Supporting Information

A unified, radical based approach for the synthesis of spiroketals

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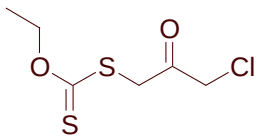
General experimental methods Anhydrous acetone was obtained by distillation from K_2CO_3 under N_2. Anhydrous CH_2Cl_2 was obtained by distillation from CaH_2 under N_2. Anhydrous THF was obtained by distillation from Na-benzophenone under N_2. Anhydrous DMSO was obtained by distillation from CaH_2 under N_2. Anhydrous DMF was obtained by distillation from $MgSO_4$ under N_2. Other solvents were used as supplied by commercial sources. Petroleum ether refers to the fraction of light petroleum ether, boiling between 40-60°C. All reagents were used as supplied by commercial sources unless stated otherwise. Purification procedures were in accordance with the instructions in D.D. Perrin and W.L.F. Armarego, "Purification of Laboratory Chemicals", Fourth edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free N_2. Flash chromatography was performed on silica gel (SDS, 60 Å C.C. 40-63 μm). Thin layer chromatography was performed on aluminium plates pre-coated with silica gel (Merck, 60 F_{254}), which were visualised by the quenching of UV fluorescence (λ_{max} = 254 nm), and/or by staining with vanillin in acidic ethanol or 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3, followed by heating. Boiling points were obtained by short path distillation and are uncorrected. Infrared spectra were recorded as solutions in CCl_4. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). Magnetic resonance spectra were recorded at ambient temperature on either a Bruker AMX 400, or Bruker Advance DPX 400 instrument. Proton magnetic resonance spectra (^{1}H NMR) were recorded at 400 MHz. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 100.6 MHz. Chemical shifts (δ_H, δ_C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. Low-resolution mass spectra (*m*/*z*) were recorded by chemical ionisation (CI) on a Hewlett-Packard HP 5989B instrument. High-resolution mass spectra were recorded by electron impact ionisation at 70 eV on a JMS-GCmate II instrument. The quoted masses are accurate to ± 5 ppm. Microanalyses were carried out by the microanalytical laboratory of the Institut de Chimie des Substances Naturelles, Gif-sur-Yvette.

Experimental procedures.

Dithiocarbonic acid (3-chloro-2-oxo-propyl) ester ethyl ester (1).



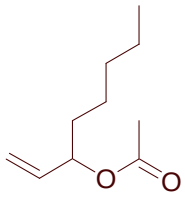
$C_6H_9ClO_2S_2$
Exact Mass: 211,97
Mol. Wt.: 212,72

A solution of dithiocarbonic acid *O*-ethyl ester potassium salt (4.8 g, 30 mmol) in water (30 mL) was cooled to 0°C before slow addition of finely powdered commercial 1,3-dichloroacetone (3.8 g, 30 mmol). Stirring was continued at 0°C for 3 h. The slightly yellow suspension thus obtained was diluted with water (70 mL) before the addition of Et_2O (100 mL). After phase separation, the organic phase

was extracted with water (1 × 100 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded pure **1** (6.0 g, 94%) as a slightly yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.2 Hz, 3 H), 4.14 (s, 2 H), 4.31 (s, 2 H), 4.63 (q, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7 (CH_3), 42.9 (CH_2), 47.9 (CH_2), 71.3 (CH_2), 195.7 (C=O), 212.8 (C=S) ppm. IR (CCl_4): *v* = 2987, 2959, 2939, 1738, 1365, 1292, 1232, 1150, 1113, 1051 cm^{-1}. MS (CI/NH_3): *m/z* 213 (MH^+, $C_6H_9{}^{35}ClO_2S_2$), 215 (MH^+, $C_6H_9{}^{37}ClO_2S_2$). HRMS: found 211.9733 (M^+). $C_6H_9{}^{35}ClO_2S_2$ requires 211.9733.

Acetic acid 1-vinyl-hexyl ester (4).

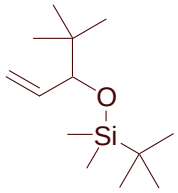


$C_{10}H_{18}O_2$
Exact Mass: 170,13
Mol. Wt.: 170,25

A solution of commercial 1-octen-3-ol (1.3 g, 10 mmol), acetic anhydride (2.1 mL, 22 mmol), and DMAP (0.27 g, 2.2 mmol) in dry CH_2Cl_2 (20 mL) was stirred at room temperature for 90 min. The mixture was then evaporated to dryness under reduced pressure. The residue was purified by flash chromatography on silica gel (Et_2O-petroleum ether, 0:100 to 5:95 v/v) to afford **4** as a slightly yellow oil (1.6 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.22-1.39 (m, 6 H), 1.52-1.68 (m, 2 H), 2.05 (s, 3 H), 5.14-5.29 (m, 3 H), 5.77 (ddd, *J* = 6.4, 10.8, 17.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 21.2 (CH_3), 22.5 (CH_2), 24.7 (CH_2), 31.6 (CH_2), 34.2 (CH_2), 74.9 (CH), 116.4 (CH_2), 136.7 (CH), 170.3 (C=O) ppm. IR (CCl_4): *v* = 3086, 3013, 2957, 2932, 2860, 1738, 1647, 1467, 1426, 1370, 1239, 1123, 1092, 1048, 1020, 988, 956, 932, 922 cm^{-1}. MS (CI/NH_3): A reasonable mass spectrum could not be obtained.

***tert*-Butyl-(1-*tert*-butyl-allyloxy)-dimethyl-silane (5).**[1]

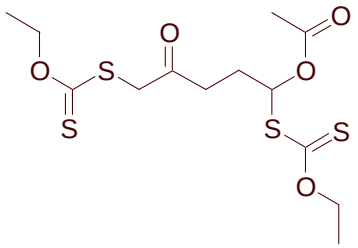


$C_{13}H_{28}OSi$
Exact Mass: 228,19
Mol. Wt.: 228,45

A solution of 4,4-Dimethyl-pent-1-en-3-ol (2.2 g, 20 mmol)[3] in freshly distilled DMF (6 mL) was cooled to 0°C before successive addition of imidazole (2.0 g, 30 mmol) and *tert*-butyl-chloro-dimethyl-silane (3.6 g, 24 mmol). After removal of the icebath, the resulting suspension was stirred at room temperature for 20 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (20 mL). Et_2O (25 mL) was then added and the resulting emulsion vigorously stirred for 5 min. After phase separation, the organic phase was washed with water (3 ×20 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. Crude **27** was obtained as a pale yellow liquid (4.0 g), which was purified by flash chromatography on silica gel (petroleum ether). Pure **27** (2.8 g, 61% over 2 steps) was obtained as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (s, 3 H), 0.04 (s, 3 H), 0.86 (s, 9 H), 0.92 (s, 9 H), 3.66 (dt, *J* = 0.8, 7.2 Hz, 1 H), 5.07-5.13 (m, 2 H), 5.76-5.84 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -4.9 (CH_3), -3.9 (CH_3), 18.3 (C_q), 26.0 (6×CH_3), 35.5 (C_q), 82.1 (CH), 115.7 (CH_2), 139.3 (CH) ppm. IR (CCl_4): *ν* = 2955, 2929, 2895, 2856, 1472, 1462, 1389, 1361, 1251, 1128, 1077, 1031, 1004, 961, 923 cm^{-1}. MS (CI/NH_3): A reasonable mass spectrum could not be obtained.

Acetic acid 1,5-bis-ethoxythiocarbonylsulfanyl-4-oxo-pentyl ester (8a).

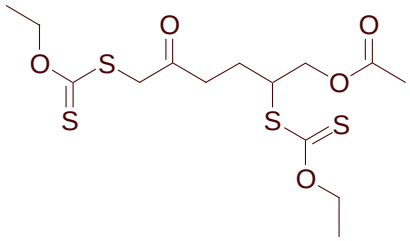


$C_{13}H_{20}O_5S_4$
Exact Mass: 384,02
Mol. Wt.: 384,56

A solution of **1** (858 mg, 4.0 mmol) and freshly distilled vinyl acetate (0.74 mL, 8.0 mmol) in 1,2-dichloro-ethane (4 mL) was refluxed for 15 min. DLP (0.05 eq.) was then added and the solution stirred for 90 min. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. The residue was dissolved in acetone (8 mL) and the solution thus obtained cooled to 0°C. A solution of dithiocarbonic acid *O*-ethyl ester potassium salt (0.71 g, 4.4 mmol) in acetone (10 mL) was added dropwise before removal of the icebath. Stirring was continued at room temperature for 2 h after which the mixture was concentrated under reduced pressure. The resulting slurry was suspended in water (25 mL) and extracted with Et_2O (3 × 25 mL). The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Crude reaction product (1.8 g) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 10:90 to 15:85 v/v) to afford **6a** (806 mg, 52% over 2 steps) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (t, *J* = 7.2 Hz, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H), 2.06 (s, 3 H), 2.13-2.30 (m, 2 H), 2.68-2.82 (m, 2 H), 3.97 (s, 2 H), 4.54-4.67 (m, 4 H), 6.59 (t, *J* = 6.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (CH_3), 13.7 (CH_3), 20.8 (CH_3), 27.9 (CH_2), 37.4 (CH_2), 45.2 (CH_2), 70.3 (CH_2), 70.9 (CH_2), 79.8 (CH), 169.3 (C=O), 201.3 (C=O), 209.7 (C=S), 213.1 (C=S) ppm. IR (CCl_4): *v* = 2987, 2959, 2938, 2900, 1752, 1721, 1471, 1442, 1369, 1292, 1227, 1149, 1113, 1052, 1020 cm^{-1}. MS (CI/NH_3): *m/z* 263 (MH^+ - $C_3H_6OS_2$), 325 (MH^+ - $C_2H_4O_2$), 385 (MH^+), 401 (MNH_4^+).

Acetic acid 2,6-bis-ethoxythiocarbonylsulfanyl-5-oxo-hexyl ester (8b).

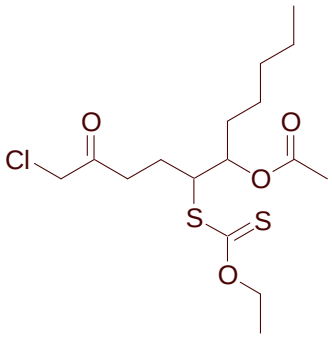


$C_{14}H_{22}O_5S_4$
Exact Mass: 398,04
Mol. Wt.: 398,59

A solution of **1** (864 mg, 4.1 mmol) and allyl acetate (0.89 mL, 8.2 mmol) in 1,2-dichloro-ethane (4 mL) was refluxed for 15 min. DLP (0.05 eq.) was then added and the solution stirred for 90 min. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. The residue was dissolved in acetone (8 mL) and the solution thus obtained cooled to 0°C. A solution of dithiocarbonic acid *O*-ethyl ester potassium salt (0.73 g, 4.5 mmol) in acetone (10 mL) was added dropwise before removal of the icebath. Stirring was continued at room temperature for 60 min. after which the mixture was concentrated under reduced pressure. The resulting slurry was suspended in water (25 mL) and extracted with Et_2O (3 × 25 mL). The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Crude reaction product (1.7 g) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 15:85 to 20:80 v/v) to afford **6b** (1.3 g, 80% over 2 steps) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (t, *J* 7.2 Hz, 3 H), 1.44 (t, *J* = 7.2 Hz, 3 H), 1.90 (ddt, *J* = 7.2, 10.0, 14.0 Hz, 1 H), 2.09 (s, 3 H), 2.20 (dtd, *J* = 5.2, 7.6, 14.0 Hz, 1 H), 2.83 (t, *J* = 7.2 Hz, 2 H), 3.96-4.02 (m, 3 H), 4.24 (dd, *J* = 6.4, 11.6 Hz, 1 H), 4.32 (dd, *J* = 4.8, 11.2 Hz, 1 H), 4.62-4.69 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (2×CH_3), 20.8 (CH_3), 24.6 (CH_2), 38.7 (CH_2), 45.4 (CH_2), 48.8 (CH), 65.6 (CH_2), 70.4 (CH_2), 70.9 (CH_2), 170.6 (C=O), 202.1 (C=O), 212.8 (C=S), 213.3 (C=S) ppm. IR (CCl_4): *v* = 2985, 2958, 2939, 2899, 2870, 1748, 1720, 1443, 1381, 1364, 1292, 1228, 1448, 1112, 1050 cm^{-1}. MS (CI/NH_3): *m/z* 339 (MH^+ - $C_2H_4O_2$), 399 (MH^+). HRMS: found 398.0352 (M^+). $C_{14}H_{22}O_5S_4$ requires 398.0350.

Acetic acid 6-chloro-2-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-hexyl ester (7c).

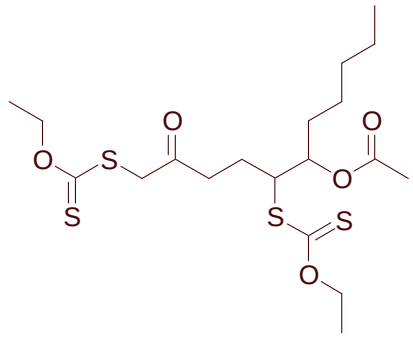


$C_{16}H_{27}ClO_4S_2$
Exact Mass: 382,10
Mol. Wt.: 382,97

A solution of **1** (431 mg, 2.0 mmol) and **4** (689 mg, 4.1 mmol) in 1,2-dichloro-ethane (2 mL) was refluxed for 15 min. DLP (0.05 eq.) was then added and the solution stirred for 90 min. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product (963 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 8:92 to 15:85 v/v) to afford **7c** (711 mg, 91%) as a pale yellow oil consisting of a 1:1 mixture of diastereomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81-0.93 (m, 6 H), 1.19-1.37 (m, 12 H), 1.42 (t, *J* = 6.8 Hz, 3 H), 1.44 (t, *J* = 6.8 Hz, 3 H), 1.56-1.73 (m, 4 H), 1.77-1.91 (m, 2 H), 2.04 (s, 3 H), 2.07 (s, 3 H), 2.10-2.24 (m, 2 H), 2.69-2.88 (m, 4 H), 4.01-4.11 (m, 6 H), 4.61-4.68 (m, 4 H), 5.10-5.19 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (2×CH_3), 14.0 (2×CH_3), 21.0 (CH_3), 21.1 (CH_3), 22.5 (2×CH_2), 22.9 (CH_2), 25.2 (CH_2), 25.3 (CH_2), 25.9 (CH_2), 31.4 (CH_2), 31.5 (2×CH_2), 32.0 (CH_2), 36.8 (CH_2), 37.0 (CH_2), 48.2 (2×CH_2), 53.8 (2×CH), 70.6 (CH_2), 70.7 (CH_2), 75.1 (CH), 75.4 (CH), 170.5 (2×C=O), 201.7 (C=O), 201.8 (C=O), 213.9 (C=S), 214.1 (C=S) ppm. IR (CCl_4): *v* = 2957, 2932, 2861, 1744, 1723, 1444, 1402, 1371, 1292, 1227, 1147, 1112, 1052, 1021 cm^{-1}. MS (CI/NH_3): *m/z* 323 (MH^+ - $C_2H_4O_2$, $C_{16}H_{27}{}^{35}ClO_4S_2$), 325 ($MH^+$ - $C_2H_4O_2$, $C_{16}H_{27}{}^{37}ClO_4S_2$), 383 ($MH^+$, $C_{16}H_{27}{}^{35}ClO_4S_2$), 385 ($MH^+$, $C_{16}H_{27}{}^{37}ClO_4S_2$), 400 ($MNH_4^+$, $C_{16}H_{27}{}^{35}ClO_4S_2$), 402 ($MNH_4^+$, $C_{16}H_{27}{}^{37}ClO_4S_2$).

Acetic acid 2,6-bis-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-hexyl ester (8c).

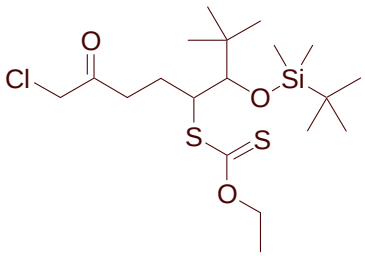


$C_{19}H_{32}O_5S_4$
Exact Mass: 468,11
Mol. Wt.: 468,72

A solution of **7c** (711 mg, 1.9 mmol) in acetone (4 mL) was cooled to 0°C. A solution of dithiocarbonic acid *O*-ethyl ester potassium salt (329 mg, 2.1 mmol) in acetone (6 mL) was added dropwise before removal of the icebath. Stirring was continued at room temperature for 2 h after which the mixture was concentrated under reduced pressure. The resulting slurry was suspended in water (20 mL) and extracted with Et_2O (3 × 20 mL). The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Crude reaction product (868 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 10:90 v/v) to afford **8c** (763 mg, 88%) as a pale yellow oil consisting of a 1:1 mixture of diastereomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88-0.93 (m, 6 H), 1.26-1.40 (m, 12 H), 1.43-1.49 (m, 12 H), 1.61-1.75 (m, 4 H), 1.78-1.91 (m, 2 H), 2.07 (s, 3 H), 2.10 (s, 3 H), 2.12-2.27 (m, 2 H), 2.75-2.92 (m, 4 H), 3.97-4.10 (m, 6 H), 4.64-4.73 (m, 8H), 5.14-5.21 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (4×CH_3), 14.0 (2×CH_3), 21.0 (CH_3), 21.1 (CH_3), 22.5 (2×CH_2), 22.9 (CH_2), 25.2 (CH_2), 25.3 (CH_2), 25.9 (CH_2), 31.4 (CH_2), 31.5 (2×CH_2), 31.9 (CH_2), 38.9 (CH_2), 39.1 (CH_2), 45.4 (2×CH_2), 53.8 (2×CH), 70.5 (CH_2), 70.6 (CH_2), 70.9 (2×CH_2), 75.1 (CH), 75.4 (CH), 170.4 (C=O), 170.5 (C=O), 202.2 (C=O), 202.4 (C=O), 213.3 (2×C=S), 213.8 (C=S), 214.0 (C=S) ppm. IR (CCl_4): ν = 2957, 2932, 2861, 1743, 1723, 1443, 1370, 1292, 1227, 1148, 1113, 1051 cm^{-1}. MS (CI/NH_3): *m/z* 486 (MNH_4^+).

Dithiocarbonic acid {1-[1-(*tert*-butyl-dimethyl-silanyloxy)-2,2-dimethyl-propyl]-5-chloro-4-oxo-pentyl} ester ethyl ester (7d).



$C_{19}H_{37}ClO_3S_2Si$
Exact Mass: 440,16
Mol. Wt.: 441,17

A solution of **1** (317 mg, 1.5 mmol) and **5** (691 mg, 3.0 mmol) in 1,2-dichloro-ethane (1.5 mL) was refluxed for 15 min. DLP (0.05 eq.) was then added. Additional DLP (0.05 eq.) was added every 90 min. until complete consumption of **1**. After addition of 0.30 eq. of DLP, the mixture was cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product (1.0 g) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 2:98 v/v) to afford **7d** (379 mg, 57%) as a pale yellow oil, consisting of a 1:3 mixture of separable diastereomers.

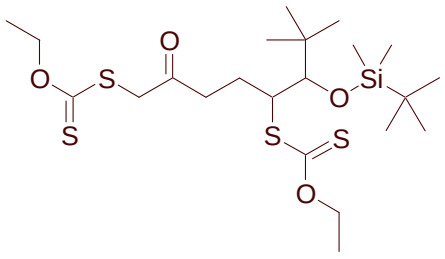
Least polar isomer (major)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3 H), 0.13 (s, 3 H), 0.92 (s, 9 H), 0.99 (s, 9 H), 1.42 (t, *J* = 7.2 Hz, 3 H), 1.71 (dddd, *J* = 5.2, 6.8, 12.0, 15.2 Hz, 1 H), 2.33 (dddd, *J* = 2.8, 6.8, 8.4, 15.6 Hz, 1 H), 2.68 (ddd, *J* = 5.2, 6.4, 18.4 Hz, 1 H), 2.79 (ddd, *J* = 6.8, 8.8, 18.4 Hz, 1 H), 3.71 (d, *J* = 1.2 Hz, 1 H), 4.07 (d, *J* = 2.0 Hz, 2 H), 4.16 (ddd, *J* = 1.2, 2.8, 15.6 Hz, 1 H), 4.58-4.71 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -4.6 (CH_3), -3.0 (CH_3), 13.9 (CH_3), 18.7 (C_q), 24.2 (CH_2), 26.3 (3×CH_3), 27.0 (3×CH_3), 37.1 (CH_2, C_q), 48.4 (CH_2), 53.2 (CH), 70.4 (CH_2), 85.3 (CH), 202.1 (C=O), 214.5 (C=S) ppm. IR (CCl_4): *v* = 2957, 2930, 2895, 2858, 1721, 1472, 1397, 1362, 1255, 1217, 1110, 1052, 1030 cm^{-1}. MS (CI/NH_3): *m/z* 307 (MH^+ - $C_6H_{16}OSi$, $C_{19}H_{37}{}^{35}ClO_3S_2Si$), 309 ($MH^+$ - $C_6H_{16}OSi$, $C_{19}H_{37}{}^{37}ClO_3S_2Si$), 441 ($MH^+$, $C_{19}H_{37}{}^{35}ClO_3S_2Si$), 443 ($MH^+$, $C_{19}H_{37}{}^{37}ClO_3S_2Si$), 458 ($MNH_4^+$, $C_{19}H_{37}{}^{35}ClO_3S_2Si$), 460 ($MNH_4^+$, $C_{19}H_{37}{}^{37}ClO_3S_2Si$).

Most polar isomer (minor)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 3 H), 0.12 (s, 3 H), 0.94 (s, 18 H), 1.42 (t, *J* = 7.2 Hz, 3 H), 2.00-2.19 (m, 2 H), 2.68 (ddd, *J* = 5.6, 7.6, 18.4 Hz, 1 H), 2.79 (dt, *J* = 7.6, 18.0 Hz, 1 H), 3.46 (s, 1 H), 4.09 (d, *J* = 1.2 Hz, 2 H), 4.17 (dd, *J* = 5.6, 9.6 Hz, 1 H), 4.55-4.70 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -3.9 (CH_3), -3.1 (CH_3), 13.9 (CH_3), 18.8 (C_q), 26.3 (3×CH_3), 26.9 (3×CH_3), 31.2 (CH_2), 36.7 (C_q), 37.1 (CH_2), 48.3 (CH_2), 53.7 (CH), 70.3 (CH_2), 82.9 (CH), 201.8 (C=O), 216.6 (C=S) ppm. IR (CCl_4): *v* = 2958, 2930, 2858, 1721, 1472, 1397, 1362, 1254, 1213, 1100, 1054 cm^{-1}. MS (CI/NH_3): *m/z* 307 (MH^+ - $C_6H_{16}OSi$, $C_{19}H_{37}{}^{35}ClO_3S_2Si$), 309 ($MH^+$ - $C_6H_{16}OSi$, $C_{19}H_{37}{}^{37}ClO_3S_2Si$), 441 ($MH^+$, $C_{19}H_{37}{}^{35}ClO_3S_2Si$), 443 ($MH^+$, $C_{19}H_{37}{}^{37}ClO_3S_2Si$).

Dithiocarbonic acid [6-(*tert*-butyl-dimethyl-silanyloxy)-5-ethoxythio-carbonyl-sulfanyl-7,7-dimethyl-2-oxo-octyl] ester ethyl ester (8d).



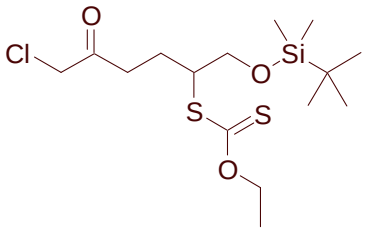
$C_{22}H_{42}O_4S_4Si$
Exact Mass: 526,17
Mol. Wt.: 526,92

A solution of **7d** (261 mg, 0.59 mmol, single diastereomer) in acetone (2 mL) was cooled to 0°C. A solution of dithiocarbonic acid *O*-ethyl ester potassium salt (105 mg, 0.65 mmol) in acetone (1 mL) was added dropwise before removal of the icebath. Stirring was continued at room temperature for 2 h after which the mixture was concentrated under reduced pressure. The resulting slurry was suspended

in water (10 mL) and extracted with Et_2O (3 × 10 mL). The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Crude reaction product (308 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 3:97 to v/v) to afford **8d** (296 mg, 95%) as a pale yellow oil, consisting of a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 3 H), 0.14 (s, 3 H), 0.92 (s, 9 H), 0.99 (s, 9 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 1.43 (t, *J* = 7.2 Hz, 3 H), 1.69 (dddd, *J* = 5.2, 6.4, 12.0, 15.6 Hz, 1 H), 2.32 (dddd, *J* = 2.4, 6.8, 8.4, 15.6 Hz, 1 H), 2.73 (ddd, *J* = 5.2, 6.8, 18.4 Hz, 1 H), 2.83 (ddd, *J* = 6.8, 8.8, 18.0 Hz, 1 H), 3.71 (d, *J* = 0.8 Hz, 1 H), 3.93 (d, *J* = 16.8 Hz, 1 H), 4.01 (d, *J* = 16.8 Hz, 1 H), 4.16 (ddd, *J* = 0.8, 2.4, 12.0 Hz, 1 H), 4.58-4.69 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -4.5 (CH_3), -3.0 (CH_3), 13.8 (CH_3), 13.9 (CH_3), 18.7 (C_q), 24.2 (CH_2), 26.3 (3×CH_3), 27.1 (3×CH_3), 37.1 (C_q), 39.3 (CH_2), 45.5 (CH_2), 53.4 (CH), 70.3 (CH_2), 70.9 (CH_2), 85.3 (CH), 202.8 (C=O), 213.5 (C=S), 214.5 (C=S) ppm. IR (CCl_4): *v* = 2957, 2930, 2895, 2857, 1718, 1472, 1362, 1218, 1147, 1112, 1052, 1030, 1008 cm^{-1}. MS (CI/NH_3): *m*/*z* 527 (MH^+).

Dithiocarbonic acid [1-(*tert*-butyl-dimethyl-silanyloxymethyl)-5-chloro-4-oxo-pentyl] ester ethyl ester (7e).



$C_{15}H_{29}ClO_3S_2Si$
Exact Mass: 384,10
Mol. Wt.: 385,06

A solution of **1** (648 mg, 3.1 mmol) and commercial TBS-protected allyl alcohol (1.1 g, 6.1 mmol) in 1,2-dichloro-ethane (3 mL) was refluxed for 15 min. DLP (0.025 eq.) was then added. Additional DLP (0.025 eq.) was added every 90 min. until complete consumption of **1**. After addition of 0.125 eq. of DLP, the mixture was cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product (1.4 g) was obtained as a brown oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 2:98 to 5:95 v/v) to afford **7e** (844 mg, 72%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 3 H), 0.07 (s, 3 H), 0.89 (s, 9 H), 1.42 (t, *J* = 7.2 Hz, 3 H), 1.91 (ddt, *J* = 7.2, 8.8, 14.8 Hz, 1 H), 2.25 (dtd, *J* = 4.8, 7.6, 14.8 Hz, 1 H), 2.79 (dt, *J* = 7.2 Hz, 2 H), 3.72 (dd, *J* = 5.6, 9.6 Hz, 1 H), 3.81-3.89 (m, 2 H), 4.09 (s, 2 H), 4.64 (q, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -5.4 (CH_3), -5.3 (CH_3), 13.8 (CH_3), 18.3 (C_q), 24.8 (CH_2), 25.9 (3×CH_3),

37.1 (CH_2), 48.2 (CH_2), 52.2 (CH), 65.3 (CH_2), 70.2 (CH_2), 201.9 (C=O), 214.3 (C=O) ppm. IR (CCl_4): ν = 2955, 2929, 2897, 2857, 1743, 1722, 1471, 1463, 1443, 1404, 1388, 1362, 1292, 1254, 1217, 1112, 1054 cm^{-1}. MS (CI/NH_3): *m/z* 254 (MH^+ - $C_6H_{16}OSi$, $C_{15}H_{29}{}^{35}ClO_3S_2Si$), 256 ($MH^+$ - $C_6H_{16}OSi$, $C_{15}H_{29}{}^{37}ClO_3S_2Si$), 385 ($MH^+$, $C_{15}H_{29}{}^{35}ClO_3S_2Si$), 387 ($MH^+$, $C_{15}H_{29}{}^{37}ClO_3S_2Si$), 402 ($MNH_4^+$, $C_{15}H_{29}{}^{35}ClO_3S_2Si$), 404 ($MNH_4^+$, $C_{15}H_{29}{}^{37}ClO_3S_2Si$).

Preparation of allylic acetates (9) – (12).

General procedure for the preparation of allylic alcohols, method A

To a solution of aldehyde (1 eq.) in dry Et_2O (7mL/mmol of aldehyde) was added dropwise at room temperature a commercial 1M solution of vinyl magnesiumbromide in THF (1.1-1.2 eq.). Stirring was continued at room temperature for 60 min. The resulting white suspension was then poured into icecold water. After phase separation, the organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude reaction products were sufficiently pure to be used without purification in the next reaction step.

General procedure for the preparation of allylic alcohols, method B

A commercial 1M solution of vinyl magnesiumbromide in THF (1.2-4.2 eq.) was cooled to 0°C before dropwise addition of a solution of aldehyde (1.0 eq.) in dry THF. The icebath was removed and stirring was continued at room temperature for 2 h. The resulting mixture was cooled to 0°C and quenched with a saturated aqueous solution of NH_4Cl. The aqueous mixture was extracted several times with either AcOEt, or Et_2O. The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude reaction products were sufficiently pure to be used without purification in the next reaction step.

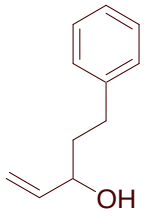
General procedure for the preparation of allylic alcohols, method C

A solution of ketone (1.0 eq.) in dry THF was cooled to 0°C before dropwise addition of a commercial 1M solution of vinyl magnesiumbromide in THF (1.1 eq.). The icebath was removed and stirring was continued at room temperature for 3 h. The resulting mixture was cooled to 0°C and quenched with a saturated aqueous solution of NH_4Cl. The aqueous mixture was extracted several times with Et_2O. The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was purified by flash chromatography on silica gel.

General acetylation procedure.

A solution of crude alcohol (1.0 eq.), acetic anhydride (2.2-4.4 eq.), and DMAP (0.22 eq.) in either dry CH_2Cl_2, or dry THF (2.0 mL/mmol of alcohol) was stirred at room temperature for 90 min. The mixture was then evaporated to dryness under reduced pressure. The residue was purified by flash chromatography on silica gel to afford acetylated alcohols **9-12**.

5-Phenyl-pent-1-en-3-ol.[2]

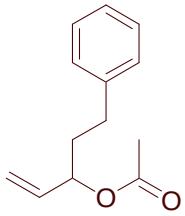


$C_{11}H_{14}O$
Exact Mass: 162,10
Mol. Wt.: 162,23

Method A - The reaction was carried out with dihydrocinnamaldehyde (1.1 g, 7.8 mmol) and a commercial 1M solution of vinyl magnesiumbromide in THF (8.5 mL). Crude reaction product (1.1 g, 85%) was obtained as a pale yellow oil and used as such in the reaction step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 3.2 Hz, 1 H), 1.85-1.91 (m, 2 H), 2.67-2.81 (m, 2 H), 4.11-4.17 (m, 1 H), 5.15 (dd, *J* = 1.2, 10.4 Hz, 1 H), 5.26 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.92 (ddd, *J* = 6.0, 10.4, 17.2 Hz, 1 H), 7.18-7.32 (m, 5 H) ppm.

Acetic acid 1-phenethyl-allyl ester (9).



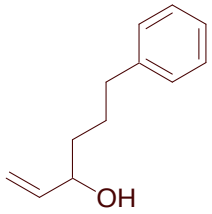
$C_{13}H_{16}O_2$
Exact Mass: 204,12
Mol. Wt.: 204,26

The reaction was carried out with a solution of allylic alcohol (1.1 g, 6.6 mmol), acetic anhydride (1.4 mL, 14.7 mmol), and DMAP (0.18 g, 1.47 mmol) in CH_2Cl_2. Flash chromatography on silica gel (EtOAc-petroleum ether, 2:98 to 4:96 v/v) afforded **9** (982 mg, 48% over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95-2.09 (m, 2 H), 2.12 (s, 3 H), 2.70-2.76 (m, 2 H), 5.25-5.37 (m, 3 H), 5.88 (ddd, *J* = 6.4, 10.4, 17.2, Hz, 1 H), 7.23-7.27 (m, 3 H), 7.31-7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3), 31.5 (CH_2), 35.8 (CH_2), 74.3 (CH), 116.9 (CH_2), 126.0 (CH),

128.4 (2×CH), 128.5 (2×CH), 136.4 (CH), 141.4 (C_q), 170.3 (C=O) ppm. IR (CCl_4): ν = 3087, 3065, 3028, 2949, 2862, 1739, 1497, 1454, 1426, 1370, 1239, 1021 cm^{-1}. MS (CI/NH_3): *m/z* 222 (MNH_4^+).

6-Phenyl-hex-1-en-3-ol.

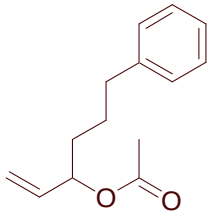


$C_{12}H_{16}O$
Exact Mass: 176,12
Mol. Wt.: 176,25

Method A - The reaction was carried out with 4-phenyl-butyraldehyde (1.4 g, 9.4 mmol) and a commercial 1M solution of vinyl magnesiumbromide in THF (11.3 mL). Crude reaction product (1.4 g, 85%) was obtained as a pale yellow oil and used as such in the next reaction step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (brs, 1 H), 1.54-1.79 (m, 4 H), 2.66 (t, *J* = 7.6 Hz, 2 H), 4.09-4.18 (m, 1 H), 5.11 (dt, *J* = 1.2, 10.4 Hz, 1 H), 5.23 (dt, *J* = 1.2, 17.2 Hz, 1 H), 5.87 (ddd, *J* = 6.4, 10.4, 17.2 Hz, 1 H), 7.14-7.32 (m, 5 H) ppm.

Acetic acid 4-phenyl-1-vinyl-butyl ester (10).

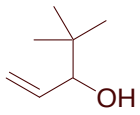


$C_{14}H_{18}O_2$
Exact Mass: 218,13
Mol. Wt.: 218,29

The reaction was carried out with a solution of allylic alcohol (1.4 g, 7.9 mmol), acetic anhydride (1.7 mL, 17.6 mmol), and DMAP (0.22 g, 1.8 mmol) in CH_2Cl_2. Flash chromatography on silica gel (EtOAc-petroleum ether, 2:98 v/v) afforded **10** (907 mg, 44% over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67-1.78 (m, 4 H), 2.12 (s, 3 H), 2.69 (t, *J* = 7.6 Hz, 2 H), 5.21-5.34 (m, 3 H), 5.83 (ddd, *J* = 6.4, 10.8, 17.2 Hz, 1 H), 7.22-7.26 (m, 3 H), 7.31-7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3 (CH_3), 26.9 (CH_2), 33.8 (CH_2), 35.6 (CH_2), 74.6 (CH), 116.7 (CH_2), 125.9 (CH), 128.4 (4×CH), 136.5 (CH), 142.1 (C_q), 170.3 (C=O) ppm. IR (CCl_4): ν = 3086, 3065, 3028, 2944, 2862, 1740, 1496, 1454, 1370, 1240, 1020 cm^{-1}. MS (CI/NH_3): *m/z* 236 (MNH_4^+).

4,4-Dimethyl-pent-1-en-3-ol.[3]

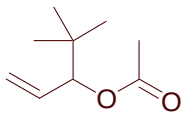


$C_7H_{14}O$
Exact Mass: 114,10
Mol. Wt.: 114,19

Method B - The reaction was carried out with a solution of pivalaldehyde (1.7 g, 20 mmol) in dry THF (5 mL) and a commercial 1M solution of vinyl magnesiumbromide in THF (24 mL). Crude reaction product (2.1 g, 92%) was obtained as a pale yellow liquid and used as such in the next reaction step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (s, 9 H), 1.77 (brs, 1 H), 3.73 (d, *J* = 7.0 Hz, 1 H), 5.15 (dt, *J* = 1.2, 10.4 Hz, 1 H), 5.21 (dt, *J* = 1.2, 17.2 Hz, 1 H), 5.91 (ddd, *J* = 7.0, 10.4, 17.2 Hz, 1 H) ppm.

Acetic acid 1-*tert*-butyl-allyl ester (11).

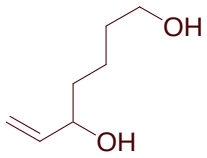


$C_9H_{16}O_2$
Exact Mass: 156,12
Mol. Wt.: 156,22

The reaction was carried out with a solution of allylic alcohol (2.3 g, 20 mmol), acetic anhydride (4.1 mL, 44 mmol), and DMAP (0.54 g, 4.4 mmol) in CH_2Cl_2. Flash chromatography on silica gel (Et_2O-petroleum ether, 3:97 v/v) afforded **11** (1.4 g, 45% over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 9 H), 2.07 (s, 3 H), 4.98 (dd, *J* = 0.4, 6.8 Hz, 1 H), 5.19-5.23 (m, 2 H), 5.79 (ddd, *J* = 7.2, 10.0, 17.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3), 25.8 (3×CH_3), 34.2 (C_q), 81.9 (CH), 118.1 (CH_2), 133.7 (CH), 170.4 (C=O) ppm. IR (CCl_4): *ν* = 3085, 3022, 2968, 2908, 2872, 1740, 1479, 1464, 1424, 1395, 1368, 1244, 1102, 1042, 1019, 974 cm^{-1}. MS (CI/NH_3): *m*/*z* 97 (MH^+ - $C_2H_4O_2$), 174 (MNH_4^+).

Hept-6-ene-1,5-diol.[4]

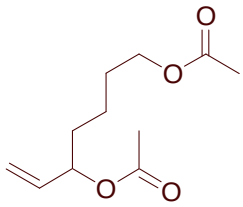


$C_7H_{14}O_2$
Exact Mass: 130,10
Mol. Wt.: 130,18

Method B - The reaction was carried out with a solution of 90% 5-hydroxy-pentanal (1.7 g, 15 mmol) in dry THF (10 mL) and a commercial 1M solution of vinyl magnesiumbromide in THF (45 mL). Crude reaction product (2.0 g, 100%) was obtained as a pale yellow liquid and used as such in the next reaction step.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31-1.60 (m, 6 H), 3.21 (brs, 2 H), 3.58 (t, *J* = 6.4 Hz, 2 H), 4.03-4.08 (m, 1 H), 5.05 (dt, *J* = 1.2, 10.4 Hz, 1 H), 5.18 (dt, *J* = 1.2, 17.2 Hz, 1 H), 5.82 (ddd, *J* = 6.0, 10.4, 17.2 Hz, 1 H) ppm.

Acetic acid 5-acetoxy-1-vinyl-pentyl ester (12).



$C_{11}H_{18}O_4$
Exact Mass: 214,12
Mol. Wt.: 214,26

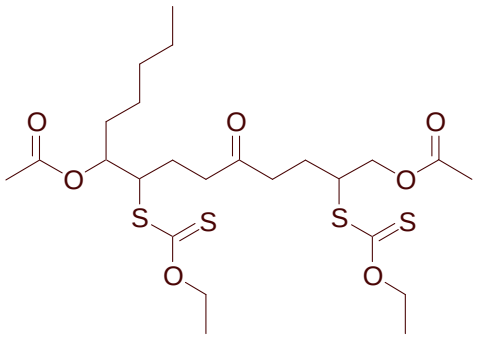
The reaction was carried out with a solution of allylic alcohol (2.0 g, 15 mmol), acetic anhydride (6.2 mL, 66 mmol), and DMAP (0.40 g, 3.3 mmol) in CH_2Cl_2. Flash chromatography on silica gel (EtOAc-petroleum ether, 15:185 v/v) afforded **12** (2.7 g, 84% over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28-1.44 (m, 2 H), 1.54-1.70 (m, 4 H), 2.02 (s, 3 H), 2.04 (s, 3 H), 4.02 (t, *J* = 6.8 Hz, 2 H), 5.13-5.24 (m, 3 H), 5.74 (ddd, *J* = 6.4, 10.4, 17.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 21.2 (CH_3), 21.5 (CH_2), 28.3 (CH_2), 33.7 (CH_2), 64.2 (CH_2), 74.5 (CH), 116.8 (CH_2), 136.3 (CH), 170.3 (C=O), 171.1 (C=O) ppm. IR (CCl_4): *v* = 3086, 2951, 2868, 1741, 1647, 1457, 1426, 1368, 1240, 1043, 1020, 989, 971, 934 cm^{-1}. MS (CI/NH_3): *m*/*z* 215 (MH^+), 232 (MNH_4^+).

Radical addition - General procedure.

A solution of bisxanthate (1.0 eq.) and olefin (2.0-2.3 eq.) in 1,2-dichloro-ethane (1.0 mL/mmol of bisxantahte) was refluxed for 15 min. DLP (0.025-0.05 eq.) was then added and additional DLP (0.025-0.05 eq.) was added every 90 min. until complete consumption of the bisxanthate. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product was obtained as a complicated mixture of inseparable diastereomers that was either purified by flash chromatography, or used as such in the next reaction step.

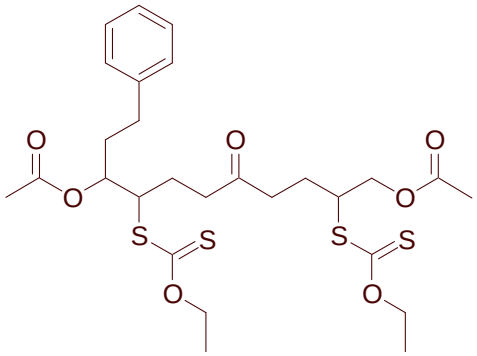
Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxotetradecyl ester (15a).



$C_{24}H_{40}O_7S_4$
Exact Mass: 568,17
Mol. Wt.: 568,83

The reaction was carried out with a solution of **8b** (705 mg, 1.8 mmol) and **4** (603 mg, 3.5 mmol) and needed 0.05 eq of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 12:88 to 20:80 v/v) afforded **15a** (885 mg, 88%) as a slightly yellow oil..

Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-11-phenyl-undecyl ester (15b).

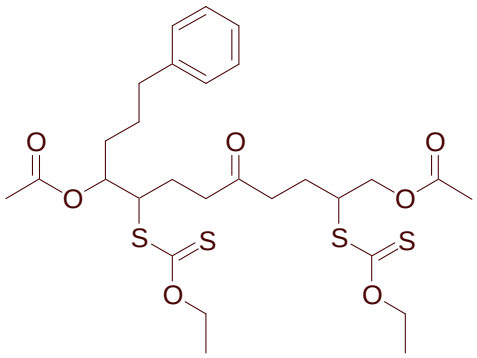


$C_{27}H_{38}O_7S_4$
Exact Mass: 602,15
Mol. Wt.: 602,85

The reaction was carried out with a solution of **8b** (439 mg, 1.1 mmol) and **9** (449 mg, 2.2 mmol) and needed 0.20 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum

ether, 15:85 to 25:75 v/v) afforded an inseparable mixture of **15b** (< 462 mg, < 70%) and a slightly more polar impurity as slightly yellow oils.

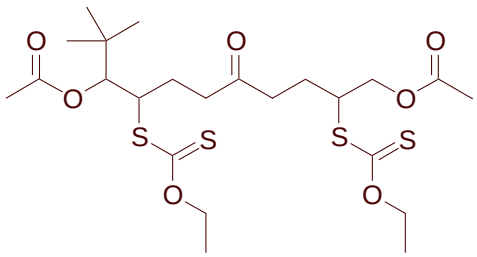
Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-12-phenyl-dodecyl ester (15c).



$C_{28}H_{40}O_7S_4$
Exact Mass: 616,17
Mol. Wt.: 616,88

The reaction was carried out with a solution of **8b** (201 mg, 0.50 mmol) and **10** (225, 1.0 mmol) and needed 0.30 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 15:85 to 20:80 v/v) afforded an inseparable mixture of **15c** (< 219 mg, < 82%) and a slightly more polar impurity as slightly yellow oils.

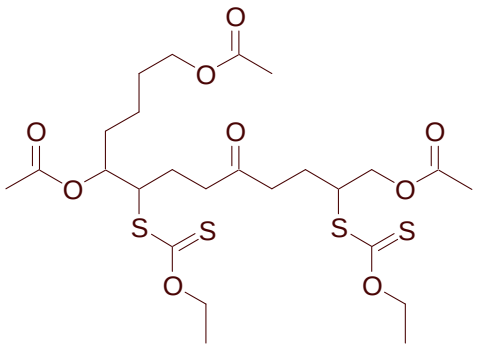
Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-10,10-dimethyl 5-oxo-undecyl ester (15d).



$C_{23}H_{38}O_7S_4$
Exact Mass: 554,15
Mol. Wt.: 554,81

The reaction was carried out with a solution of **8b** (268 mg, 0.67 mmol) and **11** (238 mg, 1.5 mmol) and needed 0.35 eq of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 10:90 to 15:85 v/v) afforded **15d** (257 mg, 69%) as a slightly yellow oil.

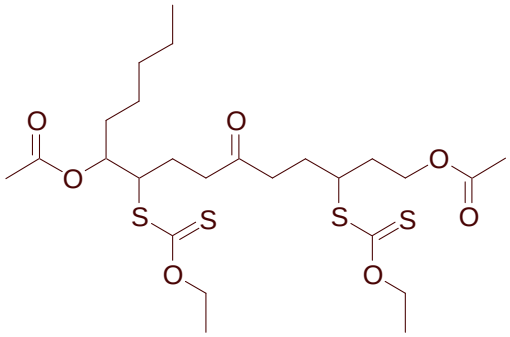
Acetic acid 9,13-diacetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo tridecyl ester (15e).



