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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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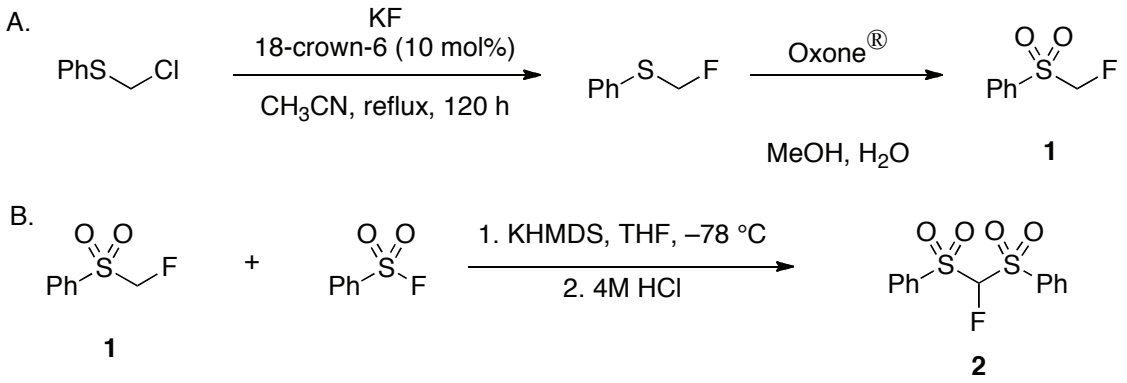
Preparation of α-Fluorobis(phenylsulfonyl)methane (FBSM)



Submitted by G. K. Surya Prakash, Nan Shao, Fang Wang, and Chuanfa Ni.[1]
Checked by Thomas D. Montgomery and Viresh H. Rawal.
Discussion Addendum: *Org. Synth.* **2019**, *96*, 474

Potassium hydride is a pyrophoric solid and must not be allowed to come into contact with the atmosphere. This reagent should only be handled by individuals trained in its proper and safe use.

1. Procedure

A. *Fluoromethyl phenyl sulfone* (**1**) (Note 1). An oven-dried (140 °C for 12 h) 100-mL round-bottomed flask equipped with a magnetic stir bar (25 x 8 mm, octagonal) is charged with spray-dried potassium fluoride (8.80 g, 152 mmol, 2.0 equiv) (Note 2) and 18-crown-6 (2.01 g, 7.6 mmol, 0.1 equiv) (Note 3). The flask is sealed with a rubber septum, into which is inserted a syringe needle attached to a nitrogen/vacuum line. The flask is evacuated and refilled with nitrogen 3 times. Anhydrous acetonitrile (50 mL) (Note 4) and chloromethyl phenyl sulfide (10.2 mL, 12.10 g, 76.0 mmol, 1.0 equiv) (Note 5) are added successively to the flask by syringe. A reflux condenser fitted with a nitrogen inlet adaptor is quickly attached and the apparatus is flushed with nitrogen three times. The stirred reaction mixture is heated to reflux in an oil bath (102–103 °C, bath temp) for 120 h (Note 6). The reaction mixture is then cooled in an ice bath (0 °C, bath temp) (Note 7), diluted with ice water (50 mL) (Note 8), and transferred to a 250 mL separatory funnel. The mixture is extracted with methylene chloride (4 x 25

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mL, Note 9) (Note 10). The combined organic layer is washed with water (30 mL), dried over magnesium sulfate (ca. 10 g, 15 min) (Note 11), and filtered. The solvent is removed on a rotary evaporator (23 °C bath temp, 2 mmHg) to give crude fluoromethyl phenyl sulfide as a brownish oil (10.04–10.25 g, 93–95%) that is directly subjected to oxidation.

To a 1-L round-bottomed flask equipped with a magnetic stir bar (50 x 8 mm, octagonal) (Note 12) is added Oxone® (116.80 g, 190 mmol $KHSO_5$, 2.6 equiv) (Note 13) and distilled water (175 mL). The flask is capped loosely with a septum and placed in an ice bath. The septum is replaced with an addition funnel and a solution of crude fluoromethyl phenyl sulfide (10.20 g, 72 mmol, 1.0 equiv) in methanol (175 mL) (Note 14) is added dropwise over ca. 1 h (Note 15). The reaction mixture is allowed to slowly warm to room temperature and stirred for an additional 12 h. Methanol is removed via rotary evaporation (45 °C bath temp, 2 mmHg) (Note 16). The resulting residue contains a large amount of insoluble white precipitate, which is removed by filtration through a Büchner funnel (Note 17). The funnel is rinsed with methylene chloride (2 x 30 mL) and the filtrate is transferred to a 250-mL separatory funnel. After layer separation, the aqueous layer is further extracted with methylene chloride (Note 18) (5 × 30 mL, Note 9). The organic layers are combined, washed with water, dried over magnesium sulfate (ca. 10 g, 15 min) (Note 11), filtered, and concentrated to ca. 40 mL of a pale yellow solution. The solution is filtered through a plug of silica gel (230–400 mesh, 100 mL), which is further washed with methylene chloride (ca. 250 mL, Note 9) to give a clear solution (Note 19). The filtrate is concentrated via rotary evaporation (23 °C, 2 mmHg) and then placed under vacuum (room temperature, ca. 0.2–0.3 mmHg, 15–30 min) to result in a clear or slightly yellowish oil, which slowly solidifies at room temperature under vacuum. The solid is stirred with hot hexanes (ca. 50 mL, 60~65 °C) (Note 20) for 20 min, which forms two layers. Upon cooling to 0 °C in an ice bath, the bottom layer gradually crystallizes to yield colorless crystals over 15 min, which are collected by filtration on a Büchner funnel and washed with cold (0 °C) hexanes (2 x 10 mL) (Note 21) to afford fluoromethyl phenyl sulfone (**1**) (10.99–12.18 g, 83–92%) (Note 22).

