

Novel oxidative coupling of 2-naphthols to 1,1'-bi-2-naphthols catalysed by solid Lewis acids using atmospheric oxygen as oxidant

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The oxidative coupling of 2-naphthol (**1a**) and 6-bromo-2-naphthol (**1b**) to 1,1'-binaphthol (**2a**) and 6,6'-dibromo-1,1'-binaphthol (**2b**), respectively, have been carried out rapidly and in excellent yield by employing a series of solid Lewis acids, FeCl₃/Al₂O₃, FeCl₃/SiO₂ and Fe³⁺ exchanged montmorillonite, as catalysts and aerial oxygen as oxidant.

Introduction

1,1'-Bi-2-naphthol derivatives have wide applications as chiral inducing agents for asymmetric synthesis.¹ There are many good methods for resolution of racemic binaphthols to give enantiomeric binaphthols.² Therefore, it is essential to establish simple, convenient, economical and environmentally-friendly methods for the preparation of racemic 1,1'-binaphthol derivatives. A number of methods have been developed for the oxidative coupling of 2-naphthols using a variety of oxidants *e.g.* FeCl₃,^{3,4} K₃[Fe(CN)₆],⁵ Mn(acac)₃,^{6,7} and Cu(II)-amine complexes⁸⁻¹⁰ as coupling reagents. The reactions were carried out in organic solvent,⁵ in the solid state³ and in aqueous Fe³⁺ solution,⁴ in each case employing excess, usually 2 equivalents, of the oxidant. The excess Fe³⁺, Cu²⁺ and the resulting Fe²⁺, Cu⁺ and HCl produced in the reactions are not acceptable from the viewpoint of environmental protection. However, a few exceptions exist where the coupling reactions proceed catalytically by solid FeCl₃,⁴ Cu(II)-amine-AgCl combinations¹¹ and the CuCl(OH)·TMEDA complex under oxygen.¹² From the practical and environmental viewpoints, heterogeneous catalysts should be advantageous and it is desirable that extra abundant aerial oxygen can be effectively used as the net oxidant in a catalytic cycle.

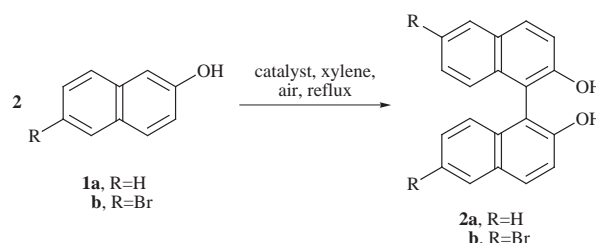
Recently, Sakamoto *et al.*¹³ and Kantam and Santhi¹⁴ independently reported two catalytic oxidative coupling procedures for preparation of 1,1'-binaphthols using aerial oxygen as oxidant and alumina-supported copper(II) sulfate and Cu²⁺-exchanged montmorillonite as catalysts. However, both procedures were carried out in chlorobenzene as solvent and a long reaction time (>2 h) and high temperature (>140 °C) were needed. Consequently, there is still a great demand for catalytic oxidative coupling of 2-naphthols to generate binaphthols under mild conditions and by a rapid process.

Herein we report novel oxidative coupling of 2-naphthols (**1a**, **1b**) to 1,1'-bi-2-naphthols (**2a**, **2b**) catalysed by a number of solid Lewis acids using aerial oxygen as oxidant.

Results and discussion

The solid Lewis acids can be easily prepared from FeCl₃·6H₂O, CuSO₄·5H₂O and commercially available alumina, montmorillonite K-10 and silica gel as shown in the Experimental section. Six types of catalysts, FeCl₃/Al₂O₃, Fe³⁺-exchanged montmorillonite, FeCl₃/SiO₂, CuSO₄/Al₂O₃, CuSO₄/montmorillonite and CuSO₄/SiO₂ were prepared. The oxidative

coupling reactions of 2-naphthol (**1a**) and 6-bromo-2-naphthol (**1b**) (Scheme 1) can be carried out rapidly and simply by



Scheme 1

heating slurries containing **1a**, **1b** and 0.2 equiv. of the catalysts in xylene at refluxing temperature whilst bubbling air through the mixture. The products can be readily isolated by removing the catalysts by filtration followed by evaporation of the solvent. The 1,1'-binaphthol (**2a**) and 6,6'-dibromo-1,1'-binaphthol (**2b**) were thus obtained in high yield and further purification can be conveniently achieved by treatment with active carbon or by simple recrystallisation from toluene. The results are listed in Table 1.

