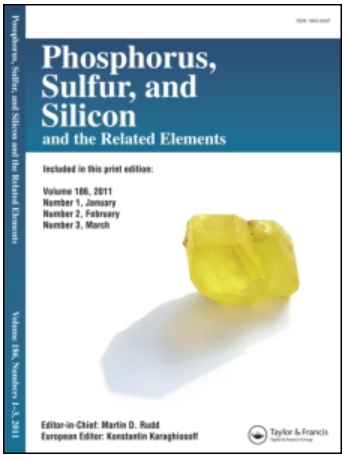

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A Convenient, One-Pot Conversion of Polyethylene Glycol-Linked *F*-Alkyl Disulfoxides into the α,β-Unsaturated Derivatives

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A CONVENIENT, ONE-POT CONVERSION OF POLYETHYLENE GLYCOL-LINKED *F*-ALKYL DISULFOXIDES INTO THE α,β-UNSATURATED DERIVATIVES

Najeh Grayaa Jaoued and Ahmed Hedhli
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The synthesis of a series of α,β-unsaturated disulfoxides having two highly fluorinated chains separated by a polyoxyethylene (POE) group is described. The reaction was carried out in basic medium, and the most relevant feature of this conversion is the enhanced acidity of SO-α-hydrogens of starting materials, leading to the observed regioselectivity.

Keywords Disulfoxide; fluorine; tosylate

INTRODUCTION

Unsaturated sulfoxides are often considered as versatile intermediates in organic synthesis,[1–7] particularly in the synthesis of complex natural products with biological activity. They are also important intermediates for the crop protection, veterinary drugs, and lubricants industries.

In the same context, some work on fluorinated sulfoxides,[8,9] sulfoximines,[10,11] and the oxidation of primary and secondary alcohols using a recyclable fluorous sulfoxide as oxidizing agent[12,13] have been described. These compounds are used in different kinds of reactions such as Michael addition reaction,[14] additive Pummerer reaction,[15,16] sigmatropic rearrangement,[17] and cycloaddition reaction.[18]

The main routes to unsaturated sulfoxides are Anderson[19] and Wittig–Horner[20–22] procedures. It has been reported from our laboratory that unsaturated *F*-alkylsulfoxides are synthesized from the corresponding hydroxylated ones, via an in situ tosylation in basic medium.[23,24] For our continuous studies on fluorinated sulfoxides,[25] we describe herein the conversion of some dihydroxyfluorinated disulfoxides derived from polyethylene glycols into the unsaturated analogues.

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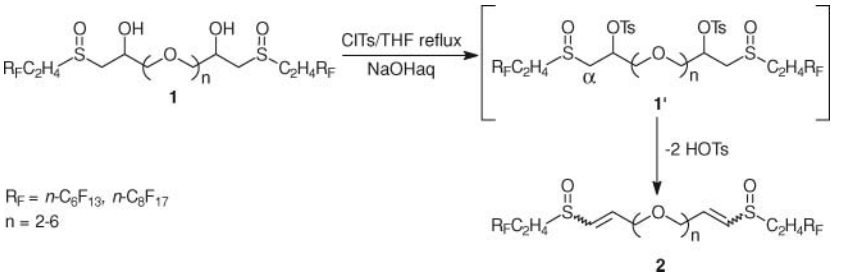
Address correspondence to Ahmed Hedhli, Laboratoire de Chimie Moléculaire Organique, Ecole Supérieure des Sciences et Techniques de Tunis, 5, avenue Taha Hussein, Montfleury, 1089 Tunis, Tunisia. E-mail: ahmed.hedhli@esstt.rnu.tn

RESULTS AND DISCUSSION

The reaction consists of a two-step, one-pot process in which the tosylation displays presumably the activation step. The synthesis of α,β-unsaturated disulfoxides **2** is outlined in Scheme 1.