B. *α-Fluorobis(phenylsulfonyl)methane (FBSM)* (**2**). An oven-dried (140 °C, 12 h) 250-mL round-bottomed flask, equipped with a magnetic stir bar (25 x 8 mm, octagonal), is charged with potassium hydride (21.80 g, 30% wt in oil, 163 mmol, 2.7 equiv) (Note 23), sealed with a rubber septum

and connected through a syringe needle to a nitrogen/vacuum line. The flask is evacuated and purged with nitrogen three times and then placed in an ice bath. Excess oil is removed as follows. Anhydrous hexanes (20 mL) (Note 24) are added to the flask via syringe. The mixture is gently stirred for 10 min and allowed to stand unstirred for another 10 min before the removal of the hexanes-oil solution with a syringe. The hexanes-oil solution is added dropwise to an isopropyl alcohol solution. This washing procedure is repeated two more times. Anhydrous THF (130 mL) is then added (Note 25). Hexamethyldisilazane (40.9 mL, 31.5 g, 195 mmol, 3.2 equiv) (Note 26) is then added portion-wise to the stirred solution via syringe over a period of 20–30 min. The hydrogen evolution ceases within 15 min after the addition. The ice bath is removed and the reaction mixture is allowed to stand without stirring for 30 min at room temperature before use (Note 27).

An oven dried (140 °C, 12 h) 500-mL round-bottomed flask equipped with a magnetic stir bar (37.5 x 8 mm, octagonal) is charged with fluoromethyl phenyl sulfone (**1**) (10.66 g, 61.2 mmol, 1.0 equiv). The flask is sealed with a rubber septum and connected through a syringe needle to a nitrogen/vacuum line. The flask is evacuated and purged with nitrogen three times. Benzenesulfonyl fluoride (7.37 mL, 9.80 g, 61.2 mmol, 1.0 equiv) (Note 28) and anhydrous tetrahydrofuran (40 mL) (Note 25) are added successively via syringe. The flask is cooled in a dry ice-acetone bath (–78 °C) and the stirred contents are treated with the KHMDS solution in tetrahydrofuran prepared above (Note 29), which is added dropwise via cannula (Note 30) over 30 min. During the course of the addition, the reaction mixture becomes brownish, cloudy, and viscous. After 30 min at –78 °C, the reaction mixture is quenched by transfer via cannula over 30 min to another 500-mL round-bottomed flask maintained under a nitrogen atmosphere containing a stirred solution of 4M HCl (185 mL) (Note 31). The resultant mixture appears as a single opaque layer and is extracted with methylene chloride in a 500 mL separatory funnel (5 × 60 mL). The combined organic layer is washed with brine (50 mL), dried over magnesium sulfate (ca. 15 g, 15 min) (Note 11), and filtered. The filtrate is concentrated via rotary evaporation (23 °C bath temp, 2 mmHg) and further dried under vacuum (room temperature, ca. 0.2–0.3 mmHg) to afford crude α-fluorobis(phenylsulfonyl)methane (**2**) as a colorless solid (18.28 g, 95%).

Examination by ^{1}H NMR and ^{19}F NMR spectroscopy shows the crude product (**2**) to be satisfactory for most preparative purposes (>98% purity) (Note 32). Compound **2** can be further purified by recrystallization in

methylene chloride and hexanes as follows. The crude product is placed in a 250-mL round-bottomed flask equipped with a stir bar and a reflux condenser. Methylene chloride (35 mL) is added and the mixture is heated to reflux to dissolve the product. Hexanes (ca. 30 mL) are slowly added portion-wise through the top of the condenser, while maintaining the reflux. The solution is slowly cooled to room temperature. The solution is then transferred to a refrigerator set to 5 °C and held for 2 h. The resulting white precipitate is collected on a Büchner funnel, rinsed with 25 mL cold methylene chloride/hexanes (1:1, v/v; 0 °C) and allowed to air dry on the funnel for 15 min and then placed on a vacuum line for 15 min (rt, 0.2–0.3 mmHg) to render 14.04 g of **2**. The mother liquor is further concentrated to approximately one-half volume. An additional 20 mL of cold hexanes (0 °C) is then added causing the solution to become cloudy. After 15 minutes without stirring an additional 2.51 g of FBSM is isolated by the above mentioned procedure (combined yield 16.55 g, 85%) (Notes 32 and 33).

2. Notes

1. Fluoromethyl phenyl sulfone can be purchased from TCI America. Alternatively, the compound can be prepared according to a reported procedure.[2] Fluoromethyl phenyl sulfide was prepared according to a known protocol.[3] The oxidation of fluoromethyl phenyl sulfide is slightly modified from this procedure.

2. Spray-dried potassium fluoride (99%) was purchased from Sigma-Aldrich and used as received. It was stored in a desiccator between uses.

3. 18-Crown-6 (99%) was purchased (Sigma-Aldrich) and used as received.

4. Acetonitrile (Optima grade) was purchased from Fisher Scientific and was dried by passing through an alumina column, as part of an Innovative Technologies PureSolv system.

5. Chloromethyl phenyl sulfide is commercially available (Aldrich Chemical Company, Inc.). It can be prepared from thiophenol according to an *Organic Syntheses* procedure.[4a] The checkers prepared this compound from thioanisole using a simpler, alternate procedure that had been used in their lab. A very similar procedure has been described by Marko *et al.,* as follows:[4c] A 500-mL three-necked round-bottomed flask equipped with a magnetic stir bar (37.5 x 10 mm, octagonal) is charged with thioanisole

