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Copper-catalyzed carbonylative Hiyama-coupling of alkyl bromides and aryl trimethoxysilanes toward arylalkyl ketones

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Ketones, especially arylalkyl ketones, represent an important structural motif with wide applications in various areas. Herein, we report a copper-catalyzed carbonylative cross-coupling reaction between alkyl bromides and arylsilanes for the synthesis of ketones. By employing a commercially available copper salt in combination with an NHC ligand as the catalyst system, a variety of the desired arylalkyl ketones were obtained in moderate to good yields with broad substrate scope and excellent functional group tolerance. This catalytic system overcomes the sluggish oxidative addition of alkyl bromides, effectively suppresses the undesired dehalogenation side reactions, and also minimizes the competing direct Hiyama coupling.

Introduction

Ketones, especially arylalkyl ketones, represent an important structural motif, widely occurring in various natural products, drug molecules, and also bioactive compounds.¹ Compared with traditional synthetic approaches such as oxidation,² condensation,³ and functional group transformations,⁴ transition-metal-catalyzed carbonylative coupling with carbon-nucleophiles has emerged as the mainstream method for ketone synthesis.⁵ This approach offers a modular reaction pathway, high functional group tolerance, and utilizes CO as an inexpensive and readily available C1 unit (Fig. 1a).⁶ However, compared with *N*- and *O*-nucleophiles, challenges in transition metal-catalyzed carbonylative coupling with carbon nucleophiles are still significant: 1) organometallic reagents are generally sensitive to air and water; 2) they require specific storage conditions and exhibit limited functional group tolerance and 3) the process usually requires expensive noble metal catalysts.⁷ Arylsilyl reagents possess several advantages, including low toxicity and environmental

benignity, insensitivity to air and water, and ease of storage.⁸ In this context, carbonylative reaction with organosilicon reagents (carbonylative Hiyama reaction) provides a more favorable and reliable approach for constructing ketones.

In earlier reports on the carbonylative Hiyama reaction, the utilization of precious metal catalysts (such as palladium) has been predominant, with fluorides as the activator (Fig. 1b).⁹ It is evident that precious metal-catalyzed systems typically proceed *via* a two-electron reaction mechanism, showing a clear preference for C(sp²) electrophiles as the substrates.¹⁰ A recent paradigm shift in research focus has been observed, with a notable emphasis placed on the conversion of alkyl reagents into more valuable C(sp³)-rich structures.¹¹ However, post-transition metals exhibit limited activation capabilities for alkyl reagents and suffer from issues such as uncontrollable β -H elimination side reactions.¹² Consequently, the exploration of novel methodologies for carbonylative transformation of alkyl halides is imperative.

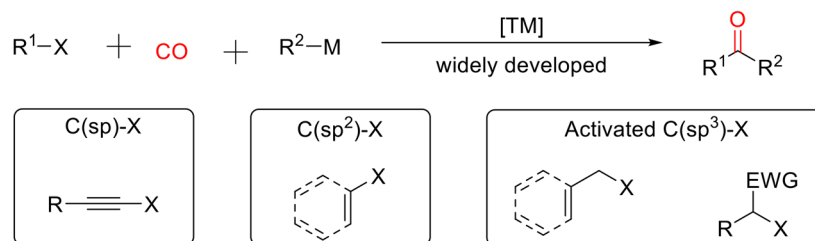
It has been reported that the first-row transition metals, including Fe,¹³ Co,¹⁴ Ni,¹⁵ Cu,¹⁶ and Mn,¹⁷ exhibit excellent catalytic activity towards C(sp³)-electrophiles. Among these, copper catalysts have garnered significant attention due to their abundant reserves, cost-effectiveness, and environmental compatibility. Notably, the single-electron-transfer (SET) mechanism effectively activates inert C(sp³)-X bonds through radical or atom-transfer pathways, fundamentally avoiding β -hydride elimination.¹⁶ Consequently, developing copper-catalyzed carbonylative reactions of alkyl halides presents a highly attractive prospect. In the field of copper-catalyzed carbonylative transformations, studies involving C-C bond formation from alkyl halides are rarely reported. In 2017, Mankad and co-workers reported a copper/manganese co-catalyzed carbonylation of alkyl iodides with arylboronic esters, which relies on a heterobimetallic C-C coupling step between aryl-copper nucleophiles and manganese-acyl species (Fig. 1c).¹⁸ Recently, our group achieved a

