Catalysis Science & Technology

PAPER

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Cite this: *Catal. Sci. Technol.*, 2018, **8**, 5963

Site-selective C–H bond carbonylation with CO_2 and cobalt-catalysis†

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Received 4th October 2018,
Accepted 22nd October 2018

DOI: 10.1039/c8cy02060d

rsc.li/catalysis

Utilization of anthropogenic greenhouse gas CO_2 for catalytic C–C bond formation *via* conversion to essentially valuable C1 synthons like CO is very challenging. The requirement of an efficient catalyst that has the ability to convert CO_2 into CO and activate inert C–H bonds is the bottleneck. We herein demonstrate a tandem approach accomplished in a two-chamber system for efficient fluoride-mediated generation of CO from CO_2 using disilane as a deoxygenating reagent and utilization of the *in situ*-produced CO gas for C–H bond carbonylation using earth-abundant cobalt catalysts. The ease of handling CO_2 gas at atmospheric pressure allows us to prepare ^{13}C labelled compounds which are otherwise difficult to achieve. The procedure developed makes it possible to utilize CO_2 as a CO source, which can be widely applied as a C1 synthon that can be incorporated between C–H and N–H bonds of aromatic, hetero-aromatic and aliphatic carboxamides for the synthesis of various cyclic imides including spirocycles in a site-selective fashion. The late-stage derivatization of a well-known angiotensin receptor blocker (ARB), Telmisartan, and a well-known drug for very low-density lipoproteins (VLDLs), Gemfibrozil, is demonstrated. Further, to showcase the generality of the reaction, various pharmacologically important and privileged scaffolds like xanthone, coumarin and isatin have been synthesized with CO_2 under atmospheric pressure.

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Introduction

Production of value-added building blocks such as alcohols, aldehydes and carboxylic acids by utilizing most abundant sources is a challenging task in synthetic organic chemistry.[1–4] In contrast to the traditional synthesis, atom-efficient carbonylation using diatomic CO gas as a C1 source is a widely practiced process for the production of oxidized hydrocarbons in both academia and industry.[5–8] However, fundamental drawbacks associated with CO such as flammability, toxicity and the requirement of high-pressure necessitate precautionary steps in its handling.[9] To circumvent this problem, CO surrogates such as formates, aldehydes, metal carbonyls, *etc.* have been employed in lieu of the poisonous diatomic gas.[10,11] Incidentally, the scope of these reactions is too narrow due to the release of additional non-innocent molecules along with the *in situ* generated CO. Alternatively, the abundant and non-flammable greenhouse gas such as CO_2 can be used instead of toxic CO, provided that effective cleavage of the carbon–oxygen (C═O) bond can be achieved.[12–16] In this regard, notable advances have been achieved through photo- as well as electrochemical methods for the conversion of CO_2 to CO.[17–19] It should be noted however that the catalytic systems in these reactions are not combined with classical catalytic carbonylations due to operational complexities. In fact, the optimization is far more challenging.

To achieve an effective carbonylation by integrating *in situ* generated CO from CO_2 or its surrogates, Skrydstrup and co-workers elegantly demonstrated carbonylative cross coupling reactions in a two-chamber system using COware, where in one chamber CO is released and in the other chamber CO is consumed (Fig. 1A).[20] To achieve such a process, the carbonylation has to occur with atmospheric CO gas. In contrast, direct carbonylation of the C–H bond can be much more elegant provided that the catalyst has the ability to activate inert C–H bonds and bind to π-acidic CO.[21] In this regard, Murahashi reported perhaps the first catalytic C–H bond carbonylation of benzaldimine using low-valent cobalt under high CO pressure and high temperature.[22] Recently, Daugulis reported the first C–H bond carbonylation of arenes catalyzed by high-valent cobalt(III) using CO at atmospheric pressure and room temperature (Fig. 1B).[23] Very recently, Sundararaju,[24] Gaunt[25] and Lei[26] independently developed cobalt-catalyzed C(sp^3)–H bond carbonylation using atmospheric CO to access various bio-active succinimide derivatives (Fig. 1B). Based on these results and the literature precedent,[27–31] we sought to couple reduction of CO_2 with C–H bond activation for direct carbonylation under cobalt catalysis.[23–26] To realize

