SUPPORTING INFORMATION

Catalytic asymmetric synthesis of mycocerosic acid

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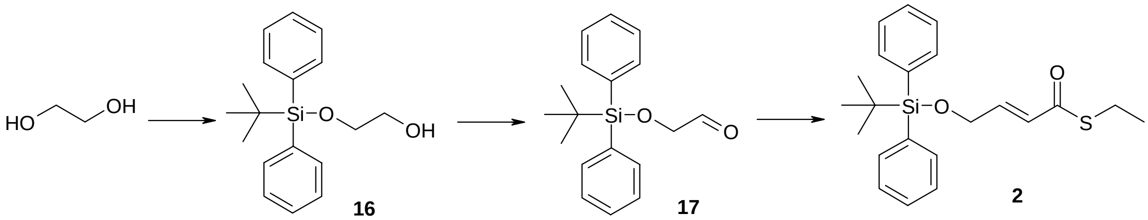
General Procedures:

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. $CuBr{\cdot}SMe_2$ 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), H_2O (500 mL) and H_2SO_4 (25mL).

Mass spectra were recorded on a AEI-MS-902 mass spectrometer. ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400, 100.59 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). 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.

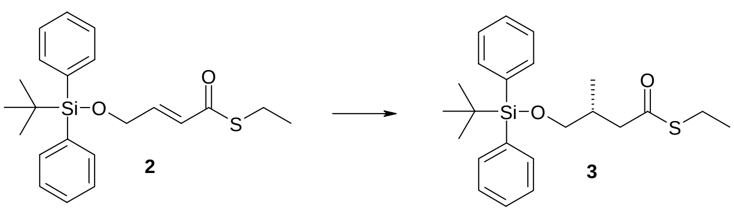
Experimental:



16 17 2

(*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 $MgSO_4$, 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 $Ph_3PCHCOSEt$ (13.99 g, 38.42 mmol) in CH_2Cl_2 (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 (9.078 g, 80% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.6, 1.2 Hz, 4H), 7.42 (m, 6H), 6.90 (dt, *J* = 15.2, 3.2 Hz, 1H), 6.55 (dt, *J* = 14.8, 2.4 Hz, 1H), 4.35 (m, 2H), 2.98 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.09 (s, 9H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 190.07 (s), 142.70 (d), 135.40 (d), 132.86 (s), 129.86 (d), 127.80 (d), 126.73 (d), 62.77 (t), 26.74 (q), 23.18 (t), 19.24 (s), 14.76 (q). MS(EI+) for $C_{22}H_{28}O_2SSi$: m/z(%) = 327 (71%, M – *t*-Butyl), 384 (100%, M). HRMS(EI+) for $C_{22}H_{28}O_2SSi$: m/z(%) = 327 (100%, M – *t*-Butyl), Measured Mass: 327.0875 Da, Calculated Mass: 327.0875 Da.

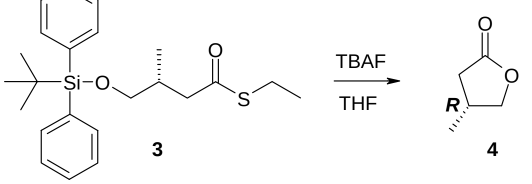


2 3

(*R*)-4-(tert-Butyl-diphenyl-silanyloxy)-3-methyl-thiobutyric acid S-ethyl ester (3)

(*S*,R_{Fe})-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 NH_4Cl 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 $MgSO_4$, concentrated under reduced pressure and purified by flash chromatography (eluent pentane/ether 40:1) to afford **3** as a colourless oil (2.968 g, 95 % yield, 98% ee, $[\alpha]_D$ = +8.0 (*c* = 1.2, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 6.8, 1.4 Hz, 4H), 7.41 (m, 6H), 3.55 (dd, *J* = 10.0, 5.3 Hz, 1H), 3.46 (dd, *J* = 9.9, 6.3 Hz, 1H), 2.88 (q, *J* = 7.4 Hz, 2H), 2.83 (dd, *J* = 14.5, 5.3 Hz, 1H), 2.38 (dd, *J* = 14.5, 8.4 Hz, 1H), 2.28 (m, 1H), 1.25 (t, *J* = 7.4 Hz, 3H), 1.15 (s, 9H), 0.98 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 199.08 (s), 135.57 (d), 133.63 (s), 129.58 (d), 127.50 (d), 67.90 (t), 47.75 (t), 33.76 (d), 26.84 (q), 23.27 (t), 19.28 (s), 16.40 (q), 14.77 (q). MS(EI+) for $C_{23}H_{32}O_2SSi$: m/z(%) = 343 (100%, M – *t*-Butyl), MS(CI+) for $C_{23}H_{32}O_2SSi$: m/z(%) = 418 (37.5%, M + NH_4^+), 401 (100%, M + H^+). HRMS(EI+) for $C_{23}H_{32}O_2SSi$: m/z(%) = 343 (100%, M – *t*-Butyl), Measured Mass: 343.1183 Da, Calculated Mass: 343.1188 Da.

E.e. and absolute configuration were determined by removal of the tert-butyldiphenylsilyl group resulting in lactone **4**. The absolute configuration of lactone **4** has been previously reported[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.]

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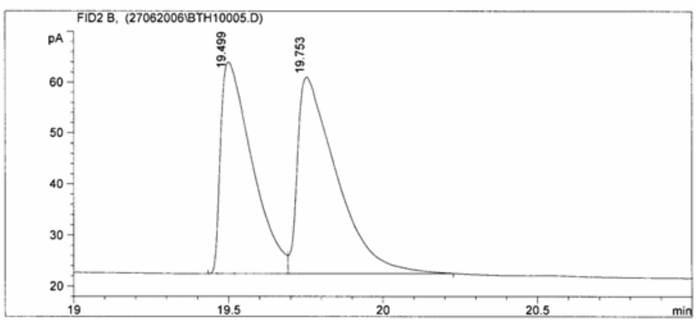

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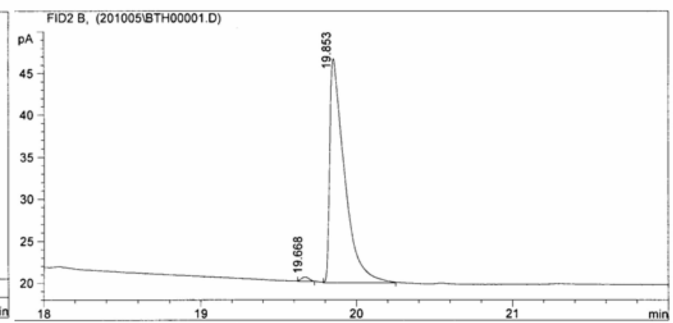

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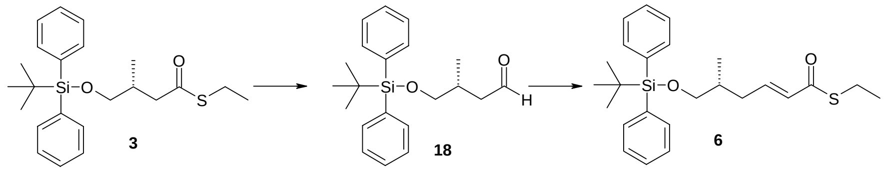
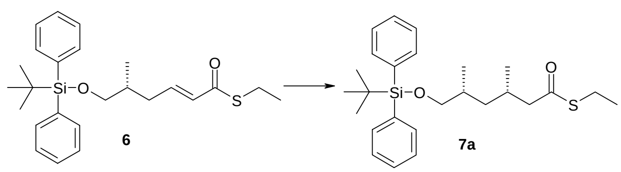


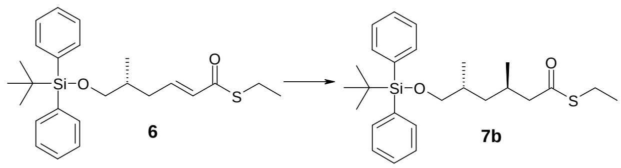
(+)-(*E*)-(*R*)-6-(tert-Butyl-diphenyl-silanyloxy)-5-methyl-hex-2-enethioic acid S-ethyl ester (6).

To a stirred mixture of **3** (2.0 g, 5 mmol) and 10% Pd-C (5 mol%, 267 mg) in CH_2Cl_2 (10 mL) was added 3 equiv of Et_3SiH (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 CH_2Cl_2. 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 $Ph_3PCHCOSEt$ (2.366 g, 6.50 mmol) in CH_2Cl_2 (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, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 $C_{25}H_{34}O_2SSi$: m/z(%) = 369 (100%, M – *t*-Butyl), MS(CI+) for $C_{25}H_{34}O_2SSi$: m/z(%) = 444 (100%, M + NH_4^+), 427 (1.5%, M + H^+). HRMS(EI+) for $C_{25}H_{34}O_2SSi$: m/z(%) = 369 (100%, M – *t*-Butyl), Measured Mass: 369.1331 Da, Calculated Mass: 369.1345 Da.



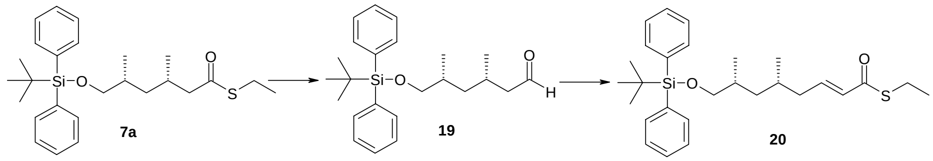
(+)-(3*S*,5*R*)-6-(tert-Butyl-diphenyl-silanyloxy)-3,5-dimethyl-hexanethioic acid S-ethyl ester (7a)

(*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 NH_4Cl 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 $MgSO_4$, 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 = (3*S*,5*R*):(3*R*,5*R*):(3*S*,5*S*):(3*R*,5*S*) = 97:2:1:0, $[\alpha]_D$ = +4.61 (*c* = 1.91, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 $C_{26}H_{38}O_2SSi$: m/z(%) = 385 (100%, M – *t*-Butyl), MS(CI+) for $C_{26}H_{38}O_2SSi$: m/z(%) = 460 (100%, M + NH_4^+), 443 (12.5%, M + H^+). HRMS(EI+) for $C_{26}H_{38}O_2SSi$: m/z(%) = 385 (100%, M – *t*-Butyl), Measured Mass: 385.1668 Da, Calculated Mass: 385.1658 Da.



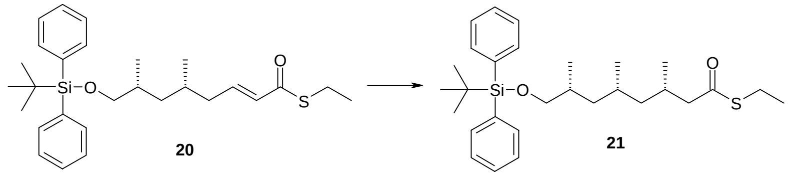
(3*S*,5*S*)-6-(tert-Butyl-diphenyl-silanyloxy)-3,5-dimethyl-hexanethioic acid S-ethyl ester (7b)

(*S*,R_{Fe})-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 NH_4Cl 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 $MgSO_4$, 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, ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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).



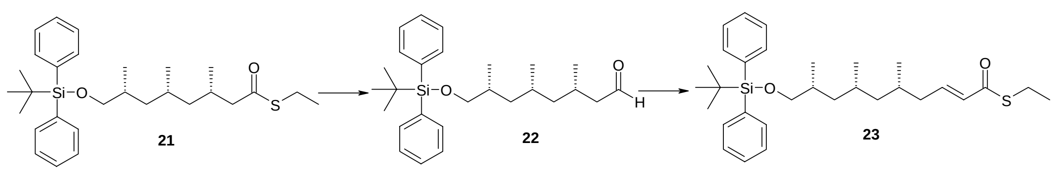
(+)-(*E*)-(5*R*,7*R*)-8-(tert-Butyl-diphenyl-silanyloxy)-5,7-dimethyl-oct-2-enethioic acid S-ethyl ester (20)

To a stirred mixture of **7a** (290 mg, 0.656 mmol) and 10% Pd-C (5 mol%, 35 mg) in CH_2Cl_2 (1.33 mL) was added 3 equiv of Et_3SiH (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 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 (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 $Ph_3PCHCOSEt$ (287 mg, 0.787 mmol) in CH_2Cl_2 (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, $[\alpha]_D$ = +7.6 (*c* = 1.97, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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), 26.86 (q), 23.01 (t), 20.12 (q), 19.28 (s), 17.59 (q), 14.81 (q). MS(EI+) for $C_{28}H_{40}O_2SSi$: m/z(%) = 411 (100%, M – *t*-Butyl), MS(CI+) for $C_{28}H_{40}O_2SSi$: m/z(%) = 486 (100%, M + NH_4^+). HRMS(EI+) for $C_{28}H_{40}O_2SSi$: m/z(%) = 411 (100%, M – *t*-Butyl), Measured Mass: 411.1812 Da, Calculated Mass: 411.1814 Da.



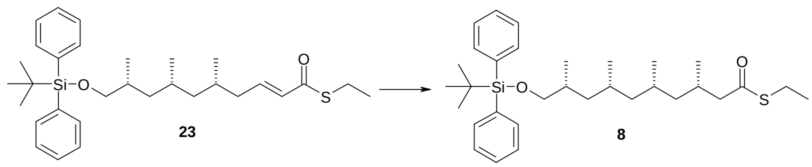
(+)-(3*S*,5*R*,7*R*)8-(tert-Butyl-diphenyl-silanyloxy)-3,5,7-trimethyl-octanethioic acid S-ethyl ester (21)

(S,R_{Fe})-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 NH_4Cl 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 $MgSO_4$, 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 = (3*S*,5*R*,7*R*):(3*R*,5*R*,7*R*):(3*S*,5*S*,7*R*):(3*S*,5*R*,7*S*) = 95:2:2:1, diastereoisomers smaller than 0.04 were neglected, $[\alpha]_D$ = +6.8 (*c* = 1.13, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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). MS(EI+) for $C_{29}H_{44}O_2SSi$: m/z(%) = 427 (100%, M – *t*-Butyl), MS(CI+) for $C_{29}H_{44}O_2SSi$: m/z(%) = 502 (100%, M + NH_4^+). HRMS(EI+) for $C_{29}H_{44}O_2SSi$: m/z(%) = 427 (100%, M – *t*-Butyl), Measured Mass: 427.2142 Da, Calculated Mass: 427.2127 Da.



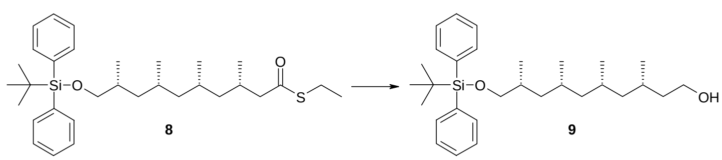
(+)-(*E*)-(5*S*,7*R*,9*R*)-10-(tert-Butyl-diphenyl-silanyloxy)-5,7,9-trimethyl-dec-2-enethioic acid S-ethyl ester (23)

To a stirred mixture of **21** (1.500 g, 3.099 mmol) and 10% Pd-C (5 mol %, 165 mg) in CH_2Cl_2 (6.4 mL) was added 3 equiv of Et_3SiH (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 (eluent pentane/ether 40:1) to give aldehyde **22** which was used in the next step without complete removal of the eluent. A solution of aldehyde **22** and $Ph_3PCHCOSEt$ (1.466 g, 4.029 mmol) in CH_2Cl_2 (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, $[\alpha]_D$ = +8.2 (*c* = 0.828, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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, 2H), 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 $C_{31}H_{46}O_2SSi$: m/z(%) = 453 (100%, M – *t*-Butyl), MS(CI+) for $C_{31}H_{46}O_2SSi$: m/z(%) = 528 (100%, M + NH_4^+). HRMS(EI+) for $C_{31}H_{46}O_2SSi$: m/z(%) = 453 (100%, M – *t*-Butyl), Measured Mass: 453.2264 Da, Calculated Mass: 453.2284 Da.



