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Synthesis of Aromatic Aldehydes by C—H Formylation of Aromatics with Silyl Formates Prepared from CO_2 and Hydrosilanes

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ABSTRACT

Despite the recent remarkable progress in CO_2 fixation reactions, the methods for the synthesis of aldehydes from CO_2 are quite limited partly because of the lability of the resulting formyl group and difficulty in the controlled deoxygenative CO_2 conversions leading to C—H and C—C bond formation. Here, we have developed the direct C—H formylation of electron-rich aromatics using silyl formates, prepared from CO_2 and hydrosilanes, in the presence of BCl_3 or BBr_3. This is the first report on the direct C—H formylation of aromatics with silyl formates. Useful compounds including a biologically active compound and octaethylporphyrin were synthesized by fixing one to four CO_2 molecules in a stepwise manner. DFT calculations have been done to elucidate the reaction mechanism including a dual role of BBr_3 in the activation of silyl formate, HCO_2SiMe_2Ph, and electrophilic aromatic substitution.

1 | Introduction

Aromatic aldehydes constitute an important class of compounds, having various applications such as synthetic intermediates for drugs and functional compounds [1–3]. Although the Gattermann–Koch reaction, Reimer–Tiemann reaction, Duff reaction, and Vilsmeier–Haack reaction are widely known as conventional synthetic methods for aromatic aldehydes [4–7], they have drawbacks such as the use of toxic gases, limited substrate scope, and severe reaction conditions. Therefore, much efforts have been made to develop green and sustainable methods for the synthesis of aromatic aldehydes [8–10].

Carbon dioxide (CO_2) is a sustainable C1 source because of abundance, renewability, and inexpensiveness, and the chemical fixation of CO_2 is a hot topic despite the kinetic and thermodynamic stability of CO_2 [11–17]. Among various CO_2 fixation reactions, reductive CO_2 conversions play a pivotal role in accessing a wide range of organic compounds [18–22]. Various reductants can be used such as H_2 [23], hydrosilanes [24–26], and hydroboranes [27]. Among them, hydrosilanes are especially useful because they show moderate reactivity and stability in air and because deoxygenative CO_2 conversions can be driven by the formation of the strong Si—O bond. The stepwise reduction of CO_2 with hydrosilanes takes place, generating silyl formates (HCO_2Si), bis(silyl)acetals ($SiOCH_2OSi$), methoxysilanes (CH_3OSi), and methane [28–34], some of which can be used as reactive species for the synthesis of value-added organic compounds [35–44].

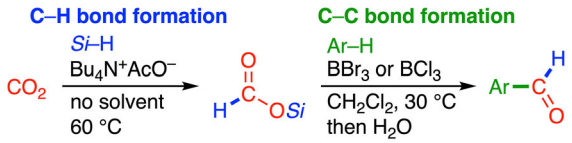
The formation of the formyl group from CO_2 is a challenging subject partly because aldehydes are labile under severe reaction conditions and because the deoxygenative transformation of CO_2 is involved. In fact, the examples of aldehyde synthesis with CO_2 are quite limited [45–56]. For example, the transition metal-catalyzed formylation of aryl halides and hydroformylation of olefins have been reported [45–53]. In most cases, CO_2 is converted

in situ into CO, which is successively used in the C—C bond formation. On the other hand, we have reported the methods for the two-step synthesis of aldehydes with CO_2 and hydrosilanes; a C—H bond is formed in the first step, and a C—C bond is formed in the second step [54–56]. For example, the *N*-formylation of amines with CO_2 and $PhSiH_3$ using tetrabutylammonium acetate (TBAA) or $Cu(OAc)_2$ as a catalyst under solvent-free conditions afforded Weinreb formamide or Comins–Meyers formamide, which were used for the one-pot synthesis of aldehydes by the reaction with Grignard reagents. In addition, *N*-methylformanilide was synthesized from *N*-methylaniline, CO_2, and $PhSiH_3$ using TBAA and $Cu(OAc)_2$ as catalysts under solvent-free conditions and was used in the one-pot Vilsmeier–Haack reaction to synthesize aromatic aldehydes. However, these reactions have a drawback of poor atom economy; the amines react with silyl formates to give formamides, which are then converted into aldehydes, giving off the amines as wastes. Here, we have developed the direct C—H formylation of aromatics using silyl formates synthesized from CO_2 and hydrosilanes (Scheme 1), which is an amine-free system with better atom economy. To the best of our knowledge, this is the first report on the direct C—H formylation of aromatics with silyl formates prepared from CO_2 and hydrosilanes. This reaction is promoted by BBr_3 or BCl_3 under mild conditions using no precious or transition metals. The reaction mechanism including the roles of silyl formates and Lewis acids has been elucidated by density functional theory (DFT) calculations.

