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Stereoselective synthesis of fluorobis(phenylsulfonyl)methyl-substituted alkenes using free radical fluoroalkylation

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ABSTRACT

$(PhSO_2)_2CFI$ was prepared in quantitative yield by the iodination of fluorobis(phenylsulfonyl)methane and utilized in facile radical bis(phenylsulfonyl)monofluoromethylation of various terminal alkenes. The synthetic methodology was further extended for the preparation of monofluoromethyl-substituted alkenes.

1. Introduction

Fluorocarbon molecules possess unique properties leading to their use in various facets of life [1]. The inductive effect, the enhancement of metabolic stability and drastic change in binding affinity and selectivity are major advantages of introducing fluorine into a drug molecule [2]. This in turn reflects in better lipophilicity, improved bioavailability and modulated physiochemical properties. Its presence has emerged to about 20% in the drug market including half of the top 10 drugs sold in 2005 over the past 50 years. This big leap can be attributed to better understanding of "fluorine effects" in drug research and also to novel methodologies to introduce fluorine in various organic molecules. Compounds with monofluoromethyl group carry significant importance in biological systems. Monofluoroacetic acid is a lethal inhibitor for the Kreb's cycle. Sevoflurane, a new generation of monofluoromethyl anesthetics has fast uptake and elimination properties [3]. Various groups have reported methods to introduce monofluoromethyl group in organic molecules using different approaches [4]. Our group has focused on developing novel fluorinating and fluoroalkylating agents for many years [5]. We recently reported a novel methodology to introduce monofluoromethyl group by Mitsunobu reaction of primary and secondary alcohols [4] and also developed a new electrophilic reagent, which can transfer "CH_2F^+" to various nucleophiles [6]. Besides electrophilic and nucleophilic pathways, radical reaction routes are also of substantial interest. Radical hydroperfluoroalkylation of alkenes using perfluoroalkyl halides was reported using copper powder, $Pd(PPh_3)_4$ and Na_2SO_4 [7]. Hu and co-workers reported the radical (phenylsulfonyl)difluoromethylation of terminal alkenes [8]. Till now, to the best of our knowledge, no report exists on radical bis(phenylsulfonyl)monofluoromethylation. In our continuing effort on fluoroalkylation, we report now the synthesis of fluoroiodobis(phenylsulfonyl)methane and its use in the radical fluoromethylation of terminal alkenes for the preparation of monofluoromethyl-substituted alkanes and alkenes.

2. Results and discussion

We have previously carried out iodination of phenylsulfonyldifluoromethane in excellent yields using potassium *t*-butoxide as the base [9]. Fluorobis(phenylsulfonyl)methane is recognized as the synthetic equivalent of monofluoromethide species and it can be easily deprotonated using a milder base such as cesium carbonate in acetonitrile. Even potassium carbonate in dimethylformamide is a suitable system to facilitate the deprotonation. Fluoroiodobis(phenylsulfonyl)methane was prepared from fluorobis(phenylsulfonyl)methane using iodine in the presence of cesium carbonate in excellent yield (Scheme 1).

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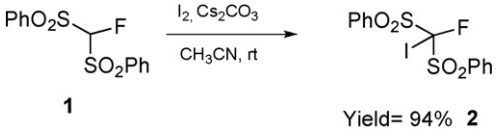
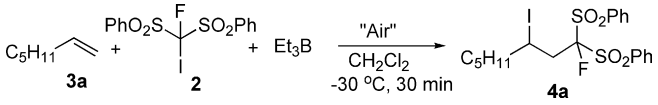


Scheme 1. Preparation of fluoroiodobis(phenylsulfonyl)methane.

Table 1
Optimization of reaction conditions



Entry	Et_3B (equiv.)	Molar ratio (**3a**:**2**)	Conditions [a]	Yield (%)[b]
1	1	2	A	33
2	3	2	A	27
3	1	2	B	40
4	0.33	2	C	56
5	1	2	C	60

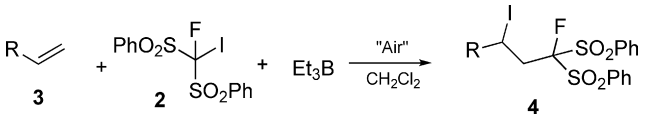
[a] Condition A: bubbling compressed air through the reaction mixture. Condition B: bubbling air through the reaction mixture. Condition C: reaction is done under air blanket.
[b] Isolated yields.

