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# Cu(II)-Promoted Palladium-Catalyzed C−H Ortho-Arylation of *N,N*-Dimethylbenzylamines

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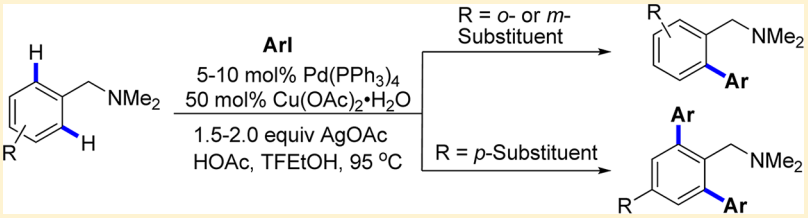
Supporting Information




**ABSTRACT:** A novel protocol for palladium-catalyzed arylation of the C($sp^2$)−H bond directed by a *N,N*-dimethylaminomethyl group in the presence of AgOAc and $Cu(OAc)_2·H_2O$ is described. Various aryl iodides proved to be efficient coupling partners, furnishing the corresponding ortho monoarylated or diarylated arenes in moderate to good yields. $Cu(OAc)_2·H_2O$ is found to be the important additive to improve the yields in this transformation.

## INTRODUCTION

Biaryls are important scaffolds in natural products, pharmaceuticals, agrochemicals, and functional materials.[1] Consequently, development of an efficient method for making biaryl motifs has been an important topic in chemical synthesis. Recently, transition-metal-catalyzed direct arylation of the aryl C($sp^2$)−H bond has emerged as an extensive research area because such reactions alleviate the need for the prefunctionalization (halogenation and/or metalation) of the aromatic substrates.[2] In particular, chelation-assisted C−H arylation has become a powerful method for effective and regioselective construction of biaryls.[3] A variety of functional groups, including anilides,[4] amides,[5] imines,[6] pyridyl,[7] 2-pyridylsulfinyl,[8] nitriles,[9] benzylamines,[10] thioethers,[11] and carboxylic acids[12] have been successfully used as directing groups in C−H arylation of arenes.

*N,N*-Dimethylaminomethyl group is well-known as a useful directing group to perform the ortho-metalation by transition metal complexes to form metallocycles and further construct C−C bonds in a stoichiometric manner.[13] Recently, *N,N*-dimethylaminomethyl as a directing group in catalytic C−H bond functionalization has received increasing attention. In a pioneering study, Murai and co-workers reported that *N,N*-dimethylaminomethyl could be used successfully as the directing group for Ru(0)-catalyzed ortho-silylation via C($sp^2$)−H activation.[14] *N,N*-Dimethylaminomethyl group-directed ortho-olefination[15] and carbonylation[16] via palladium catalysis have been developed by Shi and co-workers. This protocol was also applied to build ferrocene-functionalized naphthalenes via Pd-catalyzed direct dehydrogenative annulations of ferrocene and internal alkynes.[17] Very recently, Clark discovered *N,N*-dimethylaminomethyl-directed C−H borylation reactions using iridium catalyst.[18] Arylation is one of the most important transformations in organic synthesis. Herein, we report the palladium-catalyzed ortho-arylation of arenes directed by the *N,N*-dimethylaminomethyl group. It is important to note that $Cu(OAc)_2·H_2O$ is a crucial additive to improve the efficiency of this transformation.

## RESULTS AND DISCUSSION

In the preliminary investigation, we examined the reaction of *N,N*-dimethylbenzylamine **1a** with iodobenzene **2a** in the presence of $Pd(OAc)_2$ (10 mol %), AgOAc (2 equiv), and HOAc (15 equiv) at 95 °C (Table 1, entry 1). To our delight, diarylation product **3aa** was obtained in 41% yield. Other palladium(II) catalysts such as $PdCl_2$ and $Pd(PPh_3)_2Cl_2$ were found to be inferior for this transformation (Table 1, entries 2 and 3). Use of $Pd(PPh_3)_4$ led to an improved yield (Table 1, entry 4). In accordance with previous experience from our own study[19] as well as studies from other groups,[7b,8b,12b,c,20] the additives always significantly facilitate palladium-catalyzed C−H activation. At first we employed the copper salts as additives in this system. It was found that the introduction of 10 mol % $Cu(OAc)_2·H_2O$ under otherwise identical conditions improved the yield to 54% (Table 1, entry 5). An increase in the amount of $Cu(OAc)_2·H_2O$ to 20 mol % afforded 59% yield (Table 1, entry 6). A further increase in the amount of $Cu(OAc)_2·H_2O$ to 50 mol % delivered 70% yield (Table 1, entry 7), and *N,N*-dimethylbenzylamine was completely consumed. However, the yield of desired product dropped when more than 50 mol % of $Cu(OAc)_2·H_2O$ was added (Table 1, entry 8). $CuCO_3·Cu(OH)_2$, CuO, and $Cu(OTf)_2$ were also tested in this reaction

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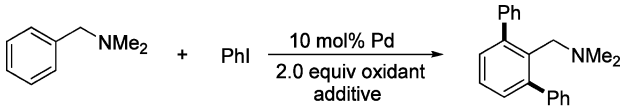
**Table 1. Optimization of the Reaction Conditions of Diarylation**[a]




1a 2a 3aa

| entry | catalyst | Ag salt | additive (mol %) | yield (%) |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | AgOAc | – | 41 |
| 2 | $PdCl_2$ | AgOAc | – | 35 |
| 3 | $Pd(PPh_3)_2Cl_2$ | AgOAc | – | 33 |
| 4 | $Pd(PPh_3)_4$ | AgOAc | – | 52 |
| 5 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (10) | 54 |
| 6 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (20) | 59 |
| 7 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 70 |
| 8 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (100) | 45 |
| 9 | $Pd(PPh_3)_4$ | AgOAc | $CuCO_3·Cu(OH)_2$ (50) | 51 |
| 10 | $Pd(PPh_3)_4$ | AgOAc | CuO (50) | 57 |
| 11 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OTf)_2$ (50) | 56 |
| 12 | $Pd(PPh_3)_4$ | AgOAc | $FeCl_3$ (50) | 0 |
| 13 | $Pd(PPh_3)_4$ | AgOAc | BQ (50) | trace |
| 14 | $Pd(PPh_3)_4$ | AgTFA | $Cu(OAc)_2·H_2O$ (50) | 62 |
| 15 | $Pd(PPh_3)_4$ | $Ag_2CO_3$ | $Cu(OAc)_2·H_2O$ (50) | 37 |
| 16 | $Pd(PPh_3)_4$ | $Ag_2O$ | $Cu(OAc)_2·H_2O$ (50) | 23 |
| 17 | – | AgOAc | $Cu(OAc)_2·H_2O$ (50) | NR |
| 18 | $Pd(PPh_3)_4$ | – | $Cu(OAc)_2·H_2O$ (50) | NR |
| 19 | $Pd(OAc)_2$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 56 |
| 20 | $PdCl_2$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 24 |
| 21 | $Pd(PPh_3)_2Cl_2$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 51 |
| 22 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 23[b] |
| 23 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 39[c] |
| 24 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 19[d] |
| 25 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 20[e] |
| 26 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 26[f] |
| 27 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | trace[g] |
| 28 | $Pd(PPh_3)_4$ | AgOAc | $Cu(OAc)_2·H_2O$ (50) | 65[h] |

[a]Unless otherwise mentioned, all the reactions were carried out using **1a** (67 mg, 0.5 mmol), **2a** (1.02 g, 5 mmol), Ag salt (1 mmol), Pd catalyst (0.05 mmol), AcOH (7.5 mmol), TFEtOH (1.5 mL), rt to 95 °C, 60 h under air. [b]*tert*-Amyl alcohol was used as solvent in place of TFEtOH. [c]Using methanol as solvent. [d]Using ethanol as solvent. [e]Using DMF as solvent. [f]Using DMA as solvent. [g]Using DMSO as solvent. [h]Under nitrogen.

system. All of them could promote the reaction but failed to give a yield better than that for $Cu(OAc)_2·H_2O$ (Table 1, entries 9–11). $FeCl_3$ and *p*-benzoquinone (BQ) were inactive additives and hampered the reaction completely (Table 1, entries 12, 13).