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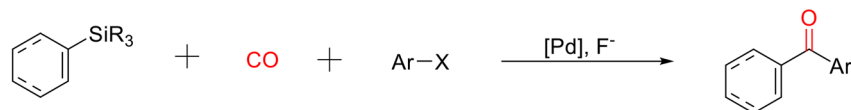
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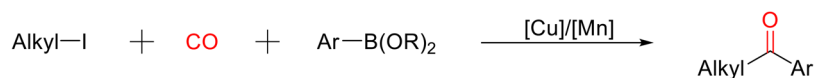
a) Transition metal-catalyzed carbonylative cross-coupling for ketone synthesis



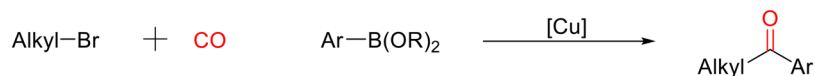
b) Pd-catalyzed carbonylative Hiyama reaction of aryl/alkyl silyl reagents



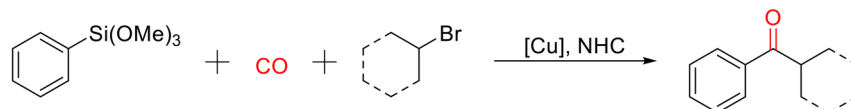
c) Cu/Mn bimetallic catalyst enables carbonylative Suzuki-Miyaura reaction



d) Cu-catalyzed carbonylative Suzuki-Miyaura reaction



e) This work: Cu-catalyzed carbonylative Hiyama reaction



- A cost-effective Cu-catalysis
- High functional group tolerance
- Simple and commercial ligand
- Broad substrate scope

Fig. 1 a) Transition metal-catalyzed carbonylative cross-coupling for ketone synthesis; b) Pd-catalyzed carbonylative Hiyama reaction of aryl/alkyl silyl reagents; c) Cu/Mn bimetallic catalyst enables the carbonylative Suzuki-Miyaura reaction; d) Cu-catalyzed carbonylative Suzuki-Miyaura reaction; e) this work: Cu-catalyzed carbonylative Hiyama reaction.

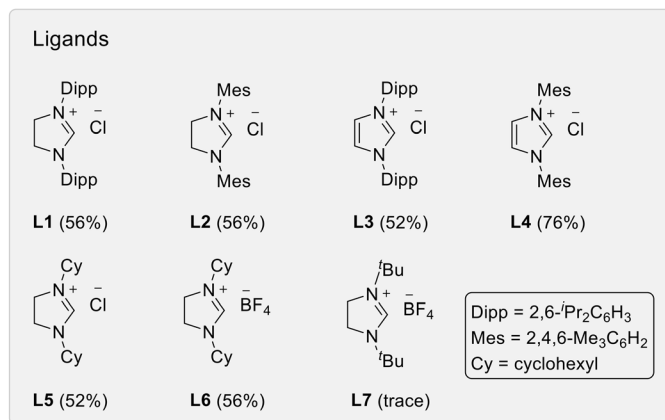
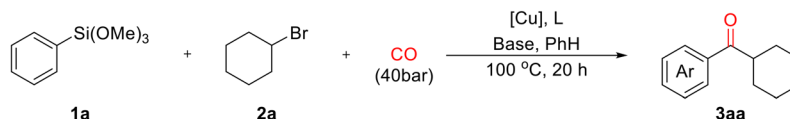
single-copper-catalyzed Suzuki-Miyaura reaction between unactivated alkyl bromides and arylboronic esters (Fig. 1d).¹⁹ Inspired by these achievements, we became interested in developing new copper-catalyzed carbonylation systems using unactivated alkyl bromides and organosilicon reagents (copper-catalyzed carbonylative Hiyama reaction/coupling) (Fig. 1e).

