Supplementary Information

Organocatalytic asymmetric oxy-Michael addition to a γ-hydroxy-α,β-unsaturated thioester *via* Hemiacetal Intermediates

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Instrumentation and Chemicals

^{1}H and ^{13}C Nuclear magnetic resonance spectra were taken on a Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane as an internal standard for ^{1}H NMR (δ = 0 ppm) and $CDCl_3$ as an internal standard for ^{13}C NMR (δ = 77.0 ppm). When a ^{13}C NMR spectrum was measured using D_2O as a solvent, CD_3OD was used as an internal standard (δ = 49.50 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration. ^{19}F NMR spectra were measured on a Varian Mercury 200 (^{19}F, 188 MHz) spectrometer with hexafluorobenzene as an internal standard (δ = 0 ppm). GC-MS analyses and High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. High performance liquid chromatography (HPLC) was performed with a SHIMADZU Prominence. Infrared (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. Melting points were determined using a YANAKO MP-500D. Optical rotations were measured on a HORIBA SEPA-200. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or such as an aqueous alkaline $KMnO_4$ solution followed by heating.

Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 μm). Unless otherwise noted, commercially available reagents were used without purification.

Experimental Procedure

General procedure for asymmetric oxy-Michael addition reaction

In a 5-mL vial, we sequentially added γ-hydroxy-α,β-unsaturated thioester **1** (0.25 mmol), cyclopentyl methyl ether (CPME, 0.25 mL), aldehyde **2** (0.5 mmol), and quinidine-derived bifunctional catalyst **4a** (0.025 mmol). The mixture was stirred in an oil bath maintained at 25 °C for 24 h. The reaction mixture was sequentially diluted with hexane/EtOAc (v/v = 1/1), passed through a short silica gel pad to remove **4a**, and concentrated in vacuo. Purification of the reaction mixture by flash silica gel column chromatography using hexane/Et_2O (v/v = 10/1) as an eluent afforded the corresponding oxy-Michael adduct **3** as a mixture of the diastereomers.

Racemic compounds were prepared using triethylamine as a catalyst.

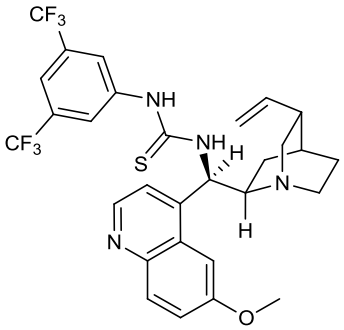
General procedure for preparation of bifunctional catalysts 4

Bifunctional organocatalysts **4** were prepared by the literature procedure.[1]

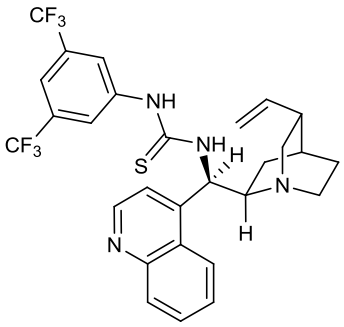
A cinchona alkaloid (5 mmol) and triphenylphosphine (1.6 g, 6 mmol) were dissolved in THF (25 mL), and the solution was cooled to 0 °C. Diethyl azodicarboxylate (1.0 g, 6 mmol) was subsequently added. To the resulting solution was added dropwise the solution of diphenyl phosphoryl azide (1.3 mL, 6 mmol) in THF (10 mL) at 0 °C. The mixture was allowed to warm to ambient temperature. After being stirred for 24 h, it was heated to 50 °C and stirred for 10 h. Triphenylphosphine (1.7 g, 6.5 mmol) was added again, and the mixture was stirred at 50 °C for additional 15 h. After the solution was cooled to ambient temperature, H_2O (0.5 mL) was added, and the solution was stirred for 24 h. The solvents were removed in vacuo, and the residue was dissolved in CH_2Cl_2/10% aqueous hydrochloric acid (25 mL/25 mL). The aqueous phase was separated and washed with CH_2Cl_2 (25 mL × 4). It was subsequently made alkaline with aqueous ammonia, and the aqueous phase was extracted with CH_2Cl_2 (25 mL × 4). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using EtOAc/CH_3OH (v/v = 9/1) then $CHCl_3$/CH_3OH (v/v = 8/2) as an eluent gave the corresponding 9-amino(9-deoxy)cinchona alkaloids. Next, to the solution of the obtained 9-amino(9-deoxy)cinchona alkaloid in THF (6 mL) was slowly added a solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (1 equiv) in THF (4 mL) at ambient temperature. The mixture was stirred overnight, and the solvents were removed in vacuo. Purification by flash silica gel column chromatography using EtOAc/CH_3OH (v/v = 95/5–97.5/2.5) or EtOAc as an eluent gave the corresponding bifunctional

organocatalyst **4**.

The characterization results are as below.

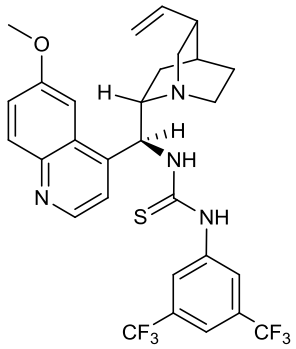


4a. White solid; 41% yield (for 2steps from quinidine). $[\alpha]_D^{23}$ +122.6 (*c* 1.33, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.65 (br s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.86 (s, 2H), 7.67 (s, 1H), 7.59 (br s, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.23 (br s, 1H), 5.86 (br s, 2H), 5.19 (br s, 1H), 5.15 (d, *J* = 9.5 Hz, 1H), 3.97 (s, 3H), 3.22 (br s, 1H), 3.10 (br s, 1H), 3.03 (m, 2H), 2.94 (m, 1H), 2.38 (m, 1H), 1.70 (s, 1H), 1.61 (m, 2H), 1.27 (br s, 1H), 1.02 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 181.0, 158.1, 147.3, 144.7, 144.5, 140.1, 139.6, 132.5 (q, *J* = 33.6 Hz), 131.6, 128.0, 123.5, 122.9 (q, *J* = 273.0 Hz), 122.3, 118.7, 115.3, 101.7, 61.4, 55.6, 48.5, 47.1, 38.7, 27.1, 26.1, 25.0. Mp. 125.0–125.2 °C. IR (KBr): 3221, 2944, 2361, 1735, 1623, 1511, 1475, 1384, 1278, 1177, 1134, 1034, 959, 916, 884, 850, 826, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{28}F_6N_4OS$: $[M+H]^+$, 595.1966. Found: *m*/*z* 595.1961.

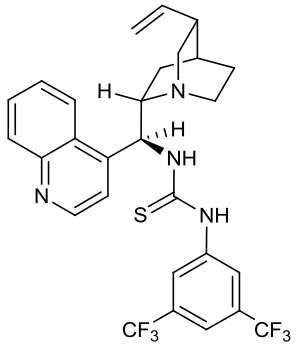


4b. White solid; 36% yield (for 2steps from cinchonine). $[\alpha]_D^{23}$ +163.3 (*c* 1.23, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.83 (br s, 1H), 8.28 (br s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.85 (br s, 2H), 7.56 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.68 (s, 1H), 7.64 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.29 (br s, 1H), 5.81 (br s, 2H), 5.14 (m, 2H), 3.21 (br s, 1H), 3.00 (m, 3H), 2.92 (br s, 1H), 2.36 (m, 1H), 1.66 (s, 1H), 1.59 (m, 2H), 1.22 (br s, 1H), 0.95 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 181.3, 150.0, 148.6, 145.8, 140.2, 139.3, 132.5 (q, *J* = 33.6 Hz), 130.5, 129.5, 127.1, 126.7, 123.4, 122.9 (q, *J* = 273.1 Hz), 122.8, 119.0, 118.7, 115.5, 61.8, 55.7, 48.5, 47.0, 38.9, 27.3, 26.0, 24.9. Mp. 189.9–190.3 °C. IR (KBr): 3428, 3246,

2944, 2360, 1622, 1588, 1512, 1474, 1386, 1281, 1183, 1126, 960, 882, 848, 752, 682 cm^{-1}. HRMS Calcd for $C_{28}H_{26}F_6N_4S$: $[M+H]^+$, 565.1861. Found: *m*/*z* 565.1855.



4c. White solid; 27% yield (for 2steps from quinine). $[\alpha]_D^{23}$ –99.0 (*c* 1.24, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 8.60 (br s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.82 (br s, 2H), 7.68 (s, 1H), 7.62 (br s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.18 (br s, 1H), 5.84 (br s, 1H), 5.70 (m, 1H), 5.01 (m, 2H), 3.96 (s, 3H), 3.37 (br s, 1H), 3.30 (br s, 1H), 3.18 (m, 1H), 2.79 (br s, 2H), 2.35 (br s, 1H), 1.72 (s, 1H), 1.68 (m, 2H), 1.41 (m, 1H), 0.92 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 181.0, 158.2, 147.4, 144.8, 144.0, 140.6, 140.0, 132.6 (q, *J* = 33.6 Hz), 131.8, 127.9, 123.6, 122.9 (q, *J* = 273.0 Hz), 122.0, 118.8, 115.1, 102.1, 61.2, 55.7, 54.9, 41.3, 39.0, 27.5, 27.1, 25.7. Mp. 121.0–121.5 °C. IR (neat): 3220, 2946, 2360, 1623, 1510, 1475, 1384, 1279, 1180, 1134, 1032, 959, 917, 885, 850, 683 cm^{-1}. HRMS Calcd for $C_{29}H_{28}F_6N_4OS$: $[M+H]^+$, 595.1966. Found: *m*/*z* 595.1961.



4d. White solid; 44% yield (for 2steps from cinchonidine). $[\alpha]_D^{23}$ –101.0 (*c* 1.24, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 8.80 (br s, 1H), 8.35 (br s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 2H), 7.74 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.69 (s, 1H), 7.63 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.27 (br s, 1H), 5.78 (br s, 1H), 5.67 (m, 1H), 4.98 (m, 2H), 3.26 (m, 1H), 3.20 (br s, 1H), 3.17 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.78 (m, 2H), 2.33 (br s, 1H), 1.70 (m, 2H), 1.63 (m, 1H), 1.33 (m, 1H), 0.93 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 180.9, 149.9, 148.5, 145.9,

140.7, 139.9, 132.6 (q, J = 33.6 Hz), 130.4, 129.5, 127.0, 123.6, 122.9 (q, J = 273.0 Hz), 119.1, 118.9, 115.0, 61.5, 56.5, 54.9, 41.1, 39.2, 27.5, 27.1, 25.7. Mp. 122.8–123.1 °C. IR (neat): 3240, 3081, 2946, 2366, 1510, 1473, 1384, 1281, 1181, 1135, 990, 958, 884, 849, 755, 683 cm^{-1}. HRMS Calcd for $C_{28}H_{26}F_6N_4S$: $[M+H]^+$, 565.1861. Found: m/z 565.1855.

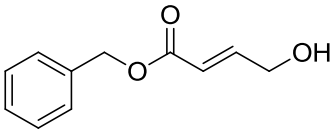
Procedure for preparation of γ-hydroxy-α,β-unsaturated ester 1a[2]

To a stirred solution of 3-butenoic acid (8.5 mL, 100 mmol) and pyridine (20.2 mL, 250 mmol) in CH_2Cl_2 (95 mL) was slowly added benzyl chloroformate (15.0 mL, 105 mmol) at room temperature, and the mixture was stirred at room temperature for 4 h. The crude was filtered with celite, and the mixture was extracted with EtOAc. The combined organic layers were washed with aqueous NH_4Cl and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 40/1) as an eluent gave benzyl 3-butenoate as a colorless oil in 67% yield.

To the solution of obtained benzyl 3-butenoate (11.8 g, 66.8 mmol) in CH_2Cl_2 (95 mL) was added *m*-CPBA (48.2 g, 201 mmol) in several portions at room temperature. After the addition of *m*-CPBA, the whole was stirred for 3 days. Aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$ were added to the solution, and the mixture was extracted with EtOAc. The combined organic layers were washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave benzyl 2-(oxiran-2-yl)acetate as a colorless oil in 84% yield.

To the solution of benzyl 2-(oxiran-2-yl)acetate (10.8 g, 56.0 mmol) in CH_2Cl_2 (200 mL) was added DBU (8.8 mL, 58.8 mmol) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. 2N Aqueous HCl was added to the solution, and the mixture was extracted with EtOAc. The combined organic layers were washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 1/1) as an eluent gave (*E*)-benzyl 4-hydroxybut-2-enoate (**1a**) in 92% yield.

(*E*)-Benzyl 4-hydroxybut-2-enoate (1a). CAS RN [586952-09-2].



Colorless oil.

^{1}H NMR ($CDCl_3$) δ 7.39–7.30 (m, 5H), 7.09 (dt, *J* =15.5, 4.0 Hz, 1H), 6.16 (dt, *J* =15.5, 4.0 Hz, 1H), 5.20 (s, 2H), 4.36 (ddd, *J* = 6.0, 4.0, 2.0 Hz, 2H), 1.65 (t, *J* = 6.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 166.2, 147.5, 135.9, 128.5, 128.2, 128.2, 119.7, 66.3, 61.8. TLC: R_f 0.20 (hexane/EtOAc = 2:1).

General Procedure for preparation of γ-hydroxy-α,β-unsaturated carboxylic acid derivatives 1b–1c, 1e–1f[3,4]

To a stirred solution of an alcohol or a thiol in CH_2Cl_2 (0.72 M) was slowly added pyridine (1.0 equiv) and bromoacetyl bromide (1.0 equiv) at 0 °C, and the mixture was stirred at 0 °C for 15 min and at room temperature for additional 20 min. H_2O was added to the solution, and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 20/1) as an eluent gave the corresponding α-bromo ester or thioester.

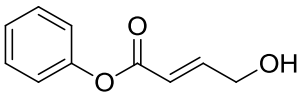
Next, the mixture of the ester or the thioester and triphenylphosphine (1.2 equiv) in benzene (1.0 M) was stirred at room temperature for 18 h. The reaction slurry was filtered, and the obtained solid was washed with benzene, and dried under reduced pressure.

This salt was dissolved in the mixture of CH_2Cl_2 (0.10 M) and 2N aqueous NaOH (0.13 M), and the solution was stirred for 30 min. The organic layers were separated, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Removal of the solvent under reduced pressure provided the corresponding stabilized ylide in nearly quantitative yield from the alcohol or the thiol.

Next, the mixture of stabilized ylide (1.2 equiv) and glycolaldehyde dimer (1.0 equiv) in THF (0.17 M) was stirred at rt–80 °C for hours. After being stirred, the solvent was evaporated. Purification by flash silica gel column chromatography using hexane/EtOAc as an eluent gave the corresponding γ-hydroxy-α,β-unsaturated carboxylic acid derivative (**1b**–**1c**, **1e**–**1f)**.

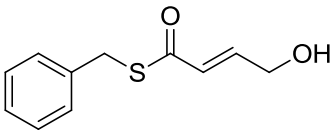
The characterization results of **1b**–**1c**, **1e**–**1f** are as below.

(*E*)-Phenyl 4-hydroxybut-2-enoate (1b).



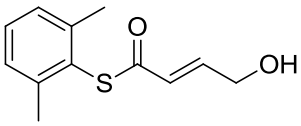
Colorless oil; 99% yield (for last step).
^{1}H NMR ($CDCl_3$) δ 7.43–7.38 (m, 2H), 7.28–7.22 (m, 2H), 7.16–7.12 (m, 2H), 6.34 (dt, *J* = 15.5, 2.0 Hz, 1H), 4.42 (m, 2H), 2.23 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 164.8, 150.6, 149.2, 129.4, 125.8, 121.5, 119.3, 61.8. TLC: R_f 0.14 (hexane/EtOAc = 2:1). IR (neat): 3443, 3043, 2903, 2362, 1737, 1659, 1592, 1494, 1299, 1276, 1197, 1164, 1146, 1098, 1023, 955, 918, 730, 690 cm^{-1}. HRMS Calcd for $C_{10}H_{10}O_3$: $[M+H]^+$, 179.0703. Found: *m*/*z* 179.0698.

(*E*)-S-Benzyl 4-hydroxybut-2-enethioate (1c).



White solid; 70% yield (for last step).
^{1}H NMR ($CDCl_3$) δ 7.33–7.27 (m, 4H), 7.26–7.22 (m, 1H), 6.98 (dt, *J* = 15.5, 4.0 Hz, 1H), 6.41 (dt, *J* = 15.5, 2.0 Hz, 1H), 4.36 (ddd, *J* = 6.0, 4.0, 2.0 Hz, 2H), 4.21 (s, 2H), 1.63 (t, *J* = 6.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 189.0, 143.1, 137.5, 128.9, 128.6, 127.3, 126.6, 61.8, 33.1. Mp. 39.1–39.4 °C. TLC: R_f 0.20 (hexane/EtOAc = 3:1). IR (KBr): 3354, 3089, 3066, 3030, 2917, 2856, 1946, 1876, 1800, 1678, 1633, 1497, 1440, 1395, 1262, 1099, 1045, 955, 902, 833, 771, 701, 612, 567, 479 cm^{-1}. HRMS Calcd for $C_{11}H_{12}O_2S$: $[M+H]^+$, 209.0631. Found: *m*/*z* 209.0629.

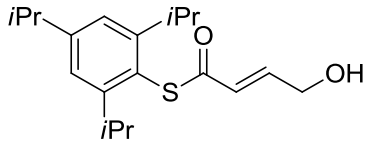
(*E*)-S-(2,6-Dimethylphenyl) 4-hydroxybut-2-enethioate (1e).



White solid; 94% yield (for last step).
^{1}H NMR ($CDCl_3$) δ 7.24 (dd, *J* = 8.0, 6.5 Hz, 1H), 7.17 (d, *J* =8.0 Hz, 2H), 7.03 (dt, *J* = 15.5, 4.0 Hz, 1H), 6.53 (dt, *J* = 15.5, 2.0 Hz, 1H), 4.39 (dd, *J* = 4.0, 2.0 Hz, 2H), 2.36 (s, 6H), 1.71 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 187.0, 143.4, 142.9, 129.9, 128.3, 126.7, 126.4, 61.8, 21.7. Mp. 73.9–74.2 °C. TLC: R_f 0.41 (hexane/EtOAc = 2:1). IR (KBr): 3424, 3054, 2910, 2826, 1682, 1636, 1462, 1438, 1374, 1255, 1102, 1036, 952, 910, 827, 775, 719, 620 cm^{-1}. HRMS Calcd for $C_{12}H_{14}O_2S$: $[M+H]^+$, 223.0784.

Found: *m*/*z* 223.0784.

(*E*)-S-(2,4,6-Triisopropylphenyl) 4-hydroxybut-2-enethioate (1f).



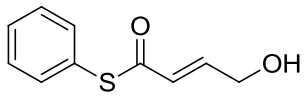
Pale yellow oil; 64% yield (for last step).
^{1}H NMR ($CDCl_3$) δ 7.09 (s, 2H), 7.03 (dt, *J* = 15.5, 4.0 Hz, 1H), 6.55 (dt, *J* = 15.5, 2.0 Hz, 1H), 4.40 (ddd, *J* = 6.0, 4.0, 2.0 Hz, 2H), 3.40 (sept, *J* = 7.0 Hz, 2H), 2.91 (sept, *J* = 7.0 Hz, 1H), 1.64 (br s, 1H), 1.27 (d, *J* = 7.0 Hz, 6H), 1.18 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$) δ 188.9, 152.5, 151.1, 143.5, 126.2, 122.0, 121.2, 61.6, 34.3, 31.9, 24.3, 23.8, 23.5. TLC: R_f 0.28 (hexane/EtOAc = 3:1). IR (neat): 3451, 2962, 2929, 2869, 2362, 1678, 1635, 1598, 1464, 1383, 1362, 1260, 1144, 1100, 1032, 955, 877, 825 cm^{-1}. HRMS Calcd for $C_{19}H_{28}O_2S$: $[M+H]^+$, 321.1883. Found: *m*/*z* 322.1877.

Procedure for preparation of γ-hydroxy-α,β-unsaturated thioester 1d

The mixture of S-phenyl 2-(triphenylphosphoranylidene)ethanethioate (3.91 g, 9.47 mmol) and 2-((triisopropylsilyl)oxy)acetaldehyde (1.77 g, 7.89 mmol) in THF (70 mL) was stirred at 50 °C for 24 h. After being stirred, the solvent was evaporated. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave (*E*)-S-phenyl 4-((triisopropylsilyl)oxy)but-2-enethioate as a pale yellow solid in 90% yield.

To the stirred solution of (*E*)-S-phenyl 4-((triisopropylsilyl)oxy)but-2-enethioate (2.50 g, 7.13 mmol) in CH_3CN (30 mL) was added aqueous HF (2.0 mL) at room temperature, and the mixture was stirred for 2 h. Aqueous $NaHCO_3$ was added to the solution, and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave (*E*)-S-phenyl 4-hydroxybut-2-enethioate (**1d**) in 48% yield.

(*E*)-S-Phenyl 4-hydroxybut-2-enethioate (1d).



Pale yellow oil.
^{1}H NMR ($CDCl_3$) δ 7.47–7.41 (m, 5H), 7.03 (dt, *J* = 15.5, 4.0 Hz, 1H), 6.48 (dt, *J* = 15.5, 2.0 Hz, 1H), 4.35 (dd, *J* = 4.0, 2.0 Hz, 2H), 2.15 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 188.2, 144.1, 134.5, 129.4, 129.2, 127.3, 125.9, 61.6. TLC: R_f 0.19 (hexane/EtOAc = 2:1). IR (neat): 3423, 3060, 2918, 2850, 2369, 1774, 1678, 1634, 1479, 1441, 1141, 1099, 1037, 951, 823, 746, 690, 493 cm^{-1}. HRMS Calcd for $C_{10}H_{10}O_2S$: $[M+H]^+$, 195.0474. Found: *m*/*z* 195.0472.

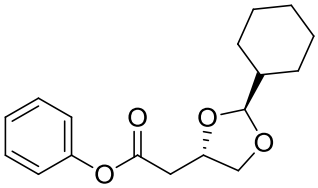
All aldehydes and ketones **2** listed in this manuscript were commercially available.

Characterization Data of Products

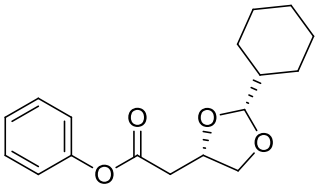
Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 10/1) as an eluent.

Yield: 13%, dr = 3.0:1.



Major diastereomer (3ba): 96% *ee*, colorless oil. $[\alpha]_D^{26}$ –32.3 (*c* 1.18, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.41–7.36 (m, 2H), 7.27–7.22 (m, 1H), 7.10–7.06 (m, 2H), 4.80 (d, *J* = 5.0 Hz, 1H), 4.54 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.26 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.64 (dd, *J* = 8.5, 6.5 Hz, 1H), 2.97 (dd, *J* = 15.5, 6.5 Hz, 1H), 2.77 (dd, *J* = 15.5, 7.0 Hz, 1H), 1.81–1.71 (m, 4H), 1.69–1.64 (m, 1H), 1.58–1.51 (m, 1H), 1.28–1.03 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 169.1, 150.3, 129.5, 126.0, 121.5, 107.4, 71.9, 70.2, 41.8, 38.3, 27.3, 27.0, 26.3, 25.7, 25.7. TLC: R_f 0.33 (hexane/Et_2O = 3:1). IR (neat): 3356, 2926, 2854, 2360, 1759, 1593, 1494, 1452, 1355, 1282, 1196, 1164, 1134, 1071, 936, 889, 815, 747, 690cm^{-1}. HRMS Calcd for $C_{17}H_{22}O_4$: $[M+H]^+$, 291.1591. Found: *m*/*z* 291.1579. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 99.5/0.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 28.4 min, t_{major} = 31.4 min.

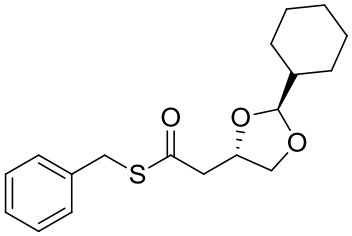


Minor diastereomer (3ba'): 84% *ee*, colorless oil. $[\alpha]_D^{26}$ –4.4 (*c* 0.20, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.41–7.36 (m, 2H), 7.27–7.22 (m, 1H), 7.11–7.07 (m, 2H), 4.68 (d, *J* = 5.0 Hz, 1H), 4.54 (dddd, *J* = 7.0, 6.5, 6.5, 5.5 Hz, 1H), 4.06 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.77 (dd, *J* = 8.0, 5.5 Hz, 1H), 2.94 (dd, *J* = 15.5, 6.5 Hz, 1H), 2.77 (dd, *J* = 15.5, 7.0 Hz, 1H), 1.82–1.73 (m, 4H), 1.69–1.57 (m, 2H), 1.32–1.06 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 169.2, 150.4, 129.5, 126.0, 121.5, 108.0, 71.9, 69.6, 41.5, 39.2, 27.3, 27.1, 26.4, 25.7, 25.7. TLC: R_f 0.30 (hexane/Et_2O = 3:1). IR (neat): 3347, 2923, 2852, 2360, 1758, 1594, 1494, 1457, 1340, 1261, 1197, 1163, 1134, 1070, 935, 890, 802, 745, 689 cm^{-1}. HRMS Calcd for $C_{17}H_{22}O_4$: $[M+H]^+$, 291.1591. Found: *m*/*z* 291.1582. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 99.5/0.5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 13.3 min, t_{major} = 15.1 min.

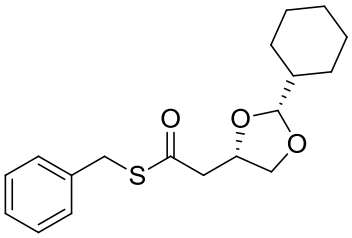
S-Benzyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using toluene/Et_2O (v/v = 80/1) as an eluent.

Yield: 18%, dr = 3.6:1.



Major diastereomer (3ca): 94% *ee*, colorless oil. $[\alpha]_D^{27}$ –23.8 (*c* 0.84, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.33–7.23 (m, 5H), 4.73 (d, *J* = 4.5 Hz, 1H), 4.46 (dddd, *J* = 7.0, 6.5, 6.5, 6.5 Hz, 1H), 4.17 (dd, *J* = 8.5, 6.5 Hz, 1H), 4.15 (s, 2H), 3.56 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.10 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.82 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.79–1.72 (m, 4H), 1.69–1.64 (m, 1H), 1.58–1.49 (m, 1H), 1.28–1.13 (m, 3H), 1.13–1.02 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 195.6, 137.2, 128.8, 128.6, 127.3, 107.3, 72.1, 70.1, 47.1, 41.8, 33.3, 27.3, 27.0, 26.4, 25.7, 25.7. R_f 0.40 (toluene/Et_2O = 80:1). IR (neat): 3356, 3064, 3031, 2926, 2853, 2362, 2347, 1685, 1603, 1497, 1452, 1240, 1187, 1153, 1135, 1072, 995, 945, 888, 770, 701, 639 cm^{-1}. HRMS Calcd for $C_{16}H_{22}O_3S$: $[M+H]^+$, 321.1519. Found: *m*/*z* 321.1504. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 98.5/1.5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 8.1 min, t_{minor} = 10.4 min.

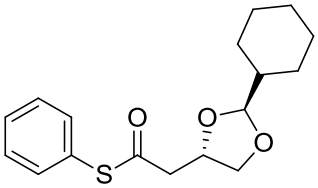


Minor diastereomer (3ca'): 61% *ee*, colorless oil. $[\alpha]_D^{27}$ –4.0 (*c* 0.63, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.32–7.22 (m, 5H), 4.62 (d, *J* = 4.5 Hz, 1H), 4.44 (dddd, *J* = 7.0, 6.5, 6.0, 5.0 Hz, 1H), 4.14 (s, 2H), 3.96 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.56 (dd, *J* = 8.0, 5.0 Hz, 1H), 2.96 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.73 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.79–1.71 (m, 4H), 1.68–1.62 (m, 1H), 1.58–1.49 (m, 1H), 1.24–1.02 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 195.7, 137.2, 128.8, 128.7, 127.3, 108.0, 72.2, 69.5, 48.0, 41.6, 33.3, 27.3, 27.1, 26.4, 25.8, 25.7. R_f 0.36 (toluene/Et_2O = 80:1). IR (neat): 3356, 3064, 3031, 2925, 2854, 2360, 2345, 1685, 1603, 1507, 1452, 1261, 1237, 1187, 1153, 1134, 1072, 998, 946, 888, 770, 700, 639 cm^{-1}. HRMS Calcd for $C_{16}H_{22}O_3S$: $[M+H]^+$, 321.1519. Found: *m*/*z* 321.1505. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 98.5/1.5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 6.4 min, t_{minor} = 7.8 min.

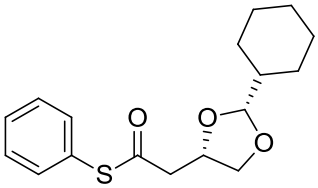
S-Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 15/1) as an eluent.

Yield: 7%, dr = 3.7:1.



Major diastereomer (3da): 97% *ee*, colorless oil. $[\alpha]_D^{26}$ –25.2 (*c* 1.20, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.45–7.39 (m, 5H), 4.75 (d, *J* = 4.5 Hz, 1H), 4.45 (dddd, *J* = 7.0, 6.5, 6.5, 6.5 Hz, 1H), 4.19 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.58 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.11 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.83 (dd, *J* = 15.0, 7.5 Hz, 1H), 1.80–1.72 (m, 4H), 1.69–1.63 (m, 1H), 1.56–1.49 (m, 1H), 1.28–1.12 (m, 3H), 1.12–1.01 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 194.8, 134.5, 129.6, 129.3, 127.1, 107.3, 72.0, 70.2, 46.8, 41.7, 27.3, 27.0, 26.3, 25.7, 25.6. R_f 0.40 (hexane/Et_2O = 5:1). IR (neat): 3385, 3061, 2926, 2853, 2757, 2669, 2360, 1701, 1584, 1479, 1441, 1410, 1344, 1304, 1267, 1225, 1187, 1153, 1135, 1068, 978, 888, 861, 843, 746, 706, 689, 631 cm^{-1}. HRMS Calcd for $C_{17}H_{22}O_3S$: $[M+H]^+$, 307.1362. Found: *m*/*z* 307.1352. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 15.8 min, t_{major} = 24.1 min.

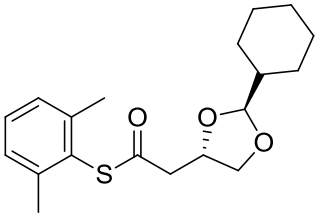


Minor diastereomer (3da'): 87% *ee*, colorless oil. $[\alpha]_D^{26}$ –10.0 (*c* 0.25, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.45–7.38 (m, 5H), 4.63 (d, *J* = 5.0 Hz, 1H), 4.45 (dddd, *J* = 7.5, 6.5, 6.0, 5.0 Hz, 1H), 3.98 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.72 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.08 (dd, *J* = 15.5, 6.0 Hz, 1H), 2.82 (dd, *J* = 15.5, 7.5 Hz, 1H), 1.80–1.72 (m, 4H), 1.70–1.64 (m, 1H), 1.60–1.55 (m, 1H), 1.32–1.06 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 194.9, 134.5, 129.6, 129.3, 127.1, 107.9, 72.1, 69.5, 47.7, 41.5, 27.3, 27.0, 26.4, 25.7, 25.7. R_f 0.36 (hexane/Et_2O = 5:1). IR (neat): 2925, 2853, 2755, 2670, 2364, 1700, 1560, 1477, 1441, 1420, 1340, 1305, 1266, 1225, 1189, 1153, 1134, 1068, 981, 888, 860, 843, 746, 706, 689, 668 cm^{-1}. HRMS Calcd for $C_{17}H_{22}O_3S$: $[M+H]^+$, 307.1362. Found: *m*/*z* 307.1351. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 19.2 min, t_{major} = 26.6 min.

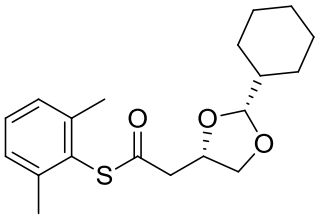
S-(2,6-Dimethylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 10/1) as an eluent.

Yield: 90%, dr = 4.4:1.



Major diastereomer (3ea): 96% *ee*, colorless oil. $[\alpha]_D^{27}$ –27.2 (*c* 2.26, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.77 (d, *J* = 5.0 Hz, 1H), 4.46 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.18 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.61 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.10 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.82 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 1.80–1.71 (m, 4H), 1.69–1.64 (m, 1H), 1.56–1.48 (m, 1H), 1.28–1.12 (m, 3H), 1.12–1.02 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 193.8, 142.7, 130.0, 128.3, 126.7, 107.4, 72.4, 70.1, 46.8, 41.9, 27.2, 27.2, 26.4, 25.7, 25.7, 21.6. TLC: R_f 0.62 (hexane/Et_2O = 2:1). IR (neat): 3368, 2926, 2854, 1699, 1583, 1464, 1452, 1412, 1376, 1344, 1304, 1264, 1225, 1186, 1153, 1135, 1079, 1033, 982, 945, 888, 802, 772, 719, 640 cm^{-1}. HRMS Calcd for $C_{19}H_{26}O_3S$: $[M+H]^+$, 335.1675. Found: *m*/*z* 335.1658. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 98.5/1.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.4 min, t_{major} = 12.9 min.



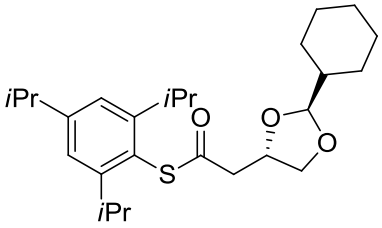
Minor diastereomer (3ea'): 81% *ee*, colorless oil. $[\alpha]_D^{27}$ –31.3 (*c* 0.40, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.63 (d, *J* = 5.0 Hz, 1H), 4.46 (dddd, *J* = 7.0, 6.5, 6.5, 5.0 Hz, 1H), 3.97 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.61 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.07 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.80 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 1.82–1.73 (m, 4H), 1.70–1.65 (m, 1H), 1.61–1.52 (m, 1H), 1.30–1.04 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 193.9, 142.7, 130.0, 128.3, 126.8, 108.0, 72.4, 69.5, 47.9, 41.6, 27.2, 27.2, 26.4, 25.7, 21.7. TLC: R_f 0.58 (hexane/Et_2O = 2:1). IR (neat): 3377, 2925, 2853, 1696, 1584, 1464, 1452, 1405, 1377, 1351, 1304, 1265, 1223, 1187, 1153, 1134, 1080, 1034, 987, 948, 888, 802, 773, 719, 639 cm^{-1} HRMS Calcd for $C_{19}H_{26}O_3S$: $[M+H]^+$, 335.1675. Found: *m*/*z* 335.1659. HPLC (Daicel Chiralcel OJ-H,

hexane/*i*-PrOH = 98.5/1.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.0 min, t_{major} = 16.5 min.

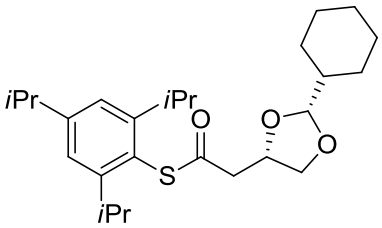
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using toluene/Et_2O (v/v = 100/1) as an eluent.

Yield: 28%, dr = 4.0:1.



Major diastereomer (3fa): 93% *ee*, colorless oil. $[\alpha]_D^{27}$ –18.2 (*c* 0.55, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.08 (s, 2H), 4.78 (d, *J* = 5.5 Hz, 1H), 4.45 (dddd, *J* = 6.5, 6.5, 6.5, 6.0 Hz, 1H), 4.16 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.59 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.38 (br s, 2H), 3.10 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.90 (sept, *J* = 7.0 Hz, 1H), 2.82 (dd, *J* = 14.5, 6.5 Hz, 1H), 1.80–1.72 (m, 4H), 1.69–1.64 (m, 1H), 1.57–1.48 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 6H), 1.24–1.19 (m, 2H), 1.18 (d, *J* = 7.0 Hz, 6H), 1.17 (d, *J* = 7.0 Hz, 6H), 1.14–1.02 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 195.4, 152.4, 151.3, 122.1, 121.3, 107.3, 72.5, 70.1, 46.6, 41.9, 34.3, 31.9, 27.2, 27.1, 26.4, 25.7, 25.7, 24.3, 23.8, 23.5. R_f 0.60 (toluene/Et_2O = 10:1). IR (neat): 3362, 2961, 2925, 2854, 2362, 2312, 1699, 1598, 1464, 1363, 1261, 1153, 1135, 1101, 1051, 988, 876, 449 cm^{-1}. HRMS Calcd for $C_{26}H_{40}O_3S$: $[M+H]^+$, 433.2771. Found: *m*/*z* 433.2765. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 100/0, flow rate = 0.8 mL/min, λ = 254 nm, 40 °C): t_{minor} = 7.4 min, t_{major} = 8.5 min.



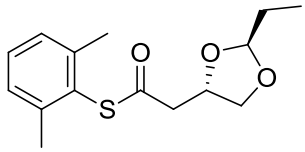
Minor diastereomer (3fa'): 85% *ee*, colorless oil. $[\alpha]_D^{27}$ –21.7 (*c* 0.23, CH_2Cl_2). ^{1}H ($CDCl_3$) δ 7.08 (s, 2H), 4.63 (d, *J* = 5.0 Hz, 1H), 4.46 (dddd, *J* = 7.0, 6.5, 6.5, 5.0 Hz, 1H), 4.12 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.71 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.38 (br s, 2H), 3.08 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.90 (sept, *J* = 7.0 Hz, 1H), 2.80 (dd, *J* = 14.5, 7.0 Hz, 1H), 1.82–1.73 (m, 4H), 1.70–1.65 (m, 1H), 1.62–1.56 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 6H), 1.24–1.19 (m, 2H), 1.17 (d, *J* = 6.5 Hz, 6H), 1.17 (d, *J* = 7.0 Hz, 6H), 1.15–1.06 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 195.5, 152.4, 151.2, 122.0, 121.3, 108.0, 72.5, 69.4, 47.7,

41.6, 34.3, 31.9, 29.7, 27.2, 26.4, 25.7, 24.3, 23.8, 23.5, 21.1. R_f 0.51 (toluene/Et_2O = 10:1). IR (neat): 3362, 2961, 2924, 2852, 2360, 2314, 1700, 1654, 1507, 1465, 1363, 1261, 1094, 1025, 877, 801, 488 cm^{-1}. HRMS Calcd for $C_{26}H_{40}O_3S$: $[M+H]^+$, 433.2771. Found: *m*/*z* 433.2766. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 100/0, flow rate = 0.8 mL/min, λ = 254 nm, 40 °C): t_{major} = 10.2 min, t_{minor} = 11.3 min.

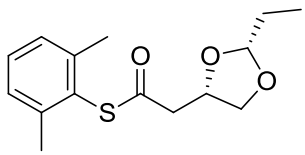
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 10/1) as an eluent.

Yield: 99%, dr = 3.4:1.



Major diastereomer (3eb): 95% *ee*, colorless oil. $[\alpha]_D^{27}$ –33.3 (*c* 2.70, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 5.00 (t, *J* = 5.0 Hz, 1H), 4.50 (dddd, *J* = 6.5, 6.5, 6.5, 6.0 Hz, 1H), 4.21 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.61 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.11 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.83 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 1.66 (qd, *J* = 7.5, 5.0 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 193.7, 142.7, 130.0, 128.3, 126.7, 105.2, 72.4, 70.1, 46.9, 27.1, 21.6, 7.9. R_f 0.39 (hexane/Et_2O = 3:1). IR (neat): 3057, 2971, 2930, 2879, 2862, 2366, 2346, 1699, 1464, 1437, 1412, 1376, 1349, 1262, 1226, 1159, 1121, 1085, 1045, 987, 933, 773 cm^{-1}. HRMS Calcd for $C_{15}H_{20}O_3S$: $[M+H]^+$, 281.1206. Found: *m*/*z* 281.1193. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 10.2 min, t_{major} = 14.8 min.



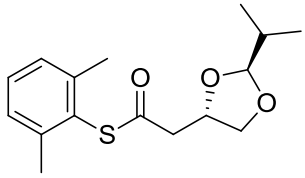
Minor diastereomer (3eb'): 88% *ee*, colorless oil. $[\alpha]_D^{27}$ +10.0 (*c* 0.25, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.85 (t, *J* = 4.5 Hz, 1H), 4.48 (dddd, *J* = 7.0, 6.5, 6.0, 5.0 Hz, 1H), 3.99 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.75 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.09 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.83 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 1.71 (qd, *J* = 7.5, 4.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 193.9, 142.7, 130.0, 128.3, 126.7, 105.8, 72.6, 69.6, 47.9, 27.1, 21.7, 7.9. R_f 0.34 (hexane/Et_2O = 3:1). IR (neat): 3057, 2965, 2926, 2880, 2856, 2360, 2343,

1701, 1465, 1375, 1260, 1228, 1160, 1122, 1089, 1034, 988, 936, 773 cm^{-1}. HRMS Calcd for $C_{15}H_{21}O_3S$: $[M+H]^+$, 281.1206. Found: *m/z* 281.1194. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 11.3 min, t_{major} = 15.8 min.

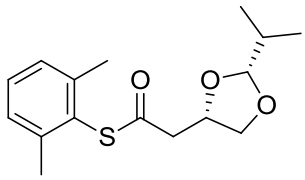
S-(2,6-Dimethylphenyl) 2-(2-isopropyl-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 10/1) as an eluent.

Yield: 99%, dr = 3.8:1.



Major diastereomer (3ec): 96% *ee*, colorless oil. $[\alpha]_D^{27}$ –39.7 (*c* 4.35, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.79 (d, *J* = 4.5 Hz, 1H), 4.49 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.19 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.75 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.11 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.82 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 1.81 (septd, *J* = 7.0, 4.5 Hz, 1H), 0.94 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 193.7, 142.7, 130.0, 128.3, 126.7, 108.0, 72.6, 70.2, 46.9, 32.2, 21.6, 16.7. R_f 0.33 (hexane/Et_2O = 3:1). IR (neat): 3057, 2962, 2927, 2875, 2360, 2314, 1699, 1472, 1464, 1376, 1272, 1192, 1088, 1053, 987, 949, 911, 853, 773, 489 cm^{-1}. HRMS Calcd for $C_{16}H_{22}O_3S$: $[M+H]^+$, 295.1362. Found: *m/z* 295.1359. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 8.1 min, t_{major} = 11.4 min.



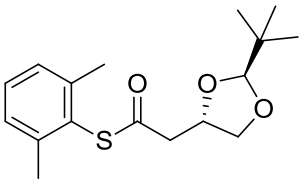
Minor diastereomer (3ec'): 87% *ee*, colorless oil. $[\alpha]_D^{27}$ –18.0 (*c* 1.11, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.65 (d, *J* = 4.5 Hz, 1H), 4.48 (dddd, *J* = 7.0, 6.5, 6.5, 5.0 Hz, 1H), 3.99 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.72 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.08 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.81 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 1.81 (septd, *J* = 7.0, 4.5 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 193.9, 142.7, 130.0, 128.3, 126.7, 108.7, 72.6, 69.6, 47.9, 31.9, 21.6, 16.8, 16.8. R_f 0.28 (hexane/Et_2O = 3:1). IR (neat): 3057, 2962, 2926, 2876, 2360, 2312, 1700, 1473, 1465, 1374, 1272, 1193, 1094, 1049, 987, 910,

852, 771, 480 cm^{-1}. HRMS Calcd for $C_{16}H_{22}O_3S$: $[M+H]^+$, 295.1362. Found: *m*/*z* 295.1358. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.0 min, t_{major} = 13.1 min.

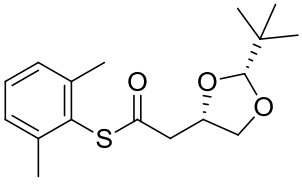
S-(2,6-Dimethylphenyl) 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 10/1) as an eluent.

Yield: 73%, dr = 3.5:1.



Major diastereomer (3ed): 99% *ee*, colorless oil. $[\alpha]_D^{27}$ –42.7 (*c* 3.51, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 4.69 (s, 1H), 4.47 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.18 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.61 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.10 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.83 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 6H), 0.91 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 193.8, 142.7, 130.0, 128.3, 126.8, 110.1, 73.0, 70.5, 46.8, 34.7, 24.1, 21.6. R_f 0.38 (hexane/Et_2O = 3:1). IR (neat): 3369, 3058, 2973, 2933, 2870, 2736, 2360, 2343, 1696, 1583, 1483, 1465, 1437, 1405, 1359, 1262, 1214, 1104, 1037, 989, 965, 849, 801, 773, 720, 668 cm^{-1}. HRMS Calcd for $C_{17}H_{24}O_3S$: $[M+H]^+$, 309.1519. Found: *m*/*z* 309.1504. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 6.4 min, t_{major} = 9.1 min.



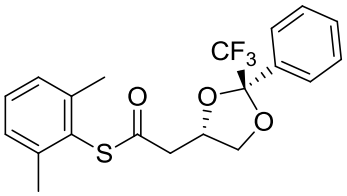
Minor diastereomer (3ed'): 97% *ee*, colorless oil. $[\alpha]_D^{27}$ –37.2 (*c* 0.74, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.54 (s, 1H), 4.49 (dddd, *J* = 7.0, 6.5, 6.5, 5.0 Hz, 1H), 4.00 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.70 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.08 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.78 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.35 (s, 6H), 0.95 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 194.1, 142.9, 130.2, 128.5, 127.0, 111.0, 72.9, 70.1, 48.1, 34.2, 24.5, 21.9. R_f 0.33 (hexane/Et_2O = 3:1). IR (neat): 3398, 3057, 2973, 2929, 2871, 2736, 2360, 2343, 1696, 1583, 1483, 1465, 1437, 1406, 1359, 1262, 1213, 1106, 1039, 988, 970, 844, 802, 773, 719, 700, 668 cm^{-1}. HRMS Calcd for $C_{17}H_{24}O_3S$: $[M+H]^+$, 309.1519. Found: *m*/*z* 309.1502. HPLC (Daicel Chiralcel OJ-H,

hexane/*i*-PrOH = 97.5/2.5, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 6.9 min, t_{major} = 11.8 min.

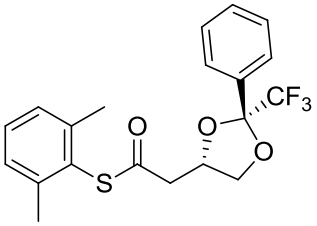
S-(2,6-Dimethylphenyl) 2-(2-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl)-ethanethioate.

The diastereomers were further separated by flash silica gel column chromatography using hexane/Et_2O (v/v = 20/1) as an eluent.

Yield: 99%, dr = 1.1:1.



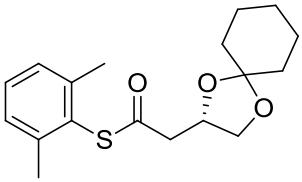
Major diastereomer (3ee): 69% *ee*, colorless oil. $[\alpha]_D^{26}$ –32.3 (*c* 0.62, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.65–7.61 (m, 2H), 7.46–7.38 (m, 3H), 7.24 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 4.91 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.48 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.82 (m, 1H), 3.12 (dd, *J* = 15.5, 6.5 Hz, 1H), 2.75 (dd, *J* = 15.5, 7.0 Hz, 1H), 2.33 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 193.1, 142.6, 134.9, 130.2, 129.8, 128.4, 128.1, 126.8, 126.3, 122.7 (q, *J* = 289.4 Hz), 104.9 (q, *J* = 32.1 Hz), 75.4, 71.1, 46.9, 21.6. ^{19}F NMR ($CDCl_3$) δ 79.9. R_f 0.38 (hexane/Et_2O = 5:1). IR (neat): 3060, 2959, 2921, 2858, 2372, 1696, 1584, 1465, 1378, 1303, 1272, 1178, 1105, 1049, 1032, 987, 955, 914, 774, 719, 696, 665 cm^{-1}. HRMS Calcd for $C_{20}H_{19}F_3O_3S$: $[M+H]^+$, 397.1080. Found: *m*/*z* 397.1068. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97/3, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 5.3 min, t_{major} = 14.5 min.



Minor diastereomer (3ee'): 72% *ee*, colorless oil. $[\alpha]_D^{26}$ –4.4 (*c* 0.57, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.62–7.57 (m, 2H), 7.44–7.37 (m, 3H), 7.25 (dd, *J* = 7.0, 8.5 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 4.57 (dddd, *J* = 7.5, 7.0, 6.5, 6.5 Hz, 1H), 4.27 (m, 1H), 3.97 (dd, *J* = 7.5, 8.0 Hz, 1H), 3.34 (dd, *J* = 15.5, 6.5 Hz, 1H), 2.98 (dd, *J* = 15.5, 7.0 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 193.3, 142.7, 134.5, 130.2, 129.8, 128.4, 128.1, 126.9, 126.4, 122.4 (q, *J* = 287.0 Hz), 104.9 (q, *J* = 32.1 Hz), 74.6, 71.2, 46.2, 21.6. ^{19}F NMR ($CDCl_3$) δ 79.9. R_f 0.38 (hexane/Et_2O = 5:1). IR (neat): 3060, 2959, 2921,

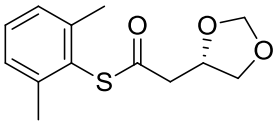
2852, 2378, 1700, 1577, 1465, 1378, 1309, 1261, 1178, 1107, 1047, 1032, 990, 955, 915, 773, 720, 696, 664 cm^{-1}. HRMS Calcd for $C_{20}H_{19}F_3O_3S$: $[M+H]^+$, 397.1080. Found: *m*/*z* 397.1068. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97/3, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.8 min, t_{major} = 29.2 min.

