DOI: 10.1002/cplu.201300307

Oxidative Coupling of 1-Naphthols over Noble and Base Metal Catalysts

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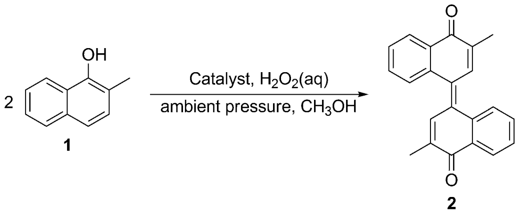
Bismuth-promoted platinum catalysts were tested for the oxidative coupling of 2- and 4-substituted 1-naphthols at different temperatures and ambient pressure. The principal final products are the 3,3′-substituted 1,1′-binaphthalenylidene-4,4′-diones and the 4,4′-substituted 2,2′-binaphthalenylidene-1,1′-diones, respectively. Hydrogen peroxide was used as the oxidant. Only naphthols with electron-donating substituents reacted. The corresponding binaphthalenyl diols can be considered as reaction intermediates. Yields of up to 99% were obtained from 2-methyl-1-naphthol as the starting material within 20 minutes. Probably for steric reasons, the diol is the final product obtained from 2-ethyl-1-naphthol. For 4-methoxy-1-naphthol the outcome is determined by the reaction temperature. At 25 °C the expected 1,1′-dione is the major product, whereas at 60 °C 1′-hydroxy-4′-methoxy-2,2′-binaphthalenyl-1,4-dione is formed; the loss of one methoxy unit and the preservation of the hydroxy group can be explained by the competitive cleavage of one of the two O–Me bonds at higher temperature. Unpromoted platinum and a range of other metallic catalysts, including gold and Raney nickel, were also found to be active. The products obtained are brightly colored solids that could be used as dyes. The method described is truly catalytic and environmentally benign. The potential of the technique justifies further research to expand on the applicability of this novel method.

Introduction

Aryl–aryl bond formation reactions are of great importance in synthetic organic chemistry. These reactions lead to the formation of coupled aromatic rings that can be used as organic dyes and for many other applications.[1,2] The oxidative coupling of naphthol compounds is an important reaction principle that can be used for this purpose. With hydroxyarene derivatives, such as phenols and naphthols, the reaction usually involves an oxidative dehydrogenation step and the subsequent C–C or C–O coupling of the resulting arenyl radicals.[3] This reaction pattern is also used in hair dyeing. For example, naphthols are coupled with a *p*-aminophenol derivative in the presence of oxidizers to make the keratin fiber (hair) bright red.[4,5] This avoids the use of oxidizing dyes, which have the problem of insufficient performance in terms of saturation or vividness of color, dyeing capability, and speed.[6] Naphthols such as 1-naphthol, 2-methyl-1-naphthol, 1,3-, 2,7- and 1,7-dihydroxynaphthalene are frequently used in hair dyeing.[7,8]

Many stoichiometric oxidants can be used for the coupling of naphthols in the liquid phase. Examples are Cr^{IV}, Mn^{III}, Fe^{III}, Cu^{II}, Ag^{I}, and Pb^{IV} compounds.[1,3] The use of stoichiometric reagents often leads to poor coupling selectivity, low yield, and the formation of by-products.[3] Another problem is the disposal of the reduced (toxic) oxidants and of the undesired side products.[9] For the sake of sustainable chemistry, these stoichiometric reactions should be replaced with environmentally friendly catalytic methods.[2,3]

In a European patent Hauck et al. describe the catalytic coupling of 2-methyl-1-naphthol (**1**) to 3,3′-dimethyl-1,1′-binaphthalenylidene-4-4′-dione (**2**) with a yield of 87% over a catalyst containing 5% platinum and 5% bismuth supported on activated carbon (5%Pt–5%Bi/AC).[10] The reaction is performed at 60 °C and ambient pressure using hydrogen peroxide as the oxidant (Scheme 1). Compound **2** is a deep red solid. In the patent only one example is described, and since then no further applications for this new coupling method have been reported. Herein, we explore the scope and the limitations of this reaction by changing the substitution pattern of the naphthol substrate and by using different metals as catalysts. This investigation is also expected to lead to a better understanding of the interaction between the substrate and the catalyst.



Scheme 1. Oxidative coupling of 2-methyl-1-naphthol (**1**) to 3,3′-dimethyl-1,1′-binaphthalenylidene-4,4′-dione (**2**).

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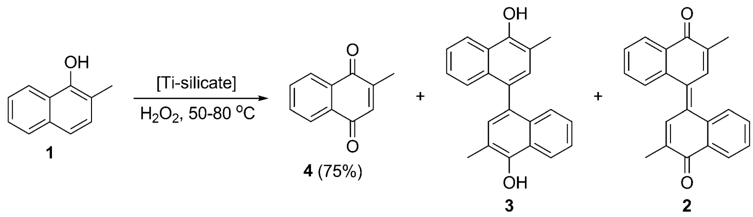
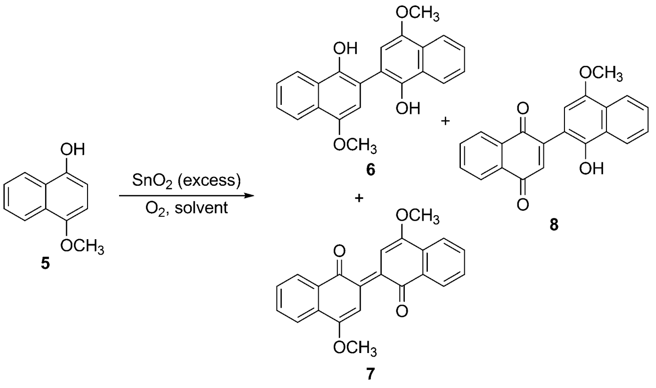


Scheme 2. Oxidation of 2-methyl-1-naphthol (**1**) to menadione (**4**) over titanium–silicate catalysts; **3** and **2** are observed as by-products.[12]

Previously, Kral and Laatsch obtained **2** with a yield of 72% by the coupling of **1** with stoichiometric amounts of AgO as the oxidant.[11] Interestingly, compounds **2** and **3** (Scheme 2) were observed by Zalomaeva et al. as by-products in the catalytic oxidation of **1** to menadione (**4**), using Ti–silicate as the catalyst and hydrogen peroxide as the oxidizing agent.[12] Menadione is a precursor to vitamin K_3. Formation of **2** and **3** also competes with the formation of **4** in the uncatalyzed oxidation of **1** with oxygen at low pressure (100 kPa) in the presence of sun light.[13] In both cases radical mechanisms were proposed for the formation of the dimers **2** and **3**.[12,13]

