SUPPORTING INFORMATION

Catalytic asymmetric synthesis of mycocerosic acid

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General Procedures:

All reactions were carried out under nitrogen atmosphere using dried glassware. All solvents were dried and distilled before use according to standard procedures. t-BuOMe was purchased as anhydrous grade, stored on 4Å MS and used without further purification. Ligand 5 was generously provided by Solvias. CuBr·SMe₂ was purchased from Aldrich or Acros and used without further purification. Grignard reagent MeMgBr was purchased from Aldrich. Grignard reagents were titrated using s-BuOH and catalytic amounts of 1,10-phenanthroline.

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by staining with Seebach’s reagent: a mixture of phosphomolybdic acid (25g), cerium (IV) sulfate (7.5g), H₂O (500 mL) and H₂SO₄ (25mL).

Mass spectra were recorded on a AEI-MS-902 mass spectrometer. ¹H- and ¹³C-NMR were recorded on a Varian AMX400 (400, 100.59 MHz, respectively) using CDCl₃ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.26 for ¹H, δ 77.0 for ¹³C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a Schmidt + Haensch polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL). Enantiomer excess was determined by capillary GC analysis (Chiraldex A-TA column (30 m x 0.25 mm) using a flame ionization detector and compared with racemic products.
Experimental:

(E)-4-(tert-Butyl-diphenyl-silanyloxy)-but-2-enethioic acid S-ethyl ester (2):
tert-Butyl-chloro-diphenyl-silane (10.0 mL, 38.5 mmol) was added to a stirred solution of 6 equiv of
ethane-1,2-diol (12.0 mL, 231 mmol) and 1.1 equiv of imidazole (2.88 g, 42.4 mmol) in 200 mL of THF
under nitrogen atmosphere. The resulting mixture was stirred for 24 h at rt and quenched with 200 mL
water followed by addition of 200 mL of diethyl ether. After phase separation and extraction of the aqueous
phase with 3 portions of 200 mL of diethyl ether, the combined organic phases were dried over MgSO₄,
concentrated under reduced pressure and purified by flash chromatography (eluent pentane/EtOAc 4:1) to
afford 16 as a colorless oil (9.14 g, 79% yield). A solution of 16 (9.14 g, 30.5 mmol) and 1.3 equiv of
iodoxybenzoic acid (IBX) (11.09 g, 39.61 mmol) in 200 mL of EtOAc was refluxed for 24 h and cooled
down to rt. IBX and benzoic acid were filtered off through a Celite pad and washed with EtOAc. The
filtrate was concentrated under reduced pressure to give the aldehyde 17 (8.81 g, 97% yield) which was
used in the next step without purification. A solution of 17 (8.81 g, 29.6 mmol) and Ph₃PCHCOSEt (13.99
352 g, 38.42 mmol) in CH₂Cl₂ (150 mL) was refluxed for 24 h. The solution was concentrated under reduced
pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford α,β-
unsaturated thioester 2 as a colourless oil (2.968 g, 95% yield, [α]D = +8.0 (c = 1.2, CHCl₃)).

(R)-4-(tert-Butyl-diphenyl-silanyloxy)-3-methyl-thiobutyric acid S-ethyl ester (3):
(S,RFe)-Josiphos (5).CuBr complex (58 mg, 0.078 mmol, 1 mol%) was dissolved in t-BuOMe (48 mL)
under nitrogen. The solution was cooled to −75 °C and methylmagnesium bromide (9.37 mmol, solution in
diethyl ether) was added dropwise over 10 min. After stirring for 10 min, a solution of thioester 2 (3.0 g,
7.81 mmol) in t-BuOMe (13.6 mL) was added via syringe pump over 1 h. The reaction mixture was stirred
at −75 °C for 17 h, then quenched by the addition of MeOH and allowed to warm to room temperature.
Saturated aqueous NH₄Cl solution was then added. After phase separation and extraction of the aqueous
phase with 3 portions of diethyl ether, the combined organic phases were dried over MgSO₄,
concentrated under reduced pressure and purified by flash chromatography (elucent pentane/ether 40:1) to
afford 3 as a colourless oil (2.968 g, 95% yield, [α]D = +8.0 (c = 1.2, CHCl₃)).