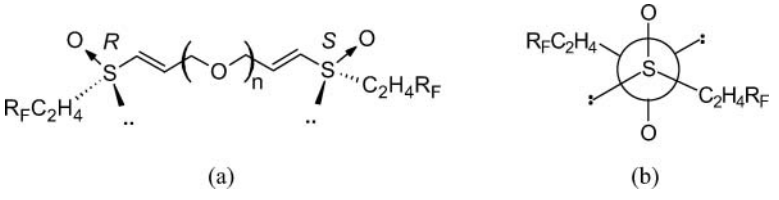
Scheme 1 Synthesis of unsaturated disulfoxides.

The first step proceeded by tosylation of hydroxyl groups[25] (Scheme 1), although the expected tosylate **1′** was not isolated.[24] In the second step, since the reaction was carried out in basic medium, compound **1′** underwent a smooth elimination of HOTs (*p*-toluene sulfonic acid) to furnish disulfoxide **2**. This latter was obtained in good yield as a mixture of *EE* and *ZZ* isomers, in almost 1:1 ratio. The isomers' proportions were evaluated by ^{1}H NMR. Attempts to separate *EE* and *ZZ* isomers by column chromatography failed. The new unsaturated disulfoxides **2** are grouped in Table I.

It is worth noting that the *EZ* isomer is not formed using this procedure, nor the β,γ-unsaturated sulfoxide involving loss of a γ-hydrogen. The absence of the former was foreseeable according to our previous results,[26] whereas the non-formation of the latter can be assumed be due to the enhanced acidity of hydrogens in position α to the sulfoxide function.

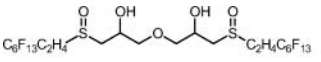
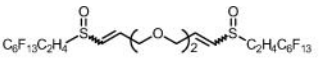
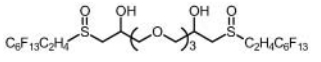
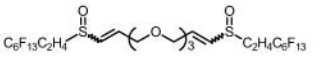
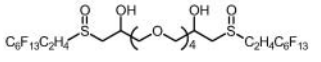
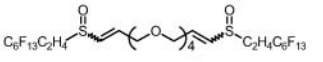
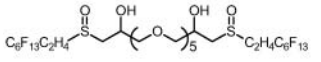
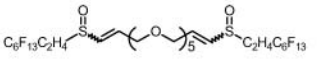
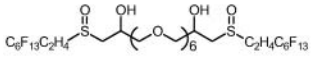
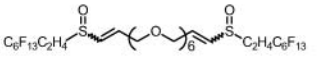
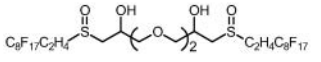
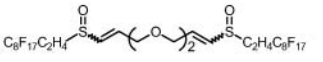
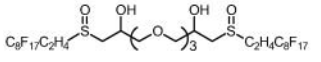
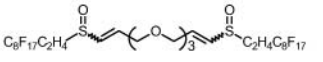
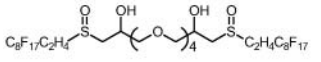
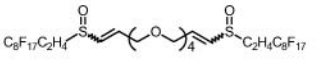
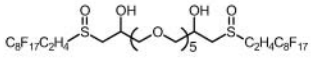
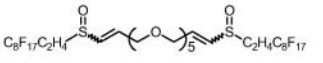
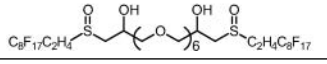
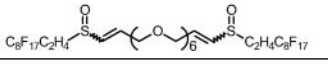
The observed stereoselectivity may be rationalized if we assume the following basic idea: In a given molecule of ditosylate, the two POE chain ends, as attached one to the other, should have the same energetic state. So, conformations leading to HOTs bimolecular elimination should be energetically equivalent and hence furnish the same kind of *E*/*Z* configurations, i.e., *EE* or *ZZ*. *EZ* configuration resulting from two different conformations and then involving different energies would not be formed.

It is important to mention that only geometric isomers *EE* and *ZZ* of compound **2** are observed by NMR. Diastereomers resulting from asymmetric sulfur atoms (Scheme 2) remain indiscernible. This may be attributed to the separation of sulfur atoms by the long



Scheme 2 Cram (a) and Newman (b) representations of *RS/EE* **2** isomer.

