ELSEVIER

Journal of Fluorine Chemistry 112 (2001) 101–108

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Design and synthesis of new fluorinated ligands for the rhodium-catalyzed hydroformylation of alkenes in supercritical CO_2 and fluorous solvents

Dominique Bonafoux, Zihao Hua, Beihan Wang, Iwao Ojima*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, USA

Abstract

Novel fluorous biphenols, 5,5′-[*n*-$C_4F_9(CH_2)_3$]$_2$-2,2′-biphenol and 5,5′-[*n*-$C_4F_9(CH_2)_3O$]$_2$-3,3′-di-*tert*-butyl-2,2′-biphenol, as well as enantiopure BINOLs, (*S*)-6,6′-[*n*-$C_4F_9(CH_2)_3$]$_2$-BINOL, (*R*)-6,6′-[*n*-$C_6F_{13}(CH_2)_3$]$_2$-BINOL, and (*S*)-6,6′-[*n*-$C_8F_{17}(CH_2)_3$]$_2$-BINOL, are synthesized. These compounds serve as key intermediates for the syntheses of a variety of new fluorous ligands for regioselective and enantioselective catalytic reactions. Novel fluorous [$Rf(CH_2)_3$]$_2$-BINAPHOS ligands (Rf = *n*-C_4F_9, *n*-C_6F_{13}, and *n*-C_8F_{17}) are successfully synthesized. These new fluorous chiral ligands when used with a rhodium catalyst can achieve comparable or even higher regioselectivity and enantioselectivity in the asymmetric hydroformylation of styrene as compared to those by the Rh-BINAPHOS system.

Keywords: Fluorous ligands; Fluorous BINOL; Fluorous BINAPHOS; Fluorous biphenol; Catalytic asymmetric synthesis; Enantioselective; Hydroformylation; Phosphine–phosphite; Diphosphite

1. Introduction

Transition metal-catalyzed hydrocarbonylation reaction of unsaturated hydrocarbons is one of the most powerful methods for the syntheses of aldehydes, alcohols, esters and carboxylic acids. The most widely used and commercially important process among these reactions is the hydroformylation of olefins [1,2]. The use of supercritical fluids, in particular $scCO_2$ as environmentally friendly reaction medium in place of conventional organic solvents has recently attracted significant interest [3–8]. On the other hand, the fluorous biphase catalysis introduced by Horváth and Rábai [9–11] provides a new and practical concept for the recovery and recycling of the expensive catalysts used in these transformations. In order to transpose the hydroformylation reaction to $scCO_2$ and/or fluorous phase, the catalyst system must be soluble in $scCO_2$ or preferentially soluble in fluorous solvents over conventional organic solvents. This can be achieved by modifying known ligands with 'solubilizing' perfluoroalkyl tails to increase the affinity of the ligands to $scCO_2$ or fluorous solvents. Accordingly, we started the design and syntheses of new diphosphite and chiral phosphine–phosphite ligands with perfluoroalkyl tails. The former ligands are the congeners of BIPHEPHOS [12–14] that is an excellent ligand for highly linear-selective hydroformylation of 1-alkenes and the latter ligands are the analogs of BINAPHOS [15,16] that is the best chiral ligand to date for the asymmetric hydroformylation of vinylarenes. While our research was in progress, Franciò and Leitner [7] reported their synthesis of a fluorous (*R*,*S*)-BINAPHOS bearing a 2-(perfluorohexyl)ethyl group at the *meta*-position of diphenylphosphinyl moiety, and its successful application to the Rh-catalyzed asymmetric hydroformylation of vinylarenes in $scCO_2$. Our design of fluorous BINAPHOS ligands is different from that of Franciò and Leitner in that perfluoroalkyl tails are attached to the peripheral naphthyl moieties, and the same approach is taken for designing fluorous BIPHEPHOS ligands (Fig. 1). Another important feature of our approach is to make a small library of fluorous ligands using biphenols as well as enantiopure binaphthols (BINOLs) bearing 3-(perfluoroalkyl)propyl tails as key common units. It should be noted that those enantiopure BINOLs bearing 3-(perfluoroalkyl)propyl tails can be applied to a variety of BINOL-based asymmetric transformations and also be converted to fluorous BINAP, MOP, BIPHENPHOS, etc. in addition to fluorous BINAPHOS.

We report here our approaches towards the syntheses of [*n*-$C_4F_9(CH_2)_3$]$_4$-BIPHEPHOS (**1a**), [*n*-$C_4F_9(CH_2)_3O$]$_2$-BIPHEPHOS (**1b**) and the successful syntheses of (*R*,*S*)-

* Corresponding author. Tel.: +1-631-632-7947; fax: +1-631-632-7942.
E-mail address: iojima@notes.cc.sunysb.edu (I. Ojima).

0022-1139/01/$ – see front matter
PII: S0022-1139(01)00473-0

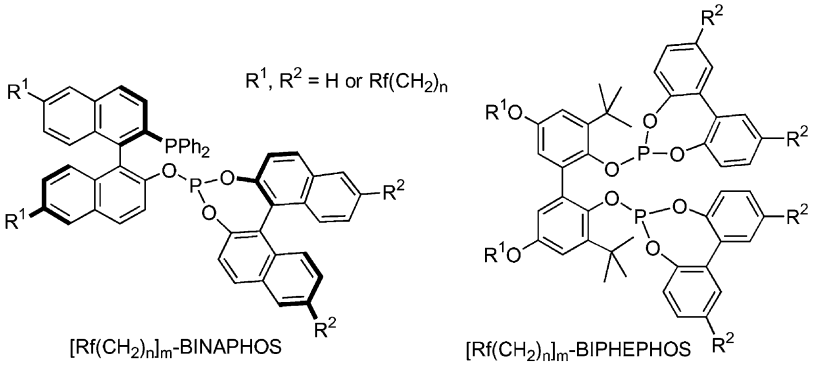


Fig. 1. New fluorous ligands.