(35.2 mL, 0.30 mol) and anhydrous methylene chloride (230 mL), added sequentially via syringe. The flask is fitted with two rubber septa and a reflux condenser. To quench the HCl (g) generated through the chlorination, a Tygon® tube is affixed to the top of the condenser, and the end of the tubing is submerged in an Erlenmeyer flask containing 500 mL of 2M aqueous NaOH. The reaction is placed under a positive pressure of nitrogen via a needle connected to a nitrogen vacuum manifold, then heated to reflux in an oil bath while stirring (50 °C, bath temp). When the reaction reaches a steady reflux, a solution of sulfuryl chloride (24.1 mL, 0.33 mol, 1.1 equiv) in methylene chloride (70 mL) is added over 1 h via cannula. The reaction is refluxed for 2 h, removed from the oil bath and allowed to cool to room temperature. The reaction mixture is then carefully diluted with water (100 mL) and transferred to a 500-mL separatory funnel. The organic phase is separated and then washed with water (3 x 75 mL) and brine (50 mL) to give a pale pink translucent solution that is dried over magnesium sulfate (15 g, 15 min). The drying agent is removed by filtration and the filtrate is concentrated by rotary evaporation (23 °C, 2 mmHg) to give the crude product as an oil (44.30 g, 93%). The product is further purified using fractional vacuum distillation at (0.2–0.3 mmHg). A small amount of starting material is collected in the first fraction (60–63 °C at distillation head; 110 °C bath temp) and this is followed by the product (87–91 °C at the distillation head; 140 °C bath temp). The distilled product (25.37 g, 53.3%) was determined to be pure enough for the following reactions (>99.7% by ^{1}H NMR). Additional fractions from the distillation contained product (14.48 g, 30.4%) that was deemed insufficiently pure (95.0% by ^{1}H NMR) for use in the present sequence of reactions. It should be noted that impurities in the starting material are problematic in subsequent reactions.

6. The reaction mixture gradually turns brownish during the course of the reaction, and a large amount of white solid precipitates onto the wall of the flask.

7. The reaction may be monitored with the addition of α,α,α-trifluorotoluene (0.49 mL, 0.59 g, 4.0 mmol) as an internal standard. A small portion of the reaction mixture (the solution, ca. 0.5 mL) is withdrawn via syringe and monitored via ^{19}F NMR spectroscopy. This method provides an approximate assessment of the reactions progress (yield +/- 10%). α,α,α-Trifluorotoluene (≥99%) was purchased from Sigma-Aldrich and used as received.

8. Distilled water was used.

9. Complete extraction was monitored by spotting a drop of the extract on a TLC plate and checking with a UV lamp to see the presence of the product.

10. Methylene chloride (Optima grade) was purchased from Fisher Scientific and was dried by passing through an alumina column, as part of an Innovative Technologies PureSolv system.

11. Anhydrous magnesium sulfate was purchased from Fisher Scientific and used as received.

12. The submitters carried this reaction out on a 5x scale and used an overhead mechanical stirrer.

13. Oxone® (potassium peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was purchased from Sigma-Aldrich and used as received.

14. Methanol (HPLC grade) was purchased from Fisher Scientific and used as received.

15. The reaction is moderately exothermic. A fast addition of fluoromethyl phenyl sulfide leads to an increase in temperature of the reaction mixture.

16. The solution was placed on the rotary evaporator for 20 min (45 °C, 2 mmHg).

17. The presence of large quantities of insoluble solids (assumed to be from Oxone®) must be removed to avoid complications with the extraction of fluoromethyl phenyl sulfone.

18. The emulsion that forms during the extraction fully or partially resolves after 5-10 min. Subsequent extractions produce less emulsion.

19. The filtration through silica gel removes impurities such as residual 18-crown-6.

20. Hexanes (ACS reagent grade) were purchased from Fisher Scientific and used as received.

21. If pure fluoromethyl phenyl sulfone is not obtained at this point it is likely contaminated with methyl phenyl sulfone. TLC analysis: 2:1, Hex:EtOAc: $R_f = 0.40$ for fluoromethyl phenyl sulfone, $R_f = 0.18$ for methyl phenyl sulfone.

22. Fluoromethyl phenyl sulfone has the following physical and spectroscopic properties: mp 51–52 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.16 (d, J = 47 Hz, 2 H), 7.62 (t, J = 8.3 Hz, 2 H), 7.74 (tt, J = 7.4, 1.2 Hz, 1 H), 7.96 (d, J = 7.3 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 92.0 (d, J = 217.5 Hz), 129.0, 129.6, 134.9. ^{19}F NMR (500 MHz, $CDCl_3$) δ: –210.0 (td, J = 50.0, 2.25 Hz); IR (KBr) 3013 (w), 2950 (w), 1587 (w), 1447 (s), 1343 (s),

1314 (s), 1220 (m), 1155 (s), 1053 (s), 937 (m), 790 (s), 751 (s), 683 (s), 556 (s), 527 (s) cm^{-1}; Anal. Calcd for $C_7H_7FO_2S$: C, 48.27; H, 4.05. Found: C, 48.28; H, 3.89. The spectral data are in agreement with the reported values.[2]

23. Potassium hydride (30 wt% in oil) was purchased from Sigma-Aldrich Inc. Potassium hydride (50 wt% in paraffin) may also be used. Potassium hydride was used as received, the oil suspension was stirred prior to use with a dry glass rod to ensure the suspension was even. The suspension was then transferred to a tared receiving flask via a wide-tipped pipette. After the desired amount of potassium hydride had been transferred the flask was sealed with a rubber septum. All contaminated glassware was carefully quenched with isopropyl alcohol in a fume hood.

24. Hexanes (95%, anhydrous grade) was purchased from Sigma-Aldrich and used as received.

25. Tetrahydrofuran (Optima grade) was purchased from Fisher Scientific and dried on an alumina column as part of an Innovative Technologies PureSolv system. Dried THF was transferred from the solvent system to the reaction flask by syringe.

