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Formation of 1,4-diphosphinobenzenes via *tele*-substitution on fluorobenzenechromium complexes

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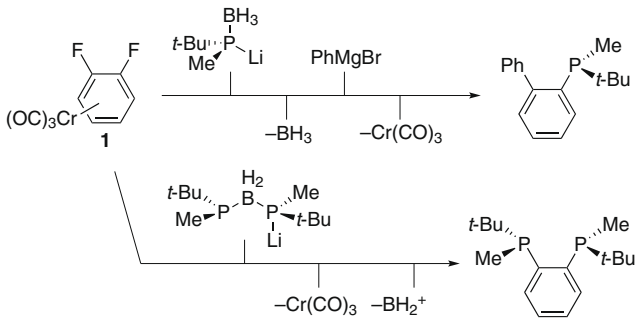
ABSTRACT

The *meta–tele*-substitution of 2-(boranatophosphino)fluorobenzenechromium complexes took place with various lithiated secondary phosphine–boranes as nucleophiles to give *para*-substituted bis(boranatophosphino)benzenechromiums. It was revealed that the yield of the *tele*-substitution product was strongly affected by the strength of a proton acid. Isotope labeling experiments indicated that 1,5-hydrogen migration was involved in this transformation.

1. Introduction

Arenechromium complexes are important aryl cation equivalents and utilized in a great number of organic transformations [1]. In particular, fluoroarenechromium complexes are frequently employed owing to their unique reactivity and high accessibility. Recently, we have demonstrated that *ortho*-difluorobenzenetricarbonylchromium (**1**) could be used as a good intermediate for the synthesis of optically active P-chiral phosphinobenzenes. In these studies, a variety of *ortho*-substituted P-chiral monophosphines were obtained via stepwise S_NAr reaction of **1** with a lithiated secondary P-chiral boranatophosphine and various nucleophiles (Eq. (1)) [2]. On the other hand, P-chiral *ortho*-diphosphinobenzenes could be prepared by the use of deprotonated bis(phosphine)boronium salts that consisted of two phosphino groups bound to each other through a boronium linkage [3]. This building block makes it possible to introduce two sterically hindered phosphino groups at proximal positions to each other. From these studies, we have shown that **1** reacted with lithiated (*S*)-*tert*-butyl(methyl)phosphine–borane (**2a**) to afford a diastereomixture of 2-(boranato-*tert*-butyl(methyl)phosphino)fluorobenzenetricarbonylchromium ((*R*$_P$,*S*)-**3a** and (*R*$_P$,*R*)-**3a**), and no bis(boranatophosphino)benzene chromium complexes could be detected under these reaction conditions. However, when this reaction was treated with an acid at low temperature, *para*-substituted bis(boranatophosphino)benzene chromium complex (*R*,*R*)-**4aa** was obtained as the main product (Scheme 1). This type of *tele*-substitution was previously reported by Rose-Munch et al., in which 2-methyl-1,3-dithian-2-yl anion was introduced at the 3-position of 2,6-dimethylfluorobenzenetricarbonylchromium [4]. Hong et al. have also studied a similar reaction using phenylacetylide anion as a nucleophile [5]. The attack of soft nucleophiles on fluoroarenechromium complexes that possess large substituents close to the fluoro group would tend to occur at *tele*-position to avoid the steric repulsion. Herein, we describe some examples of the *meta–tele*-substitution reaction of fluorobenzenechromium complexes with boranatophosphino nucleophiles, and discuss the mechanism of the reaction.



2. Results and discussion

Initially, we examined the substitution reaction using a 2-boranatophosphinofluorobenzenechromium complex with lithiated

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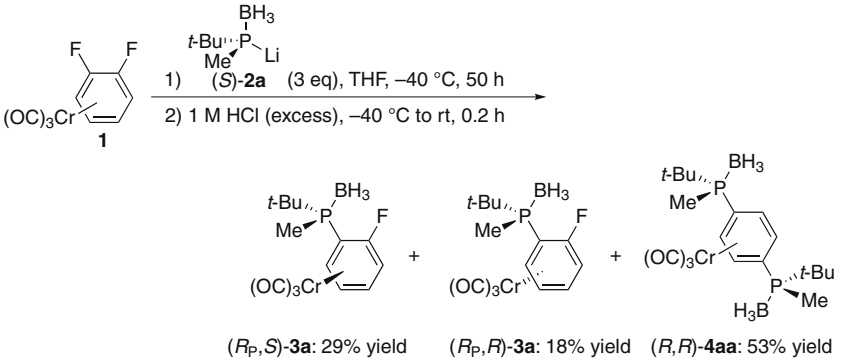
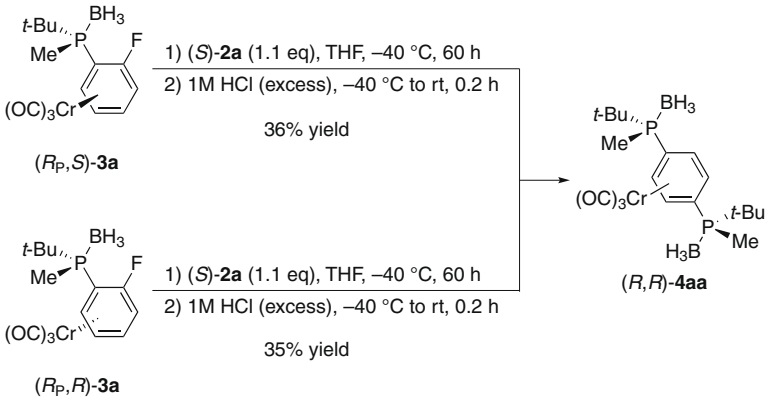


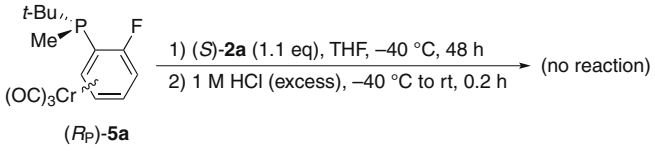
Scheme 1. The SNAr reaction of 1 with (*S*)-2a.



