

可见光促进下氟烷基砜对芳基烯烃的自由基氟烷基化反应

荣健^a 倪传法^a 王云泽^a 匡翠文^a 顾玉诚^b 胡金波^{*a}

(^a中国科学院上海有机化学研究所有机氟化学重点实验室 上海 200032)

(^b Syngenta, Jealott's Hill International Research Centre Bracknell, Berkshire UK RG42 6EY)

摘要 自由基氟烷基化是向有机分子中引入氟烷基的一类非常重要的方法,也是目前有机化学研究的热点之一。近几年来,由于广泛的官能团兼容性和温和的反应条件等优点,可见光促进的氧化还原催化反应得到了长足的发展,已经成为化学键的构建和活化的有力工具。因此,光氧化还原催化的自由基氟烷基化反应,作为向有机化合物中引入氟烷基的有效途径,受到了广泛关注。本文报道了我们发展的氟烷基砜作为一类方便易得的新型氟烷基自由基前体,在可见光氧化还原催化下实现对烯烃的自由基氟烷基化反应。该反应可以高效地向芳基烯烃中引入三氟甲基、二氟甲基、1,1-二氟乙基、苯基二氟甲基等各种含氟烷基基团,并实现对芳基烯烃的双官能团化转化。

关键词 光氧化还原催化; 氟烷基砜; 烯烃; 双官能团化; 自由基氟烷基化反应; 三氟甲基化; 二氟甲基化

Radical Fluoroalkylation of Aryl Alkenes with Fluorinated Sulfones by Visible-Light Photoredox Catalysis

Rong, Jian^a Ni, Chuanfa^a Wang, Yunze^a Kuang, Cuiwen^a Gu, Yucheng^b
Hu, Jinbo^{*a}

(^a Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032)

(^b Syngenta, Jealott's Hill International Research Centre Bracknell, Berkshire UK RG42 6EY)

Abstract The incorporation of fluorine atoms or fluorinated moieties into organic molecules can often lead to significant changes of their physical, chemical, or biological properties. Consequently, fluorinated organic molecules are widely used in areas of pharmaceuticals, agrochemicals and materials. Traditional approaches for the incorporation of fluorinated moieties into organic molecules include nucleophilic, electrophilic, and radical pathways. Among them, radical fluoroalkylations under visible-light photoredox catalysis have attracted much attention because of the mild reaction conditions and broad functional-group tolerance. In our previous work, the radical fluoroalkylation of isocyanides with fluorinated sulfones as the fluoroalkyl radical precursors via R_f-SO₂Ar bond cleavage has been achieved under visible-light photoredox catalysis (Rong, J. *et al.* *Angew. Chem., Int. Ed.* **2016**, *55*, 2743). Herein, as a logical extension of our previous research, we report the radical fluoroalkylation of aryl alkenes with fluorinated sulfones as the practical fluoroalkyl radical precursors under visible-light photoredox catalysis. Various fluoroalkyl radicals, including trifluoromethyl (CF₃), difluoromethyl (HCF₂), 1,1-difluoroethyl (CH₃CF₂) and (phenyl)difluoromethyl (PhCF₂) radicals, can be incorporated into styrene derivatives via this method, delivering the oxyfluoroalkylation products in 46%~93% yields. Typical procedures for this reaction are given as follows: to a Schlenk tube were added 2-vinylnaphthalene (**1a**) (0.20 mmol, 30.8 mg, 1.0 equiv.), trifluoromethyl 2-benzo[d]thiazolyl sulfone (**2b**) (0.24 mmol, 64.1 mg, 1.2 equiv.), *fac*-Ir(ppy)₃ (2.7 mg, 0.004 mmol, 2 mol%), H₂O (0.5 mL), and acetone (4.5 mL) sequentially. The resulting mixture was degassed with a freeze-pump-thaw procedure (3 times) and irradiated by a 6 W blue LED for 12 h. After the reaction completed, the mixture was extracted with Et₂O and dried over anhydrous MgSO₄. The organic solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a 10 : 1 (V/V) mixture of petroleum ether/EtOAc as an eluent to provide the hydroxytrifluoromethylation product **3a** (31.2 mg, 65% yield).

Keywords visible-light photoredox catalysis; fluorinated sulfones; alkenes; difunctionalization; radical fluoroalkylation; trifluoromethylation; difluoromethylation

* E-mail: jinbohu@sioc.ac.cn; Tel.: 021-54925174. Homepage: <http://hujinbo.sioc.ac.cn/en/>

Received August 14, 2016; published September 7, 2016.

