Preparation of 6,6′-Bisperfluoroalkylated BINOLs and Their Application in Asymmetric Alkylation of Benzaldehyde

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6,6′-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-BINOL and 6,6′-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-BINOL were synthesized through Suzuki coupling reaction and used in fluorous biphase asymmetric alkylation of benzaldehyde. Good enantioselectivity was obtained and the catalysts could be recovered by liquid-liquid extraction.

Keywords R_f-BINOL, fluorous biphase, asymmetric addition, recovery

Introduction

Polymer-bound or polymerized asymmetric catalysts and perfluorinated ones have been the focus of many researchers for the recovery and reuse of expensive chiral catalysts in recent years, among which BINOL has been one of the most widely studied.[1-8] Usually, polymer-bound or polymerized chiral catalyst-metal complexes are somewhat different from their monomolecular counterparts due to their solubility and changed configuration, which often result in the lower of the accessibility for substrates and reactants.[1,2] Perfluorinated chiral catalysts are superior to polymer-bound or polymerized ones for their solubility and reactivity (shorter reaction time versus polymer-bound or polymerized ones) and can be easily used under regular conditions with little or no modification.[9] Heavy-fluorinated catalysts can be used in "Fluorous Biphase System", which renders easier separation of products and recovery of catalysts.[10-13] Even light-fluorinated catalysts can be recovered by continuous extraction.[12] However, the electron-withdrawing effect of fluorine can not be totally isolated even when $(CH_2)_m$ segments exist between the fluorous domain and the organic domain.[14-16] Thus, the transition state of ligand-metal complex changes as the electron density of the catalytic site changes.

Recently, several fluorinated BINOLs have been synthesized and used in asymmetric reactions.[6-8,16,18] The 5,5′,6,6′,7,7′,8,8′-octafluoro-1,1′-binaphthol (F_8BINOL) has a similar torsion angle to that of BINOL, but its acidity increases ten fold because of the strong influence of fluorine. BINOL and F_8BINOL catalyzed asymmetric sulfoxidations give opposite chiral products.[17] What is interesting is that, when (*S*)-BINOL, (*R*)-F_8BINOL and $Ti(O^iPr)_4$ were mixed, the "pseudo-*meso*" mixture gave excellent enantioselectivity for glyoxylate-ene reaction.[18] When the perfluoroalkyl chains are attached to BINOL directly (*i.e.* without $(CH_2)_m$ segments between the perfluorous chain and the backbone of BINOL), the strong electron-withdrawing effect can not be avoided and the asymmetric induction of the catalyst is not good.[8] When ethylene spacer is introduced between the per-fluoroalkyl chain and the BINOL scaffold through C—Si bond, good enantioselectivity was obtained.[7]

Herein, we report the synthesis of 6,6′-bisperfluoroalkylated BINOLs with ethylene spacers[19] through Suzuki-coupling reaction of perfluoroalkyl iodide with BINOL derived diboronic acid and their use as fluorous catalysts in asymmetric alkylation of benzaldehyde in fluorous biphase system.

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Received February 4, 2002; revised April 25, 2002; accepted June 11, 2002.
Project supported by the National Natural Science Foundation of China (No. D20032010), QT Program and the Major State Basic Research Development Program (the Ministry of Sciences and Technology, No. G2000048007).

Results and discussion

Syntheses of bisperfluoroalkylated BINOLs

In our previous paper, the Suzuki-coupling reaction of perfluoroalkyl iodide with substituted aryl boronic acids, which gave the mono perfluoroalkylated products in good yield was described.[20] This intrigued us to use it for synthesis of bis or poly perfluoroalkylated chiral catalysts applied in fluorous biphase system (Scheme 1).

