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Catalytic applications of F_8BINOL: asymmetric oxidation of sulfides to sulfoxides

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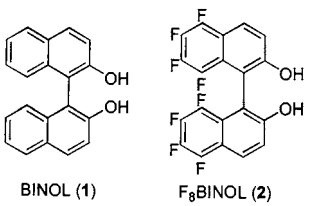
Abstract

The effect of fluorine substitution at the 5, 5′, 6, 6′, 7, 7′, 8 and 8′ positions of 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) on its catalytic activity in titanium-mediated sulfide oxidation with *tert*-butyl hydrogen peroxide and cumyl hydrogen peroxide was examined. Introduction of fluorines into the BINOL scaffold was found to increase the electrophilic character of the Lewis acidic titanium center of the catalyst. Moreover, under otherwise identical conditions, BINOL and 5,5′,6,6′,7,7′,8,8′-octafluoro-2,2′-dihydroxy-1,1′-binaphthyl (F_8BINOL) of the same absolute configuration led to opposite sense of chiral induction in the sulfoxidation process.

Keywords: Catalytic applications; BINOL; Sulfides; Sulfoxides

1. Introduction

2,2′-Dihydroxy-1,1′-binaphthyl (BINOL, **1**) and related C_2 symmetrical ligands possessing axial chirality have found wide utility in asymmetric catalysis [1]. Over the years, several modifications of the BINOL scaffold aimed at changing its steric as well as electronic properties have appeared [2]. For instance, partially hydrogenated BINOL was used in enantioselective alkylation of aldehydes [2a], conjugate addition of diethylzinc to enones [2b], and ring-opening of epoxides [2c]. Incorporation of bromine atoms at the 6 and 6′ positions of **1** was shown to increase the enantioselectivity of the corresponding titanium catalysts in glyoxylate ene reactions [2d]. Bulky triarylsilyl groups at the 3 and 3′ positions of **1** led to increased enantioselectivities in the asymmetric Diels–Alder processes [2e]. In the area of oxidation catalysis, the 3,3′-dinitrooctahydrobinaphthol ligand was applied in the titanium-catalyzed asymmetric oxidation of methyl-*p*-tolylsulfide [2f].



BINOL (1) F_8BINOL (2)

We recently designed a new class of chiral polyfluoroaryl ligands based on **1** [3]. Substitution of hydrogens by fluorines at the 5, 5′, 6, 6′, 7, 7′, 8 and 8′ positions of **1** was found to induce considerable electronic perturbation of the aromatic system in the resulting 5,5′,6,6′,7,7′,8,8′-octafluoro-2,2′-dihydroxy-1,1′-binaphthyl (F_8BINOL, **2**). The electron-deficient nature of the aromatic rings was found to raise the oxidative stability of **2** compared with **1** ($E'_2 = 2.07$ V in **2** vs. 1.47 V in **1**) as well as to increase the acidity of the ring-bound hydroxyl groups (pK'_a 9.28 in **2** vs. 10.28 of **1**). This electronic alteration in turn led to a dramatic increase in configurational stability of homochiral **2** with electronic effects playing a decisive role.

We reasoned that besides changing the physicochemical characteristics of the BINOL ligand, the structural consequences of fluorine substitution should also translate into modulated binding to metals as well as reactants in the F_8BINOL-mediated processes, especially in

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the cases where early transition metals are involved. The latter are well known to exhibit diverse aggregation equilibria in the presence of a variety of ligands [4]. Therefore, the ligands with modulated coordination ability can give rise to the catalyst systems possessing novel properties including increased catalytic activity. Since the fluorine atom is only 0.27 Å larger than the hydrogen atom [5a], one could anticipate only a small increase in the barrier to axial torsion in BINOL upon fluorine substitution. The complexes obtained from fluorinated versions of these and related ligands can be considered sterically similar to their hydrogenated counterparts, but drastically different in terms of electronics. Notably, perfluorinated ligands are known to afford stable porphyrin-derived catalysts of high turnover in catalytic oxidation processes [6]. In the present paper, we report the results of our investigations of the catalytic asymmetric sulfoxidation with F_8BINOL/Ti(O^iPr)$_4$. These catalytic experiments indicate that fluorine substitution is responsible for improved levels of enantioselectivity in the concentration range where minimum by-product sulfone is formed. In addition, reversal in the sense of chiral induction in the asymmetric sulfoxidation process takes place.

