



Rapid formation of Csp³-Csp³ bonds through copper-catalyzed decarboxylative Csp³-H functionalization

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ARTICLE INFO

Article history:

Received 28 February 2022

Revised 26 April 2022

Accepted 28 April 2022

Available online 1 May 2022

Keywords:

Copper

Cross-coupling

Csp³-H functionalization

Decarboxylation

Csp³-Csp³ bond formation

ABSTRACT

Transition-metal-catalyzed decarboxylative and C-H functionalization strategy for the construction of Csp²-Csp², Csp²-Csp, and Csp²-Csp³ bonds has been extensively studied. However, research surveys of this synthetic strategy for the Csp³-Csp³ bond forming reactions are surprisingly scarce. Herein, we present an efficient approach for the rapid formation of Csp³-Csp³ bond through copper-catalyzed decarboxylative Csp³-H functionalization. The present method should provide a useful access to C3-substituted indole scaffolds with possible biological activities. Mechanistic experiments and DFT calculations supported a dual-Cu(II)-catalytic cycle involving rate-determining decarboxylation in an outer-sphere radical pathway and spin-crossover-promoted C-C bond formation. This strategy offers a promising synthesis method for the construction of Csp³-Csp³ bond in the field of synthetic and pharmaceutical chemistry and extends the number of still limited copper-catalyzed decarboxylative Csp³-Csp³ bond forming reaction.

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Csp³-Csp³ linkages are one of the most basic chemical bonds, which are ubiquitous in a wide range of pharmaceuticals and naturally occurring products [1–3]. The introduction of Csp³ moiety with three-dimensional spread not only increases the lipophilicity, but also the hydrophilicity of the compound. As a consequence, a statistical correlation between the complexity of molecules and clinical success has been proven to be related to the number of Csp³ moieties in a drug candidate [4]. Because of its importance in drug discovery, seeking direct and selective cross-coupling approaches for the construction of Csp³-Csp³ bonds has been of continuous interest in pharmaceutical and organic chemistry. Several classical methods for the construction of Csp³-Csp³ bond have been developed, including: (1) nucleophilic substitution reactions between carbon anions and alkyl halides (Scheme 1Aa) [5]; (2) metal-catalyzed traditional cross-couplings or radical-type cross-couplings between alkyl-metallic reagents such as alkyl-magnesium, -zinc, or -boranes and alkyl halides (Scheme 1B) [6–

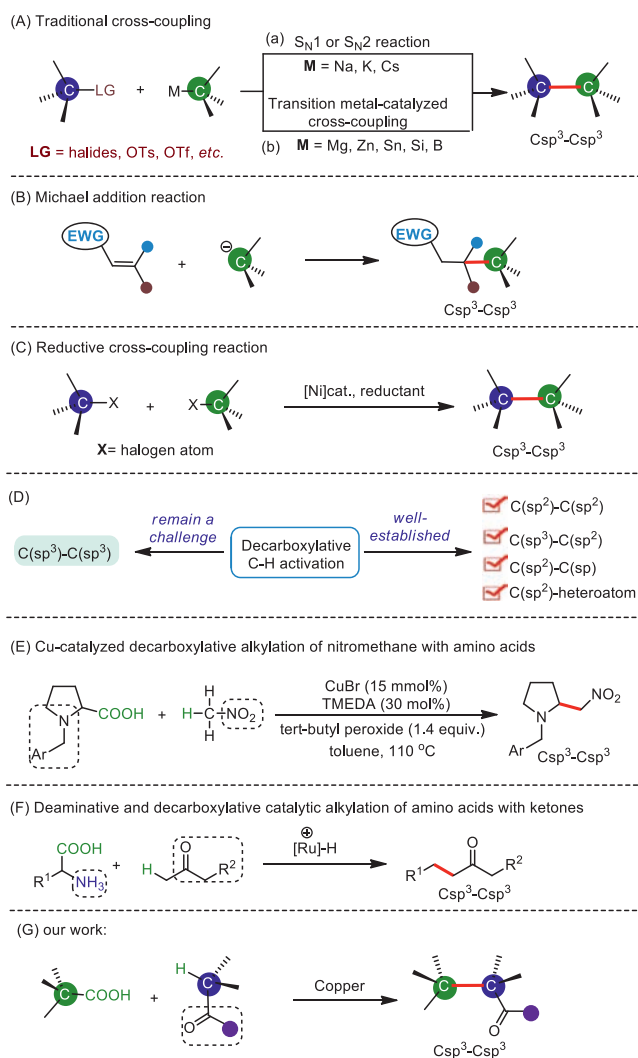
12]; (3) Michael addition reaction between carbon anions and activated olefins (Scheme 1C) [13]; and (4) reductive cross-coupling between two different alkyl halides [14–16]. Despite great achievements have been made in this field, these developed methods generally suffer from unavailability of starting substrates, harsh reaction conditions, and narrow substrate scopes. Therefore, significant space and challenges still exist for the construction of Csp³-Csp³ bond with regard to generality, reaction conditions, and catalytic efficiency.

