Organocatalytic Highly Enantioslective Synthesis of Secondary α-Hydroxyphosphonates

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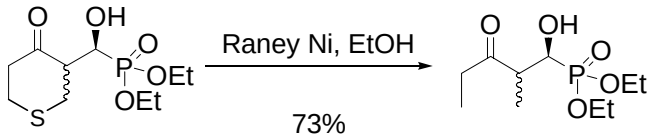
General procedure for the synthesis of secondary α-hydroxyphosphonates: To a stirred solution of the diethyl formylphosphonate hydrate (**4**, 92.0 mg, 0.5 mmol) in the ketone (0.6 mL) was added L-prolinamide (2.9 mg, 0.025 mmol, 5 mol %) at 0 °C. The reaction mixture was stirred at this temperature for 24 h. The solvent was evaporated under vacuum and the residue was purified by flash chromatography (EtOAc) over silica gel to furnish the desired secondary α-hydroxyphosphonate as a pure compound, which is characterized by its NMR spectroscopic data, such as, ^{1}H, ^{13}C, COSY and NOE.

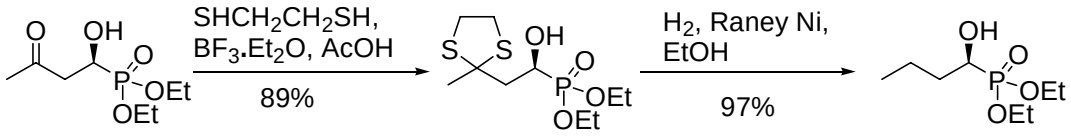
Desulfurization of diethyl [hydroxy-(4-oxo-tetrahydrothiopyran-3-yl)methyl]-phosphonate (**6k**)



6k **6l**

To a solution of compound **6k** (100 mg, 0.35 mmol) in EtOH (10 mL) at room temperature was added activated Raney nickel (0.6 g). The mixture was stirred at room temperature for 30 min and then passed through a Celite pad. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (EtOAc) to give compound **6l** as a colorless oil (65 mg, 73%).

Synthesis of diethyl (*S*)-(1-hydroxybutyl)phosphonate (**7**)



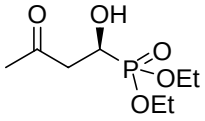
6a **A** **7**

Diethyl (*S*)-[1-hydroxy-2-(2-methyl-1,3-dithiolan-2-yl)ethyl]phosphonate (**A**): To a stirred solution of diethyl (*S*)-(1-hydroxy-3-oxobutyl)phosphonate (224 mg, 1.0 mmol),

1,2-ethanedithiol (376 mg, 4.0 mmol), and acetic acid (2.5 mL) was added $BF_3{\cdot}Et_2O$ (48%, 0.2 mL) at room temperature. The mixture was then stirred at the same temperature for 3 h. After which, acetic acid was removed under high vacuum at 40 °C and the residue was purified by flash column chromatography (EtOAc) over silica gel to give compound **A** (267 mg, 89%) as a colorless oil.

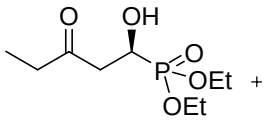
Diethyl (*S*)-(1-hydroxybutyl)phosphonate (7): To a stirred solution of compound **A** (250 mg, 0.83 mmol) in EtOH (10 mL) was added activated Raney nickel (1.5 g). The mixture was heated at 35 °C under an atmosphere of hydrogen for a period of 6 h. The reaction mixture was then passed through a Celite pad and the solvent was removed under reduced pressure at 40 °C to give compound **7** as a colorless oil (170 mg, 97%). $[\alpha]_D^{20}$ +20° (*c* 0.2, MeOH) [Lit.[17b] $[\alpha]_D^{20}$ +24° (*c* 0.6, MeOH)].

^{1}H and ^{13}C NMR data of compounds 6a-l, 7, and compound A.

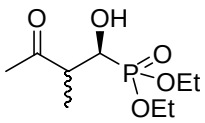


6a

Diethyl (1-hydroxy-3-oxobutyl)phosphonate (Table 2, entry 1): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28-1.35 (m, 6H), 2.21 (s, 3H), 2.78-2.93 (m, 2H), 4.13-4.18 (m, 4H), 4.43 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (2C, d, *J* = 2.6 Hz), 30.9, 44.8 (d, *J* = 1.9 Hz), 63.2 (2C, d, *J* = 6.8 Hz), 64.0 (d, J_{cp} = 168.0 Hz), 207.1 (d, *J* = 15.6 Hz).

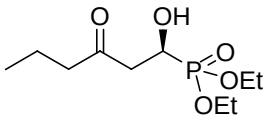


6b



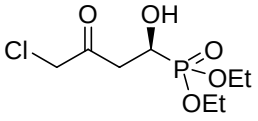
6b'

Diethyl (1-hydroxy-3-oxopentyl)phosphonate and **Diethyl (1-hydroxy-2-methyl-3-oxobutyl)phosphonate (Table 2, entry 2)** (Regioisomer mixture): Major regioisomer **6b** :^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.0 Hz, 3H), 1.29-1.34 (m, 6H), 2.48 (q, *J* = 7.5 Hz, 2H), 2.73-2.89 (m, 2H), 4.11-4.15 (m, 4H), 4.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.7, 16.6 (2C, *J* = 3.3 Hz), 37.0 (d, *J* = 1.5 Hz), 43.6 (d, *J* = 2.9 Hz), 63.3 (2C, *J* = 7.6 Hz), 64.0 (d, J_{cp} = 168.0 Hz), 209.8 (d, *J* = 15.3 Hz). Minor regioisomer **6b′**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 7.0 Hz, 3H), 1.29-1.34 (m, 6H), 2.22 (s, 3H), 3.03 (m, 1H), 3.98 (m, 1H), 4.11-4.15 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (d, *J* = 6.3 Hz), 16.7 (2C, d, *J* = 4.3 Hz), 30.1, 47.2, (d, *J* = 3.9 Hz), 62.9 (2C, d, *J* = 7.1 Hz), 70.5 (d, J_{cp} = 162.0 Hz), 212.9 (d, *J* = 10.5 Hz).



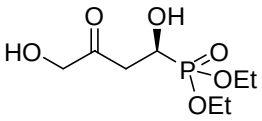
6c

Diethyl (1-hydroxy-3-oxohexyl)phosphonate (Table 2, entry 3): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3H), 1.24-1.37 (m, 6H), 1.58 (m, 2H), 2.45 (m, 2H), 2.86 (m, 2H), 4.16-4.22 (m, 4H), 4.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 16.7 (2C, d, *J* = 5.8 Hz), 17.2, 43.7, 45.6 (d, *J* = 1.4 Hz), 63.1 (2C, d, *J* = 6.8 Hz), 64.2 (d, J_{cp} = 168.8 Hz), 209.9.



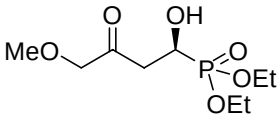
6d

Diethyl (4-chloro-1-hydroxy-3-oxobutyl)phosphonate (Table 2, entry 4): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33-1.39 (m, 6H), 2.90-3.01 (m, 1H), 3.08 (dd, *J* = 17.1, 8.1 Hz, 1H), 4.14-4.25 (m, 6H), 4.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (2C, d, *J* = 6.0 Hz), 41.7 (d, *J* = 2.9 Hz), 49.1 (d, *J* = 2.3 Hz), 63.5 (2C, d, *J* = 7.2 Hz), 64.2 (d, J_{cp} = 167.9 Hz), 200.7 (d, *J* = 15.8 Hz).



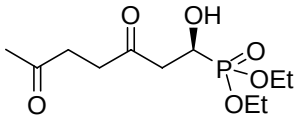
6e

Diethyl (1,4-dihydroxy-3-oxobutyl)phosphonate (Table 2, entry 5): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32-1.40 (m, 6H), 2.70-2.98 (m, 2H), 4.10-4.29 (m, 4H), 4.32 (s, 2H), 4.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2 (2C, d, *J* = 5.4 Hz), 40.7 (d, *J* = 2.6 Hz), 63.8 (2C, d, *J* = 6.0 Hz), 64.4 (d, J_{cp} = 167.6 Hz), 69.7, 208.5 (d, *J* = 14.9 Hz).



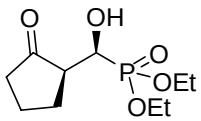
6f

Diethyl (1-hydroxy-4-methoxy-3-oxobutyl)phosphonate (Table 2, entry 6): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32-1.35 (m, 6H), 2.80-2.97 (m, 2H), 3.42 (s, 3H), 4.07 (s, 2H), 4.15-4.17 (m, 4H), 4.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (2C, d, *J* = 7.1 Hz), 40.6 (d, *J* = 2.5 Hz), 59.6, 63.2 (2C, d, *J* = 6.1 Hz), 63.8 (d, J_{cp} = 168.2 Hz), 78.2 (d, *J* = 2.0 Hz), 207.1 (d, *J* = 15.3 Hz).



6g

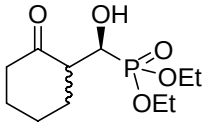
Diethyl (1-hydroxy-3,6-dioxoheptyl)phosphonate (Table 2, entry 7): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33-1.37 (m, 6H), 2.19 (s, 3H), 2.69-2.80 (m, 4H), 2.90-2.94 (m, 2H), 4.16-4.22 (m, 4H), 4.44 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.9 (2C, d, *J* = 5.5 Hz), 30.2, 37.2 (2C, d, *J* = 6.8 Hz), 44.2 (d, *J* = 2.0 Hz), 63.3 (2C, d, *J* = 7.5 Hz), 64.4 (d, J_{cp} = 168.4 Hz), 207.2, 207.9 (d, *J* = 168.5 Hz).



6h

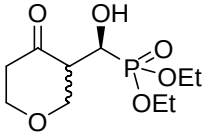
Diethyl [hydroxyl-(2-oxocyclopentyl)methyl]phosphonate (Table 2, entry 8): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.3 Hz, 6H), 1.73 (m, 1H), 2.03-2.05 (m, 2H), 2.06-2.14 (m, 1H), 2.14-2.22 (m, 1H), 2.23-2.35 (m, 1H), 2.35-2.43(m, 1H), 4.10-4.15 (m, 4H), 4.50 (dd, *J* = 7.0,

2.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (2C, d, *J* = 5.8 Hz), 20.9, 23.4, 38.5 (d, *J* = 2.3 Hz), 50.5 (d, *J* = 3.3 Hz), 62.8 (d, *J* = 7.1 Hz), 63.2 (d, *J* = 6.8 Hz), 65.6 (d, J_{cp} = 167.3 Hz), 219.3 (d, *J* = 17.1 Hz).



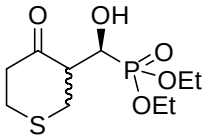
6i

Diethyl [hydroxy-(2-oxocyclohexyl)methyl]phosphonate (Table 2, entry 10): ^{1}H NMR (500 MHz, $CDCl_3$, diastereomer mixture): δ = 1.33-1.37 (m, 6H), 1.67-1.77 (m, 2H), 1.82-1.95 (m, 2H), 2.10 (m, 1H), 2.31-2.47 (m, 3H), 2.82 (anti) and 2.90 (syn) (m, 1H), 4.04 (syn) and 4.64 (anti) (m, 1H), 4.13-4.20 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8 (2C, d, J = 5.3 Hz), 20.3 (anti) and 21.2 (syn), 29.7 (anti) and 28.3 (syn), 31.9 (anti) and 30.6 (syn), 47.0 (anti) and 47.7 (syn), 52.2 (d, *J* = 2.9 Hz), 62.9 (syn) (2C, d, *J* = 7.1 Hz) and 63.2 (anti) (2C, d, *J* = 7.1 Hz), 65.4 (anti) (d, J_{cp} = 166.9 Hz) and 66.6 (syn) (d, J_{cp} = 165.9 Hz), 218.7 (anti)(d, *J* = 17.3 Hz) and 219.9 (syn)(d, *J* = 17.1 Hz).



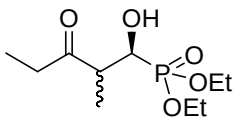
6j

Diethyl [hydroxy-(4-oxo-tetrahydropyran-3-yl)methyl]phosphonate (Table 2, entry 11): ^{1}H NMR (500 MHz, $CDCl_3$, diastereomer mixture): δ = 1.32-1.36 (m, 6H), 2.46-2.51 (m, 1H), 2.61-2.70 (m, 1H), 2.96 (anti) and 3.08 (syn) (m, 1H), 3.44 (anti) and 3.78 (syn) (bs, 1H, -OH), 3.75-3.95 (m, 2H), 4.10-4.72 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (2C, d, *J* = 5.4), 42.9 (anti) and 43.1 (syn), 52.6 (anti) (d, *J* = 4.9 Hz) and 54.0 (syn) (d, *J* = 3.5 Hz), 63.2 (anti) (2C, d, *J* = 7.4 Hz) and 63.5 (syn) (2C, d, *J* =6.8 Hz), 64.0 (anti) (d, J_{cp} = 169.0 Hz) and 65.9 (syn) (d, J_{cp} = 163.9 Hz), 68.6 (anti) (d, *J* = 2.9 Hz) and 70.5 (syn) (d, *J* = 5.32 Hz), 76.9, 206.2 (anti) (d, *J* = 13.7 Hz) and 208.0 (syn) (d, *J* = 13.3 Hz).



6k

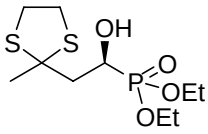
Diethyl [hydroxy-(4-oxo-tetrahydrothiopyran-3-yl)methyl]phosphonate (Table 2, entry 12): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30-1.35 (m, 6H), 2.68-2.82 (m, 2H), 2.89-3.30 (m, 5H), 3.71 (anti) and 3.90 (syn) (m, 1H, -OH), 4.13-4.17 (m, 4H), 4.68 (anti) and 4.37 (syn) (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7,(2C, d, *J* = 5.7 Hz), 30.8, 31.2 (anti) (t, *J* = 9.8 Hz), 33.7 (d, *J* = 5.3 Hz), 44.5 (t, *J* = 8.6 Hz), 54.3 (anti) (d, *J* = 4.8 Hz) and 54.8 (syn) (d, *J* = 3.9 Hz), 63.2 (anti) (d, *J* = 7.1 Hz) and 63.4 (syn) (2C, d, *J* = 7.3 Hz), 65.5 (anti) (d, J_{cp} = 167.9 Hz) and 68.0 (syn) (d, J_{cp} = 162.1 Hz), 208.9 (anti) (d, *J* = 12.4 Hz) and 210.2 (syn) (d, *J* = 11.4 Hz).



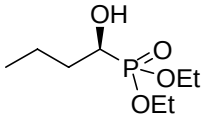
6l

Diethyl (1-hydroxy-2-methyl-3-oxopentyl)phosphonate (6l, Scheme 2): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00-1.06 (m, 3H), 1.16-1.35 (m, 9H), 2.49-2.60 (m, 2H), 2.96-3.06 (m, 1H), 4.30 (anti) and 3.97 (syn) (m, 1H), 4.11-4.17 (m, 4H); ^{13}C NMR (125 MHz,

$CDCl_3$): δ = 7.7 (anti) and 7.5 (syn), 12.5 (syn) and 15.0 (anti) (d, *J* = 8.1 Hz), 16.6 (2C, d, *J* = 5.3 Hz), 36.5 (anti) and 34.9 (syn). 46.9 (anti) and 45.6 (syn), 62.8 (syn) (2C, d, *J* = 7.5 Hz) and 63.2 (syn) (2C, d, *J* = 6.3 Hz), 68.1 (d, *J* = 164.1 Hz), 71.0 (d, J_{cp} = 161.1), 213.9 (anti) (d, *J* = 10.5 Hz) and 216.0 (syn) (d, *J* = 8.5 Hz)



Diethyl [1-hydroxy-2-(2-methyl-1,3-dithiolan-2-yl)ethyl]phosphonate (A): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 6.8 Hz, 6H), 1.84 (s, 3H), 2.32-2.42 (m, 2H), 3.33-3.39 (m, 4H), 4.15-4.22 (m, 4H), 4.36 (t, *J* = 9.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (2C, d, *J* = 2.9 Hz), 33.5, 40.1, 40.4, 45.2 (d, *J* = 1.9 Hz), 62.9 (d, *J* = 6.8 Hz), 63.1 (d, *J* = 6.6 Hz), 65.9 (d, *J* = 19.5 Hz), 67.3 (d, J_{cp} = 166.0 Hz).



