ELECTRONIC SUPPLEMENTARY INFORMATION

Stereochemistry of 10-sulfoxidation catalyzed by a soluble Δ^9 desaturase.

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Synthesis of 9-Thiafatty Acid Methyl Esters and their sulfoxy derivatives

Methyl 9-thiatridecanoate. To a solution of 8-thiooctanoic acid (1.40 g, 7.94 mmol) in 7:1 THF/HMPA (56 mL) was added 1.6 M n-butyl lithium reagent (10.9 mL, 2.2 equiv) at 0 °C under N_2. After stirring the reaction mixture for 30 min at 0 °C, 1-bromobutane (1.1 equivalents) was added. The mixture was stirred at r.t. for 20 h, quenched with dH_2O (60 mL), acidified with 3 M HCl (60 mL), and extracted with hexanes (4 x 40 mL). The combined extracts were dried over Na_2SO_4 and evaporated to give crude 9-thiatridecanoic acid, which was then methylated with 10 % BF_3/MeOH (100 mL; reflux). After evaporation of the reaction solvent, the crude product (1.28 g) was purified by flash chromatography (2.5% EtOAc/Hexane) to give the title compound (527mg, 27% yield based on 8-thiooctanoic acid), a colourless oil at room temperature. R_f = 0.14 (2.5% EtOAc/Hexanes); ^{1}H NMR (400 MHz; $CDCl_3$): δ 0.91 (t, J = 7.3, 3H), 1.26-1.45 (m, 8H), 1.52-1.66 (m, 6H), 2.30 (t, J = 7.5, 2H), 2.49 (t, J = 7.4, 2H), 2.50 (t, J = 7.4, 2H),

3.66 (s, 3H); ^{13}C NMR (100.6 MHz): δ 13.72, 22.06, 24.88, 28.73, 28.88, 29.02, 29.62, 31.82, 31.85, 32.11, 34.06, 51.48, 174.28; IR (film): 2930, 2857, 1742, 1463, 1436, 1360, 1172 cm^{-1}; EI-MS: *m/z* 246 (M^+), 215 ($[M\text{-}OMe]^+$), 189 ($[OS(CH_2)_7CO_2Me]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 246.1667 (M^+, $C_{13}H_{26}O_2S$; calc. 246.1654).

Methyl 9-thiatetradecanoate. From 8-thiooctanoic acid and 1-bromopentane: colourless oil at r.t. R_f = 0.15 (2.5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.1, 3H), 1.26-1.44 (m, 18H), 1.54-1.67 (m, 6H), 2.31 (t, *J* = 7.5, 2H), 2.51 (unresolved overlapping t, *J* = 7.4, 4H), 3.68 (s, 3H); ^{13}C NMR (100.6 MHz): δ 14.00, 22.33, 24.88, 28.73, 28.88, 29.02, 29.41, 29.63, 31.14, 32.11, 32.16, 34.03, 51.48, 174.29; IR (film): Similar to **1a** ; EI-MS: *m/z* 260 (M^+), 229 ($[M\text{-}OMe]^+$), 189 ($[OS(CH_2)_7CO_2Me]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 260.1798 (M^+, $C_{14}H_{28}O_2S$; calc. 260.1810).

Methyl 9-thiapentadecanoate. From 8-thiooctanoic acid and 1-bromohexane: colourless oil at r.t R_f = 0.15 (2.5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.9, 3H), 1.25-1.43 (m, 14H), 1.53-1.66 (m, 6H), 2.30 (t, *J* = 7.5, 2H), 2.49 (unresolved overlapping t, *J* = 7.4, 4H), 3.66 (s, 3H); ^{13}C NMR (100.6 MHz): δ 14.06, 22.57, 24.88, 28.65, 28.73, 28.88, 29.02, 29.63, 29.29, 31.47, 32.11, 32.20, 34.06, 51.48, 174.29; IR (film): Similar to **1a**; EI-MS: *m/z* 274 (M^+), 243 ($[M\text{-}OMe]^+$), 189 ($[OS(CH_2)_7CO_2Me]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 274.1938 (M^+, $C_{15}H_{30}O_2S$; calc. 274.1967).

Methyl 9-thiahexadecanoate. From 8-thiooctanoic acid and 1-bromoheptane: colourless oil at r.t. R_f = 0.17 (2.5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.9, 3H), 1.23-1.45 (m, 18H), 1.53-1.68 (m, 6H), 2.30 (t, *J* = 7.5, 2H), 2.49 (unresolved overlapping t, *J* = 7.4, 4H), 3.67 (s, 3H); ^{13}C NMR (100.6 MHz): δ 14.10, 22.63, 24.88, 28.74, 28.89, 28.93, 28.95, 29.03, 29.63, 29.73, 31.76, 32.11, 32.19, 34.06,

51.48, 174.29; IR (film): Similar to **1a**; EI-MS: *m/z* 288 (M^+), 257 ($[M\text{-}OMe]^+$), 189 ($[OS(CH_2)_7CO_2Me]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 288.2113 (M^+, $C_{16}H_{32}O_2S$; calc. 288.2123).

Methyl 9-thiaheptadecanoate. From 8-thiooctanoic acid and 1-bromooctaane: colourless oil at r.t. R_f = 0.19 (2.5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.9, 3H), 1.27-1.43 (m, 16H), 1.52-1.67 (m, 6H), 2.30 (t, *J* = 7.5, 2H), 2.49 (unresolved overlapping t, *J* = 7.4, 4H), 3.66 (s, 3H).; ^{13}C NMR (100.6 MHz): δ 14.11, 22.66, 24.89, 28.74, 28.89, 28.98, 29.03, 29.21, 29.24, 29.64, 29.74, 31.84, 32.13, 32.21, 34.07, 51.47, 174.27; IR (film): Similar to **1a**; EI-MS: *m/z* 302 (M^+), 271 ($[M\text{-}OMe]^+$), 189 ($[OS(CH_2)_7CO_2Me]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 302.2272 (M^+, $C_{17}H_{34}O_2S$; calc. 302.2280).

Methyl 9-thiaoctadecanoate. From 8-thiooctanoic acid and 1-bromononane as previously described[9]: colourless oil at r.t. R_f = 0.21 (2.5% EtOAc/Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.9, 3H), 1.27-1.43 (m, 18H), 1.53-1.66 (m, 6H), 2.30 (t, *J* = 7.5, 2H), 2.49 (unresolved overlapping t, *J* = 7.4, 4H), 3.67 (s, 3H); ^{13}C NMR (100.6 MHz): δ 14.12, 22.68, 24.89, 28.74, 28.89, 28.98, 29.03, 29.29, 29.29, 29.51, 29.65, 29.74, 31.89, 32.13, 32.21, 34.07, 51.47, 174.27; IR (film): Similar to **1a**; EI-MS: *m/z* 316 (M^+), 285 ($[M\text{-}OMe]^+$), 189 ($[OS(CH_2)_7CO_2Me]^+$), 157 ($[(CH_2)_7CO_2Me]^+$).

(*R*,*S*)-Methyl 9-thiatridecanoate S-oxide. A solution of methyl 9-thiatridecanoate (100.6 mg, 0.383 mmol in 1 mL CH_2Cl_2, was added to a solution of *meta*-chloroperbenzoic acid (0.5 equiv., 66.1 mg) in 2 mL CH_2Cl_2 at 0 °C. After standing at 0 °C for 30 min, the reaction mixture was filtered to remove a white solid precipitate (*meta*-chlorobenzoic acid). The filtrate was washed with 0.3M NaOH (2 x 2mL), dried (Na_2SO_4), and evaporated; the crude sulfoxide was purified by flash chromatography

(100% EtOAc) to give the title compound (50.4 mg, 50% yield) as a white solid. mp 35-37 °C; R_f = 0.21 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.3, 3H), 1.29-1.57 (m, 8H), 1.63 (p, *J* = 7.3, 2H), 1.69-1.81 (m, 4H), 2.31 (t, *J* = 7.5, 2H), 2.58-2.73 (m, 4H), 3.67 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.68, 22.08, 22.53, 24.60, 24.76, 28.66, 28.81, 28.84, 33.96, 51.42, 52.18, 52.35, 174.17; IR (KBr): 1008, 1020, 1174, 1437, 1471, 1739, 2850, 2922, 2955 cm^{-1}; EI-MS: *m/z* 245 ($[M\text{-}OH]^+$), 231 ($[M\text{-}OMe]^+$), 174 ($[OS(CH_2)_7CO]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 245.1528 ($[M\text{-}OH]^+$, $C_{13}H_{25}O_2S$; calc. 245.1575).

(*R*,*S*)-Methyl 9-thiatetradecanoate S-oxide. From methyl 9-thiatetradecanoate: a white solid. mp 41–43 °C; R_f = 0.29 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.3, 3H), 1.29-1.56 (m, 10H), 1.62 (p, *J* = 7.3, 2H), 1.70-1.82 (m, 4H), 2.30 (t, *J* = 7.5, 2H), 2.57-2.72 (m, 4H), 3.66 (s, H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 13.81, 22.28, 22.28, 22.51, 24.75, 28.64, 28.80, 28.80, 30.98, 33.94, 51.46, 52.31, 52.40, 174.15 (KBr): Similar to **2a**; EI-MS: *m/z* 259 ($[M\text{-}OH]^+$), 245 ($[M\text{-}OMe]^+$), 174 ($[OS(CH_2)_7CO]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 259.1714 ($[M\text{-}OH]^+$, $C_{14}H_{27}O_2S$; calc. 259.1732).

