Supporting Information

Highly Stereoselective C-Allylation of an Enantiopure α -Sulfinyl Thioacetamide

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X-ray Crystallographic Data and Chromatographic Analyses

X-ray Crystallographic Data

(2*R*,*S*_s)-4-Cyano-2-cyclohexylsulfinyl-*N,N*-dimethylpent-4-enethioamide (6c):

C₁₄H₂₂N₂OS₂; orthorhombic, space group P2₁2₁2₁, $a = 7.417$ (2), $b = 13.109$ (2), $c = 16.449$ (4) Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90$ °, $V = 1599.3$ (6) Å³, $Z = 4$, $\rho = 1.24$ g.cm⁻³, $R = 0.0392$. Enraf-Nonius CAD-4 diffractometer, MoK α radiation (highly oriented graphite crystal monochromator, $\lambda = 0.7107$ Å).

Interatomic distances: S1-C1: 1.664 (3); S2-C2: 1.861 (2); N1-C1: 1.318 (3); N1-C8: 1.456 (4); C1-C2: 1.521 (4); C3-C4: 1.488 (4); C4-C6: 1.305 (4); C9-C14: 1.513 (4); C11-C12: 1.515 (4); C13-C14: 1.503 (4); S2-O1: 1.487 (2); S2-C9: 1.833 (3); N1-C7: 1.483 (3); N2-C5: 1.123 (4); C2-C3: 1.530 (4); C4-C5: 1.433 (4); C9-C10: 1.514 (4); C10-C11: 1.521 (4); C12-C13: 1.508 (4).

Angles: O1-S2-C2: 106.9 (1); C2-S2-C9: 100.0 (1); C1-N1-C8: 121.7 (3); S1-C1-N1: 122.5 (2); N1-C1-C2: 118.8 (3); S2-C2-C3: 109.0 (2); C2-C3-C4: 113.8 (2); C3-C4-C6: 122.0 (3); N2-C5-C4: 117.7 (4); S2-C9-C14: 114.1 (2); C9-C10-C11: 110.1 (3); C11-C12-C13: 110.3 (3); C9-C14-C13: 110.6 (2); O1-S2-C9: 106.1 (1); C1-N1-C7: 124.6 (2); C7-N1-C8: 113.6 (2); S1-C1-C2: 118.7 (2); S2-C2-C1: 103.7 (2); C1-C2-C3: 114.9 (2); C3-C4-C5: 119.7 (3); C5-C4-C6: 118.2 (3); S2-C9-C10: 105.5 (2); C10-C9-C14: 110.4 (2); C10-C11-C12: 111.5 (3); C12-C13-C14: 111.1 (3).

Minor diastereoisomer

Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **178137**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

HPLC Enantiomer Analyses

Waters apparatus, M996 detector with diode array detector (200 - 300 nm), Daicel Chiralpack AD column (L = 250 mm, D = 4.6 mm, rate = 1 mL.min⁻¹), Millenium Software.

(*Rac*)-**6b**: 85% *n*-hexane - 15% 2-propanol, T = 20 °C.

6b	Retention Time (min)	λ (nm)
(2 <i>R</i> , <i>S</i> _S)	8.71	289.2
(2 <i>R</i> , <i>S</i> _R)	14.16	282.1
(2 <i>S</i> , <i>S</i> _S)	31.34	282.1
(2 <i>S</i> , <i>S</i> _R)	51.63	289.2

(*Rac*)-**6c**: 90% *n*-hexane - 10% 2-propanol, T = 20 °C.

6c	Retention Time (min)	λ (nm)
(2 <i>R</i> , <i>S</i> _S)	16.74	289.9
(2 <i>S</i> , <i>S</i> _S)	28.48	284.0
(2 <i>R</i> , <i>S</i> _R)	42.79	284.0
(2 <i>S</i> , <i>S</i> _R)	59.20	289.9

HPLC Chromatograms

(2*S*,*S*_s)-Methyl 2-[[2-cyclohexylsulfinyl]-2-(*N,N*-dimethylcarbamoyl)]ethyl}prop-2-enoate (6b)

Racemic ester (6b)

Chromatogram

UV-VIS absorptions

Enantioenriched ester (6b) from C-allylation

Chromatogram

(2*S*,*S*_c)-4-Cyano-2-cyclohexylsulfinyl-*N,N*-dimethylpent-4-enethioamide (6c)

Racemic nitrile (6c)

Chromatogram

UV-VIS absorptions

Major diastereoisomer of the enantioenriched nitrile (6c) from *C*-allylation

Chromatogram

Minor diastereoisomer of the enantioenriched nitrile (6c) from *C*-allylation

Chromatogram