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We report sodium trihydroxyaryl borates as the first robust tetracoordinate organoboron catalysts for reductive functionalization of CO_2 . Easily synthesized from condensing boronic acids with metal hydroxides, these catalysts activate main group element-hydrogen (E-H) bonds efficiently. In contrast to BX_3 type boranes, boronic acids and metal-BAr₄ salts, under transition metal-free conditions, sodium trihydroxyaryl borates exhibit high reactivity of reductive *N*-formylation toward a variety of amines (**106 examples**), including those with functional groups such as ester, olefin, hydroxyl, cyano, nitro, halogen, MeS-, ether groups etc. The over-performance to catalyze formylation of challenging pyridyl amines affords a promising alternative method to the use of traditional formylation reagents. Mechanistic investigation supports the electrostatic interaction as the key for Si/B-H activation, enabling alkali metal borates as versatile catalyst for hydroborylation, hydrosilylation, and reductive formylation/methylation of CO₂.

Introduction

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Boron-based catalysts such as BF_3 , $HB(C_6F_5)_2$ (Piers borane), $B(C_6F_5)_3$, Corey-Bakshi-Shibata oxazaborolidine reduction catalysts, boron nitrides, boronic acids and borinic acids etc are widely used in organic synthesis and/or industrial applications.¹⁻ ⁴ In the procedures using boron-based catalysts and the related borylation reactions, tetradentate borates are known as key intermediates formed due to the Lewis acidity of boron atom originated from the existence of empty 2p orbital.⁵⁻⁷ Here, these borate intermediates are treated as active species assisting the chemical reactions (Figure **1a**).

CO₂ reduction with functionalization for the preparation of formamides and methylated amines represents one of the most important ways to incorporate CO₂ into organic molecules as C1 building block. Other than the use of transition metal catalysts,⁸⁻ ¹² non-covalent weak interactions such as Van der Waals, hydrogen and halogen bondings are widely involved weak forces in organo-activation of chemical bonds.¹³⁻¹⁵ In this respect, although quite many types of transition metal-free

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catalysis mainly relies on acid-base interactions between the catalyst and reductant. For instance, FLPs (Frustrated Lewis Pairs) are used as efficient and successful catalysts to activate small molecules including even dihydrogen.¹⁷⁻¹⁸ Therefore, the presence of strong acids or bases tends to be the preferred choice to activate main group element-H (E-H) bond. However, these known systems often suffer from limited substrate scope drawbacks, especially for the acidic or basic groups containing substrates (e.g. phenolic, pyridyl amines).



Figure 1. Metal hydroxyaryl borates for activation of E-H to selectively reduce CO₂

Electrostatic catalysis refers to substrate activation by catalyst via electrostatic interactions.¹⁹⁻²¹ The strategy is late emerging approach to activate B-H bond with the recent report by Hirao and Kinjo *et al* on elegant reduction of ketone/aldehyde/CO₂ using diazadiborinine compounds as pre-catalyst.²² However, to the best of our knowledge, there is no previous report on the use of metal borates for Si-H activation and reductive

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funcationalization of CO₂, even though they contain multiple functional sites such as acidic proton, basic oxygen atom, aryl group possibly useful for catalysis. Our design strategy stem from the use of aryl bronate base catalysts to activate Si-H through electrostatic interactions, which in turn reacts with acidic CO₂ to form the silvl formate reagent required for Nformylation (Figure 1b). Such electrostatic interaction induces hydride transfer to affect hydrosilylation of CO₂ and form silyl formates. Herein, we demonstrate the use of transition metalfree arylborates, well-known Suzuki coupling reagents, for an efficient catalytic reduction of CO₂ and selective Nformylation/methylation of a broad scope of aromatic and aliphatic amines (Figure 1c).

Results and discussion

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Formates and formamides are ever present functionality in many drug intermediates, fine chemicals and polymer materials etc.²³ From the multitude of methods for the preparation of formamides, direct N-H formylation using CO₂ in the presence of reductants represents the most viable approach.24-27 Generally, selective formylation of primary amines is always challenging because of possible formation of di-formylated or methylated by-products, and moreover occurrence of serious over-reduction or side-reactions of functional groups in complex amine substrates. In our continuing interest on CO₂ utilization and of using hydrosilane as reductant²⁸⁻³² and boronic acid as catalyst,³³ we considered the use boron-contained compounds as catalyst for the N-formylation of amines.

