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A new class of C_2 chiral photodimer ligands for catalytic enantioselective diethylzinc addition to arylaldehydes

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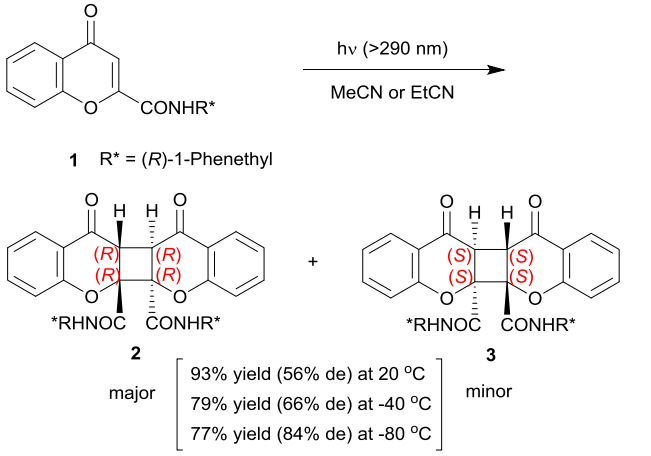
ABSTRACT

A new class of C_2 chiral materials was easily prepared by the photodimerization reaction of (*R*)-*N*-phenethyl-2-chromonecarboxamide followed by recrystallization. Reduction of the photodimer gave the corresponding alcohol stereoselectively. Both C_2 chiral materials worked effectively as ligands for enantioselective ethylation of arylaldehydes using diethylzinc.

1. Introduction

Many C_2–symmetric chiral materials have been utilized for several kinds of asymmetric syntheses as useful organic catalysts or ligands of organometallics.[1] However, most of these chiral materials are cumbersome to prepare and are expensive even if commercially available. Considering the challenging new structural motifs, we conceived of a convenient synthesis of C_2 chiral materials that may spark the creative endeavors of many synthetic organic chemists.

Recently, we reported a convenient method to construct C_2 chiral scaffolds by the diastereoselective photodimerization reaction of chromone-2-carboxamides possessing a chiral substituent on the nitrogen atom as shown in Scheme 1.[2] The reaction provided high product selectivity and stereochemistry, and the predominant dimerization products had easily modifiable carbonyl and amide groups.[3] Here, we utilized the C_2 chiral photodimers as ligands for catalytic asymmetric synthesis of secondary alcohols using diethylzinc as a typical model reaction.[4]



Scheme 1. Diastereoselective photodimerization of chromone-2-carboxamides to construct C_2 chiral scaffolds.

2. Results and discussion

Chromone-2-carboxamides possessing chiral substituents were easily obtained from the commercially available 2-chromonecarboxylic acids and corresponding chiral amines.

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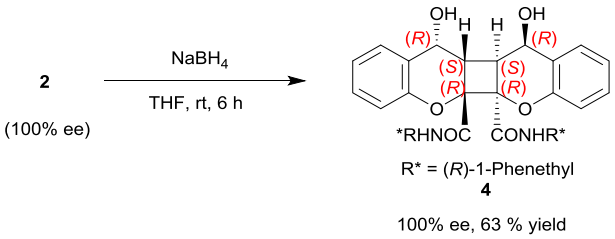
When the amide **1** was irradiated in MeCN at room temperature (20 °C), the diastereoselective formation of the *anti*-head-to-head type dimer occurred in 56% de. Decreasing the temperature of the reaction to −40 °C gave a better de value of 66%. Moreover, a higher diastereoselectivity of 84% de was obtained by irradiation at −80 °C using propionitrile as a solvent.[2]

The absolute configuration of both dimers was established by X-ray crystallographic analysis. The major isomer exhibited *R* configuration of all carbon atoms in the cyclobutane ring, and the minor isomer had an all *S* configuration in the four-membered ring. Major isomer **2** was easily optically resolved by crystallization on the basis of the big difference in crystallinity. When a 56% de mixture of photodimers was recrystallized from a mixed solvent of $CHCl_3$ and hexane, a pseudo-racemic crystal composed of a 1:1 mixture of **2** and **3** with higher crystallinity crystallized from the first crystallization. The minor isomer **3** was nearly removed by this first crystallization, and enantiopure **2** was easily obtained by a second crystallization from the mother liquor. In other words, enantiopure **2** could be isolated by crystallization twice from the photoreaction mixture. Further purification was not required to use **2** in subsequent asymmetric syntheses. On the other hand, optical resolution by preparative HPLC was required to obtain optically pure **3**.

