Formation of Enantiomerically Pure 1-Fluorovinyl and 1-Fluoromethyl Sulfoxides

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(S_S)-[Fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane oxide (**2**) was obtained with complete stereoselectivity from (fluoromethyl)diphenylphosphane oxide (**3**) and (*S*)-(–)-menthyl *p*-toluenesulfinate. 1-Fluorovinyl *p*-tolyl sulfoxides **1** were prepared in good yields by Horner–Wittig reaction of **2** with aldehydes, in excellent enantiomeric excess (*ee*). With ketones, yields were generally low. Stereoselectivity was high for aliphatic aldehydes, producing (*Z*) isomers, and for benzaldehydes, yielding the (*E*) isomers. A two-step, one-pot procedure for the conversion of **3** into **1** was also developed. Solvolysis of **2** provided the first route to enantiomerically pure (*S*)-1-(fluoromethyl)sulfinyl-4-methylbenzene (**7**).

Introduction

1-Fluorovinyl sulfoxides **1** are of potential interest as fluorinated building blocks. With vinyl sulfoxides having been used extensively in the synthesis of natural products,[1] 1-fluorovinyl sulfoxides might well be usable to prepare monofluorinated analogues. Such compounds are expected to be of importance in medicinal chemistry, as a number of fluorinated substrate analogues have been shown to be potent enzyme inhibitors.[2] For research in this field, enantiomerically pure 1-fluorovinyl sulfoxides might be of considerable value, but in contrast with other 1-halovinyl sulfoxides,[3] these have not been reported in the literature.

Research on the reactivity of 1-fluorovinyl sulfoxides has yielded promising results in the synthesis of 3-fluoropyrroles; in the conjugate addition of an isocyanide to 1-fluorovinyl sulfoxides, one of the eight possible diastereoisomers amounted to 40–50% of the product.[4] Treatment of 1-fluorovinyl sulfoxides with organometallic compounds produced vinyl fluorides through desulfurization.[5] Electrolytic reduction of 1-fluorovinyl sulfoxides in a CO_2-saturated solution afforded α-fluoroacrylates.[6] The use of the sulfinyl group as a chiral auxiliary in 1-fluorovinyl sulfoxides has thus far not been studied.

The first synthesis reported for 1-fluorovinyl sulfoxides was of limited synthetic value, as it used γ-radiation-induced addition of thiols to chlorofluoroalkenes as its key step.[7] Wittig reaction of fluoro(phenylthio)methylphosphonium ylides, formed in situ, yielded 1-fluorovinyl sulfides as 1:1 mixtures of isomers, which were oxidized to the corresponding sulfoxides with *m*CPBA.[4,5a] With racemic fluoromethyl phenyl sulfoxide, 1-fluorovinyl sulfoxides have been prepared from aldehydes with moderate to high (*E*) selectivity by means of a phosphonate reagent formed in situ (Horner–Wadsworth–Emmons reaction),[4] and from ketones through a condensation reaction.[5b,5c]

The high stereoselectivities found for vinyl sulfoxides[8] and 1-chlorovinyl sulfoxides,[9] prepared from phosphane oxides[10] (Horner–Wittig reaction), prompted us to investigate a similar route towards [fluoro(sulfinyl)methyl]diphenylphosphane oxides **2**. It was expected that 1-fluorovinyl sulfoxides **1** would be easily accessible from such compounds. For additional synthetic usefulness, an enantioselective route was envisaged. All methods reported for the synthesis of 1-fluorovinyl sulfoxides have α-fluoro sulfides or 1-fluorovinyl sulfides as intermediates. Because of the lack of a stereoselective, asymmetric oxidation of such sulfides, these routes are as yet unsuited for the synthesis of enantiomerically pure compounds.[11]

Enantiomerically pure sulfinylated Wittig-type reagents have been prepared by treating lithiated methylphosphorus compounds with menthyl *p*-toluenesulfinate.[12] To prepare α-fluorinated α-sulfinylphosphane oxides **2**, sulfinylation might take place either before or after the fluorination step. The first route has some precedent. A phosphonate analogue has been reported to be formed in 29% yield by fluorination of a deprotonated α-sulfinylphosphonate with perchloryl fluoride;[13] a corresponding sulfone was prepared using the more convenient Selectfluor™ reagent.[14] The second route would be novel. We recently prepared (fluoromethyl)diphenylphosphane oxide (**3**), which was applied in the synthesis of 1-fluoroalkenes.[15] Enantioselective sulfinylation of this phosphane oxide was expected to provide a proper reagent for the synthesis of 1-fluorovinyl sulfoxides **1** by the Horner–Wittig reaction. Fluorination, by α-metallation, of vinyl sulfoxides,[16] which can be obtained in enantiomerically pure form,[8,16] was also considered.

We would like to report here the synthesis of (S_S)-[fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane oxide (**2**), and its application in the Horner–Wittig reaction with aldehydes and ketones to prepare (*S*)-1-fluorovinyl sulfoxides **1**. The (*E*/*Z*) selectivity and enantioselectivity of the reac-

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tion have been determined. The application of **1** in the first route to enantiomerically pure 1-(fluoromethyl)sulfinyl-4-methylbenzene (**7**) is discussed.

Results and Discussion

Initially, research was aimed at the introduction of fluorine into α-phosphinoyl sulfoxides **4** or vinyl sulfoxides **5** (Figure 1), which can be prepared in an enantioselective manner with the aid of electrophilic fluorinating agents (F^+ donors).[8,12] Test reactions were carried out with racemic compounds. Anions of α-phosphinoyl sulfoxides **4** (R^1 = Me, Ph)[8] with either Li^+ or Na^+ as the counterion, gave only traces of the fluorinated analogues upon treatment with *N*-fluoropyridinium tetrafluoroborate,[17] *N*-fluorobenzenesulfonimide (NFSI),[18] or Selectfluor™.[14] Treatment of α-lithiated phenyl vinyl sulfoxide[16] (**5**: R^1 = Ph, R^2 = H) with NFSI did not result in the desired 1-fluorovinyl sulfoxide; only oligomerized products were found.

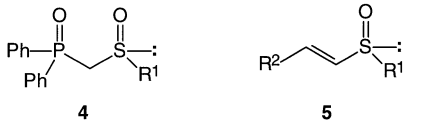
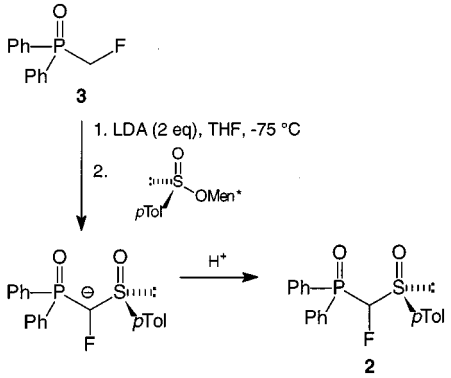


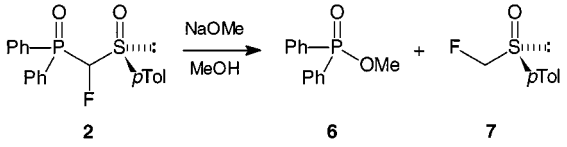
Figure 1. Model substrates for electrophilic fluorination

Treatment of lithiated (fluoromethyl)diphenylphosphane oxide (**3**) with commercially available (*S*)-(−)-menthyl *p*-toluenesulfinate[12] yielded (S_S)-[fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane oxide (**2**) as a mixture of diastereoisomers (Scheme 1). The racemic compound ***rac*-2** was similarly obtained by using methyl *p*-toluenesulfinate.[19] Purification by column chromatography yielded a mixture of diastereomers, along with starting compound **3** and, surprisingly, methyl diphenylphosphinate (**6**).[20] Phosphane oxide **1** could be obtained pure in 65% yield after overnight trituration with ether, dissolving both **3** and **6**. HPLC analysis of the diastereomeric mixture showed the *ee* of the major isomer to be > 99%. From the chemistry discussed below, it could be concluded that the minor isomer was also formed in an excellent *ee*, signifying the completely enantioselective introduction of the sulfoxide functionality. The major isomer could be obtained in pure form by recrystallization from chloroform/diisopropyl ether. Assuming that trends in solubility, diastereomeric excess, and ^{1}H NMR shifts are comparable with those found for an α-chloro-α-sulfinylphosphonate,[21] the major isomer should have the (S_C,S_S) configuration.



