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One-Pot Double Benzylation of 2-Substituted Pyridines using Palladium-Catalyzed Decarboxylative Coupling of sp^2 and sp^3 Carbons

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Abstract: An efficient and practical decarboxylative double benzylation method for various 2-picolinic acids has been established by using a bimetallic catalytic system of palladium(II) chloride ($PdCl_2$) and silver(I) oxide (Ag_2O), which offered a variety of diarylmethane derivatives with moderate to good yields.

Keywords: benzyl bromide; sp^2–sp^3 cross-coupling; decarboxylation; double benzylation; 2-picolinic acids

Functionalized pyridines and related azaarenes are important heteroarenes and key intermediates for the preparation of many biologically active compounds.[1] Particularly, 2-substituted double benzylated pyridines are useful intermediates for the synthesis of pharmaceuticals and advanced functional materials.[2] In 2006, 2-amino-substituted double benzylated pyridine derivatives were found as a new kind of inhibitor for the β-secretase enzyme (Figure 1).[2a] Traditional strategies to prepare such molecules involving the construction of double benzylated pyridines required relatively long synthetic procedures.[2a,3] Subsequently, alternative routes consisted of alkylation of 2-benzylpyridine with RX,[4] Ni-catalyzed alkenylation of triazolopyridines followed by hydrogenation-hydrolysis sequence[5] or addition of alkyllithium reagents to α-(2-pyridyloxy)styrene which triggers an anionic rearrangement to afford tertiary pyridyl carbinols.[6] Although these approaches provided elegant accesses to 2-(1,2-diphenylethyl)pyridine derivatives, they still required relatively sensitive organometallic reagents and unusual substrates for the reaction. In 2012, Kamau[7] and co-workers developed a multi-component one-pot methodology for the synthesis of tertiary carbinamines. However, this proposal required benzylmagnesium chloride as a nucleophile under a low temperature (−78 °C). Recently, Bellomo[8] et al. reported a reaction of 2-benzylpyridine with benzyl chloride, which could afford 2-(1,2-diphenylethyl)pyridine in good yield in the presence of $KN(SiMe_3)_2$ or $LiN(SiMe_3)_2$, but the applicability of this method needed to be further studied.

In the past decade, decarboxylative coupling reactions have emerged as an attractive and powerful tool for the construction of carbon-carbon and carbon-heteroatom bonds,[9] owing to the advantage of the *in*

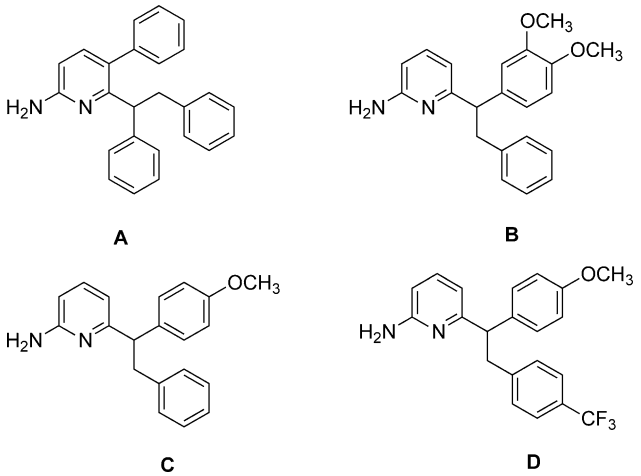
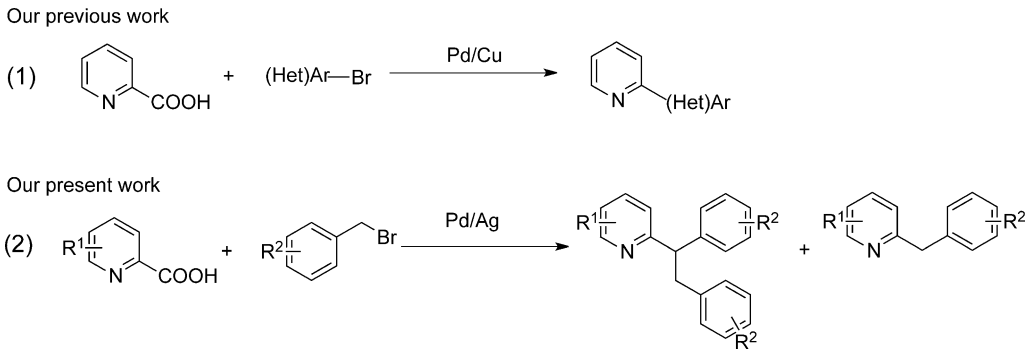


