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ENANTIOSELECTIVE SYNTHESIS OF PLANAR-CHIRAL PHOSPHINES WITH 1,*N*-DIOXA[*N*]PARACYCLOPHANE SCAFFOLD AND THEIR APPLICATION AS CHIRAL LIGANDS

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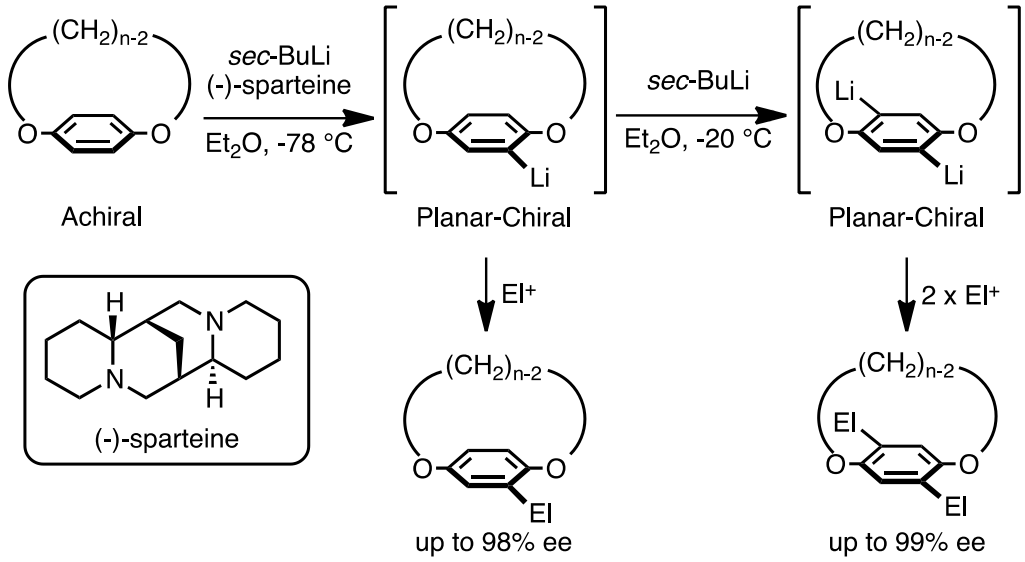
Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday.

Abstract – A new family of chiral phosphines based on planar-chiral 1,*n*-dioxa[*n*]paracyclophane scaffold was created. They were synthesized with excellent enantioselectivity via asymmetric *ortho*-lithiation using *sec*-butyllithium and (-)-sparteine. These phosphines were used as chiral ligands in three reactions: Ag-catalyzed allylation of imines, Pd-catalyzed asymmetric Sonogashira coupling of diiodoparacyclophanes, and Pd-catalyzed asymmetric Suzuki-Miyaura coupling of tricarbonyl(η^6-*ortho*-dichlorobenzene)chromium.

INTRODUCTION

Asymmetric catalysis is a powerful tool for the preparation of enantiomerically enriched compounds.[1] Especially, chiral phosphines have shown great ability as efficient ligands, which induce high enantioselectivity in a number of transition-metal-catalyzed reactions such as asymmetric hydrogenation, conjugate addition, cross coupling and cycloaddition.[1,2] Many of these chiral ligands contain some common backbones, such as binaphthyl, ferrocenyl, and spirocyclic systems. If a new chiral backbone is created, new and/or high selectivity, which cannot be achieved by conventional chiral ligands, would be expected. In this regard, planar-chiral paracyclophane structure is an attractive chiral framework.[3,4]

Actually, several [2.2]paracyclophane-based chiral ligands have been reported.[5,6] Especially, 4,12-bis(diarylphosphino)[2.2]paracyclophanes (PHANEPHOS derivatives) are commercially available and realized higher enantioselectivity than other common chiral diphosphine ligands, such as BINAP derivatives in some reactions.[7] But the enantioselective preparation of chiral [2.2]paracyclophane derivatives is still difficult. In many cases, individual and ingenious resolution procedures are necessary for racemic compounds.[5,6,8] A few protocols of other planar-chiral paracyclophane synthesis was reported,[4,9,10] however, their application for the synthesis of phosphine ligands is difficult. To the best of our knowledge, there is no phosphine ligand with planar-chiral paracyclophane scaffold other than [2.2]paracyclophane derivatives. Recently, we reported a new strategy for the planer-chiral paracyclophane synthesis: enantioselective *ortho*-lithiation of unflippable 1,*n*-dioxa[*n*]paracyclophanes ($n \leq 11$) using *sec*-butyllithium and (-)-sparteine at -78 °C and further lithiation at -20 °C gave planar-chiral monolithiated and C_2-symmetric dilithiated paracyclophanes, respectively. Subsequent treatment of these chiral lithium salts with various electrophiles gave planar-chiral mono- and disubstituted paracyclophanes with excellent to almost perfect ee (Scheme 1).[11]



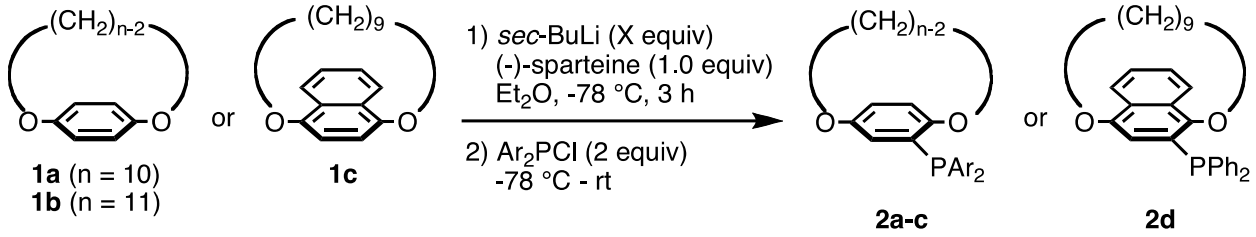
Scheme 1. Enantioselective synthesis of planar-chiral paracyclophanes via *ortho*-lithiation

We considered that this protocol can be used for the synthesis of planar-chiral phosphine derivatives. In this paper, a new family of planar-chiral phosphines with a 1,*n*-dioxa[*n*]paracyclophane backbone was synthesized by this method and used as chiral ligands in Ag-catalyzed asymmetric allylation, Pd-catalyzed Sonogashira, and Suzuki-Miyaura couplings.