Scheme 2. The *meta–tele*-substitution reaction of (R_P,*S*)-, and (R_P,*R*)-3a with (*S*)-2a.

phosphine–borane to confirm the formation of the *tele*-substitution product. Compound (R_P,*S*)-**3a** was treated with 1.1 equiv. of (*S*)-**2a** at −40 °C, and the reaction was quenched with 1 M HCl at intact temperature, and *para*-substituted product (*R*,*R*)-**4aa** was obtained in 36% yield (Scheme 2). It was also confirmed that the reactivity of (R_P,*R*)-**3a** was similar to that of (R_P,*S*)-**3a** (35% yield). On the other hand, deboranated (R_P)-(2-*tert*-butylmethylphosphino)fluorobenzenechromium ((R_P)-**5a**) gave no coupling product under these reaction conditions, probably due to the electron-donating nature of the free phosphino group (Scheme 3) [2]. The absolute configurations of (R_P,*R*)-**3a** and (*R*,*R*)-**4aa** have been unequivocally determined by single crystal X-ray analysis (Fig. 1). In each case, the two *tert*-butyl groups are oriented at opposite sides of the chromium group owing to their bulkiness. Especially in (R_P,*R*)-**3a**, the *tert*-butyl group shields the *ipso*-carbon attached to fluoro group to prevent S_NAr at this position. On the other hand, a nucleophilic attack at the meta-position to the fluoro group would be advantageous because of the stabilization of the Meisenheimer-type intermediate by boranatophosphino group, and would lead to the formation of *para*-disubstituted product.

Optimization of the reaction conditions was carried out with lithiated P-chiral secondary phosphine–borane (*S*)-**2a** and *ortho*-(dicyclohexylboranatophosphino)fluorobenzenetricarbonylchromium (**3b**, Cy: cyclohexyl). The results are summarized in Table 1. It is noted that the chemical yield of the coupling reaction was largely affected by the acid treatment [4]. When the reaction was quenched by excess amount of 1 M HCl at 0 °C for 30 min, the yield was suppressed to 22%. The use of 3.0 equiv. of trifluoromethanesulfonic acid instead of HCl produced coupling product in 44% yield. Moreover, further increase of the chemical yield (to 79%) was realized when the acid treatment was carried out at −78 °C for 24 h. In each case, *tele*-substitution product could not be



Scheme 3. The SNAr reaction with (R_P)-5a.

detected on TLC before treatment with an acid. When the reaction was treated with water instead of an acid, only starting material was recovered.

The *meta–tele*-substitution reaction of 2-(boranatophosphino)fluorobenzenechromium complexes was then carried out with various substrates and nucleophiles. The results are summarized in Table 2. In these reactions, 2-(boranatophosphino)fluorobenzenechromium complexes were treated with 3 equiv. of secondary phosphine–boranes that were previously deprotonated with *sec*-butyllithium. The reactions were then quenched with trifluoromethanesulfonic acid at −78 °C for 24 h. The products were isolated after removal of the chromium group by UV irradiation in air. In almost all cases, moderate to high yields of 1,4-bis(boranatophosphino)benzenes were obtained. When dicyclohexylphosphine–borane (**2b**) and di(*tert*-butyl)phosphine–borane (**2f**) were employed as nucleophiles, coupling products **6ab** and **6af** were afforded in 11% and 28% yields, respectively, probably owing to high steric hindrance of the nucleophiles.

To observe the features of this *tele*-S_NAr process, the reaction was conducted by treatment of *rac*-5-D-**3b** (>95% D) with **2a** (Scheme 4). Deuterated position was determined by ^1H NMR after deboranation and subsequent oxidation of the two phosphino

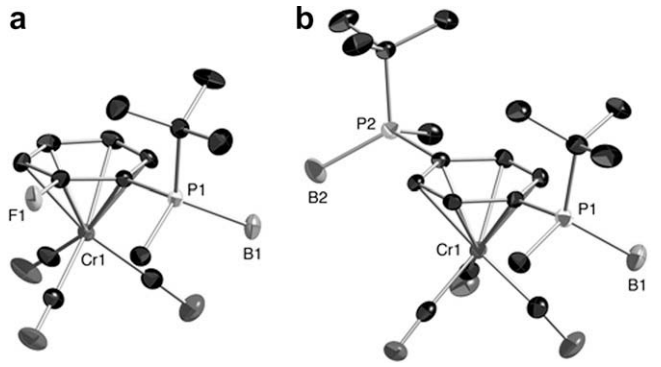
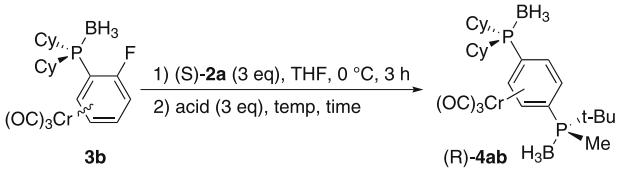


Fig. 1. ORTEP drawings of (R_P,*R*)-3a (left) and (*R*,*R*)-4aa (right). Hydrogens are omitted for clarity.

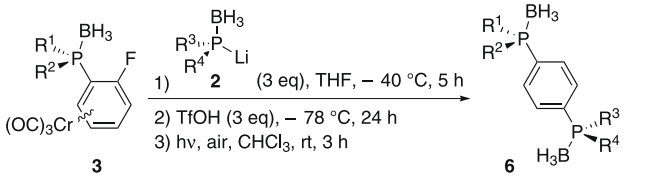
Table 1
tele-Substitution of 3b with (*S*)-**2a** under various quenching conditions[a]



Entry	Acid	Temperature (°C)	Time (h)	Yield (%)[b]
1	1 M HCl aq[c]	0	0.5	22
2	1 M HCl/MeOH	0	0.5	8
3	16 M HBF_4 aq.	0	0.5	18
4	$HBF_4 \cdot OEt_2$	0	0.5	28
5	$BF_3 \cdot OEt_2$	0	0.5	3
6	TfOH	0	0.5	44
7	TfOH	−40	3	66
8[d]	TfOH	−78	24	79

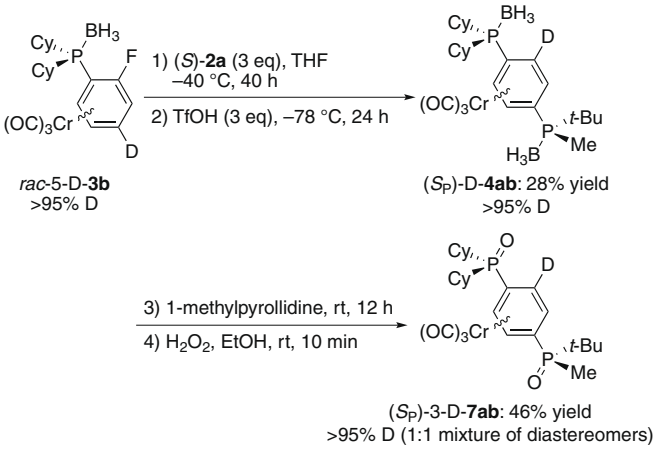
[a] All reactions were carried out with 0.2 mmol of 3b and 3.0 equiv. of 2a in 0.4 mL of THF and quenched with 3.0 equiv. of acid unless otherwise noted.
[b] Isolated yield.
[c] Excess amount of HCl was used.
[d] 1.4 mL of THF was used.

