

# A recyclable fluorous hydrazine-1,2-bis(carbothioate) with NCS as an efficient catalyst for acetalization of aldehydes

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## General remarks

<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were characterized with a Bruker Advance RX500 spectrometer. The pH was recorded on a Mettler Toledo EL2 instrument. The GC data was recorded on Agilent 7890a. All chemicals were reagent grade and used as purchased without further purifications.

## Procedure for the Preparation of Fluorous hydrazine-1,2-bis(carbothioate) **1**

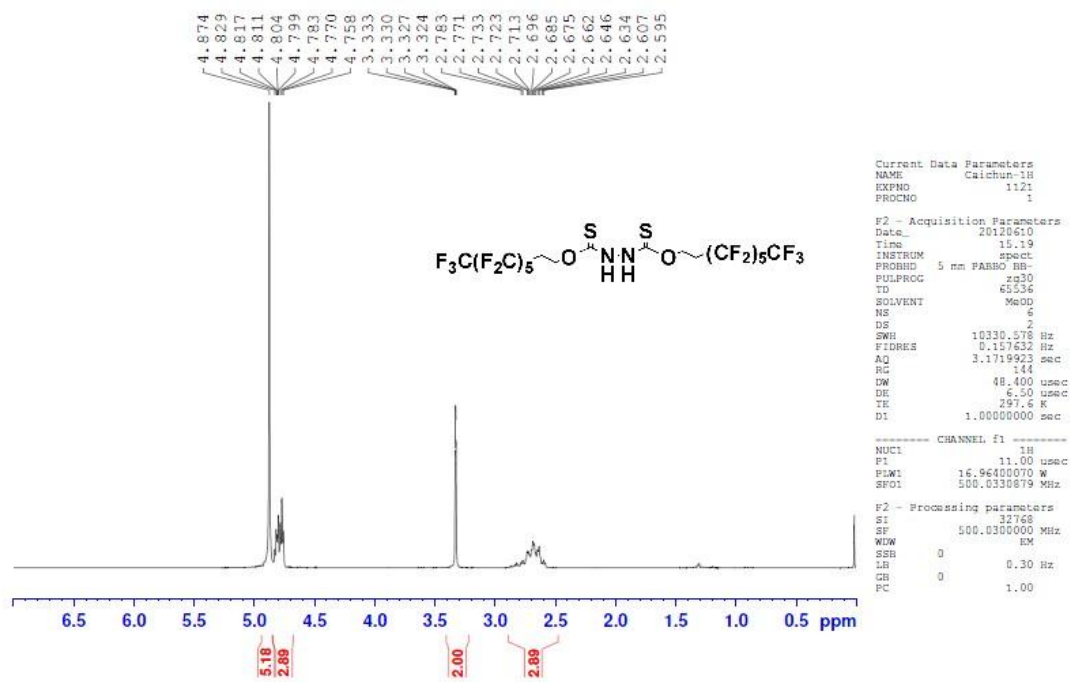
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol **II** (3.641 g, 10 mmol) was slowly added to a solution of di(1H-imidazol-1-yl)methanethione **I** (1.958 g, 11 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 12 h at room temperature, the crude reaction mixture was quenched with water and then extracted with petroleum ether (3 × 50 mL). Column chromatography, if necessary. The solvent was removed under reduced pressure and the residue was dried under high vacuum. O-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 1H-imidazole-1-carbothioate **III** was taken up in THF (50 mL) and hydrazine monohydrochloride (0.342 g, 5 mmol) and triethylamine (2.529 g, 25 mmol) were added at room temperature. After 7 d, the reaction mixture was quenched with brine (60 mL) and extracted with ether (3 × 40 mL). The organic layers were combined and loaded onto the fluorous silica gel, eluted it with 80% methanol then with ether to give the fluorous compounds. Purification in standard gel if necessary, gave *O,O*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) hydrazine-1,2-bis(carbothioate) **1** (2.363 g, 56%) as a white solid; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 4.83-4.76 (m, 4H), 2.78-2.60 (m, 4H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) δ 194.2 (b), 122.7-111.1 (m), 65.3 (t), 32.8 (b); <sup>19</sup>F NMR δ -82.5 (6F), -114.5 (4F), -122.9 (4F), -123.9 (4F), -124.6 (4F), -127.4 (4F); MS (ESI<sup>+</sup>) *m/z* 843.00 (M-H).