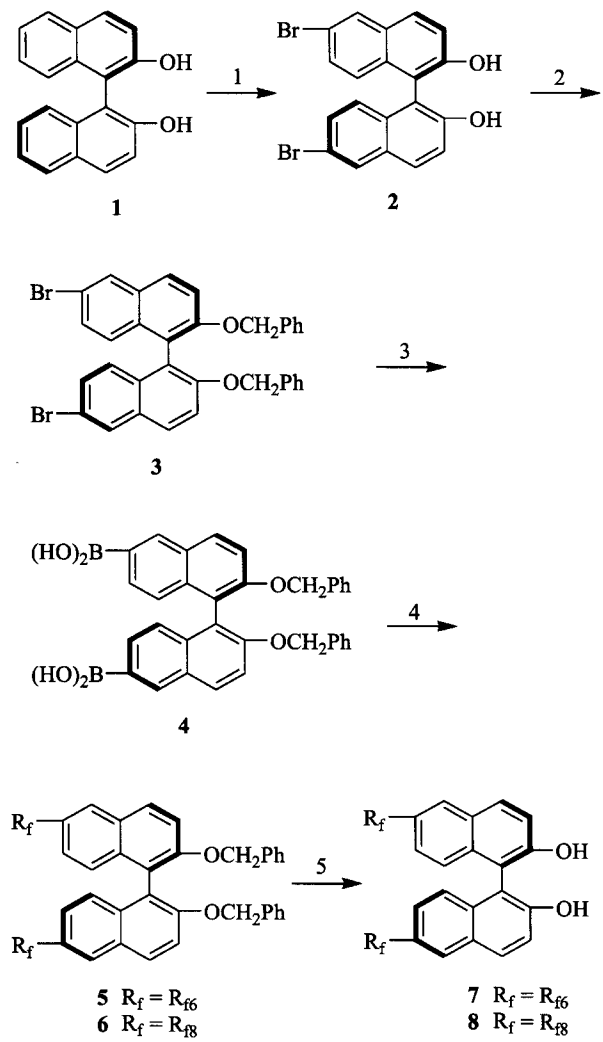
Enantio-pure (*R*)-BINOL (**1**) was brominated as described in the literature.[21a,21b] 6,6′-Dibromo-1,1′-binaphthol (**2**) was formed and the hydroxyl groups of **2** were protected through the reaction of **2** with benzyl chloride as described in the literature.[22] 2,2′-Bis(benzyloxy)-6,6′-dibromo-1,1′-binaphthyl (**3**) was converted into 2,2′-bis(benzyloxy)-6,6′-diboronic acid-1,1′-binaphthyl (**4**) by standard method.[22-24] Without purification, **4** was coupled with 1*H*,1*H*,2*H*,2*H*-perfluorooctane iodide (or 1*H*,1*H*,2*H*,2*H*-perfluorodecane iodide) in DME (ethylene glycol dimethyl ether) and aqueous $NaHCO_3$ solution under argon atmosphere using $Pd(PPh_3)_4$ as the catalyst. The desired cross-coupling products, 2,2′-bis(benzyloxy)-6,6′-bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,1′-binaphthyl (**5**) and 2,2′-bis(benzyloxy)-6,6′-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-1,1′-binaphthyl (**6**), were easily purified by column chromatography and hydrogenated under 1.013×10^5 Pa to give the expected perfluoroalkylated BINOLs (**7**) and (**8**) in good overall yield.

Alkylation of benzaldehyde

The reaction of diethyl zinc with benzaldehyde has become a classical test for screening of new ligands used in enantioselective synthesis. We used this reaction in homogenous and biphase systems to test our fluorous BINOLs.

The R_f-BINOL was dissolved in the mixed solvents as listed in Table 1. As pointed out previously,[25-27] hexane and the fluorous solvents were homogenous at room temperature even when a little proportion of toluene was added to dissolve the catalyst. When $Ti(O^iPr)_4$ was added, the mixture turned orange and an organic layer separated out, which was a little darker than the fluorous phase. Et_2Zn (15 wt%, in hexane) was added and the mixture was cooled to 0 ℃ after 0.5 h. Benzaldehyde

Scheme 1 Preparations of R_f-BINOLs

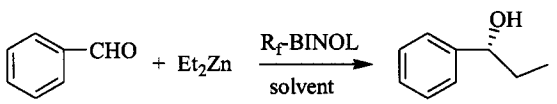


Conditions: (1) Br_2, CH_2Cl_2, −78 ℃—r.t.; (2) $PhCH_2Cl$, DMF, 80 ℃, 8 h; (3) *t*-BuLi (4 equiv.), −78 ℃, 0.5 h, $(MeO)_3B$ (6 equiv.), −78 ℃—r.t. 8 h, H_3^+O; (4) $R_{f6}I$ or $R_{f8}I$ ($R_{f6} = C_6F_{13}CH_2CH_2$, $R_{f8} = C_8F_{17}CH_2CH_2$, $Pd(PPh_3)_4$, $NaHCO_3$, DME, reflux; (5) H_2, Pd/C (10 wt%).