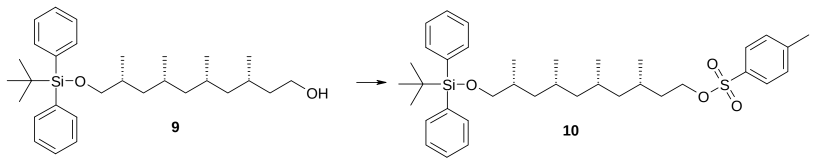
(+)-(3*S*,5*S*,7*R*,9*R*)-10-(tert-Butyl-diphenyl-silanyloxy)-3,5,7,9-tetramethyl-decanethioic acid S-ethyl ester (8)

(*S*,R_{Fe})-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 thioester **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 NH_4Cl 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 $MgSO_4$, 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 = (3*S*,5*S*,7*R*,9*R*):(3*R*,5*S*,7*R*,9*R*):(3*S*,5*R*,7*R*,9*R*):(3*S*,5*S*,7*S*,9*R*):(3*S*,5*S*,7*R*,9*S*) = 94:1:2:2:1, diastereoisomers smaller than 0.04 were neglected $[\alpha]_D$ = +6.7 (*c* = 1.14, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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), 14.81 (q). MS(EI+) for $C_{32}H_{50}O_2SSi$: m/z(%) = 469 (100%, M – *t*-Butyl), MS(CI+) for $C_{32}H_{50}O_2SSi$: m/z(%) = 544 (100%, M + NH_4^+). HRMS(EI+) for $C_{32}H_{50}O_2SSi$: m/z(%) = 469 (100%, M – *t*-Butyl), Measured Mass: 469.2590 Da, Calculated Mass: 469.2597 Da.



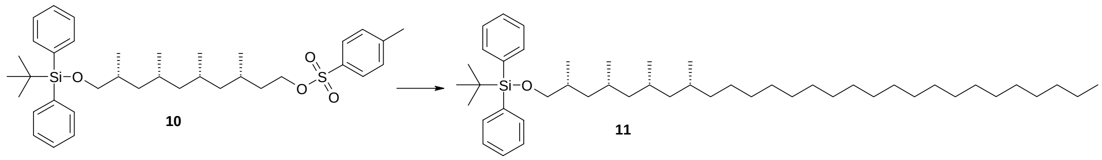
(+)-(3*S*,5*S*,7*R*,9*R*)-10-(tert-Butyl-diphenyl-silanyloxy)-3,5,7,9-tetramethyl-decan-1-ol (9)

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 CH_2Cl_2) 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 CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ 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, $[\alpha]_D$ = +3.9 (*c* = 1.17, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (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 $C_{30}H_{48}O_2Si$: m/z(%) = 411 (16%, M – *t*-Butyl), MS(CI+) for $C_{30}H_{48}O_2Si$: m/z(%) = 586 (100%, M + NH_4^+). HRMS(EI+) for $C_{30}H_{48}O_2Si$: m/z(%) = 411 (100%, M – *t*-Butyl), Measured Mass: 411.2699 Da, Calculated Mass: 411.2719 Da.



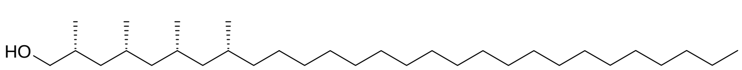
(+)-(3*S*,5*S*,7*R*,9*R*)-Toluene-4-sulfonic acid 10-(tert-butyl-diphenyl-silanyloxy)-3,5,7,9-tetramethyl-decyl ester (10)

To a stirred mixture of **9** (356 mg, 0.761 mmol) and pyridine (0.123 mL, 0.1.521 mmol) in CH_2Cl_2 (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, $[\alpha]_D$ = +3.9 (*c* = 1.17, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 (d), 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 $C_{37}H_{54}O_4SSi$: m/z(%) = 565 (4.6%, M – *t*-Butyl), MS(CI+) for $C_{37}H_{54}O_4SSi$: m/z(%) = 640 (100%, M + NH_4^+). HRMS(EI+) for $C_{37}H_{54}O_4SSi$: m/z(%) = 565 (100%, M – *t*-Butyl), Measured Mass: 565.2792 Da, Calculated Mass: 565.2808 Da.



(+)-(2*R*,4*R*,6*R*,8*R*)tert-Butyl-diphenyl-(2,4,6,8-tetramethyl-octacosyloxy)-silane (11)

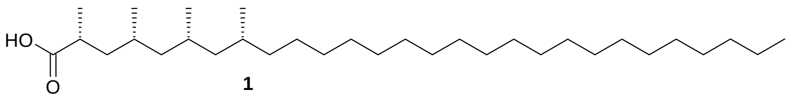
The Grignard reagent was freshly prepared as a 0.20 M solution in THF. Octadecyl bromide (400 mg, 1.20 mmol) in THF (3.0 mL) was added to a stirred solution of activated (iodine) magnesium turnings (43.7 mg, 1.80 mmol) and crushed glass in THF (3.0 mL). After 1 h at 45 °C the reaction mixture was cooled 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 $CuBr.SMe_2$ (6.6 mg, 0.032 mmol, 20 mol%) in THF (2 mL) was added $C_{18}H_{37}MgBr$ (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 NH_4Cl 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 $MgSO_4$ 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, $[\alpha]_D$ = +4.3 (*c* = 1.03, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (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), 14.12 (q) MS(EI+) for $C_{48}H_{84}OSi$: m/z(%) = 647 (88.5%, M – *t*-Butyl), MS(CI+) for $C_{48}H_{84}OSi$: m/z(%) = 722 (100%, M + NH_4^+). HRMS(EI+) for $C_{48}H_{84}OSi$: m/z(%) = 647 (100%, M – *t*-Butyl), Measured Mass: 647.5609 Da, Calculated Mass: 647.5587 Da.



12

(+)-(2*R*,4*R*,6*R*,8*R*)-Tetramethyl-octacosan-1-ol (12)

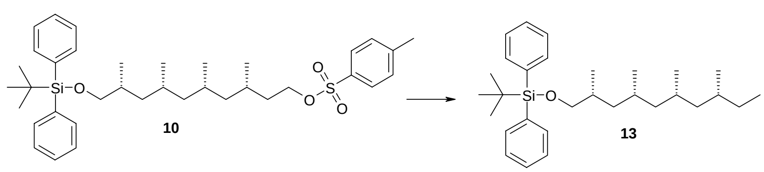
To a stirred mixture of **11** (135 mg, 0.192 mmol) in THF (1 mL) was added TBAF (0.384 mL, 0.384 mmol, 1.0 M solution in THF) at rt under nitrogen, and the mixture was stirred for 5 h. The reaction mixture was concentrated under reduced pressure and purified by chromatography (eluent pentane/ethanol 10:1) to afford **12** as a white solid (80 mg, 90% yield, $[\alpha]_D$ = +5.94 (*c* = 1.21, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): 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, 1H), 1.62 – 1.57 (m, 2H), 1.51 – 1.42 (m, 1H), 1.34 – 1.16 (m, 42H), 1.05 – 0.82 (m, 18H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 $C_{32}H_{66}O$: m/z(%) = 484 (100%, M + NH_4^+). HRMS(EI+) for $C_{32}H_{66}O$: m/z(%) = 448 (100%, M – H_2O), Measured Mass: 448.5003 Da, Calculated Mass: 448.5008 Da.



1

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

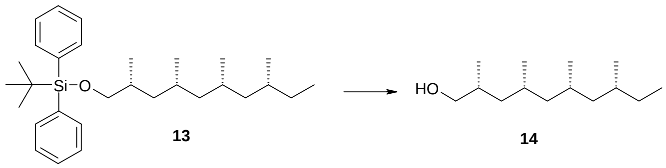
To a stirred mixture of **12** (19 mg, 0.041 mmol) in 0.3 mL CCl_4, 0.3 mL CH_3CN and 0.6 mL H_2O was added $RuCl_3.(H_2O)_x$ (1.0 mg, 0.005 mmol) and $NaIO_4$ (37 mg, 0.172 mmol) at rt under nitrogen. After 3 h the reaction mixture was poured in 2 mL CH_2Cl_2 and 0.5 mL water was added. The phases were separated and the aqueous layer was extracted with three portions of 5 mL CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ 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 ^{13}C-NMR, most probably due to chromatography steps. $[\alpha]_D$ = -6.4 (*c* = 0.94, $CHCl_3$), literature value[4] for the product isolated from *mycobacterium tuberculosis*: $[\alpha]^{21}$ = -5.62 (*c* = 8.9, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.56 (m, 1H), 1.76 (m, 1H), 0.97 – 1.80 (m, 45H), 0.78 – 0.95 (m, 17H) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 $C_{32}H_{64}O_2$: m/z(%) = 480 (63%) (M). HRMS(EI+) calcd for $C_{32}H_{64}O_2$: 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 values[5], MS(EI+) for $C_{33}H_{66}O_2$: m/z(%) = 494 (35%, M). See spectral supporting info for fragmentation details. Mass analysis matched with literature[5].



(+)-(2*R*,4*R*,6*R*,8*R*)-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 $LiAlH_4$ (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 $MgSO_4$ 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, $[\alpha]_D$ = +4.73 (*c* = 0.93, $CHCl_3$)). ^{1}H-NMR (400MHz, $CDCl_3$): 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): (135.64, 135.62) (d), (134.11, 134.08) (s), 129.44 (d), 127.53 (d), 68.70 (t), 45.79 (t), 44.57 (t), 41.22 (t), 33.18 (d), 31.52 (d), 28.72 (t), 27.61 (d), 27.43 (d), 26.88 (q), 21.06 (q), 20.99 (q), 20.05 (q), 19.31 (s), 18.18 (q), 11.15 (q). MS(EI+) for $C_{30}H_{48}OSi$: m/z(%) = 395 (100%, M – *t*-Butyl), MS(CI+) for $C_{30}H_{48}OSi$: m/z(%) = 470 (100%, M + NH_4^+).

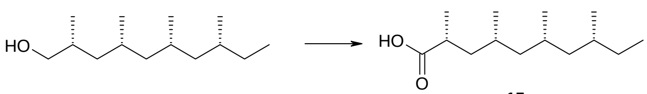
HRMS(EI+) for $C_{30}H_{48}OS$: m/z(%) = 395 (100%, M – *t*-Butyl), Measured Mass: 395.2779 Da, Calculated Mass: 395.2770 Da.



13 14

(+)-(2*R*,4*R*,6*R*,8*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, $CHCl_3$)). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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 $C_{14}H_{30}O$: m/z(%) = 232 (100%, M + NH_4^+). HRMS(EI+) for $C_{14}H_{30}O$: m/z(%) = 196 (100%, M – H_2O), Measured Mass: 196.2191 Da, Calculated Mass: 196.2191 Da.



14 15

(-)-(2*R*,4*R*,6*R*,8*R*)-Tetramethyl-decanoic acid (15)

To a stirred mixture of **14** (8.0 mg, 0.037 mmol) in 0.080 mL CCl_4, 0.080 mL CH_3CN and 0.115 mL H_2O was added $RuCl_3.(H_2O)_x$ (1.0 mg, 0.005 mmol) and $NaIO_4$ (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 $MgSO_4$ 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, $[\alpha]^{29}_D$ = -27.8 (*c* = 0.69 , $CHCl_3$) lit: Negishi *et al.*[6] $[\alpha]^{23}$ = -25.1 (*c* = 0.2 , $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 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). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 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), 20.44 (q), 19.87 (q), 18.09 (q), 11.18 (q). HRMS(EI+) for $C_{14}H_{28}O_2$: m/z(%) = 228 (19%, M), Measured Mass: 228.2100 Da, Calculated Mass: 228.2089 Da. Spectroscopic data (^{1}H, ^{13}C-NMR) corresponded with literature[6] and no diastereoisomers were observed in comparison with ^{13}C-NMR data[6], probably due to chromatography steps.

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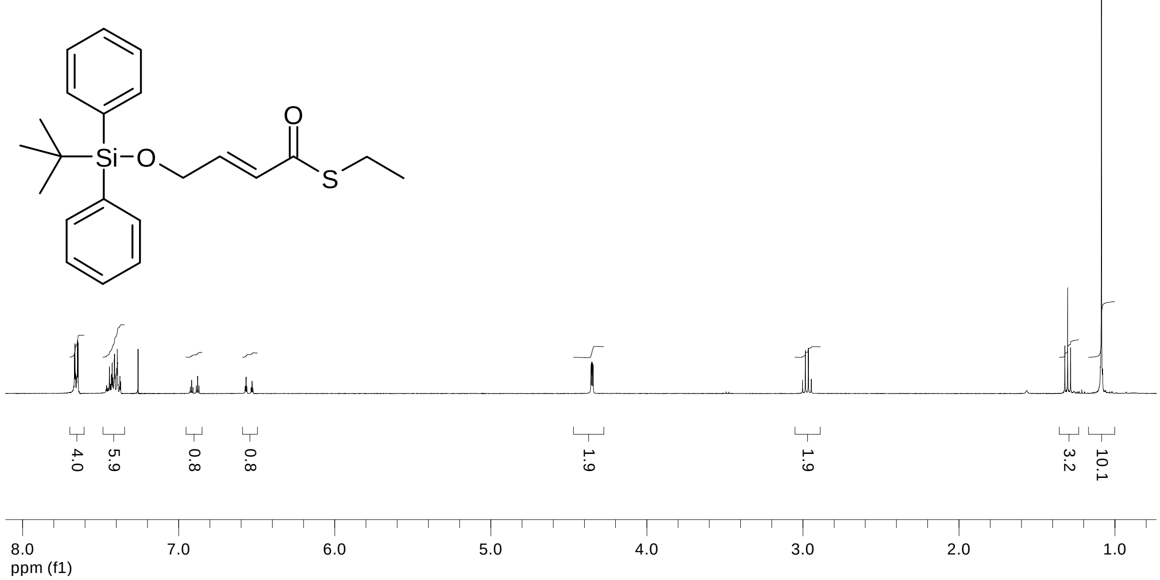
[1] H. G. W. Leuenberg, W. Boguth, R. Barner, M. Schmid and R. Zell, *Helv. Chem. Acta*., 1979, **62**, 455 – 463.
[2] T. Mukayama, K. Fujimoto, T. Hirose and T. Takeda, *Chem. Letters*, 1980, 635.
[3] K. Mori, *Tetrahedron* 1983, **39**, 3107 – 3109.
[4] N. Polgar and W. Smith, *J. Chem. Soc*., 1963, 3081 – 3085.
[5] a. S. Alugupalli, M. K. Sikka, L. Larsson and D. C. White, *Journal of Microbiological Methods*, **31**, 1998, 143 –150. b. R. Ryhage and E. Stenhagen, *J. Lipid Research*, 1960, **1**, 361 – 390.
[6] B. Liang, T. Novak, Z. Tan, and E.-I. Negishi, *J. Am. Chem. Soc.* 2006, **128**, 2770-2771.