RESULTS AND DISCUSSION

Each of 1,*n*-Dioxa[*n*]paracyclophanes **1a** (*n*=10) and **1b** (*n*=11) possesses an unflippable ansa chain,[12,13] therefore, their mono-substitution on the benzene ring generates planar chirality (Table 1). The reaction of **1a** and **1b** with *sec*-butyllithium and (-)-sparteine at -78 °C in diethyl ether followed by treatment with chlorodiphenylphosphine gave planar-chiral diphenylphosphinoparacyclophanes **2a** and **2b** with excellent ee (Entries 1 and 2).[14] The structure of **2b** was determined by X-ray analysis and its ORTEP diagram was shown in Figure 1. Treatment of monolithiated **1b** with chlorobis(3,5-bis(trifluoromethyl)phenyl)-phosphine gave corresponding electron-deficient phosphine **2c** (Entry 3). Furthermore, planar-chiral phosphine with (1.4)naphthalenophane skeleton was obtained with excellent ee from **1c** (Entry 4).

Table 1. Enantioselective synthesis of planar-chiral monophosphine



Entry	Substrate	X / equiv	Ar	Yield / %	Ee / %
1	**1a**	1.2	C_6H_5	42 (**2a**)	99
2	**1b**	2.0	C_6H_5	58 (**2b**)	98
3	**1b**	2.0	3,5-$(CF_3)_2C_6H_3$	41 (**2c**)	98
4	**1c**	1.2	C_6H_5	85 (**2d**)[a]	98[b]

[a] NMR yield. [b] Phosphine **2d** was characterized as the corresponding phosphine oxide, because **2d** could not be separated from **1c**.

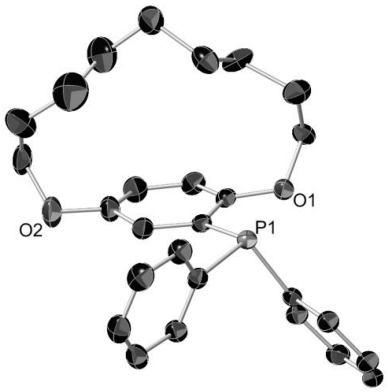
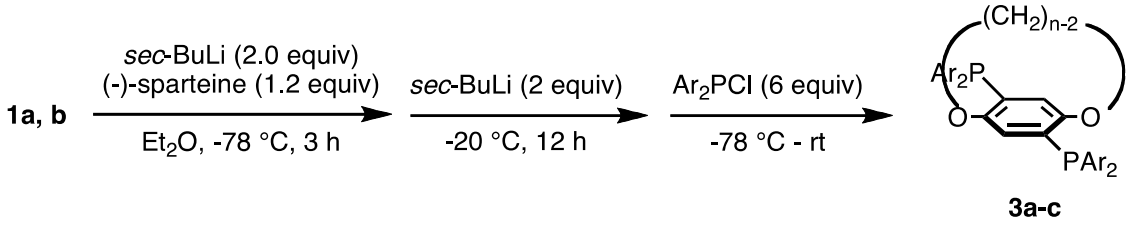


Figure 1. Thermal ellipsoid plot of **2b** is shown at the 30% probability level. The hydrogen atoms and one part of disorders on the ansa chain were omitted for clarity.

We also synthesized C_2 symmetric planar-chiral diphosphines (Table 2). After the first enantioselective lithiation of **1a** and **1b**, further addition of two equivalent amounts of *sec*-butyllithium at -20 °C induced the second lithiation. Treatment of the obtained dilithiated compounds with excess amounts of chlorodiphenylphosphine gave the corresponding diphosphines **3a** and **3b** with almost perfect ee (Entries 1 and 2). The preparation of electron-deficient diphosphine **3c** was also possible (Entry 3).

Table 2. Enantioselective synthesis of C_2 symmetric planar-chiral diphosphines

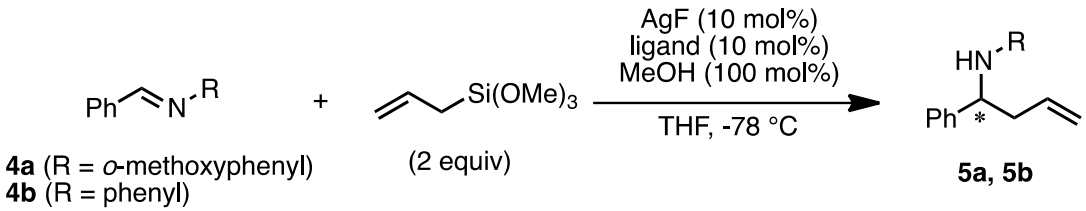


Entry	Substrate	Ar	Yield / %	Ee / %
1	**1a**	C_6H_5	55 (**3a**)	98[a]
2	**1b**	C_6H_5	55 (**3b**)	99[a]
3	**1b**	3,5-$(CF_3)_2C_6H_3$	54 (**3c**)	98[a]

[a] Ee was determined as the corresponding diphosphine oxide.