Carboxylic acids are common chemical raw materials and widely found in natural products, and biologically active molecules [17]. Recently, decarboxylative couplings for the formation of C-C and C-heteroatom bonds has been made great achievements owing to that carboxylic acids are easily prepared, easy to store, stable to air and moisture, and besides that, CO₂ is the sole waste product from the decarboxylative transformation [18–38]. On the other hand, direct activation/functionalization of C-H bonds has emerged as an environmentally friendly and economical alternative to traditional coupling reactions. Over the past few decades, great efforts have been made to develop new strategies for the direct C-H functionalizations [39–46]. The combination of decarboxylation and C-H functionalization strategy for the construction

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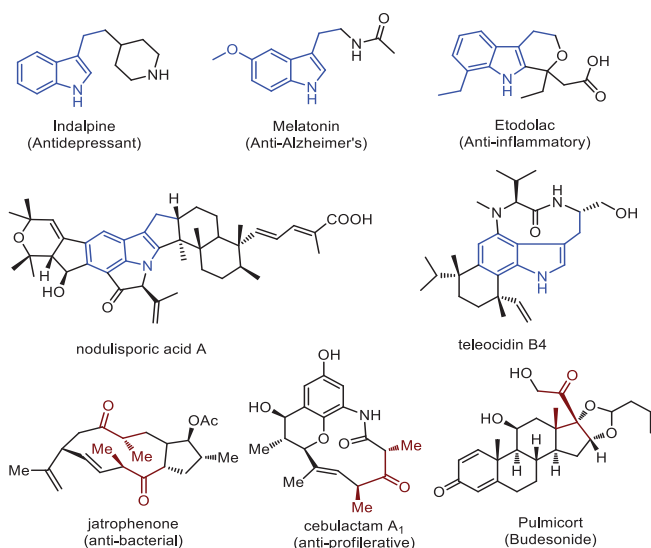
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Scheme 1. Strategies for Csp³-Csp³ bond formation.

of C-C bond, which possesses the common advantages of both, has been demonstrated as a powerful and convenient synthetic tool in organic synthesis. In this respect, most of these reactions are mainly focused on the construction of Csp²-Csp² bond, Csp²-Csp bond, and Csp²-Csp³ bond [47–53]. However, research surveys of this synthetic strategy for the Csp³-Csp³ bond forming reactions are surprisingly scarce. This is probably due to the following reasons: (1) The R-[M] species formed from aliphatic carboxylic acids is usually not stable enough, thus is prone to undergo self-coupling reaction or other side reactions; (2) Csp³-H bonds are less polar, thus have weaker coordination to metal catalysts, making them difficult to be activated; (3) Csp³-H bonds widely exist in one molecule, making the selective cleavage difficult. However, there are still sporadic reports of Csp³-Csp³ bond construction based on decarboxylative and C-H functionalization strategy. In 2009, Li and Liang reported the first CuBr-catalyzed decarboxylative Csp³-Csp³ bond coupling reaction using α -amino acids as starting materials [54]. In 2013, Yi and co-workers developed a novel and efficient Ru-catalyzed alkylation method using readily available amino acid substrates as a bio-based alkylation reagent [55]. Therefore, there is still plenty of room to develop more efficient decarboxylative and C-H functionalization strategies for the construction of Csp³-Csp³ bond using aliphatic carboxylic acids as alkylating reagents.

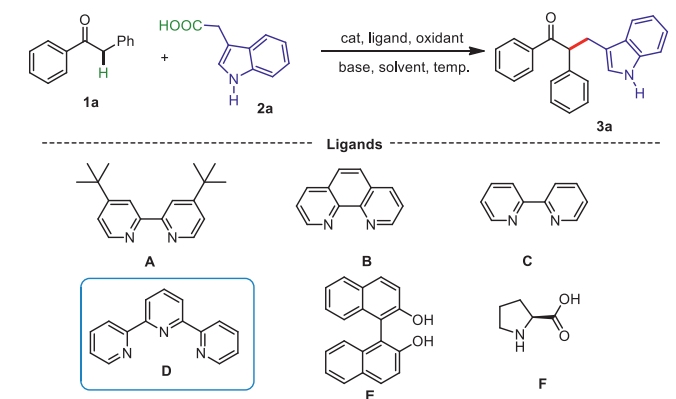
Indole is a privileged fragment, serving as an important building block in the construction of pharmaceuticals, natural products,

