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Supporting Information

A Radical Thia-Brook Rearrangement

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General experimental methods: All reactions requiring anhydrous conditions were conducted under an inert atmosphere. Reactions were monitored by TLC, using plates pre-coated with a 0.25 mm layer of silica containing a fluorescent indicator. Visualization of reaction components was achieved with 254 nm light, and with anisaldehyde reagent. Column chromatography was carried out on Kieselgel 60 (40-63 μ m). Petroleum ether refers to the fraction of petroleum boiling between 40 °C and 60 °C. IR spectra were recorded as solutions in CCl₄. Absorption maxima (v_{max}) are reported in wavenumbers (cm⁻¹) and only selected peaks are reported. Melting points were recorded on a Kofler hot block, and are uncorrected. ¹H and ¹³C NMR spectra of compounds were recorded in CDCl₃ at 25 °C. Chemical shifts (δ_H , δ_C) are guoted in parts per million (ppm) and are referenced to the residual solvent peak (CDCl₃: δ_{H} = 7.27 and δ_c = 77.14). Coupling constants (J) are given in Hz, multiplicities are given as multiplet (m), singlet (s), doublet (d), triplet (t), guartet (g), or broad (br). DEPT were use to aid spectral assignments. Low-resolution mass spectra (m/z) were recorded using HP 5989B, JMS-GCmateII and Micromass Autospec mass spectrometers and only report molecular species (M⁺, [M+H]⁺, [M+NH₄]⁺, [M+Na]⁺) and other major fragments, with intensities quoted as percentages of the base peak. High-resolution mass spectra were recorded by electron impact ionization (EI) on a JMS-GCmateII mass spectrometer. The guoted masses are accurate to \pm 5 ppm. DLP corresponds to di-lauroyl peroxide (often sold under lauroy) peroxide or laurox).



The commercially available chloromethylphthalimide (1mmol) was treated by potassium O-isopropyl xanthate (1.1 mmol.) in acetone (2 mL) at room temperature to yield the known xanthate as crystals in 90% yield. Mp (83-84°C) Mp lit. 78°C. R. R. Darji, A. Shah, *Indian J. Chem., Section B*, 1985, **24**, 685-686.



A solution of xanthate (1 mmol) and olefin **2a** (2 mmol) in ethyl acetate (1 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added portion-wise (10 mol%) and the reaction mixture was refluxed for 1.5 h. After evaporation of the solvent, the residue was purified by silica gel column chromatography using a gradient of elution (petroleum ether/ethyl acetate, 10/0 to 9/1) affording the addition product **3a** as a white solid in 83% yield. Mp 76-77°C $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$ 7.83 (m, 2H, 2CHAr), 7.69 (m, 2H, 2CHAr), 5.79 (m, 1H, CHO), 3.94 (ddd, 1H, J=5.4 Hz, J=11.5 Hz, J=13.3 Hz, NCHH), 3.81 (ddd, 1H, J=4.7 Hz, J=11.5 Hz, J=13.4 Hz, NCHH), 3.16 (dd, 1H, J=4.6 Hz, J=8.0 Hz, CHS), 2.26 (m, 1H, CHACHS), 1.96 (m, 1H, CHHCHS), 1.42 (d, 3H, J=6.4 Hz, CH_3), 1.39 (d, 3H, J=6.7 Hz, CH_3), 1.35 (s, 27H, 9CH_3). $\delta_c(100 \text{ MHz}, \text{CDCl}_3)$ 216.2 (CS), 168.3 (2NCO), 133.8 (2CHAr), 132.4 (2CqAr), 123.1 (2CHAr), 78.0 (OCHMe₂), 73.9 ([OCqMe₃]₃), 37.2 (NCH₂), 33.6 (CH₂), 31.8 (9CH₃), 30.9 (CHS), 21.5, 21.3 (2CH₃). (v_{max} /cm⁻¹, CCl₄) 1775, 1718 (NCO), 1393, 1366, 1229 (COS), 1070, 1038 (CS). HRMS (EI) calcd for C₂₇H₄₃NO₆S₂Si 569.2301 ; found 569.2292.

Compound 4a



A mixture of xanthate **3a** (0.17 g, 0.3 mmol) and diphenyl ether (2.8mL) was heated at 200°C until total consumption of the starting material. Thiol 4a was isolated as crystals in 53% yield after chromatography on a silica gel column aradient of elution (petroleum ether petroleum usina ۵ then ether/dichloromethane/diethyl ether, 1/0/0 to 6/3/1). $\delta_{H}(400 \text{ MHz}, \text{CDCl}_{3})$ 7.84 (m, 2H, 2CHAr), 7.70 (m, 2H, 2CHAr), 3.98 (ddd, 1H, J=4.4 Hz, J=8.5 Hz, J=12.9 Hz, NCHH), 3.86 (m, 1H, NCHH), 2.33 (m, 1H, CHSH), 1.70 (m, 3H, CH₂, SH), 1.32 (s, 27H, 9CH₃). δ_c (100 MHz, CDCl₃) 168.5 (2NCO), 133.9 (2CHAr), 132.3 (2CqAr), 123.2 (2CHAr), 73.4 ([OCqMe₃]₃), 37.1 (CH₂), 33.3 (CH₂), 31.7 (9CH₃), 21.8 (CHSi). (v_{max}/cm⁻¹, CCl₄) 1774, 1717 (NCO), 1391, 1365, 1188, 1065. HRMS (EI) calcd for C₂₃H₃₇NO₅SSi 467.2162; found 467.2159.

