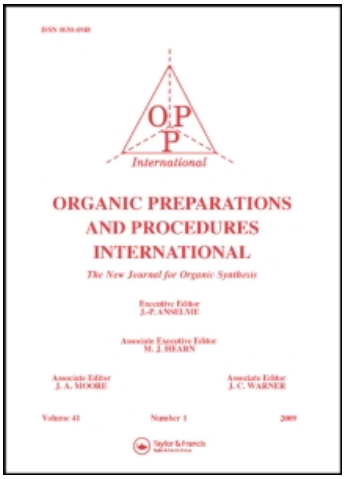

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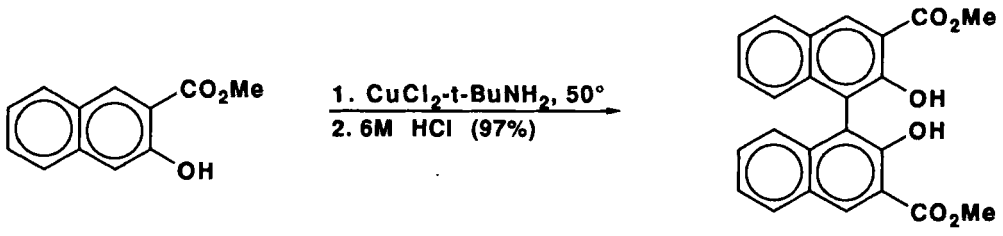
Many derivatives of 1,1'-binaphthalene-2,2'-diol are used as chiral auxiliaries in stereoselective organic reactions.[1] These compounds can be prepared by a variety of methods, the oxidative coupling of substituted 2-naphthols being the most direct. However, despite the fact that this reaction was recognized more than one hundred years ago[2] and studied many times since then, it suffers from several disadvantages: first, there is no reliable way to predict which oxidizing agent would be the best for a given substrate -an empirical approach based on analogy is unavoidable- and second, over-oxidation as well as other side-reactions[3] may often be a serious problem. Moreover, almost no attention has been paid to the possibility of preparing unsymmetrical binaphthols by oxidative cross-coupling of differently substituted 2-naphthols.[4] Thus a simple and mild procedure

allowing the preparation of binaphthols in high yields is still needed. Recently, Cu(II)



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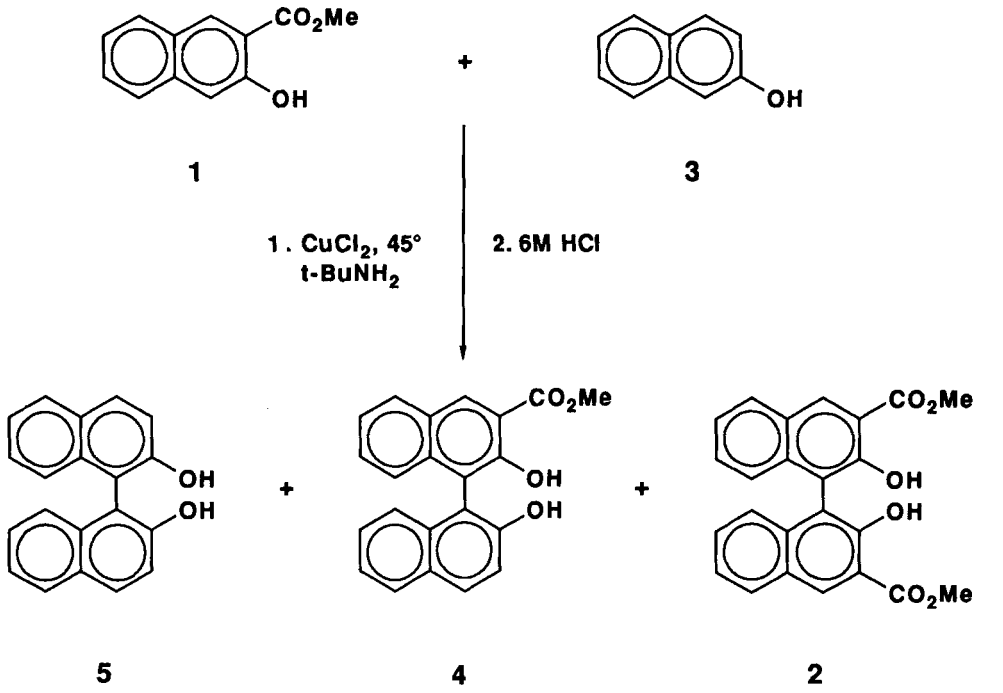
amine complexes have proven to be effective in the preparation of 1,1'-binaphthalene-2,2'-diols as well as of some other biaryl systems.[5] We now report an optimized procedure for the synthesis of dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (**2**).



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The oxidative coupling mediated by a complex of $CuCl_2$ with t-$BuNH_2$ formed *in situ* proceeds smoothly in methanol and affords the product in nearly quantitative yield. Furthermore, we found that the cross-coupling of methyl 3-hydroxy-2-naphthoate (**1**) with 2-naphthol (**3**) under the same conditions leads predominantly to methyl 2,2'-dihydroxy-1,1'-binaphthalene-3-carboxylate (**4**). The combined yield of symmetrical binaphthols **2** and **5** does not exceed 7% and these can be easily removed by a single recrystallization of the crude reaction mixture.