S-(2,6-Dimethylphenyl) 2-(1,4-dioxaspiro[4.5]decan-2-yl)ethanethioate (3eg).



Yield: 31%, 99% *ee*, colorless oil. $[\alpha]_D^{27}$ –41.2 (*c* 1.88, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.23 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.51 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.13 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.70 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.10 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.82 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.35 (s, 6H), 1.69–1.61 (m, 4H), 1.61–1.54 (m, 4H), 1.40 (br s, 2H). ^{13}C NMR ($CDCl_3$) δ 193.8, 142.7, 130.0, 128.3, 126.8, 109.9, 72.1, 68.7, 48.0, 36.7, 35.0, 25.1, 24.0, 23.8, 21.6. TLC: R_f 0.46 (hexane/EtOAc = 3:1). IR (neat): 3378, 3057, 2935, 2862, 2668, 2360, 2346, 1696, 1584, 1463, 1449, 1364, 1331, 1282, 1252, 1233, 1163, 1100, 1042, 990, 929, 847, 772 cm^{-1}. HRMS Calcd for $C_{18}H_{24}O_3S$: $[M+H]^+$, 321.1519. Found: *m*/*z* 321.1503. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.3 min, t_{major} = 12.3 min.

S-(2,6-Dimethylphenyl) 2-(1,3-dioxolan-4-yl)ethanethioate (3eh).

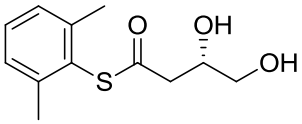


Yield: 86%, 72% *ee*, colorless oil. $[\alpha]_D^{27}$ –9.7 (*c* 4.66, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.24 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 5.06 (s, 1H), 4.88 (s, 1H), 4.46 (dddd, *J* = 7.0, 6.5, 6.5, 6.0 Hz, 1H), 4.05 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.66 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.10 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.85 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 193.7, 142.7, 130.0, 128.4, 126.6, 95.0, 72.2, 69.4, 47.0, 21.6. TLC: R_f 0.53 (hexane/EtOAc = 3:1). IR (neat): 3378, 3057, 3014, 2955, 2920, 2858, 2760, 2381, 2287, 1696, 1584, 1464, 1377, 1316, 1274, 1156, 1087, 1050, 988, 939, 911, 832, 773, 498 cm^{-1} HRMS Calcd for $C_{13}H_{16}O_3S$: $[M+H]^+$, 253.0893. Found: *m*/*z* 253.0881. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ = 254 nm, 40 °C): t_{minor} = 9.4 min, t_{major} = 15.0 min.

Procedure for synthesis of 5

To a stirred solution of **3ed** and **3ed'** (diastereomixture, *dr* = 3.8:1, 0.037 g, 0.12 mmol) in CH_2Cl_2 (5 mL) was added titanium tetrachloride (0.13 mL, 1.20 mmol) at –78 °C, and the mixture was stirred at –78 °C for 1.5 h and at –40 °C for additional 2.5 h. CH_3OH (1.5 mL) was added to the solution, and the mixture was stirred at –40 °C for 30 min and subsequently warmed to ambient temperature. H_2O was added to the solution, and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 1/2) as an eluent gave S-(2,6-dimethylphenyl) 3,4-dihydroxybutanethioate (**5**).

S-(2,6-Dimethylphenyl) 3,4-dihydroxybutanethioate (5).

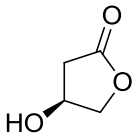


Yield: 93%, 98.7% *ee*, colorless oil. $[\alpha]_D^{26}$ –24.7 (*c* 2.63, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.25 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 4.20 (br s, 1H), 3.71 (d, *J* = 11.5 Hz, 1H), 3.56 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.05 (br s, 1H), 2.96–2.86 (m, 2H), 2.36 (s, 6H), 2.12 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 197.0, 142.6, 130.2, 128.4, 126.4, 69.0, 65.6, 46.3, 21.7. TLC: R_f 0.17 (hexane/EtOAc = 1:1). IR (neat): 3384, 3057, 2953, 2924, 2359, 2312, 1699, 1464, 1436, 1377, 1261, 1194, 1167, 1097, 1033, 997, 894, 860, 772 cm^{-1}. HRMS Calcd for $C_{12}H_{16}O_3S$: $[M+H]^+$, 241.0893. Found: *m*/*z* 241.0888. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 7.1 min, t_{major} = 8.3 min.

Procedure for synthesis of 6

The mixture of **3ed** and **3ed'** (diastereomixture, *dr* = 3.8:1, 0.077 g, 0.25 mmol) and *p*-TsOH·H_2O (0.022 g, 0.13 mmol) in 1,2-dichloroethane (9 mL) and H_2O (1 mL) was stirred at 90 °C for 8 days. The reaction mixture was sequentially diluted with EtOAc, passed through a short silica gel pad to remove *p*-TsOH, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 1/5) as an eluent gave (*S*)-4-hydroxydihydrofuran-2(3*H*)-one (**6**).

(*S*)-4-Hydroxydihydrofuran-2(3*H*)-one (6): CAS RN [7331-52-4].



Yield: 84%, 98.7% *ee*, colorless oil. $[\alpha]_D^{27}$ –73.5 (*c* 0.17, EtOH). ^{1}H NMR ($CDCl_3$) δ 4.70 (m, 1H), 4.42 (dd, *J* = 15.5, 5.0 Hz, 1H), 4.30 (m, 1H), 2.76 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.53 (m, 1H), 2.43 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 175.7, 75.8, 67.6, 37.8. TLC: R_f 0.27 (EtOAc).

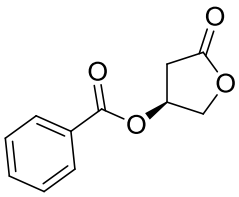
The absolute configuration of **6** was assigned as (*S*) by comparing the optical rotation with the literature value [lit.[5] (*S*)-4-hydroxydihydrofuran-2(3*H*)-one: $[\alpha]_D^{22}$ –81.0 (c 2.0, EtOH)] and by HPLC analysis after benzoylation, comparing the retention time with the value of the benzoylation product of the commercially available material (for (*S*)-5-oxotetrahydrofuran-3-yl benzoate: Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C: t_{minor} = 18.8 min, t_{major} = 20.4 min.).

The enantiomeric excess of **6** was determined by HPLC analysis after benzoylation.

Procedure for benzoylation of 6

To a solution of **6** (0.010 g, 0.10 mmol) in pyridine (0.4 mL) was added benzoyl chloride (0.070 mL, 0.60 mmol) at 0 °C, and the solution was stirred at room temperature for 3 h. After the evaporation for removal of pyridine, the reaction was quenched with H_2O, and the mixture was subsequently extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave 5-oxotetrahydrofuran-3-yl benzoate.

(*S*)-5-Oxotetrahydrofuran-3-yl benzoate: CAS RN [207985-74-8].



Yield: 16%, 98.7% *ee*, white solid. ^{1}H NMR ($CDCl_3$) δ 8.03 (m, 2H), 7.61 (m, 1H), 7.47 (m, 2H), 5.70 (m, 1H), 4.63 (dd, *J* = 11.0, 4.5 Hz, 1H), 4.54 (m, 1H), 2.98 (dd, *J* = 18.5, 6.5 Hz, 1H), 2.80 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 174.6, 165.8, 133.8, 129.8,

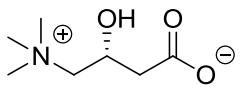
128.8, 128.6, 73.1, 70.3, 34.7. TLC: R_f 0.61 (hexane/EtOAc = 1:1). HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 18.8 min, t_{major} = 20.4 min.

Procedure for synthesis of 7[6]

To the mixture of (*S*)-4-hydroxydihydrofuran-2(3*H*)-one (0.044 g, 0.43 mmol) and methanesulfonyl chloride (0.25 g, 2.19 mmol) in CH_2Cl_2 (1 mL) was added the solution of triethylamine (0.18 g, 1.82 mmol) in CH_2Cl_2 (0.3 mL) at 0 °C, and the mixture was stirred at 0 °C for 33 h. H_2O was added to the solution, and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 1/5) as an eluent gave (*S*)-methanesulfonyl hydroxybutyrolactone as a white solid in 67% yield; CAS RN [174302-47-7]. ^{1}H NMR ($CDCl_3$) δ 5.48 (m, 1H), 4.59 (dt, *J* = 11.5, 1.5 Hz, 1H), 4.30 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.11 (s, 3H), 2.92 (dd, *J* = 18.5, 6.5 Hz, 1H), 2.83 (dt, *J* = 18.5, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 173.0, 74.2, 72.7, 38.8, 35.0.

Next, the solution of the obtained (*S*)-methanesulfonyl hydroxybutyrolactone and concentrated sulfonic acid (0.045 g, 1.84 mmol) in H_2O (1 mL) was stirred at 80 °C for 24 h. The aqueous solution was washed with CH_2Cl_2. To the aqueous solution was added 3N aqueous NaOH, and the solution was stirred at room temperature for 2 h. To the resulting solution was added aqueous trimethylamine (30% aqueous solution, 0.22 g, 1.13 mmol), and the solution was stirred at 60 °C for 2 days. The solution was concentrated in vacuo to remove water. The residue was dissolved in a small amount of water and placed in a column filled with a cation exchange resin (Dowex). Then, pure water was fluxed to the column for removal of impurities. The aqueous solution containing 2% ammonia was fluxed for obtaining the aqueous solution. Purification by decantation using CH_2Cl_2 and EtOAc gave the (*L*)-carnitine (**7**) in 17% yield for 3 steps.

(*L*)-Carnitine (7): CAS RN [541-15-1].



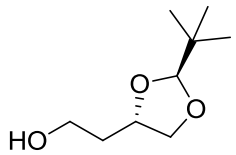
Yield: 10% (overall), pale yellow solid. $[\alpha]_D^{27}$ –30.0 (*c* 0.50, H_2O). ^{1}H NMR (D_2O) δ 4.60 (m, 1H), 3.47–3.44 (m, 3H), 3.24 (s, 9H), 2.50 (dd, *J* = 6.5, 2.5 Hz, 1H). ^{13}C

NMR (D_2O) δ 178.5, 71.6, 65.3, 55.6, 43.7.

Procedure for synthesis of 8

The mixture of **3ed** (single diastereomer, 0.046 g, 0.15 mmol) and $LiAlH_4$ (0.0061 g, 0.16 mmol) in Et_2O (2.4 mL) was stirred at room temperature for 1 h. 5% Aqueous NaOH was added to quench the reaction, and the mixture was filtered and washed with Et_2O. The combined organic layers were washed with 5% aqueous NaOH and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanol (**8**).

2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethanol (8).



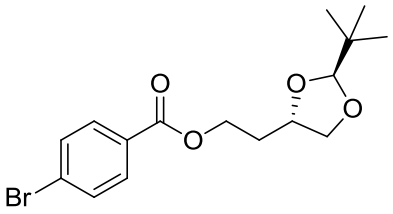
Yield: 99%, 99% *ee*, colorless oil. $[\alpha]_D^{26}$ –2.5 (*c* 2.04, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 4.64 (s, 1H), 4.22–4.13 (m, 2H), 3.83 (m, 2H), 3.51 (dd, *J* = 7.5, 7.0 Hz, 1H), 2.35 (br s, 1H), 1.86 (m, 1H), 1.73 (m, 1H), 0.90 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 109.8, 75.8, 70.9, 60.9, 35.1, 34.6, 24.2. TLC: R_f 0.18 (hexane/EtOAc = 2:1). IR (neat): 3394, 2959, 2908, 2871, 1730, 1483, 1403, 1359, 1261, 1214, 1107, 1057, 1037, 971, 903, 872, 806 cm^{-1}. HRMS Calcd for $C_9H_{18}O_3$: $[M+H]^+$, 175.1329. Found: *m*/*z* 175.1327.

The enantiomeric excess of **8** was determined by HPLC analysis after benzoylation.

Procedure for benzoylation of 8

To a solution of **8** (0.012 g, 0.07 mmol) and 4-bromobenzoylchloride (0.077 g, 0.35 mmol) in Et_2O (0.4 mL) was added pyridine (0.4 mL) at 0 °C. After the solution was stirred at room temperature for 3 h, the reaction was quenched with H_2O, and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethyl 4-bromobenzoate.

2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethyl 4-bromobenzoate.

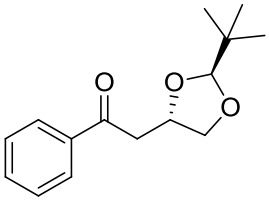


Yield: 81%, 99% *ee*, colorless oil. $[\alpha]_D^{26}$ –16.9 (*c* 1.77, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2H), 7.58 (m, 2H), 4.64 (s, 1H), 4.48 (m, 1H), 4.41 (m, 1H), 4.22–4.14 (m, 2H), 3.54 (dd, *J* = 7.5, 6.5 Hz, 1H), 2.09 (m, 1H), 1.95 (m, 1H), 0.89 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 165.8, 131.7, 131.1, 129.0, 128.1, 109.8, 73.7, 70.8, 62.3, 34.7, 32.2, 24.2. TLC: R_f 0.15 (hexane/EtOAc = 10:1). IR (neat): 2959, 2906, 2870, 2360, 1723, 1591, 1483, 1398, 1273, 1174, 1102, 1039, 1013, 971, 848, 757, 682 cm^{-1}. HRMS Calcd for $C_9H_{18}O_3$: $[M+H]^+$, 357.0701. Found: *m*/*z* 357.0710. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 99.3/0.7, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 5.8 min, t_{major} = 6.9 min.

Procedure for synthesis of 9[7]

The mixture of **3ed** (single diastereomer, 0.062 g, 0.20 mmol), $PhB(OH)_2$ (0.049 g, 0.40 mmol), CuTC (0.061 g, 0.32 mmol), tris(2-furyl)phosphine (0.0093 g, 0.04 mmol) and $Pd_2(dba)_3$ (0.0092 g, 0.01 mmol) in THF (5 mL) was stirred at 50 °C for 48 h. 5% Aqueous HCl was added to quench the reaction, and the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/toluene/EtOAc (v/v/v = 30/3/1) as an eluent gave 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)-1-phenylethanone (**9**).

2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)-1-phenylethanone (9).



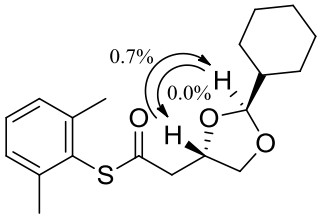
Yield: 50%, 98% *ee*, colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.95 (m, 2H), 7.58 (m, 1H), 7.48 (m, 2H), 4.66 (s, 1H), 4.58 (m, 1H), 4.39 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.59 (dd, *J* = 17.0, 5.0 Hz, 1H), 3.55 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.11 (dd, *J* = 17.0, 8.5 Hz, 1H), 0.92 (s,

9H). ^{13}C NMR ($CDCl_3$) δ 197.8, 136.6, 133.5, 128.7, 128.1, 109.7, 72.7, 71.4, 42.4, 34.7, 24.2. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm, 40 °C): t_{minor} = 18.1 min, t_{major} = 20.1 min.

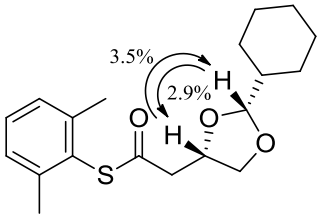
Determination of the Configurations of Products

Treatment of both **3ed** (99% *ee*) and **3ed'** (97% *ee*) as a single diastereomer with *p*-toluenesulfonic acid afforded the same enantiomer of 4-hydroxydihydrofuran-2(3*H*)-one (**6**) (the optical rotation of **6**: obtained from **3ed**, $[\alpha]_D^{26}$ –58.8 (*c* 0.17, CH_2Cl_2); obtained from **3ed'**, $[\alpha]_D^{26}$ –57.4 (*c* 0.61, CH_2Cl_2)). The absolute configurations of their benzoylation products were assigned as (*S*) by HPLC analysis, comparing the retention time with the value of the benzoylation product of the commercially available material (for (*S*)-5-oxotetrahydrofuran-3-yl benzoate: Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C: t_{minor} = 18.8 min, t_{major} = 20.4 min.). These results assigned the absolute configurations at the β-positions of the carbonyl group in both diastereomers, **3ed** and **3ed'**, as (*S*).

The relative configurations of **3ea** and **3ea'** were determined from the NOE experiments.



3ea (major diastereomer)



3ea' (minor diastereomer)

The configurations of all other examples were assigned analogously.

Electrophilicity of Thioesters

On the basis of the ^{13}C NMR chemical shifts of the carbonyl carbons, the electrophilicity of thioesters is expected to be higher than that of the corresponding esters but comparable to that of the corresponding ketones: **1a**, 166.2 ppm; **1c**, 189.0 ppm; (*E*)-4-hydroxy-1-phenylbut-2-en-1-one (shown in Scheme 1), 189.3 ppm.

Reactions of Aryl Aldehydes

The reactions of benzaldehyde or 4-methoxybenzaldehyde with **1e** gave the corresponding product in less than 10% yields, while electron-deficient 4-cyanobenzaldehyde gave the desired product in 43% yield with moderate stereoselectivity (*dr* = 1.1:1, 82% *ee* each). For quantification of the electrophilic reactivity of aldehydes, see: R. Appel and H. Mayr, *J. Am. Chem. Soc.*, 2011, **133**, 8240.

References

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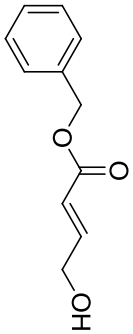
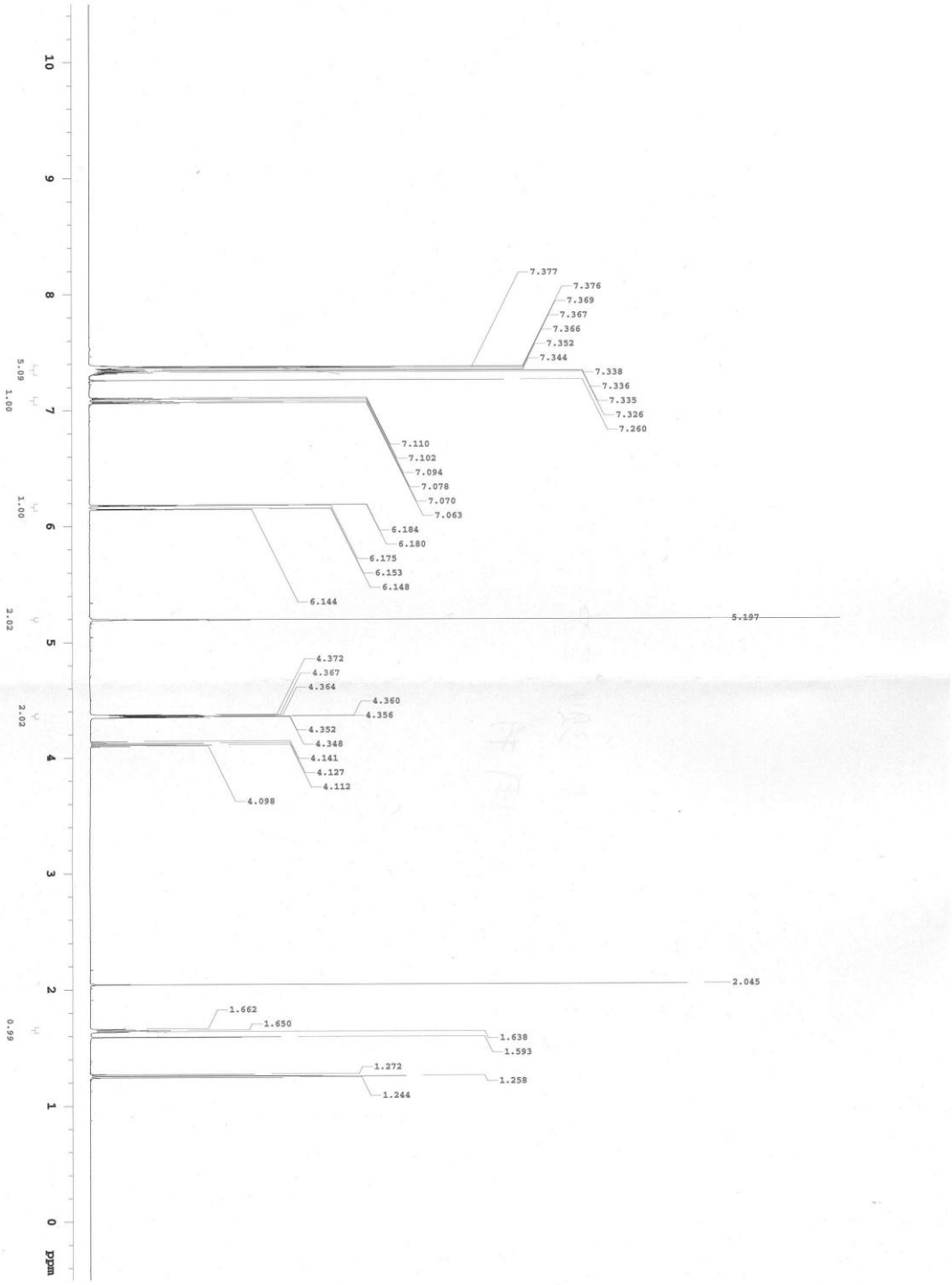
NMR Spectra (^{1}H, ^{13}C) of Products

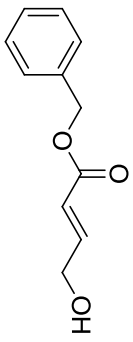
(*E*)-Benzyl 4-hydroxybut-2-enoate (1a)



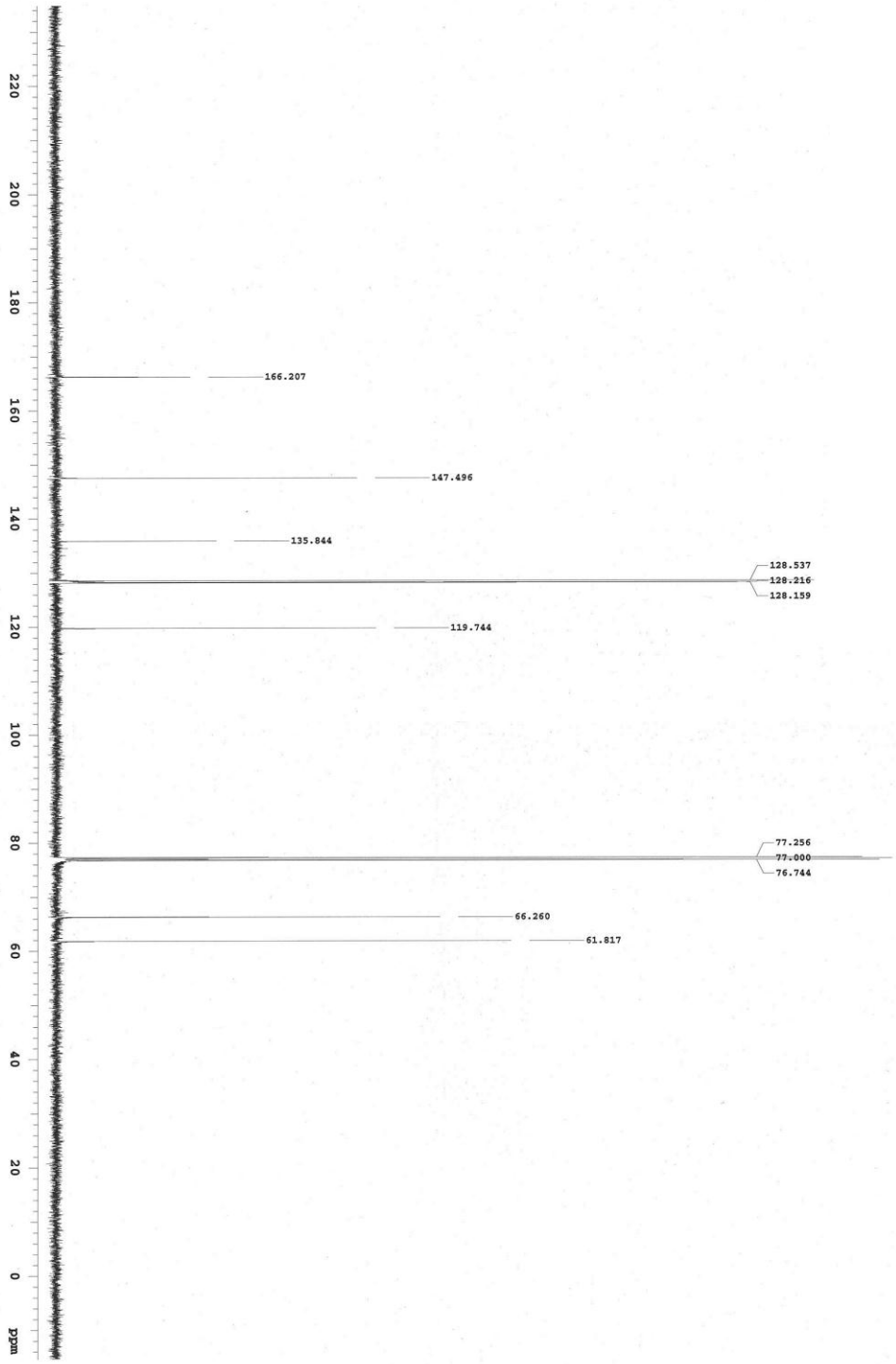
^{1}H NMR



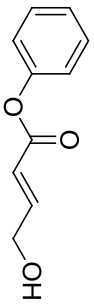
(*E*)-Benzyl 4-hydroxybut-2-enoate (1a)



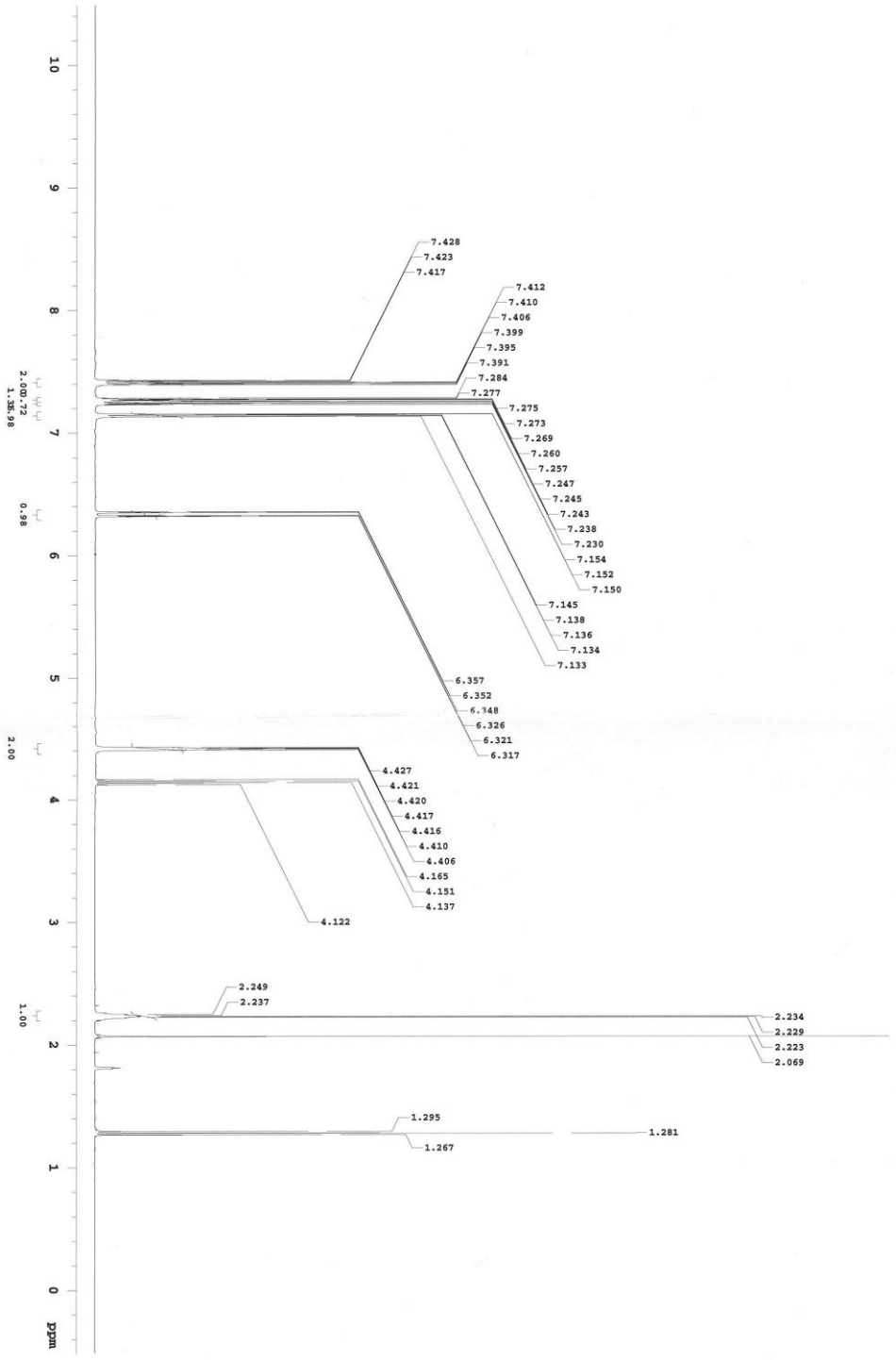
^{13}C NMR



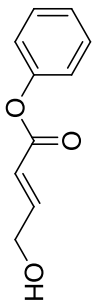
(*E*)-Phenyl 4-hydroxybut-2-enoate (1b)



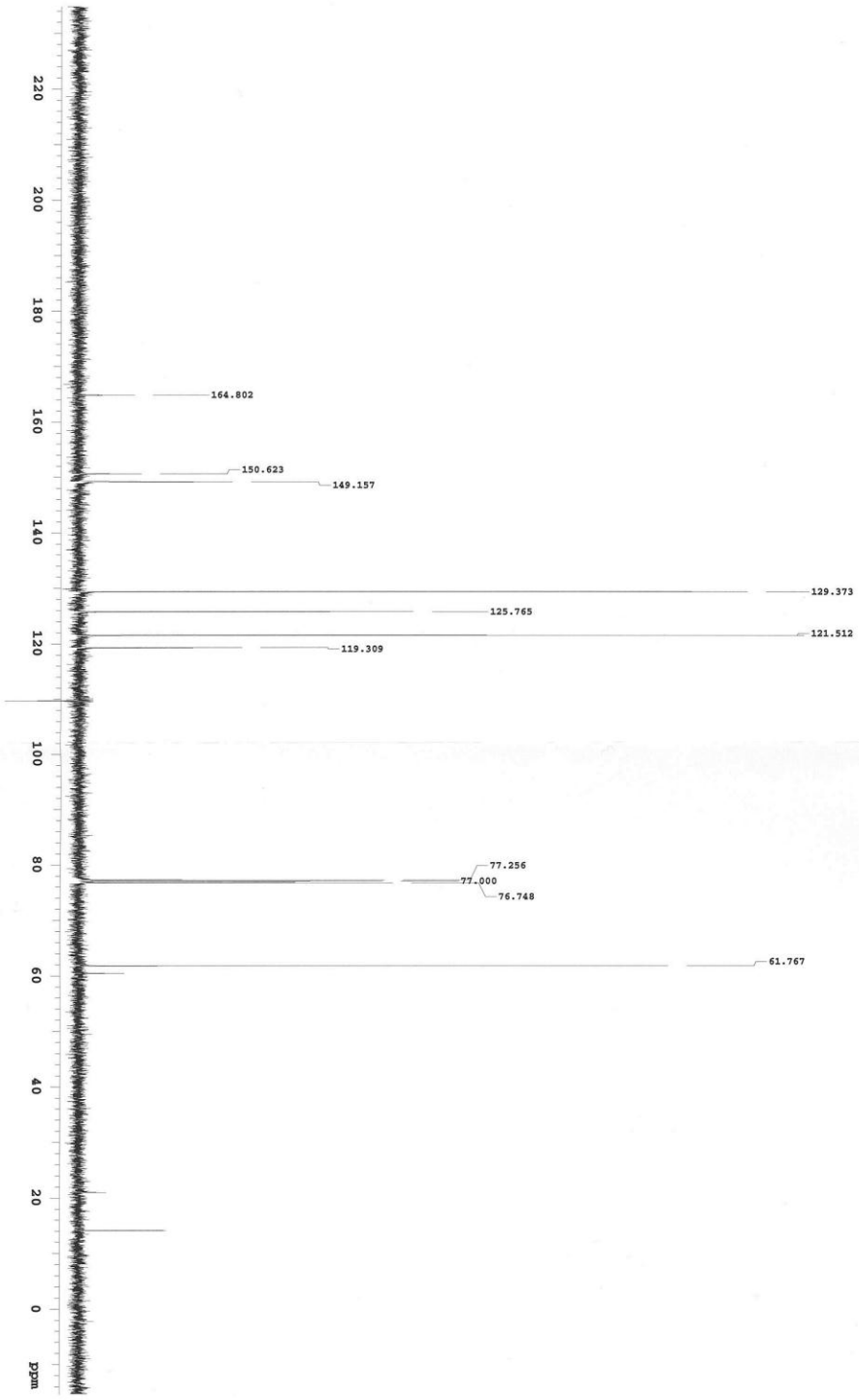
^{1}H NMR



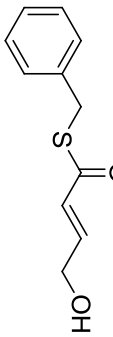
(*E*)-Phenyl 4-hydroxybut-2-enoate (1b)



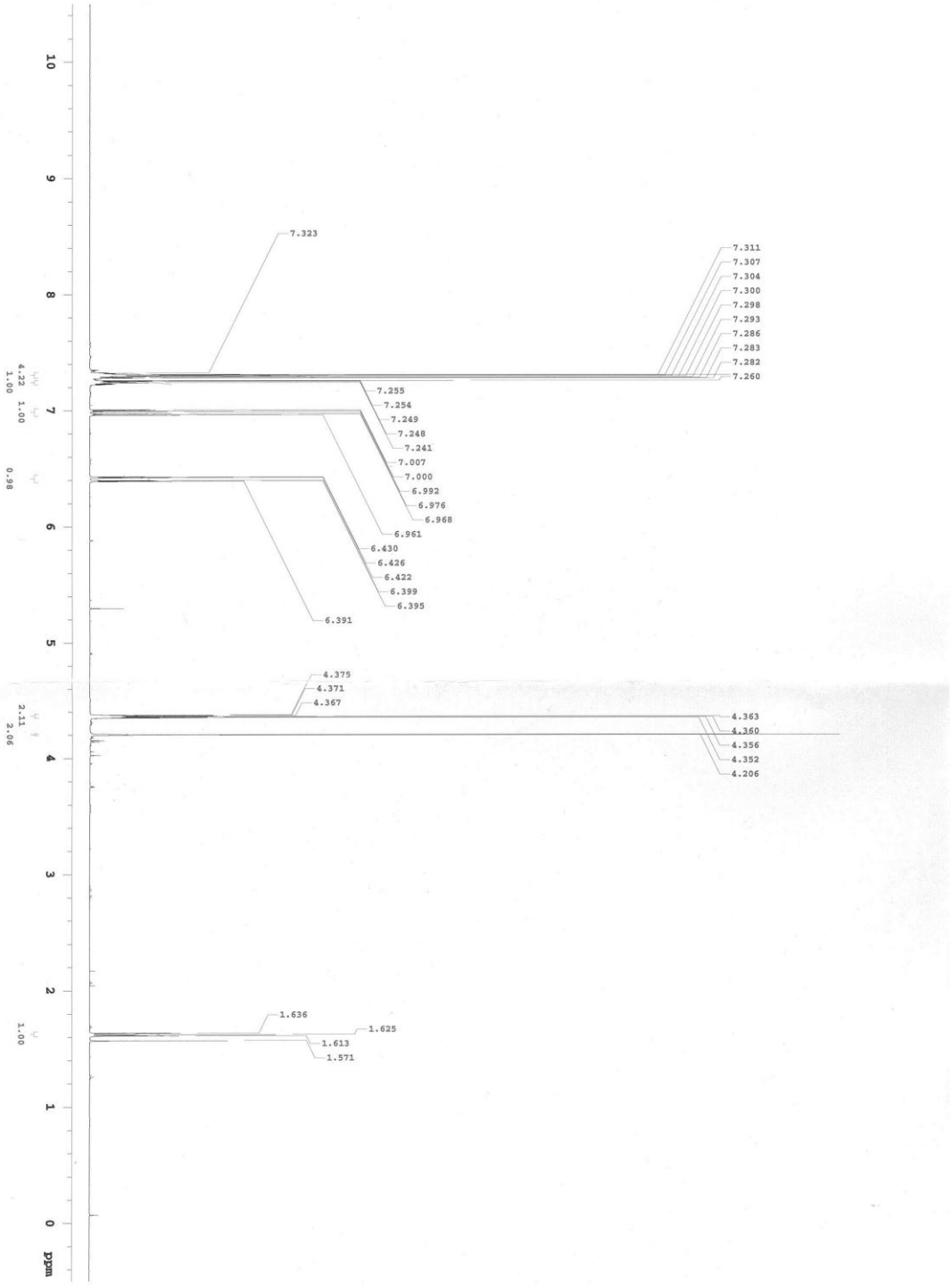
^{13}C NMR



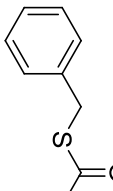
(*E*)-S-Benzyl 4-hydroxybut-2-enethioate (1c)



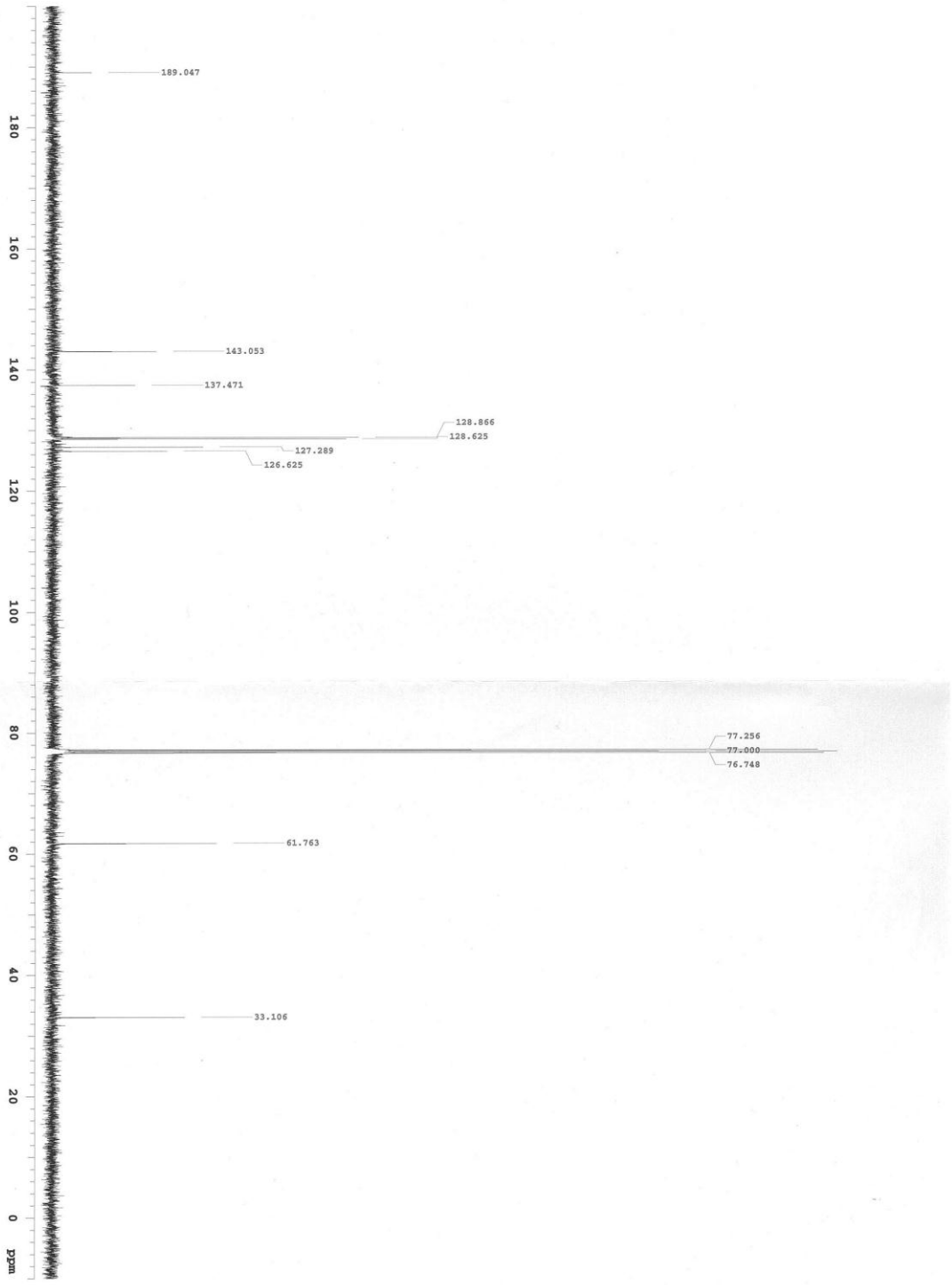
^{1}H NMR



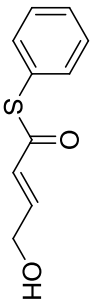
(*E*)-S-Benzyl 4-hydroxybut-2-enethioate (1c)



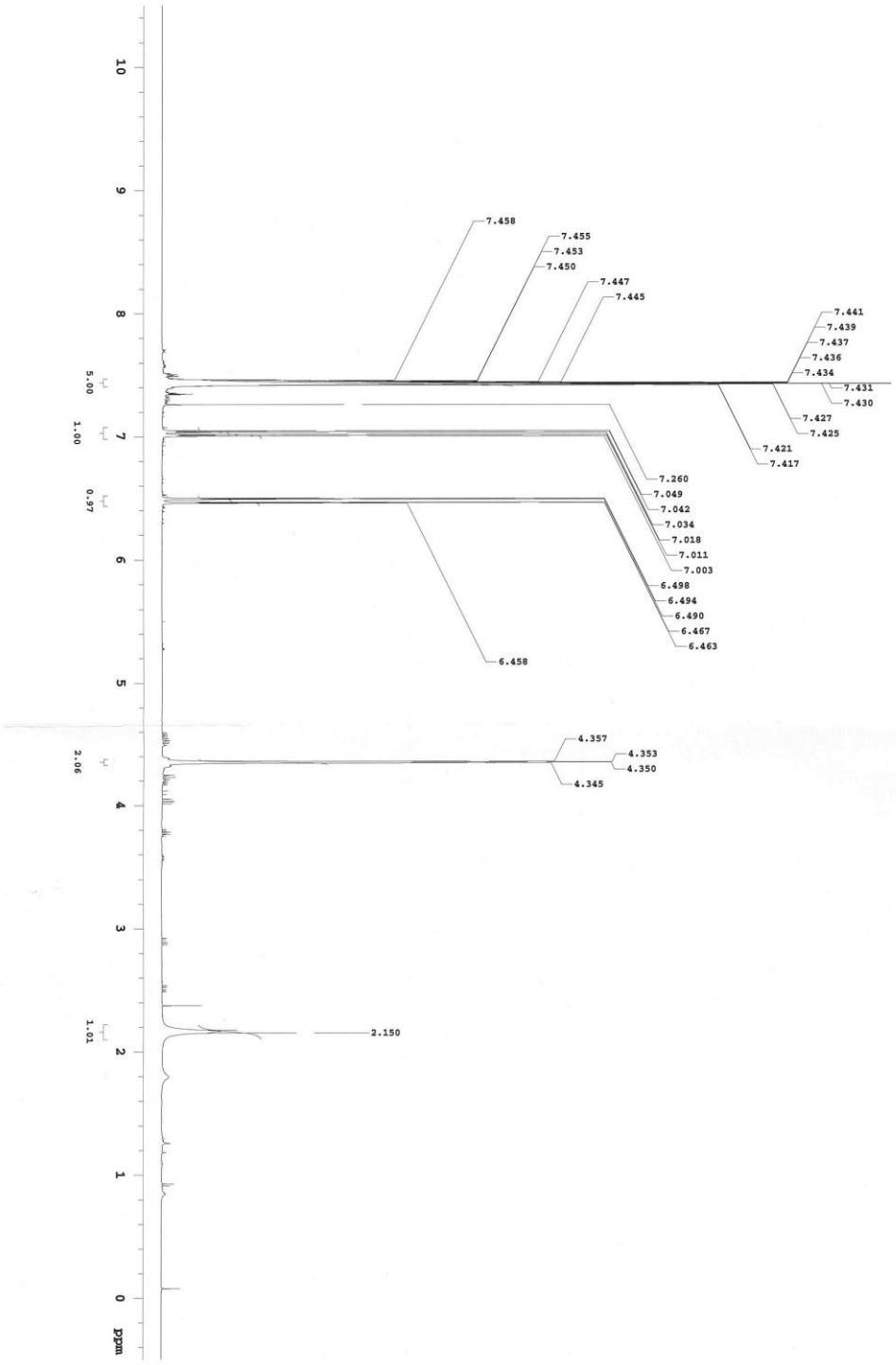
^{13}C NMR



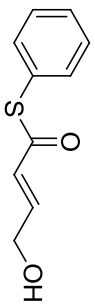
(*E*)-S-Phenyl4-hydroxybut-2-enethioate (1d)



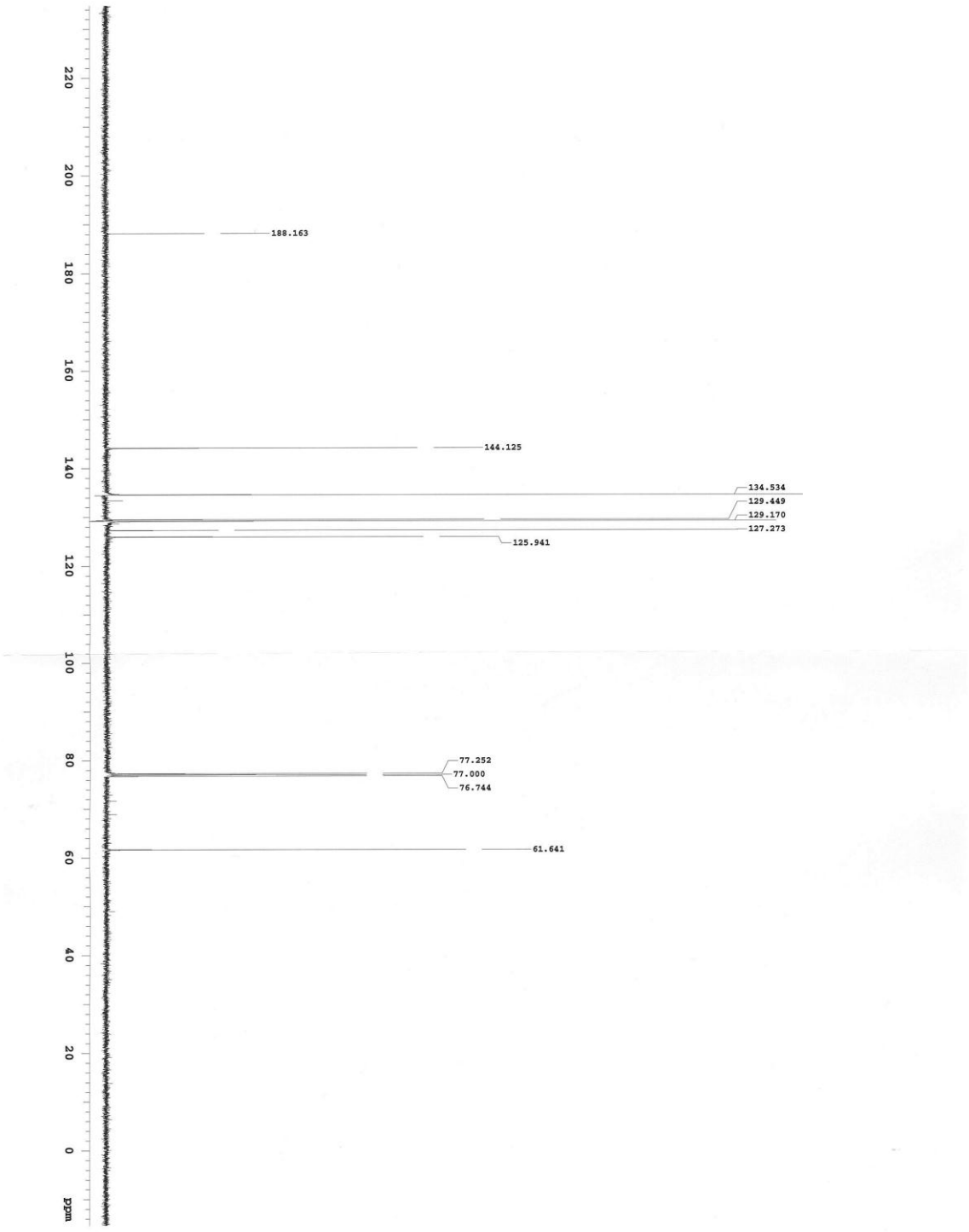
^{1}H NMR



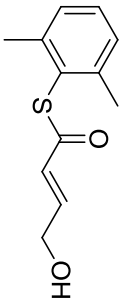
(*E*)-S-Phenyl4-hydroxybut-2-enethioate (1d)