Table 2
tele-Substitution with various substrates[a]



Entry	3	R^1	R^2	2	R^3	R^4	6	Yield (%)[b]
1	**3a**	*t*-Bu	Me	**2a**	*t*-Bu	Me	**6aa**	73
2	**3a**	*t*-Bu	Me	**2b**	Cy	Cy	**6ab**	11
3	**3a**	*t*-Bu	Me	**2c**	Cy	Me	**6ac**	70
4	**3a**	*t*-Bu	Me	**2d**	*n*-Bu	*n*-Bu	**6ad**	84
5	**3a**	*t*-Bu	Me	**2f**	*t*-Bu	*t*-Bu	**6af**	28
6	**3a**	*t*-Bu	Me	**2h**	1-Ad	Me	**6ah**	59
7	**3b**	Cy	Cy	**2a**	*t*-Bu	Me	**6ab**	86
8	**3d**	*n*-Bu	*n*-Bu	**2a**	*t*-Bu	Me	**6ad**	70
9	**3d**	*n*-Bu	*n*-Bu	**2a**	*t*-Bu	Me	**6ae**	79
10	**3e**	*i*Pr	*i*Pr	**2a**	*t*-Bu	Me	**6ae**	48
11	**3f**	*t*-Bu	*t*-Bu	**2a**	*t*-Bu	Me	**6af**	62
12	**3g**	Ph	Ph	**2a**	*t*-Bu	Me	**6ag**	83

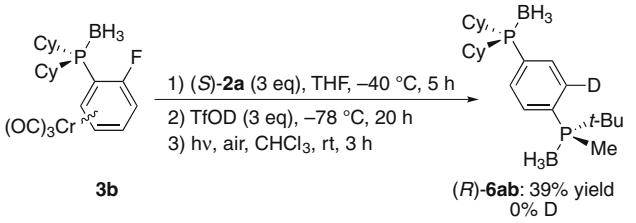
[a] All reactions were carried out with 0.1 mmol of 3 and 3.0 equiv. of 2 in 0.7 mL of THF and then treated with 3.0 equiv. of TfOH.
[b] Isolated yield.



Scheme 4. A labeling study with rac-5-D-3b.

groups. In the coupling product, the deuterium atom was found at the *ortho* position to dicyclohexyloxophosphorano group without decrease of deuteration ratio. This result strongly indicates that this *meta*–*tele*-substitution reaction proceeds via a 1,5-hydrogen shift [6]. This is also supported by the fact that the chemical yield of (S_P)-D-**4ab** (28%) was much lower than that obtained from non-deuterated **3b** (86% yield, entry 7 in Table 2). This would indicate that the shift of hydrogen/deutrium occurs as the rate-determining step of this transformation. Next, we employed deuterated trifluoromethanesulfonic acid in the reaction. Although the *para*-disubstituted product was isolated in 39% yield in its dechromination form, deuterium was not detected in the product (Scheme 5). This implies that the proton acid would promote 1,5-hydrogen migration or elimination of the fluoride anion, rather than protonate the benzene core.

Based on the results mentioned above, the mechanism of the acid-mediated formation of the *meta*–*tele*-substitution product was proposed as depicted in Fig. 2. Nucleophilic attack takes place at the *para*-position to the boranatophosphino group on the arene-chromium complex, due to the steric hindrance and the conjugatively electron-withdrawing nature of the substituent. The Meisenheimer-type intermediate thus formed undergoes subsequent 1,5-hydrogen migration before (path A) or after (path B) protonation of the fluoro group. In path A, hydrogen migration proceeds slowly and takes a longer reaction time to obtain the product in high yield. On the other hand, the reaction via path B would proceed rapidly because of the acceleration of the hydrogen migration by protonation of the fluoro group [7]. Treatment of the Meisenheimer-type intermediate with weak acid might be insufficient to protonate the fluoro group and allow the elimination of the phosphorus nucleophile required to regenerate the starting materials. The direct protonation of the benzene core is also plausible (path C). In this case, *syn*-elimination of HF from the later intermediate have to be involved because deuterium was not incorporated in the product after treatment of the reaction with trifluoromethanesulfonic acid-D.



Scheme 5. A labeling study with TfOD.

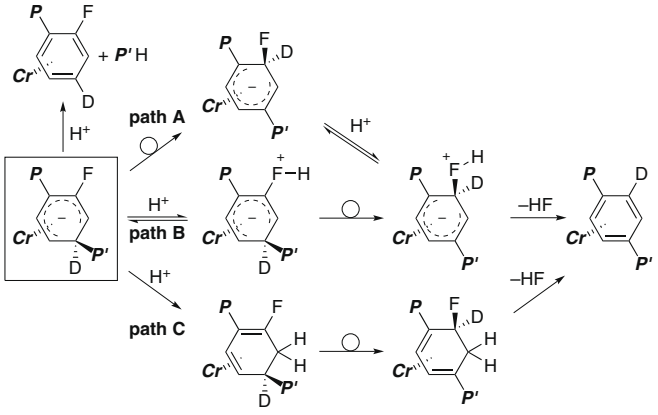


Fig. 2. Proposed mechanism of the acid-mediated *meta–tele*-substitution.

3. Conclusion

The coupling reaction with 2-(boranatophosphino)fluorobenzenechromium complexes and various lithiated secondary phosphine–boranes afforded *para*-substituted bis(boranatophosphino) benzenechromiums in moderate to high yield according to *meta–tele*-S_NAr manner. It was revealed that this transformation took place via 1,5-hydrogen migration and subsequent elimination of HF. Acid treatment is the key step for the effective formation of the product.