was added and the mixture was kept at 0 ℃ under vigorous stirring until the end of the reaction which was monitored by TLC. The organic phase was removed by syringe and quenched by 1 mol/L hydrochloric acid. To recover the catalyst, perfluorodecalin was added into the organic-water system. After the three-phase extraction, the organic phase was washed with saturated $NaHCO_3$ solution and brine, then dried over anhydrous sodium sulfate, evaporated under vacuum and purified by column chromatography. The enantioselectivity of the desired chiral alcohol,

1-phenylpropan-1-ol (**9**) was a little less than that of Nakai and coworkers (Scheme 2).[28] Catalyst recovered from the organic phase was 9% for R_{f6}-BINOL (**7**) and 7% for R_{f8}-BINOL (**8**) respectively. 88% of **7** and 89% of **8** were recovered from the two phases.

Scheme 2 Asymmetric alkylation of benzaldehyde by R_f-BINOL



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As summarized in Table 1, when FC-72 was used as the fluorous solvent, the enantioselectivity of the product was as good as that obtained when perfluorodecalin was used as the fluorous phase (Entries 1 and 3). But when $CF_3C_6F_5$ was used as the fluorous phase, extremely bad enantioselectivity was obtained (Entry 2). Although repetitions were carried out, no better results were obtained. So we decided to use the cheaper perfluorodecalin as the fluorous phase. Organic solvent effect was tested next step. When toluene and hexane were used as the combined organic phase, enantioselectivity of the product was a little less than that of CH_2Cl_2-hexane (Entry 6), but the proportion of hexane and toluene had no significant effect on enantioselectivity of the product (Entries 3—5). Because our catalysts can be easily dissolved in ordinary organic solvents, such as toluene, dichloromethane, ethyl acetate, THF, chloroform, *etc.*, we selected hexane as the organic solvent with as little toluene as possible for better recovery of the catalysts. Reactions in homogenous systems, benzotrifluoride (BTF, $CF_3C_6H_5$)-hexane and toluene-hexane, were as good as those in fluorous biphase systems, but were slower than the biphase systems (Entries 7 and 8). The selectivity of **8** was a little better than that of **7** possibly due to better solubility in fluorous phase (Entry 9). When the recovered catalysts were reused, no obvious changes were observed (Entries 10 and 11).

In conclusion, 6,6′-bisperfluoroalkylated-BINOL was synthesized by fluorous Suzuki cross-coupling reaction in overall good yield. The enantioselectivities of the ligands used in alkylation of benzaldehyde ware good. From a point of view of reactivity and selectivity, **7** and **8** are not superior to BINOL, but they are attractive for catalyst recycling by continuous extraction. Other types of asymmetric reaction are ongoing.

Experimental

General

All experiments sensitive to moisture or air were carried out under argon atmosphere using Schlenk techniques. Commercial regents were used as received without further purification. Benzaldehyde was distilled before use. Solvents were freshly distilled by standard method. Racemic BINOL was prepared and resolved as the reported procedure.[29-32] The benzyl protected dibromo derivative was made according to the method reported in the litera-

Table 1 Asymmetric alkylation of benzaldehyde catalyzed by R_f-BINOL

Entry	Catalyst (10 mol%)	Solvent [a] (mL)	Time (h)	Yield (%)	*ee*% (*R*) [b]
1	**7**	Hexane: toluene: FC-72 (1:1:5)	3	94	76
2	**7**	Hexane: toluene: $CF_3C_6F_5$ (1:1:5)	3.5	90	42
3	**7**	Hexane: toluene: $C_{10}F_{18}$ (1:1:5)	3	93	77
4	**7**	Hexane: toluene: $C_{10}F_{18}$ (2:0.4:5)	3	> 98	76
5	**7**	Hexane: toluene: $C_{10}F_{18}$ (1:0.2:5)	4	95	75
6	**6**	CH_2Cl_2: $C_{10}F_{18}$ (2:5)	4	> 98	79
7	**7**	Hexane: $C_6H_5CF_3$ (2)	6	95	76
8	**7**	Toluene (5)	7	94	76
9	**8**	Hexane: $C_{10}F_{18}$ (2:5)	1.5	88	80
10	**7**[c]	Hexane: toluene: $C_{10}F_{18}$ (2:0.4:5)	3	93	74
11	**8**[c]	Hexane: toluene: $C_{10}F_{18}$ (2:0.4:5)	2	96	75

