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Modular amino acid amide chiral ligands for enantioselective addition of diethylzinc to aromatic aldehydes

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Enantioselective addition of diethylzinc to a series of aromatic aldehydes was developed using a modular amino acid amide chiral ligand (2*S*)-3-phenyl-*N*-((*R*)-1-phenyl-ethyl)-2-(tosylamino)propanamide without using titanium complex. The catalytic system employing 10 mol% of 1g was found to promote the addition of diethylzinc ($ZnEt_2$) to a wide range of aromatic aldehydes with electron-donating and electron-withdrawing substituents, giving up to 82% ee of the corresponding secondary alcohol under mild conditions.

Keywords: addition reaction; aldehyde; amide; diethylzinc; sulfonylamino

Introduction

Enantioselective addition of diorganozinc reagents to aldehydes is a fundamental and successful area in the field of asymmetric C–C bond formation reactions, natural products and biologically active compounds.[1] Considerable progress has been made in employing diethylzinc or dimethylzinc reagents as the chiral source by many research groups using diverse chiral ligands, such as diols,[2] diamines,[3] aminothiols,[4] aminodisulfides,[5] amino alcohols,[6] diphosphoryldiols,[7] phosphoramides[8] and aminodiselenides.[9] Despite the achievements made in this field of the addition of aldehydes, it is still necessary to develop new types of catalytic system and to probe how the chiral catalysts work for the addition of diethylzinc to aldehyde.

Recently, we reported the synthesis of chiral sulfonamide-protected β-amino alcohol ligands and their application in the enantioselective addition of diethylzinc to aromatic aldehydes with good to excellent yields and enantioselectivities.[6a] Inspired by the results, we continued to search for a new highly efficient catalyst system for the enantioselective addition of diethylzinc to aromatic aldehydes. The series of chiral ligands **1a–i** (see Fig. 1; **1a–d** and **g–i** have been previously described,[10] and **1e–f** are new compounds, see Experimental section for details) were synthesized using L-phenylalanine and a chiral or achiral amine as raw material.

Results and Discussion

Catalyst System Screening

In the preliminary studies, we investigated the addition reaction of diethylzinc ($ZnEt_2$) to benzaldehyde (**2a**) in the presence of 15 mol% chiral ligand (**1a–i**) combined with 15 mol% Ti(*i*-OPr)$_4$ (1 : 1 ratio) in dry toluene at 0 °C under a nitrogen atmosphere (Table 1, entries 1–18). These titanium complexes (IV) had high reactivity and gave good to excellent isolated yields (Table 1, entries 1–9). However, the highest enantiomeric excess was only 32% ee with 91% yield employing the **1i**–Ti(IV) complex in the addition reaction of diethylzinc to benzaldehyde (Table 1, entry 9). We assumed that the titanium (IV) plays a disfavored role in the addition reaction of diethylzinc ($ZnEt_2$) to benzaldehyde. Therefore, a series of chiral ligands, **1a–i**, without Ti(*i*-OPr)$_4$ was investigated under the same conditions according to the bifunctional concept by adjusting the Lewis acid (center metal titanium and zinc) of the catalyst systems (Table 1, entries 10–18). It was found that a significant improvement was achieved when 15 mol% **1g** was employed in the enantioselective addition of diethylzinc to benzaldehyde with 68% ee and 78% yield (Table 1, entry 16). Other catalyst systems, including bigger substituents (ligands **1b,c** and **1e**), a longer carbon chain (**1d**) and stronger electron-withdrawing groups (**1f**), could also improve the ee's, although the yields were decreased dramatically (Table 1, entries 10–15, 17 and 18). In addition, the ligand **1h**, which has different configuration to **1g**, only gave 29% ee with 44% yield under same conditions (Table 1, entry 17). The **1i**, which gave the highest ee with titanium (IV) complex, only gave 46% ee with 83% yield without titanium (IV) complex (Table 3, entry 18).