4. Experimental

4.1. General

All manipulations were carried out under nitrogen atmosphere. NMR spectra were recorded on a JEOL JNM-ECX (400 MHz for ^{1}H, 162 MHz for ^{31}P, and 100 MHz for ^{13}C). Chemical shifts were reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual $CHCl_3$ (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. IR spectra were recorded on a JASCO FT/IR-6300. Optical rotations were measured with a JASCO P-1030 polarimeter with a sodium lamp. MS (ESI) spectra were obtained on JEOL JMS-T100LC spectrometers. HPLC analyses were performed on a Hitachi L-2130 pump, and L-2450 Diode Array detector with a chiral column. X-ray crystal structure data were collected using a Bruker SMART APEX II diffractometer with Mo Kα radiation. All reagents were obtained from commercial sources and used without further purification. All solvents were freshly distilled. Compound **1**, (*S*)-**2a**, (R_P,*S*)-**3a,** (R_P,*R*)-**3a,** and (R_P)-**5a** were prepared according to the literature procedure [2].

4.2. General procedure for the preparation of 2-(boranatophosphino) fluorobenzenetricarbonylchromium (**3b**–**g**)

To a solution of *sec*-phosphine–borane (2.2 equiv.) in THF was added *sec*-BuLi (1.0 M cyclohexane and *n*-hexane solution, 2.2 equiv.) at −78 °C under nitrogen atmosphere, and the reaction mixture was stirred for 1 h. To the solution was added **1** (1.0 equiv.) in THF at −40 °C, and the mixture was stirred for 20 h. The reaction mixture was diluted with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (*n*-hexane/EtOAc = 5/1–3/1) to give 2-(boranatophosphino)fluorobenzenetricarbonylchromium.

4.2.1. 2-(Boranatodicyclohexylphosphino) fluorobenzenetricarbonylchromium (**3b**)

Yield: 95% as a yellow solid; mp. 202 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.06 (dt, J = 3.64 Hz, 6.88 Hz, 1H), 5.69 (m, 1H), 5.20 (t, J = 6.40 Hz, 1H), 4.80 (dt, J = 3.20, 5.96 Hz, 1H), 2.35–2.26 (m, 2H), 2.13–2.05 (m, 1H), 2.00–1.89 (m, 4H), 1.80–1.55 (m, 7H), 1.39–1.10 (m, 8H), 1.0–0.1 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 230, 148 (d, J = 260 Hz), 99.1 (dd, J = 6.67, 124 Hz), 94.2 (d, J = 8.59 Hz), 84.2 (d, J = 7.63 Hz), 78.9 (dd, J = 19.0, 33.4 Hz), 76.9 (dd, J = 23.8, 62.9 Hz), 33.9 (d, J = 27.6 Hz), 32.6 (d, J = 31.1 Hz), 27.6 (d, J = 5.05 Hz), 27.4, 27.1, 27.0, 26.9, 26.9, 26.8, 26.7, 26.6, 25.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 37.2 (d, J = 60.4 Hz); IR (KBr) 2937, 3857, 2410, 1970, 1891 cm^{-1}; HRMS (ESI): *m/z* Calc. for $C_{21}H_{29}BClCrFO_3P$ $(M+Cl)^-$: 477.1025. Found: 477.1015; Anal. Calc. for: C, 57.03; H, 6.61. Found: C, 57.06; H, 6.67%.

4.2.2. 2-((S)-Boranatocyclohexylmethylphosphino) fluorobenzenetricarbonylchromium (**3c**)

Yield: 21% as a yellow solid; mp. 143–145 °C; $[\alpha]_D^{24}$ = 35.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.99 (dd, J = 6.88, 10.6 Hz, 1H), 5.70 (m, 1H), 5.22 (t, J = 5.96 Hz, 1H), 4.79 (m, 1H), 2.32 (m, 1H), 2.12 (q, J = 1.24 Hz, 1H), 1.87 (m, 1H), 1.74 (d, J = 11 Hz, 1H), 1.53 (d, J = 9.60 Hz, 3H), 1.48–1.18 (m, 5H), 1.1–0.2 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 230, 149 (d, J = 264 Hz), 98.2, 94.5 (d, J = 8.00 Hz), 84.0 (d, J = 8.40 Hz), 81.0 (dd, J = 18.4, 39.1 Hz), 76.6 (d, J = 23.0 Hz), 34.6 (d, J = 34.5 Hz), 26.8, 26.6, 26.1, 26.0, 25.6, 9.36 (d, J = 38.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 22.6; IR (KBr) 3104, 2931, 2855, 2342, 1972,1885 cm^{-1}; HRMS (ESI): *m/z* Calc. for $C_{16}H_{21}BClCrFO_3P$ $(M+Cl)^-$: 409.0399. Found: 409.0396.

4.2.3. Epi-**3c**

Yield: 24% as a yellow solid; mp. 141–144 °C; $[\alpha]_D^{24}$ = −65.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (m, 1H), 5.68 (m, 1H), 5.22 (t, J = 5.96 Hz, 1H), 4.80 (m, 1H), 2.00 (q, J = 1.28 Hz, 1H), 1.9–1.75 (m, 3H), 1.72 (d, J = 10.1 Hz, 4H), 1.53 (s, 1H), 1.41 (m, 2H), 1.3–1.18 (m, 3H), 1.1–0.2 (m, 3H); $CDCl_3$, 100 MHz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 230, 149 (d, J = 263 Hz), 94.3 (d, J = 8.00 Hz), 84.0 (d, J = 8.00 Hz), 80.8 (dd, J = 18.4, 40.2 Hz), 76.6 (d, J = 23.0 Hz), 35.1 (d, J = 34.5 Hz), 26.8, 26.6, 26.5, 26.4, 23, 25.6 11.1 (d, J = 44.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 25.7 (d, J = 60.7 Hz); IR (KBr) 3073, 2941, 2864, 2383, 1975, 1900, 1884 cm^{-1}; HRMS (ESI): *m/z* Calc. for $C_{16}H_{21}BClCrFO_3P$ $(M+Cl)^-$: 409.0399. Found: 409.0396.

4.2.4. 2-(Boranatodi-n-butylphosphino) fluorobenzenetricarbonylchromium (**3d**)

Yield: 53% as a yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.11 (dt, J = 3.68, 6.88 Hz, 1H), 5.69 (m, 1H), 5.23 (t, J = 5.96 Hz, 1H), 4.80 (m, 1H), 2.10–1.79 (m, 5H), 1.59–1.23 (m, 7H), 0.96 (t, J = 7.32 Hz, 3H), 0.87 (t, J = 7.32 Hz, 3H), 1.39–1.10 (m, 8H), 1.1–0.1 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.1, 147.5, 99.1 (d, J = 7.62 Hz), 94.5

(d, J = 7.63 Hz), 84.2 (d, J = 6.67 Hz), 80.6 (dd, J = 18.1, 40.0 Hz), 27.6 (d, J = 36.2 Hz), 25.4 (d, J = 11.4 Hz), 24.5 (d, J = 30.5 Hz), 24.2 (dd, J = 3.81, 13.4 Hz), 13.6; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 24.2 (d, J = 60.8); HRMS (ESI): m/z Calc. for $C_{17}H_{25}B1ClCrO_3P$ $(M+Cl)^-$ 425.0712. Found: 425.0702.