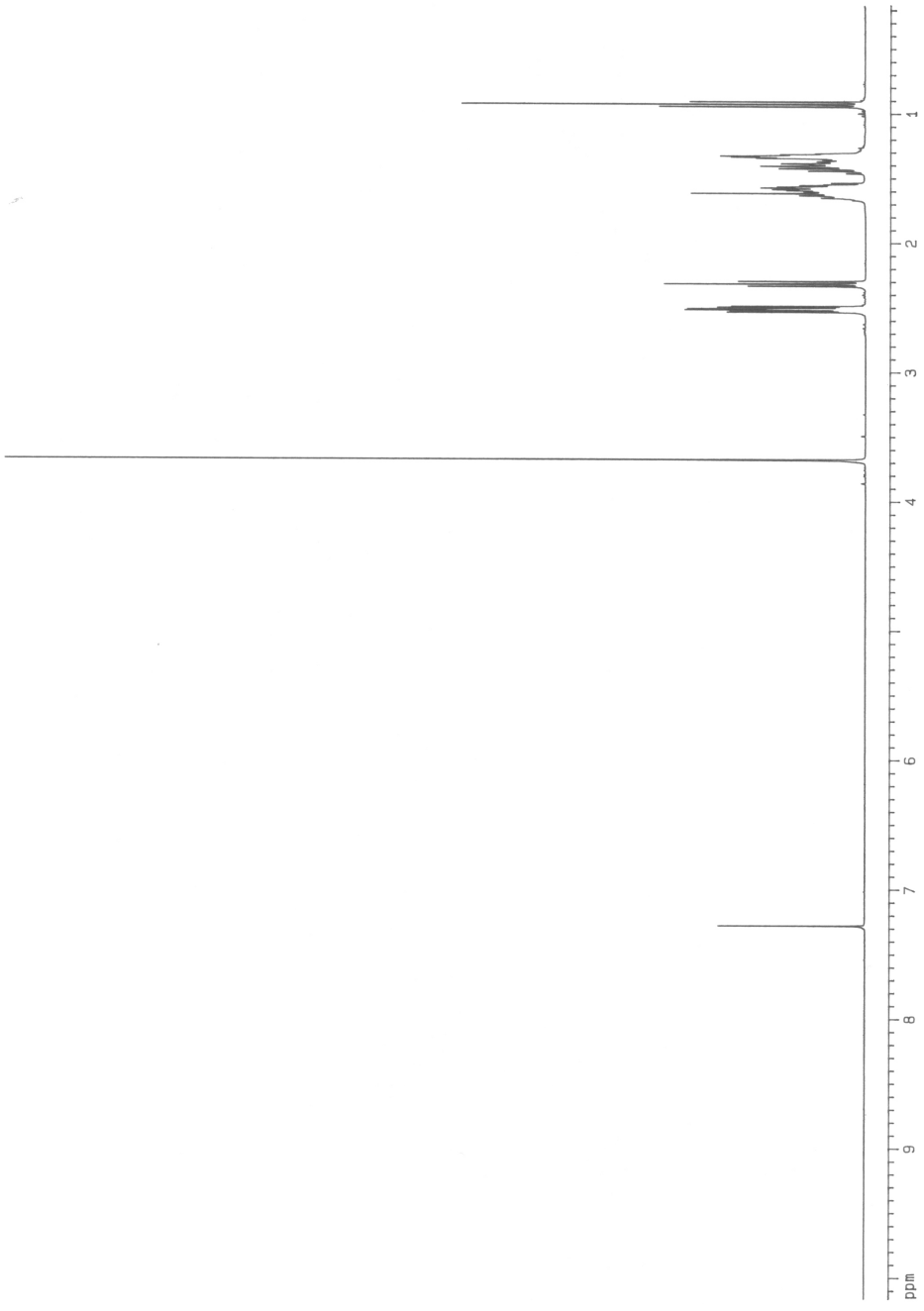
(*R*,*S*)-Methyl 9-thiapentadecanoate S-oxide. From methyl 9-thiapentadecanoate: a white solid. mp 44-46 °C; R_f = 0.31 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3, 3H), 1.27-1.56 (m, 12H), 1.62 (p, *J* = 7.3, 2H), 1.70-1.82 (m, 4H), 2.30 (t, *J* = 7.5, 2H), 2.57-2.72 (m, 4H), 3.66 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 13.93, 22.36, 22.50, 22.50 24.72, 28.50, 28.62, 28.78, 28.78, 31.32, 33.92, 51.44, 52.29, 52.42, 174.13; (KBr): Similar to **2a**; EI-MS: *m/z* 273 ($[M\text{-}OH]^+$), 259 ($[M\text{-}OMe]^+$), 174 ($[OS(CH_2)_7CO]^+$), 157 ($[(CH_2)_7CO_2Me]^+$); HR-EI-MS: 273.1929 ($[M\text{-}OH]^+$, $C_{15}H_{29}O_2S$; calc. 273.1888).

(*R*,*S*)-Methyl 9-thiahexadecanoate S-oxide. From methyl 9-thiahexadecanoate: a white solid. mp 53-55 °C; R_f = 0.32 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3, 3H), 1.25-1.56 (m, 14H), 1.62 (quin, 2H), 1.71-1.82 (m, 4H), 2.30 (t, *J* = 7.5, 2H), 2.57-2.72 (m, 4H), 3.66 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.95, 22.48, 22.48, 22.54, 24.72, 28.77, 28.78, 28.80, 28.80, 28.80, 31.48, 33.90, 51.39, 52.32, 52.45, 174.07; (KBr): Similar to **2a**; EI-MS: *m/z* 287 ($[M\text{-}OH]^+$), 273 ($[M\text{-}OMe]^+$), 174 ($[OS(CH_2)_7CO]^+$); HR-EI-MS: 287.2061 ($[M\text{-}OH]^+$, $C_{16}H_{31}O_2S$; calc. 287.2045).

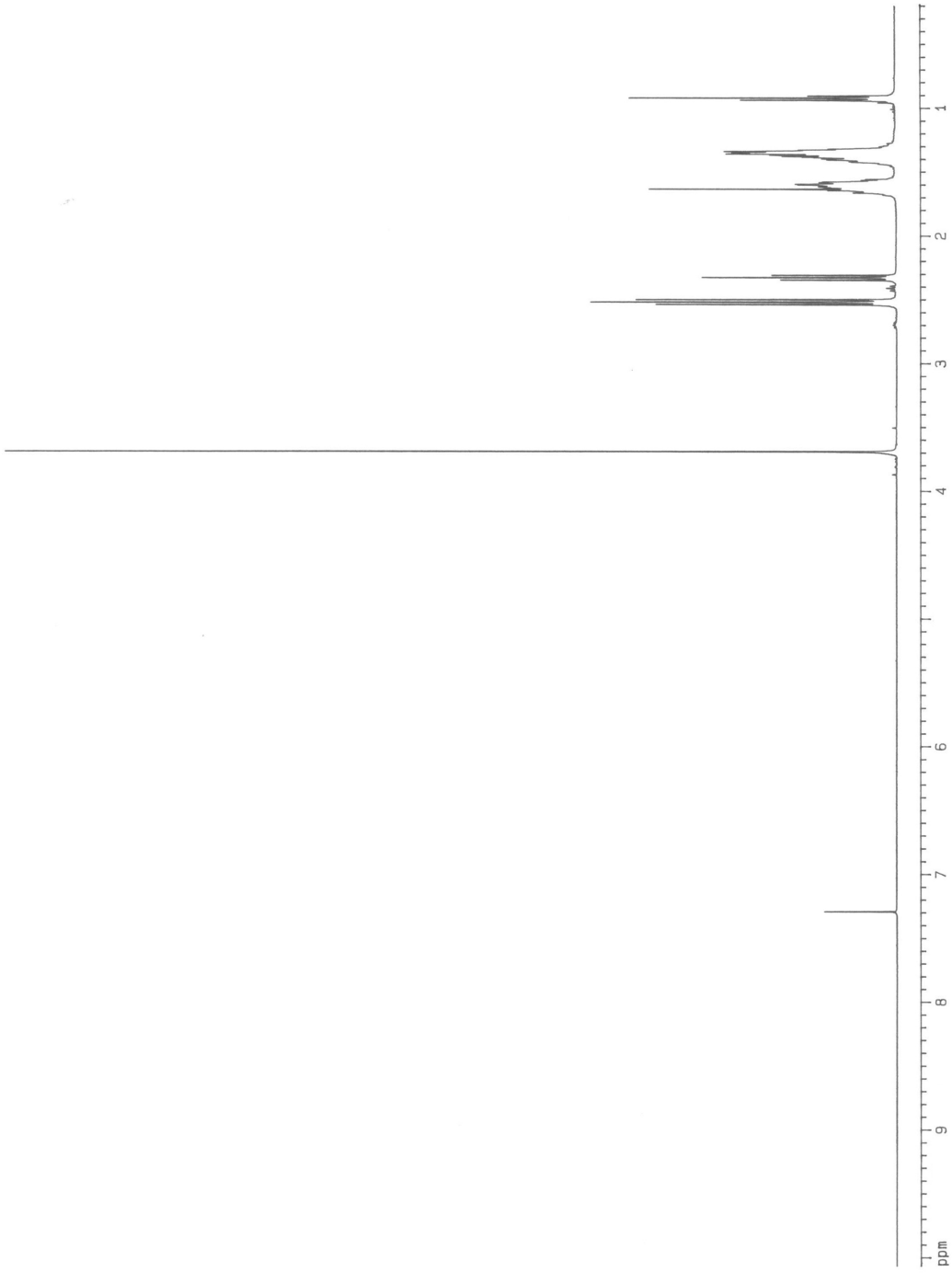
(*R*,*S*)-Methyl 9-thiaheptadecanoate S-oxide. From methyl 9-thiaheptadecanoate: a white solid. mp 56-58 °C; R_f = 0.34 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3, 3H), 1.27-1.54 (m, 16H), 1.62 (p, *J* = 7.3, 2H), 1.70-1.82 (m, 4H), 2.31 (t, *J* = 7.5, 2H), 2.57-2.72 (m, 4H), 3.67 (s, 3H); ^{13}C NMR (50.3MHz, $CDCl_3$): δ 14.05, 22.52, 22.58, 22.58, 24.75, 28.65, 28.82, 28.82, 28.82, 29.00, 29.14, 31.71, 33.94, 51.46, 52.32, 52.45, 174.15; (KBr): Similar to **2a**; EI-MS: *m/z* 301 ($[M\text{-}OH]^+$), 287 ($[M\text{-}OMe]^+$), 174 ($[OS(CH_2)_7CO]^+$); HR-EI-MS: 301.2191 ($[M\text{-}OH]^+$, $C_{17}H_{33}O_2S$; calc. 301.2201).

(*R*,*S*)-Methyl 9-thiaoctadecanoate S-oxide. From methyl 9-thiaoctadecanoate: a white solid. mp 66-68 °C (lit. 66.0 - 66.5°C)[7]; R_f = 0.36 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3, 3H), 1.27-1.54 (m, 16H), 1.62 (p, *J* = 7.3, 2H), 1.71-1.80 (m, 4H), 2.30 (t, *J* = 7.5, 2H), 2.57-2.72 (m, 4H), 3.67 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 14.09, 22.53, 22.59, 22.62, 24.76, 28.66, 28.82, 28.82, 28.82, 29.19, 29.19 29.30, 31.80, 33.95, 51.48, 52.32, 52.46, 174.17; (KBr): Similar to **2a**; EI-MS: *m/z* 315 ($[M\text{-}OH]^+$), 301 ($[M\text{-}OMe]^+$), 174 ($[OS(CH_2)_7CO]^+$).