Next, we investigated the effect of different solvents (toluene, CH_2Cl_2, THF, Et_2O, hexane and xylene) using the **1g** catalyst system (Table 2, entries 1–5). It was found that very low yield and only 3% ee were obtained in Tetrahydrofuran (THF) (Table 2, entry 2), while 99% yield and 35% ee could be afforded in Et_2O (Table 2, entry 3), which might be attributed to the different polarity. Moderate

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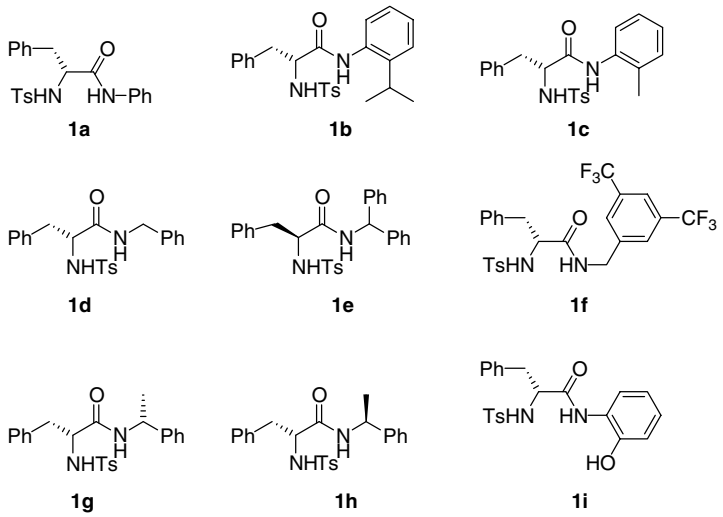
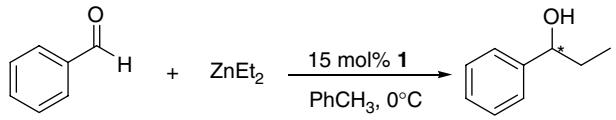


Figure 1. The structures of the chiral ligands for the addition of diethylzinc to aldehydes.

Table 1. Screening of the ligands **1a–i** for the enantioselective addition of diethylzinc to benzaldehyde



2a **3a**

Entry[a]	Ligand	Ti(*i*-OPr)$_4$ (mol%)	Yield (%)[b]	Ee (%)[c]
1	**1a**	15	93	13(*S*)
2	**1b**	15	86	0
3	**1c**	15	89	5(*S*)
4	**1d**	15	88	0
5	**1e**	15	87	8(*S*)
6	**1f**	15	90	7(*S*)
7	**1g**	15	95	0
8	**1h**	15	86	5(*S*)
9	**1i**	15	91	32(*S*)
10	**1a**	0	69	19(*S*)
11	**1b**	0	57	37(*S*)
12	**1c**	0	41	48(*S*)
13	**1d**	0	68	9(*S*)
14	**1e**	0	20	47(*S*)
15	**1f**	0	71	29(*S*)
16	**1g**	0	78	68(*S*)
17	**1h**	0	44	29(*S*)
18	**1i**	0	83	46(*S*)

[a] Conditions: concentration of **2a**, 0.25 M in $PhCH_3$; $ZnEt_2$, 1.5 equiv. in hexane solution; reaction time, 24 h.
[b] Isolated yields.
[c] The ee was determined by chiral GC G-TA column, and the *S*- or *R*-configuration was confirmed by comparison with the reported configuration.[2a,7b,11,12]

yields and low ee's could be produced employing CH_2Cl_2 and hexane (Table 2, entries 4 and 5). Similar results were observed with toluene and xylene (Table 3, entry 6 vs 1). The highest ee of 68% was obtained in toluene (Table 2, entry 1).

