Cleavage of Aromatic C−O Bonds via Intramolecular S$_N$Ar Reaction and Preparation of *P,C,Axial*-Stereogenic Menthyl Phosphine Derivatives

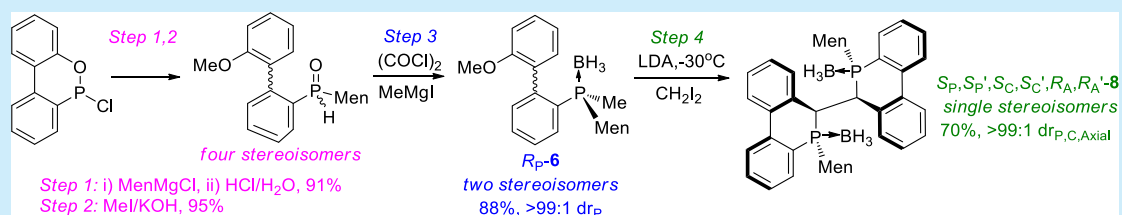Bing-Xia Yan,[∇] Yu Zhang,[∇] Hong-Xing Zheng, Jing-Jing Ye, Xiao-Ning Wang, Qiang Li,* and Chang-Qiu Zhao*

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ABSTRACT: Phosphine ligands with up to six chiral sites were prepared, starting from 2-phenylphenol, via *O*- and *P*-alkylation, cyclization, and coupling. The chirality was transferred from (*L*)-menthyl to phosphorus, α-carbon, and axis, to achieve excellent diastereoselectivities. During an intramolecular S$_N$Ar reaction with alkoxyl as the leaving groups, the C−O bond was converted to a C−C bond. Both phosphine boranes and oxides could be used for the conversions, affording a series of cyclic phosphines.

Chiral bidentate phosphines ligands form chelated complexes with metallic ions and are widely applied in asymmetric catalysis.[1] These compounds contain either a chiral carbon skeleton or chiral phosphorus.[2] Compared to those having a sole chiral element, the multiply stereogenic bidentate phosphines (MSBP) are hoped to provide more significant asymmetric circumstances and to ensure better stereo-selectivity.[3]

However, the existence of more than one chiral site in a molecule increases the difficulty to acquire MSBP. It is essential to establish a linkage, via C−C or C−P bonds, to connect chiral blocks together. A precursor suitable for MSPB, which has or will generate multichiral centers, is difficultly designed and obtained.[4] The instability of the chiral center during a reaction also restricted the availability. In order to avoid annoying racemization, harsh reaction conditions such as ultralow temperature are usually employed.[5,6] Although catalytic methods to generate chiral center are well-established,[7] their application for the preparation of MSBP is limited. Beside the restriction of reaction scope, the imperfect enantiomeric excess (ee) would be amplified in a multichiral molecule, leading to the formation of more than one diastereoisomer.

Some representative MSBPs are shown in Scheme 1. BeePHOS was prepared via cyclization of a precursor with dilithiated *o*-phenylenediphosphine. The precursor was obtained via the resolution of a chiral alcohol.[8] TangPhos was obtained from deprotonation of a P-cycle and coupling. The pure product was obtained via recrystallization of a

Scheme 1. Reported Representative MSBPs, Cleavages of C−O Bonds via S$_N$Ar Reaction, and Preparation of *P,C,Axial*-Stereogenic Menthyl Phosphines
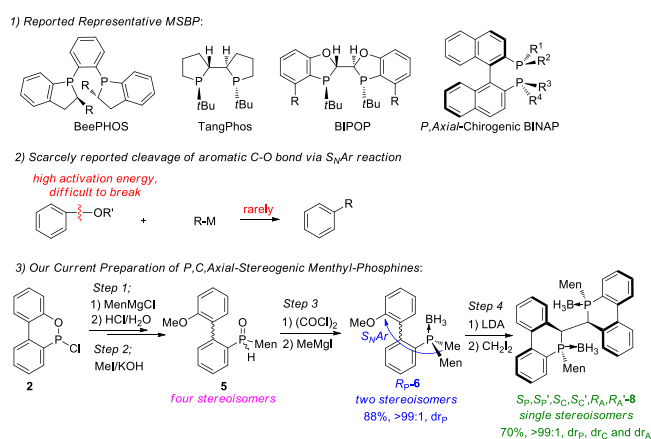
diastereomeric mixture.[9] BIBOPs and BINAPINE were also obtained via coupling of a cyclized P-precursor.[10,11] Very recently, Zuo and co-workers reported P-stereogenic BINAP

