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Headline Articles

Characterization of Enantiomeric Pairs of Optically Active 10-P-5 Phosphoranes with Asymmetry Only at Phosphorus[1)]

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Diastereomeric phosphoranes (*o*-$OC(CF_3)_2C_6H_4)_2P^*CH_2CO_2$-(−)-menthyl (**3-$R_P$** and **3-$S_P$**) of which absolute stereochemistry was determined were treated with $LiAlH_4$ to give (*o*-$OC(CF_3)_2C_6H_4)_2P^*CH_2CH_2OH$ (**4-R_P** and **4-S_P**) as the first optically active pair of enantiomeric phosphoranes of rigid stereochemistry with asymmetry only upon the pentacoordinate phosphorus atom. The high enantiomeric purities of the alcohols were confirmed by converting them to their (+)-MTPA esters. Furthermore, when diastereomeric phosphoranes (*o*-$OC(CF_3)_2C_6H_4)_2P^*CH_2NHC^*HCH_3Ph$ (**10-R_P** and **10-S_P**) of which absolute stereochemistry was also determined were treated with MeLi the first optically active pair of enantiomeric P–H phosphoranes (*o*-$OC(CF_3)_2C_6H_4)_2P^*H$ (**2-R_P** and **2-S_P**) with asymmetry only upon the pentacoordinate phosphorus atom could be obtained. The high enantiomeric purities of the P–H phosphoranes were confirmed by converting each of them to their corresponding (−)-menthyl esters **3-R_P** and **3-S_P**.

Phosphorus compounds are of significance due to their important role in numerous biological processes involving phosphoryl transfer, and recently, artificial phosphorus compounds have seen application as herbicides, insecticides, and medicines.[2)] Thus, the mechanism of reactions involving phosphorus compounds, particularly those having a P=O segment, has been a topic of interest for quite some time. Through the pioneering work of Westheimer and others it is now widely accepted that the reaction process involves a pentavalent phosphorus intermediate (or transition state) formed by nucleophilic attack upon the tetracoordinate phosphorus atom, and that the stability and stereochemistry (both steric and electronic effects combined) of the transient species (or transition state) greatly influence the outcome of the process.[3)] Therefore to deduce basic understanding of the process much attention has been focused on the stereochemistry by using various model compounds and through these studies it has been found that the permutation of the intermediate is an important factor.[4)] The permutation is usually interpreted in the terms of Berry pseudorotation.[5)] Since the process only requires simultaneous bending of bonds, the energy barrier is generally very small. Recently, due to the advent of new theoretically interesting results based upon highly sophisticated calculations[6)] and the emergence of advanced instrumentation, this field of research has gained renewed interest.[7)] In investigations of the stereochemistry, isomers arising from different configurations upon asymmetric pentavalent phosphorus atoms have been utilized by introducing chirality into at least one of the substituents thus producing diastereomers which can be monitored by spectroscopic methods such as NMR. Among these compounds there are some phosphoranes in the literature that have been successfully isolated as optically active diastereomers. These compounds bear ligands derived from optically active alcohols or aminoalcohols which are available or can be prepared easily from the chiral pool.[8)] But as for optically active pentacoordinate compounds bearing chirality only at the central phospho-

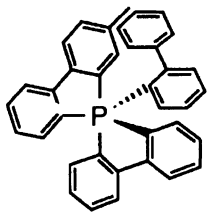

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Chart 1.

rus atom, the only one example we are aware of is the pentaarylphosphorus compound **1** (Chart 1), which was prepared by Hellwinkel.[9] This fascinating compound exhibits residual optical activity, meaning that what is observed at ambient temperatures is the averaged spectroscopic properties among interconverting positional isomers of low conversion energy barriers, and that high energy barriers between the enantiomeric groups of isomers exist. So for optically active compounds with rigid and definable stereochemistry there was no precedence. However by utilizing Martin's phosphorane **2** which meets the substituent combination requirements which permit permutation but also slows it down by allowing in principle the existence of only one configuration (along with its enantiomer) about the phosphorus atom, we have succeeded in preparing and characterizing the first configurationally stable optically active phosphoranes **4**-R_P and **4**-S_P, and **2**-R_P and **2**-S_P which bear asymmetry only upon phosphorus. Compounds **4**-R_P and **4**-S_P were obtained from a diastereomeric pair of (o-$OC(CF_3)_2C_6H_4)_2P^*CH_2CO_2$-(−)menthyl, through a transformation not directly involving chemical exchange upon the phosphorus atom, thus the stereochemistry being subject only to permutation. On the other hand, compounds **2**-R_P and **2**-S_P were obtained from (o-$OC(CF_3)_2C_6H_4)_2P^*CH_2NHC^*HCH_3Ph$ (**10**-R_P and **10**-S_P), through a transformation directly involving the phosphorus atom, thus the stereochemistry being dependent not only on permutation but also on reaction stereoselectivity. Herein we describe the details of the transformations and the characterization of the optically active compounds.

Results and Discussion

(R_P)- and (S_P)-(o-$OC(CF_3)_2C_6H_4)_2P^*CH_2CH_2OH$. The preparation of diastereomers **3**-R_P and **3**-S_P was done as shown in Scheme 1. The chiral auxiliary (−)-menthol was converted to its chloroacetate by reacting the alcohol with chloroacetyl chloride. Racemic phosphorane **2**[10] was prepared by treating phosphorus trichloride at −78 °C with lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propanolate prepared according to a published procedure[11] and then quenching the solution with 6 M (1 M=1 mol dm^{-3}) HCl before exposing the solution to the air. The use of acid was required to minimize the amount of oxidized products. The attachment of the chiral auxiliary to phosphorane **2** was achieved by treating the phosphorane with NaH in THF, followed by the addition of (−)-menthyl chloroacetate to furnish a 1:1 diastereomeric mixture of phosphoranes **3** in 87% combined yield. While a small amount of the pair could be separated by repeated use of preparative TLC, fortunately for us they could also be resolved in larger quantities by fractional crystallization using MeOH–H_2O as solvent. The diastereomers crystallized out as prisms and needles, which could easily be separated by hand. The separated crystals were repeatedly recrystallized to assure diastereomeric purity ultimately giving the diastereomer later determined to be **3**-R_P in 25% yield and the diastereomer later determined to be **3**-S_P in 22% yield. The diastereomers showed distinctive signals in both ^{1}H NMR (δ=4.53 for **3**-R_P and 4.61 for **3**-S_P in $CDCl_3$, respectively, for the methine proton geminal to the oxygen atom in the (−)-menthyl moiety; Fig. 10) and ^{31}P NMR (δ=−25.6 for **3**-R_P and −25.3 for **3**-S_P in acetone-d_6, respec-

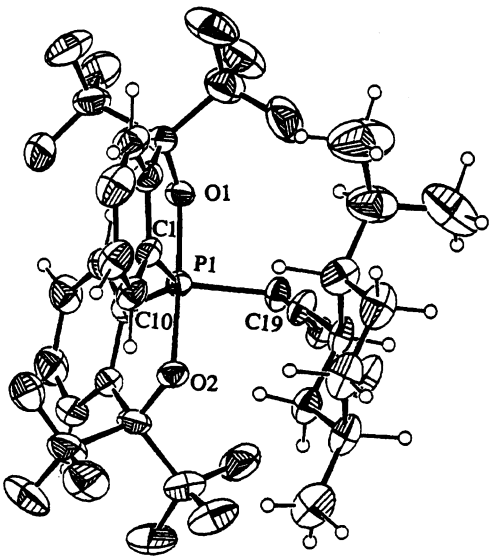
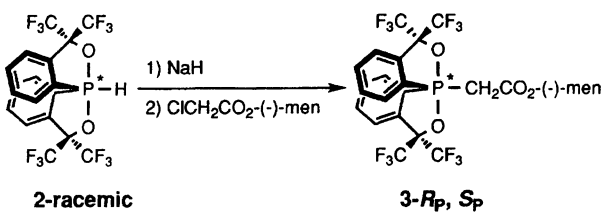


Fig. 1. ORTEP drawing of **3**-R_P showing thermal ellipsoids at the 30% probability level.

Table 1. Selected Bond Lengths and Angles for **3**-R_P, **6**-R_P, and **10**-R_P

	3-R_P	**6**-R_P	**10**-R_P
Bond lengths (Å)			
P1–O1	1.747(4)	1.768(3)	1.754(3)
P1–O2	1.751(4)	1.753(3)	1.771(3)
P1–C1	1.816(6)	1.818(5)	1.825(4)
P1–C10	1.813(5)	1.808(5)	1.821(4)
P1–C19	1.849(6)	1.817(6)	1.834(3)
Bond angles (deg)			
O1–P1–O2	177.4(2)	178.1(2)	175.8(1)
O1–P1–C1	87.9(2)	87.5(2)	87.1(1)
O2–P1–C10	87.2(2)	87.8(2)	87.3(1)
C1–P1–C10	129.1(3)	123.8(2)	127.7(1)
C1–P1–C19	118.2(3)	118.8(2)	117.4(2)
C10–P1–C19	112.6(2)	117.6(2)	114.9(2)



Scheme 1.

Table 2. Crystal Data for **3-R_P**, **6-R_P**, and **10-R_P**

	3-R_P	**6-R_P**	**10-R_P**
Formula	$C_{30}H_{29}F_{12}O_4P$	$C_{30}H_{20}F_{15}O_5P$	$C_{27}H_{20}F_{12}NO_2P$
Mol wt	712.5	776.4	649.40
Cryst syst.	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
Cryst dimens./mm	0.30×0.30×0.20	0.70×0.20×0.20	0.70×0.60×0.60
a/Å	16.922(4)	13.019(5)	14.402(2)
b/Å	19.322(7)	25.90(1)	8.949(2)
c/Å	10.036(3)	8.980(3)	10.961(2)
α/deg	90	90	90
β/deg	90	90	102.88
γ/deg	90	90	90
V/Å^3	3281(2)	3028(2)	1377.2(4)
Z	4	4	2
D_{calcd}/g cm^{-3}	1.43	1.70	1.57
Abs. coeff (ν)/cm^{-1}	1.38	1.70	1.58
F(0 0 0)	1456	1560	656
Radiation; λ/Å	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
Temp/°C	23±1	23±1	23±1
$2\theta_{max}$/deg	55.0	50.0	55.0
Scan rate/deg min^{-1}	3.0	3.0	3.0
Linear decay/%	—	—	—
Data collected	$+h$, $+k$, $+l$	$+h$, $+k$, $+l$	$\pm h$, $+k$, $+l$
Total no. of data collcd, unique, obsd	4375, 4217, 3059 (I>1.5σ(I))	3115, 3049, 2670 (I>1.0σ(I))	3584, 3373, 3005 (I>3σ(I))
R_{int}	0.00	0.00	0.03
No of params refined	494	526	393
R, R_w, S	0.075, 0.057, 1.27	0.058, 0.044, 1.18	0.047, 0.059, 1.54
Max shift in final cycle	0.17	1.53	0.15
Final diff map, max/e Å^{-3}	0.53	0.35	0.52

tively; Fig. 11) thus allowing facile determination of the diastereomeric ratio.