Table 1. Discovery of the new borate catalyst^a



^aReaction conditions: 1aa (0.2 mmol, 1 equiv.), catalyst (0.02 mmol, 10 mol %), phenylsilane (0.2 mmol, 1equiv.), CO2 (0.25 MPa) in diglyme (diethylene glycol dimethyl ether, 1 mL) at 60 °C for 12 h. ^bYields determined based on GC analysis using n-hexadecane as internal standard. "Reaction carried out at 100 °C. ^dReaction carried out using 2 equiv. of phenylsilane at 100 °C. ^eUsing 5 equiv. of

PMHS (polymethylhydrosiloxane) at 100 °C for 12 h. ^f Reaction of	Carried out at 100
°C with THF (tetrahydrofuran) as solvent. gToluene apsolvention	39/D0GC01741H

Initial investigation of N-formylation of aniline with CO₂ in the presence of hydrosilanes was examined (Table 1). Surprisingly, we find that boronic acids 3a-c were ineffective for Nformylation even though aromatic boronic acids were used for the hydrosilylation reduction of amides.³⁴ Boronic acids bearing pyridyl group were beneficial, albeit only low yields were obtained (Table 1, entries 5 - 7). The exploration of other aromatic heterocyclic boronic acids and borate esters were unsuccessful (Table 1, entries 8 - 10). To our delight, when ionic sodium trihydroxyphenyl borate 3j was used, moderate reactivity could be achieved (Table 1, entry 11). Increasing the temperature to 100 °C led to higher yield of 88% while lower yields were obtained when using other types of silanes or solvents (Table 1, entries 11 - 16). We believe that the aggregation and shielding of hydridic silanes around the catalyst induce hydride transfer to CO₂. And, the choice of hydrophobic diglyme as solvent is effective for the adsorption of CO₂ in the presence amines.³⁵ Notably, such kind of catalyst working under heating conditions in polar solvents implying special activation mode different from the known σ -hole catalysis.³⁶ Notably, when 1.0 gram of N-methylaniline was used as substrate, the desired product 2aa was obtained in 86% yield (1.1 gram) under the optimized conditions.

As shown in the work of Hall et al, aromatic borates (such as sodium trihydroxyphenyl borate, phenoxy-dialkoxy borates) were elegantly applied into base-free Pd-catalysed Suzuki coupling reactions.³⁷⁻³⁸ Here, we stress that the use of such compounds as catalysts for E-H bond activation have never been reported nor discussed before this work.³⁹ Metal borates are known as core structure of natural products (e.g. boromycin),⁴⁰ Lewis acid catalysts,⁴¹⁻⁴² and boron "ate" complex related reaction intermediates.43-44 However, borates are unstable/reactive intermediates in these reactions.

catalyst (20 mol %)

PhSiH₃ (1equiv.)

60 °C. 12 h



Figure 2. Screening of the sodium arylborates. "Reaction conditions: 1aa (0.2 mmol, 1 equiv.), catalyst (0.04 mmol, 20 mol %), phenylsilane (0.2 mmol, 1 equiv.), CO₂ (0.25 MPa)

2aa

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in diglyme at 60 °C for 12 h. ^{*b*}Phenylsilane (0.4 mmol, 2 equiv.) at 100 °C for 12 h. Yield of **2aa** shown in brackets was determined by GC analysis using *n*-hexadecane as internal standard. The catalyst was prepared quantitatively from in situ reaction of aryl boronic acids with the base.

Hence, we embarked into a systematic study probing the catalytic activity of various borates to verify the reliability of catalysis by borates, and ultimately further discover more efficient catalysts. As shown in Figure 2, a variety of sodium aromatic borates were conveniently prepared by in-situ mixing aromatic boronic acids with NaOH or sodium alkoxides.⁴⁵⁻⁴⁶ It is interesting that different reactivity was observed depending on the counter base used. Specifically, when using MeONa, EtONa, *t*BuONa or PhONa as the base (catalyst **3k-3n**), the yields ranging from 34 to 68% were obtained, with catalyst **3l** from EtONa giving better reactivity. Meanwhile, *ortho*-substitution by alkyl groups on aryl ring influenced the reactivity significantly with methyl substitution to form **3o** giving the highest yield of the desired product of 65%. *Meta or para*-substitution with methyl group decreased the reactivity (47 - 58% yields).

