A General and Facile Approach for the Synthesis of 2'-Functionalized 1,1'-Binapthyl-2-ols†

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A facile and efficient protocol for the synthesis of 2'-functionalized 1,1'-binaphthyl-2-ols has been developed. The C,O-dilithio reagent (**2**) generated by the reductive ring-opening of binaphthofuran (**1**) with lithium was treated with the corresponding electrophiles to give 2'-functionalized 1,1'-binaphthyl-2-ols including the halides (**3**), amine (**4**), acid (**5**), aldehyde (**6**), carbonate (**7**) or phosphonate (**8**), respectively, in moderate to good yields.

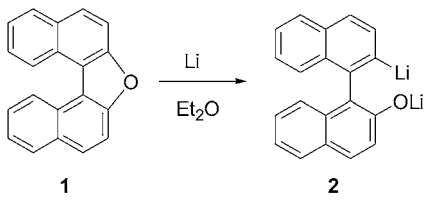
Keywords 1,1'-binaphthyl-2-ol, chiral auxiliaries, lithiation, electrophile

Introduction

2'-Functionalized 1,1'-binaphthyl-2-ols have attracted considerable interest of organic chemists due to their useful applications. The axially chiral binaphthyl skeletons of these compounds are efficient chiral auxiliaries in a variety of asymmetric reactions[1] and in the synthesis of optically active materials.[2] The phosphines of the skeleton are effective ligands in the transition-metal catalyzed C—C bond and C-hetero atom bond forming reactions;[3] the amines and their derivatives have been extensively utilized in asymmetric reactions as chiral ligands or organocatalysts;[4] the acids are used as good candidates for chiral derivatizing agents;[5] and the alcohols are potential photochromic optical triggers for liquid crystals.[6] There are several methods available for the synthesis of these binaphthyl compounds, such as oxidative coupling reactions,[7] nucleophilic aromatic substitution reactions,[2a,8] transition metal-catalyzed coupling reactions,[9] as well as the transformations from binaphthol or 2'-hydroxy-1,1-binaphthyl-2-carboxylic acid.[10] However, these methods show varying degrees of success as well as limitations such as purification difficulties, requirements of noble metal as the catalyst or expensive reagents, laborious work-up, and/or harsh reaction conditions. Furthermore, these methods are usually case-dependent. Therefore, the development of a general and facile synthetic approach for the synthesis of 2'-functionalized 1,1'-binaphthyl-2-ols has attracted our attention.

Heinicke and co-workers[11] reported the synthesis of 2'-phosphanyl-1,1'-binaphthyl-2-ols from C,O-dilithio reagents (**2**), in which the C,O-dilithio reagents was generated by the reductive ring-opening of binaphthofuran (**1**) with lithium (Scheme 1). Up to now, only a few reports for the preparation of dinaphthyl derivatives by this method were published.[3j,6b,12] Here we report an improved convenient synthesis of 2'-functionalized 1,1'-binaphthyl-2-ols based on this reaction.

Scheme 1 The reductive ring-opening of binaphthofuran (**1**) with lithium



1 **2**

Results and discussion

The C,O-dilithiated intermediate (**2**) was obtained by C—O bond cleavage of binaphthofuran (**1**) with excess of lithium at room temperature. According to the reported procedure,[11,12] we used Et_2O as solvent in the reductive ring-opening reaction. However, binaphthofuran (**1**) was not consumed completely, even when the reaction time was prolonged. Because binaphthofuran is poorly soluble in diethylether, we modified the procedure by adding a toluene solution of binaphthofuran

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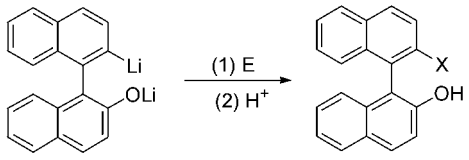
dropwise to the suspension of lithium chip in diethyl ether, the reaction was then complete at room temperature within 2.5 h.