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† Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data for all new compounds (^1H NMR, ^{13}C NMR, and HRMS), including images of NMR spectra. See DOI: 10.1039/c8cy02060d

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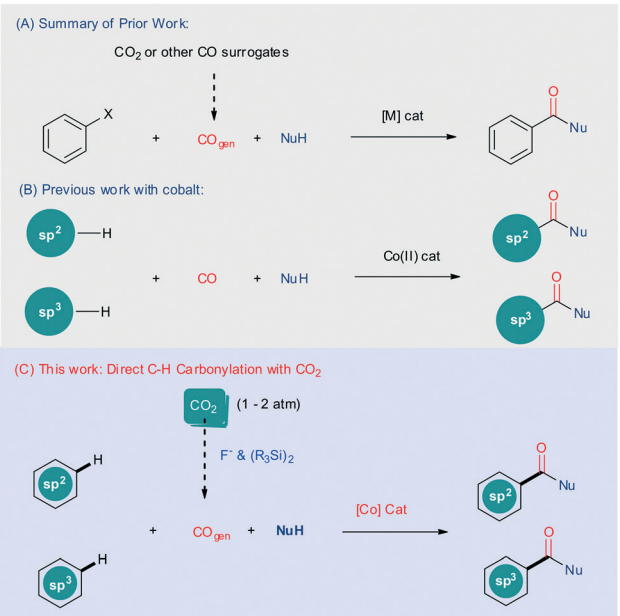
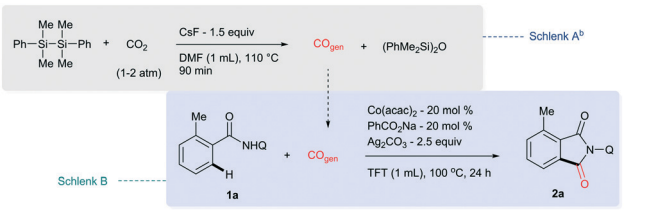


Fig. 1 Overview of catalytic C–H carbonylation.

Table 1 Optimization studies and control experiments[a]



Entry	Change in conditions	Yield[c] (%)
1	None	78
2	Chlorobenzene instead of TFT as a solvent	60
3	1 equiv. of $PhCO_2Na$ used	32
4	$Mn(OAc)_3{\cdot}2H_2O$ instead of Ag_2CO_3	30
5	No cobalt	n.d.
6	No CO_2 in chamber A	n.d.
7	10 mol% of [Co] used	64
8	$Co(acac)_3$ was used without $PhCO_2Na$	70

[a] All reactions were performed in the 0.3 mmol scale using **1a** as a limiting reagent. [b] 1.5 equivalents of disilane were used with respect to **1a**. [c] Isolated yield of **2a**; Q = 8-quinoline; TFT = α,α,α-trifluorotoluene.

this goal, we began our investigations in a two chamber system, wherein CO is released in one chamber with an appropriate reductant in the presence of fluoride and the released CO is consumed in the second chamber for C–H bond carbonylation, which is catalyzed by Co(III) (Fig. 1C). Indeed, we have achieved site-selective C(sp^2)–H and C(sp^3)–H bond carbonylation efficiently using the stated protocol, yielding phthalimide and succinimide derivatives in good-to-excellent yields.

