Synthesis and Horner−Wittig Chemistry of (Fluoromethyl)diphenylphosphane Oxide

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(Fluoromethyl)diphenylphosphane oxide (**1**) was obtained by heating (diphenylphosphinoyl)methyl *p*-toluenesulfinate (**2**) with potassium fluoride. Compound **1** is a stable, crystalline solid, suitable for application in the Horner–Wittig reaction. The compound described in the literature under this name was found to be benzylphenylphosphinic fluoride (**5**). The anion of phosphane oxide **1** readily reacted with a wide range of carbonyl compounds to yield diastereomeric mixtures of α-fluoro-β-(hydroxyalkyl)phosphane oxides **7**, which in most cases could be separated. The ease of phosphinate elimination to yield (*E*)- and (*Z*)-1-fluoroalkenes **8** stereoselectively was found to be strongly dependent upon conformation and substituent pattern. The route presented here avoids the use of hazardous fluorohalomethanes, which were employed in several earlier Wittig-related approaches to vinyl fluorides.

Introduction

The synthesis of terminal monofluoro olefins through Wittig-type reactions of fluorinated phosphorus reagents[1] has been well studied. Some routes depending on α-heterosubstituted (fluoromethyl)phosphorus intermediates have been quite successful. 1,1-Difluoroalkenes, obtained from CBr_2F_2 and HMPT[2] or from (difluoromethyl)diphenylphosphane oxide,[3] could be reduced selectively to give monofluorinated alkenes.[2] Fluorovinyl sulfones, accessible in high yields by Horner−Wadsworth−Emmons chemistry, have been desulfurized with aluminum amalgam[4] or by use of organotin chemistry.[5]

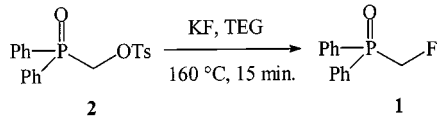
The classical Wittig reaction with (fluoromethyl)diphenylphosphonium salts gave only moderate yields and lacked stereoselectivity.[6] Simultaneous generation of the ylide and benzaldehyde gave a high yield, but no other examples were given.[6c] In other cases, addition of potassium *tert*-butoxide (KO*t*Bu) to the reaction mixture was shown to be beneficial.[6d−6f] Preparing the ylide from the (fluoroiodomethyl)phosphonium salt and zinc/copper couple provided no significant improvement.[6d] In contrast, the phosphoranium salt formed from tributylphosphane and $CFCl_3$ reacted with aldehydes with high stereoselectivity.[5b,7] Anions of (fluoromethyl)phosphonates[8] lacked both the reactivity and the stereoselectivity to be interesting alternatives to the Wittig reaction.[9] (Fluoromethyl)diphenylphosphane oxide,[10] was allegedly obtained by treating (diphenylphosphinoyl)methanol with (diethylamino)sulfur trifluoride (DAST). It was reported to be unstable and unsuitable for the synthesis of 1-fluoroalkenes.[3]

We would like to demonstrate that this last assertion is false by presenting a straightforward synthesis of (fluoromethyl)diphenylphosphane oxide, which was found to be a stable, crystalline compound. The true structure of the originally synthesized compound has been determined, and the mechanism responsible for its formation is discussed. The applicability of phosphane oxide **1** in the Horner−Wittig synthesis of β-monosubstituted and β,β-disubstituted vinyl fluorides is reported.

Results and Discussion

1. Synthesis of (Fluoromethyl)diphenylphosphane Oxide

(Diphenylphosphinoyl)methyl *p*-toluenesulfonate (**2**)[11] was prepared from the corresponding alcohol **3**[12] in 91% yield by using the modified procedure developed by De Wit.[13] Heating of sulfonate **2** with potassium fluoride (KF) in triethylene glycol (TEG) at 160 °C for 15 min provided a 70−80% yield of (fluoromethyl)diphenylphosphane oxide (**1**) after chromatographic workup (Scheme 1). When the same procedure was followed with the corresponding methanesulfonate, yields were somewhat lower.[14] Anhydrous KF was used without additional rigorous drying. Various other approaches, such as the use of tetrabutylammonium fluoride in THF, or KF in acetonitrile, DMF, or DMSO at various temperatures, either with or without 10% 18-crown-6, resulted in more lengthy procedures and lower yields.



Scheme 1

The NMR characteristics of the newly obtained phosphane oxide **1** were found to be quite different from the data originally reported.[3] This prompted us to subject the reaction between (diphenylphosphinoyl)methanol (**3**)[12] and DAST to closer scrutiny. The major compound formed turned out to be the dimeric sulfite **4** (Scheme 2). Such in-

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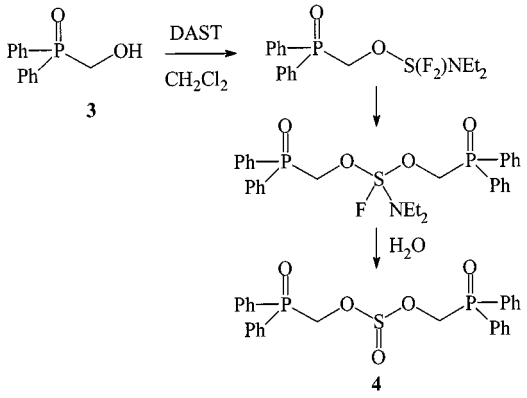
corporation of the DAST moiety into the final product by double nucleophilic attack of an oxygen function is a rare occurrence. Dialkoxy(dialkylamino)fluorosulfuranes have been prepared from silyl ethers and several DAST-type reagents,[15] but hydrolysis of these compounds resulted in sulfinamic esters and not dimeric sulfites. Formation of cyclic sulfites with DAST has been reported for diols.[16]

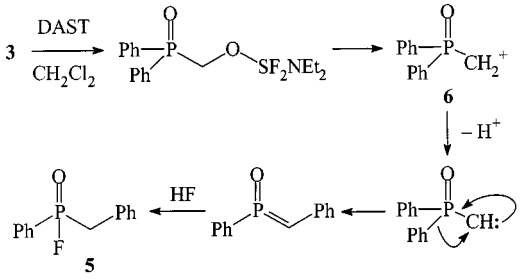


Scheme 2

Compound **5**, possessing the properties reported in the literature for (fluoromethyl)diphenylphosphane oxide, was obtained in low yield. Although the melting points were similar, it also differed markedly from phosphane oxide **2** in its chromatographic characteristics. Because the reported elemental analysis turned out to be correct, the product probably involved an isomeric form. A summary of pertinent physical properties of both compounds is presented in Table 1.

The large fluorine-phosphorus coupling constant of **5**, apparently overlooked previously,[3] definitely shows the presence of a P−F bond. The compound slowly decomposed at room temperature with formation of benzyl(phenyl)phosphinic acid.[17] By use of known chemistry,[18] the latter was transformed into benzyl(phenyl)phosphinic fluoride.[19] Analysis of spectral data proved this product to be the same as compound **5**.

The transformation of a substituted methyldiphenylphosphane oxide into a benzyl(phenyl)phosphinic acid derivative has a precedent in the photolysis of (diphenylphosphinoyl)-diazomethane in protic solvents, with (diphenylphosphinoyl)(methyl)carbene as the reactive intermediate.[20] A similar mechanism can be proposed for the DAST-induced rearrangement of (diphenylphosphinoyl)methanol (Scheme 3). Alternatively, the carbenium ion intermediate **6** might undergo rearrangement and attack by fluoride ion directly to give **5**.



Scheme 3

In a similar transformation, (hydroxymethyl)triphenylphosphonium iodide was shown to be converted into benzyldiphenylphosphane oxide on treatment with (impure)[21] sulfur tetrafluoride and subsequent hydrolysis,[6d] while the corresponding tetrafluoroborate salt was successfully fluorinated with DAST.[21] Diethyl (hydroxymethyl)-phosphonate was unreactive towards DAST,[8c] while an (α-hydroxybenzyl)phosphonate and phosphane oxide have been successfully fluorinated by this reagent.[22] It can be concluded that stabilization of a cation at the α-position by a hydrocarbon substituent appears to be a necessary condition for the successful completion of these fluorinations. This indicates transformation through an S_N1 mechanism and seems to imply that the suggested stabilization through the phosphorus moiety[22b] is negligible, at least in the case of phosphane oxides. It should be noted that a nonactivated secondary α-fluoromethylphosphonate was recently prepared with inversion of configuration, suggesting an S_N2 mechanism.[23]

2. Horner−Wittig Chemistry with 1

Deprotonation of (fluoromethyl)diphenylphosphane oxide (**1**) with lithium diisopropylamide (LDA) in THF at −70 °C resulted in the formation of a clear, orange solution. At temperatures below −80 °C, the solubility of the phosphane oxide was unsatisfactory. Addition of an aldehyde or ketone, followed by stirring at −70 °C, resulted in the formation of diastereomeric mixtures of (α-fluoro-β-hydroxyalkyl)phosphane oxides **7** in good yields (Scheme 4). The stereoselectivity of the reaction was low, with (α*R**,β*S**) (or *u*) and (α*R**,β*R**) (or *l*) isomers[24] usually formed in nearly equal amounts, although with aldehydes, *u*/*l* ratios could be as high as 3:1. With enolizable carbonyl compounds, the amount of base had to be monitored

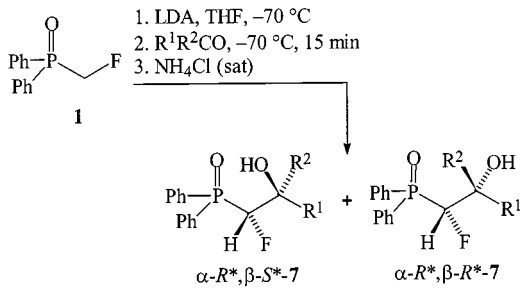
Table 1. Physical properties of (fluoromethyl)diphenylphosphane oxide (**1**) and its isomer **5**

Property[a]	**1**	**5**	**5**[3]
δ(CH_2)	5.18 (dd, 46.8, 3.7)	3.48 (dd, 18.3, 5.1)	3.47 (dd, 17.9, 5.4)
δ(*C*H_2)	80.2 (dd, 88.3, 83.1)	36.8 (dd, 56.5, 18.3)	–
δ(F)	−243.2 (dt, 49.1, 47.9)	−76.9 (d, 1034)	−75.5 (t, 5.2), −79.1 (t, 5.2)
δ(P)	23.4 (d, 49.1)	49.8 (d, 1034)	–
M.p. [°C]	95−95.5	95	93−94
R_f	0.08	0.53	–

[a] For full details see Exp. Sect.; for NMR spectroscopic data, multiplicity and coupling constants are given in parentheses.

closely, as an excess of base reduced the yield considerably. With chiral carbonyl compounds, the adducts (**7m**, Table 2, and **7s** and **7t**, Table 3) showed good stereoselectivity at the β-carbon atom, but little or no discrimination between F and H at the α-carbon atom. Similar behavior has been reported for the phosphonate analogues, although in those cases the yields were unsatisfactory.[9] Paraformaldehyde was found to be unreactive.

Conversion and diastereomeric ratios could easily be determined by ^{31}P NMR analysis of the crude product. Phosphorus shifts being highly dependent on the conformation (and therefore on the configuration) of the molecule, assignment of the signals of aldehyde derivatives **7a**−**l** was straightforward. For adduct **7m**, obtained from *ent*-Garner's aldehyde [*tert*-butyl (*R*)-(+)-4-formyl-2,2-dimethyl-3-oxazolidinecarboxylate], the spectra were complicated by the presence of rotamers that were stable on the NMR timescale. With asymmetrical ketone derivatives **7o** and **7s**−**u**, the configuration of the adducts was determined by analysis of the fluoro olefins **8** obtained after phosphinate elimination; the stereochemistry of **7v** was not elucidated. The favored mode of addition to 2-phenylcyclohexanone[25] and (*R*)-carvone[26] was deduced by comparison with literature data. Results are listed in Table 2 (aldehydes) and Table 3 (ketones).



Scheme 4

Most (α-fluoro-β-hydroxyalkyl)phosphane oxides **7** could be obtained in pure form after column chromatography. In some cases, trituration with ether was necessary to remove remaining (fluoromethyl)diphenylphosphane oxide (**1**). Separation of the diastereoisomers proved to be more difficult, as their R_f values differed only slightly in several cases. Luckily, diastereomers often showed considerable differences in solubility, enabling purification by trituration.

Pure adducts **7** were stable, with the exception of ***l*-7a** and ***l*-7c**, formed from benzaldehyde and 4-methoxybenzaldehyde; these slowly lost phosphinic acid upon standing at room temperature, even without addition of base. In contrast, 2-phenylcyclohexanone derivative 1′*R**,1*S**,2*S**-**7s** could be heated to 160 °C in [D_6]DMSO without any sign of decomposition.

Table 2. Formation of (α-fluoro-β-hydroxyalkyl)phosphane oxides from aldehydes

Compound	Aldehyde	Yield [%][a]	Isomeric ratio[b]
7a	benzaldehyde	73	62:38
7b	2-chlorobenzaldehyde	76	51:49
7c	4-methoxybenzaldehyde	74	73:27
7d	4-biphenylylcarbaldehyde	86	67:33
7e	4-nitrobenzaldehyde	61	49:51
7f	2-pyridinecarbaldehyde	81	38:62
7g	4-(dimethylamino)cinnamaldehyde	84	72:28
7h	3-(2-furyl)acrolein	79	69:31
7i	*n*-decanal	69	75:25
7j	3-phenylpropanal	66	67:33
7k	1-phenylcyclopropanecarbaldehyde	61	49:51
7l	benzyloxyacetaldehyde	73	60:40
7m	*ent*-Garner's aldehyde	67 (78)	63:37[c]

[a] Conversion is given in parentheses. − [b] *u*/*l*, unless mentioned otherwise; determined by NMR spectroscopy of the crude mixture. − [c] Major isomers; ratio of the two minor isomers could not be determined.

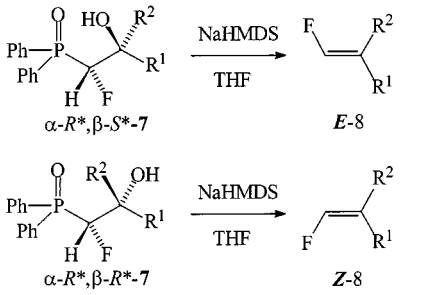
Table 3. Formation of (α-fluoro-β-hydroxyalkyl)phosphane oxides from ketones

Entry	Ketone	Yield [%][a]	Isomeric ratio
7n	9-fluorenone	83	–
7o	acetophenone	73 (85)	41:59
7p	dodecanone	45	–
7q	2-adamantanone	59	–
7r	4-*tert*-butylcyclohexanone	63	50:50
7s	2-phenylcyclohexanone	70 (78)	55:29:9:7[b]
7t	(*R*)-carvone	80 (80)	49:41:6:4[c]
7u	α,α,α-trifluoroacetophenone	94	47:53
7v	methyl benzoylformate	63 (80)	52:48

[a] Conversion is given in parentheses. − [b] (1′*R**,1*S**,2*S**)/(1′*R**,1*R**,2*R**)/(1′*R**,1*R**,2*S**)/(1′*R**,1*S**,2*R**). − [c] (1′*S*,1*R*,5*R*)/(1′*R*,1*R*,5*R*)/(1′*R*,1*S*,5*R*)/(1′*S*,1*S*,5*R*).

Conversion of (β-hydroxyalkyl)phosphane oxides into alkenes has been achieved by treatment with various sodium and potassium bases.[27] In pilot experiments, sodium bis(trimethylsilyl)amide (NaHMDS) was found to be most suitable for the conversion of (α-fluoro-β-hydroxyalkyl)-phosphane oxides **7** into fluoro olefins **8** (Scheme 5). Phosphane oxides **7** were treated with NaHMDS at 5 °C. If no precipitation of sodium phosphinate occurred, the solution was allowed to warm to room temperature. In most cases this was effective in yielding fluoroalkenes **8**. Some adducts bearing electron-withdrawing substituents resisted elimination of phosphinate even at room temperature. For these,

additional heating was necessary. In general, if adduct **7** was known not to lose phosphinate at 5 °C, it was better to add the base at room temperature in order to prevent side reactions. KO*t*Bu was used for the synthesis of ***E*-8s**, which (at lower temperatures) had given disappointing results when NaHMDS had been used.



Scheme 5

Competition to the elimination of phosphinate came from dehydrofluorination reactions. Dehydrofluorinated phosphane oxide products found were epoxides **9**, β-oxo compounds **10**, and formylphosphane oxides **11**, as shown in Figure 1.

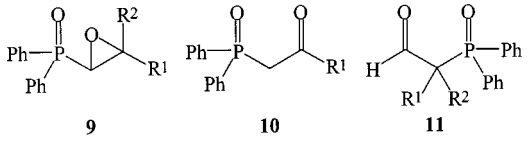


Figure 1. Dehydrofluorinated phosphane oxide products

For the synthesis of **8a** and **8j**, the possibility of a two-step, one-pot procedure was examined. In these cases, lithiated adduct **7** was not quenched at −70 °C, but allowed to warm to 0 °C. KO*t*Bu was added and the mixture was stirred overnight. Results were satisfactory but the two-step synthesis proved to be more convenient. Results of the phosphinate elimination reactions are given in Table 4 (aldehyde derivatives **7a**−**m**) and Table 5 (ketone derivatives **7n**−**v**).

