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The role of the planar chirality of iron tricarbonyl substituted homochiral amino alcohols in the asymmetric alkylation of aldehydes with diethylzinc

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Abstract—Homochiral amino alcohols bearing an iron tricarbonyl moiety were prepared from 2-amino-1,1-diphenylethanol derivatives **4a**–**d** and [(3*S*,4*S*)-$\eta^{4,7}$-octa-4,6-dien-3-ol]$Fe(CO)_3$ complex **2**. The addition of diethylzinc to aldehydes bearing electron donating substituents in the presence of these chiral ligands gave the alkylated products in good enantiomeric excess (up to 93% e.e.), whereas the addition to aldehydes bearing electron withdrawing substituents resulted in low yields and poor enantiomeric excesses.

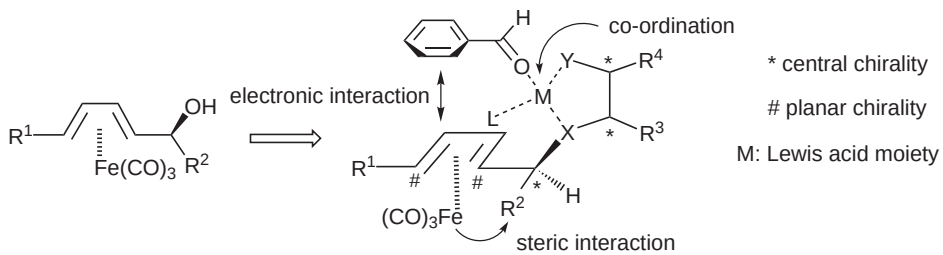
1. Introduction

The enantioselective formation of C–C bonds is one of the most important synthetic methods.[1] Among them, the addition of dialkylzinc reagents to aldehydes in the presence of small amounts of chiral ligands is the most successful catalytic reaction.[2] A number of elegant studies[3] on homochiral ligands and the reaction mechanism established the broad utility of this reaction. Recent attention has focused on the design of new ligands with both central and planar chiralities and clarification of their effect on the enantioselectivity.[4] Although tricarbonyl metal groups with planar chirality have been demonstrated to serve as powerful control elements[5] in catalyst design, there is no report of chiral ligands bearing an $Fe(CO)_3$ group. We have already reported a new and simple method for the asymmetric synthesis of homochiral [(3*S*,4*S*)-$\eta^{4,7}$-octa-4,6-dien-3-ol]$Fe(CO)_3$ complexes **2**.[6] Therefore, we undertook preparation from **2** of various amino alcohols bearing the iron tricarbonyl group with the aim of investigating the steric and electronic effects of the tricarbonyl-metal group (Scheme 1).

Herein, we describe the stereoselective synthesis of a novel class of planar chiral amino alcohols **5a**–**d**, and their application in the enantioselective addition of diethylzinc to aldehydes.

2. Results and discussion

The chiral ligands **5a**–**d** were prepared by the diastereoselective nucleophilic substitution of the acetate **3** (derived from the asymmetric alkylation of **1** with diethylzinc and the subsequent acetylation of **2**), with



Scheme 1.

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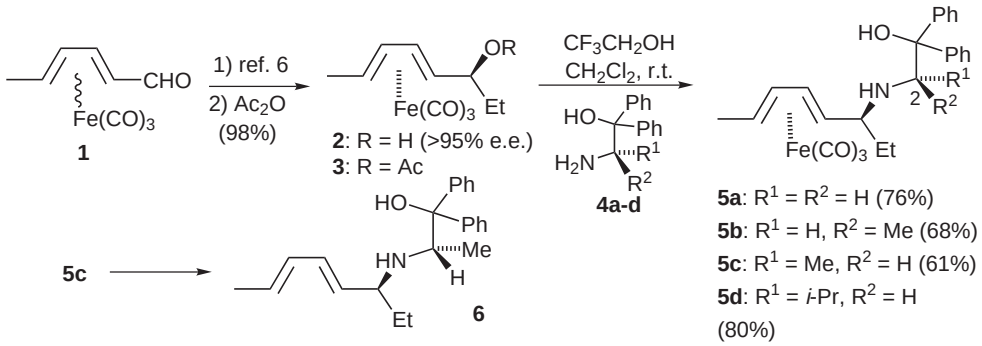