7

Diethyl (1-hydroxy-3-oxobutyl)phosphonate (7): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.45 (m, 1H), 1.64-1.74 (m, 3H), 3.87 (m, 1H), 4.14-4.20 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 16.8 (2C, d, *J* = 5.8 Hz), 19.2 (d, *J* = 13.3 Hz), 33.5, 62.8 (2C, d, *J* = 7.1 Hz), 67.9 (d, J_{cp} = 158.8 Hz).

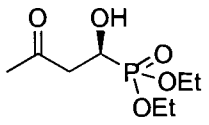
V-DR-77-1H

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

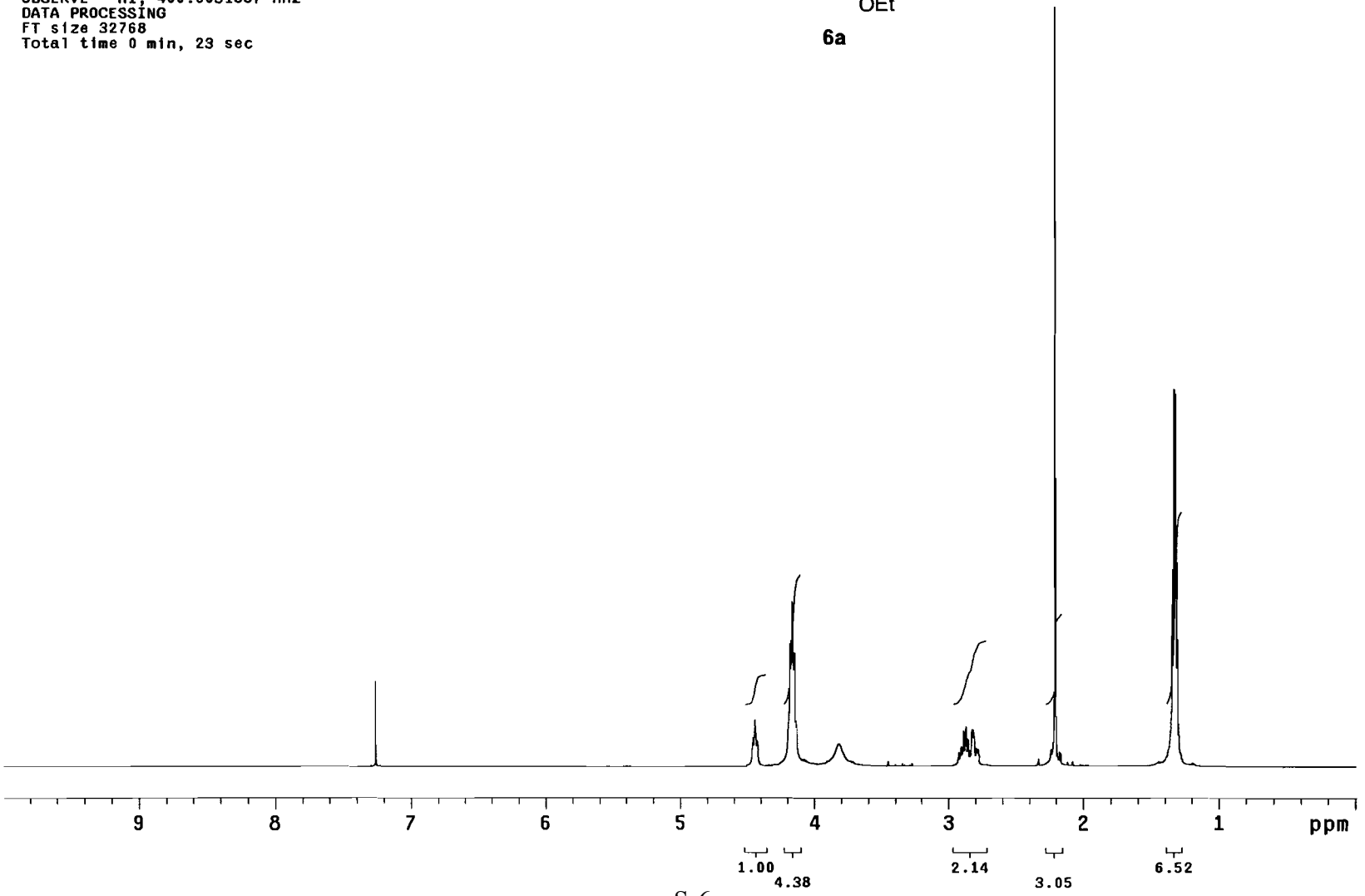
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-acetonephosphonate
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec



6a



V-DR-77-13C

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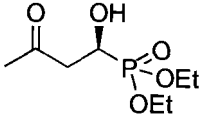
Sample directory:

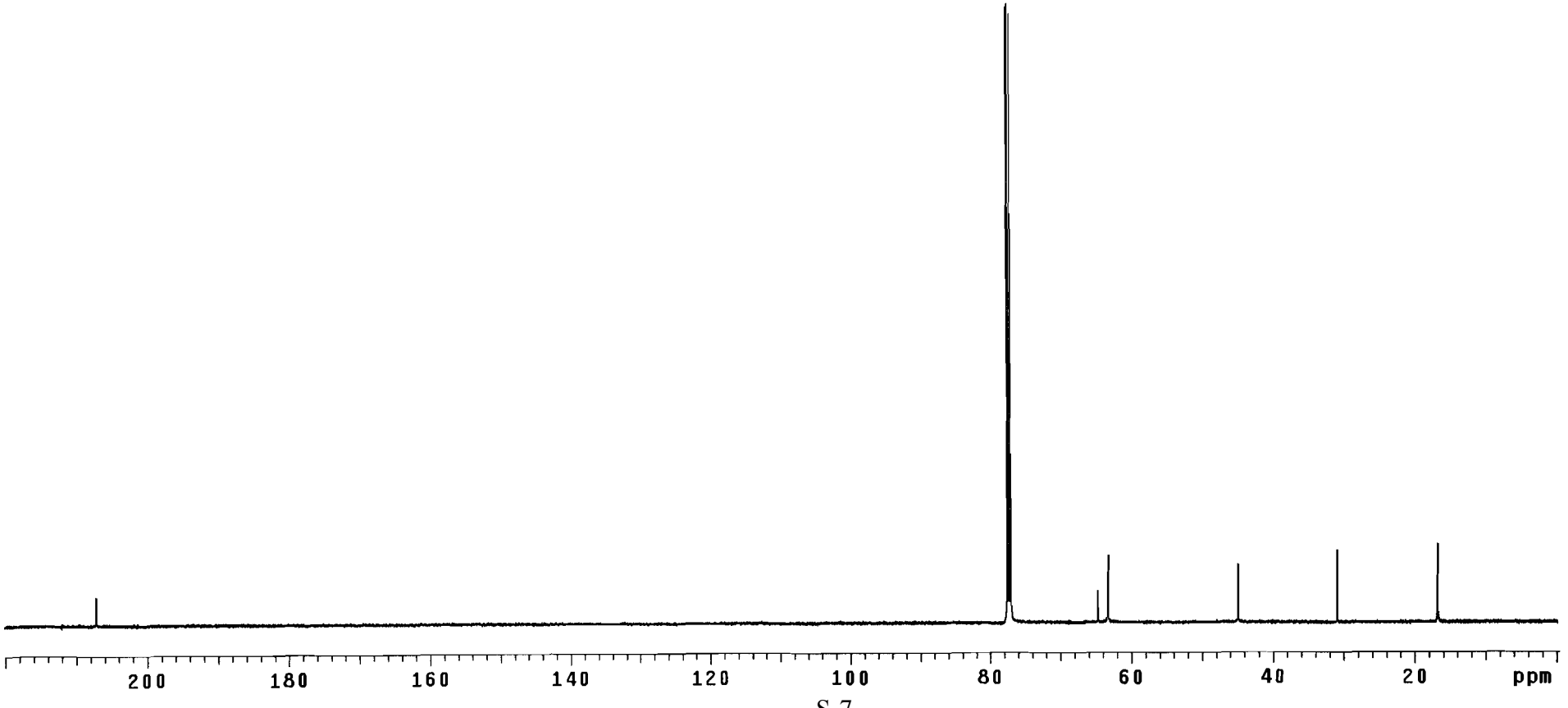
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-acetone-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
15000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 9 hr, 37 min, 20 sec



6a

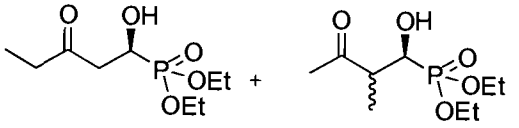


V-DR-134-1H

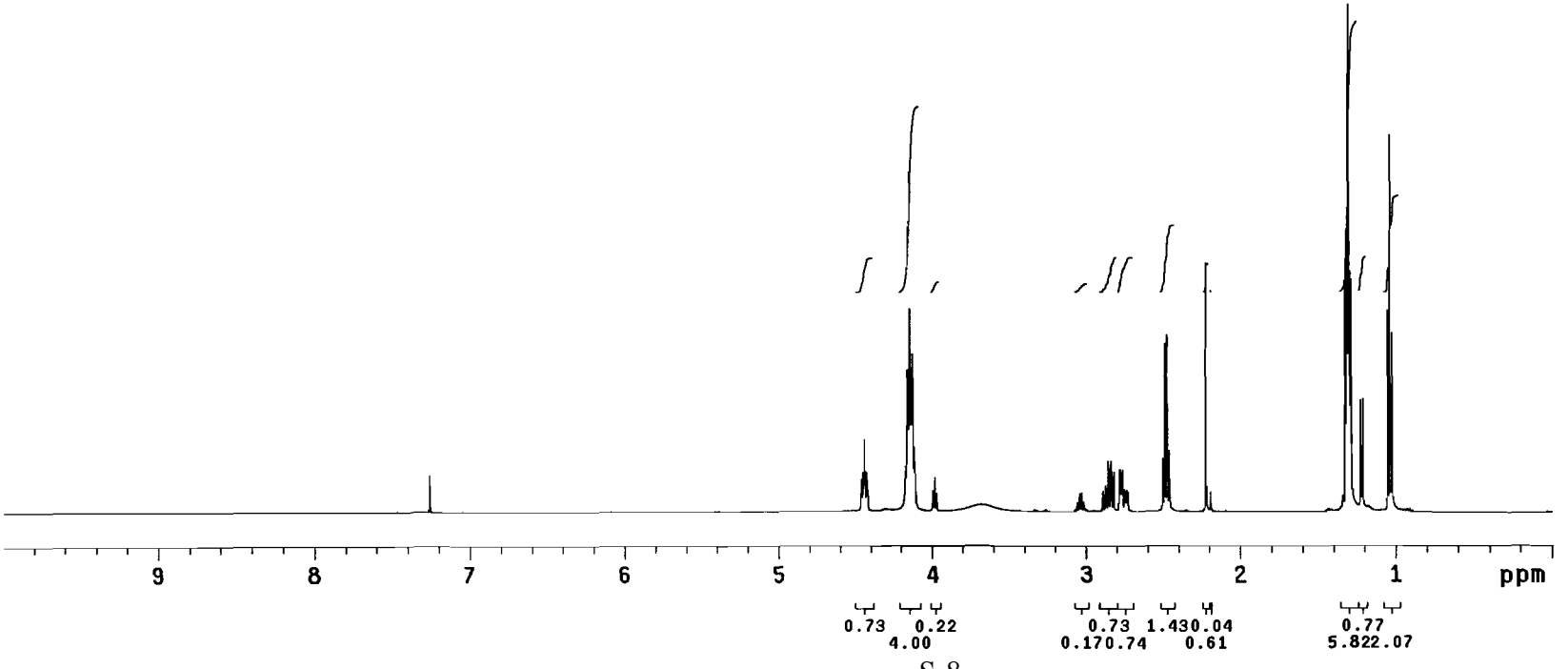
Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: V-DR-Butanone
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec



6b **6b'**



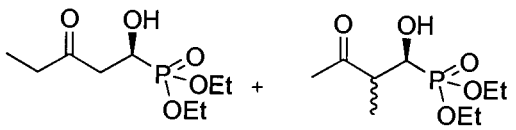
V-DR-134-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

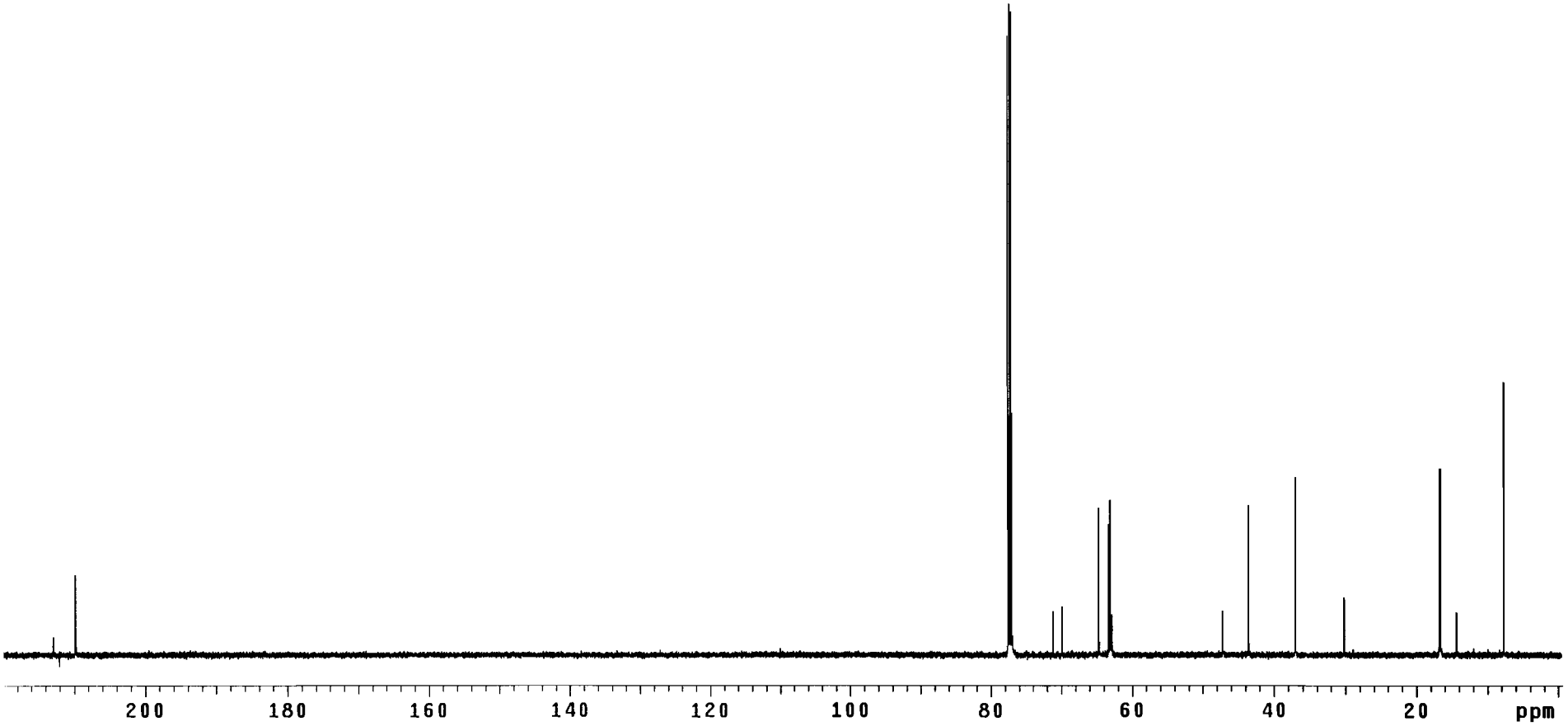
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-64-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
4864 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 6 hr, 24 min, 53 sec