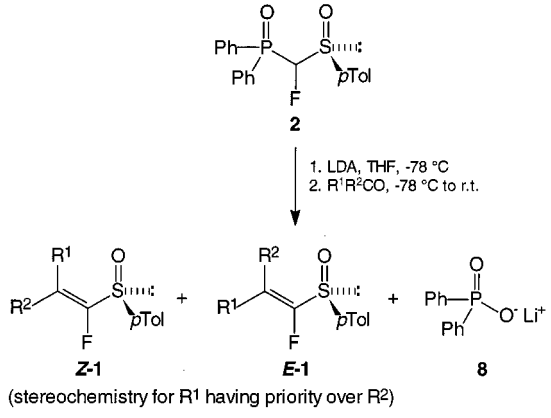
Scheme 1

Phosphinate **6** is formed during workup, by dephosphinylation of **2**. A similar reaction was reported for α-chloro-α-phosphinoylmethylphosphonates.[22] Allowing the temperature of the reaction mixture to rise also resulted in elimination of the phosphane oxide, through action of the menthylate anion formed in the sulfinylation reaction. The other product of this reaction is (*S*)-1-(fluoromethyl)sulfinyl-4-methylbenzene (**7**)[14,23] (Scheme 2). Compound **7** was prepared in nearly quantitative yield by solvolysis of **1** with sodium methoxide. The positive value found for the optical rotation is indicative of the (S_S) configuration.[12,24] HPLC analysis showed the *ee* of **7** to be 98%. This constitutes the first enantioselective synthesis of this compound, and also the first one avoiding the unstable α-fluoro sulfide. Compound **7** appears to be an interesting chiron, as its racemic analogues have been applied in a number of synthetic transformations.[25]



Scheme 2

The Horner−Wittig reaction is presented in Scheme 3. The reaction between deprotonated (by LDA at −78 °C) phosphane oxide **2** and aldehydes occurred smoothly. Upon addition of the aldehyde, reaction progress was apparent from the precipitation of lithium diphenylphosphinate (**8**), starting at −50 to −30 °C. After workup, crude 1-fluorovinyl sulfoxides **1b**−**q** were analyzed by NMR in order to establish the (*E*)/(*Z*) ratios. After purification by column chromatography, yields were usually better than 75%. For ketones, precipitation of phosphinate **8** occurred only at higher temperatures and yields were only modest.



Scheme 3

It was found that the overall yield of the reaction could be improved by performing the sulfinylation and Horner−Wittig reaction in a two-step, one-pot procedure. Instead of quenching the reaction after the anion of **2** had been formed, the carbonyl compound was added directly.

Thus, the problems of solvolysis and separation faced in the workup of phosphane oxide **2** were avoided. An overview of the results is presented in Table 1, with "Method A" being the normal Horner−Wittig reaction and "Method B" the two-step, one-pot, procedure. Note that, for a fair comparison of the yield of **1** over two steps, the yield obtained for **2** should be included for Method A.

positive $[\alpha]_D$ value, while for (*Z*) isomers the value was always negative. The products derived from ketones showed a negative optical rotation. This general trend has been noted previously for a range of vinyl sulfoxides.[26]

To obtain insight into the *ee*, HPLC analysis was carried out for several products. Olefins derived from butanal (**1c**), benzyloxyacetaldehyde (**1g**), and benzaldehyde (**1k**) showed

Table 1. Synthesis of (*S*)-1-fluorovinyl sulfoxides **1** from carbonyl compounds R^1-CO-R^2

Entry **1**	R^1	R^2	Method	Yield [%][a]	(*E*)/(*Z*) ratio[b]	δ(F, *E*)[c]	δ(F, *Z*)[c]
a	H	H	A	82	–	−114.4 (44.6, 13.9)	
b	Me	H	A	91	8:92	−130.3 (34.4)	−127.6 (16.8)
c	*n*Pr	H	A	80	9:91	−129.2 (34.7)	−127.8 (17.6)
d	*i*Pr	H	A	75	37:63	−129.7 (35.8)	−130.8 (17.5)
d	*i*Pr	H	B	60	37:63		
e	*t*Bu	H	B	57	< 2:98[d]	–	−127.8 (24.1)
f	$PhCH_2CH_2-$	H	B	58	9:91	−128.0 (35.1)	−126.3 (16.8)
g	$BzlOCH_2-$	H	A	91[e]	9:91	−123.0 (35.1)	−122.8 (16.1)
h	$CH_2=C(Me)-$	H	A	91	50:50	−124.8 (38.0)	−126.4 (19.7)
i	(*E*)-MeCH=CH−	H	A	70	62:38	−129.4 (30.5)	−132.0 (18.3)
j	(*E*)-PhCH=CH−	H	A	81	41:59	−126.7 (32.7)	−127.4 (16.1)
k[f]	Ph	H	A	85	80:20	−122.9 (37.3)	−124.5 (17.6)
l	*p*-$MeOC_6H_4$	H	B	60	> 98:2[d]	−126.7 (37.3)	–
m	*p*Tol	H	A	86	94.5:5.5	−124.4 (37.3)	−125.6 (17.6)
n	*o*Tol	H	A	88	> 98:2[d]	−124.2 (36.6)	–
o	2-Pyr	H	A	66	37:63	−118.4 (36.6)	−125.9 (16.1)
p	5-Me-2-furanyl	H	A	89	28:72	−124.6 (35.1)	−133.7 (16.8)
q	Ph	Me	A	18	52:48[g]	−130.9 (3.6)[h]	−131.9 (3.7)[h]
r	$-[CH_2]_5-$		A	26[i]	–	−139.0	
r	$-[CH_2]_5-$		B	58[j]	–		
s	$-[CH_2]_4-$		B	7	–	−131.8	

[a] Combined yield of purified isomers, with respect to **2** (Method A) or **3** (Method B). – [b] Determined by ^{19}F NMR, unless stated otherwise. – [c] Measured in $CDCl_3$ with $CFCl_3$ as an external reference, δ given in ppm; $^3J_{FH}$ (vic) given in parentheses. – [d] Only one isomer detected. – [e] ***rac*-1g** was prepared in 92% yield. – [f] Racemate ***rac*-1k** prepared in 63% yield [(*E*)/(*Z*) = 80:20] by Method B. – [g] Determined after column chromatography. – [h] $^4J_{FH}$ (Me). – [i] Main product fluoromethyl sulfoxide **7** (62%). – [j] Supported by NMR, but HRMS data unsatisfactory.

The (*E*)/(*Z*) ratios were determined from the ^{19}F NMR spectra of the crude products. The configurations of the products obtained from aldehydes were deduced from the coupling constants between the fluorine and β-hydrogen atoms. Coupling constants between vicinal *cis* H and F ranged from 14 to 23 Hz, those between vicinal *trans* H and F from 30 to 46 Hz. The configuration of acetophenone derivatives **1q** was determined on the basis of the coupling constants between the fluorine and β-methyl carbon atoms [(*E*): J_{FC} = 4.3 Hz; (*Z*): J_{FC} = 0 Hz].

Stereoselectivity was found to be highly dependent on the nature of the aldehyde used. Aliphatic aldehydes, with the exception of isobutyraldehyde, gave very high (*Z*) selectivities. Benzaldehydes, on the other hand, yielded the (*E*) isomers in large excess. The heteroaromatic and α,β-unsaturated aldehydes studied lacked stereoselectivity. The method used did not influence the stereoselectivity (Entries **1c**, **1d**, and **1k**).

Separation of the isomers by column chromatography was rather laborious, although in most cases it was at least possible to obtain the major isomer in pure form. 1-Fluorodienyl sulfoxides **1i** and **1j** could not be separated into their isomers.

A further clue to the regiochemistry of the aldehyde derivatives was found by measuring the optical activity of the purified isomers. Without exception, (*E*) isomers showed a excellent *ee* values (> 99%). Racemization through isomerization to an allyl sulfoxide, and subsequent allyl sulfoxide−sulfenite rearrangement did not appear to have occurred.[26,27] Racemization in ketone derivatives **1q**−**s** was not investigated, as the applicability of **2** in the Horner−Wittig reaction with ketones was found to be limited.

For comparative purposes, an attempt was made to synthesize enantiopure *O*,*O*-diethyl (S_S)-fluoro(*p*-tolylsulfinyl)-methylphosphonate (**9**) (Figure 2) from *O*,*O*-diethyl fluoromethylphosphonate[28] and (*S*)-(−)-menthyl toluenesulfinate. This reaction gave a disappointingly low yield. This was not due to dephosphorylation of **9**, as no **7** and only traces of diethyl methylphosphate were found in the crude reaction mixture (^1H NMR).

The Horner−Wadsworth−Emmons reaction was found to occur with complete conversion, showing only moderate, but consistent, (*E*) selectivity for butyraldehyde [**1c**: (*E*)/(*Z*) = 70:30], crotonaldehyde [**1i**: (*E*)/(*Z*) = 70:30] and benzaldehyde [**1k**: (*E*)/(*Z*) = 83:17], which agrees well with the results of the phosphonate prepared in situ.[4]

It may seem surprising that the stereoselectivity of the Horner−Wittig synthesis of 1-fluorovinyl sulfoxides shows such a strong dependence on the type of aldehyde used, while the analogous syntheses of vinyl[8] and 1-chlorovinyl[9] sulfoxides occurred with high (*E*) selectivity. A similar pat-

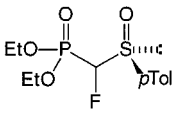


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Figure 2. *O*,*O*-Diethyl (S_S)-fluoro(*p*-tolylsulfinyl)methylphosphonate

tern of stereoselectivity has also been found for the Horner−Wittig synthesis of acrylates; 1-fluoroacrylates are formed with aldehyde-dependent stereoselectivities,[29] while the nonfluorinated compounds are formed with good (*E*) selectivities.[30] It has been suggested that the stereochemistry of olefinations of fluorinated phosphane oxides should be compared with that of nonfluorinated phosphonates.[29] Indeed, a less pronounced, aldehyde-dependent stereoselectivity has been observed for the Horner−Wadsworth−Emmons synthesis of vinyl sulfoxides.[12c]

Conclusions

The reaction between lithiated (fluoromethyl)diphenylphosphane oxide (**3**) and commercially available (*S*)-(−)-menthyl *p*-toluenesulfinate occurs with complete inversion of the configuration. [Because of a change in priorities of the substituents, the configuration descriptor remains (*S*).] (S_S)-[Fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane oxide (**2**) is an excellent starting material for the synthesis of enantiomerically pure fluoromethyl sulfoxide **7** (through solvolysis) and 1-fluorovinyl sulfoxides **1** (through the Horner−Wittig reaction). Stereoselectivity of the Horner−Wittig reaction is highly dependent on the type of aldehyde used, with aliphatic aldehydes displaying (*Z*) selectivity and benzaldehydes (*E*) selectivity.