Optimization of the reaction conditions

Initially, the reaction conditions for the carbonylative Hiyama reaction of phenyl trimethoxysilane (**1a**) and cyclohexyl bromide (**2a**) as model substrates were optimized (Fig. 2). When the reaction was carried out at 100 °C under CO pressure (40 bar) in benzene using

CuBr·SMe₂ (5 mol%), 1,10-phen (5 mol%), and NaOMe (1.5 equiv.), only trace amounts of the target product **3aa** was detected by GC-MS after 20 h (Fig. 2, entry 1). Preliminary trials indicated that conventional nitrogen-containing ligands did not afford satisfactory catalytic activity, prompting us to explore NHC-type ligands. Pleasingly, the use of IPr·HCl (**L1**) gave the target product in 56% GC yield (Fig. 2, entry 2). Subsequent screening of the ligands was conducted. When SIMes·HCl (**L4**) was employed, the yield increased to 76% (Fig. 2, entries 3–8). Subsequently, switching to different copper catalysts led to decreased yields (Fig. 2, entries 9–11). Screening of bases revealed that most bases performed poorly in this transformation; only sodium *tert*-butoxide and potassium *tert*-butoxide provided good results, though still inferior to NaOMe (Fig. 2, entries 12–17). Based on the conditions of entry 5, attempts to reduce the





^a Entry	[Cu]	Ligand	Base	Yield (%) ^b
1	CuBr·Me ₂ S	1,10-phen	NaOMe	trace
2	CuBr·Me ₂ S	L1	NaOMe	56
3	CuBr·Me ₂ S	L2	NaOMe	62
4	CuBr·Me ₂ S	L3	NaOMe	52
5	CuBr·Me ₂ S	L4	NaOMe	76
6	CuBr·Me ₂ S	L5	NaOMe	52
7	CuBr·Me ₂ S	L6	NaOMe	56
8	CuBr·Me ₂ S	L7	NaOMe	trace
9	CuBr	L4	NaOMe	65
10	CuBr ₂	L4	NaOMe	59
11	CuOTf	L4	NaOMe	31
12	CuBr·Me ₂ S	L4	NaO ^t Bu	71
13	CuBr·Me ₂ S	L4	KO ^t Bu	67
14	CuBr·Me ₂ S	L4	LiO ^t Bu	N.D.
15	CuBr·Me ₂ S	L4	NaOEt	N.D.
16	CuBr·Me ₂ S	L4	KOMe	7
17	CuBr·Me ₂ S	L4	Na ₂ CO ₃	N.D.
18 ^c	CuBr·Me ₂ S	L4	NaOMe	61
19 ^d	CuBr·Me ₂ S	L4	NaOMe	80
20 ^e	CuBr·Me ₂ S	L4	NaOMe	68
21 ^f	CuBr·Me ₂ S	L4	NaOMe	61
22 ^{c,g}	CuBr·Me ₂ S	L4	NaOMe	80 (82) ^h

Fig. 2 Investigation of the reaction conditions. ^aReaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv.), CO (40 bar), [Cu] (5 mol%), ligand (5 mol%), base (1.5 equiv.), PhH (0.5 mL), 100 °C, 20 h. ^bYield was determined by GC. ^c**2a** (1.5 equiv.). ^dCO (10 bar). ^eCO (5 bar). ^fCO (1 bar) and N₂ (9 bar). ^gToluene (0.5 mL) as the solvent. ^hThe isolated yield of **3aa** is provided in parentheses.

amount of **1a** resulted in lower yields (Fig. 2, entry 18). To increase CO utilization efficiency, various CO pressures were examined (Fig. 2, entries 19–21). The results showed that

reducing the pressure to 10 bar slightly improved the yield to 80%; further reduction in pressure progressively degraded the reaction performance. In view of the high toxicity and