2 | Results and Discussion

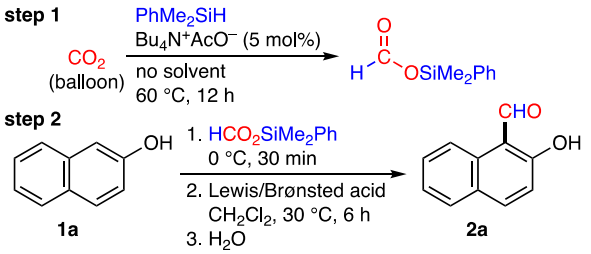
2-Naphthol (**1a**) was allowed to react with HCO_2SiMe_2Ph (3 equiv.), which was prepared from CO_2 (balloon) and $PhMe_2SiH$ using TBAA (5 mol%) as a catalyst under solvent-free conditions [54], in the presence of a Lewis acid (3 equiv.) at 30°C for 6 h (Table 1). 2-Hydroxy-1-naphthaldehyde (**2a**) was obtained in 100% and 96% yield when BBr_3 and BCl_3 (3 equiv.) were used as Lewis acids, respectively (entries 1 and 2). In sharp contrast, a trace amount of **2a** was obtained when $BF_3{\cdot}OEt_2$, $TiCl_4$, or CH_3SO_3H were used as a Lewis/Brønsted acid, and no reaction took place when the following acids were used: $AlCl_3$, $Sc(OTf)_3$, $ZnCl_2$, $Zn(OTf)_2$, $Y(OTf)_3$, $InCl_3$, $SnCl_4$, TMSCl, TMSOTf, CF_3SO_3H, or $Me_3O^+BF_4^-$ (entries 7 and 8). A decrease in the amount of BBr_3 or BCl_3 resulted in a drop in the yield (entries 3–6). Based on these results, the use of BBr_3 or BCl_3 (2–3 equiv.) is suitable for this reaction, and BBr_3 appears to be more active than BCl_3. The fact that only BBr_3 and BCl_3 promoted the formylation suggests that there is a reaction mechanism specific to BBr_3 and BCl_3 as described later.

We also examined the effect of silyl formates (Table 2). When HCO_2SiMe_2Ph, $HCO_2SiMePh_2$, and HCO_2SiPh_3 were used as a formyl source, **2a** was obtained in 100%, 90%, and 24% yield, respectively (entries 1–3). HCO_2SiMe_2Ph was more productive than $HCO_2SiMePh_2$ or HCO_2SiPh_3 probably because the former was sterically less hindered. On the other hand, the use of silyl formates prepared from $PhSiH_3$ did not afford **2a** at all (entry 4), which suggests that silyl formates bearing the primary silicon



SCHEME 1 | C–H formylation of aromatics with silyl formates derived from CO_2.

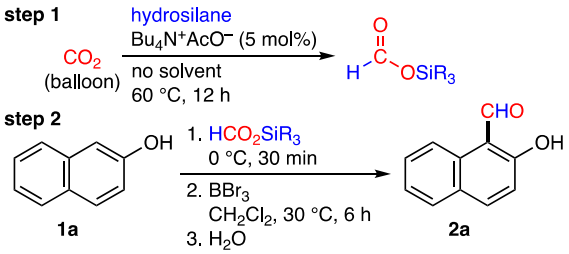
TABLE 1 | Synthesis of aldehyde **2a** by the reaction of **1a** with HCO_2SiMe_2Ph.



Entry[a]	Acid (X equiv.)	Yield (%)[b]
1	BBr_3 (3)	100
2	BCl_3 (3)	96
3	BBr_3 (2)	83
4	BCl_3 (2)	61
5	BBr_3 (1)	Trace
6	BCl_3 (1)	Trace
7	$BF_3{\cdot}OEt_2$ (3)[c]	Trace
8	$AlCl_3$ (3)[d]	0

[a]Reaction conditions: **1a** (0.3 mmol), HCO_2SiMe_2Ph (crude, 0.9 mmol), Lewis/Brønsted acid (amount indicated above), CH_2Cl_2 (0.9 mL), 30°C, 6 h, then H_2O.
[b]NMR yield of **2a**.
[c]The same results with $TiCl_4$ or CH_3SO_3H.
[d]The same results with $Sc(OTf)_3$, $ZnCl_2$, $Zn(OTf)_2$, $Y(OTf)_3$, $InCl_3$, $SnCl_4$, TMSCl, TMSOTf, CF_3SO_3H, or $Me_3O^+BF_4^-$.

TABLE 2 | Screening of hydrosilanes.



