Nickel-catalysed carbonylative homologation of aryl iodides

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Homologation is an important organic transformation which extends the carbon chain of a parent molecule, and many procedures have been established. However, although carbonylation reactions are now well developed as valuable methods for the synthesis of carbonyl-containing compounds, studies of carbonylative homologation are limited. Here we report a nickel-catalysed carbonylative homologation of aryl iodides. With molybdenum hexacarbonyl as the solid carbon monoxide source and silane as the deoxygenation reagent, benzylic units can be effectively produced. Various (hetero)arenes can be successfully benzylated and give the corresponding products in moderate to excellent yields.

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Homologation is an important organic transformation for extending the carbon chain of parent molecules, which increases their complexity and also offers the possibility for further transformations. The importance of homologation reactions has been recognized by several named reactions as well, such as Kiliani-Fischer synthesis, Arndt-Eistert reaction, Kowalski ester homologation, Seyferth-Gilbert homologation, and more[1–6].

On the other hand, transition metal-catalyzed carbonylation reactions have experienced tremendous progress since the 1940s[7–14]. Nowadays, carbonylation reactions have emerged as one of the most valuable methods for the synthesis of carbonyl-containing compounds, and many carbonylative procedures have even been industrialized. In particular, the aminohomologation of alkenes has been successfully explored, yielding a domino process consisting of three steps: (1) transition metal-catalyzed hydroformylation of alkenes into the corresponding aldehydes; (2) the aldehyde condensation with amine to give imine/enamine; and (3) transition metal-catalyzed hydrogenation of the imine/enamine intermediate to give the final aliphatic amines[15]. Conversely, carbonylative homologation of aryl halides is still challenging and rarely reported. In the latter case, benzylic units can be produced and used for the benzylation of various substrates.

Concerning the catalysts studied in carbonylation chemistry, expensive palladium and rhodium catalysts together with even more costly phosphine ligands are frequently studied. Nickel, as an abundant and non-expensive metal, has been seldom studied in carbonylative transformation[16–20]. One of the main reasons for this situation is the formation of $Ni(CO)_4$, which is a highly toxic liquid (boiling point = 43 °C). Additionally, $Ni(CO)_4$ has limited reactivity in oxidative addition with substrates, due to the full coordination of CO on the metal center. Based on our previous experience in developing new CO-gas-free carbonylation reactions[21–27], we assume the usage of $Mo(CO)_6$ as a solid CO source could be an ideal option for exploring nickel catalyst in carbonylation chemistry[28,29].

Here we describe a nickel-catalyzed carbonylative homologation of aryl iodides with $Mo(CO)_6$ as the solid carbon monoxide source and silane as the deoxygenation reagent. Various (hetero) arenes can be successfully benzylated and can produce the corresponding products in moderate to excellent yields.

Results

Optimization. In order to study this hypothesis and also the known importance of indole derivatives[30–32], we choose iodobenzene **1a** and N-methyl indole **2a** as the model substrates to establish the catalytic system (Fig. 1). To our delight, when the model substrates were treated with $Mo(CO)_6$ under the catalysis of $Ni(OTf)_2$ and 4,4′-di-tert-butyl-2,2′-bipyridine (dtbbpy) in toluene without external reductant, the desired methylene product 3-benzyl-1-methyl-1H-indole **3aa** was obtained successfully, albeit in a low yield (Table 1, entry 1). Diaryl ketone **4aa** was detected as the major product. Polar solvents such as DMF (dimethylformamide) and MeCN (acetonitrile) were not suitable for this reaction and no carbonylation products could be obtained (for details see Supplementary Table 1). Then we tested a series of reductants in this reaction. Zinc powder and formic acid were inefficient in this catalytic system and no desired product was obtained (Table 1, entry 2; for details see Supplementary Table 2). Silanes turned out to be a suitable hydrogen source, and 38% yield of **3aa** was obtained when Ph_2SiH_2 was used as the reductant (Table 1, entry 7). Increasing the amount of iodobenzene **1a** improved the total conversion and resulted in higher yield of 65% (Table 1, entry 8). Other catalyst precursors such as $NiCl_2$, NiI_2, and $Ni(acac)_2$ were all effective in catalyzing this reaction and produced **3aa** in comparable yields (for details see Supplementary
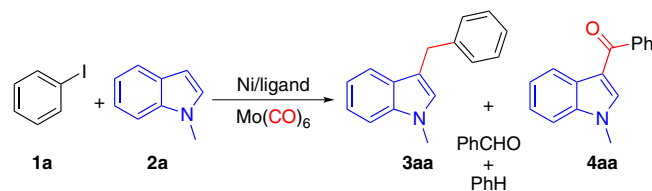
Fig. 1 Model system used for reaction optimization. Conditions used for optimization of the catalyst, ligand, and deoxygenation reagent can be found in Table 1