6b **6b'**



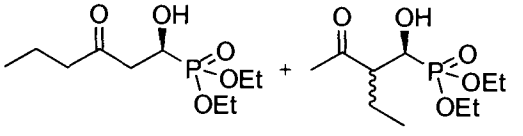
V-DR-141-1H

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

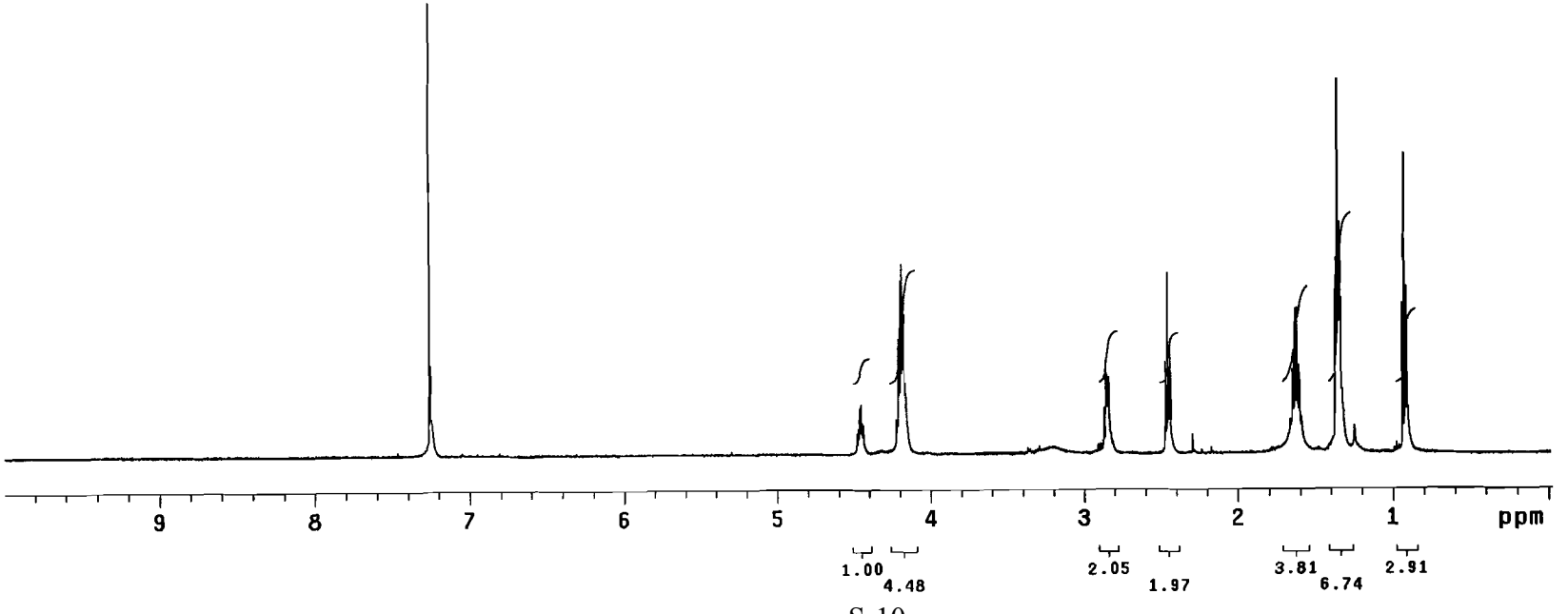
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: IV-DR-141-1Ha
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec



6c **6c'**



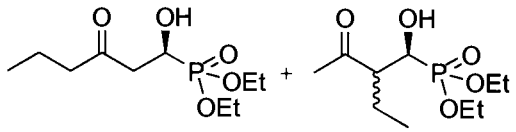
V-DR-141-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: IV-DR-141-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
5000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 3 hr, 12 min, 26 sec



6c **6c'**

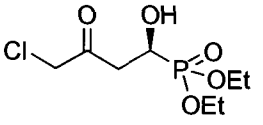
V-DR-74-1H

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

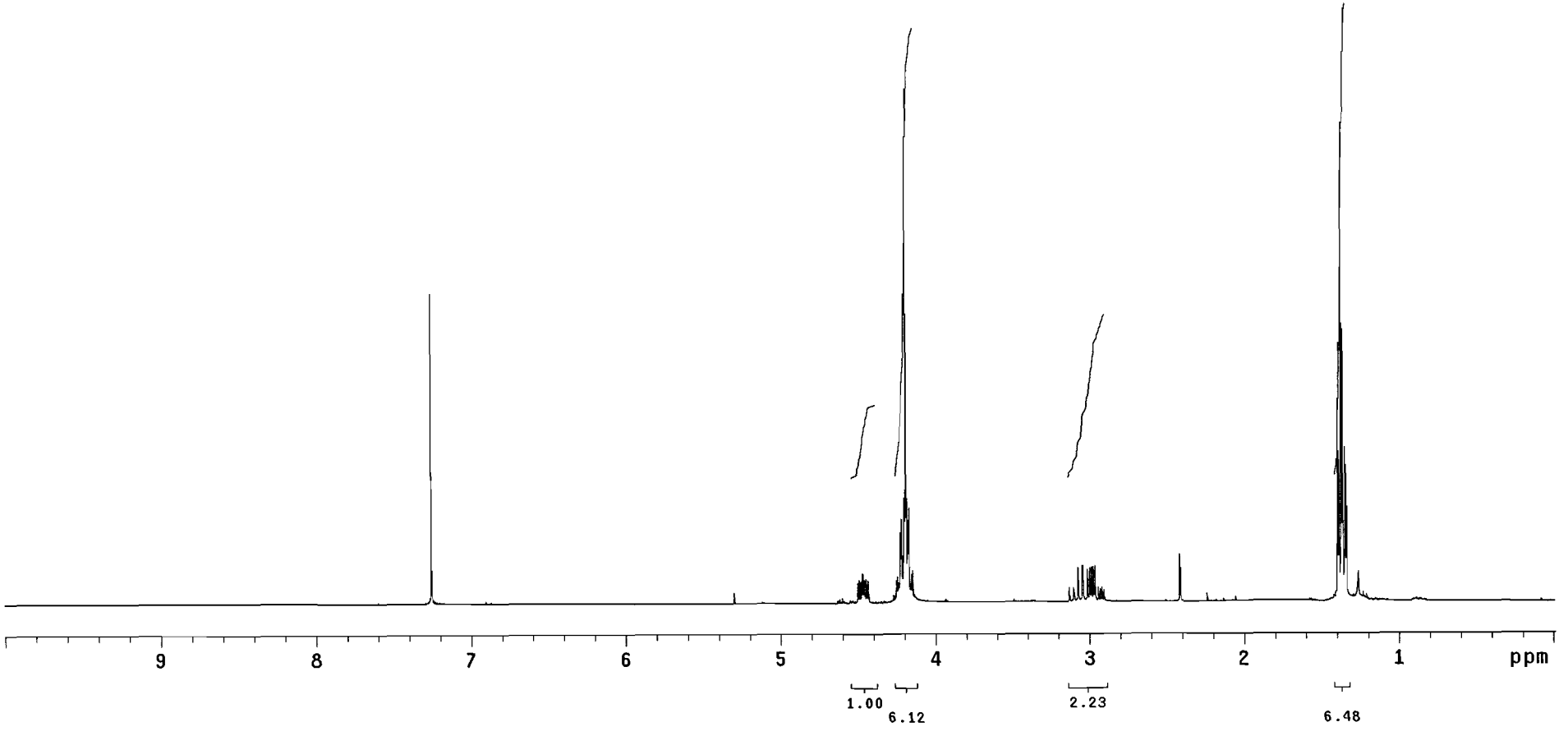
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-74-1H
Mercury-300BB "Varian300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.001 sec
Width 4789.3 Hz
16 repetitions
OBSERVE H1, 299.7452618 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



6d



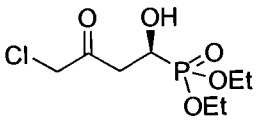
V-DR-74-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "Varian300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18832.4 Hz
15000 repetitions
OBSERVE C13, 75.3709880 MHz
DECOUPLE H1, 299.7467965 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 hr, 8 min, 37 sec



6d

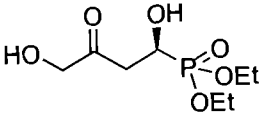
V-DR-59-1H

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

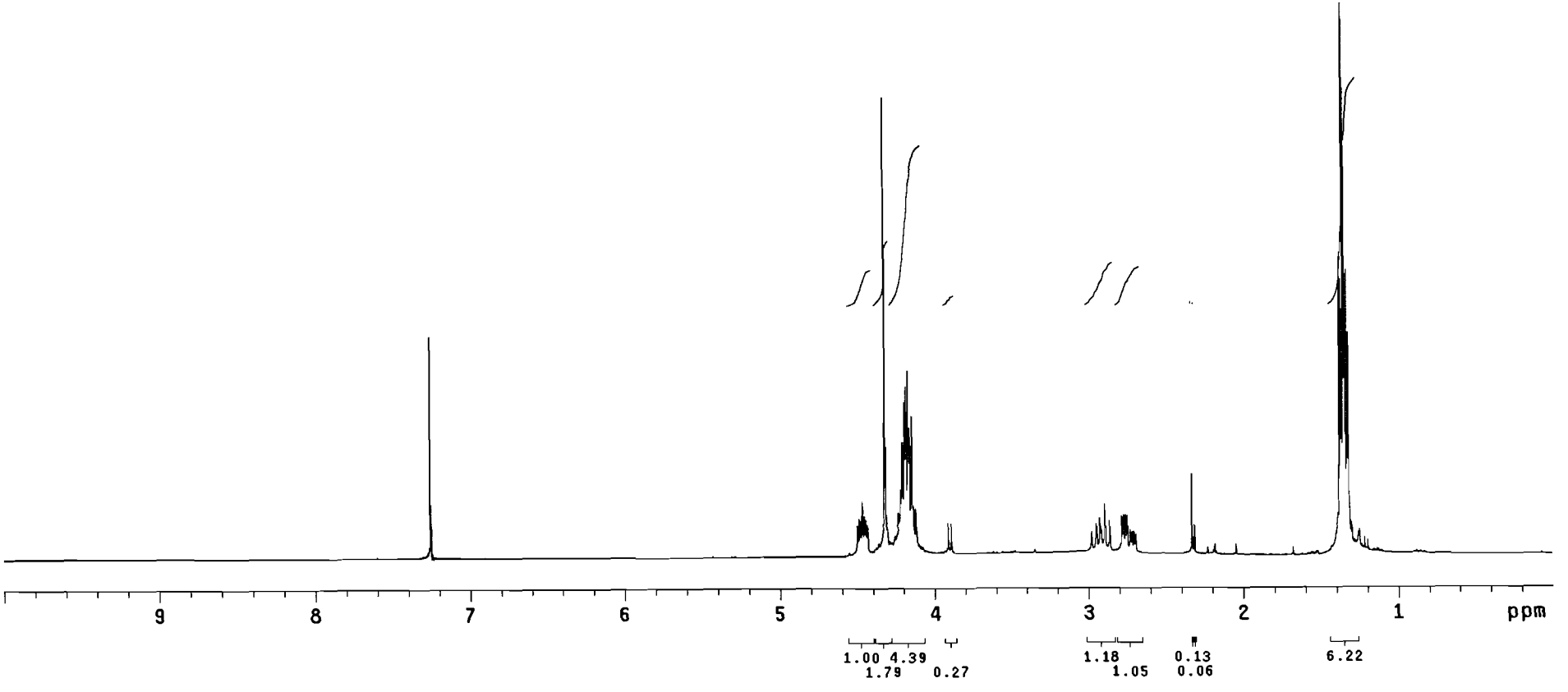
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-56-1H
Mercury-300BB "Varian300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.001 sec
Width 4789.3 Hz
16 repetitions
OBSERVE H1, 299.7452618 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



6e



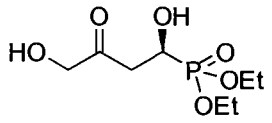
V-DR-59-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

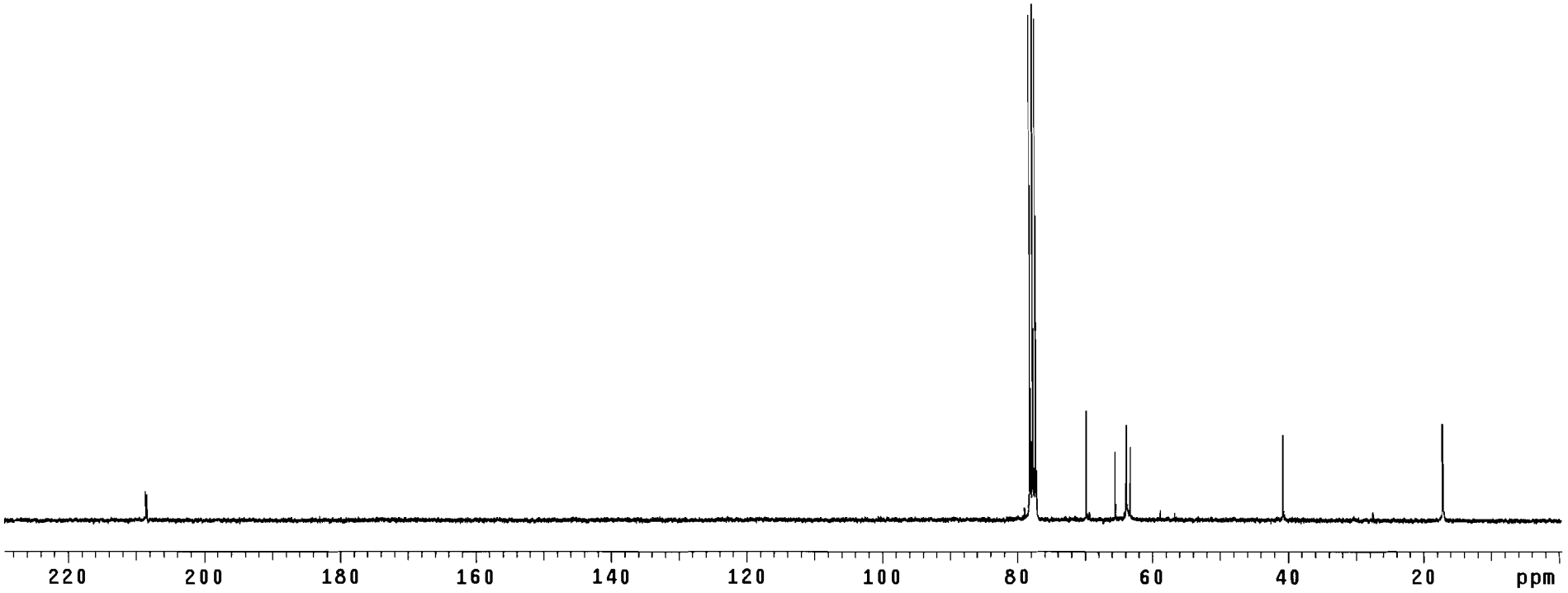
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-56-13C
Mercury-300BB "Varian300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18832.4 Hz
17000 repetitions
OBSERVE C13, 75.3709880 MHz
DECOUPLE H1, 299.7467965 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 13 hr, 45 min, 41 sec