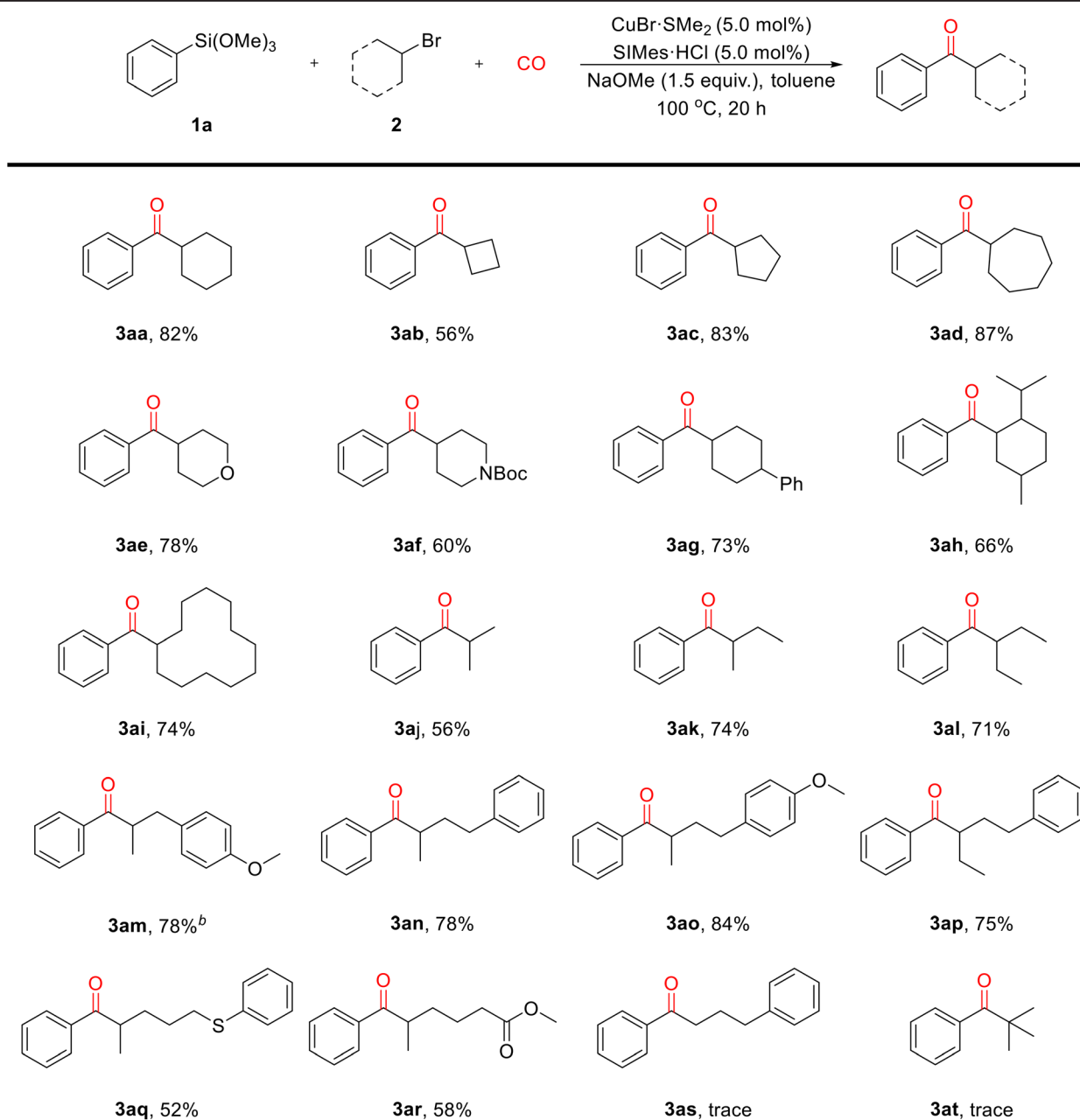
health hazards associated with benzene, toluene was evaluated as an alternative solvent (Fig. 2, entry 22). Toluene delivered comparable performance to benzene, thus establishing the final optimized reaction conditions, which afforded an 82% isolated yield of **3aa**.

Substrate scope and synthetic applications

Following the determination of the optimal reaction conditions, a range of substrates were examined to achieve a more

comprehensive understanding of the reaction's general applicability. Initially, the universality of alkyl bromides under the best reaction conditions was examined (Table 1). Bromides derived from various cyclic structures generally react well. For example, starting from ternary-, quaternary-, and quintuple-membered ring substrates, the corresponding products were obtained in yields of 56%, 83%, and 87%, respectively (**3ab**, **3ac** and **3ad**). Notably, the four-membered ring afforded only a moderate yield, likely due to its rigid geometry, whereas the even more strained three-membered ring failed to deliver the desired product. Epoxyhexyl-substituted alkyl bromides showed