Table I α,β-Unsaturated disulfoxides prepared

Disulfoxide **1**		Unsaturated disulfoxide **2**		Yield (%)
	**1a**		**2a**	93
	**1b**		**2b**	90
	**1c**		**2c**	77
	**1d**		**2d**	76
	**1e**		**2e**	87
	**1f**		**2f**	92
	**1g**		**2g**	95
	**1h**		**2h**	80
	**1i**		**2i**	82
	**1j**		**2j**	80

POE chain, as the sulfur atoms are then so far from each other that their mutual interactions are negligible. So, the corresponding diastereomeric relationship is then invisible to NMR.

Conversion of the new α,β-unsaturated disulfoxides into the lactones derivatives[27,28] is in progress.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS 66v/s. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz proton, 282 MHz fluorine, 75 MHz carbon). All spectra were obtained using $CDCl_3$ as solvent and referenced to TMS for ^{1}H and ^{13}C NMR, and $CFCl_3$ for ^{19}F NMR. The following abbreviations are used to denote multiplicity of the signals in the NMR spectra: s, singlet; d, doublet; t, triplet; m, multiplet. Analytical TLC was conducted using percolated aluminium TLC plates: silica gel/UV 254. Column chromatography was carried out with silica gel (silica gel, 0.060–0.200 mm, 40 A). The melting points were recorded on a SMAP 11 apparatus. The microanalysis was performed by Service Central d'Analyse, CNRS, Vernaison, France.

General Procedure for Preparation of Unsaturated Disulfoxides 2

Disulfoxide **1** (2 mmol) in THF (1.5 mL) was added dropwise to a stirred solution of sodium hydroxide 0.28 g (7 mmol) in water (1.5 mL), and cooled at 0°C. After 15 min of stirring at 0°C, a solution of tosyl chloride (0.43 g, 2 mmol) in THF (2 mL) was added dropwise. When the addition was complete, the reaction mixture was stirred at room temperature ($R_F = n\text{-}C_6F_{13}$) or reflux ($R_F = n\text{-}C_8F_{17}$) until completion of the reaction (TLC, eluent: chloroform:ethyl acetate 90:10). Then, it was extracted with dichloromethane (3 × 50 mL), washed with a 10% HCl aqueous solution and then water, dried over Na_2SO_4, and finally evaporated under reduced pressure. Silica gel flash chromatography (eluent: chloroform:ethyl acetate 90:10) gave unsaturated disulfoxide **2**, to which the FTIR spectroscopy showed the following main signals: ν_{COC} = 1100–1150, ν_{SO} = 1035–1050, ν_{CF} = 1000–1100, $\nu_{C=C}$ = 1690–1730 cm^{-1}.

Ethylene glycol di[3-((2-*F*-hexylethyl)sulfinyl)allyl]ether (2a). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.73 (m, 4H, 2 × $CH_2\underline{CH_2}C_6F_{13}$), 3.31 (m, 4H, 2 × $\underline{CH_2}CH_2C_6F_{13}$), 3.70 (m, 4H, $O\underline{CH_2}\underline{CH_2}$), 3.86 (m, 4H, 2 × $O\underline{CH_2}CH{=}CH$, *EE* isomer), 4.03 (m, 4H, 2 × $O\underline{CH_2}CH{=}CH$, *ZZ* isomer), 4.39 (m, 2H, 2 × $OCH_2\underline{CH}{=}CH$, *EE* isomer), 4.70 (m, 2H, 2 × $OCH_2\underline{CH}{=}CH$, *ZZ* isomer), 6.31 (m, 2H, 2 × $CH_2\underline{CH}{=}\underline{CH}SO$, *ZZ* isomer), 6.52 (m, 2H, 2 × $CH_2CH{=}\underline{CH}SO$, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.75 (t, $CH_2\underline{CH_2}C_6F_{13}$, $^2J_{C\text{-}F}$ = 25.05 Hz), 42.34 (s, $SO\underline{CH_2}CH_2C_6F_{13}$), 70.61 (m, $O\underline{CH_2}\underline{CH_2}$), 92.12 (s, $O\underline{CH_2}CH{=}CH$), 110.21–121.20 (m, $\underline{C_6F_{13}}$), 124.22 (s, $OCH_2CH{=}\underline{CH}SO$, *ZZ* isomer), 143.18 (s, $OCH_2CH{=}\underline{CH}SO$, *EE* isomer), 152.09 (s, $OCH_2\underline{CH}{=}CH$); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.77 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.48 Hz), −114.58 (m, 2F, $CF_{2\alpha}$), −122.83 (m, 2F, $CF_{2\beta}$), −123.83 (m, 2F, $CF_{2\gamma}$) −124.11 (m, 2F, $CF_{2\delta}$) −127.14 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{24}H_{20}O_4F_{26}S_2$: C, 30.98; H, 2.17. Found: C, 31.61; H, 2.28%.