^{1}H-NMR



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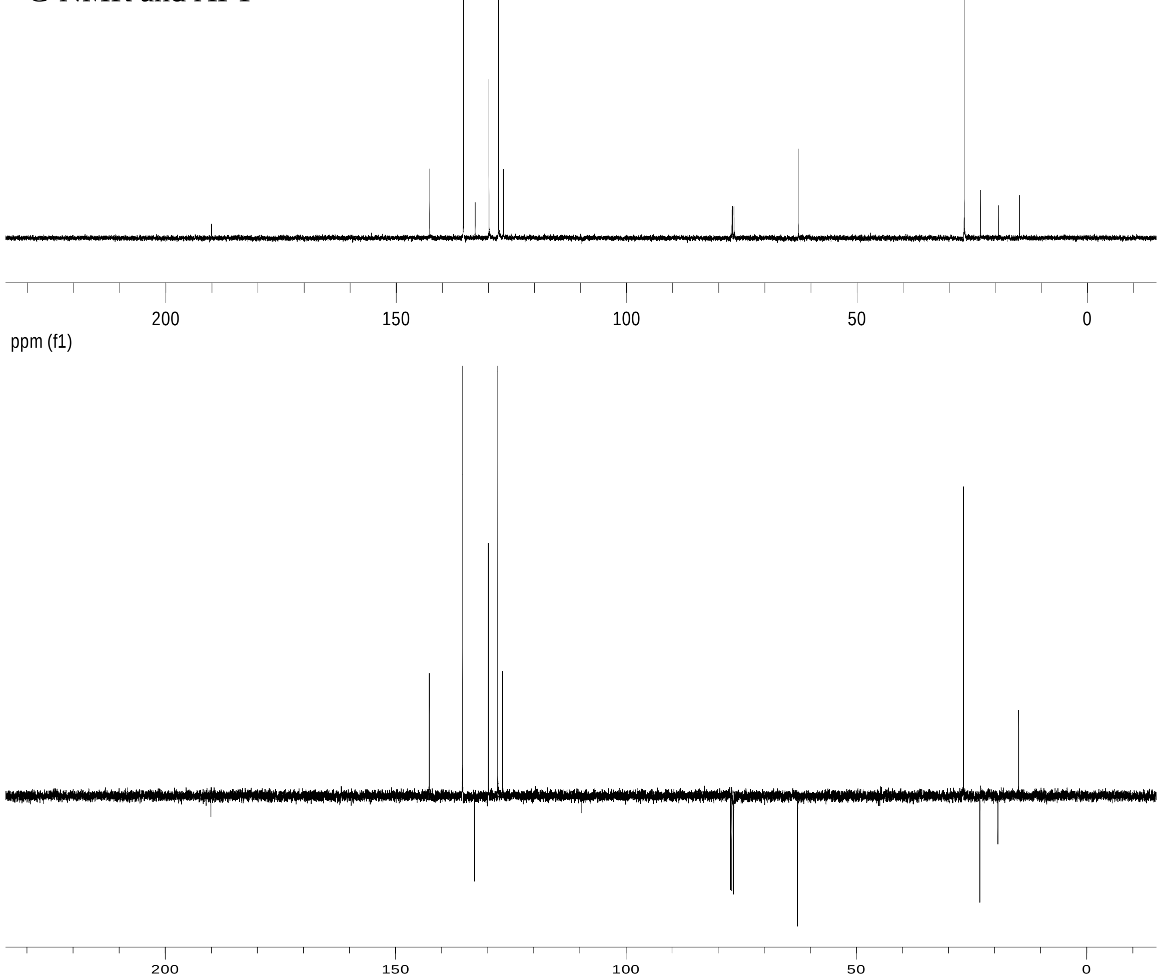

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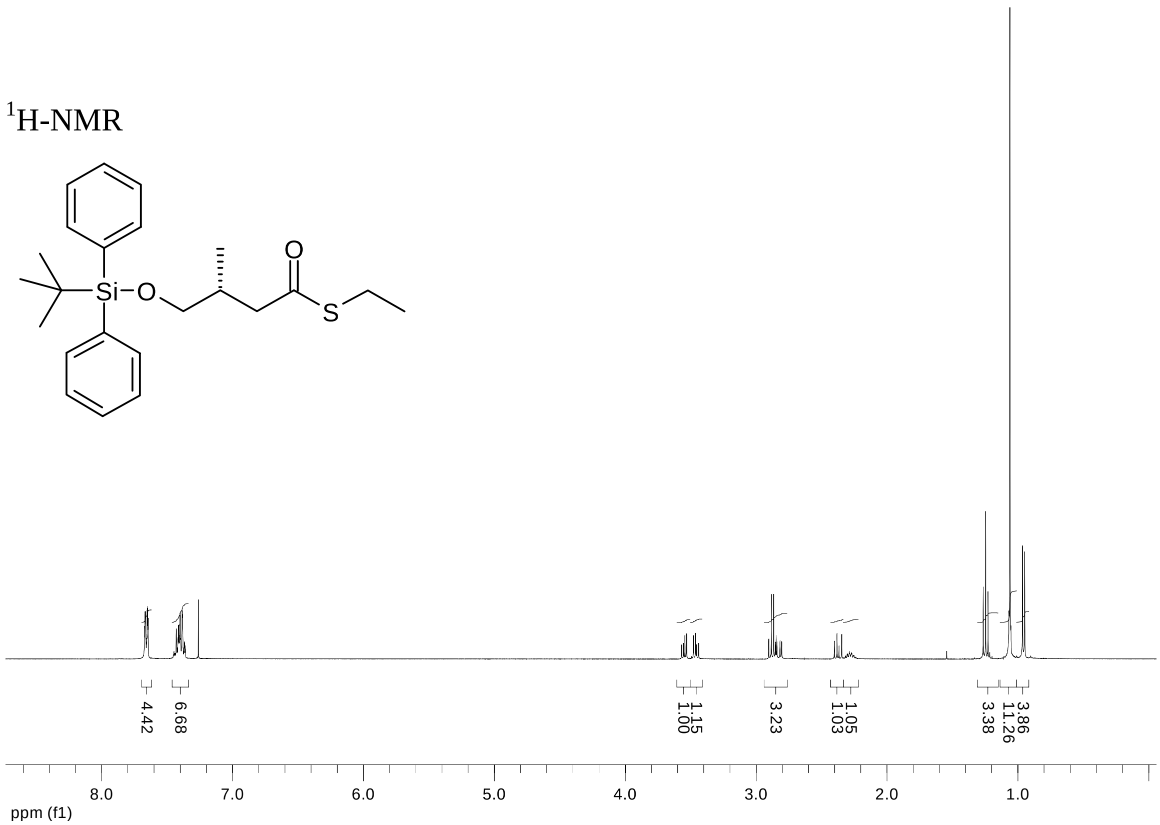

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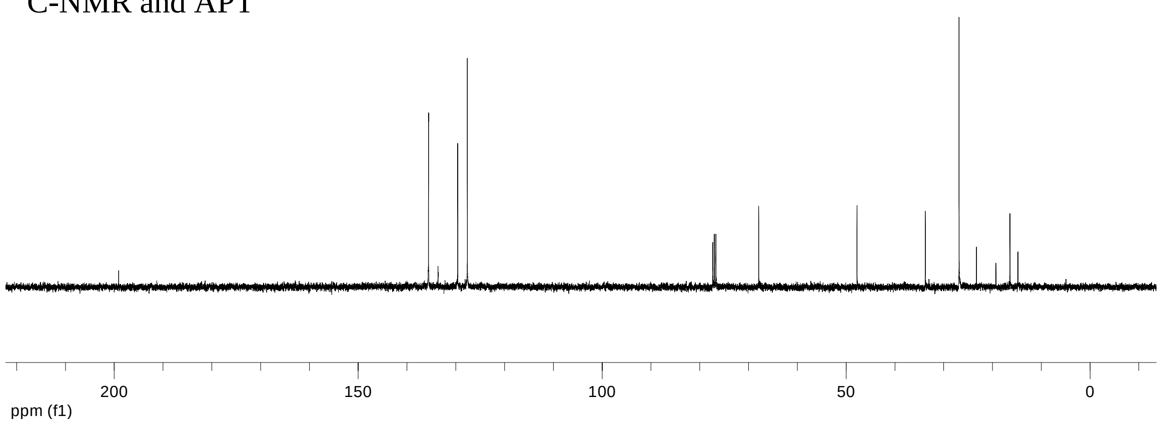

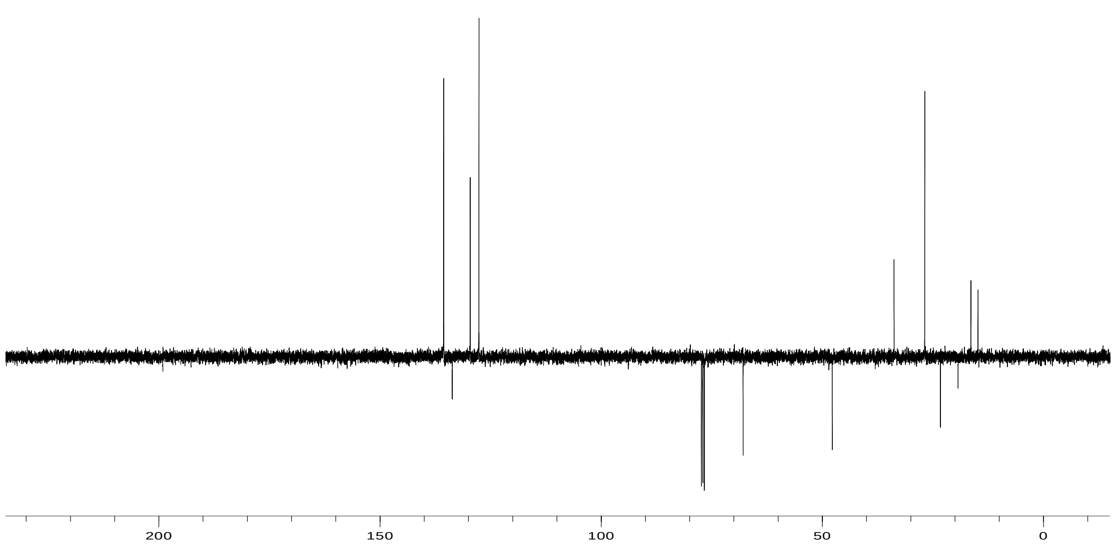

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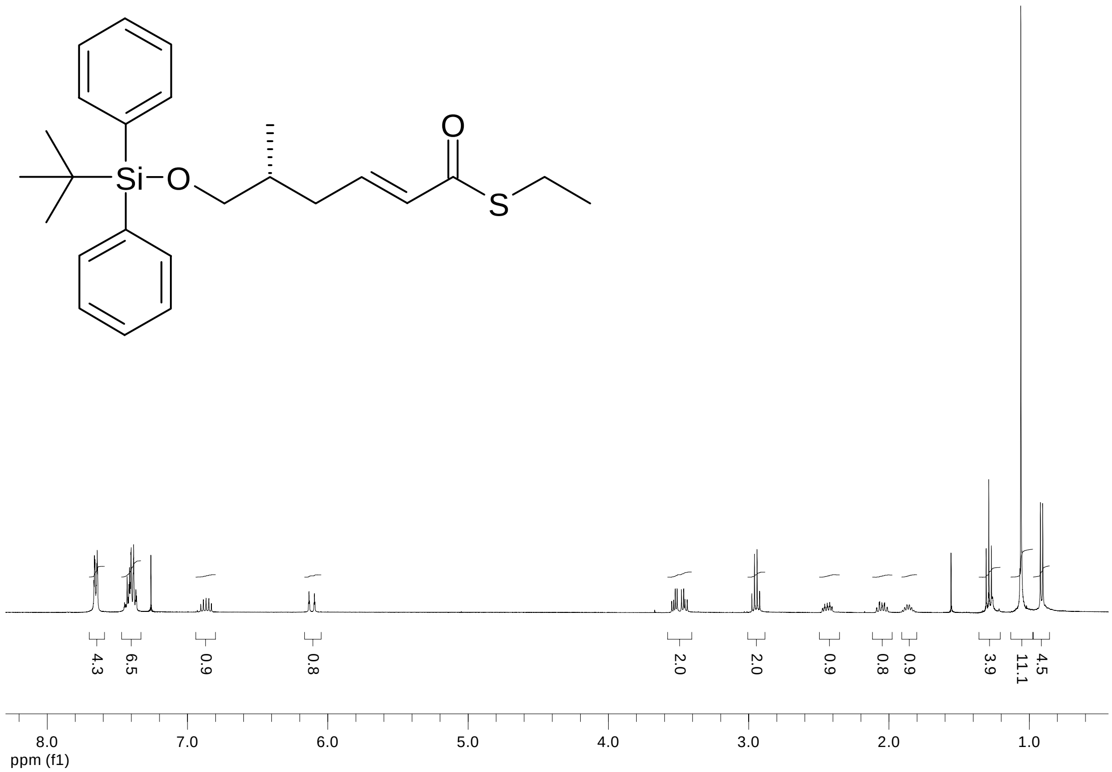

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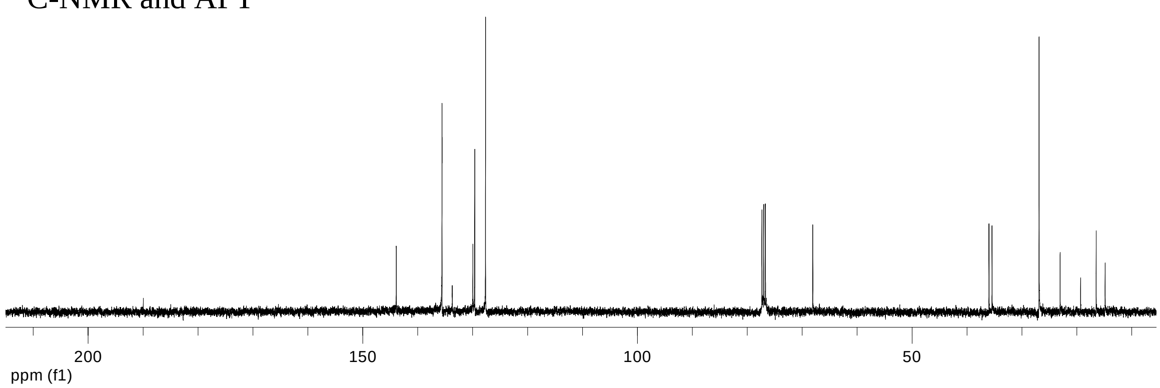

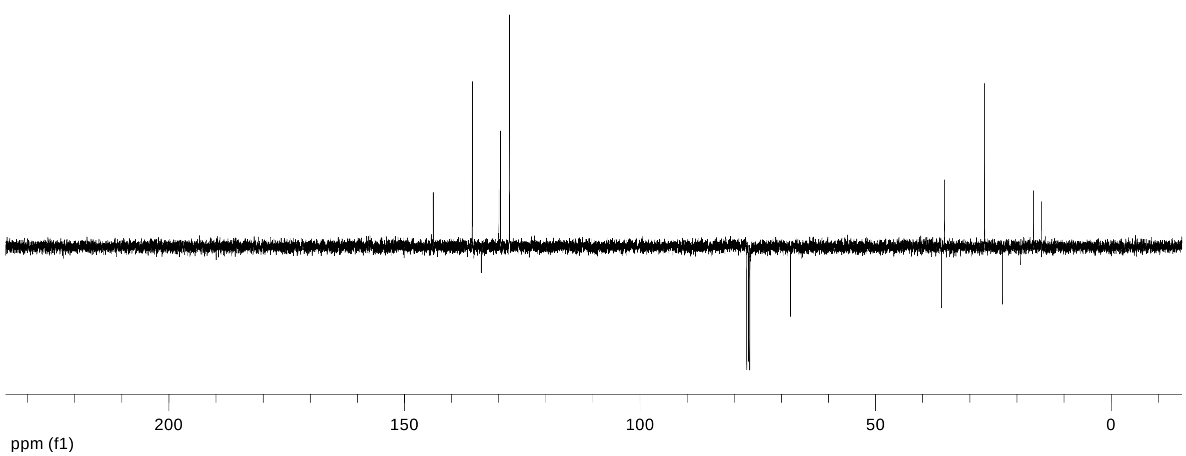

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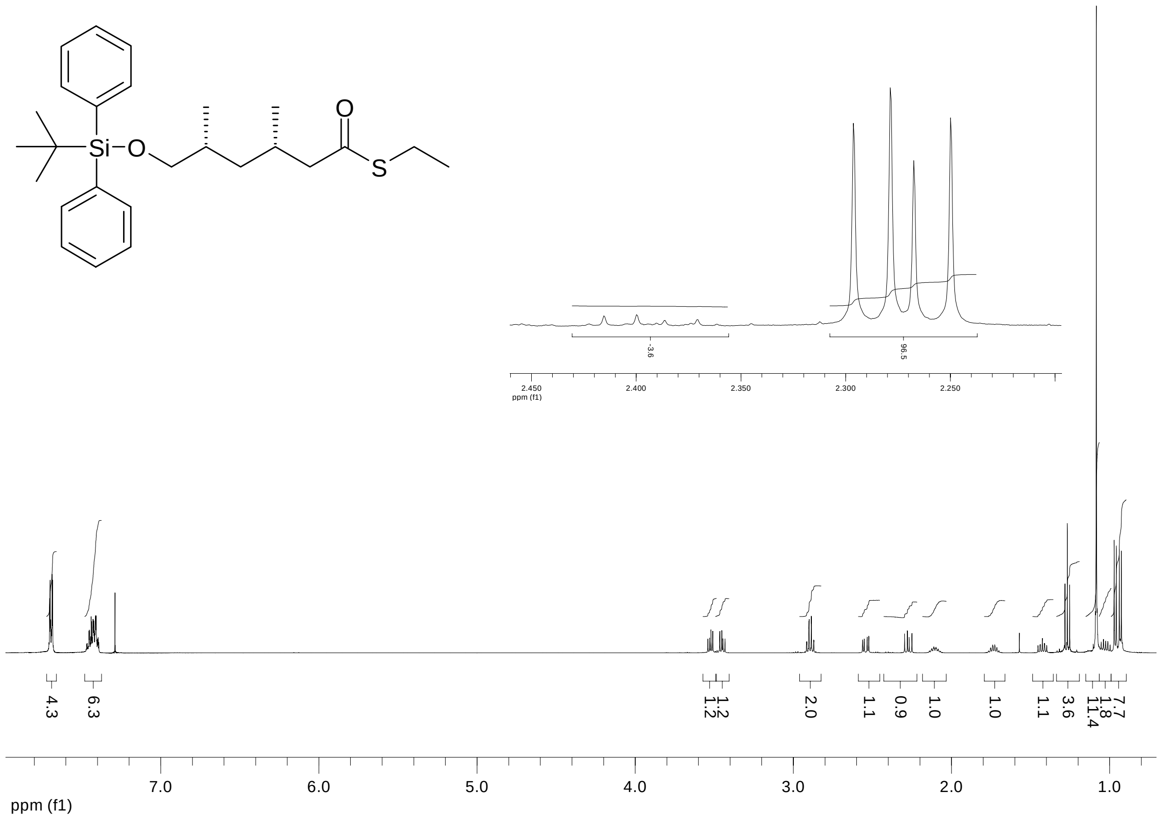

