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Efficient synthesis of α-(fluoro/chloro/methoxy)disulfonylmethane derivatives as tunable substituted methyl synthons via a new C–S bond forming strategy

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ABSTRACT

A new synthetic protocol for the preparation of α-fluoro(disulfonyl)methane and its chloro as well as methoxy analogues has been developed. Due to the synthetic utility of α-fluoro(bisphenylsulfonyl)-methane (FBSM) as a versatile synthon in the preparation of various useful fluoromethylated organic molecules, search for an easy and economic for its preparation route has been essential. The C–S bond forming strategy is utilized in this new synthetic approach, which can be applied to a variety of substrates with high efficiency and selectivity.

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1. Introduction

Sulfone-based organic compounds are widely used for the introduction of synthetically useful building blocks as well as bioactive functionalities [1]. In particular, arylsulfonylmethane derivatives have been extensively utilized in modern organic chemistry as methyl synthons [2]. Sulfonyl, a strong electron-withdrawing group, is capable of activating sp^3-hybridized C–H bond by significantly increasing the acidity of the proton. Successive substitution of protons with methyl sulfonyl groups in a methane molecule leads to pK_a values of the corresponding derivatives in water to 29, 12 and 0, respectively [3]. The resulting carbon-acids can be readily used as tunable pronucleophiles in many organic reactions [2]. On the other hand, further transformations of sulfonyl group can be achieved via a variety of methods compatible with different functional groups [4].

Incorporation of fluoromethyl groups into organic molecules has significant attention in pharmaceutical arena due to their profound influence on physical and biological properties of the molecules [5]. In recent years, phenylsulfonyl functionalized fluoromethylation reagents and related methodologies have been developed by Prakash, Hu, Shibata, and many others as highly selective and efficient fluoromethylation protocols in organo-fluorine chemistry [6]. The presence of phenylsulfonyl group in these fluoromethylation reagents can essentially suppress the α-elimination of fluoride from the corresponding carbanions and increase the thermodynamic stability of these species by delocalizing the negative charge [7]. Among these elegant reagents, α-fluorobis(phenylsulfonyl)methane (FBSM) and its analogues have been used as efficient monofluoromethyl equivalents in various transformations [6d–l]. Although FBSM has been successfully applied in numerous reactions, it is still not an easily available reagent due to the practical difficulties of its preparation. Our continuing efforts on using FBSM and its derivatives as fluoromethyl synthons have lead to a convenient synthesis of fluoro(disulfonyl)methanes as well as the chlorinated and methoxylated analogues.

Fluoro(disulfonyl)methanes were first synthesized in 1998 by Wickiser et al. as anthelmintic and insecticidal active compounds via C–F bond forming reaction between Selectfluor® and disulfonylmethide anions [8]. Realizing the potential applications of fluoro(disulfonyl)methanes in organic synthesis, FBSM was utilized by Shibata, Hu and Prakash as an efficient nucleophilic fluoromethylation reagent [6d–l]. Recently, Nagura and Fuchigami described the electrochemical reaction between NEt_4F-4HF and phenyl phenylsulfonylmethyl sulfide ($PhSO_2CH_2SPh$) to afford FBSM in 52% yield [9]. However, the major problems of the synthetic routes involving the C–F bond formation are: (a) the fluorine sources are expensive or highly hazardous; (b) the reactions can only afford the products in moderate yield (50–70%); (c) the selectivity of the reactions is unsatisfactory due to the formation of mixtures of compounds; (d) the separation,

