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磺酰氟合成研究进展

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摘 要

由于磺酰氟基团在有机合成、材料化学和材料科学相关的应用中起到重要作用，将磺酰氟基团选择性地引入到有机分子中已成为一个快速发展的领域，磺酰氟可进行六价硫氟交换反应以及可以利用磺酰基合成氨基酸的生物电子等排体，因此人们开发多种合成磺酰氟的方法，本文介绍了目前已知的合成磺酰氟的方法，包括亲核取代，卤原子交换，氧化，自由基偶联，自由基加成。

关键词

磺酰氟，卤原子交换，含硫衍生物

Progress in Synthesis of Sulfonyl Fluoride

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Abstract

Because sulfonyl fluorine groups play an important role in organic synthesis, material chemistry and material science, the selective introduction of sulfonyl fluorine groups into organic molecules has become a rapidly developing field. Sulfonyl fluorine can carry out hexavalent sulfur-fluorine exchange reactions and bioelectronic isobars of amino acids can be synthesized by the sulfonyl group. Therefore, a variety of methods for the synthesis of sulfonyl fluorine have been developed. In this paper, the known methods for the synthesis of sulfonyl fluorine are introduced, including nucleophilic substitution, halogen atom exchange, oxidation, free radical coupling and radical addition.

Keywords

Sulfonyl Fluoride, Halogen Atom Exchange, Sulfur-Containing Derivatives

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1. 引言

在各种硫(VI)卤化物中，磺酰氟化物由于其独特的性质和广泛的应用，近年来引起了越来越多的研究关注。与类似的磺酰氯相比，磺酰氟化物非常稳定，与苛刻的反应条件相容，但在特定的活化环境中对 O-和 N-亲核试剂表现出优异的亲电反应性[1]。尽管有机硫氟化物的这种独特的反应稳定性平衡早在 20 世纪 20 年代就被认识到[2]，在有机合成中，磺酰氟化物长期以来被认为是合成含磺酰基化合物(包括磺酰胺、磺酸盐和砜)的通用前体，而不是磺酰氯[3] [4] [5]。此外，磺酰氟化物已被用作一类新的选择性氟化试剂，用于脱氧氟化[6] [7] [8]和 ^{18}F 放射性标记[9] [10]。最近，氟磺酰基叠氮化物(FSO_2N_3)已被证明是一种由伯胺合成叠氮化物的优良重氮转移试剂[11]。磺酰氟化物作为反应性探针在化学生物学和分子药理学中的研究兴趣迅速增长，该类化合物是医药化学中的有效中间体，它们的高选择性抑制活性的成功鉴定促进了研究兴趣，即开发基于磺酰氟的酶抑制剂或化学探针[1] [12]-[26]，例如肽型抑制剂[1] [22] [23] [24] [25] (如图 1 所示)。在生物学中，磺酰氟已被用作化学生物学和药物发现中的特权共价探针和抑制剂[1] [12] [27] [28] [29]，为医药开发提供了大量研究素材。[23] [24] [25]它们已被广泛应用于许多领域，包括化学生物学[11] [13] [16] [18] [19] [20] [28] [30]、有机合成[6] [31]-[37]、聚合物制备[38] [39] [40]等。

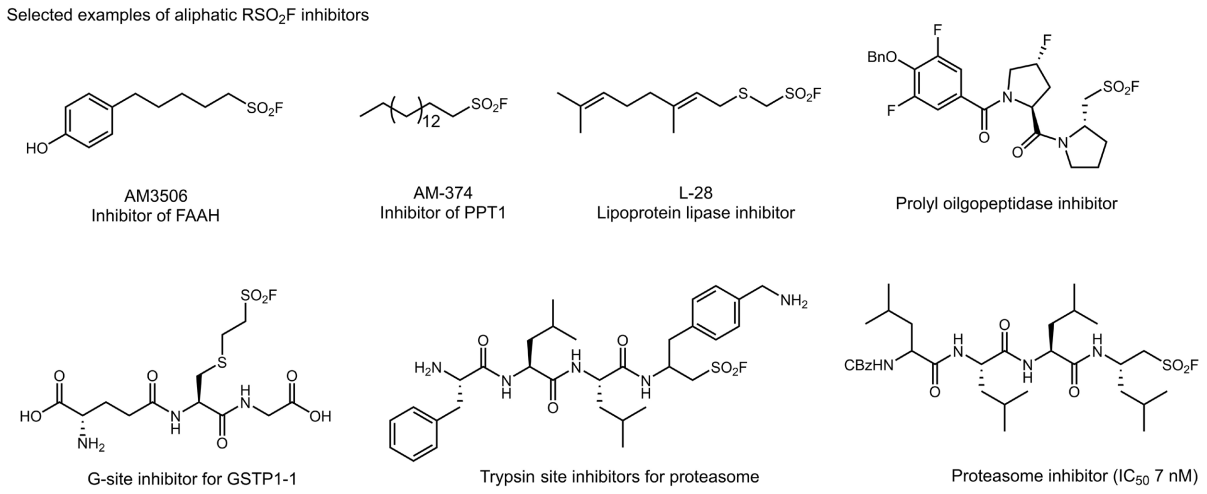


Figure 1. Selected examples of aliphatic sulfonyl fluoride inhibitors
图 1. 几种脂肪族磺酰氟抑制剂

源于磺酰基氟化物的独特性质，包括其特殊的稳定性－反应模式和对微环境敏感的质子介导反应性。磺酰基氟化物可以作为反应中间体，发生一系列的转化(如图 2 所示)。含溴和碘的芳烃磺酰基氟化物可以在溴或碘位点进行几种功能化，包括用 Chen 试剂进行三氟甲基化[41]，Heck 和 Suzuki 交叉偶联反应，得到相应的产物 3-5，SO_2F 官能团被完整保护。此外，芳烃磺酰基单元经常存在于许多药物和除草剂中，醇和胺的磺酰基化反应是药物研究中应用最广泛的五个反应之一[42]。通过这种转化获得的各种芳烃磺酰基氟化物可以作为良好的磺酰基试剂。芳烃磺酰氟与各种含氧或含氮亲核试剂的简单反应得到相应的磺酸酯 6、磺酰酰胺 7 和磺酰叠氮化物 8。用 $TMSCF_3$ 处理磺酰氟以良好产率得到所需产物 9。值得注意的是，磺酰氟也可以用作亲电磺酰化试剂，用化学计量的 $AlCl_3$ 作为路易斯

