

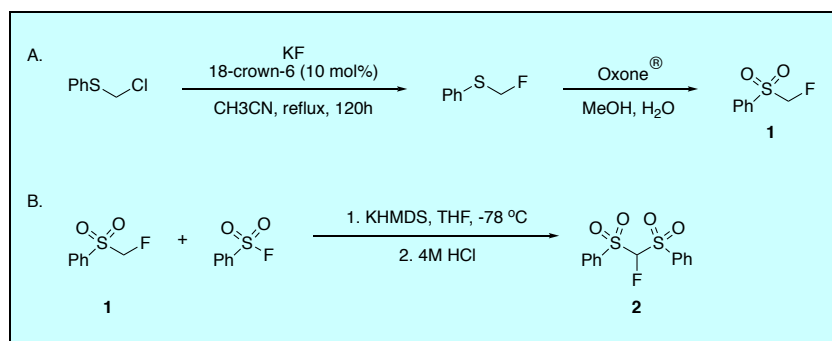
Discussion Addendum for:

Fluorobis(phenylsulfonyl)methane (FBSM)

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Monofluoromethylation is an important transformation that has been employed as a strategy to introduce fluoroalkyl functionalities into molecules.<sup>2</sup> Among the known reactions, nucleophilic monofluoromethylation stands out as an important approach in which a fluoroalkyl anion is generated and reacted with a suitable electrophile. Fluorobis(phenylsulfonyl)methane (FBSM) has been widely employed as a pronucleophile given that the electron-withdrawing nature of the phenylsulfonyl groups increases the acidity of the proton in the adjacent carbon atom, making its deprotonation facile and giving rise to a resonance-stabilized fluoromethide species<sup>3</sup> that can react with several electrophiles. This compound was first synthesized by Shibata et al., through the electrophilic fluorination of bis(phenylsulfonyl)methane<sup>4</sup> and was later used as a nucleophilic monofluoromethylating reagent. Prakash and coworkers

envisioned a large-scale procedure to synthesize FBSM in reagent quantities (Figure 1).<sup>5</sup>

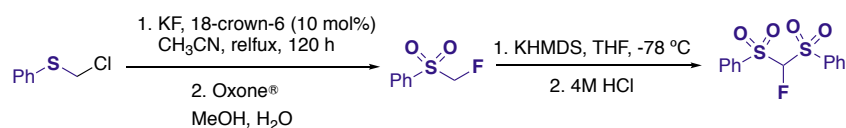
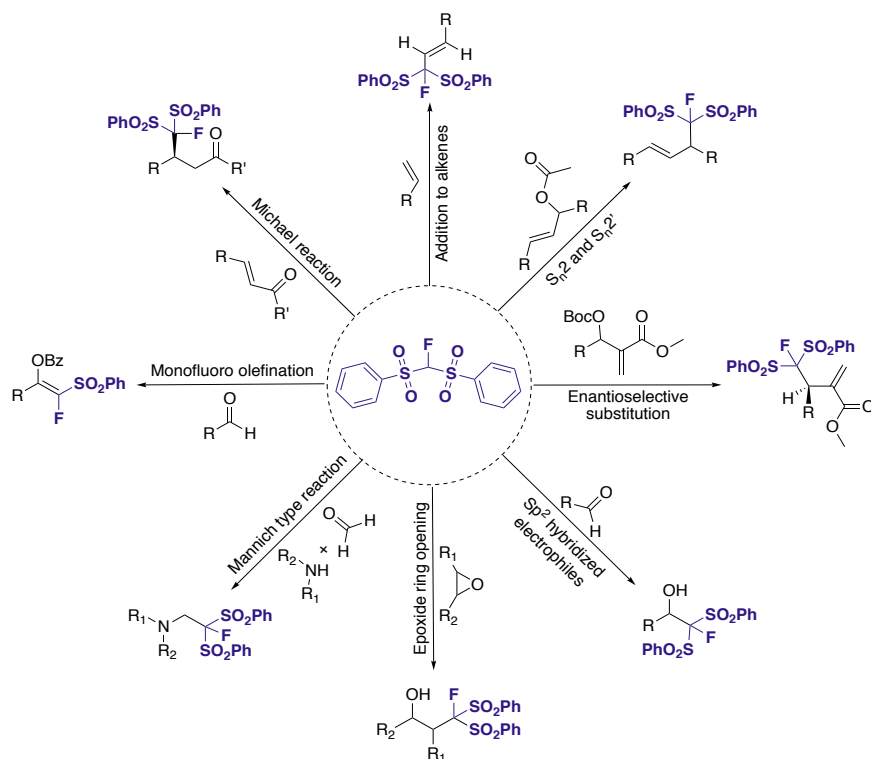