Compound 5a



The thiol **4a** (0.046 g, 0.1 mmol) in chlorobenzene (1 mL) was refluxed under nitrogen for 10 min and then di-tert-butylperoxide (3-4 drops) was added. After refluxing during 1 h, the solvent was removed under a nitrogen stream to give the pure rearranged product **5a** as a pale yellow oil in quantitative yield. $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$ 7.84 (m, 2H, 2CHAr), 7.71 (m, 2H, 2CHAr), 3.78 (t, 2H, J=7.1 Hz, NCH₂), 2.63 (t, 2H, J=7.2 Hz, CH₂), 2.04 (td, 2H, J=7.3 Hz, J=14.5 Hz, CH₂), 1.32 (s, 27H, 9CH₃). $\delta_{C}(100 \text{ MHz}, \text{CDCl}_3)$ 168.4 (2NCO), 133.9 (2CHAr), 132.2 (2CqAr), 123.2 (2CHAr), 74.1 ([OCqMe₃]₃), 37.5 (NCH₂), 31.7 (CH₂), 31.5 (9CH₃), 25.1 (CH₂S). (v_{max} /cm⁻¹, CCl₄) 1776, 1717 (NCO), 1469, 1438, 1393, 1365, 1242, 1186, 1063, 1026, 908. HRMS (EI) calcd for C₂₃H₃₇NO₅SSi 467.2162; found 467.2163.

Compound 3a'



A solution of xanthate (1 mmol) and olefin **2a**' (4 mmol) in ethyl acetate (1 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added portion-wise (20 mol%) and the reaction mixture was heated at 70°C for 1h30. After evaporation of the solvent, the residue was purified by silica gel column chromatography using a gradient of elution (petroleum ether/ethyl acetate, 10/0 to 9/1) affording the addition product **3a**' as a colorless oil and in 71% yield. $\delta_{\rm H}(400 \text{ MHz}, CDCl_3)$ 7.82 (m, 2H, 2CHAr), 7.70 (m, 2H, 2CHAr), 5.74 m, 1H, CHO), 3.81 (m, 2H, NCH₂), 3.18 (dd, 1H, J=4.8 Hz, J=9.4 Hz, CHS), 2.19 (m, 1H, CHHCHS), 1.86 (m, 1H, CHHCHS), 1.40 (t_{app}, 6H, J=5.9 Hz, 2CH₃), 0.14 (s, 9H, 3CH₃). $\delta_c(100 \text{ MHz}, CDCl_3)$ 215.4 (CS), 168.3 (2NCO), 133.9 (2CHAr), 132.2 (2CqAr), 123.2 (2CHAr), 78.5 (OCHMe₂), 37.1 (NCH₂), 33.9 (CH₂), 29.8 (CHS), 21.4, 21.3 (2CH₃), -2.4 (SiMe₃). (v_{max}/cm⁻¹, CCl₄) 1775, 1717 (NCO), 1395, 1366, 1252, 1232 (COS), 1093, 1039 (CS). HRMS (EI) calcd for $C_{18}H_{25}NO_3S_2Si$ 395.1045 ; found 395.1030.

Compound 8



A mixture of xanthate **3a'** (0.186 g, 0.47 mmol) and diphenyl ether (2 mL) was heated at 200°C under nitrogen until total consumption of the starting material. Two fractions were isolated after chromatography on a silica gel column using a gradient of elution (pentane/ ethyl acetate, 10/0 to 9/1). The known rearranged thiol **8** was obtained as crystals (Mp 46-47°C; Mp_{lit} 46-48°C) in 60% yield as well as a impure fraction containing about 10% of the thiol **4a'**. δ_{H} (400 MHz, CDCl₃) 7.80 (m, 2H, 2CHAr), 7.69 (m, 2H, 2CHAr), 3.78 (t, 2H, J=6.7 Hz, NCH₂), 2.51 (dd, 2H, J=7.3 Hz, J=14.9 Hz, CH₂S), 1.96 (q, 2H, CH₂), 1.58 (t, J=8.2 Hz, SH). δ_{C} (100 MHz, CDCl₃) 168.4 (2NCO), 134.0 (2CHAr), 131.9 (2CqAr), 123.3 (2CHAr), 36.4 (NCH₂), 32.7 (CH₂), 21.9 (CH₂). Lit. Gabriel; Lauer. *Chemische Berichte*, **1890**, *23*, 89.

