Tetrahedron 64 (2008) 9725–9732

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New synthetic approach to α-fluoro-β-arylvinyl sulfones and their application in Diels–Alder reactions

Aleksey V. Shastin [a], Valentine G. Nenajdenko [b,**], Vasiliy M. Muzalevskiy [b], Elizabeth S. Balenkova [b], Roland Fröhlich [c], Günter Haufe [c,*]

[a] Institute of Problems of Chemical Physics, Chernogolovka, Moscow Region 142432, Russia
[b] Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119992, Russia
[c] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany

ARTICLE INFO

Article history:
Received 19 July 2008
Accepted 22 July 2008
Available online 26 July 2008

Keywords:
Diels–Alder reaction
Fluoroalkynes
α-Fluoro-β-arylvinyl sulfones
Fluoronorbornadienes
Stereoselectivity
Vinyl fluorides

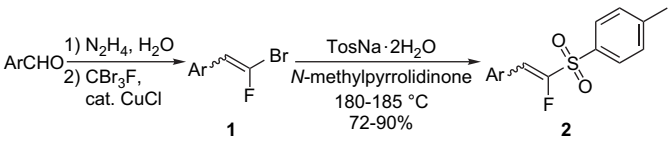
ABSTRACT

A new pathway towards α-fluoro-β-arylvinyl sulfones was elaborated. The reaction of β-bromo-β-fluorostyrenes with sodium 4-methylphenylsulfinate proceeds with maximum 94:6 stereoselectivity and 72–90% yields. The formed α-fluoro-β-arylvinyl sulfones were found to be good dienophiles for Diels–Alder reactions with simple 1,3-dienes. From corresponding (*E*)-configured dienophiles and cyclopentadiene, cycloadducts bearing the fluorine substituent in *exo*-position were formed predominantly, while with diphenylisobenzofuran the products with *endo*-orientation of the fluorine were obtained as the major products. From these cycloadducts, as a proof of principle, *p*-toluenesulfinic acid was eliminated to give 2-fluoro-3-(4-nitrophenyl)norbornadiene, the formal [4+2]-cycloadduct of cyclopentadiene and 1-fluoro-2-(4-nitrophenyl)acetylene, or the corresponding diphenylisobenzofuran cycloadducts, respectively. This reaction was not successful when other β-hydrogen atoms are accessible for elimination.

1. Introduction

Fluorine-containing organic compounds were intently investigated in recent years.[1] One reason for the particular interest in such compounds is their manifold physiological activity.[2] Numerous publications were dedicated to elaboration of new methods for their synthesis.[3] Molecules containing a vinylic fluorine atom are of special interest, both as starting materials for various syntheses[4] and as biologically active compounds. For instance, fluoroolefins are potential enzyme inhibitors[5] and can be used as a bioisosteric replacement of an amido group in peptides[6] or amino acid amides.[7]

A couple of years ago, a new catalytic olefination reaction starting from aldehydes or ketones was discovered.[8] We found that *N*-unsubstituted hydrazones of these carbonyl compounds can be smoothly transformed into various substituted alkenes by treatment with polyhalogenoalkanes in the presence of catalytic amounts of copper salts and a base (Scheme 1). Advantages over other methods[9] are inexpensive starting materials and simplicity of chemical transformation and isolation of products. Applying this reaction, we elaborated new methods for the synthesis of various fluorinated alkenes.[10] Among them β-chloro-β-(trifluoromethyl)-styrenes, $ArC(H)=C(Cl)CF_3$, β-bromo-β-(trifluoromethyl)styrenes, $ArC(H)=C(Br)CF_3$ are of particular interest, because one of the halogen atoms can be easily substituted by different nucleophiles. By way of example, the reactions with copper cyanide, alkylthiolates and arylthiolates are new approaches to α-fluoro- and α-trifluoromethylacrylonitriles[11] or to trifluoromethyl(vinylsulfides), respectively.[12]



Scheme 1. Synthesis of β-bromo-β-fluorostyrenes **1** and its reactions with sodium 4-methylphenylsulfinate.

Substitution of bromine in β-bromo-β-fluorostyrenes with 4-methylphenylsulfinate would open a new pathway to α-fluoro-β-arylvinyl sulfones, which are useful building blocks in organic synthesis. α-Fluoro-β-arylvinyl sulfones are widely used in synthesis of 1-fluorovinylstannanes,[13] fluorostyrenes,[14] 3-fluoropyrrole derivatives[15] and fluorotriazoles.[16] Due to the electron-deficient double bond and the possibility to eliminate the sulfonic

* Corresponding author. Tel.: +49 251 8333281; fax: +49 251 8339772.
** Corresponding author. Tel.: +7 495 9392276; fax: +7 495 9328846.
E-mail addresses: shastin@icp.ac.ru (A.V. Shastin), nen@acylium.chem.msu.ru (V.G. Nenajdenko), haufe@uni-muenster.de (G. Haufe).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.07.097

group, this class of compounds might be useful for both Michael additions[17] and Diels–Alder reactions.[18] Most general methods for the synthesis of α-fluorovinyl sulfones are the Wittig[19] and the Peterson olefination reactions,[20] as well as condensations of fluoromethylvinylsulfones with carbonyl compounds.[14] However, absolute solvents, inert atmosphere, application of toxic phosphorous or excess of organometallic compounds are required for the mentioned methods. Thus, the development of new, more convenient methods towards α-fluoro-β-arylvinyl sulfones is an important issue.

2. Results and discussion

2.1. Synthesis of α-fluorovinyl sulfones

Initially we found that β-bromo-β-fluorostyrenes **1** gave α-fluoro-β-arylvinyl sulfones **2** in high yields upon heating with sodium 4-methylphenylsulfinate in *N*-methylpyrrolidinone at 180–185 °C (Table 1). The reactions proceeded regioselectively providing only one regioisomer in all cases. Furthermore, the method was shown to be quite general and a variety of aromatic sulfones **2** containing both electron donating and electron withdrawing substituents at the aromatic ring were accessible. The reaction occurred stereoselectively. In most cases a slight increase of the *E*/*Z* ratio comparing to the starting **1** was observed, probably due to the better accessibility for the nucleophile of one side of the β-carbon atom. This was not further investigated.

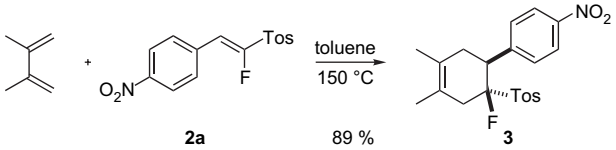
The structure of the isomeric α-fluoro-β-arylvinyl sulfones **2** was mainly determined by ^{1}H NMR spectroscopy. Most characteristically, the $^3J_{H,F}$ coupling constants between fluorine and the vinylic proton were found to be 32–35 Hz, which is typical for the transposition of the coupling nuclei. For the minor cis-isomers $^3J_{H,F}$ of 15–20 Hz were found (see Section 4).

2.2. Diels–Alder reactions of α-fluorovinyl sulfones

Though a very innovative alternative pathway was described recently,[21] the two Diels–Alder strategies combining either a fluorinated diene or a fluorinated dienophile with the corresponding non-fluorinated counterpart, remains the most convenient approach towards selectively fluorinated mono- or polycyclic cyclohexene derivatives.[4,22] Many reactions of this type have been used for syntheses of fluorinated model compounds in order to study the selectivity of such reactions,[23,24] but also for the preparation of analogues of biologically active compounds such as cantharidin, endothall[25] and D-homosteroids.[26]

Also vinylsulfones are known as active dienophiles,[27] which were used as synthetic equivalents of ethylenes[28] in [4+2]-cycloaddition reactions followed by reductive elimination of the sulfonic group (mercury amalgam in most cases[29]) or as synthetic equivalents of acetylenes[30] in case of subsequent β-elimination of sulfinic acid from the corresponding Diels–Alder adduct using a strong base (e.g., *t*-BuOK[31]). Thus, a similar synthetic sequence might be a very convenient method for selective introduction of a vinylic fluorine substituent into various carbo- and heterocyclic compounds. To the best of our knowledge only two examples of Diels–Alder reactions with α-fluorovinyl sulfones have been described in the literature so far.[19,32]

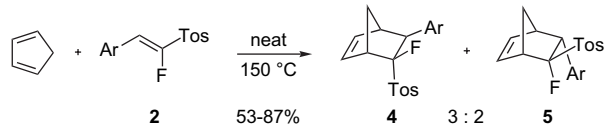
Initially, the thermal Diels–Alder reactions of the sulfone **2a** with 2,3-dimethylbutadiene and Danishefsky's diene were investigated. While the first reaction gave the desired cyclohexene **3** in 89% yield, the reaction mixture decomposed and no pure product could be isolated in case of Danishefsky's diene (Scheme 2).



Scheme 2. Reaction of sulfone **2a** with 2,3-dimethylbutadiene.

The structure of compound **3** was determined by spectroscopic methods. Most characteristic for the trans-orientation of fluorine and the vicinal proton is the big $^3J_{H,F}$ coupling constant of 32.2 Hz, found both in the ^{1}H and in the ^{19}F NMR spectra.

