

Enantioselective Addition of Diethylzinc to Aromatic Aldehydes Using Chiral Oxazoline-Based Ligands

A. E. Aydin^{a,*}

^a Department of Chemistry, Arts and Science Faculty, Hatay Mustafa Kemal University, Hatay, 31040 Turkey

*e-mail: aebruaydin@gmail.com

Received April 4, 2020; revised July 21, 2020; accepted July 22, 2020

Abstract—Chiral oxazoline ligands containing an aromatic ring were prepared from norephedrine and pyrrole-2-carbonitrile or 2-hydroxybenzoyl chloride. The synthesized ligands were used in the copper-catalyzed asymmetric addition of diethylzinc to aromatic aldehydes to provide optically active 1-arylpropan-1-ols with high conversion (92%) and enantioselectivity (up to 99% *ee*).

Keywords: asymmetric catalysis, enantioselective synthesis, chiral oxazoline-based ligands, 1,2-addition

DOI: 10.1134/S1070428020070271

INTRODUCTION

Enantioselective addition of dialkylzinc to carbonyl compounds is one of the most important reactions forming a new carbon–carbon bond in asymmetric synthesis [1–3]. The asymmetric addition of organometallic reagents to carbonyl substrates usually occurs with low enantiomeric excesses due to high chemical yields [4, 5]. On the other hand, enantioselective catalytic addition of dialkylzinc to aldehydes is by far one of the most studied enantioselective addition reactions. This reaction provides an important method for the synthesis of optically active secondary alcohols [6–9] that are widely found in nature and are also important building blocks in organic synthesis [9]. Enantioselective addition of diethylzinc to aldehydes was applied to obtain optically active lactones [10], cyclopropyl alcohols [11], as well as the natural product (+)-(*R*)-gossonorol which shows antifungal, anticancer, and antioxidant activities [12].

The enantioselectivity of a reaction depends mainly on the chiral ligand structure; therefore, search for new ligands for this important asymmetric transformation is a field of continuous interest. Among the chiral ligand families, primary amino alcohols [13–16] aminophenols [17, 18], diamines [19–21], disulfonamides [22–25], diols [26–28], and their derivatives have been widely employed in such reactions. Although a number of chiral ligands have been prepared, research focused on the development of new active, enantioselective, easily obtainable, and economically viable catalysts continues.

It is well known that oxazolines are synthetically and biologically significant molecular structures [29, 30]. These compounds are used as protecting groups for carboxylic acids and hydroxylamines [31]. Chiral oxazolines have also been extensively used in asymmetric syntheses as chiral catalysts [32, 33]. Chiral ligands containing one or more oxazoline rings have been synthesized and used to prepare enantiomerically pure compounds in many metal-catalyzed asymmetric reactions. Examples of widely used ligands of this type are pyridyloxazolines [34–37], bisoxazoline [38], bisoxazolinopyridine [39–43], BINOL-oxazoline [44–46], and phosphine-oxazoline [47–50] derivatives. These chiral ligands have been applied to a wide range of catalytic reactions including hydrosilylations [51–53], Diels–Alder reactions [54], cyclopropanations, [39, 55, 56], allylic alkylation [57], enantioselective addition of diethylzinc to aldehydes [58–61], and asymmetric Henry reactions [62–66].

However, only a few examples of chiral pyrrole oxazoline ligands have been reported so far. The first chiral pyrrolyloxazoline ligands with unsubstituted pyrrole nitrogen atom were synthesized and applied to copper-catalyzed asymmetric cyclopropanations by Brunner in 1998. However, the corresponding product was obtained with a low enantiomeric excess (3–14% *ee*) [67, 68]. The use of pyrrole-containing chiral oxazoline ligands to catalyze Henry reaction was reported by us in 2013 [69]. Chiral oxazoline-based ligands were synthesized from 1*H*-pyrrole-2-carbonitrile and 2-hydroxybenzoyl chloride and were applied

in copper-catalyzed asymmetric Henry reactions. There are a few examples of the use of oxazoline-based ligands in the addition of organozinc reagents to carbonyl compounds, and most of them utilized 4,5-dihydro-1,3-oxazoles containing a side-chain hydroxy group in the α - or β -position relative to C^2 [70–73].