In a typical run, a slurry of 0.2 equiv. of FeCl₃/Al₂O₃ and 1.0 equiv. (144 mg) of **1a** in xylene (10 cm³) was heated at refluxing temperature for 20 min whilst bubbling air through the mixture. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure to provide **2a** in 99% crude

Table 1 Oxidative coupling of 2-naphthols catalysed by solid Lewis acids using aerial oxygen as oxidant

Run	Catalyst (equiv.)	Substrate	Time/min	Product yield (%) ^a
1	FeCl ₃ /Al ₂ O ₃ (0.2)	1a	20	2a , 90
2	FeCl ₃ /Al ₂ O ₃ (0.2) ^b	1a	20	2a , 89
3	FeCl ₃ /Al ₂ O ₃ (2.0)	1a	10	2a , 94 ^c
4	FeCl ₃ /Al ₂ O ₃ (0.2)	1b	10	2b , 91
5	Fe ³⁺ /Mont. (0.2)	1a	180	2a , 93
6	Fe ³⁺ /Mont. (0.2)	1b	50	2b , 98
7	FeCl ₃ /SiO ₂ (0.2)	1a	150	2a , 98
8	FeCl ₃ /SiO ₂ (0.2)	1b	180	2b , 98
9	CuSO ₄ /Al ₂ O ₃ (0.2)	1a	240 (480) ^d	2a , 72 (97) ^d
10	CuSO ₄ /Al ₂ O ₃ (0.2)	1b	240 (120) ^d	2b , 86 (98) ^d

^a Isolated yield. ^b With recovered catalyst. ^c Carried out in toluene at 60 °C under nitrogen. ^d Chlorobenzene as solvent and at 140 °C, the data in parentheses are reported in the literature.¹³

yield. Crystallisation of the crude product from toluene gave colourless **2a**. The product in the mother liquor was further purified by short column chromatography to give another crop of **2a**, in 90% total yield (Table 1, run 1). In the case of 6-bromo-2-naphthol (**1b**), the coupling reaction was completed in only 10 min (Table 1, run 4). It should be noted that air is essential for the reaction, since with 0.2 equiv. of $\text{FeCl}_3/\text{Al}_2\text{O}_3$, **2a** was obtained only in 16% yield under a nitrogen atmosphere. However, when stoichiometric $\text{FeCl}_3/\text{Al}_2\text{O}_3$ (2.0 equiv.) was employed for the coupling reaction under deaerated conditions in toluene at 60 °C for 10 min, **1a** was converted to **2a** in 94% isolated yield (Table 1, run 3). This demonstrates that $\text{FeCl}_3/\text{Al}_2\text{O}_3$ is both a good catalyst and a very good stoichiometric reagent for the oxidative coupling reaction.

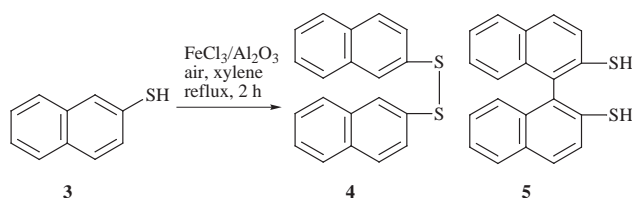
With Fe^{3+} -exchanged montmorillonite and $\text{FeCl}_3/\text{SiO}_2$ as catalysts, the coupling reactions occur in comparably excellent yield (93–98%) but are completed in a longer time (50–180 min, Table 1, run 5–8).

The present catalytic oxidative coupling of **1** to **2** can be carried out on a large scale. For example, a reaction using **1a** (14.4 g, 100 mmol), $\text{FeCl}_3/\text{Al}_2\text{O}_3$ (32.5 g, 20 mmol), and xylene (500 cm^3) provided 12.9 g of pure **2a** (90% yield) in only 50 min. The yellow colour of the initially prepared catalyst turned brown at the end of the reaction. However, the recovered catalyst showed almost equal catalytic activity without any treatment to reactivate the catalyst. Using the recovered catalyst under identical conditions, **2a** was obtained in 89% isolated yield (Table 1, run 2).

