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Enantioselective synthesis of quaternary stereogenic centers through catalytic asymmetric addition of dimethylzinc to α-ketoesters with chiral *cis*-cyclopropane-based amide alcohol as ligand

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ABSTRACT

A new amino alcohol with a chiral cyclopropane backbone has been developed and used in the catalytic asymmetric diethylzinc addition to various types of α-ketoesters. This cyclopropane-based chiral amino alcohol shows moderate enantioselectivity in the addition of organozinc to α-ketoesters. For dimethylzinc addition to α-ketoesters, up to 81% ee are obtained, respectively.

1. Introduction

The stereoselective creation of quaternary stereogenic centers in organic chemistry, especially in the synthesis of complex organic molecules, is important and highly desired. Approaches based on C–C bond formation provide a basic strategy for this target.[1] Over the past ten years, asymmetric organozinc additions to carbonyl compounds has been one of the most useful approaches. In principle, a variety of organometallic reagents can be used for the catalytic enantioselective transfer of alkyl groups. However, most of them are too reactive, and background reactions always deteriorate the enantioselectivity. The enantioselective catalytic process becomes quite difficult. In contrast, organozinc reagents are quite unreactive and can tolerate the presence of many reactive functional groups. They are highly selective in nucleophilic addition reactions to carbonyl compounds. However, because of the low reactivity of these reagents toward the ketone carbonyl group, the highly reactive catalyst has to be used to strongly activate the carbonyl group or the organometallic reagent. Therefore, although hundreds of chiral catalysts have been used for catalytic enantioselective organozinc additions to aldehydes,[2] much less work on asymmetric organozinc additions to ketones, especially additions to ketoesters, has been reported. Compared with aldehydes and ketones, a ketoester can act as a chelating ligand by itself and activate the alkylzinc reagent, which results in a strong background reaction. It is more difficult to find an excellent catalyst to afford sufficient activity, consequently, only Kozlowski's titanium–salen complex **1**,[3a] Shibashaki's proline-derived aminodiol-based ligands **2**,[3b] Hoveyda's amino acid-based ligands **3**,[3c] Pedro's amide alcohol **4**,[3d] and Uang's (−)-2-*exo*-morpholinoisobornane-10-thiol **5**[3e] (−)-MITH have been used with success for the enantioselective addition of dialkylzinc to ketoesters (Fig. 1).

In Pedro's work,[3d] deprotonated N-monosubstituted carboxy amides have been used to suppress the competition between the chiral ligand and the substrate to coordinate the zinc metal ion, and favor the formation of the chiral ligand–Zn complex. This results in a highly enantioselective addition reaction. Following this strategy, as our continuous efforts on the development of new enantioselective catalytic reactions by using cyclopropane-based ligands,[4] we herein report the synthesis of a new type of amide alcohol ligand **9** based on substituted cyclopropane and its application in Me_2Zn addition to α-ketoesters.

2. Results and discussion

The amide alcohol ligand **9** was prepared from commercially available (1*R*,5*S*)-4-hydroxy-6,6-dimethyl-3-oxa-bicyclo-[3.1.0]-hexan-2-one **6** (Fig. 2), which is a key intermediate of producing pyrethroid insecticides. Compound **6** reacted with diazomethane in diethyl ether to quantitatively give aldehydoester **7** followed by $NaBH_4$ reduction and refluxing in benzene to afford enantiomerically pure cyclopropane lactone **8** in 80% yield. Initially, we examined the direct amidation of lactone **8** by treatment with benzylamine. Unfortunately, no reaction occurred at room temperature in the presence or absence of 4-dimethylaminopyridine (DMAP) as a catalyst, even if reaction time was prolonged. Finally, the DIBAL-H-H_2NR, which is a highly efficient and mild amidating reagent in the conversion of lactones to amides, was used to furnish the synthesis of ligand **9** in more than 87% yield.[5] The structure of **9** was established unequivocally via X-ray crystallographic analysis. The absolute configuration of **9** was assigned as 1*R*,3*S* by its crystal structure (Fig. 3).[6] The –OH group and N atom are situated on the