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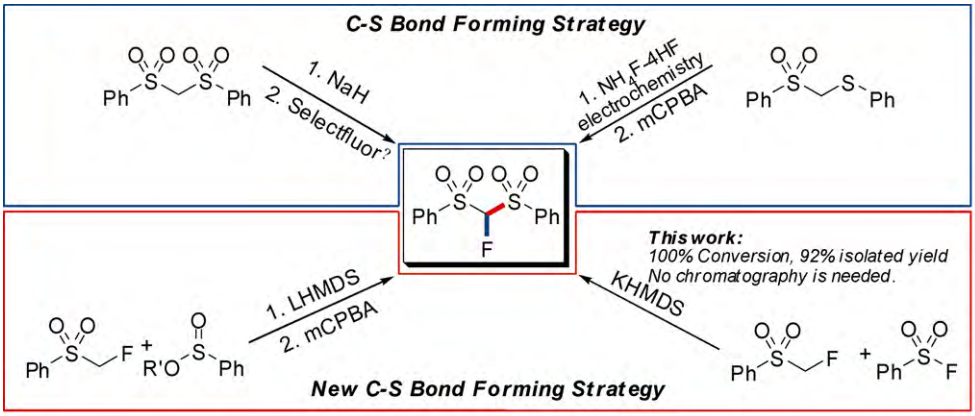


Scheme 1. Synthesis of fluorobis(phenylsulfonyl)methane (FBSM) by (a) C–F bond forming strategy and (b) C–S bond forming strategy.

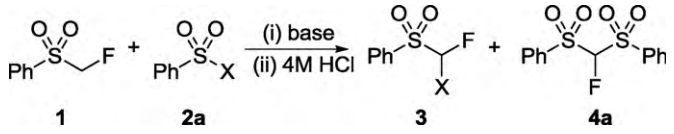
including chromatographic process, limits the application of these reactions.

Lately, Hu et al. disclosed the synthesis of FBSM by the treatment of $PhSO_2CH_2F$ with methyl benzenesulfinate followed by the oxidation using *m*-chloroperoxybenzoic acid (mCPBA) (Scheme 1) [10]. The synthetic route is a practical method for the preparation of α-fluoro(disulfonyl)methane derivatives via a "C–S bond forming strategy" instead of the conventional C–F bond forming processes. By this methodology the problems mentioned above were successfully eliminated, and the products can be obtained in high selectivity and excellent yield. However, the employed sulfinates are less available, which also introduces an additional step in the preparation. Shank et al., on the other hand, have reported the synthesis of methoxy(disulfonyl)methanes by the C–S bond forming strategy using methoxymethyl phenyl sulfone and phenylsulfonyl chloride ($PhSO_2Cl$) which significantly reduces the expense and shortens the synthetic route.

2. Results and discussion

Inspired by the earlier work of Shank et al. [11], we first performed the reaction between fluoro(phenylsulfonyl)methide anion ($PhSO_2CHF^-$) and $PhSO_2Cl$ expecting the formation of FBSM.

Table 1
Formation of fluorophenylsulfonylmethide anion under different bases and its reaction with phenyl sulfonyl halides.



1 2a 3 4a

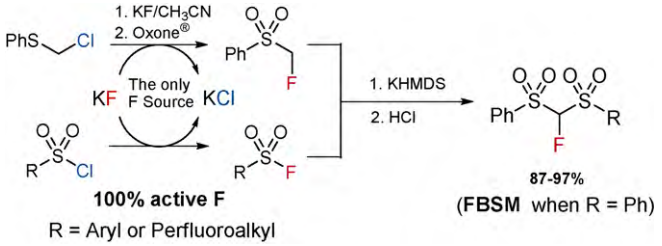
Entry	X	Base	Molar ratio **1**/**2**/base	Yield (%) **3**/**4a**[a]
1[b]	Cl	LHMDS	1.01/1.0/1.0	–
2[b]	Cl	LHMDS	1.0/1.0/2.0	–
3[b]	Cl	NaHMDS	1.0/1.2/2.0	66/0
4[c]	Cl	NaHMDS	1.0/1.2/2.0	42/0
5[b]	Cl	KHMDS	1.0/1.2/2.0	77/0
6[c]	Cl	KHMDS	1.0/1.2/2.0	85/0
7[c]	F	KHMDS	1.0/1.0/1.0	0/48
8[c]	F	KHMDS	1.0/1.0/2.0	0/99

[a] ^{19}F NMR yield.
[b] Base was added to **1** at −78 °C and stirred for 30 min followed by dropwise addition of **2a** at the same temperature and stirred for another 30 min before quenching by dil. HCl.
[c] Base was added dropwise at −78 °C to a solution of **1** and **2a** and the mixture was stirred at −78 °C for 30 min followed by quenching with HCl.