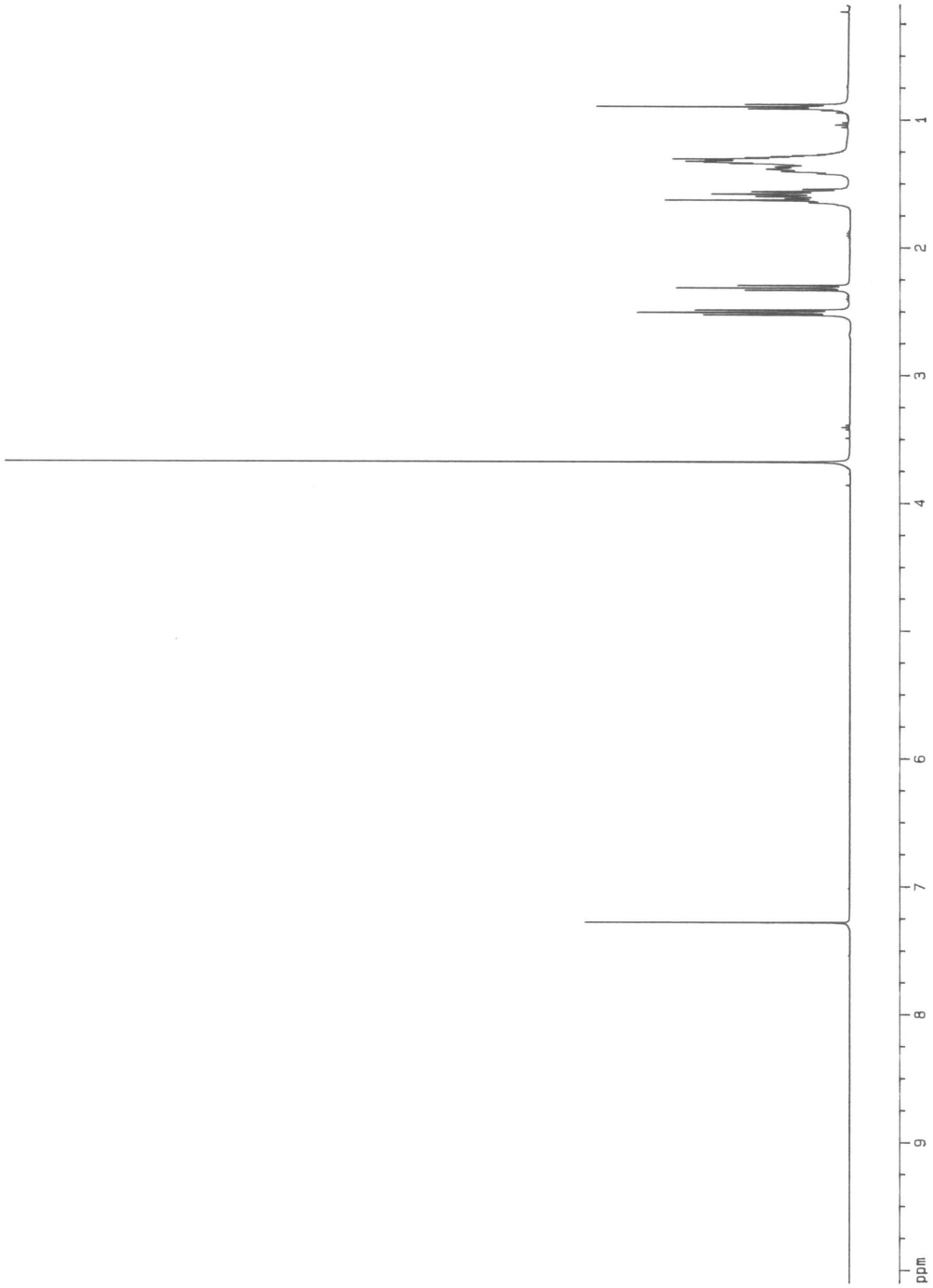
Methyl 9-thiatridecanoate



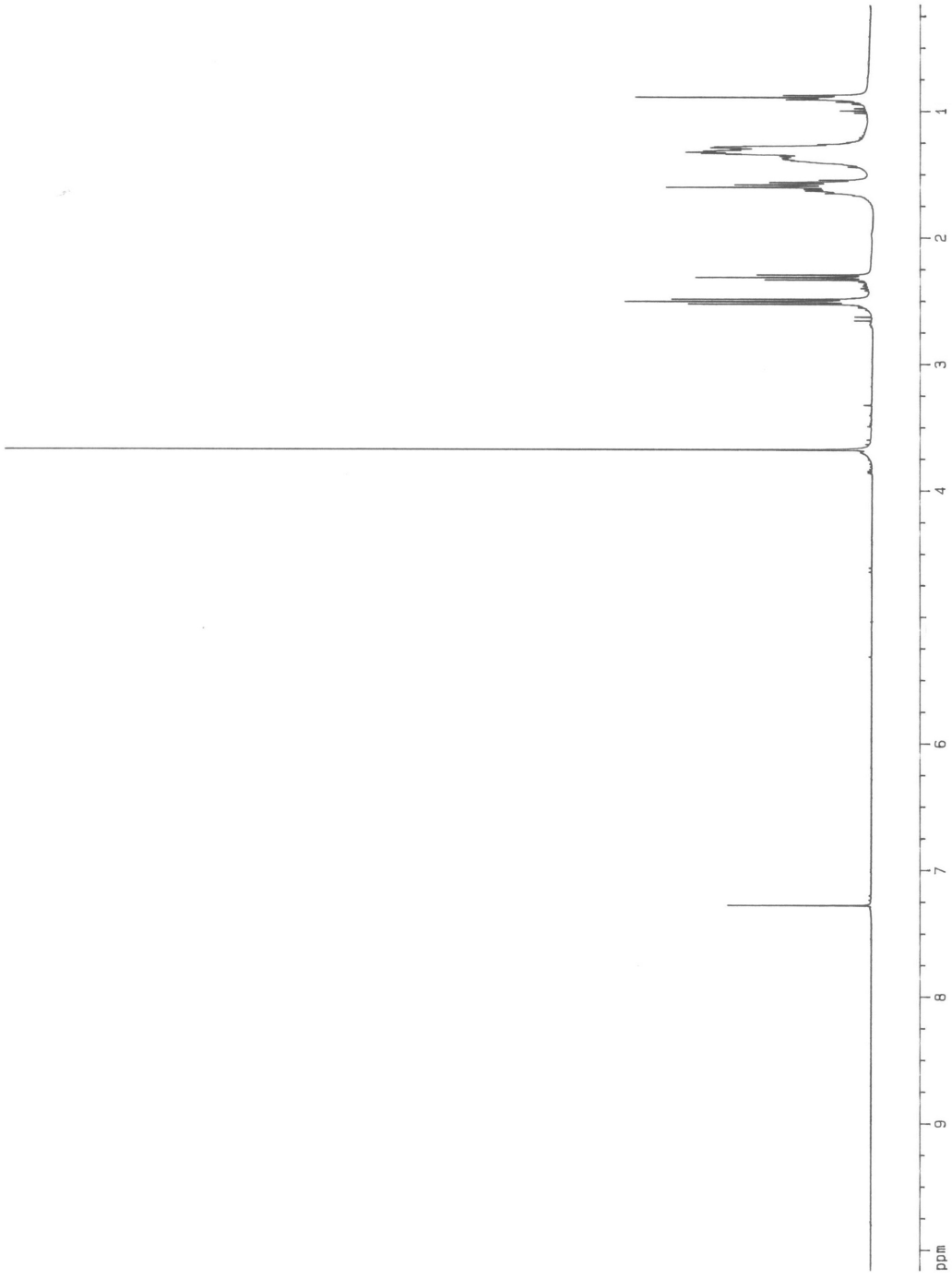
Methyl 9-thiatetradecanoate



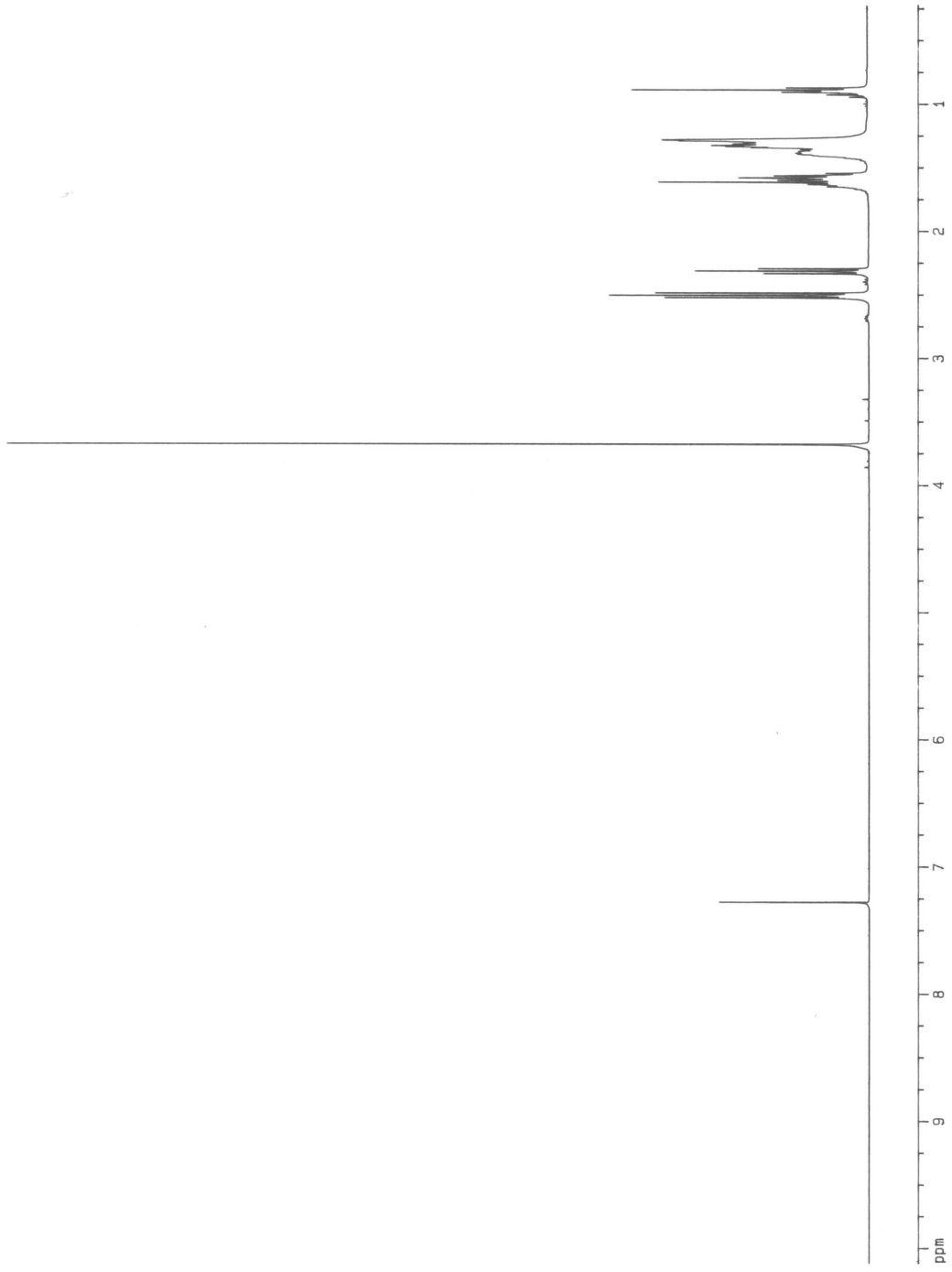
Methyl 9-thiapentadecanoate



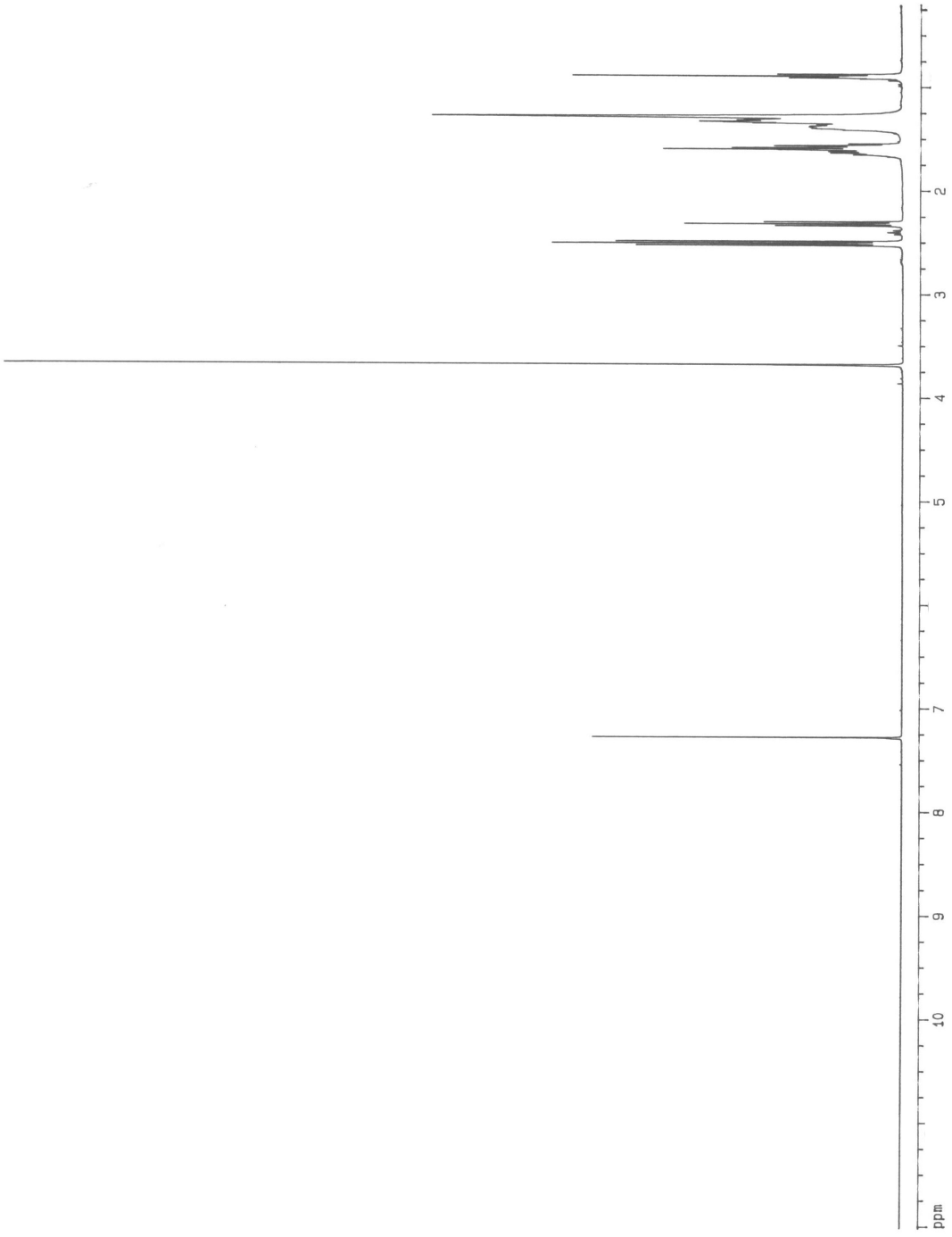
Methyl 9-thiahexadecanoate



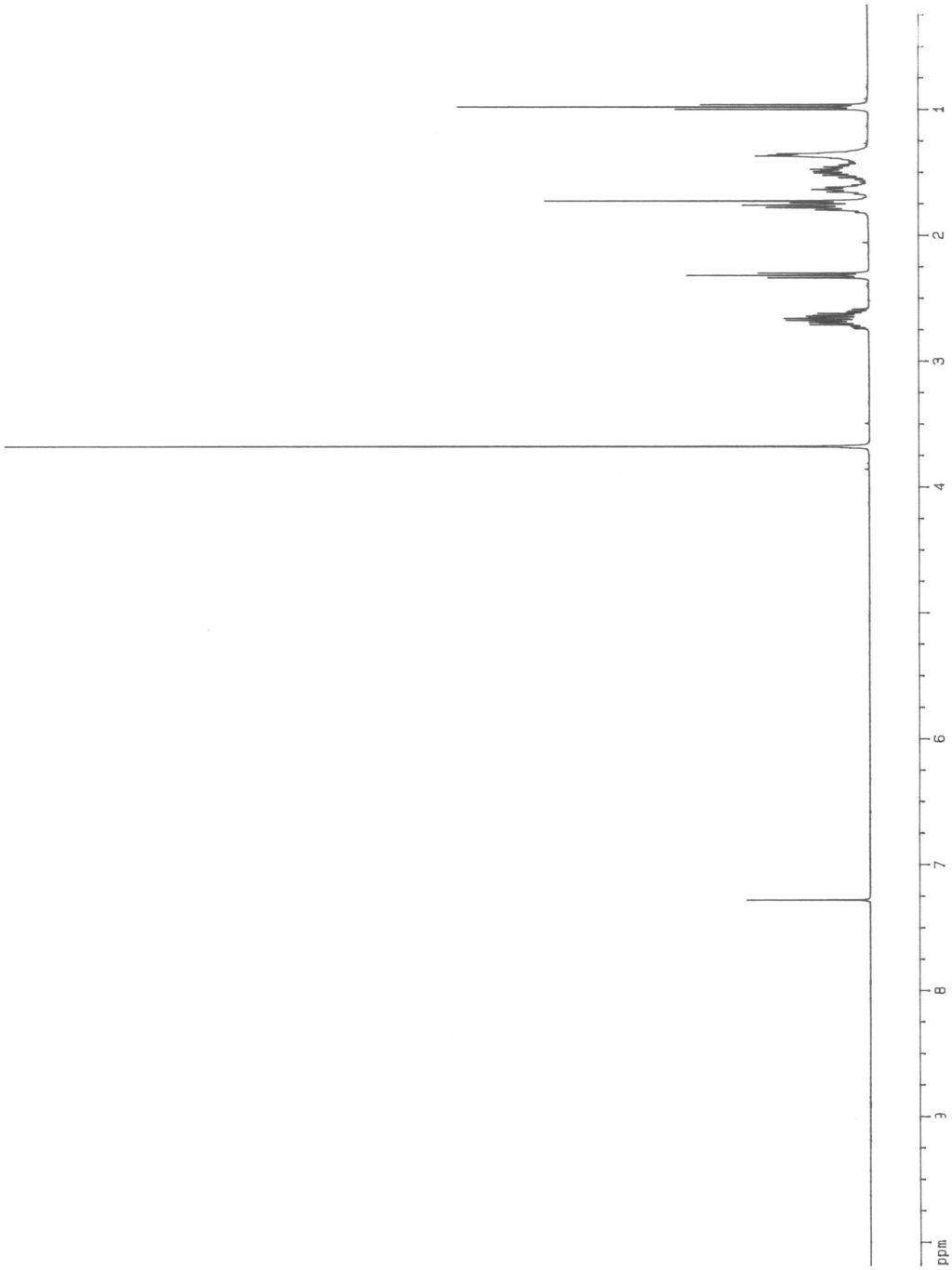
