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P-STEREOGENIC DIPHOSPHACROWNS: FACILE INCORPORATION OF AROMATIC RINGS

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Abstract – P-Stereogenic diphosphacrowns containing naphthalene and pyridine rings were synthesized. Facile incorporation of aromatic rings, and chains of different lengths, into the diphosphacrown skeleton was achieved by altering the electrophile in our previously reported synthetic method. Pyridine-containing diphosphacrown exhibited chiral recognition ability for chiral ammonium salts and carboxylic acids. This is the first example of chiral recognition using P-stereogenic diphosphacrowns. ^{1}H and ^{31}P NMR spectra indicated that the nitrogen, oxygen, and chiral phosphorus atoms contributed to the chiral recognition cooperatively.

INTRODUCTION

Phosphines are configurationally stable because of the high *s* character of the phosphorus atoms. The resulting high energy barrier for phosphines inversion allows the phosphorus atoms to become chiral centers.[1,2] Various P-stereogenic phosphines have been prepared till date, with most of them used as asymmetric ligands in transition metal-catalyzed enantioselective reactions.[2]

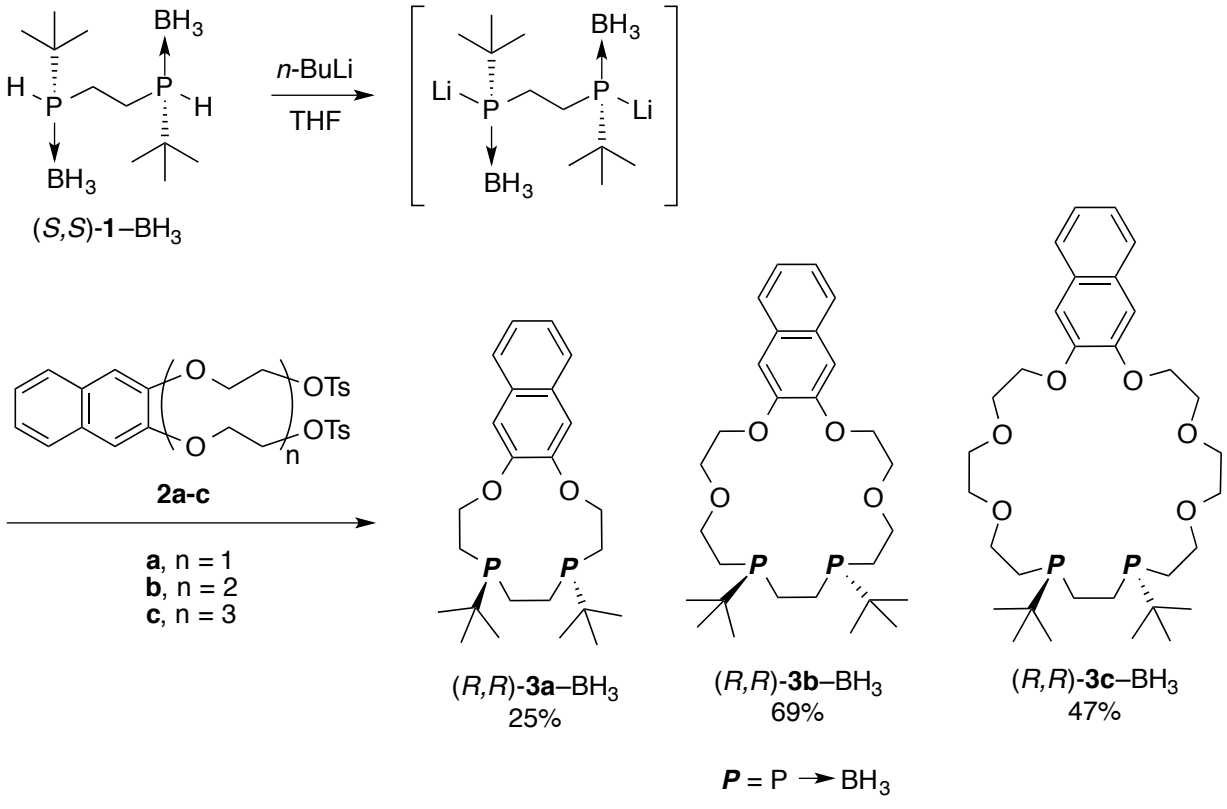
Our research has focused on P-stereogenic phosphines, employing them as chiral element-blocks[3] in the synthesis of P-stereogenic well-defined oligomers, polymers, and cyclic compounds.[4] Among these cyclic compounds, P-stereogenic phosphacrowns were the first example of crown ethers with chiral heteroatoms that interacted directly with guest molecules.[5] Since the first report of crown ether (dibenzo-18-crown-6) in 1967 by Pedersen,[6] various types and derivatives of crown ethers have been

reported.[7] Optically active crown ethers containing stereogenic carbon atoms[8] or axially chiral units[9] in the ring skeleton have been shown to exhibit chiral guest-recognition abilities.

