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Tetrahedron
Tetrahedron 62 (2006) 8559–8563

Cu(I)-catalyzed asymmetric oxidative cross-coupling of 2-naphthol derivatives

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Received 13 March 2006; revised 15 June 2006; accepted 21 June 2006
Available online 10 July 2006

Abstract—The asymmetric oxidative coupling reaction between 2-naphthol or binaphthol derivatives and 3-hydroxy-2-naphthoate derivatives with the copper(I)-(*S*)-(−)-isopropylidenebis(4-phenyl-2-oxazoline) catalyst was carried out. The reaction proceeded in a highly cross-coupling selective manner (≤99.7%) to produce the binaphthyl or quaternaphthyl derivative in good yield (≤92%) with enantioselectivity of up to 74%.

1. Introduction

The 1,1′-bi-2-naphthol derivatives bearing an axially dissymmetric structure have been widely used in asymmetric synthesis, catalysis, and resolution.[1] The oxidative coupling reaction of the 2-naphthol derivatives is a facile and effective method for their synthesis, and many studies on the homo- or self-coupling reaction with chiral metal catalysts, such as Cu(I), Ru(II), and V(IV), affording a symmetrical binaphthol framework have been reported.[2] In contrast, there have been few reports on the synthesis of the binaphthol derivatives possessing an unsymmetrical structure through the catalytic cross-coupling reaction.[3] Recently, we found that the oxidative coupling reaction between two differently substituted 2-naphthol derivatives using the CuCl-(*S*)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) [(*S*)Phbox] catalyst (Fig. 1) at room temperature under an O_2 atmosphere proceeded in a highly cross-coupling selective manner, up to 99.7%.[4] In addition, this system was successfully applied to the asymmetric oxidative cross-coupling polymerization of the methyl 6,6′-dihydroxy-2,2′-binaphthalene-7-carboxylate leading to the polybinaphthol derivative with a number average molecular weight of 1.2×10^4, which consisted of the cross-coupling unit of 96%.[5]

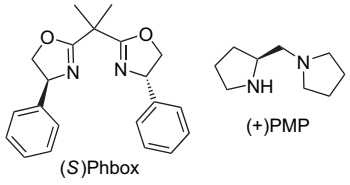

Figure 1. Chiral ligands.

On the other hand, studies on the synthesis of the oligobinaphthols, such as the ter- and quaternaphthyl derivatives, by the oxidative coupling are also available.[6] They are often prepared by the cross-coupling reaction, e.g., the ternaphthyl skeleton is constructed by coupling between the binaphthyl and naphthyl compounds, and an excess amount of one substrate to the other is generally used to maximize the yield of the desired cross-coupling oligonaphthyl product.

In this study, further investigations on the highly selective oxidative cross-coupling reaction of 2-naphthols with the copper-bisoxazoline catalyst, and its extension to the facile synthesis of the quaternaphthyl derivatives through the double oxidative cross-coupling reaction using a stoichiometric amount of the binaphthol derivatives and 2-naphthol in the ratio of 1:2.

2. Results and discussion

To optimize the reaction conditions, the oxidative cross-coupling (OCC) with the (*S*)Phbox ligand was examined using 2-naphthol **1a** and methyl 3-hydroxy-2-naphthoate **2a** as substrates (Scheme 1). The results of the OCC using CuCl-(*S*)Phbox by changing the catalyst molar ratio are listed in Table 1. In a previous report, the reaction using 0.2 equiv of the catalyst to the substrates for 3 h resulted in an 87% yield with a cross-coupling selectivity (*Y*) of 95.8% and an enantioselectivity of 10% ee (*S*) (entry 1).[4]

Keywords: Binaphthol; Cross-coupling; Asymmetric oxidative coupling.
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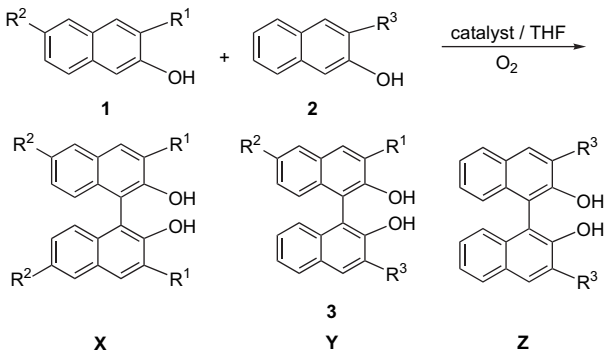
doi:10.1016/j.tet.2006.06.069



Scheme 1.

