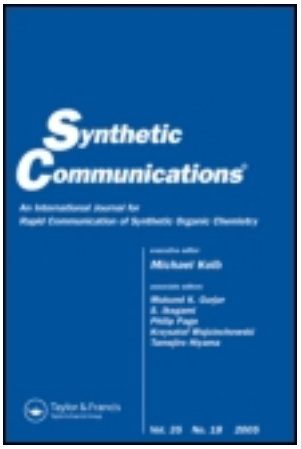

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MODULAR PROLINOL CHIRAL LIGANDS FOR ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO AROMATIC ALDEHYDES

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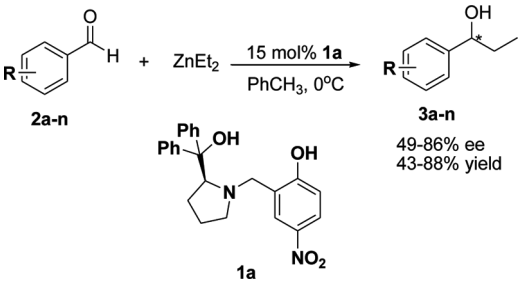
GRAPHICAL ABSTRACT



Abstract *Enantioselective addition of diethylzinc ($ZnEt_2$) to a series of aromatic aldehydes was promoted using a modular prolinol chiral ligand, 2-(*S*)-2-(hydroxydiphenylmethyl) pyrrolidin-1-yl)methyl)-4-nitrophenol (**1a**), without using titanium complex. The catalytic system employing 15 mol% of **1a** was found to promote the addition of diethylzinc to a wide range of aromatic aldehydes with electron-donating and electron-withdrawing substituents, giving up to 86%* ee *of the corresponding secondary alcohol under mild conditions.*

Keywords Addition reaction; aldehyde; C_1-symmetric; diethylzinc; prolinol

INTRODUCTION

Enantioselective addition of diethylzinc (Et_2Zn) to aldehydes is a fundamental and most successful C-C bond-formation reaction in the field of organic chemistry, natural products, and biologically active compounds.[1] It has received widespread attention because it has been one of the most efficient methods for generating optically active secondary alcohols since 1980s.[1,2] The importance of this structural

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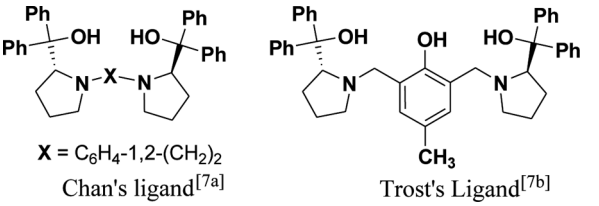


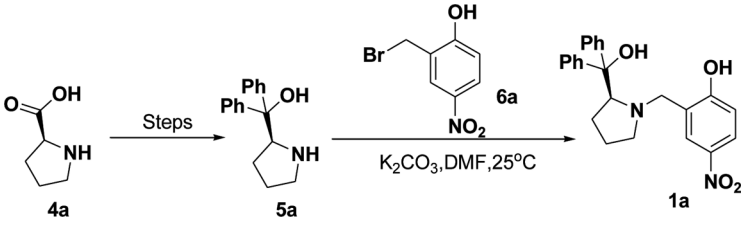
Figure 1. Reported C_2-symmetric auxiliary's ligand.

feature arises mainly from the fact that it is part of many natural products or precursors as an important synthetic intermediate.[1] For this purpose, a wide variety of chiral catalysts, such as amino alcohols,[2] diamines,[3] aminothiols,[4] aminodiselenides,[5] aminodisulfides,[6] diols,[7] 3,3′-diphsphoryl-1,1′-bi-naphthols,[8] and phosphoramides[9] have been synthesized and applied for the addition of diethylzinc to aldehydes. Despite the achievements made in this field of the addition of aldehydes, developing highly efficient catalyst systems and meeting practical application have been continuously attractive subjects for organic chemists. Among the chiral ligands reported, β-amino alcohols are the most often used chiral auxiliaries.[1,2] Recently, several C_2-symmetrical auxiliaries based on prolinol (**5a**) have been synthesized by Trost and Chan groups and applied in the catalytic enantioselective addition reaction (Fig. 1).[10] However, to our knowledge, few C_1-symmetric prolinol ligands are studied in the addition of diethylzinc to aldehyde, which derive from substituted phenol. In this article, we report the details of the synthesis of a new optically active C_1-symmetric *L*-prolinol ligand (Scheme 1) and their catalyzed asymmetric addition reaction of diethylzinc to aromatic aldehydes.