Figure 1. A new kind of inhibitor for the β-secretase enzyme.



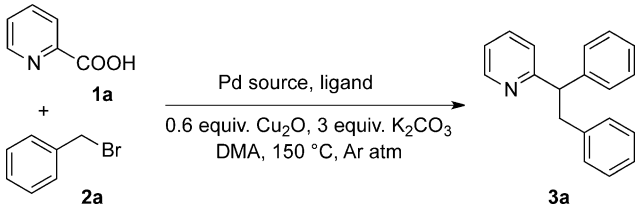
Scheme 1. Palladium-catalyzed decarboxylative coupling approaches developed by our group.

situ generated organometallic species from simple carboxylic acids. Recently, sequential decarboxylative benzylation reactions of phenols,[10a] diphenylglycinate imines,[10b] acetylides,[10c] and ketones[10c] have been achieved for the synthesis of benzylated products. Compared to toxic and expensive heterocyclic organometallics as sources of carbon nucleophiles, heterocyclic carboxylic acids are stable and available materials. Using 2-picolinic acids instead of organometallics reagents, we have successfully synthesized a series of functional 2-arylpyridines by means of the decarboxylative coupling reaction [Scheme 1, Eq. (1)].[12] Building upon this work and thinking about the fact that benzyl bromide has a higher activity than bromobenzene, we envisioned that a mechanistically related decarboxylative C(sp^2)–C(sp^3) coupling of 2-picolinic acids with benzyl bromides should be possible to form the 2-substituted benzylated pyridines [Scheme 1, Eq. (2)]. However, based on the original experimental conditions, the decarboxylative coupling of 2-picolinic acid with benzyl bromide did not give 2-benzylpyridine but offered 2-substituted double-benzylated pyridine. To the best of our knowledge, the application of 2-picolinic acids in a direct one-pot decarboxylative process to access 2-substituted double-benzylated pyridines has not been performed yet.[11]

As depicted in Table 1, the model reaction of 2-picolinic acid **1a** with benzyl bromide **2a** was first investigated by using our previously reported condition.[12] However, the transformation was inefficient and only 16% yield of the target product **3a** was detected (Table 1, entry 1). Considering a series of by-products derived from the benzyl bromide were detected by GC-MS (see the Supporting Information), the effect of the amount of benzyl bromide for the reaction was thus carefully examined. The results showed that 6.0 equiv. of benzyl bromide were the best choice to give a 57% yield of **3a** (entries 1–5).

Following that, a screening of Pd catalysts was then performed. As shown in Table 1, both Pd(0) sources and Pd(II) sources have a small effect on the decarboxylative coupling reaction and $PdCl_2$ gave the better result (entry 4, entries 6–10). 39–50% yields

Table 1. Screening of the ratios of the starting materials, catalysts and ligands for the Pd-catalyzed decarboxylative sp^2–sp^3 coupling of 2-picolinic acid **1a** with benzyl bromide **2a**.[a]



Entry	**2a** (mmol)	Pd source	Yield [%][b]
1	1.5	$PdCl_2$	16
2	2.4	$PdCl_2$	32
3	3.0	$PdCl_2$	44
4	3.6	$PdCl_2$	57
5	4.2	$PdCl_2$	33
6	3.6	$Pd(acac)_2$	51
7	3.6	$Pd(OAc)_2$	46
8	3.6	$Pd(O_2CCF_3)_2$	52
9	3.6	$Pd_2(dba)_3{\cdot}CHCl_3$	46
10	3.6	$Pd(PPh_3)_4$	53
11	3.6	$PdCl_2$	39–50[c]