	Step 1		Step 2
Entry[a]	Silyl formate	Yield (%)[b]	Yield (%)[b]
1	HCO_2SiMe_2Ph	70	100 (84)[c] (53)[d]
2	$HCO_2SiMePh_2$	45	90
3	HCO_2SiPh_3	35	24
4[e]	$(HCO_2)_nSi(H)_{3-n}Ph$	40	0

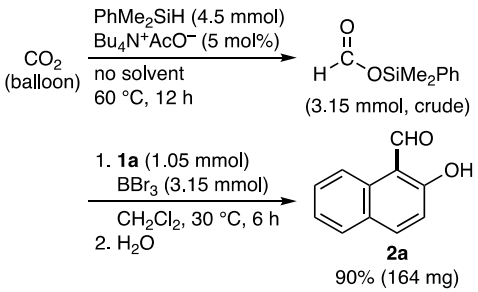
[a]Reaction conditions: **1a** (0.3 mmol), silyl formate (crude, 0.9 mmol), BBr_3 (0.9 mmol, 1 M in CH_2Cl_2), 30°C, 6 h, then H_2O.
[b]NMR yield.
[c]HCO_2SiMe_2Ph (crude, 0.6 mmol).
[d]HCO_2SiMe_2Ph (crude, 0.3 mmol).
[e]30°C in step 1, 2 h. $n = 1–3$.

atom were decomposed during the reaction. Since the reaction of **1a** with 1 or 2 equivalent of HCO_2SiMe_2Ph afforded **2a** in lower yields (53–84%) (entry 1), the use of 3 equivalent of HCO_2SiMe_2Ph was found to be the best. A one-pot reaction was conducted on a 1 mmol scale (Scheme 2). HCO_2SiMe_2Ph (3.15 mmol) was synthesized from CO_2 and $PhMe_2SiH$ (4.5 mmol) in 70% yield as determined by nuclear magnetic resonance (NMR) spectroscopy, and **1a** (1.05 mmol) and BBr_3 (3.15 mmol) were then added to the solution, and **2a** was obtained in 90% yield.

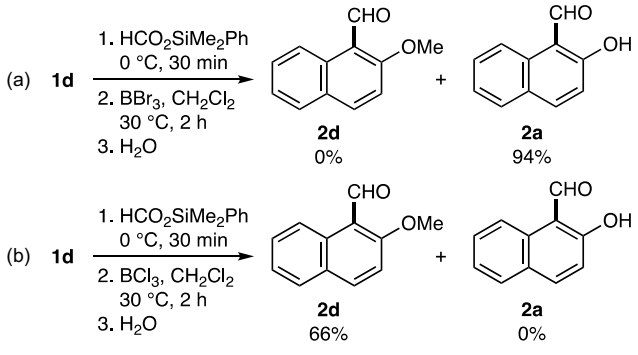
BBr_3 and BCl_3 are common reagents frequently used for the cleavage of the alkoxy group [57, 58]. To examine the effect of BBr_3 and BCl_3 on the alkoxy group, 2-methoxynaphthalene (**1d**) was subjected to the standard reaction (Scheme 3). As a result, BBr_3 effected both formylation and demethylation to deliver **2a** in 94% yield, while BCl_3 promoted the selective formation of 2-methoxy-1-naphthaldehyde (**2d**) in 66% yield, which indicates that BCl_3 is suitable for substrates having alkoxy groups.

We investigated substrate scope under the optimized reaction conditions mainly using HCO_2SiMe_2Ph and BCl_3 (Table 3). As a result, aldehydes **2a**, **2b**, and **2c** with the hydroxy group were isolated in 92%, 52%, and 49% yield, respectively. The yield of **2b** could be improved by shortening the reaction time to 2 h, which suppressed the formation of insoluble materials. As for substrates **1d**, **1e**, and **1f** with the alkoxy group, the reaction time was set to 2 h to suppress the cleavage of the alkoxy group, and **2d**, **2e**, and **2f** were obtained in 61%, 44%, and 54%, respectively. Anthracene (**1g**) was successfully converted into **2g** in 77% yield. Although pyrene (**1h**) was converted into **2h** in 32% yield under the standard reaction conditions, the use of $HCO_2SiMePh_2$ and BBr_3 instead of HCO_2SiMe_2Ph and BCl_3 increased the production of **2h** to 65% yield. In the case of perylene (**1i**), aldehyde **2i** was obtained in 58% yield by extending reaction time from 6 h to 24 h. Azulene (**1j**) was converted into **2j** in only 34% yield probably because of instability, and the yield could not be improved by changing the reaction conditions. Indoles **1k** and **1l** were transformed to **2k** and **2l** in 71% and 77%, respectively. When carbazole (**1m**) was used as a substrate, not aldehyde but *N*-formylated product **2m′** was obtained in 86% yield. 9-Methylcarbazole (**1n**) was successfully converted into aldehyde **2n** in 53% yield. The use of $HCO_2SiMePh_2$ in place of HCO_2SiMe_2Ph enabled the synthesis of **2n** in 94% yield, while the use of $HCO_2SiMePh_2$ and BBr_3 in place of HCO_2SiMe_2Ph and BCl_3 afforded **2n** in 74% yield. The moderate bulkiness of $HCO_2SiMePh_2$ and the moderate Lewis acidity of BCl_3 may suppress overreactions, leading to the improvement of the reaction yield. Ferrocene (**1o**) was a good substrate, and aldehyde **2o** was obtained in 90% yield. We employed 2,2′-biindoles **1p** and **1q** to aim for double C—H formylation. Although **1p** with the NH groups was converted into dialdehyde **2p** in a low yield, **1q** with the *N*-methyl groups was successfully converted by BBr_3 into dialdehyde **2q** in 79% yield.

