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Facile synthesis of 6-iodo-2,2′-dipivaloyloxy-1,1′-binaphthyl, a key intermediate of high reactivity for selective palladium-catalyzed monofunctionalization of the 1,1′-binaphthalene core

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ABSTRACT

A high-yielding procedure for selective monoiodination of 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) is reported. 6-Iodo-2,2′-dipivaloyloxy-1,1′-binaphthyl, obtained in three steps starting from BINOL in 88% overall yield, proved to be a highly efficient substrate in various palladium-catalyzed coupling (Stille, Heck, Sonogashira, and Suzuki coupling) and carbonylation reactions compared to the analogous 6-bromo derivative.

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Optically active 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) and its derivatives have attracted significant interest due to their application as ligands in enantioselective catalytic reactions.[1] The main drawback of these homogeneous catalytic systems is in the difficulty of recovery and recycling of the expensive chiral catalysts. Accordingly, several creative synthetic strategies toward polymer-, dendrimer-, and silica-supported BINOL-type ligands were developed.[2] Many of these use an halogenated BINOL derivative as the starting material[3–6] and often incorporate a palladium-catalyzed coupling reaction of such compounds as the key step.[7–10] According to the literature, BINOL and its derivatives can be halogenated selectively at the 6,6′-,[11] 3,3′-,[12] and 5,5′-[13] positions. However, there are fewer reports on selective monohalogenation of similar compounds. 6-Mono-bromo-BINOL derivatives were synthesized via direct bromination of BINOL[5] or 2,2′-diethoxy-1,1′-binaphthalene,[14] and, more efficiently, through mono-ester formation between BINOL and pivaloyl chloride followed by bromination.[7,15] At the same time, palladium-catalyzed coupling reactions of the bromo derivatives can be carried out efficiently usually only under harsh reaction conditions. As an example, Heck reaction of 6-bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl and butyl acrylate afforded the coupling product in 87% yield in the presence of the $Pd(OAc)_2$—(o-Tol)$_3$P catalytic system after heating for 36 h at 130 °C.[7] In spite of this, reports on the synthesis of the potentially more reactive monoiodo derivatives are scarce. A 3-iodo derivative was prepared in 44% overall yield starting from BINOL via de-iodination of an intermediate 3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene.[8] Another approach involves halogen–lithium, lithium–halogen exchange of a 6′-substituted 6-monobromo compound.[16]

As part of our ongoing research on palladium-catalyzed reactions of aryl/alkenyl halides,[17] the functionalization of 6-bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl[7] via aminocarbonylation was attempted. As we observed a sluggish reaction, we decided to explore the possibility of selective monoiodination of the binaphthyl core in order to obtain a more reactive substrate.

Recently, several direct iodinations of activated aromatic compounds were reported in the presence of a wide variety of reagents, such as $NaIO_4/KI/NaCl$,[18] $NaClO_2/NaI/HCl$,[19] $KIO_3/KI/HCl$,[20] $Py{\cdot}ICl$,[21] and IPy_2BF_4.[22] All of these reagents gave unsatisfactory results in the iodination of either BINOL (**1**) or 2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**2**). Interestingly, the solid-phase reaction of **2** with $AgNO_3/I_2$,[23] which had been reported to be a very effective method for the iodination of both activated and deactivated aromatic compounds, led to the selective formation of the 6-nitro derivative **3** in a yield of 57% after optimization (Scheme 1).[24] The presence of iodo derivatives was not detected in the reaction mixture. The position of the nitro group was proved using 2D NMR techniques (^1H–^1H COSY, HSQC, and HMBC).

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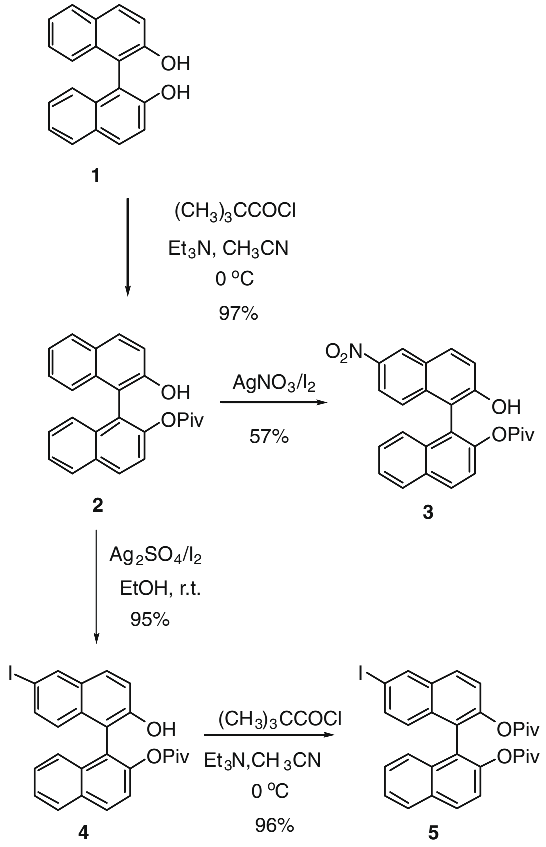


Scheme 1. Synthesis of 6-monosubstituted BINOL derivatives **3**–**5**.

