Supporting Information

Facile Barton–McCombie Deoxygenation of Alcohols with Tetrabutylammonium Peroxydisulfate and Formate Ion

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General Information. For the thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (Merck No. 5715; silica gel 60 F₂₅₄) were used. Visualization was accomplished with UV light (254 nm), typical TLC indicating solution (*p*-anisaldehyde/sulfuric acid/ethanol/acetic acid mixture), iodine, and/or phosphomolibdic acid solution. Column chromatography was performed on Silica gel 60 (0.040–0.063 mm, Merck). Melting points were taken on an Electrothermal melting point apparatus (Electrothermal Engineering Ltd) and are uncorrected. Optical rotations were taken on an Autopol III automatic polarimeter. NMR spectra were recorded on 300.4 MHz and 75.5 MHz spectrometers for ¹H and for ¹³C, respectively. The chemical shifts are reported δ unit, parts per million (ppm) relative to deteriorated solvents or Me₄Si. Splitting pattern of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), dq (doublet of quartets) and br (broadened). Coupling constant (*J* value) was reported in Hz unit. Infrared spectra were taken on a Bomen MB-100 FT-IR spectrophotometer. The low and high resolution mass spectra were recorded on a VG Autospec Ultima spectrometer or a JMS-HX110/110A Flight Resolution Tandem Mass spectrometer. HPLC data were obtained with Shimadzu 10A VP HPLC System, using a Shimadzu SPD-M10AVP diode array detector (227 nm) and a Capcell Pak C18 UG80 (4.6 × 250 mm, 5 μ m) column (Shiseido, Tokyo, Japan). The column temperature is maintained at 28 °C. Starting materials: 1-tetradecanol, 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose, (+)-dihydrocholesterol, 1-adamantanol, 1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose, 1,2-*O*-isopropylidene- α -D-xylofuranose, benzhydrol, 4-nitrophenethyl alcohol, and 1,2:5,6-Di-*O*-isopropylidene-D-mannitol were commercially available and used without further purification. Compounds ethoxymethyl 3,23-*O*-isopropylidene asiatic acid,¹ 7 α -acetyl-6,14-*endo*-ethanotetrahydrothebaine,² **11a**,³ and **12a**⁴ were prepared as described in the literature. All other chemicals were obtained commercially.

General Procedure A: Method for the Preparation of *S*-Methyl Xanthates **5a, **6a**, **7a**, **8a**, **9b**, **10b**, **11b**, **13**, **15a**, **15b**, and **17** from the Corresponding Alcohols.**⁵ The alcohol (0.3 mmol) in dry tetrahydrofuran (2 mL) was added at 0 °C under argon to a stirred suspension of sodium hydride (60% w/w in mineral oil, 30 mg, 0.75 mmol) and imidazole (1 mg, 0.015 mmol) in tetrahydrofuran (3 mL). The mixture was stirred at room temperature for 0.5 h and then carbondisulfide (45 μ L, 57 mg, 0.75 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then iodomethane (47 μ L, 106 mg, 0.75 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then quenched with acetic acid (57 μ L, 60 mg, 1 mmol) in water (10 mL). The reaction mixture was extracted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the crude product was purified by flash column chromatography on silica gel using gradient elution of 5 to 15% EtOAc in hexane to give the corresponding *S*-methyl xanthate.

General Procedure B: Deoxygenation Procedure to Obtain Compounds **5b, **6b**, **7b**, **8b**, **9c**, **10e**, **11c**, **12d**, **14**, **16a**, **16b** and **18** by (Bu₄N)₂S₂O₈/HCO₂Na.** A mixture of thiocarbonyl derivative (0.2 mmol), HCO₂Na (82 mg, 1.2 mmol), (Bu₄N)₂S₂O₈ (406 mg, 0.6 mmol), and DMF (4 mL) was stirred at 65 °C for 15 min. The mixture was then poured into water (10 mL) and the whole was extracted with CH₂Cl₂ (10 mL). The extract was washed with aqueous NaHCO₃ (10 mL) and brine (10 mL) and dried over Na₂SO₄. The solvent was removed by evaporation and the crude product was purified by flash column chromatography on silica gel using gradient elution of 5 to 15% EtOAc in hexane to give deoxy product. Similar procedures were employed for the preparation of deoxy products and the detailed reaction conditions were listed in Table 1 and Table 2.

Ethoxymethyl 3,23-*O*-isopropylidene-2-*O*-(methylthio)thiocarbonyl]asiatic acid (1).¹ Compound ethoxymethyl 3,23-*O*-isopropylidene asiatic acid¹ (29.3 g, 50 mmol) in dry tetrahydrofuran (200 mL) was added at 0 °C under argon to a stirred suspension of sodium hydride (60% w/w in mineral oil, 3 g, 75 mmol) and imidazole (100 mg, 1.5 mmol) in tetrahydrofuran (300 mL). The mixture was stirred at room temperature for 0.5 h and then carbondisulfide (4.5 mL, 5.7 g, 75 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then iodomethane (4.7 mL, 10.6 g, 75 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then quenched with acetic acid (5.7 mL, 6 g, 100 mmol) in water (1 L). The reaction mixture was extracted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the residue was chromatographed on silica gel eluted with 15% EtOAc in hexane to give **1** (28.75 g, 85%) as a white powder: *R*_f = 0.77 (EtOAc/hexane/EtOH 1/2/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 5.78–5.69 (td, *J* = 10.2, 4.2 Hz, 1H), 5.27–5.20 (m, 1H), 5.19 (s, 2H), 3.78–3.75 (d, *J* = 10.5 Hz, 1H), 3.66–3.59 (q, *J* = 6.9 Hz, 2H), 3.54–3.46 (dd, *J* = 14.4, 11.1 Hz, 2H), 2.47 (s, 3H), 2.43–2.35 (m, 1H), 2.24–2.20 (d, *J* = 11.1 Hz, 1H), 1.98–0.75 (m, 19H), 1.41 (s, 3H), 1.37 (s, 3H), 1.21–1.16 (t, *J* = 6.9 Hz, 3H), 1.11 (s, 3H), 1.07–1.06 (d, *J* = 1.8 Hz, 6H), 0.92 (s, 3H), 0.82–0.80 (d, *J* = 6.3 Hz, 3H), 0.73 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 215.0, 176.9, 138.1, 125.0, 99.4, 89.2, 78.8, 78.6, 72.6, 65.8, 52.6, 51.1, 48.1, 47.5, 43.6, 42.1, 39.6, 39.0, 38.7, 38.6, 37.8, 36.4, 32.4, 30.6, 29.7, 27.8, 24.0, 23.5, 23.2, 21.1, 19.1, 18.5, 17.4, 17.3, 16.8 (2C), 15.0, 13.6.