Scheme 2. C3-substituted indole and α,α -di-substituted ketone skeletons in natural products and biological molecules.

and functional materials [56]. Especially, the C3-substituted indole derivatives widely occur in natural products and biologically active molecules, such as antidepressant, anti-Alzheimer, and anti-inflammatory (Scheme 2) [57–60]. In addition, branched α,α -di-substituted ketones are also an important class of bioactive functional units and synthetic building blocks in multi-step organic synthesis (Scheme 2) [61–63]. We envisaged that combining the frameworks of C3-substituted indoles and α,α -di-substituted ketones might yield valuable substrates for the synthesis of biologically active compounds with different structural features from the two units separately. Inspired and encouraged by these excellent works of decarboxylative and C-H functionalization, we herein report a novel and efficient approach for the rapid construction of Csp³-Csp³ bonds through copper-catalyzed decarboxylative Csp³-H functionalization strategy between ketones and 3-indoleacetic acids (Scheme 1G).

We commenced our study by examining the reaction between deoxybenzoin (**1a**) and 2-(1*H*-indol-3-yl)acetic acid (**2a**) to investigate reaction conditions including the optimization of catalysts, ligands, oxidants, solvents, bases, and temperature under a nitrogen atmosphere. As shown in Table 1, six copper catalysts (entries 1–6) were tested at 120 °C in the presence of 0.2 equiv. of 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) (**A**) as the ligand (relative to the amount of **1a**) in DMSO, and Cu(OAc)₂ exhibited the highest reaction activity (entry 1). The reaction could not take place in the absence of a catalyst (entry 7). Next, different solvents including DMF, and NMP were examined, and DMF was found to be the best choice (entry 1 vs. entries 8 and 9). In addition, we compared various oxidants such as KMnO₄, AgOAc, and Ag₂O, and MnO₂ was showed the best result. Only 29% yield of the target product **3a** was obtained in the absence of a oxidant (entry 13). Furthermore, various ligands were screened (entries 1, 13–19), and 2,2':6',2''-terpyridine (TPY) (**D**) exhibited the highest efficiency (entry 17). In order to increase the yield of the reaction, various bases were investigated, and K₃PO₄ was superior to the others (entries 21–24). Finally, the effect of temperature was also investigated (entries 19–21), and the yields reached the maximum when the temperature was 90 °C.

With the optimal reaction conditions in hand, we began to investigate the scope and generality of the copper-catalyzed decarboxylative/Csp³-H functionalization reaction between deoxybenzoins **1** and 3-indoleacetic acids **2**, and the results are summa-

Table 1
Optimization of the reaction conditions.^{a,b}

Entry	Catalyst	Ligand	Oxidant	Solvent	Base	Yield (%) ^b
1	Cu(OAc) ₂	A	MnO ₂	DMSO	None	64
2	Cu(OTf) ₂	A	MnO ₂	DMSO	None	62
3	CuSO ₄	A	MnO ₂	DMSO	None	57
4	CuI	A	MnO ₂	DMSO	None	33
5	CuCl	A	MnO ₂	DMSO	None	32
6	CuBr ₂	A	MnO ₂	DMSO	None	28
7	None	A	MnO ₂	DMSO	None	0
8	Cu(OAc) ₂	A	MnO ₂	DMF	None	42
9	Cu(OAc) ₂	A	MnO ₂	NMP	None	31
10	Cu(OAc) ₂	A	KMnO ₄	DMSO	None	26
11	Cu(OAc) ₂	A	Ag ₂ O	DMSO	None	20
12	Cu(OAc) ₂	A	Ag ₂ O	DMSO	None	23
13	Cu(OAc) ₂	A	None	DMSO	None	29
14	Cu(OAc) ₂	None	MnO ₂	DMSO	None	55
15	Cu(OAc) ₂	B	MnO ₂	DMSO	None	53
16	Cu(OAc) ₂	C	MnO ₂	DMSO	None	51
17	Cu(OAc) ₂	D	MnO ₂	DMSO	None	69
18	Cu(OAc) ₂	E	MnO ₂	DMSO	None	31
19	Cu(OAc) ₂	F	MnO ₂	DMSO	None	46
20	Cu(OAc) ₂	D	MnO ₂	DMSO	Na ₂ CO ₃	71
21	Cu(OAc) ₂	D	MnO ₂	DMSO	Cs ₂ CO ₃	73
22	Cu(OAc) ₂	D	MnO ₂	DMSO	K ₃ PO ₄	83
23	Cu(OAc) ₂	D	MnO ₂	DMSO	K ₂ CO ₃	64
24	Cu(OAc) ₂	D	MnO ₂	DMSO	Et ₃ N	70
25	Cu(OAc) ₂	D	MnO ₂	DMSO	K ₂ CO ₃	92 ^c
26	Cu(OAc) ₂	D	MnO ₂	DMSO	K ₂ CO ₃	71 ^d