Fluoro olefins were formed in most cases, though yields were found to be strongly correlated with structural characteristics of **7** and reaction conditions. A unique feature of this route is the possibility of preparing 1-fluoro-1,3-dienes (**8g**, **8h**, and **8t**) in good yields.

It can be concluded that the conversion of *u*- and *l*-phosphane oxides **7** to (*E*)- and (*Z*)-fluoro olefins **8**, respectively, occurred with complete stereoselectivity. When the isomeric ratio of products **8** differed from that of starting compounds **7**, this was due either to the formation of side products or to incomplete conversion of one of the isomers. It was found that *l* isomers of the aldehyde adducts, yielding (*Z*)-fluoro olefins, reacted faster than the corresponding *u* isomers, giving (*E*) olefins. When using less than 1 equiv. of base with mixtures of isomers, the (*Z*)-fluoro olefins were formed preferentially with total conversion of the starting isomer, while the other isomer was converted incompletely or not at all. Separation of the (*E*) and (*Z*)-fluoro olefins by column chromatography was only successful for **8m**, which stresses the significance of the diastereoisomers of phosphane oxides **7** being separable.

As noted in the literature for **8a**[28] and ***Z*-8i**,[29] fluoro olefins can be quite unstable. Notably, 1-fluoro-1,3-dienes **8h** and ***E*-8t** rapidly turned into dark polymers after isolation, even at −20 °C.

For dehydrofluorination, two routes could be envisaged. Intramolecular nucleophilic substitution resulted in 2-(diphenylphosphinoyl)oxiranes **9**, especially if temperatures were too low for phosphinate elimination. Such behavior has previously been reported for the reaction of (chloromethyl)diphenylphosphane oxide with ketones.[30] *u* Isomers of adducts **7** had a greater tendency to form epoxides than the *l* isomers did. This could be explained by differences in conformation, deduced from NMR spectroscopic data. Coupling constants of the aldehyde derivatives indicated

Table 4. Conversion of aldehyde-derived (α-fluoro-β-hydroxyalkyl)phosphane oxides with base

Substrate[a]	Scale [mmol]	Recovery [%][a][b]	Yield (**8**) [%][c]	Yield (**9**,**10**,**11**) [%][d]
7a (75:25)	0.50	0	48[e] (62:38)	26 (***trans*-9a/11a** = 91:9)
7b (67:33)	1.0	25 (> 98:2)[f]	72 (54:46)	0
7c (92:8)	1.0	0	73 (92:8)	0
7c (22:78)	0.62	0	84 (17:83)	0
7d (67:33)	1.0	7 (> 98:2)	71 (58:42)	13 (***trans*-9d**)
7e (49:51)	1.0	32	29 (8:92)	39 (**10e**)
7f (16:84)	1.0	70 (30:70)	trace (< 2:98)	20 (**10f**)
7g (72:28)	1.0	0	84 (70:30)	0
7h (69:31)	1.0	17	54 (72:28)	4 (**10h**)
7h (69:31)[g]	0.50	0	83 (72:28)	0
7i (93:7)	1.34	0	65 (94:6)	0
7i (0:100)	1.0	0	91 (< 2:98)	0
7j (65:35)	1.0	0	78 (72:28)	0
7k (90:10)	0.63	0	49 (79:21)	45 (***trans*-9k**)
7k (< 2:98)	0.37	0	83 (3:97)	0
7l (60:40)	1.0	0	54 (60:40)	0
7m	0.50	trace	70 (48:52)	20 (**9m**)

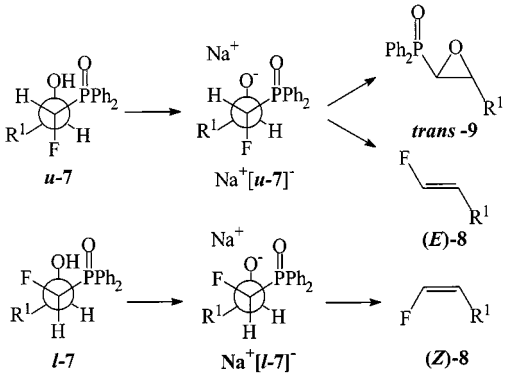
[a] Isomeric ratio (*u*/*l*) in parentheses. − [b] Recovery after column chromatography, unless noted otherwise. − [c] (*E*)/(*Z*) ratio is given in parentheses. − [d] Specified for each product. − [e] Low yield probably due to volatility. − [f] Determined by ^{1}H NMR analysis of the crude product. − [g] NaHMDS added at room temperature.

Table 5. Conversion of ketone-derived (α-fluoro-β-hydroxyalkyl)phosphane oxides by base

Entry[a]	Scale [mmol]	Recovery [%][a]	Yield (**8**) [%][b]	Yield (**9**,**11**) [%][c]
7n	1.0	0	76	none identified
7o (> 98:2)	0.90	0	60 (93:7)[d]	0
7o (3:97)	0.87	0	69 (6:94)[e]	0
7p	1.0	0	80	0
7q	1.0	22	76	0
7r-#1	0.46	0	80	0
7r-#2	0.80	0	80	0
7s (97:3)[f]	1.0	0	25 (89:11)	75 (***trans*-9s**)
7s (98:2)[g]	0.30	0	45 (91:9)	47 (***trans*-9s**)
7s (10:90)[f]	0.50	0	77 (< 2:98)	10 (***trans*-9s**)
7t (93:7)[h]	1.11	40 (70:30)[i]	42 (> 98:2)	5 (**11t**)
7t (7:93)[j]	0.47	0	68 (10:90)	0
7u (> 98:2)	1.0	5	< 5 (> 98:2)	75 (***cis*-9u**)
7u (< 2:98)	1.0	0	40 (< 2:98)[k]	0
7v (94:6)[l]	0.50	14	15 (1 isomer?)	43 (**9v**)

[a] Isomeric ratio (*u*/*l*, unless otherwise indicated) is given in parentheses. − [b] (*E*)/(*Z*) ratio is given in parentheses. − [c] Specified for each product. − [d] (*E*)/(*Z*) ratio in crude mixture was > 98:2. − [e] (*E*)/(*Z*)ratio in crude mixture was 9:91. − [f] Ratio of equatorial isomers. − [g] KO*t*Bu added at room temperature. − [h] Ratio indicated: (1′*S*,1*R*,5*R*)/(1′*R*,1*S*,5*R*) [no (1′*R*,1*R*,5*R*) and (1′*S*,1*S*,5*R*) present]. − [i] 5% of an unknown isomeric phosphane oxide containing fluorine was isolated. − [j] Ratio indicated [(1′*S*,1*R*,5*R*) + (1′*R*,1*S*,5*R*)]/(1′*R*,1*R*,5*R*). − [k] Low yield probably caused by volatility. − [l] Stereochemistry of isomers unknown.

that the OH and F substituents favored a *gauche* relationship in the *l* isomers, but a *trans* relationship in the *u* isomers, thus explaining the more facile generation of epoxides from the *u* isomers, as illustrated in Scheme 6. A similar structural relation may apply for ketone derivatives, notably **7s** and **7t**. Formylphosphane oxides **11**, formed from epoxides **9** through a known rearrangement,[30] were observed in two cases (**11a**, **11t**).



Scheme 6

With aldehyde derivatives **7e**, **7f**, and **7h**, β-oxophosphane oxides **10** were obtained. These were probably formed by dehydrofluorination of deprotonated **7**.[31] Support for the fact that ketones **10** were not formed through epoxides **9** comes from the behavior of benzaldehyde derivative **7a**. In the two-step, one-pot synthesis of **8a** from **1** with KO*t*Bu as the dephosphinating agent (2 equiv. of base), no epoxide **9a** was isolated, while oxo compound **10a** was formed in about 4% yield. However, when **7a** was treated with NaHMDS, epoxide **9a** was the main side product, along with some secondary product **11a**! Moreover, epoxides bearing electron-withdrawing groups at the α-position usually do not yield β-oxo products.[32]

Conclusions

(Fluoromethyl)diphenylphosphane oxide (**1**) is easily accessible by treatment of (diphenylphosphinoyl)methyl *p*-toluenesulfonate (**2**) with potassium fluoride. An earlier report on the synthesis of this phosphane oxide and its reactions with base was shown to be in error. Deprotonation of **1** and treatment with aldehydes and ketones resulted in stable (α-fluoro-β-hydroxyalkyl)phosphane oxides **7** in good yields. Separation of the diastereoisomers was often possible; with a sodium or potassium base, these could be stereoselectively transformed into fluoro olefins **8**. In some cases there was competition from dehydrofluorination reactions, but this tendency could be reduced by adding the base at higher temperatures. The route presented here offers the possibility of stereoselective synthesis of 1-fluoroalkenes by separation of their (stable) precursors, as well as the first high-yielding synthesis of 1-fluoroalka-1,3-dienes. Furthermore, neither harmful fluorohalomethanes nor expensive fluorinating agents were required.

Experimental Section

General Procedures: Column chromatography was performed on Baker silica gel (0.063−0.200 mm). For TLC analyses, Schleicher and Schuell F1500/LS 254 silica plates were used, with viewing under ultraviolet light or developing with $KMnO_4$ spray. R_f values were obtained with the eluent used to isolate the specified product in column chromatography, unless noted otherwise. − Melting points were determined with a Büchi melting point apparatus and are uncorrected. − ^1H (200 MHz), ^{13}C (proton-decoupled, 50 MHz), ^{31}P (proton-decoupled, 80 MHz), and ^{19}F NMR (188 MHz) spectra were recorded with a Bruker AC-200 instrument in $CDCl_3$, unless noted otherwise. Chemical shifts are given in δ (ppm) relative to tetramethylsilane (^1H, ^{13}C), $CFCl_3$ (^{19}F) or 85% phosphoric acid (^{31}P). Coupling constants (*J*) are given in Hz. Unless they could only be determined from the ^{19}F NMR spectrum,

values of J_{FH} were determined from the ^1H NMR spectroscopic data, and those of J_{PF} from the ^{31}P NMR spectroscopic data, as these values were found to be most accurate. The threshold value for ^1H NMR detection was ≤ 2%; isomeric ratios given in the Exp. Sect. are *as observed* on NMR (cf. Table 4 and 5). − High resolution mass spectrometry was performed with a Finnigan MAT 900 equipped with an Electrospray Interface (ESI). Remaining mass spectra (ESI) were recorded either with the same apparatus, or with a Finnigan MAT TSQ70 triple quadrupole mass spectrometer equipped with a custom-made ESI. GC/MS spectra were recorded with a Finnigan MAT ITD 700 coupled with a Packard 438A GC. − Commercially available aldehydes and ketones were purified if necessary. THF was distilled from $LiAlH_4$ before use. Ethanol-free dichloromethane was prepared by washing with an equal volume of water and distillation from $CaCl_2$. Diisopropylamine was dried with KOH. Remaining reagents were used without further purification. LDA was freshly prepared by addition of *n*BuLi (1.6 M) to an ice-cooled solution of diisopropylamine in THF. The concentration of base was approximately 0.5 M. KHMDS (0.5−1.0 M in THF) was prepared by dissolving pure KHMDS in THF. Petroleum ether signifies the fraction with boiling range of 40−60 °C.

(Diphenylphosphinoyl)methyl *p*-Toluenesulfonate (2):[11,13] *p*-Tosyl chloride (84.00 g, 1.1 equiv.) in THF (400 mL) was added dropwise over 1 h to a solution of (diphenylphosphinoyl)methanol (**3**)[12] (92.89 g, 400.0 mmol) and triethylamine (83.2 mL) in THF (1.2 L), at −10 °C. After stirring overnight at 5 °C, water (600 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 250 mL) and the combined layers were washed with saturated brine (500 mL). After drying ($MgSO_4$), filtration, and evaporation of the solvents, recrystallization from ether/THF (1:1−1:2, v/v) gave **2** (141.39 g, 91%) as colorless crystals, m.p.[13] 124−125 °C (ref[11] 124−126 °C). − ^1H NMR: δ = 2.44 (s, 3 H), 4.60 (d, J_{PH} = 7.2 Hz), 7.27 (d, 2 H, J_{PH} = 7.7 Hz), 7.46−7.68 (m, 8 H), 7.70−7.78 (m, 4 H). − ^{13}C NMR: δ = 21.0, 64.4 (d, J_{PC} = 82.4 Hz), 127.5−132.3, 145.0. − ^{31}P NMR: δ = 26.2.

(Fluoromethyl)diphenylphosphane Oxide (1): *p*-Toluenesulfonate **2** (19.32 g, 50 mmol) and anhydrous KF (29.05 g, 10 equiv.) were suspended in TEG (400 mL). The temperature was raised to 160 °C, and the mixture was heated for an additional 15 min. The mixture was poured into ice-cold water (1 L) and the solution was extracted with CH_2Cl_2 (4 × 150 mL). The combined organic layers were washed with water (4 × 400 mL) and saturated brine (100 mL), and dried with $MgSO_4$. After filtration, the solvent was removed under reduced pressure. Purification by column chromatography (petroleum ether/ethyl acetate, 2:3), gave 9.37 g (80%) of **1** as a colorless solid, m.p. 95−95.5 °C (petroleum ether/toluene). − R_f = 0.08. − ^1H NMR: δ = 5.18 (dd, 2 H, J_{FH} = 47.2 Hz, J_{PH} = 3.3 Hz), 7.47−7.65 (m, 6 H), 7.77−7.87 (m, 4 H). − ^{13}C NMR: δ = 80.1 (dd, J_{FC} = 189.2 Hz, J_{PC} = 83.9 Hz), 128.5 −132.4. − ^{19}F NMR: δ = −242.3. − ^{31}P NMR: δ = 25.7 (d, J_{PF} = 48.8 Hz). − HRMS; *m*/*z*: [$C_{13}H_{12}FOP^+$ + H] calcd. 235.0688; found 235.0638.

Treatment of (Diphenylphosphinoyl)methanol (3) with DAST: (Diphenylphosphinoyl)methanol (**3**) (4.1 mmol) in ethanol-free CH_2Cl_2 (20 mL) was added at 0 °C to a solution of DAST (4.0 mmol) in CH_2Cl_2 (5 mL) under nitrogen. After stirring at room temperature for 64 h, the mixture was quenched with saturated aqueous K_2CO_3, after which the organic layer was washed with water and saturated brine, and dried with $MgSO_4$. After filtration and removal of the solvent, products were separated by column chromatography (petroleum ether/ethyl acetate, 1:1), affording (in order of elution) **5**, an unidentified phosphorus difluoride [R_f = 0.21; 0.17 g; δ(P): −53.3 (t, J = 696 Hz, PF_2)], and **4**.

(Benzyl)(phenyl)phosphinic Fluoride (5):[21] R_f = 0.53. − Yield: 0.19 g (20%). − M.p., ^1H and ^{19}F NMR spectroscopic data have been reported for this compound, but with an erroneous structure assigned to them;[3] see also Table 1. − Colorless solid, m.p. 95 °C (ref.[3] 93−94 °C). − ^1H NMR: δ = 3.48 (dd, 2 H, J_{FH} = 18.3 Hz, J_{PH} = 5.1 Hz), 7.10−7.15 (m, 2 H), 7.24−7.29 (m, 3 H), 7.40−7.49 (m, 2 H), 7.57−7.67 (m, 3 H). − ^{13}C NMR: δ = 36.8 (dd, J_{FC} = 91.6 Hz, J_{PC} = 18.3 Hz), 127.1−133.3. − ^{19}F NMR: δ = −76.9 (d). − ^{31}P NMR: δ = 49.8 (J_{PF} = 1034 Hz). − A second signal in the ^{19}F NMR spectrum at δ = −54.0 (d, J_{PF} = 696 Hz) was probably due to a dimeric form, which was observed solely in a mass spectrum. − MS (ESI); *m*/*z*: 491 [(2 M)$^+$ + Na], 469 [(2 M)$^+$ + H].

Bis[(diphenylphosphinoyl)methyl] Sulfite (4): R_f = 0.01. − Yield: 0.42 g (63%). − Colorless solid, m.p. 164−166 °C. − ^1H NMR: δ = 4.41 (dd, 2 H, J_{PH} = 6.2 Hz, J = 13.2 Hz), 4.57 (dd, 2 H, J_{PH} = 4.8 Hz, J = 13.2 Hz), 7.44−7.62 (m, 12 H), 7.70−7.83 (m, 8 H). − ^{13}C NMR: δ = 54.7 (d, J_{PC} = 83.9 Hz), 128.6−132.5. − ^{31}P NMR: δ = 27.3. − MS (ESI); *m*/*z*: 510 [M$^+$ + H], 279 [M$^+$ − **3**].