$C_{25}H_{40}O_9S_4$
Exact Mass: 612,16
Mol. Wt.: 612,84

The reaction was carried out with a solution of **8b** (409 mg, 1.0 mmol) and **12** (519 mg, 2.4 mmol) and needed 0.125 eq of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 24:76 to 30:70 v/v) afforded **15e** (495 mg, 78%) as a slightly yellow oil.

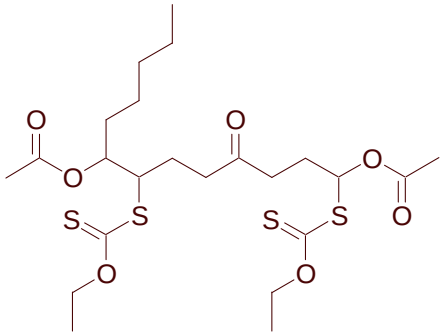
Acetic acid 10-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-decyl ester (15f).



$C_{25}H_{42}O_7S_4$
Exact Mass: 582,18
Mol. Wt.: 582,86

The reaction was carried out with a solution of **8c** (224 mg, 0.48 mmol) and homoallyl acetate (0.12 mL, 0.96 mmol) and needed 0.075 eq of DLP to go to completion. Crude **15f** was obtained as a pale yellow oil (293 mg).

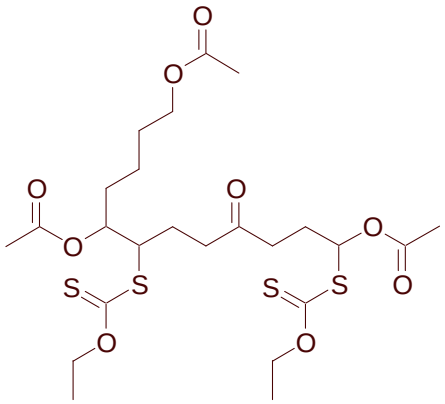
Acetic acid 8-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-octyl ester (15g).



$C_{23}H_{38}O_7S_4$
Exact Mass: 554,15
Mol. Wt.: 554,81

The reaction was carried out with a solution of **8c** (247 mg, 0.53 mmol) and freshly distilled vinyl acetate (0.15 mL, 1.6 mmol) and needed 0.075 eq of DLP to go to completion. Crude **15g** was obtained as a pale yellow oil (322 mg).

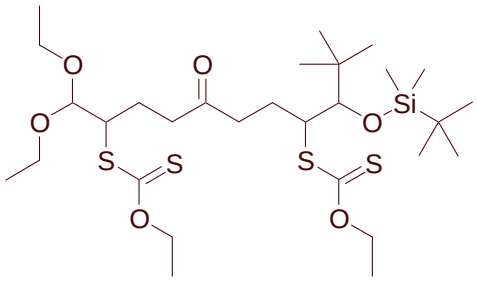
Acetic acid 8-acetoxy-1-(4-acetoxy-butyl)-2,8-bis-ethoxythiocarbonyl sulfanyl-5-oxo-octyl ester (15h).



$C_{24}H_{38}O_9S_4$
Exact Mass: 598,14
Mol. Wt.: 598,82

The reaction was carried out with a solution of **8a** (392 mg, 1.0 mmol) and **12** (466 mg, 2.0 mmol) and needed 0.275 eq of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 22:78 to 30:70 v/v) afforded **15h** (344 mg, 57%) as a pale yellow oil.

Dithiocarbonic acid {1-[1-(*tert*-butyl-dimethyl-silanyloxy)-2,2-dimethyl-propyl]-8,8-diethoxy-7-ethoxythiocarbonylsulfanyl-4-oxo-octyl} ester ethyl ester (15i).



$C_{29}H_{56}O_6S_4Si$
Exact Mass: 656,27
Mol. Wt.: 657,10

The reaction was carried out with a solution of **8d** (405 mg, 0.77 mmol) and **14** (500 mg, 3.8 mmol) and needed 0.25 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 3:97 to 4:96 v/v) afforded **15i** (283 mg, 56%) as a pale yellow mixture of inseparable diastereomers.

Reduction of bisxanthates 15a-i – General procedures.

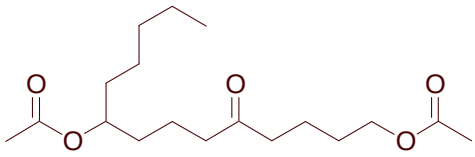
Method A

A solution of bisxanthate in isopropanol (20 mL/mmol of bisxanthate) was refluxed for 15 min. DLP (1.0 eq.) was then added and additional DLP (1.0 eq.) was added every 2 h until complete consumption of the starting material. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel.

Method B

A solution of bisxanthate (1.0 eq.) and *n*-Bu_3SnH (2.5 eq.) in heptane (20 mL/mmol bisxanthate) was refluxed for 15 min. AIBN (0.1 eq.) was then added and the yellowish solution stirred for 60 min. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel.

Acetic acid 9-acetoxy-5-oxo-tetradecyl ester (16a).

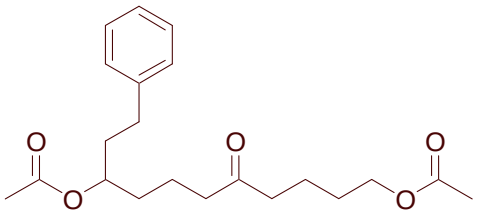


$C_{18}H_{32}O_5$
Exact Mass: 328,22
Mol. Wt.: 328,44

Method A - The reaction was carried out with a solution of **15a** (525 mg, 0.92 mmol) and needed 3.0 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 0:100 to 20:80 v/v) afforded **16a** (238 mg, 79%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.8 Hz, 3 H), 1.18-1.34 (m, 6 H), 1.40-1.67 (m, 10 H), 2.01 (s, 6 H), 2.31-2.47 (m, 4 H), 4.03 (t, *J* = 6.0 Hz, 2 H), 4.82 (tt, *J* = 5.6, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.4 (CH_2), 20.2 (CH_2), 20.9 (CH_3), 21.2 (CH_3), 22.5 (CH_2), 25.0 (CH_2), 28.1 (CH_2), 31.7 (CH_2), 33.5 (CH_2), 34.0 (CH_2), 42.1 (CH_2), 42.3 (CH_2), 64.1 (CH_2), 73.8 (CH), 170.9 (C=O), 171.1 (C=O), 210.0 (C=O) ppm. IR (CCl_4): *v* = 2957, 2932, 2860, 1739 (3×C=O), 1458, 1412, 1367, 1243, 1122, 1023, 950 cm^{-1}. MS (CI/NH_3): *m*/*z* 209 (MH^+ - 2 $C_2H_4O_2$), 269 (MH^+ - $C_2H_4O_2$), 329 (MH^+), 346 (MNH_4^+).

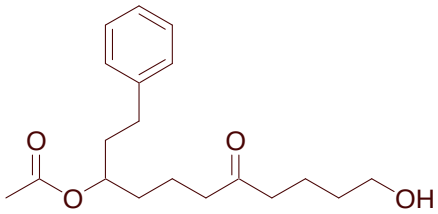
Acetic acid 9-acetoxy-5-oxo-1-phenethyl-nonyl ester (16b).



$C_{21}H_{30}O_5$
Exact Mass: 362,21
Mol. Wt.: 362,46

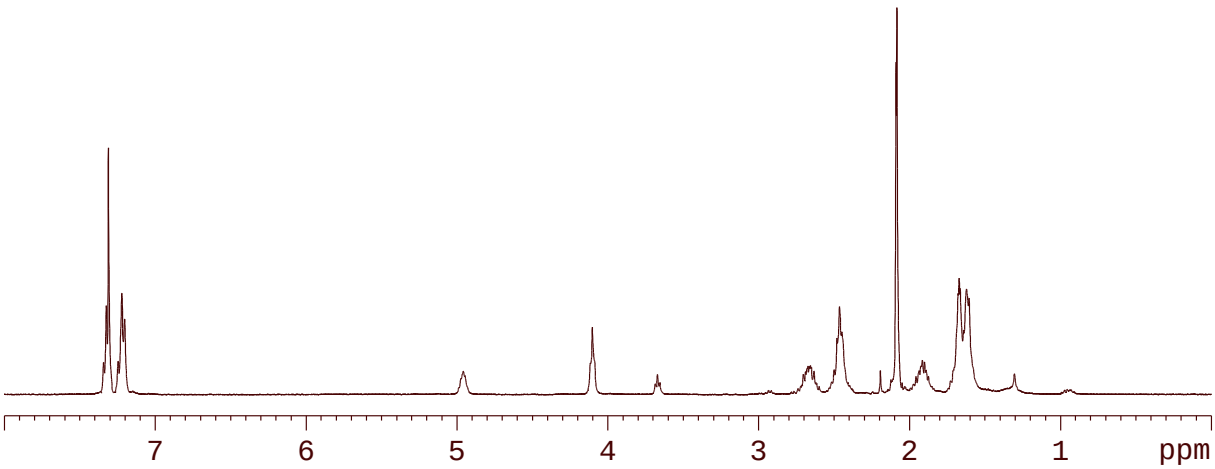
Method B - The reaction was carried out with a solution of **15b** (449 mg, 0.74 mmol). Flash chromatography on silica gel (EtOAc-petroleum ether, 0:100 to 50:50 v/v) afforded **16b** (174 mg, 65%), together with a more polar side-product **16b'** (48 mg, 20%) as pale yellow oils, which were combined and used as a mixture in the next recation step.

Side-product **16b'**:

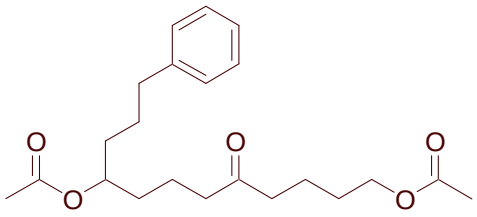


$C_{19}H_{28}O_4$
Exact Mass: 320,20
Mol. Wt.: 320,42

^{1}H NMR (400 MHz, $CDCl_3$), mixture of **16b** and **16b'**:



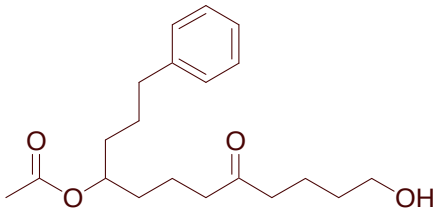
Acetic acid 9-acetoxy-5-oxo-1-(3-phenyl-propyl)-nonyl ester (16c).



$C_{22}H_{32}O_5$
Exact Mass: 376,22
Mol. Wt.: 376,49

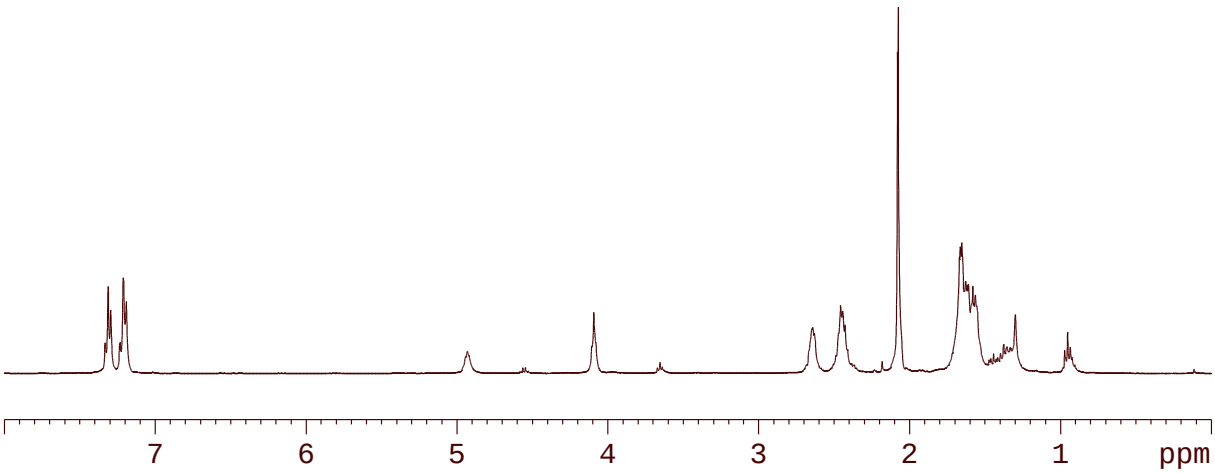
Method B - The reaction was carried out with a solution of **15c** (101 mg, 0.16 mmol). Flash chromatography on silica gel (EtOAc-petroleum ether, 0:100 to 50:50 v/v) afforded **16c** (45 mg, 75%), together with a more polar side-product **16c'** (8 mg, 15%) as pale yellow oils, which were combined and used as a mixture in the next recation step.

Side-product **16c'**:

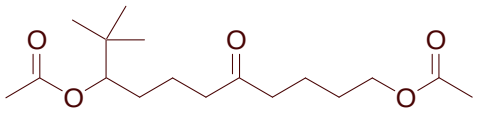


$C_{20}H_{30}O_4$
Exact Mass: 334,21
Mol. Wt.: 334,45

^{1}H NMR (400 MHz, $CDCl_3$), mixture of **16c** and **16c'**:



Acetic acid 9-acetoxy-1-*tert*-butyl-5-oxo-nonyl ester (16d).

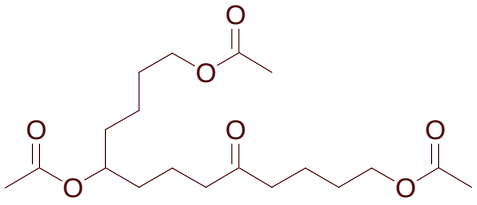


$C_{17}H_{30}O_5$
Exact Mass: 314,21
Mol. Wt.: 314,42

Method A - The reaction was carried out with a solution of **15d** (257 mg, 0.46 mmol) and needed 3.0 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 0:100 to 20:80 v/v) afforded **16d** (119 mg) as a pale yellow oil, which had to be purified again by flash chromatography on silica gel (EtOAc-petroleum ether, 15:85 v/v). Pure **16d** (111 mg, 76%) was obtained as a clear, pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (s, 9 H), 1.42-1.72 (m, 8 H), 2.06 (s, 3 H), 2.09 (s, 3 H), 2.33-2.54 (m, 4 H), 4.01-4.12 (m, 2 H), 4.73 (dd, *J* = 2.0, 9.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (CH_2), 20.5 (CH_2), 21.0 (2×CH_3), 25.9 (3×CH_3), 28.1 (CH_2), 29.0 (CH_2), 34.6 (CH_2), 42.1 (CH_2), 42.3 (CH_2), 64.1 (CH_2), 80.0 (CH), 171.2 (2×C=O), 210.2 (C=O) ppm. IR (CCl_4): *v* = 2961, 2872, 1741 (3×C=O), 1478, 1459, 1412, 1396, 1369, 1243, 1041, 1020 cm^{-1}. MS (CI/NH_3): *m*/*z* 255 (MH^+ - $C_2H_4O_2$), 315 (MH^+), 332 (MNH_4^+).

Acetic acid 9,13-diacetoxy-5-oxo-tridecyl ester (16e).

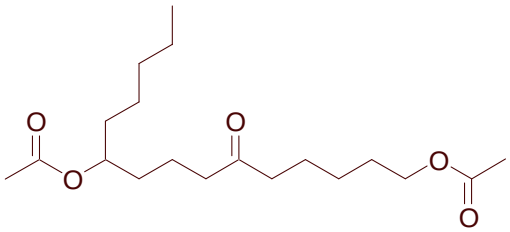


$C_{19}H_{32}O_7$
Exact Mass: 372,21
Mol. Wt.: 372,45

Method A - The reaction was carried out with a solution of **15e** (486 mg, 0.79 mmol) and needed 3.0 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 25:75 to 30:70 v/v) afforded **16e** (246 mg, 84%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29-1.37 (m, 2 H), 1.46-1.67 (m, 12 H), 2.02 (s, 9 H), 2.36-2.46 (m, 4 H), 3.99-4.05 (m, 4H), 4.83 (tt, *J* = 5.6, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_2), 20.1 (CH_2), 21.0 (2×CH_3), 21.2 (CH_3), 21.8 (CH_2), 28.1 (CH_2), 28.4 (CH_2), 33.4 (CH_2), 33.6 (CH_2), 42.1 (CH_2), 42.2 (CH_2), 64.1 (CH_2), 64.2 (CH_2), 73.4 (CH), 170.9 (C=O), 171.2 (2×C=O), 210.1 (C=O) ppm. IR (CCl_4): *v* = 2955, 2869, 1740 (4×C=O), 1457, 1412, 1366, 1240, 1040 cm^{-1}. MS (CI/NH_3): *m*/*z* 253 (MH^+ - 2 $C_2H_4O_2$), 313 (MH^+ - $C_2H_4O_2$), 389 (MNH_4^+).

Acetic acid 10-acetoxy-5-oxo-1-pentyl-decyl ester (16f).

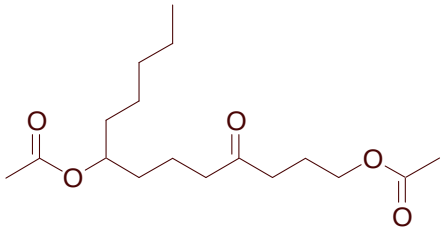


$C_{19}H_{34}O_5$
Exact Mass: 342,24
Mol. Wt.: 342,47

Method A - The reaction was carried out with a solution of crude **15f** (279 mg, 0.48 mmol) and needed 3.0 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 8:92 to 15:85 v/v) afforded **16f** (119 mg) as a clear, pale yellow oil, which had to be purified again by flash chromatography on silica gel (CH_2Cl_2, then Et_2O). Pure **16f** (95 mg, 58% over 2 steps) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.19-1.36 (m, 8 H), 1.45-1.65 (m, 10 H), 2.02 (s, 6 H), 2.38 (t, *J* = 7.2 Hz, 4 H), 4.03 (t, *J* = 6.8 Hz, 2 H), 4.83 (dq, *J* = 6.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.4 (CH_2), 21.0 (CH_3), 21.3 (CH_3), 22.5 (CH_2), 23.4 (CH_2), 25.0 (CH_2), 25.6 (CH_2), 28.5 (CH_2), 31.7 (CH_2), 33.5 (CH_2), 34.0 (CH_2), 42.3 (CH_2), 42.6 (CH_2), 64.3 (CH_2), 73.8 (CH), 170.9 (C=O), 171.2 (C=O), 210.4 (C=O) ppm. IR (CCl_4): *v* = 2955, 2932, 2860, 1738 (3×C=O), 1458, 1366, 1242, 1044 cm^{-1}. MS (CI/NH_3): *m/z* 283 (MH^+ - $C_2H_4O_2$), 343 (MH^+), 360 (MNH_4^+).

Acetic acid 8-acetoxy-4-oxo-tridecyl ester (16g).



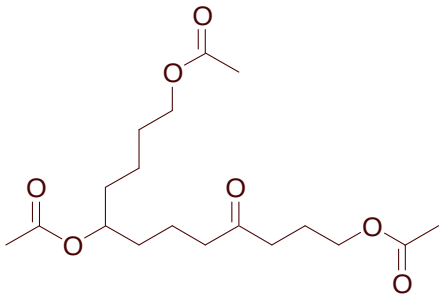
$C_{17}H_{30}O_5$
Exact Mass: 314,21
Mol. Wt.: 314,42

Method A - The reaction was carried out with a solution of crude **15g** (292 mg, 0.53 mmol) and needed 3.0 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 5:95 to 15:85 v/v) afforded **16g** (83 mg, 50% over 2 steps) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.8 Hz, 3 H), 1.31-1.34 (m, 6 H), 1.42-1.64 (m, 6 H), 1.88 (dq, *J* = 6.8 Hz, 2 H), 2.01 (s, 6 H), 2.38-2.47 (m, 4 H), 4.03 (t, *J* = 6.4 Hz, 2 H), 4.83 (dq, *J* = 6.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.4 (CH_2), 20.9 (CH_3), 21.2 (CH_3), 22.5

(CH_2), 22.7 (CH_2), 25.0 (CH_2), 31.7 (CH_2), 33.4 (CH_2), 34.0 (CH_2), 38.9 (CH_2), 42.3 (CH_2), 63.6 (CH_2), 73.8 (CH), 170.9 (C=O), 171.0 (C=O), 209.4 (C=O) ppm. IR (CCl_4): ν = 2957, 2931, 2859, 1740 (3×C=O), 1458, 1414, 1366, 1243, 1025 cm^{-1}. MS (CI/NH_3): *m/z* 255 (MH^+ - $C_2H_4O_2$), 315 (MH^+), 332 (MNH_4^+).

Acetic acid 8-acetoxy-1-(4-acetoxy-butyl)-5-oxo-octyl ester (16h).

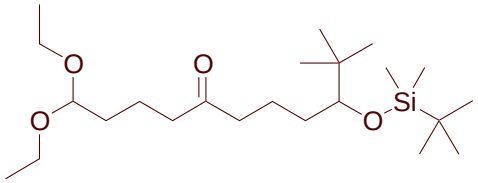


$C_{18}H_{30}O_7$
Exact Mass: 358,20
Mol. Wt.: 358,43

Method A - The reaction was carried out with a solution of **15h** (344 mg, 0.57 mmol) and needed 3.0 eq. of DLP to go to completion. Flash chromatography on silica gel (EtOAc-petroleum ether, 28:72 to 35:65 v/v) afforded **16h** (118 mg, 58%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27-1.37 (m, 2 H), 1.45-1.65 (m, 8 H), 1.87 (dq, *J* = 6.8 Hz, 2 H), 2.01 (s, 9 H), 2.33-2.51 (m, 4 H), 3.99-4.04 (m, 4 H), 4.82 (tt, *J* = 5.6, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_2), 20.9 (CH_3), 21.0 (CH_3), 21.2 (CH_3), 21.8 (CH_2), 22.7 (CH_2), 28.4 (CH_2), 33.4 (CH_2), 33.6 (CH_2), 38.9 (CH_2), 42.2 (CH_2), 63.6 (CH_2), 64.2 (CH_2), 73.4 (CH), 170.9 (C=O), 171.0 (C=O), 171.2 (C=O), 209.3 (C=O) ppm. IR (CCl_4): ν = 2954, 1741 (4×C=O), 1457, 1366, 1240, 1039 cm^{-1}. MS (CI/NH_3): *m/z* 239 (MH^+ - 2 $C_2H_4O_2$), 300 (MH^+ - $C_2H_4O_2$), 376 (MNH_4^+).

9-(*tert*-Butyl-dimethyl-silanyloxy)-1,1-diethoxy-10,10-dimethyl-undecan-5-one (16i).



$C_{23}H_{48}O_4Si$
Exact Mass: 416,33
Mol. Wt.: 416,71

A solution of **15i** (289 mg, 0.44 mmol) and *n*-Bu_3SnH (2.5 eq.) in heptane (9 mL) was refluxed for 15 min. AIBN (0.1 eq.) was then added and the yellowish solution stirred for 60 min. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. Flash chromatography on silica gel (EtOAc-petroleum ether, 5:95 v/v) afforded **16i** (156 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 3 H), 0.06 (s, 3 H), 0.85 (s, 9 H), 0.90 (s, 9 H), 1.21 (t, *J* = 7.2 Hz, 6 H), 1.23-1.34 (m, 2 H), 1.44-1.55 (m, 2 H), 1.56-1.80 (m, 4 H), 2.37 (t, *J* = 6.8 Hz, 2 H), 2.43 (t, *J* = 6.8 Hz, 2 H), 3.21 (dd, *J* = 2.8, 6.8 Hz, 1 H), 3.49 (dq, *J* = 7.2, 9.2 Hz, 2 H), 3.65 (dq, *J* = 7.2, 9.2 Hz, 2 H), 4.48 (t, *J* = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -3.9 (CH_3), -3.3 (CH_3), 15.4 (2×CH_3), 18.4 (C_q), 19.1 (CH_2), 22.1 (CH_2), 26.2 (3×CH_3), 26.5 (3×CH_3), 33.1 (2×CH_2), 35.9 (C_q), 42.4 (CH_2), 43.3 (CH_2), 61.1 (2×CH_2), 80.5 (CH), 102.8 (CH), 210.8 (C=O) ppm. IR (CCl_4): *v* = 2956, 2929, 2884, 2857, 1717, 1472, 1462, 1408, 1391, 1373, 1361, 1256, 1127, 1095, 1067, 1028, 1006 cm^{-1}. MS (CI/NH_3): *m*/*z* 324 (MH^+ - 2 C_2H_6O), 371 (MH^+ - C_2H_6O).

Cyclisation of compounds 16a-i - General procedure.

Method A

A solution of bisacetate (1.0 eq.) and KOH (1.1 eq.) in methanol (2.5 mL/mmol of bisacetate) was stirred overnight at room temperature. The resulting pale yellow solution was diluted with CH_2Cl_2, neutralised with concentrated H_2SO_4, and washed with water. The organic phase was then dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel.

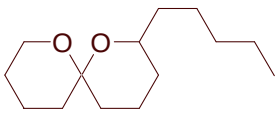
Method B

A solution of bisacetate (1.0 eq.) and NaOH (20 eq.) in a 1:1 mixture of water and methanol (10 mL/mmol of bisacetate) was stirred overnight at room temperature. The resulting pale yellow solution was neutralised with concentrated H_2SO_4, diluted with water, and extracted with Et_2O. The organic phase was then dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel.

Method C

A solution of mono- (n eq.) and bisacetate (m eq.) and KOH (1.1 × (n + m) eq.) in methanol (2.5 mL/mmol of mono- and bisacetate) was stirred overnight at room temperature. The resulting pale yellow solution was diluted with CH_2Cl_2, neutralised with concentrated H_2SO_4, and washed with water. The organic phase was then dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel.

2-Pentyl-1,7-dioxa-spiro[5.5]undecane (17a).

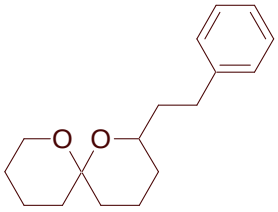


$C_{14}H_{26}O_2$
Exact Mass: 226,19
Mol. Wt.: 226,36

Method A - The reaction was carried out with a solution of **16a** (523 mg, 1.6 mmol) and KOH (99 mg, 1.8 mmol) in methanol (4.1 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 1:99 to 5:95 v/v) afforded **17a** (255 mg, 71%) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 3 H), 1.10-1.23 (m, 1 H), 1.26-1.67 (m, 17 H), 1.77-1.94 (m, 2H), 3.54-3.60 (m, 2 H), 3.66 (dt, *J* = 2.4, 11.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 18.7 (CH_2), 19.0 (CH_2), 22.7 (CH_2), 25.6 (2×CH_2), 31.4 (CH_2), 32.1 (CH_2), 35.6 (CH_2), 36.1 (CH_2), 36.6 (CH_2), 60.4 (CH_2), 69.2 (CH), 95.5 (C_q) ppm. IR (CCl_4): *v* = 2938, 2870, 14.64, 1455, 1438, 1384, 1350, 1280, 1255, 1227, 1210, 1196, 1182, 1102, 1089, 1066, 1048, 990 cm^{-1}. MS (CI/NH_3): *m*/*z* 227 (MH^+). HRMS: found 226.1942 (M^+). $C_{14}H_{26}O_2$ requires 226.1933.

2-Phenethyl-1,7-dioxa-spiro[5.5]undecane (17b).

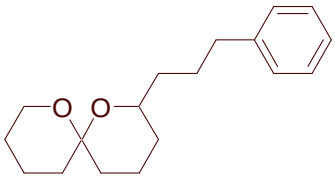


$C_{17}H_{24}O_2$
Exact Mass: 260,18
Mol. Wt.: 260,37

Method C - The reaction was carried out with a solution of **16b** (174 mg, 0.48 mmol), **16b'** (48 mg, 0.15 mmol), and KOH (46 mg, 0.82 mmol) in methanol (1.9 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 3:197 to 5:95 v/v) afforded **17b** (123 mg, 64% over 2 steps) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23-1.34 (m, 1 H), 1.41-2.00 (m, 13 H), 2.71 (ddd, *J* = 6.0, 10.8, 13.6 Hz, 1 H), 2.99 (ddd, *J* = 5.6, 10.8, 13.6 Hz, 1 H), 3.61-3.75 (m, 3 H), 7.22-7.36 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7 (CH_2), 18.9 (CH_2), 25.5 (CH_2), 31.3 (CH_2), 32.4 (CH_2), 35.5 (CH_2), 36.0 (CH_2), 38.2 (CH_2), 60.4 (CH_2), 68.8 (CH), 95.5 (C_q), 125.7 (CH), 128.3 (2×CH), 128.4 (2×CH), 142.7 (C_q) ppm. IR (CCl_4): *v* = 3086, 3064, 3027, 2941, 2869, 1602, 1496, 1454, 1439, 1385, 1367, 1350, 1279, 1255, 1227, 1210, 1196, 1181, 1114, 1096, 1090, 1066, 1047, 993, 971, 950, 934, 916 cm^{-1}. MS (CI/NH_3): *m*/*z* 261 (MH^+). HRMS: found 260.1779 (M^+). $C_{17}H_{24}O_2$ requires 260.1776.

2-(3-Phenyl-propyl)-1,7-dioxa-spiro[5.5]undecane (17c).

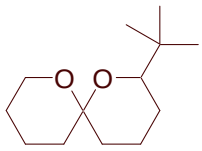


$C_{18}H_{26}O_2$
Exact Mass: 274,19
Mol. Wt.: 274,40

Method C - The reaction was carried out with a solution of **16c** (45 mg, 0.12 mmol), **16c'** (8 mg, 24 µmol), and KOH (10 mg, 0.17 mmol) in methanol (0.39 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 2:98 v/v) afforded **17c** (30 mg, 67% over 2 steps) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17-1.28 (m, 1 H), 1.38-1.78 (m, 12 H), 1.83-2.01 (m, 3 H), 2.65-2.77 (m, 2 H), 3.61-3.74 (m, 3 H), 7.20-7.28 (m, 3 H), 7.29-7.37 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7 (CH_2), 18.9 (CH_2), 25.5 (CH_2), 27.9 (CH_2), 31.4 (CH_2), 35.6 (CH_2), 36.0 (CH_2), 36.2 (2×CH_2), 60.5 (CH_2), 69.0 (CH), 95.5 (C_q), 125.7 (CH), 128.4 (2×CH), 128.5 (2×CH), 142.8 (C_q) ppm. IR (CCl_4): ν = 3086, 3064, 3027, 2940, 2869, 1604, 1496, 1453, 1439, 1385, 1367, 1350, 1279, 1255, 1227, 1210, 1182, 1094, 1066, 1047, 1030, 986 cm^{-1}. MS (CI/NH_3): *m/z* 275 (MH^+). HRMS: found 274.1928 (M^+). $C_{18}H_{26}O_2$ requires 274.1933.

2-*tert*-Butyl-1,7-dioxa-spiro[5.5]undecane (17d).

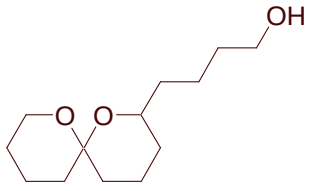


$C_{13}H_{24}O_2$
Exact Mass: 212,18
Mol. Wt.: 212,33

Method B - The reaction was carried out with a solution of **16d** (111 mg, 0.35 mmol) and NaOH (280 mg, 7.0 mmol) in a 1:1 mixture of water and methanol (3.5 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 1:99 v/v) afforded **17d** (45 mg, 61%) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (s, 9 H), 1.13-1.34 (m, 2 H), 1.38-1.64 (m, 8 H), 1.72-1.94 (m, 2 H), 3.25 (dd, *J* = 0.8, 12.0 Hz, 1 H), 3.52-3.59 (m, 1 H), 3.67-3.73 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (CH_2), 19.1 (CH_2), 24.8 (CH_2), 25.7 (CH_2), 26.2 (3×CH_3), 34.2 (C_q), 35.6 (CH_2), 36.3 (CH_2), 60.4 (CH_2), 76.1 (CH), 95.5 (C_q) ppm. IR (CCl_4): ν = 2953, 2869, 1479, 1464, 1455, 1439, 1392, 1382, 1362, 1280, 1257, 1231, 1208, 1194, 1181, 1131, 1112, 1099, 1075, 1061, 1046, 1038, 1026, 1009, 997 cm^{-1}. MS (CI/NH_3): *m/z* 213 (MH^+), 230 (MNH_4^+).

4-(1,7-Dioxa-spiro[5.5]undec-2-yl)-butan-1-ol (17e).[5]

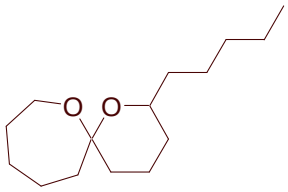


$C_{13}H_{24}O_3$
Exact Mass: 228,17
Mol. Wt.: 228,33

Method A - The reaction was carried out with a solution of **16e** (246 mg, 0.66 mmol) and KOH (41 mg, 0.73 mmol) in methanol (1.7 mL). Flash chromatography on silica gel (EtOAc-petroleum ether, 30:70 v/v) afforded **17e** (108 mg, 72%) as single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$)[i]: δ = 1.11-1.21 (m, 1 H), 1.31-1.67 (m, 15 H), 1.76-1.88 (m, 2 H), 3.53-3.61 (m, 2 H), 3.62-3.68 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7 (CH_2), 18.9 (CH_2), 22.1 (CH_2), 25.5 (CH_2), 31.3 (CH_2), 32.9 (CH_2), 35.5 (CH_2), 35.9 (CH_2), 36.2 (CH_2), 60.4 (CH_2), 62.8 (CH_2), 69.1 (CH), 95.5 (C_q) ppm. IR (CCl_4): ν = 3637, 3472, 2939, 2870, 1741, 1455, 1439, 1385, 1350, 1279, 1228, 1210, 1182, 1096, 1066, 1048, 1025, 988 cm^{-1}. MS (CI/NH_3): *m/z* 211 (MH^+ - H_2O), 229 (MH^+). HRMS: found 228.1727 (M^+). $C_{13}H_{24}O_3$ requires 228.1726.

2-Pentyl-1,7-dioxa-spiro[5.6]dodecane (17f).



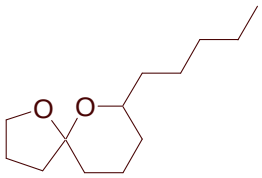
$C_{15}H_{28}O_2$
Exact Mass: 240,21
Mol. Wt.: 240,38

Method A - The reaction was carried out with a solution of **16f** (95 mg, 0.28 mmol) and KOH (17 mg, 0.30 mmol) in methanol (0.70 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 2:98 v/v) afforded **17f** (50 mg, 75%) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3 H), 1.10-1.21 (m, 1 H), 1.23-1.49 (m, 11 H), 1.51-1.67 (m, 5 H), 1.68-1.91 (m, 5 H), 3.51-3.58 (m, 1 H), 3.60-3.68 (m, 1 H), 3.70-3.76 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 19.4 (CH_2), 22.6 (CH_2), 22.8 (CH_2), 25.4 (CH_2), 29.9 (CH_2), 30.6 (CH_2), 31.4 (CH_2), 32.0 (CH_2), 35.4 (CH_2), 36.4 (CH_2), 42.0 (CH_2), 61.2 (CH_2), 69.8 (CH), 100.3 (C_q) ppm. IR (CCl_4): ν = 2932, 2857, 1454, 1440, 1378, 1345, 1280, 1202, 1150, 1103, 1056, 1040, 968 cm^{-1}. MS (CI/NH_3): *m/z* 241 (MH^+). HRMS: found 240.2100 (M^+). $C_{15}H_{28}O_2$ requires 240.2089.

[i] The signal corresponding to OH was not observed.

7-Pentyl-1,6-dioxa-spiro[4.5]decane (17g).

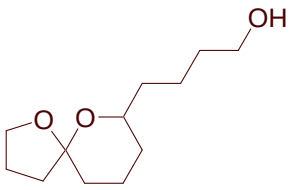


$C_{13}H_{24}O_2$
Exact Mass: 212,18
Mol. Wt.: 212,33

Method A - The reaction was carried out with a solution of **16g** (83 mg, 0.26 mmol) and KOH (17 mg, 0.30 mmol) in methanol (0.70 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 2:98 to 3:97 v/v) afforded **17g** (38 mg, 68%) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.11-1.46 (m, 9 H), 1.53-1.74 (m, 5 H), 1.75-1.95 (m, 3 H), 1.99-2.10 (m, 1 H), 3.65-3.73 (m, 1 H), 3.83-3.92 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 20.6 (CH_2), 22.7 (CH_2), 23.8 (CH_2), 25.4 (CH_2), 31.1 (CH_2), 31.9 (CH_2), 33.0 (CH_2), 36.3 (CH_2), 37.3 (CH_2), 66.7 (CH_2), 70.3 (CH), 105.9 (C_q) ppm. IR (CCl_4): *ν* = 2935, 2872, 1457, 1439, 1386, 1368, 1309, 1270, 1235, 1214, 1161, 1117, 1098, 1076, 1042, 1011 cm^{-1}. MS (CI/NH_3): *m/z* 213 (MH^+). HRMS: found 212.1782 (M^+). $C_{13}H_{24}O_2$ requires 212.1776.

4-(1,6-Dioxa-spiro[4.5]dec-7-yl)-butan-1-ol (17h).

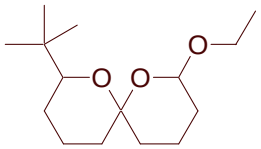


$C_{12}H_{22}O_3$
Exact Mass: 214,16
Mol. Wt.: 214,30

Method A - The reaction was carried out with a solution of **16h** (118 mg, 0.33 mmol) and KOH (22 mg, 0.39 mmol) in methanol (0.90 mL). Flash chromatography on silica gel (Et_2O-petroleum ether, 50:50 v/v) afforded **17h** (65 mg, 92%) as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11-1.22 (m, 1 H), 1.31-1.49 (m, 4 H), 1.51-1.70 (m, 7 H), 1.73-1.97 (m, 3 H), 2.01-2.09 (m, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 3.66-3.72 (m, 1 H), 3.81-3.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_2), 21.9 (CH_2), 23.7 (CH_2), 31.0 (CH_2), 32.6 (CH_2), 32.9 (CH_2), 35.8 (CH_2), 37.8 (CH_2), 62.8 (CH_2), 66.7 (CH_2), 70.3 (CH), 105.9 (C_q) ppm. IR (CCl_4): *ν* = 3637, 3475, 2939, 2872, 1458, 1439, 1387, 1368, 1310, 1270, 1234, 1215, 1161, 1114, 1086, 1040, 1009, 959 cm^{-1}. MS (CI/NH_3): *m/z* 197 (MH^+ - H_2O), 215 (MH^+). HRMS: found 214.1561 (M^+). $C_{12}H_{22}O_3$ requires 214.1569.

2-*tert*-Butyl-8-ethoxy-1,7-dioxa-spiro[5.5]undecane (17i).



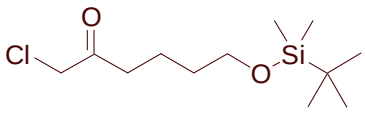
$C_{15}H_{28}O_3$
Exact Mass: 256,20
Mol. Wt.: 256,38

To a solution of **16i** (40 mg, 96µmol) in dry THF (0.47 mL) was added a commercial 1M solution of TBAF in THF (0.29 mL). The resulting mixture was heated to reflux and stirred for 6 h. After cooling to room temperature, the mixture was diluted with Et_2O (10 mL) and washed with water (2 × 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The residue (28 mg) was dissolved in dry CH_2Cl_2 (2.2 mL) and cooled to 0°C before addition of Amberlyst-15® (5 mg). Stirring was continued at 0°C for 7 h. The icebath was then removed and the mixture stirred at room temperature for 12 h. The resin was removed by filtration and the filtrate evaporated to dryness under reduced pressure. Crude reaction product (24 mg) was obtained as a yellow oil, which was purified by flash chromatography on deactivated silica gel (Et_2O-petroleum ether, 2:98 v/v)[i] to afford **17i** (14 mg, 57% over 2 steps) as a pale yellow oil, consisting of a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 9 H), 1.16-1.45 (m, 4 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.53-1.65 (m, 4 H), 1.68-1.75 (m, 1 H), 1.76-1.82 (m, 1 H), 1.83-1.97 (m, 2 H), 3.32 (dd, *J* = 2.2, 11.6 Hz, 1 H), 3.52 (dq, *J* = 7.2, 9.6 Hz, 1 H), 4.01 (dq, *J* = 6.8, 9.2 Hz, 1 H), 4.73 (dd, *J* = 2.4, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (CH_3), 18.2 (CH_2), 19.1 (CH_2), 24.9 (CH_2), 26.2 (3×CH_3), 31.2 (CH_2), 34.2 (C_q), 35.3 (2×CH_2), 64.3 (CH_2), 76.8 (CH), 96.5 (CH), 98.2 (C_q) ppm. IR (CCl_4): *ν* = 2954, 2869, 1479, 1457, 1440, 1414, 1392, 1379, 1363, 1281, 1256, 1228, 1210, 1185, 1167, 1146, 1111, 1096, 1078, 1059, 1041, 1024, 1006, 982, 966 cm^{-1}. MS (CI/NH_3): *m*/*z* 211 (MH^+ - C_2H_6O), 239 (MH^+ - H_2O), 257 (MH^+). HRMS: found 256.2043 (M^+). $C_{15}H_{28}O_3$ requires 256.2039.

[i] A few drops of triethylamine were added to the eluent.

6-(*tert*-Butyl-dimethyl-silanyloxy)-1-chloro-hexan-2-one (18).

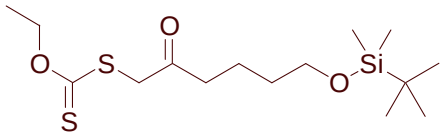


$C_{12}H_{25}ClO_2Si$
Exact Mass: 264,13
Mol. Wt.: 264,86

A solution of **7e** (566 mg, 1.5 mmol) and AIBN (24 mg, 0.15 mmol) in degassed heptane (21 mL) was heated to reflux before dropwise addition of a solution of *n*-Bu_3SnH (0.42 mL, 1.54 mmol) in degassed heptane (8 mL). After 60 min. of additional stirring at reflux temperature, the mixture was cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product (922 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 2:98 v/v) to afford **18** (269 mg, 69%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 6 H), 0.89 (s, 9 H), 1.49-1.56 (m, 2 H), 1.65-1.72 (m, 2 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 4.07 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -5.3 (2×CH_3), 18.4 (C_q), 20.3 (CH_2), 26.0 (3×CH_3), 32.1 (CH_2), 39.5 (CH_2), 48.2 (CH_2), 62.7 (CH_2), 202.7 (C=O) ppm. IR (CCl_4): *ν* = 2954, 2929, 2895, 2856, 1743, 1722, 1471, 1462, 1404, 1388, 1361, 1255, 1102, 1005, 972 cm^{-1}. MS (CI/NH_3): *m/z* 385 (MH^+, $C_{15}H_{25}{}^{35}ClO_2Si$), 387 ($MH^+$, $C_{15}H_{25}{}^{37}ClO_2Si$).

Dithiocarbonic acid [6-(*tert*-butyl-dimethyl-silanyloxy)-2-oxo-hexyl] ester ethyl ester (19).



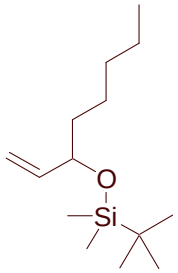
$C_{15}H_{30}O_3S_2Si$
Exact Mass: 350,14
Mol. Wt.: 350,61

A solution of **18** (377 mg, 1.4 mmol) in acetone (3 mL) was cooled to 0°C. A solution of dithiocarbonic acid *O*-ethyl ester potassium salt (252 mg, 1.6 mmol) in acetone (4 mL) was added dropwise before removal of the icebath. Stirring was continued at room temperature for 2 h after which the mixture was concentrated under reduced pressure. The resulting slurry was suspended in water (20 mL) and extracted with Et_2O (3 × 20 mL). The collected organic phases were dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Crude reaction product (486 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 2:98 to 10:90 v/v) to afford **19** (442 mg, 89%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 6 H), 0.88 (s, 9 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 1.49-1.56 (m, 2 H), 1.64-1.72 (m, 2 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 3.98 (s, 2 H), 4.62 (q, *J* =

7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -5.3 (2×CH_3), 13.8 (CH_3), 18.4 (C_q), 20.3 (CH_2), 26.0 (3×CH_3), 32.1 (CH_2), 41.7 (CH_2), 45.4 (CH_2), 62.7 (CH_2), 70.8 (CH_2), 203.2 (C=O), 213.4 (C=S) ppm. IR (CCl_4): *v* = 2955, 2929, 2895, 2857, 1719, 1471, 1462, 1387, 1361, 1293, 1223, 1149, 1112, 1052 cm^{-1}. MS (CI/NH_3): *m*/*z* 351 (MH^+).

tert-Butyl-dimethyl-(1-vinyl-hexyloxy)-silane (20).

