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Glycolaldehyde as a Bio-Based C_1 Building Block for Selective *N*-Formylation of Secondary Amines

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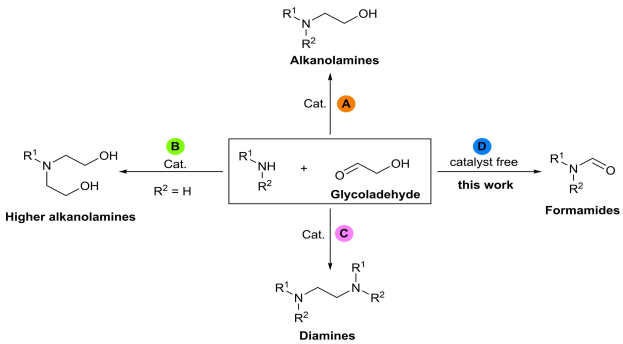
Biomass derived glycolaldehyde was employed as C1 building block for the *N*-formylation of secondary amines using air as oxidant. The reaction is atom economic, highly selective and proceeds under catalyst free conditions. This strategy can be used for the synthesis of cyclic and acyclic formylamines, including DMF. Mechanistic studies suggest a radical oxidation pathway.

Introduction

Nature generates yearly about 170 billion metric tons of biomass, 75% of which being carbohydrates.[1] This represents the biggest source of renewable carbon on earth, and is consequently seen as the most promising alternative to fossil stocks for the production of chemicals and fuels.[2] The addition of C_1 building block represents an important strategy for the synthesis of new products. Several C_1 building blocks have been used; carbon mono- and dioxide, methanol, and formic acid-all potentially obtainable from renewable resources-being the most ubiquitous examples.[3]

N-Formamides are an important class of chemicals with widespread industrially relevant applications as solvents and raw materials for fine chemicals such as drugs, fertilizers, cosmetics and softeners.[4] Traditionally, the C–N bond is formed by reaction of amines with C_1 sources, such as formic acetic anhydride, chloral or carbon monoxide.[5] Various routes have been reported for the synthesis of formamides employing CO_2 as carbon source and hydrogen as reducing agent.[6] Notwithstanding the importance and applicability of the latter, we aimed to develop a practical procedure for the *N*-formylation of amines which avoids the use of gaseous reactants and directly utilizes biomass-derived small molecules. This approach presents some immediate limitations: 1) biomass is typically a mixture of multi-carbon compounds, and it needs to be further transformed to obtain a C_1 building block; 2) transition metal catalysts are usually needed for the conversion of biomass into small chemicals, thus generating extra costs. A seminal work in this regard comes from Shi and co-workers, who reported the use of glycerol and glycerol-derived compounds (dihydroxyacetone, glyceraldehyde and glycolic acid) for the *N*-formylation of amines over copper-containing heterogeneous catalysts under oxidative conditions.[7] In our attempts to prepare cleavable conjugated polymers, we serendipitously found that glycolaldehyde (GA) reacted with secondary amines to yield the *N*-formylated products with very good yields. This use of glycolaldehyde as C_1 building block is unprecedented and we decided to investigate this reaction in depth. GA is the smallest of the reducing sugars homologous series; it can be obtained by cracking of glucose in good yield or from biomass pyrolysis oil, where it is a major component, and it displays low toxicity.[8] GA is widely used as a bio-based platform chemical for the addition of C_2 chains on amines (Scheme 1A–C), but its use as C_1 building block is, to the best of our knowledge, unprecedented.[9] Herein, we report a highly efficient strategy for the *N*-formylation of secondary amines using GA as C_1 source (Scheme 1D). This process offers several advantages over conventional methods. The reaction does not require a catalyst, is highly selective for secondary amine groups, and proceeds under mild conditions, using air as oxidant.



Scheme 1. Reactions of secondary amines with glycolaldehyde.