that was obtained from *axis* to P chirality-transferring, via multistep conversions.[12] The above approaches to generate MSBPs usually involved tedious resolution and included multistep reactions. Sometimes the poisonous, flammable, and very air-sensitive phosphines were employed.

In addition, nucleophilic aromatic substitution (S_NAr) reactions offer a convenient access to benzenoid functionalization. However, the utility is limited to the arenes bearing strong EWG and with halides as the leaving groups.[13] The S_NAr reaction with alkoxyl as the leaving group is rare, likely due to the high activation energy barrier for breaking the C–O bond.[14] The reported activations of aromatic C–O bonds usually use O, N, and S nucleophiles.[15] To the best of our knowledge, the direct conversions of aromatic C–O bonds to C–C bonds are quite limited (see Scheme 1).[16]

We were engaged in developing facile routes to acquire MSPBs.[17] The enclosed work presented a procedure that utilized (*L*)-menthyl to induce the chiralities on phosphorus, carbon, and axis. An intramolecular S_NAr reaction was studied, and the conversion of C–O bonds to C–C bonds was realized (see Scheme 1). The preparation avoided the resolution process, and the title compound had C, P, and axial chiral elements, up to six chiral sites.

The research was started with **2** that was obtained from 2-phenylphenol **1** and phosphorus trichloride. Reaction of **2** with (1*R*,2*S*,5*R*)-menthyl Grignard reagent afforded **3**. After hydrolysis in situ, **3** was converted to secondary menthyl phosphine oxide **4**, as a mixture of four stereoisomers that were derived from chiral biphenyl axis and phosphorus. Four single peaks were observed at 48.20, 37.79, 24.47, and 24.04 ppm in the ³¹P NMR spectrum. The (1*R*,2*S*,5*R*)-structure of menthyl remained unchanged.[17i] Besides **4**, other byproducts were not detected.[18]

When reacted with methyl iodide in ethanol in the presence of KOH, 2′-hydroxyl of **4** was methylated and P–H remained unchanged, affording **5** in excellent yield. The ³¹P NMR spectrum indicated that **5** also was formed as a mixture of four stereoisomers. Both *O,P*-methylated products were not detected when 1 equiv of KOH was used (see Scheme 2A).[19]

Scheme 2. Preparation of Four Stereoisomers of 5 and the Conversion to Two Isomers of 6
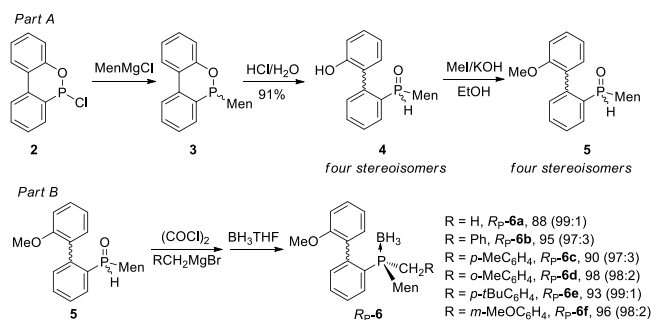

Treatment of **5** with oxalyl chloride, followed by reaction with Grignard reagents at −80 °C and the addition of borane, afforded **6**. During the process, the R_P- and S_P-stereoisomers of **5** were converted to R_P-**6**; thus, *the four stereoisomers were converted to two stereoisomers that were derived from the chiral axis.*[20] When methyl magnesium iodide was used, the two stereoisomers R_A-**6a** and S_A-**6a** were formed in 88% yield, as indicated by the two peaks at 20.35 and 17.50 ppm in the ³¹P

NMR spectrum. Various benzyl Grignard reagents afforded **6b**–**6f** in excellent yields and diastereomeric ratio (dr$_P$) values (see Scheme 2B).

