Electronic Supplementary Information

Enantioselective synthesis of gabapentin analogues via organocatalytic asymmetric Michael addition of α-branched aldehydes to β-nitroacrylates.

Masanori Yoshida,*[a,b] Erika Masaki,[c] Hiroto Ikehara[b] and Shoji Hara[a,b]

Division of Chemical Process Engineering, Faculty of Engineering,[a]
Molecular Chemistry and Engineering Course, Graduate School of Chemical Sciences and Engineering,[b]
Department of Applied Science and Engineering, School of Engineering,[c]
Hokkaido University
Kita 13-jo Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628 Japan.

myoshida@eng.hokudai.ac.jp

Contents

(A) General

IR spectra were recorded using a JASCO FT/IR-5300 or FT/IR-410 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM-A400II, JNM-ECX400P or JNM-ECS400 FT NMR. Chemical shifts, δ are referred to TMS ($CDCl_3$ and CD_3OD) or 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt (TSP) (D_2O). ESI high-resolution mass spectra were measured on a Thermo Exactive spectrometer. Specific rotation was measured by a JASCO P-2200 or HORIBA SEPA-300. Melting points are measured by Yanagimoto micro melting point apparatus and are uncorrected. HPLC was carried out using a JASCO PU-2089 Plus intelligent pump and a UV-2075 Plus UV detector. X-Ray analysis was performed with a RIGAKU R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation.

(B) Synthesis of cycloheptanecarboxaldehyde (2d)[1]

In a round-bottomed flask, a solution of 1,2-dibromoethane (0.56 g, 3 mmol) in dry THF (5 mL) was added to Mg chip (2.43 g, 100 mmol) under nitrogen atmosphere. A solution of bromocycloheptane (16.0 g, 90 mmol) in dry THF (60 mL) was then added to the reaction mixture and refluxed for 2.5 h. After cooling the resulting solution to 0 °C with an ice-water bath, *N*-formylpiperidine (10.2 g, 90 mmol) was added to the reaction mixture. After stirring for 1 h at room temperature, 3N-HCl (50 mL) was added to the reaction mixture to acidify, and the whole reaction mixture was extracted with Et_2O (50 mL×3). The combined organic phase was successively washed with H_2O, sat. aq. $NaHCO_3$ and brine, and then, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (silicagel, hexane–Et_2O) gave cycloheptanecarboxaldehyde (**2d**) in a pure form (36%, 3.65 g, 33 mmol). $\delta_H(CDCl_3)$ 1.46–1.72 (10H, m), 1.92–1.99 (2H, m), 2.33–2.40 (1H, m), 9.62 (1H, s); $\delta_C(CDCl_3)$ 26.2, 27.2, 28.5, 51.8, 204.7.

(C) Synthesis of β-nitroacrylates 3

Benzyl (*E*)-β-nitroacrylate (3a)[2,3]

In a round-bottomed flask, cold 3N-NaOH (105 mL) and nitromethane (32 mL, 595 mmol) were successively added to glyoxylic acid monohydrate (27.6 g, 300 mmol). The reaction mixture was stirred for 14 h at room temperature, then, 1 h at 70 °C. After cooling the resulting solution with an ice-water bath, cold 6N-H_2SO_4 (100 mL) was added to the reaction mixture at 0 °C and extracted with EtOAc (100 mL×1, then, 50 mL×9). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure at 40 °C to give brown oil. Addition of CH_2Cl_2 to the crude reaction mixture gave a brown solid. The precipitate was filtered and dried in air to give pure 2-hydroxy-3-nitropropionic acid (86%, 35.0 g, 259 mmol).[2] In a round-bottomed flask, K_2CO_3 (13.8 g, 100 mmol) was added portionwise to a solution of 2-hydroxy-3-nitropropionic acid (13.5 g, 100 mmol) in DMF (100 mL) with cooling in a water bath. To the reaction mixture, KI (0.83 g, 5 mmol) and benzyl bromide (17.1 g, 100 mmol) were successively added and the resulting solution was stirred for 14 h at room temperature. The resulting solution was poured into 1.5M-NH_4Cl (200 mL) and extracted with EtOAc (100 mL×1, then, 50 mL×3). The combined organic phase was washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. After the residue was dissolved in a small amount of EtOAc, a large amount of hexane was added to the solution to obtain a product, benzyl 2-hydroxy-3-nitropropionate (75%, 16.8 g, 74.7 mmol), as a solid. In a round-bottomed flask, methanesulfonyl chloride (17.3 mL, 224 mmol) was added to a solution of benzyl 2-hydroxy-3-nitropropionate (16.8 g, 74.7 mmol) in dry CH_2Cl_2 (75 mL) under nitrogen atmosphere. Triethylamine (31 mL, 224 mmol) was added dropwise to the reaction mixture at –20 °C and stirred for 1 h at the same temperature. The resulting mixture was poured into water (100 mL) and extracted with Et_2O (50 mL×3). The combined organic phase was washed with sat. $CuSO_4$, sat. $NaHCO_3$ and brine successively and dried over $MgSO_4$. Volatile organics were removed by evaporation to give a crude product. Benzyl (*E*)-β-nitroacrylate (**2a**) (59%, 9.12 g, 44 mmol) was isolated by column chromatography (silicagel, hexane–EtOAc). $\delta_H(CDCl_3)$ 5.28 (2H, s), 7.12 (1H, d, *J* 13.1 Hz), 7.39 (5H, s), 7.69 (1H, d, *J* 13.1 Hz); $\delta_C(CDCl_3)$ 68.1, 127.4, 128.6, 128.7, 128.9, 134.3, 149.1, 162.4.

Methyl (*E*)-β-nitroacrylate (3b) and Ethyl (*E*)-β-nitroacrylate (3c)[3,4]

In a round-bottomed flask, thionyl chloride (11.9 g, 100 mmol) was added dropwise to a solution of 2-hydroxy-3-nitropropionic acid (6.75 g, 50 mmol) in MeOH (50 mL) at 0 °C. After stirring for 14 h, the reaction mixture was concentrated under reduced pressure to give methyl 2-hydroxy-3-nitropropionate which was pure enough for further transformation. In a round-bottomed flask, acetic anhydride (14 mL, 150 mmol) was added to a solution of methyl 2-hydroxy-3-nitropropionate in DMSO (50 mL) at room temperature.[3] After stirring for 3 days at 30 °C, the reaction mixture was poured into water (300 mL) and extracted with CH_2Cl_2 (50 mL×3). The combined organic phase was washed with sat. aq. $NaHCO_3$ (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Methyl (*E*)-β-nitroacrylate (**3b**) (2 steps, 13%, 0.86 g, 6.6 mmol) was isolated by column chromatography (silicagel, hexane–Et_2O). Ethyl (*E*)-β-nitroacrylate (**3b**) (2 steps, 11%, 0.82 g, 5.6 mmol) was also synthesized by using EtOH as a solvent for the esterification reaction. Spectroscopic data of **3b**[4a] and **3c**[4b] are in agreement with the published data.

t-Buthyl (*E*)-β-nitroacrylate (**3d**) was synthesized according to the literature.[5]

Benzyl (*E*)-3-nitropent-2-enoate (3e)[6]

2-Hydroxy-3-nitropentanoic acid was prepared from glyoxylic acid monohydrate (9.2 g, 100 mmol) and 1-nitropropane (10.0 g, 111

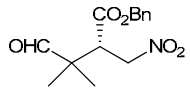
mmol) according to the procedure for 2-hydroxy-3-propionic acid described in the recipe of **3a**. The obtained crude 2-hydroxy-3-pentanoic acid was used for further transformation without purification. Esterification of 2-hydroxy-3-pentanoic acid with benzyl bromide by the same procedure as that for benzyl 2-hydroxy-3-propionate described in the recipe of **3a** gave benzyl 2-hydroxy-3-pentanoate (2 steps, 86%, 23.4 g, 86 mmol). In a round-bottomed flask, methanesulfonyl chloride (10 mL, 130 mmol) was added to a solution of benzyl 2-hydroxy-3-nitropentanoate (23.4 g, 86 mmol) in dry CH_2Cl_2 (86 mL) under nitrogen atmosphere. Triethylamine (35.7 mL, 258 mmol) was slowly added to the reaction mixture at –20 °C and stirred for 1 h at the same temperature. The resulting solution was poured into water (100 mL) and extracted with Et_2O (50 mL×3). The combined organic phase was washed with sat. $CuSO_4$, sat. $NaHCO_3$ and brine successively, and then, dried over $MgSO_4$. Volatile organics were removed by evaporation to give a crude product. Benzyl (*E*)-3-nitropent-2-enoate (**3e**) (55%, 12.0 g, 47 mmol) was isolated by column chromatography (silicagel, hexane–EtOAc). $\delta_H(CDCl_3)$ 1.18 (3H, t, *J* 7.3 Hz), 3.07 (2H, q, *J* 7.3 Hz), 5.24 (2H, s), 7.00 (1H, s), 7.37–7.39 (5H, m); $\delta_C(CDCl_3)$ 12.3, 21.1, 67.4, 120.2, 128.4, 128.7, 134.7, 163.7, 165.6.

Methyl (*E*)-2-methyl-3-nitroacrylate (3f)[3]

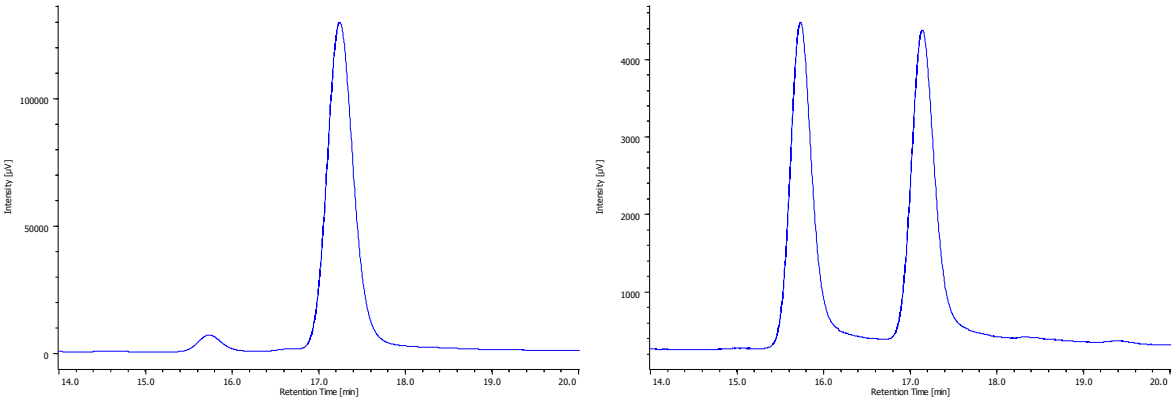
In a round-bottomed flask, triethylamine (0.4 g, 4 mmol) was added to a solution of methyl pyruvate (2.04 g, 20 mmol) in $MeNO_2$ (80 mL) at room temperature. After stirring for 3 days at room temperature, the reaction mixture was concentrated under reduced pressure to give methyl 2-hydroxy-2-methyl-3-nitropropionate which was pure enough for further transformation. In a round-bottomed flask, acetic anhydride (5.7 mL, 60 mmol) was added to a solution of methyl 2-hydroxy-2-methyl-3-nitropropionate in DMSO (70 mL) at room temperature. After stirring for 2 days at room temperature, the reaction mixture was poured into water (300 mL) and extracted with CH_2Cl_2 (50 mL×3). The combined organic phase was washed with sat. aq. $NaHCO_3$ (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Methyl (*E*)-2-methyl-3-nitroacrylate (**3f**) (2 steps, 50%, 1.45 g, 10 mmol) was isolated by column chromatography (silicagel, hexane–EtOAc). $\delta_H(CDCl_3)$ 2.10 (3H, s), 3.87 (3H, s), 6.87 (1H, s); $\delta_C(CDCl_3)$ 17.5, 53.1, 135.8, 140.6, 166.5.

(D) HPLC data of 4, 6 and 7

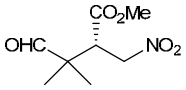
Benzyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4a)



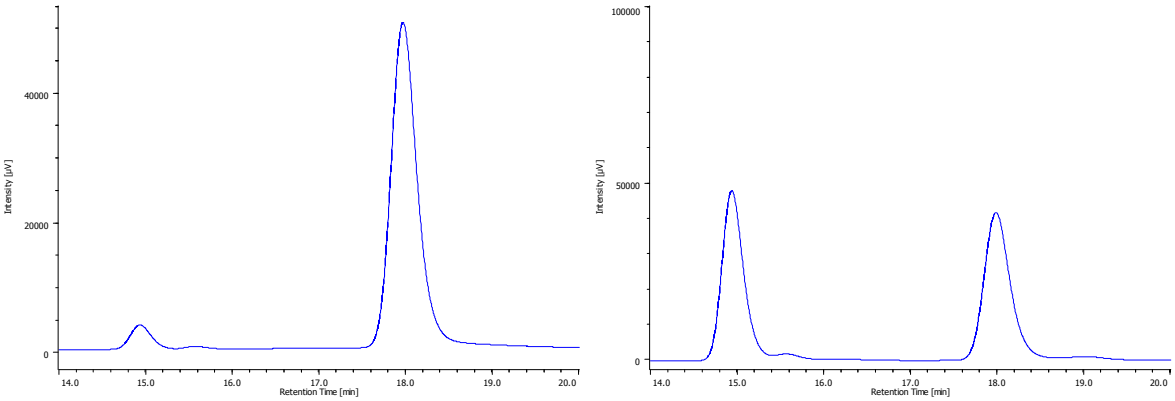
Daicel CHIRALPAK AD-H, hexane/isopropanol (93:7, v/v), 0.8 mL/min, 215 nm; t_r(major enantiomer) = 17.2 min, t_r(minor enantiomer) = 15.7 min



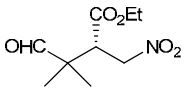
Methyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4b)



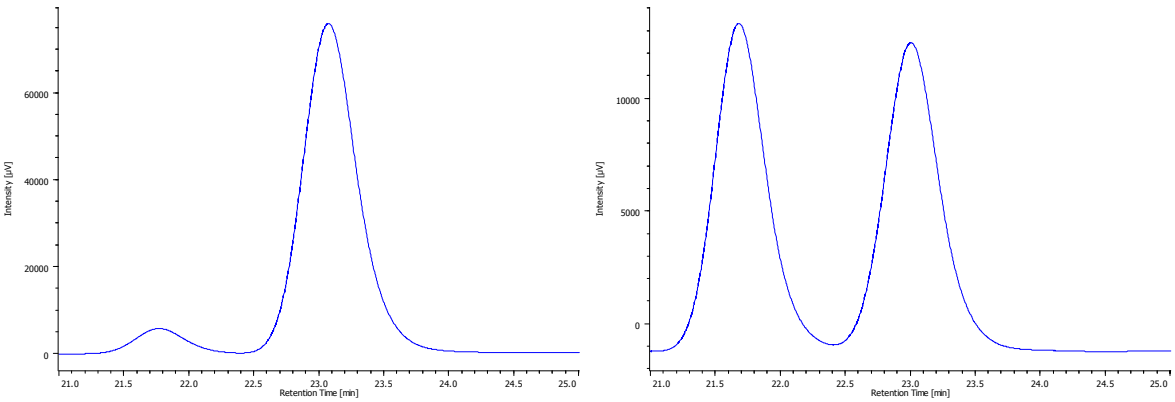
Daicel CHIRALPAK AD-H, hexane/isopropanol (93:7, v/v), 0.8 mL/min, 215 nm; t_r(major enantiomer) = 18.0 min, t_r(minor enantiomer) = 14.9 min



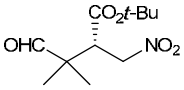
Ethyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4c)



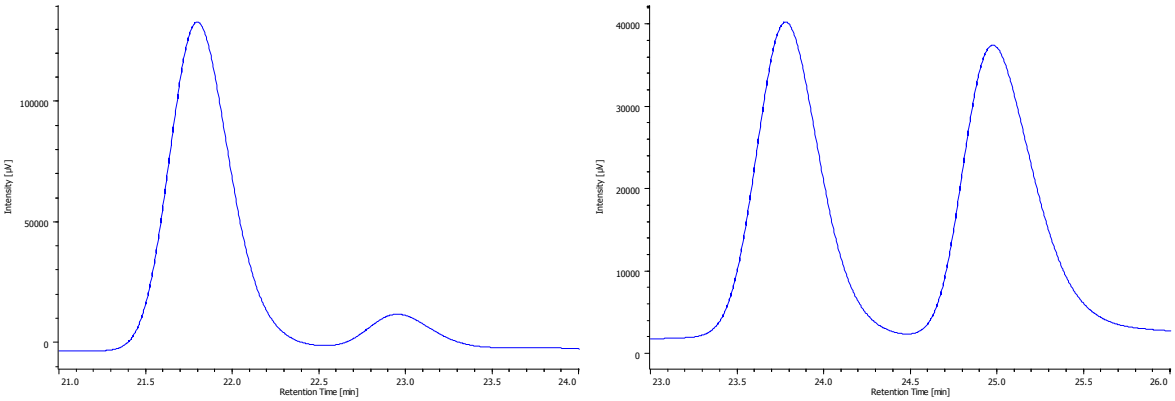
Daicel CHIRALPAK AD-H, hexane/isopropanol (98:2, v/v), 0.8 mL/min, 215 nm; t_r(major enantiomer) = 23.1 min, t_r(minor enantiomer) = 21.8 min



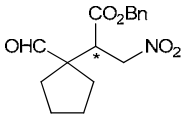
_t_-Butyl (_S_)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4d)



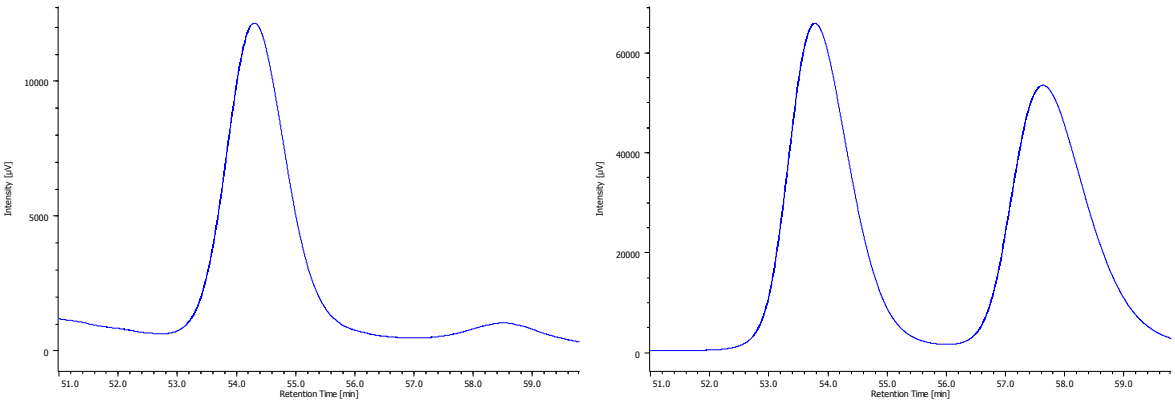
Daicel CHIRALPAK AD-H, hexane/isopropanol (99:1, v/v), 0.7 mL/min, 208 nm; t_r(major enantiomer) = 21.8 min, t_r(minor enantiomer) = 23.0 min



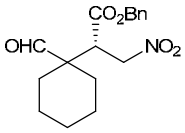
Benzyl 2-(1-formylcyclopentyl)-3-nitropropionate (4e)



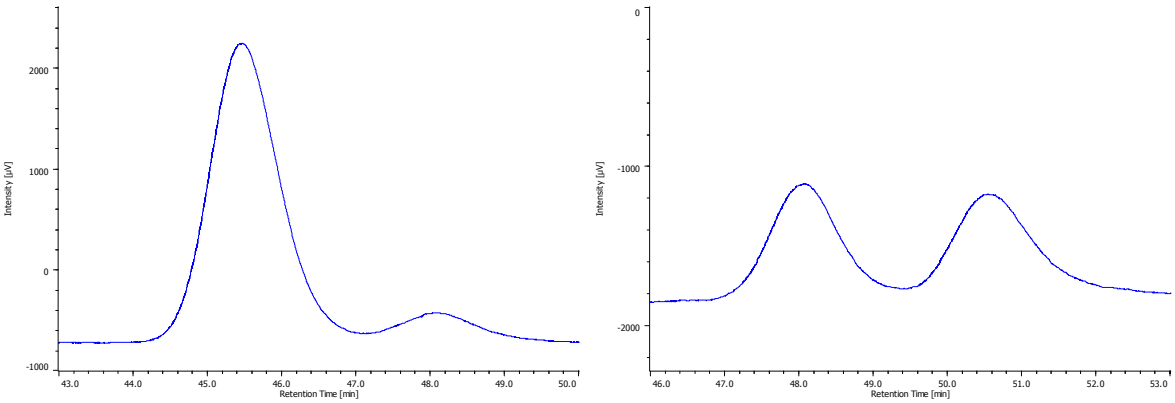
Daicel CHIRALCEL AS-H, hexane/isopropanol (97:3, v/v), 0.7 mL/min, 215 nm; t_r(major enantiomer) = 54.3 min, t_r(minor enantiomer) = 58.5 min



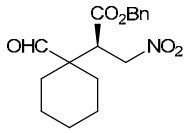
Benzyl (_S_)-2-(1-formylcyclohexyl)-3-nitropropionate (4f)



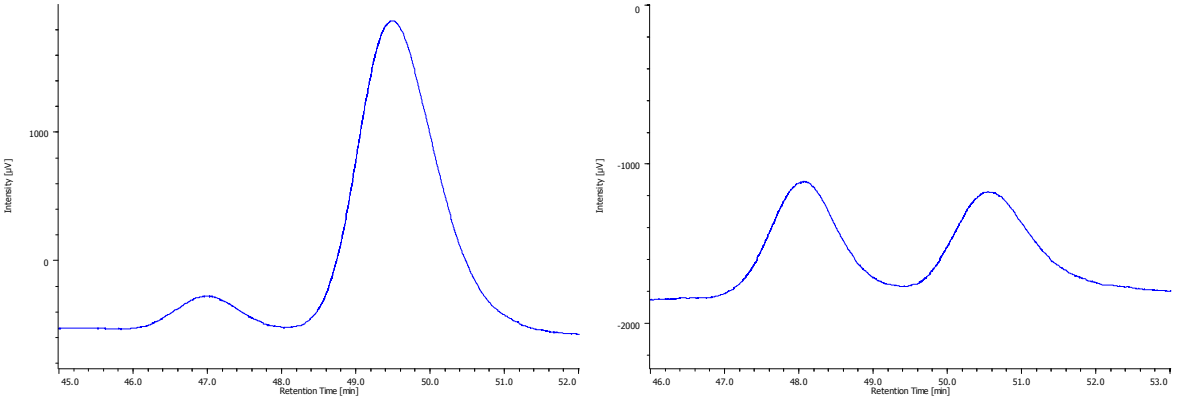
Daicel CHIRALCEL AS-H, hexane/isopropanol/ethanol (98.5:1.0:0.5 v/v/v), 0.8 mL/min, 229 nm; t_r(major enantiomer) = 45.5 min, t_r(minor enantiomer) = 48.1 min



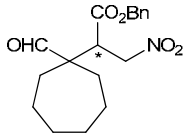
Benzyl (*R*)-2-(1-formylcyclohexyl)-3-nitropropionate (4f-*R*)



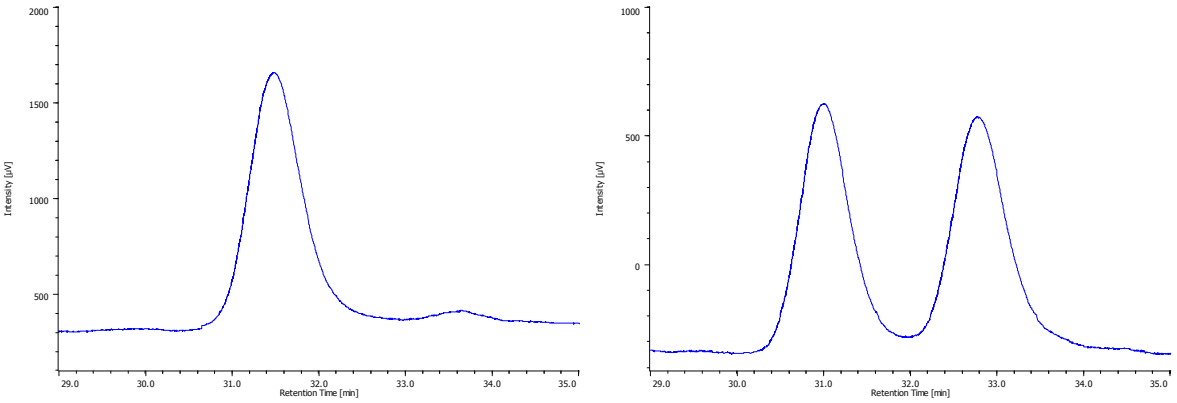
Daicel CHIRALCEL AS-H, hexane/isopropanol/ethanol (98.5:1.0:0.5 v/v/v), 0.8 mL/min, 229 nm; t_r(major enantiomer) = 49.5 min, t_r(minor enantiomer) = 47.0 min