26. Hexamethyldisilazane (>96%) was purchased from Alfa Aesar and used as received.

27. More hydrogen evolution may occur on warming to room temperature and continue for several minutes. The solution should not be used until hydrogen evolution has stopped for at least 10 min.[5]

28. Benzenesulfonyl fluoride can be purchased from Aldrich Chemical Company, Inc. Access to high-purity benzenesulfonyl fluoride (>99%) is required for clean formation of the final product. As this compound is a liquid at room temperature, the known method for its synthesis, which calls for purification by recrystallization, was modified as follows:[6] A 500-mL round-bottomed flask equipped with a magnetic stirring bar (50 mm x 8 mm, octagonal) is charged with benzenesulfonyl chloride (39.0 mL, 53.90 g, 0.3 mol, 1.0 equiv), potassium fluoride (22.70 g, 0.39 mol, 1.3 equiv) and 18-crown-6 (3.96 g, 15 mmol, 0.05 equiv). The flask is then sealed with a rubber septum and connected via a syringe needle to nitrogen/vacuum line. The flask is evacuated/flushed with nitrogen three times, then acetonitrile (300 mL) is added via syringe and the mixture is stirred at room temperature for 24 h. The reaction mixture is then diluted with water (150 mL) and transferred to a 1L separatory funnel and extracted with diethyl ether (3 x 75 mL). The combined organic layer is washed with brine (30 mL) and dried over magnesium sulfate (15 g, 15 min). The drying agent is removed

by filtration and the solvent is removed by rotary evaporation (23 °C, 2 mmHg) to give a clear low-viscosity liquid. This product is dissolved in hexanes (50 mL) and washed with HCl solution (1 N, 5 x 20 mL) to remove residual 18-crown-6. The organic phase is dried over magnesium sulfate (15 g, 15 min), the drying agent is removed by filtration and the filtrate is concentrated by rotary evaporation (23 °C, 2 mmHg) and then further under high vacuum (room temp, 0.2–0.3 mmHg) to give benzenesulfonyl fluoride (28.2 mL, 37.50 g, 78 % yield).

29. Solid potassium bis(trimethylsilyl)amide (KHMDS, 95%) can also be purchased from Aldrich Chemical Company, Inc. and formulated into a 1M solution in THF, which can be employed to render similar results.

30. FBSM (**2**) is more acidic than fluoromethyl phenyl sulfone (**1**). The FBSM generated under the reaction conditions readily undergoes deprotonation, which consumes an extra equivalent of base. Thus, the reaction theoretically requires 2 equivalents of base. Employment of less than 2.5 equivalents of KHMDS resulted in an incomplete reaction.

31. HCl (12.1 N, ACS Plus) was purchased from Fisher Scientific.

32. Bis(phenylsulfonyl)methane was identified as the major impurity based on the characteristic signal of the methylene appearing in the ^{1}H NMR spectroscopy in $CDCl_3$ (δ = 4.73 ppm). According to the ^{1}H NMR integration, the amount of bis(phenylsulfonyl)methane was ca. 2 wt%.

33. α-Fluorobis(phenylsulfonyl)methane has the following physical and spectroscopic properties: mp 106.5–107.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.81 (d, J = 45.7 Hz, 1 H), 7.60 (t, J = 7.8 Hz, 4 H), 7.76 (t, J = 7.2 Hz, 2 H), 7.98 (d, J = 7.9 Hz, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 105.6 (d, J = 264 Hz), 129.6, 130.2, 135.3, 135.8. ^{19}F NMR (500 MHz, $CDCl_3$) δ: –167.4 (d, J = 48.6 Hz); IR (KBr) 3096 (w), 3071 (w), 2955 (m), 1581 (m), 1450 (s), 1358 (s), 1172 (s), 1077 (s), 797 (s), 683 (s), 533 (s), 520 (s) cm^{-1}; HRMS for $(C_{13}H_{11}FO_4S_2)Na^+$: Calcd 336.997500; Found 336.997129. Anal. Calcd for $C_{13}H_{11}FO_4S_2$: C, 49.67; H, 3.53. Found: C, 49.39; H, 3.45. The spectral data are in agreement with the reported values.[7,8]

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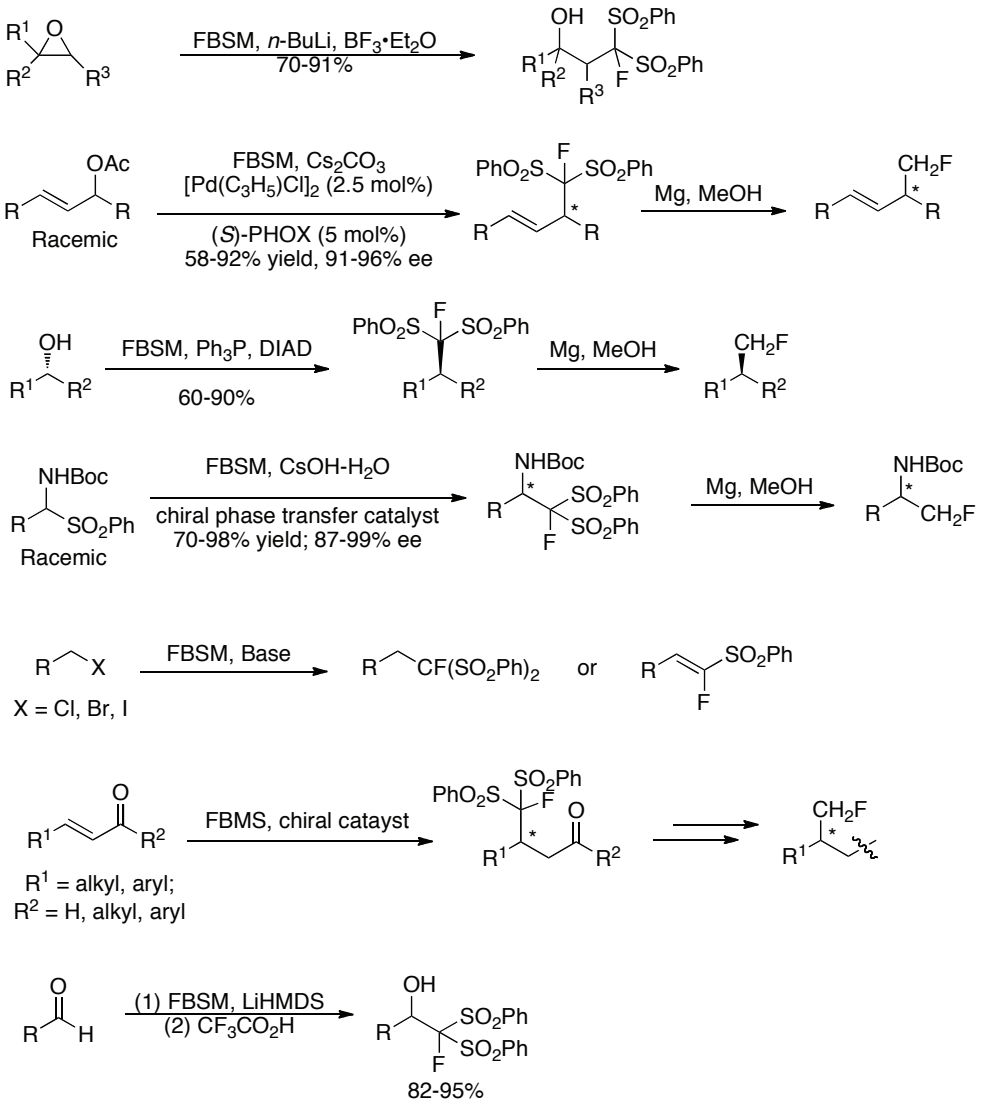
3. Discussion