酸作用下生成砜[43]。

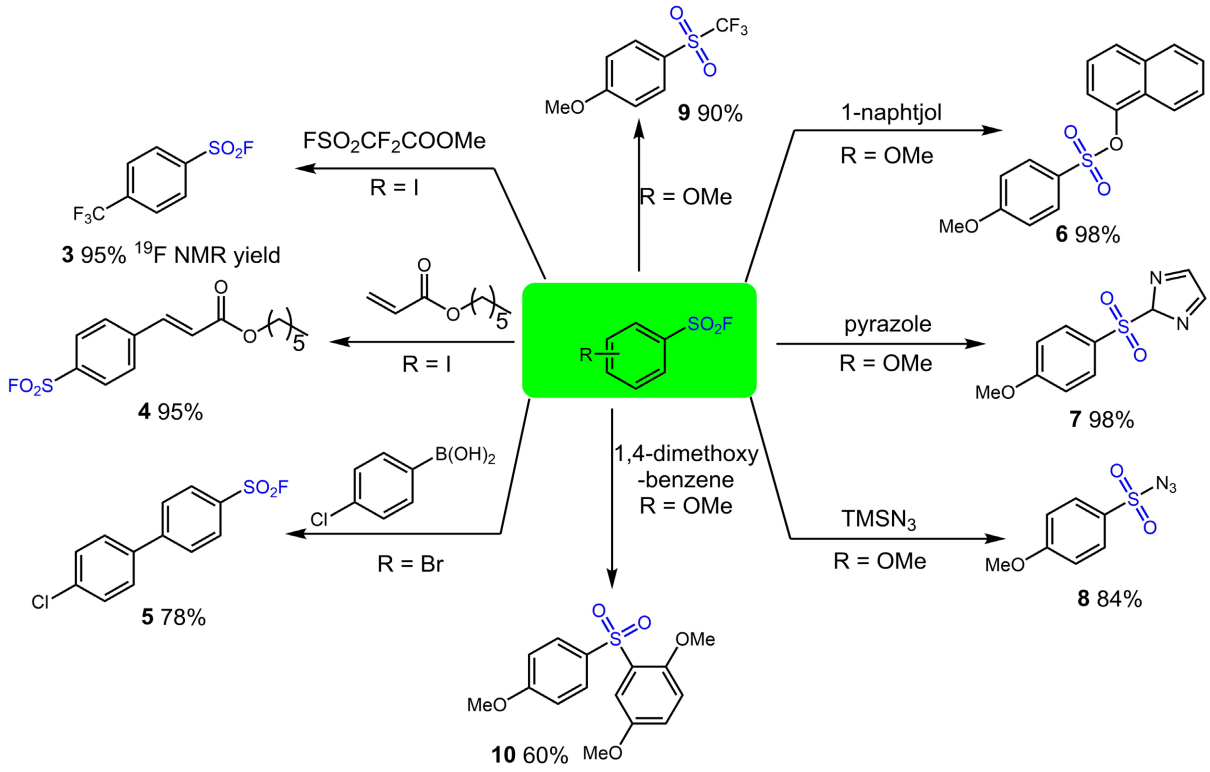


Figure 2. Derivatization reactions of the arenesulfonyl fluorides
图 2. 磺酰氟的衍生化反应

2. 合成黄酰氟的常见方法

鉴于磺酰氟的广泛应用在各个领域中的广泛应用，开发获得磺酰氟的有效方法无疑是高需求的，并已成为有机化学中的热门话题。在这篇综述中，我们旨在及时总结磺酰氟化物的合成方法，本文根据亲核取代反应，F/Cl 卤原子交换反应，含硫衍生物的氧化氟磺酰化，自由基的偶联，黄酰氟自由基对烯烃的加成等不同反应类型合成 RSO2F 的方法进行了概括。

2.1. 亲核取代反应

早在 1979 年，Hyatt 课题组就研究了 ESF 与胺、硫醇以及活性亚甲基亲核试剂的 Michael 反应，以优异的产率得到广泛的脂肪族磺酰基氟化物[44]。2014 年，Sharpless 课题组顺利扩展了 ESF 与各种亲核试剂的 Michael 反应，这些亲核试剂包括活性胺、含胺两性离子、磺酰胺、醇和 1,3-二羰基化合物[45] (如图 3 所示)。2019 年，Leung 课题组报道了第一个 Pd 催化的 β-芳基乙磺酰基氟化物的对映选择性加氢膦化反应[46]。以优异的产率获得了一系列手性磺酰氟衍生的膦，其 ee 值高达 93%。同年，该小组实现了 Rh 催化的芳基硼酸与 2-芳基乙烯磺酰基氟化物的不对称共轭加成[47]。获得了一系列具有手性偕二芳基甲烷部分的新型磺酰基氟化物，其对映选择性高达 99.8%。2019 年，Yan 课题组在 ESF 中实现了 3-氨基-2-氧吲哚的有机催化对映选择性 Michael 加成[48]。以 3,3-二取代吲哚为骨架，制备了一系列手性磺酰氟化合物，产率高，对映选择性好。提出奎宁衍生的芳酰胺可以通过氢键相互作用同时激活两种底物。此外，在不损失光学纯度的情况下，产物顺利转化为手性螺环氧吲哚舒坦、磺酰胺

和磺酸盐。

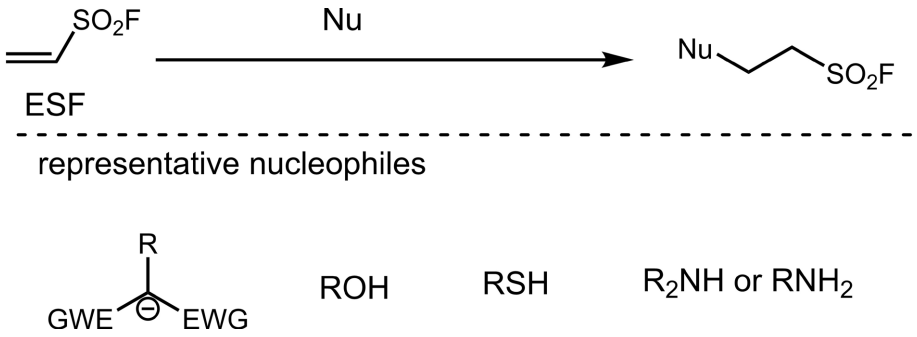


Figure 3. Conjugate addition of carbon, oxygen, and nitrogen nucleophiles to ESF
图 3. 碳、氧和氮亲核试剂与 ESF 的共轭加成

2019 年，Michael C. Willis 课题组报道了一种氧化还原中性 Ni(II)催化的易得芳基和杂芳基硼酸的硫化反应[49] (如图 4 所示)。使用 $NiBr_2$.(glyme)和 DABSO 组合，硼酸可以有效地转化为相应的亚磺酸盐，通过使用 N-氟苯磺酰亚胺(NFSI)作为亲电组分，能够以良好至适度的产率制备一系列磺酰氟化物。

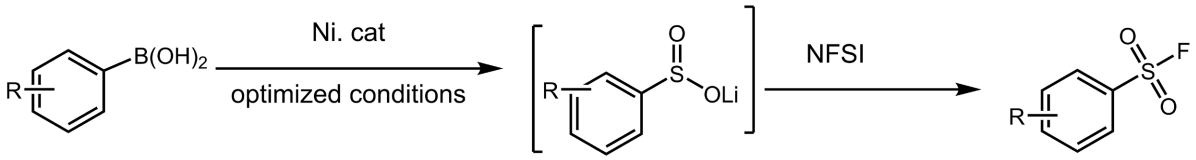


Figure 4. Sulfonyl fluoride was prepared with NFSI as electrophilic reagent
图 4. 以 NFSI 为亲电试剂制备磺酰氟化物