Compound 1b



To a solution of the commercially available 2-chloro-5-(chloromethyl)pyridine (6.2 mmol) in acetone (12 mL) was added potassium O-isopropyl xanthate (6.8 mmol, 1.1 eq.) portion-wise under nitrogen. After addition of ice water, the precipitate was filtered off and dried to afford the desired xanthate **1b** in 81% and as yellow crystals which were recrystallised from diethy ether/pentane. Mp 62-63°C. $\delta_{H}(400 \text{ MHz}, \text{CDCl}_{3})$ 8.37 (d, 1H, J=2.5 Hz, CHAr), 7.66 (dd, 1H, J=2.6 Hz, J=8.2 Hz, CHAr), 7.28 (d, 1H, J=8.3 Hz, CHAr), 5.73 (m, 1H, CHO), 4.29 (s, 2H, CH₂S), 1.37 (d, 6H, J=6.2 Hz, 2CH₃). $\delta_{C}(100 \text{ MHz}, \text{CDCl}_{3})$ 211.8 (CS), 150.4 (CqAr), 149.9 (CHAr), 139.2 (CHAr), 131.4 (CqAr), 124.1 (CHAr), 78.6 (CHO), 36.2 (CH₂S), 21.2 (2CH₃). m/z (CI, NH₃) 262, 264 (MH⁺), HRMS (EI) calcd for $C_{10}H_{12}NClOS_2$ 261.0049; found 261.0048.

Compound 3b

Si(OtBu)₃ S CI N S O

A solution of xanthate **1b** (1 mmol) and olefin **2a** (2 mmol) in ethyl acetate (1 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added

portion-wise (3x10 mol% and 2x5 mol%) every hour. After evaporation of the solvent, the residue was purified by silica gel column chromatography using a gradient of elution (diethyl ether/pentane, 100/0 to 95/5) affording the addition product as a colorless oil and in 68% yield. $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$ 8.21 (d, 1H, J=2.3 Hz, CHAr), 7.46 (dd, 1H, J=2.5 Hz, J=8.1 Hz, CHAr), 7.22 (d, 1H, J=8.1 Hz, CHAr), 5.79 (m, 1H, CHO), 3.18 (dd, 1H, J=4.6 Hz, J=7.2 Hz, CHS), 2.85 (ddd, 1H, J=5.0 Hz, J=12.0 Hz, J=13.7 Hz, CHAr), 2.73 (ddd, 1H, J=5.3 Hz, J=11.9 Hz, J=13.9 Hz, CHHAr), 2.13 (m, 1H, CHHCHS), 1.89 (m, 1H, CHHCHS), 1.39 (d, 3H, J=6.2 Hz, CH₃), 1.37 (d, 1H, J=6.2 Hz, CH₃), 1.33 (s, 27H, 9CH₃). $\delta_c(100 \text{ MHz}, \text{CDCl}_3)$ 216.2 (CS), 149.7 (CHAr), 148.9 (CqAr), 138.9 (CHAr), 137.2 (CqAr), 123.9 (CHAr), 78.0 (CHO), 73.9 (OCqMe₃), 35.6, 33.9 (CHS, CH₂), 31.8 (9 CH₃), 30.5 (CH₂), 21.5, 21.4 (2CH₃). (v_{max} /cm⁻¹, CCl₄) 1459, 1388, 1365, 1228 (COS), 1071, 1037 (CS). HRMS (EI) calcd for C₂₄H₄₂NClO₄S₂Si 535.2013; found 535.2005.

Compounds 4b and 5b



A mixture of xanthate **3b** (0.3 g, 0.56 mmol) and diphenyl ether (2.8mL) was heated at 200°C under nitrogen until total consumption of the starting material. Two products were isolated as colorless oils after chromatography on a silica gel column using a gradient of elution (petroleum/ diethyl ether, 100/0 to 95/5). The thiol **4b** was obtained in 42% yield and the rearranged product **5b** in 28% yield.

Compounds 4b $\delta_{H}(400 \text{ MHz}, \text{CDCI}_{3})$ 8.23 (d, 1H, J=2.4 Hz, CHAr), 7.48 (dd, 1H, J=2.5 Hz, J=8.1 Hz, CHAr), 7.23 (d, 1H, J=8.1 Hz, CHAr), 2.95 (ddd, 1H, J=4.4 Hz, J=9.6 Hz, J=14.0 Hz, CHAr), 2.69 (ddd, 1H, J=7.3 Hz, J=9.2 Hz, J=13.9 Hz, CHHAr), 2.11 (m, 1H, CHSH), 1.73 (m, 1H, CHHCHS), 1.64 (m, 1H, CHHCHS), 1.53 (d, 1H, J=9.1 Hz, CHSH), 1.32 (s, 27H, 9CH_3). δ_c (100 MHz, CDCI₃) 149.8 (CHAr), 148.9 (CqAr), 139.1 (CHAr), 136.7 (CqAr), 123.9 (CHAr), 73.4 ([OCqMe₃]₃), 36.1 (CH₂Ar), 31.8 (9CH₃), 30.4 (CHSH), 23.6 (CH₂CHSi). (v_{max} /cm⁻¹, CCI₄) 1586, 1563, 1459, 1388, 1365, 1241, 1209, 1187, 1107, 1063, 1026, 908. HRMS (EI) calcd for $C_{20}H_{36}NCIO_3SSi$ 433.1874 ; found 433.1884.

