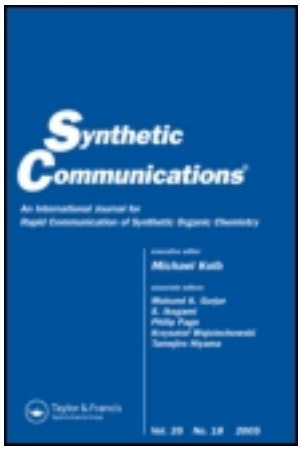

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ABSTRACT

Microwave-assisted oxidative coupling of 2-naphthols at solid state gave the corresponding coupling products in high yields, which provides a simple, rapid and efficient approach to the preparation of binaphthols.

Optically active 1,1′-binaphthalene-2,2′-diol and its derivatives have been of synthetic interest associated with wide applicability of the enantiomers in chirality induction,[1] since a convenient and economic way for obtaining the enantiomers is the resolution of the racemic 1,1′-binaphthalene-2,2′-diol.[2] There have been some known methods for the oxidative coupling of 2-naphthols to give 1,1′-binaphthalene-2,2′-diol using $FeCl_3$,[3] $K_3Fe(CN)_6$,[4] $Mn(acac)_3$,[5] $CuCl(OH)$,[6] $CuSO_4(Al_2O_3)$[7] and Cu(II)–amine complexes[8–10] as coupling reagents. In most cases, however, the oxidative couplings of 2-naphthol are usually carried out by treatment of

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naphthol in solution with stoichiometric amount of metal salts such as $FeCl_3$ or manganese *tris*(acetyl acetonate), which reaction times are longer (9–120 h),[11] or by the use of a Cu(II)–amine complex combined with AgCl.[12] Recently, molecular oxygen as the oxidant in the presence of a catalytic amount (10%) of $VO(acac)_2$ in solution have been investigated.[11] The coupling reaction of aerated powder mixtures of 2-naphthols and $FeCl_3$ under ultrasound irradiation at 50°C has been reported by Toda et al.[3a] and Villemin's group has reported the oxidative coupling of 2-naphthol using an excess amount of $FeCl_3$ under microwave irradiation.[3b] However, the effect of a variety of amount $FeCl_3{\cdot}6H_2O$ for oxidative coupling of 2-naphthols under microwave intermittent irradiation in the solid state have not yet been reported.

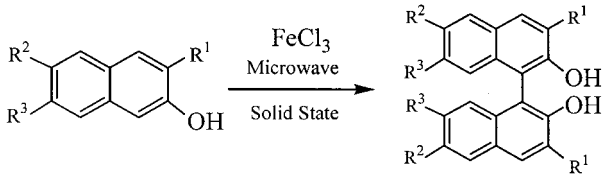
Since the appearance of first article on the use of microwave energy in chemical synthesis,[13] the approach has now developed into a useful technique for a variety of applications in organic synthesis.[14–17] Especially, the solvent-free reactions can be conducted on the solid supports, which has been intensively investigated.[16,17] During the course of our studies, we have investigated microwave-assisted copolymerization, reduction, and synthesis of one-dimensional polymeric complex in solid state.[18] We herein wish to report a simple, rapid and efficient method for oxidative coupling reaction of 2-naphthols in the solid state in the presence of coupling agents (i.e., $FeCl_3$) under microwave irradiation to give 1,1′-binaphthalene-2,2′-diol in high yields.

In a typical procedure, a mixture of 2-naphthols (0.72 g, 5 mmol) and $FeCl_3{\cdot}6H_2O$ (1.35 g, 5 mmol) was finely powdered by grinding in an agate mortar. The mixture was transferred to an Erlenmeyer flask and placed in a commercial microwave oven operating at 2450 MHz frequency while adopting intermission irradiation. The reaction process was monitored by TLC with pre-coated plates of silica gel in a one-minute time slot. After specify the usual workup, decomposition the reaction mixture with dilute HCl and purified by column chromatography (hexane–EtOAc = 4 : 1) to afford the coupling product **2a** in 97% yield. Similar treatment of other naphthol derivatives gave the corresponding binaphthols in 80–97% yields and the results are summarized in Table 1.

The use of 2 equiv. of $FeCl_3{\cdot}6H_2O$ (Table 1, Entry 3) did not increase the yield of coupling product **2a**. Further increasing the reaction time had no significant effect on the yield and resulted in minor amount of decomposition (Table 1, Entry 2). The coupling reaction of 3-(methoxycarbonyl)-2-naphthol **1f** was very sluggish. It gave 80% yield of **2f** after 20 min irradiation and 13% of **1f** was recovered (Table 1, Entry 8).