Supporting information for this article is available free of charge via the Internet at <http://sioc-journal.cn>.

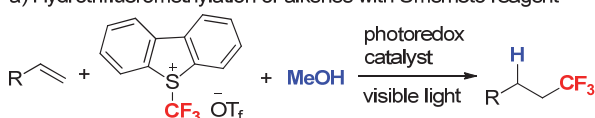
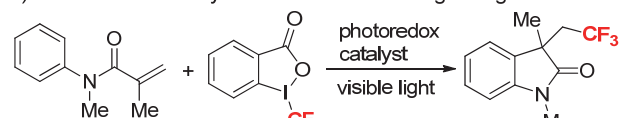
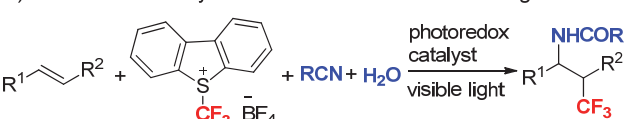
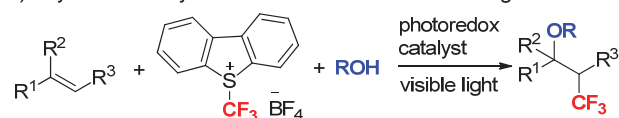
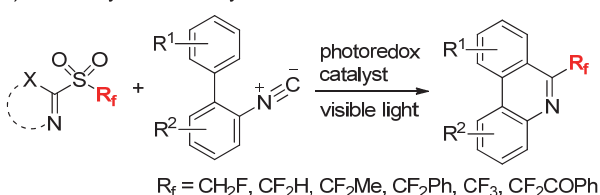
Project supported by the 973 Program (2015CB931900), the National Natural Science Foundation of China (21372246, 21421002, 21472221), Shanghai Academic Research Leader Program (15XD1504400), the Youth Innovation Promotion Association CAS (2014231), and a Syngenta Ph.D. Studentship.

项目受 973 计划(2015CB931900)、国家自然科学基金(21372246, 21421002, 21472221)、上海市学术带头人计划(15XD1504400)、中国科学院青年创新促进会(2014231)与 Syngenta 博士生奖学金资助。

1 引言

向生物活性分子中引入氟原子或者含氟基团往往可以有效地改善其生物活性^[1], 这也是医药、农药研究中提高药物药效的常用方法. 由此, 发展新的高效的向有机分子中引入含氟基团的方法也成为了有机化学的研究热点^[2]. 近年来, 可见光促进的氧化还原催化的自由基氟烷基化反应, 由于其在单电子氧化还原电势方面的巨大优势以及温和的反应条件和良好官能团兼容性等优点, 受到了化学家们的极大关注^[3]. 烯烃是重要的基础原料, 实现简单烯烃高效地向复杂官能团化产物转化具有重要意义. 烯烃的双官能团化反应可以区域选择性地一步向双键两端各引入一个官能团, 是构建复杂结

Representative previous work

a) Hydrotrifluoromethylation of alkenes with Umemoto reagent^[5a]b) Carbontrifluoromethylation of alkenes with Togni reagent^[6a]c) Aminotrifluoromethylation of alkenes with Umemoto reagent^[7a]d) Oxytrifluoromethylation of alkenes with Umemoto reagent^[8a]e) Halotrifluoromethylation of alkenes with CF3I^[9a]f) Fluoroalkylation of isocyanides with fluorinated sulfones^[11]

This work

g) Oxyfluoroalkylation of alkenes with fluorinated sulfones

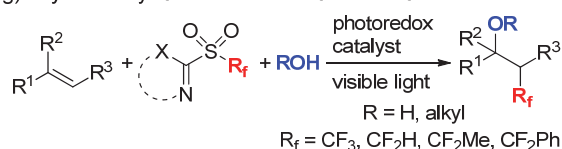


图1 可见光氧化还原催化下涉及自由基氟烷基化的双官能团化反应
Figure 1 Visible-Light photoredox catalyzed difunctionalization involving radical fluoroalkylation