Takeya et al. found that 4-methoxy-1-naphthol (**5**) couples in the presence of oxygen and semiconductors, such as SnO_2 and ZrO_2, to give binaphthols and binaphthoquinones, which are of importance for the pharmaceutical industry (Scheme 3).[2,3] These compounds are also useful intermediates for the preparation of naturally occurring substances, such as diosindigo B, biramentaceone, and violet-quinone.[2]

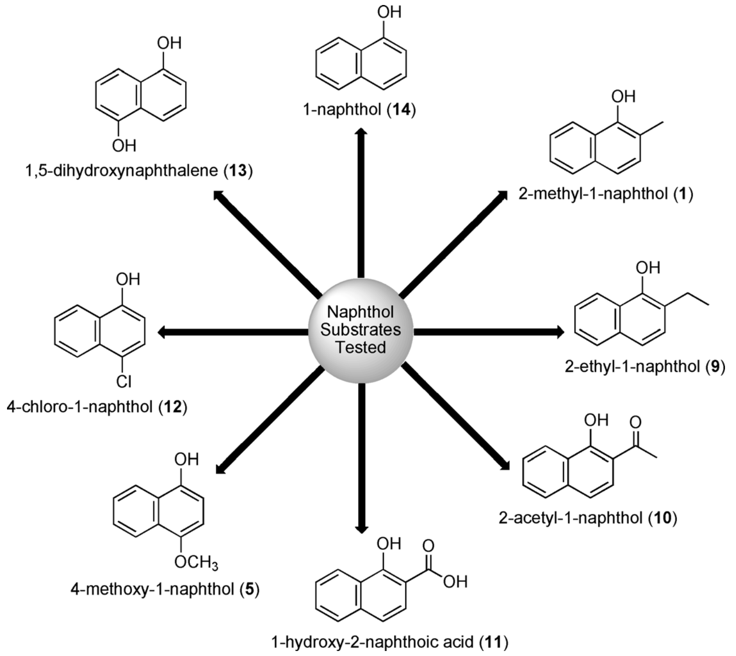
The substrates employed in our study include compounds **1**, **5**, and other readily accessible *ortho*- or *para*-substituted 1-naphthols (see Scheme 4). The substituents used were both electron donating (Me, Et, OMe) and electron withdrawing (COMe, COOH, Cl). Unsubstituted 1-naphthol and 1,5-dihydroxynaphthalene were also tested.



Scheme 3. Oxidation of 4-methoxy-1-naphthol (**5**) in the presence of semiconductors, such as SnO_2.[2,3]

Results and Discussion

A variety of metals (see Figure 1) were tested as supported or unsupported catalysts for the oxidative coupling of 2-methyl-1-naphthol (**1**) according to Scheme 1. Commercially available catalysts that were used are listed in the Experimental Section. Other catalysts (including 5%Pt–5%Bi/AC) were prepared according to the procedures given in the Experimental Section. Aqueous H_2O_2 (30%) was used as the oxidizing agent. Substrate **1** was found to couple both at 60 °C and at room temperature over 5%Pt–5%Bi/AC and gave **2** (red leaflets with a green metallic luster), and yields of up to 99% were obtained (Table 1). Unpromoted (bismuth free) 5%Pt/AC and 10%Pd/AC show similar activities (at 60 °C). In Table 1 the results obtained over Pt and Pd catalysts are summarized by recording the yields and the turnover frequencies (TOF). No conversion took place over the support material (AC) on its own, or in the absence of a catalyst (Table 1, entries 5 and 6).



Scheme 4. Naphthol substrates tested for the oxidative coupling over a 5%Pt–5%Bi/AC catalyst at 60 °C.

The catalysts 5%Ag/AC, 5%Au/AC, 5%Ru/AC, 5%Ru/Al_2O_3, 5%Rh/Al_2O_3, 30%Ir/Al_2O_3, and Raney Ni were also found to be active when qualitatively tested in a test tube according to the procedure given in the Experimental Section. In contrast, Fe powder, Cu powder, and 5%Ni/Al_2O_3–SiO_2 were inactive under these conditions. Figure 1 summarizes the effectiveness of the metals tested.

2-Ethyl-1-naphthol (**9**, Scheme 5) couples over the in-house prepared 5%Pt–5%Bi/AC catalyst at room temperature to give a purple/red compound that was identified as 3,3′-diethyl-1,1′-binaphthalenyl-4,4′-diol (**15**; Table 1, entry 9). A yield of 37% was obtained (TOF = 2.8 min^{-1}). The balance was unconverted

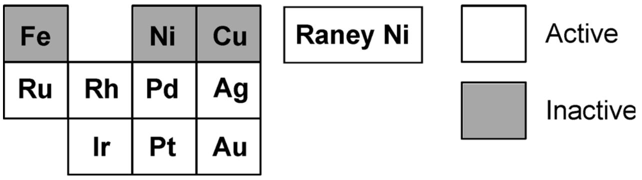
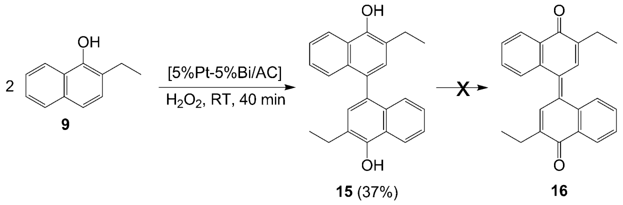
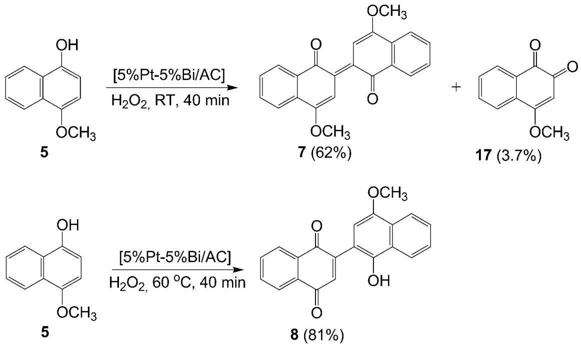


Figure 1. Effectiveness of metals for the oxidative coupling of 2-methyl-1-naphthol (**1**) to the dione **2**, according to Scheme 1.