2. Results and discussion

The racemic form of **2** was prepared in five steps and 30% overall yield from the commercially available chloropentafluorobenzene [3]. The diastereomeric bis[(−)-menthoxycarbonyl] derivatives were obtained by reacting racemic **2** with excess (−)-menthyl chloroformate in quantitative yield. Subsequent deprotection furnished the *R*- and *S*-enantiomers of **2** in 99 + % ee each.

Our investigations commenced with the NMR studies aimed at characterizing the titanium/F_8BINOL adducts. Upon addition of Ti(O^iPr)$_4$ (one equivalent) to the 0.133 M solution of F_8BINOL (one equivalent) in $CDCl_3$, the reaction mixture turned yellow–orange and resonances at −148.3, −149.1, −156.6, and −161.8 ppm in the ^{19}F-NMR spectrum, corresponding to free F_8BINOL, disappeared. A new set of peaks at −143.8, −149.8, −158.6, and −162.4 ppm was observed (Fig. 2). This change is consistent with the formation of the C_2 symmetrical 1:1 adduct **4** between Ti(O^iPr)$_4$ and F_8BINOL. The ^{13}C spectrum features a resonance at 159.0 ppm, which is very close to the value of 158.8 ppm reported for the corresponding 1:1 adduct **3** in the Ti(O^iPr)$_4$/BINOL system in $CDCl_3$ (Fig. 1) [7]. Thus, despite a tenfold decrease in acidity of the hydroxyl groups in BINOL upon fluorine substitution, binding to the oxophilic titanium atoms still takes place. The ^{19}F-NMR spectrum obtained by mixing Ti(O^iPr)$_4$ and F_8BINOL in a 1:2 ratio featured an additional set of eight peaks corresponding to the formation of a new species having C_1 symmetry [8].

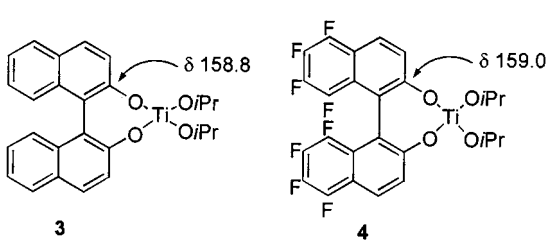


Fig. 1. ^{13}C chemical shifts of the 2 and 2′ carbons in BINOL/Ti(O^iPr)$_4$ and F_8BINOL/Ti(O^iPr)$_4$ adducts.

The replacement of aromatic hydrogens for fluorines is known to increase barriers to axial torsion in substituted biphenyls. For example, fluorination of the 4 and 5 positions of 9,10-dihydrophenanthrene raises the torsion barrier from 4.1 to 10.3 kcal mol^{-1} [6]. The torsion angle between the tetrafluoronaphthol planes in the molecular structure of *R*-(−)-2 (79.7°) is only 1.4° larger than in the parent protio-derivative *R*-(−)-1 (78.3°) [3,9]. This indicates that fluorine substitution at the 5, 5′, 6, 6′, 7, 7′, 8 and 8′ positions of BINOL has fairly insignificant steric influence on the torsion angle and the observed effect on the catalytic activity of **2** must be primarily electronic in nature. The desired conformational flexibility, one of the most important characteristics of BINOL allowing it to coordinate a wide variety of metals [1], is preserved in **2**, which is evident from the NMR characterization of the F_8BINOL/Ti(O^iPr)$_4$ adducts.