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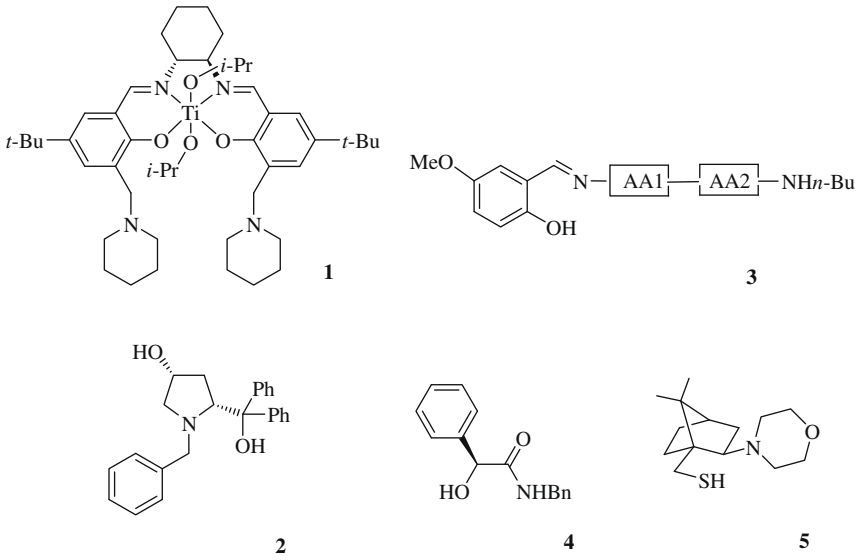


Figure 1. Catalysts of catalytic addition of dialkylzinc to α-ketoesters.

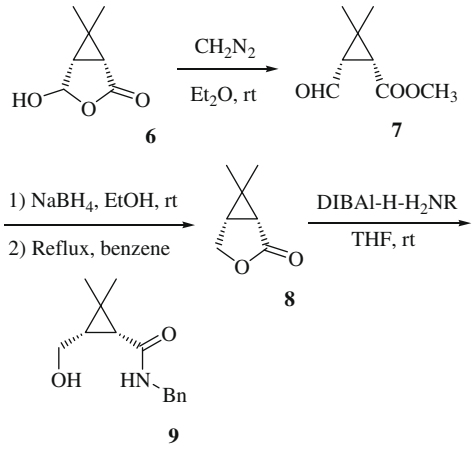


Figure 2. Synthesis of amide alcohol ligand.

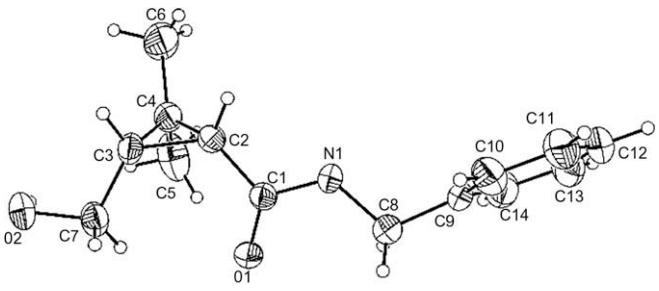
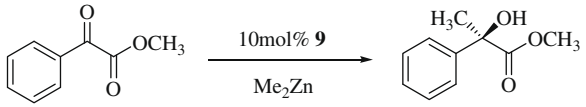


Figure 3. ORTEP diagram of amino alcohol (1*R*,3*S*)-**9**.

same side of cyclopropane backbone. This clearly indicated that metal can easily chelate to both of the groups despite the highly rigid cyclopropane backbone.