Table 1 Optimization of the reaction conditions for carbonylative homologation of iodobenzene[a]

Entry	Catalyst	Ligand	[H]	Conv. (%)[b]	Yield 3aa (%)[b]
1	$Ni(OTf)_2$	dtbbpy	–	31	8
2	$Ni(OTf)_2$	dtbbpy	HCO_2H	52	0
3	$Ni(OTf)_2$	dtbbpy	PHMS	75	6
4	$Ni(OTf)_2$	dtbbpy	$HSi(OCH_3)_3$	30	10
5	$Ni(OTf)_2$	dtbbpy	Et_3SiH	53	6
6	$Ni(OTf)_2$	dtbbpy	$PhSiH_3$	37	12
7	$Ni(OTf)_2$	dtbbpy	Ph_2SiH_2	50	38
8[c]	$Ni(OTf)_2$	dtbbpy	Ph_2SiH_2	100	65
9[c]	$NiBr_2$	dtbbpy	Ph_2SiH_2	79	67
10[c]	$NiBr_2$	bpy	Ph_2SiH_2	92	88
11[c]	$NiBr_2$	1,10-phen	Ph_2SiH_2	82	79
12[c]	$NiBr_2$	PPh_3	Ph_2SiH_2	80	79
13[c]	$NiBr_2$	bpy	^iPrOH	42	20
14[c]	$NiBr_2$	bpy	NH_3BH_3	29	23
15[c]	$Ni(OTf)_2$	bpy	Ph_2SiH_2	100	93(91)[d]

dtbbpy 4,4′-di-tert-butyl-2,2′-bipyridine, *bpy* 2,2′-bipyridine, *1,10-phen* 1,10-phenanthroline
[a]Reaction conditions: N-methyl indole (0.5 mmol), iodobenzene (0.5 mmol), [Ni] (5 mol%), ligand (5 mol%), $Mo(CO)_6$ (0.5 mmol), [H] (1.0 mmol), toluene (2 mL), 120 °C, 24 h
[b]Conversion and yield were determined by GC analysis using dodecane as an internal standard
[c]Iodobenzene (0.75 mmol)
[d]Isolated yield

Table 3). A slightly higher yield of 67% was obtained when $NiBr_2$ was used as the catalyst (Table 1, entry 9). Subsequently, the ligand effect was investigated with a series of nitrogen- and phosphine-ligands. To our delight, when 2,2′-bipyridine (bpy) was used as the ligand, the desired product **3aa** was obtained in a high yield of 88% (Table 1, entry 10). Other ligands including 1,10-phenanthroline and PPh_3 were also effective for this transformation, but with lower yields (Table 1, entries 11 and 12, for details see Supplementary Table 4). Screening of the amount of CO and reductant revealed that 0.5 equivalent of $Mo(CO)_6$ and 2 equivalents of Ph_2SiH_2 were the optimal concentrations (see Supplementary Tables 5, 7, 8). Further screening of non-silane-based hydrogen sources such as isopropanol and ammonia borane failed to improve the yields (Table 1, entries 13 and 14, for details see Supplementary Table 6). Considering that $Ni(OTf)_2$ leads to complete conversion of the substrate, we tested it again under our new system and found that $Ni(OTf)_2$/bpy catalyst system provides better yield. The desired product **3aa** was isolated in an excellent yield of 91% (Table 1, entry 15). Notably, benzaldehyde could be detected as well during the optimization process.