In order to determine the absolute stereochemistry of the diastereomers, X-ray crystal structure analysis was carried out on the diastereomer of the prism crystal. The ORTEP structure of **3-R_P** is shown in Fig. 1 along with selected structural parameters in Table 1 and crystal parameters in Table 2. As the drawing shows the compound assumes a trigonal bipyramidal structure with the two oxygen atoms occupying the two apical positions and the three carbon atoms occupy the three equatorial positions. The angles around the phosphorus atom are nearly ideal with the apical O(1)–P(1)–O(2) angle being 177.4°, and the sum of the angles formed by the equatorial atoms and phosphorus being 359.9° implying coplanarity of the phosphorus atom and the three equatorial carbon atoms. The absolute stereochemistry of the phosphorus atom determined from its relative stereochemistry to the known (−)-menthyl moiety turned out to be R_P.[12]

The optical rotation values measured with 589 nm (Na-D) radiation were near zero, therefore the measurements were carried out with 436 nm (Hg). The values were $[\alpha]_{436}^{21}$ +11.1° (c 1.02, $CHCl_3$) for **3-R_P** and $[\alpha]_{436}^{21}$ −70.0° (c 1.02, $CHCl_3$) for **3-S_P**. Since benzene rings were attached directly to the asymmetric phosphorus atom in a C_2 symmetry style, it was speculated that opposite Cotton effects arising from the isoenergetic exciton dipole coupling of light polarization due to π–π^* transition of the two benzene rings would be observed between the two diastereomers in CD spectroscopy.[13] The UV measurements of the phosphoranes showed absorption maximums at 224 (log ε=4.26), 229 (4.26), 266 (3.16), and 273 nm (3.10) for **3-R_P** and 224 (4.32), 229 (4.32), 267 (3.23), and 274 nm (3.16) for **3-S_P** while the absorption of (−)-menthyl chloroacetate alone was observed as a shoulder at ca. 220 nm (strong solvent absorption is inevitable in this low wavelength region). The CD spectra of (−)-menthyl chloroacetate showed a single monotone positive peak at 221 nm ($\Delta\varepsilon$=+0.42), therefore implying a slight signal overlap in the positive region. The measured spectra of **3-R_P** and **3-S_P** have been calibrated so that the vertical coordinate gives the $\Delta\varepsilon$ values as shown in Fig. 2. The spectrum of **3-R_P** showed a negative Cotton effect (a negative primary Cotton effect and a positive secondary Cotton effect) with peaks at λ ($\Delta\varepsilon$)=214 (+8.2), 229 (−5.4), 235 (+3.5), 265 (+1.7), and 271 nm (+1.3), while that for **3-S_P** exhibited a positive Cotton effect (a positive primary Cotton effect and a negative secondary Cotton effect) with peaks at 214 (−6.5), 229 (+8.2), 235 (−3.5), 265 (−2.0), and 272 nm (−1.5). The expected small differences in intensity due to the (−)-menthyl moiety could be observed at 214 and 229 nm. These Cotton

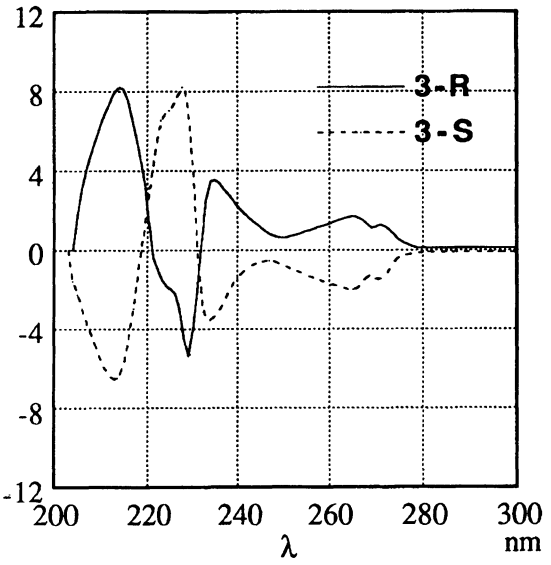


Fig. 2. CD spectra of **3-R_P** (solid line, 4.98×10^{-5} M) and **3-S_P** (broken line, 5.38×10^{-5}) in cyclohexane. The original data has been replotted in terms of $\Delta\varepsilon$. The random noise level in the <230 nm region was $\Delta\varepsilon$=ca. ±30 while in the >230 nm region it was $\Delta\varepsilon$=ca. ±10.

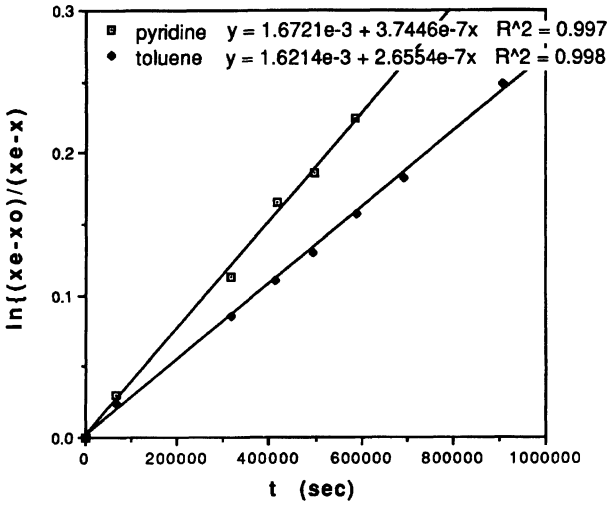


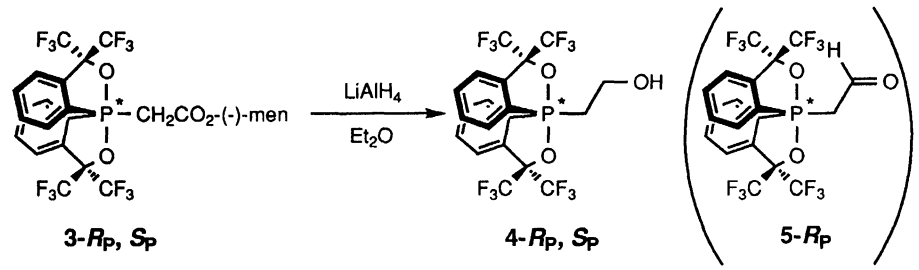
Fig. 3. Plot of $\ln\{(x_e-x_o)/(x_e-x)\}$ vs. time. (x_e= ratio at equilibrium, x_o=ratio observed at t=0, x= observed ratio at arbitrary intervals).

effects imply that **3-R_P** has an overall left-handed helical electron transition moment, while that of **3-S_P** is the opposite.

Before proceeding on to the removal of the chiral auxiliary and subsequent reactions, the rates of epimerization of the compounds were measured at 100 °C using toluene and pyridine as solvent by monitoring ^{31}P NMR. The observed change in diastereomer ratio is shown in Fig. 3. Martin et al. had already measured the permutation rate of a similar compound having a phenyl group in the equatorial position in the place of the chiral auxiliary in compound **3** and have come up with the value $\Delta G^{\neq}$=28.3 kcal mol^{-1} (424 K).[14] In our case the rates were found to be 1.3×10^{-7} s^{-1} in toluene, and 1.9×10^{-7} s^{-1} in pyridine, corresponding to activation free energies of $\Delta G^{\neq}$=33.8 kcal mol^{-1} (373 K) and 33.5 kcal mol^{-1} (373 K), respectively. These results show that the process is very slow and that there is little dependence of solvent polarity or donor ability upon the rate. This is in contrast with results obtained in kinetic studies of permutation of pentacoordinate antimony compounds, which showed strong solvent dependence with large rate acceleration when donating solvents were used.[15] Thus it was concluded that by avoiding high temperatures and prolonged reaction periods epimerization could be avoided.

The removal of the chiral menthyl moiety was achieved by treating the diastereomers with an excess amount of $LiAlH_4$ in refluxed Et_2O as depicted in Scheme 2, thereby generating the first pair of rigid optically active phosphoranes with asymmetry only at phosphorus. The yields of **4-R_P** and **4-S_P** were 81 and 84%, respectively. Since it was found that complete removal of (−)-menthol from the product mixture was difficult using chromatographic means the final purification of the alcohols **4-R_P** and **4-S_P** was carried out by sublimation under reduced pressure at temperatures at or below 50 °C. Since this process required a rather lengthy amount of time, partial epimerization could be detected when heating was carried out at temperatures over 50 °C. ^{1}H, ^{13}C, and ^{31}P NMR (δ=−22.7 in acetone-d_6) showed identical spectra for the two compounds and were fully compatible with the assigned structure. The hydroxyl proton could be observed at δ=1.86 as a broad singlet and the carbon bonded to this hydroxyl group was observed at δ=58.2. The IR spectra also showed the presence of a hydroxyl group with OH stretching at 3410 cm^{-1} and alcoholic CO stretching at 1197 cm^{-1}. The reaction of other nucleophilic reagents such as Grignard and alkyllithium reagents turned out to be sluggish probably due to steric hindrance and were not suitable for the conversion. In the reaction of **3-R_P**, the use of less amounts of $LiAlH_4$ led to partial formation of aldehyde **5-R_P** (aldehyde proton at δ=9.63; carbonyl stretching at 1719 cm^{-1}), the partially reduced product.

The optical rotation values of **4-R_P** and **4-S_P** were $[\alpha]_{436}^{21}$+108° (*c* 1.02, $CHCl_3$) and $[\alpha]_{436}^{21}$−107° (*c* 0.83, $CHCl_3$), respectively. The UV spectra showed λ_{max} ($\log\varepsilon$) at 223 (4.36), 228 (4.38), and 266 (3.21) nm. The CD spectra (Fig. 4) of **4-R_P** showed the expected negative Cotton effect with peaks at λ ($\Delta\varepsilon$)=210 (+10.2), 227 (−10.9), 264 (+1.8), and 270 (+1.3), while that of **4-S_P** showed the expected positive Cotton effect with peaks at the same wavelengths with identical absolute intensities and opposite signs. The small intensity differences could be ascribed primarily to uncertainty of the measurements, therefore implying the high enantiomeric purities of the compounds.