2-*O*-(Methylthio)thiocarbonyl]asiatic acid (3). To a solution of **1** (6.77 g, 10 mmol) in methanol (200 mL) was added 1N HCl solution (20 mL). After refluxing for 2 h, the reaction mixture was concentrated. Purification of the residue by recrystallization with methanol provided 5.56 g (96%) of the title compound as a white crystalline solid: mp 207–209 °C (methanol); *R*_f = 0.59 (EtOAc/hexane/EtOH 1/1/0.1); [α]_D = –36.7 (*c* 1.0, CHCl₃, 25 °C); ¹H NMR (300.4 MHz, DMSO-*d*₆) δ 5.69 (td, *J* = 10.2, 4.2 Hz, 1H), 5.10 (s, 1H), 4.91 (d, *J* = 5.4 Hz, 1H), 4.63 (s, 1H), 3.75 (dd, *J* = 9.9, 5.1 Hz, 1H), 3.31 (d, *J* = 10.5 Hz, 1H), 3.10 (d, *J* = 10.2 Hz, 1H), 2.52 (s, 3H), 2.11 (m, 2H), 2.00–1.70 (m, 4H), 1.65–1.15 (m, 12H), 1.10–0.70 (m, 19H), 0.59 (s, 3H); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 214.9, 178.4, 138.3, 124.4, 84.3, 71.2, 63.4, 52.5, 46.9, 46.8, 45.8, 43.7, 42.2, 41.9, 39.2, 38.6, 38.5, 37.9, 36.4, 32.1, 30.3, 27.6, 23.9, 23.4, 23.1, 21.2, 17.9, 17.5, 17.1, 17.0, 16.6, 13.8; IR (KBr, cm^{–1}) 3474 (br), 2924 (s), 1689 (s), 1454 (m), 1393 (w), 1223 (s), 1191 (m), 1050 (s); HRMS (EI) calcd for C₃₂H₅₀O₅S₂ (M⁺) 578.3100, found *m/z* 578.3103.

2-Deoxyasiatic acid (4):¹

Method 1. Deoxygenation Using Barton–McCombie Procedure. Compound **3** (1.16 g, 2 mmol) and AIBN (131 mg, 0.8 mmol) were dissolved in dry toluene (25 mL) and degassed by passing argon through the solution with stirring (15 min). Bu₃SnH (2.2 mL, 2.42 g, 8.3 mmol) was added. The reaction mixture was stirred for 4 h at 105 °C. The mixture was cooled to room temperature, and then poured with vigorous stirring into a 1.5 N NaOH solution (50 mL). The precipitated solid was collected, and the solid dissolved in methanol (10 mL). The solution was neutralized with conc. HCl, and filtered to remove NaCl. The filtrate was concentrated in vacuo, and the residue was recrystallized from methanol to give **4** (0.72 g) in 76% yield as a white crystalline solid.

Method 2. Deoxygenation Using Diphenylsilane and AIBN.⁶ A solution of AIBN (197 mg, 1.2 mmol) in dry toluene (5 mL) was added five times over 1 h (12 min intervals) to a solution of xanthate **1** (2.03 g, 3 mmol) and diphenylsilane (1.19 mL, 1.11 g, 6 mmol) in dry toluene (5 mL) at refluxing temperature under argon. Then, the solution was stirred for 30 min at the same temperature and concentrated under reduced pressure. Without isolation of ethoxymethyl 2-deoxy-2,23-*O*-isopropylideneasiatic acid (**2**), the residue dissolved in methanol (8 mL). Then conc. HCl (2 mL) was added to deprotect the alcohol and acid function of **2**. The mixture heated at reflux for 2 h, and cooled to room temperature. To the mixture was added water (2 mL). The precipitated solid was collected, and then added with vigorous stirring into 6 N NaOH solution (2 mL). The precipitated solid was filtered off, and the filtrate was neutralized with conc. HCl to pH 5–6. Then, the resulting white precipitate was filtered and washed with water (4 × 25

mL). The solid residue was recrystallized from methanol to give **4** (993 mg) in 70% yield as a white crystalline solid.

