DOI: 10.1002/adsc.200600481

Asymmetric Hydrosilylation of Prochiral Ketones Catalyzed by Nanocrystalline Copper(II) Oxide

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Received: September 19, 2006; Revised: April 26, 2007

Abstract: Asymmetric hydrosilylation of aryl alkyl ketones to afford chiral secondary alcohols with good yields and excellent enantioselectivity is realized by using nanocrystalline copper(II) oxide and BINAP in the presence of organosilanes as the stoichiometric reducing agents.

Keywords: asymmetric hydrosilylation; heterogeneous catalysis; nanocrystalline copper(II) oxide; reduction; secondary alcohols

Introduction

Asymmetric reduction of ketones represents one of the most important methodologies for obtaining enantiomerically enriched alcohols, which are key intermediates for numerous biologically active molecules.[1] Asymmetric hydrogenation and transfer hydrogenation of carbonyl compounds have been reported by Mikami et al. and Tu and co-workers using ruthenium catalysts with excellent yields and enantiomeric excess.[2] Asymmetric hydrosilylation (AHS) reactions employing organosilanes as the stoichiometric reducing agents lead to very high enantiomeric excesses on a large range of substrates, employing catalytic amounts of complexes of transition metal such as rhodium or titanium.[3] Highly enantioselective hydrosilylations of prochiral ketones were reported by Fu and co-workers using the planar chiral P,N-ferrocene-based rhodium catalyst at room temperature in the presence of mesitylphenylsilane as the hydride source.[4] The AHS reaction is also catalyzed by ruthenium complexes in the presence of chiral tridentate ligands.[5] The AHS reaction of prochiral ketones using inexpensive hydride sources such as polymethylhydrosiloxane (PMHS) and easily accessible and economical catalysts such as zinc diamine complexes[6] or tin[7] has also been reported.

The AHS reaction using CuH and DIOP, a chiral phosphine ligand, was first described by Brunner in 1984.[8] The utility of copper for hydride delivery was studied with the Stryker reagent $[CuH{\cdot}PPh_3]_6$, a stoichiometric reducing agent for the reduction of enones.[9] The catalytic version of the reaction was achieved when a phosphine-copper(I) system such as $[CuH{\cdot}PPh_3]_6$ was treated with hydrogen gas[10] or silanes[11] which enabled the generation of the Cu−H complex. Buchwald described a highly enantioselective 1,4- reduction of α, β-unsaturated esters and β-substituted enones using an active catalyst generated *in situ* from CuCl/NaO-*t*-Bu/chiral diphosphine ligand and PMHS.[12] The effectiveness of $[CuH{\cdot}PPh_3]_6$ for the hydrosilylation of carbonyl compounds was reported by Lipshutz.[13] Subsequent studies by the same group led to the development of the highly enantioselective hydrosilylation of ketones based on CuCl/NaO-*t*-Bu and chiral diphosphine ligands.[14] Besides Stryker's reagent and copper alkoxides, copper fluoride[15] and copper(II) acetate[16] also catalyze the AHS reaction of prochiral ketones in the presence of BINAP ligand. Recently, Bellemin-Laponnaz and co-workers reported an efficient AHS reaction using a chiral BINAP-copper(I)-phenyl(methyl)silane system.[17]

Although homogeneous catalysts are desirable because of their high activity and selectivity, separation of homogeneous catalysts from the products of reaction and/or recovery of the catalysts are inherent problems associated with conventional catalysts. Heterogeneous catalysis has potential advantages, such as easy separation, efficient recycling and minimization of metal traces in the product. Very recently Lipshutz reported the heterogeneous copper-catalyzed AHS reaction.[18]

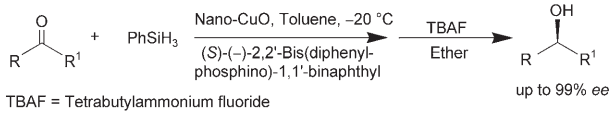
Results and Discussion

Nanocrystalline metal oxides find excellent applications as active adsorbents for gases and destruction of hazardous chemicals[19] and catalysts for various organic transformations.[20,21] Very recently, CO and NO oxidations were reported by CuO nanoparticles[22] and we reported asymmetric epoxidation, Henry and Michael addition reactions using nanocrystalline MgO.[23]

We herein report the nanocrystalline copper oxide (nano-CuO)-catalyzed asymmetric hydrosilylation of prochiral ketones to chiral secondary alcohols in good yields with excellent enantioselectivity (Scheme 1).