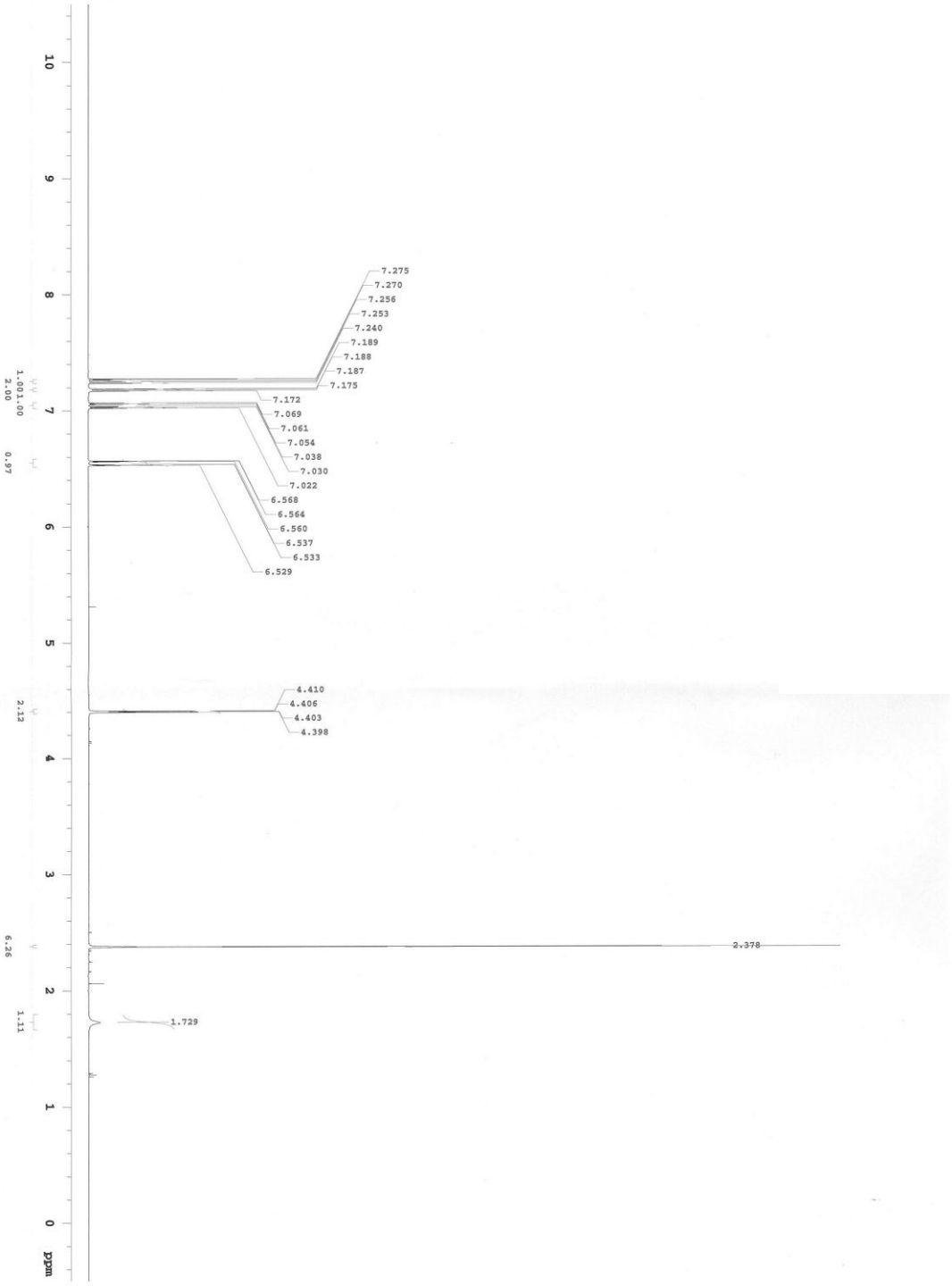
^{13}C NMR



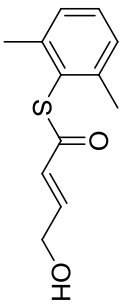
(*E*)-S-(2,6-Dimethylphenyl) 4-hydroxybut-2-enethioate (1e)



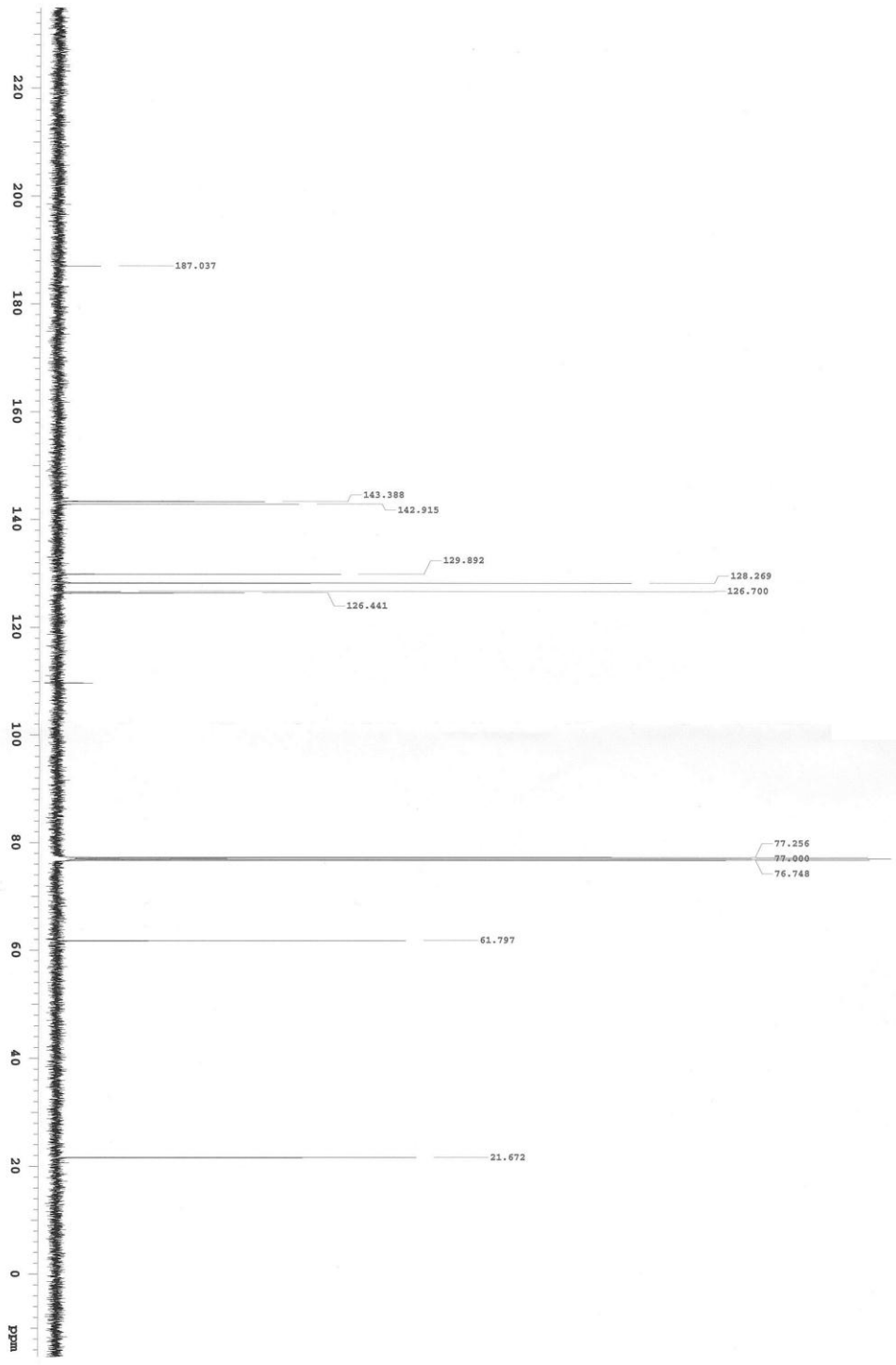
^{1}H NMR



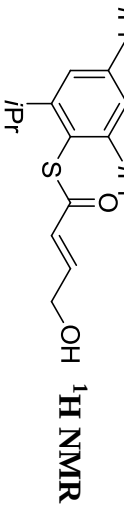
(*E*)-S-(2,6-Dimethylphenyl) 4-hydroxybut-2-enethioate (1e)



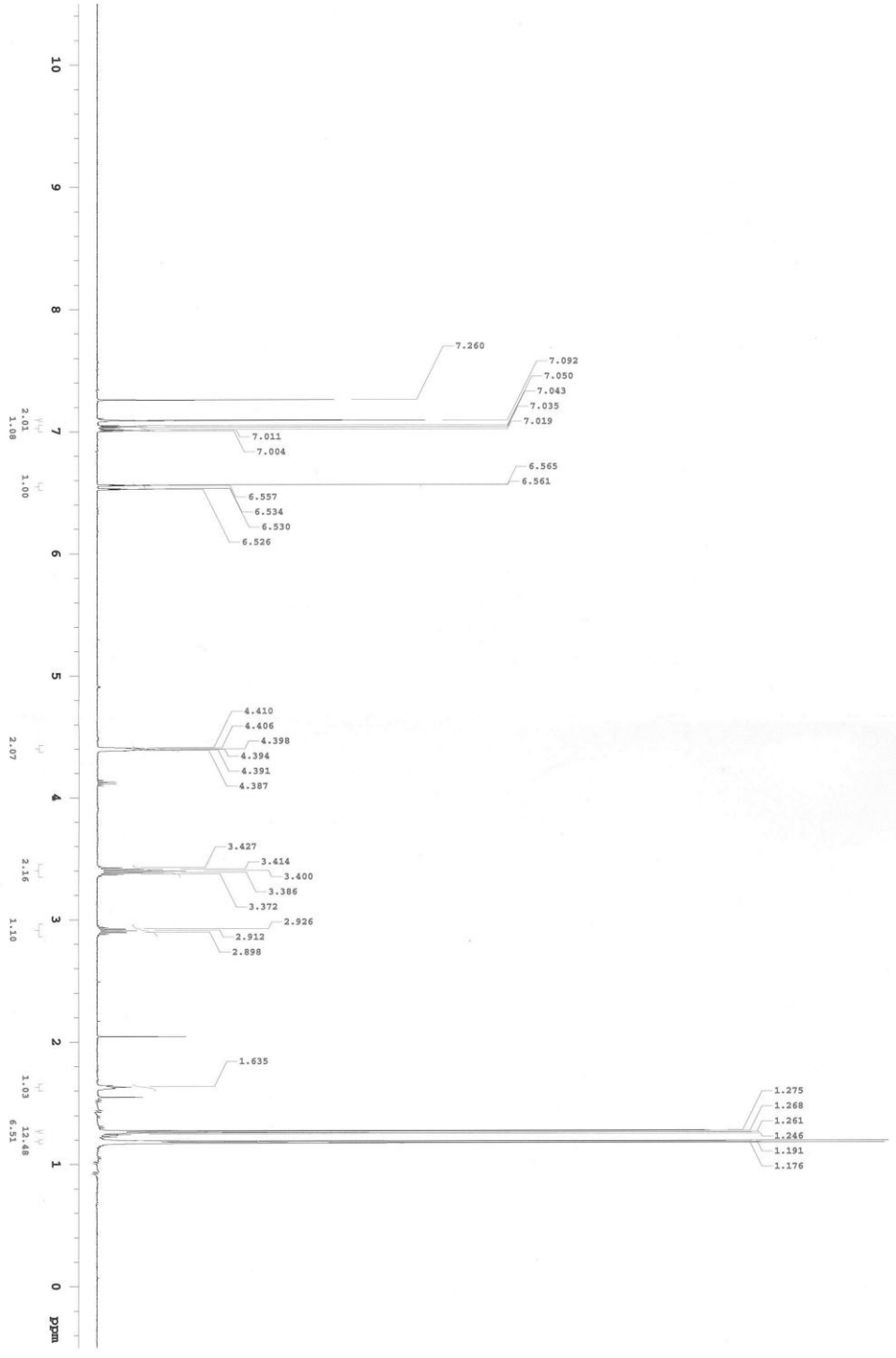
^{13}C NMR



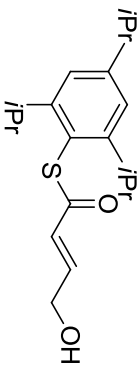
(*E*)-S-(2,4,6-Triisopropylphenyl) 4-hydroxybut-2-enethioate (1f)



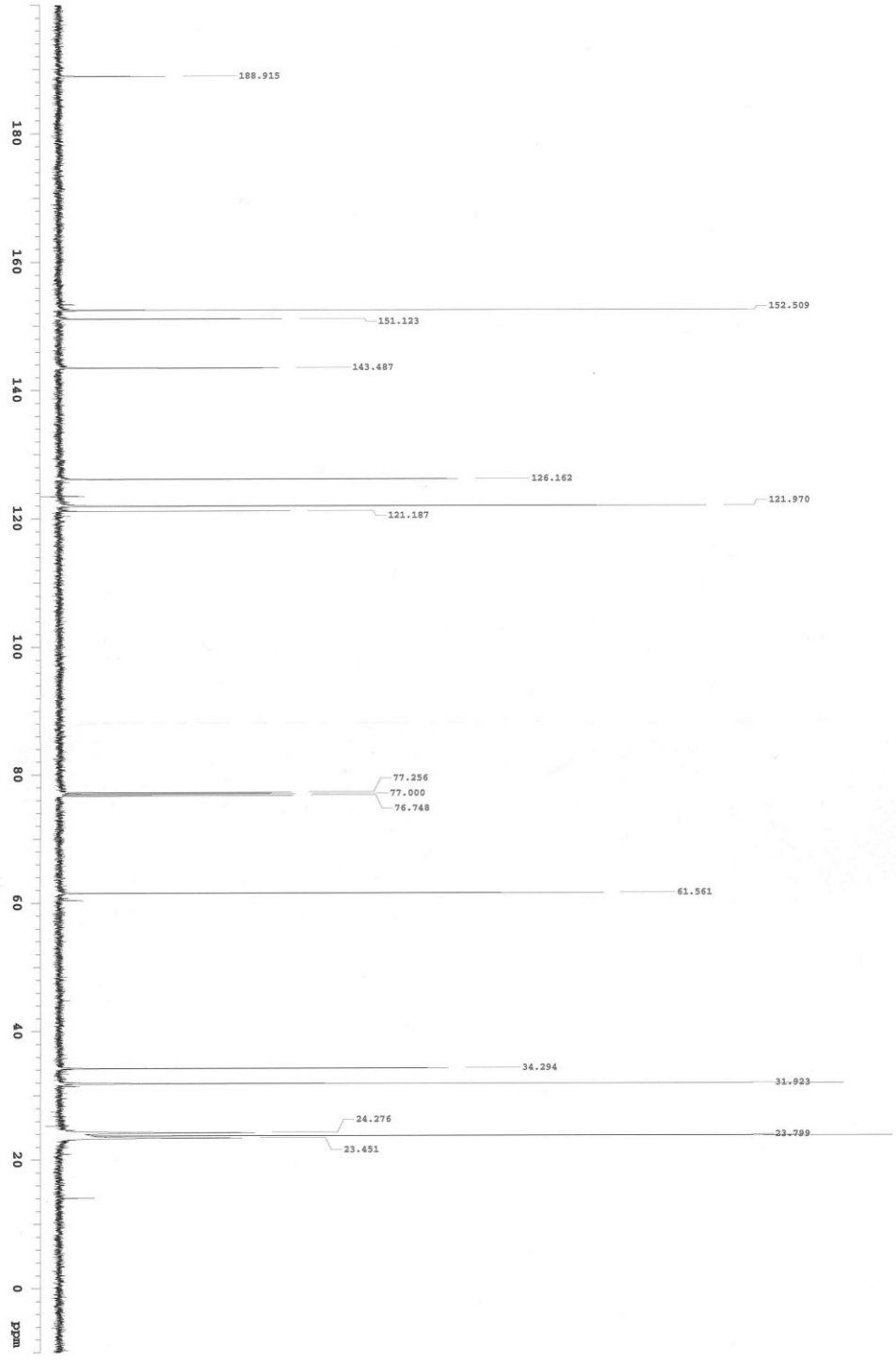
^{1}H NMR



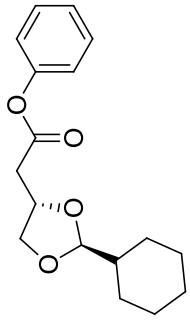
(*E*)-S-(2,4,6-Triisopropylphenyl) 4-hydroxybut-2-enethioate (1f)



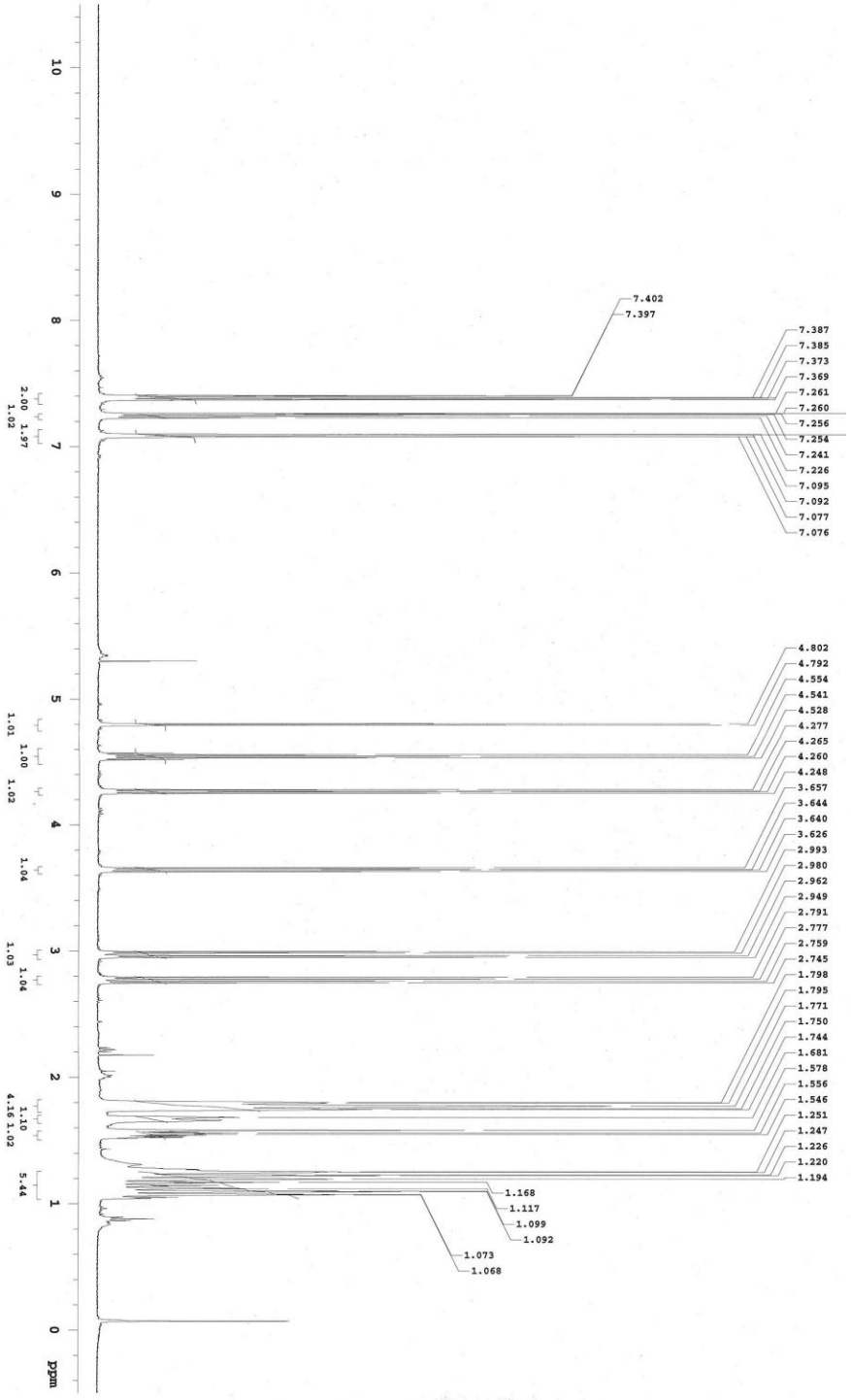
^{13}C NMR



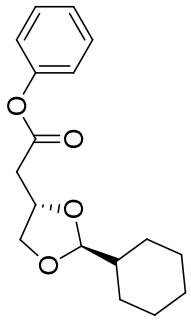
Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate (3ba)



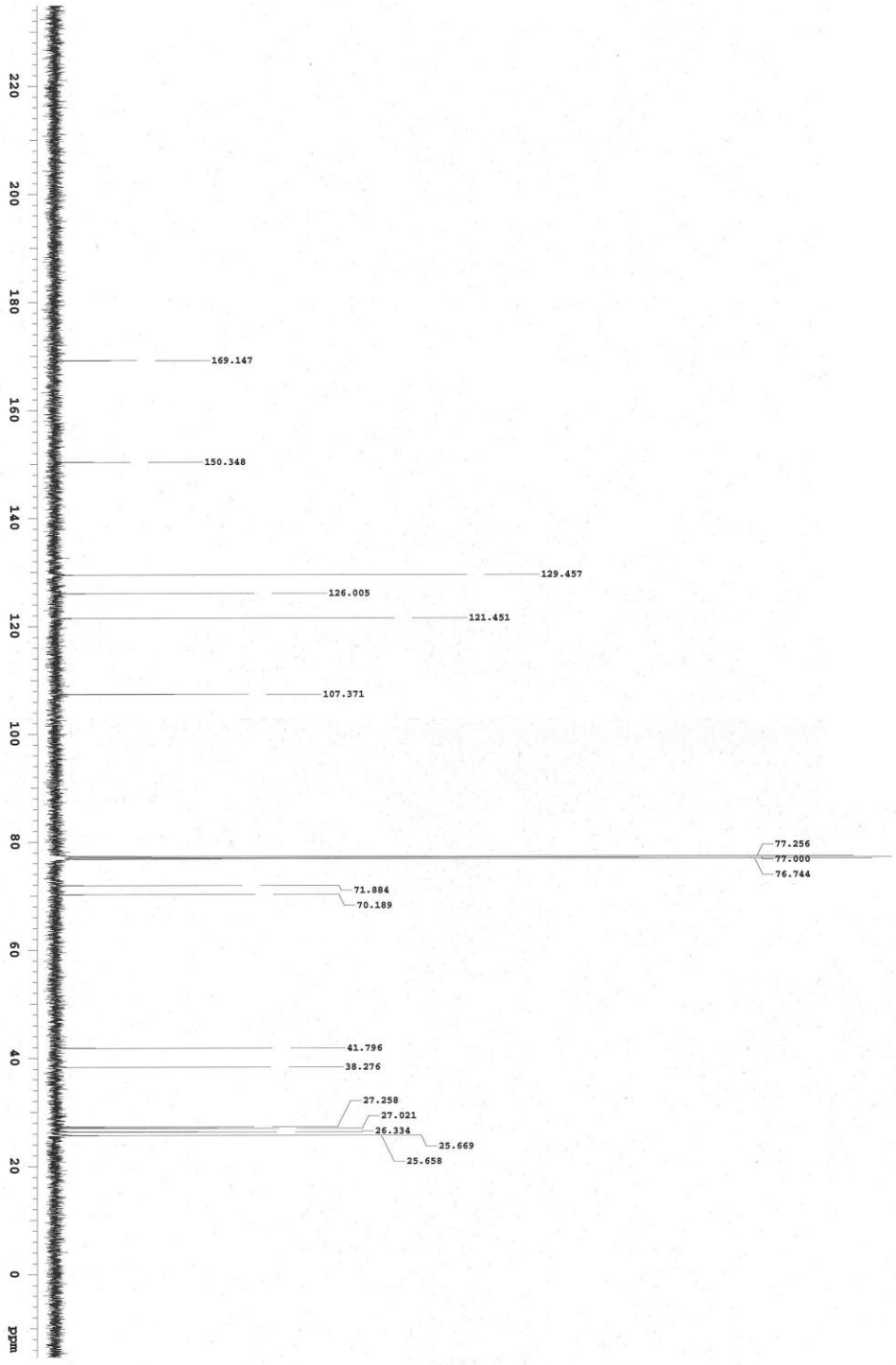
^{1}H NMR



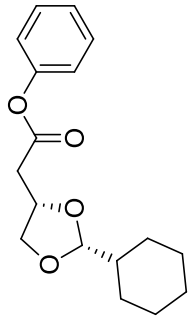
Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate (3ba)



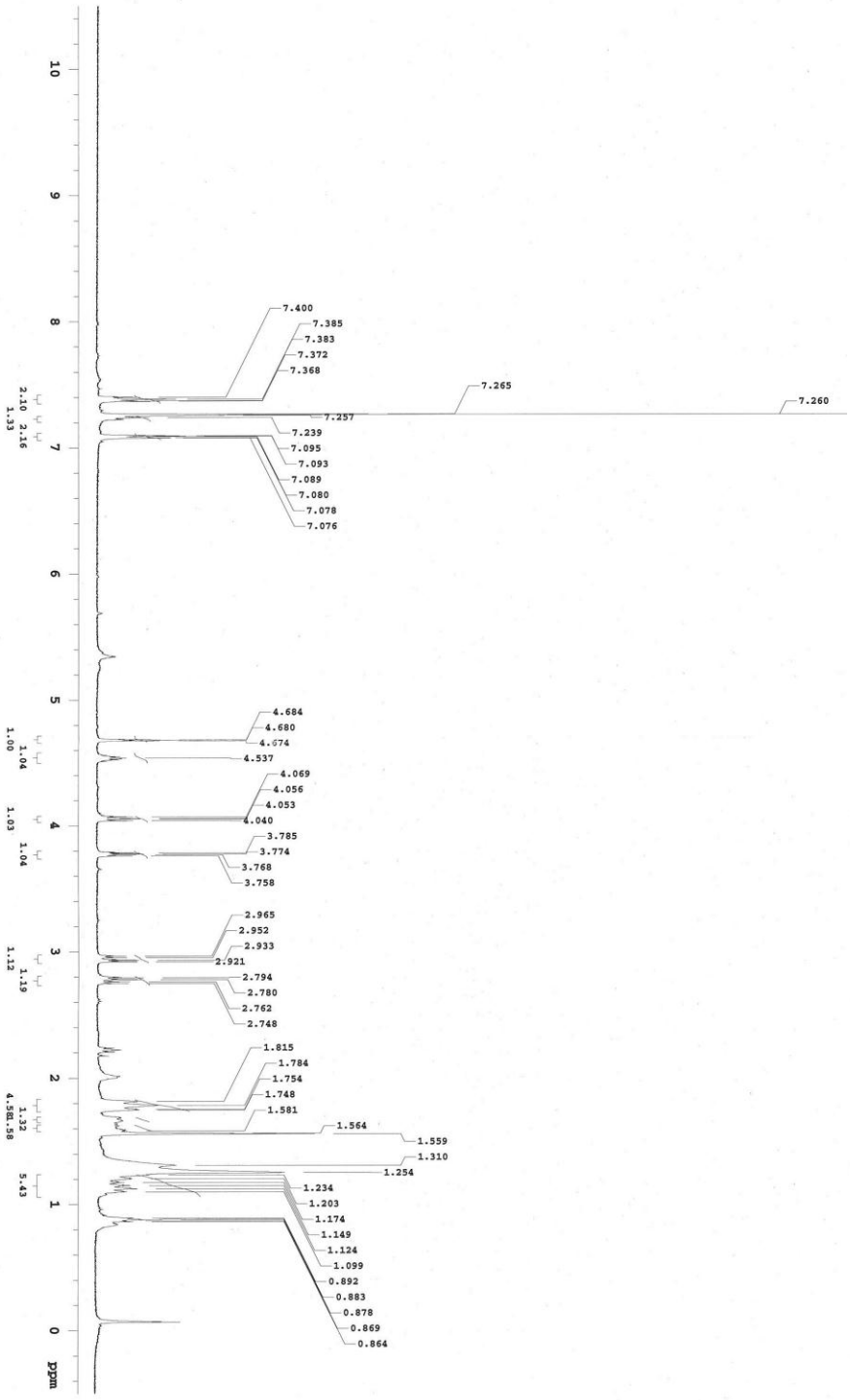
^{13}C NMR



Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate (3ba')



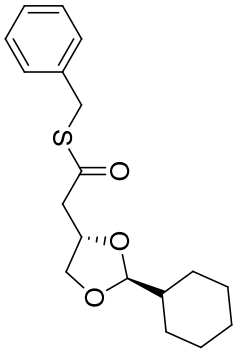
^{1}H NMR



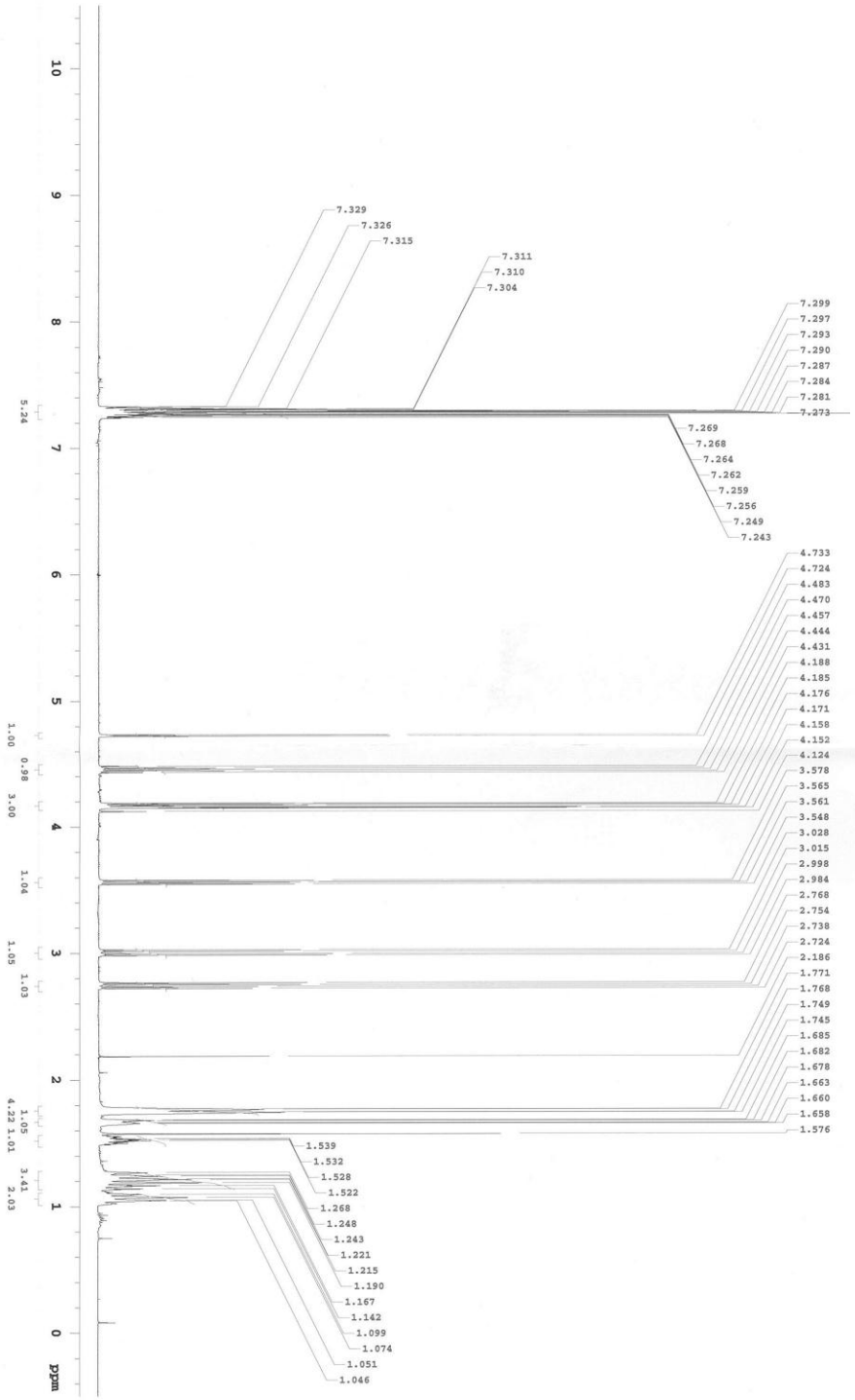
Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate (3ba')

^{13}C NMR

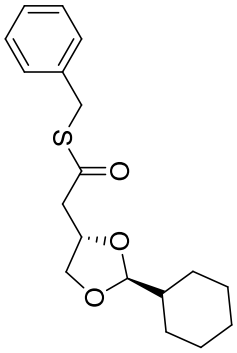
S-Benzyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ca)



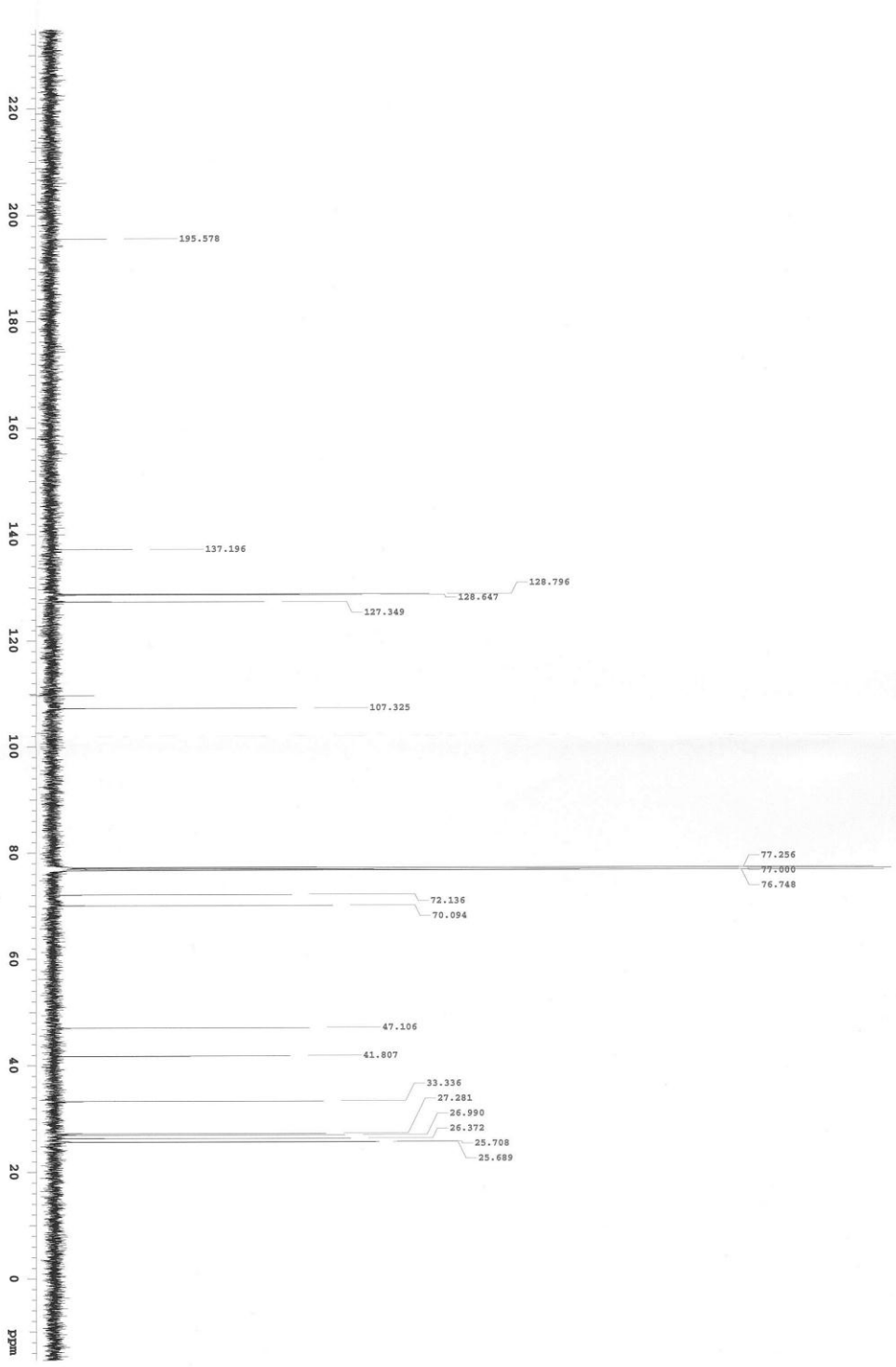
^{1}H NMR



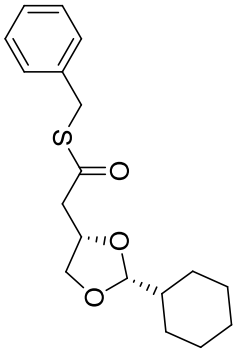
S-Benzyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ca)



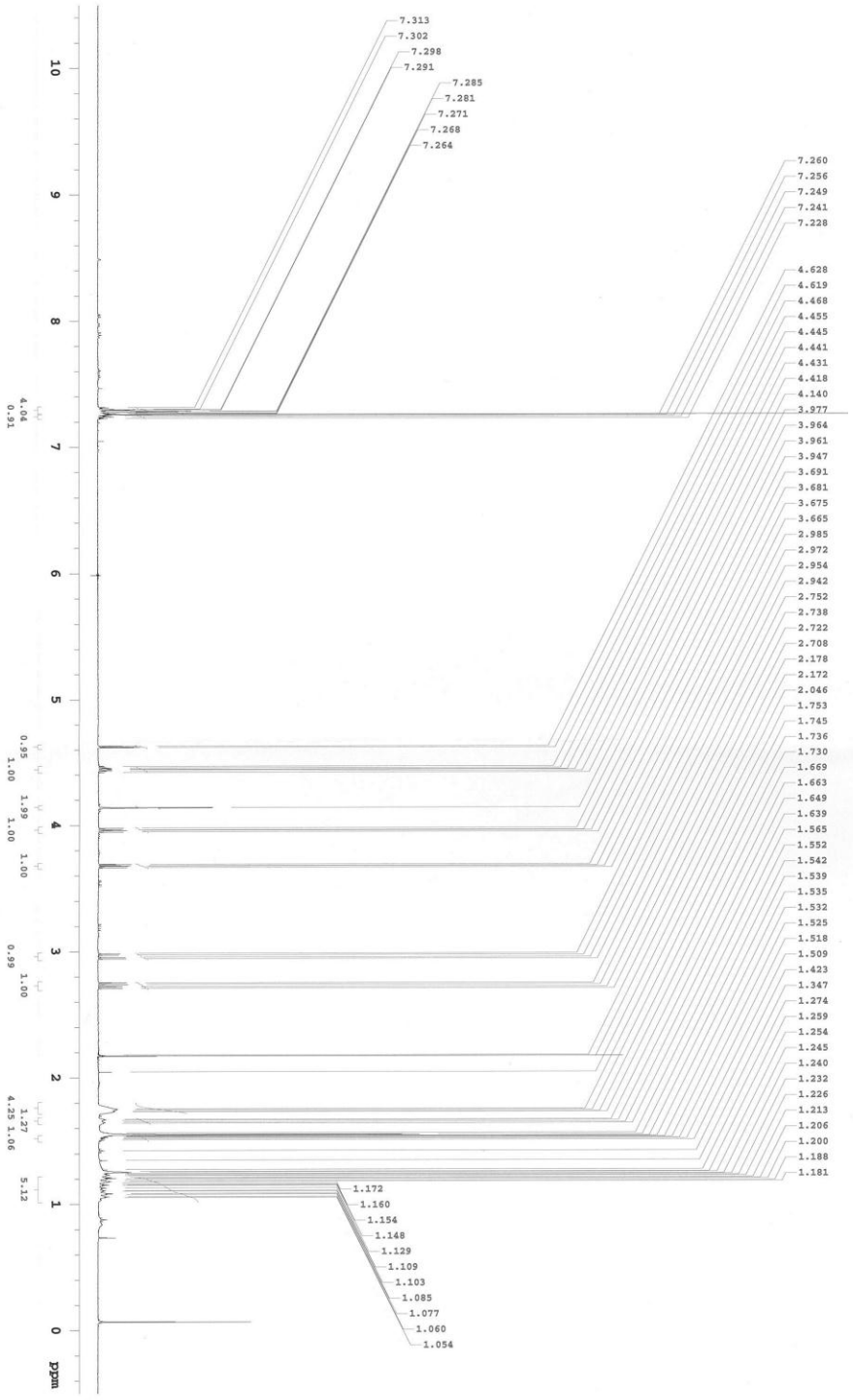
^{13}C NMR



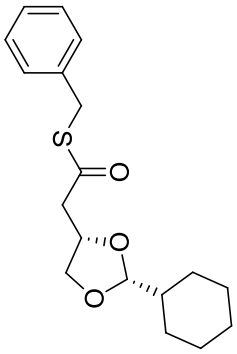
S-Benzyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ca')



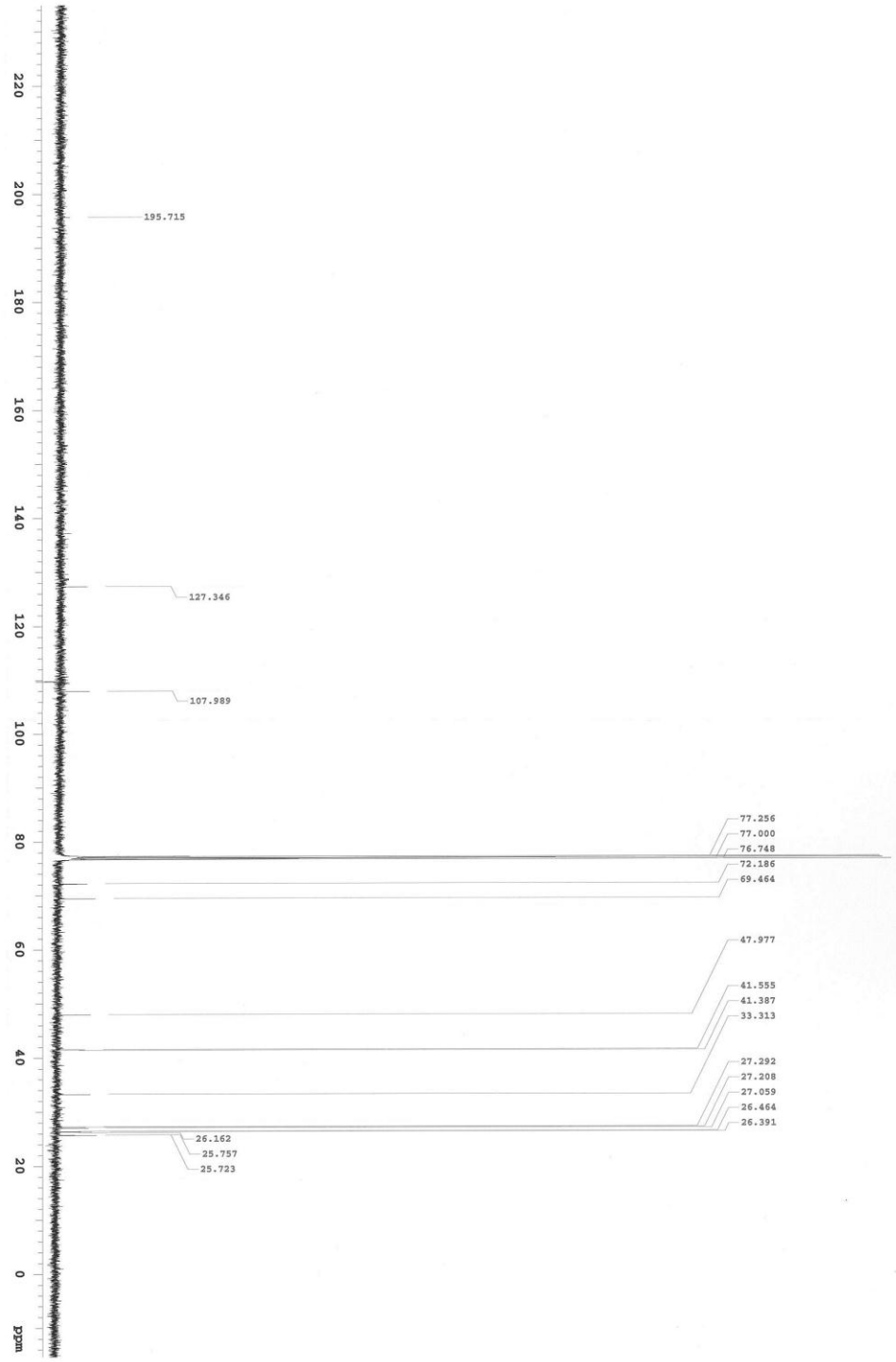
^{1}H NMR



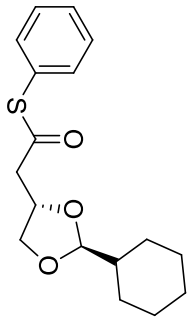
S-Benzyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ca')



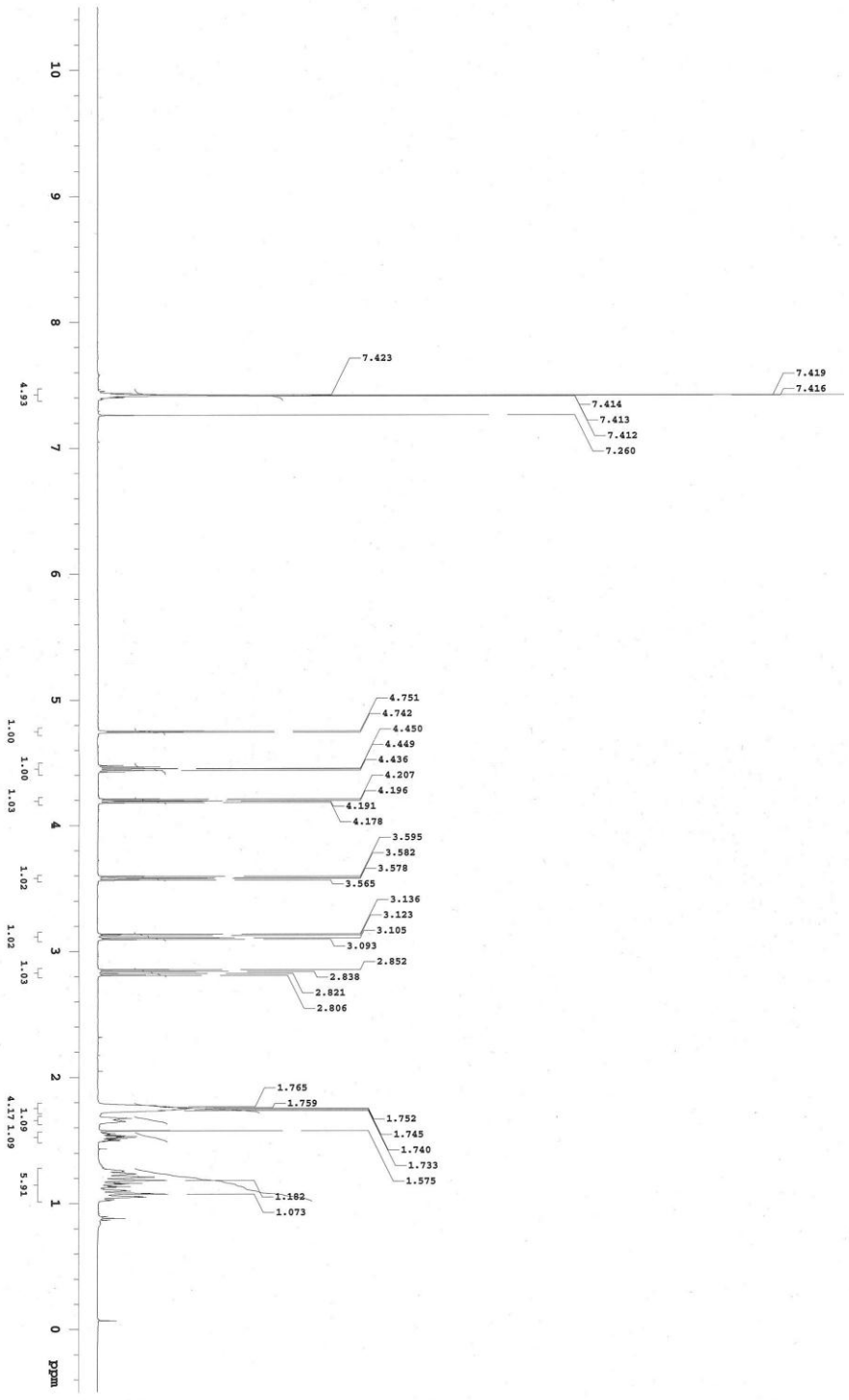
^{13}C NMR



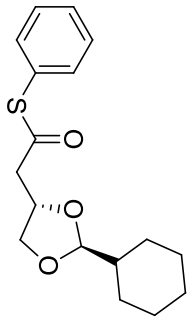
S-Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3da)