Next we considered the use of the obtained mono- and diphosphines as chiral ligands in transition-metal-catalyzed reactions and paid attention to the similarity as P,O-ligands between our developed phosphines and 2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MOP). We first chose Ag-catalyzed enantioselective allylation of imines with allylsilanes, where MOP was the preferable ligand (Table 3).[15] We used *N*-benzylidene-2-methoxyaniline (**4a**), which was a good substrate in the literature,[15] and we examined asymmetric Ag-catalyzed allylation using monophosphines **2a**, **2b** and diphosphines **3a**, **3b**, but both of the yield and ee were low in all cases (Entries 1-4).[16] In contrast, the reaction of *N*-benzylideneaniline (**4b**) smoothly proceeded and chiral homoallyl amine **5b** was obtained in good yield with moderate ee (Entries 5-8). These results suggest that our developed planar-chiral phosphines could be used as chiral ligands and show the different selectivity with conventional ligands.

Table 3. Ag-catalyzed allylation of imines using paracyclophane-based phosphine ligands



4a (R = *o*-methoxyphenyl)
4b (R = phenyl)

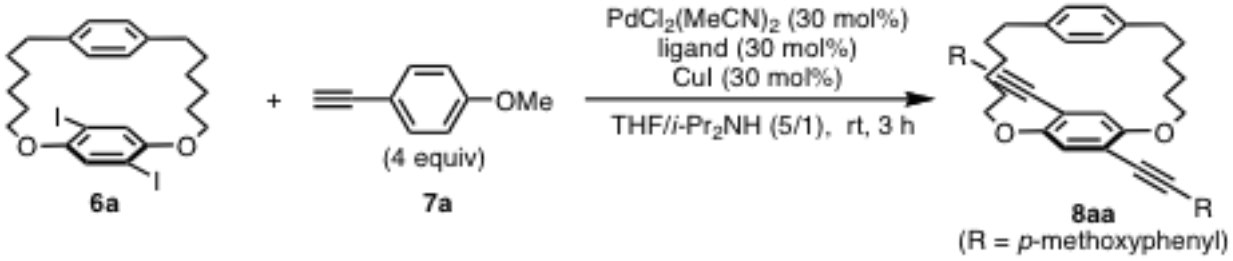
(2 equiv)

5a, 5b

Entry	Imine	Ligand	Yield / %	Ee / %
1	**4a**	**2a**	5 (**5a**)	11
2	**4a**	**2b**	22 (**5a**)	15
3	**4a**	**3a**	10 (**5a**)	10
4	**4a**	**3b**	11 (**5a**)	38
5	**4b**	**2a**	90 (**5b**)	51
6	**4b**	**2b**	89 (**5b**)	57
7	**4b**	**3a**	89 (**5b**)	48
8	**4b**	**3b**	62 (**5b**)	59

Next we focused attention on the planar chirality of our ligands. One of the typical chiral phosphine ligands with planar chirality is a ferrocenyl ligand, and various types of chiral ligands are now commercially available. We also used a ferrocenyl phosphine ligand, (R_P)-1-[(*R*)-α-(dimethylamino)-2-(diphenylphosphino)benzyl]-2-diphenylphosphinoferrocene (TANIAPHOS) as the best ligand in the Pd-catalyzed asymmetric double Sonogashira coupling of diiodoparacyclophanes possessing a flippable ansa chain.[10c] Based on this background, we chose the asymmetric Sonogashira coupling as the second model reaction. Under the optimal reaction conditions, the coupling of diiodoparacyclophane **6a** with 4-ethynylanisole (**7a**) gave dialkynylated product **8aa** with 57% ee in the presence of cesium carbonate as a base (Table 4, Entry 1). When organic base such as diisopropylamine was used, the reaction proceeded smoothly at room temperature, but ee was low (Entry 2). Under the same reaction conditions, Sonogashira coupling was examined using paracyclophane-based ligands (Entries 3-6). As a result, monophosphine **2b** realized the highest ee of 72% (Entry 4), which was higher than the previous best result (57% ee) (Entry 1). Even when the amount of the catalyst was lowered from 30 mol% to 10 mol%, comparable yield and ee were achieved (Entry 7).

Table 4. Pd-catalyzed asymmetric Sonogashira coupling of **6a**

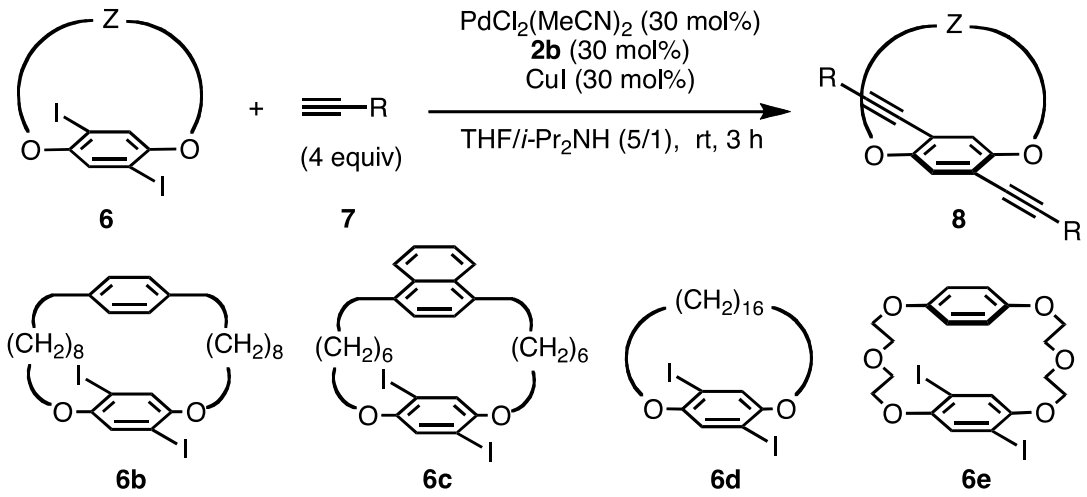


Entry	Ligand	Yield / %	Ee / %
1[a]	TANIAPHOS	98	57
2	TANIAPHOS	81	22
3	**2a**	74	53
4	**2b**	**93**	**72**
5	**3a**	70	50
6	**3b**	78	64
7[b]	**2b**	93	70

[a] Cesium carbonate (4 equiv) was used as a base in place of diisopropylamine and the reaction time was 6 h. [b] Less amounts of $PdCl_2(MeCN)_2$ (10 mol%), **2b** (10 mol%), and CuI (10 mol%) were used.

