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# Facile Synthesis of 3,3′-Disubstituted 2,2′-Binaphthyls by Transition-metal-catalyzed Double Benzannulation

Rui Umeda,[1] Hiromasa Tabata,[1] Yoshito Tobe,[2] and Yutaka Nishiyama*[1]
[1]*Faculty of Chemistry, Materials and Bioengineering, Kansai University, Osaka 564-8680*
[2]*Graduate School of Engineering Science, Osaka University, Osaka 560-8531*

(E-mail: nishiya@kansai-u.ac.jp)

3,3′-Disubstituted 2,2′-binaphthyls were prepared by the Cu- or Re-catalyzed double benzannulation reaction of 2-(phenylethynyl)benzaldehyde with various butadiynes in the presence of trichloroacetic acid, in moderate to good yields. Acceleration of the second benzannulation was clearly observed.

1,1′-Binaphthyl (Chart 1) is one of the most versatile organic frameworks due to its axial chirality. The synthetic methods of various 1,1′-binaphthyl derivatives and their applications, such as chiral ligands and sensors, have been reported.[1] On the other hand, although 2,2′-binaphthyl derivatives can be promising candidates for chiral frameworks, there are only a few reports on their synthesis and application.[2] From this point of view, we planned to develop the synthesis of 2,2′-binaphthyls by Cu[3]- or Re[4]-catalyzed double benzannulation reactions. Although the synthesis of dihalo-2,2′-binaphthyl derivatives by the [4 + 2] benzannulation of 1,4-diphenylbutadiyne and 2-(phenylethynyl)benzaldehyde in the presence of $CuX_2$ (X = Cl and Br) has been shown,[5] to the best of our knowledge, there is no catalytic synthetic method for 2,2′-binaphthyl derivatives via the double benzannulation reaction of 2-(phenylethynyl)benzaldehyde with butadiynes.[6] In this report, we describe the catalytic synthetic method for 3,3′-disubstituted 2,2′-binaphthyl derivatives by the Cu- or Re-catalyzed reaction of 2-(phenylethynyl)benzaldehyde with various butadiynes in the presence of trichloroacetic acid as a Brønsted acid.

The reaction of 1,4-diphenylbutadiyne (**2a**) with 3.0 equiv of 2-(phenylethynyl)benzaldehyde (**1**) using $[ReCl(CO)_5]$ as a catalyst in the presence of trichloroacetic acid under our previous optimized conditions[4] gave 3,3′-diphenyl-2,2′-binaphthyl (**3a**) in 44% yield (Entry 1 in Table 1).[7,8] When $Cu(OTf)_2$ instead of the Re complex was used as a catalyst, the yield of **3a** decreased due to the formation of uncharacterized polymeric products (Entry 1). To study the scope and limitations of the substrates, various butadiynes **2** were treated with **1** (3.0 equiv) using $Cu(OTf)_2$ or $[ReCl(CO)_5]$ as the catalyst in the presence of trichloroacetic acid; the results are shown in Table 1.

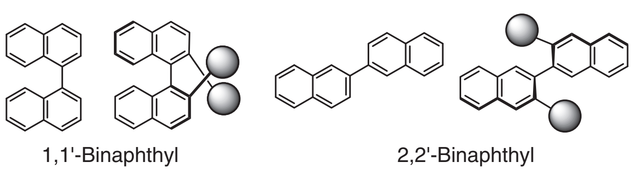
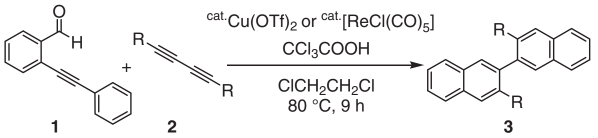