To illustrate the utility of the F_8BINOL-derived catalysts in asymmetric catalysis, we chose sulfide oxidation as a model reaction. Enantiomerically pure sulfoxides constitute an important target in asymmetric synthesis [10]. At the beginning, we compared the activities of (*R*)-F_8BINOL and (*R*)-BINOL ligands in titanium-catalyzed asymmetric oxidation of *p*-tolyl sulfide with *tert*-butyl hydrogen peroxide (TBHP) [10b]. The results of this study are summarized in Table 1. Gratifyingly, the catalyst produced in the (*R*)-F_8BINOL/Ti system (10 mol%) was found to catalyze the sulfoxidation process with higher enantioselectivity than the (*R*)-BINOL/Ti species at 0.05 M concentration. Uemura's sulfoxidation protocol [10] leads to high enantioselectivities at high concentrations, albeit at the expense of a significant production of the sulfone by-product, which decreases the yield of the sulfoxide. Due to the highly electrophilic character of F_8BINOL, Ti(O^iPr)$_4$/F_8BINOL-catalyzed reactions tend to produce more sulfone than the BINOL-mediated reaction arising from over oxidation. The lack of enantioselectivity for the (*R*)-BINOL/Ti species (Table 1, entry 2) suggests that the species responsible for enantioselective oxygen atom transfer is not produced in the 1:1 system. To our biggest surprise, the *opposite* sense of induction was