Method 3. Deoxygenation Using (Bu₄N)₂S₂O₈ and HCO₂Na. A mixture of xanthate **3** (5.79 g, 10 mmol), HCO₂Na (4.08 g, 60 mmol), (Bu₄N)₂S₂O₈ (20.31 g, 30 mmol), and DMF (150 mL) was stirred at 50 °C for 2 h. The mixture was then poured into water (400 mL) and the whole was extracted with CH₂Cl₂ (300 mL). The extract was washed with water (400 mL) and dried over Na₂SO₄. The solvent was removed by evaporation and the residue was recrystallized from methanol to give deoxy product **4** (4.49 g) in 95% yield as a white crystalline solid: mp 272–274 °C (methanol) [lit.⁷ mp 264–265 °C (methanol)]; *R_f* = 0.21 (EtOAc/hexane/EtOH 1/2/0.1); [α]_D = 84.5 (*c* 1.00, DMF, 20 °C) [lit.⁷ [α]_D = 64 (*c* 0.27, methanol, 25 °C)]; ¹H NMR (300.4 MHz, DMSO-*d*₆) δ 14.5–13.2 (br s, 1H), 5.14–5.12 (m, 1H), 3.48–3.41 (dd, *J* = 10.8, 5.1 Hz, 1H), 2.84–2.81 (d, *J* = 10.8 Hz, 1H), 2.61–2.57 (d, *J* = 10.2 Hz, 1H), 1.51–1.48 (d, *J* = 10.8 Hz, 1H), 1.45–1.16 (m, 4H), 1.02–0.85 (m, 7H), 0.82–0.57 (m, 5H), 0.46–0.42 (m, 4H), 0.36–1.16 (m, 8H), 0.19–0.14 (m, 6H); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 178.5, 138.5, 124.9, 70.6, 64.8, 52.6, 47.3, 47.1, 46.7, 42.1, 41.9, 39.3, 38.7 (2C), 38.3, 36.6, 36.5, 32.5, 30.4, 27.8, 26.8, 24.1, 23.6, 23.1, 21.3, 17.7, 17.3, 17.2, 15.8, 12.9; IR (KBr, cm⁻¹) 3414 (br), 2926 (s), 1695 (s), 1454 (m), 1389 (w), 1233 (s), 1191 (m), 1045 (s), 662 (w).

S-Methyl O-tetradecyl xanthate (5a).⁸ Procedure A; 95% yield; oil; ¹H NMR (300.4 MHz, DMF-*d*₇) δ 4.66–4.61 (t, *J* = 6.3 Hz, 2H), 2.61 (s, 3H), 1.81 (pentet, *J* = 6.6 Hz, 2H), 1.50–1.25 (m, 22H), 0.89–0.85 (t, *J* = 6.9 Hz, 3H); *m/z* 304 (M⁺, 8%), 271 (59), 257 (50), 244 (67), 229 (59), 196 (92), 109(95) and 56 (100).

Tetradecane (5b).⁵ Procedure B; 100% yield; oil; ¹H NMR (300.4 MHz, CDCl₃) δ 1.32–1.21 (br s, 24H), 0.87–0.82 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 32.0, 29.8, 29.7, 29.4, 22.7, 14.1.

1,2:3,4-Di-O-isopropylidene-3-O-[(methylthio)thiocarbonyl]- α -D-galactopyranose (6a). Procedure A; 98% yield; oil; *R_f* = 0.48 (EtOAc/hexane/EtOH 1/5/0.1); [α]_D = –58.7 (*c* 1.00, CHCl₃, 19 °C) [lit.⁹ [α]_D = –63.1 (*c* 1.51, CHCl₃, 20 °C)]; ¹H NMR (300.4 MHz, CDCl₃) δ 5.56–5.54 (d, *J* = 5.1 Hz, 1H), 4.87–4.81 (dd, *J* = 11.7, 4.5 Hz, 1H), 4.71–4.62 (m, 2H), 4.35–4.33 (m, 1H), 4.30–4.22 (m, 2H), 2.56 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 215.70, 109.7, 108.9, 96.3, 71.9, 71.0, 70.7, 70.4, 65.6, 26.0, 25.9, 24.9, 24.4, 19.0.

6-Deoxy-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (6b).¹⁰ Procedure B; 86% yield; oil; *R_f* = 0.40 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 5.53–5.52 (d, *J* = 4.8 Hz, 1H), 4.60–4.58 (d, *J* = 7.8 Hz, 1H), 4.30–4.29 (m, 1H), 4.10–4.07 (d, *J* = 8.1 Hz, 1H), 3.95–3.89 (q, *J* = 6.6 Hz, 1H), 1.53 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.27–1.25 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 109.0, 108.3, 96.6, 73.5, 70.9, 70.4, 63.5, 26.0 (2C), 24.9, 24.4, 15.9.

O-Cholestanyl S-methyl xanthate (7a).¹¹ Procedure A; 92% yield; a white solid; *R_f* = 0.48 (hexane); ¹H NMR (300.4 MHz, CDCl₃) δ 5.53–5.42 (septet, *J* = 5.4 Hz, 1H), 2.51 (s, 3H), 2.03–0.78 (m, 31H), 0.89–0.87 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 1.2 Hz, 3H), 0.83 (s, 6H), 0.63 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 215.2, 83.6, 56.4, 56.2, 54.1, 44.6, 42.6, 39.9, 39.5, 36.6, 36.1, 35.8, 35.5, 35.4, 33.2, 31.9, 28.6, 28.2, 28.0, 26.8, 24.2, 23.8, 22.8, 22.5, 21.2, 18.8, 18.6, 12.2, 12.0.

