

A Highly Selective Synthesis of 1,1'-Bi-2-naphthol by Oxidative Coupling of Naphthol on Mesoporous Fe,Cu/MCM-41 Aluminosilicates

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The oxidative coupling of 2-naphthol to 2,2'-dihydroxy-1,1'-binaphthyl (binaphthol) by air or oxygen has been carried out in the presence of Cu²⁺- and Fe³⁺-doped MCM-41 aluminosilicate as catalyst. Fe-exchanged MCM-41 was found to be a very efficient catalyst; excellent mass balances (> 95%) with almost total conversion and selectivity to binaphthol were achieved. The same reaction has also been carried out on Cu²⁺- and Fe³⁺-Y zeolites. Taking into account the relative dimensions of binaphthol and the catalyst pores, molecular modeling predicts that binaphthol can be accommodated inside the zeolite Y supercages (1.3 nm), but

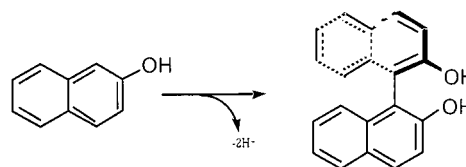
it cannot diffuse outside the zeolite cavities through the smaller pore apertures (0.74 nm). This prediction has been confirmed by dissolving a Y zeolite after the reaction, whereby unextractable binaphthol entrapped within the cavities was recovered. Variable amounts of two secondary by-products have also been detected, and their structure assigned to (2,8'); (8,2')-dioxo-1,1'-binaphthyl and binaphthofuran based on analytical and spectroscopic data. Their percentage is particularly high when alumina-supported CuSO₄ is used as the catalyst.

Introduction

2,2'-Dihydroxy-1,1'-binaphthyl (binaphthol) and a large variety of its derivatives are among the most widely used chiral inductors for highly stereoselective catalytic reactions.^[1–5] A large series of highly efficient enantioselective catalytic complexes are based on binaphthol in order to create the stereogenic space surrounding the active center. The list of asymmetric reactions catalyzed by binaphthol derivatives includes Diels–Alder cycloadditions,^{[6][7]} ene reactions,^{[8][9]} Lewis acid catalyzed transformations,^{[10][11]} enantioselective reduction of ketones,^{[12][13]} synthesis of chiral macrocycles,^[14] asymmetric protonation,^[15] and enantioselective group transfer polymerization.^[16]

The most straightforward synthesis of binaphthols is the oxidative coupling of the corresponding 2-naphthols (Scheme 1).^{[17][18]} This coupling is usually promoted by treating 2-naphthols with a molar excess of transition-metal ions such as Fe^{III},^[19] Mn^{III},^[20] and Cu^{II}.^[21] It has, however, been reported that binaphthol can be obtained by using either catalytic amounts of FeCl₃ upon aerated ultrasound irradiation of 2-naphthols^[22] or substoichiometric amounts of Cu^{II}–amine complexes.^{[23][24]} More recently, heterogeneous catalytic processes have been developed by supporting a CuSO₄–^[25] and CuCl–amine complex^[26] on amorphous alumina.

Zeolites are crystalline aluminosilicates whose structure is constructed by linking AlO₄ and SiO₄ tetrahedra creating an open framework that defines channels and cages of various shapes and sizes.^[27] These internal voids are accessible



Scheme 1. Oxidative coupling of 2-naphthol

to organic molecules provided that their molecular sizes are smaller than the dimensions of the pores. The application of zeolites in their H⁺ form as solid acids in organic synthesis for the production of fine chemicals is an active area of research in heterogeneous catalysis.^[28–31] In contrast, much less attention has been paid to the use of ion-exchanged zeolites as catalysts for oxidation reactions.

Herein, we report a study of the catalytic coupling of 2-naphthol to binaphthol in the presence of a series of Cu²⁺- and Fe³⁺-exchanged mesoporous MCM-41 aluminosilicates as well as microporous Y zeolite. The selectivities to binaphthol have been compared with those attained using CuSO₄ or Fe(NO₃)₃ supported on silica and alumina. As could be anticipated based on the relative molecular size of binaphthol and the internal voids, mesoporous MCM-41 was found to be a much more convenient catalyst than microporous Y zeolite, where a considerable portion of binaphthol remains trapped inside the pores and is not extractable by solid–liquid extraction.