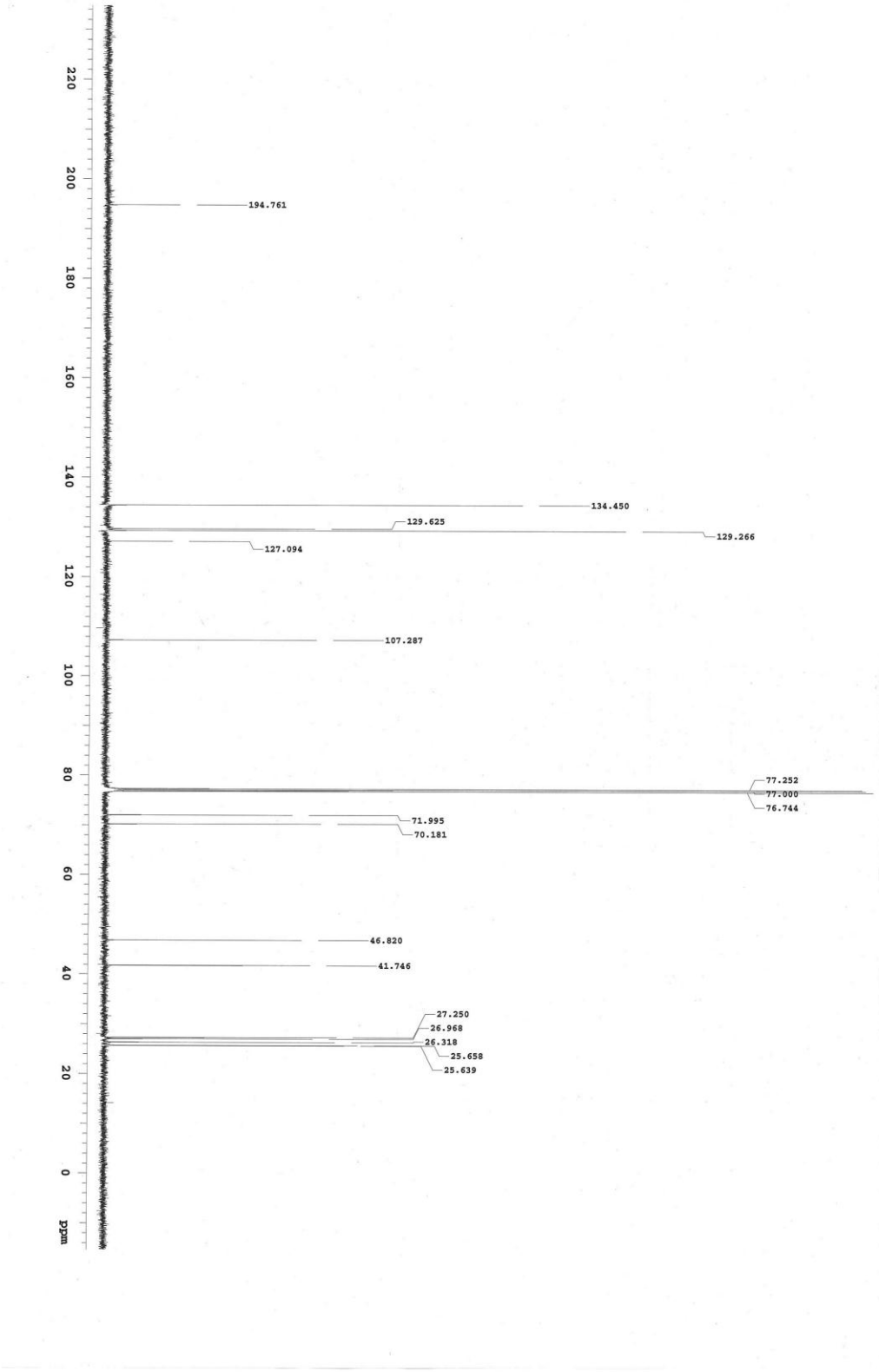
^{1}H NMR



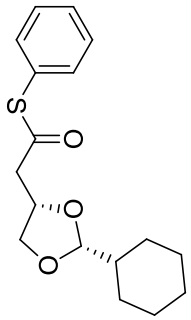
S-Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3da)



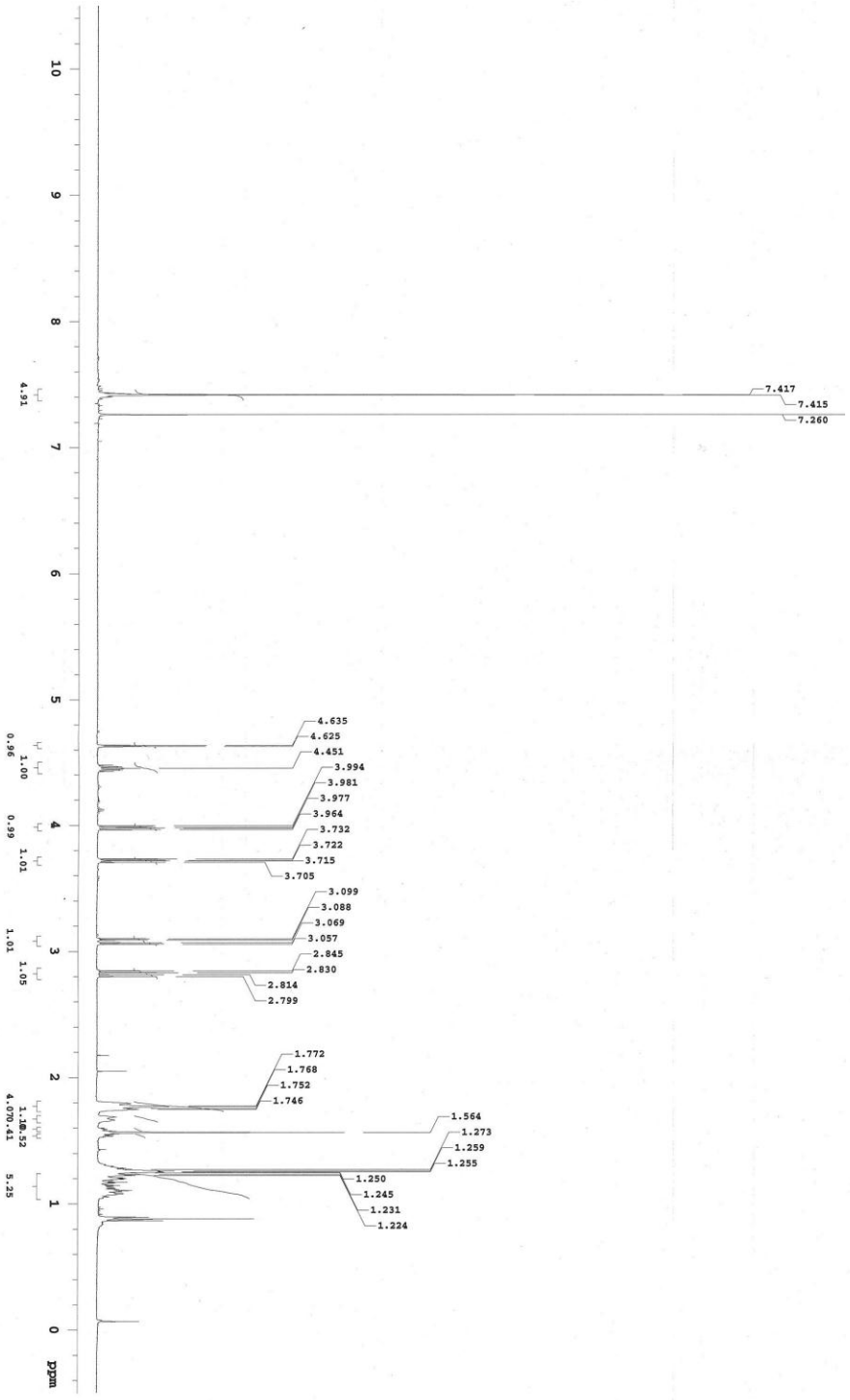
^{13}C NMR



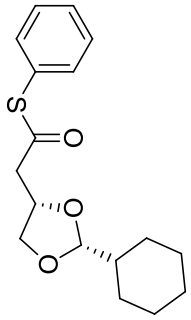
S-Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3da')



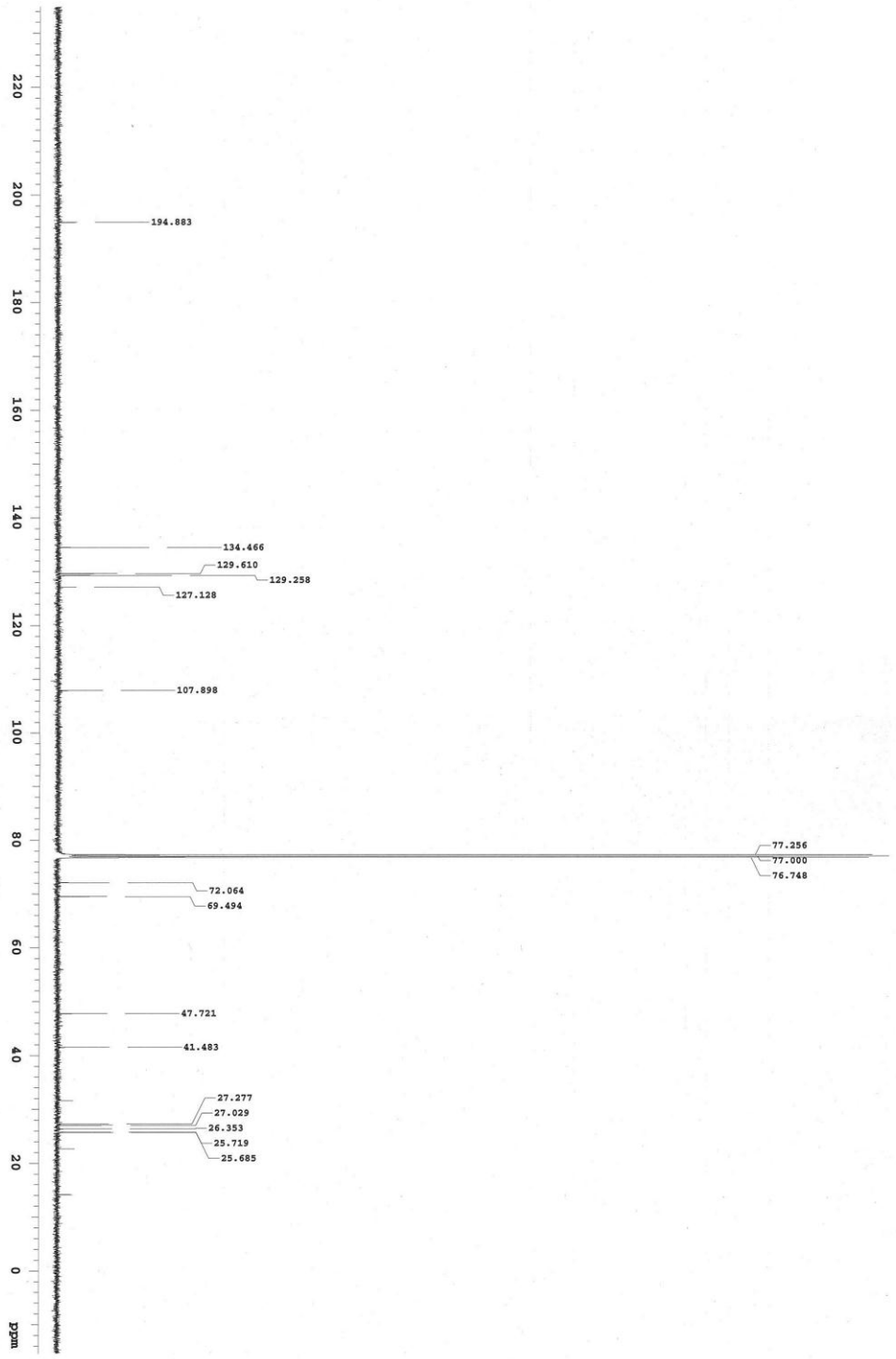
^{1}H NMR



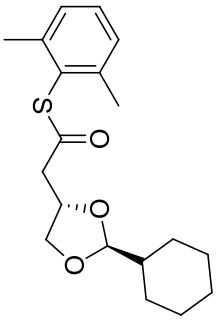
S-Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3da')



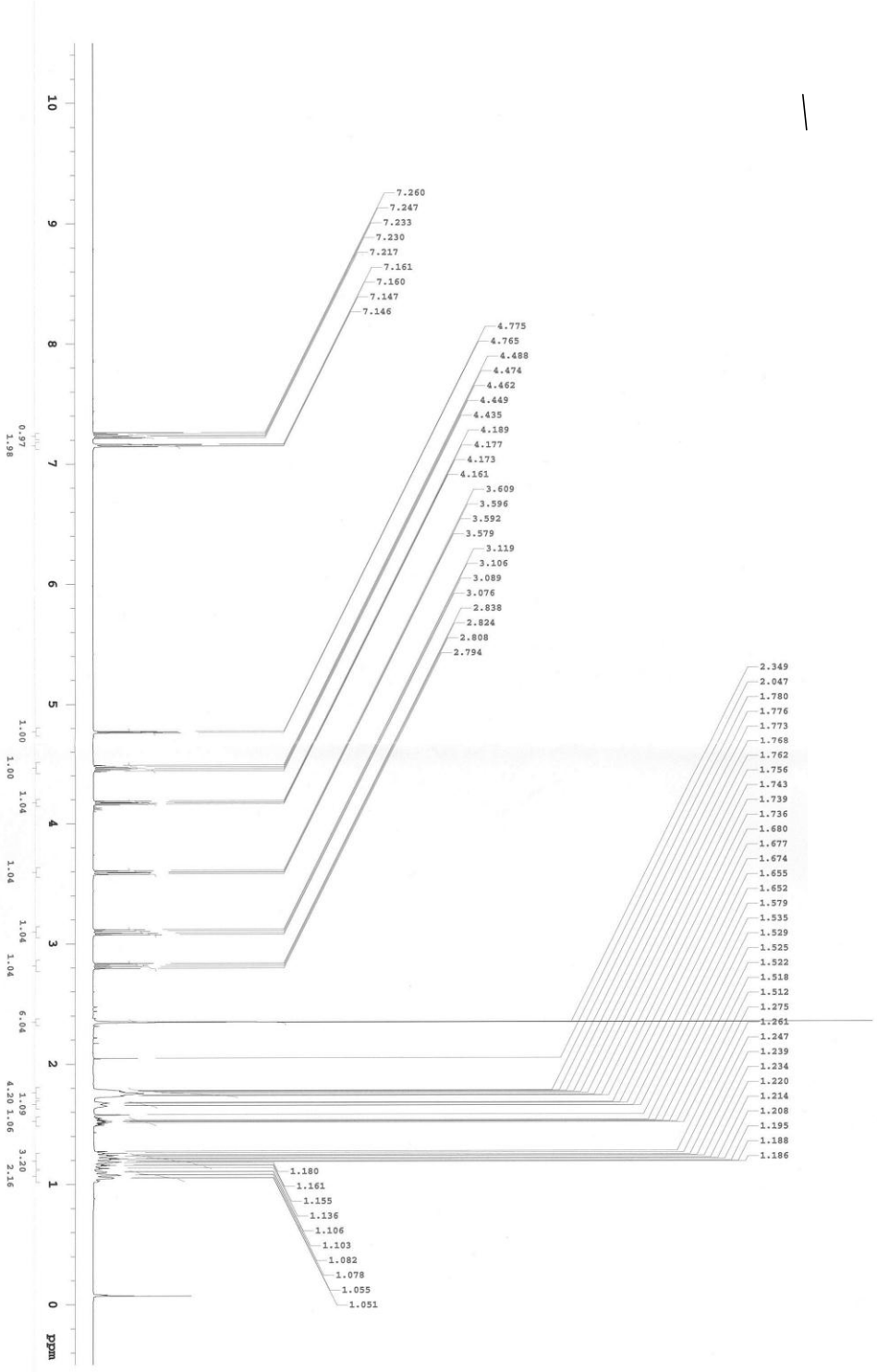
^{13}C NMR



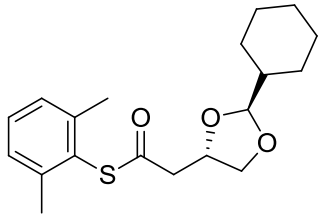
S-(2,6-Dimethylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ea)



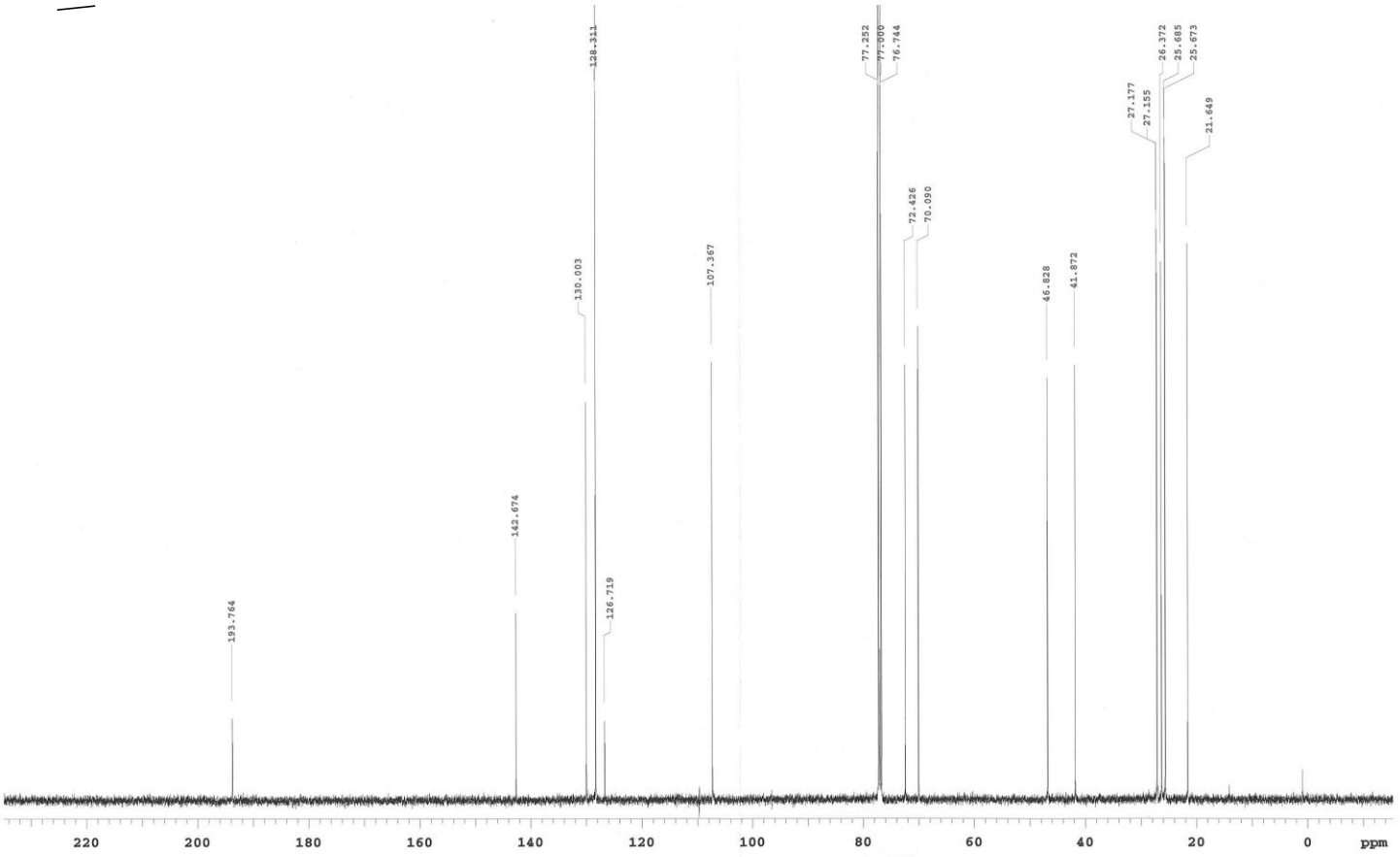
^{1}H NMR



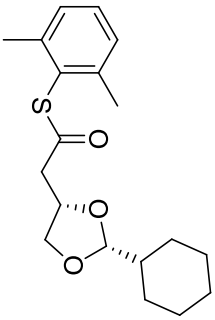
S-(2,6-Dimethylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ea)



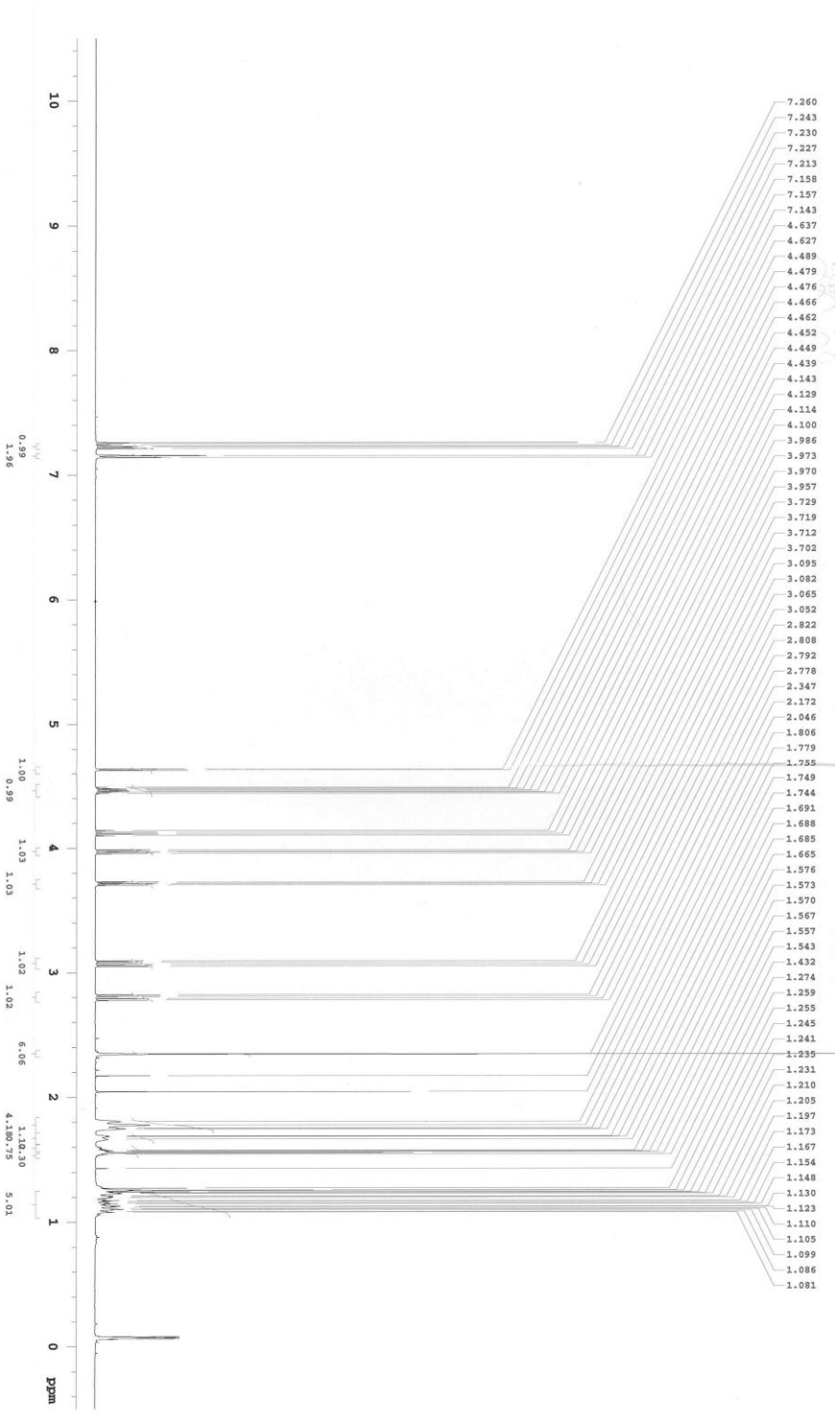
^{13}C NMR



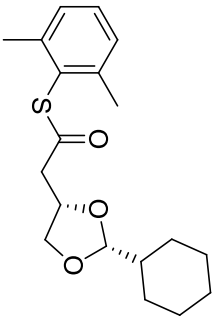
S-(2,6-Dimethylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ea')



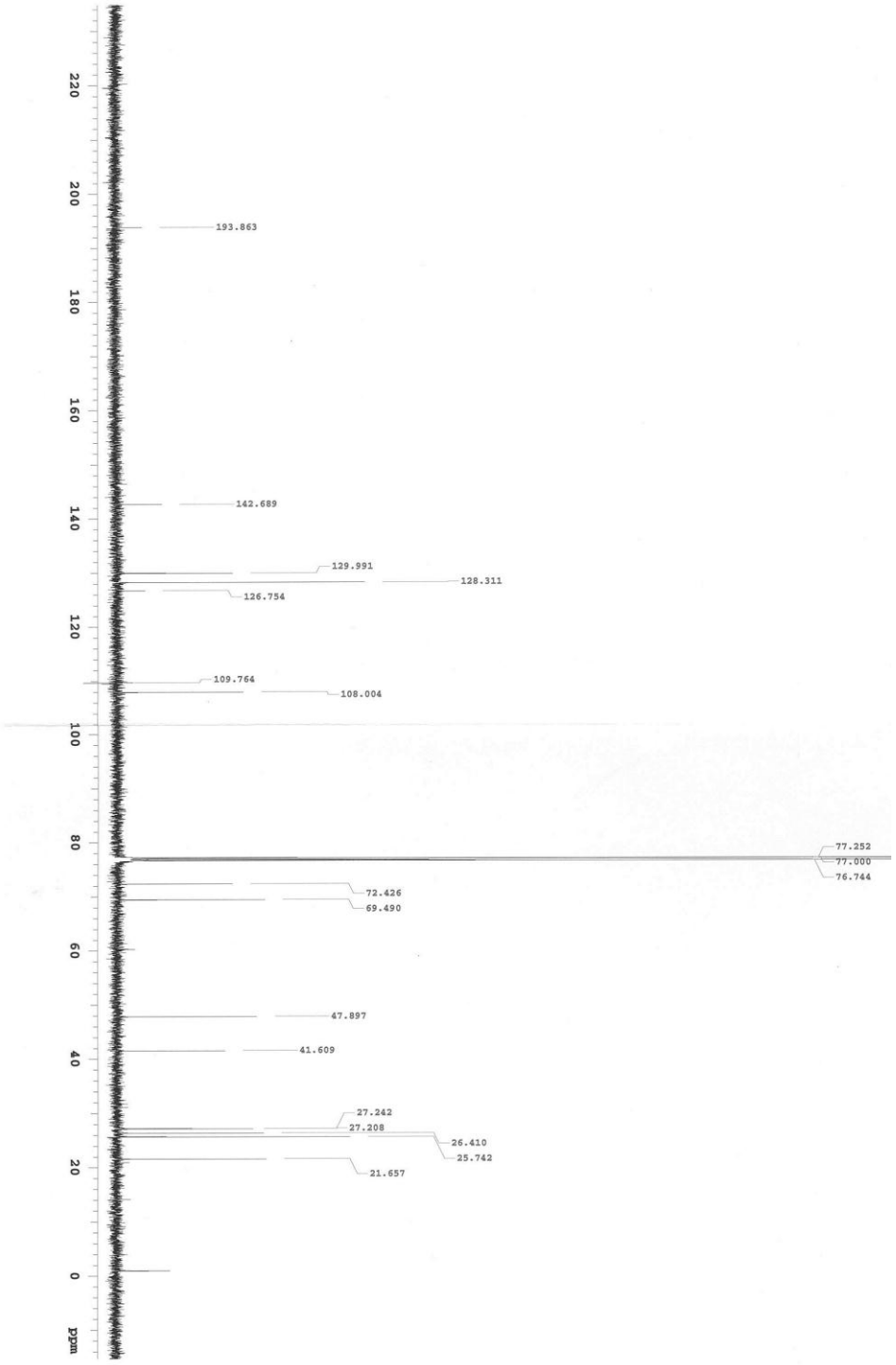
^{1}H NMR



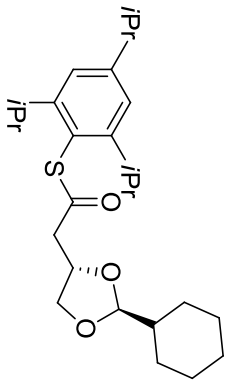
S-(2,6-Dimethylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ea')



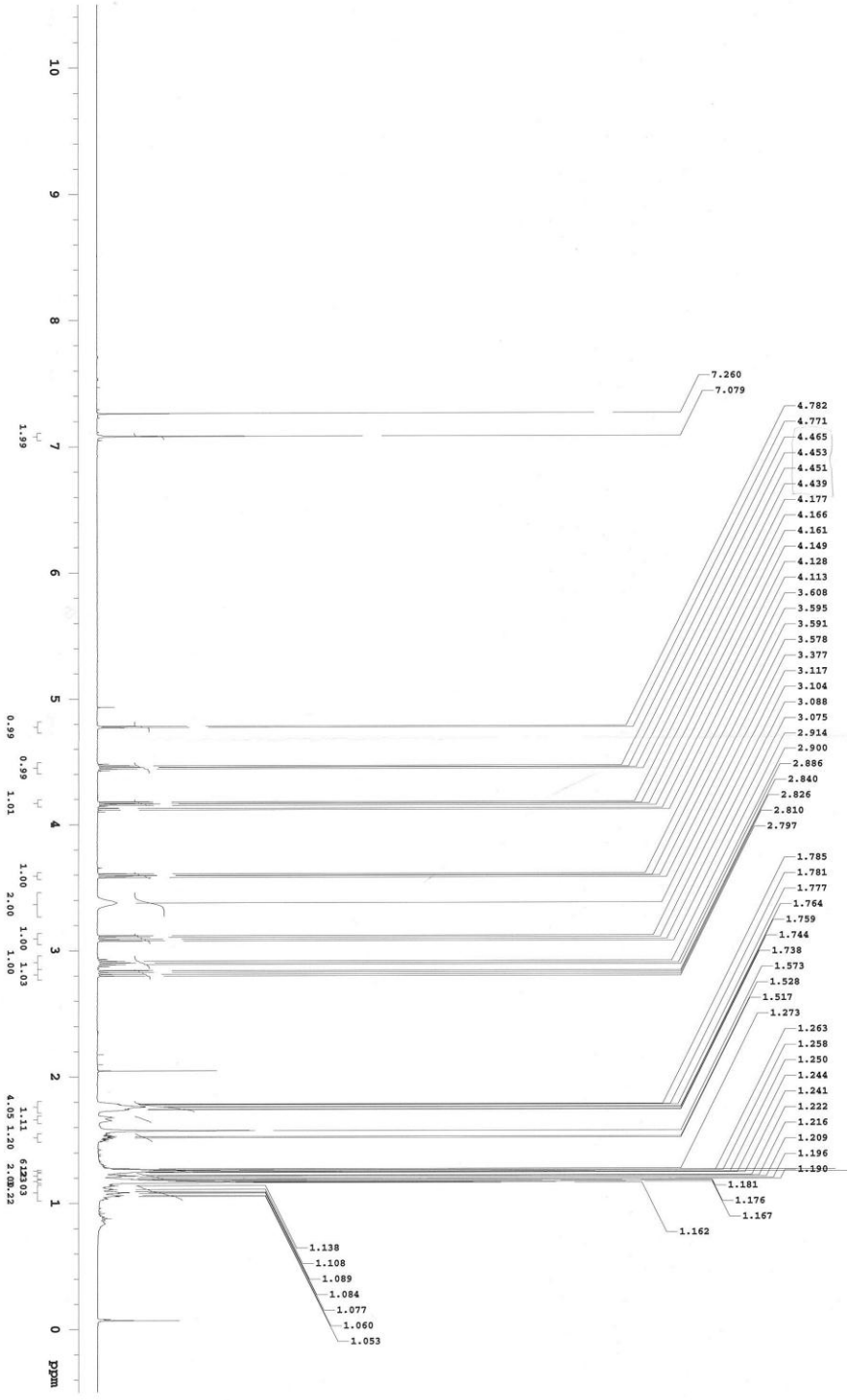
^{13}C NMR



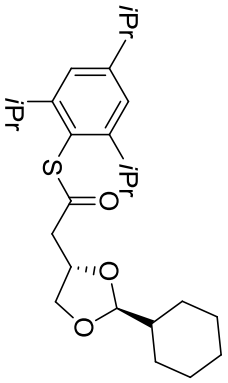
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3fa)



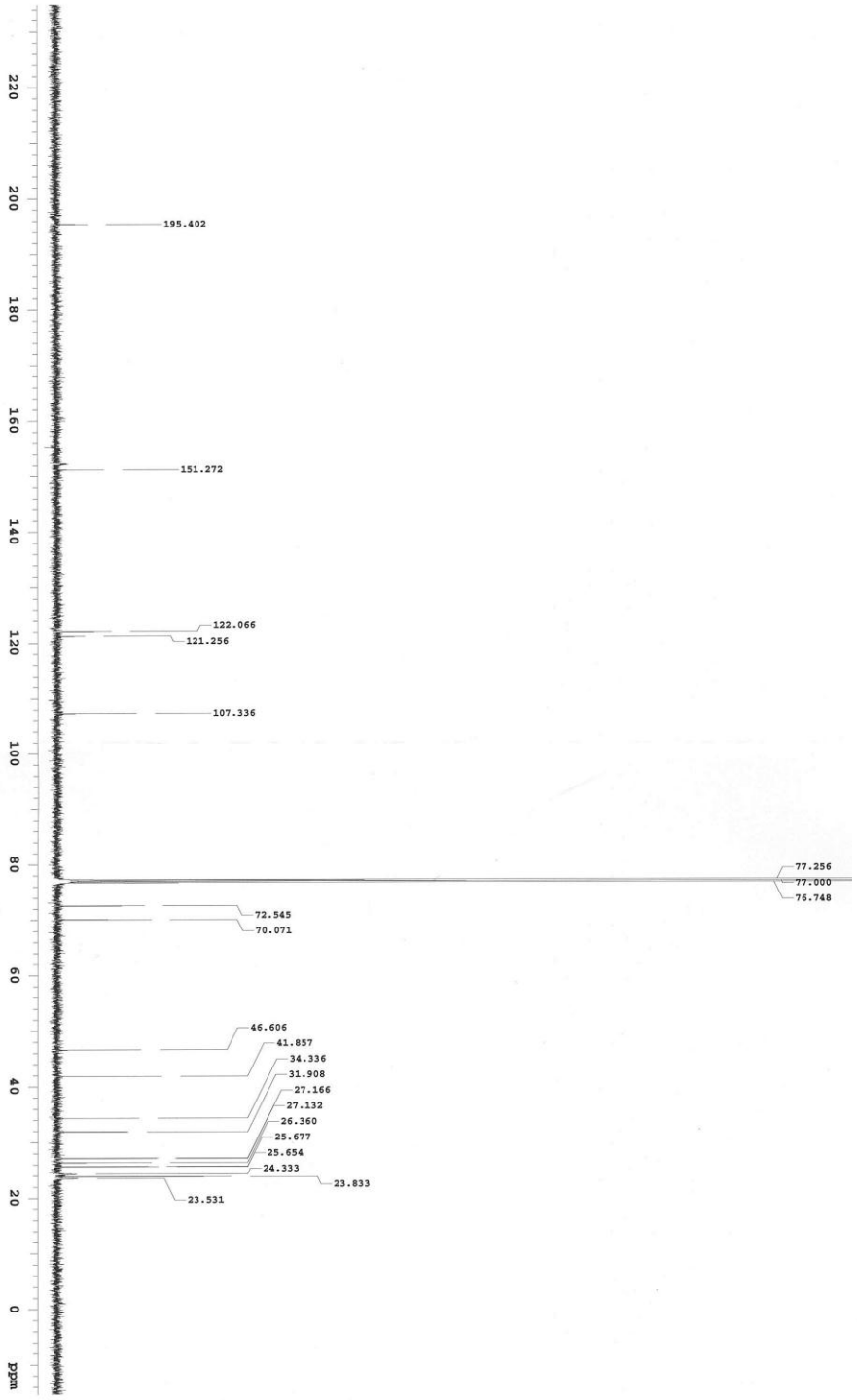
^{1}H NMR



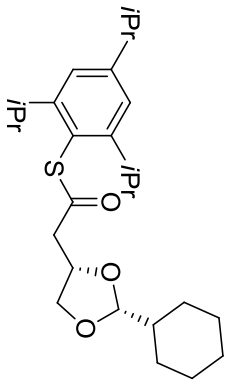
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3fa)



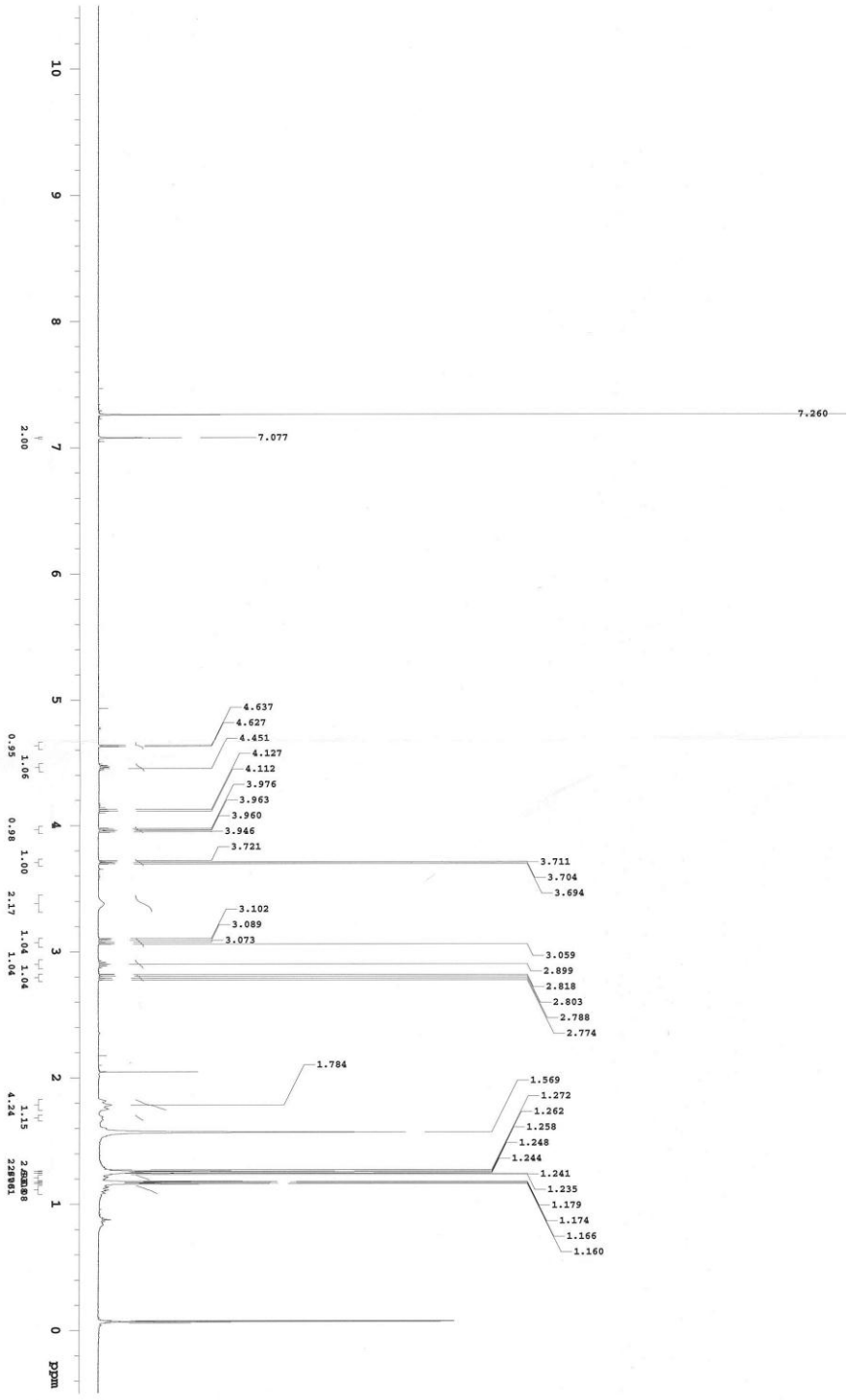
^{13}C NMR



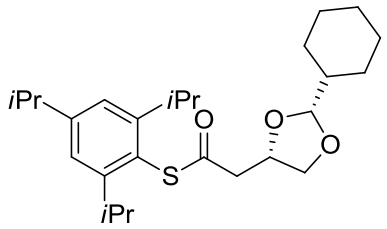
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3fa')



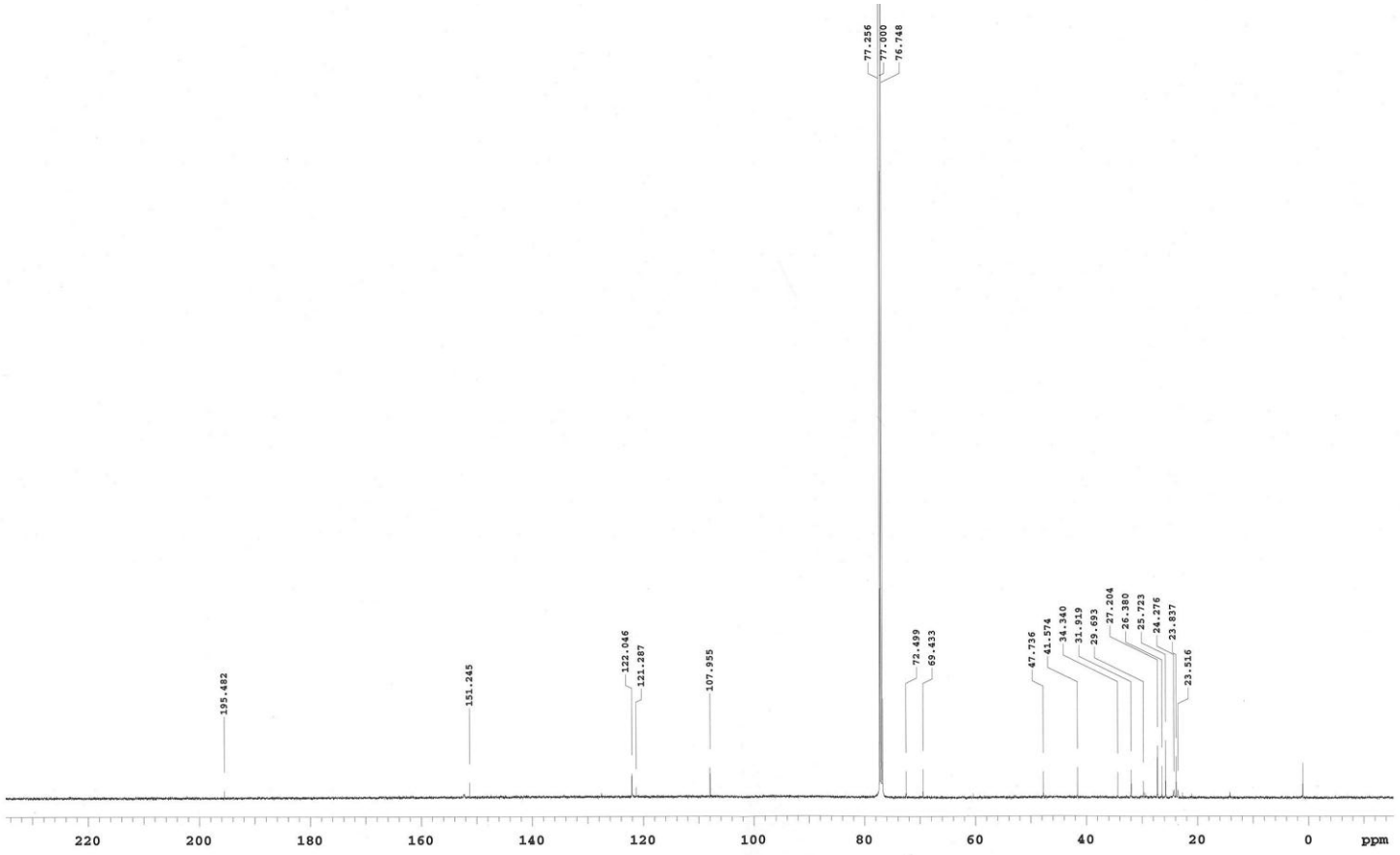
^{1}H NMR



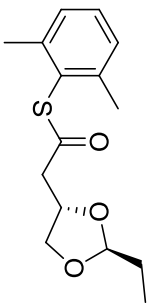
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3fa')



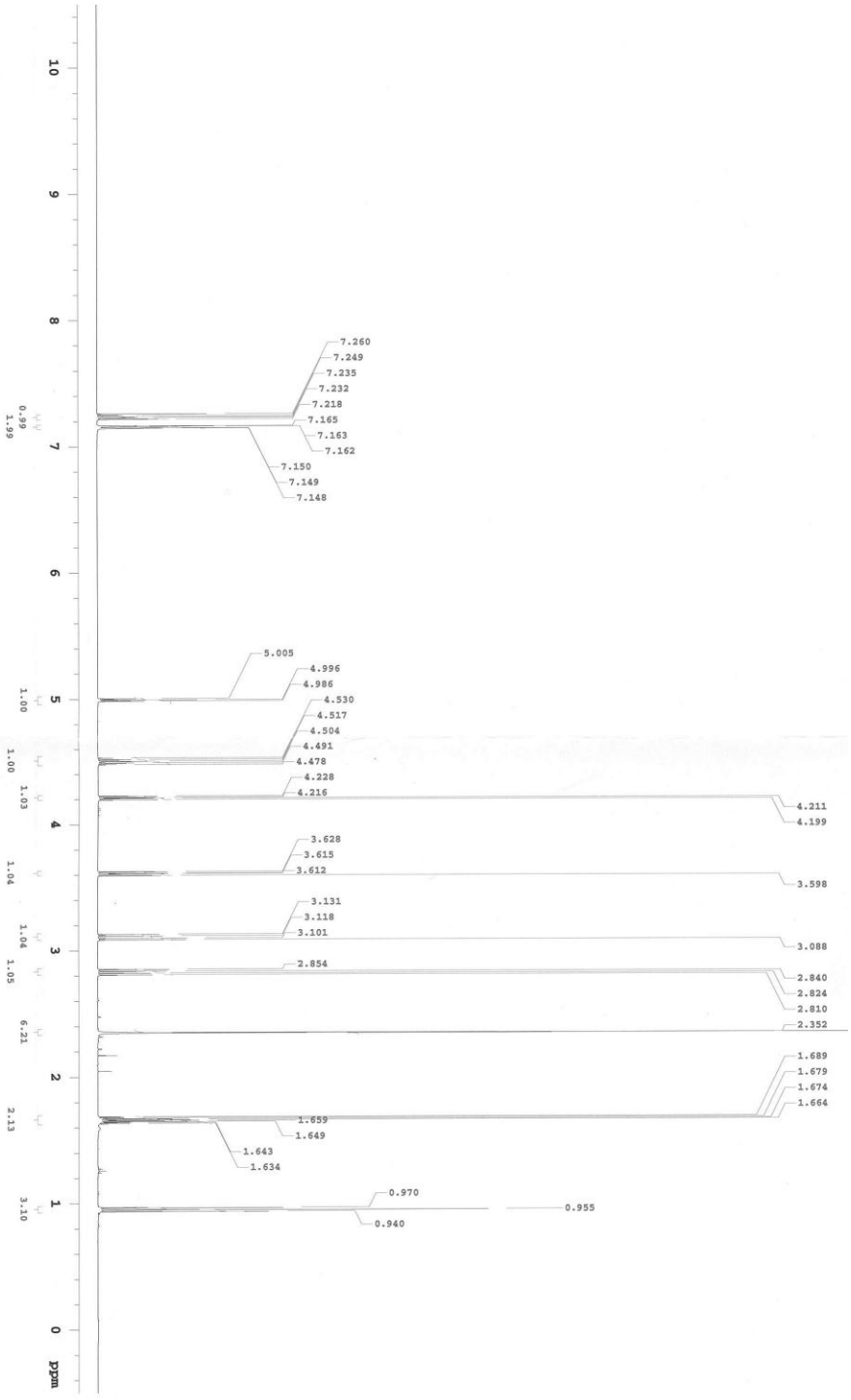
^{13}C NMR



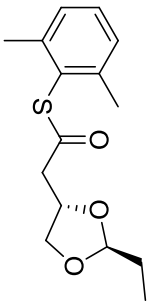
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate (3eb)



