## **Supporting Information**

## Reductive Insertion of Sulfur Dioxide for the Synthesis of Trifluoromethyl thiolsulphonates Through One-pot Reaction of Aniline and Trifluoromethanesulfanylamide

Jie Sheng<sup>a</sup> Yuewen Li<sup>b</sup> and Guanyinsheng Qiu<sup>b\*</sup>

<sup>a</sup> College of Food Science and Technology, Shanghai Ocean University, 999

Huchenghuan Road, Shanghai, China

<sup>b</sup>College of Biological, Chemical Science and Engineering, Jiaxing University,

118 Jiahang Road, Jiaxing 314001, China. E-mail: 11110220028@fudan.edu.cn

- 1. General experimental methods (S2).
- 2. <sup>19</sup>F, <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **3** (S7-S46).

## **General experimental methods:**

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20Torr (house vacuum) at 25–35°C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

S-trifluoromethyl benzenesulfonothioate  $(3a)^{[1]}$ 

*S*-trifluoromethyl 4-bromobenzenesulfonothioate (**3b**)<sup>[1]</sup>

Ethyl 4-(trifluoromethylthiosulfonyl)benzoate (3c)

S-trifluoromethyl 4-cyanobenzenesulfonothioate (3d) [1]

S-trifluoromethyl 4-nitrobenzenesulfonothioate (3e) [1]

S-trifluoromethyl 4-(trifluoromethyl)benzenesulfonothioate (3f)

$$C_2H_5O$$

S-trifluoromethyl 4-ethoxybenzenesulfonothioate (3g)

S-trifluoromethyl 4-methoxybenzenesulfonothioate (3h)<sup>[1]</sup>

S-trifluoromethyl 2-chlorobenzenesulfonothioate (3i)

S-trifluoromethyl 2-methylbenzenesulfonothioate (3j)

S-trifluoromethyl 3-methoxybenzenesulfonothioate (3k)

S-trifluoromethyl 2,4,6-trimethylbenzenesulfonothioate (31)

S-trifluoromethyl 2-(2-phenylethynyl)benzenesulfonothioate (3m)

S-trifluoromethyl quinoline-8-sulfonothioate  $8^{[1]}$ 

## Reference:

1. X. Shao, C. Xu, L. Lu, Q. Shen, J. Org. Chem. 2015, 80, 3012.



















































