Substrate scope. With the optimized reaction conditions in hand (Table 1, entry 15), we examined the substrate scope of this reaction with respect to aryl iodides, and these results are summarized in Fig. 2. Both electron-donating (**3aa-3la**) and electron-
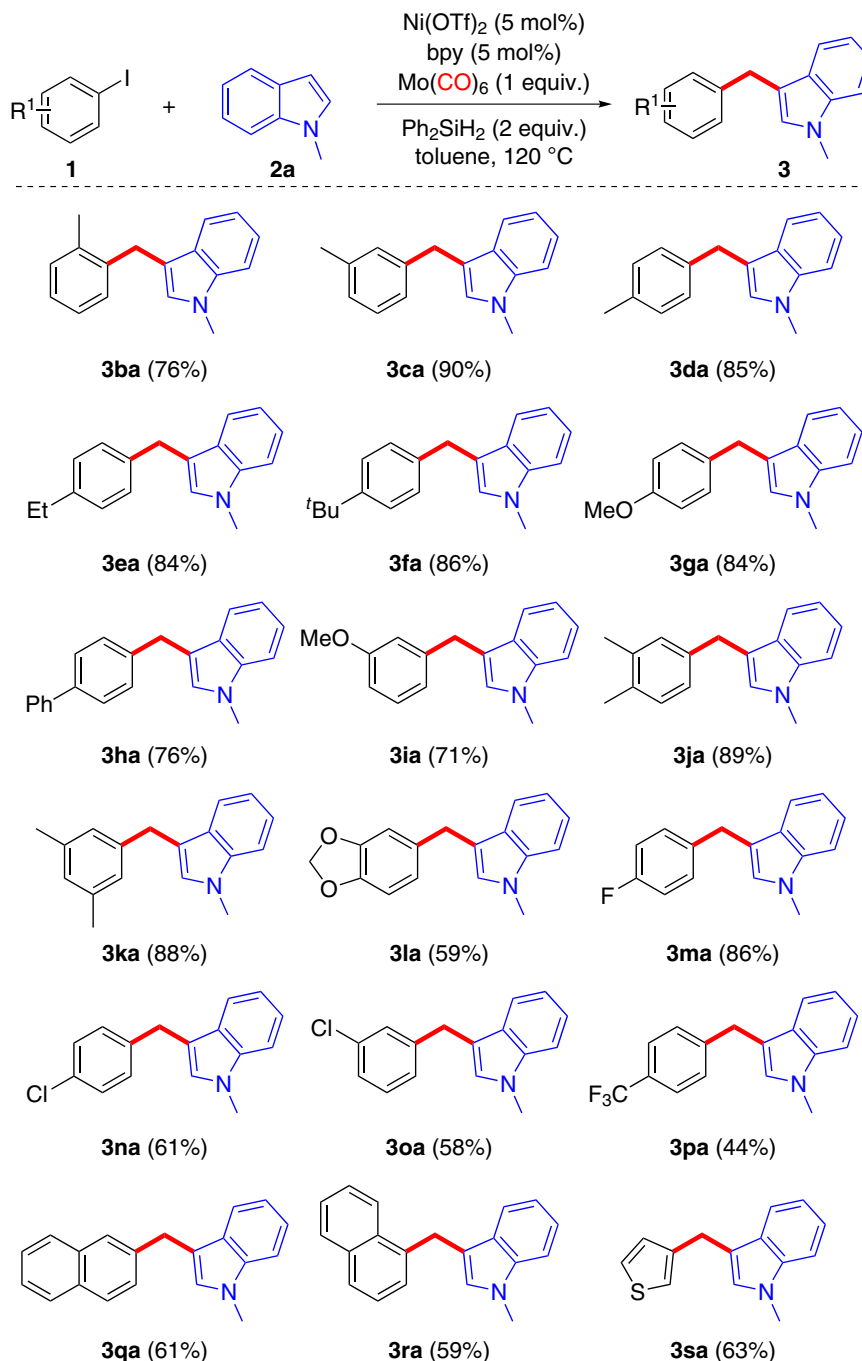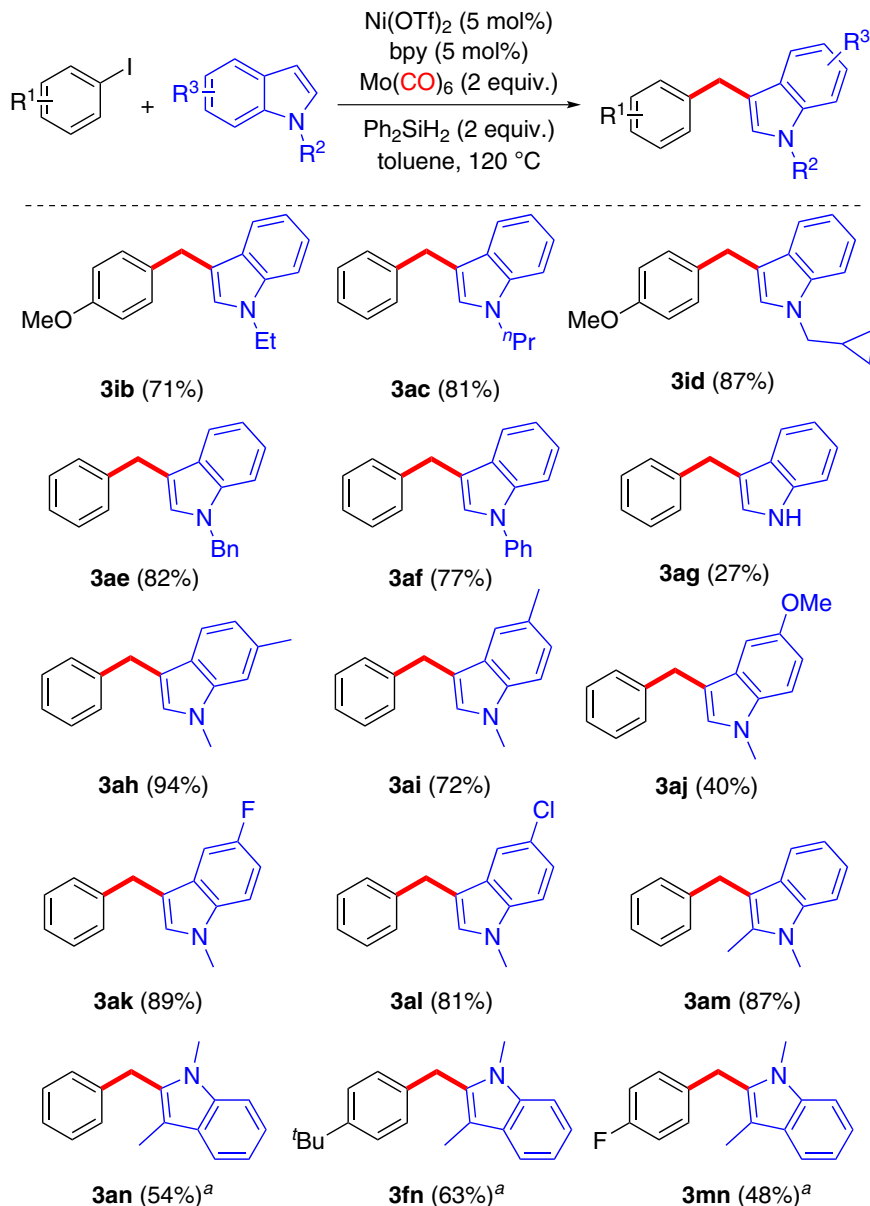
Fig. 2 Carbonylative homologation of aryl iodides. Reaction conditions: *N*-methyl indole (0.5 mmol), aryl iodide (0.75 mmol), Ni(OTf)$_2$ (5 mol%), bpy (5 mol%), Mo(CO)$_6$ (0.5 mmol), Ph$_2$SiH$_2$ (1.0 mmol), toluene (2 mL), 120 °C, 24 h, isolated yield