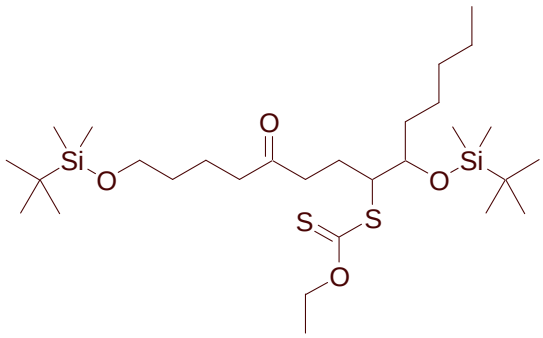


$C_{14}H_{30}OSi$
Exact Mass: 242,21
Mol. Wt.: 242,47

A solution of *tert*-butyl-chloro-dimethyl-silane (3.6 g, 24 mmol) and imidazole (2.0 g, 30 mmol) in freshly distilled DMF (6.4 mL) was cooled to 0°C before addition of commercial 1-octen-3-ol (2.6 g, 20 mmol). After removal of the icebath, the resulting suspension was stirred at room temperature for 68 h. As was evident from TLC, starting material was still present after 68 h of stirring at room temperature. The mixture was then heated to 75°C and stirred for 5 h. After cooling to room temperature, the reaction was quenched by addition of a saturated solution of NH_4Cl (20 mL). Et_2O (20 mL) was then added and the resulting emulsion vigorously stirred for 5 min. After phase separation, the organic phase was successively washed with water (3 ×20 mL) and a 2% aqueous solution of HCl (2 × 20 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. Crude **20** was obtained as a colourless liquid (5.2 g), which was purified by flash chromatography on silica gel (petroleum ether). Pure **20** (4.7 g, 97%) was obtained as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 3 H), 0.06 (s, 3 H), 0.88-0.96 (m, 12 H), 1.22-1.57 (m, 8 H), 4.08 (q, *J* = 6.0 Hz, 1 H), 5.02 (dt, *J* = 1.2, 10.4 Hz, 1 H), 5.14 (dt, *J* = 1.2, 17.2 Hz, 1 H), 5.81 (ddd, *J* = 6.0, 10.4, 16.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -4.7 (CH_3), -4.3 (CH_3), 14.1 (CH_3), 18.4 (C_q), 22.7 (CH_2), 25.0 (CH_2), 26.0 (3×CH_3), 31.9 (CH_2), 38.2 (CH_2), 74.0 (CH), 113.4 (CH_2), 142.0 (CH) ppm. IR (CCl_4): *v* = 2956, 2930, 2857, 1471, 1462, 1421, 1403, 1388, 1378, 1360, 1253, 1102, 1079, 1031, 1005, 992, 921 cm^{-1}. MS (CI/NH_3): A reasonable mass spectrum could not be obtained.

Dithiocarbonic acid {8-(*tert*-butyl-dimethyl-silanyloxy)-1-[1-(*tert*-butyl-dimethyl-silanyloxy)-hexyl]-4-oxo-octyl} ester ethyl ester (21).

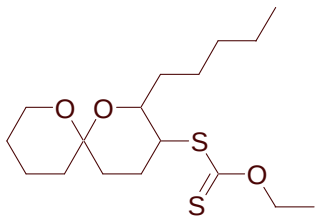


$C_{29}H_{60}O_4S_2Si_2$
Exact Mass: 592,35
Mol. Wt.: 593,09

A solution of **19** (442 mg, 1.3 mmol) and **20** (611 mg, 2.5 mmol) in 1,2-dichloro-ethane (1.3 mL) was refluxed for 15 min. DLP (0.05 eq.) was then added. Additional DLP (0.025-0.05 eq.) was added every 90 min. until complete consumption of **19**. After addition of 0.175 eq. of DLP, the mixture was cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product (1.1 g) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (Et_2O-petroleum ether, 3:97 to 10:90 v/v) to afford **21** (505 mg, 68%) as a pale yellow oil consisting of an inseparable 1:1.1 mixture of diastereomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 15 H), 0.06 (s, 3 H), 0.07 (s, 3 H), 0.11 (s, 3 H), 0.85-0.91 (m, 42 H), 1.20-1.86 (m, 20 H), 1.41 (t, *J* = 7.2 Hz, 6 H), 1.42 (t, *J* = 7.2 Hz, 6 H), 2.09-2.21 (m, 2 H), 2.39-2.43 (m, 4 H), 2.52-2.65 (m, 4 H), 3.60 (t, *J* = 6.4 Hz, 4 H), 3.83-3.97 (m, 4 H), 4.59-4.67 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -5.2 (4×CH_3), -4.5 (CH_3), -4.2 (2×CH_3), -4.1 (CH_3), 13.9 (2×CH_3), 14.1 (2×CH_3), 18.1 (C_q), 18.2 (C_q), 18.4 (2×C_q), 20.3 (2×CH_2), 22.0 (CH_2), 22.6 (CH_2), 22.7 (CH_2), 25.3 (CH_2), 25.5 (CH_2), 25.8 (CH_2), 25.9 (3×CH_3), 26.0 (9×CH_3), 31.8 (CH_2), 31.9 (CH_2), 32.3 (2×CH_2), 34.4 (CH_2), 35.2 (CH_2), 39.9 (CH_2), 40.3 (CH_2), 42.6 (CH_2), 42.7 (CH_2), 56.2 (CH), 56.3 (CH), 62.9 (2×CH_2), 69.9 (CH_2), 70.2 (CH_2), 74.7 (CH), 75.3 (CH), 210.1 (C=O), 210.3 (C=O), 215.4 (C=S), 215.6 (C=S) ppm. IR (CCl_4): *v* = 2955, 2929, 2895, 2857, 1717, 1471, 1462, 1409, 1388, 1361, 1255, 1214, 1111, 1052, 1006 cm^{-1}. MS (CI/NH_3): *m*/*z* 593 (MH^+), 462 (MH^+ - $C_6H_{16}OSi$).

Dithiocarbonic acid ethyl ester (2-pentyl-1,7-dioxa-spiro[5.5]undec-3-yl) ester (22).

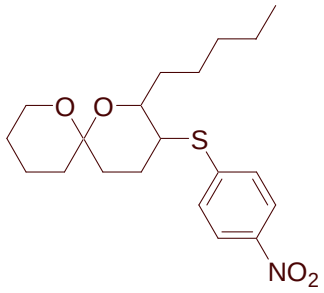


$C_{17}H_{30}O_3S_2$
Exact Mass: 346,16
Mol. Wt.: 346,55

A solution of **21** (480 mg, 0.81 mmol) in a 1.3 M aqueous solution of HF in acetonitrile (5 mL) was stirred at room temperature for 17 h. The resulting pale yellow solution was diluted with Et_2O (10 mL) and extracted with water (3 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Crude reaction product (290 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (Et_2O-petroleum ether, 3:97 to 5:95 v/v) to afford **22** (252 mg, 90%) as a pale yellow oil consisting of an inseparable 1:1 mixture of diastereomers

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85-0.91 (m, 6 H), 1.25-1.36 (m, 10 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 1.42 (t, *J* = 7.2 Hz, 3 H), 1.45-1.74 (m, 19 H), 1.76-2.04 (m, 6 H), 2.30 (tt, *J* = 4.0, 13.6 Hz, 1 H), 3.50-3.64 (m, 6 H), 3.94-4.01 (m, 2 H), 4.57-4.70 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (2×CH_3), 14.1 (2×CH_3), 18.5 (CH_2), 18.7 (CH_2), 22.6 (CH_2), 22.7 (CH_2), 25.3 (2×CH_2), 25.6 (2×CH_2), 25.7 (CH_2), 26.1 (CH_2), 31.9 (3×CH_2), 33.2 (CH_2), 33.7 (CH_2), 35.3 (2×CH_2), 36.3 (CH_2), 50.6 (CH), 51.7 (CH), 60.7 (2×CH_2), 69.9 (CH_2), 70.0 (CH_2), 70.5 (CH), 71.1 (CH), 95.0 (C_q), 95.7 (C_q), 213.2 (C=S), 215.1 (C=S) ppm. IR (CCl_4): *ν* = 2940, 2871, 1446, 1384, 1289, 1271, 1216, 1181, 1146, 1112, 1082, 1050, 1006, 978, 948 cm^{-1}. MS (CI/NH_3): *m/z* 347 (MH^+), 364 (MNH_4^+). HRMS: found 346.1634 (M^+). $C_{17}H_{30}O_3S_2$ requires 346.1637.

3-(4-Nitro-phenylsulfanyl)-2-pentyl-1,7-dioxa-spiro[5.5]undecane (24).



$C_{20}H_{29}NO_4S$
Exact Mass: 379,18
Mol. Wt.: 379,51

A solution of **22** (155 mg, 0.45 mmol) and ethylene diamine (0.12 mL, 1.8 mmol) in a 1:1 mixture of Et_2O and ethanol (0.45 mL) was stirred at room temperature for 40 min. Water (25 mL) was then added and the aqueous mixture extracted with Et_2O (3 × 25 mL). The collected organic phases were washed with a saturated solution of NH_4Cl (1 × 25 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was dissolved in dry THF (1 mL) before addition of DBU (76 µL, 0.50 mmol). After 10 min. of stirring at room temperature, commercial 1-fluoro-4-nitro-benzene (77 mg, 0.54 mmol) was added and the resulting yellow solution refluxed for 90 min. After cooling to room temperature, the reaction was quenched by addition of a saturated solution of NH_4Cl (10 mL) and the aqueous mixture extracted with Et_2O (3 × 10 mL). The collected organic phases were washed with water (2 × 15 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under

reduced pressure. Crude reaction product (166 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (EtOAc-petroleum ether, 6:94 v/v) to afford **24** (136 mg, 80% over 2 steps) as a pale yellow oil consisting of a separable 1:1 mixture of diastereomers

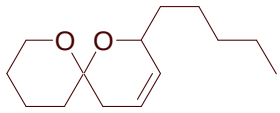
Least polar isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3 H), 1.22-1.68 (m, 13 H), 1.74 (ddd, *J* = 2.8, 4.0, 13.6 Hz, 1 H), 1.78-2.08 (m, 4 H), 3.11 (ddd, *J* = 4.4, 10.4, 11.6 Hz, 1 H), 3.58-3.64 (m, 3 H), 7.39-7.43 (m, 2 H), 8.10-8.14 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 18.7 (CH_2), 22.7 (CH_2), 25.3 (CH_2), 25.5 (CH_2), 27.0 (CH_2), 31.9 (CH_2), 33.7 (CH_2), 35.3 (CH_2), 36.3 (CH_2), 47.8 (CH), 60.8 (CH_2), 72.1 (CH), 95.0 (C_q), 124.0 (2×CH), 128.5 (2×CH), 145.5 (C_q), 146.2 (C_q) ppm. IR (CCl_4): *v* = 2942, 2872, 1596, 1582, 1520, 1478, 1466, 1452, 1439, 1384, 1340, 1287, 1274, 1225, 1180, 1113, 1081, 1048, 1036, 1012, 977, 949 cm^{-1}. MS (CI/NH_3): *m*/*z* 380 (MH^+).

Most polar isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3 H), 1.28-1.38 (m, 6 H), 1.45-1.65 (m, 6 H), 1.68-1.98 (m, 5 H), 2.34 (tt, *J* = 4.0, 13.2 Hz, 1 H), 3.52-3.56 (m, 1 H), 3.60-3.68 (m, 2 H), 4.05 (ddd, *J* = 2.0, 4.4, 8.8 Hz, 1 H), 7.36-7.40 (m, 2 H), 8.10-8.14 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 18.5 (CH_2), 22.6 (CH_2), 25.1 (CH_2), 25.3 (CH_2), 25.7 (CH_2), 30.8 (CH_2), 31.9 (CH_2), 34.0 (CH_2), 35.3 (CH_2), 47.5 (CH), 60.8 (CH_2), 70.6 (CH), 95.8 (C_q), 124.0 (2×CH), 127.6 (2×CH), 145.1 (C_q), 147.5 (C_q) ppm. IR (CCl_4): *v* = 2940, 2872, 1595, 1580, 1518, 1479, 1465, 1444, 1383, 1366, 1339, 1293, 1270, 1244, 1227, 1211, 1181, 1111, 1088, 1049, 1012, 986, 948 cm^{-1}. MS (CI/NH_3): *m*/*z* 380 (MH^+).

2-Pentyl-1,7-dioxa-spiro[5.5]undec-3-ene (26).



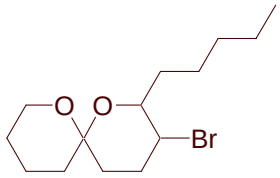
$C_{14}H_{24}O_2$
Exact Mass: 224,18
Mol. Wt.: 224,34

A solution of **24** (338 mg, 0.89 mmol) in CH_2Cl_2 (3 mL) was cooled to 0°C before dropwise addition of a solution of 73% *m*CPBA (222 mg, 0.94 mmol) in CH_2Cl_2 (3 mL). Stirring was continued at 0°C for 5 min. The reaction was then quenched by addition of a saturated solution of $NaHCO_3$ (15 mL) and the aqueous mixture extracted with CH_2Cl_2 (3 × 25 mL). The collected organic phases were dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. Part of the residue (125 mg) was dissolved in toluene (6.4 mL) and PPh_3 (92 mg, 0.35 mmol) was added. The resulting mixture was

refluxed for 21 h. After cooling to room temperature, the mixture was evaporated to dryness under reduced pressure. The residue was was purified by flash chromatography on silica gel (Et_2O-petroleum ether, 2:98 v/v) to afford **26** as a pale yellow oil, which had to be purified again by flash chromatography on silica gel (EtOAc-petroleum ether, 5:95 v/v). Pure **26** (58 mg, 81%) was obtained as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.8 Hz, 3 H), 1.20-1.54 (m, 5 H), 1.47-1.66 (7 H), 1.67-1.75 (m, 1 H), 1.88-2.05 (m, 2 H), 2.12-2.18 (m, 1 H), 3.63-3.70 (m, 1 H), 3.75 (dt, *J* = 2.8, 11.2 Hz, 1 H), 4.05-4.14 (m, 1 H), 5.63-5.70 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 18.9 (CH_2), 22.7 (CH_2), 25.2 (CH_2), 25.4 (CH_2), 32.0 (CH_2), 35.2 (CH_2), 35.4 (CH_2), 36.0 (CH_2), 61.5 (CH_2), 67.7 (CH), 95.0 (C_q), 121.7 (CH), 129.2 (CH) ppm. IR (CCl_4): *ν* = 3035, 2936, 2870, 1663, 1521, 1464, 1439, 1423, 1392, 1380, 1368, 1334, 1286, 1272, 1236, 1213, 1189, 1180, 1148, 1116, 1096, 1078, 1049, 1007, 962, 942 cm^{-1}. MS (CI/NH_3): *m*/*z* 225 (MH^+). HRMS: found 224.1771 (M^+). $C_{14}H_{24}O_2$ requires 224.1776.

3-Bromo-2-pentyl-1,7-dioxa-spiro[5.5]undecane (27).



$C_{14}H_{25}BrO_2$
Exact Mass: 304,10
Mol. Wt.: 305,25

A solution of **22** (84 mg, 0.24 mmol) and 2-bromo-2-methyl-propionic acid ethyl ester (236 mg, 1.2 mmol) in chlorobenzene (3.4 mL) was refluxed for 15 min. Cumyl peroxide (0.50 eq.) was then added and additional cumyl peroxide (0.50 eq.) was added every 2 h until complete consumption of the starting material. The reaction needed 1.50 eq. of cumyl peroxide to go to completion. The mixture was then cooled to room temperature and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (Et_2O-petroleum ether, 2:98 v/v) to afford **27** (53 mg, 72%) as a 1:1.2 mixture (NMR analysis) of separable diastereomers.

Least polar isomer

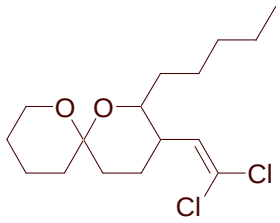
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.8 Hz, 3 H), 1.30-1.48 (m, 7 H), 1.51-1.65 (m, 6 H), 1.69 (ddd, *J* = 2.8, 4.4, 13.6 Hz, 1 H), 1.76-1.89 (m, 1 H), 2.00-2.07 (m, 1 H), 2.10-2.16 (m, 1 H), 2.31-2.41 (m, 1 H), 3.61-3.66 (m, 2 H), 3.68-3.76 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 18.8 (CH_2), 22.7 (CH_2), 25.3 (2×CH_2), 31.2 (CH_2), 31.9 (CH_2), 33.6 (CH_2), 35.1 (CH_2), 37.8 (CH_2), 53.1 (CH), 60.8 (CH_2), 73.1 (CH), 95.2 (C_q) ppm. IR (CCl_4): *ν* = 2951, 2869, 1728, 1456,

1383, 1272, 1227, 1178, 1151, 1108, 1079, 1045, 999, 977, 949, 910 cm^{-1}. MS (EI, 70eV): *m/z* 304 (M^+, 82%, $C_{14}H_{25}{}^{79}BrO_2$), 306 (M^+, 82%, $C_{14}H_{25}{}^{81}BrO_2$). HRMS: found 304.1045 (M^+, $C_{14}H_{25}{}^{79}BrO_2$). $C_{14}H_{25}{}^{79}BrO_2$ requires 304.1038.

Most polar isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 6.8 Hz, 3 H), 1.33-1.82 (m, 14 H), 1.88-2.06 (m, 3 H), 2.40-2.51 (m, 1 H), 3.56-3.69 (m, 3 H), 4.27-4.32 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 18.5 (CH_2), 22.7 (CH_2), 25.2 (CH_2), 25.3 (CH_2), 28.8 (CH_2), 30.5 (CH_2), 31.9 (CH_2), 35.2 (CH_2), 35.3 (CH_2), 56.4 (CH), 60.7 (CH_2), 70.2 (CH), 95.7 (C_q) ppm. IR (CCl_4): *ν* = 2950, 2866, 1728, 1442, 1381, 1269, 1228, 1179, 1148, 1093, 1053, 1006, 983, 949 cm^{-1}. MS (EI, 70 eV): *m/z* 304 (M^+, 100%, $C_{14}H_{25}{}^{79}BrO_2$), 306 (M^+, 100%, $C_{14}H_{25}{}^{81}BrO_2$). HRMS: found 304.1038 (M^+, $C_{14}H_{25}{}^{79}BrO_2$). $C_{14}H_{25}{}^{79}BrO_2$ requires 304.1038.

3-(2,2-Dichloro-vinyl)-2-pentyl-1,7-dioxa-spiro[5.5]undecane (28).



$C_{16}H_{26}Cl_2O_2$
Exact Mass: 320,13
Mol. Wt.: 321,28

A solution of **22** (96 mg, 0.28 mmol) and ethyl-2,2-dichlorovinyl sulfone (210 mg, 1.1 mmol) in a 1:3 mixture of chlorobenzene and heptane (0.60 mL) was refluxed for 15 min. DLP (0.025 eq.) was then added. Additional DLP (0.025 eq.) was added every 60 min. until complete consumption of **22**. After addition of 0.40 eq. of DLP, the mixture was cooled to room temperature and the solvent evaporated under reduced pressure. Crude reaction product (222 mg) was obtained as a yellow oil, which was purified by flash chromatography on silica gel (Et_2O-petroleum ether, 1:99 to 2:98 v/v) to afford **28** (46 mg, 51%) as a pale yellow oil consisting of a 1:4 mixture of diastereomers, the most polar of which could be isolated and characterised.

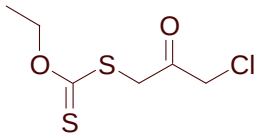
Most polar isomer (major)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.8 Hz, 3 H), 1.24-1.76 (m, 17 H), 1.80-1.92 (m, 1 H), 2.33 (dtd, *J* = 4.4, 10.0, 11.6 Hz, 1 H), 3.40 (dt, *J* = 2.0, 10.0 Hz, 1 H), 3.55-3.67 (m, 2 H), 5.62 (d, *J* = 10.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 18.7 (CH_2), 22.8 (CH_2), 24.4 (CH_2), 25.4 (CH_2), 25.6 (CH_2), 32.1 (CH_2), 34.1 (CH_2), 34.8 (CH_2), 35.7 (CH_2), 43.0 (CH), 60.6 (CH_2), 71.5

(CH), 95.0 (C_q), 120.7 (C_q), 131.3 (CH) ppm. IR (CCl_4): ν = 2938, 2870, 1621, 1465, 1450, 1439, 1383, 1351, 1312, 1286, 1272, 1244, 1224, 1196, 1182, 1171, 1112, 1100, 1084, 1047, 996, 979, 948, 924 cm^{-1}. MS (CI/NH_3): *m*/*z* 321 (MNH_4^+, $C_{16}H_{26}{}^{35}Cl_2O_2$), 323 ($MNH_4^+$, $C_{16}H_{26}{}^{35}Cl^{37}ClO_2$), 325 ($MNH_4^+$, $C_{16}H_{26}{}^{37}Cl_2O_2$). HRMS: found 320.1304 (M^+). $C_{16}H_{26}Cl_2O_2$ requires 320.1310.

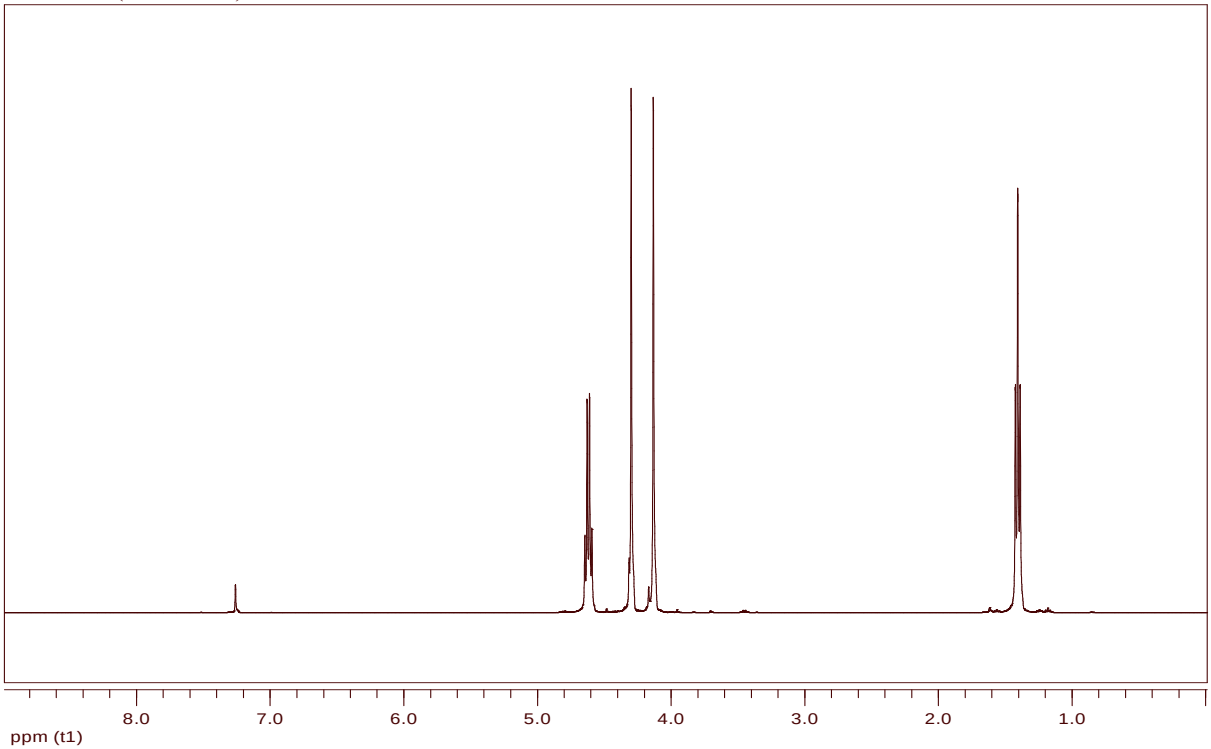
Spectral data.

Dithiocarbonic acid (3-chloro-2-oxo-propyl) ester ethyl ester (1).

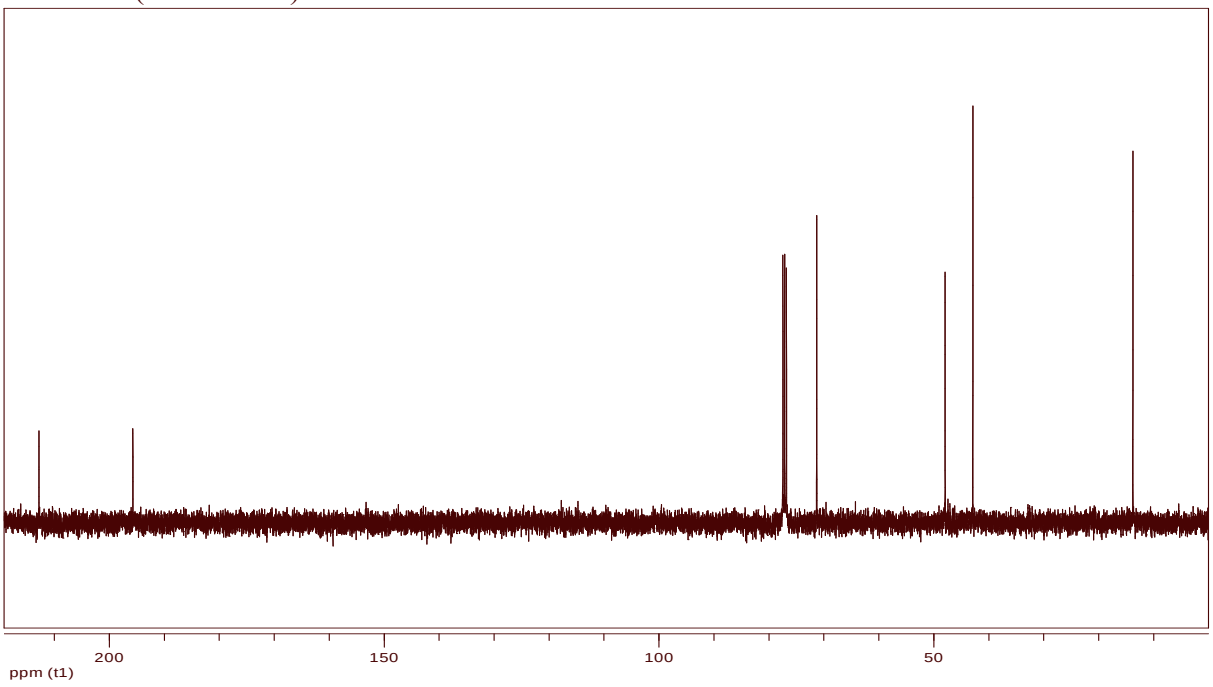


$C_6H_9ClO_2S_2$
Exact Mass: 211,97
Mol. Wt.: 212,72

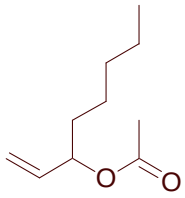
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

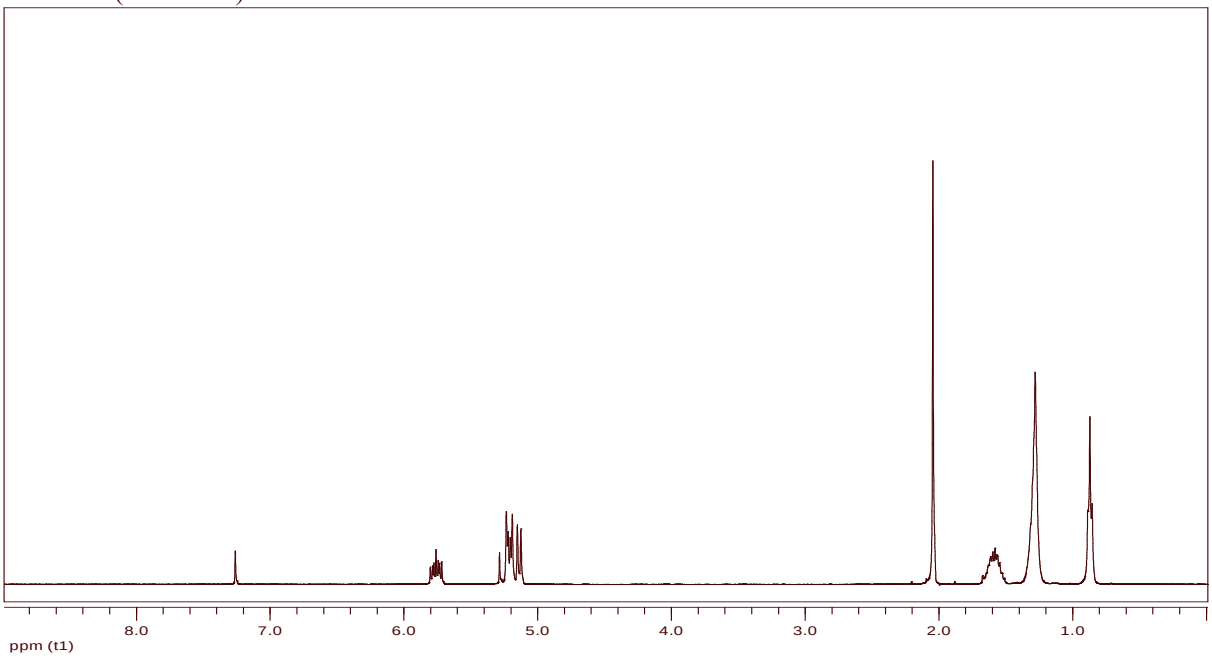


Acetic acid 1-vinyl-hexyl ester (4).

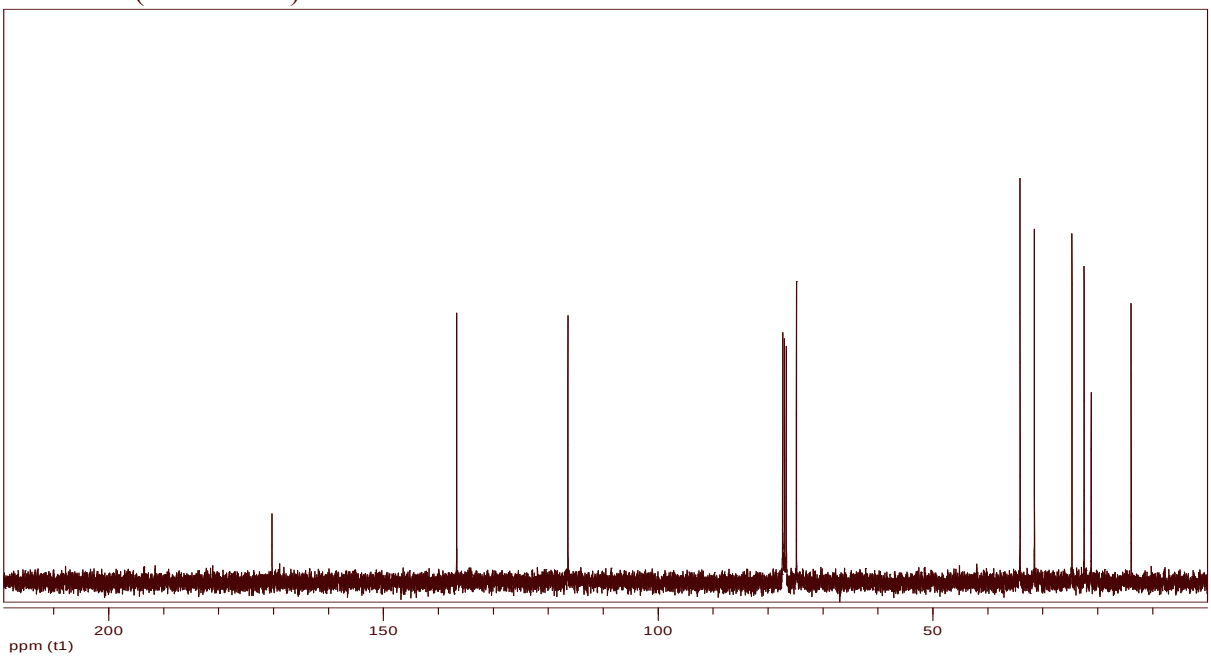


$C_{10}H_{18}O_2$
Exact Mass: 170,13
Mol. Wt.: 170,25

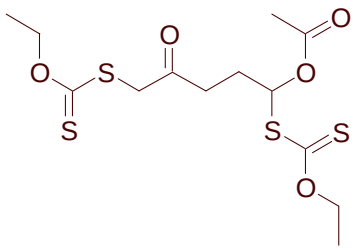
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

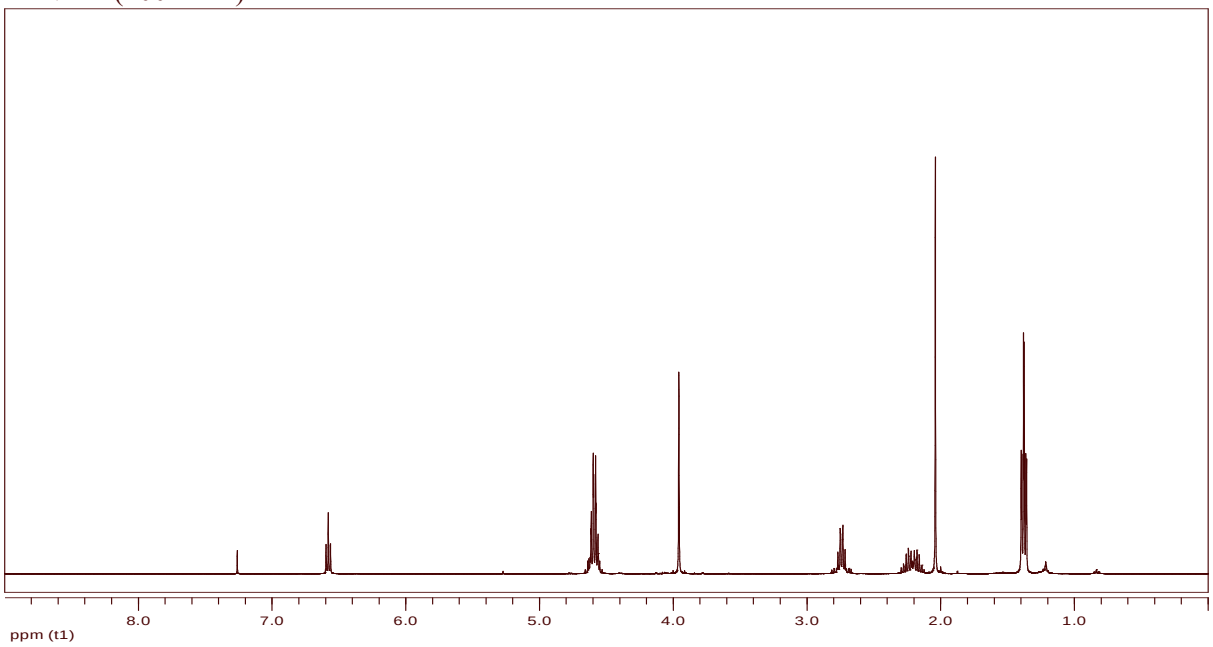


Acetic acid 1,5-bis-ethoxythiocarbonylsulfanyl-4-oxo-pentyl ester (8a).

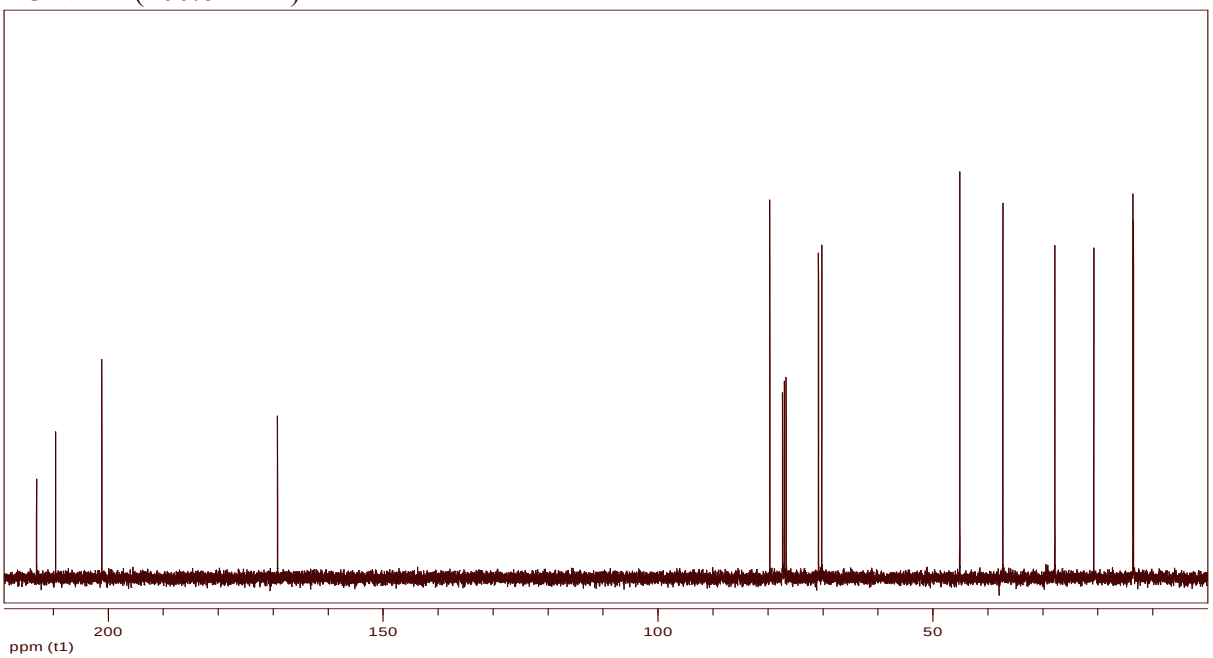


$C_{13}H_{20}O_5S_4$
Exact Mass: 384,02
Mol. Wt.: 384,56

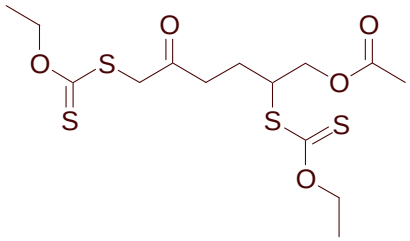
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

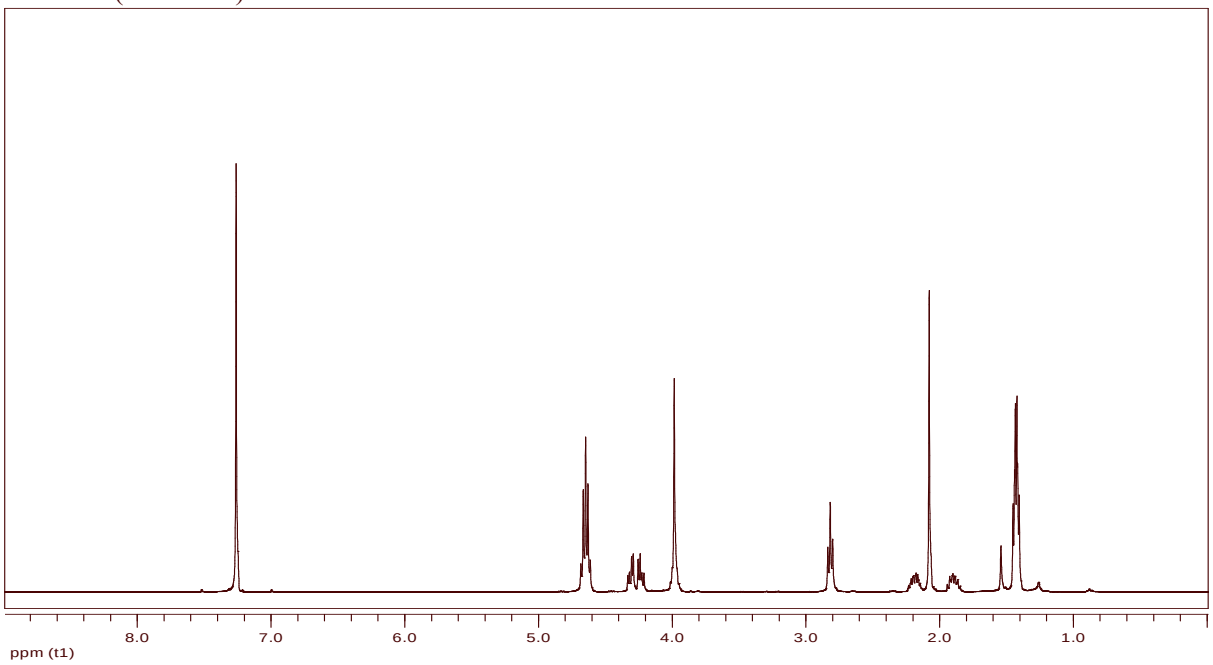


Acetic acid 2,6-bis-ethoxythiocarbonylsulfanyl-5-oxo-hexyl ester (8b).

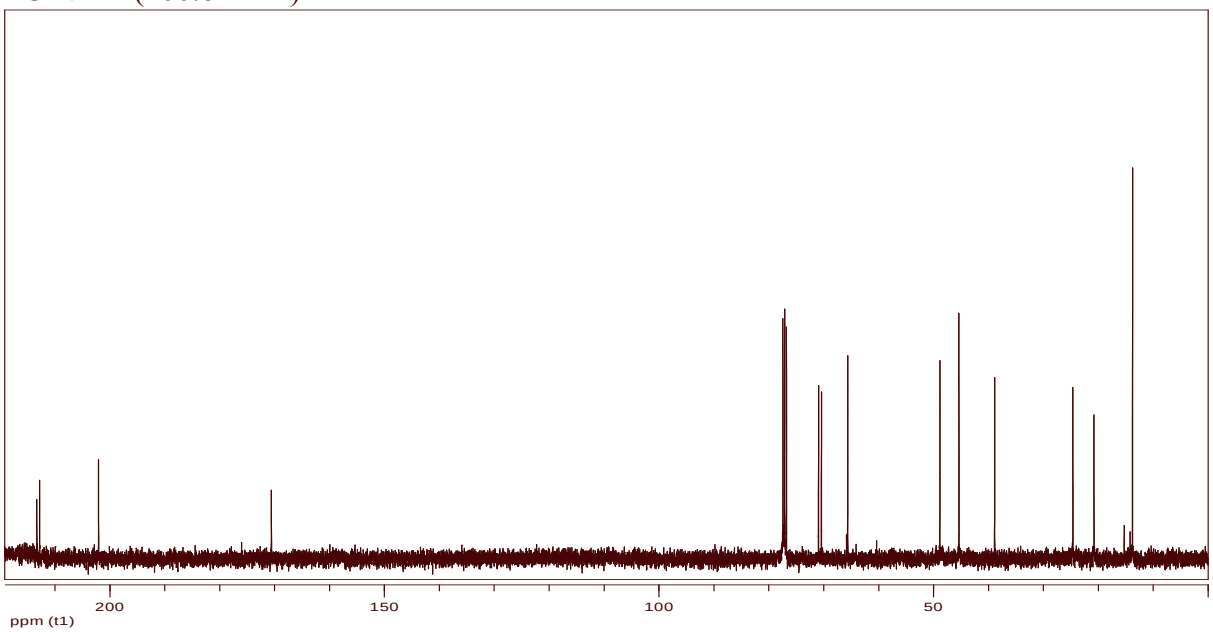


$C_{14}H_{22}O_5S_4$
Exact Mass: 398,04
Mol. Wt.: 398,59

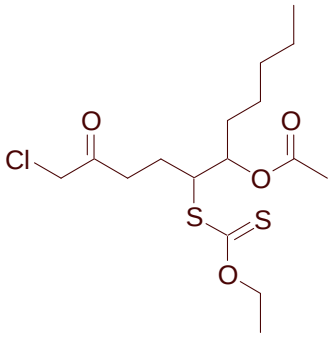
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

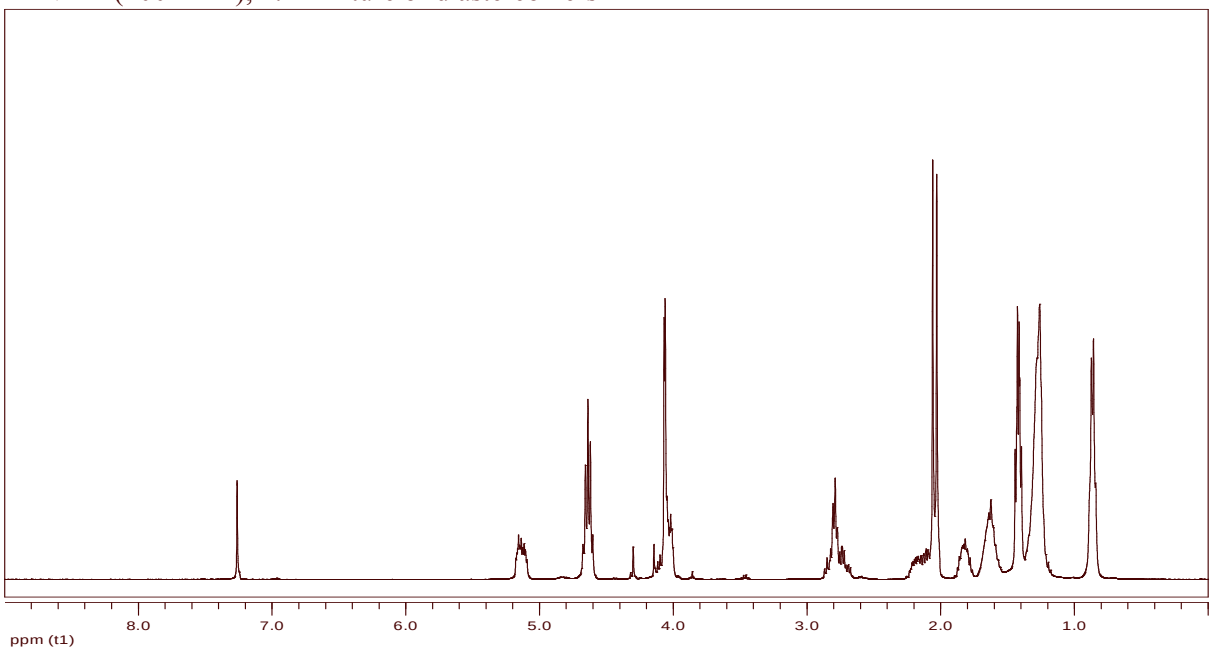


Acetic acid 6-chloro-2-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-hexyl ester (7c).