Results and discussion

To begin with, we wanted to consider a known reaction that delivers CO from CO_2 for adaptation to a two-chamber protocol for C–H bond carbonylation (Table 1). The reduction of CO_2 by 1,1,2,2-tetramethyl-1,2-diphenylsilane at 1–2 atmospheric pressure is one such reaction that is well known to produce CO,[31] *cf.* Table 1. We, therefore, utilized this process for generation of CO in one chamber. The CO released in one chamber, *i.e.*, A, was carried forward to the second chamber, *i.e.*, B, in which C–H bond carbonylation of benzamides is accomplished with a Co-catalyst, *cf.* Table 1. To start with, 8-aminoquinoline substituted benzamide was employed as a representative substrate and carbonylation was investigated using CO_2 as a CO source in the two-chamber setup. The carbonylation was conducted in α,α,α-trifluorotoluene as the solvent at 100 °C for 24 h using the catalytic system that comprised of $Co(acac)_2$ (20 mol%), $PhCO_2Na$ (20 mol%) and Ag_2CO_3 (2.5 equiv.). Remarkably, the formation of expected phthalimide **2a** occurred in a facile manner leading to an isolation of the product in 78% (Table 1, entry 1). When chlorobenzene was used as the solvent in place of TFT, a rather lower yield of **2a** was obtained (entry 2). Increasing the amount of base proved to be deleterious to the product formation (entry 3). Changing the oxidant from Ag(I) to Mn(III) dramatically reduced the yield of phthalimide **2a** (entry 4). Based on control experiments, we found that the cobalt and CO_2 are mandatory for the carbonylation to proceed (entries 5 and 6). Reduction in the catalyst loading or usage of Co(III) as a catalyst without any additional carboxylate ligand provided results (entries 7–8) lower than those of the initial experiment (entry 1). Overall, our optimized result is gratifyingly comparable to that reported by Daugulis and co-workers, who employed CO directly for carbonylation of benzamide derivatives.[23,32]

With the optimized conditions, the efficiency of the reaction was further scrutinized for various arylamides substituted at the *para*-position with diverse electron-releasing (–Me, –^{t}Bu, –OMe and –SMe) and withdrawing groups (F, Cl, Br, CF_3 and CO_2Me) (Scheme 1). Notably, only a marginal difference was observed in terms of the reactivity with electron-rich amides yielding rather better yields (**2c–2f**) than the e-poor amides (**2g–2k**). A similar trend was observed for *meta*- as well as *ortho*-substituted amides, indicating a marginal influence of the inductive effect (**2l–2s**). Benzo-annulation as well as heteroarylannulation yielded the products with comparable efficacy (**2t–2u**). Under the same reaction conditions, the carbonylation of sulfonamides led to saccharins (**2v–2z**), albeit in moderate yields. Next, we undertook the challenge of introducing heterocycles, which could potentially poison the catalyst by strongly coordinating to cobalt as depicted in Scheme 1 (bottom). The versatile groups and their presence facilitate their functioning as pharmacological agents. Heterocycles such as pyrimidine and pyridine afforded carbonylated products in excellent yields, but the reaction of 7-azaindole led to the product in a lower yield (**3a–3c**). Substitution of the amide with five membered

