Synthesis of Fluoroalkyl Vinyl Sulfoxides and their Use in Diels–Alder Reactions

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Abstract: Condensation of various dienes with fluoroalkyl vinyl sulfoxides was studied. Four diastereoisomers were obtained in the case of cyclopentadiene and their structures were assigned by 2D NMR experiments. Diels–Alder cycloaddition occurred with cyclohexadiene, in comparison to phenyl vinyl sulfoxide, without thermal extrusion of fluoroalkylsulfenic acid. Condensation with anthracene led to a mixture of compounds **11** and **12**.

Key words: acetylene equivalent, Diels–Alder reactions, eliminations, fluorine, sulfoxides

α,β-unsaturated sulfoxides are interesting dienophiles in the Diels–Alder reaction and are widely used in synthesis.[1–5] For example, phenyl vinyl sulfoxide (**1**) has been proposed by Paquette et al.[6] as an acetylene equivalent in Diels–Alder cycloadditions. Indeed, the thermal extrusion of phenylsulfenic acid (C_6H_5SOH) can occur from the adduct during the condensation of **1** with dienes. Consequently, this reagent reacts, in one step, in the same manner as acetylene which is a very poor dienophile. However, the scope of the method[6–11] is limited by the weak dienophilicity of **1**. It has thus been reported that cyclohexa-1,3-diene does not react under the conditions of Paquette et al.[11] Owing to the electron-withdrawing effect of the fluorine atoms, we postulated that a fluoroalkylsulfinyl group would influence a double bond more strongly than would a phenylsulfinyl group [σ_p = 0.69 for $S(O)CF_3$ versus 0.44 for $S(O)C_6H_5$[12]]. With this aim in view, we undertook the synthesis of the fluoroalkyl vinyl sulfoxides **2** and **3** (Figure 1) and the study of their reactivity as dienophiles. A long perfluoroalkyl chain was initially chosen for reagent **2** in order to avoid the use of low-boiling reactants. We have also studied compound **3** which gave readily interpreted ^{19}F NMR spectra, thus simplifying identification of the various adducts. The present study is mainly devoted to the preparation of reagent **3** and to the Diels–Alder condensations of **2** and **3** with various dienes.

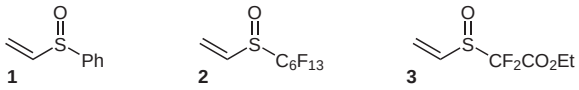

Figure 1 Vinyl sulfoxides **1**–**3**

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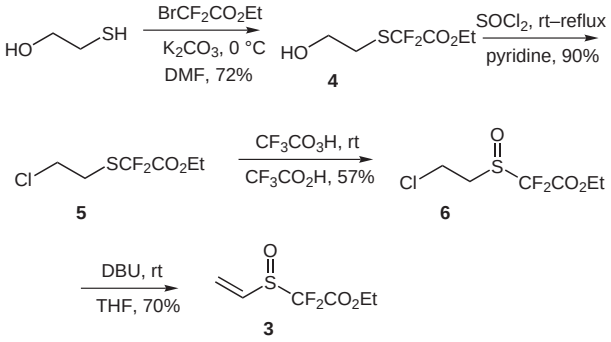
The dienophile **3** was prepared following the method previously described for the synthesis of the compound **2**.[13] The fluorinated precursor **4** was obtained by reaction of 2-mercaptoethanol with ethyl bromodifluoroacetate under mild conditions, using potassium carbonate as base.[14] The time and temperature of this reaction were monitored carefully in order to obtain the most acceptable yield. It was not necessary to add a sulfoxylate anion precursor as in the alkylation with a perfluoroalkyl halide, due to the different mechanism of the reaction.[13] The alcohol **4** was transformed into the chlorine derivative **5**, then the sulfur atom was oxidized using trifluoroperacetic acid. Treatment of sulfoxide **6** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in tetrahydrofuran gave the dienophile **3** in 26% overall yield (Scheme 1).

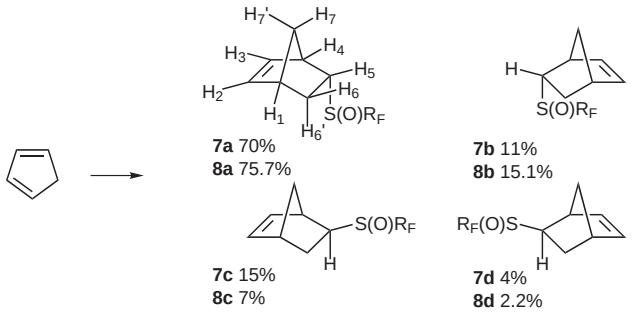


Scheme 1

The reactivity of compounds **2** and **3** as dienophile was then studied with various dienes. The main goal of this study was to compare the reactivity of dienophiles **2** and **3** with that of dienophile **1**. For this reason selected dienes (cyclopentadiene, cyclohexadiene and anthracene), already studied in cycloaddition with phenyl vinyl sulfoxide (**1**), were examined. The reaction between **2** and **3** and 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (Danishefsky's diene) was also attempted, though the structure of the products formed in the cycloaddition of this diene with **1** was not defined.[15,16] With dienophiles **2** and **3**, condensations gave a complex mixture of aromatic non-fluorinated adducts after 4 days reflux in toluene.

