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Synthesis and Diels–Alder Cycloaddition Reactions of [(2,2-Dichloro-1-fluoroethenyl)sulfinyl] Benzene and [(2-Chloro-1,2-difluoro ethenyl)sulfinyl] Benzene☆

Madabhushi Sridhar, K. Leela Krishna and Jampani Madhusudana Rao*

Organic Chemistry Division-II, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Abstract—Synthesis of [(2,2-dichloro-1-fluoroethenyl)sulfinyl] benzene and [(2-chloro-1,2-difluoro ethenyl)sulfinyl] benzene and their Diels–Alder cycloadditions with cyclopentadiene, furan and 1,3-diphenylisobenzofuran under thermal and microwave irradiation conditions are described. © 2000 Elsevier Science Ltd. All rights reserved.

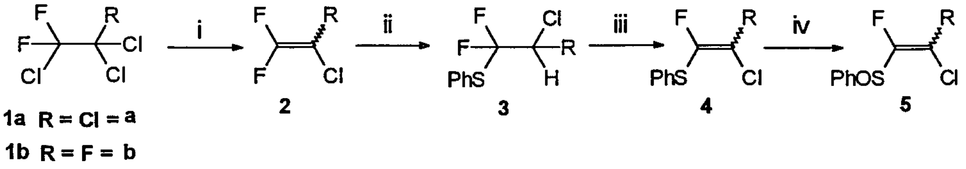
Though fluorine substituted vinyl compounds are not very reactive species, they are considered to be important building blocks in construction of fluorine substituted carbocycles.[1,2] This has prompted extensive studies in recent years in developing novel and reactive fluorovinyl compounds.[3]

Vinyl sulfoxides are valuable dienophiles[4] and widely in use in asymmetric Diels–Alder reaction studies.[5] Reactions of these dienophiles are also highly sluggish but their reactivity could improve considerably when they are activated further with a functionality such as –COOR,[6] $-NO_2$,[7] $-SO_2Ph$[8] etc. In the literature no reports are known on Diels–Alder cycloaddition reactions of fluorine substituted vinylsulfoxides and hence, the cumulative effect of sulfoxide functionality and fluorine functionality on the reactivity of these dienophiles has remained unknown. Here we report the results of our study with the novel fluorovinyl sulfoxides viz., [(2,2-dichloro-1-fluoroethenyl)sulfinyl] benzene, **5a** and [(2-chloro-1,2-difluoro ethenyl)sulfinyl] benzene, **5b** in Diels–Alder cycloadditions with typical dienes such as cyclopentadiene, furan and 1,3-diphenylisobenzofuran under conventional heating and microwave irradiation conditions.

The dienophiles **5a** and **5b** are prepared starting from 1,1,1,2-tetrachloro-2,2-difluoroethane and 1,1,2-trichloro-1,2,2-trifluoroethane respectively using the reported procedure[9] as shown in Scheme 1.

In the present study, vinyl sulfoxides, **5a** and **5b**[10] have shown good reactivity as dienophiles forming [4+2] adducts with cyclopentadiene and 1,3-diphenylisobenzofuran under conventional heating as well as under microwave irradiation (BPL BMO 700T domestic microwave oven, 600 W) giving the corresponding cycloadducts in >70% yield. Furan resisted cycloaddition with **5a** and **5b** when subjected to conventional heating (sealed tube at 130°C for 24 h). It did, however, undergo cycloaddition with >35% conversion (Yield >70% based on recovered **5**) in relatively short reaction times (25 min) when treated with microwave radiation[11] (Scheme 2).

Cycloaddition of cyclopentadiene with **5a** gave mixtures of



Scheme 1. (i) **2a**: Zn/EtOH, 60°C, 3h, 80%; **2b**: Zn/EtOH, 50°C, 3 h, 75%; (ii) **3a**: PhSH, NaOH, autoclave, 120°C, 8 h, 90%; **3b**: PhSH, NaOH, autoclave, 120°C, 6 h, 85%; (iii) **4a**: KOH, autoclave, 120°C, 10 h, 85%; **4b**: KOH, autoclave, 120°C, 8 h, 80%; (iv) **5a** and **5b**: *m*-CPBA, DCM, RT, 24 h, 90%.

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Keywords: Diels–Alder cycloaddition reaction; vinylphenyl sulfoxides; fluorovinyl.

* Corresponding author. Tel.: +91-40-717-3933; fax: +91-40-717-3387; e-mail: sridharm@iict.ap.nic.in