Subsequently, we investigated reactions of α-fluoro-β-arylvinyl sulfones **2** with cyclopentadiene. The reactions were carried out without solvent using excess of the diene in a sealed tube at 150 °C leading to mixtures of the corresponding Diels–Alder adducts **4** and **5** in about 3:2 ratio and 53–87% yields (Scheme 3). About 7–8 h of reaction time were needed for complete consumption of the starting material in case of the sulfones **2a** and **2e** with electron withdrawing substituents at the aromatic ring. As expected, the reaction time increased dramatically for the electron donor substituted compound **2d** (Table 2).



Scheme 3. Reaction of the α-fluoro-β-arylvinyl sulfones **2** with cyclopentadiene.

In addition to spectroscopic investigations, the structure of the diastereomers **4** and **5** was confirmed by X-ray analysis of the pure diastereomers **4a** and **5a** containing a 4-nitrophenyl group. For the major diastereomer **4a** unexpectedly the *exo*-F-*endo*-Tos-*exo*-Ar configuration was determined. The minor diastereomer **5a** was found to have the *endo*-F-*exo*-Tos-*endo*-Ar configuration (Figs. 1 and 2). The preferred formation of the cycloadduct with *exo*-orientation of the fluorine substituent was also found in the reaction of cyclopentadiene with 3-fluorofuran-2(5*H*)-one.[33]

In contrast, for the Diels–Alder reaction of diphenylisobenzofuran with the dienophiles **2a** and **2b** the reverse stereoselection was found (Scheme 4). The 4-chloro substituted dienophile **2b** gave an 89:11 mixture of diastereomers **6b** and **7b** in favour of the *endo*-fluoro diastereomer.

The structure of diastereomer **6a** was confirmed by X-ray analysis (Fig. 3).

Table 1
Synthesis of α-fluoro-β-arylvinyl sulfones **2**

	Ar	*E*/*Z* ratio **1**[a]	*E*/*Z* ratio **2**[a]	Yield of **2** (%)
a	4-$O_2NC_6H_4$–	78:22	89:11	90
b	4-ClC_6H_4–	86:14	94:6	86
c	Ph	85:15	88:12	89
d	4-$MeOC_6H_4$–	83:17	89:11	88
e	4-$MeO_2CC_6H_4$–	78:22	91:9	79
f	2-$MeOC_6H_4$–	83:17	80:20	72
g	4-MeC_6H_4–	85:15	92:8	75

[a] determined by ^{1}H NMR spectroscopy.

Table 2
Synthesis of the Diels–Alder adducts **4** and **5**

	Ar	Reaction time (h)	Yield of **4**+**5** (%)
a	4-$O_2NC_6H_4$-	7	87
b	4-ClC_6H_4–	12	65
c	Ph	23	53
d	4-$MeOC_6H_4$–	54	81
e	4-$MeO_2CC_6H_4$–	8	67

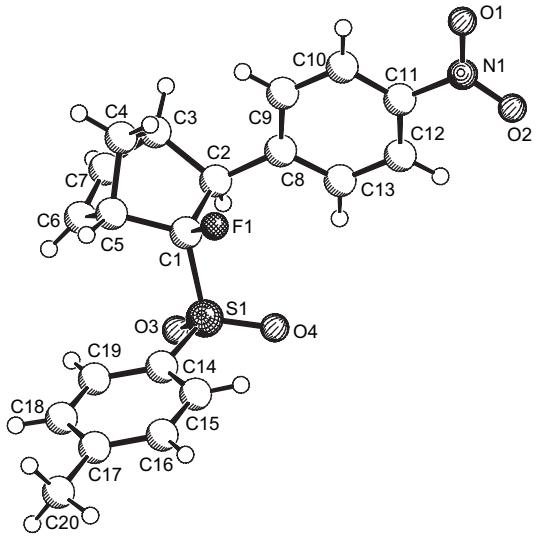


Figure 1. X-ray structure of **4a**.

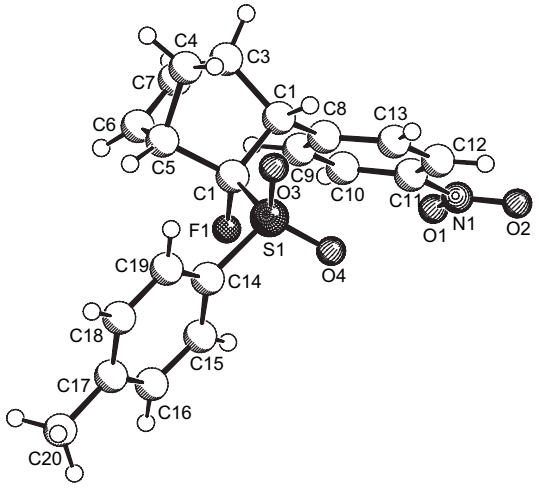
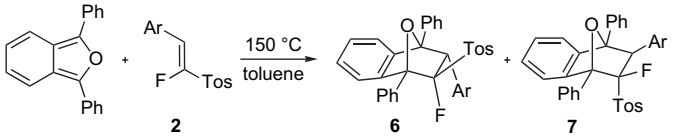


Figure 2. X-ray structure of **5a**.

It should be noted, that in neither of the mentioned reactions any product derived from the minor *Z*-alkenes was isolated. We consider that the most probable explanation of this fact could be the loss of corresponding products during purification due to their low amount (less than 10%) in reaction mixture.



a Ar = 4-O_2N-C_6H_4	94 %	75	:	25
b Ar = 4-Cl-C_6H_4	82 %	89	:	11

Scheme 4. Reaction of the α-fluoro-β-arylvinyl sulfones **2** with diphenylisobenzofuran.

2.3. Elimination reactions of 4-methylphenylsulfonyl group

We have seen above that the arylsulfonyl group and the vicinal proton are in a cis-configuration. Thus, β-elimination of arylsulfinic acid from the Diels–Alder adducts should provide a formal access to

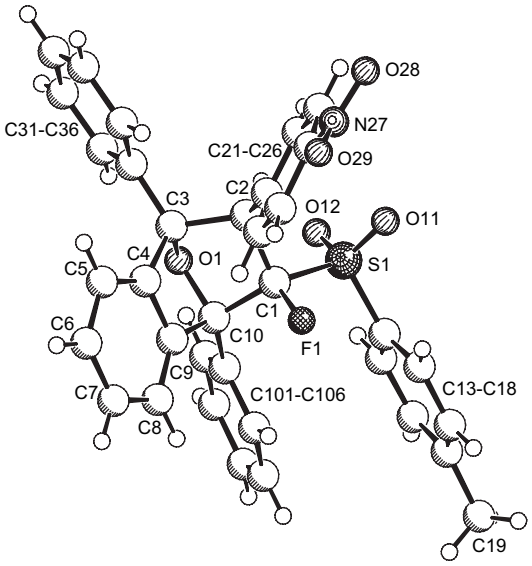
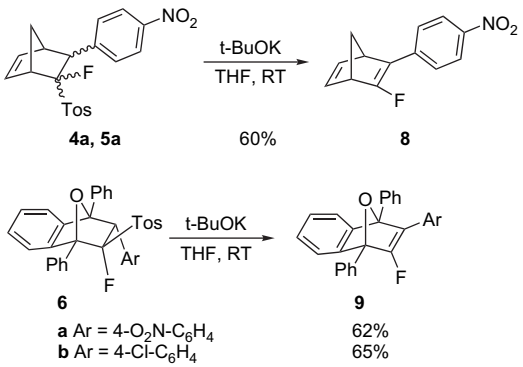


Figure 3. X-ray structure of **6a**.

the [4+2]-cycloadducts of 1,3-dienes and 1-aryl-2-fluoroacetylenes. The chemistry of fluoroacetylenes is almost not investigated. This might be due to the instability and explosive behaviour of some fluoroacetylenes. Only perfluoro-3-methylbut-1-yne and perfluoropropyne have been used in cycloadditions so far.[34] 2-Fluoro-1-phenylacetylene itself was formed as one of the products of thermal decomposition of the lithium derivative of *trans*-α,β-difluorostyrene. However, the compound was not isolated and the spectroscopic properties and reactivity were not investigated.[35]

In order to prove the above-mentioned hypothetic pathway towards 2-fluoronorbornadienes and corresponding 7-oxa-derivatives, we treated the mixture of the cycloadducts **4a** and **5a** and pure diastereomers **6a** and **6b**, which all have the proton and the arylsulfonyl group in cis-position, with potassium *tert*-butoxide in THF. In all cases, the elimination was complete at room temperature in few minutes and the target compounds **8**, **9a** and **9b** were isolated in 60–65% yields. The 2-fluoronorbornadiene **8** is a thermolabile compound, which decomposed at room temperature in a few hours. The corresponding 7-oxa analogues **9a** and **9b** were found to be more stable at room temperature, but complete decomposition was observed after several days (Scheme 5).

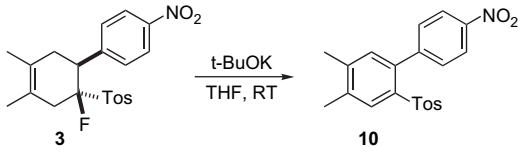
We also tried *p*-toluenesulfinic acid elimination from the Diels–Alder adduct **3**. In this case the formation of the non-fluorinated product **10** occurred by HF elimination. Subsequent spontaneous oxidation of the intermediary cyclohexadiene leads to the biphenyl



a Ar = 4-O_2N-C_6H_4	62%
b Ar = 4-Cl-C_6H_4	65%

Scheme 5. Elimination of *p*-toluenesulfinic acid from Diels–Alder adducts.