We applied the present method to the synthesis of biologically active compound, 5,11-dimethylindolo[3,2-*b*]carbazole-6-carboxaldehyde (**2r**) (Scheme 4a). **2r** is known as an agonist for the aryl hydrocarbon receptor (AhR) [59]. The binding of **2r** to AhR induces the translocation of AhR from the cytoplasm into the nucleus and then the formation of a heterodimer with ARNT (AhR nuclear translocator), leading to the binding to specific DNA sequences in the promoter regions and the transcription of genes such as CYP1A1. Based on the assay with ethoxyresorufin-*O*-deethylase, **2r** was found to show 39-fold activity relative to blank even at a low concentration of 80 nM [59]. We synthesized 5,11-dimethylindolo[3,2-*b*]carbazole (**1r**) from 1-methylindole (**1l**), CO_2, and $PhSiH_3$ using BPh_3 as a catalyst in acetonitrile at 40°C as reported previously [60], and **1r** was then subjected to C—H formylation. As a result, AhR agonist **2r** with three CO_2 molecules fixed, regioisomer **2r′**, and diformyl derivative **2r″** with four CO_2 molecules fixed were obtained in 14%, 35%, and 8% yield, respectively. This modest regioselectivity probably originated from the comparable electron-rich sites at the 2-, 6-, 8-, and 12-positions of the indolo[3,2-*b*]carbazole framework, and the two formyl groups were attached to the 2- and 8-positions, forming **2r″**, because these two sites are distant enough. To further understand this reaction, the Vilsmeier–Haack reaction of **1r** was also done for comparison (Scheme 4c) [61]. The Vilsmeier–Haack reaction of **1r** with *N*-methylformanilide and $POCl_3$ produced **2r** and **2r′** in 26% and 36% yield, respectively, without formation of **2r″**. The fact that **2r″** was produced only in the present method suggests that a reactive species made up of HCO_2SiMe_2Ph and BBr_3 is more electrophilic than the Vilsmeier reagent. On the other hand, the fact that the selectivity of **2r** over **2r′**/**2r″** was lower in the present method than in the Vilsmeier–Haack reaction performed at higher temperature suggests that the reactive species made up of HCO_2SiMe_2Ph and BBr_3 is bulkier than the Vilsmeier reagent because the 6- and 12-positions are more sterically hindered than the 2- and 8-positions. We also synthesized 2,5,8,11-tetramethylindolo[3,2-*b*]carbazole (**1s**) from 1,5-dimethylindole, CO_2, and $PhSiH_3$ in the same way [60], and **1s** was used as a substrate for the direct C—H formylation (Scheme 4b). As a result,