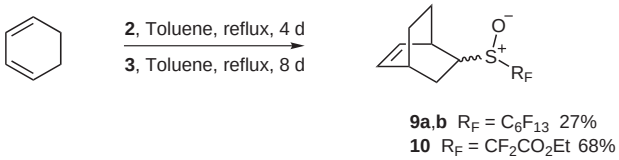
Treatment of the vinylic compounds **2** and **3** with a large excess of cyclopentadiene (10 equiv) in dichloromethane at room temperature led to corresponding diastereoisomeric adducts mixtures **7a**–**d** and **8a**–**d** in yields of 79 and 75%, respectively (Scheme 2). In the case of the conden-

sation with the initial dienophile **2**, the 79% yield was improved to 84% by the addition of ytterbium triflate. Four diastereoisomers were obtained, as in dienophile **1** cycloaddition:[17] compounds **7a–d** were isolated as a 70:11:15:4 ratio which represented 81% of the *endo* product and 19% of the *exo* product; compounds **8a–d** were isolated as a 75.7:15.1:7:2.2 ratio which represented 80.8% of the *endo* product and 9.2% of the exo product. Formation of a mixture of adducts is explained by the existence of *s-cis* and *s-trans* conformations of the vinyl sulfoxides.[18] For each mixture, the four isomers were separated, except for compounds **7a** and **7b**, by column chromatography and fully characterized (see structural analysis).



Scheme 2

Cyclohexadiene is less reactive than cyclopentadiene in Diels–Alder reactions.[19] In this case, it was necessary to use a solvent having a higher boiling point than dichloromethane. Condensations were performed in toluene at reflux for several days (Scheme 3). For dienophile **2**, a 27% yield of the *endo*/*exo* (ratio 8:2) isomeric mixture **9a**,**b** was obtained after 4 days heating. For the condensation using dienophile **3**, compound **10** was isolated in a 68% yield as a single *endo* isomer by portionwise addition of cyclohexadiene during 8 days refluxing in toluene. The stereochemistry of the adducts **9a**,**b** and **10** was deduced by comparison of the NMR data with those of the cyclopentadiene adducts (see below).



Scheme 3

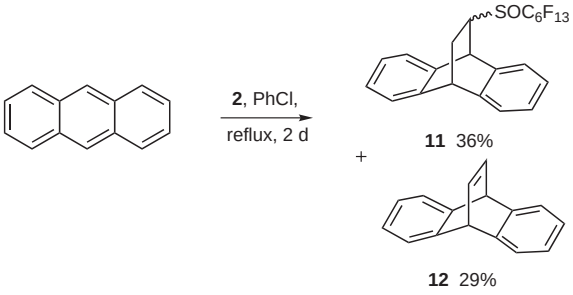
The structure and stereochemistry of the four diastereomers **7a–d** and **8a–d** were established from the information provided by a detailed analysis of the ^1H and ^{13}C NMR spectra recorded in $CDCl_3$ (see experimental section). The resonances of the protons were assigned on the basis of two dimensional homonuclear chemical shift correlation (COSY) and those of carbon atoms on the basis of J-modulation and two dimensional heteronuclear chemical shift correlation (HETCOR). Finally, NOE experiments allowed us to confirm the *endo* stereochemistry (4:1 ratio) and to discriminate between the two bridge protons H_7 and $H_{7'}$ and between the two protons H_6 and $H_{6'}$.

Interestingly, the chemical shifts (see selected data reported in Table 1) as well as the coupling constants observed in the NMR spectra for the *endo* conformation (for example, H_4 and H_5 more deshielded) are in full agreement with those reported in a previous study of the cyclopentadiene/*p*-tolyl vinyl sulfoxide condensation.[20]

Table 1 ^1H NMR Data of Adducts **7a–d**

δ, *J* (Hz)	**7a**	**7b**	**7c**	**7d**
δ_{H-1}	3.09	3.24	3.52	3.23
δ_{H-2}	6.35	6.29	6.17	6.19
δ_{H-3}	6.23	5.94	6.33	6.34
δ_{H-4}	3.51	3.51	3.14	3.08
δ_{H-5}	4.01	3.89	3.23	2.85
δ_{H-6}	1.14	1.69	1.54	1.55
$\delta_{H-6'}$	1.95	1.45	1.67	1.55
δ_{H-7}	1.40	1.85	1.54	1.55
$\delta_{H-7'}$	1.68	2.15	1.54	2.46
J (Hz)	$J_{H-5,H-6}$ = 9.2 $J_{H-5,H-6}$ = 3.9	$J_{H-5,H-6}$ = 9.1 $J_{H-5,H-6}$ = 3.7	$J_{H-5,H-6}$ = 3.6 $J_{H-5,H-6}$ = 8.2	$J_{H-5,H-6}$ = 3.6 $J_{H-5,H-6}$ = 8.1