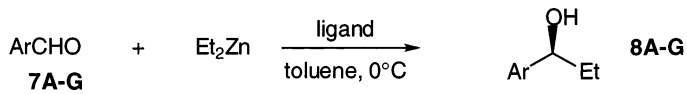
Scheme 2.

chiral amino alcohols **4a–d** (Scheme 2). In contrast to that of ferrocene derivatives,[7] the nucleophilic substitution of acetate **3** by primary amines has not been reported. In fact, no substituted adducts were obtained under standard reaction conditions such as heating and addition of a Lewis acid. After many experiments, we found that addition of trifluoroethanol dramatically promoted the substitution reaction of **3** to afford **4a–d**. The reaction of **3** and **4a** in dichloromethane in the presence of trifluoroethanol (40 equiv.) at room temperature gave the desired product **5a** in good yield with high stereoselectivity. The choice of solvent and amount of trifluoroethanol were crucial for this reaction. When using solvents other than dichloromethane and chloroform, the desired product **4a** was not obtained, even if a large excess of trifluoroethanol was added. The same reaction of **3** with other amino alcohols **4b–d** bearing a C-(2) substituent proceeded smoothly to afford the corresponding adducts **5b–d**. Stereochemical assignment of **5a–d** was elucidated from the known literature outcomes.[8] In addition, the decomplexed product **6** was synthesized in 57% yield by treatment of **5c** with 30% hydrogen peroxide in the presence of 1N NaOH solution in methanol.

The catalytic efficiency of the amino alcohols **5a–d** and **6** was evaluated in the addition of diethylzinc to benzaldehyde, and the results are summarized in Table 1. The reaction was carried out in toluene at 0°C in the presence of 10 mol% of the catalyst using benzaldehyde and diethylzinc in 1:2 ratio. The chiral amino alcohol–$Fe(CO)_3$ complexes were found to efficiently catalyze the addition of diethylzinc to benzaldehyde **7A** and afforded 1-phenyl-1-propanol **8A** in reasonable yields and with moderate to good enantiomeric excesses (41–84% e.e.).

The results showed that the enantioselectivity was affected by the structure of the chiral ligand. It was apparent that the chirality induced by the catalyst was controlled essentially by the planar chirality of the $Fe(CO)_3$ group. The central chirality of the C-(2) of the amino alcohol moiety had only a marginal effect on the e.e. For example, the same (*S*)-1-phenylpropanol was

Table 1. Addition of diethylzinc to benzaldehyde in the presence of chiral catalysts **5a–d** and **6**



Entry	R	Ligand	Time (h)	Yield[a] (%)	E.e. (%)	Configuration[e]
1	Ph (**7A**)	**5a**	18	24 (**8A**)	58[b]	*S*
2		**5b**	18	36 (**8A**)	41[b]	*S*
3		**5c**	78	67 (**8A**)	84[b]	*S*
4		**5d**	45	45 (**8A**)	70[b]	*R*
5	4-MeC_6H_4 (**7B**)	**5c**	40	66 (**8B**)	79[c]	*S*
6	4-$MeOC_6H_4$ (**7C**)	**5c**	48	70 (**8C**)	91[b]	*S*
7	3,4-$(MeO)_2C_6H_4$ (**7D**)	**5c**	45	54 (**8D**)	93[b]	*S*
8		**6**	45	27 (**8D**)	70[b]	*S*
9	4-ClC_6H_4 (**7E**)	**5c**	43	20 (**8E**)	25[b]	*S*
10	2-Naphthyl (**7F**)	**5c**	45	56 (**8F**)	87[b]	*S*
11	*trans*-PhCH=CH (**7G**)	**5c**	45	86 (**8G**)	81[b]	*S*
12	$PhCH_2CH_2$ (**7H**)	**5c**	48	69 (**8H**)	72[b]	*S*
13	$CH_3(CH_2)_5$(**7I**)	**5c**	45	53 (**8I**)	43[d]	*S*

[a] Isolated yields.
[b] Determined by HPLC with a Daicel CHIRALCEL-OD column.
[c] Determined by HPLC with a Daicel CHIRALCEL-AS column.
[d] Based on the reported value of optical rotation. $[\alpha]_D^{20}=+4.2$ ($c=10.2$, $CHCl_3$); lit. 3k), e.e. 74%: $[\alpha]_D^{20}=+7.1$ ($c=8.3$, $CHCl_3$).
[e] Determined from the comparison of the sign of the specific rotation with the literature data.