Figure 1. Prakash's large-scale synthesis of FBSM

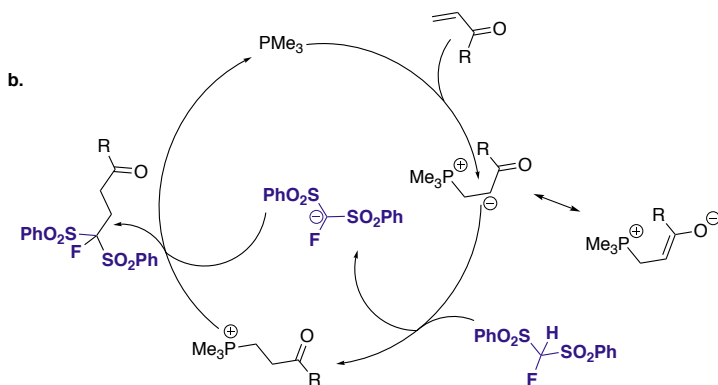
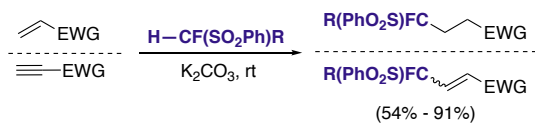
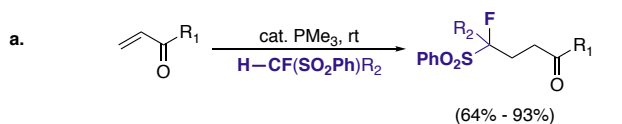
The present addendum discloses the transformations available employing FBSM as a monofluoromethylation reagent (Scheme 1).



Scheme 1. FBSM as a masked nucleophile

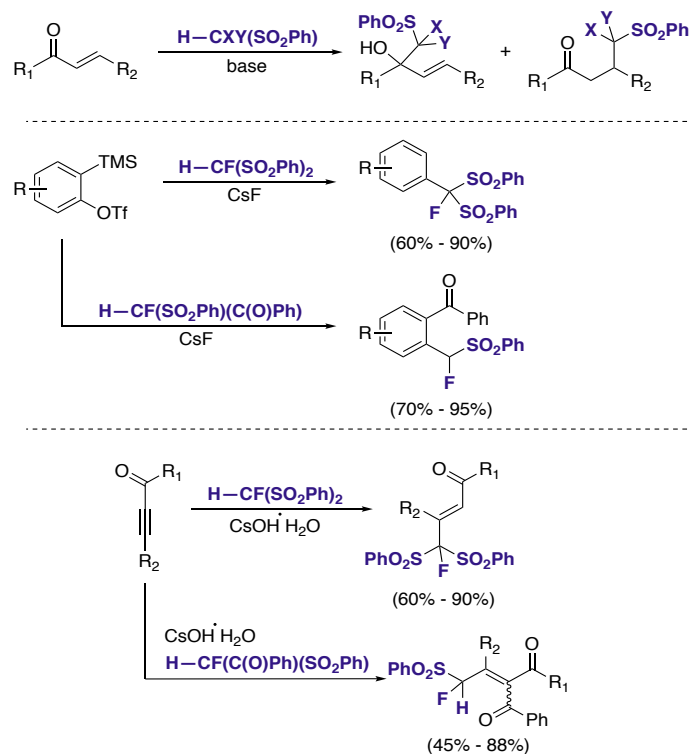
*Michael Reactions with FBSM*

Michael reactions are one of the most important synthetic avenues to impart structural complexity to organic molecules. The acidity of FBSM enables its facile deprotonation even when using mild bases, with the resultant anion being a good nucleophile which has been reacted with a variety of Michael acceptors, furnishing C-protected monofluoromethyl compounds. One of the earliest of such transformations was performed by Prakash and coworkers in 2008 (**Scheme 2**).<sup>6</sup> The authors prepared and screened a variety of fluoro(phenylsulfonyl)methanes, with the third substituent being a phenylsulfonyl, nitro, cyano, ester or ketone group. In reactions with  $\alpha,\beta$ -unsaturated compounds, trimethylphosphine was found to be the most efficient catalyst, furnishing the desired products in moderate to excellent yields (**Scheme 2a**). The reaction is proposed to proceed *via* initial addition of the electron-rich phosphine to the electrophilic carbon of the Michael acceptor, producing the active base: a  $\beta$ -phosphonio enolate. Note that analogous intermediates are well documented in the Morita-Baylis-Hillman reaction. Deprotonation of FBSM by the formed base, followed by subsequent attack of the newly-formed nucleophile at the C-P<sup>+</sup> carbon results in the formation of the desired products, along with the regeneration of the phosphine catalyst (**Scheme 2b**).