The efficiency of other silver salts was also examined. AgTFA, $Ag_2CO_3$, and $Ag_2O$ were less effective, providing **3aa** in 62%, 37%, and 23% yields, respectively (Table 1, entries 14–16). It is important to note that $Pd(PPh_3)_4$ and AgOAc are essential for this arylation reaction; no desired product could be obtained in the absence of $Pd(PPh_3)_4$ or AgOAc (Table 1, entries 17 and 18). Other palladium catalysts such as $Pd(OAc)_2$, $PdCl_2$, and $Pd(PPh_3)_2Cl_2$ were found less effective for the reaction, and lower yields were obtained (Table 1, entries 19–21). In addition, the amount of aryl iodide was examined, and we found 10 equiv of aryl iodide was required to obtain a successful yield. The influence of the reaction solvent was also investigated. *tert*-Amyl alcohol, methanol, ethanol, DMF, DMA, and DMSO were ineffective for the reaction (Table 1, entries 22–27). Trifluoroethanol (TFEtOH) proved to be the most suitable solvent for the reaction. The reaction delivered the diarylated products in 65% yield under $N_2$ atmosphere (Table 1, entry 28). Finally, the optimal reaction conditions were obtained: $Pd(PPh_3)_4$ (10 mol %), AgOAc (2.0 equiv), $Cu(OAc)_2·H_2O$ (0.5 equiv), and HOAc (15 equiv) under air in TFEtOH (1.5 mL) at 95 °C for 60 h.

On the basis of the optimization studies, we evaluated the scope and generality of this transformation using *N*,*N*-dimethylbenzylamine **1a** and a variety of aryl iodides **2**. The results are shown in Table 2. Various aryl iodides were suitable substrates to give the desired diarylation products in moderate to good yields. Many useful functional groups, including methyl (Table 2 entry 2), methoxy (Table 2, entry 3), trifluoromethyl (Table 2, entry 4), fluoride (Table 2, entry 5), chloride (Table 2, entry 6), bromide (Table 2, entry 7), ester (Table 2, entry 8), and ketone (Table 2, entry 9), were compatible with this diarylation transformation. It appears that aryl iodides bearing an electron-donating substituent show efficiency higher than those with an electron-withdrawing group. For example, 1-iodo-4-methylbenzene and 1-iodo-4-methoxybenzene underwent smooth diarylation to give products **3ab** and **3ac** in 73% and 72% yields, respectively (Table 2, entries 2 and 3). The presence of strong electron-withdrawing groups such as $CF_3$, Cl, Br, F, ester, and acetyl groups in the aromatic ring of aryl iodides led to slightly lower yield (Table 2, entries 4–9). The steric hindrance of aryl iodides affected the diarylation reaction. Aryl iodides with a meta substituent generally afforded lower yields (Table 2, entries 10 and 12). The ortho-substituted aryl iodide, such as 2-methyl iodobenzene **2k**, was inactive, and attempted arylation resulted in the recovery of the unreacted starting material (Table 2, entry 11). Unfortunately, other aryl halides such as aryl chloride, aryl bromide, and heteroaryl halide were inactive under the standard reaction conditions.

We next examined the reactivity of other benzylamines. As shown in Table 3, the reaction of iodobenzene **2a** with various substituted benzylamines **1** furnished the diarylation products **3** in moderate to good yields. The electron-rich substituents were helpful for this ortho-diarylation due to the enhancement of electron density of phenyl rings. Arenes containing an electron-withdrawing substituent gave yields of arylation lower than those with electron-rich group, which was consistent with the electrophilic palladation mechanism hypothesis. For example, methyl- and methoxy-substituted arenes gave the corresponding diarylation products in 55% and 45% yields, respectively (Table 3, entries 1 and 2). A strong electron-withdrawing trifluoromethyl substituent significantly decreased the yield to 17% (Table 3, entry 6). 4-Fluorobenzylamine gave the desired products in 31% (Table 3, entry 3). Notably, bromide and chloride were tolerated in this transformation, which provided sites for further elaboration of the products (Table 3, entries 4 and 5).

The meta-substituted arenes underwent exclusive monoarylation at the less hindered ortho position of the dimethylaminomethyl groups owing to the steric effect. We explored the reaction conditions of monoarylation between *N*,*N*-dimethyl-3-methylbenzylamine **1h** with iodobenzene (Table 4, entry 1). It was found that the monoarylation reaction could proceed successfully in the presence of 5 mol % $Pd(PPh_3)_4$, 1.5 equiv of AgOAc, 0.5 equiv of $Cu(OAc)_2·H_2O$, and 15 equiv of HOAc in TFEtOH at 95 °C. Similar to diarylation transformation, electron-rich aryl iodides such as $CH_3$ and $OCH_3$ in the aromatic ring gave good yields (Table 4, entries 1–3). Aryl iodides with electron-withdrawing groups such as $CF_3$, F, Cl, Br, and ester


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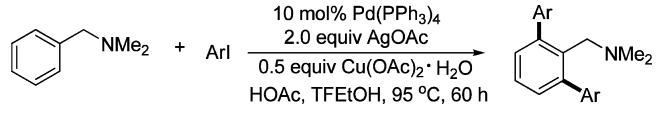
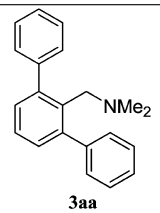
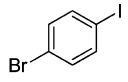
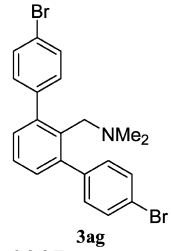
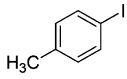
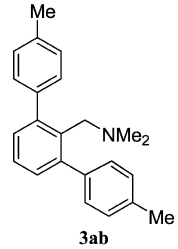
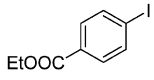
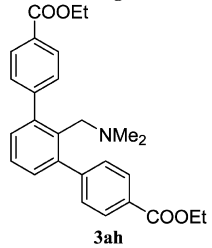
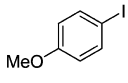
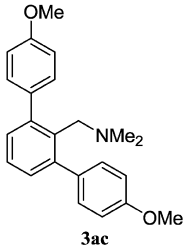
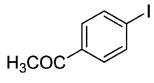
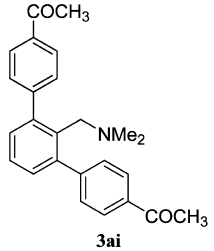
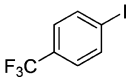
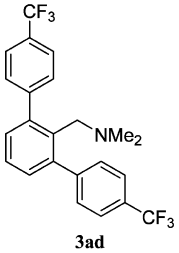
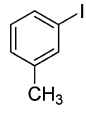
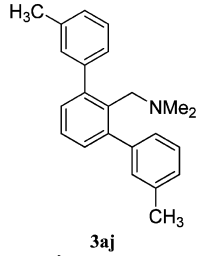
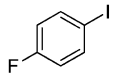
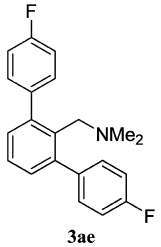
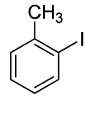
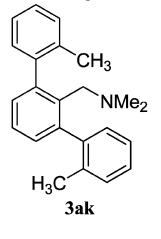
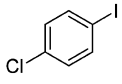
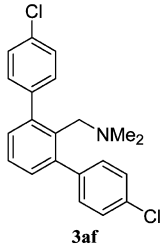
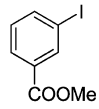
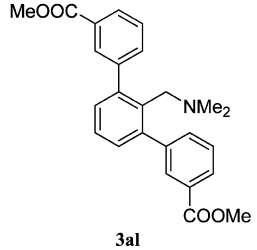
**Table 2. Diarylation of *N,N*-Dimethylbenzylamine with Aryl Iodides[a]**




**1a** **2** **3**

| entry | substrate 2 | product | yields (%) | entry | substrate 2 | product | yields (%) |
|---|---|---|---|---|---|---|---|
| 1 |  **2a** |  **3aa** | 70 | 7 |  **2g** |  **3ag** | 43 |
| 2 |  **2b** |  **3ab** | 73 | 8 |  **2h** |  **3ah** | 61 |
| 3 |  **2c** |  **3ac** | 72 | 9 |  **2i** |  **3ai** | 38 |
| 4 |  **2d** |  **3ad** | 61 | 10 |  **2j** |  **3aj** | 57 |
| 5 |  **2e** |  **3ae** | 55 | 11 |  **2k** |  **3ak** | 0 |
| 6 |  **2f** |  **3af** | 49 | 12 |  **2l** |  **3al** | 54 |

[a]Reaction conditions: *N,N*-dimethylbenzylamine **1a** (67 mg, 0.5 mmol), aryl iodide **2** (5 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol), AgOAc (166 mg, 1.0 mmol), $Cu(OAc)_2{\cdot}H_2O$ (50 mg, 0.25 mmol), HOAc (450 mg, 7.5 mmol), and TFEtOH (1.5 mL), at 95 °C for 60 h under air.