6e

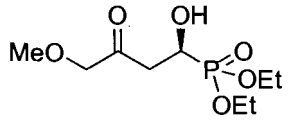


V-DR-62-1H

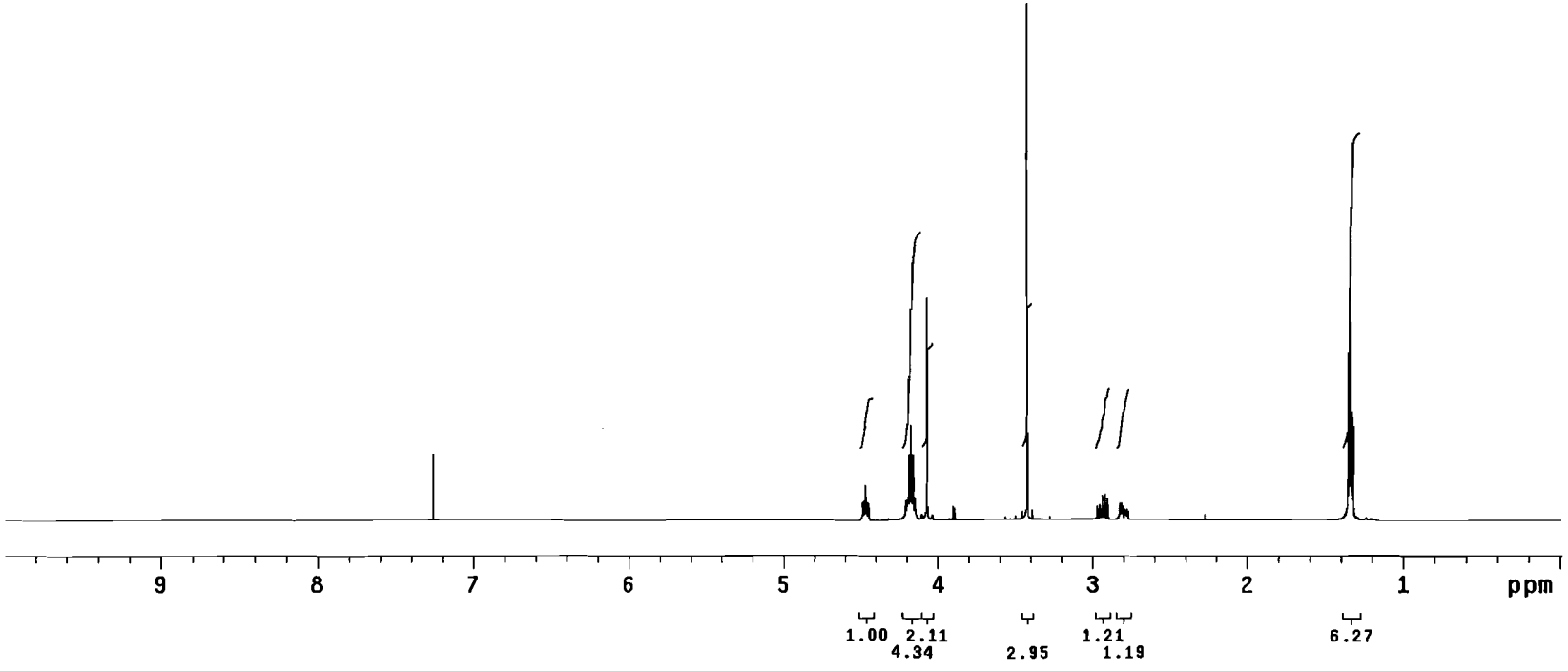
Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: COCl3
Ambient temperature
File: V-DR-62-1H
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
16 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



6f

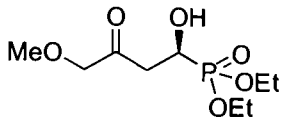


V-DR-62-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-62-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
16000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 10 hr, 15 min, 49 sec



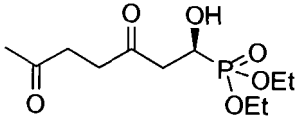
6f

V-DR-31-1H

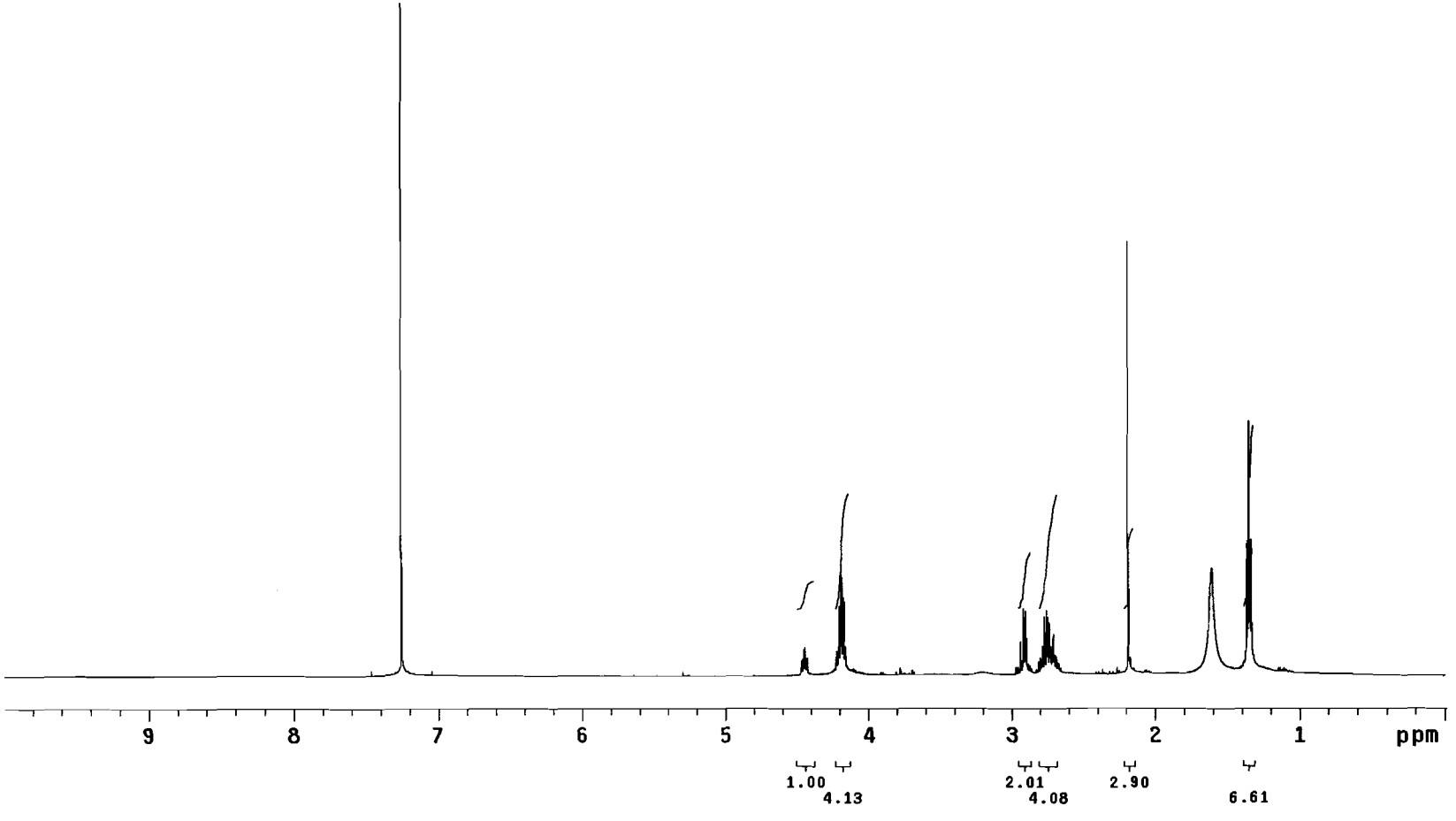
Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: V-DR-28-1H
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
128 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 11 sec



6g



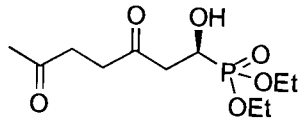
V-DR-31-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:
File: CARBON

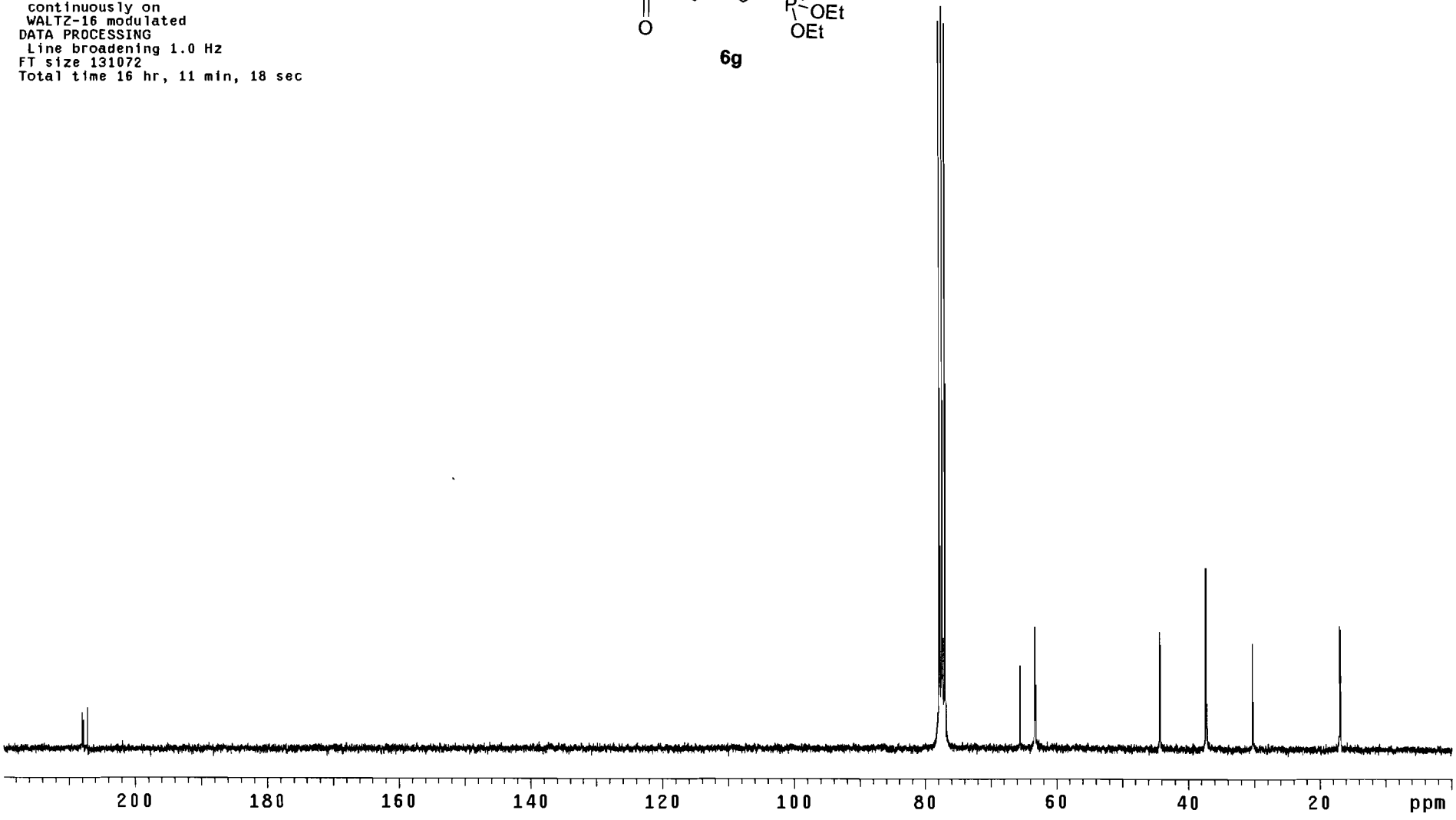
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "Varian300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18832.4 Hz
14144 repetitions
OBSERVE C13, 75.3709880 MHz
DECOUPLE H1, 299.7467965 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 16 hr, 11 min, 18 sec



6g



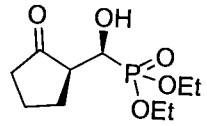
V-DR-27-1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

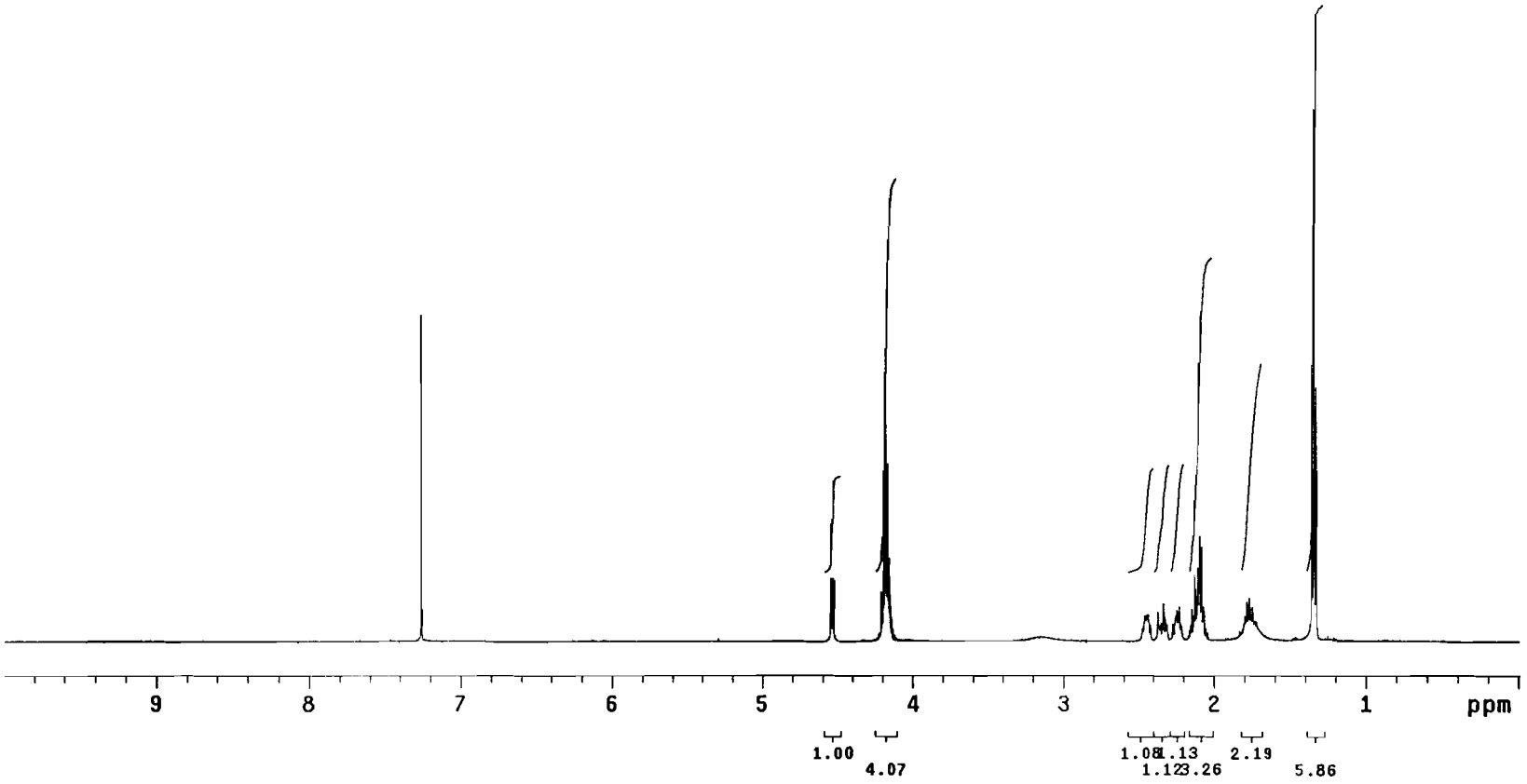
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 36.4 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
4 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 11 sec



6h



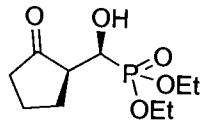
V-DR-27-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

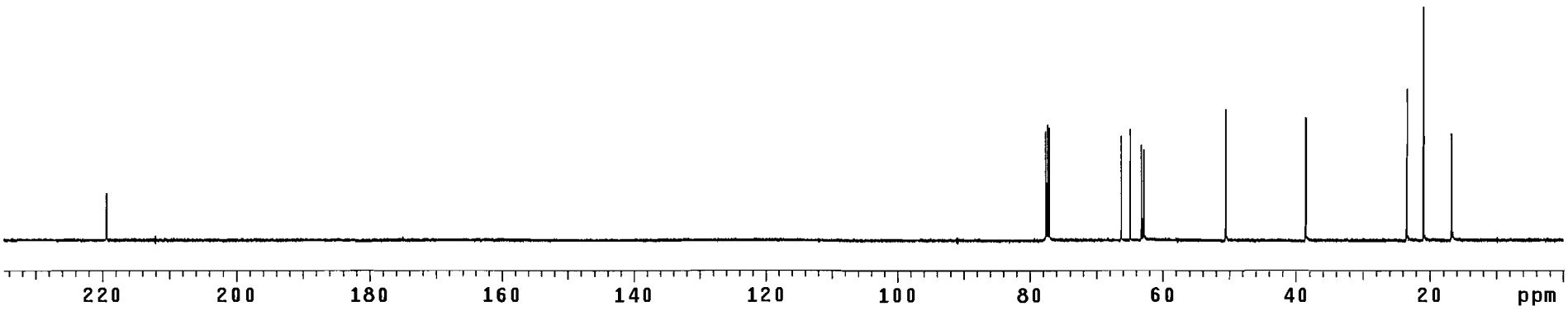
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-27-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
960 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 3 hr, 12 min, 26 sec