After establishing an easy and efficient preparation of **2**, we explored its free radical bis(phenylsulfonyl)monofluoromethylation of terminal alkenes using triethylborane and air to initiate the reaction. Triethylborane has been extensively used in asymmetric radical reactions at low temperatures [10]. We explored various conditions using 1-heptene as the model system and found that the reaction gave the best yield when carried out under an air blanket using 1 equiv. of the initiator relative to **2** [7] (Table 1).

After establishing the optimal conditions for the reaction, we reacted various terminal alkenes to generate their corresponding adducts in moderate to good yields. The reactions were monitored using ^{19}F NMR and found to be completed in less than 30 min. The reaction was found to be applicable towards alkenes bearing ketones, esters and silyl groups. However, in the case of nitriles, hydroxyl groups and ethers, the reaction was non-selective and gave multiple products. Styrene and dienes were found to be sluggish towards the radical reaction and the desired products were isolated only in minor amounts (Table 2).

It has been reported that tributyltinhydride can be used for deiodination reaction to generate the corresponding alkanes from the iodoalkanes [9]. In our case, the use of neither Bu_3SnH nor tris(trimethylsilyl)silyl hydride was successful in generating bis(phenylsulfonyl)monofluoromethyl-substituted alkanes. The

Table 2
Reaction of terminal alkenes using triethylborane



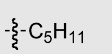
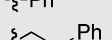
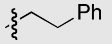
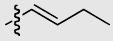
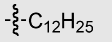
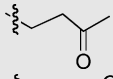
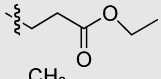
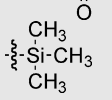
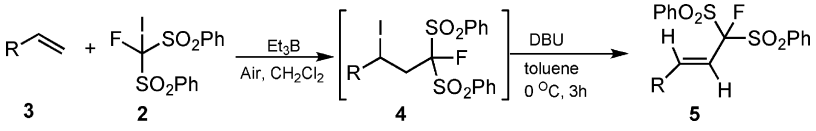
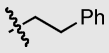
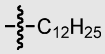
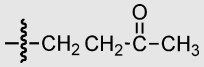
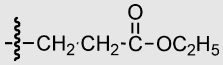
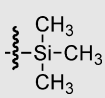
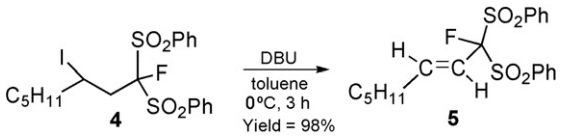
Entry	R	Products	Isolated yield (%)
1		**4a**	60
2		**4b**	15
3		**4c**	75
4		**4d**	15
5		**4e**	69
6		**4f**	70
7		**4g**	40
8		**4h**	71

Table 3
Stereoselective synthesis of bis(phenylsulfonyl)monofluoromethyl-substituted alkenes



Entry	R	Products	Yield (%)[a]
1		**5a**	60
2		**5b**	63
3		**5c**	68
4		**5d**	63
5		**5e**	38
6		**5f**	64

[a] Isolated yields.



Scheme 2. Stereoselective synthesis of bis(phenylsulfonyl)monofluoromethyl-substituted alkenes.

adducts from the radical reaction, however, underwent facile dehydroiodination using 1,5-diazabicyclo[4,3,0]non-5-ene (DBU) to generate stereoselectively the bis(phenylsulfonyl)monofluoromethyl-substituted alkenes in high yields (Scheme 2).

Encouraged by this result, we also investigated a one-pot stereoselective synthesis of bis(phenylsulfonyl)monofluoromethyl-substituted alkenes starting from terminal alkenes. After completion of the first addition step, the second HI elimination step can be indeed carried out in one pot without isolation of the intermediate adduct **4**. After screening various conditions, we found that DBU in toluene at 0 °C gave the desired alkenes in good to moderate overall yields. The reaction is found to be compatible with functionalities such as ketones, esters and silyl groups (Table 3).