Initially, the activities of various silanes were tested in the AHS reaction of acetophenone in presence of (*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand and nano-CuO at room temperature (Table 1). Although it can be seen from Table 1 that the level of enantiomeric excess (*ee*) does not depend too much on the nature of the reducing agent, the rate of the reaction is highly dependent on the choice of the reducing agent. Monoarylsilanes such as phenylsilane ($PhSiH_3$) afforded good enantioselectivity and excellent yield in a short period of time (Table 1, entry 1), while the use of diaryl- and dialkylsilanes furnished lower yields, but the stereoselectivity remained almost unchanged (Table 1, entries 2 and 5). However, with triaryl- or trialkylsilanes, only a trace amount of product was obtained even after prolonged reaction time (Table 1, entries 3 and 6). While $PhSiH_3$ is the most active reducing agent with our catalytic system, the cheaper and readily available siloxanes such as PMHS (Table 1, entry 7), a by-product of silicone industry, can also be employed albeit with a slower reaction rate.

In the process of optimization for the AHS reaction, we explored the use of different solvents (Table 2) and also the reaction was done at different temperatures (Table 3). From Table 2 it is evident that toluene is the best solvent both in terms of product yield and *ee*. A significant effect was observed when the reaction temperature was decreased. As the temperature decreases, the *ee* increases with a decrease in the rate of reaction (Table 3). The solvent



Scheme 1. Asymmetric hydrosilylation reaction of ketones using nano-CuO in the presence of a chiral ligand.

Table 1. Asymmetric hydrosilylation reaction of acetophenone by different silanes at room temperature.[a]

Entry	Silane	Time [h]	Yield [%][b]	*ee* [%][c]
1.	$PhSiH_3$	0.5	95	77
2.	Ph_2SiH_2	24	30	76
3.	Ph_3SiH	24	trace	-
4.	$(EtO)_3SiH$	24	15	67
5.	Et_2SiH_2	24	39	73
6.	Et_3SiH	24	trace	-
7.	PMHS	10	78	81[d]

[a] *Reaction conditions*: acetophenone (2 mmol), silane (2 equivs.), nano-CuO (0.010 g), toluene (3 mL), chiral ligand (BINAP) (0.1 mmol, 0.062 g).

[b] Isolated yields.

[c] Absolute configurations were determined to be (*S*). *ee* were measured by Diacel Chiralcel HPLC using OJ-H column with 5 % 2-propanol in hexane.

[d] 5 mmol of PMHS were used.

Table 2. Asymmetric hydrosilylation reaction of acetophenone catalyzed by nano-CuO with different solvents at −20 °C.[a]

Entry	Solvent	Time [h]	Yield [%][b]	*ee* [%][c]
1.	THF	12	40	31
2.	DCM	12	32	25
3.	Ether	10	72	76
4.	Toluene	3	85	99

[a] *Reaction conditions*: acetophenone (2 mmol), phenylsilane (2 equivs), nano-CuO (0.010 g), solvent (3 mL) chiral ligand (BINAP) (0.1 mmol, 0.062 g).

[b] Isolated yields.

[c] Absolute configurations were determined to be (*S*). *ee* were measured by Diacel Chiralcel HPLC using OJ-H column with 5 % 2-propanol in hexane.

Table 3. Asymmetric hydrosilylation reaction of acetophenone catalyzed by nano-CuO at different temperatures.[a]

Entry	*T* [°C]	Time [h]	Yield [%][b]	*ee* [%][c]
1.	25	0.5	95	77
2.	0	2	89	85
3.	−20	3	85	99
4.	−20	24	38[d]	72
5.	−20	18	29[e]	77

[a] *Reaction conditions*: acetophenone (2 mmol), phenylsilane (2 equivs), nano-CuO (0.010 g), toluene (3 mL), chiral ligand (BINAP) (0.1 mmol, 0.062 g).

[b] Isolated yields.

[c] The *ee* were measured by Diacel Chiralcel HPLC using OJ-H column with 5 % 2-propanol in hexane.

[d] Using commercial CuO.

[e] Using 0.275 g of Cu/C.