Table 2. Screening of the solvent enantioselective addition of diethylzinc to benzaldehyde

Entry[a]	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]	Ee (%)[c]
1	$PhCH_3$	0	24	78	68(*S*)
2	THF	0	24	trace	3(*S*)
3	Et_2O	0	24	99	35(*S*)
4	CH_2Cl_2	0	24	58	15(*S*)
5	Hex	0	24	79	18(*S*)
6	Xylene	0	24	73	66(*S*)

[a] Conditions: concentration of **2a**, 0.25 M in $PhCH_3$; $ZnEt_2$, 1.5 equiv. in hexane solution; **1g**, 15 mol%.
[b] Isolated yields.
[c] The ee was determined by chiral GC G-TA column, and the (*S*)-configuration was confirmed by comparison with the reported configuration.[2a,7b,11,12]

The loading of **1g** and $ZnEt_2$, optimum temperature and the concentration of **2a** were also investigated using chiral ligand **1g** (Table 3, entries 1–10). Better enantioselectivity was not obtained when lowering or increasing the concentration of **2a** (Table 3, entries 2 and 3). Changing the loadings of $ZnEt_2$ and reaction temperature (20 or −20 °C) also did not improve the enantioselectivity (Table 3, entries 4–7). Better enantioselectivity was obtained when the loading of **1g** decreased from 20 to 10 mol%, although a longer reaction time was required (Table 3, entry 9). Greater loading of **1g** (increased from 15 to 25 mol%) caused significant improvement in the reactivity (Table 3, entry 8). Smaller loading of **1g** (5 mol%) gave very bad reactivity and low enantioselectivity after 80 h (Table 3, entry 10). The optimal catalyst system and reaction conditions were 10 mol% **1g**, 1.5 equiv. $ZnEt_2$ and 0.25 M of **2a** in $PhCH_3$ at 0 °C.

Substrate Generality

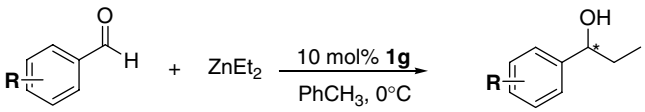
To study the generality of the **1g** catalyst system for the enantioselective addition of diethylzinc to various aromatic aldehydes, a number of aromatic aldehydes having electron-donating or electron-withdrawing groups, *a*- and *β*-naphthaldehydes and (*E*)-cinnamaldehyde were examined under the optimized conditions

Table 3. Optimization of the catalytic system for the enantioselective addition of diethylzinc to benzaldehyde catalyzed by **1g**

Entry[a]	**1g** (mol%)	Concentration of **2a**	$ZnEt_2$ (equiv.)	Temperature (°C)	Time (h)	Yield (%)[b]	Ee (%)[c]
1	15	0.25	1.5	0	24	78	68
2	15	0.5	1.5	0	10	83	63
3	15	0.1	1.5	0	48	49	57
4	15	0.25	1.8	0	24	68	67
5	15	0.25	1.0	0	48	43	54
6	15	0.25	1.5	−20	48	38	71
7	15	0.25	1.5	20	10	88	54
8	25	0.25	1.5	0	20	94	65
9	10	0.25	1.5	0	40	71	75
10	5	0.25	1.5	0	80	40	66

[a] Conditions: solvent, $PhCH_3$; $ZnEt_2$, hexane solution.
[b] Isolated yields.
[c] The ee was determined by chiral GC G-TA column and the (*S*)-configuration was confirmed by comparison with the reported configuration.[2a,7b,11,12]

Table 4. Enantioselective addition of diethylzinc to various aromatic aldehydes catalyzed by **1g**



