

Supporting Information

Catalyst-free radical fluorination of sulfonyl hydrazides in water

Lin Tang,^{*a} Yu Yang,^b Lixian Wen,^b Xingkun Yang^a and Zhiyong Wang^{*b}

^a *College of Chemistry and Chemical Engineering, Xinyang Normal University,
Xinyang, Henan 464000, China. E-mail: lintang@xynu.edu.cn*

^b *Hefei National Laboratory for Physical Sciences at Microscale, CAS Key
Laboratory of Soft Matter Chemistry and Department of Chemistry, University of
Science and Technology of China, Hefei, Anhui 230026, China. E-mail:
zwang3@ustc.edu.cn*

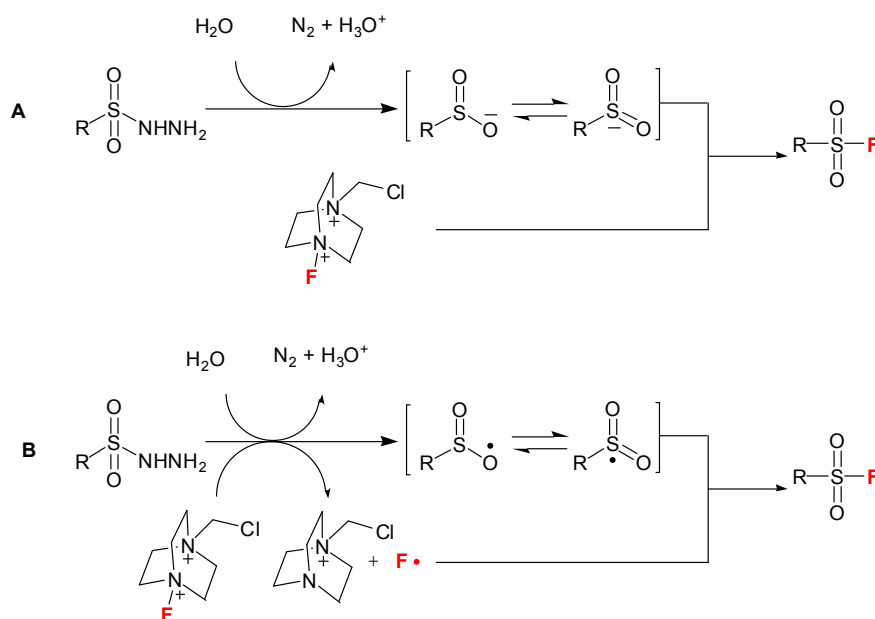
Contents:

General experimental procedures.....	S2
Two possible reaction pathways.....	S2
Characterization data of products 2a-2u	S3
¹ H, ¹³ C and ¹⁹ F NMR spectra of products 2a-2u	S8

General experimental procedures

Solvent of water (1.0 ml) was added to the mixture of 4-methylbenzenesulfonohydrazide (46.5mg, 0.25 mmol), Selectfluor (115.1 mg, 0.325 mmol) in a Schlenk tube. The reaction mixture was stirred at 60 °C for 14 h. After cooling to room temperature, 5 times the volume of EtOAc was added to the reaction mixture under vigorous stirring conditions. Then, the solvent of the organic phase was removed under vacuum and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 8:1) to give the product as a white solid in 94% yield. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AC-400 FT (^1H NMR 400 MHz, ^{13}C NMR 100 MHz) using TMS as an internal reference. ^{19}F fluorine spectra were recorded on either a Bruker AC-400 FT (^{19}F NMR 376 MHz) using CFCl_3 as an external reference.

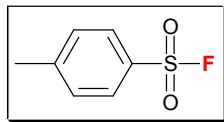
Two possible reaction pathways



Scheme S1 the possible processes for this fluorination.

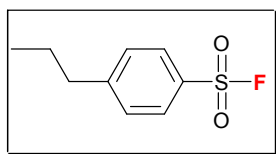
Characterization data of products 2a-2u

4-methyl-benzenesulfonyl fluoride (**2a**)



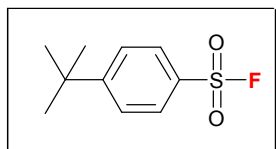
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.89 (d, 8.0 Hz, 2H), 7.42 (d, 8.0 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 147.2, 130.4, 130.3, 130.1, 128.6, 22.0; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.2. This compound was known.^[1]

4-propyl-benzenesulfonyl fluoride (**2b**)



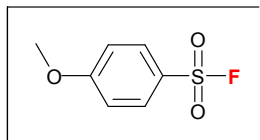
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.91 (d, 8.0 Hz, 2H), 7.42 (d, 8.0 Hz, 2H), 2.71 (t, 7.8 Hz, 2H), 1.73-1.64 (m, 2H), 0.96 (t, 7.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 151.8, 130.5, 130.2, 129.8, 128.6, 38.2, 24.2, 13.8; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.3. This compound was known.^[1]

4-tert-butyl-benzenesulfonyl fluoride (**2c**)