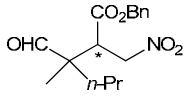
Benzyl 2-(1-formylcycloheptyl)-3-nitropropionate (4g)



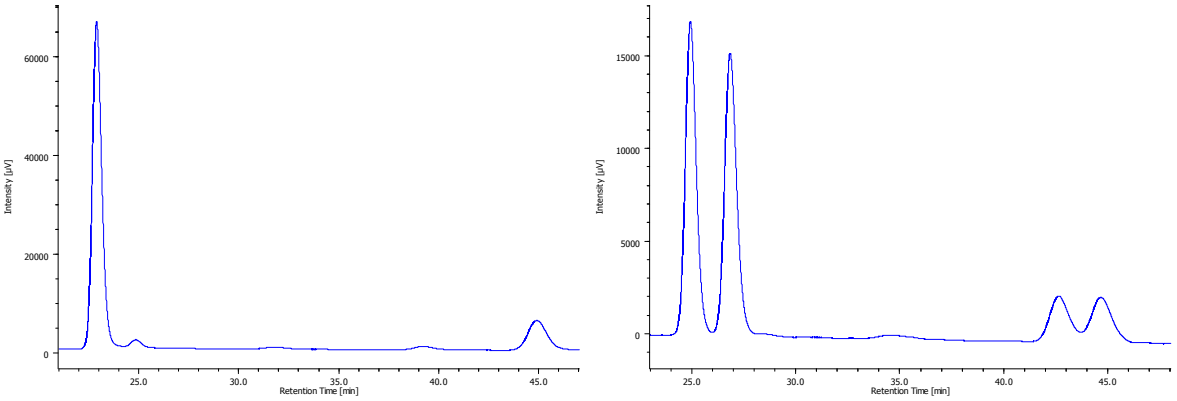
Daicel CHIRALPAK AD-H, hexane/isopropanol/ethanol (97.5:2.0:0.5 v/v/v), 1.0 mL/min, 229 nm; t_r(major enantiomer) = 31.5 min, t_r(minor enantiomer) = 33.6 min



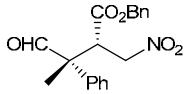
Benzyl 3-formyl-3-methyl-2-nitromethylhexanoate (4h)



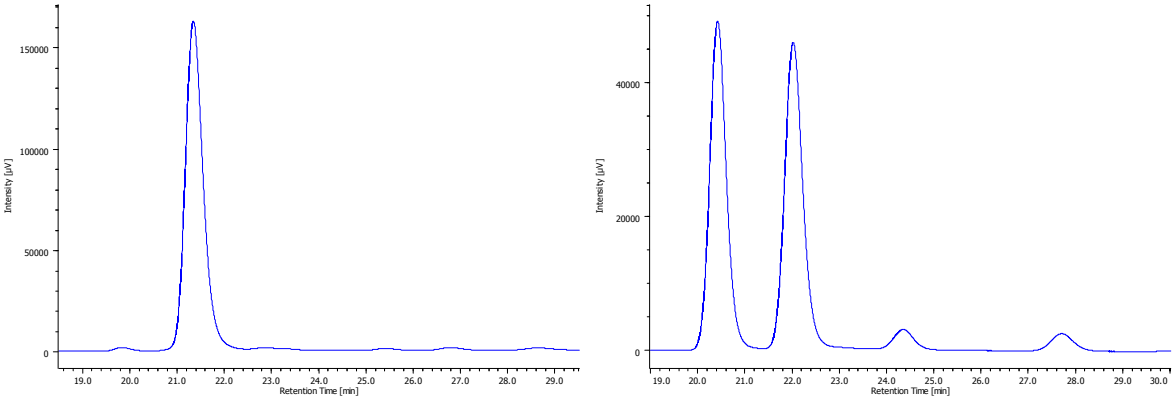
Daicel CHIRALCEL AS-H, hexane/isopropanol (97:3, v/v), 0.8 mL/min, 215 nm; t_r(major enantiomer) = 22.9 min, t_r(minor enantiomer) = 24.8 min



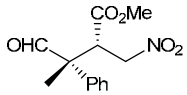
Benzyl (2*S*,3*R*)-3-methyl-3-phenyl-2-nitromethyl-4-oxobutyrate (4i)



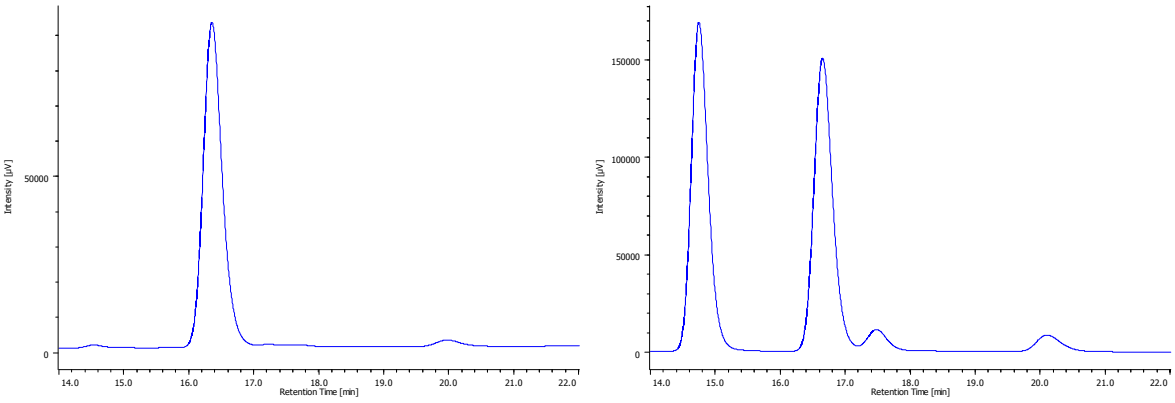
Daicel CHIRALPAK AD-H, hexane/isopropanol (90:10, v/v), 0.6 mL/min, 215 nm; t_r(major enantiomer) = 21.3 min, t_r(minor enantiomer) = 19.8 min



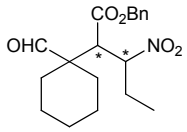
Methyl (2*S*,3*R*)-3-methyl-3-phenyl-2-nitromethyl-4-oxobutyrate (4j)



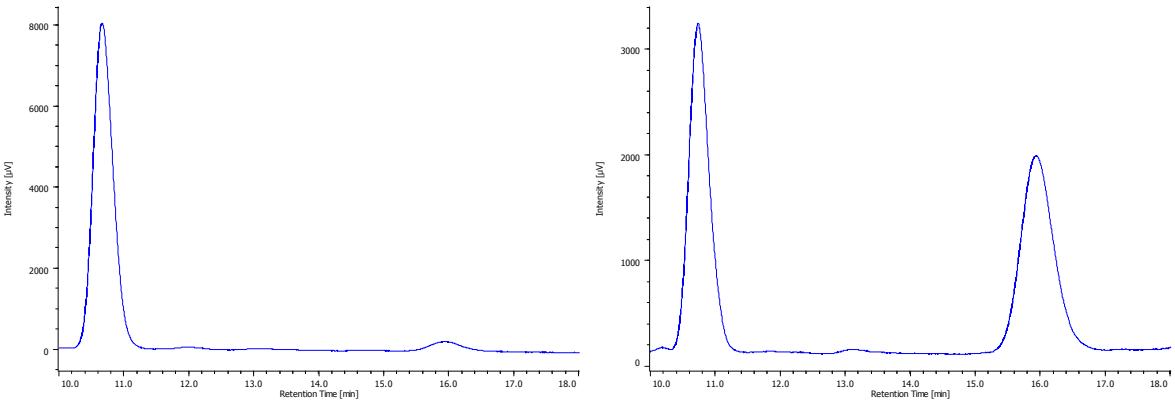
Daicel CHIRALPAK AD-H, hexane/isopropanol (93:7, v/v), 0.8 mL/min, 215 nm; t_r(major enantiomer) = 16.4 min, t_r(minor enantiomer) = 14.5 min



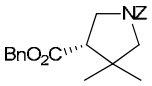
Benzyl 2-(1-formylcyclohexyl)-3-nitropentanoate (4k)



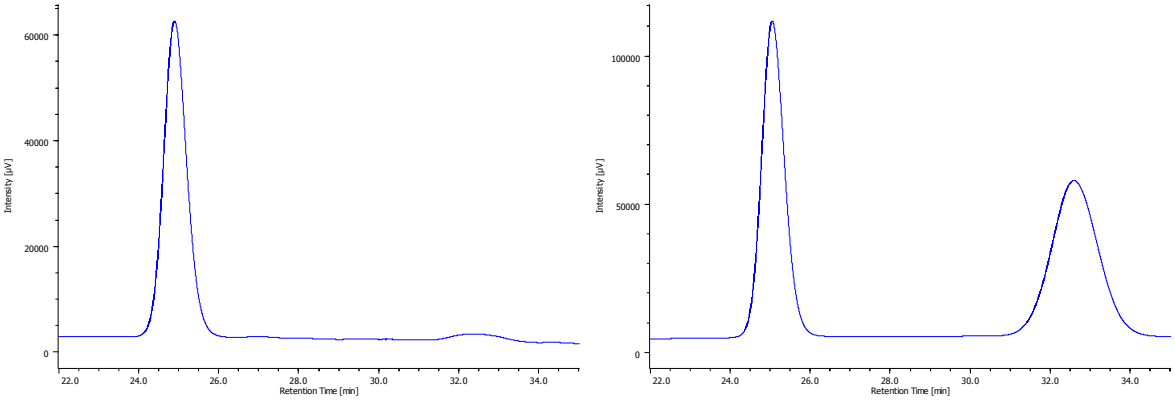
Daicel CHIRALCEL AS-H, hexane/isopropanol (95:5 v/v), 1.0 mL/min, 229 nm; t_r(major enantiomer) = 10.7 min, t_r(minor enantiomer) = 15.9 min



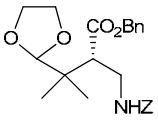
Benzyl *N*-(*S*)-benzyloxycarbonyl 4,4-dimethylpyrrolidine-3-carboxylate (6)



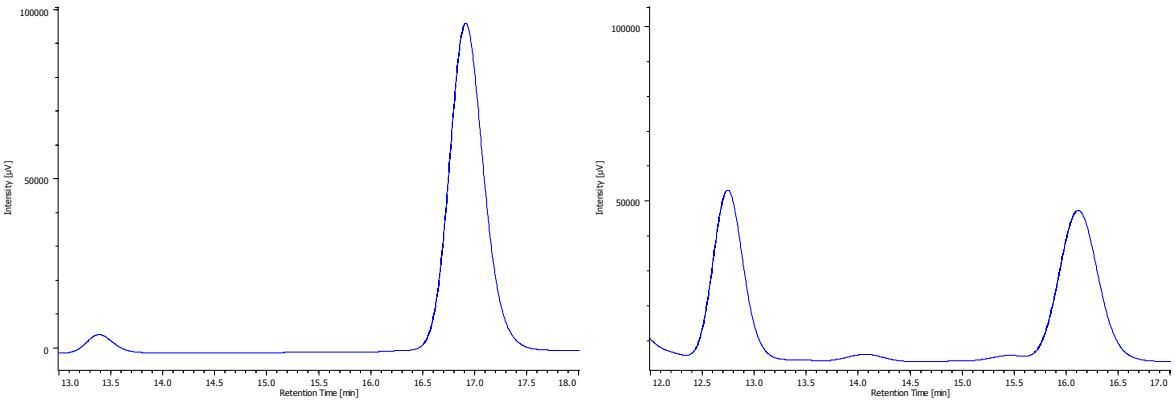
Daicel CHIRALCEL AS-H, hexane/isopropanol (90:10, v/v), 0.7 mL/min, 210 nm; t_r(major enantiomer) = 24.9 min, t_r(minor enantiomer) = 32.4 min]



Benzyl *N*-benzyloxycarbonyl (*S*)-2-aminomethyl-3-[1,3]dioxolan-2-yl-3-methyl butyrate (7)

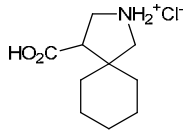


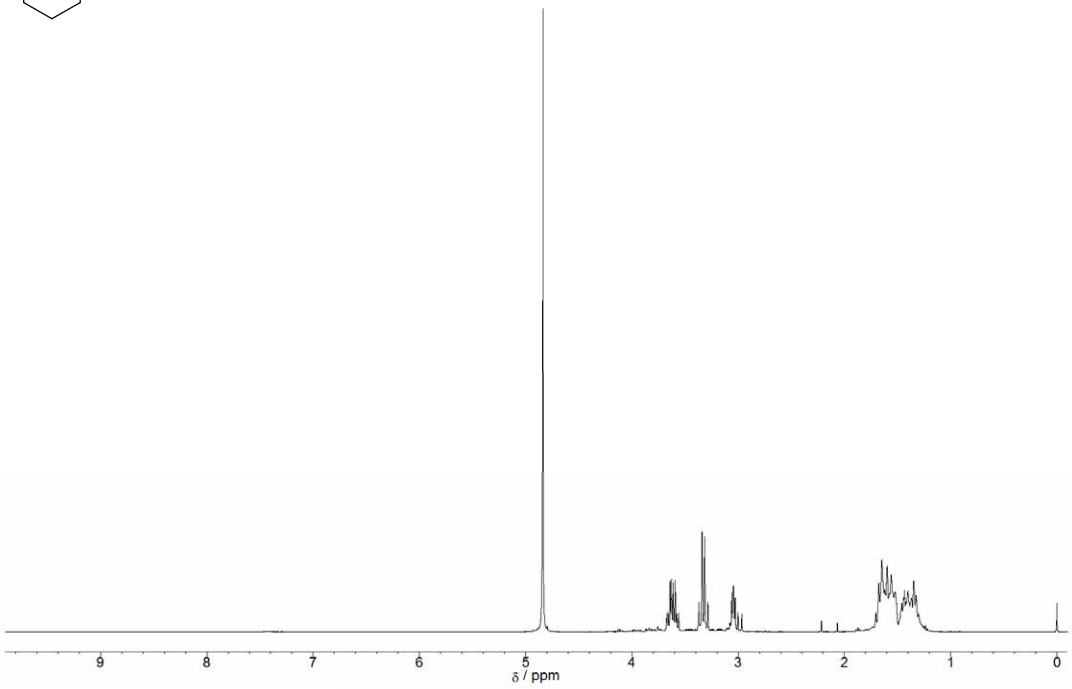
Daicel CHIRALPAK AD-H, 20% isopropanol/hexane, 0.8 mL/min, 209 nm; t_r(major enantiomer) = 16.9 min, t_r(minor enantiomer) = 13.4 min



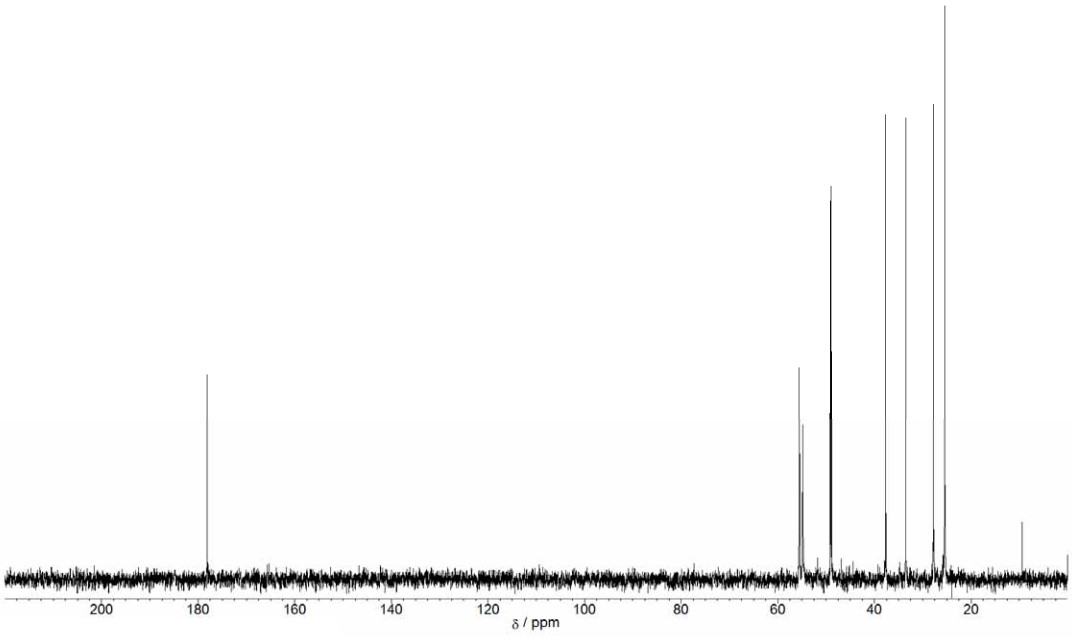
(E) ^{1}H and ^{13}C NMR spectra

Aza-spiro[4,5]decane-4-carboxylic acid hydrochloride (1a)



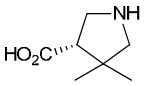


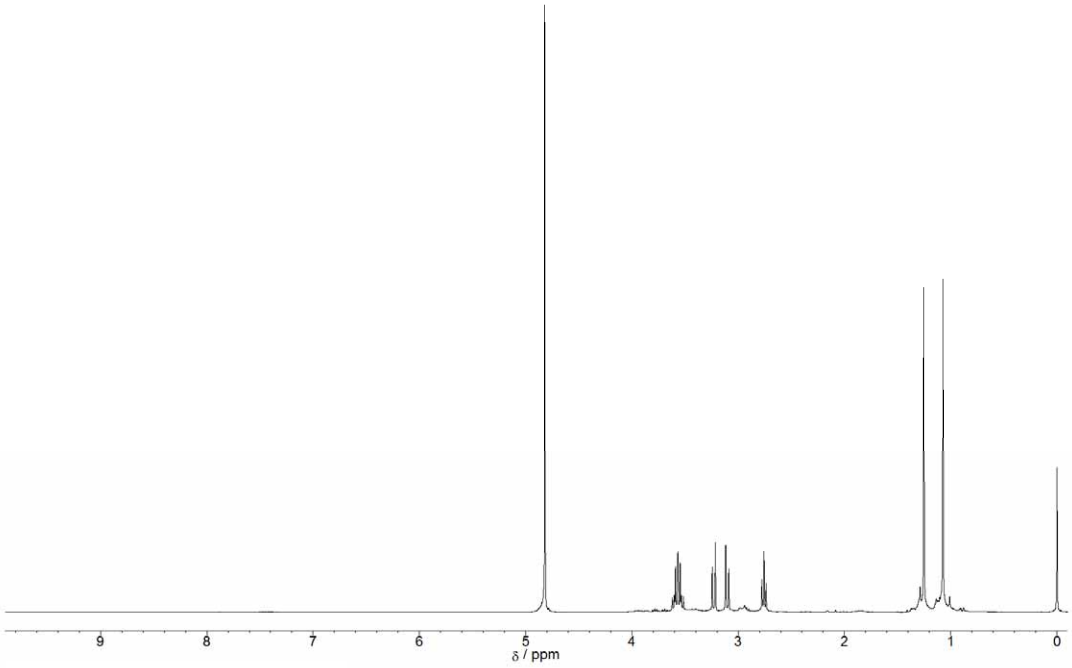
(400 MHz, D_2O, TSP)



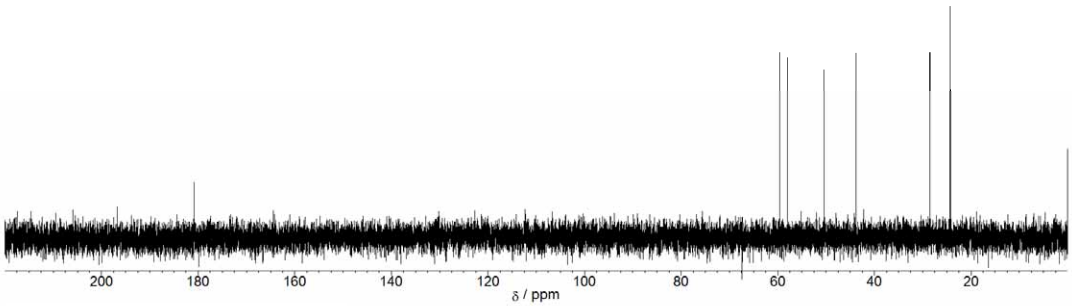
(100 MHz, D_2O, TSP)

(*S*)-4,4-Dimethylpyrrolidine-3-carboxylic acid (1b)



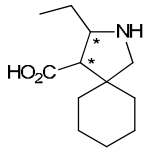


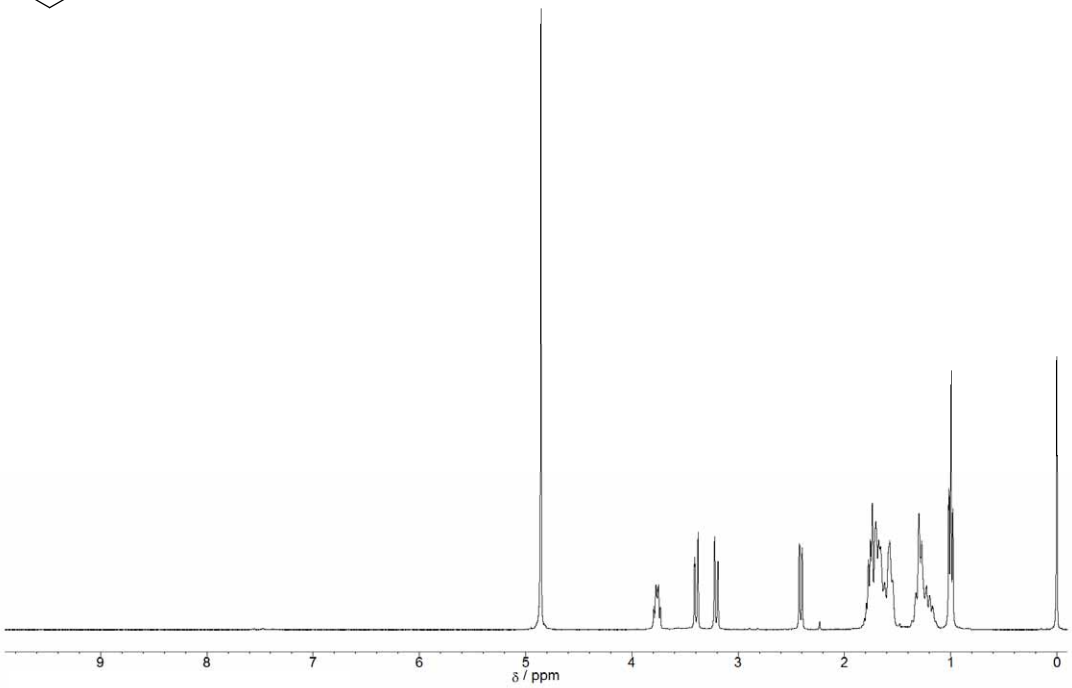
(400 MHz, D_2O, TSP)



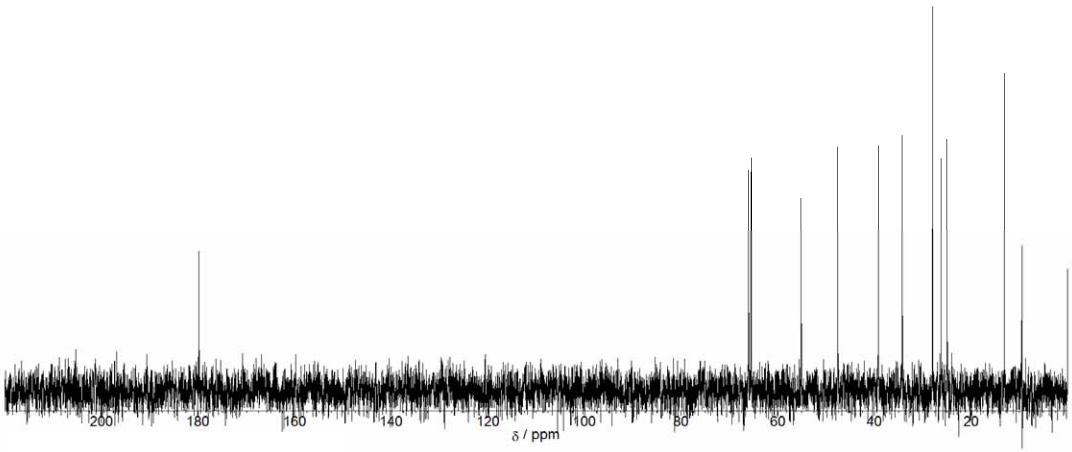
(100 MHz, D_2O, TSP)