构的有效方法. 直接向烯烃中引入氟烷基并实现其双官能团化的反应类型包括: 氢氟烷基化^[4]、碳氟烷基化^[5]、氮氟烷基化^[6]、氧氟烷基化^[7]和卤氟烷基化^[8]等; 在光氧化还原催化的温和条件下向烯烃中引入氟烷基并实现其双官能团化反应也成为了近几年的研究热点^[4-8]. 有机化学家们利用 Umemoto 试剂、Togni 试剂、Langlois 试剂、氟烷基卤化物、氟烷基磺酰氯、氟烷基膦盐以及氟烷基亚胺等氟烷基自由基前体实现了对烯烃的氢氟烷基化、碳氟烷基化、氮氟烷基化、氧氟烷基化以及卤氟烷基化等双官能团化反应^[4-8]. 我们小组长期致力于利用氟烷基磺试剂向有机分子中引入氟烷基^[9]. 最近, 我们发展了光氧化还原催化下氟烷基磺参与的异腈的自由基氟烷基化反应^[10]. 在光氧化还原催化的温和条件下, 使用氟烷基磺作为氟烷基自由基前体, 可以高效地向异腈中引入 $-\text{CF}_3$, $-\text{CF}_2\text{H}$, $-\text{CF}_2\text{Me}$, $-\text{CF}_2\text{Ph}$, $-\text{CF}_2\text{COPh}$, $-\text{CH}_2\text{F}$ 等各种含氟基团. 在光氧化还原催化的条件下, 氟烷基磺作为氟烷基自由基前体有以下优点: (1)稳定性好, 操作简单; (2)制备方法高效、简便, 可大量合成; (3)氟烷基端可以灵活多变, 适合多种氟烷基化反应, 可作为各种氟烷基自由基的新型实用的统一前体. 为进一步拓宽氟烷基磺作为氟烷基自由基前体的应用, 本文报道在光氧化还原催化下氟烷基磺对芳基烯烃的自由基氟烷基化反应.

2 结果与讨论

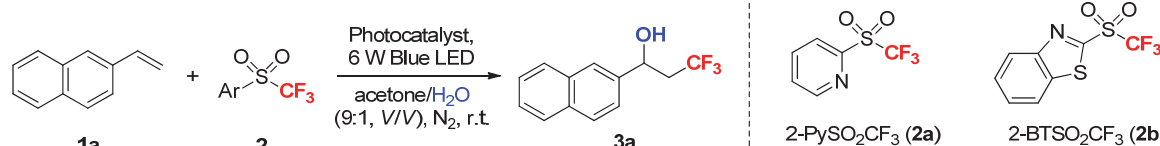
2.1 反应条件的优化

以 2-乙烯基萘(**1a**)作为模板底物, 以三氟甲基磺试剂作为自由基三氟甲基化试剂, 选用丙酮/水(9:1, *V/V*)作为溶剂. 通过对三氟甲基磺和光催化剂的筛选, 发现选用还原能力强的 *fac*-Ir(ppy)₃ 催化剂和更容易产生三氟甲基自由基的三氟甲基磺 **2b** 能得到更好的反应结果(表 1, Entries 1~4). 反应的时间可以缩短到 12 h(表 1, Entries 5~6); 三氟甲基磺 **2b** 的用量降低时, 反应的产率也随之下降(表 1, Entries 7~8).

2.2 芳基烯烃底物普适性的考察

在优化后的条件下, 我们首先考察了芳环上取代基对反应的影响. 从表 2 的数据中可以发现, 给电子基取代的苯乙烯能以优秀的产率给出目标产物 **3c**, **3d**; 吸电子基取代的苯乙烯仅能以中等到良好的产率给出目标产物 **3e**~**3i**. 1,1-双取代的芳基乙烯能以良好到优秀的产率给出目标产物 **3j**~**3l**. 1,2-双取代的芳基乙烯能以中等到良好的产率给出一对非对映异构体 **3m**~**3o**. 杂芳基乙烯、乙烯基取代的较复杂天然产物衍生物以及乙烯基二茂铁也能以中等到良好的产率给出目标产物 **3p**~**3s**. 除了可以得到羟基三氟甲基双取代的产物, 反应也能以中等的产率给出烷氧基三氟甲基双取代的产物 **3t**.

