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Pd-catalyzed asymmetric Wacker-type cyclization of *o*-trisubstituted allylphenols by use of tetraoxazoline ligands

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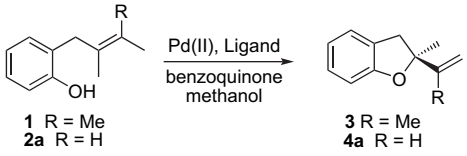
ABSTRACT

Pd(II)-catalyzed intramolecular Wacker-type cyclizations of *o*-trisubstituted allylphenols were studied. The chelation-induced axially chiral catalytic system, $Pd(CF_3COO)_2$-**8** (1:1 molar ratio), showed excellent catalytic activities and enantioselectivities in the Wacker-type cyclizations of *o*-trisubstituted allylphenols with up to 94% ee.

1. Introduction

Pd(II)-catalyzed intramolecular Wacker-type cyclizations have emerged as a versatile strategy in the construction of a range of heterocycles,[1] such as number of biologically active compounds[2] having a 2-isopropenyl-2,3-dihydrobenzofuran skeleton that contains an asymmetric carbon at the 2-position. However, asymmetric oxidative cyclizations catalyzed with chiral Pd(II)-complexes have received relatively little attention for stereoselective syntheses of these skeletons.[3] Previous attempts at asymmetric version of this oxidative cyclizations were reported by Hosokawa and Murahashi,[4] nevertheless, whose Wacker-type cyclization of *o*-allylphenols by use of a chiral π-allylpalladium complex afforded dihydrobenzofurans with only 29% ee. Recently, Hayashi and co-workers reported an important breakthrough in the Pd(II)-catalyzed enantioselective Wacker-type cyclization of *o*-allylphenols with chiral bisoxazoline ligands based on binaphthyl backbone (boxax) (Scheme 1).[5] Their researches, however, showed that the enantioselectivity of this oxidative cyclization largely depended on the substituent circumstances of allyl group at a substrate. In the cyclization of *o*-tetrasubstituted allylphenol **1**, 96% ee was obtained in the presence of *p*-benzoquinone in methanol by using boxax **5a** (see Fig. 1), but only 9% ee for *o*-trisubstituted allylphenols **2a** was obtained. Therefore, they developed boxax **5b**,[6] which introduced several functional groups at the C3 and C3′ positions of binaphthyls (see Fig. 1). Using boxax **5b** as a ligand, up to 97% ee was obtained for catalytic cyclization of **2a**, but only 9% ee was obtained for *o*-tetrasubstituted allylphenol **1**. Stoltz and co-workers also reported this reaction with Pd(II)/sparteine as a catalyst system under aerobic conditions, however, the enantioselectivities for cyclizations of *o*-trisubstituted allylphenols are not sufficiently high.[7] Very recently, we reported a series of novel biphenyl oxazoline ligands **6**, **7**, and **8** (see Figs. 1 and 2) and their applications in the Wacker-type cyclization of *o*-tetrasubstituted allylphenols.[8,9] The best result was gained with ligands **8**, which have four identical chiral oxazoline groups at four *ortho* positions in biphenyl. Although ligands **8** have no any axial chirality due to the molecular symmetry, only one diastereomer as (*S*)-axial configuration was obtained upon the complexing process whether the monometallic (*S*,a*S*)-**9** or bimetallic palladium complexes (*S*,a*S*)-**10** was formed.[9] The catalytic



1 R = Me
2a R = H

3 R = Me
4a R = H

Scheme 1. Pd(II)-catalyzed Wacker-type cyclization.

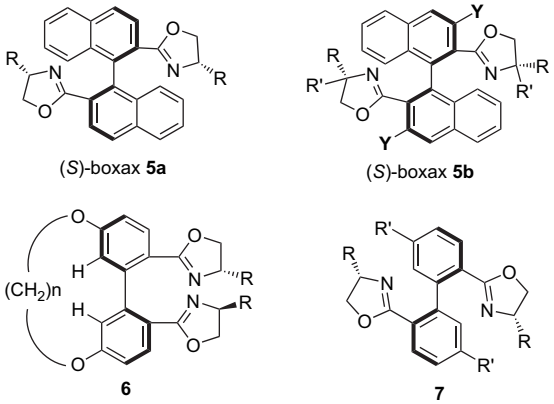


Figure 1. Bisoxazoline ligands with a biaryl backbone.

