Chemical Papers
https://doi.org/10.1007/s11696-020-01308-w

SHORT COMMUNICATION

Synthesis of (±)-3,3′-diphenyl-2,2′-binaphthol via different routes using Pd and Ni as catalyst respectively

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Received: 15 April 2020 / Accepted: 10 August 2020

Abstract

3,3′-Biphenyl-2,2′-binaphthols (BINOLs) are precursors of phosphoric acids that are widely used as ligands and catalysts in organic reactions. In this report, two routes for the synthesis of (±)-3,3′-diphenyl BINOLs via (±)-3,3′ bis-halogenated BINOLs intermediates using (±)-BINOL as starting material have been established. Both routes are four-step reactions, characterized by the use of different catalysts in the third step, the total yield of the first route is 45%, while overall yield of the second route is 51% yield.

Keywords BINOLs · (±)-3,3′-Diphenyl BINOL · (±)-3,3′ Bis-halogenated BINOLs · Organic reactions

Due to the chiral auxiliaries and ligands with *C2*-symmetry, chiral 3,3′-disubstituted-2,2′-binaphthol derivatives (BINOLs) have been widely employed as important ligands in catalytic asymmetric reactions since the several decades, additionally, they have also been used as axially chiral backbones for the development of phosphoric acids through synthetic sequences (Brunel 2005, 2007; Yamamoto and Futatsugi 2005; Luan and Schaus 2012; Zhou et al. 2012; Yu et al. 2011). In this regard, chiral phosphoric acids derived from BINOLs have bifunctional catalytic performance, namely Brønsted acids sites play roles in capturing electrophiles via hydrogen bonding interactions without formation of loose ion pair, whereas phosphoryl oxygens act as Lewis bases sites to capture another component, just as we have known, phosphoric acids are prevalent organocatalysts that have attracted increasing attention (Yu et al. 2008; Bartoli et al. 2010; Mori et al. 2013; Yin and You 2011; Li 2013; Dong et al. 2017). Furthermore, intensive studies have been revealed that the substituents at 3 and 3′ positions of the BINOLs backbone have considerable electronic and/or steric influence on chiral phosphoric acids catalytic performance through theoretical and experimental methods. According to this concept, changing the substituent groups at 3 and 3′ positions can, to a large extent, influence the steric and electronic properties of the BINOLs framework (Brunel 2005; Kaupmees et al. 2013; Yang et al. 2013; Bisht et al. 2019). Therefore, 3,3′ bis-arylated BINOLs are valuable precursors for an array of phosphoric acids organocatalysts that are applied in catalytic asymmetric reactions.

Although many 3,3′ bis-arylated BINOLs are commercial outside, lengthy synthetic sequences and tedious manipulations lead to high price-to-sales for 3,3′ bis-arylated BINOLs, and the used 3,3′ bis-arylated BINOLs in most laboratory are usually synthesized by themselves. Generally, there are two protocols for synthesis of 3,3′ bis-arylated BINOLs, one via 3,3′ bis-metalled BINOLs intermediate (Simonsen et al. 1998; Wipf et al. 2000; Ahmed and Clark 2014) and the other through 3,3′ bis-halogenated BINOLs intermediate (Cox et al. 1992; Tsang et al. 2001; Ooi et al. 2003; Bartoszek et al. 2008; Klussmann et al. 2010; Albini et al. 2014), both 3,3′ bis-metalled BINOLs intermediate and 3,3′ bis-halogenated BINOLs intermediate could undertake coupling reactions with aryl sources to furnish 3,3′ bis-arylated BINOLs (Simonsen et al. 1998; Wipf et al. 2000; Ahmed and Clark 2014; Cox et al. 1992; Tsang et al. 2001; Ooi et al. 2003; Bartoszek et al. 2008; Klussmann et al. 2010; Albini et al. 2014). Herein, we describe two different

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11696-020-01308-w) contains supplementary material, which is available to authorized users.