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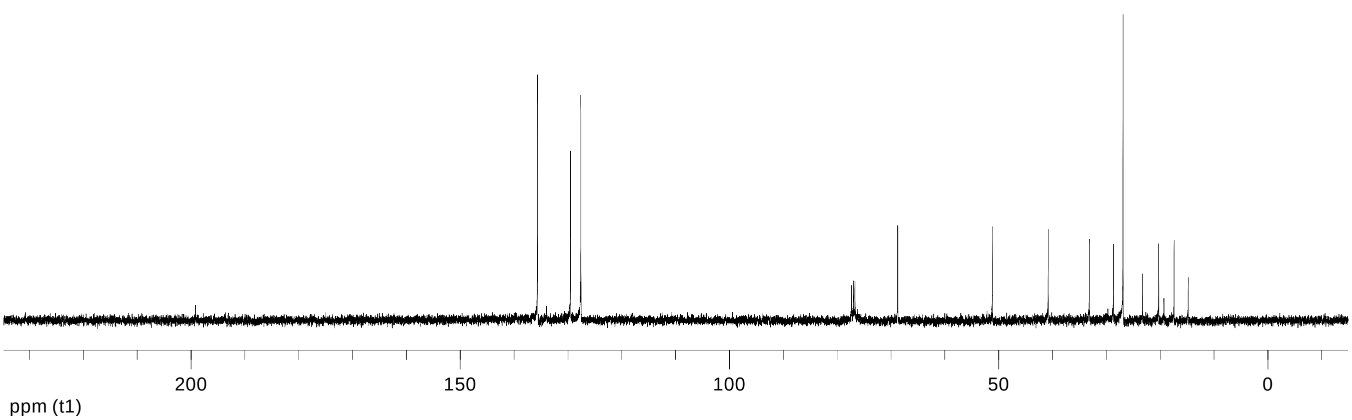

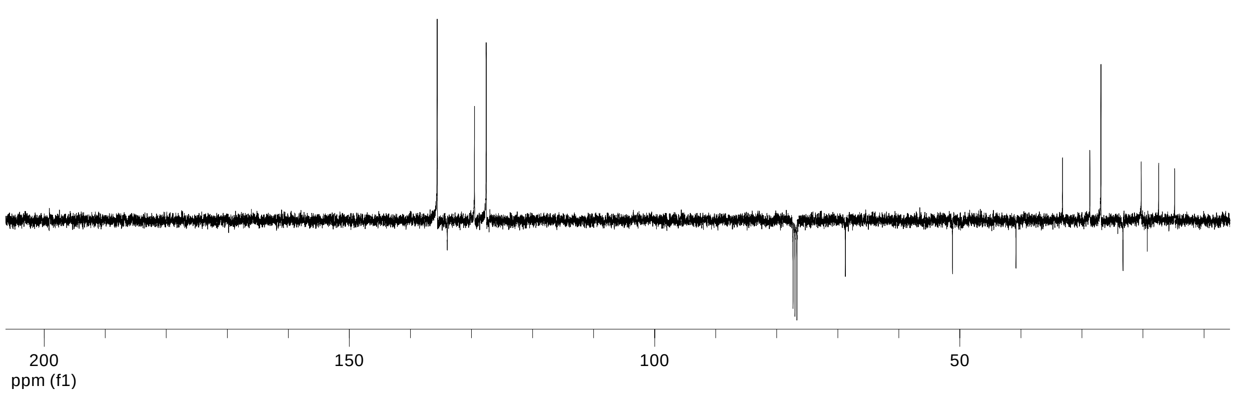

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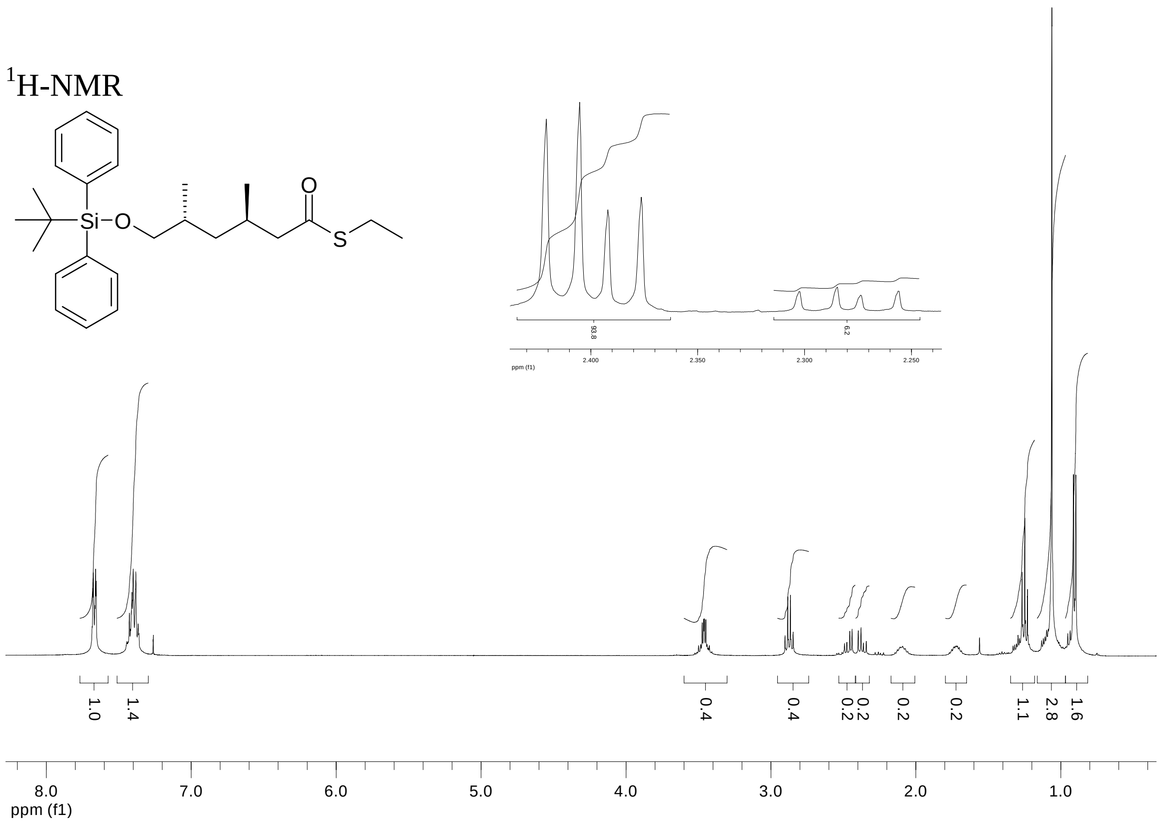

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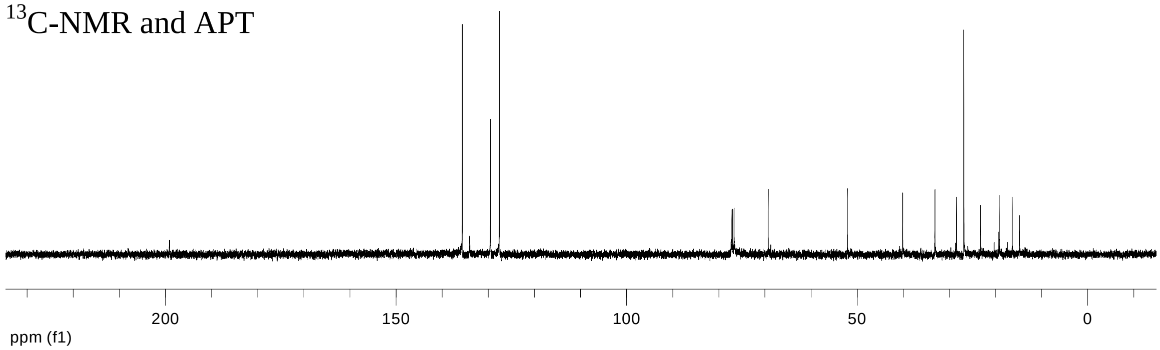
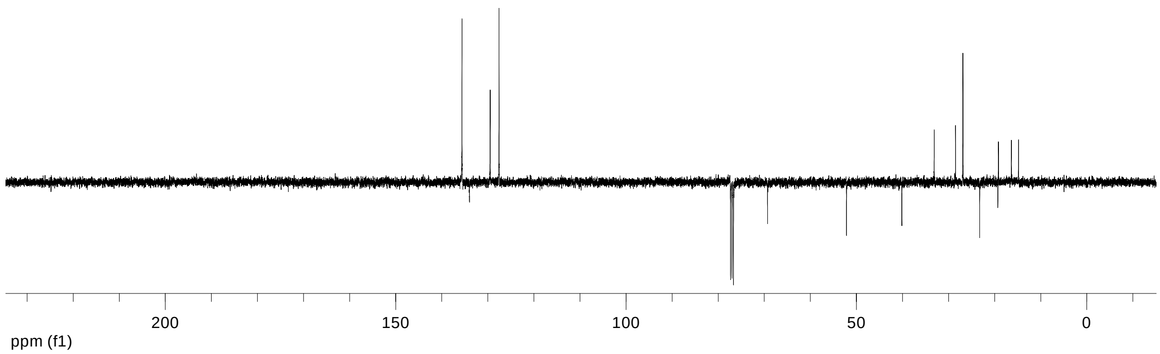
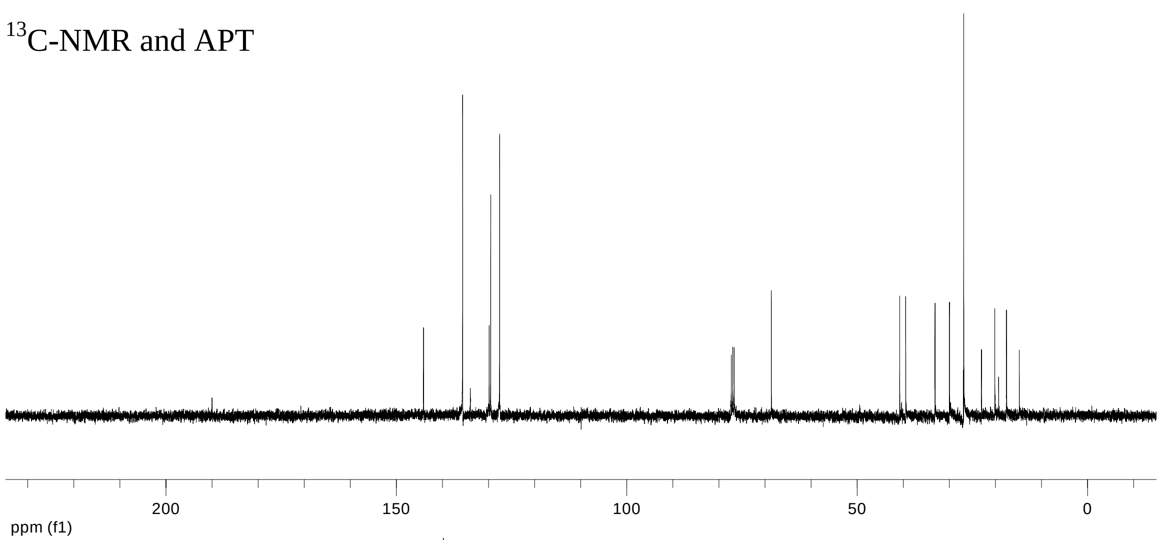
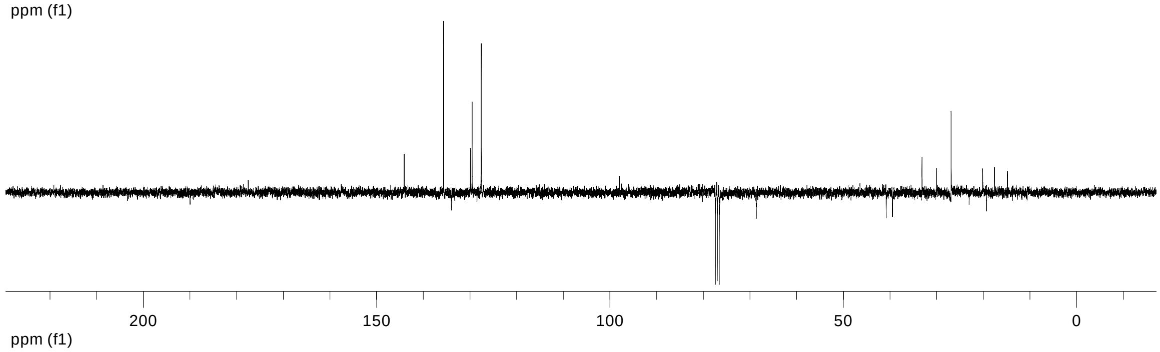




