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Convenient and Efficient Reduction of 1,1′-Binaphthyls to H_8-1,1′-Binaphthyl Derivatives with Pd and Ru Catalysts on Solid Support

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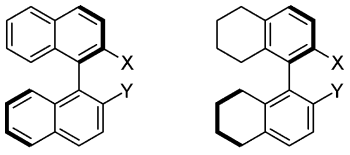
Abstract: Hydrogenation of chiral 2,2′-functionalized 1,1′-binaphthyls with Pd and Ru solid-supported metal catalysts was found to be a clean and convenient pathway to 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-dinaphthyl derivatives. In most cases no racemization was observed in the course of the reaction.

Optically active 1,1′-bi-2-naphthol (BINOL), 1,1′-bi-2-naphthylamine (BINAM), and their numerous derivatives (**I**) have found extensive application as chiral ligands for asymmetric catalysis.[1] During the last years, it was found that several ligands based on the H_8-binaphthalene core (**II**) show higher asymmetric induction than those based on parent 1,1′-binaphthyls in asymmetric hydrogenations, alkylations of aldehydes, hetero-Diels−Alder, and Morita−Baylis−Hillman reactions.[2]

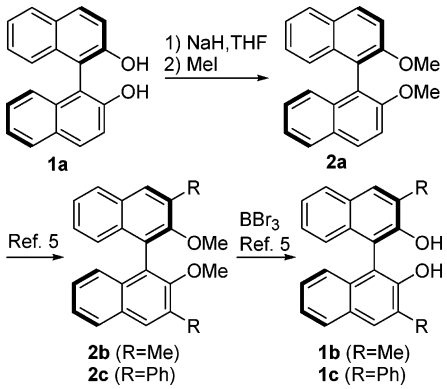


(**I**) (**II**)

X,Y = OH, OR, NH_2, NHR, NR_2, SR

Therefore, optically active H_8-1,1′-bi-2-naphthol (H_8-BINOL) and H_8-1,1′-bi-2-naphthylamine (H_8-BINAM) represent extremely useful starting materials for the synthesis of relevant chiral ligands. But, to the best of our knowledge, only H_8-BINOL is commercially available (at nearly 10 times the cost of (*R*)- or (*S*)-BINOL) and most research groups prefer to synthesize chiral H_8-1,1′-binaphthyl blocks in-house by reduction of corresponding 1,1′-binaphthyls. The procedure developed by Cram[3] is widely used for the synthesis of H_8-BINOL, but requires 15 mol % of expensive PtO_2 catalyst and the reaction must be carried out at 25 °C for 7 days, because higher temperatures cause racemization of the product. Recently, Ding et al. reported on the reduction of binaphthyls using Raney Ni/Al alloy in H_2O/*i*-PrOH alkaline solution.[4] But this alternative method also leads to a partial racemization of the product. Moreover it seems to be difficult to scale-up this procedure, since large amounts of catalyst and solvent are necessary. Finally, Sigimura et al. reported a single example of partial hydrogenation of a binaphthyl derivative using Pd/C as a catalyst,[5] but somewhat low yield (70%), long reaction time (2 days at 80 °C), and the necessity to purify the product by MPLC make it difficult to consider the technique as convenient and well-developed. We report here a practical, efficient, and scalable process for hydrogenation of various 1,1′-binaphthyls using common solid supported metal catalysts, namely Pd/C, Ru/C, Pd/Al_2O_3, and Ru/Al_2O_3 (5 wt % metal in all cases).

SCHEME 1



Commercially available (*R*)-BINOL (**1a**) and its 3,3′-disubstituted derivatives (**1b**,**c**) which are readily obtainable from **1a** in 3 steps (Scheme 1) were chosen.[6]

The hydrogenation of enantiopure binaphthols of type **1** was carried out with a metal loading of 7 mol % in ethanol at 50−100 °C under 50−60 bar of H_2 pressure (Table 1). Under these conditions the reaction proceeds very cleanly and gives partially saturated products in nearly quantitative yield and excellent ee values. The catalysts could be easily recovered by filtration. Combined with remarkably simple workup, this makes the process very practical. Surprisingly, the efficiency of the metal catalysts depends on the solid support employed. Pd/C and Ru/C turned out to be significantly more active than Pd/Al_2O_3 and Ru/Al_2O_3. Pd/C and Ru/C showed virtually identical catalytic activity ensuring full conversion of **1a** and **1b** at 70 °C after 1 h. Longer reaction time

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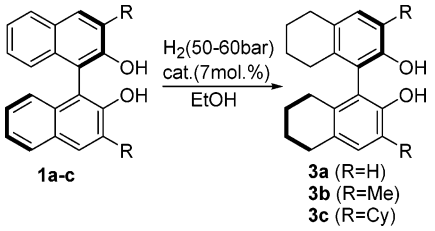
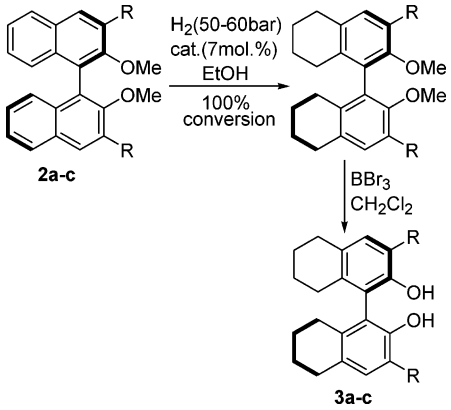
TABLE 1. Catalytic Hydrogenation of 1a−c