Aza-spiro[4,5]decane-3-ethyl-4-carboxylic acid (1c)



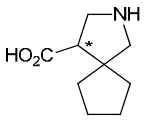


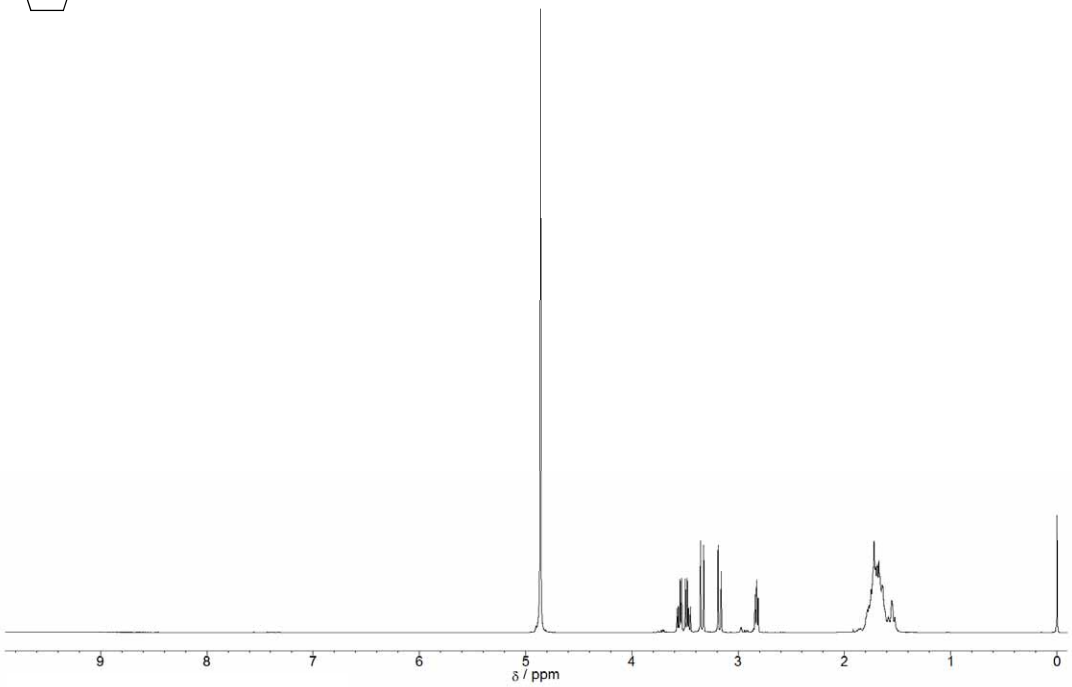
(400 MHz, D_2O, TSP)



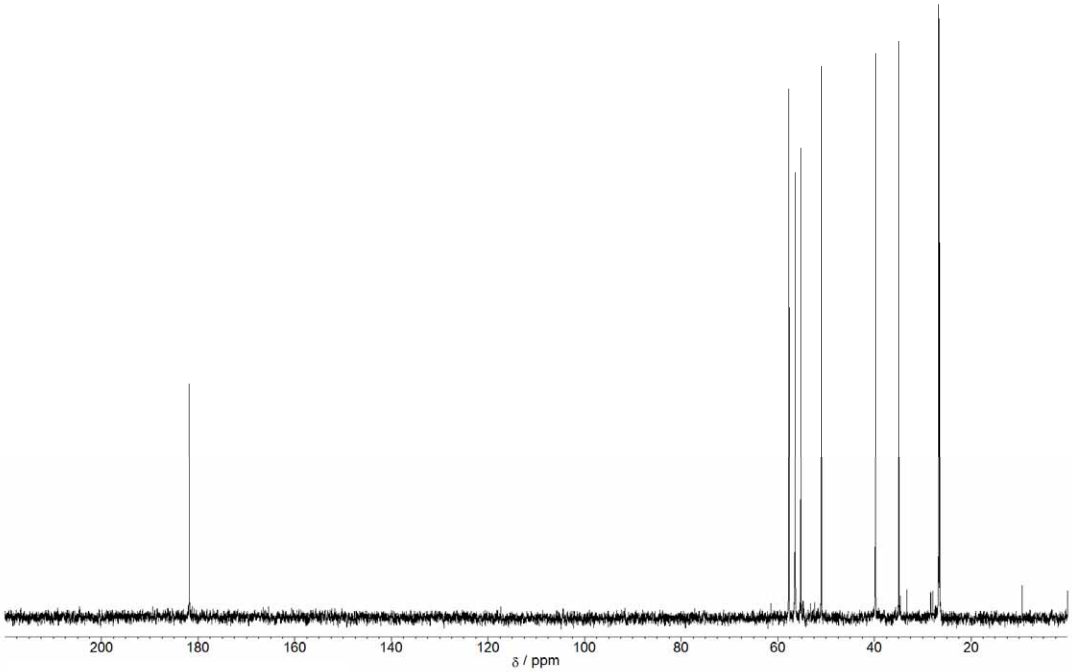
(100 MHz, D_2O, TSP)

Aza-spiro[4,4]nonane-4-carboxylic acid (1d)



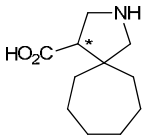


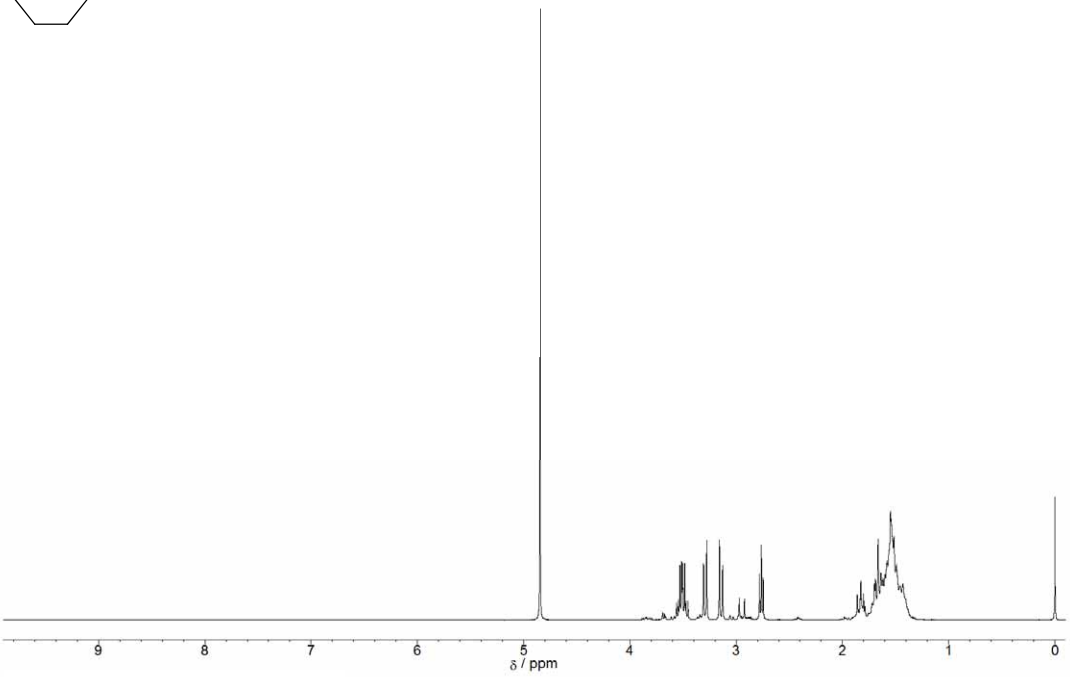
(400 MHz, D_2O, TSP)



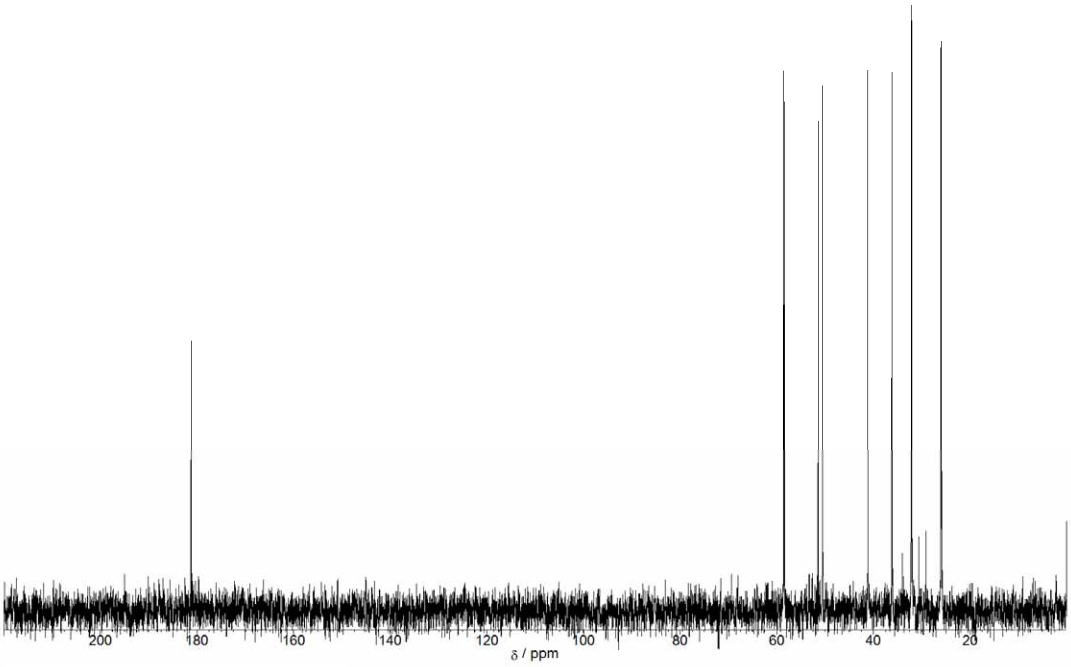
(100 MHz, D_2O, TSP)

Aza-spiro[4,6]undecane-4-carboxylic acid (1e)



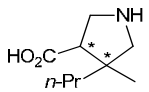


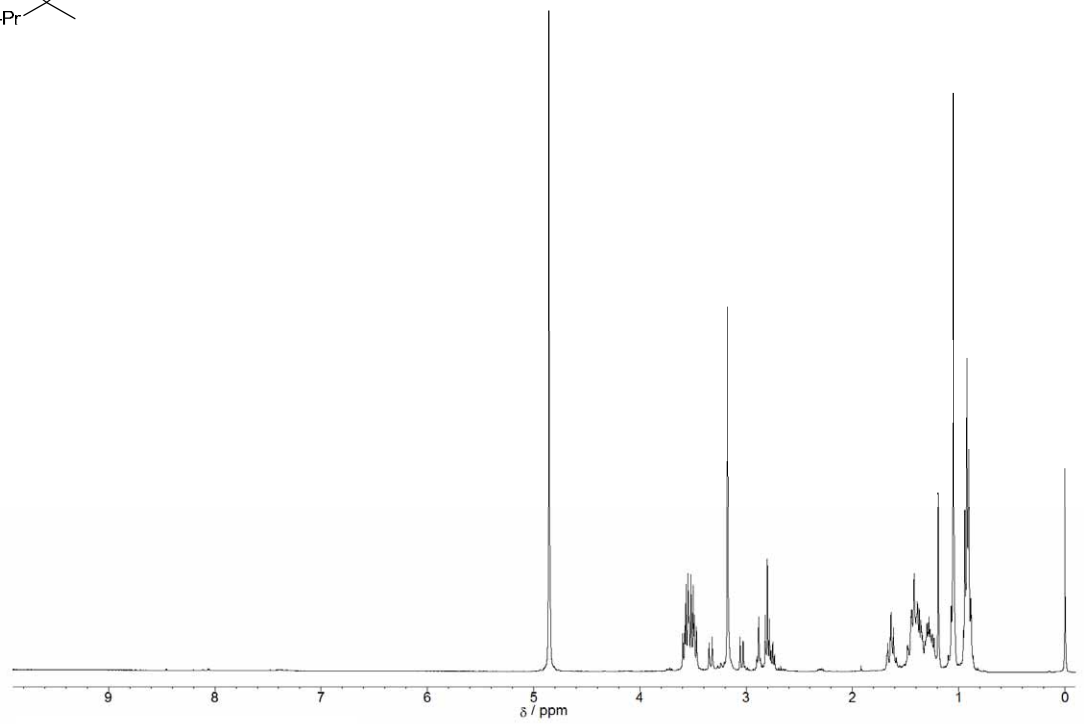
(400 MHz, D_2O, TSP)



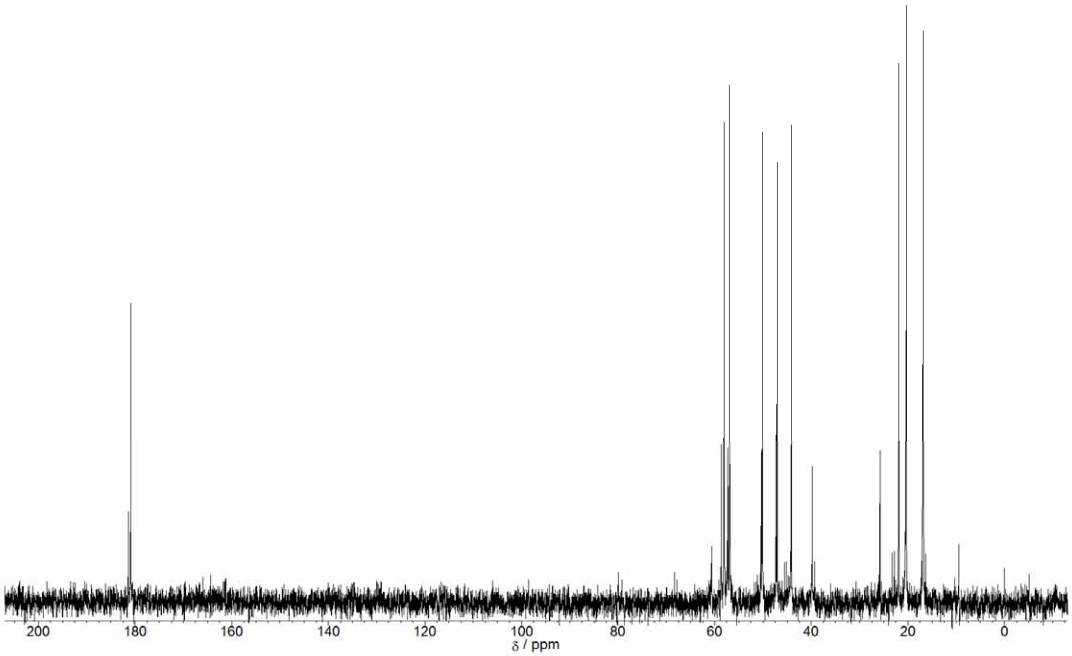
(100 MHz, D_2O, TSP)

4-Methyl-4-propylpyrrolidine-3-carboxylic acid (1f)



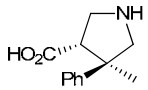


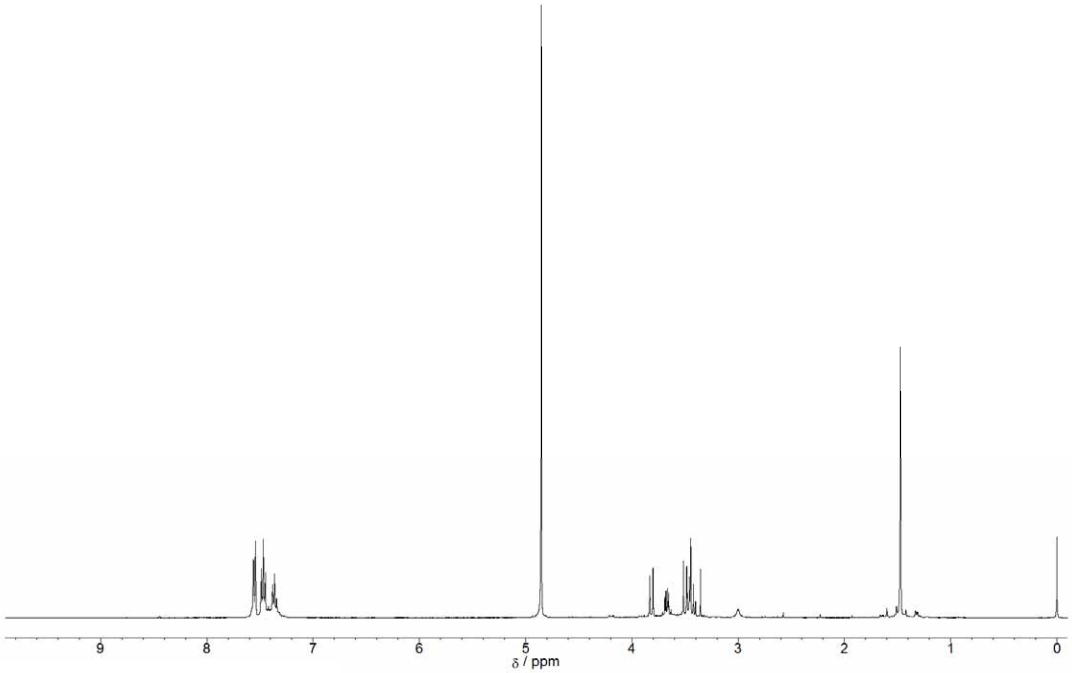
(400 MHz, D_2O, TSP)



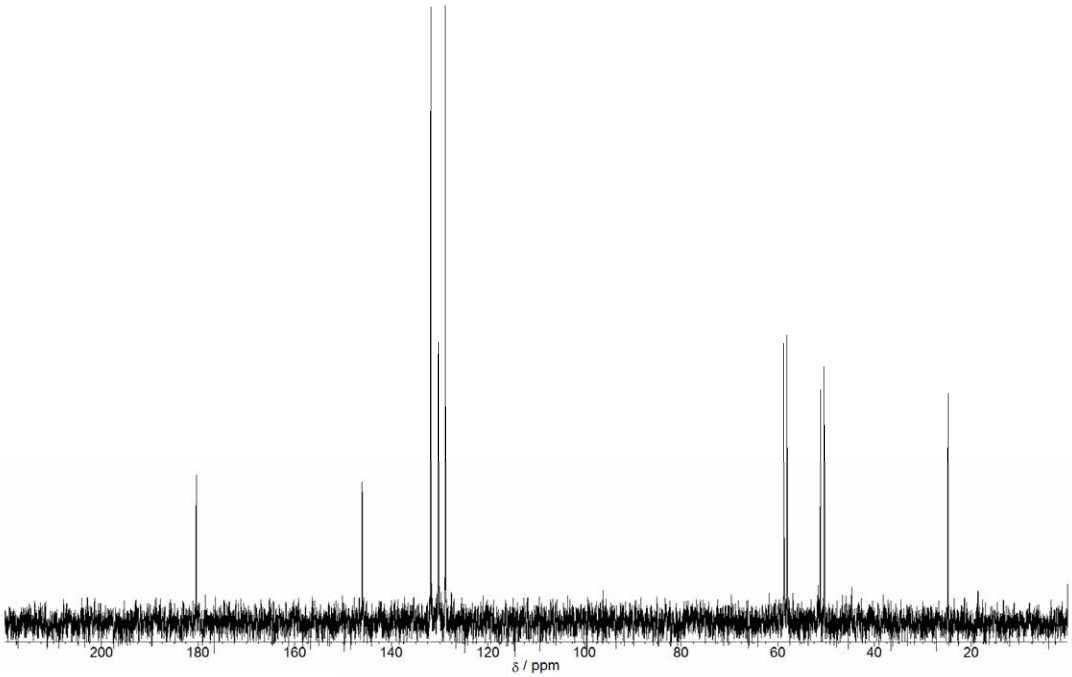
(100 MHz, D_2O, TSP)

(3*S*,4*R*)-4-Methyl-4-phenylpyrrolidine-3-carboxylic acid (1g)



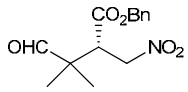


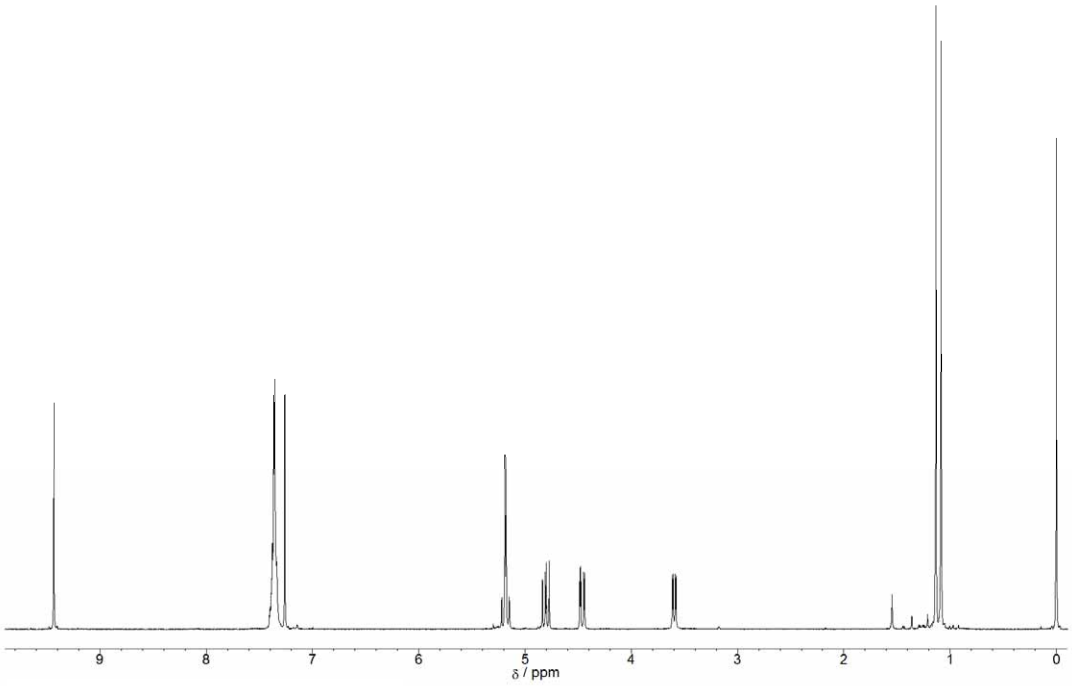
(400 MHz, D_2O, TSP)



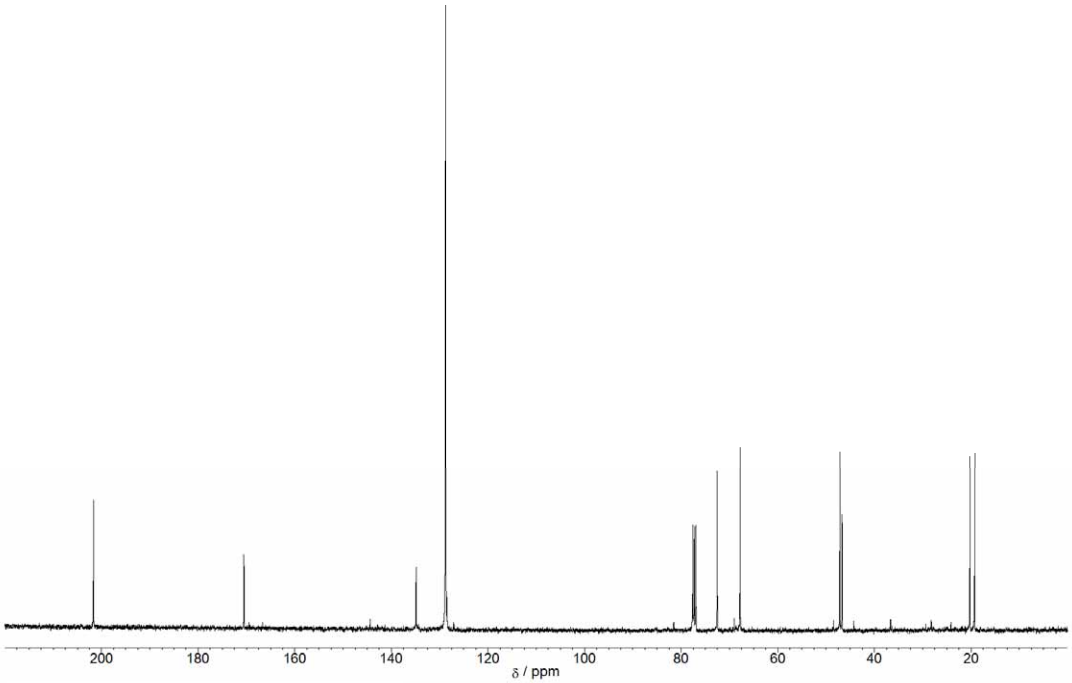
(100 MHz, D_2O, TSP)

Benzyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4a)



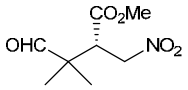


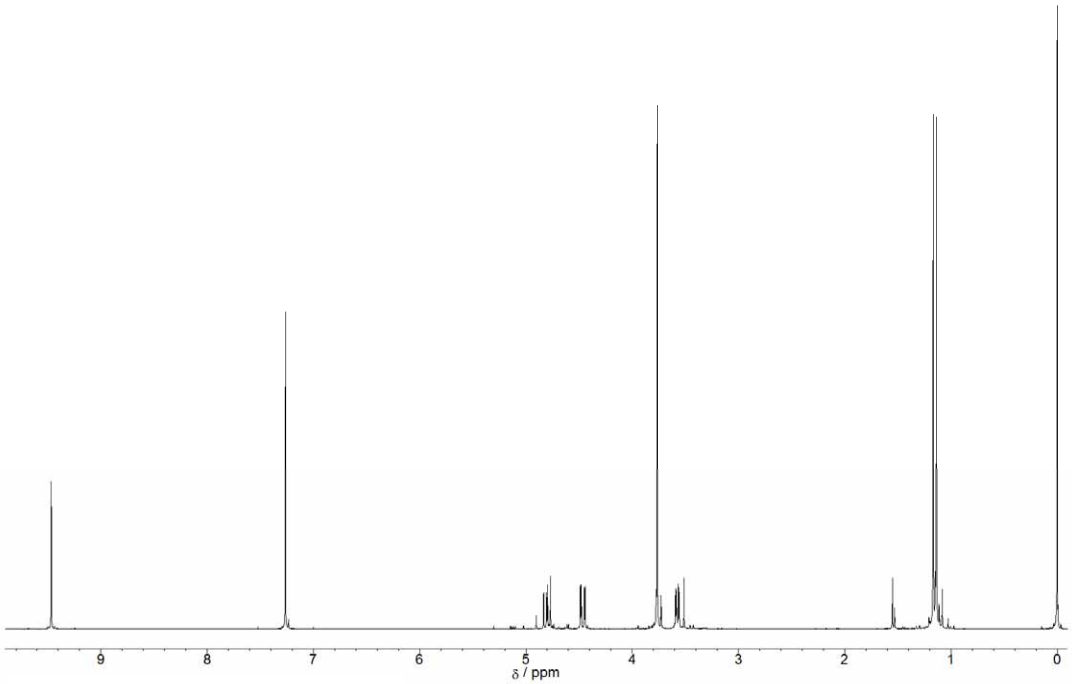
(400 MHz, $CDCl_3$, TMS)



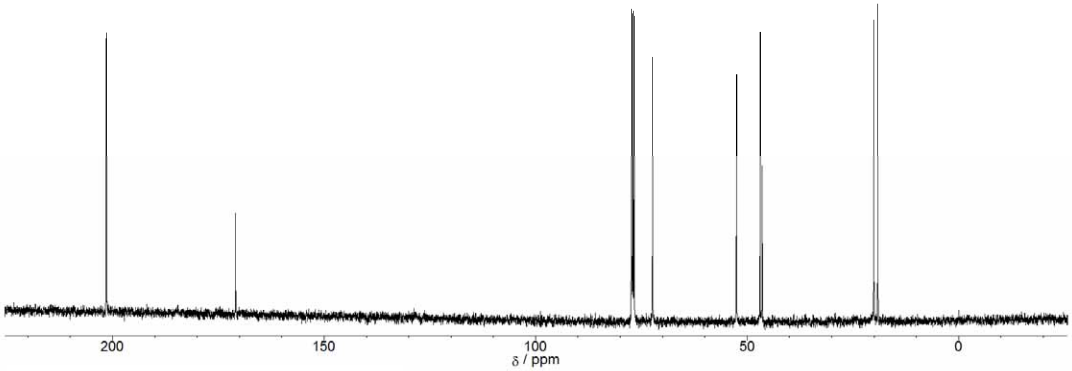
(100 MHz, $CDCl_3$)

Methyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4b)



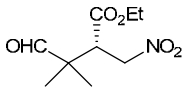


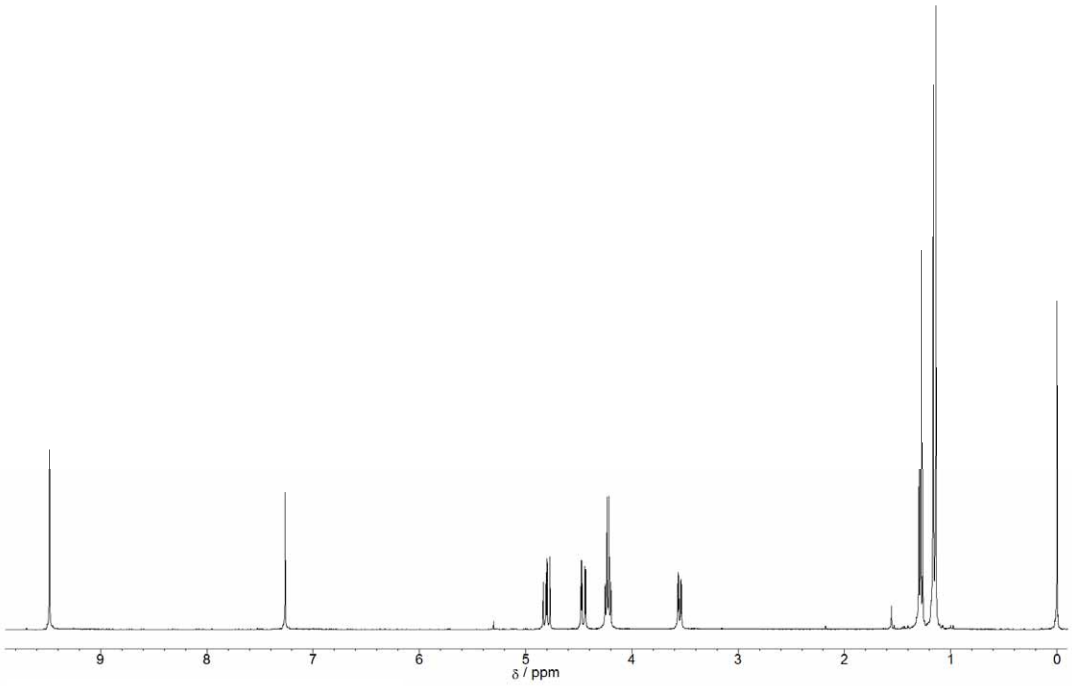
(400 MHz, $CDCl_3$, TMS)



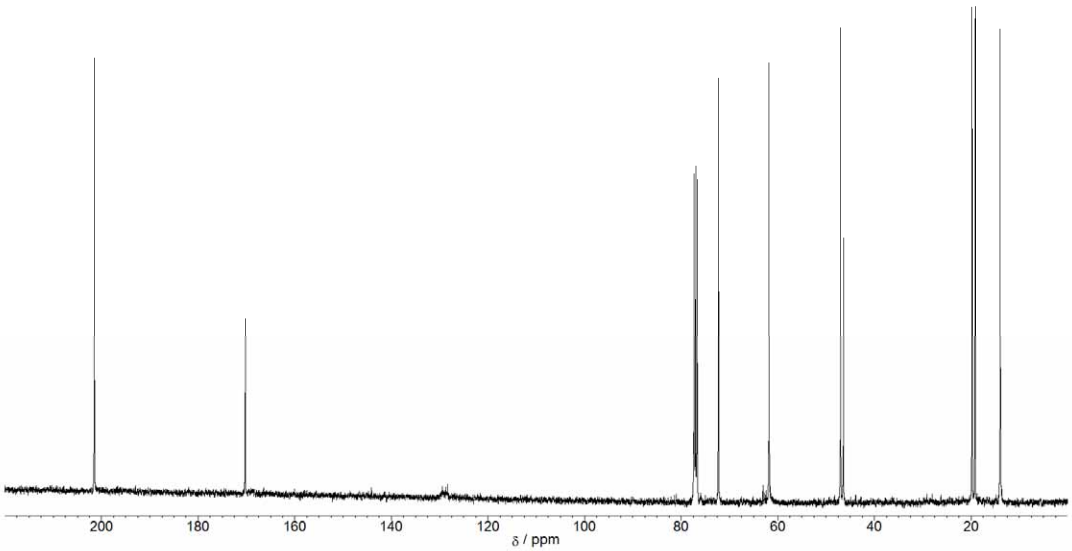
(100 MHz, $CDCl_3$)

Ethyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4c)



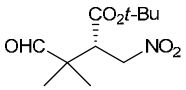


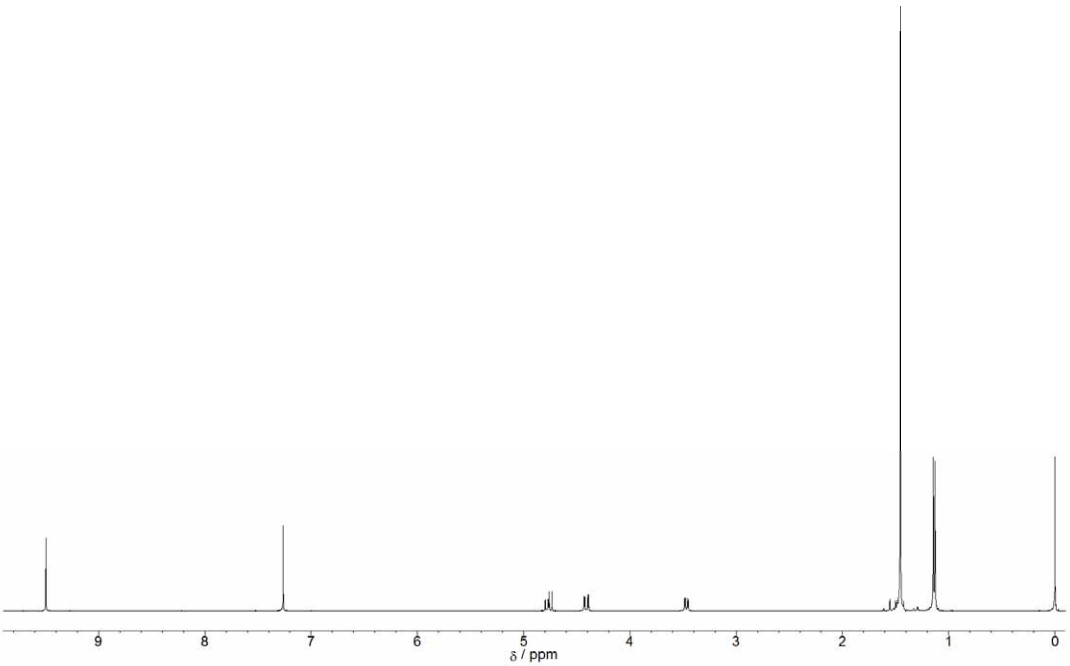
(400 MHz, $CDCl_3$, TMS)



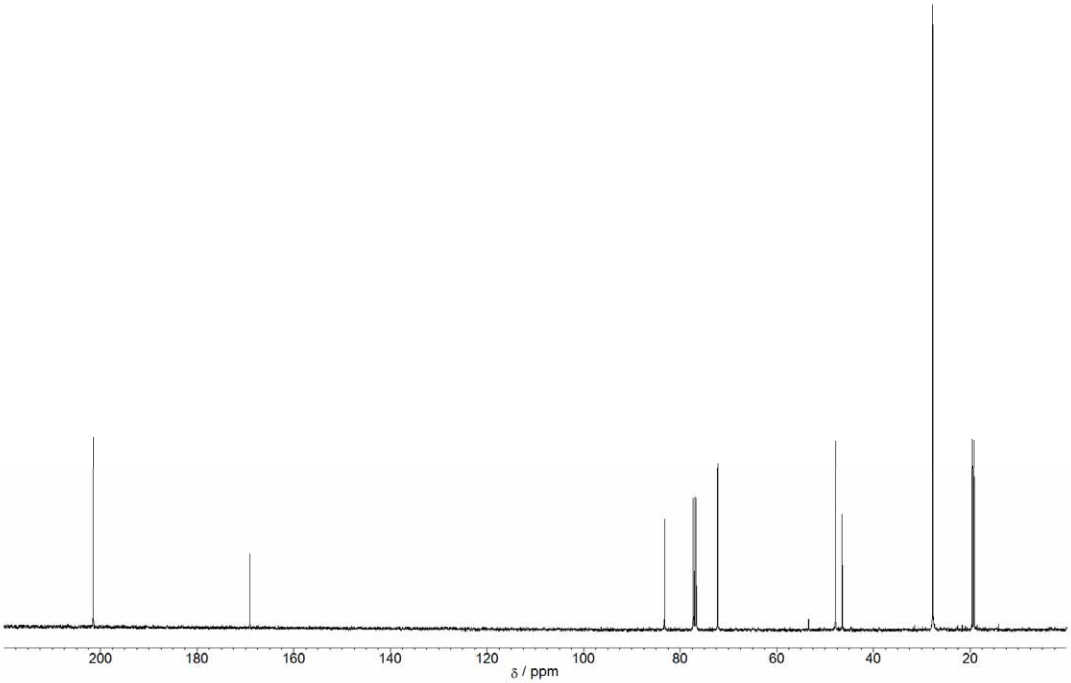
(100 MHz, $CDCl_3$)

***t*-Butyl (*S*)-3,3-dimethyl-2-nitromethyl-4-oxobutyrate (4d)**



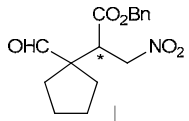


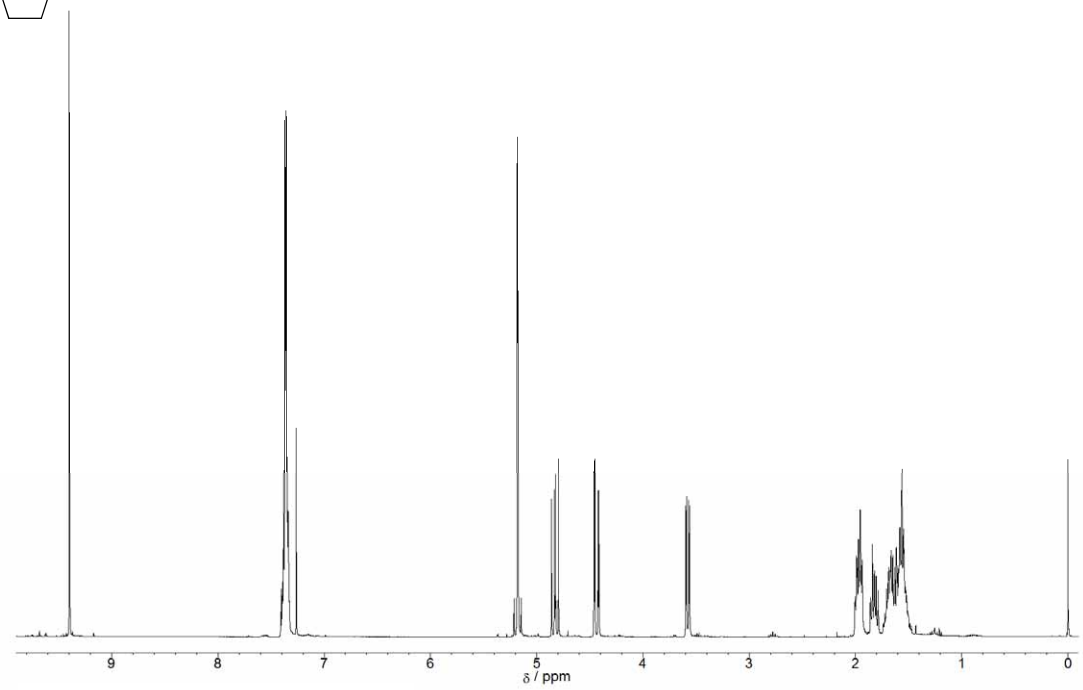
(400 MHz, $CDCl_3$, TMS)



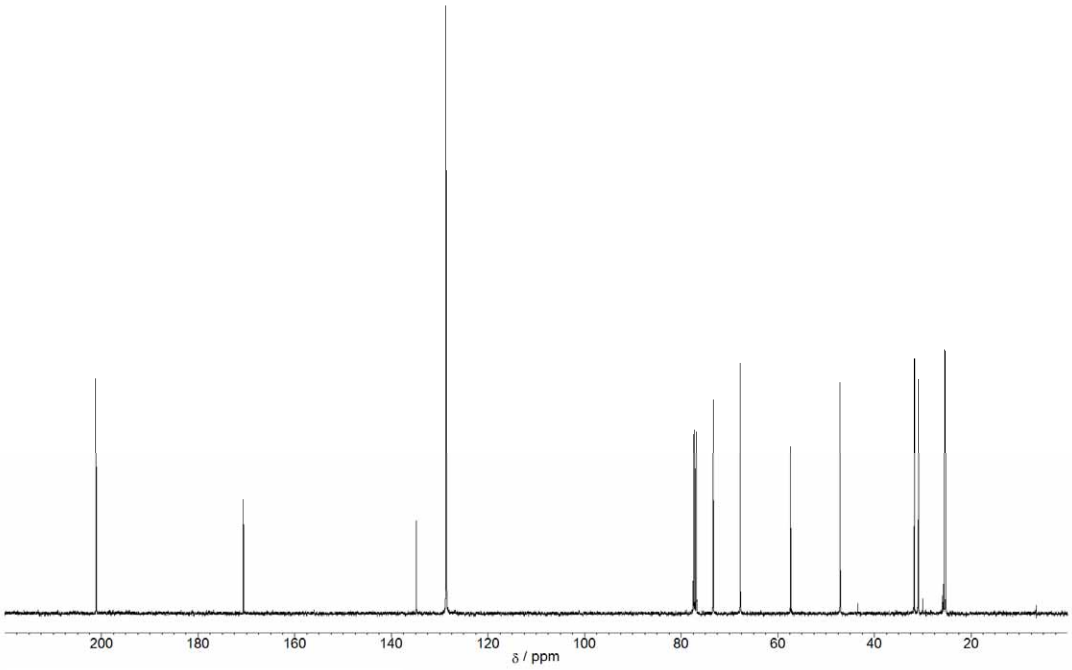
(100 MHz, $CDCl_3$)

Benzyl 2-(1-formylcyclopentyl)-3-nitropropionate (4e)



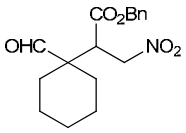


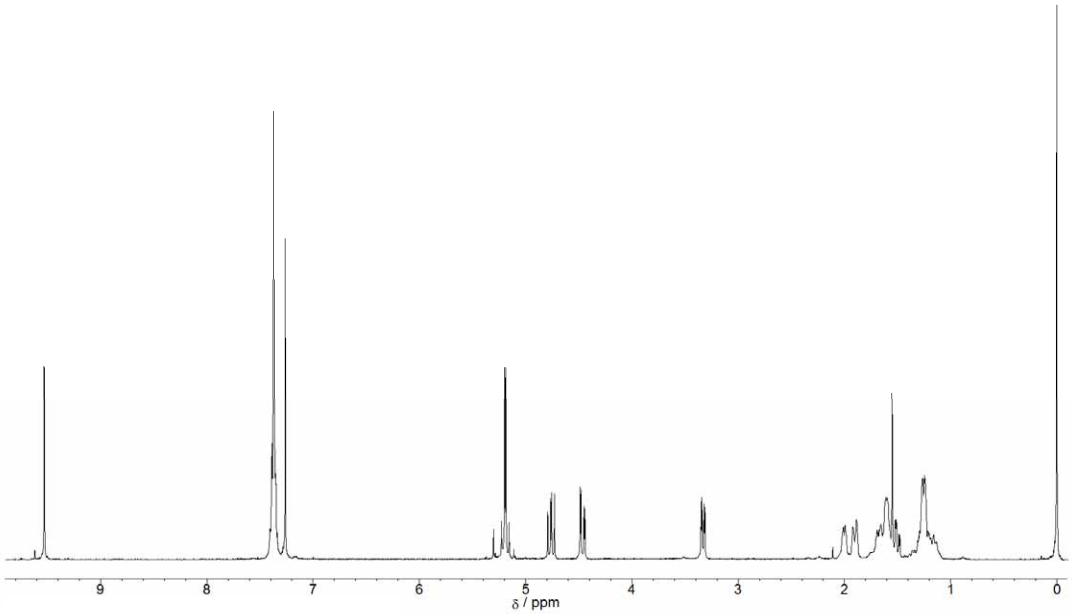
(400 MHz, $CDCl_3$, TMS)



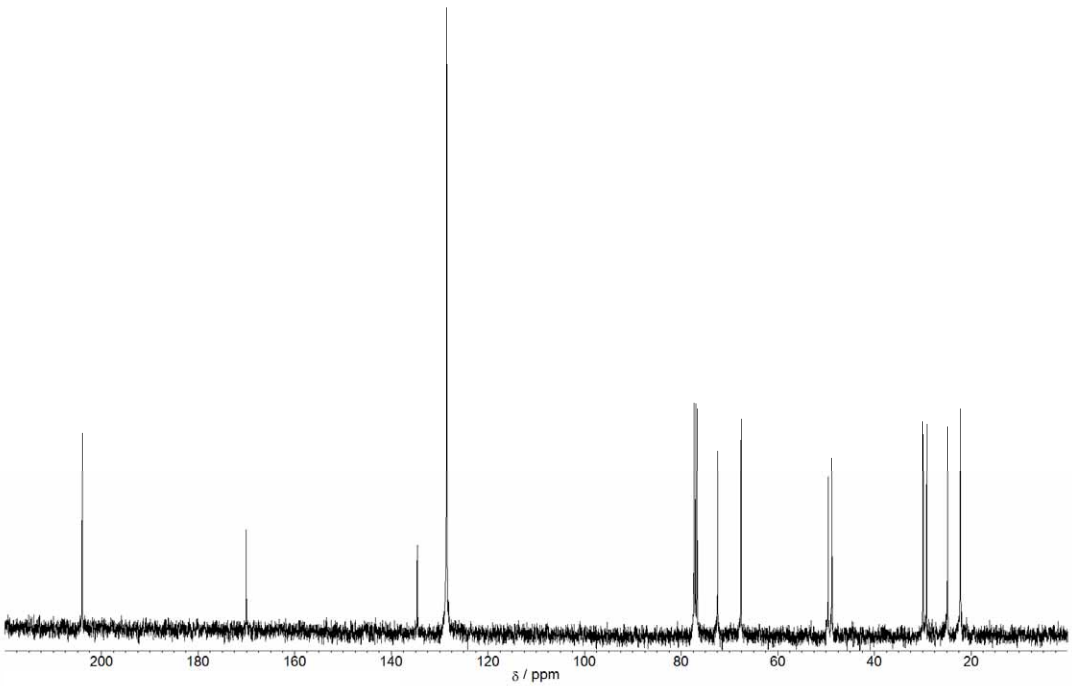
(100 MHz, $CDCl_3$)

