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Cobalt catalyzed carbonylation of unactivated C(sp<sup>3</sup>)–H bonds†

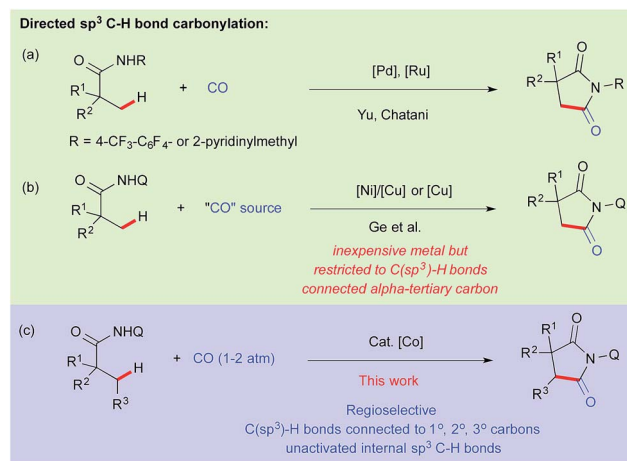
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A general efficient regioselective cobalt catalyzed carbonylation of unactivated C(sp<sup>3</sup>)–H bonds of aliphatic amides was demonstrated using atmospheric (1–2 atm) carbon monoxide as a C1 source. This straightforward approach provides access to  $\alpha$ -spiral succinimide regioselectively in a good yield. Cobalt catalyzed sp<sup>3</sup> C–H bond carbonylation is reported for the first time including the functionalization of ( $\beta$ )-C–H bonds of  $\alpha$ -1°, 2°, 3° carbons and even internal ( $\beta$ )-C–H bonds. Our initial mechanistic investigation reveals that the C–H activation step is irreversible and will possibly be the rate determining step.

## Introduction

Catalytic carbonylation is one of the most straightforward processes for the production of carbonyl compounds both in academia and industry.<sup>1</sup> Insertion of CO into carbon–hydrogen bonds has become even more interesting provided that the catalyst has the ability to activate both inert C–H bonds and to bind  $\pi$ -acidic carbon monoxide.<sup>2</sup> In this regard, Shunsuke Murahashi reported the first effective catalytic C–H carbonylation of benzaldimine in 1955 using a low valent cobalt(0) complex.<sup>3</sup> Since then, several reports have been documented for catalytic C(sp<sup>2</sup>)–H bond carbonylation.<sup>4</sup> However the corresponding extension to carbonylation of C(sp<sup>3</sup>)–H bonds is rare and only a handful of examples have been reported in the literature.<sup>5</sup> After the pioneering work of Tanaka *et al.* for photocatalytic carbonylation of alkanes,<sup>6</sup> Chatani reported the directing group assisted C–H carbonylation of  $\alpha$ -C(sp<sup>3</sup>)–H bonds adjacent to nitrogen.<sup>7</sup> In 2010–11, Yu and Chatani independently reported the site-selective C(sp<sup>3</sup>)–H carbonylation of aliphatic amide using Pd and Ru based catalysts, while the former used oxidative conditions, the latter proceeded through a metal-hydride pathway (Scheme 1a).<sup>8–10</sup> We assumed that it would be more rational to choose a metal abundantly present in nature compared to precious metals in terms of cost effectiveness and the unexploited inherent properties exhibited by them.<sup>11</sup> Utilization of 8-aminoquinoline as a bidentate auxiliary for C–H bond functionalization was first reported by Daugulis,<sup>12</sup> and later developed by Chatani<sup>13</sup> and others<sup>14</sup> for several profitable applications using first row late transition metal precursors.

Using this approach, Ge *et al.* reported recently the carbonylation of unactivated C(sp<sup>3</sup>)–H bonds with Ni–Cu/Cu as a catalyst using DMF and nitromethane as a carbonyl sources.<sup>15</sup> But the presented nickel–copper/copper catalyzed carbonylation was limited to  $\beta$ -C(sp<sup>3</sup>)–H bonds connected to  $\alpha$ -tertiary carbon (Scheme 1b). On the other hand, cobalt seems to be a very promising alternative metal catalyst for various C(sp<sup>2</sup>)–H bond functionalizations.<sup>11a,b,16</sup> Very recently Ge and Zhang independently reported cobalt catalyzed intramolecular cyclization through activation of directed C(sp<sup>3</sup>)–H bonds.<sup>17</sup> Daugulis reported lately, cobalt catalyzed *o*-C(sp<sup>2</sup>)–H bond carbonylation of benzamides at room temperature.<sup>16n</sup> We have previously demonstrated the activation of C(sp<sup>3</sup>)–H bonds using Cp\*Co(III) for C–H alkenation with alkynes and C–H amidation with oxazolone.<sup>18</sup> Inspired by these results and based on our continuous efforts on the development of cobalt catalyzed C–H bond functionalization,<sup>19</sup> we report herein the first regio- and site-