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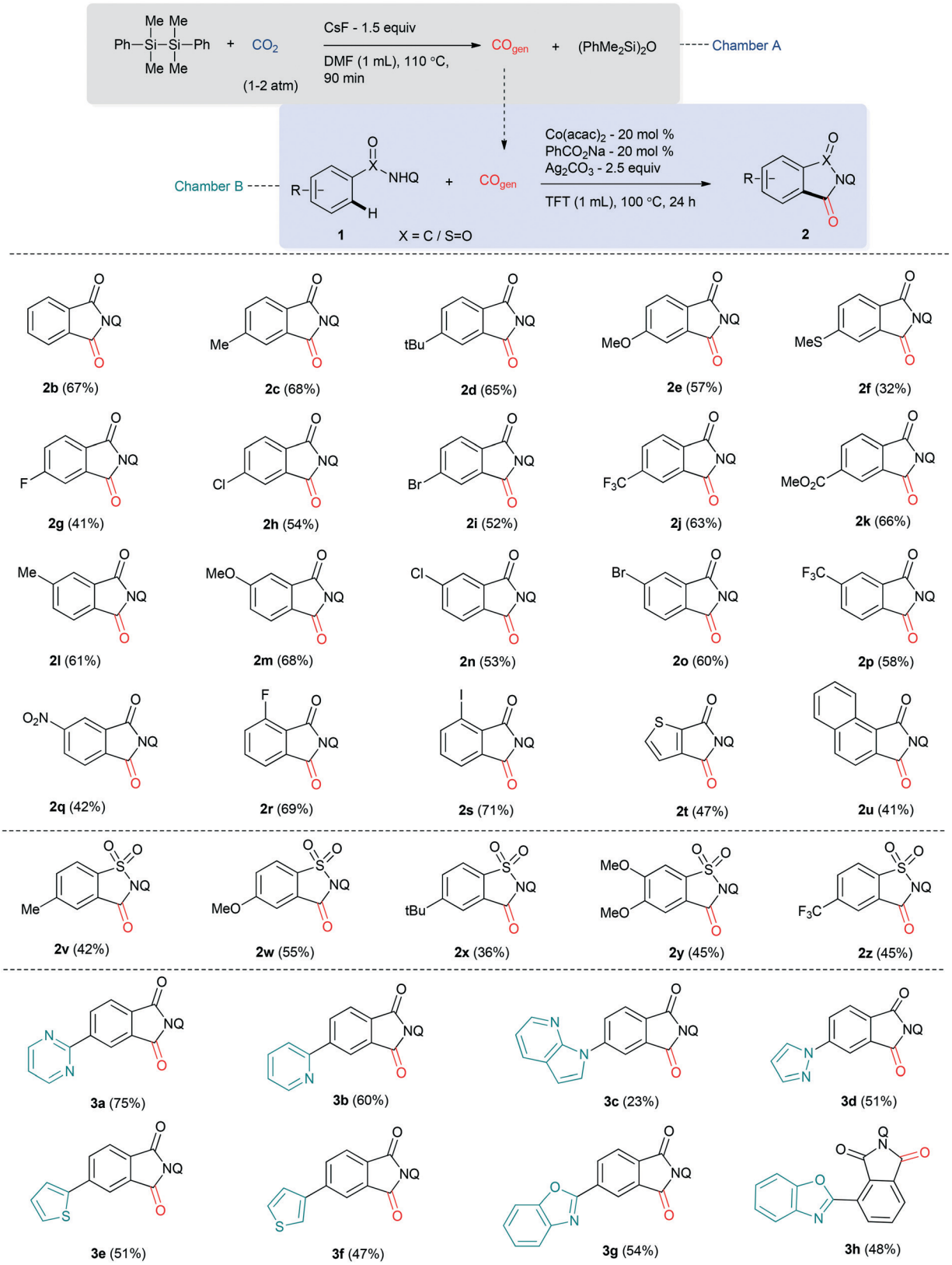

Scheme 1 Cobalt-catalyzed C(sp^2)–H bond carbonylation – scope of carboxamides and sulfonamides.

heterocyclic rings, namely, pyrazole, 2-thiophene and 3-thiophene, did not affect the reactions, leading to products in good yields (**3d–3f**). In the same vein, substitution of benzamides at the *para*-position and at the hindered *ortho*-position with other biologically active scaffolds like oxazoline gave moderate yields of the products (**3g–3h**).