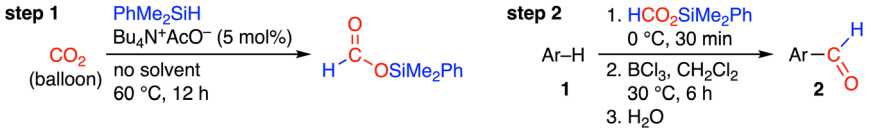


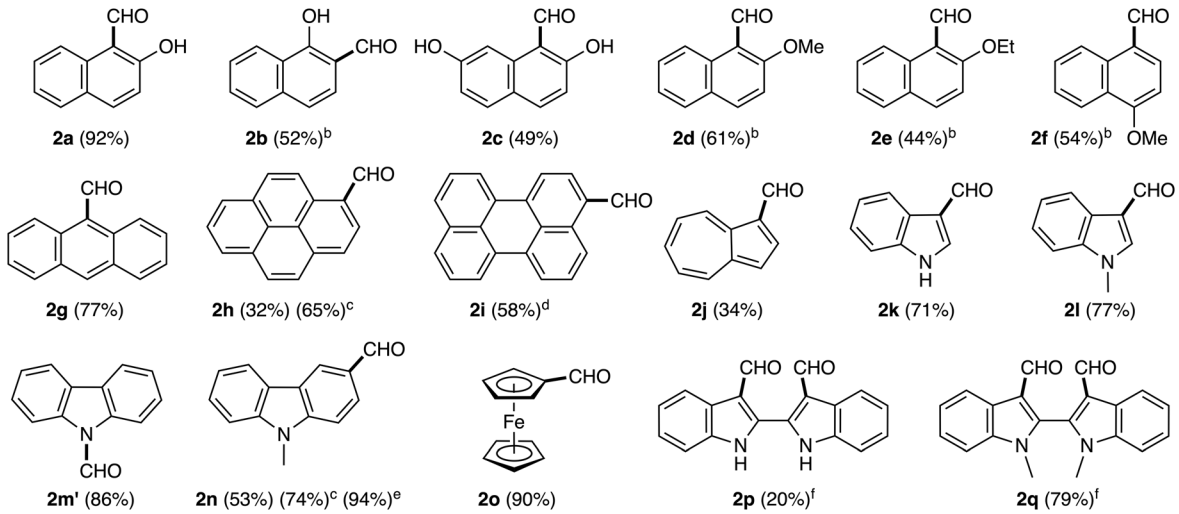
SCHEME 2 | One-pot synthesis of **2a** on a 1 mmol scale.



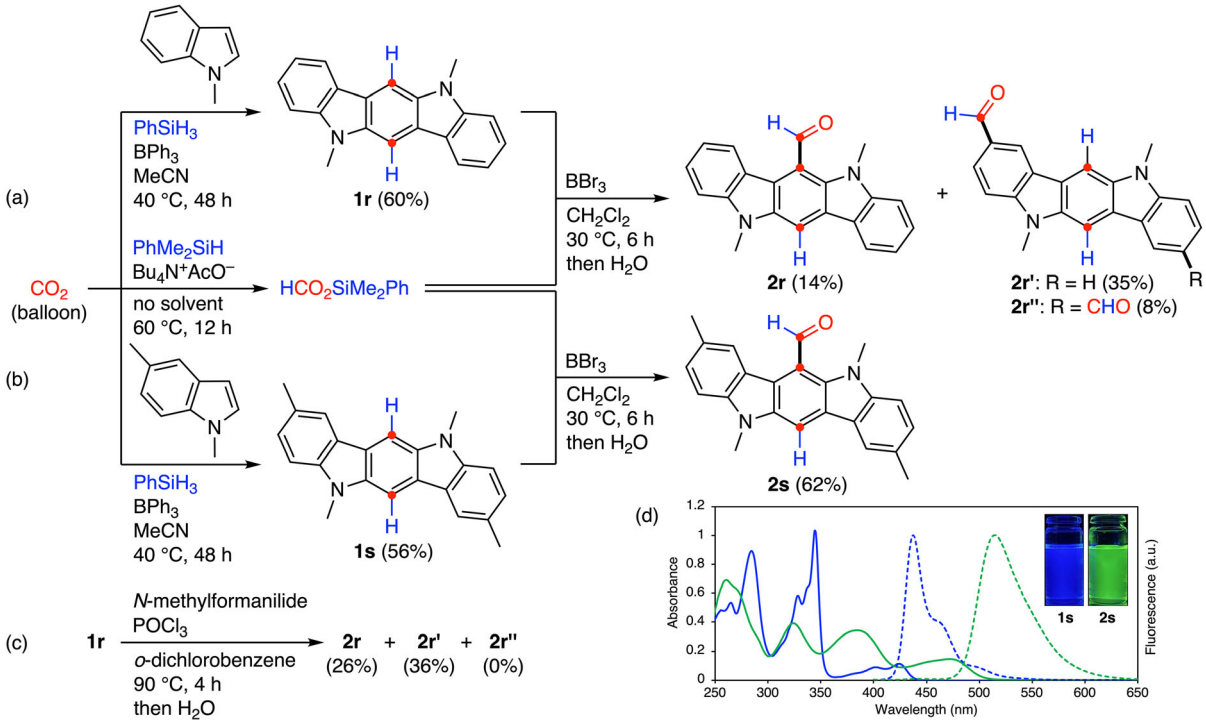
SCHEME 3 | Difference in reactivity and outcome between (a) BBr_3 and (b) BCl_3.