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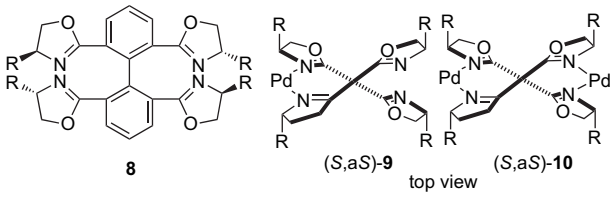


Figure 2. Tetraoxazoline ligands and their palladium complexes.

system, $Pd(CF_3COO)_2$-**8** in a 1:1 molar ratio, showed excellent catalytic activities and enantioselectivities in the Wacker-type cyclizations of *o*-tetrasubstituted allylphenols with up to 99% ee. Thus, to investigate the generality of this catalytic system, we report herein asymmetric Wacker-type cyclizations of *o*-trisubstituted allylphenols by using of Pd-**8** complex as a catalyst.[10]

2. Results and discussion

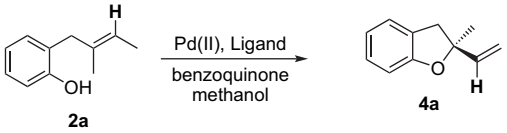
Previous work showed that phenyl-substituted tetraoxazoline (Ph-**8**) was the best ligand in Pd-catalyzed Wacker-type cyclizations of *o*-tetrasubstituted allylphenols, so Ph-**8** was used in the same reaction but the allyl group at the phenols is trisubstituted. Typically, 2-(2-methyl-2-butenyl)phenol (**2a**) was used as a model substrate for the oxidative cyclization. The reactions were catalyzed by 10 mol % of the Pd(II) complexes generated in situ by mixing $Pd(CF_3COO)_2$ with oxazoline-based biphenyl ligands in the presence of *p*-benzoquinone as reoxidant in methanol at 60 °C. As shown in Table 1, it was noteworthy that the chelation-induced axially chiral Pd-catalyst, $Pd(CF_3COO)_2$-**8** (1:1 molar ratio), is more effective than bipalladium catalyst for asymmetric cyclization of **2a** (entries 1 and 2). In order to optimize reaction conditions, the influence of palladium source, solvent, and reaction temperature was also studied. The catalytic efficiencies were largely depended on palladium source, solvent, and reaction temperature. The Pd(II) complexes formed from $Pd(OAc)_2$ and $Pd(CF_3COO)_2$ exhibited similar catalytic efficiencies (entries 1 and 3). However, markedly decreased enantioselectivity has been observed with the Pd(II)-complexes bearing chloride (entry 4). Higher catalytic activities and enantioselectivities were observed by using acetone or methanol as reaction solvents (entries 1 and 8), but the enantioselectivities markedly decreased by using THF, toluene, and TFE (2,2,2-trifluoroethanol) (entries 5–7). Furthermore, the presence of water did not affect the catalytic efficiency obviously (entry 9). It is also found that the enantioselectivity was largely depended on the reaction temperature. The enantioselectivity was significantly improved by decreasing the reaction temperature (entries 10 and 11). The reaction was also carried out at 20 °C for 3 days in acetone, the highest enantioselectivity 94% ee was acquired (entry 12). Under the same reaction conditions with entry 1, our ligands **6** with different axial configuration and the length of the bridge across the 5,5′-position of biphenyls were also used to Pd-catalyzed Wacker-type cyclizations of *o*-trisubstituted allylphenol **2a** (entries 13–15). However, only 27% ee was obtained in the cyclization of allylphenol **2a**.

With optimized reaction conditions in hand, the generality of this catalytic system, $Pd(CF_3COO)_2$-**8** (1:1 molar ratio), was studied through the Wacker-type cyclization of a series of *o*-trisubstituted allylphenols **2b**–**2e** and *o*-trisubstituted allyl naphthols **2f**–**2g**, providing corresponding chiral 2,3-dihydrobenzofurans **4b**–**4e**, dihydronaphtho[1,2-*b*]furan **4f**, and dihydronaphtho[2,1-*b*]furan **4g**. For the substrate **2b** with methyl group at 5-position of *o*-allylphenol, excellent enantioselectivity was obtained, but only 60% of isolated yield was afforded (Table 2, entry 1). The electronic property of the group at 4-position of *o*-allylphenols slightly effected the enantioselectivity of cyclizations of **2c**–**2e** (entries 2–4). When 4-position of *o*-allylphenols was substituted by phenyl (**2c**) or fluoro (**2d**) group, excellent enantioselectivities were obtained, but slightly lower enantioselectivity was obtained for cyclization of **2e**, which is substituted by methoxy group. The cyclizations of naphthol derivatives, **2f** and **2g**, gave the corresponding cyclized products **4f** and **4g** with good isolated yields and moderate enantioselectivities (entries 5 and 6).