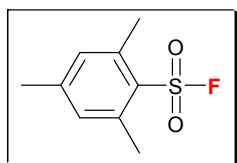
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.93 (d, 8.0 Hz, 2H), 7.63 (d, 8.0 Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 160.1, 130.2, 130.0, 128.5, 126.8, 35.7, 31.1; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.2. This compound was known.^[1]

2-(4-Methoxyphenyl)-benzoxazole (**2d**)



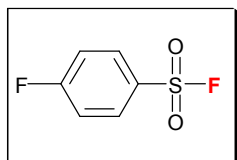
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.94 (d, 8.5 Hz, 2H), 7.06 (d, 8.5 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 165.3, 131.0, 124.3, 124.1, 115.0, 56.0; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 67.3. This compound was known.^[1]

2,4,6-trimethyl-benzenesulfonyl fluoride (**2e**)



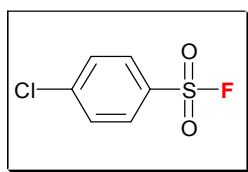
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.03 (s, 2H), 2.64 (d, 1.2 Hz, 6H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 145.2, 140.2, 132.0, 132.0, 129.3, 129.1, 22.5, 22.5, 21.3; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 68.2. This compound was known.^[1]

4-fluoro-benzenesulfonyl fluoride (2f)



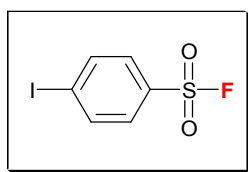
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.08-8.04 (m, 2H); 7.32 (t, 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 168.3, 165.7, 131.8, 131.7, 117.5, 117.3; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 66.8. This compound was known.^[1]

4-chloro-benzenesulfonyl fluoride (2g)



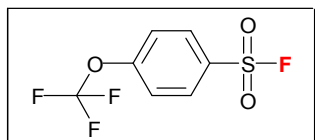
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.98-7.94 (m, 2H), 7.63-7.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 142.7, 131.5, 131.2, 130.1, 129.9; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 66.5. This compound was known.^[1]

4-iodo-benzenesulfonyl fluoride (2h)



¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.01 (d, 8.0 Hz, 2H), 7.71 (d, 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 139.2, 132.9, 129.6, 104.2; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 66.2. This compound was known.^[1]

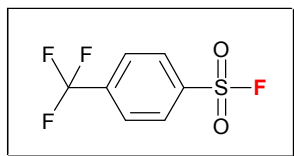
4-trifluoromethoxy-benzenesulfonyl fluoride (2i)



¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.09 (d, 8.0 Hz, 2H), 7.46 (8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 154.3, 131.1, 130.9, 130.8, 124.0, 121.4, 121.2, 118.8, 116.2; ¹⁹F NMR

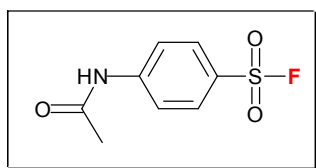
(376 MHz, CDCl₃): δ [ppm] = 66.5, -57.7. HRMS (M⁺) calcd for C₇H₄F₄O₃S: 243.9817 found 243.9811.

4-trifluoromethyl-benzenesulfonyl fluoride (**2j**)



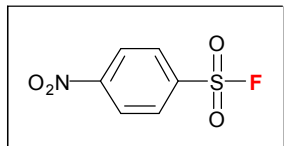
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.17 (d, 8.0 Hz, 2H), 7.92 (d, 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 137.5, 137.2, 136.8, 129.3, 127.1, 127.1, 127.0, 127.0, 124.2, 121.5; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 65.9, -63.5. This compound was known.^[2]

4-acetyl-amino-benzenesulfonyl fluoride (**2k**)



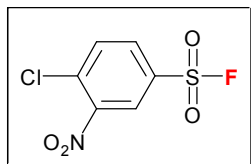
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.96 (d, 8.8 Hz, 2H), 7.79 (d, 8.8 Hz, 2H), 7.57 (s, 1H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 168.8, 144.5, 130.2, 127.2, 119.5, 25.0; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 66.8. This compound was known.^[1]

4-nitro-benzenesulfonyl fluoride (**2l**)



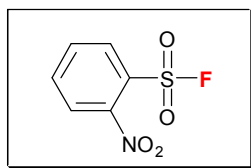
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.49 (d, 8.4 Hz, 2H), 8.25 (d, 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 142.8, 131.7, 131.4, 130.3, 130.0; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 66.3. This compound was known.^[1]

4-chloro-3-nitro-benzenesulfonyl fluoride (**2m**)



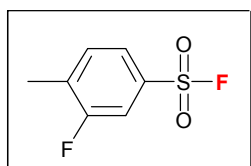
¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.52 (d, 2.0 Hz, 1H), 8.16-8.14 (m, 1H), 7.89 (d, 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 148.3, 135.5, 134.0, 133.0, 132.7, 132.3, 126.1; ¹⁹F NMR (376 MHz, CDCl₃): δ [ppm] = 67.0. HRMS (M⁺) calcd for C₆H₃ClFNO₄S: 238.9455 found 238.9459.