Results and Discussion

In zeolites, the large majority of the active sites (in our case the transition-metal ions) are located in the interior of the pores. Hence, zeolites are generally efficient catalysts when the molecular size of reagents and reaction products

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are smaller than the dimensions of the micropores and intracrystalline diffusion is, then, allowed. For large-pore zeolites having apertures defined by 12-membered-ring oxygen atoms, such as faujasites, the limiting diameter of the pores is around 7.4 Å.^[32] However, the crystal structure of tridirectional Y zeolites encompasses much larger spherical cavities (13 Å in diameter). Therefore, it is possible to envisage a situation in which a bulky reaction product formed inside a large cage remains immobilized and trapped without any possibility of diffusing outside the cage. This is, in fact, the case in this study, where a large binaphthol molecule can be formed from a smaller 2-naphthol precursor. Binaphthol is a bulky, fairly rigid molecule in which free rotation around the 1–1' C–C bond connecting the two naphthyl moieties is restricted. Our semiempirical calculations at the AM1 level suggest that the dimensions of binaphthol are $11.53 \times 9.14 \times 10.05$ Å along the principal three Cartesian axes of the molecule. Accordingly, molecular modeling predicts that while binaphthol can be accommodated inside the supercages of Y zeolites, it would be too bulky to diffuse through the smaller 7.4 Å windows of the Y supercage (Figure 1). Therefore, if binaphthol is formed inside the supercages, it should remain immobilized and unextractable inside the zeolite Y catalyst.

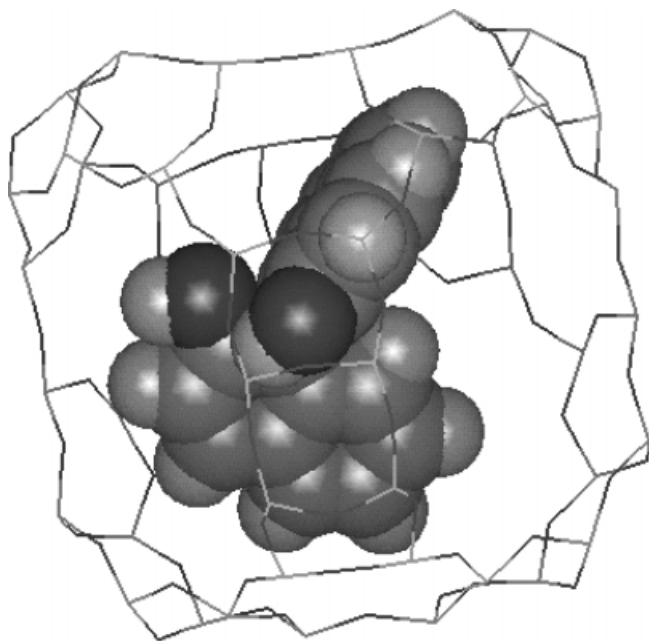


Figure 1. Molecular modeling visualization of binaphthol encapsulated inside the zeolite Y supercage

The same model predicts that diffusion of binaphthol inside the 35 Å channels of MCM-41 is not impeded. The geometry of internal voids of mesoporous MCM-41 is formed by an array of parallel hexagonal channels, the diameter of which can be varied at will during the synthesis from 25 to 80 Å depending on the chain length and concentration of the alkyltrimethylammonium surfactant used as the template.^{[27][33]}

The results obtained for the coupling of naphthol to binaphthol in the presence of Y and MCM-41 aluminosil-

icates containing Cu^{2+} or Fe^{3+} ions under the different conditions studied are collected in Table 1. Previous blank reactions performed without any catalyst under our experimental conditions showed that spontaneous, uncatalyzed formation of binaphthol from 2-naphthol only takes place to a very minor extent ($< 2\%$). For the sake of comparison, Table 1 also contains the results achieved using CuSO_4 or $\text{Fe}(\text{NO}_3)_3$ deposited on the external surface of nonporous silica and alumina.