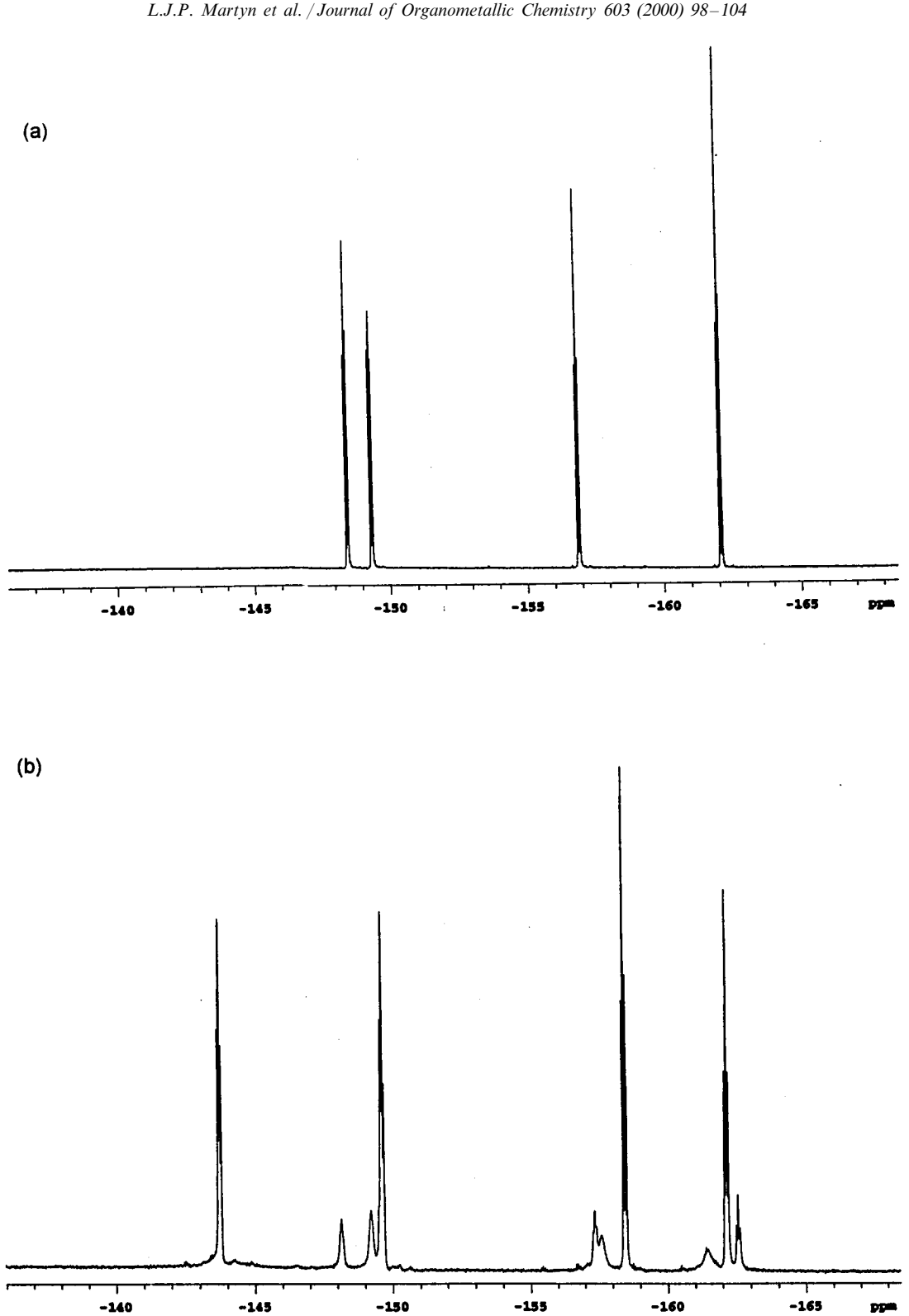


Fig. 2. ^{19}F-NMR spectra of (a) F_8BINOL in $CDCl_3$ (0.133 M); (b) 1:1 adduct between F_8BINOL and $Ti(O^iPr)_4$.

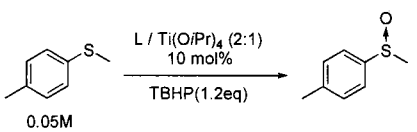
observed upon fluorine substitution: (*R*)-BINOL gave preferentially the *R*-sulfoxide, whereas (*R*)-F_8BINOL produced an excess of the *S*-enantiomer. This intriguing observation warrants further investigation into the nature of the catalytically active species as well as the scope of the F_8BINOL-based catalysts. It is conceivable that different aggregation is a likely cause for the observed change in enantioselectivity. Notably, reversal of asymmetric induction in the titanium-mediated oxidation of sulfides upon introduction of the CF_3 sub-

stituents into the backbone of 1,2-diarylethane-1,2-diols was documented [11]. In addition, introduction of the *ortho*-nitro groups into BINOL was previously found to reverse the enantioselectivity of the sulfoxidation [2f].

We also compared the reactivities of BINOL and F_8BINOL by generating the conversion/time diagrams for the BINOL/Ti(O^iPr)$_4$ and F_8BINOL/Ti(O^iPr)$_4$ oxidations at 0.05 M substrate concentration and 5 mol% catalyst loading. Fig. 3 features comparison of the catalyzed oxidation of methyl-*p*-tolyl sulfide to methyl-*p*-tolyl sulfoxide. The build-up of the sulfoxide was monitored by gas chromatography over 8 h. Ethyl phenyl sulfone was chosen as an internal standard in both runs due to its resistance to further oxidation. Although the initial rates were not measured, Fig. 3 clearly demonstrates that the electronic influence of fluorines dictates higher activity of the F_8BINOL-based titanium catalyst.

The use of a 1:2 ratio of Ti(O^iPr)$_4$–F_8BINOL at room temperature (r.t.) constitutes optimal reaction conditions. Experiments were conducted in order to determine the optimal amount and the nature of the oxidant in the sulfoxidation of methyl-*p*-tolyl sulfide (Table 2). The largest increase in % ee was obtained when cumyl hydrogen peroxide was substituted for *tert*-butyl hydrogen peroxide. Optimized reaction conditions call for the use of cumyl hydrogen peroxide (1.1 equivalents) and chloroform as solvent. In this case,

Table 1
Comparison of the BINOL/Ti(O^iPr)$_4$ and F_8BINOL/Ti(O^iPr)$_4$ catalyzed oxidation of methyl-*p*-tolyl sulfide to methyl-*p*-tolyl sulfoxide



Entry	Solvent	Ti:ligand ratio	Temperature (°C)	Time (h)	(*R*)-F_8BINOL % ee	(*R*)-BINOL % ee
1	CH_2Cl_2	1:2	0–RT	4	61 (*S*)	7 (*R*)
2	CH_2Cl_2	1:1	0–RT	4	0	0
3	CCl_4	1:2	0–RT	3	31 (*S*)	22 (*R*)
4	CH_2Cl_2	1:2	−50 to −5	20	60 (*S*)	0 (*R*)
5	CH_2Cl_2	1:4	0–RT	5	64 (*S*)	17 (*R*)