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Published online: 05 September 2020

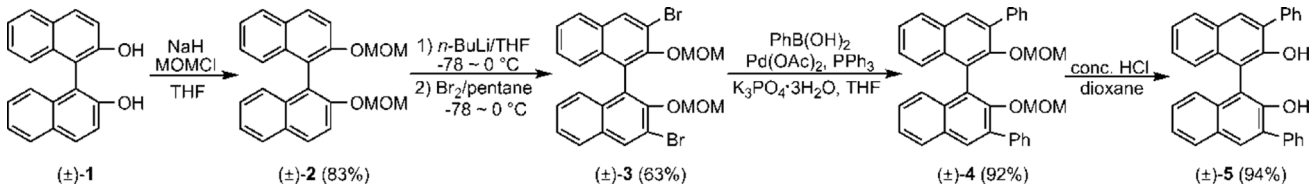
methodologies for synthesis of (±)-3,3′-diphenyl BINOL (±)-**5** via (±)-3,3′ bis-halogenated BINOLs intermediate. The presented methods are complementary to previously established procedures in the aspects of briefness and efficiency (Yang et al. 2016).

(±)-**1**—(±)-**2**: (i) (±)-BINOL (1 equiv), NaH (60% dispersion in mineral oil, 2.5 equiv), THF, 0 °C, 1 h; (ii) MOMCl (2.5 equiv), 0 °C, 5 h. (±)-**2**—(±)-**3**: (i) *n*-BuLi (1.6 M in hexane, 2.5 equiv), − 78 °C—0 °C, THF, 1 h; (ii) Br_2/pentane (4 equiv), − 78 °C—rt, 10 h. (±)-**3**—(±)-**4**: $PhB(OH)_2$ (2.4 equiv), $K_3PO_4 \bullet 3H_2O$ (3 equiv), PPh_3 (0.22 equiv), $Pd(OAc)_2$ (0.05 equiv), THF, 85 °C, 20 h. (±)-**4**—(±)-**5**: conc. HCl, 1,4-dioxane, 50 °C ~ rt, several minutes.

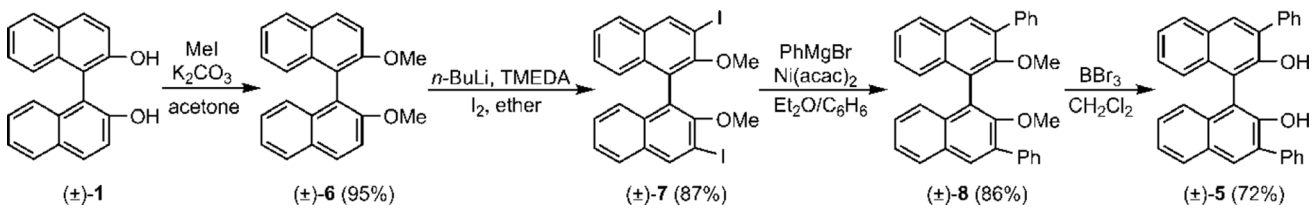
As shown in Scheme 1, the first route to synthesize (±)-**5** started with the commercially available (±)-BINOL. First, the (±)-BINOL (±)-**1** was treated with stoichiometric amounts of sodium hydride (NaH) and chloromethyl methyl ether (MOMCl) in THF to give 83% yield of (±)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (±)-**2**. Based on known literatures (Ooi et al. 2003; Xu et al. 2005; Osorio-Planes et al. 2014), the (±)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (±)-**2** was then carried out with *n*-butyllithium in low temperature for half an hour, followed by dibromination with the solution of bromine in pentane to afford (±)-3,3′-dibromo-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (±)-**3** in 63% yield along with some monobromination byproduct at room temperature (rt). Subsequently, a Suzuki coupling transformation of dibromo functional groups of (±)-**3** was accomplished with stoichiometric amounts of phenylboronic acid and potassium phosphate tribasic trihydrate in THF via palladium acetate/triphenylphosphine catalyst system to give (±)-3,3′-diphenyl-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (±)-**4** in 92% yield, which was much higher than that Snieckus reported (Cox et al. 1992). After treatment of (±)-**4** with concentrated HCl in 1,4-dioxane, 94% yield of (±)-3,3′-diphenyl(1,1′-binaphthalene)-2,2′-diol (±)-**5** was formed, which could be readily converted to phosphoric acid bearing an axially binaphthyl backbone with sterically demanding substituents at 3 and 3′ positions.