5 α -Cholestane (7b).⁵ Procedure B; 96% yield; white crystals; *R_f* = 0.90 (hexane); ¹H NMR (300.4 MHz, CDCl₃) δ 1.97–1.90 (dt, *J* = 12.0, 2.4 Hz, 1H), 1.85–0.61 (m, 32H), 0.89–0.87 (d, *J* = 6.6 Hz, 3H), 0.86–0.85 (d, *J* = 1.5 Hz, 3H), 0.84–0.83 (d, *J* = 1.5 Hz, 3H), 0.76 (s, 3H), 0.63 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 56.6, 56.3, 54.7, 47.0, 42.6, 40.1, 39.5, 38.7, 36.2, 36.1, 35.8, 35.5, 32.2, 29.1, 29.0, 28.2, 28.0, 26.8, 24.2, 23.8, 22.8, 22.5, 22.2, 20.8, 18.6, 12.2, 12.1.

O-Adamantanyl S-methyl xanthate (8a).¹² Procedure A; 100% yield; white crystals; *R_f* = 0.49 (hexane); ¹H NMR (300.4 MHz, CDCl₃) δ 2.49–2.43 (m, 9H), 2.24 (br s, 3H), 1.73–1.64 (br s, 6H); *m/z* 242 (M⁺, 47%), 231 (14), 182 (6), 135 (100), 107 (6), 93 (14), and 79 (20).

Adamantane (8b).⁵ Procedure B; 100% yield; white crystals; R_f = 0.92 (hexane); ^1H NMR (300.4 MHz, CDCl_3) δ 1.94–1.79 (br s, 4H), 1.80–1.72 (br s, 12H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 37.7, 28.3.

6,14-endo-Ethano-7 α -(1-(*R*)-hydroxyethyl)tetrahydrothebaine (9a). To a solution of 7 α -acetyl-6,14-endo-ethanotetrahydrothebaine² (383 mg, 1 mmol) in THF (20 mL) was added dropwise DIBAL-H (2.5 mmol; 1 mol/L toluene solution) at -78°C under argon. After stirring for 3 h at the temperature, the solution was neutralized with 10% HCl solution. The reaction mixture was extracted with CH_2Cl_2 and washed with saturated brine. The organic phase was dried over Na_2SO_4 . After evaporation of the solvent, the residual oil was chromatographed on silica gel eluted with 50% EtOAc in hexane to give **9a** (366 mg) in 95% yield: prisms; mp 79–81 $^\circ\text{C}$ [lit.¹³ mp 49–51 $^\circ\text{C}$ (aqueous methanol)]; R_f = 0.15 (EtOAc/hexane/EtOH 1/1/0.1); $[\alpha]_{\text{D}} = -101$ (c 1.00, methanol, 19 $^\circ\text{C}$); ^1H NMR (300.4 MHz, CDCl_3) δ 6.72 (d, J = 8.1 Hz, 1H), 6.58 (d, J = 8.1 Hz, 1H), 5.28 (s, 1H), 4.48 (s, 1H), 3.99–3.94 (m, 1H), 3.87 (d, 3H), 3.52 (d, 3H), 3.11 (d, J = 18.3 Hz, 1H), 2.77 (m, 1H), 2.64 (d, J = 6.3 Hz, 1H), 2.46 (dd, J = 11.8, 5.1 Hz, 1H), 2.34–2.19 (m, 5H), 2.11–2.00 (m, 1H), 1.76–1.55 (m, 4H), 1.28–1.21 (m, 3H), 1.07–0.88 (m, 2H), 0.79–0.71 (m, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 146.5, 141.6, 132.3, 128.3, 119.0, 113.8, 94.2, 79.7, 69.9, 61.2, 56.6, 52.1, 45.1, 44.9, 43.4, 42.7, 35.2, 34.9, 32.2, 29.0, 21.7, 21.0, 17.7; IR (liquid film, cm^{-1}) 3445 (br), 2932 (br), 1633 (s), 1601 (s), 1504 (s); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_4$ (M^+) 385.2253, found m/z 385.2256.

6,14-endo-Ethano-7 α -{1-(*R*)-*O*-[(methylthio)thiocarbonyl]ethyl}tetrahydrothebaine (9b). Procedure A; 95% yield; white crystalline solid; mp 176–178 $^\circ\text{C}$ (hexane); R_f = 0.45 (EtOAc/hexane/EtOH 1/1/0.1); $[\alpha]_{\text{D}} = -96$ (c 1.0, CHCl_3 , 19 $^\circ\text{C}$); ^1H NMR (300.4 MHz, CDCl_3) δ 6.71 (d, J = 8.1 Hz, 1H), 6.59 (d, J = 8.1 Hz, 1H), 6.10 (pentet, J = 6.0 Hz, 1H), 4.54 (s, 1H), 3.87 (s, 3H), 3.46 (s, 3H), 3.12 (d, J = 18.3 Hz, 1H), 2.78–2.70 (m, 2H), 2.57 (s, 3H), 2.53–2.44 (m, 2H), 2.33–2.23 (m, 5H), 2.03 (td, J = 12.0, 6.0 Hz, 1H), 1.71–1.34 (m, 7H), 1.05 (td, J = 12.9, 6.6 Hz, 1H), 0.78 (t, J = 12.3 Hz, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 215.1, 147.0, 141.8, 132.4, 128.5, 119.1, 113.8, 91.3, 81.0, 76.3, 61.5, 56.6, 51.2, 45.3, 44.9, 43.5, 37.9, 35.6, 35.5, 29.5, 29.4, 21.9, 20.5, 19.0, 16.8; IR (KBr, cm^{-1}) 2828 (br), 1602 (s), 1629 (s), 1502 (s), 1453 (s), 1227 (s), 999 (s), 957 (s), 788(m); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{33}\text{NO}_4\text{S}_2$ (M^+) 475.1851, found m/z 475.1844.