To our dismay, FBSM was not formed under these conditions, however, chlorofluoromethyl phenyl sulfone ($PhSO_2CHClF$) was found as the major product (Table 1, entries **3–6**). In comparison with NaHMDS and LiHMDS, KHMDS was the base affording higher yields which presumably diminishes the defluorination of $PhSO_2CHF^-$ because of the weaker coordination between fluoride and potassium ions (Table 1, entries **1–6**). It appears that the formation of $PhSO_2CHClF$ is due to the lower electrophilicity of the $PhSO_2$ group compared to that of the Cl toward the $PhSO_2CHF^-$ anion, in accordance with a previous report [12].

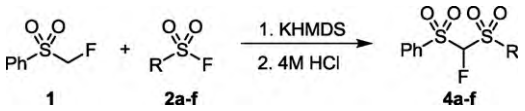
The results indicate that the sulfur atom on the phenylsulfonyl halides $PhSO_2X$ needed to be more electrophilic toward $PhSO_2CHF^-$ anion. Among various sulfonating reagents, we decided to utilize $PhSO_2F$, which has been shown as a superior precursor due to the strong electronegativity of F [13]. As anticipated, the halogenation process was suppressed, and FBSM was obtained in almost quantitative yield with high NMR purity (>95%) by the treatment of $PhSO_2CH_2F$ and $PhSO_2F$ with 2 equiv. of KHMDS (Table 1, entry **8**). The extra amount of the base was required, as it was consumed during the facile deprotonation of the (disulfonyl)methanes.

Furthermore, the product can be easily isolated in high purity by extraction technique since all the by-products are water-soluble or volatile. The newly developed synthetic strategy successfully avoids tedious separation processes or utilization of any expensive or low efficient reagents. RSO_2CH_2F is readily synthesized on a large scale from fairly inexpensive substrate, chloromethyl phenyl sulfide and KF followed by oxidation with Oxone® [14]. Phenylsulfonyl fluoride can be prepared from the corresponding chlorine-containing counterpart (phenylsulfonyl chloride) by chlorine–fluorine exchange using KF. It is important to note that KF is the only fluorine source used in the new protocol, which increases the atom efficiency and remarkably reduces the cost of the reaction. Compared to the utilization of Selectfluor® as electrophilic fluorinating agent, the application of KF as the fluorine source is economic, efficient and advantageous (Scheme 2).



Scheme 2. The new C–S bond forming strategy for the preparation of fluorobis(phenylsulfonyl)methane (FBSM) and its derivatives.

Table 2
Synthesis of 1-fluorobis(phenylsulfonyl)methane derivatives by the new C–S bond forming strategy[a].



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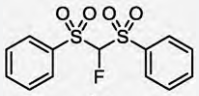
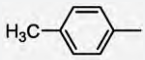
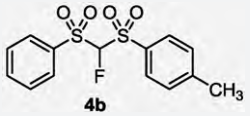
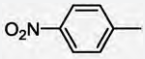
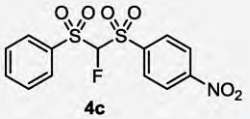
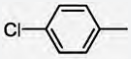
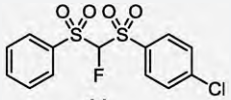
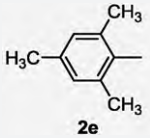
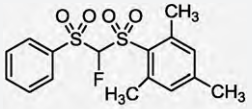
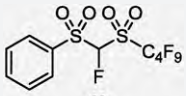
Entry	Substrate	Product	Yield (%)[b]
1	 2a	 4a	95
2	 2b	 4b	93
3	 2c	 4c	90
4	 2d	 4d	97
5	 2e	 4e	73
6	 2f	 4f	86

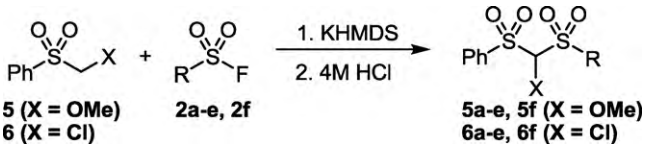
[a] Conversion was 100% in all cases.
[b] Isolated yields.