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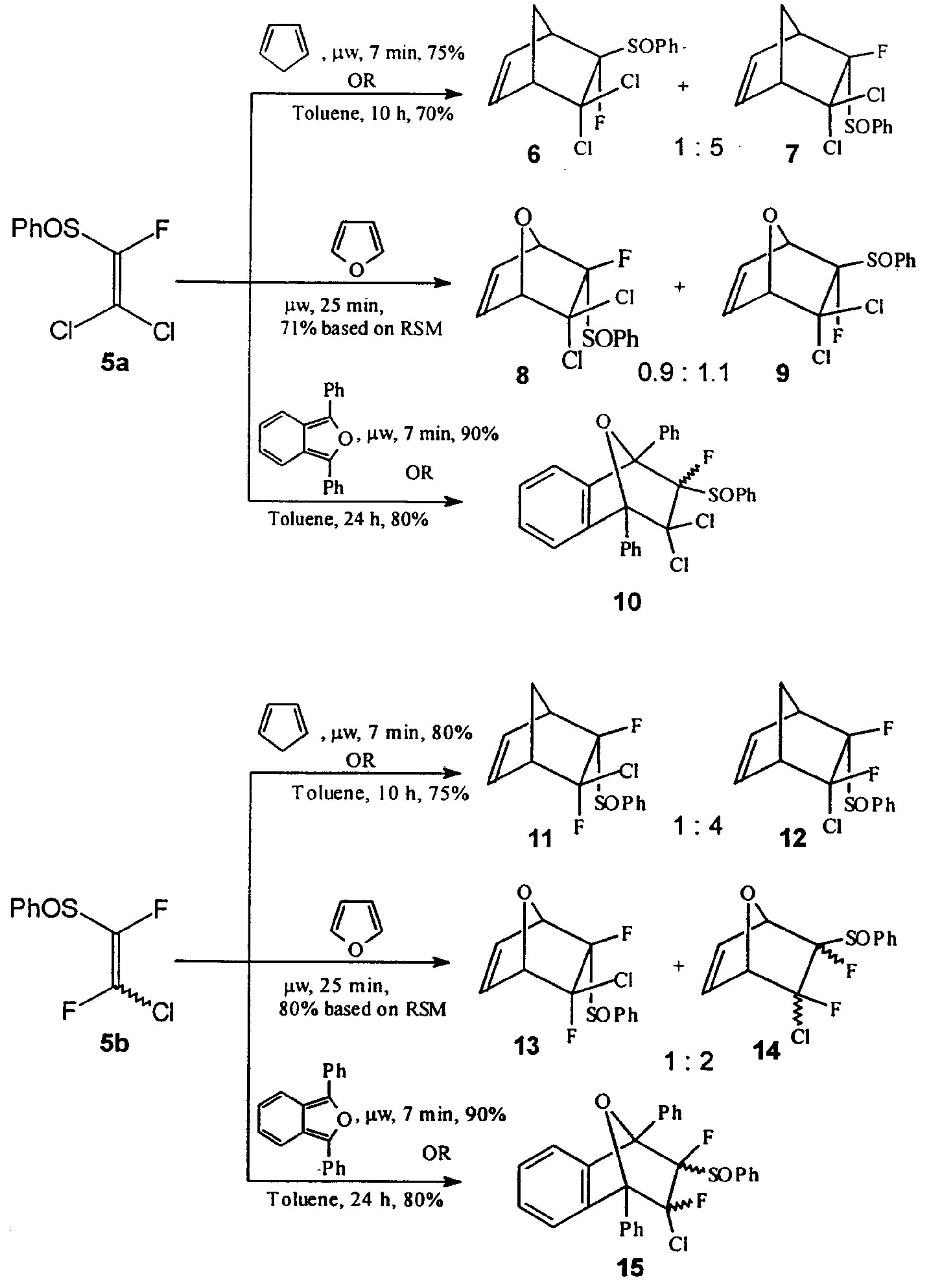
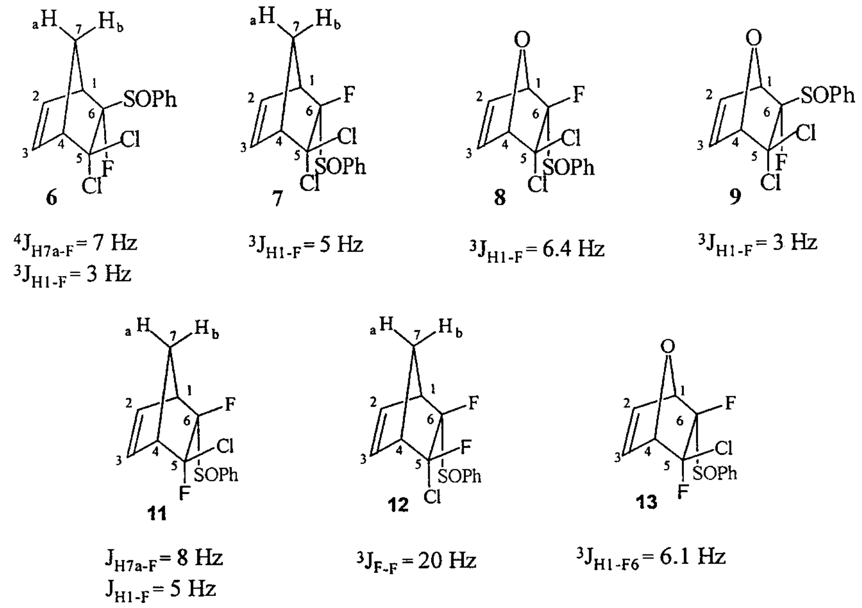


Scheme 2.