Scheme 1 Carbonylation of unactivated C(sp<sup>3</sup>)–H bonds.

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selective cobalt catalyzed carbonylation of unactivated C(sp<sup>3</sup>)-H bonds including terminal and internal C-H bond connected  $\alpha$ -1°, 2° and 3° carbons (Scheme 1c).

## Results and discussion

We began our investigation using aliphatic amide **1a**, 2 atm CO gas as a C1 source with a catalytic amount of simple Co(OAc)<sub>2</sub>, metal carboxylate and silver carbonate as an oxidant at 150 °C for 36 h in chlorobenzene (0.5 mL). The optimization results are summarized in Table 1. Initial screening of different metal carboxylates revealed that a good yield of **2a** was obtained with sodium benzoate (50 mol%) as an additive, which is also an optimal reaction parameter for intramolecular  $\beta$ -sp<sup>3</sup> C-H bond amidation<sup>17a</sup> (Table 1, entry 1–4). Lowering the reaction concentration did not provide any further improvement (entry 5). A small amount of sodium benzoate turned out to be crucial for high product formation with cobalt(II) (entry 6 and 7).

There was no significant change in yield when the reaction time was reduced to 24 h or by increasing the catalyst loading to 20 mol% (entries 8 and 9). To our delight, a small increment in the silver carbonate gave excellent product formation after 24 h (entry 10). Next, we examined various cobalt sources from different oxidation states. It was revealed that Co(II) and Co(III) gave excellent yields whereas Co(0) and Co(II)Br<sub>2</sub> gave moderate

yields (entries 11–14). After a brief solvent screening,<sup>20</sup> we found out that  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT) was the best solvent, which provided 95% of the succinimide **2a** under our optimized reaction parameters (entry 15). A well-defined, isolated cobalt-pivalate dimer<sup>21</sup> was used as a catalyst without any additive and this resulted in a 55% yield (entry 16). We further confirmed that the direct use of the Co(III) precursor in the absence of the sodium benzoate provides **2a** in 92% yield and the structure of **2a** was confirmed by X-ray crystallography (entry 17).<sup>22</sup>

Prior to the scope of the reaction, we examined the scalability of the reaction. A gram scale reaction was performed with **1a** using atmospheric CO gas and provides succinimide **2a** in 71% yield after 36 h (Scheme 2) and silver carbonate was regenerated from the residue in 69% (2.5 g) yield using the known literature procedure.<sup>16e,23</sup> The recycled silver carbonate was used for C-H carbonylation and resulted in 83% of **2a** under standard conditions (Scheme 2).

With the optimized conditions in hand, we next investigated the scope of the aliphatic amides and the results are depicted in Scheme 3. Architecturally interesting spiral succinimides possessing a 4-, 5-, 6-membered ring on the backbone were achieved in good yields (**2b–d**). Replacing one of the methyl groups from **1a** with a benzyl, 4-OMe-benzyl, cyclopentyl, isopropyl or alkyl chain at the  $\alpha$ -tertiary center gave the desired succinimides in high yields (**2e–j**). Phenyl, ester, and -Br substituents on the backbone were tolerated (**2k–m**). Next, the reactivity difference between C(sp<sup>2</sup>)-H and C(sp<sup>3</sup>)-H bonds was investigated for cyclocarbonylation. It was found out that carbonylation of unactivated C(sp<sup>3</sup>)-H bonds was favoured over C(sp<sup>2</sup>)-H bonds (**2n–o**) and only **2o'** was obtained in 15% yield in addition to **2o** (50%). This may be due to the fact that the former proceeds *via* facile 5-membered cyclocobaltation while the latter proceeds through a 6-membered metallocycle. Furthermore, we explore the possibility of activating  $\beta$ -C(sp<sup>3</sup>)-H bonds next to an  $\alpha$ -secondary and primary carbon center, which is much more challenging (this has not been explored before for carbonylation using first row transition metals) than a C-H bond next to an  $\alpha$ -tertiary carbon. Gratifyingly, propanamide (**1p**) and  $\alpha$ -methylpropanamide (**1q**) underwent cyclocarbonylation albeit in a moderate yield (**2p**, **2q**) but the mass of the product can be improved if we prolong the reaction to 36 h with a 20 mol% cobalt catalyst.