1H-NMR (400 MHz, CDCl₃): δ 7.66 (dd, J = 6.8, 1.4 Hz, 4H), 7.41 (m, 6H), 2.88 (q, J = 7.4 Hz, 2H), 2.38 (dd, J = 14.5, 5.3 Hz, 1H), 2.28 (dd, J = 14.5, 8.4 Hz, 1H), 2.29 (m, 1H), 1.25 (t, J = 7.4 Hz, 3H), 1.15 (s, 9H), 0.98 (d, J = 6.6 Hz, 3H). MS(EI⁺) for C₂₃H₃₂O₂SSi: m/z(%) = 343 (100%, M – tert-Butyl), MS(CI⁺) for C₂₃H₃₂O₂SSi: m/z(%) = 418 (37.5%, M + NH₄⁺), 401 (100%, M + H⁺). HRMS(EI⁺) for C₂₃H₃₂O₂SSi: m/z(%) = 343 (100%, M – tert-Butyl), Measured Mass: 343.1183 Da, Calculated Mass: 343.1188 Da.
E.e. and absolute configuration were determined by removal of the tert-butylidiphenylsilyl group resulting in lactone 4. The absolute configuration of lactone 4 has been previously reported\textsuperscript{1,2,3}. Lit: $[\alpha]_D = -24.7$ (c = 1.7, MeOH) for the $S$-configuration. Found: $[\alpha]_D = +21.6$ (c = 0.5, MeOH). Determination of enantiomeric excess was achieved by GC analysis [ChiralDEX AT-A (30.0 m x 0.25 mm), 1.0 ml min$^{-1}$, initial temp. 50 °C then 5 °C min$^{-1}$ to final temp. 170 °C, 19.7 min (minor), 19.9 (major) shows 98% ee.]
To a stirred mixture of 3 (2.0 g, 5 mmol) and 10% Pd-C (5 mol%, 267 mg) in CH₂Cl₂ (10 mL) was added 3 equiv of Et₃SiH (2.41 mL, 15.0 mmol) at rt under nitrogen. Stirring was continued at rt until the reduction was completed (10-30 min). The catalyst was filtered off through a Celite pad and washed with CH₂Cl₂. The filtrate was concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to give 18 which was used in the next step without complete removal of the eluent. A solution of 18 and Ph₃PCHCOSEt (2.366 g, 6.50 mmol) in CH₂Cl₂ (30 mL) was refluxed for 24 h. The solution was concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford α,β-unsaturated thioester 6 as a colourless oil (1.491 g, 70% yield over 2 steps, \([\alpha]_D = +5.73 (c = 1.57, \text{CHCl}_3)\). 1H-NMR (400 MHz, CDCl₃): δ 7.65 (d, \(J = 7.9\) Hz, 4H), 7.41 (m, 6H), 6.87 (dt, \(J = 15.4, 7.6\) Hz, 1H), 6.11 (dt, \(J = 15.5, 1.4\) Hz, 1H), 3.53 (dd, \(J = 10.0, 5.4\) Hz, 1H), 3.46 (dd, \(J = 10.0, 6.4\) Hz, 1H), 2.95 (q, \(J = 7.4\) Hz, 2H), 2.44 (m, 1H), 2.05 (m, 1H), 1.86 (m, 1H), 1.29 (t, \(J = 7.4\) Hz, 3H), 1.06 (s, 9H), 0.92 (d, \(J = 6.8\) Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 189.97 (s), 143.89 (d), 135.57 (d), 133.70 (s), 129.95 (d), 129.61 (d), 127.64 (d), 68.07 (t), 35.97 (t), 35.42 (d), 26.86 (q), 23.03 (t), 19.29 (s), 16.46 (q), 14.83 (q). MS(EI+) for C₂₅H₃₄O₂SSi: m/z(%) = 369 (100%, M – tert-Butyl), MS(CI+) for C₂₅H₃₄O₂SSi: m/z(%) = 444 (100%, M + NH₄⁺), 427 (1.5%, M + H⁺). HRMS(EI+) for C₂₅H₃₄O₂SSi: m/z(%) = 369 (100%, M – tert-Butyl), Measured Mass: 369.1331 Da, Calculated Mass: 369.1345 Da.

(S,R Fe)-Josiphos (5).CuBr complex (16.8 mg, 0.023 mmol, 1 mol%) was dissolved in t-BuOMe (13.8 mL) under nitrogen. The mixture was cooled to –75 °C and methylmagnesium bromide (2.73 mmol, solution in diethyl ether) was added dropwise over 10 min. After stirring for 10 min, a solution of thioester 6 (969 mg, 2.275 mmol) in t-BuOMe (3.9 mL) was added via syringe pump over 1 h. The reaction mixture was stirred at –75 °C for 17 h, then quenched by the addition of MeOH and allowed to warm to room temperature. Saturated aqueous NH₄Cl solution was then added. After phase separation and extraction of the aqueous phase with 3 portions of diethyl ether, the combined organic phases were dried over MgSO₄, concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford 7a as a colourless oil (900 mg, 90% yield, syn/anti by NMR = 96/4, d.r. calculated from syn/anti ratio = (3S,5R):(3R,5R):(3S,5S):(3R,5S) = 97:2:1:0, \([\alpha]_D = +4.61 (c = 1.91, \text{CHCl}_3)\).

1H-NMR (400 MHz, CDCl₃): δ 7.67 (dd, \(J = 7.7, 1.6\) Hz, 4H), 7.41 (m, 6H), 3.50 (dd, \(J = 9.9, 5.5\) Hz, 1H), 3.43 (dd, \(J = 9.9, 6.4\) Hz, 1H), 2.87 (q, \(J = 7.4\) Hz, 2H), 2.52 (dd, \(J = 14.4, 5.1\) Hz, 1H), 2.25 (dd, \(J = 14.4, 8.8\) Hz, 1H), 2.08 (m, 1H), 1.71 (m, 1H), 1.41 (m, 1H), 1.24 (t, \(J = 7.4\) Hz, 3H), 1.06 (s, 9H), 1.03 (m, 1H), 0.94 (d, \(J = 6.7\) Hz, 3H), 0.91 (d, \(J = 6.6\) Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 199.15 (s), 135.61 (d), 133.94 (s), 129.50 (d), 127.57 (d), 68.74 (t), 51.19 (t), 40.79 (t), 33.16 (d), 28.69 (d), 26.88 (q), 23.26 (t), 20.28 (q), 19.29 (s), 17.42 (q), 14.79 (q). MS(EI+) for C₂₆H₃₄O₂SSi: m/z(%) = 385 (100%, M – tert-Butyl), MS(Cl⁻) for C₂₆H₃₄O₂SSi: m/z(%) = 460 (100%, M + NH₄⁺), 443 (12.5%, M + H⁺). HRMS(EI+) for C₂₆H₃₄O₂SSi: m/z(%) = 385 (100%, M – tert-Butyl), Measured Mass: 385.1668 Da, Calculated Mass: 385.1658 Da.
(3S,5S)-6-(tert-Butyl-diphenyl-silyloxy)-3,5-dimethyl-hexanethioic acid S-ethyl ester (7b)