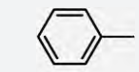
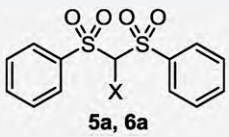
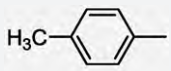
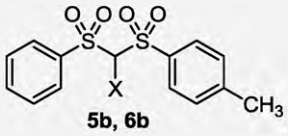
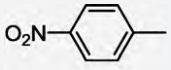
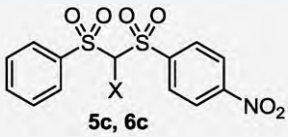
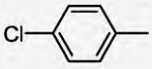
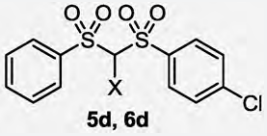
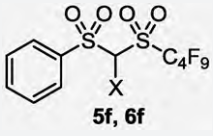
To examine the scope of the methodology, we carried out the reaction between $PhSO_2CH_2F$ and other sulfonyl fluorides. It has been shown that the method can be successfully applied to a variety of sulfonyl fluorides including perfluoroalkylsulfonyl fluorides, the arylsulfonyl fluorides bearing both electron-withdrawing and electron-donating groups, and even the hindered sulfonyl fluoride. The reaction generally affords the products in good to excellent yield with high NMR purity (>95%, Table 2).

It has been demonstrated that alkoxymethyl sulfonylmethanes can be readily applied as a carbonyl 1,1-dipole synthon [15] and methoxymethyl synthon [16]. Diekmann, in 1965, reported the synthesis of alkoxybis(phenylsulfonyl)methanes by photolysis of bis(phenylsulfonyl)diazomethane in alcohols [17]. The drawbacks of this method appear to be: (a) the availability of bis(phenylsulfonyl)diazomethane is limited; (b) the alcoholysis has to be performed under UV irradiation, a setup which may be not generally available in many organic chemistry laboratories. The 2-alkoxybenzo-1,3-disulfone was prepared by the oxidation of the corresponding sulfide with MoO_5·HMPA·H_2O [15]. However, attempts to oxidize methoxybis(phenylthio)methane under the similar conditions lead to the decomposition of the starting material. As mentioned above, methoxydisulfonylmethanes can also be obtained by the treatment of methoxyphenylsulfonylmethide with the corresponding sulfonyl chlorides in moderate yield (50–70%) [11]. Encouraged by the successful preparation of fluoro(disulfonyl)methanes by the new C–S bond forming strategy, we explored the synthesis of methoxy(disulfonyl)methanes using similar strategy. The desired products were obtained in higher yields by the sulfonylation of methoxyphenylsulfonylmethide using sulfonyl fluorides instead of sulfonyl chlorides (Table 3, entries **5a–d, 5f**).

On the other hand, Gibson reported the synthesis of chloro(disulfonyl)methanes from the reaction between disulfonylmethide salts and $PhSO_2Cl$ [18]. Symmetric chloro(disulfo-

Table 3
Synthesis of α-methoxy and α-chloro derivatives of bis(phenylsulfonyl)methane by the new sulfonylation protocol.