[a] $C_{10}F_{18}$ is perfluorodecalin. [b] Chiralcel OD column, V_{hexane}: $V_{2\text{-propanol}}$ = 97.5:2.5, flow rate = 1.0 mL/min, configuration was determined by optical rotation compared with that in Ref. 28. [c] Recovered catalyst.

ture.[21a,21b] ^1H, ^{13}C and ^{19}F NMR spectra were obtained on a Bruker, AMX-300 spectrometer (TMS as ^1H internal reference, signal of $CDCl_3$ as ^{13}C internal standard and $CFCl_3$ as ^{19}F external reference). IR spectra were recorded with a Bio-Rad FTS-185 spectrometer as KBr discs. Mass spectra (EI) were taken on an HP5989-A spectrometer.

Preparation of 2,2′-*bis*(*benzyloxy*)-6,6′-*diboronic acid*-1,1′-*binaphthyl* (**4**)

2,2′-Bis(benzyloxy)-6,6′-dibromo-1,1′-binaphthyl (2.496 g, 4 mmol) was dissolved in dry THF (70 mL). The solution was cooled to − 78 ℃ under argon atmosphere and *t*-BuLi (13 mL, 1.5 mol/L, 16 mmol) was added dropwise. The solution turned dark brown and was stirred at − 78 ℃ for 0.5 h. Trimethyl borate (2.7 mL, 24 mmol) was added at − 78 ℃ and stirred for 8 h while the temperature was allowed to warm to room temperature. The reaction was quenched by HCl (1 mol/L, 40 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic solution was neutralized by saturated $NaHCO_3$ and washed with water, then evaporated to about 5 mL of solvents left. Dithyl ether (40 mL) was added and the solid was filtrated. Then the solution was washed with water (3 × 20 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated under vacuum. The white solid obtained was used for coupling without further purification. A little portion of crude **4** was purified by column purification and 74.8% of **4** was obtained.

4 White powder, m.p. 254—255 ℃, $[\alpha]_D^{20}$ + 33.3 (*c* 0.78, CH_3OH); ^1H NMR (Acetone-d_6) δ: 8.53 (s, 2H, H-5 and H-5′), 8.07 (d, J = 9.1 Hz, 2H, H-4 and H-4′), 7.72 (d, J = 8.6 Hz, 2H, H-3 and H-3′), 7.56 (dd, J = 9.1, 1.9 Hz, 4H), 7.04—7.18 (m, 12H), 5.19 (s, 4H, OCH_2); IR (KBr) ν: 3450, 1620, 1475, 1373, 1315, 1245, 1222, 1026, 830, 802, 730, 696 cm^{-1}.

Preparation of 2,2′-*dibenzyloxy*-6,6′-*bis*(*perfluoroalkyl*)-1,1′-*binaphthyl* (**5**) *and* (**6**)

Typical proceduce 2,2′-Bis(benzyloxy)-6,6′-diboronic acid-1,1′-binaphthyl (**4**) (554 mg, 1 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctane iodide (1.043 g, 2.2 mmol) were dissolved in DME (7 mL) under argon atmosphere. $Pd(PPh_3)_4$ (58 mg, 5 mol%) and 1 mol/L $NaHCO_3$ (5 mL) were added. The mixture was refluxed for 5 h and cooled to ambient temperature. Ethyl ether (10 mL) and water (5 mL) were added. The organic layer was separated out and the aqueous layer was extracted by ethyl ether (2 × 15 mL). The combined organic solution was washed with water and brine, then dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash chromatography eluted by hexane and dichloromethane. The coupling of **4** with 1*H*,1*H*,2*H*,2*H*-perfluorodecane iodide was as good as that of 1*H*,1*H*,2*H*,2*H*-perfluorooctane iodide. The yields were 61% and 57% respectively.