2'-Halogen substituted 1,1'-binaphthyl-2-ols are important intermediates for MOP type ligands, however, only a few synthetic methods were reported.[2a,10d,10e,13] In order to efficiently introduce a halogen atom, we investigated the reaction of the dianion (**2**) with several halogenating under various conditions. The results were listed in Table 1. When the dianion (**2**) was reacted with bromine, the expected 2'-bromo-derivative (**3a**) could not be detected (Table 1, Entry 1). When NBS was the electrophile only a trace of the product was obtained (Table 1, Entry 2). When $Br_2CHCHBr_2$ as the electrophile, the expected product was obtained in 47% yield at −15 ℃ (Table 1, Entry 3). Lowering the temperature to −30 ℃ led to increased yield, but when the temperature was further decreased to −78 ℃, no obvious yield improvement was observed (Table 1, Entries 4 vs. 5). Under the optimized conditions, −30 ℃ and 1.1 equivalent of $BrCH_2CH_2Br$, 80% yield of the desired product was obtained (Table 1, Entry 6). To synthesize the iodide **3b**, ICl was the electrophile of choice. At −30 ℃, the dianion (**2**) was reacted with ICl to afford **3b** in 42% yield. As the temperature was increased to −15 ℃, the yield was increased to 53% (Table 1, Entries 8, 9). Higher temperature resulted in low yield, and large excess of ICl is unnecessary in improving the yield (Table 1, Entries 11, 12).

Table 1 Synthesis of 2'-bromo(or iodo)-1,1'-binaphthyl-2-ols



2 **3**

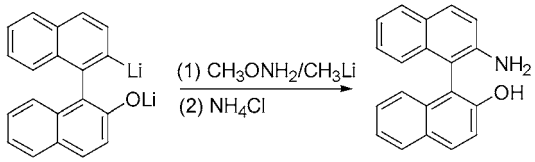
3a: X = Br; **3b**: X = I

Entry	Electrophile	Temp.[a]/℃	Product and yield/ %
1	Br_2 (1.1 equiv.)	−15	—
2	NBS (1.1 equiv.)	−15	**3a**, 5.6
3	$Br_2CHCHBr_2$ (0.55 equiv.)	−15	**3a**, 47
4	$Br_2CHCHBr_2$ (0.55 equiv.)	−30	**3a**, 60
5	$Br_2CHCHBr_2$ (0.55 equiv.)	−78	**3a**, 52
6	$Br_2CHCHBr_2$ (1.1 equiv.)	−30	**3a**, 80
7	I_2 (1.1 equiv.)	−15	—
8	ICl (1.1 equiv.)	−30	**3b**, 42
9	ICl (1.1 equiv.)	−15	**3b**, 53
10	ICl (1.1 equiv.)	r.t.	**3b**, 43
11	ICl (1.5 equiv.)	−15	**3b**, 47

[a] Refers to the addition of electrophiles to the dilithium salt and the subsequent reaction temperature.

Following the success of the synthesis of halides, we desired to synthesize 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN, **4**), an important ligand and intermediate for other ligands in organic synthesis,[4] whose synthesis has been reported by several methods,[7,9,10] but not yet by electrophilic amination method.[14] The dianion (**2**) was treated with 2.0 equiv. of the electrophilic amination reagent, $CH_3ONH_2/2CH_3Li$, at −50 ℃. Subsequent quenching with a saturated aqueous solution of ammonium chloride afforded the expected product, NOBIN, in 60% yield (Scheme 2).

Scheme 2 Synthesis of NOBIN (**4**) by the reaction of the dianion (**2**) with $CH_3ONH_2/2CH_3Li$