As can be seen in Table 1 (entries 3–6), binaphthol is present in the organic phase when the reaction is conducted in the presence of Y zeolites as catalyst. This amount of binaphthol is believed to correspond to that formed at those centers located in the more accessible outermost surface of the particles. Leaching out of some Cu^{2+} or Fe^{3+} ions from the zeolite to the organic solution, which might lead to some degree of homogeneous catalysis, was ruled out by filtering at 140°C a suspension of the zeolite and the reaction mixture in chlorobenzene at 40% conversion and subsequently observing that this mixture does not vary in composition upon heating in the absence of the solid catalyst. Furthermore, chemical analysis of the organic phase by atomic absorption spectroscopy revealed that the concentrations of Cu or Fe metals was under the detection limit for the technique (< 2 ppm).

Taking into account the results of the molecular modeling and given that binaphthol was present in the organic phase using ion-exchanged Y zeolites as catalysts, we anticipated that another fraction of binaphthol could have been formed inside the voids of the solid, but it would remain trapped inside the big cavities. This is consistent with the poor mass balances obtained when considering exclusively the amount of reactants and products recovered from the organic phases after the catalytic reaction. Indeed, thermogravimetric analysis revealed that after the reaction the Y zeolites contained between 10–20 wt-% of adsorbed organic material. Adding the weights of the organic material retained in the catalyst estimated by thermogravimetry to those of the organic material present in the liquid phase (see footnote a in Table 1), the final mass balances were excellent ($> 95\%$) in all cases. IR spectra of self-supported wafers of these catalysts exhibit absorption bands in the aromatic region compatible either with 2-naphthol, binaphthol, or a mixture of both compounds (Figure 2). However, owing to the similarity between the IR spectra of naphthol and binaphthol in the spectral window available where the zeolite framework does not interfere, the exact nature and composition could not be definitively determined by *in situ* spectroscopy.

In order to conclusively establish that the material trapped inside the zeolite Y corresponds, at least in part, to binaphthol, we proceeded to dissolve a sample of FeY in HF after its use as a catalyst (sample corresponding to entry 3 in Table 1). Previous controls indicate that neither naphthol or binaphthol are affected by this treatment. After dissolving a thoroughly Soxhlet-extracted FeY solid, only binaphthol was recovered. This shows that the oxidative coupling had also occurred inside the micropores, but the

Table 1. Results of the formation of binaphthol from 2-naphthol in the presence of solid catalysts after 8 h reaction time

Entry	Catalyst	Conditions	Mass Balance ^[a] (%)	Conversion 2-Naphthol (%)	Selectivity Binaphthol ^[b] (%)
1	NaY	oxygen	100	< 2	—
2	HY	oxygen	80	15	— ^[c]
3	FeY	oxygen	100	65	46 (49) ^[d]
4	FeY	air	100	62	42 (34) ^[e]
5	CuY	oxygen	98	48	42 (25) ^[e]
6	CuY	air	98	26	12 (21) ^[e]
7	MCM-41 ^[f]	oxygen	100	68	52
8	FeMCM-41	oxygen	92	99	100
9	FeMCM-41	air	50 ^[g]	86	94
10	FeMCM-41 ^[h]	oxygen	100	99	100
11	FeMCM-41	autoclave	100	79	47
12	CuMCM-41	oxygen	100	98	61
13	CuMCM-41 ^[h]	oxygen	100	37	43
14	CuMCM-41	autoclave	100	84	33
15	SiO ₂	oxygen	100	0	—
16	CuSO ₄ /SiO ₂	oxygen	98	46	80
17	CuSO ₄ /Al ₂ O ₃	oxygen	99	97	88 (10) ^[i]
18	CuSO ₄ /Al ₂ O ₃	air	84	94	87 (15) ^[i]
19	Fe(NO ₃) ₃ /SiO ₂	oxygen	86	39	39
20	Fe(NO ₃) ₃ /Al ₂ O ₃	oxygen	100	65	83

^[a] Including the weight of organic material retained in the catalyst measured by thermogravimetry. — ^[b] Secondary by-products account for 100%. — ^[c] 2,2'-Dinaphthyl ether was formed in 75% selectivity. — ^[d] The number within brackets corresponds to amount of binaphthol recovered after HF disaggregation of the solid. — ^[e] The number in brackets corresponds to binaphthol retained in the solid measured by thermogravimetry. — ^[f] Only traces of binaphthol (yield < 2%) were obtained in the absence of any catalyst. — ^[g] The poor mass balance is due to the presence of unidentified polymeric material. — ^[h] The pore size of this MCM-41 was 50 Å. — ^[i] The number in brackets corresponds to the selectivity of **DOB**.