For comparison with the method reported by Sakamoto *et al.*, the $\text{CuSO}_4/\text{Al}_2\text{O}_3$ catalyst¹³ was employed for the coupling reaction following their procedures. After refluxing the catalyst and reagents in chlorobenzene for 4 h we obtained **2a** and **2b** in 72 and 86% isolated yield respectively (Table 1, runs 9 and 10). The reaction was repeated using xylene in place of chlorobenzene and refluxed for 3 h to give **2a** and **2b** in 53 and 79% isolated yield respectively. Thus, $\text{FeCl}_3/\text{Al}_2\text{O}_3$, Fe^{3+} -exchanged montmorillonite and $\text{FeCl}_3/\text{SiO}_2$ are better catalysts than $\text{CuSO}_4/\text{Al}_2\text{O}_3$.

$\text{CuSO}_4/\text{montmorillonite}$ and $\text{CuSO}_4/\text{SiO}_2$ proved to be much less efficient than $\text{FeCl}_3/\text{Al}_2\text{O}_3$, $\text{FeCl}_3/\text{SiO}_2$, Fe^{3+} -exchanged montmorillonite and $\text{CuSO}_4/\text{Al}_2\text{O}_3$ for the coupling reactions. Under similar conditions using $\text{CuSO}_4/\text{montmorillonite}$, **2a** and **2b** were obtained in 20 and 22% isolated yield respectively, whereas the $\text{CuSO}_4/\text{SiO}_2$ catalyst gave **2a** and **2b** in 28 and 36% isolated yield respectively.

We have also made preliminary investigations into the use of $\text{FeCl}_3/\text{Al}_2\text{O}_3$ as a catalyst for oxidative coupling naphthalene-2-thiol (**3**) to bis(2-naphthyl) disulfide (**4**). A mixture of **3** and 0.2 equiv. of $\text{FeCl}_3/\text{Al}_2\text{O}_3$ in xylene was heated at refluxing temperature for 2 h whilst bubbling air through the mixture to provide **4** in 96% yield without detectable formation of 1,1'-binaphthalene-2,2'-dithiol (**5**) (Scheme 2).



Scheme 2

Conclusions

In summary, we have shown that $\text{FeCl}_3/\text{Al}_2\text{O}_3$, $\text{FeCl}_3/\text{SiO}_2$, and $\text{Fe}^{3+}/\text{montmorillonite}$ are very good catalysts for oxidative coupling of 2-naphthols to 1,1'-bi-2-naphthols. The present methods have the additional advantages of high yield, short reaction time, and inexpensive and reusable catalysts.

Experimental

Materials and methods

All reagents and chemicals were obtained from commercial suppliers without further purification. Melting points were uncorrected. ^1H NMR spectra were measured on Varian-INOVA-500 spectrometers by using TMS as internal standard and CDCl_3 as solvent. J Values are given in Hz. $\text{Fe}^{3+}/\text{Montmorillonite}$ catalyst was prepared according to the literature.¹⁵ $\text{CuSO}_4/\text{Al}_2\text{O}_3$ and $\text{CuSO}_4/\text{SiO}_2$ catalysts were prepared according to the literature.¹³

Preparation of FeCl_3 adsorbed on Al_2O_3 or SiO_2

To a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.7 g, 61.7 mmol) in acetone (250 cm^3) was added neutral alumina (90 g, 200–300 mesh) or silica gel (90 g, 200–300 mesh) and the slurry was stirred at room temperature for 30 min. The solvent was removed by a rotary evaporator at 40 °C and then at 80 °C under reduced pressure. The resulting yellow powder was further dried over P_2O_5 in a vacuum desiccator to provide *ca.* 98 g of $\text{FeCl}_3/\text{Al}_2\text{O}_3$ or 95 g of $\text{FeCl}_3/\text{SiO}_2$.