Fluorinated organic compounds have received increasing interest in recent years due to their unique biological and physicochemical properties. Other than fluorinations of organic compounds via C-F bond forming reactions, the incorporation of fluorinated motifs using various fluoroalkylating reagents is of particular importance because of their synthetic advantages.[9] Among these reagents, the title compound, FBSM (**2**), has been developed as a versatile nucleophilic monofluoromethylating reagent. Notably, owing to the presence of the two phenylsulfonyl groups, FBSM possesses superior acidity than fluoromethyl phenyl sulfone (**1**) and can undergo feasible deprotonation to render a rather stable α-fluorocarbanion.[10] Thus, a variety of nucleophilic monofluoromethylation reactions have been achieved using FBSM, such as the ring-opening of epoxides and aziridines,[7] the allylic monofluoromethylation reaction,[8] the Mitsunobu reaction,[11] conjugate addition reactions,[12] the Mannich reaction,[13] the aldol reaction,[14] as well as many others (Scheme 1).[15] In particular, the facile reductive removal of the sulfonyl groups allows for the introduction of the unfunctionalized CH_2F motif using FBSM, thereby prevailing over many other monofluoromethylating reagents. In addition, FBSM can be further converted to fluoroiodobis(phenylsulfonyl)methane, which has been utilized as a viable radical monofluoromethylating reagent.[16]

Although extensively utilized in nucleophilic monofluoromethylation reactions, the synthetic approaches toward FBSM had been rather limited since the initial documentation of this compound. FBSM was originally synthesized in 49–60% yields through the reaction between Selectfluor® and bis(phenylsulfonyl)methide anion.[7,8] An alternative method was later

achieved via the electrochemical reaction of phenyl phenylsulfonylmethyl sulfide using tetraethylammonium fluoride-hydrogen fluoride mixture as the fluorine source.[17] The afforded product, α-fluoro-α-phenylthiomethyl phenyl sulfonyl, was further oxidized to generate FBSM in 44% yield in two steps. However, the major problems of the synthetic routes through the C-F bond formation are a) the fluorine sources are expensive and/or hazardous; b) the reactions can only afford the products in moderate yield (44–60%); c) the selectivity of the reactions is unsatisfactory due to the incomplete consumption of bis(phenylsulfonyl)methane and the formation of difluorinated product; d) the purification of the crude product necessitates the use of chromatography, which significantly limits the scalability of these methods.

Scheme 1. Synthetic Applications of FBSM (**2**)



Lately, instead of applying the C-F bond forming strategy, an improved synthetic protocol has been reported by treating fluoromethyl phenyl sulfone with methyl benzenesulfinate followed by the oxidation of the intermediate. Facilitated by the C-S bond formation reaction, such a methodology has been demonstrated with remarkable selectivity, and affords FBSM with high purity and excellent yield without sophisticated purification processes. Although this method triumphs over the previous approaches, its practicality is somewhat diminished due to the employment of less available sulfinate, which also introduces an additional step in the preparation.

Inspired by the C-S bond forming strategy, our laboratory has achieved the aforementioned preparative-scale method[18] using readily available starting materials to yield FBSM with excellent yield and high purity.

Appendix
Chemical Abstracts Nomenclature; (Registry Number)

Chloromethyl phenyl sulfide: Benzene, [(chloromethyl)thio]-; (7205-91-6)
Potassium fluoride (KF); (7789-23-3)
Fluoromethyl phenyl sulfide: Benzene, [(fluoromethyl)thio]-; (60839-94-3)
α,α,α-Trifluorotoluene: Benzene, (trifluoromethyl)-; (98-08-8)
18-Crown-6: 1,4,7,10,13,16-Hexaoxacyclooctadecane; (17455-13-9)
Oxone: Potassium peroxymonosulfate sulfate ($K_5(HSO_5)_2(HSO_4)(SO_4)$); (70693-62-8)
Fluoromethyl phenyl sulfone: Benzene, [(fluoromethyl)sulfonyl]-; (20808-12-2)
Potassium hydride (KH); (7693-26-7)
Hexamethyldisilazane: Silanamine, 1,1,1-trimethyl-*N*-(trimethylsilyl)-; (999-97-3)
Potassium bis(trimethylsilyl)amide: Silanamine, 1,1,1-trimethyl-*N*-(trimethylsilyl)-, potassium salt (1:1); (40949-94-8)
Benzenesulfonyl fluoride; (368-43-4)
α-Fluorobis(phenylsulfonyl)methane (FBSM): Benzene, 1,1'-[(fluoromethylene)bis(sulfonyl)]bis-; (910650-82-7)

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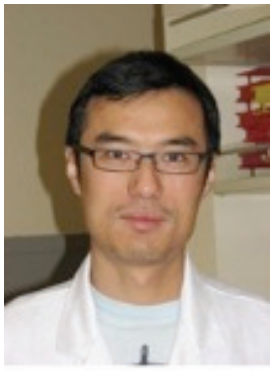
G. K. Surya Prakash, born 1953 in India, earned a Bachelor's degree from Bangalore University and a Master's degree from the Indian Institute of Technology. Prakash joined George Olah's group at Case Western Reserve University to pursue graduate work in 1974. He moved with Olah to the University of Southern California (USC) in 1977 and obtained his Ph.D. in Physical Organic Chemistry in 1978. He joined the faculty of USC in 1981 and is currently a Professor and the holder of the Olah Nobel Laureate Chair in Hydrocarbon Chemistry and serves as the Director of the Loker Hydrocarbon Research Institute.