Entry	Substrate	Product	Yield (%)[a,b]
1	 **2a**	 **5a, 6a**	(**5a**) 78 (**6a**) 78
2	 **2b**	 **5b, 6b**	(**5b**) 82 (**6b**) 75
3	 **2c**	 **5c, 6c**	(**5c**) 62 (**6c**) 83
4	 **2d**	 **5d, 6d**	(**5d**) 77 (**6d**) 74
5	 **2f**	 **5f, 6f**	(**5f**) 79 (**6f**) 52

[a] Conversion was 100% in all cases.
[b] Isolated yields.

nyl)methanes can be also achieved by treatment of disulfonylmethanes in aqueous NaOH solution with NaOCl [19]. Our attempts to obtain chloro(disulfonyl)methanes via the oxidation of the corresponding disulfides failed due to the high instability of the chloro(disulfonyl)methanes. Since the disulfonylmethanes are much less acidic than the monochlorinated intermediates, chlorination of disulfonylmethide with stoichiometric amount of N-chlorosuccinimide (NCS) always leads to a mixture of mono- and dichlorinated products along with unreacted starting material. However, when we followed the new C–S bond forming protocol using $PhSO_2CH_2Cl$ and RSO_2F, the corresponding chloro(disulfonyl)methanes were feasibly formed in good yields and purity (Table 3, **6a–d, 6f**).

3. Conclusions

A practical and highly efficient "C–S bond forming strategy" for the synthesis of α-substituted disulfonylmethane derivatives was developed. The novel methodology achieves the one-step synthesis of the substituted disulfonylmethanes as useful methyl synthons for various reactions. Particularly, the practical synthesis of FBSM and its analogues based on the nucleophilic nature of fluorine (the starting materials are derived only from KF) successfully diminishes the problems encountered in the conventional synthetic approaches, employing electrophilic fluorine-based reagents.

4. Experimental

Unless otherwise mentioned, all chemicals were purchased from commercial sources. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz superconducting NMR spectrometer. All the unknown compounds have been fully characterized by NMR spectroscopy and MS analysis, whereas structures of all known products were confirmed by comparison of their NMR spectra with the reported data. ^1H NMR chemical shifts (δ) were determined relative to internal tetramethylsilane at δ 0.0 ppm or to the signal of a residual solvent in $CDCl_3$ (δ 7.26 ppm). ^{13}C NMR chemical shifts

were determined relative to internal tetramethylsilane at δ 0.0 ppm or to the ^{13}C signal of $CDCl_3$ at δ 77.16 ppm.

4.1. Typical procedure for the preparation of α-fluorobis(phenylsulfonyl)methane (4a)

$PhSO_2CH_2F$ (**1**, 348 mg, 2 mmol) and phenyl sulfonyl fluoride (**2a**, 320 mg, 2 mmol) were dissolved in anhydrous THF (10 mL) in a Schlenk flask under inert atmosphere. The solution was cooled to −78 °C. KHMDS (499 mg, 5 mmol) was dissolved in anhydrous THF (5 mL) and added to the Schlenk flask dropwise. The reaction mixture was stirred for 30 min at the same temperature before poured into 4 M HCl aqueous solution (20 mL). The resultant mixture was washed with water and was extracted with CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over $MgSO_4$, and the solvent was evaporated to afford an oil which crystallized after standing for a while as the product (**4a**, 598 mg, 95%). ^1H NMR and ^{19}F NMR spectroscopy showed the high purity (>95%) of the product.

4.1.1. α-Fluorobis(phenylsulfonyl)methane (4a)

As white solid ^1H NMR ($CDCl_3$) δ 5.70 (d, J = 45.8 Hz, 1H), 7.60–7.66 (t, J = 7.6 Hz, 4H), 7.74–7.83 (t, J = 7.6 Hz, 2H), 7.95–8.03 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −168.2 (d, J = 45.6 Hz, 1F). The data are consistent with Ref. [6d].

4.1.2. 1-(Fluoro(phenylsulfonyl)methylsulfonyl)-4-methylbenzene (4b)

As white solid in 93% yield isolated. ^1H NMR ($CDCl_3$) δ 2.48 (s, 3H), 5.70 (d, J = 45.6 Hz, 1H), 7.39–7.41 (m, 2H), 7.59–7.63 (m, 2H), 7.74–7.78 (m, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.97–8.00 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −168.87 (d, J = 45.5 Hz, 1F). The data are consistent with Ref. [9].