10. Its structure was established by ESI-MS and ^{1}H NMR spectra (Scheme 6).



Scheme 6. Elimination of HF from Diels–Alder adduct **3**.

3. Conclusions

We discovered a new synthetic pathway towards α-fluoro-β-arylvinyl sulfones **2** by direct nucleophilic substitution of bromine in β-bromo-β-fluorostyrenes **1** with 4-methylphenylsulfinate. The reactions proceeded stereoselectively with 72–90% yields. The isomers with (*E*)-configuration of the double bond were formed preferentially with retention of the configuration. The presence of the strong electron-withdrawing 4-methylphenylsulfonyl group at the double bond enables compounds **2** to react as dienophiles in Diels–Alder reactions with active dienes, like 2,3-dimethylbutadiene and cyclopentadiene giving diastereomeric cycloadducts in the latter case. In the major product the fluorine substituent is attached in *exo*-position. In contrast, the corresponding reactions of **2a** and **2b** with diphenylisobenzofuran gave preferentially the Diels–Alder adducts with fluorine in the *endo*-position. As a proof of principle, the elimination of the 4-methylphenylsulfonyl group from the Diels–Alder adducts **4a**,**5a** and **6a**,**6b** gave a 2-fluoronorbornadiene **8** and the 7-oxa analogues **9**, respectively, which are the formal Diels–Alder products of cyclopentadiene or diphenylisobenzofuran with the 1-aryl-2-fluoroacetylenes.

4. Experimental

4.1. General

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker ARX 300 and Bruker AMX 400 spectrometers in $CDCl_3$ with TMS, $CDCl_3$ and CCl_3F as internal standards. IR spectra were obtained with an UR-20 spectrometer. Mass spectra (ESI-MS) were measured on a MicroTof Bruker Daltonics. Column and TLC chromatographies were performed on silica gel Merck 60 and Merck 60F_{254} plates, respectively. β-Bromo-β-fluorostyrenes **1** were synthesized according to our previously reported procedure.[10d] 2,3-Dimethylbutadiene and cyclopentadiene were distilled prior to use.

4.2. General procedure for the synthesis of the β-bromo-β-fluorostyrenes 1

A solution of the corresponding aldehyde (2 mmol) in ethanol (8 ml) was added dropwise to a solution of hydrazine hydrate (0.11 ml, 2.1 mmol) in ethanol (4 ml) with intensive stirring. After completion of hydrazone formation (TLC monitoring), ethylenediamine (0.2 ml, 1.5 equiv) and CuCl (0.002 g, 1 mol %) were added. The reaction mixture was cooled to 0 °C and CBr_3F (0.3 ml, 1.5 equiv) was added dropwise with stirring. The reaction mixture was stirred for 4–48 h at room temperature to the completion (TLC monitoring) and 5% aq HCl (50 ml) was added. The reaction products were extracted with CH_2Cl_2 (3×30 ml) and the combined extract was dried with Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, gradient). The (*E*)- and (*Z*)-isomers of β-bromo-β-fluorostyrenes **1**[10d] could not be separated by column chromatography.

4.3. General procedure for the synthesis of the α-fluoro-β-arylvinyl sulfones 2

A one-neck 50 ml round bottom flask was charged with the corresponding β-bromo-β-fluorostyrene **1** (5 mmol), $TosNa\cdot 2H_2O$ (0.60 g, 6 mmol), dry *N*-methylpyrolidinone (5 ml) and flushed with argon. The reaction mixture was heated under reflux at 180–185 °C for 8–10 h (TLC control). After cooling down to room temperature, the reaction mixture was quenched with water (100 ml). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3×20 ml). The combined extract was washed with brine and dried over sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 2:1) to afford the corresponding sulfones **2**. The (*E*)- and (*Z*)-isomers of **2** could not be separated by column chromatography.

*4.3.1. 1-Fluoro-2-(4-nitrophenyl)vinyl-4-methylphenyl sulfone (**2a**)*

Mixture of *E*/*Z* isomers (89:11 after purification); yellowish solid (1.44 g, 90%). IR (Nujol): ν=1350, 1520, 1600 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, Me), 7.12 (d, 1H, *CH*=CF, *J*=33.5 Hz), 7.43 (d, 2H, Tos, *J*=8.0 Hz), 7.74 (d, 2H, 4-$NO_2C_6H_4$–, *J*=8.1 Hz), 7.91 (d, 2H, Tos, *J*=8.0 Hz), 8.25 (d, 2H, 4-$NO_2C_6H_4$–, *J*=8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8 (Me), 112.4 (CH), 124.1 (CH), 129.0 (CH), 130.3 (CH), 130.8 (d, CH, *J*=7.3 Hz), 133.6, 135.7 (d, *J*=3.7 Hz), 146.4, 148.2, 156.3 (d, CH=*C*F, *J*=311.0 Hz). (*Z*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, Me), 6.90 (d, 1H, *CH*=CF, *J*=20.2 Hz), 7.40 (d, 2H, Tos, *J*=8.0 Hz), 7.62 (d, 2H, 4-$NO_2C_6H_4$–, *J*=8.3 Hz), 7.78 (d, 2H, Tos, *J*=8.0 Hz), the other signals are identical to those of the (*E*)-isomer; ESI-MS (*m*/*z*): calcd for $C_{15}H_{12}FNO_4SNa$ $[M]^+$ 344.0369, found 344.0363.

*4.3.2. 1-Fluoro-2-(4-chlorophenyl)vinyl-4-methylphenyl sulfone (**2b**)*

Mixture of *E*/*Z* isomers (94:6 after purification); yellowish solid (1.33 g, 86%). IR (Nujol): ν=1600 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H, Me), 7.01 (d, 1H, *CH*=CF, *J*=34.4 Hz), 7.38 (d, 2H, 4-ClC_6H_4–, *J*=8.6 Hz), 7.41 (d, 2H, Tos, *J*=8.4 Hz), 7.51 (d, 2H, 4-ClC_6H_4–, *J*=8.6 Hz), 7.91 (d, 2H, Tos, *J*=8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7 (Me), 113.8 (CH), 128.1 (d, *J*=4.4 Hz), 128.8 (CH), 129.3 (CH), 130.2 (CH), 131.4 (d, CH, *J*=2.2 Hz), 134.3, 136.3 (d, *J*=2.9 Hz), 145.9, 154.3 (d, CH=*C*F, *J*=305.9 Hz). (*Z*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (d, 1H, *CH*=CF, *J*=21.5 Hz), 7.78 (d, 2H, Tos, *J*=8.3 Hz), the other signals are identical to those of the (*E*)-isomer; ESI-MS (*m*/*z*): calcd for $C_{15}H_{12}ClFO_2SNa$ $[M^+]$ 333.0123, found 333.0128.

*4.3.3. 1-Fluoro-2-phenylvinyl-4-methylphenyl sulfone (**2c**)*

Mixture of *E*/*Z* isomers (88:12 after purification); white solid (1.12 g, 86%). IR (Nujol): ν=1620 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H, Me), 7.05 (d, 1H, *CH*=CF, *J*=34.6 Hz), 7.38–7.44 (m, 5H, Ph, Tos), 7.56–7.62 (m, 2H, Ph), 7.91 (d, 2H, Tos, *J*=8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7 (Me), 115.1, 128.7, 129.0, 130.1, 130.2, 130.3, 130.3 (d, *J*=2.2 Hz), 134.5, 145.7, 153.9 (d, CH=*C*F, *J*=305.2 Hz). (*Z*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (d, 1H, *CH*=CF, *J*=21.7 Hz), 7.78 (d, 2H, Tos, *J*=8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.1, 129.6 (d, *J*=3.7 Hz), the other signals are identical to those of the (*E*)-isomer; ESI-MS (*m*/*z*): calcd for $C_{15}H_{13}FO_2SNa$ $[M^+]$ 299.0518, found 299.0512.

*4.3.4. 1-Fluoro-2-(4-methoxyphenyl)vinyl-4-methylphenyl sulfone (**2d**)*

Mixture of *E*/*Z* isomers (88:11 after purification); white solid (1.35 g, 88%). IR (Nujol): ν=1610 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H, Me), 3.85 (s, 3H, MeO), 6.92 (d, 2H,

4-MeOC$_6$H$_4$–, J=8.8 Hz), 7.01 (d, 1H, C*H*=CF, J=35.1 Hz), 7.39 (d, 2H, Tos, J=8.2 Hz), 7.54 (d, 2H, 4-MeOC$_6$H$_4$–, J=8.8 Hz), 7.90 (d, 2H, Tos, J=8.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.7 (Me), 55.6 (MeO), 114.4, 115.0 (CH), 122.2 (d, *C*–CH=CF, J=3.7 Hz), 128.6 (CH), 130.1 (CH), 131.9 (d, CH, J=7.3 Hz), 134.9, 145.5, 149.7 (CH=*C*F, J=300.1 Hz), 161.5 (d, J=2.9 Hz). (*Z*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.86 (s, 3H, MeO), 6.83 (d, 1H, C*H*=CF, J=23.0 Hz), 7.36 (d, 2H, Tos, J=8.3 Hz), 7.48 (d, 2H, 4-MeOC$_6$H$_4$–, J=8.6 Hz), 7.81 (d, 2H, Tos, J=8.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 55.3 (MeO), 113.6 (CH), 118.7 (CH), 128.6 (CH), 129.9 (CH), the other signals are identical to those of the (*E*)-isomer; ESI-MS (m/z): calcd for C$_{16}$H$_{15}$FO$_3$SNa [M$^+$] 329.0624, found 329.0618.