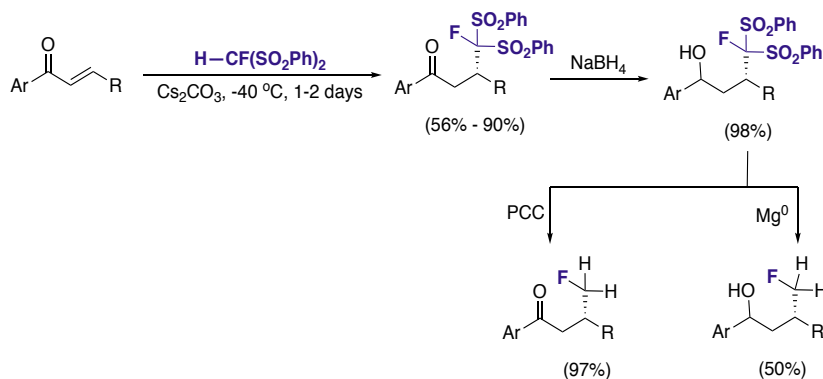
**Scheme 2. Phosphine-catalyzed FBSM addition to  $\alpha,\beta$ -unsaturated compounds**

Shortly after this seminal work, Hu and coworkers investigated FBSM-type molecules as pronucleophiles in the fluoromethylation of  $\alpha,\beta$ -unsaturated ketones, arynes, and alkynes.<sup>7</sup> Each transformation provided a mixture of products, with the ratio of formed species dependent on the hardness/softness of the nucleophile (**Scheme 3**).



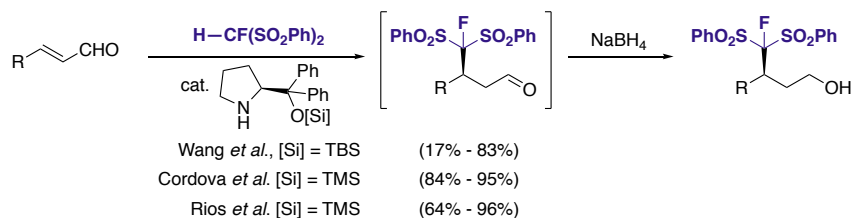
**Scheme 3.** Addition of FBSM to arynes, alkynes and  $\alpha,\beta$ -unsaturated ketones

A reaction system for the long-elusive chiral monofluoromethylation came from the 2008 work by Shibata and coworkers, wherein FBSM was used as a pronucleophile in an asymmetric 1,4-addition to  $\alpha,\beta$ -unsaturated ketones, with the stereochemistry set by a Cinchona alkaloid-derived ammonium salt.<sup>8</sup> Generally high (*ee*: 84% – 98%) enantiomeric excesses were observed along with good yields. Further functionalization at the carbonyl group was demonstrated *via* a  $\text{NaBH}_4$ -mediated reduction, keeping the phenylsulfonyl groups intact. Following this, oxidation to restore the carbonyl group results in simultaneous desulfurization, forming a monofluoromethyl group. Alternatively, a  $\text{Mg}^0$ -mediated reduction of the alcohol results in desulfurization to yield the monofluoromethyl derivative (**Scheme 4**).



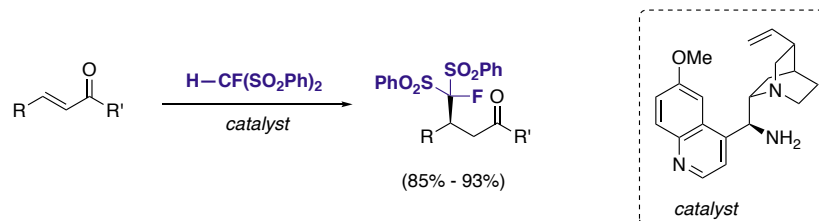
**Scheme 4. Chiral monofluoromethylation of  $\alpha,\beta$ -unsaturated ketones with FBSM**

Chiral enamine catalysis has been extensively employed in the asymmetric functionalization of aldehydes and ketones (**Scheme 5**). In 2009, the Wang group documented an asymmetric conjugate addition of FBSM to enals, catalyzed by a chiral proline derivative.<sup>9</sup> The active electrophile; the in-situ formed  $\alpha,\beta$ -unsaturated iminium ion; is trapped by FBSM to form a  $\beta$ -substituted enamine. Subsequent hydrolysis of the enamine (loss of the proline derivative) affords the desired products in moderate to good yields and in excellent enantiomeric excess. Adding to the slew of enantioselective fluoromethylations of Michael acceptors, Córdova and coworkers added FBSM to 1,2-enals using chiral proline-type catalysts,<sup>10</sup> similar to the work of Wang and coworkers.<sup>9</sup> The authors used an  $-\text{OTMS}$ -containing catalyst in place of an  $-\text{OTBS}$ -containing one, generating the desired monofluoromethyl compounds in good yields. At the same time, Rios and coworkers also published a near-identical synthesis of  $\beta$ -monofluoromethyl aldehydes.<sup>11</sup>



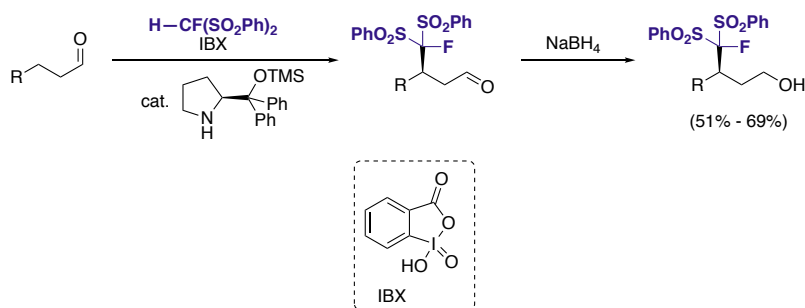
**Scheme 5. Asymmetric monofluoromethylation of  $\alpha,\beta$ -unsaturated aldehydes and ketones**