6,14-endo-Ethano-7 α -ethyltetrahydrothebaine (9c).¹⁴ Procedure B; 95% yield; oil; R_f = 0.40 (EtOAc/hexane/EtOH 1/1/0.1); $[\alpha]_{\text{D}} = -79$ (c 1.0, CHCl_3 , 19 $^\circ\text{C}$); ^1H NMR (300.4 MHz, CDCl_3) δ 6.71 (d, J = 8.1 Hz, 1H), 6.58 (d, J = 8.1 Hz, 1H), 4.51 (s, 1H), 3.87 (s, 3H), 3.34 (s, 3H), 3.12 (d, J = 18.3 Hz, 1H), 2.87 (m, 1H), 2.67 (d, J = 6.6 Hz, 1H), 2.47 (dd, J = 11.7, 5.1 Hz, 1H), 2.37–2.21 (m, 5H), 2.05 (td, J = 12.6, 5.7 Hz, 1H), 1.83–1.73 (m, 1H), 1.70–1.58 (m, 2H), 1.43–1.31 (m, 2H), 1.20–0.95 (m, 6H), 0.79–1.74 (m, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 147.0, 141.8, 132.6, 128.5, 118.8, 113.3, 91.3, 76.5, 61.7, 56.4, 49.9, 45.4, 44.7, 43.6, 36.4, 35.7, 35.3, 34.5, 29.1, 23.1, 21.8, 19.6, 11.9; IR (liquid film, cm^{-1}) 2929 (br), 1501 (s), 1440 (s), 1256 (m), 1152 (m), 1106 (s), 1053 (m); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_3$ (M^+) 369.2304, found m/z 369.2307.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(methylthio)thiocarbonyl]- α -D-glucofuranose (10b).¹⁵ Procedure A; 94% yield; a colorless syrup; R_f = 0.61 (EtOAc/hexane/EtOH 1/5/0.1); ^1H NMR (300.4 MHz, CDCl_3) δ 5.97–5.91 (m, 2H), 4.69–4.68 (d, J = 3.6 Hz, 1H), 4.36–4.27 (m, 2H), 4.13–4.04 (m, 2H), 2.60 (s, 3H), 1.54 (s, 3 H), 1.42 (s, 3H), 1.33 (s, 6 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 214.7, 112.4, 109.3, 105.0, 84.2, 82.7, 79.7, 72.3, 66.9, 26.8, 26.6, 26.2, 25.2, 19.3.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-phenyl carbonothioate- α -D-glucofuranose (10c). Prepared via literature procedure;¹⁶ 94% yield; white crystals; R_f = 0.55 (EtOAc/hexane/EtOH 1/5/0.1); ^1H NMR (300.4 MHz, CDCl_3) δ 7.46–7.40 (t, J = 8.1 Hz, 2H), 7.33–7.29 (t, J = 7.2 Hz, 1H), 7.14–7.10 (d, J = 9.0 Hz, 2H), 5.98–5.96 (d, J = 3.9 Hz, 1H), 5.65–5.64 (d, J = 1.8 Hz, 1H), 4.79–4.78 (d, J = 3.6 Hz, 1H), 4.36–4.31 (m, 2H), 4.15–4.05 (m, 2H), 1.55 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 193.6, 153.2, 129.6, 126.8, 121.7, 112.4, 109.4, 105.0, 85.0, 82.8, 79.6, 72.2, 67.0, 26.9, 26.6, 26.2, 25.3.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-thiocarbonylimidazole- α -D-glucofuranose (10d). To a stirred solution of **10a** (52 mg, 0.2 mmol) in 4 mL of dry DMF were added DMAP (49 mg, 0.4 mmol) and 1,1'-thiocarbonyldiimidazole (107 mg, 0.6 mmol). After the reaction mixture had been stirred for 30 h at 65 °C, it was partitioned between water (5 mL) and EtOAc (5 mL), and the phases were separated. Aqueous layer was extracted with EtOAc (5 mL). The combined organic extracts were washed with aqueous NaHCO₃ followed by brine. The organic extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on silica gel eluted with 20% EtOAc in hexane to give **10d** (62 mg) in 82% yield; oil;¹⁷ R_f = 0.75 (EtOAc/hexane/EtOH 1/1/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 8.33 (s, 1H), 7.61 (s, 1H), 7.07 (s, 1H), 5.96–5.94 (d, J = 3.9 Hz, 1H), 5.84–5.83 (d, J = 2.7 Hz, 1H), 4.77–4.75 (d, J = 3.9 Hz, 1H), 4.36–4.30 (m, 2H), 4.16–4.04 (m, 2H), 1.57 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.29 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 182.4, 136.7, 131.1, 117.8, 112.7, 109.8, 105.0, 84.4, 82.7, 79.7, 72.3, 67.5, 26.9, 26.5, 26.2, 25.0.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene- α -D-ribo-hexofuranose (10e). Procedure B; a colorless syrup;¹⁵ R_f = 0.35 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (CDCl₃) δ 5.83–5.81 (d, J = 6.9 Hz, 1H), 4.77–4.75 (t, J = 6.9 Hz, 1H), 4.20–4.08 (m, 3H), 3.86–3.79 (m, 1H), 2.22–2.16 (dd, J = 13.0, 3.5 Hz, 1H), 1.83–1.73 (m, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 111.3, 109.6, 105.6, 80.4, 78.6, 76.8, 67.1, 35.2, 26.7, 26.4, 26.1, 25.1.