4.2.5. 2-(Boranatodiisopropylphosphino) fluorobenzenetricarbonylchromium (**3e**)

Yield: 79% as a yellow solid; mp. 141–143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (m, 1H), 5.69 (m, 1H), 5.21 (t, J = 6.40 Hz, 1H), 4.82 (m, 1H), 2.60 (m, 1H), 2.37 (m, 1H), 1.47 (dd, J = 6.88, 16.5 Hz, 3H), 1.36 (dd, J = 6.88, 16.0 Hz, 3H), 1.17 (dd, J = 6.88, 16.0 Hz, 3H), 1.04 (ddd, J = 1.84, 6.88, 14.2 Hz, 3H), 0.9–0.14 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149, 147, 98.8 (dd, J = 6.68, 12.4 Hz), 94.3 (d, J = 7.63 Hz), 84.3 (d, J = 6.67 Hz), 78.3 (dd, J = 19.0, 32.4 Hz), 23.7 (d, J = 4.77 Hz), 23.6, 23.5 (d, J = 4.76 Hz), 23.3, 17.6 (dd, J = 25.8, 25.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 45.8 (d, J = 65.0 Hz); IR (KBr) 3102, 2979, 2392, 1975, 1930 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{15}H_{21}BClCrO_3P$ $(M+Cl)^-$: 397.0399. Found: 397.0412; Anal. Calc. for: C, 49.75; H, 5.85. Found: C, 49.73; H, 5.39%.

4.2.6. 2-(Boranatodi-tert-butylphosphino) fluorobenzenetricarbonylchromium (**3f**)

Yield: 85% as a yellow solid; mp. 180–182 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.44 (dt, J = 3.68, 7.32 Hz, 1H), 5.74 (m, 1H), 5.22 (t, J = 6.88 Hz, 1H), 4.80 (dt, J = 3.68, 6.44 Hz, 1H), 1.54 (dd, J = 1.84, 14.7 Hz, 2H), 1.24 (d, J = 13.8 Hz, 1H), 1.1–0.3 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 230 (s), 147.2 (dd, J = 3.21, 263 Hz), 100.2 (dd, J = 7.50, 11.8 Hz), 94.5 (d, J = 7.50 Hz), 80.0 (dd, J = 22.5, 25.7 Hz, 2H), 76.5 (d, J = 25.7 Hz), 35.4 (d, J = 2.10 Hz), 35.2 (d, J = 4.30 Hz), 29.5 (m), 28.8 (m); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 60.0 (d, J = 64.8); IR (KBr) 3080, 2969, 2400, 1976, 1906 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{17}H_{25}BClCrO_3P$ $(M+Cl)^-$: 425.0712. Found 425.0714; Anal. Calc. for: C, 52.33; H, 6.46. Found: C, 52.35; H, 6.39%.

4.2.7. 2-(Boranatodiphenylphosphino) fluorobenzenetricarbonylchromium (**3g**)

Yield: 69% as a yellow solid; mp 145–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (m, 2H), 7.63–7.40 (m, 8H), 6.19 (t, J = 6.88 Hz, 1H), 5.69 (m, 1H), 5.15 (t, J = 5.96 Hz, 1H), 4.79 (m, 1H), 1.7–0.7 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150, 148, 134 (d, J = 10.5 Hz), 132 (d, J = 9.54 Hz), 132, 131, 129 (d, J = 10.5 Hz), 129 (d, J = 11.4), 128, 98.7 (dd, J = 4.77, 14.3 Hz), 94.4 (d, J = 7.63 Hz), 83.5 (d, J = 7.63 Hz), 81.9 (dd, J = 17.2, 45.7 Hz), 75.9 (d, J = 21.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 22.86 (d, J = 24.1 Hz); IR (KBr) 3089, 2384, 1984, 1926 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{21}H_{17}BClCrFO_3P$ $(M+Cl)^-$: 465.0086. Found: 465.0083; Anal. Calc. for: C, 58.64; H, 3.98. Found: C, 58.63; H, 3.80%.

4.3. General procedure for the tele-S_NAr

To a solution of *sec*-phosphine–borane (0.3 mmol) in THF (0.5 mL) was added a solution of *sec*-BuLi (0.3 mL, 1.0 M cyclohexane solution, 0.3 mmol) at −78 °C under nitrogen atmosphere, and the reaction mixture was stirred for 1 h. To the solution was added 2-boranatophosphinofluorobenzenetricarbonylchromium (0.1 mmol) in THF (0.2 mL) at −40 °C, and the mixture was stirred for 5 h. Trifluoromethanesulfonic acid (0.3 mmol) was then added slowly to the solution at −78 °C. After stirring at intact temperature for 24 h, the mixture was diluted with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The resulting yellow solid was dissolved in chloroform, and the solution was exposed to air under irradiation of light for 3 h. After removal of green precipitates by filtration, the filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (n-hexane/EtOAc = 5/1) to give 1,4-bis(boranatophosphino) benzene.

4.3.1. 1,4-Bis(boranato-tert-butylmethylphosphino)benzene (**6aa**)

Yield: 73% as a A white solid; mp 230 °C (decomp.); $[\alpha]_D^{23}$ = −16.8 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (m, 4H), 1.57 (d, J = 9.64 Hz, 6H), 1.09 (d, J = 14.2 Hz, 18H), 1.0–0.2 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.6 (t, J = 8.6 Hz), 131.6 (d, J = 45.8 Hz), 28.7 (d, J = 32.4 Hz), 25.3 (d, J = 2.90 Hz), 5.26 (d, J = 37.2); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 33.9 (m); IR (KBr) 2954, 2866, 2370 cm^{-1}; Anal. Calc. for: C, 61.99; H, 11.05. Found: C, 61.75; H, 11.11%.