Benzyl 2-(1-formylcyclohexyl)-3-nitropropionate (4f and **4f-*R*)**



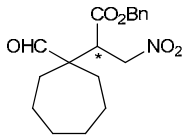


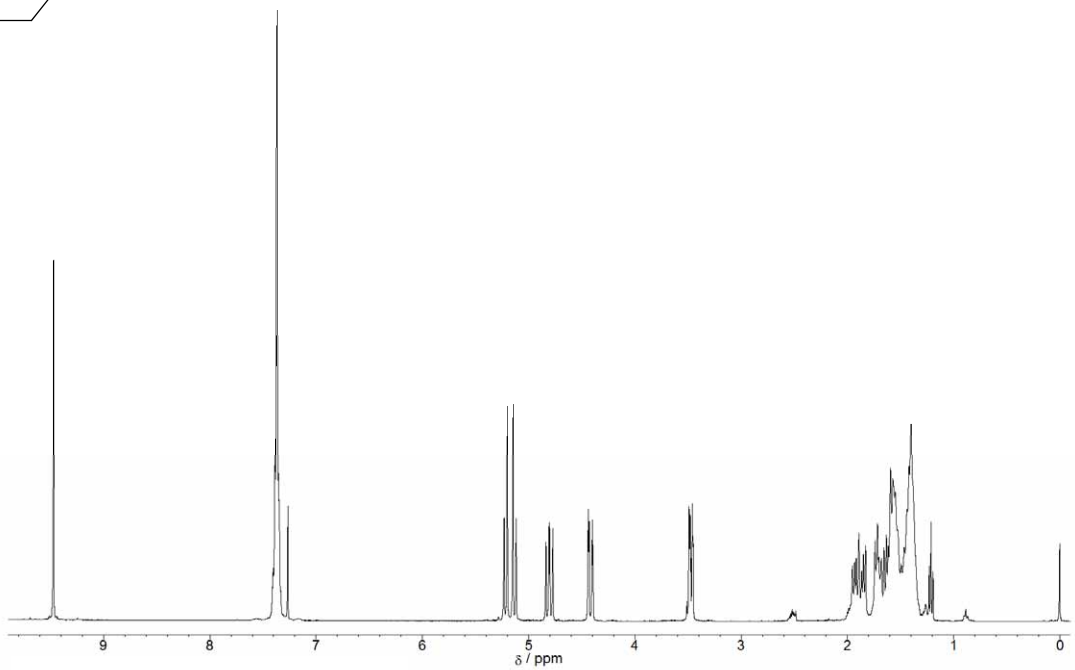
(400 MHz, $CDCl_3$, TMS)



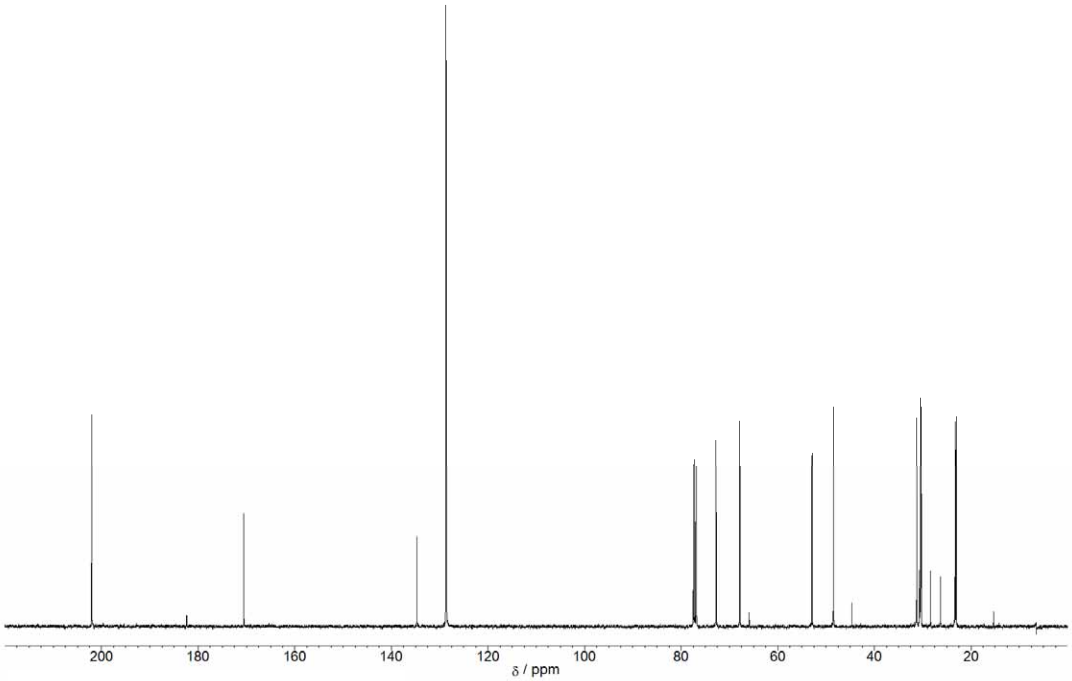
(100 MHz, $CDCl_3$)

Benzyl 2-(1-formylcycloheptyl)-3-nitropropionate (4g)



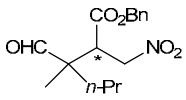


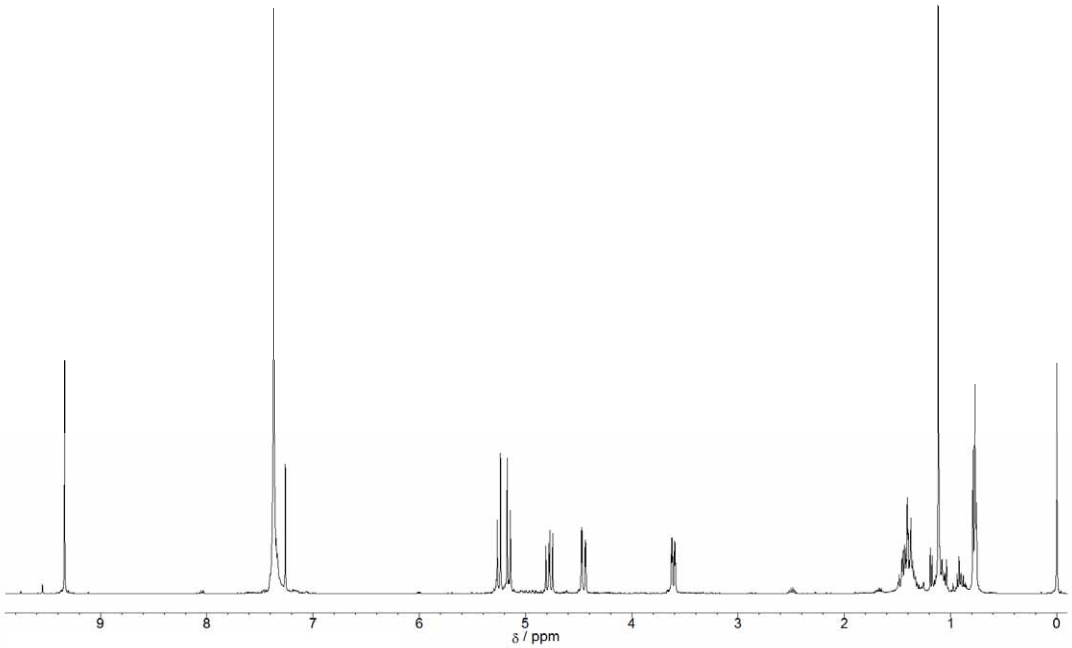
(400 MHz, $CDCl_3$, TMS)



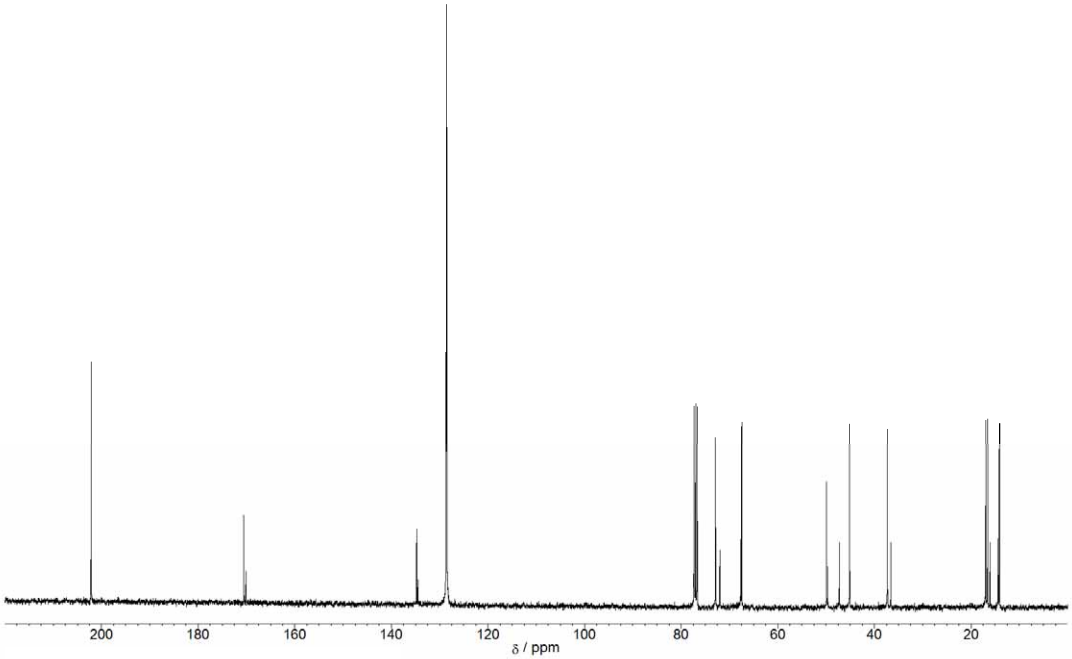
(100 MHz, $CDCl_3$)

Benzyl 3-formyl-3-methyl-2-nitromethylhexanoate (4h)



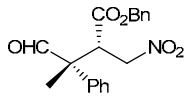


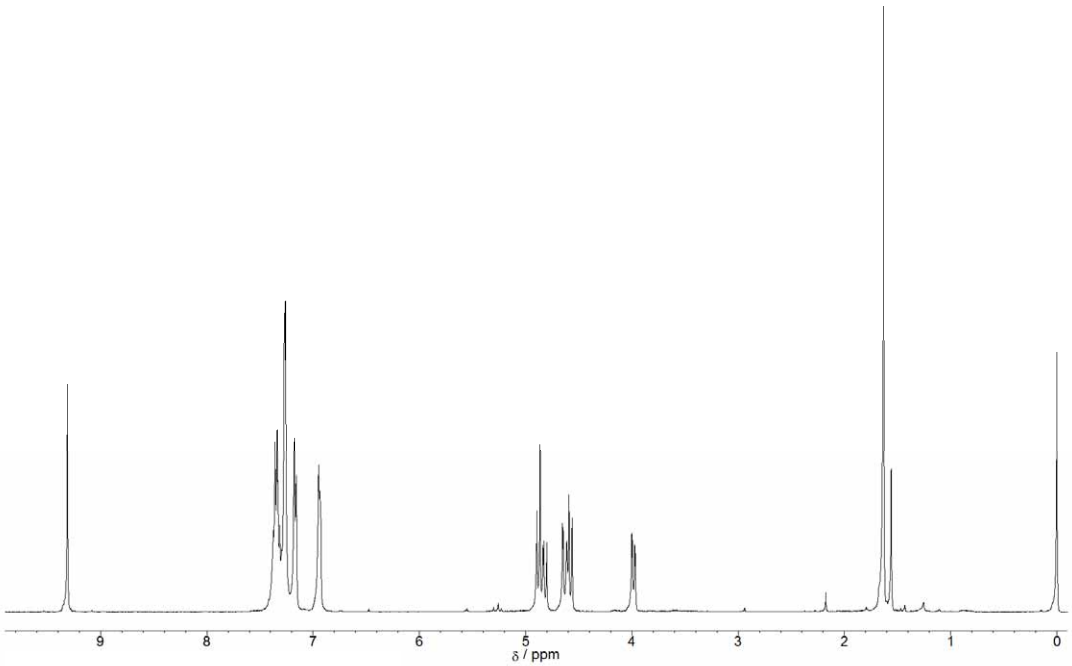
(400 MHz, $CDCl_3$, TMS)



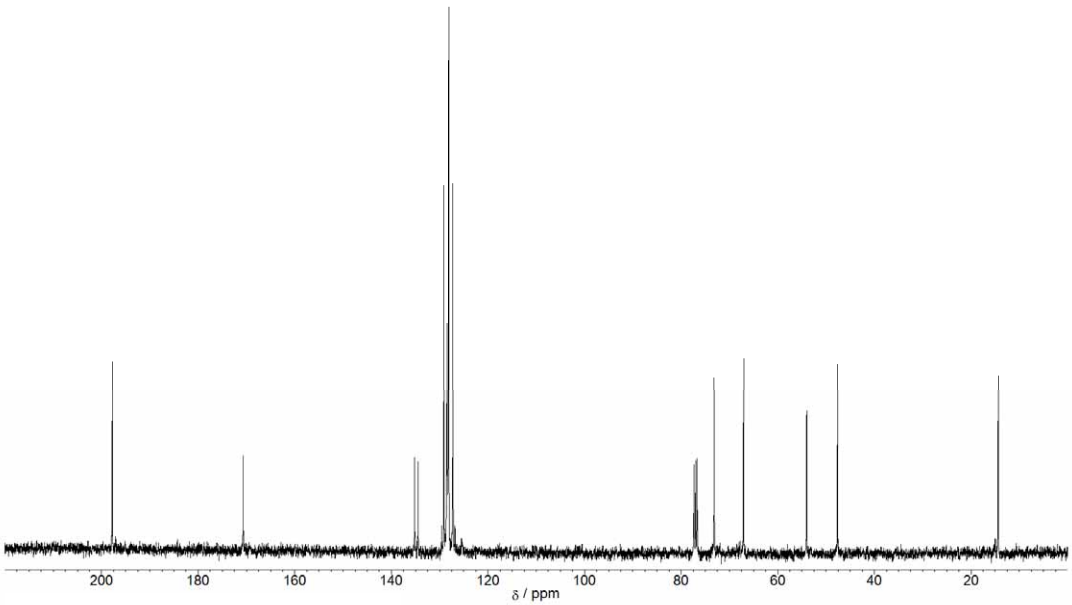
(100 MHz, $CDCl_3$)

Benzyl (2*S*,3*R*)-3-methyl-3-phenyl-2-nitromethyl-4-oxobutyrate (4i)



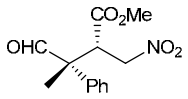


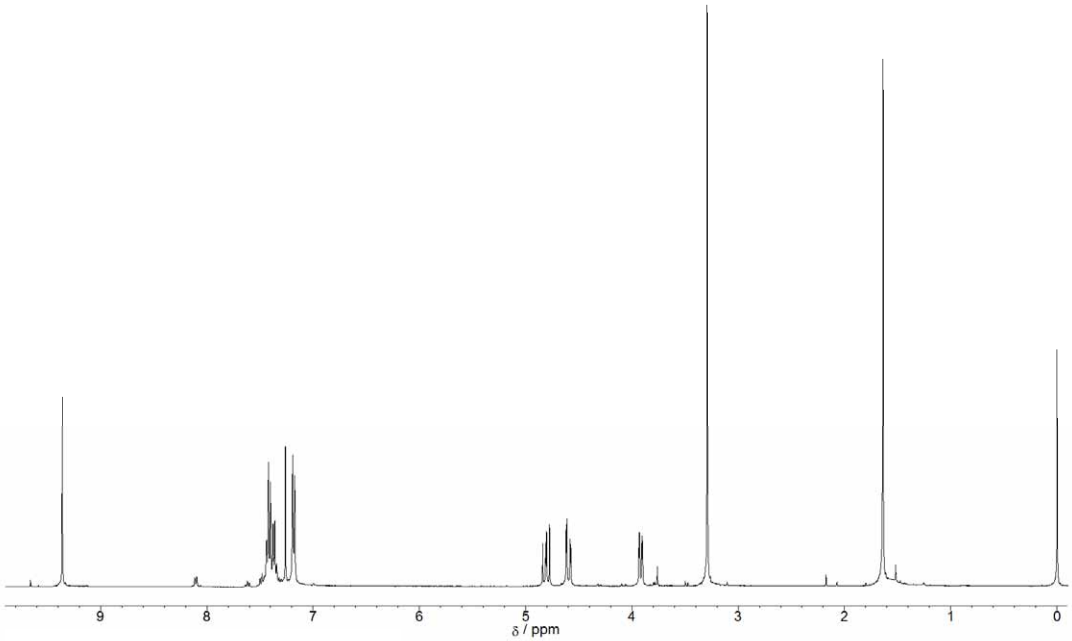
(400 MHz, $CDCl_3$, TMS)



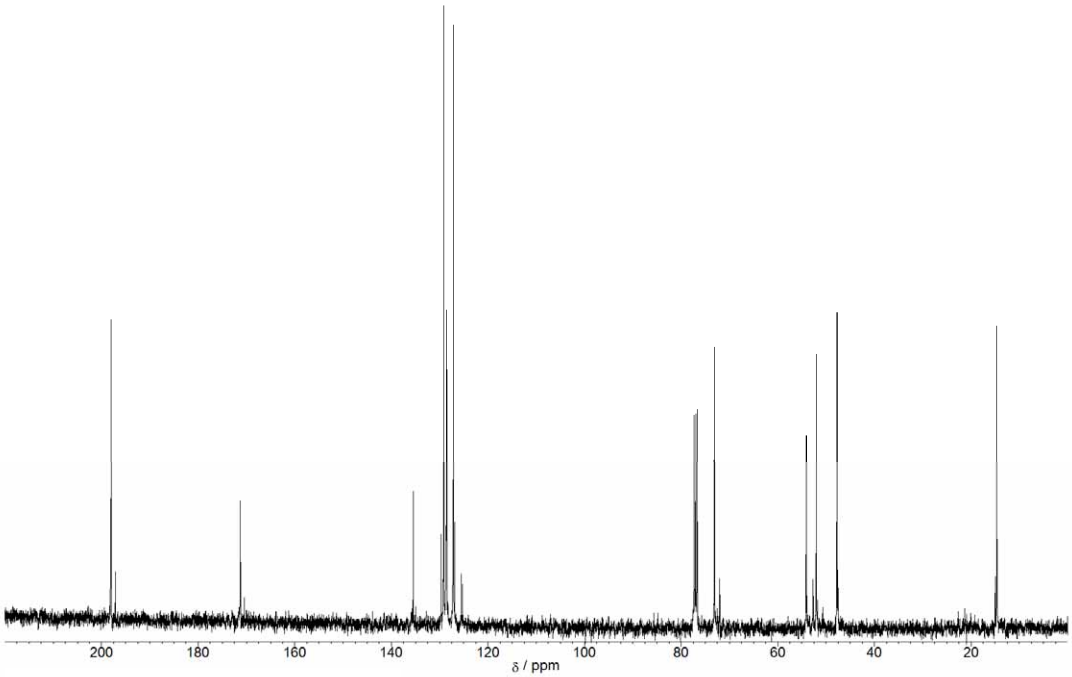
(100 MHz, $CDCl_3$)

Methyl (2*S*,3*R*)-3-methyl-3-phenyl-2-nitromethyl-4-oxobutyrate (4j)



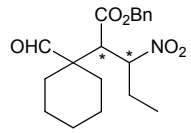


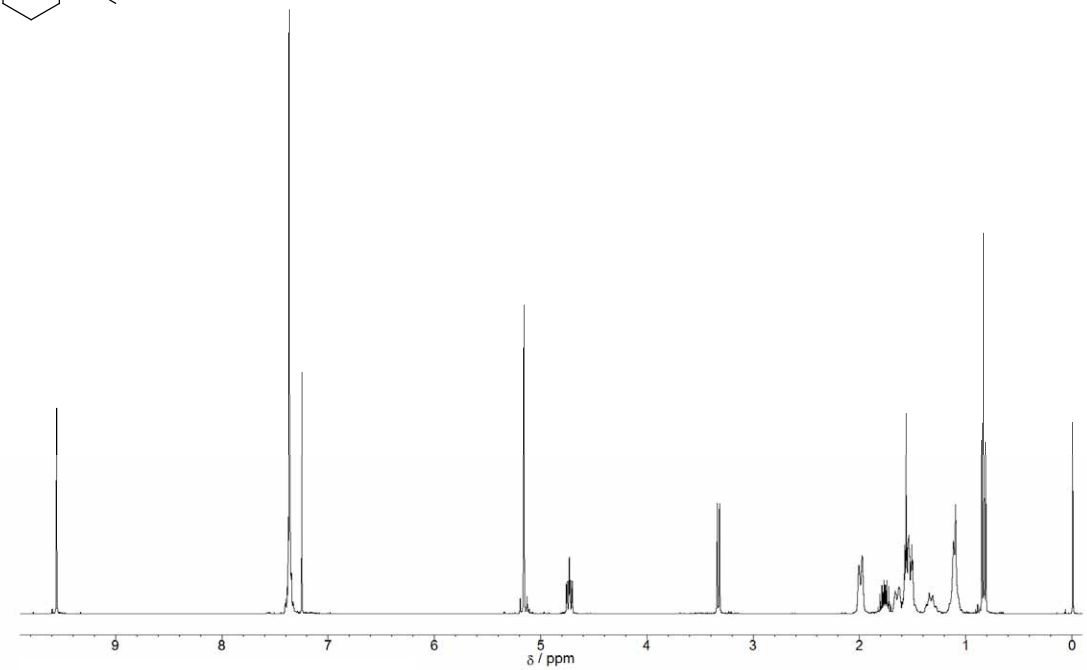
(400 MHz, $CDCl_3$, TMS)



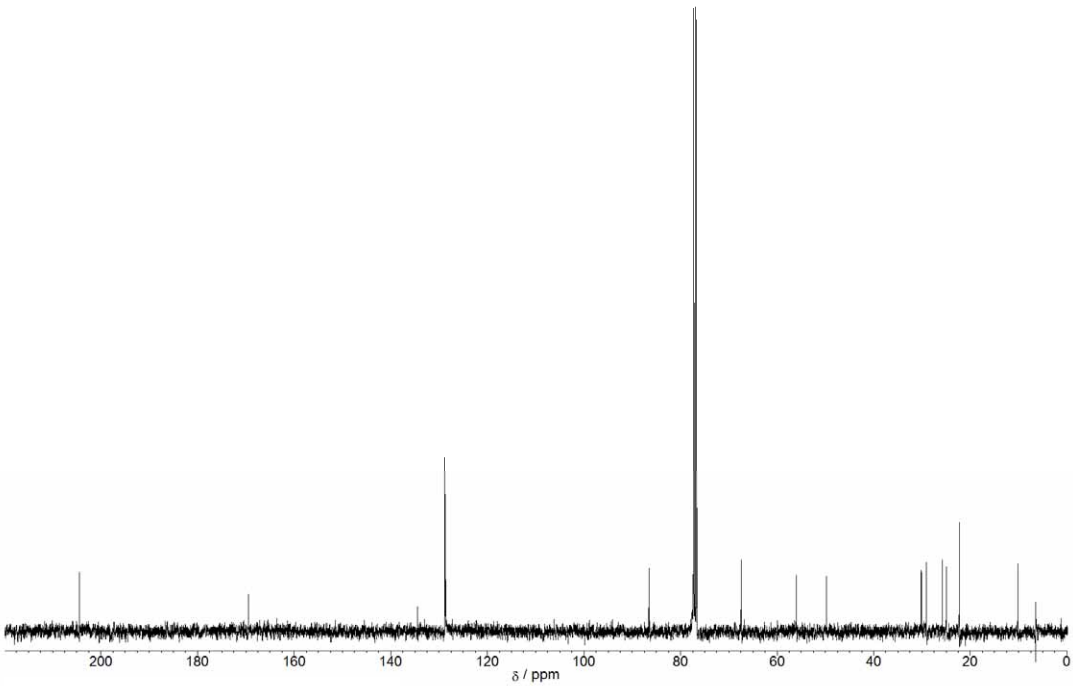
(100 MHz, $CDCl_3$)

Benzyl 2-(1-formylcyclohexyl)-3-nitropentanoate (4k)