Initial experiments were performed with compound **10** as substrate for catalyst evaluation. Generally, 10 mol % catalyst and 1.8 equiv of Me_2Zn had been used. Some screening results are listed in Table 1. The reaction of Me_2Zn and **10** in toluene at 20 °C gave the corresponding product in 94% yield and 40% ee (Table 1, entry 1). The ee value was further improved to 70% when the

Table 1
Catalytic asymmetric addition of dimethylzinc to methyl oxo(phenyl)acetate **10**, using cyclopropane-based amide alcohols as ligands **9**[a]



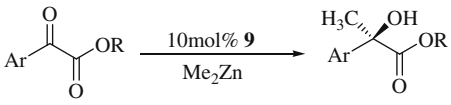
Entry	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1	Toluene	20	24	94	40
2	CH_2Cl_2	20	24	93	54
3	CH_2Cl_2	0	24	90	60
4	CH_2Cl_2	−20	48	70	70
5[d]	CH_2Cl_2	−20	48	62	66
6[e]	CH_2Cl_2	−20	48	77	59
7	CH_2Cl_2	−20	60	70	63
8	CH_2Cl_2	−35	48	55	28
9[f]	CH_2Cl_2	0	24	64	57
10[f]	CH_2Cl_2	−20	48	49	69

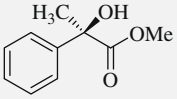
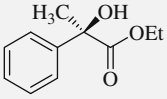
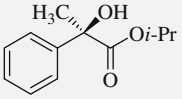
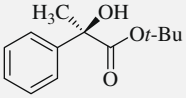
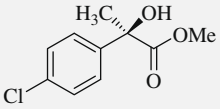
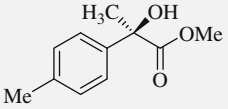
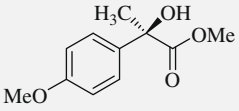
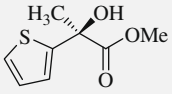
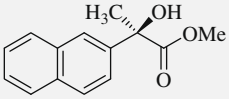
[a] Me_2Zn: 1.8 equiv; ligand: 10 mol %.
[b] Isolated yields after column chromatography.
[c] Determined by chiral GLC and the absolute configuration of major enantiomer was assigned as (*R*)-configuration by the comparison with literature data.
[d] 5% Ligands was used.
[e] 20% Ligands was used.
[f] 5 mol % DiMPEG was used.

reaction was carried out at −20 °C in CH_2Cl_2 (entry 4). Lower reaction temperature (−35 °C) or more ligand (20 mol %) did not improve the enantioselectivity. Because polyethers could improve enantioselectivity of the aryl transfer reaction in several reports, the DiMPEG was used as an additive in this reaction.[7] However, when 5 mol % of DiMPEG (M = 2000 g/mol) was used, ee value remained nearly the same (70% vs 69%), and the yield decreased significantly from 70% to 49%. (Table 1, entry 10 vs 4).

Under the optimized conditions, a series of α-ketoesters were examined for the enantioselective Me_2Zn additions in the presence of ligand **9** as shown in Table 2. The catalyst exhibited a remarkably broad substrate scope, and the corresponding products were obtained in good yield (60–87%) and moderate enantioselectivities (41–81%) (entries 1–9). Phenyl groups in the substrates featuring electron-withdrawing or -donating substituents worked well (entries 1–7), as did a thiophen-2-yl or 2-naphthyl group (entries 8 and 9). It is worth noting that methyl (phenyl)oxoacetate and isopro-

Table 2
Catalytic asymmetric addition of dimethylzinc to α-ketoesters[a]



Entry	Ketoesters	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1		−20	48	70	70
2		−20	48	75	54
3		−20	48	70	70
4		−20	48	85	81
5		−20	48	66	41
6		−20	48	68	61
7		−20	48	60	67
8		−20	48	87	45
9		−20	48	69	64

[a] Me_2Zn: 1.8 equiv, 10 mol % ligands. CH_2Cl_2.
[b] Isolated yields after column chromatography.
[c] Determined by chiral GC.

pyl (phenyl)oxoacetate can afford the same enantiomeric excesses (70% vs 70%), while in sharp contrast, ethyl (phenyl)oxoacetate reacted with Me_2Zn at −20 °C to give 54% ee (Table 2, entry 2), and *tert*-butyl (phenyl)oxoacetate provided 81% ee (Table 2, entry 4).