Recently, a practical synthetic route to P-stereogenic benzodiphosphacrowns was developed using P-stereogenic secondary bisphosphine precursors. In this study, we expand the substrate scope in the synthesis of P-stereogenic diphosphacrowns to incorporate different aromatic units (naphthalene and pyridine) and ring sizes. Their preparation and characterization, including chiral recognition studies, are reported.

RESULTS AND DISCUSSION

The synthetic route to naphthalene-containing P-stereogenic diphosphacrowns is shown in Scheme 1. P-Stereogenic secondary bisphosphine borane complex (*S,S*)-**1**–BH_3 was prepared as previously described.[10] Bisphosphine (*S,S*)-**1**–BH_3 was readily lithiated with *n*-BuLi, and successive treatment with electrophiles **2a-c** under diluted conditions afforded the corresponding P-stereogenic (*R,R*)-naphthodiphosphacrowns (*R,R*)-**3a-c**–BH_3,[11] after purification by SiO_2 column chromatography. The products were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and high-resolution mass spectrometry (HRMS). The absolute configuration of the phosphine was unaltered during this procedure; however, a change in the priority of the P-substituents resulted in different *R*/*S* labels for the optical isomers.



Scheme 1

A suitable single crystal of (*R*,*R*)-**3c**–BH_3 was obtained, and its structure was confirmed by X-ray crystallography. The ORTEP drawing is shown in Figure 1; crystallographic data are listed in Tables S1 and S2 in the Supporting Information[12] X-Ray crystallographic analysis revealed that the crystal structure of (*R*,*R*)-**3c**–BH_3 was similar to that of (*R*,*R*)-benzo-24-diphosphacrown-8 previously. We confirmed that the 1:1 reaction stoichiometry in Scheme 1 resulted in preferential construction of 24-diphosphacrown-8 over the 48- or 72-membered rings. The 24-diphosphacrown-8 ring possessed two P-stereogenic centers, both with *R* absolute configuration, and two *tert*-butyl substituents on the phosphorus atoms located at diagonal quadrants.