[*n*-$C_4F_9(CH_2)_3$]$_2$-BINAPHOS(*R*,*S*-**2a**),(*S*,*R*)-[*n*-$C_6F_{13}(CH_2)_3$]$_2$-BINAPHOS (*S*,*R*-**2b**), (*R*,*S*)-[*n*-$C_8F_{17}(CH_2)_3$]$_2$-BINAPHOS (*R*,*S*-**2c**). Preliminary results on the use of **2a–c** for the asymmetric hydroformylation of styrene are also discussed.

2. Results and discussion

2.1. Towards the syntheses of [n-$C_4F_9(CH_2)_3$]$_4$-BIPHEPHOS and [n-$C_4F_9(CH_2)_3O$]$_2$-BIPHEPHOS

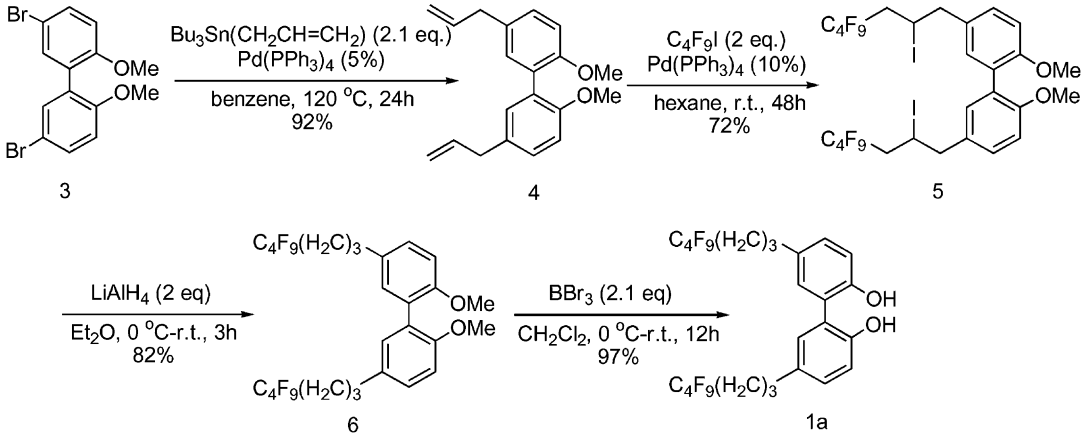
5,5′-Diallyl-2,2′-dimethoxybiphenyl (**4**) was prepared through the Stille coupling of 5,5′-dibromo-2,2′-dimethoxybiphenyl (**3**) [17] with allyltributyltin catalyzed by $Pd(PPh_3)_4$ [8], which was then submitted to a Pd-catalyzed coupling [18] with perfluorobutyl iodide to afford diodide **5**. The subsequent reduction of **5** with $LiAlH_4$ and deprotection with BBr_3 afforded 5,5′-[*n*-$C_4F_9(CH_2)_3$]$_2$-2,2′-biphenol (**1a**) in 52% overall yield in four steps from **3** (Scheme 1).

The attempted synthesis of 5,5′-diallyloxy-3,3′-di-*tert*-butyl-2,2′-biphenol (**9**) by direct allylation of 2,2′,5,5′-tetrahydroxy-3,3′-di-*tert*-butyl-2,2′-biphenyl was found to be troublesome. Thus, **9** was synthesized by oxidative coupling of **8**, which had been prepared by the allylation of *tert*-butylhydroquinone (**7**). After protection of **9** as diacetate, diallyldiacetoxybiphenyl **10** was subjected to Pd-catalyzed addition of perfluorobutyl iodide to give the corresponding diodide **11**, which was reduced by Bu_3SnH and deacetylated to afford 5,5′-[*n*-$C_4F_9(CH_2)_3O$]$_2$-3,3′-di-*tert*-butyl-2,2′-biphenol (**1b**) in 10% overall yield for five steps from **7** (Scheme 2).