Diethylene glycol di[3-((2-*F*-hexylethyl)sulfinyl)allyl]ether (2b). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.58 (m, 4H, 2 × $CH_2\underline{CH_2}C_6F_{13}$), 3.23 (m, 4H, 2 × $\underline{CH_2}CH_2C_6F_{13}$), 3.69 (m, 8H, 2 × $O\underline{CH_2}\underline{CH_2}$), 3.96 (m, 4H, 2 × $O\underline{CH_2}CH{=}CH$, *EE* isomer), 4.12 (m, 4H, 2 × $O\underline{CH_2}CH{=}CH$, *ZZ* isomer), 4.31 (m, 2H, 2 × $OCH_2\underline{CH}{=}CH$, *EE* isomer), 4.42 (m, 2H, 2 × $OCH_2\underline{CH}{=}CH$, *ZZ* isomer), 6.27 (m, 2H, 2 × $CH_2\underline{CH}{=}\underline{CH}SO$, *ZZ* isomer), 6.57 (m, 2H, 2 × $CH_2CH{=}\underline{CH}SO$, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.75 (t, $CH_2\underline{CH_2}C_6F_{13}$, $^2J_{C\text{-}F}$ = 24.82 Hz), 43.14 (s, $SO\underline{CH_2}CH_2C_6F_{13}$), 70.91 (m, $O\underline{CH_2}\underline{CH_2}$), 93.13 (s, $O\underline{CH_2}CH{=}CH$), 110.21–121.20 (m, $\underline{C_6F_{13}}$), 125.15 (s, $OCH_2CH{=}\underline{CH}SO$, *ZZ* isomer), 149.38 (s, $OCH_2CH{=}\underline{CH}SO$, *EE* isomer), 153.29 (s, $OCH_2\underline{CH}{=}CH$); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −80.27 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.88 Hz), −115.18 (m, 2F, $CF_{2\alpha}$), −123.63 (m, 2F, $CF_{2\beta}$), −124.13 (m, 2F, $CF_{2\gamma}$) −126.01 (m, 2F, $CF_{2\delta}$) −127.94 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{26}H_{24}F_{26}O_5S_2$: C, 32.04; H, 2.48. Found: C, 31.41; H, 2.37%.

Triethylene glycol di[3-((2-*F*-hexylethyl)sulfinyl)allyl]ether (2c). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.63 (m, 4H, 2 × $CH_2\underline{CH_2}C_6F_{13}$), 3.23 (m, 4H, 2 × $\underline{CH_2}CH_2C_6F_{13}$), 3.66 (m, 12H, 3 × $O\underline{CH_2}\underline{CH_2}$), 3.83 (dm, 4H, 2 × $O\underline{CH_2}CH{=}CH$, $^3J_{HH}$ = 7.80 Hz, *ZZ* isomer), 4.01 (m, 2H, 2 × $O\underline{CH_2}CH{=}CH$, *EE* isomer), 4.31 (m, 2H, 2 × $OCH_2\underline{CH}{=}CH$, *EE* isomer), 4.59 (dt, 2H, 2 × $OCH_2\underline{CH}{=}CH$, $^3J_{HH}$ = 5.88 Hz, *ZZ* isomer), 6.46 (dm, 2H, 2 × $CH_2CH{=}\underline{CH}SO$, $^3J_{HH}$ = 5.89 Hz, *ZZ* isomer), 6.87 (dm, 2H, 2 × $OCH_2CH{=}\underline{CH}SO$, $^3J_{HH}$ = 18.46 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.75 (t, $CH_2\underline{CH_2}C_6F_{13}$, $^2J_{C\text{-}F}$ = 25.05Hz), 45.98 (s, $SO\underline{CH_2}CH_2C_6F_{13}$), 70.45 (m, $(O\underline{CH_2}\underline{CH_2})_3$), 92.12 (s, $O\underline{CH_2}CH{=}CH$), 110.21–121.20 (m, $\underline{C_6F_{13}}$), 127.11 (s, $OCH_2CH{=}\underline{CH}SO$, *ZZ* isomer), 147.08 (s, $OCH_2CH{=}\underline{CH}SO$, *EE* isomer), 152.09 (s, $OCH_2\underline{CH}{=}CH$); ^{19}F NMR