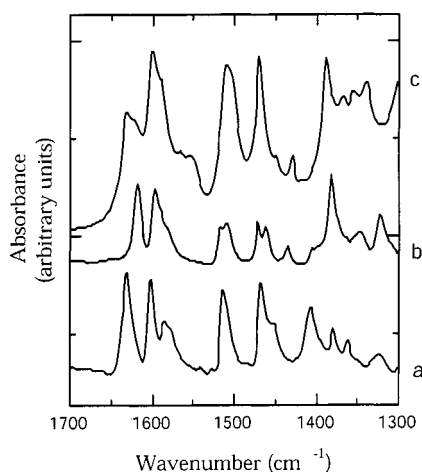


Figure 2. Aromatic region of the FT-IR spectra recorded at room temperature of 2-naphthol (a), 2,2'-binaphthol (b) in KBr disks and a self-supported wafer of CuMCM-41 aluminosilicate after being used as catalyst for oxidative coupling of 2-naphthol and outgased at 200°C under 10^{−2} Pa for 1 h

bulky product was unrecoverable by solid–liquid extraction. An estimation of the number of binaphthols per supercage indicates that at the maximum loading of the Y catalysts (entry 3, Table 1) there is an average of one binaphthol for every three supercages. The successful immobilization of binaphthol inside the zeolite Y supercages constitutes a new example of a ship-in-a-bottle synthesis of an organic molecules by creation of new C–C bonds.^[34–36]

Interestingly, the H⁺ form of the Y zeolite behaves in a totally different way and does not promote the formation of binaphthol (entry 2, Table 1). Using HY as the catalyst

the main product identified was 2,2'-dinaphthyl ether.^[37] Thus, it is the hydroxy group rather than the aromatic ring that is the reactive functionality under acid catalysis, suggesting that the reaction mechanism of binaphthol formation is related to the oxidizing ability of the active sites.

Both Cu^{II} and Fe^{III} salts have previously been found to be convenient reagents for the formation of binaphthol in homogeneous phase in stoichiometric amounts.^[19,21,22] Table 1 reveals that the activity of Fe^{III}-exchanged aluminosilicates is consistently significantly higher than those containing Cu^{II} at similar levels of ion exchange.

As anticipated from their pore dimensions and molecular sizes, the performance, based on the product found in the organic phase, of ion exchanged MCM-41 catalysts is better than that of zeolite Y. Eventually, under optimum conditions, essentially 100% mass balances were achieved after solid–liquid extraction of the catalysts with excellent (> 90%) conversion and selectivity (entries 8 and 10, Table 1). At the end of each run the ion-exchanged MCM-41 catalysts became heavily deactivated. However, an almost complete recovery of the activity of FeMCM-41 for a second run was achieved upon calcination of the deactivated catalyst at 500°C overnight under an oxygen stream.

To learn about the influence of the pore size, we compared the results using two different batches of MCM-41 having diameters of 35 and 50 Å, respectively. No significant improvement in the catalytic performance was observed. This indicates that once the limiting diameter for the diffusion of binaphthol is reached, an increase in the dimensions of the pore does not exert an appreciable influence on the course of the reaction.

We also noticed a beneficial influence of the oxygen partial pressure on the rate of formation of binaphthol and the yield achieved (Figure 3). However, it is worth mentioning that the coupling of naphthol could also be conducted to a lesser extent using a sealed autoclave or under Ar in the absence of oxygen (entries 11 and 14 in Table 1). It is reasonable to assume that in the absence of oxygen, the reaction is no longer catalytic, but stoichiometric and eventually the oxidizing capacity of the zeolites has to be exhausted. According to the Cu^{2+} or Fe^{3+} content of MCM-41 (0.532 and $0.770 \text{ mmol} \times \text{g}^{-1}$, respectively) and the weights of naphthol and catalyst used (see Experimental Section), the maximum yield of binaphthol for a stoichiometric transformation would be 27 and 38%, respectively. These predicted maximum yields agree quite well with the experimental values achieved in the autoclave experiments (yields of binaphthol in entries 11 and 14 of Table 1 are 37 and 28, respectively; product yield = mass balance $\times$ conversion $\times$ selectivity). For those runs carried out in the presence of oxygen where the yield of binaphthol exceeded these values, the reaction is truly catalytic and dioxygen is required to regenerate the active oxidation states of the metal ions.