3. Conclusion

In summary, Pd(II)-catalyzed intramolecular Wacker-type cyclizations of *o*-trisubstituted allylphenols using tetraoxazoline ligands were studied. High catalytic activity and excellent enantioselectivity for cyclization of *o*-trisubstituted allylphenols

Table 1
Pd(II)-catalyzed intramolecular Wacker-type cyclizations of *o*-trisubstituted allylphenol **2a**[a]

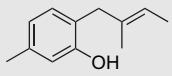
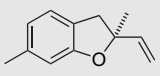
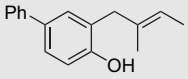
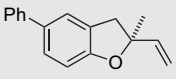
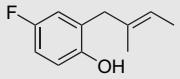
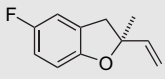
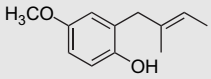
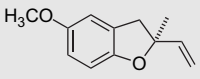
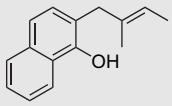
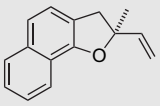
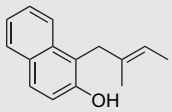
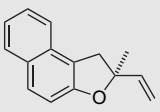


2a **4a**

Entry	Ligand	Pd source	Pd(II)/L (mol %/mol %)	Solvent	Temperature (°C)	Time (h)	Yield[b] %	ee[c] %
1	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	Methanol	60	24	94	82
2	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/5	Methanol	60	24	92	23
3	**8** (R=Ph)	$Pd(AcO)_2$	10/10	Methanol	60	24	95	79
4	**8** (R=Ph)	$PdCl_2$	10/10	Methanol	60	24	35	4
5	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	THF	60	24	27	68
6	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	Toluene	60	24	39	49
7	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	TFE	60	24	78	16
8	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	Acetone	Reflux	24	93	83
9	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	5% H_2O in methanol	60	24	91	77
10	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	Methanol	40	72	90	86
11	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	Methanol	20	72	79	93
12	**8** (R=Ph)	$Pd(CF_3COO)_2$	10/10	Acetone	20	72	87	94
13	(*S*,a*R*,*S*)-**6** (*n*=8, R=*i*-Pr)	$Pd(CF_3COO)_2$	10/20	Methanol	60	24	94	27
14	(*S*,a*S*,*S*)-**6** (*n*=8, R=*i*-Pr)	$Pd(CF_3COO)_2$	10/20	Methanol	60	24	12	2
15	(*S*,a*R*,*S*)-**6** (*n*=10, R=*i*-Pr)	$Pd(CF_3COO)_2$	10/20	Methanol	60	24	91	23

[a] The reactions were catalyzed by Pd(II)-**8** complex generated in situ by mixing palladium source with tetraoxazoline **8** in the presence of 4 equiv of *p*-benzoquinone.
[b] Isolated yield by column chromatography.
[c] The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min). The *S* absolute configuration was assigned by comparison of optical rotations with the known reported data.[6]

Table 2
Pd(II)-catalyzed intramolecular Wacker-type cyclizations of *o*-trisubstituted allylphenols **2b**–**2e** and *o*-trisubstituted allyl naphthols **2f**–**2g**[a]

Entry	Substrate	Product[b]	Yield[c] %	ee[d] %
1	 **2b**	 **4b**	60	92
2	 **2c**	 **4c**	87	90
3	 **2d**	 **4d**	89	90
4	 **2e**	 **4e**	90	83
5	 **2f**	 **4f**	88	54
6	 **2g**	 **4g**	92	71

[a] All reactions were catalyzed by 10 mol % of the Pd(II)-**8** complex generated in situ by mixing $Pd(CF_3COO)_2$ with tetraoxazoline **8** (Pd/ligand 1:1) in the presence of 4 equiv of *p*-benzoquinone in acetone at 20 °C for 72 h.
[b] Absolute configurations for these products were assigned by analogy through comparison of HPLC elution order with compounds **4a**.
[c] Isolated yield by column chromatography.
[d] The ee was determined by HPLC on a Daicel Chiralcel OD-H column.

were observed by using $Pd(CF_3COO)_2$-**8** (1:1 molar ratio) with up to 94% ee. It is demonstrated that our tetraoxazoline ligand **8** is of more general utility for Wacker-type cyclization than others that have been reported previously. The applications of tetraoxazoline ligands in other asymmetric reactions are underway.