Reaction of dienophile **2** with anthracene was performed in chlorobenzene as in the condensation with phenyl vinyl sulfoxide **(1)**.[6] After refluxing for two days, two compounds were separated by chromatography (Scheme 4). The major product isolated in a 36% yield was the cycloadduct **11** and the minor product, obtained in a 29% yield, was the dibenzobarrelene **(12)** formed by thermal extrusion of perfluorohexyl sulfenic acid. Owing to the high acidity of this by-product, it was not possible to continue heating up to 5 days, as in the case of phenyl vinyl sulfoxide (**1**), without degradation of the mixture.



Scheme 4

In contrast to phenyl vinyl sulfoxide (**1**),[11] fluoroalkyl vinyl sulfoxides **2** and **3** are able to give the corresponding adducts with cyclohexadiene, showing a higher reactivity in the Diels–Alder reaction. However, any advantage of these dienophiles as acetylene equivalents is counterbalanced by the difficulty of the fluoroalkyl sulfenic acid elimination. Contrary to the case of phenyl vinyl sulfoxide (**1**)/anthracene,[6] formation of dibenzobarrelene (**12**) in the condensation of perfluorohexyl vinyl sulfoxide (**2**) with the same dienophile is not complete. Moreover, this elimination reaction does not occur in the condensation between cyclohexadiene and dienophile **2** in refluxing toluene. This unexpected result may be rationalized if one considers that the loss of the sulfenic acid occurs by attack of the oxygen atom of the sulfinyl group on a vicinal hydrogen atom (Figure 2).[21]

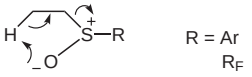


Figure 2 Mechanism of elimination of sulfenic acid in Diels–Alder reaction with fluoroalkyl vinyl sulfoxides

We suppose that the electron-withdrawing effect of the fluorinated group probably reduces the basicity of the sulfoxide oxygen; consequently, the elimination step becomes more difficult, enabling the isolation of adducts susceptible to further functionalization.

As indicated very recently by Jenks and McCulla, the introduction of a vicinal silyl substituent allows for easier elimination of the sulfinyl group.[22] We plan to examine the effect of an additional silyl group on the ease of fluoroalkylsulfinyl elimination. Alternatively, reagents **2** and **3** should behave as Michael acceptors as does phenyl vinyl sulfoxide (**1**).[23] Moreover, the ethoxycarbonyl group of **3** should allow further chemical functionalization of the obtained adducts.

Melting points were determined on a Mettler FP61 apparatus. NMR spectra were recorded in $CDCl_3$ solutions, on a Bruker AC-300 spectrometer. Reported coupling constants and chemicals shifts were based on a first-order analysis. Internal reference was the residual peak of $CHCl_3$ (7.27 ppm) for ^1H (300 MHz) NMR spectra, central peak of $CDCl_3$ (77 ppm) for ^{13}C (75 MHz) NMR spectra, internal $CFCl_3$ (0 ppm) for ^{19}F (282 MHz) NMR spectra. Chemical shifts are reported in parts per million (ppm) and constants *J* in Hertz (Hz). Mass spectra were carried out at the Ecole Normale Supérieure (Paris). IR spectra were recorded on a Nicolet 400SD spectrometer. Elemental analyses were determined by the Microanalytical Laboratory of the CNRS (Gif sur Yvette). Column chromatography was performed with Merck silica gel (70–230 mesh). Reagents were commercially available and used as received. All solvents were distilled prior use and reactions were usually carried out under argon except in the case of perfluoroalkylation reactions.

Ethyl Difluoro-(2-hydroxyethylsulfanyl)acetate (4)

To a solution of ethyl bromodifluoroacetate (5.2 g, 25.6 mmol) and K_2CO_3 (3.54 g, 25.6 mmol) in DMF (24 mL) was added mercaptoethanol (2.0 g, 25.6 mmol) dropwise under argon at 0 °C. After 2 h, H_2O (40 mL) was added and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with 5% aq solution of $NaHCO_3$ (3 × 100 mL), H_2O (100 mL) and dried ($MgSO_4$). The solvent was removed at reduced pressure and the residue was purified by column chromatography using pentane–Et_2O (5:5) as eluent to give 3.7 g (72%) of **4** as a colorless oil.

