catalysts

MDPI

*Article*

# Efficient S-Formylation of Thiols with $CO_2$ Catalyzed by Carboxylate Salt Compounds

**Yu Chen [1], Xuan Chen [1], Huimei Wu [1], Hai-Jian Yang [1,*], Qingqing Jiang [1], Juncheng Hu [1] and Cun-Yue Guo [2,*]**

[1] Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, College of Chemistry and Materials Science, South-Central Minzu University, Wuhan 430074, China; 2023120683@mail.scuec.edu.cn (Y.C.); 2024110231@mail.scuec.edu.cn (X.C.); 2025110288@mail.scuec.edu.cn (H.W.); qqjiang@mail.scuec.edu.cn (Q.J.); jchu@mail.scuec.edu.cn (J.H.)

[2] School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 101408, China

* Correspondence: yanghj@mail.scuec.edu.cn (H.-J.Y.); cyguo@ucas.ac.cn (C.-Y.G.)

## Abstract

The formylation of mercaptans using $CO_2$ as a C1 source represents a sustainable and efficient strategy for converting $CO_2$ into value-added chemicals. However, to date, S-formylation still remains scarcely explored with $CO_2$ as the starting material, despite its important role in various biological processes. In this work, the S-formylation reaction between $CO_2$ and mercaptans was successfully carried out to construct C-S bonds using an inexpensive and commercially available carboxylate salt (sodium edetate) as the catalyst under mild conditions (25 °C and 0.1 MPa). Further investigations demonstrated that the present catalytic system applies to a broad substrate scope, affording moderate to excellent yields in the S-formylation of both aliphatic and aromatic thiols with $CO_2$. To clarify the excellent catalytic performance of carboxylates in these S-formylation reactions, reaction intermediates as well as the activating effects of carboxylates on carbon dioxide and phenylsilanes were identified through control experiments and spectroscopic analysis. Based on these findings, the reaction pathway of the S-formylation process was determined, and a corresponding reaction mechanism is proposed.

**Keywords:** carboxylate salts; $CO_2$ conversion; phenylsilane; S-formylation; thiols

## 1. Introduction

The development of synthetic methods for constructing C-S bonds under mild, inexpensive, and operationally simple reaction conditions is attracting widespread attention, due to the ubiquitous presence of sulfur in natural products, bioactive molecules, and materials [1–3]. Esterification of thiols is one of the most common and favored reactions in organic synthesis, enabling the preparation of thioester derivatives [4–7]. S-Acylation of thiols further provides an efficient and economical strategy for protecting sulfhydryl groups during multi-step synthetic processes [8,9]. Thioesters are an important class of organosulfur compounds that play a fundamental role in the construction of pharmaceuticals, biological molecules [10,11], industrial products [12–14], and natural products [15,16]. Their central role in biological processes (e.g., formyl-CoA) and industrial applications has further driven research into their synthetic methods [17,18]. Traditional thioester synthesis typically relies on the activation of carboxylic acid derivatives under strong bases (e.g., triethylamine, pyridine, and DMAP) at elevated temperatures. However, recent advances



Academic Editor: Morris D. Argyle

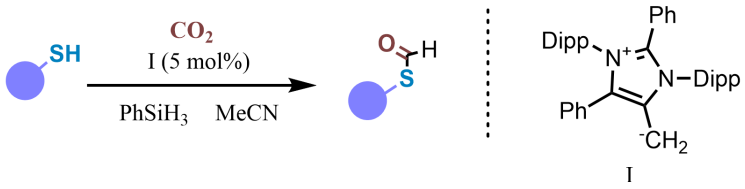
Received: 27 February 2026
Revised: 28 March 2026
Accepted: 2 April 2026
Published: 7 April 2026

have expanded the catalytic toolkit to include Lewis acids, NBS, CsF, zeolites, dodecylbenzenesulfonic acid, ionic liquids, and rongalite for the acylation of thiols [19–27]. Despite these developments, most methods still face challenges such as harsh reaction conditions, costly catalysts, or a narrow substrate scope. Consequently, the exploration of inexpensive and safe starting materials combined with efficient catalytic systems remains a significant challenge for researchers.

The concentration of greenhouse gases (GHGs) in the atmosphere is steadily rising, leading to environmental degradation phenomena such as global warming, sea-level rise, weakened thermohaline circulation, ocean acidification, and the loss of coral reefs. Ultimately, these changes are triggering climate shifts. As the most prevalent greenhouse gas, carbon dioxide ($CO_2$) accounts for 76.7% (by volume) of such emissions. Since the onset of industrialization, its concentration has increased sharply due to human activities such as deforestation, fossil fuel combustion, transportation, and land-use changes. Nowadays, $CO_2$ utilization has been successfully applied to numerous synthetic procedures [28,29], particularly in formylation reactions, where excellent results have been obtained under relatively mild conditions. However, most reported formylation methods focus on the construction of C-N bonds between amines and $CO_2$, while S-formylation remains scarcely explored [30,31], despite its important role in various biological processes [32–35].

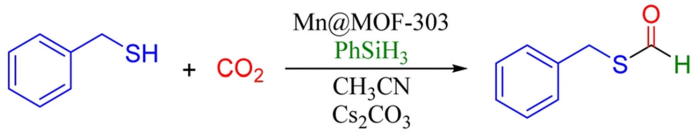
As shown in Scheme 1a, in 2024, Mandal and coworkers developed a metal-free process under ambient conditions for the S-formylation of various thiols using $CO_2$ as the C1 source [36]. In 2025, Zhao and coworkers prepared a novel Mn@MOF-303 as the catalyst for the S-formylation of benzyl thiols with $CO_2$ at room temperature. As a heterogeneous catalyst, Mn@MOF-303 exhibited highly efficient catalytic activity and excellent cycling performance (Scheme 1b) [37]. The synthesis of catalysts involved in the aforementioned S-formylation reactions is relatively complex. While EDTA (edetic acid) has been successfully employed as a catalyst for the N-formylation of amines [38], its application in the synthesis of S-formylated products remains significantly more challenging. Thiols, although reasonably effective nucleophiles, possess very low basicity. Moreover, the thioester bond (C–S bond) formed during the reaction exhibits greater susceptibility to hydrolysis and lower thermodynamic stability compared to the corresponding amide bond. In salt-catalyzed systems, most reactions generate key pentacoordinate silicon intermediates ($PhSiH_3X$), which drive nucleophilic attack of hydrides on $CO_2$. The formation of pentacoordinate high-valent silicon intermediates requires only one nucleophile ($X^-$) to activate hydrosilane. Therefore, salts containing nucleophilic anions exhibit excellent catalytic efficiency. Particularly noteworthy, carboxylates demonstrate favorable catalytic activity due to their strong nucleophilic nature [39,40], enabling both efficient adsorption of $CO_2$ and effective activation of hydrosilane, thereby significantly promoting the S-formylation of thiols with $CO_2$ (Scheme 1c).