Methyl 9-thiaheptadecanoate



Methyl 9-thiaoctadecanoate



(*R*,*S*)-Methyl 9-thiatridecanoate S-oxide



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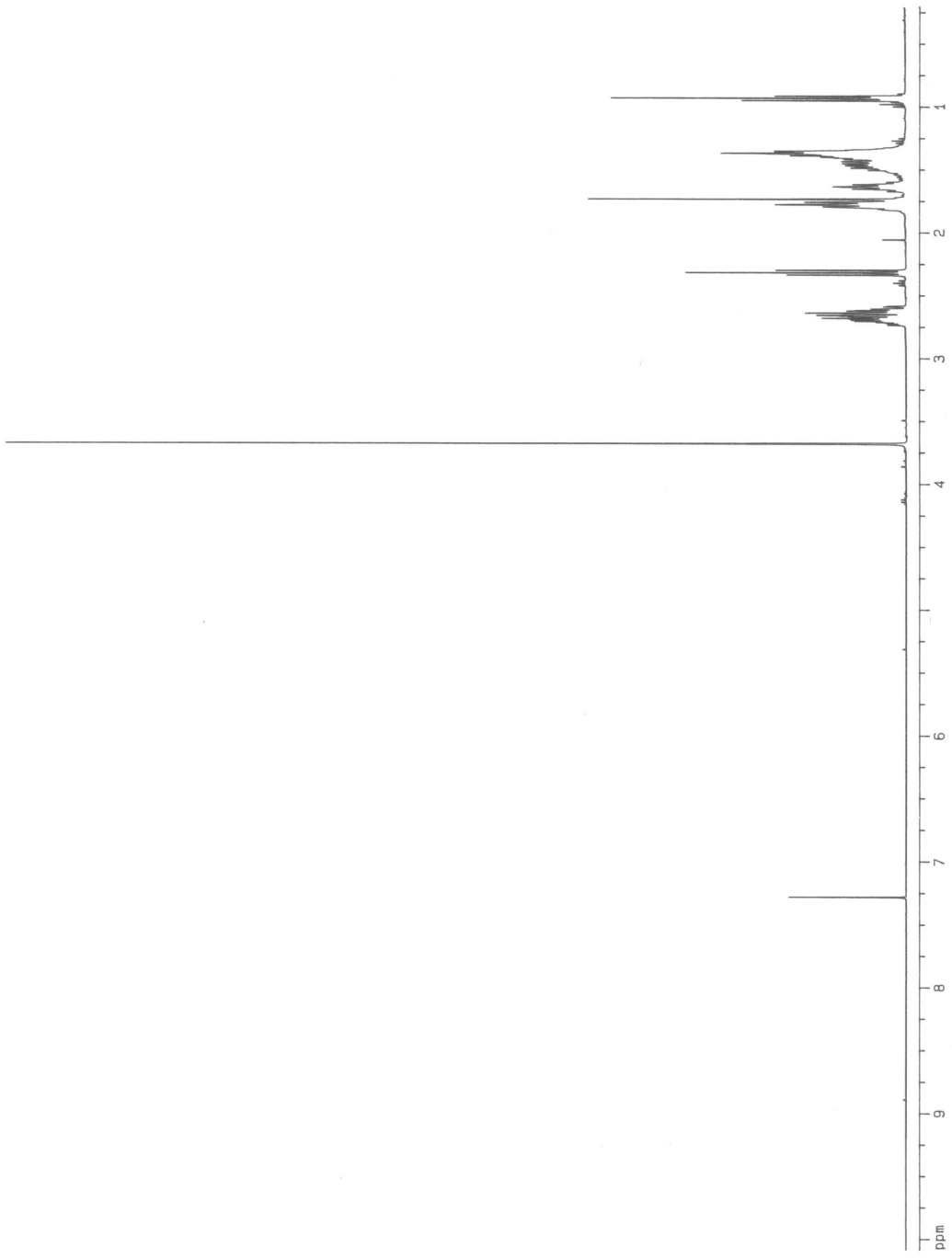

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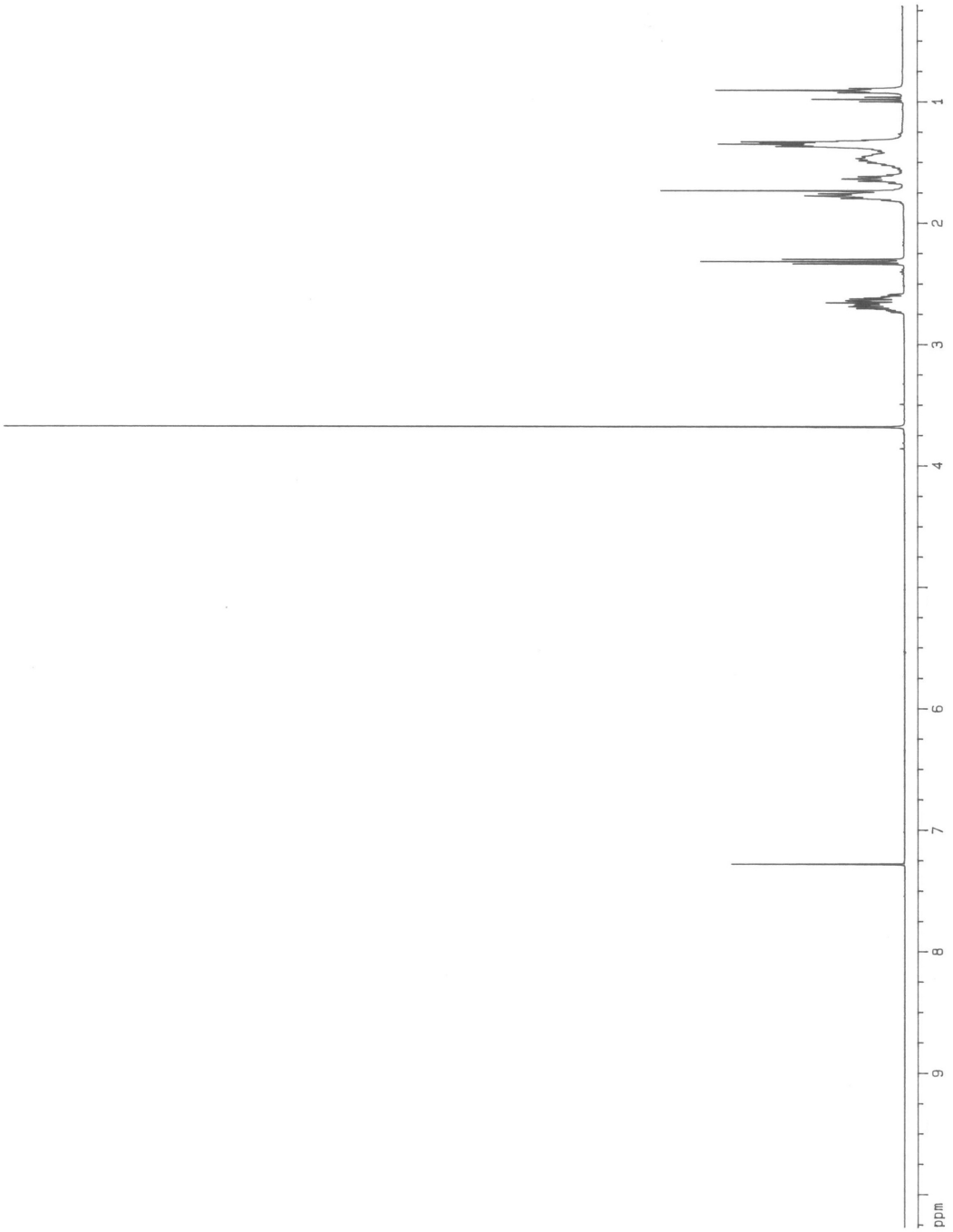