3. Conclusions

We report the preparation of fluoroiodobis(phenylsulfonyl)-methane and its use for the radical addition to terminal alkenes. The adducts undergo dehydroiodination to provide the *E* isomers of bis(phenylsulfonyl)monofluoromethyl-substituted alkenes in preparatively acceptable yields in the presence of DBU. This methodology is found to be compatible with ketones, esters and silyl functional groups.

4. Experimental

4.1. General

Unless otherwise mentioned, all reagents were purchased from commercial sources. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian Mercury-400 NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to the ^{13}C signal of the solvent: $CDCl_3$ (77.16 ppm). $CFCl_3$ was used as internal standard for ^{19}F NMR. High-resolution mass spectra were recorded in EI+ or FAB+ mode on a high-resolution mass spectrometer.

4.2. Typical procedure for the preparation of fluoroiodobis(phenylsulfonyl)methane (2)

Into acetonitrile solution (20 mL) of bis(phenylsulfonyl)fluoromethane (**1**) Cs_2CO_3 (3.2 mmol) was added and stirred for 10 min. Subsequently, iodine (3.5 mmol) was added to the reaction mixture and stirred until all starting material was consumed based on ^{19}F NMR (20 min). The solvent was evaporated and the remaining material was dissolved in CH_2Cl_2 (10 mL) and it was washed with water (2× 20 mL), 10% $Na_2S_2O_3$ solution (2× 20 mL) and dried using $MgSO_4$. (The water washing should precede the washing with thiosulfate solution otherwise the starting material will be recovered.) After evaporation the pure bis(phenylsulfonyl)iodofluoromethane (**2**) was isolated in high yield.

4.3. Typical procedure for the radical addition of fluoroiodobis(phenylsulfonyl)methane with alkenes

A flask containing fluoroiodobis(phenylsulfonyl)methane (**2**) (0.3 mmol) and the alkene (**3**) (0.6 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and purged with pure air from a balloon. (Only the atmosphere of the flask was affected, the air was not bubbled into the solution.) Meanwhile the solution was cooled down to −30 °C and Et_3B solution (0.3 mmol, 1 M hexane solution) was added dropwise via syringe. The reaction mixture was stirred for additional 30 min at this temperature. After the removal of volatile solvents under vacuum, the crude product was purified by gradient silica gel column chromatography (Sorbent silica gel, 65–250 mesh) using hexane/ethyl acetate as the eluents to give the desired product **4**.

4.4. Typical one-pot procedure for the preparation of 1-fluoro-1,1-bis(phenylsulfonyl)alkenes

A flask containing bis(phenylsulfonyl)iodofluoromethane (**2**) (0.3 mmol) and the alkene (**3**) (0.6 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and was purged with pure air from a balloon. (Only the atmosphere of the flask was affected, the air was not bubbled into the solution.) Meanwhile the solution was cooled down to −30 °C and Et_3B solution (0.3 mmol, 1 M hexane solution) was added dropwise via syringe. The reaction mixture was stirred for additional 30 min at this temperature. After the removal of volatile solvents under vacuum the residue was dissolved in toluene (5 mL) and DBU (0.36 mmol) was added dropwise at 0 °C and the solution was stirred at this temperature for 3 h. After evaporation the remaining material was purified by gradient silica gel column chromatography (Sorbent silica gel, 65–250 mesh) using hexane/ethyl acetate as the eluents to give the desired product **5**.

4.5. Fluoroiodobis(phenylsulfonyl)methane (2)

^{1}H NMR ($CDCl_3$): 8.03 (m, 4H, J = 7.4 Hz), 7.77 (t, 2H, J = 7.5 Hz), 7.60 (m, 4H). ^{19}F NMR ($CDCl_3$): −110.56 (s, 1F). ^{13}C NMR ($CDCl_3$): 136.04, 133.09, 131.87, 129.26, 105.28 (d, $J_{(C-F)}$ = 337.8 Hz). HRMS calcd. for $C_{13}H_{11}FIO_4S_2$ 441.2628, found 441.2613.