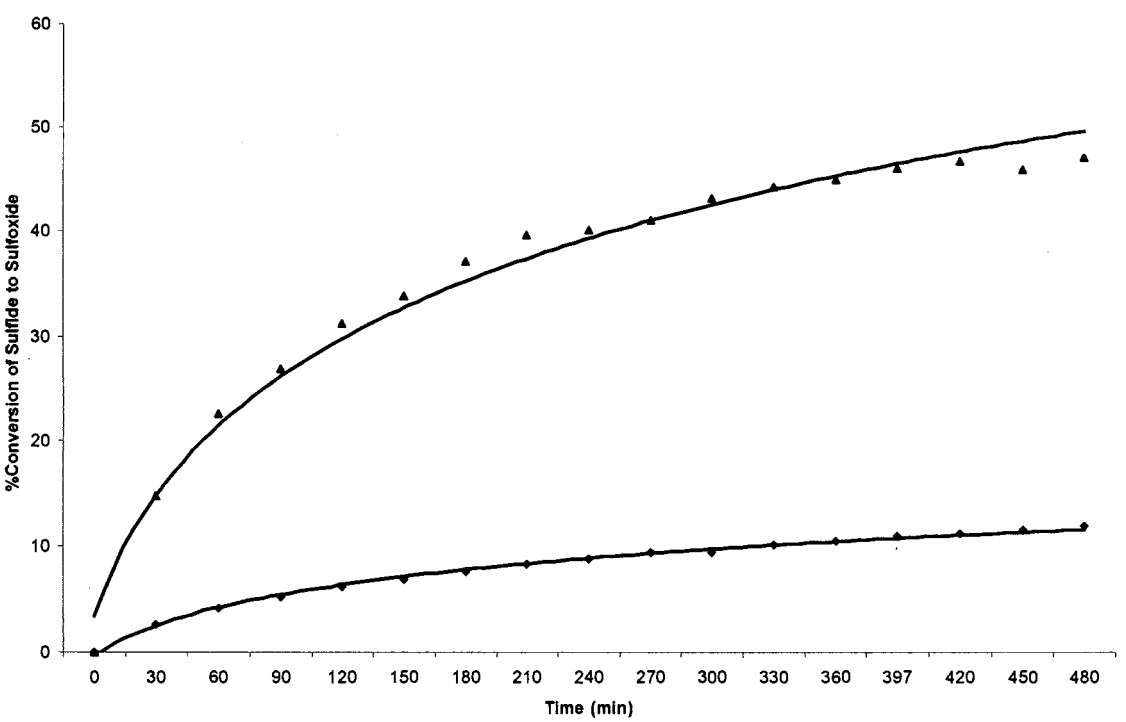


Fig. 3. Comparison of the BINOL/F_8BINOL catalyzed oxidation of methyl-*p*-tolyl sulfide to methyl-*p*-tolyl sulfoxide (▲: F_8BINOL reaction; ◆: BINOL reaction).

Table 2
Comparison of titanium sources, oxidants and ligand:titanium ratios

Entry	Titanium source	Oxidant	Ti:F_8BINOL ratio	% ee
1	$Ti(O^iPr)_4$	2.2 equivalents TBHP [a]	1:4	64 (*S*)
2	$Ti(O^iPr)_4$	1.1 equivalents TBHP	1:4	67 (*S*)
3	$Ti(O^iPr)_4$	1.1 equivalents TBHP	1:2	64 (S)
4	$Ti(O^iPr)_4$	2.2 equivalents CHP [b]	1:2	75 (*S*)
5	$TiCl_4$	2.2 equivalents TBHP	1:2	0
6	$TiCl_4$	2.2 equivalents CHP	1:2	0

[a] TBHP, *tert*-butyl hydrogen peroxide.
[b] CHP, cumyl hydrogen peroxide.

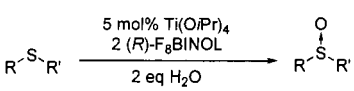
maximum enantioselectivity of 76–86% was observed for the oxidation of phenyl methyl sulfide (Table 3, entries 10–13). Kagan and co-workers had previously established that water is essential to ensure rapid turnover in the titanium/diethyl tartrate oxidation system [10a]. In our case, water was also found to be crucial and, according to the optimized protocol, two equivalents of water with respect to sulfide are necessary for the turnover to take place. As far as alternative sources of titanium(IV), titanium(IV) chloride was tested but did not lead to the production of the catalytically active species, presumably due to the premature hydrolysis of titanium(IV) chloride under the reaction conditions [12]. An increase in the ligand-to-titanium ratio (Table 2, entry 1) was found to have little to no effect on the %ee of the sulfoxide. Similarly, a decrease in the amount of oxidant showed no change in the %ee, although better yields were observed due to the lower amounts of sulfone produced.