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, or Merck 60 F_{254} silica gel plates were used, viewing with ultraviolet light. Differences in R_f values between the two types were negligible. − Melting points were determined with a Büchi melting point apparatus and are uncorrected. − ^{1}H- (200 MHz), ^{13}C- (50 MHz), ^{31}P- (80 MHz), and ^{19}F-NMR (188 MHz) spectra were recorded in $CDCl_3$ with a Bruker AC-200 instrument. Chemical shifts are given in δ (ppm) relative to TMS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), or 85% phosphoric acid (^{31}P). Coupling constants (*J*) are given in Hz. For the 1D NOE (diff) experiment (**1e**), a Bruker WM-300 instrument was used. − The enantiomeric excess (*ee*) of selected compounds was determined by HPLC analysis, performed on a Daicel column (type specified), using mixtures of *n*-hexane (H) and isopropyl alcohol (I) as eluents (λ_{det} = 254 nm). − Optical rotations were measured with a Propol automatic polarimeter at 589 nm. − High resolution mass spectrometry was performed with a Finnigan Matt 900, equipped with a direct insertion probe (DIP), or with an Electron Spray Interface (ESI). − Elemental analyses were obtained with a Perkin−Elmer 2400 II CHNS Analyzer. − Methyl *p*-toluenesulfinate[19] and *O*,*O*-diethyl fluoromethylphosphonate[31] were prepared by literature procedures. LDA (ca. 0.5 M) was freshly prepared by addition of *n*BuLi (1.6 M) to an ice-cooled solution of diisopropylamine in THF. Aldehydes and ketones were distilled or washed with base before use. THF was distilled from $LiAlH_4$. Diisopropylamine was dried with KOH. Remaining reagents were used without further purification. Petroleum ether signifies the fraction boiling at 40−60 °C. All reactions requiring dry conditions were performed under an inert gas.

Sulfinylation of (Fluoromethyl)diphenylphosphane Oxide (3): Phosphane oxide **3** (20 mmol) was dissolved in THF (400 mL). After cooling to −78 °C, LDA (2.2 equiv.) was added. The *p*-toluenesulfinate (22 mmol) in THF (50 mL) was added rapidly. Stirring was continued for 2 min, after which the reaction was quenched with acetic acid (6 mL) in methanol (200 mL). Water (200 mL) was added, and the mixture was extracted with dichloromethane (3 × 200 mL). The combined organic layers were washed with water (200 mL) and saturated brine (200 mL), and dried ($MgSO_4$). After filtration and evaporation of the solvents, a yellowish oil remained, which was purified further by column chromatography (ether or ethyl acetate/petroleum ether, 3:2), giving a solid or semi-solid mixture of phosphane oxides [R_f = 0.10 (ether)]. After overnight stirring with ether, compound **2** was obtained pure, as a colorless solid. Invariably, a diastereomeric mixture was formed, usually in a 3:1 ratio.

(*R*/S_C),(S_S)-[Fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane Oxide (2): Prepared with (−)-(*S*)-menthyl *p*-toluenesulfinate. − Yield 4.84 g (65%). − An analytically pure sample of the major isomer could be obtained by recrystallization of 0.39 g from diisopropyl ether/chloroform. Yield 0.20 g of colorless crystals, m.p. 159−162 °C. − ^{1}H NMR: δ = 2.39 (s, 3 H, *Me*), 5.58 (dd, 1 H, J_{FH} = 46.0, J_{PH} = 1.5, PC*H*F), 7.30 (d, 2 H, *J* = 8.0, H_m, Tol), 7.42−7.65 (m, 6 H, $H_{m,p}$, PhP), 7.60 (d, 2 H, *J* = 8.0, H_o, Tol), 7.73−7.83 (ddd, 2 H, J_{PH} = 12.1, *J* = 6.9, 0.7, H_o, PhP), 7.90−8.00 (dddd, 2 H, J_{PH} = 12.2, *J* = 7.5, 2 × 0.7, H_o, PhP). − ^{13}C NMR: δ = 21.2 (*Me*), 104.2 (dd, J_{FC} = 251.8, J_{PC} = 71.7, P*C*HF), 125.3 (*C*H, Tol), 128.2−132.8 (*C*H, PhP), 135.8 (*C*S), 142.4 (*C*Me). − ^{31}P NMR: δ = 25.3 (J_{FP} = 54.9). − ^{19}F NMR: δ = −201.4. − $[\alpha]_D^{20}$ = +193 (*c* = 1.0, CH_2Cl_2). − *ee* > 99% (major) [HPLC, Chiralpak AD (eluent: H/I = 85:15; 1.00 mL/min): $t'_{R,1}$ = 26.82 min (R_S), $t'_{R,2}$ = 36.10 min (S_S); α = 1.35]. − The minor isomer was not obtained in pure form: ^{1}H NMR: δ = 2.36 (s, 3 H, *Me*), 5.85 (dd, 1 H, J_{FH} = 47.2, J_{PH} = 1.8, PC*H*F), 7.18 (d, 2 H, *J* = 8.0, H_m, Tol), 7.40−7.59 (m, 8 H, H-arom.), 7.66−7.88 (m, 4 H, H_o, PhP). − ^{13}C NMR: δ = 21.2 (*Me*), 103.5 (dd, J_{FC} = 250.2, J_{PC} = 70.2, P*C*HF), 126.0 (*C*H, Tol), 128.2−132.8 (*C*H, Ph), 135.7 (*C*S), 142.7 (*C*Me). − ^{31}P NMR: δ = 23.8 (J_{FP} = 52.5). − ^{19}F NMR: δ = −196.6. − The *ee* could not be determined by chromatography [HPLC, Chiralpak AD (eluent: H/I = 85:15; 1.00 mL/min): t'_R = 51.68 min (S_S and R_S)]. − HRMS (DIP): *m*/*z* [$C_{20}H_{18}FO_2PS^+$] calcd. 372.0772; found 372.0749.

[Fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane Oxide (*rac*-2): Prepared in a similar way on a 32-mmol scale, using methyl *p*-toluenesulfinate.[19] − Yield 8.36 g (70%).

Synthesis of 1-Fluorovinyl Sulfoxides 1a−s. − Method A: Phosphane oxide **2** (2.0 mmol, mixture of isomers) was dissolved in THF (50 mL). Non-enolizable aldehydes (1.1 equiv.) were dissolved in the same flask before deprotonation of the phosphane oxide. After cooling to −78 °C, LDA (1.1 equiv.) was added. Enolizable aldehydes and ketones (1.1 equiv.) were added as THF solutions

(5 mL) through a dropping funnel. Paraformaldehyde (3 equiv.) was added in portions over a period of 15 min. The mixture was allowed to warm to room temperature. Progress of the reaction was apparent by the precipitation of phosphinate **8**. Stirring was continued until the reaction had reached completion. This usually took about 1 h. For ketones and pivaldehyde the reaction required stirring overnight to reach completion. A saturated NH_4Cl solution (50 mL) was added, and the reaction mixture was extracted with ether (3 × 30 mL). The combined organic layers were dried with $MgSO_4$ (for **1o**: Na_2SO_4). After filtration and evaporation of the solvents, the crude compound was analyzed by ^1H and ^{19}F NMR. Pure compounds were obtained after column chromatography, though the isomers could not always be separated. − **Method B:** (Fluoromethyl)diphenylphosphane oxide (**3**) (2.0 mmol) was converted into lithiated **2** using the procedure described before. Instead of quenching the reaction, the appropriate aldehyde or ketone (2.0 equiv.), dissolved in THF (5 mL), was added at −70 °C. Use of less aldehyde resulted in lower yields. Further treatment was identical to that described for Method A. Method used, yields, (*E*)/(*Z*) ratios, and ^{19}F- NMR-spectroscopic data are all given in Table 1.

(*S*)-1-Fluoro-1-(*p*-tolylsulfinyl)ethene (1a): R_f = 0.42 (petroleum ether/ether, 1:1). − Colorless oil. − ^1H NMR: δ = 2.43 (s, 3 H, *Me*), 5.30 (dd, 1 H, J_{FH} = 13.9, J = 4.4, H_E), 5.55 (dd, 1 H, J_{FH} = 44.6, J = 4.4, H_Z), 7.35 (d, 2 H, J = 8.0, H_m), 7.63 (d, 2 H, J = 8.0, H_o). − ^{13}C NMR: δ = 20.8 (*Me*), 95.1 (d, J_{FC} = 7.6, CH_2=CF_2), 124.9 (*C*H, Tol), 129.6 (*C*H, Tol), 136.8 (*C*S), 142.4 (*C*Me), 165.6 (d, J_{FC} = 311.2, *C*F). − $[\alpha]_D^{20}$ = +310 (c = 1.0, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_9H_9FOS^+$ + H] calcd. 185.0436; found 185.0434.