Table 1. Asymmetric OCC between **1a** and **2a**[a]

Entry	[CuCl-(*S*)Phbox]/[**1**+**2**]	Time (h)	Coupling ratio **X**:**Y**:**Z**[b]	Cross-coupling product **Y**	
				Yield (%)[c]	ee (%)[d]
1	0.2	3	0.3:95.8:3.9	87	10 (*S*)
2	0.1	6	0:97.4:2.6	82	8 (*S*)
3	0.05	9	0:98.5:1.5	81	7 (*S*)
4	0.01	24	0:99.6:0.4	79	8 (*S*)

[a] [**1a**]/[**2a**]=1:1, [**1a**]=0.18 M, temp=rt, O_2 atmosphere.
[b] Ratio of isolated yields.
[c] Isolated yield.
[d] Determined by HPLC analysis (Chiralpak AD).

With the decreasing molar ratio of the catalyst, the cross-coupling selectivity slightly increased with almost no decrease in the yield, as well as the enantioselectivity of the cross-coupling product. The OCC with 1.0 mol % of CuCl-(*S*)Phbox catalyst showed the highest cross-coupling selectivity of 99.6% (entry 4).

The reaction with various copper salts (1.0 mol %) in THF at room temperature was also conducted (Table 2). In every catalyst system, the cross-coupling bond formation preferentially took place. However, the yield and stereoselectivity were significantly reduced during the reaction with the copper(II) salt (entry 1). The counter-anion of the copper salt

Table 2. Asymmetric OCC between **1a** and **2a**[a]

Entry	CuX	Time (h)	Coupling ratio **X**:**Y**:**Z**[b]	Cross-coupling product **Y**	
				Yield (%)[c]	ee (%)[d]
1	$CuCl_2$	48	0:98.1:1.9	21	1 (*R*)
2	CuBr	24	0:99.1:0.9	76	3 (*S*)
3	CuI	24	0:97.9:2.1	66	1 (*S*)
4	CuOTf	24	0:97.2:2.8	41	7 (*S*)
5	$[(CH_3CN)_4Cu]PF_6$	24	0:95.5:4.5	53	5 (*R*)

[a] [CuX]/[(*S*)Phbox]/[**1a**]/[**2a**]=0.010:0.013:0.5:0.5, [**1a**]=0.18 M, temp=rt, O_2 atmosphere.
[b] Ratio of isolated yields.
[c] Isolated yield.
[d] Determined by HPLC analysis (Chiralpak AD).

Table 3. Asymmetric OCC between **1** and **2**[a]

Entry	**1**	**2**	Coupling ratio **X**:**Y**:**Z**[b]	Cross-coupling product **Y**		
				3	Yield (%)[c]	ee (%)[d]
1	**1b**	**2a**	5.2:88.7:6.1	**3b**	74	8 (*S*)
2	**1c**	**2b**	0:99.7:0.3	**3c**	87	16 (*S*)
3	**1d**	**2a**	0:99.7:0.3	**3d**	94	10 (*S*)
4	**1d**	**2b**	0:97.3:2.7	**3e**	76	46 (*R*)
5	**1e**	**2b**	12.0:86.3:1.7	**3f**	71	67 (*R*)
6[e]	**1e**	**2b**	11.1:87.0:1.9	**3f**	70	70 (*R*)
7[f]	**1e**	**2b**	13.5:85.5:1.0	**3f**	67	73 (*R*)
8[g]	**1e**	**2b**	12.8:85.1:2.1	**3f**	44	74 (*R*)