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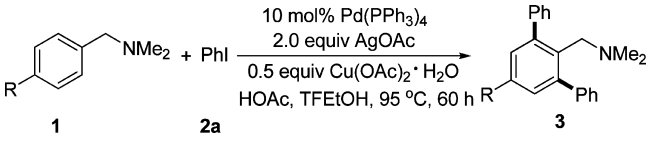
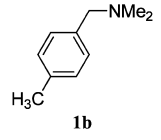
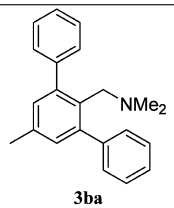
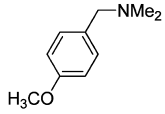
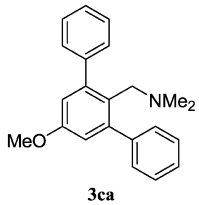
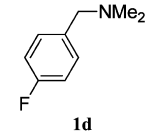
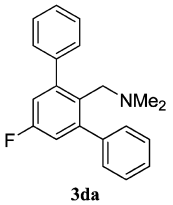
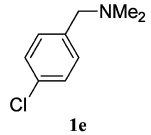
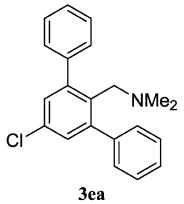
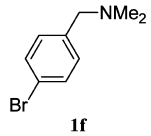
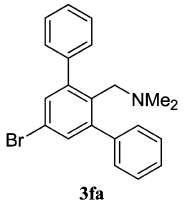
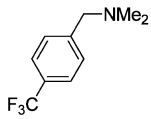
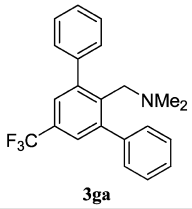
**Table 3. Diarylation of Differently Substituted Benzylamines with Iodobenzene**[a]




1 2a 3

| entry | substrate 1 | product | yields (%) |
|---|---|---|---|
| 1 |  1b |  3ba | 55 |
| 2 |  1c |  3ca | 45 |
| 3 |  1d |  3da | 31 |
| 4 |  1e |  3ea | 34 |
| 5 |  1f |  3fa | 35 |
| 6 |  1g |  3ga | 17 |

[a]Reaction conditions: *N,N*-dimethylbenzylamine **1** (0.5 mmol), iodobenzene **2a** (1.02 g, 5 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol), AgOAc (166 mg, 1.0 mmol), $Cu(OAc)_2·H_2O$ (50 mg, 0.25 mmol), HOAc (450 mg, 7.5 mmol), and TFEtOH (1.5 mL), at 95 °C for 60 h under air.

group showed less reactivity (Table 4, entries 4−8). Meta-substituted aryl iodides gave a slightly lower yield (Table 4, entry 9) presumably due to steric hindrance. Benzylamines bearing electron-withdrawing substituents gave lower yields compared to their electron-rich analogues (Table 4, entry 10). The introduction of substituents on the ortho-position of benzylamine **1j** had a strong steric effect on the reactions, offering the desired product with obviously lower yield compared with its meta-substituted counterpart **1h** (Table 4, entries 11 and 1). When *N,N*-dimethyl-2-naphthalenemethylamine **1k** was employed, the reaction with iodobenzene **2a** proceeded in a regioselective manner to give monoarylated product **3ka** in 61% yield (Table 4, entry 12).

The *N,N*-dimethylaminomethyl group could be readily converted into a methyl group by catalytic hydrogenation using Pd/C as a catalyst (Scheme 1).[15,16] The corresponding derivative of toluene **4aa** was obtained in 73% yield, which is not easily prepared through the traditional Friedel−Crafts method.

Next, we investigate the roles of Ag and Cu salts in this new arylation reaction. Silver salts may serve as the oxidant for Pd(0) to Pd(II), the abstraction reagent for halide, or both.[21] To further elucidate this, the reaction residue was subjected to XRD analysis. It revealed that no Ag(0) was observed, and AgI was the only species detected in the residue. The palladacycle **5**[15,22] could undergo ortho-arylation to form the desired product **3aa** in 83% yield without AgOAc (eq 4). The above results indicated that silver salt may act as a halide scavenger to remove iodide which could promote the formation of the palladacycle in this reaction.[21c] To investigate the role of Cu salt during this transformation, we tested the reaction in the absence or presence of Cu salt and acetic acid (eqs 1 and 2, Scheme 2). Only less than 10% yield of diarylated product was obtained in the absence of HOAc and $Cu(OAc)_2·H_2O$ (eq 1). The reaction carried out with 0.5 equiv of $Cu(OAc)_2·H_2O$ in the absence of HOAc afforded diarylated product in 43% yield (eq 2), which is an approximate yield compared with Table 1 entry 4 (with HOAc, no $Cu(OAc)_2·H_2O$). Furthermore, the reaction of palladacycle **5** with aryl iodide could give the desired product **3aa** in 41% yield and less than 10% yield of **3aa** was obtained without HOAc and $Cu(OAc)_2$ (eqs 3 and 5). From these results, it seems that both $Cu(OAc)_2·H_2O$ and HOAc can promote the arylation reaction. Moreover, the combination of $Cu(OAc)_2·H_2O$ with HOAc is the most efficient system for this reaction. Whereas the role of Cu salt in this transformation is not entirely clear, it likely acts as a Lewis acid which may serve to liberate the Pd(II) from the palladacycle complex.

## CONCLUSION

In summary, we have developed an efficient protocol for arylation of arenes via the *N,N*-dimethylaminomethyl chelation-assisted C−H bond activation by the palladium catalysis. This method allows the ortho-arylation with an aryl iodide coupling partner in the presence of silver acetate and $Cu(OAc)_2·H_2O$. The addition of $Cu(OAc)_2·H_2O$ was found to be important to the efficiency of this transformation. Further studies to expand the scope of this transformation are currently in progress.

## EXPERIMENTAL SECTION

**General.** *N,N*-Dimethylbenzylamines **1b−k** were prepared according to the literature.[15,16] The other materials and solvents were purchased from common commercial sources and used without additional purification. NMR spectra were recorded for $^1H$ NMR at 400 or 500 MHz and $^{13}C$ NMR at 100 or 125 MHz using TMS as internal standard. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), multiplet (m), broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-EI instrument. Infrared spectra were recorded on a FTIR spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using Cu K$\alpha$1 radiation (0.1540 nm), operated at 40 kV and 40 mA.


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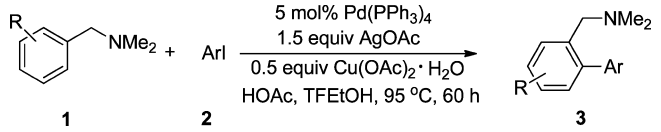
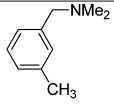
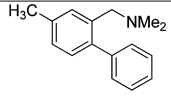
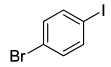
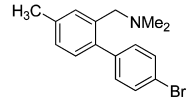
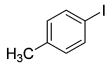
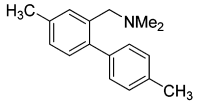
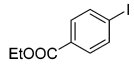
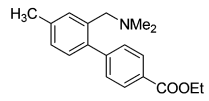
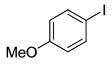
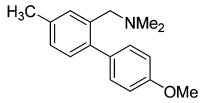
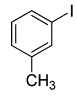
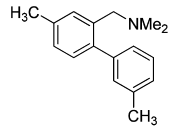
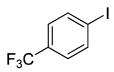
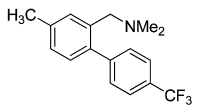
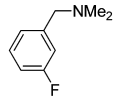
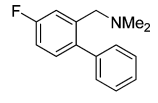
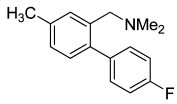
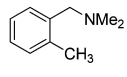
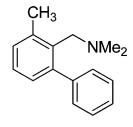
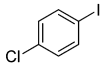
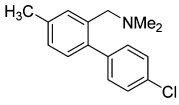
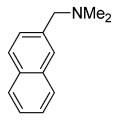
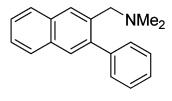
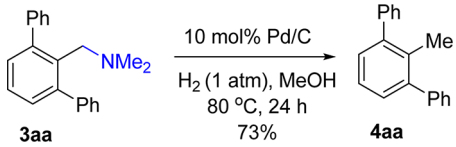
**Table 4. Monoarylation of *N,N*-Dimethylbenzylamines**[a]




| entry | substrate 1 | substrate 2 | product | yields (%) | entry | substrate 1 | substrate 2 | product | yields (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 |  **1h** |  **2a** |  **3ha** | 66 | 7 | **1h** |  **2g** |  **3hg** | 56 |
| 2 | **1h** |  **2b** |  **3hb** | 67 | 8 | **1h** |  **2h** |  **3hh** | 50 |
| 3 | **1h** |  **2c** |  **3hc** | 65 | 9 | **1h** |  **2j** |  **3hj** | 59 |
| 4 | **1h** |  **2d** |  **3hd** | 52 | 10 |  **1i** | **2a** |  **3ia** | 22 |
| 5 | **1h** |  **2e** |  **3he** | 57 | 11 |  **1j** | **2a** |  **3ja** | 31 |
| 6 | **1h** |  **2f** |  **3hf** | 58 | 12 |  **1k** | **2a** |  **3ka** | 61 |

[a]Reaction conditions: *N,N*-dimethylbenzylamine **1** (0.5 mmol), aryl iodide **2** (5 mmol), $Pd(PPh_3)_4$ (57 mg, 0.025 mmol), AgOAc (124.5 mg, 0.75 mmol), $Cu(OAc)_2{\cdot}H_2O$ (50 mg, 0.25 mmol), HOAc (450 mg, 7.5 mmol), and TFEtOH (1.5 mL), at 95 °C for 60 h under air.