(S,R,R)-Josiphos (5).CuBr complex (3 mg, 0.004 mmol, 5 mol%) was dissolved in t-BuOMe (0.8 mL) under nitrogen. The mixture was cooled to −75 °C and methylmagnesium bromide (0.12 mmol, solution in diethyl ether) was added dropwise over 10 min. After stirring for 10 min, a solution of thioester 6 (40 mg, 0.094 mmol) in t-BuOMe (0.2 mL) was added via syringe pump over 1 h. The reaction mixture was stirred at −75 °C for 17 h, then quenched by the addition of MeOH and allowed to warm to room temperature. Saturated aqueous NH₄Cl solution was then added. After phase separation and extraction of the aqueous phase with 3 portions of diethyl ether, the combined organic phases were dried over MgSO₄, concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford 7b as a colourless oil (38 mg, 90% yield, syn/anti by NMR > 5/95, 1H-NMR (400 MHz, CDCl₃): δ 7.67 (dd, J = 7.7, 1.6 Hz, 4H), 7.41 (m, 6H), 3.47 (m, 2H), 2.87 (q, J = 7.5 Hz, 2H), 2.47 (dd, J = 14.4, 6.3 Hz, 1H), 2.37 (dd, J = 14.5, 7.7 Hz, 1H), 2.10 (m, 1H), 1.73 (m, 1H), 1.28 (m, 1H), 1.25 (t, J = 7.4 Hz, 3H), 1.08 (m, 1H), 1.06 (s, 9H), 0.90 (d, J = 6.6 Hz, 6H). 13C-NMR (100.6 MHz, CDCl₃): 199.10 (s), 135.61 (d), 134.00 (s), 129.49 (d), 127.56 (d), 69.29 (t), 52.14 (t), 40.13 (t), 33.11 (d), 28.4 (d), 26.88 (q), 23.25 (t), 19.30 (s), 19.17 (q), 16.36 (q), 14.81 (q).

(+)-(E)-(5R,7R)-8-(tert-Butyl-diphenyl-silyloxy)-5,7-dimethyl-oct-2-enethioic acid S-ethyl ester (20)

To a stirred mixture of 7a (290 mg, 0.656 mmol) and 10% Pd-C (5 mol%, 35 mg) in CH₂Cl₂ (1.33 mL) was added 3 equiv of Et₃SiH (0.316 mL, 1.968 mmol) at rt under nitrogen. Stirring was continued at rt until the reduction was completed (10-30 min). The catalyst wa s filtered off through a Celite pad and washed with the solvent of the reaction. The filtrate was concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to give aldehyde 19 which was used in the next step without complete removal of the eluent. A solution of aldehyde 19 and Ph₃PCHCOSEt (287 mg, 0.787 mmol) in CH₂Cl₂ (6.7 mL) was refluxed for 24 h. The solution was concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford α,β-unsaturated thioester 20 as a colourless oil (214 mg, 70% yield over 2 steps, [α]D = +7.6 (c = 1.97, CHCl₃)). 1H-NMR (400 MHz, CDCl₃): δ 7.66 (dd, J = 7.7, 1.6 Hz, 4H), 7.41 (m, 6H), 6.83 (dt, J = 15.4, 7.6 Hz, 1H), 6.08 (dt, J = 15.5, 1.4 Hz, 1H), 3.50 (dd, J = 9.8, 5.3 Hz, 1H), 3.42 (dd, J = 9.8, 6.3 Hz, 1H), 2.94 (q, J = 7.4 Hz, 2H), 2.18 (m, 1H), 1.92 (m,1H), 1.69 (m,2H), 1.39 (m, 1H), 1.28 (t, J = 7.4 Hz, 3H), 1.06 (s, 9H), 1.02 (m, 1H), 0.93 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 189.97 (s), 144.07 (d), 135.59 (d), 133.93 (s), 129.84 (d), 129.51 (d), 127.57 (d), 68.61 (t), 40.76 (t), 39.45 (t), 33.08 (d), 29.96 (d), 26.88 (q), 23.01 (t), 20.12 (q), 19.28 (s), 17.59 (q), 14.81 (q). MS(El+) for C₂₈H₄₀O₂SSi: m/z(%) = 411 (100%, M – t-Butyl), MS(Cl+) for C₂₈H₄₀O₂SSi : m/z(%) = 411 (100%, M – t-Butyl), Measured Mass: 411.1812 Da, Calculated Mass: 411.1814 Da.
(S,R,R)-Josiphos (5). CuBr complex (3.2 mg, 0.004 mmol, 1 mol%) was dissolved in t-BuOMe (0.8 mL) under nitrogen. The mixture was cooled to −75 °C and methylmagnesium bromide (0.541 mmol, solution in diethyl ether) was added dropwise over 10 min. After stirring for 10 min, a solution of thioester 20 (211 mg, 0.451 mmol) in t-BuOMe (2.76 mL) was added via syringe pump over 1 h. The reaction mixture was stirred at −75 °C for 17 h, then quenched by the addition of MeOH and allowed to warm to room temperature. Saturated aqueous NH₄Cl solution was then added. After phase separation and extraction of the aqueous phase with 3 portions of diethyl ether, the combined organic phases were dried over MgSO₄, concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford 21 as a colourless oil (185 mg, 85 % yield, syn/anti by NMR = >96/4, d.r.calculated from syn/anti ratio = (3S,5R,7R):(3R,5R,7R):(3S,5S,7S):(3S,5R,7S) = 95:2:2:1, diastereoisomers smaller than 0.04 were neglected, [α]D = +6.8 (c = 1.13, CHCl₃)). 1H-NMR (400 MHz, CDCl₃): δ 7.67 (dd, J = 1.7, 7.7 Hz, 4H), 7.41 (m, 6H), 3.46 (dd, J = 9.8, 5.1 Hz, 1H), 3.41 (dd, J = 9.8, 6.5 Hz, 1H), 2.87 (q, J = 7.4 Hz, 2H), 2.52 (dd, J = 5.0, 14.3 Hz, 1H), 2.23 (dd, J = 8.8, 14.3 Hz, 1H), 2.10 (m, 1H), 1.72 (m, 1H), 1.49 (m, 1H), 1.35 (m, 1H), 1.25 (t, J = 7.4 Hz, 3H), 1.21 (m, 1H), 1.06 (s, 12H), 0.94 (d, J = 6.7 Hz, 3H), 0.92 (m, 2H), 0.91 (d, J = 6.5 Hz, 3H), 0.84 (d, J = 6.5 Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 199.22 (s), 135.60 (d), 134.03 (s), 129.47 (d), 127.54 (d), 68.74 (t), 50.93 (t), 44.71 (t), 41.18 (t), 33.08 (d), 28.59 (d), 27.61 (d), 26.88 (q), 23.24 (t), 20.53 (q), 20.46 (q), 19.29 (s), 17.98 (q), 14.80 (q), 13.00 (q). MS(EI+) for C₂₉H₄₄O₂SSi: m/z(%) = 427 (100%, M – t-Butyl), MS(CI+) for C₂₉H₄₄O₂SSi: m/z(%) = 502 (100%, M + NH₄⁺). HRMS(EI+) for C₂₉H₄₄O₂SSi: m/z(%) = 427 (100%, M – t-Butyl), Measured Mass: 427.2142 Da, Calculated Mass: 427.2127 Da.