[a] *Reaction conditions:* 0.6 mmol **1a**, 1.5–4.2 mmol **2a**, 5 mol% catalyst, 5 mol% BINAP, 1.8 mmol K_2CO_3, 3.5 mL DMA, 0.36 mmol Cu_2O, 150 °C, 24 h, argon atmosphere, 200 mg 3 Å MS.
[b] Detected by GC.
[c] BINAP was replaced by ligand **L1–L6** (Figure 2).

were obtained by using phosphine ligands with various steric and electronic properties [**L1–L6**, Figure 2, (see the Supporting Information)] (entry 11). The best yield (57%) was obtained when BINAP was used as ligand (entry 4).

The influence of bases, solvents and additives were also tested and summarized in Table 2. Several bases were examined in the reaction (see the Supporting Information), while the excellent yield was obtained when 3.0 equiv. of Na_2CO_3 was used as base (entries 5, 8 and 9). Screening of various solvents revealed that DMA gave the desired product **3a** in 66% yield and DMSO showed only a trace yield (en-

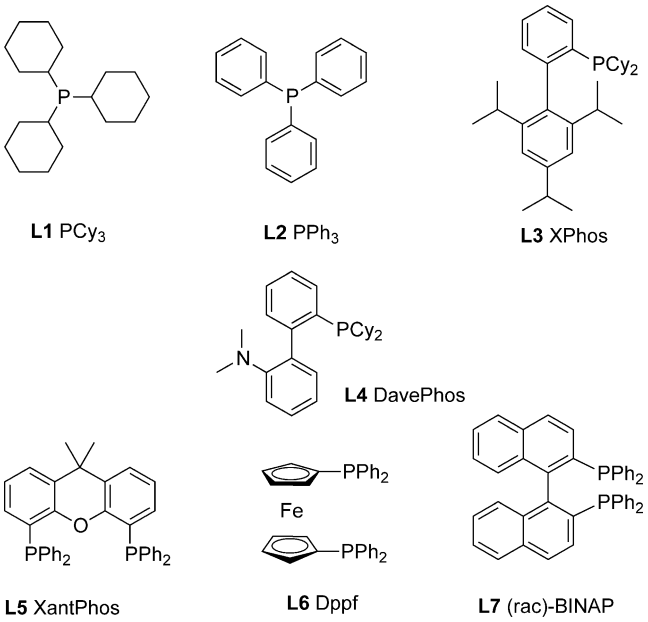
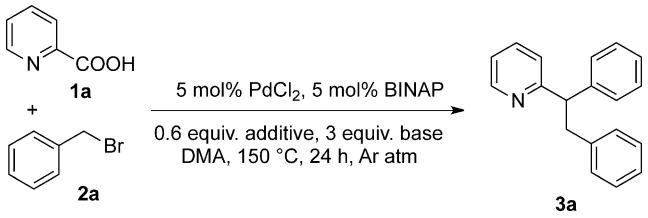


Figure 2. The structures of different phosphine ligands.

Table 2. Screening of the bases, solvents and additives for the Pd-catalyzed decarboxylative coupling of 2-picolinic acid **1a** with benzyl bromide **2a**.[a]



Entry	Base	Additive	Solvent	Yield [%][b]
1	Na_2CO_3	Cu_2O	DMA	66
2	Na_2CO_3	Cu_2O	NMP	55
3	Na_2CO_3	Cu_2O	DMF	51
4	Na_2CO_3	Cu_2O	DMSO	trace
5	Na_2CO_3	Ag_2O	DMA	99 (86[c])
6	Na_2CO_3	–	DMA	33
7	–	Ag_2O	DMA	trace
8	Na_2CO_3	Ag_2O	DMA	47[d]
9	Na_2CO_3	Ag_2O	DMA	87[e]
10	Na_2CO_3	Ag_2O	DMA	90[f]