2a-n **3a-n**

Entry[a]	Aldehyde	Time (h)	Yield (%)[b]	Ee (%)[c]
1	Benzaldehyde (**2a**)	40	71	75(*S*)
2	4-Methyl-benzaldehyde (**2b**)	60	51	59(*S*)
3	2-Methyl-benzaldehyde (**2c**)	60	48	50(*S*)
4	4-Methoxy-benzaldehyde (**2d**)	60	38	60(*S*)
5	3-Methoxy-benzaldehyde (**2e**)	60	41	57(*S*)[d]
6	4-Fluoro-benzaldehyde (**2f**)	40	76	71(*S*)
7	4-Chloro-benzaldehyde (**2g**)	40	74	73(*S*)
8	2-Chloro-benzaldehyde (**2h**)	40	60	65(*S*)
9	4-Bromobenzaldehyde (**2i**)	40	69	74(*S*)
10	4-Iodobenzaldehyde (**2j**)	40	76	76(*S*)
11	4-(Trifluoromethyl)benzaldehyde (**2k**)	40	60	51(*S*)[e]
12	(*E*)-Cinnamaldehyde (**2l**)	60	37	42(*S*)[d]
13	Naphthalene-2-carbaldehyde (**2m**)	40	83	82(*S*)[d]
14	Naphthalene-1-carbaldehyde (**2n**)	40	85	70(*S*)[d]

[a] Conditions: solvent, $PhCH_3$; 0 °C; concentration of **2**, 0.25 M; $ZnEt_2$, in hexane solution.
[b] Isolated yields.
[c] The ee was determined by chiral GC G-TA column, and the (*S*)-configuration was confirmed by comparison with the reported configuration.[2a,7b,11,12]
[d] The ee was determined by using a Chiral OD-H or OD column.[2a,7b,11,12]
[e] The ee was determined by using a Chiral OJ-H column.[2a,7b,11,12]

summarized in Table 3. In comparison to the results obtained with **2a**, the electron-donating substituents, the methyl group, led to a decrease in the ee of the products **3b** and **c** after a longer time (Table 4, entries 2 and 3 vs entry 1). In the case of stronger electron-donating substituents, the MeO group, lower yields but comparable ee to **3b** (Table 4, entries 4 and 5 vs entry 2) were obtained. Electron-withdrawing groups (F, Cl, Br, I and CF_3, Table 4, entries 6–11) showed variation in the yields, but no major differences in the ees of **3f–j**. (*E*)-cinnamaldehyde only gave 37% yield with 42% ee (Table 4, entry 12). Reaction of *α*- and *β*-naphthaldehydes **2j** and **2k** resulted in up to 82 and 70% ee, respectively (Table 4, entries 13 and 14). In general, moderate to good yields and enantioselectivities of the secondary alcohols **3a–n** were obtained (Table 4), with electron-donating and bigger substituted aromatic aldehydes giving less favorable results than electron-withdrawing substituted aromatic aldehydes. These results revealed that the **1g** catalyst system was effective for the 1,2-addition of diethylzinc to various aromatic aldehydes.

Catalytic Cycle Considerations

According to previous works in the field of the enantioselective addition of diethylzinc to aromatic aldehydes,[1–9] the Zn (II) complex might play multiple roles in the 1,2-addition reaction, as described in our previous report. [6a] The expected active species could be generated from the solution of **1g** and $ZnEt_2$

by coordination between the TsNH and CONH groups.[6a,11–14] When the benzaldehyde (**2a**) is added to the mixture, the metal moiety (Zn) might act as a Lewis acid to activate the benzaldehyde (**2a**) and engender other species. Then the product **3a** could be obtained by working up with aqua acid (HCl) and one catalytic cycle accomplished.

Conclusion

In summary, the chiral ligand **1g**, the sulfonamide-protected derivative of (2*S*)-3-phenyl-*N*-((*R*)-1-phenylethyl)-2-(tosylamino)propanamide readily prepared in several steps from commercially available (*R*)-α-phenylethylamine and L-phenylalanine, showed good catalytic activities and moderate enantioselectivities (up to 82% ee) with asymmetric addition of diethylzinc to various aromatic aldehydes. Further investigation on the applications of these ligands for other asymmetric reactions is ongoing.