4.3.5. Methyl 4-(2-fluoro-2-[(4-methylphenyl)-sulfonyl]vinyl)benzoate (**2e**)

Mixture of *E*/*Z* isomers (91:9 after purification); white solid (1.32 g, 79%). IR (Nujol): ν=1610, 1720 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.49 (s, 3H, Me), 3.94 (s, 3H, CO$_2$CH$_3$), 7.08 (d, 1H, C*H*=CF, J=34.4 Hz), 7.42 (d, 2H, Tos, J=8.2 Hz), 7.64 (d, 2H, 4-MeO$_2$CC$_6$H$_4$–, J=8.2 Hz), 7.92 (d, 2H, Tos, J=8.2 Hz), 8.06 (d, 2H, 4-MeO$_2$CC$_6$H$_4$–, J=8.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.8 (Me), 52.4 (CO$_2$CH$_3$), 113.8 (CH), 128.9 (CH), 129.9 (CH), 130.0 (CH), 130.3 (CH), 131.3 (d, J=2.2 Hz), 133.8 (d, J=3.7 Hz), 134.0, 146.1, 155.2 (d, CH=*C*F, J=308.1 Hz), 166.2 (*C*O$_2$CH$_3$). (*Z*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.90 (d, 1H, C*H*=CF, J=20.1 Hz), 7.52 (d, 2H, 4-MeO$_2$CC$_6$H$_4$–, J=8.2 Hz), 7.76 (d, 2H, Tos, J=8.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 52.0 (CO$_2$*C*H$_3$), 129.6 (CH), 129.8 (CH), 134.5, 167.2 (*C*O$_2$CH$_3$), the other signals are identical to those of the (*E*)-isomer; ESI-MS (m/z): calcd for C$_{17}$H$_{15}$FO$_4$SNa [M]$^+$ 357.0567, found 357.0573.

4.3.6. 1-Fluoro-2-(2-methoxyphenyl)vinyl-4-methylphenyl sulfone (**2f**)

Mixture of *E*/*Z* isomers (80:20 after purification); white solid (1.10 g, 72%). IR (Nujol): ν=1610 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.47 (s, 3H, Me), 3.89 (s, 3H, MeO), 6.94 (t, 1H, 2-MeOC$_6$H$_4$–, J=8.0 Hz), 7.33–7.37 (m, 2H, 2-MeOC$_6$H$_4$–), 7.39 (d, 2H, Tos, J=8.0 Hz), 7.59 (d, 1H, C*H*=CF, J=36.4 Hz), 7.73 (dd, 1H, 2-MeOC$_6$H$_4$–, J=8.0, 1.3 Hz), 7.92 (d, 2H, Tos, J=8.0 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.7 (Me), 55.6 (MeO), 114.1, 109.2 (CH), 110.9 (CH), 118.5 (d, *C*–CH=CF, J=4.4 Hz), 120.8 (CH), 128.7 (CH), 130.1 (CH), 130.4 (d, CH, J=13.2 Hz), 131.8 (CH), 134.8, 145.5, 153.6 (CH=*C*F, J=303.0 Hz), 157.6. (*Z*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.46 (s, 3H, MeO), 3.82 (s, 3H, MeO), 7.79 (d, 2H, Tos, J=8.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 55.4 (MeO), 110.1 (CH), 120.0 (CH), 128.8 (CH), 129.8 (CH), 132.2 (CH), 135.1, 145.4, 157.1. Anal. Calcd for C$_{16}$H$_{15}$FO$_3$S: C, 62.73; H, 4.94. Found: C, 62.60; H 4.75.

4.3.7. 1-Fluoro-2-(4-methylphenyl)vinyl-4-methylphenyl sulfone (**2g**)

Mixture of *E*/*Z* isomers (92:8 after purification); white solid (1.09 g, 75%). IR (Nujol): ν=1610 (C=C) cm^{-1}. (*E*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.36 (s, 3H, Me), 2.45 (s, 3H, Me), 7.04 (d, 1H, C*H*=CF, J=35.4 Hz), 7.19 (d, 2H, 4-MeC$_6$H$_4$–, J=8.1 Hz), 7.38 (d, 2H, Tos, J=8.3 Hz), 7.46 (d, 2H, 4-MeC$_6$H$_4$–, J=8.1 Hz), 7.91 (d, 2H, Tos, J=8.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.3 (Me), 21.5 (Me), 115.1, 128.5, 128.7, 129.6, 130.0, 130.1, 134.5, 140.7 (d, J=2.2 Hz), 145.5, 153.1 (CH=*C*F, J=303.0 Hz). (*Z*)-Isomer: ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.36 (s, 3H, Me), 2.45 (s, 3H, Me), 6.85 (d, 1H, C*H*=CF, J=22.5 Hz), 7.33 (d, 2H, J=8.3 Hz), 7.79 (d, 2H, 4-, J=8.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.2 (Me), 126.6 (d, J=3.7 Hz), 128.6, 129.8, 129.9 (d, J=2.9 Hz), 134.9, 139.2, 145.6, 152.7 (CH=*C*F, J=288.3 Hz), the other signals are identical to those of the (*E*)-isomer. Anal. Calcd for C$_{16}$H$_{15}$FO$_2$S: C, 66.19; H, 5.21. Found: C, 66.02; H 5.04.

4.4. General procedure for cycloaddition reactions of the α-fluoro-β-arylvinyl sulfones 2 with 2,3-dimethylbutadiene and cyclopentadiene

The corresponding α-fluoro-β-arylvinyl sulfone **2** (1 mmol) and the diene (1.0 ml) were heated in a sealed glass tube with a Young-tap. The excess of the diene was evaporated at reduced pressure and the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 20:1).

4.4.1. 1-(6-Fluoro-3,4-dimethyl-6-[(4-methylphenyl)-sulfonyl]cyclohex-3-en-1-yl)-4-nitrobenzene (**3**)

Obtained from **2a** by heating with 2,3-dimethylbutadiene at 150 °C for 7 h. Pale brown solid (0.36 g, 89%). Mp 155–157 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.68 (s, 6H, Me), 2.28 (dd, 1H, –CH$_2$–, J=17.3, 5.7 Hz), 2.36 (s, 3H, CH$_3$), 2.38–2.53 (m, 2H, –CH$_2$–), 2.85–3.05 (m, 1H, –CH$_2$–), 3.65 (dq, 1H, –CH–Ar, J=32.3, 5.9 Hz), 7.07 (d, 2H, Ar, J=8.1 Hz), 7.32 (d, 2H, Ar, J=8.1 Hz), 7.37 (d, 2H, Tos, J=8.5 Hz), 7.90 (d, 2H, Tos, J=8.5 Hz); ^{19}F NMR (282 MHz, CDCl$_3$): δ −160.5; ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.6 (Me, Tos), 18.2 (Me), 18.5 (Me), 36.8 (d, –CH$_2$–, J=22.3 Hz), 38.2 (d, –CH$_2$–, J=4.7 Hz), 44.0 (–CH–, J=18.6 Hz), 109.4 (d, –CF–, J=225.8 Hz), 120.6, 123.0 (CH), 125.1, 129.2 (CH), 129.7 (d, CH, J=1.8 Hz), 130.2 (d, CH, J=2.7 Hz), 132.4, 145.2 (Ar), 146.2, 147.0 (–*C*H=*C*H–); ESI-MS (m/z): calcd for C$_{21}$H$_{21}$FNO$_4$SNa [M$^+$] 426.1151, found 426.1141.

4.4.2. 5-Fluoro-5-[(4-methylphenyl)sulfony]-6-(4-nitrophenyl)-bicyclo[2.2.1]hept-2-ene (**4a**,**5a**)