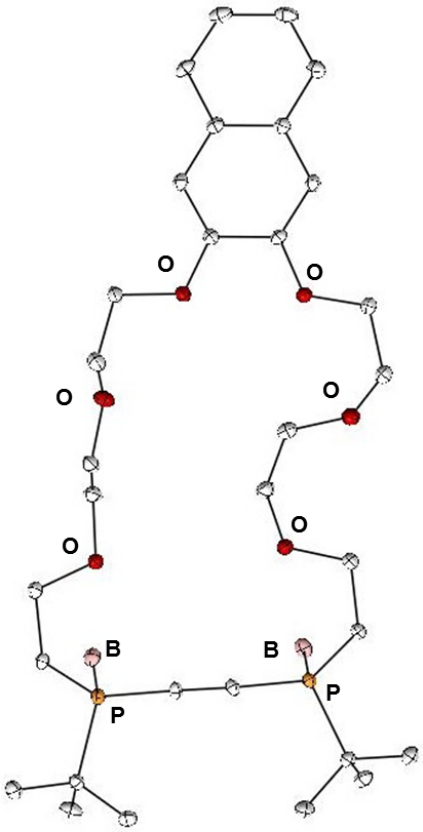
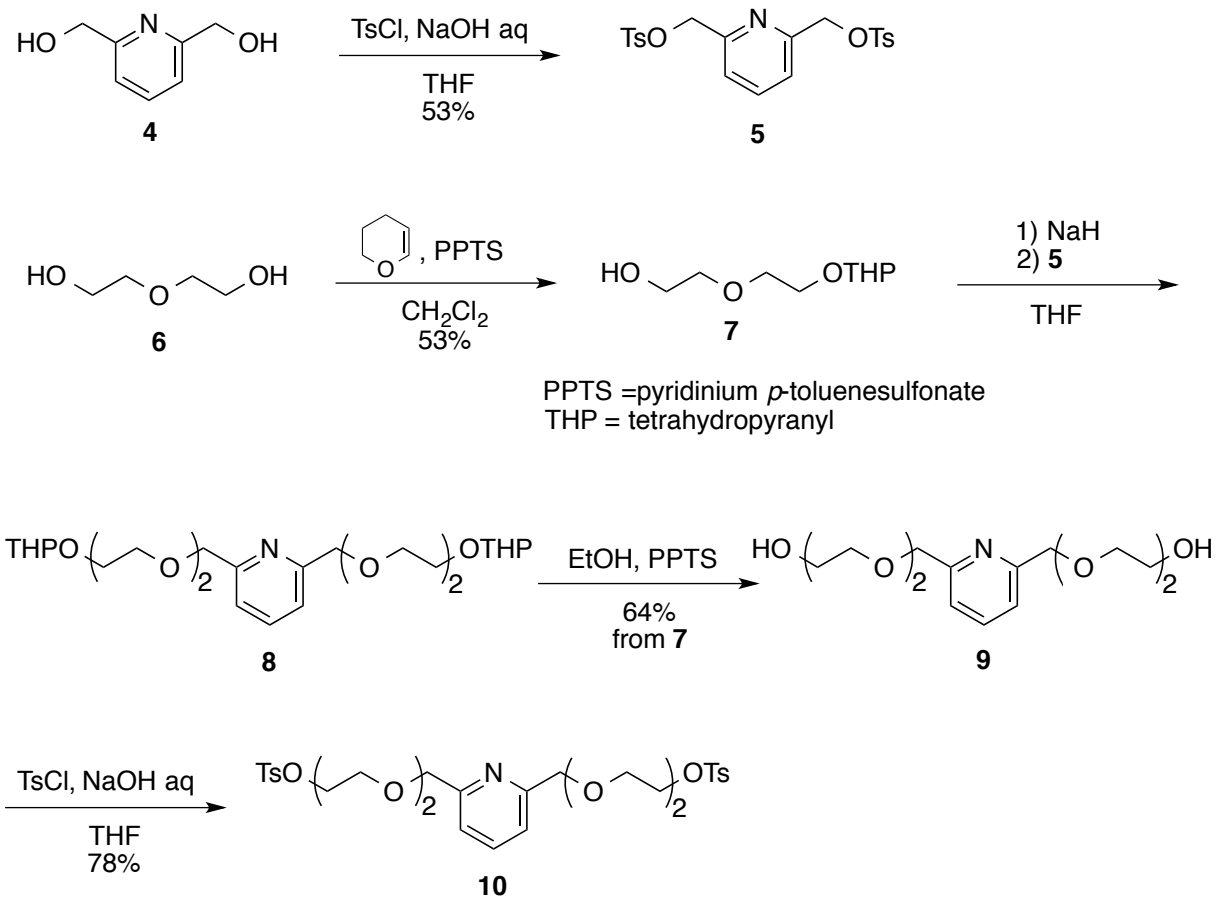
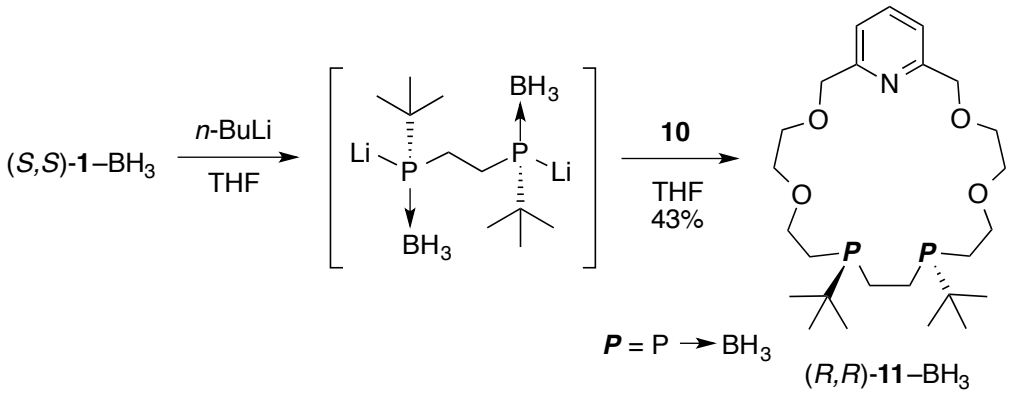


Figure 1. ORTEP drawing of (*R*,*R*)-**3c**–BH_3. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Pyridine-containing electrophile **10** was synthesized from commercially available 2,6-bis(hydroxymethyl)pyridine **6**, as shown in Scheme 2. P-Stereogenic diphosphacrown containing a pyridine ring was synthesized using the same procedure as that used for the naphthodiphosphacrowns. Accordingly, treatment of (*S,S*)-**1**–BH_3 with *n*-BuLi, followed by the addition of electrophile **10**, afforded (*R,R*)-pyrido-21-diphosphacrown-7 (*R,R*)-**11**–BH_3 in 43% isolated yield (Scheme 3). The structure of (*R,R*)-**11**–BH_3 was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR, and HRMS spectra.