[$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.80 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.43 Hz), −114.75 (m, 2F, $CF_{2\alpha}$), −122.85 (m, 2F, $CF_{2\beta}$), −123.86 (m, 2F, $CF_{2\gamma}$) −124.23 (m, 2F, $CF_{2\delta}$) −127.15 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{28}H_{28}F_{26}O_6S_2$: C, 33.02; H, 2.77. Found: C, 32.63; H, 2.49%.

Tetraethylene glycol di[3-((2-*F*-hexylethyl)sulfinyl)allyl]ether (2d). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.62 (m, 4H, 2 × $CH_2CH_2C_6F_{13}$), 3.32 (m, 4H, 2 × $CH_2CH_2C_6F_{13}$), 3.68 (m, 4H, 2 × $OCH_2CH{=}CH$, *EE* isomer), 3.72 (m, 16H, 4 × (OCH_2CH_2)), 3.96 (m, 4H, 2 × $OCH_2CH{=}CH$, *ZZ* isomer), 4.29 (dm, 2H, 2 × $OCH_2CH{=}CH$, $^3J_{HH}$ = 16.28 Hz, *EE* isomer), 4.65 (m, 2H, 2 × $OCH_2CH{=}CH$, *ZZ* isomer), 6.42 (dm, 2H, 2 × $CH_2CH{=}CHSO$, $^3J_{HH}$ = 12.01 Hz, *ZZ* isomer), 6.86 (dm, 2H, 2 × $CH_2CH{=}CHSO$, $^3J_{HH}$ = 16.49 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.42 (t, $CH_2CH_2C_6F_{13}$, $^2J_{C\text{-}F}$ = 25.05 Hz), 42.13 (s, $SOCH_2CH_2C_6F_{13}$), 70.63 (m, $(OCH_2CH_2)_4$), 110.21–121.20 (m, C_6F_{13}), 152.86 (s, $OCH_2CH{=}CH$), 92.03 (s, $OCH_2CH{=}CH$), 147.22 (s, $OCH_2CH{=}CHSO$, *EE* isomer), 128.06 (s, $OCH_2CH{=}CHSO$, *ZZ* isomer); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.86 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.06 Hz), −114.53 (m, 2F, $CF_{2\alpha}$), −122.96 (m, 2F, $CF_{2\beta}$), −123.35 (m, 2F, $CF_{2\gamma}$) −124.14 (m, 2F, $CF_{2\delta}$) −126.42 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{30}H_{32}F_{26}O_7S_2$: C, 33.91; H, 3.04. Found: C, 33.87; H, 3.01%.