[a] [CuCl]/[(*S*)Phbox]/[**1**]/[**2**]=0.010:0.013:0.50:0.50, [**1**]=0.18 M, temp=rt, time=24 h, O_2 atmosphere.
[b] Ratio of isolated yields.
[c] Isolated yield.
[d] Determined by HPLC analysis (Chiralpak AS or AD).
[e] [CuCl]/[(*S*)Phbox]/[**1**]/[**2**]=0.05:0.06:0.50:0.50, temp=0 °C, 48 h.
[f] [CuCl]/[(*S*)Phbox]/[**1**]/[**2**]=0.05:0.06:0.50:0.50, temp=−20 °C, 72 h.
[g] [CuCl]/[(*S*)Phbox]/[**1**]/[**2**]=0.1:0.13:0.50:0.50, temp=−40 °C, 72 h.

also significantly affected the catalyst activity and stereocontrol.

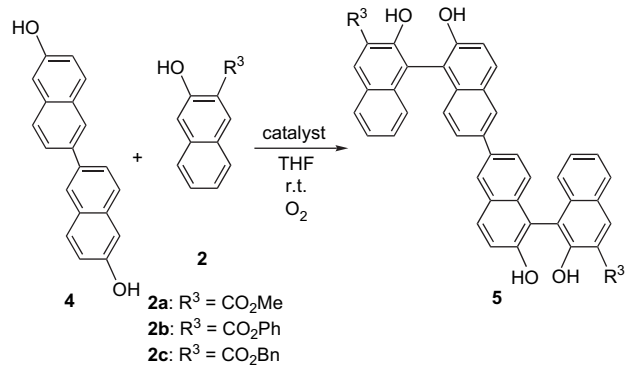
Table 3 shows the results of the OCC between the 2-naphthol derivatives **1** and 3-hydroxy-2-naphthoate derivatives **2** using the CuCl-(*S*)Phbox catalyst (1.0 mol %). The reaction of 6-substituted-2-naphthol **1c**, **1d** demonstrated the excellent cross-coupling selectivity of 99.7% (entries 2 and 3), whereas the reaction of 2-naphthol having a substituent at the 3-position **1e** showed the highest enantioselectivity of 67% ee (*R*) (entry 3). By lowering the reaction temperature to −40 °C, the enantioselectivity was further improved to 74% ee (*R*), although the yield of the cross-coupling product was reduced (entry 6).

The results of the OCC between the 6,6′-dihydroxy-2,2′-binaphthalene **4** and **2a** (**4**:**2**=1:2 ratio) with various copper complexes of (+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)-PMP] (Fig. 1), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and (*S*)Phbox, in THF at room temperature under an O_2 atmosphere are listed in Table 4 (Scheme 2). The stereoselectivity of the quaternaphthyl derivatives was determined by circular dichroism (CD)[7] and high-performance-liquid-chromatography (HPLC) analyses. The reaction with CuCl-(+)PMP hardly produced any coupling product (entry 1), whereas the quaternaphthyl **5a** was obtained in

Table 4. Asymmetric OCC between **4** and **2**[a]

Entry	Catalyst	**2**	Time (h)	Quaternaphthyl **5**		
				5	Yield (%)[b]	*RR*:*RS*:*SS*[c]
1	CuCl-(+)PMP	**2a**	24	**5a**	<1	—
2	CuCl(OH)-TMEDA	**2a**	10	**5a**	32	19:62:19
3	CuCl-(*S*)Phbox	**2a**	5	**5a**	85	11:45:44
4[d]	CuCl-(*S*)Phbox	**2a**	24	**5a**	80	9:42:49
5[e]	CuCl-(*S*)Phbox	**2a**	48	**5a**	92	10:43:47
6	CuCl-(*S*)Phbox	**2b**	5	**5b**	60	40:48:12
7	CuCl-(*S*)Phbox	**2c**	5	**5c**	79	12:47:41