Another method for the enantioselective conjugate addition of FBSM to  $\alpha,\beta$ -unsaturated ketones comes in the form of the 2009 paper by Kim and coworkers, wherein chiral primary amine catalysts were used to steer the stereochemical outcome of the reaction towards one enantiomer (**Scheme 6**).<sup>12</sup> The thus formed products were obtained in moderate stereoselectivity and good to excellent yields. Noteworthy is the work of Hu and coworkers on the reversibility of 1,2-additions of FBSM across  $\alpha,\beta$ -unsaturated carbonyl compounds, wherein the formation of 1,4-adducts was observed following the disappearance of the 1,2-adducts.<sup>13</sup>



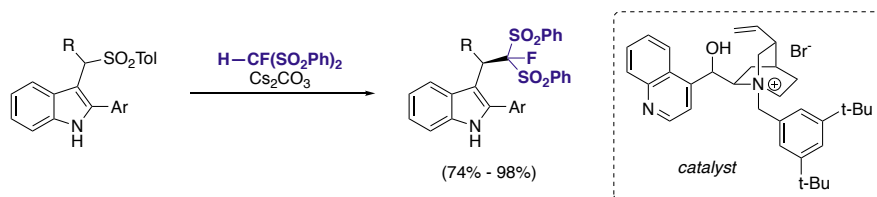
**Scheme 6.**  $\beta$ -Monofluoromethyl ketones *via* chiral primary amine catalysis

Despite iminium catalysis being widespread in organic chemistry, the converse process had not been studied (the conversion of an enamine to an iminium ion). That is, until the 2011 paper by Zhang et al., wherein *in situ* generated enamines were oxidized by a hypervalent iodine compound (IBX) (**Scheme 7**). The thus formed iminium ions were then reacted with FBSM, generating  $\beta$ -fluoromethyl compounds, which were then reduced to the corresponding alcohols using  $\text{NaBH}_4$ .<sup>14</sup>



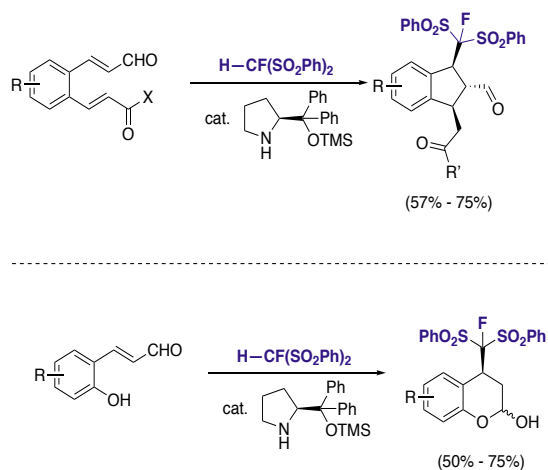
**Scheme 7.**  $\text{I}^{\text{V}}$ -mediated oxidative monofluoromethylation

An *in situ* generated iminium ion, stemming from the desulfurization of an indole derivative, has been used as an electrophile in reactions with FBSM. In this work by Shibata and coworkers, the monofluoromethyl indole derivatives were prepared in excellent yields and generally displayed high enantiomeric excess (**Scheme 8**).<sup>15</sup> As in previous work, radical desulfurization proceeds with retention of stereochemistry.



**Scheme 8. Enantioselective monofluoromethylation of indole derivatives**

Finally, in a collaborative effort, the labs of Yang and Rios jointly developed a cascade reaction for the synthesis of fluoroindane and fluorchromanol derivatives.<sup>16</sup> The cascade begins with a conjugate addition of FBSM to the iminium ion born as a consequence of condensation between the aldehyde and the chiral amine. Upon the occurrence of a second Michael reaction, the fluoroindane is formed. Using (2-hydroxy)cinnamic acids results in the formation of fluorchromanols (**Scheme 9**).