**Typical Procedure for Fluorous hydrazine-1,2-bis(carbothioate) **1** with NCS catalyzed the acetalization reaction of aldehydes and the recycling of catalyst **1****

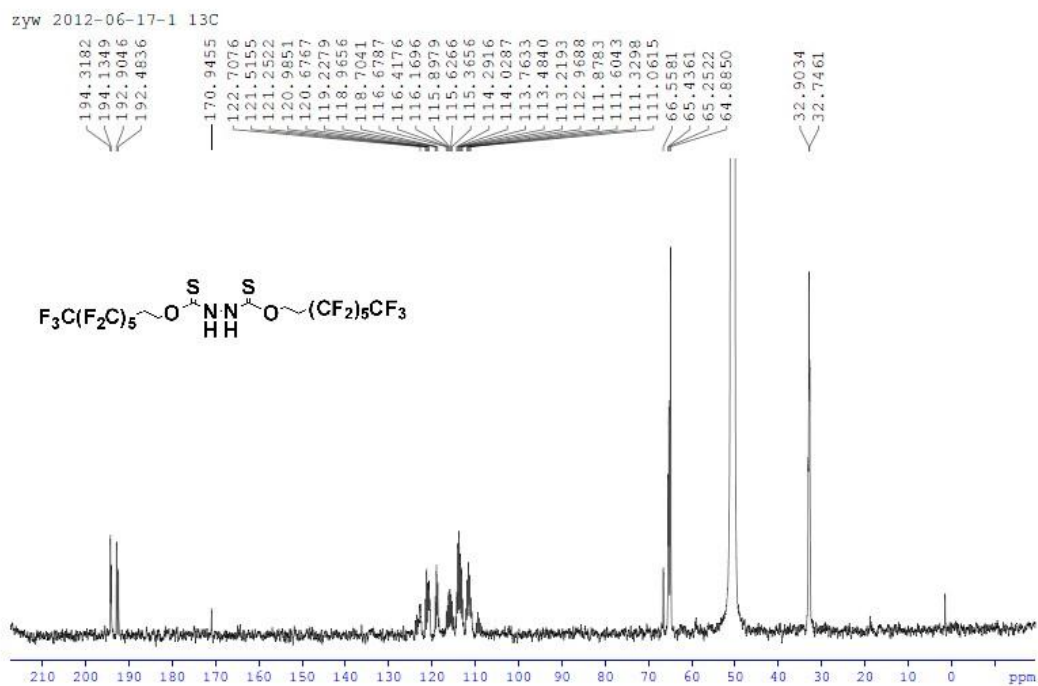
Fluorous hydrazine-1,2-bis(carbothioate) **1** (0.084 g, 0.1 mmol) with NCS (0.013 g, 0.1 mmol) was added in MeOH (6 mL) was stirred at 25 °C for 10 min. Then 3-phenylpropionaldehyde (0.268 g, 2 mmol) was added and the resulting mixture was stirred at 25 °C for 1 h. After the reaction completed, the mixture was concentrated and then loaded onto a FluoroFlash<sup>®</sup> silica gel cartridge (5 g), eluted by 80% methanol at first for non-fluorous components. Then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated for GC analysis. Ether was then added onto the fluorous gel column to wash out the fluorous hydrazine-1,2-bis(carbothioate) **1**. After removal the ether, compound **1** was dried in vacuo at 40 °C for 8 h and could be directly used in the next run.

# $^1\text{H}$ NMR

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# $^{13}\text{C}$ NMR



# 1 <sup>19</sup>F NMR