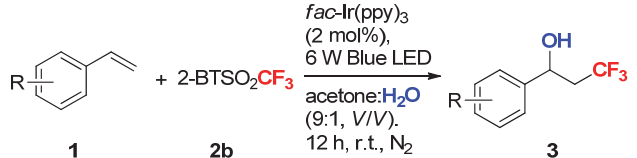
表1 光氧化还原催化下三氟甲基磺对芳基烯烃的自由基三氟甲基化反应的条件优化

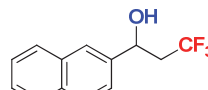
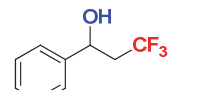
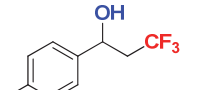
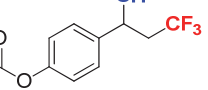
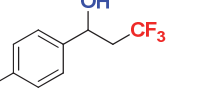
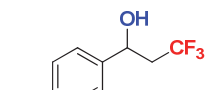
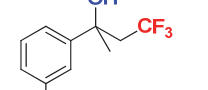
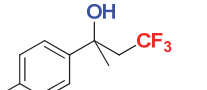
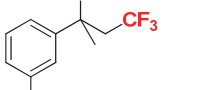
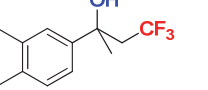
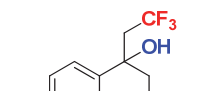
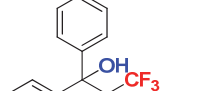
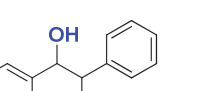
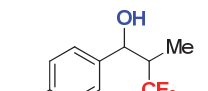
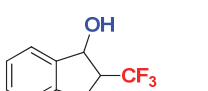
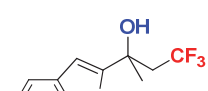
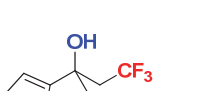
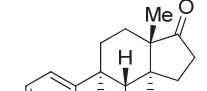
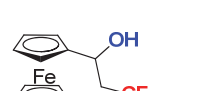
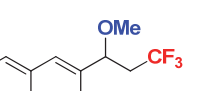
Table 1 Optimization of reaction conditions for radical trifluoromethylation of aryl alkene **1a** with trifluoromethyl sulfones **2** by visible-light photoredox catalysis^a


Entry ^a	2 (equiv.)	Photocatalyst	Time/h	Yield ^b /%
1	2a (1.2 equiv.)	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	24	0
2	2a (1.2 equiv.)	<i>fac</i> -Ir(ppy) ₃	24	8
3	2b (1.2 equiv.)	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	24	0
4	2b (1.2 equiv.)	<i>fac</i> -Ir(ppy) ₃	24	75
5	2b (1.2 equiv.)	<i>fac</i> -Ir(ppy) ₃	12	73
6	2b (1.2 equiv.)	<i>fac</i> -Ir(ppy) ₃	6	68
7	2b (1.1 equiv.)	<i>fac</i> -Ir(ppy) ₃	12	67
8	2b (1.0 equiv.)	<i>fac</i> -Ir(ppy) ₃	12	56

^aReaction conditions: **1a** (0.20 mmol), **2**, photocatalyst (2 mol%) in acetone (4.5 mL) and H₂O (0.5 mL) were irradiated with a 6 W blue LED at room temperature under N₂ atmosphere; ^bYield was determined by ¹⁹F NMR spectroscopy using PhCF₃ as internal standard.

表2 光氧化还原催化下三氟甲基磺对芳基烯烃自由基三氟甲基化反应的普适性考察

Table 2 Scope of radical trifluoromethylation of aryl alkenes **1** with trifluoromethyl sulfone **2b** by visible-light photoredox catalysis^a


				
3a , 65%	3b , 75%	3c , 92%	3d , 88%	3e , 58%
				
3f , 76% ^b	3g , 70%	3h , 70%	3i , 61%	3j , 80%
				
3k , 89% ^b	3l , 90% ^c	3m , 75%, <i>d.r.</i> , 7:1 ^e	3n , 82%, <i>d.r.</i> , 1.25:1 ^{d,e}	3o , 65%, <i>d.r.</i> 3.41:1 ^e
				