Compounds 5b The thiol **4b** (0.06 g, 0.14 mmol) in chlorobenzene (1.4 mL) was refluxed under nitrogen for 10 min and then di-tert-butylperoxide (3 drops) was

added. After refluxing during 2 h, the mixture was filtered over silica gel to remove the solvent and yielded the rearranged product **5b** as a colorless oil in 78%. $\delta_{H}(400 \text{ MHz}, \text{CDCl}_{3})$ 8.23 (d, 1H, J=2.4 Hz, CHAr), 7.49 (dd, 1H, J=2.5 Hz, J=8.1 Hz, CHAr), 7.23 (d, 1H, J=8.1 Hz, CHAr), 2.72 (m, 2H, CH₂), 2.60 (t, 2H, J=7.1 Hz, CH₂), 1.95 (td, 2H, J=7.1 Hz, J=14.5 Hz, CH₂), 1.33 (s, 27H, 9CH₃). $\delta_{C}(100 \text{ MHz}, \text{CDCl}_{3})$ 149.8 (CHAr), 149.1 (CqAr), 139.0 ((CHAr), 136.2 (CqAr), 123.9 (CHAr), 74.2 ([OCqMe₃]₃), 33.4 (CH₂Ar), 31.6 (9CH₃), 31.1 (CH₂), 26.9 (CH₂). (v_{max} /cm⁻¹, CCl₄).1586, 1563, 1460, 1389, 1365, 1242, 1206, 1185, 1106, 1066, 1026. HRMS (EI) calcd for C₂₀H₃₆NClO₃SSi 433.1874 ; found 433.1867.

Compound 1c



The commercial available 1-(Chloromethyl)-1H-benzotriazole (2g, 11.9 mmol) was treated with potassium O-isopropylxanthate (2.28g, 1.1 equiv) in acetone (24 mL) at room temperature to yield the desired xanthate 1c as crystals in 95% yield. Mp 76-77°C. $\delta_{H}(400 \text{ MHz}, \text{ CDCl}_{3})$ 8.04 (d, 1H, J=8.4 Hz, CHAr), 7.70 (d, 1H, J=8.4 Hz, CHAr), 7.50 (m, 1H, CHAr), 7.38 (m, 1H, CHAr), 6.37 (s, 2H, CH₂S), 5.75 (m, 1H, CHO), 1.38 (d, 6H, J=6.2 Hz, 2CH₃). $\delta_{C}(100 \text{ MHz}, \text{CDCl}_{3})$ 209.5 (CS), 146.1 (CqAr), 132.3 (CqAr), 127.9 (br, CHAr), 124.4, 124.3 (CHAr), 120.2, 120.1 (CHAr), 110.4, 110.2 (CHAr), 79.8, 79.7 (CHO), 51.6 (br, CH₂S), 21.25, 21.20 (2CH₃). (v_{max}/cm^{-1} , CCl₄) 1241 (COS), 1038 (CS). HRMS (EI) calcd for $C_{11}H_{13}ON_{3}S_{2}$ 267.0500 ; found 267.0512.

Compound 3c



A solution of xanthate 1c (0.5g, 1.87 mmol) and olefin 2a (2 mmol) in ethyl acetate (1.9 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added portion-wise (2x10 mol% and 1x5 mol%) every hour. After evaporation of the solvent, the residue was purified by silica gel column

chromatography using a gradient of elution (petroleum ether/ethyl acetate, 10/0 to 9/1) affording the addition product **3c** as a yellow oil and in 58% yield. $\delta_{H}(400 \text{ MHz}, \text{CDCl}_3)$ 8.04 (d, 1H, J=8.4 Hz, CHAr), 7.56 (dd, 1H, J=0.7 Hz, J=8.4 Hz, CHAr), 7.45 (t, 1H, J=7.6 Hz, CHAr), 7.34 (m, 1H, CHAr), 5.76 (m, 1H, CHO), 4.83 (m, 2H, NCH₂), 3.24 (dd, 1H, J=4.8 Hz, J=7.0 Hz, CHS), 2.57 (m, 1H, CHHCHS), 2.30 (m, 1H, CHHCHS), 1.39 (d, 6H, J=6.1 Hz, 2CH₃), 1.35 (s, 27H, 9CH₃). $\delta_{c}(100 \text{ MHz}, \text{CDCl}_3)$ 215.7 (CS), 145.9 (CqAr), 132.9 (CqAr), 127.08, 127.02 (CHAr), 123.8, 123.7 (CHAr), 120.0, 119.9 (CHAr), 109.7, 109.5 (CHAr), 78.4, 78.3 (CHO), 74.2 (SiOCq), 46.8 (NCH₂), 33.3 (CHS), 32.0 (CH₂CHS), 31.8, 31.7 (9CH₃), 21.43, 21.38, 21.30, 21.2 (2CH₃). (v_{max} /cm⁻¹, CCl₄) 1455, 1389, 1366, 1230 (COS), 1070, 1036 (CS). HRMS (EI) calcd for C₂₅H₄₃O₄N₃S₂Si 541.2464; found 541.2475.