Systematic increase of bulkiness by incorporating a -Et and -*t*-Bu group did not significantly alter the isomeric ratio (**2r–s**). Furthermore, to our delight, an internal C(sp<sup>3</sup>)-H bond was carbonylated in the case of **1t** and **1u**, and it resulted in the formation of substituted and structurally strained succinimides (**2t** & **2u**) and X-ray crystallography further confirmed the structure of **2t**.<sup>22</sup> The reactivity of **1u** was documented for the

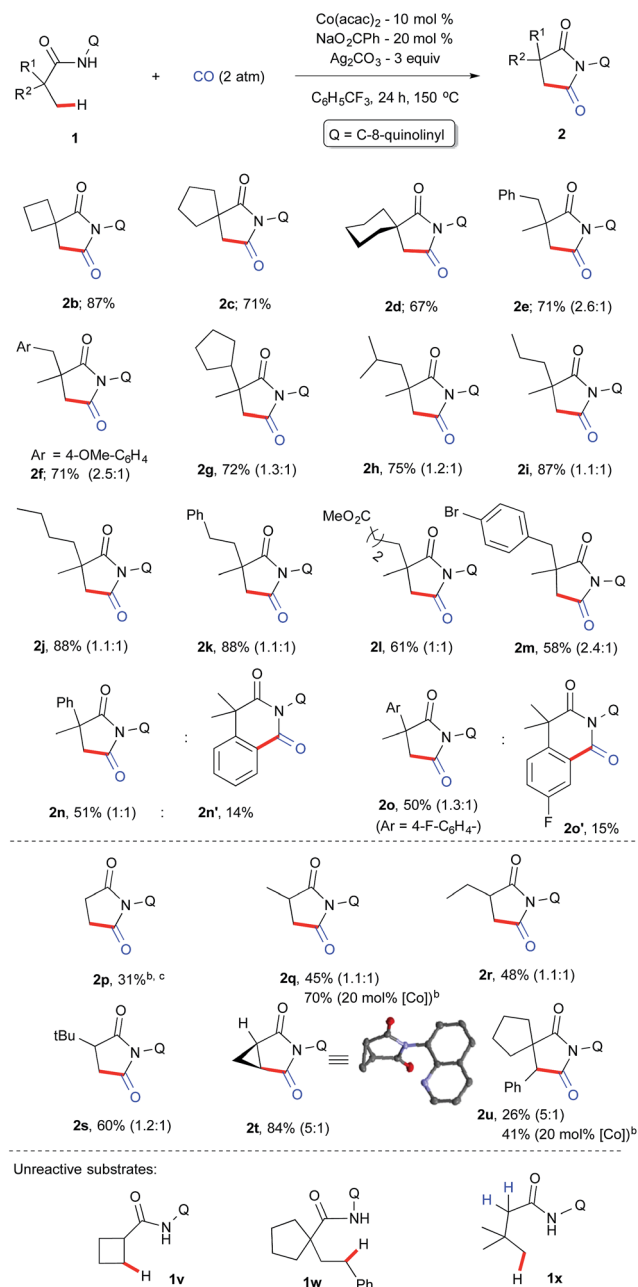
Table 1 Optimization studies and control experiments<sup>a</sup>