(±)-**1**—(±)-**6**: (±)-BINOL (1 equiv), K_2CO_3 (3.5 equiv), MeI (4 equiv), anhydrous acetone, reflux, 20 h; (±)-**6**—(±)-**7**: (i) TMEDA (3.5 equiv), *n*-BuLi (1.6 M in hexane, 2.5 equiv), ether, 1.5 h, rt; (ii) I_2/ether (6 equiv), − 78 °C ~ rt, 10 h; (±)-**7**—(±)-**8**: $Ni(acac)_2$ (0.1 equiv), PhMgBr/ether (5 equiv), benzene, rt ~ reflux, 20 h; (±)-**8**—(±)-**5**: BBr_3 (1.0 M in CH_2Cl_2, 6.5 equiv), 0 °C ~ rt, 20 h.

Considering the bromination of (±)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (±)-**2** provided desired (±)-3,3′-dibromo-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (±)-**3** in moderate yield in the Scheme 1, another methodology was highly desirable to handle this unsatisfied result. As illustrated in Scheme 2, the starting synthetic sequence was based on the use of (±)-2,2′-dimethoxy-1,1′-binaphthalene (±)-**6**, which was first obtained from the nearly complete conversion of the corresponding (±)-BINOL (±)-**1** in the presence of stoichiometric amounts of potassium carbonate and methyl iodide in anhydrous acetone under reflux conditions. Afterwards, dilithiation of (±)-2,2′-dimethoxy-1,1′-binaphthalene (±)-**6** was done with tetramethylethylenediamine and *n*-butyllithium in low temperature for an hour, followed by diiodination with iodine in ether to afford (±)-3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene (±)-**7** in 87% yield. The yield of diiodination in our route is higher than those in literatures (Zheng et al. 2012; Đorđević et al. 2015). Although Pd-catalyzed reactions have occupied a central role for forming new C–C bonds, Ni-catalyzed transformations have witnessed



Scheme 1 The first route to synthesize (±)-3,3′-diphenyl BINOL (±)-**5**



Scheme 2 The second route to synthesize (±)-3,3′-diphenyl BINOL (±)-**5**

considerable development and become one of the most promising synthetic tools, partially due to the nonprecious and earth-abundant nature of nickel versus its noble counterpart palladium. Thereafter, the subsequent approach involved Ni-catalyzed Kumada transformation of the (±)-3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene (±)-**7** into desired 3,3′-diphenyl-2,2′-dimethoxy-1,1′-binaphthalene (±)-**8** in 86% yield with stoichiometric amounts of phenylmagnesium bromide in mixed solvents, and the obtained yield was superior to previous reports (Cram et al. 1981; Wipf et al. 2000). Finally, quantities of boron tribromide were slowly added into the solution of (±)-3,3′-diphenyl-2,2′-dimethoxy-1,1′-binaphthalene (±)-**8** in anhydrous dichloromethane, which afforded (±)-3,3′-diphenyl(1,1′-binaphthalene)-2,2′-diol (±)-**5** in 72% yield.

In summary, we have reported two different methods to furnish (±)-3,3′-diphenyl BINOL via (±)-3,3′ bis-halogenated BINOL intermediates using (±)-BINOL as starting material in this paper. Additionally, the described protocols to synthesize (±)-3,3′-diphenyl BINOL here are likely to provide access to several varieties of phosphoric acids which can be used in the development of ligands and catalysts precursors for organic catalytic reactions.