Compound 5c



A mixture of xanthate **3c** (0.5 g, 0.92 mmol) and diphenyl ether (5 mL) was heated at 200°C under nitrogen until total consumption of the starting material. After removal of the diphenyl ether by filtration on a pad of silica gel, the crude reaction mixture was taken up in chlorobenzene (7 mL) and refluxed in the presence of di-tert-butylperoxide (3-4 drops) under nitrogen. The reaction mixture was purified on a silica gel column (petroleum ether/ ethyl acetate 10/0 to 9/1) to yield the rearranged product **5c** as a yellow oil in 62% yield. $\delta_{H}(400 \text{ MHz}, CDCl_3)$ 8.03 (td, 1H, J=0.9 Hz, J=8.4 Hz, CHAr), 7.61 (td, 1H, J=0.9 Hz, J=8.3 Hz, CHAr), 7.46 (m, 1H, CHAr), 7.34 (m, 1H, CHAr), 4.78 (t, 2H, J=6.9 Hz, NCH₂), 2.60 (t, 2H, J=6.8 Hz, CH₂S), 2.36 (m, 2H, J=6.8 Hz, CH₂CHS), 1.30 (s, 27H, 9CH₃). δ_C (100 MHz, CDCl₃) 145.9 (CqAr), 133.2 (CqAr), 127.27, 127.22 (CHAr), 123.84, 123.81 CHAr), 119.99, 119.87 (CHAr), 109.69, 109.54 (CHAr), 74.3 (SiOCq), 46.7 (NCH₂), 32.1 (CH₂S), 31.5, 31.44 (9CH₃), 24.7 (CH₂). (v_{max}/cm⁻¹, CCl₄) 2977, 1455, 1390, 1366, 1243, 1206, 1185, 1066, 1026. HRMS (EI) calcd for $C_{21}H_{37}O_3N_3SSi$ 439.2325; found 439.2322.

Compound 1d



See the following reference : B. Quiclet-Sire and S. Z. Zard, Org. Lett., 2013, 15, 5886-5889.

Compound 3d



A solution of xanthate **3d** (1.62 mmol) and olefin **2a** (2 equiv) in ethyl acetate (1.62 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added (10 mol%) and the reaction mixture was heated under reflux for 1h. After evaporation of the solvent, the residue was purified by silica gel column chromatography using a gradient of elution (pentane/ethyl acetate, 10/0 to 8/2) affording the addition product as a colorless oil and in 76% yield. $\delta_H(400 \text{ MHz}, CDCl_3) 8.73$ (d, 1H, J=8.1 Hz, CHAr), 8.08 (d, 1H, J=4.5 Hz, CHAr), 7.65 (brs, 1H, NH), 7.23 (dd, 1H, J=4.7 Hz, J=8.0 Hz, CHAr), 5.76 (m, 1H, CHO), 3.20 (dd, 1H, J=4.3 Hz, J=7.6 Hz, CHS), 2.66 (m, 2H, CH₂CO), 2.38 (m, 1H, CHHCHS), 2.04 (m, 1H, CHHCH), 1.36 (brs, 33H, CH(CH₃)₂, 9CH₃). $\delta_C(100 \text{ MHz}, CDCl_3) 216.4$ (CS), 172.0 (NCO), 143.7, 143.5 (CHAr), 139.7 (CqAr), 132.1 (CqAr), 129.1, 129.0 (CHAr), 123.4 (CHAr), 78.2, 78.1 (CHO), 74.0 (SiOCq), 36.2 (CHS), 35.3 (CH₂CO), 31.8 (9CH₃), 27.5 (CH₂), 21.5, 21.5, 21.3 (2CH₃). (v_{max}/cm^{-1} , CCl₄) 3421 (NH), 1709 (NHCO), 1227 (COS), 1074 (CS). HRMS (EI) calcd for (M-C₄H₁₀O) $C_{21}H_{33}N_2O_4S_2CISi$ 504.1340; found 504.1338.