For enantioselective alkylations using dialkylzinc, diols have commonly been used as effective chiral ligands.[5] The chromone dimer has a convertible functional carbonyl group, and reduction was examined to provide chiral alcohols. When optically pure **2** was reacted with $NaBH_4$ in THF and the reaction mixture was separated by column chromatography on silica gel, enantiopure **4** was obtained in 63% yield without any cumbersome experimental procedures. The stereochemistry of the newly formed chiral center was determined as (*R*) by X-ray structural analysis. The hydride attacked from the vacant side so as to avoid the bulk of the chromone structure (Scheme 2, Fig. 1).



Scheme 2. Synthesis of diol **4** by stereoselective reduction of **2**.

We herein report the behavior of these chiral chromone derivatives **2**–**4** as a new class of ligands in the enantioselective alkylation of aryl aldehydes as a representative model asymmetric reaction because many chiral ligands effectively catalyze the asymmetric alkylation of aldehydes with high ees.[6]

Before the asymmetric reaction using the chiral photodimers, we tried the reaction using the monomer **1**; however, **1** did not work as an effective ligand for the asymmetric ethylation (Scheme 3, Table 1, entry 1). Next, when chiral dimer **2** was used, 70% ee of (*R*)-1-phenyl-1-propanol was obtained in 75% yield (entry 2). Diastereomeric dimer **3**, with a different stereochemistry of the cyclobutane ring, also worked, and 65% ee of enantiomeric (*S*)-alcohol was obtained in a better chemical yield of 81%. The chiral phenethyl group did not affect the enantioselectivity, suggesting that the dimer structure controlled the enantioselectivity considerably.

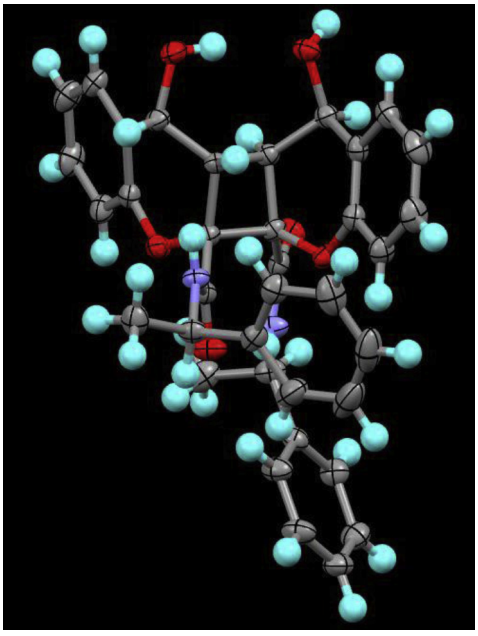
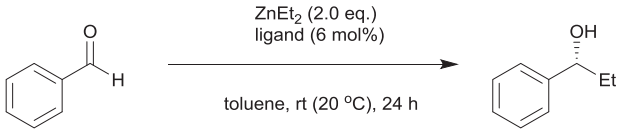


Fig. 1. Perspective view of reduced chromone dimer **4**.



Scheme 3. Asymmetric ethylation of benzaldehyde using chromone ligands.