Experimental

Chloromethyl methyl ether (Amato et al. 1979) and phenylmagnesium bromide (Gülak et al. 2012) were prepared following literature procedures. All other reagents were commercially available. All reactions were performed under nitrogen atmosphere unless otherwise noted. Column chromatography was performed on silica gel 300–400 mesh. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz with $CDCl_3$ as solvent, respectively, and all coupling constants (*J* values) were reported in Hertz (Hz). Elemental analyses were performed by Comprehensive Laboratory Center of College of Chemistry.

Preparation of (±)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene [(±)-2, in Scheme 1]

100-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with sodium hydride (NaH) (0.5 g, 60% dispersion in mineral oil, 12.5 mmol, 2.5 equiv), (±)-BINOL (1.43 g, 5 mmol, 1 equiv) and THF (30 mL). The mixture was stirred at 0 °C for 1 h, and then chloromethyl methyl ether (MOMCl) (0.95 mL, 12.5 mmol, 2.5 equiv) was slowly added via syringe at this temperature. After the addition, the reaction mixture was stirred at 0 °C for 5 h. Subsequently, the reaction mixture was warmed to room temperature and diluted with saturated aqueous NH_4Cl, filtered through a pad of celite and then washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (15% ether in hexane) to afford 1.42 g (83%) corresponding product as a white solid.

Preparation of (±)-3,3′-dibromo-2,2′-bis(methoxymethyl)-1,1′-binaphthalene [(±)-3, in Scheme 1]

50-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with (±)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (1.42 g, 4.2 mmol, 1 equiv) and THF (20 mL). The mixture was cooled to -78 °C with stirring, and *n*-butyllithium (*n*-BuLi) (6.6 mL, 1.6 M in hexane, 10.5 mmol, 2.5 equiv) was slowly added via syringe at this temperature. Then, the reaction mixture was allowed to warm to 0 °C and stirred for 1 h. After 1 h, the reaction mixture was re-cooled to -78 °C, and the solution of bromine (Br_2) (0.43 mL, 16.8 mmol, 4 equiv) in pentane (5 mL) was slowly added in to reaction mixture via syringe. Subsequently, the reaction mixture was allowed to warm to room temperature and stirred for 10 h. Then, the reaction mixture was diluted with saturated aqueous Na_2SO_3, filtered through a pad of celite and then washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (3% ether in hexane) to afford 1.33 g (63%) dibromination product as a white solid and 0.19 g (11%) monobromination byproduct as a white solid.

Preparation of (±)-3,3′-diphenyl-2,2′-bis(methoxymethyl)-1,1′-binaphthalene [(±)-4, in Scheme 1]

A 50-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with phenylboronic acid ($PhB(OH)_2$) (0.79 g, 6.5 mmol, 2.4 equiv), potassium phosphate tribasic trihydrate ($K_3PO_4 \bullet 3H_2O$) (2.16 g, 8.1 mmol, 3 equiv), triphenylphosphine (PPh_3) (0.16 g, 0.6 mmol, 0.22 equiv), palladium acetate ($Pd(OAc)_2$) (0.030 g, 8.1 mmol, 0.05 equiv), (±)-3,3′-dibromo-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (1.33 g, 2.7 mmol, 1 equiv) and THF (20 mL). With stirring, the reaction mixtures were heated at 85 °C for 20 h, and then cooled down to room temperature. The reaction mixtures were diluted with deionized water, filtered through a pad of celite and then washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (6% ether

in hexane) to afford 1.21 g (92%) corresponding product as a white solid.

Synthesis of (±)-3,3′-diphenyl(1,1′-binaphthalene)-2,2′-diol [(±)-5, in Scheme 1]

A 50-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with (±)-3,3′-diphenyl-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (1.30 g, 2.6 mmol, 1 equiv), concentrated HCl solution (10 mL) and 1,4-dioxane (20 mL). With stirring, the reaction mixture was heated at 50 °C for several minutes, and then cooled down to room temperature. The reaction mixtures were diluted with deionized water and washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (6% ether in hexane) to afford 1.01 g (94%) corresponding product as a white solid.