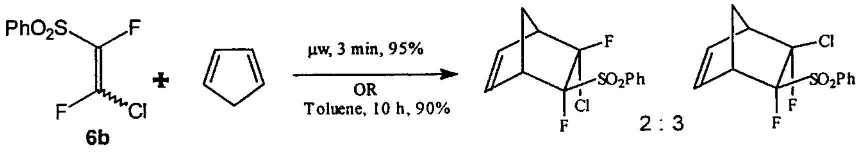
diastereomers **6** and **7**, and with **5b** it gave **11** and **12**, which were easily purified by normal column chromatography. In the case of furan also we have obtained mixtures of adducts upon its cycloaddition with **5a** and **5b**. Here, with the exception of **13**, the other components of the mixtures were found to be difficult to resolve by column chromatography.[12] Each of these components were, however, clearly characterisable from the ^{1}H NMR and ^{19}F NMR spectra of their adduct mixtures.

The stereochemistry of the adducts, **6–13** was assigned based on literature reports[2,11,13] on vicinal and long range couplings of fluorine with bridgehead and apical protons respectively in each of these adducts. For example, for compound **6**, we have assigned *endo* position to fluorine as it gave $^4J_{\mathrm{H7a-F}}=7$ Hz and $^3J_{\mathrm{H1-F}}=3$ Hz. Similarly, for furan adduct **9** also we observed $^3J_{\mathrm{H1-F}}=3$ Hz. When fluorine is in *exo* position, the $^3J_{\mathrm{H1-F}}$ coupling is usually >3 Hz. In the case of adduct **7**, it is found to be 5 Hz and for **8** it is 6.4 Hz (Scheme 3).

In our study we have noticed an unusual reversal of stereochemistry in cycloadditions of vinyl sulfoxide **5a** and **5b** and the corresponding sulfones **6a**[14] and **6b**[11] with cyclopentadiene. The cycloaddition of **5b** proceeded disposing the phenylsulfoxide group exclusively in the *endo* orientation, while **6b** formed adducts with the phenyl sulfone group only in *exo* position (Scheme 4).



Scheme 3.



Scheme 4.

In conclusion, this work is the first study on the Diels–Alder cycloaddition reaction using fluorine substituted vinylphenyl sulfoxides as dienophiles. Under microwave irradiation these dienophiles showed remarkable reactivity even with unreactive dienes like furan-forming cycloadducts.

Experimental

Infrared spectra were scanned on a Shimadzu Perkin–Elmer 1310 spectrometer. Proton magnetic resonance spectra were recorded on Varian FT-200 (Gemini) and Unity 400 spectrometers in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in ppm units downfield from TMS. Fluorine NMR was recorded on a Unity 400 spectrometer at an operating frequency of 376.3 MHz in $CDCl_3$ using trichlorofluoromethane ($CFCl_3$) as an internal standard. Chemical shifts are expressed in ppm units downfield from $CFCl_3$. Electron Impact (EI) and gas chromatographic mass spectra (GCMS) were recorded on VG 7070 H instrument at 70 eV. Chemical ionization mass spectra (CIMS) were recorded on VG 7070 H at 70 eV using acetone as CI reagent. Liquid secondary ion mass spectrometry (LSIMS) was carried out on VG Autospec M using Cs^+ ion gun. High-resolution mass spectra (HRMS) were recorded on VG Autospec M at 5000 resolution and perfluoro kerosine was used as an internal standard. Gas chromatography was carried out on HP-5890 Series II gas chromatograph with helium as a carrier gas (30 mL/min). Microwave irradiations were carried out on BPL BMO-700T (600 W) domestic microwave oven in a sealed tube (Aldrich, Ace pressure tube with a teflon plug, 10.2 cm, 15 mL).

1,1,-Dichloro-2,2-difluoroethene, 2a

Alkene **2a** was prepared[15] by the dehalogenation of 2,2-difluoro-1,1,1,2-tetrachloroethane **1a** in a reactive cryogenic distillation set up which consisted of a two-necked 1 litre round bottom flask. One neck was equipped with a fractionating column and a condenser and the other with a dropping funnel. A coolant at −40°C was circulated through the condenser. Activated zinc dust (163.47 g, 2.5 mol) was suspended in ethanol (200 mL) in the round bottom flask then 1,1,1,2-tetrachloro-2,2-difluoroethane, **1a** (101.91 g, 0.5 mol) in 100 mL ethanol was added dropwise over a period of 30 min. The mixture was treated with 10 mL of a 10% ethanolic solution of zinc chloride and warmed to 40–50°C with continuous stirring until a spontaneous reaction set in, after which the temperature was maintained at 70°C. The gaseous product liberated over a period of 3 h was collected in a trap cooled with a dry ice–acetone bath. The crude product was purified by cryogenic fractional distillation over P_2O_5 and the fraction boiling at 19–20°C (lit.[16] boiling point 19°C) was collected as a colourless liquid. Yield: 53.20 g (80%).