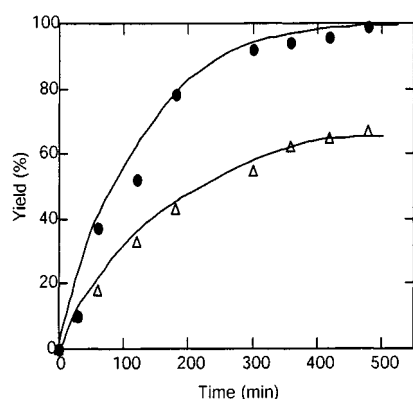


Figure 3. Time conversion plot of the formation of binaphthol catalyzed by FeMCM-41 in the presence of oxygen (●) or air (Δ)

At least two secondary by-products can be formed at high 2-naphthol conversions. The percentage of these by-products is particularly high using the CuSO_4 -supported catalyst (entries 17 and 18, Table 1). The secondary nature of these by-products was established by following their evolution with the reaction time (Figure 4) and by carrying out a test reaction starting with pure binaphthol where the same by-products were produced.

Although the formation of by-products in the oxidative coupling of naphthol using $\text{CuSO}_4/\text{Al}_2\text{O}_3$ had been previously reported,^[25] their chemical structure had not been disclosed. We carried out chromatographic isolation of these two products and their structures were assigned to (2,8'); (8,2')-dioxo-1,1'-binaphthyl (**DOB**) and dinaphtho[2,1-*b*:1',2'-*d*]furan (**DNF**) based on their MS, ^1H -NMR and ^{13}C -NMR spectroscopic and analytical data (see Experimental Section). Compound **DOB** would be the overoxidized product of binaphthol, while **DNF** can be rationalized as the dehydration product of binaphthol. Analogous attack of the OH group of one naphthol group to the 2'

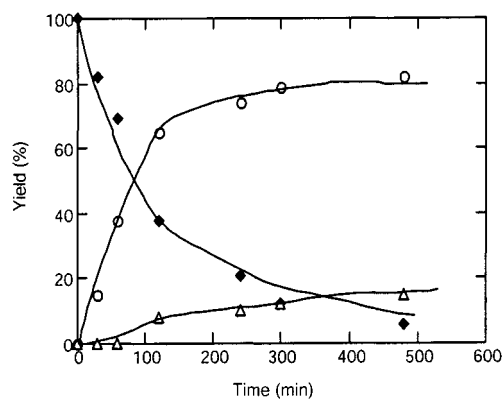
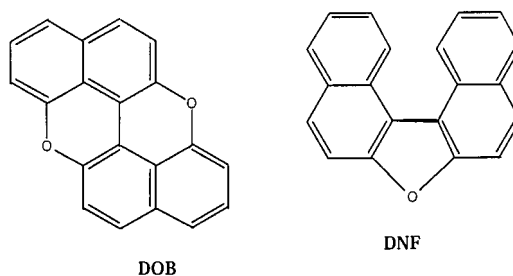


Figure 4. Time conversion plot for the oxidative coupling of 2-naphthol in the presence of $\text{CuSO}_4/\text{Al}_2\text{O}_3$ as catalyst showing the secondary nature of DOB; 2-Naphthol (◆), binaphthol (○), DOB (Δ)

carbon of the other naphthyl ring is not without precedent in the literature.^{[38][39]}