[a] *Reaction conditions:* 0.6 mmol **1a**, 3.6 mmol **2a**, 5 mol% $PdCl_2$, 5 mol% BINAP, 1.8 mmol base, 3.5 mL solvent, 0.36 mmol additive, 24 h, argon atmosphere, 200 mg 3 Å MS.
[b] Detected by GC.
[c] Isolated yields based on **1a**.
[d] 1.5 equiv. base (0.9 mmol).
[e] 4.0 equiv. base (2.4 mmol).
[f] Reaction temperature was 140 °C.

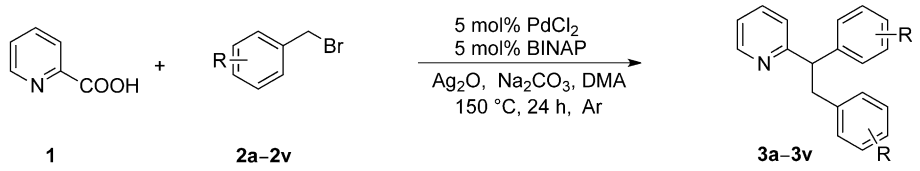
tries 1–4). Considering the additive was always used as a critical parameter in the decarboxylation step,[13] the additive was switched from Cu_2O to Ag_2O. To our delight, 86% yield of **3a** was obtained (entry 5). It was noteworthy that only 33% yield of **3a** was obtained without any additional additive (entry 6). Decreasing the reaction temperatures (entry 10) or not using protective gas (see the Supporting Information) led to a decrease of the yields. Therefore, the optimized reaction conditions are 5 mol% $PdCl_2$, 5 mol% BINAP in DMA in the presence of 3.0 equiv. Na_2CO_3 and 0.6 equiv. Ag_2O at 150 °C under an argon atmosphere.

Under the optimized conditions (Table 2, entry 5), a series of benzyl bromides was investigated for this reaction. The results are shown in Table 3. In most cases, the products were obtained in moderate to good yields. Benzyl bromide afforded the desired product **3a** in 86% isolated yield, while the introduction of a methyl group as *ortho*-, *meta*- and *para*-substituted benzyl bromides produced the corresponding products **3b**, **3c** and **3d** in 68%, 73% and 65% yields, respectively.