Substrate scope of alkynes and diiodoparacyclophanes was examined, and the enantiomeric excesses under the previous optimal conditions were listed in the rightmost row for comparison (Table 5). A few MeO-substituted arylalkynes **7b-7d** were submitted to the reaction with paracyclophane **6a** and the corresponding dialkynylated products **8ab-8ad** were obtained in excellent yield (Entries 1-3). Among them, 2-ethynylanisole (**7c**) induced the highest enantioselectivity of 76% (Entry 2). Phenylacetylene (**7e**) was also a good coupling partner (Entry 4). Propargyl ethers **7f** and **7g** could be used, but the yield was low to moderate because of the formation of 1,3-diynes as by-products (Entries 5 and 6). In the reaction of other diiodoparacyclophanes **6b-6e** with alkyne **7a** (Entries 7-10), 1,4-naphthylene-tethered paracyclophane **6c** was a preferable substrate and the highest ee of 90% was achieved, which is the highest value among all previous results using TANIAPHOS as a chiral ligand.[10c]

Table 5. Asymmetric Sonogashira coupling of various diiodoparacyclophanes and alkynes using **2b**

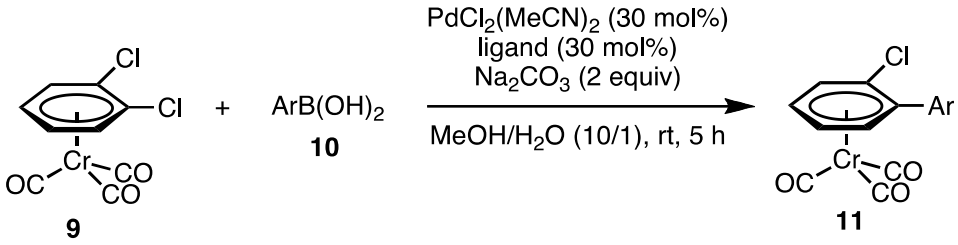


Entry	Substrate	R	Yield / %	Ee / %	Ee / %[a]
1	**6a**	3-MeOC$_6$H$_4$ (**7b**)	97 (**8ab**)	55	59
2	**6a**	2-MeOC$_6$H$_4$ (**7c**)	94 (**8ac**)	76	69
3	**6a**	2,6-(MeO)$_2$C$_6$H$_3$ (**7d**)	95 (**8ad**)	62	66
4	**6a**	C$_6$H$_5$ (**7e**)	80 (**8ae**)	79	56
5	**6a**	BnOCH$_2$ (**7f**)	34 (**8af**)	66	78
6	**6a**	MeOCH$_2$ (**7g**)	51 (**8ag**)	79	79
7	**6b**	4-MeOC$_6$H$_4$ (**7a**)	92 (**8ba**)	76	55
8	**6c**	4-MeOC$_6$H$_4$ (**7a**)	80 (**8ca**)	90	54
9	**6d**	4-MeOC$_6$H$_4$ (**7a**)	87 (**8da**)	72	52
10	**6e**	4-MeOC$_6$H$_4$ (**7a**)	81 (**8ea**)	68	58

[a] The result under the optimal reaction conditions using TANIAPHOS: $PdCl_2(MeCN)_2$ (10 mol%), TANIAPHOS (10 mol%), CuI (10 mol%) Cs_2CO_3 (4 equiv) in THF at 25 °C.[10c]

Finally, we investigated enantioselective desymmetrization of tricarbonyl(η^6-*ortho*-dichlorobenzene)-chromium **9** by Suzuki-Miyaura coupling because planar chiral ligand, *N*,*N*-dimethyl-1-[2-(diphenylphosphino)ferrocenyl]ethylamine (PPFA) realized good enantioselectivity in this reaction, but toxic TlOH was used as a base.[17] We examined the coupling of the chromium arene complex with phenylboronic acid (**10a**) using much less toxic Na_2CO_3 as a base. According to the screening of planar-chiral phosphines (Table 6, Entries 1-4), diphosphine **3b** was optimal and high enantioselectivity was achieved.[18] The coupling of **9** with 4-methoxyphenylboronic acid (**10b**) also proceeded in high enantioselectivity (Entry 5).

Table 6. Asymmetric Suzuki-Miyaura coupling of tricarbonyl(η^6-*ortho*-dichlorobenzene)chromium



Entry	Ligand	Ar	Yield / %	Ee / %
1	**2a**	C_6H_5 (**10a**)	59 (**11a**)	55
2	**2b**	C_6H_5 (**10a**)	48 (**11a**)	24
3	**3a**	C_6H_5 (**10a**)	58 (**11a**)	59
4	**3b**	C_6H_5 (**10a**)	66 (**11a**)	85
5[a]	**3b**	4-$MeOC_6H_4$ (**10b**)	59 (**11b**)	79

[a] The reaction time was 2 h.

In conclusion, a new family of [*n*]paracyclophane-based planar-chiral phosphines was synthesized by enantioselective *ortho*-lithiation of 1,*n*-dioxa[*n*]paracyclophane using *sec*-butyllithium and (-)-sparteine. Treatment of the chiral monolithiated- and dilithiated 1,*n*-dioxa[*n*]paracyclophane with a chlorophosphine derivatives gave planar-chiral monophosphines and C_2-symmetric diphosphines, respectively, with excellent ee. These phosphines were used as chiral ligands in Ag-catalyzed allylation of imines and Pd-catalyzed couplings. As a result, good to high enantioselectivities were achieved in the asymmetric Sonogashira coupling of diiodoparacyclophanes possessing a flippable ansa chain (up to 90% ee) and asymmetric desymmetrization of tricarbonyl(η^6-*ortho*-dichlorobenzene)chromium by Suzuki-Miyaura coupling (up to 85% ee).