^a Reaction conditions: **1a** (0.2 mmol), **2b** (0.4 mmol), catalyst (10 mol%), ligand (10 mol%), oxidant (0.4 mmol), base (0.4 mmol), solvent (2.0 mL), 120 °C, reaction time (0.5 h), under N₂ atmosphere.

^b Isolated yield.

^c At 90 °C.

^d At 60 °C.

rized in Scheme 3. We were pleased to find that diverse deoxybenzoin **1** bearing either electron-donating groups, or electron-withdrawing groups smoothly reacted with 3-indoleacetic acids **2**, affording the corresponding alkylation products in good to excellent yields. The hindrance effect of this decarboxylative/Csp³-H functionalization transformation was not obvious; the deoxybenzoin bearing methyl at different positions could react with 3-indoleacetic acids efficiently (**3e** and **3f**). Notably, a strong electron withdrawing group such as nitro was also tolerated under the reaction standard conditions (**3o**). It should be noted that the electron-effect of the substituted groups in 3-indoleacetic acids including electron-rich, -deficient, and -neutral groups did not display evident difference of reactivity.

Subsequently, the coupling reactions of other ketones such as 1,3-diphenylpropan-1-ones and 1-phenylpropan-2-ones with 3-indoleacetic acids **2** were evaluated in the present transformation (Scheme 4). To our delight, the reaction proceeded well, and afforded the desired products in moderate yield (**5a-5h**). In addition, 1,3-dicarbonyl compounds are also amenable to the reaction,