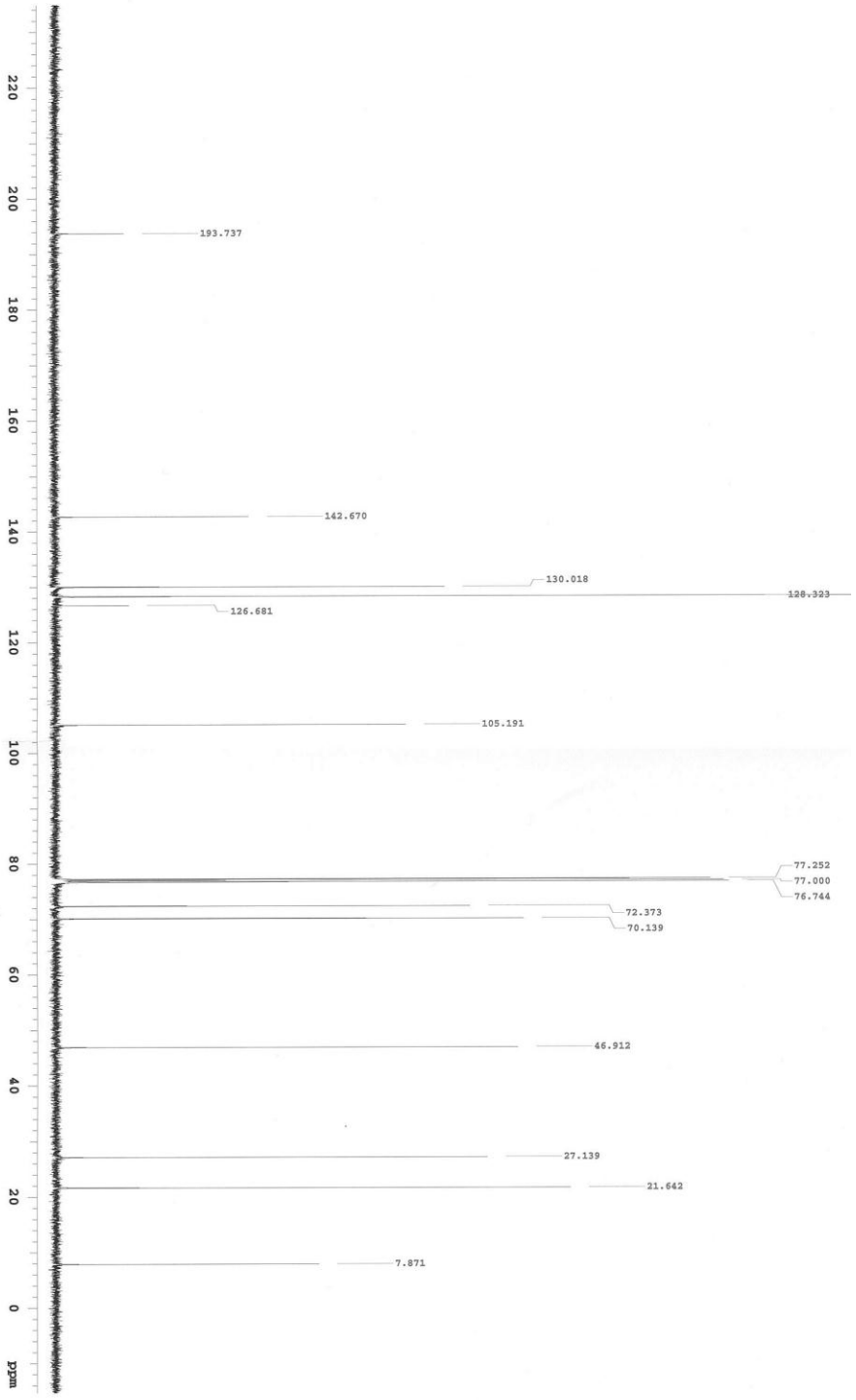
^{1}H NMR



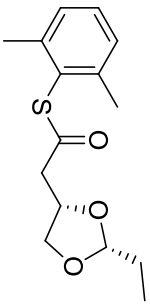
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate (3eb)



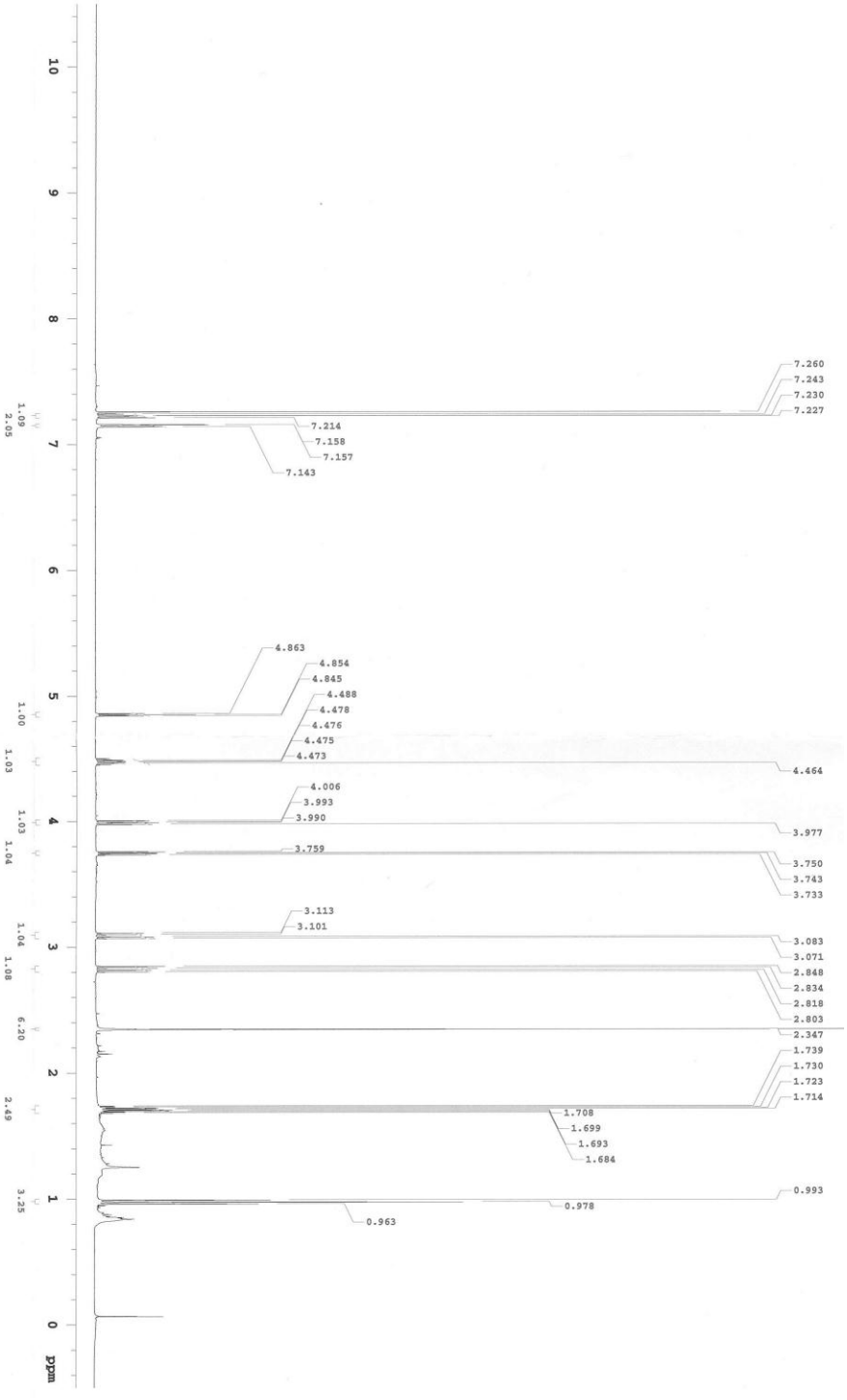
^{13}C NMR



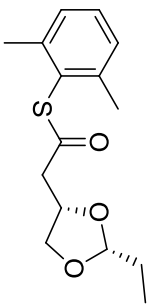
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate (3eb')



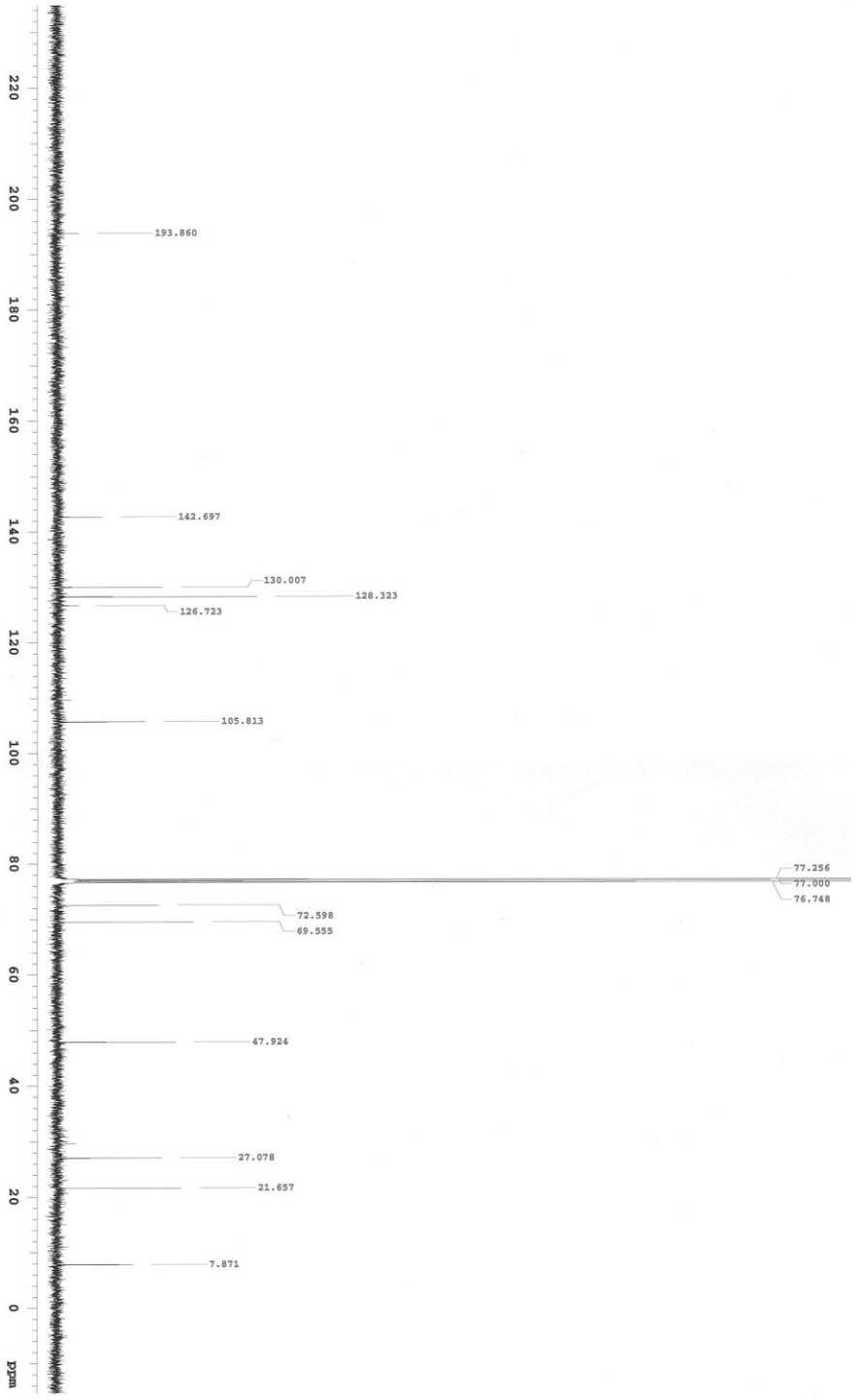
^{1}H NMR



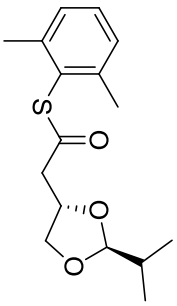
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate (3eb')



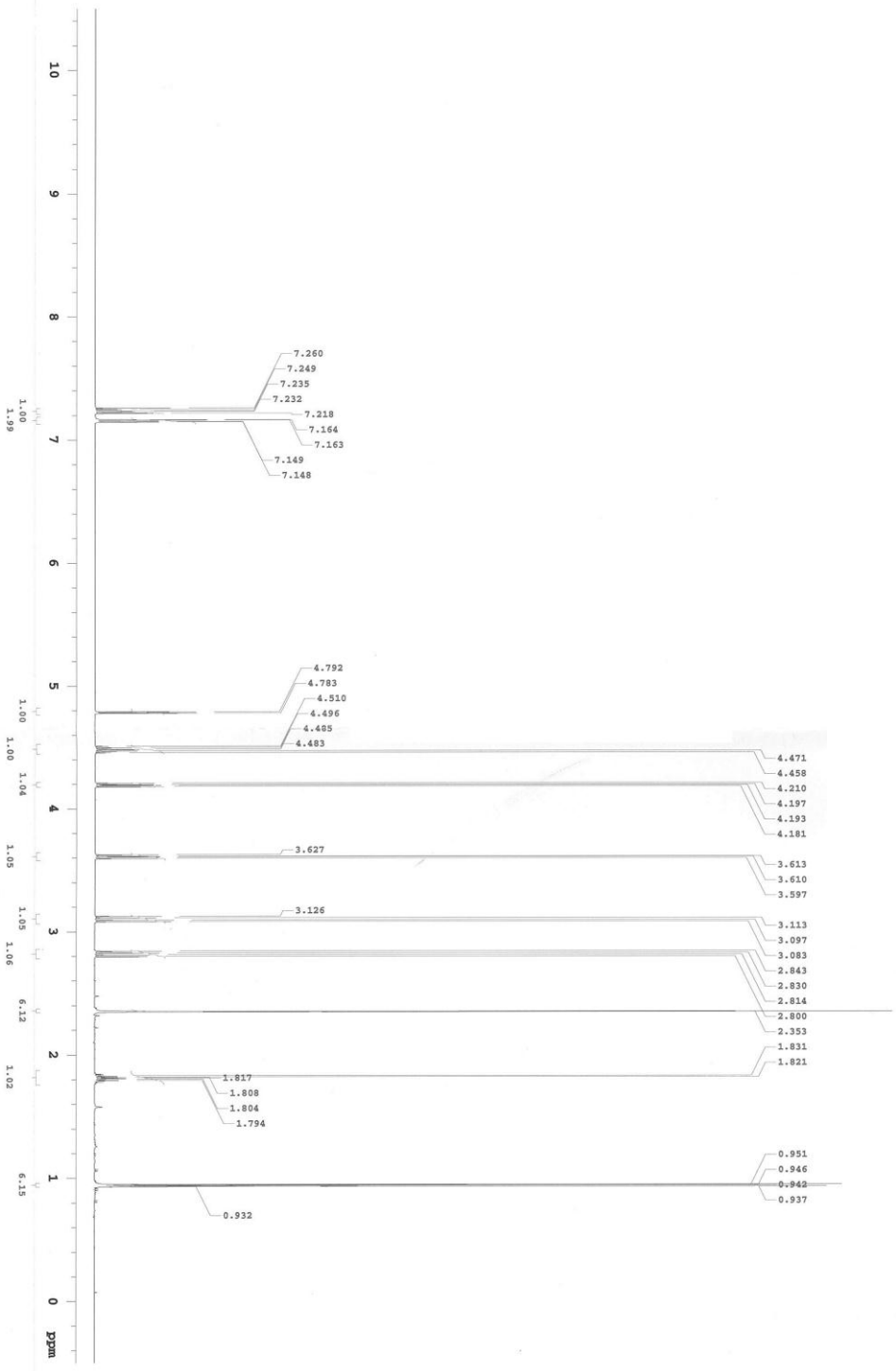
^{13}C NMR



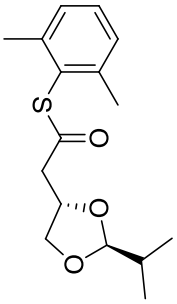
S-(2,6-Dimethylphenyl) 2-(2-isopropyl-1,3-dioxolan-4-yl)ethanethioate (3ec)



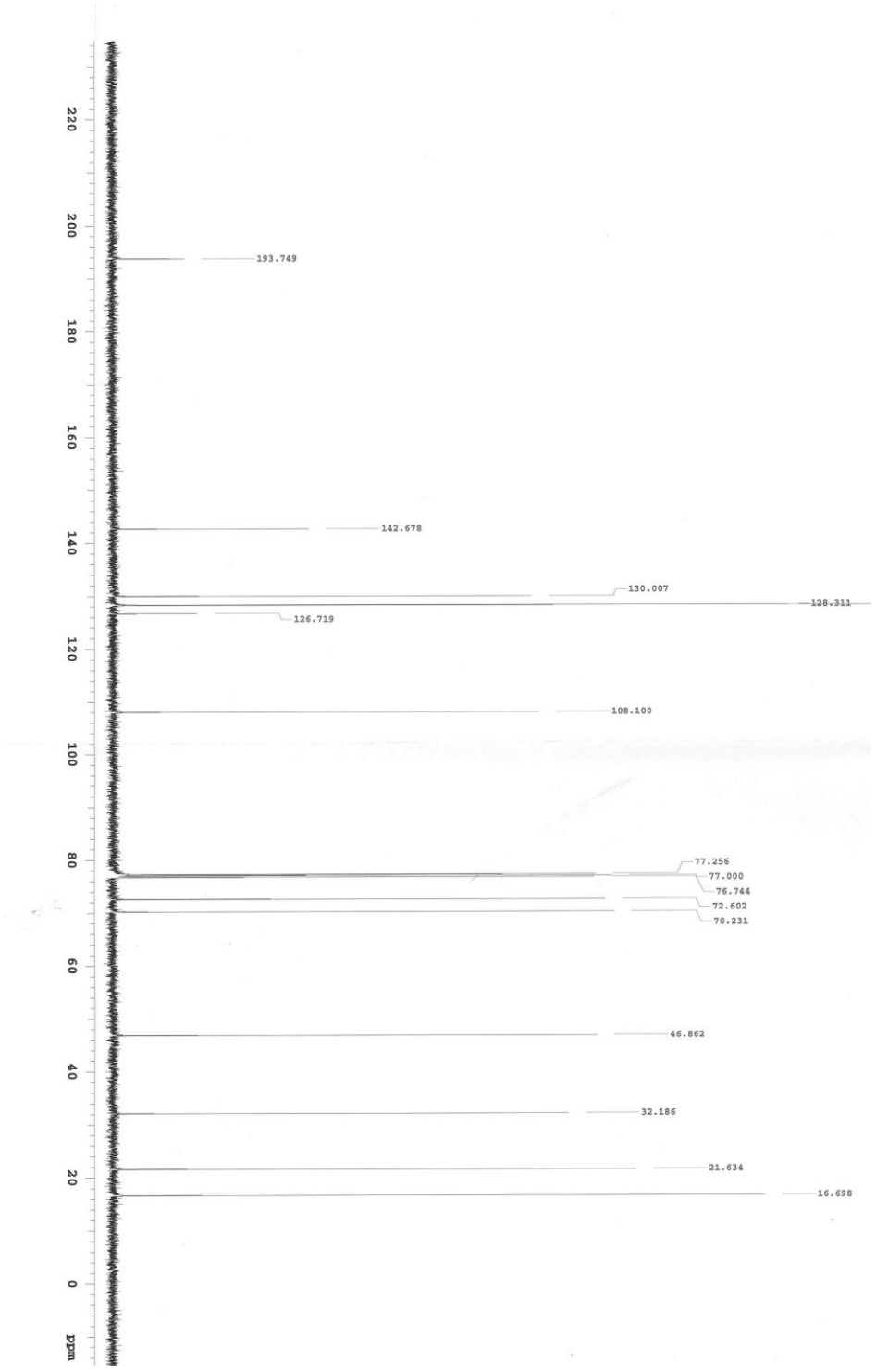
^{1}H NMR



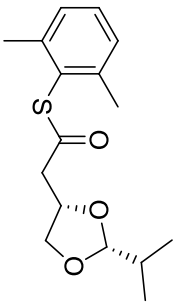
S-(2,6-Dimethylphenyl) 2-(2-isopropyl-1,3-dioxolan-4-yl)ethanethioate (3ec)



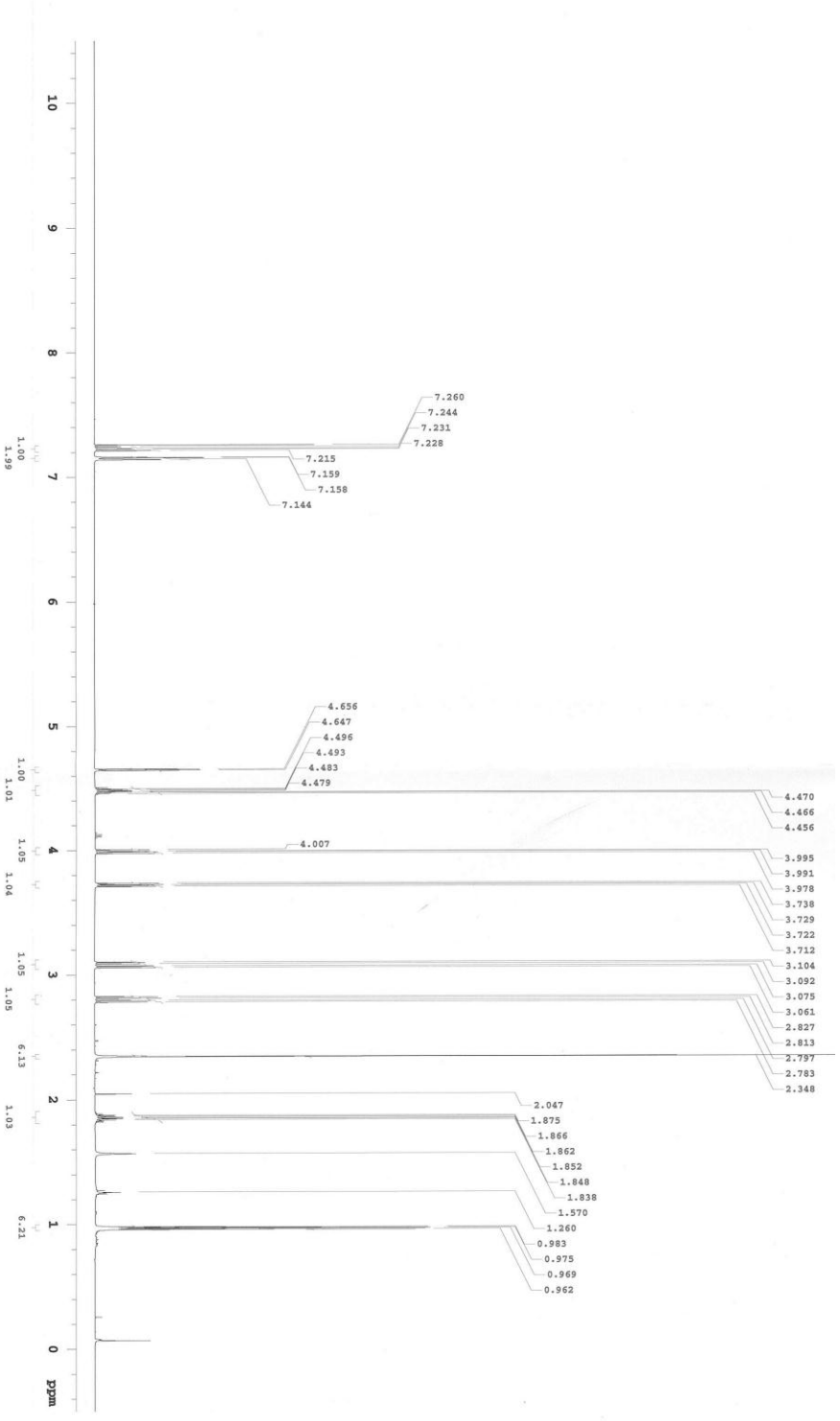
^{13}C NMR



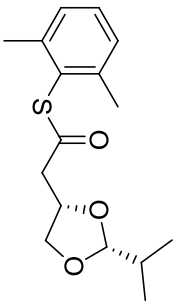
S-(2,6-Dimethylphenyl) 2-(2-isopropyl-1,3-dioxolan-4-yl)ethanethioate (3ec')



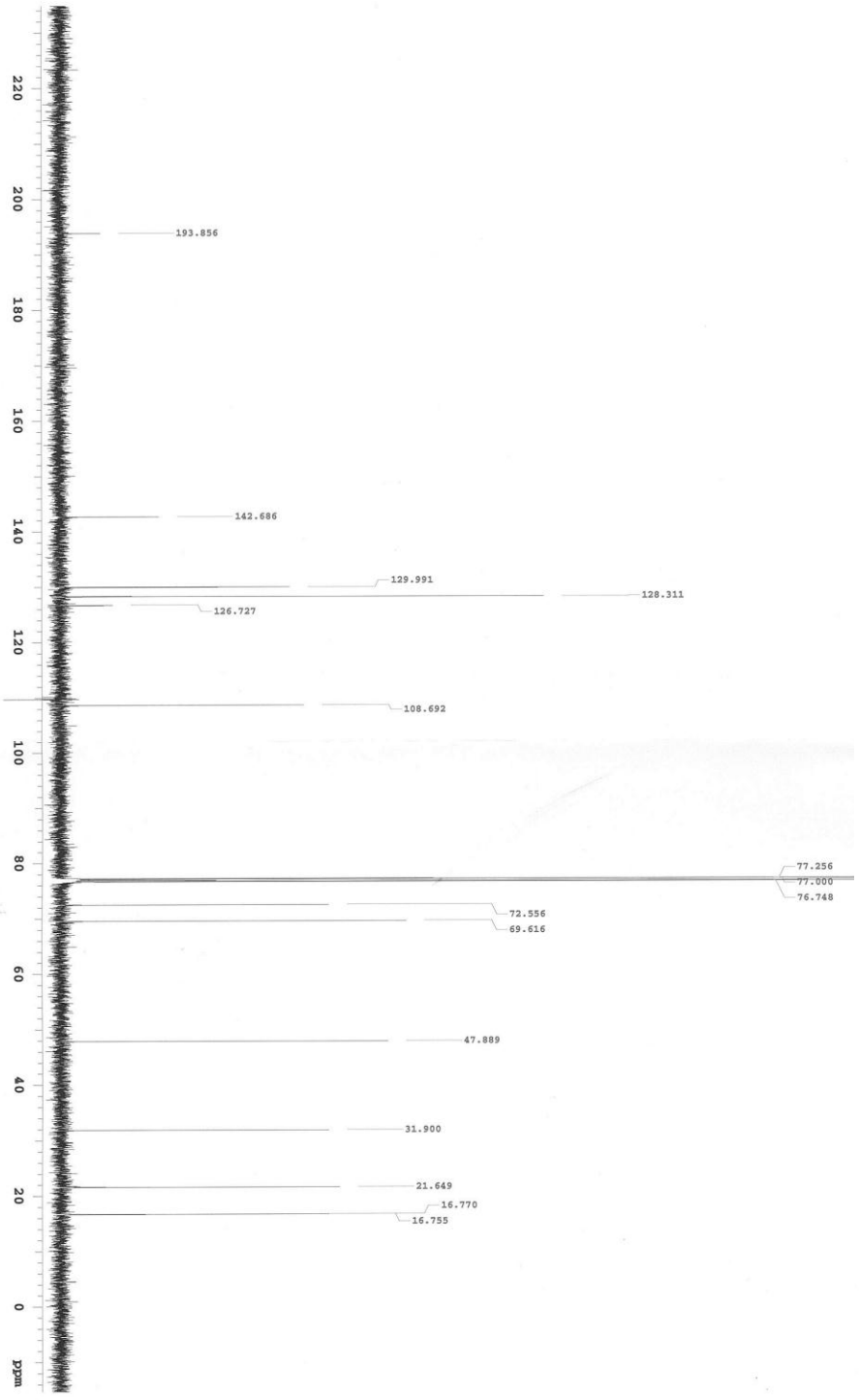
^{1}H NMR



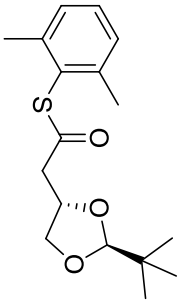
S-(2,6-Dimethylphenyl) 2-(2-isopropyl-1,3-dioxolan-4-yl)ethanethioate (3ec')



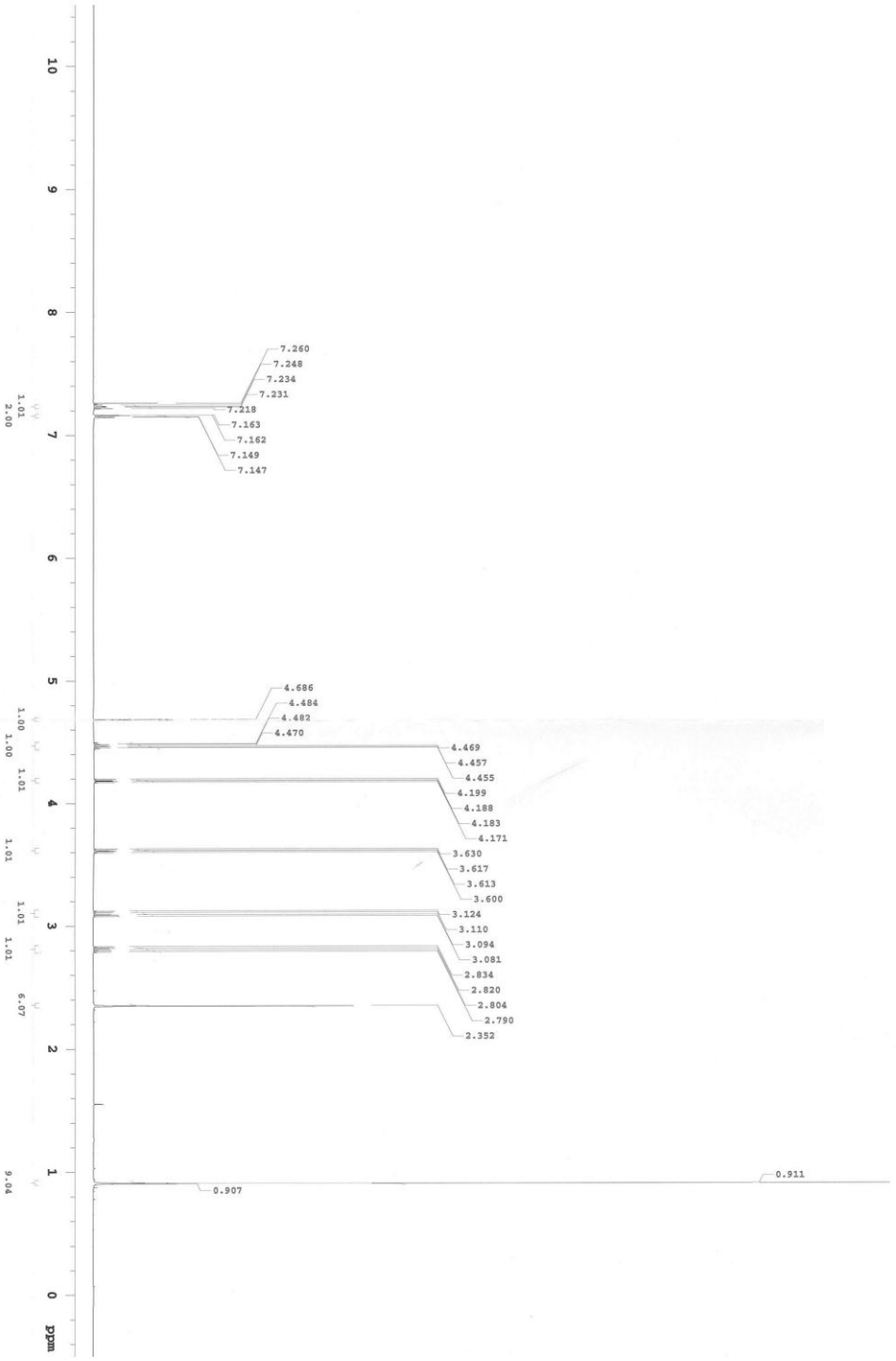
^{13}C NMR



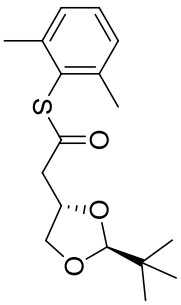
S-(2,6-Dimethylphenyl) 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanethioate (3ed)



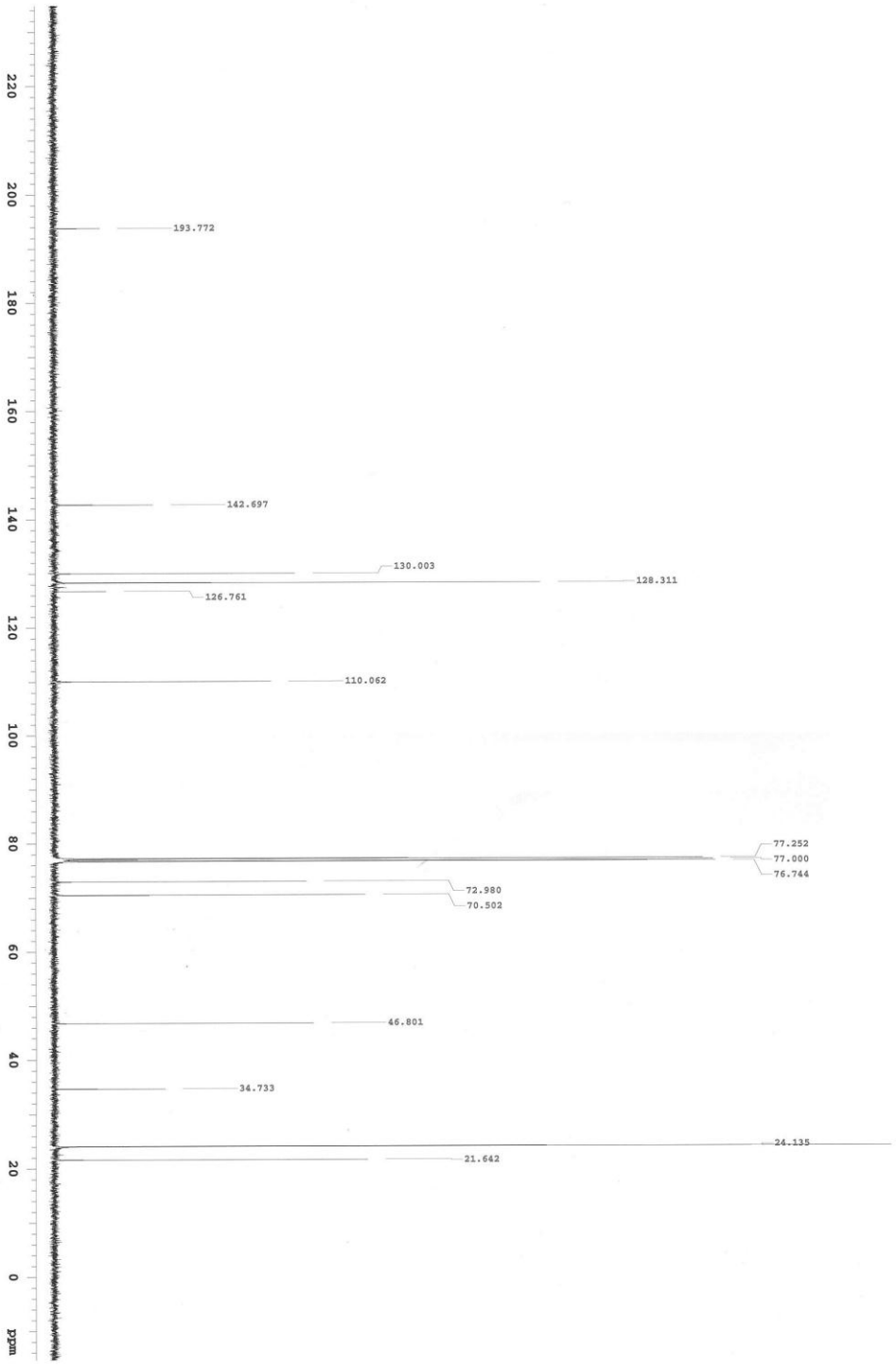
^{1}H NMR



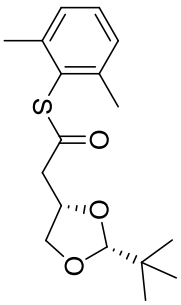
S-(2,6-Dimethylphenyl) 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanethioate (3ed)



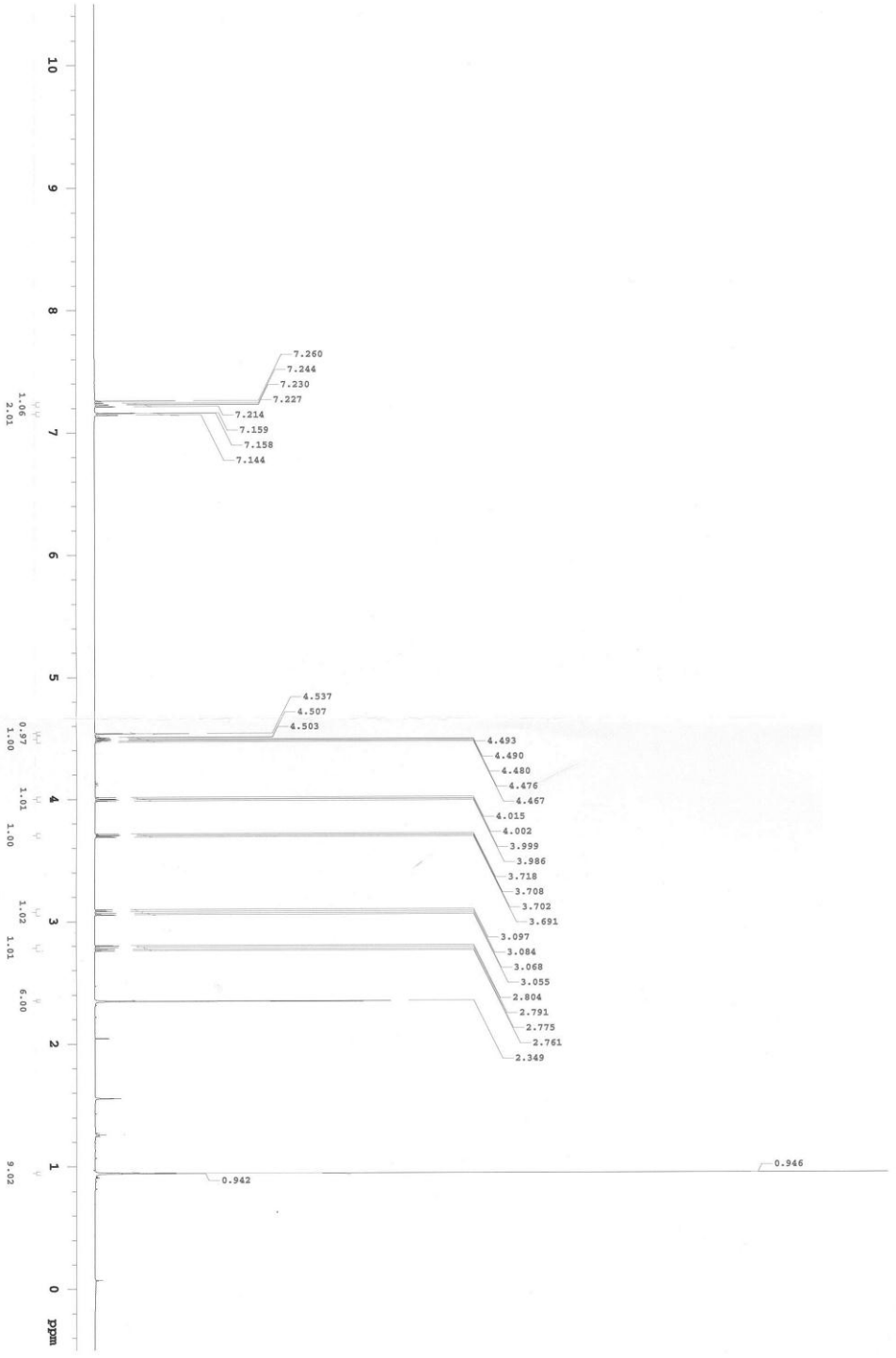
^{13}C NMR



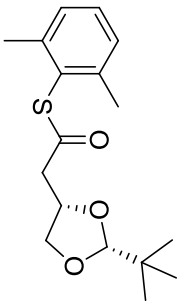
S-(2,6-Dimethylphenyl) 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanethioate (3ed')



^{1}H NMR



S-(2,6-Dimethylphenyl) 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanethioate (3ed')



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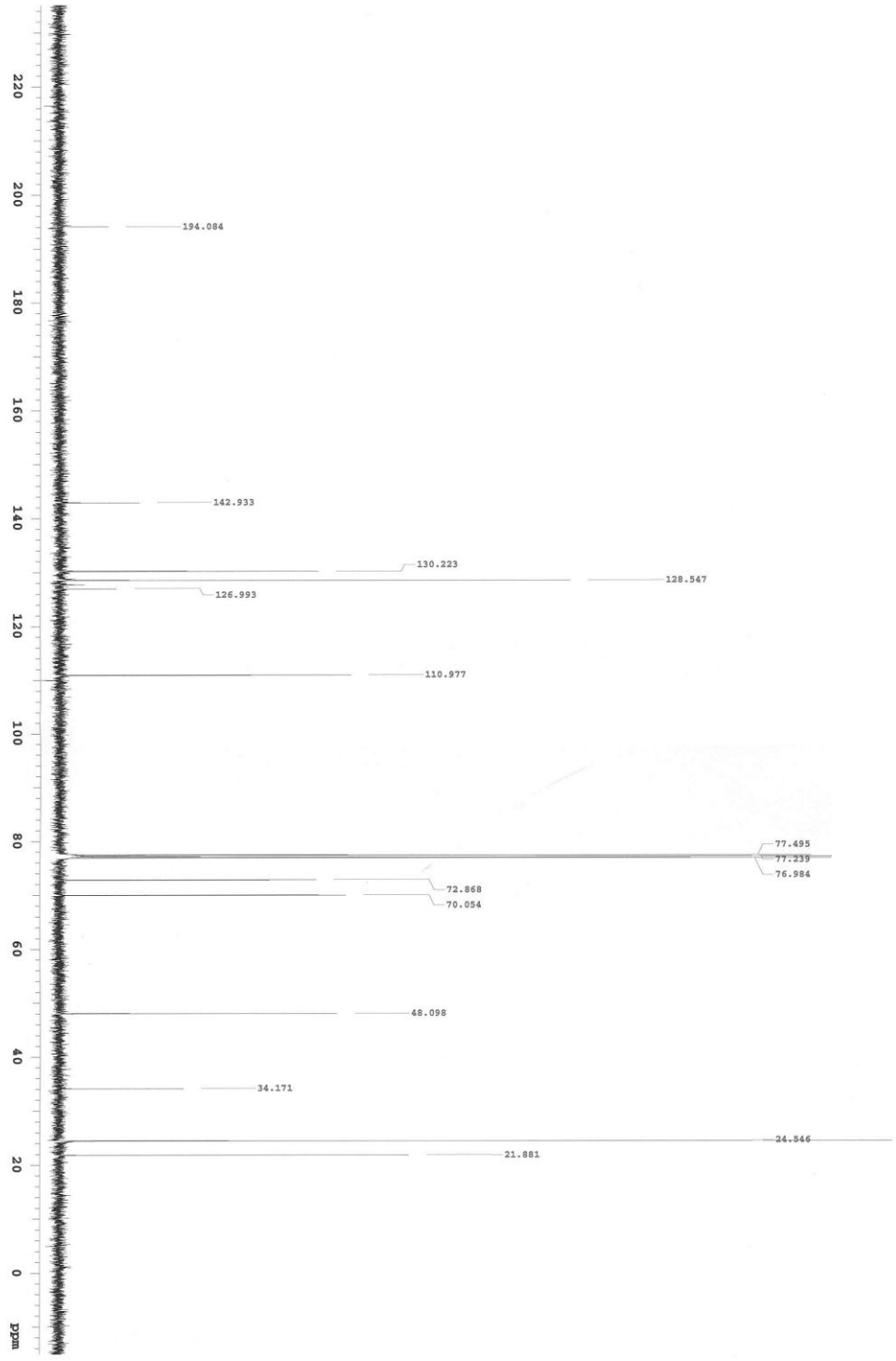
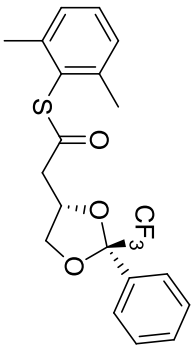
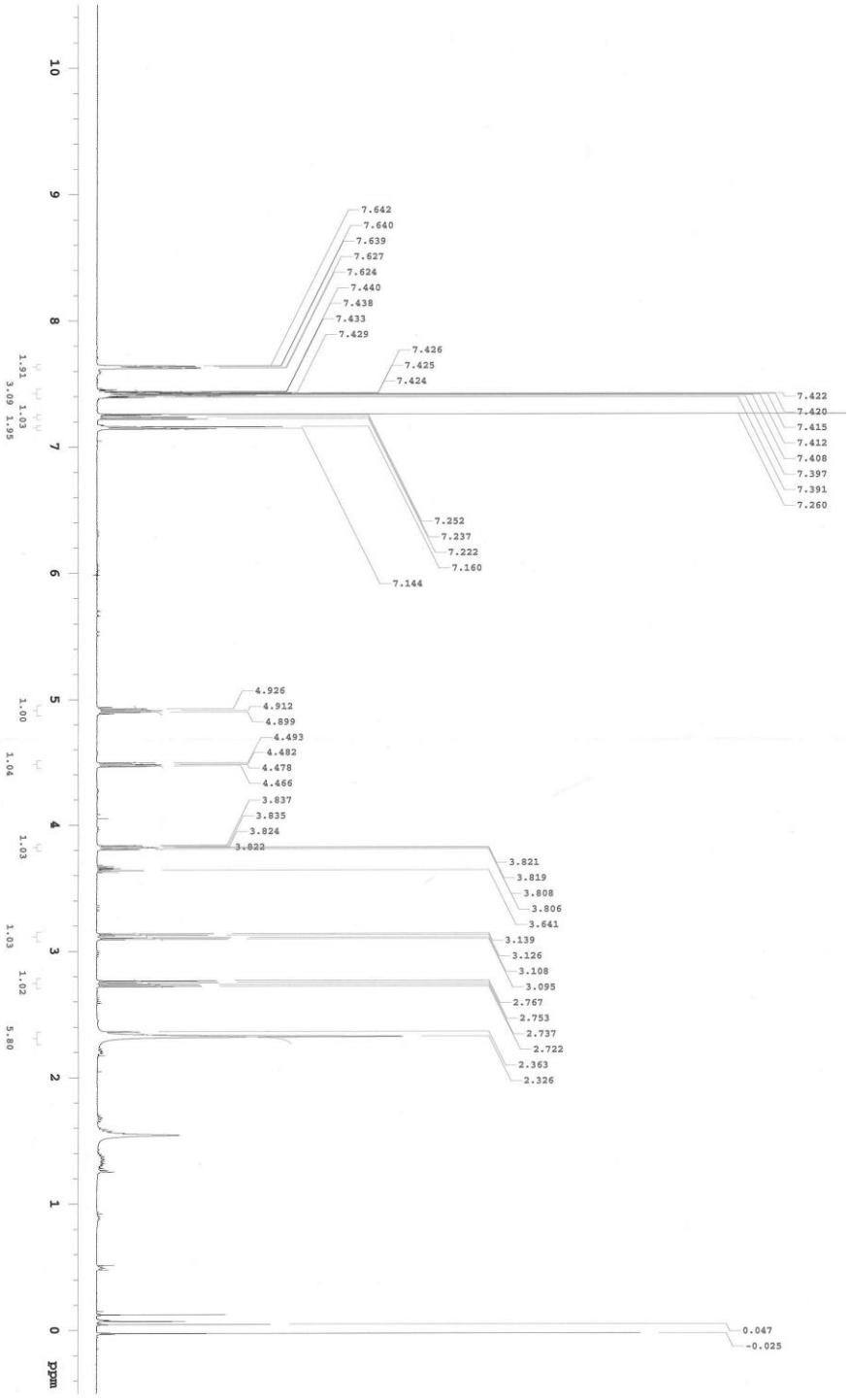


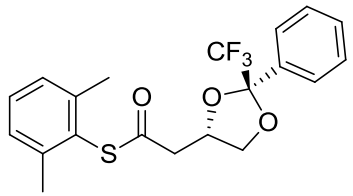
S-(2,6-Dimethylphenyl) 2-(2-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl)ethanethioate (3ee)



