

Supplementary Materials: A Recyclable Fluorous Hydrazine-1,2-Bis(Carbothioate) Organocatalyst for the Synthesis of β -Chloroethers with *N*-Chlorosuccinimide

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General remarks

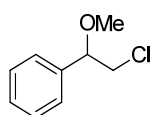
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were characterized with a Bruker Advance RX500 spectrometer. All chemicals were reagent grade and used as purchased without further purifications. All the β -chloroether products are known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.

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_2Cl_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). The solvent was removed under reduced pressure and the residue was dried under high vacuum. The crude *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) **1** (2.363 g, 56%) as a white solid; ^1H NMR (500 MHz, CD_3OD): δ 4.83-4.76 (m, 4H), 2.78-2.60 (m, 4H); ^{13}C NMR (125 MHz, CD_3OD): δ 194.2 (b), 122.7-111.1 (m), 65.3 (t), 32.8 (b); ^{19}F NMR: δ -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).

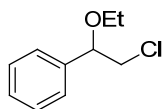
Typical procedure for fluorous hydrazine-1,2-bis(carbothioate) 1 catalyzed the synthesis of β -chloroethers and the recycling of fluorous organocatalyst

Fluorous hydrazine-1,2-bis(carbothioate) **1** (0.042 g, 0.05 mmol) with NCS (0.267 g, 2 mmol) was added in MeOH (3 mL) and stirred at 25 $^\circ\text{C}$ for 10 min. Then olefin (1 mmol) was added and the resulting mixture was stirred at 25 $^\circ\text{C}$ for 0.5–48 h. After the reaction completed, the mixture was concentrated and then loaded onto a FluoroFlash $^\circ$ silica gel cartridge (5 g), eluted by 80% methanol at first for non-fluorous components. Then dried over Na_2SO_4 and evaporated for silica gel chromatography to provide a clear oil. 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 $^\circ\text{C}$ for 8 h and could be directly used in the next run.



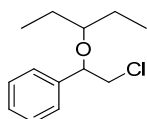
Clear oil.

^1H NMR (500 MHz, CDCl_3): δ 7.41-7.31 (m, 5H), 4.37 (dd, 1H, J = 8.0, 4.5), 3.65 (dd, 1H, J = 11.5, 8.0), 3.57 (dd, 1H, J = 11.5, 4.5), 3.31 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 138.1, 128.8, 128.3, 126.8, 83.7, 57.1, 47.9



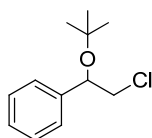
Clear oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.42-7.29 (m, 5H), 4.43 (dd, 1H, $J = 8.0, 4.5$), 3.66 (dd, 1H, $J = 11.5, 8.0$), 3.59 (dd, 1H, $J = 11.5, 4.5$), 3.44 (m, 2H), 1.21 (t, 3H, $J = 7.0$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 139.3, 128.5, 128.2, 126.9, 81.7, 64.9, 48.1, 15.3



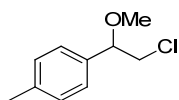
Clear oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.36-7.30 (m, 5H), 4.51 (dd, 1H, $J = 8.0, 5.0$), 3.67 (dd, 1H, $J = 11.0, 8.0$), 3.54 (dd, 1H, $J = 11.0, 5.0$), 3.21-3.18 (m, 1H), 1.67-1.51 (m, 2H), 1.48-1.36 (m, 2H), 0.92 (t, 3H, $J = 7.5$), 0.77 (t, 3H, $J = 7.5$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 140.1, 128.5, 128.1, 127.1, 80.2, 79.7, 48.6, 26.1, 24.9, 9.8, 8.8



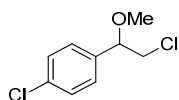
Clear oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.38-7.24 (m, 5H), 4.62 (dd, 1H, $J = 8.0, 4.5$), 3.52 (dd, 1H, $J = 11.0, 8.0$), 3.47 (dd, 1H, $J = 11.0, 4.5$), 1.16 (s, 9H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 142.3, 128.1, 127.5, 126.4, 75.0, 74.6, 49.2, 28.5



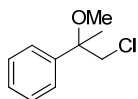
Clear oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.21-7.15 (m, 4H), 4.32 (dd, 1H, $J = 8.25, 4.0$), 3.63 (dd, 1H, $J = 11.5, 8.0$), 3.53 (dd, 1H, $J = 11.5, 4.0$), 3.27 (s, 3H), 2.35 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 138.1, 135.3, 129.1, 126.5, 83.4, 57.0, 48.2, 21.2



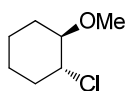
Clear oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.35 (d, 2H, $J = 8.5$), 7.26 (d, 2H, $J = 8.5$), 4.33 (dd, 1H, $J = 7.25, 8.0$), 3.63 (dd, 1H, $J = 11.5, 7.5$), 3.54 (dd, 1H, $J = 11.5, 4.5$), 3.30 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 137.1, 134.3, 128.6, 128.1, 82.7, 57.2



Clear oil.