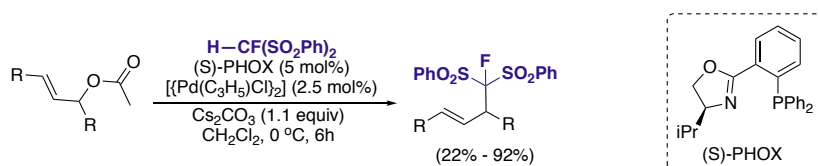


**Scheme 9. Preparation of fluoroindanes and fluorchromanols**



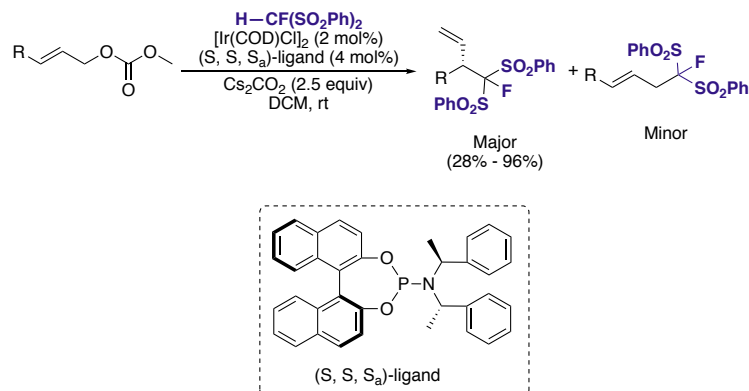
## Substitution Reactions with FBSM

$S_N2'$ :  $S_N2'$  chemistry offers a viable route to obtain functionalized allylic compounds. The application of this concept to FBSM pronucleophile has facilitated the synthesis of various  $\beta,\gamma$ -unsaturated- $\alpha$ -fluoromethyl compounds. The first transformation of this type was disclosed collaboratively by Shibata and Toru in 2006 (**Scheme 10**).<sup>4</sup> The authors performed an enantioselective allylic monofluoromethylation of allyl acetates using FBSM in combination with a palladium catalyst and chiral ligand, producing the desired allyl monofluoromethanes in moderate to good yields with high enantioselectivities.



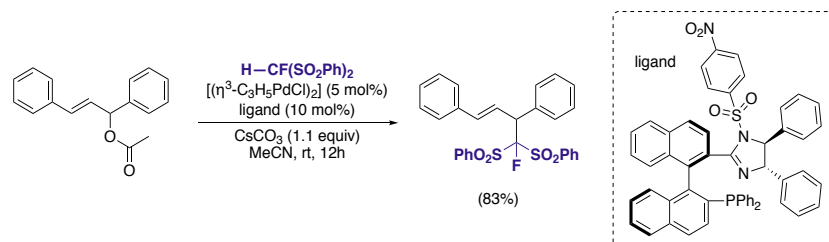
**Scheme 10.** Enantioselective Pd-catalyzed allylic monofluoromethylation

An analogous reaction catalyzed by iridium in place of palladium was devised by Liu et al., wherein FBSM-containing terminal alkenes were prepared in excellent yields with good enantioselectivity (**Scheme 11**).<sup>17</sup> The authors then proceeded to apply their methodology to the synthesis of monofluoromethyl ibuprofen, which was found to have enhanced analgesic properties.<sup>18</sup>



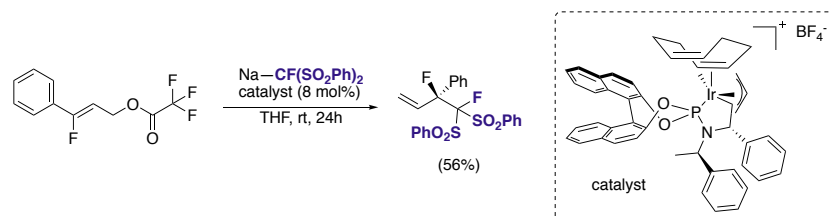
**Scheme 11.** Enantioselective Ir-catalyzed monofluoromethylation of allylic carbonates

As part of an investigation into the potency of phosphine-imidazoline ligands when applied to allylic substitution reactions, FBSM was reacted with an allylic acetate to generate the allyl-monofluoromethyl compound in good yield with excellent *ee*.<sup>19</sup> Mei et al. discovered that the optimal catalyst for this system was  $\eta^3$ -allyl palladium(II)chloride dimer, and a series of axially-chiral BINAP-type ligands were found suitable for the transformation (**Scheme 12**).



**Scheme 12.** Chiral ligand-assisted Pd-catalyzed  $\alpha$ -fluoromethylation

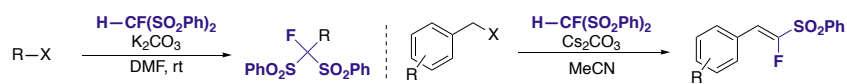
Finally, Hartwig and coworkers developed a method for the production of tertiary allylic fluorides from tri-substituted alkene derivatives (**Scheme 13**).<sup>20</sup> Catalyzed by an iridium species, the reaction system provided the desired products in moderate to excellent yields.