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Results and Discussion

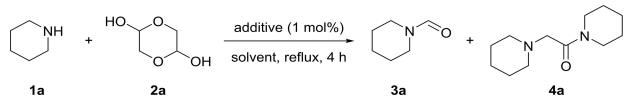
In preliminary experiments piperidine (**1a**) was chosen as the model substrate and the commercially available dimer of GA (**2a**) as the formylating agent (Table 1). Initial screening of solvents (Table 1, entries 1–6) revealed that acetonitrile is the best one under the given reaction conditions. Formamide **3a** was obtained in 92% yield (Table 1, entry 5). Surprisingly, when typical oxidation catalysts (Table 1, entries 7 and 8) were added, lower yields of the desired product **3a** were obtained (55 and 78% respectively). When oxygen gas was used instead of air, the yield of **3a** was not improved (Table 1, entry 9). Presence of oxygen was shown to be crucial, as the reaction does not proceed under argon (Table 1, entry 10). The absence of light does not have an impact on the yield of **3a** (Table 1, entry 11). Further variations in temperature and reaction time were also studied but did not lead to any improvement (see the Supporting Information for details, Tables S1 and S2).

Having optimal reaction conditions in hand, we explored the scope of the *N*-formylation of different secondary amines (Table 2). Cyclic amines afforded good to high yields (**3a**–**d**, up to 92%). Remarkably, this protocol also works well for acyclic secondary amines (**1e**–**l**) which are usually less reactive or not reactive at all in *N*-formylation reactions. In the case of secondary phenylamines, such as 2-(methylamino)pyridine (**1e**), *N*-methylaniline (**1f**) and diphenylamine (**1g**), the corresponding products (**3e**–**g**) were obtained in good yields (up to 73%). Secondary fatty amines were also formylated obtaining **3h**–**l** in yields up to 70%. Ephedrine was formylated to give a mixture of rotamers in 27% yield. However, the reaction does not proceed for primary amines such as aniline (**1m**), benzylamine (**1n**) and *n*-hexylamine (**1o**; see the Supporting Information for details, Scheme S1).

Given the paramount importance of dimethylformamide (DMF),[10] we applied our protocol for the *N*-formylation of dimethylamine. Different dimethylamine solutions were tested using O_2 as oxidant at atmospheric pressure at 95 °C and 8 h (Table 3, entries 1–4). Only dimethylamine solution in THF (2.0 M) afforded DMF in low yield (24%). In previous studies, dimethylammonium dimethyl carbamate is usually chosen as starting material for the synthesis of DMF.[6b] Under the same conditions, DMF was obtained in 21% yield (Table 3, entry 5). As we assumed that the low yields were due to the low boiling point of dimethylamine, we performed the reaction in a sealed autoclave in the presence of pressurized air as oxygen source (Table 3, entries 6 and 7). DMF was obtained in higher yields (57 and 45% yield). This demonstrates the potential of the shown procedure for further practical applications in DMF manufacturing.

To gain mechanistic insights, the reaction between **1a** and **2a** was monitored over time (Scheme 2). When piperidine **1a** and glycolaldehyde dimer were reacted under standard reac-

Table 1. Optimization of the reaction conditions.