Scheme 2.

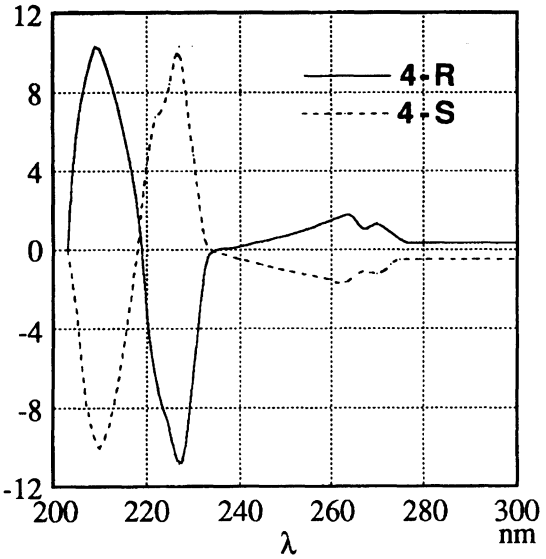
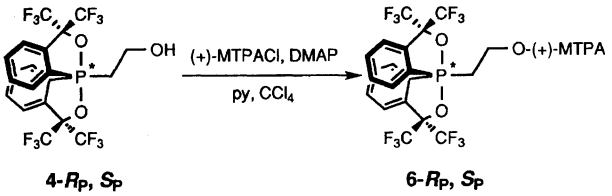


Fig. 4. CD spectra of **4-R_P** (solid line, 1.73×10^{-5} M) and **4-S_P** (broken line, 1.26×10^{-5}) in cyclohexane. The original data has been replotted in terms of $\Delta\varepsilon$. The random noise level in the <230 nm region was $\Delta\varepsilon$=ca. ±30 while in the >230 nm region it was $\Delta\varepsilon$=ca. ±10.



Scheme 3.

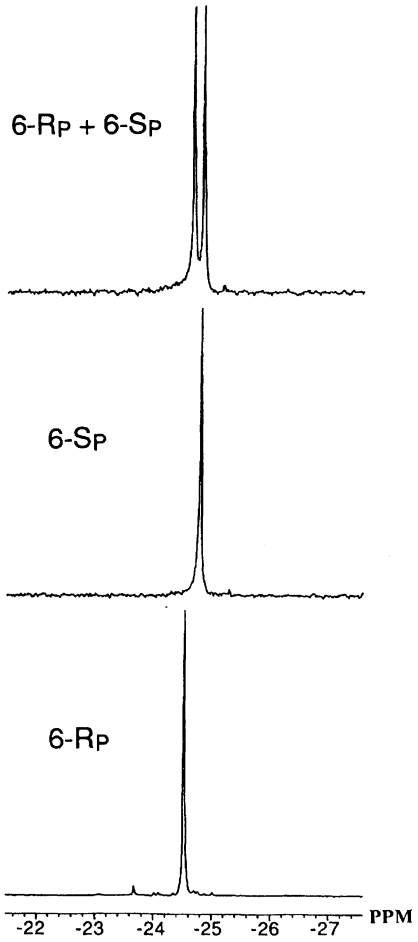


Fig. 5. ^{31}P NMR of a mixture of **6-R_P**+6-**S_P** (upper chart), **6-S_P** derived from **4-S_P** (middle chart), and **6-R_P** derived from **4-R_P** (lower chart).

In order to assure the high enantiomeric purity of the chiral alcohols, the alcohols **4** were converted to their (*R*)-(+)-Mosher ester as described in Scheme 3, using the acid chloride derived from (*R*)-(+)-2-methoxy-2-(trifluoromethyl)phenylacetic acid. The isolated yields were at best 54 and 31%, respectively, and were not optimized. To facilitate assignments and make comparisons a mixture of **3-R_P** and **3-S_P** was exposed to the same sequence of reactions, to give **4** in 92% yield and the following **6** in 57%. Resolution of the ^{31}P NMR signals could be achieved in acetone ($\delta=-24.5$ for **6-R_P** and $\delta=-24.7$ for **6-S_P**). ^{1}H NMR of the protons of the benzene ring ortho to phosphorus (δ=8.38 for **6-R_P** and δ=8.28 for **6-S_P**) and the methoxyl protons (δ=3.37 for **6-R_P** and δ=3.26 for **6-S_P**) could also be distinguished. Other common solvents were not appropriate.

A comparison of the ^{31}P NMR charts (Fig. 5) of the diastereomeric mixture (top), the Mosher ester **6-S_P** derived from **4-S_P** (middle), and the Mosher ester **6-R_P** derived from **4-R_P** (bottom) clearly shows that both optically active esters are of high diastereomeric purity. The spectra of the crude samples of neither **6-S_P** nor **6-R_P** showed the presence of the opposing diastereomer. This implies the fact that epimerization had not occurred either during the two consecutive transforma-

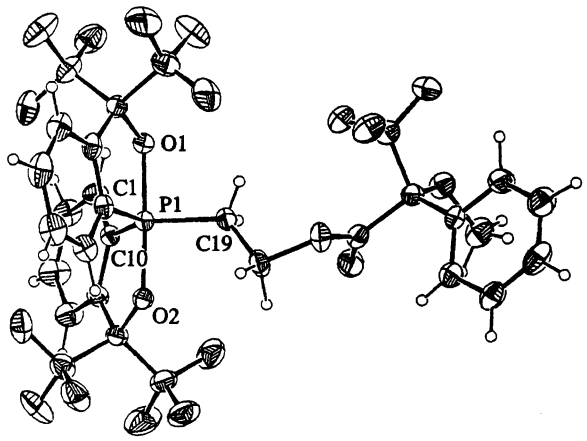


Fig. 6. ORTEP drawing of **6-R_P** showing the thermal ellipsoids at the 30% probability level.

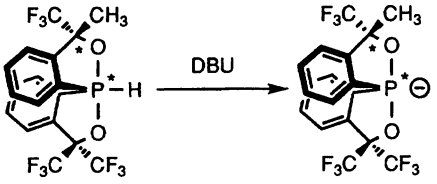
tions of esters **3-R_P** and **3-S_P** to **6-R_P** and **6-S_P**, respectively, or during purification procedures. Thus we could confirm the high enantiomeric purity of the alcohols **4-R_P** and **4-S_P**.

Recrystallization of **6-R_P** from hexane–CH_2Cl_2 afforded single crystals, and were thus structurally analyzed. Figure 6 shows the ORTEP drawing and selected parameters are listed in Tables 1 and 2 along side those of **3-R_P**. Compound **6-R_P** was found to have a nearly ideal trigonal bipyramidal structure just as **3-R_P**. The *R* configuration of the phosphorus atom was determined from its relative stereochemistry to that of the Mosher moiety of known absolute stereochemistry. Through analogy the absolute stereochemistry of the alcohols **4-R_P** and **4-S_P** were again affirmed. The structural features of the two compounds, **3-R_P** and **6-R_P**, are quite similar in principle, but **3-R_P** was found to have a rather longer P(1)–C(19) bond length (1.849 to 1.817 Å; Δ=0.032 Å) and a smaller sum of apical bond lengths (3.498 Å to 3.521 Å; Δ=−0.023 Å). The former is probably due to the steric bulk of the equatorial ligand moiety in **3-R_P** and the presence of the electron withdrawing carbonyl group, whereas the latter is due to the counter balance of the electron density upon the phosphorus atom, i.e., **3-R_P** having shorter bonds due to the presence of the carbonyl group, a kind of push-pull effect.

Thus, we were able to establish the absolute stereochemistry and high enantiomeric purity of the first single structured chiral pentacoordinate phosphorus compound with asymmetry located solely on the phosphorus atom through successive conversions, i.e., reduction and esterification, under rather mild conditions without the accompaniment of epimerization (racemization).

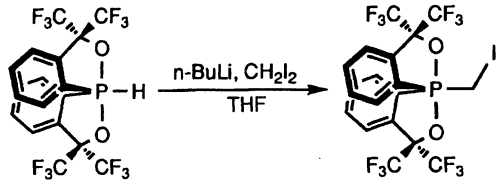
(R_P)- and (S_P)-(o-OC(CF_3)$_2$$C_6H_4$)$_2$P*H. To further gain a general picture of the nature of optically active phosphoranes we reasoned that it would be desirable to have a larger amount of available optically active compounds with differing functionalities. In order to do so a parent compound that would allow transformation without losing optical activity was required. To this end we turned our attention to P–H phosphorane **2** because the hydrogen could potentially be replaced with other substituents, and the compound itself is unique due to the possibility of giving a ring opened tautomer. Before seeking the optically active compound we examined the stereochemical features of an analogous diastereomeric compound **7** which has a methyl group in the place of one of the four trifluoromethyl groups.[16] The permutation of **7** was found to be much faster than ester **3** with the activation parameters being $\Delta H^{\neq}$=24.3 kcal mol^{-1}, $\Delta S^{\neq}$=−4.5 eu, and $\Delta G^{\neq}$=25.7 kcal mol^{-1} (298 K) in toluene, and the values were essentially unchanged in pyridine or acetic acid although the compound has the potential to undergo proton abstraction or tautomerize to an open-ring P(III) species. This implied that it would be highly desirable to carry out the transformations at as low temperature as possible. It was also found that the alkylation reaction of the conjugate base of **7**, namely **8** proceeded with full retention of configuration provided that the reaction temperature was kept at or below ambient temperature (Scheme 4).

The attachment of the chiral auxiliary to phosphorane **2** was achieved in two steps (Scheme 5). Phosphorane **2** was first treated with CH_2I_2 after deprotonation with *n*-BuLi to give **9** [^{31}P NMR ($CDCl_3$) δ=−24.6] in 82% yield. This compound was found to gradually decompose on standing. Compound **9** was then treated with optically active (+)-1-phenylethylamine in acetonitrile to give a diastereomeric mixture of **10** in 56%

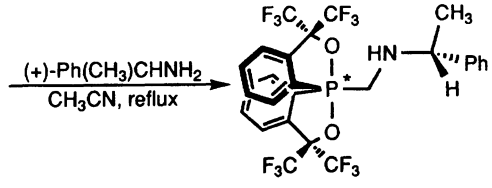


7 **8**

Scheme 4.