**Scheme 13.** Ir-catalyzed synthesis of allylic fluorides

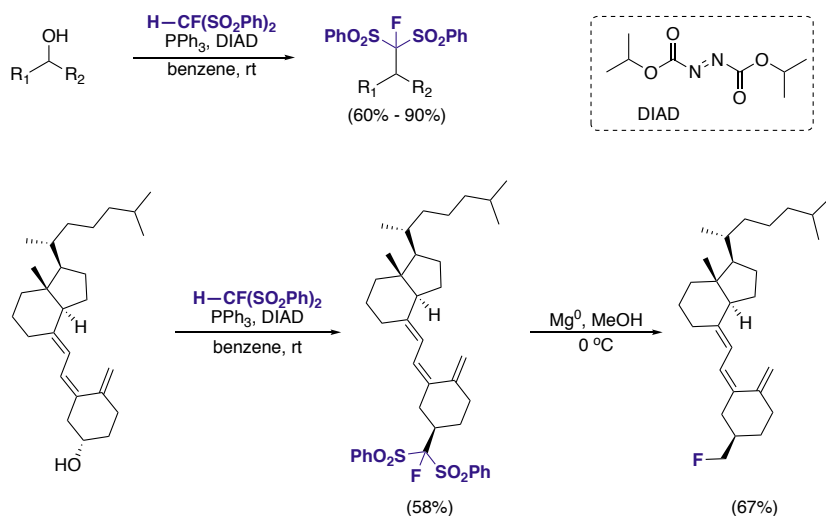
$S_N2$ : Perhaps one of the most studied reactions,  $S_N2$  chemistry has become standard textbook science: the reaction of a nucleophile with a primary or secondary carbon with a good leaving group proceeding with inversion of stereochemistry. In 2009, Prakash and coworkers developed a base-mediated monofluoromethylation of primary alkyl halides using FBSM as the pronucleophile.<sup>21</sup> The results of this chemistry are substrate-dependent: aliphatic alkyl halides produced the expected  $S_N2$  product, and benzyl

halides afforded monofluoroolefins instead, facilitating the synthesis of  $\beta$ -fluorostyrenes (**Scheme 14**).



**Scheme 14. Nucleophilic monofluoromethylation of primary alkyl halides**

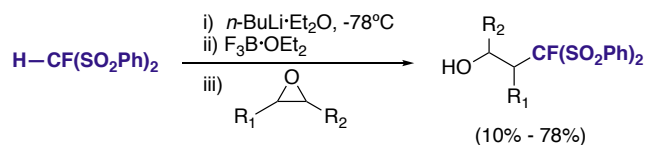
*Mitsunobu-type:* Mitsunobu chemistry has been used extensively in the deoxygenative functionalization of primary and secondary alcohols. In 2007, Prakash and coworkers delineated a DIAD/ $\text{PPh}_3$ -mediated deoxygenation-monofluoromethylation of secondary alcohols, producing monofluoromethyl compounds in good to excellent yields (**Scheme 15**).<sup>22</sup> In the case of enantiopure alcohols, the transformation proceeds with inversion of stereochemistry at the chiral alcohol carbon.



**Scheme 15. Stereospecific deoxymonofluoromethylation of secondary alcohols**

### Epoxide Ring-opening

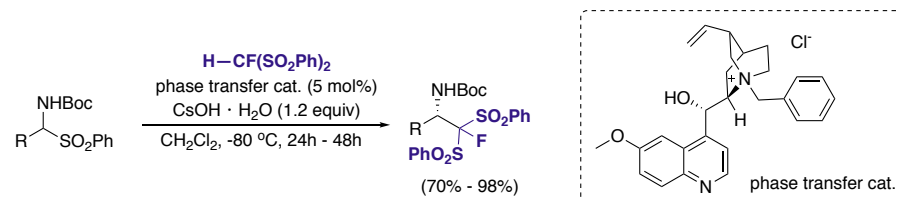
Epoxide ring-opening reactions have seen use primarily in the synthesis of  $\beta$ -substituted alcohols. One approach to  $\beta$ -monofluoromethyl alcohols was disclosed by Hu and coworkers in 2006.<sup>23</sup> On deprotonation with *n*-BuLi, FBSM was reacted with various epoxides, of which the corresponding monofluoromethane derivatives were obtained in good to excellent yields (**Scheme 16**).



**Scheme 16. Epoxide ring-opening with FBSM**

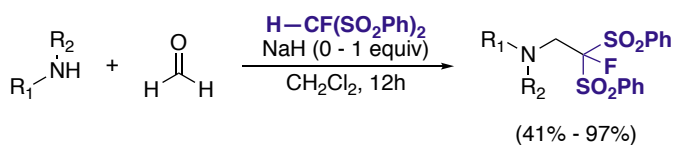
### Multicomponent Reactions with FBSM

The propensity of FBSM to behave as a pronucleophile has encouraged its implementation in multicomponent reactions. The first such system was developed by Shibata and coworkers in 2007, which allowed for the synthesis of  $\beta$ -monofluoromethyl amines starting from  $\beta$ -sulfonyl amines and using a chiral phase-transfer catalyst (**Scheme 17**). The products were furnished in good to excellent yields.



**Scheme 17. Monofluoromethylation of amines by phase-transfer catalysis**

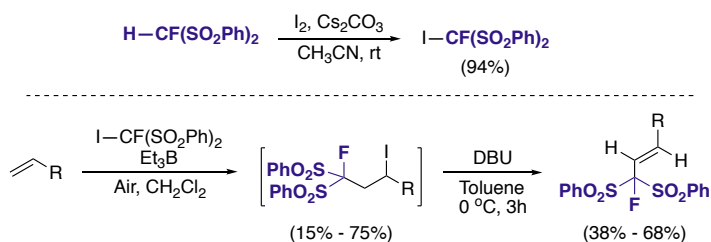
In 2013, Prakash and coworkers presented a Mannich-type reaction between an aldehyde, a secondary amine, and FBSM, producing a variety of monofluoromethyl amines in moderate to good yields.<sup>24</sup> The addition of NaH as a base was required for challenging substrates (**Scheme 18**).