IR (neat): 3500, 3011, 1757, 1203 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.32 (2 H, q, *J* = 7.2 Hz, OCH_2), 3.79 (2 H, t, *J* = 6.6 Hz, $HOCH_2$), 3.01 (2 H, t, SCH_2), 2.88 (1 H, br s, OH), 1.33 (3 H, t, CH_3).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 161.8 (t, *J* = 32.8 Hz), 120.5 (t, *J* = 285.9 Hz), 63.8, 61.2, 33.3, 13.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –82.6 (m, CF_2).

MS (CI, NH_3): *m*/*z* = 218 $(M + NH_4)^+$, 201 $(M + H)^+$.

HRMS: *m*/*z* calcd for $C_6H_{11}F_2O_3S$: 201.0397 $(M + H)^+$; found: 201.0400.

Anal. Calcd for $C_6H_{10}F_2O_3S$: C, 36.00; H, 5.03. Found: C, 35.54; H, 4.77.

Ethyl Difluoro(2-chloroethylsulfanyl)acetate (5)

To a solution of ethyl difluoro-(2-hydroxyethylsulfanyl)acetate (**4**; 8.75 g, 43.7 mmol) in pyridine (3.5 ml, 43.7 mmol) was added dropwise $SOCl_2$ (6.38 mL, 87.4 mmol). The reaction mixture was stirred at r.t. for 1 h and then refluxed for an additional hour. After cooling, H_2O (50 mL) was added. The mixture was then extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with a solution of 5% aq NaOH (3 × 100 mL), H_2O (100 mL) and then dried ($MgSO_4$). The solvent was removed at reduced pressure and the oily residue was distilled at reduced pressure to give 8.6 g (90%) of **5** as a colorless liquid; bp 105 °C/15 mmHg.

IR (neat): 2975, 2929, 1767, 1301 and 1173 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.34 (2 H, q, *J* = 7.2 Hz, OCH_2), 3.70 (2 H, t, *J* = 7.7 Hz, $ClCH_2$), 3.19 (2 H, t, SCH_2), 1.34 (3 H, t, CH_3).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 161.2 (t, *J* = 32.2 Hz), 120.2 (t, *J* = 287.1 Hz), 63.8, 42.6, 30.7, 13.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –82.4 (m, CF_2).

MS (CI, NH_3): *m*/*z* = 219 $(M + H)^+$.

HRMS: *m*/*z* calcd for $C_6H_{10}ClF_2O_2S$: 219.0058 $(M + H)^+$; found: 219.0061.

Anal. Calcd for $C_6H_9ClF_2O_2S$: C, 32.96; H, 4.15. Found: C, 32.86; H, 4.17.

Ethyl Difluoro(2-chloroethylsulfinyl)acetate (6)

To a solution of ethyl difluoro(2-chloroethylsulfanyl)acetate (**5**; 7.8 g, 35.6 mmol) in trifluoroacetic acid (12 mL) at r.t. was added freshly prepared trifluoroperacetic acid (8.9 mL, 35.6 mmol) and the reaction mixture was stirred overnight. After completion of the reaction, H_2O (100 mL) was added, then the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with aq sat. solution of $NaHCO_3$ (150 mL), H_2O (100 mL), dried ($MgSO_4$) and concentrated at reduced pressure to give without further purification 4.8 g (57%) of the compound **6** as a colorless liquid.

IR (neat): 2986, 1767, 1306, 1157 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.46 (2 H, q, *J* = 7.2 Hz, OCH_2), 3.96 (2 H, m, $ClCH_2$), 3.47 [1 H, dt, ^2J = 13.5, 4.6 Hz, $S(O)CH_aH_b$], 3.23 [1 H, m, $S(O)CH_aH_b$], 1.41 (3 H, t, CH_3).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 159.4 (t, *J* = 27.7 Hz), 118.5 (t, *J* = 300.0 Hz), 64.7, 51.0, 36.0, 13.9.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –109.7 (1 F, d, *J* = 233 Hz), –111.5 (1 F, d).

MS (CI, NH_3): *m*/*z* = 252 $(M + NH_4)^+$.

HRMS: *m*/*z* calcd for $C_6H_{10}ClF_2O_3S$: 235.0007 $(M + H)^+$; found: 235.0003.

Ethyl Difluoro(vinylsulfinyl)acetate (3)

DBU (2.75 mL, 18.4 mmol) was added dropwise to a solution of **6** (4.3 g, 18.4 mmol) in THF (73 mL). The reaction mixture was stirred overnight and was fractionally distilled under reduced pressure to give 2.52 g (70%) of **3** as a colorless liquid; bp 113–115 °C/ 15 mmHg.