Typical procedure for catalytic oxidative coupling of 2-naphthols

1,1'-Binaphthalene-2,2'-diol (2a). A 25 cm^3 three-necked round-bottom flask was charged with $\text{FeCl}_3/\text{Al}_2\text{O}_3$ (0.325 g, 0.20 mmol), **1a** (144 mg, 1.0 mmol), and xylene (10 cm^3). The mixture was stirred vigorously at refluxing temperature (138 °C) for 20 min whilst bubbling air through the mixture. TLC showed that **1a** was completely converted to **2a**. After cooling, the catalyst was removed by filtration and washed with hot toluene (10 $\text{cm}^3 \times 2$) and then with dichloromethane (10 $\text{cm}^3 \times 2$). The solvent of the combined filtrate was evaporated under reduced pressure to give crude **2a** (142 mg, 99%) as a brownish solid. This was treated with active carbon and crystallised from toluene to provide colourless needles **2a** (105 mg, 73%), mp 219–221 °C (lit.,¹³ 214–216 °C); δ_{H} (500 MHz) 5.03 (2H, br s, -OH), 7.15 (2H, d, J 9.0, 3 and 3'- H_2), 7.31 (2H, ddd, J 8.5, 7.0, and 1.5, 6 and 6'- H_2), 7.38 (2H, ddd, J 8.0, 7.0, and 1.5, 7 and 7'- H_2), 7.39 (2H, d, J 9.0, 4 and 4'- H_2), 7.895 (2H, d, J 8.0, 8 and 8'- H_2) and 7.98 (2H, d, J 8.5, 5 and 5'- H_2). The mother liquor was concentrated to dryness and the residue was purified by column chromatography on silica gel to give another crop of **2a** (24 mg, 17%).

6,6'-Dibromo-1,1'-binaphthalene-2,2'-diol (2b). Mp 206–208 °C (lit.,¹³ 208–209 °C); δ_{H} (300 MHz) 5.01 (2H, br s, -OH), 6.95 (2H, d, J 8.4, 3 and 3'- H_2), 7.36 (2H, dd, J 9.0 and 2.1, 7 and 7'- H_2), 7.38 (2H, d, J 8.4, 4 and 4'- H_2), 7.87 (2H, d, J 9.0, 8 and 8'- H_2) and 8.03 (2H, br s).

Stoichiometric coupling of **1a**

A 25 cm^3 three-necked round-bottom flask was charged with $\text{FeCl}_3/\text{Al}_2\text{O}_3$ (3.25 g, 2.0 mmol), **1a** (144 mg, 1.0 mmol) and toluene (10 cm^3). The mixture was stirred vigorously at 60 °C for 50 min under a nitrogen atmosphere. The catalyst was removed by filtration and washed with hot toluene (10 $\text{cm}^3 \times 2$) and then with dichloromethane (10 $\text{cm}^3 \times 2$). The solvent was evaporated under reduced pressure to give crude **2a** (142 mg, 99%) as a brownish solid. The same purification method as described in the typical procedure was applied to give pure **2a** (134 mg, 94%).

Large scale synthesis of **2a**

A 1 dm^3 three-necked round-bottom flask was charged with $\text{FeCl}_3/\text{Al}_2\text{O}_3$ (32.5 g, 20 mmol), **1a** (14.42 g, 100 mmol), and xylene (500 cm^3). The mixture was stirred vigorously at

refluxing temperature (138 °C) for 50 min whilst bubbling air through the mixture. TLC showed that **1a** was completely converted to **2a**. The catalyst was removed by filtration whilst hot and washed with hot toluene (100 cm³ × 2). The combined filtrate was cooled to room temperature to give colourless needles **2a** (8.87 g, 62%). The mother liquor was concentrated to dryness and the residue was treated with active carbon and crystallised from toluene to afford a second crop of **2a** (4.02 g, 28%), in 90% total yield.

Bis(2-naphthyl) disulfide (4): Catalytic oxidative coupling of naphthalene-2-thiol (3)

A 25 cm³ three-necked round-bottom flask was charged with FeCl₃/Al₂O₃ (0.325 g, 0.20 mmol), **3** (0.160 g, 1.0 mmol), and chlorobenzene (5 cm³). The mixture was stirred vigorously at refluxing temperature for 2 h whilst bubbling air through the mixture. After cooling, the catalyst was removed by filtration and washed with dichloromethane (10 cm³ × 2). The solvent was evaporated under reduced pressure to give crude **4** (0.157 g, 99%) as a yellowish solid. This was further purified with active carbon to provide pure **4** (0.153 g, 96%) as colourless platelets, mp 139–141 °C (lit.,¹⁶ 139–140 °C).

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