3p , 75%	3q , 70%	3r , 80%	3s , 60% ^f	3t , 66% ^g

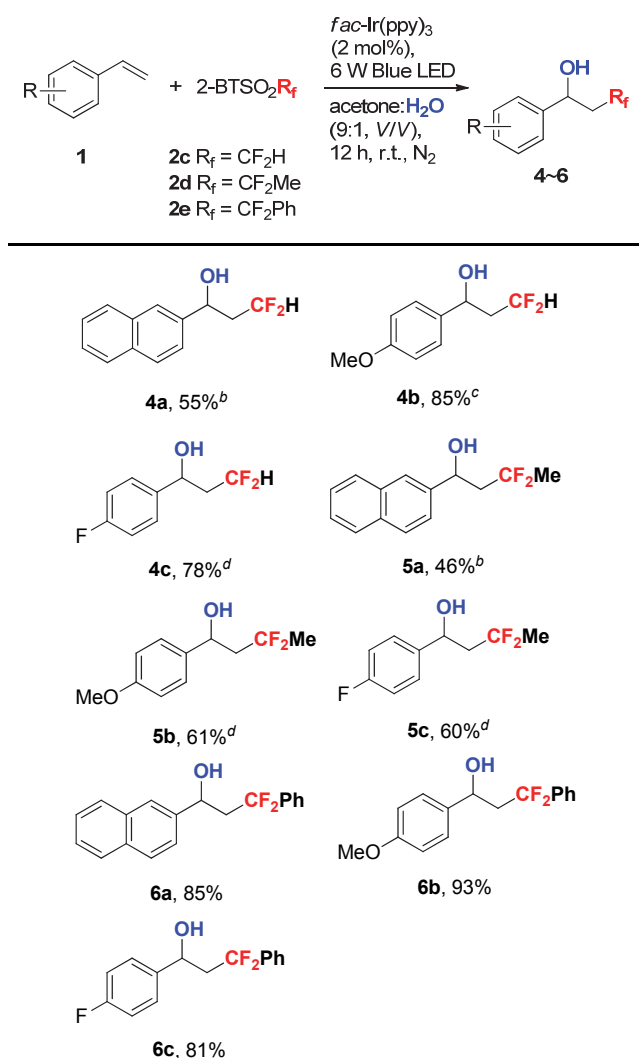
^aReaction conditions: **1** (0.20 mmol), **2b** (0.24 mmol), photocatalyst (2 mol%) in acetone (4.5 mL) and H₂O (0.5 mL) were irradiated with a 6 W blue LED for 12 h at room temperature under N₂ atmosphere, isolated yield; ^bReaction was irradiated for 24 h; ^cReaction was irradiated for 36 h; ^dReaction was irradiated for 48 h; ^eThe diastereomeric ratio was determined by ¹⁹F NMR spectroscopy; ^fYield was determined by ¹⁹F NMR spectroscopy using PhCF₃ as internal standard; ^g**2b** (0.30 mmol) and CH₂Cl₂/MeOH (4.5 mL/0.5 mL) were used.

2.3 氟烷基自由基普适性的考察

从表2中我们可以发现,以三氟甲基磺 2b 为三氟甲基自由基前体可以与各种不同取代的烯烃发生自由基三氟甲基化反应. 在优化后的条件下,我们又选用电中性的 2-乙炔基萘(1a)、富电子的 4-甲氧基苯乙烯(1c)以及缺电子的 4-氟苯乙烯(1e)作为模板底物,分别考察了以二氟甲基、1,1-二氟乙基、苯基二氟甲基取代的磺作为多种氟烷基自由基前体与芳基烯烃的自由基氟烷基化反应的情况. 从表3中我们可以发现,以二氟甲基、1,1-二氟乙基取代的磺 2c、2d 作为二氟甲基、1,1-二氟乙基自由基源,在光氧化还原催化的条件下,可以顺利

表3 光氧化还原催化下各种含氟磺对芳基烯烃的自由基氟烷基化反应

Table 3 Radical fluoroalkylation of aryl alkenes **1** with fluorinated sulfones **2** by visible-light photoredox catalysis^a



^a Reaction conditions: **1** (0.20 mmol), **2b** (0.30 mmol), photocatalyst (2 mol%) in acetone (4.5 mL) and H₂O (0.5 mL) were irradiated with a 6 W blue LED for 12 h at room temperature under N₂ atmosphere, isolated yield; ^b Reaction was irradiated for 24 h; ^c Reaction was irradiated for 96 h; ^d Reaction was irradiated for 36 h.

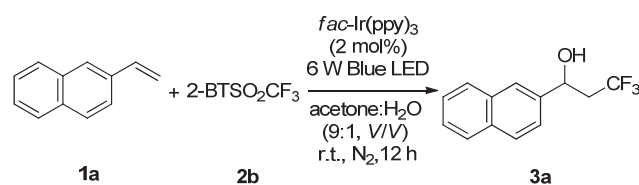
地与不同取代的芳基烯烃进行自由基氟烷基化反应并以中等到良好的产率得到相应的目标产物 **4a~4c** 以及 **5a~5c**. 苯基二氟甲基磺 **2e** 作为苯基二氟甲基自由基前体,可以非常高效地与不同取代的芳基烯烃进行自由基氟烷基化反应并以良好到优秀的产率得到相应的目标产物 **6a~6c**.