2019 年，Sammis 课题组报道了一锅法合成磺酰氟的新方法[50]。在环境温度下，将烷基、芳基或杂芳基格氏试剂加入磺酰氟溶液中，可获得中等产率的磺酰氟产物(如图 5 所示)。然而，底物范围相对有限，对强吸电子取代的苯基衍生物没有效果。

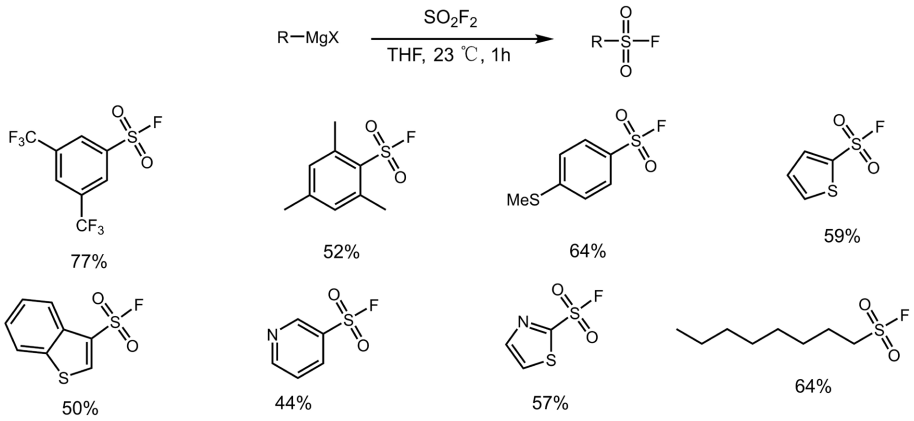


Figure 5. Sulfonyl fluoride was obtained by one-pot method
图 5. 一锅法制备磺酰氟

2021 年，Tang 课题组[51]报道了用铜催化三组分反应。将喹啉、异喹啉和吡啶转化为一类独特的含中氮茚的烷基磺酰基氟化物(如图 6 所示)。该方法具有底物范围广、官能团兼容性强、原子经济性，反应条件温和等特点。重氮盐与铜催化剂反应形成铜卡宾物质 A，同时释放 N_2。随后，中间体 A 受到喹啉分

子的亲核攻击，形成喹啉叶立德中间体 B，该中间体 B 进一步转化为前体 1,3-偶极子 C；随后 1,3-偶极子 C 与 ESF 的 1,3-双极环加成生成环化脂肪族磺酰氟 D。中间体 D 在喹啉的协助下去质子化，得到 E，其与另一分子 ESF 进行典型的 Michael 加成产生中间体 F。随后磺酰氟基团水解得到 G，最后，通过消除 SO_3 和在铜/O_2 下的氧化过程得到预期产物。

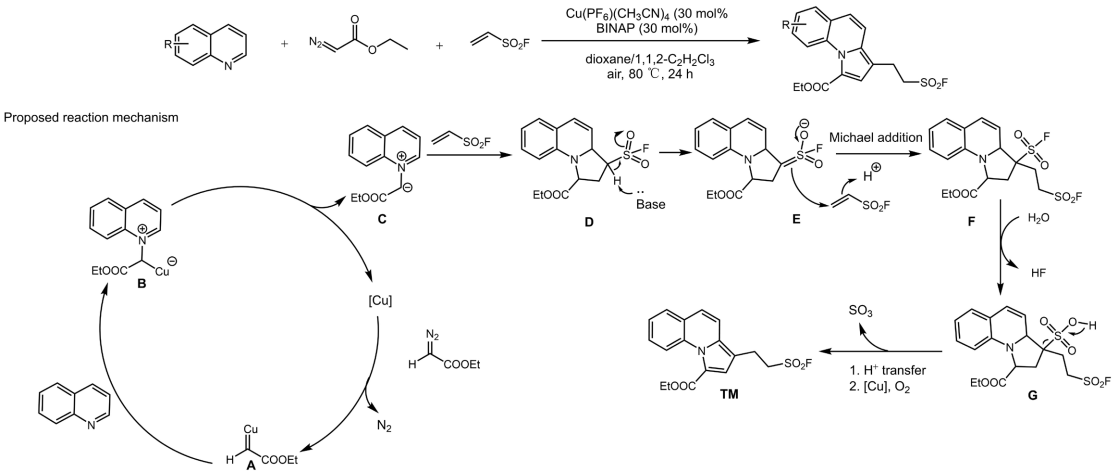


Figure 6. To construct an aliphatic sulfonyl fluoride containing indene and mechanism
图 6. 构建含氮茚的脂肪族磺酰氟化物和反应机理

2.2. F/Cl 卤原子交换反应

鉴于磺酰氟的高价值和广泛应用，包括硫醇与 KF 的电化学偶联[52] [53]、二硫化物与磺酰基氟化物的氧化[54]、磺酰肼的氟化[55]、芳基二氮鎓盐的氟磺酰化[56] [57] [58] [59]，芳基卤化物[60] [61]和硼酸[62] [63]催化氟化。SO_2F_2 与格氏试剂[64]和芳基重氮盐[65]反应表现出良好的产率。此外，包括 BESF [66] [67] [68]、SASF [69]和 MDF [70]在内的几种 SO_2F 共催化合成子的有效环加成反应也被认为是构建各种杂环磺酰氟的替代方法。然而，尽管目前有大量生成磺酰氟分子的方案，但使用不同氟源和磺酰氯进行 F/Cl 交换反应仍然占主导地位，并且易于操作。最传统的 F/Cl 交换反应通常用磺酰氯与有毒的钾盐组合进行，Davies 和 Dick 于 1931 年报道芳香族或脂肪族磺酰氯与氟化钾水溶液的混合物煮沸，可以容易地制备相应的磺酰氟化物[70]。1977 年，Cate 课题组开发了一种有效的“裸氟”方法(在干燥乙腈中使用 KF 和 18-冠-6)来制备磺酰氟化物[71] (如图 7 所示)。然而，在这种条件下发生的副反应和烷基磺酰基氟