2-mixture **9**



10-R_P, S_P

Scheme 5.

combined yield. Fortunately, recrystallization from hexane gave each diastereomer as differently shaped crystals. The diastereomer of the flat plate like crystal [^{31}P NMR ($CDCl_3$) $\delta=-25.1$] was obtained in 11% overall yield, while the diastereomer of the prism shaped crystal [^{31}P NMR ($CDCl_3$) $\delta=-26.9$] was obtained in 20% overall yield. ^{1}H NMR of almost all of the protons of the monodentate amine moiety were characteristically different between the two diastereomers. The UV spectra was very similar to those of **3** and **4** with an additional absorption maximum at 203 nm ($\log\varepsilon=4.37$) for the compound later determined to be **10-R_P** and 208 nm ($\log\varepsilon=4.39$) for the compound later determined to be **10-S_P** presumably arising from the absorbance of the phenyl group of the amine moiety. The optical rotation values were $[\alpha]_{436}^{20}$ +73° (*c* 1.22, $CHCl_3$) for **10-R_P** and $[\alpha]_{436}^{20}$ +104° (*c* 0.66, $CHCl_3$) for **10-S_P**. The fact that the values both turned out to be large with the same plus sign implied that the optically active amine moiety would have a large bearing on the CD Spectra. The CD charts calibrated to give the $\Delta\varepsilon$ values are shown in Fig. 7. The spectrum for **10-R_P** could be considered to have a negative Cotton effect with an overlap from the amine moiety in the positive region. The peaks were at λ ($\Delta\varepsilon$)=211 (+3.6), 228 (−9.9), 242 (−1.0), 245 (−0.9), 260 (+1.9), 265 (+2.46), and 272 (+2.4) nm. However it was rather difficult to tell for the **10-S_P** compound with peaks at λ ($\Delta\varepsilon$)=221(+6.8), 225 (+6.2), 232 (−0.4), 245 (+2.8), 260 (−0.5), 226 (−0.5), 271 (+1.3), and 278 (+3.1). Therefore the absolute stereochemistry upon phosphorus could not be determined with certainty. Thus we made recourse to X-ray crystallographic analysis.

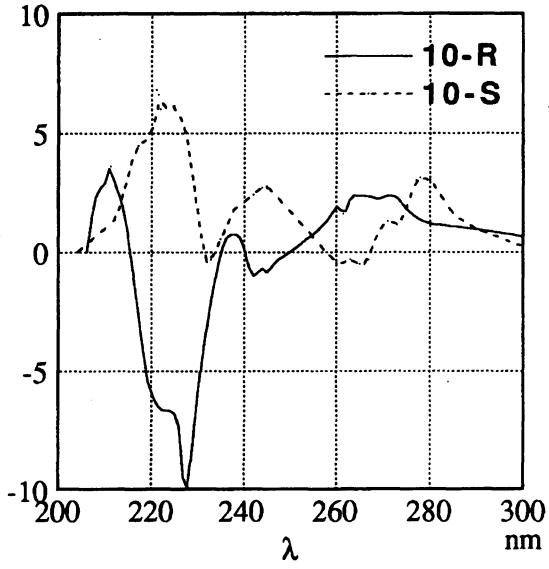


Fig. 7. CD Spectra of **10-R_P** (solid line, 3.85×10^{-5} M) and **10-S_P** (broken line, 5.41×10^{-5}) in cyclohexane. The original data has been replotted in terms of $\Delta\varepsilon$. The random noise level in the <230 nm region was $\Delta\varepsilon$=ca. ±1 while in the >230 nm region it was $\Delta\varepsilon$=ca. ±0.3.

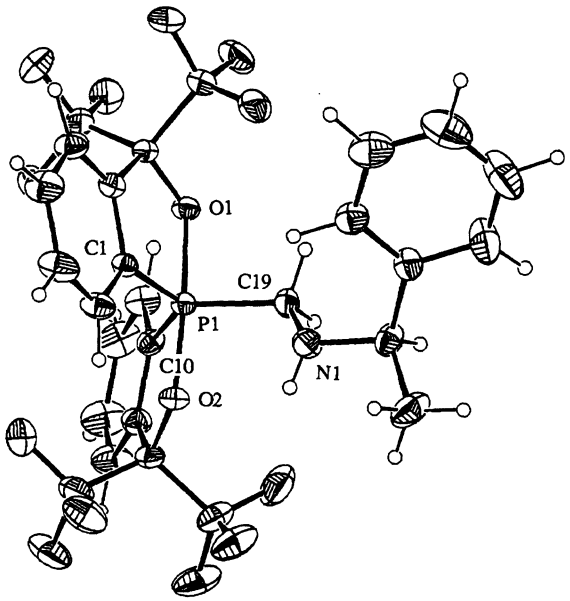
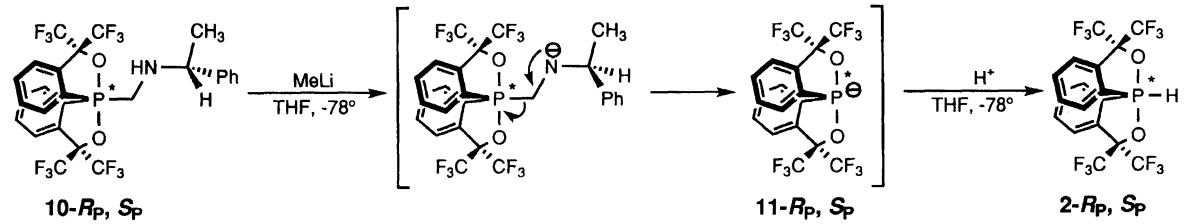


Fig. 8. ORTEP drawing of **10-R_P** showing the thermal ellipsoids at the 30% probability level.

X-Ray crystallographic analysis was conducted with the diastereomer of the plate-like crystals. The ORTEP structure is shown in Fig. 8 with selected structural parameters in Table 1. The above compound was also found to have a trigonal bipyramidal structure and the absolute stereochemistry of the phosphorus atom determined from its relative stereochemistry to the known (+)-1-phenylethylamine moiety turned out to be R_P, i. e., **10-R_P**. The bond angle between the two apical bonds was somewhat more acute (175.8°) than the corresponding angles in **3-R_P** (177.4°) and **6-R_P** (178.1°). This implies that compound **10-R_P** has slightly more of a square pyramidal nature compared with the other two compounds, thus leading to slight overall elongation of the bonds about phosphorus in comparison with **6-R_P**.

We anticipated that the generation of phosphoranide **11** would be effected by deprotonation of the proton upon the nitrogen atom followed by spontaneous imine elimination. A similar type of reaction has been applied in the generation of a simple germanium anion.[17] However, there also existed the possibility that a phosphoramide would be produced via a Brook-type rearrangement.[18] When each diastereomer **10-R_P** and **10-S_P** was treated separately with MeLi (3 equiv) at −78 °C as illustrated in Scheme 6, the corresponding phosphoranides **11-R_P** and **11-S_P** [^{31}P NMR (THF) $\delta=+43$ for the Li^+ salt], respectively, were formed quantitatively. Treatment of these compounds with aq NH_4Cl without raising the temperature furnished the desired P–H phosphoranes **2-R_P** and **2-S_P**. The yields of **2-R_P** and **2-S_P** were 67 and 87%, respectively, after chromatographic purification. Less amounts of base or use of *n*-BuLi was less effective in generating the phos-



Scheme 6.

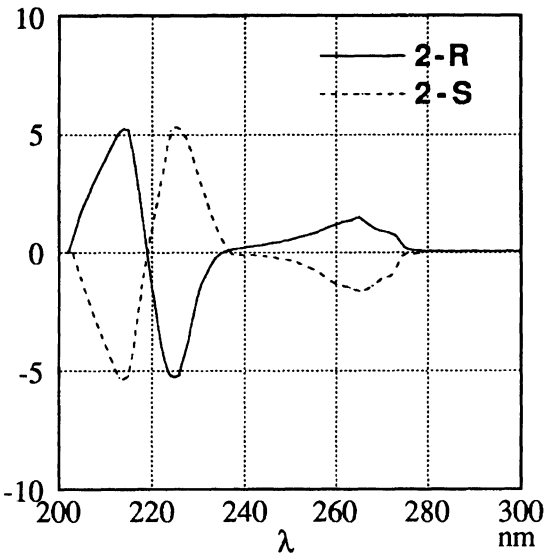
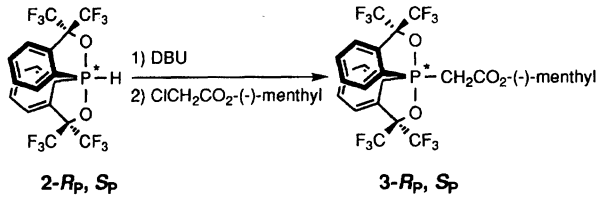


Fig. 9. CD Spectra of **2-R_P** (solid line, 1.09×10^{-5} M) and **2-S_P** (broken line, 1.49×10^{-5}) in cyclohexane. The original data has been replotted in terms of $\Delta\varepsilon$. The random noise level in the $\leq$230 nm region was $\Delta\varepsilon$=ca.$\pm$1 while in the >230 nm region it was $\Delta\varepsilon$=ca.$\pm$0.3.



Scheme 7.

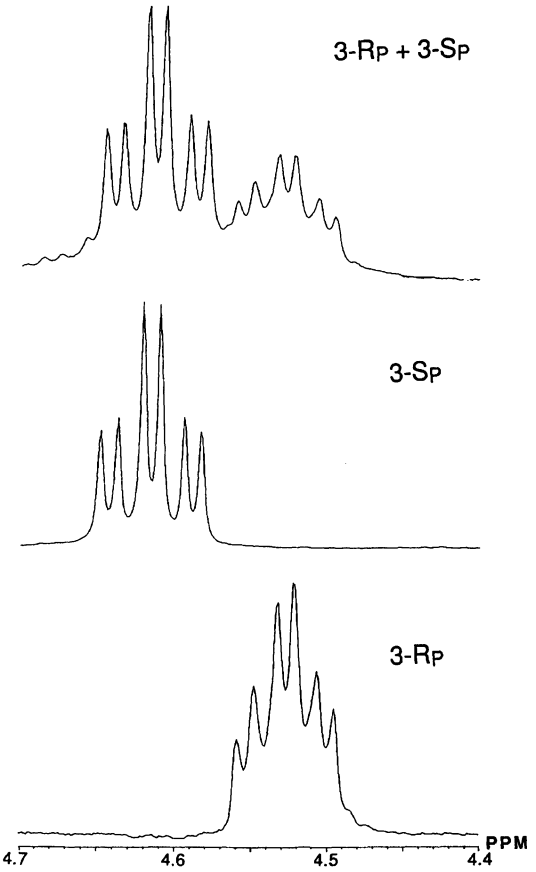


Fig. 10. ^{1}H NMR ($CDCl_3$) of the methine proton of the (−)-menthyl moiety. From top to bottom, a 3 : 7 mixture of **3-R_P**+**3-S_P**, **3-R_P** derived from **2-S_P**, and **3-R_P** derived from **2-R_P**.

phoranides. The enantiomers both exhibited identical ^{1}H, ^{13}C, and ^{31}P NMR spectra with racemic **2** used as the starting material. The optical rotation values were $[\alpha]_{436}^{20}$ −16° (*c* 1.07, $CHCl_3$) for **2-R_P** and $[\alpha]_{436}^{20}$ +17° (*c* 1.09, $CHCl_3$) for **2-S_P**. The CD spectrum showed peaks for **2-R_P** at λ ($\Delta\varepsilon$)=214 (+5.3), 225 (−5.3), 267 (+1.5), 269 and (+1.0), corresponding to a negative Cotton effect. The enantiomer **2-S_P** showed a mirror image spectrum with a positive Cotton effect. Thus the handedness of the Cotton effect could be considered the same as the amine reactant (Fig. 9).