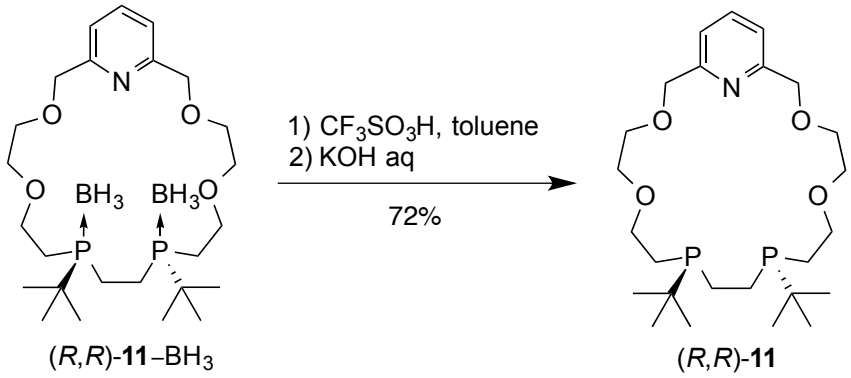
Scheme 2



Scheme 3

Boranes, which protect the phosphorus lone pairs, can be readily removed using strong acids (e.g. trifluoromethanesulfonic acid or tetrafluoroboric acid)[13] or organic bases (e.g. morpholine or 1,4-diazabicyclo[2.2.2]octane)[14] without causing pyramidal inversion. In this study, borane was removed from (*R,R*)-**11**–BH_3 using trifluoromethanesulfonic acid and aqueous potassium hydroxide, as shown in Scheme 4. Extraction with diethyl ether and purification by Al_2O_3 column chromatography

afforded free phosphine (*R,R*)-**11** in 72% yield as an air-sensitive colorless liquid, which was characterized by ^{1}H NMR, ^{31}P NMR, and HRMS spectra.



Scheme 4

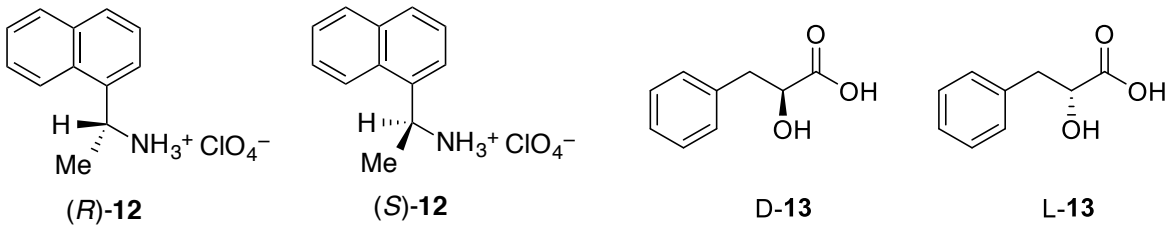


Figure 2. Structures of guest molecules

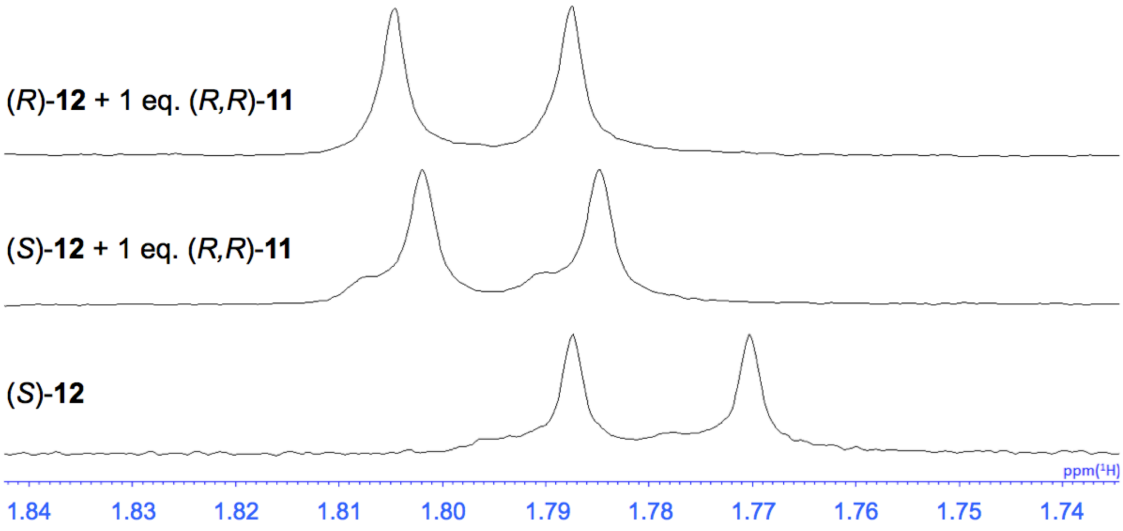


Figure 3. The CH_3 proton peaks around 1.8 ppm in (*R*)-**12** with 1 eq .of (*R,R*)-**11**, (*S*)-**12** with 1 eq. of (*R,R*)-**11**, and (*S*)-**12** in $CDCl_3/CD_3CN$ (1:1, v/v)