Bolm et al. [74] described the application of the ferrocene ligand containing a chiral oxazoline unit to catalyze the reaction of diethylzinc with aromatic, aliphatic, and α,β -unsaturated aldehydes at 0°C in toluene with 83–94% yield and 78–95% *ee*. Reiser and co-workers [75] reported the activity of bis-oxazolines in the addition of diethylzinc to aromatic and aliphatic aldehydes. High enantioselectivities (83–95% *ee*) have been achieved, especially with aromatic aldehydes. In the case of aliphatic aldehydes, both yield and enantioselectivity could be considerably increased in the presence of a catalytic amount of *n*-BuLi.

To the best of our knowledge, chiral oxazoline ligands containing a pyrrole ring have not been used previously in the enantioselective addition of diethylzinc to aldehydes. Herein, chiral oxazolines synthesized from pyrrole-2-carbonitrile and 2-hydroxybenzoyl chloride were applied as ligands in the copper-catalyzed asymmetric addition of diethylzinc to aldehydes with excellent enantioselectivities.

RESULTS AND DISCUSSION

As described previously [69], chiral 2-oxazolines **3a**, **3b**, **4a**, and **4b** were synthesized by reacting both enantiomers of norephedrine with 1*H*-pyrrole-2-carbonitrile (**1**) or 2-hydroxybenzoyl chloride as shown in Scheme 1. Taking into account successful application of these ligands in the enantioselective Henry reaction [69], we envisioned that this catalytic system should also be suitable for the addition of diethylzinc to aldehydes. We started our investigation by using benzalde-

hyde (**5a**) as a model substrate and the addition reaction was performed at 0°C in toluene for 12 h in the presence of 2 mol % of chiral ligands **3a**, **3b**, **4a**, and **4b**. The results are summarized in Table 1. The use of enantiomeric chiral ligands (4*S*,5*R*)-**3a** and (4*R*,5*S*)-**3b** led to the opposite configurations of the resulting secondary alcohol **6a** with 80 and 78% *ee*, respectively. It was found that the absolute configuration of **6a** is determined mainly by the stereogenic centers of norephedrine on chiral ligands. Chiral ligand (4*S*,5*R*)-**3a** with the *R* configuration at the OH-bearing carbon gave the *S* isomer, whereas chiral ligand (4*R*,5*S*)-**3b** gave rise to (*R*)-**6a** (Table 1, entry nos. 1, 2). Thus, the configuration of **6a** depended on the configuration of the alcohol part of the chiral ligand. In the presence of ligands (4*S*,5*R*)-**4a** and (4*R*,5*S*)-**4b**, addition product **6a** was obtained in 82% yield with 78 and 79% *ee*, respectively (Table 1, entry nos. 3, 4).

Since (4*R*,5*S*)-**3b** showed the highest enantioselectivity in the addition of diethylzinc to benzaldehyde, it was selected for further optimization of the reaction conditions, including solvent, chiral ligand loading, metal catalyst, reaction time, and temperature. The results are listed in Tables 2 and 3. Moderate yields and medium enantioselectivities were obtained in chlorinated solvents such as chloroform and methylene chloride (Table 2, entry nos. 1 and 2), as well as in a polar protic solvent such as methanol (entry no. 6). Lower enantioselectivity was also achieved in diethyl ether, acetonitrile, and THF (entry nos. 3–5). The highest enantioselectivity (84% *ee*) and 83% yield were observed in toluene (entry no. 7). When the loading of chiral ligand (4*R*,5*S*)-**3b** was increased to 20 mol %, both yield and *ee* value increased to 79 and 87%, respectively (entry no. 8). An increase in the loading of chiral ligand from 10 to 30 mol % led to a significant increase in the yield (from 83 to 87%; entry nos. 8, 9) without any change

Scheme 1.