As described in Scheme 7 the optical purities and the stereochemistries of the enantiomers were confirmed by converting the P–H phosphoranes **2-R_P** and **2-S_P** to their menthyl esters, **3-R_P** and **3-S_P**, the stereochemistries of which we had already established as mentioned above. The use of DBU as base turned out to give most satisfactory results, giving **3-R_P** and **3-S_P** in 80 and 95% yields, respectively, without the accompaniment of racemization. The use of metal-oriented bases such as *n*-BuLi and NaH resulted in partial racemization. However, it could not be determined whether the result was due to permutation of the intermediate phosphoranide or to stereochemical leakage in the sequential alkylation process. Figure 10 shows the ^{1}H NMR spectra of the methine proton geminal to the oxygen atom in the (−)-menthyl moiety. A comparison of the charts of a diastereomeric mixture (top), the menthyl

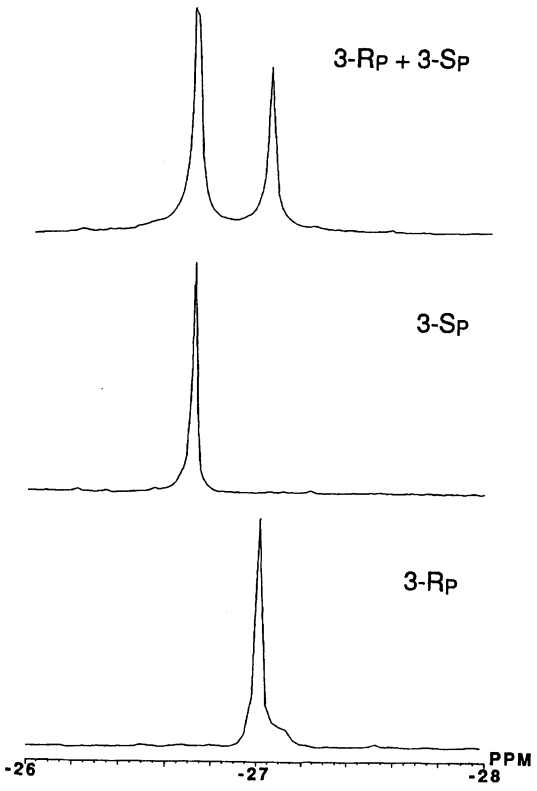


Fig. 11. ^{31}P NMR ($CDCl_3$) of a mixture of 3 : 7 mixture of **3-R_P**+**3-S_P** (upper chart), **3-S_P** derived from **2-S_P** (middle chart), and **3-R_P** derived from (lower chart).

ester derived from **2-S_P** (middle), and the menthyl ester derived from **2-R_P** (bottom) clearly shows that the former ester is **3-S_P** and the latter ester is **3-R_P**, and not a trace of the other diastereomer could be observed in the chart of either diastereomer. The same can be concluded from the comparison of the ^{31}P NMR spectra shown in Fig. 11. These facts imply that **2-R_P**, **2-S_P**, **3-R_P**, and **3-S_P** are all stereochemically pure. Thus no racemization had occurred during the two conversion processes or during their purification procedures and the stereochemistry upon the phosphorus atom was completely retained. In other words, the stereochemical identity of the first enantiomeric pair of optically active P–H phosphoranes with only a single stereocenter could be established as designated in the text having >99% enantiomerical purity. We could also conclude that there is a tendency for these compounds with an *R* configuration to have a negative Cotton effect while those of *S* configuration have a positive Cotton effect.

In summary, we have successfully obtained and characterized the first enantiomeric pair of stereochemically definable 10-P-5 phosphoranes **4-R_P** and **4-S_P**, and P–H phosphoranes **2-R_P** and **2-S_P**. It was also found that the P–H phosphoranes could be converted to alkylated derivatives with complete retention of configuration via the optically active phosphoranide intermediates **11-R_P** and **11-S_P** to give optically pure derivatives. Phosphoranes with other ligand combinations are currently under investigation.

Experimental

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz), and ^{31}P (162 MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^{1}H NMR (90 MHz) and ^{19}F NMR (85 MHz) spectra were also routinely recorded on a Hitachi R-90H spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from internal Me_4Si, or from residual chloroform (δ=7.26) or acetone (δ=2.0). ^{13}C NMR chemical shifts (δ) are given in ppm downfield from internal Me_4Si, or from internal chloroform-*d* (δ=77.0), benzene-d_6 (δ=128.0) or acetone-d_6 (δ=30.3). ^{19}F NMR chemical shifts (δ) are given in ppm downfield from internal $CFCl_3$. ^{31}P NMR chemical shifts (δ) are given in ppm downfield from external 85% H_3PO_4. Elemental analyses were performed on a Perkin–Elmer 2400CHN elemental analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. UV spectra were measured on a Shimadzu UV-160A spectrometer. Optical rotations were measured on a Union Giken PM-71 polarimeter. CD spectra were measured on a JASCO J-40CS polarimeter.

All reactions were carried out under N_2. THF and Et_2O were freshly distilled from Na-benzophenone, and benzene was freshly distilled from CaH_2 prior to use. All other solvents and liquid reagents were distilled from CaH_2. (−)-Menthol (Wako Chemicals), (*R*)-(+)-2-methoxy-2-(trifluoromethyl)phenylacetic acid (Aldrich), and (+)-1-phenylethylamine (Tokyo Kasei) were used as received. Preparative thin layer chromatography was carried out on plates of Merck silica gel 60 GF254.

(−)-Menthyl Chloroacetate. Chloroacetyl chloride (12.0 mL, 151 mmol) was added to (−)-menthol (23.6 g, 151 mmol) in benzene (60 mL) and the solution was refluxed for one day. Removal of the solvent under reduced pressure, followed by distillation (161 °C, 13 mmHg, 1 mmHg=133.322 Pa) yielded the ester (32.4 g, 86%) as a colorless liquid. $[\alpha]_{436}^{21}$ −159° (*c* 0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.70 (dt, *J*=4.4, 11.0 Hz, 1H), 3.97 (d, *J*=14.7 Hz, 1H), 3.96 (d, *J*=14.7 Hz, 1H), 1.96—1.32 (m, 6H), 1.04—0.94 (m, 2H), 0.91—0.76 (m, 1H), 0.85 (d, *J*=5.9 Hz, 3H), 0.83 (d, *J*=7.8 Hz, 3H), 0.70 (d, *J*=7.3 Hz, 3H).

3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (2). Lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propanolate prepared according to a reported procedure from *n*-BuLi (*c* 1.62 mol L^{-1}, 143 mL, 233 mmol), TMEDA (3.52 mL, 23.3 mmol), and 1,1-bis(trifluoromethyl)benzyl alcohol (23.6 mL, 116 mmol) in THF (50 mL) was transferred dropwise via cannula to a THF (30 mL) solution of PCl_3 (5.08 mL, 58.2 mmol) at −78 °C. After removal of the cooling bath, the solution was stirred at r.t. for 24 h. The solution was quenched with 6 M HCl (20 mL), extracted with Et_2O (3×200 mL), dried with $MgSO_4$, and concentrated in vacuo. Recrystallization (hexane) of the residue gave the product (17.6 g, 59%) as white powder. Mp 162 °C; ^{1}H NMR ($CDCl_3$) δ=8.41—8.27 (m, 2H), 8.38 (d, J_{PH}=729 Hz, 1H), 7.79—7.68 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ=137.4 (d, $^2J_{PC}$=22.0 Hz), 136.7 (d, $^3J_{PC}$=11.0 Hz), 134.4, 131.8 (d, $^2J_{PC}$=14.7 Hz), 126.4 (d, $^1J_{PC}$=158.1 Hz), 125.3 (d, $^3J_{PC}$=16.6 Hz), 122.6 (q,

$^1J_{FC}$=286.8 Hz), 122.4 (q, $^1J_{FC}$=286.8 Hz), 82.0 (sept, $^2J_{FC}$=31.3 Hz); ^{19}F NMR ($CDCl_3$) δ=−75.0 (q, J=9.8 Hz, 6F), −76.2 (q, J=9.8 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ=−45.8.

[(1′*R*, 2′*S*, 5′*R*)-1*R*]- and [(1′*R*, 2′*S*, 5′*R*)-1*S*]-1-[(2-Isopropyl-5-methylcyclohexyloxycarbonyl)methyl]-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*, 2,1λ^5-benzoxaphosphole] (3-*R*$_P$ and 3-*S*$_P$). Phosphorane **2** (4.00 g, 7.75 mmol) was added to a suspension of NaH (0.205 g, 8.54 mmol) in THF (50 mL) at 0 °C. After removing the cooling bath and stirring for 30 m, (−)-methyl chloroacetate (1.93 g, 7.75 mmol) was added to the suspension. After stirring for one hour at r.t., the mixture was quenched with 1 M HCl (30 mL). Extraction with Et_2O (3×40 mL), followed by washing with brine, drying with $MgSO_4$, and removal of solvent under reduced pressure gave a diastereomeric mixture of **3** as a white solid (4.81 g, 87%). Recrystallization from MeOH–H_2O (repeated 5 times) furnished **3-*R*$_P$** (1.38 g, 25%) as prisms and **3-*S*$_P$** (1.19 g, 22%) as needles in diastereomerically pure state.