(*S*)-1-Fluoro-1-(*p*-tolylsulfinyl)prop-1-ene (1b): The (*E*) isomer (***E*-1b**) was eluted first: R_f = 0.16 (petroleum ether/ethyl acetate, 9:1). − Colorless solid, m.p. 49.5−50 °C. − ^1H NMR: δ = 1.78 (dd, 3 H, J_{FH} = 2.9, J = 7.3, *Me*-3), 2.43 (s, 3 H, *Me*, Tol), 5.83 (dq, 1 H, J_{FH} = 34.4, J = 7.3, C*H*=CF), 7.34 (d, 2 H, J = 8.8, H_m), 7.60 (d, 2 H, J = 8.8, H_o). − ^{13}C NMR: δ = 9.50 (*Me*-3), 21.5 (*Me*, Tol), 110.0 (d, J_{FC} = 7.6, *C*H=CF), 125.2 (*C*H, Tol), 130.0 (*C*H, Tol), 137.2 (*C*S), 142.5 (*C*Me, Tol), 158.8 (d, J_{FC} = 309.8, *C*F). − $[\alpha]_D^{20}$ = +145 (c = 0.15, CH_2Cl_2). − $C_{10}H_{11}FOS$ (198.26): calcd. C 60.58, H 5.59; found C 60.91, H 5.70. − Next, the (*Z*) isomer (***Z*-1b**) was obtained: R_f = 0.10 (petroleum ether/ethyl acetate, 9:1). − Colorless solid, m.p. 76−76.5 °C. − ^1H NMR: δ = 2.05 (dd, 3 H, J_{FH} = 2.9, J = 7.3, CH*Me*), 2.43 (s, 3 H, *Me*, Tol), 5.77 (dq, 1 H, J_{FH} = 16.8, J = 7.3, C*H*=CF), 7.35 (d, 2 H, J = 8.4, H_m), 7.58 (d, 2 H, J = 8.4, H_o). − ^{13}C NMR: δ = 10.1 (d, J_{FC} = 6.1, *Me*-3), 20.7 (*Me*, Tol), 113.2 (d, J_{FC} = 13.7, *C*H=CF), 124.1 (*C*H, Tol), 129.5 (*C*H, Tol), 136.0 (*C*S), 141.5 (*C*Me), 157.2 (d, J_{FC} = 311.3, *C*F). − $[\alpha]_D^{20}$ = −202 (c = 1.0, CH_2Cl_2). − $C_{10}H_{11}FOS$ (198.26): calcd. C 60.58, H 5.59; found C 60.65, H 5.74.

(*S*)-1-Fluoro-1-(*p*-tolylsulfinyl)pent-1-ene (1c): Column chromatography (petroleum ether/ethyl acetate, 9:1), gave the (*E*) isomer (***E*-1c**) first: R_f = 0.17 (petroleum ether/ethyl acetate,10:1). − Colorless solid, m.p. 35−37 °C. − ^1H NMR: δ = 0.92 (t, 3 H, J = 7.3, *Me*-5), 1.48 (tq, 2 H, J = 7.3 (2 ×), CH_2-4), 2.19 (ddt, 2 H, J = 7.3, 2.0, CH_2-3), 2.42 (*Me*, Tol), 5.80 (dt, 1 H, J_{FH} = 34.7, J = 7.6, C*H*=CF), 7.34 (d, 2 H, J = 8.0, H_m), 7.60 (d, 2 H, J = 8.0, H_o). − ^{13}C NMR: δ = 13.5 (*Me*-5), 21.5 (*Me*, Tol), 21.8 (CH_2-4), 26.1 (CH_2-3), 114.5 (d, J_{FC} = 7.6, *C*H=CF), 125.3 (*C*H, Tol), 130.1 (*C*H, Tol), 137.5 (*C*S), 142.5 (*C*Me), 158.3 (d, J_{FC} = 309.8, *C*F). − $[\alpha]_D^{20}$ = +109 (c = 0.23, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{12}H_{15}FOS^+$ + H] calcd. 227.0906; found 227.0857. − The (*Z*) isomer (***Z*-1c**) was eluted as the second fraction: R_f = 0.14 (petroleum ether/ethyl acetate,10:1). − Colorless oil. − ^1H NMR: δ = 1.01 (t, 3 H, J = 7.3, *Me*-5), 1.55 (m, 2 H, CH_2-4), 2.43 (s, 3 H, *Me*, Tol), 2.45 (m, 2 H, CH_2-3), 5.73 (dt, 1 H, J_{FH} = 17.6, J = 8.0, C*H*=CF), 7.34 (d, 2 H, J = 8.0, H_m), 7.58 (d, 2 H, J = 8.0, H_o). − ^{13}C NMR: δ = 13.1 (*Me*-5), 21.0 (*Me*, Tol), 22.3 (CH_2-4), 26.8 (CH_2-3), 118.2 (d, J_{FC} = 10.9, *C*H=CF), 124.3 (*C*H, Tol), 129.6 (*C*H, Tol), 136.0 (*C*S), 141.6 (*C*Me), 157.2 (d, J_{FC} = 314.2, *C*F). − $[\alpha]_D^{20}$ = −186 (c = 1.0, CH_2Cl_2). − *ee* > 99% [HPLC, Chiralcel OJ (eluent: H/I = 95:5; 1.00 mL/min): $t'_{R,1}$ = 6.05 min (*S*), $t'_{R,2}$ = 8.19 min (*R*); α = 1.35].

1-Fluoro-1-(*p*-tolylsulfinyl)pent-1-ene (*rac*-1c): Prepared as an HPLC reference by Method A. − Yield 90%.

(*S*)-1-Fluoro-3-methyl-1-(*p*-tolylsulfinyl)but-1-ene (1d): Chromatography first afforded the (*E*) isomer (***E*-1d**) as a colorless oil, R_f = 0.43 (petroleum ether/ether, 1:1). − ^1H NMR: δ = 1.07 (d, 6 H, J = 5.8, CHMe_2), 2.43 (s, 3 H, *Me*, Tol), 2.80 (dh, 1 H, J = 5.8, J = 9.5, C*H*Me_2, 5.67 (dd, 1 H, J_{FH} = 35.8, J = 9.5, C*H*=CF), 7.34 (d, 2 H, J = 8.4, H_m), 7.6 (d, 2 H, J = 8.4, H_o). − ^{13}C NMR: δ = 20.7 (*Me*, Tol), 21.8 (CHMe_2), 24.5 (*C*HMe_2), 120.7 (d, J_{FC} = 6.1, *C*H=CF), 124.9 (*C*H, Tol), 129.7 (*C*H, Tol), 137.1 (*C*S), 142.1 (*C*Me), 156.6 (d, J_{FC} = 309.8, *C*F). − $[\alpha]_D^{20}$ = +56 (c = 0.60, CH_2Cl_2). − The (*Z*) isomer (***Z*-1d**) was obtained afterwards as a colorless solid, melting at room temperature [R_f = 0.37 (petroleum ether/ether, 1:1)]. − ^1H NMR: δ = 1.12 (d, 3 H, J = 6.6, CHMe_2), 1.17 (d, 3 H, J = 6.6, CHMe_2), 2.43 (s, 3 H, *Me*, Tol), 3.13 (dtt, 1 H, J = 11.0, 6.6 (2 ×), C*H*Me_2), 5.55 (dd, 1 H, J_{FH} = 17.5, J = 11.0, C*H*=CF), 7.34 (d, 2 H, J = 7.9, H_m), 7.57 (d, 2 H, J = 7.9, H_o). − ^{13}C NMR: δ = 21.3 (*Me*, Tol), 23.0 (CHMe_2, one of two), 23.1 (CHMe_2, one of two), 25.6 (d, J_{FC} = 4.6, *C*HMe_2, 124.6 (*C*H, Tol), 124.0 (d, J_{FC} = 7.6, *C*H=CF), 129.9 (*C*H, Tol), 136.4 (*C*S), 142.0 (*C*Me), 156.0 (d, J_{FC} = 314.3, *C*F). − $[\alpha]_D^{20}$ = −160 (c = 2.0, CH_2Cl_2). − HRMS (ESI): *m*/*z*: [$C_{12}H_{15}FOS^+$ + H] calcd. 227.0906; found 227.0854.