Experimental Section

General Remarks

All reactions were conducted in oven-dried glassware under an inert atmosphere of nitrogen with anhydrous solvents unless stated otherwise. The solvents were purified and dried according to standard procedures. Analytical thin-layer chromatography (TLC) was performed on alumina- or glass-backed silica plates (GF254, 250 micron thickness) and visualized with UV light. Flash column chromatography was carried out on silica gel 60 (250–400 mesh) under air pressure. Enantiomeric ratios of the products were determined using chiral GC G-TA and HPLC OJ-H, OD-H or OD columns (UV detector, 254 nm). Specific rotations were determined as $[\alpha]_D^{22}$ (c = 0.5 g/ml in CH_2Cl_2). Melting points are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) chemical shifts in $CDCl_3$ are quoted as δ values relative to TMS (δ = 0.00) and $CDCl_3$ (δ = 77.0), respectively, in ppm and coupling constants in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were obtained using positive electrospray ionization (*m/z* values are given).

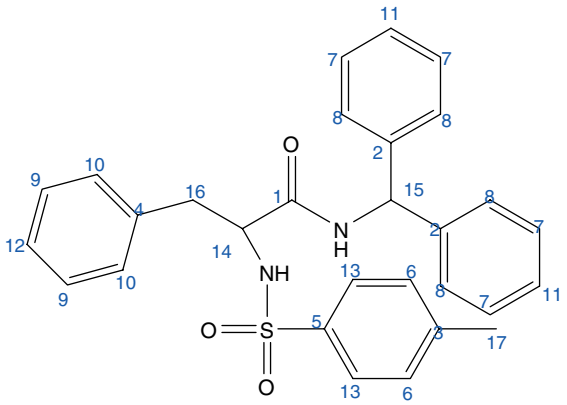
Materials

L-Phenylalanine, diethylzinc ($ZnEt_2$), PCl_5, Ti(*i*-OPr)$_4$, all aromatic aldehydes and all amines were commercially available and used without further purification, unless otherwise noted. 3-Phenyl-2-(toluene-4-sulfonylamino) propionyl chloride (**4a**) was synthesized according to the literature.[6a,10] The ligands **1a–d** and **g–i** are known compounds and were synthesized according to the literature procedures.[6a,10]

General Procedure for the Synthesis of Ligands 1e–f

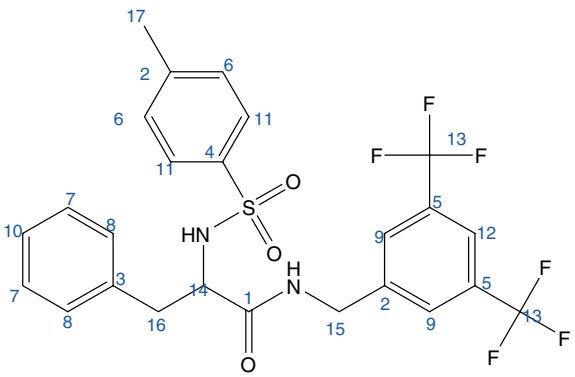
3-Phenyl-2-(toluene-4-sulfonylamino)-propionyl chloride (405 mg, 1.2 mmol) was added to a solution of the corresponding amine (1.0 mmol) and Et_3N (0.21 ml, 1.5 mmol) in CH_2Cl_2 (10 ml) at 22 °C. After stirring for 2 h (TLC), the reaction mixture was diluted with CH_2Cl_2 (50 ml), washed with aqueous HCl (1.0 M, 2 × 20 ml), aqueous K_2CO_3 (1.0 M, 2 × 20 ml) and then brine (2 × 20 ml). The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness on a rotary evaporator. The crude products were purified using column chromatography on silica gel (EA-hexane) and recrystallized from a mixture of EA : hexane (10 : 1 to 5 : 1, v/v). The corresponding products were obtained as white solids in 85–87% yield.