15 (37%)
16

Scheme 5. Oxidative coupling of 2-ethyl-1-naphthol (**9**) over the in-house prepared 5%Pt–5%Bi/AC catalyst.



Scheme 6. Oxidative coupling of 4-methoxy-1-naphthol (**5**) over the in-house prepared 5%Pt–5%Bi/AC catalyst.

starting material. The formation of the diol **15** showed that **9**, in contrast to **1**, dimerized but further oxidation to the dione **16** did not take place.

4-Methoxy-1-naphthol (**5**, Scheme 6) was found to couple at room temperature over the in-house prepared 5%Pt–5%Bi/AC catalyst and gave the deep blue 4,4′-dimethoxy-2,2′-binaphthalenylidene-1,1′-dione (**7**, Russig's Blue) as the major product (62%), along with trace amounts of the deep violet 1′-hydroxy-4′-methoxy-2,2′-binaphthalenyl-1,4-dione (**8**; Table 1, entry 10). The yellow 4-methoxy-1,2-naphthoquinone (**17**) was formed as a minor by-product (3.7%). Interestingly, at 60 °C **8** became the major product (81%); **7** and **17** were not formed under these conditions (Table 1, entry 11).

Apart from 2-methyl-, 2-ethyl-, and 4-methoxy-1-naphthol (**1**, **9,** and **5**), all the other naphthols shown in Scheme 4 did not react when tested over the in-house prepared 5%Pt–5%Bi/AC catalyst at 60 °C. A possible rationale for the difference in substrate reactivity with respect to dependence on the substitution pattern is discussed below.

Activity of the catalysts

Transition metals with relatively low standard electrode potentials (Cu, Fe, and Ni were tested) are inactive for the coupling reaction (compare Figure 1). These metals are readily oxidized, which renders them inactive. This outcome is confirmed by the fact that Raney nickel (Raney Ni contains nickel in the metallic state.) is active, whereas 5%Ni/SiO_2–Al_2O_3 is inactive. On the surface of the latter material (prior to a prereduction step) nickel is present in the oxidized form. All precious metals were found to be active, surely because they remain in the metallic state because of their high electrode potentials.

According to Table 1, almost complete conversion of **1** into **2** was achieved over all promoted and unpromoted Pt and Pd catalysts when the reaction was carried out at 60 °C. However, at room temperature and with the amount of catalyst decreased by half, the yields were lower and thin layer chromatography (TLC) indicated that some of the starting material was still present.

Under both conditions (RT and 60 °C) a commercial 5%Pt–5%Bi/AC catalyst supplied by Evonik was also tested (see Table 1, entries 1 and 7). The results obtained for this catalyst are similar to those for the in-house prepared 5%Pt–5%Bi/AC

Table 1. Yields and TOFs obtained for the oxidative coupling of 1-naphthols over various Pt and Pd catalysts, according to Schemes 1, 5, and 6.

Entry	Substrate	Catalyst	Ratio[b]	*t* [min]	*T* [°C]	Yield [%] (TOF/min^{-1})[c]				
						2	**15**	**7**	**8**	**17**
1	**1**	5%Pt–5%Bi/AC[a]	0.08	20	60	99.4 (7.7)	–	–	–	–
2	**1**	5%Pt–5%Bi/AC	0.08	20	60	99.4 (7.7)	–	–	–	–
3	**1**	5%Pt/AC	0.08	20	60	99.0 (7.6)	–	–	–	–
4	**1**	10%Pd/AC[a]	0.08	20	60	99.0 (2.1)	–	–	–	–
5	**1**	AC	0.08	20	60	0	–	–	–	–
6	**1**	no catalyst	0.08	20	60	0	–	–	–	–
7	**1**	5%Pt–5%Bi/AC[a]	0.04	40	RT	97.2 (7.5)	–	–	–	–
8	**1**	5%Pt–5%Bi/AC	0.04	40	RT	96.6 (7.4)	–	–	–	–
9	**9**	5%Pt–5%Bi/AC	0.04	40	RT	–	37.0 (2.9)	–	–	–
10	**5**	5%Pt–5%Bi/AC	0.04	40	RT	–	–	62.0 (4.8)	trace	3.7 (0.60)
11	**5**	5%Pt–5%Bi/AC	0.04	40	60	–	–	0	81.0 (6.2)	0

[a] Commercial catalyst. [b] Mass of catalyst over mass of substrate. [c] TOF in $mol_{product}mol_{precious\ metal}^{-1}t^{-1}$. AC = activated carbon.

sample (Table 1, entries 2 and 8). The absence of a significant difference seems to indicate that the reaction is not very structure sensitive with respect to the catalyst; these two materials were surely not made by the same method, nor can they be expected to be based on the same activated carbon.

The TOFs indicate that the metal utilization of a 10%Pd/AC catalyst (Table 1, entry 4, TOF = 2.1 min^{-1}) is significantly lower than that of the catalysts containing 5%Pt (TOF > 7.6 min^{-1}). It has to be kept in mind that these numbers were calculated based on the total amount of precious metal present on each catalyst. Higher metal loadings can be expected to lead to lower metal dispersions, that is, to more unutilized subsurface metal that does not directly contribute to catalysis, thus resulting in lower turnover frequencies. However, the results could be a better indication of the intrinsic relative activities of Pd and Pt if the calculation of the TOFs was based on the exposed metal surface areas, but these were not measured.

The use of a 5%Pt–5%Bi/AC catalyst was predetermined by the procedure given in the prior-art patent.[10] Our results do, however, not point to a significant influence of bismuth on the performance of the catalysts (Table 1). In addition, bismuth plays no role in the mechanisms proposed below. Nevertheless, platinum–bismuth catalysts are of considerable commercial importance. Although the exact role of bismuth is still controversial, bismuth appears to enhance the efficiency of the active metal (Pt) by protecting it from poisoning, sintering, leaching, and overoxidation.[14–17] This, at least, is the role attributed to bismuth promoters added to platinum and palladium catalysts used for the selective oxidation of alcohols into ketones, aldehydes, and carboxylic acids.[14,17] A positive influence of bismuth on the oxidative coupling reactions described here can therefore only be established by a combination of catalyst recycling and characterization experiments. Such experiments, together with the use of other catalyst supports, are currently in progress and will be the subject of a forthcoming contribution.