**Scheme 1. Transformation of Tertiary Amine to Functionalized Toluene**




**General Procedure for Preparation of Functionalized *N,N*-Dimethylbenzylamines (1b–k).**[15,16] To a solution of $Et_3N$ (4.2 mL, 30 mmol) in absolute EtOH (23 mL) was added dimethylamine hydrochloride (2.48 g, 30 mmol), and then $Ti(i\text{-}PrO)_4$ (9.0 mL, 30 mmol) and the corresponding aldehyde (15 mmol) were added. After the mixture was stirred at 25 °C for 12 h, $NaBH_4$ (0.86 g, 22.5 mmol) was added and the resulting mixture was further stirred for 12 h at 25 °C. The reaction was quenched by pouring the mixture into 30 mL of water, the white suspension was filtered through a Celite pad, and the resulting inorganic solid was washed with $CH_2Cl_2$ (100 mL). The filtrate was extracted with $CH_2Cl_2$ (3 × 50 mL), and the organic layer was washed with saturated NaCl. The organic phase was combined, dried over $Na_2SO_4$, and then evaporated. The residue was purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

**Characterization Data of the *N,N*-Dimethylbenzylamines.** *N,N,4-Trimethylbenzylamine*[15,16] ***(1b):*** light yellow oil (1.3 g, 65% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.24 (s, 6H), 2.35 (s, 3H), 3.39 (s, 2H), 7.14 (d, 2H, $J$ = 7.6 Hz), 7.20 (d, 2H, $J$ = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 21.1, 45.3, 64.1, 128.9, 129.1, 135.7, 136.6.

*4-Methoxy-N,N-dimethylbenzylamine*[15,16] ***(1c):*** light yellow oil (1.0 g, 45% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.22 (s, 6H), 3.36 (s, 2H), 3.80 (s, 3H), 6.86 (d, 2H, $J$ = 8.4 Hz), 7.22 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.2, 55.2, 63.7, 113.6, 130.3, 130.8, 158.7.

*4-Fluoro-N,N-dimethylbenzylamine*[15,16] ***(1d):*** light yellow oil (1.4 g, 61% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.23 (s, 6H), 3.38 (s, 2H), 6.98–7.02 (m, 2H), 7.25–7.28 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.2, 63.5, 114.9–115.1, 130.6 (d, $J$ = 8.3 Hz), 134.5, 162.0 (d, $J$ = 243.6 Hz).

*4-Chloro-N,N-dimethylbenzylamine*[15,16] ***(1e):*** light yellow oil (1.6 g, 64% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.23 (s, 6H), 3.39 (s, 2H), 7.26–7.27 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.3, 63.6, 128.4, 130.4, 132.8, 137.3.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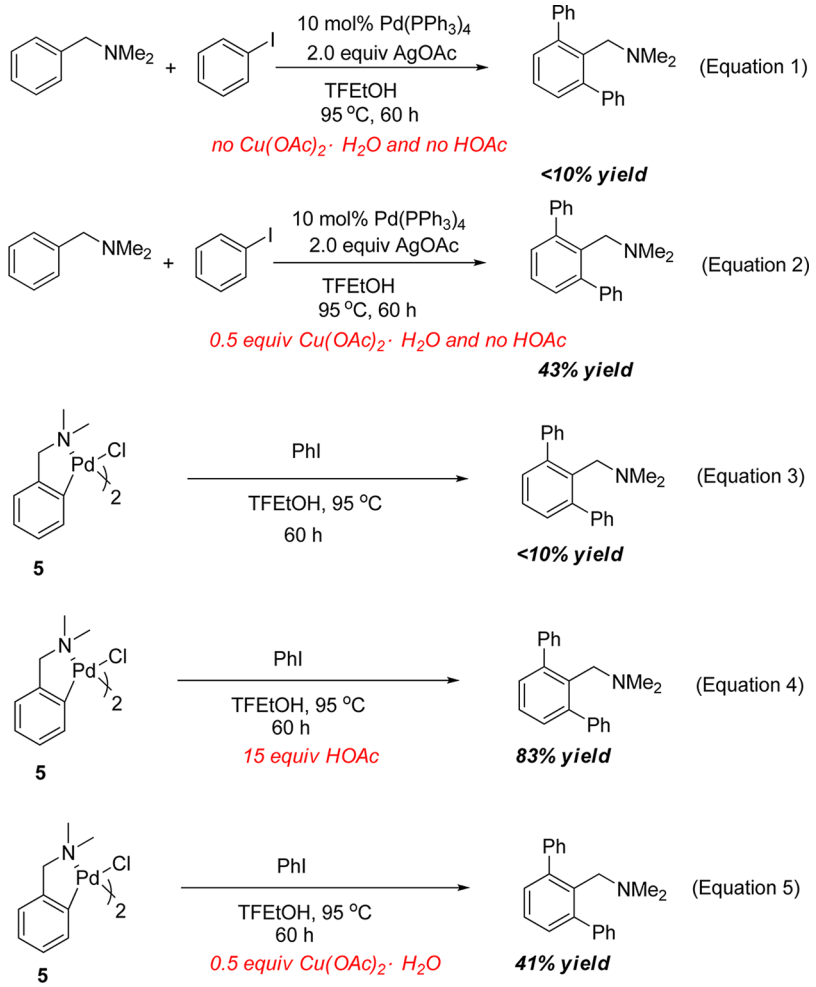
**Scheme 2. Control Experiment for Investigating the Role of $Cu(OAc)_2 \cdot H_2O$**




*4-Bromo-N,N-dimethylbenzylamine*[23] ***(1f):*** light yellow oil (2.1 g, 65% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.21 (s, 6H), 3.35 (s, 2H), 7.17 (d, 2H, $J$ = 8.4 Hz), 7.42 (d, 2H, $J$ = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.3, 63.6, 120.9, 130.8, 131.3, 137.9.

*4-(Trifluoromethyl)-N,N-dimethylbenzylamine*[15,16] ***(1g):*** light yellow oil (1.8 g, 58% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.24 (s, 6H), 3.46 (s, 2H), 7.42 (d, 2H, $J$ = 8.0 Hz), 7.57 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.4, 63.8, 125.2, 129.2, 132.7, 143.2.

*N,N,3-Trimethylbenzylamine*[15,16] ***(1h):*** red oil (1.3 g, 58% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.25 (s, 6H), 2.35 (s, 3H), 3.39 (s, 2H), 7.07−7.10 (m, 2H), 7.14 (s, 2H), 7.19−7.23 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 21.4, 45.4, 64.4, 126.2, 127.8, 128.1, 129.8, 137.9, 138.7.

*3-Fluoro-N,N-dimethylbenzylamine*[16] ***(1i):*** light yellow oil (1.4 g, 61% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.23 (s, 6H), 3.40 (s, 2H), 6.91−6.96 (m, 1H), 7.02−7.08 (m, 2H), 7.24−7.28 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.4, 63.8 (d, $J$ = 1.7 Hz), 114.0 (d, $J$ = 20.8 Hz), 115.8 (d, $J$ = 21.8 Hz), 124.5 (d, $J$ = 2.9 Hz), 129.6 (d, $J$ = 8.1 Hz), 141.54, 163.0 (d, $J$ = 256.2 Hz).

*N,N,2-Trimethylbenzylamine*[15,16] ***(1j):*** light yellow oil (1.2 g, 54% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.26 (s, 6H), 2.39 (s, 3H), 3.39 (s, 2H), 7.18 (m, 3H), 7.26−7.28 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 19.2, 45.6, 62.0, 125.6, 127.1, 129.9, 130.3, 137.0, 137.3.