(*S*),(*Z*)-1-Fluoro-3,3-dimethyl-1-(*p*-tolylsulfinyl)but-1-ene (*Z*-1e): R_f = 0.16 (petroleum ether/ethyl acetate, 10:1). − Colorless solid, m.p. 39.0−39.5 °C. − ^1H NMR: δ = 1.33 (s, 9 H, CMe_3), 2.41 (s, 3 H, *Me*, Tol), 5.82 (d, 1 H, J_{FH} = 24.1, C*H*=CF), 7.33 (d, 2 H, J = 8.0, H_m), 7.59 (d, 2 H, J = 8.0, H_o). − ^{13}C NMR: δ = 21.1 (*Me*, Tol), 31.6 (CMe_3), 124.8 (*C*H, Tol), 129.1 (d, J_{FC} = 10.7, *C*H=CF), 129.8 (*C*H, Tol), 136.1 (*C*S), 141.7 (*C*Me), 155.7 (d, J_{FC} = 312.8, *C*F), δ (*C*Me_3) not determined. − $[\alpha]_D^{20}$ = −194 (c = 1.0, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{12}H_{17}FOS^+$ + Na] calcd. 262.0803; found 262.0773. − Confirmation of the stereochemistry of the double bond was obtained by 1D-NOE (diff) 300-MHz ^1H-NMR spectroscopy; the $[\alpha]_D^{20}$ value is also indicative of the (*Z*) configuration.

(*S*)-1-Fluoro-4-phenyl-1-(*p*-tolylsulfinyl)but-1-ene (1f): The (*E*) isomer (***E*-1f**) was eluted first, but could not be obtained in pure form [R_f = 0.27 (petroleum ether/ether, 1:1)]. − Continued elution afforded the (*Z*) isomer (***Z*-1f**) [R_f = 0.20 (petroleum ether/ether, 1:1)]. − Colorless solid, m.p. 63.5−64 °C. − ^1H NMR: δ = 2.40 (s, 3 H, *Me*), 2.68−2.95 (m, 4 H, CH_2-3,4), 5.72 (dt, 1 H, J_{FH} = 16.8, J = 8.0, C*H*=CF), 7.18−7.37 (m, 9 H, H-arom.). − ^{13}C NMR: δ = 21.0 (*Me*), 26.9 (d, J_{FC} = 3.0, CH_2), 35.0 (CH_2), 117.5 (d, J_{FC} = 12.2, *C*H=CF), 124.3 (*C*H, Tol), 126.1 (*C*H, Ph), 128.0 (d, J_{FC} = 6.1, *C*H, Ph), 128.3 (*C*H, Ph), 129.6 (*C*H, Tol), 135.7 (d, J_{FC} = 3.0, C_i, Ph), 139.6 (*C*S), 141.5 (*C*Me), 157.6 (d, J_{FC} = 315.9, *C*F). − $[\alpha]_D^{20}$ = −181 (c = 1.0, CH_2Cl_2). − $C_{17}H_{17}FOS$ (288.38): calcd. C 70.80, H 5.94; found C 70.48, H 6.13.

(*S*)-3-Benzyloxy-1-fluoro-1-(*p*-tolylsulfinyl)prop-1-ene (1g): A fraction containing primarily the (*E*) isomer (***E*-1g**) was eluted first: R_f = 0.33 (petroleum ether/ether, 1:1). − Colorless oil, contamin-

ated with some (*Z*) isomer. − ^{1}H NMR: δ = 2.43 (s, 3 H, *Me*), 4.20 (dd, 1 H, *J* = 12.0, 6.6, C*H*$_2$-3), 4.25 (dd, 1 H, *J* = 12.0, 6.6, C*H*$_2$-3), 4.50 (s, 2 H, C*H*$_2$Ph), 6.03 (dt, 1 H, J_{FH} = 35.1, *J* = 6.6, C*H*=CF), 7.29−7.36 (m, 5 H, Ph), 7.35 (d, 2 H, *J* = 8.0, H$_m$, Tol), 7.62 (d, 2 H, *J* = 8.0, H$_o$, Tol). − ^{13}C NMR: δ = 21.5 (*Me*), 62.2 (d, J_{FC} = 3.1, *C*H$_2$-3), 72.6 (*C*H$_2$Ph), 109.7 (d, J_{FC} = 4.6, *C*H=CF), 125.4 (*C*H, Tol), 127.8 (*C*H, Ph), 127.9 (*C*H, Ph), 128.4 (*C*H, Ph), 130.1 (*C*H, Tol), 137.1 (*C*$_i$, Ph), 137.4 (*C*S), 142.9 (*C*Me), 160.4 (d, J_{FC} = 312.8, *C*F). − Continued elution afforded the majority of the (*Z*) isomer (***Z*-1g**) in pure form: R_f = 0.29 (petroleum ether/ether, 1:1). − Colorless solid, m.p. 35−36 °C (hexanes). − ^{1}H NMR: δ = 2.42 (s, 3 H, *Me*), 4.33 (ddd, 1 H, J_{FH} = 2.0, *J* = 12.4, 7.5, C*H*$_2$-3), 4.51 (ddd, 1 H, J_{FH} = 2.0, *J* = 12.4, 7.5, C*H*$_2$-3), 4.58 (d, 1 H, *J* = 11.7, C*H*$_2$Ph), 4.62 (d, 1 H, *J* = 11.7, C*H*$_2$Ph), 5.90 (ddd, 1 H, J_{FH} = 16.1, *J* = 8.0, 7.3, C*H*=CF), 7.32 (d, 2 H, *J* = 8.0, H$_m$), 7.37 (m, 5 H, Ph), 7.57 (d, 2 H, *J* = 8.0, H$_o$). − ^{13}C NMR: δ = 20.7 (*Me*), 61.9 (d, J_{FC} = 7.6, *C*H$_2$-3), 72.0 (*C*H$_2$Ph), 113.2 (d, J_{FC} = 12.2, *C*H=CF), 124.3 (*C*H, Tol), 127.3 (*C*H, Ph), 127.9 (*C*H, Ph), 129.5 (*C*H, Tol), 135.7 (*C*$_i$, Ph), 136.9 (*C*S), 141.6 (*C*Me), 159.9 (d, J_{FC} = 320.4, *C*F). − $[\alpha]_D^{20}$ = −161 (*c* = 0.55, CH_2Cl_2). − *ee* > 99% [HPLC, Chiralcel OJ (eluent: H/I = 90:10; 1.00 mL/min): $t'_{R,1}$ = 22.80 min (*S*), $t'_{R,2}$ = 25.58 min (*R*); α = 1.12]; the sample should not contain any (*E*) isomer [t'_R = 25.69 (*R* and *S*)], as overlap of the signals would render exact determination of the *ee* impossible. − HRMS (ESI): *m*/*z* [$C_{17}H_{17}FO_2S^+$ + Na] calcd. 327.0831; found 327.0775.

3-Benzyloxy-1-fluoro-1-(*p*-tolylsulfinyl)prop-1-ene (***rac*-1g**): Prepared as an HPLC reference by Method A. − Yield 92%.

(*S*)-1-Fluoro-3-methyl-1-(*p*-tolylsulfinyl)buta-1,3-diene (1h): Chromatography afforded the (*E*) isomer (***E*-1h**) first: R_f = 0.48 (petroleum ether/ether, 1:1). − Colorless solid, melting near room temperature. − ^{1}H NMR: δ = 1.98 (d, 3 H, *J* = 2.2, H$_2$C=C*Me*), 2.43 (s, 3 H, *Me*, Tol), 5.12 (dq, 1 H, *J* = 1.5, *H*$_2$C=CMe), 5.23 (m, 1 H, *H*$_2$C=CMe), 6.27 (d, 1 H, J_{FH} = 38.0, C*H*=CF), 7.35 (d, 2 H, *J* = 8.0, H$_m$), 7.62 (d, 2 H, *J* = 8.0, H$_o$). − ^{13}C NMR: δ = 20.9 (d, J_{FC} = 4.6, H$_2$C=C*Me*), 21.2 (*Me*, Tol), 113.5 (*C*H=CF), 121.5 (d, J_{FC} = 4.6, H$_2$*C*=CMe), 125.1 (*C*H, Tol), 129.9 (*C*H, Tol), 136.3 (d, J_{FC} = 3.0, H$_2$C=*C*Me), 137.2 (*C*Me), 142.5 (*C*S), 157.7 (d, J_{FC} = 318.9, *C*F). − $[\alpha]_D^{20}$ = +237 (*c* = 1.7, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{12}H_{13}FOS^+$ + H] calcd. 225.0749; found 225.0694. − The (*Z*) isomer (***Z*-1h**) was obtained next: R_f = 0.34 (petroleum ether/ether, 1:1). − Colorless oil. − ^{1}H NMR: δ = 2.11 (m, 3 H, H$_2$C=C*Me*), 2.43 (s, 3 H, *Me*, Tol), 5.24 (m, 1 H, *H*$_2$C=CMe), 5.27 (dq, 1 H, *J* = 2.2, 1.5, *H*$_2$C=CMe), 6.32 (d, J_{FH} = 19.7, C*H*=CF), 7.34 (d, 2 H, *J* = 8.4, H$_m$), 7.60 (d, 2 H, *J* = 8.4, H$_o$). − ^{13}C NMR: δ = 21.0 (H$_2$C=C*Me*), 22.6 (*Me*, Tol), 120.8 (d, J_{FC} = 18.3, *C*H=CF), 122.8 (d, J_{FC} = 6.1, H$_2$*C*=CMe), 124.6 (*C*H, Tol), 129.7 (*C*H, Tol), 134.8 (d, J_{FC} = 7.6, H$_2$C=*C*Me), 136.2 (d, J_{FC} = 3.0, *C*S), 141.8 (*C*Me), 157.6 (d, J_{FC} = 317.4, *C*F). − $[\alpha]_D^{20}$ = −302 (*c* = 1.8, CH_2Cl_2).