Nan Shao was born 1979 in Shanghai, China. He received his B.S. degree in biochemical engineering at the East China University of Science and Technology in 2001. After earning his M.S. degree in chemistry at the University of Minnesota Duluth in 2006, he started to pursue his Ph. D. in the laboratory of Professor G. K. Surya Prakash and Professor George A. Olah at the University of Southern California, where he has conducted research involving the development of novel fluoromethylating reagents and fluoromethylation protocols.

Fang Wang was born in 1983 in Shenyang, China. He received a B.S. degree in chemistry in 2006 from the Zhejiang University, China, where he began undergraduate research with Professor Ping Lu. While there, he also attended the Shanghai Institute of Organic Chemistry as a visiting student performing research under the guidance of Professor Jinbo Hu. Since 2006, he has been pursuing his doctoral degree in the laboratory of Professor G. K. Surya Prakash and Professor George A. Olah at the University of Southern California. His research focuses on asymmetric fluoromethylations and the related mechanistic studies.

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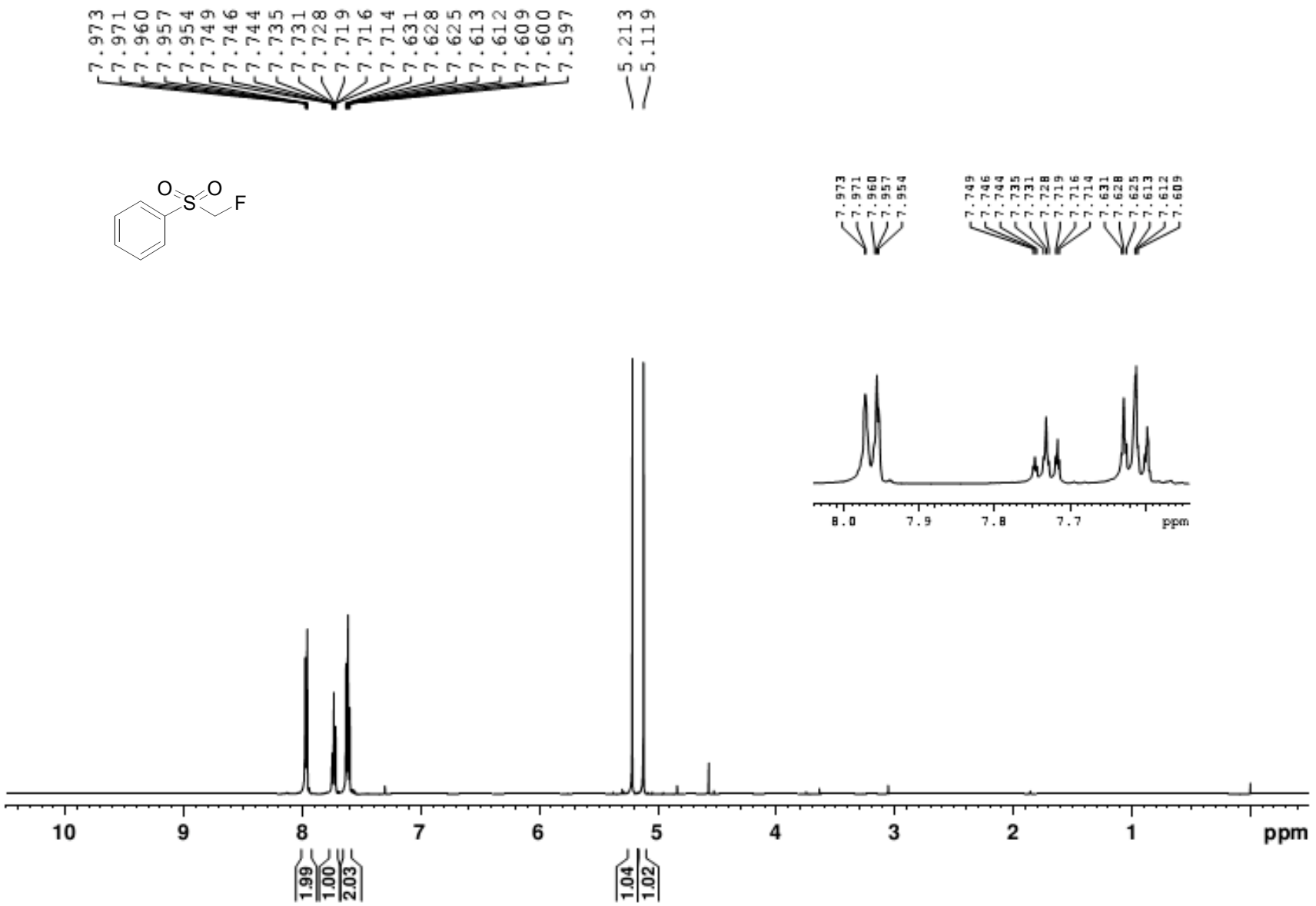