*N,N-Dimethyl-2-naphthalenemethylamine*[15,16] ***(1k):*** light yellow oil (1.2 g, 43% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.31 (s, 6H), 3.60 (s, 2H), 7.47−7.51 (m, 3H), 7.75 (s, 1H), 7.82−7.84 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 45.4, 64.5, 125.7, 126.0, 127.4, 127.7, 127.7, 127.8, 128.0, 132.8, 133.4, 136.1.

**General Procedure for the Diarylation Reaction of *N,N*-Dimethylbenzylamines (3aa−al and 3ba−ga).** A flask with a magnetic stir bar was charged with *N,N*-dimethylbenzylamine (0.5 mmol), aryl iodide (5 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol), AgOAc (166 mg, 1.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (50 mg, 0.25 mmol), HOAc (450 mg, 7.5 mmol), and TFEtOH (1.5 mL). The mixture was stirred for 30 min at room temperature and then heated at 95 °C in an oil bath for 60 h under air. After the reaction was finished, the mixture was cooled, neutralized to slightly alkaline with a saturated $Na_2CO_3$ solution (5 mL), and stirred for 30 min. Then the suspension was filtered through a Celite pad and extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 30 mL) and dried over anhydrous $Na_2SO_4$. The desired products **3** were obtained in the corresponding yields after purification by flash chromatography on silica gel using PE and EtOAc as eluent.

**Characterization Data of the Products.** *2,6-Diphenyl-N,N-dimethylbenzylamine* ***(3aa):*** light yellow oil (101 mg, 70% yield); $^1$H NMR (400 Hz, $CDCl_3$, TMS) $\delta$ 1.74 (s, 6H), 3.56 (s, 2H), 7.25 (d, 2H, $J$ = 6.4 Hz), 7.33−7.36 (m, 3H), 7.38−7.44 (m, 8H); $^{13}$C NMR (100 Hz, $CDCl_3$, TMS) $\delta$ 44.4, 56.0, 126.5, 127.6, 129.5, 129.8, 142.4, 144.2; IR $\nu$ 2937, 2854, 2763, 1494, 1457, 1020, 914, 850, 802, 758, 701 $cm^{-1}$; HRMS (EI) calcd for $C_{21}H_{21}N$ ($M^+$) 287.1674, found 287.1672.

*2,6-Bis(4-methylphenyl)-N,N-dimethylbenzylamine* ***(3ab):*** light yellow solid (115 mg, 73% yield); mp (°C): 110−111 (uncorrected); $^1$H NMR (400 Hz, $CDCl_3$, TMS) $\delta$ 1.77 (s, 6H), 2.42 (s, 6H), 2.37 (s, 2H), 7.21−7.24 (m, 6H), 7.31−7.34 (m, 5H); $^{13}$C NMR (100 Hz, $CDCl_3$, TMS) $\delta$ 21.1, 44.6, 56.1, 126.4, 128.2, 129.4, 129.7, 134.1, 136.0, 139.6, 144.1; IR $\nu$ 2921, 2851, 2771, 1512, 1456, 1368, 1018, 847, 814, 747 $cm^{-1}$; HRMS (EI) calcd for $C_{23}H_{25}N$ ($M^+$) 315.1987, found 315.1985.

*2,6-Bis(4-methoxyphenyl)-N,N-dimethylbenzylamine* ***(3ac):*** light yellow solid (125 mg, 72% yield); mp (°C): 89−90 (uncorrected);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$^1$H NMR (400 Hz, $CDCl_3$, TMS) $\delta$ 1.80 (s, 6H), 3.38 (s, 2H), 3.88 (s, 6H), 6.97 (d, 4H, $J$ = 8.8 Hz), 7.24 (d, 2H, $J$ = 7.6 Hz), 7.36−7.32 (m, 1H), 7.39 (d, 4H, $J$ = 8.4 Hz); $^{13}$C NMR (100 Hz, $CDCl_3$, TMS): $\delta$ 44.6, 55.2, 56.1, 126.5, 129.5, 130.9, 134.4, 134.9, 143.8, 158.3; IR $\nu$ 2936, 2836, 2761, 1609, 1511, 1457, 1288, 1242, 1177, 1023, 835, 813, 745 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{25}NO_2$ ($M^+$) 347.1885, found 347.1888.

*2,6-Bis(4-(trifluoromethyl)phenyl)-N,N-dimethylbenzylamine (**3ad**):* light yellow solid (125 mg, 72% yield); mp (°C): 63−64 (uncorrected); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.71 (s, 6H), 3.25 (s, 2H), 7.24 (d, 2H, $J$ = 8.8 Hz), 7.38 (t, 1H, $J$ = 8.0 Hz), 7.52 (d, 4H, $J$ = 8.4 Hz), 7.66 (d, 4H, $J$ = 8.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 140.1, 139.0, 136.7, 130.0 (q, $J$ = 32.0 Hz), 129.7, 128.0, 125.7 (d, $J$ = 3.9 Hz), 125.5 (q, $J$ = 270.6 Hz), 122.6, 121.0, 120.5, 110.0, 103.0, 31.5; IR $\nu$ 2946, 1616, 1463, 1403, 1322, 1160, 1109, 1065, 1017, 848, 800, 748 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{19}F_6N$ ($M^+$) 423.1423, found 423.1424.

*2,6-Bis(4-fluorophenyl)-N,N-dimethylbenzylamine (**3ae**):* light yellow solid (89 mg, 72% yield); mp (°C): 134−135 (uncorrected); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.74 (s, 6H), 3.26 (s, 2H), 7.06−7.10 (m, 4H), 7.21 (d, 2H, $J$ = 7.2 Hz), 7.31−7.33 (m, 1H), 7.36−7.39 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 44.5, 56.2, 114.4 (d, $J$ = 21.8 Hz), 126.5, 129.6, 131.2 (d, $J$ = 7.9 Hz), 134.4, 138.1, 143.2, 161.9 (d, $J$ = 270.9 Hz); IR $\nu$ 2981, 2853, 2774, 1601, 1506, 1454, 1218, 1157, 1044, 835, 805, 750 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{19}F_2N$ ($M^+$) 323.1486, found 323.1478.

*2,6-Bis(4-chlorophenyl)-N,N-dimethylbenzylamine (**3af**):* light yellow solid (87 mg, 49% yield); mp (°C): 139−140 (uncorrected); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.75 (s, 6H), 3.26 (s, 2H), 7.20 (d, 2H, $J$ = 7.2 Hz), 7.35−7.36 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 44.4, 56.2, 126.7, 127.7, 129.6, 131.0, 132.6, 134.3, 140.6, 143.0; IR $\nu$ 2924, 2850, 2778, 1490, 1453, 1088, 1016, 821, 797, 751 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{19}Cl_2N$ ($M^+$) 355.0895, found 355.0900.

*2,6-Bis(4-bromophenyl)-N,N-dimethylbenzylamine (**3ag**):* light yellow solid (95 mg, 43% yield); mp (°C): 123−124 (uncorrected); $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 1.77 (s, 6H), 3.28 (s, 2H), 7.22 (d, 2H, $J$ = 7.5 Hz), 7.30 (d, 4H, $J$ = 8.5 Hz), 7.35 (t, 1H, $J$ = 7.5 Hz), 7.54 (d, 4H, $J$ = 8.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 44.7, 56.5, 56.1, 121.2, 127.0, 129.9, 131.0, 131.7, 134.4, 141.5, 143.3; IR $\nu$ 2930, 2820, 2775, 1487, 1453, 1388, 1361, 1069, 1041, 1013, 816, 796, 749, 721 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{19}Br_2N$ ($M^+$) 442.9884, found 442.9880.

*Diethyl 2′-((dimethylamino)methyl)-[1,1′:3′,1″-terphenyl]-4,4″-dicarboxylate (**3ah**):* light yellow solid (131 mg, 61% yield); mp (°C): 120−121 (uncorrected); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.42 (t, 6H, $J$ = 7.2 Hz), 1.69 (s, 6H), 3.29 (s, 2H), 4.40 (m, 4H), 7.24 (d, 2H, $J$ = 8.0 Hz) 7.38 (t, 1H, $J$ = 8.0 Hz), 7.48 (d, 4H, $J$ = 8.4 Hz) 8.08 (d, 4H, $J$ = 8.4 Hz); $^{13}$ C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 14.3, 44.3, 56.2, 60.9, 126.9, 128.8, 128.9, 129.6, 143.3, 146.9, 166.5; IR $\nu$ 2974, 2823, 1709, 1607, 1267, 1177, 1099, 1021, 863, 770, 710 cm$^{-1}$; HRMS (EI) calcd for $C_{27}H_{29}NO_4$ ($M^+$) 431.2097, found 431.2099.