5 Colorless waxy solid, $[\alpha]_D^{20}$ + 23.0 (*c* 0.73, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 7.88 (d, J = 8.8 Hz, 2H, H-4 and H-4′), 7.69 (s, 2H, H-5 and H-5′), 7.41 (d, J = 9.1 Hz, 2H, H-3 and H-3′), 7.12—6.95 (m, 14H), 5.06 (s, 4H, OCH_2), 2.95—3.07 (m, 4H, CF_2CH_2), 2.32—2.54 (m, 4H); ^{19}F NMR ($CDCl_3$, TFC) δ: − 81.2 (m, 6F), − 115.1 (m, 4F), − 122.3 (m, 4F), − 123.3 (m, 4F), − 124.0 (m, 4F), − 126.5 (m, 4F); IR (KBr) ν: 2928, 2860, 1600, 1236, 1189, 1143 cm^{-1}; MS *m*/*z* (%) 1160 (M + 2, 33.53), 1159 (M + 1, 57.90), 1158 (M^+, 100), 1157 (M − 1, 76.26). Anal. clacd for $C_{50}H_{32}F_{26}O_2$: C 51.81, H 2.76, F 42.66; found C 51.98, H 2.82, F 42.57.

6 Colorless waxy solid, $[\alpha]_D^{20}$ + 28.5 (*c* 0.48, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 7.89 (d, J = 9.2 Hz, 2H, H-4 and H-4′), 7.70 (s, 2H, H-5 and H-5′), 7.42 (d, J = 9.2 Hz, 2H, H-3 and H-3′), 7.12—6.96 (m, 14H), 5.06 (s, 4H, OCH_2), 2.96—3.08 (m, 4H, CF_2CH_2), 2.32—2.56 (m, 4H); ^{19}F NMR ($CDCl_3$, TFC) δ: − 81.2 (m, 6F), − 115.0 (m, 4F), − 122.2 (m, 12F), − 123.2 (m, 4F), − 123.9 (m, 4F), − 126.6 (m, 4F); IR (KBr) ν: 2928, 1599, 1204, 1148 cm^{-1}; MS *m*/*z* (%): 1360 (M + 2, 25.82), 1359 (M + 1, 38.06), 1358 (M^+, 45.06), 1357 (M − 1, 45.74), 91 ($C_7H_7^+$, 100). Anal. clacd for $C_{54}H_{32}F_{34}O_2$: C 47.72, H 2.36, F 47.57; found C 47.87, H 2.31, F 47.80.

Preparation of 6,6′-*bis*(*perfluoroalkyl*)-1,1′-*binaphthyl* (**7**) *and* (**8**)

Typical procedure 2,2′-Dibenzyloxy-6,6′-bis

(1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl)-1,1′-binaphthyl (**5**) (579 mg, 0.5 mmol) was dissolved in ethyl acetate (5 mL), Pd/C (10 wt%, 58 mg) was added. The mixture was hydrogenated under 1.013×10^5 Pa at room temperature for 4 h. After filtration and evaporation, the residue was purified by flash chromatography (hexane: ethyl acetate = 3:1) to give a colorless solid quantitively.

7 Colorless waxy solid, $[\alpha]_D^{20}$ − 13.1 (*c* 0.63, THF); ^{1}H NMR ($CDCl_3$) δ: 7.89 (d, J = 9.0 Hz, 2H, H-4 and H-4′), 7.58 (s, 2H, H-5 and H-5′), 7.27 (d, J = 8.9 Hz, 2H, H-3 and H-3′), 7.04—7.16 (m, 4H), 5.07 (s, 2H, OH), 3.11 (t, J = 8.4 Hz, 4H, CF_2CH_2), 2.27—2.53 (m, 4H); ^{13}C NMR ($CDCl_3$) δ: 152.7, 134.9, 132.4, 131.1, 129.8, 128.4, 127.4, 124.9, 118.3, 111.0, 33.1, 26.4; ^{19}F NMR ($CDCl_3$, TFC) δ: − 80.7 (m, 6F), − 114.5 (m, 4F), − 121.8 (m, 4F), − 122.8 (m, 4F), − 123.4 (m, 4F), − 126.0 (m, 4F); IR (KBr) ν: 3516, 3477, 2953, 1602, 1238, 1206, 1145 cm^{-1}; MS *m/z* (%): 980 (M + 2, 23.9), 979 (M + 1, 48.9), 978 (M^+, 100), 977 (M − 1, 94.2), 976 (M − 2, 64.0). Anal. calcd for $C_{36}H_{20}F_{26}O_2$: C 44.27, H 2.04, F 50.51; found C 44.23, H 2.05, F 50.35.