always obtained in the presence of **5a**–**c** irrespective of the central chirality of C-(2) (entries 1–3). Interestingly, increasing the bulk of the C-(2) substituent induced reversal of enantioselectivity, even though **5d** has the same central and planar chiralities as **5c**, to give (*R*)-1-phenylpropanol with a slight decrease in e.e. (comparing entries 3 and 4). When the reaction was carried out in dichloromethane, both reaction rate and enantioselectivity significantly decreased to 45% yield and an e.e. of 57%. As a result toluene was the solvent of choice in the remaining reactions.

We next examined the same asymmetric alkylation of several aromatic and aliphatic aldehydes **7B**–**I** with the best ligand from the initial investigations, **5c**. Most interestingly, the substitution of the aromatic ring of aldehydes with an electron donating group resulted in greater enantiomeric purity of alkylated products (entries 5–13). For example, the alkylation of 4-methylbenzaldehyde **7B** with diethylzinc produced the alkylation product **8B** with a slightly lower e.e. of 79%, the same reactions of 4-methoxybenzaldehyde **7C** and 3,4-dimethoxybenzaldehyde **7D** gave the corresponding alkylated products **8C** and **8D** with higher e.e.s of 86–93% (entries 5–7), whilst the reactions of 4-chlorobenzaldehyde **7E** and hexanylaldehyde **7I** afforded the desired products **8E** and **8I** in low yields and e.e.s (entries 9 and 13). In the case of other aromatic and α,β-unsaturated aldehydes **7F**–**H** (entries 10–12), good enantioselectivity was observed.

To investigate the importance of co-ordination of the $Fe(CO)_3$ group to the ligands, asymmetric alkylation of **7c** with the decomplexed chiral ligand **6** was performed, giving the alkylated adduct **8C** in 27% yield with only 70% e.e. (entry 8). This result indicates that complexation of a metal carbonyl group to the ligands is very important for enhancing not only the reaction rate, but also increasing the e.e. of products. From these results, we speculate that the beneficial effect on the enantioselectivity of the asymmetric alkylation of aromatic aldehydes bearing electron donating groups may be attributed to π–π-stacking between the (diene)$Fe(CO)_3$ group and the electron rich aromatic ring, as shown in Fig. 1.[3e] Such a strong interaction of the aldehyde and the chiral catalyst could serve to stabilize the transition state leading to (*S*)-**8A**, and enhancing both the reaction rate and the enantioselectivity of the reaction.

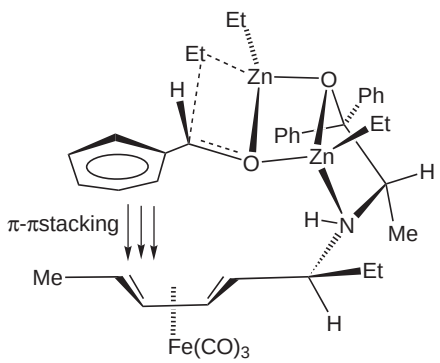


Figure 1. Transition state model of the asymmetric alkylation of **5c**.

3. Conclusion

We have succeeded in the asymmetric synthesis of new iron tricarbonyl complexed amino alcohols by using trifluoroethanol to promote reaction. When these ligands were applied as catalysts in the addition of diethylzinc to several aldehydes, **5c** was shown to provide the corresponding alcohols with good to high e.e., especially in the case of electron rich aromatic aldehydes. These results indicate that the chirality and π–π-stacking interaction of the (diene)$Fe(CO)_3$ moiety are important factors for the asymmetric alkylation.

4. Experimental

4.1. General

IR spectra were obtained using a Jasco FT/IR-420 spectrometer. ^{1}H NMR spectra were obtained using Jeol JNM-GX-500 (500 MHz) and JNM-EX-270 (270 MHz) spectrometers. ^{13}C NMR spectra were obtained using a Jeol JNM-EX-270 (67.8 MHz) spectrometer. Optical rotations were measured with a Jasco DIP-360 polarimeter. Mass spectra (MS) were measured with a Shimadzu GCMS-QP-1000 spectrometer. High-resolution mass spectra (HR-MS) were measured with a Jeol JMS-D300 spectrometer. HPLC analyses were performed on a Shimadzu LC-10AT equipped with SPD-10A UV–vis detector. A 1.0 M solution of diethylzinc in hexane was purchased from Kanto Chemicals. Column chromatography was carried out using Merck Kieselgel 60. Dry toluene, dichloromethane, ether and THF were obtained from Kanto Chemicals.