*2,6-Bis(4-acetylphenyl)-N,N-dimethylbenzylamine (**3ai**):* light yellow oil (70 mg, 38% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.71 (s, 6H), 2.67 (s, 6H), 3.31 (s, 2H), 7.25 (d, 2H, $J$ = 8.4 Hz), 7.39 (t, 1H, $J$ = 8.0 Hz) 7.51 (t, 4H, $J$ = 8.0 Hz), 8.01 (d, 4H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 26.6, 44.3, 56.3, 126.9, 127.8, 129.7, 129.8, 135.4, 143.2, 147.3, 197.9; IR $\nu$ 2938, 2816, 2765, 1678, 1602, 1357, 1264, 1016, 956, 844, 800, 747, 701 cm$^{-1}$; HRMS (EI) calcd for $C_{25}H_{25}NO_2$ ($M^+$) 371.1885, found 371.1889.

*2,6-Bis(3-methylphenyl)-N,N-dimethylbenzylamine (**3aj**):* light yellow oil (90 mg, 57% yield); $^1$H NMR (400 Hz, CDCl3, TMS) $\delta$ 1.78 (s, 6H), 2.43 (s, 6H), 2.37 (s, 2H), 7.17 (d, 2H, $J$ = 7.5 Hz), 7.24−7.26 (m, 3H), 7.28−7.36 (m, 7H); $^{13}$C NMR (100 Hz, $CDCl_3$, TMS) $\delta$ 21.5, 44.6, 56.3, 126.4, 127.0, 127.2, 127.5, 129.4, 130.7, 134.5, 137.0, 142.5, 144.3; IR $\nu$ 2935, 2855, 2763, 1456, 1019, 781, 745, 707 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{25}N$ ($M^+$) 315.1987, found 315.1989.

*Dimethyl 2′-((dimethylamino)methyl)-[1,1′:3′,1″-terphenyl]-3,3″-dicarboxylate (**3al**):* light yellow solid (108 mg, 54% yield); mp (°C): 82−83 (uncorrected); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.70 (s, 6H), 3.28 (s, 2H), 3.93 (s, 6H), 7.25 (d, 2H, $J$ = 7.2 Hz), 7.37 (t, 1H, $J$ = 7.6 Hz) 7.47 (t, 2H $J$ = 7.8 Hz), 7.62 (d, 2H, $J$ = 7.6 Hz), 8.03 (d, 2H, $J$ = 7.8 Hz), 8.10 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 44.3, 52.1, 56.2, 126.7, 127.7, 127.9, 129.5, 129.7, 130.7, 134.2, 142.5, 143.1, 167.1; IR $\nu$ 2942, 2813, 2762, 1709, 1440, 1300, 1253, 1196, 1086, 1042, 805, 755, 699 cm$^{-1}$; HRMS (EI) calcd for $C_{25}H_{25}NO_4$ ($M^+$) 403.1784, found 403.1786.

*2,6-Diphenyl-4-methyl-N,N-dimethylbenzylamine (**3ba**):* light yellow oil (83 mg, 55% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.71 (s, 6H), 2.43 (s, 3H), 3.45 (s, 2H), 7.12 (s, 2H), 7.37−7.39 (m, 2H), 7.41−7.47 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 21.0, 44.7, 56.1, 126.5, 127.6, 129.9, 129.8, 130.4, 131.4, 136.0, 142.8, 144.2; IR $\nu$ 2936, 2813, 2764, 1599, 1492, 1456, 1018, 867, 851, 771, 752, 700 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{23}N$ ($M^+$) 301.1830, found 301.1827.

*4-Methoxyl-2,6-diphenyl-N,N-dimethylbenzylamine (**3ca**):* light yellow oil (71 mg, 45% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.73 (s, 6H), 3.27 (s, 2H), 3.84 (s, 3H), 6.83 (s, 2H), 7.36−7.46 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 44.4, 55.2, 55.6, 114.9, 126.6, 127.6, 129.7, 142.4, 145.5, 157.4; IR $\nu$ 2936, 2813, 2762, 1592, 1460, 1429, 1338, 1205, 1170, 1040, 1018, 849, 752, 700 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{23}NO$ ($M^+$) 317.1780, found 317.1782.

*4-Fluoro-2,6-diphenyl-N,N-dimethylbenzylamine (**3da**):* light yellow oil (47 mg, 31% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.70 (s, 6H), 3.27 (s, 2H), 6.96 (d, 2H, $J$ = 8.8 Hz), 7.35−7.41 (m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 44.4, 56.6, 116.1 (d, $J$ = 20.37 Hz), 127.0, 127.8, 129.6, 141.6, 146.2, 15.8 (d, $J$ = 254.37 Hz); IR $\nu$ 2936, 2855, 2765, 1592, 1495, 1455, 1427, 1335, 1164, 1020, 921, 871, 849, 752, 700 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}FN$ ($M^+$) 305.1580, found 305.1580.

*4-Chloro-2,6-diphenyl-N,N-dimethylbenzylamine (**3ea**):* light yellow oil (54 mg, 34% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.71 (s, 6H), 3.28 (s, 2H), 7.26 (s, 2H), 7.36−7.40 (m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 44.5, 55.7, 127.0, 127.8, 129.2, 129.6, 131.9, 141.3, 145.8; IR $\nu$ 2937, 2855, 2765, 1568, 1493, 1459, 1307, 1019, 875, 852, 754, 727, 699 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}ClN$ ($M^+$) 321.1284, found 321.1287.

*4-Bromo-2,6-diphenyl-N,N-dimethylbenzylamine (**3fa**):* light yellow solid (64 mg, 35% yield); mp (°C) 64−65 (uncorrected); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.71 (s, 6H), 3.27 (s, 2H), 7.26 (s, 2H), 7.35−7.39 (m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 44.4, 55.7, 120.3, 127.0, 129.5, 132.0, 133.2, 141.0, 146.0; IR $\nu$ 2930, 2754, 1564, 1492, 1454, 1304, 1029, 877, 846, 748, 718 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}BrN$ ($M^+$) 365.0779, found 365.0774.

*4-Trifluoromethyl-2, 6-diphenyl-N,N-dimethylbenzylamine (**3ga**):* light yellow oil (64 mg, 35% yield); $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.72 (s, 6H), 3.35 (s, 2H), 7.37−7.42 (m, 10H), 7.49(s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 44.6, 55.1, 126.1, 127.2, 127.9, 129.7, 141.2, 144.9; IR $\nu$ 2940, 2818, 2768, 1358, 1263, 1168, 1122, 1092, 896, 794, 753, 701 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{20}F_3N$ ($M^+$) 355.1548, found 355.1548.

**General Procedure for the Monoarylation Reaction of *N,N*-Dimethylbenzylamines (3ha−hj and 3ia−ka).** A flask with a magnetic stir bar was charged with *N,N*-dimethylbenzylamine (0.5 mmol), aryl iodide (5 mmol), $Pd(PPh_3)_4$ (28 mg, 0.025 mmol), AgOAc (124.5 mg, 0.75 mmol), $Cu(OAc)_2{\cdot}H_2O$ (50 mg, 0.25 mmol), HOAc (450 mg, 7.5 mmol), and TFEtOH (1.5 mL), and the mixture was stirred for 30 min at room temperature and then heated at 95 °C in an oil bath for 60 h under air. After the reaction was finished, the mixture was cooled and neutralized to slightly alkaline with a saturated $Na_2CO_3$ solution (5 mL) and stirred for 30 min. Then the suspension was filtered through a Celite pad and extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 30 mL) and dried over anhydrous $Na_2SO_4$. The desired products **3** were obtained in the corresponding yields after purification by flash chromatography on silica gel using PE and EtOAc as eluent.

*N,N-Dimethyl-1-(4-methylbiphenyl-2-yl)methanamine (**3ha**):* light yellow oil (74 mg, 66% yield); $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 2.15 (s, 6H), 2.40 (s, 3H), 3.34 (s, 2H), 7.10−7.15 (m, 2H), 7.32−7.33 (m, 3H), 7.37−7.38 (m, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 45.4, 60.8, 126.6, 127.4, 127.9, 129.7, 129.9, 130.2, 136.1, 137.0, 139.5, 141.5; IR $\nu$ 2937, 2814, 2764, 1480, 1172, 1073, 824, 762,


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703 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{19}N$ ($M^+$) 225.1517, found 225.1520.