**Scheme 18. Synthesis of  $\beta$ -monofluoromethyl amines through Mannich-type intermediate**

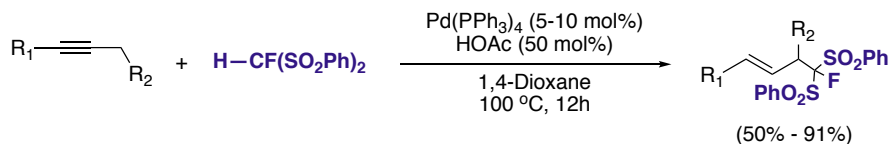
### Additions to Alkenes and Alkynes

Fluoriodobis(phenylsulfonyl)methane (FBSM-I) has been prepared by a deprotonation-iodination sequence developed by Prakash and coworkers (**Scheme 19**),<sup>25</sup> and this methodology was later used by Shibata and coworkers in developing novel halogen-bonding catalysts.<sup>26</sup> In Prakash's work, the iodomethane derivative was demonstrated to be a viable radical monofluoromethylation reagent, affording the desired monofluoromethyl products in good to excellent yields.



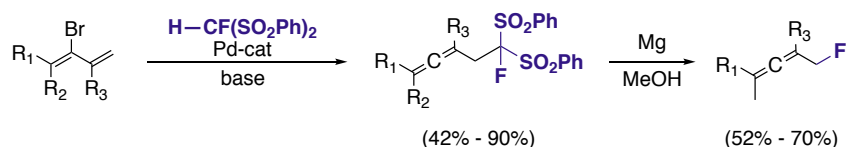
**Scheme 19. Radical monofluoromethylation of olefins using FBSM-I**

A palladium-catalyzed allylation of FBSM was later developed by Hu and coworkers.<sup>27</sup> Mediated by HOAc, this method furnished the linear products in high yields and excellent regioselectivity (**Scheme 20**).



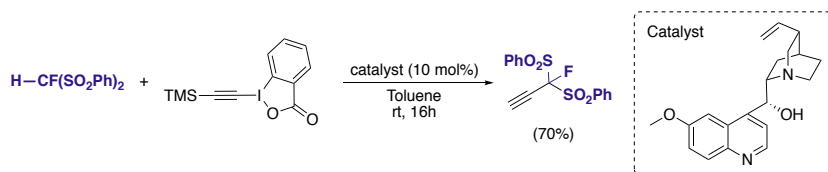
**Scheme 20. Allylic monofluoromethylation of alkynes**

In 2009, Shibata and coworkers devised a synthesis of monofluoromethyl allenes from 2-halo-1,3-dienes and FBSM, catalyzed by a palladium species.<sup>28</sup> The desired allenes were synthesized in excellent yields (**Scheme 21**).



**Scheme 21. Monofluoromethylation of conjugated dienes**

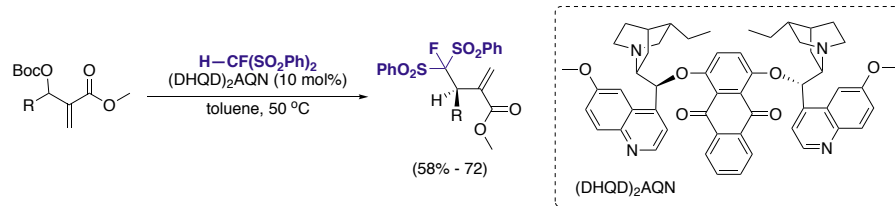
A transition metal-free, chiral ammonium salt catalyzed, electrophilic alkynylation method was developed by Kamlar et al, yielding alkynyl monofluoromethanes in high yields (**Scheme 22**).<sup>29</sup>



**Scheme 22. Electrophilic alkynylation of FBSM**

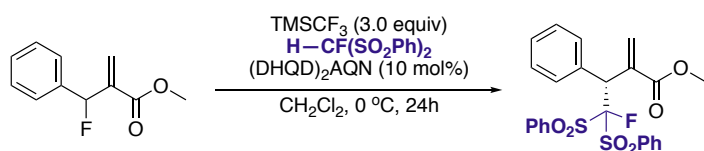
#### *Addition to Morita-Baylis-Hillman Products*

Morita-Baylis-Hillman (MBH) products have been extensively used as versatile synthons for the introduction of molecular complexity in substrates of interest. The first fluoromethylation of an MBH-carbonate was reported by Shibata and coworkers in 2011, wherein FBSM was used as a nucleophilic monofluoromethyl source (**Scheme 23**).<sup>30</sup> The use of an axially chiral anthraquinone allowed the authors to obtain allyl-fluoromethyl compounds in moderate to good yields, with high enantioselectivity. Similar work is reported by Yang et al.<sup>31</sup>