Synthesis of (α-Fluoro-β-hydroxyalkyl)phosphane Oxides 7: LDA (4.2 mmol) was added to a solution of phosphane oxide **1** (1.02 g. 4.3 mmol) in THF (100 mL), at −70 °C. Use of excess base resulted in significantly lower yields with enolizable aldehydes and ketones. After 5 min, the appropriate carbonyl compound (4.0 mmol) in THF (5 mL) was added. Stirring was continued at −70 °C for 15 min. The reaction was quenched with saturated aqueous NH_4Cl. After addition of water to dissolve remaining solids, the layers were separated. The aqueous layer was extracted with ether (3 × 20 mL), and the combined organic layers were washed with saturated brine and dried ($MgSO_4$). After filtration, solvents were removed under reduced pressure, and the crude reaction product was analyzed by NMR. The compounds were purified by column chromatography: eluents were as specified. Trituration was applied in various cases for (further) purification, as mentioned for the individual compounds. Adducts **7** were usually white solids; exceptions are mentioned. Conversion, overall yields, and diastereomeric ratios are given in Table 2 (aldehydes, **7a**−**m**) and Table 3 (ketones, **7n**−**v**).

2-(Diphenylphosphinoyl)-2-fluoro-1-phenylethanol (7a): Chromatography (ether) gave **7a** as a mixture of isomers. The *l* isomer decomposed slowly at room temperature into fluoro olefin ***Z*-8a** and diphenylphosphinic acid. − R_f = 0.36 (petroleum ether/ethyl acetate, 1:1). − ^1H NMR: δ = 4.10 (br., 1 H), 4.93−5.04 (m, 1 H), 5.10 (m, 0.6 H, *u*), 5.35 (m, 0.4 H, *l*), 7.23−7.42 (m, 5 H), 7.43−7.70 (m, 6 H), 7.78−7.95 (m, 4 H). − ^{13}C NMR: δ = 71.3 (d, J_{FC} = 15.3 Hz, *l*), 71.4 (d, J_{FC} = 21.6 Hz, *u*), 90.2 (dd, J_{FC} = 196.8 Hz, J_{PC} = 80.9 Hz, *u*), 93.6 (dd, J_{FC} = 199.9 Hz, J_{PC} = 82.4 Hz, *u*), 125.6−132.6, 138.7 (d, J_{FC} = 10.7 Hz, *u*), 139.1 (d, J_{FC} = 6.1 Hz, *l*). − ^{19}F NMR: δ = −217.8 (J_{FH} = 45.8 Hz, 27.7 Hz, *l*), −202.0 (J_{FH} = 44.3 Hz, *u*). − ^{31}P NMR: δ = 29.4 (J_{PF} = 64.7 Hz, *l*), 32.3 (J_{PF} = 61.0 Hz, *u*). − MS (ESI): *m*/*z* = 363 [M$^+$ + Na], 341 [M$^+$ + H].

1-(2-Chlorophenyl)-2-(diphenylphosphinoyl)-2-fluoroethanol (7b): Chromatography (ether) gave Fraction 1 (**7b**, impure mixture of isomers); (→ ethyl acetate) gave Fraction 2 (**1/7b** = 33:67). Fraction 1 was purified by trituration with petroleum ether [0.90 g (59%), *u*/*l* = 67:33]. Trituration of Fraction 2 with ether gave pure **7b** [0.21 g (14%), *u*/*l* = 10:90]. − **(1*R**,2*S**) Isomer (*u*-7b):** R_f = 0.54 (ether). − ^1H NMR: δ = 5.00 (br., 1 H), 5.20 (ddd, 1 H, J_{FH} = 46.0 Hz, J_{PH} = 8.8 Hz, J = 2.2 Hz), 5.66 (ddd, 1 H, J_{PH} = 19.7 Hz,

J_{FH} = 10.9, J = 2.2), 7.13−7.35 (m, 3 H), 7.49−7.71 (m, 7 H), 7.76−7.97 (m, 4 H). − ^{13}C NMR: δ = 68.0 (d, J_{FC} = 21.4 Hz), 90.6 (dd, J_{FC} = 198.4 Hz, J_{PC} = 82.4 Hz), 126.7−132.6, 136.3. − ^{19}F NMR: δ = −202.5 (J_{FH} = 46.0 Hz). − ^{31}P NMR: δ = 32.3 (d, J_{PF} = 61.0 Hz). − **(1*R**,2*R**) Isomer (*l*-7b):** R_f = 0.42 (ether). − ^{1}H NMR: δ = 5.42 (dd, 1 H, J_{FH} = 45.3 Hz, J_{PH} = 5.8 Hz), 5.62 (d, 1 H, J_{FH} = 30.0 Hz), 7.19−7.36 (m, 2 H), 7.50−7.71 (m, 7 H), 7.77−7.96 (m, 5 H). − ^{13}C NMR ([D$_4$]methanol): δ = 68.2 (d, J_{FC} = 16.8 Hz), 92.3 (dd, J_{FC} = 198.4, J_{PC} = 83.9), 127.3−133.2, 137.0. − ^{19}F NMR: δ = −224.1 (J_{FH} = 45.3 Hz, 30.0). − ^{31}P NMR: δ = 31.7 (d, J_{PF} = 65.9 Hz). − MS (ESI); *m*/*z*: 397 [M$^+$ + Na], 375 [M$^+$ + H].

2-(Diphenylphosphinoyl)-2-fluoro-1-(4-methoxyphenyl)ethanol (7c): Chromatography (ether) gave Fraction 1 [0.80 g (54%), *u*/*l* = 92:8], and Fraction 2 [0.30 g (20%), *u*/*l* = 22:78]. The compound was unstable at room temperature, slowly losing diphenylphosphinic acid to give fluoro olefin **8c**. The *l* isomer was the more labile. − **(1*R**,2*S**) Isom**er **(*u*-7c):** R_f = 0.50. − ^{1}H NMR: δ = 3.78 (s, 3 H), 4.89 (s, 1 H), 4.88−4.98 (m, 1 H), 5.10 (ddd, 1 H, J_{FH} = 44.3 Hz, J_{PH} = 2.2 Hz, J = 9.5 Hz), 6.85 (d, 2 H, J = 8.0 Hz), 7.28 (d, 2 H, J = 8.0 Hz), 7.50−7.64 (m, 6 H), 7.82−7.94 (m, 4 H). − ^{13}C NMR: δ = 54.3, 70.4 (d, J_{FC} = 21.4 Hz), 91.3 (dd, J_{FC} = 193.8 Hz, J_{PC} = 83.9 Hz), 112.8, 127.8−132.0, 158.9. − ^{19}F NMR: δ = −203.9 (J_{FH} = 44.3 Hz). − ^{31}P NMR: δ = 32.1 (d, J_{PF} = 62.3 Hz). − **(1*R**,2*R**) Isomer (*l*-7c):** R_f = 0.40. − ^{1}H NMR: δ = 3.77 (s, 3 H), 3.93 (br., 1 H), 5.30 (ddd, 1 H, J_{FH} = 46.0 Hz, J_{PH} = 2.9 Hz, J = 2.9 Hz), 5.30 (m, 1 H), 6.79 (d, 2 H, J = 8.8 Hz), 7.28 (d, 2 H, J = 8.8 Hz), 7.47−7.61 (m, 6 H), 7.76−7.91 (m, 4 H). − ^{13}C NMR: δ = 54.9, 70.8 (d, J_{FC} = 18.3 Hz), 94.0 (dd, J_{FC} = 198.4 Hz, J_{PC} = 83.9 Hz), 113.4, 128.1−132.1, 159.1. − ^{19}F NMR: δ = −214.7 (J_{FH} = 46.0 Hz, 24.4 Hz). − ^{31}P NMR: δ = 29.0 (d, J_{PF} = 64.7 Hz). − MS (ESI): *m*/*z* = 393 [M$^+$ + Na], 371 [M$^+$ + H], 353 [M$^+$ − OH].

1-(Biphenyl-4-yl)-2-(diphenylphosphinoyl)-2-fluoroethanol (7d): Chromatography (petroleum ether/ethyl acetate, 1:1) gave **7d** as a mixture of isomers: R_f = 0.34, 0.29. − ^{1}H NMR: δ = 4.16 (br., 0.3 H, *l*), 5.00 (br., 0.7 H, *u*), 5.10 (m, 1 H), 5.16 (ddd, 0.7 H, J_{FH} = 44.6 Hz, J_{PH} = 2.2 Hz, J = 8.8 Hz, *u*), 5.40 (m, 0.3 H, *l*), 7.33−7.65 (m, 15 H), 7.82−7.96 (m, 4 H). − ^{13}C NMR: δ = 70.7 (*u*), 71.1 (*l*), 91.2 (dd, J_{FC} = 195.3 Hz, J_{PC} = 80.9 Hz, *u*), 94.0 (dd, J_{FC} = 199.9 Hz, J_{PC} = 83.9 Hz, *l*), 126.4−132.2, 137.8, 140.3 (*l*), 140.6 (*u*). − ^{19}F NMR: δ = −215.5 (J_{FH} = 45.3 Hz, 26.5 Hz, *l*), −203.1 (J_{FH} = 44.6 Hz, 8.9 Hz, *u*). − ^{31}P NMR: δ = 29.3 (d, J_{PF} = 63.5 Hz, *l*), 32.2 (d, J_{PF} = 61.0 Hz, *u*). − MS (ESI); *m*/*z*: 439 [M$^+$ + Na], 417 [M$^+$ + H].

2-(Diphenylphosphinoyl)-2-fluoro-1-(4-nitrophenyl)ethanol (7e): Chromatography (ethyl acetate) afforded **7e** as a mixture of isomers, along with some remaining **1** (R_f = 0.48). Trituration with ether gave pure **7e** as a pale yellow solid. Although the *u* isomer appeared to be more soluble than the *l* isomer in methanol and chloroform, permitting the preparation of mixtures enriched in one isomer, complete separation was not achieved. − ^{1}H NMR: δ = 4.77−5.50 (m, 2 H), 7.42−7.61 (m, 8 H), 7.69−7.95 (m, 4 H), 8.07−8.19 (m, 2 H). − Other NMR spectroscopic data could be assigned to the individual isomers. − **(1*R**,2*S**) Isomer (*u*-7e):** ^{13}C NMR ([D$_4$]methanol): δ = 70.6 (d, J_{FC} = 19.8 Hz), 90.6 (dd, J_{FC} = 198.4 Hz, J_{PC} = 82.4 Hz), 122.8, 128.0−132.6, 146.2 (d, J_{FC} = 7.6 Hz), 147.3. − ^{19}F NMR: δ = −205.5 (J_{FH} = 49.7 Hz, 7.9). − ^{31}P NMR: δ = 32.2 (d, J_{PF} = 59.8 Hz). − **(1*R**,2*R**) Isomer (*l*-7e):** ^{13}C NMR: δ = 70.1 (d, J_{FC} = 6.1 Hz), 93.7 (dd, J_{FC} = 199.9 Hz, J_{PC} = 83.9 Hz), 122.8, 123.0, 127.7−132.0, 146.5, 147.3. − ^{19}F NMR: δ = −215.9 (J_{FH} = 45.3 Hz, 18.3 Hz). − ^{31}P NMR: δ = 30.0 (d, J_{PF} = 62.3 Hz). − MS (ESI); *m*/*z*: 408 [M$^+$ + Na], 386 [M$^+$ + H], 235 [**1**$^+$ + H].

2-(Diphenylphosphinoyl)-2-fluoro-1-(pyridin-2-yl)ethanol (7f): Chromatography (petroleum ether/ethyl acetate/triethylamine, 40:60:1 → ethyl acetate/triethylamine, 50:1) gave Fraction 1 [0.54 g (40%), *u*/*l* = 79:21; slightly brown oil] and Fraction 2 [0.56 g (41%), *u*/*l* = 16:84]. − **(1*R**,2*S**) Isomer (*u*-7f):** R_f = 0.18 (ethyl acetate). − ^{1}H NMR: δ = 5.20 (s, 1 H), 5.18−5.30 (m, 1 H), 5.57 (ddd, 1 H, J_{FH} = 45.6 Hz, J_{PH} = 3.0 Hz, J = 3.6 Hz), 7.11−7.18 (m, 1 H), 7.43−7.66 (m, 11 H), 7.74−7.93 (m, 5 H), 8.48 (d, 1 H, J = 4.9 Hz). − ^{13}C NMR: δ = 72.3 (d, J_{FC} = 21.4 Hz), 91.0 (d, J_{FC} = 193.8 Hz, J_{PC} = 83.9 Hz), 121.7, 122.2, 127.7−131.4, 135.8, 147.8, 157.3. − ^{19}F NMR: δ = −205.6 (J_{FH} = 45.6 Hz, 10.2 Hz). − ^{31}P NMR: δ = 31.1 (J_{PF} = 62.2 Hz). − **(1*R**,2*R**) Isomer (*l*-7f):** R_f = 0.15 (ethyl acetate). − ^{1}H NMR: δ = 5.16 (d, 1 H, J_{FH} = 3.7 Hz), 5.41 (br. d, 1 H, J_{FH} = 30.7 Hz), 5.76 (ddd, 1 H, J_{FH} = 45.3 Hz, J_{PH} = 2.9 Hz, J = 1.5 Hz), 7.11−7.21 (m, 1 H), 7.44−7.74 (m, 11 H), 7.77−7.94 (m, 5 H), 8.45−8.51 (m, 1 H). − ^{13}C NMR: δ = 71.4 (d, J_{FC} = 18.3 Hz), 93.0 (dd, J_{FC} = 198.4 Hz, J_{PC} = 85.4 Hz), 121.4, 122.4, 128.1−132.3, 136.7, 148.0, 158.2 (d, J_{FC} = 4.6 Hz) − ^{19}F NMR: δ = −220.8 (J_{FH} = 45.3 Hz, 30.7 Hz). − ^{31}P NMR: δ = 30.1 (J_{PF} = 64.7 Hz). − MS (ESI); *m*/*z*: 364 [M$^+$ + Na], 342 [M$^+$ + H], 322 [M$^+$ − F].

4-[4-(Dimethylamino)phenyl]-1-(diphenylphosphinoyl)-1-fluorobut-3-en-2-ol (7g): Chromatography (petroleum ether/ethyl acetate, 2:3) gave a mixture of **7g** and starting material (R_f = 0.09; *u*/*l*/**1** = 65:25:10), which after trituration with ether afforded pure **7g** as an orange-yellow solid. − ^{1}H NMR: δ = 2.94 (s, 6 H), 3.64 (d, 0.3 H, J = 5.1 Hz, *l*), 4.44 (br., 0.7 H, *u*), 4.67 (m, 0.7 H, *u*), 5.12 (ddd, 0.7 H, J_{FH} = 46.0 Hz, J_{PH} = 2.2 Hz, J = 8.4 Hz, *u*), 5.20−5.26 (m, 0.3 H, *l*), 5.31 (ddd, 0.3 H, J_{FH} = 46.0 Hz, J_{PH} = 2.2 Hz, J = 3.7 Hz, *l*), 5.89−6.04 (m, 2 H), 7.40−7.61 (m, 10 H), 7.80−7.92 (m, 4 H). − ^{13}C NMR: δ = 40.3, 71.0 (d, J_{FC} = 19.8 Hz, *u*), 71.6 (d, J_{FC} = 18.3 Hz, *l*), 90.2 (dd, J_{FC} = 196.8 Hz, J_{PC} = 80.9 Hz, *u*), 92.7 (dd, J_{FC} = 197.6 Hz, J_{PC} = 83.2 Hz, *l*), 112.0, 121.3−133.4, 150.2. − ^{19}F NMR: δ = −213.1 (J_{FH} = 46.0 Hz, 22.6 Hz, *l*), −204.3 (J_{FH} = 46.0 Hz, *u*). − ^{31}P NMR: δ = 28.6 (d, J_{PF} = 68.3 Hz, *l*), 31.5 (d, J_{PF} = 61.0 Hz, *u*). − MS (ESI); *m*/*z*: 432 [M$^+$ + Na], 410 [M$^+$ + H], 392 [M$^+$ − OH].

1-(Diphenylphosphinoyl)-1-fluoro-4-(furan-2-yl)but-3-en-2-ol (7h): Chromatography (ether → ethyl acetate) gave **7h** as a mixture of isomers: R_f = 0.51 (ethyl acetate). − ^{1}H NMR: δ = 3.82 (d, 0.3 H, J = 6.2 Hz, *l*), 4.60 (s, 0.7 H, *u*), 4.67 (m, 1 H), 5.07 (ddd, 0.7 H, J_{FH} = 45.9 Hz, J_{PH} = 2.4 Hz, J = 8.8 Hz, *u*), 5.31 (m, 0.3 H, *l*), 6.00−6.23 (m, 2 H), 6.32−6.36, (m, 1 H), 6.54 (d, 1 H, J = 16.1), 7.31 (d, 1 H, J = 1.5), 7.39−7.66 (m, 6 H), 7.78−7.91 (m, 4 H). − ^{13}C NMR: δ = 69.6 (d, J_{FC} = 18.3 Hz, *u*), 69.9 (d, J_{FC} = 15.3 Hz, *l*), 91.1 (dd, J_{FC} = 195.3 Hz, J_{PC} = 83.4 Hz, *u*), 92.8 (dd, J_{FC} = 198.4 Hz, J_{PC} = 87.0 Hz, *l*), 108.2, 110.8, 120.1 (*l*), 120.5 (*u*), 124.6−132.1, 141.5, 151.7. − ^{19}F NMR: δ = −212.4 (J_{FH} = 45.2 Hz, 22.6 Hz, *l*), −207.1 (J_{FH} = 45.9 Hz, 11.3 Hz, *u*). − ^{31}P NMR: δ = 29.1 (d, J_{PF} = 61.0 Hz, *l*) 31.8 (d, J_{PF} = 59.8 Hz, *u*). − MS (ESI); *m*/*z*: 379 [M$^+$ + Na], 357 [M$^+$ + H], 339 [M$^+$ − OH].