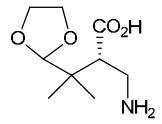


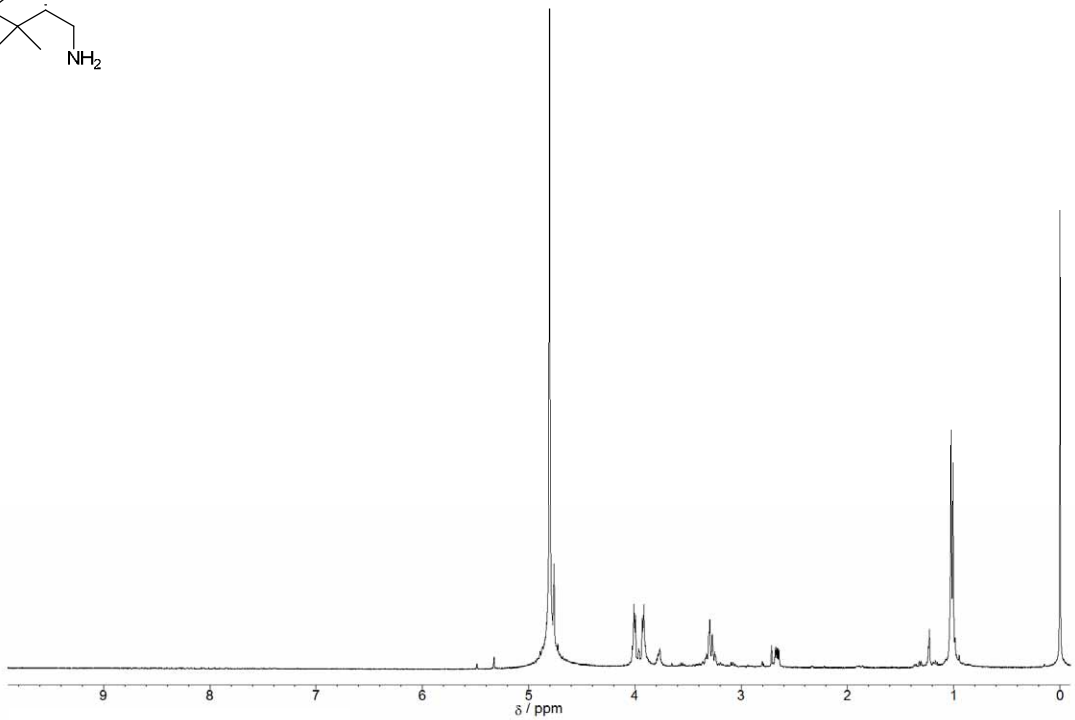
(400 MHz, $CDCl_3$, TMS)



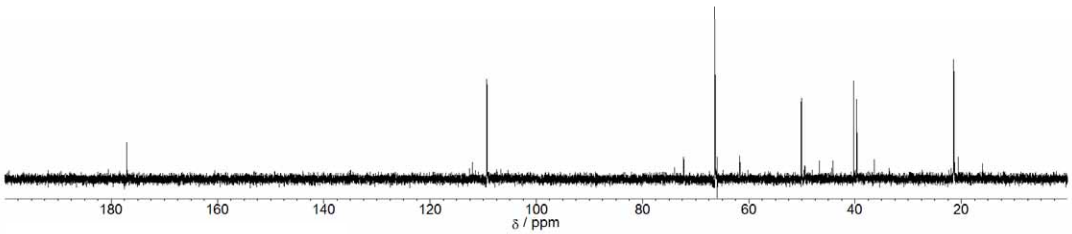
(100 MHz, $CDCl_3$)

(*S*)-2-Aminomethyl-3-[1,3]dioxolan-2-yl-3-methyl butyric acid (5)



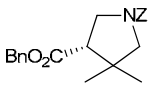


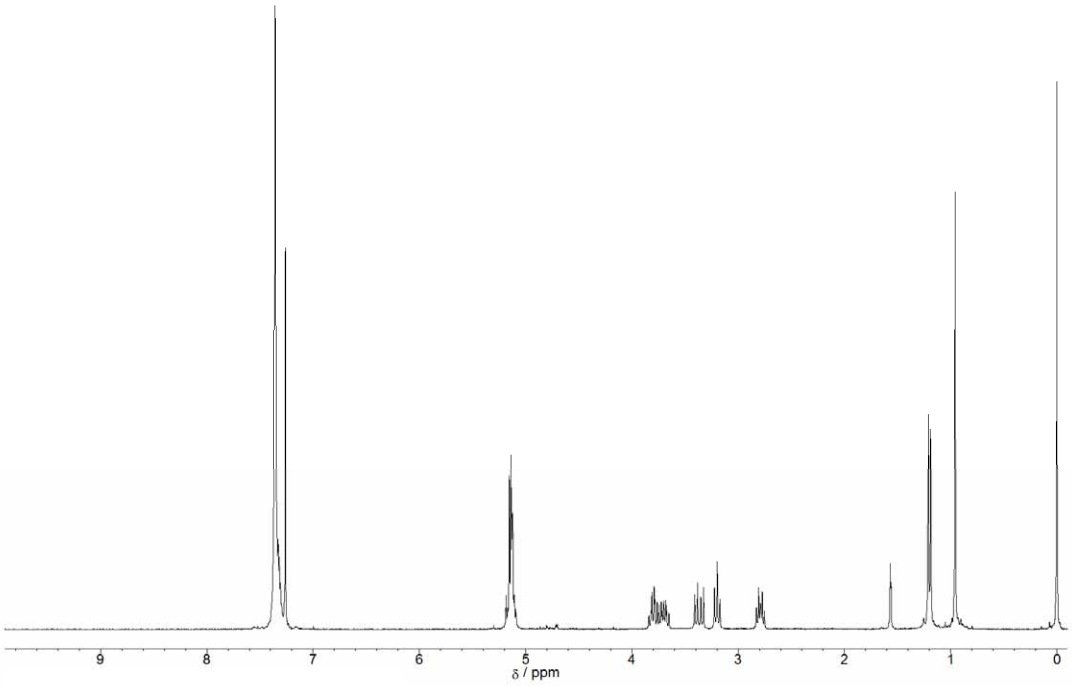
(400 MHz, D_2O, TSP)



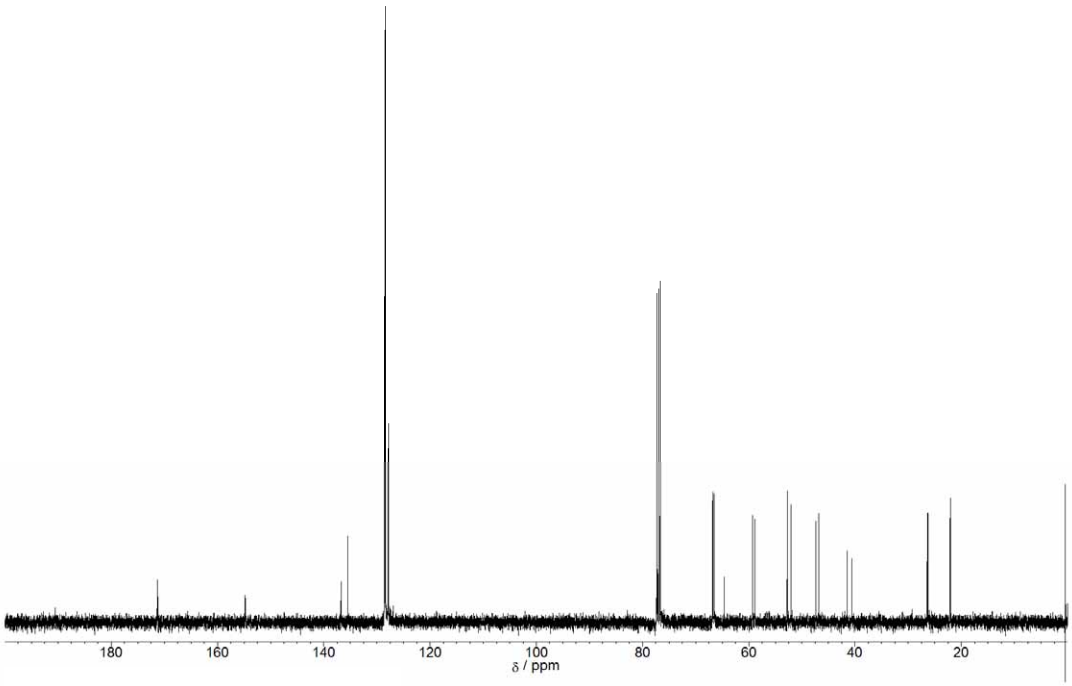
(100 MHz, D_2O, TSP)

Benzyl *N*-benzyloxycarbonyl (*S*)-4,4-dimethylpyrrolidine-3-carboxylate (6)



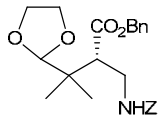


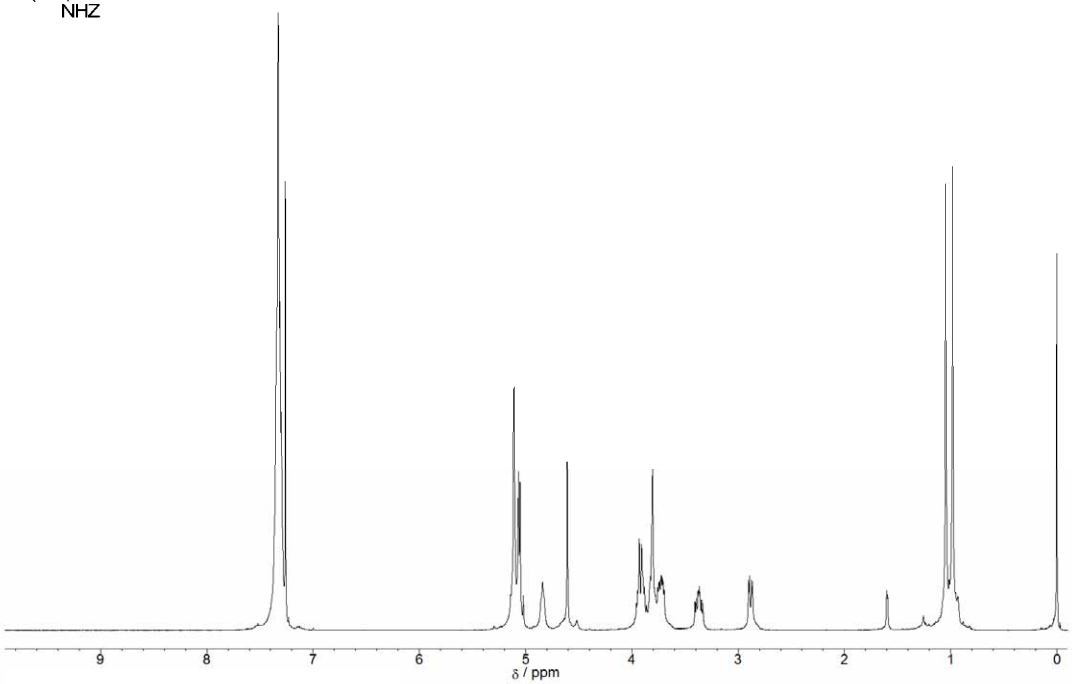
(400 MHz, $CDCl_3$, TMS)



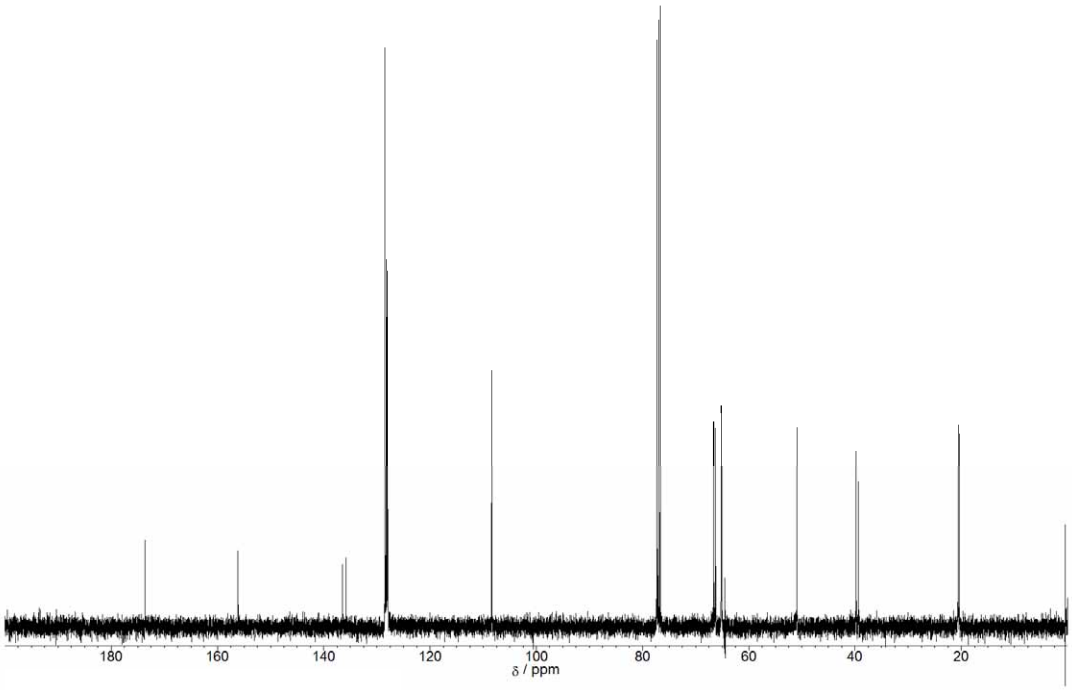
(100 MHz, $CDCl_3$)

Benzyl *N*-benzyloxycarbonyl (*S*)-2-aminomethyl-3-[1,3]dioxolan-2-yl-3-methyl butyrate (7)



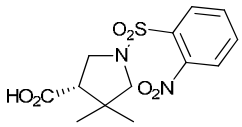


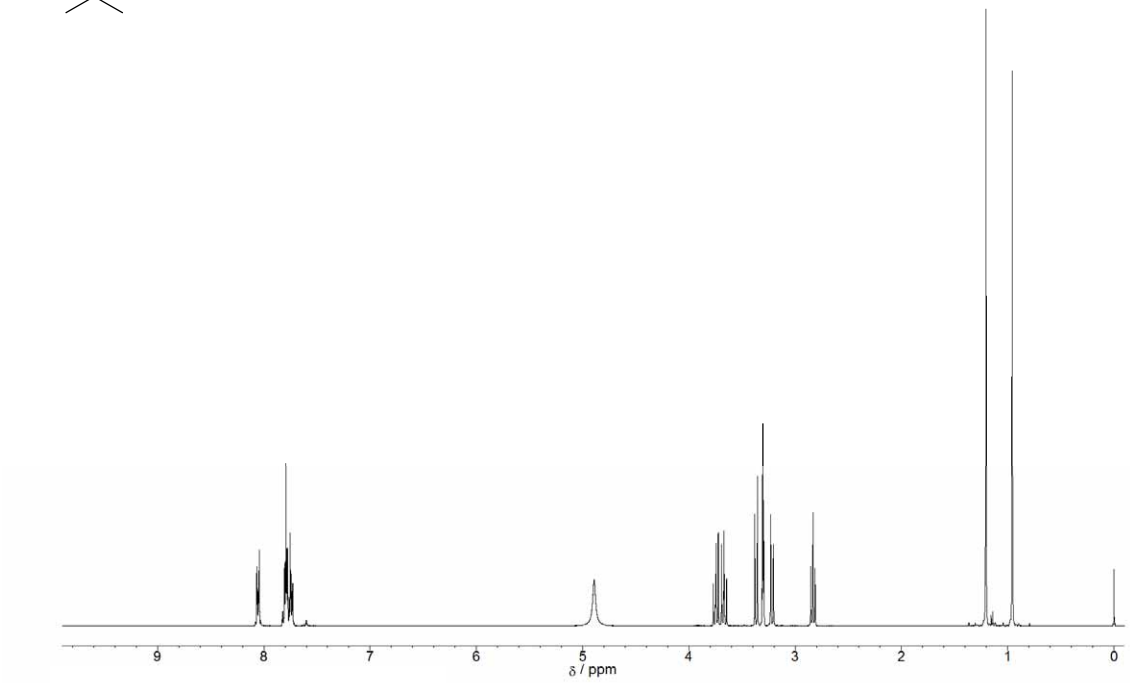
(400 MHz, $CDCl_3$, TMS)



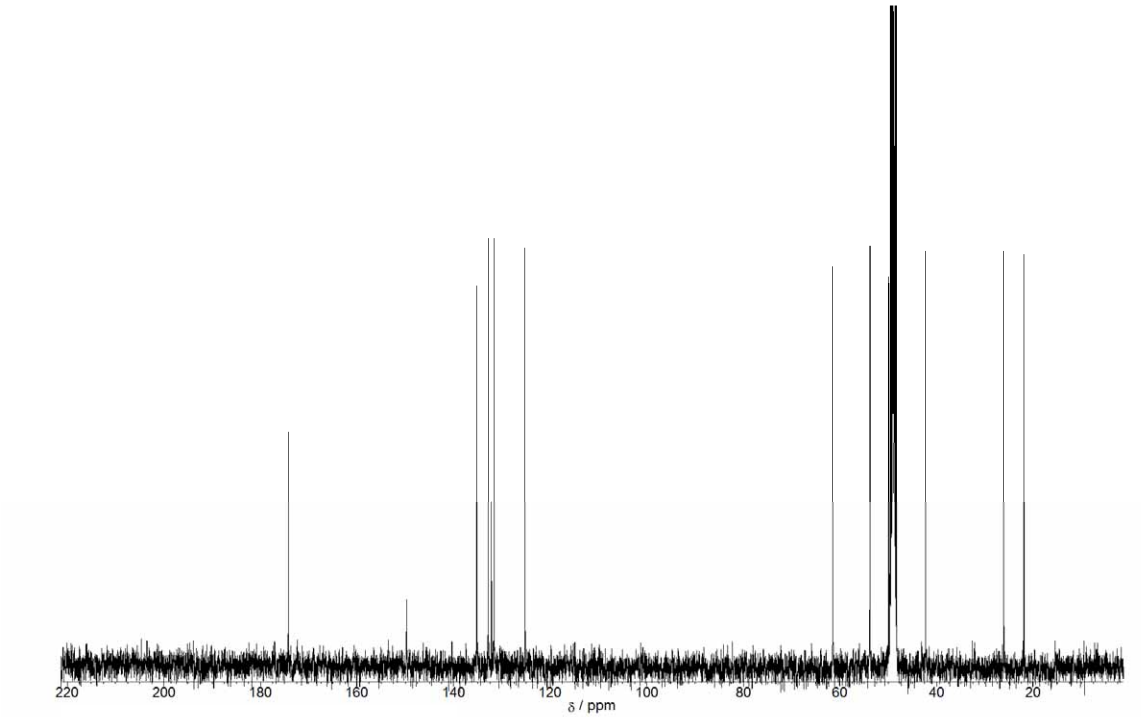
(100 MHz, $CDCl_3$)

(*S*)-*N*-(2-Nitrophenylsulfonyl)-4,4-dimethylpyrrolidine-3-carboxylic acid (*N*-nosyl 1b)





(400 MHz, CD_3OD, TMS)



(100 MHz, CD_3OD)

(F) X-Ray Structure Report for *N*-nosyl 1b

Experimental

Data Collection

A white block crystal of $C_{13}H_{16}N_2O_6S$ having approximate dimensions of 0.500 x 0.300 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a	=	7.5722(4) Å	α	=	75.744(2)°
b	=	9.8018(5) Å	β	=	72.735(2)°
c	=	10.6602(5) Å	γ	=	80.784(2)°
V	=	729.04(6) Å^3			

For Z = 2 and F.W. = 328.34, the calculated density is 1.496 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P1 (#1)

The data were collected at a temperature of -150 $\pm$ 1°C to a maximum 2θ value of 54.9°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at χ=45.0° and ϕ = 0.0°. The exposure rate was 90.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at χ=45.0° and ϕ = 180.0°. The exposure rate was 90.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 7153 reflections that were collected, 5411 were unique (R_{int} = 0.0156); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 2.537 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.826 to 0.975. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 5411 observed reflections and 402 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0453$$

$$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.1267$$

The standard deviation of an observation of unit weight[3] was 1.10. A Sheldrick weighting scheme was used. The maximum and minimum peaks on the final difference Fourier map corresponded to 47.56 and -2.46 $e^-/Å^3$, respectively. The absolute structure was deduced based on Flack parameter, 0.03(8), refined using 2118 Friedel pairs.[4]

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL-97[10].

References

(1) SIR2004: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna (2005)

(2) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2-F_c^2)^2$$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$$

where N_o = number of observations
N_v = number of variables

(4) Flack, H. D. (1983), Acta Cryst. A39, 876-881.

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(10) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{13}H_{16}N_2O_6S$
Formula Weight	328.34
Crystal Color, Habit	white, block
Crystal Dimensions	0.500 X 0.300 X 0.100 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.5722(4) Å b = 9.8018(5) Å c = 10.6602(5) Å α = 75.744(2) ^{o} β = 72.735(2) ^{o} γ = 80.784(2) ^{o} V = 729.04(6) Å^3
Space Group	P1 (#1)
Z value	2
D_{calc}	1.496 g/cm^3
F_{000}	344.00
μ(MoKα)	2.537 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0^{o}C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0^{o}
Exposure Rate	90.0 sec./^{o}
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0^{o}
Exposure Rate	90.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.9^{o}
No. of Reflections Measured	Total: 7153 Unique: 5411 (R_{int} = 0.0156) Friedel pairs: 2118
Corrections	Lorentz-polarization Absorption (trans. factors: 0.826 - 0.975)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0779 \cdot P)^2 + 0.4054 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5411
No. Variables	402
Reflection/Parameter Ratio	13.46
Residuals: R1 (I>2.00σ(I))	0.0453
Residuals: R (All reflections)	0.0481
Residuals: wR2 (All reflections)	0.1267
Goodness of Fit Indicator	1.095
Flack Parameter (Friedel pairs = 2118)	0.03(8)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	47.56 $e^-/Å^3$
Minimum peak in Final Diff. Map	-2.46 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S1	0.45668(8)	0.43386(7)	0.39877(6)	1.52(2)
S2	-0.02619(8)	0.16522(7)	1.25185(6)	1.48(2)
O1	-0.1840(3)	0.0869(3)	1.2859(3)	1.76(4)
O2	0.4158(4)	0.3795(3)	0.2986(3)	2.22(5)
O3	0.0104(4)	0.2230(3)	1.3519(3)	1.98(5)
O4	0.6167(3)	0.5107(3)	0.3643(3)	1.94(5)
O5	-0.0380(4)	-0.0052(3)	1.0290(3)	2.45(5)
O6	0.4742(4)	0.6082(3)	0.6198(3)	2.50(5)
O7	-0.0602(4)	0.7535(3)	0.8727(3)	2.56(5)
O8	0.4707(4)	0.8184(3)	0.4940(3)	2.86(5)
O16	0.1531(4)	-0.0409(3)	0.7244(3)	2.78(5)
O35	-0.0582(4)	-0.2089(3)	1.1672(3)	2.53(5)
O36	0.2037(4)	0.6560(3)	0.9241(3)	2.70(5)
O37	0.3799(5)	-0.1188(3)	0.8231(4)	3.88(6)
N2	0.4701(5)	0.3050(4)	0.5208(4)	2.06(6)
N32	0.0114(4)	-0.0986(4)	1.1170(3)	1.74(5)
N33	-0.0378(4)	0.2896(4)	1.1224(4)	2.08(6)
N34	0.4150(4)	0.6995(4)	0.5379(4)	1.87(5)
C3	0.3234(5)	-0.1751(4)	1.1401(4)	2.04(6)
C6	0.0924(5)	0.5262(4)	0.4320(4)	1.77(6)
C7	0.4935(5)	-0.0280(5)	1.2029(5)	2.39(7)
C8	0.1713(4)	-0.0731(4)	1.1577(4)	1.64(6)
C9	0.2549(5)	0.5510(4)	0.4530(3)	1.41(5)
C10	0.2561(5)	0.6718(4)	0.4994(3)	1.53(5)
C11	0.1035(5)	0.7694(4)	0.5180(4)	2.15(6)
C12	0.3402(5)	0.0692(5)	1.2256(4)	1.99(6)
C13	0.0615(7)	0.4163(5)	1.0911(5)	3.00(8)
C14	-0.0673(5)	0.6195(5)	0.4581(4)	2.37(7)
C15	0.0390(5)	0.6522(4)	0.9356(3)	1.94(5)
C17	0.3419(6)	0.1926(4)	0.5633(5)	2.69(7)
C18	-0.0601(5)	0.7415(5)	0.4986(5)	2.65(7)
C19	-0.1876(5)	0.3096(4)	1.0549(4)	1.86(6)
C20	0.5596(5)	0.1428(4)	0.7006(4)	1.83(6)
C21	-0.0646(5)	0.5289(3)	1.0246(3)	1.69(5)
C22	0.4853(5)	-0.1503(5)	1.1631(4)	2.40(7)
C23	0.5829(6)	0.2928(4)	0.6143(5)	2.62(7)
C24	-0.1536(5)	0.4496(4)	0.9508(4)	1.73(6)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C25	0.2898(6)	-0.0223(4)	0.7500(4)	2.92(7)
C26	-0.0153(6)	0.4225(4)	0.8208(4)	2.55(6)
C27	0.3582(5)	0.1233(4)	0.7052(4)	2.89(7)
C28	-0.3359(5)	0.5236(4)	0.9273(5)	3.16(7)
C29	0.7013(6)	0.0377(5)	0.6309(5)	3.53(8)
C30	0.1736(5)	0.0481(4)	1.2033(4)	1.54(5)
C31	0.5796(8)	0.1311(6)	0.8431(5)	4.5(1)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H1	0.3161	-0.2590	1.1132	2.44
H2	0.0893	0.4448	0.3995	2.12
H3	0.6067	-0.0106	1.2149	2.86
H4	0.1096	0.8544	0.5436	2.58
H5	0.3474	0.1507	1.2565	2.39
H6	-0.1804	0.5992	0.4482	2.85
H7	-0.1674	0.8068	0.5132	3.18
H8	0.5909	-0.2176	1.1515	2.88
H9	-0.1661	0.5645	1.0968	2.03
H10	0.2732	0.1825	0.7668	3.47
H11	0.1866	0.4046	1.0289	3.60
H12	0.0731	0.4390	1.1736	3.60
H13	0.3817	0.1241	0.5035	3.23
H14	0.2132	0.2330	0.5644	3.23
H15	-0.3113	0.3164	1.1199	2.23
H16	-0.1793	0.2305	1.0102	2.23
H17	0.5368	0.3647	0.6704	3.14
H18	0.7148	0.3043	0.5653	3.14
H19	0.0101	0.5128	0.7573	3.07
H20	-0.0674	0.3632	0.7816	3.07
H21	0.1006	0.3742	0.8398	3.07
H22	-0.3919	0.4638	0.8912	3.79
H23	-0.3135	0.6138	0.8631	3.79
H24	-0.4203	0.5412	1.0125	3.79
H25	0.6938	0.0508	0.5384	4.24
H26	0.6750	-0.0588	0.6795	4.24
H27	0.8263	0.0535	0.6300	4.24
H28	0.5317	0.0435	0.9018	5.42
H29	0.5088	0.2123	0.8792	5.42
H30	0.7109	0.1302	0.8387	5.42
H31	-0.1698	0.7322	0.8931	3.08
H38	0.334(8)	-0.213(7)	0.859(6)	5(2)