4. Experimental

4.1. General comments

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. Methanol and 2,2,2-trifluoroethanol (TFE) were distilled from CaH_2. The commercially available reagents were used without further purification. The substrates of Wacker-type cyclization, **2a**–**2g**, were prepared according to the literature procedures.[5a] TLC was run on 2 cm×5 cm silica plate. Column chromatography was run on silica gel (100–200 mesh). ^{1}H NMR (400 MHz) spectra and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer. The ee values were determined by HPLC using a Daicel Chiralcel OD-H. HRMS were performed on a Micromass LCTTM at the Analysis and Research Center of East China University of Science and Technology.

4.2. General procedure for the Pd(II)-catalyzed asymmetric Wacker-type cyclization of *o*-trisubstituted allylphenols and naphthols

A typical procedure is given for the reaction of 2-(2-methyl-2-butenyl)phenol (**2a**) with a palladium(II) complex of ligand **8** forming (*S*)-2-ethenyl-2-methyl-2,3-dihydrobenzofuran (**4a**). To a solution of palladium bis(trifluoroacetate) (14.0 mg, 0.042 mmol) and **8** (31.1 mg, 0.042 mmol) in methanol (1.0 mL) were added *p*-benzoquinone (181.6 mg, 1.68 mmol) and 2-(2-methyl-2-butenyl)phenol (**2a**) (68.2 mg, 0.42 mmol) in methanol (0.5 mL) at room temperature. The reaction mixture was stirred at 60 °C for 24 h, concentrated in vacuo, and then chromatographed on silica gel (eluent: ethyl acetate and petroleum ether) to give compound **4a**.

*4.2.1. (S)-2-Ethenyl-2-methyl-2,3-dihydrobenzofuran (**4a**)*

Yield 94% (63.0 mg), 82% ee, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11–7.16 (m, 2H, ArH), 6.76–6.88 (m, 2H, ArH), 6.05 (dd, *J*=17.6, 11.2 Hz, 1H, CH), 5.31 (dd, *J*=17.2, 0.8 Hz, 1H, CH), 5.10 (dd, *J*=10.4, 0.8 Hz, 1H, CH), 3.18 (d, *J*=14.2 Hz, 1H, CH_2), 3.06 (d, *J*=15.6 Hz, 1H, CH_2), 1.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 141.8, 128.2, 126.6, 125.2, 120.4, 113.0, 109.6, 87.7, 42.2, 26.3. The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min).

*4.2.2. (S)-2-Ethenyl-2,6-dimethyl-2,3-dihydrobenzofuran (**4b**)*

Yield 60%, 92% ee, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (dd, *J*=7.6, 15.2 Hz, 1H, ArH), 6.66 (d, *J*=7.2 Hz, 1H, ArH), 6.63 (d, *J*=8.0 Hz, 1H, ArH), 6.00–6.09 (m, 1H, CH), 5.27–5.33 (m, 1H, CH), 5.06–5.10 (m, 1H, CH), 3.09 (d, *J*=15.6 Hz, 1H, CH_2), 2.97 (d, *J*=15.6 Hz, 1H, CH_2), 2.20 (s, 3H, CH_3), 1.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 142.0, 128.1, 124.7, 121.4, 121.1, 112.7, 110.4, 87.8, 41.9, 26.5, 21.7; HRMS (Micromass LCT) calcd for $C_{12}H_{14}O$: 174.1045, found: 174.1046. The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min).

*4.2.3. (S)-2-Ethenyl-2-methyl-5-phenyl-2,3-dihydrobenzofuran (**4c**)*

Yield 87%, 90% ee, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.57 (m, 2H, ArH), 7.27–7.41 (m, 5H, ArH), 6.85 (d, *J*=8.8 Hz, 1H, ArH), 6.08 (dd, *J*=17.6, 10.8 Hz, 1H, CH), 5.34 (dd, *J*=17.2, 0.8 Hz, 1H, CH), 5.11 (dd, *J*=10.8, 0.8 Hz, 1H, CH), 3.23 (d, *J*=15.6 Hz, 1H, CH_2), 3.10 (d, *J*=15.6 Hz, 1H, CH_2), 1.58 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 141.7, 141.5, 134.0, 128.8, 127.3, 127.2, 126.9, 126.6, 124.1, 113.1, 109.8, 82.2, 42.2, 26.3; HRMS (Micromass LCT) calcd for $C_{17}H_{16}O$: 236.1201, found: 236.1204. The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min).