Finally, when catalyst 3u was used, the highest yield of 82% was achieved. When lowering catalyst loading (10 mol%) under elevated temperature, higher yields were obtained for both 3j and **3u**. Notably, in principle, unlimited number of metal aromatic borates type compounds could be obtained by combining different aromatic boronic acids with metal hydroxide/alkoxides. To the best of our knowledge, metal borates have never been used for catalytic reduction reactions. We also compared the reactivity of other types of boroncontained compounds. As shown in Table 2, only the use of borate 3r led to high reactivity under similar conditions. Even the use of strong base NaOH or strong Lewis acids such as BF₃ or $B(C_6F_5)_3$ resulted in poor reactivity for the desired reaction, with significant amounts of aniline starting material recovered. Substrate-catalyst activation via weak interactions could be tested by NMR techniques. Therefore, ¹H NMR measurement of mixtures of CO₂, PhSiH₃ or N-Me aniline, individually with 3jwere performed (See the SI). Initially, when 3j was added to PhSiH₃, chemical shift changes of Si-H of PhSiH₃ and C-H on phenyl ring of 3i were not observed (Si-H at 4.03 ppm for PhSiH₃). Control experiments suggested that borates could be stabilized by silane molecules. Specifically, without silane, CO₂ reacts with borate salt 3j to form free phenyl boronic acid and NaHCO₃. In contrast, with PhSiH₃, no decomposition of 3j occurred in the presence of CO2. This result suggests the occurrence of weak interactions (not able to be detected in ¹H NMR time scale) between silane and borate catalysts offering a protective shield to the borate catalyst from decomposition by CO₂. In this respect, silane might be activated via the stabilization of borate catalyst with the formation of the energized favored intermediate. Regarding the role of alkali metal cation (*i.e.* Na⁺), no influence on reactivity was observed in the reaction of *N*-Me aniline with **3***j* in the presence of other alkali metals CsCl, LiCl or KCl. Hence, we envision that the borate anion plays the key role in the activation of Si-H bond.



Reaction conditions: **1aa** (0.2 mmol, 1 equiv.), catalyst (0.04 mmol, 20 mol %), phenylsilane (0.2 mmol, 1 equiv.), CO₂ (0.25 MPa) in diglyme (1 mL) at 60 °C for 12 h. Yields determined by GC analysis using *n*-hexadecane as internal standard.

Moreover, in ¹H NMR experiments B-H formation was undetected unlike with the recent development of alkali metal hydridotriphenylborate catalysts for the hydroboration of CO_2 via B-H and B-OR interconversion.⁷ Therefore, we advance the involvement of weak interactions seemingly weaker than classical hydrogen bonding. Meanwhile, it is interesting to note that in the Pd-catalysed Suzuki coupling reaction of acyl chlorides or aryl iodides with sodium trihydroxyphenylborate, the presence of PhSiH₃ strongly suppressed the C-C coupling reaction. This result implies that the interaction between silanes and borates influence the original coupling reaction (Figure **S1**, see the SI).

To further understand the mechanism, density functional theory (DFT) calculations on the interaction of silanes with borates were examined. It is suggested that the weak attraction between borate catalysts and hydrosilanes is through Si-H...H-O, Si-H...H-C and Si...O interactions, I and II as illustrated in Figure 3. The stabilized energy is at the level of 4-5 kcal mol⁻¹ belonging to the energy strength of electrostatic interaction. Besides, the electrostatic potential map illustrated in Figure 4 also suggest that the negatively charged hydride of phenylsilane interacts with the positively charged hydrogen atoms connected by oxygen atoms and carbon atoms in sodium aryl borates. This is also consistent with the results of NMR experiments that interactions weaker than hydrogen bonding could exist and were undetectable in ¹H NMR time scale. Besides, as mentioned above, the presence of methyl group at ortho-position to the boron (catalyst 30) or methoxy group on boron atom (catalyst