RESULTS AND DISCUSSION

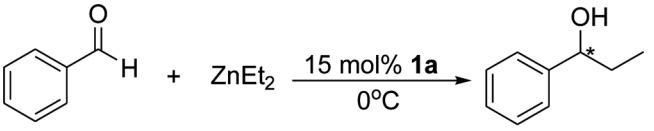
Catalyst System Screening

In the preliminary studies, we investigated the addition reaction of diethylzinc (Et_2Zn) to benzaldehyde (**2a**) in the presence of 15 mol% chiral ligand (**1a**) in varying solvent at 0 °C under nitrogen atmosphere (Table 1, entries 1–11). It was found that solvent drastically affected the enantiomeric excess (ee) of this asymmetric reaction. In contrast to the general results that hexane can give good results, a hexane solution of benzaldehyde reacting with 1.5 equiv. of diethylzinc (Et_2Zn, in hexane solution) in



Scheme 1. Modular proline C_1-symmetric chiral ligands.

Table 1. Effect of **1a** for the enantioselective addition of diethylzinc to benzaldehyde



2a **3a**

Entry[a]	Solvent	Time (h)	Yield (%)[b]	Ee (%)[c]
1	Hexane	30	12	56(*S*)
2	Toluene	24	78	74(*S*)
3	Toluene/hexane (*v*/*v*, 1:1)	24	68	58(*S*)
4	Toluene/hexane (*v*/*v*, 1:2)	24	57	55(*S*)
5	Toluene/hexane (*v*/*v*, 1:3)	24	48	54(*S*)
6	Xylene	24	59	52(*S*)
7	Xylene/hexane (*v*/*v*, 1:1)	24	57	53(*S*)
8	THF	24	30	60(*S*)
9	THF/hexane (*v*/*v*, 1:1)	24	26	56(*S*)
10	Et_2O	24	10	51(*S*)
11	CH_2Cl_2	30	16	23(*S*)
12[d]	Toluene	24	77	86(*S*)

[a]Conditions: concentration of **2a**, 0.25 M; Et_2Zn: 1.5 equiv. in hexane solution.
[b]Isolated yields.
[c]The *ee* was determined with a chiral GC G-TA column, and the (*S* or *R*)-configuration was confirmed by comparison with the reported configuration.[11a,b]
[d]Et_2Zn: 1.5 equiv. in $PhCH_3$. For details, see the Experimental section.

the presence of 15 mol% of chiral ligand **2a** at 0 °C can only give (*S*)-1-phenyl-1-propanol in 12% isolated yield with 56% ee (Table 1, entry 1). However, when the same reaction was employed in toluene under otherwise identical conditions, both the isolated yield and ee of the reaction product were considerably improved to 78% and 65%, respectively (Table 1, entry 2). The isolated yields and ee's of the reactions decreased with an increase of hexane content when a mixed solvent of toluene-hexane was used (Table 1, entries 3–5). It is might be arritibuted to the chiral ligand **1a** can be dissolved in toluene easily and dissolved in hexane slightly. The same phenomena were also observed when xylene-hexane was used as solvent (Table 1, entries 6–7). For THF, Et_2O and THF-hexane as solvent, because of their coordination to diethylzinc, low yields and moderate enantioselectivities were observed (Table 1, entries 8–10). However, for dichloromethane (CH_2Cl_2) as the solvent, poor yield and enantioselectivity were obtained (Table 1, entry 11). Gratifyingly, a significant improvement (86% *ee*, 77% yield) was achieved when the hexane solvent was evaporated with the addition of diethylzinc to benzaldehyde (Table 1, entry 12; for details see the experimental section).