4.2. General procedure for preparation of amino alcohol–$Fe(CO)_3$ complexes 5a–d and 6

4.2.1. (2*S*,1′*S*,2′*S*)-*N*-Tricarbonyliron[(η^4-2-5)-1-ethyl-2,4-hexadienyl]-2-amino-1,1-diphenylpropanol 5c. To a stirred solution of **3** (188 mg, 0.61 mmol) and **4c** (277 mg, 1.22 mmol) in CH_2Cl_2 (3.6 mL) was added trifluoroethanol (1.8 ml, 24.4 mmol) under an argon atmosphere and the resulting mixture was stirred at room temperature for 18 h. After removal of the solvents in vacuo, the obtained residue was purified by flash column chromatography (hexane/ethyl acetate = 10/1) to give **5c** (230 mg, 79%). **5c**: $[\alpha]_D^{21}$ −21.90 (*c* 0.719, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 0.69 (dd, 1H, *J* = 8.6 Hz), 0.77 (t, 3H, *J* = 7.3 Hz), 0.97 (d, 3H, *J* = 6.5 Hz), 1.11 (qd, 1H, *J* = 8.6, 6.2 Hz), 1.15–1.21 (m, 2H), 1.38 (d, 3H, *J* = 6.2 Hz), 1.50–1.66 (m, 1H), 2.06 (ddd, 1H, *J* = 8.6, 6.2, 3.9 Hz), 3.87 (q, 1H, *J* = 6.5 Hz), 4.55–4.79 (m, 1H), 5.01 (dd, 1H, *J* = 8.6, 4.9 Hz), 5.10 (dd, 1H, *J* = 8.6, 4.9 Hz), 7.10–7.70 (m, 10H); ^{13}C NMR

($CDCl_3$, 67.8 MHz) δ: 8.8, 16.5, 19.1, 28.5, 56.0, 57.8, 58.5, 65.8, 78.5, 82.6, 85.4, 125.8, 126.1, 126.4, 126.8, 127.9, 128.2, 144.8, 146.6; IR ($CHCl_3$) 3341, 3039, 2969, 2040, 1968, 1454, 1375 cm^{-1}; MS FAB: (m/z) 476 (MH^+, 67), 391 (71), 249 (100), 193 (58); HR-MS (FAB+) calcd for $C_{26}H_{30}FeNO_4$ (MH^+): 476.1524. Found: 476.1530.

4.2.2. (1′*S*,2′*S*)-*N*-Tricarbonyliron[(η⁴-2-5)-1-ethyl-2,4-hexadienyl]-2-amino-1,1-diphenylethanol 5a. Compound **5a** was prepared by the same procedure described above: $[\alpha]_D^{28}$ +12.17 (*c* 0.641, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.76 (dd, 1H, $J=8.9$, 8.1 Hz), 0.89 (dd, 3H, $J=7.3$, 7.0 Hz), 1.18 (qd, 1H, $J=5.9$, 7.6 Hz), 1.29–1.45 (m, 2H), 1.39 (d, 3H, $J=5.9$ Hz), 1.60–1.82 (m, 1H), 2.19 (ddd, 1H, $J=8.9$, 3.0 Hz), 3.07 (d, 1H, $J=11.9$ Hz), 3.52 (d, 1H, $J=11.9$ Hz), 5.01 (dd, 1H, $J=7.6$, 12.4 Hz), 5.04 (dd, 1H, $J=8.1$, 12.4 Hz), 7.18–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 10.1, 19.1, 29.9, 56.1, 58.0, 62.5, 65.5, 76.2, 82.7, 85.4, 125.9, 126.1, 126.9, 127.0, 128.2, 128.3, 145.4, 145.5; IR ($CHCl_3$) ν: 3410, 3040, 2965, 2865, 2040, 1968, 1454, 1375 cm^{-1}; MS FAB: (m/z) 462 (MH^+, 92), 377 (100), 249 (82), 193 (53); HR-MS (FAB+) calcd for $C_{25}H_{28}FeNO_4$ (MH^+): 462.1367. Found: 462.1364.