5-*O*-[(1,1-Dimethylethyl)diphenylsilyl]-1,2-*O*-isopropylidene-3-*O*-[(methylthio)thiocarbonyl]- α -D-xylofuranose (11b). The starting material 5-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1,2-*O*-isopropylidene- α -D-xylofuranose **11a**³ was prepared via literature procedures. Compound **11a** was subjected to the procedure A: 92% yield; oil; R_f = 0.59 (EtOAc/hexane/EtOH 1/5/0.1); $[\alpha]_D$ = –28 (c 1.0, CHCl₃, 20 °C); ¹H NMR (300.4 MHz, CDCl₃) δ 7.68–7.62 (m, 4H), 7.43–7.33 (m, 6H), 6.07 (d, J = 3.0 Hz, 1H), 5.91 (d, J = 3.9 Hz, 1H), 4.67 (d, J = 3.9 Hz, 1H), 4.57–4.51 (m, 1H), 3.91–3.87 (m, 2H), 2.50 (s, 3H), 1.64 (s, 3H), 1.32 (s, 3H), 1.02 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃) δ 214.6, 135.4, 132.8, 129.7, 129.6, 127.7, 112.2, 104.8, 83.8, 82.7, 79.0, 60.1, 26.6, 26.2, 19.1, 19.0; IR (liquid film, cm^{–1}) 2931 (m), 2858 (m), 1428 (m), 1202 (s), 1077 (s), 1022 (m), 703 (m); HRMS (EI) calcd for C₂₆H₃₄O₅S₂Si (M⁺) 518.1617, found m/z 518.1572.

3-Deoxy-5-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1,2-*O*-isopropylidene- α -D-xylofuranose (11c).³ Procedure B; colorless crystals; R_f = 0.55 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 7.69–7.65 (m, 4H), 7.43–7.35 (m, 6H), 5.84–5.83 (d, J = 3.6 Hz, 1H), 4.77–4.35 (dd, J = 4.6, 3.6 Hz, 1H), 4.35–4.31 (m, 1H), 3.83–3.73 (m, 2H), 2.10–2.04 (dd, J = 13.2, 4.2 Hz, 1H), 1.92–1.85 (ddd, J = 13.4, 10.3, 4.8 Hz, 1H), 1.51 (s, 3H), 1.33 (s, 3H), 1.05 (s, 9H).

1,2-*O*-Isopropylidene-3-*O*-[(methylthio)thiocarbonyl]- α -D-xylofuranose (12b). 1,2-*O*-Isopropylidene-5-*O*-pivaloyl- α -D-xylofuranoside **12a**⁴ (137 mg, 0.5 mmol) in dry tetrahydrofuran (2 mL) was added at 0 °C under argon to a stirred suspension of sodium hydride (60% w/w in mineral oil, 30 mg, 0.75 mmol) and imidazole (1 mg, 0.015 mmol) in tetrahydrofuran (3 mL). The mixture was stirred at room temperature for 0.5 h and then carbondisulfide (45 μ L, 57 mg, 0.75 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then iodomethane (47 μ L, 106 mg, 0.75 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then quenched with water (10 mL). The reaction mixture was extracted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na₂SO₄. After evaporation of the solvent, the crude product was purified by flash column chromatography on silica gel using gradient elution of 5 to 30% EtOAc in hexane to give deprotected xanthate **12b** (123 mg) in 88% yield: a white powder; mp 88–89 °C (hexane); R_f = 0.60 (EtOAc/hexane/EtOH 2/1/0.1); $[\alpha]_D$ = –16.5 (c 1.0, methanol, 19 °C); ¹H NMR (300.4 MHz, CDCl₃) δ 5.97 (d, J = 3.3 Hz, 1H), 4.98 (dd, J = 11.4, 5.7 Hz, 1H), 4.74 (dd, J = 11.7, 5.7 Hz, 1H), 4.56–4.48 (m, 2H), 4.29 (s, 1H), 2.59 (s, 3H), 2.55–2.42 (m, 1H), 1.52 (s, 3H), 1.33 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 216.3, 112.0, 104.8, 85.1, 77.7, 74.8, 70.2, 26.7, 26.1, 19.3; IR (KBr, cm^{–1}) 3406 (br), 2975 (m), 1385 (m), 1228 (s), 1108 (s), 1065 (s), 864 (m), 791 (m); HRMS (EI) calcd for C₁₀H₁₆O₅S₂ (M⁺) 280.0439, found m/z 280.0384.

1,2-*O*-Isopropylidene- α -D-xylofuranose 3,5-*O*-thionocarbonate (12c). To a stirred solution of 1,2-*O*-isopropylidene- α -D-xylofuranoside (80 mg, 0.5 mmol) in 5 mL of dry CH₃CN were added DMAP (122 mg, 1 mmol) and 1,1'-thiocarbonyldiimidazole (214 mg, 1.2 mmol). After the reaction mixture had been stirred for 24 h at room temperature, it was partitioned between water (10 mL) and EtOAc (10 mL), and the phases were separated. Aqueous layer was extracted with EtOAc (5 mL). The combined organic extracts were washed with water followed by brine. The organic extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on silica gel eluted with 10% EtOAc in hexane to give **12c** (81 mg) in 70% yield. In CDCl₃ **12c** exists as a mixture of conformers, which complicates the NMR spectrum. In the text below the chemical shifts of the carbons of the major isomer only are given: oil; R_f = 0.76 (EtOAc/hexane/EtOH 2/1/0.1); $[\alpha]_D$ = -6.4 (c 0.8, CHCl₃, 26 °C); ¹H NMR (300.4 MHz, CDCl₃, mixture of conformers) δ 6.04–5.95 (m, 1H), 4.89–4.03 (m, 5H), 1.52–1.50 (m, 3H), 1.35–1.32 (m, 3H); ¹³C NMR (75.5 MHz, CDCl₃, mixture of conformers) δ 187.3, 113.2, 105.2, 83.4, 82.5, 69.3, 67.4, 26.6, 26.2; IR (liquid film, cm⁻¹) 2988 (m), 2938 (m), 1456 (m), 1378 (m), 1276 (s), 1200 (s), 1163 (s), 1080 (s), 1020 (s), 892(m), 864 (m), 826 (m), 540 (w), 525 (w); HRMS (EI) calcd for C₉H₁₂O₅S (M⁺) 232.0506, found m/z 232.0505; HPLC: 1 mL/min, 0.1% *N,N*-diisopropylethylamine/CH₃CN/MeOH (1:0.5:0.5), injection in 20 μ L of MeOH, retention time of 7.78 min, purity 99.6%.