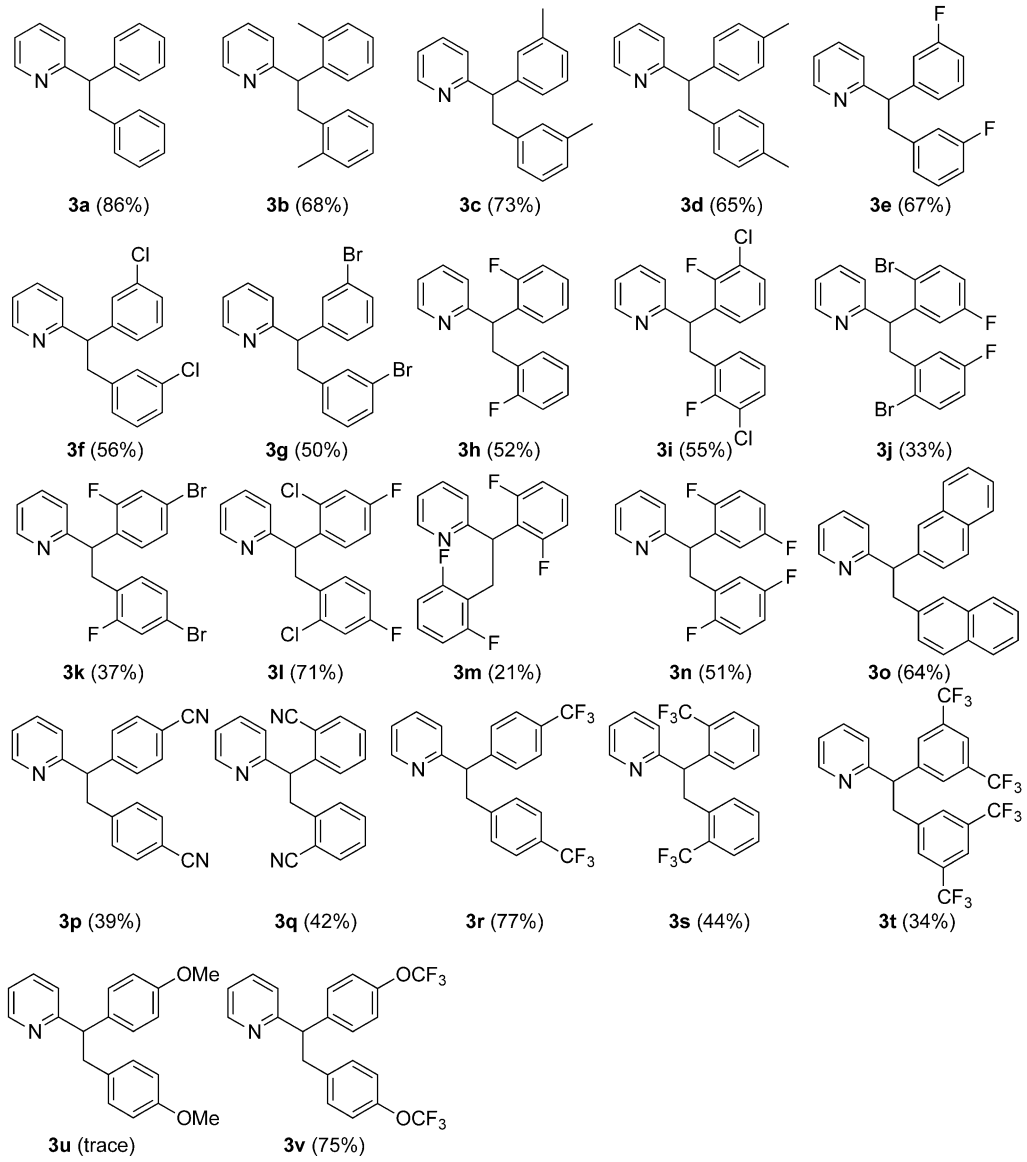
Following that, benzyl bromides containing a 3-substituted fluoride, chloride or bromide atom underwent chemoselective coupling reactions to give 50–67% yields with 3-substituted halides still intact (**3e**–**3g**). Dihalogen-substituted benzyl bromides were found to be tolerated in the reaction and afforded moderate yields. 1-(Bromomethyl)-2-chloro-4-fluorobenzene gave a 71% yield. However, 2-(bromomethyl)-1,3-difluorobenzene gave a low yield. These results showed that the Pd/Ag catalysis system could be well compatible with halide substituents, which provide an opportunity for further functionalizations. 2-(Bromomethyl)naphthalene provided the desired product **3o** in 64% yield. To further reveal the compatibility of the conditions, 4-(bromomethyl)benzonitrile and 2-(bromomethyl)benzonitrile were tested. These results showed that the nitrile group was also tolerated. In addition, benzyl bromides containing 4-trifluoromethyl or 4-trifluoromethoxy groups on the aromatic rings provided the corresponding products **3r**, **3v** in 77%, 75% yields, respectively. 2-Trifluoromethyl and disubstituted trifluoromethyl groups gave 44% and 34% yields (**3s**, **3t**). Unfortunately, 1-(bromomethyl)-4-methoxybenzene gave only trace amount of the desired product **3u**, even with elevated reaction temperature and prolonged reaction time. It was possibly because that 1-(bromomethyl)-4-methoxybenzene is unstable and especially perishable.