^{1}H-NMR

^{13}C-NMR and APT





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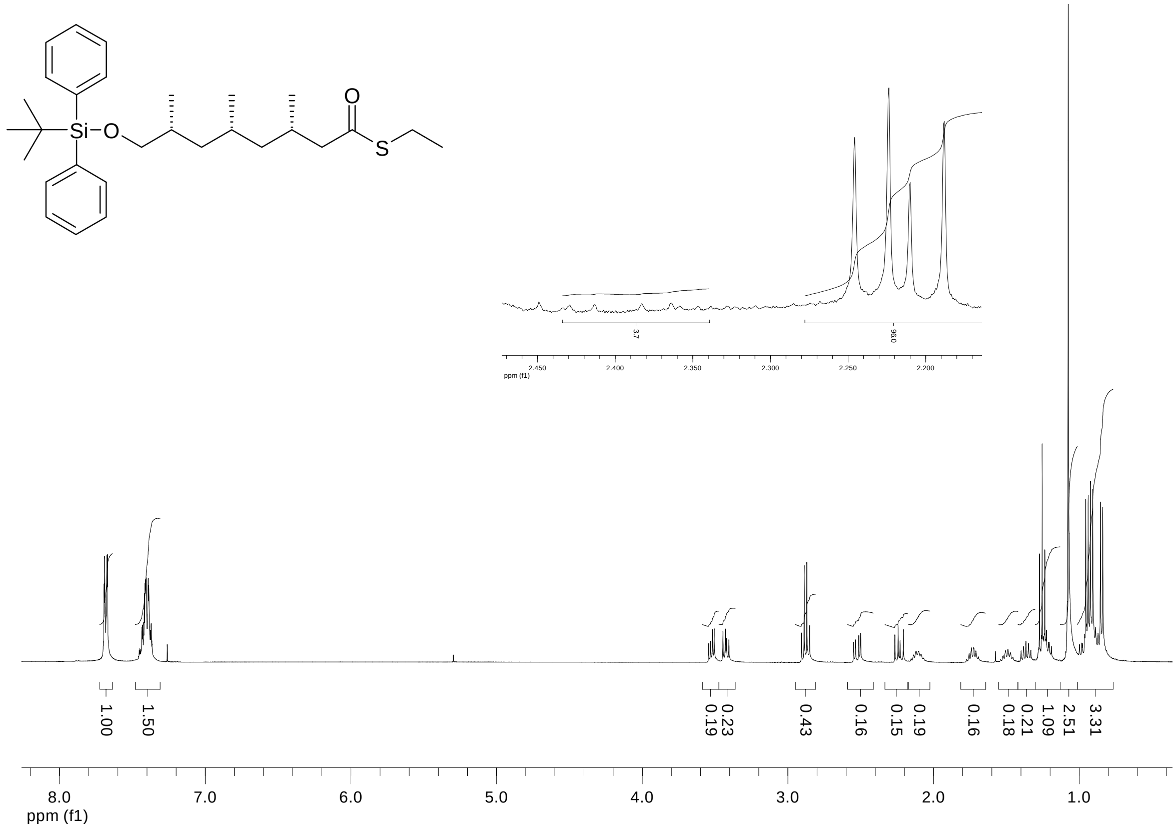

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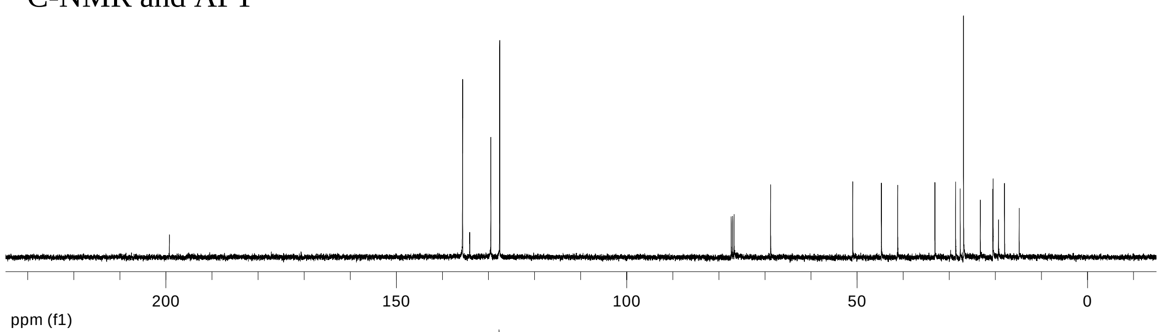

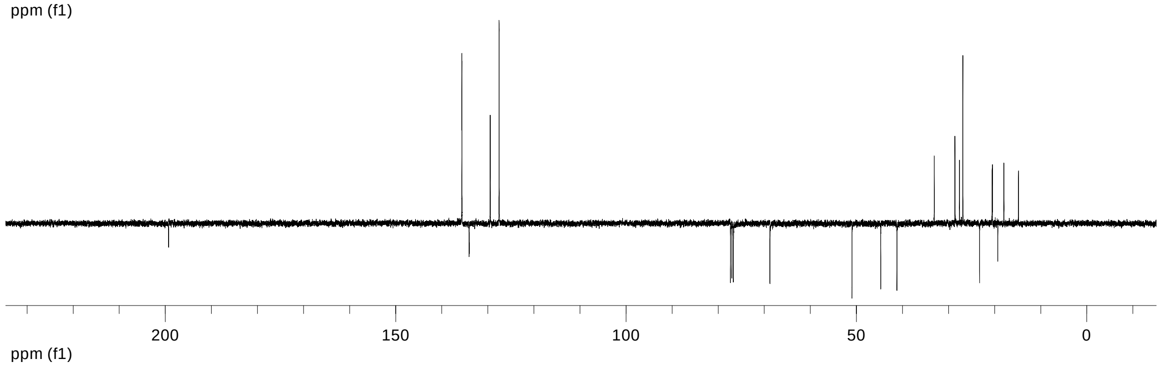

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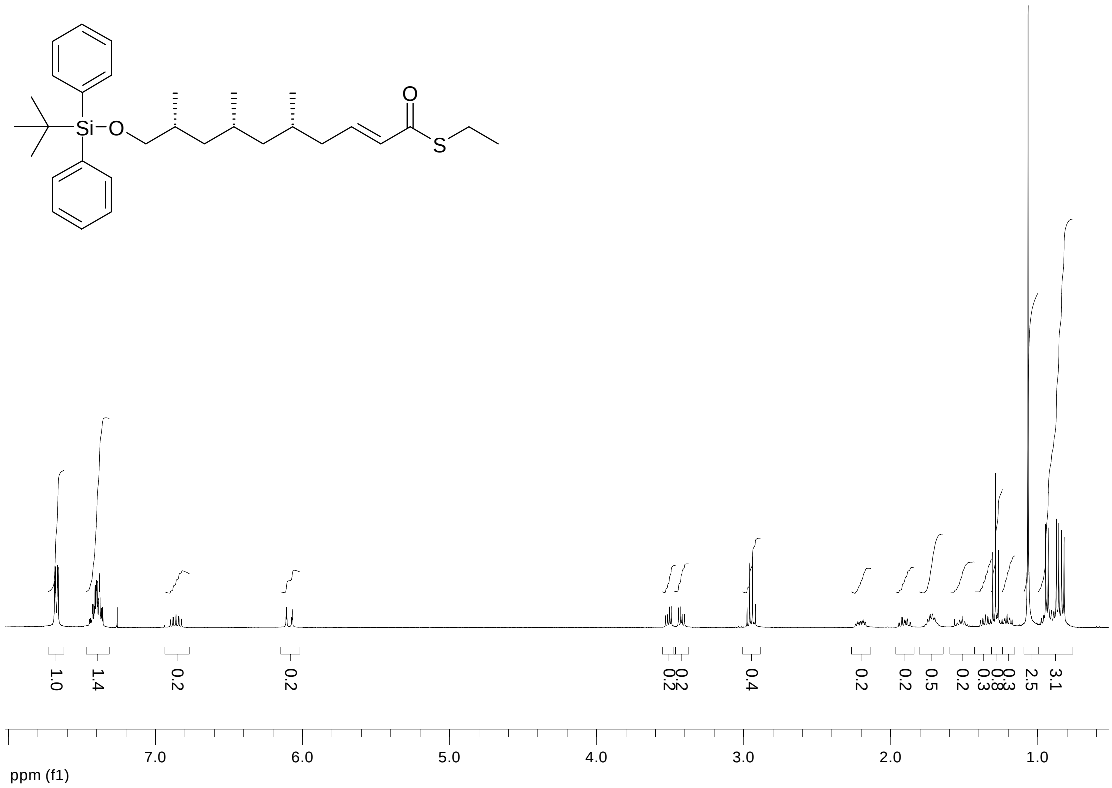

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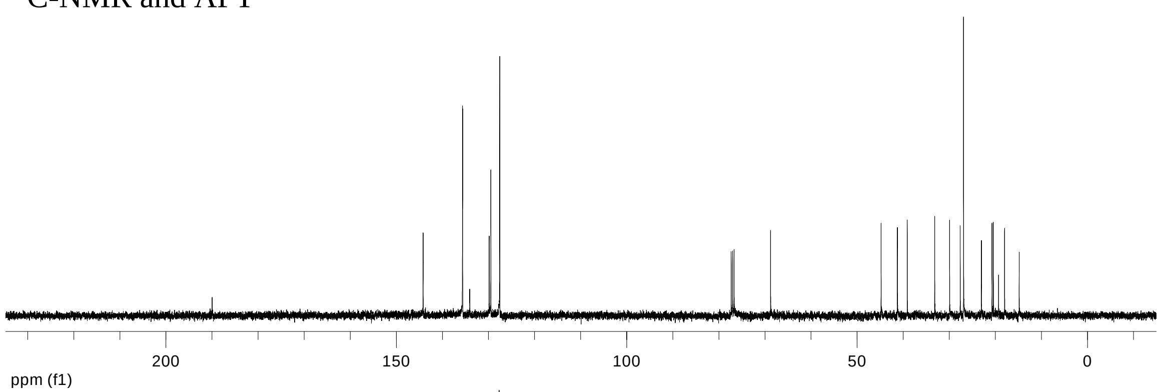

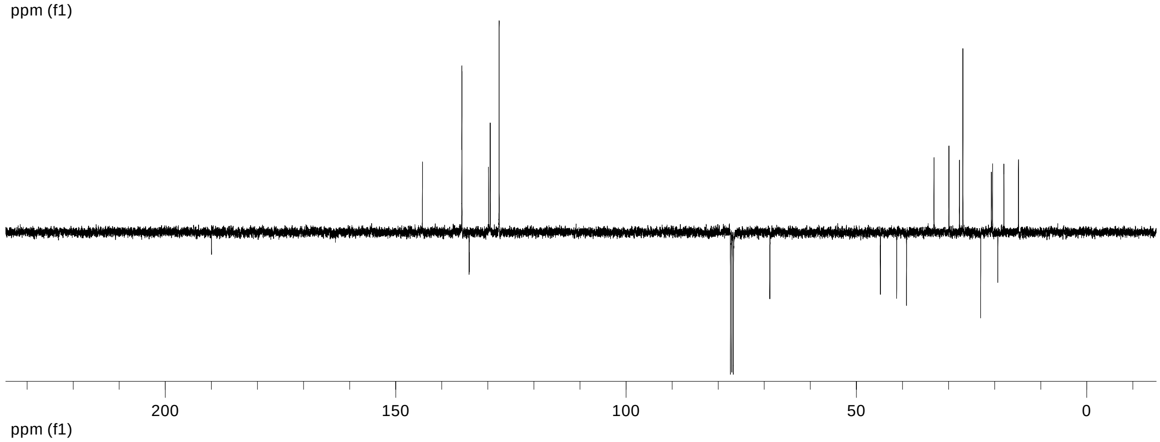

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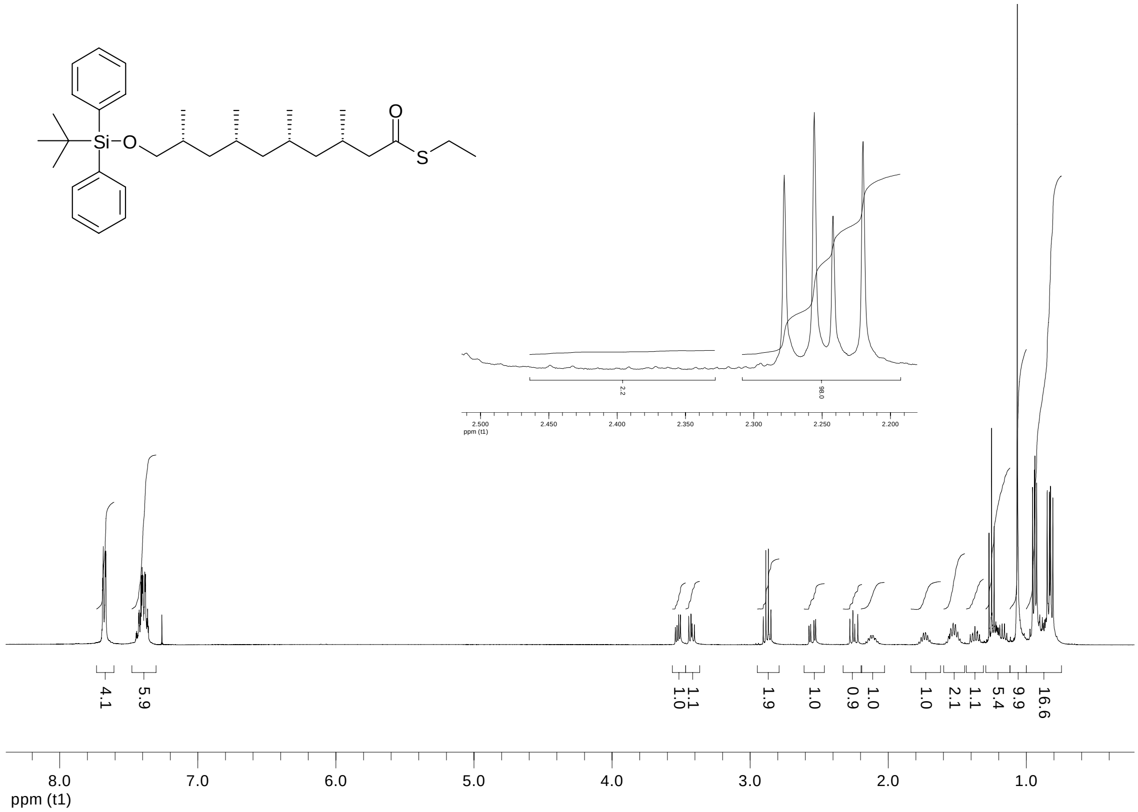

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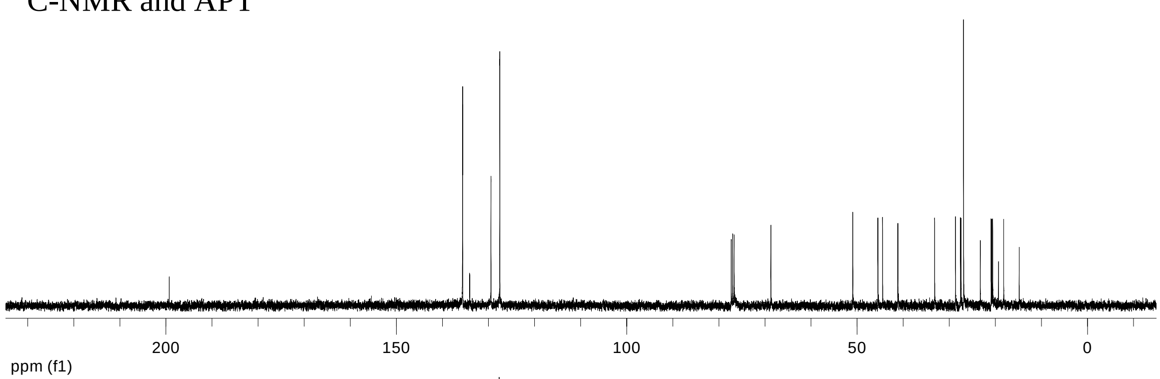