Table 4. Asymmetric hydrosilylation reaction of acetophenone catalyzed by nano-CuO with different ligands at −20 °C.[a]

Entry	Ligand	Time [h]	Yield [%][b]	*ee* [%][c]
1.	(*S*)-(−)-BINAP	3, 24[d]	85, 15[d]	99, 0[d]
2.	(*S*)-(−)-BINAM	24	76	54
3.	2,2'-Isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline]	24	74	70
4.	(*S*)-(−)-BINOL	24	trace	-

[a] *Reaction conditions*: acetophenone (2 mmol), phenylsilane (2 equivs), nano-CuO (0.010 g), toluene (3 mL), chiral ligand (0.1 mmol).

[b] Isolated yields.

[c] Absolute configurations were determined to be (*S*). *ee* were measured by Diacel Chiralcel HPLC using OJ-H column with 5 % 2-propanol in hexane.

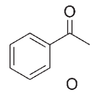
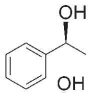
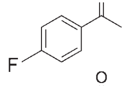
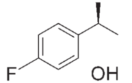
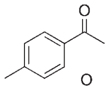
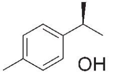
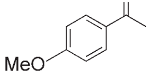
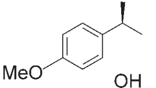
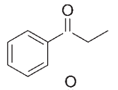
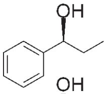
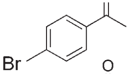
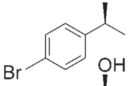
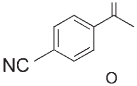
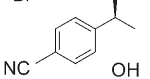
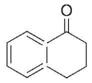
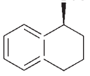
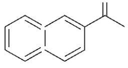
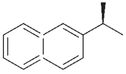
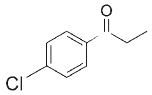
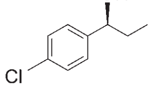
[d] Without ligand at room temperature.

toluene and a temperature of −20 °C gave the best result.

The AHS reaction of acetophenone with commercial CuO afforded 38 % of the desired product with 72 % *ee* after 24 h at −20 °C (Table 3). The nano-CuO with higher surface area (136 m^2/g)[24] and smaller crystallite size (7–9 nm) than the commercial CuO (SA: 1.952 m^2/g) displayed higher activity. The higher enantioselectivity is correlated to the smaller crystallite size which effectively complexes with the chiral auxiliary.

Different types of chiral auxiliaries were also tested and the results are summarized in (Table 4). It was important to note that diphosphine ligands such as BINAP were crucial for the catalytic activity of nano-CuO both in terms of yield as well as *ee* (Table 4, entry 1). The use of bidentate nitrogen-based ligands (Table 4, entries 2 and 3), gave poor yield of product and also the *ee* decreased significantly. Moreover, the bidentate oxygen-based ligand BINOL produced only

Table 5. Asymmetric hydrosilylation reaction of prochiral ketones catalyzed by nano-CuO with phenylsilane at −20 °C.[a]

Entry	Substrate	Time [h]	Product	Yield [%][b]	*ee* (%)[c]	TOF (sec^{-1}) [d]
1.		3		85	99	12.56 x 10^{-4} (92.35 x 10^{-25})
2.		3		88	78	13.01 x 10^{-4} (95.70 x 10^{-25})
3.		5		81	96	7.19 x 10^{-4} (52.86 x 10^{-25})
4.		7		79	83	5.02 x 10^{-4} (36.85 x 10^{-25})
5.		7		75	96	4.76 x10^{-4} (35.01 x 10^{-25})
6.		3		91	76	13.48 x 10^{-4} (99.71 x 10^{-25})
7.		2.5		92	63	16.32 x 10^{-4} (12.00 x 10^{-24})
8.		9		73	88	3.6 x 10^{-4} (26.49 x 10^{-25})
9.		8		78	74	4.33 x 10^{-4} (31.82 x 10^{-25})
10.		6		83	98	6.14 x 10^{-4} (45.20 x 10^{-25})

[a] *Reaction conditions*: ketone (2 mmol), phenylsilane (2 equivs), nano-CuO (0.010 g), toluene (3 mL), chiral ligand (BINAP) (0.1 mmol, 0.062 g).

[b] Isolated yields.

[c] Absolute configurations were determined to be (*S*).

[d] TOF based on moles of CuO and in parenthesis TOF calculated based on surface area (turnover/nm^2/sec).