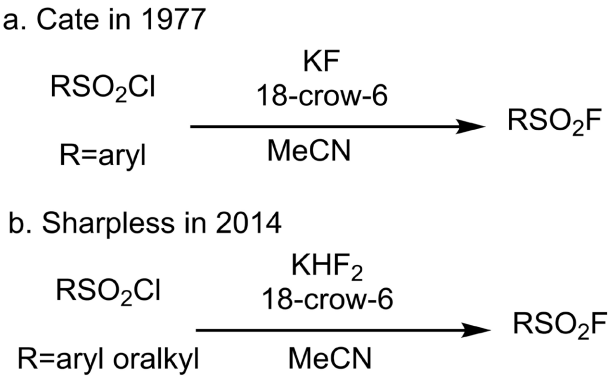


Figure 7. Synthesis of sulfonyl fluorides via F/Cl exchange
图 7. 通过 F/Cl 交换合成黄酰氟

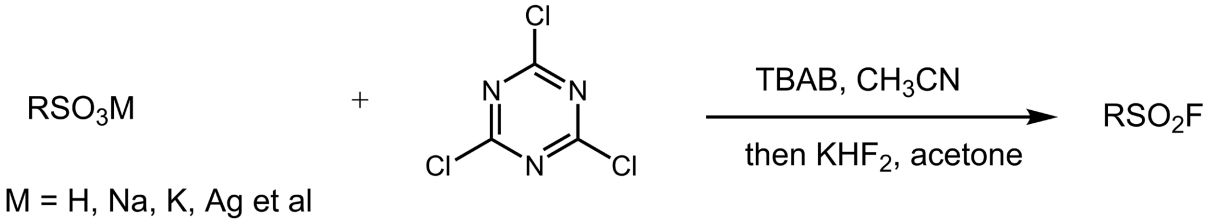


Figure 8. Sulfonyl fluoride was synthesized from sulfonate or sulfonic acid in one pot
图 8. 由磺酸盐或磺酸一锅法简便合成磺酰氟

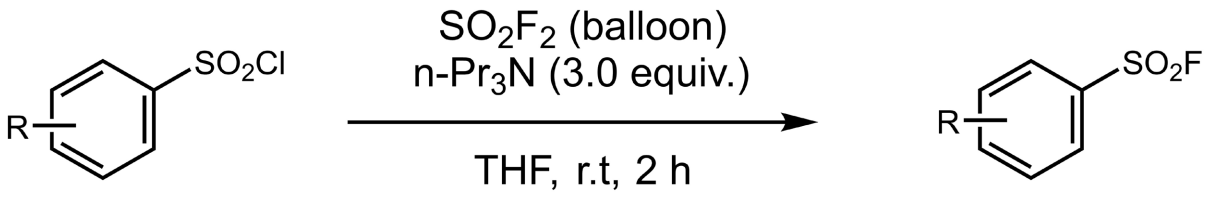


Figure 9. F/Cl exchange of SO_2F_2 alternative fluorine source
图 9. SO_2F_2 替代氟源的 F/Cl 交换

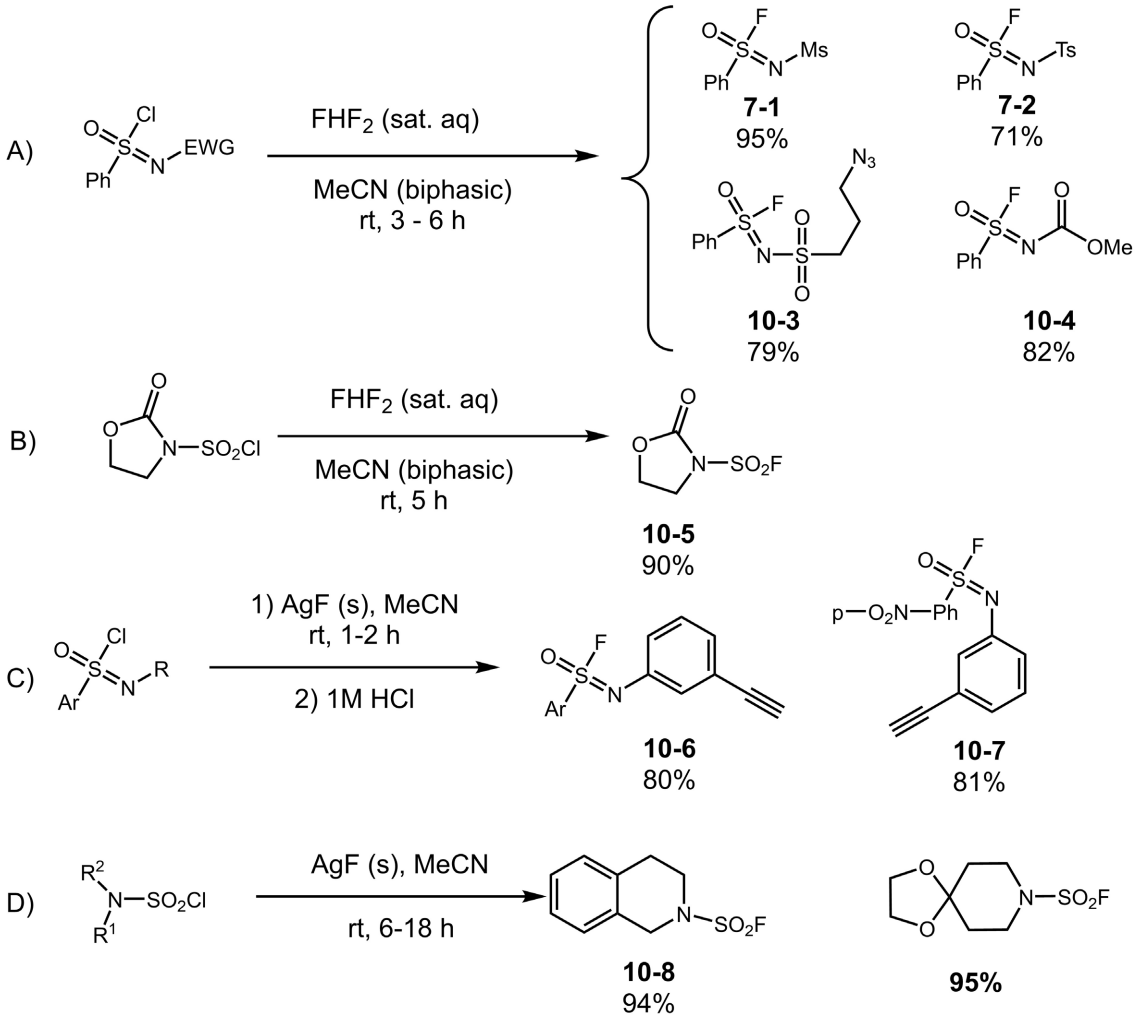


Figure 10. Sulfonimide and aminosulfonyl fluorides were prepared from chlorides
图 10. 由氯化物制备磺酰亚胺基和氨磺酰基氟化物