(a) Mesoionic N-heterocyclic olefin-catalyzed S-formylation

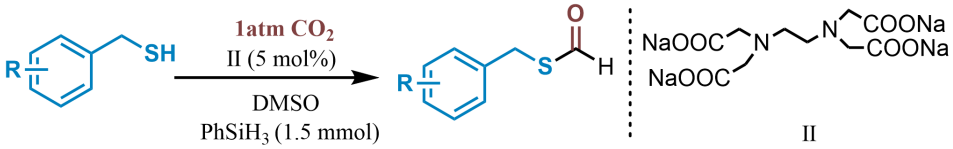



I

(b) The synthesis of S-formyl aryl thiols via MOF material-catalyzed S-formylation




(c) Carboxylate-catalyzed synthesis of S-formylation (this work)




II

**Scheme 1.** Methods of S-formylation [36,37].

## 2. Results

### *2.1. Optimization of Reaction Conditions*

As summarized in Table 1, no reaction occurred in the absence of a catalyst, confirming that a catalyst is essential for the S-formylation process (entry 1). Upon addition of $Na_4EDTA$, the desired product was obtained in 89% yield (entry 2). When EDTA (edetic acid) or DTPA (pentetic acid), which lacks metal ion exchange capability, were employed as catalysts, the reaction was significantly suppressed due to their reduced nucleophilicity (entries 3, 4) [41]. Further screening of organic bases revealed that DBU, a strong base, afforded a moderate yield of 74% (entry 5), whereas N-butyldiethanolamine (BDEA) proved ineffective, yielding only trace amounts of the product (entry 6). It should be noted that increasing the $CO_2$ pressure from 0.1 MPa to 2 MPa resulted in a yield of 71% yield with $Na_4EDTA$ as the catalyst (entry 7). The reduced yield of **2a** is likely attributable to the high $CO_2$ pressure, which diluted the interaction between 1a and the $Na_4EDTA$ catalyst. This dilution effect lowered the local concentration of 1a near the active sites [42]. This trend is further supported by the yields obtained under other $CO_2$ pressures, as detailed in Table S1. Control experiments showed that the reaction could not proceed in the absence of phenylsilane as a reducing agent (entry 8). When other silanes such as $Ph_2SiH_2$ or $Ph_3SiH$ were used, lower conversion rates were obtained (entries 9, 10). Further substitution with $Me_2PhSiH$, $(EtO)_3SiH$, or PMHS as the hydrogen source afforded only trace amounts of the thioester (entries 11–13) [43,44].

As shown in Table 2, the reaction failed to proceed under solvent-free conditions (Table 2, entry 1). Polar aprotic solvents demonstrated superior performance, with DMSO, DMF, and DMAC affording product yields of 89%, 69%, and 72%, respectively (Table 2, entries 2, 5, 6) [45–47]. Low-polarity solvents (THF, $CH_3CN$) provided only trace yields (Table 2, entries 3, 4). Notably, strongly polar protic solvents (MeOH, $H_2O$) completely suppressed product formation (Table 2, entries 7, 8) [48]. This inhibition is attributed to the acidic environment generated by the dissolution of $CO_2$ in $H_2O$, which hinders the S-formylation reaction [49]. After adding a small amount of dimethyl sulfoxide (1 mL) to acetonitrile, the product yield was significantly enhanced. Polar solvents that effec-

tively dissolve both the catalyst $Na_4EDTA$ and the reactant $CO_2$ simultaneously create a homogeneous environment with optimal reactant concentrations. The reaction exhibited temperature dependence, with yield decreasing at elevated temperatures (Table 2, entries 10, 11). This decrease is likely attributable to the limited solubility of $Na_4EDTA$ in DMSO at elevated temperatures, which leads to increased viscosity and catalyst aggregation [50]. As the reaction time was extended, the yield of 2a gradually increased (Table 2, entries 12–15). When the reaction time was extended to 48 h, a decrease in yield was observed (Table 2, entry 15 vs. entry 2). The slight drop in yield after 48 h is attributed to the over-reduction of the silyl formate intermediate over extended reaction times, which generates trace S-methylated byproducts and reduces the target product yield (Figure S1).

**Table 1.** Optimal reaction conditions for S-formylation catalysts and reducing agents [a,b].

| Entry | Catalyst | Hydrosilane | Yield (%) |
|---|---|---|---|
| 1 | None | $PhSiH_3$ | - |
| 2 | $Na_4EDTA$ | $PhSiH_3$ | 89% |
| 3 | EDTA | $PhSiH_3$ | 2% |
| 4 | DTPA | $PhSiH_3$ | 2% |
| 5 | DBU | $PhSiH_3$ | 74% |
| 6 | BDEA | $PhSiH_3$ | trace |
| 7 [c] | $Na_4EDTA$ | $PhSiH_3$ | 71% |
| 8 | $Na_4EDTA$ | None | - |
| 9 | $Na_4EDTA$ | $Ph_2SiH_2$ | 76% |
| 10 | $Na_4EDTA$ | $Ph_3SiH$ | trace |
| 11 | $Na_4EDTA$ | $Me_2PhSiH$ | 24% |
| 12 | $Na_4EDTA$ | $(EtO)_3SiH$ | trace |
| 13 | $Na_4EDTA$ | PMHS | - |

[a] Reaction conditions: thiol **1a** (1 mmol), $Na_4EDTA$ (5 mol%), DMSO (1 mL), hydrosilane. (1.5 mmol), temperature: 25 °C, $CO_2$ pressure: 0.1 MPa, time: 24 h. [b] The yields of the products were determined by $^1H$ NMR spectroscopy using TMS as an internal standard. [c] $CO_2$ (2 MPa).