Compounds 4d and 5d



First approach :

A mixture of xanthate 3d (0.610 g, 1.055 mmol) and diphenyl ether (5 mL) was heated at 200°C under nitrogen until total consumption of the starting material. Two fractions were isolated after chromatography on a silica gel column using a gradient of elution (pentane/ ethyl acetate, 10/0 to 6/4). The first fraction was isolated as a colorless oil and corresponds to thiolactone 12 (0.143 g, 39%) and the second one is composed of 0.280 g of a mixture of the thiol derivative 4d and 2-chloro-3-aminopyridine 13. This mixture was heated under reflux of chlorobenzene and 3-4 drops of di-tert-butylperoxide were added under nitrogen. The reaction mixture was filtered on a silica gel column (pentane/ ethyl acetate 10/0 to 7/3) to yield the rearranged product as an oil in 55% yield and 2-chloro-3-aminopyridine **13** in 41% yield.

Second approach :

The xanthate **3d** (0.3 g, 0.5 mmol) in a degased solution of 1:1 mixture of diethyl ether-ethanol (1 mL) was added ethylenediamine (0.14 mL, 4 equiv). After consumption of the starting xanthate, the reaction mixture was diluted with diethyl ether and neutralised with aqueous citric acid solution, the organic phase washed with brine and dried over $MgSO_4$ and the resulting organic phase was evaporated under reduced pressure to yield thiol **4d**. This latter was taken up in chlorobenzene (5 mL) and refluxed under nitrogen in the presence of di-tert-butyl peroxide (3-4 drops). After concentration of the solvent and purification on a silica gel column (petroleum ether/ ethyl acetate 10/0 to 8/2), the rearranged product **5d** was isolated as an oil in 74% yield over 2 steps.

Compound 5d

 $δ_{H}(400 \text{ MHz}, \text{CDCI}_{3})$ 8.71 (d, 1H, J=8.1 Hz, CHAr), 8.06 (dd, 1H, J=1.8 Hz, J=4.7 Hz, CHAr), 7.74 (brs, 1H, NH), 7.22 (dd, 1H, J=4.7 Hz, J=8.1 Hz, CHAr), 2.69 (t, 2H, J=6.7 Hz, CH₂CO), 2.61 (t, 1H, J=7.4 Hz, CH₂S), 2.07 (m, 1H, CH₂), 1.31 (s, 27H, 9CH₃). $δ_{C}(100 \text{ MHz}, \text{CDCI}_{3})$ 171.5 (NHCO), 143.7 (CHAr), 139.7 (CqAr), 132.0 (CqAr), 129.0 (CHAr), 123.3 (CHAr), 74.2 (Si(OCMe)_3), 36.4 (CH₂CO), 31.5 (9CH₃), 27.4, 27.0 (2CH₂). (v_{max} /cm⁻¹, CCI₄) 3420, 2977, 1709, 1583, 1503, 1454, 1389, 1365, 1297, 1243, 1206, 1185, 1066, 1026. HRMS (EI) calcd for $C_{21}H_{37}CIO_4N_2SSi$ 476.1932; found 476.1929.

Compound 12 and 13



Compound 12 $\delta_{H}(400 \text{ MHz}, \text{CDCl}_{3})$ 2.97 (dd, 1H, J=5.2 Hz, J=11.2 Hz), 2.58 (m, 1H), 2.46 (m, 1H), 2.33 (m, 1H), 2.17 (m, 1H), 1.33 (s, 27H, 9CH_3). $\delta_{C}(100 \text{ MHz}, \text{CDCl}_{3})$ 212.1 (CO), 73.6 (SiOCMe₃), 42.8 (CHS), 35.9 (CH₂CO), 31.8 (9CH₃), 28.2 (CH₂). (v_{max}/cm^{-1} , CCl₄) 1705 (SCO). HRMS (EI) calcd for C₁₆H₃₂O₄SSi 348.1791 ; found 348.1797.

Compound 13 δ_H(400 MHz, CDCl₃) 7.75 (dd, 1H, J=2.4 Hz, J=3.8 Hz, CHAr), 7.01 (m, 2H, 2CHAr), 4.05 (brs, 2H, NH₂). Ref : Zhang, T.Y. ; Stout, J.R. ; Keay, J.G. ; Striven, E.F.V. ; Toomey, J. E. ; Goe, G. Tetrahedron, 1995, **51**, 13177-13184.

Compound 1c'



See the following reference : A. R. Katritzky, M. A. C. Button and S. N. Denisenko, *Heterocyl.*, 2001, **54**, 301.

Compound 3c'