Thomas D. Montgomery was born in 1988 in Maryland, USA. He received a B.A. degree in chemistry and biology in 2010 from St. Mary's College of Maryland where he performed undergraduate research with Professor Andrew Koch. Since the fall of 2010 he has been pursuing his doctoral degree in Professor Viresh H. Rawal's lab at the University of Chicago. His research has focused on metal catalyzed functionalization of substituted indole cores and related compounds.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7.628
7.625
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7.600
7.597
5.213
5.119
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O
S
F
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7.9
7.8
7.7
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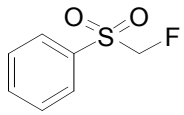
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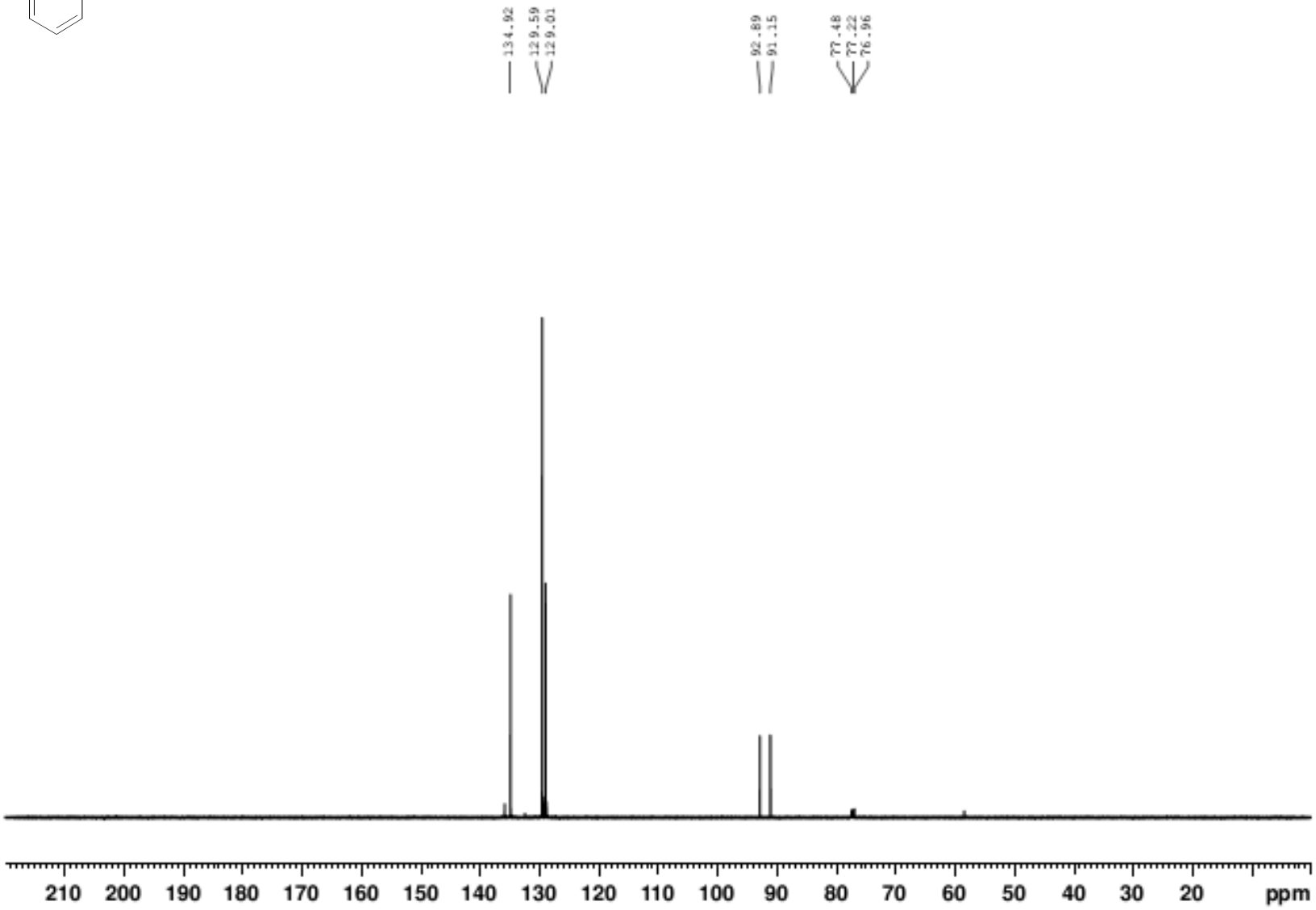
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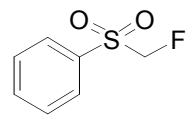
30
20
ppm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O
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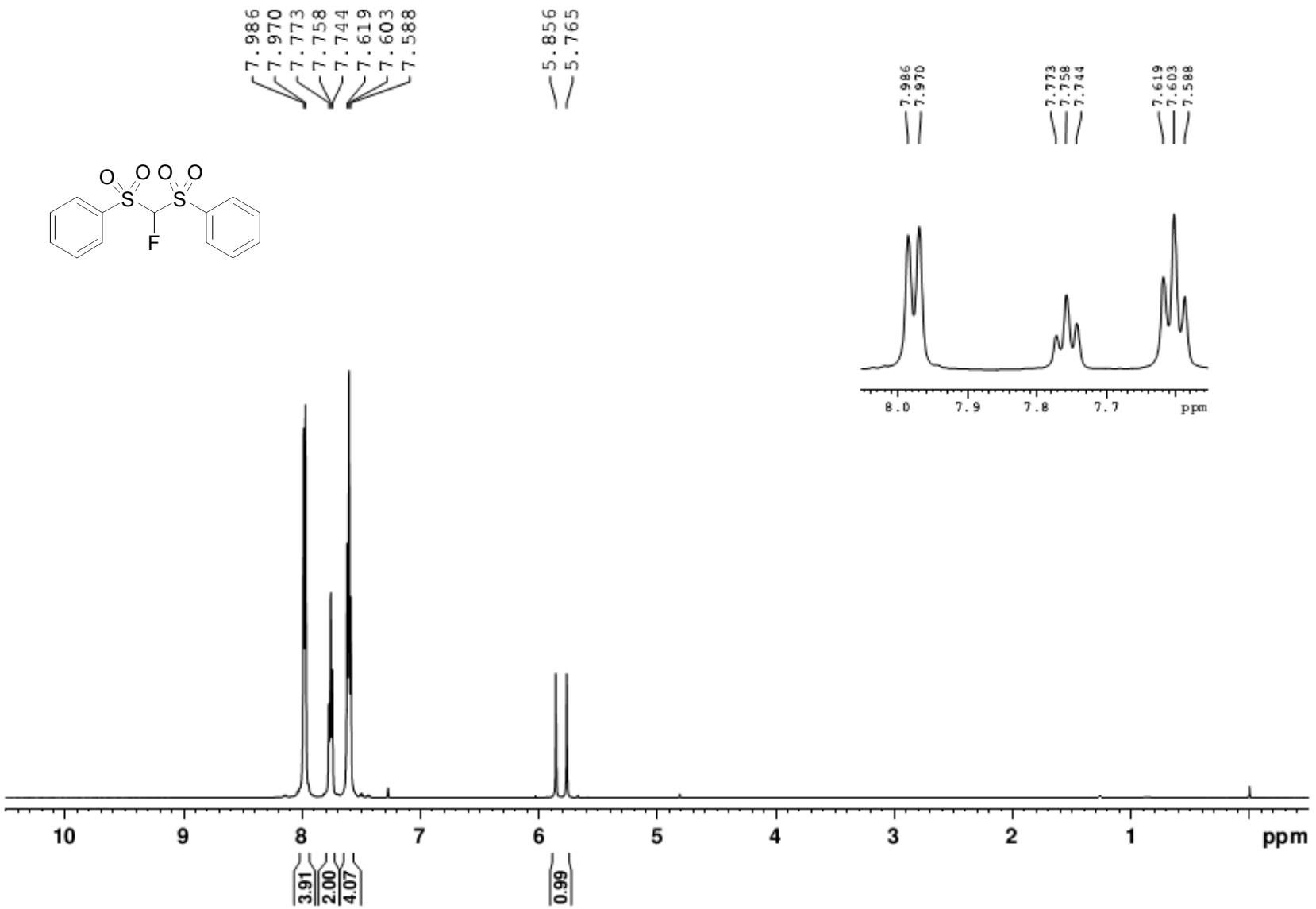
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S
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7.9
7.8
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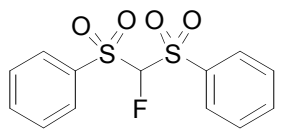