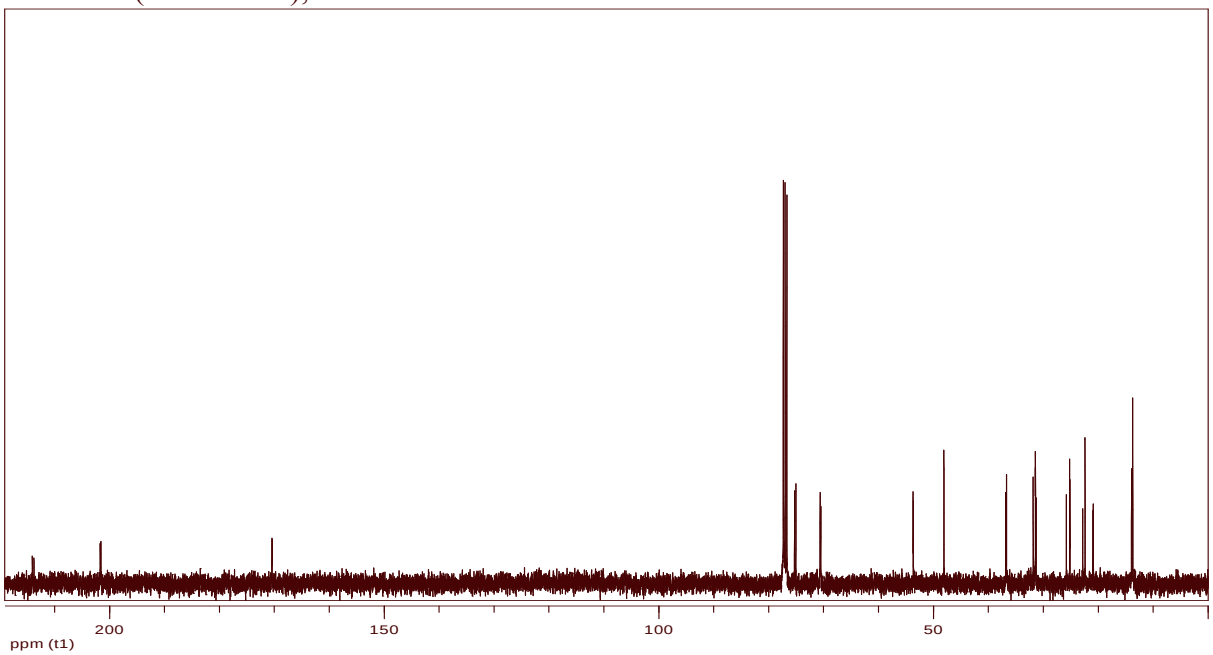


$C_{16}H_{27}ClO_4S_2$
Exact Mass: 382,10
Mol. Wt.: 382,97

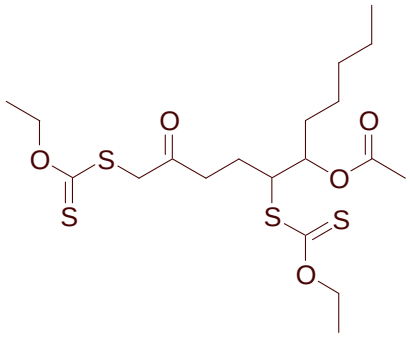
^{1}H NMR (400 MHz), 1:1 mixture of diastereomers



^{13}C NMR (100.6 MHz), 1:1 mixture of diastereomers

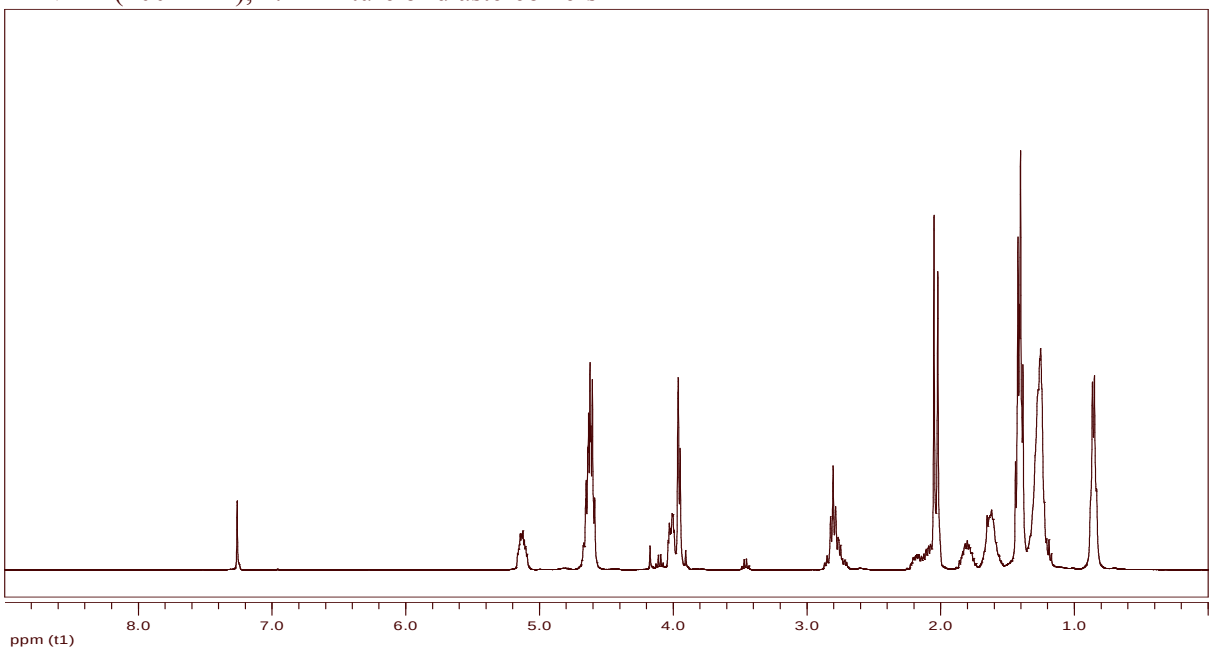


Acetic acid 2,6-bis-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-hexyl ester (8c).

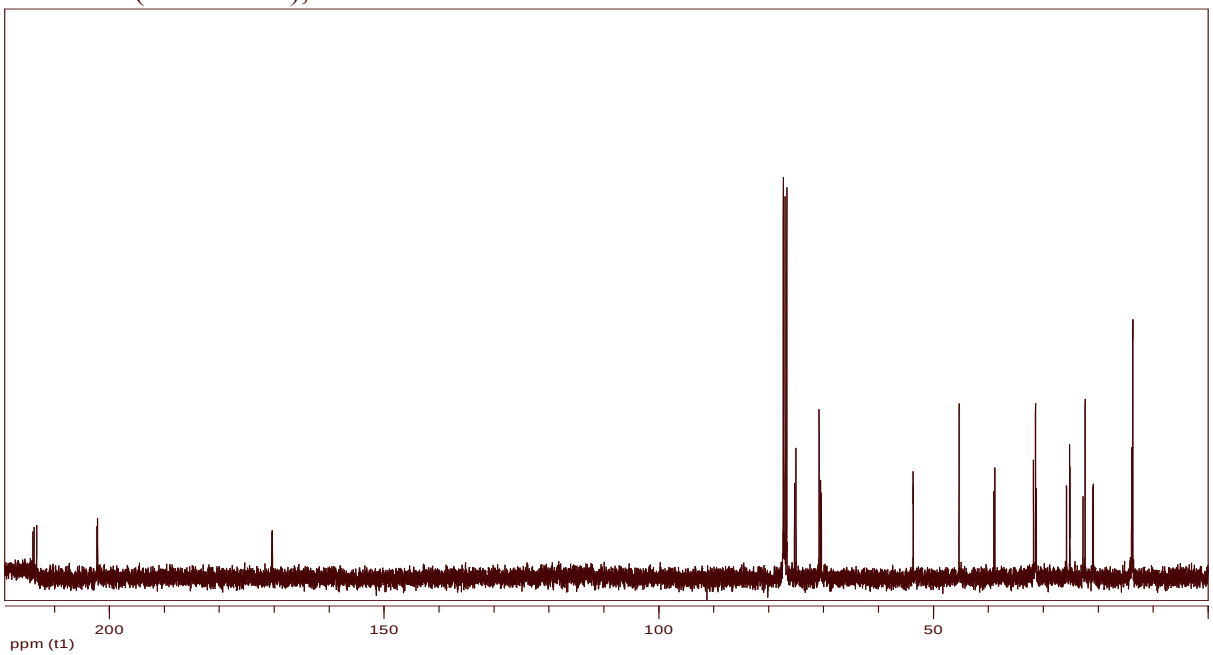


$C_{19}H_{32}O_5S_4$
Exact Mass: 468,11
Mol. Wt.: 468,72

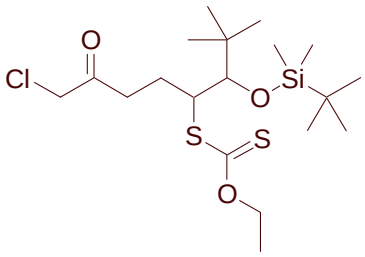
^{1}H NMR (400 MHz), 1:1 mixture of diastereomers



^{13}C NMR (100.6 MHz), 1:1 mixture of diastereomers

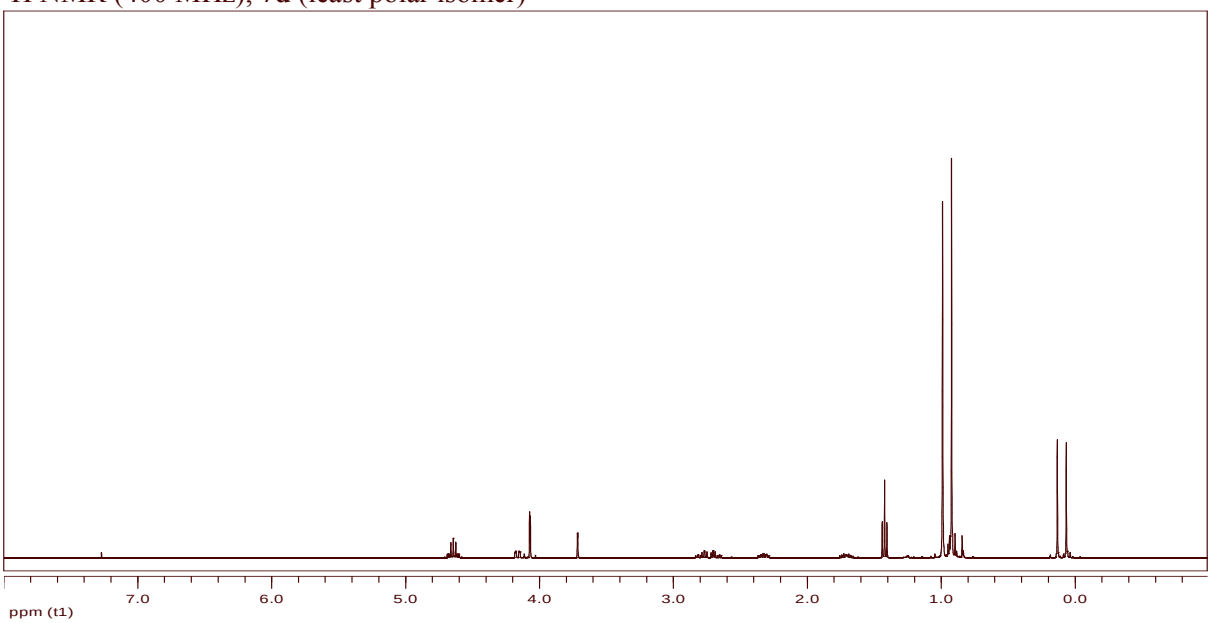


Dithiocarbonic acid {1-[1-(*tert*-butyl-dimethyl-silanyloxy)-2,2-dimethyl-propyl]-5-chloro-4-oxo-pentyl} ester ethyl ester (7d).

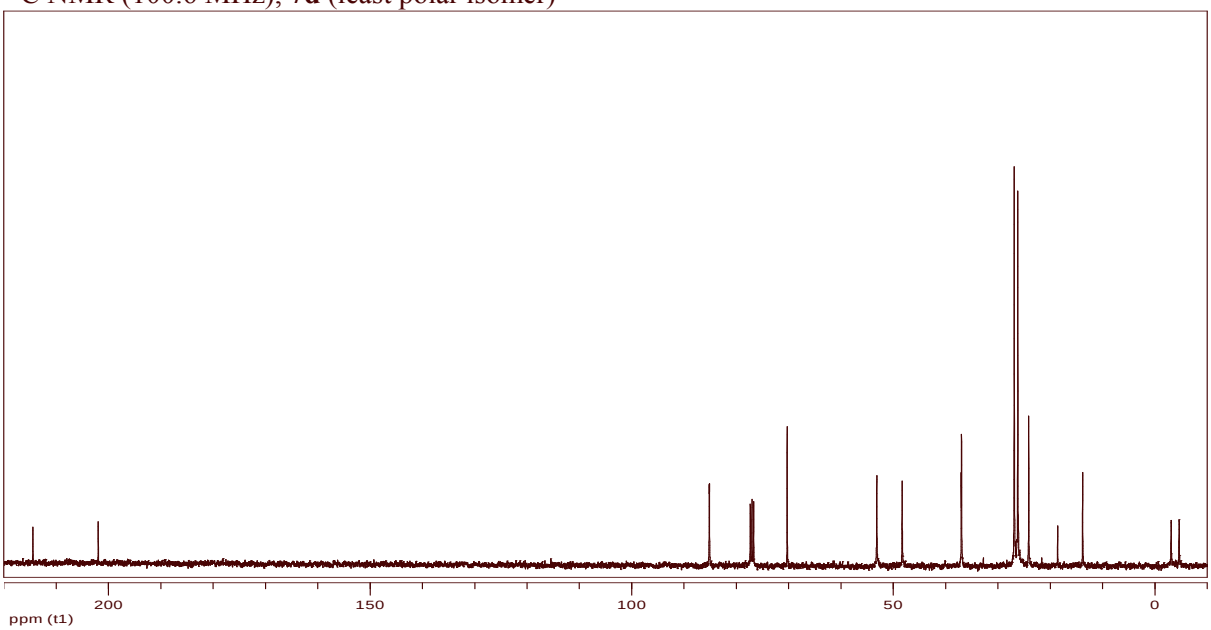


$C_{19}H_{37}ClO_3S_2Si$
Exact Mass: 440,16
Mol. Wt.: 441,17

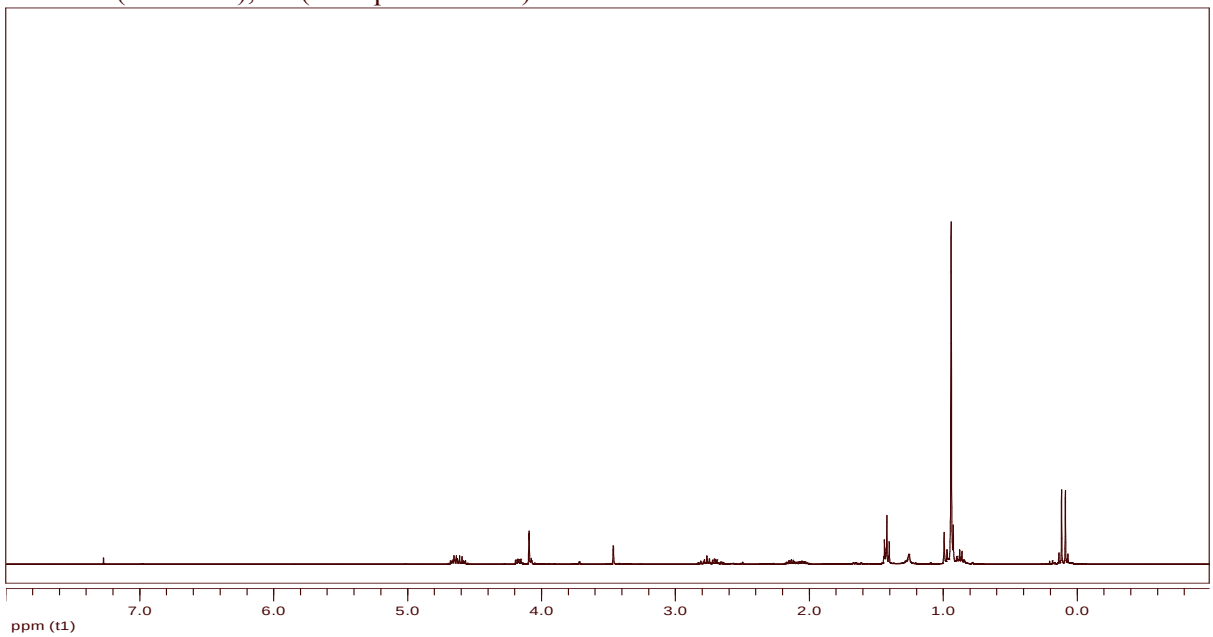
^{1}H NMR (400 MHz), **7d** (least polar isomer)



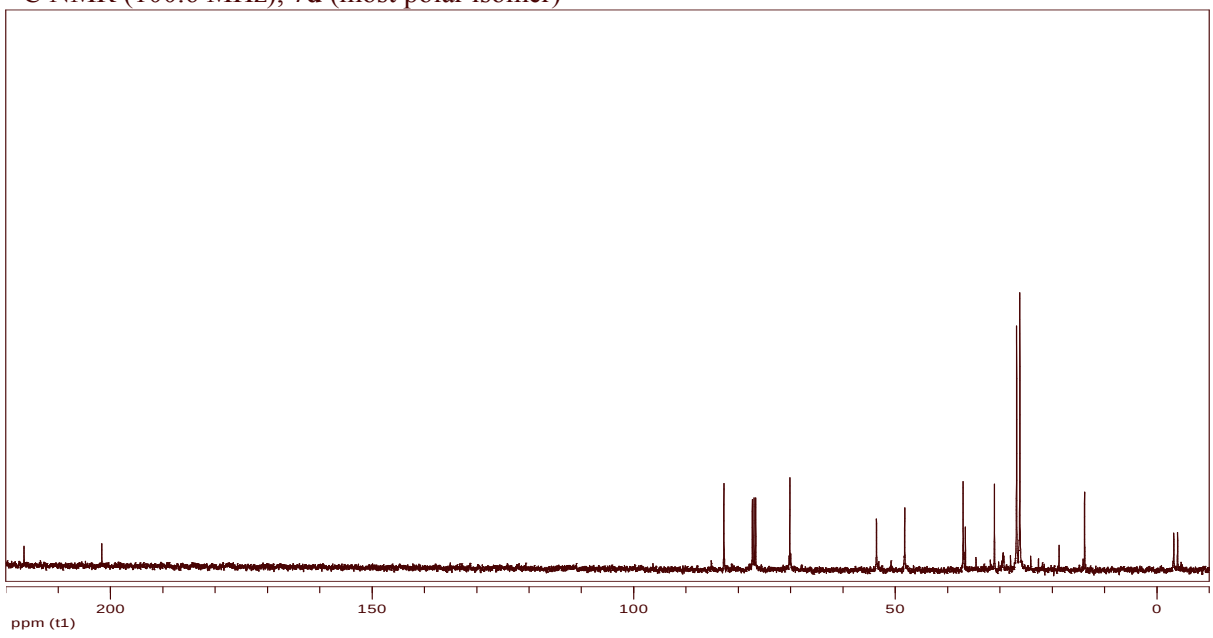
^{13}C NMR (100.6 MHz), **7d** (least polar isomer)



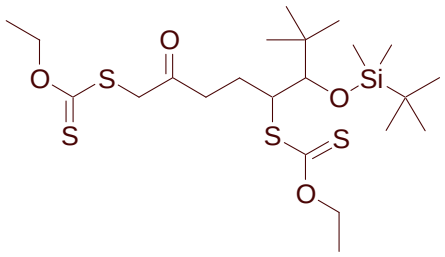
^{1}H NMR (400 MHz), **7d** (most polar isomer)



^{13}C NMR (100.6 MHz), **7d** (most polar isomer)

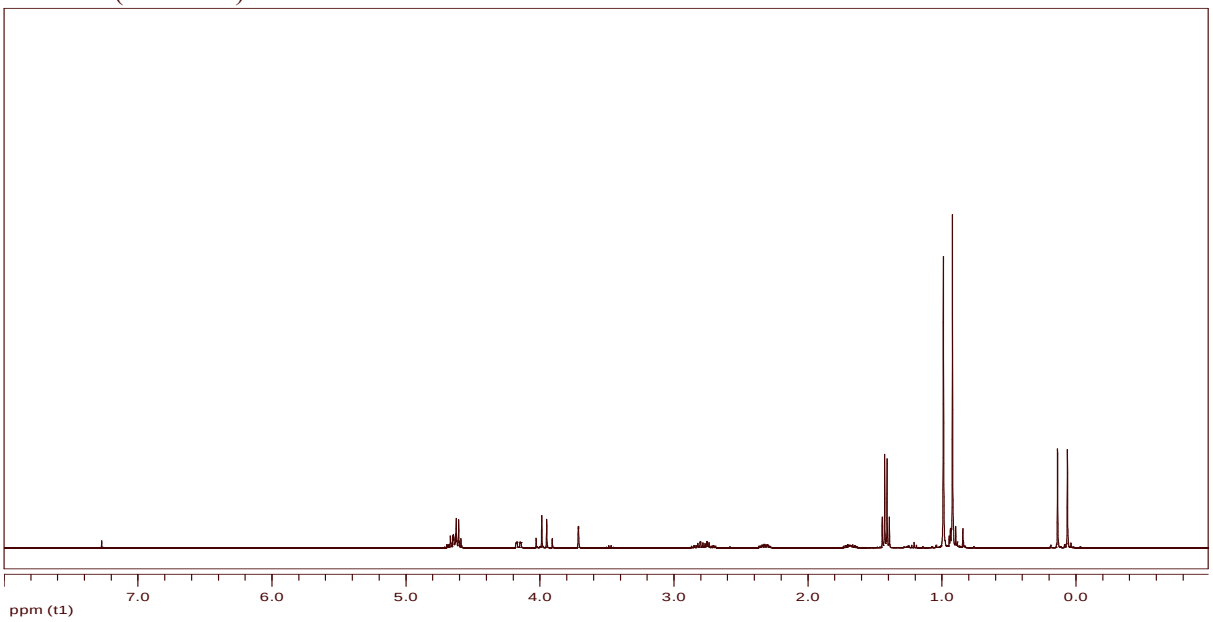


Dithiocarbonic acid [6-(*tert*-butyl-dimethyl-silanyloxy)-5-ethoxythio-carbonyl-sulfanyl-7,7-dimethyl-2-oxo-octyl] ester ethyl ester (8d).

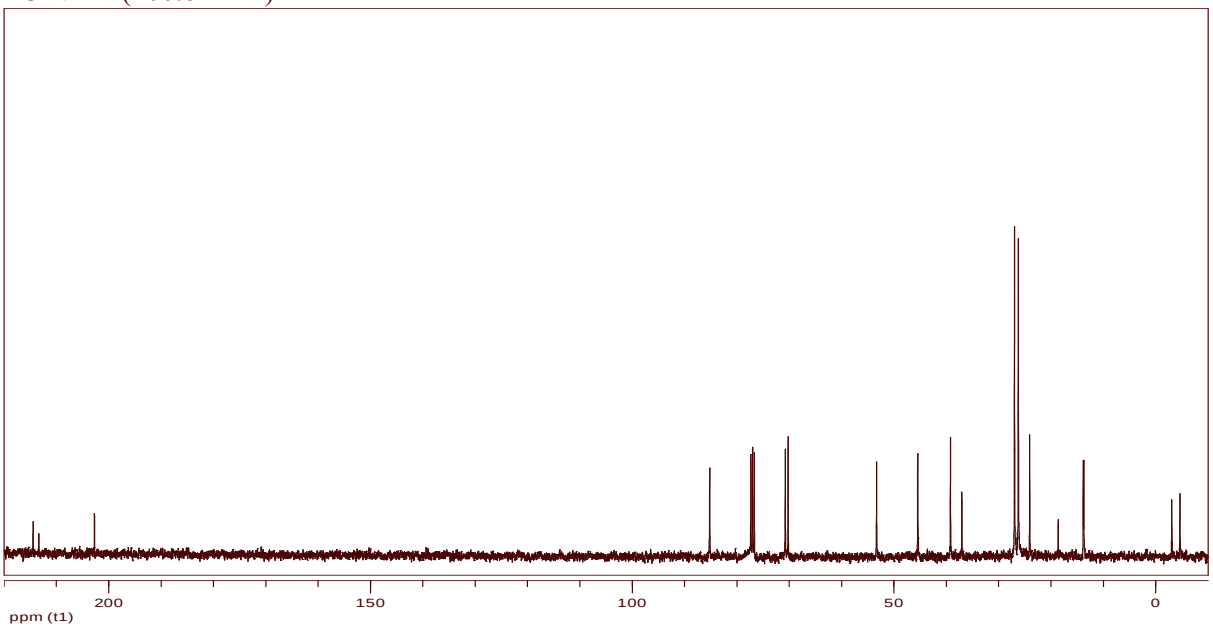


$C_{22}H_{42}O_4S_4Si$
Exact Mass: 526,17
Mol. Wt.: 526,92

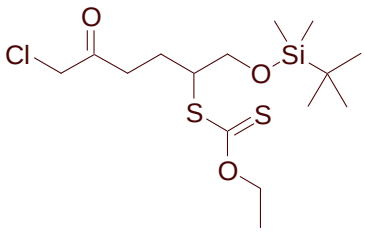
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

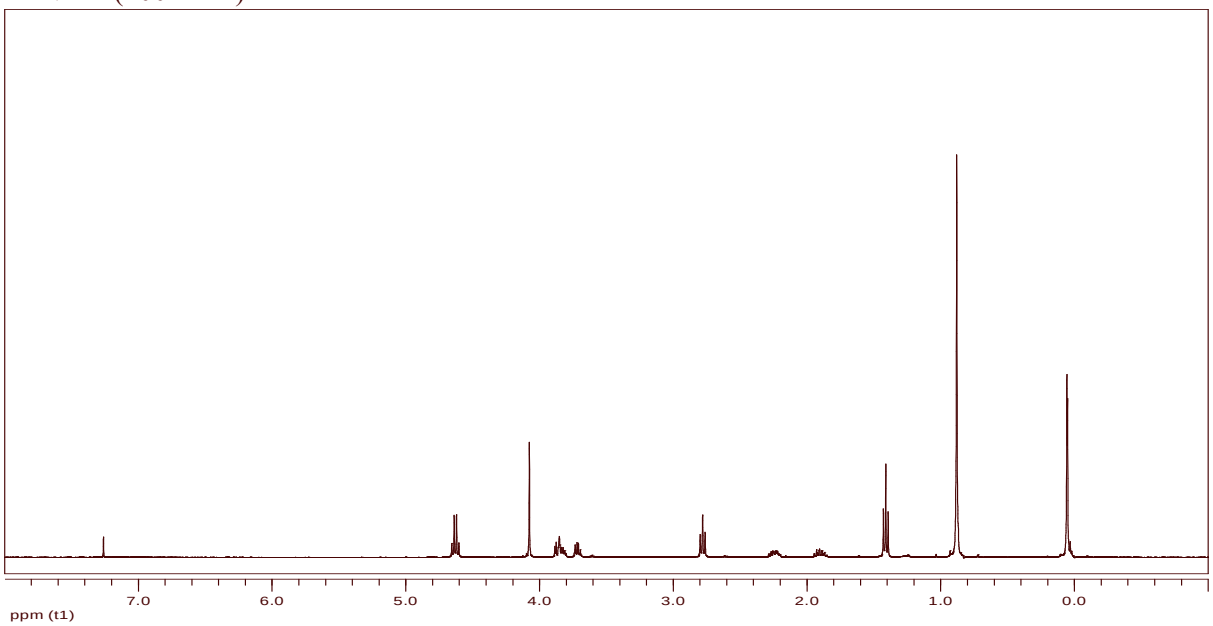


Dithiocarbonic acid [1-(*tert*-butyl-dimethyl-silanyloxymethyl)-5-chloro-4-oxo-pentyl] ester ethyl ester (7e).

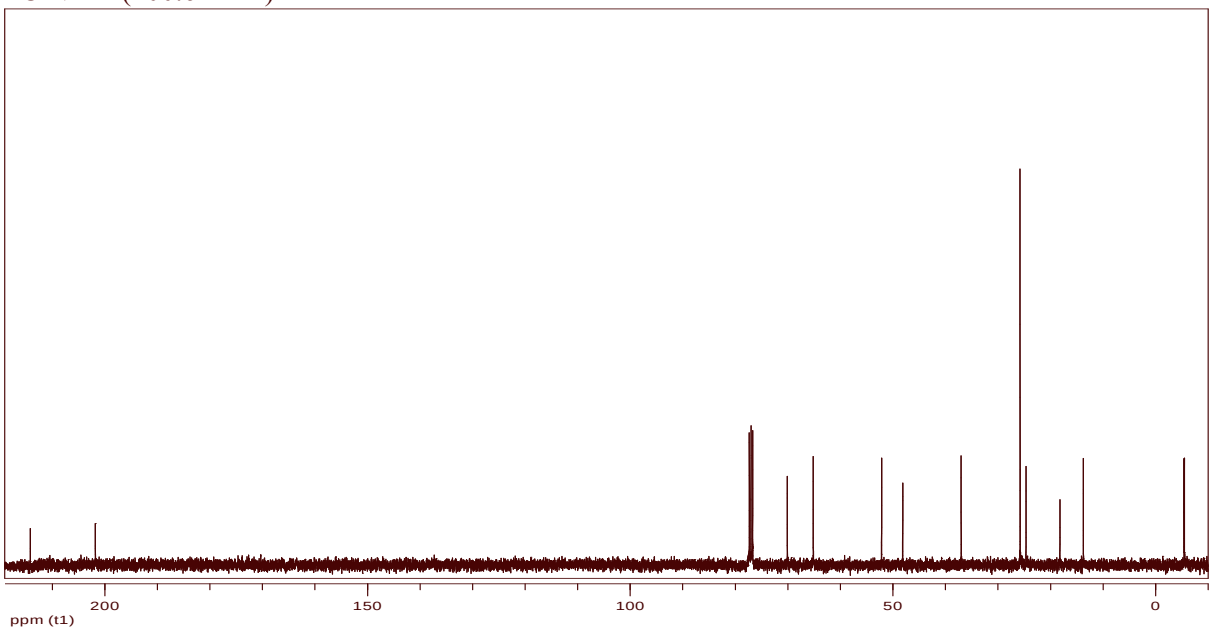


$C_{15}H_{29}ClO_3S_2Si$
Exact Mass: 384,10
Mol. Wt.: 385,06

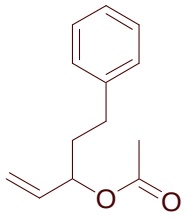
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

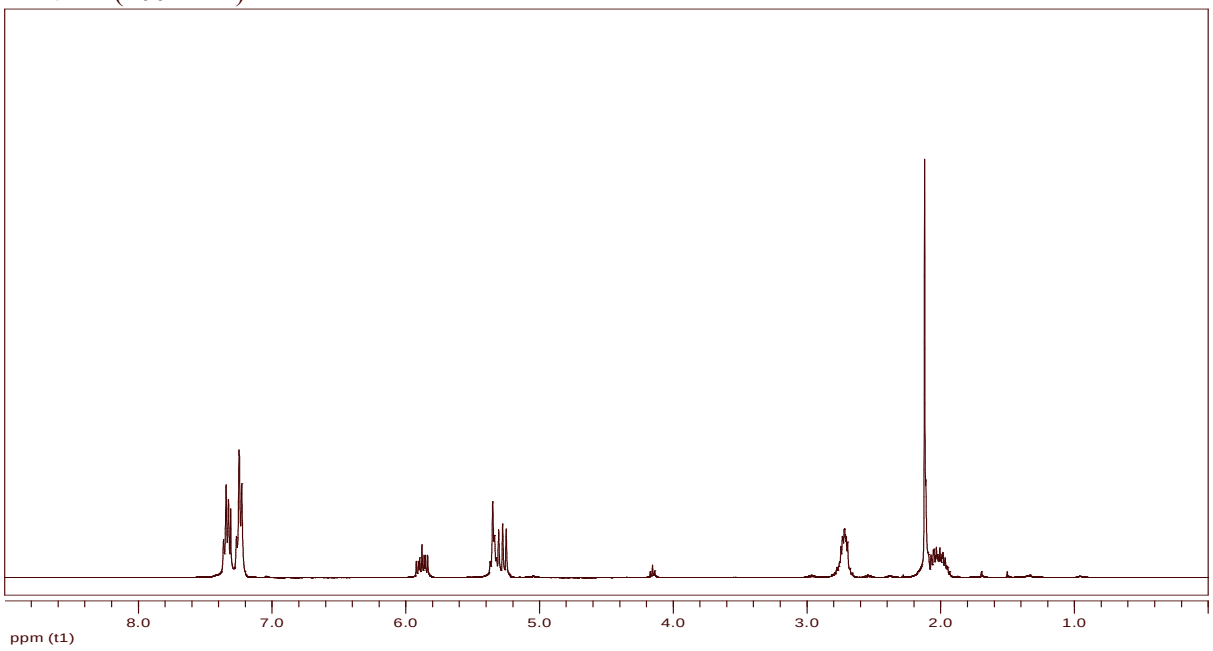


Acetic acid 1-phenethyl-allyl ester (9).

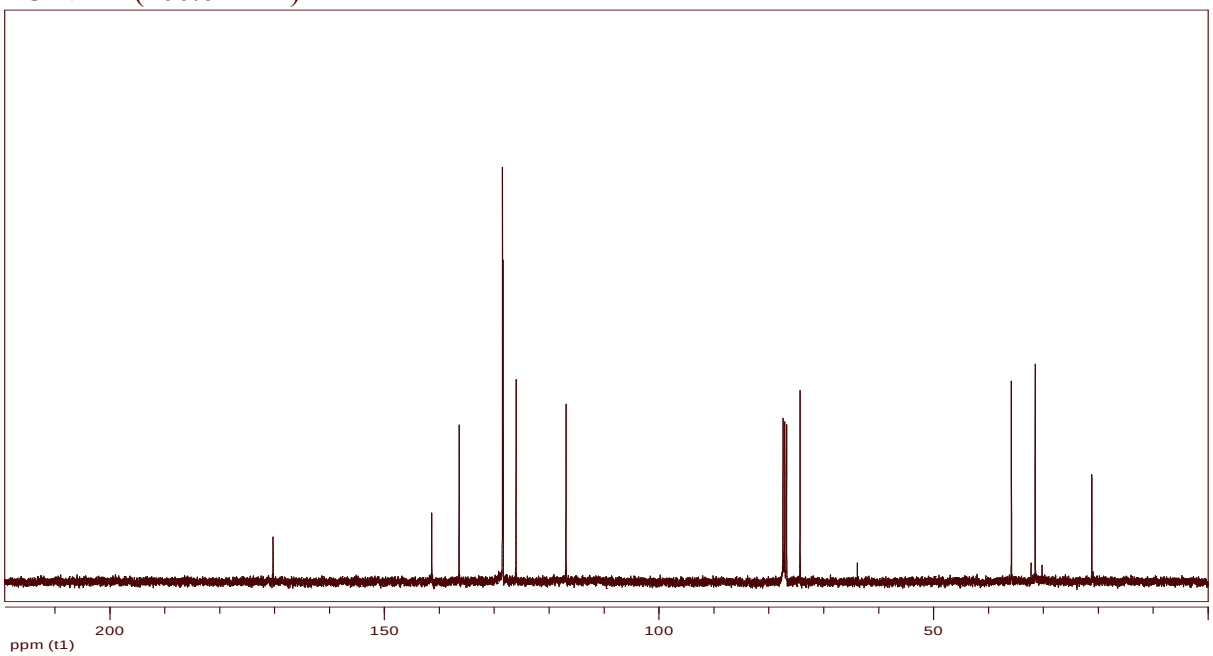


$C_{13}H_{16}O_2$
Exact Mass: 204,12
Mol. Wt.: 204,26

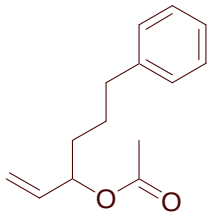
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

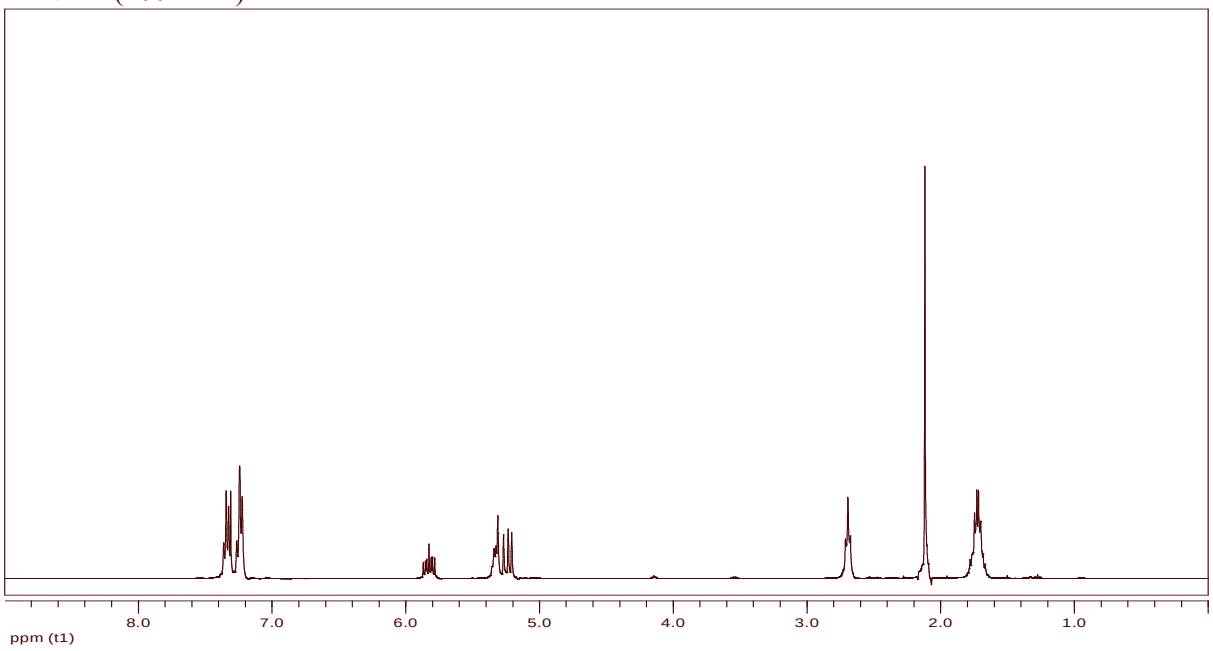


Acetic acid 4-phenyl-1-vinyl-butyl ester (10).

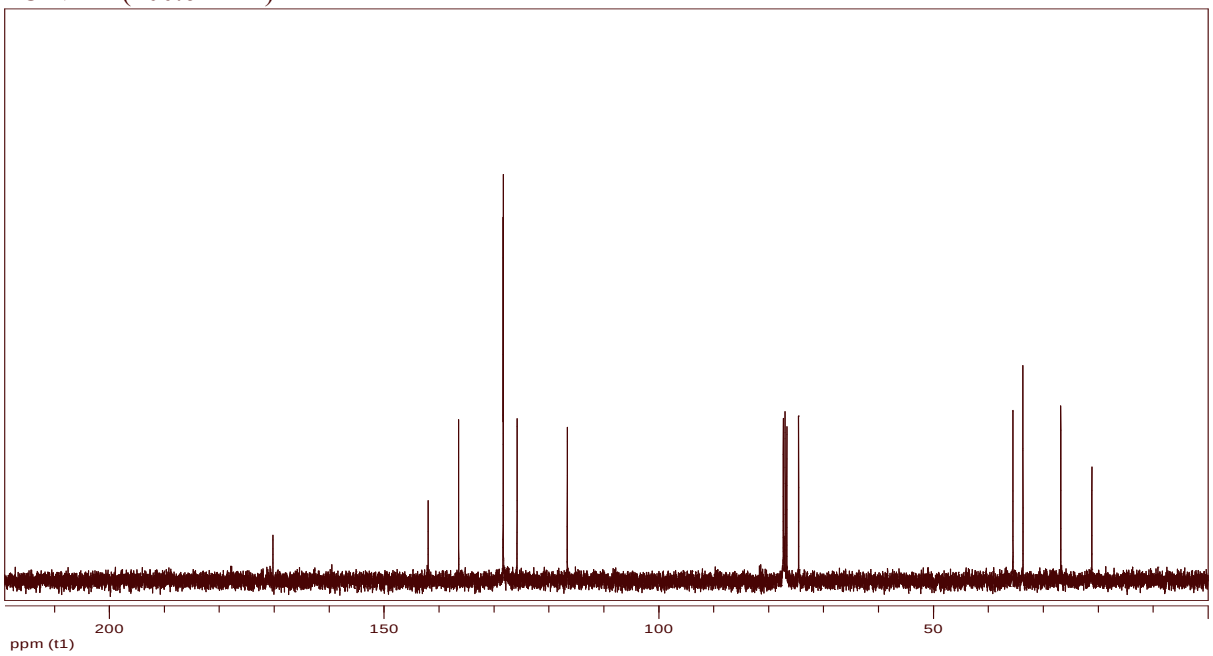


$C_{14}H_{18}O_2$
Exact Mass: 218,13
Mol. Wt.: 218,29

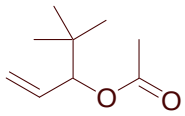
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

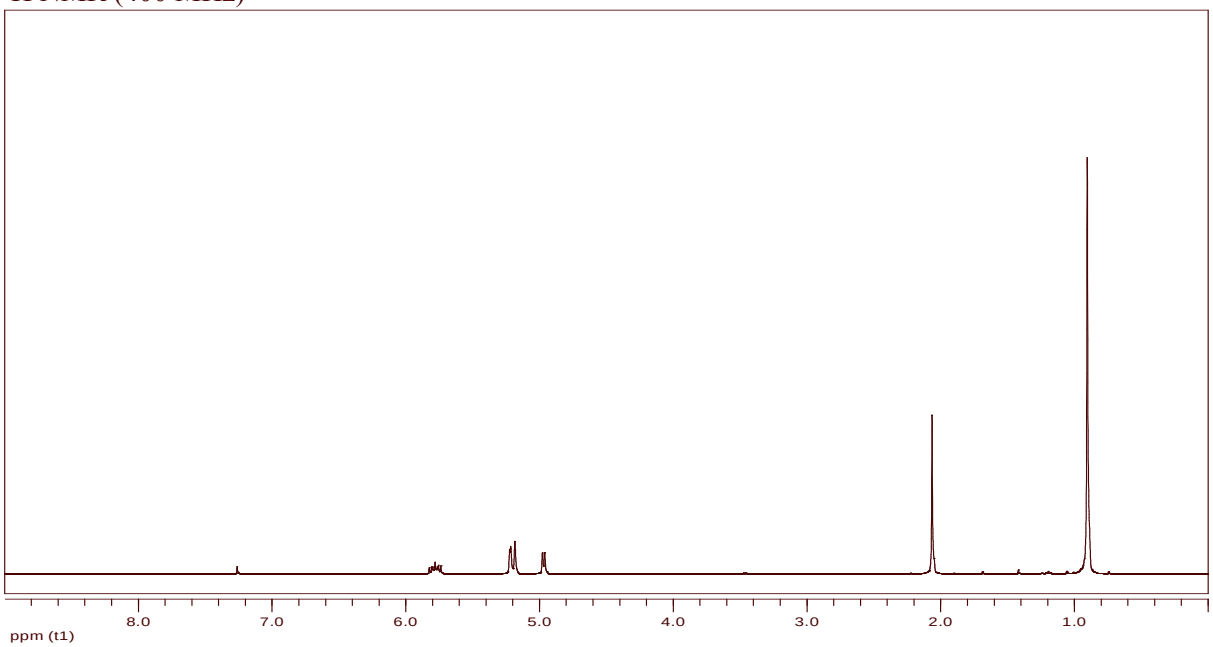


Acetic acid 1-*tert*-butyl-allyl ester (11).