1-(Diphenylphosphinoyl)-1-fluoroundecan-2-ol (7i): Chromatography (petroleum ether/ethyl acetate, 1:1) gave Fraction 1 [0.73 g (48%), *u*/*l* = 97:3], overlapping Fractions 1−2 [0.11 g (7%), *u*/*l* = 56:44], and Fraction 2 [0.20 g (14%), *u*/*l* = 0:100]. − **(1*R**,2*S**) Isomer (*u*-7i):** R_f = 0.64. − ^{1}H NMR: δ = 0.87 (t, 3 H, J = 6.6 Hz), 1.24−1.30 (m, 10 H), 1.42−1.60 (m, 6 H), 4.02−4.10 (m, 1 H), 4.24 (br., 1 H), 5.00 (ddd, 1 H, J_{FH} = 46.8 Hz, J_{PH} = 2.2 Hz, J = 9.5 Hz), 7.47−7.65 (m, 6 H), 7.80−7.92 (m, 4 H). − ^{13}C NMR:

δ = 13.6, 22.1, 24.2, 28.8, 29.0 (3 ×), 31.3, 32.3 (d, J_{FC} = 4.6 Hz), 68.6 (d, J_{FC} = 21.4 Hz), 90.9 (dd, J_{FC} = 196.0 Hz, J_{PC} = 83.1 Hz), 127.9−132.1. − ^{19}F NMR: δ = −204.9 (J_{FH} = 46.8 Hz). − ^{31}P NMR: δ = 31.6 (J_{PF} = 62.2 Hz). − MS (ESI); *m/z*: 413 [M$^+$ + Na], 391 [M$^+$ + H]. − **(1*R**,2*R**) Isomer (*l*-7i):** R_f = 0.55. − ^{1}H NMR: δ = 0.87 (t, 3 H, *J* = 6.6 Hz), 1.22−1.29 (m, 14 H), 1.53−1.67 (m, 2 H), 4.17 (m, 1 H), 5.15 (dd, J_{FH} = 46.1 Hz, J_{PH} = 1.5 Hz), 7.44−7.60 (m, 6 H), 7.79−7.93 (m, 4 H). − ^{13}C NMR: δ = 13.9, 22.4, 25.2, 29.0, 29.2 (3 ×), 31.6, 32.6, 69.5 (d, J_{FC} = 18.3 Hz), 92.9 (dd, J_{FC} = 194.6 Hz, J_{PC} = 85.5 Hz), 128.2−132.3. − ^{19}F NMR: δ = −217.8 (J_{FH} = 46.1 Hz, 26.5 Hz). − ^{31}P NMR: δ = 28.7 (J_{PF} = 63.4 Hz).

1-(Diphenylphosphinoyl)-1-fluoro-4-phenylbutan-2-ol (7j): Prepared on a 10-mmol scale. Chromatography (petroleum ether/ethyl acetate, 2:3) gave **7j** as a mixture of isomers: R_f = 0.39, 0.28. − ^{1}H NMR: δ = 1.75−2.12 (m, 2 H), 2.58−2.97 (m, 2 H), 4.10 (ddt, J_{FH} = 9.5 Hz, *J* = 9.1 Hz, 2.9 Hz, *u*), 4.20−4.25 (m, *l*) [comb.: 1 H], 4.38 (br., 1 H), 5.04 (ddd, 0.7 H, J_{FH} = 46.8 Hz, J_{PH} = 1.8 Hz, *J* = 9.5 Hz, *u*), 5.12 (ddd, 0.3 H, J_{FH} = 46.4 Hz, J_{PH} = 1.9 Hz, *J* = 1.5 Hz, *l*), 7.19−7.28 (m, 5 H), 7.45−7.65 (m, 6 H), 7.76−7.91 (m, 4 H). − ^{13}C NMR: δ = 30.4 (*u*), 30.9 (*l*), 33.9, 67.9 (d, J_{FC} = 19.8 Hz, *u*), 68.2 (d, J_{FC} = 16.8 Hz, *l*), 91.1 (dd, J_{FC} = 195.3 Hz, J_{PC} = 87.9 Hz, *u*), 93.1 (dd, J_{FC} = 193.8 Hz, J_{PC} = 95.4 Hz, *l*), 125.1−132.0, 140.9 (*l*), 141.2 (*u*). − ^{19}F NMR: δ = −216.7 (J_{FH} = 46.4 Hz, 27.1 Hz, *l*), −205.0 (J_{FH} = 46.8 Hz, 9.5 Hz, *u*). − ^{31}P NMR: δ = 29.0 (J_{PF} = 63.5 Hz, *l*), 31.9 (J_{PF} = 61.0 Hz, *u*). − MS (ESI); *m/z*: 391 [M$^+$ + Na], 369 [M$^+$ + H].

2-(Diphenylphosphinoyl)-2-fluoro-1-(1-phenylcyclopropyl)ethanol (7k): Trituration of the crude product from CH_2Cl_2 gave a proportion of the *l* isomer [0.21 g (13%)] in pure form. Chromatography (petroleum ether/ethyl acetate, 1:1) gave remaining **7k** as a mixture of isomers [0.69 g (45%)]. A pure sample of the *u* isomer was obtained by trituration with ether/CH_2Cl_2. − **(1*R**,2*S**) Isomer (*u*-7k):** ^{1}H NMR: δ = 0.60−1.04 (m, 4 H), 3.34 (dd, 1 H, *J* = 9.5 Hz, *J* = 9.2 Hz), 4.42 (s, 1 H), 4.79 (ddd, 1 H, J_{FH} = 46.0 Hz, J_{PH} = 1.5 Hz, *J* = 10.2 Hz), 7.24−7.34 (m, 5 H), 7.45−7.66 (m, 6 H), 7.71−7.90 (m, 4 H). − ^{13}C NMR: δ = 10.5, 11.3, 29.6 (d, J_{FC} = 10.7 Hz), 76.7 (d, J_{FC} = 22.9 Hz), 90.5 (dd, J_{FC} = 190.7 Hz, J_{PC} = 85.4 Hz), 127.8, 128.7, 129.2−129.7, 131.9−133.5, 132.4, 141.2. − ^{19}F NMR: δ = −202.8 (J_{FH} = 46.0 Hz). − ^{31}P NMR: δ = 29.2 (J_{PF} = 63.5 Hz). − MS (ESI); *m/z*: 403 [M$^+$ + Na], 381 [M$^+$ + H], 343 [M$^+$ − H_2O − F]. − **(1*R**,2*R**) Isomer (*l*-7k):** ^{1}H NMR: δ = 0.56−0.62 (m, 1 H), 0.86−0.97 (m, 1 H), 0.99−1.09 (m, 1 H), 1.15−1.20 (m, 1 H), 3.44 (d, 1 H, *J* = 5.1 Hz), 4.25 (ddd, 1 H, J_{FH} = 30.0 Hz, *J* = 4.4 Hz), 5.19 (ddd, 1 H, J_{FH} = 48.0 Hz, J_{PH} = 1.6 Hz, *J* = 3.0 Hz), 7.24−7.34 (m, 5 H); 7.45−7.90 (m, 10 H). − ^{13}C NMR ([D$_4$]methanol): δ = 8.8, 8.9, 29.0 (d, J_{FC} = 10.7 Hz), 72.2 (d, J_{FC} = 16.8 Hz), 92.6 (dd, J_{FC} = 196.8 Hz, J_{PC} = 87.0 Hz), 127.6−133.4, 143.1. − ^{19}F NMR: δ = −223.8 (J_{FH} = 48.0 Hz, 30.0 Hz). − ^{31}P NMR: δ = 32.0 (J_{PF} = 59.8 Hz).

3-Benzyloxy-1-(diphenylphosphinoyl)-1-fluoropropan-2-ol (7l): Chromatography (ethyl acetate) afforded **7l** (mixture of isomers), as a colorless oil: R_f = 0.57. − ^{1}H NMR: δ = 3.66 (m, 1.2 H, *u*), 3.72 (m, 0.8 H, *l*), 4.28−4.64 (m, 3 H), 5.39 (ddd, 0.6 H, J_{FH} = 45.3 Hz, J_{PH} = 2.2 Hz, *J* = 2.2 Hz, *u*), 5.43 (d, 0.4 H, J_{FH} = 46.0 Hz, *l*), 7.28−7.32 (m, 5 H), 7.37−7.58 (m, 6 H), 7.82 (m, 4 H). − ^{13}C NMR: δ = 67.2 (d, J_{FC} = 16.8 Hz, *l*), 68.4 (d, J_{FC} = 21.4 Hz, *u*), 68.6 (*l*), 69.4 (*u*), 72.1 (*l*), 72.4 (*u*), 88.4 (dd, J_{FC} = 193.0 Hz, J_{PC} = 84.7 Hz, *u*), 90.4 (dd, J_{FC} = 193.7 Hz, J_{PC} = 85.5 Hz, *l*), 126.7−131.6, 137.1, 137.2. − ^{19}F NMR: δ = −221.6 (J_{FH} = 46.0 Hz, 24.4 Hz, *l*), −208.5 (J_{FH} = 45.3 Hz, *u*). − ^{31}P NMR: δ = 29.7 (J_{PF} = 63.5 Hz, *l*), 31.5 (J_{PF} = 59.8 Hz, *u*). − MS (ESI); *m/z*: 407 [M$^+$ + Na], 385 [M$^+$ + H].

***tert*-Butyl 4-[2-(Diphenylphosphinoyl)-2-fluoro-1-hydroxyethyl]-2,2-dimethyl-3-oxazolidinecarboxylate (7m):** NMR analysis was hampered by the occurrence of rotamers. Chromatography (ether → ether/ethyl acetate, 1:1) afforded **7m** as a mixture of isomers: R_f = 0.18 (ether). − ^{1}H NMR: δ = 0.83−0.96 (br. m, 3 H), 1.25 (br., 9 H), 1.43−1.49, 1.67−1.79 (2 × br. m, 3 H), 3.93 (dd, 1 H, *J* = 9.1 Hz, 7.2 Hz), 4.14 (br., 1 H), 4.20−4.34 (m, 2 H), 4.48 (br., 0.6 H, *pro-E*), 4.54 (br., 0.4 H, *pro-Z*), 5.12 (br. d, 0.6 H, J_{FH} = 46.4 Hz, *J* = 8.0 Hz, *pro-E*), 5.50 (br., 50% of 0.4 H,), 7.52−7.56 (m, 6 H), 7.82−7.91 (m, 4 H). − ^{19}F NMR: δ = −221.8 (*pro-Z*, *major*), −206.6 (*pro-E*, *major*, 1 rotamer), −204.3 (*minor*), −203.7 (*pro-E*, *major*, 1 rotamer). − ^{31}P NMR: δ = 28.9 (J_{PF} = 65.9 Hz, *pro-Z*, *major*); 30.5 (J_{PF} = 62.3 Hz, *pro-E*, *major*); no other isomers noted; saturated sample (at low concentrations, rotamers made assignments impossible). − MS (ESI); *m/z*: 486 [M$^+$ + Na], 464 [M$^+$ + H], 386 [M$^+$ − BOC + Na], 364 [M$^+$ + H − BOC].

9-[(Diphenylphosphinoyl)fluoromethyl]-9*H*-fluoren-9-ol (7n): Purified by chromatography (ether). − ^{1}H NMR: δ = 5.47 (dd, 1 H, J_{FH} = 45.0 Hz, J_{PH} = 2.6 Hz), 6.99−7.12 (m, 2 H), 7.24−7.78 (m, 16 H). − ^{13}C NMR: δ = 82.2 (d, J_{FC} = 19.8 Hz), 93.4 (dd, J_{FC} = 200.6 Hz, J_{PC} = 81.6 Hz), 119.0, 124.5−131.2, 139.2, 139.3, 143.6, 143.8. − ^{19}F NMR: δ = −199.7. − ^{31}P NMR: δ = 30.0 (J_{PF} = 67.1 Hz). − MS (ESI); *m/z*: 437 [M$^+$ + Na], 415 [M$^+$ + H].

1-(Diphenylphosphinoyl)-1-fluoro-2-phenylpropan-2-ol (7o): Chromatography (petroleum ether/ether, 1:1) gave **7o** as a mixture of isomers. During evaporation of the eluent, the major isomer precipitated and could be obtained in pure form [0.62 g (44%), *u*]. The minor isomer was isolated pure after repeated chromatography [0.41 g (29%), *u*/*l* = 3:97]. Correct stereochemistry of the products was deduced from the final outcome of the Horner−Wittig reaction. − **(1*R**,2*S**) Isomer (*u*-7o):** ^{1}H NMR: δ = 1.69 (d, 3 H, J_{FH} = 2.2 Hz), 5.78 (dd, 1 H, J_{FH} = 44.6 Hz, J_{PH} = 5.1 Hz), 7.04−7.09 (m, 3 H), 7.32−7.60 (m, 10 H), 7.73−7.83 (m, 2 H). − ^{13}C NMR: δ = 27.2 (dd, J_{FC} = J_{PC} = 4.6 Hz), 77.5 (d, J_{FC} = 18.3 Hz), 95.4 (dd, J_{FC} = 197.6 Hz, J_{PC} = 83.2 Hz), 127.0−133.4, 144.4. − ^{19}F NMR: δ = −201.9. − ^{31}P NMR: δ = 30.8 (d, J_{PF} = 65.9 Hz). − **(1*R**,2*R**) Isomer (*l*-7o):** ^{1}H NMR ([D$_4$]methanol): δ = 1.78 (d, 3 H, J_{FH} = 1.5 Hz), 5.70 (dd, 1 H, J_{FH} = 44.6 Hz, J_{PH} = 2.9 Hz), 7.06−7.14 (m, 3 H), 7.33−7.49 (m, 8 H), 7.60−7.74 (m, 4 H). − ^{13}C NMR ([D$_4$]methanol): δ = 26.9, 76.7 (d, J_{FC} = 18.3 Hz), 96.2 (dd, J_{FC} = 197.6 Hz, J_{PC} = 83.2 Hz), 127.0−133.3, 144.1. − ^{19}F NMR: δ = −199.4. − ^{31}P NMR: δ = 30.1 (d, J_{PF} = 61.0 Hz). − MS (ESI); *m/z*: 377 [M$^+$ + Na], 355 [M$^+$ + H], 337 [M$^+$ − OH].

1-[(Diphenylphosphinoyl)fluoromethyl]cyclododecanol (7p): Purified by chromatography (ether). − ^{1}H NMR: δ = 1.30 (br., 18 H), 1.62−1.79 (m, 4 H), 3.97 (s, 1 H), 5.09 (dd, 1 H, J_{FH} = 46.0 Hz, J_{PC} = 2.2 Hz), 7.42−7.57 (m, 6 H), 7.83−7.93 (m, 4 H). − ^{13}C NMR: δ = 18.4, 19.1, 21.9, 22.0, 22.5 (2 ×), 25.8, 26.2 (2 ×), 31.7, 32.8, 77.6 (d, J_{FC} = 18.3 Hz), 94.7 (dd, J_{FC} = 199.1 Hz, J_{PC} = 81.6 Hz), 128.2−132.3. − ^{19}F NMR: δ = −204.0. − ^{31}P NMR: δ = 30.4 (d, J_{PF} = 68.4 Hz). − MS (ESI); *m/z*: 439 [M$^+$ + Na], 417 [M$^+$ + H], 399 [M$^+$ − OH], 379 [M$^+$ − H_2O − F].

2-[(Diphenylphosphinoyl)fluoromethyl]adamantan-2-ol (7q): Trituration of the crude product from CH_2Cl_2 gave part of adduct **7q** in pure form. The remainder was purified by chromatography (ether). − ^{1}H NMR: δ = 1.38−1.53 (br. m, 4 H), 1.65 (br., 2 H), 1.77 (br., 4 H), 2.19−2.37 (br. m, 4 H), 4.10 (s, 1 H), 5.71 (dd, 1 H, J_{FH} = 46.8 Hz, J_{PH} = 3.7 Hz), 7.43−7.63 (m, 6 H), 7.82−7.96 (m, 4 H). − ^{13}C NMR: δ = 26.7, 26.8, 32.1 (2 ×), 33.2 (dd, J_{PC} = J_{FH} =

6.1 Hz), 33.6, 34.2, 34.9 (d, J = 3.1 Hz), 37.9, 78.4 (d, J_{FC} = 16.8 Hz), 91.4 (dd, J_{FC} = 193.8, J_{PC} = 83.9), 128.3−132.3. − ^{19}F NMR: δ = −213.0. − ^{31}P NMR: δ = 31.1 (d, J_{PF} = 72.0 Hz). − MS (ESI); *m/z*: 407 [M^+ + Na], 385 [M^+ + H], 367 [M^+ − OH].