1,2-*O*-Isopropylidene-5-deoxy- α -D-xylofuranose (12d).¹⁸ Procedure B; 73–75% yield from **12b** and **12c**; a colorless syrup; R_f = 0.48 (EtOAc/hexane/EtOH 2/1/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 5.88–5.87 (d, J = 3.7 Hz, 1H), 4.60–4.59 (d, J = 3.8 Hz, 1H), 4.34–4.27 (m, 1H), 3.98 (s, 1H), 2.20–1.90 (br s, 1H), 1.49 (s, 3H), 1.30–1.20 (m, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 111.4, 104.3, 85.4, 76.3, 75.9, 26.5, 26.1, 12.7.

***O*-Benzhydryl *S*-methyl xanthate (13).**¹⁹ Procedure A; 95% yield; ¹H NMR (300.4 MHz, CDCl₃) δ 7.67 (s, 1H), 7.37–7.27 (m, 10H), 2.59 (s, 3H); m/z 274 (M⁺, 10%), 214 (8), 199 (30), 184 (8), 167 (100), 152 (70), 121 (39).

Tetraphenyl ethane (14).²⁰ Procedure B; 95% yield; ¹H NMR (300.4 MHz, CDCl₃) δ 7.23–6.98 (m, 20H), 4.76 (s, 3H); m/z 334 (M⁺, 38%), 167 (100), 152 (25), 58 (12), 229 (59).

***O*-(4-Nitrophenethyl) *S*-methyl xanthate (15a).** Procedure A; 96% yield; a pale yellow crystalline solid; mp 70–72 °C (methanol); R_f = 0.48 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 8.18 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 4.85 (t, J = 6.6 Hz, 2H), 3.23 (t, J = 6.6 Hz, 2H), 2.54 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 215.7, 146.9, 145.1, 129.8, 123.7, 72.5, 34.4, 19.0; IR (KBr, cm⁻¹) 3079 (w), 2960 (w), 1598 (m), 1517 (s), 1285 (s), 1173 (s), 1108 (s), 1014 (s), 851 (m), 699 (m); HRMS (EI) calcd for C₁₀H₁₁NO₃S₂ (M⁺) 257.0180, found m/z 257.0184.

***O*-Phenethyl *S*-methyl xanthate (15b).**^{19a} Procedure A; 95% yield; a pale yellow liquid; R_f = 0.63 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (300.4 MHz, DMSO-*d*₆) δ 7.33–7.21 (m, 5H), 4.80–4.76 (t, J = 6.6 Hz, 2H), 3.34 (s, 3H), 3.11–3.07 (d, J = 6.6 Hz, 2H); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 215.2, 137.5, 128.9, 128.4, 126.5, 74.3, 33.7, 18.3.

4-Nitrostyrene (16a).²¹ Procedure B; 95% yield; a yellow liquid; ¹H NMR (300.4 MHz, CDCl₃) δ 8.21–8.18 (d, J = 9.0 Hz, 2H), 7.77–7.74 (d, J = 9.0 Hz, 2H), 6.93–6.84 (dd, J = 18.0, 10.8 Hz, 1H), 6.13–6.07 (d, J = 18.0 Hz, 1H), 5.55–5.52 (d, J = 10.8 Hz, 1H).

Styrene (16b).²² Procedure B; 90% yield; a yellow liquid; R_f = 0.14 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ 7.41–7.18 (m, 5H), 6.75–6.66 (dd, J = 17.4, 10.5 Hz, 1H), 5.77–5.71 (d, J = 17.7 Hz, 1H), 5.25–5.21 (d, J = 11.1 Hz, 1H).

1,2:5,6-Di-*O*-isopropylidene-3,4-bis-*O*-[(methylthio)thiocarbonyl]-D-mannitol (17).²³ Procedure A; 90% yield; colorless crystals; R_f = 0.51 (EtOAc/hexane/EtOH 1/5/0.1); ¹H NMR (300.4 MHz, CDCl₃) δ

5.88–5.87 (d, $J = 3.7$ Hz, 2H), 4.38–4.32 (m, 2H), 4.00–3.98 (d, $J = 6.0$ Hz, 4H), 2.61 (s, 6H), 1.38 (s, 6H), 1.32 (s, 6H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 215.7, 109.5, 79.1, 74.7, 65.1, 26.3, 25.2, 19.3.