IR (neat): 2986, 2929, 1777, 1372, 1311, 1127 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.66 (1 H, dd, *J* = 16.4, 9.9 Hz), 6.27 (2 H, m), 4.39 (2 H, q, *J* = 7.2, OCH_2), 1.36 (3 H, t, CH_3).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 158.8 (t, *J* = 28.3 Hz), 134.3 (t, *J* = 4.0 Hz), 127.6 (t, *J* = 1.1 Hz), 118.1 (t, *J* = 300.7 Hz), 64.2, 13.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –109.4 (1 F, d, *J* = 234 Hz), –105.4 (1 F, d).

MS (CI, NH_3): *m*/*z* = 199 $(M + H)^+$.

HRMS: *m*/*z* calcd for $C_6H_9F_2O_3S$: 199.0240 $(M + H)^+$; found: 199.0238.

Anal. Calcd for $C_6H_8F_2O_3S$: C, 36.96; H, 4.07. Found: C, 36.63; H, 3.98.

5-(Tridecafluorohexane-1-sulfinyl)bicyclo[2.2.1]hept-2-ene (7)

A solution of the dienophile **2** (0.20 g, 0.51 mmol), freshly distilled cyclopentadiene (0.34 g, 5.10 mmol) and ytterbium triflate (0.32 g, 0.51 mmol) in CH_2Cl_2 (2 mL) was stirred overnight and filtered through Celite 545®. After concentration at reduced pressure, the residue was purified by chromatography on preparative plates using pentane–Et_2O (9:1) as eluent to afford 4 diastereomers in a 70:11:15:4 ratio and an 84% (235 mg) overall yield as a white solid; mp 68.3–68.6 °C.

IR (Nujol): 2966, 2848, 1460, 1373 cm^{-1}.

MS (CI, NH_3): *m*/*z* = 461 $(M + H)^+$, 478 $(M + NH_4)^+$.

HRMS: *m*/*z* calcd for $C_{13}H_{10}F_{13}OS$: 461.0245 $(M + H)^+$; found: 461.0243.

Anal. Calcd for $C_{13}H_9F_{13}OS$: C, 33.93; H, 1.97. Found: C, 34.02; H, 2.05.

Compound 7a

^1H NMR (300 MHz, $CDCl_3$): δ = 6.35 (1 H, dd, *J* = 3.9, 5.6 Hz, H_2), 6.23 (1 H, dd, *J* = 2.6, 5.6 Hz, H_3), 4.01 (1 H, ddd, *J* = 3.6, 3.9, 9.1 Hz, H_5), 3.51 (1 H, m, H_4), 3.09 (1 H, m, H_1), 1.95 (1 H, dd, *J* = 3.6, 7.2 Hz, $H_{6'}$), 1.68 (1 H, m, $H_{7'}$), 1.40 (1 H, m, H_7), 1.14 (1 H, ddd, *J* = 3.6, 6.6 Hz, H_6).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 139.5 (C_2), 132.0 (C_3), 58.8 (C_5), 48.1 (C_7), 44.9 (C_4), 42.3 (C_1), 26.0 (C_6).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.4 (3 F, m, CF_3), –111.5 (1 F, d, *J* = 251 Hz, $SOCF_2$), –121.2 (2 F, m, CF_2), –121.7 (1 F, d, $SOCF_2$), –122.5 (2 F, m, CF_2), –123,3 (2 F, m, CF_2), –126.7 (2 F, m, CF_2).

Compound 7b

^1H NMR (300 MHz, $CDCl_3$): δ = 6.29 (1 H, dd, *J* = 3.3, 5.6 Hz, H_2), 5.94 (1 H, dd, *J* = 3.0, 5.9 Hz, H_3), 3.89 (1 H, dt, *J* = 3.7, 9.1 Hz, H_5), 3.51 (1 H, m, H_4), 3.24 (1 H, m, H_1), 2.15 (1 H, m, $H_{7'}$), 1.85 (1 H, m, H_7), 1.69 (1 H, m, H_6), 1.45 (1 H, m, $H_{6'}$).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 139.4 (C_2), 131.3 (C_3), 59.2 (C_5), 49.8 (C_7), 44.9 (C_4), 41.8 (C_1), 26.3 (C_6).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.4 (3 F, m, CF_3), –113.5 (1 F, d, *J* = 251 Hz, $SOCF_2$), –120.5 (1 F, d, $SOCF_2$), –121.2 (2 F, m, CF_2), –122.5 (2 F, m, CF_2), –123.3 (2 F, m, CF_2), –126.7 (2 F, m, CF_2).