Entry	[Co]	MCO <sub>2</sub> R (mol%)	Oxidant	Yield <sup>b</sup>
1	Co(OAc) <sub>2</sub>	NaOPiv (50)	Ag <sub>2</sub> CO <sub>3</sub>	27
2	Co(OAc) <sub>2</sub>	Mn(OAc) <sub>3</sub> (50)	Ag <sub>2</sub> CO <sub>3</sub>	n.r.
3	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (50)	Ag <sub>2</sub> CO <sub>3</sub>	67
4	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CMe (50)	Ag <sub>2</sub> CO <sub>3</sub>	49
5	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (50)	Ag <sub>2</sub> CO <sub>3</sub>	53 <sup>c</sup>
6	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (100)	Ag <sub>2</sub> CO <sub>3</sub>	43
7	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	76
8	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	70 <sup>d</sup>
9	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	79 <sup>d,e</sup>
10	Co(OAc) <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	87 <sup>d,f</sup>
11	Co(acac) <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	86 <sup>d,f</sup>
12	Co(acac) <sub>3</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	87 <sup>d,f</sup>
13	Co <sub>2</sub> (CO) <sub>8</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	68 <sup>d,f</sup>
14	CoBr <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	61 <sup>d</sup>
15	Co(acac) <sub>2</sub>	NaO <sub>2</sub> CPh (20)	Ag <sub>2</sub> CO <sub>3</sub>	95 <sup>d,g</sup>
16	[Co(Piv) <sub>2</sub> ] <sub>2</sub>	—	Ag <sub>2</sub> CO <sub>3</sub>	55 <sup>d,g</sup>
17	Co(acac) <sub>3</sub>	—	Ag <sub>2</sub> CO <sub>3</sub>	92 <sup>d,g</sup>

<sup>a</sup> All reactions reagents were added under argon atmosphere unless otherwise stated using **1a**/[Co]/NaO<sub>2</sub>CR/Ag<sub>2</sub>CO<sub>3</sub> in 0.2/0.02/0.02–0.05/0.5 mmol using chlorobenzene (0.5 mL) as a solvent at room temperature and then pressurized with CO (2 atm) at 150 °C for 36 h. <sup>b</sup> Isolated yield. <sup>c</sup> 1 mL of PhCl was used. <sup>d</sup> Reaction performed for 24 h. <sup>e</sup> 20 mol% of [Co] was used. <sup>f</sup> 3 equiv. of Ag<sub>2</sub>CO<sub>3</sub> was used. <sup>g</sup> TFT (0.5 mL) was used as a solvent.



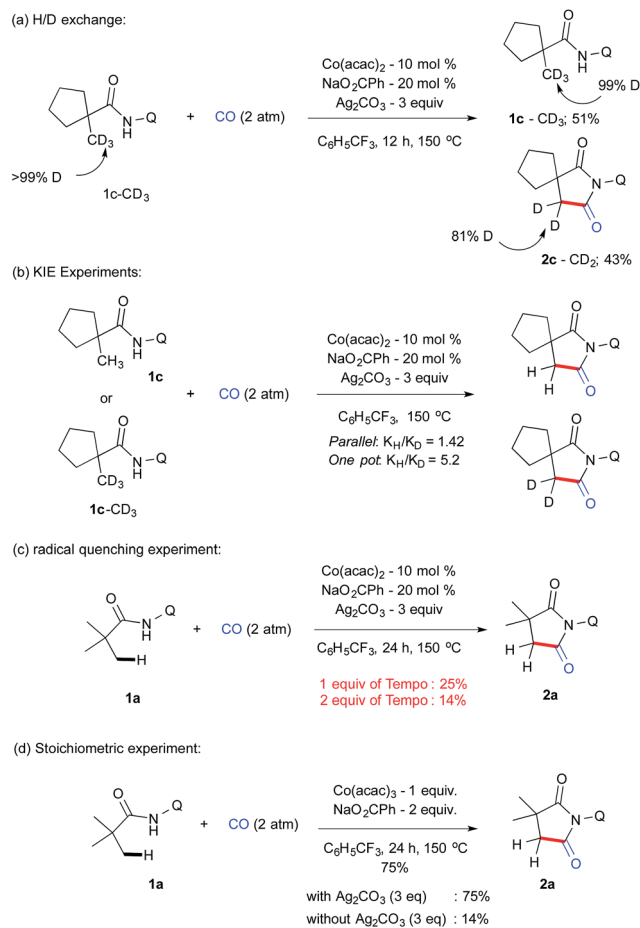
Scheme 2 Gram scale synthesis of succinimide.



**Scheme 3** Scope and limitation. <sup>a</sup>The number in parenthesis is the ratio of diastereomer. <sup>b</sup>36 h instead of 24 h. <sup>c</sup>PhCl as a solvent.

first time *via* internal  $\beta\text{-C}(\text{sp}^3)\text{-H}$  carbonylation. To understand the reaction mechanism, several experiments were carried out as displayed in Scheme 4.