4.1.3. 1-(Fluoro(phenylsulfonyl)methylsulfonyl)-4-nitrobenzene (4c)

As white solid in 90% yield isolated. ^1H NMR ($CDCl_3$) δ 5.83 (d, J = 45.6 Hz, 1H), 7.61–7.65 (m, 2H), 7.77–7.81 (m, 1H), 7.94–7.96 (m, 2H), 8.22–8.24 (m, 2H), 8.43–8.46 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 105.8 (d, J = 265.4 Hz), 124.7, 130.0, 130.2, 132.2, 135.2, 136.3, 140.7, 152.1. ^{19}F NMR ($CDCl_3$) δ −168.47 (d, J = 45.8 Hz, 1F). MS (ESI, m/z): 357.9 ($M-H^-$), 202.1, 157.0, 137.9. HRMS: calcd for $C_{13}H_9FNO_6S_2$ 357.9861 ($M-H^-$) found: m/z 357.9859.

4.1.4. 1-Chloro-4-(fluoro(phenylsulfonyl)methylsulfonyl)benzene (4d)

As white solid in 97% yield isolated. ^1H NMR ($CDCl_3$) δ 5.72 (d, J = 46.0 Hz, 1H), 7.58–7.64 (m, 4H), 7.76–7.80 (m, 1H), 7.92–7.98 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 105.8 (d, J = 265.0 Hz), 129.7, 130.0, 130.2, 131.9, 133.6, 135.4, 136.0, 143.1. ^{19}F NMR ($CDCl_3$) δ −168.61 (d, J = 45.8 Hz, 1F). MS (ESI, m/z): 371.0 ($M+Na^+$). HRMS: calcd for $C_{13}H_{10}ClFO_4S_2Na$ 370.9591 ($M+Na^+$) found: m/z 370.9590.

4.1.5. 2-(Fluoro(phenylsulfonyl)methylsulfonyl)-1,3,5-trimethylbenzene (4e)

As pale powder in 73% yield isolated. ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.61 (s, 6H), 5.68 (d, J = 46.4 Hz, 1H), 6.99 (s, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.77 (t, J = 7.7 Hz, 1H), 8.04 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.4, 23.2, 106.4 (d, J = 265.9 Hz), 129.4, 130.4, 130.5, 132.8, 135.4, 135.7, 142.4, 145.9. ^{19}F NMR ($CDCl_3$) δ −168.02 (d, J = 46.4 Hz, 1F). MS (ESI, m/z): 379.1 ($M+Na^+$), 338.3. HRMS: calcd for $C_{16}H_{18}FO_4S_2$ 357.0631 ($M+H^+$) found: m/z 357.0625.

4.1.6. (Fluoro(perfluorobutylsulfonyl)methylsulfonyl)benzene (4f)

As white waxy solid in 86% yield isolated. ^1H NMR ($CDCl_3$) δ 6.15 (d, J = 46.5 Hz, 1H), 7.67–7.71 (m, 2H), 7.85 (tq, ^1J = 7.7 Hz, ^2J = 1.2 Hz, 1H), 8.05–8.08 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 103.4 (d, J = 274.5 Hz), 105.1–121.6 (m, 4C), 130.0, 130.7, 134.3, 136.9. ^{19}F NMR ($CDCl_3$) δ −81.2 (t, J = 9.7 Hz, 3F), −109.9 (m, 2F), −121.5 (m, 2F), −126.3 (m, 2F), −166.5 (m, 1F). MS (ESI, m/z): 932.5 (2M + Na-2H$^-$), 455.0 ($M-H^-$), 282.8. HRMS: calcd for $C_{11}H_5F_{10}O_4S_2$ 454.9475 ($M-H^-$) found: m/z 454.9469.