Table 6. Recycling of the catalytic system for the asymmetric Hydrosilylation reaction of acetophenone at −20 °C.

Run	Time [h]	Yield [%][b]	*ee* [%][c]
1.	3	84	99
2.	3	82	95
3.	3	80	96
4.	3	82	97

[a] *Reaction conditions*: ketone (2 mmol), phenylsilane (2 equivs), nano-CuO (0.010 g), toluene (3 mL), chiral ligand (BINAP) (0.1 mmol, 0.062 g).

[b] Isolated yields.

[c] Absolute configurations were determined to be (*S*).

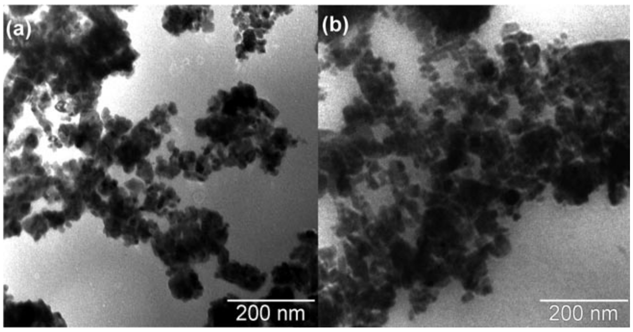


Figure 1. TEM images of nano CuO (**a**) fresh nano-CuO (**b**) used nano-CuO.

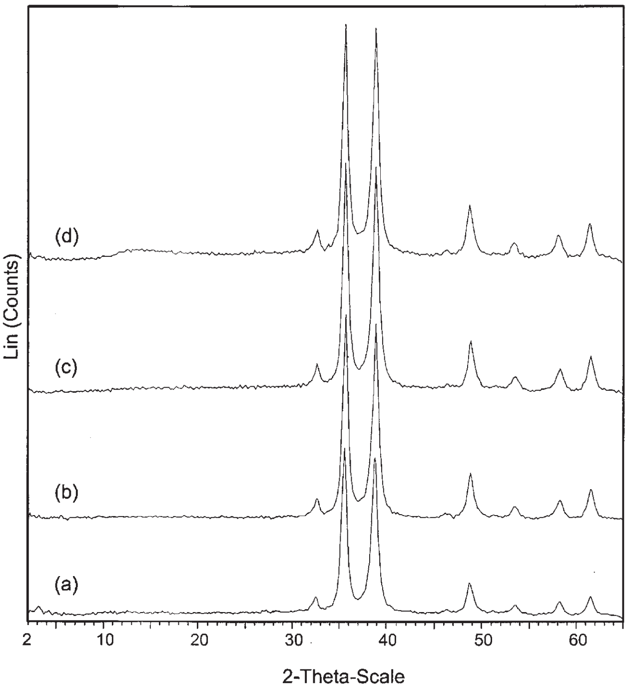


Figure 2. XRD patterns of nano-CuO (**a**) 1st cycle, (**b**) 2nd cycle, (**c**) 3rd cycle, (**d**) 4th cycle.

trace amounts of product despite a prolonged reaction time.

To widen the scope, the catalytic activity of nano-CuO was tested in the AHS reaction of an array of aryl alkyl ketones using (*S*)-(−)-BINAP as chiral auxiliary and phenylsilane as the stoichiometric reducing agent, which resulted in excellent enantioselectivity. Acetophenone is hydrosilylated cleanly with high enantioselectivity (Table 5, entry 1). Introduction of electron-withdrawing groups at the *para* position of acetophenone (Table 5, entries 2, 6 and 7) produced a decrease in enantioselectivity although total conversion was achieved in a shorter period of time. Conversely, the presence of electron-donating groups at te *para*-position of acetophenone (Table 5, entries 3 and 4) has little effect on enantioselectivity but a longer reaction time is needed for full conversion. Sterically demanding 2-acetonaphthone (Table 5, entry 9) also afforded good yields with excellent enantioselectivity. When the methyl group of the aryl alkyl ketone is substituted with an ethyl group, the AHS reaction still gave excellent enantioselectivity albeit with moderate yields (Table 5, entries 5 and 10). It is significant to note that other substituents like fluoro, bromo, cyano, and chloro (Table 5, entries 2, 6, 7 and 10) were not affected during the hydrosilylation reaction. The corresponding chiral alcohols are obtained after hydrolysis (see Experimental Section).