(5S,7R,9R)-10-(tert-Butyl-diphenyl-silanyloxy)-5,7,9-trimethyl-dec-2-enethioic acid S-ethyl ester (23)

To a stirred mixture of 21 (1.500 g, 3.099 mmol) and 10% Pd-C (5 mol %, 165 mg) in CH₂Cl₂ (6.4 mL) was added 3 equiv of Et₃SiH (1.494 mL, 9.297 mmol) at rt under nitrogen. Stirring was continued at rt until the reduction was completed (10-30 min). The catalyst was filtered off through a Celite pad and washed with the solvent of the reaction. The filtrate was concentrated under reduced pressure and purified by flash chromatography to give aldehyde 22 which was used in the next step without complete removal of the eluent. A solution of aldehyde 22 and Ph₃PCHCOSEt (1.466 g, 4.029 mmol) in CH₂Cl₂ (32 mL) was refluxed for 24 h. The solution was concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford α,β-unsaturated thioester 23 as a colourless oil (1.102 g, 70 % yield over 2 steps, [α]D = +8.2 (c = 0.828, CHCl₃)). 1H-NMR (400 MHz, CDCl₃): δ 7.67 (dd, J = 7.9, 1.6 Hz, 4H), 7.40 (m, 6H), 6.86 (dt, J = 15.5, 8.0 Hz, 1H), 6.09 (dt, J = 15.5, 1.4 Hz, 1H), 3.51 (dd, J = 9.8, 5.2 Hz, 1H), 3.42 (dd, J = 9.8, 6.4 Hz, 1H), 2.95 (q, J = 7.4 Hz, 2H), 2.21 (m, 1H), 1.90 (m, 1H), 1.72 (m, 1H), 1.52 (m, 1H), 1.36 (m, 1H), 1.29 (t, J = 7.4 Hz, 3H), 1.21 (m, 1H), 1.07 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H), 0.91 (m, 2H), 0.86 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.5 Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 189.96 (s), 144.17 (d), 135.59 (d), 134.03 (s), 129.83 (d), 129.47 (d), 127.53 (d), 68.76 (t), 44.78 (t), 41.24 (t), 39.10 (t), 33.14 (d), 29.90 (d), 27.61 (d), 26.88 (q), 23.01 (t), 20.70 (q), 20.42 (q), 19.30 (s), 17.97 (q), 14.81 (q). MS(EI+) for C₃₁H₄₆O₂SSi: m/z(%) = 453 (100%, M – t-Butyl), MS(CI+) for C₃₁H₄₆O₂SSi: m/z(%) = 528 (100%, M + NH₄⁺). HRMS(EI+) for C₃₁H₄₆O₂SSi: m/z(%) = 453 (100%, M – t-Butyl), Measured Mass: 453.2264 Da, Calculated Mass: 453.2284 Da.
(+)-(3S,5S,7R,9R)-10-(tert-Butyl-diphenyl-silanyloxy)-3,5,7,9-tetramethyl-decanethioic acid S-ethyl ester (8)

(S,R_e)-Josiphos (5).CuBr complex (15.9 mg, 0.022 mmol, 1 mol%) was dissolved in t-BuOMe (13.6 mL) under nitrogen. The mixture was cooled to −75 °C and methylmagnesium bromide (2.593 mmol, solution in diethyl ether) was added dropwise. After stirring for 10 min, a solution of thioster 23 (1.102 g, 2.161 mmol) in t-BuOMe (3.9 mL) was added via syringe pump over 1 h. The reaction mixture was stirred at −75 °C for 17 h, then quenched by the addition of MeOH and allowed to warm to room temperature. Saturated aqueous NH₄Cl solution was then added. After phase separation and extraction of the aqueous phase with 3 portions of diethyl ether, the combined organic phases were dried over MgSO₄, concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford 8 as a colourless oil (1.010 mg, 88% yield, syn/anti by NMR = >96/4, d.r.calculated from syn/anti ratio = (3S,5S,7R,9R):(3S,5S,7R,9R):(3S,5S,7S,9R):(3S,5S,7S,9S) = 94:1:2:2, diastereoisomers smaller than 0.04 were neglected [α]D = +6.7 (c = 1.14, CHCl₃)).

1H-NMR (400 MHz, CDCl₃): δ 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.41 (m, 6H), 3.53 (dd, J = 9.8, 5.0 Hz, 1H), 3.43 (dd, J = 9.8, 6.4 Hz, 1H), 2.88 (q, J = 7.4 Hz, 2H), 2.56 (dd, J = 14.3 Hz, J = 5.0 Hz, 1H), 2.26 (dd, J = 14.3, 8.8 Hz, 1H), 2.12 (m, 1H), 1.74 (m, 1H), 1.54 (m, 2H), 1.38 (m, 1H), 1.26 (t, J = 7.4 Hz, 3H), 1.20 (m, 2H), 1.17 (s, 9H), 0.95 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.89 (m, 3H), 0.85 (d, J = 6.5 Hz, 3H), 0.82 (d, J = 6.5 Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 199.24 (s), 135.61 (d), 134.04 (s), 129.44 (d), 127.52 (d), 68.69 (t), 50.93 (t), 45.48 (t), 44.46 (t), 41.15 (t), 33.16 (d), 28.63 (d), 27.55 (d), 27.43 (d), 26.88 (q), 23.25 (t), 20.92 (q), 20.75 (q), 20.55 (q), 19.30 (s), 18.18 (q). MS(EI+) for C₃₂H₅₀O₂SSi: m/z(%) = 469 (100%, M – tert-Butyl), MS(CI+) for C₃₂H₅₀O₂SSi: m/z(%) = 544 (100%, M + NH₄⁺). HRMS(EI+) for C₃₂H₅₀O₂SSi : m/z(%) = 469 (100%, M – tert-Butyl), Measured Mass: 469.2590 Da, Calculated Mass: 469.2597 Da.