Prompted by these results, an array of 2-picolinic acids was investigated for this reaction (Table 4). Firstly, the coupling reactions of substrates with a methyl group at 3-, 4-, 5- and 6-positions of 2-picolinic acid with **2a** were studied. 2-Picolinic acids with a methyl group at the 3-position and 5-position proceeded to give products (**3w**, **3x**) in moderate yields.

Table 3. Pd-catalyzed decarboxylative sp^2–sp^3 coupling of 2-picolinic acid with various benzyl bromides.[a,b]



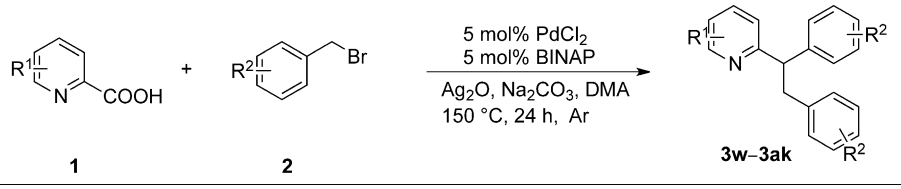
1 **2a–2v** **3a–3v**

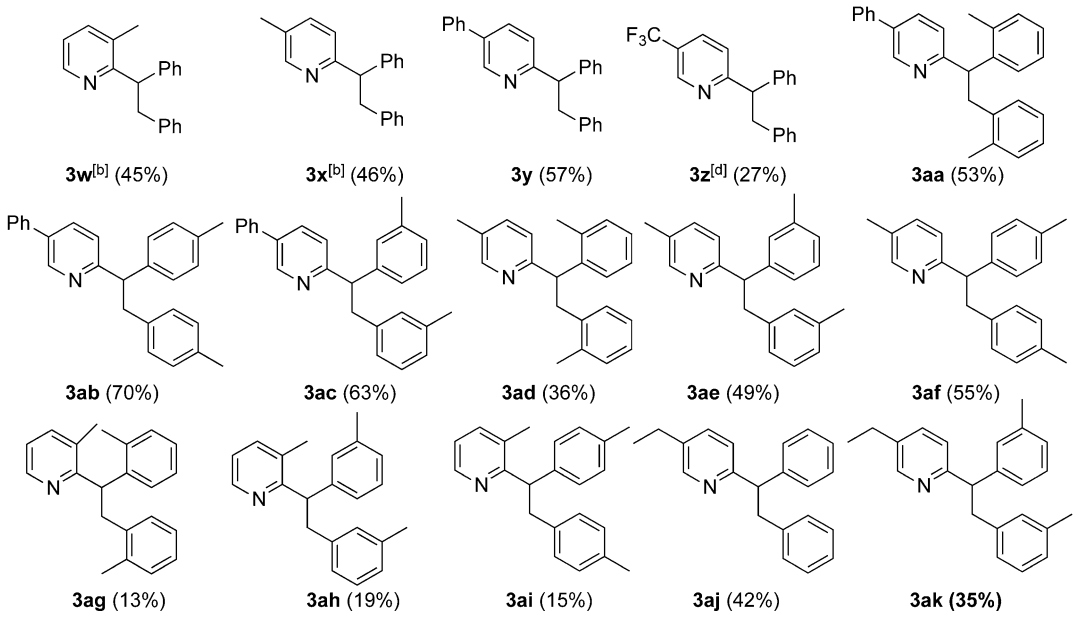


[a] *Reaction conditions:* 0.6 mmol **1**, 3.6 mmol **2a–2v**, 5 mol% $PdCl_2$, 5 mol% BINAP, 1.8 mmol Na_2CO_3, 3.5 mL DMA, 0.36 mmol Ag_2O, 150 °C, 24 h, argon atmosphere, 200 mg 3 Å MS.
[b] Isolated yields based on **1**.