EXPERIMENTAL

General. All reactions were examined under an argon atmosphere in oven-dried glassware with a magnetic stirring bar. A hexane-cyclohexane solution of *sec*-butyllithium (1.0 M) was purchased from Kanto Chemical Co., Inc. Dehydrated diethyl ether and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries Ltd. (Wako), and purified by passing thorough a purification system (Glass Contour) before use.[19] (-)-Sparteine was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Other reagents were purchased from Wako, Kanto, TCI, or Aldrich and were used without further purification. Flash column chromatography was performed with silica gel (Kanto Chemical Co., Inc. 60 N 40-50 μm). Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory. Gel permeation chromatography (GPC) was

performed on JAI LC-908. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 (400 MHz), JEOL ECS400 (400 MHz), JEOL ECX500 (500 MHz), or JEOL Lambda 500 (500 MHz) using TMS as an internal standard and $CDCl_3$ was used as a solvent. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-SX102A with FAB (Fast Atomic Bombardment) method or JMS-T100CS with ESI (Electro Spray Ionization) method. Optical rotations were measured with Jasco DIP-1000 polarimeter. Physical properties of phosphines **2a** and **3b**, and Sonogashira-coupling products **8aa-8ag** were omitted, because they were already listed in the precedent report.[10c,11]

Typical Experimental Procedure of Enantioselective Monolithiation for the Synthesis of Monophosphine 2 (Table 1). A cyclohexane-hexane solution of *sec*-butyllithium (1.0 M, 1.2 or 2.0 mL, 1.2 or 2.0 mmol) was added dropwise to an ether solution (5 mL) of a 1,*n*-dioxa[*n*]paracyclophane **1** (1.0 mmol) and (-)-sparteine (230 μL, 1.0 mmol) at -78 °C and the reaction mixture was stirred for 3 h at -78 °C. To the mixture was added dropwise chlorodiarylphosphine (2 mmol) at -78 °C, and the reaction mixture stirred for 2 h at room temperature. It was filtered through a short plug of silica gel with CH_2Cl_2 and the filtrate was evaporated under reduced pressure. The crude products were purified by flash column chromatography (hexane/CH_2Cl_2= 3/1) to give the corresponding paracyclophane **2**.

13-(Diphenylphosphino)-1,11-dioxa[11]paracyclophane (2b). White solid. Mp 110 °C; IR (CH_2Cl_2) 2925, 2854, 1473, 1456, 1194, 742, 696 cm^{-1}; ^1H NMR (500 MHz) δ 0.67-0.79 (m, 1H), 0.79-1.08 (m, 8H), 1.10-1.23 (m, 1H), 1.35-1.47 (m, 1H), 1.50-1.67 (m, 2H), 1.81-1.93 (m, 1H), 3.87-3.96 (m, 1H), 3.99-4.07 (m, 1H), 4.20-4.334 (m, 2H), 6.32-6.37 (m, 1H), 7.00-7.07 (m, 2H), 7.26-7.40 (m, 10H); ^{13}C NMR (125 MHz) δ 25.8, 26.0, 26.0, 26.2, 26.5, 27.9, 29.8, 71.7, 72.0 (d, *J*= 2.1 Hz), 119.8 (d, *J*= 2.1 Hz), 122.1, 125.2, 128.3 (d, *J*= 6.2 Hz), 128.4, 128.5 (d, *J*= 6.2 Hz), 128.9, 130.9 (d, *J*= 13.4 Hz), 133.1 (d, *J*= 19.7 Hz), 134.5 (d, *J*= 20.7 Hz), 136.4 (d, *J*= 10.3 Hz), 137.1 (d, *J*= 11.3 Hz), 154.5, 156.6 (d, *J*= 16.6 Hz); ^{31}P NMR (200 MHz) δ -17.9; HRMS (FAB^+) for M^+ found *m/z* 418.2057, calcd for $C_{27}H_{31}O_2P$: 418.2056. $[\alpha]^{26}_D$ 5.8 (*c* 1.21 $CHCl_3$, 98% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 0.5 mL/min, retention time: 9.1 min for major isomer and 9.8 min for minor isomer). The crystal data of **2b**: $C_{27}H_{31}O_2P$, *M*=418.51, monoclinic, space group $P2_1$ (no. 4), a = 8.7764(3) Å, b = 12.7465(4) Å, c = 10.3739(3) Å, β = 98.110(2) °, V = 1148.91(6) $Å^3$, *T*=173 K, *Z*=2, μ(Cu Kα) 12.086 cm^{-1}; number of reflections measured: total 12,015 and unique 4026, *R*1=0.0490, *wR*2=0.1295, Flack parameter (Friedel pairs=1823) 0.01(3). CCDC 953143.