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3k) increased the reaction efficiency significantly. From the DFT study, it is clear that the CH₃ moiety interact with hydride of silane. The Si-H...H-O and Si-H...H-C distances are shortened in comparison with those in I and II. Moreover, the binding energies are -7.6, -5.7, and -6.2 kcal mol⁻¹ for I-MeO, II-MeO, and I-Me, while they are -5.6 and -4.0 kcal mol⁻¹ for I and II, respectively (Table S5). These results demonstrate that the interactions between PhSiH₃ and sodium aromatic borates are effectively strengthened by the introduction of methoxy group on boron atom or *ortho*-methyl substitution to boron, being beneficial for the activation of Si-H bonds for the key CO₂ reduction step. The present results rationalize the experiment findings.



Figure 3. DFT-Calculated Interaction Modes. (**A**) Optimized complex structures of sodium aryl borates (**3***j*, **3***k*, **30**) with phenylsilane at the M06-2X-D3/6-311G(d, p) level of theory in solvent. Values in parenthesis denote the binding energies (in kcal mol⁻¹) calculated at DSD-PBEP86/def2-TZVPP level in solvent. Bond lengths are in Å. (**B**) Electrostatic potential map for the catalyst-silane interaction.

From experimental results and theoretical studies, we propose that the ionic borate moiety of sodium phenyl trihydroxy borate could interact with hydrosilane selectively via electrostatic interactions (Figure 3). This is a key step for CO₂ reduction to give silyl formate intermediates, which further undergo additive substitution reaction with amine substrates to give the desired formamide product (Pathway **A**). Besides, the formation of carbamate intermediates followed by reduction to give the formamide product is also possible (Pathway B). The use of borates to promote the activation of Si-H or B-H bond is unique. In addition, it is suggested that the non-coordinating nature of tetrahedral borate makes them suitable for tasks that involve ion-pairing with sensitive organometallic complexes or reactive cationic intermediates.

With the optimized reaction conditions in hands, investigation of substrate scope was performed. Firstly, different aromatic aniline substrates were tested (Table 3). It was found that good to excellent reactivity and selectivity for the desired *N*-formylation reaction was achieved for most aromatic primary amines at 60 °C, with occasionally aromatic primary amines requiring 100 °C. Electron donating aromatic amines such as Me, Et, *i*Pr, *t*Bu, di-Me, MeS and OMe derivatives afforded the desired compounds (**2b** - **f**, **2k** - **o**, **2u**) in 80 - 86% yields respectively. The reaction also underwent smooth conversion



with electron-withdrawing aromatic amines substituents like F.

Cl, Br, I, CF₃, 3,5-di-F, 3,5-di-Cl and NO₂DO: afford the desired

compounds (2g - j, 2p - r) in 70 - 88% yields. To our surprise, the

reaction gave the desired compounds 2z in 77% yields using

allylamine without affecting the double bond which is often

sensitive to reductants. Fortunately, this method was also

successful in the N-formylation of amines which contain

Figure 4. Proposed Reaction Mechanism

In light of the success with aromatic primary amine derivatives, we extended the scope to aromatic secondary amine substrates, as also presented in Table 3. To our delight, the reactions also underwent smooth conversion to afford the expected *N*-formylated product. Similarly to aromatic primary amines, aromatic secondary amines also exhibit functional group tolerance and display good to excellent reactivity. The reaction underwent smooth conversion regardless of electron-withdrawing and donating substituents affording the desired compounds in good to excellent yields (**2ab - ac, 2ae - ai,** 73% - 91%). Conversely, we find that the product conversion is slightly lowered with ortho position substituted substrate, presumably due to steric hindrance **2ad** (68% yield).