Fortunately, iodination of **2** with Ag$_2$SO$_4$/I$_2$[25] gave a selective reaction affording **4** in 95% yield (Scheme 1).[26] The structure of **4** was proved by 2D NMR methods.

Electron-deficient aryl halides are usually more reactive substrates in palladium-catalyzed coupling reactions because of the more facile oxidative addition of these compounds to the nucleophilic Pd(0) complex. In order to obtain a substrate with high reactivity, compound **4** was converted into the dipivaloyloxy derivative **5**[27] using a standard procedure.[28]

It should be mentioned that the attempted iodination of BINOL (**1**) resulted in a complex mixture of several unidentified side products and no conversion of 2,2′-dipivaloyloxy-1,1′-binaphthyl was observed under the same reaction conditions.

The reactivity of **5** was examined in various palladium-catalyzed reactions (Scheme 2, Table 1). As a comparison, carbonylation/coupling reactions of 6-bromo-2,2′-dipivaloyloxy-1,1′-binaphthyl (**6**), obtained by pivaloylation[28,29] of known 6-bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl,[7] were carried out under the same conditions. The reactions were followed by GC and the formation of the products confirmed by GC–MS. The reactions were completely selective in each case, besides the carbonylation/coupling products, no other derivatives were obtained. The reaction conditions for the conversion of **5** were not optimized.

In the aminocarbonylation using morpholine as the nucleophilic reagent, a marked difference in the reactivities of **5** (Table 1, entry 1) and **6** (entry 2) was observed. A poor conversion of **6** was obtained even after 12 h. As expected, under carbonylation conditions, the formation of **7a** was accompanied by a double carbonylation leading to ketoamide **7b**, even at atmospheric CO pressure, in both cases.[17b]

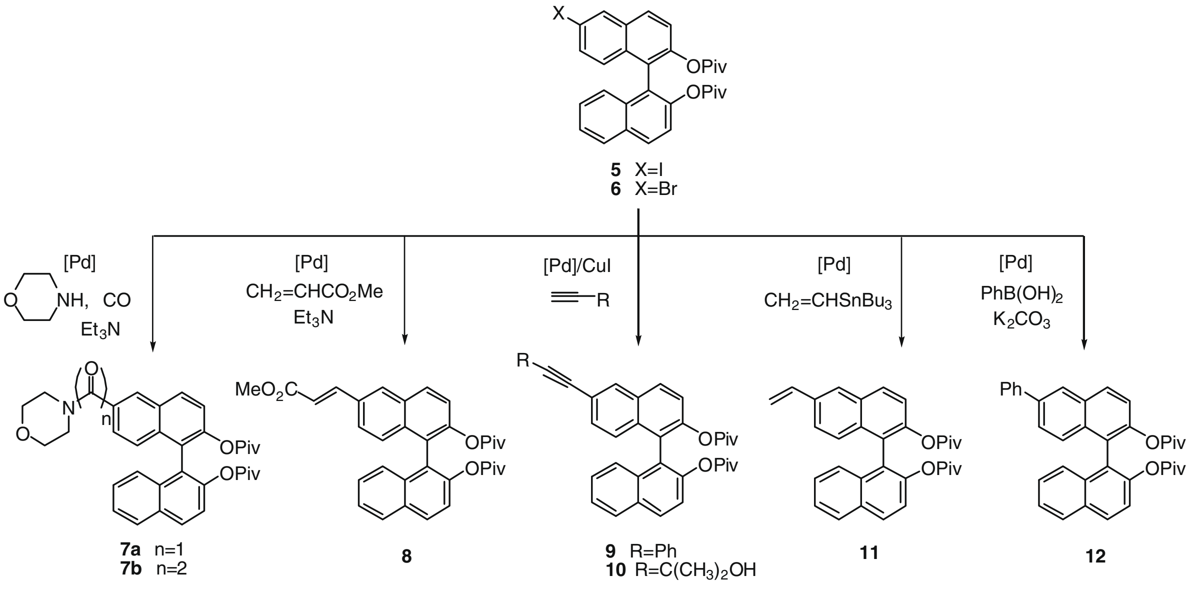
Compound **5** was also found to be a superior substrate in Heck and Sonogashira reactions (entries 3–10). The reactivity difference between **5** and **6** is especially evident when using less active reagents, such as 2-methyl-3-butyn-2-ol in the Sonogashira coupling (entries 8–10).

Although Sonogashira and Stille reactions of **6** gave the expected products in reasonable to excellent yields, respectively (entries 6 and 12), total conversion of the 6-iodo derivative **5** was observed even upon reducing the reaction temperature (entries 7 and 13).

The only example where **5** and **6** gave identical results under the conditions used was in the Suzuki coupling with PhB(OH)$_2$ (entries 15 and 16).

It should be mentioned that derivative **4** was found to be an almost equally reactive substrate in these couplings, but the formation of side products was observed. Clarification of the effect of protecting groups on the reactivity of 6-halogeno-2,2′-dihydroxy-1,1′-binaphthyl derivatives as well as exploration of the side reactions observed in couplings of **4** is in progress.

In summary, 6-iodo-2,2′-dipivaloyloxy-1,1′-binaphthyl (**5**) was synthesized in high yield starting from 2,2′-dihydroxy-1,1′-binaph-



Scheme 2. Palladium-catalyzed reactions of 6-iodo-(**5**) and 6-bromo-(**6**) derivatives of BINOL.

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