Next, we investigated the varying loadings of **1a** and Et_2Zn, optimum temperature, and concentration of **2a** using a **1a** catalyst system (Table 2, entries 1–10). It was found that better enantioselectivity could not be obtained when lowering or increasing the loading of **1a** (Table 2, entries 2–4), although better yields could be obtained when increasing the loading of **1a** from 15 to 20 mol% (Table 2, entry 4).

Table 2. Optimization of the catalytic system for the enantioselective addition of diethylzinc to benzaldehyde catalyzed by **1a**

Entry[a]	**1a** (mol%)	Concentration of **2a**	Et_2Zn (equiv.)	Temp. (°C)	Time (h)	Yield (%)[b]	Ee (%)[c]
1	15	0.25	1.5	0	24	77	86(*S*)
2	10	0.25	1.5	0	30	70	71(*S*)
3	5	0.25	1.5	0	48	46	53(*S*)
4	20	0.25	1.5	0	20	83	78(*S*)
5	15	0.25	1.5	−20	40	75	85(*S*)
6	15	0.25	1.5	20	10	96	58(*S*)
7	15	0.5	1.5	0	10	91	74(*S*)
8	15	0.15	1.5	0	40	69	73(*S*)
9	15	0.25	2.0	0	20	91	85(*S*)
10	15	0.25	1.2	0	40	65	73(*S*)

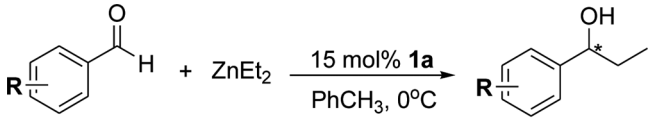
[a]Conditions: solvent: $PhCH_3$; Et_2Zn–hexane solution, similar to Table 1, entry 12.
[b]Isolated yields.
[c]The *ee* was determined with a chiral GC G-TA column, and the (*S*)-configuration was confirmed by comparison with the reported configuration.[11a,b]

Changing the reaction temperature (20 or −20 °C) could also not improve the enantioselectivity (Table 2, entries 5 and 6). Similarly, changing the concentration of **2a** and loading of Et_2Zn could not also improve the enantioselectivity (Table 2, entries 7–10). Herein, the $ZnEt_2$ may act as a Lewis acid and **1a** may act as a Lewis base in the catalyst system; increasing or decreasing the loading of **1a** or $ZnEt_2$ could not afford a best pKa value for the enantioselective addition of diethylzinc to aldehydes.[2e] The optimal catalyst system and reaction conditions were 15 mol% **1a**, 1.5 equiv. Et_2Zn, and 0.25 M of **2a** in $PhCH_3$ at 0 °C.

Substrate Generality

To study the generality of the **1a** catalyst system for the enantioselective addition of diethylzinc to various aromatic aldehydes, a number of aromatic aldehydes having electron-donating and electron-withdrawing groups, α- and β-naphthaldehydes, and (*E*)-cinnamaldehyde were examined under the optimized conditions summarized in Table 3. In comparison to the results obtained with **2a**, the poor electron-donating substituents, 4-Methyl group, gave similar results to **2a** (Table 3, entry 2 *vs* 1). However, the 2-methyl group led to a decrease in the *ee* and yield of the products **3c** after a longer time (Table 3, entry 3 *vs* entry 1). In the case of stronger electron-donating substituents, MeO group, lower yields with moderate *ee* (Table 3, entries 4 and 5) were obtained. Electron-withdrawing groups (F, Cl, Br, I, and CF_3, Table 4, entries 6–11) showed variation in the yields (67–81%) and *ees* (53–82%). In particular, the 4-(trifluoromethyl)benzaldehyde gave only 53% *ee* and yields (Table 3, entry 11). (*E*)-Cinnamaldehyde only gave 47% yield with 49% *ee* (Table 4, entry 12). Reaction of *a*- and β-naphthaldehydes **2j** and **2k** resulted with up to 83% *ee* and 72% *ee*, respectively (Table 4, entries 13 and 14). In general, moderately to good yields and enantioselectivities of the secondary alcohols **3a–n** were obtained (Table 4); electron-donating and bigger substituted aromatic aldehydes gave less favorable results than electron-withdrawing substituted aromatic