When the mixture of R_A-**6a**/S_A-**6a** was treated with *n*-butyl lithium at −30 °C, followed by the addition of CuCl$_2$, three compounds **7a**, **8**, and **9** were obtained (see Scheme 3A). It

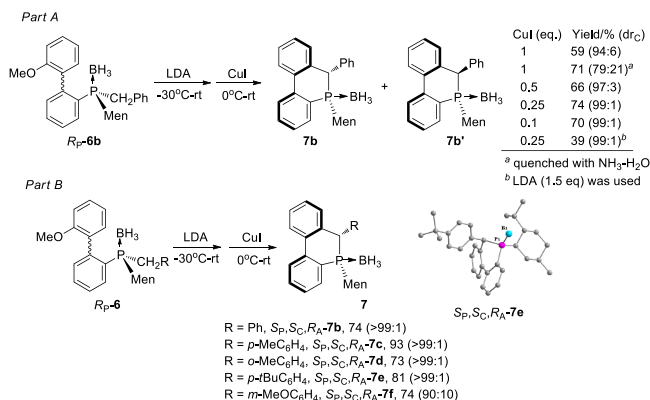**Scheme 3. Conversion of R_A-6a and S_A-6a to Single Stereoisomers of 7, 8, and 9**
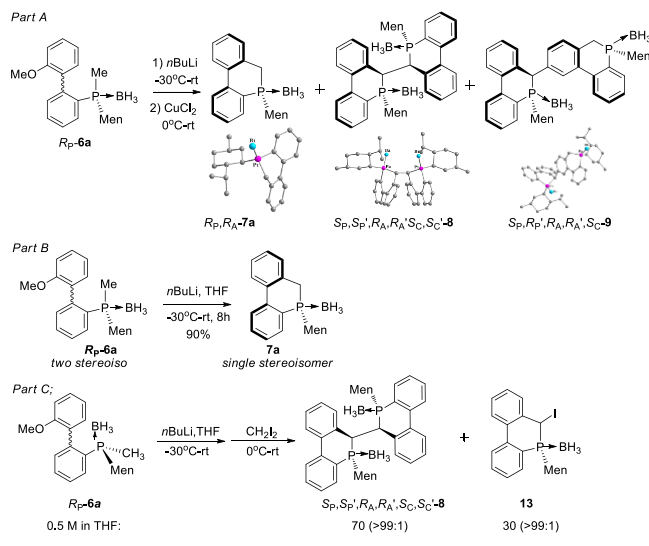
was interesting that the three products were detected as single stereoisomers, respectively, whose structures were confirmed by NMR spectrum and X-ray diffraction (XRD). Obviously, R_P,R_A-**7a** was initially formed via intramolecular cyclization, which was converted to **8** and **9** via coupling or substitution. The results indicated that *the two stereoisomers R_A-6a/S_A-6a derived from chiral axis were converted to the single stereoisomer R_A-7a.*

Further investigation indicated the cyclization of R_A-**6a**/S_A-**6a** could be realized in the absence of copper. When the reaction was performed at −30 °C, with *n*-butyl lithium as a base, R_P,R_A-**7a** was formed in 90% yield and >99:1 dr$_A$ (see Scheme 3B). It was believed that the chiral menthyl-phosphorus moiety induced and fixed the flexibly axial chirality via a six-membered cycle. As we previously reported, the effective asymmetric induction was also observed for the seven-membered cycle or metallic linkage.[16c,19]

The cyclization of *P*-benzyl-substituted compounds **6b**–**6f** cannot occur without a catalyst. In the presence of CuI, the cyclization occurred. The reaction was optimized with **6b** (Scheme 4A). After treatment with LDA and the addition of 1 equiv of CuI, **6b** was converted to a product that gave two signals at 18.89 and 8.11 ppm, in a ratio of 96:4, in a ³¹P NMR spectrum. The two signals were assigned as the stereoisomers **7b**/**7b′** derived from chiral α-carbon. Quenching the reaction with aqueous ammonia led to a poor ratio of **7b**/**7b′**, perhaps because of water freezing at the quenching temperature (run 2). The ratio was improved when quenched with a solution of acetic acid in tetrahydrofuran (THF).