**Table 2.** Optimal reaction conditions of solvent, time and temperature for S-formylation reaction [a,b].

| Entry | *T* (°C) | Time (h) | Solvent | Yield (%) |
|---|---|---|---|---|
| 1 | 25 | 24 | None | - |
| 2 | 25 | 24 | DMSO | 89% |
| 3 | 25 | 24 | THF | trace |
| 4 | 25 | 24 | $CH_3CN$ | 5.6% |
| 5 | 25 | 24 | DMF | 69% |
| 6 | 25 | 24 | DMAC | 72% |
| 7 | 25 | 24 | MeOH | - |
| 8 | 25 | 24 | $H_2O$ | - |
| 9 [c] | 25 | 24 | $CH_3CN$:DMSO (4:1) | 81% |
| 10 | 40 | 24 | DMSO | 12% |
| 11 | 60 | 24 | DMSO | trace |
| 12 | 25 | 4 | DMSO | 33% |
| 13 | 25 | 12 | DMSO | 52% |
| 14 | 25 | 18 | DMSO | 61% |
| 15 | 25 | 48 | DMSO | 75% |

[a] Reaction conditions: thiol **1a** (1 mmol), $Na_4EDTA$ (5 mol%), Solvent (1 mL), $PhSiH_3$. (1.5 mmol), temperature: 25 °C, $CO_2$ pressure: 0.1 MPa, time: 24 h. [b] The yields of the products were determined by $^1H$ NMR spectroscopy using TMS as an internal standard. [c] 0. 8 mL $CH_3CN$ and 0.2 mL DMSO.

### *2.2. S-Formylation of Benzyl Thiols with $CO_2$ Catalyzed by Sodium Edetate*

With benzyl mercaptan derivatives, ortho-substituted methyl groups afforded a high yield (86%, **4b**), compared to meta- (81%, **4c**) and para-substituted (78%, **4d**) analogs.

Notably, electron-donating methoxy substitution enhanced reactivity, achieving 91% yield (**4e**). Conversely, electron-withdrawing groups (−F, −Cl, $-NO_2$) substantially decreased yields (**4f**–**4h**). Subsequently, when using heteroaryl mercaptans as substrates, such as 2-furylmethanethiol and 2-methyl-3-furylthiol (**4i**,**4j**), the corresponding S-(furan-2-ylmethyl) methanethioate can be produced in 67% yield in our reaction scheme. When the methyl group is located at the ortho position of the furan, increased steric hindrance results in only trace yields of the final S-formylated product, The furan ring is an aromatic heterocycle with electron-rich properties, and its oxygen atom can influence the electron density at the reaction site through electron-withdrawing conjugation effects. Compared to the phenyl group, the introduction of a furan moiety may reduce the nucleophilicity of the thiol, thereby weakening its ability to attack the reaction intermediates (Figure 1).

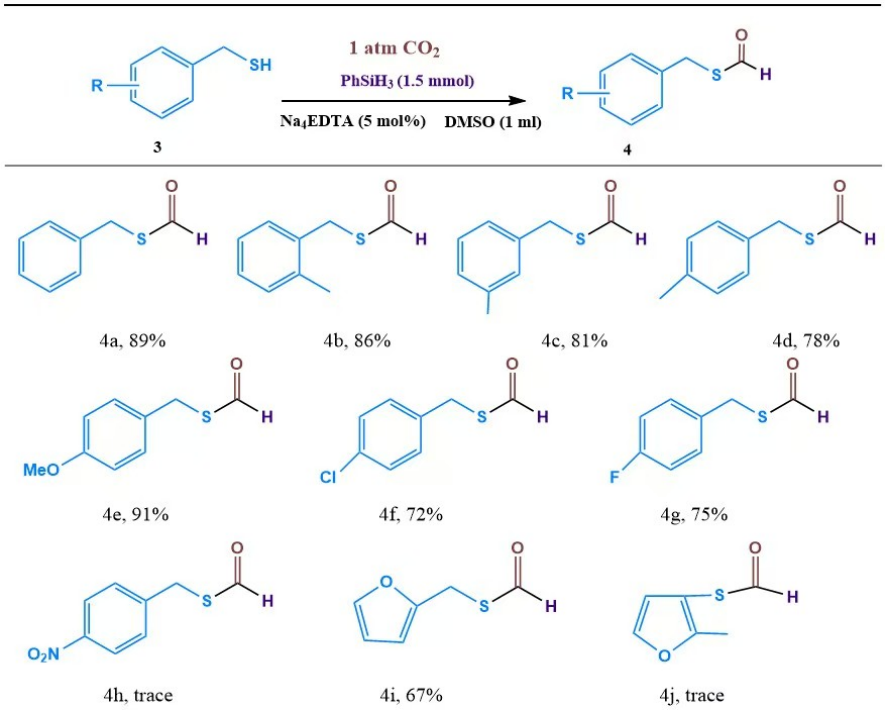



**Figure 1.** S-formylation of benzyl thiols with $CO_2$ [a,b]. [a] Reaction conditions: thiol **1a** (1 mmol), $Na_4EDTA$ (5 mol%), DMSO (1 mL), $CO_2$ (0.1 MPa), $PhSiH_3$ (1.5 mmol), 25 °C, 24 h. [b] The yields of the products were determined by $^1H$ NMR spectroscopy using TMS as an internal standard. All products are known compounds [36,37], and their yields were determined by NMR spectroscopy without further purification.

### *2.3. S-Formylation of Aliphatic Thiols with $CO_2$ Catalyzed by Sodium Edetate*

Linear and branched aliphatic thiols (isobutyl, butyl, and isoamyl mercaptans, **6a**–**6c**) afforded moderate to good yields (63–83%). However, as the alkyl carbon chain length increased, the product yield decreased [51]. 3-methyl-2-butanethiol and tert-butanethiol gave substantially lower yields (48% and 7%, respectively) after 24 h. After extending the reaction time to 48 h, the formylation yield of 3-methyl-2-butanethiol was increased to 53%, but there was no enhancement in the formylation yield of tert-butanethiol (**6d**,**6e**) (Figure 2).

Dithiols like 1,3-propanedithiol afforded both mono- and di-S-formylated products in 27% and 48% yield, respectively (**6f**). Linear thiols with a bulky terminal group, exemplified by 2-phenylethanethiol and 2-pyrazinylethanethiol, also underwent S-formylation, yielding the corresponding products in 39% and 19% yield [52]. Under the optimized conditions, cyclohexanethiol and 2-methyl-3-tetrahydrofuranethiol were also reactive, with the latter giving a 69% yield (**6i**–**6j**).