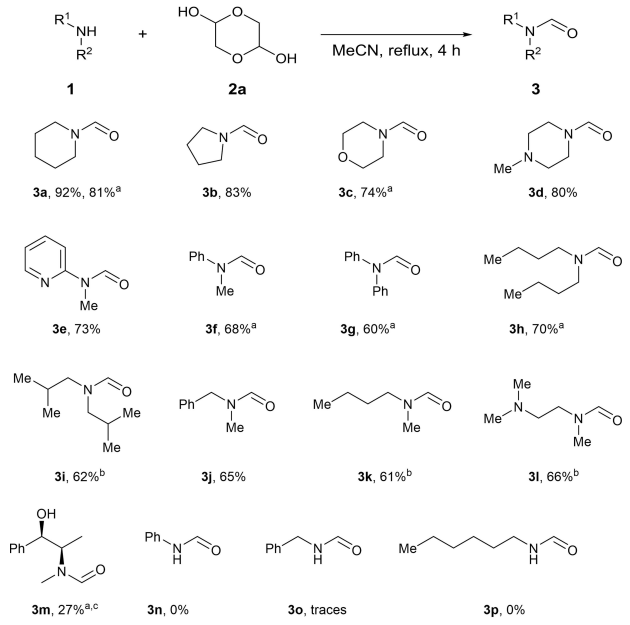


1a 2a 3a 4a

Entry	Solvent	Additive	Conv. [%]	**3a** [%]	**4a** [%]
1	THF	–	>99	64	31
2	CH_2Cl_2	–	75	71	3
3	$CHCl_3$	–	84	81	2
4	toluene	–	81	73	6
5	MeCN	–	99	92	5
6	acetone	–	81	75	5
7	MeCN	CuCl	72	55	7
8	MeCN	$Pd(OAc)_2$	88	78	10
9[a]	MeCN	–	97	92	3
10[b]	MeCN	–	90	–	–
11[c]	MeCN	–	99	91	4

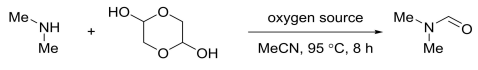
Reaction conditions: **1a** (2.0 mmol), **2a** (0.5 mmol), solvent (5 mL), reflux, 4 h. Yields were determined by GC using mesitylene as internal standard. [a] Using O_2 balloon with Schlenk flask. [b] Under argon. [c] Reaction in the dark.

Table 2. Substrate scope of *N*-formylation of amines **1**.



Reaction conditions: **1** (2.0 mmol), **2a** (0.5 mmol), MeCN (5.0 mL), reflux, 4 h. Yields were determined by GC using mesitylene as internal standard. [a] Isolated yields. [b] **1** (1.0 mmol), **2a** (0.5 mmol), 12 h. [c] 16 h, O_2 (1 atm).

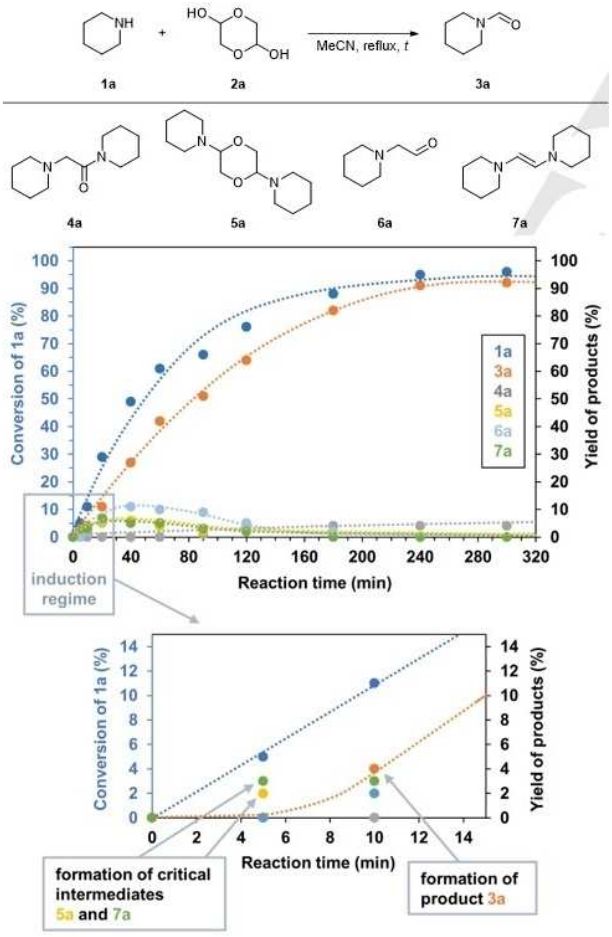
Table 3. Synthesis of DMF from dimethylamine and glycolaldehyde.



