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Bifunctional Schiff base/Ti(IV) catalysts for enantioselective cyanoformylation of aldehydes with ethyl cyanoformate

Nan Ji[a], Lin Yao[a], Wei He[a]* and Yurong Li[b]*

A new bifunctional titanium/Schiff base catalyst was developed for the enantioselective cyanoformylation of aldehydes with ethyl cyanoformate. The reaction proceeded smoothly with a mild reaction condition to afford the cyanohydrin ethyl carbonates in high yields (up to 96%) and good enantioselectivities (up to 85% enantiomeric excess). Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: Schiff base; asymmetric catalysis; titanium; cyanoformylation; ethyl cyanoformate

Introduction

Optically active cyanohydrins serve as highly versatile synthetic building blocks in biologically active products.[1] They are stable in the presence of moisture and air, and can therefore be widely used in the synthesis of α-amino alcohols and β-substituted unsaturated nitriles.[2] In the last two decades, HCN, K(Na)CN and TMSCN (trimethylsilyl cyanide) have been used as the cyanide source to react with carbonyl compounds to provide the optically active cyanohydrins.[3,4] Recently, scientists have investigated some more promising cyanide candidates in this reaction. Ethyl cyanoformate[5] ($NCCO_2Et$) has been applied in the enantioselective cyanoformylation of aldehydes more frequently than others because it is more stable and less toxic. The groups of Deng,[6] Shibasaki,[7] North,[8] Saá,[9] Chinchilla,[10] Johnson[11] and Moberg[12] have devoted much effort to this field. Although their experiments have generally achieved high enantioselectivities and yields, some of them still needed the multicomponent metal complex,[13] harsh reaction conditions[14] and sometimes the presence of alkaline additives.[10,12]

More recently, Feng reported the enantioselective cyanoformylation of aldehydes activated by a series of combined catalyst systems based on bifunctional catalysis methods[13,15] and the self-assembly concept[16] (Fig. 1). Focusing on these catalyst systems, the combination of BINOL derivatives (1) with chiral amines (2,3) or 2,2′-biphenol derivatives (5) with Cinchona alkaloid (4) or use of Schiff base (6) together with cinchonine (2) could improve enantioselectivity and reactivity. Based on these reports, we hope to synthesize a series of single molecules made up of the two interesting parts (uncovered hydroxyl and Cinchona alkaloid) and explore whether they can activate the cyanoformylation of aldehydes with ethyl cyanoformate. This study may also help us to understand the possible transition state in this transformation more easily.

Very recently, we have developed a series of novel Schiff base ligands from Cinchona alkaloids and salicylaldehyde derivatives,[17,18] and the experimental results showed that they could be successfully applied in the copper-catalyzed asymmetric Henry reaction of various aldehydes. Herein, we wish to report the catalytic performance of these Schiff base ligands in the asymmetric addition of ethyl cyanoformate to aldehydes.

Results and Discussion

The Schiff base ligands 1a–g were synthesized according to our previous reports[17,18] and 1 h was synthesized following Jacobsen's procedure[19] (Fig. 2). 1a–d and 1f were prepared by condensation of the Cinchona alkaloid-derived 9-amino compounds with salicylaldehyde derivatives. 1b was methylated with dimethyl sulfate to afford 1e. 1 g was obtained by the reaction of 1,2-benzenedialdehyde with (8S,9S)-9-amino-(9-deoxy)-epiquinine.[17] The catalytic performance of these ligands was evaluated.

Initially, the addition of $NCCO_2Et$ to benzaldehyde in CH_2Cl_2 at −20°C in the presence of chiral Schiff base 1a (5 mol%) was investigated. Unfortunately, no reaction was observed after 48 h (Table 1, entry 1), which indicated that 1a alone could not promote this reaction. Interestingly, in the presence of 1a (5 mol%) and tetraisopropyl titanate [Ti(O*i*-Pr)$_4$] (5 mol%) (in situ), the reaction proceeded smoothly and gave the product in 75% yield and 10% enantiomeric excess (ee) (Table 1, entry 2) under the same conditions. Other metal precursors were also investigated. It was found that when Ti(O*i*-Pr)$_4$ was replaced by $TiCl_4$, enantioselectivity reduced from 10% to 7% ee (Table 1, entry 3). When $Cu(OTf)_2$ was used in this reaction, only trace products could be observed (Table 1, entry 4). Although the use of $Cu(OAc)_2.H_2O$