3. Conclusion

In conclusion, we have designed and prepared a new *cis*-cyclopropane-based amide alcohol ligand. With this ligand, the addition of dimethylzinc to α-ketoesters under mild conditions can give moderate enantioselectivities and moderate to good yields.

4. Experimental

4.1. General experimental method

All reactions were carried out under an atmosphere of dry argon. Dimethylzinc (1.2 M solution in toluene), was purchased from Acros. CH_2Cl_2 was distilled from $LiAlH_4$ under argon. All ketoesters were either commercially available or prepared according to the literature.[8] NMR spectra were recorded by a 500 MHz NMR instrument; Mass spectra were recorded on an Agilent instrument by the TOF MS technique. Enantiomeric excesses (ee) were determined by

chiral GC analysis. The optical rotations were measured on PERKIN ELEMER 341 Polarimeter.

4.2. General procedure for synthesis of *cis*-cyclopropane aminoalcohol 9

4.2.1. (1*R*,3*S*)-Methyl-3-formyl-2,2-dimethylcyclopropanecarboxylate 7

(1*R*,5*S*)-4-Hydroxy-6,6-dimethyl-3-oxa-bicyclo[3.1.0]-hex-an-2-one **6** (2.8 g, 20 mmol) was dissolved in the mixture of 30 mL of Et_2O and 5 mL of MeOH. This solution was cooled to 0 °C and a solution of diazomethane in ether was slowly added with stirring, until the solution did not bubble and the color of solution remained yellow. The solution was slowly allowed to warm to room temperature without additional heating. The reaction mixture was concentrated under reduced pressure. The crude product was passed through a silica gel column (ethyl acetate/hexanes = 1:6) to afford **7** as a colorless oil (2.9 g, 93% yield). $[\alpha]_D^{18} = -73.4$ (*c* 0.99, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (d, 1H, *J* = 9.5 Hz), 3.71 (s, 3H), 2.12 (d, 1H, *J* = 9.5 Hz), 1.86–1.83 (m, 1H), 1.55 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4, 170.4, 52.2, 40.9, 36.1, 29.8, 28.3, 15.5. HRMS (TOF) calcd for $C_8H_{13}NO_3$ [M+H$^+$]: 157.0859, found: 157.0865.

4.2.2. (1*R*,5*S*)-6,6-Dimethyl-3-oxa-bicyclo[3.1.0]hexan-2-one 8

At first, $NaBH_4$ (3.8 g, 100 mmol) was dissolved in 60 mL of dry MeOH, and a solution of **7** (15.6 g, 100 mmol) in MeOH was added slowly into the above mixture. Next, the reaction was kept for 30 min. Then, concentrated HCl (1 mL) was added to stop the reaction and extracted with ether (40 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and then, concentrated to give a light yellow oil (13.7 g, 87% yield).

To a solution of benzene (60 mL) was added the light yellow oil (8.0 g, 50 mmol). The mixture was refluxed for 2 h, then, concentrated under reduced pressure (2 mmHg, 56 °C) to give **8** (90% yield). ^{1}H NMR (500 MHz, DMSO): δ 4.38–4.35 (m, 1H), 4.16–4.14 (d, 1H, *J* =10 Hz), 2.06–2.03 (m, 1H), 1.96–1.94 (m, 1H), 1.18 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 174.9, 66.5, 30.5, 30.0, 25.2, 23.0, 14.4.

4.2.3. (1*R*,3*S*)-*N*-Benzyl-3-(hydroxymethyl)-2,2-dimethylcyclopropanecarboxamide 9