*4.2.4. (S)-2-Ethenyl-2-methyl-5-fluoro-2,3-dihydrobenzofuran (**4d**)*

Yield 89%, 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77–6.85 (m, 2H, ArH), 6.68 (dd, *J*=4.4, 8.8 Hz, 1H, ArH), 6.02 (dd, *J*=17.2, 10.8 Hz, 1H, CH), 5.30 (dd, *J*=17.2, 0.8 Hz, 1H, CH), 5.10 (dd, *J*=10.8, 1.2 Hz, 1H, CH), 3.15 (d, *J*=16.0 Hz, 1H, CH_2), 3.04 (d, *J*=15.6 Hz, 1H, CH_2), 1.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 114.3, 114.1, 113.1, 112.4, 112.1, 109.7, 109.6, 88.4, 42.3, 26.2; HRMS (Micromass LCT) calcd for $C_{11}H_{11}FO$: 178.0794, found: 178.0795. The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.5:0.5, flow=0.5 mL/min).

*4.2.5. (S)-2-Ethenyl-2-methyl-5-methoxy-2,3-dihydrobenzofuran (**4e**)*

Yield 90%, 83% ee, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64–6.73 (m, 3H, ArH), 6.03 (dd, *J*=17.2, 10.4 Hz, 1H, CH), 5.30 (dd, *J*=17.2, 0.8 Hz, 1H, CH), 5.08 (dd, *J*=8.4, 1.2 Hz, 1H, CH), 3.74 (s, 3H, OCH_3), 3.15 (d, *J*=16.0 Hz, 1H, CH_2), 3.03 (d, *J*=15.2 Hz, 1H, CH_2), 1.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 153.1, 141.8, 127.6, 113.0, 112.9, 111.5, 109.5, 87.8, 56.1, 42.6, 26.2; HRMS (Micromass LCT) calcd for $C_{12}H_{14}O_2$: 190.0994, found: 190.0994. The ee was

determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min).

*4.2.6. (S)-2-Ethenyl-2-methyl-2,3-dihydronaphtho[1,2-b]furan (**4f**)*

Yield 88%, 54% ee, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J=7.6 Hz, 1H, ArH), 7.69 (d, J=9.2 Hz, 1H, ArH), 7.54 (d, J=8.4 Hz, 1H, ArH), 7.43–7.47 (m, 1H, ArH), 7.25–7.31 (m, 1H, ArH), 7.12 (d, J=8.4 Hz, 1H, ArH), 6.14 (dd, J=17.6, 10.8 Hz, 1H, CH), 5.37 (dd, J=17.2, 1.2 Hz, 1H, CH), 5.12 (dd, J=10.8, 1.2 Hz, 1H, CH), 3.46 (d, J=5.6 Hz, 1H, CH_2), 3.33 (d, J=15.6 Hz, 1H, CH_2), 1.64 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 141.9, 131.1, 129.3, 129.2, 128.9, 126.7, 122.9, 122.7, 117.9, 112.9, 112.4, 88.6, 41.2, 26.6; HRMS (Micromass LCT) calcd for $C_{15}H_{14}O$: 210.1045, found: 210.1045. The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min).

*4.2.7. (S)-2-Ethenyl-2-methyl-2,3-dihydronaphtho[2,1-b]furan (**4g**)*

Yield 92%, 71% ee, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J=8.8 Hz, 1H, ArH), 7.69 (d, J=9.2 Hz, 1H, ArH), 7.52 (d, J=8.0 Hz, 1H, ArH), 7.44 (dd, J=6.8, 8.0 Hz, 1H, ArH), 7.28 (dd, J=7.2, 8.4 Hz, 1H, ArH), 7.12 (d, J=8.8 Hz, 1H, ArH), 6.12 (dd, J=17.2, 10.4 Hz, 1H, CH), 5.36 (d, J=17.2 Hz, 1H, CH), 5.11 (d, J=10.8 Hz, 1H, CH), 3.43 (d, J=15.2 Hz, 1H, CH_2), 3.30 (d, J=15.6 Hz, 1H, CH_2), 1.63 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 141.9, 131.1, 129.3, 129.2, 128.9, 126.7, 122.8, 122.7, 117.9, 112.9, 112.4, 88.6, 41.1, 26.5; HRMS (Micromass LCT) calcd for $C_{15}H_{14}O$: 210.1045, found: 210.1045. The ee was determined by HPLC on a Daicel Chiralcel OD-H column (hexane/2-propanol=99.0:1.0, flow=0.5 mL/min).

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References and notes

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