(*S*),(1*Z*/*E*),(3*E*)-1-Fluoro-1-(*p*-tolylsulfinyl)penta-1,3-diene (1i): Obtained as a mixture of isomers after column chromatography (petroleum ether/ether, 1:1; or petroleum ether/ethyl acetate, 10:1). − R_f = 0.20 (petroleum ether/ethyl acetate, 10:1). − Colorless oil. − ^{1}H NMR: δ = 1.83 (d, *J* = 8.8, *Me*-5), 1.84 (dd, *J* = 8.8, 2.2, *Me*-5) (comb. 3 H), 2.42 (s, 3 H, *Me*, Tol), 5.88−6.12 (m, 1 H, H-4), 6.18−6.42 (m, 1.6 H, H-2, H-3 {*E*}), 6.63 (ddq, 0.4 H, *J* = 13.2, 11.0, 1.8, H-3 {*Z*}), 7.33 (d, 2 × 2 H, *J* = 8.0, Tol), 7.58 (d, 2 H, *J* = 8.0, Tol), 7.59 (d, 2 H, *J* = 8.0, Tol). − ^{13}C NMR: δ = 17.6 (*Me*-5), 20.3 (*Me*, Tol), 113.1 (d, J_{FC} = 4.6, *C*H-2, *Z*), 118.4 (d, J_{FC} = 16.8, *C*H-2, *E*), 119.7 (*C*H-4, *E*), 120.2 (d, J_{FC} = 4.6, *C*H-4, *Z*), 123.7 (*C*H, Tol, *E*), 124.2 (*C*H, Tol, *Z*), 129.1 (*C*H, Tol), 135.7 (d, J_{FC} = 3.0, *C*H-3, *Z*), 136.0 (d, J_{FC} = 10.7, *C*H-3, *E*), 136.5 (*C*S), 141.0 (*C*Me, *E*), 141.4 (*C*Me, *Z*), 155.4 (d, J_{FC} = 317.4, *C*F, *Z*), 156.8 (d, J_{FC} = 317.4, *C*F, *E*). − HRMS (ESI): *m*/*z* [$C_{12}H_{13}FOS^+$ + H] calcd. 225.0749; found 225.0707.

(*S*),(1*Z*/*E*),(3*E*)-1-Fluoro-4-phenyl-1-(*p*-tolylsulfinyl)buta-1,3-diene (1j): Obtained as a mixture of isomers after column chromatography (petroleum ether/ether, 1:1; or petroleum ether/ethyl acetate, 10:1). − R_f = 0.16 (petroleum ether/ethyl acetate, 10:1). − Off-white solid. − ^{1}H NMR: δ = 2.43 (s, 3 H, *Me*, both isomers), 6.41−6.63 (m), and 6.71−6.92 (m) (comb. 3 H, diene), 7.28−7.51 (m, 7 H, H-arom.), 7.61 (d, *J* = 8.0), and 7.63 (d, *J* = 8.0) (comb. 2 H, H$_o$, Tol). − ^{13}C NMR: δ = 21.4 (*Me*), 113.5 (d, J_{FC} = 3.1, *C*H-2, *E*), 117.4 (*C*H-2, *Z*), 117.9 (d, J_{FC} = 4.6, *C*H-3, *E*), 119.4 (d, J_{FC} = 18.3, *C*H-3, *Z*), 124.8 (*C*H, Tol), 125.3 (*CH*$_p$, 126.8 (*C*H, Ph), 128.7 (*C*H, Ph), 130.0 (*C*H, Tol), 137.5 (d, J_{FC} = 3.0, *C*H-4, *E*), 138.1 (d, J_{FC} = 9.2, *C*H-4, *Z*), 142.2 (*C*S, *Z*), 142.6 (*C*S, *E*), 158.2 (d, J_{FC} = 318.0, *E*), 158.4 (d, J_{FC} = 318.9, *Z*). − $C_{17}H_{15}FOS$ (286.36): calcd. C 71.30, H 5.28, S 11.20; found C 70.43, H 5.03, S 11.14.

(*S*)-1-Fluoro-2-phenyl-1-(*p*-tolylsulfinyl)ethene (1k): The (*E*) isomer (***E*-1k**) was eluted first: R_f = 0.49 (petroleum ether/ether, 1:1). − Colorless solid, m.p. 73−76 °C. − ^{1}H NMR: δ = 2.43 (s, 3 H, *Me*), 6.64 (d, 1 H, J_{FH} = 37.3, C*H*=CF), 7.34−7.37 (m, 5 H, H-arom.), 7.54 (dd, 2 H, *J* = 8.0, 1.5, Ph), 7.67 (d, 2 H, *J* = 8.0, H$_o$, Tol). − ^{13}C NMR: δ = 20.8 (*Me*), 111.2 (*C*H=CF), 124.8 (*C*H, Tol), 128.2 (*C*H, Ph), 128.9 (d, J_{FC} = 6.1, *C*H, Ph), 129.6 (*C*H, Tol), 130.0 (*C*$_i$, Ph), 136.8 (*C*S), 142.1 (*C*Me), 158.3 (d, J_{FC} = 320.4, *C*F). − $[\alpha]_D^{20}$ = +79 (*c* = 1.0, CH_2Cl_2). − *ee* > 99% [HPLC, Chiralcel OJ (eluent: H/I = 95:5; 0.80 mL/min): $t'_{R,1}$ = 10.91 min (*R*), $t'_{R,2}$ = 15.58 min (*S*); α = 1.42]. − $C_{15}H_{13}FOS$ (260.33): calcd. C 69.21, H 5.03; found C 69.15, H 5.35. −The (*Z*) isomer (***Z*-1k**) was obtained afterwards as part of a 3:2 (*Z*)/(*E*) mixture: R_f = 0.45 (petroleum ether/ether, 1:1). − ^{1}H NMR: δ = 6.83 (d, J_{FH} = 17.6, C*H*=CF). − ^{13}C NMR: δ = 118.8 (d, J_{FC} = 19.8, *C*H=CF), 135.7 (*C*S), 141.6 (*C*Me). − The *ee* was not determined exactly [HPLC, Chiralcel OJ (eluent: H/I = 95:5; 0.80 mL/min): $t'_{R,1}$ = 12.89 min (*R*), $t'_{R,2}$ = 13.50 min (*S*)].

1-Fluoro-2-phenyl-1-(*p*-tolylsulfinyl)ethene (***rac*-1k**): Prepared as an HPLC reference by Method B. − Yield 63%, (*E*)/(*Z*) ratio 80:20.

(*S*),(*E*)-1-Fluoro-2-(4-methoxyphenyl)-1-(*p*-tolylsulfinyl)ethene (*E*-1l): R_f = 0.19 (petroleum ether/ethyl acetate, 5:1). − Colorless solid, m.p. 97.5−98.5 °C. − ^{1}H NMR: δ = 2.43 (s, 3 H, *Me*, Tol), 3.82 (s, 3 H, *Me*O), 6.57 (d, 1 H, J_{FH} = 37.3, C*H*=CF), 6.89 (d, 2 H, *J* = 8.8, MeOC_6H_4), 7.35 (d, 2 H, *J* = 8.4, H$_m$, Tol), 7.50 (d, 2 H, *J* = 8.8, MeOC_6H_4), 7.66 (d, 2 H, *J* = 8.4, H$_o$, Tol). − ^{13}C NMR: δ = 21.0 (*Me*, Tol), 54.7 (*Me*O), 112.1 (*C*H=CF), 113.8 (*C*H-3,5, MeOC_6H_4), 122.7 (*C*-4, MeOC_6H_4), 124.9 (*C*H, Tol), 129.7 (*C*H, Tol), 130.7 (d, J_{FC} = 7.1, *C*H-4,6, MeOC_6H_4), 137.0 (*C*S), 142.1 (*C*Me), 156.6 (d, J_{FC} = 330.4, *C*F), 159.7 (*C*OMe). − $[\alpha]_D^{20}$ = +76 (*c* = 1.0, CH_2Cl_2). − $C_{16}H_{15}FO_2S$ (290.35): calcd. C 66.19, H 5.21, S 11.04; found C 66.16, H 4.98, S 10.93.