* *Correspondence to: Wei He, Department of Chemistry, School of Pharmacy, Fourth Military Medical University, Xi'an 710032, People's Republic of China. E-mail: weihechem@fmmu.edu.cn; Yurong Li, Department of Radiation Medicine, Fourth Military Medical University, Xi'an 710032, People's Republic of China. E-mail: 722lyr@fmmu.edu.cn*

a *Department of Chemistry, School of Pharmacy, Fourth Military Medical University, Xi'an 710032, People's Republic of China*

b *Department of Radiation Medicine, Fourth Military Medical University, Xi'an 710032, People's Republic of China*

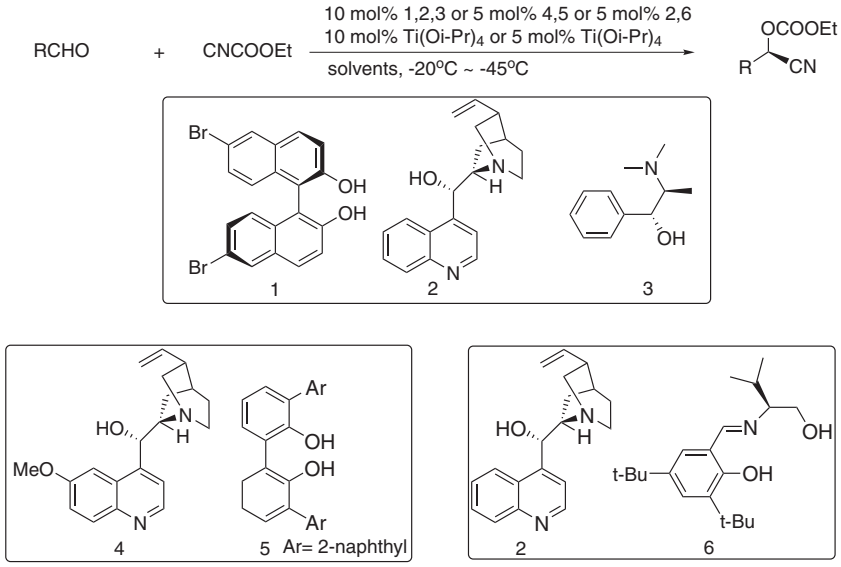


Figure 1. Feng's combined catalyst systems for cyanoformylation of aldehydes with ethyl cyanoformate.

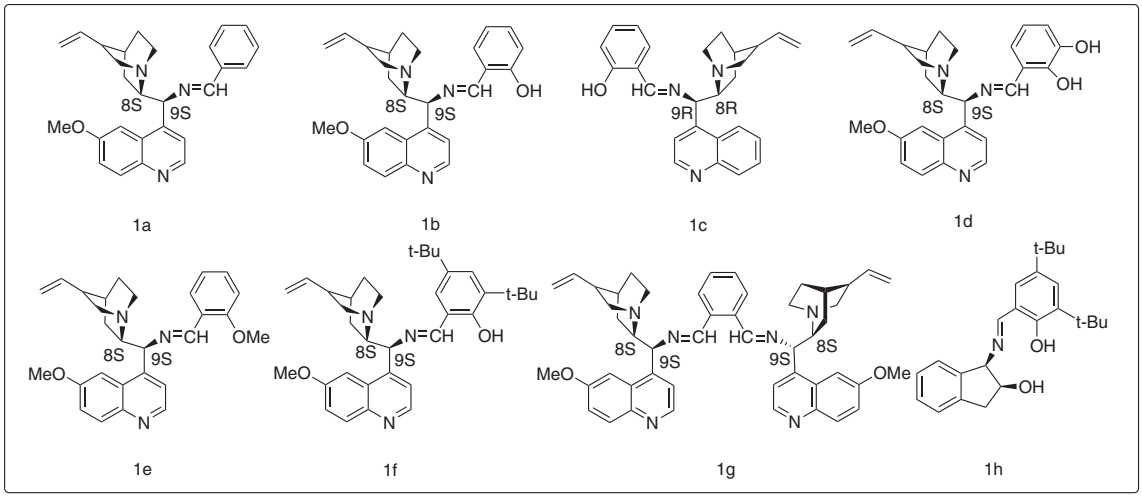


Figure 2. Schiff base ligands 1a–h.