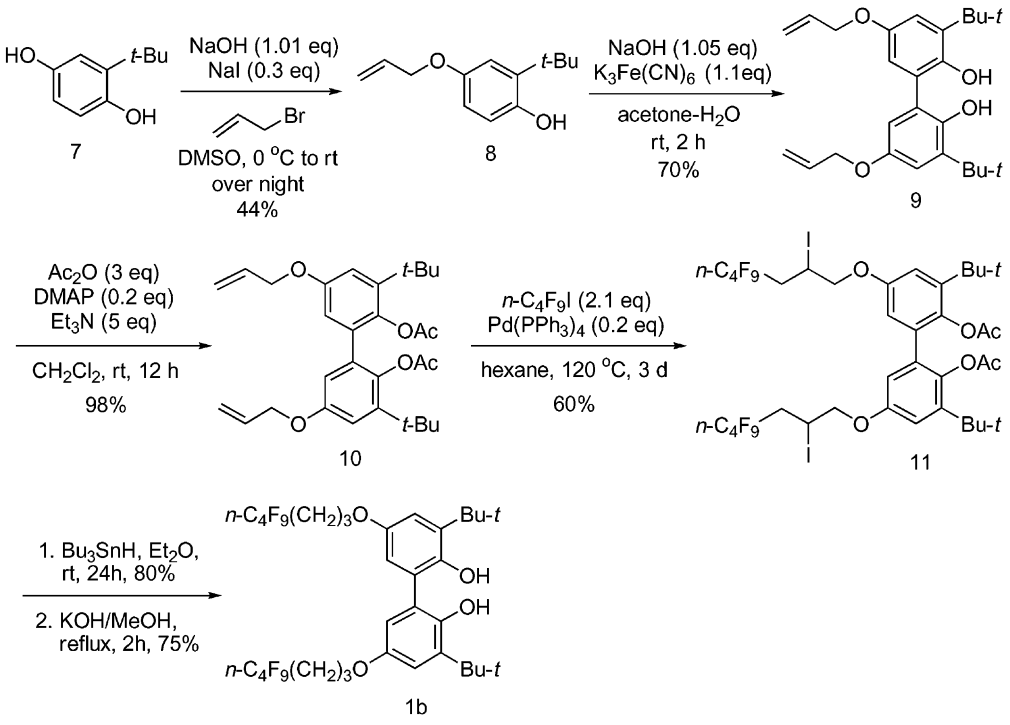
[*n*-$C_4F_9(CH_2)_3$]$_2$-Biphenol (**1a**), thus obtained, was converted to biphenyl-2,2′-dioxyphosphorous chloride **12**, which was coupled with 3,3′-di-*tert*-butyl-5,5′-dimethoxy-2,2′-biphenol (**13**) (**12/13** = 2/1), following the literature procedure for the synthesis of BIPHEPHOS [14]. In the same manner, [*n*-$C_4F_9(CH_2)_3O$]$_2$-biphenol **1b** was coupled with biphenyl-2,2′-dioxyphosphorous chloride (**14**) (**1b/14** = 1/10). Both attempted coupling reactions led to the formation of a mixture of phosphites that are most likely formed through skeletal rearrangements on the basis of ^{31}P NMR analyses. Because of their instability during column chromatography on silica gel, the elucidation of the structures of these products requires further elaboration (Scheme 3).

2.2. Syntheses of (R,S)- and (S,R)-[Rf(CH$_2$)$_3$]$_2$-BINAPHOS ligands

Only a few fluorous chiral ligands have been reported to date [7,19–21]. Recently Nakamura et al. reported the first



Scheme 1.

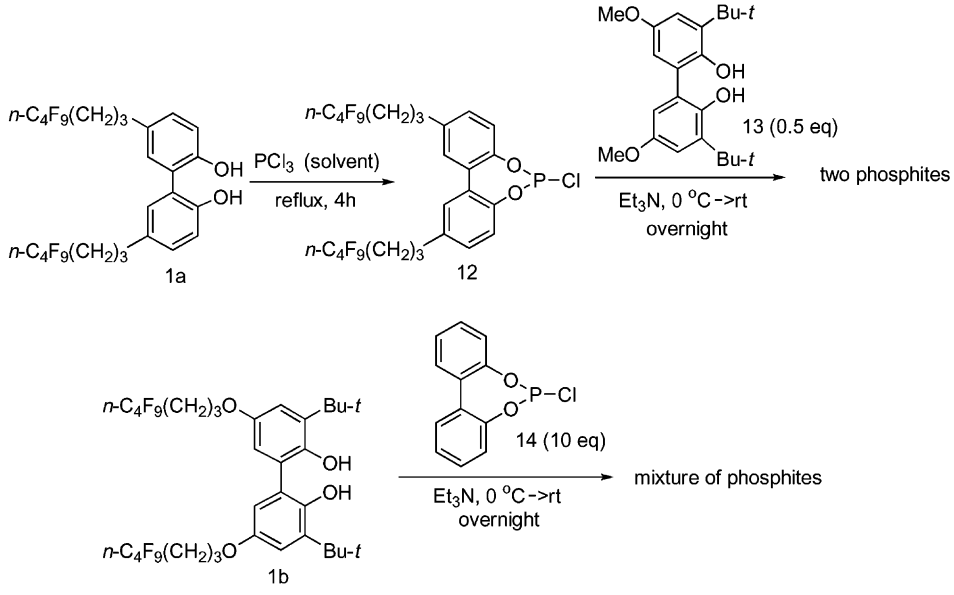


Scheme 2.