2.4 可能的反应机理

为了理解该反应的机理,我们做了对照实验和自由基抑制实验. 在对照实验中(表4),我们发现反应在空气中进行时,反应的产率急剧下降到4%(表4, Entry 1); 在没有光催化剂或者光照时,反应是不能够进行的(表4, Entries 2, 3). 在自由基抑制实验中(图2),向反应体系中加入自由基抑制剂 TEMPO 可以有效地抑制该反应,产率下降到15%(图2).

表4 对照实验

Table 4 The controlled experiment^a



Entry ^a	Difference from standard conditions	Yield ^b /%
1	in air	4
2	without <i>fac</i> -Ir(ppy) ₃	0
3	in dark (without Blue LED)	0

^a Reaction conditions: **1a** (0.20 mmol), **2**, photocatalyst (2 mol%) in acetone (4.5 mL) and H₂O (0.5 mL) were irradiated with a 6 W blue LED at room temperature under N₂ atmosphere; ^b Yield was determined by ¹⁹F NMR spectroscopy using PhCF₃ as internal standard.



图2 自由基抑制实验

Figure 2 Radical inhibition experiment

基于以上实验事实和相关文献的报道^[7]以及本组以前的工作^[10],我们对该反应提出了一个可能的反应机理(图3): 首先,光催化剂 *fac*-Ir^{III}(ppy)₃ 在光照下激发成 *Ir^{III}, 氟烷基磺 **2** 经 *Ir^{III} 单电子还原得到氟烷基自由基·R_f 与芳基烯烃 **1** 进行自由基加成得到自由基中间体 **A**, 中间体 **A** 可能与 Ir^{IV} 发生单电子转移得到碳正离子中间体 **B** 和催化剂 *fac*-Ir^{III}(ppy)₃ 完成催化循环(path a, 催化路径); 中间体 **A** 也可能与氟烷基磺 **2** 发生单电子转移得到氟烷基自由基·R_f 与碳正离子中间体 **B** (path b, 自由基链反应); 最后, 碳正离子中间体 **B** 被含氧亲核试剂捕获得到目标产物 **3~6**.

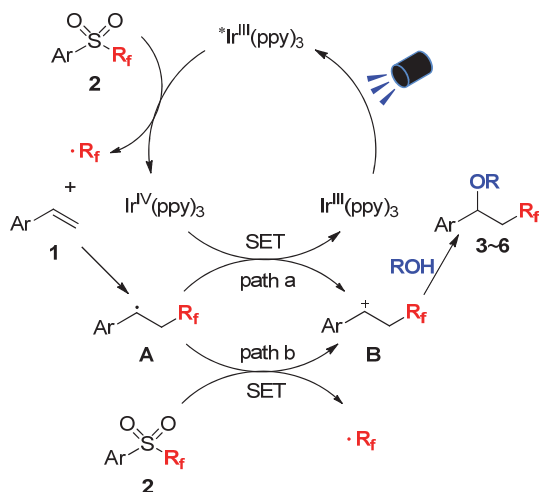


图3 光氧化还原催化的芳基烯烃的自由基氟烷基化反应的机理
Figure 3 Proposed mechanism for radical fluoroalkylation of aryl alkene with fluorinated sulfones by visible-light photoredox catalysis

3 结论

我们利用氟烷基砷作为一类方便易得的新型氟烷基自由基前体, 发展了光氧化还原催化条件下对芳基烯烃的自由基氟烷基化反应. 在可见光和光氧化还原催化剂的共同作用下, 各种氟烷基砷作为氟烷基自由基源, 对芳基烯烃发生氟烷基自由基加成反应, 然后单电子氧化为碳正离子, 最后与含氧亲核试剂反应, 得到氧氟烷基化产物. 该反应可以高效地向芳基烯烃中引入三氟甲基、二氟甲基、1,1-二氟乙基、苯基二氟甲基等各种含氟烷基基团, 实现对芳基烯烃的双官能团化转化.

4 实验部分

光氧化还原催化的芳基烯烃的自由基氟烷基化反应的实验方法: 室温下, 向 Schlenk 管中依次加入烯烃 **1a** (0.20 mmol, 30.8 mg, 1.0 equiv.)、氟烷基砷 **2b** (0.24 mmol, 64.1 mg, 1.2 equiv.)、催化剂 *fac*-Ir(ppy)₃ (2.7 mg, 0.004 mmol, 2 mol%)、H₂O (0.5 mL) 和丙酮 (4.5 mL). 体系经过三次液氮冷冻-抽真空-充氮气-解冻循环, 在 6 W LED 蓝光照射下反应 12 h. 反应完成后, 加入水和饱和氯化钠水溶液各 20 mL, 用乙醚萃取三次(每次 30 mL 乙醚). 合并有机相, 用无水硫酸镁干燥. 减压浓缩后得到的混合物在硅胶柱上, 以石油醚/乙酸乙酯(V/V = 10 : 1) 为淋洗剂进行柱层析分离纯化, 以 65% 收率得到目标产物 **3a** (31.2 mg).