Obtained from **2a** by heating with cyclopentadiene at 150 °C for 7 h. White solid (0.34 g, 87%). Major diastereomer **4a**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.73–1.82 (m, 1H, –CH$_2$–), 2.35–2.48 (m, 1H, –CH$_2$–), 2.43 (s, 3H, CH$_3$), 3.29 (br s, 1H, –CH–), 3.44 (br s, 1H, –CH–), 4.15 (dd, 1H, –CH–Ar, J=13.7, 2.9 Hz), 6.23 (dd, 1H, –CH=, J=5.5, 3.3 Hz), 6.62 (dd, 1H, –CH=, J=5.5, 2.9 Hz), 7.29–7.39 (m, 4H, Tos, Ar), 7.80 (d, 2H, Tos, J=8.1 Hz), 8.04 (d, 2H, Ar, J=8.8 Hz); ^{19}F NMR (282 MHz, CDCl$_3$): δ −155.9 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.7 (Me), 48.5 (–CH$_2$–), 48.6 (–CH–), 50.4 (d, –CH–, J=20.4 Hz), 51.4 (d, –CH–, J=16.5 Hz), 114.9 (d, –CF–, J=236.5 Hz), 122.9 (CH), 129.8 (CH), 130.1 (CH), 130.6 (CH), 131.9, 143.9 (d, J=3.8 Hz), 145.9, 146.9 (Ar), 134.1 (d, J=6.4 Hz), 140.0 (–*C*H=*C*H–). Minor diastereomer **5a**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.96 (d, 1H, –CH$_2$–, J=9.5 Hz), 2.30 (d, 1H, –CH$_2$–, J=9.5 Hz), 2.47 (s, 3H, CH$_3$), 2.78 (br s, 1H, –CH–), 3.28 (br s, 1H, –CH–), 3.78 (dd, 1H, –CH–Ar, J=15.5, 2.4 Hz), 6.36 (br s, 1H, –CH=), 6.62 (br s, 1H, –CH=), 7.37 (d, 2H, Tos, J=8.0 Hz), 7.58 (d, 2H, Ar, J=8.8 Hz), 7.77 (d, 2H, Tos, J=8.0 Hz), 8.17 (d, 2H, Ar, J=8.8 Hz); ^{19}F NMR (282 MHz, CDCl$_3$): δ −149.3 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.3 (Me), 48.1 (–CH–), 48.4 (–CH$_2$–), 50.6 (d, –CH–, J=6.4 Hz), 50.9 (d, –CH–, J=16.5 Hz), 113.4 (d, –CF–, J=239.1 Hz), 123.7 (CH), 130.2 (CH), 130.3 (CH), 130.8 (CH), 132.4, 133.5, 147.1 (Ar), 133.9 (d, J=6.4 Hz), 141.2 (–*C*H=*C*H–); ESI-MS (m/z): calcd for C$_{20}$H$_{18}$FNO$_4$SNa [M$^+$] 410.0838, found 410.0831. Anal. Calcd for C$_{20}$H$_{18}$FNO$_4$S: C, 62.00; H, 4.68; N, 3.62. Found: C, 61.99; H, 4.45; N, 3.54.

4.4.3. 5-Fluoro-5-[(4-methylphenyl)sulfonyl]-6-(4-chlorophenyl)-bicyclo[2.2.1]hept-2-ene (**4b**,**5b**)

Obtained from **2b** by heating with cyclopentadiene at 150 °C for 12 h. White solid (0.24 g, 65%). Major diastereomer **4b**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.67–1.76 (m, 1H, –CH$_2$–), 2.33 (d, 1H, –CH$_2$–, J=9.8 Hz), 2.42 (s, 3H, CH$_3$), 3.20 (br s, 1H, –CH–), 3.43 (br s, 1H, –CH–), 3.99 (dd, 1H, –CH–Ar, J=14.1, 3.0 Hz), 6.18 (dd, 1H, –CH=, J=5.2, 3.4 Hz), 6.60 (dd, 1H, –CH=, J=5.2, 2.9 Hz), 7.04–7.38 (m, 6H, Tos, Ar), 7.78 (d, 2H, Tos, J=7.9 Hz); ^{19}F NMR (282 MHz, CDCl$_3$): δ −156.1 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.2 (Me), 48.9 (–CH$_2$–), 49.0 (–CH–), 50.7 (d, –CH–, J=20.3 Hz), 51.7 (d, –CH–, J=17.8 Hz), 115.1 (d, –CF–, J=236.5 Hz), 128.3 (CH), 131.5 (CH), 130.2

(CH), 132.7, 135.1, 136.7, 146.0 (Ar), 134.0 (d, J=5.1 Hz), 140.8 (–*C*H=*C*H–). Minor diastereomer **5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (d, 1H, –CH_2–, J=9.3 Hz), 2.45 (s, 3H, CH_3), 2.76 (br s, 1H, –CH–), 3.64 (dd, 1H, –CH–Ar, J=15.6, 2.1 Hz), 6.32 (br s, 1H, –CH=); ^{19}F NMR (282 MHz, $CDCl_3$): δ −149.4 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2 (Me), 48.3 (–CH–), 48.5 (–CH_2–), 50.3 (d, –CH–, J=6.4 Hz), 114.0 (d, –CF–, J=236.5 Hz), 128.7 (CH), 131.1 (CH), 130.2 (CH), 130.5 (CH), 133.2, 135.2, 137.0, 146.0 (Ar); 133.6 (d, J=5.1 Hz), 141.5 (–*C*H=*C*H–); ESI-MS (m/z): calcd for $C_{20}H_{18}ClFO_2SNa$ [M^+] 399.0598, found 399.0595. Anal. Calcd for $C_{20}H_{18}ClFO_2S$: C, 63.74; H, 4.81. Found: C, 63.42; H 4.58.

*4.4.4. 5-Fluoro-5-((4-methylphenyl)sulfonyl)-6-phenyl-bicyclo[2.2.1]hept-2-ene (**4c**,**5c**)*

Obtained from **2c** by heating with cyclopentadiene at 150 °C for 23 h. White solid (0.18 g, 53%). Major diastereomer **4c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66–1.74 (m, 1H, –CH_2–), 2.35 (d, 1H, –CH_2–, J=9.4 Hz), 2.40 (s, 3H, CH_3), 3.23 (br s, 1H, –CH–), 3.46 (br s, 1H, –CH–), 4.00 (dd, 1H, –CH–Ar, J=14.3, 3.1 Hz), 6.18 (dd, 1H, –CH=, J=5.5, 3.5 Hz), 6.64 (dd, 1H, –CH=, J=5.5, 2.9 Hz), 7.08–7.38 (m, 7H, Tos, Ar), 7.79 (d, 2H, Tos, J=7.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −156.0 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1 (Me), 48.9 (–CH_2–), 49.1 (–CH–), 50.7 (d, –CH–, J=17.8 Hz), 52.2 (d, –CH–, J=17.8 Hz), 115.3 (d, –CF–, J=236.5 Hz), 127.6, 128.1 (CH), 127.4 (CH), 130.1 (CH), 130.2 (CH), 130.5 (CH), 136.6, 145.8 (Ar), 133.6 (d, J=5.1 Hz), 141.2 (–*C*H=*C*H–). Minor diastereomer **5c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (d, 1H, –CH_2–, J=9.3 Hz), 2.44 (s, 3H, CH_3), 2.78 (br s, 1H, –CH–), 3.23 (br s, 1H, –CH–), 3.67 (dd, 1H, –CH–Ar, J=15.7, 2.3 Hz), 6.29–6.35 (m, 1H, –CH=), 6.57–6.62 (m, 1H, –CH=); ^{19}F NMR (282 MHz, $CDCl_3$): δ −149.5 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1 (Me), 48.5 (–CH–), 48.6 (–CH_2–), 51.0 (d, –CH–, J=17.8 Hz), 114.0 (d, –CF–, J=239.1 Hz), 127.6 (CH), 128.6 (CH), 129.8 (CH), 130.7 (CH), 136.7 (Ar); 141.7 (–*C*H=*C*H–); ESI-MS (m/z): calcd for $C_{20}H_{19}FO_2SNa$ [M^+] 365.0987, found 365.0971. Anal. Calcd for $C_{20}H_{19}FO_2S$: C, 70.15; H, 5.59. Found: C, 70.62; H, 5.57.

*4.4.5. 5-Fluoro-5-[(4-methylphenyl)sulfonyl]-6-(4-methoxyphenyl)-bicyclo[2.2.1]hept-2-ene (**4d**,**5d**)*

Obtained from **2d** by heating with cyclopentadiene at 150 °C for 54 h. White solid (0.30 g, 81%). Major diastereomer **4d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61–1.72 (m, 1H, –CH_2–), 2.32 (d, 1H, –CH_2–, J=9.4 Hz), 2.41 (s, 3H, CH_3), 3.18 (br s, 1H, –CH–), 3.42 (br s, 1H, –CH–), 3.74 (s, 3H, CH_3O), 3.96 (dd, 1H, –CH–Ar, J=14.3, 3.1 Hz), 6.16 (dd, 1H, –CH=, J=5.3, 3.3 Hz), 6.63 (dd, 1H, –CH=, J=5.3, 3.0 Hz), 6.69 (d, 2H, Ar, J=8.7 Hz), 7.03 (d, 2H, Ar, J=8.7 Hz), 7.28 (d, 2H, Tos, J=8.0 Hz), 7.78 (d, 2H, Tos, J=8.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −156.1 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1 (Me), 48.9 (–CH_2–), 49.2 (–CH–), 50.8 (d, –CH–, J=20.4 Hz), 51.4 (d, –CH–, J=17.8 Hz), 55.6 (MeO), 113.5 (CH), 127.9, 130.1 (CH), 130.5 (CH), 131.2 (CH), 136.1, 145.1, 158.3 (Ar), 133.6 (d, J=5.1 Hz), 141.2 (–*C*H=*C*H–). Minor diastereomer **5d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87 (d, 1H, –CH_2–, J=9.3 Hz), 2.44 (s, 3H, CH_3), 2.75 (br s, 1H, –CH–), 3.18 (br s, 1H, –CH–), 3.65 (dd, 1H, –CH–Ar, J=15.5, 2.1 Hz), 3.78 (s, 3H, CH_3O), 6.27–6.33 (m, 1H, –CH=), 6.55–6.60 (m, 1H, –CH=), 6.82 (d, 2H, Ar, J=8.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −149.4 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1 (Me), 48.5 (–CH_2–), 48.6 (–CH–), 50.3 (d, –CH–, J=17.8 Hz), 50.7 (d, –CH–, J=20.4 Hz), 113.9 (CH), 127.8, 130.2 (CH), 130.8 (CH), 136.3, 145.0, 157.9 (Ar), 133.4 (d, J=5.1 Hz), 141.8 (–*C*H=*C*H–); ESI-MS (m/z): calcd for $C_{21}H_{21}FO_3SNa$ [M^+] 395.1093, found 395.1089.