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0221(4)	0.0170(4)	0.0203(4)	-0.0044(3)	-0.0056(3)	-0.0054(3)
S2	0.0211(4)	0.0166(4)	0.0198(4)	-0.0051(3)	-0.0055(3)	-0.0043(3)
O1	0.023(2)	0.023(2)	0.023(2)	-0.008(1)	-0.004(1)	-0.007(1)
O2	0.031(2)	0.030(2)	0.028(2)	-0.002(1)	-0.008(1)	-0.015(2)
O3	0.030(2)	0.024(2)	0.025(2)	-0.007(1)	-0.008(1)	-0.009(1)
O4	0.022(2)	0.022(2)	0.029(2)	-0.005(1)	-0.005(1)	-0.004(1)
O5	0.033(2)	0.031(2)	0.037(2)	0.005(2)	-0.021(2)	-0.013(2)
O6	0.040(2)	0.027(2)	0.034(2)	-0.001(2)	-0.021(2)	-0.007(2)
O7	0.039(2)	0.021(2)	0.035(2)	-0.007(1)	-0.009(1)	-0.002(1)
O8	0.036(2)	0.027(2)	0.050(2)	-0.014(1)	-0.015(2)	-0.004(2)
O16	0.048(2)	0.028(2)	0.033(2)	-0.015(2)	-0.014(2)	-0.000(1)
O35	0.031(2)	0.024(2)	0.049(2)	-0.009(1)	-0.016(2)	-0.011(2)
O36	0.037(2)	0.021(2)	0.040(2)	-0.010(1)	-0.007(2)	0.002(1)
O37	0.062(2)	0.032(2)	0.060(2)	-0.023(2)	-0.034(2)	0.012(2)
N2	0.032(2)	0.017(2)	0.035(2)	-0.009(2)	-0.019(2)	0.003(2)
N32	0.022(2)	0.025(2)	0.024(2)	-0.000(1)	-0.009(2)	-0.014(2)
N33	0.029(2)	0.023(2)	0.032(2)	-0.010(2)	-0.017(2)	0.001(2)
N34	0.022(2)	0.022(2)	0.030(2)	-0.005(2)	-0.006(2)	-0.009(2)
C3	0.023(2)	0.026(2)	0.034(2)	-0.001(2)	-0.012(2)	-0.012(2)
C6	0.025(2)	0.021(2)	0.025(2)	-0.007(2)	-0.010(2)	-0.005(2)
C7	0.023(2)	0.037(2)	0.036(2)	-0.008(2)	-0.013(2)	-0.006(2)
C8	0.017(2)	0.023(2)	0.022(2)	-0.006(2)	-0.005(2)	-0.005(2)
C9	0.022(2)	0.016(2)	0.016(2)	-0.003(2)	-0.006(2)	-0.002(2)
C10	0.023(2)	0.020(2)	0.018(2)	-0.005(2)	-0.007(2)	-0.005(2)
C11	0.030(2)	0.025(2)	0.029(2)	0.002(2)	-0.009(2)	-0.012(2)
C12	0.025(2)	0.030(2)	0.025(2)	-0.009(2)	-0.007(2)	-0.008(2)
C13	0.052(3)	0.027(2)	0.045(3)	-0.021(2)	-0.031(2)	0.010(2)
C14	0.023(2)	0.035(2)	0.037(2)	-0.004(2)	-0.012(2)	-0.013(2)
C15	0.033(2)	0.018(2)	0.022(2)	-0.005(2)	-0.002(2)	-0.007(1)
C17	0.041(2)	0.017(2)	0.051(3)	-0.015(2)	-0.026(2)	0.007(2)
C18	0.026(2)	0.037(3)	0.042(3)	0.004(2)	-0.011(2)	-0.018(2)
C19	0.027(2)	0.019(2)	0.029(2)	-0.005(2)	-0.016(2)	0.001(2)
C20	0.030(2)	0.018(2)	0.022(2)	-0.007(2)	-0.008(2)	0.000(2)
C21	0.032(2)	0.015(2)	0.018(2)	-0.007(1)	-0.004(2)	-0.005(1)
C22	0.021(2)	0.034(2)	0.038(3)	0.002(2)	-0.011(2)	-0.012(2)
C23	0.040(2)	0.019(2)	0.048(3)	-0.008(2)	-0.026(2)	-0.002(2)
C24	0.024(2)	0.018(2)	0.027(2)	-0.001(2)	-0.011(2)	-0.008(2)

Table 3. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C25	0.052(3)	0.027(2)	0.035(2)	-0.014(2)	-0.019(2)	0.003(2)
C26	0.046(2)	0.028(2)	0.023(2)	-0.011(2)	0.001(2)	-0.011(2)
C27	0.035(2)	0.029(2)	0.048(2)	-0.006(2)	-0.009(2)	-0.012(2)
C28	0.034(2)	0.026(2)	0.060(3)	-0.002(2)	-0.025(2)	0.006(2)
C29	0.040(2)	0.036(2)	0.046(2)	0.001(2)	-0.003(2)	0.000(2)
C30	0.020(2)	0.021(2)	0.019(2)	-0.006(2)	-0.006(2)	-0.004(2)
C31	0.085(4)	0.054(3)	0.041(3)	-0.030(3)	-0.022(3)	-0.004(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Fragment Analysis

fragment: 1

S(1)	O(2)	O(4)	O(6)	O(8)
O(16)	O(37)	N(2)	N(34)	C(6)
C(9)	C(10)	C(11)	C(14)	C(17)
C(18)	C(20)	C(23)	C(25)	C(27)
C(29)	C(31)			

fragment: 2

S(2)	O(1)	O(3)	O(5)	O(7)
O(35)	O(36)	N(32)	N(33)	C(3)
C(7)	C(8)	C(12)	C(13)	C(15)
C(19)	C(21)	C(22)	C(24)	C(26)
C(28)	C(30)			

Table 5. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O2	1.431(4)	S1	O4	1.436(3)
S1	N2	1.590(3)	S1	C9	1.797(3)
S2	O1	1.431(3)	S2	O3	1.434(3)
S2	N33	1.615(4)	S2	C30	1.774(4)
O5	N32	1.238(4)	O6	N34	1.217(4)
O7	C15	1.316(4)	O8	N34	1.236(5)
O16	C25	1.196(6)	O35	N32	1.210(4)
O36	C15	1.223(5)	O37	C25	1.309(6)
N2	C17	1.482(6)	N2	C23	1.468(7)
N32	C8	1.477(5)	N33	C13	1.471(6)
N33	C19	1.479(6)	N34	C10	1.463(6)
C3	C8	1.399(5)	C3	C22	1.388(6)
C6	C9	1.383(6)	C6	C14	1.395(5)
C7	C12	1.381(5)	C7	C22	1.382(7)
C8	C30	1.395(6)	C9	C10	1.393(6)
C10	C11	1.376(5)	C11	C18	1.393(7)
C12	C30	1.406(6)	C13	C21	1.520(6)
C14	C18	1.382(7)	C15	C21	1.508(4)
C17	C27	1.530(7)	C19	C24	1.541(5)
C20	C23	1.537(5)	C20	C27	1.552(6)
C20	C29	1.521(6)	C20	C31	1.545(7)
C21	C24	1.568(6)	C24	C26	1.523(5)
C24	C28	1.513(5)	C25	C27	1.512(6)

Table 6. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
O7	H31	0.840	O37	H38	0.99(6)
C3	H1	0.950	C6	H2	0.950
C7	H3	0.950	C11	H4	0.950
C12	H5	0.950	C13	H11	0.990
C13	H12	0.990	C14	H6	0.950
C17	H13	0.990	C17	H14	0.990
C18	H7	0.950	C19	H15	0.990
C19	H16	0.990	C21	H9	1.000
C22	H8	0.950	C23	H17	0.990
C23	H18	0.990	C26	H19	0.980
C26	H20	0.980	C26	H21	0.980
C27	H10	1.000	C28	H22	0.980
C28	H23	0.980	C28	H24	0.980
C29	H25	0.980	C29	H26	0.980
C29	H27	0.980	C31	H28	0.980
C31	H29	0.980	C31	H30	0.980

Table 7. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O2	S1	O4	119.94(15)	O2	S1	N2	107.46(18)
O2	S1	C9	104.18(17)	O4	S1	N2	108.56(17)
O4	S1	C9	107.62(16)	N2	S1	C9	108.61(15)
O1	S2	O3	119.78(14)	O1	S2	N33	107.77(17)
O1	S2	C30	106.94(16)	O3	S2	N33	109.50(18)
O3	S2	C30	104.42(17)	N33	S2	C30	107.85(15)
S1	N2	C17	120.8(3)	S1	N2	C23	126.0(3)
C17	N2	C23	112.6(3)	O5	N32	O35	124.6(4)
O5	N32	C8	116.4(3)	O35	N32	C8	119.0(3)
S2	N33	C13	120.8(4)	S2	N33	C19	123.2(3)
C13	N33	C19	113.2(3)	O6	N34	O8	123.9(4)
O6	N34	C10	117.9(3)	O8	N34	C10	117.9(3)
C8	C3	C22	118.1(4)	C9	C6	C14	120.6(4)
C12	C7	C22	121.2(4)	N32	C8	C3	115.2(4)
N32	C8	C30	122.1(3)	C3	C8	C30	122.6(4)
S1	C9	C6	116.2(3)	S1	C9	C10	124.8(3)
C6	C9	C10	118.6(3)	N34	C10	C9	122.5(3)
N34	C10	C11	115.8(4)	C9	C10	C11	121.7(4)
C10	C11	C18	118.9(4)	C7	C12	C30	120.3(4)
N33	C13	C21	101.9(4)	C6	C14	C18	119.6(4)
O7	C15	O36	123.2(3)	O7	C15	C21	115.4(3)
O36	C15	C21	121.4(3)	N2	C17	C27	102.6(4)
C11	C18	C14	120.5(4)	N33	C19	C24	104.1(3)
C23	C20	C27	101.6(3)	C23	C20	C29	109.7(3)
C23	C20	C31	112.0(4)	C27	C20	C29	111.9(4)
C27	C20	C31	111.3(4)	C29	C20	C31	110.1(4)
C13	C21	C15	111.7(3)	C13	C21	C24	105.3(3)
C15	C21	C24	114.9(3)	C3	C22	C7	120.3(4)
N2	C23	C20	103.7(4)	C19	C24	C21	100.5(3)
C19	C24	C26	110.3(3)	C19	C24	C28	110.0(3)
C21	C24	C26	110.5(3)	C21	C24	C28	113.2(3)
C26	C24	C28	111.7(4)	O16	C25	O37	124.0(4)
O16	C25	C27	119.4(4)	O37	C25	C27	116.5(5)
C17	C27	C20	104.2(3)	C17	C27	C25	111.0(4)
C20	C27	C25	120.4(3)	S2	C30	C8	123.8(3)
S2	C30	C12	118.4(3)	C8	C30	C12	117.4(3)

Table 8. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C15	O7	H31	109.5	C25	O37	H38	118(4)
C8	C3	H1	121.0	C22	C3	H1	120.9
C9	C6	H2	119.7	C14	C6	H2	119.7
C12	C7	H3	119.4	C22	C7	H3	119.4
C10	C11	H4	120.5	C18	C11	H4	120.5
C7	C12	H5	119.9	C30	C12	H5	119.9
N33	C13	H11	111.4	N33	C13	H12	111.4
C21	C13	H11	111.4	C21	C13	H12	111.4
H11	C13	H12	109.3	C6	C14	H6	120.2
C18	C14	H6	120.2	N2	C17	H13	111.3
N2	C17	H14	111.3	C27	C17	H13	111.3
C27	C17	H14	111.3	H13	C17	H14	109.2
C11	C18	H7	119.8	C14	C18	H7	119.8
N33	C19	H15	110.9	N33	C19	H16	110.9
C24	C19	H15	110.9	C24	C19	H16	110.9
H15	C19	H16	109.0	C13	C21	H9	108.2
C15	C21	H9	108.2	C24	C21	H9	108.2
C3	C22	H8	119.9	C7	C22	H8	119.9
N2	C23	H17	111.0	N2	C23	H18	111.0
C20	C23	H17	111.0	C20	C23	H18	111.0
H17	C23	H18	109.0	C24	C26	H19	109.5
C24	C26	H20	109.5	C24	C26	H21	109.5
H19	C26	H20	109.5	H19	C26	H21	109.5
H20	C26	H21	109.5	C17	C27	H10	106.8
C20	C27	H10	106.8	C25	C27	H10	106.8
C24	C28	H22	109.5	C24	C28	H23	109.5
C24	C28	H24	109.5	H22	C28	H23	109.5
H22	C28	H24	109.5	H23	C28	H24	109.5
C20	C29	H25	109.5	C20	C29	H26	109.5
C20	C29	H27	109.5	H25	C29	H26	109.5
H25	C29	H27	109.5	H26	C29	H27	109.5
C20	C31	H28	109.5	C20	C31	H29	109.5
C20	C31	H30	109.5	H28	C31	H29	109.5
H28	C31	H30	109.5	H29	C31	H30	109.5

Table 9. Torsion Angles(O)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O2	S1	N2	C17	-38.4(3)	O2	S1	N2	C23	151.5(3)
O2	S1	C9	C6	22.9(3)	O2	S1	C9	C10	-149.5(3)
O4	S1	N2	C17	-169.5(2)	O4	S1	N2	C23	20.4(3)
O4	S1	C9	C6	151.29(19)	O4	S1	C9	C10	-21.1(3)
N2	S1	C9	C6	-91.4(3)	N2	S1	C9	C10	96.2(3)
C9	S1	N2	C17	73.8(3)	C9	S1	N2	C23	-96.4(3)
O1	S2	N33	C13	158.3(2)	O1	S2	N33	C19	-1.3(3)
O1	S2	C30	C8	22.4(3)	O1	S2	C30	C12	-150.3(2)
O3	S2	N33	C13	26.5(3)	O3	S2	N33	C19	-133.2(3)
O3	S2	C30	C8	150.3(3)	O3	S2	C30	C12	-22.4(3)
N33	S2	C30	C8	-93.2(3)	N33	S2	C30	C12	94.1(3)
C30	S2	N33	C13	-86.6(3)	C30	S2	N33	C19	113.8(3)
S1	N2	C17	C27	-161.7(2)	S1	N2	C23	C20	-174.2(2)
C17	N2	C23	C20	14.9(4)	C23	N2	C17	C27	9.7(4)
O5	N32	C8	C3	-121.1(3)	O5	N32	C8	C30	55.6(4)
O35	N32	C8	C3	56.6(4)	O35	N32	C8	C30	-126.8(3)
S2	N33	C13	C21	-149.0(3)	S2	N33	C19	C24	173.1(2)
C13	N33	C19	C24	12.0(4)	C19	N33	C13	C21	12.6(4)
O6	N34	C10	C9	-53.4(4)	O6	N34	C10	C11	123.6(3)
O8	N34	C10	C9	132.5(3)	O8	N34	C10	C11	-50.5(4)
C8	C3	C22	C7	0.3(5)	C22	C3	C8	N32	173.5(3)
C22	C3	C8	C30	-3.2(5)	C9	C6	C14	C18	3.4(5)
C14	C6	C9	S1	-173.6(3)	C14	C6	C9	C10	-0.6(5)
C12	C7	C22	C3	2.5(6)	C22	C7	C12	C30	-2.6(6)
N32	C8	C30	S2	13.9(5)	N32	C8	C30	C12	-173.3(3)
C3	C8	C30	S2	-169.7(3)	C3	C8	C30	C12	3.1(5)
S1	C9	C10	N34	-14.3(4)	S1	C9	C10	C11	168.89(19)
C6	C9	C10	N34	173.5(3)	C6	C9	C10	C11	-3.4(5)
N34	C10	C11	C18	-172.5(3)	C9	C10	C11	C18	4.5(5)
C10	C11	C18	C14	-1.6(6)	C7	C12	C30	S2	173.0(3)
C7	C12	C30	C8	-0.2(5)	N33	C13	C21	C15	-157.3(3)
N33	C13	C21	C24	-32.0(4)	C6	C14	C18	C11	-2.3(6)
O7	C15	C21	C13	179.0(3)	O7	C15	C21	C24	59.2(4)
O36	C15	C21	C13	-1.1(5)	O36	C15	C21	C24	-120.9(4)
N2	C17	C27	C20	-30.2(4)	N2	C17	C27	C25	-161.2(3)

N33	C19	C24	C21	-30.3(3)	N33	C19	C24	C26	86.4(4)
N33	C19	C24	C28	-149.9(3)	C23	C20	C27	C17	39.3(4)

Table 9. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C23	C20	C27	C25	164.6(4)	C27	C20	C23	N2	-32.6(4)
C29	C20	C23	N2	86.0(4)	C31	C20	C23	N2	-151.5(3)
C29	C20	C27	C17	-77.6(4)	C29	C20	C27	C25	47.6(5)
C31	C20	C27	C17	158.7(3)	C31	C20	C27	C25	-76.0(5)
C13	C21	C24	C19	39.2(3)	C13	C21	C24	C26	-77.4(3)
C13	C21	C24	C28	156.4(3)	C15	C21	C24	C19	162.5(3)
C15	C21	C24	C26	45.9(4)	C15	C21	C24	C28	-80.3(3)
O16	C25	C27	C17	-40.9(5)	O16	C25	C27	C20	-162.9(4)
O37	C25	C27	C17	143.4(3)	O37	C25	C27	C20	21.4(5)

Table 10. Possible hydrogen bonds

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A
O37	H38	O36[1]	2.594(5)	0.99	1.63(6)	165(5)

Symmetry Operators:

(1) X,Y-1,Z

Table 11. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	O6	3.275(4)	S1	N34	3.231(4)
S2	O5	3.251(4)	S2	N32	3.192(4)
O1	O5	2.939(4)	O1	O35	3.335(4)
O1	N32	2.812(4)	O1	C8	3.015(4)
O1	C19	2.865(4)	O2	C6	2.810(4)
O2	C17	2.911(5)	O3	C12	2.849(4)
O3	C13	2.911(5)	O4	O6	2.949(4)
O4	O8	3.508(5)	O4	N34	2.878(5)
O4	C10	3.070(4)	O4	C23	2.949(5)
O5	N33	3.280(5)	O5	C3	3.340(5)
O5	C19	3.161(5)	O5	C30	2.968(6)
O6	N2	3.397(5)	O6	C9	2.961(6)
O6	C11	3.331(5)	O6	C23	3.079(5)
O7	C24	3.028(5)	O7	C26	3.371(5)
O7	C28	3.148(5)	O8	C9	3.477(6)
O8	C11	2.824(5)	O16	C17	2.808(5)
O35	C3	2.882(5)	O35	C30	3.446(6)
O36	C13	2.732(5)	O36	C24	3.537(5)
O36	C26	3.569(6)	O37	C20	2.923(5)
O37	C29	3.027(5)	O37	C31	3.158(8)
N2	C6	3.520(5)	N2	C29	3.089(5)
N33	C12	3.576(5)	N33	C26	3.121(5)
C3	C12	2.797(7)	C6	C11	2.778(7)
C7	C8	2.744(6)	C9	C17	3.442(5)
C9	C18	2.783(5)	C10	C14	2.759(6)
C13	C26	3.088(7)	C13	C30	3.560(5)
C15	C26	2.947(6)	C15	C28	3.317(6)
C17	C29	3.087(6)	C22	C30	2.806(5)
C25	C29	3.088(6)	C25	C31	3.339(9)

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H2	2.764	S1	H13	3.049
S1	H14	2.813	S1	H17	3.026
S1	H18	2.957	S2	H5	2.824
S2	H11	3.153	S2	H12	2.763
S2	H15	2.930	S2	H16	3.018
O1	H15	2.734	O1	H16	2.922
O2	H2	2.435	O2	H13	2.878
O2	H14	2.927	O3	H5	2.507
O3	H11	3.438	O3	H12	2.475
O4	H17	3.141	O4	H18	2.751
O5	H1	3.518	O5	H16	2.372
O6	H4	3.512	O6	H17	2.317
O6	H18	3.319	O7	H9	2.634
O7	H19	2.828	O7	H23	2.567
O7	H24	3.444	O8	H4	2.609
O16	H10	2.683	O16	H13	2.785
O16	H14	2.828	O16	H38	2.45(6)
O35	H1	2.708	O36	H9	2.994
O36	H11	2.449	O36	H12	2.984
O36	H19	3.274	O36	H21	3.373
O36	H31	2.903	O37	H10	2.896
O37	H25	3.482	O37	H26	2.372
O37	H28	2.525	N2	H2	3.455
N2	H10	2.691	N2	H25	2.778
N32	H1	2.572	N32	H16	3.385
N33	H5	3.556	N33	H9	2.690
N33	H20	3.593	N33	H21	2.834
N34	H4	2.548	N34	H17	3.337
C3	H3	3.255	C6	H7	3.258
C6	H14	3.002	C7	H1	3.264
C8	H5	3.257	C8	H8	3.253
C9	H4	3.274	C9	H6	3.268
C9	H14	3.082	C9	H17	3.587
C10	H2	3.247	C10	H7	3.243
C11	H6	3.266	C12	H8	3.259
C13	H5	3.574	C13	H15	3.041
C13	H16	3.186	C13	H19	3.571

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C13	H21	2.732	C14	H4	3.267
C15	H11	2.595	C15	H12	2.912
C15	H19	2.673	C15	H21	3.060
C15	H23	3.091	C17	H2	3.341
C17	H17	3.012	C17	H18	3.195
C17	H25	2.771	C17	H26	3.510
C18	H2	3.256	C19	H9	2.682
C19	H11	3.038	C19	H12	3.192
C19	H19	3.361	C19	H20	2.723
C19	H21	2.679	C19	H22	2.698
C19	H23	3.350	C19	H24	2.673
C20	H13	2.866	C20	H14	3.265
C21	H15	2.818	C21	H16	3.232
C21	H19	2.774	C21	H20	3.385
C21	H21	2.673	C21	H22	3.408
C21	H23	2.815	C21	H24	2.716
C21	H31	2.313	C22	H5	3.260
C23	H10	2.645	C23	H13	3.049
C23	H14	3.167	C23	H25	2.625
C23	H26	3.345	C23	H27	2.745
C23	H28	3.379	C23	H29	2.649
C23	H30	2.864	C24	H11	2.873
C24	H12	3.292	C24	H31	2.677
C25	H13	2.612	C25	H14	2.879
C25	H25	3.282	C25	H26	2.774
C25	H28	3.008	C26	H9	3.378
C26	H11	3.004	C26	H15	3.339
C26	H16	2.560	C26	H22	2.715
C26	H23	2.697	C26	H24	3.353
C26	H31	3.264	C27	H17	2.804
C27	H18	3.241	C27	H25	2.736
C27	H26	2.737	C27	H27	3.388
C27	H28	2.688	C27	H29	2.806
C27	H30	3.394	C27	H38	3.31(6)
C28	H9	2.641	C28	H15	2.535
C28	H16	2.954	C28	H19	2.710
C28	H20	2.706	C28	H21	3.351