8 Colorless waxy solid, $[\alpha]_D^{20}$ − 11.5 (*c* 0.79, THF),^{321}H NMR ($CDCl_3$) δ: 7.90 (d, J = 9.0 Hz, 2H, H-4 and H-4′), 7.72 (s, 2H, H-5 and H-5′), 7.38 (d, J = 8.9 Hz, 2H, H-3 and H-3′), 7.05—7.18 (m, 4H), 5.02 (s, 2H, OH), 2.95—3.09 (m, 4H, CF_2CH_2), 2.31—2.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ: 152.7, 134.9, 132.4, 131.1, 129.7, 128.4, 127.4, 124.9, 118.3, 110.9, 33.1, 26.5; ^{19}F NMR ($CDCl_3$, TFC) δ: − 80.7 (m, 6F), − 114.4 (m, 4F), − 121.6 (m, 12F), − 122.5 (m, 4F), − 123.4 (m, 4F), − 126.0 (m, 4F); IR (KBr) ν: 3516, 1604, 1479, 1241, 1206, 1149, 1115 cm^{-1}; MS *m/z* (%): 1180 (M + 2, 34.1), 1179 (M + 1, 57.9), 1178 (M, 98.3), 1177 (M − 1, 100.0). Anal. calcd for $C_{40}H_{20}F_{34}O_2$: C 40.75, H 1.70, F 54.80; found C 40.90, H 1.31, F 54.20.

Typical procedure for asymmetric alkylation of benzaldehyde

Entry 4 as an example, R_{f6}-BINOL (**7**) (98 mg, 0.1 mmol) was dissolved in the mixed solvents (perfluorodecalin: hexane: toluene = 5:2:0.4), $Ti(O^iPr)_4$ (210 μL, 0.7 mmol) was added and the mixture was stirred at room temperature for 0.5 h. Et_2Zn (3.4 mL, 15 wt%, 3 mmol) in hexane was added and stirred for 10 min. Then the mixture was cooled to 0 ℃ and benzaldehyde (102 μL, 1 mmol) was added. The reaction was kept at 0 ℃ until TLC inferred the disappearance of benzaldehyde. The organic layer was syringed out and quenched by 1 mol/L HCl (4 mL). Perfluorodecalin (5 mL) and toluene (1 mL) were added into the filtrate for three-phase liquid-liquid extraction. Another 5 mL of perfluorodecalin was added for a second extraction. The separated organic layer was washed with saturated $NaHCO_3$ and brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by flash chromatography. Optical rotation of the product was $[\alpha]_D^{20}$ − 38.0 (*c* 0.94, $CHCl_3$). Catalyst **7** recovered from the organic phase was 9%. The combined fluorous solvent was distilled with a little $C_{10}F_{18}$ left. Ethyl acetate and 1 mol/L HCl were added. 79% of **7** was obtained after column purification. ^{1}H NMR ($CDCl_3$) δ: 7.25—7.35 (m, 5H, Ph), 4.58 (t, J = 6.6 Hz, 1H, CHOH), 1.93 (s, 1H, OH), 1.65—1.90 (m, 2H, CH_2), 0.92 (t, J = 7.4 Hz, 3H, CH_3).

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33 The optical rotation of **8** in Ref. 19 is $[\alpha]_D^{10} - 33.33$ (*c* 1.1, $CHCl_3$). Our results are $[\alpha]_D^{20} - 28.6$ (*c* 0.97, $CHCl_3$) for R_{65}-BINOL and $[\alpha]_D^{20} - 23.5$ (*c* 0.96, $CHCl_3$) for R_{68}-BINOL. HPLC confirmed the purity of **7** and **8** (chiracel AD column, $V_{hexane}: V_{2\text{-propanol}} = 9:1$, flow rate = 0.75 mL/min).

(E0202045 ZHAO, X. J.)