Experiments to establish the substrate scope were also carried out (Table 3). Several commercially available sulfides were subjected to the Ti/F_8BINOL catalyzed sulfoxidation protocol. The highest levels of ee were observed with the sulfide moiety bearing a methyl substituent. The oxidation of electron deficient systems, known to proceed slowly, was sluggish in our case accounting for the low conversion of methyl 2-nitrophenyl sulfide. Longer reaction times were required in order to drive this reaction to completion. The attempt to optimize this process by decreasing the reaction temperature resulted in lower enantioselectivity. Expanding on the observation that carrying out the reactions at −20°C reduced the %ee, we carried out the reactions at r.t. Having obtained reasonably good enantiomeric excess at the 0.05 mmol scale, the process was then scaled up to 1 mmol and isolated yields for selected substrates were determined (Table 4).

3. Conclusions

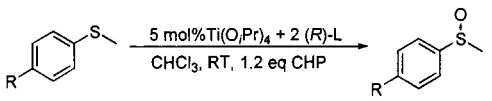
In summary, fluorine substitution, which confers remarkable configurational stability on homochiral 5,5′,6,6′,7,7′,8,8′-octafluoro-2,2′-dihydroxy-1,1′-binaphthyl, also has an interesting effect on the catalytic activity and selectivity of the titanium-based catalysts. F_8BINOL efficiently catalyzes the titanium-mediated sulfoxidation process. The most intriguing difference between the F_8BINOL and BINOL systems is the reversal in the sense of chiral induction upon fluorine substitution. Most importantly, the tenfold increase in acidity of the ring-bound hydroxyl groups still allows coordination to Ti(IV) centers. Similar trends should operate

Table 3
Substrate scope of the sulfoxidation reaction catalyzed by F_8BINOL/$Ti(O^iPr)_4$



Entry	R	R′	Solvent	Oxidant	Reaction time (h)	Temperature (°C)	% ee (*S*)
1	4-MePh	Me	CH_2Cl_2	2.2 equivalents TBHP	18	−20	35
2	Phenyl	Me	CH_2Cl_2	2.2 equivalents TBHP	18	−20	41
3	2-BrPh	Me	CH_2Cl_2	2.2 equivalents TBHP	18	−20	0
4	4-BrPh	Me	CH_2Cl_2	2.2 equivalents TBHP	18	−20	54
5	2-NO_2Ph	Me	CH_2Cl_2	2.2 equivalents TBHP	18	−20	51
6	Ph	Et	CH_2Cl_2	2.2 equivalents TBHP	18	−20	17
7	Ph	CH_2Cl	CH_2Cl_2	2.2 equivalents TBHP	18	−20	NR
8	Ph	Bn	CH_2Cl_2	2.2 equivalents TBHP	18	−20	14
9	Ph-SO_2CH_2-	Me	CH_2Cl_2	2.2 equivalents TBHP	18	−20	NR
10	4-MePh	Me	$CHCl_3$	1.1 equivalents CHP	4.5	0	76
11	4-BrPh	Me	$CHCl_3$	1.1 equivalents CHP	4.5	0	82
12	4-MePh	Me	$CHCl_3$	1.1 equivalents CHP	4.5	23	86
13	4-BrPh	Me	$CHCl_3$	1.1 equivalents CHP	4.5	23	77

Table 4
Isolated yields for selected sulfoxides in the BINOL- and F_8BINOL-mediated oxidations



Entry	R	F_8BINOL			BINOL		
		Time (h)	% Yield	% ee (*S*)	Time (h)	Yield	% ee (*R*)
1	Me	18	55	80	42	69	3
2	Br	18	77	76	42	74	14
3	H	18	74	70	42	66	0

for other substituents at the 2 and 2′ positions as well as the coordinated metals, eventually providing novel catalysts with modulated reactivities [13]. Reactions that involve highly acidic and/or oxidative conditions [14] under which **1** could become configurationally or structurally unstable seem to be particularly interesting. Noteworthy, both enantiomers of **2** can be readily prepared from commercially available starting materials.