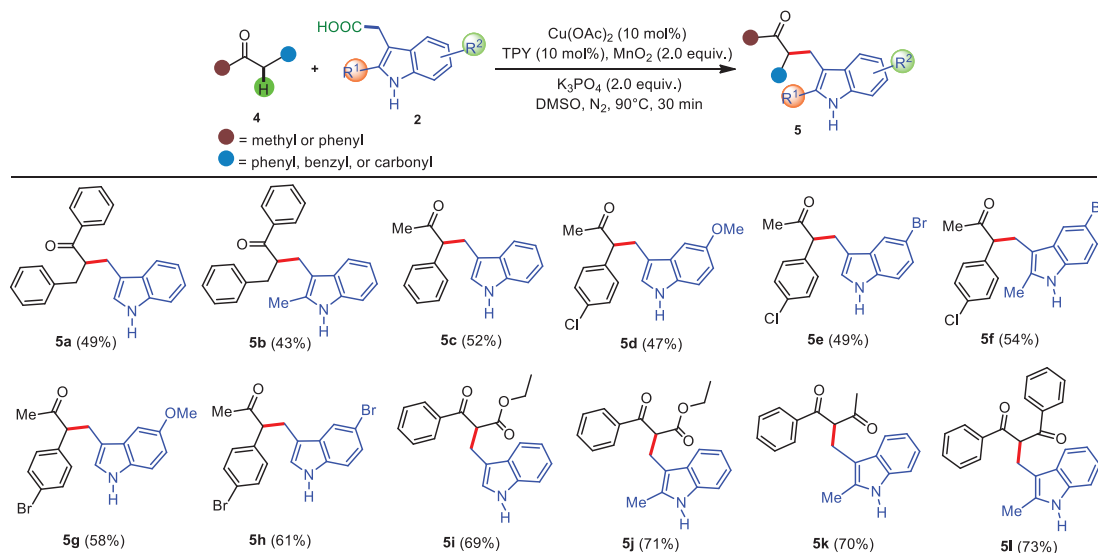
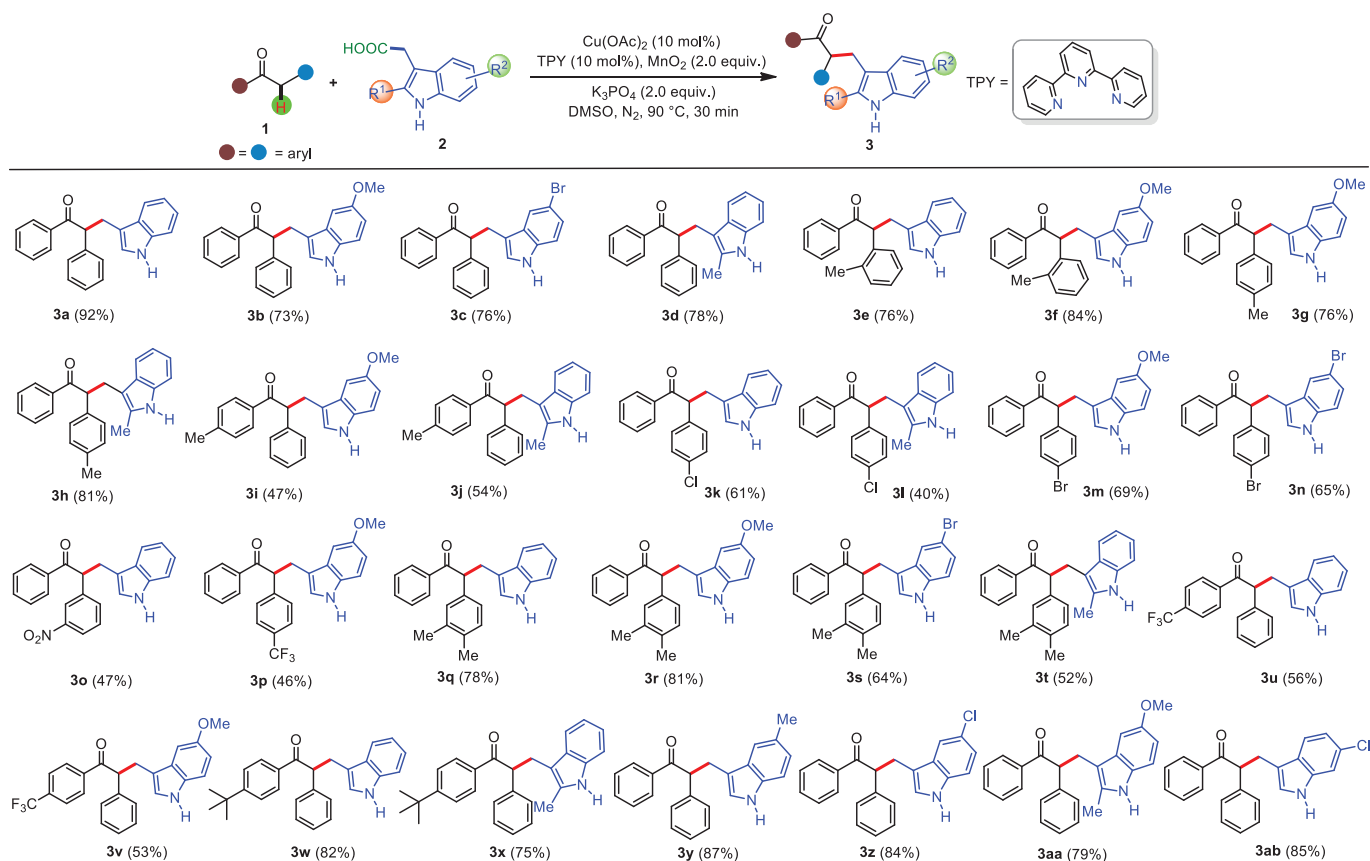
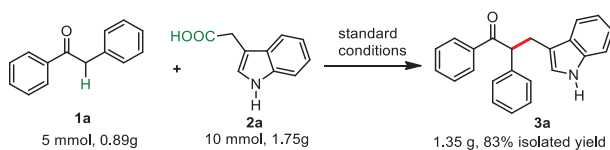
delivering the products (**5i-5l**) in good yields. Furthermore, the present transformation could tolerate some functional groups such as methoxy groups, methyl groups, NO₂ group, CF₃ group, and C-Br bond, which provided great opportunities for further modifications.

Next, gram scale applications for the copper-catalyzed decarboxylative/Csp³-H functionalization reaction between deoxybenzoin **1a** and 3-indoleacetic acid **2a** were investigated. As shown in Scheme 5, the proposed reaction proceeded smoothly under the standard conditions, which could afford 1.35 g of **3a** in 83% yield. Therefore, this copper-catalyzed protocol could be used as a practical approach for the synthesis of alkylating ketones.