1H-NMR (400 MHz, CDCl₃): 1H-NMR (400 MHz, CDCl₃): δ 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.41 (m, 6H), 3.53 (dd, J = 9.8, 5.0 Hz, 1H), 3.43 (dd, J = 9.8, 6.4 Hz, 1H), 2.88 (q, J = 7.4 Hz, 2H), 2.56 (dd, J = 14.3 Hz, J = 5.0 Hz, 1H), 2.26 (dd, J = 14.3, 8.8 Hz, 1H), 2.12 (m, 1H), 1.74 (m, 1H), 1.54 (m, 2H), 1.38 (m, 1H), 1.26 (t, J = 7.4 Hz, 3H), 1.20 (m, 2H), 1.17 (s, 9H), 0.95 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.89 (m, 3H), 0.85 (d, J = 6.5 Hz, 3H), 0.82 (d, J = 6.5 Hz, 3H). 13C-NMR (100.6 MHz, CDCl₃): 199.24 (s), 135.61 (d), 134.04 (s), 129.44 (d), 127.52 (d), 68.69 (t), 50.93 (t), 45.48 (t), 44.46 (t), 41.15 (t), 33.16 (d), 28.63 (d), 27.55 (d), 27.43 (d), 26.88 (q), 23.25 (t), 20.92 (q), 20.75 (q), 20.55 (q), 19.30 (s), 18.18 (q). MS(EI+) for C₃₂H₅₀O₂SSi: m/z(%) = 469 (100%, M – tert-Butyl), MS(CI+) for C₃₂H₅₀O₂SSi: m/z(%) = 544 (100%, M + NH₄⁺). HRMS(EI+) for C₃₂H₅₀O₂SSi : m/z(%) = 469 (100%, M – tert-Butyl), Measured Mass: 469.2590 Da, Calculated Mass: 469.2597 Da.

To a stirred mixture of 8 (99.0 mg, 0.188 mmol) in THF (3 mL) was added DIBAL-H (0.388 mL, 0.388 mmol, 1.0 M solution in CH₂Cl₂) at -20 °C under nitrogen. Stirring was continued until the reduction was completed (3-4 h). The reaction mixture was quenched in 30 mL saturated Rochelle solution (potassium sodium tartrate) and stirred for 30 min. The phases were separated and the aqueous layer was extracted with three portions of 30 mL CH₂Cl₂. The combined organic phases were dried over MgSO₄ and concentrated under reduced pressure to yield crude aldehyde. The above reduction/work-up was repeated to yield crude alcohol 9 as a colourless oil which was purified by flash chromatography (eluent pentane/ether 40:1) to afford 9 as a colourless oil (83.2 mg, 95% yield, [α]D = +3.9 (c = 1.17, CHCl₃)). 1H-NMR (400 MHz, CDCl₃): δ 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.41 (m, 6H), 3.68 (m, 2H), 3.43 (dd, J = 9.8, 5.0 Hz, 1H), 3.44 (dd, J = 9.8, 6.5 Hz, 1H), 1.79 – 1.15 (m, 10H), 1.08 (s, 9H), 0.97 – 0.82 (m, 15H). 13C-NMR (100.6 MHz, CDCl₃): 135.60, 135.58 (d), (134.06, 134.02) (s), (129.44, 129.42) (d), 127.51 (d), 68.65 (t), 61.19 (t), 45.60 (t), 45.14 (t), 41.14 (t), 39.37 (t), 33.14 (d), 27.54 (d), 27.31 (d), 26.91 (d), 26.86 (q), 20.96 (q), 20.92 (q), 20.54 (q), 19.29 (s), 18.19 (q). MS(EI+) for C₃₀H₄₈O₂Si: m/z(%) = 411 (16%, M – tert-Butyl), MS(Cl+) for C₃₀H₄₈O₂Si: m/z(%) = 586 (100%, M + NH₄⁺). HRMS(El+) for C₃₀H₄₈O₂Si : m/z(%) = 411 (100%, M – tert-Butyl), Measured Mass: 411.2699 Da, Calculated Mass: 411.2719 Da.
To a stirred mixture of 9 (356 mg, 0.761 mmol) and pyridine (0.123 mL, 1.521 mmol) in CH2Cl2 (5 mL) was added tosyl chloride (290 mg, 1.521 mmol) at rt under nitrogen, and the mixture was stirred for 24 h. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 9:1) to afford 10 as a colourless oil (452 mg, 95% yield, [α]D = +3.9 (c = 1.17, CHCl3)).

1H-NMR (400 MHz, CDCl3): δ 7.80 (d, J = 8.3 Hz, 2H), 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.39 (m, 8H), 4.07 (m, 2H), 3.52 (dd, J = 9.8, 5.0 Hz, 1H), 3.43 (dd, J = 9.8, 6.4 Hz, 1H), 2.44 (s, 3H), 1.73 (m, 2H), 1.61 (m, 1H), 1.49 (m, 2H), 1.33 (m, 2H), 1.18 (m, 2H), 1.06 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H), 0.84 (m, 12H).

13C-NMR (100.6 MHz, CDCl3): 144.53 (s), (135.58, 135.56) (d), (134.03, 133.99) (s), 133.25 (s), 129.74 (d), (129.44, 129.43) (d), 127.82 (d), 127.50 (d), 69.05 (t), 68.63 (t), 45.39 (t), 44.65 (t), 41.07 (t), 35.14 (t), 33.12 (t), 27.49 (d), 27.17 (d), 26.65 (q), 26.58 (d), 21.58 (q), 20.91 (q), 20.77 (q), 19.98 (q), 19.27 (s), 18.17 (q). MS(EI+) for C37H54O4SSi: m/z(%) = 565 (4.6%, M – t-Butyl), MS(CI+) for C37H54O4SSi: m/z(%) = 640 (100%, M + NH4+).

HRMS(EI+) for C37H54O4SSi: m/z(%) = 565 (100%, M – t-Butyl), Measured Mass: 565.2792 Da, Calculated Mass: 565.2808 Da.