4-*tert*-Butyl-1-[(diphenylphosphinoyl)fluoromethyl]cyclohexanol (7r): Trituration of the crude product from CH_2Cl_2 gave a proportion of the less soluble isomer in pure form [0.23 g (16%)]. The remainder was purified by chromatography (ether): Fraction 1 [0.13 g, (7%), less-soluble isomer], overlapping Fractions 1−2 [0.15 g (10%)], Fraction 2 [0.43 g (30%), soluble isomer]. Configuration of isomers (**1α,4β** or **1α,4β**) not assigned. − **Fraction 1 (7r-#1):** R_f = 0.54. − ^{1}H NMR: δ = 0.82 (s, 9 H), 1.26−1.78 (m, 7 H), 1.88 (br. d, 2 H, J = 10.2 Hz), 4.04 (s, 1 H), 5.02 (dd, 1 H, J_{FH} = 45.7 Hz, J_{PH} = 1.8 Hz), 7.46−7.58 (m, 6 H), 7.80−7.96 (m, 4 H). − ^{13}C NMR: δ = 21.1, 21.2, 26.0, 31.8, 33.0, 34.0, 46.7, 72.1 (d, J_{FC} = 18.3), 94.8 (dd, J_{FC} = 196.8 Hz, J_{PC} = 82.4 Hz), 128.2−132.1. − ^{19}F NMR: δ = −204.3. − ^{31}P NMR: δ = 29.0 (d, J_{PF} = 63.5). − **Fraction 2 (7r-#2):** R_f = 0.33. − ^{1}H NMR: δ = 0.78 (s, 9 H), 0.85−1.11 (m, 2 H), 1.21−1.63 (m, 5 H), 2.27 (br. d, 2 H, J = 13.9 Hz), 4.21 (s, 1 H), 5.36 (dd, 1 H, J_{FH} = 46.0 Hz, J_{PH} = 2.9 Hz), 7.48−7.62 (m, 6 H), 7.84−7.97 (m, 4 H). − ^{13}C NMR: δ = 23.1, 23.5, 27.1, 31.7, 34.8, 34.9, 36.5, 46.2, 74.4 (d, J_{FC} = 16.8 Hz), 91.3 (dd, J_{FC} = 196.1 Hz, J_{PC} = 83.2 Hz), 127.9−132.1. − ^{19}F NMR: δ = −210.3. − ^{31}P NMR: δ = 30.5 (d, J_{PF} = 70.8 Hz). − MS (ESI); *m/z*: 411 [M^+ + Na], 389 [M^+ + H], 371 [M^+ − OH], 351 [M^+ − H_2O − F].

1-[(Diphenylphosphinoyl)fluoromethyl]-2-phenylcyclohexanol (7s): The crude product consisted of four components, in a 55:29:9:7 ratio (^{31}P NMR). Chromatography (petroleum ether/ether, 1:1) resulted in partial separation of the isomers: Fraction 1 (0.84 g, mixture of two isomers), overlapping Fractions 1−2 [0.11 g (10%), 28:48:0:24], Fraction 2 [0.06 g (5%), 0:20:0:80]; (→ ether): Fraction 3 [0.10 g (9%), 0:0:100:0]. Fraction 1 was purified further by trituration from ether: soluble isomer [0.58 g (51%), 97:3:0:0), insoluble isomer [0.29 g (25%), 10:90:0:0]. − The stereochemistry of the products was deduced from the favored mode of addition[25] and final outcome of the Horner−Wittig reaction. − **Fraction 1, Soluble Isomer (1′*R**,1*S**,2*S**-7s):** R_f = 0.21. − ^{1}H NMR: δ = 1.18−1.94 (m, 6 H), 2.18 (dt, 1 H, J = 13.2 Hz, 3.1 Hz), 2.83 (br. d, 1 H, J = 13.2 Hz), 4.18 (dd, 1 H, J = 1.8 Hz, 1.5 Hz), 4.85 (d, 1 H, J_{FH} = 45.0 Hz). − ^{13}C NMR: δ = 20.7, 25.7, 28.3, 33.6, 48.7 (d, J_{FC} = 7.6 Hz), 74.9 (d, J_{FC} = 18.3 Hz), 90.8 (dd, J_{FC} = 199.9 Hz, J_{PC} = 83.9 Hz), 126.4−132.1, 141.2. − ^{19}F NMR: δ = −204.5. − ^{31}P NMR: δ = 29.2 (J_{PF} = 61.0 Hz). − **Fraction 1, Insoluble Isomer (1′*R**,1*R**,2*R**-7s):** R_f = 0.21. − ^{1}H NMR: δ = 1.45−1.77 (m, 6 H), 2.07−2.20 (m, 2 H), 3.55 (dd, 1 H, J = 12.8 Hz, 3.3 Hz), 4.96 (d, 1 H, J_{FH} = 45.0 Hz), 7.14−7.34 (m, 3 H), 7.36−7.70 (m, 10 H), 7.84−7.99 (m, 2 H). − ^{13}C NMR: δ = 20.7, 25.7, 29.0, 34.1, 47.5, 75.1 (dd, J_{FC} = 17.6 Hz, J_{PC} = 5.4 Hz), 94.8 (dd, J_{FC} = 187.7 Hz, J_{PC} = 80.9 Hz), 126.4−132.2, 142.2. − ^{19}F NMR: δ = −214.5. − ^{31}P NMR: δ = 24.2 (d, J_{PF} = 65.9 Hz). − MS (ESI); *m/z*: 431 [M^+ + Na], 409 [M^+ + H]. − **Fraction 2 (1′*R**,1*S**,2*R**-7s):** R_f = 0.14. − ^{1}H NMR: δ = 1.64−1.78 (m, 4 H), 2.44 (br. d, 1 H, J = 13.5 Hz), 2.87 (ddd, 1 H, J = 13.5 Hz, 4.8 Hz, 4.0 Hz), 4.58 (d, 1 H, J = 2.2 Hz), 5.19 (dd, 1 H, J_{FH} = 45.7 Hz, J_{PH} = 1.8 Hz), 7.21−7.65 (m, 13 H), 7.89−7.99 (m, 2 H). − ^{13}C NMR: δ = 22.1, 25.4, 28.6, 28.8 (d, J_{FC} = 12.2 Hz), 38.1, 54.5, 74.1 (d, J_{FC} = 16.8 Hz), 92.5 (dd, J_{FC} = 202.9 Hz, J_{PC} = 82.4 Hz), 126.6−132.3, 140.8. − ^{19}F NMR: δ = −196.6. − ^{31}P NMR: δ = 29.0 (J_{PF} = 63.5 Hz). − **Fraction 3 (1′*R**,1*R**,2*S**-7s):** R_f = 0.48. − ^{1}H NMR: δ = 1.43−2.30 (m, 8 H), 3.13 (t, 1 H, J = 4.8 Hz), 3.84 (br., 1 H), 5.08 (dd, 1 H, J_{FH} = 45.3 Hz, J_{PH} = 3.3 Hz), 7.22−7.56 (m, 11 H), 7.65−7.98 (m, 4 H). − ^{13}C NMR: δ = 20.8, 21.5, 27.8, 32.3, 49.6 (dd, J = 6.1 Hz, 4.6 Hz), 76.8 (d, J_{FC} = 16.8 Hz), 92.2 (dd, J_{FC} = 195.3 Hz, J_{PC} = 82.4 Hz), 126.4−132.3, 142.3. − ^{19}F NMR: δ = −209.7. − ^{31}P NMR: δ = 30.8 (d, J_{PF} = 70.8 Hz).

1-[(Diphenylphosphinoyl)fluoromethyl]-5-isopropenyl-2-methylcyclohex-2-enol (7t): The crude product consisted of four components, in a 49:41:6:4 ratio (^{31}P NMR). Chromatography (petroleum ether/ether, 1:1) afforded partially separated isomers of **7t**: Fraction 1 [0.18 g (12%), 90:0:10:0], overlapping and combined Fractions 1−2 [0.95 g (64%)]; (→ ether): Fraction 3 [0.06 g (4%), 0:0:0:100]. Trituration of overlapping Fractions 1−2 with ether afforded pure Fraction 2 [0.36 g (24%), 0:100:0:0]. The remaining mixture of isomers (0.59 g) was subjected to a second chromatographic workup (petroleum ether/ether, 1:1): Fraction 1 [0.43 g (29%), 85:0:15:0], overlapping Fractions 1−2 [0.12 g (8%), 46:19:35:0], Fraction 2 [0.05 g (3%), 0:100:0:0]. Deduction of the stereocenters was based on the preference of *re*-side attack on (*R*)-carvone[26] and final outcome of the Horner−Wittig reaction. − **Fraction 1, Major Isomer (1′*S*,1*R*,5*R*-7t):** Colorless oil. − R_f = 0.73 (ether). − ^{1}H NMR: δ = 1.29 (s, 3 H), 1.72 (dd, 1 H, J = 13.2 Hz, 1.8 Hz), 1.76−1.88 (m, 1 H), 1.80 (s, 3 H), 1.96−2.09 (m, 2 H), 2.36 (d, 1 H, J = 13.2 Hz), 4.14 (s, 1 H), 4.35 (q, 1 H, J = 1.5 Hz), 4.77 (d, 1 H, J_{FH} = 1.8 Hz), 5.36 (dd, 1 H, J_{FH} = 45.3 Hz, J_{PH} = 1.8 Hz), 5.71 (br., 1 H), 7.42−7.62 (m, 6 H), 7.82−8.01 (m, 4 H). − ^{13}C NMR: δ = 16.1, 19.4, 30.5, 37.0 (d, J_{FC} = 4.6 Hz), 39.1, 74.7 (d, J_{FC} = 18.3 Hz), 90.8 (dd, J_{FC} = 202.9 Hz, J_{PC} = 80.9 Hz), 108.4, 128.4−132.7 (d, J_{FC} = 9.2 Hz), 147.4. − ^{19}F NMR: δ = −195.6. − ^{31}P NMR: δ = 28.7 (d, J_{PF} = 63.5 Hz, 49%). − **Fraction 1, Minor Isomer (1′*R*,1*S*,5*R*-7t):** R_f = 0.73 (ether). − ^{1}H NMR: δ = 1.50 (s), 4.72 (s), 5.51 (d, J_{FH} = 45.0 Hz). − ^{13}C NMR: δ = 17.1, 20.2, 35.8, 37.6, 90.2 (dd, J_{FC} = 201.4 Hz, J_{PC} = 82.4 Hz), 133.2, 148.4. − Other signals eclipsed by major fraction. − ^{19}F NMR: δ = −203.2 (J_{FH} = 45.2 Hz). − ^{31}P NMR: δ = 28.8 (d, J_{PF} = 57.4 Hz, 6%). − **Fraction 2 (1′*R*,1*R*,5*R*-7t):** R_f = 0.67 (ether). − ^{1}H NMR: δ = 1.46 (s, 3 H), 1.81 (s, 3 H), 1.66−2.16 (m, 4 H), 2.30 (d, 1 H, J = 12.8 Hz), 4.33 (s, 1 H), 4.46 (q, 1 H, J = 1.5 Hz), 4.73 (s, 1 H), 5.37 (dd, J_{FH} = 46.3 Hz, J_{PH} = 5.1 Hz), 5.54 (br., 1 H), 7.44−7.58 (m, 6 H), 7.81−7.95 (m, 4 H). − ^{13}C NMR: δ = 18.5 (d, J_{FC} = 6.1), 19.5, 30.4, 38.1, 39.1, 76.1 (d, J_{FC} = 21.4 Hz), 95.5 (dd, J_{FC} = 197.1 Hz, J_{PC} = 78.1 Hz), 108.7, 125.4, 128.1−132.2, 136.1, 147.0. − ^{19}F NMR: δ = −206.0 (J_{FH} = 45.2 Hz). − ^{31}P NMR: δ = 31.3 (d, J_{PF} = 73.2 Hz, 41%). − MS (ESI); *m/z*: 407 [M^+ + Na], 385 [M^+ + H], 367.1 [M^+ − OH], 347 [M^+ − H_2O − F]. − **Fraction 3 (1′*S*,1*S*,5*R*-7t):** R_f = 0.46. − ^{1}H NMR: δ = 1.50 (s, 3 H), 1.63−1.82 (m, 2 H), 1.82 (s, 3 H), 2.09 (m, 1 H), 2.35 (m, 1 H), 3.27 (s, 1 H), 4.31 (s, 1 H), 4.55 (s, 1 H), 5.42 (dd, 1 H, J_{FH} = 45.3 Hz, J_{PH} = 2.6 Hz), 5.67 (d, 1 H, J = 6.2 Hz), 7.46−7.56 (m, 6 H), 7.84−7.95 (m, 4 H). − ^{13}C NMR: δ = 19.4 (d, J_{FC} = 3.0 Hz), 20.3, 31.0, 36.2, 38.4, 74.9 (dd, J_{FC} = 18.3 Hz, J_{PC} = 3.0 Hz), 95.1 (dd, J_{FC} = 194.6 Hz, J_{PC} = 79.1 Hz), 108.9, 128.4−133.1 (dd, J_{FC} = J_{PC} = 3.0 Hz), 148.5. − ^{19}F NMR: δ = −208.9. − ^{31}P NMR: δ = 26.8 (d, J_{PF} = 68.4 Hz, 4%).

1-(Diphenylphosphinoyl)-1,3,3,3-tetrafluoro-2-phenylpropan-2-ol (7u): Assignment of the stereocenters was based on the final outcome of the Horner−Wittig reaction. Chromatography (petroleum ether/ether, 1:1) first afforded the **(1*R**,2*S**) Isomer (*u*-7u):** R_f = 0.42. − ^{1}H NMR: δ = 5.88 (dd, 1 H, J_{FH} = 47.0 Hz, J_{PH} = 1.3 Hz), 6.55 (s, 1 H), 6.97−7.04 (m, 2 H), 7.11−7.20 (m, 5 H), 7.33−7.40 (m, 2 H), 7.48 (br. d, 2 H, J = 7.7 Hz), 7.53−7.64 (m, 2 H), 7.81−7.90 (m, 2 H). − ^{13}C NMR: δ = 79.2 (dq, J_{FC} = 18.3 Hz, 12.2 Hz), 89.3 (dd, J_{FC} = 206.7 Hz, J_{PC} = 80.1 Hz), 120.9

(d, J_{FC} = 10.7 Hz), 128.1−132.9. − ^{19}F NMR: δ = −208.0 (m, 1 F), −75.8 (s, 3 F). − ^{31}P NMR: δ = 30.8 (J_{PF} = 58.6 Hz). − Continued chromatography gave the **(1*R**,2*R**) Isomer (*l*-7u):** R_f = 0.24. − ^{1}H NMR: δ = 5.74 (dd, 1 H, J_{FH} = 46.8 Hz, J_{PH} = 3.7 Hz), 7.10 (s, 1 H), 7.24−7.29 (m, 2 H), 7.34−7.59 (m, 10 H), 7.80−7.90 (m, 2 H). − ^{13}C NMR: δ = 76.0 (dq, J_{FC} = 17.3 Hz, 12.2 Hz), 88.2 (dd, J_{FC} = 210.6 Hz, J_{PC} = 82.4 Hz), 120.8 (d, J_{FC} = 15.3 Hz), 127.3−133.0. − ^{19}F NMR: δ = −203.2 (m, 1 F), −79.0 (d, 3 F, J_{FF} = 18.3 Hz). − ^{31}P NMR: δ = 33.8 (J_{PF} = 68.3 Hz). − MS (ESI); *m*/*z*: 409 [M$^+$ + H].

Methyl 3-(Diphenylphosphinoyl)-3-fluoro-2-hydroxy-2-phenylpropionate (7v): Chromatography (ether) gave Fraction 1 [0.56 g (35%), **#1/#2** = 94:6], Fraction 2 [0.44 g (28%), **#2**]; (→ ether/methanol, 10:1): Fraction 3 (starting material **1**, ≤ 15%), and Fraction 4 (probably 2:1 adducts, traces). − **Fraction 1 (7v-#1):** R_f = 0.29. − ^{1}H NMR: δ = 3.71 (s, 3 H), 5.93 (dd, 1 H, J_{FH} = 44.5 Hz, J_{PH} = 3.7 Hz), 6.06 (s, 1 H), 7.09 (m, 3 H), 7.25−7.55 (m, 10 H), 7.76−7.87 (m, 2 H). − ^{13}C NMR: δ = 53.0, 80.5 (d, J_{FC} = 18.3 Hz), 91.9 (dd, J_{FC} = 202.9 Hz, J_{PC} = 81.9 Hz), 125.9−132.4, 135.5 (d, J_{FC} = 4.6 Hz), 170.8 (d, J_{FC} = 9.2 Hz). − ^{19}F NMR: δ = −202.1. − ^{31}P NMR: δ = 31.5 (d, J_{PF} = 67.1 Hz). − **Fraction 2 (7v-#2):** R_f = 0.18. − ^{1}H NMR: δ = 3.76 (s, 3 H), 4.83 (s, 1 H), 6.08 (d, 1 H, J_{FH} = 45.3 Hz), 7.31−7.40 (m, 4 H), 7.43−7.65 (m, 6 H), 7.77−7.92 (m, 5 H). − ^{13}C NMR: δ = 53.4, 79.2 (d, J_{FC} = 19.8 Hz), 93.9 (dd, J_{FC} = 201.4 Hz, J_{PC} = 88.4 Hz), 125.8−132.4, 137.0, 171.3 (d, J_{FC} = 7.6 Hz). − ^{19}F NMR: δ = −210.6. − ^{31}P NMR: δ = 29.2 (d, J_{PF} = 64.7 Hz). − MS (ESI); *m*/*z*: 421 [M$^+$ + Na], 399 [M$^+$ + H]. − The stereochemistry of the adducts has not been resolved.