withdrawing substituents (**3ma**-**3pa**) on iodobenzene were well-tolerated and produced the methylene products in moderate to excellent yields. The electronic property of the substituent played an important role in the reaction yields. Generally, substrates with electron-donating groups gave higher yields than those with electron-withdrawing groups. Steric effect on aryl iodides also affected the reaction yields. For example, *ortho*-methyl iodo-benzene gave a lower yield than *meta*- and *para*-methyl iodo-benzene (**3ba** vs **3ca**, **3da**). Fluoro- and chloro-substituents were compatible in this reaction and produced the desired products in 58–86% yields (**3ma**, **3na**, and **3oa**). In addition to iodobenzene, β- and α-iodo-naphthalene were also subjected to the optimized reaction conditions, and the corresponding products were

conveniently obtained in 61% and 59% yields, respectively (**3qa** and **3ra**). Moreover, heteroaryl iodides such as 3-iodothiophene were tolerated as well, and the corresponding product **3sa** was delivered in 63% yield. However, no desired transformation could be detected when bromobenzene was applied as the substrate.

Then, we turned our attention to test the generality of the indole coupling partner of the arylmethylation reaction. As highlighted in Fig. 3, firstly, we examined a series of different *N*-substituted indoles. *N*-alkyl, *N*-benzyl, and *N*-phenyl-indoles were all suitable substrates and produced the corresponding products in good yields (**3ib**–**3af**). Interestingly, when non-protected indole was applied in this reaction, the C3-arylmethylated product **3ag** was obtained in 27% yield. A *N*-benzoyl-indoline

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Fig. 3 Carbonylative homologation of aryl iodides with indoles. Reaction conditions: indole (0.5 mmol), aryl iodide (0.75 mmol), Ni(OTf)$_2$ (5 mol%), bpy (5 mol%), Mo(CO)$_6$ (0.5 mmol), Ph$_2$SiH$_2$ (1.0 mmol), toluene (2 mL), 120 °C, 24 h, isolated yield. ^{a}Et$_3$SiH was used instead of Ph$_2$SiH$_2$
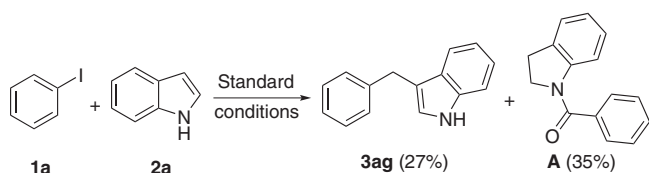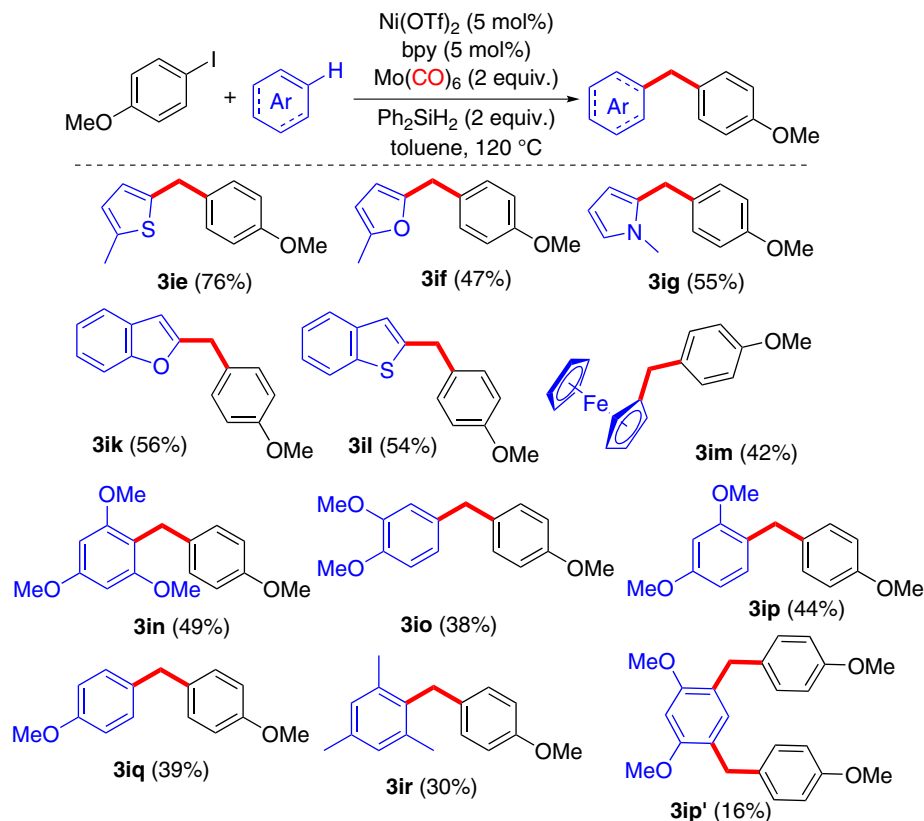