References

[1] (a) Uneyama, K. *Organofluorine Chemistry*, Blackwell, Oxford, 2006. (b) Chambers, D. R. *Fluorine in Organic Chemistry*, Blackwell, Oxford, 2004. (c) Kirsch, P. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*, 2nd Ed., Wiley-VCH, Weinheim, 2013.
[2] (a) Qing, F.-L. *Chin. J. Org. Chem.* **2012**, *32*, 815. (卿凤翎, 有机化学, **2012**, *32*, 815.) (b) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 8214. (c) Ni, C.; Hu, J. *Chem. Soc. Rev.* **2016**, DOI: 10.1039/C6CS00351F.

[3] For recent reviews, see: (a) Koike, T.; Akita, M. *Top. Catal.* **2014**, *57*, 967. (b) Belhomme, M.-C.; Besset, T.; Poisson, T.; Pannecoucke, X. *Chem. Eur. J.* **2015**, *21*, 12836. (c) Ni, C.; Zhu, L.; Hu, J. *Acta Chim. Sinica* **2015**, *73*, 90. (倪传法, 朱林桂, 胡金波, 化学学报, **2015**, *73*, 90.) (d) Barata-Vallejo, S.; Bonesi, M. S.; Postigo, A. *Org. Biomol. Chem.* **2015**, *13*, 11153. (e) Pan, X.; Xia, H.; Wu, J. *Org. Chem. Front.* **2016**, *3*, 1163. (f) Tan, F.; Xiao, W. *Acta Chim. Sinica* **2015**, *73*, 85. (谭芬, 肖文精, 化学学报, **2015**, *73*, 85.)
[4] (a) Mizuta, S.; Verhoog, S.; Engle, K. M.; Khotavivattana, T.; O'Duill, M.; Wheelhouse, K.; Rassias, G.; Médebielle, M.; Gouverneur, V. *J. Am. Chem. Soc.* **2013**, *135*, 2505. (b) Wilger, D. J.; Gesmundo, N. J.; Nicewicz, D. A. *Chem. Sci.* **2013**, *4*, 3160. (c) Pitre, S. P.; McTiernan, C. D.; Ismaili, H.; Scaiano, J. C. *ACS Catal.* **2014**, *4*, 2530. (d) Yu, B.; Iqbal, N.; Park, S.; Cho, E. J. *Chem. Commun.* **2014**, *50*, 12884. (e) Tang, X.-J.; Zhang, Z.; Dolbier, W. R., Jr. *Chem. Eur. J.* **2015**, *21*, 18961. (f) Lin, Q.-Y.; Xu, X.-H.; Zhang, K.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2016**, *55*, 1479. (g) Panferova, L. I.; Tsybmal, A. V.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2016**, *18*, 996. (h) Zhu, L.; Wang, L.-S.; Li, B.; Fu, B.; Zhang, C.-P.; Li, W. *Chem. Commun.* **2016**, *52*, 6371. (i) Lin, Q.; Chu, L.; Qing, F.-L. *Chin. J. Chem.* **2013**, *31*, 885.
[5] (a) Xu, P.; Xie, J.; Xue, Q.; Pan, C.; Cheng, Y.; Zhu, C. *Chem. Eur. J.* **2013**, *19*, 14039. (b) Carboni, A.; Dagousset, G.; Magnier, E.; Masso, G. *Org. Lett.* **2014**, *16*, 1240. (c) Tang, X.-J.; Thomason, C. S.; Dolbier, W. R., Jr. *Org. Lett.* **2014**, *16*, 4594. (d) Wang, J.-Y.; Su, Y.-M.; Yin, F.; Bao, Y.; Zhang, X.; Xu, Y.-M.; Wang, X.-S. *Chem. Commun.* **2014**, *50*, 4108. (e) Carboni, A.; Dagousset, G.; Magnier, E.; Masson, G. *Chem. Commun.* **2014**, *50*, 14197. (f) Wang, J.-Y.; Zhang, X.; Bao, Y.; Xu, Y.-M.; Cheng, X.-F.; Wang, X.-S. *Org. Biomol. Chem.* **2014**, *12*, 5582. (g) Gao, F.; Yang, C.; Gao, G.-L.; Zheng, L.; Xia, W. *Org. Lett.* **2015**, *17*, 3478. (h) Thomason, C. S.; Tang, X.-J.; Dolbier, W. R., Jr. *J. Org. Chem.* **2015**, *80*, 1264. (i) Fu, W.; Zhu, M.; Zou, G.; Xu, C.; Wang, Z.; Ji, B. *J. Org. Chem.* **2015**, *80*, 4766. (j) Zheng, L.; Yang, C.; Xu, Z.; Gao, F.; Xia, W. *J. Org. Chem.* **2015**, *80*, 5730. (k) Song, R.-J.; Liu, Y.; Xie, Y.-X.; Li, J.-H.; Synthesis **2015**, *47*, 1195. (l) An, Y.; Li, Y.; Wu, J. *Org. Chem. Front.* **2016**, *3*, 570.