*4.4.6. Methyl 4-(3-Fluoro-3-[(4-methylphenyl)sulfonyl]-bicyclo[2.2.1]hept-5-en-2-yl)benzoate (**4e**,**5e**)*

Obtained from **2e** by heating with cyclopentadiene at 150 °C for 8 h. White solid (0.27 g, 67%). Major diastereomer **4e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.69–1.78 (m, 1H, –CH_2–), 2.33–2.38 (m, 1H, –CH_2–), 2.40 (s, 3H, CH_3), 3.25 (br s, 1H, –CH–), 3.47 (br s, 1H, –CH–), 3.88 (s, 3H, CO_2CH_3), 4.06 (dd, 1H, –CH–Ar, J=14.1, 3.1 Hz), 6.21 (dd, 1H, –CH=, J=5.5, 3.5 Hz), 6.62 (dd, 1H, –CH=, J=5.5, 2.9 Hz), 7.25–7.41 (m, 4H, Tos, Ar), 7.78 (d, 2H, Tos, J=8.1 Hz), 7.83 (d, 2H, Ar, J=8.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −156.0 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (Me), 48.5 (–CH_2–), 48.7 (–CH–), 50.4 (d, –CH–, J=20.4 Hz), 51.7 (d, –CH–, J=15.3 Hz), 52.1 (CO_2*Me*), 114.9 (d, –CF–, J=236.5 Hz), 129.7 (CH), 128.9 (CH), 130.0 (CH), 132.2, 136.4, 145.6 (Ar), 133.6 (d, J=7.6 Hz), 140.5 (–*C*H=*C*H–), 167.0 (*C*O_2Me). Minor diastereomer **5e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (d, 1H, –CH_2–, J=9.5 Hz), 2.41 (s, 3H, CH_3), 2.77 (br s, 1H, –CH–), 3.25 (br s, 1H, –CH–), 3.72 (dd, 1H, –CH–Ar, J=15.4, 2.4 Hz), 3.90 (s, 3H, CO_2CH_3), 6.31–6.36 (m, 1H, –CH=), 6.58–6.60 (m, 1H, –CH=); ^{19}F NMR (282 MHz, $CDCl_3$): δ −149.4 (d, J=15.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (Me), 48.2 (–CH_2–), 48.4 (–CH_2–), 50.5 (d, –CH–, J=17.8 Hz), 51.8 (d, –CH–, J=15.3 Hz), 113.9 (d, –CF–, J=239.1 Hz), 129.4 (CH), 129.1 (CH), 130.3 (CH), 132.7, 136.6, 145.5 (Ar), 133.3 (d, J=5.1 Hz), 141.1 (–*C*H=*C*H–), 166.0 (*C*O_2Me); ESI-MS (m/z): calcd for $C_{22}H_{21}FO_4SNa$ [M^+] 423.1042, found 423.1037.

4.5. General procedure for cycloaddition reactions of the α-fluoro-β-arylvinyl sulfones 2 with 1,3-diphenylisobenzofuran

The corresponding α-fluoro-β-arylvinyl sulfone **2** (1 mmol), 1,3-diphenylisobenzofuran (270 mg, 1 mmol) and toluene (1.0 ml) were heated in a sealed glass tube with a Young-tap. Toluene was evaporated at reduced pressure and the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 10:1).

*4.5.1. 2-Fluoro-2-[(4-methylphenyl)sulfonyl]-3-(4-nitrophenyl)-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**6a**,**7a**)*

Obtained from **2a** by heating with 1,3-diphenylisobenzofuran at 150 °C for 17 h. Major diastereomer **6a**: white crystals (0.416 g, 70%), mp 224–226 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 4.69 (d, 1H, –CH–Ar, J=14.0 Hz), 6.37 (dd, 2H, J=8.9, 2.1 Hz), 6.99 (d, 2H, J=7.9 Hz), 7.04 (d, 1H, J=7.2 Hz), 7.16 (dd, 2H, J=8.3, 1.5 Hz), 7.26–7.43 (m, 10H), 7.53 (d, 1H, J=7.4 Hz), 7.61 (d, 2H, J=7.4 Hz), 7.94 (d, 2H, J=8.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −148.53 (d, J=14.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (Me), 59.5 (d, J=16.0 Hz), 90.3 (d, J=22.8 Hz), 90.9, 112.3 (d, J=250.4 Hz), 122.5, 122.6, 123.3, 125.6, 126.3, 128.0, 128.1, 128.4, 128.7, 129.4, 129.6 (d, J=1.0 Hz), 131.8, 132.3 (d, J=2.9 Hz), 133.1, 135.7, 139.8, 143.4, 145.0, 147.5; ESI-MS (m/z): calcd for $C_{35}H_{26}FNO_5SNa$ [M^+] 614.1395, found 614.1408.

Minor diastereomer **7a**: white crystals (0.138 g, 24%), mp 131–133 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 4.47 (d, 1H, –CH–Ar, J=11.0 Hz), 7.10–7.27 (m, 8H), 7.31–7.41 (m, 4H), 7.47–7.56 (m, 3H), 7.62 (dd, 2H, J=8.3, 1.5 Hz), 7.68–7.76 (m, 3H), 8.14 (dd, 2H, J=7.7, 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −151.08 (d, J=11.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (Me), 59.0 (d, J=16.7 Hz), 91.8, 93.2 (d, J=23.4 Hz), 113.4 (d, J=253.6 Hz), 119.5, 122.2, 123.8, 126.0, 127.8, 128.0, 128.2, 128.4, 129.0, 129.7, 130.0 (d, J=2.0 Hz), 131.6, 132.4, 133.3, 134.9, 146.1, 146.7, 148.6. ESI-MS (m/z): calcd for $C_{35}H_{26}FNO_5SNa$ [M^+] 614.1395, found 614.1408.

*4.5.2. 2-Fluoro-2-[(4-methylphenyl)sulfonyl]-3-(4-chlorophenyl)-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**6b**,**7b**)*

Obtained from **2b** by heating with 1,3-diphenylisobenzofurane at 150 °C for 67 h. Major diastereomer **6b**: white crystals (0.424 g, 73%), mp 103–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H, CH_3), 4.50 (d, 1H, –CH–Ar, J=14.4 Hz), 6.08 (dd, 2H, J=8.6, 2.0 Hz), 6.95–7.05 (m, 5H), 7.16–7.41 (m, 12H), 7.50 (d, 1H, J=7.5 Hz), 7.64 (d, 2H, J=6.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −148.43 (d, J=14.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6 (Me), 59.4 (d, J=16.4 Hz), 90.2 (d, J=22.8 Hz), 90.7, 112.0 (d, J=249.7 Hz), 122.6, 123.1, 125.7, 126.4,

127.7, 127.8, 128.3, 128.4, 128.5, 129.3, 129.5 (d, J=1.3 Hz), 130.8 (d, J=1.9 Hz), 132.1, 132.7 (d, J=2.6 Hz), 133.5, 134.0, 136.1, 143.5, 144.8, 145.5; ESI-MS (m/z): calcd for $C_{35}H_{26}ClFNO_3SNa$ [M^+] 603.1173, found 603.1153.

Minor diastereomer **7b**: white crystals (0.052 g, 9%), mp 91–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 4.33 (d, 1H, –CH–Ar, J=11.0 Hz), 6.81 (d, 2H, J=8.1 Hz), 7.06–7.26 (m, 6H), 7.29–7.40 (m, 6H), 7.45–7.55 (m, 3H), 7.61 (dd, 2H, J=8.3, 1.3 Hz), 7.72 (dd, 1H, J=6.0, 1.5 Hz), 8.17 (d, 2H, J=6.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −151.11 (d, J=11.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (Me), 58.6 (d, J=17.3 Hz), 91.8, 93.0 (d, J=24.1 Hz), 113.2 (d, J=252.9 Hz), 119.4, 123.7, 126.2, 127.5, 127.7, 128.2, 128.5, 128.8, 129.6, 130.0 (d, J=1.9 Hz), 132.1, 133.5, 135.5, 141.0 (d, J=5.5 Hz), 145.8, 149.2; ESI-MS (m/z): calcd for $C_{35}H_{26}ClFNO_3SNa$ [M^+] 603.1173, found 603.1167.

4.6. General procedure for the reactions of cycloadducts 3, 4, 5 and 6 with *t*-BuOK

A 10 ml round bottom flask was charged with a mixture of adducts **4**,**5** (1 mmol) or pure adducts **3** and **6** (0.2 mmol) and dry THF (2 ml) and a solution of *t*-BuOK (120 mg, 1.05 mmol) (or 27 mg, 0.24 mmol) in dry THF (2 ml) was added dropwise. After completion of the reaction (TLC control), THF was evaporated in vacuum. The residue was dissolved in cyclohexane and passed through a short filter with silica gel in case of **8** and **10** or was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 10:1) in case of **9**.