*1-(4,4′-Dimethylbiphenyl-2-yl)-N,N-dimethylmethanamine (**3hb**):* light yellow oil (80 mg, 67% yield); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.16 (s, 6H), 2.39 (s, 6H), 2.40 (s, 6H), 3.52 (s, 2H), 7.11−7.12 (m, 2H), 7.21−7.24 (m, 4H), 7.37 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 21.2, 45.3, 60.8, 127.4, 128.6, 129.6, 123.0, 130.2, 136.0, 136.2, 136.8, 138.5, 139.5; IR $\nu$ 2923, 2813, 2764, 1489, 1456, 1362, 1256, 1027, 810 $cm^{-1}$; HRMS (EI) calcd for $C_{17}H_{21}N$ ($M^+$) 239.1674, found 239.1672.

*1-(4′-Methoxy-4-methylbiphenyl-2-yl)-N,N-dimethylmethanamine (**3hc**):* light yellow oil (83 mg, 65% yield); $^1H$ NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 2.15 (s, 6H), 2.39 (s, 3H), 3.33 (s, 2H), 3.85 (s, 3H), 6.93 (d, 2H, $J$ = 8.5 Hz), 7.08−7.13 (m, 2H), 7.26 (d, 2H, $J$ = 9.0 Hz), 7.35 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 45.4, 55.3, 61.0, 113.3, 127.5, 130.1, 130.3, 130.8, 133.9, 136.3, 136.7, 139.2, 158.5; IR $\nu$ 2939, 2813, 2764, 1609, 1518, 1489, 1459, 1295, 1243, 1176, 1038, 816 $cm^{-1}$; HRMS (EI) calcd for $C_{17}H_{21}NO$ ($M^+$) 255.1623, found 255.1626.

*N,N-Dimethyl-1-(4-methyl-4′-(trifluoromethyl)biphenyl-2-yl)-methanamine (**3hd**):* light yellow solid (76 mg, 52% yield); mp (°C) 88−89 (uncorrected); $^1H$ NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 2.16 (s, 6H), 2.42 (s, 3H), 3.30 (s, 2H), 7.14−7.15 (m, 2H), 7.38 (s, 1H), 7.50 (d, 2H, $J$ = 8.5 Hz), 7.66 (d, 2H, $J$ = 8.5 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 18.7, 42.7, 58.4, 122.3, 125.2, 127.2, 127.5, 128.2, 133.5, 135.2, 135.7, 145.5; IR $\nu$ 2933, 2814, 2759, 1614, 1319, 1157, 1115, 1066, 1020, 836, 815 $cm^{-1}$; HRMS (EI) calcd for $C_{17}H_{18}F_3N$ ($M^+$) 293.1391, found 293.1393.

*1-(4′-Fluoro-4-methylbiphenyl-2-yl)-N,N-dimethylmethanamine (**3he**):* light yellow oil (69 mg, 57% yield); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.14 (s, 6H), 2.39 (s, 3H), 3.28 (s, 2H), 7.04−7.09 (m, 2H), 7.10−7.24 (m, 2H), 7.30−7.33 (m, 2H), 7.34 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 45.3, 60.9, 114.7 (d, $J$ = 20.4 Hz), 127.6, 130.0, 130.6, 131.2 (d, $J$ = 8 Hz), 136.2, 137.1, 137.4 (d, $J$ = 3 Hz), 138.6, 162.0 (d, $J$ = 243.8 Hz); IR $\nu$ 2927, 2815, 2766, 1751, 1694, 1600, 1574, 1515, 1492, 1214, 1028, 841, 817, 773 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{18}FN$ ($M^+$) 243.1423, found 243.1423.

*1-(4′-Chloro-4-methylbiphenyl-2-yl)-N,N-dimethylmethanamine (**3hf**):* light yellow solid (75 mg, 58% yield); mp (°C) 44−45 (uncorrected); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.18 (s, 6H), 2.42 (s, 3H), 3.32 (s, 2H), 7.14 (s, 2H), 7.31−7.33 (m, 2H), 7.37−7.39 (m, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 45.3, 60.9, 127.7, 128.1, 129.8, 130.7, 131.1, 132.8, 136.0, 137.3, 138.4, 139.9; IR $\nu$ 2925, 2811, 2766, 1476, 1090, 1006, 814 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{18}ClN$ ($M^+$) 259.1128, found 259.1130.

*1-(4′-Bromo-4-methylbiphenyl-2-yl)-N,N-dimethylmethanamine (**3hg**):* light yellow solid (85 mg, 56% yield); mp (°C) 54−55 (uncorrected); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.15 (s, 6H), 2.39 (s, 3H), 3.29 (s, 2H), 7.11 (s, 2H), 7.24 (d, 2H, $J$ = 8.8 Hz), 7.35 (s, 1H), 7.51 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 45.2, 60.8, 120.9, 127.7, 129.8, 130.6, 131.0, 131.4, 135., 137.4, 138.3, 140.3; IR $\nu$ 2928, 2810, 2764, 1475, 1002, 835, 812 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{18}BrN$ ($M^+$) 303.0623, found 303.0622.

*Ethyl 2′-((dimethylamino)methyl)-4′-methylbiphenyl-4-carboxylate (**3hh**):* light yellow oil (74 mg, 50% yield); $^1H$ NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 1.43 (t, 3H, $J$ = 7.2 Hz), 2.15 (s, 6H), 2.42 (s, 3H), 3.32 (s, 2H), 4.14−4.31 (m, 2H), 7.15 (s, 2H), 7.39 (s, 1H), 7.45 (d, 2H, $J$ = 8.0 Hz), 8.09 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 14.4, 21.2, 45.3, 60.9, 61.0, 127.7, 128.8, 129.2, 129.7, 129.7, 130.6, 136.0, 137.6, 138.6, 146.3, 166.7; IR $\nu$ 2940, 2814, 2765, 1715, 1609, 1459, 1365, 1269, 1176, 1101, 1026, 1007, 821, 774, 708 $cm^{-1}$; HRMS (EI) calcd for $C_{19}H_{23}NO_2$ ($M^+$) 297.1729, found 297.1732.

*1-(3′,4-Dimethylbiphenyl-2-yl)-N,N-dimethylmethanamine (**3hj**):* light yellow oil (71 mg, 59% yield); $^1H$ NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 2.16 (s, 6H), 2.39 (s, 6H), 3.33 (s, 2H), 7.09−7.15 (m, 5H), 7.27 (t, 1H, $J$ = 7.5 Hz), 7.37 (s, 1H); $^{13}$ C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 21.2, 21.6, 45.4, 60.7, 126.8, 127.4, 127.8, 129.9, 130.2, 130.5, 136.2, 136.9, 137.4, 139.7, 141.5. IR $\nu$ 2924, 2814, 2764, 1608, 1474, 1170, 1028, 823, 787, 708 $cm^{-1}$; HRMS (EI) calcd for $C_{17}H_{21}N$ ($M^+$) 239.1674, found 239.1677.

*1-(4-Fluorobiphenyl-2-yl)-N,N-dimethylmethanamine (**3ia**):* light yellow oil (25 mg, 22% yield); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.18 (s, 6H), 3.35 (s, 2H), 6.97−7.02 (m, 1H), 7.19−7.23 (m, 1H), 7.37 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 45.3, 60.7, 113.5 (d, $J$ = 20.5 Hz), 115.9 (d, $J$ = 22 Hz) 127.0, 128.0, 129.6, 131.4 (d, $J$ = 7.75 Hz), 138.0 (d, $J$ = 1.87 Hz), 138.9 (d, $J$ = 8.5 Hz), 140.5, 161.3 (d, $J$ = 246.75 Hz); IR $\nu$ 2922, 2853, 1609, 1479, 1260, 1224, 1028, 821, 765, 704 $cm^{-1}$; HRMS (EI) calcd for $C_{15}H_{16}FN$ ($M^+$) 229.1267, found 229.1270.

*N,N-Dimethyl-1-(3-methylbiphenyl-2-yl)methanamine (**3ja**):* light yellow oil (35 mg, 31% yield); $^1H$ NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 1.98 (s, 6H), 2.50 (s, 3H), 3.37 (s, 2H), 7.03−7.05 (m, 1H), 7.18 (m, 2H), 7.23−7.26 (m, 2H), 7.30−7.33 (m, 1H), 7.35−7.40 (m, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 20.0, 45.1, 57.3, 126.5, 126.6, 127.6, 127.7, 129.8, 130.0, 134.7, 139.1, 142.4, 143.5; IR $\nu$ 2937, 2814, 2763, 1586, 1461, 1362, 1254, 1172, 1019, 848, 789, 758, 701 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{19}N$ ($M^+$) 225.1517, found 225.1517.