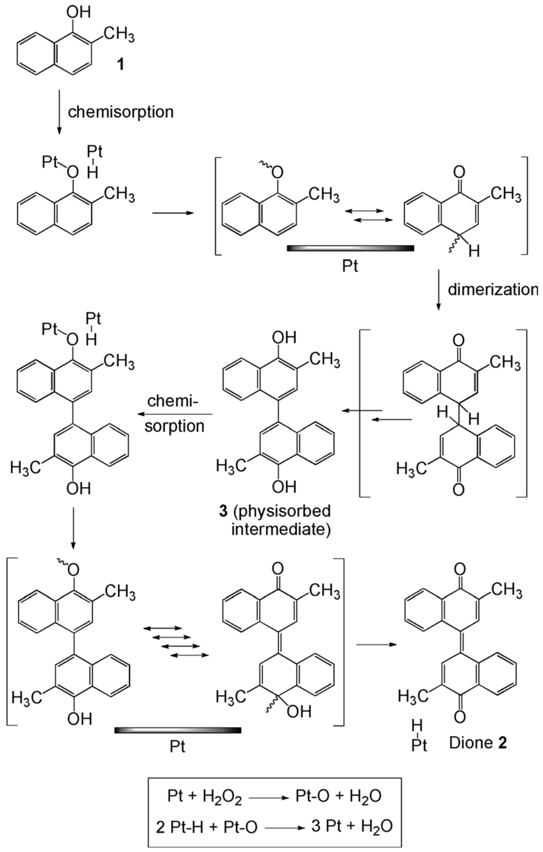
Influence of the substituents on the substrate reactivity

Of the 1-naphthol derivatives shown in Scheme 4 all unsubstituted 1-naphthols (**13**, **14**), and those with -$COCH_3$, -COOH, and -Cl substituents in 2- or 4-positions (**10**, **11**, and **12**) did not react. This observation suggests that an electron-donating group in the 2- or 4-position is required for the reaction to occur. This finding is in agreement with the study conducted by Tanoue et al. on the oxidative coupling of 4-substituted 1-naphthols using a tenfold excess of AgO–40%HNO_3 reagent.[18] They found that electron-withdrawing substituents deactivate the aromatic ring and inhibit the coupling process. The presence and the type of functional groups determine, therefore, whether the coupling reaction takes place or not.

The literature does not provide information with respect to the oxidative coupling of 1,5-dihydroxynaphthalene (**13**). Nonetheless, 2,7-dihydroxynaphthalene is known to couple readily to give 7,7′-dihydroxy-1,1′-binaphthalene-2,2′-diol. Catalytic procedures include the use of $CuSO_4/Al_2O_3$[19] and $FeCl_3{\cdot}6H_2O$[20] as catalysts. Just like **13**, the 2,7-derivative did, however, not react over our metallic-state catalysts.

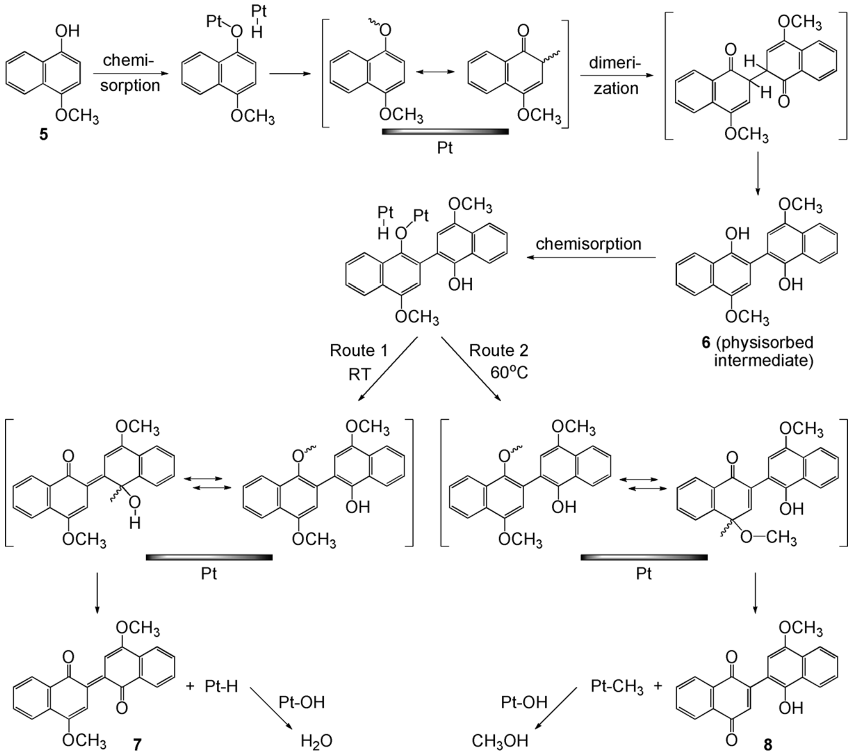
Proposed reaction mechanisms

Most mechanisms proposed in the literature for both oxide-mediated and uncatalyzed oxidative coupling reactions of 2- and 4-substituted naphthols involve radicals.[2,3,12,13] The reaction sequence proposed (Scheme 7) for the metal catalyzed reaction of **1** is related to this group of mechanisms, but the "radical" is stabilized by bonding to the metal surface (e.g. Pt). In the suggested mechanism, Pt abstracts the hydrogen atom from the hydroxy group of the naphthol substrate, thus leading to chemisorbed aryloxide and hydrogen. By resonance the "aryloxy" species can be bonded through the oxygen atom and also through the carbon in *ortho* and *para* position (compare Scheme 7) without disturbing the aromaticity of the second ring. Coupling at the *para* position (reductive elimination from the Pt surface) leads to a dimer. Hydrogen shift gives the diol (**3**), which can be considered as a physisorbed intermediate. Chemisorption of **3** leads to another resonance stabilized aryl species bonded to the Pt surface. Oxidation (abstraction of the second hydroxy hydrogen atom) leads to the final product, which is the fully conjugated quinoid dione (**2**).



Scheme 7. Proposed reaction sequence for the oxidative coupling of 2-methyl-1-naphthol on a platinum surface, using H_2O_2 as the oxidant. (The wavy bonds represent bonds to the platinum surface.)