Conclusion

Oxidative coupling of naphthol to binaphthol can be conveniently carried out with almost total conversion and selectivity using Fe^{3+} -exchanged MCM-41 in the presence of oxygen. In the case of large-pore Y zeolites, the conversions and selectivities measured in the liquid phase are moderate and, additionally, a significant amount of the binaphthol is trapped and immobilized inside the zeolite cavities. Potential applications in catalysis of this ship-in-a-bottle synthesis of binaphthol within the zeolite Y supercages could be developed in the future. This report constitutes a further example of the opportunities of mesoporous MCM-41 materials not only as acids but as oxidizing catalysts in organic synthesis for the production of bulky fine chemicals

Experimental Section

Catalysts – Preparation of CuSO_4 or $\text{Fe}(\text{NO}_3)_3$ Adsorbed on Alumina or Silica: Neutral alumina (Merck) or silica (Degussa Aerosil 200, 100% SiO_2) (10 g) were added to a solution of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (1.56 g) or $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (2.52 g) in distilled water (100 mL) and the suspension stirred at room temperature for 30 min. The water was evacuated at 80°C under reduced pressure. The resulting moist solid was finally dried under vacuum at 150°C for 8 h.

Preparation of Fe³⁺- and Cu²⁺-Exchanged Y Zeolite and MCM-41 Aluminosilicate: The initial NaY (Si/Al = 2.6, unit cell size 24.65 Å) was a commercial sample (PQ Industries, CBV-100). MCM-41 was synthesized by using amorphous silica (Degussa Aerosil 200) and a 25% aqueous solution of tetramethylammonium hydroxide and hexadecyltrimethylammonium bromide as templates following the procedure reported in the literature.^{[27][40]} The Si/Al ratio determined by chemical analysis was 15, while the pore size distribution measured by Ar adsorption were 35 and 50 Å for two different samples. The ion exchange was carried out starting from NaY or MCM-41 (0.7 g) using aqueous solutions (200 mL) of Cu(CH₃COO)₂ · H₂O (0.4 g) or Fe(NO₃)₃ · 9 H₂O (0.8 g). The suspensions were stirred at room temperature for 24 h. The resulting solids were filtered, washed, dried, and calcined at 500°C.

Acid zeolite HY was prepared from NaY by exhaustive Na⁺-to-NH₄⁺ ion exchange using NH₄AcO solutions and subsequent calcination as previously described.^[41] The final Na₂O content measured by atomic absorption spectroscopy was less than 0.05 wt-%.

XRD established that the crystallinity of the Cu²⁺ and Fe³⁺-exchanged Y zeolites was 85% of that of the original NaY. This loss of crystallinity indicates a partial framework dealumination of NaY during the calcination steps and is well-documented in the literature.^{[29][42]} In the case of ion-exchanged MCM-41 the number of counts of the most characteristic XRD at 2θ = 2.4° decreased to 40% after ion doping.^[43] This significant diminution in the XRD intensity of the doped MCM-41 with respect to the original sample can be attributed to a decrease in the long-range order of the aluminosilicate structure. Comparison of the isothermal Ar adsorption/desorption measurements with that of the original as-synthesized MCM-41 showed that the mesoporosity of the material was maintained after ion exchange. The new values of BET area of ion-exchanged MCM-41 were 750 m² × g⁻¹, only slightly smaller than those of the initial calcined MCM-41 (820 m² × g⁻¹) and the typical pattern of the isotherms for mesoporous material maintained. It has been reported in the literature that the decrease of the XRD intensity of MCM-41 may not be related to a massive destruction of the porous structure.^[44]

Reaction Procedure: Previously dehydrated (for zeolites: 500°C, overnight; for alumina and silica 200°C for 2 h under 1 Torr) catalyst (350 mg) was added to a chlorobenzene solution (20 mL) of 2-naphthol (100 mg). Nitrobenzene (100 mg) was added as internal standard. The reactions were carried out in the presence of air, oxygen, or in an autoclave as indicated in Table 1 for each run. The resulting suspension was magnetically stirred at 140°C. The course of the reaction was periodically followed by analyzing the organic phase using a HP 5890 gas chromatograph equipped with a 25 m capillary column of 5% phenylmethylsilicone. At the end of the reaction (8 h), the catalyst was filtered and submitted to exhaustive solid-liquid extraction using a micro-Soxhlet equipment and dichloromethane as the solvent. The extracted solid catalyst was analysed by FT-IR and thermogravimetric-analysis differential-scanning calorimetry (Netzsch-STA 409 EP thermobalance under air stream using kaolin as inert standard).

