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

Yi-Wei Zhu, Wen-Bin Yi*, Chun Cai

School of Chemical Engineering, Nanjing University of Science and Technology, Xiao Ling Wei Street, Nanjing 210094, People’s Republic of China

*Corresponding author. Fax: +86-25-84315030; Tel.: +86-25-84315514; E-mail: yiwenbin@mail.njust.edu.cn

General remarks

$^1$H NMR, $^{13}$C NMR and $^{19}$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-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$_2$Cl$_2$. After stirring for 12 h at room temperature, the crude reaction mixture was quenched with water and then extracted with petroleum ether ($3 \times 50$ 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 ($3 \times 40$ 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) I (2.363 g, 56%) as a white solid; $^1$H NMR (500 MHz, CD$_3$OD) $\delta$ 4.83-4.76 (m, 4H), 2.78-2.60 (m, 4H); $^{13}$C NMR (125 MHz, CD$_3$OD) $\delta$ 194.2 (b), 122.7-111.1 (m), 65.3 (t), 32.8 (b); $^{19}$F NMR $\delta$ -82.5 (6F), -114.5 (4F), -122.9 (4F), -123.9 (4F), -124.6 (4F), -127.4 (4F); MS (ESI$^+$) $m/z$ 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 ºC for 10 min. Then 3-phenylpropionaldehyde (0.268 g, 2 mmol) was added and the resulting mixture was stirred at 25 ºC for 1 h. After the reaction completed, the mixture was concentrated and then loaded onto a FluoroFlash® silica gel cartridge (5 g), eluted by 80% methanol at first for non-fluorous components. Then dried over Na₂SO₄ 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 ºC for 8 h and could be directly used in the next run.
$^1$H NMR
$^{13}$C NMR

\[
\text{F}_3\text{C} (\text{F}_2\text{C})_5 \text{S} \sim \text{O} \overset{\text{N}}{\text{N}} \overset{\text{O}}{\text{N}} \sim (\text{CF}_2)_p \text{CF}_3
\]
$^{19}$F NMR

$F_3C\{(F_2C)\}_5\rightarrow S \rightarrow S \rightarrow O \rightarrow \{(CF_2)\}_5CF_3$

---

**Current Data Parameters**

- **Sample**: Carboxin-100
- **Temperature**: 25.0

**$^{13}C$ – Assignments Parameters**

- **Data**: 2012.06.10
- **Time**: 15:26

---

**BRUKER**

Current Data Parameters

Sample: Carboxin-100

Temperature: 25.0

---

**Electronic Supplementary Material (ESI) for New Journal of Chemistry**

This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

---

$F_3C\{(F_2C)\}_5\rightarrow S \rightarrow S \rightarrow O \rightarrow \{(CF_2)\}_5CF_3$