4.2. Typical procedure for the preparation of methoxy(disulfonyl)methanes (5a–d, 5f)

Methoxy(disulfonyl)methanes (**5a–d, 5f**) were prepared by the same procedure for fluoro(disulfonyl)methane synthesis. The products were obtained with a small amount of $PhSO_2CH_2OCH_3$ which can be removed by chromatography with hexanes–CH_2Cl_2 as the eluent.

4.2.1. α-Methoxybis(phenylsulfonyl)methane (5a)

As white solid in 78% yield isolated. ^1H NMR ($CDCl_3$) δ 3.61 (s, 3H), 5.03 (s, 1H), 7.55–7.59 (m, 4H), 7.68–7.73 (m, 2H), 7.94–8.96 (m, 4H), ^{13}C NMR ($CDCl_3$) δ 64.6, 106.1, 129.2, 130.3, 135.1, 136.3. MS (ESI, m/z): 349.0 ($M+Na^+$). HRMS: calcd for $C_{14}H_{14}NaO_5S_2$ 349.0175 ($M+Na^+$) found: m/z 349.0173.

4.2.2. 1-Chloro-4-(methoxy(phenylsulfonyl)methylsulfonyl)benzene (5b)

As white solid in 82% yield isolated. ^1H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.60 (s, 3H), 5.00 (s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.55–7.58 (m, 2H), 7.67–7.73 (m, 1H), 7.82–7.84 (m, 2H), 7.94–7.96 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 21.9, 64.5, 106.1, 129.1, 129.9, 130.2, 133.3, 135.0, 136.4, 146.4. MS (ESI, m/z): 702.7 ($2M+Na^+$), 363.0 ($M+Na^+$). HRMS: calcd for $C_{15}H_{16}NaO_5S_2$ 363.0331 ($M+Na^+$) found: m/z 363.0334.

4.2.3. 1-(Methoxy(phenylsulfonyl)methylsulfonyl)-4-nitrobenzene (5c)

As white solid in 62% yield isolated. ^1H NMR ($CDCl_3$) δ 3.66 (s, 3H), 5.08 (s, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.74 (m, 1H), 7.93 (m, 2H), 8.18 (d, J = 8.8 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 64.8, 106.2, 124.1, 129.5, 130.1, 132.2, 135.4, 136.2, 141.5, 151.6. MS (ESI, m/z): 370.0 ($M-H^-$), 153.6, 145.8. HRMS: calcd for $C_{14}H_{12}NO_7S_2$ 370.0061 ($M-H^-$) found: m/z 370.0066.

4.2.4. 1-Chloro-4-(methoxy(phenylsulfonyl)methylsulfonyl)benzene (5d)

As white solid in 74% yield isolated. ^1H NMR ($CDCl_3$) δ 3.62 (s, 3H), 5.07 (s, 1H), 7.51–7.59 (m, 4H), 7.72 (m, 1H), 7.86–7.94 (m, 4H) ^{13}C NMR ($CDCl_3$) δ 64.6, 106.1, 129.3, 129.5, 130.2, 131.8, 134.5, 135.1, 136.3, 142.1. MS (ESI, m/z): 382.9 ($M+Na^+$). HRMS: calcd for $C_{14}H_{13}ClNaO_5S_2$ 382.9785 ($M + Na^+$) found: m/z 382.9784.

4.2.5. (Methoxy(perfluorobutylsulfonyl)methylsulfonyl)benzene (5f)

As white waxy solid in 74% yield isolated. ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H), 5.55 (s, 1H), 7.63 (t, J = 7.6 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 64.4, 105.3–121.8 (m, 4C), 104.6, 129.5, 130.7, 135.1, 136.0. ^{19}F NMR ($CDCl_3$) δ −81.2 (t, J = 9.0 Hz, 3F), −110.5 to −108.5 (m, 2F), −122.6 to −120.5 (m, 2F), −127.3 to −125.4 (m, 2F). MS (ESI, m/z): 620.9 (2M + Na-2H$^-$), 299.2 ($C_4F_9SO_3^-$). HRMS: calcd for $C_{12}H_8F_9O_5S_2$ 466.9675 ($M-H^-$) found: m/z 466.9670.