13-(Bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-1,11-dioxa[11]paracyclophane (2c). White solid. Mp 85 °C; IR (CH_2Cl_2) 2924, 1279, 1185, 1136, 899, 802, 682 cm^{-1}; ^1H NMR (400 MHz) δ 0.65-0.72 (m,

1H), 0.84-0.97 (m, 5H), 0.98-1.06 (m, 1H), 1.07-1.13 (m, 1H), 1.19-1.34 (m, 1H), 1.39-1.43 (m, 1H), 1.58-1.67 (m, 3H), 1.72-1.84 (m, 1H), 3.95-3.99 (m, 1H), 4.09-4.13 (m, 1H), 4.22-4.31 (m, 2H), 6.28-6.30 (m, 1H), 7.11-7.18 (m, 2H), 7.68-7.74 (m, 4H), 7.91 (d, *J*= 15.9 Hz, 2H); ^{13}C NMR (125 MHz) δ 25.7, 25.8, 26.1, 26.6, 27.8, 29.5, 72.1 (d, *J*= 14.4 Hz), 119.9, 121.7 (d, *J*= 8.5 Hz), 123.4, 124.1-124.7 (m), 126.1 (d, *J*= 14.2 Hz), 131.9-132.5 (m), 133.1 (d, *J*= 26.3 Hz), 133.6 (d, *J*= 25.2 Hz), 138.5 (d, *J*= 22.4 Hz), 139.8 (d, *J*= 22.4 Hz), 154.9, 156.6 (d, *J*= 20.3 Hz); ^{31}P NMR (200 MHz) δ -12.2; ^{19}F NMR (470 MHz) δ -62.6, -62.9; HRMS (FAB$^+$) for $[M+H]^+$ found *m/z* 691.1627, calcd for $C_{31}H_{28}O_2F_{12}P$: 691.1630. $[\alpha]^{37}_D$ -28.5 (*c* 1.09 $CHCl_3$, 98% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 0.5 mL/min, retention time: 6.0 min for major isomer and 8.3 min for minor isomer).

13-(Diphenylphosphinic)-1,11-dioxa[11](1,4)naphthalenophane (oxide of 2d). To a mixture of **1c** and **2d** in CH_2Cl_2-acetone (1/1, 0.5 mL), H_2O_2 (0.5 mL) was added and stirred for 1 h at room temperature. The solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 and the combined organic layer was dried over Na_2SO_4. The solvent was removed under the reduced pressure and the crude products were purified by PTLC (AcOEt) to give the oxide of **2d**. White solid. Mp 57 °C; IR (CH_2Cl_2) 3060, 1586, 1499, 1230, 1025, 728, 699 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.26-0.29 (m, 3H), 0.60-0.63 (m, 3H), 0.77-0.82 (m, 3H), 0.88-0.90 (m, 1H), 1.19-1.24 (m, 1H), 1.34-1.39 (m, 1H), 1.70-1.76 (m, 1H), 1.80-1.86 (m, 1H), 4.17-4.28 (m, 2H), 4.31-4.40 (m, 2H), 6.98-7.02 (m, 1H), 7.45-7.47 (m, 4H), 7.51-7.53 (m, 3H), 7.58-7.60 (m, 1H), 7.71-7.78 (m, 4H), 8.12-8.17 (m, 1H), 8.24-8.28 (m, 1H); ^{13}C NMR (125 MHz) δ 24.9, 25.9, 26.2, 26.3, 27.6, 29.4, 30.6, 72.4, 75.9, 115.6 (d, *J*= 11.7 Hz), 119.8, 120.9, 122.4, 124.3, 126.4, 128.0, 128.3 (d, *J*= 15.6 Hz), 128.5 (d, *J*= 14.4. Hz), 130.5 (d, *J*= 12.7 Hz), 131.1, 131.5, 131.6, 131.7, 132.0 (d, *J*= 12.0 Hz), 133.0, 152.0, 154.6; ^{31}P NMR (200 MHz) δ 33.8; HRMS (FAB$^+$) for $[M+H]^+$ found *m/z* 485.2242, calcd for $C_{31}H_{34}O_3P$: 485.2240. $[\alpha]^{34}_D$ -106.8 (*c* 1.58 $CHCl_3$, 98% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IC: 4 x 250 mm, 254 nm UV detector, rt, eluent: 50% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 5.7 min for major isomer and 7.0 min for minor isomer).

Typical Experimental Procedure of Enantioselective Dilithiation for the Synthesis of Diphosphine 3 (Table 2). A cyclohexane-hexane solution of *sec*-butyllithium (1.0 M, 2.0 mL, 2.0 mmol) was added dropwise to an ether solution (5 mL) of a 1,*n*-dioxa[*n*]paracyclophane **1** (1 mmol) and (-)-sparteine (275 μL, 1.2 mmol) at -78 °C and the reaction mixture was stirred for 3 h at -78 °C. Then A cyclohexane-hexane solution of *sec*-butyllithium (1.0 M, 2.0 mL, 2.0 mmol) was added dropwise and the resulting mixture was stirred for 12 h at -20 °C. To the mixture was added dropwise chlorodiphenylphosphine (6 mmol) at -78 °C, and the reaction mixture was stirred for 2 h at room temperature. It was filtered through a short plug of silica gel with CH_2Cl_2 and the filtrate was evaporated

under reduced pressure. The crude products were purified by flash column chromatography (hexane/CH_2Cl_2 = 5/1) to give the corresponding paracyclophane **3**.

12,15-Bis(diphenylphosphino)-1,10-dioxa[10]paracyclophane (3a). White solid. Mp 218 °C; IR (CH_2Cl_2) 2926, 2854, 1465, 1433, 1384, 1348, 1331, 1265, 1244, 743, 696, 416 cm^{-1}; ^1H NMR (400 MHz) δ 0.49-0.55 (m, 2H), 0.80-0.86 (m, 2H), 1.03-1.04 (m, 4H), 1.50-1.51 (m, 2H), 1.52-1.53 (m, 2H), 3.73-3.77 (m, 2H), 4.08-4.13 (m, 2H), 6.28-6.30 (m, 2H), 7.25-7.36 (m, 20H); ^{13}C NMR (125 MHz) δ 24.0, 26.6, 27.5 (d, *J*= 3.9 Hz), 72.3, 128.0 (d, *J*=7.2 Hz), 128.5 (d, *J*= 7.5 Hz), 129.1, 133.13, 134.6 (d, *J*= 19.9 Hz), 136.9, 155.1; ^{31}P NMR (200 MHz) δ -12.2; HRMS (FAB^+) for $[M+H]^+$ found *m/z* 589.2446, calcd for $C_{38}H_{39}O_2P_2$: 589.2420. $[\alpha]^{37}_D$ -78.6 (*c* 0.1 $CHCl_3$, 97% ee). Ee was determined by HPLC analysis of the oxidized product using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 70% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 7.5 min for major isomer and 12.9 min for minor isomer).