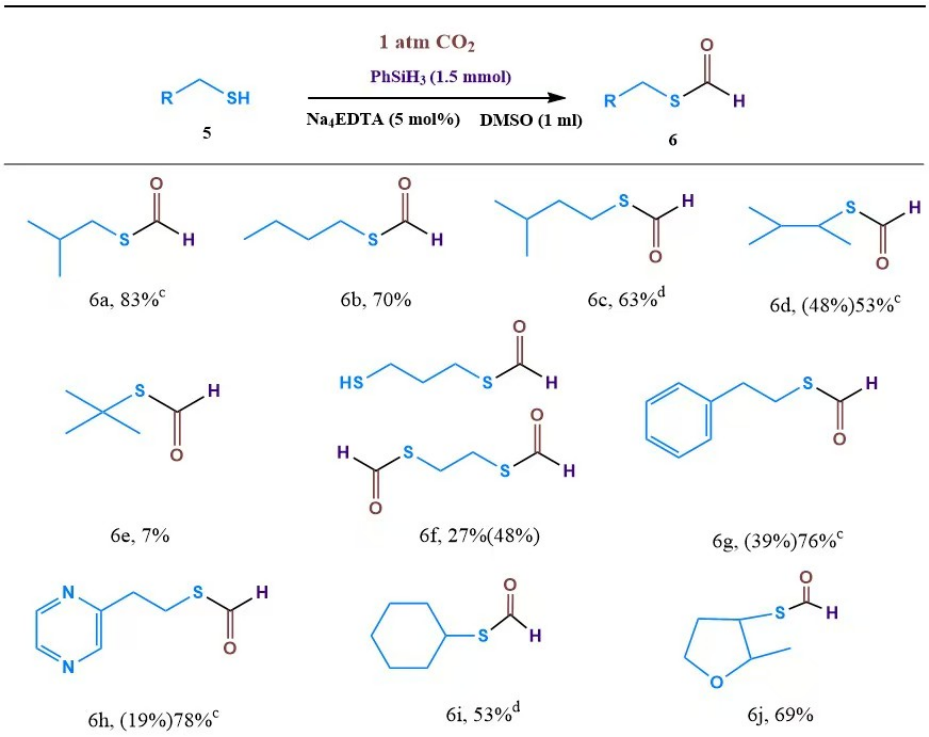



**Figure 2.** S-formylation of aliphatic linear thiols and aliphatic cyclic thiols with $CO_2$ [a,b]. [a] Reaction conditions: thiol **1a** (1 mmol), $Na_4EDTA$ (5 mol%), DMSO (1 mL), $CO_2$ (0.1 MPa), $PhSiH_3$ (1.5 mmol), 25 °C, 24 h. [b] The yields of the products were determined by $^1H$ NMR spectroscopy using TMS as an internal standard. [c] 48 h. [d] 35 °C. All products are known compounds [36], and their yields were determined by NMR spectroscopy without further purification.

### *2.4. Mechanistic Study of the S-Formylation Reaction of Thiols Catalyzed by Ethylene Diaminetetra Acetic Acid Tetrasodium Salt*

To elucidate the reaction mechanism, we performed a series of control experiments. When $N_2$ was substituted for $CO_2$ under identical conditions, no thiocarbonate product was detected by spectroscopic analysis after 24 h (Figure 3a). This confirms that $CO_2$ is indispensable as the exclusive carbon source for the S-formylation reaction. In situ $^1H$ NMR analysis of the reaction mixture revealed a distinct singlet signal at $\delta = 8.17$ ppm. This chemical shift is consistent with the formyl proton of a silyl formate intermediate, thereby directly capturing and confirming the formation of this key reactive species (Figures 3b, 4 and S2). The detected silyl formate species is consistent with the key intermediate proposed by Mandal et al. [36] in their metal-free system and by Zhao et al. [37] in their Mn@MOF-303 catalytic cycle.

To probe the catalytic activation pathway, we systematically examined the interactions between the catalyst ($Na_4EDTA$), phenylsilane, and $CO_2$. Reaction of $Na_4EDTA$ with $PhSiH_3$ for 12 h induced a detectable downfield shift in the Si–H bond resonance ($^1H$ NMR, Figure 5), confirming nucleophilic activation of phenylsilane by the carboxylate moiety. In our previous study on the N-formylation reaction catalyzed by alkanolamine (MDEA), MDEA first reacts with $CO_2$ to generate a zwitterionic intermediate, which then activates the silane to form a pentacoordinate silicon species, ultimately leading to the formation of silyl formate [29]. In contrast, the present study reveals that the carboxylate anion itself possesses sufficient nucleophilicity to directly activate phenylsilane and generate a pentacoordinate silicon species without the need for prior coordination with $CO_2$, which subsequently converts to silyl formate.

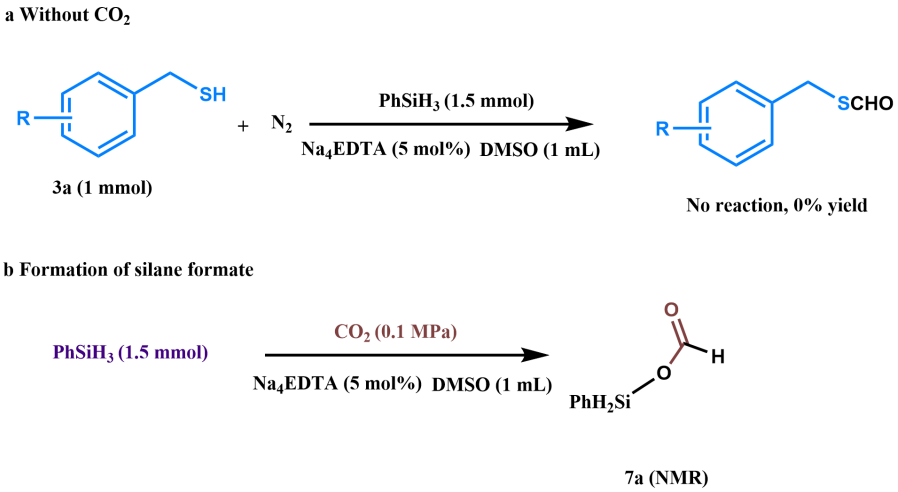



**Figure 3.** Step-by-step experiment of S-formylation reaction. (**a**) S-formylation reaction in $N_2$ (without $CO_2$). (**b**) Formation of silane formate.