4.6. 1-Fluoro-3-iodo-1,1-bis(phenylsulfonyl)octane (4a)

^{1}H NMR ($CDCl_3$): 7.94 (m, 4H), 7.76 (m, 2H), 7.60 (m, 4H), 4.46 (m, 1H), 3.21 (dd, 2H, J = 6.0 Hz, $J_{(H-F)}$ = 17 Hz) 1.65 (m, 2H), 1.26 (m, 6H), 0.88 (m, 3H). ^{19}F NMR ($CDCl_3$): −149.84 (t, 1F, $J_{(H-F)}$ = 17 Hz). ^{13}C NMR ($CDCl_3$): 135.72, 135.62, 134.56, 134.33, 131.10, 131.0, 129.41, 129.24, 114.78 (d, $J_{(C-F)}$ = 272.3 Hz), 40.95 (d, J = 1.8 Hz), 40.42 (d, J = 16.4 Hz), 30.71, 29.12, 24.86 (d, J = 3.4 Hz), 22.49, 14.11. HRMS calcd. for $C_{20}H_{25}O_4FS_2I$ 539.0223, found 539.0220.

4.7. 1-Fluoro-3-iodo-3-phenyl-1,1-bis(phenylsulfonyl)propane (4b)

^{1}H NMR ($CDCl_3$): 7.97 (m, 2H), 7.90 (m, 2H), 7.75 (m, 2H), 7.58 (m, 4H), 7.29 (m, 5H), 5.40 (dd, 1H, J = 2.1 Hz, J = 9.0 Hz), 2.86 (m, 1H), 2.71 (m, 1H). ^{19}F NMR ($CDCl_3$): −143.47 (dd, $J_{(H_B-F)}$ = 13.2 Hz, $J_{(H_A-F)}$ = 22.4 Hz). ^{13}C NMR ($CDCl_3$): 142.87, 135.74, 135.68, 134.93, 134.58, 131.27, 131.09, 129.40, 129.36, 128.80, 128.09, 125.62, 115.17 (d, $J_{(C-F)}$ = 268.0 Hz), 68.79 (d, J = 6.0 Hz), 40.77 (d, J = 16.5 Hz). HRMS calcd. for $C_{21}H_{19}FO_4S_2$ $(M-I)^+$ 417.0631, found 417.0648.

4.8. 1-Fluoro-3-iodo-5-phenyl-1,1-bis(phenylsulfonyl)pentane (4c)

^{1}H NMR ($CDCl_3$) 7.92 (d, 2H, J = 8.5 Hz), 7.84 (d, 2H, J = 8.5 Hz), 7.73 (m, 2H), 7.56 (m, 4H), 7.28 (m, 2H), 7.22 (m, 1H), 7.14 (m, 2H), 4.12 (m, 1H), 3.26 (m, 2H), 2.75 (m, 1H), 2.57 (m, 1H), 1.95 (m, 2H). ^{19}F NMR ($CDCl_3$): −149.39 (t, 1F, J = 16.6 Hz). ^{13}C NMR ($CDCl_3$): 140.1, 135.6, 135.5, 134.3, 134.1, 130.9, 130.8, 129.3, 129.1, 128.5,

128.4, 126.1, 114.6 (d, J = 272 Hz), 42.3, 40.2 (d, J = 16 Hz), 35.5, 23.7. HRMS calcd. for $C_{23}H_{23}O_4FS_2I$ 573.0067, found 573.0093.

4.9. 7-Fluoro-5-iodo-7,7-bis(phenylsulfonyl)hept-3-ene (**4d**)

^{1}H NMR ($CDCl_3$): 7.92 (d, 4H, J = 8.5 Hz), 7.73 (t, 2H, J = 7.5 Hz), 7.57 (m, 4H), 5.60 (m, 2H), 3.97 (m, 1H), 3.14 (m, 2H), 1.50 (m, 2H), 0.89 (m, 3H). ^{19}F NMR ($CDCl_3$): −142.27 (t, 1F, $J_{(H-F)}$ = 17.1 Hz). ^{13}C NMR ($CDCl_3$): 140.05, 139.04, 135.43, 135.38, 131.02, 129.19, 119.49, 119.43, 114.50 (d, $J_{(C-F)}$ = 267.3 Hz), 73.71, 33.49 (d, J = 18.9 Hz), 29.83, 9.71. HRMS calcd. for $C_{19}H_{20}FO_4S_2$ $(M-I)^+$ 395.0787, found 395.0790.