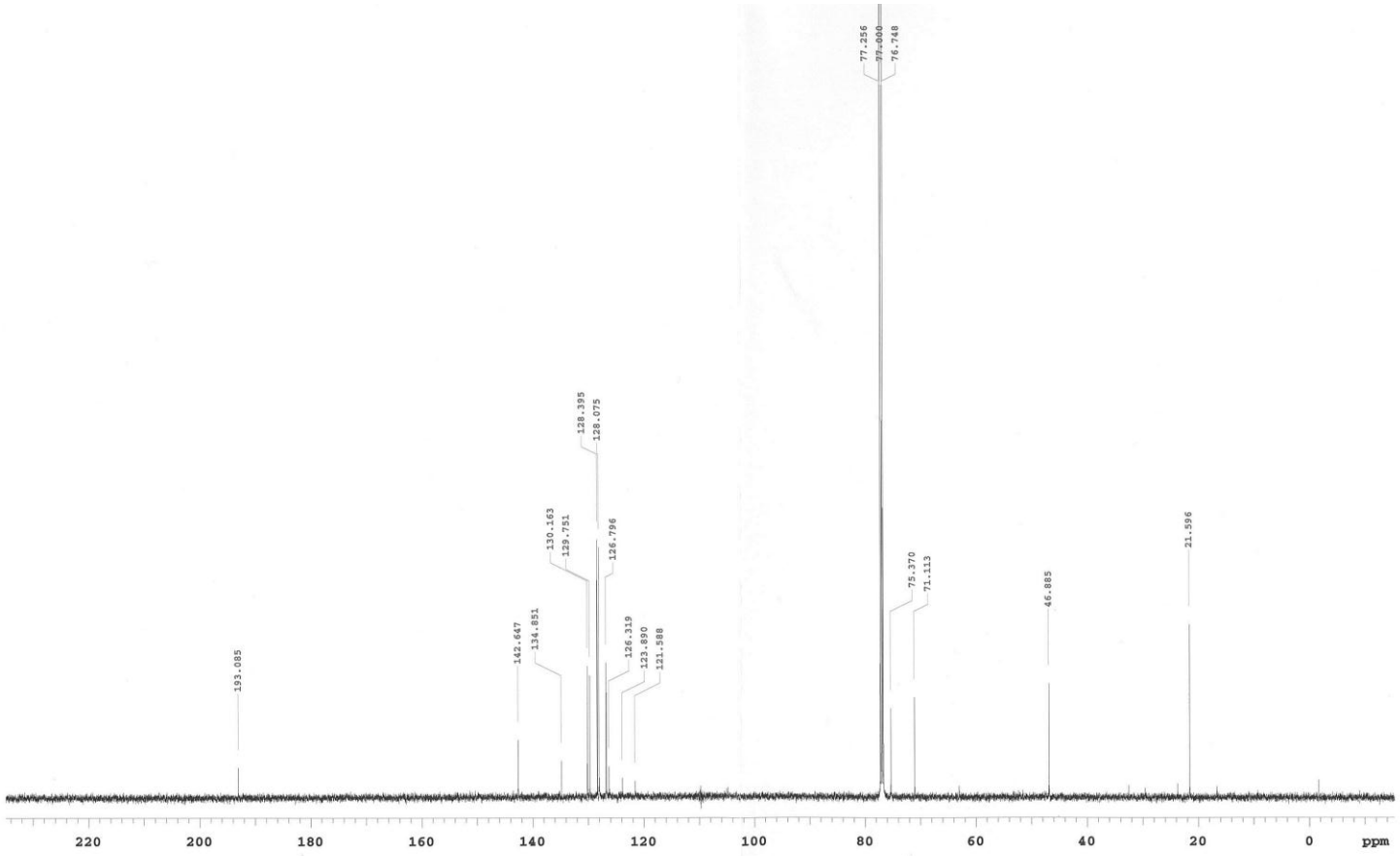
^{1}H NMR



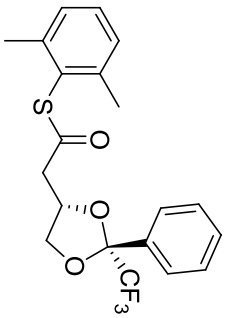
S-(2,6-Dimethylphenyl) 2-(2-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl)ethanethioate (3ee)



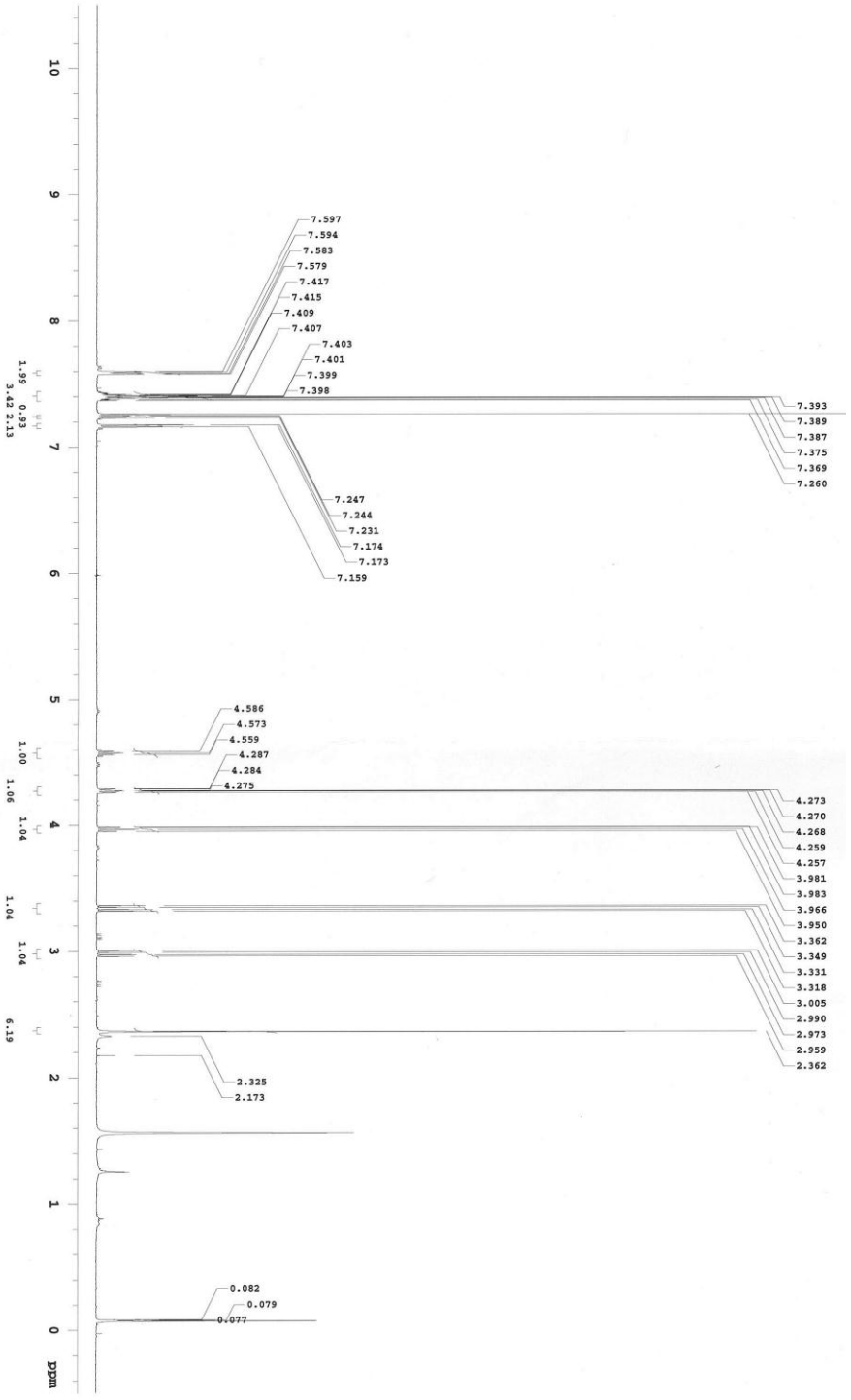
^{13}C NMR



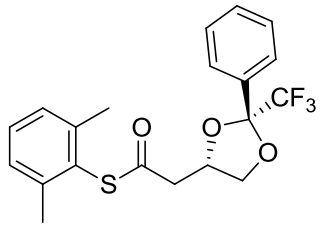
S-(2,6-Dimethylphenyl) 2-(2-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl)ethanethioate (3ee')



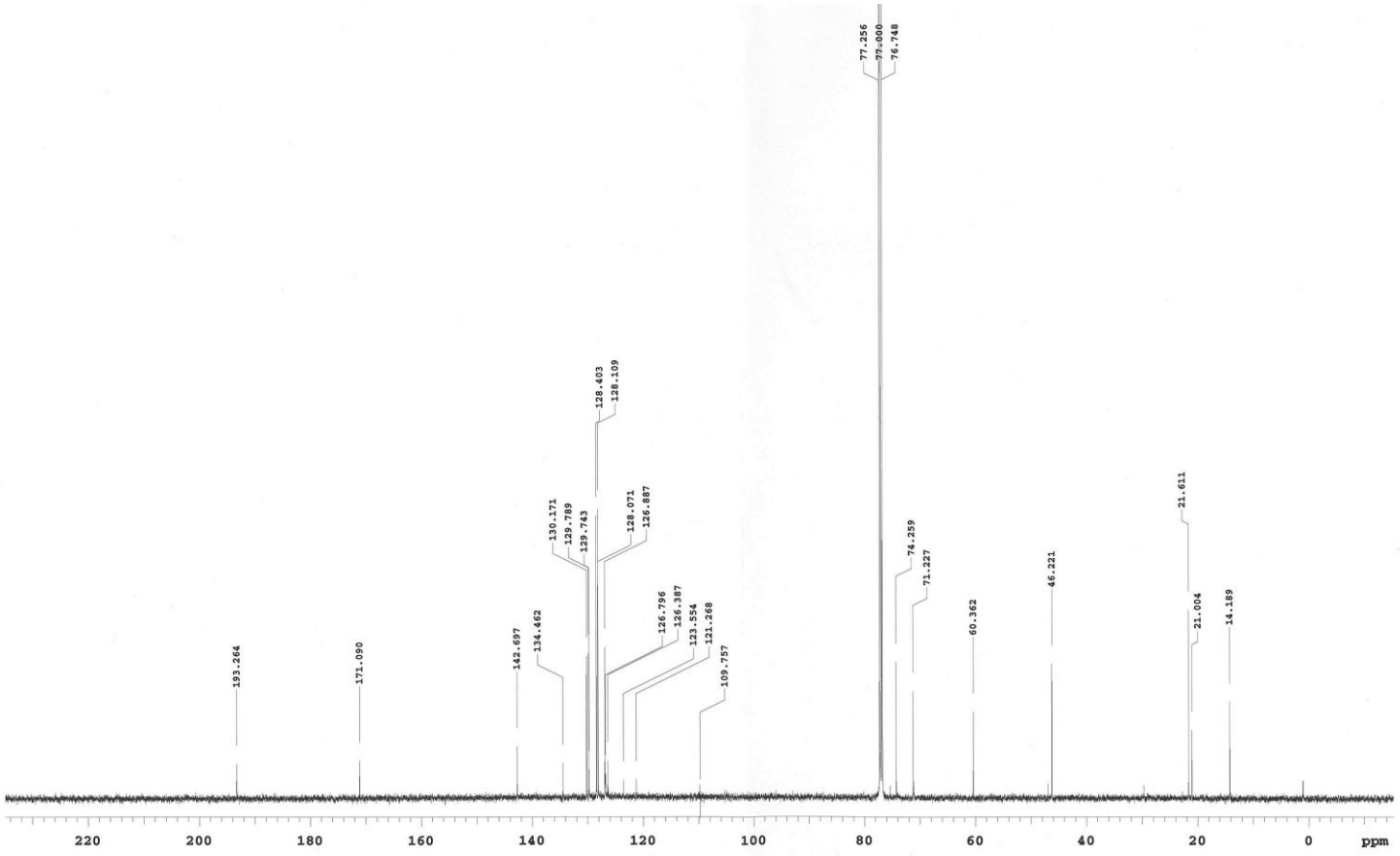
^{1}H NMR



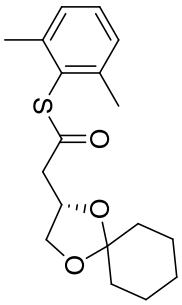
S-(2,6-Dimethylphenyl) 2-(2-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl)ethanethioate (3ee')



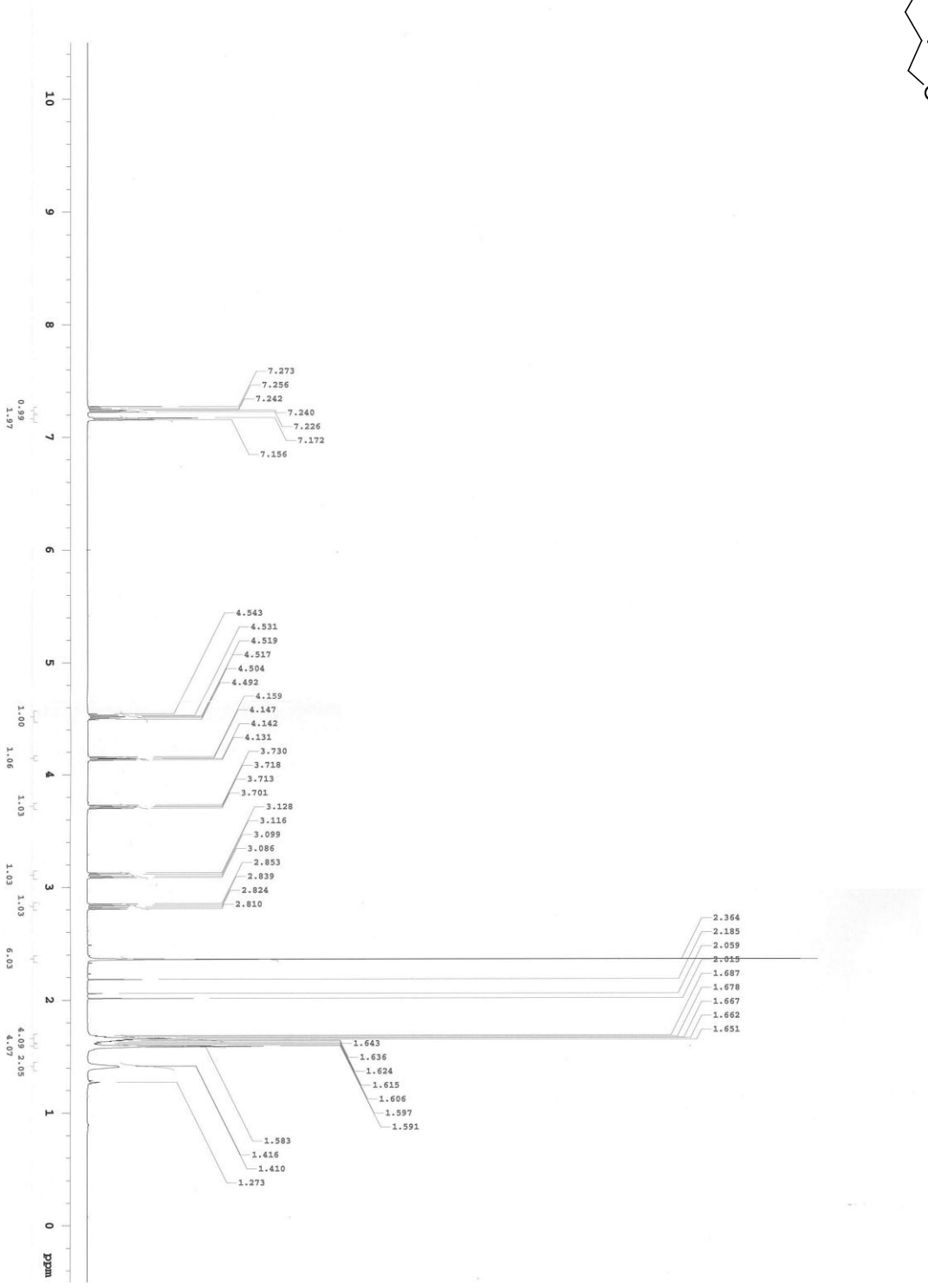
^{13}C NMR



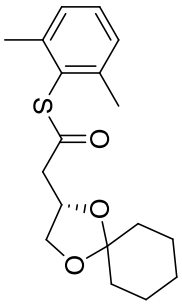
S-(2,6-Dimethylphenyl) 2-(1,4-dioxaspiro[4.5]decan-2-yl)ethanethioate (3eg)



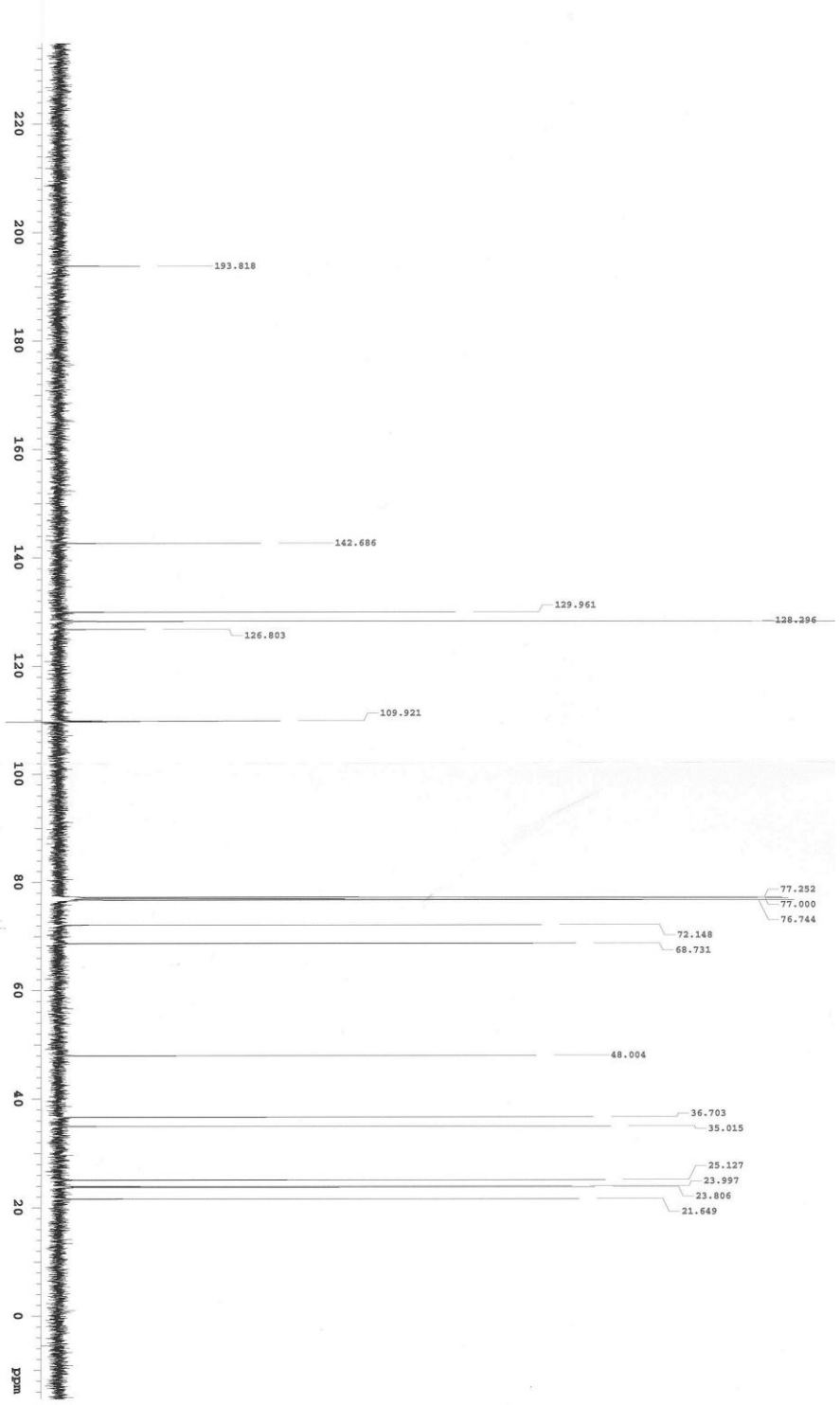
^{1}H NMR



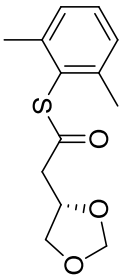
S-(2,6-Dimethylphenyl) 2-(1,4-dioxaspiro[4.5]decan-2-yl)ethanethioate (3eg)



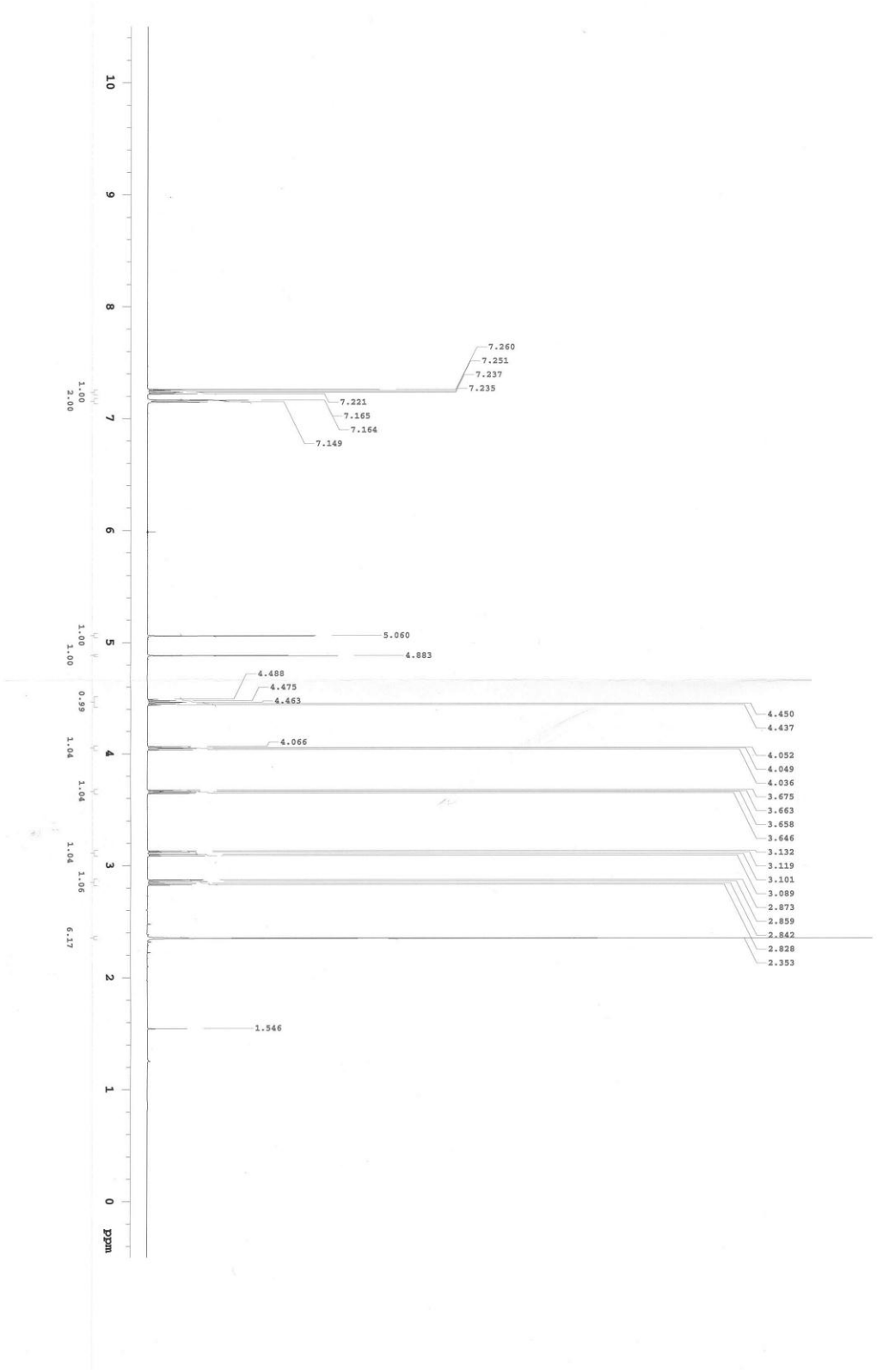
^{13}C NMR



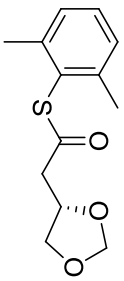
S-(2,6-Dimethylphenyl) 2-(1,3-dioxolan-4-yl)ethanethioate (3eh)



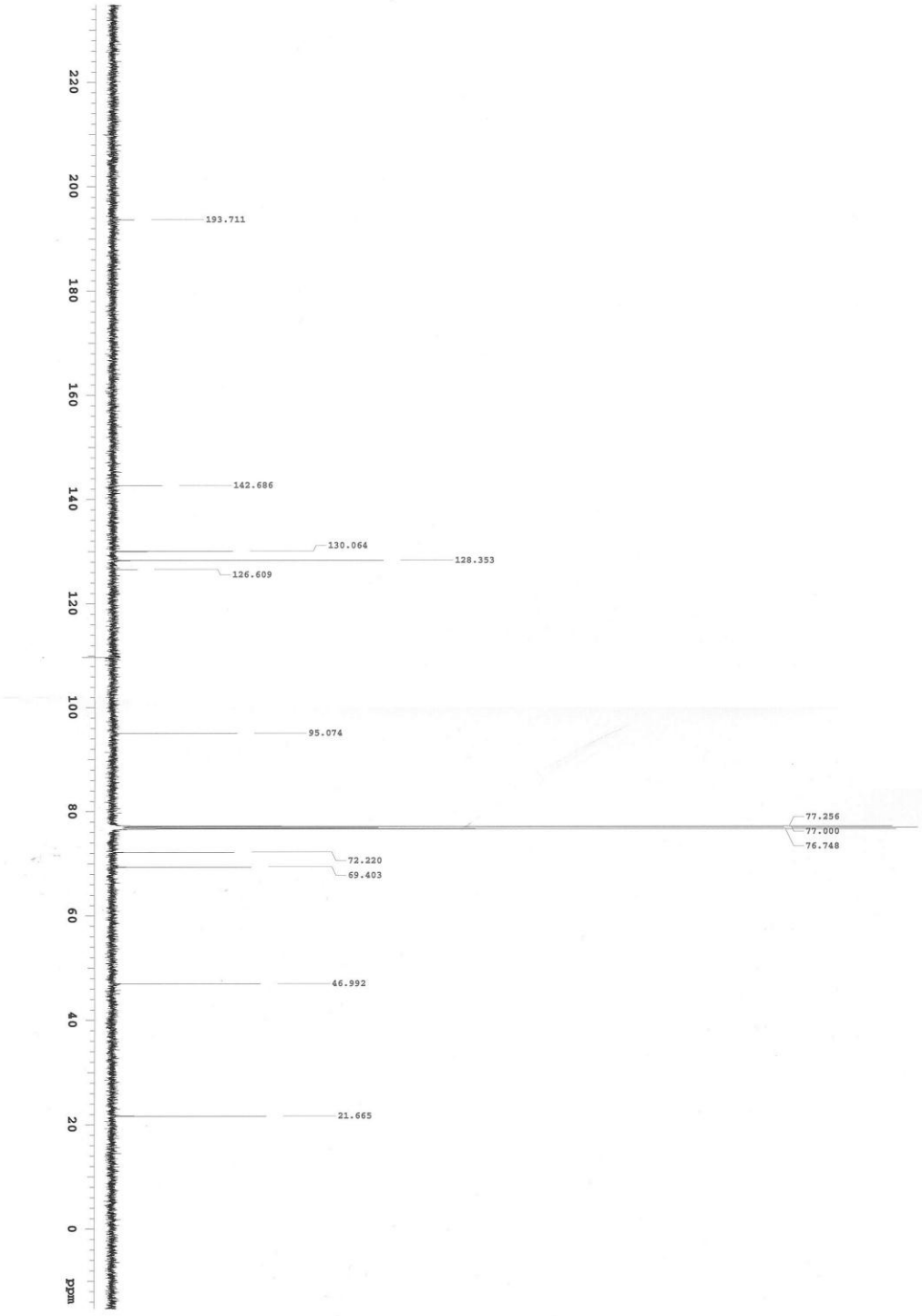
^{1}H NMR



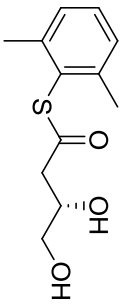
S-(2,6-Dimethylphenyl) 2-(1,3-dioxolan-4-yl)ethanethioate (3eh)



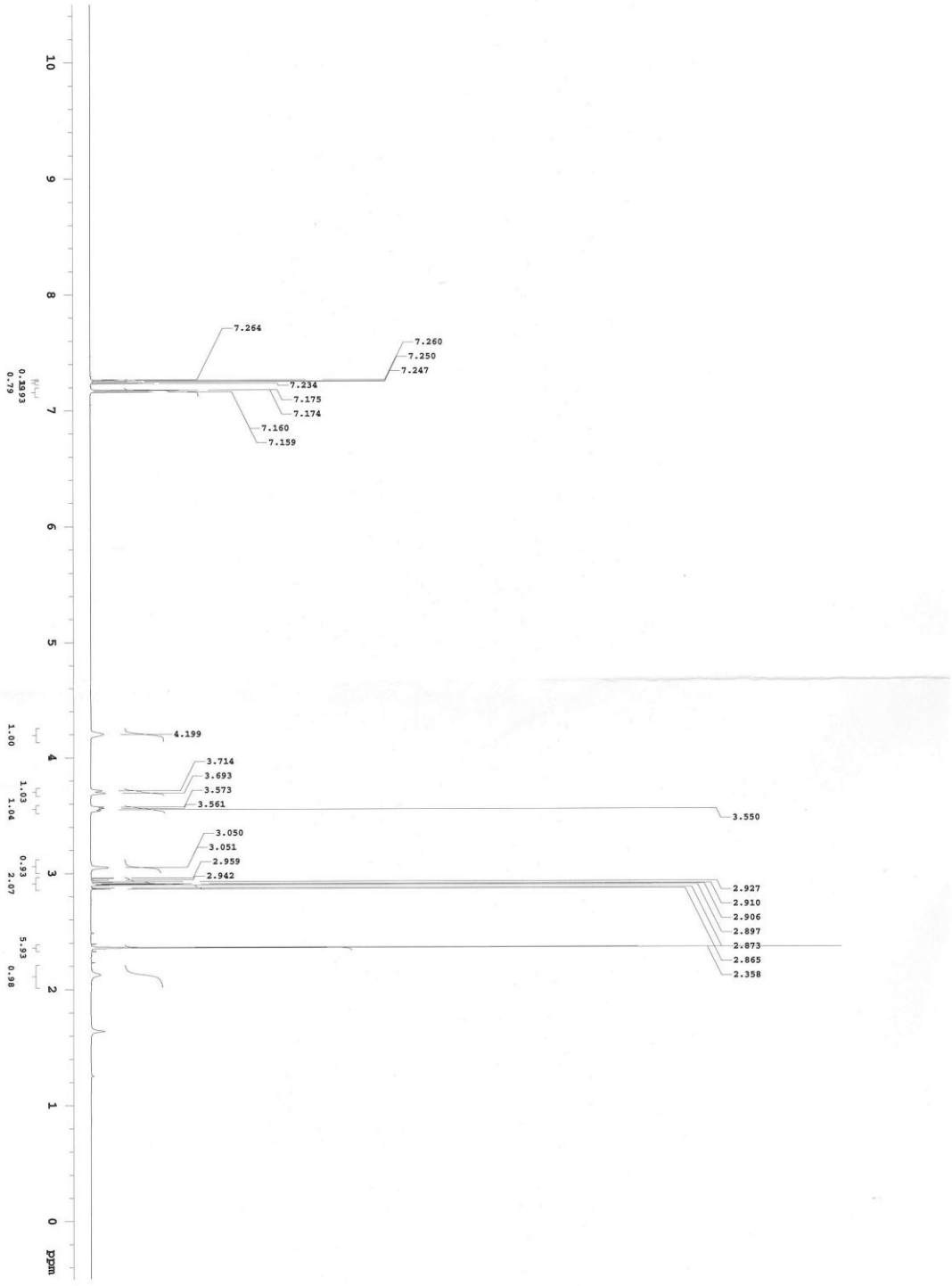
^{13}C NMR



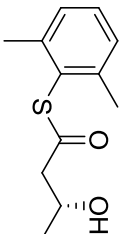
S-(2,6-Dimethylphenyl) 3,4-dihydroxybutanethioate (5)



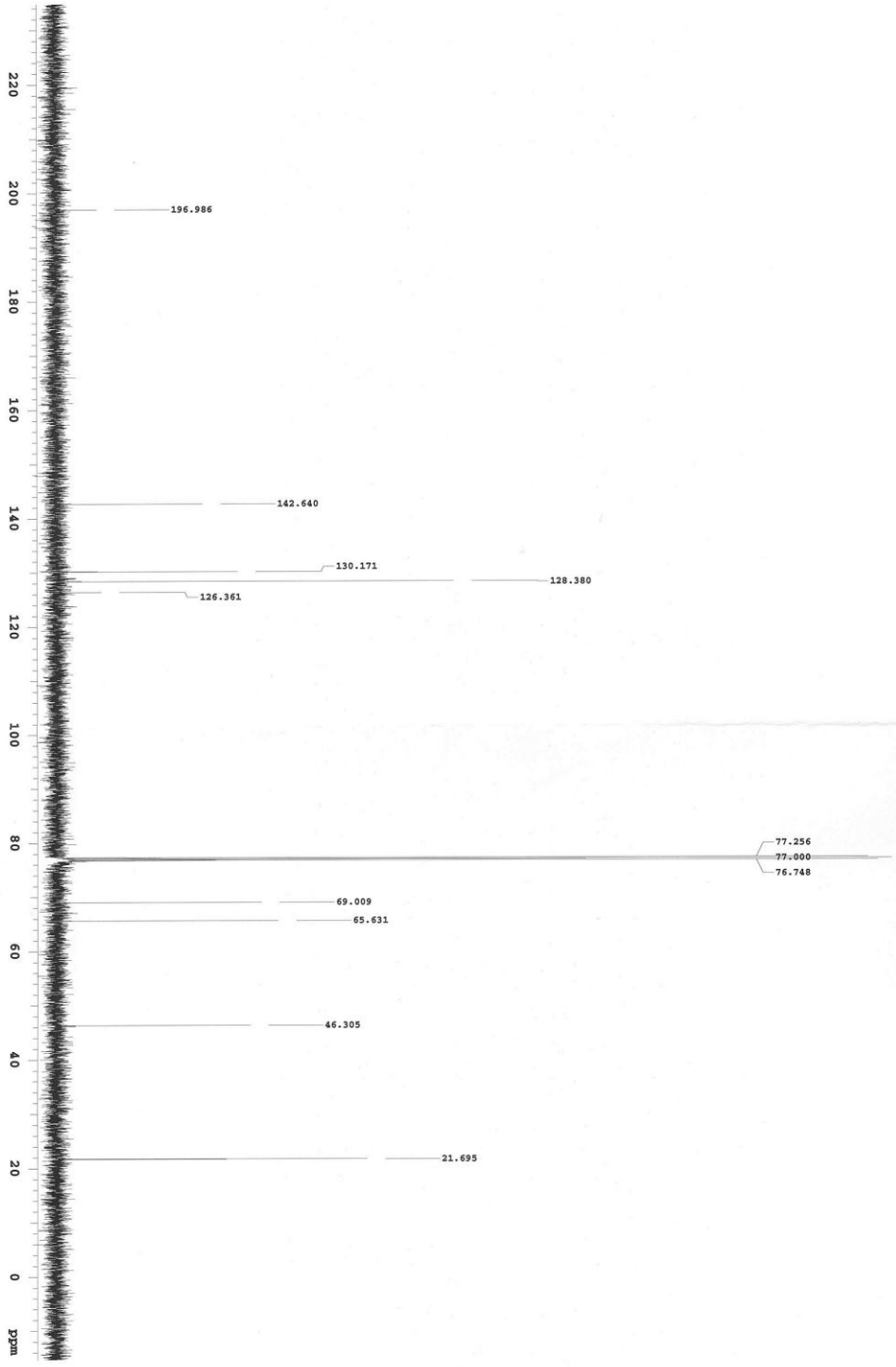
^{1}H NMR



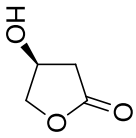
S-(2,6-Dimethylphenyl) 3,4-dihydroxybutanethioate (5)



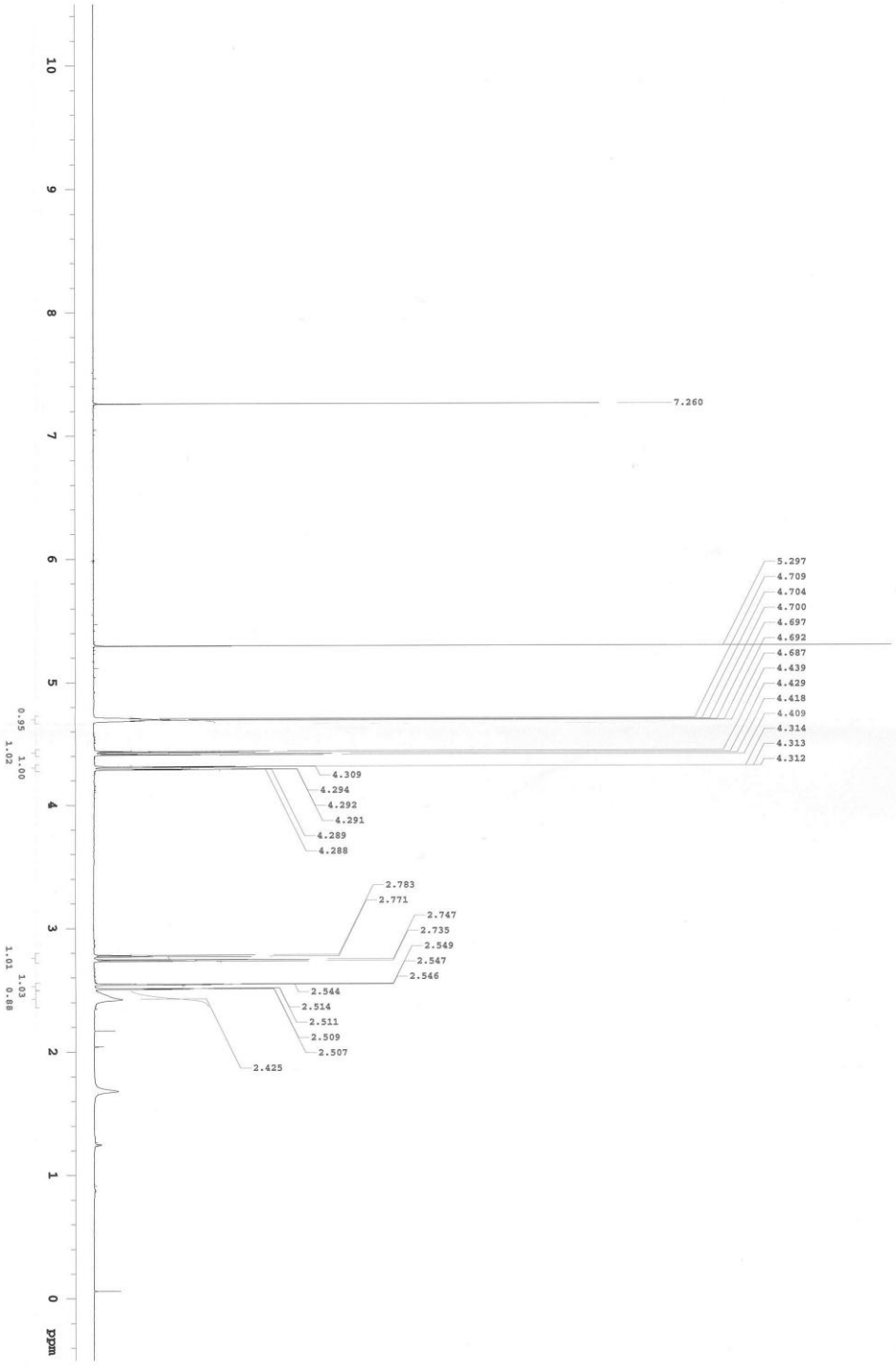
^{13}C NMR



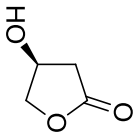
(*S*)-4-Hydroxydihydrofuran-2(3*H*)-one (6)



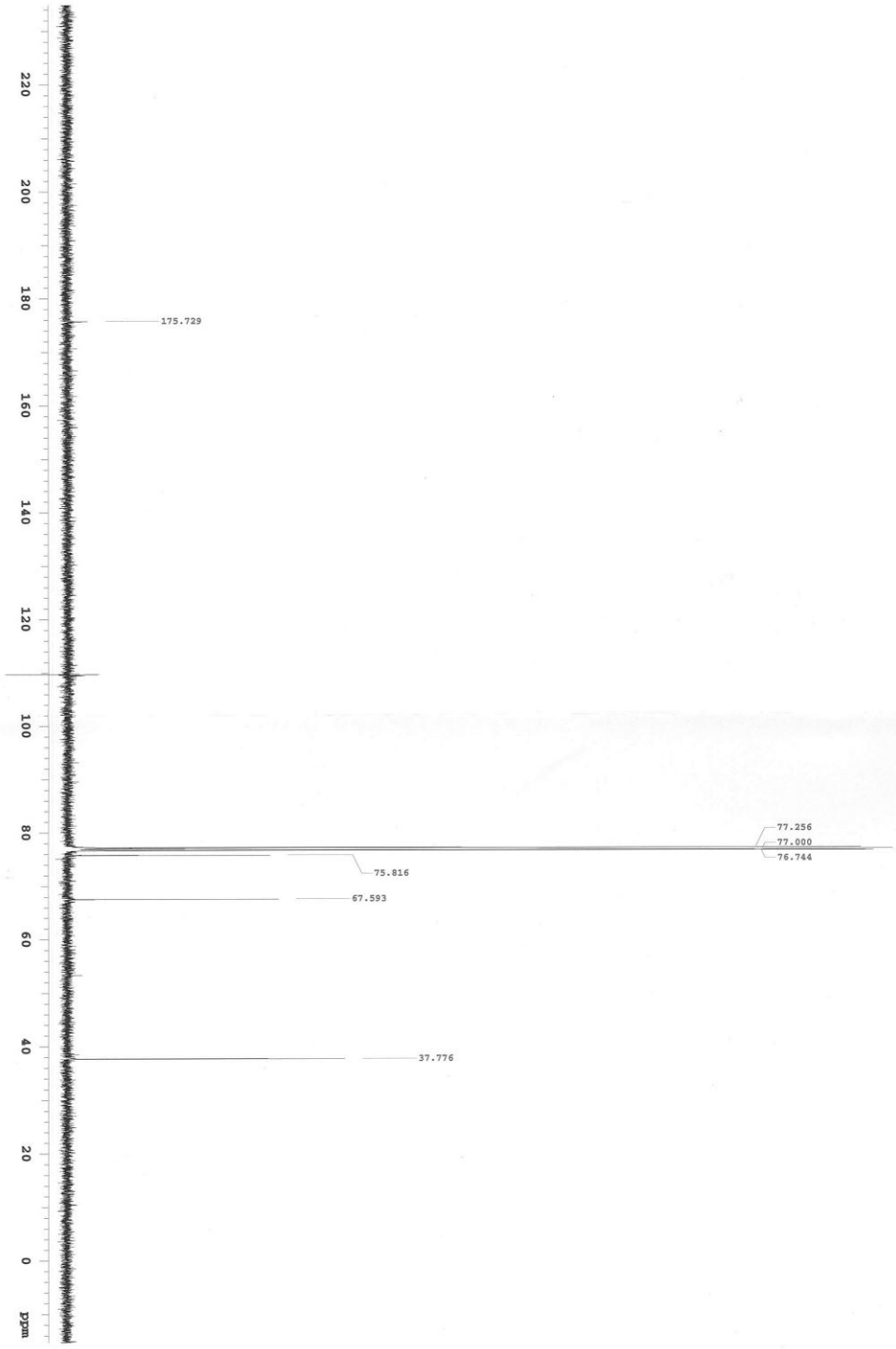
^{1}H NMR



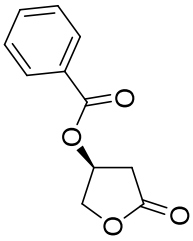
(*S*)-4-Hydroxydihydrofuran-2(3*H*)-one (6)



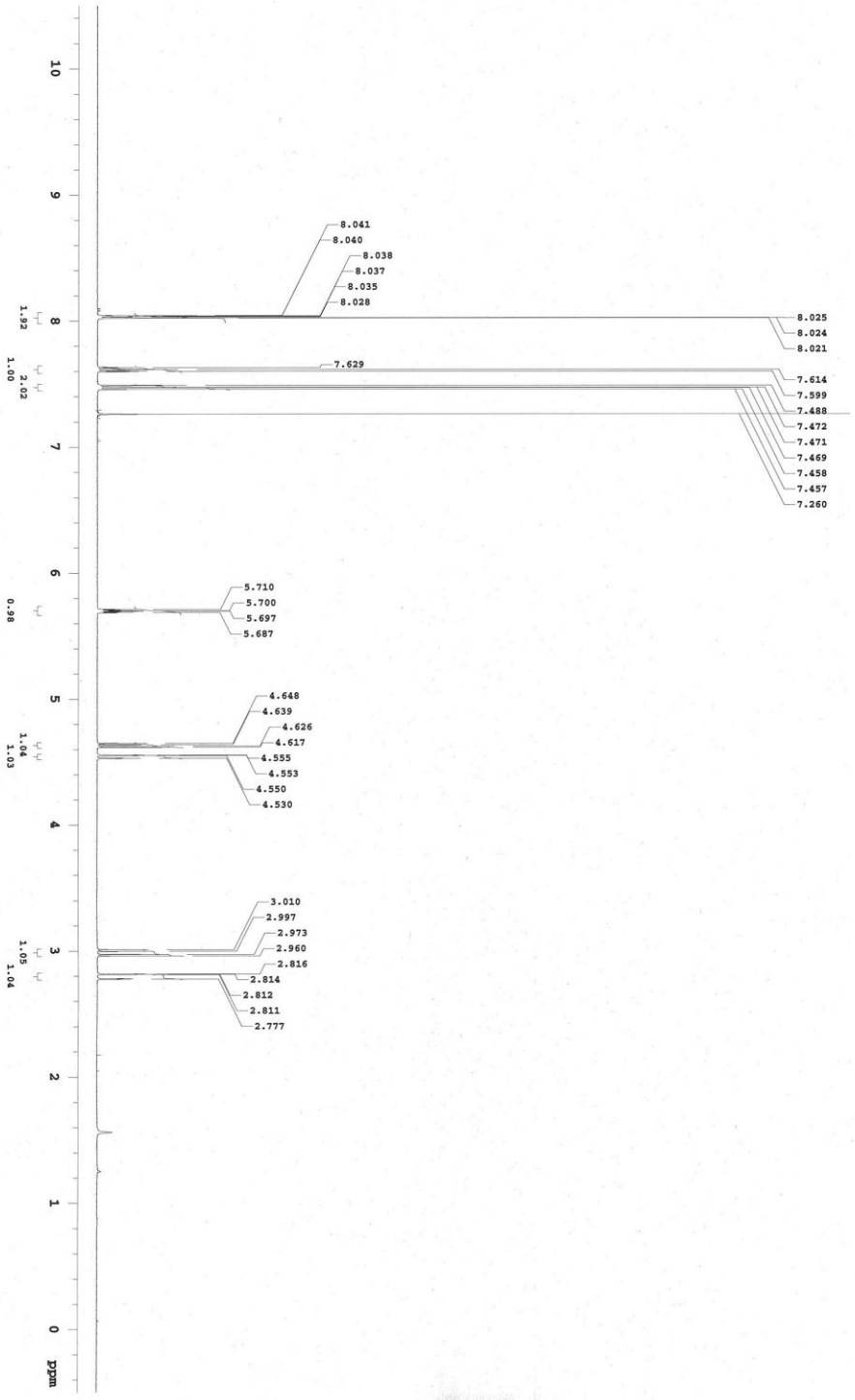
^{13}C NMR



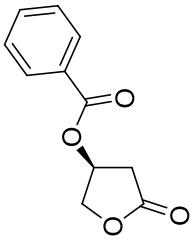
(S)-5-Oxotetrahydrofuran-3-yl benzoate



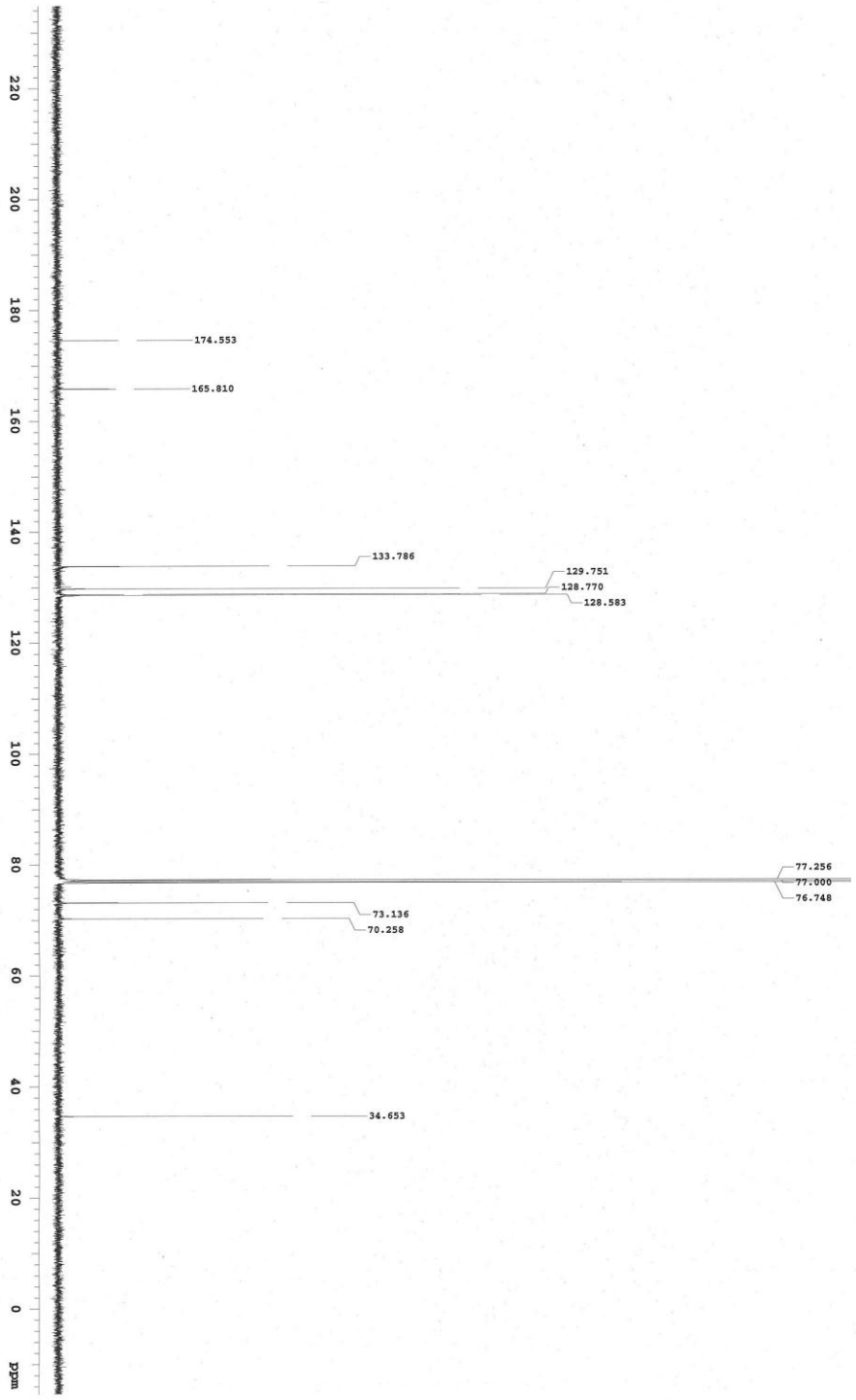
^{1}H NMR



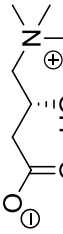
(S)-5-Oxotetrahydrofuran-3-yl benzoate



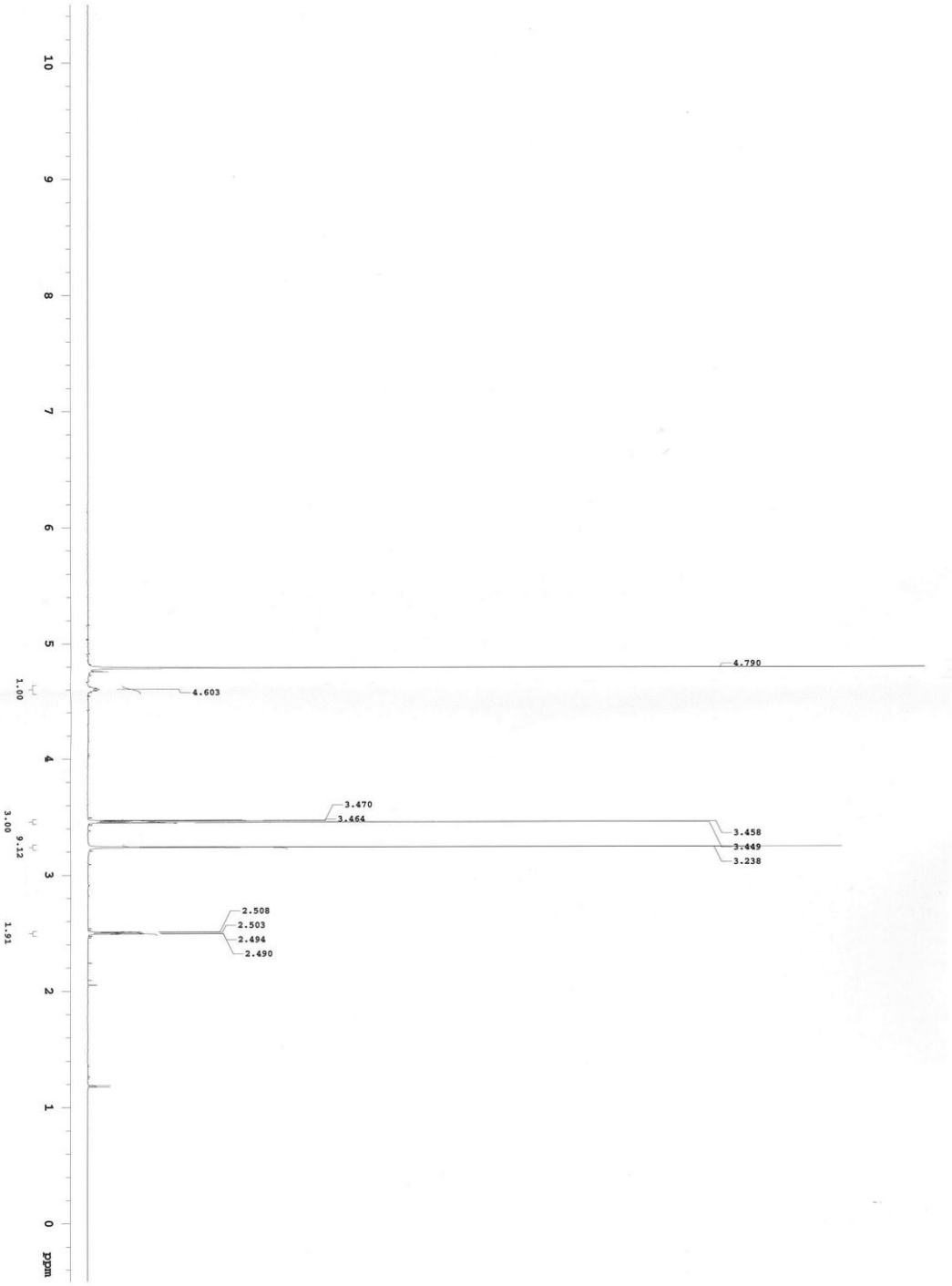
^{13}C NMR



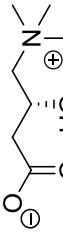
(*L*)-Carnitine (7)