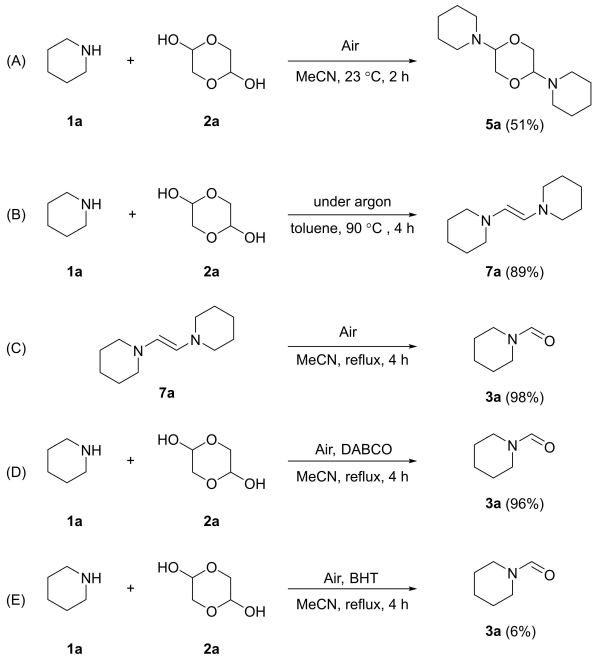
4 2a 5a

Entry	Dimethylamine solution **4**	Oxygen source	**5a** [%]
1	2.0 M in THF	O_2 balloon	24
2	40 wt. % in H_2O	O_2 balloon	0
3	2.0 M in methanol	O_2 balloon	0
4	5.6 M in ethanol	O_2 balloon	0
5	$(CH_3)_2NH\cdot(CH_3)_2NCOOH$	O_2 balloon	21
6	2.0 M in THF	air (10 bar)[a]	57
7	$(CH_3)_2NH\cdot(CH_3)_2NCOOH$	air (10 bar)[a]	45

Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), MeCN (5 mL), 95 °C, 8 h. Yields were determined by GC using mesitylene as the internal standard. [a] Autoclave instead of Schlenk flask.



Scheme 2. Reaction profile of the *N*-formylation from amine with glycolaldehyde.



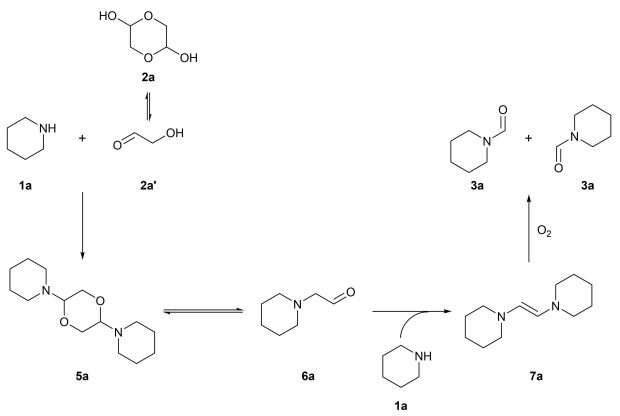
Scheme 3. Control experiments.

tion conditions, four types of compounds were detected. As early as after 5 min the desired product starts to form. Amide **4a** is detected only after 90 min. Its concentration increases with time, reaching a plateau after 180 min. This suggests that **4a** is not an intermediate towards the desired product, but more likely a by-product coming from another reaction path. The compounds **5a**, **6a**, and **7a** are all produced at the initial stage of the reaction, but their concentration stays low (< 15%) and they get eventually consumed in the later stage of the reaction. After 4 h all intermediates are converted into either **3a** or **4a**. From this observation it can be postulated that **5a**, **6a**, and **7a** are all intermediates to the product as well as to the unwanted **4a**.

To form a more conclusive mechanistic picture, several control experiments were performed (Scheme 3). Firstly, piperidine **1a** and glycolaldehyde dimer **2a** were stirred at room temperature until a homogeneous solution was formed. Colorless crystals were formed after stirring was halted. They were collected by filtration and washed with ice-cold acetonitrile, and **5a** was obtained in 51% yield (Scheme 3A). Notably, **5a** monomerizes over time in $CDCl_3$ (even faster in C_6D_6), to form 2-(piperidin-1-yl) acetaldehyde **6a** (Supporting Information, Figures S1 and S2). As mentioned before (Table 1, entry 10 and Scheme 3B), the reaction under inert conditions does not lead to the formylated product, but the enamine **7a** could be obtained in 89% yield as a low-melting solid that gradually turned yellow over the course of the next 2 days (Figure S3). This suggests that oxygen is the actual oxidizing agent in the reaction. In addition, using isolated **7a** as starting materials under our standard conditions, the corresponding product **3a** can be obtained in excellent yield (Scheme 3C). This is a further indication that the oxygen atom on the formyl group does not come from water (that is produced upon condensation between the aldehyde and the amine), but rather from oxygen itself.