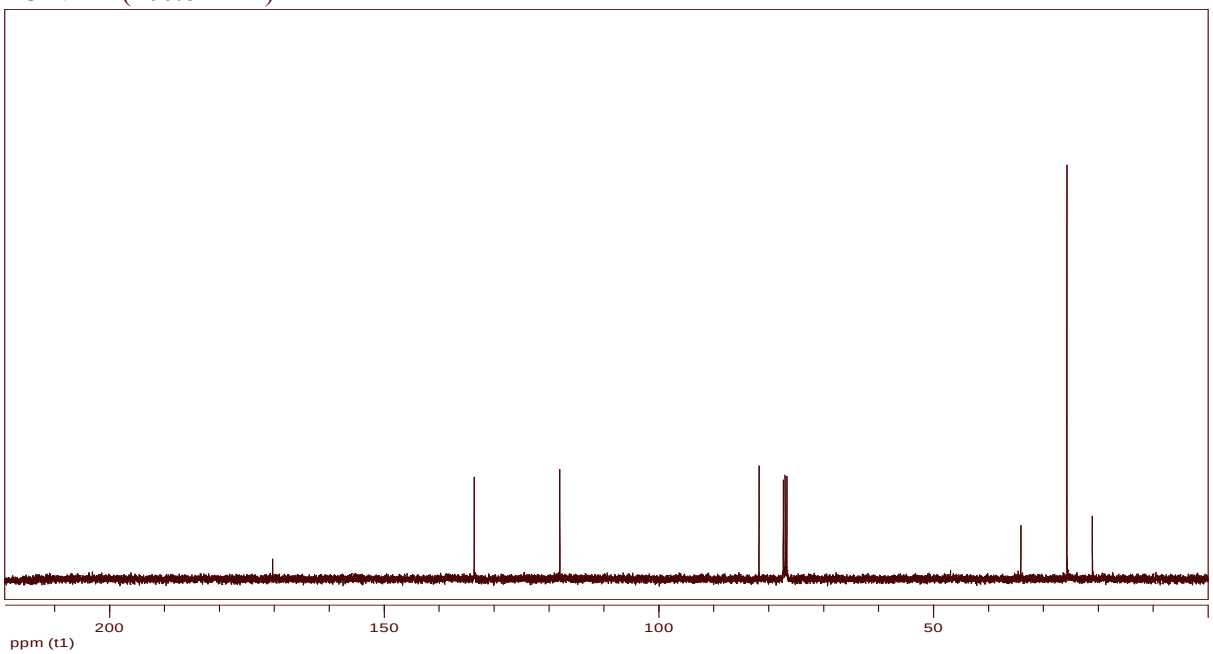


$C_9H_{16}O_2$
Exact Mass: 156,12
Mol. Wt.: 156,22

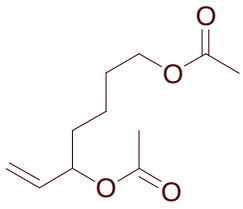
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

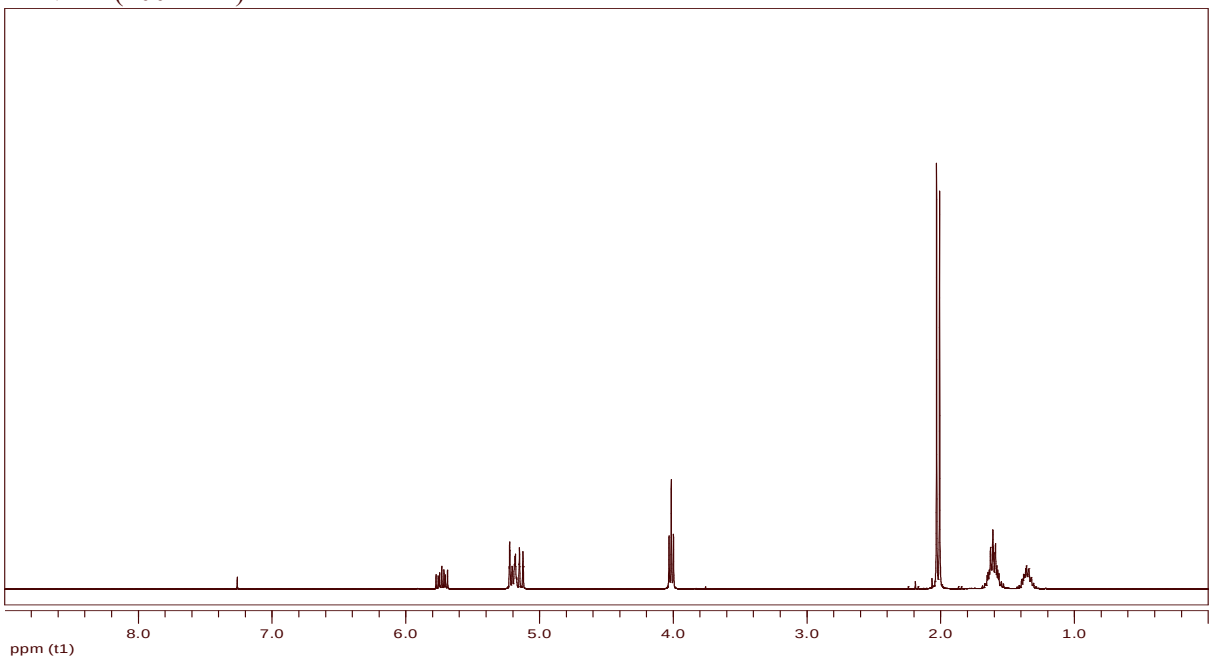


Acetic acid 5-acetoxy-1-vinyl-pentyl ester (12).

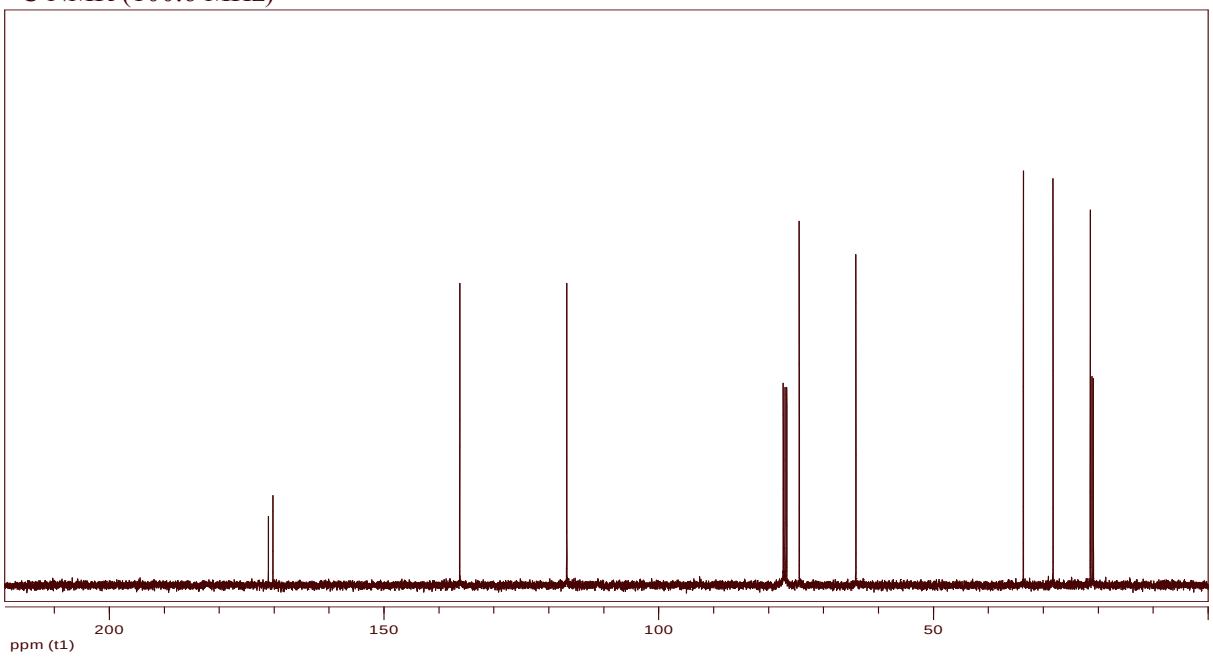


$C_{11}H_{18}O_4$
Exact Mass: 214,12
Mol. Wt.: 214,26

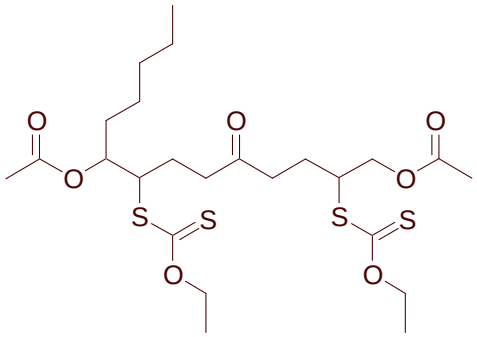
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

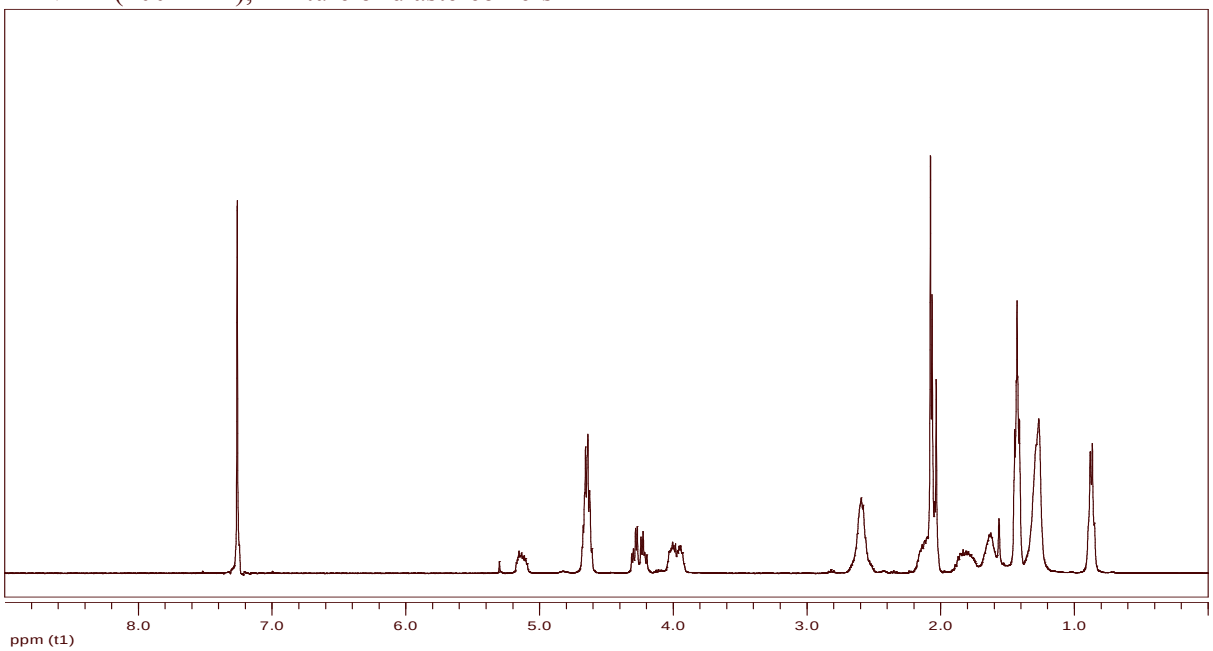


Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxotetradecyl ester (15a).

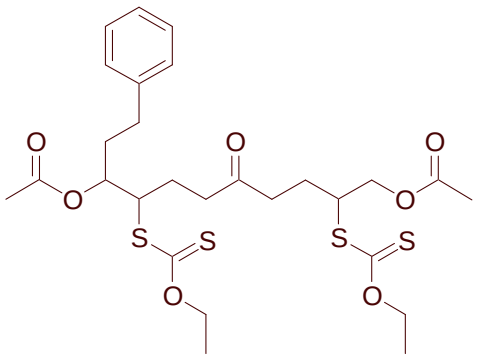


$C_{24}H_{40}O_7S_4$
Exact Mass: 568,17
Mol. Wt.: 568,83

^{1}H NMR (400 MHz), mixture of diastereomers

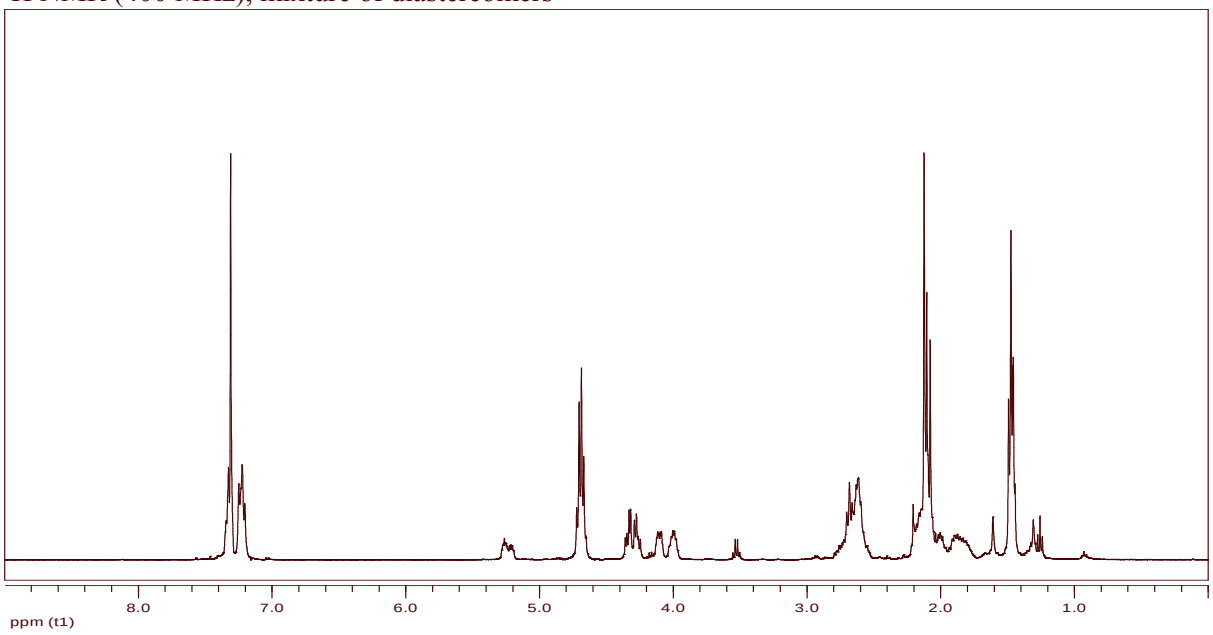


Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-11-phenyl-undecyl ester (15b).

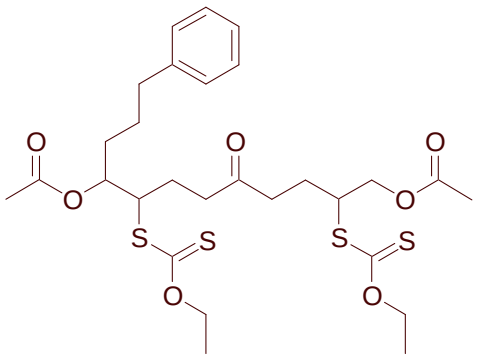


$C_{27}H_{38}O_7S_4$
Exact Mass: 602,15
Mol. Wt.: 602,85

^{1}H NMR (400 MHz), mixture of diastereomers

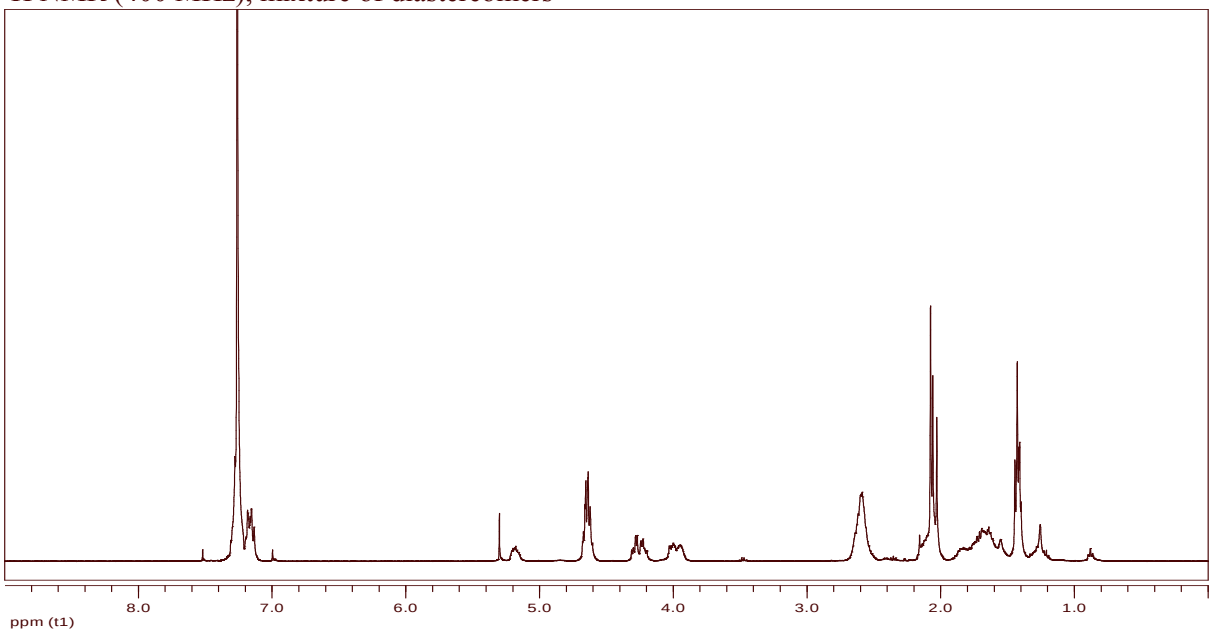


Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-12-phenyl-dodecyl ester (15c).

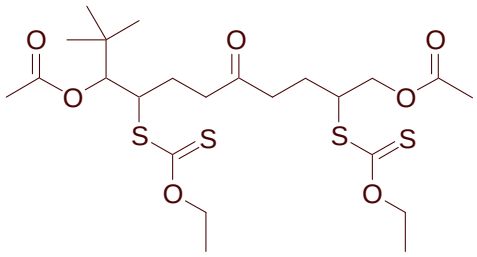


$C_{28}H_{40}O_7S_4$
Exact Mass: 616,17
Mol. Wt.: 616,88

^{1}H NMR (400 MHz), mixture of diastereomers

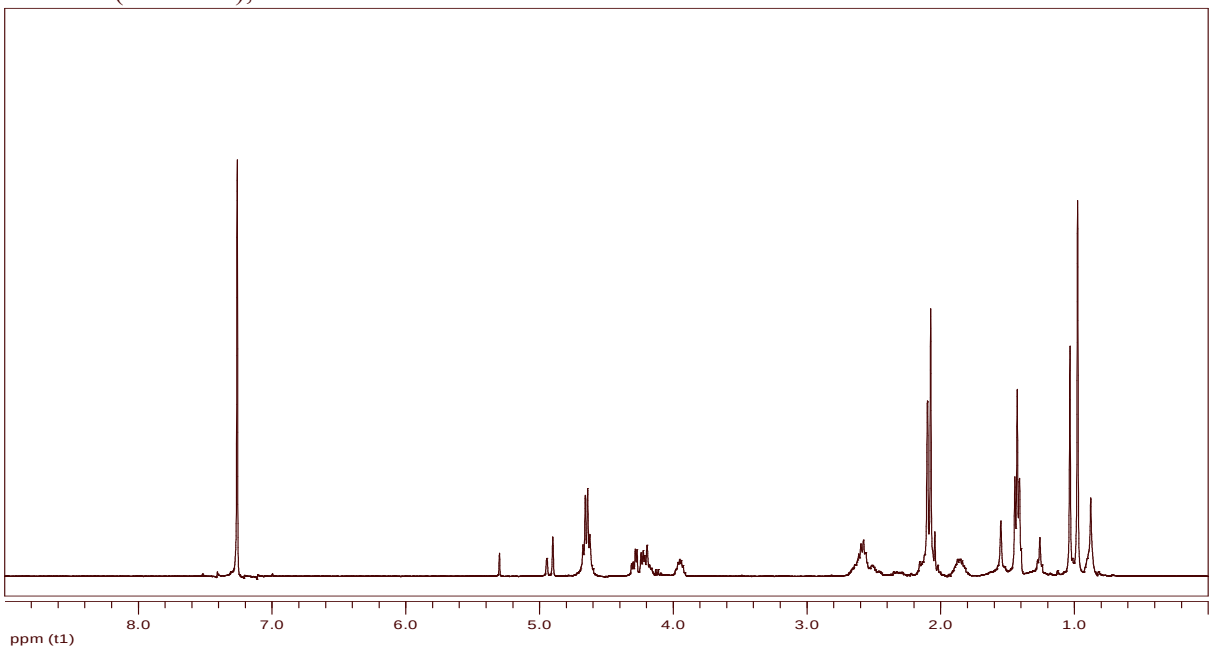


Acetic acid 9-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-10,10-dimethyl 5-oxo-undecyl ester (15d).

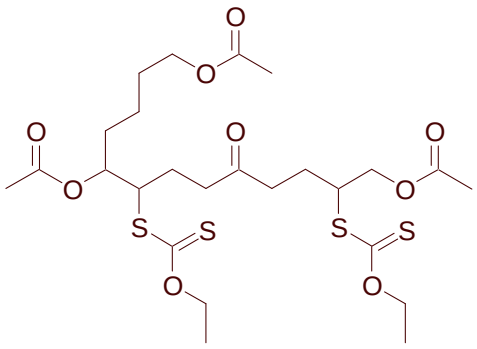


$C_{23}H_{38}O_7S_4$
Exact Mass: 554,15
Mol. Wt.: 554,81

^{1}H NMR (400 MHz), mixture of diastereomers

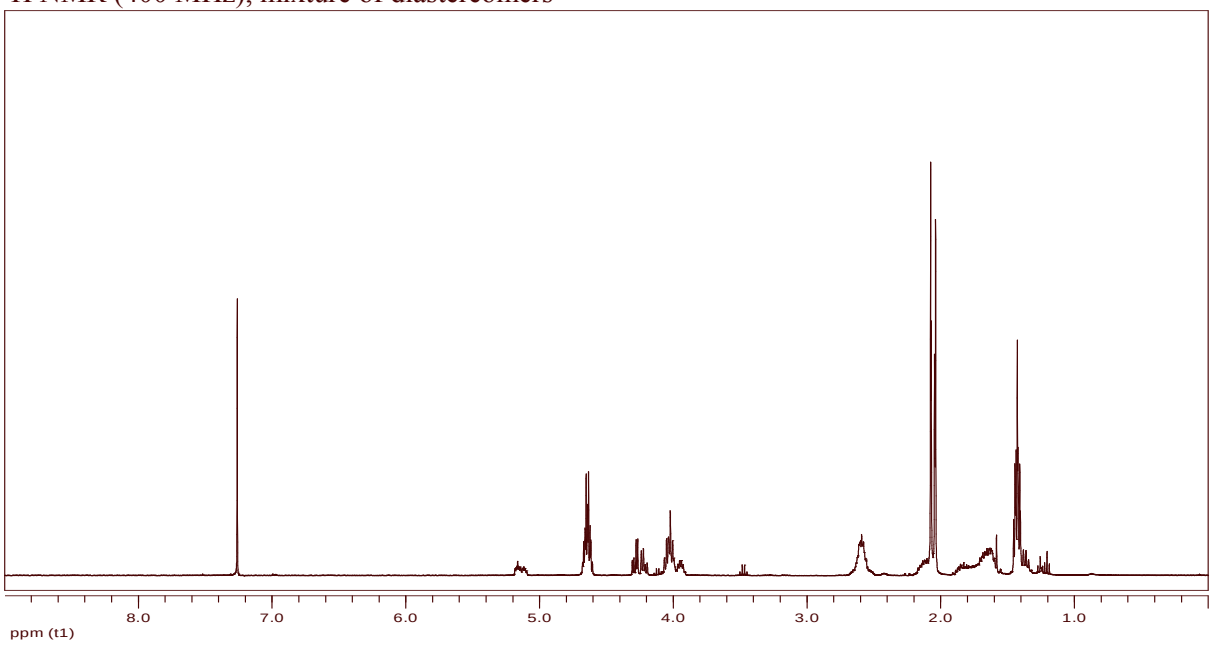


Acetic acid 9,13-diacetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo tridecyl ester (15e).

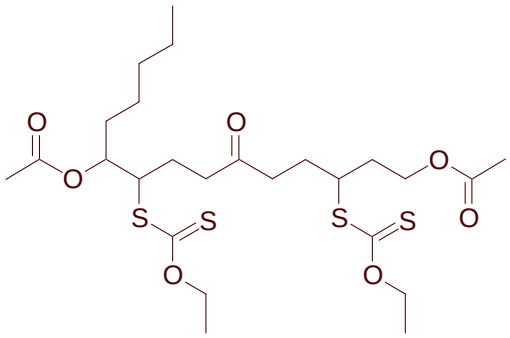


$C_{25}H_{40}O_9S_4$
Exact Mass: 612,16
Mol. Wt.: 612,84

^{1}H NMR (400 MHz), mixture of diastereomers

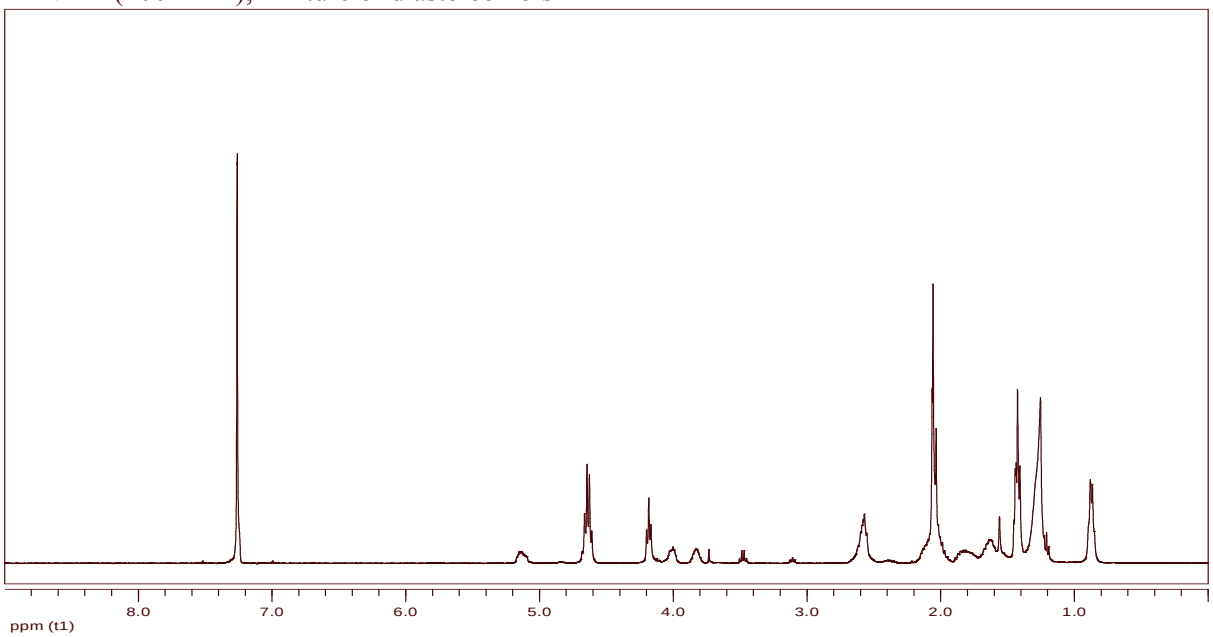


Acetic acid 10-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-decyl ester (15f).

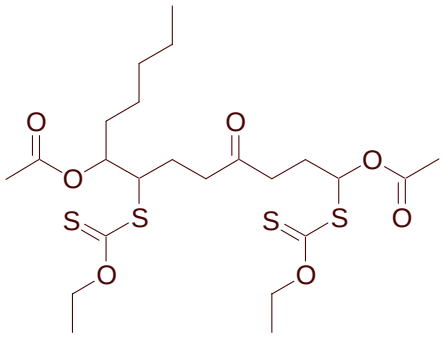


$C_{25}H_{42}O_7S_4$
Exact Mass: 582,18
Mol. Wt.: 582,86

^{1}H NMR (400 MHz), mixture of diastereomers

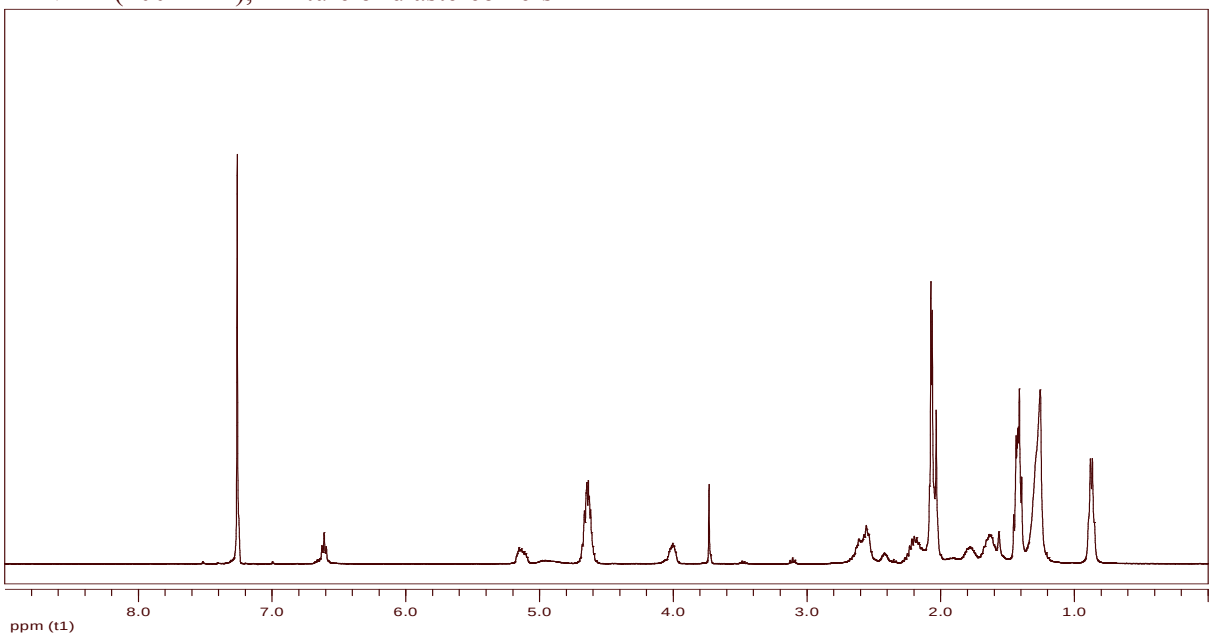


Acetic acid 8-acetoxy-2,8-bis-ethoxythiocarbonylsulfanyl-5-oxo-1-pentyl-octyl ester (15g).

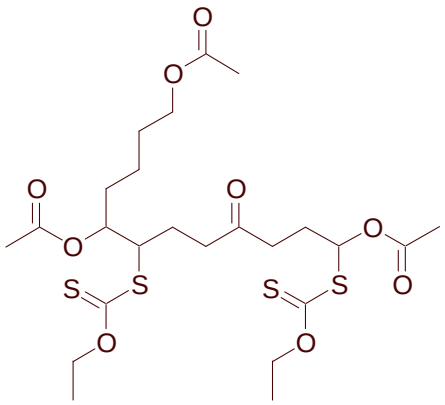


$C_{23}H_{38}O_7S_4$
Exact Mass: 554,15
Mol. Wt.: 554,81

^{1}H NMR (400 MHz), mixture of diastereomers

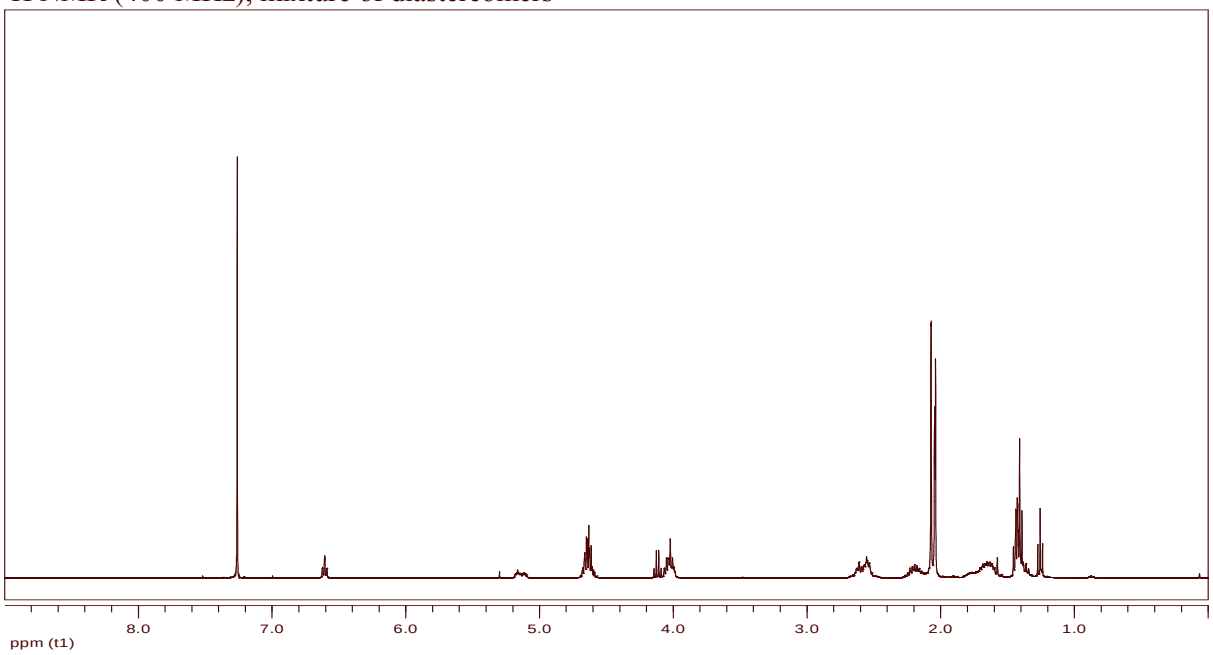


Acetic acid 8-acetoxy-1-(4-acetoxy-butyl)-2,8-bis-ethoxythiocarbonyl sulfanyl-5-oxo-octyl ester (15h).

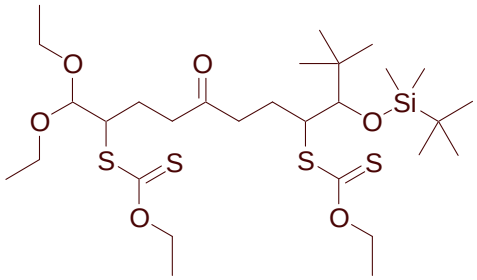


$C_{24}H_{38}O_9S_4$
Exact Mass: 598,14
Mol. Wt.: 598,82

^{1}H NMR (400 MHz), mixture of diastereomers

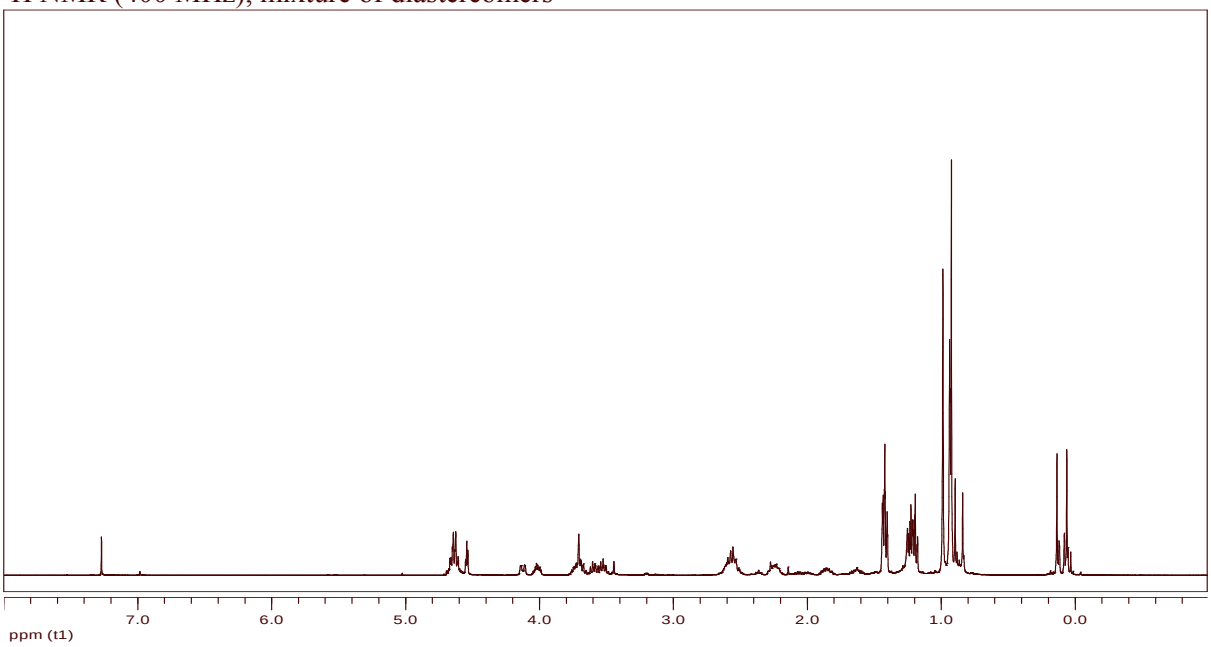


Dithiocarbonic acid {1-[1-(*tert*-butyl-dimethyl-silanyloxy)-2,2-dimethyl-propyl]-8,8-diethoxy-7-ethoxythiocarbonylsulfanyl-4-oxo-octyl} ester ethyl ester (15i).

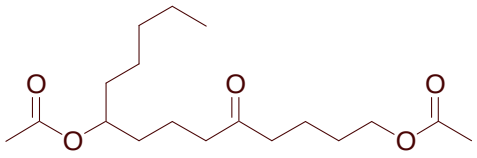


$C_{29}H_{56}O_6S_4Si$
Exact Mass: 656,27
Mol. Wt.: 657,10

^{1}H NMR (400 MHz), mixture of diastereomers

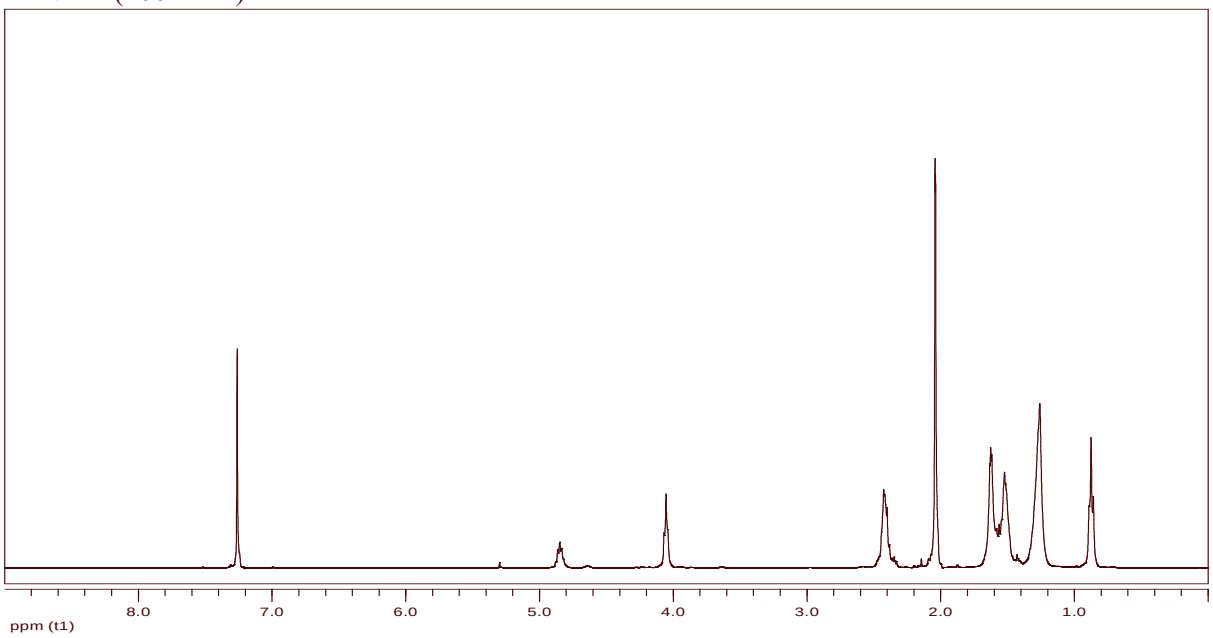


Acetic acid 9-acetoxy-5-oxo-tetradecyl ester (16a).

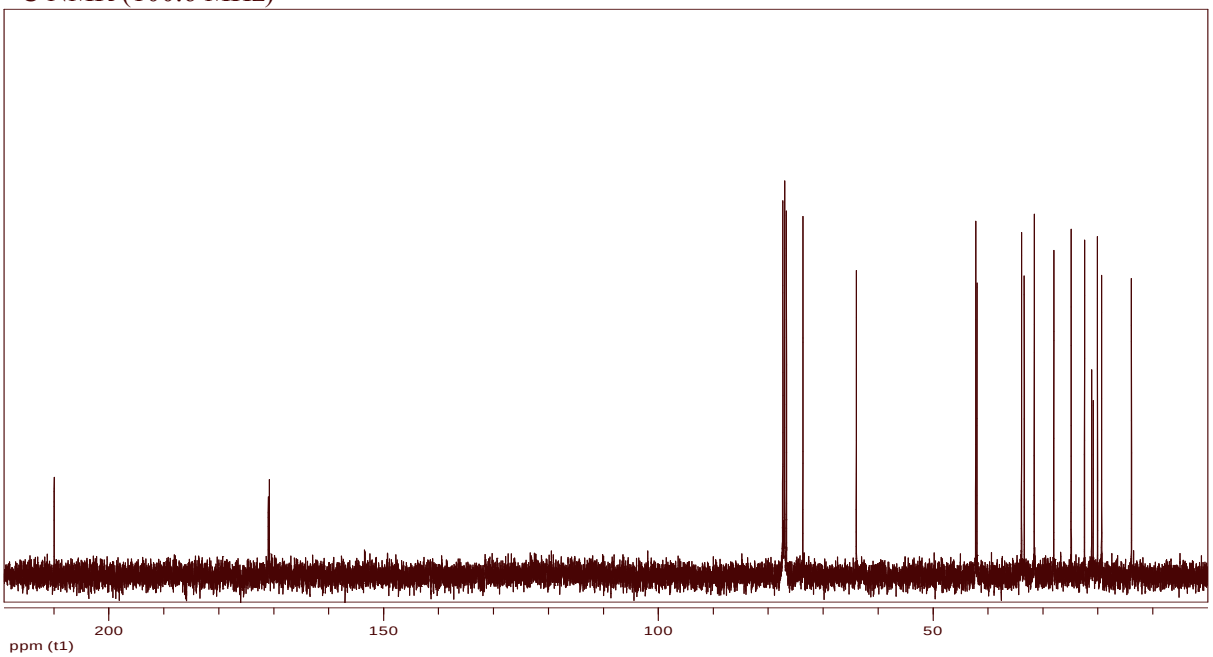


$C_{18}H_{32}O_5$
Exact Mass: 328,22
Mol. Wt.: 328,44

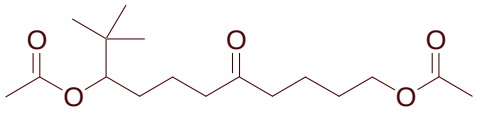
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

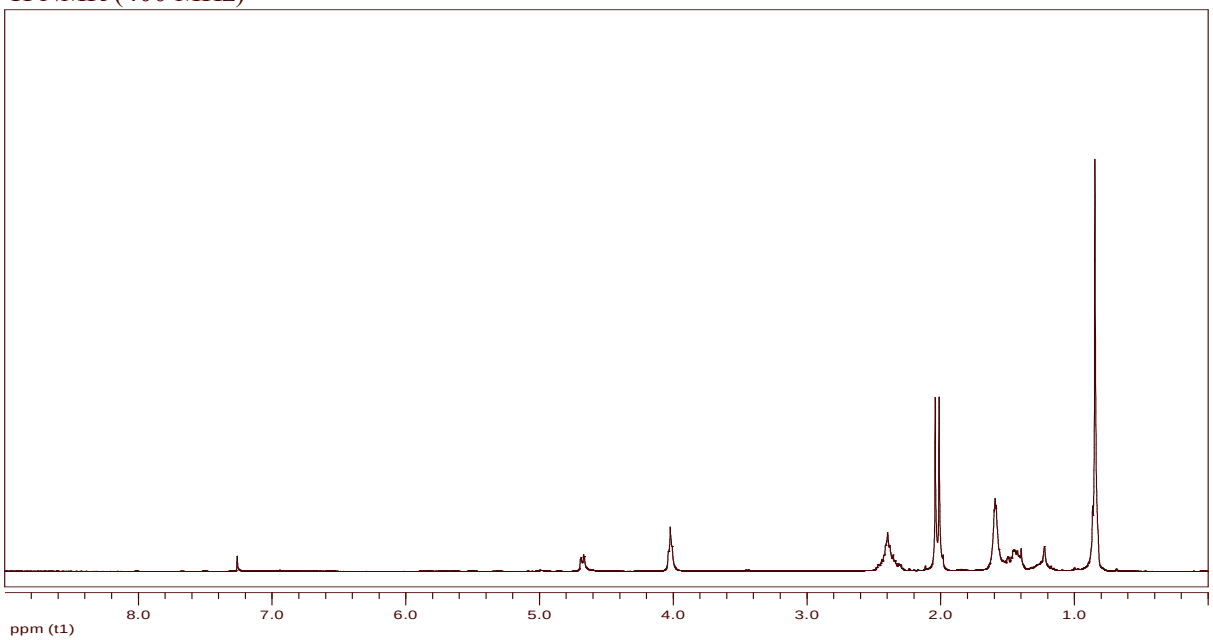


Acetic acid 9-acetoxy-1-*tert*-butyl-5-oxo-nonyl ester (16d).