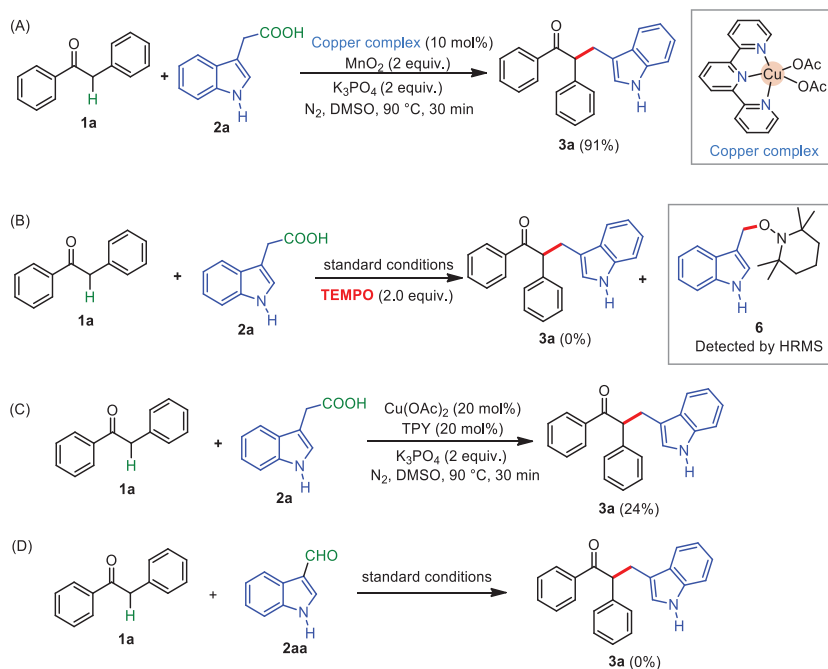
Several control experiments were conducted to investigate the mechanism. First, in order to demonstrate the role of the Cu(II)-based catalyst, the copper complex **9** was synthesized according to the previous report [64]. This copper catalyst **9** was then applied in place of the combination of Cu(OAc)₂ and TPY as the catalyst for the reaction. To our delight, the desired product **3a** was obtained in almost the same yield as that under the standard conditions. This preliminary experimental result indicated that this Cu(II) complex generated *in situ* was the active catalyst in the present transformation (Scheme 6A). When 2 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, a well-known radical capture) was added to the reaction system, the reaction was completely suppressed and a TEMPO-trapped complex **9** was detected by HRMS analysis (see Supporting information for details), thus indicating that a radical process might be involved in the present transformation (Scheme 6B). When the reaction of **1a** with **2a** was carried out in the absence of MnO₂, the present reaction proceeded sluggishly and gave the desired product **3a** in 24% isolated yield only, suggesting that MnO₂ might be used as an oxidant for the copper catalyst (Scheme 6C). Treatment of **1a** with 2-(1*H*-indol-3-yl)acetaldehyde **2aa** under the standard conditions did not afford the product **3a**, indicating **2aa** was not the intermediate in the present transformation (Scheme 6D).

Furthermore, to gain mechanistic insights into this copper-catalyzed Csp³-Csp³ bond forming reaction, a kinetic isotope effect (KIE) study was performed. As shown in Scheme 7, two parallel reactions of deoxybenzoin **1a** and D-**1a** with 3-indoleacetic acid **2a** were carried out, and no kinetic isotope effect ($k_H/k_D = 1.81017/1.01695 = 1.78$) was observed, which suggested that Csp³-H bond cleavage might not take place during the turnover-limiting step [65].

The mechanistic details were further clarified with the aid of computational methods (see Supporting information for more details). The potassium acetate **2a'** can be *in situ* generated from the reaction of **2a** and K₃PO₄ with a free energy change of -19.1 kcal/mol (Scheme S1 in Supporting information), and then undergoes anion exchange with **Int1** to form copper(II) acetate **Int2** with an energy decrease of 5.0 kcal/mol (Fig. 1) [53,66,67]. In contrast to the inner-sphere anionic mechanism [68], **Int2** undergoes decarboxylation *via* an outer-sphere radical mechanism (**TS1**) [69,70], in which no Cu-C bond forms. The decarboxylation has a free energy barrier of 28.7 kcal/mol and generates CO₂, radical **R1** and **Int3**. The radical rebound of **R1** *via* **TS2** to generate **Int4** is fast but is slightly exergonic by only 2.1 kcal/mol, meaning that this step can be reversible at the reaction temperature. This result is consistent with the free radical capture experiment (Scheme 6B). In the next, the C_α-H bond of **1a** is activated by another **Int1** *via* **TS3** to generate copper(II) enolate **Int6** with an energy barrier of 23.2 kcal/mol. Then **R1** is released again from **Int4** *via* **TS2**, and combines with **Int6** to form the triplet complex **Int7-T**. From **Int7-T**, the outer-sphere C-C bond formation *via* the triplet transition state **TS4-T** is less likely as the corresponding overall energy barrier is 32.1 kcal/mol. It was found that the geometry optimization starting from **Int7-T** as singlet minimum spontaneously forms