TABLE 3 | C–H formylation of aromatics.[a]



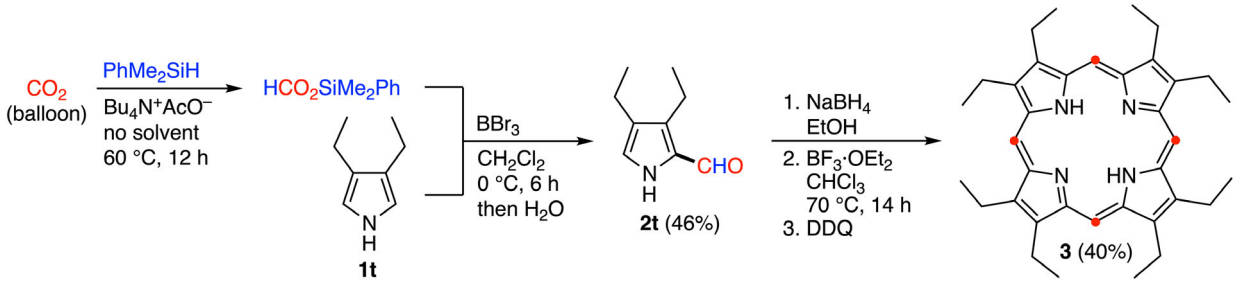


[a]Reaction conditions: **1** (0.3 mmol), HCO_2SiMe_2Ph (crude, 0.9 mmol), BCl_3 (0.9 mmol, 1 M in CH_2Cl_2), 30°C, 6 h. Isolated yields of **2**.
[b]2 h.
[c]$HCO_2SiMePh_2$ and BBr_3 instead of HCO_2SiMe_2Ph and BCl_3.
[d]24 h.
[e]$HCO_2SiMePh_2$ instead of HCO_2SiMe_2Ph.
[f]**1** (0.15 mmol). BBr_3 instead of BCl_3.



SCHEME 4 | Synthesis of (a) biologically active substance **2r** and (b) analog **2s** by the sequential CO_2 fixation reactions. (c) The Vilsmeier–Haack reaction of **1r** for comparison. (d) UV–vis absorption spectra (solid line) and fluorescence spectra (dotted line) of **1s** (blue) and **2s** (green) in DMSO (2.0×10^{-5} M). $\lambda_{ex} = 395$ nm. Photographs of solutions of **1s** and **2s** in DMSO under UV light (365 nm) are also shown.

2,5,8,11-tetramethylindolo[3,2-*b*]carbazole-6-carboxaldehyde (**2s**) was selectively obtained in 62% yield. Fortunately, **2s** was stable under air despite the possession of the formyl group probably because of steric protection. **2s** showed absorption and fluorescence bands at longer wavelengths than **1s**, and almost colorless and slightly yellow solutions of **1s** and **2s** in DMSO exhibited blue



SCHEME 5 | C–H formylation of 3,4-diethylpyrrole (**1t**) and the transformation of the resulting 2-formylpyrrole **2t** to porphyrin **3**.

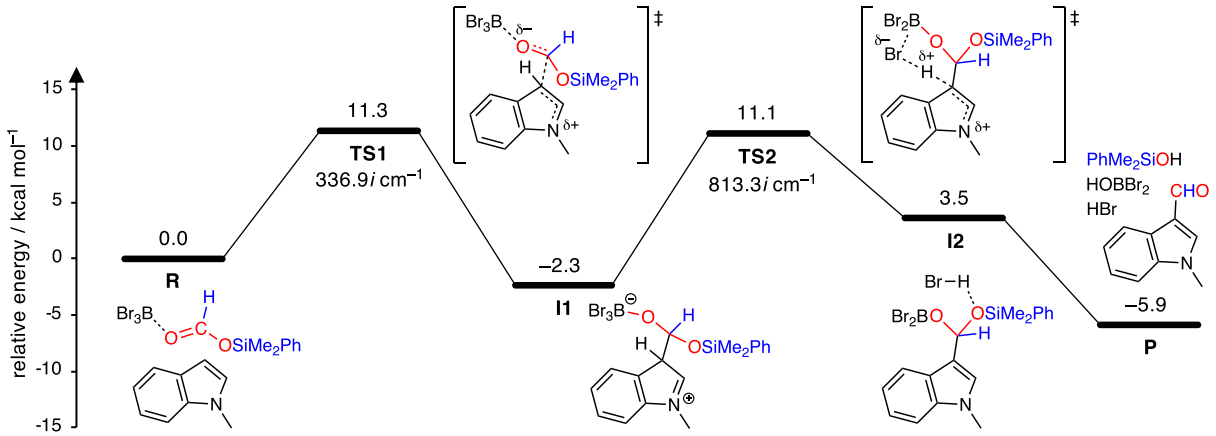


FIGURE 1 | Energy profile for the C–H formylation of 1-methylindole (**1l**). Relative free energies (303 K) are shown in kcal mol^{-1}. DFT calculations were performed at the ωB97XD/6-31G(d) level of theory. The self-consistent reaction field (SCRF) method with the polarizable continuum model (PCM) was adopted to take the solvation effect into account, and the PCM parameters for dichloromethane were employed. The energy of H_2O is included in the former steps where it does not appear explicitly in the computational model.