Compound 7c

^1H NMR (300 MHz, $CDCl_3$): δ = 6.33 (1 H, dd, *J* = 2.9, 5.6 Hz, H_3), 6.17 (1 H, dd, *J* = 3.3, 5.6 Hz, H_2), 3.52 (1 H, m, H_1), 3.23 (1 H, dd, *J* = 3.6, 8.2 Hz, H_5), 3.14 (1 H, m, H_4), 1.67 (1 H, dd, *J* = 3.6, 7.5 Hz, $H_{6'}$), 1.54 (3 H, m, H_6, H_7, $H_{7'}$).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 140.2 (C_2), 134.0 (C_3), 57.6 (C_5), 45.3 (C_7), 43.2 (C_1), 42.8 (C_4), 27.4 (C_6).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.3 (3 F, m, CF_3), –111.6 (1 F, d, *J* = 251 Hz, $SOCF_2$), –121.1 (2 F, m, CF_2), –121.3 (1 F, d, $SOCF_2$), –122.4 (2 F, m, CF_2), –123.3 (2 F, m, CF_2), –126.6 (2 F, m, CF_2).

Compound 7d

^1H NMR (300 MHz, $CDCl_3$): δ = 6.34 (1 H, dd, *J* = 3.0, 5.6 Hz, H_3), 6.19 (1 H, dd, *J* = 3.0, 5.6, H_2), 3.23 (1 H, m, H_1), 3.08 (1 H, m, H_4), 2.85 (1 H, m, H_5), 2.46 (1 H, m, $H_{7'}$), 1.55 (3 H, m, H_6, $H_{6'}$, H_7).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.2 (3 F, m, CF_3), –112.8 (1 F, d, *J* = 251 Hz, $SOCF_2$), –119.3 (1 F, d, $SOCF_2$), –121.2 (2 F, m, CF_2), –122.4 (2 F, m, CF_2), –123.2 (2 F, m, CF_2), –126.6 (2 F, m, CF_2).

Ethyl Difluoro(bicyclo[2.2.1]hept-5-ene-2-sulfinyl)acetate (8)

A solution of the dienophile **3** (0.45 g, 2.29 mmol) and freshly distilled cyclopentadiene (1.51 g, 22.92 mmol) in CH_2Cl_2 (9 ml) was stirred at r.t. Cyclopentadiene (1.51 g, 22.92 mmol) was added every 12 h during 2 d. After concentration of the mixture at reduced pressure, the residue was purified by column chromatography using pentane–Et_2O (9:1) as eluent to afford 4 diastereomers in a 75.7:15.1:7:2.2 ratio and in 75% (605 mg) overall yield as a colorless oil.

IR (neat): 2991, 2934, 1751, 1311, 1152, 1127 cm^{-1}.

MS (CI, NH_3): *m*/*z* = 265 $(M + H)^+$.

HRMS: *m*/*z* calcd for $C_{11}H_{15}F_2O_3S$: 265.0710 $(M + H)^+$; found: 265.0708.

Anal. Calcd for $C_{11}H_{14}F_2O_3S$: C, 49.99; H, 5.34. Found: C, 49.61; H, 5.36.

Compound 8a

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (1 H, dd, *J* = 3.2, 5.8 Hz, H_2), 6.21 (1 H, dd, *J* = 2.6, 5.9 Hz, H_3), 4.45 (2 H, q, *J* = 6.9 Hz, OCH_2), 3.82 (1 H, ddd, *J* = 3.7, 3.9, 7.5 Hz, H_5), 3.44 (1 H, m, H_4), 3.01 (1 H, m, H_1), 1.92 (1 H, m, $H_{6'}$), 1.65 (1 H, m, H_7), 1.40 (4 H, m, CH_3, $H_{7'}$), 1.03 (1 H, m, H_6).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 160.1 (t, *J* = 27.7 Hz, CO) 139.26 (C_2), 132.1 (C_3), 119.6 (t, *J* = 304.5 Hz, CF_2), 64.3 (OCH_2), 58.7 (C_5), 48.1 (C_7), 44.5 (C_4), 42.3 (C_1), 25.8 (C_6), 13.9 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –107.1 (1 F, d, *J* = 226.3 Hz, CF_2), –109.8 (1 F, d, CF_2).

Compound 8b

^1H NMR (300 MHz, $CDCl_3$): δ = 6.30 (1 H, dd, *J* = 2.90, 5.6 Hz, H_2), 6.02 (1 H, dd, *J* = 3.0, *J* = 5.9 Hz, H_3), 4.45 (2 H, q, *J* = 6.9 Hz, OCH_2), 3.79 (1 H, ddd, *J* = 3.6, 3.7, 8.9 Hz, H_5), 3.23 (1 H, m, H_4), 3.06 (1 H, m, H_1), 2.13 (1 H, m, $H_{6'}$), 1.75 (1 H, m, H_6), 1.60 (1 H, m, H_7), 1.40 (4 H, m, CH_3, $H_{7'}$).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 160.0 (t, *J* = 28.0 Hz, CO) 139.0 (C_2), 131.8 (C_3), 118.8 (t, *J* = 296.5 Hz, CF_2), 64.3 (OCH_2), 59.1 (C_5), 49.6 (C_7), 44.8 (C_4), 41.7 (C_1), 26.6 (C_6), 14.0 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –107.5 (1 F, d, *J* = 233.9 Hz, CF_2), –112.5 (1 F, d, CF_2).