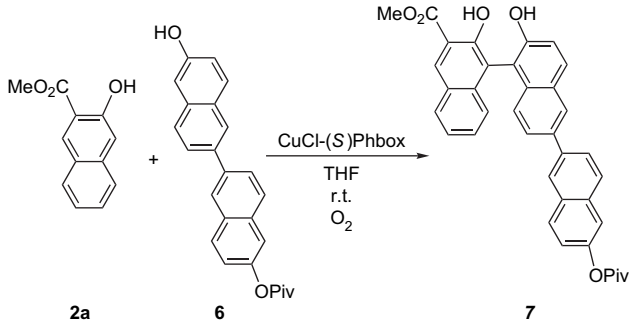
[a] Conditions: [CuCl]/[diamine]/[**4**]/[**2a**]=0.20:0.25:0.33:0.66, [**4**]=0.12 M, solvent=THF, O_2 atmosphere, temp=rt.
[b] Isolated yield.
[c] Determined by HPLC (Chiralpak AD) and CD measurements.
[d] [CuCl]/[diamine]/[**4**]/[**2a**]=0.010:0.013:0.33:0.66.
[e] Reaction temp=−20 °C.



Scheme 2.

a low yield (32%) as a mixture of *dl* and *meso* during the reaction with the CuCl(OH)-TMEDA catalyst for 10 h (entry 2). In marked contrast, the CuCl-(*S*)Phbox catalyst effectively produced the double cross-coupling product **5a** in good yield (85%, reaction time=5 h), accompanied by the sole homo-coupling by-product of **2a** in 8% yield (entry 3). Therefore, the cross-coupling selectivity was calculated to be 95.5%, whose value is quite consistent with that observed for the coupling reaction between **1a** and **2a**. The stereoselectivity (*RR*/*RS*/*SS*) of the obtained **5a** was determined to be 11:45:44, that is, *R*/*S*=33.5:66.5 [33% ee (*S*)]. When 1.5 mol % of the catalyst to **2a** was used, **5a** was again obtained in a good yield [80%, 40% ee (*S*), entry 4]. The reaction at the lower temperature of −20 °C for 48 h produced the excellent yield of **5a** of 92% and a high cross-coupling selectivity of 99% (yield of the homo-coupling product: 2%, entry 5).

The model reaction using the mono-pivaloylated compounds **6** and **2a** (1:1) was also carried out [[**6**]/[**2a**]/[CuCl]/[(*S*)Phbox]=0.5/0.5/0.2/0.25, rt, 5 h] (Scheme 3). The cross-coupling product **7** was obtained in 87% yield with a cross-coupling selectivity of 95.8% and an enantioselectivity of 42% ee (*S*). These results are roughly comparable to those observed for the double cross-coupling process. Accordingly, the second cross-coupling reaction should be slightly affected by the structure formed during the first cross-coupling process.



Scheme 3.

The OCC of the phenyl ester **2b** or benzyl ester **2c** with **4** also afforded a quaternaphthyl in a moderate or good yield, whereas the stereoselectivity for the cross-coupling reaction

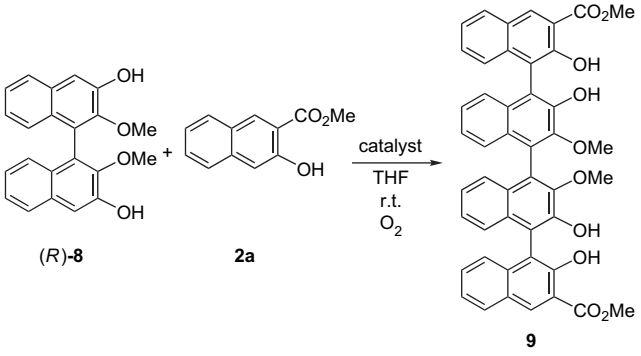
Table 5. Asymmetric OCC between (*R*)-**8** and **2a**[a]

Entry	Catalyst	Time (h)	Quaternaphthyl **9**	
			Yield (%)[b]	*RRR*:*RRS*:*SRS*[c]
1	CuCl(OH)-TMEDA	24	45	45:45:10
2	CuCl-(*S*)Phbox	6	65	56:38:6
3[d]	CuCl-(*S*)Phbox	24	60	62:34:4
4[d]	CuCl-(*R*)Phbox	24	56	15:35:50

[a] Conditions: [CuCl]/[diamine]/[**8**]/[**2a**]=0.20:0.25:0.33:0.66, [**8**]=0.12 M, solvent=THF, O_2 atmosphere, temp=rt.
[b] Isolated yield.
[c] Ratio of isolated yield.
[d] [CuCl]/[diamine]/[**8**]/[**2a**]=0.010:0.013:0.33:0.66.

was the opposite of each other, i.e., 28% ee (*R*) for the former and 29% ee (*S*) for the latter (entries 6 and 7). The structure of the ester groups on the 2-naphthol significantly affected the coupling stereochemistry.