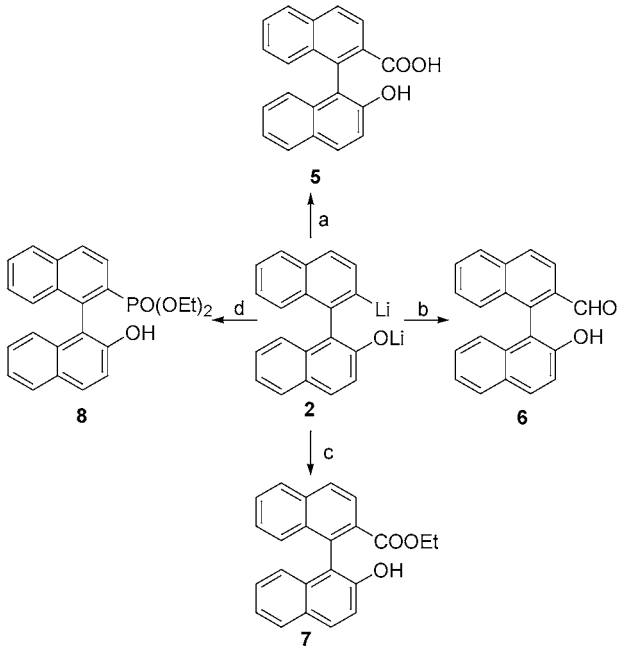


2 **4**

Yield 60%

We also investigated the reaction of the dianion (**2**) with varying carbonyl compounds. The results are shown in Scheme 3. Treatment of the dianion (**2**) with CO_2 (s) at −15 ℃ afforded the expected acid (**5**) in 69% yield simply by acidifying the reaction mixture, filtration and washing. Similarly, the corresponding aldehyde (**6**) was obtained in satisfactory yield by treating the dianion (**2**) with *N*,*N*-dimethylformamide, whereas when the dianion (**2**) was treated with ethyl chloroformate under the same reaction conditions, only a trace of

Scheme 3 The reaction of the dianion (**2**) with carbonyl compounds



a: (i) CO_2, (ii) H^+, yield 69%; b: (i) DMF, (ii) H^+, yield 83%; c: (i) CuI, ClCOOEt , (ii) H^+, yield 71%; d: (i) CuI, $ClPO(OEt)_2$, (ii) H^+, yield 59%.

the expected product was detected. However, when catalytic amounts of CuI were added to the dianion (**2**), followed by ethyl chloroformate at −15 ℃, the expected ester (**7**) was obtained in 71% yield. This strategy is also applicable to the synthesis of the phosphonate which serves as a universal starting material for the synthesis of MOP derivatives. In the presence of catalytic amounts of CuI, the dianion (**2**) reacted with 1.1 equiv. of diethyl chlorophosphate at −15 ℃ to generate product (**8**) in 59% yield, whereas in the absence of CuI only a 5% yield of the desired product was isolated under otherwise identical reaction conditions.

Conclusion

In summary, we have developed a simple and efficient one-pot, two-step method for the synthesis of various 2'-functionalized 1,1'-binaphthyl-2-ols by reductive ring-opening of binaphthofuran (**1**) with lithium to give the C,O-dilithium reagent (**2**), followed by reacting it with the corresponding electrophiles.

Experimental

General

All of reactions were carried out under a nitrogen atmosphere in glassware that had been dried in an oven and cooled under nitrogen. Toluene and Et_2O were distilled under nitrogen from sodium and benzophenone. All other chemicals were purchased commercially. NMR (^1H, ^{13}C and ^{31}P) spectra were recorded on a 400 MHz machine.

Typical procedure for the preparation of 2'-bromo-1,1'-binaphthyl-2-ol (3a)

To a suspension of lithium chip (2.6 g, 0.372 mol, 10 equiv.) in Et_2O (150 mL), a solution of binaphthofuran (10.0 g, 37.3 mmol) in toluene (150 mL) was added dropwise, and then the mixture was stirred at room temperature for 2.5 h. After excess lithium was removed by filtration, the solution of dianion (**2**) was cooled to −30 ℃, and then $C_2H_2Br_4$ (14.2 g, 41.0 mmol) in Et_2O (20 mL) was added dropwise. After the addition, the mixture was stirred for 2 h at −30 ℃, and then it was warmed to room temperature and stirred overnight. After the reaction was quenched with 2 mol/L hydrochloric acid, the aqueous layer was extracted with Et_2O (30 mL×2). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude product which was purified by column chromatography on silica gel [*V*(hexane)∶*V*(EA)=20∶1] to give the product (**3a**) (10.5 g, 80%). ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.74 (s, 1H), 6.96 (d, J=8.0 Hz, 1H), 7.24—7.27 (m, 2H), 7.32—7.35 (m, 3H), 7.49—7.53 (m, 1H), 7.84—7.90 (m, 3H), 7.92—7.95 (m, 2H); ^{13}C MNR ($CDCl_3$, 100 MHz) δ: 117.6, 118.2, 123.6, 124.2, 124.7, 126.0, 126.7, 126.9, 127.7, 128.2, 128.3, 129.0, 130.3, 130.4, 130.5, 131.8, 132.7, 132.9, 134.1, 150.6.