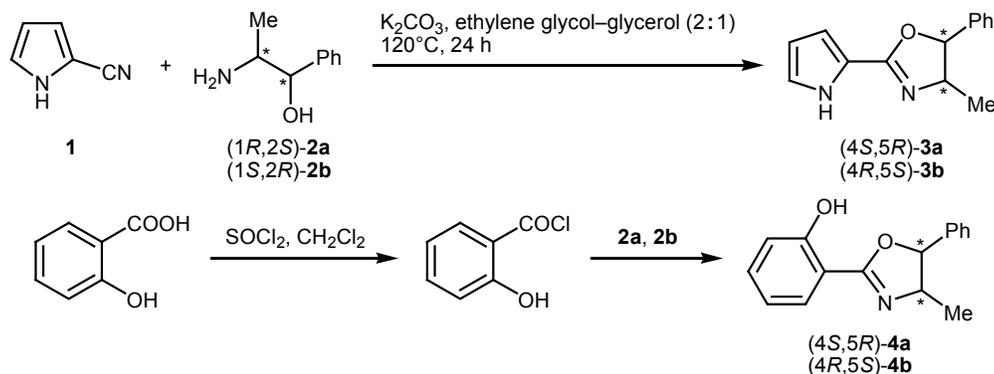
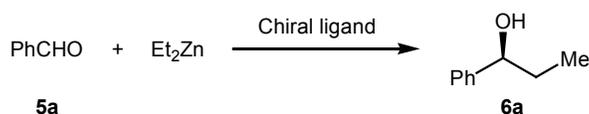


Table 1. Enantioselective addition of diethylzinc to benzaldehyde in the presence of chiral ligands **3a**, **3b**, **4a**, and **4b**^a

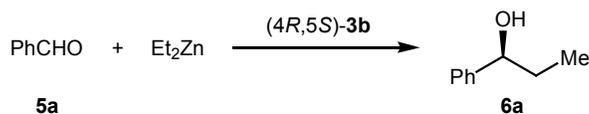
Entry no.	Ligand no.	Yield, ^b %	<i>ee</i> , ^c %	Configuration ^d
1	(4 <i>S</i> ,5 <i>R</i>)- 3a	75	78	<i>S</i>
2	(4 <i>R</i> ,5 <i>S</i>)- 3b	74	80	<i>R</i>
3	(4 <i>S</i> ,5 <i>R</i>)- 4a	82	78	<i>S</i>
4	(4 <i>R</i> ,5 <i>S</i>)- 4b	82	79	<i>R</i>

^a The reactions were carried out in methylene chloride using 1 mmol of benzaldehyde (**5a**), 10 mol % of Cu(OAc)₂·H₂O, and 2.2 mmol of diethylzinc (1 M solution in hexane) at 0°C to room temperature.

^b Yield refers to the pure product after column chromatography.

^c The *ee* values were determined by HPLC with a Chiralcel OD-H column.

^d The absolute configurations were assigned by comparison of HPLC retention time with literature data [76–78].

Table 2. Enantioselective addition of diethylzinc to benzaldehyde (**5a**) under different conditions

Entry no.	Ligand, mol %	Solvent	Temperature, °C	Yield, ^a %	<i>ee</i> , ^b %
1	10	Methylene chloride	0 to room temp.	74	80
2	10	Chloroform	0 to room temp.	68	72
3	10	Diethyl ether	0 to room temp.	75	48
4	10	Acetonitrile	0 to room temp.	73	52
5	10	Tetrahydrofuran	0 to room temp.	65	50
6	10	Methanol	0 to room temp.	80	65
7	10	Toluene	0 to room temp.	83	84
8	20	Toluene	0 to room temp.	79	87
9	30	Toluene	0 to room temp.	87	85
10	20	Toluene	0	82	78
11	20	Toluene	–20	62	55
12	20	Toluene	–50	36	0

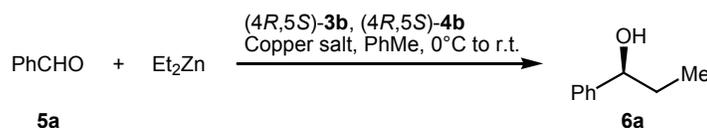
^a Yield of **6a** isolated by column chromatography.