**1c-CD<sub>3</sub>** employed under our reaction conditions gave the corresponding carbonylation product **2c-CD<sub>2</sub>** (43%) along with the recovered starting material **1c-CD<sub>3</sub>** (51%) after 12 h (Scheme 4a). Analysis of the isolated compound revealed that **1c-CD<sub>3</sub>** did not have any H/D exchange, which indicates that the C-H activation step is irreversible. KIE values of 1.42 and 5.2 were determined from parallel and one-pot experiments using **1c-CH<sub>3</sub>** and **1c-CD<sub>3</sub>** (Scheme 4b). This value possibly suggests that the cleavage of C-H bonds is the rate-determining step.



**Scheme 4** H/D exchange, KIE and control experiments.

Next, we performed a series of control experiments *e.g.* addition of a stoichiometric amount of a radical scavenger such as TEMPO (1 eq.), which drastically reduces the yield of **2a**, which further reduced to 14% when 2 equiv. of TEMPO was employed (Scheme 4c). Although there is no adduct possible to isolate from the mixture, the present result suggests that the possibility of the SET pathway may also to be considered. In addition, we have also carried out the reaction with a stoichiometric amount of Co(III) to gain insight into the possibility of Co(III) or Co(IV) intermediates involved in the catalytic cycle with and without  $\text{Ag}_2\text{CO}_3$ . In line with radical experiments, 1 eq. of  $\text{Co}^{\text{III}}(\text{acac})_3$  without silver carbonate gave 14% of **2a** compared to a 75% mass of **2a** which was isolated with silver carbonate. These results indicate that Co(IV) was involved in reductive elimination instead of Co(III) (scheme 4d).

Based on the control experiments and previous reports on  $\beta\text{-C}(\text{sp}^3)\text{-H}$  bond activation,<sup>17</sup> we propose the plausible mechanism as shown in Scheme 5. Initial oxidation of Co(II) to Co(III) instigated by  $\text{Ag}^+$  (confirmed by UV-Vis spectra),<sup>20</sup> which subsequently coordinated with **1a** *via* *N,N*-coordination (initial deprotonation possibly by silver carbonate) led to intermediate **A**. Then, carboxylate/carbonate assisted deprotonation provides cobaltacycle **B**. Co(III) intermediate **B** coordinates with CO followed by insertion into the C-Co(III), which gave the





Scheme 5 Proposed mechanism.

intermediate **C**, which may either undergo reductive elimination to Co(I) and reoxidized by silver to active Co(III) species as depicted in path a.<sup>16a-g</sup> Alternatively, intermediate **C** will undergo one electron oxidation to Co(IV), which will undergo reductive elimination to **2a** and regenerate Co(II) (path b). At the same time, one may also consider that intermediate **B** will undergo one electron oxidation to **C'** which then subsequently insert CO between Co–C and lead to **D** (path c), which further undergoes reductive elimination. Although the final solution cannot be given for the mechanism at this stage, control experiments suggest that path b or c may be favoured over path a.

To validate the synthetic utility of this method, we have performed a two ring opening reaction with **1a** to obtain 1,4-dicarbonyl compound **3** and 1,4-dicarboxylic acid **4** in good yields under the standard reaction conditions (Scheme 6).

## Conclusions

We have developed a new protocol for cobalt catalyzed site-selective carbonylation of unactivated C(sp<sup>3</sup>)–H bonds under atmospheric CO pressure to access various succinimide derivatives that are active against seizures (anticonvulsant ethosuximide). Our initial mechanistic investigation reveals that the involvement of a one electron process operated in the catalytic cycle and the reaction may proceed through Co(IV) to Co(II) (Scheme 5, path b or c). Studies to further extend this new reactivity to develop new medicinal compounds and materials are

currently underway. Further understanding of the mechanism including the SET process, isolation of stoichiometric intermediates is presently on going in our laboratory.

## Acknowledgements

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Scheme 6 Synthetic applications.





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- 22 See notes for more information.†
- 23 Catalytic carbonylation was performed using recycled silver carbonate, which resulted in 83% isolated yield of succinimide **2a** under the standard reaction conditions.