Preparation of 2'-iodo-1,1'-binaphthyl-2-ol (3b)

By the procedure similar to that for the preparation of **3a**, ICl (3.3 g, 20.5 mmol) in Et_2O (20 mL) was added to the dianion (**2**, 18.6 mmol) solution at −15 ℃, and kept stirring for 2 h at −15 ℃. **3b** was obtained in 53% yield (3.92 g). ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.72 (s, 1H), 6.94 (d, J=8.0 Hz, 1H), 7.25—7.37 (m, 5H), 7.51—7.55 (m, 1H), 7.74 (d, J=8.8 Hz, 1H), 7.88—7.95 (m, 3H), 8.10 (d, J=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 102.1, 118.0, 122.1, 124.0, 124.5, 126.8, 127.20, 127.23, 128.0, 128.4, 128.5, 129.3, 130.74, 130.77, 133.0, 133.5, 134.2, 136.3, 137.0, 150.6.

Preparation of NOBIN (4)

By the procedure similar to that for the preparation of **3a**, the dianion (**2**) solution was added dropwise to a mixture, which was made by addition of methyllithium (40 mL, 1.6 mol/L) to a suspension of *O*-methylhydroxylamine hydrochloride (2.18 g, 26.1 mmol) in Et_2O, at −50 ℃, and then the reaction mixture was warmed to −15 ℃ and stirred for 2 h. **4** was obtained in 60% yield (2.23 g). ^1H NMR (DMSO, 400 MHz) δ: 4.56 (br, 2H), 6.74—6.77 (m, 1H), 6.94 (d, J=8.4, 1H), 7.05—7.11 (m, 2H), 7.17—7.27 (m, 3H), 7.37 (d, J=8.8 1H), 7.72—7.74 (m, 2H), 7.86—7.91 (m, 2H), 9.33 (s, 1H); ^{13}C NMR (DMSO, 100 MHz) δ: 112.0, 115.6, 119.2, 119.5, 121.5, 123.2, 124.2, 124.8, 126.4, 126.8, 127.7, 128.4, 128.7, 128.8, 129.2, 129.8, 134.4, 134.7, 144.7, 154.0

Preparation of 2'-hydroxy-1,1'-binapthyl-2-carboxylic acid (5)

CO_2 (s) was added in several portions to the dianion (**2**) solution at −15 ℃, and then the mixture was warmed to room temperature naturally and stirred overnight. NaOH (2 mol/L, 80 mL) was added to the reaction mixture carefully, and then the organic phase was separated off. The aqueous phase was adjusted to pH=1 with 2 mol/L HCl, and the solid was precipitated. After filtration, washing the cake with water, and dried, the product **5** was obtained (4.03 g, 69%). ^1H NMR (DMSO, 400 MHz) δ: 6.75 (d, J=8.4 Hz, 1H), 7.12—7.35 (m, 5H), 7.55—7.60 (m, 1H), 7.84—7.88 (m, 2H), 8.02—8.10 (m, 3H), 9.40 (s, 1H), 12.30 (br, 1H); ^{13}C NMR (DMSO, 100 MHz) δ: 118.89, 118.97, 123.0, 124.8, 126.8, 126.9, 127.3, 127.7, 128.1, 128.3, 128.5, 128.6, 128.7, 129.5, 131.1, 133.2, 134.9, 135.3, 136.9, 152.9, 169.3.