Table 5 summarizes the results of the OCC between **2a** and the chiral 1,1′-binaphthyl derivative, (*R*)-**8**, (**2a**:**8**=2:1 ratio) with the Cu(I)-diamine catalyst (Scheme 4). The absolute configuration of the quaternaphthyls **9** was assigned on the basis of the spectral pattern and absorption intensity at around 240, 260, and 340 nm for the CD, in addition to the NMR analysis.[4,6d,h]



Scheme 4.

The reaction with the CuCl(OH)-TMEDA catalyst afforded a quaternaphthyl **9** in the low yield of 45%, and the *R*-structure is predominantly formed [*RRR*/*RRS*/*SRS*=45:45:10, 35% ee (*R*), entry 1]. The CuCl-(*S*)Phbox catalyst produced **9** in the yield of 65%, which is also rich in the *R*-configuration [*RRR*/*RRS*/*SRS*=56:38:6, 50% ee (*R*), entry 2]. The OCC with 1.5 mol % of CuCl-(*S*)Phbox catalyst also afforded **9** in a 60% yield with a stereoselectivity of 62:34:4 [58% ee (*R*), entry 3]. The reaction with the (*R*)Phbox catalyst produced a quaternaphthyl with an *S*-selectivity [35% ee (*S*), entry 4]. Accordingly, the *R*-structure was preferentially constructed using the CuCl-(*S*)Phbox, and this selectivity is consistent with that observed for the reaction between the 3-alkoxy-2-naphthols and 3-hydroxy-2-naphthoates.[4] The stereoselectivity was influenced by the structure of the binaphthol used as a substrate, as well as the ligand.

During the reaction using the CuCl-(*S*)Phbox catalyst, the cross-coupling bond formation predominantly proceeded. It is postulated that the naphthol bearing an ester group

may act as an acceptor molecule due to its electron-deficient character, while the one-electron oxidation should be preferentially promoted on the other substrate, the 2-naphthols, to generate an intermediate radical species, and then the cross-coupling reaction may selectively take place.[3e,4] The cross-coupling- or enantioselectivity increased to some extent with a decrease in the molar ratio of the catalyst. These may be due to the fact that the minor coupling of the intermediate radical generated from the 3-hydroxy-2-naphthoates in a less stereoselective manner occurs and produces the cross- and homo-coupling compounds during the reaction with a higher catalyst loading.

3. Conclusion

In conclusion, the CuCl-(*S*)Phbox is a very effective catalyst for the oxidative coupling reaction between two differently substituted 2-naphthols leading to the cross-coupling product with a high selectivity. In addition, the quaternaphthyl derivatives can be directly prepared from stoichiometric amounts of the binaphthols and 2-naphthols (1:2 in feed) by the double oxidative cross-coupling reaction. The yields of the cross-coupling products, cross-coupling selectivity, and stereoselectivity were significantly affected by the structure of the substrates and copper salts.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were measured on a Varian Unity Inova (500 MHz for ^{1}H) or Mercury 200 (200 MHz for ^{1}H) spectrometer. The infrared (IR) spectra were recorded on a Horiba FT-720 spectrometer. The mass (MS) spectra were obtained using a JEOL AX505H. The optical rotation was measured on a Jasco P-1010 polarimeter at 25 °C. The circular dichroism (CD) spectra were obtained with a Jasco J-720WI apparatus. The high-performance-liquid-chromatography (HPLC) analyses were performed on a Jasco 986-PU chromatograph equipped with UV (Jasco 970-UV) and polarimetric (Jasco OR-990) detectors at room temperature.