However, the corresponding products were not detected when 2-picolinic acids containing methyl groups at the 4-position or 6-position were used as coupling partners. Secondly, the effects of different substituents at the 5-position of 2-picolinic acid were investigated. It was found that phenyl or methyl groups at the 5-position of 2-picolinic acid could afford moderate yields, a trifluoromethyl group at the 5-position of 2-picolinic acid gave a low yield (products **3y** 57%, **3x** 46%, **3z** 27%). To our disappointment, only trace amounts of the corresponding products were detected by GC-MS, when halogen groups

Table 4. Pd-catalyzed decarboxylative sp^2–sp^3 coupling of 2-picolinic acid derivatives with various benzyl bromides.[a,c]





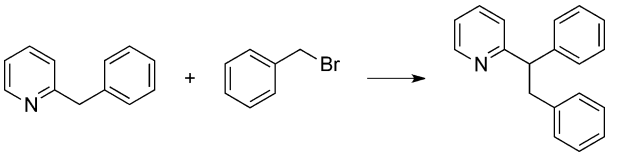
[a] *Reaction conditions:* 0.6 mmol **1**, 3.6 mmol **2**, 5 mol% $PdCl_2$, 5 mol% BINAP, 1.8 mmol Na_2CO_3, 3.5 mL DMA, 0.36 mmol Ag_2O, 150 °C, 24 h, argon atmosphere, 200 mg 3 Å MS.
[b] Carboxylic acids are hydrochloride salts, 2.4 mmol Na_2CO_3 as the base.
[c] Isolated yields based on **1**.
[d] GC yield.

(F, Cl, Br) or methoxy group were present at the 5-position of the 2-picolinic acid used. When coupling with substituted 2-picolinic acid, *ortho*-methylbenzyl bromide afforded lower yields than *meta*-methylbenzyl bromide and *para*-methylbenzyl bromide (**3ag**–**3ai**, **3ad**–**3af**, **3aa**–**3ac**). Only 13–19% isolated yields were obtained in the coupling reactions of 3-methylpicolinic acid with *ortho*-, *meta*- and *para*-methyl-substituted benzyl bromides (**3ag**–**3ai**), which could be rationalized by the steric effect of 3-methyl on the 2-picolinic acid.

Subsequently, nicotinic acid, isonicotinic acid, thiophene-2-carboxylic acid and quinoline-2-carboxylic acid were employed as the substrates in the decarboxylative coupling reaction. Unfortunately, the corresponding products were not detected. The current method needs further optimization to be suitable for more carboxylic acid substrates in our following research.

To further explore the possible reaction mechanism, some experiments were carried out and the results are summarized in Table 5. When the reaction of 2-

Table 5. The reaction of 2-benzylpyridine with benzyl bromide.



Entry	Base	Yield [%][d]
1	Na_2CO_3	97[a]
2	–	19[b]
3	Na_2CO_3	91[c]

[a] *Reaction conditions:* 0.6 mmol 2-benzylpyridine, 0.9 mmol benzyl bromide, 5 mol% $PdCl_2$, 5 mol% BINAP, 1.8 mmol Na_2CO_3, 3.5 mL DMA, 0.36 mmol Ag_2O, 150 °C, 24 h, argon atmosphere, 200 mg 3 Å MS.
[b] *Reaction conditions:* same as for footnote[a] but without Na_2CO_3.
[c] *Reaction conditions:* 0.6 mmol 2-benzylpyridine, 0.9 mmol benzyl bromide, 1.8 mmol Na_2CO_3, 3.5 mL DMA, 24 h, argon atmosphere.
[d] GC yield.

