Highly Enantiospecific Oxyfunctionalization of Non Activated Hydrocarbon Sites by Perfluoro *cis*-2,3-dialkyloxaziridines

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Supporting Information Available

Techniques and conditions for enantiomer separation of compounds 2, 3, 5, 6, 7, 8.

2a; See refs.[13, 14] of the paper: The optical purity of **2a** was assigned through the optical purity of (*R*) – 2,6–dimethyl–2–octanol **3d**.
Analytical Technique: The ^{1}H – NMR spectrum of a solution obtained from 2 mg of (*R*) – **3d** and 15 mg of Eu(hfc)$_3$ in 0.5 mL of degassed $CDCl_3$ was recorded after 1 h on a Bruker ARX 400 spectrometer with TMS as internal standard.
Chemical Shifts: (*R*) – **3d**: 1.328 ppm (C*H*$_3$–C-6); (*S*) – **3d**: 1.336 ppm (C*H*$_3$–C-6).

3a; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with MEGADEX 5 (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 20 °C min^{-1} /75 °C - 2' / 1 °C min^{-1} / 90 °C.
Retention Times: (*S*) – **3a**: 16.12 min; (*R*) – **3a**: 16.81 min.

3b; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 20 °C min^{-1} / 110 °C - 2' / 1 °C min^{-1} / 160 °C.
Retention Times: (*S*) – **3b**: 43.26 min; (*R*) – **3a**: 43.82 min.

2c; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 20 °C min^{-1} / 85 °C - 2' / 1 °C min^{-1} / 130 °C.
Retention Times: (*S*) – **2c**: 43.82 min; (*R*) – **2c**: 44.00 min.

3c; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 20 °C min^{-1} / 125 °C - 2' / 1 °C min^{-1} / 165 °C.
Retention Times: (*S*) – **3c**: 27.00 min; (*R*) – **3c**: 31.00 min.

5; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 20 °C min^{-1} / 100 °C - 2' / 1 °C min^{-1} / 140 °C.
Retention Times: (*S*) – **5**: 33.50 min; (*R*) – **5**: 33.85 min.

6; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 20 °C min^{-1} / 125 °C - 2' / 1 °C min^{-1} / 160 °C.
Retention Times: (*S*) – **6**: 31.48 min; (*R*) – **6**: 31.75 min.

8a; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 °C - 1'/ 1.5 °C min^{-1} / 75 °C.
Retention Times: (*S*) – **8a**: 34.88 min; (*R*) – **8a**: 35.70 min.

7b; Analtyical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with DEtTBSil βCDX (d_f = 0.25 μm).
Temperature Gradient: 40 ^{o}C - 1'/ 1 ^{o}C min^{-1} / 70 ^{o}C.
Retention Times: (*S*) – **7b**: 35.70 min; (*R*) – **7b**: 36.15 min.

8b; Analytical Technique: Chiral GLC on Dani mod. 8610.
Used Column: 25 m x 0.25 mm i.d. fused silica capillary column coated with MEGADEX 5 (d_f = 0.25 μm).
Temperature Gradient: 40 ^{o}C - 1'/ 1.5 ^{o}C min^{-1} / 75 ^{o}C.
Retention Times: (*S*) – **8b**: 28.58 min; (*R*) – **8b**: 28.97 min.

General procedure for the oxyfunctionalization of substrates 2, 5, and 7 with oxaziridine 1.

A solution of freshly distilled **1** (4.0 meq.) in $CFCl_3$ (2.9 mL) was added dropwise to a solution of the substrate **2** or **5** or **7** (1.0 meq.) in the same solvent (1.5 ml). The reaction mixture was stirred at 20 °C and the progress of the reaction was monitored by GLC. After the reaction times reported in the Schemes, a fair conversion had been obtained (18-62%). The solvent was removed under reduced pressure, excess ethyl acetate and perfluoromethylciclohexane were added and the hydrocarbon phase was separated. The perfluorinated phase was extracted twice with ethyl acetate and collected organic phases were evaporated to give a crude residue which was purified through flash-chromatography. Isolated yields in pure **3**, **6**, **8** were 15-56%.

Spectral data for the products 3, 6, and 8.

(*S*)-3a: ^{1}H NMR identical with an authentic sample (Aldrich).

(*R*)-3b: ^{1}H NMR and ^{13}C NMR: see ref. 19 of the paper

(*R*)-3c: ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.49 (m, 2H), 2.08 (m, 2H), 1.8-1.2 (m, 7H), 1.23 (s, 6H), 1.21 (s, 3H).

^{13}C NMR (62.9 MHz, $CDCl_3$) δ 73.08 (o), 70.99 (o), 45.05 (o), 44.05 (o), 42.70 (o), 29.39 (e), 28.20 (o), 26.64 (e), 18.58 (o).

(*R*)-3d: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.85 (brs, 1H), 1.5-1.2 (m, 9H), 1.22 (s, 6H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.3 Hz, 3H).

(*S*)-6: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.24 (m, 2H), 4.09 (m, 2H), 2.06 (s, 6H), 1.96 (brs, 1H), 1.83 (m, 2H), 1.72 (m, 2H), 1.54 (m, 2H), 1.24 (s, 3H).

^{13}C NMR (62.9 MHz, $CDCl_3$) δ 171.32 (o), 171.14 (o), 71.77 (o), 64.72 (o), 61.14 (o), 39.67 (o), 38.50 (o), 26.87 (e), 23.23 (o), 21.06 (e), 21.00 (e).

(*S*)-8b: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.09 and 4.06 (d, *J* = 10.6 Hz, 2H), 1.95 (s, 6H), 1.74 (brs, 1H), 1.60 (q, *J* = 7.5 Hz, 2H), 1.24 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (62.9 MHz, $CDCl_3$) δ 171.59 (o), 72.16 (o), 71.86 (o), 55.76 (o), 31.58 (o), 30.79 (e), 23.23 (e), 7.88 (e).