Pentaethylene glycol di[3-((2-*F*-hexylethyl)sulfinyl)allyl]ether (2e). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.61 (m, 4H, 2 × $CH_2CH_2C_6F_{13}$), 3.32 (m, 4H, 2 × $CH_2CH_2C_6F_{13}$), 3.69 (m, 20H, $CH_2(OCH_2CH_2)OCH_2$), 4.31 (dm, 2H, 2 × $OCH_2CH{=}CH$, $^3J_{HH}$ = 16.28 Hz, *EE* isomer), 4.65 (dm, 2H, 2 × $OCH_2CH{=}CH$, $^3J_{HH}$ = 5.88 Hz, *ZZ* isomer), 6.58 (dm, 2H, 2 × $CH_2CH{=}CHSO$, $^3J_{HH}$ = 6.08 Hz, *ZZ* isomer), 6.86 (dm, 2H, 2 × $CH_2CH{=}CHSO$, $^3J_{HH}$ = 16.12 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.90 (t, $CH_2CH_2C_6F_{13}$, $^2J_{C\text{-}F}$ = 25.05 Hz), 42.43 (s, $SOCH_2CH_2C_6F_{13}$), 70.51 (m, $(OCH_2CH_2)_5$), 92.03 (s, $OCH_2CH{=}CH$), 110.21–121.20 (m, C_6F_{13}), 128.06 (s, $OCH_2CH{=}CHSO$, *ZZ* isomer), 152.09 (s, $OCH_2CH{=}CH$), 144.32 (s, $OCH_2CH{=}CHSO$, *EE* isomer); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.82 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.26 Hz), −114.47 (m, 2F, $CF_{2\alpha}$), −122.85 (m, 2F, $CF_{2\beta}$), −123.86 (m, 2F, $CF_{2\gamma}$) −124.10 (m, 2F, $CF_{2\delta}$) −127.14 (m, 2F, $CF_2\omega$); Anal. calcd for $C_{32}H_{36}F_{26}O_8S_2$: C, 34.73; H, 3.28. Found: C, 34.69; H, 3.23%.

Ethylene glycol di[3-((2-*F*-octylethyl)sulfinyl)allyl]ether (2f). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.56 (m, 4H, 2 × $CH_2CH_2C_8F_{17}$), 3.29 (m, 4H, 2 × $CH_2CH_2C_8F_{17}$), 3.68 (m, 4H, OCH_2CH_2), 3.86 (m, 4H, 2 × $OCH_2CH{=}CH$, *EE* isomer), 4.05 (m, 4H, 2 × $OCH_2CH{=}CH$, *ZZ* isomer), 4.39 (dm, 2H, 2 × $OCH_2CH{=}CH$, $^3J_{HH}$ = 15.17 Hz, *EE* isomer), 4.70 (m, 2H, 2 × $OCH_2CH{=}CH$, *ZZ* isomer), 6.50 (m, 2H, 2 × $CH_2CH{=}CHSO$, *ZZ* isomer), 6.72 (dm, 2H, 2 × $CH_2CH{=}CHSO$, $^3J_{HH}$ = 15.83 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.78 (t, $CH_2CH_2C_8F_{17}$, $^2J_{C\text{-}F}$ = 25.05 Hz), 42.83 (s, $SOCH_2CH_2C_8F_{17}$), 70.72 (m, OCH_2CH_2), 92.03 (s, $OCH_2CH{=}CH$), 129.45 (m, C_8F_{17}), 130.06 (s, $OCH_2CH{=}CHSO$, *ZZ* isomer), 151.88 (s, $OCH_2CH{=}CH$), 145.03 (s, $OCH_2CH{=}CHSO$, *EE* isomer); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.87 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.43 Hz), −114.53 (m, 2F, $CF_{2\alpha}$), −122.81 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.56 (m, 2F, $CF_{2\varepsilon}$) −124.12 (m, 2F, $CF_{2\xi}$) −127.11 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{28}H_{20}F_{34}O_4S_2$: C, 29.75; H, 2.53. Found: C, 29.99; H, 2.48%.

Diethylene glycol di[3-(2-*F*-octylethyl)sulfinyl)allyl]ether (2g). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.65 (m, 4H, 2 × $CH_2CH_2C_8F_{17}$), 3.30 (m, 4H, 2 × $CH_2CH_2C_8F_{17}$), 3.70 (m, 8H, 2 × OCH_2CH_2), 3.68 (m, 4H, 2 × $OCH_2CH{=}CH$, *EE* isomer), 4.05 (m, 4H, 2 × $OCH_2CH{=}CH$, *ZZ* isomer), 4.40 (dm, 2H, 2 × $OCH_2CH{=}CH$, $^3J_{HH}$ = 13.62 Hz, *EE* isomer), 4.65 (m, 2H, 2 × $OCH_2CH{=}CH$, *ZZ* isomer), 6.50 (m, 2H, 2 × $OCH_2CH{=}CHSO$, *ZZ* isomer), 6.70 (dm, 2H, 2×$CH_2CH{=}CHSO$,