4.3.2. 1-(Boranato-tert-butylmethylphosphino)-4-(boranatodicyclohexylphosphino)benzene (**6ab**)

Yield: 86% as a white solid; mp 300 °C (decomp.); $[\alpha]_D^{24}$ = −3.7 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (m, 4H), 2.08 (m, 2H), 1.94 (m, 2H), 1.82–1.67 (m, 6H), 1.59 (d, J = 9.60 Hz, 3H), 1.54 (m, 2H), 1.34–1.15 (m, 10H), 1.11 (d, J = 6.80 Hz, 9H), 1.0–0.1 (br, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.1 (t, J = 8.58 Hz), 132.7 (t, J = 8.58 Hz), 131.4 (d, J = 47.7 Hz), 129.6 (d, J = 44.8 Hz), 31.4 (d, J = 21.9 Hz), 31.1 (d, J = 22.9 Hz), 28.8 (d, J = 32.4 Hz), 26.8, 26.7, 26.6, 26.3 (d, J = 5.72 Hz), 25.91, 25.86, 5.24 (d, J = 37.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.9 (d, J = 60.7 Hz), 26.8 (d, J = 65.1 Hz); IR (KBr) 2938, 3855, 2390 cm^{-1}; MS (ESI): m/z 439.3 $(M+Cl)^-$; Anal. Calc. for: C, 67.81; H, 10.90. Found: C, 68.32; H, 11.19%.

4.3.3. 1-(Boranato-tert-butylmethylphosphino)-4-(boranatocyclohexylmethylphosphino)benzene (**6ac**)

Yield: 70% as a white solid; mp 179–180 °C; $[\alpha]_D^{24}$ = −14.7 (c 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (m, 4H), 1.85–1.74 (m, 4H), 1.73–1.61 (m, 2 H), 1.59 (d, J = 9.60 Hz, 3H), 1.54 (d, J = 10.0 Hz, 3H), 1.29–1.17 (m, 5H), 1.12 (d, J = 14.2 Hz, 9H), 1.1–0.1 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.9 (dd, J = 8.58, 8.58 Hz), 132.7 (d, J = 49.6 Hz), 131.7 (dd, J = 8.58, 8.58 Hz), 131.6 (d, J = 48.6 Hz), 35.7 (d, J = 35.3 Hz), 28.8 (d, J = 32.4 Hz), 26.5, 26.4, 25.7, 25.3, 7.69 (d, J = 38.1 Hz), 5.26 (d, J = 36.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 34.0 (m), 32.5 (m); IR (KBr) 2930, 2857, 2388 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{18}H_{36}B_2ClP_2$ $(M+Cl)^-$: 371.2167. Found: 371.2168.

4.3.4. 1-(Boranato-tert-butylmethylphosphino)-4-(boranatodi-n-butylphosphino)benzene (**6ad**)

Yield: 84% as a white solid; mp 168 °C; $[\alpha]_D^{24}$ = −7.3 (c 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (m, 4H), 1.9–1.79 (m, 4H), 1.59 (d, J = 9.60 Hz, 3H), 1.50–1.42 (m, 2H,) 1.38–1.28 (m, 6H), 1.11 (d, J = 13.8 Hz, 9H), 0.87 (t, J = 7.32 Hz, 6H) 0.9–0.2 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133 (dd, J = 8.60, 8.60 Hz), 133 (d), 132 (dd, J = 8.60, 8.60 Hz), 132 (d, J = 47.7 Hz), 28.8 (d, J = 32.4 Hz), 25.4, 25.3, 25.2, 24.95, 24.95, 24.9, 24.4, 24.3, 13.6, 5.25 (d, J = 36.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.0 (d, J = 65.0 Hz), 16.6 (d, J = 56.4 Hz); IR (KBr) 2957, 2869, 2378 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{19}H_{40}B_2ClP_2$ $(M+Cl)^-$: 387.2480. Found 387.2474.; Anal. Calc. for: C, 64.81; H, 11.45. Found: C, 64.89; H, 11.26%.

4.3.5. 1-(Boranato-tert-butylmethylphosphino)-4-(boranatodiisopropylphosphino)benzene (**6ae**)

Yield: 48% as a white solid; mp 179–180 °C; $[\alpha]_D^{24}$ = −10.5 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (m, 4H), 2.37 (m, 2H), 1.59 (d, J = 9.64 Hz, 3H), 1.10 (d, J = 14.2 Hz, 9H), 1.20–1.02 (m, 12H), 1.0–0.1 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.1 (dd,

J = 7.60, 7.60 Hz), 132.7 (dd, J = 8.6, 8.6 Hz), 131.7 (d, J = 46.7 Hz), 129.4 (d, J = 44.8 Hz), 28.7 (d, J = 32.4 Hz), 25.2, 22.0, 16.8, 5.23 (d, J = 36.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 35.7 (d, J = 65.0 Hz), 26.9 (d, J = 69.4 Hz); IR (KBr) 2971, 2871, 2380 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{17}H_{36}B_2ClP_2$ $(M+Cl)^-$: 359.2167. Found: 359.2168.; Anal. Calc. for: C, 63.01; H, 11.20. Found: C, 62.93; H, 10.94%.

4.3.6. 1-(Boranato-tert-butylmethylphosphino)-4-(boranatodi-tert-butylphosphino)benzene (**6af**)

Yield: 62% as a white solid; mp 167–169 °C; $[\alpha]_D^{24}$ = −9.0 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (t, J = 8.28 Hz, 2H), 7.79 (t, J = 8.68 Hz, 2H), 1.59 (d, J = 9.64 Hz, 3H), 1.31 (d, J = 13.3 Hz, 18H), 1.10 (d, J = 14.2 Hz, 9H), 1.0–0.1 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.7, 132.2 (t, J = 8.58 Hz), 131.4 (d, J = 18.1 Hz), 131.0 (d, J = 7.63 Hz), 33.4 (d, J = 4.77 Hz), 33.1 (d, J = 4.77 Hz), 28.9 (d, J = 2.86 Hz), 28.5, 25.3 (d, J = 2.86 Hz), 5.19 (d, J = 36.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 46.2 (d, J = 82.4 Hz), 26.6 (d, J = 75.8 Hz); IR (KBr) 2971, 2385 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{19}H_{40}B_2ClP_2$ $(M+Cl)^-$: 387.2480. Found: 387.2484. Anal. Calc. for: C, 64.81; H, 11.45. Found: C, 65.06; H, 11.27%.