The organic phases (from the reaction and the catalyst extraction) were separately concentrated under vacuum, weighed, and analysed by gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) (Varian Saturn II, same column and conditions as CG), ¹H-NMR spectroscopy (Varian Gemini, 300 MHz, CDCl₃ as solvent, TMS as internal standard), and GC-FT-IR (HP 5890 gas chromatograph, same column as GC-MS, coupled with a FT-IR HP 5965A detector).

Purification of the reaction mixtures and product isolation was accomplished by column chromatography (silica gel Merck) using a 1:1 mixture hexane-dichloromethane as eluent. 2,2'-Dinaphthyl ether was identified by comparison with an authentic commercial sample (TCI America).

Spectroscopic Data of the Reaction By-products: Dinaphtho[2,1-b:1',2'-d]furan (DNF):^{[38][45]} ¹H NMR δ: 9.20–9.15 (d, 2 H, J = 8.4 Hz), 8.11–8.06 (dd, 2 H, J₁ = 1.2; J₂ = 8.1 Hz), 8.00–7.95 (d, 2 H, J = 8.7 Hz); 7.88–7.83 (d, 2 H, J = 9 Hz), 7.80–7.72 (td, 2 H, J₁ = 6.9; J₂ = 1.5 Hz); 7.64–7.56 (td, 2 H, J₁ = 7.2; J₂ = 1.5 Hz). – High-resolution mass spectrum, calcd. for C₂₀H₁₂O m/z 268.0834, found 268.0837. MS: 268(25) [M⁺], 239(100), 119(89).

(2,8'):(8,2')-Dioxo-1,1'-binaphthyl (DOB):^{[46][47]} IR (cm⁻¹): 2940, 1100, 780, 700, 620. – ¹H NMR δ: 7.31 (d, 1 H, J = 9 Hz), 7.10 (d, 1 H, J = 4.8 Hz), 7.08 (d, 1 H, J = 3.6 Hz), 6.92 (d, 1 H, J = 9 Hz), 6.65 (dd, 1 H, J₁ = 3.9 Hz; J₂ = 3.9 Hz). – ¹³C NMR (CDCl₃, 75 MHz) δ: 108.6; 117.3; 120.0; 126.3; 127.1. – High-resolution mass spectrum, calcd. for C₂₀H₁₀O₂ m/z 282.0680, found 282.0687. MS: 282(100) [M⁺], 253(4), 224(6), 141(18).

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- [1] G. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, 503.
- [2] J. Bao, W. D. Wulff, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 3814.
- [3] R. Noyori, H. Takaya, *Acc. Chem. Res.* **1990**, *23*, 345.
- [4] H.-U. Blaser, *Chem. Rev.* **1992**, *92*, 935.
- [5] G. Kaupp, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 728.
- [6] D. Seebach, R. Dahindeu, R. E. Marti, A. K. Beck, D. A. Plattner, F. N. M. Kuhnle, *J. Org. Chem.* **1995**, *60*, 1788.
- [7] S. Kobayashi, H. Ishitani, *J. Am. Chem. Soc.* **1994**, *116*, 4083.
- [8] M. Terada, Y. Motoyana, K. Mikami, *Tetrahedron Lett.* **1994**, *35*, 6693.
- [9] E. M. Carreira, W. Lee, R. A. Singer, *J. Am. Chem. Soc.* **1995**, *117*, 3649.
- [10] K. Maruoka, T. Itoh, T. Shirasaka, M. Yamamoto, *J. Am. Chem. Soc.* **1988**, *110*, 310.
- [11] M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1237–1256.
- [12] R. Noyori, I. Tomino, M. Nishizana, *J. Am. Chem. Soc.* **1984**, *106*, 6709.
- [13] M. Periasamy, J. V. B. Kanth, C. K. Reddy, *J. Chem. Soc., Perkin Trans. I* **1995**, 427.
- [14] G. D. Y. Sogah, D. J. Cram, *J. Am. Chem. Soc.* **1979**, *101*, 3035.
- [15] K. Ishihara, M. Kaneeda, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 11179.
- [16] T. Nakano, D. Y. Sogah, *J. Am. Chem. Soc.* **1995**, *117*, 534.
- [17] R. Pummerer, A. Rieche, E. Prell, *Chem. Ber.* **1926**, *59*, 2159.
- [18] M. J. S. Dewar, T. Nakaya, *J. Am. Chem. Soc.* **1968**, *90*, 7134.
- [19] D. Kuiling, W. Yang, Z. Lijun, W. Yangjie, *Tetrahedron* **1996**, *52*, 1005.
- [20] H. Yamamoto, H. Fukushima, Y. Okamoto, K. Hatada, M. Nakazaki, *J. Chem. Soc., Chem. Commun.* **1984**, 1111.
- [21] B. Feringa, H. Wynbery, *Bioorg. Chem.* **1978**, *7*, 397.
- [22] F. Toda, K. Tanaka, S. Iwata, *J. Org. Chem.* **1989**, *54*, 3007–3009.
- [23] M. Smrcina, J. Polakova, S. Vyskocil, P. Kocovsky, *J. Org. Chem.* **1993**, *58*, 4534.
- [24] M. Noji, M. Nakajima, K. Koga, *Tetrahedron Lett.* **1994**, *35*, 7983–7984.
- [25] T. Sakamoto, H. Yonehara, C. Pac, *J. Org. Chem.* **1994**, *59*, 6859–6861.