^b The *ee* values were determined by HPLC with a Chiralcel OD-H column.

in the *ee* value. When the reaction was performed at 0°C, the *ee* value of the addition product was 78% with 82% yield (Table 2, entry no. 10). When the reaction temperature was reduced from room temperature to –20°C, the product was obtained in 62% yield with 55% *ee* (entry no. 11). A racemic mixture of (*R*)- and (*S*)-secondary alcohol was obtained when the reaction was carried out at –50°C (entry no. 12).

On the basis of the above experimental data, the optimized reaction conditions were toluene as solvent, 0°C to room temperature, 24 h, 20 mol % of (4*R*,5*S*)-**3b** as chiral ligand.

The effect of various copper salts was examined using ligands (4*R*,5*S*)-**3b** and (4*R*,5*S*)-**4b**. The results are summarized in Table 3. The copper source significantly affected the reactivity and enantioselectivity (Table 3, entry nos. 2–8). The reactions with CuI, CuCl, CuBr, Cu(OAc)₂·H₂O, Cu(MeCN)ClO₄, and Cu(OTf)₂ afforded moderate to good yields and high *ee* values (Table 3, entry nos. 2–3). In the presence of 20 mol % Cu(OAc)₂·H₂O and (4*R*,5*S*)-**3b** and (4*R*,5*S*)-**4b**, the corresponding products were obtained in 77 and 78% yield with 94 and 93% *ee*, respectively (entry no. 5). By keeping the ligand (4*R*,5*S*)-**3b** and

Table 3. Enantioselective addition of diethylzinc to benzaldehyde (**5a**) in the presence of different copper salts and ligands **3b** and **4b**^a

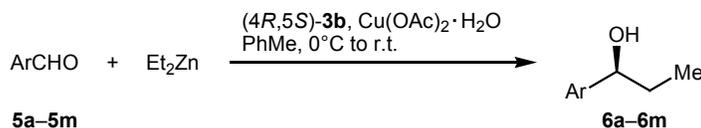
Entry no.	Copper salt	(4R,5S)-3b		(4R,5S)-4b	
		yield, ^b %	ee, ^c %	yield, ^b %	ee, ^c %
1	None	79	87	76	85
2	CuI	78	93	77	92
3	CuCl	75	91	75	90
4	CuBr	72	92	74	92
5	Cu(OAc) ₂ ·H ₂ O	77	94	78	93
6	Cu(OTf) ₂	70	65	72	68
7	Cu(MeCN)ClO ₄	75	88	76	90
8 ^d	Cu(OAc) ₂ ·H ₂ O	77	96	77	95

^a The reactions were carried out in toluene using 1 mmol of benzaldehyde (**5a**), 20 mol % of copper salt, 20 mol % of ligand **3b** or **4b**, and 2.2 mmol of diethylzinc (1 M solution in hexane) at 0°C to room temperature.

^b Yield refers to pure product after column chromatography.

^c The *ee* values were determined by HPLC with a Chiralcel OD-H column.

^d 10 mol % Cu(OAc)₂·H₂O.

Table 4. Enantioselective addition of diethylzinc to aromatic aldehydes in the presence of chiral ligand (4R,5S)-3b^a

Entry no.	Aldehyde	Product	Yield, ^b %	ee, ^c %
1	Benzaldehyde (5a)	6a	77	96
2	2-Methoxybenzaldehyde (5b)	6b	80	84
3	3-Methoxybenzaldehyde (5c)	6c	78	89
4	4-Methoxybenzaldehyde (5d)	6d	75	94
5	2-Methylbenzaldehyde (5e)	6e	85	80
6	3-Methylbenzaldehyde (5f)	6f	75	90
7	4-Methylbenzaldehyde (5g)	6g	76	90
8	3-Chlorobenzaldehyde (5h)	6h	72	90
9	4-Chlorobenzaldehyde (5i)	6i	75	92
10	4-(Trifluoromethyl)benzaldehyde (5j)	6j	68	99
11	Naphtalene-1-carbaldehyde (5k)	6k	72	86
12	Naphtalene-2-carbaldehyde (5l)	6l	83	60
13	Thiophene-2-carbaldehyde (5m)	6m	74	83

^a The reactions were carried out in toluene using 1 mmol of benzaldehyde (**5a**), 20 mol % of copper salt, 20 mol % of ligand **3b** or **4b**, and 2.2 mmol of diethylzinc (1 M solution in hexane) at 0°C to room temperature.