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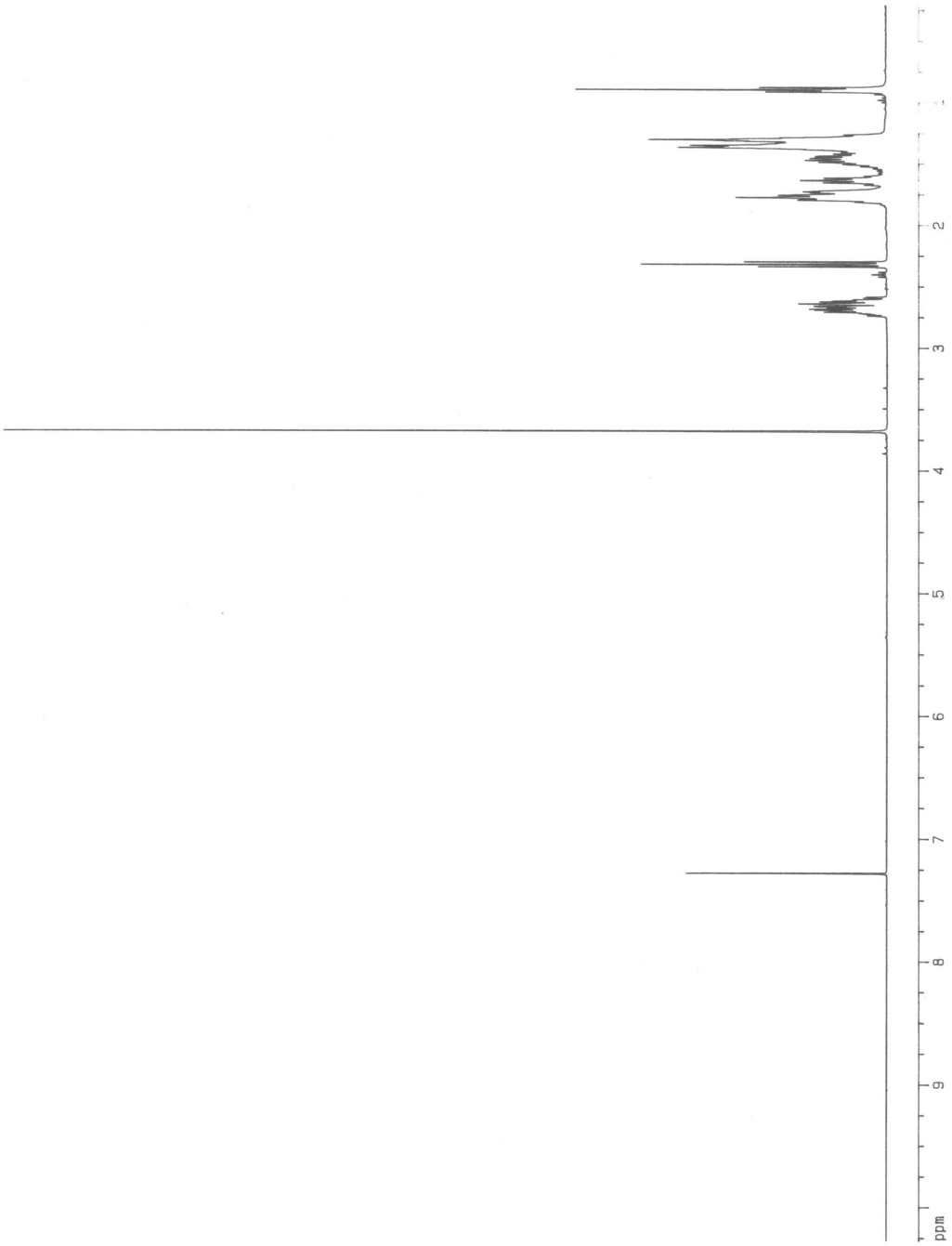

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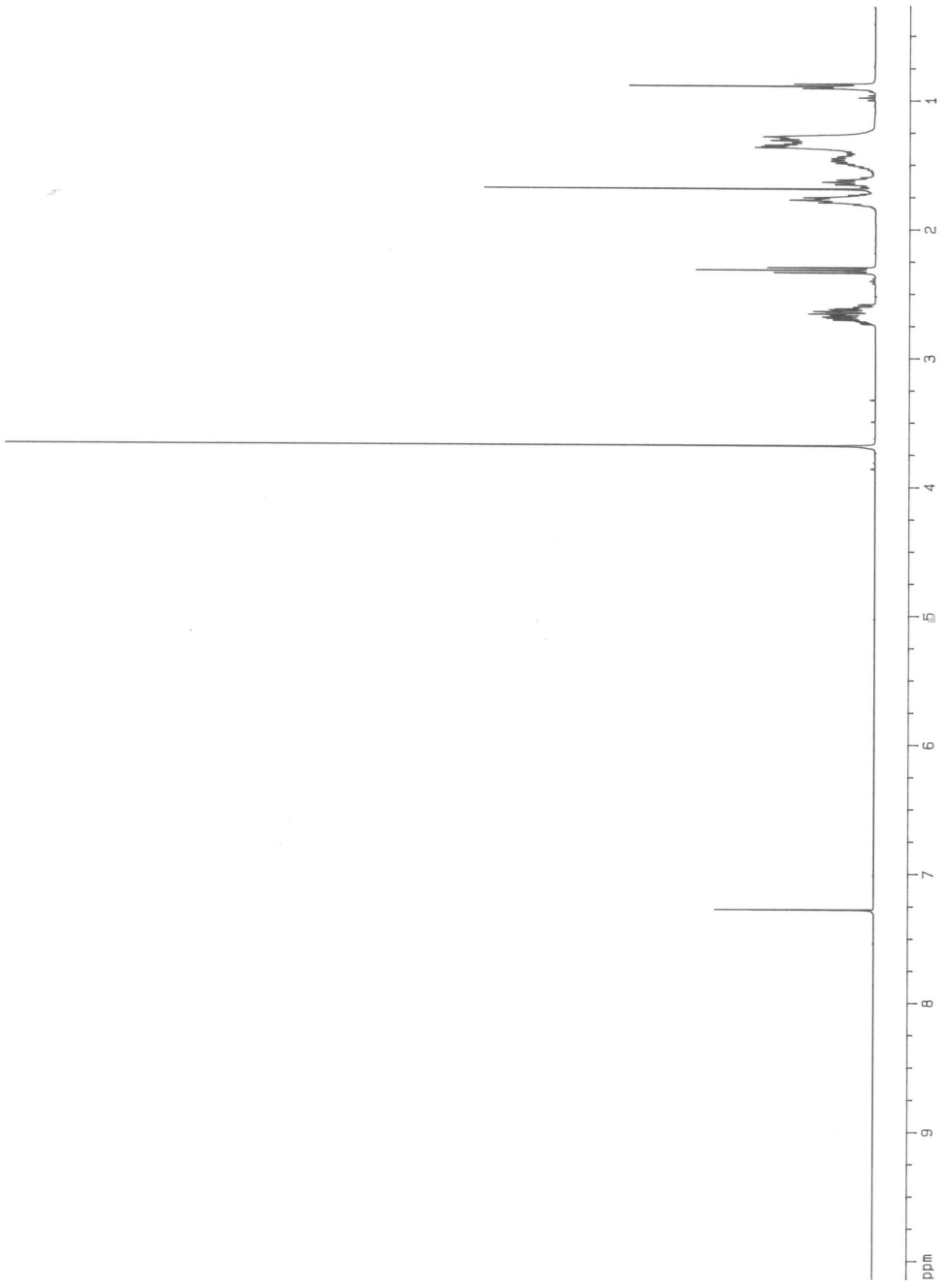
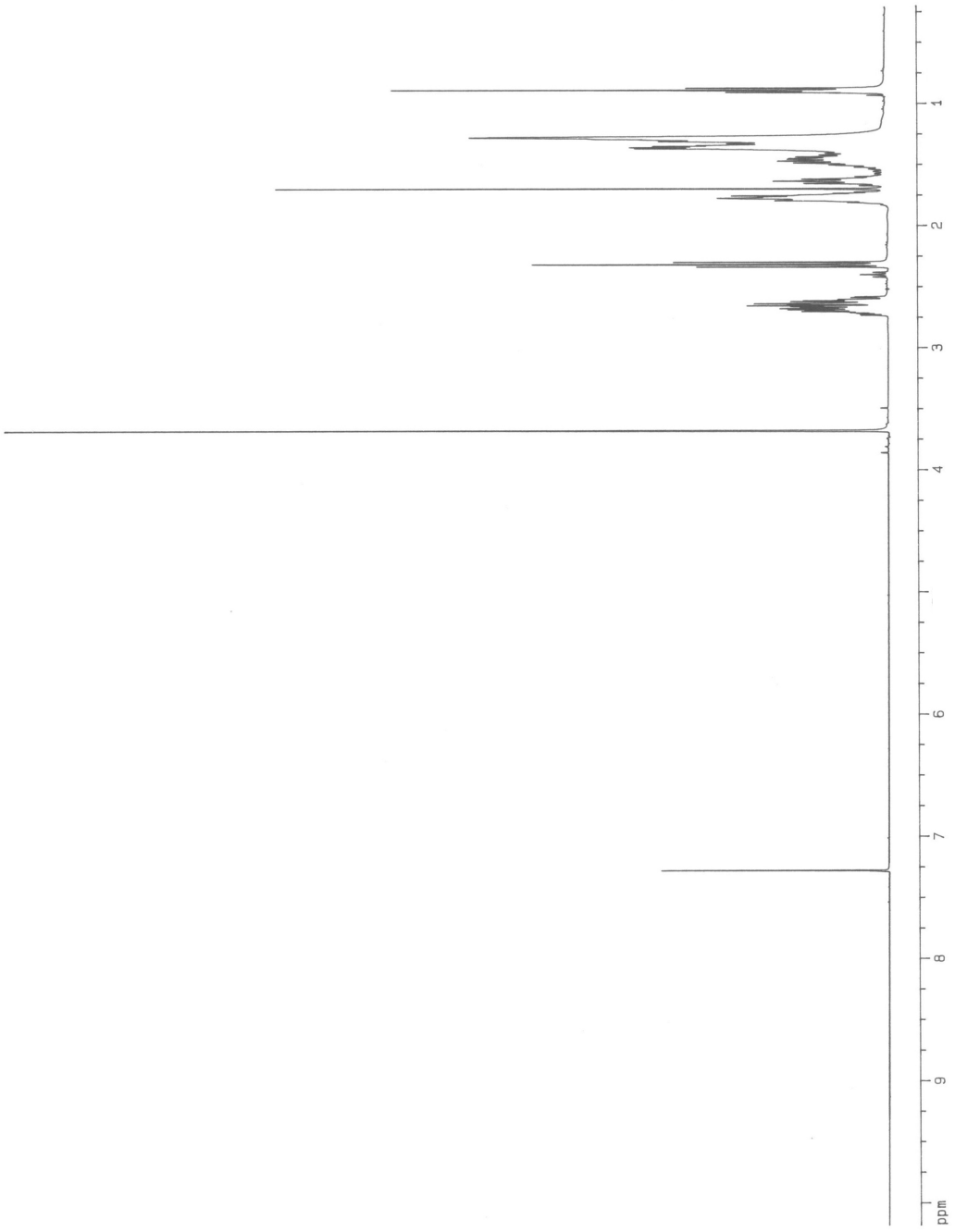
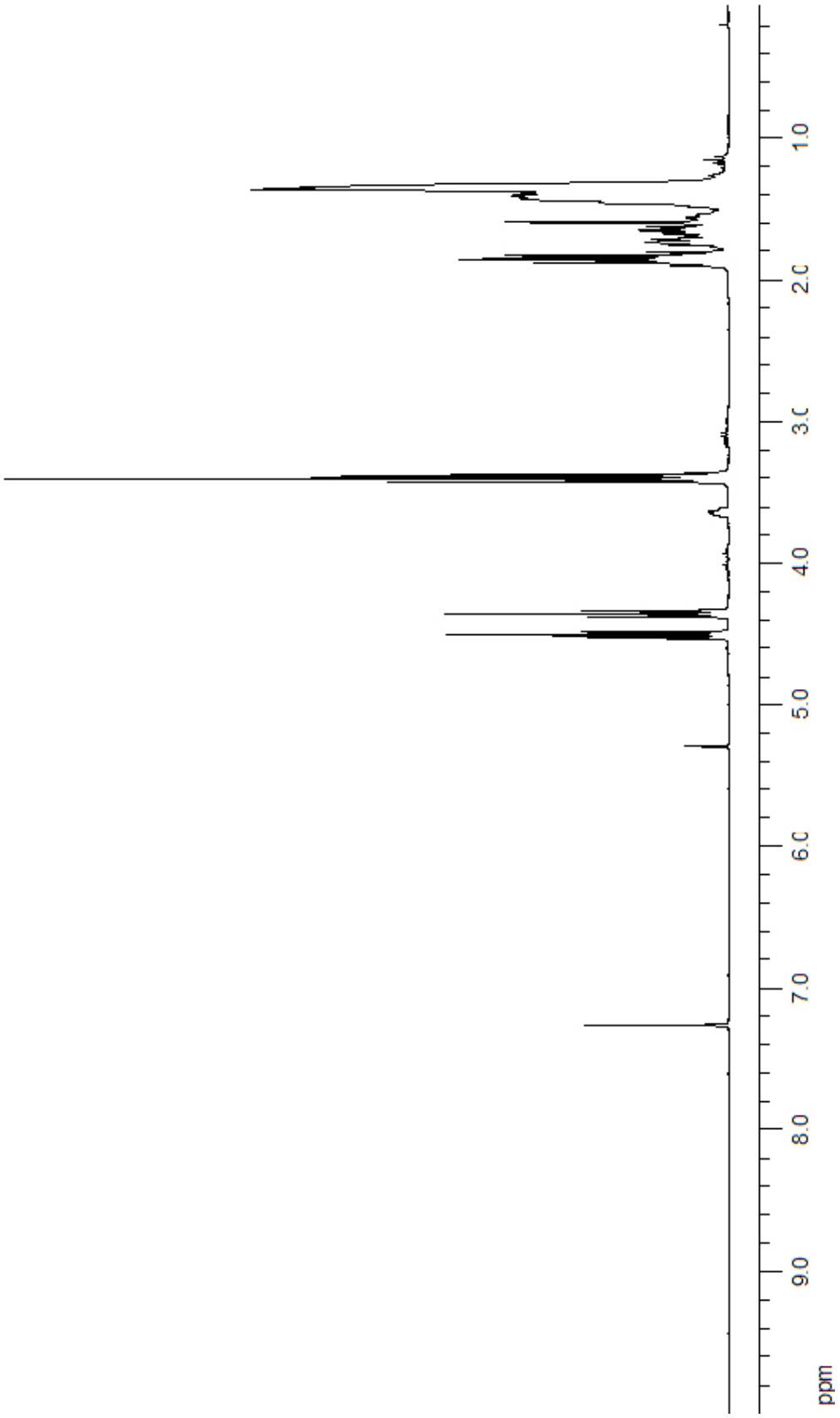