(*S*)-*N*-Benzhydryl-3-phenyl-2-(toluene-4-sulfonylamino)-propionamide (1e)



White solid, 85% yield, m.p.181–183 °C, $[a]_D^{20}$ = −13.32 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55 (d, J = 8.4 Hz, 2H, NH), 7.07–7.39 (m, 16H, ArH), 6.87–6.94 (m, 3H, ArH), 6.11 [d, J = 8.1 Hz, 1H, -NHC*H*(Ph)$_2$], 3.96 [dd, J_1 = 6.6 Hz, J_2 = 19.2 Hz, 1H, -CH$_2$C*H*(NHTS)CO-], 3.02–3.09 [m, 2H, PhC*H*$_2$CH(TsNH)CO-], 2.38 (s, 3H, -NHTsPhC*H*$_3$).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 169.2 (C1), 144.1 (C2), 141.1 (C3), 140.7 (C4),134.5 (C5), 129.5 (C6), 129.3 (C7), 129.1 (C8), 128.7 (C9), 128.6 (C10), 127.6 (C11), 127.5 (C12), 127.3 (C13), 57.2 (C14), 57.6 (C15), 38.2 (C16), 21.6 (C17) ppm. HRMS (ESI): calcd for (M^+ + 1) for $C_{29}H_{29}N_2O_3S$, 485.1899; found, 485.1908. Anal. calcd for $C_{29}H_{29}N_2O_3S$, C, 71.87%; found, 71.99%; H, 5.82%, found, 5.96%; N, 5.78%, found, 5.96%.

(*S*)-*N*-(3,5-Bis-trifluoromethyl-benzyl)-3-phenyl-2-(toluene-4-sulfonylamino)-propionamide (1f)



Slightly yellow solid, 87% yield, m.p.142–144 °C, $[a]_D^{20}$ − 15.08 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.71 (s, 1H, ArH), 7.50 (d, J = 5.4 Hz, 2H, NH), 7.24 (d, J = 8.1 Hz, 2H,ArH), 6.86–7.21 (m, 7H, ArH), 6.84 (d, J = 6.9 Hz, 2H), 4.51 [d, J = 6.0 Hz, 2H, -CONHC*H*$_2$(3,5,-CF$_3$Ph)], 3.90 [dd, J_1 = 6.3 Hz, J_2 = 12.6 Hz, 1H, TsNHC*H*(Bn)CONH-], 2.85–3.01 [m, 2H, PhC*H*$_2$CH(TsNH)CONH-], 2.44 (s, 3H, -PhC*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 170.7 (C1), 144.3 (C2), 141.1 (C2), 140.6 (C3), 134.7 (C4), 129.9 (C5), 129.0 (C6), 128.9 (C7), 127.5 (C8), 127.2 (9), 125.7 (C10), 125.1 (C11), 121.4

(C12), 120.2 (C13), 57.8 (C14), 50.2 (C15), 37.7 (C16), 22.6 (C17) ppm. HRMS (ESI): calcd for ($M^+ + 1$) for $C_{25}H_{23}F_6N_2O_3S$, 545.1334; found, 545. 1349. Anal. calcd for $C_{25}H_{23}F_6N_2O_3S$, C, 55.14%; found, 55.23%; H, 4.07%, found, 4.18%; N, 5.14%, found, 5.26%.

A Typical Procedure for the Catalytic Addition of Diethylzinc to Aromatic Aldehydes

To a solution of **1g** (10.6 mg, 0.025 mmol) in $PhCH_3$ (1.0 ml), a solution of diethylzinc (1.0 M in hexane, 0.375 ml, 0.375 mmol) was added under a nitrogen atmosphere at 0 °C, and the reaction mixture was stirred for 30 min at room temperature (about 20 °C). The reaction mixture was then cooled to 0 °C, and the corresponding aromatic aldehyde (0.25 mmol) was added and stirring was continued for stated times. The reaction mixture was quenched with HCl (1.0 M, 2.0 ml) at 0 °C, and the product was extracted with (3 × 5 ml) ethyl acetate. The combined ethyl acetate extracts were dried over Na_2SO_4 and evaporated to dryness under vacuum pressure. The residue was purified by silica gel column chromatography (hexane : ethyl acetate, 10 : 1, v/v) to afford the secondary alcohol products. The enantioselectivities of the reactions were determined by chiral GC G-TA, OJ-H or OD-H columns. Compounds **3a–n** are known compounds; they were characterized by comparing their ^1H and ^{13}C NMR spectra with the literature.[2a,6a,7b,11,12]

*(S)-1-Phenyl-propan-1-ol (**3a**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral GC G-TA column (100 °C, 2.0 ml/min, t_R = 9.0 min, t_R = 9.2 min).