2-nitro-benzenesulfonyl fluoride (**2n**)



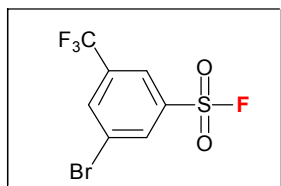
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 8.88 (s, 1H), 8.65 (d, 8.0 Hz, 1H), 8.36 (d, 8.0 Hz, 1H), 7.94-7.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 148.6, 135.2, 134.9, 133.9, 131.5, 130.1, 124.0; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.5. This compound was known.^[2]

3-fluoro-4-methyl-benzenesulfonyl fluoride (**2o**)



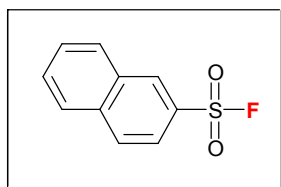
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.72-7.70 (m, 1H), 7.65 (d, 8.0 Hz, 1H), 7.47 (t, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 162.2, 159.7, 134.7, 134.5, 132.9, 132.9, 131.9, 131.9, 131.7, 131.6, 124.3, 124.2, 115.6, 115.4, 15.2, 15.2; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.3, -111.9. HRMS (M^+) calcd for $\text{C}_7\text{H}_6\text{F}_2\text{O}_2\text{S}$: 192.0057 found 192.0065.

3-bromo-5-trifluoromethyl-benzenesulfonyl fluoride (**2p**)



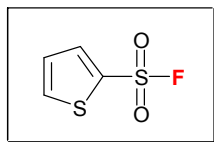
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 8.34 (s, 1H), 8.20 (s, 1H), 8.16 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 136.0, 135.7, 135.6, 135.6, 135.6, 134.7, 134.4, 134.0, 133.7, 126.1, 124.6, 124.3, 124.3, 124.2, 124.2, 123.3, 120.6, 117.9; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.6, -63.1. This compound was known.^[2]

naphthalene-2-sulfonyl fluoride (**2q**)



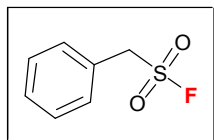
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 8.62 (s, 1H), 8.08-8.02 (m, 2H), 7.99-7.92 (m, 2H), 7.78-7.68 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 136.2, 132.0, 131.1, 130.5, 130.2, 130.1, 129.8, 129.8, 128.5, 128.3, 122.3; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.3. This compound was known.^[3]

thiophene-2-sulfonyl fluoride (**2r**)



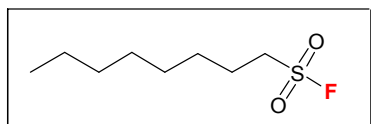
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.94 (d, 4.0 Hz, 1H), 7.90 (d, 4.8 Hz, 1H), 7.27 (t, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 137.0, 136.6, 136.6, 131.8, 131.5, 128.3; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 71.8. This compound was known.^[1]

phenyl-methanesulfonyl fluoride (**2s**)



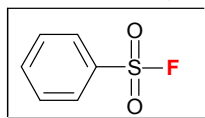
^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.47-7.43 (m, 5H), 4.60 (d, 3.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 130.8, 130.1, 129.5, 125.6, 57.1, 56.9; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 51.4. This compound was known.^[4]

octanesulfonyl fluoride (**2t**)



^1H NMR (400 MHz, CDCl_3): δ [ppm] = 3.38-3.33 (m, 2H), 1.98-1.91 (m, 2H), 1.51-1.44 (m, 2H), 1.33-1.28 (m, 8H), 0.89 (t, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 51.1, 50.9, 31.8, 29.0, 29.0, 28.0, 23.5, 22.7, 14.2; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 53.2. This compound was known.^[5]

benzenesulfonyl fluoride (**2u**)



^1H NMR (400 MHz, CDCl_3): δ [ppm] = 8.20 (d, 6.8 Hz, 2H), 7.96 (t, 6.8 Hz, 1H), 7.82 (t, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 132.8, 130.3, 130.0, 126.9, 125.6; ^{19}F NMR (376 MHz, CDCl_3): δ [ppm] = 66.2. This compound was known.^[1]

References:

- [1] L. Matesic, N. A. Wyatt, B. H. Fraser, M. P. Roberts, T. Q. Pham, I. Greguric, *J. Org. Chem.*, 2013, **78**, 112625.
- [2] G. Palumbo, R. Caputo, *Synthesis*, 1981, 888.
- [3] D. N. Harpp, S. J. Bodzay, *Sulfur Lett.*, 1987, 73.
- [4] M. Kirihaara, S. Naito, Y. Nishimura, Y. Ishizuka, T. Iwai, H. Takeuchi, T. Ogata, H. Hanai, Y. Kinoshita, M. Kishida, K. Yamazaki, T. Noguchi, S. Yamashoji, *Tetrahedron*, 2014, **70**, 2464.
- [5] J. Burdon, I. Farazmand, M. Stacey, J. C. Tatlow, *J. Chem. Soc.*, 1957, 2574.

^1H , ^{13}C and ^{19}F NMR spectra of products 2a-2u