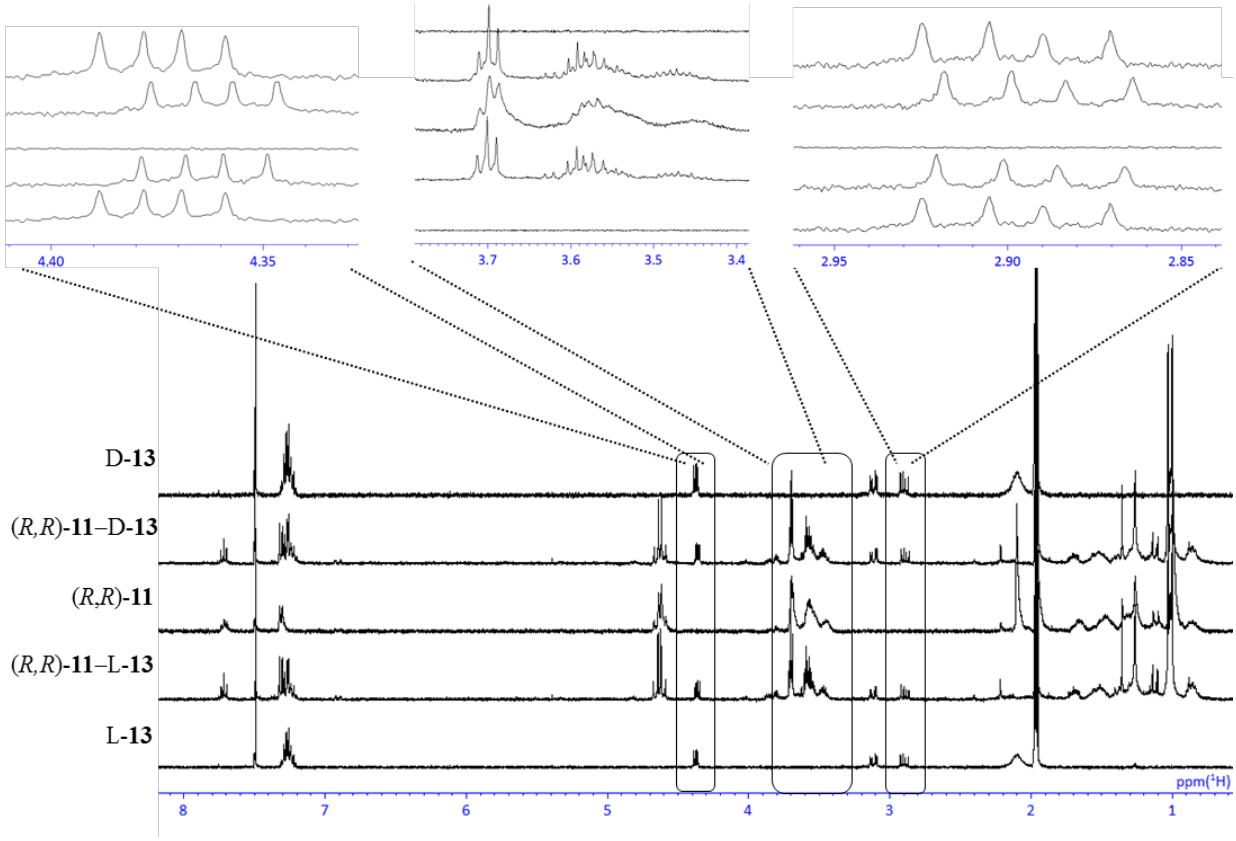


Figure 4. ^{1}H NMR spectra of D-**13**, (*R,R*)-**11**–D-**13**, (*R,R*)-**11**, (*R,R*)-**11**–L-**13**, and L-**13**

We investigated the chiral recognition ability of (*R,R*)-**11** by monitoring changes in ^{1}H NMR spectra after treatment with perchlorate salts of enantiomers of (1-naphthyl)ethylammonium ((*R*)/(*S*)-**12**) and 3-phenyllactic acid (D/L-**13**), as shown in Figure 2. When an equimolar amount of guest **12** was added to (*R,R*)-**11** in $CDCl_3/CD_3CN$ solution (v/v = 1/1), peak shifts ($\Delta\delta$) were observed for the O-CH_2 (Figure S17 in the Supporting Information), and pyridyl protons in (*R,R*)-**11** as well as the C*H* and CH_3 protons in **12**. As shown in Figure 3, the CH_3 proton peak in **12**, usually around 1.8 ppm, was distinctly shifted downfield by host-guest interactions, giving $\Delta\delta$ values of 0.0172 ppm for (*R,R*)-**11**–(*R*)-**12** and 0.0145 ppm for (*R,R*)-**11**–(*S*)-**12**. Despite the small differences in $\Delta\delta$ between (*R,R*)-**11**–(*R*)-**12** and (*R,R*)-**11**–(*S*)-**12**, this was clear evidence of (*R,R*)-**11** exhibiting chiral recognition; the complexation constants were estimated to be approximately 64.5 and 46.9 M^{-1}, respectively. In addition, (*R,R*)-**11** recognized enantiomers D-**13** and L-**13**, as confirmed by ^{1}H NMR spectra (Figure 4). In both cases, the (*R,R*)-**11** methylene (O–CH_2) peaks at around 3.4-3.8 and 4.6 ppm shifted noticeably, suggesting hydrogen bonding between ether oxygen atoms and acidic protons, in addition to those between pyridyl nitrogen and acidic protons. To elucidate the interaction between the phosphorus atoms and the guest molecule, ^{31}P NMR spectra of (*R,R*)-**11** and (*R,R*)-**11**–D-**13** were obtained (Figure S20 in the Supporting Information). The ^{31}P NMR signal became broader and appeared at a slightly lower magnetic field in (*R,R*)-**11**–D-**13** than in (*R,R*)-**11**. Adding an excess of trifluoroacetic acid (TFA), a strong acid, caused a