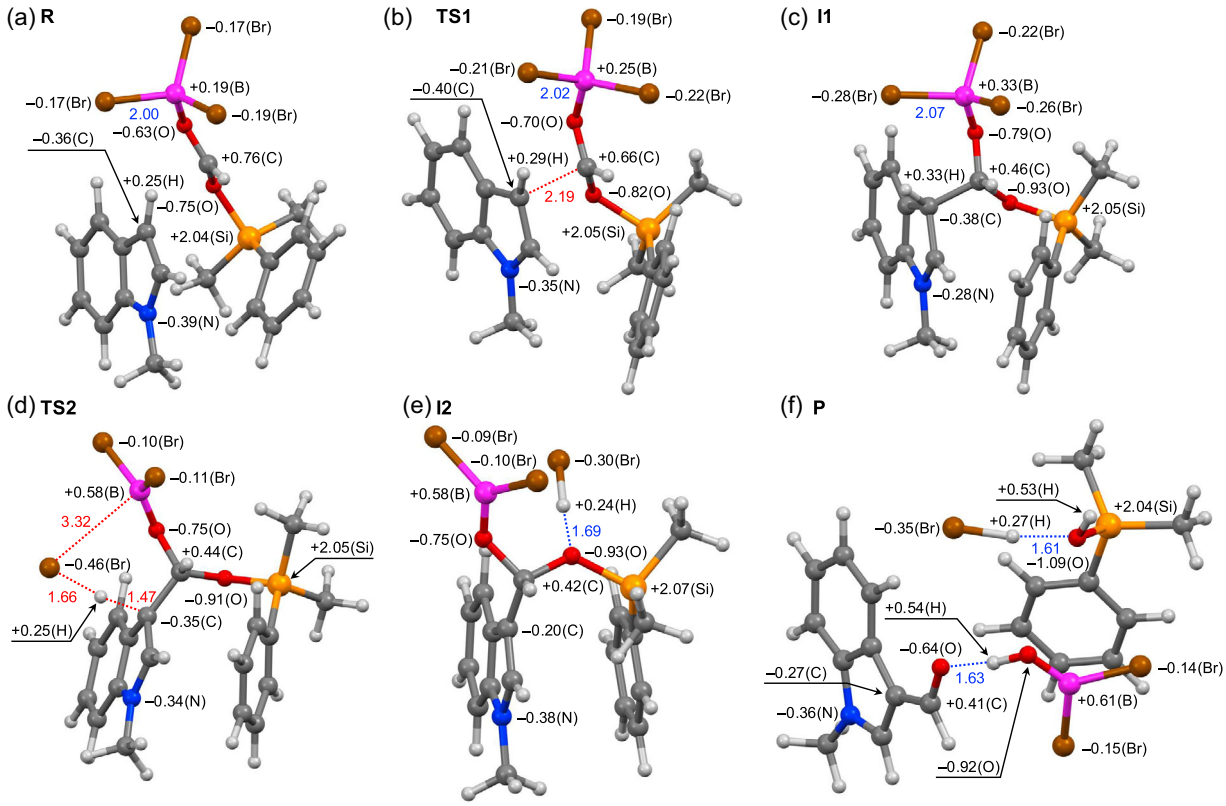


FIGURE 2 | DFT-optimized structures of (a) **R**, (b) **TS1**, (c) **I1**, (d) **TS2**, (e) **I2**, and (f) **P**. Distances (Å) are shown in blue or red, and natural bond orbital (NBO) charges are shown in black.

and green fluorescence, respectively, upon UV light irradiation under dark (Scheme 4d). These aldehydes **2r**, **2r′**, **2r″**, and **2s** are potential precursors for optoelectronic materials since the derivatization of similar compounds has previously been reported [62, 63].

Because porphyrins and metalloporphyrins are important and useful pigments showing unique physicochemical properties, catalytic activities, and supramolecular behaviors, we decided to construct the porphyrin framework using CO_2 as a building block. 3,4-Diethylpyrrole (**1t**) was converted into aldehyde **2t** at 0°C in 46% yield, and the reduction of **2t** with $NaBH_4$ followed by the macrocyclization of the resulting alcohol and oxidation with DDQ afforded 2,3,7,8,12,13,17,18-octaethylporphyrin (**3**) with four CO_2 molecules fixed in the π system (Scheme 5). Since several aromatic aldehydes shown in Table 3, such as **2a** and **2h**, have previously been used for the synthesis of *meso*-aryl-substituted porphyrins [64, 65], the formal synthesis of them with CO_2 has been achieved.