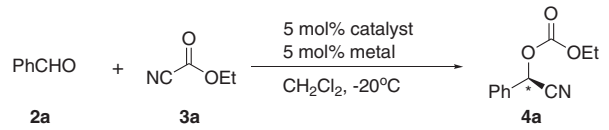
or $VOSO_4.XH_2O$ respectively as the metal source together with 1a could drive the reaction with good reactivity, only racemic products were obtained (Table 1, entries 5 and 6). Apparently, Ti(O*i*-Pr)$_4$ was the best choice.

Subsequently, catalytic cyanoformylation using a series of chiral Schiff bases 1a–h (Fig. 2) combined with Ti(O*i*-Pr)$_4$ was examined. As shown in Table 1, it was noteworthy that the skeleton of the quinine has a more perceptible influence on enantioselectivity than cinchonine (Table 1, entry 7 vs. 8), and the absolute configuration of the product is determined by the C_8-position and C_9-position configuration of Cinchona alkaloids. Moreover, by comparison of the catalytic performance of the ligands 1a, 1b, 1d, 1e, 1f, all of which were derived from quinine, we can conclude that the hydroxyl group from salicylaldehyde was crucial for chiral induction (Table 1, entries 2, 10 vs.7, 9, 11), which is consistent with Feng's observation. Chiral Schiff base 1f derived from 9-aminoquinine and 3,5-di-tert-butylsalicylaldehyde[18] turned out to have the best architecture (Table 1, entry 11). C_2 symmetric chiral Schiff base 1 g gave the product with high yield but poor enantioselectivity (Table 1, entry 12). When the skeleton of quinine was replaced by chiral indene derivative (1 h),[19] the rate of this reaction was enhanced, while enantioselectivity declined to a great extent (Table 1, entry 13).

It was found that the solvent frequently influenced reactivity and enantioselectivity in various catalytic processes.[20] In order to improve enantioselectivity, the catalytic activity of chiral Schiff base 1f with Ti(O*i*-Pr)$_4$ has been further evaluated for this reaction in various solvents (Table 2). Lower enantioselectivity was obtained from ether, acetonitrile and hexane (Table 2, entries 1–3). In the chlorinated solvents $CHCl_3$ and CH_2Cl_2, moderate yields and medium enantioselectivities were observed (Table 2, entries 4 and 5). No corresponding product had been detected in toluene or THF (Table 2, entries 6 and 7). Polar protic solvents isopropanol, *n*-propanol and ethanol showed a similar level of activity enantioselectivity (Table 2, entries 8–10). Surprisingly, performing the reaction in glycerol led to a racemic product. Other conditions such as alkaline additives and reaction time were also examined. However, the enantiomeric excesses of the products were not satisfactory. Considering the balance between enantioselectivity and yield, ethanol was selected as the optimized solvent for this reaction (Table 2, entry 10).

The effect of several concentrations of benzaldehyde was also tested under our catalytic system (Table 3), and experiments

Table 1. Screening of the Schiff base ligands and metals in the enantioselective cyanoformylation of benzaldehyde



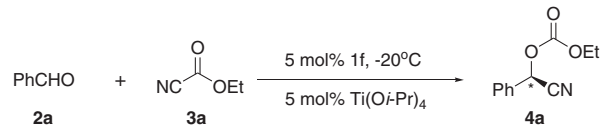
Entry[a]	Catalyst	Metal	Time (h)	Yield (%)[b]	ee (%)[c]
1	1a	—	48	trace	—
2	1a	Ti(O*i*-Pr)$_4$	12	75	10 (*R*)
3	1a	$TiCl_4$	12	70	7 (*R*)
4	1a	$Cu(OTf)_2$	48	Trace	—
5	1a	$Cu(OAc)_2 \cdot H_2O$	12	72	Rac.
6	1a	$VOSO_4 \cdot XH_2O$	10	76	Rac.
7	1b	Ti(O*i*-Pr)$_4$	12	71	17 (*R*)
8	1c	Ti(O*i*-Pr)$_4$	12	73	12 (*S*)
9	1d	Ti(O*i*-Pr)$_4$	12	70	21 (*R*)
10	1e	Ti(O*i*-Pr)$_4$	12	75	11 (*R*)
11	1f	Ti(O*i*-Pr)$_4$	12	70	55 (*R*)
12	1 g	Ti(O*i*-Pr)$_4$	12	83	Rac.
13	1 h	Ti(O*i*-Pr)$_4$	7	81	5 (*R*)

[a]All reaction were performed with benzaldehyde (0.25 mmol) and $NCCO_2Et$ (0.375 mmol) in CH_2Cl_2 (1 ml) at −20°C.