*(S)-1-p-Tolyl-propan-1-ol (**3b**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral GC G-TA column (115 °C, 2.0 ml/min, t_R = 13.7 min, t_R = 13.4 min).

*(S)-1-o-Tolyl-propan-1-ol (**3c**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral GC G-TA column (115 °C, 2.0 ml/min, t_R = 14.2 min, t_R = 12.7 min).

*(S)-1-(4-Methoxy-phenyl)-propan-1-ol (**3d**)*[2b,6a,11,12]

Enantiomeric excess was determined on a chiral GC G-TA column (110 °C, 2.0 ml/min, t_R = 41.1 min, t_R = 39.7 min).

*(S)-1-(3-Methoxy-phenyl)-propan-1-ol (**3e**)*[2b,6a,12]

Enantiomeric excess was determined on a chiral HPLC OD (UV detector, 254 nm, hexane : *i*-PrOH = 9 : 1, 1.0 ml/min, t_R = 10.8 min, t_R = 10.0 min).

*(S)-1-(4-Fluoro-phenyl)-propan-1-ol (**3f**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral GC G-TA column (110 °C, 2.0 ml/min, t_R = 10.9 min, t_R = 10.1 min).

*(S)-1-(4-Chloro-phenyl)-propan-1-ol (**3g**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral GC G-TA column (135 °C, 3.0 ml/min, t_R = 7.5 min, t_R = 8.3 min).

*(S)-1-(2-Chloro-phenyl)-propan-1-ol (**3h**)*[2b,6a,7b,12–13]

Enantiomeric excess was determined on a chiral GC G-TA column (135 °C, 3.0 ml/min, t_R = 11.2 min, t_R = 11.7 min).

*(S)-1-(4-Bromo-phenyl)-propan-1-ol (**3i**)*[2b,6a]

Enantiomeric excess was determined on a chiral GC G-TA column (130 °C, 3.0 ml/min, t_R = 15.9 min, t_R = 15.2 min).

*(S)-1-(4-Iodo-phenyl)-propan-1-ol (**3j**)*[2b,6a]

Enantiomeric excess was determined on a chiral GC G-TA column (130 °C, 3.0 ml/min, t_R = 29.5 min, t_R = 28.0 min).

*(S)-1-(4-Trifluoromethyl-phenyl)-propan-1-ol (**3k**)*[2b,6a,7b]

Enantiomeric excess was determined on a chiral HPLC OJ-H (UV detector, 254 nm, hexane : *i*-PrOH = 98 : 2, 1.0 ml/min, t_R = 17.9 min, t_R = 16.4 min).

*(S)-(E)-1-Phenyl-pent-1-en-3-ol (**3l**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral HPLC OD-H (UV detector, 254 nm, hexane : *i*-PrOH = 9 : 1, 1.0 ml/min, t_R = 13.5 min, t_R = 9.1 min).

*(S)-2-Naphthalen-2-yl-propan-1-ol (**3m**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiral HPLC OD-H (UV detector, 254 nm, hexane : *i*-PrOH = 9 : 1, 1.0 ml/min, t_R = 10.1 min, t_R = 9.4 min).

*(S)-1-Naphthalen-2-yl-propan-1-ol (**3n**)*[2b,6a,7b,11,12]

Enantiomeric excess was determined on a chiralcel HPLC OD column (UV detector, 254 nm, 4 : 96 *i*-PrOH : hexane, 0.5 ml/min t_R = 31 min, t_R = 27 min).

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