To elucidate the reaction mechanism, we performed DFT calculations on the reaction of 1-methylindole (**1l**) with HCO_2SiMe_2Ph in the presence of BBr_3 and obtained an energy diagram as shown in Figure 1. All the DFT-optimized structures including the intermediate and transition-state structures are presented in Figure 2. Binding of BBr_3 to HCO_2SiMe_2Ph forms an activated species, which triggers the formation of zwitterionic Wheland intermediate **I1** via transition state **TS1** with a $\Delta G^{\ddagger}$ value of 11.3 kcal mol^{-1}. In **TS1**, the newly forming C—C bond is relatively long (2.19 Å), and the carbon atom of the carbonyl group is close to sp^2 hybridization rather than sp^3 hybridization. Upon transformation of **R** into **I1**, the positive charge on the boron atom increases, and the negative charge on the bromine atoms increases. The resulting intermediate **I1** is then converted into intermediate **I2** via **TS2** with a $\Delta G^{\ddagger}$ value of 13.4 kcal mol^{-1}. The proton at the 3-position is abstracted by the negatively charged bromine atom released from the boron atom in **TS2**. In this way, BBr_3 has two roles: the Lewis acid for the activation of HCO_2SiMe_2Ph and the base (Br^-) for the proton abstraction. The resulting HBr forms a hydrogen bond with the oxygen atom of the siloxy group of **I2**, where π–π stacking occurs between the indole ring and the phenyl group with the shortest distance of 3.32 Å. Finally, **I2** is hydrolyzed to deliver the aldehyde product. Considering that both transition states (**TS1** and **TS2**) have small $\Delta G^{\ddagger}$ values and that the whole reaction of the C—H formylation is exothermic, this reaction is likely to occur at ambient temperature.

3 | Conclusion

Various synthetic methods for CO_2 fixation are required to create more sustainable societies. It is still difficult to convert CO_2 into the formyl group partly because CO_2 needs to undergo both C—H and C—C bond formation. Here, we have developed the method for the synthesis of aromatic aldehydes by the direct C—H formylation of electron-rich aromatics using silyl formates prepared from CO_2 and hydrosilanes in the presence of BCl_3 or BBr_3. This is the first example of the C—H formylation of aromatics with silyl formates derived from CO_2, and good substrate scope was confirmed. Useful compounds including a biologically active compound and octaethylporphyrin were synthesized by fixing one to four CO_2 molecules in a stepwise manner. Because of the synthetic utility of aldehydes, the further derivatization of CO_2-derived aldehydes will be possible. Further study is under way to develop sustainable organic synthesis based on effective and efficient CO_2 fixation.

4 | Experimental Section

4.1 | General Procedure for the Synthesis of Aldehydes with CO_2

4.1.1 | Step 1. Synthesis of Silyl Formate

In a glovebox (purge type) under N_2 atmosphere, TBAA (68 mg, 0.23 mmol, 5 mol%) was put in a 30 mL Schlenk flask (dried at 150°C for a few hours and cooled down) fitted with a magnetic stirring bar and a rubber septum, and the flask was taken out from the glovebox. After the flask was evacuated and filled with CO_2 (balloon), $PhMe_2SiH$ (696 μL, 4.5 mmol, stored over molecular sieves 3A) was added via a syringe. The reaction mixture was stirred at 60°C for 12 h and cooled to room temperature to give a crude solution (ca. 700 μL) containing HCO_2SiMe_2Ph, which was used in the subsequent reaction without purification. 1,2-Dichloroethane (39 μL, 0.50 mmol) was added as an internal standard to quantify the amount of HCO_2SiMe_2Ph by means of ^1H NMR spectroscopy (typically, 70% NMR yield).

4.1.2 | Step 2. Synthesis of Aldehyde

To a 5 mL two-neck round-bottom flask (dried at 150°C for a few hours and cooled down) fitted with a magnetic stirring bar and a rubber septum, aromatic substrate **1** (0.30 mmol) was added, and the flask was quickly evacuated and filled with N_2 (balloon). The reaction mixture obtained in step 1 (200 μL) containing HCO_2SiMe_2Ph (0.90 mmol, 3 equiv.) was added to the flask via a syringe, and the mixture was stirred at 0°C for 30 min. A solution of BCl_3 or BBr_3 (1 M solution in CH_2Cl_2, 0.9 mL, 0.90 mmol, 3 equiv.) was added. The mixture was stirred at 30°C for 6 h. The mixture was cooled in an ice bath, and the reaction was quenched with water (3 mL). The mixture was neutralized with saturated aqueous $NaHCO_3$ (3 mL). The product was extracted with CH_2Cl_2 (10 mL × 2). The organic layers were combined, washed with water (10 mL), and dried over Na_2SO_4. After the evaporation of the solvent, mesitylene (14 μL, 0.10 mmol) was added as an internal standard to quantify the amount of the product by means of ^1H NMR spectroscopy. Purification by silica gel column chromatography gave aldehyde **2**.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. Experimental procedures, compound data, and DFT calculations.