- [26] M. Nakajima, K. Kanayama, I. Miyoshi, S. Hashimoto, *Tetrahedron Lett.* **1995**, 36, 9519–9520.
- [27] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, Chu, T.-W. C. D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, 114, 10834.
- [28] P. B. Venuto, *Microporous Mater.* **1994**, 2, 297.
- [29] A. Corma, *Chem. Rev.* **1995**, 95, 559–614.
- [30] A. Corma, *Chem. Rev.* **1997**, 97, 2373–2419.
- [31] A. Corma, H. García, *Catal. Today* **1997**, 38, 257–308.
- [32] W. M. Meier, D. H. Olson, *Atlas of Zeolite Structure Types*; Butterworths: London, **1992**.
- [33] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, 359, 710.
- [34] For related examples of ship-in-a-bottle synthesis of organic compounds wherein the key step is the formation of new C–C bonds see the following two references.
- [35] A. Sanjuán, M. Alvaro, G. Aguirre, H. García, J. C. Scaiano, *J. Am. Chem. Soc.* **1998**, 120, 7351–7352.
- [36] F. Algarra, M. A. Esteves, V. Fornés, H. García, J. Primo, *New J. Chem.* **1998**, 333–338.
- [37] S. R. Kirby, C. Song, H. H. Schobert, *Catal. Today* **1996**, 31, 121–135.
- [38] A. Arienti, F. Bigi, R. Maggi, P. Moggi, M. Rastelli, G. Sartori, A. Treré, *J. Chem. Soc., Perkin Trans. 1* **1997**, 9, 1391–1393.
- [39] S. Yijian, W. Peter, *J. Chem. Soc., Chem. Commun.* **1997**, 273.
- [40] A. Corma, V. Fornés, M. T. Navarro, J. Pérez-Pariente, *J. Catal.* **1994**, 148, 569.
- [41] A. Corma, H. García, S. Iborra, J. Primo, *J. Catal.* **1989**, 120, 78–87.
- [42] J. K. Thomas, H. He, J. Klinowski, *J. Am. Chem. Soc.* **1994**, 116, 11811–11818.
- [43] X. S. Zhao, F. Audslei, G. Q. Lu, *J. Phys. Chem. B* **1998**, 102, 4143–4146.
- [44] I. Kinski, H. Gies, F. Marlow, *Zeolites* **1997**, 19, 373–381.
- [45] D. Fabbri, A. Dore, S. Gladiali, O. De Lucchi, G. Valle, *Gazz. Chim. Ital.* **1996**, 126, 11–18.
- [46] G. R. Clemo, R. Spence, *J. Chem. Soc.* **1928**, 2811.
- [47] G. M. Guseva, B. N. Kolokolov, R. A. Khmel'nitskii, *Zh. Org. Khim.* **1980**, 16, 141–146.

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