A solution of xanthate 1c' (0.506 g, 2 mmol) and olefin 2a (4 mmol) in ethyl acetate (1 mL) was refluxed under nitrogen for 10 min. Then dilauroyl peroxide (DLP) was added portion-wise (2x10 mol%) every hour. After cooling the reaction mixture, the crystals were filtered to give the pure xanthate as a white in 52% yield. Mp 104-105°C. δ_{H} (400 MHz, CDCl₃) 8.06 (d, 1H, J=8.4 Hz, CHAr), 7.57 (d, 1H, J=8.3 Hz, CHAr), 7.47 (t, 1H, J=7.6 Hz, CHAr), 7.36 (m, 1H, CHAr), 4.84 (dd, 1H, J=7.2 Hz, J=9.1 Hz, NCH₂), 4.66 (m, 1H, OCHHCH₃), 4.55 (m, 1H, OCHHCH₃), 3.20 (dd, 1H, J=4.9 Hz, J=7.1 Hz, CHS), 2.62 (m, 1H, CHHCHS), 2.31 (m, 1H, CHHCHS), 1.36 (br, 30H, 9CH₃, OCH₂CH₃). δ_C (100 MHz, CDCl₃) 216.3 (CS), 145.9 (CqAr), 133.0 (CqAr), 127.0 (CHAr), 123.8 (CHAr), 120.0, 119.9 (CHAr), 109.6, 109.5 (CHAr), 74.3 (SiOCq), 70.4 (OCH₂CH₃), 46.8 (NCH₂), 33.3 (CHS), 31.8 (CH₂CHS, 9CH₃), 13.8 (OCH₂CH₃). (v_{max}/cm^{-1} , CCl₄) 1219 (CO), 1066 (CS). HRMS (EI) calcd for C₂₄H₄₁O₄N₃S₂Si 527.2308;found 527.2298.

Compound 4c



Xanthate 3c' (0.3 g, 0.5 mmol) in a degased solution of 1:1 mixture of diethyl ether-ethanol (2 mL) was added ethylenediamine (0.18 mL, 4 equiv). After consumption of the starting xanthate, the reaction mixture was diluted with diethyl ether and neutralised with aqueous citric acid solution, the organic phase was washed with brine and dried over MgSO₄ and the resulting organic phase

was evaporated under reduced pressure to yield thiol 4c as a solid in 76% yield after chromatography on a silica gel column (pentane/ethyl acetate; 10/0 to 9/1). Mp 73-74°C. δ_H(400 MHz, CDCl₃) 8.05 (d, 1H, J=8.4 Hz, (CHAr), 7.63 (d, 1H, J=8.3 Hz, (CHAr), 7.48 (t, 1H, J=7.6 Hz, (CHAr), 7.35 (m, 1H, (CHAr), 4.96 (m, 1H, NCHH), 4.86 (m, 1H, NCHH), 2.62 (m, 1H, CHS), 2.00 (m, 1H, CHH), 1.65 (d, 1H, J=10.1 Hz, SH), 1.53 (dt, 1H, J=2.6 Hz, J=10.6 Hz, CHH), 1.28 (s, 27H, 9CH₃). $\delta_c(100 \text{ MHz}, \text{ CDCl}_3)$ 145.9 (CqAr), 133.2 (CqAr), 127.2 (CHAr), 123.8 (CHAr), 120.0, 119.9 (CHAr), 109.6, 109.5 (CHAr), 73.5 (3SiOCq), 46.3 (NCH₂), 34.8 (CHS), 31.7 (9CH₃), 21.2 (CH₂). (v_{max} /cm⁻¹, CCl₄) 2976, 2930, 1455, 1389, 1365, 1242, 1208, 1187, 1060, 1026. HRMS (EI) calcd for C₂₁H₃₇O₃N₃SSi 439.2325 ; found 439.2321.

Compound 5c from thiol 4c



The thiol **4c** (0.178 g, 0.4 mmol) in chlorobenzene (4 mL) was refluxed under nitrogen for 10 min and then di-tert-butylperoxide (3-4 drops) was added. After removal of the solvent under a nitrogen stream, the rearranged product **5c** was isolated as a yellow oil in quantitative yield. See data above.

Compound 3e



See the following reference : B. Quiclet-Sire and S. Z. Zard, *Org. Lett.*, 2013, **15**, 5886-5889.

Compound 5e



Xanthate **3e** (0.34 g, 0.6 mmol) in a degased solution of 1:1 mixture of diethyl ether-ethanol (0.6 mL) was added ethylenediamine (0.16 mL, 4 equiv). After consumption of the starting xanthate, the reaction mixture was diluted with

diethyl ether and neutralised with aqueous citric acid solution, the organic phase was washed with brine and dried over MgSO₄ and the resulting organic phase was evaporated under reduced pressure to yield the corresponding thiol. This latter was taken up in chlorobenzene (5 mL) and refluxed under nitrogen in the presence of di-tert-butyl peroxide (3-4 drops). After concentration of the solvent and purification on a silica gel column (petroleum ether/ ethyl acetate 10/0 to 9/1), the rearranged product **5e** was isolated as an oil in 36% yield over 2 steps. $\delta_{\rm H}(400 \text{ MHz}, \text{CDCl}_3)$ 7.15 (m, 4H, 4CHAr), 3.79 (t, 2H, J=6.6 Hz, CH₂), 2.72 (t, 2H, J=6.6 Hz, CH₂), 2.63 (m, 4H, 2CH₂), 1.99 (m, 4H, 2CH₂), 1.32 (s, 27H, 9CH₃). $\delta_{\rm C}(100 \text{ MHz}, \text{CDCl}_3)$ 172.5 (NCO), 139.3 (br, CqAr), 128.5, 126.1, 125.1, 124.8 (4CHAr), 74.1 (Si(OCq)₃), 43.1 (m, CH₂), 33.4 (CH₂), 31.5,(9CH₃), 28.2, 27.4, 26.9, 24.2 (4CH₂). (v_{max} /cm⁻¹, CCl₄) 2976, 1656 (NCO), 1492, 1389, 1365, 1241, 1186, 1063. HRMS (EI) calcd for C₂₅H₄₃O₄NSSi 481.2682; found 481.2691.