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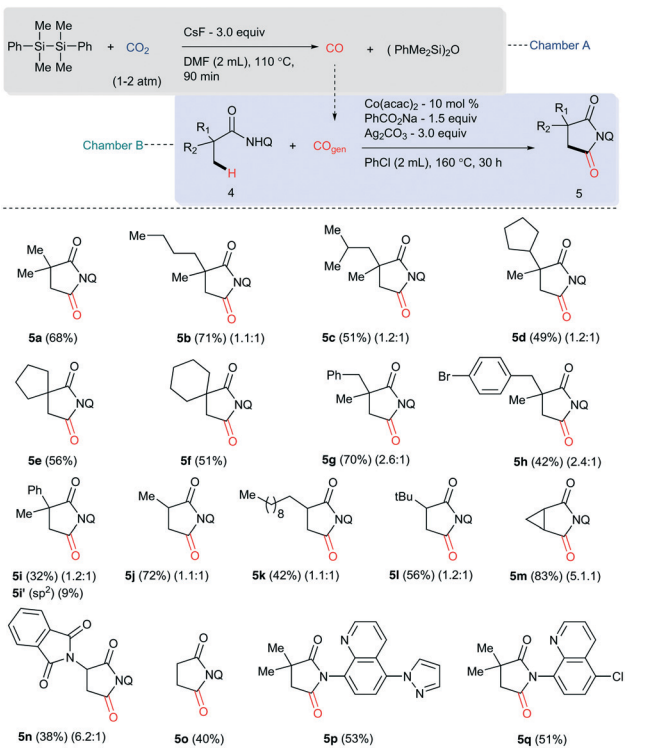
To further expand the scope of the two-chamber protocol, carbonylation was tested for amide containing C(sp^3)–H bonds with a slight modification of the conditions. Accordingly, the reactions were conducted at atmospheric pressure of CO_2 in the presence of 10 mol% $Co(acac)_2$, 1.5 equiv. $PhCO_2Na$ and 3.0 equiv. of Ag_2CO_3 in chlorobenzene for 30 h at 160 °C. The products were isolated in respectable yields for substrates containing quaternary alpha carbon atoms (Scheme 2, **5a–i** & **p–q**). Carbonylation of α,α-disubstituted propanamide with varied substituents that range from dimethyl to alkyl to cycloalkyl groups led to the products in moderate-to-excellent yields (**5a–d**). 5/6-Membered spirocyclic succinimides were accessed in good yields (**5e–f**). Next the reactivity comparison of the internal C(sp^3)–H bond *versus* the terminal C(sp^3)–H bond was investigated. The results suggest that the activation of the terminal β-C–H bond is facile compare to that of the internal benzylic β-C–H bond for direct carbonylation (**5g–h**). Subsequently, we examined the substrates containing the aryl C–H (sp^2-H) bond and aliphatic C–H (sp^3-H) bond. The results suggest that the activation of the C(sp^3)–H bond is favoured over C(sp^2)–H bonds, possibly due to favored 5-membered metallacycles, leading to anticonvulsant 3-methyl-3-phenyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione as the major product (**5i**).

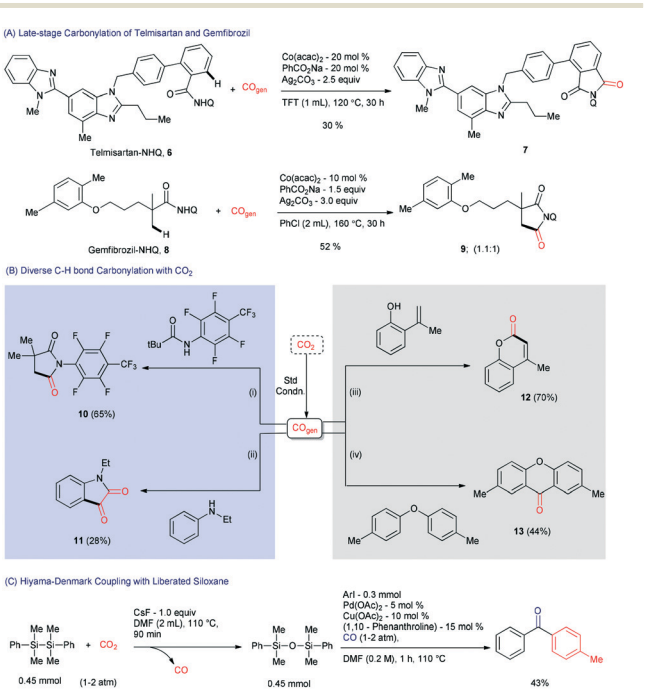
Further extension of the scope towards amide-containing α-monosubstituted propanamides yielded the desired succinimides (**5j–n**) in moderate yields. Moreover, privileged scaffolds like phthalimide protected amino acid (**5n**) could be activated to yield the corresponding product in a respectable yield. Furthermore, challenging unsubstituted propanamides could also be activated due to higher relative strength, yielding the product (**5o**). The reaction of amides substituted with C5-functionalized quinoline proceeded smoothly leading to the products in decent yields (**5p–q**).