6h



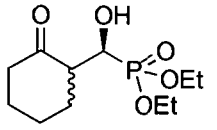
V-DR-46-1H

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

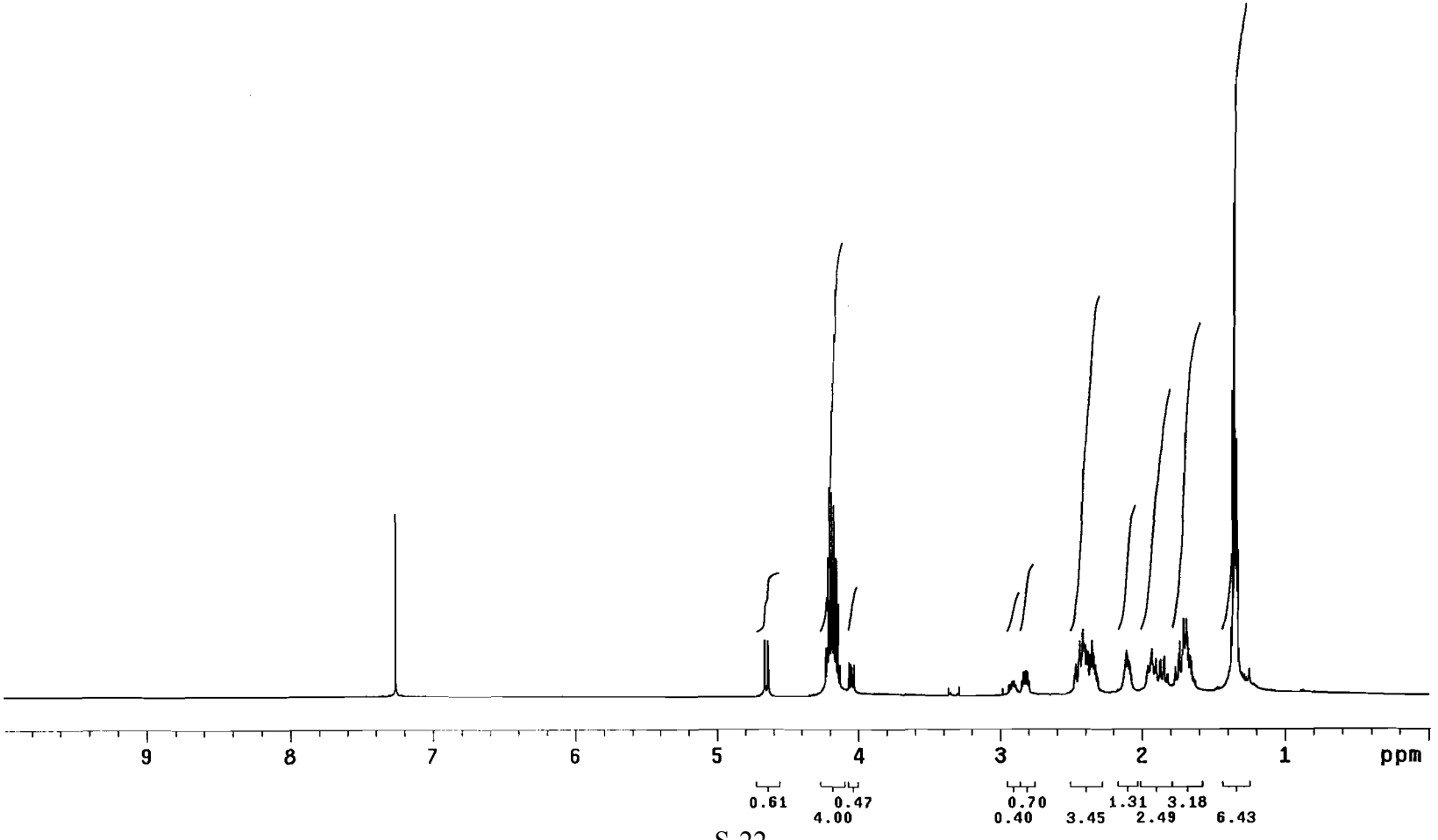
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-cyclohexanone-proton
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec



6i



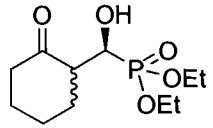
V-DR-46-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

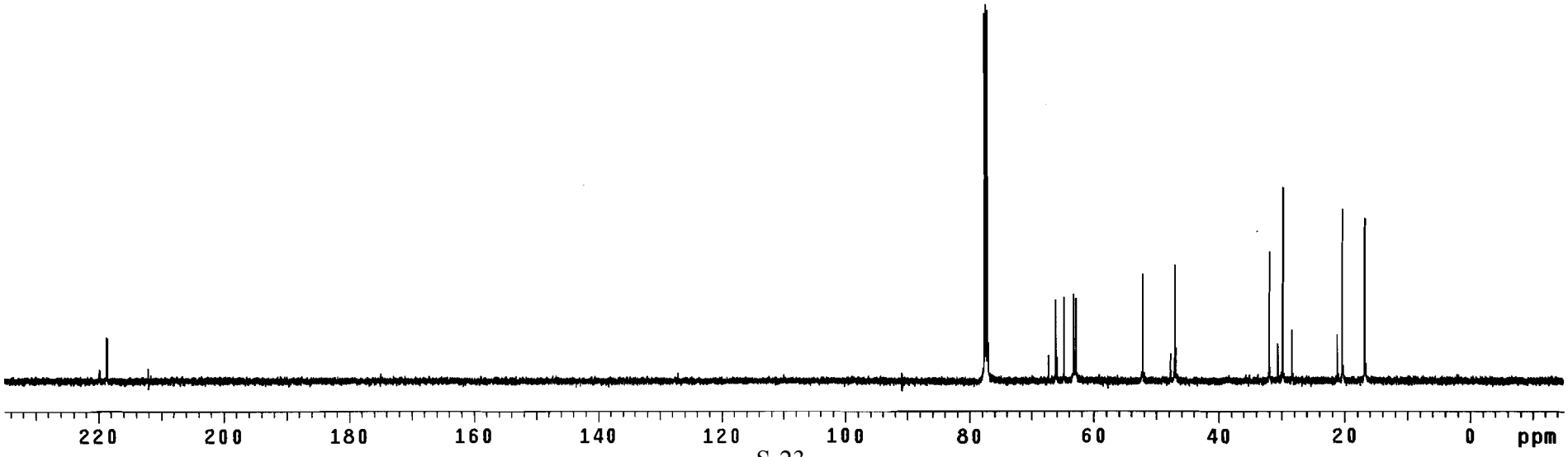
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-50-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3136 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 33 min, 57 sec



6i

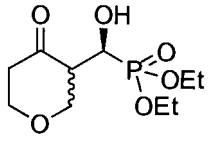


V-DR-45-1H

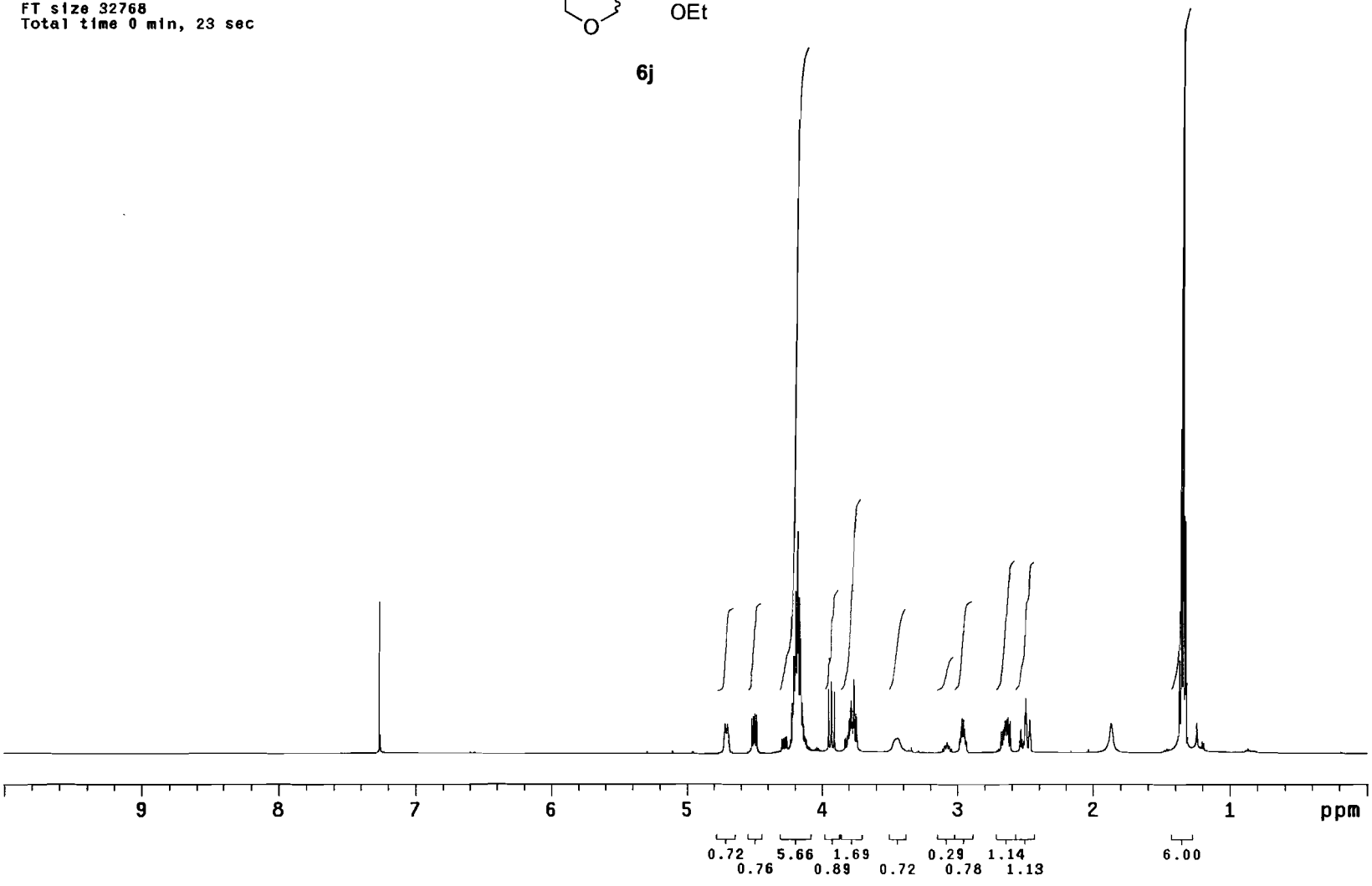
Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: V-DR-45-1H
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec



6j



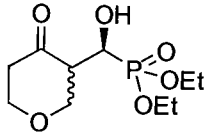
V-DR-45-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

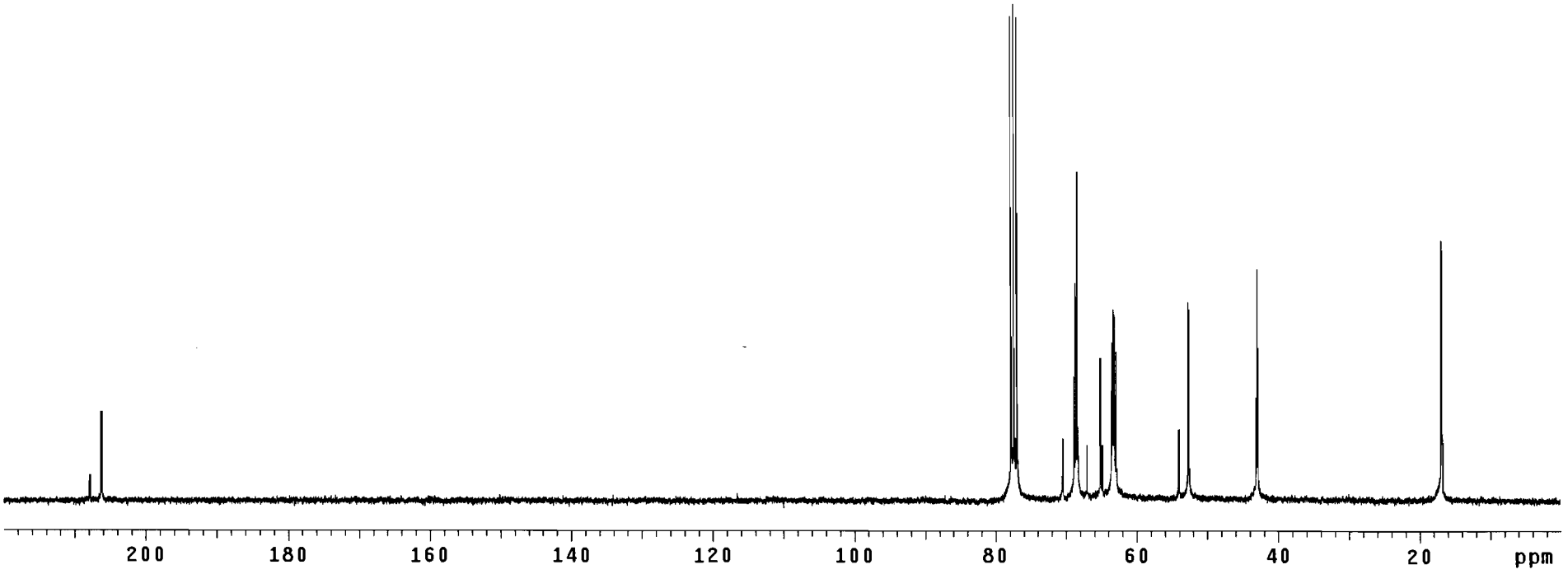
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-38-13C
Mercury-300BB "Varian300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18832.4 Hz
12000 repetitions
OBSERVE C13, 75.3709880 MHz
DECOUPLE H1, 299.7467965 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 42 min, 59 sec



6j



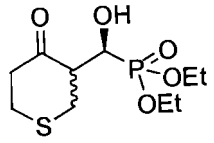
V-DR-44-1H

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:

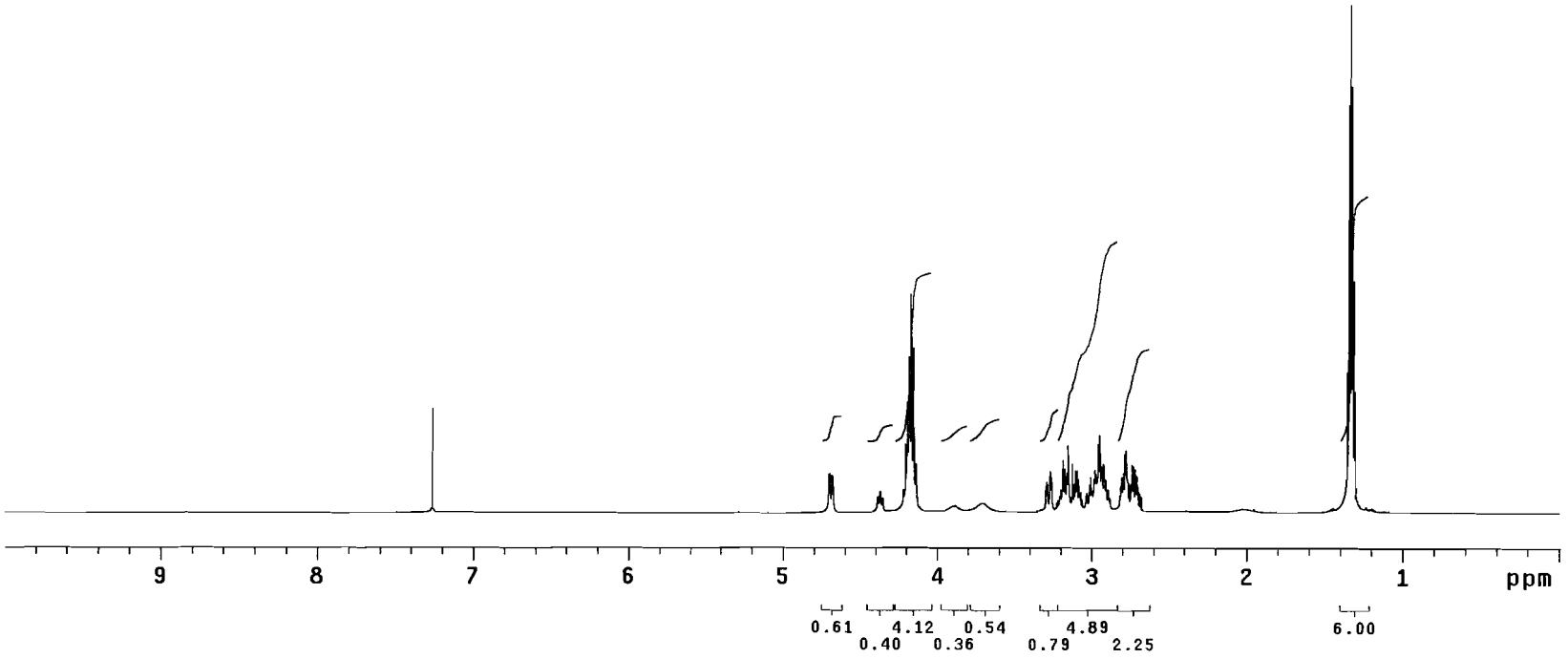
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: V-DR-40-1Ha
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 36.4 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec



6k



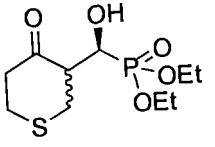
V-DR-44-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

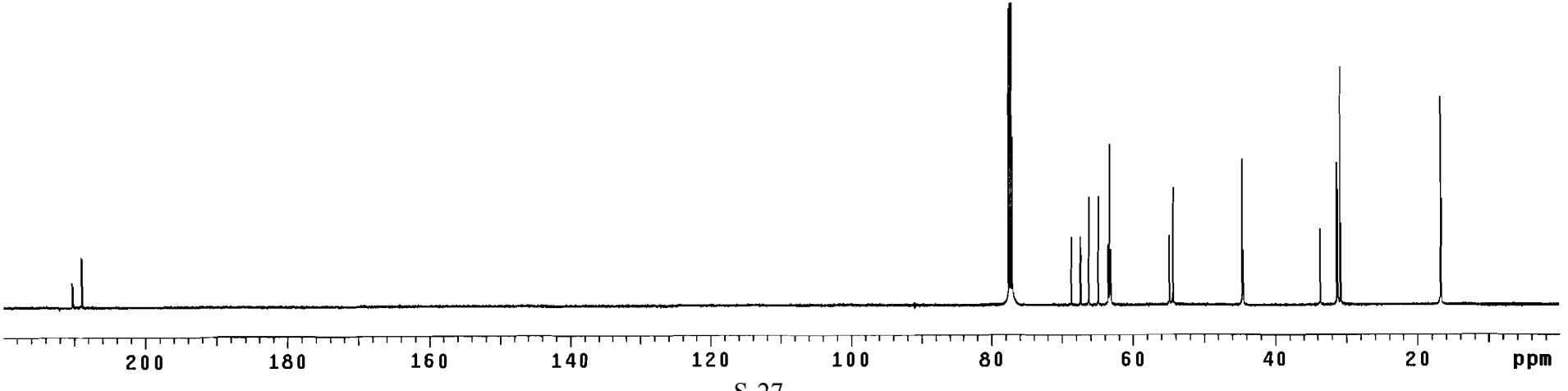
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-40-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
20000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 hr, 49 min, 47 sec



6k



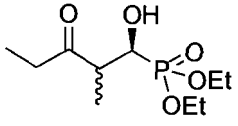
V-DR-84-1H

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
32 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec



6l

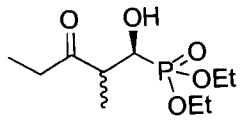
V-DR-84-13Ca

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:
File: CARBON

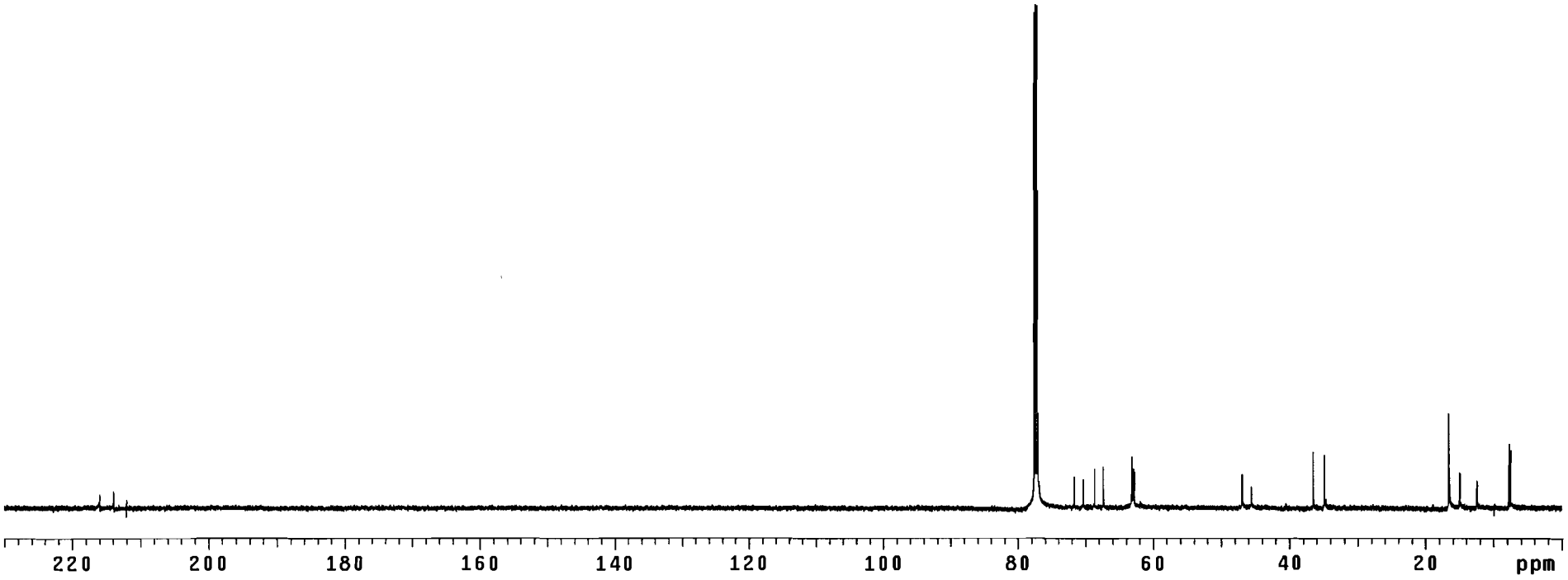
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
22000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 14 hr, 6 min, 46 sec



6l



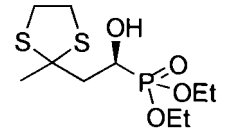
V-DR-75-1H

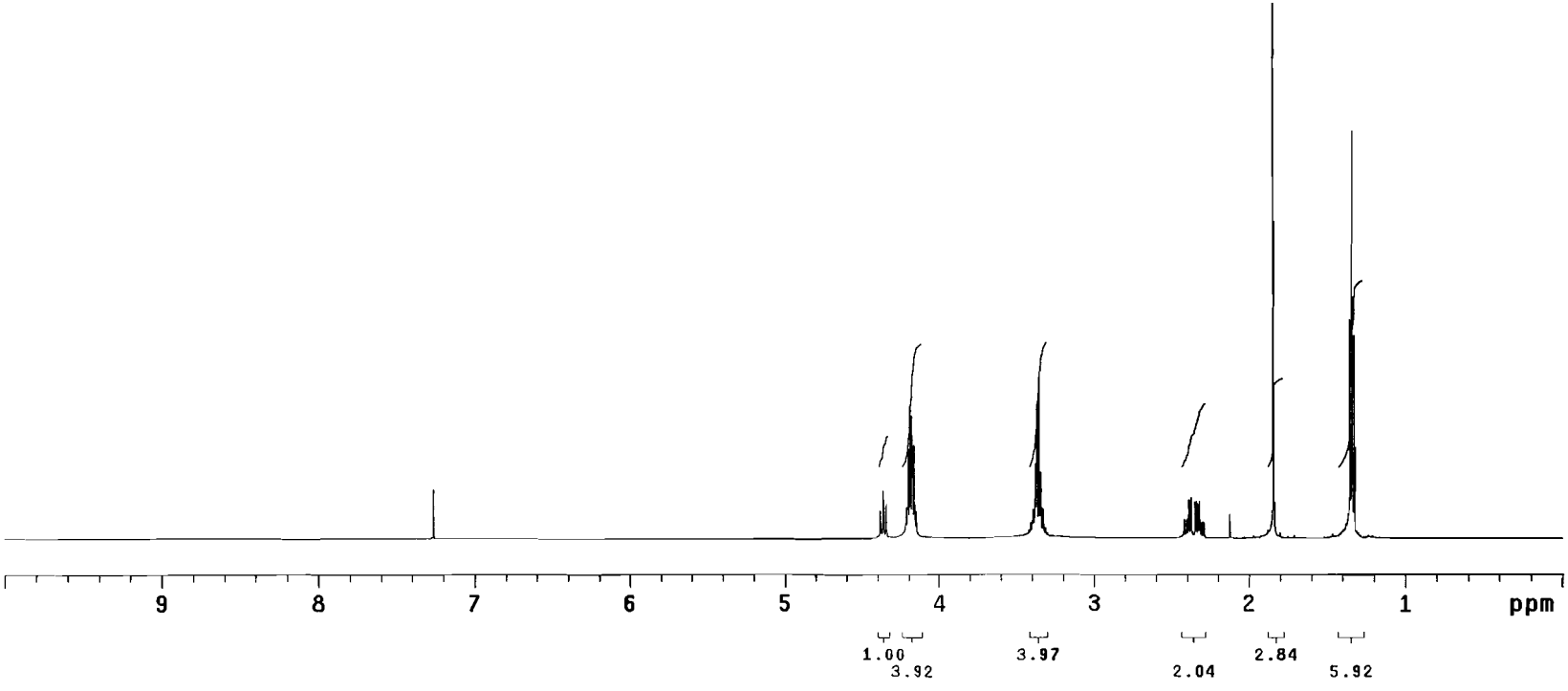
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 36.4 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
16 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec





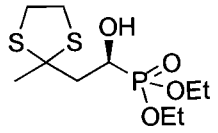
V-DR-75-13C

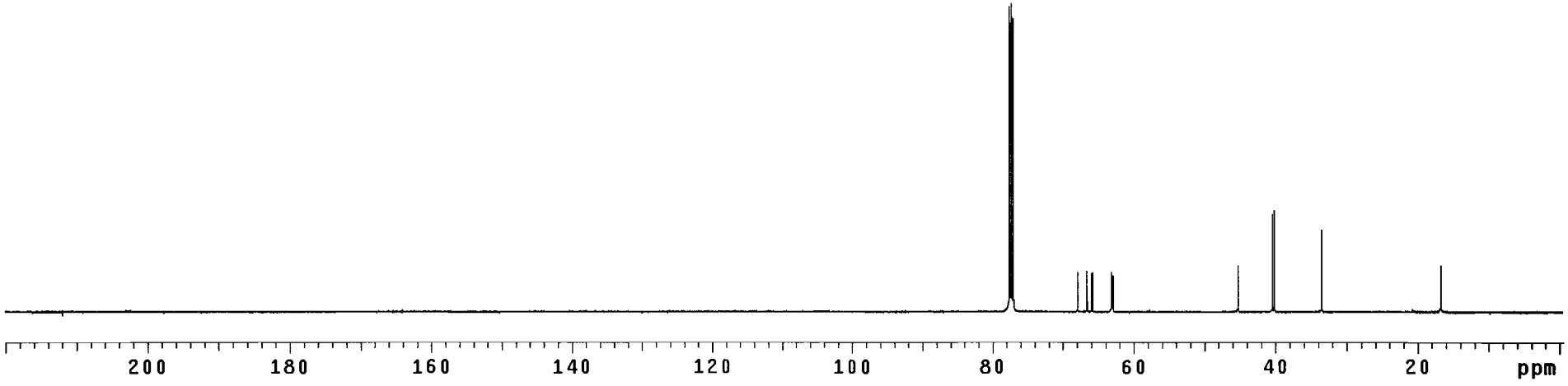
Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-75-13C
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
20000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 12 hr, 49 min, 47 sec



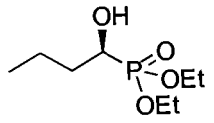


V-DR-79-1H

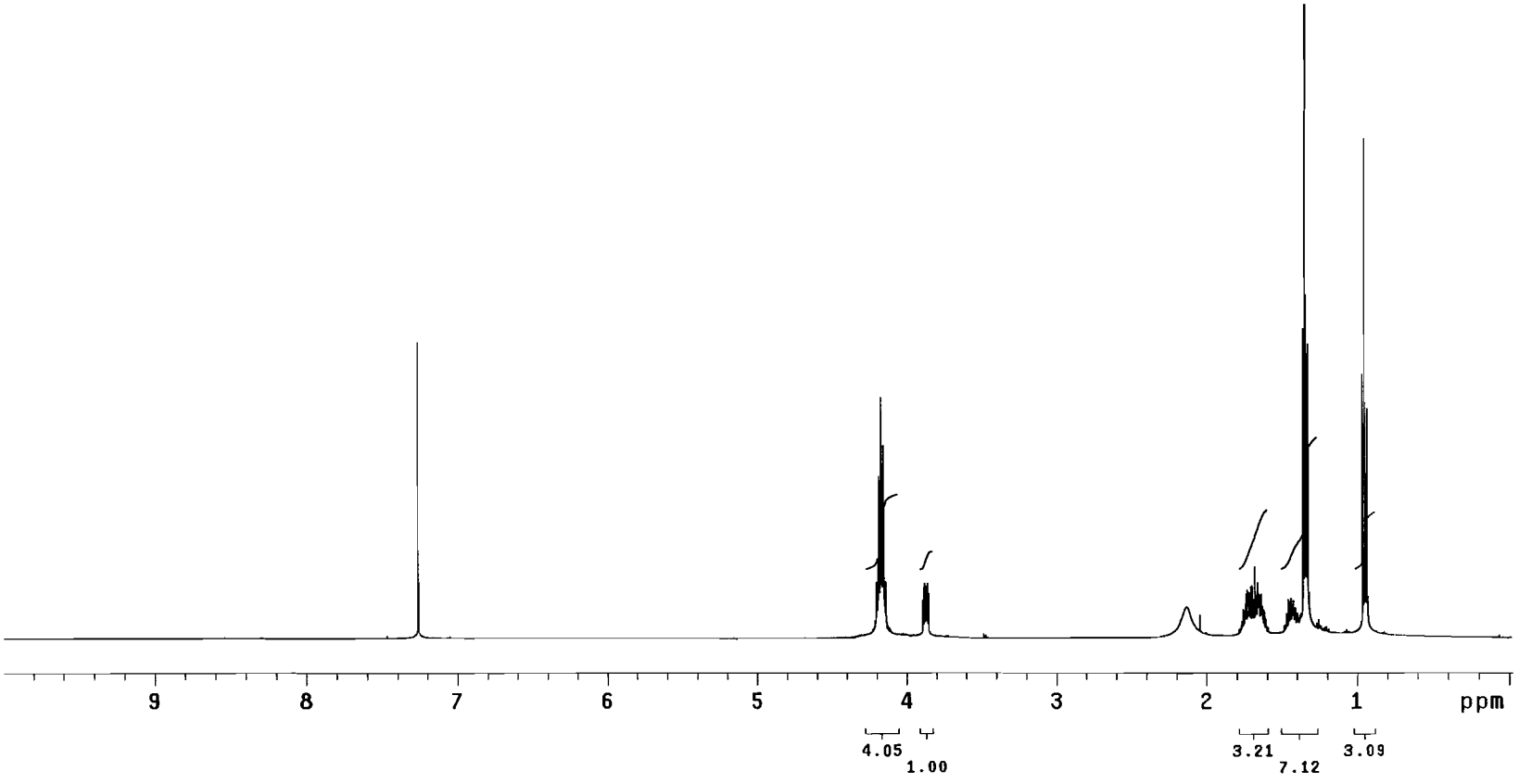
Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: V-DR-76-1H
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
32 repetitions
OBSERVE H1, 499.6931887 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec



7



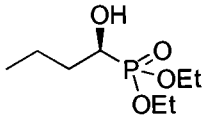
V-DR-79-13C

Archive directory: /home/drajasek/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: V-DR-76-13Ca
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
30000 repetitions
OBSERVE C13, 125.6479222 MHz
DECOUPLE H1, 499.6956872 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 hr, 14 min, 41 sec

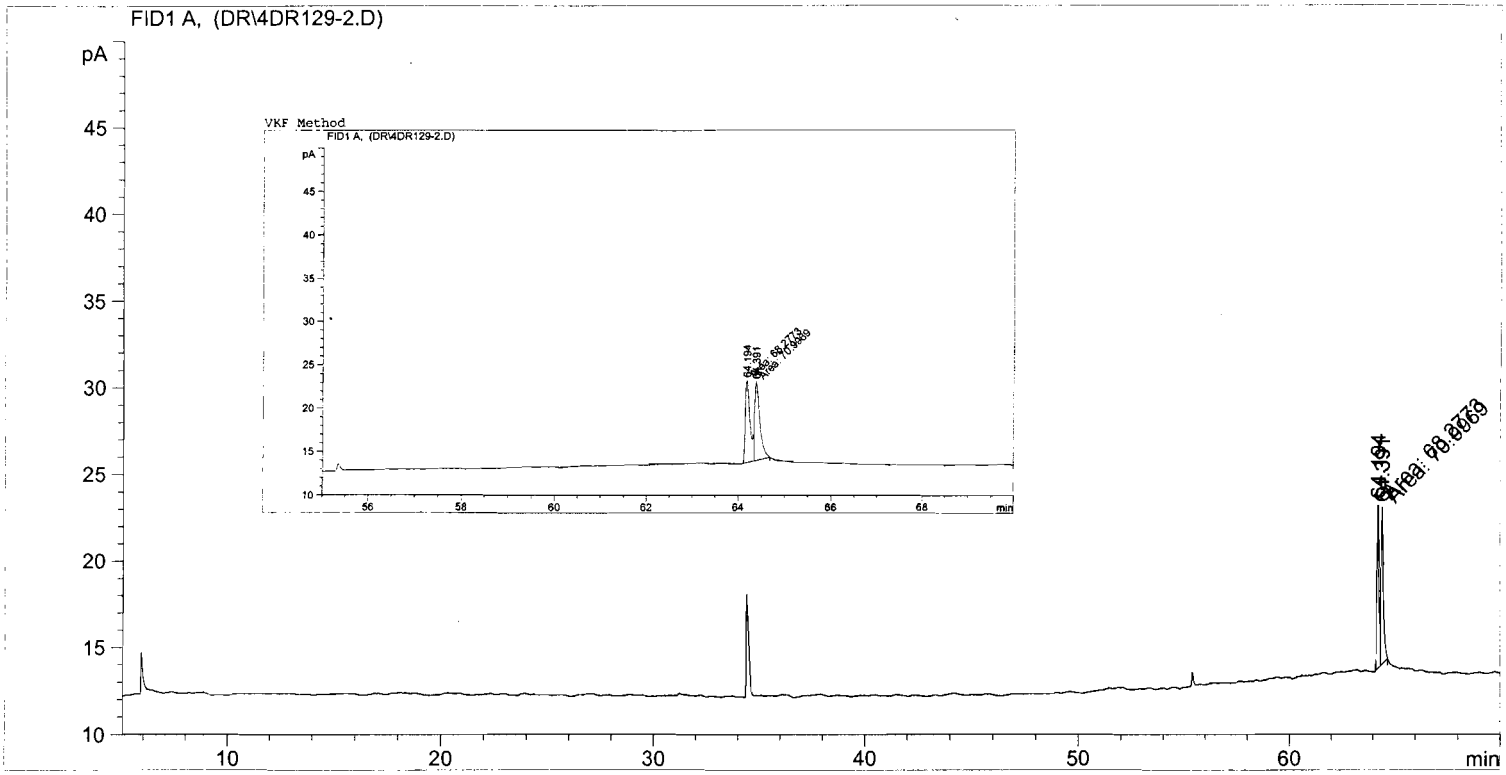


7

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE(ACETONE)

```
==========================================================================
Injection Date  : 3/22/2006 4:02:14 PM
Sample Name     : IV-DR-129                    Location : Vial 1
Acq. Operator   : dodda                           Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 3/22/2006 3:59:56 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 5/13/2006 10:34:28 PM by dodda
                  (modified after loading)
```

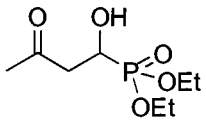
VKF Method




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	64.194	MF	0.1196	68.27729	9.51382	49.02365
2	64.391	FM	0.1300	70.99689	9.10277	50.97635
Totals :				139.27419	18.61659	

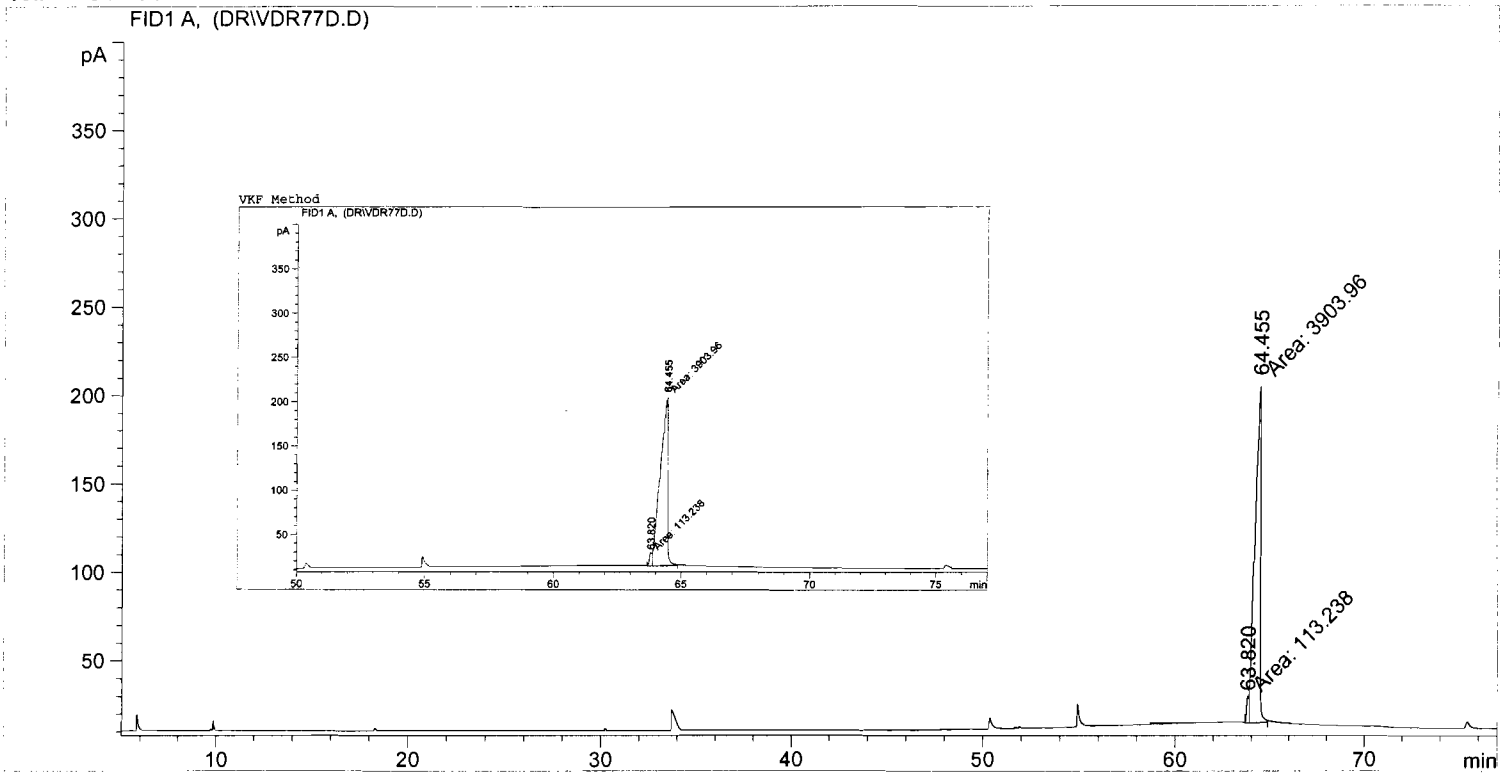


racemic

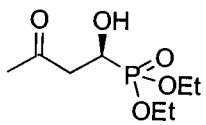
```
 Results obtained with standard integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================
```

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE

```
==========================================================================
Injection Date  : 6/5/2006 11:26:07 AM
Sample Name     : V-DR-77-D                        Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/5/2006 11:23:11 AM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/6/2006 9:31:07 AM by dodda
                  (modified after loading)
VKF Method
```



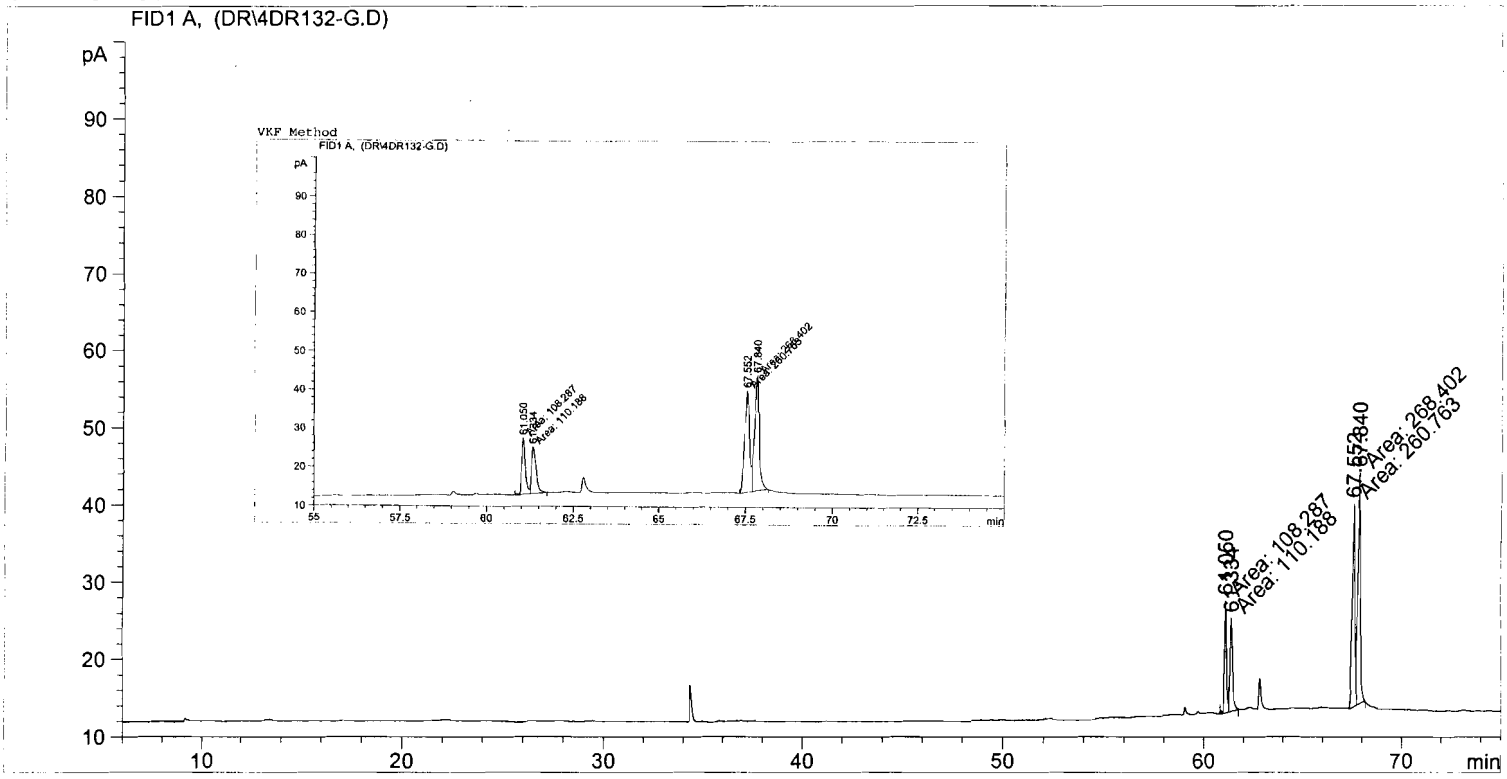

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  63.820 MF    0.1257  113.23793   15.01011  2.81883
   2  64.455 FM    0.3374 3903.96094  192.85309 97.18117

Totals :                  4017.19887  207.86320

 Results obtained with standard integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================
```



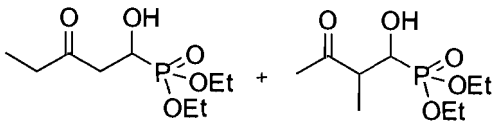
6a (94% ee)

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE(butanone)

```
==========================================================================
Injection Date  : 3/30/2006 11:29:25 AM
Sample Name     : IV-DR-132-G                    Location : Vial 1
Acq. Operator   : dodda                             Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 3/27/2006 2:42:01 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 4/3/2006 11:20:47 AM by dodda
                  (modified after loading)
VKF Method
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  61.050 MF    0.1239  108.28665   14.56791 14.48379
   2  61.334 FM    0.1515  110.18818   12.12047 14.73813
   3  67.552 MF    0.1654  260.76282   26.28061 34.87812
   4  67.840 FM    0.1500  268.40247   29.82926 35.89996

Totals :                   747.64011   82.79825
```

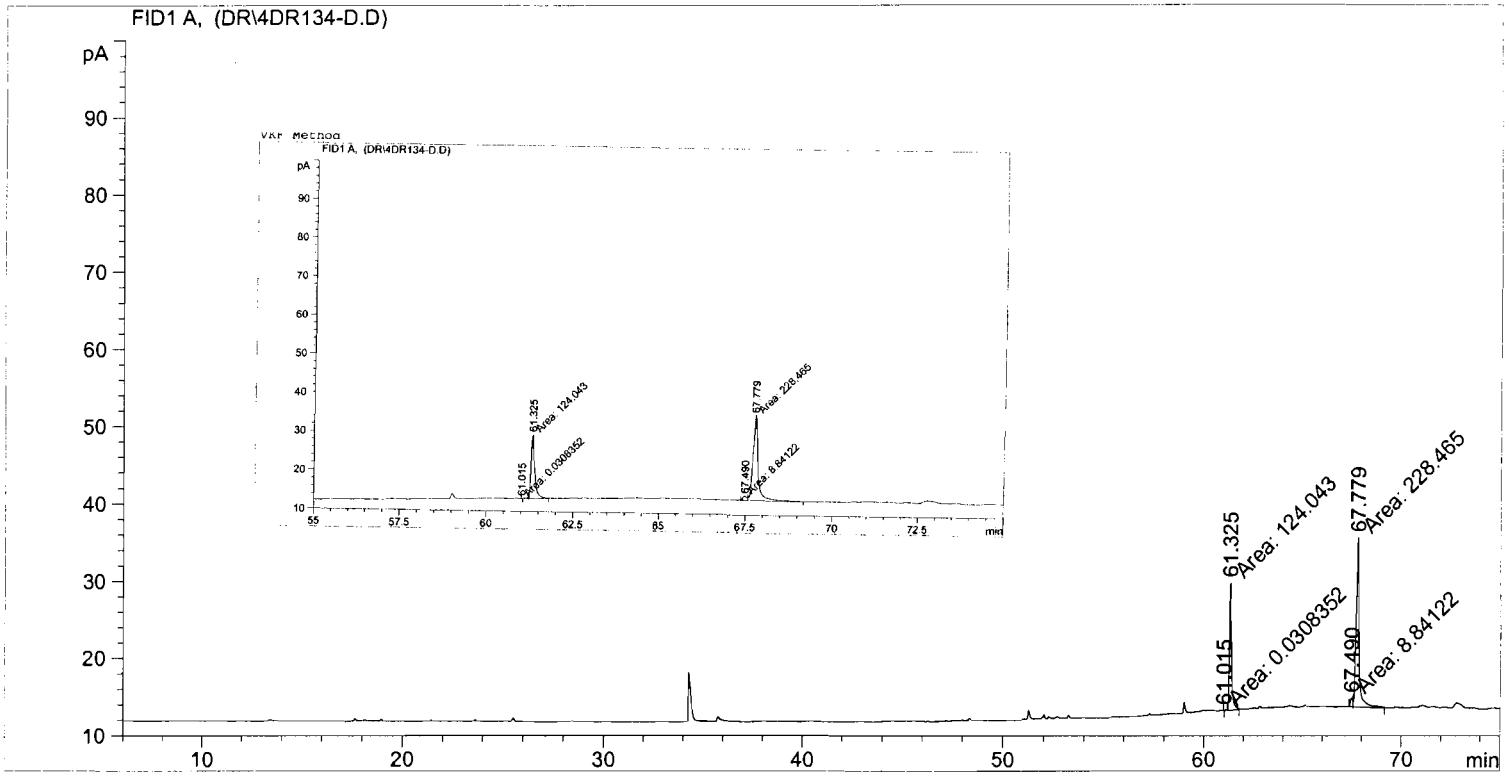