As shown in the insert of Scheme 7, the chemisorbed hydrogen is converted into water by chemisorbed oxygen, which originates from the catalytic decomposition of hydrogen peroxide (the oxidant used for the overall reaction). Water is the only by-product.



Scheme 8. Proposed reaction sequence for the oxidative coupling of 4-methoxy-1-naphthol on a platinum surface, using H_2O_2 as the oxidant. (The wavy bonds represent bonds to the platinum surface.)

Coupling of 2-substituted 1-naphthols takes place selectively at the *para* position. Coupling at the *ortho* position can neither lead to a dione nor to a binaphthol (diol), because no hydrogen atom is available in that position. Apart from this, coupling could be sterically hindered as a result of the *ortho* substituent. However, as seen in Scheme 8, coupling occurs *ortho* to the OH group for 4-substituted 1-naphthols, such as 4-methoxy-1-naphthol (**5**). Otherwise, the coupling of 4-substituted naphthols follows the mechanistic principle proposed for 2-substituted naphthols.

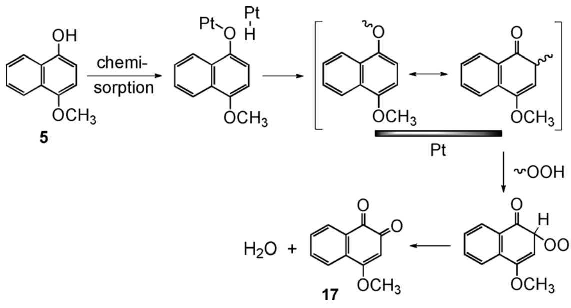
Under identical conditions (RT and ambient pressure) there is a major difference in the reactivity of the methyl- (**1**) and the ethyl-substituted substrate (**9**). Compound **1** couples readily and the intermediate binaphthol **3** is not observed, but oxidized further and gave the dione **2** as the final product (Scheme 7). In contrast, compound **9** forms only the "intermediate" diol (**15**) with a comparatively low yield (Scheme 5). It appears therefore that **1** is more reactive than **9**. The ethyl group is more electron-donating, but sterically more demanding than the methyl group. At this stage, the difference in reactivity between the two compounds can only be explained in terms of a trade-off between electron-donation and steric factors. According to the first step of the reaction sequence shown in Scheme 7, a hydrogen atom is abstracted from a hydroxy group *ortho* to the alkyl group. On a metal surface this step might be more difficult if the alkyl group is more bulky. Although some of compound **9** is able to react and form the binaphthol **15** with a relatively low yield of 37 %, the even more sterically demanding binaphthol cannot react further to form the corresponding dione (**16**). Interestingly, Kral and Laatsch obtained both, **2** with a yield of 72 % and **16** with a yield of 75 %, by coupling of the corresponding 2-alkyl-1-naphthols using stoichiometric amounts of AgO as the oxidant.[11] Their results seem to confirm that in our case steric hindrance on the catalyst surface retards the reaction of **9**. Obviously, steric factors would then also contribute to the non-reactivity of compounds **10** and **11** (Scheme 4).

When 4-methoxy-1-naphthol (**5**) is the substrate (Scheme 6), the expected dione **7** is only observed at room temperature. At 60 °C **8** becomes the principal reaction product. According to Takeya et al., **8** is formed from **7** in the presence of Brønsted acids.[2] These can be present as acidic sites on the surface of semiconductor oxides used as reaction mediators (compare Scheme 3), or added as HCl. Activated carbon was found to be inactive for this purpose. Under our reaction conditions (at RT or 60 °C) compound **7** did not convert into compound **8**. Consequently, for the reaction catalyzed by Pt, **7** cannot be regarded as an intermediate to **8**. We therefore propose that in our case the binaphthol **6** (Scheme 8) is the intermediate for both compound **7** and **8**. As seen in Scheme 8, Route 1 leads to dione **7**, and the reaction sequence follows the principle shown in Scheme 7 for the formation of **2**. Route 2 leads to the formation of **8**. The difference between Routes 1 and 2 is straight forward. In the last step of Route 2 one of the two O–Me bonds is cleaved rather than the remaining O–H bond. This leads directly to **8**. In place of water, methanol is formed as the by-product. (Pt–OH stems from the homolytic cleavage of the oxidant H_2O_2 on the metal surface.[21])

The formation of by-product **17** (Scheme 6) can be explained by the scavenging of an *ortho*-bonded aryl intermediate by perhydroxide, as shown in Scheme 9. Adsorbed perhydroxide (Pt–OOH) is one of the expected intermediates in the decomposition of H_2O_2 on platinum surfaces.[22]

Conclusion

The oxidative coupling of 2-methyl-1-naphthol (**1**) at 60 °C and ambient pressure over bismuth-promoted 5 %Pt–5 %Bi/AC cat-



Scheme 9. Proposed mechanism for the formation of the *ortho*-naphthoquinone **17** during the oxidative coupling of 4-methoxy-1-naphthol (**5**) on a platinum surface, using H_2O_2 as the oxidant. (The wavy bonds represent bonds to the platinum surface.)

alysts gave 3,3′-dimethyl-1,1′-binaphthalylidene-4,4′-dione (**2**) with yields of >99% within 20 minutes (TOF = 7.7 min^{-1}). Aqueous H_2O_2 (30%) was used as the oxidant. Two unpromoted AC-supported Pt and Pd catalysts also gave very high yields (99%). Other supported noble metal catalysts (Ru, Rh, Ir, Ag, and Au) were also found to be active when qualitatively tested in a test tube at room temperature. Raney nickel (Ni in the metallic state) was the only base–metal catalyst that showed activity. It is concluded that the reaction proceeds only over catalysts that contain the active metal in the oxidation state zero.

Substituents at the 2- or 4-position have a decisive influence on the reactivity of the substrate. All unsubstituted 1-naphthols and those containing electron-withdrawing groups (-$COCH_3$, -COOH, and -Cl were tested) did not react. 2-Ethyl-1-naphthol (**9**) was found to couple at room temperature and gave 3,3′-diethyl-1,1′-binaphthalenyl-4,4′-diol (**15**) with a relatively low yield of 37%; in contrast with **1** as substrate the corresponding dione (**16**) was not observed. The binaphthalenyl diols are regarded as intermediates for the formation of the binaphthalenylidene diones. It is therefore assumed that the more bulky ethyl group *ortho* to the hydroxy group sterically hinders the further reaction of the diol on the catalyst surface.