^b Yield refers to pure product after column chromatography.

^c The *ee* values were determined by HPLC with a Chiralcel OD-H column.

(4*R*,5*S*)-**4b** at 20 mol % and reducing the Cu(OAc)₂·H₂O loading from 20 to 10 mol %, the enantioselectivity was increased to 96 and 95% *ee*, respectively, without any change in the yield (entry nos. 5, 8). Thus, the most suitable metal-to-ligand ratio proved to be 2:1 (entry no. 8).

Since ligand (4*R*,5*S*)-**3b** showed the highest enantioselectivity, it was used in the enantioselective additions of diethylzinc to different aromatic aldehydes with electron-withdrawing and electron-donating substituents. The results are summarized in Table 4. It appeared that the position of substituent on the phenyl ring had significant effect on the reaction. *para*-Substituted substrates (entry nos. 4, 7, 9) tended to give higher enantioselectivities. Lower *ee* values were observed for aromatic aldehydes bearing substituents at the *ortho* position (entry nos. 2, 5), presumably due to steric hindrance. Electron-withdrawing substituents (e.g., CF₃; entry no. 10) gave higher enantioselectivity than did electron-donating groups. It is known that electron-withdrawing groups in aromatic aldehydes increase the electrophilicity of the carbonyl carbon atom, while electron-donating groups reduce it. Substrates with an electron-withdrawing substituent were expected to react at a higher rate, leading to higher enantioselectivity. For instance, heteroaromatic thiophene-2-carbaldehyde in the presence of chiral ligand (4*R*,5*S*)-**3b** afforded diethylzinc addition product with 83% *ee* (Table 4, entry no. 13).

In summary, the use of chiral oxazoline ligands containing a pyrrole ring in copper-catalyzed enantioselective addition of diethylzinc to aromatic aldehydes has been reported for the first time. The reactions provide high yields and enantioselectivities. Studies aimed at defining the utility of these ligands for other substrates and reactions are now in progress.

EXPERIMENTAL

All reactions were carried out under argon atmosphere. Commercially available reagents and solvents were used as received. Tetrahydrofuran and diethyl ether were purified by distillation over sodium in the presence of benzophenone; methylene chloride and toluene were dried by distillation over calcium hydride. Column chromatography was performed on silica gel 60 (230–400 mesh). Analytical thin-layer chromatography was performed on silica gel 60 F254 plates (Merck); spots were visualized under UV light and by staining with phosphomolybdic acid. The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 400

spectrometer (400 MHz for ¹H) using CDCl₃ as solvent and tetramethylsilane as internal standard. Enantiomeric excesses (% *ee*) were determined by HPLC with an Agilent 1100 Series liquid chromatograph using different chiral columns (see below).

Chiral ligands **3a**, **3b**, **4a**, and **4b** were synthesized according to our previous report [69] (Scheme 1).

General procedure for enantioselective addition of diethylzinc to aromatic aldehydes. A 1.0 M solution of diethylzinc in hexane (2.2 mmol) was added via a syringe over a period of 5 min to a solution of chiral ligand **3a**, **3b**, **4a**, or **4b** (20 mol %) and Cu(OAc)₂·H₂O (20 mol %) in dry toluene (5 mL) at 0°C under argon. The mixture was stirred for 1 h at that temperature, aldehyde **5a–5m** (1 mmol) was added, and the mixture was stirred for 24 h at room temperature (TLC). The reaction was quenched with 5 mL of 1 M aqueous HCl. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3×15 mL), and the combined organic phases were washed with 10 mL of brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The crude product was purified by flash column chromatography (EtOAc–hexane, 1:5). Known compounds were characterized by comparing their ¹H NMR spectra with those given in [79–85]. The absolute configuration of the products was assigned by comparison with published data [79–85]. For details, see Supplementary Materials.