Compound 8c

^{1}H NMR (300 MHz, acetone-d_6): δ = 6.33 (1 H, dd, *J* = 2.9, 5.6 Hz, H_3), 6.17 (1 H, dd, *J* = 3.3, 5.6 Hz, H_2), 4.45 (2 H, q, *J* = 6.8 Hz, OCH_2), 3.35 (1 H, m, H_1), 3.10 (1 H, m, H_4), 3.03 (1 H, dd, *J* = 3.6, 8.2 Hz, H_5), 1.70 (1 H, m, $H_{6'}$), 1.55 (1 H, m, $H_{7'}$), 1.45 (2 H, m, $H_{6,7}$).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 160.5 (t, *J* = 28.2 Hz, CO), 140.5 (C_3), 134.7 (C_2), 120.4 (t, *J* = 300.3 Hz, CF_2), 65.0 (OCH_2), 58.1 (C_5), 45.7 (C_7), 43.8 (C_1), 43.6 (C_4), 27.5 (C_6), 14.1 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –106.2 (1 F, d, *J* = 236.5 Hz, CF_2), –110.4 (1 F, d, CF_2).

Compound 8d

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.30 (1 H, dd, *J* = 3.0, 5.6 Hz, H_3), 6.14 (1 H, dd, *J* = 3.0, 5.6 Hz, H_2), 4.44 (2 H, q, *J* = 6.9 Hz, OCH_2), 3.04 (1 H, m, H_1), 3.18 (1 H, m, H_4), 2.86 (1 H, m, H_5), 2.46 (1 H, m, $H_{7'}$), 1.55 (3 H, m, H_6, $H_{6'}$, H_7)

^{13}C NMR (77 MHz, $CDCl_3$): δ = 160.0 (t, *J* = 28.0 Hz, CO), 140.3 (C_3), 134.4 (C_2), 118.6 (t, *J* = 298.6 Hz, CF_2), 64.4 (OCH_2), 56.7 (C_5), 46.0 (C_7), 46.2 (C_1), 41.4 (C_4), 24.7 (C_6), 13.9 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –107.1 (1 F, d, *J* = 231.4 Hz, CF_2), –110.6 (1 F, d, CF_2).

5-(Tridecafluorohexane-1-sulfinyl)bicyclo[2.2.2]oct-2-ene (9)

A solution of the dienophile **2** (0.10 g, 0.26 mmol) and cyclohexadiene (20.5 mg, 2.60 mmol) in toluene (1 mL) was refluxed for 4 d. After concentration at reduced pressure, the residue was purified by chromatography on preparative plates using pentane–Et_2O (9:1) as eluent to afford 32 mg (27%) of an inseparable mixture of *endo* and *exo* adducts (8:2) as a white solid; mp 72.4–72.6 °C.

IR (Nujol): 2976, 2848, 1760, 1283 cm^{-1}.

MS (CI, NH_3): *m*/*z* = 492 $(M + NH_4)^+$.

HRMS: *m*/*z* calcd for $C_{14}H_{15}F_{13}OS$: 492.0667 $(M + CH_4)^+$; found: 492.0660.

Compound *endo*-9a

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.52 (1 H, dd, *J* = 7.3, 7.6 Hz, H_2), 6.29 (1 H, dd, *J* = 6.9, 7.6 Hz, H_3), 3.73 (1 H, m, H_5), 3.22 (1 H, m, H_4), 2.73 (1 H, s, H_1), 1.84 (1 H, m, $H_{6'}$ or H_6), 1.56–1.72 (4 H, m, H_7, $H_{7'}$, H_8, $H_{8'}$), 1.40 (1 H, m, H_7), 1.36 (1 H, m, $H_{6'}$ or H_6).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 137.1 (C_2), 130.0 (C_3), 57.3 (C_5), 28.9 (C_4), 28.8 (C_1), 25.9 (C_6), 24.5 (C_8), 24.3 (C_7).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.2 (3 F, m, CF_3), –111.8 (1 F, d, *J* = 246 Hz, $SOCF_2$), –121.2 (2 F, m, CF_2), –122.3 (2 F, m, CF_2), –122.5 (1 F, d, $SOCF_2$), –123.3 (2 F, m, CF_2), –126.6 (2 F, m, CF_2).

