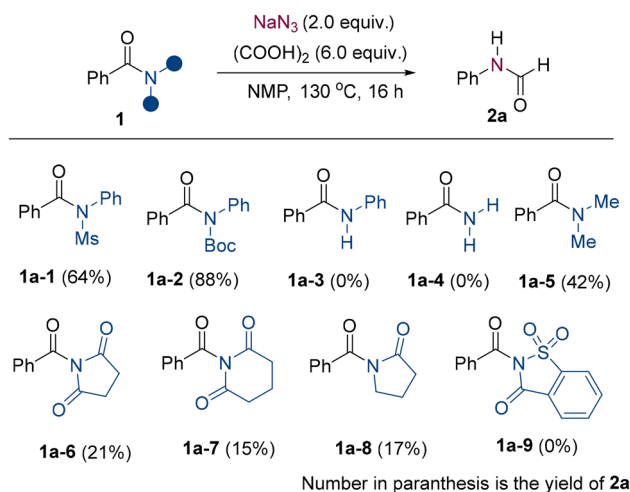
To investigate the reactivity of benzamide derivatives bearing various substituents on their nitrogen atom, a series of

substrates were examined under the optimized reaction conditions (Scheme 3). Among the activated benzamides, *N*-mesityl-*N*-phenylbenzamide and *N*-Boc-*N*-phenylbenzamide successfully underwent the transformation, affording **2a** in 64% and 88% yields, respectively. Among deactivated benzamides, *N*-phenylbenzamide and benzamide did not produce the desired product, whereas *N,N*-dimethylbenzamide afforded **2a** in 42% yield. *N*-Acyl-substituted activated amides, namely *N*-benzoyl succinimide, *N*-benzoyl glutarimide, and *N*-benzoyl pyrrolidin-2-one, produced **2a** in 21%, 15%, and 17% yields, respectively. However, *N*-benzoyl saccharin did not transform to **2a**.

To gain further insights into the reaction mechanism, a series of control experiments were conducted. To investigate the origin of the hydrogen atoms in the formamide product, a control experiment was conducted using deuterated oxalic acid. Under the standard reaction conditions, the desired product **2a-D** was obtained in 85% yield. <sup>1</sup>H NMR analysis of the crude reaction mixture revealed 51% deuterium incorporation<sup>9</sup> at the formyl hydrogen and 3% incorporation at the N–H position of the aniline moiety. These results indicate that the hydrogen at the formyl position is partially derived from oxalic acid, supporting its role as a hydride source in the proposed mechanism (Scheme 4a). To examine the unique role of oxalic acid as a hydride source, we tested alternative reducing agents under the same reaction conditions. When sodium



**Scheme 2** Substrate scope for the synthesis of *N*-formanilide derivatives. Reaction conditions: **1** (1.0 mmol), NaN<sub>3</sub> (2.0 mmol), and (CO<sub>2</sub>H)<sub>2</sub> (6.0 mmol) reacted in NMP (3.0 mL) at 130 °C for 16 h. The numbers in parentheses are the isolated yields.



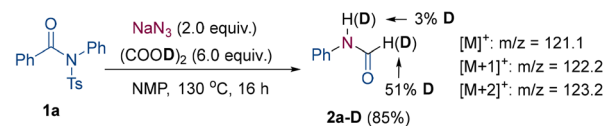
**Scheme 3** Reactions involving various benzamides for the synthesis of **2a**.

hydride (NaH) or triethylsilane was used in place of oxalic acid, no formation of the target *N*-formanilide product was observed. These control experiments underscore the essential and specific role of oxalic acid in facilitating the reduction step in this transformation (Scheme 4b). In one experiment, *N*-phenyl-*N*-tosylbenzamide and oxalic acid were placed in separate reaction vessels connected to one another. The oxalic acid-containing vessel was heated to 130 °C, while the *N*-phenyl-*N*-tosylbenzamide- and  $\text{NaN}_3$ -containing vessel was maintained at 50 °C. Under these conditions, no detectable formation of **2a** was observed. When  $\text{NaN}_3$  was introduced into the oxalic acid-containing vessel, only a trace amount of **2a** was detected by gas chromatography. These findings indicate that hydrogen gas generated solely from the thermal decomposition of oxalic acid is insufficient to promote the formylation reaction (Scheme 4c). To further investigate the influence of electronic effects, a competitive experiment was performed using an electron-donating methyl-substituted amide (**1d**) and an electron-withdrawing fluoro-substituted amide (**1j**). When these substrates were reacted under identical conditions (130 °C) in the presence of  $\text{NaN}_3$  and oxalic acid, the corresponding *N*-formanilide products **2d** and **2j** were obtained in 25% and 86% yields, respectively.