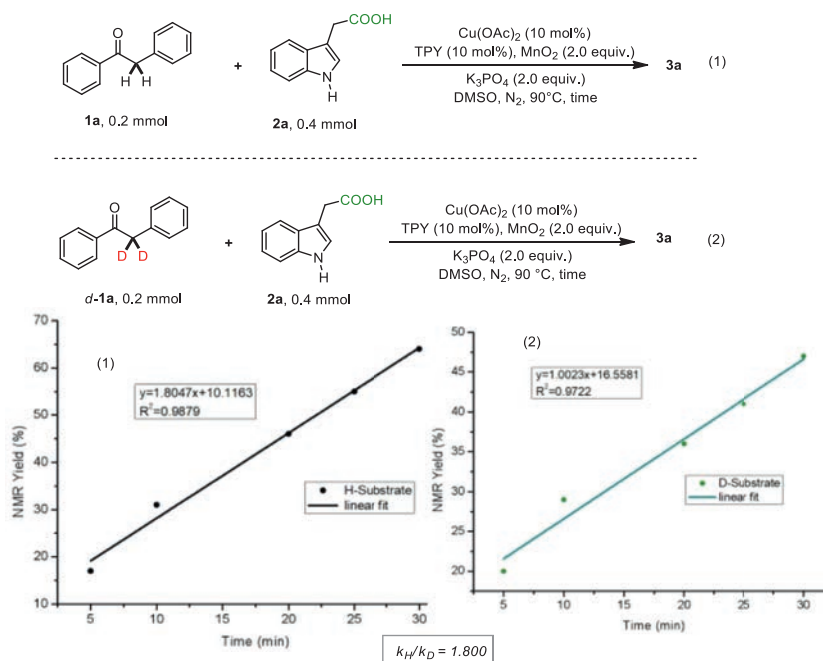
Synthesis of **3a** on a gram scale

the C–C bond to afford **Int8**. Inspired by this phenomenon and our previous works [71,72], a spin-crossover pathway via the minimum energy crossing point **MECP1** that turns the triplet **Int7-T** into singlet **Int8** was proposed for the C–C bond formation (Geometry optimization starting from **MECP1** as singlet minimum also spontaneously formed **Int8**). The electronic energy of **MECP1** is higher than that of **Int7-T** by only 5.2 kcal/mol, indicating that this step is feasible. We also considered C–C reductive elimination from



Scheme 6. Control experiments.

Kinetic isotopic effect studies: parallel experiments



Scheme 7. Mechanistic studies.

a Cu(III) complex but this pathway seems to be less favored according to the estimated energy barrier (about 32.6 kcal/mol, Fig. S4 in Supporting information). The calculated energy profile indicates that the decarboxylation is the rate-determining step, and is in line with the absence of H/D primary kinetic isotope effect (Scheme 7).

Based on these experimental findings, a possible reaction mechanism for this copper-catalyzed decarboxylative cross-coupling pathway was proposed in Scheme 8. First, treatment of $\text{Cu}(\text{OAc})_2$ with TPY produces a chelated Cu(II) complex LCu(II). Next, ligand exchange reaction of LCu(II) with **2** leads to the intermediate **A**. Then, the intermediate **A** is decarboxylated to deliver the ac-

tive copper species **B**, which undergoes homolytic reaction to give the radical **C** and LCu(I). Meanwhile, the substrate **1a** reacts with LCu(II) with the assistance of a base to afford the intermediate Cu(II)-O-enolate **D**. Subsequently, the intermediate **D** reacts with radical **C** to give the desired product **3**, together with a release of the LCu(I) complex. Finally, the LCu(I) complex is oxidized to a catalytic LCu(II) species by MnO_2 to finish the catalytic cycle.