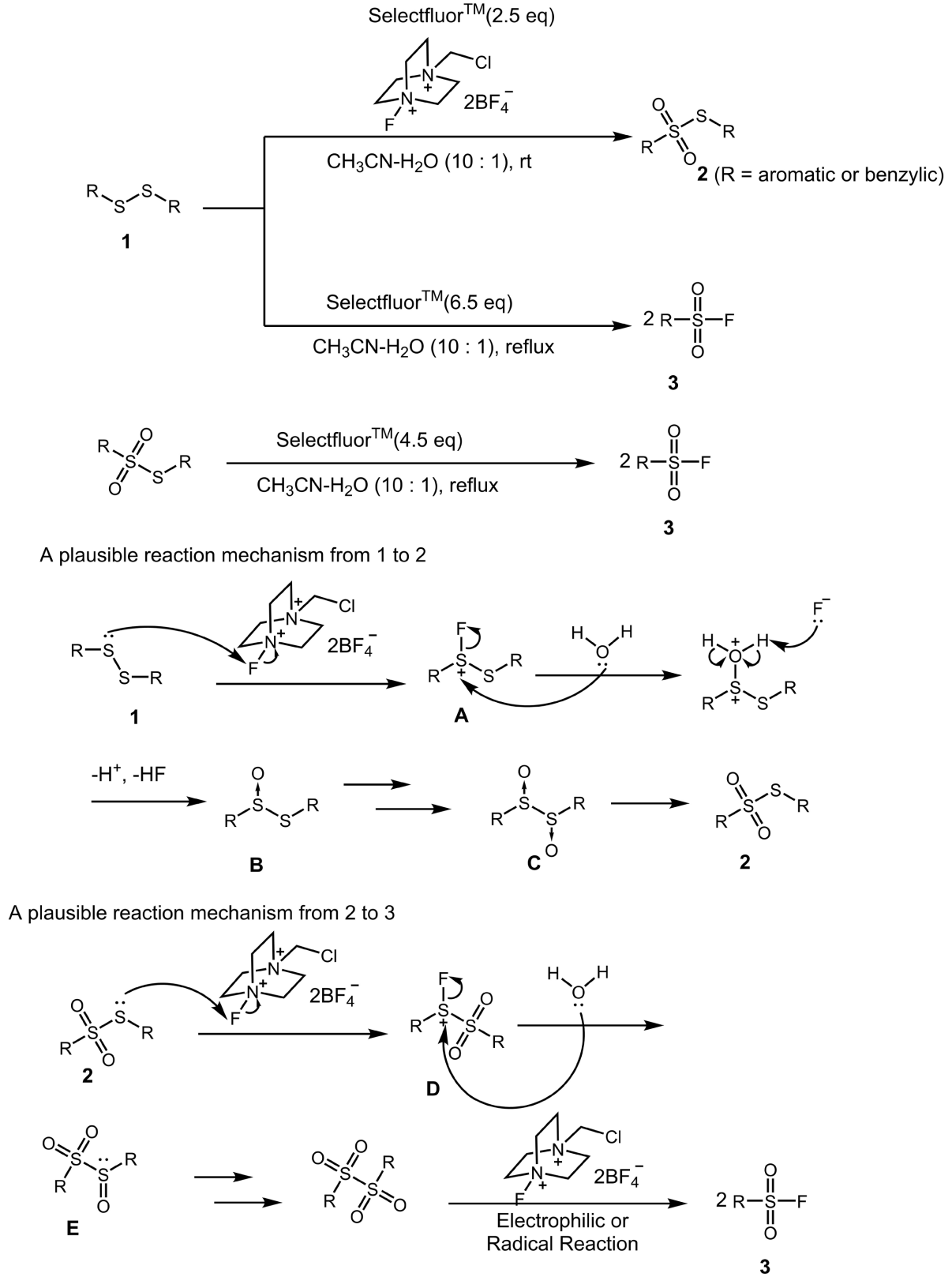


Figure 11. Oxidation of disulfide with electrophilic halogenated reagent and mechanism
图 11. 亲电卤化试剂氧化二硫化物和反应机理

化物的水解可能会掩盖这种方法的优势[72] [73]。为了应对这一挑战，2014 年，Sharpless 及其同事开发了一种使用二氟化钾作为替代氟化物来源的改进方法[74]。用这种方法，烷基和芳基磺酰氯可以在温和的条件下高效地转化为相应的磺酰氟化物，而不会水解磺酰氟化物产物。溶剂和氢键在水/有机界面上对提高氟离子对氟氯交换的亲核性起着重要作用。

2019 年，Qin 课题组[75]开发了一种新的不含过渡金属催化的一锅法，在温和的反应条件下，由丰富而廉价的磺酸盐(或磺酸)直接转化为高价值的磺酰氟化物(如图 8 所示)。这一新方案的特点是使用易于获得和操作的试剂在温和的反应条件下进行。制备了一套不同的磺酰氟化物，促进了磺酰氟化物库的富集。

2022 年，Tang 课题组[76]报道了在合适的碱的促进，以 SO_2F_2 为氟源，由芳基磺酰氯合成芳基磺酰氟化物的高效方案(如图 9 所示)。该方法条件温和、效率高、适用范围广、官能团相容性好，在有机合成等相关学科中有很大的应用潜力。

氮上具有吸电子取代基的磺酰亚胺酰氯和氨磺酰氯[77] [78] [79] [80]与磺酰氯的反应性非常相似[81] [82]，并且可以通过用饱和 KHF_2 水溶液处理转化为相应的氟化物(如图 10A，B 所示)。当氮上存在给电子基团时，氟化二反应性不足，在标准条件下产率低。在这些情况下，氟化银在乙腈条件下用于制备克级规模的磺酰氟(如图 10C，D 所示) [83]。

2.3. 含硫衍生物的氧化氟磺酰化

鉴于磺酰氯的高灵敏度反应性和低可及性，通过使用一种稳定廉价的起始原料合成磺酰氟化物极为重要。芳香硫化合物，如硫醇[52]、二硫化物[53]、磺酸[56]、磺酸钠[57]，亚磺酸盐[58]、磺酰肼[55]和磺酰胺[59]已被证明是相应磺酰氟化物的替代合成前体。

2006 年，Wright 和 Hallstrom 开发了一种由硫醇合成杂环磺酰基氟化物的有效方法[84]。该方法包括氧化氯化步骤，使用次氯酸钠水溶液原位氧化后提供磺酰氯中间体，然后进行氟氯交换形成磺酰氟化物。该反应使用容易获得的试剂，并避免使用氯气。然而，在该方法中仅证明了杂芳硫醇可以合成磺酰氟。

2011 年，Kirihara 课题组将二硫化物转化为磺酰氟化物，Selectfluor 既是氧化剂又是氟源[85] [86] [87]。在该体系中，芳香族和烷基二硫化物可以以良好的产率转化为相应的磺酰基氟化物。对照实验表明，在该过程中产生了硫代硫酸盐中间体 a，Selectfluor 的负载是关键。尽管确切的机制尚不清楚，但作者提出，硫代硫酸盐 A 的硫原子亲电氟化形成氟化锍盐 B，然后加水得到二硫代亚磺酸盐 C，随后进行自由基或亲电氟化得到最终产物磺酰氟(如图 11 所示)。

为了使反应条件更加绿色温和，2019 年，Noël 及其同事报道了一种有效的电化学氧化方法，用 KF 作为廉价的氟源，从广泛可用的硫醇和二硫化物中制备磺酰氟化物[88]。该方法不需要额外的氧化剂或催化剂，并且显示出广泛的底物范围，包括芳基、杂芳基、苄基和烷基硫醇或二硫化物(如图 12 所示)。