Reducing the amount of CuI could improve the yield and dr$_C$ of **7b** (runs 3–5). When 25 equiv of CuI was used, **7b** was formed in 74% yield and >99:1 dr$_C$. When the amount of LDA was reduced, the yield became poor (run 6).

Scheme 4. Cyclization of P-Benzyl-Substituted 6

CuI (eq.)	Yield/% (dr_C)
1	59 (94:6)
1	71 (79:21)[a]
0.5	66 (97:3)
0.25	74 (99:1)
0.1	70 (99:1)
0.25	39 (99:1)[b]

[a] quenched with NH₃·H₂O
[b] LDA (1.5 eq) was used

R = Ph, S_P,S_C,R_A-7b, 74 (>99:1)
R = p-MeC₆H₄, S_P,S_C,R_A-7c, 93 (>99:1)
R = o-MeC₆H₄, S_P,S_C,R_A-7d, 73 (>99:1)
R = p-tBuC₆H₄, S_P,S_C,R_A-7e, 81 (>99:1)
R = m-MeOC₆H₄, S_P,S_C,R_A-7f, 74 (90:10)

Table 1. Investigation of the Coupling Reaction of 7a

			8		13	
entry	base	additive (equiv)	yield[a] (%)	dr_C[a]	stereoisomer	yield[a] (%)
1	nBuLi	CuCl₂/1	39	99:1	13a	34
2	nBuLi	CH₂I₂/1	36	99:1	13b	43
3	LDA	CH₂I₂/0.5	11	99:1	13b	43
4	nBuLi	CH₂I₂/0.5	69	99:1	13b	24
5	nBuLi	I₂/0.5	47	99:1	13b	23
6	nBuLi	DMF/1	52	99:1	NA	NA

[a]The yield and dr_C were estimated using the ¹H{³¹P}NMR spectrum.

Under the above optimized conditions, various α-substituted compounds **7b**−**7f** were obtained (Scheme 4B). The excellent dr_C values that were exhibited by the chiral α-carbon were successfully controlled by the menthyl phosphorus moiety, whose S-configuration was confirmed by XRD analysis of S_P,S_C,R_A-**7e**.

The cyclization was proposed as an intramolecular nucleophilic attack of the α-carbon anion toward an adjacent phenyl, and alkoxyl was displaced as a leaving group (see Scheme 5). It was well-known that the cleavage of the C_sp2−O

Scheme 5. Proposed Mechanism of Intramolecular Cyclization and the Subsequent Formation of 8 and 9
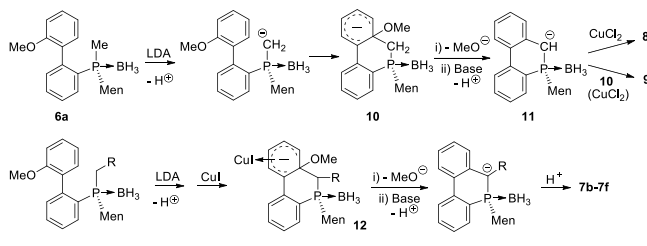
bond via S_NAr reaction was difficult. However, the facile cyclization, especially for **6a**, probably benefitted from a six-membered cyclic transition state **10**. The cleavage of the C−O bond of **10** afforded **11**. When the reaction was performed in the presence of CuCl₂, the subsequent oxidative coupling of **11** afforded **8**. The formation of **9** probably was relevant to a copper-promoted C−H activation and further attack of **11** to the para-position of **10**.