Table 3. 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**)	24	77	86(*S*)
2	4-Methyl-benzaldehyde (**2b**)	24	79	84(*S*)
3	2-Methyl-benzaldehyde (**2c**)	30	70	68(*S*)
4	4-Methoxy-benzaldehyde (**2d**)	48	68	60(*S*)
5	3-Methoxy-benzaldehyde (**2e**)	48	43	59(*S*)[d]
6	4-Fluoro-benzaldehyde (**2f**)	30	81	82(*S*)
7	4-Chloro-benzaldehyde (**2g**)	30	78	78(*S*)
8	2-Chloro-benzaldehyde (**2h**)	40	69	67(*S*)
9	4-Bromobenzaldehyde (**2i**)	40	72	71(*S*)
10	4-Iodobenzaldehyde (**2j**)	40	78	85(*S*)
11	4-(Trifluoromethyl)benzaldehyde (**2k**)	48	67	53(*S*)[e]
12	(*E*)-Cinnamaldehyde (**2l**)	48	47	49(*S*)[d]
13	Naphthalene-2-carbaldehyde (**2m**)	24	88	83(*S*)[d]
14	Naphthalene-1-carbaldehyde (**2n**)	30	77	72(*S*)[d]

[a]Conditions: solvent: $PhCH_3$; 0 °C; concentration of **2**: 0.25 M; Et_2Zn in hexane solution. The procedure is the same as in Table 1, entry 12.

[b]Isolated yields.

[c]The *ee* was determined with a chiral GC G-TA column, and the (*S*)-configuration was confirmed by comparison with the reported configuration.[11a–c]

[d]The *ee* was determined using a chiral OD-H or OD column.[8a–d]

[e]The *ee* was determined using a chiral OJ-H column.[11f–g]

aldehydes. These results revealed that the **1a** catalyst system was effective for the 1,2-addition of diethylzinc to various aromatic aldehydes.

Catalytic Mechanism Considerations

According to the previous works in the field of the enantioselective addition diethylzinc to aromatic aldehydes,[1–12] herein the Zn(II) complex might play a multifunctional role in this reaction. The metal moiety of the Zn(II) catalyst system act as a Lewis acid to activate the aldehyde and engender one species. On the other hand, the tertiary amine and OH groups of the catalyst system might act as a Lewis base to activate the $ZnEt_2$ and engender another species (Et^-). Then the activated $ZnEt_2$ transfers the species (Et^-) to the activated aldehyde and affords the corresponding product.

CONCLUSION

In summary, the chiral ligand **1a**, which derives from *L*-proline and was readily prepared in several steps from commercially available starting materials, showed

good catalytic activities and moderate enantioselectivities (up to 86% *ee*) in the asymmetric additions of diethylzinc to various aromatic aldehydes. Further investigation on the applications of these ligands for other asymmetric reactions is ongoing.

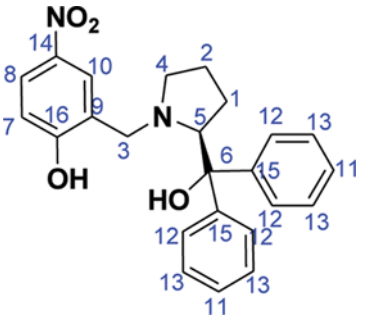
EXPERIMENTAL

All reactions were conducted in oven-dried glassware under an inert atmosphere of nitrogen with anhydrous solvents unless otherwise stated. The solvents were purified and dried according to standard procedures. Analytical thin-layer chromatography (TLC) was performed on alumina- or glass-backed silica plates (F254, 250-micron thickness) and visualized with untraviolet (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 gas chromatography (GC) and high-performance liquid chromatography (HPLC) techniques. Specific rotations were determined as $[\alpha]_D^{22}$ ($c = 0.5\,g/mL$ in CH_2Cl_2). Melting points are uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) chemical shifts in $CDCl_3$ are quoted as δ values relative to tetramethylsilane (TMS) ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.0$), respectively, in parts per million (ppm), and coupling constants are in hertz (Hz). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. High-resolution mass spectra (HRMS) were obtained using HPLC-Mass electrospray ionization (ESI) mode.

