

Efficient synthesis of β -hydroxy sulfides by microwave-promoted ring opening in (+)-3-carene *trans*-epoxide with sodium thiolates

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(1*S*,3*S*,4*S*,6*R*)-4-Benzylthiocaran-3-ol **3**: yield 95%, colourless oil, $[\alpha]_{589}^{25} +91$ (*c* 1.04, CHCl₃). IR (*c* 2% in CHCl₃, $\nu_{\max}/\text{cm}^{-1}$): 3581, 1134. ¹H NMR (300 MHz, CDCl₃) δ : 0.60–0.75 (m, 2H, H-1, H-6), 0.96 (s, 3H, H-8 or H-9), 0.98 (s, 3H, H-8 or H-9), 1.11 (m, 1H, H_{pro-S-2}), 1.20 (s, 3H, H-10), 1.25 (m, 1H, H_{pro-S-2}), 1.91 (dd, 1H, H_{pro-R-5}, *J* 15.6 and 8.6 Hz), 2.12 (ddd, 1H, H_{pro-S-5}, *J* 15.6, 8.6 and 5.5 Hz), 2.20 (s, 1H, OH), 2.64 (dd, 1H, H-4, *J* 9.5 and 5.6 Hz), 3.72 (d, 1H, H_{a-11}, *J* 13.2 Hz), 3.77 (d, 1H, H_{b-11}, *J* 13.2 Hz), 7.17–7.33 (m, 5H, H-13, H-14, H-15). ¹³C NMR (75 MHz, CDCl₃) δ : 15.70 (C⁸), 17.65 (C⁶), 18.09 (C⁵), 21.6 (C¹), 25.20 (C⁷), 26.73 (C⁹), 28.01 (C¹⁰), 32.22 (C²), 36.64 (C¹¹), 51.88 (C⁴), 71.93 (C³), 126.59 (C¹⁵), 128.03 (C¹⁴), 128.40 (C¹³), 137.93 (C¹²). MS, *m/z* (%): 276.1548 (3, [M]⁺, calc for [C₁₇H₂₄OS]⁺: 276.1542), 233 (6), 185 (28), 127 (31), 109 (6), 93 (10), 92 (8), 91 (100), 83 (13), 71 (5), 67 (6), 65 (8), 43 (23), 41 (8).

(1*S*,3*S*,4*S*,6*R*)-4-*n*-Heptylthiocaran-3-ol **4**: yield 91%, colourless oil, $[\alpha]_{589}^{29} +95$ (*c* 1.8, CHCl₃). IR (*c* 2% in CHCl₃, $\nu_{\max}/\text{cm}^{-1}$): 3587. ¹H NMR (300 MHz, CDCl₃) δ : 0.6–0.7 (m, 2H, H-1 and H-6), 0.87 (t, 3H, H-17, *J* 6.7 Hz), 0.94 (s, 3H, H-8 or H-9), 0.95–1.05 (m, 1H, H_{pro-R-5}), 0.98 (s, 3H, H-8 or H-9), 1.04 (dd, 1H, H_{pro-R-2}, *J* 15.2 and 6.8 Hz), 1.10 (s, 3H, H-10), 1.20–1.39 (m, 8H, H-13, H-14, H-15, H-16), 1.52 (dddd, 2H, H-12, *J* 4×7.4 Hz), 1.76 (dd, 1H, H_{pro-S-2}, *J* 15.2 and 8.3 Hz), 2.06–2.15 (m, 1H, H_{pro-S-5}), 2.45 (dddd, 1H, H_{a-11}, *J* 14.6, 2×7.4 and 2.4 Hz), 2.49 (dddd, 1H, H_{b-11}, *J* 14.6, 2×7.4 and 2.4 Hz), 2.58 (dd, 1H, H-4, *J* 9.5 and 5.7 Hz), 3.61 (s, 1H, OH). ¹³C NMR (75 MHz, CDCl₃) δ : 13.9 (C¹⁷), 15.3 (C⁸), 17.9 (C¹ or C⁶), 18.4 (C⁷), 22.1 (C¹ or C⁶), 22.4 (C¹⁶), 25.8 (C⁵), 26.8 (C¹⁰), 28.2 (C⁹), 28.7, 28.7, 29.7, 31.5, 32.4, 32.4 (C¹¹, C¹², C¹³, C¹⁴, C¹⁵), 32.6 (C²), 53.2 (C⁴), 72.4 (C³). MS, *m/z* (%): 284.2167 (11, [M]⁺, calc. for [C₁₇H₃₂OS]⁺: 284.2168), 241 (100), 201 (20), 185 (40), 173 (62), 159 (24), 152 (25), 137 (26), 135 (30), 127 (35), 119 (20), 109 (45), 107 (23), 93 (41), 83 (74), 71 (20), 67 (25), 55 (36).