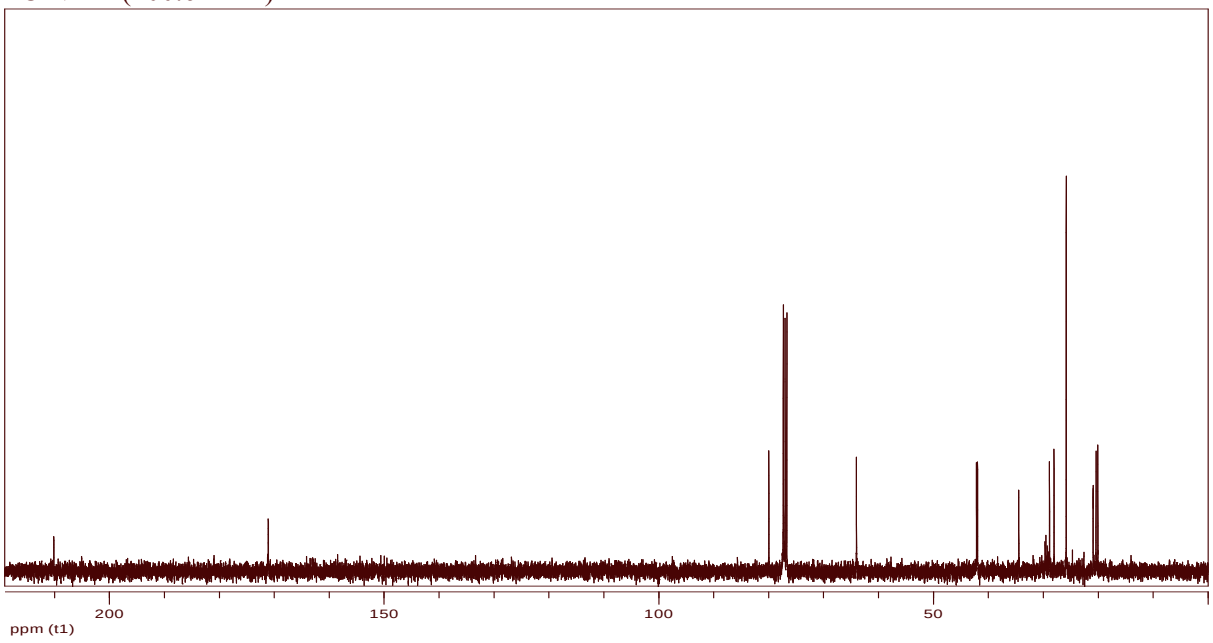


$C_{17}H_{30}O_5$
Exact Mass: 314,21
Mol. Wt.: 314,42

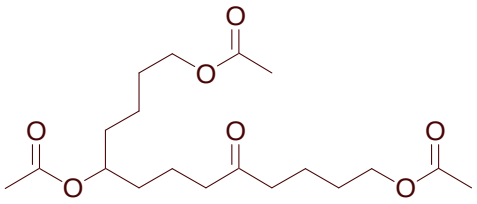
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

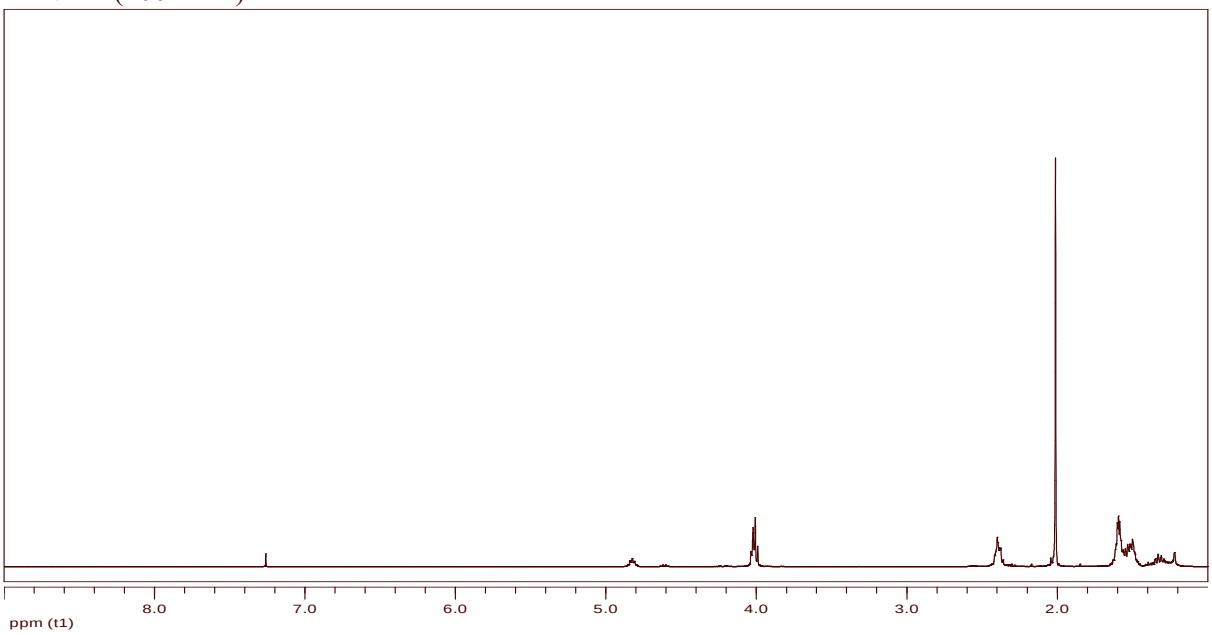


Acetic acid 9,13-diacetoxy-5-oxo-tridecyl ester (16e).

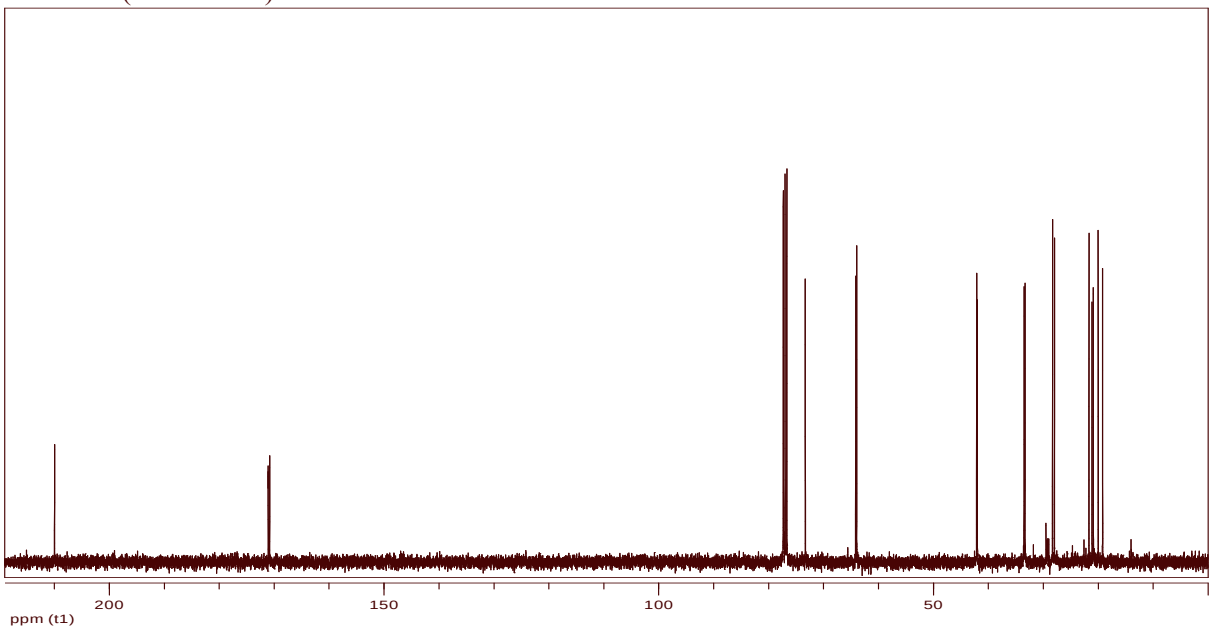


$C_{19}H_{32}O_7$
Exact Mass: 372,21
Mol. Wt.: 372,45

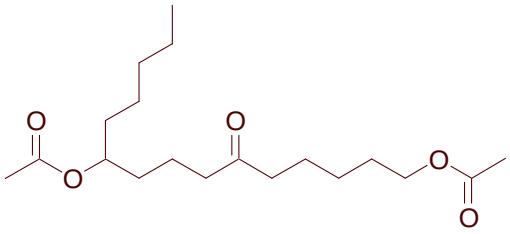
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

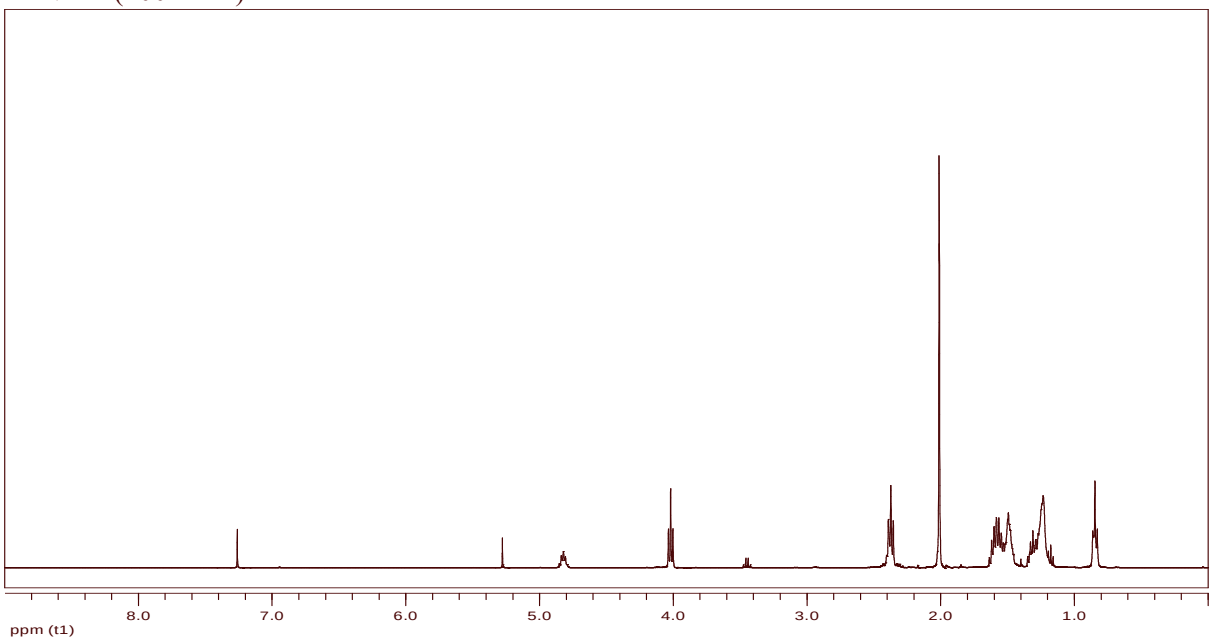


Acetic acid 10-acetoxy-5-oxo-1-pentyl-decyl ester (16f).

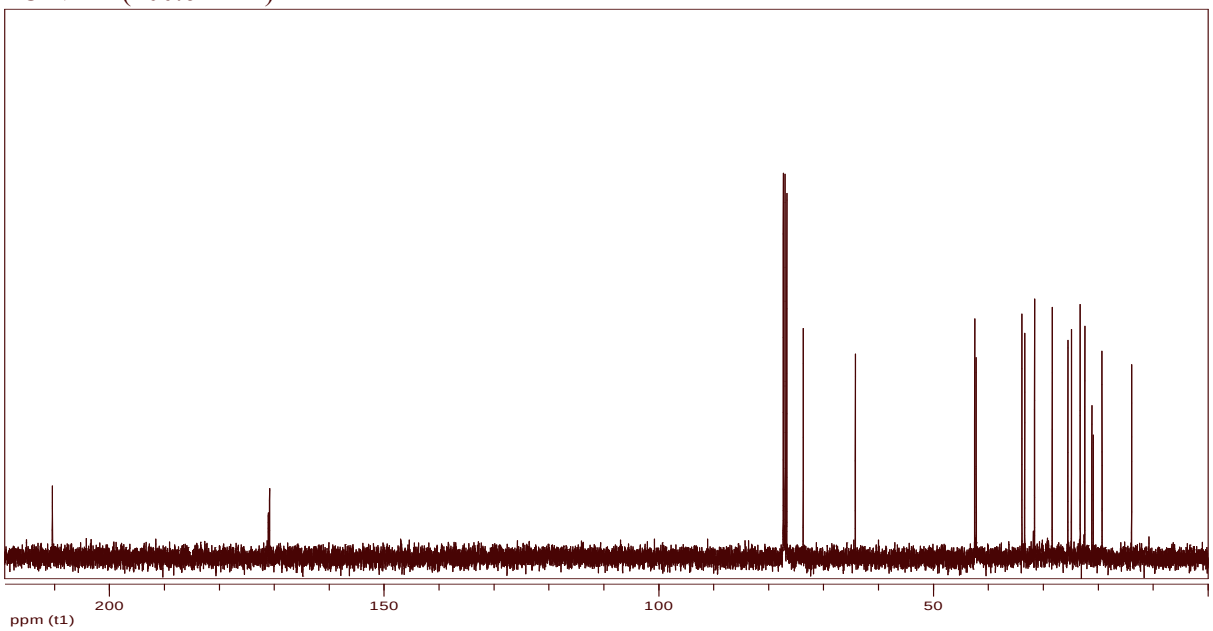


$C_{19}H_{34}O_5$
Exact Mass: 342,24
Mol. Wt.: 342,47

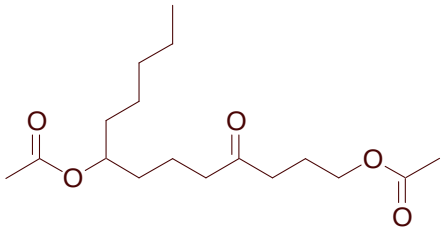
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

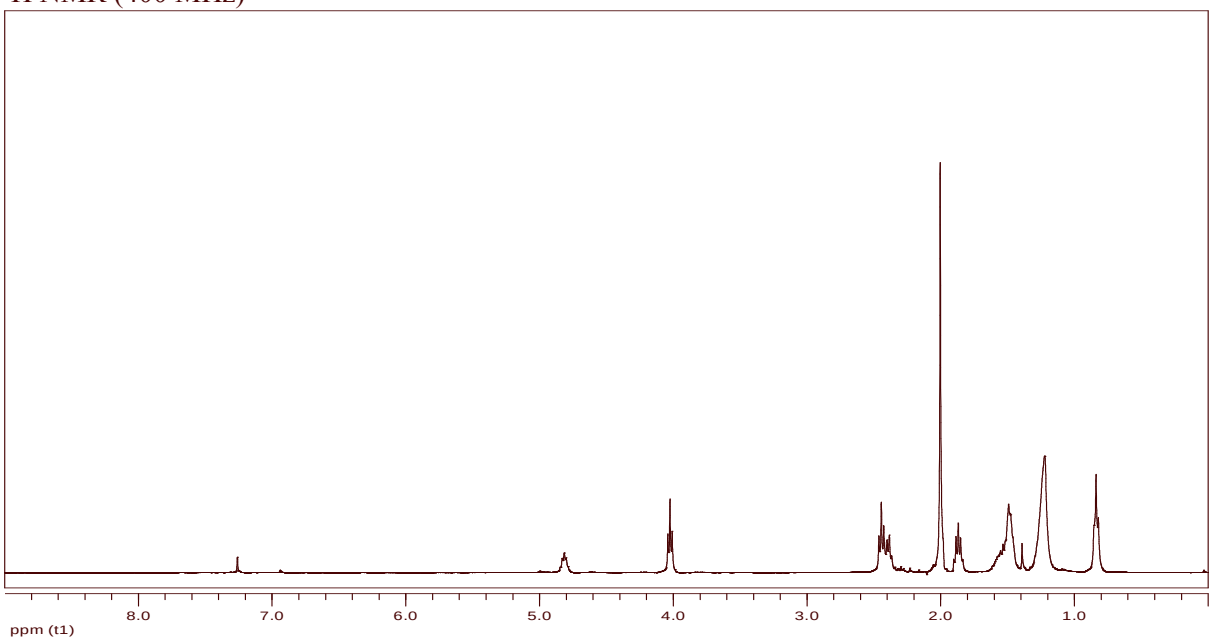


Synthesis of Acetic acid 8-acetoxy-4-oxo-tridecyl ester (16g).

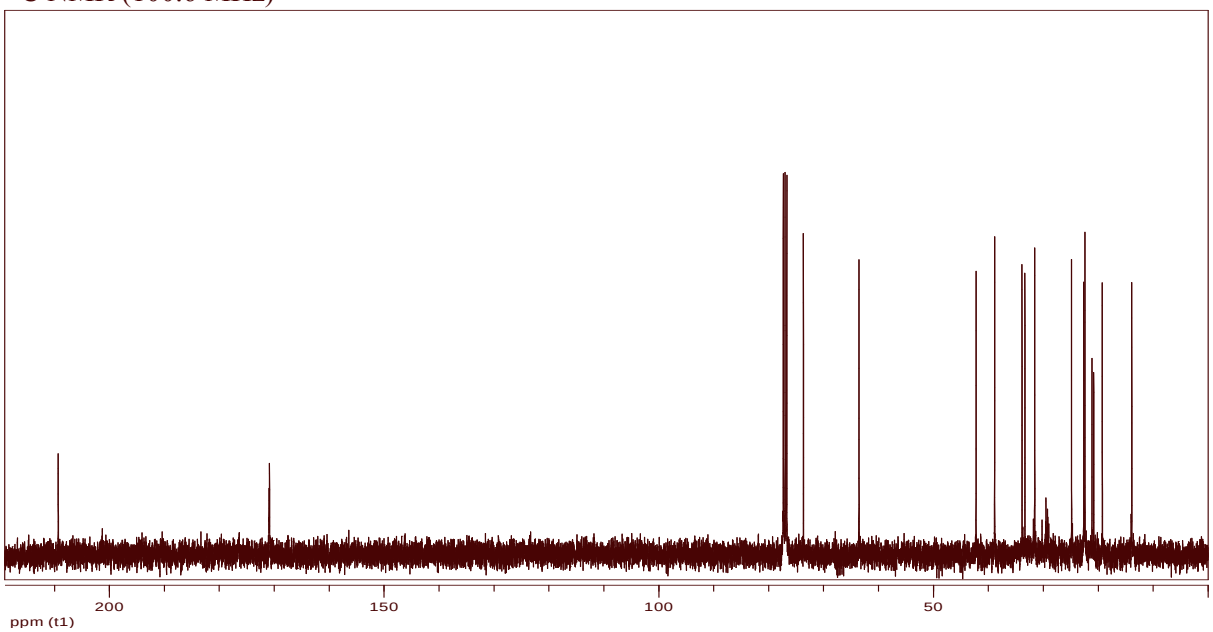


$C_{17}H_{30}O_5$
Exact Mass: 314,21
Mol. Wt.: 314,42

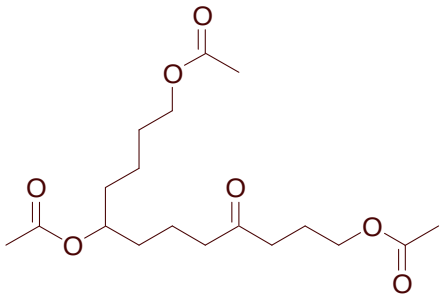
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

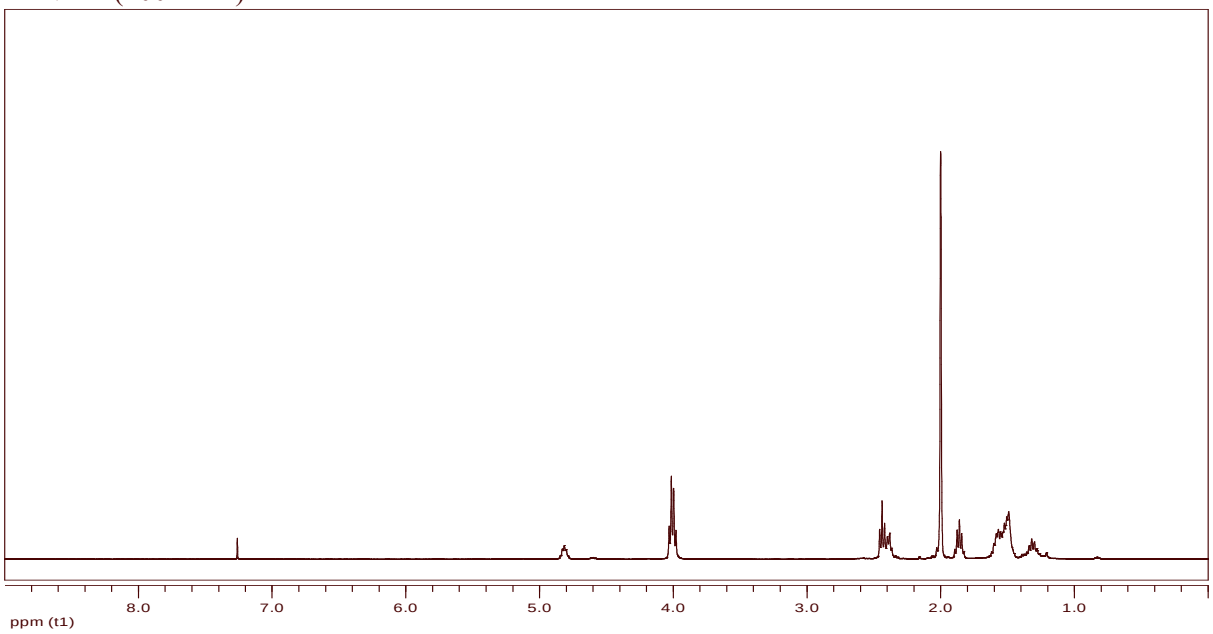


Acetic acid 8-acetoxy-1-(4-acetoxy-butyl)-5-oxo-octyl ester (16h).

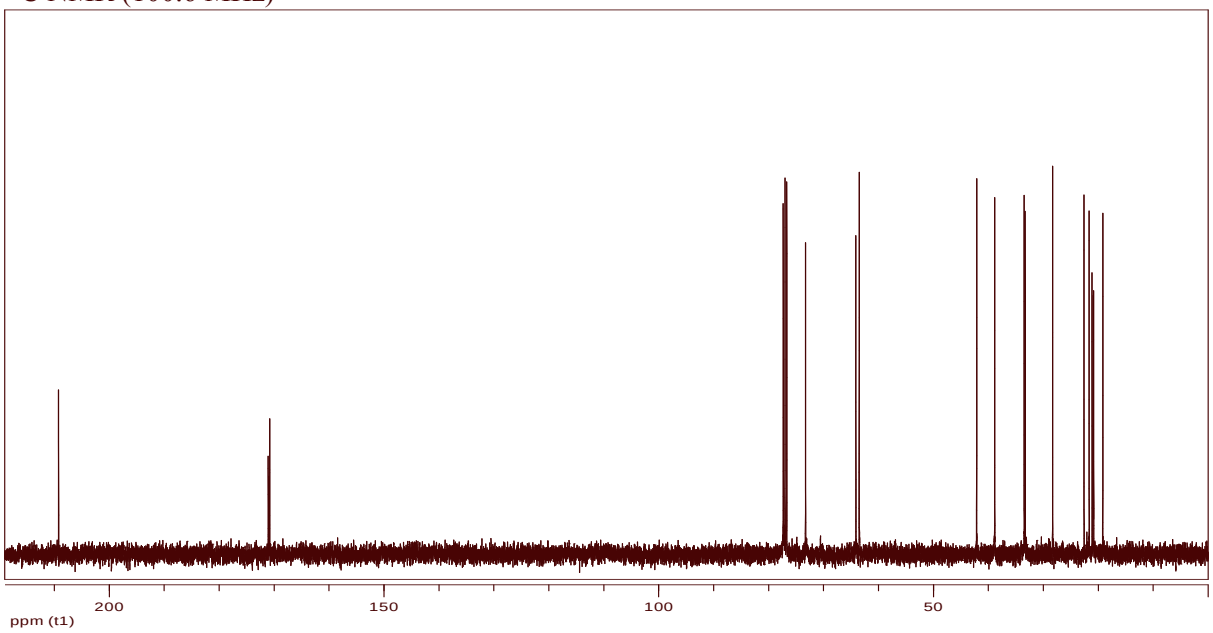


$C_{18}H_{30}O_7$
Exact Mass: 358,20
Mol. Wt.: 358,43

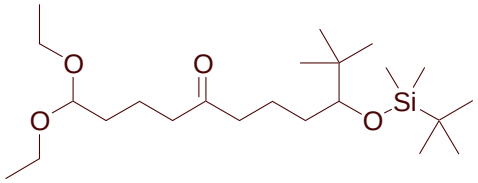
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

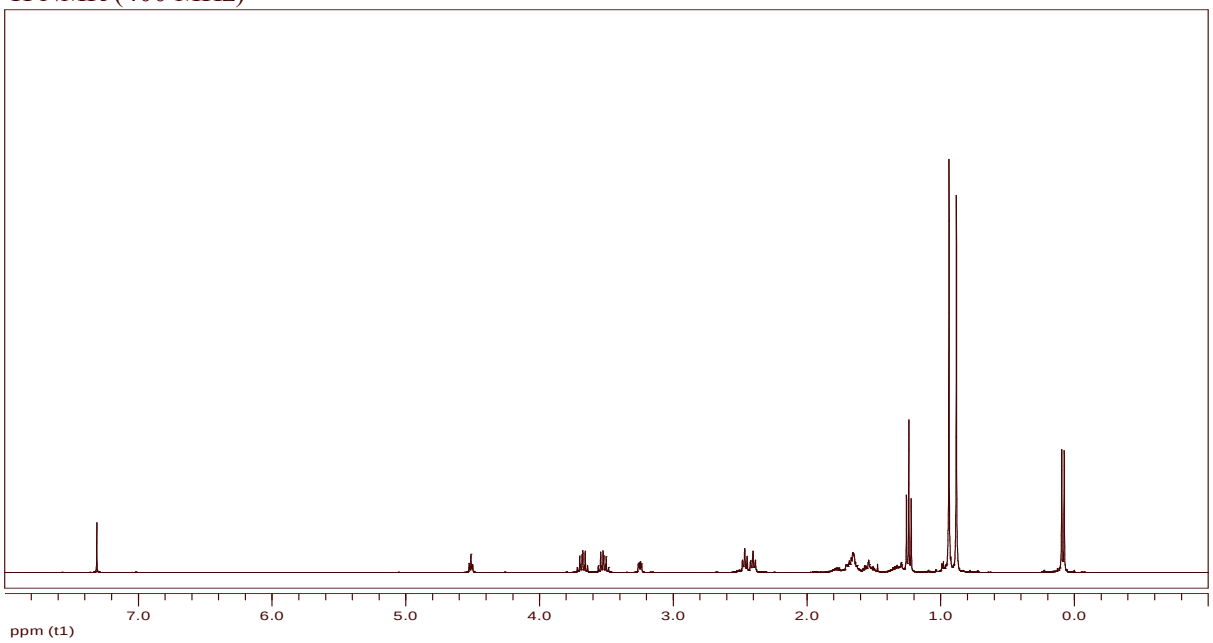


9-(*tert*-Butyl-dimethyl-silanyloxy)-1,1-diethoxy-10,10-dimethyl-undecan-5-one (16i).

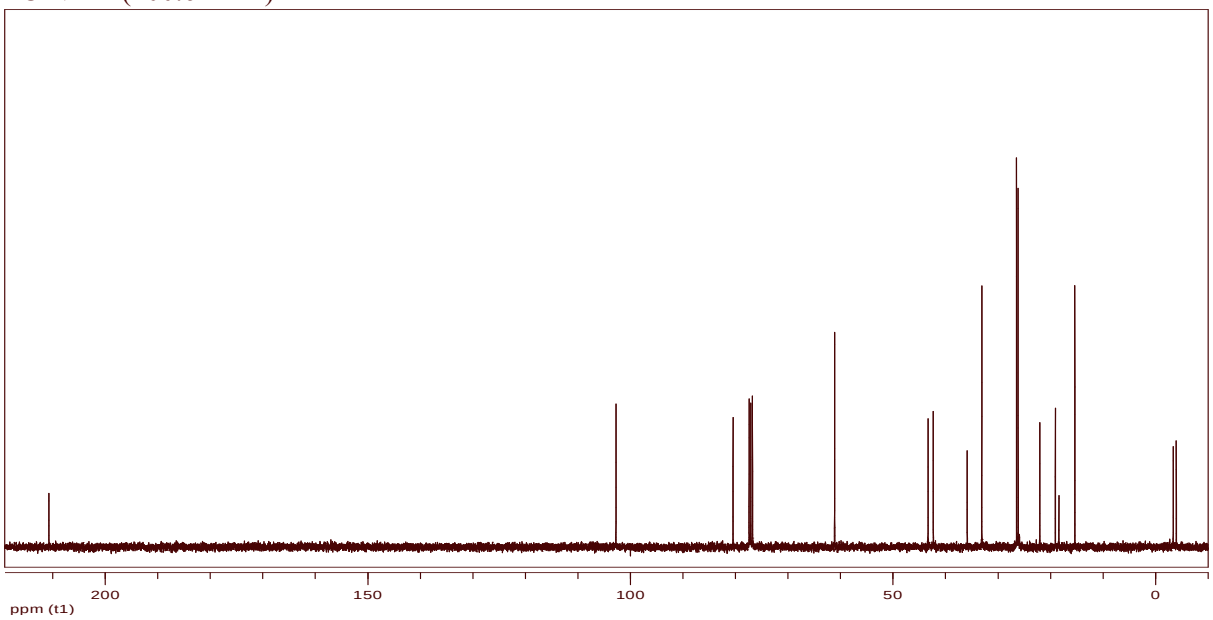


$C_{23}H_{48}O_4Si$
Exact Mass: 416,33
Mol. Wt.: 416,71

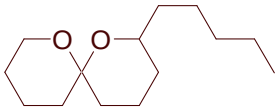
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

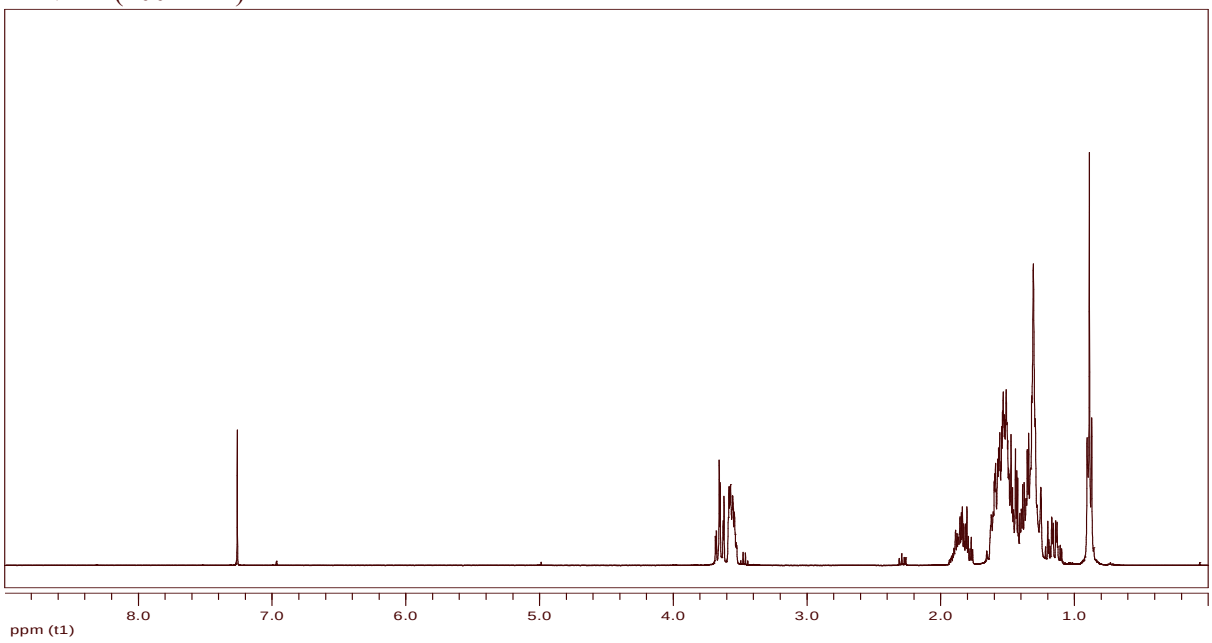


2-Pentyl-1,7-dioxa-spiro[5.5]undecane (17a).

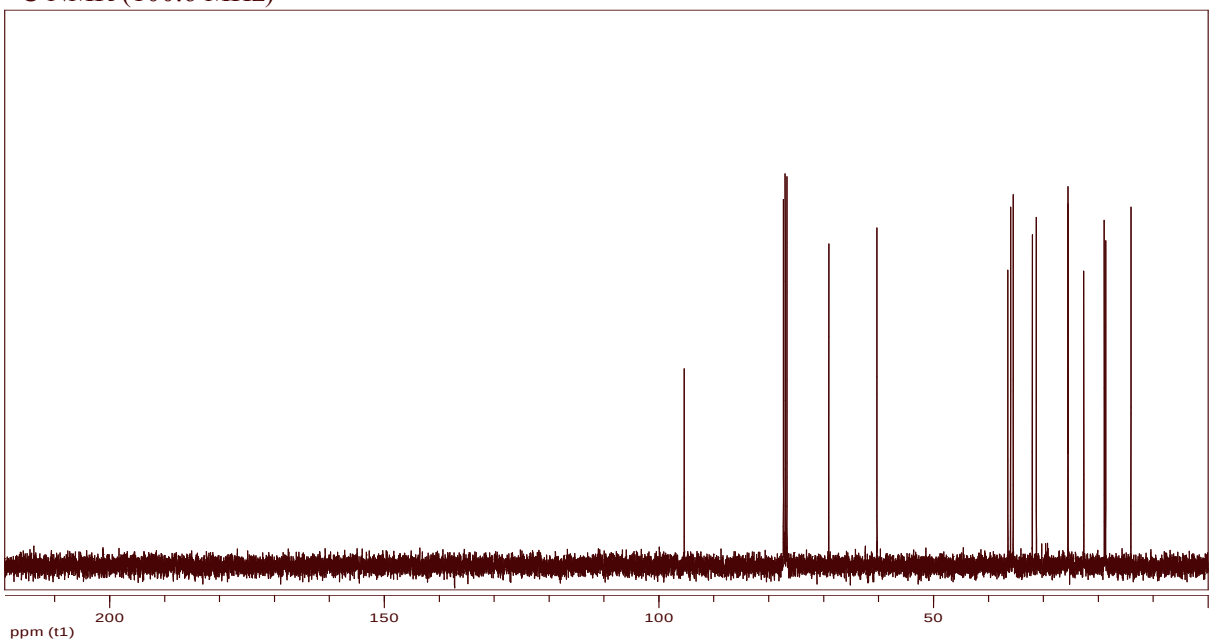


$C_{14}H_{26}O_2$
Exact Mass: 226,19
Mol. Wt.: 226,36

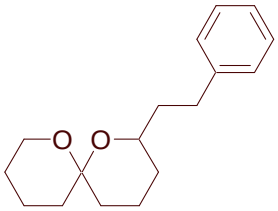
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

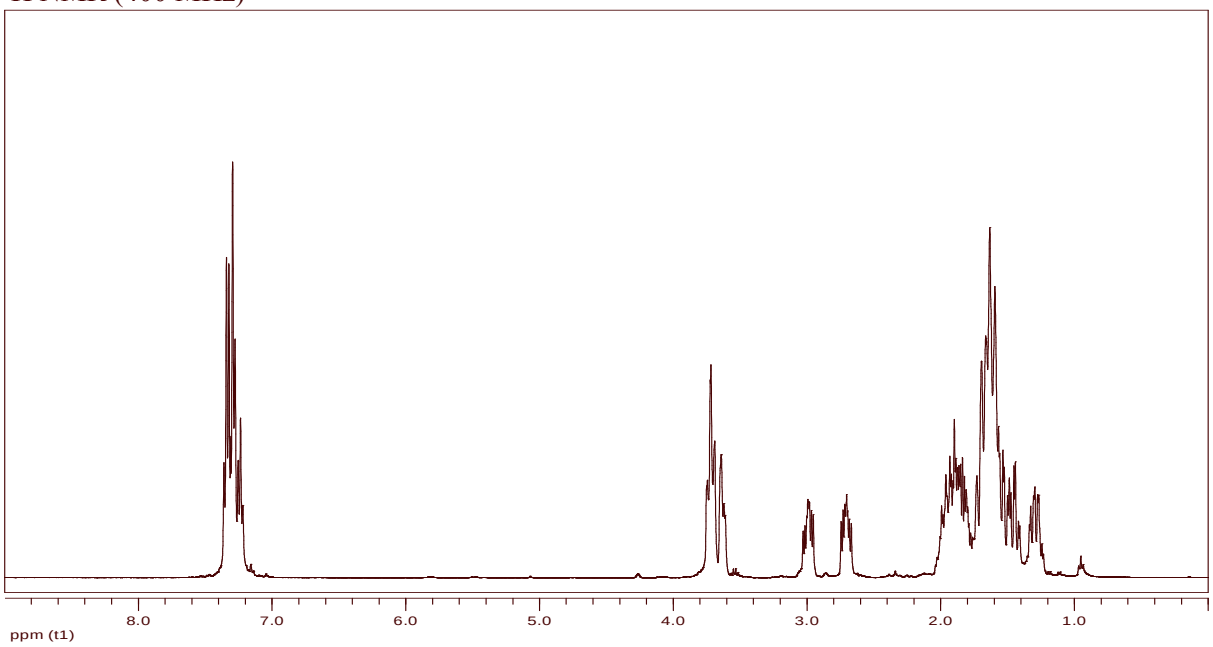


2-Phenethyl-1,7-dioxa-spiro[5.5]undecane (17b).

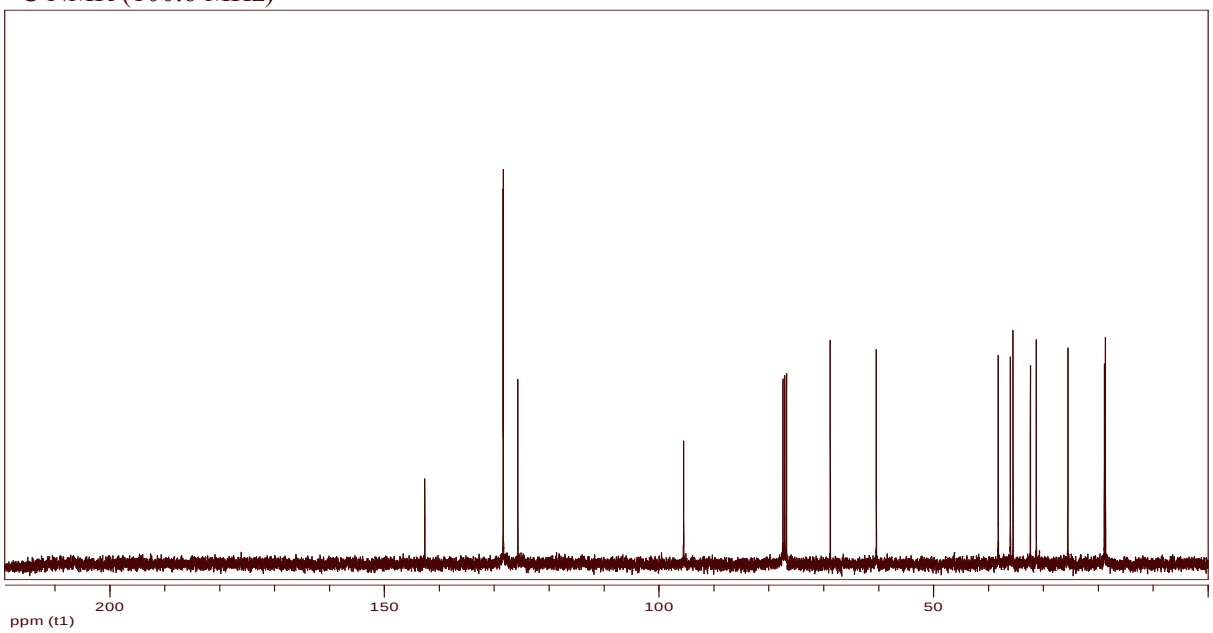


$C_{17}H_{24}O_2$
Exact Mass: 260,18
Mol. Wt.: 260,37

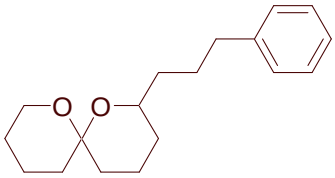
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

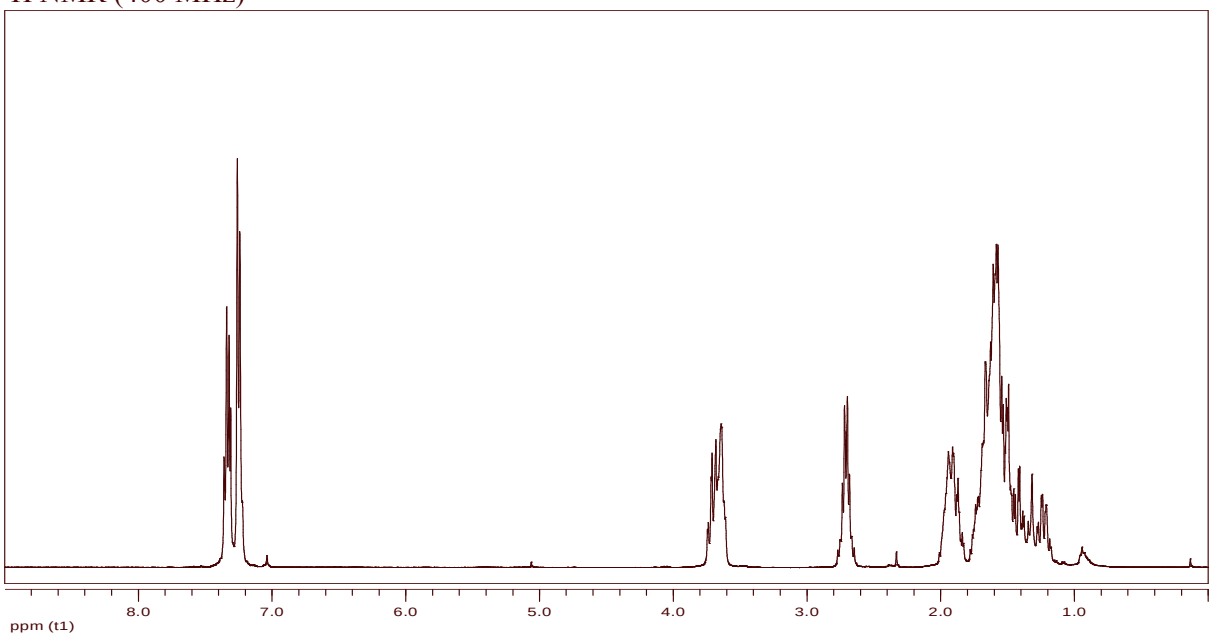


2-(3-Phenyl-propyl)-1,7-dioxa-spiro[5.5]undecane (17c).

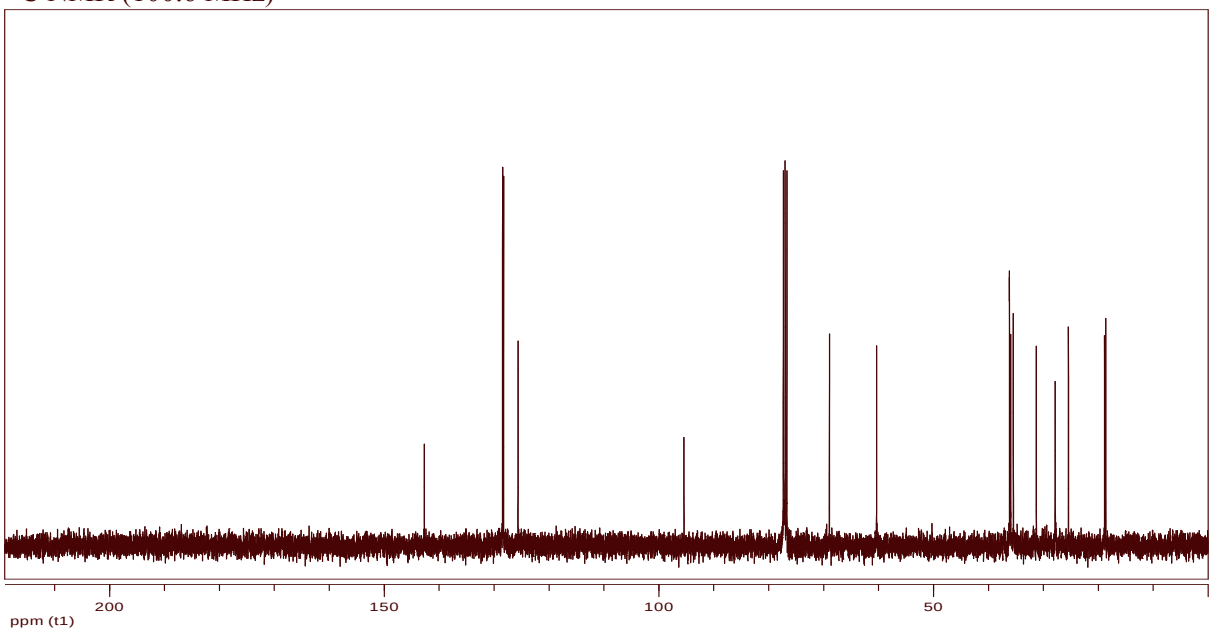


$C_{18}H_{26}O_2$
Exact Mass: 274,19
Mol. Wt.: 274,40

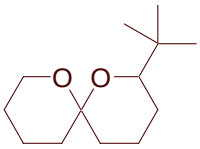
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

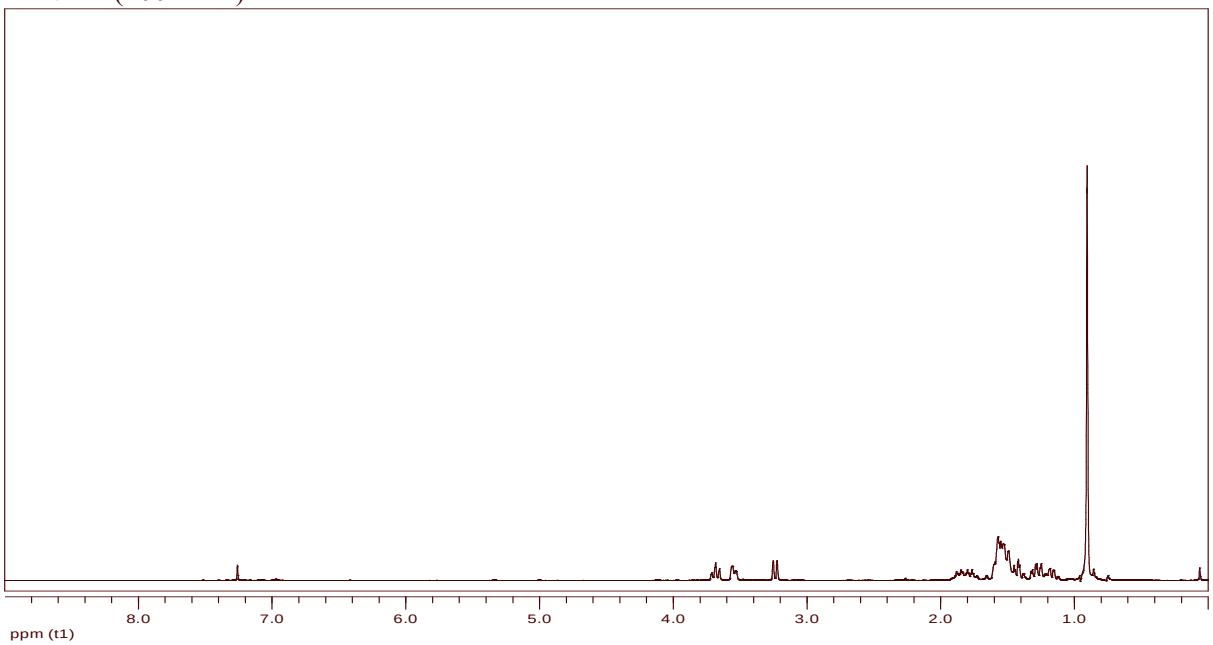


2-*tert*-Butyl-1,7-dioxa-spiro[5.5]undecane (17d).