4.3.7. 1-(Boranato-tert-butylmethylphosphino)-4-(boranatodiphenylphosphino)benzene (**6ag**)

Yield: 83% as a white solid; mp. 144–145 °C; $[\alpha]_D^{24}$ = 14.8 (c 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (t, J = 6.88 Hz, 2H), 7.66–7.50 (m, 8H), 7.45 (t, J = 7.32 Hz, 4H), 1.57 (d, J = 9.60 Hz, 3H), 1.10 (d, J = 17.0 Hz, 9H), 1.8–0.2 (br, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134, 133.3 (d, J = 9.53 Hz), 133.1 (t, J = 9.54 Hz), 132.8 (t, J = 9.54 Hz), 131.7 (d, J = 44.8 Hz), 131.7, 28.8 (d, J = 32.4 Hz), 25.3 (d, J = 2.86 Hz), 5.26 (d, J = 37.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.2 (d, J = 45.5 Hz), 21.8 (d, J = 32.1 Hz); IR (KBr) 2963, 2902, 2381, 2341, 2264 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{23}H_{32}B_2Cl_1P_2$ $(M+Cl)^-$: 427.1854. Found: 427.1850. Anal. Calc. for: C, 70.46; H, 8.23. Found: C, 70.47; H, 7.98%.

4.3.8. 1-(Boranato-tert-butylmethylphosphino)-4-(boranato-1-adamantylmethylphosphino)benzene (**6ah**)

Yield: 59% as a white solid; mp 277–279 °C; $[\alpha]_D^{24}$ = −12.4 (c 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (m, 4H), 1.98 (s, 3H), 1.27 (s, 6H), 1.69 (s, 3H), 1.63 (s, 3H), 1.59 (d, J = 9.6 Hz, 3H), 1.53 (d, J = 9.2 Hz, 3H), 1.12 (d, J = 14.2 Hz, 9H), 1.1–0.2 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.8 (t, J = 9.53 Hz), 132.5 (t, J = 8.58 Hz), 131.4 (d, J = 46.7 Hz), 130.7 (d, J = 46.7 Hz), 36.3, 35.9, 31.4 (d, J = 32.4 Hz), 21.8 (d, J = 32.4 Hz), 27.7 (d, J = 8.58 Hz), 25.3 (d, J = 1.90 Hz), 5.24 (d, J = 37.2 Hz), 3.70 (d, J = 37.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 26.9 (d, J = 60.8 Hz), 23.4 (d, J = 73.8 Hz); IR (KBr) 2905, 2851, 2376 cm^{-1}; HRMS (ESI): m/z Calc. for $C_{22}H_{40}B_2ClP_2$ $(M+Cl)^-$: 409.0399. Found: 409.0396.

4.4. Preparation of 2-boranatodicyclohexylphosphino-5-deuteriofluorobenzenetricarbonylchromium (rac-5-D-**3b**)

4.4.1. 1-Dicyclohexylphosphino-2,3-difluorobenzenetricarbonylchromium (rac-**8**)

To a solution of **1** (707 mg, 2.8 mmol) in Et_2O (28 mL) was added n-BuLi (1.8 mL of 1.6 M n-hexane solution, 2.8 mmol) at −78 °C under nitrogen atmosphere. After stirring for 0.5 h, chlorodicyclohexylphosphine (630 μL, 2.8 mmol) was added at −78 °C, and the mixture was stirred for 3 h at intact temperature. The reaction was quenched with 1 M HCl aq., and the mixture was extracted three times with EtOAc. The combined extracts were washed with saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel (n-hexane/EtOAc = 10/1) to give *rac*-**8** (627 mg, 50% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.67 (m, 1H), 5.07 (m, 1H), 4.91 (t, J = 6.44 Hz, 1H), 2.18 (t, J = 10.1 Hz, 1H), 2.01 (t, J = 11.0 Hz, 2H), 1.92–1.76 (m, 7H), 1.69 (d, J = 11.9 Hz, 2H), 1.37–1.1 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131 (d, J = 269 Hz), 133 (d, J = 269 Hz), 93.4 (dd, J = 4.76, 21.9 Hz), 90.5 (dd, J = 20.0, 47.7 Hz), 84.9, 81.7 (d, J = 17.1 MHz), 33.4, 33.0, 30.2, 30.0, 29.9, 29.8, 27.3, 27.2, 27.0, 26.9, 26.3, 26.2; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 7.92 (d, J = 13.0 Hz).

4.4.2. 1-Dicyclohexylphosphino-4-duterio-2,3-difluorobenzenetricarbonylchromium (rac-**9**)

To a solution of *rac*-**8** (722 mg, 1.6 mmol) in Et_2O (10 mL) was added n-BuLi (1.2 mL of 1.6 M n-hexane solution, 1.9 mmol) at −78 °C under nitrogen atmosphere. After stirring for 0.5 h, the reaction was quenched with D_2O (10 mL), and the mixture was extracted three times with EtOAc. The combined extracts were washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (n-hexane/EtOAc = 10/1) to give *rac*-**9** (641 mg, 88% yield, >99% D) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.67 (m, 0.01H), 5.07 (m, 1H), 4.91 (d, J = 6.4 Hz, 1H), 2.15 (t, J = 10.1 Hz, 1H), 2.01 (t, J = 11.0 Hz, 2H), 1.92–1.76 (m, 7H), 1.69 (d, J = 11.9 Hz, 2H), 1.37–1.1 (m, 10H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 7.92 (d, J = 13.0 Hz).

4.4.3. 2-Dicyclohexylphosphino-5-duteriofluorobenzenetricarbonylchromium (rac-**10**)

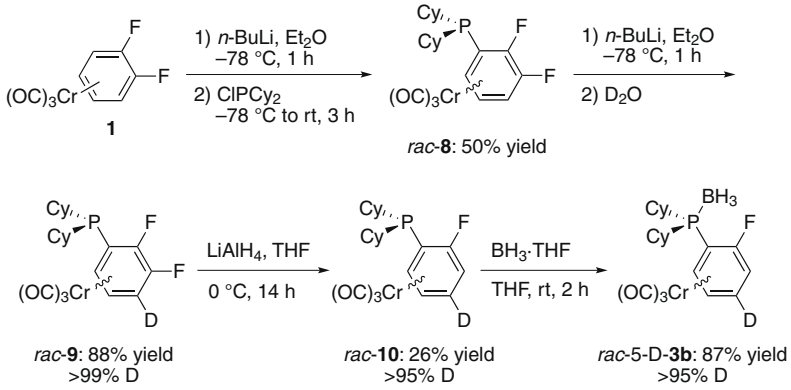
A solution of *rac*-**9** (641 mg, 1.43 mmol) in Et_2O (30 mL) was slowly added to a stirred suspension of lithium aluminum hydride (270 mg, 7.2 mmol) in Et_2O (10 mL) at 0 °C, and the mixture was stirred at intact temperature for 14 h. The reaction mixture was diluted with EtOAc, and washed with water, and the aqueous phase was extracted twice with EtOAc. The combined extracts were washed with saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (n-hexane/EtOAc = 10/1) to give *rac*-**10** (162 mg, 26% yield, >95% D) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.54 (m, 1.02H), 5.25 (d, J = 5.04 Hz, 1H), 4.84 (m, 1H), 2.1–1.6 (m, 12H), 1.4–1.1 (m, 10H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 5.44 (d, J = 26.0 Hz).