	catalyst	*T*/°C	time/h	yield/%[a]	ee/%[b]
1a	Pd/Al_2O_3	50	4	<20	n.d.
1a	Ru/Al_2O_3	100	4	100	97.2
1a	Ru/C	50	1.5	98	99.4
1a	Ru/C	70	1	98	99.6
1a	Pd/C	50	2.5	99	99.5
1a	Pd/C	70	1	99	99.6
1b	Ru/Al_2O_3	100	2	100	99.0
1b	Ru/C	50	7	99	99.4
1b	Ru/C	70	1	97	99.4
1b	Pd/C	70	1	98	99.3
1c	Ru/C	70	7	96	98.5
1c	Pd/C	70	7	100	99.2
1c	Pd/C	100	0.75	100	99.0

[a] Isolated yield. [b] HPLC was used for determination. For analysis of **3a**: Chiralcel OD-H, *n*-hexane/EtOH 90/10. For analysis of **3b**: Chiralcel OD-H, *n*-hexane/EtOH 99.5/0.5. For analysis of **3c**: (*R*,*R*)-Whelk-01, *n*-hexane/EtOH 99.95/0.05.

SCHEME 2



in the case of **1c** as substrate is caused by additional phenyl rings, which also undergo hydrogenation under the conditions applied. HPLC on chiral columns revealed that no racemization occurred during the reaction and products **2a**−**c** were thus obtained with >99% ee. Remarkably, the metal catalysts could be reused several times. Thus, when five consecutive hydrogenation cycles of **1a** were run with the same portion of the Pd/C catalyst, identical activity and selectivity were observed in each cycle.

Another possible approach to 3,3′-disubstituted chiral H_8-BINOLs **3b**,**c** is the hydrogenation of bis-methylated binaphthols **2b**,**c** prior to demethylation. This reaction would also extend the scope of the new technique. Therefore, 2,2′-dimethoxy-1,1′-binaphthyls **3a**−**c** were subjected to hydrogenation followed by deprotection with BBr_3 (Scheme 2).

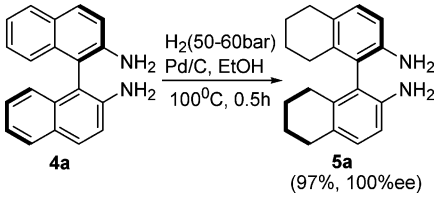
Hydrogenation of 2,2′-dimethoxybinaphthyls **2a**−**c** also proceeded smoothly and quantitatively, but required some longer time or more severe reaction conditions in comparison to the reduction of their 2,2′-dihydroxy analogues **1a**−**c** (Table 2). The reason is probably the lower solubility of **2a**−**c** in ethanol. The products **3a**−**c** isolated after demethylation contained 1−5% of the opposite enantiomer. Therefore, for the synthesis of enantiomerically pure H_8-BINOL and its 3,3′-disubstituted derivatives, direct hydrogenation of 2,2′-dihydroxybinaphthyls seems to be the method of choice.

TABLE 2. Catalytic Hydrogenation of 2,2′-Dimethoxybinaphthyls 2a−c

	catalyst	*T*/°C	time/h	yield/%[a]	ee/%[b]
2a	Ru/C	100	0.5	74	95.4
2a	Pd/C	50	3	80	97.0
2a	Pd/C	70	1.5	77	97.2
2b	Ru/C	100	1.5	71	93.3
2b	Pd/C	100	1	75	90.2
2c	Ru/C	100	0.5	69	98.8
2c	Pd/C	100	1	74	98.5

[a] Isolated yield of deprotected binaphthols **3a**−**c**. [b] Determined by chiral HPLC of deprotected binaphthols **3a**−**c** (see Table 1).

SCHEME 3



The new methodology also proved to be efficient for the hydrogenation of (*R*)-2,2′-diamino-1,1′-binaphthyl (**4a**), which was quantitatively converted into its H_8-derivative **5a** at 100 °C with Pd/C (7 mol %) within 30 min (Scheme 3). No traces of the starting material or of the opposite enantiomer of **5a** could be detected by HPLC. The NMR spectral data, optical rotation, and melting point of the product were in good agreement with the parameters previously reported.[7]

To evaluate the applicability of the new technique to a multigram scale synthesis, we performed the hydrogenation of 20 g of **1a** with 1 mol % of Pd/C (2.97 g of 5% Pd/C, 50% wet) as a catalyst (100 °C, 80 bar of H_2). Full conversion was achieved within 5.5 h and spectroscopically pure **3a** (99.7% ee) was isolated in 98% yield.

In conclusion, we have developed a simple, highly effective and readily scalable hydrogenation procedure for conversion of chiral binaphthyls into H_8-binaphthyl derivatives catalyzed by solid-supported Pd and Ru metal catalysts.

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Supporting Information Available: Two representative hydrogenation procedures, full characterization of **3c** including copies of ^1H and ^{13}C NMR spectra, elemental analysis data for **3b**, and ^1H and ^{13}C spectra of **3a** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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