Table 1
Asymmetric ethylation of benzaldehyde using chromone ligands

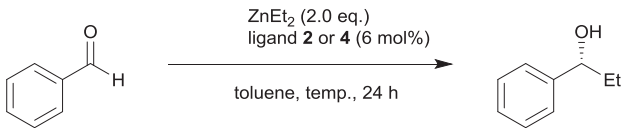
Entry	Ligand	Yield (%)[a]	ee (%)[b]	Config[c]
1	**1**	20	0	—
2	**2**	75	70	*R*
3	**3**	81	−65	*S*
4	**4**	77	71	*R*

[a] Isolated yield.
[b] Determined by HPLC analysis using a CHIRALCEL OD column.
[c] Determined by comparison with an authentic sample.

It is known that many diols serve as good ligands for catalytic asymmetric alkylation using diethylzinc, and it was expected that the dimeric diol **4** would be more effective for the asymmetric reaction.[5] The chiral diol **4** was slightly more stereoselective for the asymmetric reaction (entry 4), and gave the (*R*)-alcohol in 71% ee.

We then examined the effect of the reaction temperature by using the dimer ligands, **2** and **4** (Scheme 4). Decreasing the temperature to 0 °C from 20 °C resulted in decreased reactivity (Table 2, entries 3 and 4), but the ee value was almost the same (entries 2 and 4). On the other hand, increasing the temperature decreased the stereoselectivity, and the ee values were reduced (entries 5 and 6). These results showed that a temperature of 20 °C was the best condition for ethylation using photodimer ligands. Furthermore, there was little difference between the reactions using **2** and the diol **4** in the chemical yields, ees, and stereochemistry.

Next, enantioselective addition using a variety of arylaldehydes was examined with the photodimer ligands at 20 °C (Scheme 5, Table 3). In the case of the reaction of 2-chlorobenzaldehyde, both ligands worked and gave moderate chemical yields and ee values



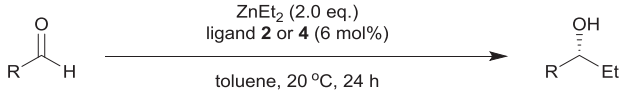
Scheme 4. Asymmetric ethylation of benzaldehyde using chromone ligands.

Table 2
Asymmetric ethylation of benzaldehyde using chromone ligands

Entry	Ligand	Temp (°C)	Yield (%)[a]	ee (%)[b]	Config[c]
1	**2**	20	75	70	*R*
2	**4**	20	77	71	*R*
3	**2**	0	Trace	—	—
4	**4**	0	38	71	*R*
5	**2**	40	74	63	*R*
6	**4**	40	77	46	*R*

[a] Isolated yield.
[b] Determined by HPLC analysis using a CHIRALCEL OD column.
[c] Determined by comparison with an authentic sample.

(entries 3 and 4). However, introduction of a substituent at the *ortho*-position prevented the reaction and decreased the chemical yields. In the case of 4-chlorobenzaldehyde, better chemical yields were obtained with almost the same ee values (entries 5 and 6). An electron-rich methyl group at the *ortho*-position decreased the reactivity (entries 7 and 8), whereas the reaction with 4-methylbenzaldehyde gave moderate chemical yields and ees (entries 9 and 10). In the cases of the reactions with an electron-rich methoxy group at the 2- or 4-position, lower reactivity and stereoselectivity resulted (entries 11–14). On the other hand, the reaction with 1-naphthaldehyde gave the best results of 95% ee by the use of **2** and **4** with good chemical yields (entries 15 and 16). 2-Naphthaldehyde gave moderate stereoselectivity. In all cases, the stereochemistry of the resulting alcohol was the *R*-configuration.



Scheme 5. Asymmetric alkylation of arylaldehydes using chromone dimer ligands.