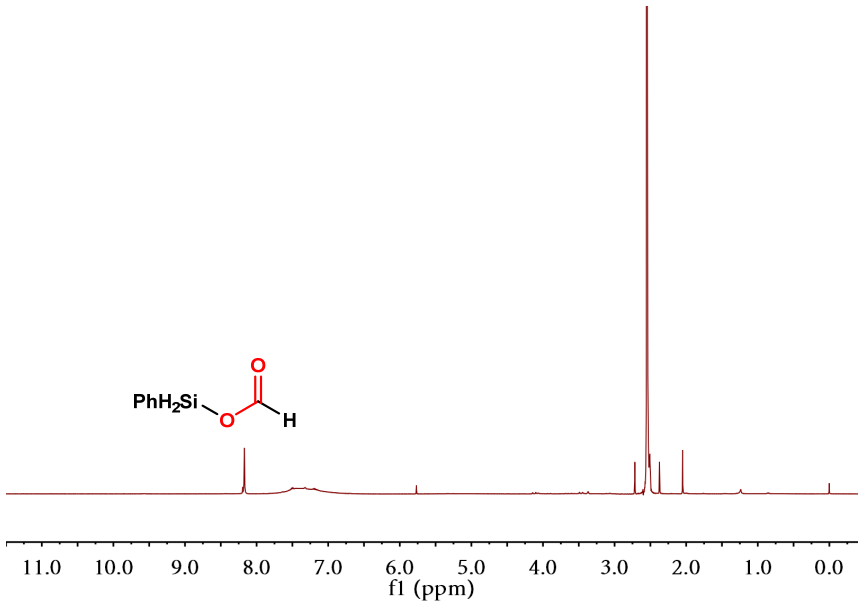



**Figure 4.** Si-H $^1$H NMR spectra of the formyl proton signal of the silyl formate intermediate.

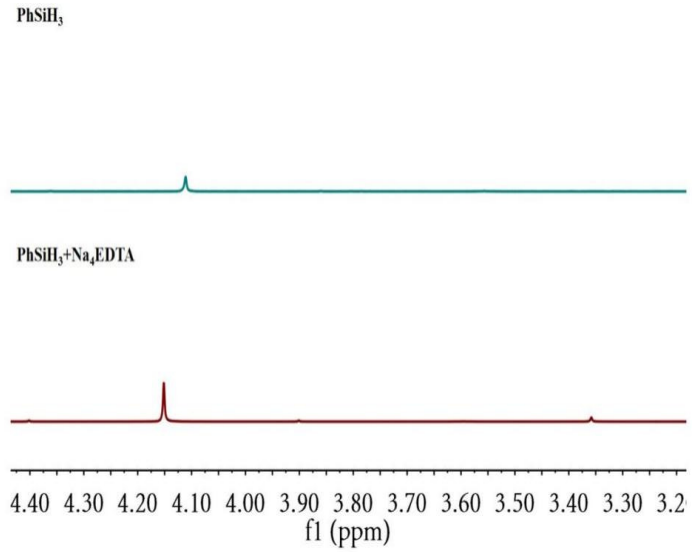



**Figure 5.** $^1$H NMR spectra of phenylsilane and phenylsilane/sodium edetate mixtures.

FT-IR analysis of the $Na_4EDTA/CO_2$ system revealed two diagnostic absorptions at 1646 $cm^{-1}$ and 1335 $cm^{-1}$ after 12 h (Figure 6), attributed to the asymmetric stretching vibration formed by the interaction between carbon dioxide and $Na_4EDTA$ [53,54].

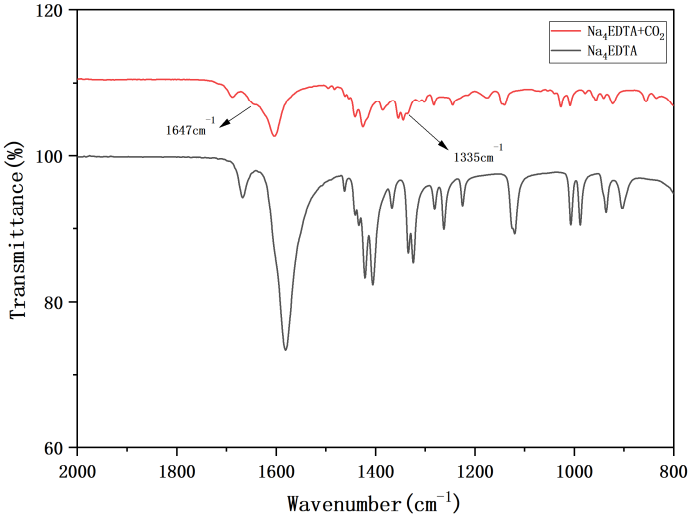
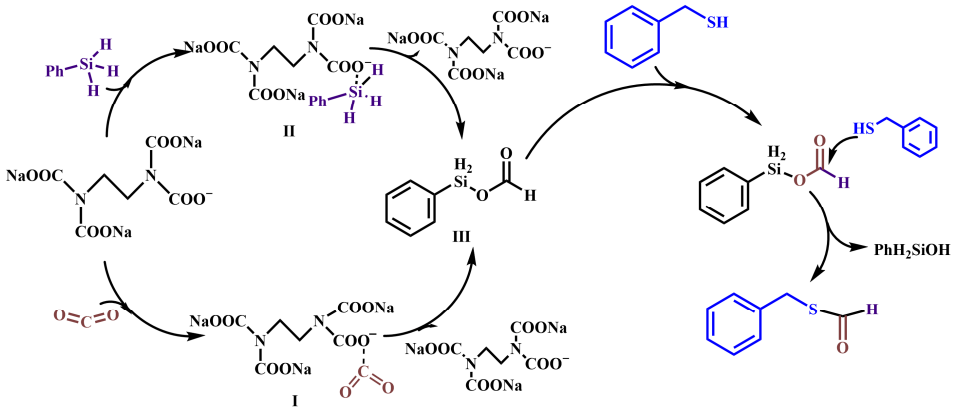



**Figure 6.** FT-IR spectra of $CO_2$ and $CO_2/Na_4EDTA$ mixtures.

As depicted in Scheme 2, the proposed mechanism begins with the dual activation of carbon dioxide and phenylsilane by the same carboxylate unit: the carboxylate moiety first activates $CO_2$ to generate intermediate I, while its nucleophilic oxygen anion concurrently activates phenylsilane to form the more reactive pentavalent silicon species II. Subsequent proton migration (H-transfer) within intermediate II facilitates the insertion of $CO_2$ into the Si–H bond, generating the key silyl formate intermediate III while regenerating the carboxylate catalyst. Finally, nucleophilic attack of the thiol substrate on intermediate III results in C–O bond cleavage, selectively affording the S-formylated product and completing the catalytic cycle.




**Scheme 2.** Mechanism of S-formylation of $CO_2$ with thiols catalyzed by sodium edetate.

## 3. Materials and Methods

### *3.1. Chemicals and Analytical Methods*

All thiol chemicals used were purchased from Aladdin (Shanghai, China) and used directly, while some solvents and chemicals were sourced from Bellingway (Beijing, China) and Macklin (Shanghai, China). NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer (Bruker Corporation, Billerica, MA, USA) using tetramethylsilane (TMS) as an internal standard. The data were processed using TopSpin 4.1.4 (Bruker).