2,2-Dichloro-1,1-difluoro-1-(phenyl thio) ethane,[17] 3a

Alkene **2a** (33.23 g, 250 mmol), thiophenol (30.30 g, 275 mmol) and powdered NaOH (1.2 g, 30 mmol) were taken in an autoclave and heated at 120°C for 8 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, discharged and extracted with diethyl ether (2×100 mL). The ether layer was washed successively with 10% aqueous sodium hydroxide solution (2×50 mL), water (2×100 mL) and brine solution (50 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was distilled under vacuum (80–85°C/0.6 mmHg) to obtain **3a** (54.70 g, 90%) as a colourless liquid. IR (Neat) $\nu_{\max}$: 1480, 1430, 1160, 1070 cm^{-1}; ^{1}H NMR (200 MHz): δ 5.7 (t, J=7 Hz, 1H), 7.4–7.6 (m, 5H, Ar-H); ^{19}F NMR: δ −82.5 (d, J=7 Hz); MS (EI): m/z 242 (M^+,15), 159 (80), 109 (100), 83 (15); HRMS: Calculated for $C_8H_6Cl_2F_2S$ 241.9535, found: 241.9525.

2,2-Dichloro-1-fluoro-1-(phenyl thio) ethylene,[17] 4a

Thioether **3a** (24.31 g, 100 mmol) and powdered KOH (11.2 g 200 mmol) were placed in an autoclave and heated at 120°C for 10 h under nitrogen atmosphere. The mixture was cooled to room temperature, discharged and extracted with diethyl ether (2×100 mL). The ether layer was washed successively with water (2×100 mL) and brine (50 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was distilled under vacuum to yield **4a** as a colourless liquid (18.96 g, 85%, bp: 60–65°C/1 mmHg). IR (neat) $\nu_{\max}$: 1600, 1500, 1420, 1120, 980 cm^{-1}; ^{1}H NMR (200 MHz): δ 7.3–7.5 (m, Ar-H); ^{19}F NMR: δ −85.0 (s); MS (EI): m/z 222 (M^+, 10), 152 (100), 109 (20), 77 (80); HRMS: Calculated for $C_8H_5Cl_2FS$ 221.9473, found: 221.9474

[(2,2-Dichloro-1-fluoroethenyl)sulfinyl] benzene 5a

A mixture consisting of alkene **4a** (4.46 g, 20 mmol) and *m*-CPBA (60%: 5.75 g, 20 mmol) was stirred in dry dichloromethane (100 mL) for 24 h at room temperature. The ether layer was washed successively with saturated sodium bicarbonate solution (2×50 mL), water (2× 100 mL), brine (50 mL) and then dried over anhydrous sodium sulfate. The crude product obtained after the removal of the solvent was purified by column chromatography (silica gel, 60–120 mesh, 10% EtOAc in petroleum ether) to obtain **5a** (4.30 g, 90%) in the form of an oil. IR (neat) $\nu_{\max}$: 3150, 1650, 1060 (S=O) and 950 cm^{-1}; ^{1}H NMR (200 MHz): δ 7.5–7.8 (m, Ar-H); ^{19}F NMR: δ −121.66 (s); MS (EI): m/z 238 [M^+, 0.7] 222 (29), 190 (75), 125 (47), 109 (97), 77 (100); HRMS: Calculated for $C_8H_5Cl_2FOS$ 237.9422, found 237.9416.

1-Chloro-1,2,2-trifluoroethene,[18] 2b

Activated zinc dust (143.86 g, 2.2 mol) was suspended in 230 mL of ethanol in the round bottom flask then 1,1,2-trichloro-1,2,2-trifluoroethane, **1b** (290.44 g, 1.55 mol) was added dropwise at room temperature. After addition was complete, the mixture was treated with 10 mL of 10% alcoholic solution of zinc chloride and warmed to 40–50°C with continuous stirring until a spontaneous reaction sets in, after which the temperature was maintained at 50°C. The gaseous product liberated over a period of 3 h was collected in a cold trap at −78°C using a dry ice–acetone bath. The crude product was further purified by cryogenic fractional distillation over P_2O_5 and **2b** is collected as a fraction boiling at −24−−26°C as a colourless liquid. Yield: 135.40 g (75%).

2-Chloro-1,1,2-trifluoro-1-(phenyl thio) ethane,[19] 3b

Alkene **2b** (29.12 g, 250 mmol), thiophenol (30.30 g, 275 mmol) and powdered NaOH, (1.2 g, 30 mmol) were taken in an autoclave and heated at 120°C for 6 h under nitrogen atmosphere. The reaction mixture was cooled, the reactor was discharged and extracted with diethyl ether (2×100 mL). The ether layer was washed successively with 10% aq. NaOH solution (2×50 mL), water (2×100 mL) and brine solution (50 mL). The organic layer was dried over anhydrous sodium sulfate and ether was removed under reduced pressure. Distillation of the crude furnished pure **3b** (48.16 g, 85%; bp: 70°C/0.6 mmHg) as a colourless liquid. IR (neat) $\nu_{\max:}$ 1480, 1430, 1160 and 1080 cm^{-1}; MS (EI): m/z 226 (M^+, 45), 159 (100), 109 (60), 77 (40); ^{1}H NMR (200 MHz): δ 5.9–6.3 (dm, J=50 Hz, 1H); 7.4–7.7 (m, 5H, Ar-H); HRMS: Calculated for $C_8H_6ClF_3S$ 225.9830, found: 225.9830.