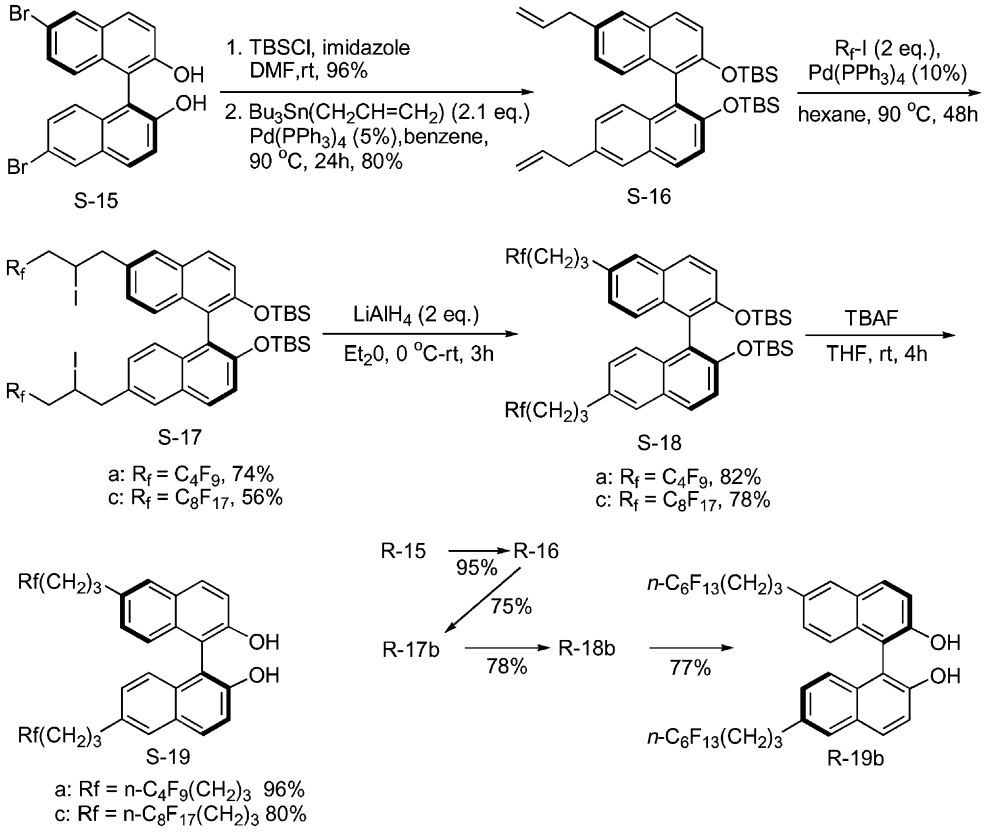
enantiopure fluorous BINOL, (*R*)-[(*n*-$C_6F_{13}(CH_2)_3)_3Si]_2$-BINOL, in which two units of three perfluoroalkyl tails per silicon atom are tethered to binaphthol [19,20]. In our design, two 3-(perfluoroalkyl)propyl tails are directly attached to binaphthol.

Our syntheses of enantiopure fluorous BINOLs use (*S*)- and (*R*)-6,6′-diallyl-2,2′-di(*tert*-butyldimethylsiloxy)binaphthyl, *S*-**16** and *R*-**16**, as the common key intermediate. (*S*)- and (*R*)-diallyldi-TBSO-BINOLs **16** were synthesized through the Stille coupling of (*S*)- and (*R*)-6,6′-dibromo-2,2′-di-TBSO-binaphthyls (TBS-15), which were prepared by the TBS protection of (*S*)- and (*R*)-6,6′-dibromo-2,2′-binaphthols (**15**). (*S*)- and (*R*)-Dibromobinaphthols **15** were obtained through the optical resolution of racemic **15**, which was prepared by oxidative coupling of 2-bromonaphthol [22], using *N*-benzylcinchonidium chloride [23] as the resolving agent.

Palladium-catalyzed addition of perfluorobutyl iodide to *S*-**16**, followed by reduction of the resulting diodide *S*-**17a**



Scheme 3.



Scheme 4.

and subsequent deprotection with tetrabutylammonium fluoride (TBAF) gave (*S*)-6,6′-[*n*-$C_4F_9(CH_2)_3]_2$-BINOL (*S*-**19a**) in 45% overall yield for five steps from *S*-**15** (Scheme 4). In the same manner, (*R*)-6,6′-[*n*-C_6F_{13}-$(CH_2)_3]_2$-BINOL (*R*-**19b**) and (*S*)-6,6′-[*n*-$C_8F_{17}(CH_2)_3]_2$-BINOL (*S*-**19c**) were synthesized in 37 and 27% overall yield for five steps from *R*-**15** and *S*-**15**, respectively (Scheme 4).

(*S*)-6,6′-[*n*-$C_4F_9(CH_2)_3]_2$-BINOL (*S*-**19a**) was converted to (*S*)-6,6′-[*n*-$C_4F_9(CH_2)_3]_2$-binaphthyl-2,2-dioxyphosphorous chloride (*S*-**20a**), which was then coupled with (*R*)-2-hydroxy-2′-diphenylphosphinobinaphthol [24][1] (*R*-**21**) (0.5 eq.), following the literature procedure for the synthesis of BINAPHOS [16], in the presence of triethylamine in ether to afford (*R*,*S*)-[*n*-$C_4F_9(CH_2)_3]_2$-BINAPHOS (*R*,*S*-**2a**) as white solid in 60% yield for two steps (Scheme 5). In the same manner, (*S*,*R*)-[*n*-$C_6F_{13}(CH_2)_3]_2$-BINAPHOS (*S*,*R*-**2b**) and (*R*,*S*)-[*n*-$C_8F_{17}(CH_2)_3]_2$-BINAPHOS (*R*,*S*-**2c**) were obtained in 71 and 67% yields for two steps from (*R*)-6,6′-[*n*-$C_6F_{13}(CH_2)_3]_2$-BINOLand(*S*)-6,6′-[*n*-$C_8F_{17}(CH_2)_3]_2$-BINOL, respectively (Scheme 5).