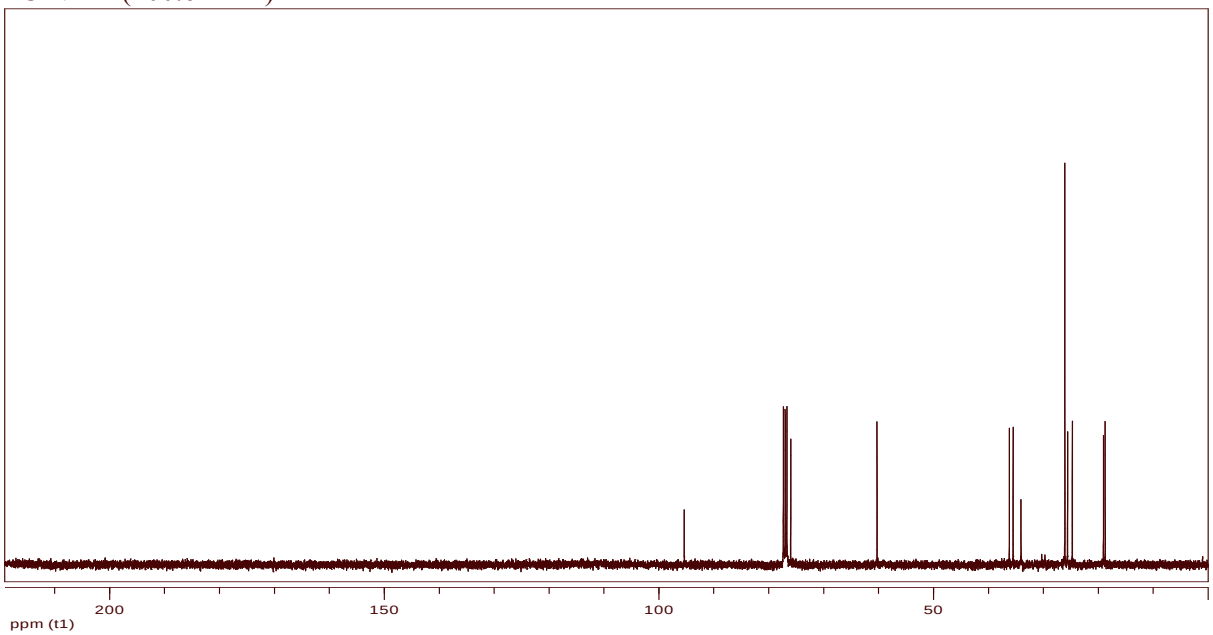


$C_{13}H_{24}O_2$
Exact Mass: 212,18
Mol. Wt.: 212,33

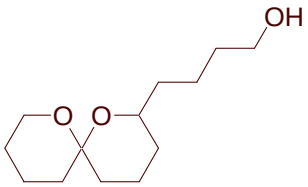
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

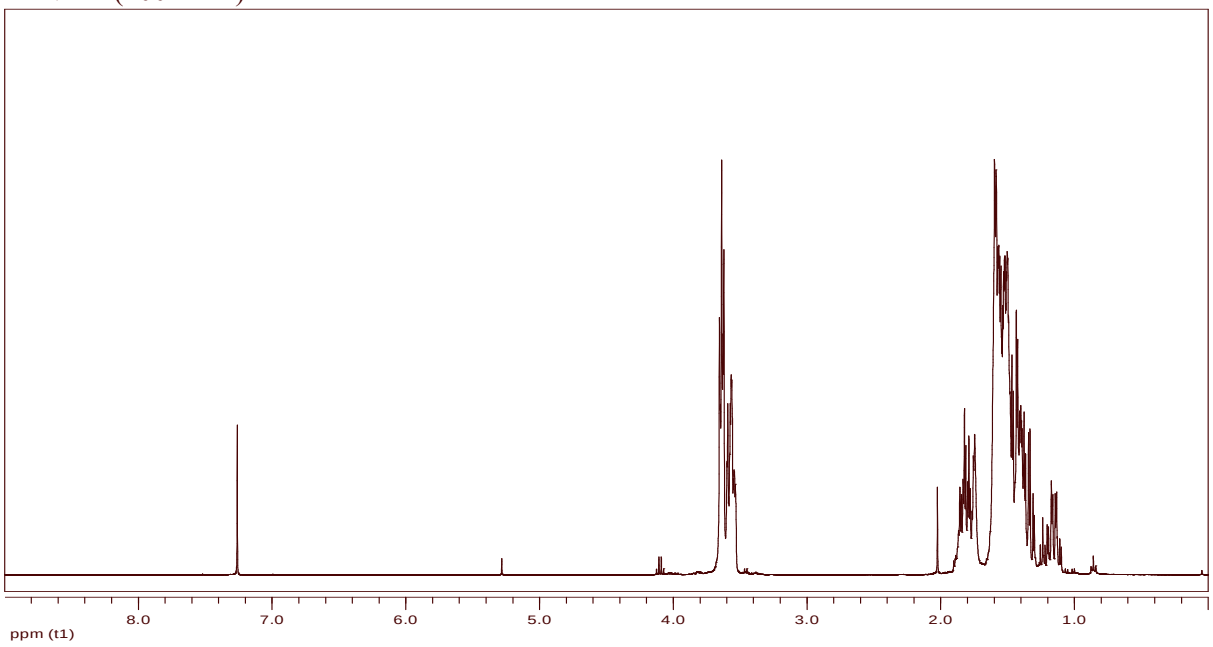


4-(1,7-Dioxa-spiro[5.5]undec-2-yl)-butan-1-ol (17e).[5]

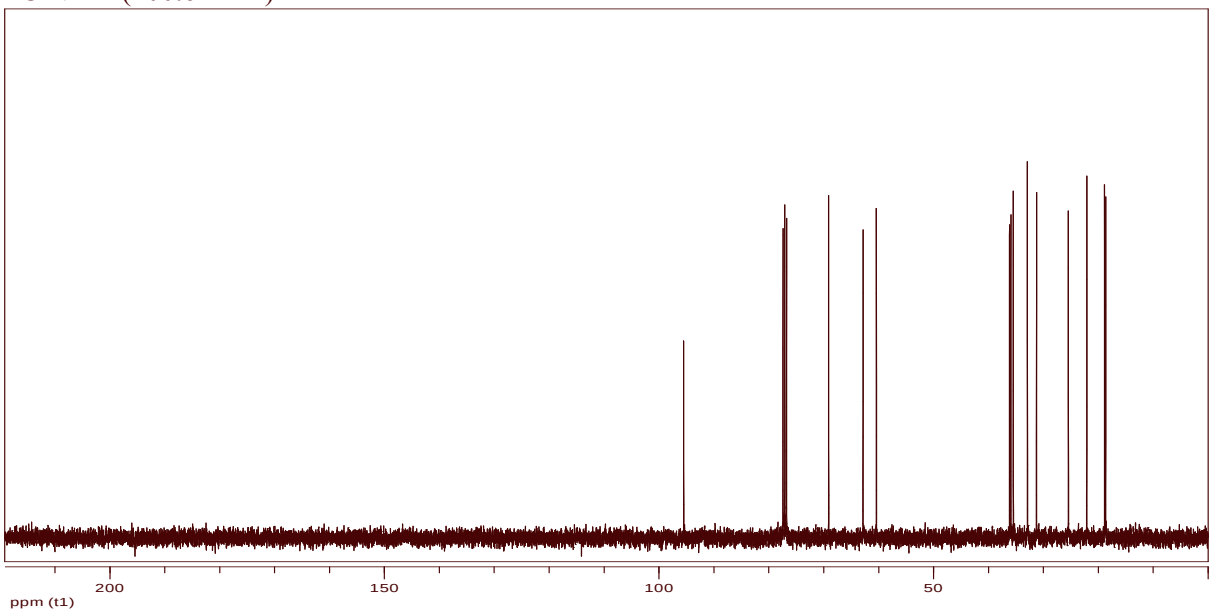


$C_{13}H_{24}O_3$
Exact Mass: 228,17
Mol. Wt.: 228,33

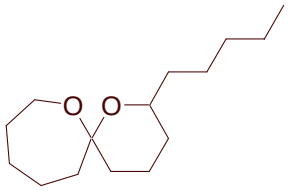
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

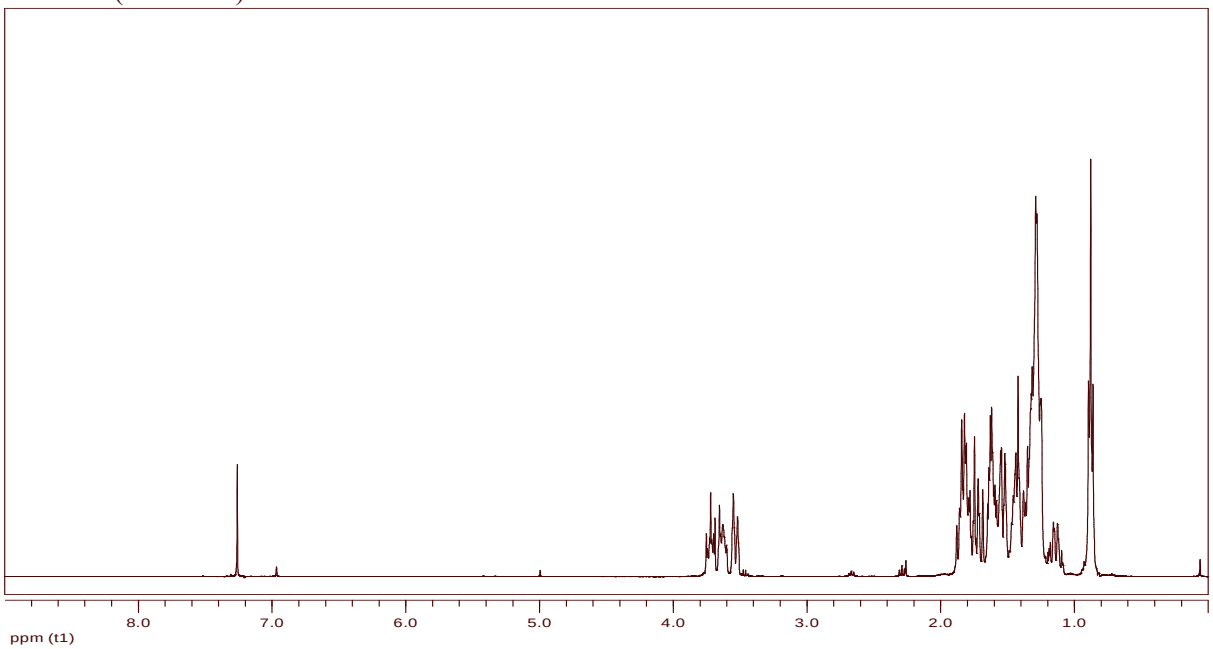


2-Pentyl-1,7-dioxa-spiro[5.6]dodecane (17f).

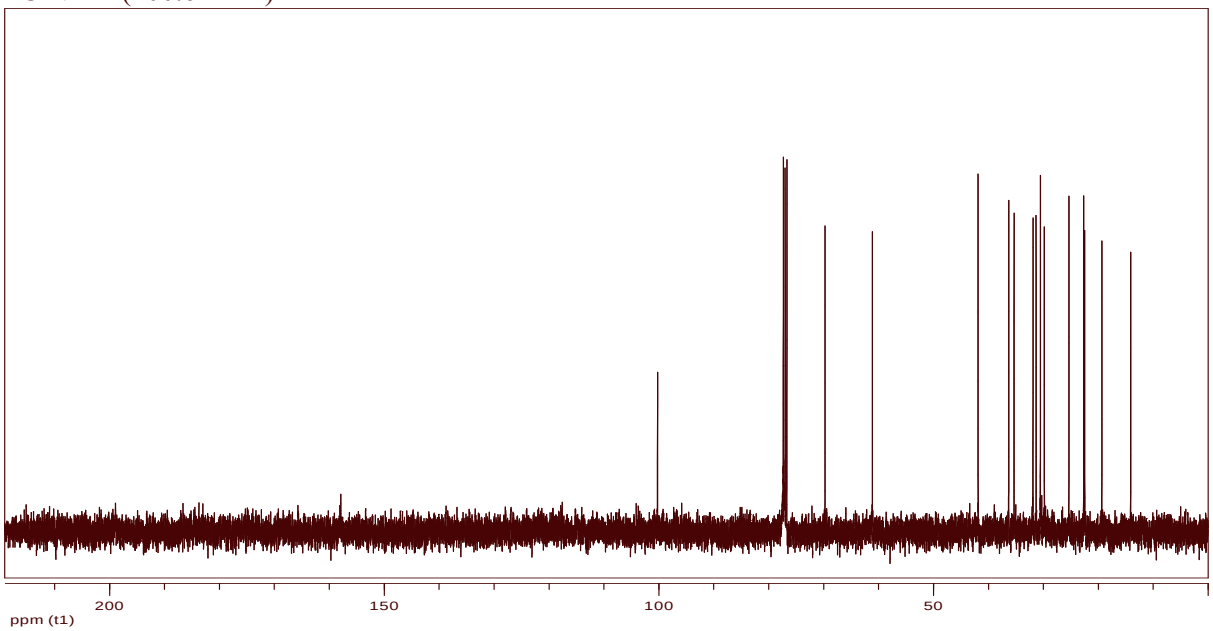


$C_{15}H_{28}O_2$
Exact Mass: 240,21
Mol. Wt.: 240,38

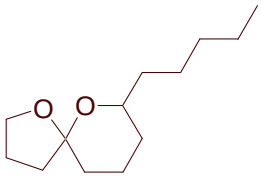
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

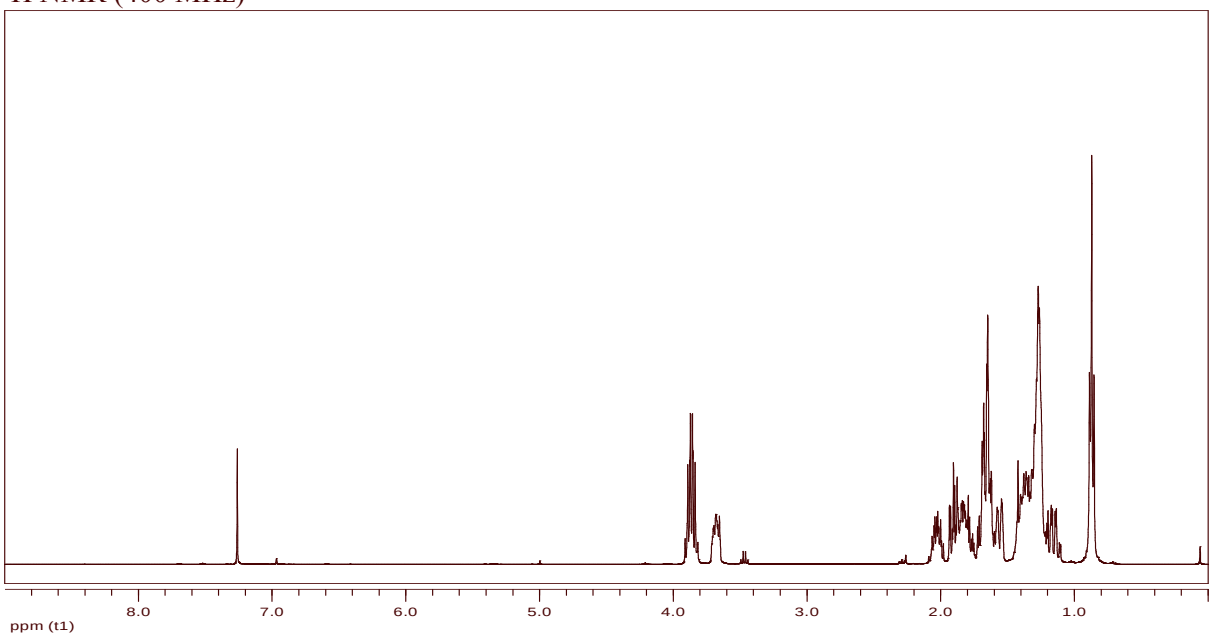


7-Pentyl-1,6-dioxa-spiro[4.5]decane (17g).

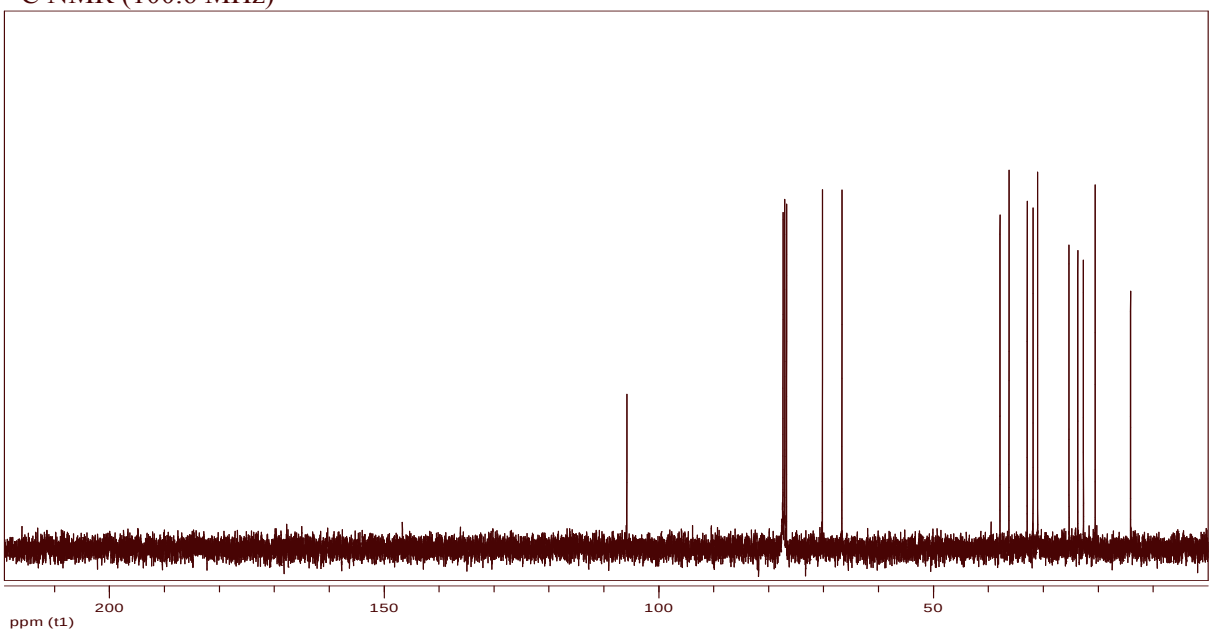


$C_{13}H_{24}O_2$
Exact Mass: 212,18
Mol. Wt.: 212,33

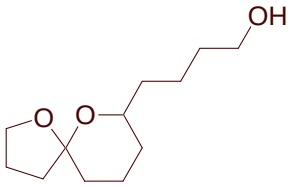
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

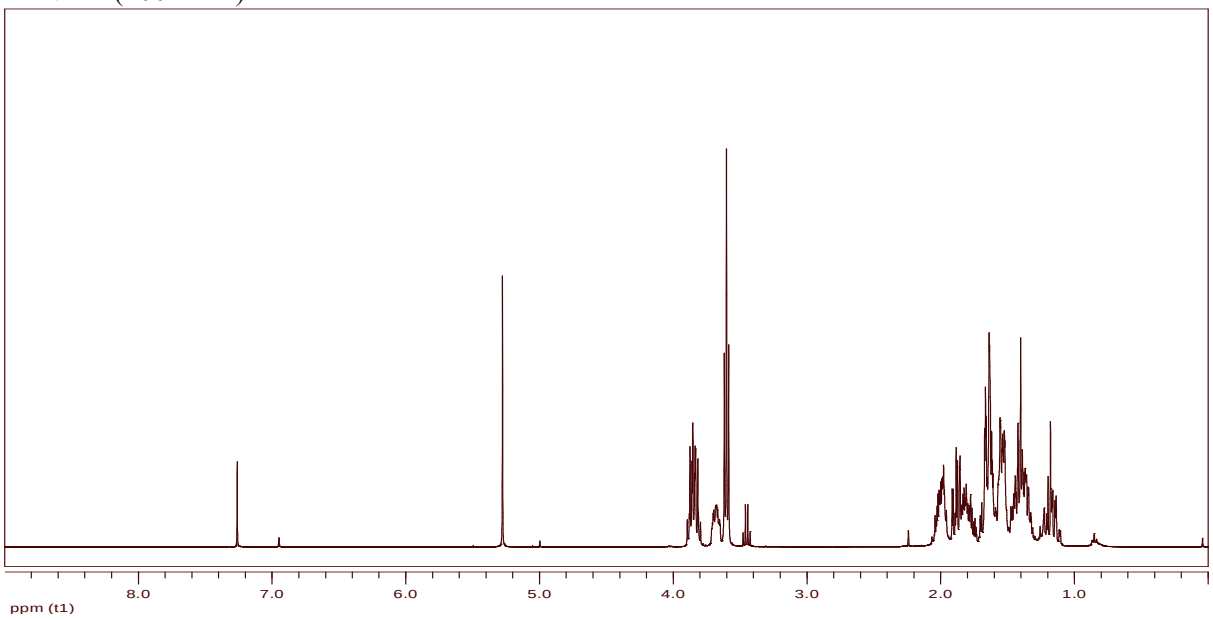


4-(1,6-Dioxa-spiro[4.5]dec-7-yl)-butan-1-ol (17h).

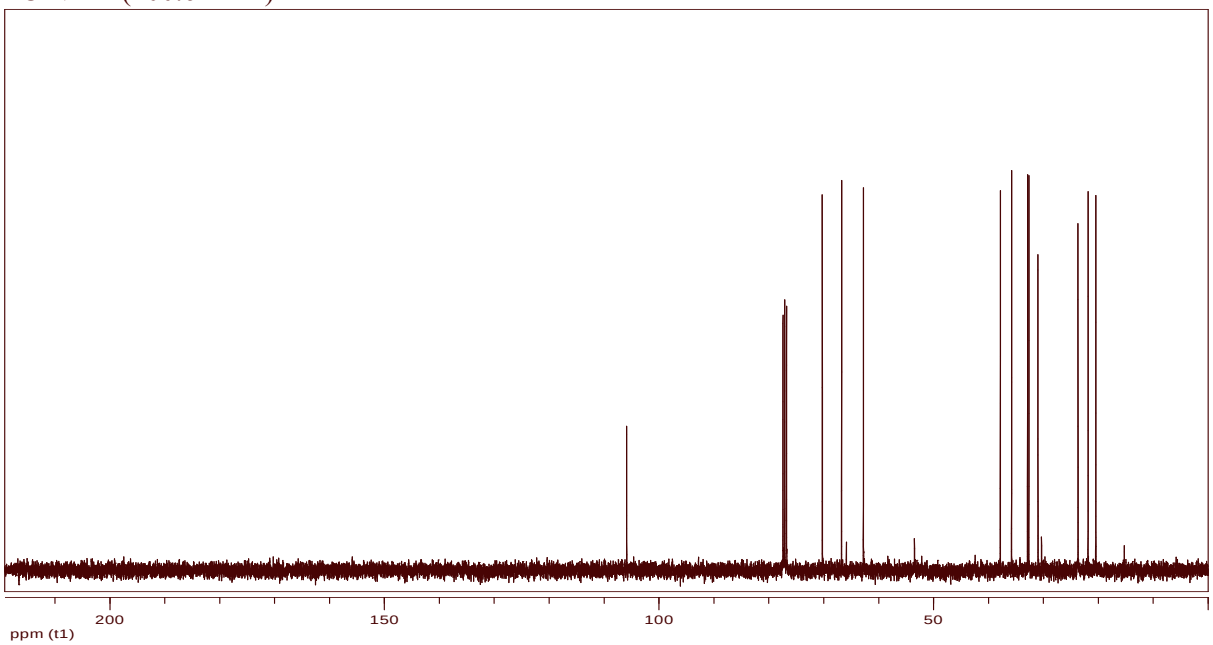


$C_{12}H_{22}O_3$
Exact Mass: 214,16
Mol. Wt.: 214,30

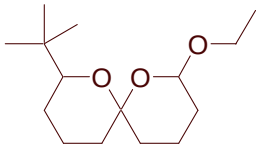
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

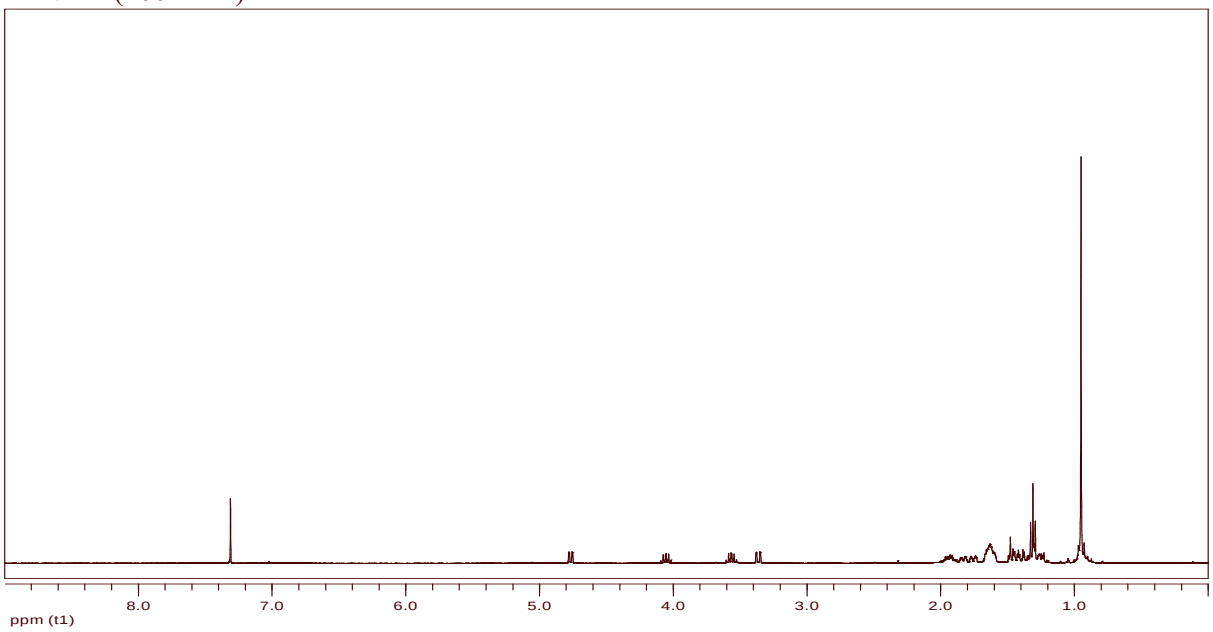


2-*tert*-Butyl-8-ethoxy-1,7-dioxa-spiro[5.5]undecane (17i).

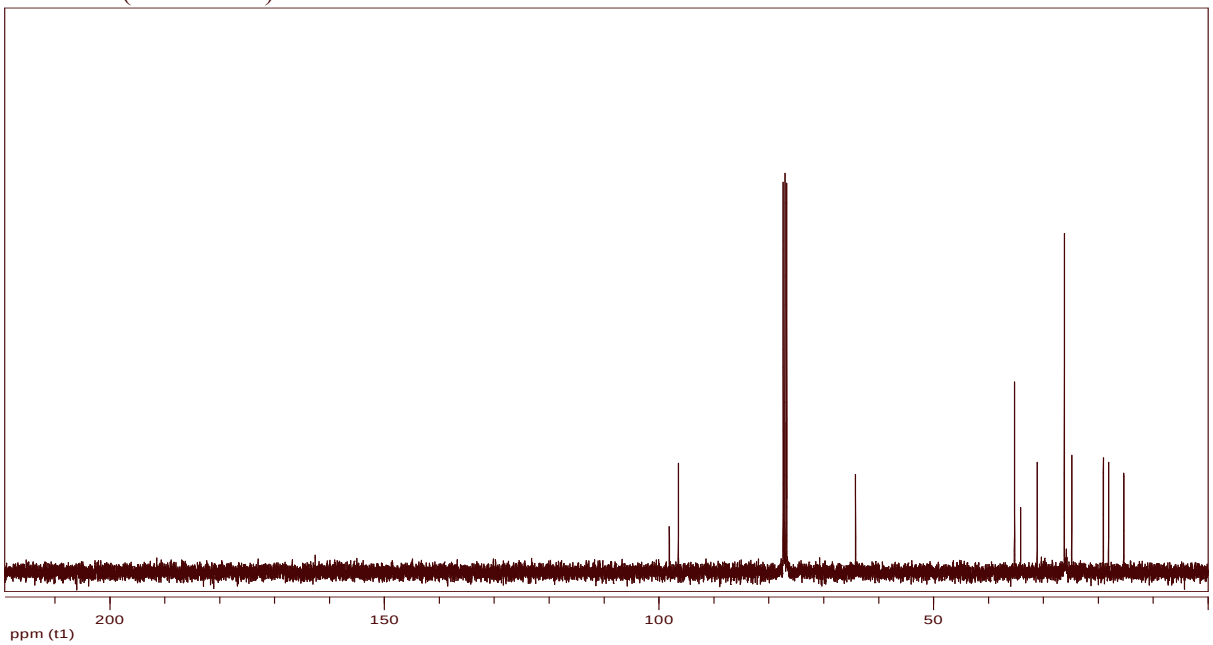


$C_{15}H_{28}O_3$
Exact Mass: 256,20
Mol. Wt.: 256,38

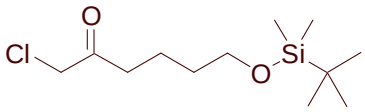
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

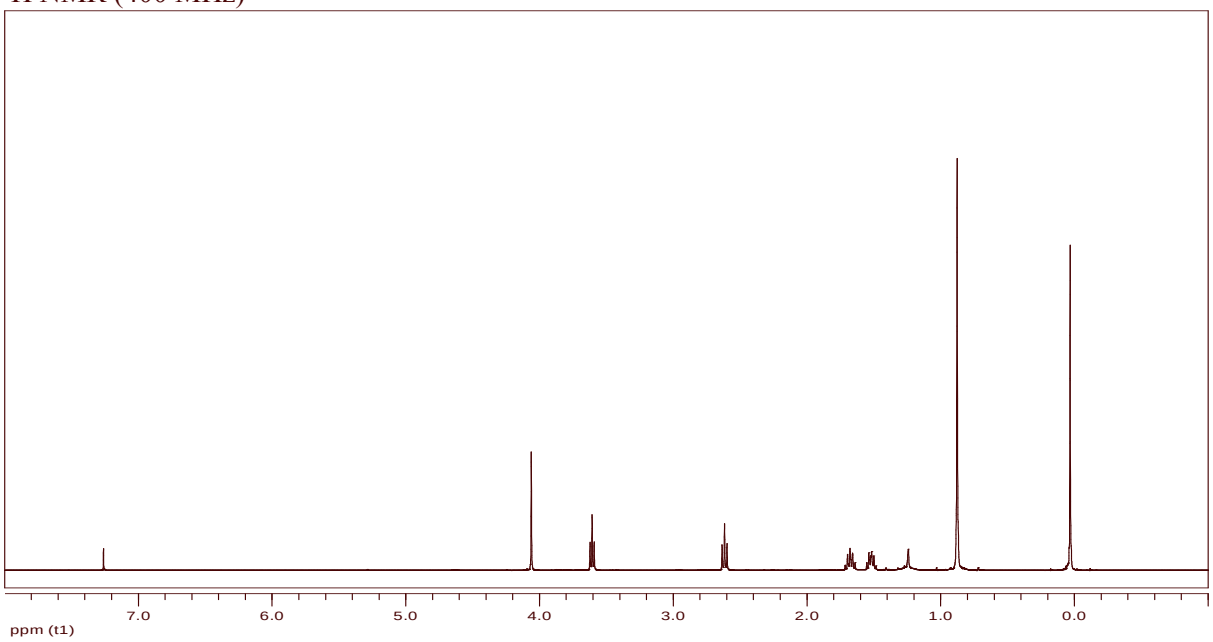


6-(*tert*-Butyl-dimethyl-silanyloxy)-1-chloro-hexan-2-one (18).

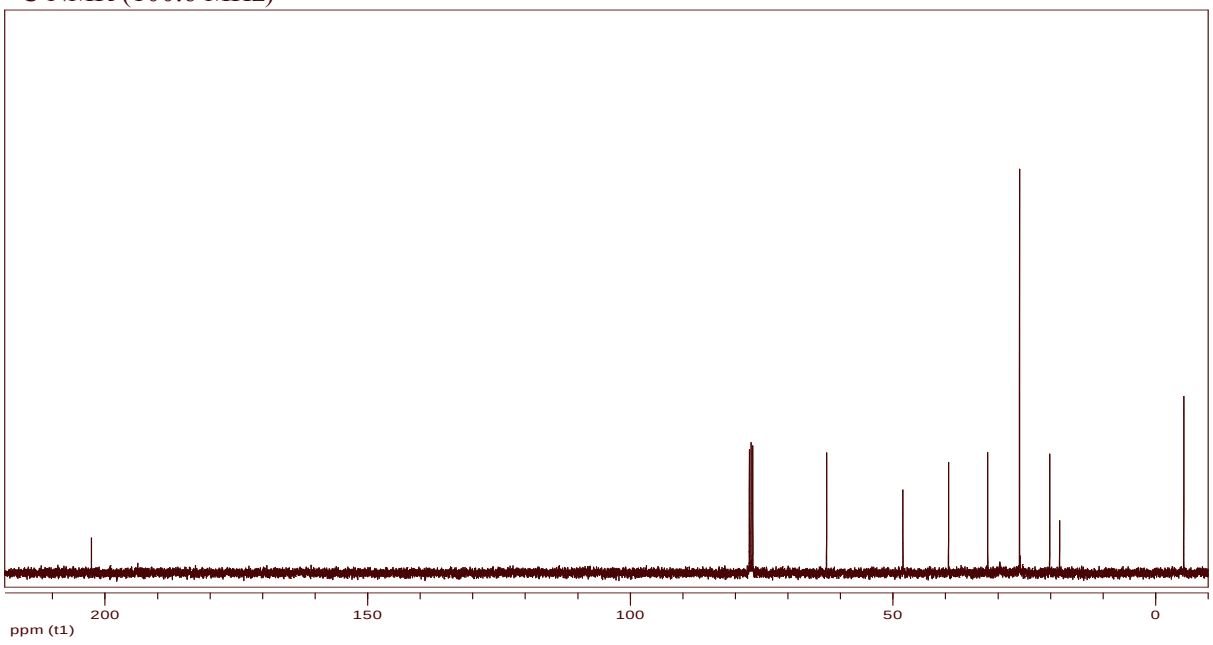


$C_{12}H_{25}ClO_2Si$
Exact Mass: 264,13
Mol. Wt.: 264,86

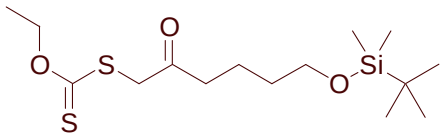
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

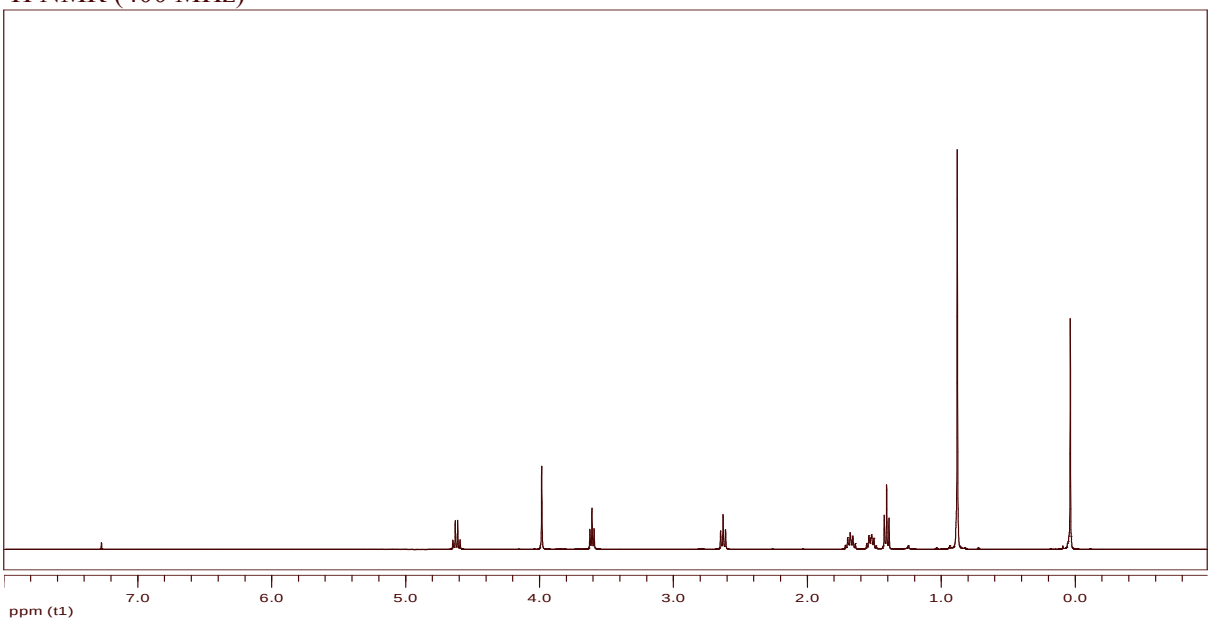


Dithiocarbonic acid [6-(*tert*-butyl-dimethyl-silanyloxy)-2-oxo-hexyl] ester ethyl ester (19).

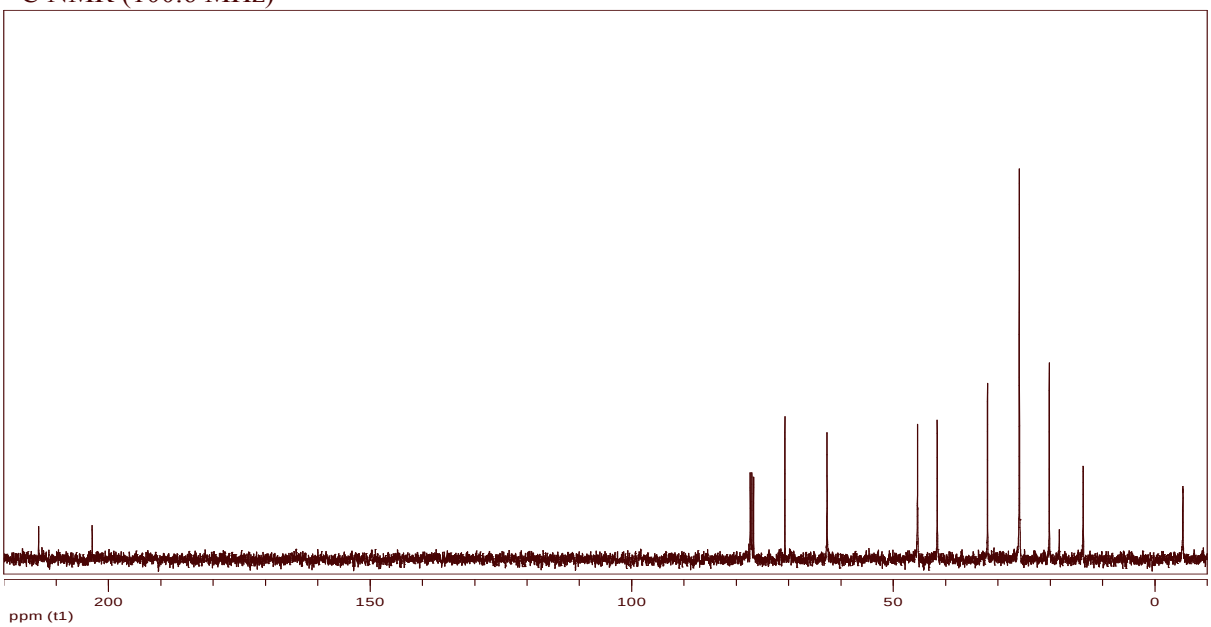


$C_{15}H_{30}O_3S_2Si$
Exact Mass: 350,14
Mol. Wt.: 350,61

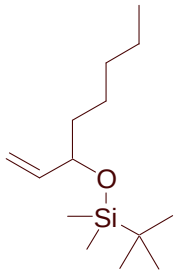
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

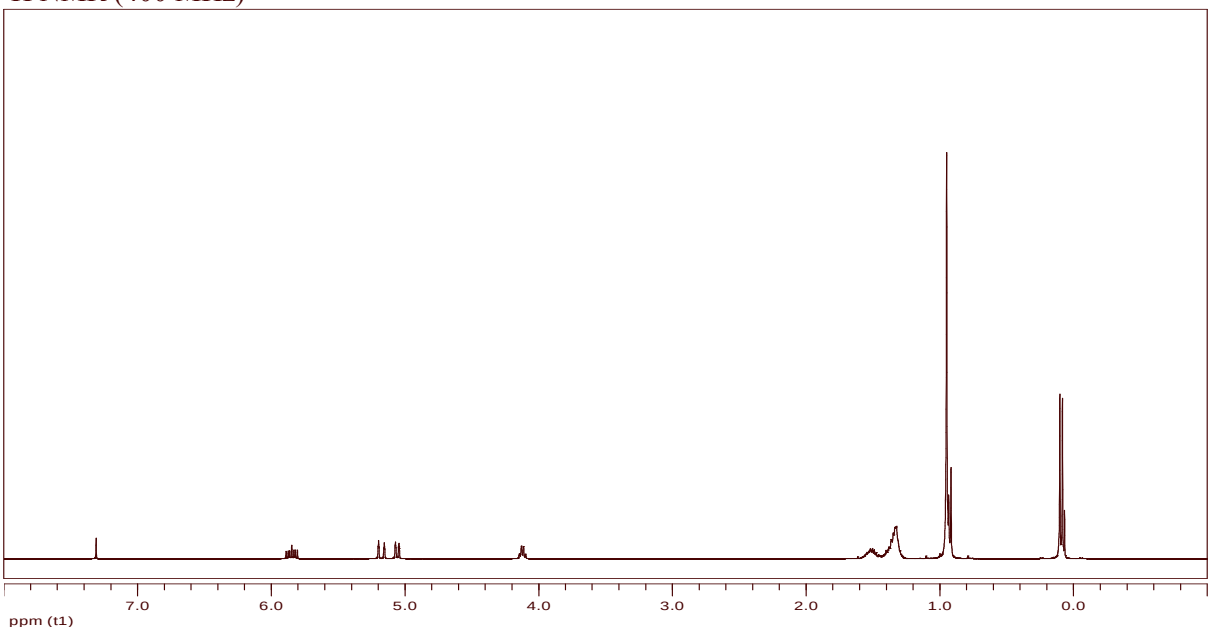


tert-Butyl-dimethyl-(1-vinyl-hexyloxy)-silane (20).