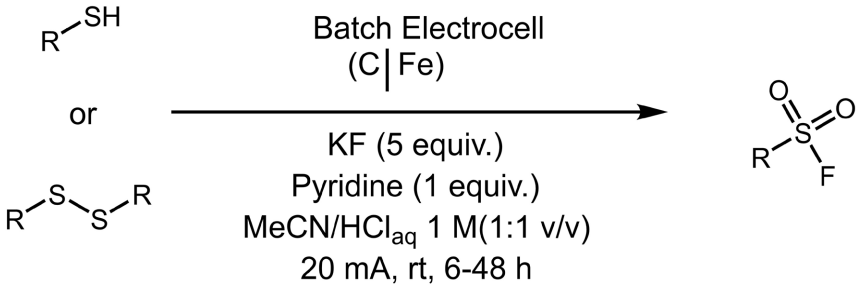
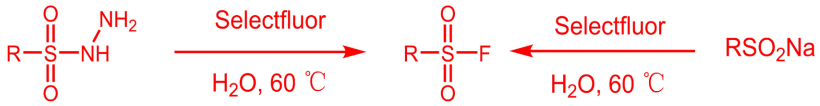


Figure 12. Synthesis of sulfonyl fluorides via electrochemical oxidative of thiols
图 12. 硫醇或二硫化物电化学氧化合成磺酰氟

2.4. 自由基的偶联

2016 年，Wang 课题组使用磺酰肼的无催化剂氟化，用 Selectfluor 作为氟源合成磺酰氟化物[89]。这种方法显示出广泛的底物范围，并且不需要任何金属催化剂和其他添加剂(如图 13 所示)。所有这些转化在温和的条件下进行，磺酰肼可以在水存在下通过释放氮气与 Selectfluor 反应形成氟自由基和磺酰基自由基，然后磺酰基自由基可快速捕获氟生成磺酰氟。在值得注意的是，在相同条件下，苯亚磺酸钠也可以与 Selectfluor 顺利反应生成苯磺酰氟，甚至不受自由基抑制剂 TEMPO 的影响。在这种条件下实现几种芳基亚硫酸钠有效合成苯磺酰氟。



Plausible reaction mechanism

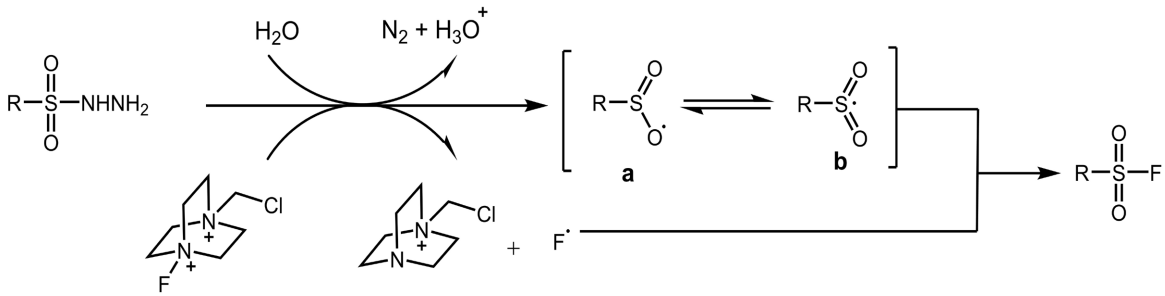


Figure 13. Sulfonyl fluoride is synthesized from sulfonyl hydrazine or sodium benzenesulfonate in water
图 13. 磺酰肼或苯亚磺酸钠在水中合成磺酰氟化物

2019 年，Willis 课题组[90]用烯基三氟甲磺酸酯为原料，高效地合成了一系列低分子量、结构紧凑的多官能团环状烯基磺酰氟。使用 DABSO 作为磺酰基源的替代试剂，在钯催化下二氧化硫插入生成亚磺酸盐，然后被亲电试剂捕获，生成磺酰氟，该体系具有广泛的官能团兼容性(如图 14 所示)。

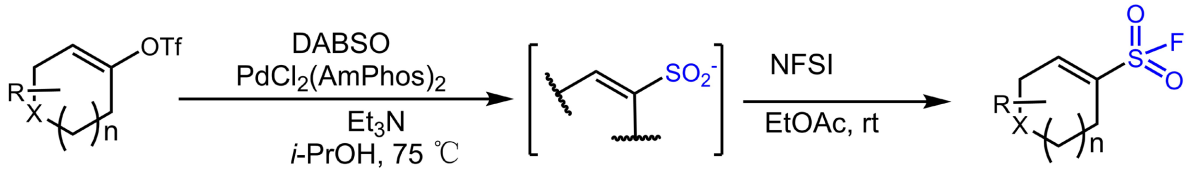


Figure 14. Synthesis of cycloenyl sulfonyl fluoride catalyzed by palladium
图 14. 钯催化合成环烯基磺酰基氟化物

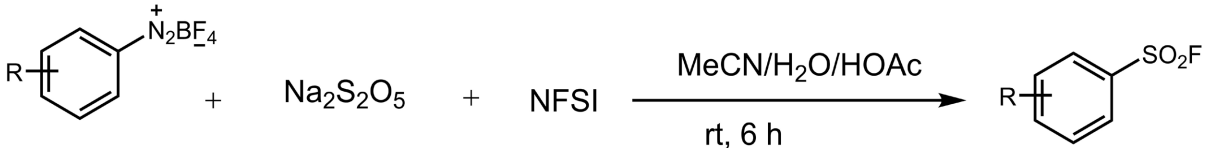


Figure 15. Synthesis of sulfonyl fluoride by copper-free Sandmeyer type fluorosulfonylation
图 15. 无铜 Sandmeyer 型氟磺酰化合成磺酰氟

2020 年，liu 课题组[91]报道了一种温和有效的无铜 Sandmeyer 型氟磺酰化反应，用 $K_2S_2O_5$ 作为还原剂和实用的磺酰源，与 N-氟苯磺酰亚胺作为有效的氟源相结合，制备有价值的芳烃磺酰氟化物(如图 15 所示)。考虑到整体的实用性和范围，该方法为制备各种重要的芳烃磺酰氟化物提供了一条有吸引力的途径。

2022 年，Weng 课题组[92]报道了一种催化脱羧氟磺酰化方法，将丰富的脂肪族羧酸转化为相应的磺酰氟化物(如图 16 所示)。这种转化是通过醛肟酯的简单预活化和能量转移介导的光催化实现的。这种操作简单的方法在温和和氧化还原中性条件下具有高官能团耐受性。

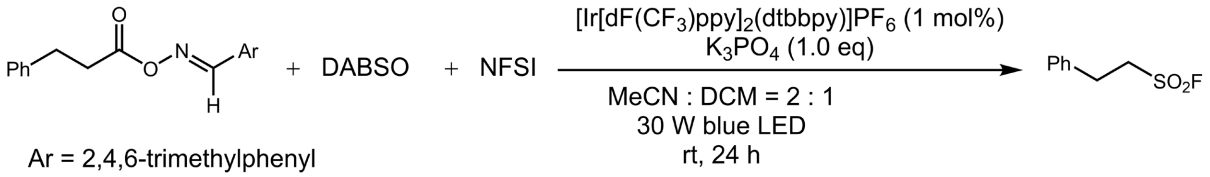


Figure 16. Photocatalytic mediated Energy transfer fluorosulfonylation of decarboxylation
图 16. 能量转移介导的光催化脱羧氟磺酰化反应