Heterocyclic secondary amines were also amenable to this transformation and converted to the corresponding carboxamide products in good to excellent yields (**2aj** - **al**, 73 - 95%). For alkylated secondary amines, we found that the length and branching of the carbon chain of the alkyl substituent on the N atom has influence on the yield. For instance, amine substrates with sterically hindered isopropyl or *t*-butyl substituents afford desired products with lower yields, while side reaction methylation products increase (**2an** - **aq**, 53 - 73%). Acceptable yields were obtained when secondary amine substrates (substituent (**2ar** - **as**, 47 - 70%). Notably, the presence of nitro group often inhibits *N*-formylation Using CO₂ in previous reports. Substituted amines (anilines) with either electron donating or electron

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^{*a*}Reaction conditions: **1** (0.2 mmol, 1 equiv.), catalyst (0.02 mmol, 10 mol %), phenylsilane (0.4 mmol, 2 equiv.), CO₂ (0.25 MPa) in diglyme (1 mL) at 60 °C for 12 h. ^{*b*}Phenylsilane (0.4 mmol, 2 equiv.) at 100 °C for 12 h. ^{*c*}Phenylsilane (0.4 mmol, 2 equiv.) at 100 °C for 24 h. ^{*d*}Yields determined based on GC analysis using *n*-hexadecane as internal standard. Other yields refer to isolated yields.

withdrawing groups afforded the desired products/in moderate to good yields (2ba, 83%; 2au - 2az, 68 - 89%). Secondary alkenty amines allylphenylamine was also transformed to the corresponding formylated products in lower moderate yield (2at, 44%). Secondary amines bearing bulky substituents regarded incompatible for such transformation also afforded the desired products in moderate yields (2bc - be, 40 - 58%). Lastly, when substrate is an ortho-diamine, the corresponding benzimidazole or benzothiazole compounds were formed in moderate yields (2bf, 46%; 2bg, 55%; 2bh, 52%). Here, it is important to note that under elevated temperature the catalyst remained stable after the reaction showing the robustness of the borate catalyst in this catalytic system. With respect to the concept of green chemistry, the development of reusable heterogeneous catalysts is highly attractive.⁴⁷ In our system, the catalyst recycling test shows that the catalytic activity is still high after two times of reuse with the yields of the desired product as 88%, 75%, 70% respectively.

Table 4. N-Formylation of aliphatic amines^a



^{*a*}Reaction conditions: **1** (0.2 mmol, 1 equiv.), catalyst (0.02 mmol, 10 mol %), phenylsilane (0.3 mmol, 1.5 equiv.), CO₂ (0.25 MPa) in diglyme (1 mL) at 60 °C for 12 h. ^{*b*}Phenylsilane (0.2 mmol, 1 equiv.). ^CYields refer to isolated yield. Other yields determined based on GC analysis using *n*-hexadecane as internal standard.

We further investigated a wide range of aliphatic amines (Table 4). Reactions with both aliphatic and benzylic primary and secondary amines afforded the corresponding formylated products in good to excellent yields, including substrates with bulky tBu group substitution. Notably, functional groups such as ether, nitrile, cyclopropyl, halogen, phenol and trifluoromethyl groups were well tolerated. Cyclohexamine, benzylamine, aminopropylbenzene and aminobutylbenzene were converted successfully to *N*-formylated derivatives in good to excellent

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yields (2bi, 81%; 2cj - cl, 61 - 88%). Cyclic heterocyclic amines aza-cyclohexane, oxazine and piperazines afforded the desired products in moderate to good yields (2bj - bo, 56 - 80%). Dialkylated amine substrates, N-butyl amine, di-isopropylamine, N,N,N-trimethyl diaminoethane and bis(2-cyanoethyl)amine were transformed in excellent yields (2bp - bs, 75 - 93%). N-Methyl benzylamine and derivatives bearing electronwithdrawing or electron-donating groups were also amenable to this transformation in good yields (2bt - cd, 72 - 92%). It is interesting to note that aminomethyl phenol 2bx undergoes chemoselective *N*-formylation smoothly. N-Substituted benzylamines with various alkyl groups (ethyl, isopropyl, butyl and benzyl) gave the corresponding N-formylated products in moderate yields with bulky t-butyl one at the lower end of the range (2cc, 2ce - cg, 41 - 87%). Reactions of chiral substrates (S)and (*R*)-2-Pyrrolidinemethyl-methyl ether (2cn. 2cm) proceeded smoothly with the chiral properties maintained in the product.