3-*R*$_P$: Mp 127—128 °C; $[\alpha]_{436}^{21}$ +11.1° (c 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=8.41—8.37 (m, 2H), 7.75—7.70 (m, 6H), 4.53 (dt, J=4.4, 10.8 Hz, 1H), 3.53 (dd, $^2J_{PH}$=18.1 Hz, J=14.7 Hz, 1H), 3.36 (dd, $^2J_{PH}$=17.1 Hz, J=14.7 Hz, 1H), 2.02 (d, J=12.2 Hz, 1H), 1.65—1.48 (m, 5H), 0.94—0.80 (m, 3H), 0.90 (d, J=6.8 Hz, 3H), 0.66 (d, J=6.8 Hz, 3H), 0.60 (d, J=6.8 Hz, 3H); ^{13}C{^{1}H} NMR (C_6D_6) δ=164.8 (d, $^2J_{PC}$=7.4 Hz), 137.8 (d, $^3J_{PC}$=9.2 Hz), 136.4 (d, $^2J_{PC}$=20.2 Hz), 134.3 (d, $^4J_{PC}$=3.6 Hz), 133.5 (d, $^2J_{PC}$=14.7 Hz), 129.6 (d, $^1J_{PC}$=165.4 Hz), 125.0 (d, $^3J_{PC}$=16.6 Hz), 123.2 (q, $^1J_{FC}$=288.6 Hz), 123.1 (q, $^1J_{FC}$=288.6 Hz), 82.2 (sept, $^2J_{FC}$=31.3 Hz), 75.5, 47.1, 46.7 (d, $^1J_{PC}$=123.1 Hz), 40.8, 34.5, 31.4, 26.0, 23.4, 22.1, 20.8, 16.2; ^{19}F NMR ($CDCl_3$) δ=−74.7 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−25.6; IR (KBr, cm^{-1}) 1735 (ν_{CO}); UV (c-hexane) [λ_{max}, nm (log ε)] 224 (4.26), 229 (4.26), 266 (3.16), 273 (3.10). Anal. Calcd for $C_{30}H_{29}F_{12}O_4P$: C, 50.57; H, 4.10%. Found: C, 50.40; H, 4.03%.

3-*S*$_P$: Mp 125—127 °C; $[\alpha]_{436}^{21}$=−70.0° (c 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=8.40—8.35 (m, 2H), 7.75—7.67 (m, 6H), 4.61 (dt, J=4.4, 10.8 Hz, 1H), 3.55 (dd, $^2J_{PH}$=18.1 Hz, J=14.7 Hz, 1H), 3.36 (dd, $^2J_{PH}$=16.6 Hz, J=14.7 Hz, 1H), 1.96—1.93 (m, 1H), 1.78—1.75 (m, 1H), 1.62—1.54 (m, 2H), 1.42—1.30 (m, 1H), 1.16—1.10 (m, 1H), 1.01—0.95 (m, 1H), 0.90 (d, J=7.3 Hz, 3H), 0.82 (d, J=6.8 Hz, 3H), 0.76—0.69 (m, 1H), 0.71 (d, J=6.8 Hz, 3H), 0.57—0.48 (m, 1H); ^{13}C{^{1}H} NMR (C_6D_6) δ=165.1, 137.8 (d, $^3J_{PC}$=9.2 Hz), 136.3 (d, $^2J_{PC}$=22.2 Hz), 134.3, 131.5 (d, $^2J_{PC}$=14.7 Hz), 130.0 (d, $^1J_{PC}$=165.5 Hz), 125.0 (d, $^3J_{PC}$=14.7 Hz), 123.2 (q, $^1J_{FC}$=288.6 Hz), 123.1 (q, $^1J_{FC}$=288.6 Hz), 87.0 (sept, $^2J_{FC}$=31.3 Hz), 75.5, 47.2, 46.9 (d, $^1J_{PC}$=125.0 Hz), 40.7, 34.3, 31.3, 26.0, 23.3, 22.0, 20.9, 16.2; ^{19}F NMR ($CDCl_3$) δ=−74.7 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−25.3; IR (KBr, cm^{-1}) 1735 (ν_{CO}); UV (c-hexane) [λ_{max}, nm (log ε)] 224 (4.32), 229 (4.32), 266 (3.23), 273 (3.16). Anal. Calcd for $C_{30}H_{29}F_{12}O_4P$: C, 50.57; H, 4.10%. Found: C, 50.43; H, 3.91%.

(*R*)-1-(2-Hydroxyethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (4-*R*$_P$). Compound **3-*R*$_P$** (500 mg, 0.702 mmol) in Et_2O (30 mL) was added to a suspension of $LiAlH_4$ (79.7 mg, 2.10 mmol) in Et_2O. After refluxing for 2 h, the mixture was quenched with 1 M HCl, extracted with Et_2O (3×30 mL) and washed with brine. Drying with $MgSO_4$ followed by removal of solvent under reduced pressure and preparative TLC separation (hexane–CH_2Cl_2, 1 : 2) gave **4-*R*$_P$** (320 mg, 81%) as a white solid. An analytical sample was prepared by sublimation (50 °C, ca. 0.1 mmHg) of the separated product.

4-*R*$_P$: Mp 103—105 °C; $[\alpha]_{436}^{21}$+108° (c 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=8.42—8.38 (m, 2H), 7.74—7.67 (m, 6H), 3.84 (ddt, $^3J_{PH}$=4.88 Hz, J=13.7, 6.8 Hz, 2H), 2.75 (ddt, $^2J_{PH}$=17.1 Hz, J=13.7, 6.8 Hz, 1H), 2.60 (ddt, $^2J_{PH}$=13.2 Hz, J=13.7, 6.8 Hz, 1H), 1.79 (bs, 1H); ^{13}C{^{1}H} NMR (acetone-d_6) δ=138.3 (d, $^3J_{PC}$=9.2 Hz), 137.1 (d, $^2J_{PC}$=20.2 Hz), 135.9, 133.3 (d, $^2J_{PC}$=12.9 Hz), 131.3 (d, $^1J_{PC}$=160 Hz), 126.4 (d, $^3J_{PC}$=14.7 Hz), 124.1 (q, $^1J_{FC}$=288.6 Hz), 123.9 (q, $^1J_{FC}$=288.6 Hz), 82.8 (sept, $^2J_{FC}$=31.3 Hz), 58.2, 44.0 (d, $^1J_{PC}$=114.0 Hz); ^{19}F NMR ($CDCl_3$) δ=−74.9 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−22.7, ($CDCl_3$) δ=−21.5; IR (KBr, cm^{-1}) 3410 (ν_{OH}), 1197 (ν_{CO}); UV (c-hexane) [λ_{max}, nm (log ε)] 223 (4.36), 228 (4.38), 266 (3.21). Anal. Calcd for $C_{20}H_{13}F_{12}O_3P$: C, 42.88; H, 2.34%. Found: C,43.16; H, 2.17%.

(*S*)-1-(2-Hydroxyethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (4-*S*$_P$). Following the procedure of **4-*R*$_P$**, **3-*S*$_P$** (300 mg, 0.421 mmol) and $LiAlH_4$ (47.9 mg, 1.26 mmol) yielded **4-*S*$_P$** (198 mg, 84%) as a white solid. Sublimation (vide supra) gave an analytical sample.

4-*S*$_P$: Mp 103—105 °C; $[\alpha]_{436}^{21}$−107° (c 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=8.42—8.38 (m, 2H), 7.74—7.67 (m, 6H), 3.84 (ddt, $^3J_{PH}$=4.88 Hz, J=13.7, 6.8 Hz, 2H), 2.75 (ddt, $^2J_{PH}$=17.1 Hz, J=13.7, 6.8 Hz, 1H), 2.60 (ddt, $^2J_{PH}$=13.2 Hz, J=13.7, 6.8 Hz, 1H), 1.86 (bs, 1H); ^{13}C{^{1}H} NMR (acetone-d_6) δ=138.3 (d, $^3J_{PC}$=9.2 Hz), 137.0 (d, $^2J_{PC}$=20.2 Hz), 136.0, 133.4 (d, $^2J_{PC}$=12.9 Hz), 131.2 (d, $^1J_{PC}$=160 Hz), 126.3 (d, $^3J_{PC}$=14.7 Hz), 124.1 (q, $^1J_{FC}$=288.6 Hz), 123.9 (q, $^1J_{FC}$=288.6 Hz), 82.7 (sept, $^2J_{FC}$=31.3 Hz), 58.1, 43.9 (d, $^1J_{PC}$=114.0 Hz); ^{19}F NMR ($CDCl_3$) δ=−74.9 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−22.7, ($CDCl_3$) δ=−21.5; IR (KBr, cm^{-1}) 3410 (ν_{OH}), 1197 (ν_{CO}); UV (c-hexane) [λ_{max}, nm (log ε)] 223 (4.38), 228 (4.40), 266 (3.21). Anal. Calcd for $C_{20}H_{13}F_{12}O_3P$: C, 42.88; H, 2.34%. Found: C, 43.00; H, 2.61%. Under similar conditions, a diastereomeric mixture of **3** (800 mg, 1.12 mmol) and $LiAlH_4$ (128 mg, 3.36 mmol) gave **4** (577 mg, 92%) as a mixture of enantiomers.

4-Rac: Mp 133—134 °C; ^{1}H NMR ($CDCl_3$) δ=8.42—8.38 (m, 2H), 7.74—7.67 (m, 6H), 3.84 (ddt, $^3J_{PH}$=4.88 Hz, J=13.7, 6.8 Hz, 2H), 2.75 (ddt, $^2J_{PH}$=17.1 Hz, J=13.7, 6.8 Hz, 1H), 2.60 (ddt, $^2J_{PH}$=13.2 Hz, J=13.7, 6.8 Hz, 1H), 1.86 (bs, 1H); ^{19}F NMR ($CDCl_3$) δ=−74.9 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−22.7, ($CDCl_3$) δ=−21.5.

5-*R*$_P$: Mp 154—157 °C; ^{1}H NMR δ=9.63 (s, 1H), 8.33—8.23 (m, 2H), 7.70—7.65 (m, 6H), 3.67 (ddd, $^2J_{PH}$=23.9 Hz, J=13.7, 2.4 Hz, 1H), 3.17 (ddd, $^2J_{PH}$=18.6 Hz, J=14.2, 3.4 Hz, 1H); ^{31}P NMR ($CDCl_3$) δ=−28.6; IR (KBr, cm^{-1}) 1719 (ν_{CO}).