Preparation of 2'-hydroxy-1,1'-binaphthyl-2-carbaldehyde (6)

By the procedure similar to that for the preparation of **3a**, DMF (1.5 g, 20.5 mmol) in Et_2O (20 mL) was added to the dianion (**2**) solution at −15 ℃, and kept stirring for 2 h at the same temperature. The product of **6** was obtained in 83% yield (4.83 g). ^1H NMR (DMSO,

400 MHz) δ: 6.76 (d, J=8.0 Hz, 1H), 7.21—7.33 (m, 3H), 7.40—7.45 (m, 2H), 7.67—7.71 (m, 1H), 7.95 (d, J=8.5 Hz, 1H), 8.03 (d, J=8.4 Hz, 2H), 8.11—8.18 (m, 2H), 9.62 (s, 1H), 9.94 (s, 1H); ^{13}C NMR (DMSO, 100 MHz) δ: 113.9, 118.9, 122.6, 123.7, 124.7, 127.6, 127.8, 128.0, 128.5, 129.0, 129.30, 129.34, 129.9, 131.2, 132.5, 133.1, 135.3, 136.9, 142.8, 154.3, 193.1.

Preparation of ethyl 2'-hydroxy-1,1'-binaphthyl-2-carboxylate (7)

By the procedure similar to that for the preparation of **3a**, CuI (0.18 g, 0.93 mmol) was added to the dianion (**2**) solution, and then ethyl chloroformate (1.5 g, 20.5 mmol) in Et_2O (20 mL) was added to the solution at −15 ℃ and kept stirring for 2 h at the same temperature. The product of **7** was obtained in 71% yield (4.52 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.70 (t, J=6.8 Hz, 3H), 3.9 (q, J=7.2 Hz, 2H), 4.85 (s, 1H), 6.88—6.91 (m, 1H), 7.17—7.21 (m, 1H), 7.26—7.36 (m, 4H), 7.55—7.60 (m, 1H), 7.84 (d, J=8.4 Hz, 1H), 7.90 (d, J=8.8 Hz, 1H), 7.97 (d, J=8.4 Hz, 1H), 8.05—8.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.5, 61.3, 117.9, 118.3, 123.6, 124.9, 126.4, 126.8, 127.4, 127.7, 128.2, 128.4, 128.5, 129.1, 129.4, 130.0, 131.4, 133.1, 133.6, 134.2, 135.5, 151.1, 168.2.

Preparation of diethyl 2'-hydroxy-1,1'-binaphthyl-2-ylphosphonate (8)

By the procedure similar to that for the preparation of **3a**, CuI (0.18 g, 0.93 mmol) was added, and then diethyl chlorophosphate (3.5 g, 20.5mmol) in Et_2O (20 mL) was added to the dianion (**2**) solution at −15 ℃. The reaction mixture was warmed to room temperature naturally and stirred overnight. The product of **8** was obtained in 59% yield (4.46 g). ^{1}H NMR (DMSO, 400 MHz) δ: 0.65 (t, J=6.8 Hz, 3H), 0.97 (t, J=6.8 Hz, 3H), 3.46—3.74 (m, 4H), 6.64 (d, J=8.4 Hz, 1H), 7.10—7.14 (m, 2H), 7.20—7.23 (m, 1H), 7.30—7.36 (m, 2H), 7.60 (t, J=8.0 Hz, 1H), 7.83—7.90 (m, 2H), 8.04—8.14 (m, 3H), 9.46 (s, 1H); ^{13}C NMR (DMSO, 100 MHz) δ: 16.0, 16.1, 16.4, 16.5, 61.57, 61.61, 61.89, 61.94, 117.6, 118.8, 122.8, 125.4, 126.3, 126.6, 127.3, 127.5, 127.9, 128.0, 128.2, 128.3, 128.4, 128.6, 128.7, 129.4, 129.5, 130.0, 133.2, 133.4, 135.2, 135.4, 141.3, 141.4, 153.7; ^{31}P NMR (DMSO, 162 MHz) δ: 18.19.

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