To exclude the involvement of singlet oxygen the reaction was performed in the presence of an excess (5 equiv. with respect to piperidine) of 1,4-diazabicyclo[2.2.2]octane (DABCO, Scheme 3D), which is a known quencher for $^1O_2$.[11] The reaction proceeded to full conversion to the desired product, thus excluding that $^1O_2$ has an active role. Considering these results and previous reports, we propose the reaction pathway shown in Scheme 4.

Initially, glycolaldehyde dimer **2a** and glycolaldehyde **2a'** rapidly interconvert in solution. Then, piperidine **1a** quickly reacts with glycolaldehyde **2a'** forming **5a**. Compounds **5a** and **6a** exist in equilibrium in solution. The latter undergoes a second amination reaction with **1a** to form **7a**. The actual oxidation should then take place via a radical mechanism. To prove this hypothesis the formylation of **1a** was run in the presence of 2 equivalents of butylated hydroxytoluene (BHT), a common quenching agent for radical species. Indeed, the yield of the reaction dropped to 6%, which indicates that the



Scheme 4. Putative reaction pathway.

reaction was effectively inhibited by BHT. To further support this assumption, in situ EPR experiments using **7a** and the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were conducted in the presence and absence of O_2. No radical intermediates have been detected under Ar at the reaction temperature (80 °C). However, in the presence of O_2, a multiline EPR signal(triplet-of-sextets) appeared at $g = 2.006$. This signal can be fitted (Bruker-SpinFit package) by assuming the coupling to $A_N = 14.0$, $A_H = 16.7$, and $A_{Ng} = 1.7$ G (Figure 1) indicating the formation of a DMPO-•N spin adduct.[12] This suggests that a nitrogen-centered radical is formed upon interaction of **7a** with O_2. Additionally, there is a weak three-line signal (1:1:1) at $g = 2.006$ with $A_N = 13.8$ G attributed to the formation of aminoxyl radical (DMPOX), indicating small extent of degradation of DMPO.

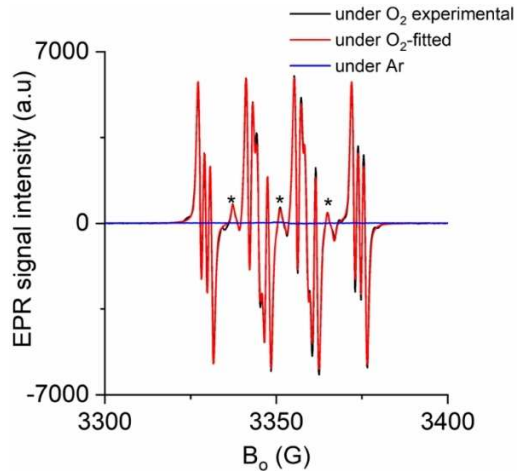
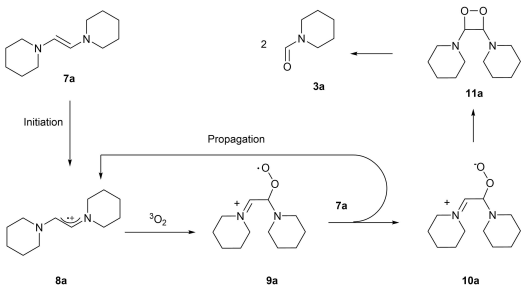


Figure 1. EPR spectra of 0.2 M dienamine **7a** + 10 μL DMPO measured at 20 °C after heating 4 h at 80 °C under a) Ar (blue-line); b) O_2 (black-line); c) Fitted spectrum of (b) using Bruker SpinFit package program (red line). *EPR signal of DMPOX due to the oxidation of DMPO.