Treatment of (α-Fluoro-β-hydroxyalkyl)phosphane Oxides 7 with Base: Base (1.0 equiv.; NaHMDS, unless stated otherwise) was added to a solution of phosphane oxide **7** in THF (20 mL/mmol) under argon, cooled in an ice bath (exceptions mentioned). If no suspension of sodium diphenylphosphinate developed, the solution was allowed to warm to room temp. The mixture was stirred overnight, either at 4 °C or room temp., after which saturated NH_4Cl was added. The layers were separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were dried with $MgSO_4$. After filtration, solvents were carefully removed under reduced pressure, and the crude product was analyzed by NMR spectroscopy. Product mixtures were purified by column chromatography (eluent: petroleum ether/ether, 10:1; exceptions mentioned in text) to isolate fluoro olefins **8**, usually as colorless oils (exceptions mentioned). To obtain the phosphane oxide fractions, chromatography was continued with a more polar eluent (mentioned for the individual compounds), to yield phosphane oxides **9**−**11** as white solids. Isomeric ratios of the starting material, conversion, yields and stereochemistry of **8**−**11** are all given in Table 4 (**7a**−**m**) and Table 5 (**7n**−**v**). For known compounds, references are provided.

Conversion of 7a. − Experiment 1: 4 °C → room temp. Chromatography: **8a**; (→ ethyl acetate): mixture of phosphane oxides (**9a**/**11a** = 91:9). − **2-(Diphenylphosphinoyl)-2-phenylethanal (11a):**[35] This was identified on the basis of its NMR spectroscopic data [δ (C*H*O) = 9.92 (br. d, *J* = 4.4 Hz); δ (P) = 24.9]. − **Two-Step, One-Pot Procedure:** Performed with 3.0 mmol of **1**. The temperature of the reaction mixture (containing lithiated **7a**) was allowed to reach 0 °C, after which KO*t*Bu was added. Stirring was continued overnight at 5 °C, and the usual workup procedure was followed. Chromatography: **8a** [0.17 g (46%); (*E*)/(*Z*) = 56:44]; (→ petroleum ether/ethyl acetate, 1:1): ***u*-7a** [R_f = 0.36; 0.24 g (23%)], mixture of phosphane oxides (R_f = 0.17; 0.10 g, **1/10a** = 67:33). Conversion of **1** was 92%. − **α-(Diphenylphosphinoyl)acetophenone (10a)** was identified on the basis of its NMR spectroscopic data [δ (CH_2) = 4.19 (d, J_{FH} = 15.4 Hz)].[36]

(2-Fluorovinyl)benzene (8a): ^{1}H (for ***Z*-8a**) and ^{19}F NMR spectroscopic data agree with those reported.[29,33] − ^{1}H NMR: δ = 6.40 (dd, 1 H, J_{FH} = 19.0 Hz, *J* = 11.7 Hz, *E*), 7.17 (dd, 1 H, J_{FH} = 83.3 Hz, *J* = 11.7 Hz, *E*), 7.20−7.54 (m, 5 H). − ^{13}C NMR:[34] δ = 110.8 (*Z*), 113.8 (d, J_{FC} = 16.8 Hz, *E*), 126.1−128.9, 132.6, 148.2 (d, J_{FC} = 270.1 Hz, *Z*), 150.1 (d, J_{FC} = 257.9 Hz, *E*).

(2*R,3*R**)-2-(Diphenylphosphinoyl)-3-phenyloxirane (*trans*-9a):**[35] Obtained as a mixture with **11a**. − ^{1}H NMR: δ = 3.60 (dd, 1 H, J_{PC} = 30.7 Hz, *J* = 2.2 Hz), 4.09 (dd, 1 H, J_{PC} = 4.4 Hz, *J* = 2.2 Hz), 7.27−7.34 (m, 5 H), 7.45−7.62 (m, 6 H), 7.80−7.91 (m, 4 H). − ^{31}P NMR: δ = 24.9.

Conversion of 7b: Fraction 1 (*u*/*l* = 67:33): 4 °C → room temp. Conversion 75%; unconverted starting material ***u*-7b** not isolated.

1-Chloro-2-(2-fluorovinyl)benzene (8b):[7] ^{1}H NMR: δ = 6.07 (dd, 0.4 H, J_{FH} = 43.9 Hz, *J* = 5.5 Hz, *Z*), 6.72 (dd, 0.6 H, J_{FH} = 19.4 Hz, *J* = 11.3 Hz, *E*), 6.74 (dd, 0.4 H, J_{FH} = 82.6 Hz, *J* = 5.5 Hz, *Z*), 7.13 (dd, 0.6 H, J_{FH} = 82.2 Hz, *J* = 11.3 Hz, *E*), 7.15−7.26 (m, 2 H), 7.29−7.41 (m, 1.4 H), 7.83 (dd, 0.6 H, *J* = 7.8 Hz, 2.0, *E*). − ^{13}C NMR: δ = 106.7 (*Z*), 111.1 (d, J_{FC} = 19.8 Hz, *E*), 126.7−130.8, 132.6 (*Z*), 133.0 (d, J_{FC} = 4.6 Hz, *E*), 134.7 (*Z*), 135.0 (*E*), 149.2 (d, J_{FC} = 273.1 Hz, *E*), 151.2 (d, J_{FC} = 260.9 Hz, *Z*). − ^{19}F NMR: δ = −124.9 (*E*), −122.1 (*Z*).

Conversion of 7c: Fraction 1 (*u*/*l* = 92:8): Reaction performed with 1.0 mmol; 4 °C → room temp.. Chromatography: **8c** (R_f = 0.28); (→ methanol): complex mixture of phosphane oxides (0.12 g). − Fraction 2 (*u*/*l* = 22:78*)*: Reaction performed with 0.62 mmol; room temp. Chromatography: **8c**; (→ methanol): mixture of unidentified phosphane oxides (0.03 g).

1-(2-Fluorovinyl)-4-methoxybenzene (8c): ^{1}H and ^{19}F NMR spectroscopic data agreed with those reported, but we obtained separate data for both isomers, and used a different reference for ^{19}F NMR.[29,37] − ***E*-8c:** ^{1}H NMR: δ = 3.80 (s, 3 H), 6.35 (dd, 1 H, J_{FH} = 19.7 Hz, *J* = 11.0 Hz), 6.85 (d, 2 H, *J* = 8.8 Hz), 7.09 (dd, 1 H, J_{FH} = 83.7 Hz, *J* = 11.0 Hz), 7.18 (d, 2 H, *J* = 8.8 Hz). − ^{13}C NMR: δ = 55.1, 113.2 (d, J_{FC} = 15.4 Hz), 114.1, 124.9 (d, J_{FC} = 12.2 Hz), 127.2 (d, J_{FC} = 3.0 Hz), 148.9 (d, J_{FC} = 256.3 Hz), 159.0. − ^{19}F NMR: δ = −133.1. − ***Z*-8c:** ^{1}H NMR: δ = 5.55 (dd, 1 H, J_{FH} = 35.3 Hz, *J* = 5.1 Hz), 6.60 (dd, 1 H, J_{FH} = 83.3 Hz, *J* = 5.8 Hz), 6.87 (d, 2 H, *J* = 8.8 Hz), 7.46 (d, 2 H, *J* = 8.8 Hz). − ^{13}C NMR: δ = 55.1, 110.2, 113.8, 125.3, 130.1 (d, J_{FC} = 7.6 Hz), 146.9 (d, J_{FC} = 267.0 Hz), 158.8. − ^{19}F NMR: δ = −125.7.

Conversion of 7d. − Experiment 1: Performed with 1.5 mmol; 4 °C → room temp. Chromatography: **4-(2-Fluorovinyl)biphenyl (8d)**[38] [mixture of isomers: R_f = 0.35, 0.32; 0.22 g (74%); (*E*)/(*Z*) = 1.8:1; spectral data (^{1}H, ^{13}C, ^{19}F) in accordance with those reported]; byproducts not analyzed. − **Experiment 2:** Performed with 1.0 mmol, results given in Table 4. Chromatography: **8d**; (→ ethyl acetate): mixture of phosphane oxides (***u*-7d**/***trans*-9d** = 28:72).

(2*R,3*R**)-3-(4-Biphenylyl)-2-(diphenylphosphinoyl)oxirane (*trans*-9d):** Obtained as a mixture with ***u*-7d**. − ^{1}H NMR: δ = 3.64 (dd, 1 H, J_{PH} = 20.7 Hz, *J* = 2.2 Hz), 4.15 (dd, 1 H, J_{PH} = 4.0 Hz, *J* = 2.2 Hz), 7.27−7.59 (m, 15 H), 7.83−7.91 (m, 4 H). − ^{31}P NMR: δ = 24.7. − MS (ESI); *m*/*z*: 397 [M$^+$ + H].

Conversion of 7e: Conditions: 4 °C → room temp.. Chromatography (CH_2Cl_2): **8e**; (→ CH_2Cl_2/methanol, 50:1): mixture of phos-

phane oxides (R_f = 0.13; ***u*-7e/10e** = 45:55); unknown compound (R_f = 0.06; 0.05 g).

1-(2-Fluorovinyl)nitrobenzene (8e):[39] Pale yellow solid. − R_f = 0.85 (CH_2Cl_2/methanol, 50:1) − Primarily contained the (*Z*) isomer (***Z*-8e**): ^{1}H NMR: δ = 5.74 (dd, 1 H, J_{FH} = 43.1 Hz, J = 5.1 Hz), 6.80 (dd, 1 H, J_{FH} = 81.1 Hz, J = 5.1 Hz), 7.66 (d, 2 H, J = 8.8 Hz), 8.21 (d, 2 H, J = 8.8 Hz). − ^{13}C NMR: δ = 109.4, 123.8, 129.4 (d, J_{FC} = 7.6 Hz), 132.9, 139.0, 150.7 (d, J_{FC} = 276.2 Hz). − ^{19}F NMR: δ = −116.4. − The (*E*) isomer (***E*-8e**) was present as a minor fraction: ^{19}F NMR: δ = −122.5 (dd, J_{FH} = 80.9 Hz, 17.6 Hz).

2-(Diphenylphosphinoyl)-1-(4-nitrophenyl)ethanone (10e):[36] Obtained as a mixture with ***u*-7e**. − ^{1}H NMR: δ = 4.17 (d, 2 H, J_{PH} = 15.4 Hz), 7.50−7.68 (m, 8 H), 7.75−7.90 (m, 4 H), 8.14−8.25 (m, 2 H); data agree well with the reported ones. − ^{13}C NMR: δ = 43.6 (d, J_{PC} = 56.4 Hz), 123.3, 128.0−132.6, 141.0, 150.0, 191.4 (d, J_{PC} = 4.6 Hz). − ^{31}P NMR: δ = 27.0.

Conversion of 7f: Fraction 2 (*u*/*l* = 16:84)*:* Conditions: 4 °C → room temp. Chromatography (petroleum ether/ether, 1:1): **(*Z*)-2-(2-Fluorovinyl)pyridine (*Z*-8f)** [^{19}F NMR: δ = −117.9 (dd, J_{FH} = 82.4 Hz, 45.8 Hz)]; (→ ether/methanol/triethylamine, 50:5:1): mixture of phosphane oxides (R_f = 0.32; ***u*-7f/*l*-7f/10f** = 23:56:21). Elimination of phosphinate from Fraction 1 (*u*/*l* = 79:21) was not investigated, as no ***E*-8f** was detected in the experiment described.

2-(Diphenylphosphinoyl)-1-(pyridin-2-yl)ethanone (10f): ^{1}H NMR: δ = 4.58 (d, 2 H, J_{PH} = 15.4 Hz), 7.19−7.94 (m, 13 H), 8.56 (d, 1 H, J = 4.4 Hz). − ^{31}P NMR: δ = 27.9. − MS (ESI); *m*/*z*: 322 (64%) [M^+ + H]; note that this signal was also found for **7f** (intensity: 31%).

1-(Dimethylamino)-4-[(1*E*/*Z*,3*E*)-4-fluorobuta-1,3-dienyl]benzene (8g): Conditions: 4 °C. Chromatography afforded ***Z*-8g** (R_f = 0.45) and ***E*-8g** (R_f = 0.43) as a mixture of isomers. − Colorless solid, decaying slowly when stored at −20 °C. − ^{1}H NMR: δ = 2.96 (s, *E*), 2.97 (s, *Z*) (comb. 6 H), 5.55 (ddd, 0.3 H, J_{FH} = 40.9 Hz, J = 11.0 Hz, J = 4.4 Hz, *Z*), 6.07−6.32 (m, 1.4 H), 6.37 (dd, 1 H, J = 8.0 Hz, 1.5), 6.64−6.71 (m, 2 H), 6.86 (dd, 0.3 H, J = 15.7 Hz, 11.3 Hz), 7.10 (d, 0.7 H, J = 11.0 Hz, *E*), 7.23−7.35 (m, 2.3 H). − From the other NMR spectra, signals of the single isomers were elucidated. − ***E*-8g:** ^{13}C NMR: δ = 40.2, 112.2, 114.8 (d, J_{FC} = 15.3 Hz), 116.3 (d, J_{FC} = 12.2 Hz), 125.3, 127.1, 132.4, 149.9, 150.8 (d, J_{FC} = 259.4 Hz). − ^{19}F NMR: δ = −129.8 (J_{FH} = 85.4 Hz, 18.3 Hz), − ***Z*-8g:** ^{13}C NMR: δ = 40.2, 112.2, 114.5 (d, J_{FC} = 4.6 Hz), 125.1, 127.5, 132.2, 146.8 (d, J_{FC} = 264.0 Hz), 150.0. − ^{19}F NMR: δ = −129.0 (J_{FH} = 79.4 Hz, 36.6 Hz). − MS (ESI); *m*/*z*: 192 [M^+ + H], 177 [$M^+ - CH_2$].

Conversion of 7h. − Experiment 1: Conditions: 4 °C → room temp. Chromatography: **8h** (54%); (→ ethyl acetate): mixture of **7h** and **10h** (0.12 g; **7h/10h** = 70:30). Repeated chromatography (ethyl acetate) gave pure β-oxophosphane oxide **10h**. − **Experiment 2:** Conditions: room temp. Column chromatography gave **8h** as the only product.

2-(4-Fluorobuta-1,3-dienyl)furan (8h): Yellowish oil. − The compound was very unstable, turning into a dark polymer within 24 h at −20 °C. − ^{1}H NMR: δ = 5.53 (ddd, 0.3 H, J_{FH} = 39.8 Hz, J = 11.0 Hz, 4.4 Hz, *Z*), 6.13 (ddd, 0.7 H, J_{FH} = 16.8 Hz, J = 2 × 11.0 Hz, *E*), 6.22−6.40 (m, 2 H), 6.52 (dd, 0.3 H, J_{FH} = 82.3 Hz, J = 4.4 Hz, *Z*), 6.52 (ddd, 0.7 H, J = 15.4 Hz, 11.0, 1.5, *E*), 6.92 (dd, 0.7 H, J_{FH} = 83.0 Hz, J = 11.0 Hz, *E*), 6.95 (dd, 0.3 H, J = 15.7 Hz, 11.3, *Z*), 7.35 (d, 0.7 H, J = 1.5 Hz, *E*), 7.37 (d, 0.3 H, J = 1.8 Hz, *Z*). − ^{13}C NMR: δ = 108.0 (*E*), 108.7 (*Z*), 111.5, 114.1 (d, J_{FC} = 15.3 Hz, *E*), 117.6 (d, J_{FC} = 4.6 Hz, *Z*), 119.5, 119.8, 120.0, 121.5, 142.0 (*E*), 142.3 (*Z*), 148.5 (d, J_{FC} = 258.6 Hz, *Z*), 152.4 (d, J_{FC} = 262.4 Hz, *E*), 152.8. − ^{19}F NMR: δ = −125.7 (both isomers).

1-(Diphenylphosphinoyl)-4-(furan-2-yl)but-3-en-2-one (10h): R_f = 0.41. − ^{1}H NMR: δ = 3.78 (d, 2 H, J_{PH} = 15.4 Hz), 6.46 (m, 1 H), 6.69 (d, 1 H, J = 3.6 Hz), 6.77 (d, 1 H, J = 16.1 Hz), 7.38 (d, 1 H, J = 16.1 Hz, 7.48−7.50 (m, 7 H), 7.74−7.83 (m, 4 H). − ^{31}P NMR: δ = 27.7.