2.5. 黄酰氟自由基对烯烃的加成

与芳香族磺酰基氟化物相比，脂肪族、烯基和炔基磺酰基氟化物的合成方法相对较少。通过使用自由基对烯烃磺酰氟化合物的加成可以得到脂肪族磺酰氟化合物，将有助于扩大这些磺酰氟的应用。2016 年，Sharpless 课题组[93]报道合成 β-芳基乙烯磺酰氟化合物的 Heck-Matsuda 法(如图 17 所示)。乙烯磺酰氟(即，乙烯基磺酰氟或 ESF)在催化剂乙酸钯(II)存在下与稳定且容易制备的芳烃重氮四氟硼酸盐进行芳基化，得到肉桂酰氟的异构体磺酰类似物。但是由于芳烃重氮盐在光催化生成自由基过程中会产生氮气，不利于安全生产，另外容易吸水，不利于长期保存，因此该反应在工业生产中具有一定的限制性。

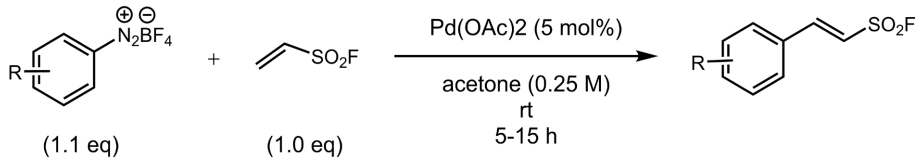


Figure 17. Synthesis of ß-arylvinyl sulfonyl fluoride by Heck-Matsuda method
图 17. Heck-Matsuda 法合成 ß-芳基乙烯磺酰氟化物

羧酸在自然界中普遍存在，广泛存在于天然产物、药物和材料中。羧酸的稳定性、低毒性和商业可用性等优点使其成为有机合成中理想的构建块类型[27]。2019 年，Liao 课题组[94]报道了一种通过可见光介导的脱羧氟磺酰基乙烯基化合成脂肪族磺酰基氟化物(如图 18 所示)。利用一种快速、无金属的方法来构建具有多样性的磺酰氟化合物库。还证明了含有 SO_2F 的产物进一步转化，可以获得一系列药学上的重要基序，如舒坦、磺酸盐和磺酰胺。

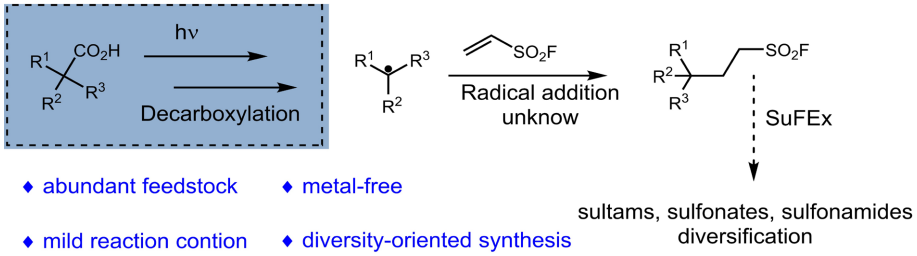


Figure 18. Synthesis of aliphatic sulfonyl fluoride by decarboxylation of carboxylic acid
图 18. 羧酸脱羧合成脂肪族磺酰氟

2020 年，Qin 课题组报道了一种可见光诱导的烷基碘化物与 ESF 的还原加成反应，使用 Hantzsch 酯作为氢源[95]。广泛烷基碘化物被有效地转化为相应的脂肪族磺酰基氟化物，包括酶抑制剂、天然产物和药物的衍生物。所得脂肪族磺酰氟化物的进一步衍生也通过氟化硫交换(SuFEx)反应实现，以获得磺酸盐和磺酰胺药物结构中间体。在光照射下，$Mn_2(CO)_{10}$ 被激发发生均裂，形成[$Mn(CO)_5$]自由基。随后，[$Mn(CO)_5$]自由基与烷基碘(1)反应生成亲核烷基自由基 A 和 $Mn(CO)_5I$。随后，A 自由基加成到乙烯基磺酰氟(2)中以形成中间体 B，B 从 Hantzsch 酯中捕获氢自由基以形成不同的烷基磺酰基氟化物(3)，最后在 $Mn(CO)_5I$ 存在下，二烯基自由基 C 通过芳构化得到吡啶盐 D，伴随着[$Mn(CO)_5$]自由基的再生以启动下一个催化循环(如图 19 所示)。