Fig. 4 Carbonylative homologation of iodobenzene with indole. When non-protected indole was used, the C3-arylmethylated product **3ag** was obtained (27%) and N-benzoyl-indoline was observed as a by-product (35%)

was observed as a by-product (Fig. 4). However, when electron-withdrawing groups (such as Boc, Piv and Ts) were attached to the nitrogen of indole, no desired products were obtained. This might have resulted from the decreased nucleophilicity of the indoles due to the strong electron-withdrawing effect. Subsequently, a range of substitutes *N*-methylindoles were subjected to

the optimized conditions. All reactions proceeded smoothly and provided the corresponding products in moderate to excellent yields (**3ah–3al**). Interestingly, the steric effect on indole did not affect the yield. For example, 2-methylindole substrate reacted smoothly and afforded the desired product **3am** in 87% yield. It should be noted that C3-alkyl substituted indole was also tolerated in this reaction, where the arylmethylation took place at the C2-position of the indole. For example, 1,3-dimethyl-1*H*-indole **2n** reacted with different substituted iodobenzenes and provided the corresponding C2-benzylated products in acceptable yields (**3an, 3fn,** and **3mn**).

Besides indoles, other (hetero)arenes are proper substrates for this transformation as well (Fig. 5). Five-membered heterocycles, including thiophene, furan, pyrrole, benzofuran, and benzothio-phene, are all suitable reaction partners, and moderate to good yields of the corresponding products can be obtained (Fig. 5, **3ie–3il**). Ferrocene can be selectively benzylated as well; the corresponding product **3im** was isolated in 42% yield. Simple arenes were tested under standard conditions; it was found that

Fig. 5 Carbonylative homologation of aryl iodides with (hetero)arenes. Reaction conditions: arenes (0.5 mmol), 4-methoxyl iodobenzene (0.75 mmol), Ni (OTf)$_2$ (5 mol%), bpy (5 mol%), Mo(CO)$_6$ (0.5 mmol), Ph$_2$SiH$_2$ (1.0 mmol), toluene (2 mL), 120 °C, 24 h, isolated yield

moderate yields of the desired products can be obtained (Fig. 5, **3in–3ir**). Interestingly, in the case of 1,3-dimethoxybenzene, 16% of double benzylated product (**3ip′**) can be obtained as well.