4.2. General procedure for oxidative cross-coupling

The 2-naphthols **1** and 3-hydroxy-2-naphthoates **2** were added to a mixture of CuCl and a diamine in THF ([**1**+**2**]=0.35 M, [Cu(I)]/[diamine]/[**1**]/[**2**]=0.010:0.012:0.50:0.50). After room-temperature stirring under an O_2 atmosphere, the reaction mixture was diluted with $CHCl_3$ and then washed with 1 N HCl. The organic solutions were then dried over $MgSO_4$. Filtration and concentration afforded the crude products. Purification was accomplished by silica gel column chromatography that produced the binaphthol derivatives.

Compound **3d**: ^{1}H NMR (500 MHz, $CDCl_3$) 10.84 (s, 1H, –OH), 8.73 (s, 1H, aromatic), 7.95–7.86 (s, 2H, aromatic), 7.58–6.97 (m, 7H, aromatic), 4.99 (s, 1H, –OH), 4.08 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) 170.26, 169.76, 154.85, 151.37, 146.59, 137.25, 133.96, 131.49, 130.23, 129.83, 129.79, 129.42, 127.29, 126.11, 124.71, 124.56, 121.55, 118.93, 118.54, 114.28, 114.20, 114.18, 52.90, 21.18; IR (KBr, cm^{-1}) 3208, 2954, 1756, 1677, 1604, 1504, 1340, 1321, 1207, 1149; $[\alpha]_D^{25}$ −12 (*c* 1.0, THF) for 10% ee (*S*) (Chiralpak AD-H column, hexane/2-propanol=3:1, 0.50 mL/min, 245 nm UV detector), t_R=22.6 min for (*S*) and t_R=24.3 min for (*R*). Mass (FAB): 403 *m*/*z* $[M]^+$. Anal. Calcd for $C_{24}H_{18}O_6$: C, 71.64; H, 4.51. Found: C, 71.51; H, 4.58.

Compound **3e**: ^{1}H NMR (500 MHz, $CDCl_3$) 10.54 (s, 1H, –OH), 9.00 (s, 1H, aromatic), 8.02–7.87 (s, 2H, aromatic), 7.59–6.99 (m, 12H, aromatic), 4.97 (s, 1H, –OH), 2.32 (s, 3H, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) 169.77, 168.71, 155.01, 151.35, 150.03, 146.64, 137.66, 134.68, 131.46, 130.68, 130.03, 129.91, 129.79, 129.46, 127.40, 126.68, 126.08, 124.82, 121.65, 121.59, 118.99, 118.55, 114.59, 114.58, 114.07, 113.80, 21.18; IR (KBr, cm^{-1}) 3268, 1756, 1689, 1602, 1504, 1338, 1315, 1274, 1205, 1145; $[\alpha]_D^{25}$ +63 (*c* 1.0, THF) for 46% ee (*R*) (Chiralpak AD-H column, hexane/2-propanol=3:1, 0.50 mL/min, 245 nm UV detector), t_R=23.0 min for (*R*) and t_R=25.5 min for (*S*). Mass (FAB): 465 *m*/*z* $[M]^+$. Anal. Calcd for $C_{29}H_{20}O_6$: C, 74.99; H, 4.34. Found: C, 74.91; H, 4.52.

Compound **5a**: ^{1}H NMR (200 MHz, $CDCl_3$) 10.87 (s, 2H, –OH), 8.74 (s, 2H, aromatic), 8.13 (s, 2H, aromatic), 8.01–7.93 (m, 4H, aromatic), 7.60–7.13 (m, 12H, aromatic), 4.98 (s, 2H, –OH), 4.08 (s, 6H, $-CH_3$); IR (KBr, cm^{-1}) 3434, 1679, 1625, 1502, 1442, 1340, 1322, 1226, 1209, 1151; $[\alpha]_D^{25}$ −70 (*c* 1.0, THF) for the mixture (*RR*/*RS*/*SS*=11:45:44) (Chiralpak AD-H column, hexane/EtOH=1:1, 0.45 mL/min, 245 nm UV detector), t_R=36.2 min for (*RR*) and t_R=66.4 min for (*RS*) and t_R=127.9 min for (*SS*). Mass (FAB): *m*/*z* 687 $[M]^+$. Anal. Calcd for $C_{44}H_{30}O_8$: C, 76.96; H, 4.40. Found: C, 76.96; H, 4.51.