*4.6.1. 2-Fluoro-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**8**)*

Obtained from the mixture of **4a** and **5a**. Colourless, unstable solid (0.14 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25–2.30 (m, 1H, –CH_2–), 2.43 (dt, 1H, –CH_2–, J=6.4, 1.4 Hz), 3.48–3.52 (m, 1H, –CH–), 3.88–3.92 (m, 1H, –CH–), 7.07 (d, 2H, Ar, J=8.1 Hz), 6.95 (ddd, 1H, –CH=, J=5.0, 3.1, 0.5 Hz), 7.05 (pent, 1H, –CH=, J=2.4 Hz), 7.51 (d, 2H, Ar, J=8.8 Hz), 8.18 (d, 2H, Ar, J=8.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −110.5; ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.1 (d, –CH_2–, J=4.5 Hz), 48.8 (d, –CH_2–, J=19.7 Hz), 67.3 (–CH–, J=5.6 Hz), 121.7 (CH), 123.4 (d, CH, J=6.7 Hz), 126.7, 132.0 (Ar); 137.4 (d, C=*C*–Ar, J=5.1 Hz), 139.1 (d, –*C*H=*C*H–, J=4.2 Hz), 141.0 (d, –*C*H=*C*H–, J=5.9 Hz), 176.1 (d, –CF–, J=311.3 Hz); ESI-MS (m/z): calcd for $C_{13}H_{10}FNO_2Na$ [M^+] 254.0593, found 254.0588.

*4.6.2. 2-Fluoro-3-(4-nitrophenyl)-1,4-diphenyl-1,4-dihydro-1,4-epoxynaphthalene (**9a**)*

Obtained from **6a**. Yellow solid (54 mg, 62%), mp 80–81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09–7.77 (m, 16H), 8.09 (d, 2H, J=8.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −118.42; ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.7 (d, J=25.7 Hz), 93.2 (d, J=7.7 Hz), 121.3, 121.4, 125.9, 126.4, 126.7 (d, J=4.2 Hz), 127.1, 127.6, 128.7, 128.9, 129.0, 129.2, 129.5, 129.8, 130.2, 132.7, 137.7, 146.3, 149.5 (d, J=3.2 Hz), 150.4 (d, J=2.4 Hz), 171.8 (d, J=321.4 Hz); ESI-MS (m/z): calcd for $C_{28}H_{18}FNO_3Na$ [M^+] 458.1168, found 458.1188.

*4.6.3. 2-Fluoro-3-(4-chlorophenyl)-1,4-diphenyl-1,4-dihydro-1,4-epoxynaphthalene (**9b**)*

Obtained from **6b**. Yellow solid (56 mg, 65%), mp 84–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04–7.28 (m, 7H), 7.39–7.51 (m, 6H), 7.58 (d, 1H, J=6.8 Hz), 7.63–7.68 (m, 2H), 7.74 (d, 2H, J=8.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −124.27; ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.7 (d, J=21.5 Hz), 93.2 (d, J=7.7 Hz), 120.9, 121.2, 125.6, 126.0, 127.2 (d, J=1.3 Hz), 127.5, 127.6, 128.6, 128.7, 128.8, 129.0, 129.5, 130.3, 131.9 (d, J=3.2 Hz), 132.9, 133.1, 133.3, 150.1 (d, J=2.9 Hz), 150.9 (d, J=2.6 Hz), 173.5 (d, J=315.1 Hz); ESI-MS (m/z): calcd for $C_{28}H_{18}FNO_3Na$ [M^+] 447.0928, found 447.0922.

*4.6.4. 4,5-Dimethyl-4′-nitro-1,1′-biphenyl-2-yl 4-methylphenyl sulfone (**10**)*

Obtained from **3**. Yellow oil (not purified). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H, Me), 2.28 (s, 3H, Me), 2.35 (s, 3H, Tos), 6.87 (s, 1H, Ar), 6.96 (d, 2H, J=8.3 Hz, 4-$NO_2C_6H_4$), 7.09 (d, 2H, J=8.7 Hz, Tos), 7.11 (d, 2H, J=8.3 Hz, 4-$NO_2C_6H_4$), 7.99 (d, 2H, J=8.7 Hz, Tos), 8.07 (s, 1H, Ar); ESI-MS (m/z): calcd for $C_{21}H_{19}NNaO_4S$ [M^+] 404.0932, found 404.0930.

4.7. X-ray crystal structure analyses

*4.7.1. exo-5-Fluoro-5-[(4-methylphenyl)sulfonyl]-exo-6-(4-nitrophenyl)-bicyclo[2.2.1]hept-2-ene (**4a**)*

$C_{20}H_{18}FNO_4S$, M=387.41, colourless crystal 0.35×0.15×0.15 mm, a=11.258(1), b=8.839(1), c=18.517(1) Å, β=103.14(1)°, V=1794.4(3) Å^3, ρ_{calcd}=1.434 g cm^{-3}, μ=1.932 mm^{-1}, empirical absorption correction ($0.551 \le T \le 0.760$), Z=4, monoclinic, space group $P2_1/c$ (No. 14), λ=1.54178 Å, T=223(2) K, ω and φ scans, 11,830 reflections collected ($\pm h,\pm k,\pm l$), [(sin θ)/λ]=0.60 Å^{-1}, 3153 independent (R_{int}=0.039) and 2870 observed reflections [$I \ge 2\sigma(I)$], 245 refined parameters, R=0.042, wR^2=0.116, max. residual electron density 0.34(−0.33) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*4.7.2. endo-5-Fluoro-5-[(4-methylphenyl)sulfonyl]-endo-6-(4-nitrophenyl)-bicyclo[2.2.1]hept-2-ene (**5a**)*

$C_{20}H_{18}FNO_4S$, M=387.41, colourless crystal 0.50×0.30×0.10 mm, a=8.237(1), b=20.207(1), c=11.746(1) Å, β=110.41(1)°, V=1832.3(3) Å^3, ρ_{calcd}=1.404 g cm^{-3}, μ=1.892 mm^{-1}, empirical absorption correction ($0.451 \le T \le 0.833$), Z=4, monoclinic, space group $P2_1/n$ (No. 14), λ=1.54178 Å, T=223(2) K, ω and φ scans, 8736 reflections collected ($\pm h,\pm k,\pm l$), [(sin θ)/λ]=0.60 Å^{-1}, 3072 independent (R_{int}=0.040) and 2848 observed reflections [$I \ge 2\sigma(I)$], 245 refined parameters, R=0.056, wR^2=0.145, max. residual electron density 0.54(−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*4.7.3. endo-2-Fluoro-2-[(4-methylphenyl)sulfonyl]-endo-3-(4-nitrophenyl)-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epoxy-naphthalene (**6a**)*

$C_{35}H_{26}FNO_5S$, M=591.63, colourless crystal 0.35×0.25×0.12 mm, a=13.2017(5), b=19.1893(7), c=11.3914(4) Å, β=91.410(2)°, V=2884.9(2) Å^3, ρ_{calcd}=1.362 g cm^{-3}, μ=1.432 mm^{-1}, empirical absorption correction ($0.634 \le T \le 0.847$), Z=4, monoclinic, space group $P2_1/c$ (No. 14), λ=1.54178 Å, T=223 K, ω and φ scans, 22,073 reflections collected ($\pm h,\pm k,\pm l$), [(sin θ)/λ]=0.60 Å^{-1}, 5079 independent (R_{int}=0.051) and 4528 observed reflections [$I \ge 2\sigma(I)$], 389 refined parameters, R=0.046, wR^2=0.121, max. (min.) residual electron density 0.33(−0.34) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

The data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[36] absorption correction Denzo,[37] structure solution SHELXS-97,[38] structure refinement SHELXL-97,[39] graphics SCHAKAL.[40]

CCDC 675468, 675469 and 688574 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336 033, e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

This project was supported by the Deutsche Forschungsgemeinschaft (DFG) through grant Gz: 436 RUS 113/858/

0-1 and the Russian Foundation for Basic Research (grants no. 08-03-00736-a, RFBR-DFG 07-03-91562-NNIO_a).