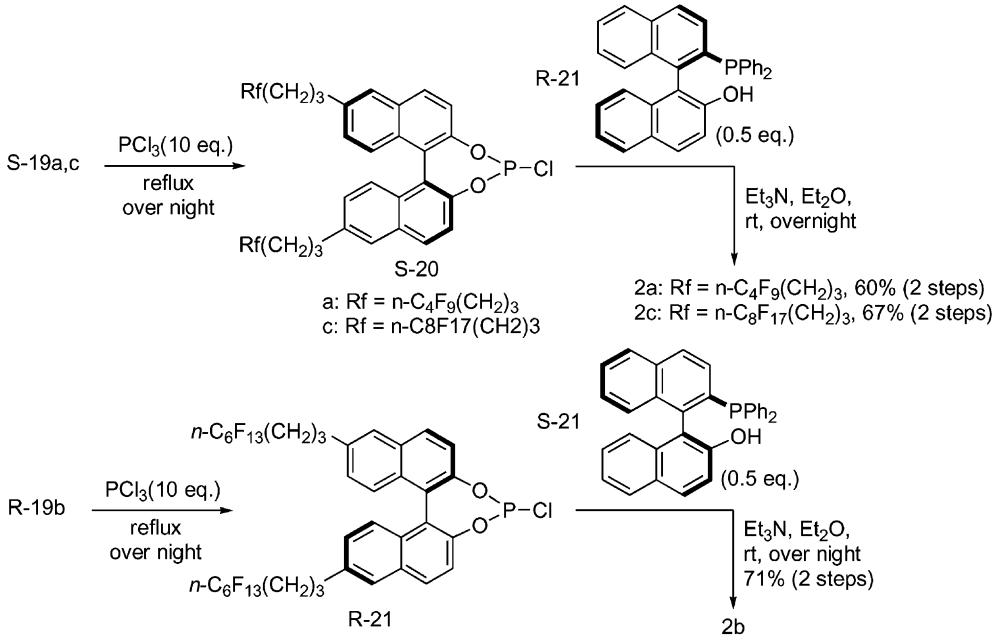
The $^{31}P\{^1H\}$ NMR spectra of fluorous chlorophosphines **19a–c** as well as **2a–c** are very similar to those of the parent non-fluorinated compounds [7,16], which suggests that the introduction of 3-(perfluoroalkyl)propyl tails does not affect the electronic properties of the phosphorus moieties (Table 1).

2.3. Asymmetric hydroformylation of styene catalyzed by Rh-catalysts with fluorous BINAPHOSs

(*R*,*S*)- and (*S*,*R*)-[$Rf(CH_2)_3]_2$-BINAPHOS ligands thus synthesized were examined their efficiency in the asymmetric hydroformylation of styrene. First, the reactions were carried out in benzene that has been the standard solvent for the reactions catalyzed by Rh-BINAPHOS [16]. As Table 2 shows, fluorous BINAPHOS ligands when used with Rh(acac)$(CO)_2$ exhibit catalytic activity, regioselectivity, and enantioselectivity comparable to those achieved by BINAPHOS (b/l: 88/12, 94% e.e.) [16] and (*R*,*S*)-3-*n*-$C_6F_{13}(CH_2)_2$-BINAPHOS (b/l: 92.7/7.3, 90.6% e.e.) [7] in the formation of 2-phenylpropanal.

[$Rf(CH_2)_3]_2$-BINAPHOS ligands showed good solubility in $scCO_2$. The reaction of styrene catalyzed by Rh(acac)$(CO)_2$/*S*,*R*-**2b** was carried out in $scCO_2$ at 60°C and 100 atm total pressure ($CO/H_2 = 1$, 20 atm) for 24 h [catalyst concentration $= 3.9 \times 10^{-5}$ M; styrene concentration $= 3.7 \times 10^{-2}$ M; styrene/Rh = 969] to give (*S*)-1-phenylpropanal with 89/11–90/10 regioselectivity and 70–74% e.e. The observed reduced enantioselectivity appears to be due to

[1] The enantiopurities of *R*-**21** (92% e.e.) and *S*-**21**, (98.8% e.e.) were checked by chiral HPLC using a Chiracel OD column and hexane/2-propanol (95/5) as the eluant.



Scheme 5.

Table 1
^{31}P MNR data of **20a–c** and **2a–c** (in $CDCl_3$)

Chlorophosphine	^{31}P (δ, ppm)	Ligand	^{31}P (δ, ppm)
S-**20a**	179	*R*,*S*-**2a**	−12,5 (d), 146.9 (d) (J_{P-P} = 30.6 Hz)
R-**20b**	179	*S*,*R*-**2b**	−12.4 (d), 146 (d) (J_{P-P} = 30.4 Hz)
S-**20c**	180	*R*,*S*-**2c**	−12.4 (d), 147.1 (d) (J_{P-P} = 30.4 Hz)
(1,1′-binaphtalene-2,2′-dioxy)chlorophosphine [16]	174	BINAPHOS	−13.3 (d), 146.2 (d) (J_{P-P} = 29 Hz) [16]

racemization during the reaction. A detailed investigation into this phenomenon is underway and will be reported elsewhere.

Although $[Rf(CH_2)_3]_2$-BINAPHOS ligands include reasonable number of fluorines, it was found that these fluorous ligands were preferentially soluble in toluene over perfluoromethylcyclohexane (PFMC). This may be ascribed to strong aromatic/aromatic interactions between the two naphthalene moieties and toluene as well as moderate fluorine content [25]. All $[Rf(CH_2)_3]_2$-BINAPHOS ligands were found to dissolve in perfluorotoluene (PFT) very well. We investigated the asymmetric hydroformylation of styrene catalyzed by $Rh(acac)(CO)_2$/*S*,*R*-**2b** in PFMC/toluene binary solvent system, PFMC, and PFT. Results are summarized in Table 3.