(*S*)-1-Fluoro-2-(*p*-tolyl)-1-(*p*-tolylsulfinyl)ethene (1m): Column chromatography gave **1m** as a mixture of isomers: R_f = 0.20 (petroleum ether/ethyl acetate, 9:1). Trituration from diisopropyl ether/hexanes gave pure (*E*) isomer (***E*-1m**): Colorless solid, m.p. 111 °C. − ^{1}H NMR: δ = 2.35 (s, 3 H, *Me*, Tol-2), 2.42 (s, 3 H, *Me*, STol), 6.60 (d, 1 H, J_{FH} = 37.3, C*H*=CF), 7.17 (d, 2 H, *J* = 8.0, H$_m$, Tol-2), 7.29 (d, 2 H, *J* = 8.0, H$_m$, TolS), 7.44 (d, 2 H, *J* = 8.0, H$_o$, Tol-2), 7.66 (d, 2 H, *J* = 8.0, H$_o$, TolS). − ^{13}C NMR: δ = 21.2 (*Me*, Tol), 21.3 (*Me*, Tol), 111.9 (*C*H=CF), 124.7 (*C*H, TolS), 127.6 (d, J_{FC} = 3.0, *C*$_i$, Tol), 129.3 (d, J_{FC} = 7.6, *C*H, Tol-2), 129.3 (*C*H,

Tol), 130.0 (*C*H, Tol), 137.3 (*C*S), 139.3 (*C*Me), 142.5 (*C*Me), 158.8 (d, J_{FC} = 317.4, *C*F). − $[\alpha]_D^{20}$ = +106 (*c* = 1.0, CH_2Cl_2). − $C_{16}H_{15}FOS$ (274.35): calcd. C 70.05, H 5.51, S 11.69; found C 69.66, H 5.29, S 11.68. − Data for the (*Z*) isomer (***Z*-1m**) could be obtained from the remaining (*E*)/(*Z*) mixture: ^{1}H NMR: δ = 6.79 (d, J_{FH} = 17.6, C*H*=CF).

(*S*),(*E*)-1-Fluoro-2-(*o*-tolyl)-1-(*p*-tolylsulfinyl)ethene (*E*-1n): R_f = 0.21 (petroleum ether/ethyl acetate, 9:1). − Colorless solid, m.p. 57 °C. − ^{1}H NMR: δ = 2.41 (s, 3 H, *Me*, *o*Tol), 2.44 (s, 3 H, *Me*, *p*Tol), 6.84 (d, 1 H, J_{FH} = 36.6, C*H*=CF), 7.13−7.21 (m, 3 H, *o*Tol), 7.36 (d, 2 H, *J* = 8.0, H_m, *p*Tol), 7.60 (d, 1 H, *J* = 6.6, *o*Tol), 7.68 (d, 2 H, *J* = 8.0, H_m, *p*Tol). − ^{13}C NMR: δ = 19.6 (*Me*, *o*Tol), 21.0 (*Me*, *p*Tol), 108.4 (*C*H=CF), 125.0 (*C*H, *p*Tol), 125.8 (*C*H, *o*Tol), 128.7 (*C*H, *o*Tol), 128.9 (*C*H, *o*Tol), 129.8 (*C*H, *p*Tol), 130.1 (*C*H, *o*Tol), 136.4 (*C*S), 137.1 (*C*Me, *o*Tol), 142.3 (*C*Me, *p*Tol), 158.5 (d, J_{FC} = 318.9, *C*F), δ (C_i, *o*Tol) not determined. − $[\alpha]_D^{20}$ = +97 (*c* = 1.0, CH_2Cl_2). − $C_{16}H_{15}FOS$ (274.35): calcd. C 70.05, H 5.51; found C 69.74, H 5.83.

(*S*)-1-Fluoro-2-(2-pyridinyl)-1-(*p*-tolylsulfinyl)ethene (1o): Column chromatography (ether, with 1% triethylamine) gave the (*Z*) isomer (***Z*-1o**) first: R_f = 0.38 (ether). − Colorless oil, turning reddish on standing. − ^{1}H NMR: δ = 2.41 (s, 3 H, *Me*), 6.71 (d, 1 H, J_{FH} = 16.1, C*H*=CF), 7.24−7.40 (m, 2 H, Pyr), 7.32 (d, 2 H, *J* = 8.0, H_m), 7.71 (m, 1 H, Pyr), 7.93 (d, 2 H, *J* = 8.0, H_o), 8.66 (m, 1 H, H-6, Pyr). − ^{13}C NMR: δ = 21.2 (*Me*), 114.8 (d, J_{FC} = 18.3, *C*H=CF), 122.8 (*C*H, Pyr), 123.9 (d, J_{FC} = 4.6, *C*H, Pyr), 125.4 (*C*H, Tol), 129.6 (*C*H, Tol), 136.5 (*C*H, Pyr), 138.6 (*C*S), 141.5 (*C*Me), 148.9 (*C*H-6, Pyr), 150.0 (d, J_{FC} = 13.7, *C*-2, Pyr), 162.5 (d, J_{FC} = 320.4, *C*F). − $[\alpha]_D^{20}$ = −390 (*c* = 1.4, CH_2Cl_2). − The (*E*) isomer (***E*-1o**) was obtained next: R_f = 0.29 (ether). − Colorless solid, m.p. 67.5−68 °C. − ^{1}H NMR: δ = 2.43 (s, 3 H, *Me*), 6.85 (d, 1 H, J_{FH} = 36.6, C*H*=CF), 7.21−7.30 (m, 2 H, Pyr), 7.35 (d, 2 H, *J* = 8.0, H_m), 7.60−7.73 (m, 1 H, Pyr), 7.68 (d, 2 H, *J* = 8.0, H_o), 8.64 (m, 1 H, H-6, Pyr). − ^{13}C NMR: δ = 21.3 (*Me*), 111.7 (*C*H=CF), 123.1 (*C*H, Pyr), 124.5 (d, J_{FC} = 9.2, *C*H, Pyr), 125.3 (*C*H, Tol), 130.1 (*C*H, Tol), 136.4 (*C*H, Pyr), 136.9 (*C*S), 142.8 (*C*Me), 149.8 (*C*H-6, Pyr), 150.3 (d, J_{FC} = 3.0, *C*-2, Pyr), 161.6 (d, J_{FC} = 323.5, *C*F). − $[\alpha]_D^{20}$ = +124 (*c* = 0.40, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{14}H_{12}FNOS^+$ + H] calcd. 262.0702; found 262.0741.

(*S*)-1-Fluoro-2-[2-(5-methylfuranyl)]-1-(*p*-tolylsulfinyl)ethene (1p): Chromatography first afforded the (*E*) isomer (***E*-1p**): R_f = 0.19 (petroleum ether/ethyl acetate, 9:1). − Colorless oil, rapidly turning reddish brown on standing. − ^{1}H NMR: δ = 2.31 (s, 3 H, *Me*, Fur), 2.42 (s, 3 H, *Me*, Tol): 6.06 (d, 1 H, *J* = 2.9, Fur), 6.56 (d, 1 H, *J* = 2.9, Fur), 6.60 (d, 1 H, J_{FH} = 35.1, C*H*=CF), 7.34 (d, 2 H, *J* = 8.0, H_m), 7.64 (d, 2 H, *J* = 8.0, H_o). − ^{13}C NMR: δ = 13.4 (*Me*, Fur), 21.3 (*Me*, Tol), 103.0 (d, J_{FC} = 3.0, *C*H, Fur), 108.4 (*C*H, Fur), 114.9 (d, J_{FC} = 7.6, *C*H=CF), 125.2 (*C*H, Tol), 130.0 (*C*H, Tol), 137.0 (*C*S, Tol), 142.5 (*C*Me), 144.3 (d, J_{FC} = 3.0, *C*-2, Fur), 154.0 (d, J_{FC} = 3.0, *C*Me, Fur), 155.6 (d, J_{FC} = 328.9, *C*F). − $[\alpha]_D^{20}$ = +68 (*c* = 1.3, CH_2Cl_2). − Further elution gave the (*Z*) isomer (***Z*-1p**): R_f = 0.11 (petroleum ether/ethyl acetate, 9:1). − Colorless solid, rapidly turning reddish brown on standing. − ^{1}H NMR: δ = 2.39 (s, 3 H, *Me*, Fur), 2.43 (s, 3 H, *Me*, Tol), 6.10 (d, 1 H, *J* = 2.9, Fur), 6.43 (d, 1 H, J_{FH} = 16.8, C*H*=CF), 6.48 (d, 1 H, *J* = 3.7, Fur), 7.34 (d, 2 H, *J* = 8.0, H_m), 7.66 (d, 2 H, *J* = 8.0, H_o). − ^{13}C NMR: δ = 13.2 (*Me*, Fur), 20.8 (*Me*, Tol), 106.6 (d, J_{FC} = 24.4, *C*H, Fur), 108.0 (*C*H, Fur), 115.2 (d, J_{FC} = 7.6, *C*H=CF), 124.1 (*C*H, Tol), 129.5 (*C*H, Tol), 136.7 (*C*S, Tol), 141.5 (*C*Me, Tol), 142.7 (d, J_{FC} = 9.2, *C*-2, Fur), 154.4 (d, J_{FC} = 3.0, *C*Me, Fur), 155.8 (d, J_{FC} = 317.4, *C*F). − $[\alpha]_D^{20}$ = −544 (*c* = 1.0, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{14}H_{13}FO_2S^+$ + H] calcd. 265.0698; found 265.0711.