Table 1 Substrate scope for alkyl bromides^a



^a Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), CO (10 bar), CuBr·SMe₂ (5 mol%), SIMes·HCl (5 mol%), NaOMe (1.5 equiv.), toluene (0.5 mL), 100 °C, 20 h. ^b CuBr·SMe₂ (10 mol%) and SIMes·HCl (10 mol%).



no adverse effect on reactivity, and substrates bearing the NBoc group also proceeded smoothly (**3ae** and **3af**). Alkyl bromides substituted with a *para*-phenyl or an *ortho*-isopropyl group furnished the corresponding products in moderate yields (**3ag** and **3ah**). Notably, macrocyclic substrates remained compatible, providing the target product in 74% yield (**3ai**). Subsequent evaluation of acyclic alkyl bromides, such as isopropyl bromide, *sec*-butyl bromide, and 3-bromopentane, delivered the corresponding products in moderate to good yields (**3aj–3al**). Linear alkyl bromides generally exhibited good compatibility, even with those containing sulfur or ester functional groups (**3an–3ar**). Among them, 1-(2-bromopropyl)-4-methoxybenzene displayed poor reactivity, presumably due to the electronic influence of the benzene ring; however, increasing the catalyst and ligand loading to 10 mol% raised the product yield to 78% (**3am**). The reaction demonstrates pronounced selectivity for secondary alkyl bromides, while primary and tertiary alkyl bromides perform poorly (**3as** and **3at**).

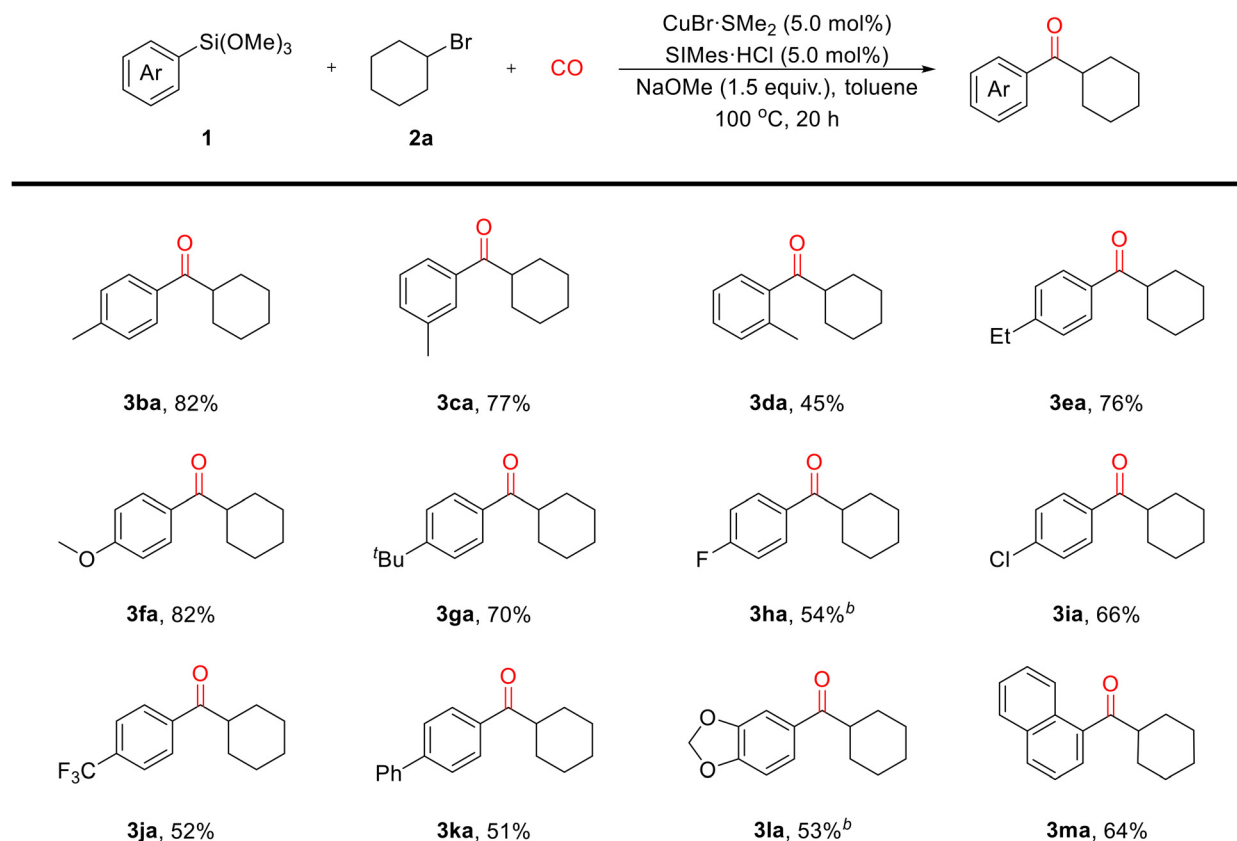
Subsequently, the substrate scope of aryl silanes was systematically investigated (Table 2). Methyl groups introduced at the *para*-, *meta*-, or *ortho*-positions of the aryl ring afforded the corresponding products in yields ranging from 45% to 82% (**3ba–3da**). As hypothesized, the *ortho*-methyl substrate gave a significantly lower yield,