EXPERIMENTAL SECTION

Melting points were determined on a Kofler block and are uncorrected. ^{1}H NMR spectra were obtained with Varian HA 100 spectrometer (100 MHz) using tetramethylsilane as internal standard and $CDCl_3$ as solvent. MS spectra were recorded on a ZAB EQ spectrometer (VG Analytical) in EI mode. For TLC analysis, pre-coated plastic sheets POLYGRAM^R SIL G/UV$_{254}$ (Macherey-Nagel, Düren) were used. Flash chromatography was performed on SGX silica gel (spherical, 20-40μm, TESSEK Corp., Prague, static pressure up to 150kPa). 2-Naphthol was purchased from Aldrich and methyl 3-hydroxy-2-naphthoate was prepared from 3-hydroxy-2-naphthoic acid following a previously described procedure.[6]

Dimethyl 2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (**2**).- A solution of methyl 3-hydroxy-2-naphthoate (**1**) (100 g, 0.495 mol) and copper(II) chloride (133 g, 0.990 mol) in methanol (3 L) was placed into a four-necked 6 L flask equipped with a mechanical stirrer, a 500 mL dropping funnel, a nitrogen inlet and a Dimroth condenser. The apparatus was flushed with nitrogen and tert-butylamine (415.5 mL, 289.1 g, 3.96 mol) was added over a period of 5 minutes to the vigorously stirred mixture (slightly exothermic). When the addition was complete, the dropping funnel was replaced by a thermometer and the green-brown suspension was heated with stirring to 50° until the starting material disappeared (100 min); TLC (5% EtOAc in toluene) was used to monitor the reaction. Then, the reaction mixture was cooled to about 10° and decomposed with 6N HCl (1 L). When recooled to 10°, the reaction mixture deposited a lemon-yellow precipitate which was collected. After thorough washing with water, the product was dissolved in chloroform (1200 mL) and the solution washed several times with water and sat. aqueous $NaHCO_3$ and then dried over $MgSO_4$. Evaporation of the solvent gave a dirty-yellow solid which after boiling, for 5 minutes with methanol (1 L), was cooled to 0° and collected. The product (dried at 80°/27Pa for 3 hrs) weighed 97 g (97%), mp. 282-283°, lit.[6] 276-278°. HPLC analysis [RPODS column, elution with 80% (v/v) aq. methanol, UV detection at 254nm] showed only a single product peak; t_R 25.4 min. MS: m/e 402 (M^+); ^{1}H NMR: δ 4.04 (s, 6H, -CO_2CH_3), 7.01-7.46 (m, 6H, ArH), 7.76-8.05 (m, 2H, ArH), 8.68 (s, 2H, ArH), 10.69 (s, 2H, exchangeable with CD_3CO_2D, -OH).

Anal. Calcd for $C_{24}H_{18}O_6$: C, 71.64; H, 4.48 . Found: C, 71.76; H, 4.52

Methyl 2,2'-Dihydroxy-1,1'-binaphthalene-3-carboxylate (**4**) .- A mixture of 2-naphthol (**3**) (14.4 g, 100 mmol), methyl 3-hydroxy-2-naphthoate (**1**) (20.2 g, 100 mmol) and copper(II) chloride (53.8 g, 400 mmol) was dissolved in methanol (1 L) and placed into a three-necked 2 L flask equipped as described above. After the apparatus was flushed with argon, tert-butylamine (168.1 mL, 116.8 g, 1.6 mol) was added to the rapidly stirred solution over a period of 5 minutes (slightly exothermic). The mixture was heated to 50° and the progress of the reaction monitored by TLC (5% EtOH in toluene). After 45 minutes, the dark-brown suspension was cooled to 10° and quenched with 6M HCl (450 mL). Methanol was removed on an evaporator and the residue extracted with chloroform (3 x 200 mL). The extracts were collected, washed with water and sat. aqueous $NaHCO_3$ and then dried over $MgSO_4$. Evaporation of chloroform gave a brown-yellow solid which was recrystallized from

toluene (200 mL). The microcrystalline yellowish precipitate was collected and dried (50°/27Pa for 3 hrs) to give 26 g (76%) of **4**, mp. 182-183°. GC analysis (capillary column HP 1 methyl silicone, 5 m) showed that the product was more than 99% pure. A further 4.0 g of **4** as well as 0.8 g of **5** and 1.2 g of **2** were obtained by flash chromatography of the residue after evaporation of mother liquors (silica gel, elution with toluene to 5% EtOAc in toluene). The overall yield of **4** was 87%. MS: m/e 344 (M^+); ^1H NMR: δ 4.06 (s, 3H, -$COCH_3$), 4.96 (s, 1H, exchangeable with CD_3CO_2D, -OH), 6.83-7.55 (m, 7H, ArH), 7.72-8.10 (m, 3H, ArH), 8.73 (s, 1H, ArH), 10.83 (s, 1H, exchangeable with CD_3CO_2D, -OH).

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.74; H, 4.65. Found: C, 76.85; H, 4.70

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3. For example, in the oxidative dimerization of 3-hydroxy-2-naphthoic acid (**6**) mediated by iron(III) chloride in aqueous solution, 4-chloro-3-hydroxy-2-naphthoic acid (**8**) is always formed together with the desired 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid (**7**). According to Ioffe,[7] the yield and distribution of products depend on the pH of the reaction mixture, the diacid **7** being favored in alkaline media (Na salt of **6**). In our hands, however, this method proved to be irreproducible, even under the conditions recommended by Ioffe. The yield of **7** varied from one experiment to another and the chloro acid (**8**) was always present in the reaction mixture. Using this reaction, Cram et al.[8] obtained **7** in a 41% yield (after purification of **7** via Et_3N salt).

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