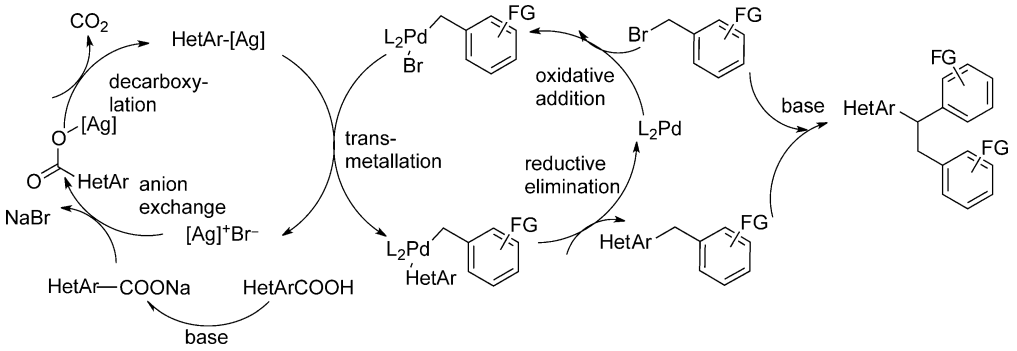


Figure 3. A proposed catalytic cycle for the decarboxylative coupling of 2-picolinic acid derivatives with various benzyl bromides

benzylpyridine and benzyl bromide was carried out under our optimized reaction conditions, **3a** was detected in 97% yield (entry 1). In the absence of Na_2CO_3, only 19% of **3a** was obtained under the same conditions (entry 2). When the reaction was carried out with Na_2CO_3 in the absence of other additives, a 91% yield was detected (entry 3). These results indicated that 2-benzylpyridine was possibly a key intermediate for the construction of 2-substituted double-benzylated pyridines.

Thus, the reaction of 2-picolinic acid with benzyl bromide possibly went through such a process: 2-picolinic acid reacted with benzyl bromide firstly to form 2-benzylpyridine according to the conventional decarboxylative cross-coupling mechanism, and then 2-benzylpyridine reacted with benzyl bromide to produce 2-substituted double-benzylated pyridine under the promotion of Na_2CO_3. Based on this observation and the literature reports,[13a,b,14] we propose a plausible catalytic cycle for the decarboxylative coupling of 2-picolinic acid derivatives with various benzyl bromides (Figure 3).

In conclusion, a new one-pot protocol for the preparation of 2-substituted double-benzylated pyridine-related skeletons has been developed by the palladium-catalyzed decarboxylative sp^2–sp^3 cross-coupling reaction. In most cases, the isolated yields are moderate to good. Various functional groups on the benzyl bromides are compatible. Further investigation on the synthetic application of this protocol is still in progress in our laboratory.

Experimental Section

Palladium-Catalyzed Decarboxylative Coupling Reaction of 2-Picolinic Acid with Benzyl Bromide; Typical Reaction Procedure

An oven-dried glass reaction tube equipped with a magnetic stir bar was firstly charged with the 2-picolinic acid (73.8 mg, 0.6 mmol, 1.0 equiv.), $PdCl_2$ (5.3 mg, 0.03 mmol, 5 mol%), BINAP (18.7 mg, 0.03 mmol, 5 mol%), Na_2CO_3 (190.8 mg, 1.8 mmol, 3 equiv.), Ag_2O (83.4 mg, 0.36 mmol, 0.6 equiv.) and 3 Å molecular sieve (200 mg). Secondly, anhydrous DMA (2.0 mL) was added and the mixture was charged with argon gas three times. Thirdly, benzyl bromide was added *via* syringe, additional anhydrous DMA (1.5 mL) was added by syringe. The reaction mixture was finally stirred at 150 °C for 24 h under argon gas. The reaction progress was monitored by TLC and the yield was determined by GC analysis, using di-*n*-pentyl phthalate as the internal standard. After cooling to room temperature, the reaction mixture was filtered through a pad of celite, and washed with 10 mL ethyl acetate/H_2O (1:1) three times. The filtrate was extracted with ethyl acetate. The combined organic layer was washed with brine, dried with $MgSO_4$ and filtered. The filtrate was concentrated under vacuum and the residue was purified by silica gel flash chromatography to produce the desired product. The products were characterized by ^1H NMR, ^{13}C NMR and LC-MS.

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