Infrared spectra were recorded on a PerkinElmer 2000 FT-IR spectrometer (PerkinElmer, Inc., Waltham, MA, USA). The IR data were analyzed using Spectrum software (version 10.5.2, PerkinElmer).

### *3.2. Experiment Procedure*

**High-pressure experimental procedure:** A clean and dry 50 mL high-pressure autoclave was purged three times with $CO_2$ gas. Under a protective $CO_2$ atmosphere, precise quantities of the catalyst, thiol, and hydrosilane were added to the autoclave. The sealed autoclave equipped with a stirrer was then placed in an oil bath at the set temperature. After 30 min, $CO_2$ gas was introduced into the autoclave to reach the specified pressure, and stirring was initiated. The reaction was terminated upon reaching the predetermined time, and the autoclave was immersed in ice water to slowly release the gas. Finally, a small aliquot of the reaction mixture was directly taken for NMR analysis to determine the yield of the S-formylated product.

**Atmospheric pressure experimental procedure:** An appropriate amount of solid catalyst was added to a 75 mL Schlenk flask. The apparatus was sealed and subjected to three cycles of vacuum purging under a nitrogen atmosphere. After evacuation, the Schlenk flask was maintained under vacuum, and a $CO_2$ balloon was connected to fill the flask with carbon dioxide. The solvent was then injected into the flask using a syringe. If the hydrosilane and thiol were solids at room temperature, they were added along with the catalyst prior to the nitrogen purging and evacuation. If they were liquids at room temperature, they were injected into the flask together with the solvent via syringe after the nitrogen purging and evacuation. Subsequently, the reaction vessel was resealed. The prepared Schlenk flask was preheated in a constant-temperature oil bath for 20 min to initiate the reaction, which was terminated upon reaching the predetermined reaction time.

IHa denotes the signal peak area integral of Ha for the reactant thiol in $^1$H NMR spectra, and IHb denotes the signal peak area integral of Hb for the formyl group of the product in $^1$H NMR spectra (Figure 7).

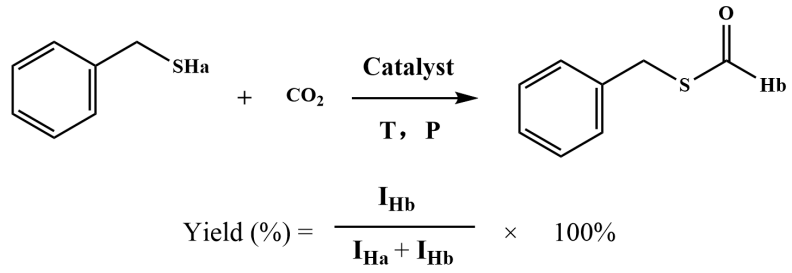



**Figure 7.** Determination of the yield of S-formylation products.

## 4. Conclusions

Although S-formylation plays a crucial role in various pharmaceutical and biological processes, its synthetic utilization remains underdeveloped. Herein, we report a mild and efficient carboxylate-catalyzed S-formylation of diverse thiols with $CO_2$. This protocol is applicable to both benzyl mercaptans and aliphatic thiols (including mono- and dithiols), enabling their catalytic reductive transformation with $CO_2$ into the corresponding S-formylated products. Controlled experiments, supported by spectroscopic analysis, identified key intermediates and verified that the carboxylate catalyst activates both $CO_2$ and phenylsilane. Based on these findings, a plausible reaction mechanism is proposed.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal16040334/s1, Figure S1: $^1$H NMR spectrum of S-methylated

product; Figure S2: $^1$H NMR spectra of a mixture of silicone formate; Figures S3–S8: $^1$H NMR spectrum of S-formylation; Table S1: Yields at different $CO_2$ loadings; Table S2: Effect of $Na_4EDTA$ and $PhSiH_3$ loading on the reaction outcome; Table S3: Advantages of the $Na_4EDTA$ Catalytic System [36,37,44,55].

**Author Contributions:** Y.C.: Formal analysis, Resources, Validation, Writing—original draft. X.C.: Data curation. H.W.: Methodology. H.-J.Y.: Conceptualization, Funding acquisition, Project administration, Validation, Writing—review and editing. Q.J.: Software, Visualization. J.H.: Investigation. C.-Y.G.: Conceptualization, Project administration, Validation. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (grant number 51073175) and the Fund for Academic Innovation Teams of South-Central Minzu University (No. XTZ24016).

**Data Availability Statement:** Experimental data and materials used in this study are available upon reasonable request from the corresponding author.