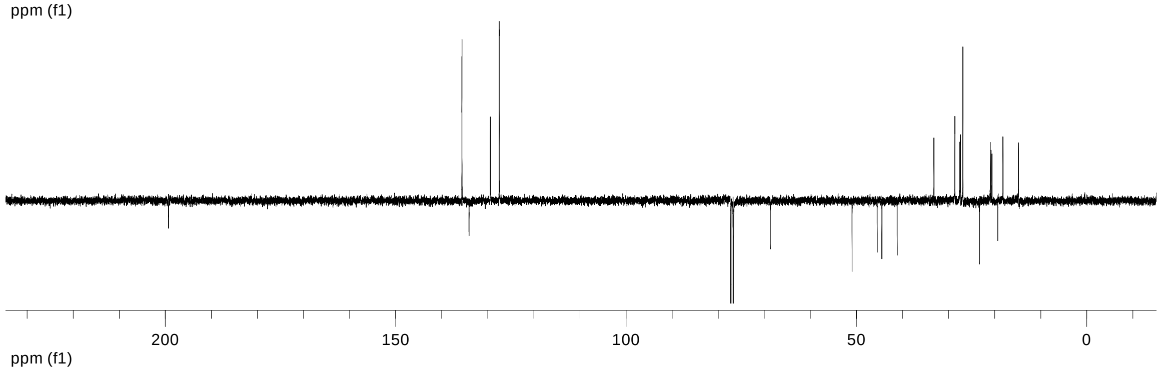

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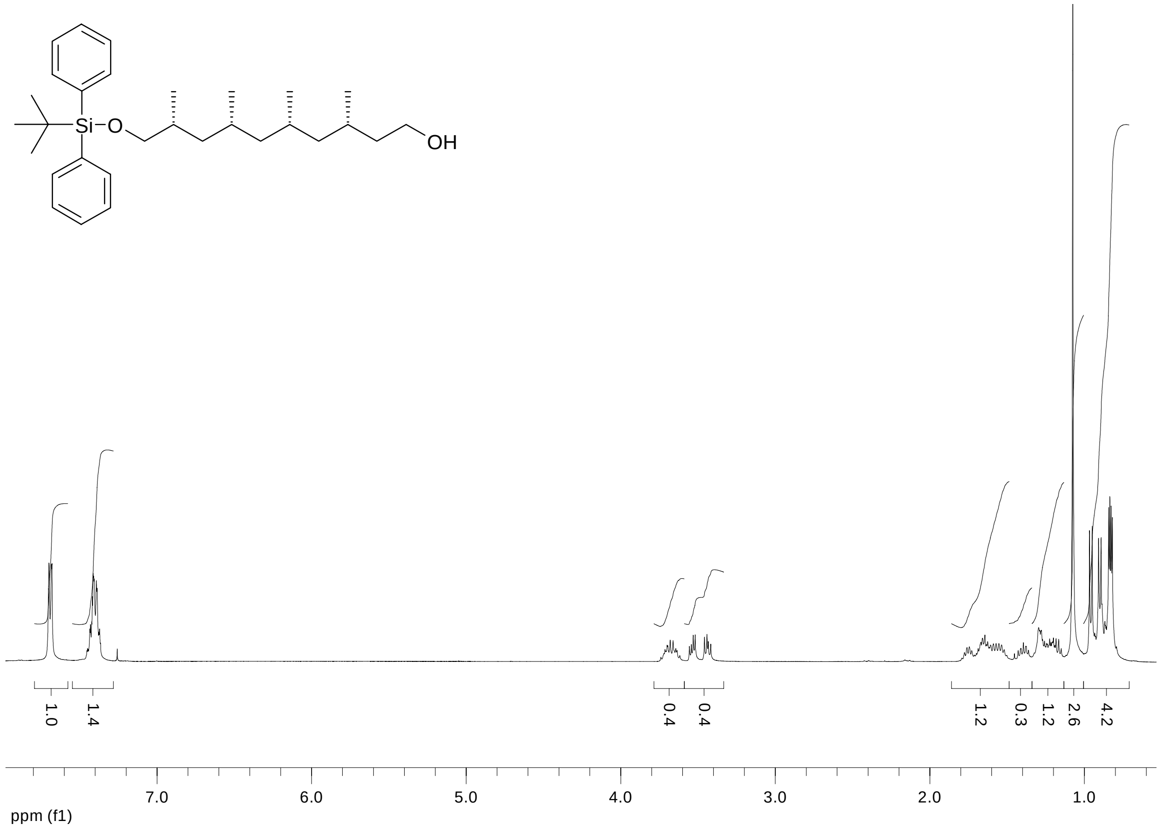

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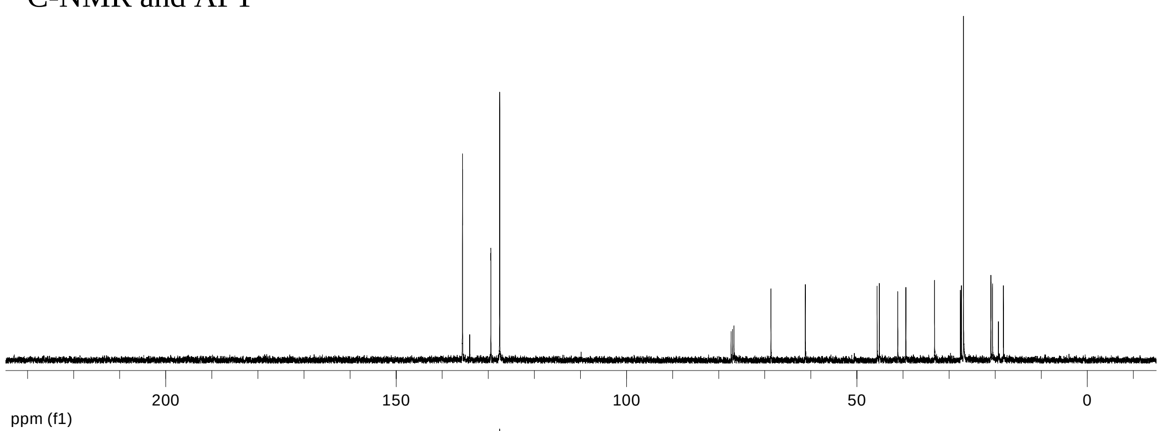

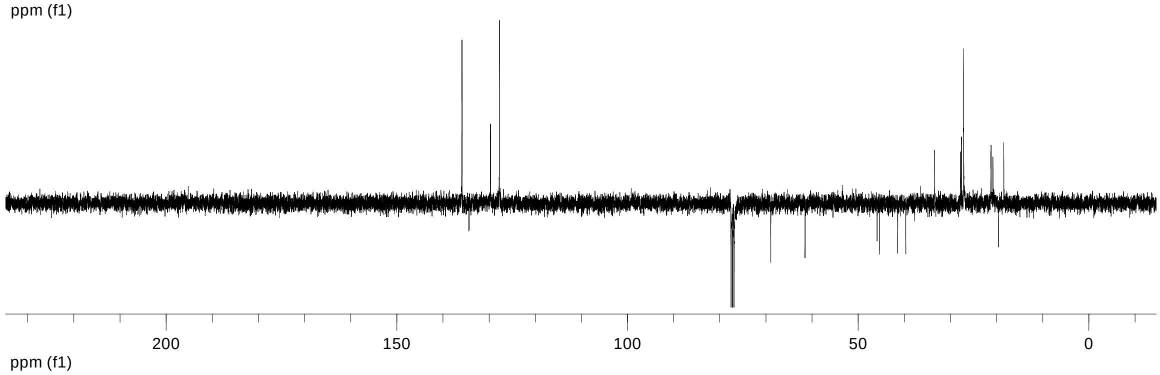

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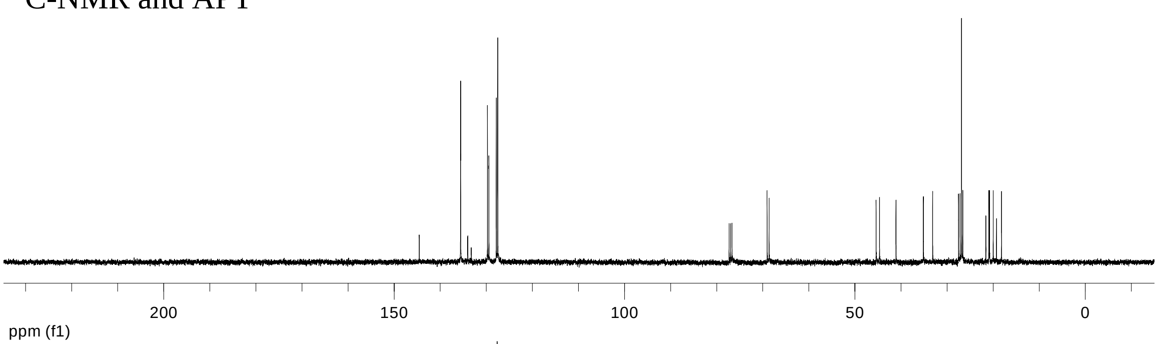
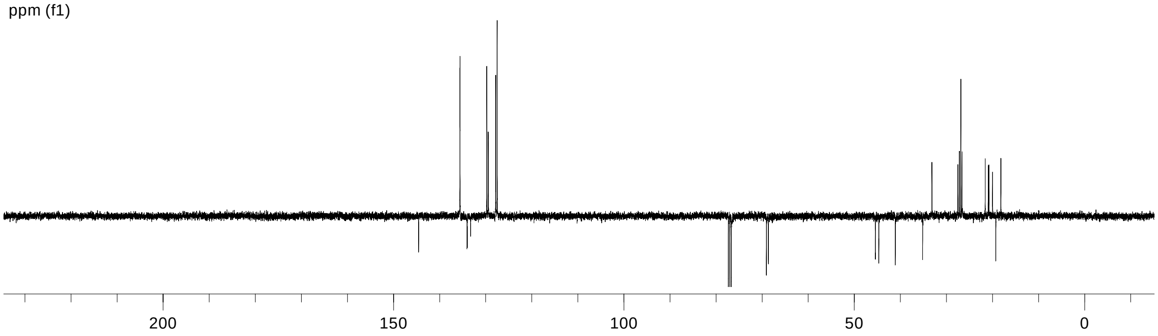
[13]C-NMR and APT





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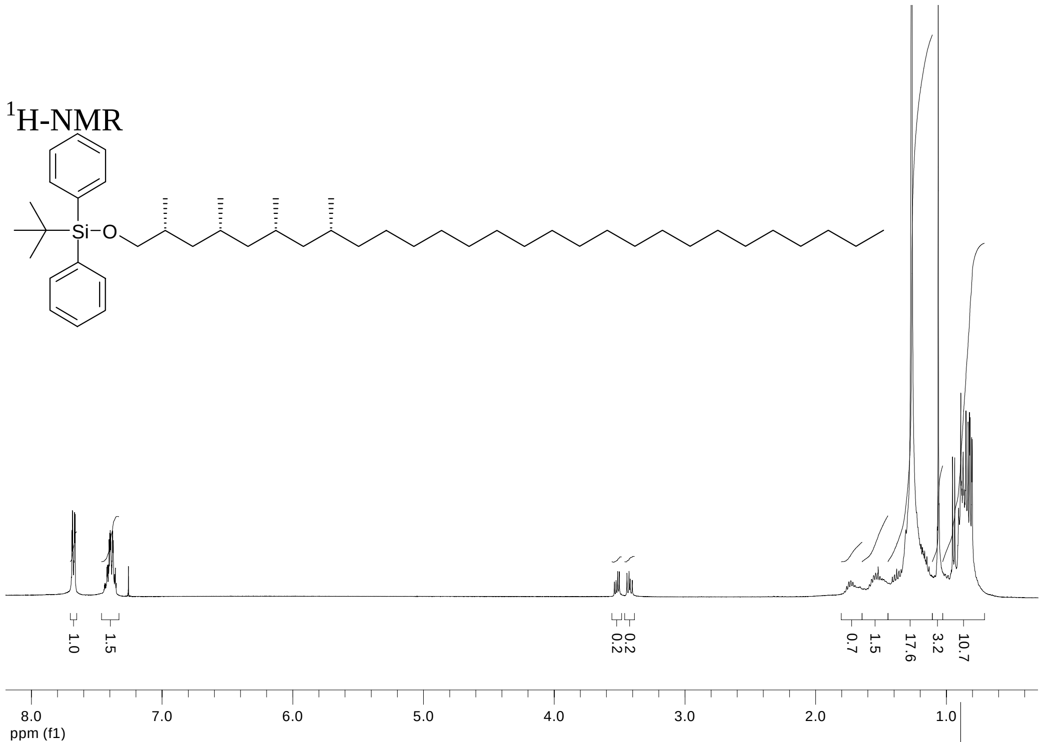

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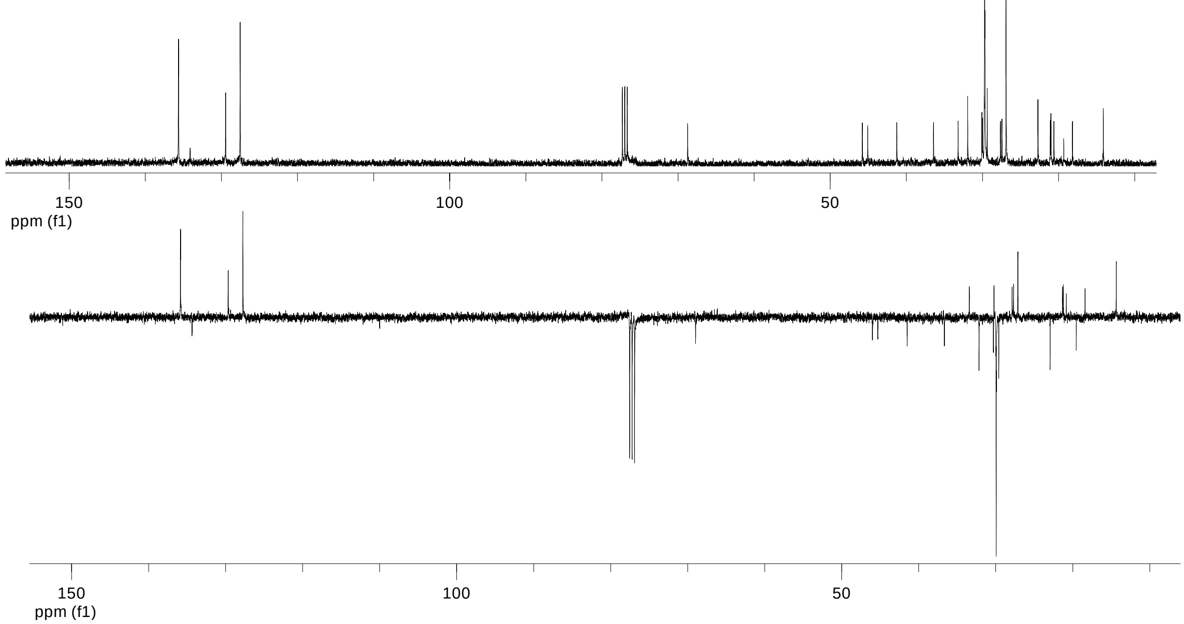

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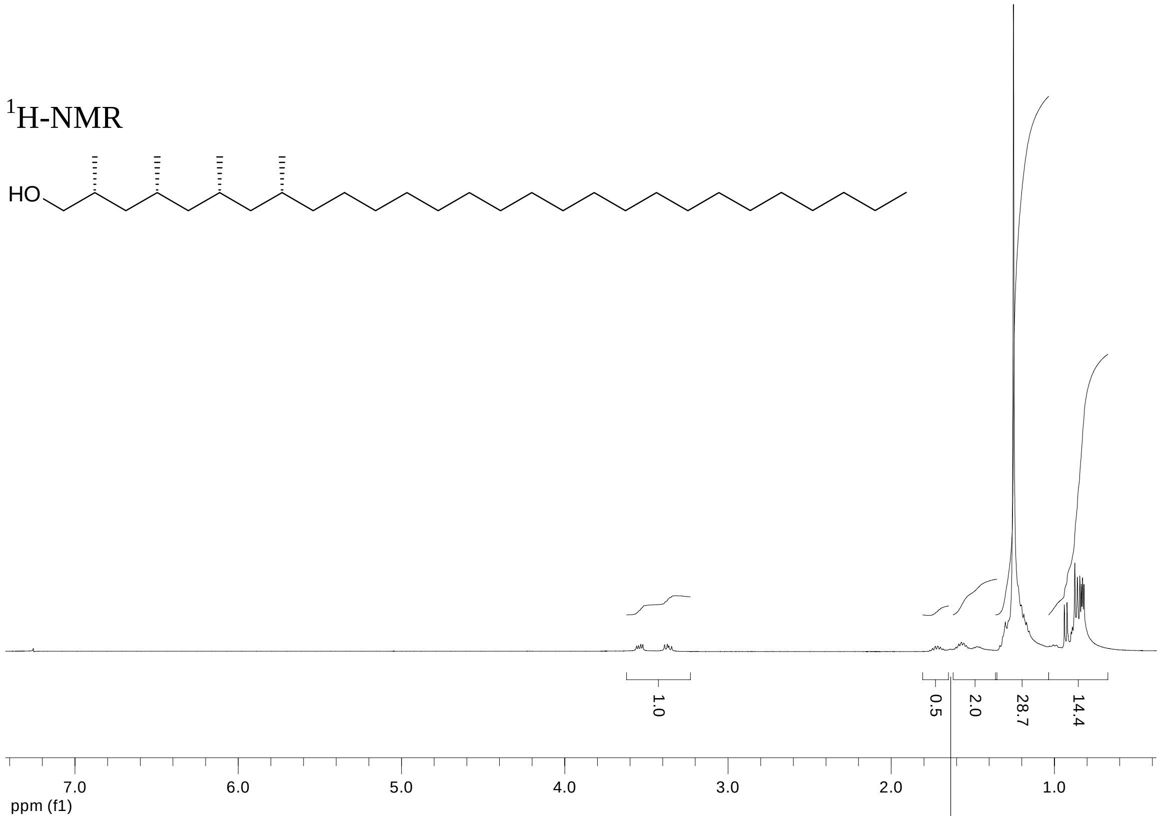