Pyridine based derivatives represent key motifs in drug and fine chemicals including ligands for catalysis. It is noteworthy to mention that the presence of pyridyl group is always problematic in catalytic transformations. Satisfyingly, we found that heterocyclic substrates such as substituted aminopyridine and derivatives could be transformed to the desired product in good to excellent yields (2co - ct, 48% - 92%; Table 5). Notably, the Meyers formylating agent 2cq was produced in 58% yield.^{48a} These results implied that a new mechanism pathway is involved to have basic pyridine group well tolerated.

Table 5. Application to the synthesis of heteroaromatic formamides^a



^aReaction conditions: 1 (0.2 mmol, 1 equiv.), catalyst (0.02 mmol, 10 mol %), phenylsilane (0.3 mmol, 1.5 equiv.), CO₂ (0.25 MPa) in diglyme (1 mL) at 60 °C for 12 h.^b. Phenylsilane (0.2 mmol, 1 equiv.). 'Yields refer to isolated yield. Other yields determined based on GC analysis using *n*-hexadecane as internal standard.

Moreover, we successfully transformed more complex structures such quinolinamine and pyridinemethanamine

derivatives in excellent yields (2cu - cy, 75 - 95%), Also, the reaction of thiophenemethylamine or Purary methylamines afforded the desired products in good yields (2cz - db, 62 - 85%).



Figure 5. Comparison results of borate-catalysis approach with non-catalytic methods





B) N-methylation of aromatic amines



C) HBpin as the reductant



Figure 6. Further applications on reduction, N-methylation and activation of hydroborane.

To further demonstrate the usefulness of this new method, the *N*-formylation of valuable pyridyl amines^{48b} **3co** and primary amine 2t were carried out using the known non-catalytic methods⁴⁹ to demonstrate the applicability of this work (Figure 5). Notably, the presence of pyridyl group is often problematic to the transition metal catalysed reactions that proceed via the formation of metal-H species. Most of non-catalytic methods tested were unsuccessful and only trace amounts of product was observed using ethyl formate for the formylation of 3co (Figure 5). Also for the reaction of 2t, poorer yields were obtained compared to the approach this work based on borate 3j and PhSiH₃. The generality of this approach is unprecedented as shown above for substrate scope tolerance. Interestingly, in spite of the presence of basic pyridyl group or acidic phenolic

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group good reactivity was maintained. This is in a striking contrast to the known base-acid interaction strategy.

The control experiment for the reduction of CO2 in the absence2of amines gave the silyl formate product in high yield (99%;3Figure 6A). Under slightly higher temperatures, the reductive N-5methylation using CO2 was also achieved with good reactivity6(76 - 87 yields; Figure 6B). To further prove the activation of7main group element-hydrogen bond using ionic borates, the7catalytic formylation of amines using hydroborane was8performed. Using HBpin as the reductant, the formylation of N-8Me aniline proceeded smoothly giving the desired product in 89% 99yield. Similarly, when using phenyl boronic acid or NaOH as the10catalyst, much lower reactivity was observed (Figure 6C).10

Conclusions

This work developed a general methodology of a transition metal-free pathway based on alkali metal arylborate electrostatic catalysts for hydroborylation, hydrosilylation, and reductive formylation/methylation of CO₂. Sodium trihydroxyphenylborate was found to be superior catalyst in the activation of main group element-hydrogen bond. This method of *N*-formylation is broad in scope applicable to both aromatic and aliphatic amine substrates (total 106 examples), especially the unexplored pyridyl amine substrates. Notably, this is the first example of using hydroxyborate for catalytic reductions of carbon dioxide for N-formylation/methylation reactions. Experimental data and DFT calculations show the action of catalysts is presumably through the dual activation of Si and H atoms in hydrosilane as proposed in the mechanism.

Experimental

General procedure for reductive formylation of amines with CO₂: To a 4 mL sealing tube in a nitrogen-filled glovebox, the substrate (0.2 mmol), **3j** and phenylsilane were added followed by addition of solvent diglyme (1 mL). Then the tube was sealed, taken out of the glovebox and placed into the autoclave. The autoclave was sealed and purged three times with CO₂ gas, then pressurized to 2.5 atm. At last, the autoclave was heated at 60 - 100 °C for 12 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The yield was determined by GC analysis or the product was purified by silica gel giving the isolated yield.

Conflicts of interest

There are no conflicts to declare.

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