[6] (a) 5b. (b) Yasu, Y.; Koike, T.; Akita, M. *Org. Lett.* **2013**, *15*, 2136. (c) Zhang, Z.; Tang, X.; Thomason, C. S.; Dolbier, W. R., Jr. *Org. Lett.* **2015**, *17*, 3528. (d) Wei, Q.; Chen, J.-R.; Hu, X.-Q.; Yang, X.-C.; Lu, B.; Xiao, W.-J. *Org. Lett.* **2015**, *17*, 4464. (e) Kim, E.; Choi, S.; Kim, H.; Cho, E. J. *Chem. Eur. J.* **2013**, *19*, 6209. (f) Yu, X.-L.; Chen, J.-R.; Chen, D.-Z.; Xiao, W.-J. *Chem. Commun.* **2016**, *52*, 8275.
[7] (a) Yasu, Y.; Koike, T.; Akita, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 9567. (b) 6e. (c) Wei, X.-J.; Yang, D.-T.; Wang, L.; Song, T.; Wu, L.-Z.; Liu, Q. *Org. Lett.* **2013**, *15*, 6054. (d) Yasu, Y.; Arai, Y.; Tomita, R.; Koike, T.; Akita, M. *Org. Lett.* **2014**, *16*, 780. (e) 5b. (f) Fu, W.; Zhu, M.; Zou, G.; Xu, C.; Wang, Z. *Asian J. Org. Chem.* **2014**, *3*, 1273. (g) 6d. (h) Deng, Q.-H.; Chen, J.-R.; Wei, Q.; Zhao, Q.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Commun.* **2015**, *51*, 3537. (i) Noto, N.; Miyazawa, K.; Koike, T.; Akita, M. *Org. Lett.* **2015**, *17*, 3710. (j) Arai, Y.; Tomita, R.; Ando, G.; Koike, T.; Akita, M. *Chem. Eur. J.* **2016**, *22*, 1262. (k) Ran, Y.; Lin, Q.-Y.; Xu, X.-H.; Qing, F.-L. *J. Org. Chem.* **2016**, *81*, 7001. (l) Noto, N.; Koike, T.; Akita, M. *J. Org. Chem.* **2016**, *81*, 7064.
[8] (a) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160. (b) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875. (c) Oh, S. H.; Malpani, Y. R.; Ha, N.; Jung, Y.-S.; Han, S. B. *Org. Lett.* **2014**, *16*, 1310. (d) Tang, X.-J.; Dolbier, W. R., Jr. *Angew. Chem. Int. Ed.* **2015**, *54*, 4246. (e) Bagal, D. B.; Kachkovskiy, G.; Knorn, M.; Rawner, T.; Bhanage, M. B.; Reiser, O. *Angew. Chem. Int. Ed.* **2015**, *54*, 6999. (f) Carboni, A.; Dagousset, G.; Magnier, E.; Masson, G. *Synthesis* **2015**, *47*, 2439. (g) Lin, Q.-Y.; Ran, Y.; Xu, X.-H.; Qing, F.-L. *Org. Lett.* **2016**, *18*, 2419.
[9] (a) Prakash, G. K. S.; Hu, J. *Acc. Chem. Res.* **2007**, *40*, 921. (b) Hu, J. *J. Fluorine Chem.* **2009**, *130*, 1130. (c) Zhang, W.; Ni, C.; Hu, J. *Top. Curr. Chem.* **2012**, *308*, 25. (d) Ni, C.; Hu, M.; Hu, J. *Chem. Rev.* **2015**, *115*, 765.
[10] Rong, J.; Deng, L.; Tan, P.; Ni, C.; Gu, Y.; Hu, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 2743.

(Cheng, B.)