sharp peak to appear at +30 ppm, indicating protonated phosphorus atoms. These results implied that phosphorus atoms constructed a chiral environment rather than had an affinity for hydrogen atoms in the guest molecule.

CONCLUSION

We have demonstrated the facile incorporation of aromatic rings into P-stereogenic diphosphacrowns, affording naphthalene- and pyridine-containing diphosphacrowns. Various naphthalene-containing P-stereogenic diphosphacrown ring sizes were obtained by altering the electrophile used for cyclization. A preliminary chiral recognition experiment, involving mixing of chiral ammonium salts and carboxylic acids with the pyridine-containing diphosphacrown, revealed different chemical shifts for each guest enantiomer. It was confirmed that, in addition to nitrogen and oxygen, phosphorus atoms contributed to the capture of guest molecules. Studies on the synthesis of optically active diphosphacrowns containing a variety of heteroaromatic rings, and their applications as NMR chiral shift reagents, are underway.

EXPERIMENTAL

General. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a 400 MHz spectrometer, and samples were analyzed in $CDCl_3$ or CD_2Cl_2 using Me_4Si as an internal standard. ^{31}P (161.5 MHz) NMR spectra were also recorded on a 400 MHz spectrometer, and samples were analyzed in $CDCl_3$ using H_3PO_4 as an external standard. High-resolution mass spectra (HRMS) were obtained by electron spray ionization (ESI) or direct analysis in real time (DART) technique using an Orbitrap mass spectrometer (EXACTIVE, Thermo Fisher Scientific). Optical rotation was measured using $CHCl_3$ as a solvent. Analytical thin-layer chromatography was performed with MERCK SiO_2 plates. Column chromatography was performed with Wakogel C-300 SiO_2 or MERCK Al_2O_3 90 active basic.

Materials. THF and Et_2O were purchased and purified by the GlassContour solvent purification system.[15] Compound (*S*,*S*)-**1**–BH_3[10] was synthesized as described in the literatures. The other materials were purchased and used without further purification.

Synthesis of (*R*,*R*)-3a–BH_3. A THF solution (60 mL) of (*S*,*S*)-**1**–BH_3 (233.9 mg, 1.0 mmol) was cooled to –78 °C. *n*-BuLi (1.6 M in *n*-hexane, 1.40 mL, 2.2 mmol) was added with a syringe. After stirring for 1 h, a THF solution (20 mL) of electrophile **2a** (556.6 mg, 1.0 mmol) was added with a syringe. The reaction mixture was allowed to warm to room temperature. After stirring for 48 h, the reaction was quenched with 2 N HCl aq (50 mL). The organic layer was extracted with AcOEt (50 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ aq, brine, and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on

SiO_2 with AcOEt and hexane (v/v = 1/3) as an eluent. Removal of the solvent gave (*R,R*)-**3a**–BH_3 (109.9 mg, 0.25 mmol, 25%) as a colorless solid. R_f = 0.75 (hexane/AcOEt, v/v = 1:1); $[\alpha]_D^{23}$ +48.6 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.38 (br q, $J_{H\text{-}B}$ = 80.8 Hz, 6H, BH_3), 1.17 (d, J = 13.5 Hz, 18H, C(CH_3)$_3$), 1.96-2.04 (m, 4H, PCH_2), 2.20-2.30 (m, 2H, PCH_2), 2.47-2.56 (m, 2H, PCH_2), 4.36-4.50 (m, 4H, OCH_2), 7.03 (s, 2H, $C_{10}H_6$), 7.31-7.33 (m, 2H, $C_{10}H_6$), 7.64-7.66 (m, 2H, $C_{10}H_6$) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.3 (d, $J_{C\text{-}P}$ = 30.0 Hz), 21.3 (d, $J_{C\text{-}P}$ = 30.0 Hz), 25.3, 28.4 (d, $J_{C\text{-}P}$ = 34.4 Hz), 63.1, 106.6 (d, J = 9.7 Hz), 124.3, 126.2 (d, J = 5.8 Hz), 129.0, 147.5 ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.5 MHz) δ +34.6 (br) ppm. HRMS (ESI) calcd for $[C_{24}H_{42}B_2O_2P_2+NH_4]^+$: 464.3193, found 464.3188.