4.2.3. (2*R*,1′*S*,2′*S*)-*N*-Tricarbonyliron[(η⁴-2-5)-1-ethyl-2,4-hexadienyl]-2-amino-1,1-diphenylethanol 5b. Compound **5b** was prepared by the same procedure described above: $[\alpha]_D^{31}$ +30.42 (*c* 0.933, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.59 (dd, 1H, $J=8.9$, 9.2 Hz), 0.86 (t, 3H, $J=7.3$ Hz), 0.95 (d, 3H, $J=6.2$ Hz), 1.14 (qd, 1H, $J=5.9$, 3.5 Hz), 1.20–1.37 (m, 2H), 1.43 (d, 3H, $J=5.9$ Hz), 1.60–1.80 (m, 1H), 2.18 (ddd, 1H, $J=3.5$, 9.2, 9.7 Hz), 3.95 (q, 1H, $J=6.2$ Hz), 4.20–4.50 (m, 1H), 4.95 (dd, 1H, $J=8.9$, 4.9 Hz), 5.07 (dd, 1H, $J=3.5$, 4.9 Hz), 7.10–7.60 (m, 10H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 10.1, 14.8, 19.1, 30.7, 54.7, 58.1, 58.3, 65.8, 79.1, 82.1, 85.4, 125.7, 126.1, 126.4, 126.9, 127.9, 128.3, 144.7, 146.2; IR ($CHCl_3$): ν 3448, 3037, 2970, 2041, 1968, 1452, 1373 cm^{-1}; MS FAB: (m/z) 476 (MH^+, 65), 391 (80), 249 (100), 193 (62); HR-MS (FAB^+) calcd for $C_{26}H_{30}FeNO_4$ (MH^+): 476.1524. Found: 476.1511.

4.2.4. (2*S*,1′*S*,2′*S*)-*N*-Tricarbonyliron[(η⁴-2-5)-1-ethyl-2,4-hexadienyl]-2-amino-1,1-diphenyl-3-methylbutanol 5d. Compound **5d** was prepared by the same procedure described above: $[\alpha]_D^{31}$ +38.24 (*c* 1.037, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.57 (t, 1H, $J=8.9$ Hz), 0.71 (d, 3H, $J=7.0$ Hz), 0.79 (dd, 3H, $J=6.8$, 7.6 Hz), 0.84 (d, 3H, $J=7.3$ Hz), 1.07 (qd, 1H, $J=5.9$, 8.4 Hz), 1.13–1.30 (m, 2H), 1.39 (d, 3H, $J=5.9$ Hz), 1.42–1.51 (m, 1H), 1.52–1.60 (m, 1H), 2.05–2.22 (m, 1H), 3.80 (d, 1H, $J=2.2$ Hz), 5.04 (dd, 1H, $J=8.9$, 15.1 Hz), 5.06 (dd, 1H, $J=8.4$, 15.1 Hz), 5.20–5.35 (m, 1H), 7.06–7.74 (m, 10H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 10.7, 16.0, 19.1, 22.4, 28.3, 32.2, 57.9, 59.5, 64.5, 67.5, 78.3, 81.9, 84.7, 125.7, 126.07, 126.15, 126.6, 127.9 (×2), 145.4, 148.9; IR ($CHCl_3$) ν: 3348, 3060, 2963, 2039, 1968, 1454, 1379 cm^{-1}; MS FAB: (m/z) 504 (MH^+, 78), 249 (100), 221 (24), 193 (35); HR-MS (FAB+) calcd for $C_{28}H_{34}FeNO_4$ (MH^+): 504.1837. Found: 504.1847.