4.10. 1-Fluoro-3-iodo-1,1-bis(phenylsulfonyl)pentadecane (**4e**)

^{1}H NMR ($CDCl_3$): 7.94 (dd, 4H, J = 8.5 Hz, J = 17.8 Hz), 7.75 (dd, 2H, J = 7.2 Hz, J = 13.4 Hz), 7.60 (t, 4H, J = 7.3 Hz), 4.28 (m, 1H), 3.21 (dd, 2H, J = 6.1 Hz, $J_{(H-F)}$ = 16.9 Hz), 1.64 (m, 2H), 1.26 (m, 20H), 0.88 (t, 3H, J = 6.8 Hz). ^{19}F NMR ($CDCl_3$): −149.85 (t, 1F, $J_{(H-F)}$ = 16.8 Hz). ^{13}C NMR ($CDCl_3$): 135.73, 135.64, 134.4, 134.2, 131.17, 131.1, 129.44, 129.26, 114.79 (d, $J_{(C-F)}$ = 272.3 Hz), 41.05, 40.54, 40.37, 32.06, 29.79, 29.76, 29.68, 29.50, 28.62, 24.91 (d, J = 3.3 Hz), 22.84, 14.28. HRMS calcd. for $C_{27}H_{39}O_4FS_2I$ 637.1319, found 637.1317

4.11. 7-Fluoro-5-iodo-7,7-bis(phenylsulfonyl)heptan-2-one (**4f**)

^{1}H NMR ($CDCl_3$): 7.92 (t, 4H, J = 8.7 Hz), 7.76 (q, 2H, J = 7.3 Hz), 7.59 (t, 4H, J = 7.8 Hz), 4.35 (m, 1H), 3.21 (m, 2H), 2.56 (m, 2H), 2.14 (s, 3H), 2.00 (m, 1H), 1.90 (m, 1H). ^{19}F NMR ($CDCl_3$): −149.14 (t, 1F, $J_{(H-F)}$ = 16.8 Hz). ^{13}C NMR ($CDCl_3$): 206.78, 135.77, 135.72, 134.32, 134.26, 131.13, 131.10, 129.44, 129.31, 114.68 (d, $J_{(C-F)}$ = 272.5 Hz), 43.66, 40.42 (d, J = 16.4 Hz), 34.69 (d, J = 2.4 Hz), 30.19, 23.16 (d, J = 3.4 Hz). HRMS calcd. for $C_{19}H_{21}O_5FS_2I$ 538.9859, found 538.9847.

4.12. Ethyl-6-fluoro-4-iodo-6,6-bis(phenylsulfonyl)hexanoate (**4g**)

^{1}H NMR ($CDCl_3$): 7.94 (t, 4H), 7.76 (m, 2H), 7.59 (m, 4H), 4.37 (m, 1H), 4.13 (q, 2H, J = 7.2 Hz), 3.23 (m, 2H), 2.40 (m, 2H), 2.06 (m, 1H), 1.94 (m, 1H), 1.26 (t, 3H, J = 7.2 Hz). ^{19}F NMR ($CDCl_3$): −149.42 (t, $J_{(H-F)}$ = 16 Hz). ^{13}C NMR ($CDCl_3$): 172.14, 135.78, 135.72, 131.15, 131.13, 130.31, 129.63, 129.45, 129.31, 114.66 (d, $J_{(C-F)}$ = 272.2 Hz), 60.78, 40.48 (d, J = 16.4 Hz), 35.99, 34.64, 22.86, 14.33. HRMS calcd. for $C_{20}H_{23}O_6FS_2I$ 568.9965, found 568.9979.