4.3. Typical procedure for the preparation of chloro(disulfonyl)methanes (6a–d, 6f)

Chloro(disulfonyl)methanes were obtained according to the same procedure for fluoro(disulfonyl)methane synthesis. The reactions afforded the products in high purity (>95%) by a simple extraction technique.

*4.3.1. α-Chlorobis(phenylsulfonyl)methane (**6a**)*

As white solid in 78% yield isolated. ^{1}H NMR ($CDCl_3$) δ 5.56 (s, 1H), 7.61–7.65 (m, 4H), 7.75–7.80 (m, 2H), 8.03–8.05 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 84.0, 129.4, 130.7, 135.6, 135.7. The data are consistent with Ref. [20].

*4.3.2. 1-(Chloro(phenylsulfonyl)methylsulfonyl)-4-methylbenzene (**6b**)*

As white solid in 82% yield isolated. ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3H), 5.56 (s, 1H), 7.40 (d, J = 8.0 Hz 2H), 7.59–7.63 (m, 2H), 7.73–7.78 (m, 1H), 7.90 (d, J = 8.0 Hz, 2H), 8.01–8.04 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 22.0, 84.0, 129.3, 130.0, 130.7, 130.8, 132.5, 135.6, 135.7, 147.2. MS (ESI, m/z): 710.5 ($2M + Na^+$), 367.0 ($m + Na^+$). HRMS: calcd for $C_{14}H_{13}ClO_4S_2Na$ 366.9836 ($M + Na^+$) found: m/z 366.9831

*4.3.3. 1-(Chloro(phenylsulfonyl)methylsulfonyl)-4-nitrobenzene (**6c**)*

As white solid in 77% yield isolated. ^{1}H NMR ($CDCl_3$) δ 5.63 (s, 1H), 7.62–7.66 (m, 2H), 7.77–7.81 (m, 1H), 7.99–8.02 (m, 2H), 8.27–8.30 (m, 2H), 8.45–8.47 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 83.9, 124.3, 129.6, 130.6, 132.6, 135.3, 136.0, 140.8, 151.9. MS (ESI, m/z): 374.0 ($M-H^-$). HRMS: calcd for $C_{13}H_9ClNO_6S_2$ 373.9565 (M−H) found: m/z 373.9561.

*4.3.4. 1-Chloro-4-(chloro(phenylsulfonyl)methylsulfonyl)benzene (**6d**)*

As white solid in 74% yield isolated. ^{1}H NMR ($CDCl_3$) δ 5.58 (s, 1H), 7.58–7.64 (m, 4H), 7.75–7.79 (m, 1H), 7.96–8.03 (m, 4H), ^{13}C NMR ($CDCl_3$) δ 83.9, 129.5, 129.7, 130.6, 132.3, 133.8, 135.5, 135.8, 142.8. MS (ESI, m/z): 386.9 ($M + Na^+$). HRMS: calcd for $C_{13}H_{11}Cl_2O_4S_2$ 364.9470 ($M + H^+$) found: m/z 364.9476.

*4.3.5. (Chloro(perfluorobutylsulfonyl)methylsulfonyl)benzene (**6f**)*

As white waxy solid in 52% yield isolated. ^{1}H NMR ($CDCl_3$) δ 5.93 (s, 1H), 7.66 (t, J = 7.8 Hz, 2H), 7.83 (t, J = 7.7 Hz, 1H), 8.08 (d, J = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 81.0, 106.6–119.8 (m, 4C), 129.7, 131.2, 134.5, 136.6. ^{19}F NMR ($CDCl_3$) δ −81.1 (m, 3F), −106.1 (m, 2F), −122.2 (m, 2F), −126.2 (m, 2F). MS (ESI, m/z): 964.5 ($2M + Na^+ - 2H^-$), 471.1 ($M-H^-$). HRMS: calcd for $C_{11}H_5ClF_9O_4S_2$ 470.9180 ($M-H^-$) found: m/z 470.9183.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.07.006.

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