Table 3
Asymmetric ethylation of arylaldehydes using chromone dimer ligands

Entry	R	Ligand	Yield (%)[a]	ee (%)[b]	Config[c]
1	C_6H_5	**2**	75	70	*R*
2	C_6H_5	**4**	77	71	*R*
3	2-ClC_6H_4	**2**	63	68	*R*
4	2-ClC_6H_4	**4**	60	67	*R*
5	4-ClC_6H_4	**2**	72	68	*R*
6	4-ClC_6H_4	**4**	83	67	*R*
7	2-MeC_6H_4	**2**	36	72	*R*
8	2-MeC_6H_4	**4**	42	73	*R*
9	4-MeC_6H_4	**2**	69	63	*R*
10	4-MeC_6H_4	**4**	76	70	*R*
11	2-$MeOC_6H_4$	**2**	51	58	*R*
12	2-$MeOC_6H_4$	**4**	51	67	*R*
13	4-$MeOC_6H_4$	**2**	41	30	*R*
14	4-$MeOC_6H_4$	**4**	56	50	*R*
15	1-Naphthyl	**2**	82	95	*R*
16	1-Naphthyl	**4**	88	95	*R*
17	2-Naphthyl	**2**	63	62	*R*
18	2-Naphthyl	**4**	90	74	*R*

[a] Isolated yield.
[b] Determined by HPLC analysis using a chiral column.
[c] Determined by comparison with an authentic sample. The major enantiomer in all cases had the (*R*)-configuration.

We provided a new class of C_2 chiral ligands that were easily prepared by photodimerization, recrystallization, and reduction without cumbersome procedures. The difference between photodimers **2** and **3** was the stereochemistry of the cyclobutane ring. Each reaction using **2** or **3** gave opposite selectivity (Table 1, entries 2 and 3), which indicated that the chiral phenethyl group did not affect the enantioselectivity and the dimer structure controlled the stereoselectivity. Furthermore, there was no significant difference in the reactivity and the stereoselectivity between the reactions using ligands **2** and **4**, as the results show in Tables 1–3. In these reactions, we cannot provide the exact structure of the active intermediate complex without precise evidence by X-ray or spectral techniques.

3. Conclusion

We provided a convenient method to construct a C_2 chiral scaffold by the diastereoselective photodimerization reaction of chiral chromone-2-carboxamides followed by recrystallization and reduction with sodium borohydride. Enantioselective ethylation of arylaldehydes was examined using the new class of C_2 chiral ligands as a typical model of an asymmetric reaction. It was confirmed that the C_2 chiral dimer ligands could be utilized as ligands for catalytic asymmetric ethylation of arylaldehydes using diethylzinc.

4. Experimental section

4.1. General

NMR spectra were recorded in $CDCl_3$ solution on a Bruker 300 instrument operating at 300 MHz for ^1H and ^{13}C NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Specific rotation was measured using a DIP 370 polarimeter (JASCO). X-ray single crystallographic analysis was conducted using a SMART APEX II (Bruker AXS).

4.2. Preparation and photochemical procedure of 2-chromonecarboxamides (1)[2]

Chromone-2-carboxamide **1** was obtained in 85% yield according to the reported procedure.[2] A 0.02 M solution of 2-chromonecarboxamide **1** was deoxygenated by bubbling argon for 20 min and was irradiated for 2 h at 20 °C. After irradiation the solvent was removed in vacuo and dimeric products were obtained in 98% yield at 85% conversion. The diastereoselectivity of 56% was determined on the basis of NMR spectra. Crystallization of a mixture of 56% de of diastereomeric dimers from a mixed solvent of $CHCl_3$ and hexane gave pseudo-racemic crystals composed of a 1:1 mixture of **2** and **3** in 35% yield. Crystallization from the mother liquor afforded optically pure **2** in 42% yield.

4.3. Reduction of photodimer 2 by $NaBH_4$ leading to diol (4)

After $NaBH_4$ (4.0 equiv) was added to a THF solution of the photodimer 2 portion by portion, the solution was stirred for 2 h at room temperature. Aqueous HCl was added and treated with usual work up process. The diol **4** was separated by column chromatography on silica gel with the mixed solvent of hexane and ethyl acetate as an eluent. Solid diol **4** was recrystallized from a mixture of hexane and diethyl ether. The chemical yield was 63%.