(1*R*,1′*R*)-[2-(3,3,3-Trifluoro-2-methoxy-2-phenylpropanoyloxy)ethyl]-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spiorobi[3*H*,2,1λ^5-benzoxaphosphole] (6-*R*$_P$). A mixture of (*R*)-(+)-2-methoxy-2-(trifluoromethyl)-

phenylacetic acid (63 mg, 0.268 mmol), thionyl chloride (1 mL) and a trace of NaCl was refluxed for 50 h. After removing the excess thionyl chloride in vacuo, a mixture of **4-R_P** (100 mg, 0.179 mmol), DMAP (38.6 mg, 0.357 mmol), pyridine (0.5 mL), and CCl_4 (0.5 mL) was added to the crude (*R*)-2-methoxy-2-(trifluoromethyl)phenylacetyl chloride and the solution was stirred for 24 h. Quenching with sat. NH_4Cl followed by extraction with Et_2O (3×30 mL), washing with brine, drying with $MgSO_4$, and removal of solvent under reduced pressure yielded a crude product, which was subjected to preparative TLC (hexane–CH_2Cl_2, 1 : 1). **6-R_P** (75.6 mg, 54%) was obtained as a white solid. Recrystallization from hexane–CH_2Cl_2 gave an X-ray sample.

6-R_P: Mp 128—130 °C; ^{1}H NMR (acetone-d_6) δ=8.38 (dd, J=11.2, 7.8 Hz, 2H), 7.91—7.88 (m, 2H), 7.84—7.79 (m, 3H), 7.38—7.37 (m, 4H), 4.70 (dddd, $^3J_{PH}$=14.7 Hz, J=11.2, 8.8, 5.9 Hz, 1H), 4.43 (dddd, $^3J_{PH}$=15.6 Hz, J=11.2, 8.8, 6.8 Hz, 1H), 3.37 (s, 3H), 3.05 (dddd, $^2J_{PH}$=20.0 Hz, J=14.2, 8.8, 5.9 Hz, 1H), 2.68 (dddd, $^2J_{PH}$=21.0 Hz, J=14.2, 8.8, 6.8 Hz, 1H); ^{13}C{^{1}H} NMR (acetone-d_6) δ=167.2, 138.7 (d, $^3J_{PC}$=12.9 Hz), 137.0 (d, $^2J_{PC}$=20.3 Hz), 136.3, 133.6 (d, $^2J_{PC}$=12.8 Hz), 133.4, 131.1, 130.4 (d, $^1J_{PC}$=159.9 Hz), 130.0, 128.6, 126.4 (d, $^3J_{PC}$=14.7 Hz), 124.7 (q, $^1J_{FC}$=288.6 Hz), 124.1 (q, $^1J_{FC}$=286.8 Hz), 123.8 (q, $^1J_{FC}$=288.6 Hz), 85.9 (q, $^2J_{FC}$=27.6 Hz), 82.6 (sept, $^2J_{FC}$=31.3 Hz), 63.0, 56.1, 39.4 (d, $^1J_{PC}$=119.5 Hz); ^{19}F NMR (CDCl$_3$) δ=−72.2 (s, 3F), −74.9 (q, J=9.8 Hz, 6F), −75.2 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−24.5; IR (KBr, cm^{-1}) 1719 (ν_{CO}). Anal. Calcd for $C_{30}H_{20}F_{15}O_5P$: C, 46.41; H, 2.60%. Found: C, 46.53; H, 2.29%.

(1*S*,1′*R*)-[2-(3,3,3-Trifluoro-2-methoxy-2-phenylpropanoyloxy)ethyl]-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (6-S_P). From (*R*)-2-methoxy-2-(trifluoromethyl)phenylacetyl chloride (prepared from (*R*)-(+)-2-methoxy-2-(trifluoromethyl)-phenylacetic acid (50.1 mg, 0.214 mmol), thionyl chloride (1 mL), NaCl (trace)), **4-S_P** (60.0 mg, 0.107 mmol), DMAP (26.1 mg, 0.214 mmol), pyridine (0.5 mL), and CCl_4 (0.5 mL) was obtained **6-S_P** (26.2 mg, 31%).

6-S_P: Mp 128—129 °C; ^{1}H NMR (acetone-d_6) δ=8.28 (dd, J=11.2, 7.8 Hz, 2H), 7.91—7.87 (m, 2H), 7.80—7.75 (m, 3H), 7.46—7.41 (m, 4H), 4.67 (dddd, $^3J_{PH}$=14.7 Hz, J=11.2, 8.8, 5.9 Hz, 1H), 4.45 (dddd, $^3J_{PH}$=15.6 Hz, J=11.2, 8.8, 6.8 Hz, 1H), 3.26 (s, 3H), 3.05 (dddd, $^2J_{PH}$=20.0 Hz, J=14.2, 8.8, 5.9 Hz, 1H), 2.74 (dddd, $^2J_{PH}$=21.0 Hz, J=14.2, 8.8, 6.8 Hz, 1H); ^{13}C{^{1}H} NMR (acetone-d_6)[19] δ=167.2, 138.3 (d, $^3J_{PC}$=14.7 Hz), 136.9 (d, $^2J_{PC}$=18.4 Hz), 135.6, 133.4, 132.9 (d, $^2J_{PC}$=14.7 Hz), 131.9, 130.5 (d, $^1J_{PC}$=163.6 Hz), 130.5, 129.3, 125.6 (d, $^3J_{PC}$=15 Hz), 124.7 (q, $^1J_{FC}$=286.8 Hz), 124.0 (q, $^1J_{FC}$=288.6 Hz), 123.8 (q, $^1J_{FC}$=288.6 Hz), 83.0 (sept, $^2J_{FC}$=31.3 Hz), 63.0, 55.7, 39.3 (d, $^1J_{PC}$=139.9 Hz); ^{19}F NMR (CDCl$_3$) δ=−72.6 (s, 3F), −74.9 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (acetone-d_6) δ=−24.7; IR (KBr, cm^{-1}) 1719 (ν_{CO}). Anal. Calcd for $C_{30}H_{20}F_{15}O_5P$: C, 46.41; H,2.60%. Found: C, 46.50; H, 2.21%.

1-(Iodomethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (9). To a THF (30 mL) solution of P–H phosphorane **2** (3.0 g, 5.81 mmol) was added *n*-BuLi (3.63 mL, 5.81 mmol) at −78 °C. After stirring at r.t. for 1 h, CH_2I_2 (0.47 mL, 5.83 mmol) was added and stirring was continued for 24 h. The mixture was quenched with water, extracted with Et_2O (30 mL×3). The combined ethereal layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Recrystallization of the residue from hexane gave the product (3.13 g, 82%) as a white solid. Mp 101—102 °C. ^{1}H NMR (CDCl$_3$) δ=8.44—8.33 (m, 2H), 7.76—7.71 (m, 6H), 3.62 (dd, $^2J_{PH}$=7.3 Hz, J=9.8 Hz, 1H), 3.48 (dd, $^2J_{PH}$=3.9 Hz, J=9.8 Hz, 1H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ=137.5 (d, $^3J_{PC}$=12.9 Hz), 136.3 (d, $^2J_{PC}$=20.3 Hz), 134.4 (d, $^4J_{PC}$=6.5 Hz), 131.4 (d, $^1J_{PC}$=173.8 Hz), 131.4 (d, $^2J_{PC}$=20.2 Hz), 125.9 (d, $^3J_{PC}$=16.5 Hz), 119.6 (q, $^1J_{FC}$=286.8 Hz), 119.4 (q, $^1J_{FC}$=286.8 Hz), 81.1 (sept, $^2J_{FC}$=31.3 Hz), 25.2 (d, $^1J_{PC}$=125 Hz); ^{19}F NMR (CDCl$_3$) δ=−75.1 (q, J=9.8 Hz, 6F), −75.5 (q, J=9.8 Hz, 6F); ^{31}P NMR (CDCl$_3$) δ=−24.6.

(1*R*,1*R*′) and (1*S*,1*R*′)-1-(1-Phenylethylaminomethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (10-R_P and 10-S_P). To a CH_3CN solution (30 mL) of **9** (2.32 g, 3.54 mmol) was added (+)-1-phenylethylamine (0.46 mL, 3.544 mmol) and the resulting solution was stirred for 14 d. The solution was quenched with aq NH_4Cl, and extracted with ether (30 mL×3). After drying the combined solution the solvent was removed under reduced pressure. Treatment of the residue on silica gel column chromatography (hexane–CH_2Cl_2=1 : 1) gave the desired product (1.29 g, 56%) as a 1 : 1 diastereomeric mixture. Recrystallization from hexane gave colorless plates (250 mg, 11%) and prisms (456 mg, 20%).

10-R_P: Mp 124—126 °C; $[\alpha]_{436}^{20}$ +73° (*c* 1.22, $CHCl_3$); ^{1}H NMR (CDCl$_3$) δ=8.42—8.38 (m, 2H), 7.71—7.68 (m, 6H), 7.23—7.16 (m, 5H), 3.74 (dq, J=6.8, 2.4 Hz, 1H), 3.61 (dd, $^2J_{PH}$=14.7 Hz, J=7.3 Hz, 1H), 3.53 (dd, $^2J_{PH}$=14.7 Hz, J=7.3 Hz, 1H), 2.09 (bs, 1H), 1.12 (d, J=6.4 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ=136.9 (d, $^3J_{PC}$=9.2 Hz), 136.1 (d, $^2J_{PC}$=20.3 Hz), 133.8, 131.5 (d, $^2J_{PC}$=14.7 Hz), 131.4, 130.1 (d, $^1J_{PC}$=154.4 Hz), 128.2, 126.9, 126.5, 124.8 (d, $^3J_{PC}$=14.7 Hz), 122.6 (q, $^1J_{FC}$=288.6 Hz), 122.4 (q, $^1J_{FC}$=288.6 Hz), 81.6 (sept, $^3J_{FC}$=31.3 Hz), 58.1 (d, $^3J_{PC}$=12.9 Hz), 55.7 (d, $^1J_{PC}$=114.0 Hz), 22.9; ^{19}F NMR (CDCl$_3$) δ=−74.8 (q, J=9.8 Hz, 6F), −75.1 (q, J=9.8 Hz, 6F); ^{31}P NMR (CDCl$_3$) δ=−24.6 (THF) δ=−23.7, (CH_3CN) δ=−23.3; UV (*c*-hexane) [λ_{max}, nm (log ε)] 223 (4.32), 227 (4.33), 267 (3.59), 274 (3.54). Anal. Calcd for $C_{27}H_{20}F_{12}NO_2P$: C, 49.94; H, 3.10; N, 2.16%. Found: C, 49.82; H, 3.02; N, 2.10%.