1,2:5,6-Di-*O*-isopropylidene-3,4-bis-*O*-[(methylthio)thiocarbonyl]- β -mannitol (18).^{23a, 24} Procedure B; 86% yield; a colorless syrup; $R_f = 0.21$ (EtOAc/hexane/EtOH 1/5/0.1); ^1H NMR (300.4 MHz, CDCl_3) δ 5.82–5.80 (dd, $J = 3.9, 1.8$ Hz, 2H), 4.57–4.49 (m, 2H), 4.12–4.07 (t, $J = 6.6$ Hz, 2H), 3.62–3.57 (t, $J = 7.8$ Hz, 2H), 1.43 (s, 6H), 1.39 (s, 6H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 130.8, 109.4, 76.0, 69.3, 26.6, 25.9.

Reaction of $(\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ and $(\text{HCO}_2)_2\text{Cu}$ with 10b. A mixture of **10b** (35 mg, 0.1 mmol), $(\text{HCO}_2)_2\text{Cu}$ (92 mg, 0.6 mmol), $(\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ (203 mg, 0.3 mmol), and DMF (2 mL) was stirred at 65 °C for 60 min. The mixture was then poured into water (5 mL) and the whole was extracted with CH_2Cl_2 (5 mL). The extract was washed with brine (5 mL) and dried over Na_2SO_4 . After evaporation of the solvent, the residue was subjected to flash column chromatography on silica gel using gradient elution of 5 to 30% EtOAc in hexane to recover the starting material **10b** (33 mg, 95%).

Reaction of $(\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ and HCO_2NH_4 with 10b. A mixture of **10b** (35 mg, 0.1 mmol), HCO_2NH_4 (38 mg, 0.6 mmol), $(\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ (203 mg, 0.3 mmol), and DMF (2 mL) was stirred at 65 °C for 20 min. The mixture was then poured into water (5 mL) and the whole was extracted with CH_2Cl_2 (5 mL). The extract was washed with aqueous NaHCO_3 (5 mL) and brine (5 mL) and dried over Na_2SO_4 . After evaporation of the solvent, the residue was subjected to flash column chromatography on silica gel using gradient elution of 5 to 30% EtOAc in hexane to give the deoxy product **10e** (2 mg) in 8% yield.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(deuteromethylthio)thiocarbonyl]- α -D-glucofuranose (19). The alcohol (1 mmol) in dry tetrahydrofuran (4 mL) was added at 0 °C under argon to a stirred suspension of sodium hydride (60% w/w in mineral oil, 60 mg, 1.5 mmol) and imidazole (2 mg, 0.03 mmol) in tetrahydrofuran (6 mL). The mixture was stirred at room temperature for 0.5 h and then carbondisulfide (90 μL , 114 mg, 1.5 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then deuteromethyl iodide (93 μL , 217 mg, 1.5 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then quenched with acetic acid (114 μL , 120 mg, 2 mmol) in water (20 mL). The reaction mixture was extracted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na_2SO_4 . After evaporation of the solvent, the residue was subjected to flash column chromatography on silica gel using gradient elution of 5 to 30% EtOAc in hexane to give **19** (343 mg) in 97% yield: oil; $R_f = 0.60$ (EtOAc/hexane/EtOH 1/5/0.1); $[\alpha]_D = -16.3$ (c 1.0, CHCl_3 , 19 °C); ^1H NMR (300.4 MHz, CDCl_3) δ 5.97 (d, $J = 3.3$ Hz, 1H), 4.98 (dd, $J = 11.4, 5.7$ Hz, 1H), 4.74 (dd, $J = 11.7, 5.7$ Hz, 1H), 4.56–4.48 (m, 2H), 4.29 (s, 1H), 2.59 (s, 3H), 2.55–2.42 (m, 1H), 1.52 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 214.5, 112.2, 109.1, 104.8, 84.0, 82.6, 79.5, 72.2, 66.7, 26.6, 26.5, 26.1, 25.1; IR (liquid film, cm^{-1}) 2988 (m), 1374 (m), 1200 (s), 1163 (m), 1079 (s), 1022 (m), 845 (m); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{D}_3\text{O}_6\text{S}_2$ (M^+) 353.1043, found m/z 353.1061.

Deoxydeuteration of Thiocarbonyl Derivatives 10b and 10c Using $(\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ and DCO_2Na . A deuteration of **10c** is exemplary. A mixture of phenyl thionocarbonate **10c** (40 mg, 0.1 mmol), Na_2CO_3 (85 mg, 0.8 mmol), DCO_2Na (41 mg, 0.6 mmol), $(\text{Bu}_4\text{N})_2\text{S}_2\text{O}_8$ (203 mg, 0.3 mmol), and DMSO (2 mL) was stirred at 65 °C for 30 min. The mixture was then poured into water (5 mL) and the whole was extracted with CH_2Cl_2 (10 mL). The extract was washed with aqueous NaHCO_3 (10 mL) and brine (10 mL) and dried over Na_2SO_4 . After evaporation of the solvent, the residue was subjected to flash column chromatography on silica gel using gradient elution of 5 to 30% EtOAc in hexane to give the deuterated mixture **20** (22 mg) in 90 % yield as a viscous oil. The atom % deuterium incorporation (91%) and the position of the deuterium in the product **20** were determined by 300.4 MHz ^1H NMR: $R_f = 0.35$ (EtOAc/hexane/EtOH 1/5/0.1); ^1H NMR (300.4 MHz, CDCl_3) δ 5.82 (d, $J = 3.6$ Hz, 1H), 4.76 (d, $J = 3.6$ Hz, 1H), 4.17–4.08 (m, 3H), 3.86–3.79 (m, 1H), 2.18 (m, 1H), 1.76 (m, 0.09 H), 1.52 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H).

Deoxydeuterations of **10b** were conducted similarly. The detailed reaction conditions were listed in Table 2.

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3

$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$
5b

20: mixture of β D and β H