For 4-methoxy-1-naphthol as the substrate the outcome of the coupling reaction is determined by the reaction temperature: at room temperature the expected 4,4′-dimethoxy-2,2′-binaphthalenylidene-1,1′-dione (**7**) was the major product (62%), whereas at 60 °C 1′-hydroxy-4′-methoxy-2,2′-binaphthalenyl-1,4-dione (**8**) was formed (81%). The loss of one methoxy group and the preservation of the hydroxy group can be explained by the competitive cleavage of an O–Me bond (rather than the second O–H bond) on the platinum surface at elevated temperature.

The products obtained are brightly colored solids that could be used as organic dyes and as intermediates for the fine chemicals industry.

In conclusion, heterogeneous noble metal catalysts can effectively replace conventional stoichiometric oxidants used for the oxidative coupling of naphthols. This method will contribute to the development of more ecological and sustainable chemical processes. The results and discussions presented here form the basis for ongoing improvements of the catalytic system and for expanding the applicability of this promising new method.

Experimental Section

Materials

A commercial 5%Pt–5%Bi/AC catalyst (CF105RA/W) was obtained from Evonik (Germany). Activated carbon (Darko KB-G 174), 10%Pd/AC, 5%Rh/Al_2O_3, 5%Ru/Al_2O_3, 5%Ru/AC, 5%Ni/SiO_2–Al_2O_3, Raney nickel, copper powder (99%, mesh size 325), bismuth(III) nitrate pentahydrate (98%), hydrogen tetrachloroaurate(III) trihydrate (99.9%), 4-chloro-1-naphthol (97%), 1,5-dihydroxynaphthalene (99%), 2,7-dihydroxynaphthalene (98%), 2-acetyl-1-naphthol (99%), 4-methoxy-1-naphthol (97%), 2-methyl-1-naphthol (98%, used as reference material), 1-naphthol (98%), and hydrazine monohydrate (98%) were purchased from Sigma–Aldrich. Hexachloroplatinic acid (metal content 40.31%) was purchased from SA Precious Metals, and Fe powder (99%) from Glassworld. 30%Ir/Al_2O_3 is a proprietary catalyst. 1-Hydroxy-2-naphthoic acid (98%) and 2-methyl-1-naphthyl acetate (98%) were purchased from Tokyo Chemical Industry. Hydrogen peroxide (30%), silver nitrate (99.9%), and methanol (99.5%) were purchased from SMM Instruments. Triton X-100 (98–102%) was purchased from BDH.

Analytical methods

The amount of metal that remained in solution during catalyst preparation was determined with a Spectro Arcos FHS ICP-OES instrument in order to indirectly determine the amount of metal loaded onto the support. The FTIR spectra were recorded from 4000 to 450 cm^{-1} on a PerkinElmer Spectrum Two spectrometer equipped with KBr windows and a $LiTaO_3$ detector. The samples were mounted onto the diamond and a force gauge between 130 and 150 N was applied. A 400/54/ASP Varian 400 MHz premium-shielded NMR spectrometer was used to obtain ^1H NMR (100 MHz) and ^{13}C NMR (400 MHz) spectra. Maximum absorption wavelengths (λ_{max}) over the range from 200 to 700 nm were determined using a single-beam Pharmacia Biotech Ultrospec 3000-UV/Visible spectrophotometer with a tungsten filament lamp.

Preparation of catalysts

All in-house made catalysts were synthesized using an electroless deposition method. The 5%Pt–5%Bi/AC catalyst was prepared by dissolving $H_2PtCl_6{\cdot}6H_2O$ (0.1328 g, 0.2564 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1162 g, 0.2396 mmol) in a 50% H_2O/50% CH_3OH mixture (100 mL) to give a cloudy primrose/yellow suspension. Triton X-100 (3 mL) was added and the mixture was placed in an ultrasonic bath for 45 min to dissolve bismuth nitrate. After the salts were dissolved, activated carbon (0.9005 g) was added and the mixture was agitated using a magnetic stirrer. After 10 min, $N_2H_4{\cdot}H_2O$ (0.2 mL, 4.041 mmol N_2H_4) was added to reduce the metal ions. Stirring continued for 48 h and the catalyst was filtered, washed with deionized water to pH 7, and dried under vacuum. 5%Pt/AC, 5%Ag/AC, and 5%Au/AC catalysts were prepared in the same way. The metal composition of the catalysts was found by ICP-OES to be close to the expected values of 5 mass% (4.7–5.3%).

Preparation of naphthol substrates

2-Methyl-1-naphthol (**1**) was prepared by reducing 2-methyl-1-naphthyl acetate (**18**) with $LiAlH_4$. Lithium aluminum hydride (1.89 g, 49.8 mmol) was transferred into a three-necked round-bottomed flask (250 mL). The flask was placed in an ice bath and equipped with a condenser and a dropping funnel. The air was replaced with nitrogen, and distilled THF (30 mL) was added to the $LiAlH_4$ powder by syringe through a septum on the dropping funnel, while agitating with a magnetic stirrer. Compound **18** (4.50 g, 22.5 mmol) was dissolved in THF (20 mL), the solution was injected into the dropping funnel through the septum, and added dropwise to the $LiAlH_4$ slurry. The ice bath was replaced with an oil bath, and the reaction mixture was refluxed at 66 °C. After 4 h 50 % THF/50 % water was added dropwise (to protonate the intermediate) until the grey color disappeared and a greenish/yellow color emerged. The mixture was filtered through a celite layer on a fritted glass funnel. The filtrate was partitioned in ethyl acetate/water. The organic phase was dried with $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The product purity was checked on a UV-active TLC plate using 5 % ethyl acetate/95 % petroleum ether as the mobile phase. Commercial samples of **1** and **18** were used as reference materials. The product was recrystallized from CH_2Cl_2/ *n*-hexane (10 mL/30 mL) and orange crystals formed. Yield: 88 % (3.13 g). Characterization results are summarized further below.