10-S_P: Mp 134—137 °C; $[\alpha]_{436}^{20}$ +104° (*c* 0.66, $CHCl_3$); ^{1}H NMR (CDCl$_3$) δ=8.43—8.39 (m, 2H), 7.73—7.71 (m, 6H), 7.10 (m, 3H), 6.81—6.79 (m, 2H), 3.92 (dq, J=5.4, 5.4 Hz, 1H), 3.65 (dd, $^2J_{PH}$=15.6 Hz, J=5.4 Hz, 1H), 3.33 (bd, $^2J_{PH}$=15.6 Hz, 1H) 2.21 (bs, 1H), 1.25 (d, J=6.8 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ=136.7 (d, $^3J_{PC}$=11.0 Hz), 136.0 (d, $^2J_{PC}$=18.4 Hz), 133.6, 131.5 (d, $^2J_{PC}$=12.9 Hz), 130.1, 129.1 (d, $^1J_{PC}$=152.6 Hz), 128.1, 126.8, 126.7, 124.8 (d, $^3J_{PC}$=14.7 Hz), 122.6 (q, $^1J_{FC}$=286.8 Hz), 122.4 (q, $^1J_{FC}$=288.6 Hz), 81.7 (sept, $^2J_{FC}$=31.2 Hz), 57.4 (d, $^3J_{PC}$=5.6 Hz), 55.0 (d, $^1J_{PC}$=99.3 Hz), 24.6; ^{19}F NMR (CDCl$_3$) δ=−74.8 (q, J=9.8 Hz, 6F), −75.0 (q, J=9.8 Hz, 6F); ^{31}P NMR (CDCl$_3$) δ=−26.9, (THF) δ=−25.8, (CH_3CN) δ=−25.2; UV (*c*-hexane) [λ_{max}, nm (log ε)] 223 (4.37), 227 (4.38), 267 (3.64), 274 (3.59). Anal. Calcd for $C_{27}H_{20}F_{12}NO_2P$: C, 49.94; H, 3.10; N, 2.16%. Found: C, 49.75; H, 2.92; N, 2.05%.

Reaction of 10-R_P with MeLi. MeLi (*c* 1.14 in

hexane, 0.49 mL, 0.558 mmol) was added to a solution of amine **10-R_P** (100.4 mg, 0.155 mmol) in THF (10 mL) at −78 °C and the solution was stirred for 15 min. After quenching with aq NH_4Cl (10 mL), the solution was extracted with ether (30 mL×3), washed with brine, and dried with $MgSO_4$. Purification of the residue obtained after removal of the solvent was carried out on TLC (hexane) to give **2-R_P** (53.7 mg, 67%) as white powder. Mp 127—128 °C; $[\alpha]_{436}^{20}$ −16° (*c* 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=8.36 (d, J_{PH}=729 Hz, 1H), 8.31—8.26 (m, 2H), 7.79—7.68 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=137.4 (d, $^2J_{PC}$=22.1 Hz), 136.7 (d, $^3J_{PC}$=9.2 Hz), 134.4, 131.8 (d, $^2J_{PC}$=14.8 Hz), 126.4 (d, $^1J_{PC}$=158.1 Hz), 125.3 (d, $^3J_{PC}$=17.6 Hz), 122.6 (q, $^1J_{FC}$=286.8 Hz), 122.4 (q, $^1J_{FC}$=286.7 Hz), 81.9 (sept, $^2J_{FC}$=31.3 Hz); ^{19}F NMR ($CDCl_3$) δ=−75.0 (q, J=9.8 Hz, 6F), −76.2 (q, J=9.8 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ=−45.9. UV (*c*-hexane) [λ_{max}, nm (log ε)] 223 (4.32), 228 (4.38), 267 (3.30), 274 (2.97). Anal. Calcd for $C_{18}H_9F_{12}O_2P$: C, 41.88; H, 1.76%. Found: C, 41.86; H, 1.58%.

Reaction of 10-S_P with MeLi. Using the same procedure described above, **10-S_P** (160 mg, 0.247 mmol) treated with MeLi (1.14 M, 0.78 mL, 0.889 mmol) furnished **2-S_P** (111 mg, 87%). Mp 129—130 °C; $[\alpha]_{436}^{20}$ +17° (*c* 1.09, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=8.36 (d, J_{PH}=729 Hz, 1H), 8.32—8.27 (m, 2H), 7.79—7.69 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=137.3 (d, $^2J_{PC}$=22.1 Hz), 135.9 (d, $^3J_{PC}$=9.2 Hz), 134.4, 131.7 (d, $^2J_{PC}$=18.4 Hz), 126.4 (d, $^1J_{PC}$=156.3 Hz), 125.3 (d, $^3J_{PC}$=14.7 Hz), 122.6 (q, $^1J_{FC}$=286.8 Hz), 122.4 (q, $^1J_{FC}$=286.8 Hz), 81.9 (sept, $^2J_{FC}$=31.3 Hz); ^{19}F NMR ($CDCl_3$) δ=−75.0 (q, J=9.8 Hz, 6F), −76.2 (q, J=9.8 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ=−45.9. UV (*c*-hexane) [λ_{max}, nm (log ε)] 223 (4.36), 228 (4.41), 267 (3.37), 274 (3.36). Anal. Calcd for $C_{18}H_9F_{12}O_2P$: C, 41.88; H, 1.76%. Found: C, 41.92; H, 1.36%.

Reaction of a Mixture of 10-R_P and 10-S_P with MeLi. A diastereomeric mixture (*R*:*S*=26:74) of **10** (450 mg, 0.693 mmol) treated with MeLi (1.14 M, 2.58 mL, 2.49 mmol) gave **2**, quantitatively. Mp 162 °C; ^{1}H NMR ($CDCl_3$) δ=8.36 (d, J_{PH}=729 Hz, 1H), 8.31—8.26 (m, 2H), 7.79—7.68 (m, 6H); ^{19}F NMR ($CDCl_3$) δ=−75.0 (q, J=9.8 Hz, 6F), −76.2 (q, J=9.8 Hz, 6F). ^{31}P NMR ($CDCl_3$) δ=−45.9.

3-R_P from 2-R_P. To **2-R_P** (37.7 mg, 0.073 mmol) in CH_3CN (10 mL) was added DBU (0.02 mL, 0.14 mmol) at r.t. After stirring for one minute (−)-menthyl chloroacetate (17.0 mg, 0.073 mmol) in THF (1 mL) was added and the solution was stirred for 30 min. The solution was quenched with aq NH_4Cl and extracted with ether (30 mL×3). The residue obtained after drying with $MgSO_4$ and removal of solvent was subjected to PTLC (hexane:CH_2Cl_2=1:1) to yield **3-R_P** (52 mg, 99%) slightly contaminated with (−)-menthyl chloroacetate. ^{1}H NMR ($CDCl_3$) δ=8.40—8.36 (m, 2H), 7.74—7.69 (m, 6H), 4.52 (dt, J=4.4, 10.8 Hz, 1H), 3.53 (dd, $^2J_{PH}$=18.1 Hz, J=14.7 Hz, 1H), 3.36 (dd, $^2J_{PH}$=17.1 Hz, J=14.7 Hz, 1H), 2.01 (d, J=12.2 Hz, 1H), 1.67—1.42 (m, 5H), 0.92—0.80 (m, 3H), 0.90 (d, J=5.9 Hz, 3H), 0.66 (d, J=6.8 Hz, 3H), 0.59 (d, J=6.8 Hz, 3H); ^{31}P NMR ($CDCl_3$) δ=−27.0.

3-S_P from 2-S_P. In the same manner, **2-S_P** (87.5 mg, 0.17 mmol) in CH_3CN (15 mL), DBU (0.05 mL, 0.33 mmol), and (−)-menthyl chloroacetate (39.4 mg, 0.17 mmol) in THF (2 mL) gave **3-S_P** (106 mg, 87%) slightly contaminated with (−)-menthyl chloroacetate. ^{1}H NMR ($CDCl_3$) δ=8.40—8.36 (m, 2H), 7.74—7.67 (m, 6H), 4.62 (dt, J=4.4, 10.7 Hz, 1H), 3.55 (dd, $^2J_{PH}$=18.1 Hz, J=15.1 Hz, 1H), 3.37 (dd, $^2J_{PH}$=15.6 Hz, J=15.1 Hz, 1H), 1.97—1.94 (m, 1H), 1.78—1.75 (m, 1H), 1.68—1.60 (m, 2H), 1.34—1.26 (m, 1H), 1.17—1.14 (m, 1H), 1.11—0.96 (m, 2H), 0.90 (d, J=7.3 Hz, 3H), 0.82 (d, J=6.4 Hz, 3H), 0.72 (d, J=6.8 Hz, 3H), 0.58—0.49 (m, 1H); ^{31}P NMR ($CDCl_3$) δ=−26.7.

A Diastereomeric Mixture of 3-R_P and 3-S_P from a Mixture of 2-S_P and 2-R_P. Similarly, **2** (*R*:*S*=26:74, 87.5 mg, 0.17 mmol) in CH_3CN (20 mL), DBU (0.04 mL, 0.27 mmol), and (−)-menthyl chloroacetate (30.8 mg, 0.133 mmol) in THF (2 mL) gave **3** (106 mg, 87%) slightly contaminated with (−)-menthyl chloroacetate.

Kinetic Measurements. Solutions enriched with **3-R_P** (ca. 50 mg in 0.6 mL of solvent) were sealed in NMR tubes. Temperatures for the kinetic runs were maintained at 100 °C (±2 °C). The composition of the diastereomers was monitored by integration of ^{31}P NMR signals. The data was analyzed assuming first order kinetics using the equation, $\ln\{(x_e-x_o)/(x_e-x)\}=k(K+1)t$, in which x_e=ratio at equilibrium, x_o=ratio observed at t=0, x=observed ratio at arbitrary intervals, k=rate constant to be determined, and K=equilibrium ratio. The equilibrium ratio K was determined to be 1.0.

Crystallographic Studies. Crystal data and numerical details of the structural determinations are given in Table 2. Crystals were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) for data collection. Lattice parameters were determined by least-squares fitting of 27 reflections in the range of $23°<2\theta<32°$ for **3-R_P**, 31 reflections in the range of $26°<2\theta<30°$ for **6-R_P**, and 31 reflections in the range of $31°<2\theta<35°$ for **10-R_P**. Data were collected with the $2\theta/\omega$ scan mode. Data for **6-R_P** and **10-R_P** were corrected for absorption.[20] Compound **3-R_P** was solved by a direct method with the Monte Carlo–Multan program[21] whereas Shelx86 was used for **6-R_P** and **10-R_P**. Refinement on F was carried out by the full-matrix least squares method. All computations were carried out on a Titan 750 computer. Tables of positional and thermal parameters and complete interatomic distances and angles have been deposited as Document No. 68026 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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