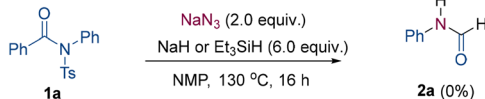
A similar reaction was then conducted with a modified sequence, where  $\text{NaN}_3$  was first allowed to react at 25 °C for 6 h before oxalic acid was added. Under these conditions, **2d** and **2j** were obtained in yields nearly identical to those observed in the original experiment (Scheme 4d). These results suggest that the electronic properties of the substituents do not significantly influence the initial acyl substitution reaction with  $\text{NaN}_3$ . However, at elevated temperatures, benzamides with electron-withdrawing groups exhibit enhanced reactivity, likely due to the more efficient formation and subsequent reaction of the isocyanate intermediate generated *via* the Curtius rearrangement.

Based on our experimental findings and previous literature reports, a plausible reaction mechanism is proposed in

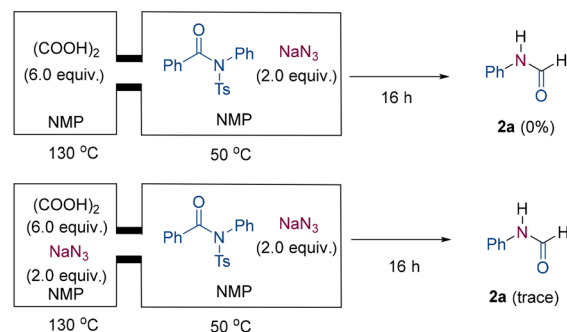
a) Deuterated oxalic acid



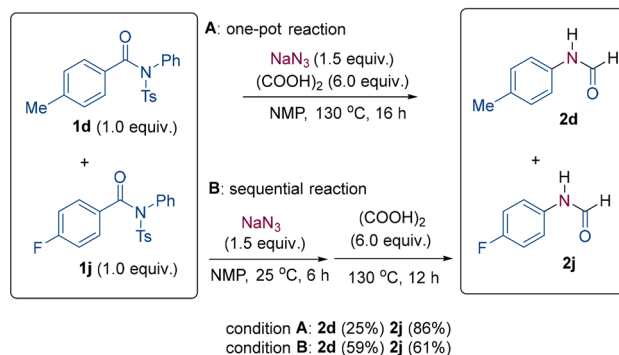
b) Hydride source



c) Two chamber reactions



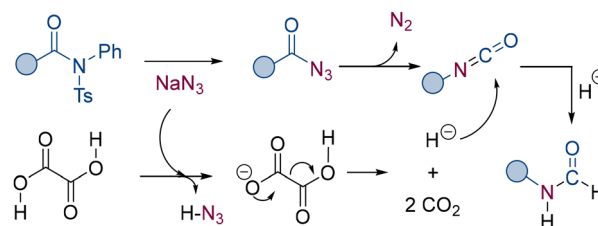
d) Competitive reactions under one-pot & sequential conditions<sup>a</sup>



<sup>a</sup>Note: Due to the use of two equivalents of amide substrates, total isolated yields exceed 100%

**Scheme 4** Control experiments.

Scheme 5. The reaction begins when the amide substrate reacts with  $\text{NaN}_3$ , leading to the formation of an acyl azide intermediate. Upon heating, the acyl azide intermediate undergoes a Curtius rearrangement, generating an isocyanate intermediate. Concurrently, oxalic acid thermally decomposes or reacts with  $\text{NaN}_3$  to generate a hydride source. The isocyanate



**Scheme 5** Proposed mechanism.



intermediate then reacts sequentially with the hydride source and a proton, ultimately yielding the final *N*-formylated product.

## Conclusions

In summary, we report a one-step strategy to synthesize *N*-formanilide derivatives from activated amides using oxalic acid as a hydride source. The process involves sodium azide-mediated C–N bond cleavage, forming a benzyl azide intermediate, which undergoes a Curtius rearrangement to yield an isocyanate. This isocyanate is then reduced *in situ* by oxalic acid to produce the target *N*-formylated products. Substrate scope studies showed that electron-withdrawing groups enhance the reaction, while sterically hindered or alkyl amides show reduced reactivity. Optimization focused on reagent equivalents, temperature, and solvent. Control experiments confirmed that oxalic acid acts directly as a hydride donor, not *via* hydrogen gas. This method expands the utility of acyl azides and offers insight into amide bond activation. By using *N*-tosylated or *N*-Boc-protected amides, this approach provides a practical route to formylated anilines, even under mild conditions.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Acknowledgements

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- 9 The formation of only 50% deuterated product is attributed to trace amounts of water present in the reaction system, despite our efforts to rigorously exclude moisture under carefully controlled conditions.