^1H NMR (500 MHz, CDCl_3): δ 7.41-7.35 (m, 5H), 3.71 (d, 1H, $J = 11.0$), 3.56 (d, 1H, $J = 11.0$), 3.12 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 141.6, 128.3, 127.9, 126.2, 78.5, 53.3, 50.8, 20.8



obtained as a anti diastereoisomer

Clear oil. Reaction time

^1H NMR (500 MHz, CDCl_3): δ 3.88-3.82 (m, 1H), 3.45 (s, 3H), 3.19-3.15 (m, 1H), 2.21-2.13 (m, 2H), 1.74-1.64 (m, 3H), 1.32-1.30 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 82.9, 62.5, 57.1, 34.7, 29.8, 24.2, 23.1

1 ^1H NMR

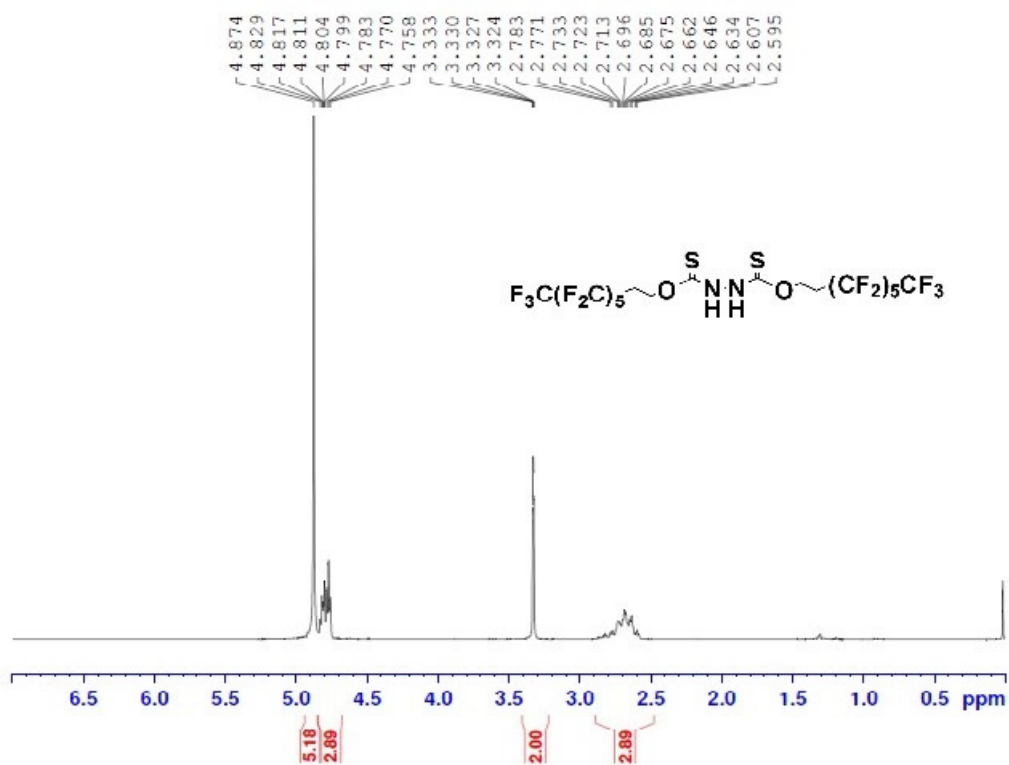
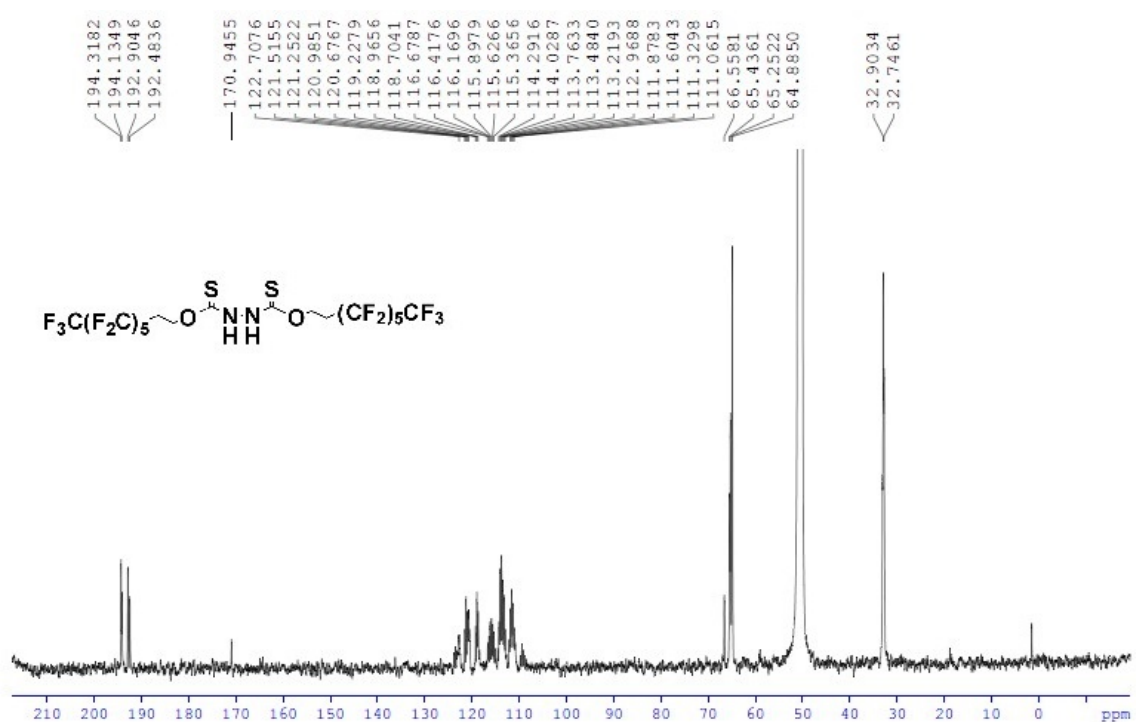
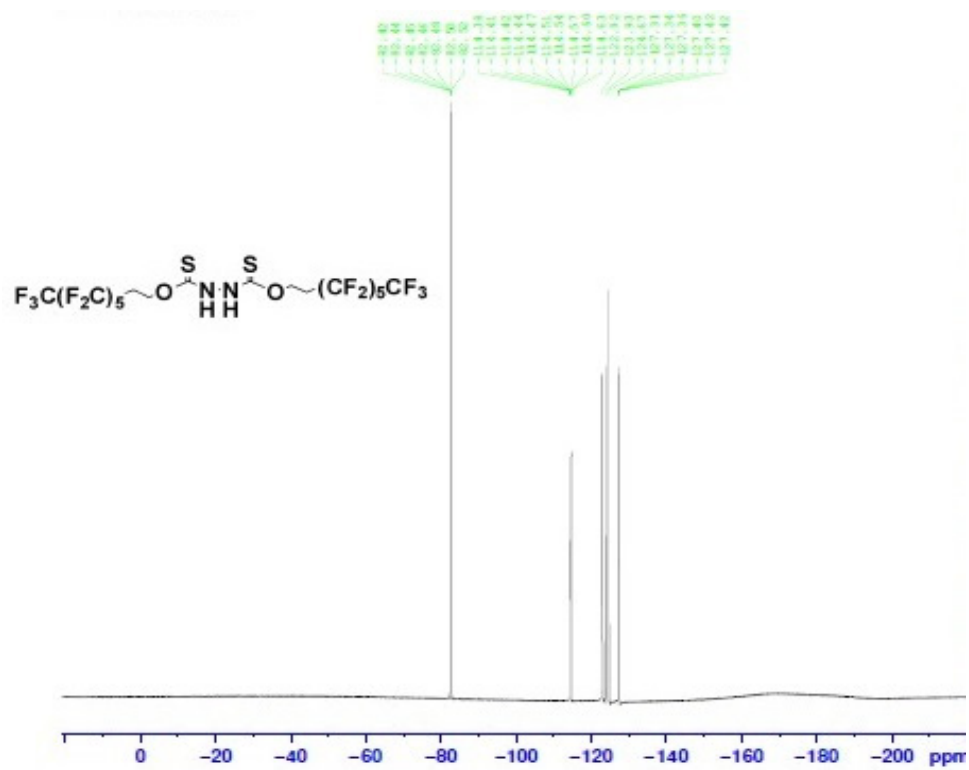


Figure S1. ^1H NMR of the fluorine hydrazine-1,2-bis(carbothioate) 1.

1 ¹³C NMR**Figure S2.** ¹³C NMR of the fluoruous hydrazine-1,2-bis(carbothioate) **1**.**1 ¹⁹F NMR****Figure S3.** ¹⁹F NMR of the fluoruous hydrazine-1,2-bis(carbothioate) **1**.