Table 2
Asymmetric hydroformylation of styrene in benzene[a]

Ligand	Time (h)	Conversion[b] (%)	Selectivity[c] (%)	(b/l)[d]	e.e. (%)[e]
R,*S*-**2a**[f]	12	86	100	90/10	90 (*R*)
R,*S*-**2a**[f]	38	100	100	88/12	88 (*R*)
S,*R*-**2b**	12	84	100	90/10	94.8 (*S*)
S,*R*-**2b**	38	100	100	90/10	93 (*S*)

[a] All reactions were run with styrene (390 mg, 3.75 mmol), $Rh(acac)(CO)_2$ (0.5 mg, 1.94×10^{-3} mmol), ligand **2** (7.76×10^{-3} mmol) in benzene (0.2 ml) at 60°C and 40 atm of CO and H_2 (1:1); styrene/Rh = 2235, styrene concentration = 20−23 M, Rh concentration = $(1.02-1.24) \times 10^{-2}$ M.

[b] Determinated by GC analysis on a DB-1701 capillary column and by ^{1}H NMR using the vinylic protons of styrene and the aldehyde protons of 2-phenylpropanal and 3-phenylpropanal as the internal standard.

[c] Product (aldehyde) selectivity determinated by GC analysis using a DB-1701 capillary column.

[d] Branched/linear aldehyde ratio determinated by ^{1}H NMR analysis.

[e] Determinated by chiral GC analysis of the corresponding 2-phenylpropanoic acid using a Supelco Dex-225 column. Absolute configuration of the aldehyde is shown in parentheses.

[f] Enantiomeric purity of **2a** is 92% e.e.

Table 3
Asymmetric hydroformylation of styrene catalyzed by (*S*,*R*-**2b**)-Rh complex in fluorous solvents[a]

Entry	Solvent	S/Rh[b]	[S][c] M	[Rh][d] M	Time (h)	Conv.[e] (%)	Select.[f]	b/l[g]	e.e. (%)[h]
1	PFMC/toluene	2235	9.4	4.2×10^{-3}	24	84	100	91/9	90
2	PFMC/toluene	1042	4.3	4.2×10^{-3}	18	100	100	92/8	85
3	PFMC	1042	8.7	8.3×10^{-3}	18	88	100	94/6	87
4	PFT	2235	23	1.0×10^{-2}	2	11	100	91/9	94
5	PFT	2235	23	1.0×10^{-2}	16	73	100	91/9	82

[a] Reactions were run with styrene (1.75–3.75 mmol), $Rh(acac)(CO)_2$ (1.67×10^{-3} mmol), *S*,*R*-**2b** (6.71×10^{-3} mmol) in a fluorous solvent (0.16–0.2 ml) with or without toluene (0.2 ml) at 50–60°C and 40 atm of CO and H_2 (1:1).
[b] Styrene/Rh ratio.
[c] Concentration of styrene.
[d] Concentration of $Rh(acac)(CO)_2$.
[e] Determinated by GC analysis on a DB-1701 capillary column and by ^{1}H NMR using the vinylic protons of styrene and the aldehyde protons of 2-phenylpropanal and 3-phenylpropanal as the internal standard.
[f] Determinated by GC analysis on a DB-1701 capillary column.
[g] Determinated by ^{1}H NMR analysis.
[h] Determinated by chiral GC analysis of the corresponding (*S*)-2-phenylpropanoic acid with a Supelco Dex-225 column.

As Table 3 shows, the regioselectivity of the reaction is improved as compared to the reactions in benzene. Enantioselectivity in PFMC and PFMC/toluene binary system is in the same range, but slightly lower than that observed in benzene. In PFT, the reaction gave high enantioselectivity (94% e.e.) at low conversion (entry 4). However, apparent racemization was observed as the reaction proceeds, while maintaining high branched/linear ratio. Investigation into this phenomenon in this particular solvent is underway and will be reported elsewhere.

In conclusion, novel fluorous biphenols and enantiopure BINOLs have been synthesized, which serve as key intermediates for the syntheses of a variety of new fluorous ligands for regioselective and enantioselective catalytic reactions. Syntheses of fluorous BIPHEPHOS ligands were attempted using these fluorous biphenols, but further investigation is necessary to complete the syntheses. Novel fluorous $[Rf(CH_2)_3]_2$-BINAPHOS ligands (Rf = *n*-C_4F_9, *n*-C_6F_{13}, and *n*-C_8F_{17}) were successfully synthesized. These new fluorous chiral ligands when used with a rhodium catalyst have achieved comparable or even higher regioselectivity and enantioselectivity as compared to those by the Rh-BINAPHOS system. Further investigation along this line is actively underway in these laboratories.

3. Experimental

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 or Varian Gemini 2300 using $CDCl_3$ as the internal standard. The ^{31}P NMR and ^{19}F NMR were recorded on a Brucker AC-250 with phosphoric acid and hexafluorobenzene, respectively, as external references. Mass spectra (MS) and high resolution mass spectra (HRMS) were recorded by the Mass Spectrometry Facility, University of Illinois at Urbana-Champaign. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. Chiral GC analyses were carried out on a Hewlett-Packard 5890 Series II chromatograph (FID) with a Hewlett-Packard HP 3396A Chemstation using a Supelco Dex-225 column. Chiral HPLC analyses were on a Waters HPLC 600E assembly including a Workstation with the Millenium 32 chromatography manager program using a Daicel-Chiracel OD column employing hexane/2-propanol (95/5, v/v) as the solvent system. Acetylacetonatorhodium was obtained from the Mitsubishi Chemical Corporation and use as received.