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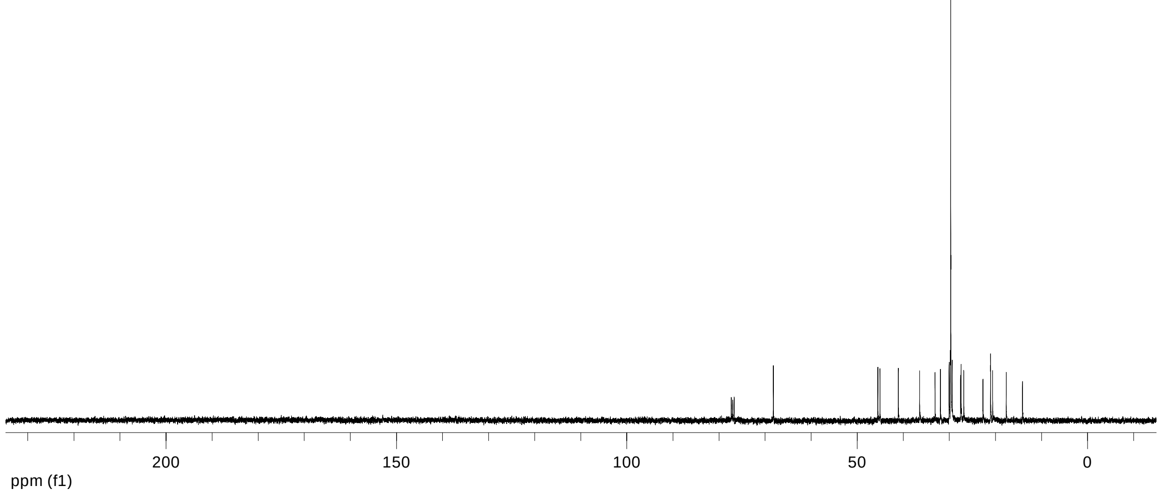

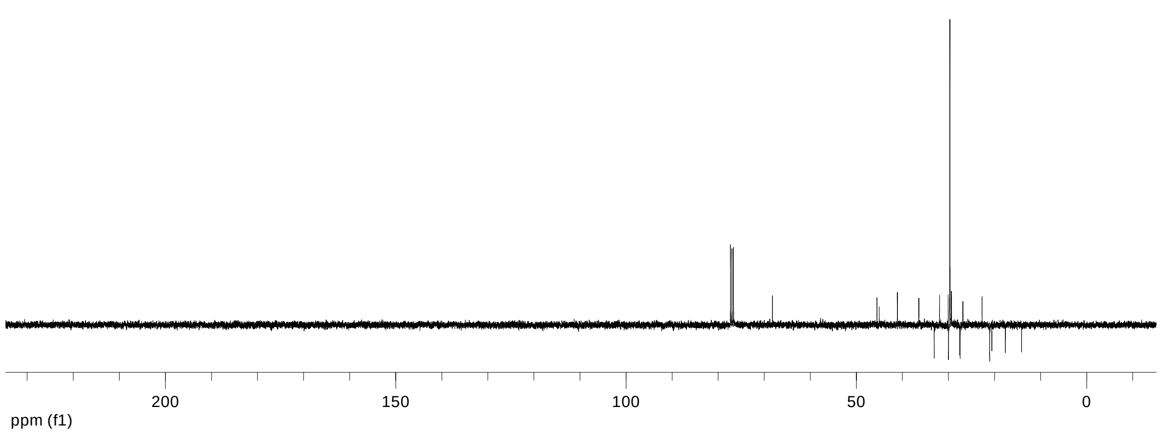

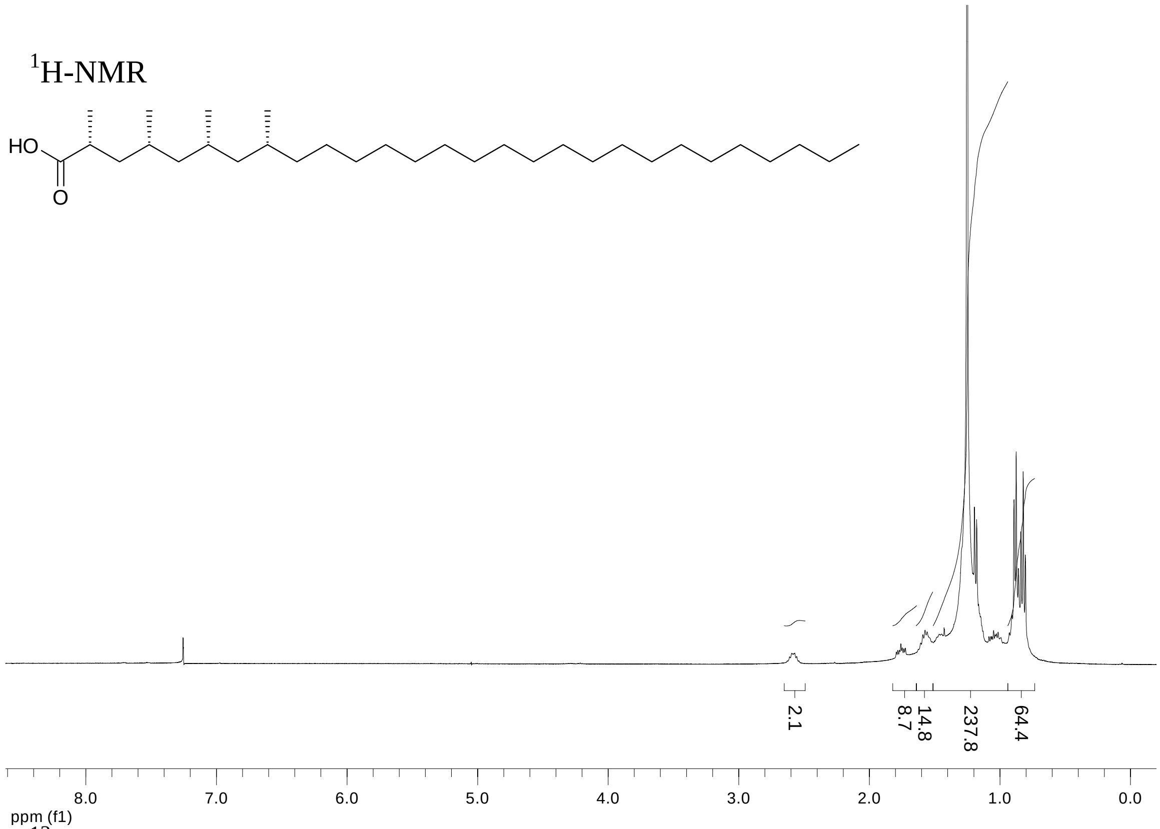

1H-NMR
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O
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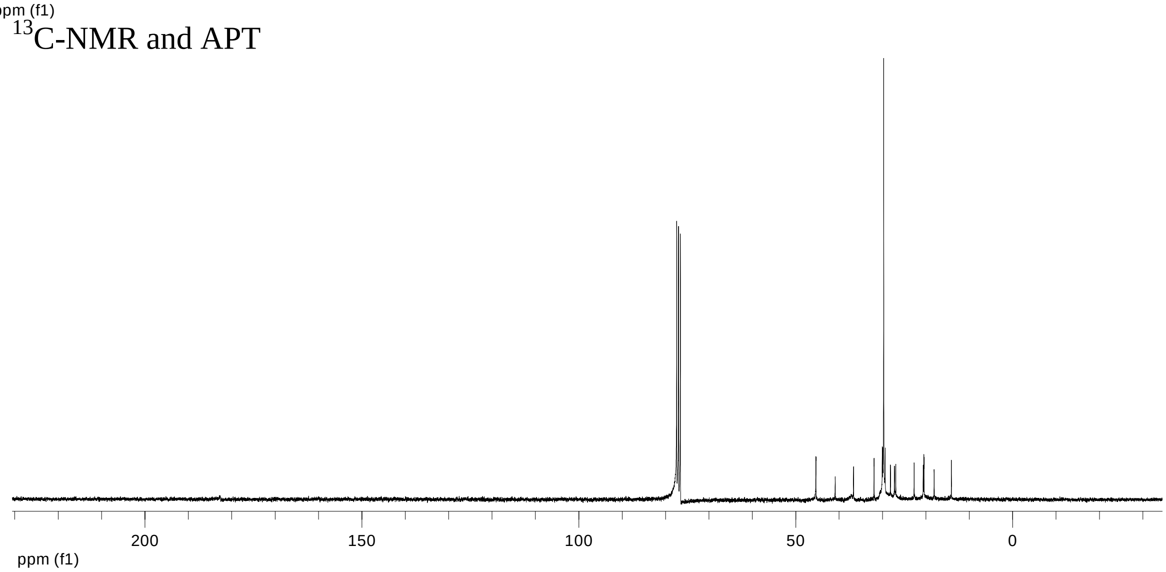
8.7
14.8
237.8
64.4
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)



13C-NMR and APT
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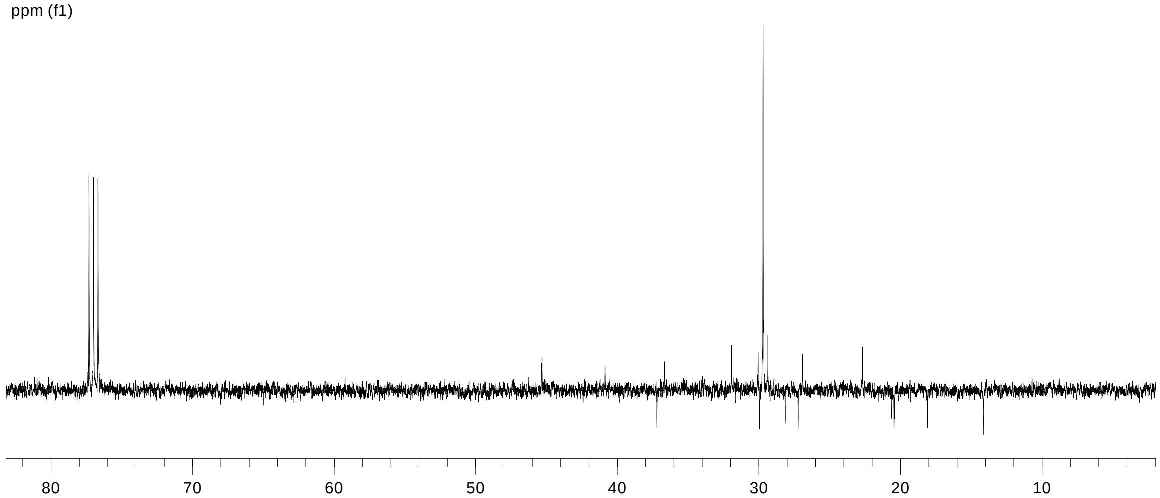
50
0
ppm (f1)



80
70
60
50
40
30
20
10
ppm (f1)

RUG

2/15/06 3:17:18 AM

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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

RUG

4/5/06 4:20:09 PM

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

05
n/z 111; 1%FS TIC: 498368

R.T.: 4:26.3

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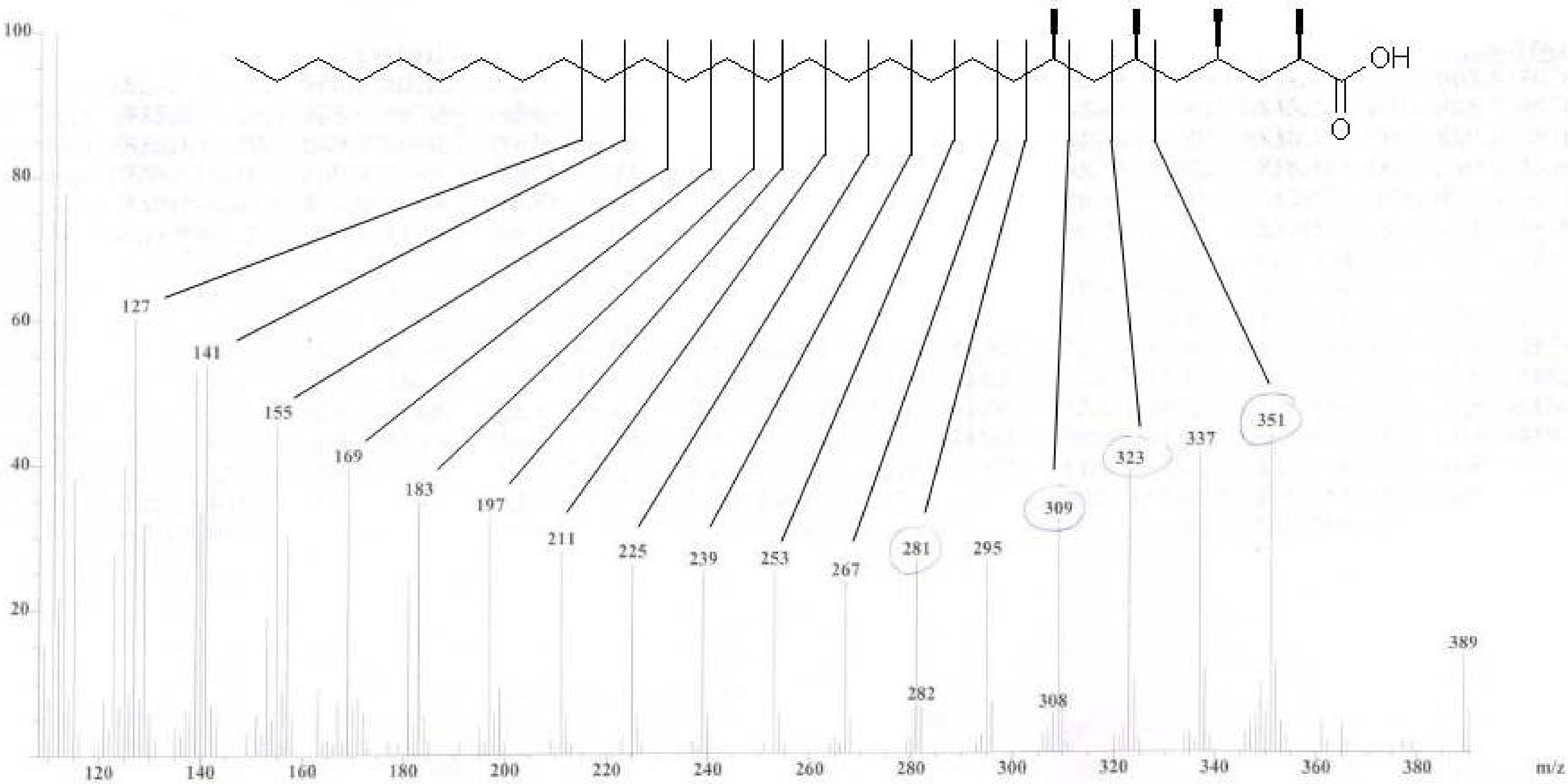