Preparation of (±)-2,2′-dimethoxy-1,1′-binaphthalene [(±)-6, in Scheme 2]

A 100-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with potassium carbonate (K_2CO_3) (2.42 g, 17.5 mmol, 3.5 equiv), methyl iodide (MeI) (1.25 mL, 20 mmol, 4 equiv), (±)-BINOL (1.43 g, 5 mmol, 1 equiv) and anhydrous acetone (40 mL). With stirring, the reaction mixture was heated for 20 h under reflux conditions, and then cooled down to room temperature. The reaction mixtures were diluted with deionized water and washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to afford 1.49 g (95%) corresponding product as a pale yellow solid.

Preparation of (±)-3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene [(±)-7, in Scheme 2]

A 250-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with tetramethylethylenediamine (TMEDA) (2.6 mL, 17.5 mmol, 3.5 equiv) and ether (70 mL), *n*-butyllithium (*n*-BuLi) (7.8 mL, 1.6 M in hexane, 12.5 mmol, 2.5 equiv) was slowly added via syringe at room temperature and the mixture stirred for 0.5 h. Then (±)-2,2′-dimethoxy-1,1′-binaphthalene (1.56 g, 5 mmol, 1 equiv) was added and the mixture was stirred for another 1 h. After 1 h, the mixture was cooled to -78 °C with stirring, the solution of iodine (I_2) (7.6 g, 30 mmol, 6 equiv) in ether (10 mL) was slowly added via syringe for several minutes. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 10 h. Then, the reaction mixture was diluted with saturated aqueous Na_2SO_3, filtered through a pad of celite and then washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (8% ether in hexane) to afford 2.34 g (87%) corresponding product as a yellow solid.

Preparation of (±)-3,3′-diphenyl-2,2′-dimethoxy-1,1′-binaphthalene [(±)-8, in Scheme 2]

A 50-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with nickel (II) acetylacetonate ($Ni(acac)_2$) (0.11 g, 0.43 mmol, 0.1 equiv), (±)-3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene (2.45 g, 4.3 mmol, 1 equiv) and benzene (10 mL). With stirring, the solution of phenylmagnesium bromide (PhMgBr) (3.90 g, 21.5 mmol, 5 equiv) in ether was slowly added via syringe at room temperature. After the addition, the reaction mixture was stirred for 0.5 h at room temperature, and then heated for 20 h under reflux conditions. After 20 h, the reaction mixture was slowly diluted with saturated aqueous NH_4Cl (20 mL), filtered through a pad of celite and then washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (8% ether in hexane) to afford 1.66 g (86%) corresponding product as a yellow solid.

Preparation of (±)-3,3′-diphenyl(1,1′-binaphthalene)-2,2′-diol [(±)-5, in Scheme 2]

A 100-mL, one-necked, round-bottomed flask equipped with a stir bar was charged with (±)-3,3′-diphenyl-2,2′-dimethoxy-1,1′-binaphthalene (1.71 g, 3.7 mmol, 1 equiv) and dichloromethane (30 mL). Then the mixture was cooled to 0 °C by ice bath with stirring, boron tribromide (BBr_3) (24 mL, 1.0 M in CH_2Cl_2, 24 mmol, 6.5 equiv) was slowly added via syringe at 0 °C and the mixture was stirred for 20 h at room temperature. Then, the mixture was re-cooled to 0 °C again via ice bath, the reaction mixture was diluted with deionized water with stirring and washed with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel (20% ether in hexane) to afford 1.12 g (72%) corresponding product as a white solid.

Acknowledgements Financial support from the National Natural Science Foundation of China (NSFC) (21761021 and 21861026), project of teaching reform in colleges and universities of Jiangxi Province (JXJG-18-1-56), innovative special funds project for graduate sudents of Nanchang University (CX2019061) and scientific research and training program of Nanchang University (3664) is gratefully acknowledged.

Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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