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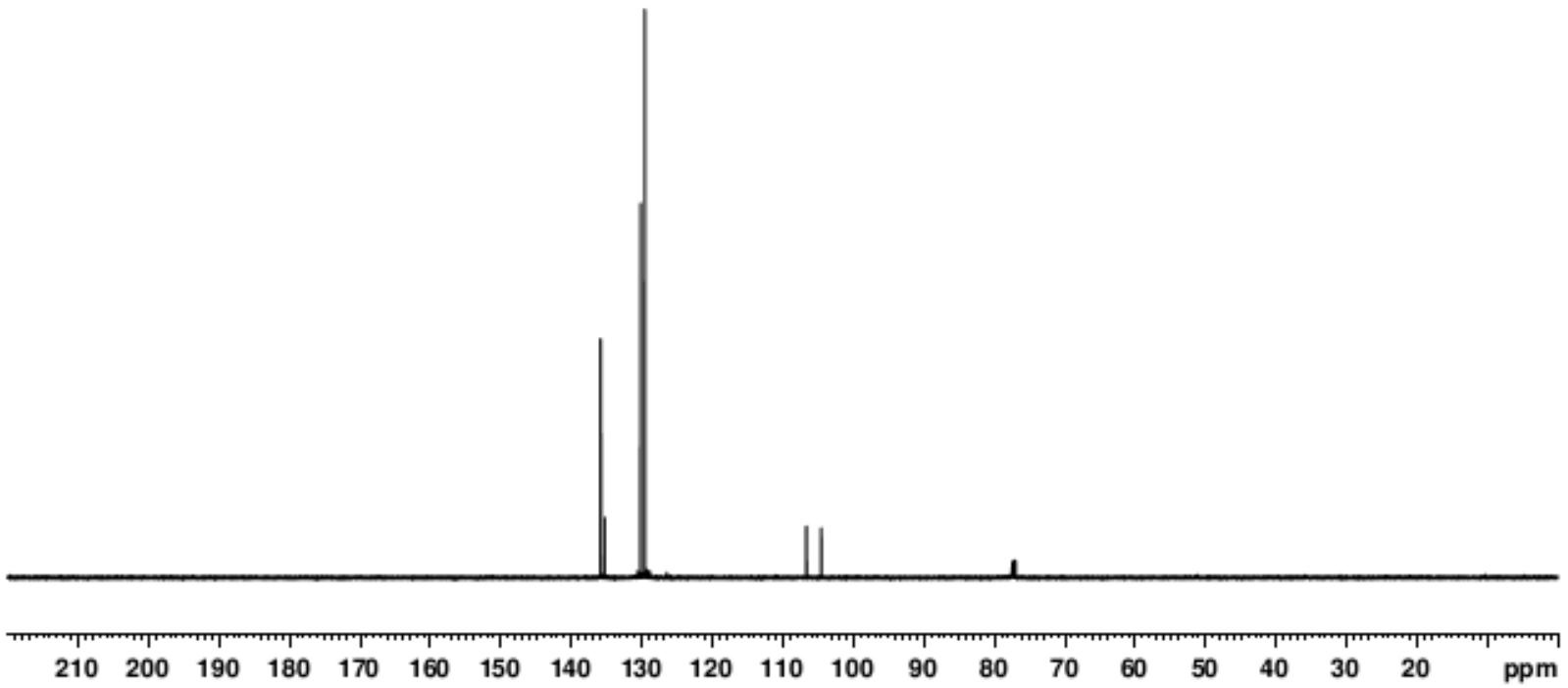

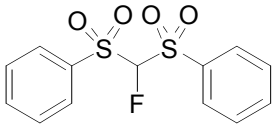
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ppm