*N,N-Dimethyl-1-(3-phenylnaphthalen-2-yl)methanamine (**3ka**):* light yellow oil (79 mg, 61% yield); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.26 (s, 6H), 3.54 (s, 2H), 7.48−7.52 (m, 7H), 7.76 (s, 1H), 7.85−7.87 (m, 1H), 7.91−7.93 (m, 1H), 8.05 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 45.3, 61.3, 125.9, 125.9, 127.0, 127.5, 127.6, 127.9, 128.8, 129.7, 132.3, 132.7, 134.5, 140.8, 141.3; IR $\nu$ 2939, 2814, 2765, 1679, 1491, 1449, 1364, 1173, 1148, 1024, 892, 747, 701 $cm^{-1}$; HRMS (EI) calcd for $C_{19}H_{19}N$ ($M^+$) 261.1517, found 261.1516.

**General Procedure for the Reduction of the 2,6-Diphenyl-*N,N*-dimethylbenzylamine to 2′-Methyl-1,1′:3′,1″-terphenyl[15,24] (4aa).** A mixture of **3aa** (143.5 mg, 0.5 mmol) and Pd/C catalyst (10 wt % Pd, 106 mg, 10 mol %) in MeOH (5 mL) was stirred under $H_2$ at balloon pressure at 80 °C for 24 h. After the catalyst was filtered, the filtrate was evaporated to get the crude product. Further purification by flash chromatography on silica gel with PE afforded product **4aa**.

*2′-Methyl-1,1′:3′,1″-terphenyl[24] (**4aa**):* colorless oil (90 mg, yield 73%); $^1H$ NMR (400 Hz, $CDCl_3$, TMS) $\delta$ 2.03 (s, 3H), 7.14−7.19 (m, 3H), 7.23−7.35 (m, 10H); $^{13}C$ NMR (100 Hz, $CDCl_3$, TMS) $\delta$ 18.8, 125.4, 126.9, 128.1, 129.1, 129.4, 133.0, 142.5, 142.9.

**Preparation of $\mu$-(Dichloro)-bis(*N,N*-dimethylbenzylamine-C,N)dipalladium[15,22] (5).** A mixture of **1a** (540 mg, 4 mmol) and palladium dichloride (354 mg, 2 mmol) in methanol (15 mL) was stirred at room temperature. After 5 h, all of the palladium dichloride had dissolved and was replaced by a yellow solid. This solid was recrystallized from benzene and *n*-hexane to obtain the product **5.**

*$\mu$-(Dichloro)-bis(N,N-dimethylbenzylamine-C,N)dipalladium[15,22] (**5**):* yellow solid (368 mg, 22% yield); mp (°C) 186−188 (uncorrected); $^1H$ NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.85 (d, 6H, $J$ = 10.8 Hz), 3.93 (s, 2H), 6.85−6.89 (m, 2H), 6.95−6.97 (m, 1H), 7.14−7.20 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 52.6, 52.9, 73.2, 73.4, 121.5, 124.7, 125.2, 132.9, 133.4, 143.0, 147.0

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1H$ NMR and $^{13}C$ NMR spectra for all relevant compounds and XRD spectra for the reaction mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES


(1) For selected reviews, see: (a) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (b) Bringmann, G.; Price Mortimer, A. J.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5384. (c) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (d) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.

(2) For recent reviews on direct arene C−H arylation, see: (a) Miura, M.; Satoh, T. *Top. Organomet. Chem.* **2005**, *14*, 55. (b) Campeau, L. C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (c) Seregin, I. Y.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (d) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (e) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269. (f) Daugulis, O.; Do, H. Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (g) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (h) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (i) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447. (j) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (k) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824. (l) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (m) Fagnou, K. *Top. Curr. Chem.* **2010**, *292*, 35. (n) Daugulis, O. *Top. Curr. Chem.* **2010**, *292*, 57. (o) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215.

(3) Ackermann, L. In *Topics in Organometallic Chemistry*; Chatani, N., Ed.; Springer: Berlin, 2007; Vol *24*, p 35.

(4) Daugulis, O.; Zaitsev, V. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4046.

(5) (a) Daugulis, O.; Zaitsev, V. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4046. (b) Yang, S.; Li, B.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 6066. (c) Li, B.-J.; Tian, S.-L.; Fang, Z.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1115. (d) Li, D.-D.; Yuan, T.-T.; Wang, G.-W. *J. Org. Chem.* **2012**, *77*, 3341. (e) Péron, F.; Fossey, C.; Cailly, T.; Fabis, F. *Org. Lett.* **2012**, *14*, 1827.

(6) (a) Yoshikai, N.; Matsumoto, A.; Norinder, J.; Nakamura, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 2925. (b) Tredwell, M. J.; Gulias, M.; Bremeyer, N. G.; Johansson, C. C. C.; Collins, B. S. L.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1076.

(7) (a) Vogler, T.; Studer, A. *Org. Lett.* **2007**, *10*, 129. (b) Li, H.; Wei, W.; Xu, Y.; Zhang, C.; Wan, X. *Chem. Commun.* **2011**, *47*, 1497.

(8) (a) Yu, M.; Liang, Z.; Wang, Y.; Zhang, Y. *J. Org. Chem.* **2011**, *76*, 4987. (b) Romero-Revilla, J. A.; García-Rubia, A.; Arrayás, R. G.; Fernández-Ibáñez, M. Á.; Carretero, J. C. *J. Org. Chem.* **2011**, *76*, 9525. (c) Zhang, X.; Yu, M.; Yao, J.; Zhang, Y. *Synlett* **2012**, *3*, 463.

(9) Li, W.; Xu, Z.; Sun, P.; Jiang, X.; Fang, M. *Org. Lett.* **2011**, *13*, 1286.

(10) Lazareva, A.; Daugulis, O. *Org. Lett.* **2006**, *8*, 5211.

(11) Yao, J.; Yu, M.; Zhang, Y. *Adv. Synth. Catal.* **2012**, *354*, 3205.

(12) (a) Chiong, H. A.; Pham, Q. N.; Daugulis, O. *J. Am. Chem. Soc.* **2007**, *129*, 9879. (b) Giry, R.; Maugel, N.; Li, J.-J.; Wang, D.-H.; Breazzano, S. P.; Saunders, L. B.; Yu, J.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 3510. (c) Wang, D.-H.; Mei, T. S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2008**, *130*, 17676. (d) Engle, K. M.; Thuy-Boun, P. S.; Dang, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 18183.

(13) (a) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909. (b) Tsuji, J. *Acc. Chem. Res.* **1969**, *2*, 144. (c) Holton, R. A.; Davis, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 4175. (d) Holton, R. A. *Tetrahedron Lett.* **1977**, *4*, 355. (e) Grove, D. M.; van Koten, G.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4285. (f) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1511. (g) Dunina, V. V.; Kuzmina, L. G.; Kazakova, M. Y.; Gorunova, O. N.; Grishin, Y. K.; Kazakova, E. I. *Eur. J. Org. Chem.* **1999**, 1029.

(14) Kakiuchi, F.; Igi, K.; Matsumoto, M.; Hayamizu, T.; Chatani, N.; Murai, S. *Chem. Lett.* **2002**, 396.

(15) Cai, G.; Fu, Y.; Li, Y.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 7666.

(16) Li, H.; Cai, G.-X.; Shi, Z.-J. *Dalton Trans.* **2010**, *39*, 10442.

(17) Zhang, H.; Cui, X.; Yao, X.; Wang, H.; Zhang, J.; Wu, Y. *Org. Lett.* **2012**, *14*, 3012.

(18) Roering, A. J.; Hale, L. V. A.; Squier, P. A.; Ringgold, M. A.; Wiederspan, E. R.; Clark, T. B. *Org. Lett.* **2012**, *14*, 3558.

(19) Zhao, J.; Zhang, Y.; Cheng, K. *J. Org. Chem.* **2008**, *73*, 7428.

(20) Shi, Z.; Li, B.; Wan, X.; Cheng, J.; Fang, Z.; Cao, B.; Qin, C.; Wang, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5554.

(21) (a) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643. (b) Albano, V. G.; Di Serio, M.; Monari, M.; Orabona, I.; Panunzi, A.; Ruffo, F. *Inorg. Chem.* **2002**, *41*, 2672. (c) Lebrasseur, N.; Larrosa, L. *J. Am. Chem. Soc.* **2008**, *130*, 2926. (d) Thirunavukkarasu, V. S.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9462.

(22) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

(23) Saidi, M. R.; Stan Brown, R.; Ziyaei-Halimjani, A. *J. Iran. Chem. Soc.* **2007**, *4*, 194.

(24) (a) Azzena, U.; Cattari, M.; Melloni, G.; Pisano, L. *Synthesis* **2003**, 2811. (b) Hilt, G.; Danz, M. *Synthesis* **2008**, 2257.