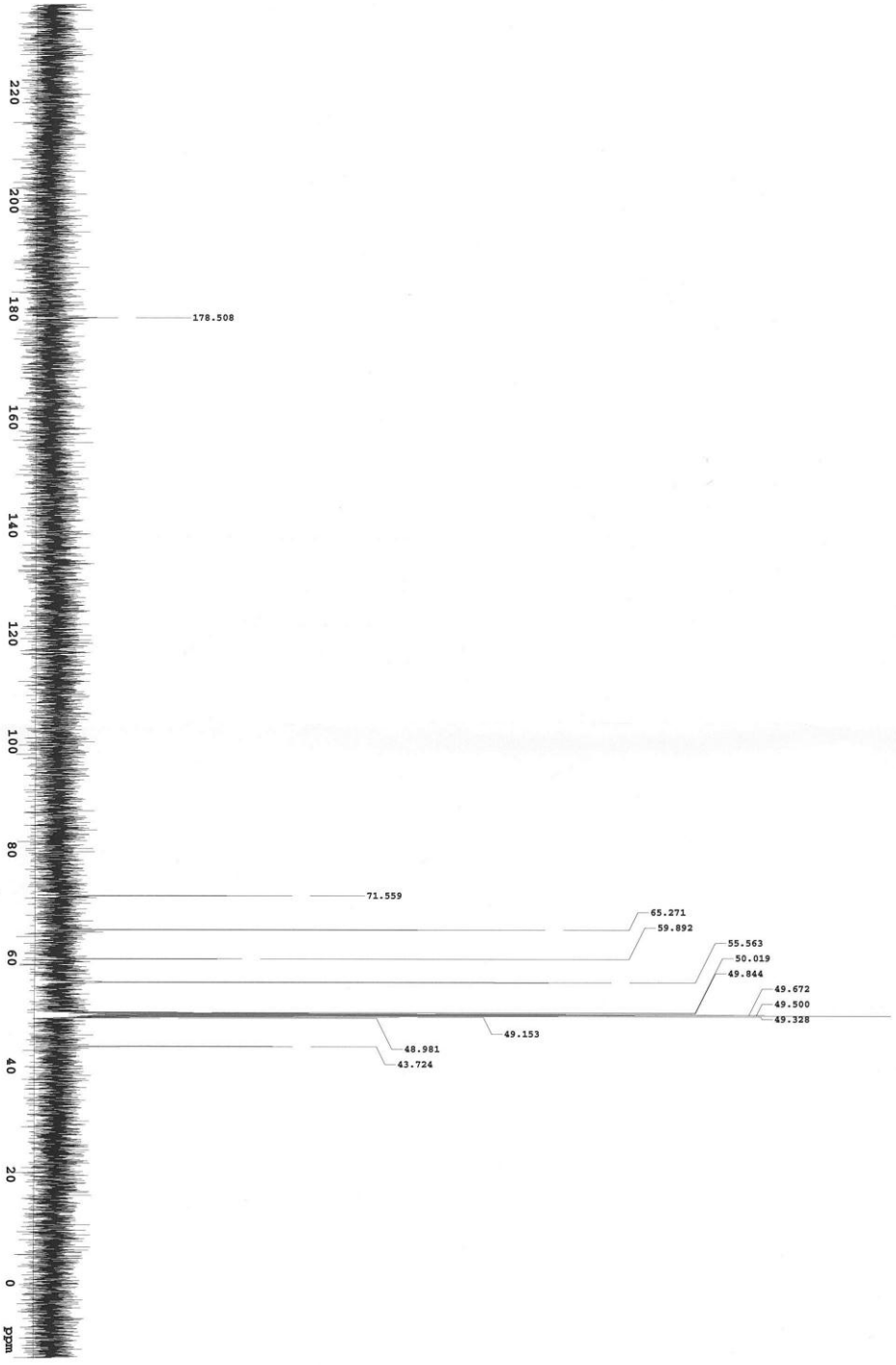
^{1}H NMR



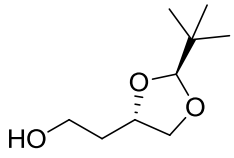
(*L*)-Carnitine (7)



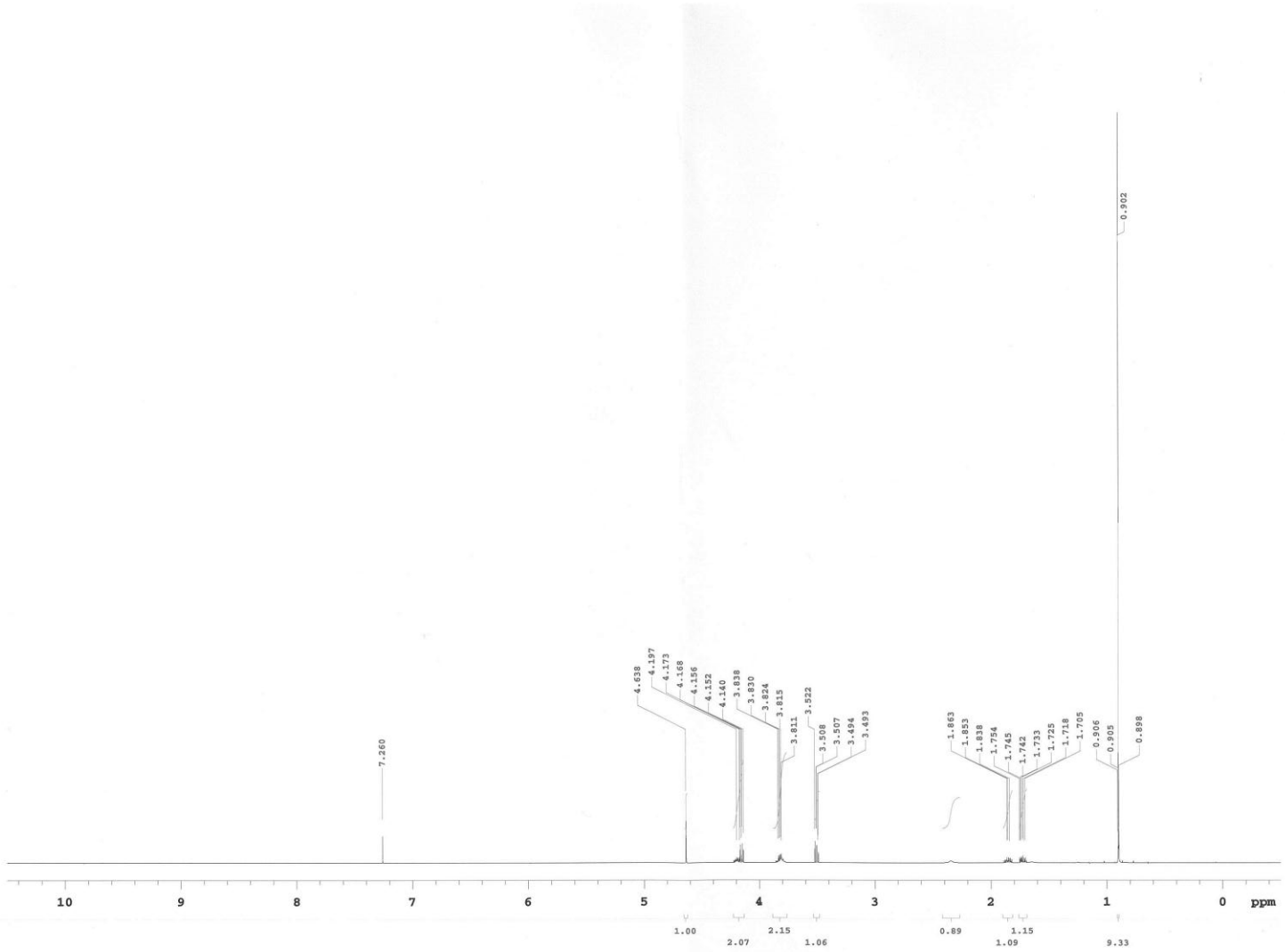
^{13}C NMR



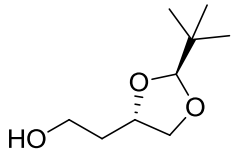
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethanol (8)



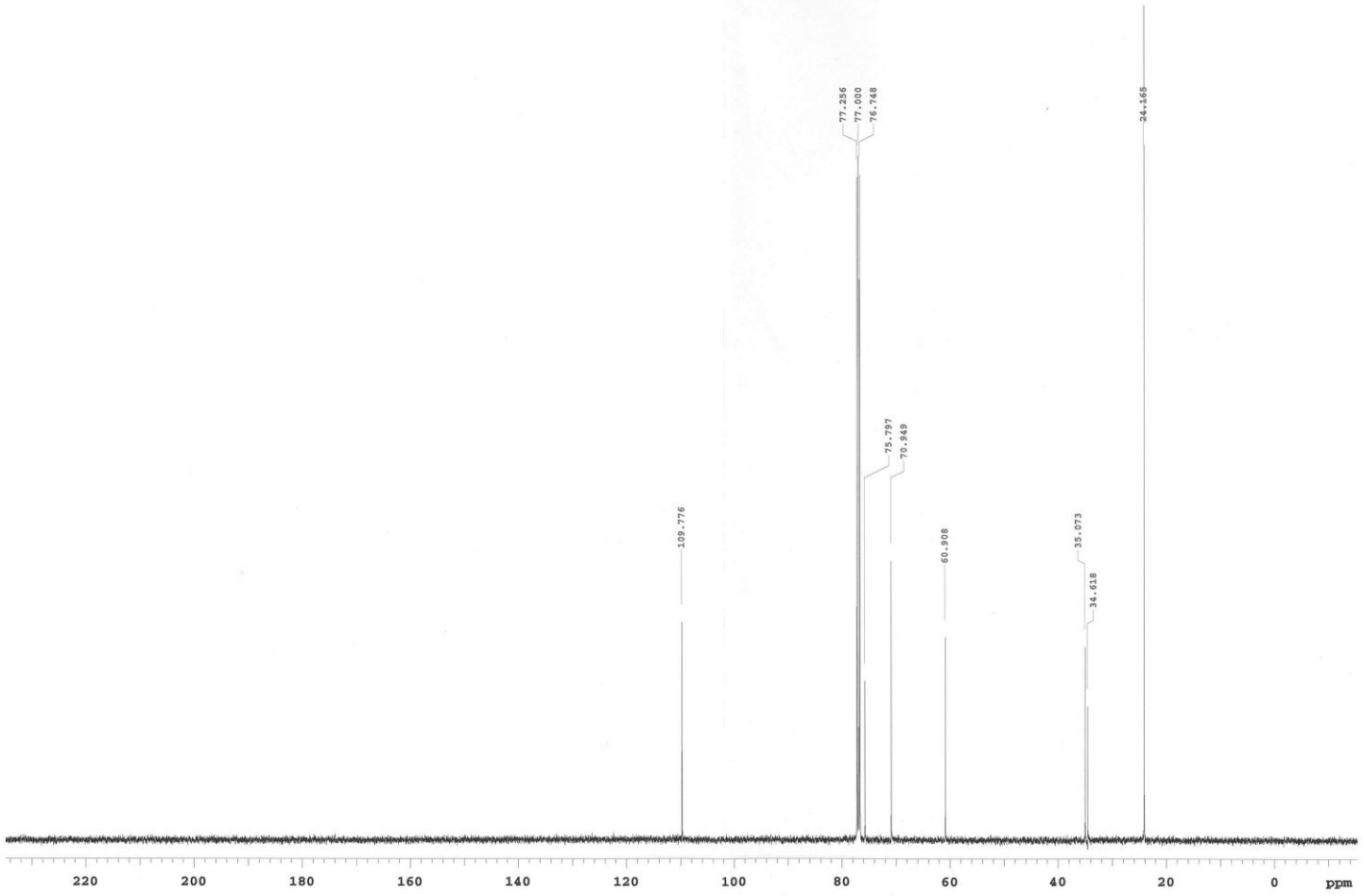
^{1}H NMR



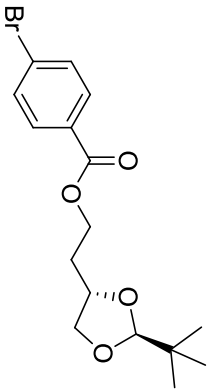
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethanol (8)



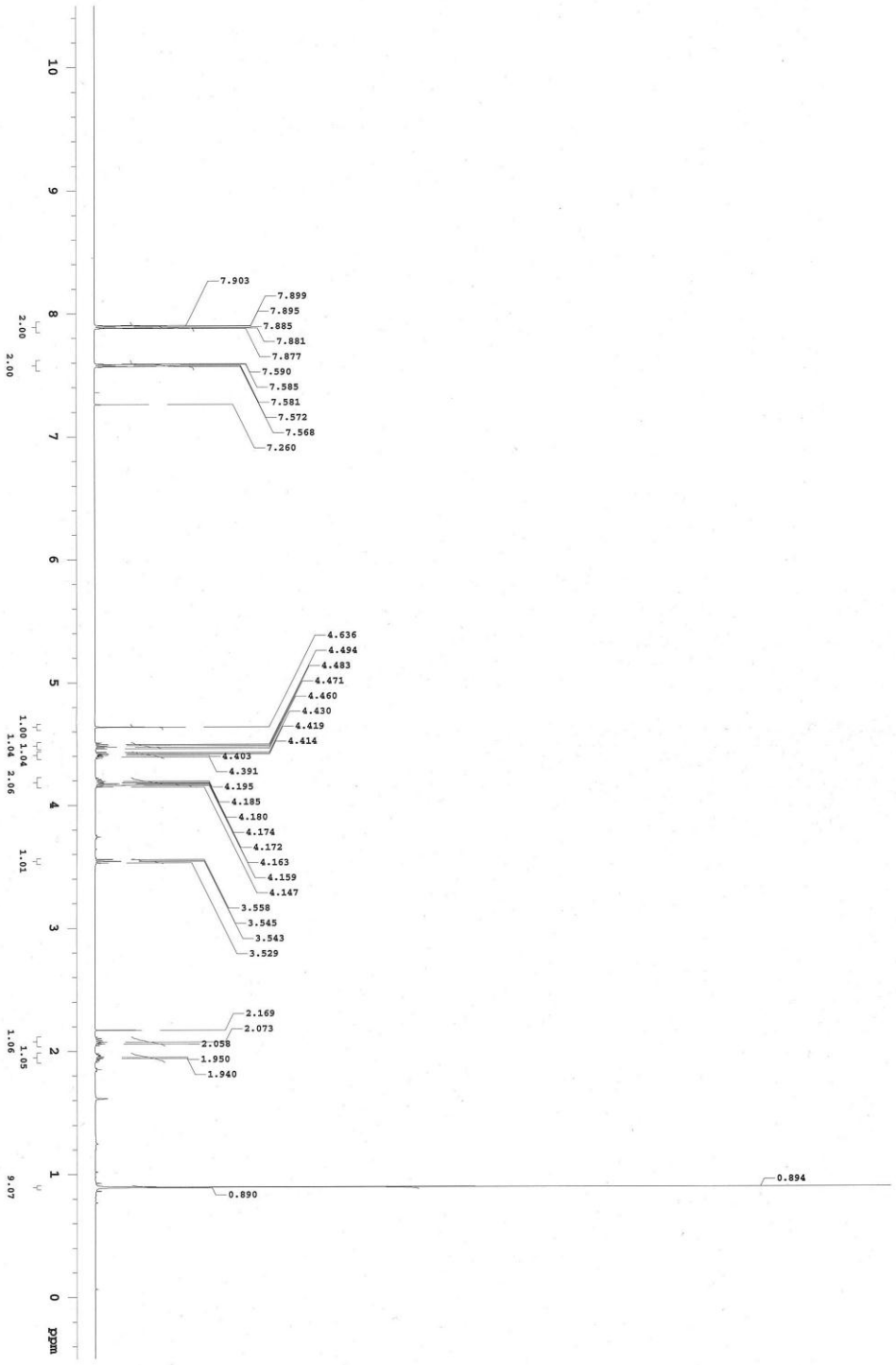
^{13}C NMR



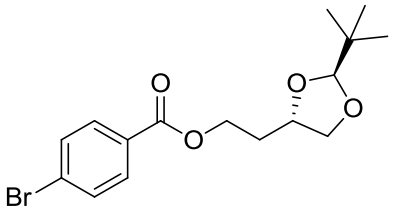
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethyl 4-bromobenzoate



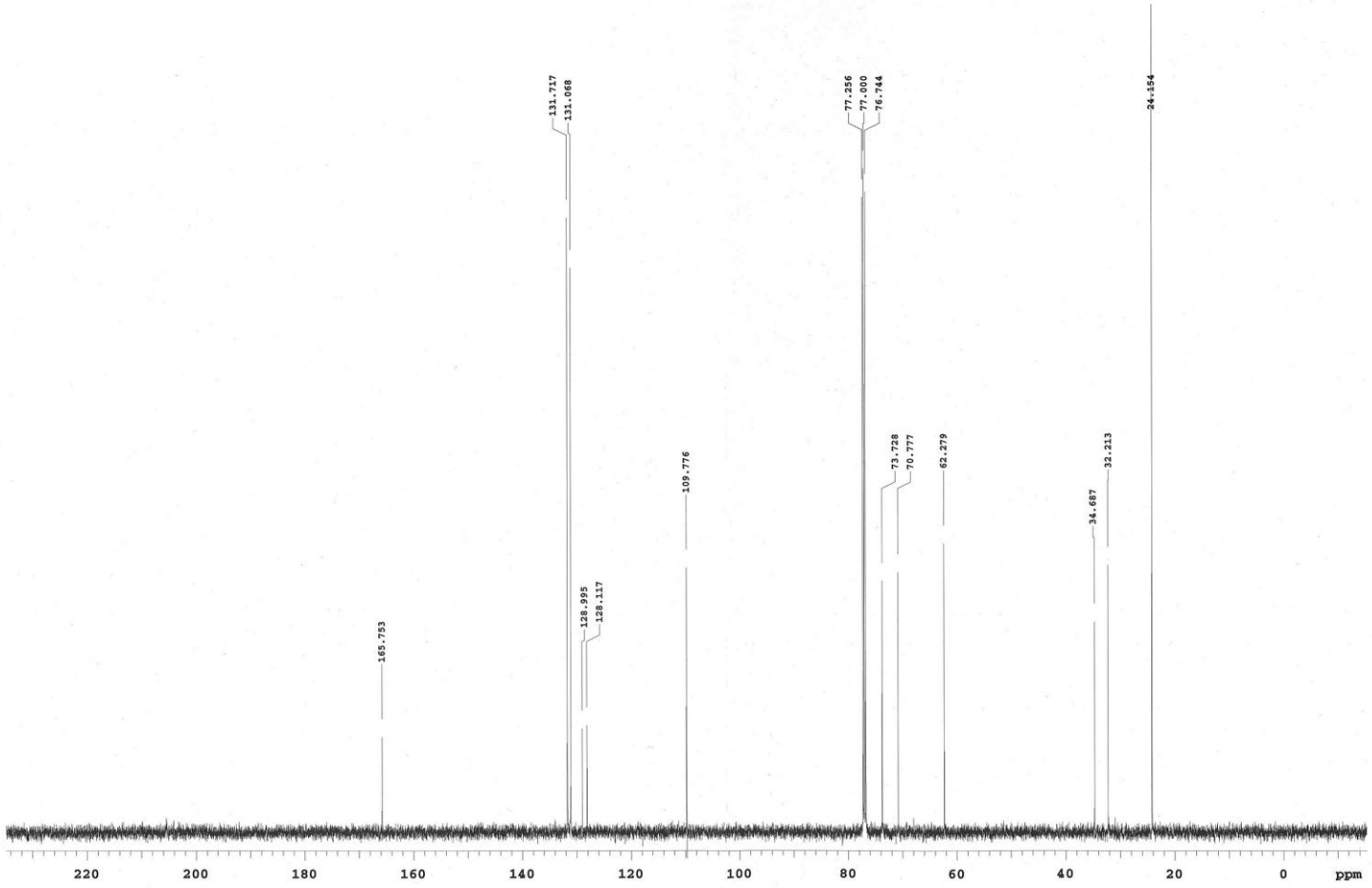
^{1}H NMR



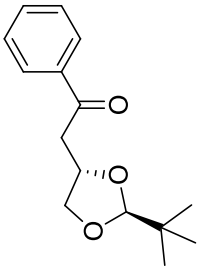
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethyl 4-bromobenzoate



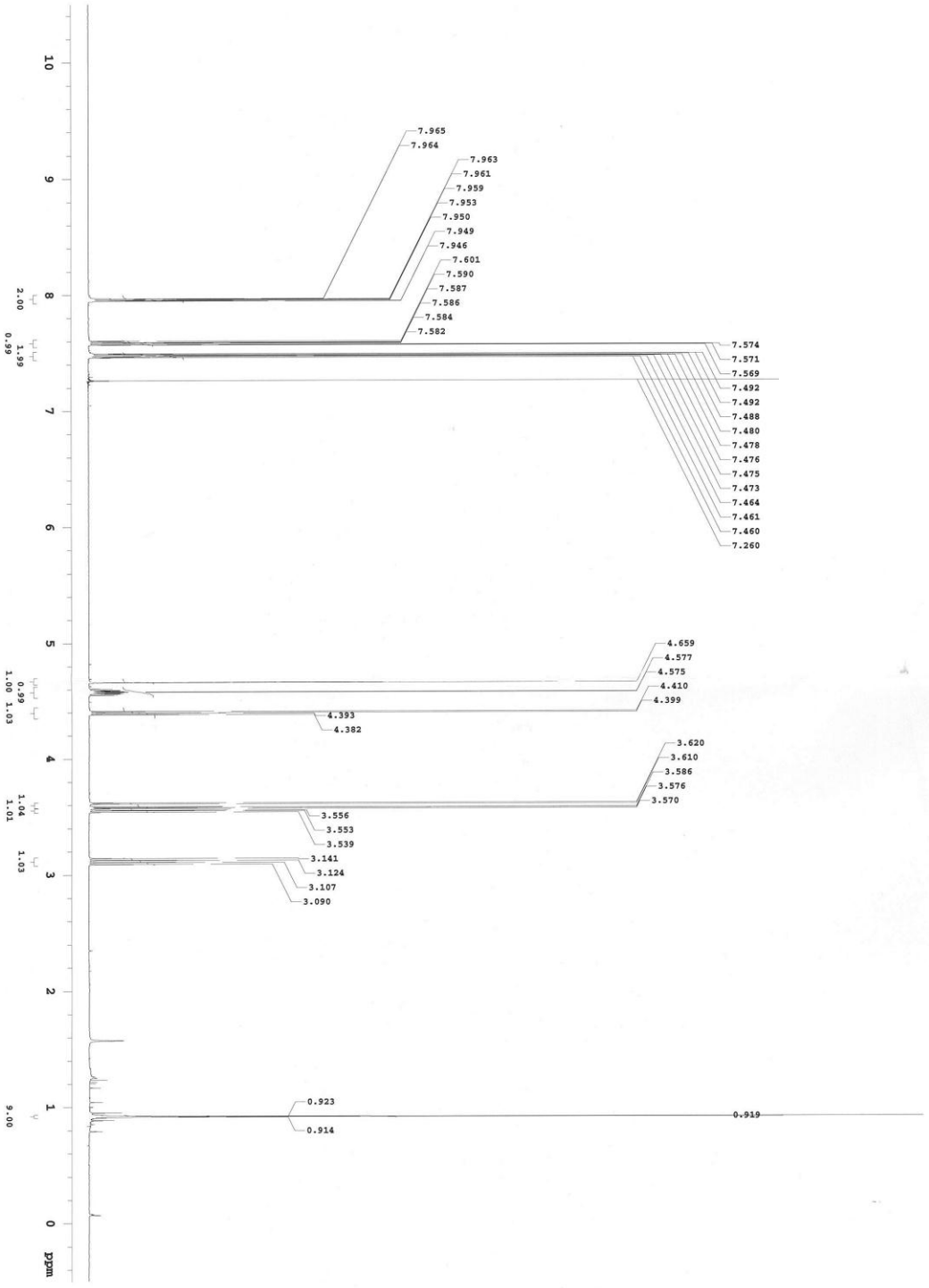
^{13}C NMR



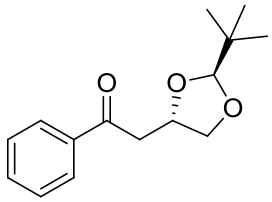
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)-1-phenylethanone (9)



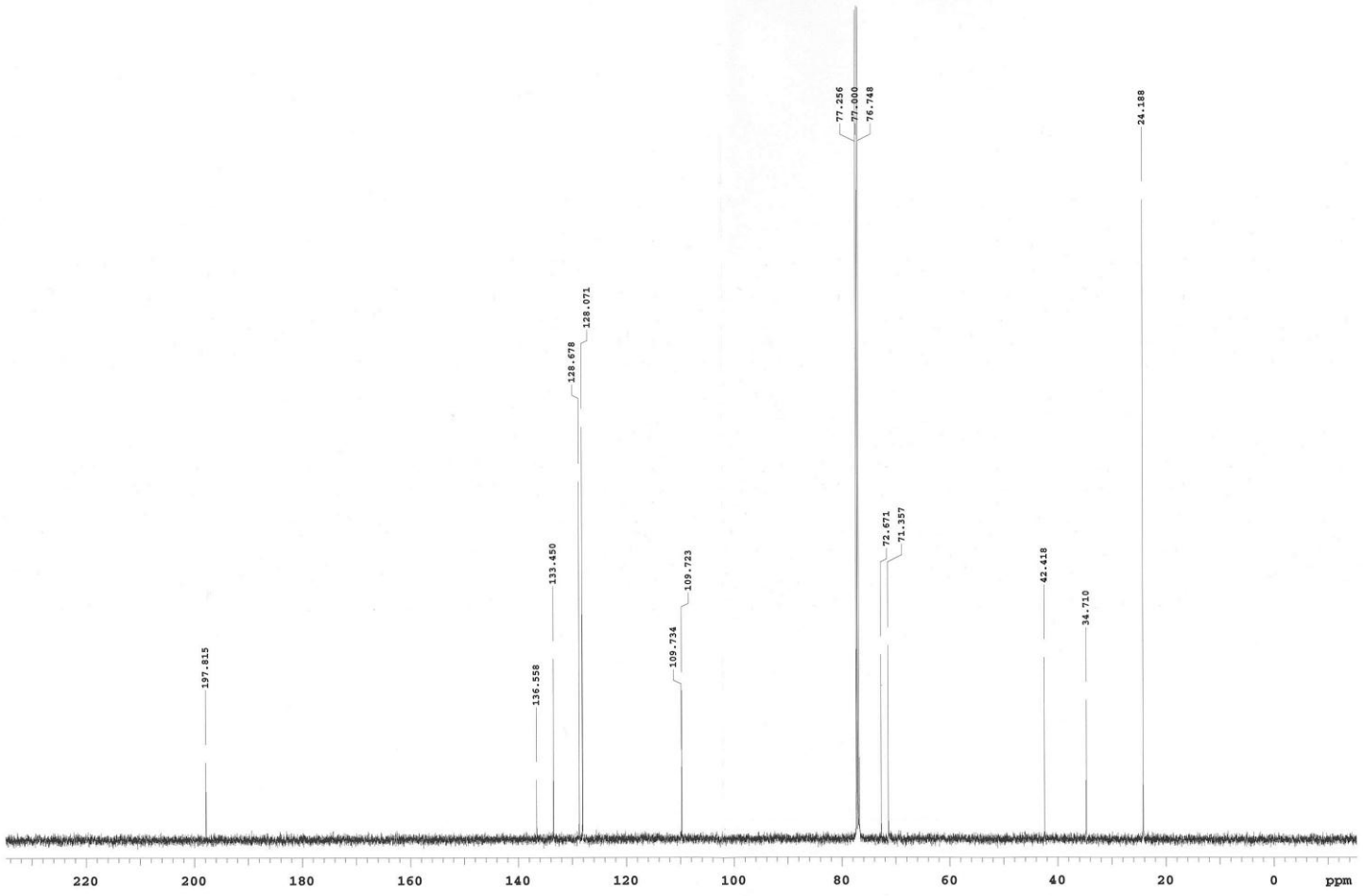
^{1}H NMR



2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)-1-phenylethanone (9)

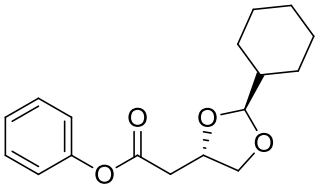


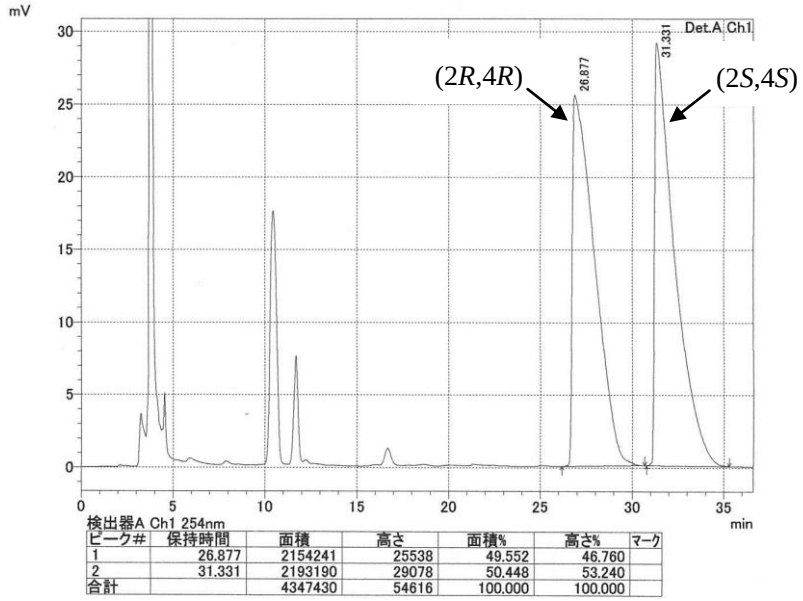
^{13}C NMR



HPLC Chromatogram Profiles

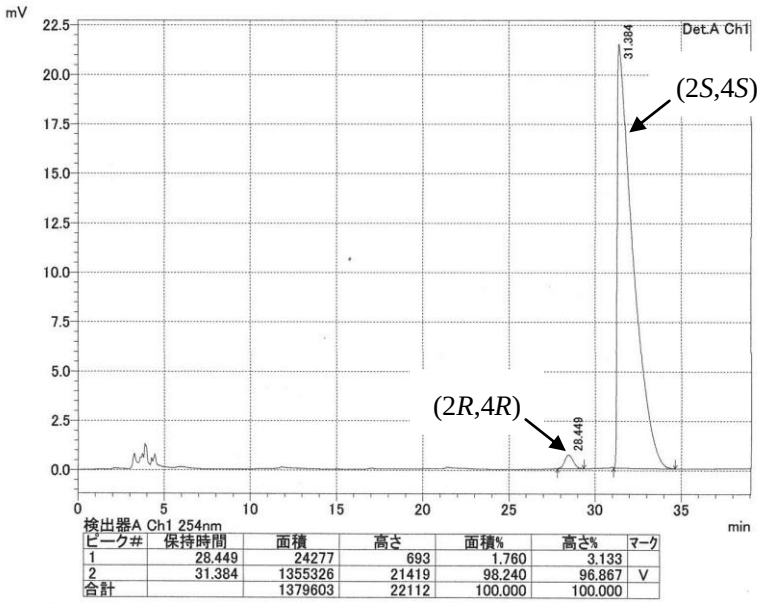
Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate (3ba)





検出器A Ch1 254nm

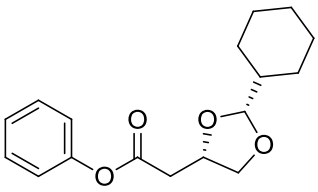
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	26.877	2154241	25538	49.552	46.760	
2	31.331	2193190	29078	50.448	53.240	
合計		4347430	54616	100.000	100.000	

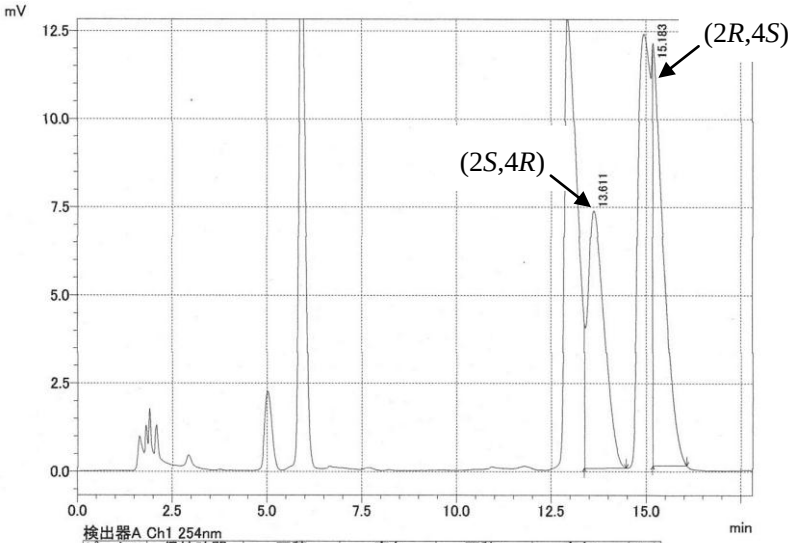


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	28.449	24277	693	1.760	3.133	
2	31.384	1355326	21419	98.240	96.867	V
合計		1379603	22112	100.000	100.000	

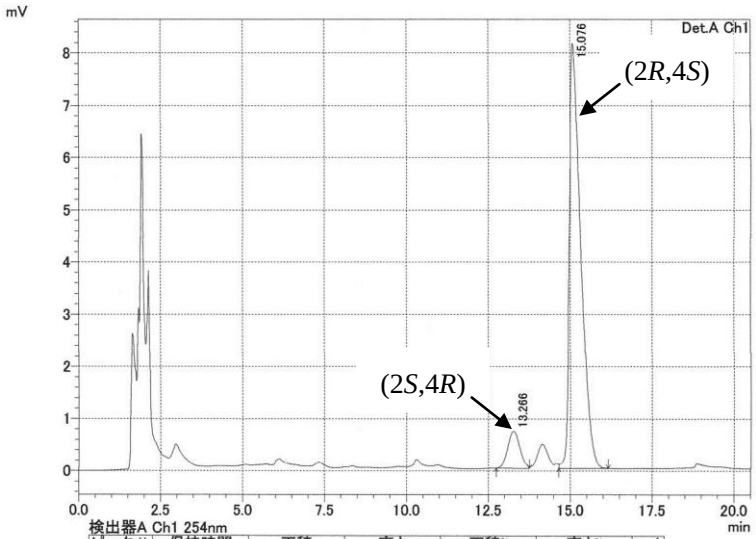
Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)acetate (3ba')





検出器A Ch1 254nm

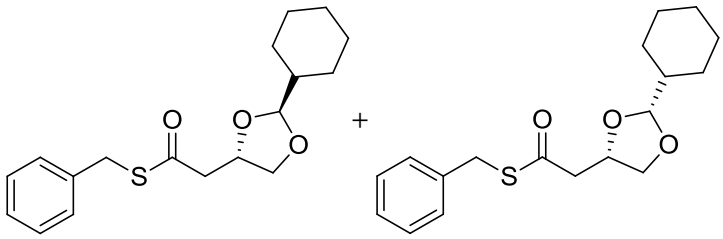
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	13.611	221794	7297	49.590	37.857	
2	15.183	225466	11978	50.410	62.143	
合計		447260	19274	100.000	100.000	

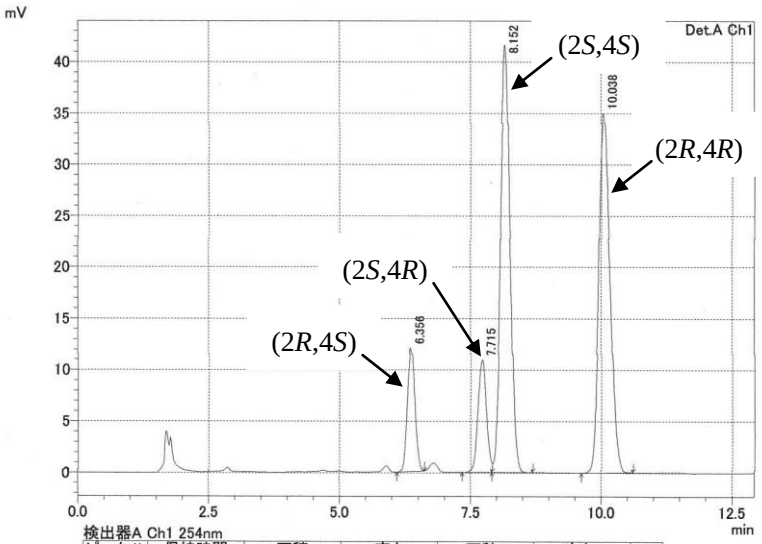


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	13.266	18271	708	8.487	8.004	
2	15.076	197017	8133	91.513	91.996	
合計		215288	8840	100.000	100.000	

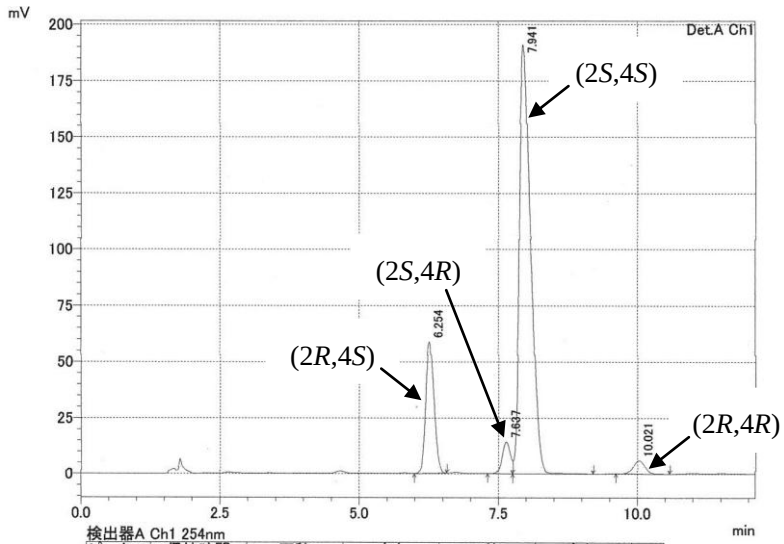
S-Benzyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ca + 3ca') (diastereomixture)





検出器A Ch1 254nm

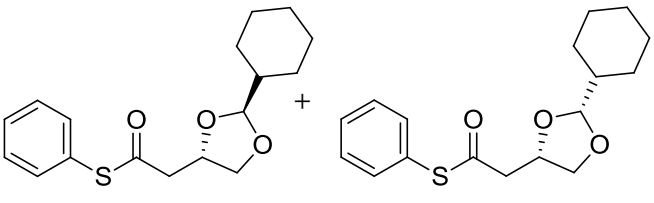
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	6.356	121913	12030	9.433	12.086	
2	7.715	123610	10912	9.564	10.963	
3	8.152	524864	41576	40.611	41.769	V
4	10.038	522043	35018	40.392	35.182	
合計		1292430	99536	100.000	100.000	

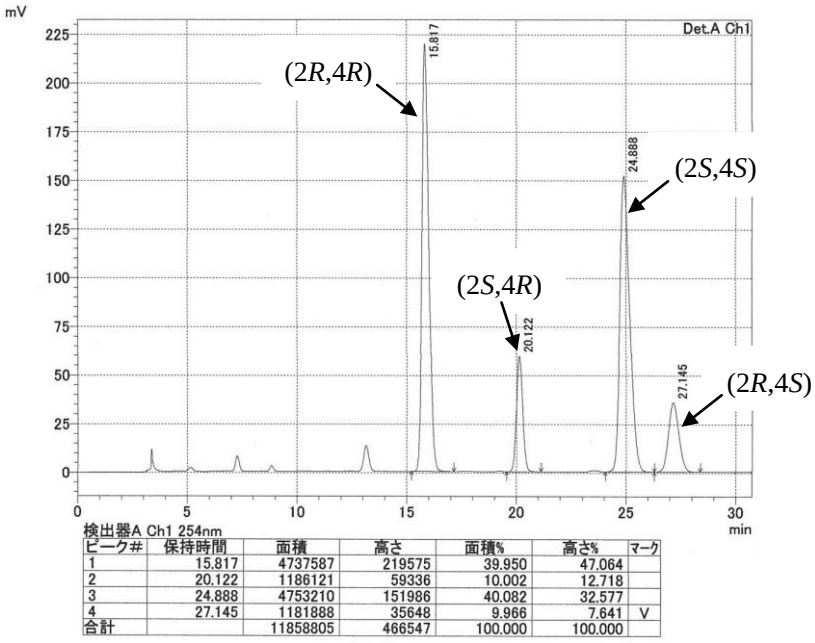


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	6.254	613531	58647	17.354	21.739	
2	7.637	146674	14316	4.149	5.307	
3	7.941	2688279	190825	76.040	70.734	SV
4	10.021	86848	5988	2.457	2.220	
合計		3535332	269777	100.000	100.000	

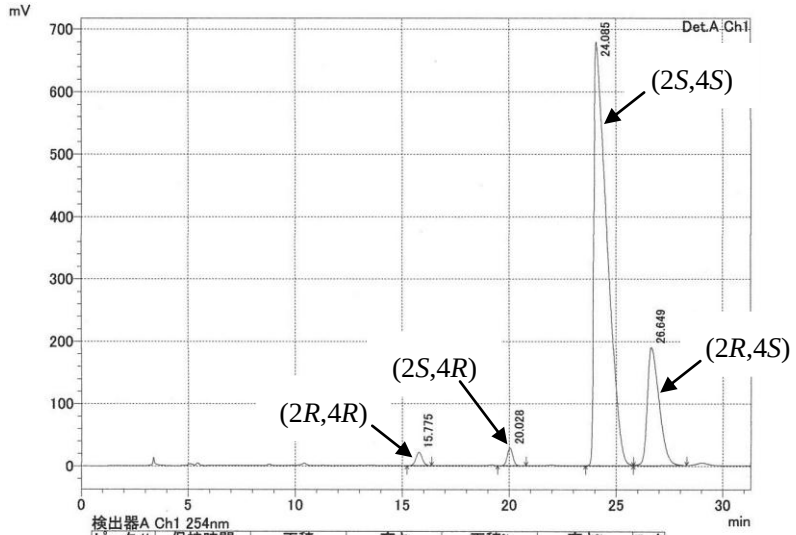
S-Phenyl 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3da + 3da') (diastereomixture)





検出器A Ch1 254nm

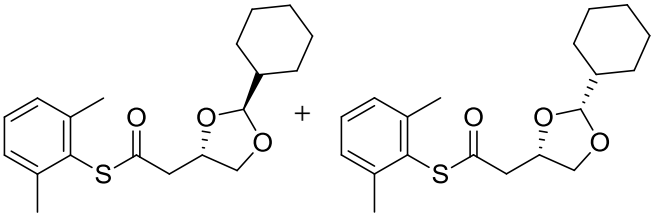
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	15.817	4737587	219575	39.950	47.064	
2	20.122	1186121	59336	10.002	12.718	
3	24.888	4753210	151986	40.082	32.577	
4	27.145	1181888	35648	9.966	7.641	V
合計		11858805	466547	100.000	100.000	