In order to choose the ideal reaction condition, 2-naphthol (**1a**) was chosen as model compound. Oxidizing reagent, irradiation time, and

Table 1. Microwave Assisted Oxidative Coupling of 2-Naphthols[a]



1a-1f **2a-2f**

	Naphthol						
Entry	Substrate	R^1	R^2	R^3	Time/min	Product/%[b]	
1	**1a**	H	H	H	5	**2a**	(97)
2	**1a**	H	H	H	10	**2a**	(93)
3	**1a**	H	H	H	5[c]	**2a**	(95)
4	**1b**	H	Br	H	8	**2b**	(89)
5	**1c**	H	H	OCH_3	4	**2c**	(93)
6	**1d**	H	H	OH	4	**2d**	(90)
7	**1e**	Me	H	H	7	**2e**	(89)
8	**1f**	CO_2Me	H	H	20	**2f**	(80)

[a]All the reactions were performed on 5 mmol scale at ambient pressure; [b]Compounds **2a–f** were identified according to data reported in Ref. [7,10]; [c]2 equiv. of $FeCl_3{\cdot}6H_2O$ was employed.

irradiation power were found to be important factor which influence the coupling reaction. These results are summarized in Table 2. On the basis of these results, it was found that the coupling reaction also proceeds in the presence of a catalytic amount of $FeCl_3{\cdot}6H_2O$. For example, irradiation with microwave to a mixture of finely powdered **1a** and a 0.2 molar amount of $FeCl_3{\cdot}6H_2O$ for 20 min gave **2a** in 90% yield and 31% yield under a nitrogen atmosphere (Table 2, Entries 4,5). This result shows that oxidation of Fe^{2+} to Fe^{3+} under the air occurs easily for open system and intermission irradiation. In the case of same irradiation time and same amounts of oxidant reagent (Table 2, Entries 6,7 and Table 1, Entry 1), it seems that the effect of microwave energy for the present coupling reaction is evident.

The results obtained by the microwave-assisted solid-state process are rather different compared to those attained by the traditional thermal method in the solid and in solution, of which the yields were lower (Table 2, Entries 12–14). It appears that, aside from the thermal effect, the microwave energy may also have other non-thermal effect. In case of $CuCl_2{\cdot}2H_2O$, $K_3Fe(CN)_6$ and $(NH_4)_2Ce(NO_3)_6$, the oxidative coupling reaction also

Table 2. Oxidative Coupling of 2-Naphthol at Different State[a]

Entry	Reagent (mmol)	Method	Time/min	Product/%[d]
1	$FeCl_3 \cdot 6H_2O$ (1.0)	700 W	1	45
2	$FeCl_3 \cdot 6H_2O$ (1.0)	700 W	3	69
3	$FeCl_3 \cdot 6H_2O$ (0.5)	700 W	11	95
4	$FeCl_3 \cdot 6H_2O$ (0.2)	700 W	20	90
5	$FeCl_3 \cdot 6H_2O$ (0.2)	700 W	20	31[e]
6	$FeCl_3 \cdot 6H_2O$ (1.0)	100 W	5	24
7	$FeCl_3 \cdot 6H_2O$ (1.0)	450 W	5	68
8	$Mn(OAc)_3$ (1.0)	700 W	5	90
9	$CuCl_2 \cdot 2H_2O$ (1.0)	700 W	10	81
10	$K_3Fe(CN)_6$ (1.0)	700 W	10	85
11	$(NH_4)_2Ce(NO_3)_6$ (1.0)	700 W	10	85
12	$FeCl_3 \cdot 6H_2O$ (2.0)	Δ/35°C[b]	60	64
13	$FeCl_3 \cdot 6H_2O$ (2.0)	Δ/35°C[b]	180	68
14	$FeCl_3 \cdot 6H_2O$ (2.0)	Reflux[c]	180	60

[a]All the reactions were performed on 5 mmol scale at ambient pressure; [b]The mixture was put in a test tube and kept at 35°C; [c]The reaction was performed in ethanol–water (1 : 1); [d]Isolated yield; [e]Carried out under nitrogen.

proceeded smoothly to give binaphthols in high yields, (Table 2, Entries 8–11). Especially, the successive coupling reaction is very interesting by using the $(NH_4)_2Ce(NO_3)_6$ as oxidative coupling reagent.

In conclusion, we have developed an improved oxidative coupling of naphthol by microwave-assisted solid-state process, which provides an efficient, simple and rapid methods for the synthesis of 1,1′-binaphthalene-2,2′-diol. The study of non-thermal effect of microwave energy and the application of cerium compounds for microwave reaction are now in progress in our laboratory.

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