4.4.4. rac-5-D-**3b**

To a solution of *rac*-**10** (161 mg, 0.4 mmol) in THF (1 mL) was added BH_3·THF complex (0.4 mL of 1.0 M THF solution, 0.4 mmol) at 0 °C under nitrogen atmosphere. After stirring at room temperature for 2 h, the reaction was quenched with 1 M HCl aq., and the mixture was extracted three times with EtOAc. The combined extracts were washed with saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (n-hexane/EtOAc = 10/1) to give *rac*-5-D-**3b** (154 mg, 87% yield, >95% D) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.06 (dt, J = 3.64, 6.88 Hz, 1H), 5.69 (m, 0.05H), 5.20 (d, J = 6.4 Hz, 1H), 4.80 (dd, J = 3.20, 5.96 Hz, 1H), 2.35–2.26 (m, 2H), 2.13–2.05 (m, 1H), 2.00–1.89 (m, 4H), 1.80–1.55 (m, 7H), 1.39–1.10 (m, 8H), 1.0–0.1 (m, 3H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 37.2 (d, J = 60.4 Hz).

4.4.5. Procedure for the labeling studies (Scheme 4)

To a solution of (*S*)-*tert*-butylmethylphosphine–borane (34.9 mg, 0.3 mmol) in THF (0.5 mL) was added *sec*-BuLi (0.3 mL, 1.0 M cyclohexane and n-hexane solution, 0.3 mmol) at −78 °C under nitrogen atmosphere, and the reaction mixture was stirred for 1 h. To the solution was added *rac*-5-D-**3b** (45 mg, 0.1 mmol), and THF (0.2 mL) at −40 °C, and the mixture was stirred for 40 h. Trifluoromethanesulfonic acid (27 μL, 0.3 mmol) was then added slowly to the solution at −78 °C, and the reaction was stirred at intact temperature. After 24 h, the reaction mixture was diluted with



Scheme 6. Preparation of *rac*-5-D-**3b**.

water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (*n*-hexane/EtOAc = 5/1).

A mixture of the purified product (27.5 mg) and 1-methylpyrrolidine (2 mL) was stirred under nitrogen atmosphere at room temperature for 12 h. The volatiles were removed under reduced pressure, and the residue was passed through a column of silica gel with degassed toluene elution. The eluent was evaporated under reduced pressure to give free phosphine. To a solution of free phosphine (18 mg) in EtOH (1.0 mL) was added H_2O_2 at 0 °C and the mixture was stirred for 10 min at intact temperature. The reaction was quenched with 1 M HCl aq., and the mixture was extracted three times with EtOAc. The combined extracts were washed with saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel ($CHCl_3$/MeOH = 10/1) to give a diastereomeric mixture of 3-D-**7ab** (7.2 mg, 13% yield, >95% D). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 (t, J = 5.96 Hz, 1H), 5.66 (t, J = 6.40 Hz, 0.48H), 5.59 (t, J = 6.40 Hz, 0.55H), 5.05 (t, J = 5.96 Hz, 1H), 2.1–1.8 (m, 10H), 1.73 (d, J = 13.6 Hz, 3H), 1.5–1.2 (m, 12H), 1.18 (d, J = 15.1 Hz, 9H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 48.4, 43.5.

4.4.6. Procedure for the labeling studies (Scheme 5)

To a solution of (*S*)-*tert*-butylmethylphosphine–borane (36 mg, 0.3 mmol) in THF (0.5 mL) was added *sec*-BuLi (0.3 mL, 1.0 M cyclohexane and *n*-hexane solution, 0.3 mmol) at −78 °C under nitrogen atmosphere, and the reaction mixture was stirred for 1 h. To the solution was added **3b** (44.2 mg, 0.1 mmol) in THF (0.2 mL) at −40 °C, and the mixture was stirred for 5 h. Trifluoromethanesulfonic acid-D (27 μL, 0.3 mmol) was then added slowly to the solution at −78 °C, and the reaction was stirred at intact temperature. After 24 h, the mixture was diluted with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The resulting yellow solid was dissolved in $CHCl_3$, and the solution was exposed to air under irradiation of light for 3 h. After removal of green precipitates by filtration, the filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (*n*-hexane/EtOAc = 5/1) to give **6ab** (15.8 mg, 39% yield) (see Scheme 6).

*4.4.7. Crystal data of (R_P,R)-**3a***

Crystal dimensions 0.25 × 0.40 × 0.50 mm^3; $C_{14}H_{19}BCrFO_3P$, M_r = 348.08; orthorhombic space group $P2_12_12_1$, a = 9.276(5), b = 10.764(6), c = 16.627(9) Å, V = 1660.3(15) Å^3, Z = 4, D_{calc} = 1.392 g cm^{-3}, T = 120 K, 3762 unique and 3524 observed [$I > 2\sigma(I)$] reflections, 196 parameters, final [$I > 2\sigma(I)$] R_1 = 0.0249, wR_2 = 0.0775. S = 0.606. Flack parameter = –0.011(15), CCDC-685999.

*4.4.8. Crystal data of (R,R)-**4aa***

Crystal dimensions 0.20 × 0.20 × 0.10 mm^3; $C_{19}H_{34}B_2CrO_3P_2$, M_r = 446.02; orthorhombic space group $P2_12_12_1$, a = 8.1336(5), b = 10.9987(7), c = 26.7003(16) Å, V = 2388.6(3) Å^3, Z = 4, D_{calc} = 1.240 g cm^{-3}, T = 120 K, 4673 unique and 4391 observed [$I > 2\sigma(I)$] reflections, 276 parameters, final [$I > 2\sigma(I)$] R_1 = 0.0267, wR_2 = 0.0632. S = 1.029. Flack parameter = –0.004(14), CCDC-686000.

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Appendix A. Supplementary material

CCDC 685999 and 686000 contain the supplementary crystallographic data from this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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