4.13. 1-Fluoro-1,1-bis(phenylsulfonyl)-3-iodo-3-trimethylsilylpropane (**4h**)

^{1}H NMR ($CDCl_3$): 8.03 (d, 2H, J = 8.5 Hz), 7.82 (d, 2H, J = 8.5 Hz), 7.73 (td, 2H, J = 7.5 Hz, J = 20.8 Hz), 7.58 (td, 4H, J = 7.9 Hz, J = 14.0 Hz), 3.54 (ddd, 1H, J = 1.9 Hz, J = 17.8 Hz, $J_{(H-F)}$ = 24.6 Hz), 3.40 (dd, 1H, J = 1.9 Hz, J = 10.2 Hz), 2.76 (ddd, 1H, J = 3.1 Hz, J = 10.2 Hz, J = 17.8 Hz), 0.18 (s, 9H). ^{19}F NMR ($CDCl_3$): −151.76 (d, 1F, $J_{(H-F)}$ = 24.5 Hz). ^{13}C NMR ($CDCl_3$): 135.64, 135.49, 135.17, 133.44, 131.29, 131.15, 129.40, 129.05, 114.37 (d, $J_{(C-F)}$ = 273.4 Hz), 34.15 (d, J = 17.7 Hz), 6.06 (d, J = 3.2 Hz), −2.32. HRMS calcd. for $C_{18}H_{23}O_4FSiS_2I$ 540.9836, found 540.9841.

4.14. 1-Fluoro-1,1-bis(phenylsulfonyl)-oct-2-ene (**5a**)

^{1}H NMR ($CDCl_3$): 7.92 (m, 4H), 7.71 (m, 2H), 7.56 (m, 4H), 5.98 (ddt, 1H, J = 1.4 Hz, $J_{(H-H)}$ = 15.6 Hz, $J_{(H-F)}$ = 22.2 Hz), 5.83 (dt, 1H, J = 7.1 Hz, $J_{(H-H)}$ = 15.5 Hz), 2.51 (m, 2H), 1.23 (m, 4H), 1.08 (m, 2H), 0.83 (m, 3H). ^{19}F NMR ($CDCl_3$): −150.67 (d, $J_{(H-F)}$ = 22.2 Hz). ^{13}C NMR ($CDCl_3$): 144.48, 144.39, 135.29, 135.12, 130.96, 128.96, 114.43, 114.29, 113.23 (d, $J_{(C-F)}$ = 267 Hz), 32.66, 31.13, 27.79, 22.46, 14.03. HRMS calcd. for $C_{20}H_{24}FO_4S_2$ 411.1100, found 411.1110.

4.15. 1-Fluoro-5-phenyl-1,1-bis(phenylsulfonyl)pent-2-ene (**5b**)

^{1}H NMR ($CDCl_3$): 7.90 (d, 4H, J = 8.1 Hz), 7.72 (t, 2H, J = 7.5 Hz), 7.55 (t, 4H, J = 8.0 Hz), 7.28 (m, 2H), 7.22 (m, 1H), 7.05 (d, 2H, J = 7.3 Hz), 6.06 (dd, 1H, $J_{(H-H)}$ = 15.6 Hz, $J_{(H-F)}$ = 22.4 Hz), 5.88 (td, 1H, J = 6.6 Hz, $J_{(H-H)}$ = 15.6 Hz), 2.51 (t, 2H, J = 7.7 Hz), 2.35 (dd, 2H, J = 7.1 Hz, J = 14.3 Hz). ^{19}F NMR ($CDCl_3$): −150.97 (d, $J_{(H-F)}$ = 22.3 Hz). ^{13}C NMR ($CDCl_3$): 143.16, 143.08, 140.51, 135.42, 135.11, 131.08, 129.22, 129.06, 128.52, 126.44, 115.23, 115.09, 113.36 (d, $J_{(C-F)}$ = 267 Hz), 34.43, 34.36. HRMS calcd. for $C_{23}H_{22}O_4FS_2$ 445.0944, found 445.0934.

4.16. 1-Fluoro-1,1-bis(phenylsulfonyl)pentadec-2-ene (**5c**)

^{1}H NMR ($CDCl_3$): 7.93 (d, 4H, J = 8.4 Hz), 7.71 (t, 2H, J = 7.5 Hz), 7.56 (t, 4H, J = 7.9 Hz), 5.98 (dd, 1H, $J_{(H-H)}$ = 15.7 Hz, $J_{(H-F)}$ = 22.5 Hz), 5.81 (dt, 1H, J = 6.8 Hz, $J_{(H-H)}$ = 15.7 Hz), 2.01 (dd, 2H, J = 6.8 Hz, J = 13.7 Hz), 1.26 (m, 20H), 0.88 (t, 3H, J = 6.8 Hz). ^{19}F NMR ($CDCl_3$): −150.68 (d, $J_{(H-F)}$ = 22.5 Hz). ^{13}C NMR ($CDCl_3$): 144.44, 144.36, 135.26, 135.06, 130.91, 128.93, 114.40, 114.26, 113.31 (d, $J_{(C-F)}$ = 266.9 Hz), 32.69, 32.01, 29.77, 29.74, 29.73, 29.57, 29.45, 29.43, 29.00, 28.11, 22.79, 14.24. HRMS calcd. for $C_{27}H_{38}O_4FS_2$ 509.2196, found 509.2213.