2-Ethyl-1-naphthol (**9**) was prepared by reducing the carbonyl group in 2-acetyl-1-naphthol (**10**). KOH pellets (5.06 g, 90.2 mmol) were transferred into a two-necked round-bottomed flask (250 mL) containing diethylene glycol (100 mL). The flask was placed in an oil bath and equipped with a condenser. The mixture was heated to 140 °C to dissolve the KOH. The solution was allowed to cool to 90 °C and **10** (5.03 g, 27.0 mmol) was added together with $N_2H_4{\cdot}H_2O$ (15 mL, 303 mmol N_2H_4), followed by heating at reflux (130 °C). After 1 h excess hydrazine and water were distilled off until the temperature of the solution reached 205 °C. The remaining solution was heated at reflux (205 °C) for 3 h and, after cooling to 100 °C, poured into an Erlenmeyer flask containing deionized water (90 mL). The mixture was acidified to pH 2 by slow addition of HCl (6 mol L^{-1}) and allowed to cool down to room temperature. The organic compounds were extracted with diethyl ether and the organic phase was washed with water, dried with $MgSO_4$, and filtered. The volume of the filtrate was reduced (rotary evaporator). The purity of the residue was checked on a UV-active TLC plate using 90 % petroleum ether/10 % ethyl acetate as the mobile phase. The product was purified by column chromatography on silica gel. The fractions containing **9** were combined and the volume reduced. The residue was allowed to stand and dark orange crystals formed. Yield: 45.3 % (2.10 g). Characterization results are summarized further below.

Oxidative coupling reactions

At room temperature: the reactions were carried out by adding the naphthol substrate (18.96 mmol) and 5 %Pt–5 %Bi/AC (0.12 g) to a three-necked round-bottomed flask (100 mL), equipped with a dropping funnel. Methanol (40 mL) was added. While stirring, 30 % aqueous H_2O_2 (4.1 mL, 29.2 mmol H_2O_2) was added dropwise directly into the solution within 20 min. Stirring was continued for another 20 min. The reaction mixture was filtered through a celite coated fritted glass funnel, and the filter cake was washed with $CHCl_3$. The solvent was evaporated (rotary evaporator). The residual liquid was analyzed on an UV-active TLC plate using the starting material as the reference and 90 % petroleum ether/10 % ethyl acetate as the mobile phase. The products were purified by column chromatography on silica gel.

At 60 °C: The naphthol substrate (31.60 mmol), CH_3OH (64 mL), and the catalyst (0.40 g) were heated at reflux, and within 15 min 30 % aqueous H_2O_2 (6.8 mL, 48.5 mmol H_2O_2) was dropped directly into the mixture while stirring. Refluxing and stirring continued for another 5 min. The work-up process was carried out as described above.

For all reactions with 4-methoxy-1-naphthol (**5**) as the substrate only 1.00 g (5.74 mmol) starting material was used. The stoichiometric ratio of all ingredients was kept the same as for the other substrates.

The same procedures as described above were followed in the attempts to convert **7** into **8** (both at RT and at 60 °C).

Test tube reactions: 1 (tip of a spatula) and a "pinch" of the catalyst were mixed in a test tube that contained methanol (ca. 3 mL). A few drops of 30 % aqueous H_2O_2 were added while swirling the tube. Appearance of a red color indicated that the catalyst was active. The red solution was tested on a TLC plate against the expected product (**2**) as the reference.

Characterization of organic compounds

2-Methyl-1-naphthol (**1**):[23] $R_f = 0.20$ (petroleum ether/ethyl acetate 9.5:0.5); m.p. 64–66 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 2.31$ (s, 3H, CH_3), 5.00 (bs, 1H, OH), 7.13 (d, ^3J(H,H) = 8 Hz, 1H, H^3), 7.28–7.38 (m, 3H, $H^{4,6,7}$), 7.67–7.69 (m, 1H, H^5), 8.02 ppm (dd, J(H,H) = 8.4–1.2 Hz, 1H, H^8); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 15.64$ (CH_3), 116.3 (C^4), 120.2 (C^9), 120.9 (C^2), 124.3 (C^3), 125.4 (C^7), 125.4 (C^{10}), 127.6 (C^8), 128.9 (C^6), 133.4 (C^5), and 148.5 (C^1); IR (KBr): $\nu = 3334$ (OH), 3051, 2951, 2930, 1599, 1573 cm^{-1}.

2-Ethyl-1-naphthol (**9**): $R_f = 0.54$ (petroleum ether/ethyl acetate 9:1); m.p. 66–68 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 1.30$ (t, ^3J(H,H) = 7.6 Hz, 3H, CH_3), 2.76 (q, ^3J(H,H) = 7.6 Hz, 2H, CH_2), 5.18 (bs, 1H, OH), 7.27 (d, ^3J(H,H) = 8.4 Hz, 1H, H^3), 7.42–7.50 (m, 3H, $H^{4,6,7}$), 7.78 (d, ^3J(H,H) = 7.2 Hz, 1H, H^5), 8.12 ppm (d, ^3J(H,H) = 8 Hz, 1H, H^8); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 14.39$ (CH_3), 23.00 (CH_2), 120.4 (C^4), 120.9 (C^9), 122.6 (C^2), 124.4 (C^3), 125.3 (C^7), 125.4(C^{10}), 127.4 (C^8), 127.7 (C^6),133.3 (C^5), 147.9 ppm (C^1); IR (KBr): $\nu = 3378$ (OH), 3054, 2959, 2930, 2867, 1602, 1573 cm^{-1}.

3,3′-Dimethyl-1,1′-binaphthalenylidene-4,4′-dione (**2**):[11] $R_f = 0.27$ (petroleum ether/ethyl acetate 8:2); m.p. 250 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 2.38$ (s, 6H, $2CH_3$), 7.58 (m, 4H, $H^{6,6',7,7'}$), 7.80 (d, ^3J(H,H) = 6.4 Hz, 2H, $H^{5,5'}$), 7.87 (s, 2H, $H^{3,3'}$), 8.27 ppm (m, 2H, $H^{8,8'}$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 17.16$ (CH_3), 127.7 ($C^{4,4'}$), 130.2 ($C^{6,6'}$), 130.8 ($C^{10,10'}$), 131.1 ($C^{8,8'}$), 132.1 ($C^{9,9'}$), 134.3 ($C^{5,5'}$), 136.5 ($C^{7,7'}$), 138.9 ($C^{2,2'}$), 140.2 ($C^{3,3'}$), 184.2 ppm ($C^{1,1'}$); IR (KBr): $\nu = 2921$, 2851, 1615 (CO), 1580 cm^{-1}; UV/Vis (CH_3Cl): $\lambda_{max} = 490$ nm.