4. Experimental

4.1. General

Anhydrous dichloromethane was obtained using the method described by Grubbs [15]. All sulfides as well as *tert*-butyl hydrogen peroxide (TBHP) and cumyl hydrogen peroxide (CHP) were purchased from Aldrich Chemical Company. Column chromatography was carried out using 230–400 mesh silica gel. ^{1}H-NMR spectra were referenced to residual $CHCl_3$ and ^{19}F-NMR spectra were referenced to $CFCl_3$.

4.2. Methyl-p-tolyl sulfoxide

(a) 0.05 mmol scale. Into an oven dried 1 ml flask was placed F_8BINOL (2.2 mg, 0.5 μmol). $CHCl_3$ (1 ml) was added, followed by the addition of $Ti(O^iPr)_4$ (0.74 μl, 0.25 μmol) via syringe. The reaction turned dark red–orange. Water (1.8 μl, 0.1 mmol) was added and the resulting mixture was allowed to stir for 15 min. Methyl-*p*-tolyl sulfide (6.7 μl, 0.05 mmol) was introduced, followed by the addition of cumene hydrogen peroxide (80%) (11 μl, 0.06 mmol). The reaction was allowed to stir for 4–5 h at r.t. The mixture was then quenched with 0.5 ml of water and was allowed to stir for an additional 5 min. Subsequent filtration through a plug of Celite was followed by concentration under reduced pressure. The residue was taken up in HPLC grade hexane and chromatographed using 7:3 hexane–*i*-propanol as eluent on a Daicel Chiralpak AS column (flow rate 1 ml min^{-1}).

(b) 1 mmol scale. Into an oven-dried 10 ml flask was placed F_8BINOL (4.3 mg, 0.1 mmol). $CHCl_3$ (5 ml) was added, followed by the addition of $Ti(O^iPr)_4$ (14.7 μl, 0.05 mmol). Water (36 μl, 2 mmol) was added and the reaction mixture was allowed to stir for 15 min. Methyl *p*-tolyl sulfide (134 μl, 1 mmol) was then introduced, followed by the addition of cumene hydrogen peroxide (80%) (220 μl, 1.2 mmol). The reaction was allowed to stir for 4–5 h at r.t. The reaction was then quenched with 1 ml of water and the resulting mixture was allowed to stir for additional 5 min. Celite was added to the reaction mixture and the solvent was concentrated under reduced pressure. The product, adsorbed on Celite, was added to the top of a silica gel column and was chromatographed with 4:1 hexanes–diethyl ether. After the F_8BINOL and sulfone by-product had eluted, the eluent was changed to pure ether and the sulfoxide was obtained as an analytically pure material in 55% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 2.70 (s, 3H), 2.42 (s, 3H).

4.3. Methyl 4-bromophenyl sulfoxide

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.68 (d, $J = 8.6$ Hz, 2H), 7.66 (d, $J = 8.6$ Hz, 2H), 2.72 (s, 3H).

4.4. Methyl phenyl sulfoxide

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, $J = 8.1$ Hz, 2H), 7.54 (m, 3H), 2.73 (s, 3H).

4.5. NMR study of the F_8BINOL/ $Ti(O^iPr)_4$ equilibrium

To (*R*)-F_8BINOL (29 mg, 0.067 mmol) was added 0.5 ml of $CDCl_3$ in an NMR tube at r.t. Subsequent addition of $Ti(O^iPr)_4$ (20 μl, 0.068 mmol) resulted in color change to yellow–orange and the formation of

the 1:1 adduct **4** along with isopropanol (two equivalents) observed by NMR spectroscopy. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.9, 144.7 (dm, $J = 253$ Hz), 143.3 (dm, $J = 253$ Hz), 140.2 (dm, $J = 252$ Hz), 137.2 (dm, $J = 249$ Hz), 122.1, 120.9, 120.6, 116.3 (d, $J = 13$ Hz), 115.8.

Acknowledgements

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