presumably due to steric hindrance. Substrates bearing electron-donating groups (*e.g.*, ethyl, methoxy, and *tert*-butyl) showed little influence on the reaction and delivered favourable yields (**3ea–3ga**). Electron-withdrawing groups (*e.g.*, fluorine, chlorine, and trifluoromethyl) were also compatible, providing moderate yields (**3ha–3ja**). Substrates bearing a phenyl group at the *para*-position of the benzene ring have been shown to yield the corresponding product in a 52% yield (**3ka**). Moreover, the reaction exhibited good tolerance toward oxygen-containing heterocycles and naphthalene-based silanes, giving the respective products in 53% and 64% yields (**3la** and **3ma**). Phenyltrimethylsilane and vinyltrimethoxysilane were also tested here, but no desired product was detected.

Mechanistic investigations

Following the investigation of the substrate scope, studies were initiated to elucidate the reaction mechanism of this carbonylative Hiyama reaction (Fig. 3). Under standard conditions, addition of the radical scavenger TEMPO (3.0 equiv.) completely suppressed the reaction, and products arising from the TEMPO-trapping of alkyl radicals were detected, indicating the involvement of a radical pathway.

Table 2 Substrate scope for arylsilanes^a



^a Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), CO (10 bar), CuBr·SMe₂ (5 mol%), SIMes·HCl (5 mol%), NaOMe (1.5 equiv.), toluene (0.5 mL), 100 °C, 20 h. ^b CuBr·SMe₂ (10 mol%) and SIMes·HCl (10 mol%).