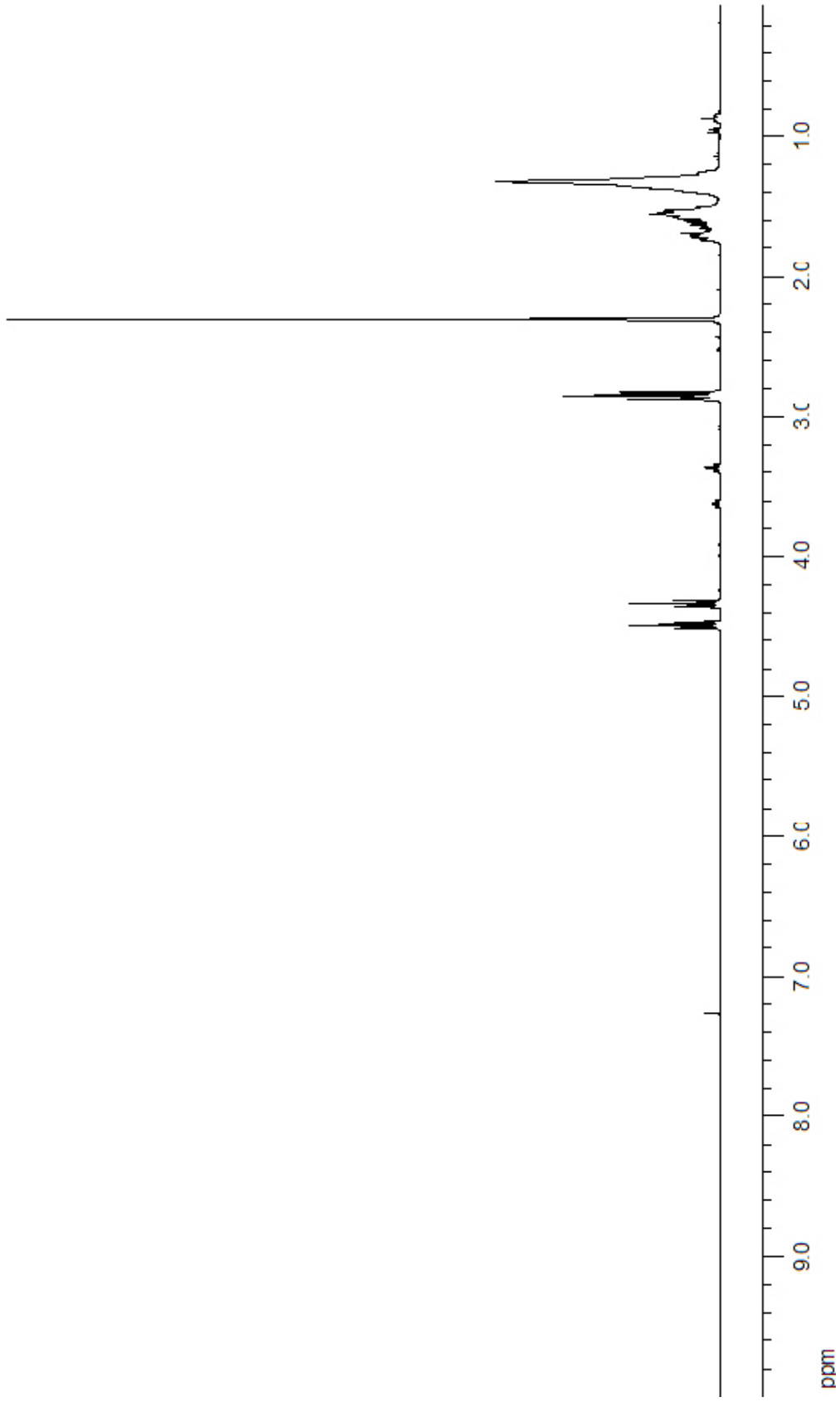
(*R*,*S*)-Methyl 9-thiaoctadecanoate S-oxide