*4.3.1. ((5aR,5bR,11R,11aS,11bS,12R)-11,12-dihydroxy-11,11a,11b,12-tetrahydrocyclobuta[1,2-b:4,3-b′]dichromene-5a,5b-diyl)bis((((R)-1-phenylethyl)-l2-azanyl)methanone) (**4**).* Colorless crystal; mp

106–107 °C; $[\alpha]_D^{20}$ −20.23 (*c* 0.48, $CHCl_3$); IR: (cm^{-1}, KBr) 3420, 3292, 1671; ^1H NMR: (300 MHz, $CDCl_3$) δ 1.62 (d, *J*=6.8 Hz, 6H), 3.74 (s, 2H), 4.60 (m, 4H), 5.14 (m, 2H), 6.95 (d, *J*=8.1 Hz, 2H), 6.87 (t, *J*=7.9 Hz, 4H), 7.06 (t, *J*=7.4 Hz, 2H), 7.19–7.29 (m, 12H), 7.45 (d, *J*=7.5 Hz, 2H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 21.26, 49.42, 112.24, 118.05, 124.26, 125.94, 126.04, 126.34, 127.89, 134.47, 141.85, 154.58, 155.14, 158.34, 178.08; HRMS(ESI-MS) *m*/*z* calcd for $C_{36}H_{34}N_2O_6$+H 591.2490, found 591.2471.

4.4. X-ray diffraction analysis data of diol (4)

Colorless prismatic crystals from ether–hexane, including each equimolar amount of ether and water, monoclinic space group *C*2, *a*=24.9503(3) Å, *b*=10.01740(10) Å, *c*=17.3961(2) Å, β=124.4275(4)°, *V*=3586.38(7) $Å^3$, *Z*=4, ρ=1.265 g/cm^3, μ=0.714 mm^{-1}, Flack parameter=0.03(3) The structure was solved by the direct method of full matrix least-squares, where the final *R* and *wR* were 0.0315 and 0.0875 for 5753 reflections. CCDC1400554.

4.5. Asymmetric ethylation of arylaldehyde with diethylzinc

Diethylzinc (1.1 ml, 1 M solution in hexane) was added to a stirred solution of ligand (0.033 mmol) in toluene (1.0 ml) under Ar at room temperature. After stirring the resulting reaction mixture at this temperature for 15 min, benzaldehyde (0.05 ml, 0.55 mmol) was added. Stirring was continued for 24 h at room temperature. At the end of this period, the reaction mixture was diluted with ethyl acetate (10 ml), quenched with a saturated aqueous solution of NH_4Cl (10 ml), and the two layers were separated. The aqueous layer was extracted with ethyl acetate (2×10 ml). The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel using hexane–ethyl acetate. 1-Phenyl-1-propanol was obtained in 81% yield (61 mg, 0.446 mmol). Chiral HPLC was used to determine the ee. Other asymmetric reaction using various aldehydes and ligands were examined with the same procedure.

4.5.1. 1-Phenyl-1-propanol (Table 2, entry 2). $[\alpha]_D^{20}$ +33.68 (*c* 0.47, $CHCl_3$), ($[\alpha]_D^{25}$ +42.4 (*c* 2.50, $CHCl_3$) for 99% ee (*R*));[7] 71% ee by HPLC analysis (CHIRALCEL OD column, hexane:2-propanol=98:2, 1 ml/min, 254 nm UV detector), t_R=14.72 min for (*R*) and t_R=20.04 min for (*S*).

4.5.2. 1-(2′-Chrorophenyl)-1-propanol (Table 3, entry 3). $[\alpha]_D^{20}$ +36.63 (*c* 0.58, $CHCl_3$), ($[\alpha]_D^{25}$ +52.31 (*c* 3.46, $CHCl_3$) for 96% ee (*R*));[8] 68% ee by HPLC analysis (CHIRALCEL OB-H column, hexane:2-propanol=99:1, 1 ml/min, 254 nm UV detector), t_R=30.46 min for (*R*) and t_R=20.04 min for (*S*).