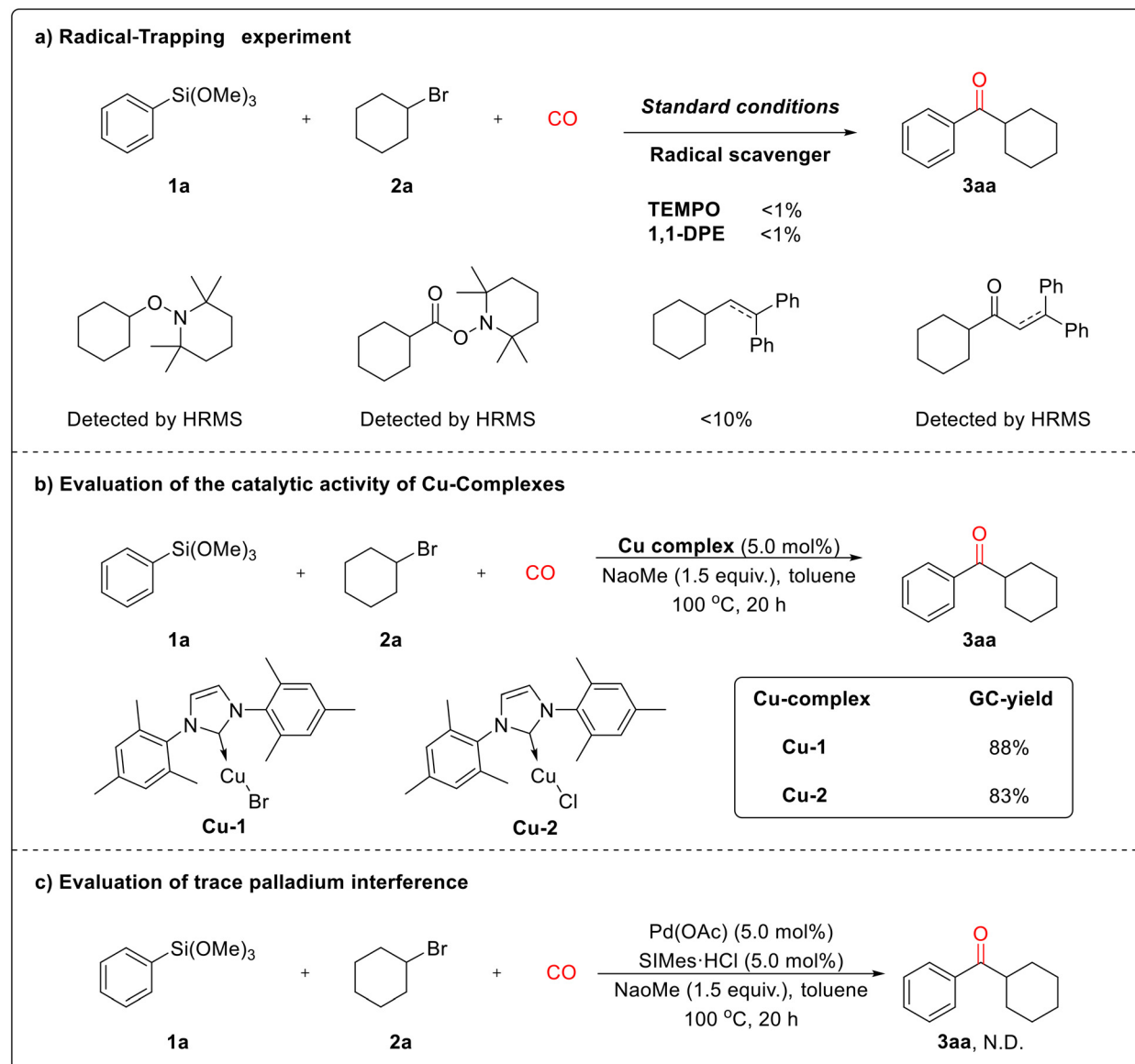


Fig. 3 a) Radical-trapping experiment; b) evaluation of the catalytic activity of Cu complexes; c) evaluation of trace palladium interference.

Similarly, when the radical inhibitor 1,1-diphenylethylene (3.0 equiv.) was added, the reaction proceeded with great difficulty, with both alkyl and acyl radicals being captured. CuBr(SIMes) (**Cu-1**) and CuCl(SIMes) (**Cu-2**) were synthesized and evaluated under the model reaction conditions.²⁰ Replacing the catalyst and ligand with these pre-formed complexes gave higher yields than the *in situ* formed system, suggesting that such species may serve as key catalytic intermediates. Furthermore, replacing the copper catalyst with Pd(OAc)₂ (5 mol%) in the reaction failed to yield the target product, thereby ruling out the influence of trace palladium catalyst residues in commonly used reagents.

Based on the experimental results and relevant literature,^{19,21} a plausible reaction mechanism is proposed as follows (Fig. 4): At the onset of the reaction, the *in situ*-formed Cu-NHC species **A** is converted into the alkoxy-

copper intermediate **B** in the presence of NaOMe. **B** then undergoes transmetalation with the arylsilane to afford the aryl-copper species **C**. Subsequently, **C** reduces the alkyl halide to generate an alkyl radical, while itself being oxidized to the [aryl-Cu-Br] species **D**. Under a CO atmosphere, the alkyl radical captures CO to form an acyl radical, which is intercepted by **D** to give the high-valent copper intermediate **E**. Finally, reductive elimination from **E** delivers the desired carbonylative coupling product and regenerates the catalytic Cu-NHC species **A**, closing the catalytic cycle.