[b]Isolated yield.

[c]Enantiomeric excess, determined by HPLC on a Chiralcel OD-H column. The absolute configurations were determined by comparison with the literature data.[15]

Table 2. Screening the solvents in the enantioselective cyanoformylation of benzaldehyde



Entry[a]	Solvent	Time (h)	Yield (%)[b]	Ee (%)[c]
1	Et_2O	12	75	17
2	CH_3CN	12	80	9
3	Hexane	12	73	25
4	$CHCl_3$	12	75	35
5	CH_2Cl_2	12	70	55
6	toluene	48	Trace	—
7	THF	48	Trace	—
8	*i*-PrOH	8	78	71
9	*n*-PrOH	8	77	73
10	ethanol	8	82	77
11	glycerol	8	90	Rac.

[a]All reactions were performed with benzaldehyde (0.25 mol) and $NCCO_2Et$ (0.375 mmol) in solvent (1 ml) with 1f (5 mol%) and Ti(O*i*-Pr)$_4$ (5 mol%) at −20°C for 8–48 h.

[b]Isolated yield.

[c]Determined by HPLC on a Chiralcel OD-H column. The absolute configuration was *R* was determined by comparison with literature data.[15]

Table 3. Effects of concentration and temperature on the Ti(O*i*-Pr)$_4$ /1f system catalyzed enantioselective cyanoformylation of benzaldehyde

Entry[a]	Benzaldehyde conc. (mol L^{-1})	Temperature (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	0.25	−20	8	82	77
2	0.125	−20	8.5	80	85
3	0.08	−20	8.5	78	73
4	0.06	−20	8.5	78	70
5	0.125	−30	12	70	79
6	0.125	0	6	93	83
7	0.125	r.t.	4.5	95	71

[a]Reactions were carried out on varied content of benzaldehyde in ethanol with catalyst (5 mol%) and $NCCO_2Et$ (1.5 equiv.).

[b]Isolated yield.

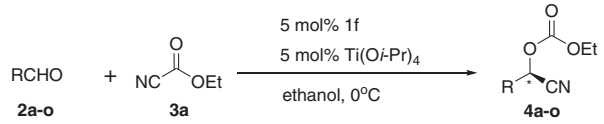
[c]Enantiomeric excess, determined by HPLC on a Chiralcel OD-H column. The absolute configuration was *R*, determined by comparison with literature data.[15]

revealed that the concentration of benzaldehyde had an important effect on the reaction rate and enantioselectivity. When the concentration of benzaldehyde was reduced from 0.25 M to 0.125 M, the enantioselectivity increased up to 85% ee (Table 3, entry 1 vs. 2). Further lowering the concentration of benzaldehyde was detrimental to ee value (Table 3, entry 2 vs. entries 3 and 4). We also tested the effects of reaction temperature. Reducing the temperature from −20°C to −30°C did not improve the enantioselectivity and lowered the yield (Table 3, entry 5). On the other hand, when the temperature was enhanced from −20°C to 0°C, the yield of the reaction increased to 93%, while the enantioselectivity was not significantly reduced (Table 3, entry 6). When the reaction temperature was further increased to room temperature from 0 °C, the enantioselectivity decreased from 83% to 71% ee (Table 3, entry 7). To summarize, the optimized reaction conditions for the model reaction were Ti(O*i*-Pr)$_4$ (5 mol%), Schiff base 1f (5 mol%), 0.125 M aldehydes, at 0°C in ethanol.