Compound **5b**: ^{1}H NMR (200 MHz, $CDCl_3$) 10.57 (s, 2H, –OH), 9.01 (s, 2H, aromatic), 8.14 (s, 2H, aromatic), 8.05–7.97 (m, 4H, aromatic), 7.63–7.17 (m, 22H, aromatic), 5.00 (s, 2H, –OH); IR (KBr, cm^{-1}) 3434, 1689, 1625, 1596, 1336, 1315, 1203, 1187, 1151, 1133; $[\alpha]_D^{25}$ +73 (*c* 1.0, THF) for the mixture (*RR*/*RS*/*SS*=40:48:12) (Chiralpak AD-H column, hexane/EtOH=1:1, 0.65 mL/min, 245 nm UV detector), t_R=26.1 min for (*RR*) and t_R=51.7 min for (*RS*) and t_R=95.0 min for (*SS*). Mass (FAB): *m*/*z* 811 $[M]^+$. Anal. Calcd for $C_{54}H_{34}O_8$: C, 79.99; H, 4.23. Found: C, 79.99; H, 4.28.

Compound **5c**: ^{1}H NMR (200 MHz, $CDCl_3$) 10.86 (s, 2H, –OH), 8.77 (s, 2H, aromatic), 8.12 (s, 2H, aromatic), 8.01–7.92 (m, 4H, aromatic), 7.60–7.37 (m, 18H, aromatic), 7.26–7.13 (m, 4H, aromatic), 5.51 (s, 4H, $-CH_2-$), 4.96 (s, 2H, –OH); IR (KBr, cm^{-1}) 3434, 1675, 1596, 1500, 1338, 1311, 1274, 1205, 1153, 1089; $[\alpha]_D^{25}$ −50 (*c* 1.0, THF) for the mixture (*RR*/*RS*/*SS*=12:47:41) (Chiralpak AD-H column, hexane/EtOH=1:1, 0.50 mL/min, 245 nm UV detector), t_R=64.3 min for (*RR*) and t_R=111.9 min for (*RS*) and t_R=127.6 min for (*SS*). Mass (FAB): *m*/*z* 839 $[M]^+$. Anal. Calcd for $C_{56}H_{38}O_8$: C, 80.18; H, 4.57. Found: C, 80.17; H, 4.66.

Compound **7**: ^{1}H NMR (200 MHz, $CDCl_3$) 10.89 (s, 1H, –OH), 8.75 (s, 1H, aromatic), 8.19–8.20 (m, 7H, aromatic), 7.65–7.54 (m, 2H, aromatic), 7.43–7.38 (m, 3H, aromatic), 7.27–7.17 (m, 3H, aromatic), 5.03 (s, 1H, –OH), 4.07 (s, 3H, CH_3), 1.41 (s, 9H, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) 177.25, 170.30, 154.94, 151.66, 148.76, 138.27, 137.36, 135.83, 133.96, 132.82, 132.74, 131.67, 130.57, 130.23, 129.89, 129.57, 129.52, 128.07, 127.37, 126.56, 126.35, 126.34, 125.57, 125.27, 124.72, 124.57, 121.55, 118.25, 118.18, 114.37, 114.34, 114.00, 52.92, 39.15, 27.18; IR (KBr, cm^{-1}) 3426, 2969, 1718, 1681, 1604, 1506, 1442, 1284, 1205, 1145; $[\alpha]_D^{25}$ −38 (*c* 1.0, THF) for 42% ee (*S*) (Chiralpak AD-H column, hexane/2-propanol=2:1, 0.50 mL/min, 245 nm UV detector), t_R=29.6 min for (*R*) and t_R=61.0 min for (*S*). Mass (FAB): 571 *m/z* $[M]^+$. Anal. Calcd for $C_{37}H_{30}O_6$: C, 77.88; H, 5.30. Found: C, 77.84; H, 5.22.