$^3J_{HH}$ = 13.01 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.77 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^2J_{C\text{-}F}$ = 25.05 Hz), 42.37 (s, $SO\underline{C}H_2CH_2C_8F_{17}$), 70.44 (m, $O\underline{C}H_2\underline{C}H_2$), 120.45 (m, $\underline{C}_8F_{17}$), 151.06 (s, $OCH_2\underline{C}H{=}CH$), 92.12 (s, $O\underline{C}H_2CH{=}CH$), 140.13 (s, $OCH_2CH{=}\underline{C}H$, *EE* isomer), 129.38 (s, $OCH_2CH{=}\underline{C}H$, *ZZ* isomer); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.85 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.43 Hz), −114.78 (m, 2F, $CF_{2\alpha}$), −122.69 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.77 (m, 2F, $CF_{2\varepsilon}$) −124.16 (m, 2F, $CF_{2\xi}$) −127.18 (m, 2F, $CF_{2\omega}$). Anal. calcd for $C_{30}H_{24}F_{34}O_5S_2$: C, 30.68; H, 1.78. Found: C, 30.95; H, 1.47%.

Triethylene glycol di[3-((2-*F*-octylethyl)sulfinyl)allyl]ether (2h). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.52 (m, 4H, 2 × $CH_2\underline{C}H_2C_8F_{17}$), 3.22 (m, 4H, 2 × $C\underline{H}_2CH_2C_8F_{17}$), 3.65 (m, 12H, 3 × $OC\underline{H}_2\underline{C}H_2$), 3.72 (m, 4H, 2 × $OC\underline{H}_2CH{=}CH$, *EE* isomer), 3.91 (m, 4H, 2 × $OC\underline{H}_2CH{=}CH$, *ZZ* isomer), 4.31 (dm, 2H, 2 × $OCH_2C\underline{H}{=}CH$, $^3J_{HH}$ = 13.01 Hz, *EE* isomer), 4.90 (m, 2H, 2 × $OCH_2C\underline{H}{=}CH$, *ZZ* isomer), 6.50 (m, 2H, 2 × $OCH_2CH{=}C\underline{H}SO$, *ZZ* isomer), 6.73 (dm, 2H, 2 × $CH_2CH{=}C\underline{H}SO$, $^3J_{HH}$ = 13.68 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.62 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^2J_{C\text{-}F}$=26.63 Hz), 42.74 (s, $SO\underline{C}H_2CH_2C_8F_{17}$), 70.63 (m, $(O\underline{C}H_2\underline{C}H_2)_3$), 92.33 (s, $O\underline{C}H_2CH{=}CH$), 122.38 (s, $OCH_2CH{=}\underline{C}HSO$, *ZZ* isomer), 125.45 (m, $\underline{C}_8F_{17}$), 144.33 (s, $OCH_2CH{=}\underline{C}HSO$, *EE* isomer), 149.93 (s, $OCH_2\underline{C}H{=}CH$); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.83 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.72 Hz), −113.99 (m, 2F, $CF_{2\alpha}$), −122.96 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.74 (m, 2F, $CF_{2\varepsilon}$) −124.32 (m, 2F, $CF_{2\xi}$) −127.23 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{32}H_{28}F_{34}O_6S_2$: C, 31.54; H, 2.32. Found: C, 31.96; H, 2.65%.