4.17. 7-Fluoro-7,7-bis(phenylsulfonyl)-hept-6-en-2-one (**5d**)

^{1}H NMR ($CDCl_3$): 7.92 (d, 4H, J = 8.4 Hz), 7.73 (t, 2H, J = 7.5 Hz), 7.57 (t, 4H, J = 8.0 Hz), 6.02 (tdd, 1H, J = 1.4 Hz, $J_{(H-H)}$ = 15.6 Hz, $J_{(H-F)}$ = 22.2 Hz), 5.82 (td, 1H, J = 6.6 Hz, $J_{(H-H)}$ = 15.7 Hz), 2.39 (t, 2H, J = 6.9 Hz), 2.28 (dd, 2H, J = 6.7 Hz, J = 13.7 Hz), 2.10 (s, 3H). ^{19}F NMR ($CDCl_3$): −150.83 (d, 1F, $J_{(H-F)}$ = 22.3 Hz). ^{13}C NMR ($CDCl_3$): 206.54, 142.35, 142.26, 135.36, 134.94, 130.96, 128.99, 115.45, 115.27, 113.17 (d, $J_{(C-F)}$ = 267.2 Hz), 41.38, 30.05, 26.39. HRMS calcd. for $C_{19}H_{20}FO_5S_2$ 411.0736, found 411.0733.

4.18. Ethyl-6-fluoro-6,6-bis(phenylsulfonyl)hex-2-enoate (**5e**)

^{1}H NMR ($CDCl_3$): 7.92 (d, 4H, J = 7 Hz), 7.30 (t, 2H, J = 7 Hz), 7.57 (t, 4H, J = 8 Hz), 6.05 (dd, 1H, J = 23 Hz, $J_{(H-H)}$ = 15.8 Hz), 5.40 (m, 1H), 4.13 (q, 2H, J = 7 Hz), 2.36 (m, 2H), 2.23 (m, 2H), 1.26 (m, 3H). ^{19}F NMR ($CDCl_3$): −150.83 (t, 1F, $J_{(H-F)}$ = 22.5 Hz). ^{13}C NMR ($CDCl_3$): 172.04, 141.78, 141.69, 135.37, 134.93, 130.98, 128.98, 115.82, 115.68, 113.13 (d, $J_{(C-F)}$ = 267 Hz), 60.84, 32.44, 27.7, 14.29. HRMS calcd. for $C_{20}H_{22}FO_6S_2$ 441.0842, found 441.0841.

4.19. 1-Fluoro-1,1-bis(phenylsulfonyl)-3-trimethylsilylprop-2-ene (**5f**)

^{1}H NMR ($CDCl_3$): 7.91 (td, 4H, J = 1.1 Hz, J = 8.6 Hz), 7.71 (t, 2H, J = 7.5 Hz), 7.55 (dd, 4H, J = 7.5 Hz, J = 8.1 Hz), 6.42 (dd, 1H, $J_{(H-H)}$ = 19.0 Hz, $J_{(H-F)}$ = 20.2 Hz), 6.05 (d, 1H, $J_{(H-H)}$ = 19.0 Hz), −0.05 (s, 9H). ^{19}F NMR ($CDCl_3$): −151.65 (d, 1F, $J_{(H-F)}$ = 20.3 Hz). ^{13}C NMR ($CDCl_3$): 144.65, 144.61, 135.35, 135.03, 130.95, 130.94, 128.92, 128.18, 128.01, 112.97 (d, $J_{(C-F)}$ = 266.8 Hz), −1.94. HRMS calcd. for $C_{18}H_{22}FO_4S_2Si$ 413.0713, found 413.0710.

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