Compound (*R*,*R*,*R*)-**9**: Mp >300 °C; pale-yellow prisms (recrystallized from *n*-hexane/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) 10.93 (s, 2H, –OH), 8.75 (s, 2H, aromatic), 7.99–7.94 (m, 2H, aromatic), 7.54–7.49 (m, 2H, aromatic), 7.42–7.37 (m, 4H, aromatic), 7.24–7.18 (m, 8H, aromatic), 6.18 (s, 2H, –OH), 4.10 (s, 6H, CH_3), 3.59 (s, 6H, $-CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) 170.56, 154.25, 146.29, 145.82, 137.14, 133.20, 130.72, 129.88, 129.64, 129.12, 127.30, 126.52, 125.73, 124.86, 124.64, 124.42, 124.09, 123.08, 116.61, 116.05, 114.25, 61.24, 52.81; IR (KBr, cm^{-1}) 3496, 1675, 1504, 1436, 1413, 1398, 1340, 1317, 1222, 1151; $[\alpha]_D^{25}$ +179 (*c* 1.0, THF). Mass (FAB): 746 *m/z* $[M]^+$. Anal. Calcd for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4.59. Found: C, 74.00; H, 4.58.

Compound (*R*,*R*,*S*)-**9**: Mp >300 °C; pale-yellow needles (recrystallized from *n*-hexane/$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) 10.92 (s, 1H, –OH), 10.77 (s, 1H, –OH), 8.75 (s, 2H, aromatic), 7.99–7.94 (m, 2H, aromatic), 7.54–7.36 (m, 8H, aromatic), 7.26–7.20 (m, 6H, aromatic), 6.22 (s, 1H, –OH), 6.15 (s, 1H, –OH), 4.09 (s, 3H, $-CH_3$), 4.08 (s, 3H, $-CH_3$), 3.62 (s, 3H, $-CH_3$), 3.55 (s, 3H, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) 170.56, 170.48, 154.27, 154.24, 146.40, 146.33, 145.90, 145.82, 137.24, 137.15, 133.17, 133.15, 130.79, 130.70, 129.87, 129.86, 129.68, 129.60, 129.16, 129.11, 127.29, 127.23, 126.51, 126.03, 125.67, 125.58, 124.96, 124.90, 124.89, 124.69, 124.36, 124.34, 124.10, 124.07, 123.08, 122.71, 116.66, 116.64, 116.18, 115.91, 114.26, 114.24, 61.28, 61.17, 52.80, 52.77; IR (KBr, cm^{-1}) 3494, 1681, 1504, 1446, 1396, 1338, 1317, 1224, 1211, 1153; $[\alpha]_D^{25}$ +66 (*c* 1.0, THF). Mass (FAB): 746 *m/z* $[M]^+$. Anal. Calcd for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4.59. Found: C, 73.99; H, 4.57.

Compound (*S*,*R*,*S*)-**9**: Mp >300 °C; pale-yellow needles (recrystallized from *n*-hexane/THF); ^{1}H NMR (200 MHz, $CDCl_3$) 10.76 (s, 2H, –OH), 8.75 (s, 2H, aromatic), 7.99–7.95 (m, 2H, aromatic), 7.49–7.40 (m, 8H, aromatic), 7.27–7.20 (m, 6H, aromatic), 6.20 (s, 2H, –OH), 4.09 (s, 6H, $-CH_3$), 3.58 (s, 6H, $-CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) 170.50, 154.26, 146.43, 145.91, 137.26, 133.12, 130.77, 129.84, 129.68, 129.13, 127.23, 126.04, 125.54, 124.99, 124.82, 124.28, 124.09, 122.65, 116.71, 116.04, 114.26, 61.20, 52.77; IR (KBr, cm^{-1}) 3502, 1679, 1502, 1446, 1396, 1338, 1317, 1224, 1211, 1151; $[\alpha]_D^{25}$ −55 (*c* 1.0, THF). Mass (FAB): 746 *m/z* $[M]^+$. Anal. Calcd for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4.59. Found: C, 73.98; H, 4.60.

Acknowledgements

This work was partially supported by Grants-in-Aid for Scientific Research (No. 15350066) from the Ministry of Education, Science, Sports, and Culture of Japan.

Supplementary data

CD spectra of **5a–c**, **7**, and **9** are available. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.06.069.

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