Control experiments. To examine the reaction pathway of this nickel-catalyzed arylmethylation reaction, a series of control experiments were conducted. First, when benzylic alcohol **5** was treated with *N*-methyl indole **2a** under the standard condition, no methylated product **3aa** could be observed (Fig. 6a). However, when benzaldehyde **6** was used in this reaction, the desired product **3aa** was obtained in 32% yield (Fig. 6b). During the optimization of the reaction conditions, a diaryl ketone **4aa** was detected as a by-product. So we examined the direct transformation of the ketone to the methylene group. When **4aa** was subjected to the standard condition, the desired product **3aa** was obtained in 20% yield (Fig. 6c). Besides, **3aa** was obtained in 50% yield when alcohol **7** was treated under the standard condition (Fig. 6d). These observations indicate that benzaldehyde **6**, diaryl ketone **4,** and diaryl methanol **7** can serve as intermediates in this catalytic transformation. In addition, no desired product **3aa** was obtained when diaryl ketone **4aa** was treated under standard condition without nickel catalyst (Fig. 6e). Moreover, decreased yield was obtained from alcohol **7** in the absence of nickel catalyst (Fig. 6f). These results indicate that nickel catalyst plays a crucial role in the deoxygenation step.

Discussion

Based on these observations and previous literatures, a plausible mechanism is proposed and shown in Fig. 7. Initially, the oxidative addition of aryl iodide to the in situ-generated Ni(O) forms an aryl nickel complex **8**, which was converted to the acyl nickel intermediate **9** after coordination and insertion of CO. Then,
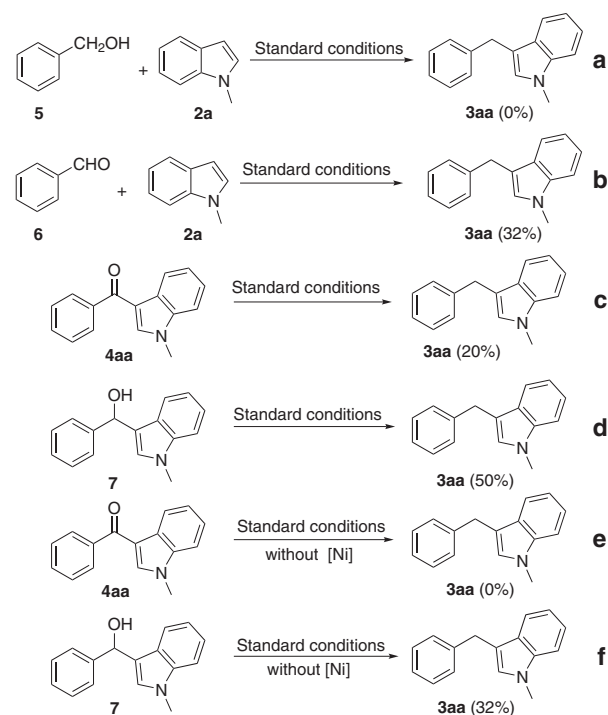
Fig. 6 Control experiments. The experiments support the intermediacy of a benzylic carbonyl, which undergoes two-step reduction, and the necessity of the nickel catalyst for reduction. **a** Benzyl alcohol does not react under standard conditions. **b** Benzaldehyde undergoes homologation under standard conditions. **c** Diaryl ketone, observed as a reaction by-product, is reduced under standard conditions. **d** Diaryl alcohol is reduced under standard conditions. Nickel is required for the reduction of **e** diaryl ketone and **f** diaryl alcohol
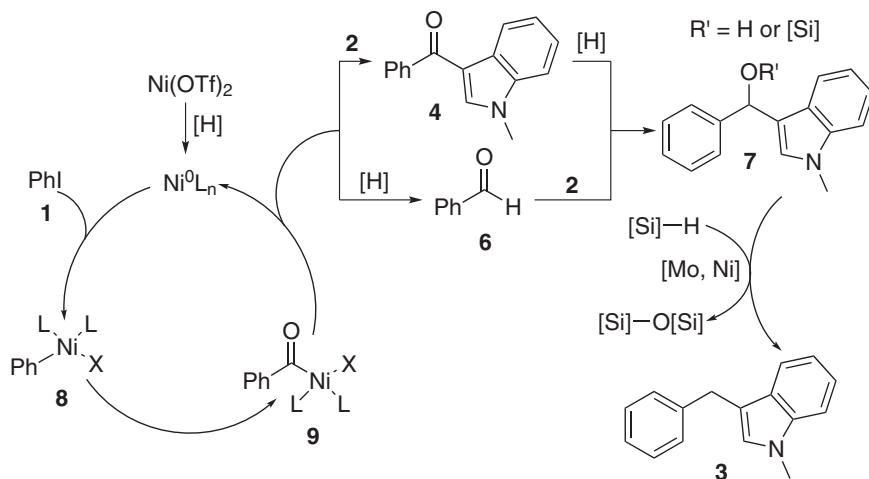
Fig. 7 Proposed mechanism. Based on control experiments, (Fig. 6) a plausible mechanism involving oxidative addition to in situ generated Ni(O) followed by insertion of CO reaction to form a ketone or aldehyde, and finally Ni-mediated hydrogenation by silane