Benzylamine (2.2 mL, 20 mmol) was dissolved in dry THF (10 mL), cooled to −15 °C, and DIBAL-H (13 mL, 20 mmol) was injected. After the mixture was stirred for 20 min, the solution was allowed to warm to 30 °C and left to react for 3 h. Then, it was cooled to −5 °C, and a solution of **8** (2.2 mL) in THF (7.5 mL) was added with stirring for 10 min. After 20 h at room temperature, the reaction was quenched with water (10 mL) and 4 N HCl, (15 mL) and the mixture was extracted several times with Et_2O. The combined organic phases were washed with 1 N HCl, then, dried over Na_2SO_4 and concentrated under reduced pressure to give the products **9** (3.5 g, 87% yield). $[\alpha]_D^{20} = +41.0$ (*c* 1.14, $CHCl_3$). ^{1}H NMR (500 MHz, DMSO): δ 7.36–7.33 (m, 2H), 7.30–7.26 (m, 3H), 6.07 (br, 1H), 4.46–4.44 (m, 2H), 4.03–3.97 (m, 1H), 3.88–3.84 (m, 1H), 3.15–3.12 (m, 1H), 1.42–1.37 (m, 2H), 1.20 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 171.3, 138.2, 128.7, 127.8, 127.6, 59.1, 43.8, 32.6, 31.8, 28.6, 24.2, 15.5.

4.3. General procedure for the asymmetric addition of dimethylzinc to α-ketoesters

A solution of Me_2Zn (1.5 mL, 1.2 M in toluene, 1.8 mmol, 1.8 equiv) was added to a solution of amine alcohol ligand **9** (23 mg, 0.1 mmol, 0.1 equiv) at 0 °C under an atmosphere of argon. After 30 min, the mixture was cooled to −20 °C and ketoester (1 mmol) was added. The reaction was kept for 48 h. Then, saturated NH_4Cl (10 mL) was added to stop the reaction and extracted with ether (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, then, concentrated, and purified by Flash column chromatography (ethyl acetate/hexanes = 1:3) to give a colorless oil.

4.3.1. (*R*)-Methyl 2-hydroxy-2-phenylpropanoate

70% Yield, 70% ee determined by chiral GC analysis (CYCLODEX-B column, 115 °C). Retention time: t_{major} = 31.9 min, t_{minor} = 33.1 min. $[\alpha]_D^{20} = -44.2$ (*c* 3.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.56–7.53 (m, 2H), 7.36–7.25 (m, 3H), 3.77 (s, 3H), 3.75 (s, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 176.1, 142.7, 128.3, 127.8, 125.1, 75.8, 53.2, 26.7. HRMS (TOF) calcd for $C_{10}H_{12}O_3$+Na$^+$: 203.0684, found: 203.0679.

4.3.2. (*R*)-Ethyl 2-hydroxy-2-phenylpropanoate

75% Yield, 54% ee determined by chiral GC analysis (CYCLODEX-B column, 115 °C). Retention time: t_{major} = 38.3 min, t_{minor} = 39.4 min. $[\alpha]_D^{20} = -29.6$ (*c* 2.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.54 (m, 2H), 7.38–7.26 (m, 3H), 4.29–4.17 (m, 2H), 3.79 (s, 1H), 1.78 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.6, 142.9, 128.3, 127.7, 125.1, 75.6, 62.4, 26.7, 14.0. HRMS (TOF) calcd for $C_{11}H_{14}O_3$+Na$^+$: 217.0841, found: 217.0834.

4.3.3. (*R*)-Isopropyl 2-hydroxy-2-phenylpropanoate

70% Yield, 70% ee determined by chiral GC analysis (G-TA column, 95 °C). Retention time: t_{major} = 76.0 min, t_{minor} = 82.4 min. $[\alpha]_D^{20} = -42.5$ (*c* 1.85, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.54 (m, 2H), 7.38–7.26 (m, 3H), 5.10–5.01 (m, 1H), 3.81 (s, 1H), 1.76 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.1, 143.0, 128.2, 127.6, 125.1, 75.5, 70.2, 26.6, 21.6, 21.4. HRMS (TOF) calcd for $C_{12}H_{16}O_3$+Na$^+$: 231.0997, found: 231.0995.

4.3.4. (*R*)-*tert*-Butyl 2-hydroxy-2-phenylpropanoate

85% Yield, 81% ee determined by chiral GC analysis (G-TA column, 100 °C). Retention time: t_{major} = 57.5 min, t_{minor} = 60.0 min. $[\alpha]_D^{20} = -54.0$ (*c* 4.35, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57–7.54 (m, 2H), 7.37–7.26 (m, 3H), 3.87 (s 1H), 1.79 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.8, 143.3, 128.1, 127.5, 125.2, 83.0, 75.6, 27.8, 26.6. HRMS (TOF) calcd for $C_{13}H_{18}O_3$+Na$^+$: 245.1154, found: 245.1152.