We propose the following radical mechanism based on Scheme 5. As initiation step, we assume the enediamine **7a** is oxidized to the radical cation **8a** by oxygen. This most likely is the species that is trapped by the spin trap. This type of reactivity is well-precedented from the work of Wiberg who showed that reaction of tetra(dimethylamino)ethylene with oxygen leads to the formation of a radical cation.[13] Reaction of **8a** with oxygen leads to formation of the peroxo radical **9a**. This compound may abstract an electron from **7a** in the propagating step leading to the species **10a** and the regeneration of **8a**.

Ring-closure of **10a** to the dioxetane **11a** is well-precedented from earlier work of Foote and others on the reaction between enamines and singlet oxygen.[14] Thermal decomposition of the dioxetane to 2 equivalents of formamide is again well-precedented. To obtain more information about the structure of the spin trap adduct we subjected the reaction mixture to ESI-MS (see Supporting Information for details). Although a signal for the spin trapped **8a** (m/z = 307) was not visible, we found a small signal at m/z = 309, possibly due to reduction by the formic acid that was used in the MS sample preparation. More interesting, a signal at m/z = 339 fits very well with the spin-trapped intermediate **9a** (Scheme 5, Figure 2). Dioxetanes are not very long-lived intermediates, certainly not at the temperature of the reaction. For that reason, we followed the reaction of **7a** in CD_3CN at room temperature over 16 h. In the ^{1}H NMR (Figure 2) we see the signal of the olefinic proton of **7a** and slowly over time the formation of the formamide **3a** with the characteristic formyl proton at 7.92 ppm. Interestingly, in the first 9 h of the reaction, we also see a small peak at 4.92 ppm which fits very well with the anticipated adsorption of the dioxetane protons.



Scheme 5. Proposed mechanism for the radical oxidation of **7a**.

Conclusions

Bio-based glycolaldehyde was used for the first time as a C_1 building block for the selective catalyst-free *N*-formylation of secondary amines to formamides under mild experimental conditions. The protocol is highly selective for secondary amines, with several aromatic and aliphatic (both cyclic and linear) being *N*-formylated. Based on control experiments, a spin trap experiment, MS and ^{1}H NMR spectroscopz, we propose a radical oxidation mechanism that leads to formation of a dioxetane that splits in two formamide molecules.