References and notes

1. Recent textbooks: (a) Hiyama, T. *Organofluorine Compounds: Chemistry and Applications*; Springer: Berlin, 2000; (b) Chambers, R. D. *Fluorine in Organic Chemistry*; Blackwell: Oxford, 2004; (c) Kirsch, P. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*; Wiley-VCH: Weinheim, 2004; (d) Uneyama, K. *Organofluorine Chemistry*; Blackwell: Oxford, 2006.
2. Recent reviews: (a) Welch, J. T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemistry*; Wiley and Sons: Chichester, UK, 1991; (b) *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*; Filler, R., Kobayashi, Y., Yagupolskii, L. M., Eds.; Elsevier: Amsterdam, 1993; (c) *Fluorine-containing Amino Acids: Synthesis and Properties*; Kukhar, V. P., Soloshonok, V. A., Eds.; Wiley and Sons: Chichester, UK, 1995; (d) *Biomedical Frontiers of Fluorine Chemistry*; Ojima, I., McCarthy, J. R., Welch, J. T., Eds.; ACS Symposium Series 639; American Chemical Society: Washington, DC, 1996; (e) Fluorine in the Life Sciences. (Multiauthor Special Issue) *ChemBioChem* **2004**, *5*, 559–722; (f) Fluorine in the Life Science Industry. (Multiauthor Special Issue) *Chimia* **2004**, *58*, 92–162; (g) Theodoridis, G. Fluorine-containing Agrochemicals: An Overview of Recent Developments. In *Advances in Fluorine Science*; Tressaud, A., Ed.; Elsevier: Amsterdam, 2006; Vol. 2, pp 121–175; (h) *Fluorine and Health: Molecular Imaging, Biomedical Materials and Pharmaceuticals*; Tressaud, A., Haufe, G., Eds.; Elsevier: Amsterdam, 2008; pp 553–778.
3. (a) Hudlický, M.; Pavlak, A. P. *Chemistry of Organic Fluorine Compounds II*. ACS Symposium Series 187; American Chemical Society: Washington, DC, 1995; (b) *Enantiocontrolled Synthesis of Fluoro-organic Compounds*; Soloshonok, V. A., Ed.; Wiley and Sons: Chichester, UK, 1999; (c) *Asymmetric Fluoroorganic Chemistry. Synthesis, Applications, and Future Directions*; Ramachandran, P. V., Ed.; ACS Symposium Series 746; American Chemical Society: Washington, DC, 2000; (d) *Fluorine-containing Synthons*; Soloshonok, V. A., Ed.; ACS Symposium Series 911; American Chemical Society: Washington, DC, 2005; (e) *Science of Synthesis*; Percy, J. M., Ed.; Fluorine; Thieme: Stuttgart, 2006; Vol. 34; (f) *Current Fluoroorganic Chemistry. New Synthetic Directions, Technologies, Materials, and Biological Applications*; Soloshonok, V. A., Mikami, K., Yamazaki, T., Welch, J. T., Honek, J. F., Eds.; ACS Symposium Series 949; American Chemical Society: Washington, DC, 2006.
4. Haufe, G. Vinyl Fluorides in Cycloadditions. In *Fluorine-containing Synthons*; Soloshonok, V. A., Ed.; ACS Symposium Series 911; American Chemical Society: Washington, DC, 2005; pp 155–172.
5. Bégué, J.-P.; Bonnet-Delpon, D. *Chimie Bioorganique et Médicinale du Fluor, Savoirs Actuels*; EDP Sciences/CNRS Editions: Paris, 2005; pp 229–286.
6. (a) Allmendinger, Y.; Felder, E.; Hungerbuehler, E. Fluoroolefin Dipeptide Isosteres. In *Selective Fluorination in Organic and Bioorganic Chemistry*; Welch, J. T., Ed.; American Chemical Society: Washington, DC, 1991; (b) Welch, J. T.; Lui, J.; Boros, L. G.; Decorte, B.; Bergmann, K.; Gimi, R. Fluoro-olefin Isosteres as Peptidomimetics. In *Biomedical Frontiers of Fluorine Chemistry*; Ojima, I., McCarthy, J. R., Welch, J. T., Eds.; ACS Symposium Series 639; American Chemical Society: Washington, DC, 1996; pp 129–141; (c) Cieplak, P.; Kollman, P. A.; Radomski, J. P. Molecular Design of Fluorine Containing Peptide Mimetics. In *Biomedical Frontiers of Fluorine Chemistry*; Ojima, I., McCarthy, J. R., Welch, J. T., Eds.; ACS Symposium Series 639; American Chemical Society: Washington, DC, 1996; pp 143–168.
7. (a) Abraham, R. J.; Ellison, S. L. R.; Schonholzer, P.; Thomas, W. A. *Tetrahedron* **1986**, *42*, 2101–2110; (b) Gharat, L. A.; Martin, A. R. *J. Heterocycl. Chem.* **1996**, *33*, 197–201; (c) Takeuchi, Y.; Yamada, A.; Suzuki, T.; Koizumi, T. *Tetrahedron* **1996**, *52*, 225–232; (d) Laue, K. W.; Mück-Lichtenfeld, C.; Haufe, G. *Tetrahedron* **1999**, *55*, 10413–10424.
8. Shastin, A. V.; Korotchenko, V. N.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 6557–6563.
9. For reviews of carbonyl olefination see: (a) Kuhn, F. E.; Santos, A. M. *Mini-Rev. Org. Chem.* **2004**, *1*, 55–64; (b) Korotchenko, V. N.; Nenajdenko, V. G.; Shastin, A. V.; Balenkova, E. S. *Russ. Chem. Rev.* **2004**, *73*, 957–989; (c) Takeda, T. *Modern Carbonyl Olefination*; Wiley-VCH: Weinheim, 2004.
10. (a) Nenajdenko, V. G.; Shastin, A. V.; Korotchenko, V. N.; Varseev, G. N.; Balenkova, E. S. *Eur. J. Org. Chem.* **2003**, 302–308; (b) Korotchenko, V. N.; Shastin, A. V.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2001**, *57*, 7519–7527; (c) Nenajdenko, V. G.; Varseev, G. N.; Korotchenko, V. N.; Shastin, A. V.; Balenkova, E. S. *J. Fluorine Chem.* **2003**, *124*, 115–118; (d) Nenajdenko, V. G.; Varseev, G. N.; Korotchenko, V. N.; Shastin, A. V.; Balenkova, E. S. *J. Fluorine Chem.* **2004**, *124*, 1339–1345; (e) Nenajdenko, V. G.; Varseev, G. N.; Shastin, A. V.; Balenkova, E. S. *J. Fluorine Chem.* **2005**, *126*, 907–913; (f) Shastin, A. V.; Muzalevsky, V. M.; Balenkova, E. S.; Nenajdenko, V. G. *Mendeleev Commun.* **2006**, *16*, 179–180.
11. Nenajdenko, V. G.; Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Haufe, G. *J. Fluorine Chem.* **2007**, *128*, 818–826.
12. Muzalevskiy, V. M.; Shastin, A. V.; Balenkova, E. S.; Nenajdenko, V. G. *Russ. Chem. Bull.* **2007**, *56*, 1526–1533.
13. Chen, C.; Wilcoxen, K.; Kim, K.; McCarthy, J. R. *Tetrahedron Lett.* **1997**, *38*, 7677–7680.
14. Inbasekaran, M.; Peet, N. P.; McCarthy, J. R.; Le Tourneau, M. E. *J. Chem. Soc., Chem. Commun.* **1985**, 678–679.
15. Uno, H.; Sakamoto, K.; Tominaga, T.; Ono, N. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1441–1448.
16. Carini, D. J.; Duncia, J. V.; Aldrich, P. E.; Chiu, A. T.; Johnson, A. L. *J. Med. Chem.* **1991**, *34*, 2525–2547.
17. Tolman, V.; Spronglowa, P. S. *Collect. Czech. Chem. Commun.* **1983**, *48*, 319–326.
18. Al'bekov, V. A.; Benda, A. F.; Gontar, A. F.; Sokol'skii, G. A.; Knunyants, I. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1988**, 765–769.
19. Koizumi, T.; Hagi, T.; Horie, Y.; Takeuchi, Y. *Chem. Pharm. Bull.* **1987**, *35*, 3959–3962.
20. Asakura, N.; Usuki, Y.; Iio, H. *J. Fluorine Chem.* **2003**, *124*, 81–88.
21. Gouverneur, V.; Lam, Y.-H. *Angew. Chem.* **2007**, *119*, 5198–5202; *Angew. Chem., Int. Ed.* **2007**, *46*, 5106–5610.
22. (a) Percy, J. M. *Top. Curr. Chem.* **1997**, *193*, 131–195; (b) Patrick, T. B.; Gorrell, K.; Rogers, J. *J. Fluorine Chem.* **2007**, *128*, 710–713; (c) Rock, M. H. In *Methods of Organic Chemistry (Houben-Weyl)*, 4th ed.; Baasner, B., Hagemann, H., Tatlow, J. C., Eds.; Thieme: Stuttgart, 1999; Vol. E/10b, pp 513–515.
23. (a) Ernet, T.; Haufe, G. *Tetrahedron Lett.* **1996**, *37*, 7251–7252; (b) Ernet, T.; Maulitz, A. H.; Würthwein, E.-U.; Haufe, G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1929–1938; (c) Essers, M.; Mück-Lichtenfeld, C.; Haufe, G. *J. Org. Chem.* **2002**, *67*, 4715–4721.
24. Bogachev, A. A.; Kobrina, L. S.; Meyer, O. G. J.; Haufe, G. *J. Fluorine Chem.* **1999**, *97*, 135–143.
25. Essers, M.; Wibbeling, B.; Haufe, G. *Tetrahedron Lett.* **2001**, *42*, 5429–5433.
26. Essers, M.; Haufe, G. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2719–2728.
27. Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951–6984.
28. Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853–855.
29. Paquette, L. A.; Kunzer, H.; Kesselmayer, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 6521–6527.
30. Lucchi, O. D.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596–604.
31. Bradley, P. J.; Grayson, D. H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1794–1799.
32. Crowley, P. J.; Percy, J. M.; Stansfield, K. *Tetrahedron Lett.* **1996**, *37*, 8233–8236.
33. Hajduch, J.; Paleta, O.; Kvíčala, J.; Haufe, G. *Eur. J. Org. Chem.* **2007**, 5101–5111.
34. (a) Chambers, R. D.; Shepherd, T.; Tamura, M.; Bryce, M. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1657–1658; (b) Blackwell, G. B.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2207–2210.
35. Kobayashi, Y.; Yamashita, T.; Takahashi, K.; Kuroda, H.; Kumadaki, I. *Chem. Pharm. Bull.* **1984**, *32*, 4402–4409.
36. Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.
37. Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228–234.
38. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.
39. Sheldrick, G. M. Structure refinement program, University of Göttingen, 1997.
40. Keller, E. Graphics program, University of Freiburg, 1997.