Synthesis of (*R,R*)-3b–BH_3 and (*R,R*)-3c–BH_3. Synthetic procedures are same as that of (*R,R*)-**3a**–BH_3; compound data are as follows.

(*R,R*)-3b–BH_3: R_f = 0.65 (AcOEt and hexane, v/v = 1/1). $[\alpha]_D^{23}$ +44.8 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.36 (br q, $J_{H\text{-}B}$ = 111.2 Hz, 6H, BH_3), 1.15 (d, J = 13.7 Hz, 18H, C(CH_3)$_3$), 1.84-2.05 (m, 8H, PCH_2), 3.81-3.97 (m, 8H, OCH_2), 4.22-4.26 (m, 4H, OCH_2), 7.13 (s, 2H, $C_{10}H_6$), 7.30-7.35 (m, 2H, $C_{10}H_6$), 7.64-7.67 (m, 2H, $C_{10}H_6$) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ15.2 (d, $J_{C\text{-}P}$ = 30.6 Hz,), 21.3 (d, $J_{C\text{-}P}$ = 30.2 Hz), 25.2, 28.4 (d, $J_{C\text{-}P}$ = 34.1 Hz), 66.4, 68.1, 69.6, 108.8, 124.4, 126.3, 129.3, 149.1 ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz) δ +32.3 (br d, $J_{P\text{-}B}$ = 35.0 Hz) ppm. HRMS (ESI) calcd for $[C_{28}H_{50}B_2O_4P_2+NH_4]^+$: 552.3709, found 552.3699.

(*R,R*)-3c–BH_3: R_f = 0.20 (hexane/AcOEt, v/v = 1:1); $[\alpha]_D^{23}$ +1.2 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.34 (br q, $J_{H\text{-}B}$ = 117.4 Hz, 6H, BH_3), 1.14 (d, J = 13.8 Hz, 18H, C(CH_3)$_3$), 1.84-2.02 (m, 8H, PCH_2), 3.60-3.87 (m, 12H, OCH_2), 3.95-3.97 (m, 4H, OCH_2), 4.25-4.27 (m, 4H, OCH_2), 7.12 (s, 2H, $C_{10}H_6$), 7.31-7.33 (m, 2H, $C_{10}H_6$), 7.64-7.67 (m, 2H, $C_{10}H_6$) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.3 (d, $J_{C\text{-}P}$ = 30.8 Hz), 21.4 (d, $J_{C\text{-}P}$ = 30.4 Hz), 25.3, 28.5 (d, $J_{C\text{-}P}$ = 33.7 Hz), 66.3, 69.0, 69.6, 70.4, 70.9, 108.4, 124.2, 126.3, 129.4, 149.1 ppm; ^{31}P{^{1}H}NMR ($CDCl_3$, 161.5 MHz) δ +32.3 (br) ppm. HRMS (ESI) calcd for $[C_{32}H_{58}B_2O_6P_2+NH_4]^+$: 640.4233, found 640.4222.

Synthesis of 10. A mixture of an aqueous solution (10 mL) of NaOH (1.7 g, 42 mmol) and a THF solution (20 mL) of **9** (1.65 g, 5.23 mmol) was cooled to 0 °C. To this solution was added a THF solution (20 mL) of TsCl (5.0 g, 26 mmol) in one portion. The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched with H_2O, and the organic layer was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with H_2O three times and brine, and then dried over Na_2SO_4. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2 with AcOEt and hexane (v/v = 4/1) as an eluent. The solvent was evaporated to obtain **10** (2.55 g, 4.08 mmol, 78%) as colorless oil. R_f = 0.10 (hexane/AcOEt, v/v = 1:4); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H, Ar-CH_3), 3.6-3.8 (m, 12H, -O-CH_2), 4.18 (t, J = 4.9

Hz, 4H, Ar-SO_3-CH_2), 4.63 (s, 4H, Ar-CH_2-O), 7.3-7.4 (m, 6H, *Ar*), 7.72 (t, *J* = 7.6 Hz, 1H, *Ar*), 7.79 (d, *J* = 8.6 Hz, 4H, *Ar*) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 68.8, 69.2, 70.2, 70.7, 74.1, 120.0, 128.0, 129.8, 133.2, 137.4, 144.7, 157.8 ppm; HRMS (ESI) calcd for $[C_{29}H_{37}NO_{10}S_2+H]^+$ 624.1932, found 624.1917.