Compound 3f

See the following reference : B. Quiclet-Sire and S. Z. Zard, *Org. Lett.,* 2013, **15**, 5886-5889.

Compound 5f

∽^S_Si(O*t*Bu)₃

Xanthate 3f (0.28 g, 0.58 mmol) in a degased solution of 1:1 mixture of diethyl ether-ethanol (1.2 mL) was added ethylenediamine (0.16 mL, 4 equiv). After consumption of the starting xanthate, the reaction mixture was diluted with diethyl ether and neutralised with aqueous citric acid solution, the organic phase was washed with brine and dried over MgSO₄ and the resulting organic phase was evaporated under reduced pressure to yield the corresponding thiol. This latter was taken up in chlorobenzene (2 mL) and refluxed under nitrogen in the presence of di-tert-butyl peroxide (3-4 drops). After concentration of the solvent and purification on a silica gel column (petroleum ether/ diethyl ether 10/0 to 95/5), the rearranged product **5f** was isolated as an oil in 84% yield over 2 steps. δ_H(400 MHz, CDCl₃) 2.70 (t, 2H, J=7.4 Hz, CH₂), 2.62 (t, 2H, J=6.9 Hz, CH₂), 1.94 (m, 3H, CH₂, CHCO), 1.34 (s, 27H, 9CH₃), 1.00 (m, 2H, CH₂), 0.85 (m, 2H, CH₂). $\delta_c(100 \text{ MHz}, \text{CDCl}_3)$ 210.7 (CO), 74.1 (Si(OCq)₃), 42.2 (CH₂CO), 31.5 $(9CH_3)$, 27.3 (CH_2) , 26.3 (CH_2) , 20.5 (CHCO), 10.7 $(2CH_2)$. $(v_{max}/cm^{-1}, CCl_4)$ 1702 (CO), 1471, 1459, 1242, 1186, 1066. HRMS (EI) calcd for C₁₉H₃₈O₄SSi 390.2260; found 390.2267.

Compound 3g

See the following reference : B. Quiclet-Sire and S. Z. Zard, *Org. Lett.*, 2013, **15**, 5886-5889.

Compound 5g

$$\underbrace{\overset{O}{\underset{H}{\overset{}}}}_{H} \overset{CF_{3}}{\underset{S}{\overset{}}} Si(OtBu)_{3}$$

Xanthate **3g** (0.14 g, 0.26 mmol) in a degased solution of 1:1 mixture of diethyl ether-ethanol (0.5 mL) was added ethylenediamine (0.07 mL, 4 equiv). After consumption of the starting xanthate, the reaction mixture was diluted with diethyl ether and neutralised with aqueous citric acid solution, the organic phase was washed with brine and dried over MgSO₄ and the resulting organic phase was evaporated under reduced pressure to yield the corresponding thiol 4d. This latter was taken up in chlorobenzene (2.6 mL) and refluxed under nitrogen in the presence of di-tert-butyl peroxide (3-4 drops). After concentration of the solvent and purification on a silica gel column (petroleum ether/ diethyl ether 10/0 to 7/3), the rearranged product **5g** was isolated as an oil in 78% yield over 2 steps. Mp 79-81°C. δ_H(400 MHz, CDCl₃) 6.22 (d, 1H, J=9.4 Hz, NH), 4.68 (m, 1H, CHCF₃), 2.63 (†, 2H, J=7.5 Hz, CH₂S), 2.20 (m, 1H, CHCHCF₃), 2.03 (s, 3H, COCH₃), 1.87 (m, 1H, , CHHCHCF₃), 1.33 (s, 27H, 9CH₃). δ_c(100 MHz, CDCl₃) 170.4 (CO), 125.1 (q, J=281.7 Hz, CF₃), 74.5 (Si(OCq)₃), 50.2 (q, 1H, J=30.4 Hz, $CHCF_3$), 31.51 (9 CH_3), 31.47 (CH_2S), 23.5, 23.1 (CH_2CHCF_3 , CH_3CO). (v_{max}/cm^{-1} , CCl₄) 3447 (NH), 1704 (NHCO), 1505, 1390, 1366, 1242, 1187, 1067, 1026. HRMS (EI) calcd for C₁₈H₃₆O₄NSSiF₃ 447.2086; found 447.2086.

NMR Spectra





S16























Compound 5b



Compound 1c



Compound 3c



Compound 5c





S27





Compound 12







1.322

1.0

24.250 26.912 27.390 27.390 31.537 33.399

Т

0.0





Compound 5f