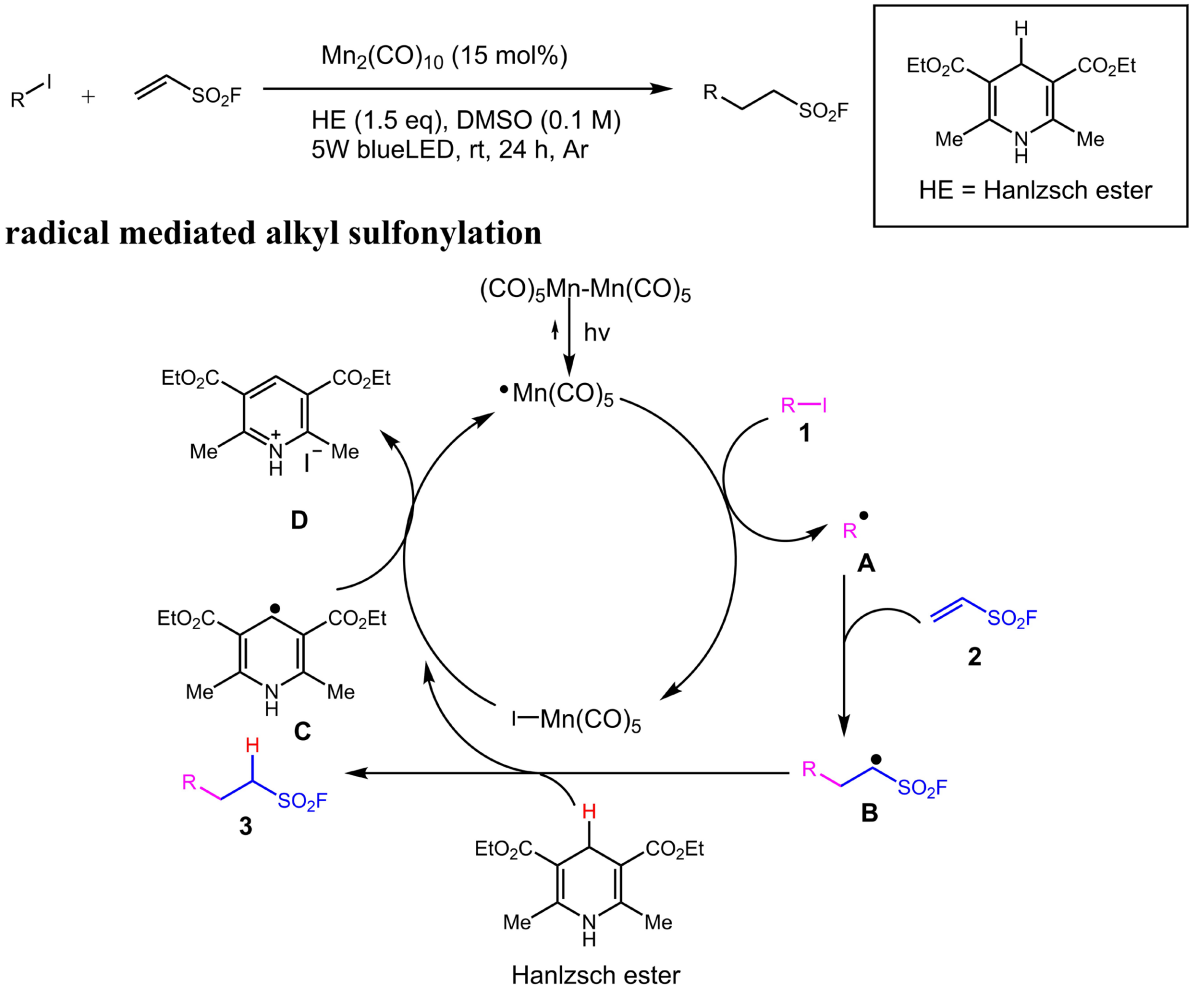


Figure 19. Sulfonyl fluoride is synthesized by reductive addition of alkyl iodine
图 19. 烷基碘通过还原加成合成黄酰氟

2022 年，Liao 课题组[96]报道了一种新的氟磺酰基自由基试剂——1-氟磺酰基，2-芳基苯并咪唑鎓三氟酸盐(FABI)，它能够在光氧化还原条件下使烯烃氟磺酰基化。与已知的自由基前体气态 FSO_2Cl 相比，FABI 盐是更稳定的，易于处理，在之前具有挑战性的底物烯烃的氟磺酰基化中实现更高产率(如图 20 所示)。在光照下，光催化剂(IrIII)被激发，然后通过单电子转移(SET)到氧化还原活性自由基前体，在得到一个电子后，发生 N-S 键的均裂，产生 FSO_2 自由基，随后 FSO_2 自由基加成到苯乙烯中生成自由基中间体 Int-1，通过 IrIV 氧化 Int-1 得到阳离子中间体 Int-2，其发生去质子化得到 3aa，而用醇(ROH)捕获 Int-2

可以得到双官能化产物(如图 21 所示)。

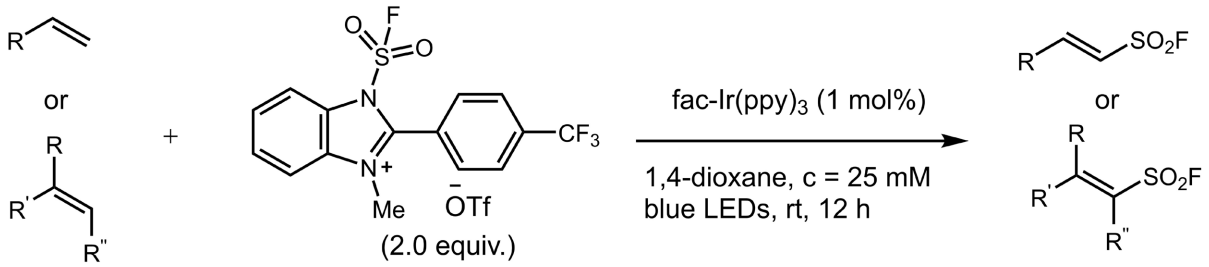


Figure 20. Photoredox fluorsulfonation catalyzed by fluorosulfonyl radical precursors
图 20. 氟磺酰基自由基前驱体催化的光氧化还原氟磺化反应

Mechanism

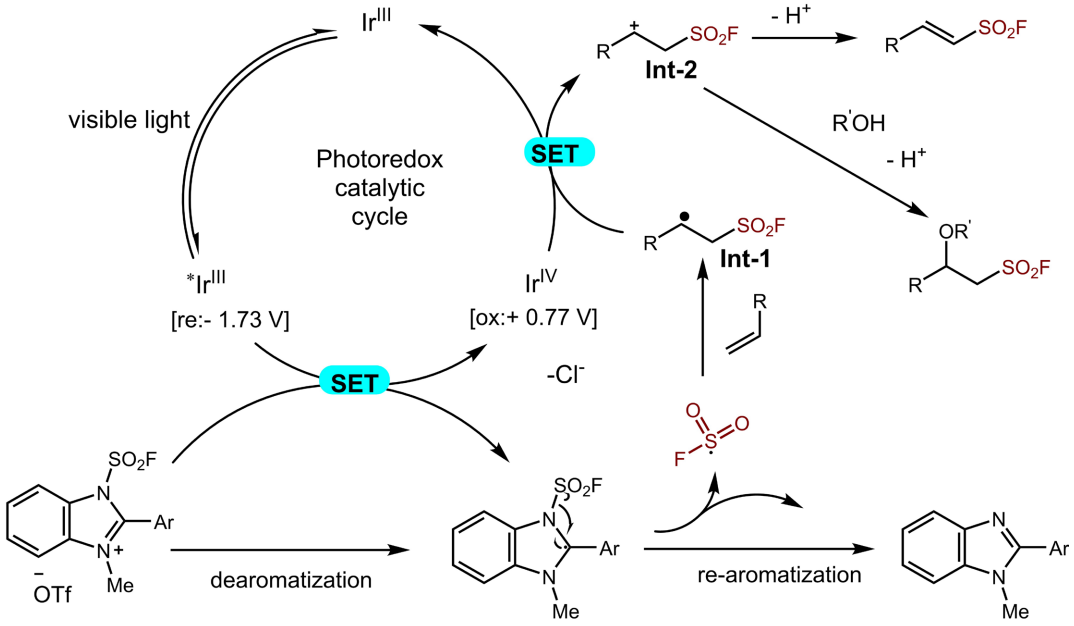


Figure 21. Photoredox fluorsulfonation catalyzed by fluorosulfonyl radical precursors
图 21. 氟磺酰基自由基前驱体催化的光氧化还原氟磺化反应

3. 总结

磺酰氟化物由于其独特的反应稳定性平衡，在一系列领域得到了广泛的应用。特别是为 Sharpless 的开创性报告许多研究工作奠定了基础，进一步证明了氟硫酸盐的实用性。虽然已经取得了一些进展，但利用新的合成策略，如直接的 C-H 功能化、后期转化和自由基反应，在类药物分子中区域选择性地安装 SO_2F 基序仍然有限。毫无疑问，磺酰氟的合成方法和应用在不久的将来将得到进一步发展。我们希望这篇简短的综述能引起人们对磺酰氟化学的浓厚研究兴趣，并帮助化学家将所开发的方法应用于相关领域。

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