Conclusion

In summary, we have developed a copper-catalyzed carbonylative Hiyama reaction that enables the efficient synthesis of arylalkyl ketones from readily available alkyl



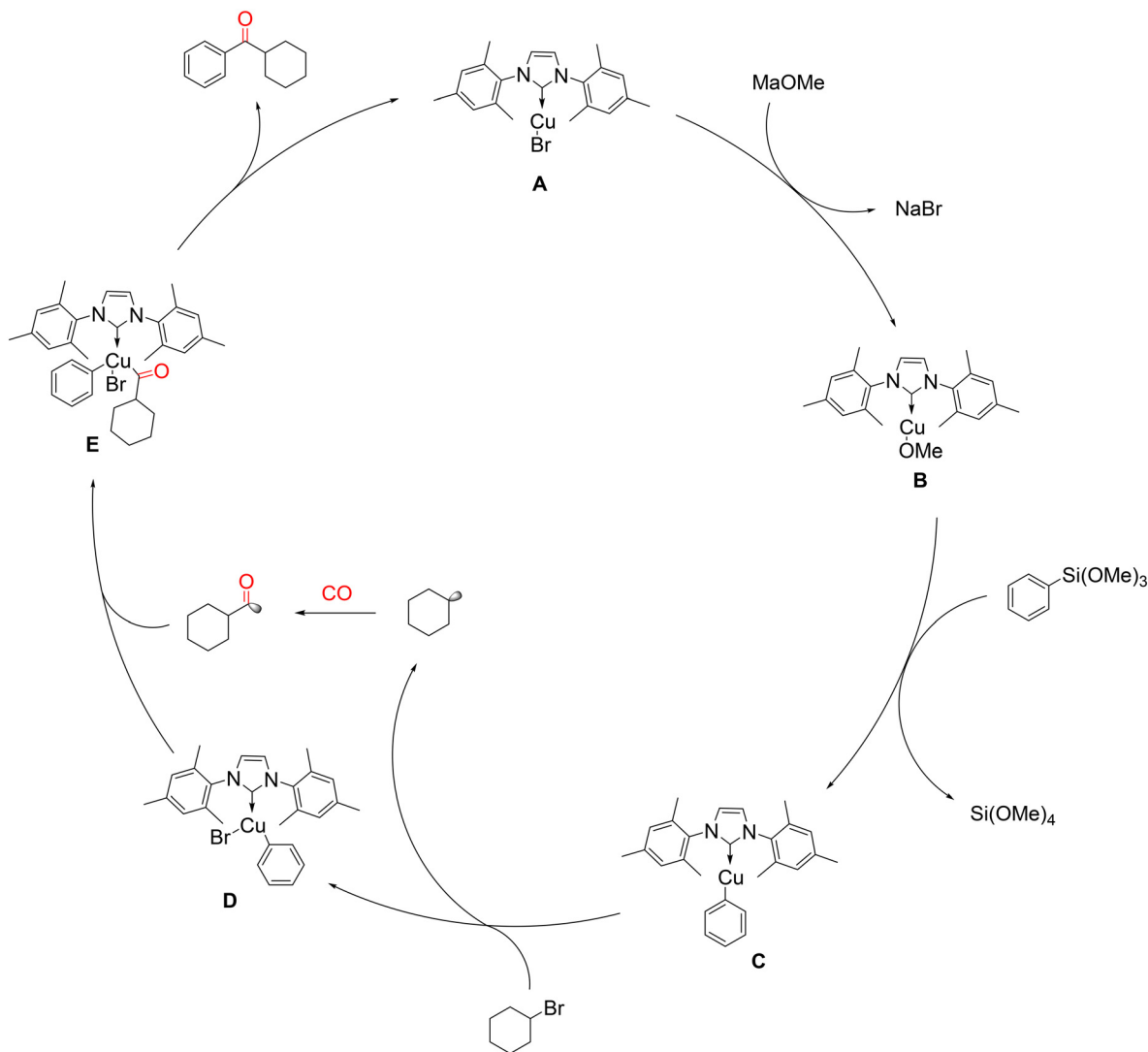


Fig. 4 Proposed mechanism.

bromides and arylsilanes. The reaction exhibits a broad substrate scope and furnishes a diverse range of arylalkyl ketones in moderate to good yields. Moreover, commercially available copper and NHC ligands not only effectively suppress side reactions, including direct Hiyama coupling, reductive dehalogenation and β -hydride elimination, but also play an essential role in promoting the transmetalation of arylsilanes.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI).

Supplementary information is available. See DOI: <https://doi.org/10.1039/d6cy00177g>.

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