To underscore the synthetic utility of this two-chamber methodology, the carbonylation reaction was applied for late-stage functionalization of drug molecules such as Gemfibrozil and Telmisartan (Scheme 3A). The former serves to lower the lipid level and the latter functions as an angiotensin II receptor blocker. The carbonylation of these drugs yielded the corresponding products in 52 and 30% isolated yields, respectively (Scheme 3A). Further diversity of the two-chamber reaction was demonstrated by applying the methodology for the synthesis of various biologically active scaffolds such as succinimide (**10**),[33] isatin (**11**),[34] coumarin (**12**)[35] and xanthone (**13**)[36] in moderate-to-good yields (Scheme 3B). Additionally, the method was proved to be more sustainable by successfully performing Hiyama–Denmark carbonylative cross-coupling between liberated disiloxane from the first chamber and aryl iodide under the reported conditions of the reaction (Scheme 3C).[37]

To gain insights into the reaction mechanism, control experiments and preliminary mechanistic investigations were conducted (Scheme 4).



Scheme 2 Cobalt-catalyzed C(sp^3)–H bond carbonylation. The number in parenthesis is the ratio of diastereomers.



Scheme 3 Diversification. Reaction conditions for the synthesis of **10–13**: for succinimide (**10**): (i) 0.2 mmol of amide, $Pd(OAc)_2$ (10 mol%), AgOAc (2 equiv.), TEMPO (2 equiv.), KH_2PO_4 (2 equiv.), hexane (0.1 M) for 24 h at 130 °C; for isatin (**11**): (ii) 0.3 mmol of amine, $PdCl_2(PPh_3)_2$ (5 mol%), $Cu(OPiv)_2$ (2 equiv.), DMSO/toluene (1 : 1) for 30 h at 100 °C; for coumarin (**12**): (iii) 0.3 mmol of phenol, Cp·Co(CO)I_2 (10 mol%), Ag_2CO_3 (1 equiv.), $Cu(OAc)_2$·H_2O (1 equiv.), *o*-xylene (0.2 M) for 24 h at 30 °C; for xanthone (**13**): (iv) 0.3 mmol of ether, $Pd(OAc)_2$ (5 mol%), $K_2S_2O_8$ (2 equiv.), 2,2,2-trifluoroacetic acid (0.2 M) for 6 h at 50 °C.

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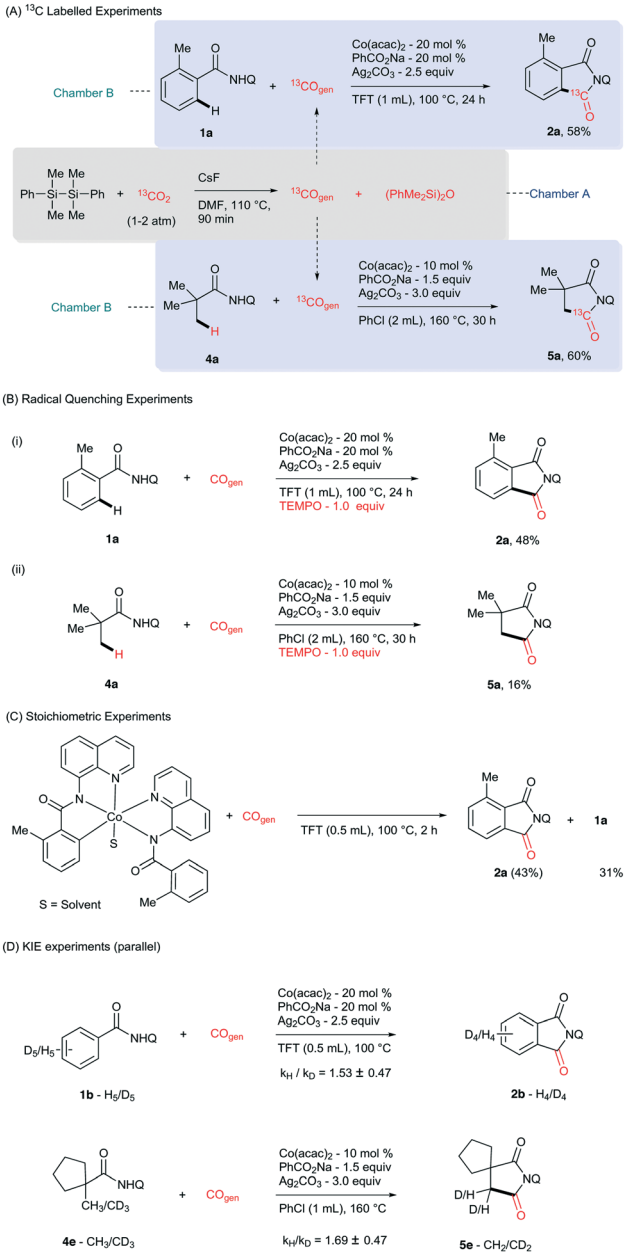