**Chart 1.**

**Table 1.** Reaction of 2-(phenylethynyl)benzaldehyde (**1**) with various butadiynes **2**[a]

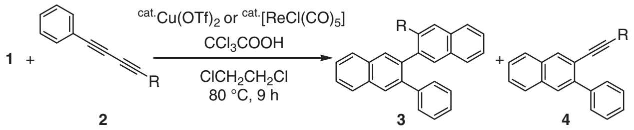


| Entry | R | **3**, Yield [%][b] | |
|---|---|---|---|
| | | cat. Cu | cat. Re |
| 1 | **a**, Ph | 25 | 44 |
| 2 | **b**, 4-$t$-Bu$C_6H_4$ | 53 | 78 |
| 3 | **c**, 4-Me$OC_6H_4$ | 61 | 60 |
| 4 | **d**, 2,4,6-triMe$C_6H_2$ | 83 | 94 |
| 5 | **e**, 3,5-di-$t$-Bu-4-Me$OC_6H_2$ | 25 | 55 |
| 6 | **f**, 4-Cl$C_6H_4$ | trace | trace |
| 7 | **g**, 4-F$C_6H_4$ | <5 | <5 |
| 8 | **h**, 1-Naphthyl | 24 | 43 |
| 9 | **i**, 2-Naphthyl | 23 | 55 |
| 10 | **j**, 9-Anthryl | N.D. | 43 |
| 11 | **k**, 2-Thienyl | N.D. | N.D. |
| 12 | **l**, 3-Thienyl | <10 | 24 |
| 13 | **m**, $n$-Bu | 61 | 73 |
| 14 | **n**, $(CH_3)_3Si$ | 31[c] | 58 |

[a]Reaction conditions: **1** (0.90 mmol), **2** (0.30 mmol), catalyst (16 mol %), $CCl_3COOH$ (0.90 mmol), and $ClCH_2CH_2Cl$ (10 mL) at 80 °C for 9 h. [b]Isolated yields based on **2**. [c]2,2′-Binaphthyl was obtained in 13% yield.

When **1** was allowed to react with 1,4-di(4-$t$-butylphenyl)- and 1,4-di(4-methoxyphenyl)butadiynes using $[ReCl(CO)_5]$ catalyst, the corresponding 2,2′-binaphthyl derivatives, **3b** and **3c**, were obtained in 78% and 60% yields, respectively (Entries 2 and 3). Similarly, the Cu-catalyzed double benzannulation of **3b** and **3c** took place to give the 2,2′-binaphthyl derivatives in moderate yields (Entries 2 and 3). For both the Cu and Re catalysts, the reaction of the sterically hindered butadiyne, 1,4-bis(2,4,6-trimethylphenyl)butadiyne (**2d**), with **1** efficiently occurred to give **3d** in high yield (Entry 4). For the benzannulation of **1** with 1,4-bis(3,5-di-$t$-butyl-4-methoxyphenyl)butadiyne or dinaphthyl-substituted butadiynes, the yields of **3e**, **3h**, and **3i** were almost the same as those of **3a** (Entries 1, 5, 8, and 9). On the other hand, for the reaction of 1,4-diarylbutadiynes substituted with chloro and fluoro groups on the phenyl moieties, **2f** and **2g**, the yields of the corresponding binaphthyls **3f** and **3g** were quite low (Entries 6 and 7). The Re-catalyzed double benzannulation reaction of **1** with 1,4-di(9-anthryl)butadiyne (**2j**) occurred to give **3j** in 43% yield; however, the use of $Cu(OTf)_2$ as a catalyst led to the formation of only uncharacterized polymeric materials (Entry 10). Although 2-thienyl-substituted naphthalene **3k** was not formed from **2k**, 3-thienyl-substituted naphthalene **3l** was obtained by the reaction of 1,4-

**Table 2.** Effect of the ratio of **1** and butadiynes **2**[a]



| Entry | R | **1** /mmol | Catalyst | Product amount /mmol | |
|---|---|---|---|---|---|
| | | | | **3** | **4** |
| 1 | **a**, Ph | 0.90 | Cu | 0.075 | N.D. |
| 2 | **a**, Ph | 0.90 | Re | 0.13 | N.D. |
| 3 | **a**, Ph | 0.60 | Cu | 0.069 | N.D. |
| 4 | **a**, Ph | 0.60 | Re | 0.099 | N.D. |
| 5 | **a**, Ph | 0.30 | Cu | 0.050 | N.D. |
| 6 | **a**, Ph | 0.30 | Re | 0.090 | N.D. |
| 7 | **o**, *n*-Bu | 0.90 | Cu | 0.18 | N.D. |
| 8 | **o**, *n*-Bu | 0.90 | Re | 0.22 | N.D. |
| 9 | **o**, *n*-Bu | 0.30 | Cu | 0.060 | trace[b] |
| 10 | **o**, *n*-Bu | 0.30 | Re | 0.10 | trace[b] |