3,3′-Diethyl-1,1′-binaphthalenyl-4,4′-diol (**15**):[24] $R_f = 0.33$ (petroleum ether/ethyl acetate 9:1); m.p. 166–168 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 1.33$ (t, ^3J(H,H) = 7.8 Hz, 6H, $2CH_3$), 2.84 (q, ^3J(H,H) = 7.6 Hz, 4H, $2CH_2$), 5.24 (bs, 2H, 2OH), 7.25–7.28 (m, 4H, $H^{6,6',7,7'}$), 7.34 (d, ^3J(H,H) = 8 Hz, 2H, $H^{5,5'}$), 7.44 (t, ^3J(H,H) = 7.2 Hz, 2H, $H^{3,3'}$), 8.21 ppm (d, ^3J(H,H) = 8.4 Hz, 2H, $H^{8,8'}$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 14.41$ (CH_3), 23.02 (CH_2), 121.0 ($C^{4,4'}$), 122.0 ($C^{9,9'}$), 124.3 ($C^{2,2'}$), 125.1 ($C^{3,3'}$), 125.4 ($C^{7,7'}$), 126.6 ($C^{10,10'}$), 129.5 ($C^{8,8'}$), 131.0 ($C^{6,6'}$), 132.7 ($C^{5,5'}$), 147.5 ppm ($C^{1,1'}$); IR (KBr): $\nu = 3261$ (OH), 2965, 2927, 2870, 1576, 1506 cm^{-1}; UV/Vis (CH_3Cl): $\lambda_{max} = 320$ nm.

4,4′-Dimethoxy-2,2′-binaphthalenylidene-1,1′-dione (**7**):[25] $R_f = 0.75$ (petroleum ether/ethyl acetate 8:2); m.p. 259–260 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 4.06$ (s, 6H, 2OCH_3), 7.47 (t, ^{3}J(H,H) = 7.2–7.6 Hz, 2H, H$^{5,5'}$), 7.60 (t, ^{3}J(H,H) = 7.6 Hz, 2H, H$^{5,5'}$), 7.78 (d, ^{3}J(H,H) = 7.6 Hz, 2H, H$^{5,5'}$), 8.15 (d, ^{3}J(H,H) = 7.6 Hz, 2H, H$^{5,5'}$), 8.39 ppm (s, 2H, H$^{8,8'}$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 55.85$ (OCH_3), 103.1 (C$^{3,3'}$), 121.9 (C$^{6,6'}$), 127.6 (C$^{10,10'}$), 128.9 (C$^{8,8'}$), 131.4 (C$^{9,9'}$), 131.7 (C$^{5,5'}$), 131.8 (C$^{7,7'}$), 133.1 (C$^{2,2'}$), 157.3 (C$^{4,4'}$), 189.3 ppm (C$^{1,1'}$); IR (KBr): $\nu = 3007$, 2969, 2937, 2838, 1602 (CO), 1583, 1557 cm^{-1}; UV/Vis (CH_3Cl): $\lambda_{max} = 630$ nm.

1′-Hydroxy-4′-methoxy-2,2′-binaphthalenyl-1,4-dione (**8**):[26] $R_f = 0.64$ (petroleum ether/ethyl acetate 8:2); m.p. 187–188 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 3.97$ (s, 3H, OMe), 6.54 (s, 1H, H$^{3'}$), 7.12 (s, 1H, H^{3}), 7.55–7.58 (m, 2H, ArH), 7.78–8.25 (m, 5H, ArH), 8.37–8.40 (m, 1H, ArH), 8.49 ppm (s, 1H, OH); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 55.79$ (OMe), 104.6 (C$^{3'}$), 114.4 (C$^{9'}$), 121.7 (C$^{6'}$), 123.7 (C$^{2'}$), 126.3 (C$^{7'}$), 126.7 (C$^{10'}$), 127.3 (C$^{8'}$), 127.5 (C$^{5'}$), 127.7 (C^{6} or C^{9}), 127.9 (C^{6} or C^{9}), 131.7 (C^{5} or C^{10}), 132.5 (C^{5} or C^{10}) 134.0 (C^{7} or C^{8}), 134.8 (C^{7} or C^{8}), 138.9 (C^{3}), 145.5 (C^{2}), 149.7 (C$^{4'}$), 149.9 (C$^{1'}$), 184.5 (C^{1}), 188.5 ppm (C^{4}); IR (KBr): $\nu = 3328$ (OH), 3070, 2952, 2924, 2854, 1656 (CO), 1589 cm^{-1}; UV/Vis (CH_3Cl): $\lambda_{max} = 570$ nm.

4-Methoxy-1,2-naphthoquinone (**17**):[26] $R_f = 0.09$ (petroleum ether/ethyl acetate 8:2); m.p. 190–191 °C; ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 4.00$ (s, 6H, OCH_3), 5.96 (s, 1H, H^{3}), 7.57 (dt, J(H,H) = 7.6, 1.2 Hz, 2H, H^{7} or H^{9}), 7.68 (dt, J(H,H) = 7.6, 1.2 Hz, 1H, H^{7} or H$^{9'}$), 7.84 (d, ^{3}J(H,H) = 8 Hz, 1H, H^{6}), 8.10 ppm (dd, J(H,H) = 7.6, 1.2 Hz, 1H, H^{9}); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 56.83$ (OCH_3), 103.1 (C^{3}), 124.7 (C^{6}), 129.1 (C^{10}), 130.3 (C^{8}), 131.5 (C^{9}), 131.9 (C^{5}), 134.9 (C^{7}), 168.7(C^{4}), 179.4 (C^{2}), 179.5 ppm (C^{1}); IR (KBr): $\nu = 3060$, 2956, 2924, 2851, 1701 1641 (CO), 1608, 1561 cm^{-1}.

Acknowledgements

This work was financially supported by the National Research Foundation of South Africa under Grant Unique No. 63266. We thank Makhosazana Gamedze for the NMR analyses and Evonik (Germany) for a free catalyst sample. M. V. Maphoru is grateful for financial support through a CSIR-TUT bursary.

Keywords: 1-naphthols · C–C coupling · heterogeneous catalysis · oxidation · platinum

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Received: September 2, 2013