For P-benzyl-substituted subtrates, the formation of **10** became difficult, likely because of spatial hindrance on the α-carbon anion. The presence of CuI was supposed to decrease the electron cloud density on the benzene ring via the formation of a π-complex **12**, and enabling the nucleophilic attack of the α-anion became easy.

In order to dominantly obtain **8**, various coupling reagents were examined. When **7a** was treated with LDA, followed by the addition of CuCl₂, **8** was formed in 39% yield. Other diasteroisomer of **8** were not detected (see Table 1, entry 1).[21]

Diiodomethane (DIM) was initially attempted to connect two molecules of **7a** with methylene. However, when 0.5 equiv of DIM was used, **8** was obtained as the major product (Table 1, entries 2−4). Iodine was employed as a coupling reagent to afford **8** and **13b** (Table 1, entry 5). It was strange when

dimethylformamide (DMF) was used: **8** was also obtained in 52% yield (Table 1, entry 6).

Tandem reaction of cyclization and coupling, i.e., direct formation of **8** from **6a**, could be realized in a diluted solution. When the reaction was carried out in a 1.4 M solution of **6a** in THF, the mixture of **8** and **13b** was formed, similar to the results of Table 1. In a 0.5 M solution, **8** was formed as a major product (see Scheme 3C).
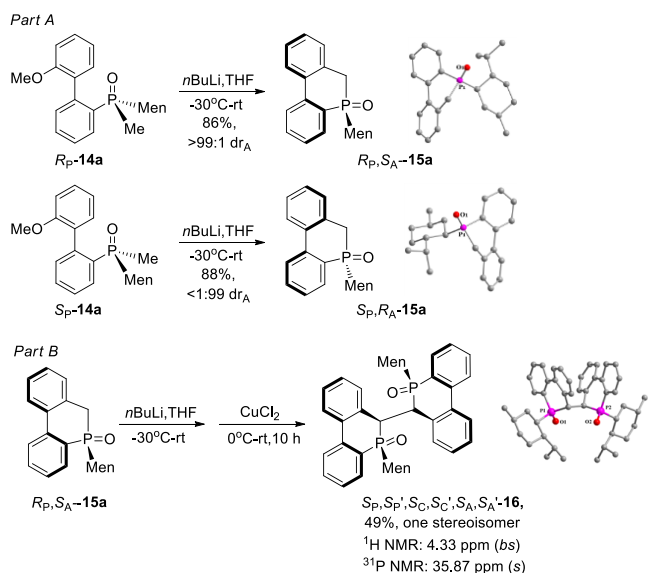
The XRD result of **8** indicated that the chiral α- and α'-carbon atoms had the same S-configuration, which was similar to **7e**. The chirality on α-carbon was controlled by chiral phosphorus. It could be observed that the bulky menthyl located at a position trans to the α-alkyl group in the X-ray structures of **7e** and **8** (see Schemes 2A and 3B).

The intramolecular cyclization of phosphines oxide R_P-**14a** (R = Me) also occurred in the absence of CuI, and the two axial stereoisomers were converted to the same R_P,S_A-**15a** in >99:1 dr_A, as indicated by the two peaks of R_P-**14a** at 45.17 and 42.32 ppm becoming one peak at 33.85 ppm in the ³¹P NMR spectrum. Similarly, S_P-**14a** afforded S_P,R_A-**15a** in 88% yield and <1:99 dr_A. The structures of R_P,S_A-**15a** and S_P,R_A-**15a** were confirmed by XRD (see Scheme 6A).
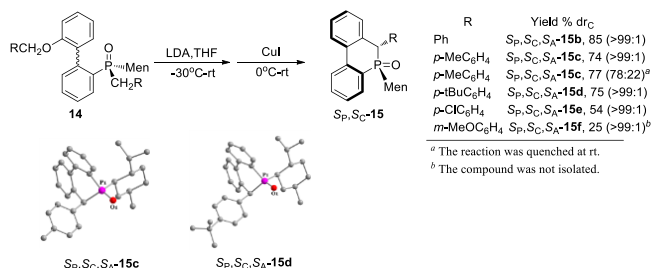
After deprotonation and treatment with CuCl₂, R_P,S_A-**15a** was converted to **16** in excellent dr_C (Scheme 6B). The sole peak at 35.87 ppm in the ³¹P NMR spectrum indicated that only one stereoisomer was formed. The bs peak at 4.33 ppm in the ¹H NMR spectrum indicated that the two α-C atoms have the same configuration. The structure of **16** was also confirmed by XRD.