(*R*)-1-Phenylpropan-1-ol (6a). Yield 77%, *ee* 96% (Chiralcel OD-H column; eluent 10% propan-2-ol in hexane, flow rate 0.5 mL/min; detection at λ 254 nm; retention times 9.04 min for the *R* enantiomer and 11.79 min for the *S* enantiomer). ¹H NMR spectrum, δ, ppm: 0.94 t (3H, *J* = 7.4 Hz), 1.71–1.88 m (2H), 1.92–1.99 br.s (1H), 4.61 t (1H, *J* = 6.6 Hz, 1H), 7.26–7.42 m (5H).

(*R*)-1-(2-Methoxyphenyl)propan-1-ol (6b). Yield 80%, *ee* 84% [Chiralcel OD-H; 10% propan-2-ol in hexane, 0.5 mL/min; λ 254 nm; 12.21 min (*R*), 13.77 min (*S*)]. ¹H NMR spectrum, δ, ppm: 0.98 t (3H), 1.78–1.89 m (2H), 2.81 d (1H), 3.87 s (3H), 4.80–4.86 m (1H), 6.88–7.37 m (4H).

(*R*)-1-(3-Methoxyphenyl)propan-1-ol (6c). Yield 78%, *ee* 89% [Chiralpak OD-H; 2% propan-2-ol in hexane, 0.8 mL/min; λ 210 nm; 9.09 min (*R*), 11.97 min (*S*)]. ¹H NMR spectrum (300 MHz), δ, ppm: 0.96 t (3H, *J* = 7.5 Hz), 1.75–1.89 m (3H), 3.85 s (3H), 4.61 t (1H, *J* = 6.5 Hz), 6.79–6.89 m (1H), 6.90–6.99 m (2H), 7.25–7.32 m (1H).

(R)-1-(4-Methoxyphenyl)propan-1-ol (6d). Yield 75%, *ee* 94% [Chiralpak AD-H; 2% propan-2-ol in hexane, 0.8 mL/min; λ 210 nm; 14.26 min (*R*), 18.49 min (*S*)]. ^1H NMR spectrum, δ , ppm: 0.88 t (3H), 1.63–1.90 m (2H), 2.26–2.68 br.s (1H), 3.81 s (3H), 4.51 s (1H), 6.82–7.28 m (4H).

(R)-1-(2-Methylphenyl)propan-1-ol (6e). Yield 85%, *ee* 80% [Chiralpak AD-H, 1% propan-2-ol in hexane, 0.8 mL/min; λ 215 nm; 25.41 min (*R*), 30.08 min (*S*)]. ^1H NMR spectrum, δ , ppm: 1.02 t (3H, $J = 7.4$ Hz), 1.74–1.83 m (2H), 2.18 br.s (1H), 2.38 s (3H), 4.88 t (1H), 7.12–7.51 m (4H).

(R)-1-(3-Methylphenyl)propan-1-ol (6f). Yield 75%, *ee* 90% [Chiralcel OD-H; 5% propan-2-ol in hexane, 0.8 mL/min; λ 215 nm; 8.79 min (*R*), 10.14 min (*S*)]. ^1H NMR spectrum, δ , ppm: 0.95 t (3H, $J = 7.5$ Hz), 1.73–1.90 m (2H), 1.91 s (1H), 2.38 s (3H), 4.59 t (1H, $J = 6.7$ Hz), 7.09–7.23 m (3H), 7.23–7.29 m (1H).

(R)-1-(4-Methylphenyl)propan-1-ol (6g). Yield 76%, *ee* 90% [Chiralpak AD-H; 1% propan-2-ol in hexane, 0.8 mL/min; λ 215 nm; 28.86 min (*R*), 33.46 min (*S*)]. ^1H NMR spectrum, δ , ppm: 0.95 t (3H, $J = 7.5$ Hz), 1.73–1.91 m (2H), 1.92 br.s (1H), 2.39 s (3H), 4.59 t (1H, $J = 6.7$ Hz), 7.20 d (2H, $J = 8.1$ Hz), 7.27 d (2H, $J = 8.1$ Hz).