**Acknowledgments:** We acknowledge the technical support provided by the Colledge of Chemistry and Materials Science at South-Central Minzu University in characterization testing.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Fontecave, M.; Ollagnier-de-Choudens, S.; Mulliez, E. Biological radical sulfur insertion reactions. *Chem. Rev.* **2003**, *103*, 2149–2166. [CrossRef] [PubMed]
2. Schaumann, E. Sulfur is more than the fat brother of oxygen. An overview of organosulfur chemistry. *Sulfur-Mediat. Rearrange. I* **2007**, *1*, 1–34.
3. Agnieszka, L.; Christian, H. Enzymatic carbon–sulfur bond formation in natural product biosynthesis. *Chem. Rev.* **2017**, *117*, 5521–5577. [CrossRef] [PubMed]
4. Kim, S.; Yang, S. A facile preparation of thiol esters from carboxylic acids and thiols. *Chem. Lett.* **1981**, *10*, 133–134. [CrossRef]
5. Liu, H.J.; Sabesan, S.I. Direct transformation of carboxylic acids to thiol esters induced by phenyl dichlorophosphate. *Can. J. Chem.* **1980**, *58*, 2645–2648. [CrossRef]
6. Liebeskind, L.S.; Yang, H.; Li, H. A copper-catalyzed, pH-neutral construction of high-enantiopurity peptidyl ketones from peptidic S-acylthiosalicylamides in air at room temperature. *Angew. Chem. Int. Ed.* **2009**, *121*, 1445–1449. [CrossRef]
7. Wakasugi, K.; Iida, A.; Misaki, T. Simple, Mild, and Practical esterification, Thioesterification, and amide formation utilizing *p*-toluenesulfonyl chloride and N-methylimidazole. *Adv. Synth. Catal.* **2003**, *345*, 1209–1214. [CrossRef]
8. Fowelin, C.; Schüpbach, B.; Terfort, A. Aromatic thioesters as protecting groups for thiols against 1,2-didehydrobenzenes. *Eur. J. Org. Chem.* **2007**, *6*, 1013–1017. [CrossRef]
9. Goux, C.; Lhoste, P.; Sinou, D. Palladium (O)-catalyzed alkylation of thiols. *Tetrahedron* **1994**, *50*, 10321–10330. [CrossRef]
10. Bar-Even, A. Formate assimilation: The metabolic architecture of natural and synthetic pathways. *Biochemistry* **2016**, *55*, 3851–3863. [CrossRef] [PubMed]
11. Ilardi, E.A.; Vitaku, E.; Njardarson, J.T. Data-mining for sulfur and fluorine: An evaluation of pharmaceuticals to reveal opportunities for drug design and discovery: Miniperspective. *J. Med. Chem.* **2014**, *57*, 2832–2842. [CrossRef] [PubMed]
12. Liu, X.L.; Shi, Y.; Kang, J.S. Amino acid thioester derivatives: A highly promising scaffold for the development of metallo-β-lactamase L1 inhibitors. *ACS Med. Chem. Lett.* **2015**, *6*, 660–664. [CrossRef]
13. Modha, S.G.; Mehta, V.P.; Van der Eycken, E.V. Transition metal-catalyzed C–C bond formation via C–S bond cleavage: An overview. *Chem. Soc. Rev.* **2013**, *42*, 5042–5055. [CrossRef] [PubMed]
14. Denes, F.; Schiesser, C.H.; Renaud, P. Thiols, thioethers, and related compounds as sources of C-centred radicals. *Chem. Soc. Rev.* **2013**, *42*, 7900–7942. [CrossRef] [PubMed]
15. Ozaki, S.; Adachi, M.; Sekiya, S. Cyclization of aryl acyl radicals generated from S-(4-cyano) phenyl thiolesters by a nickel complex catalyzed electroreduction. *J. Org. Chem.* **2003**, *68*, 4586–4589. [CrossRef]
16. Shimizu, T.; Seki, M. A novel synthesis of functionalized ketones via a nickel-catalyzed coupling reaction of zinc reagents with thiolesters. *Tetrahedron Lett.* **2002**, *43*, 1039–1042. [CrossRef]
17. Kullin, B.; Tannock, G.W.; Loach, D.M. A functional analysis of the formyl-coenzyme A (frc) gene from *Lactobacillus reuteri* 100-23C. *J. Appl. Microbiol.* **2014**, *116*, 1657–1667. [CrossRef]

18. Katritzky, A.R.; Shestopalov, A.A.; Suzuki, K. A new convenient preparation of thiol esters utilizing N-acylbenzotriazoles. *Synthesis* **2004**, *11*, 1806–1813. [CrossRef]
19. Kawakami, J.; Mihara, M.; Kamiya, I. Platinum-catalyzed highly selective thiocarbonylation of acetylenes with thiols and carbon monoxide. *Tetrahedron* **2003**, *59*, 3521–3526. [CrossRef]
20. Mapp, A.K.; Dervan, P.B. Preparation of thioesters for the ligation of peptides with non-native substrates. *Tetrahedron Lett.* **2000**, *41*, 9451–9454. [CrossRef]
21. Romanelli, G.P.; Bennardi, D.O.; Autino, J.C. A simple and mild acylation of alcohols, phenols, amines, and thiols with a reusable heteropoly acid catalyst ($H_6P_2W_{18}O_{62}\cdot 24H_2O$). *J. Chem.* **2008**, *5*, 641–647. [CrossRef]
22. Iranpoor, N.; Firouzabadi, H.; Khalili, D. Easily prepared azopyridines as potent and recyclable reagents for facile esterification reactions. An efficient modified Mitsunobu reaction. *J. Org. Chem.* **2008**, *73*, 4882–4887. [CrossRef]
23. Weingärtner, H. Understanding ionic liquids at the molecular level: Facts, problems, and controversies. *Angew. Chem. Int. Ed.* **2008**, *47*, 654–670. [CrossRef]
24. Lee, J.W.; Shin, J.Y.; Chun, Y.S. Toward understanding the origin of positive effects of ionic liquids on catalysis: Formation of more reactive catalysts and stabilization of reactive intermediates and transition states in ionic liquids. *Acc. Chem. Res.* **2010**, *43*, 985–994. [CrossRef] [PubMed]
25. Kochetkov, S.V.; Kucherenko, A.S.; Kryshtal, G.V. Simple ionic liquid supported C2-symmetric bisprolinamides as recoverable organocatalysts for the asymmetric aldol reaction in the presence of water. *Eur. J. Org. Chem.* **2012**, *36*, 7129–7134. [CrossRef]
26. Xi, Z.; Hao, W.; Wang, P. Ruthenium (III) chloride catalyzed acylation of alcohols, phenols, and thiols in room temperature ionic liquids. *Molecules* **2009**, *14*, 3528–3537. [CrossRef] [PubMed]
27. Gotor-Fernández, V.; Busto, E.; Gotor, V. Candida antarctica lipase B: An ideal biocatalyst for the preparation of nitrogenated organic compounds. *Adv. Synth. Catal.* **2006**, *348*, 797–812. [CrossRef]
28. Li, Y.; Wang, Y.; Zhang, L. Iridium-catalyzed hydrocarboxylation of olefins with $CO_2$ and $H_2$. *Molecules* **2025**, *30*, 1599. [CrossRef]
29. Wen, Q.; Yuan, X.; Zhou, Q.; Yang, H.J.; Jiang, Q.; Hu, J.; Guo, C.Y. Efficient N-formylation of carbon dioxide and amines with alkanolamine as eco-friendly catalyst under mild conditions. *J. $CO_2$ Util.* **2023**, *69*, 102398. [CrossRef]
30. Ping, R.; Zhao, P.; Zhang, Q. Catalytic conversion of $CO_2$ from simulated flue gases with aminophenol-based protic ionic liquids to produce quinazoline-2,4(1H,3H)-diones under mild conditions. *ACS Sustain. Chem. Eng.* **2021**, *9*, 5240–5249. [CrossRef]
31. Liu, F.; Ping, R.; Gu, Y. Efficient one pot capture and conversion of $CO_2$ into quinazoline-2,4(1H,3H)-diones using triazolium-based ionic liquids. *ACS Sustain. Chem. Eng.* **2020**, *8*, 2910–2918. [CrossRef]
32. Zhu, K.; Li, Y.; Li, Z. In situ activation of COOH-functionalized ZIF-90-enabled reductive $CO_2$ N-formylation. *Chem. Commun.* **2022**, *58*, 12712–12715. [CrossRef] [PubMed]
33. Rahman, M.M.; Dutta, I.; Gholap, S.S. Ruthenium catalyzed additive-free N-Formylation of amines with $CO_2$ and $H_2$: Exploring carbon neutral hydrogen Cycle. *ChemCatChem* **2024**, *16*, e202401202. [CrossRef]
34. Mullins, E.A.; Starks, C.M.; Francois, J.A. Formyl-coenzyme A (CoA): Oxalate CoA-transferase from the acidophile *Acetobacter aceti* has a distinctive electrostatic surface and inherent acid stability. *Protein Sci.* **2012**, *21*, 686–696. [CrossRef]
35. Legler, P.M.; Kumaran, D.; Swaminathan, S. Structural characterization and reversal of the natural organophosphate resistance of a D-type esterase, *Saccharomyces cerevisiae S*-formylglutathione hydrolase. *Biochemistry* **2008**, *47*, 9592–9601. [CrossRef]
36. Maji, S.; Das, A.; Bhatt, M.M. Metal-free organocatalytic S-formylation of thiols using $CO_2$. *Nat. Catal.* **2024**, *7*, 375–385. [CrossRef]
37. Liu, Y.S.; Wang, Z.Q.; Zhang, Y.P. A novel Mn@MOF-303 as a catalyst for the highly efficient *S*-formylation of benzyl thiols with $CO_2$. *Chem. Commun.* **2025**, *61*, 4678–4681. [CrossRef]
38. Zhou, Q.Q.; Chen, Y.; Yuan, X.X.; Yang, H.J. N-Formylation of carbon dioxide and amines with EDTA as a recyclable catalyst under ambient conditions. *Catalysts* **2024**, *14*, 492. [CrossRef]
39. Liu, X.F.; Li, X.Y.; Qiao, C. Betaine catalysis for hierarchical reduction of $CO_2$ with amines and hydrosilane to form formamides, aminals, and methylamines. *Angew. Chem. Int. Ed.* **2017**, *56*, 7425–7429. [CrossRef]
40. Zhang, C.; Lu, Y.; Zhao, R. A comparative DFT study of TBD-catalyzed reactions of amines with $CO_2$ and hydrosilane: The effect of solvent polarity on the mechanistic preference and the origins of chemoselectivities. *Chem. Commun.* **2018**, *54*, 10870–10873. [CrossRef]
41. Hulla, M.; Chamam, S.M.A.; Laurenczy, G. Delineating the mechanism of ionic liquids in the synthesis of quinazoline-2, 4 (1H, 3H)-dione from 2-aminobenzonitrile and $CO_2$. *Angew Chem.* **2017**, *56*, 10559–10563. [CrossRef]
42. Prasad, D.; Patil, K.N.; Bhanushali, J.T. Sustainable fixation of $CO_2$ into epoxides to form cyclic carbonates using hollow marigold $CuCO_2O_4$ spinel microspheres as a robust catalyst. *Catal. Sci. Technol.* **2019**, *9*, 4393–4412. [CrossRef]
43. Nicholls, R.L.; McManus, J.A.; Rayner, C.M. Guanidine-catalyzed reductive amination of carbon dioxide with silanes: Switching between pathways and suppressing catalyst deactivation. *ACS Catal.* **2018**, *8*, 3678–3687. [CrossRef]
44. Xie, C.; Song, J.; Wu, H. Natural product glycine betaine as an efficient catalyst for transformation of $CO_2$ with amines to synthesize N-substituted compounds. *ACS Sustain. Chem. Eng.* **2017**, *5*, 7086–7092. [CrossRef]