Materials

S-Proline (**4a**), 2-(bromomethyl)-4-nitrophenol **6a**, diethylzinc (Et_2Zn), and all aldehydes were commercially available and used without further purification unless otherwise noted. (*S*)-Prolinol (**5a**) was synthesized according to the literatures procedure.[13]

General Procedure for the Synthesis of Chiral Ligand 1a (see Scheme 1)



2-(Bromomethyl)-4-nitrophenol **6a** (0.3 g, 1.3 mmol) was added in one portion to a stirred and cooled solution of (*S*)-prolinol **5a** (1.32 g, 5.21 mmol) and K_2CO_3

(2.88 g, 20.84 mmol) in dry dimethylformamide (DMF, 10 mL). The ice bath was removed after the addition, and the resulting solution was allowed to stir at room temperature (about 25 °C) for 24 h before it was diluted with water (100 mL) and ethyl acetate (EA, 100 mL). The two phrases were separated, and the aqueous phase was extracted with EA (3 × 20 mL). The combined organic phases were washed with water (2 × 20 mL) and brine, dried (Na_2SO_4), and evaporated. The crude products were purified using column chromatography on silica gel (EA–hexane); the corresponding products were obtained as yellow solid in 71% yield, mp 85–87 °C, $[a]_D^{20} = +25.90$ (CH_2Cl_2, c = 0.5 g/mL). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95 (d, J = 2.4 Hz, 1H, Ar-H, C8-*H*), 7.92 (d, J = 2.7 Hz, 1H, Ar-H, C10-*H*), 7.08–7.68 (m, 10H, Ar-H, C11-C15-*H*), 6.69 (d, 1H, J = 9.0 Hz, ArH, C7-*H*), 4.95 (s, 2H, 2O*H*), 3.52 (s, 2H, -N-CH_2-), 2.11 (m, 2H, -CH_2CH_2N-), 1.61–1.64 (m, 4H, -CH_2CH_2CH_2N-), 1.25–1.27 (m, 1H, Ph_2CC*H*OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.9 (C16), 145.7 (C15), 140.1 (C14), 128.6 (C13), 128.5 (C12), 127.3 (C11), 126.1 (C10), 125.9 (C9), 121.8 (C8), 116.3 (C7), 80.1 (C6), 72.1 (C5), 44.1 (C4), 35.1 (C3), 29.3 (C2), 24.1 (C1) ppm. HRMS (ESI, CH_3OH): calcd. for ($M^+ + 1$) for $C_{24}H_{25}N_2O_4$: exact mass: 405.1814, molecular weight: 405.4663, found: 405.1800. Anal. for $C_{24}H_{24}N_2O_4$: C, 71.27%, found: 71.42%; H, 5.98%, found: 6.11%; and N%: 6.93%, found: 7.11%.

Typical Procedure for the Catalytic Addition of Diethylzinc to Aromatic Aldehydes

A solution ofdiethylzinc (1.0 M in hexane, 0.375 mL, 0.375 mmol) was added to a solution of **1a** (10.1 mg, 0.025 mmol) in $PhCH_3$ (1.0 mL) under a nitrogen atmosphere at 0 °C, and the reaction mixture was stirred for 30 min at room temperature (about 25 °C). Then, 1.0 mL dry $PhCH_3$ was added after the mixture completely evaporated under vacuum evaporation. The reaction mixture was then cooled to 0 °C, and the corresponding aromatic aldehyde (0.25 mmol) was added. Stirring continued for the 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 ^{1}H and ^{13}C NMR spectra with those published in the literature.[10a–h]

Selected Data

(*S*)-1-Phenyl-propan-1-ol (3a)[8c,11a–c]. 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)[8c,11a–c]. 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)[8c,11a–c]. 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)[8c,11a–c]. Enantiomeric excess was determined on a Chiral GC G-TA column (110 °C, 2.0 mL/min, $t_R = 41.1$ min, min, $t_R = 39.7$ min).

(*S*)-1-(3-Methoxy-phenyl)-propan-1-ol (3e)[11a–d]. 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)[11a–c]. 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)[8c,11a–c]. 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)[8c,11a–c]

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)[8c,11a–c]

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)[11a–c]

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)[8c,11a–h]

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)[8c,11a–h]

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)[8c,11a–h]

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)[8c,11a–h]

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).

ACKNOWLEDGMENT

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