The Grignard reagent was freshly prepared as a 0.20 M solution in THF. Octadecyl bromide (400 mg, 1.20 mmol) in THF (3.0 mL) was added to a stirred solution of activated (iodine) magnesium turnings (43.7 mg, 1.80 mmol) and crushed glass in THF (3.0 mL). After 1 h at 45 °C the reaction mixture was cooled to rt and 0.5 ml of the Grignard solution was titrated by using sec-BuOH and catalytic amounts of 1,10-phenanthroline. To a stirred mixture of 10 (100 mg, 0.161 mmol) and CuBr.SMe2 (6.6 mg, 0.032 mmol, 20 mol%) in THF (2 mL) was added C18H37MgBr (2.415 mL, 0.483 mmol, 0.2 M) at 0 °C under nitrogen. The reaction mixture was warmed to rt and stirred for 24 h. After quenching with 2.0 mL of saturated NH4Cl solution, 5 ml of diethyl ether was added. The phases were separated and the aqueous layer was extracted with three portions of 10 mL diethyl ether. The combined organic phases were dried over MgSO4 and concentrated under reduced pressure to yield crude 11, which was purified by flash chromatography (eluent pentane) to afford 11 as a colourless oil (91 mg, 80% yield, [α]D = +4.3 (c = 1.03, CHCl3)).

1H-NMR (400 MHz, CDCl3): δ 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.40 (m, 6H), 3.52 (dd, J = 9.8, 5.0 Hz, 1H), 3.42 (dd, J = 9.8, 6.4 Hz, 1H), 1.80 – 1.10 (m, 45H), 1.06 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H), 0.92 – 0.78 (m, 15H).

13C-NMR (100.6 MHz, CDCl3): (135.64, 135.62) (d), (134.13, 134.10) (s), 129.43 (d), 127.25 (d), 66.74 (t), 45.78 (t), 45.08 (t), 41.26 (t), 36.43 (t), 33.19 (d), 31.94 (t), 30.07 (t), 29.99 (d), 29.77 (t), 29.71 (12*C), 29.67 (t), 29.37 (t), 27.63 (d), 27.44 (d), 26.89 (q), 22.70 (t), 21.09 (q), 20.99 (q), 20.61 (q), 19.31 (s), 18.17 (q). MS(EI+) for C48H84OSi: m/z(%) = 647 (88.5%, M – t-Butyl), MS(CI+) for C48H84OSi: m/z(%) = 647 (100%, M + NH4+).

HRMS(EI+) for C48H84OSi: m/z(%) = 647 (100%, M – t-Butyl), Measured Mass: 647.5609 Da, Calculated Mass: 647.5587 Da.

The Grignard reagent was freshly prepared as a 0.20 M solution in THF. Octadecyl bromide (400 mg, 1.20 mmol) in THF (3.0 mL) was added to a stirred solution of activated (iodine) magnesium turnings (43.7 mg, 1.80 mmol) and crushed glass in THF (3.0 mL). After 1 h at 45 °C the reaction mixture was cooled to rt and 0.5 ml of the Grignard solution was titrated by using sec-BuOH and catalytic amounts of 1,10-phenanthroline. To a stirred mixture of 10 (100 mg, 0.161 mmol) and CuBr.SMe2 (6.6 mg, 0.032 mmol, 20 mol%) in THF (2 mL) was added C18H37MgBr (2.415 mL, 0.483 mmol, 0.2 M) at 0 °C under nitrogen. The reaction mixture was warmed to rt and stirred for 24 h. After quenching with 2.0 mL of saturated NH4Cl solution, 5 ml of diethyl ether was added. The phases were separated and the aqueous layer was extracted with three portions of 10 mL diethyl ether. The combined organic phases were dried over MgSO4 and concentrated under reduced pressure to yield crude 11, which was purified by flash chromatography (eluent pentane) to afford 11 as a colourless oil (91 mg, 80% yield, [α]D = +4.3 (c = 1.03, CHCl3)).

1H-NMR (400 MHz, CDCl3): δ 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.40 (m, 6H), 3.52 (dd, J = 9.8, 5.0 Hz, 1H), 3.42 (dd, J = 9.8, 6.4 Hz, 1H), 1.80 – 1.10 (m, 45H), 1.06 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H), 0.92 – 0.78 (m, 15H).

13C-NMR (100.6 MHz, CDCl3): (135.64, 135.62) (d), (134.13, 134.10) (s), 129.43 (d), 127.25 (d), 66.74 (t), 45.78 (t), 45.08 (t), 41.26 (t), 36.43 (t), 33.19 (d), 31.94 (t), 30.07 (t), 29.99 (d), 29.77 (t), 29.71 (12*C), 29.67 (t), 29.37 (t), 27.63 (d), 27.44 (d), 26.89 (q), 22.70 (t), 21.09 (q), 20.99 (q), 20.61 (q), 19.31 (s), 18.17 (q). MS(EI+) for C48H84OSi: m/z(%) = 647 (88.5%, M – t-Butyl), MS(CI+) for C48H84OSi: m/z(%) = 647 (100%, M – t-Butyl), Measured Mass: 647.5609 Da, Calculated Mass: 647.5587 Da.
To a stirred mixture of 11 (135 mg, 0.192 mmol) in THF (1 mL) was added TBAF (0.384 mL, 0.384 mmol, 1.0 M solution in THF) at rt under nitrogen, and the mixture was stirred for 5 h. The reaction mixture was concentrated under reduced pressure and purified by chromatography (eluent pentane/pentan-2-one 10:1) to afford 12 as a white solid (80 mg, 90% yield, [α]D = +5.94 (c = 1.21, CHCl3)). 1H-NMR (400 MHz, CDCl3): δ ppm 3.55 (dd, J = 10.5, 4.9 Hz, 1H), 3.37 (dd, J = 10.5, 6.9 Hz, 1H), 1.78 – 1.73 (m, 2H), 1.62 – 1.57 (m, 2H), 1.51 – 1.42 (m, 2H), 1.34 – 1.16 (m, 41H), 1.05 – 0.82 (m, 18H). 13C-NMR (100.6 MHz, CDCl3): 68.20 (t), 45.52 (t), 45.04 (t), 41.07 (t), 36.43 (t), 33.10 (d), 31.92 (t), 30.06 (t), 29.99 (d), 29.70 (13*C), 29.36 (t), 27.56 (d), 27.46 (d), 26.86 (t), 22.69 (t), 21.04 (q), 21.06 (q), 20.59 (q), 17.65 (q), 14.11 (q). MS(CI+) for C32H66O: m/z(%) = 484 (100%, M + NH4+). HRMS(EI+) for C32H66O : m/z(%) = 448 (100%, M – H2O), Measured Mass: 448.5003 Da, Calculated Mass: 448.5008 Da.