Characterization data for new fluorous biphenols, binaphthols, and phosphine–phosphites are shown below.

3.1. 5,5′-Di(perfluorobutylpropyl)-2,2′-biphenol (*1a*)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.1 (8H, m), 2.69 (4H, t, $J = 7.5$ Hz), 5.39 (2H, s), 6.96 (2H, d, $J = 7.8$ Hz), 7.12 (4H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 30.2 (t, $J = 89.6$ Hz), 34.1, 116.9, 124.4, 129.6, 131.1, 133.9, 151.0; ^{19}F NMR (235.4 MHz, $CDCl_3$): δ −126.7 (4F, t, $J = 11.3$ Hz), 125.1 (4F, s), −115.0 (4F, t, $J = 14.6$ Hz), −81.7 (6F, t, $J = 8.6$ Hz).

3.2. 5,5′-Di(perfluorobutylpropyl)-3,3′-di-tert-butyl-2,2′-biphenol (*1b*)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (8H, m), 3.99 (4H, t, $J = 6$ Hz), 5.01 (2H, s), 6,61 (2H, d, $J = 3$ Hz), 7.12 (2H, d, $J = 3$ Hz).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ 20.7, 27.9 (t, $J = 22$ Hz), 29.4, 35.2, 66.9, 112.6, 115.8, 123.1, 139.1, 146.2, 152.2.

^{19}F NMR (235.4 MHz, $CDCl_3$): δ −81.7 (6F, t, $J = 8.7$ Hz), −115.2 (4F, s), −125.1 (4F, s), −126.7 (4F, s).

HRMS (EI) calcd for $C_{34}H_{36}F_{18}O_4$ (M^+) 850.2326, found 850.2327 ($\Delta = -0.1$ ppm).

3.3. (S)-6,6′-di(perfluorobuthylpropyl)-2,2′-binaphthol (S-**19a**)

^{1}H NMR (250 MHz, $CDCl_3$): δ 1.99–2.21 (8H, m), 2.83 (4H, t, $J = 7.3$ Hz), 5.02 (2H, s), 7.13 (4H, m), 7.37 (2H, d, $J = 8.9$ Hz), 7.67 (2H, s), 7.92 (2H, d, $J = 8.9$ Hz).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ 21.7, 30.28 (t, $J = 22$ Hz), 34.8, 110.8, 118, 124,6, 127,2, 128.5, 129.6, 130.9, 132, 136.3, 152.4.

^{19}F NMR (235.4 MHz, $CDCl_3$): δ −126.7 (4F, t, $J = 11.8$ Hz), −125 (4F, bs), −114.9 (4F, bs) −81.7 (6F, t, $J = 8.7$ Hz).

HRMS (EI) calcd for $C_{34}H_{24}F_{18}O_2$ (M^+) 806.1489, found 806.1489, ($\Delta = 0$ ppm).

3.4. (R)-6,6′-di(perfluorohexylpropyl)-2,2′-binaphthol (R-**19b**)

^{1}H NMR (250 MHz, $CDCl_3$): δ 1.99–2.22 (8H, m), 2.85 (4H, t, $J = 6.9$ Hz), 5.1 (2H, s), 7.14 (4H, m), 7.32 (2H, d, $J = 8.9$ Hz), 7.69 (2H, s), 7.87 (2H, d, $J = 8.9$ Hz).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ 21.8, 30.4 (t, $J = 22$ Hz), 34.8, 111, 117.9, 124.6, 127.1, 128.4, 129.6, 130.8, 132.2, 136.3, 152.4.

^{19}F NMR (235.4 MHz, $CDCl_3$): δ −126 (4F, m), −124 (4F, b), −123 (4F, b), −122 (4F, b), −114 (4F, b) −81.4 (6F, t, $J = 9.3$ Hz).

HRMS (EI) calcd for $C_{38}H_{24}F_{26}O_2$ (M^+) 1006.1365, found 1006.1361, ($\Delta = -0.4$ ppm).

3.5. (S)-6,6′-di(perfluorooctylpropyl)-2,2′-binaphthol (S-**19c**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95–2.21 (8H, m), 2.83 (4H, t, $J = 7.5$ Hz), 4.98 (2H, s), 7.09–7.17 (4H, m), 7.38 (2H, d, $J = 9$ Hz), 7.68 (2H, s), 7.93 (2H, d, $J = 9$ Hz).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ 21.8, 30.8 (t, $J = 22.4$ Hz), 34.8, 110.9, 117.9, 124.6, 127.1, 128.5, 129.6, 130.8, 132.1, 136.4, 152.4.

^{19}F NMR (235.4 MHz, $CDCl_3$): δ −95.6 (4F, b), −92.9 (4F, b), −92.2 (4F, b), −91.4 (12F, b), −83.6 (4F, b), −50.3 (6F, t, $J = 10.4$ Hz).

HRMS (EI) calcd for $C_{42}H_{24}F_{34}O_2$ (M^+) 1206.1233, found 1206.1233, ($\Delta = 0.0$ ppm).

3.6. (R,S)-[n-$C_4F_9(CH_2)_3$]$_2$-BINAPHOS (R,S-**2a**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02–2.19 (8H, m), 2.83 (4H, m), 6 (1H, d, $J = 8.5$ Hz), 5.96–8.06 (31H, m).

^{19}F NMR (235.4 MHz, $CDCl_3$): δ −126.7 (4F, t, $J = 11.8$ Hz), −125 (4F, bs), −114.9 (4F, bs) −81.7 (6F, t, $J = 8.7$ Hz).