Synthesis of (*R,R*)-11–BH_3. A THF solution (30 mL) of (*S,S*)-**1**–BH_3 (0.093 g, 0.39 mmol) was cooled to –78 °C under Ar atmosphere. To this solution, *n*-BuLi (1.60 M in cyclohexane and *n*-hexane, 0.6 mL, 1.0 mmol) was added by a syringe. After the solution was stirred for 1 h, a THF solution (20 mL) of **10** (0.25 g, 0.39 mmol) was added over a period of 5 min by a syringe. After 1 h, the mixture was allowed to warm to room temperature and stirred for 72 h. The reaction was quenched with H_2O (30 mL), and the organic layer was extracted with AcOEt (50 mL × 3). The combined organic layers were washed with brine, and then dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2 with AcOEt and hexane (v/v = 4/1) as an eluent. The solvent was evaporated to obtain (*R,R*)-**11**–BH_3 (0.085 g, 0.17 mmol, 43%) as colorless oil. R_f = 0.20 (hexane/AcOEt, v/v = 1:4); $[\alpha]^{23}_D$ +4.3 (c 0.25, $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ –0.5-0.8 (br q, $J_{H\text{-}B}$ = 75 Hz, 6H, BH_3), 1.0 (br, 18H, *t*-Bu), 1.5-2.0 (m, 8H, P-CH_2), 3.2-3.8 (m, 12H, O-CH_2), 4.4-4.6 (q, *J* = 9.5 Hz, 4H, Ar-CH_2-O), 7.18 (d, *J* = 7.4 Hz, 2H, *Ar*), 7.59 (t, *J* = 7.4 Hz, 1H, *Ar*) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.3 (d, $J_{C\text{-}P}$ = 30 Hz), 20.4 (d, $J_{C\text{-}P}$ = 30 Hz), 25.3, 28.6 (d, $J_{C\text{-}P}$ = 33 Hz), 66.1, 70.0, 70.6, 74.4, 121.0, 136.9, 158.0 ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.5 MHz) δ +33.0 (br d, $J_{P\text{-}B}$ = 47 Hz) ppm; HRMS (ESI) calcd for $[C_{25}H_{51}B_2NO_4P_2+H]^+$ 514.3552, found 514.3549.

Removal of BH_3 from (*R,R*)-11–BH_3. To a solution of (*R,R*)-**11**–BH_3 (0.016 g, 0.032 mmol) in degassed dry toluene (0.5 mL) was added trifluoromethanesulfonic acid (0.5 mL, 6 mmol) by a syringe under Ar atmosphere. After stirring for 2 h at room temperature, toluene was removed in vacuo. The residue was dissolved in degassed EtOH (6 mL) and added to degassed KOH aq (0.6482 g, 12 mmol KOH in 10 mL H_2O). After the reaction for 5 h at 50 °C under Ar atmosphere, the solution was allowed to cool to room temperature. Extraction with degassed dry Et_2O was carried out, and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by column chromatography on Al_2O_3 (active basic) to obtain (*R,R*)-**11** (0.011 g, 0.023 mmol, 72%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.0 (br, 18H, *t*-Bu), 1.4-1.8 (m, 8H , P-CH_2), 3.4-3.8 (m, 12H, O-CH_2), 4.6-4.8 (q, *J* = 13 Hz, 4H, Ar-CH_2-O), 7.31 (d, *J* = 7.7 Hz, 2H, *Ar*), 7.67 (t, *J* = 7.7 Hz, 1H, *Ar*) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.5 MHz) δ –0.6 ppm; HRMS (DART) calcd for $[C_{25}H_{45}NO_4P_2+H]^+$ 486.2897, found 486.2893.

Host-guest reaction. Sample preparation was performed under Ar atmosphere. A $CDCl_3$ solution of (*R,R*)-**11** was prepared. The concentration of this solution was determined as 27.16 mM by the quantitative ^{1}H NMR method using dimethyl sulfone as an internal standard. A CD_3CN solution of

(*R*)-**12** or (*S*)-**12** (9.05 mM) was prepared. $CDCl_3$ and CD_3CN solutions were mixed and stirred for 1 h at room temperature; then, ^1H NMR measurement was carried out.

A $CDCl_3$ solution of (*R,R*)-**11** was prepared. The concentration of this solution was determined as 4.44 mM by the quantitative ^1H NMR method using dimethyl sulfone as an internal standard. A CD_3CN solution of D-**13** or L-**13** (4.44 mM) was prepared. $CDCl_3$ and CD_3CN solutions were mixed, and then ^1H and ^{31}P NMR measurements were carried out. After NMR measurement, excess CF_3CO_2H (ca. 10 μl) was added to the solution, and the solution was shaken for a minute; then, ^1H and ^{31}P NMR measurements were carried out.

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