In summary, we have established a new strategy for constructing the Csp³-Csp³ bonds through copper-catalyzed decarboxylative Csp³-H functionalization. A series of potentially biological C3-substituted indole scaffolds could be efficiently and conveniently obtained in moderate and good yields with ex-

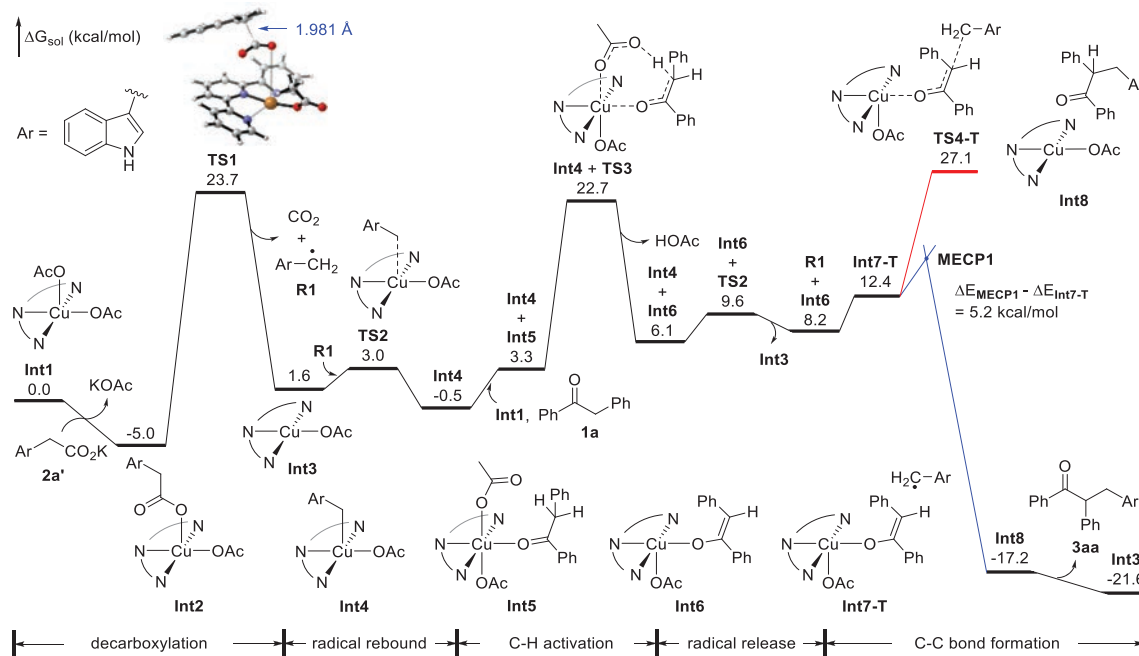
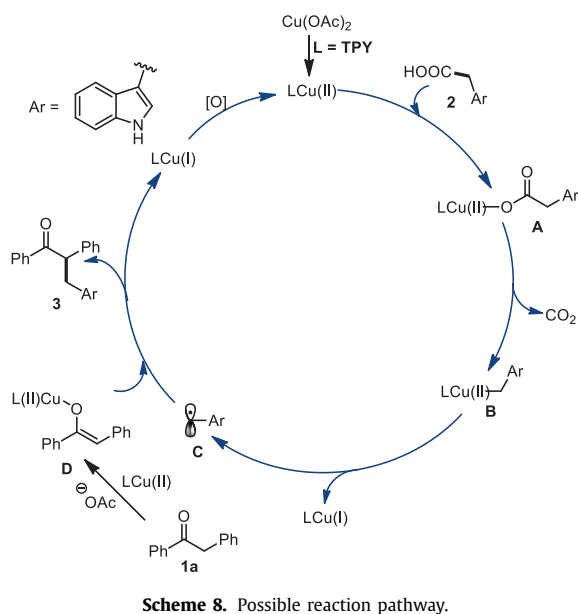


Fig. 1. Calculated relative solution-phase Gibbs free energies of Cu-catalyzed decarboxylative Csp³-Csp³ cross-coupling of deoxybenzoin and 3-indoleacetic acid (kcal/mol).



Scheme 8. Possible reaction pathway.

cellent functional group tolerance. Preliminary mechanistic experiments and DFT calculations suggest that this reaction was likely to proceed *via* Cu(II)-catalyzed rate-determining outer-sphere radical decarboxylation while the C-C bond formation is achieved through a spin-crossover pathway. We anticipate that this strategy will open a new avenue for the formation of Csp³-Csp³ bonds and will also find wide applicability on synthetic and pharmaceutical chemistry. Further investigations on the practical application of this method are ongoing in our laboratory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21702119), Natural Science Foundation of Shandong Province (Nos. ZR2016JL012, ZR2020JQ07), and the Scientific Research Foundation of Qingdao University of Science and Technology (No. 1203043003457).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.04.075.

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