45. Xie, W.; Zhao, M.; Cui, C. Cesium carbonate-catalyzed reduction of amides with hydrosilanes. *Organometallics* **2013**, *32*, 7440–7444. [CrossRef]
46. Wang, X.; Yan, H.; Liang, X. Schiff base-mediated dual active site catalyst for efficient N-formylation of amines with $CO_2$. *J. Phys. Chem. Lett.* **2025**, *16*, 468–474. [CrossRef] [PubMed]
47. Lv, H.; Xing, Q.; Yue, C. Solvent-promoted catalyst-free N-formylation of amines using carbon dioxide under ambient conditions. *Chem. Commun.* **2016**, *52*, 6545–6548. [CrossRef]
48. Withnall, R.; Andrews, L. Matrix reactions of silane and oxygen atoms. Infrared spectroscopic evidence for the silanol, silanone, and silanoic and silicic acid molecules. *J. Phys. Chem. Lett.* **1985**, *89*, 3261–3268. [CrossRef]
49. Kang, X.; Wang, Z.; Shi, X. Effective reduction of $CO_2$ with aromatic amines into N-formamides triggered by noble-rree metal–organic framework catalysts under mild conditions. *Small* **2024**, *20*, 2311511. [CrossRef]
50. Tartari, T.; Borges, M.M.B.; Araújo, L.B.B. Effects of heat in the properties of NaOCl alone and mixed with etidronate and alkaline tetrasodium EDTA. *Int. Endod. J.* **2021**, *54*, 616–627. [CrossRef]
51. Fang, J.; Wang, Z.Q.; Wei, X. N-Formylation of amines with carbon dioxide and hydrogen catalyzed by ionic liquid-assisted Ru complexes. *ACS Sustain. Chem. Eng.* **2021**, *9*, 13256–13267. [CrossRef]
52. Luo, R.; Lin, X.; Chen, Y. Cooperative catalytic activation of Si–H bonds: $CO_2$-based synthesis of formamides from amines and hydrosilanes under mild conditions. *ChemSusChem* **2017**, *10*, 1224–1232. [CrossRef] [PubMed]
53. Zhu, X.; Chen, C.; Wang, Q. Roles for $K_2CO_3$ doping on elevated temperature $CO_2$ adsorption of potassium promoted layered double oxides. *Chem. Eng. J.* **2019**, *366*, 181–191. [CrossRef]
54. Zhao, W.; Li, H.; Li, Y. Low-cost acetate-catalyzed efficient synthesis of benzimidazoles using ambient $CO_2$ as a carbon source under mild conditions. *Sustain. Chem. Pharm.* **2020**, *17*, 100276. [CrossRef]
55. Zhao, W.; Chi, X.; Li, H. Eco-friendly acetylcholine-carboxylate bio-ionic liquids for controllable N-methylation and N-formylation using ambient $CO_2$ at low temperatures. *Green Chem.* **2019**, *21*, 567–577.