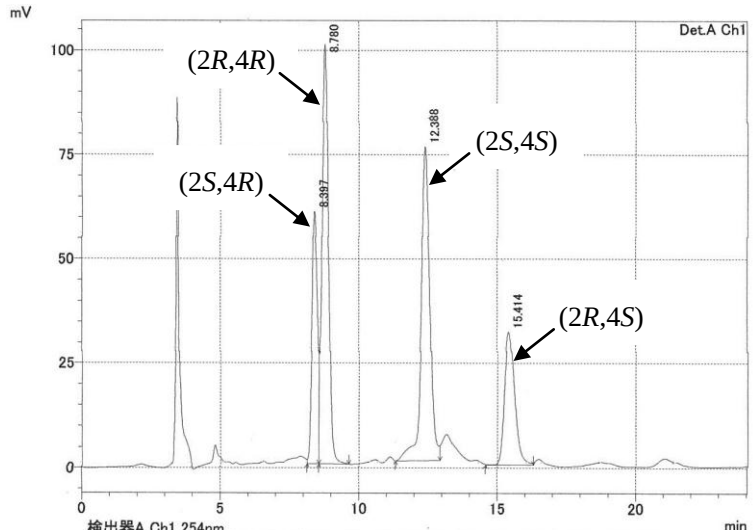


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	15.775	449510	21830	1.212	2.375	
2	20.028	528473	28823	1.425	3.136	
3	24.085	28828951	678739	77.747	73.852	
4	26.649	7273402	189662	19.615	20.637	V
合計		37080336	919055	100.000	100.000	

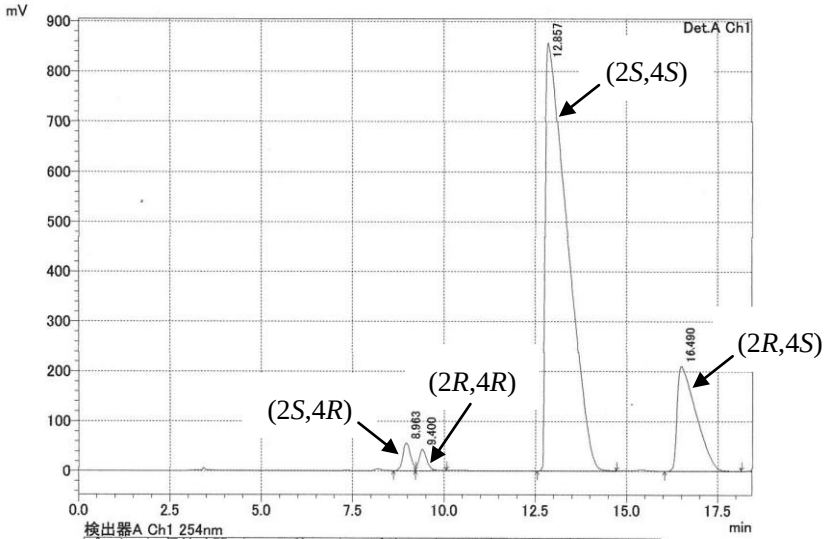
S-(2,6-Dimethylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3ea + 3ea') (diastereomixture)





検出器A Ch1 254nm

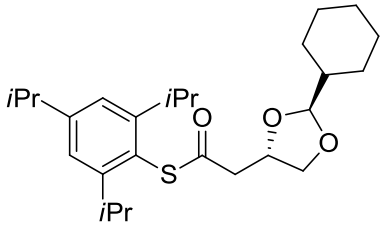
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	8.397	819757	60427	16.663	22.565	
2	8.780	1641991	100448	33.377	37.509	V
3	12.388	1642949	75089	33.397	28.040	
4	15.414	814823	31831	16.563	11.886	
合計		4919520	267794	100.000	100.000	

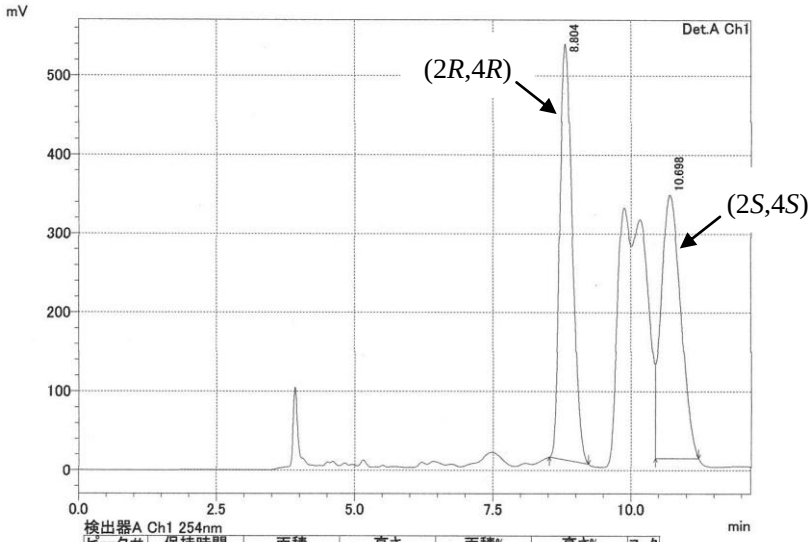


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	8.963	824036	56063	1.843	4.805	
2	9.400	635352	43317	1.421	3.713	V
3	12.857	35665519	856814	79.752	73.442	
4	16.490	7595432	210463	16.984	18.040	
合計		44720339	1166657	100.000	100.000	

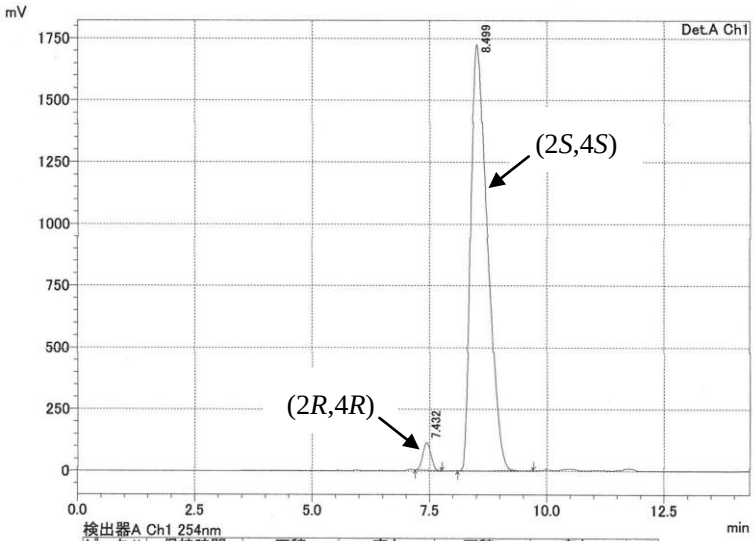
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3fa)





検出器A Ch1 254nm

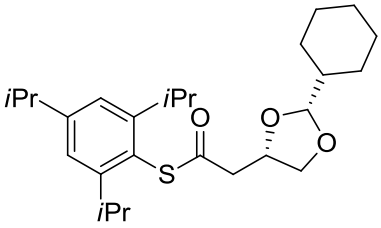
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	8.804	8320249	526740	50.336	61.201	
2	10.698	8209092	333934	49.664	38.799	
合計		16529340	860674	100.000	100.000	

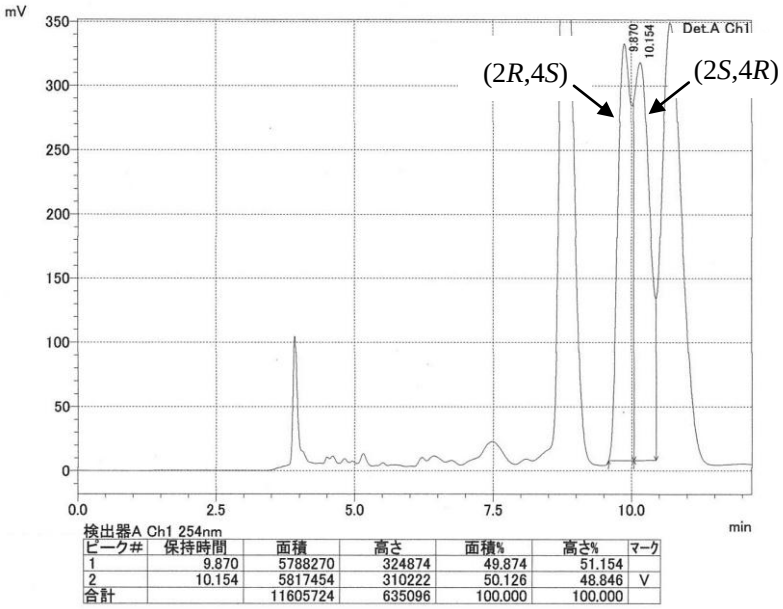


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	7.432	1368382	112417	3.092	6.119	
2	8.499	42884342	1724756	96.908	93.881	
合計		44252724	1837173	100.000	100.000	

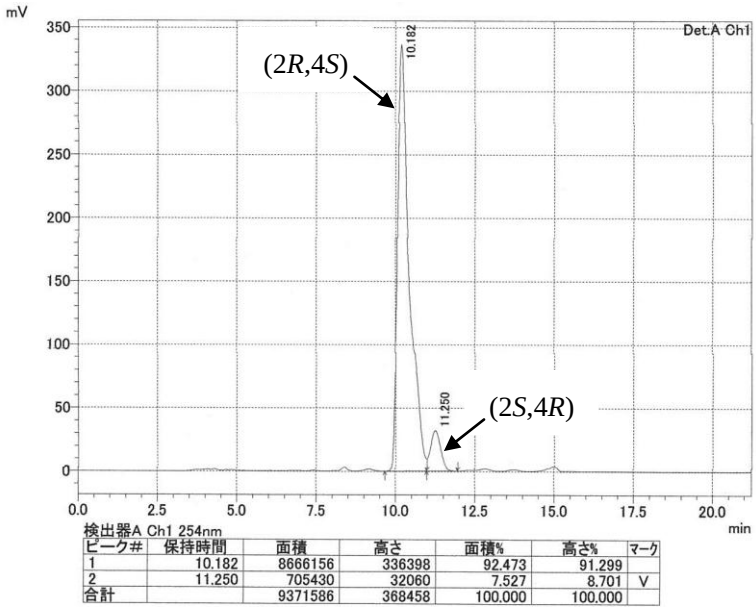
S-(2,4,6-Triisopropylphenyl) 2-(2-cyclohexyl-1,3-dioxolan-4-yl)ethanethioate (3fa')





検出器A Ch1 254nm

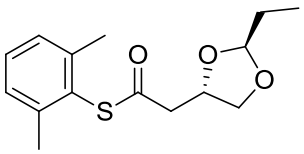
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.870	5788270	324874	49.874	51.154	
2	10.154	5817454	310222	50.126	48.846	V
合計		11605724	635096	100.000	100.000	

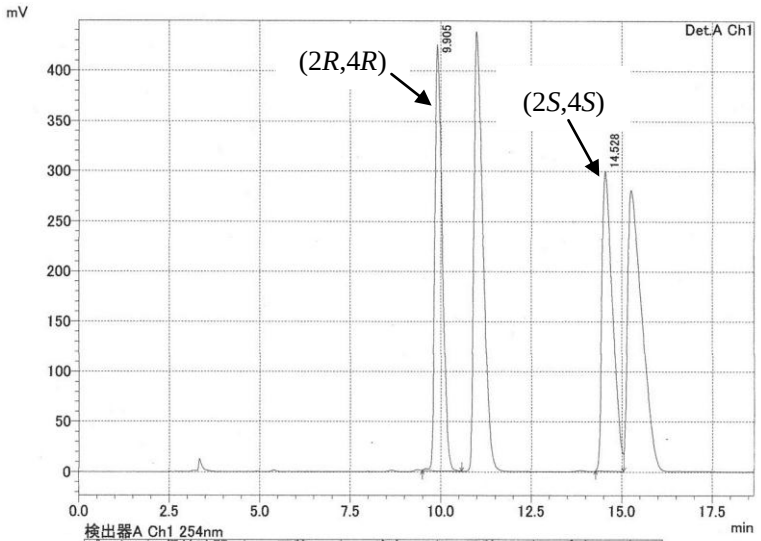


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.182	8666156	336398	92.473	91.299	
2	11.250	705430	32060	7.527	8.701	V
合計		9371586	368458	100.000	100.000	

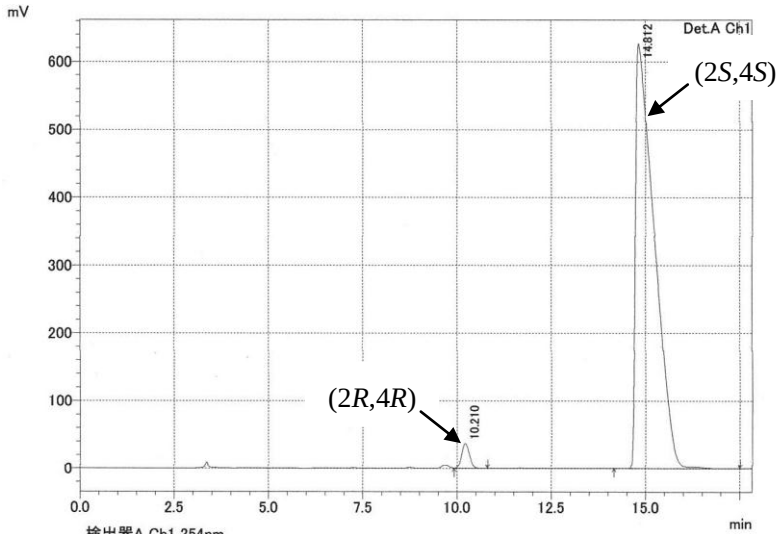
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate (3eb)





検出器A Ch1 254nm

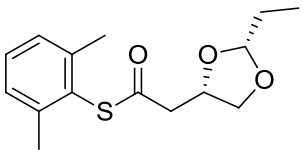
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.905	6092219	424946	49.826	58.673	
2	14.528	6134774	299309	50.174	41.327	
合計		12226993	724255	100.000	100.000	

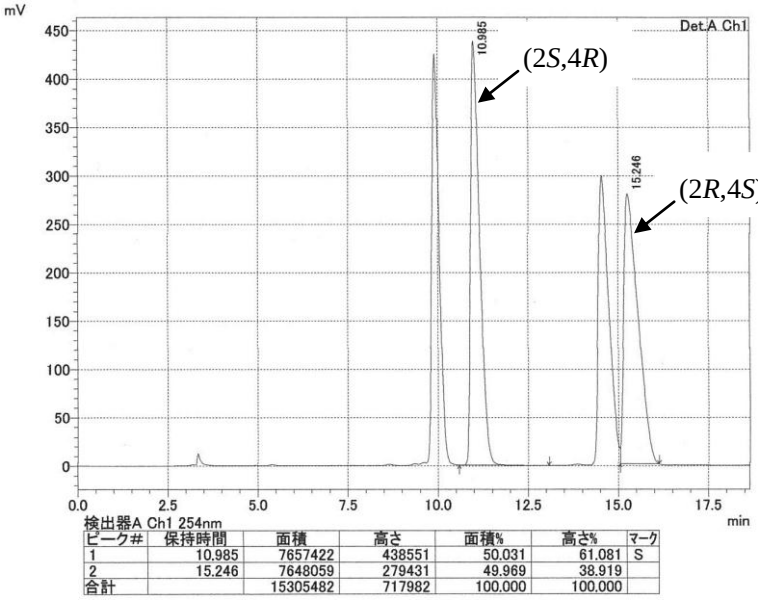


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.210	513703	36599	2.321	5.519	
2	14.812	21617386	626485	97.679	94.481	
合計		22131089	663084	100.000	100.000	

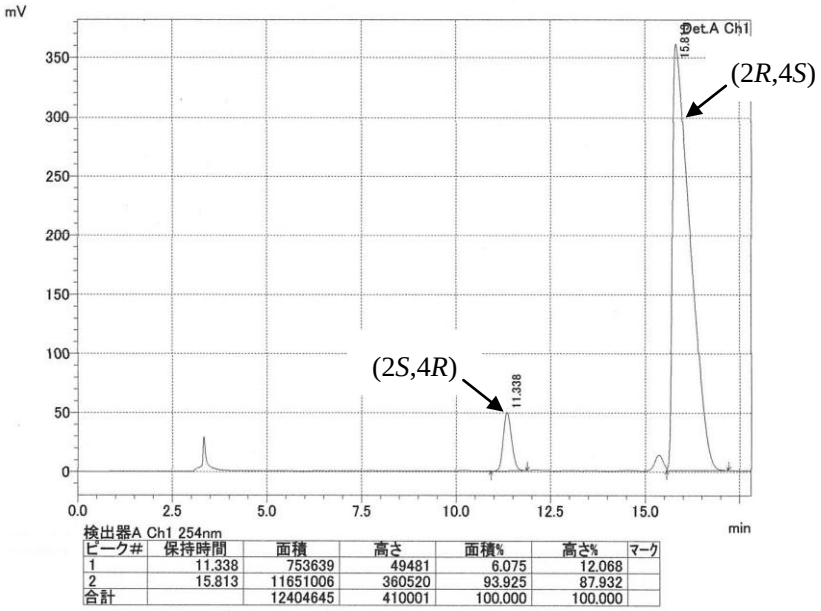
S-(2,6-Dimethylphenyl) 2-(2-ethyl-1,3-dioxolan-4-yl)ethanethioate (3eb')





検出器A Ch1 254nm

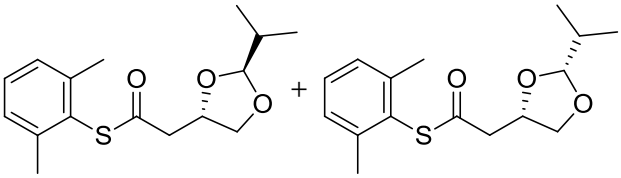
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	10.985	7657422	438551	50.031	61.081	S
2	15.246	7648059	279431	49.969	38.919	
合計		15305482	717982	100.000	100.000	

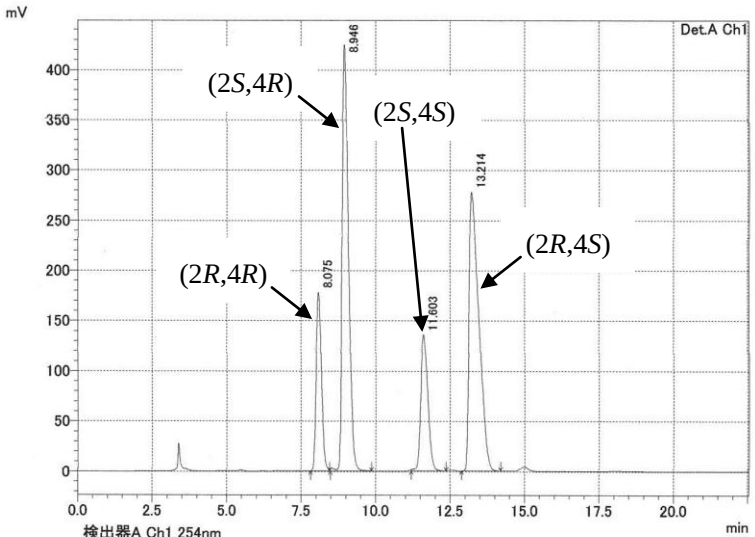


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	11.338	753639	49481	6.075	12.068	
2	15.813	11651006	360520	93.925	87.932	
合計		12404645	410001	100.000	100.000	

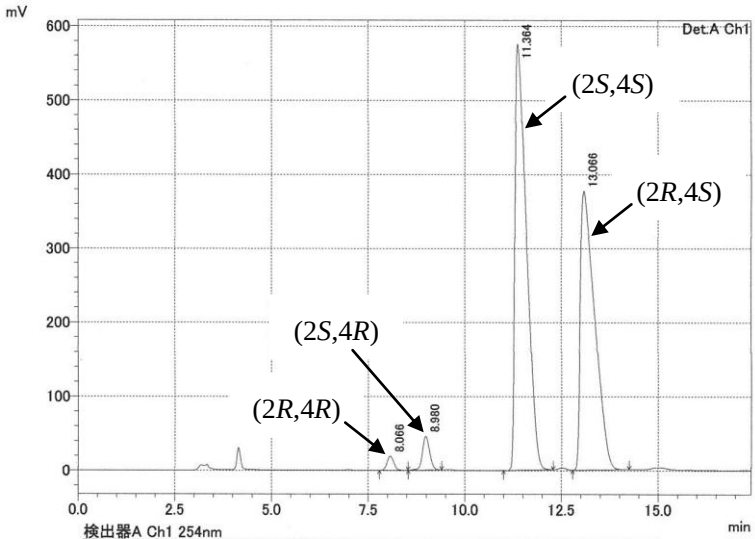
S-(2,6-Dimethylphenyl) 2-(2-isopropyl-1,3-dioxolan-4-yl)ethanethioate (3ec + 3ec') (diastereomixture)





検出器A Ch1 254nm

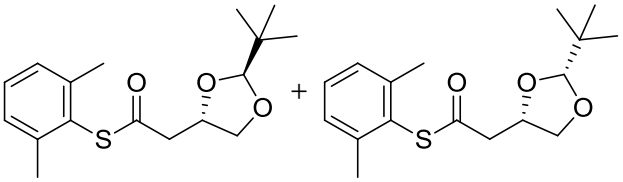
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	8.075	2213551	178167	13.023	17.522	
2	8.946	6223832	424826	36.616	41.780	
3	11.603	2245119	136055	13.208	13.381	
4	13.214	6315243	277766	37.153	27.317	
合計		16997746	1016814	100.000	100.000	

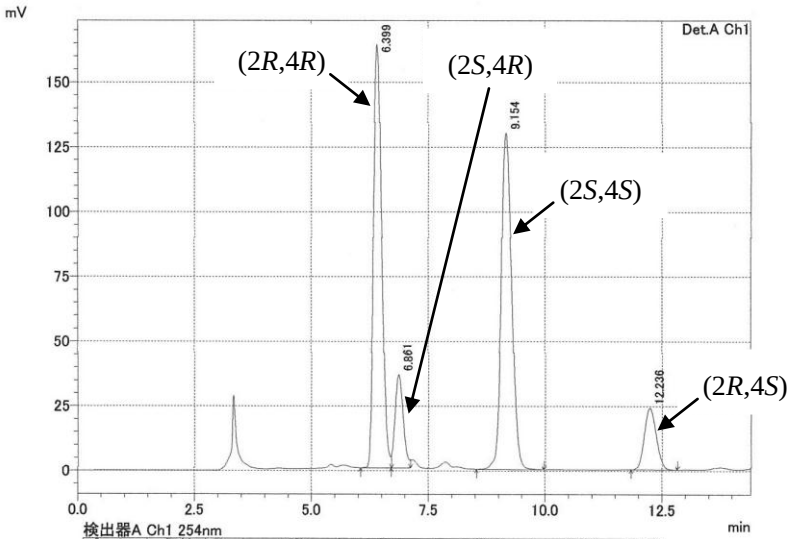


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	8.066	235438	19498	1.052	1.915	S
2	8.980	605974	45903	2.708	4.509	
3	11.364	11932432	575452	53.327	56.531	
4	13.066	9602320	377094	42.913	37.045	
合計		22376163	1017948	100.000	100.000	

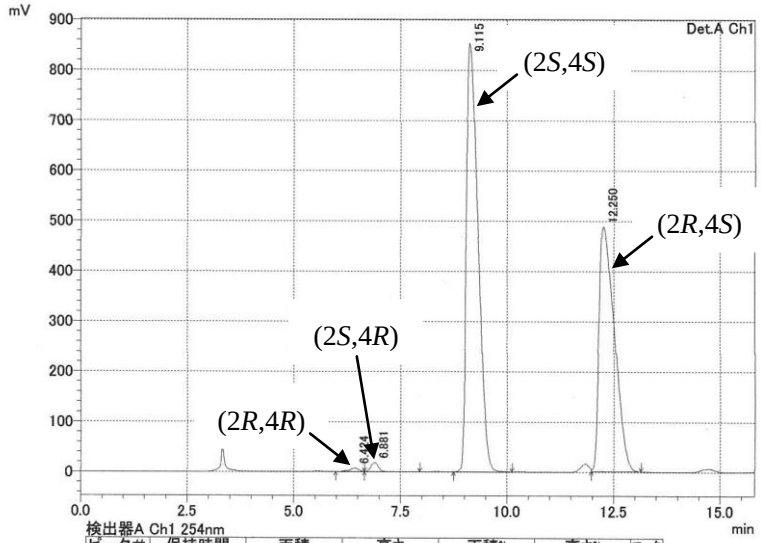
S-(2,6-Dimethylphenyl) 2-(2-(*tert*-butyl)-1,3-dioxolan-4-yl)ethanethioate (3ed + 3ed') (diastereomixture)





検出器A Ch1 254nm

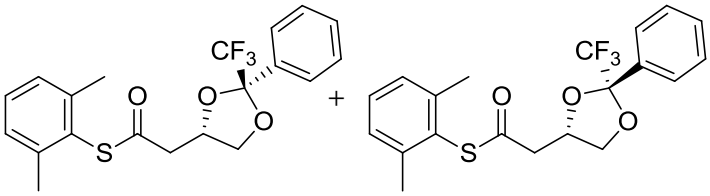
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	6.399	1999963	163437	40.746	46.256	
2	6.861	440676	36079	8.978	10.211	V
3	9.154	2038489	129827	41.531	36.744	
4	12.236	429188	23988	8.744	6.789	
合計		4908315	353331	100.000	100.000	

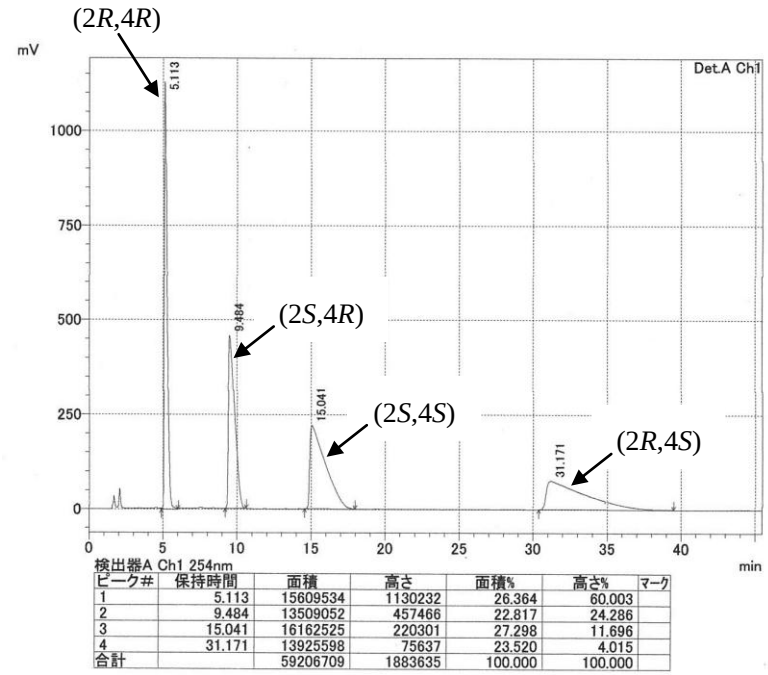


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	6.424	114767	7633	0.398	0.558	
2	6.881	232250	18859	0.805	1.380	SV
3	9.115	16208920	852838	56.147	62.391	
4	12.250	12312756	487587	42.651	35.671	
合計		28868693	1366918	100.000	100.000	

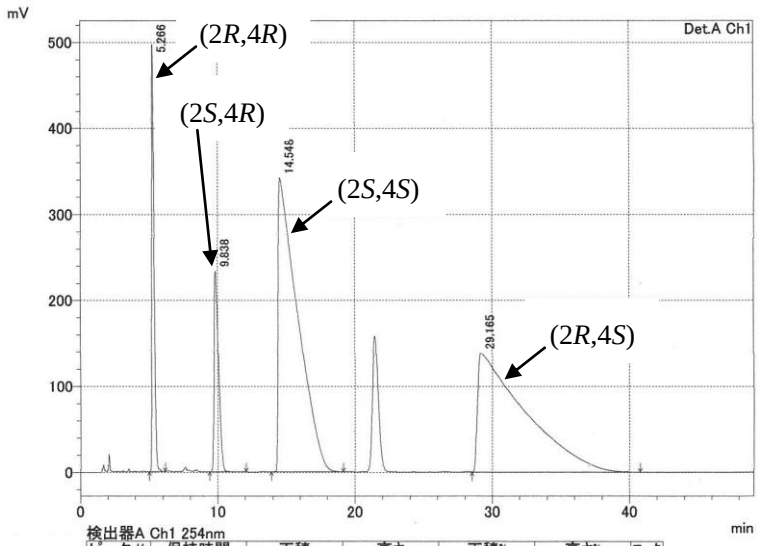
S-(2,6-Dimethylphenyl) 2-(2-phenyl-2-(trifluoromethyl)-1,3-dioxolan-4-yl) ethanethioate (3ee + 3ee') (diastereomixture)





検出器A Ch1 254nm

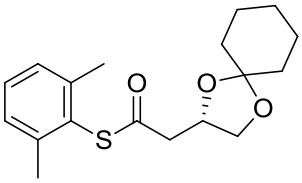
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.113	15609534	1130232	26.364	60.003	
2	9.484	13509052	457466	22.817	24.286	
3	15.041	16162525	220301	27.298	11.696	
4	31.171	13925598	75637	23.520	4.015	
合計		59206709	1883635	100.000	100.000	

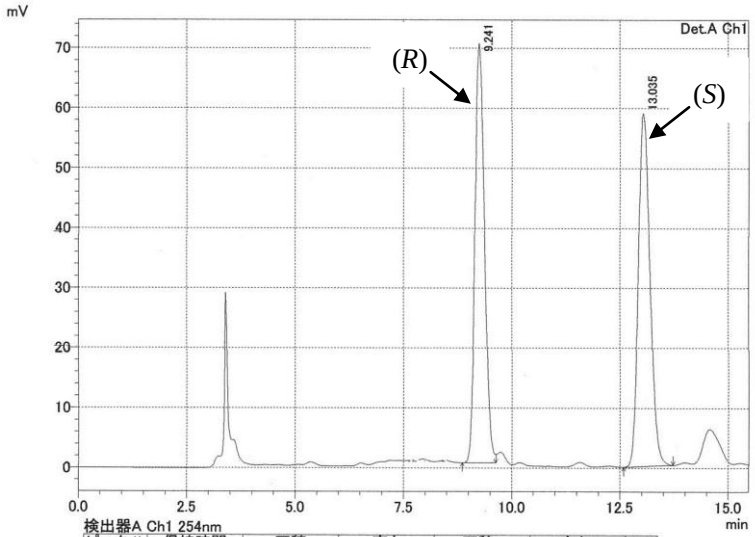


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.266	5764887	497065	7.422	41.031	
2	9.838	5315313	233799	6.843	19.299	S
3	14.548	33572239	342153	43.222	28.244	
4	29.165	33022166	138418	42.513	11.426	
合計		77674606	1211435	100.000	100.000	

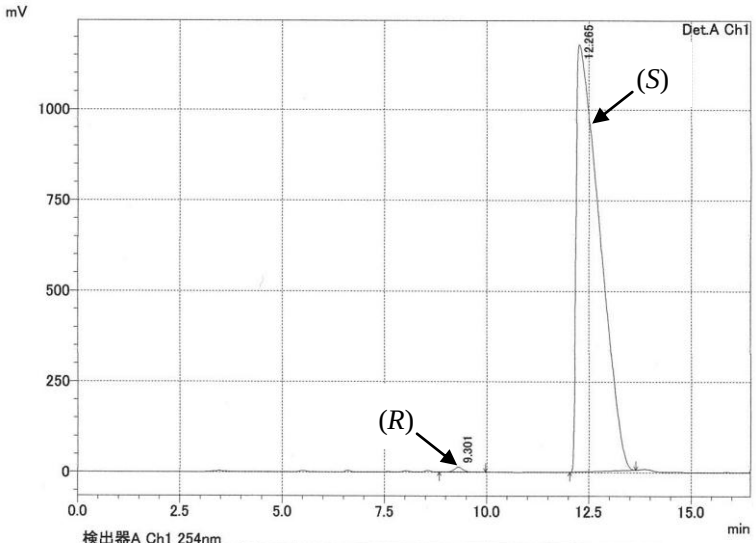
S-(2,6-Dimethylphenyl) 2-(1,4-dioxaspiro[4.5]decan-2-yl)ethanethioate (3eg)





検出器A Ch1 254nm

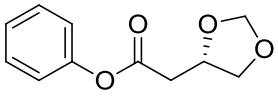
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.241	1072766	69919	49.219	54.291	
2	13.035	1106818	58868	50.781	45.709	
合計		2179584	128787	100.000	100.000	

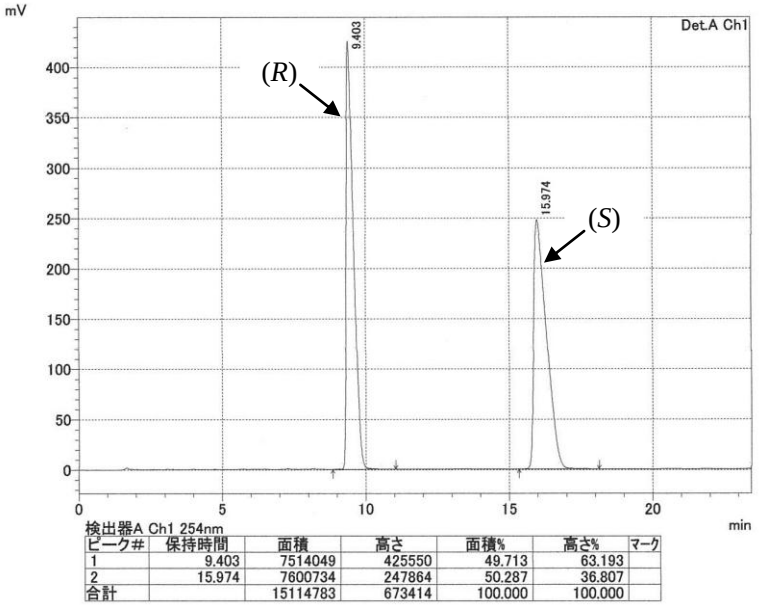


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.301	209043	14332	0.445	1.201	
2	12.265	46812815	1178517	99.555	98.799	
合計		47021858	1192849	100.000	100.000	

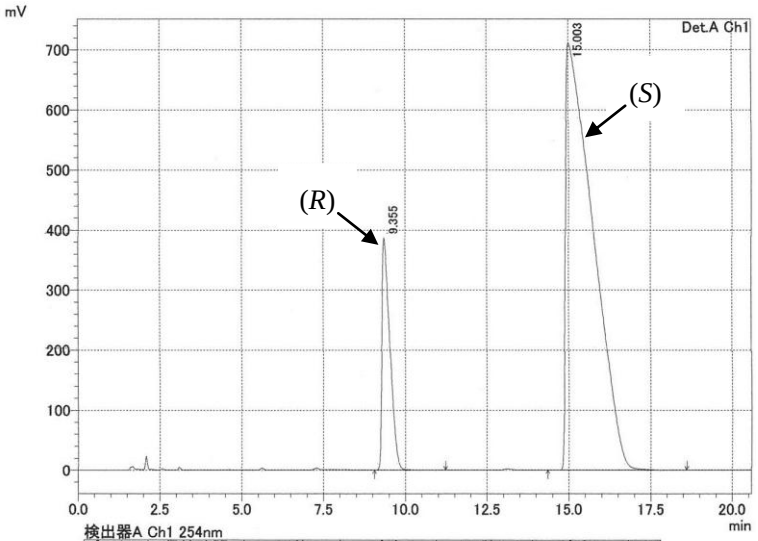
S-(2,6-Dimethylphenyl) 2-(1,3-dioxolan-4-yl)ethanethioate (3eh)





検出器A Ch1 254nm

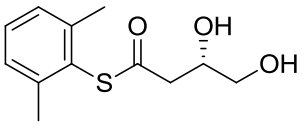
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.403	7514049	425550	49.713	63.193	
2	15.974	7600734	247864	50.287	36.807	
合計		15114783	673414	100.000	100.000	

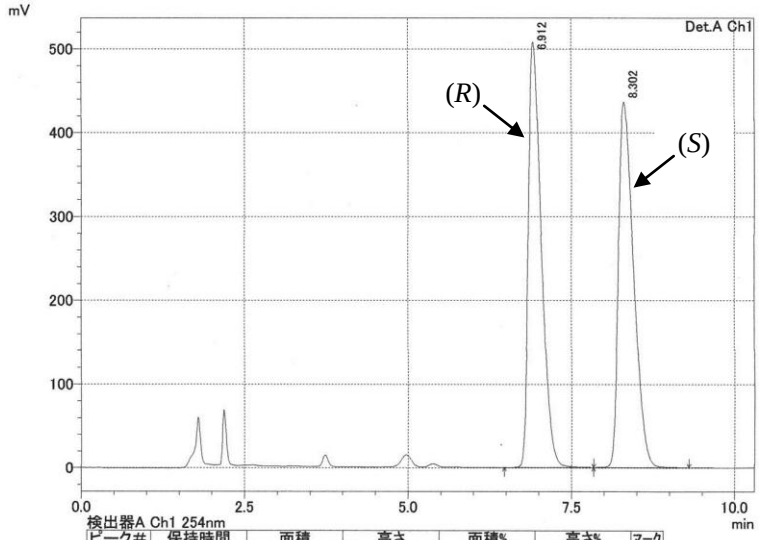


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	9.355	6515637	386984	13.644	35.231	
2	15.003	41237625	711441	86.356	64.769	
合計		47753262	1098426	100.000	100.000	

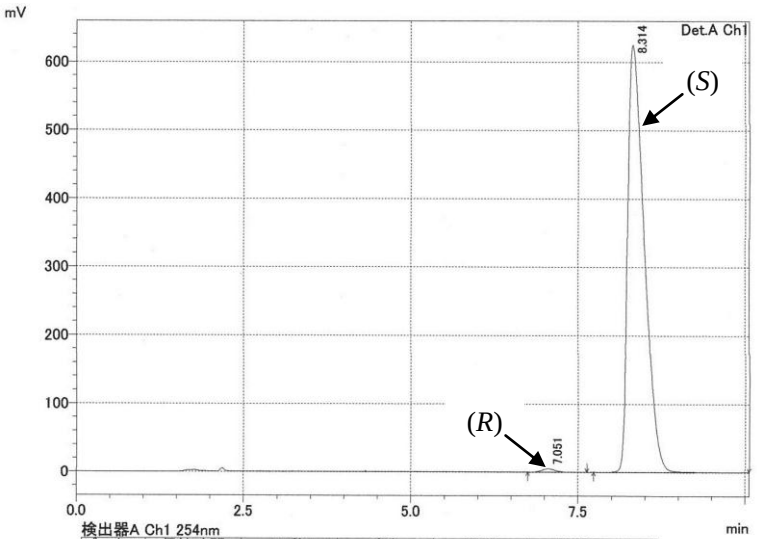
S-(2,6-Dimethylphenyl) 3,4-dihydroxybutanethioate (5)





検出器A Ch1 254nm

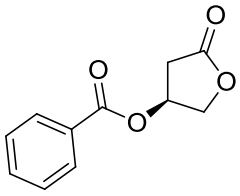
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	6.912	7011391	507895	49.880	53.789	
2	8.302	7045104	436343	50.120	46.211	V
合計		14056495	944238	100.000	100.000	

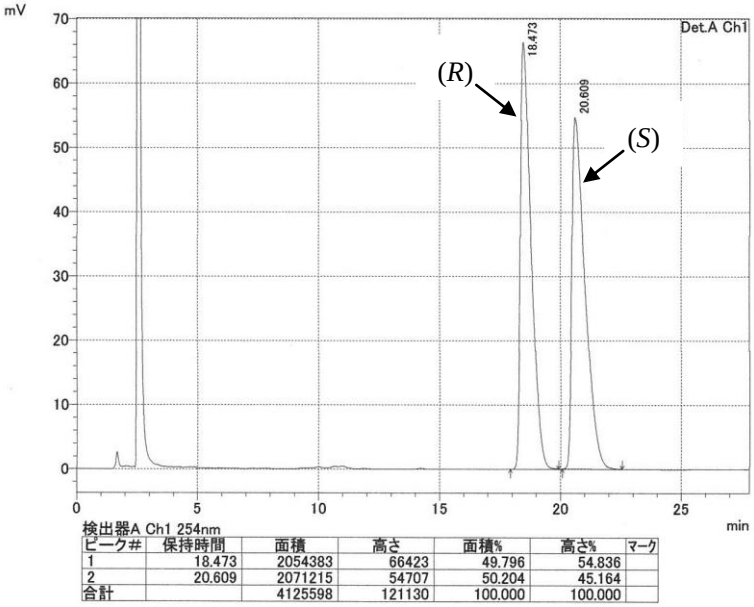


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	7.051	69170	5198	0.640	0.826	
2	8.314	10742424	624395	99.360	99.174	
合計		10811594	629593	100.000	100.000	

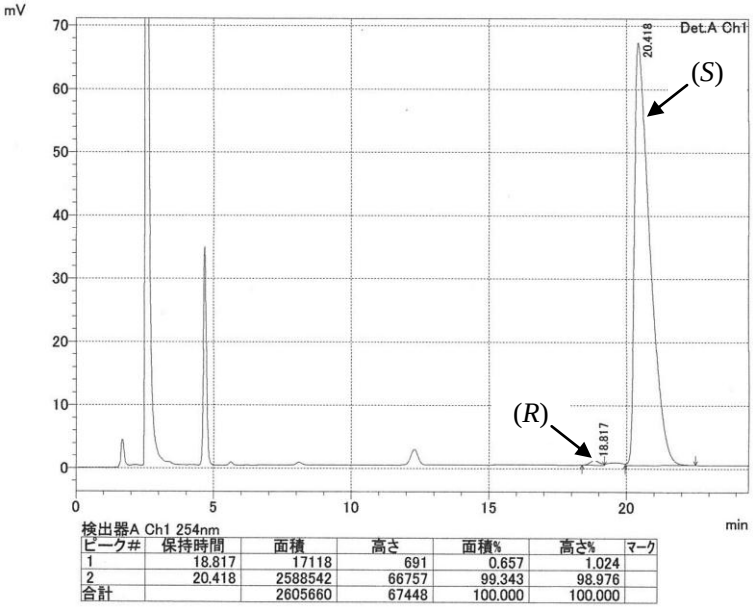
(*S*)-5-Oxotetrahydrofuran-3-yl benzoate





検出器A Ch1 254nm

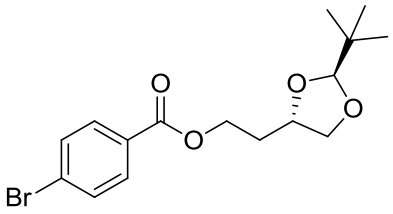
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	18.473	2054383	66423	49.796	54.836	
2	20.609	2071215	54707	50.204	45.164	
合計		4125598	121130	100.000	100.000	

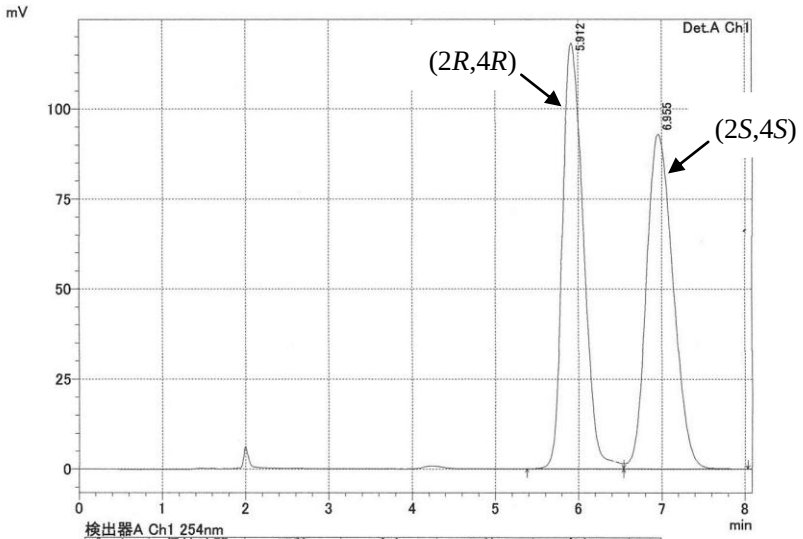


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	18.817	17118	691	0.657	1.024	
2	20.418	2588542	66757	99.343	98.976	
合計		2605660	67448	100.000	100.000	

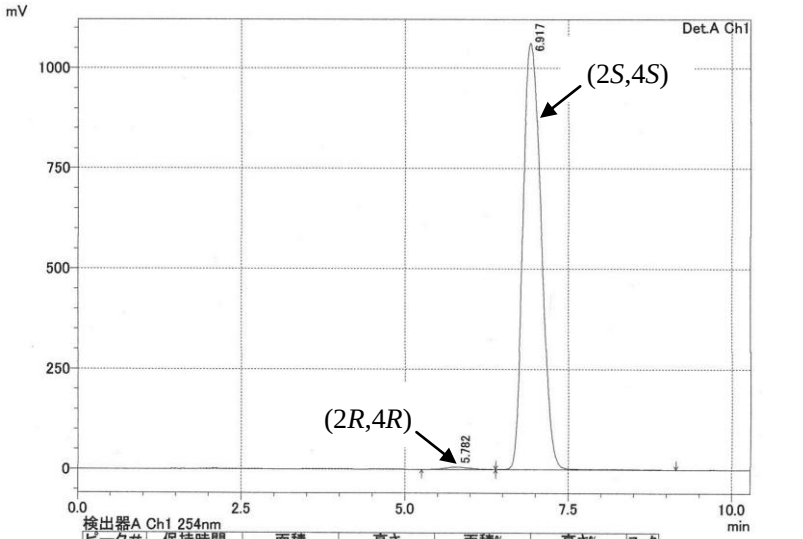
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)ethyl 4-bromobenzoate





検出器A Ch1 254nm

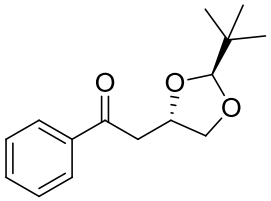
ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.912	2066253	118107	49.932	56.006	
2	6.955	2071916	92777	50.068	43.994	V
合計		4138170	210884	100.000	100.000	

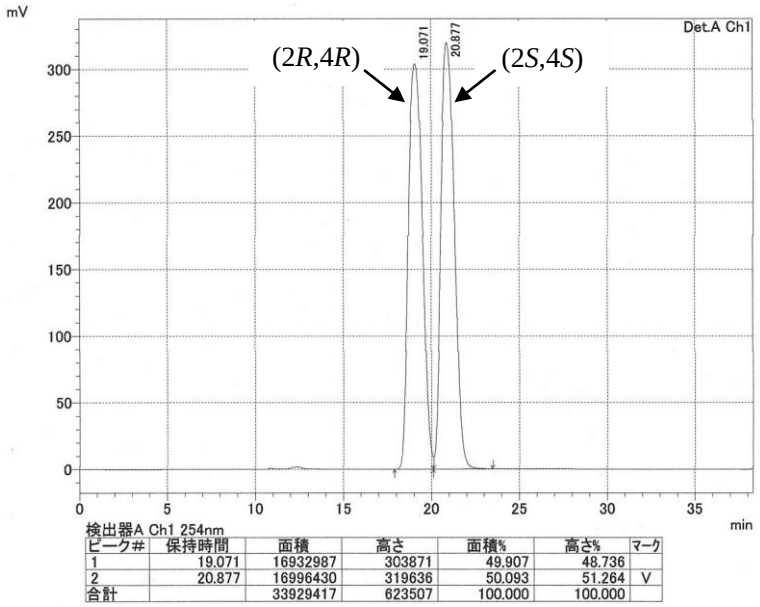


検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	5.782	131427	5435	0.634	0.509	
2	6.917	20588413	1062195	99.366	99.491	SV
合計		20719839	1067630	100.000	100.000	

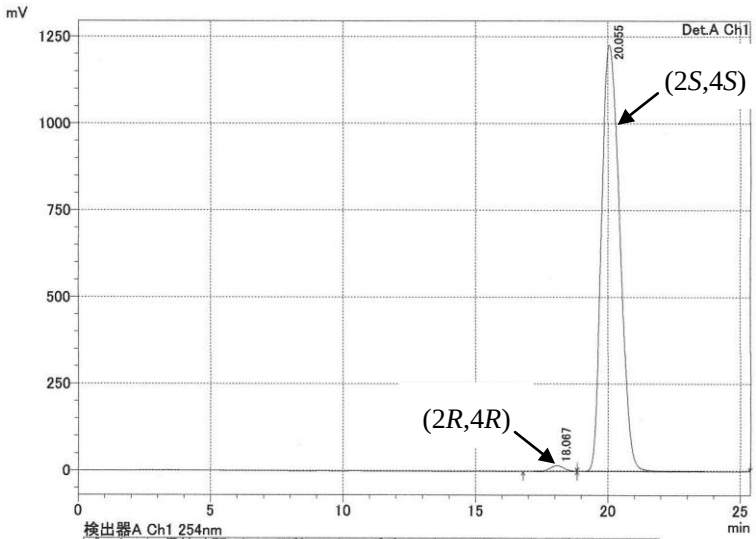
2-(2-(*tert*-Butyl)-1,3-dioxolan-4-yl)-1-phenylethanone (9)





検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	19.071	16932987	303871	49.907	48.736	
2	20.877	16996430	319636	50.093	51.264	V
合計		33929417	623507	100.000	100.000	



検出器A Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	高さ%	マーク
1	18.067	673056	17542	1.125	1.407	
2	20.055	59173800	1229370	98.875	98.593	V
合計		59846855	1246912	100.000	100.000	