acyl-nickel complex reacted with indole to produce the ketone **4**; the catalytic active Ni(O) was regenerated in this step. Ketone **4** was reduced by silane to give the alcohol or its silyl ether **7**. It should be mentioned that the formation of **7** via the intermediacy of aldehyde **6** cannot be excluded. Subsequently, hydrogenation of **7** by silane provided the final methylene product **3**. It is also important to state that molybdenum hexacarbonyl is not only a solid carbon monoxide source but also participates in the deoxygenation process as a catalyst.

In summary, we have developed an interesting nickel-catalyzed carbonylative homologation of aryl iodides. With Mo(CO)₆ as the solid CO source and silane as the deoxygenation reagent, benzylic units can be effectively produced. Various (hetero)arenes can be successfully benzylated and can produce the corresponding products in moderate to excellent yields.

Methods

Synthesis and characterization. See Supplementary Methods for general information about chemicals and analytical methods, synthetic procedures and characterization for substrates and products. For ^1H and ^{13}C NMR data see Supplementary Figures 1-46.

Optimization. See Supplementary Table 1 (Optimization of solvent), Supplementary Table 2 (Optimization of additives), Supplementary Table 3 (Optimization of catalysts), Supplementary Table 4 (Optimization of ligands), Supplementary Table 5 (Optimization of CO source), Supplementary Table 6 (Optimization of reductants), Supplementary Table 7 (Optimization of the amount of Mo(CO)₆), and Supplementary Table 8 (Optimization of the amount of Ph₂SiH₂).

General procedure. Ni(OTf)₂ (8.9 mg, 5.0 mol%), bpy (3.9 mg, 5 mol%), and Mo (CO)₆ (132.0 mg, 1.0 equiv.) were transferred into a 15-mL tube filled with nitrogen. N-methyl indole (63 μL, 0.5 mmol), iodobenzene (143 μL, 1.5 mmol) and toluene (2 mL) were added to the reaction tube. Then the tube was sealed and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction tube was adding sodium hydroxide methanol solution (0.2 mol/L, 10 mL) and stirred for 1 h. The reaction was quenched with H₂O and diluted with EtOAc. The phases were separated and the aqueous phase was washed with EtOAc (30 mL). Combined organic phases was dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

Data availability

The data sets generated and analyzed during the current study are included in the Supplementary Information file and also available from the corresponding authors on request.

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Author contributions

X.-F.W. and J.-B.P. conceived and supervised the project. F.-P.W. performed experiments and prepared the supporting information. X.Q. and J.Y. participated in the discussions. X.-F.W. and J.-B.P. wrote and revised the manuscript.

Additional information

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