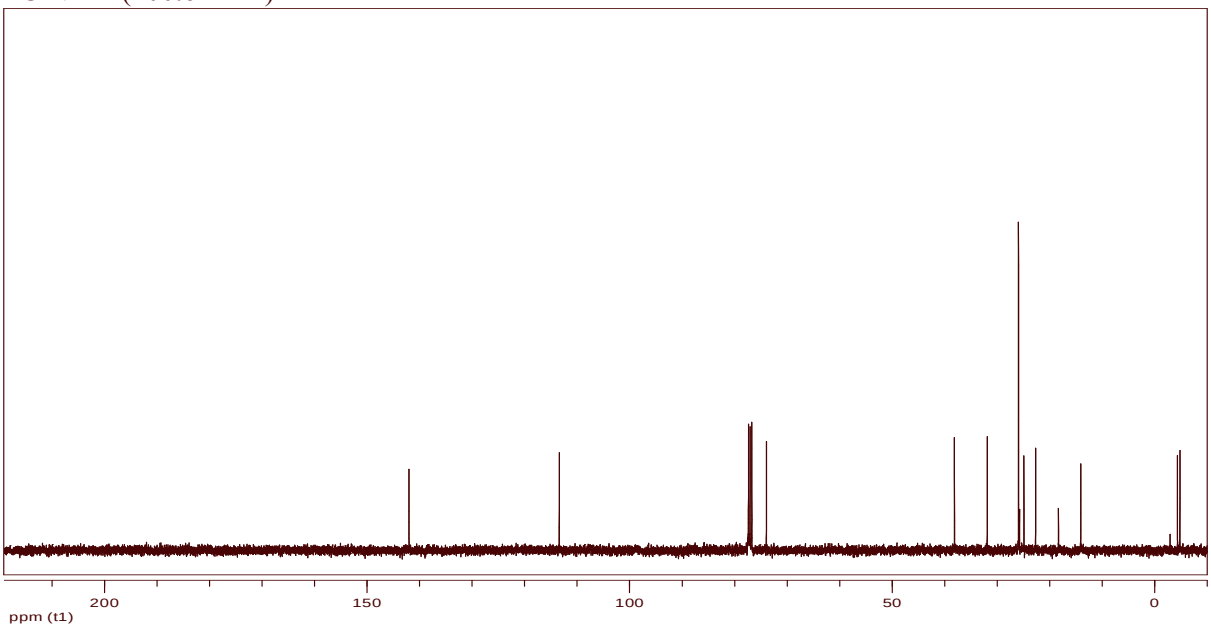


$C_{14}H_{30}OSi$
Exact Mass: 242,21
Mol. Wt.: 242,47

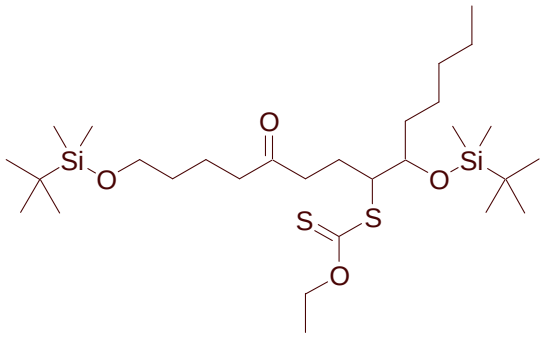
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

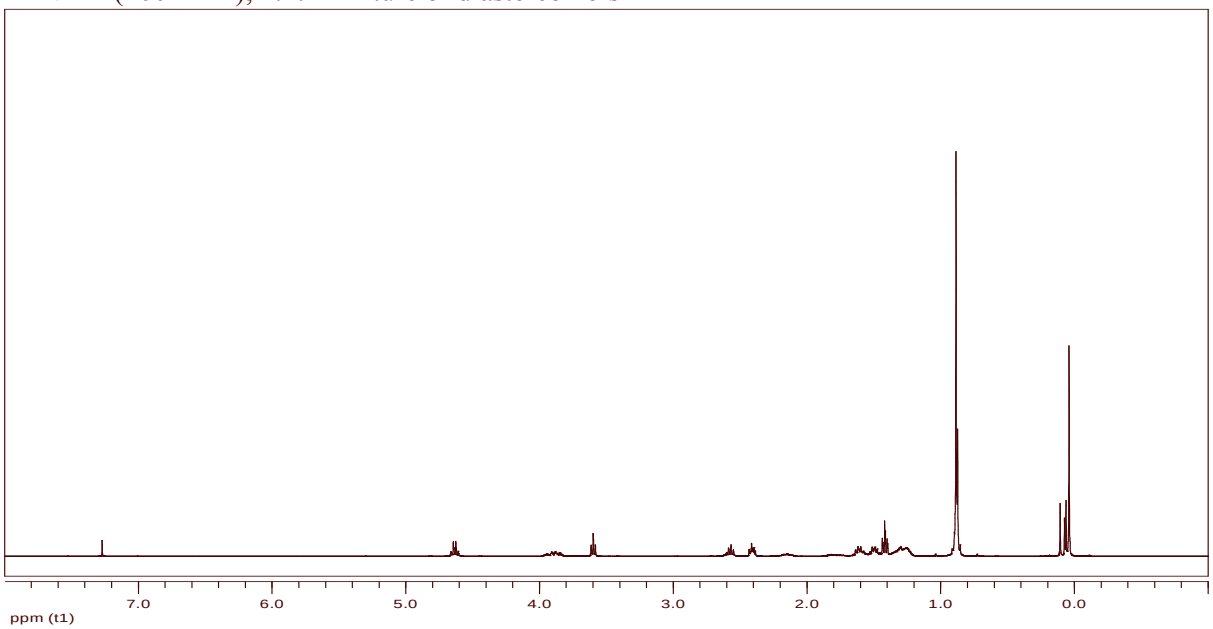


Dithiocarbonic acid {8-(*tert*-butyl-dimethyl-silanyloxy)-1-[1-(*tert*-butyl-dimethyl-silanyloxy)-hexyl]-4-oxo-octyl} ester ethyl ester (21).

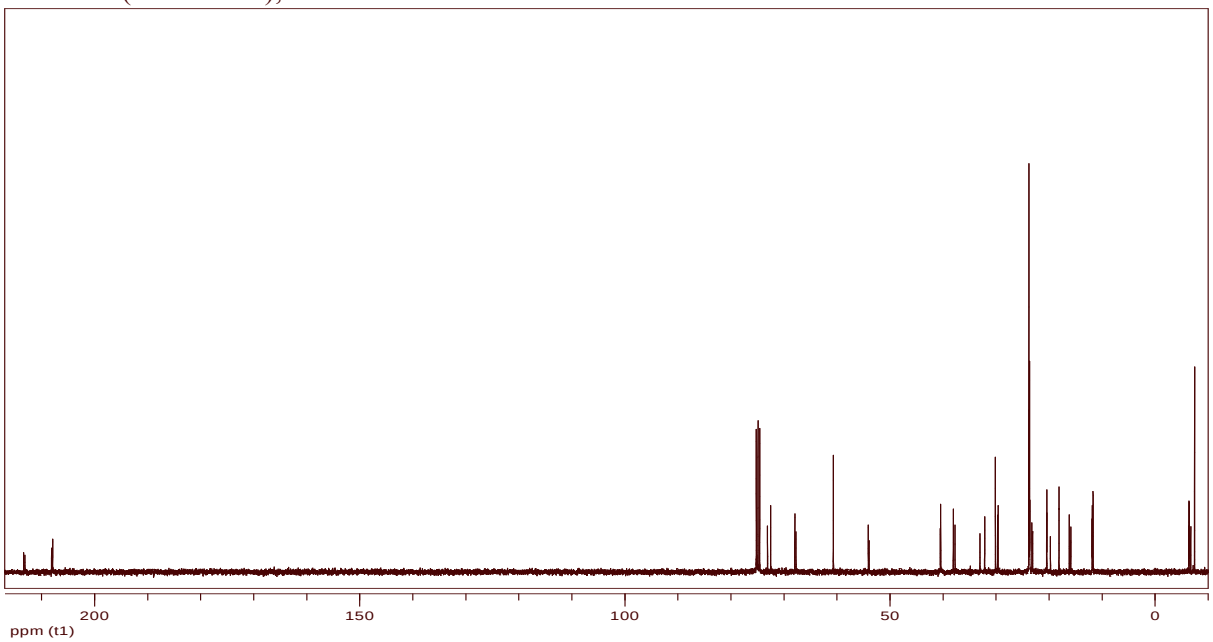


$C_{29}H_{60}O_4S_2Si_2$
Exact Mass: 592,35
Mol. Wt.: 593,09

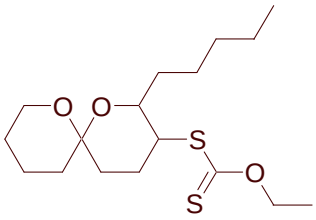
^{1}H NMR (400 MHz), 1:1.1 mixture of diastereomers



^{13}C NMR (100.6 MHz), 1:1.1 mixture of diastereomers

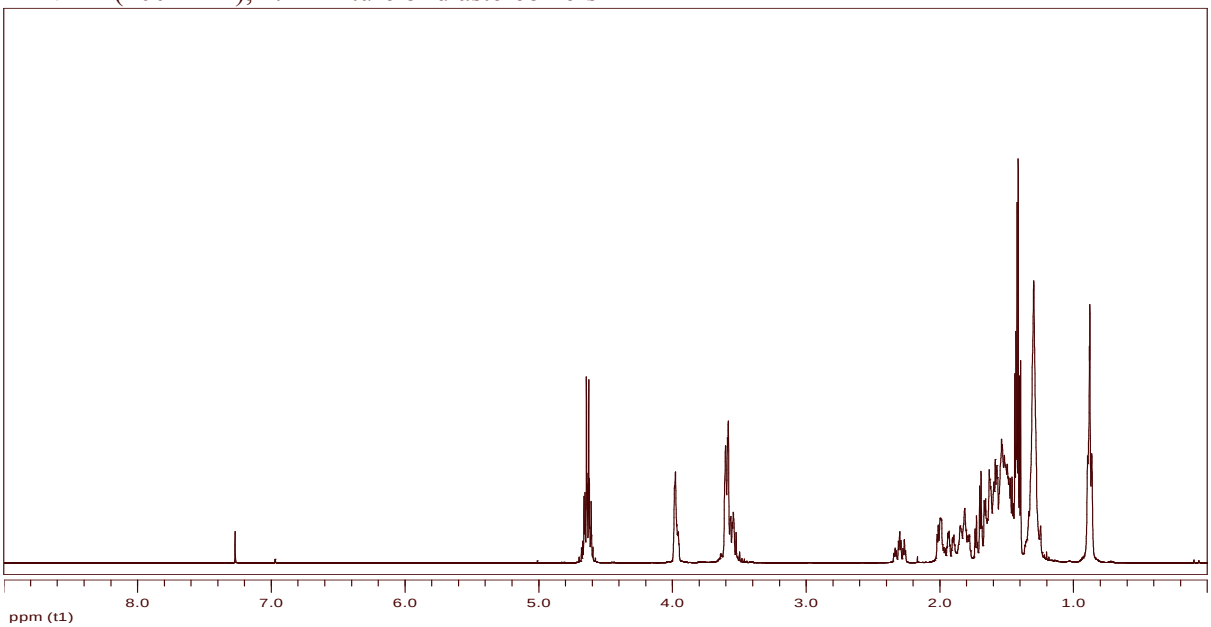


Dithiocarbonic acid ethyl ester (2-pentyl-1,7-dioxa-spiro[5.5]undec-3-yl) ester (22).

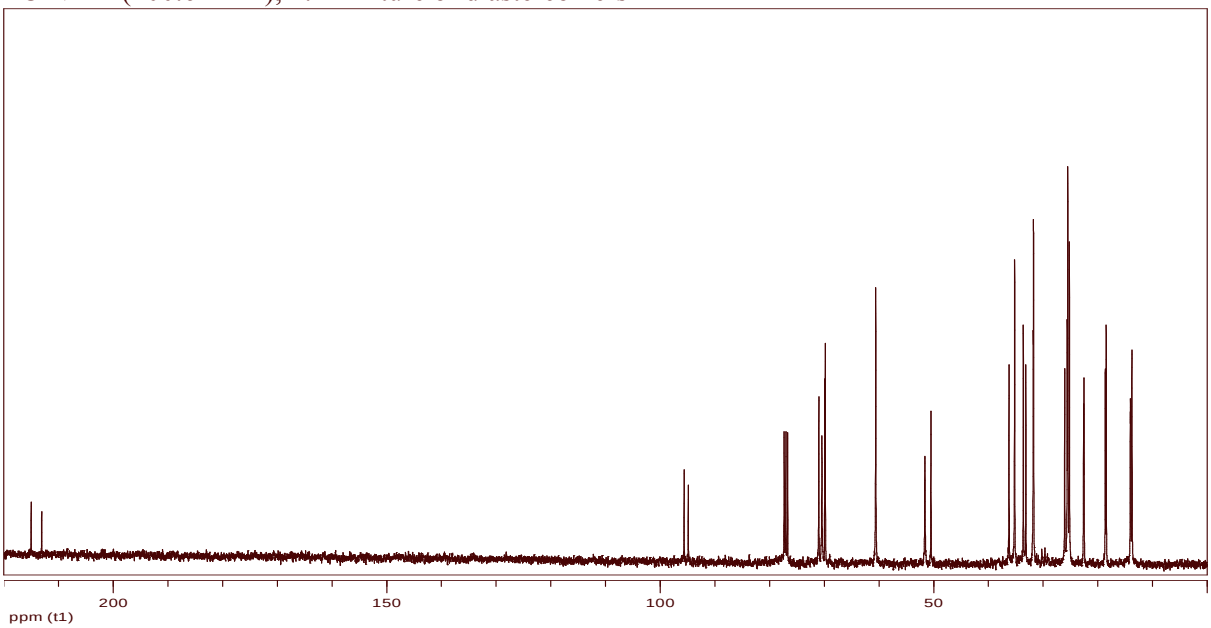


$C_{17}H_{30}O_3S_2$
Exact Mass: 346,16
Mol. Wt.: 346,55

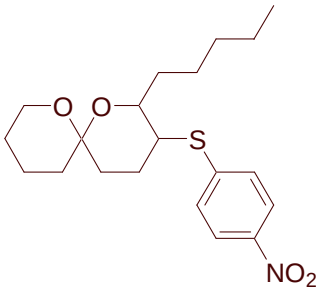
^{1}H NMR (400 MHz), 1:1 mixture of diastereomers



^{13}C NMR (100.6 MHz), 1:1 mixture of diastereomers

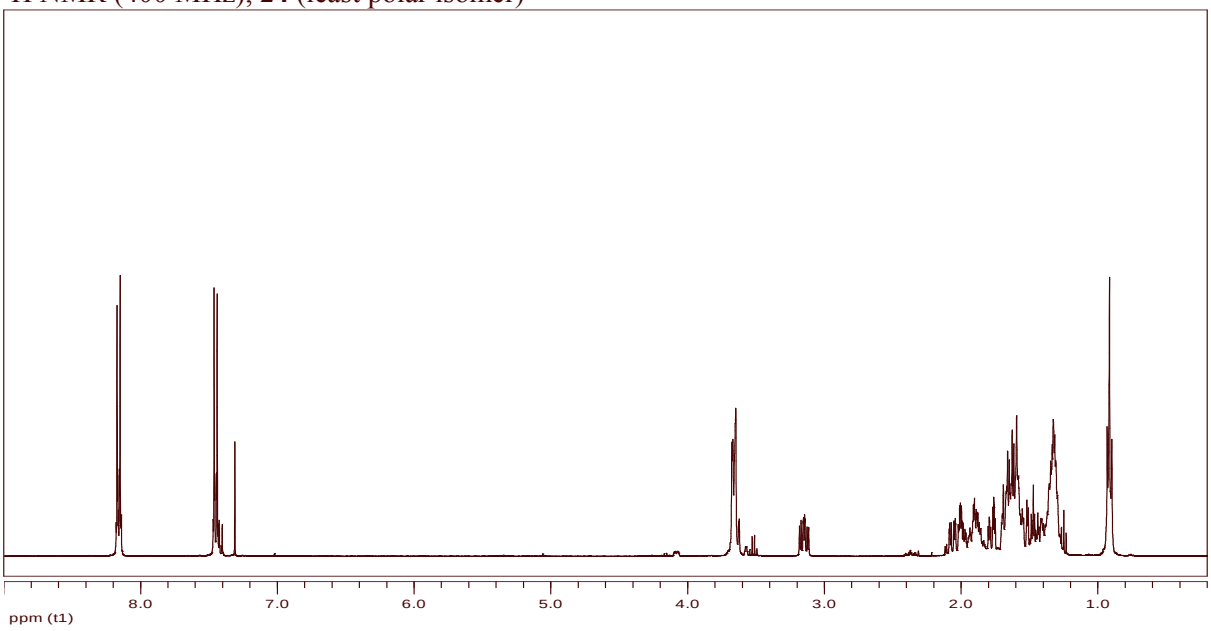


3-(4-Nitro-phenylsulfanyl)-2-pentyl-1,7-dioxa-spiro[5.5]undecane (24).

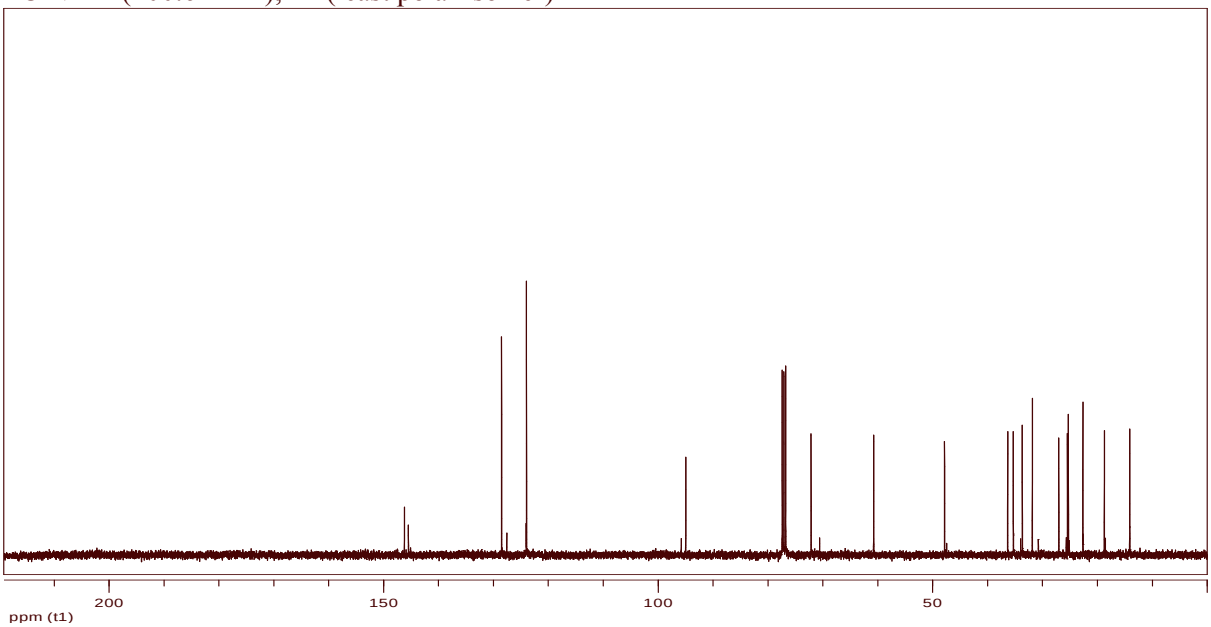


$C_{20}H_{29}NO_4S$
Exact Mass: 379,18
Mol. Wt.: 379,51

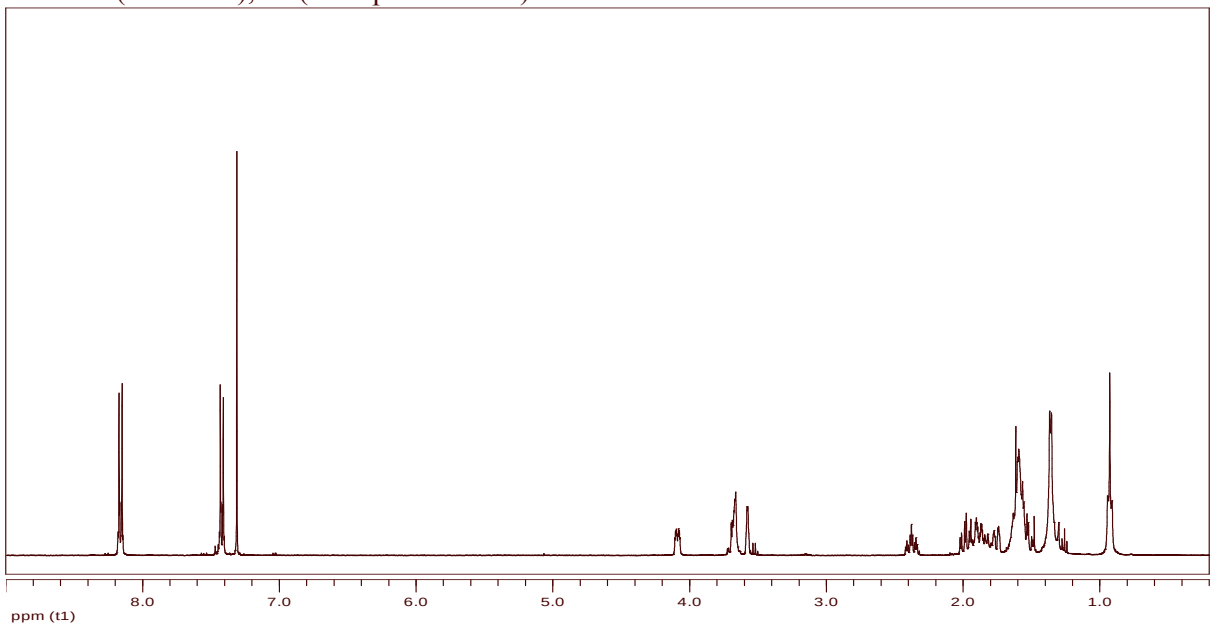
^{1}H NMR (400 MHz), **24** (least polar isomer)



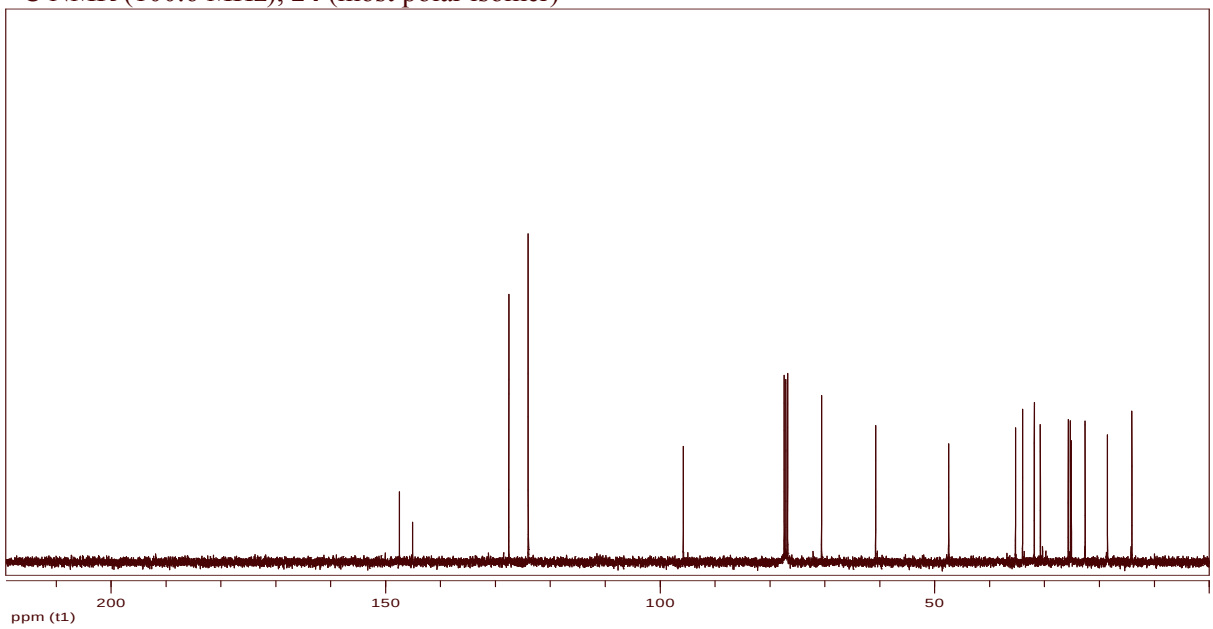
^{13}C NMR (100.6 MHz), **24** (least polar isomer)



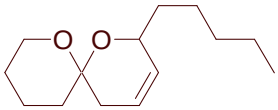
^{1}H NMR (400 MHz), **24** (most polar isomer)



^{13}C NMR (100.6 MHz), **24** (most polar isomer)

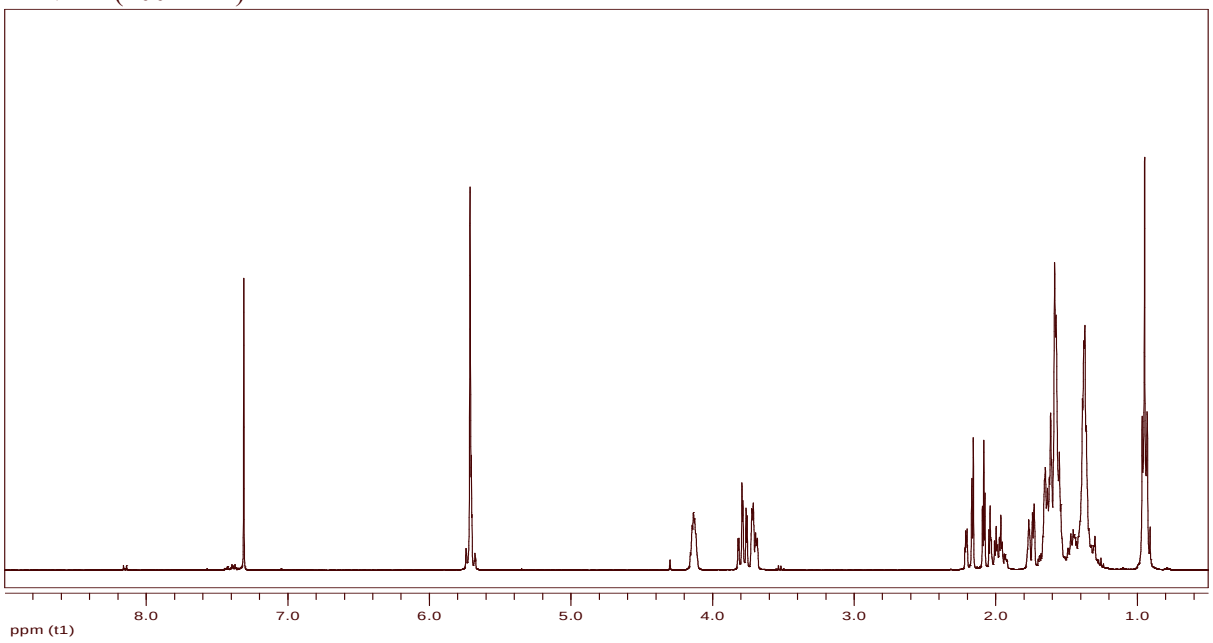


2-Pentyl-1,7-dioxa-spiro[5.5]undec-3-ene (26).

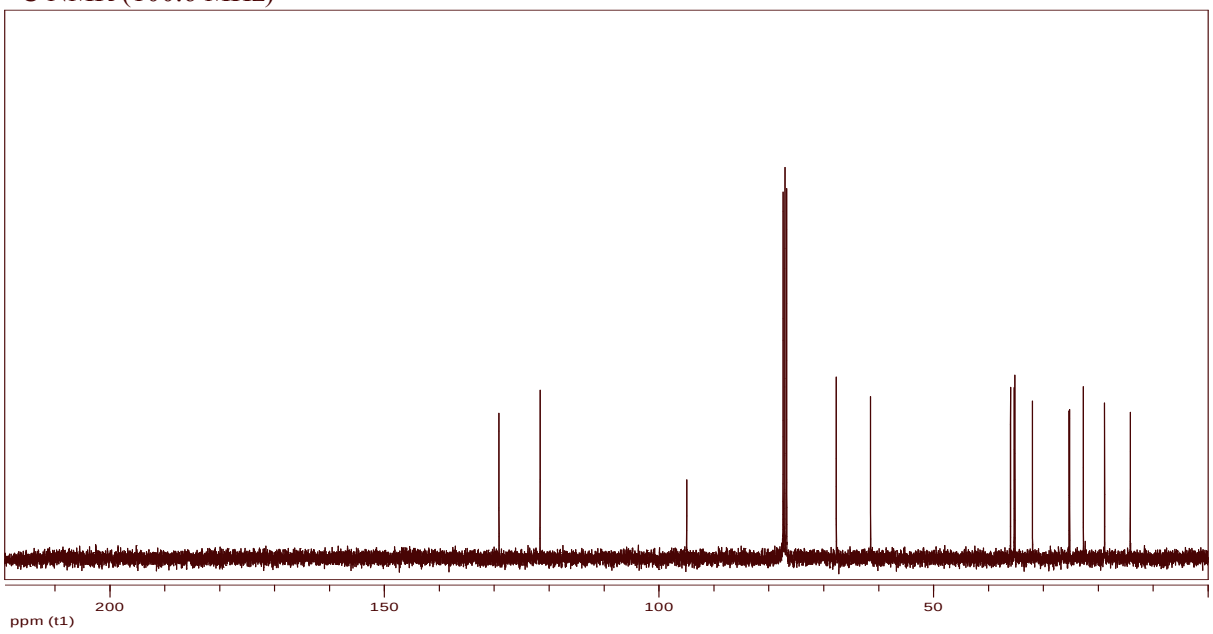


$C_{14}H_{24}O_2$
Exact Mass: 224,18
Mol. Wt.: 224,34

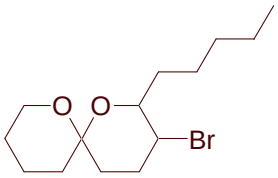
^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)

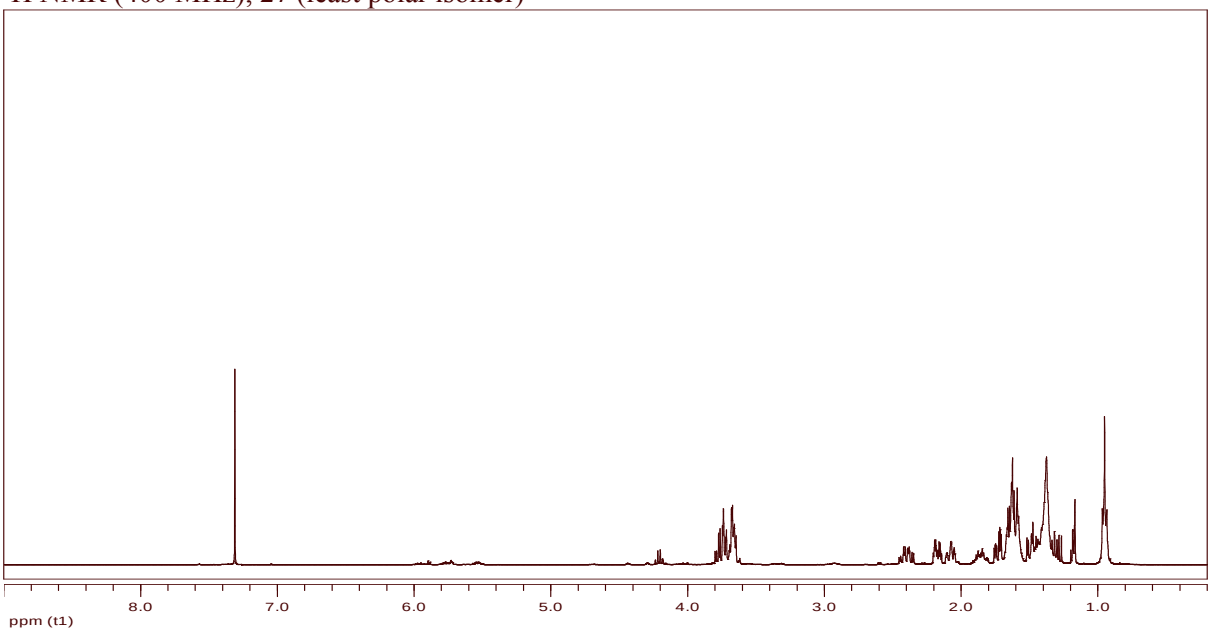


3-Bromo-2-pentyl-1,7-dioxa-spiro[5.5]undecane (27).

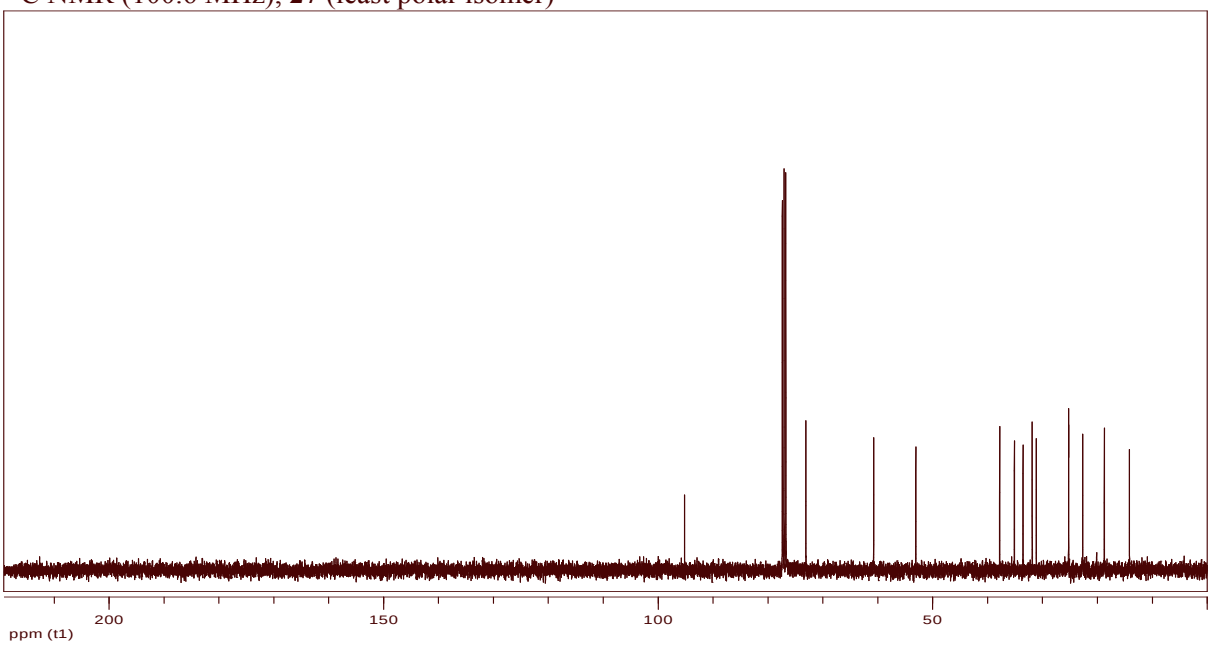


$C_{14}H_{25}BrO_2$
Exact Mass: 304,10
Mol. Wt.: 305,25

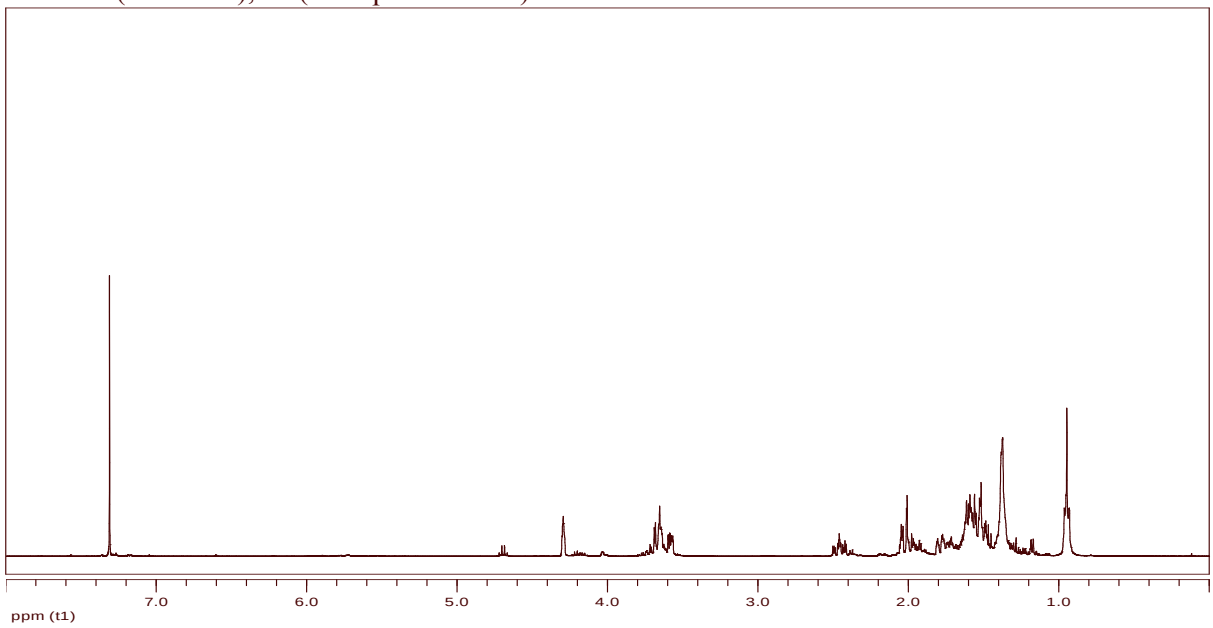
^{1}H NMR (400 MHz), **27** (least polar isomer)



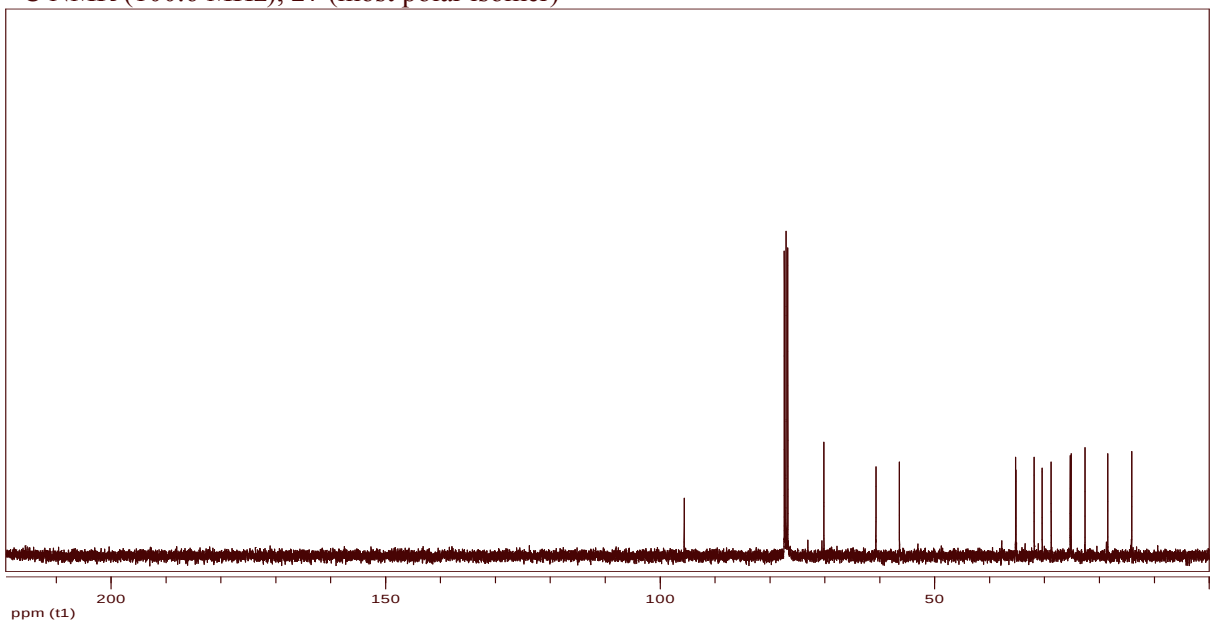
^{13}C NMR (100.6 MHz), **27** (least polar isomer)



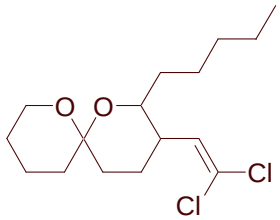
^{1}H NMR (400 MHz), **27** (most polar isomer)



^{13}C NMR (100.6 MHz), **27** (most polar isomer)

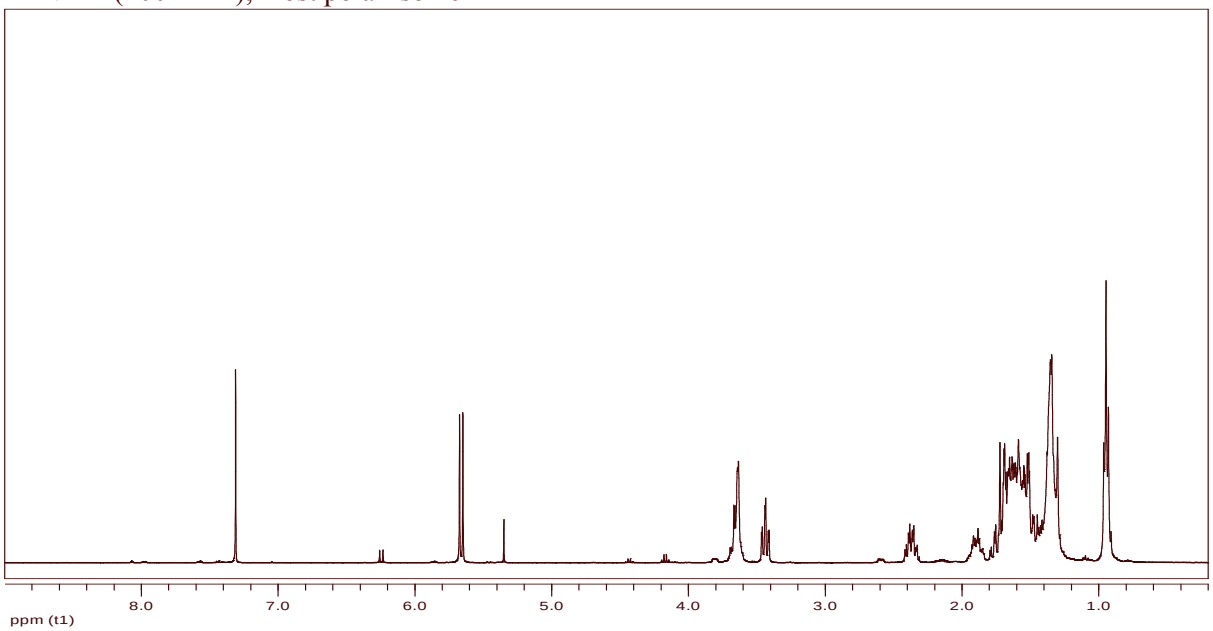


3-(2,2-Dichloro-vinyl)-2-pentyl-1,7-dioxa-spiro[5.5]undecane (28).

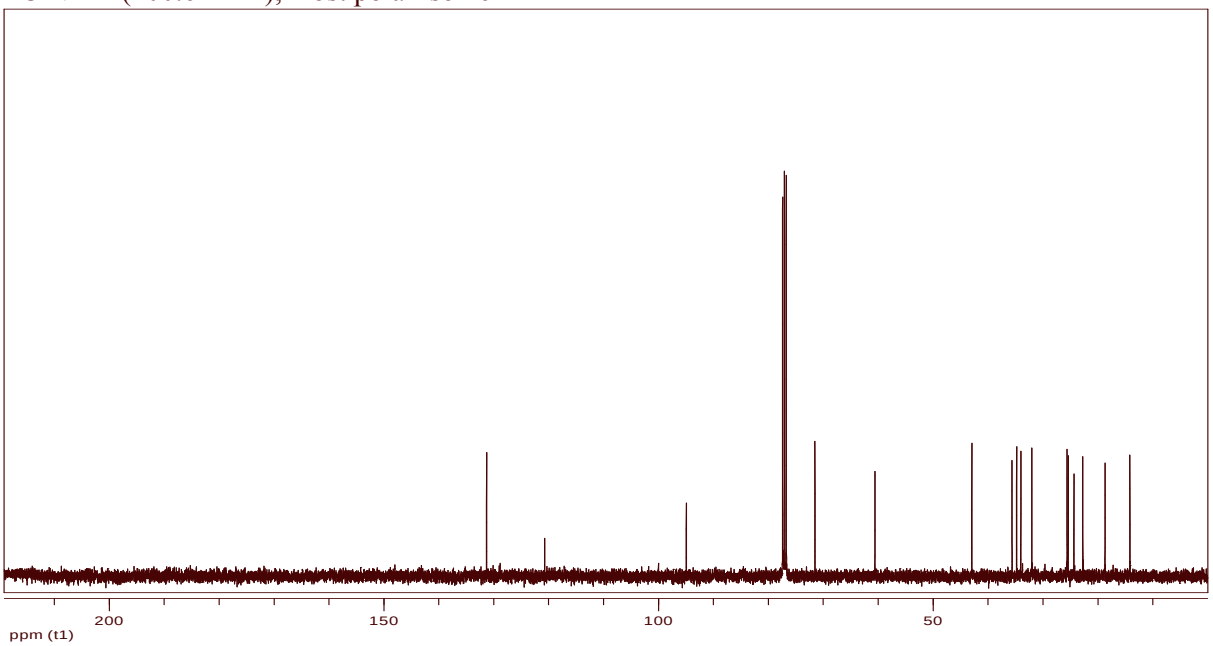


$C_{16}H_{26}Cl_2O_2$
Exact Mass: 320,13
Mol. Wt.: 321,28

^{1}H NMR (400 MHz), most polar isomer



^{13}C NMR (100.6 MHz), most polar isomer



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[2] Schmidt, B. *J. Org. Chem.* **2004**, *69*, 7672.

[3] Craig, D.; Pennington, M. W.; Warner, P. *Tetrahedron* **1999**, *55*, 13495.

[4] Murphy, P. J.; Williams, H. L.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *Tetrahedron* **1996**, *52*, 8315.

[5] Brimble, M. A.; Rush, C. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 497.