**Scheme 23. Enantioselective monofluoromethylation of MBH-carbonates**

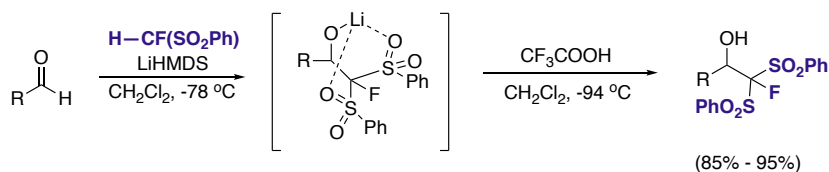
Later, Shibata conducted a similar transformation, wherein the base used to deprotonate FBSM was trifluoromethide generated in-situ from (trifluoromethyl)trimethylsilane (TMSCF<sub>3</sub>) (**Scheme 24**).<sup>32</sup>



**Scheme 24. Trifluoromethide-promoted monofluoromethylation**

#### Additional Reactions of FBSM

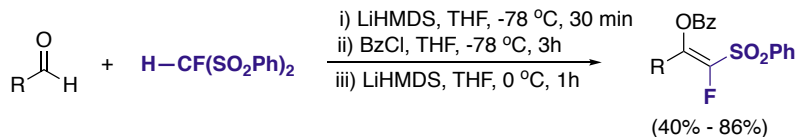
FBSM has been added to C(sp<sup>2</sup>) electrophiles. In 2011, Hu and coworkers disclosed an addition of FBSM to aldehydes, mediated by Li<sup>+</sup> coordination (**Scheme 25**).<sup>33</sup> The nature of the cation was found essential in facilitating the addition, as Na<sup>+</sup> and K<sup>+</sup> bases did not produce favorable results. The desired monofluoromethyl carbinols were obtained in excellent yields.



**Scheme 25. Li<sup>+</sup>-promoted FBSM addition to aldehydes**

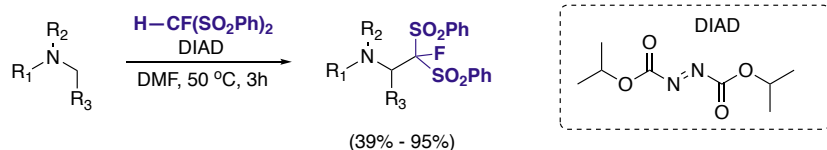
Further elaboration on this type of chemistry was presented by the same group, two years later. Synthesized by the above method,<sup>33</sup>

monofluoromethyl carbinols were transformed into monofluoroolefins through step-wise treatment with benzyl chloride and then LiHMDS. The olefins were predominantly obtained in the *Z* configuration, and in good yields (**Scheme 26**).<sup>34</sup>



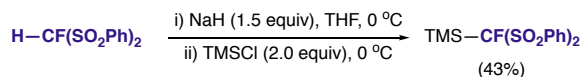
**Scheme 26. Monofluoroolefination using FBSM**

A DIAD-mediated  $\alpha$ -fluoromethylation of tertiary amines is reported by Hu and coworkers, *via* a dehydrogenative coupling of the amines with FBSM (**Scheme 27**).<sup>35</sup> The reaction is postulated to involve an iminium ion intermediate, which acts as the electrophile to react with FBSM nucleophile. The monofluoromethyl products were obtained in moderate to excellent yields.



**Scheme 27. Dehydrogenative monofluoromethylation of amines**

Perfluoroalkylsilanes have been extensively used as sources of nucleophilic fluoroalkyl species. The deprotonation-silylation of FBSM, as conducted by Prakash et al., provides access to a reagent requiring mild activation for nucleophilic monofluoromethylation of carbonyl compounds (**Scheme 28**).<sup>36</sup>



**Scheme 28. Silylation of FBSM**



## References

1. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA-90089-1661 (USA). \*Corresponding author: [gprakash@usc.edu](mailto:gprakash@usc.edu). ORCID G. K. Surya Prakash: 0000-0002-6350-8325. The work is supported by the Loker Hydrocarbon Research Institute. †These authors contributed equally to the work. ‡Undergraduate research participant.
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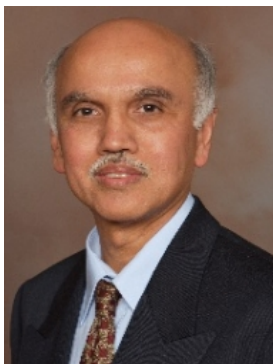
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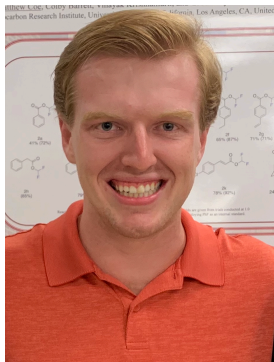
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