2-Chloro-1,2-difluoro-1-(phenyl thio) ethylene,[19] 4b

Thioether **3b** (22.66 g, 100 mmol) and powdered KOH (11.2 g, 200 mmol) were taken in an autoclave and heated at 120°C for 8 h under nitrogen atmosphere. The mixture was cooled to room temperature, discharged and extracted with diethyl ether (2×100 mL). The organic layer was washed successively with water (2×50 mL), brine solution (50 mL), and dried over anhydrous sodium sulphate and solvent was removed under reduced pressure. The crude product upon distillation gave **4b** as a colourless liquid (16.53 g, 80%; bp: 206–208°C, lit. bp:[19] 208°C). IR (neat) $\nu_{\max:}$ 3050, 1700, 1125 cm^{-1}; MS (EI): m/z 206 (M^+, 40), 171 (50), 143 (26), 127 (100), 109 (15); ^{1}H NMR (200 MHz): δ 7.2–7.5 (m, Ar-H). GC-mass analysis of **4b** indicated it to be a mixture of its geometrical isomers in 2:3 ratio. HRMS: Calculated for $C_8H_5ClF_2S$ 205.9768, found: 205.9775.

[(2-Chloro-1,2-difluoro ethenyl)sulfinyl]benzene, 5b

A mixture consisting of alkene **4b** (4.13 g, 20 mmol) and *m*-CPBA (60%, 5.75 g, 20 mmol) was stirred in dry dichloromethane (100 mL) for 24 h at room temperature. The organic layer was washed successively with saturated $NaHCO_3$ solution (2×50 mL), water (2×50 mL) and saturated brine solution (50 mL) and then dried over anhydrous sodium sulphate. The crude product obtained after removal of solvent was purified by column chromatography (silica gel, 60–120 mesh, 10% EtOAc in petroleum ether) to obtain **5b** (4.01 g, 90%) in the form of colourless oil. IR (neat) $\nu_{\max:}$ 3075, 1680, 1200, and 1080 cm^{-1}; ^{1}H NMR (200 MHz): δ 7.5–7.8 (m, Ar-H); Mass (EI): m/z 222 (M^+, 3.6), 206 (25), 174 (100), 125 (53), 109 (75), 77 (97). HRMS: Calculated for $C_8H_5ClF_2OS$ 221.9723, found: 221.9717.

Diels–Alder cycloaddition reactions of [(2,2-dichloro-1-fluoroethenyl)sulfinyl] benzene, 5a with cyclopentadiene

(a) *Thermal cycloaddition*. Sulfoxide **5a** (0.238 g, 1 mmol) and dry toluene (15 mL) were placed in a two-necked round bottom flask fitted with a rubber septum and a cold water condenser. To this freshly cracked cyclopentadiene, (0.660 g, 10 mmol) was added and the mixture was refluxed for 10 h under nitrogen atmosphere. Toluene and the unreacted cyclopentadiene were removed under reduced pressure and the crude product was subjected to column chromatography (silica gel, finer than 200 mesh, 100 mL of petroleum ether followed by 3–5% EtOAc in petroleum ether) to obtain 33 mg. (10.9%) of pure 5,5-dichloro-6-fluoro-*exo*-6-(phenylsulfinyl)-bicyclo[2.2.1]hept-2-ene, **6** followed by 15 mg (4.9%) of mixture of **6** and **7** and 165 mg (54.3%) of pure 5,5-dichloro-6-fluoro-*endo*-6-(phenylsulfinyl)bicyclo[2.2.1]hept-2-ene, **7**. Ratio of **6** and **7** (1:5) was determined by the relative peak intensities in the ^{1}H NMR spectrum of the adduct mixture.

(b) *Microwave assisted cycloaddition*. Sulfoxide **5a** (0.119 g, 0.5 mmol) and freshly cracked cyclopentadiene (0.330 g, 5 mmol) were taken in sealed pressure tube under nitrogen atmosphere. The reaction mixture was subjected to microwave irradiation in a domestic microwave oven (BPL BMO 700T, 600 W) for 7 min and then cooled. After attaining room temperature the crude reaction product was subjected to column chromatography (silica gel, 60–120 mesh, 100 mL petroleum ether followed by 5–10% EtOAc in petroleum ether) to afford cycloadduct 0.114 g (75%) as a mixture of two diastereomers **6** and **7** in the ratio of 1:5 based on relative peak intensities in ^{1}H NMR of the mixture.