Similar to **7b**−**7f**, the cyclization of P-benzyl-substituted **14b**−**14f** did not occur in the absence of a catalyst. When catalyzed by CuI, the reaction readily occurred to afford **15b**−**15e** in moderate to good yields (see Scheme 7). As seen in run 3, quenching the reaction of **14c** at room temperature afforded **15c**/**15c'** in 78:22 dr_C, which indicated that the chirality on α-carbon was influenced by temperature. The dr_C was improved to >99:1 at a reduced quenching temperature (run 2).

The cyclization was supposed to proceed via a mechanism similar to that described in Scheme 5, except the benzyloxy was displaced by the α-C anion. The poor yield of **15f** was ascribed to the electronically enriched m-methoxyl benzyl, which behaved as a worse leaving group. XRD analysis of the S_P,S_C,S_A-**15c** and S_P,S_C,S_A-**15d** confirmed the S-configuration on α-C.

Scheme 6. Cyclization/Coupling of R_P-14a and S_P-14a

Part A

Part B

Scheme 7. Cyclization of 14 to Form 15

	R		Yield % dr_C
	Ph	S_P,S_C,S_A-**15b**,	85 (>99:1)
	p-MeC$_6$H$_4$	S_P,S_C,S_A-**15c**,	74 (>99:1)
	p-MeC$_6$H$_4$	S_P,S_C,S_A-**15c**,	77 (78:22)^a
	p-tBuC$_6$H$_4$	S_P,S_C,S_A-**15d**,	75 (>99:1)
	p-ClC$_6$H$_4$	S_P,S_C,S_A-**15e**,	54 (>99:1)
	m-MeOC$_6$H$_4$	S_P,S_C,S_A-**15f**,	25 (>99:1)^b

^{a} The reaction was quenched at rt. ^{b} The compound was not isolated.

S_P,S_C,S_A-**15c** S_P,S_C,S_A-**15d**

In summary, a new family of P,C,*axial*-stereogenic menthyl phosphines was obtained, starting from 2-phenylphenol, via four pots of reactions. The secondary phosphine oxide **4** was formed from a reaction with (L)-menthyl Grignard reagent, which was converted to **5** via O-alkylation. After treatment with oxalyl chloride and reaction with Grignard reagents, the R_P and S_P stereoisomers of **5** were converted to R_P-**6**. An intramolecular cyclization of **6a** occurred when deprotonated, and the two axial stereoisomers of R_P-**6a** were converted to single R_P,R_A-**7a**. In the presence of diiodomethane, the coupling of R_A-**7a** afforded **8**. **8** could be directly formed from R_P-**6** in a diluted solution. The intramolecular cyclization of P-benzyl-substituted **6** was realized when catalyzed by CuI, affording α-substituted **7** in excellent diastereoselectivity. Similar cyclization and coupling also occurred for the corresponding phosphine oxides **14**, which afforded S_P,R_A-**15a**, R_P,S_A-**15a**, and **16** as single diastereoisomers.

Our research has provided a facile and convenient method for the formation of a new family of chiral phosphine ligands. The various structures and multiply chiral elements of the compounds could enable a fine-tuning of the asymmetric induction. In addition, because of the potential ability to be modified, the products could be further converted to more diverse structures suitable for asymmetric catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02861.

Experimental details; photocopies of ^{1}H, ^{31}P, and ^{13}C NMR spectra (PDF)

Accession Codes

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