Scheme 4 Mechanistic investigations.

First, validation of the fact that a stoichiometric amount of CO is produced from CO_2 in the two-chamber protocol was established by employing ^{13}C-labelled CO_2 in both sp^2 and sp^3 C–H carbonylations (Scheme 4A). The incorporation of ^{13}C-labelled CO in the respective products was confirmed by ^{13}C NMR and mass spectrometric analysis. This clearly endorses the role of CO_2 as a C-1 source. Second, to examine the involvement of a radical in the reaction pathways, carbonylation reactions were conducted in the presence of 1 equiv. of TEMPO with benzamide and pivalamide under standard reaction conditions, where the former provided the phthalimide product without any reduction in the yield, while the latter led to succinimide in a significantly lower yield. These results suggest the possibility of involvement of the radical in the reaction pathways for C(sp^3)–H bond carbonylation of pivalamide and not with C(sp^2)–H carbonylation of benzamide (Scheme 4B). Third, stoichiometric experiments were conducted with an isolated cobaltacycle for carbonylation using *in situ*-generated CO in α,α,α-trifluorotoluene for 2 h. The expected phthalimide **2a** was obtained in 43% yield along with the recovery of the starting benzamide **1a** in 31% yield. This result suggests that the isolated cobaltacycle is possibly involved in the catalytic cycle (Scheme 4C). Fourth, KIE experiments were conducted in parallel for carbonylation of benzamide (**1b**), aliphatic amide (**4e**), and their deuterium analogues under standard reaction conditions. These experiments provided k_H/k_D values of 1.53 ± 0.47 and 1.69 ± 0.47, respectively. Although the KIE values are low, they are significant enough and hence it is very difficult to conclude at this stage that the C–H activation is not the rate-determining step (Scheme 4D).

Conclusions

In summary, direct conversion of CO_2 to CO, and its incorporation between C–H and N–H bonds of amides to yield useful succinimides, phthalimides, saccharins and their derivatives is compellingly demonstrated by a two-chamber protocol. This unconventional deoxygenation of CO_2 and the insertion of CO between C–H bonds in a simple laboratory setup are heretofore unprecedented. With the developed protocol, direct handling of toxic carbon monoxide is avoided. The site-selective C–H functionalization could be applied to other carbonylation reactions to access diverse valuable products like isatins, coumarins and xanthones. Furthermore, the reaction could be applied for late-stage functionalization of blockbuster drugs such as Telmisartan and Gemfibrozil.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Financial support provided by SERB (EMR2016/000136) to carry out this work is gratefully acknowledged. N. B. and D. K. thank CSIR and IITK for their fellowship. The PK Kelkar Young Faculty Award given to B. S. is gratefully acknowledged. B. S. acknowledges Johnson Matthey for generously providing the precious metals.

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