Under the optimized conditions, the generalities of this methodology for a series of aldehydes were investigated, and the results are summarized in Table 4. Almost all the tested substrates, including aromatic, heteroaromatic and aliphatic aldehydes, gave high yields (up to 96%) and moderate to good enantioselectivities (up to 85% ee). It can be seen that the aromatic aldehydes with electron-donating group gave similar results to benzaldehyde, except for heliotropin (Table 4, entries 2–11). Among them, 2-methoxybenzaldehyde (Table 4, entry 6) gave the highest enantioselectivity (85% ee). On the other hand, the aromatic aldehydes with electron-withdrawing group gave lower ee value, even when adjusting the temperature to −50°C (Table 4, entries 10 and 11). The substrate scope was also expanded to heterocyclic aldehydes and aliphatic aldehydes (Table 4, entries 12–15). Furfural 2l gave the product in highest yield with 73% ee under −20°C (Table 4, entry 12). Under the same temperature, pyridylaldehyde 2m gave the product in 93% yield with 61% ee (Table 4, entry 13). The aliphatic 3-phenylpropionaldehyde 2n resulted also in a moderate enantioselectivity (Table 4, entry 14). When amylcinnamaldehyde 2o was subjected to this reaction, 1,2-addition product was afford in 90% yield and 71% ee (Table 4, entry 15).

Based on previous mechanism studies[5,7,13] of the cyanoformylation of aldehydes with $NCCO_2Et$ and the experiments above, we proposed a potential transition state to reveal the possible

Table 4. $Ti(Oi\text{-}Pr)_4$ /1f system-catalyzed enantioselective cyanoformylation of aldehydes



Entry[a]	Substrate	Time (h)	Yield (%)[b]	ee (%)[c]
1	benzaldehyde (2a)	6	93	83
2	3-methylbenzaldehyde (2b)	6	91	77
3	4-methylbenzaldehyde (2c)	6	92	75
4	3-methoxybenzaldehyde (2d)	6	94	71
5	4-methoxybenzaldehyde (2e)	6	93	73
6	2-methoxybenzaldehyde (2f)	6	90	85
7	4-tert-butylbenzaldehyde (2 g)	6	91	75
8	4-isobutylbenzaldehyde (2 h)	6	92	71
9	heliotropin (2i)	10	94	65
10[d]	4-fluorobenzaldehyde (2j)	12	95	71
11[d]	4-chlorobenzaldehyde (2 k)	12	95	63
12[e]	furfural (2 l)	10	96	73
13[e]	pyridylaldehyde (2 m)	10	93	61
14	3-Phenylpropionaldehyde (2n)	6	91	67
15[e]	amylcinnamaldehyde (2o)	10	90	71

[a]All reactions were performed with aldehydes (0.25 mmol) and $NCCO_2Et$ (0.375 mmol) in ethanol (2 ml) at 0°C, unless otherwise indicated.

[b]Isolated yield.

[c]Determined by HPLC on a Chiralcel OD-H or Chiralcel AD-H column.

[d]Reaction temperature −50°C.

[e]Reaction temperature −20°C.

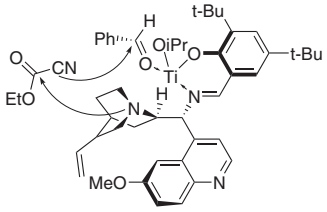


Figure 3. Proposed transition state for this reaction.

mechanism of this asymmetric catalytic reaction. As shown in Fig. 3, we considered that the hydroxyl group of salicylaldehyde and nitrogen from the Schiff base double bond coordinated with $Ti(Oi\text{-}Pr)_4$ might act as a Lewis acid to activate the carbonyl group, and the tertiary nitrogen atom of Cinchona alkaloid might act as a base to activate the $NCCO_2Et$. In this proposed working model, the activated cyanide would attack the aldehydes through the less hindered Re face, and then the corresponding product would be afforded. Nevertheless, the detailed catalytic mechanism still needs further investigation.

Conclusion

In summary, a new enantioselective catalytic cyanoformylation of aldehydes with $NCCO_2Et$ through an additive-free process was developed. By using the catalyst in situ prepared by chiral Schiff base 1f and $Ti(Oi\text{-}Pr)_4$, the reaction proceeded smoothly under mild conditions to provide products with high yields and good enantioselectivities (up to 96% yield and up to 85% ee). Further application and mechanism studies are ongoing in our laboratory.