(R)-1-(3-Chlorophenyl)propan-1-ol (6h). Yield 72%, *ee* 90% [Daicel Chiralcel OJ-H; 2% propan-2-ol in hexane, 0.8 mL/min; λ 210 nm; 8.79 min (*S*), 10.14 min (*R*)]. ^1H NMR spectrum, δ , ppm: 0.93 t (3H, $J = 7.5$ Hz), 1.73–1.88 m (3H), 4.62 t (1H, $J = 6.4$ Hz), 7.21–7.28 m (2H), 7.28–7.34 m (1H), 7.34–7.38 m (1H).

(R)-1-(4-Chlorophenyl)propan-1-ol (6i). Yield 75%, *ee* 92% [Chiralcel OD-H; 5% propan-2-ol in hexane, 0.8 mL/min; λ 215 nm; 8.98 min (*S*), 9.56 min (*R*)]. ^1H NMR spectrum, δ , ppm: 0.86 t (3H, $J = 7.5$ Hz), 1.63–1.82 m (2H), 2.31–2.39 br.s (1H), 4.54 t (1H, $J = 6.8$ Hz), 7.18–7.34 m (4H).

(R)-1-[4-(Trifluoromethyl)phenyl]propan-1-ol (6j). Yield 68%, *ee* 99% [Chiralcel OD-H column; 10% propan-2-ol in hexane, 1.0 mL/min; λ 220 nm; 12.58 min (*R*), 14.38 min (*S*)]. ^1H NMR spectrum, δ , ppm: 0.92 t (3H, $J = 7.4$ Hz), 1.69–1.82 m (2H), 2.30 br.s (1H), 4.65 t (1H, $J = 6.2$ Hz), 7.38–7.68 m (4H).

(R)-1-(Naphthalen-1-yl)propan-1-ol (6k). Yield 72%, *ee* 86% [Chiralcel AD-H; 5% propan-2-ol in

hexane, 0.8 mL/min; λ 210 nm; 18.33 min (*S*), 21.41 min (*R*)]. ^1H NMR spectrum, δ , ppm: 1.05 t (3H, $J = 7.5$ Hz), 1.91–2.08 m (2H), 2.16 s (1H), 5.44 d.d (1H, $J = 7.5, 5.0$ Hz), 7.48–7.59 m (3H), 7.67 d (1H, $J = 7.1$ Hz), 7.82 d (1H, $J = 8.1$ Hz), 7.88–7.95 m (1H), 8.11–8.18 m (1H).

(R)-1-Naphthalen-2-yl)propan-1-ol (6l). Yield 83%, *ee* 60% [Chiralcel AS-H; 2% propan-2-ol in hexane, 0.8 mL/min; λ 210 nm; 9.84 min (*S*), 17.73 min (*R*)]. ^1H NMR spectrum, δ , ppm: 1.02 t (3H, $J = 7.3$ Hz), 1.83–2.07 m (2H), 2.96 s (1H), 5.31 t (1H, $J = 6.4$ Hz), 7.43–8.16 m (7H).

(R)-1-(Thiophen-2-yl)propan-1-ol (6m). Yield 74%, *ee* 92% [Chiralcel OD-H; 10% propan-2-ol in hexane, 1.0 mL/min; λ 220 nm; 32.72 min (*R*), 34.61 min (*S*)]. ^1H NMR spectrum, δ , ppm: 0.97 t (3H, $J = 7.4$ Hz), 1.75–1.96 m (2H), 3.15 br.s (1H), 4.79 t (1H, $J = 6.5$ Hz), 6.91–7.28 m (3H).

FUNDING

This research (1005M0115) is financially supported by the Scientific Research Commission of Mustafa Kemal University.

CONFLICT OF INTEREST

The author declares the absence of conflict of interest.

SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at <https://doi.org/10.1134/S1070428020070271> and are accessible for authorized users.

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