(--(2R,4R,6R,8R)-Tetramethyl-octacosanoic acid (1)/ mycocerosic acid

To a stirred mixture of 12 (19 mg, 0.041 mmol) in 0.3 mL CCl4, 0.3 mL CH3CN and 0.6 mL H2O was added RuCl3.(H2O)x (1.0 mg, 0.005 mmol) and NaIO4 (37 mg, 0.172 mmol) at rt under nitrogen. After 3 h the reaction mixture was poured in 2 mL CH2Cl2 and 0.5 mL water was added. The phases were separated and the aqueous layer was extracted with three portions of 5 mL CH2Cl2. The combined organic phases were dried over MgSO4 and concentrated under reduced pressure to yield crude 1, which was purified by flash chromatography (eluent pentane/diethyl ether 9:1) to afford 1 as a white solid (16.7 mg, 85% yield, the product did not contain other diasteroisomers by 13C-NMR, most probably due to chromatography steps. [α]D = -6.4 (c = 0.94, CHCl3), literature value4 for the product isolated from mycobacterium tuberculosis: [α]D = -5.62 (c = 8.9, CHCl3)). 1H-NMR (400 MHz, CDCl3): δ ppm 2.56 (m, 1H), 1.76 (m, 1H), 0.97 – 1.80 (m, 45H), 0.78 – 0.95 (m, 17H) ppm. 13C-NMR (100.6 MHz, CDCl3): 182.87 (s), 45.34 (t), 45.31 (t), 40.86 (t), 37.19 (d), 36.64 (t), 31.92 (t), 30.05 (t), 29.93 (d), 29.75 (t), 29.70 (12*C), 29.35 (t), 28.13 (d), 27.21 (d), 26.91 (t), 22.68 (t), 20.59 (q), 20.44 (q), 20.40 (q), 18.08 (q), 14.10 (q). MS(EI+) for C32H64O2 : m/z(%) = 480 (63%) (M). HRMS(EI+) calcd for C32H64O2: 480.4906, found: 480.4904.

A small sample (1 mg) was converted into the methyl ester of 1 (treatment with trimethylsilyldiazomethane) for mass analysis to compare with literature values5, MS(EI+) for C33H66O2 : m/z(%) = 494 (35%, M). See spectral supporting info for fragmentation details. Mass analysis matched with literature5.

(+-)(2R,4R,6R,8R)-tert-Butyl-diphenyl-(2,4,6,8-tetramethyl-decyloxy)-silane (13)

To a stirred mixture of 10 (46 mg, 0.074 mmol) in THF (1.5 mL) was added LiAlH4 (14.0 mg, 0.370 mmol) at rt under nitrogen. After 24 h the reaction mixture was quenched with MeOH and 1.0 mL of 1 M HCl solution and 2.0 mL diethyl ether were added. The phases were separated and the aqueous layer was extracted with three portions of 3 mL diethyl ether. The combined organic phases were dried over MgSO4 and concentrated under reduced pressure to yield crude 13, which was purified by flash chromatography (eluent pentane/diethyl ether 9:1) to afford 13 as a colourless oil (30 mg, 90% yield, [α]D = +4.73 (c = 0.93, CHCl3)). 1H-NMR (400 MHz, CDCl3): δ ppm 7.68 (dd, J = 7.8, 1.6 Hz, 4H), 7.41 (m, 6H), 3.53 (dd, J = 9.8, 5.0 Hz, 1H), 3.43 (dd, J = 9.8, 6.4 Hz, 1H), 1.75 (m, 1H), 1.54 (m, 2H), 1.39 (m, 3H), 1.22 (m, 3H), 1.07 (s, 9H), 0.95 (d, J = 6.7 Hz, 3H), 0.86 (m, 15H). 13C-NMR (100.6 MHz, CDCl3): (135.64, 135.62) (d), (134.11, 134.08) (s), 129.44 (d), 127.53 (d), 68.70 (t), 45.79 (q), 45.07 (t), 31.92 (t), 30.05 (t), 29.93 (d), 29.75 (t), 29.70 (12*C), 29.35 (t), 28.13 (d), 27.21 (d), 26.91 (t), 22.68 (t), 20.59 (q), 20.44 (q), 20.40 (q), 18.08 (q), 14.10 (q). MS(EI+) for C32H48O2: m/z(%) = 480 (63%) (M). HRMS(EI+) calcd for C32H48O2: 480.4906, found: 480.4904.
HRMS(EI+) for C\textsubscript{30}H\textsubscript{48}O\textsubscript{2}S : m/z(\%) = 395 (100\%, M – t-Butyl), Measured Mass: 395.2779 Da, Calculated Mass: 395.2770 Da.

(+)-(2\textit{R},4\textit{R},6\textit{R},8\textit{R})-Tetramethyl-decan-1-ol (14)

To a stirred mixture of 13 (82 mg, 0.181 mmol) in THF (2 mL) was added TBAF (0.363 mL, 0.363 mmol, 1.0 M solution in THF) at rt under nitrogen, and the mixture was stirred for 3 h. The reaction mixture was concentrated under reduced pressure and purified by column flash chromatography (eluent pentane/diethyl ether 9:1) to afford 14 as a white solid (33.4 mg, 86\% yield, [\alpha]_D = +6.4 (c = 1.093, CHCl\textsubscript{3})). \textsuperscript{1}\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \delta ppm 3.53 (dd, J = 10.4, 4.9 Hz, 1H), 3.36 (dd, J = 10.4, 6.9 Hz, 1H), 1.73 (m, 1H), 1.57 (m, 2H), 1.47 – 1.14 (m, 6H), 1.04 (m, 2H), 0.97 – 0.78 (m, 17H). \textsuperscript{13}C-NMR (100.6 MHz, CDCl\textsubscript{3}): 68.13 (t), 45.51 (t), 44.54 (t), 41.02 (t), 33.07 (d), 31.51 (d), 28.73 (t), 27.51 (d), 27.42 (d), 21.03 (q), 20.98 (q), 20.02 (q), 17.64 (q), 11.12 (q).