Experimental

General Remarks

All reactions were run under an atmosphere of nitrogen using oven-dried glassware. Solvents were prepared before use by standard procedures. ^1H and ^{13}C NMR spectra were recorded on Mercury 400 MHz or JEOL JNM-LA 100 MHz spectrometers. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as internal standard, and coupling constants are reported in hertz. Mass spectrometry was performed on a Waters Q Tof Premier Micromass (ESI) spectrometer. Routine monitoring of reactions was performed by thin-layer chromatography, and visualization was done by fluorescence quenching at 254 nm or exposure to iodine vapor. Flash chromatography was carried out on silica gel (Acme, 60–120 mesh). Melting points were determined using YG252A apparatus and were uncorrected. Optical rotations were measured on a PerkinElmer 343 polarimeter in the solvent indicated. IR spectra were recorded as KBr disks on an FT-IR-8400S (CE). High-performance liquid chromatography (HPLC) was performed using an Agilent 1260 interfaced to a HP71 series computer workstation with Daicel Chiralcel OD-H column.

Preparation of the Ligands (Fig. 2)

The ligands 1a–1h (Fig. 2) were synthesized according to previous reports[17–19] and the structures of these compounds were confirmed by ^1H NMR (see supporting information).

General Procedure for the Asymmetric Addition of Ethyl Cyanoformate to Aldehydes

$Ti(Oi\text{-}Pr)_4$ (1.0 M in toluene, 0.0125 mmol, 12.5 μl), Schiff base ligand 1f (0.0125 mmol, 6.75 mg) were dissolved in ethanol (2 ml) at room temperature. The mixture was stirred at room temperature for 0.5 h. Then, the corresponding aldehyde (0.25 mmol) was added, and $NCCO_2Et$ (1.5 equiv.) was added after 10 min at 0°C. Stirring was continued for the time indicated in Table 4, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 15:1) to provide the corresponding cyanohydrin carbonates. These adducts (4a–o) were compared with those published in the literature by using ^1H and ^{13}C NMR spectra. The ee were determined by HPLC analysis on a Chiralcel OD-H or AD-H column (see supporting information), and the absolute configurations were determined by comparison with the literature data.[12–15]

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-phenyl-acetonitrile (4a), 93% yield, 83% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 15.3 (major) and 19.0 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(3-methylphenyl)-acetonitrile (4b), 91% yield, 77% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 7.2 (major) and 8.4 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(4-methylphenyl)-acetonitrile (4c), 92% yield, 75% ee. HPLC analysis (Chiralpak OD-H

column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 11.9 (major) and 13.8 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(3-methoxylphenyl)-acetonitrile (4d), 94% yield, 71% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 16.5 (major) and 24.5 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(4-methoxylphenyl)-acetonitrile (4e), 93% yield, 73% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 18.9 (major) and 25.8 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(2-methoxylphenyl)-acetonitrile (4f), 90% yield, 85% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 6.8 (major) and 9.7 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(4-tert-butylphenyl)-acetonitrile (4 g), 91% yield, 75% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 10.9 (major) and 12.8 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(4-isobutylphenyl)-acetonitrile (4 h), 92% yield, 71% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 8.5 (major) and 9.7 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(benzo[*d*][1,3]dioxole-5-yl)-acetonitrile (4i), colorless oil; 94% yield, 65% ee. Physical and spectroscopic data consistent with those previously reported. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 20.5 (major) and 22.3 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(4-fluorophenyl)-acetonitrile (4j), 95% yield, 71% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 12.3 (major) and 15.5 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-(4-chlorophenyl)-acetonitrile (4 k), 95% yield, 63% ee. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 16.9 (major) and 23.8 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-furyl-acetonitrile (4 l), colorless oil; 96% yield, 73% ee. Physical and spectroscopic data consistent with those previously report. HPLC analysis (Chiralpak AD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 15.6 (major) and 18.0 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-2-pyridyl-acetonitrile (4 m), yellow oil; 93% yield, 61% ee. Physical and spectroscopic data consistent with those previously reported. HPLC analysis (Chiralpak AD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 15.5 (major) and 18.2 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-4-phenyl-butanenitrile (4n), colorless oil; 91% yield, 67% ee. Physical and spectroscopic data consistent with those previously report. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 28.6 (major) and 29.4 min (minor).

2-Ethoxycarbonyl (*R*)-2-hydroxy-3-amyl-4-phenyl-but-3-enonitrile (4o), yellow oil; 90% yield, 71% ee. Physical and spectroscopic data consistent with those previously reported. HPLC analysis (Chiralpak OD-H column, hexane:*i*-PrOH = 99:1, 1 ml min^{-1}, 254 nm). t_R = 16.7 (major) and 17.7 min (minor).

Acknowledgments

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