^{31}P NMR (101.3 MHz, $CDCl_3$): δ −12.5 (d, $J = 30.6$ Hz), +146.9 (d, $J = 30.6$ Hz).

HRMS (FAB) calcd for $C_{66}H_{44}F_{18}O_3P_2$ $[M+H]^+$ 1289.2561, found 1289.2557 ($\Delta = -0.4$ ppm).

$[\alpha]_D^{22}$ + 97.8° (c 0.46, $CHCl_3$).

3.7. (S,R)-[n-$C_6F_{13}(CH_2)_3$]$_2$-BINAPHOS (S,R-**2b**)

^{1}H NMR (250 MHz, $CDCl_3$): δ 2.01–2.19 (8H, m), 2.83 (4H, m), 6 (1H, d, $J = 8.8$ Hz), 6.7–8 (31H, m).

^{19}F NMR (235.4 MHz, $CDCl_3$): δ −126 (4F, m), −124 (4F, b), −123 (4F, b), −122 (4F, b), −114 (4F, b) −81.4 (6F, t, $J = 9.3$ Hz).

^{31}P NMR (101.3 MHz, $CDCl_3$): δ −12.5 (d, $J = 30.4$ Hz), +146.9 (d, $J = 30.4$ Hz).

HRMS (FAB) calcd for $C_{70}H_{44}F_{26}O_3P_2$ $[M+H]^+$ 1489.2432, found 1489.2429 ($\Delta = -0.3$ ppm).

$[\alpha]_D^{21}$–55.3° (c 1.7, $CHCl_3$).

3.8. (R,S)-[n-$C_8F_{17}(CH_2)_3$]$_2$-BINAPHOS (R,S-**2c**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.26–1.90 (8H, m), 2.85 (4H, m), 8.07–6.70 (32H, m).

^{19}F NMR (235.4 MHz, $CDCl_3$) δ −126.7 (4F, b), −124.1 (4F, b), −123.4 (4F, b), −122.6 (12F, b), −114.7 (4F, b), −81.4 (6F, t, 9.4 Hz).

^{31}P NMR (101.3 MHz, $CDCl_3$) δ −12.4 (d, $J = 30.4$ Hz), 147.1 (d, $J = 30.4$ Hz).

HRMS (FAB) calcd for $C_{74}H_{44}F_{34}O_3P_2$ $[M+H]^+$ 1689.2301, found 1689.2296, ($\Delta = 0.3$ ppm).

$[\alpha]_D^{23}$ + 110° (c 0.29, $CHCl_3$).

Acknowledgements

This work was supported by grants from the National Science Foundation and the National Institutes of Health (NIGMS). Generous support from the Mitsubishi Chemical Corporation is also gratefully acknowledged.

References

[1] I. Ojima, C.-Y. Tsai, M. Tzamarioudaki, D. Bonafoux, in: L.E. Overman (Ed.), Organic Reactions, Vol. 56, 2000, pp. 1–354.
[2] B. Breit, W. Seiche, Synthesis (2000) 1–36.
[3] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 99 (1999) 475–493.
[4] S. Kainz, W. Leitner, Catal. Lett. 55 (1998) 223–225.
[5] D. Koch, W. Leitner, J. Am. Chem. Soc. 120 (1998) 133398–133404.
[6] S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem. Int. Ed. Engl. 36 (1997) 1628–1630.
[7] G. Franciò, W. Leitner, Chem. Comun. (1999) 1663–1664.
[8] D.R. Palo, C. Erkey, Organometallics 19 (2000) 81–86.
[9] I.T. Horváth, J. Rábai, Science 266 (1994) 72–75.
[10] I.T. Horváth, Acc. Chem. Res. 31 (1998) 641–650.
[11] I.T. Horváth, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rábai, E.J. Mozeleski, J. Am. Chem. Soc. 120 (1998) 3133–3143.
[12] E. Billig, A.G. Abatjoglou, D. Bryant, US Patent 4 769 498 (1988).
[13] I. Ojima, M. Tzamarioudaku, M. Egushi, J. Org. Chem. 60 (1995) 7078–7079.
[14] G.D. Cuny, S.L. Buchwald, J. Am. Chem. Soc. 115 (1993) 2066–2068.
[15] N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033–7034.

[16] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, J. Am. Chem. Soc. 119 (1997) 4413–4423.
[17] M.R. Agharahimi, N.A. Lebel, J. Org. Chem. 60 (1995) 1856–1863.
[18] T. Ishihara, M. Kuroboshi, Y. Okada, Chem. Lett. (1986) 1895–1896.
[19] Y. Nakamura, S. Takeuchi, Y. Ohgo, D.P. Curran, Tetrahedron 56 (2000) 351–356.
[20] Y. Nakamura, S. Takeuchi, Y. Ohgo, D.P. Curran, Tetrahedron Lett. 41 (2000) 57–60.
[21] A. Klose, J.A. Gladysz, Tetrahedron: Asymm. 10 (1999) 2667–2674.
[22] K. Ding, Y. Wang, L. Zhang, Y. Wu, Tetrahedron 52 (1996) 1005–1009.
[23] D. Cai, D.L. Hughes, T.R. Verhoeven, P.J. Reider, Tetrahedron Lett. 44 (1995) 7991–7994.
[24] Y. Uozumi, A. Tanashi, S.-Y. Lee, T. Hayashi, J. Org. Chem. 58 (1993) 1945–1948.
[25] Q. Zhang, Z. Luo, D.P. Curran, J. Org. Chem. 65 (2000) 8866–8873.