5,5-Dichloro-6-fluoro-*exo*-6-(phenylsulfinyl)-bicyclo-[2.2.1]hept-2-ene, 6

White solid; mp: 99–100°C; IR (KBr) ν_{max}: 1052 cm^1 (SO Stretch); ^{1}H NMR (400 MHz): δ 1.9–2.1 (m, $^2J_{\text{H7a–H7b}}$=10.9 Hz, $^3J_{\text{H–H}}$=1.83 Hz, $^4J_{\text{H7a–F}}$=7.0 Hz irradiation, H-7a), 2.52 (dm, $^2J_{\text{H7b–H7a}}$=10.9 Hz, $^3J_{\text{H–H}}$=1.80 Hz, irradiation, H-7b), 3.48 (m, H-1), 3.56 (m, H-4), 6.1–6.2 (m, $^3J_{\text{H–H}}$=5.7 Hz, irradiation, H-2), 6.4–6.5 (m, $^3J_{\text{H–H}}$=5.7 Hz, irradiation, H-3); 7.6–7.9 (m, 5H, Ar-H); MS (LSIMS): *m/z* 305 (M$^+$+H, 100), 269 (10), 179 (30), 77 (40), 66 (30%); HRMS: Calculated for [M$^+$+H] $C_{13}H_{12}Cl_2FOS$ 304.9970, found: 304.9991.

5,5,-Dichloro-6-fluoro-*endo*-6-(phenylsulfinyl)-bicyclo-[2.2.1]hept-2-ene, 7

White solid; mp: 163–165°C; IR (KBr) ν_{max}:1050 cm^1 (SO Stretch); ^{1}H NMR (400 MHz): δ 2.1 (ddd, $^2J_{\text{H7a–H7b}}$=10.26 Hz, J_2=3.3 Hz, J_3=1.46 Hz, irradiation, H-7a), 2.30 (dd, $^2J_{\text{H7b–H7a}}$=10.26 Hz, $J_{2\text{b}}$=1.4 Hz, irradiation, H-7b), 3.4 (m, H-1), 3.5 (m, H-4), 6.4 (m, H-2), 6.6 (m, H-3), 7.6–7.8 (m, 5H, Ar-H); MS (LSIMS): *m/z* 305 (M$^+$+H, 100), 288 (10), 269 (20), 179 (60), 77 (60), 66 (30); HRMS (LSIMS): Calculated for (M$^+$+H) $C_{13}H_{12}Cl_2FOS$ 304.9970, found: 304.9990.

Diels–Alder cycloaddition reactions of 5a with furan

Microwave assisted cycloaddition. Sulfoxide **5a** (0.119 g, 0.5 mmol) and furan (2 mL, 27 mmol) were taken in a sealed pressure tube under a nitrogen atmosphere. The mixture was subjected to microwave irradiation for 5×5 min and then cooled. After attaining room temperature the reaction mixture was discharged, excess furan distilled off and the product was subjected to column chromatography (silica gel, finer than 200 mesh, 3–5% EtOAc in pet ether) to obtain 60 mg. of unreacted **5a** followed by 54 mg of cycloadduct in 70.7% yield based on recovered starting material (35% conversion) as an inseparable mixture of two diastereomers 5,5,-dichloro-6-fluoro-*endo*-6-(phenyl-sulfinyl)-7-oxabicyclo[2.2.1]hept-2-ene, **8** and 5,5,-dichloro-6-fluoro-*exo*-6-(phenyl-sulfinyl)-7-oxabicyclo-[2.2.1]-hept-2-ene, **9** in the ratio 0.9:1.1 based on relative peak intensities in ^{1}H NMR and ^{19}F NMR of their mixture. In these spectra the signals of **8** and **9** are clearly distinguishable.

5,5,-Dichloro-6-fluoro-*endo*-6-(phenyl sulfinyl)-7-oxabicyclo[2.2.1]hept-2-ene, 8

Waxy solid (mixture); IR (KBr) $\nu_{\text{max:}}$1050 cm^1 (SO Stretch); ^{1}H NMR (200 MHz): δ 5.0–5.1 (dd, $^3J_{\text{H1–F6}}$=6.40 Hz, $^3J_{\text{H1–H2}}$=1.5 Hz, H-1), 5.2 (d, $^3J_{\text{H4–H3}}$=1.6 Hz, H-4), 6.7–6.8 (m, H-2), 6.9–7.0 (m, H-3), 7.5–8.0 (m, 5H, Ar-H); ^{19}F NMR: −144.26 (d, $J_{\text{F–H}}$=6.40 Hz); MS (LSIMS): *m/z* 307 (M$^+$+H, 40), 238 (30), 125 (20), 109 (100); HRMS: Calculated for (M$^+$+H) $C_{12}H_{10}O_2FSCl_2$ 306.9762, found: 306.9766.

5,5,-Dichloro-6-fluoro-*exo*-6-(phenyl sulfinyl)-7-oxabicyclo[2.2.1]hept-2-ene, 9

^{1}H NMR (200 MHz): δ 5.2–5.3 (dd, $^3J_{\text{H1–F}}$=3.0 Hz, $^3J_{\text{H1–H2}}$=1.5 Hz, H-1), 5.6–5.7 (d, $^3J_{\text{H4–H3}}$=1.7 Hz, H-4), 6.5–6.6 (m, H-2), 6.7 (m, H-3), 7.5–8.0 (m, 5H, Ar-H); ^{19}F NMR: δ −141.20 (s). HRMS: Calculated for (M$^+$+H) $C_{12}H_{10}O_2FSCl_2$ 306.9762, found: 306.9766.