(*S*)-1-Fluoro-2-phenyl-1-(*p*-tolylsulfinyl)prop-1-ene (1q): Chromatography first afforded the (*E*) isomer (***E*-1q**): Colorless, viscous oil, R_f = 0.14 (petroleum ether/ethyl acetate, 5:1). − ^{1}H NMR: δ = 2.13 (d, 3 H, J_{FH} = 3.6, *Me*-3), 2.41 (s, 3 H, *Me*, Tol), 7.30−7.47 (m, 5 H, Ph), 7.39 (d, 2 H, *J* = 8.0, H_m), 7.54 (d, 2 H, *J* = 8.0, H_o). − ^{13}C NMR: δ = 17.88 (d, J_{FC} = 4.3, *Me*-3), 21.4 (*Me*, Tol), 125.0 (*C*H, Tol), 128.6 (*C*H, Ph), 128.8 (*C*H, Ph), 129.2 (C_i, Ph), 129.8 (*C*H, Tol), 135.8 (d, J_{FC} = 4.7, *C*=CF), 136.8 (*C*S, Tol), 141.8 (*C*Me, Tol), 155.0 (d, J_{FC} = 317.3, C=*C*F). − $[\alpha]_D^{20}$ = −285 (*c* = 0.58, CH_2Cl_2). − The (*Z*) isomer (***Z*-1q**) was obtained next: R_f = 0.08 (petroleum ether/ethyl acetate, 5:1). − Colorless solid, m.p. 100−101 °C (*n*-pentane) − ^{1}H NMR: δ = 2.41 (s, 3 H, *Me*, Tol), 2.45 (d, 3 H, J_{FH} = 3.7, *Me*-3), 7.34 (d, 2 H, *J* = 8.0, H_m), 7.32−7.38 (m, 5 H, Ph), 7.62 (d, 2 H, *J* = 8.0, H_o). − ^{13}C NMR: δ = 17.0 (*Me*-3), 21.4 (*Me*, Tol), 124.6 (*C*H, Tol), 127.9 (d, J_{FC} = 4.3, *C*H, Ph), 128.3 (*C*H, Ph), 128.8 (*C*H, Ph), 130.0 (*C*H, Tol), 135.0 (*C*=CF), 136.8 (*C*S), 141.9 (*C*Me, Tol), 153.6 (d, J_{FC} = 314.6, C=*C*F); δ (C_i, Ph) not determined. − $[\alpha]_D^{20}$ = −7.7 (*c* = 1.1, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{16}H_{15}FOS^+$ + H] calcd. 275.0906; found 275.0946.

(*S*)-[Fluoro(*p*-tolylsulfinyl)methylene]cyclohexane (1r): Prepared by Method A. Obtained as the first fraction after chromatography, as a colorless oil, R_f = 0.43 (petroleum ether/ether, 1:1). −^{1}H NMR: δ = 1.61 (bm, 6 H, CH_2), 2.28 (m, 2 H, CH_2-6′), 2.42 (s, 3 H, *Me*), 2.61 (m, 2 H, CH_2-2′), 7.33 (dd, 1 H, *J* = 8.4, 1.8, H_m), 7.34 (dd, 1 H, *J* = 8.4, 1.8, H_m), 7.55 (dd, 2 H, *J* = 8.4, 1.8, H_o). − ^{13}C NMR: δ = 21.1 (*Me*), 25.6, 26.3, 26.6 (d, J_{FC} = 6.1), 27.2, 28.0 (each *C*H_2), 124.4 (*C*H, Tol), 129.7 (*C*H, Tol), 131.9 (d, J_{FC} = 7.6, *C*=CF), 136.8 (*C*S), 141.4 (*C*Me), 150.2 (d, J_{FC} = 306.7, C=*C*F). − $[\alpha]_D^{20}$ = −105 (*c* = 0.79, CH_2Cl_2). − HRMS: *m*/*z* [$C_{14}H_{17}FOS^+$ + H] calcd. 253.1062; found 253.1103. − As the second fraction, fluoromethyl sulfoxide **7** was obtained, data for which are provided below. For the product prepared by Method B, NMR-spectroscopic data are similar, but HRMS analysis failed.

(*S*)-[Fluoro(*p*-tolylsulfinyl)methylene]cyclopentane (1s): R_f = 0.07 (petroleum ether/ethyl acetate, 10:1). − Viscous, colorless oil. − ^{1}H NMR: δ = 1.62 (m, 4 H, CH_2-3′,4′), 2.42 (s, 3 H, *Me*), 2.48 (m, 4 H, CH_2-2′,5′), 7.33 (d, 2 H, *J* = 8.0, H_m), 7.57 (d, 2 H, *J* = 8.0, H_o). − ^{13}C NMR: δ = 21.3 (*Me*), 25.4, 26.7, 29.2, 29.2 (each *C*H_2), 124.6 (*C*H, Tol), 129.8 (*C*H, Tol), 135.8 (d, J_{FC} = 10.7, *C*=CF), 136.7 (*C*S), 141.7 (*C*Me), 149.5 (d, J_{FC} = 308.2, C=*C*F). − $[\alpha]_D^{20}$ = −142 (*c* = 0.37, CH_2Cl_2). − HRMS (ESI): *m*/*z* [$C_{13}H_{15}FOS^+$ + H] calcd. 239.0906; found 239.0800.

Solvolysis of [Fluoro(*p*-tolylsulfinyl)methyl]diphenylphosphane Oxide: Phosphane oxide **2** (1.0 mmol) was dissolved in methanol/THF (10 mL, 1:1 v/v), and sodium methoxide (0.81 g, 1.5 mmol) was added. The mixture was stirred until the reaction was complete (1 h, TLC). A saturated NH_4Cl solution was added, and the mixture was extracted with dichloromethane (3 × 20 mL). After drying with $MgSO_4$, solvents were removed. Column chromatography gave **7** [R_f = 0.47 (ether)], and **6** [R_f = 0.21 (ether)], as pure products. Properties found for methyl diphenylphosphinate (**6**) agree with known data.[20]

(*S*)-1-(Fluoromethyl)sulfinyl-4-methylbenzene (7): Prepared from **2**. Yield 165 mg (96%). − Colorless crystals, m.p. 58.5−59.5 °C (petroleum ether/ether). − ^{1}H NMR: δ = 2.44 (s, 3 H, *Me*), 5.04 (dd, 1 H, J_{FH} = 47.8, *J* = 8.4, CH_2F), 5.07 (dd, 1 H, J_{FH} = 47.8, *J* = 8.4, CH_2F), 7.37 (d, 2 H, *J* = 8.0, H_m), 7.57 (d, 2 H, *J* = 8.0, H_o). − ^{13}C NMR: δ = 21.0 (*Me*), 98.0 (d, J_{FC} = 219.7, *C*H_2F), 124.4

(*C*H, Tol), 129.9 (*C*H, Tol), 134.9 (d, J_{FC} = 6.1, *C*S), 142.4 (*C*Me). − ^{19}F NMR: δ = −212.9. − $[\alpha]_D^{20}$ = +214 (*c* = 1.0, CH_2Cl_2). − *ee* = 98% [HPLC, Chiralcel OJ (eluent: H/I = 90:10; 1.00 mL/min): $t'_{R,1}$ = 9.58 min (*R*), $t'_{R,2}$ = 10.85 min (*S*); α = 1.13]. − HRMS (ESI): *m*/*z* [$C_8H_9FOS^+$ + H] calcd. 173.0436; found 173.0477.

1-(Fluoromethyl)sulfinyl-4-methylbenzene (*rac*-7): Prepared from ***rac*-2** as a reference compound. − Colorless crystals, m.p. 52.5−53 °C (ether/petroleum ether) (ref.[22a] 52 °C).

***O*,*O*-Diethyl (*S*$_S$)-[Fluoro(*p*-tolylsulfinyl)methyl]phosphonate (9):** Prepared from *O*,*O*-diethyl (fluoromethyl)phosphonate, according to the procedure described for the preparation of phosphane oxide **2**. After column chromatography (ether → ether/methanol, 9:1), phosphonate **9** was obtained as a colorless solid, containing some unidentified phosphonate impurities. Yield ≤ 35% (isomeric ratio 3:1). − ^{1}H NMR: δ = 1.26−1.42 (m, 6 H, CH_2*Me*), 2.44 (s, *Me*, Tol, major), and 2.48 (s, *Me*, Tol, minor) (comb. 3 H), 4.04−4.23 (m, 2 H, C*H*$_2$Me), 4.25−4.40 (m, 2 H, C*H*$_2$Me), 5.18 (dd, J_{FH} = 46.4, J_{PH} = 3.7, PC*H*F, major), and 5.24 (dd, J_{FH} = 46.6, J_{PH} = 1.6, PC*H*F, minor) (comb. 1 H), 7.37 (d, *J* = 8.0, H$_m$ Tol), 7.64 (d, *J* = 8.0, H$_o$, major), and 7.68 (d, *J* = 8.0, H$_o$, minor) (comb. 2 H). − ^{13}C NMR: δ = 16.1 (*Me*CH_2), 21.4 (*Me*, Tol), 63.4−64.6 (*C*H_2), 100.9 (dd, J_{FC} = 238.8, J_{PC} = 162.5, P*C*HF, minor), 101.5 (dd, J_{FC} = 242.6, J_{PC} = 163.3, P*C*HF, major), 125.5 (*C*H, Tol, major), 125.9 (*C*H, Tol, minor), 129.7 (*C*H, Tol, minor), 129.9 (*C*H, Tol, major), 135.6 (*C*S), 142.9 (*C*Me, major), 143.0 (*C*Me, minor). − ^{19}F NMR: δ = −174.4 (major), −167.2 (minor). − ^{31}P NMR: 8.6 (J_{FP} = 71.8, major), 9.0 (J_{FP} = 71.8, minor).

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