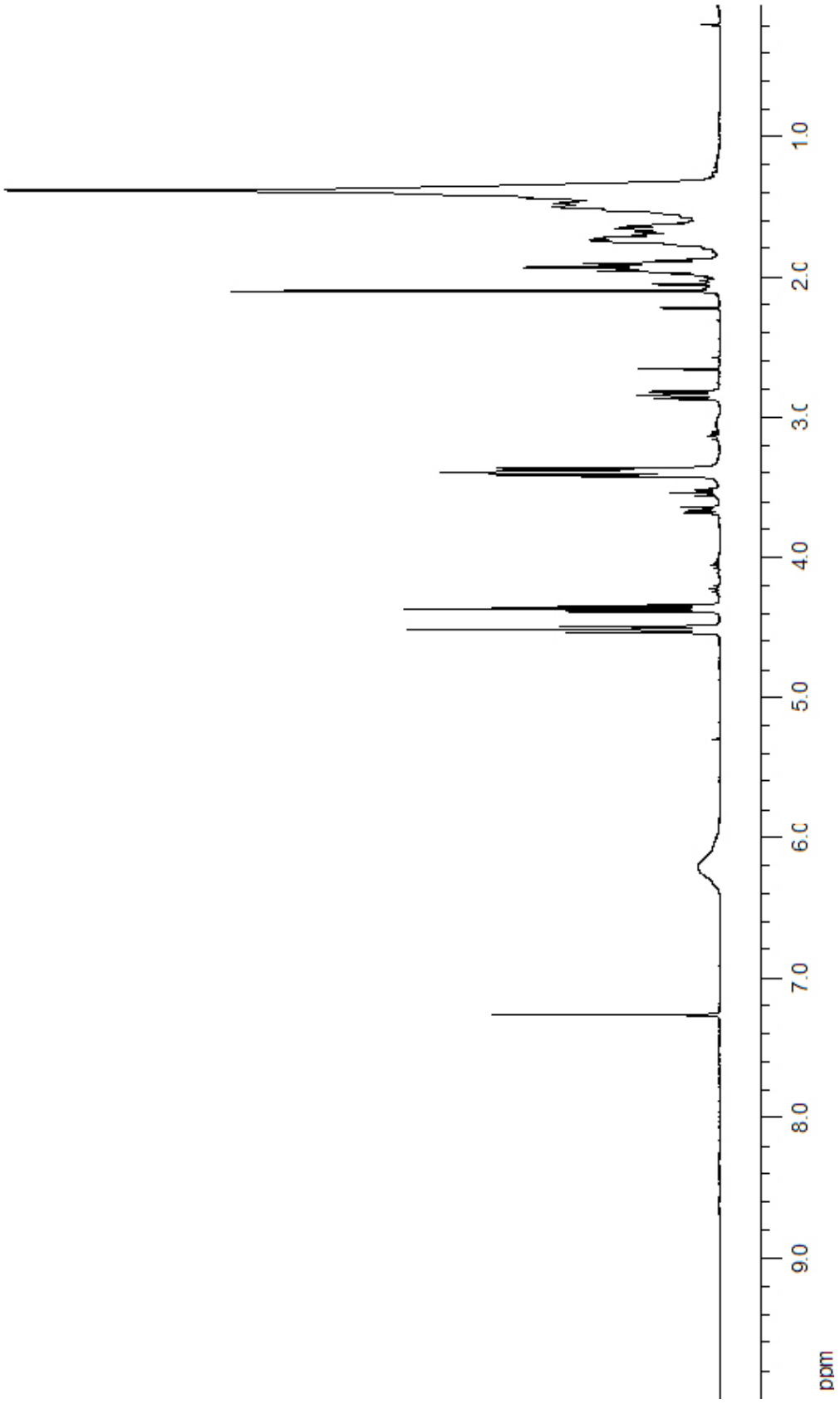
1-Bromo-8-fluorooctane



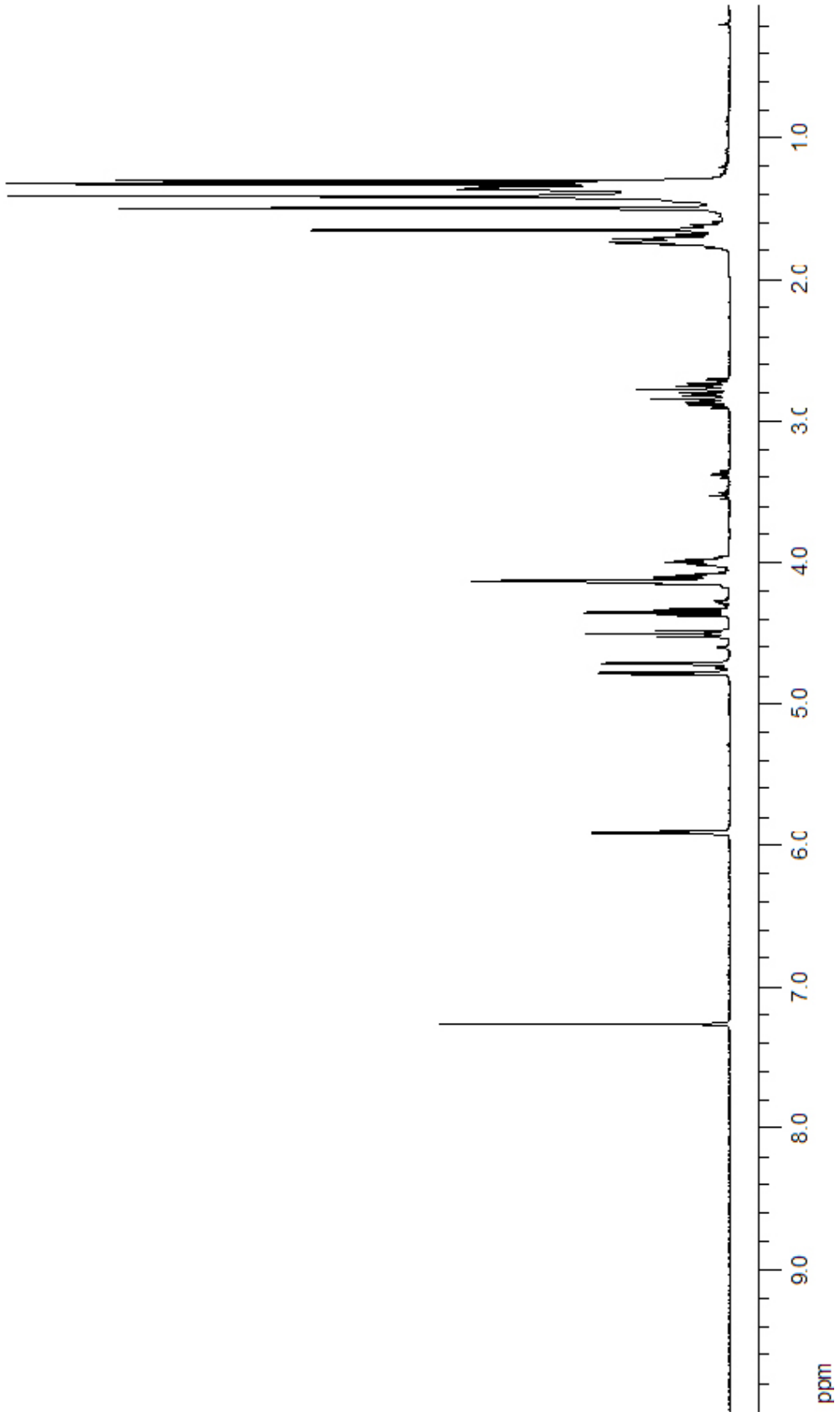
Thioacetic acid S-(8-fluoro-octyl) ester



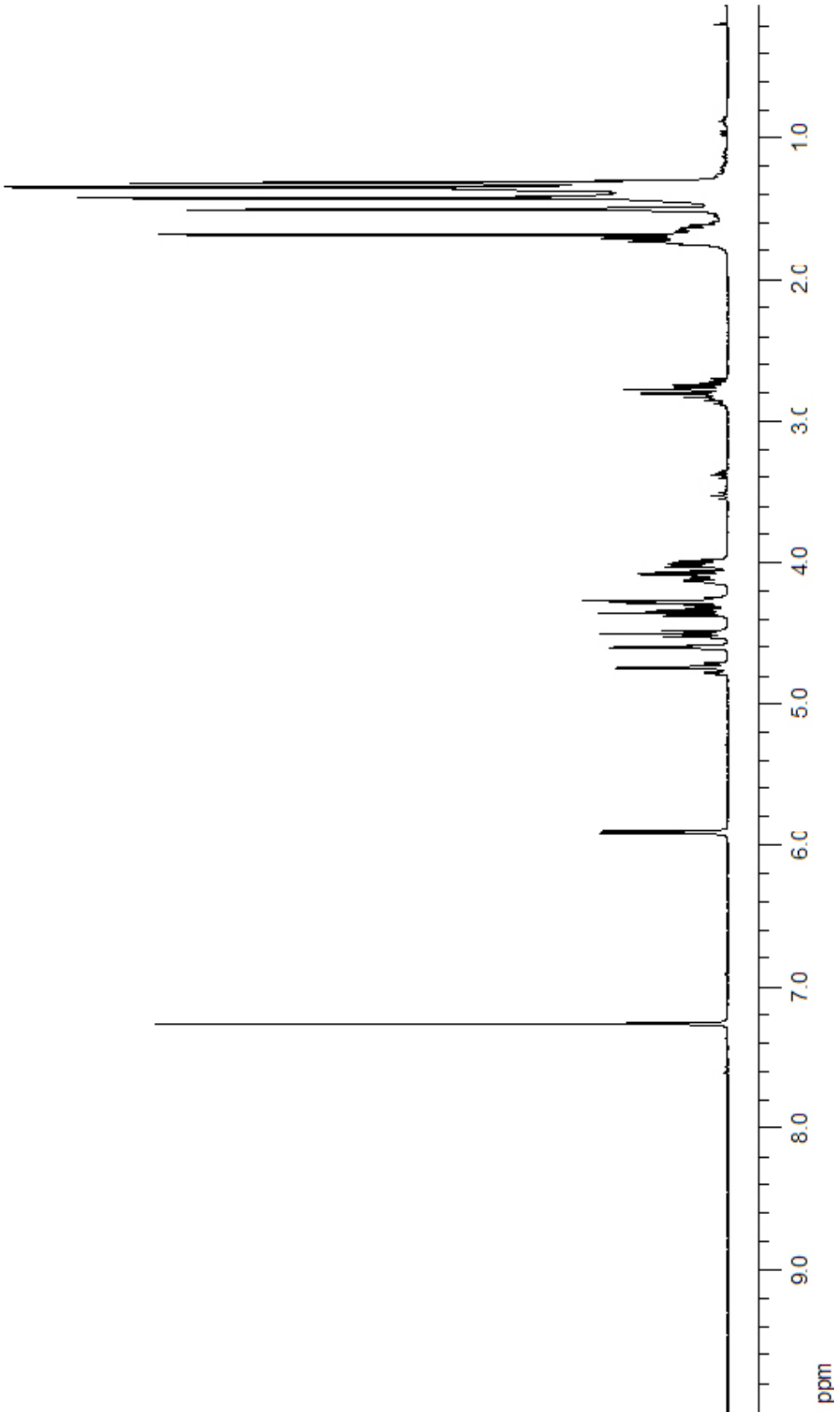
8-Fluorooctanesulfinyl chloride



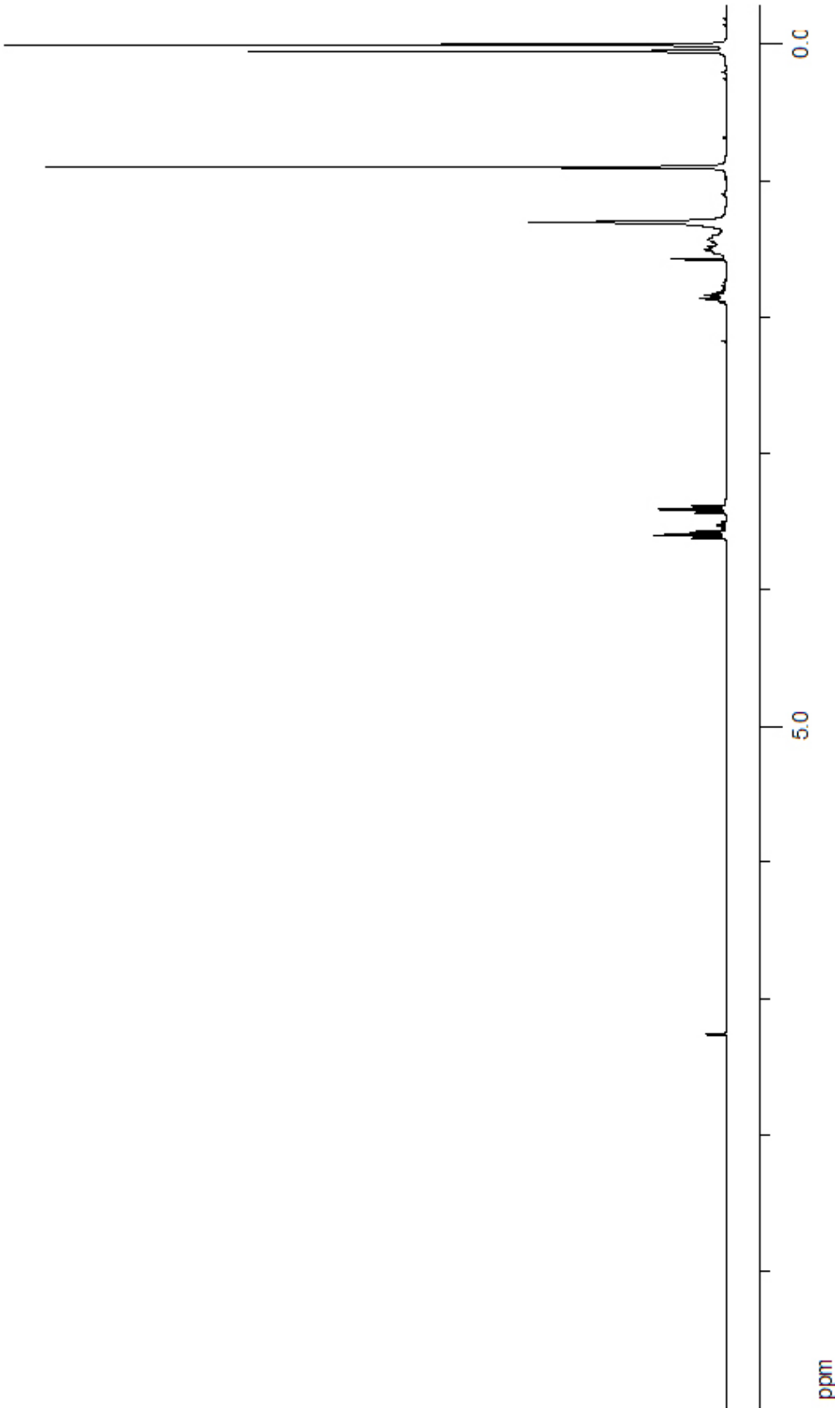
1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl (+)-(*R*)-8-fluorooctanesulfinate