Diels–Alder cycloaddition reactions of 5a with 1,3-diphenylisobenzofuran

(a) *Thermal cycloaddition.* Sulfoxide **5a** (0.238 g, 1 mmol) and 1,3-diphenylisobenzofuran (0.270 g, 1 mmol) were refluxed in dry toluene (15 mL) for 24 h under nitrogen atmosphere. Toluene was removed under reduced pressure and the mixture was subjected to column chromatography (silica gel, 60–120 mesh, 10% EtOAc in petroleum ether) to afford 0.406 g (80%) of cycloadduct 2,2-dichloro-3-fluoro-1,2,3,4-tetrahydro-1,4-diphenyl-3-(phenyl sulfinyl) 1,4-epoxy napthalene, **10** as a white solid.

(b) *Microwave assisted cycloaddition.* A mixture of **5a** (0.119 g, 0.5 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol) were taken in a sealed tube and subjected to microwave irradiation for 7 min and crude product subjected to column chromatography (silica gel, 60–120 mesh, 10% EtOAc in petroleum ether) to afford 0.228 g (90%) of cycloadduct, **10**.

2,2-Dichloro-3-fluoro-1,2,3,4-tetrahydro-1,4-diphenyl-3-(phenyl sulfinyl)1,4-epoxy napthalene, 10

White solid; mp: 180–181°C; IR (KBr) $\nu_{max:}$1050 cm^{-1}; ^{1}H NMR (200 MHz):δ 7.3–8.0 (m, Ar-H); MS (LSIMS): *m/z* 509 [(M^++H), 30], 270 (100), 238 (20); HRMS (LSIMS): Calculated for (M^++H) $C_{28}H_{20}Cl_2FO_2S$ 509.0545, found: 509.0555.

Diels–Alder cycloaddition reactions of sulfoxide 5b with cyclopentadiene

(a) *Thermal cycloaddition.* Sulfoxide **5b** (0.222 g, 1 mmol) and dry toluene (10 mL) were taken in a two-necked flask equipped with a rubber septum and a cold water condenser. Freshly cracked cylopentadiene (0.660 g, 10 mmol) was added and the mixture was refluxed for 10 h under nitrogen atmosphere. Solvent was removed under reduced pressure and the crude product was subjected to column chromatography (silica gel, 60–120 mesh, 100 mL petroleum ether followed by 3–5% EtOAc in petroleum ether) to obtain 38 mg (13.2%) of pure *exo*-5-chloro-5,6-difluoro-*endo*-6-(phenyl sulfinyl)-bicyclo[2.2.1]hept-2-ene, **11** followed by 17 mg (5.9%) of mixture of **11** and **12** and 160 mg (55.6%) of pure *endo*-5-chloro-5,6-difluoro-*endo*-6-(phenyl sulfinyl)-bicyclo[2.2.1]hept-2-ene, **12**.

(b) *Microwave assisted cycloaddition.* Sulfoxide **5b** (0.110 g, 0.5 mmol) and freshly cracked cyclopentadiene, (0.33 g, 5 mmol) were taken in an sealed pressure tube under a nitrogen atmosphere and subjected to microwave irradiation for 7 min and then cooled. The crude reaction product was purified by column chromatography (silica gel, 60–120 mesh, 50 mL pet ether followed by 10% EtOAc in petroleum ether) to obtain 115 mg. (80%) of cycloadduct as a mixture of two diastereomers **11** and **12** in the ratio 1:4 based on relative peak intensities in ^{1}H NMR of their mixture.

exo-5-Chloro-5,6-difluoro-*endo*-6-(phenyl sulfinyl)-bicyclo[2.2.1]hept-2-ene, 11

White solid; mp: 98–99°C; IR (KBr) ν_{max}: 1075 cm^{-1} (SO stretch); ^{1}H NMR (200 MHz): δ 1.85 – 2.0 (brm, $^2J_{H7a-7b}$= 11 Hz, $^4J_{7a-F}$=8 Hz, $^3J_{H7a-H-1}$=$^3J_{H7a-H-4}$=1.5 Hz, irradiation, H-7a), 2.3–2.4 (dd, $^2J_{7b-7a}$=11 Hz, $^3J_{H7b-H-1}$=$^3J_{H7b-H-4}$= 1.5 Hz, irradiation, H-7b), 3.3 (m, $^3J_{H1-F6}$=5 Hz, irradiation, H-1), 3.4 (m, H-4), 6.1–6.2 (m, H-2), 6.3–6.4 (m, H-3), 7.6–7.9 (m, 5H, Ar-H); MS (EI): *m/z* 288 (M^+, 30), 163 (50), 125 (100), 66 (40); HRMS: Calculated for $C_{13}H_{11}ClF_2OS$ 288.0187, Found: 288.0177.

endo-5-Chloro-5,6-difluoro-*endo*-6-(phenyl sulfinyl)-bicyclo[2.2.1]hept-2-ene, 12

White solid; mp: 110°C; IR (KBr) ν_{max}:1075 cm^{-1} (SO stretch); ^{1}H NMR (200 MHz): δ 2.0–2.1 (m, H-7a, 7b), 3.2–3.3 (m, H-1), 3.4–3.5 (m, H-4), 6.4–6.5 (m, H-2), 6.6–6.7 (m, H-3), 7.4–7.8 (m, 5H, Ar-H); ^{19}F NMR δ −108 (d, $^3J_{F-F}$=20 Hz, 1F), −154 (d, $^3J_{F-F}$=20 Hz, 1F); MS (EI): *m/z* 288 (M^+, 30), 163 (70), 125 (100), 66 (30); HRMS: Calculated for $C_{13}H_{11}ClF_2OS$ 288.0187, Found: 288.0203.