4.3.5. (*R*)-Methyl 2-(4-chlorophenyl)-2-hydroxypropanoate

66% Yield, 41% ee determined by chiral GC analysis (CYCLODEX-B column, 150 °C). Retention time: t_{major} = 21.5 min, t_{minor} = 22.2 min. $[\alpha]_D^{20} = -22.6$ (*c* 3.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51–7.48 (m, 2H), 7.34–7.26 (m, 2H), 3.78 (s, 3H), 3.77 (s, 1H), 1.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.8, 141.2, 133.8, 128.4, 126.8, 75.4, 53.4, 26.9. HRMS (TOF) calcd for $C_{10}H_{11}O_3Cl$+Na$^+$: 237.0397, found: 237.0293.

4.3.6. (*R*)-Methyl 2-hydroxy-2-*p*-tolylpropanoate

68% Yield, 61% ee determined by chiral GC analysis (CYCLODEX-B column, 130 °C). Retention time: t_{major} = 30.1 min, t_{minor} = 31.2 min. $[\alpha]_D^{20} = -34.0$ (*c* 2.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44–7.41 (m, 2H), 7.18–7.15 (m, 2H), 3.77 (s, 3H), 3.69 (s, 1H), 2.34 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 176.2, 139.8, 137.5, 129.0, 125.0, 75.6, 53.1, 26.6, 20.9. HRMS (TOF) calcd for $C_{11}H_{14}O_3$+Na$^+$: 217.0841, found: 217.0845.

4.3.7. (*R*)-Methyl 2-hydroxy-2-(4-methoxyphenyl) propanoate

60% Yield, 67% ee determined by chiral GC analysis (CYCLODEX-B column, 155 °C). Retention time: t_{major} = 25.2 min, t_{minor} = 25.5 min. $[\alpha]_D^{20} = -38.3$ (*c* 2.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47–7.44 (m, 2H), 6.89–6.86 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.70 (s, 1H), 1.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 176.3,

159.2, 134.9, 126.4, 113.7, 75.4, 55.2, 53.1, 26.7. HRMS (TOF) calcd for $C_{11}H_{14}O_4$+Na^+: 233.0790, found: 233.0784.

4.3.8. (*R*)-Methyl 2-hydroxy-2-(thiophen-2-yl) propanoate

87% Yield, 45% ee determined by chiral GC analysis (CYCLODEX-B column, 115 °C). Retention time: t_{major} = 32.7 min, t_{minor} = 33.4 min. $[\alpha]_D^{20} = -25.4$ (*c* 2.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.26–7.23 (m, 1H), 7.08–7.06 (m, 1H), 6.98–6.95 (m, 1H), 4.00 (s, 1H), 3.82 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.1, 147.5, 126.9, 125.0, 124.0, 74.3, 53.4, 27.8. HRMS (TOF) calcd for $C_8H_{10}O_3S$+Na^+: 209.0248, found: 209.0248.

4.3.9. (*R*)-Methyl 2-hydroxy-2-(naphthalen-2-yl) propanoate

69% Yield, 64% ee determined by chiral GC analysis (CYCLODEX-B column, 145 °C). Retention time: t_{major} = 152.0 min, t_{minor} = 155.6 min. $[\alpha]_D^{20} = -36.0$ (*c* 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.03–8.02 (m, 1H), 7.84–7.81 (m, 3H), 7.64 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.49–7.46 (m, 2H), 3.88 (s, 1H), 3.78 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 176.0, 140.0, 133.0, 132.8, 128.3, 128.1, 127.5, 126.2, 124.1, 123.4, 76.0, 53.3, 26.7. HRMS (TOF) calcd for $C_{14}H_{14}O_3$+Na^+: 253.0831, found: 253.0841.

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