Compound *exo*-9a

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.43 (2 H, m, H_3, H_2), 3.36 (1 H, m, H_5), 3.16 (1 H, m, H_4), 2.71 (1 H, m, H_1), 1.1–2.2 (6 H, m, H_6, $H_{6'}$,H_7, $H_{7'}$, H_8, $H_{8'}$).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 137.0 (C_2), 132.5 (C_3), 55.5 (C_5), 28.7 (C_4), 28.3 (C_1), 26.6 (C_6), 25.1 (C_8), 19.9 (C_7).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.3 (3 F, m, CF_3), –111.8 (1 F, d, *J* = 246 Hz, $SOCF_2$), –121.1 (2 F, m, CF_2), –121.5 (1 F, d, $SOCF_2$), –122.3 (2 F, m, CF_2), –123.4 (2 F, m, CF_2), –126.6 (2 F, m, CF_2).

Ethyl Difluoro(bicyclo[2.2.2]oct-5-ene-2-sulfinyl)acetate (10)

A solution of the dienophile **3** (0.4 g, 2.02 mmol) and cyclohexadiene (0.80 g, 10.1 mmol) in toluene (4 mL) was refluxed under argon. Cyclohexadiene (0.80 g, 10.1 mmol) was added every 2 d during 8 d. After concentration at reduced pressure, the residue was purified by column chromatography using pentane–Et_2O (9:1) as eluent to afford 0.38 g (68%) of the *endo* adduct as a colorless oil.

IR (neat): 2945, 2863, 1767, 1449, 1367, 1301 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.48 (1 H, dd, *J* = 6.9, 7.3 Hz, H_2), 6.28 (1 H, dd, *J* = 7.3, 7.6 Hz, H_3), 3.59 (1 H, m, H_5), 3.17 (1 H, m, H_4), 2.68 (1 H, s, H_1), 1.84 (1 H, m, $H_{6'}$ or H_6), 1.56–1.72 (4 H, m, H_7, $H_{7'}$, H_8, $H_{8'}$), 1.40 (1 H, m, H_7), 1.36 (1 H, m, $H_{6'}$ or H_6).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 136.95 (C_2), 130.3 (C_3), 64.3 (CH_2), 57.3 (C_5), 28.9 (C_4), 28.7 (C_1), 25.6 (C_6), 24.6 (C_8), 24.4 (C_7), 13.9 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –105.49 (1 F, d, *J* = 229.7 Hz, CF_2), –109.9 (1 F, d, *J* = 230 Hz, CF_2).

MS (CI, NH_3): *m*/*z* = 279 $(M + H)^+$.

HRMS: *m*/*z* calcd for $C_{12}H_{17}F_2O_3S$: 279.0866 $(M + H)^+$; found: 279.0863.

2,3:5,6-Dibenzo-8-(tridecafluorohexanesulfinyl)bicyclo[2.2.2]octadiene (11)

A solution of the dienophile **2** (0.10 g, 0.26 mmol) and anthracene (45 mg, 0.26 mmol) in chlorobenzene (1 mL) was refluxed for 2 d. After concentration at reduced pressure, the residue was purified by chromatography on preparative plates using pentane–Et_2O (9:1) as eluent to afford 145 mg (36%) of compound **11** as a yellow oil and 52 mg (29%) of compound **12**.

Compound 11

IR (neat): 2966, 2863, 2715 and 1301 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (2 H, m, Ar), 7.35 (2 H, m, Ar), 7.25 (4 H, m, Ar), 4.98 (1 H, d, *J* = 2.6 Hz, H_1), 4.46 (1 H, t, *J* = 2.6 Hz, H_4), 3.87 (1 H, m, H_8) 1.56–2.10 (1 H, m, H_7 or $H_{7'}$), 1.64 (1 H, m, H_7 or $H_{7'}$).

^{13}C NMR (77 MHz, $CDCl_3$): δ = 143.6, 143.0, 139.6, 137.0 (C_q), 127.5,127.0, 126.6, 126.2, 125.8, 125.3, 124.3, 123.6 (CH), 56.9 (C_5), 43.2 (C_4), 42.5 (C_1), 28.3 (C_7).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.3 (3 F, m, CF_3), –110.1 (1 F, d, *J* = 244 Hz, $SOCF_2$), –120.7 (1 F, d, $SOCF_2$), –121.2 (2 F, m, CF_2), –122.3 (2 F, m, CF_2), –123.3 (2 F, m, CF_2), –126.6 (2 F, m, CF_2).

MS (CI, NH_3): *m*/*z* = 590 $(M + NH_4)^+$.

HRMS: *m*/*z* calcd for $C_{22}H_{17}F_{13}NOS$: 590.0823 $(M + NH_4)^+$; found: 590.0826.

Anal. Calcd for $C_{22}H_{13}F_{13}OS$: C, 46.17; H, 2.29. Found: C, 46.71; H, 2.56.

Compound 12

^{1}H NMR: δ = 7.30 (5 H, m, Ar), 7.08–6.80 (5 H, m, Ar, CH=CH), 5.16 (2 H, m, H_1, H_4).

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