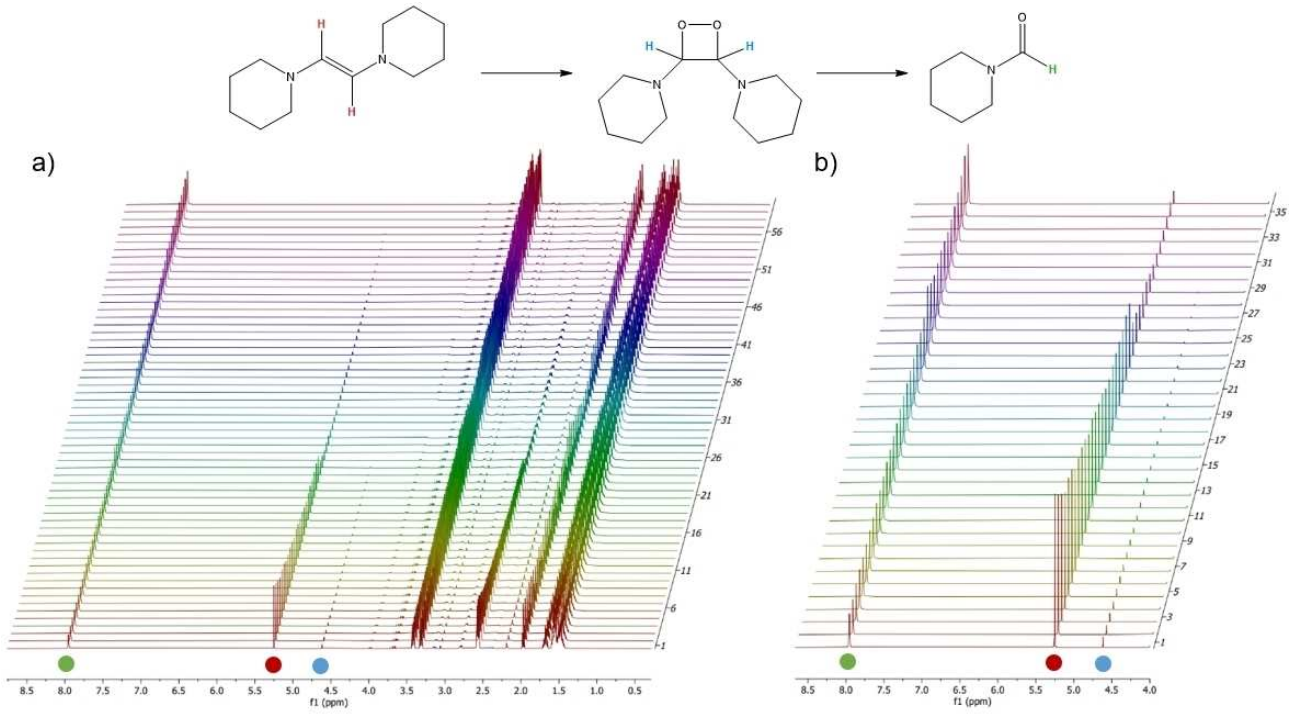


Figure 2. Reaction monitoring by ^{1}H NMR in CD_3CN over 16 h: a) full spectrum; b) characteristic region between 4.0 and 8.5 ppm. Reaction conditions: **7a** in CD_3CN, room temperature, 1 atm O_2.

Experimental Section

All experiments were performed under argon atmosphere by using standard Schlenk technique or in a glove box, if not stated otherwise. For further details, see Supporting Information.

Synthesis of intermediate 5a

Glycolaldehyde dimer **2a** (60 mg, 0.5 mmol) was suspended in MeCN (2 mL) to make an 0.5 M solution. Then **1a** (0.1 mL, 1.0 mmol) was added, and the mixture stirred at room temperature until a homogeneous solution formed. The reaction was then left without stirring at room temperature, depositing colorless crystals after 1 h. The reaction was left standing overnight and cooled to 0 °C for 1 h. The crystals were collected by filtration and washed with ice-cold MeCN, and **5a** was obtained in 51% yield. ^{1}H NMR (300 MHz, CDCl3) $\delta = 3.99$ (dd, $J = 9.6$, 2.5 Hz, 1H), 3.86–3.76 (m, 1H), 3.70 (dd, $J = 11.3$, 9.6 Hz, 1H), 2.83–2.73 (m, 2H), 2.64–2.52 (m, 2H), 1.59–1.50 (m, 4H), 1.48–1.40 (m, 2H) ppm.

Synthesis of intermediate 7a

Glycolaldehyde dimer **2a** (300 mg, 2.5 mmol) was suspended in anhydrous toluene (50 mL) under argon. The toluene was degassed by bubbling argon for 30 min, and then **1a** (1.0 mL, 10.1 mmol) was added. The reaction mixture was heated to 90 °C for 2 h. Removal of the solvent under high vacuum gave a pale-yellow crystalline residue 7a in 89% yield. This residue could be distilled under vacuum to yield a colorless oil, which crystallized to a low-melting solid at room temperature and turned yellow over the course of 1–2 days while standing at room temperature under argon. ^{1}H NMR (300 MHz, Toluene-d8) $\delta = 5.31$ (s, 2H), 2.61–2.52 (m, 8H), 1.59–1.48 (m, 8H), 1.39–1.33 (m, 4H) ppm.

General Procedure for the N-formylation of amines

In a Schlenk tube (20 mL), glycolaldehyde dimer **2a** (60 mg, 0.5 mmol) was suspended in acetonitrile (5 mL), and secondary amine **1** (2.0 mmol) was added. The reaction mixture was heated to reflux under air for 4 h. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the isolated yield of products.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: amines · formylation · glycolaldehyde · oxidation · platform chemicals

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