13,16-Bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-1,11-dioxa[11]paracyclophane (3c). White solid. Mp 210 °C; IR (CH_2Cl_2) 2923, 1470, 1278, 1177, 1096, 898, 765 cm^{-1}; ^1H NMR (400 MHz) δ 0.71-0.75 (m, 2H), 0.91-1.12 (m, 6H), 1.38-1.43 (m, 2H), 1.53-1.62 (m, 2H), 1.67-1.72 (m, 2H), 3.81-3.87 (m, 2H), 4.11-4.17 (m, 2H), 6.31-6.33 (m, 2H), 7.64-7.65 (m, 4H), 7.72-7.74 (m, 4H), 7.93 (d, *J*= 5.5 Hz, 4H); ^{13}C NMR (125 MHz) δ 25.5 (d, *J*= 4.8 Hz), 26.5, 27.9, 28.9, 72.2, 121.6 (d, *J*= 2.4 Hz), 122.8, 123.6-123.9 (m), 124.3, 127.0, 130.0 (d, *J*= 16.8 Hz), 133.0-133.5 (m), 137.2 (d, *J*= 21.5 Hz), 139.0 (d, *J*= 23.5 Hz), 156.4 (d, *J*= 20.3 Hz); ^{31}P NMR (200 MHz) δ -11.4; ^{19}F NMR (470 MHz) δ -63.1, -62.9; HRMS (FAB^+) for $[M+H]^+$ found *m/z* 1147.1578, calcd for $C_{47}H_{33}F_{24}O_2P_2$: 1147.1567. $[\alpha]^{36}_D$ -82.5 (*c* 0.465 $CHCl_3$, 98% ee). Ee was determined by HPLC analysis of the oxidized product using a chiral column (Doubly-arrayed Daicel Chiralcel IC and IC-3: 4 x 250 mm, 254 nm UV detector, rt, eluent: 50% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 6.1 min for major isomer and 6.8 min for minor isomer).

Typical Experimental Procedure for Enantioselective Allylation of Imines 4b Using Phosphine Ligands (Table 3, Entries 5-8). A MeOH solution (1.0 mL) of AgF (6.3 mg, 0.05 mmol) and planar-chiral phosphine (0.05 mmol) was stirred for 10 min and then MeOH was excluded under vacuum for 1 h. After cooling of the resulting white solid to -78 °C, MeOH (20 μL, 0.5 mmol) and THF (1.5 mL) were added and the mixture was stirred for 10 min. To the resulting clear solution, allyltrimethoxysilane (1.0 mmol) and imine **4b** (91.0 mg, 0.50 mmol) were added successively at -78 °C and the mixture was stirred at -78 °C for 12 h. The reaction mixture was passed through a short silica gel column using Et_2O as an eluent. The solvent was excluded under the reduced pressure, and the crude products were purified by thin-layer chromatography to give allylated product **5b**.[20]

Typical Experimental Procedure for Enantioselective Sonogashira Coupling (Table 5). A THF solution (0.2 mL) of $PdCl_2(MeCN)_2$ (3.9 mg, 0.015 mmol) and **2b** (10.2 mg, 0.015 mmol) was stirred for 10 min. To the solution were added diiodoparacyclophane **6** (0.05 mmol) in THF (0.8 mL), *i*-Pr_2NH (0.2 mL), alkyne **7** (0.2 mmol) and CuI (2.9 mg, 0.015 mmol) in order. The resulting mixture was stirred at room temperature. After the reaction was complete, H_2O was added to the reaction mixture, and organic materials were extracted with AcOEt. The organic layer was washed with brine and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the crude products were purified by thin-layer chromatography to give dialkynylated product **8**.

22,25-Bis{2-(4-methoxyphenyl)ethynyl}-1,20-dioxa[9.9]paracyclophane (8ba). Yellow oil; IR (CH_2Cl_2) 2929, 2854, 2227, 1516, 1248, 1031, 831; ^{1}H NMR δ 1.12-1.55 (m, 18H), 1.63-1.77 (m, 4H), 1.84-2.01 (m, 2H), 2.36-2.50 (m, 4H), 3.83 (s, 6H), 3.92-4.02 (m, 2H), 4.06-4.19 (m, 2H), 6.88 (d, *J*= 9.0 Hz, 4H), 6.95 (s, 4H), 6.99 (s, 2H), 7.47 (d, *J*= 9.0 Hz, 4H); ^{13}C NMR δ 24.7, 27.1, 27.8, 28.0, 28.3, 30.7, 35.0, 55.3, 66.4, 84.8, 94.7, 113.9, 114.1, 115.7, 116.9, 128.3, 133.0, 139.7, 153.3, 159.5; HRMS (FAB^+) for M^+ found *m/z* 668.3848, calcd for $C_{46}H_{52}O_4$: 668. 3860. $[\alpha]^{12}_D$ -23.9 (*c* 1.62 $CHCl_3$, 55% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 7.5 min for major isomer and 13.1 min for minor isomer).