1-Fluoroundec-1-ene (8i): Conditions for conversion of Fraction 1 (*u*/*l* = 93:7) (1.34 mmol), and Fraction 2 (***l*-7i**) (0.30 mmol): 4 °C → room temp. Column chromatography gave **8i** as the sole product, both isomers almost stereochemically pure. − ***E*-8i:** ^{1}H NMR: δ = 0.88 (t, J = 6.4 Hz), 1.26 (br., 14 H), 1.84−1.91 (m, 2 H), 5.34 (ddt, 1 H, J_{FH} = 19.2 Hz, J = 11.0 Hz, 7.7), 6.49 (ddt, 1 H, J_{FH} = 86.2 Hz, J = 11.0 Hz, 1.5 Hz). − ^{13}C NMR: δ = 14.1, 22.4, 22.7, 25.0 (d, J_{FC} = 9.2 Hz), 29.0, 29.4, 29.4, 29.6, 31.9, 111.6 (d, J_{FC} = 7.6 Hz), 148.5 (d, J_{FC} = 253.3 Hz). − ^{19}F NMR: δ = −131.5. − MS (ESI); *m*/*z*: 173 [M^+ + H]. − ***Z*-8i:** ^{1}H NMR spectroscopic data as reported in the literature.[29] − ^{13}C NMR: δ = 14.1, 22.7, 29.1, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 111.1 (d, J_{FC} = 4.6 Hz), 147.5 (d, J_{FC} = 254.8 Hz). − ^{19}F NMR: δ = −131.9.

(4-Fluorobut-3-enyl)benzene (8j):[38] Conversion of **7j** was achieved in two ways. − **Experiment 1:** Conditions: 4 °C → room temp.: compound **8j** obtained as sole product after chromatography. − **Experiment 2:** KHMDS, 4 °C → room temp.: small amount of phosphane oxide **9j** seemingly present, not analyzed. − **One-Pot Procedure:** compound **8j** was isolated in 49% yield [(*E*)/(*Z*) = 74:26], at 67% conversion, by-products not analyzed. − ^{1}H and ^{19}F NMR spectroscopic data similar to those reported. − ^{13}C NMR: δ = 24.3 (d, J_{FC} = 4.6 Hz, *Z*), 26.9 (d, J_{FC} = 9.2 Hz, *E*), 35.3 (*Z*), 36.0 (d, J_{FC} = 3.0 Hz, *E*), 110.0 (d, J_{FC} = 6.1 Hz, *Z*), 110.7 (d, J_{FC} = 9.2 Hz, *E*), 125.9, 126.0, 128.4, 141.1 (*E*), 141.3 (*Z*), 147.8 (d, J_{FC} = 257.9 Hz, *Z*), 148.9 (d, J_{FC} = 254.8 Hz, *E*).

Conversion of 7k: Insoluble fraction (*u*/*l* = ≤ 2:98): Reaction performed with 0.37 mmol, as an 18 mM solution, at room temp. Chromatography (petroleum ether) gave **8k** as the sole product. − Soluble fraction (*u*/*l* = 90:10): performed with 0.63 mmol; room temp. → 40 °C (2.5 h). Chromatography (petroleum ether): **8k**; (→ ethyl acetate): ***trans*-9k**; (→ methanol): unidentified product (0.03 g).

[1-(2-Fluorovinyl)cyclopropyl]benzene (8k): Both isomers obtained in good stereochemical purity. − ***Z*-8k:** ^{1}H NMR: δ = 1.14 (m, 4 H), 5.02 (dd, 1 H, J_{FH} = 43.1 Hz, J = 4.8 Hz), 6.43 (dd, 1 H, J_{FH} = 83.3 Hz, J = 5.1 Hz), 7.17−7.29 (m, 5 H). − ^{13}C NMR: δ = 16.1, 114.9, 125.9, 127.2, 128.2, 144.6, 148.4 (d, J_{FC} = 264.0 Hz). − ^{19}F NMR: δ = −127.2. − MS/GC (EI); *m*/*z*: 162 [M^+]. − ***E*-8k:** ^{1}H NMR: δ = 0.96 (m, 2 H), 1.06 (m, 2 H), 5.49 (dd, 1 H, J_{FH} = 19.0 Hz, J = 11.0 Hz), 6.22 (dd, 1 H, J_{FH} = 84.8 Hz, J = 11.0 Hz), 7.20−7.30 (m, 5 H). − ^{13}C NMR: δ = 14.4, 119.1 (d, J_{FC} = 13.7 Hz), 126.5, 128.4, 128.7, 143.0, 150.4 (d, J_{FC} = 251.8 Hz). − ^{19}F NMR: δ = −135.8.

(2*R,3*R**)-2-(Diphenylphosphinoyl)-3-(1-phenylcyclopropyl)oxirane (*trans*-9k):** ^{1}H NMR: δ = 0.88−1.02 (m, 4 H), 3.18 (dd, 1 H, J_{PH} = 34.7 Hz, J = 2.6 Hz), 3.27 (dd, 1 H, J_{PH} = 9.1 Hz, J = 2.6 Hz), 7.25−7.28 (m, 5 H), 7.40−7.59 (m, 6 H), 7.64−7.78 (m, 4 H). − ^{13}C NMR: δ = 9.7, 10.9, 24.8, 52.8 (d, J_{PC} = 100.7 Hz), 59.4, 126.9−132.3, 140.0. − ^{31}P NMR: δ = 25.7. − MS (ESI); *m*/*z*: 383 [M^+ + Na], 361 [M^+ + H].

[(3-Fluoroallyloxy)methyl]benzene (8l): Obtained from **7l** at room temp., as the only product. Column chromatography (petroleum ether/ether, 20:1) afforded **8l** as a mixture of isomers. Spectra of the individual isomers could be elucidated. − ***E*-8l:** ^{1}H NMR: δ = 3.95 (ddd, 1.2 H, J_{FH} = 2.9 Hz, J = 7.3 Hz, 1.5), 4.50 (s, 1.2 H), 5.56 (ddt, 0.6 H, J_{FH} = 17.2 Hz, J = 11.3 Hz, 7.3), 6.71 (ddt, 0.6 H, J_{FH} = 83.3 Hz, J = 11.3 Hz, 1.5 Hz), 7.28−7.36 (m, 60% of 2 H). − ^{13}C NMR: δ = 64.4 (d, J_{FC} = 13.7 Hz), 71.8, 108.5 (d, J_{FC} = 10.7 Hz), 127.7−128.4, 127.8, 151.7 (d, J_{FC} = 260.9 Hz). − ^{19}F NMR: δ = −125.4. − ***Z*-8l:** ^{1}H NMR: δ = 4.18 (ddd, 0.8 H, J_{FH} = 2.2 Hz, J = 6.9 Hz, 1.5 Hz), 4.51 (s, 0.8 H), 5.04 (ddt, 0.4 H, J_{FH} = 41.7 Hz, J = 6.9 Hz, 4.8 Hz), 6.57 (ddt, 0.4 H, J_{FH} = 84.1 Hz, J = 4.8 Hz, 1.5 Hz), 7.28−7.36 (m, 40% of 2 H). − ^{13}C NMR: δ = 61.5 (d, J_{FC} = 7.6 Hz), 72.1, 108.1 (d, J_{FC} = 3.0 Hz), 127.7−128.4, 149.5 (d, J_{FC} = 262.4 Hz). − ^{19}F NMR: δ = −126.1. − MS (ESI); *m*/*z*: 167 [M$^+$ + H].

Conversion of 7m: Reaction performed with 0.50 mmol; room temp. Chromatography (petroleum ether/ether, 9:1) afforded Fraction 1 [**8m**, 40 mg (34%); (*E*)/(*Z*) = 0:100]; and Fraction 2 [**8m**, 57 mg (48%); (*E*)/(*Z*) = 82:18]; (→ ethyl acetate): **7m**, (< 8 mg); (→ methanol): **9m** [mixture of isomers, 25 mg (11%)].

***tert*-Butyl (4*S*)-4-(2-Fluorovinyl)-2,2-dimethyl-3-oxazolidinecarboxylate (8m):**[5d] Both isomers obtained in satisfactory stereochemical purity. − ***Z*-8m:** R_f = 0.24. − ^{1}H NMR ([D$_6$]DMSO, 113 °C): δ = 1.45 (s, 9 H), 1.49 (s, 3 H), 1.55 (s, 3 H), 3.70 (dd, 1 H, J = 8.8 Hz, 2.9 Hz), 4.09 (dd, 1 H, J = 8.8 Hz, 5.8 Hz), 4.74 (m, 1 H), 4.96 (ddd, 1 H, J_{FH} = 42.4 Hz, J = 8.8 Hz, 4.8 Hz), 6.67 (ddd, 1 H, J_{FH} = 84.4 Hz, J = 4.8 Hz, 1.1). − ^{13}C NMR ([D$_6$]DMSO, 113 °C): δ = 23.7, 25.9, 27.5, 50.5 (d, J_{FC} = 6.1 Hz), 67.4, 81.4, 92.5, 111.4, 145.8 (d, J_{FC} = 259.4 Hz). − ^{19}F NMR ([D$_6$]DMSO, 113 °C): δ = −144.2. − ***E*-8m:** R_f = 0.18. − ^{1}H NMR ([D$_6$]DMSO, 113 °C): δ = 1.46 (s, 9 H), 1.48 (s, 3 H), 1.54 (s, 3 H), 3.72 (dd, 1 H, J = 9.1 Hz, 2.6 Hz), 4.05 (ddd, 1 H, J = 9.1 Hz, 6.2 Hz, 1.5 Hz), 4.34 (bddd, 1 H, J = 8.0 Hz, 6.2 Hz, 2.6 Hz), 5.45 (ddd, 1 H, J_{FH} = 19.0 Hz, J = 11.0 Hz, 8.0 Hz), 6.85 (dd, 1 H, J_{FH} = 84.4 Hz, J = 11.0 Hz). − ^{13}C NMR ([D$_6$]DMSO, 113 °C): δ = 23.6, 26.2, 27.6, 52.6 (d, J_{FC} = 13.7 Hz), 67.2, 78.8, 92.6, 111.2 (d, J_{FC} = 9.2 Hz), 150.9 (d, J_{FC} = 256.4 Hz). − ^{19}F NMR ([D$_6$]DMSO, 113 °C): δ = −147.0.

***tert*-Butyl (4*R*)-4-[3-(Diphenylphosphinoyl)oxiranyl]-2,2-dimethyloxazolidine-3-carboxylate (9m):** Mixture of isomers. − ^{1}H NMR: δ = 1.26−1.59 (m, 15 H), 3.36−4.14 (m, 5 H), 7.50−7.54 (m, 6 H), 7.74−7.86 (m, 4 H). − ^{31}P NMR: δ = 25.4 (55%); 25.6 (7%); 26.2 (38%). − MS (ESI); *m*/*z*: 466 [M$^+$ + Na], 444 [M$^+$ + H], 388 [M$^+$ + 2 H − *t*Bu], 344 [M$^+$ + H − BOC], 330 [M$^+$ + 2 H − O*t*Bu − CMe$_2$].

Conversion of 7n: Reaction conducted at 4 °C. Column chromatography afforded **8n**, and unidentified apolar by-products (R_f = 0.30; 0.01 g); (→ ethyl acetate) unidentified phosphane oxides (0.06 g).

9-Fluoromethylene-9*H*-fluorene (8n): Colorless to yellowish solid. − R_f = 0.62. − ^{1}H NMR: δ = 7.23−7.45 (m, 4 H), 7.57 (d, 1 H, J = 7.3 Hz), 7.70 (d, 1 H, J_{FH} = 79.7 Hz), 7.72−7.76 (m), 7.98 (dd, 1 H, J = 6.2 Hz, 1.7 Hz). − ^{13}C NMR: δ = 119.7, 120.1, 125.7, 125.9, 126.9, 127.4, 128.0, 128.4, 134.5, (d, J_{FC} = 19.8), 135.9 (d, J_{FC} = 12.2 Hz), 139.3, 139.4, 147.9 (d, J_{FC} = 276.2 Hz). − ^{19}F NMR: δ = −125.6. − MS (ESI); *m*/*z*: 196 [M$^+$ + H].

Conversion of 7o. − Insoluble Fraction (*u*-7o): 4 °C. Crude product contained only ***E*-8o**, but after column chromatography, an (*E*)/(*Z*) ratio of 93:7 was found. − **Soluble Fraction (*u*/*l* = 97:3):** 4 °C. Crude product contained only **8o** [(*E*)/(*Z*) = 9:91], after column chromatography, the (*E*)/(*Z*) ratio had changed to 6:94. Obviously, there is some silica-induced (*E*) → (*Z*) isomerization.

[2-(1-Fluoroprop-1-enyl)]benzene (8o):[6d] ***E*-8o:** ^{1}H NMR: δ = 2.04 (dd, 3 H, J_{FH} = 3.7 Hz, J = 1.5 Hz), 6.90 (dq, 1 H, J_{FH} = 85.2 Hz, J = 1.5 Hz), 7.24−7.37 (m, 5 H). − ^{13}C NMR: δ = 12.2, 120.0 (d, J_{FC} = 10.7 Hz), 125.8 (d, J_{FC} = 3.0 Hz), 127.4, 128.5, 137.4, 146.0 (d, J_{FC} = 56.4 Hz). − ^{19}F NMR: δ = −131.6. − ***Z*-8o:** ^{1}H NMR: δ = 1.91 (dd, 3 H, J_{FH} = 4.8 Hz, J = 1.5 Hz), 6.66 (dq, 1 H, J_{FH} = 84.1 Hz, J = 1.5 Hz), 7.25−7.41 (m, 3 H), 7.48−7.52 (m, 2 H). − ^{13}C NMR: δ = 15.9 (d, J_{FC} = 6.1), 116.9, 127.5 (d, J_{FC} = 12.2), 127.8, 128.2, 135.9 (d, J_{FC} = 4.6 Hz), 144.2 (d, J_{FC} = 262.4 Hz). − ^{19}F NMR: δ = −129.5.

(Fluoromethylene)cyclododecane (8p): Obtained from **7p**, at 4 °C, as the sole product after chromatography. − ^{1}H-, ^{13}C-, and ^{19}F NMR spectroscopic data agreed with those reported.[40]

2-(Fluoromethylene)adamantane (8q): Obtained from **7q**, at 4 °C, as the sole product (at 78% conversion) after chromatography: Colorless solid. − ^{1}H NMR: δ = 1.71−1.98 (br. m, 12 H), 2.27 (d, 1 H, J = 2.2 Hz), 3.04 (s, 1 H,), 6.43 (d, 1 H, J_{FH} = 88.1 Hz). − ^{13}C NMR: δ = 28.1 (d, J_{FC} = 4.6 Hz), 28.4, 31.6 (d, J_{FC} = 7.6), 37.0, 38.0, 39.3, 129.4, 137.2 (d, J_{FC} = 247.1 Hz). − ^{19}F NMR: δ = −148.4. − MS (ESI); *m*/*z*: 166 [M$^+$ + H].

4-*tert*-Butyl-1-(fluoromethylene)cyclohexane (8r):[41] Obtained from either fraction of **7r**, at 4 °C, as the sole product and in identical yield after chromatography: ^{1}H NMR: δ = 0.85 (s, 9 H), 0.85−1.20 (m, 3 H), 1.43−1.68 (m, 1 H), 1.82−1.89 (m, 3 H), 2.07−2.15 (m, 1 H), 2.82−2.89 (m, 1 H), 6.38 (dt, 1 H, J_{FH} = 87.7 Hz, J = 2.2 Hz). − ^{13}C NMR: δ = 24.5 (d, J_{FC} = 4.6 Hz), 27.4, 27.5, 28.1 (d, J_{FC} = 6.1 Hz), 28.5, 32.4), 48.2, 121.6 (d, J_{FC} = 4.6 Hz), 140.1 (d, J_{FC} = 250.2 Hz). − ^{19}F NMR: δ = −142.1. − GC/MS (EI); *m*/*z*: 170 [M$^+$].

Conversion of 7s. − Fraction 1, Soluble Isomer [(1′*R,1*S**,2*S**)/(1′*R**,1*R**,2*R**) = 97:3], Experiment 1:** 4 °C → room temp. − **Experiment 2:** KO*t*Bu, room temp. Chromatography (ether): **8s**, ***trans*-9s**. − **Fraction 1, Insoluble Isomer [(1′*R**,1*S**,2*S**)/(1′*R**,1*R**,2*R**) = 10:90]:** 4 °C. Chromatography: **8s**; (→ ethyl acetate): ***trans*-9s**.

(2-Fluoromethylenecyclohexyl)benzene (8s): R_f = 0.80. − Both isomers obtained in good stereochemical purity. − ***Z*-8s:** Spectral data (^{1}H NMR, ^{13}C NMR, ^{19}F NMR) as reported.[5c] − ***E*-8s:** ^{1}H NMR: δ = 1.32−1.92 (m, 7 H), 2.72 (br. d, 1 H, J = 13.2 Hz), 3.22 (m, 1 H), 5.80 (d, 1 H, J_{FH} = 87.4 Hz), 7.17−7.36 (m, 5 H). − ^{13}C NMR: δ = 24.4 (d, J_{FC} = 6.1 Hz), 25.5, 26.4, 33.2, 44.6 (d, J_{FC} = 7.6 Hz), 125.9 (d, J_{FC} = 6.1 Hz), 126.4, 128.1, 128.3, 141.7, 143.9 (d, J_{FC} = 248.7 Hz). − ^{19}F NMR: δ = −142.1. − MS (ESI); *m*/*z*: 191 [M$^+$ + H].