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C28	H31	2.465	C29	H10	3.372
C29	H13	3.024	C29	H17	3.328
C29	H18	2.543	C29	H28	2.801
C29	H29	3.347	C29	H30	2.615
C30	H1	3.305	C30	H3	3.271
C30	H11	3.532	C31	H10	2.615
C31	H17	2.603	C31	H18	2.996
C31	H25	3.360	C31	H26	2.730
C31	H27	2.666	H1	H8	2.349
H2	H6	2.345	H2	H14	2.615
H3	H5	2.321	H3	H8	2.321
H4	H7	2.347	H5	H11	3.371
H5	H12	3.325	H6	H7	2.331
H9	H11	2.861	H9	H12	2.266
H9	H15	2.755	H9	H19	3.599
H9	H22	3.540	H9	H23	2.928
H9	H24	2.415	H9	H31	2.384
H10	H13	2.856	H10	H14	2.256
H10	H17	2.692	H10	H26	3.580
H10	H28	2.758	H10	H29	2.512
H10	H30	3.550	H11	H16	3.556
H11	H19	3.410	H11	H21	2.391
H12	H15	3.563	H13	H18	3.592
H13	H25	2.468	H13	H26	3.347
H14	H17	3.510	H15	H20	3.483
H15	H22	2.697	H15	H23	3.475
H15	H24	2.363	H16	H19	3.505
H16	H20	2.432	H16	H21	2.681
H16	H22	2.835	H16	H24	3.292
H17	H25	3.581	H17	H27	3.499
H17	H28	3.486	H17	H29	2.327
H17	H30	2.939	H18	H25	2.605
H18	H26	3.497	H18	H27	2.465
H18	H29	3.211	H18	H30	2.986
H19	H22	3.014	H19	H23	2.527
H19	H24	3.594	H19	H31	2.828
H20	H22	2.542	H20	H23	2.981

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H21	H22	3.600	H21	H23	3.588
H22	H31	3.349	H23	H31	1.851
H24	H31	2.694	H25	H30	3.517
H26	H28	2.664	H26	H30	2.893
H26	H38	3.086	H27	H28	3.078
H27	H29	3.509	H27	H30	2.395
H28	H38	3.315			

Table 13. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	C7[1]	3.267(6)	O1	C29[2]	3.446(5)
O2	O3[3]	3.485(4)	O2	C12[3]	3.488(6)
O2	C19[4]	3.439(4)	O3	O2[5]	3.485(4)
O3	C6[5]	3.479(5)	O3	C29[2]	3.492(5)
O4	C14[6]	3.259(6)	O5	O7[7]	3.261(5)
O5	O16	3.220(4)	O5	O37	3.468(4)
O5	C7[1]	3.495(5)	O5	C25	3.281(5)
O6	O36	3.382(4)	O6	C14[6]	3.393(5)
O7	O5[8]	3.261(5)	O7	O16[8]	2.670(4)
O7	O35[8]	3.255(5)	O7	O37[8]	3.594(5)
O7	N32[8]	3.483(5)	O7	C11	3.585(5)
O7	C25[8]	3.458(5)	O8	O16[8]	3.289(4)
O8	O37[8]	3.557(5)	O8	C7[9]	3.064(5)
O8	C12[9]	3.555(5)	O8	C18[6]	3.524(5)
O8	C22[9]	3.434(6)	O8	C25[8]	3.309(6)
O16	O5	3.220(4)	O16	O7[7]	2.670(4)
O16	O8[7]	3.289(4)	O16	O36[7]	3.241(4)
O16	N34[7]	3.590(5)	O16	C11[7]	3.342(6)
O16	C15[7]	3.347(4)	O35	O7[7]	3.255(5)
O35	O36[7]	3.193(4)	O35	C7[1]	3.528(5)
O35	C14[10]	3.129(5)	O35	C15[7]	2.957(5)
O35	C18[10]	3.441(6)	O35	C21[7]	3.306(5)
O35	C22[1]	3.423(5)	O36	O6	3.382(4)
O36	O16[8]	3.241(4)	O36	O35[8]	3.193(4)
O36	O37[8]	2.594(5)	O36	N32[8]	3.416(5)
O36	C3[8]	3.529(6)	O36	C25[8]	3.297(5)
O36	C28[6]	3.527(5)	O37	O5	3.468(4)
O37	O7[7]	3.594(5)	O37	O8[7]	3.557(5)
O37	O36[7]	2.594(5)	O37	N32	3.547(4)
O37	C3	3.195(6)	O37	C8	3.554(5)
O37	C15[7]	3.440(5)	N32	O7[7]	3.483(5)
N32	O36[7]	3.416(5)	N32	O37	3.547(4)
N32	C15[7]	3.416(5)	N34	O16[8]	3.590(5)
C3	O36[7]	3.529(6)	C3	O37	3.195(6)
C6	O3[3]	3.479(5)	C7	O1[6]	3.267(6)
C7	O5[6]	3.495(5)	C7	O8[10]	3.064(5)
C7	O35[6]	3.528(5)	C8	O37	3.554(5)

Table 13. Intermolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C11	O7	3.585(5)	C11	O16[8]	3.342(6)
C12	O2[5]	3.488(6)	C12	O8[10]	3.555(5)
C14	O4[1]	3.259(6)	C14	O6[1]	3.393(5)
C14	O35[9]	3.129(5)	C15	O16[8]	3.347(4)
C15	O35[8]	2.957(5)	C15	O37[8]	3.440(5)
C15	N32[8]	3.416(5)	C18	O8[1]	3.524(5)
C18	O35[9]	3.441(6)	C18	C29[11]	3.537(7)
C19	O2[2]	3.439(4)	C21	O35[8]	3.306(5)
C22	O8[10]	3.434(6)	C22	O35[6]	3.423(5)
C25	O5	3.281(5)	C25	O7[7]	3.458(5)
C25	O8[7]	3.309(6)	C25	O36[7]	3.297(5)
C28	O36[1]	3.527(5)	C29	O1[4]	3.446(5)
C29	O3[4]	3.492(5)	C29	C18[12]	3.537(7)

Symmetry Operators:

(1) X-1,Y,Z
(2) X-1,Y,Z+1
(3) X,Y,Z-1
(4) X+1,Y,Z-1
(5) X,Y,Z+1
(6) X+1,Y,Z
(7) X,Y-1,Z
(8) X,Y+1,Z
(9) X,Y+1,Z-1
(10) X,Y-1,Z+1
(11) X-1,Y+1,Z
(12) X+1,Y-1,Z

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H15[1]	3.345	S2	H25[2]	3.212
O1	H3[3]	2.357	O1	H5[3]	3.597
O1	H7[4]	3.197	O1	H13[2]	3.440
O1	H25[2]	2.527	O2	H5[5]	2.551
O2	H12[5]	3.168	O2	H15[1]	2.473
O2	H24[1]	3.059	O3	H2[6]	2.546
O3	H13[6]	3.537	O3	H14[6]	3.118
O3	H18[2]	2.849	O3	H25[2]	3.059
O3	H27[2]	3.059	O4	H6[7]	2.353
O4	H8[8]	3.065	O4	H9[1]	2.806
O4	H12[1]	3.511	O4	H15[1]	3.462
O5	H3[3]	2.828	O5	H8[3]	3.506
O5	H10	3.420	O5	H30[3]	3.107
O5	H38	3.51(6)	O6	H6[7]	2.713
O6	H7[7]	3.350	O6	H19	3.563
O6	H22[7]	3.266	O6	H23[7]	3.448
O6	H38[9]	3.27(7)	O7	H4	3.311
O7	H8[10]	3.378	O7	H26[10]	3.325
O7	H27[10]	3.583	O7	H38[9]	3.01(6)
O8	H3[8]	3.000	O8	H6[7]	3.126
O8	H7[7]	2.790	O8	H8[8]	3.583
O8	H13[9]	2.984	O8	H25[9]	3.241
O8	H26[9]	3.366	O16	H4[11]	2.517
O16	H27[3]	2.877	O16	H30[3]	3.507
O16	H31[11]	3.364	O35	H3[3]	2.935
O35	H6[4]	3.083	O35	H7[4]	3.570
O35	H8[3]	2.727	O35	H9[11]	2.816
O35	H12[11]	3.425	O35	H31[11]	3.470
O36	H1[9]	2.748	O36	H22[7]	3.300
O36	H23[7]	3.492	O36	H24[7]	3.210
O36	H38[9]	1.63(6)	O37	H1	2.986
O37	H23[12]	3.245	N32	H3[3]	2.987
N32	H8[3]	3.452	N32	H38	3.39(6)
N34	H6[7]	3.005	N34	H7[7]	3.408
N34	H38[9]	3.58(7)	C3	H24[12]	3.452
C3	H28	3.092	C3	H38	3.09(7)
C6	H12[5]	3.127	C6	H19	3.310

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C6	H20	3.594	C7	H28	3.047
C8	H28	3.352	C8	H38	3.59(7)
C9	H1^{8}	3.573	C9	H19	3.187
C10	H19	3.039	C11	H19	3.110
C11	H26^{10}	3.563	C11	H27^{10}	3.444
C12	H13^{6}	3.249	C12	H28	3.380
C12	H29	3.529	C13	H2^{6}	3.437
C14	H18^{3}	3.514	C14	H19	3.298
C15	H1^{9}	3.535	C15	H38^{9}	2.59(6)
C17	H5^{5}	3.383	C18	H19	3.218
C18	H25^{10}	3.347	C18	H26^{10}	3.143
C18	H27^{10}	3.550	C19	H3^{3}	3.541
C19	H30^{3}	3.532	C21	H8^{10}	3.507
C22	H9^{12}	3.576	C22	H28	2.919
C22	H31^{12}	3.555	C23	H6^{7}	3.548
C25	H4^{11}	3.433	C26	H10	2.986
C26	H14	3.547	C27	H21	3.233
C28	H1^{10}	3.548	C28	H38^{10}	3.40(6)
C29	H4^{12}	3.315	C29	H7^{12}	2.761
C30	H4^{4}	3.586	C30	H28	3.542
C31	H16^{7}	3.288	C31	H20^{7}	3.595
C31	H22^{7}	3.472	H1	O36^{11}	2.748
H1	O37	2.986	H1	C9^{4}	3.573
H1	C15^{11}	3.535	H1	C28^{12}	3.548
H1	H12^{11}	3.558	H1	H23^{12}	3.550
H1	H24^{12}	2.735	H1	H28	3.552
H1	H38	2.605	H2	O3^{5}	2.546
H2	C13^{5}	3.437	H2	H12^{5}	2.462
H2	H18^{3}	3.185	H3	O1^{7}	2.357
H3	O5^{7}	2.828	H3	O8^{4}	3.000
H3	O35^{7}	2.935	H3	N32^{7}	2.987
H3	C19^{7}	3.541	H3	H13^{6}	3.504
H3	H15^{7}	3.216	H3	H16^{7}	3.091
H3	H28	3.449	H4	O7	3.311
H4	O16^{9}	2.517	H4	C25^{9}	3.433
H4	C29^{10}	3.315	H4	C30^{8}	3.586
H4	H13^{9}	3.476	H4	H25^{10}	3.425

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H4	H26[10]	3.246	H4	H27[10]	2.762
H5	O1[7]	3.597	H5	O2[6]	2.551
H5	C17[6]	3.383	H5	H13[6]	2.668
H5	H14[6]	3.395	H5	H15[7]	3.063
H6	O4[3]	2.353	H6	O6[3]	2.713
H6	O8[3]	3.126	H6	O35[8]	3.083
H6	N34[3]	3.005	H6	C23[3]	3.548
H6	H12[5]	3.561	H6	H17[3]	3.372
H6	H18[3]	2.986	H7	O1[8]	3.197
H7	O6[3]	3.350	H7	O8[3]	2.790
H7	O35[8]	3.570	H7	N34[3]	3.408
H7	C29[10]	2.761	H7	H25[10]	2.498
H7	H26[10]	2.385	H7	H27[10]	2.967
H8	O4[4]	3.065	H8	O5[7]	3.506
H8	O7[12]	3.378	H8	O8[4]	3.583
H8	O35[7]	2.727	H8	N32[7]	3.452
H8	C21[12]	3.507	H8	H9[12]	2.647
H8	H24[12]	3.108	H8	H28	3.290
H8	H31[12]	2.921	H9	O4[2]	2.806
H9	O35[9]	2.816	H9	C22[10]	3.576
H9	H8[10]	2.647	H10	O5	3.420
H10	C26	2.986	H10	H19	3.515
H10	H20	2.872	H10	H21	2.275
H11	H22[7]	3.173	H11	H24[7]	3.396
H11	H29	3.122	H12	O2[6]	3.168
H12	O4[2]	3.511	H12	O35[9]	3.425
H12	C6[6]	3.127	H12	H1[9]	3.558
H12	H2[6]	2.462	H12	H6[6]	3.561
H13	O1[1]	3.440	H13	O3[5]	3.537
H13	O8[11]	2.984	H13	C12[5]	3.249
H13	H3[5]	3.504	H13	H4[11]	3.476
H13	H5[5]	2.668	H14	O3[5]	3.118
H14	C26	3.547	H14	H5[5]	3.395
H14	H20	3.028	H14	H21	3.376
H14	H27[3]	3.464	H15	S1[2]	3.345
H15	O2[2]	2.473	H15	O4[2]	3.462
H15	H3[3]	3.216	H15	H5[3]	3.063

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H16	C31[3]	3.288	H16	H3[3]	3.091
H16	H29[3]	3.127	H16	H30[3]	2.655
H17	H6[7]	3.372	H17	H20[7]	3.532
H17	H21	3.259	H17	H22[7]	2.970
H18	O3[1]	2.849	H18	C14[7]	3.514
H18	H2[7]	3.185	H18	H6[7]	2.986
H18	H20[7]	3.404	H19	O6	3.563
H19	C6	3.310	H19	C9	3.187
H19	C10	3.039	H19	C11	3.110
H19	C14	3.298	H19	C18	3.218
H19	H10	3.515	H20	C6	3.594
H20	C31[3]	3.595	H20	H10	2.872
H20	H14	3.028	H20	H17[3]	3.532
H20	H18[3]	3.404	H20	H29[3]	3.514
H20	H30[3]	2.888	H21	C27	3.233
H21	H10	2.275	H21	H14	3.376
H21	H17	3.259	H21	H29	3.334
H22	O6[3]	3.266	H22	O36[3]	3.300
H22	C31[3]	3.472	H22	H11[3]	3.173
H22	H17[3]	2.970	H22	H29[3]	2.732
H22	H30[3]	3.382	H22	H38[10]	3.497
H23	O6[3]	3.448	H23	O36[3]	3.492
H23	O37[10]	3.245	H23	H1[10]	3.550
H23	H26[10]	3.325	H23	H38[10]	2.931
H24	O2[2]	3.059	H24	O36[3]	3.210
H24	C3[10]	3.452	H24	H1[10]	2.735
H24	H8[10]	3.108	H24	H11[3]	3.396
H24	H38[10]	3.222	H25	S2[1]	3.212
H25	O1[1]	2.527	H25	O3[1]	3.059
H25	O8[11]	3.241	H25	C18[12]	3.347
H25	H4[12]	3.425	H25	H7[12]	2.498
H26	O7[12]	3.325	H26	O8[11]	3.366
H26	C11[12]	3.563	H26	C18[12]	3.143
H26	H4[12]	3.246	H26	H7[12]	2.385
H26	H23[12]	3.325	H26	H31[12]	3.047
H27	O3[1]	3.059	H27	O7[12]	3.583
H27	O16[7]	2.877	H27	C11[12]	3.444

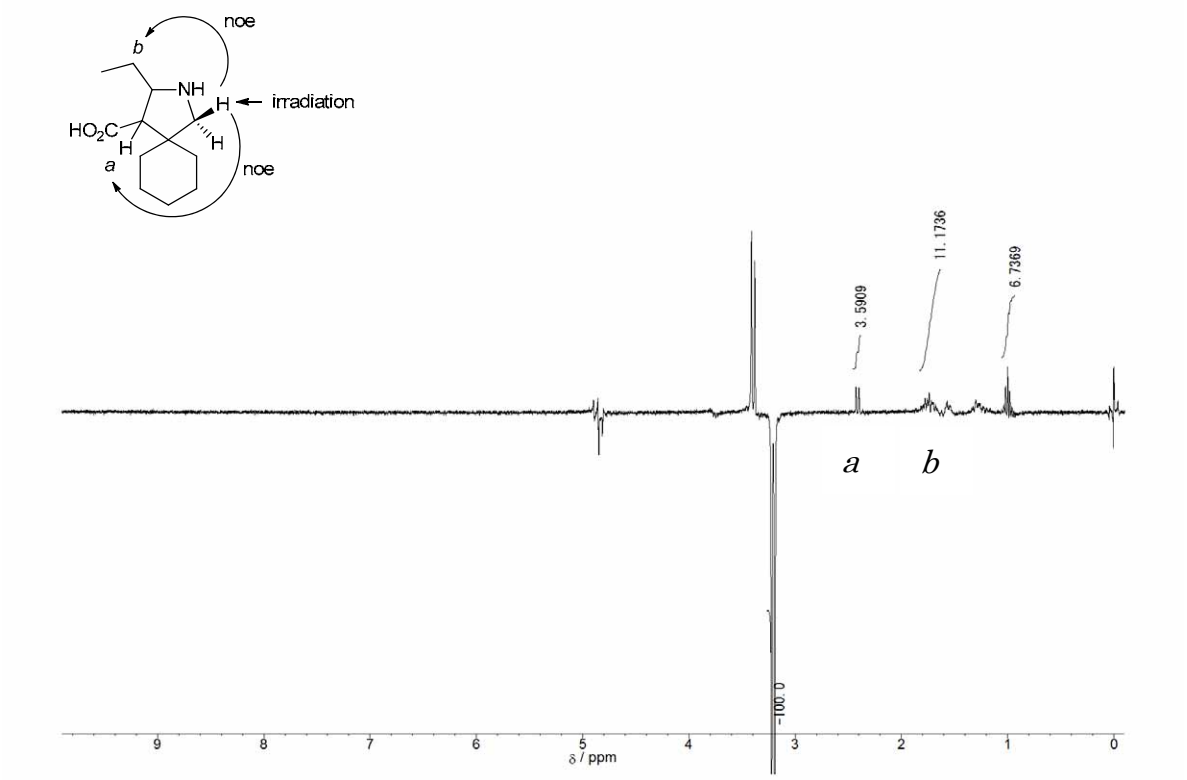
Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

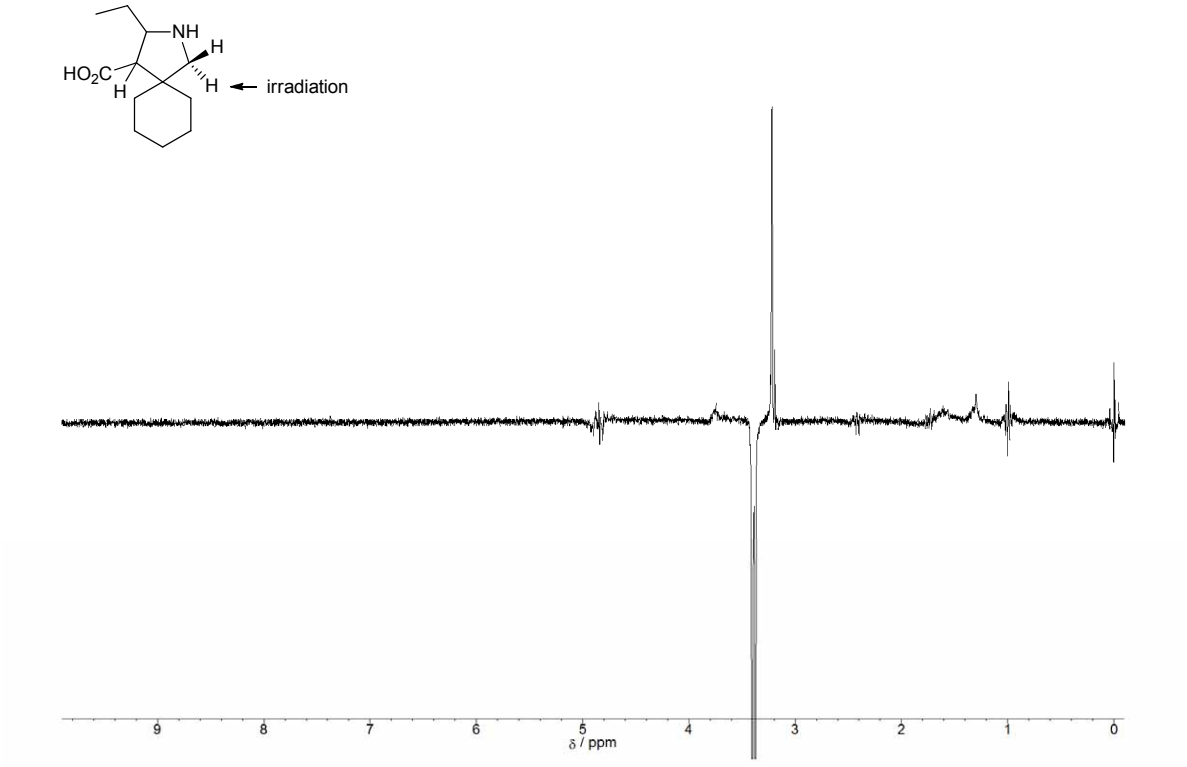
atom	atom	distance	atom	atom	distance
H27	C18[12]	3.550	H27	H4[12]	2.762
H27	H7[12]	2.967	H27	H14[7]	3.464
H28	C3	3.092	H28	C7	3.047
H28	C8	3.352	H28	C12	3.380
H28	C22	2.919	H28	C30	3.542
H28	H1	3.552	H28	H3	3.449
H28	H8	3.290	H28	H31[12]	3.498
H29	C12	3.529	H29	H11	3.122
H29	H16[7]	3.127	H29	H20[7]	3.514
H29	H21	3.334	H29	H22[7]	2.732
H30	O5[7]	3.107	H30	O16[7]	3.507
H30	C19[7]	3.532	H30	H16[7]	2.655
H30	H20[7]	2.888	H30	H22[7]	3.382
H31	O16[9]	3.364	H31	O35[9]	3.470
H31	C22[10]	3.555	H31	H8[10]	2.921
H31	H26[10]	3.047	H31	H28[10]	3.498
H38	O5	3.51(6)	H38	O6[11]	3.27(7)
H38	O7[11]	3.01(6)	H38	O36[11]	1.63(6)
H38	N32	3.39(6)	H38	N34[11]	3.58(7)
H38	C3	3.09(7)	H38	C8	3.59(7)
H38	C15[11]	2.59(6)	H38	C28[12]	3.40(6)
H38	H1	2.605	H38	H22[12]	3.497
H38	H23[12]	2.931	H38	H24[12]	3.222

Symmetry Operators:

(1) X+1,Y,Z-1
(2) X-1,Y,Z+1
(3) X-1,Y,Z
(4) X,Y-1,Z+1
(5) X,Y,Z-1
(6) X,Y,Z+1
(7) X+1,Y,Z
(8) X,Y+1,Z-1
(9) X,Y+1,Z
(10) X-1,Y+1,Z
(11) X,Y-1,Z
(12) X+1,Y-1,Z

(G) noe analysis of 1c





(H) References

1) G. A. Olah and M. Arvanaghi, *Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 878.
2) H. Shechter and F. Conrad, *J. Am. Chem. Soc.*, 1953, **75**, 5610.
3) N. J. A. Martin, X. Cheng and B. List, *J. Am. Chem. Soc.*, 2008, **130**, 13862.
4) (*a*) R. G. Pritchard, R. J. Stoodley and W.-H. Yuen, *Org. Biomol. Chem.*, 2005, **3**, 162; (*b*) J. K. Addo, P. Teesdale-Spittle and J. O. Hoberg, *Synthesis*, 2005, **12**, 1923.
5) H. Ishikawa, T. Suzuki and Y. Hayashi, *Angew. Chem. Int. Ed.*, 2009, **48**, 1304.
6) A. Palmieri1, S. V. Ley, A. Polyzos, M. Ladlow and I. R. Baxendale, *Beilstein J. Org. Chem.*, 2009, **5**, No. 23. doi:10.3762/bjoc.5.23