[a]Reaction conditions: **1**, **2** (0.30 mmol), catalyst (16 mol %), and $ClCH_2CH_2Cl$ (10 mL) at 80 °C for 9 h. $CCl_3COOH$ was used in the same amount of **1**. [b]Compound **4** (R = *n*-Bu) was detected by GC-MS analysis.

di(3-thienyl)butadiyne (**2l**) in low yields (Entries 11 and 12). 3,3′-Di-*n*-butyl-2,2′-binaphthyl (**3m**) was obtained in good yield by the benzannulation of **1** with the corresponding butadiyne **2m** (Entry 13). The Cu-catalyzed reaction of **1** and 1,4-bis(trimethylsilyl)butadiyne (**2n**) produced the mixtures of **3n** (31%) and a desilylated compound, 2,2′-binaphthyl (13%). On the other hand, it is important to note that when the Re complex was used, 3,3′-bis(trimethylsilyl)-2,2′-binaphthyl (**3n**) was formed in 58% yield as the sole product (Entry 14). To confirm the reaction pathway of the formation of 2,2′-binaphthyl, **3n** was exposed to 16 mol % of $Cu(OTf)_2$ and 3.0 equiv of $CCl_3COOH$ in $CH_2ClCH_2Cl$ solvent at 80 °C for 9 h. The protodesilylation of **3n** proceeded to give 2,2′-binaphthyl (38%) together with the recovered **3n** (50%). Based on these results, we suggested that 2,2′-binaphthyl was formed by the benzannulation reaction of **1** and **2n**, followed by the protodesilylation of **3n** with TFA derived from $Cu(OTf)_2$.[9]

Next, to estimate the reactivity and selectivity of the triple bonds of the butadiynes **2**, the investigation of the ratio between **1** and **2** was carried out (Table 2). First, when 2 equiv of **1** and 1,4-diphenylbutadiyne (**2a**) was used, in both cases using the Cu and Re catalysts, the yield of **3a** slightly decreased as compared to Entries 1 and 2; however, the monobenzannulated product 2-(phenylethynyl)-3-phenylnaphthalene (**4a**) was not detected by both $^1$H NMR and GC-MS analysis (Entries 1–4). Even when **1** was used in the same amount as **2a**, **4a** was not obtained at all (Entries 5 and 6). The Cu- and Re-catalyzed benzannulation reaction of **1** (3 equiv) with the asymmetric butadiyne 1-*n*-butyl-4-phenylbutadiyne (**2o**) (3.0 mmol) afforded the corresponding 2,2′-binaphthyl **3o** as the sole product in good yield (Entries 7 and 8), but when **1** was used in the same amount as **2a**, only a trace amount of **4o**[10] was observed in the case of using both Cu and Re catalysts (Entries 9 and 10). These results clearly indicated that the second benzannulation step is much faster than the first.

In conclusion, the Cu- or Re-catalyzed double benzannulation of 2-(phenylethynyl)benzaldehyde (**1**) with butadiynes **2** in the presence of trichloroacetic acid gave the corresponding 3,3′-disubstituted 2,2′-binaphthyls **3**. The possibility of an asymmetric catalytic reaction using chiral ligands is an intriguing consideration, which is currently under investigation.

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6 In a preliminary our examination, we have shown the one example on the Re-catalyzed benzannulation of 1,4-diphenylbutadiyne and 2-(phenylethynyl)benzaldehyde, see ref 4.

7 Other Lewis acid- or metal complex-catalyzed reaction of 1,4-diphenylbutadiyne (**2a**) with 2-(phenylethynyl)benzaldehyde (**1**) in the presence of trichloroacetic acid were also investigated. These results are shown in Supporting Information.

8 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 The protodesilylation of the trimethylsilyl-substituted aryls can be achieved by TFA. As an example, see: R. Diercks, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1986**, *108*, 3150.

10 Another isomer, 2-*n*-butyl-3-(phenylethynyl)naphthalene, was also observed during the reaction process. Therefore, we could not explain the reactivity and selectivity of the triple bonds of **2o**.