Catalyst recycle experiments were also carried out using acetophenone as a model substrate. As can be seen in Table 6, the nano-CuO catalyst can be reused for several cycles without loss of activity and selectivity. No reaction occurred when the reaction was conducted with the filtrate obtained after removal of the solid catalyst. This indicates that the active catalyst species was not leached out of the solid catalyst. The absence of copper in the filtrate was also confirmed by AAS studies.

Transmission electron microscopic (TEM) studies of both fresh and used catalysts were carried out to understand the shape and size of the particles. Figure 1 a and b shows the TEM images of the fresh and the used catalyst after the fourth cycle. Interestingly it is observed that the shape and size of the particles remain unchanged. This supports the proposal that the morphology of the catalyst remains the same even after recycling. The X-ray powder diffraction (XRD, Figure 2) patterns of the fresh and used nano-CuO do not differ in the range $2\theta = 0^{\circ}$–80° which confirms the fact that the structure and morphology of the catalyst remains the same during the course of the reaction.

The plausible mechanism of hydrosilylation may be through the formation of copper hydride species from the reduction of ligated nano-CuO by the silane. At this stage, we are not sure whether the active catalytic species is a copper(I) hydride or a copper(II) hy-

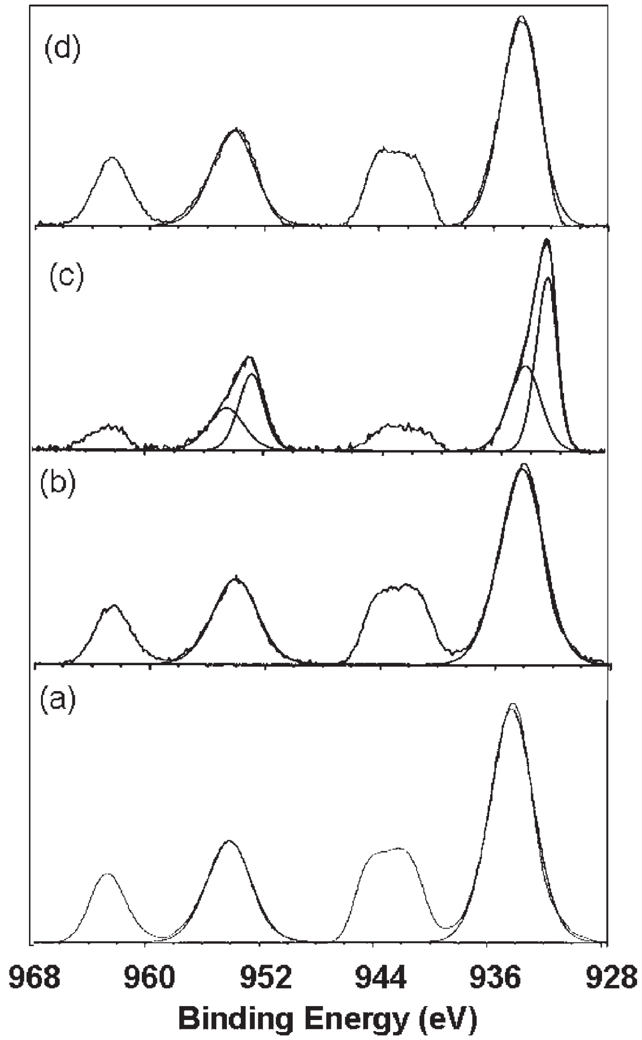


Figure 3. XPS high resolution narrow scans of Cu $2p_{3/2}$ for (**a**) fresh nano-CuO, (**b**) nano-CuO treated with BINAP, (**c**) nano-CuO treated with BINAP and silane, and (**d**) used nano-CuO.

dride.[16] X-ray photoelectron spectroscopic (XPS) investigations of fresh nano-CuO and nano-CuO treated with BINAP ligand at the Cu 2*p* level show $2p_{3/2}$ lines at 934.4 eV and 934.2 eV, respectively, which correspond to the +2 oxidation state (Figure 3 a),[25] whereas XPS spectra of nano-CuO treated with BINAP and silane under an inert atmosphere show two Cu $2p_{3/2}$ peaks at 934.4 and 933.1 eV, which correspond to Cu in +2 and +1 oxidation states, respectively (Figure 3 c). The approximate amounts of copper in the +1 and +2 oxidation states were found to be 57% and 43%, respectively. from the area under the curve of the Cu 2*p* XPS high resolution narrow scan. The copper hydride species reacts with the ketone resulting in the formation of a copper alkoxide that subsequently undergoes σ-bond metathesis with the organosilane to afford the silyl ether.[16] After the reaction, the XPS of the recovered nano-CuO (Figure 3 d) shows the $2p_{3/2}$ peak at 934.3 eV which corresponds to Cu in the +2 oxidation state only.