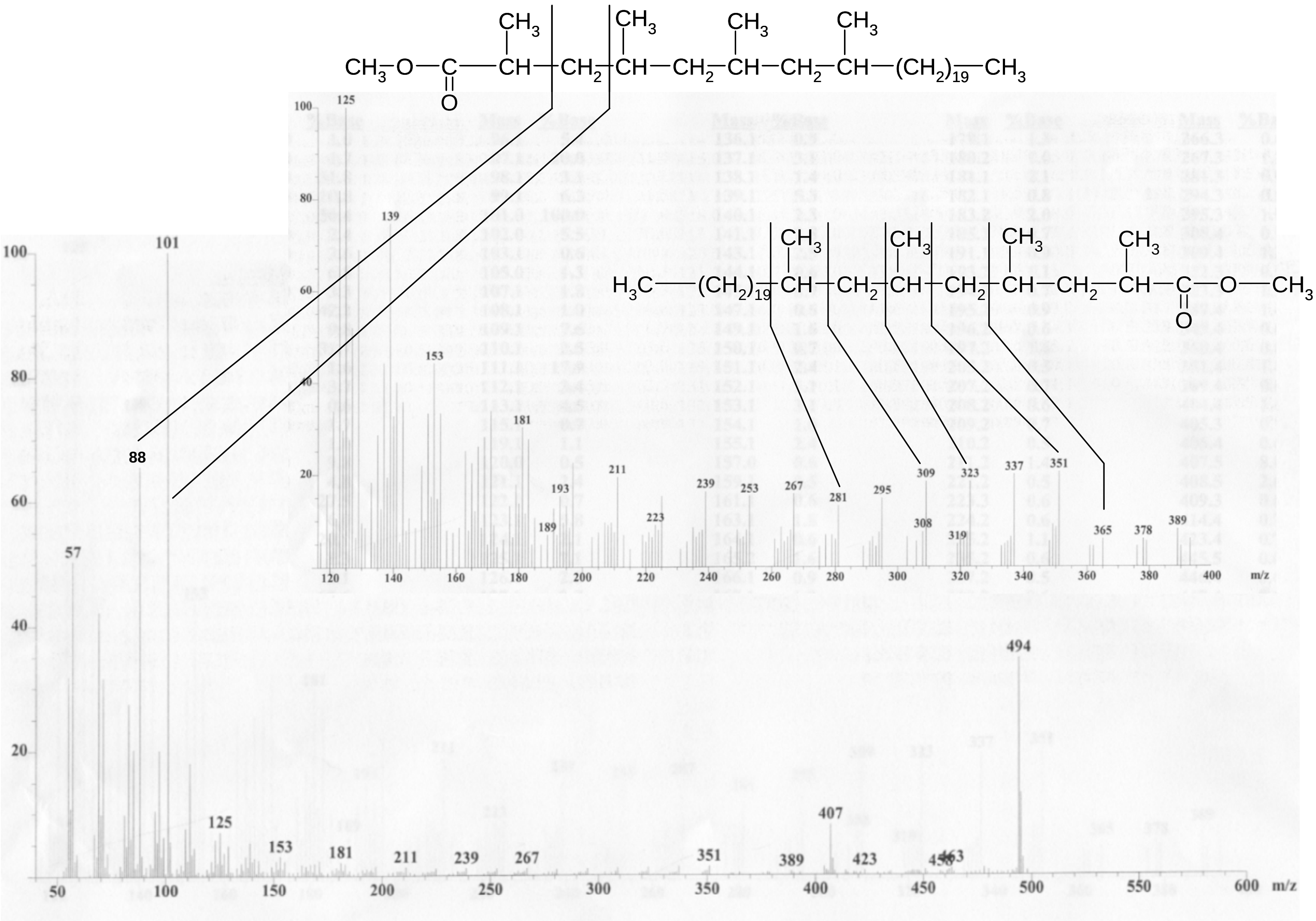

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CH3
O
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139
153
181
193
189
211
223
239
253
267
281
295
309
308
323
319
337
351
365
378
389
m/z
101
88
57
407
423
451
463
494
100
80
60
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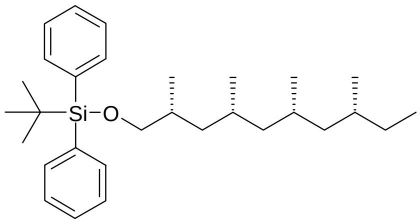
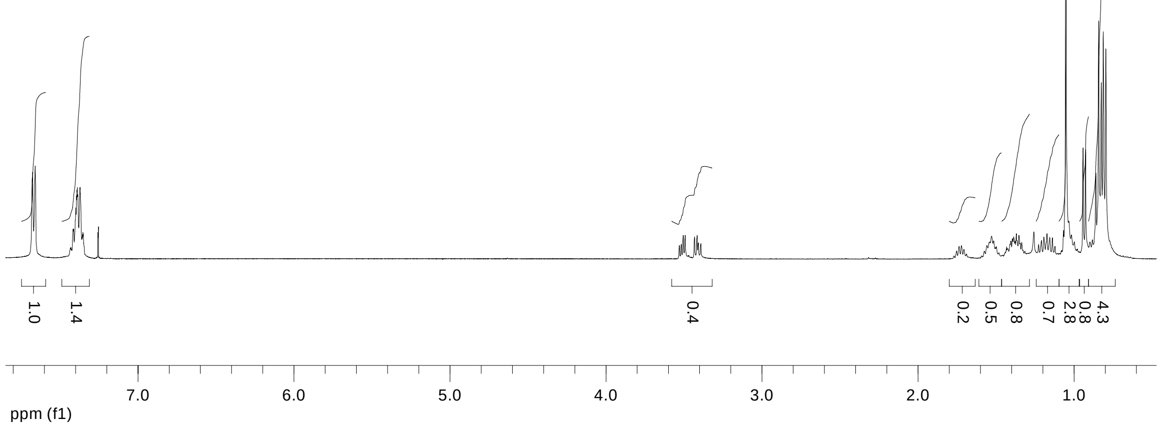
^{1}H-NMR





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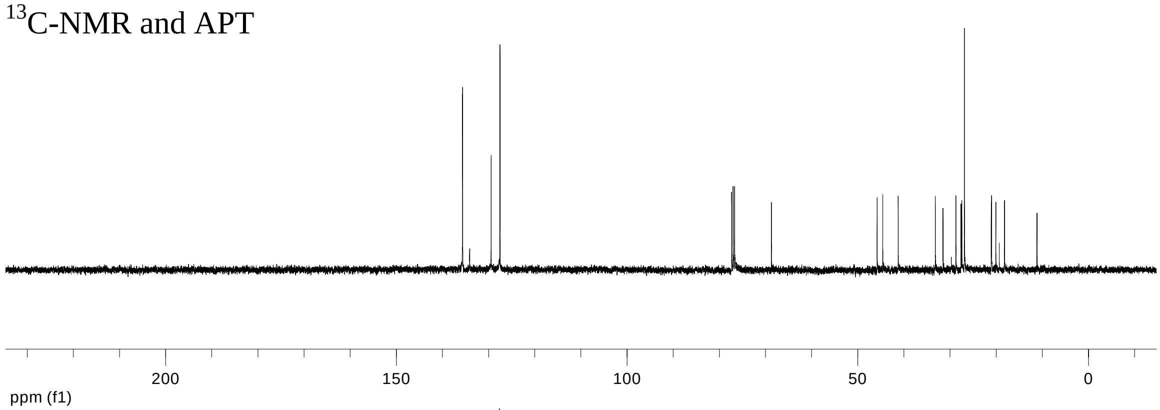

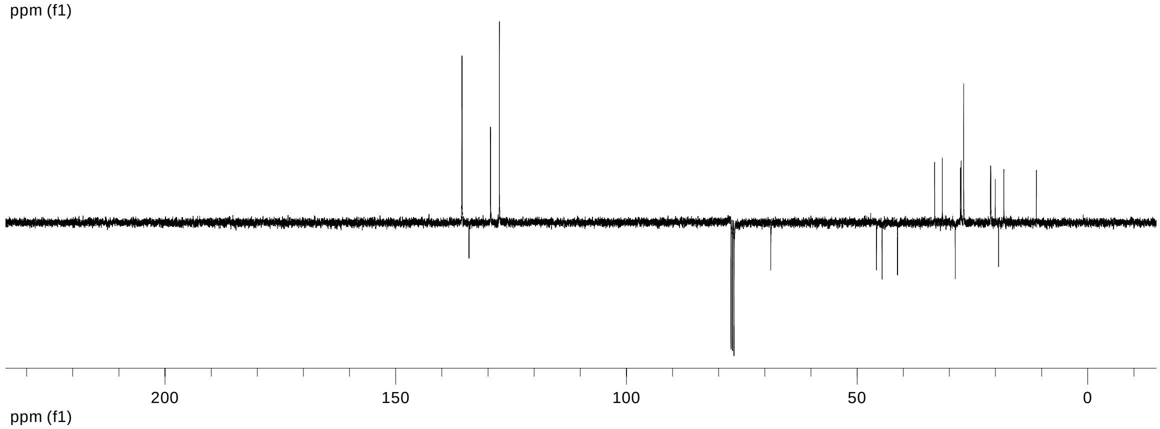

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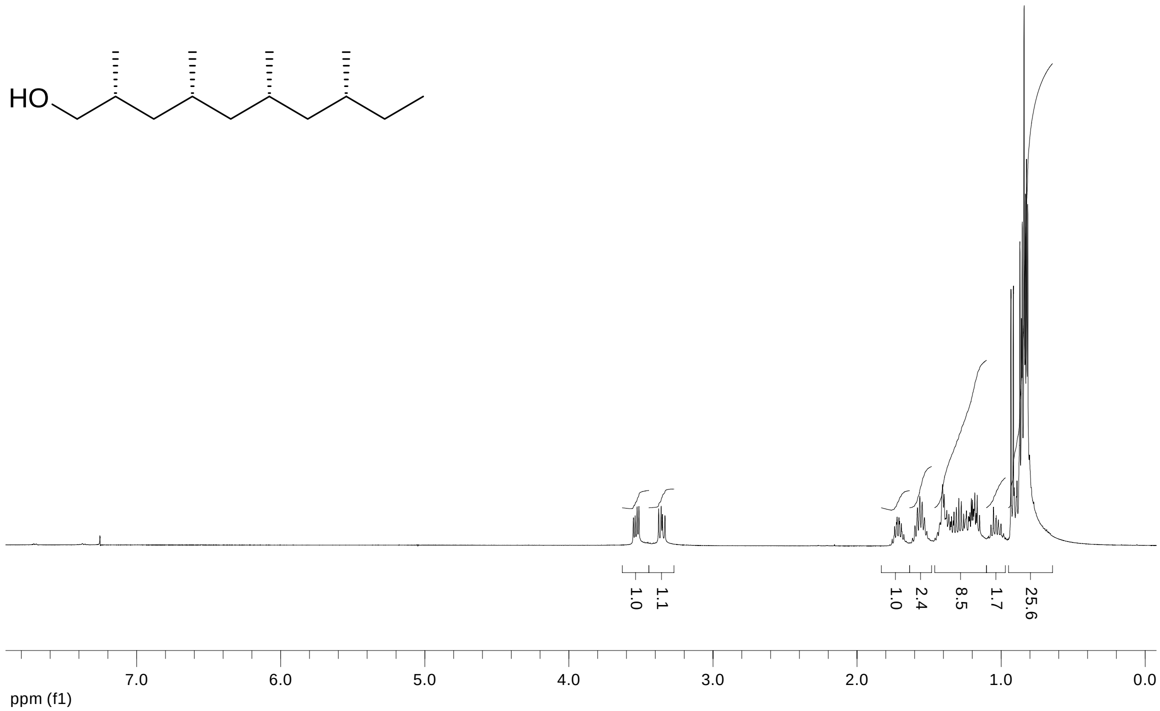

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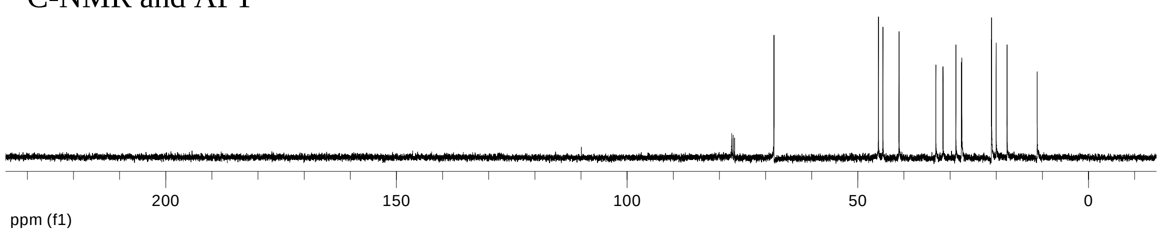

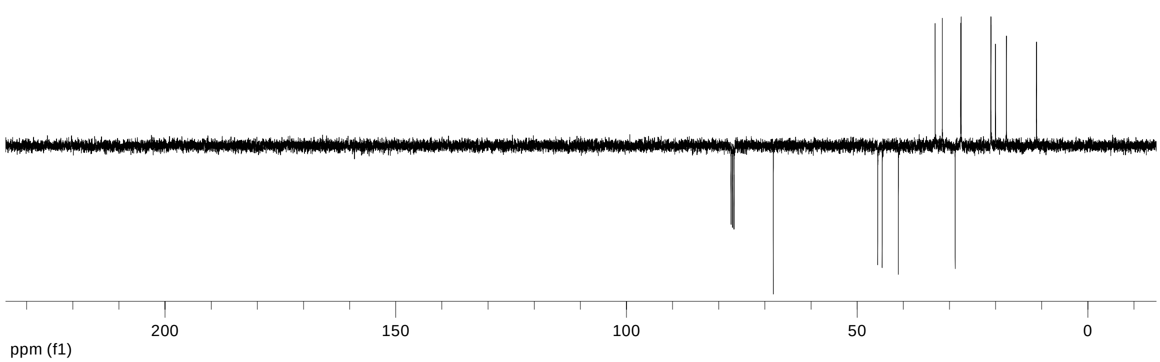

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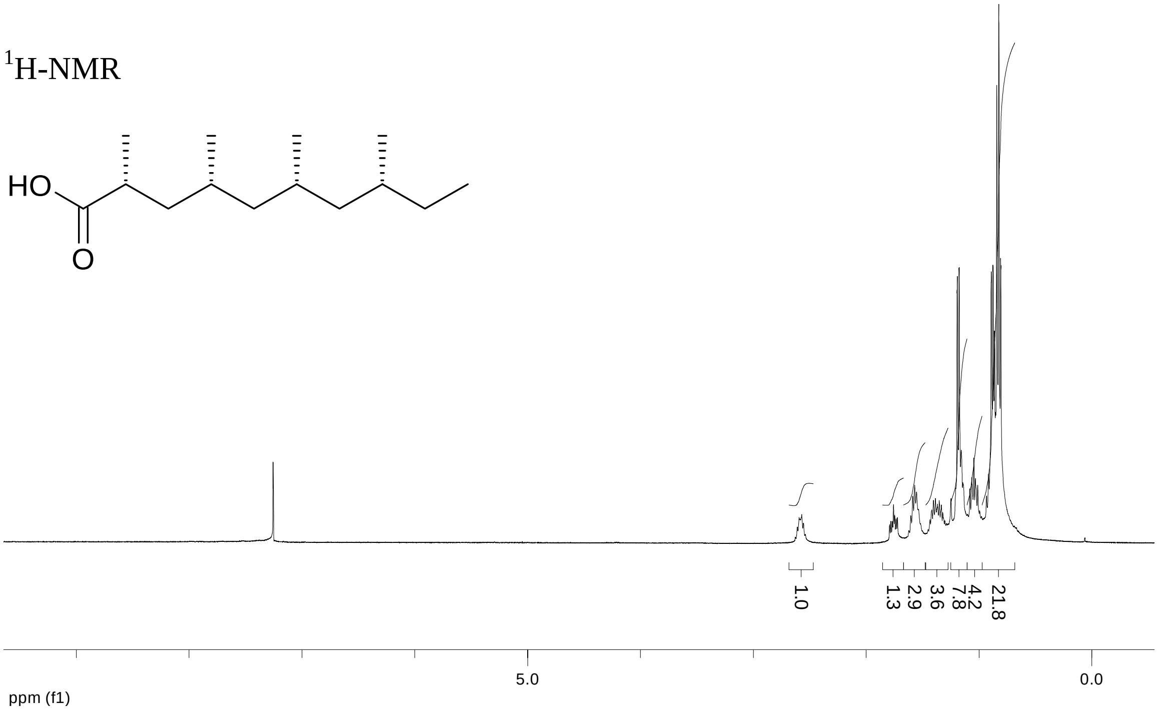

^{13}C-NMR and APT