Diels–Alder cycloaddition reactions of sulfoxide 5b with furan

Sulfoxide **5b** (0.110 g, 0.5 mmol) and furan (2 mL, 27 mmol) were taken in an pressure tube under a nitrogen atmosphere and subjected to microwave irradiation for 5×5 min and cooled to room temperature. Excess furan was distilled off and the reaction mixture was subjected to column chromatography (silica gel, finer than 200 mesh, 3–5% EtOAc in petroleum ether) to afford successively 56 mg of unreacted **5b** followed by 20 mg of cycloadduct *exo*-5-chloro-5,6-difluoro-*endo*-6-(phenyl-sulfinyl)-7-oxa-bicyclo[2.2.1]hept-2-ene, **13** and 37 mg of cycloadduct 5-chloro-5,6-difluoro-6-(phenyl sulfinyl)-7-oxabicyclo[2.2.1]hept-2-ene, **14** which is a mixture of inseparable diastereomers. Yield: 80% based on recovered starting material

exo-5-Chloro-5,6-difluoro-*endo*-6-(phenyl sulfinyl)-7-oxabicyclo[2.2.1]hept-2-ene, 13

White solid; mp: 102°C; IR (KBr) $\nu_{max:}$1075 cm^{-1} (SO stretch); ^{1}H NMR (200 MHz): δ 5.1–5.2 (d, $^3J_{H-F}$= 6.10 Hz, H-1), 5.60 (brs, H-4), 6.5–6.6 (m, H-2), 6.7–6.8 (m, H-3), 7.5–8.0 (m, 5H, Ar-H); ^{19}F NMR: δ −111 (s, 1F), −154.75 (d, $^3J_{F-H}$=6.10 Hz); MS (EI) *m/z* 290 (M^+, 5), 165 (20), 125 (100), 68 (60); HRMS: Calculated for $C_{12}H_9ClF_2O_2S$ 289.9979, Found: 289.9971.

5-Chloro-5,6-difluoro-6-(phenyl sulfinyl)-7-oxabicyclo-[2.2.1]hept-2-ene, 14

IR (KBr) ν_{max}:1070 cm^{-1} (SO stretch); ^{1}H NMR (200 MHz): δ 4.9–5.0 (m, 1H), 5.2–5.3 (m, 1H), 6.6–6.9 (m, 2H), 7.5–7.9 (m, 5H, Ar-H); MS (EI) *m/z* 290 (M^+, 10), 165 (20), 125 (100), 68 (60); HRMS: Calculated $C_{12}H_9ClF_2O_2S$ 289.9979, Found: 289.9968.

Diels–Alder cycloaddition reaction of sulfoxide 5b with 1,3-diphenylisobenzofuran

(a) *Thermal cycloaddition.* A solution consisting of sulfoxide **5b** (0.222 g, 1 mmol) and diphenylisobenzofuran, (0.270 g, 1 mmol) in dry toluene (15 mL) was refluxed for 24 h under nitrogen atmosphere. Toluene was removed under reduced pressure and the reaction product was subjected to column chromatography (silica gel, 60–120 mesh, 10% EtOAc in petroleum ether) to obtain 0.394 g (80%) of the cycloadduct [2-chloro-2,3-difluoro-1,2,3,4-tetrahydro-1,4-diphenyl-3-(phenyl sulfinyl)]-1,4-epoxy naphthalene, **15** which is a mixture of inseparable diastereomers.

(b) *Microwave assisted cycloaddition.* A mixture consisting of sulfoxide **5b** (0.111 g, 0.5 mmol), 1,3 diphenylisobenzofuran, (0.135 g, 0.5 mmol) were subjected to microwave irradiation for 7 min and the reaction mixture upon column chromatography (silica gel, 60–120 mesh, 10% EtOAc in petroleum ether) afforded 0.225 g (90%) of the cycloadduct, **15** as a white solid.

[2-Chloro-2,3-difluoro-1,2,3,4-tetrahydro-1,4-diphenyl-3-(phenyl sulfinyl)] 1,4 epoxy naphthalene, 15

White solid mp: 116–117°C; IR (KBr) ν_{max} 1060 cm^{-1} (SO stretch); ^{1}H NMR (200 MHz) δ 7.4–8.2 (m, Ar-H); MS (LSIMS) *m/z* 493 [(M$^+$+H), 15], 287 (90), 270 (60), 149 (100); HRMS: Calculated for (M$^+$+H) $C_{28}H_{20}ClF_2O_2S$ 493.084, Found 493.082.

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