In conclusion, the enantioselective hydrosilylation of aryl alkyl ketones to afford chiral secondary alcohols with good yields and excellent enantioselectivity is realized by using nanocrystalline copper oxide and BINAP in the presence of organosilanes as the stoichiometric reducing agents without any inorganic base.

Experimental Section

General Remarks

Nanocrystalline CuO (NanoActive™ CuO abbreviated as nano-CuO S.A: 136 m²/g) samples were obtained from Nano-Scale Materials Inc., Manhattan, Kansas, USA. The commercial CuO (CM-CuO, S.A: 1.952 m²/g) was purchased from Loba Chemie. India. Cu(II)/C was prepared by a process previously reported by Lipshutz[18]. Activated Carbon (100 mesh size, having surface area = 1001 m²/g and contains 30% H_2O) was provided by Sud-Chemie India Pvt. Ltd. $Cu(NO_3)_2{\cdot}3H_2O$ was purchased from S D Fine – Chem Limited, India. From AAS studies the copper loading was found to be 3.07 wt% of Cu. Rest of the chemicals were purchased from Aldrich and used as received. All solvents were purchased as analytical grade and used as received from Merck India Pvt. Ltd. Dry toluene was used for all reactions. ACME silica gel (100–200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F254 plates.

All reactions were conducted at –20 °C in dry toluene under nitrogen atmosphere. The ^{1}H NMR spectra were recorded on Varian Gemini 200 MHz and Bruker Avance 300 MHz spectrometers. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard in $CDCl_3$. High performance liquid chromatography (HPLC) was performed using the following apparatus; Shimadzu LC-10 AT (liquid chromatograph), Shimadzu SPD-10 A (UV detector), and Shimadzu C-R6 A Chromatopac. Optical rotations were obtained on Jasco P-1020 Polarimeter and reported in absolute reactions: $[\alpha]_D^{\text{temperature}}$ (concentration c = g/100 mL of solvent). X-ray photoelectron spectra (XPS) were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg-Kα anode. X-ray powder diffraction (XRD) data were collected on a Simens D-5000 diffractometer using Cu-Kα radiation. The external morphologies of fresh and used catalyst were observed on a Philips TECNAI F12 FEI transmission electron microscope (TEM).

General Procedure for the Asymmetric Hydrosilylation Reaction

Nano-CuO (0.010 g) and (*S*)-BINAP (0.1 mmol, 0.062 g) were placed in a dried Schlenk flask containing dry toluene (3 mL) at room temperature and stirred for 1 h under nitrogen atmosphere. The resulting mixture was cooled to –20 °C and $PhSiH_3$ (2 equivs.) was added. To the reaction mixture, ketone (2 mmol) was added at that temperature and stirring was continued. After completion of the reaction, (as monitored by TLC), the reaction mixture was centrifuged to separate the catalyst. The catalyst was washed with ether and was reused for another cycle after vacuum drying. The reaction mixture was quenched with water with the aid of Et_2O (10 mL), and then tetrabutylammonium fluoride solution (TBAF) (1.0 M in THF, 1.2 mL) was added. The reaction mixture was stirred vigorously for 0.5 h. The organic layer was separated and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography to afford pure (*S*)-1-phenylethanol; yield: 85%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.50$ (d, 3H, $J = 6.6$ Hz, CH_3), 1.95 (br, 1H, OH), 4.89 (q, 1H, $J = 6.6$ Hz, CH), 7.22–7.40 (m, 5H, ArH); HPLC (Diacel Chiralcel OJ-H, 5% 2-propanol in hexane, flow rate 0.5 mL min^{-1}): $t_R = 22.252$ min (major), 24.301 min (minor).

Acknowledgements

We wish to thank the CSIR for financial support under the Task Force Project COR-0003 and Soumi Laha and Jagjit Yadav thank CSIR, India for their fellowships. Nanocrystalline CuO samples were obtained from NanoScale Materials Inc., Manhattan, KS 66502, USA.

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