(2*R,3*R**,4*R**)-2-(Diphenylphosphinoyl)-4-phenyl-1-oxaspiro[2.5]-octane (*trans*-9s):** R_f = 0.07 (ether). − ^{1}H NMR: δ = 1.43−2.12 (m, 7 H), 2.42 (br. d, 1 H, J = 12.8 Hz), 2.64 (d, 1 H, J_{PH} = 32.5 Hz), 3.06 (dd, 1 H, J = 12.0, 3.7), 7.18−7.27 (m, 3 H), 7.39−7.67 (m, 12 H). − ^{13}C NMR: δ = 24.0, 25.5, 29.8, 31.4, 47.9, 56.4 (d, J_{PC} = 99.2), 66.8, 126.6−131.8, 139.0. − ^{31}P NMR: δ = 23.8. − MS (ESI); *m*/*z*: 411 [M$^+$ + Na], 389 [M$^+$ + H], 371 [M$^+$ − OH].

Conversion of 7t. − Fraction 1 [(1′*S*,1*R*,5*R*)/(1′*R*,1*S*,5*R*) = 93:7): 4 °C. Chromatography (petroleum ether): ***E*-8t**; (→ ether): Unknown phosphane oxide derivative (R_f = 0.62; 0.03 g); recovered **7t** (R_f = 0.55), **11t**. **1′*R*,1*S*,5*R*-7t** proved unreactive. − **Fraction 2**

{[(1′*S*,1*R*,5*R*) + (1′*R*,1*S*,5*R*)]/(1′*R*,1*R*,5*R*) = 7:93}: 4 °C. Chromatography (petroleum ether) afforded **8t** as the sole product.

(4*R*)-6-Fluoromethylene-4-isopropenyl-1-methylcyclohexene (8t): Both isomers obtained in good stereochemical purity. Smell reminiscent of *Tsuga heterophylla* (western hemlock). − ***E*-8t:** Unstable, decaying slowly while kept at −20 °C. − ^{1}H NMR: δ = 1.73 (s, 3 H), 1.76 (s, 3 H), 1.91−2.28 (m, 5 H), 2.86 (m, 1 H), 4.76 (s, 2 H), 5.61 (br., 1 H), 6.68 (d, 1 H, J_{FH} = 85.2 Hz). − ^{13}C NMR: δ = 18.6, 20.7, 26.4 (d, J_{FC} = 4.6 Hz), 30.9, 40.2, 109.3, 121.6 (d, J_{FC} = 9.2 Hz), 127.2 (d, J_{FC} = 12.2 Hz), 127.9 (d, J_{FC} = 6.1 Hz), 144.4 (d, J_{FC} = 253.3 Hz), 148.7. − ^{19}F NMR: δ = −140.0. − ***Z*-8t:** ^{1}H NMR: δ = 1.73 (s, 3 H), 2.01 (dd, 3 H, J = 5.1 Hz, 0.7 Hz), 1.92−2.26 (m, 5 H), 4.72 (m, 1 H), 4.74 (m, 1 H), 5.54 (t, 1 H, J = 1.5 Hz), 6.36 (d, 1 H, J_{FH} = 84.8 Hz). − ^{13}C NMR: δ = 20.6, 22.1 (d, J_{FC} = 7.6 Hz), 31.0 (d, J_{FC} = 7.6 Hz), 31.5, 41.3, 109.3, 118.3, 127.9 (d, J_{FC} = 3.2 Hz), 129.4 (d, J_{FC} = 3.0 Hz), 143.1 (d, J_{FC} = 267.0 Hz), 148.7. − ^{19}F NMR: δ = −130.5.

(5*R*)-1-(Diphenylphosphinoyl)-5-isopropenyl-2-methylcyclohex-2-enecarbaldehyde (11t): Stereochemistry at C-1 not known. − R_f = 0.27. − ^{1}H NMR: δ = 1.25 (s, 3 H), 1.76 (m, 3 H), 1.91−2.04 (m, 1 H), 2.14−2.32 (m, 2 H), 2.52 (m, 1 H), 4.56 (s, 1 H), 4.64 (q, 1 H, J = 1.1 Hz), 5.94−5.98 (m, 1 H), 7.43−7.59 (m, 6 H), 7.89−8.02 (m, 4 H), 9.84 (d, J_{PH} = 4.8 Hz). − ^{13}C NMR: δ = 20.7, 22.1, 30.0, 32.3, 62.0 (d, J_{PC} = 58.0 Hz), 109.9, 126.5−132.4, 147.8, 200.0. − ^{31}P NMR: δ = 29.6. − MS (ESI); *m*/*z*: 387 [M$^+$ + Na], 365 [M$^+$ + H].

Conversion of 7u. − Fraction 1 (*u*-7u): Room temp. → 50 °C, 1 h. Clouding occurred at temperatures over 27 °C, with color changing from brown through purple to gray. Chromatography (petroleum ether): fluoro olefin ***E*-8u** isolated in disappointing yield, probably due to its volatility.[6d] − **Fraction 2 (*l*-7u):** Room temp. Little clouding occurred. Fluoro olefin ***Z*-8u** (< 5%), noted in the crude product [^{19}F NMR: δ = −125.1 (dq, 1 F, J_{FF} = 12.2 Hz, J_{FH} = 79.4 Hz), −63.8 (d, 3 F, J_{FF} = 12.2 Hz)],[6d] was not isolated. Chromatography (petroleum ether → petroleum ether/ether, 1:1): Recovered ***l*-7u**; (→ ether): ***cis*-9u**.

(*E*)-(2-Fluoro-1-trifluoromethylvinyl)benzene (*E*-8u):[6d] ^{1}H NMR: δ = 6.81 (d, 1 H, J_{FH} = 77.5 Hz), 7.29−7.35 (m, 2 H), 7.36−7.44 (m, 3 H). − ^{13}C NMR: δ = 128.8, 129.2, 151.8 (dq, J_{FC} = 286.9 Hz, 3.1 Hz). − ^{19}F NMR: δ = −113.1 (dq, 1 F, J_{FF} = 23.7 Hz), −60.0 (d, 3 F, J_{FF} = 23.7 Hz).

(2*R,3*S**)-2-(Diphenylphosphinoyl)-3-phenyl-3-trifluoromethyloxirane (*cis*-9u):** ^{1}H NMR: δ = 4.15 (d, 1 H, J_{PH} = 22.7), 7.03−7.33 (m, 9 H), 7.49−7.64 (m, 4 H), 7.79−7.90 (m, 2 H). − ^{13}C NMR: δ = 55.9 (d, J_{PC} = 97.7 Hz), 62.4 (q, J_{FC} = 36.6 Hz), 122.2 (q, J_{FC} = 280.2 Hz), 126.0, 127.4−132.2. − ^{19}F NMR: δ = −76.5. − ^{31}P NMR: δ = 22.7. − MS (ESI); *m*/*z*: 411 [M$^+$ + Na], 389 [M$^+$ + H].

Conversion of 7v. − Fraction 1 (7v-#1/7v#2 = 94:6): 5 °C → 47 °C, 2 h. Chromatography: **8v**; (→ ether): Three unidentified products, possibly resulting from polymerization (R_f = 0.86, 0.79, 0.70; 18 mg); phosphane oxides (R_f = 0.10; **7v/9v-major/9v-minor** = 25:64:11). Adding the base at 50 °C did not improve the yield of fluoro olefin. Phosphinate elimination of Fraction 2 (**7v-#2**) was not investigated, as the small amount present in Fraction 1 was converted only to the epoxide.

Methyl 3-Fluoro-2-phenylprop-2-enoate (8v): Stereochemistry not determined. − R_f = 0.34. − ^{1}H NMR: δ = 3.85 (s, 3 H), 7.00 (d, 1 H, J_{FH} = 91.4 Hz), 7.28−7.39 (m, 5 H). − ^{19}F NMR: δ = −109.7.

Methyl 3-(Diphenylphosphinoyl)-2-phenyloxirane-2-carboxylate (9v): Mixture of isomers. − ^{1}H NMR: δ = 3.56 (d, 1 H, J_{PH} = 31.1 Hz), 3.75 (s, 3 H), 7.34−7.40 (m, 3 H), 7.50−7.60 (m, 8 H), 7.80−7.94 (m, 4 H); signals of minor isomer probably eclipsed by those of the major one. − ^{13}C NMR: δ = 52.8 (*major*), 53.6 (*minor*), 61.6 (d, J_{PC} = 94.6 Hz, *major*), 64.8 (d, J_{PC} = 99.2 Hz, *minor*). 68.0, 126.0, 128.5−132.6, 166.3. − ^{31}P NMR: δ = 22.4 (0.85 P), 23.1 (0.15 P). − MS (ESI); *m*/*z*: 401 [M$^+$ + Na], 379 [M$^+$ + H], 347 [M$^+$ − MeO].

[1] D. J. Burton, Z.-Y. Yang, W. Qiu, *Chem. Rev.* **1996**, *96*, 1641−1715.

[2] S. Hayashi, T. Nakai, N. Ishikawa, D. J. Burton, D. G. Naae, H. S. Kesling, *Chem. Lett.* **1979**, 983−986.

[3] M. L. Edwards, D. M. Stemerick, E. T. Jarvi, D. P. Matthews, J. R. McCarthy, *Tetrahedron Lett.* **1990**, *31*, 5571−5574.

[4] J. R. McCarthy, D. P. Matthews, M. L. Edwards, D. M. Stemerick, E. T. Jarvi, *Tetrahedron Lett.* **1990**, *31*, 5449−5452.

[5] [5a] J. R. McCarthy, D. P. Matthews, D. M.Stemerick, E. W. Huber, P. Bey, B. J. Lippert, R. D. Snyder, P. S. Sunkara, *J. Am. Chem. Soc.* **1991**, *113*, 7439−7440. − [5b] A. P. Khrimian, A. B. DeMilo, R. M. Waters, N. J. Liquido, J. M. Nicholson, *J. Org. Chem.* **1994**, *59*, 8034−8039. − [5c] J. R. McCarthy, D. P. Matthews, J. P. Paolini, *Org. Synth.* **1995**, *72*, 216−224. − [5d] J. R. McCarthy, E. W. Huber, T.-B. Le, M. Laskovics, D. P. Matthews, *Tetrahedron* **1996**, *52*, 45−58.

[6] [6a] M. Schlosser, M. Zimmermann, *Synthesis* **1969**, 75−76. − [6b] F. Manfré, J. M. Kern, J.-F. Biellmann, *J. Org. Chem.* **1992**, *57*, 2060−2065. − [6c] Q. Wang, H.-x.Wei, M. Schlosser, *Eur. J. Org. Chem.* **1999**, 3263−3268. − [6d] D. J. Burton, P. E. Greenlimb, III, *J. Org. Chem.* **1975**, *40*, 2796−2801. − [6e] Z. Du, M. J. Haglund, L. A. Pratt, K. L. Erickson, *J. Org. Chem.* **1998**, *63*, 8880−8887. − [6f] M. El-Khoury, Q. Wang, M. Schlosser, *Tetrahedron Lett.* **1996**, *37*, 9047−9050.

[7] D. G. Cox, N. Gurusamy, D. J. Burton, *J. Am. Chem. Soc.* **1985**, *107*, 2811−2812.

[8] [8a] R. Waschbüsch, J. Carran, A. Marinetti, P. Savignac, *Synthesis* **1997**, 727−743; and references therein. − [8b] A. P. Tomilov, B. I. Martynov, Yu. D. Smirnov, F. M. Semchenko, *J. Fluorine Chem.* **1997**, *82*, 39−41. − [8c] C. J. Hamilton, S. M. Roberts, *J. Chem. Soc., Perkin Trans. 1* **1999**, 1051−1056.

[9] G. M. Blackburn, M. J. Parratt, *J. Chem. Soc., Chem. Commun.* **1983**, 886−888.

[10] For the use of "phosphane" instead of "phosphine", see IUPAC recommendations: G. P. Moss, P. A. S. Smith, D. Tavernier, *Pure Appl. Chem.* **1995**, *67*, 1307−1375.

[11] W. Wegener, *Z. Chem.* **1971**, *11*, 262.

[12] P. P. de Wit, T. A. M. van Schaik, A. van der Gen, *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 369−370. − Reaction performed in THF under reflux, according to a procedure described in ref.[13]

[13] P. P. de Wit, Ph. D. Dissertation, Leiden University, **1987**.

[14] E. D. Bergmann, I. Shahak, *Chem. Ind.* **1958**, 157.

[15] L. N. Markovskii, L. S. Bobkova, V. E. Pasnik, *J. Org. Chem. USSR* **1981**, *17*, 1699−1703.

[16] D. F. Shellhamer, D. T. Anstine, K. M. Gallego, B. R. Ganesh, A. A. Hanson, K. A. Hanson, R. D. Henderson, J. M. Prince, V. L. Heasley, *J. Chem. Soc., Perkin Trans. 2* **1995**, 861−866.

[17] NMR spectroscopic data conform to those reported. − ^{1}H NMR, ^{31}P NMR: [17a] M. P. Coogan, M. J. P. Hager, *J. Chem. Soc., Perkin Trans. 2* **1994**, 2101−2107. − ^{13}C NMR: [17b] D. J. Collins, P. F. Drygala, J. M. Swan, *Aust. J. Chem.* **1983**, *36*, 2517−2536.

[18] R. J. Brooks, C. A. Bunton, *J. Org. Chem.* **1975**, *40*, 2059−2064.

[19] P. J. Weidert, E. Geyer, L. Horner, *Phosphorus Sulfur Silicon* **1989**, *45*, 55−59.

[20] M. Regitz, A. Liedhegener, W. Anschütz, H. Eckes, *Chem. Ber.* **1971**, *104*, 2177−2194.

[21] D. J. Burton, D. M. Wiemers, *J. Fluorine Chem.* **1985**, *27*, 85−90.

[22] [22a] G. M. Blackburn, D. E. Kent, *J. Chem. Soc., Chem. Commun.* **1981**, 511−513. − [22b] G. M. Blackburn, D. E. Kent, *J. Chem. Soc., Perkin Trans. 1* **1986**, 913−917.
[23] D. B. Berkowitz, M. Bose, T. J. Pfannenstiel, T. Doukov, *J. Org. Chem.* **2000**, *65*, 4498−4508.
[24] For reasons of brevity, (α*R**,β*R**) isomers containing no other chiral centers are referred to as *l* isomers, and the corresponding (α*R**,β*S**) isomers as *u* isomers.
[25] For example: [25a] C. R. Johnson, J. R. Zeller, *Tetrahedron* **1984**, *40*, 1225−1233. − [25b] J. T. Negri, L. A. Paquette, *J. Am. Chem. Soc.* **1992**, *114*, 8835−8841. − [25c] N. Greeves, L. Lyford, J. E. Pease, *Tetrahedron Lett.* **1994**, *35*, 285−288. − [25d] K. M. Depew, S. J. Danishefsky, N. Rosen, L. Sepp-Lorenzino, *J. Am. Chem. Soc.* **1996**, *118*, 12463−12464.
[26] For example: [26a] G. Stork, J. M. Stryker, *Tetrahedron Lett.* **1983**, *24*, 4887−4890. − [26b] B. M. Trost, D. J. Jebaratnam, *Tetrahedron Lett.* **1987**, *28*, 1611−1614. − [26c] M. D. Preite, M. González-Sierra, J. Zinczuk, E. A. Rúveda, *Tetrahedron: Asymmetry* **1994**, *5*, 503−506.
[27] For example: A. D. Buss, S. Warren, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2307−2325.
[28] F. Bergmann, A. Kalmus, E. Breuer, *J. Am. Chem. Soc.* **1958**, *80*, 4540−4543.
[29] K. Kataoka, S. Tsuboi, *Synthesis* **2000**, 452−456.
[30] J. Park, S. F. Pedersen, *J. Org. Chem.* **1990**, *55*, 5924−5926.
[31] T. Satoh, T. Fujii, K. Yamakawa, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1266−1268.
[32] N. Radembino, P. M. Loiseau, M.-C. Dessalles, L. Marchat, C. Bories, P. Gayral, G. Mahuzier, *Arzneim.-Forsch./Drug Res.* **1998**, *48 (I)*, 294−299.
[33] W. R. Dolbier, Jr., M. D. Bartberger, *J. Org. Chem.* **1995**, *60*, 4984−4985.
[34] S. H. Lee, J. Schwartz, *J. Am. Chem. Soc.* **1986**, *108*, 2445−2447.
[35] V. K. Byistro, L. A. Krichevskii, Z. M. Mildakhmetov, *J. Gen. Chem. USSR* **1976**, *46*, 781−782.
[36] M. Regitz, W. Anschütz, *Chem. Ber.* **1969**, *102*, 2216−2229.
[37] E. Elkik, C. Francesch, *C. R. Acad. Sci. Paris* **1970**, *270 C*, 443−445.
[38] H. Uno, K. Sakamoto, F. Semba, H. Suzuki, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 210−217.
[39] G. Marchese, F. Naso, *Boll. Sci. Fac. Chim. Ind. Bologna* **1968**, *26*, 283−293.
[40] M. A. Tius, J. K. Kawakami, *Tetrahedron* **1995**, *51*, 3997−4010.
[41] M. L. Boys, E. W. Collington, H. Finch, S. Swanson, J. F. Whitehead, *Tetrahedron Lett.* **1988**, *29*, 3365−3368.

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