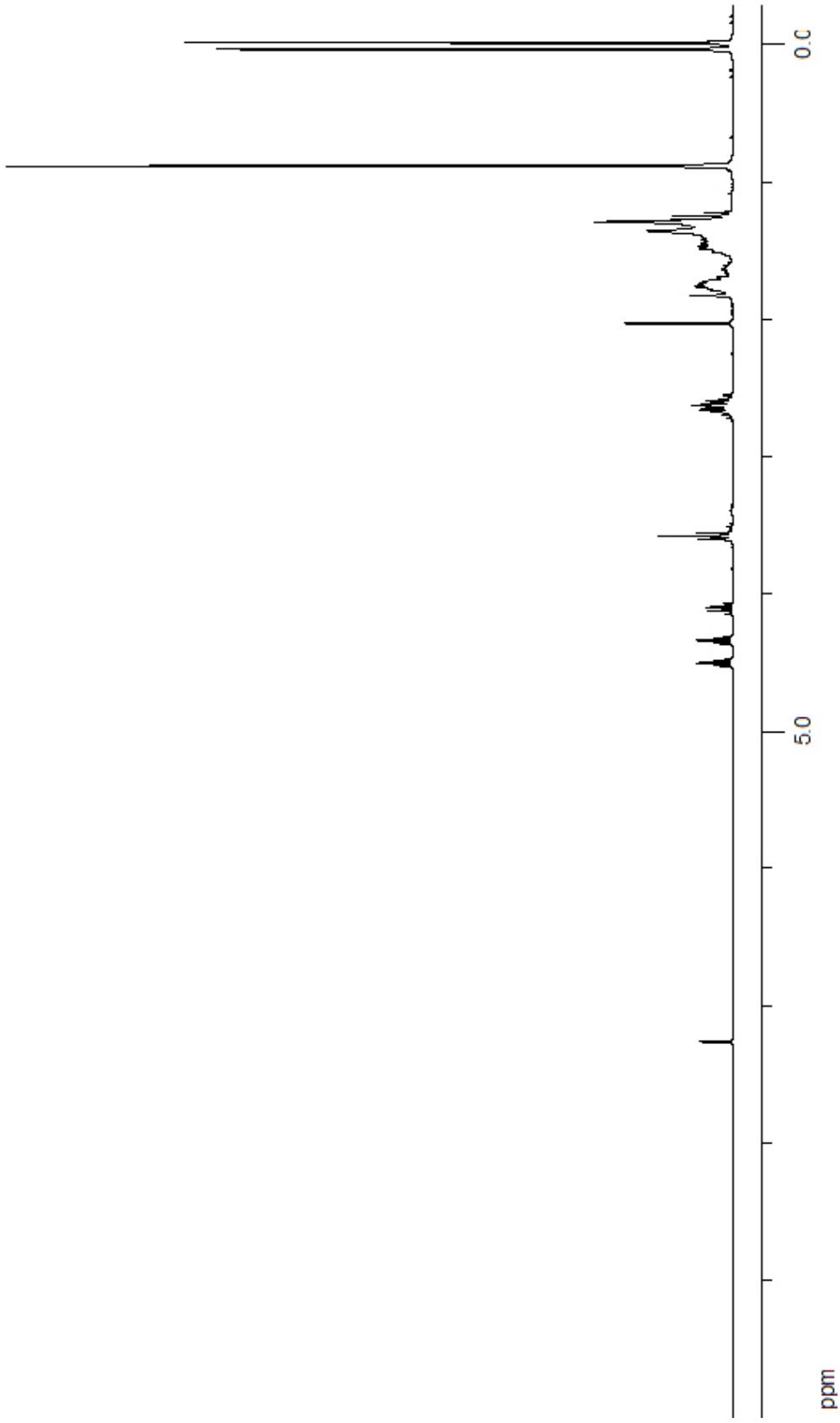


1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl (-)-(*S*)-8-fluorooctanesulfinate



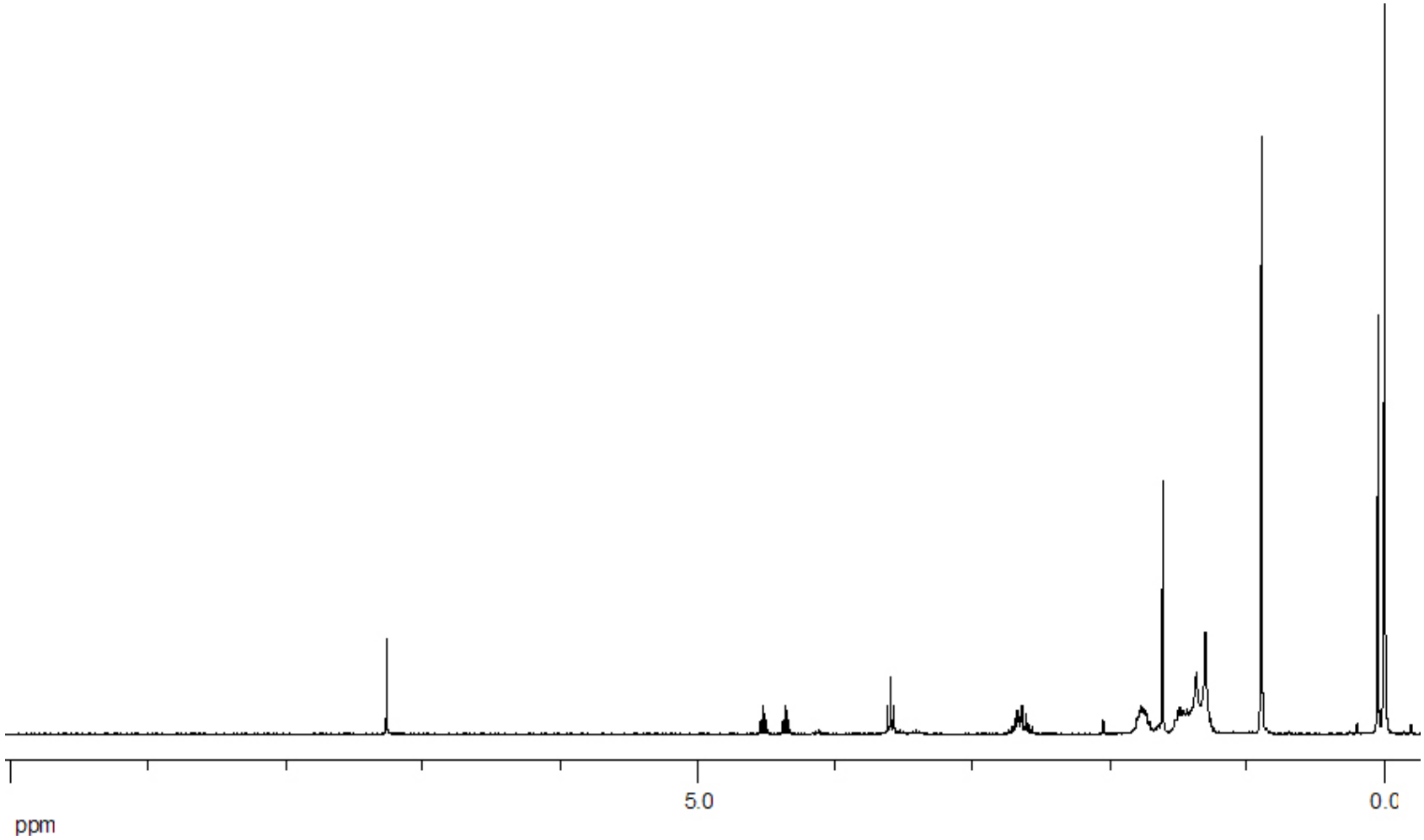
(9-Bromo-nonyloxy)-*tert*-butyl-dimethyl-silane.



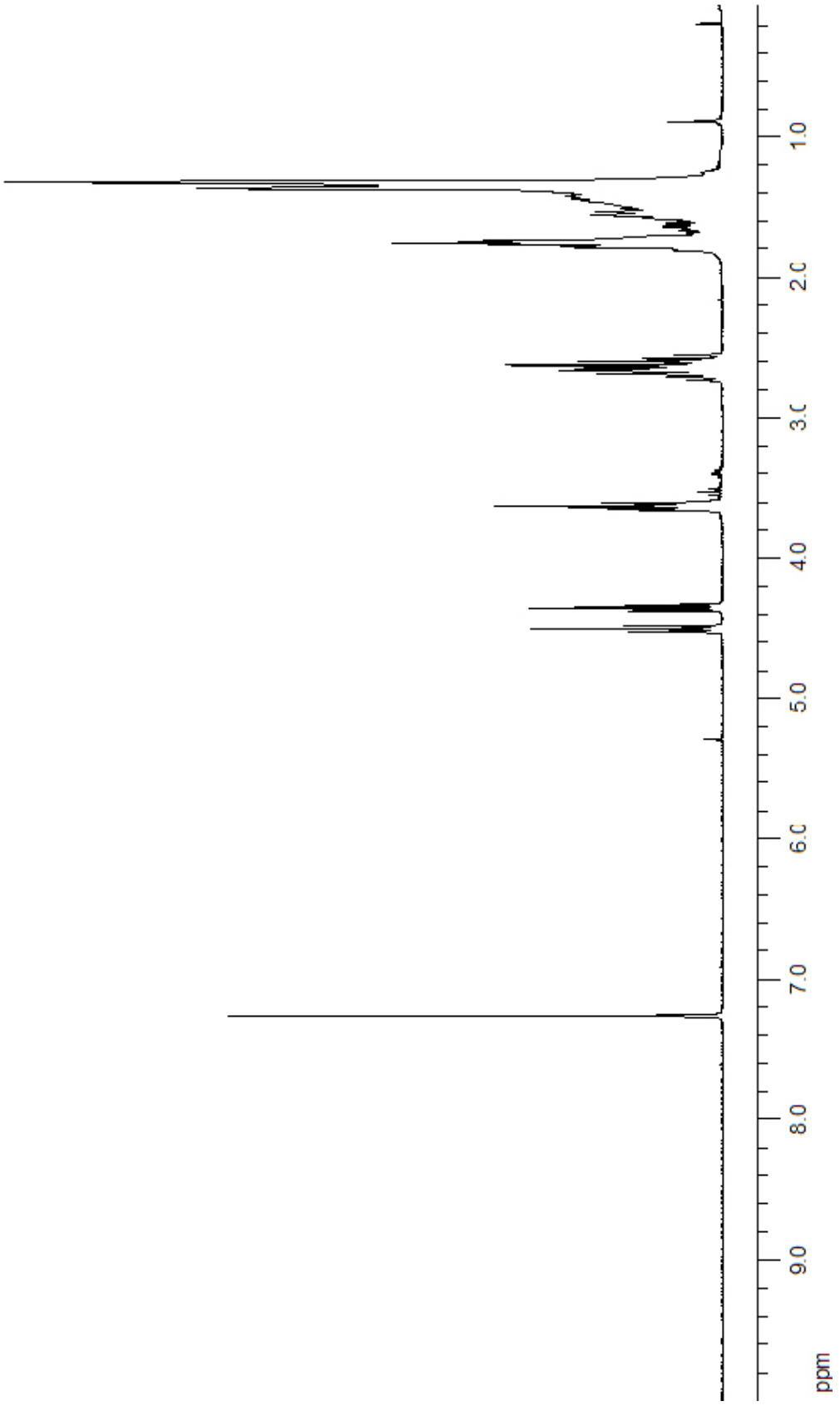


***tert*-Butyl-[10-(8-fluoro-octane-1-(*S*)-sulfinyl)-decyloxy]-dimethyl-silane**

***tert*-Butyl-[10-(8-fluoro-octane-1-(*R*)-sulfinyl)-decyloxy]-dimethyl-silane.**



10-(8-Fluoro-octane-1-(*S*)-sulfinyl)-decan-1-ol.



10-(8-Fluoro-octane-1-(*R*)-sulfinyl)-decan-1-ol.