MS(CI+) for C\textsubscript{14}H\textsubscript{30}O: m/z(\%) = 232 (100\%, M + NH\textsubscript{4}\textsuperscript{+}).

HRMS(EI+) for C\textsubscript{14}H\textsubscript{30}O: m/z(\%) = 196 (100\%, M – H\textsubscript{2}O), Measured Mass: 196.2191 Da, Calculated Mass: 196.2191 Da.

(-)-(2\textit{R},4\textit{R},6\textit{R},8\textit{R})-Tetramethyl-decanoic acid (15)

To a stirred mixture of 14 (8.0 mg, 0.037 mmol) in 0.080 mL CCl\textsubscript{4}, 0.080 mL CH\textsubscript{3}CN and 0.115 mL H\textsubscript{2}O was added RuCl\textsubscript{3}(H\textsubscript{2}O)\textsubscript{x} (1.0 mg, 0.005 mmol) and NaIO\textsubscript{4} (33.7 mg, 0.150 mmol) at rt under nitrogen. After 3 h the reaction mixture was poured into 5 mL of diethyl ether and 0.5 mL of water was added. The phases were separated and the aqueous layer was extracted with three portions of 5 mL diethyl ether. The combined organic phases were dried over MgSO\textsubscript{4} and concentrated under reduced pressure to yield crude 15, which was purified by flash chromatography (eluent pentane/diethyl ether 9:1) to afford 15 as a white solid (7 mg, 82\% yield, [\alpha]\textsubscript{29}D = -27.8 (c = 0.69, CHCl\textsubscript{3})), lit: Negishi \textit{et al.}\textsuperscript{6} [\alpha]\textsubscript{23}D = -25.1 (c = 0.2, CHCl\textsubscript{3}).

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \delta ppm 2.59 (m, 1H), 1.75 (m, 1H), 1.57 (m, 2H), 1.47 – 1.00 (m, 8H), 0.99 – 0.78 (m, 15H).

\textsuperscript{13}C-NMR (100.6 MHz, CDCl\textsubscript{3}): 182.95 (s), 45.41 (t), 44.85 (t), 40.88 (t), 37.21 (d), 31.53 (d), 28.98 (t), 28.16 (d), 27.25 (t), 20.60 (t), 18.09 (q), 11.18 (q).

HRMS(EI+) for C\textsubscript{14}H\textsubscript{28}O\textsubscript{2}: m/z(\%) = 228 (19\%, M), Measured Mass: 228.2100 Da, Calculated Mass: 228.2089 Da.

Spectroscopic data (\textsuperscript{1}H, \textsuperscript{13}C-NMR) corresponded with literature\textsuperscript{6} and no diastereoisomers were observed in comparison with \textsuperscript{13}C-NMR data\textsuperscript{6}, probably due to chromatography steps.


$^1$H-NMR

$^{13}$C-NMR and APT
$^1$H-NMR

$^1$H-NMR and APT

$^{13}$C-NMR and APT
$^1$H-NMR

\[
\begin{align*}
\text{Si-O-} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} \\
\text{CH}_3 & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} \\
\text{CH}_2 & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} \\
\text{CH}_3 & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} \\
\text{Si} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} \\
\text{O} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} & \quad \text{---} \\
\end{align*}
\]

$^{13}$C-NMR and APT
$^1$H-NMR

13C-NMR and APT
$^1$H-NMR

$^{13}$C-NMR and APT
$^{1}$H-NMR

![H-NMR spectrum]

$^{13}$C-NMR and APT

![13C-NMR and APT spectra]
$^1$H-NMR

$^{13}$C-NMR and APT
$^1$H-NMR

$^{13}$C-NMR and APT
$^{13}$C-NMR and APT

$^{1}$H-NMR
$^{1}H$-NMR

\[
\text{Structure Image}
\]

$^{13}C$-NMR and APT

\[
\text{Spectra Image}
\]
$^{1}H$-NMR

$^{13}C$-NMR and APT
$^1$H-NMR

$^{13}$C-NMR and APT
$^1$H-NMR

$^{13}$C-NMR and APT
$^{1}H$-NMR

$^{13}C$-NMR and APT
File: K6021411
Sample: TER HORST/BTH 120
Instrument: JEOL JMS600
Inlet: My Inlet

Date Run: 02-15-2006
Ionization mode: EI+

Time Run: 03:08:39
Run By: RUG
Printed by: RUG

Scan: 105
Base: m/z 87; 4.5%FS TIC: 498368

R.T.: 4:26.3

#Ions: 208
Date Run: 02-15-2006
Time Run: 03:08:39
Ionization mode: EI+
R.T.: 4:26:3

#Ions: 208
$^{1}$H-NMR

\[
\text{\begin{tikzpicture}
  \path[use as bounding box] (0,0) rectangle (3,2);
  \draw[thick] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
  \draw[thick] (1,0) -- (2,0) -- (2,1) -- (1,1) -- cycle;
  \draw[thick] (2,0) -- (3,0) -- (3,1) -- (2,1) -- cycle;
  \draw[thick] (0,1) -- (1,1) -- (1,2) -- (0,2) -- cycle;
  \draw[thick] (1,1) -- (2,1) -- (2,2) -- (1,2) -- cycle;
  \draw[thick] (2,1) -- (3,1) -- (3,2) -- (2,2) -- cycle;
\end{tikzpicture}}
\]

$^{13}$C-NMR and APT
$^1$H-NMR

$^{13}$C-NMR and APT
$^1$H-NMR

$^{13}$C-NMR and APT