4.2.5. (2*S*,1′*S*)-*N*-(1-Ethyl-2,4-hexadienyl)-2-amino-1,1-diphenyl-3-propanol 6. To a solution of **5c** (100 mg, 0.21 mmol) in methanol (7 mL) was added 30% aqueous H_2O_2 (3 ml) and 3N aqueous NaOH (1 mL) at 0°C, and then the resulting mixture was stirred at 0°C for 1 h and at room temperature for 45 min. After $NaHSO_3$ was added to the mixture, methanol was removed under reduced pressure and the residue was extracted with AcOEt. The combined extracts were washed with a saturated $NaHCO_3$ solution and a saturated NaCl solution, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 40/1) to give **6** (39.9 mg, 57%): $[\alpha]_D^{21}$ −58.02 (*c* 0.329, $CHCl_3$); ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.67 (dd, 3H, $J=7.3$, 7.6 Hz), 0.95 (d, 3H, $J=6.5$ Hz), 1.11–1.39 (m, 4H), 1.76 (d, 3H, $J=6.8$ Hz), 2.36–2.44 (m, 1H), 3.78 (q, 1H, $J=6.5$ Hz), 5.20 (dd, 1H, $J=8.1$, 14.9 Hz), 5.69 (qd, 1H, $J=6.8$, 13.5 Hz), 5.84–6.08 (m, 2H), 7.12–7.62 (m, 10H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 10.3, 17.8, 18.1, 28.8, 56.6, 60.1, 78.1, 125.9, 126.2 (×2), 126.6, 127.8, 128.0, 128.7, 131.0, 131.1, 134.1, 145.2, 147.3; IR ($CHCl_3$) ν: 3335, 3061, 2965, 2928, 2865, 1454, 1374 cm^{-1}; MS FAB: (m/z) 336 (MH^+, 60), 210 (10), 152 (32), 109 (100); HR-MS (FAB+) calcd for $C_{23}H_{30}NO$ (MH^+): 336.2327. Found: 336.2325.

4.3. General procedure for catalytic ethylation of aldehydes with 5a–d and 6

A typical procedure for enantioselective addition of diethylzinc to aldehydes: (*S*)-1-phenyl-1-propanol **7A**. To a solution of **5a** (40 mg, 0.087 mmol) in toluene (2 ml) was added diethylzinc (1.1 M solution in toluene, 1.19 ml, 1.3 mmol) under an argon atmosphere at 0°C and the resulting solution was stirred at room temperature for 1 h. A solution of benzaldehyde (92.3 mg, 0.87 mmol) in toluene (0.8 ml) was added to the mixture at 0°C and the resulting mixture was stirred for 18 h. After being quenched with a saturated NH_4Cl solution, the resulting mixture was extracted with AcOEt. The combined extracts were washed with a saturated NH_4Cl solution and a saturated NaCl solution, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 5/1) to give (*S*)-1-phenyl-1-propanol **7A** (27.3 mg, 24%). The e.e. was determined to be 58% by HPLC analysis using a DAICEL Chiralcel OD column (hexane/*i*-PrOH 99/1, flow rate: 1 ml/min):[3g] (*R*)-**7A** 20.3 min, (*S*)-**7A** 29.1 min. For 1-(4-methylphenyl)-1-propanol **7B**:[3m] AS column (hexane/*i*-PrOH 99/1, flow rate: 0.5 ml/min); (*R*)-**7B** 29.8 min, (*S*)-**7B** 35.2 min. For 1-(4-methoxyphenyl)-1-propanol **7C**:[3g] OD column (hexane/*i*-PrOH 97.5/2.5, flow rate: 0.7 ml/min); (*R*)-**7C** 33.2 min, (*S*)-**7C** 39.6 min. For 1-(3,4-dimethoxyphenyl)-1-propanol **7D**:[3e] OD column (hexane/*i*-PrOH 97.5/2.5, flow rate: 1 ml/min); (*R*)-**7D** 59.7 min, (*S*)-**7D** 54.9 min. For 1-(4-chlorophenyl)-1-propanol **7E**:[3d] OD column (hexane/*i*-PrOH 99/1, flow rate: 1 ml/min); (*R*)-**7E** 13.1 min, (*S*)-**7E** 14.0 min. For 1-(2-naphthyl)-1-propanol **7F**:[3g] OD column (hexane/*i*-PrOH 96/4, flow rate: 1 ml/min); (*R*)-**7F** 19.6 min, (*S*)-**7F** 15.4 min. For *trans*-1-phenyl-1-penten-3-ol **7G**:[3g]

OD column (hexane/*i*-PrOH 95/5, flow rate: 1 ml/min); (*R*)-**7G** 11.9 min, (*S*)-**7G** 19.4 min. For 1-phenyl-1-pentanol **7H**:[3g] OD column (hexane/*i*-PrOH 95/5, flow rate: 1 ml/min); (*R*)-**7H** 9.4 min, (*S*)-**7H** 13.7 min.

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