24,27-Bis{2-(4-methoxyphenyl)ethynyl}-1,22-dioxa[7](1,4)naphthalene[7]paracyclophane (8ca). Yellow oil; ^{1}H NMR δ 1.17-1.32 (m, 4H) 1.33-1.49 (m, 2H), 1.59-1.79 (m, 6H), 1.81-1.96 (m, 2H), 1.97-2.13 (m, 2H), 2.74-2.92 (m, 2H), 3.02-3.18 (m, 2H), 3.83 (s, 6H), 3.96-4.22 (m, 4H), 6.28 (s, 2H), 6.89 (d, *J*= 8.8 Hz, 4H), 6.98 (s, 2H), 7.40 (dd, *J*= 3.3 Hz, 6.6 Hz, 2H), 7.50 (d, *J*= 8.8 Hz, 4H), 7.98 (dd, *J*= 3.3 Hz, 6.6 Hz, 2H); ^{13}C NMR δ 23.1, 25.6, 27.7, 28.5, 30.6, 55.4, 67.7, 84.9, 95.0, 114.1, 114.6, 115.8, 117.4, 124.7, 124.8, 126.4, 132.2, 133.1, 135.5, 153.0, 159.7; HRMS (FAB^+) for $[M+Na]^+$ found *m/z* 685.3284, calcd for $C_{46}H_{46}O_4Na$: 685.3288. $[\alpha]^{28}_D$ 16.5 (*c* 1.38 $CHCl_3$, 54% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5.5 min for major isomer and 8.4 min for minor isomer).

20,23-Bis{2-(4-methoxyphenyl)ethynyl}-1,18-dioxa[18]paracyclophane (8da). Pale yellow solid. Mp 134 °C; IR (CH_2Cl_2) 2925, 2852, 2208, 1604, 1515, 1463, 1248, 1172, 1032, 831 cm^{-1}; ^{1}H NMR δ 0.99-1.14 (m, 8H) 1.14-1.28 (m, 8H), 1.28-1.47 (m, 6H), 1.60-1.77 (m, 4H), 1.80-1.96 (m, 2H), 3.83 (s, 6H), 4.05-4.16 (m, 2H), 4.16-4.27 (m, 2H), 6.87 (d, *J*= 8.7 Hz, 4H), 7.00 (s, 2H), 7.47 (d, *J*= 8.7 Hz, 4H); ^{13}C NMR δ 24.1, 26.9, 27.7, 28.0, 28.2, 28.7, 29.4, 55.2, 68.6, 84.8, 94.6, 113.9, 114.3, 115.8, 117.6, 133.0, 153.0, 159.6; HRMS (FAB^+) for M^+ found *m/z* 592.3550. calcd for $C_{40}H_{48}O_4$: 592.3547. $[\alpha]^{26}_D$ -34.0 (*c* 1.55 $CHCl_3$, 54% ee). Ee was determined by HPLC analysis using a chiral column (Daicel

Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 7.8 min for major isomer and 11.9 min for minor isomer).

22,25-Bis{2-(4-methoxyphenyl)ethynyl}-1,4,7,14,17,20-hexaoxa-[7.7]paracyclophane (8ea). Yellow solid. Mp 95 °C; IR (CH_2Cl_2) 2927, 2862, 2210, 1604, 1515, 1463, 1248, 1209, 1062, 1029, 833 cm^{-1}; ^1H NMR δ 3.72-3.80 (m, 2H), 3.83 (s, 6H), 3.83-3.92 (m, 2H), 3.92-4.10 (m, 8H), 4.18-4.25 (m, 4H), 6.58 (s, 4H), 6.88 (d, *J*= 9.1 Hz, 4H), 6.89 (s, 2H), 7.43 (d, *J*= 9.1 Hz, 4H); ^{13}C NMR δ 55.3, 69.1, 69.5, 70.0, 70.0, 85.0, 94.5, 113.8, 114.0, 115.6, 116.4, 117.4, 132.9, 152.2, 152.9, 159.6; HRMS (FAB^+) for M^+ found *m/z* 620.2394, calcd for $C_{38}H_{36}O_8$: 620.2405. $[\alpha]^{13}_D$ 10.5 (*c* 1.41 $CHCl_3$, 58% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 50% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5.1 min for major isomer and 6.1 min for minor isomer).

Typical Procedure for Enantioselective Suzuki Coupling (Table 6). A MeOH solution (0.5 mL) of $PdCl_2(MeCN)_2$ (3.9 mg, 0.015 mmol) and phosphine ligand (0.015 mmol) was stirred for 30 min. To the solution were added chromium complex **9** (14.2 mg, 0.05 mmol) and arylboronic acid **10** (0.1 mmol) in MeOH (0.5 mL) and Na_2CO_3 (10.6 mg, 0.1 mmol) in water (0.1 mL) in order. The resulting mixture was stirred at room temperature. After the reaction was complete, it was filtered through a short plug of silica gel with Et_2O as an eluent and the filtrate was evaporated under reduced pressure. The crude products were purified by thin-layer chromatography (hexane/EtOAc = 5/1) to give mono-arylated product **11**.

(*1S,2R*)-Tricarbonyl(2-phenylchlorobenzene)chromium (11a). The physical properties of this compound were consistent with those in the literature.[11b]

Tricarbonyl(2-(4-methoxyphenyl)chlorobenzene)chromium (11b). Yellow oil; IR (CH_2Cl_2) 1970, 1893, 1338, 1249, 1179 cm^{-1}; ^1H NMR δ 3.85 (s, 3H), 5.13 (dd, *J*= 6.0, 6.0 Hz, 1H), 5.45-5.54 (m, 2H), 5.62 (d, *J*= 6.0 Hz, 1H), 6.94 (d, *J*= 8.2 Hz, 2H), 7.45 (d, *J*= 8.2 Hz, 2H); ^{13}C NMR δ 55.3, 87.8, 90.6, 93.2, 96.1, 110.3, 113.4, 113.6, 126.9, 131.7, 160.1, 231.7; HRMS (FAB^+) for M^+ found *m/z* 353.9744, calcd for $C_{16}H_{11}O_4ClCr$: 353.9745; $[\alpha]^{27}_D$ 19.6 (*c* 1.44 $CHCl_3$, 79% ee). Ee was determined by HPLC analysis using a chiral column (Doubly-arrayed Daicel Chiralpak AD-H: 4 x 250 mm, 254 nm UV detector, rt, eluent: 2% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 9 min for minor isomer and 10 min for major isomer).

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