Tetraethylene glycol di[3-((2-*F*-octylethyl)sulfinul)allyl]ether (2i). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.50 (m, 4H, 2 × $CH_2\underline{C}H_2C_8F_{17}$), 3.32 (m, 4H, 2 × $C\underline{H}_2CH_2C_8F_{17}$), 3.69 (m, 16H, 4 × $(OC\underline{H}_2\underline{C}H_2)$), 3.72 (m, 4H, 2 × $OC\underline{H}_2CH{=}CH$, *ZZ* isomer), 3.98 (m, 4H, 2 × $OC\underline{H}_2CH{=}CH$, *EE* isomer), 4.71 (dm, 2H, 2 × $OCH_2C\underline{H}{=}CH$, $^3J_{HH}$=13.66 Hz, *EE* isomer), 5.10 (m, 2H, 2 × $OCH_2C\underline{H}{=}CH$, *ZZ* isomer), 6.51 (m, 2H, 2 × $CH_2CH{=}C\underline{H}SO$, *ZZ* isomer), 6.86 (dm, 2H, 2 × $CH_2CH{=}C\underline{H}SO$, $^3J_{HH}$ = 14.02 Hz, *EE* isomer); ^{13}C NMR: 29.30 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^2J_{C\text{-}F}$ = 25.33 Hz), 45.23 (s, $SO\underline{C}H_2CH_2C_8F_{17}$), 70.62 (m, $(O\underline{C}H_2\underline{C}H_2)_4$), 129.03 (m, $\underline{C}_8F_{17}$), 150.82 (s, $OCH_2\underline{C}H{=}CH$), 91.82 (s, $O\underline{C}H_2CH{=}CH$), 142.33 (s, $CH_2CH{=}\underline{C}HSO$, *EE* isomer), 132.26 (s, $OCH_2CH{=}\underline{C}HSO$, ZZ isomer); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.56 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.86 Hz), −112.35 (m, 2F, $CF_{2\alpha}$), −122.73 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.74 (m, 2F, $CF_{2\varepsilon}$) −124.43 (m, 2F, $CF_{2\xi}$) −127.11 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{34}H_{32}F_{34}O_7S_2$: C, 32.34; H, 2.55. Found: C, 32.59; H, 2.62%.

Pentaethylene glycol di[3-((2-*F*-octylethyl)sulfinyl)allyl]ether (2j). ^{1}H NMR [$CDCl_3$, δ (ppm/TMS)]: 2.70 (m, 4H, 2 × $CH_2\underline{C}H_2C_8F_{17}$), 3.30 (m, 4H, 2 × $C\underline{H}_2CH_2C_8F_{17}$), 3.68 (m, 20H, 5 × $(OC\underline{H}_2\underline{C}H_2)$), 3.86 (m, 4H, 2 × $OC\underline{H}_2CH{=}CH$, *EE* isomer), 4.01 (m, 4H, 2×$OC\underline{H}_2CH{=}CH$, *ZZ* isomer), 4.63 (dm, 2H, 2 × $OCH_2C\underline{H}{=}CH$, $^3J_{HH}$=11.45 Hz, *EE* isomer), 5.01 (m, 2H, 2 × $OCH_2C\underline{H}{=}CH$, *ZZ* isomer), 6.43 (m, 2H, 2 × $CH_2CH{=}C\underline{H}SO$, *ZZ* isomer), 6.50 (dm, 2H, 2 × $CH_2CH{=}C\underline{H}SO$, $^3J_{HH}$ = 12.02 Hz, *EE* isomer); ^{13}C-{^{1}H} NMR: 29.49 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^2J_{C\text{-}F}$ = 25.12 Hz), 42.25 (s, $SO\underline{C}H_2CH_2C_8F_{17}$), 70.66 (m, $(O\underline{C}H_2\underline{C}H_2)_5$), 92.06 (s, $O\underline{C}H_2CH{=}CH$), 110.03–127.23 (m, $\underline{C}_8F_{17}$), 131.32 (s, $OCH_2CH{=}\underline{C}HSO$, *ZZ* isomer), 141.32 (s, $OCH_2CH{=}\underline{C}HSO$, *EE* isomer), 152.04 (s, $OCH_2\underline{C}H{=}CH$); ^{19}F NMR [$CDCl_3$, δ (ppm/$CFCl_3$)]: −81.82 (t, 3F, CF_3, $^3J_{F\text{-}F}$ = 9.26 Hz), −114.47 (m, 2F, $CF_{2\alpha}$), −122.85 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.86 (m, 2F, $CF_{2\varepsilon}$) −124.10 (m, 2F, $CF_{2\xi}$) −127.15 (m, 2F, $CF_{2\omega}$); Anal. calcd for $C_{36}H_{36}F_{34}O_8S_2$: C, 33.09; H, 2.78. Found: C, 32.90; H, 2.47%.

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