4.5.3. 1-(4′-Chrorophenyl)-1-propanol (Table 3, entry 5). $[\alpha]_D^{20}$ +22.02 (*c* 0.52, $CHCl_3$), ($[\alpha]_D^{25}$ +37.3 (*c* 1.57, $CHCl_3$) for 96% ee (*R*));[9] 68% ee by HPLC analysis (CHIRALCEL OD column, hexane:2-propanol=99:1, 0.5 ml/min, 254 nm UV detector), t_R=52.72 min for (*R*) and t_R=49.10 min for (*S*).

4.5.4. 1-(2′-Tolyl)-1-propanol (Table 3, entry 8). $[\alpha]_D^{20}$ +40.28 (*c* 0.51, $CHCl_3$), ($[\alpha]_D$ +60.1 (*c* 5.0, $CHCl_3$) for 95% ee (*R*));[10] 73% ee by HPLC analysis (CHIRALPAK AD-H column, hexane:2-propanol=99:1, 1 ml/min, 254 nm UV detector), t_R=15.30 min for (*R*) and t_R=18.58 min for (*S*).

4.5.5. 1-(4′-Tolyl)-1-propanol (Table 3, entry 10). $[\alpha]_D^{20}$ +30.25 (*c* 0.56, $CHCl_3$), ($[\alpha]_D^{25}$ +37.2 (*c* 1.00, $CHCl_3$) for 85% ee (*R*));[11] 70% ee by HPLC analysis (CHIRALPAK AD-H column, hexane:2-propanol=98:2, 1 ml/min, 254 nm UV detector), t_R=12.94 min for (*R*) and t_R=14.18 min for (*S*).

4.5.6. 1-(2′-Methoxyphenyl)-1-propanol (Table 3, entry 12). $[\alpha]_D^{20}$ +13.16 (*c* 0.50, $CHCl_3$), ($[\alpha]_D^{26}$ +23.7 (*c* 1.40, $CHCl_3$) for 95% ee (*R*));[11] 67% ee by HPLC analysis (CHIRALCEL OD-H column, hexane:2-propanol=99:1, 0.5 ml/min, 254 nm UV detector), t_R=66.91 min for (*R*) and t_R=59.80 min for (*S*).

4.5.7. 1-(4′-Methoxyphenyl)-1-propanol (Table 3, entry 14). $[\alpha]_D^{20}$ +22.70 (*c* 0.59, $CHCl_3$), ($[\alpha]_D^{26}$ +38.9 (*c* 1.23, $CHCl_3$) for 96% ee (*R*));[11] 50% ee by HPLC analysis (CHIRALCEL OD column, hexane:2-propanol=97:3, 1 ml/min, 254 nm UV detector), t_R=19.71 min for (*R*) and t_R=24.23 min for (*S*).

4.5.8. 1-(1′-Naphthyl)-1-propanol (Table 3, entry 15). $[\alpha]_D^{20}$ +53.66 (*c* 0.50, $CHCl_3$), ($[\alpha]_D^{25}$ +51.10 (*c* 4.10, $CHCl_3$) for 98% ee (*R*));[11] 95% ee by HPLC analysis (CHIRALCEL OD column, hexane:2-propanol=90:10, 1 ml/min, 254 nm UV detector), t_R=15.40 min for (*R*) and t_R=8.80 min for (*S*).

4.5.9. 1-(2′-Naphthyl)-1-propanol (Table 3, entry 18). $[\alpha]_D^{20}$ +30.53 (*c* 0.57, $CHCl_3$), ($[\alpha]_D^{20}$ +35.1 (*c* 2.4, $CHCl_3$) for 92% ee (*R*));[12,13] 74% ee by HPLC analysis (CHIRALCEL OD column, hexane:2-propanol=95:5, 1 ml/min, 254 nm UV detector), t_R=18.34 min for (*R*) and t_R=16.13 min for (*S*).

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Supplementary data

Supplementary data (Crystal structure for compound **4** and copies of ^1H and ^{13}C NMR spectra of new compounds.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.06.084.

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