```
 Results obtained with standard integrator!
==========================================================================
```

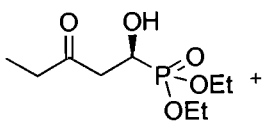
DIETHYL ALPHAHYDROXYKETOPHOSPHONATE(butanone)

```
==========================================================================
Injection Date  : 3/31/2006 5:28:52 PM
Sample Name     : IV-DR-134-D                    Location : Vial 1
Acq. Operator   : dodda                             Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 3/31/2006 5:22:03 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 4/3/2006 11:16:08 AM by dodda
                  (modified after loading)
```

VKF Method

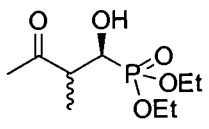



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  61.015 MM    0.0383 3.08352e-2 1.34014e-2  0.00853
   2  61.325 MM    0.1256  124.04306   16.45497 34.32481
   3  67.490 MF    0.1375    8.84122    1.07175  2.44651
   4  67.779 FM    0.1744  228.46507   21.82769 63.22014

Totals :                   361.38019   39.36782

 Results obtained with standard integrator!
==========================================================================
```



6b (93% ee)

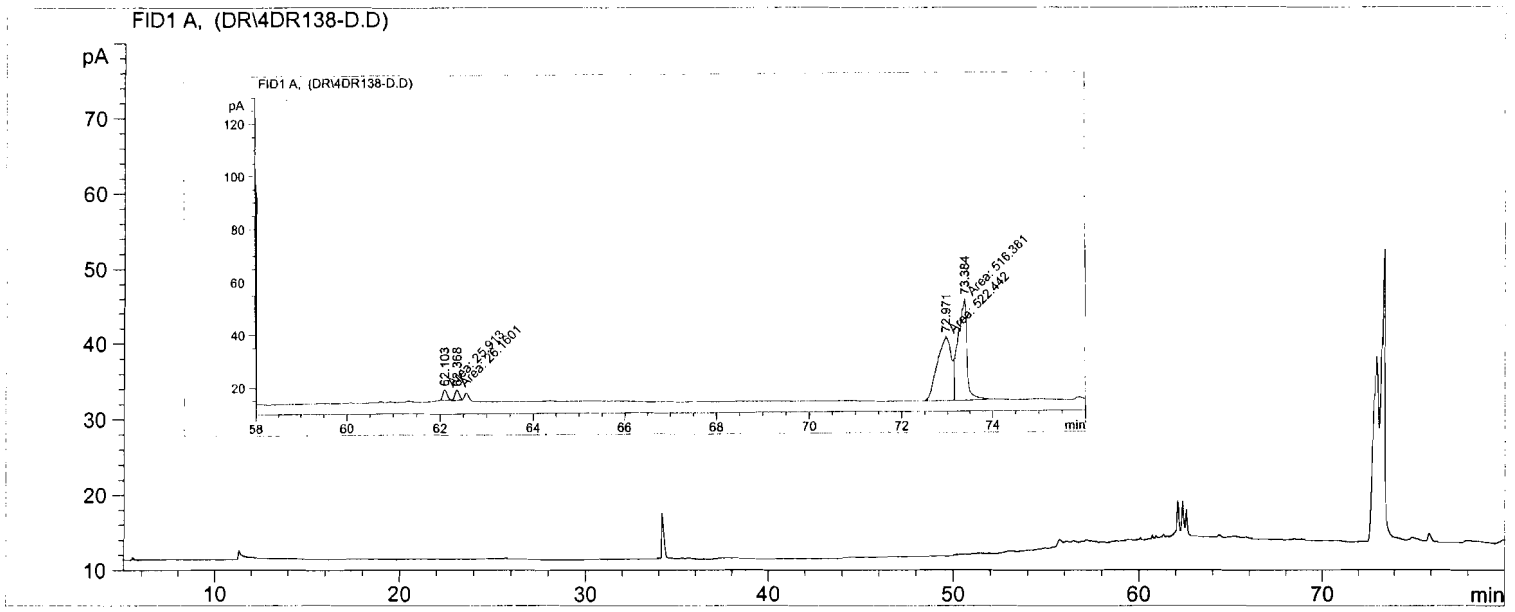
+



6b' (99% ee)

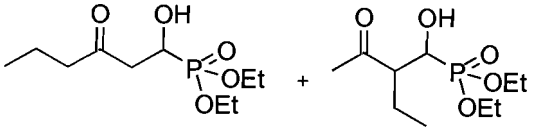
DIETHYL ALPHAHYDROXYKETOPHOSPHONATE(2-PENTANONE)

```
==========================================================================
Injection Date  : 4/4/2006 1:50:36 PM
Sample Name     : IV-DR-138-D                      Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 4/4/2006 10:33:24 AM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 9/6/2006 5:51:54 PM by dodda
                  (modified after loading)
VKF Method
==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,
```

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	62.103	MM	0.1060	25.91303	4.07581	2.37539
2	62.368	MM	0.1064	26.16009	4.09629	2.39804
3	72.971	MF	0.3568	522.44153	24.40538	47.89105
4	73.384	FM	0.2232	516.38135	38.56390	47.33552
Totals :				1090.89600	71.14138	

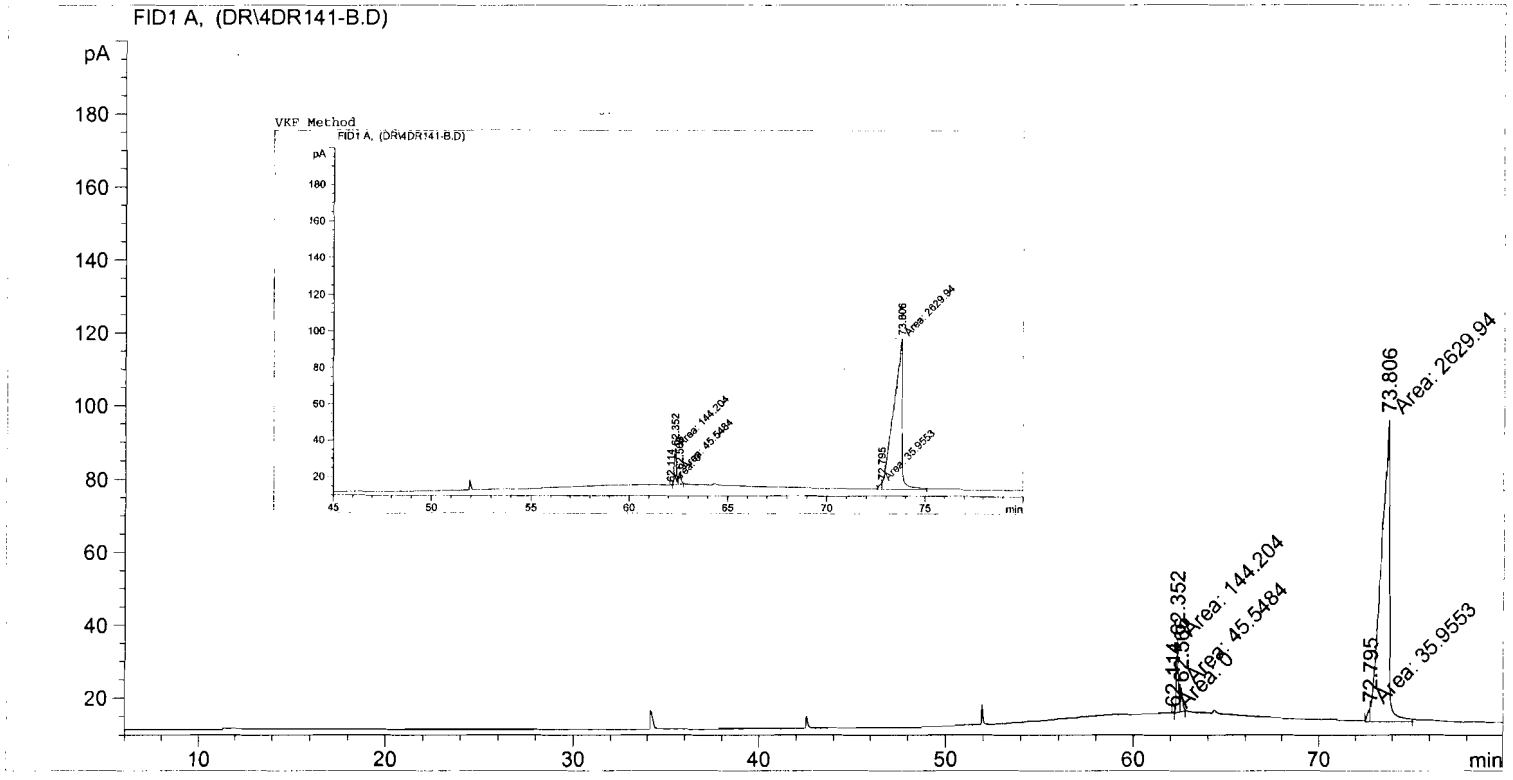


racemic

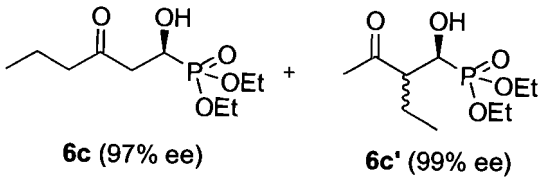
```
 Results obtained with standard integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================

Signal 1: FID1 A,
```

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE(2-PENTANONE)

```
==========================================================================
Injection Date  : 4/5/2006 9:26:03 AM
Sample Name     : IV-DR-141-B                    Location : Vial 1
Acq. Operator   : dodda                             Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 4/5/2006 8:47:50 AM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 5/13/2006 10:26:31 PM by dodda
                  (modified after loading)
VKF Method
```



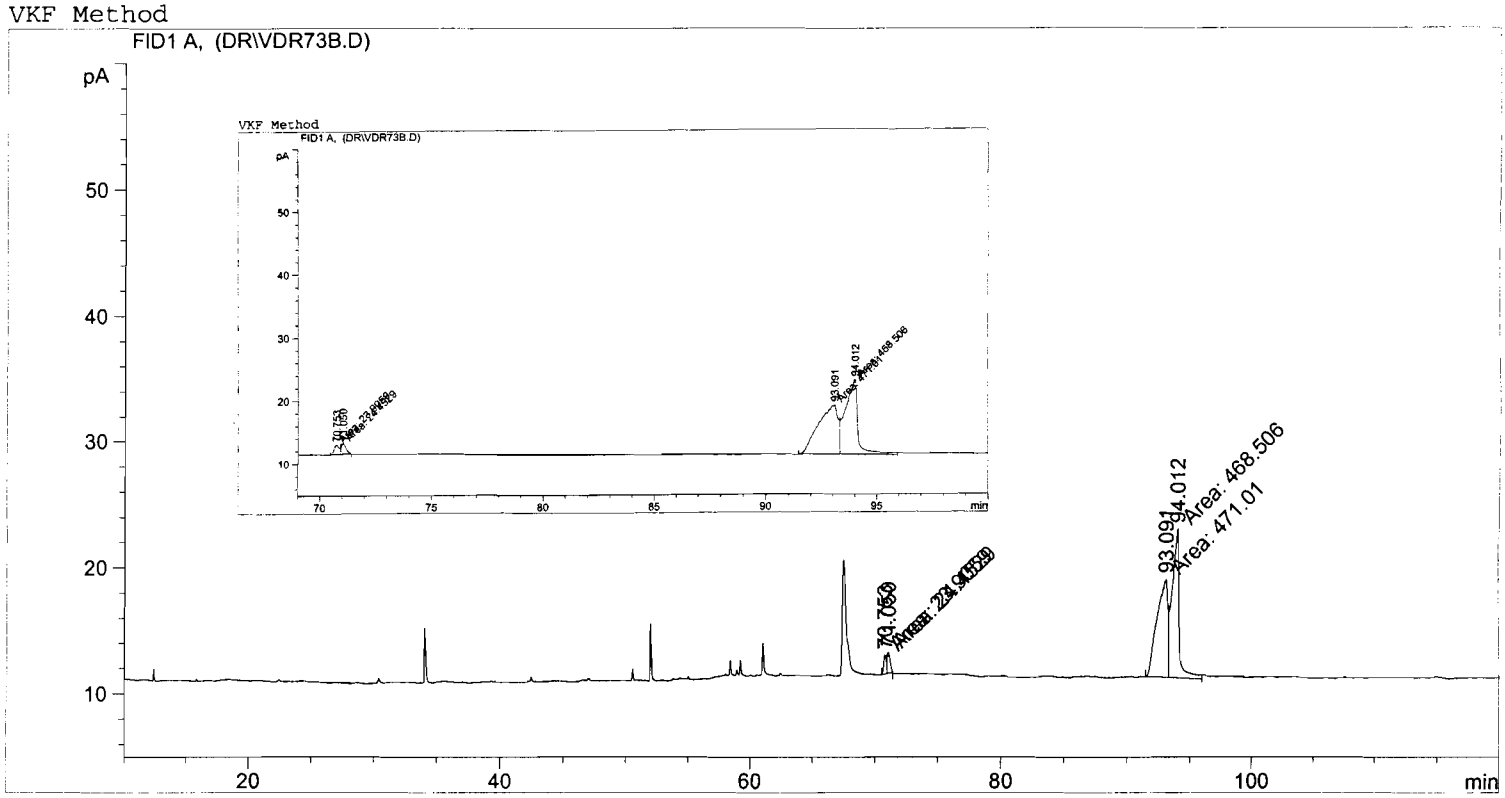

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  62.114 MM    0.0000    0.00000 7.91976e-2  0.00000
   2  62.352 MF    0.1231  144.20358   19.52109  5.04978
   3  62.566 FM    0.1182   45.54842    6.42212  1.59503
   4  72.795 MF    0.1624   35.95532    3.68982  1.25910
   5  73.806 FM    0.5286 2629.93604   82.92406 92.09610

Totals :                  2855.64336  112.63629

 Results obtained with standard integrator!
```



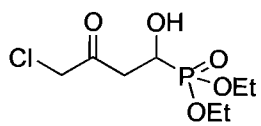
6c (97% ee) **6c'** (99% ee)

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE

```
==========================================================================
Injection Date  : 5/31/2006 5:59:04 PM
Sample Name     : V-DR-73-b                          Location : Vial 1
Acq. Operator   : dodda                                 Inj :   1
Acq. Instrument : Instrument 1                    Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 5/31/2006 5:58:07 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/1/2006 10:40:14 AM by dodda
                  (modified after loading)
VKF Method
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```



racemic

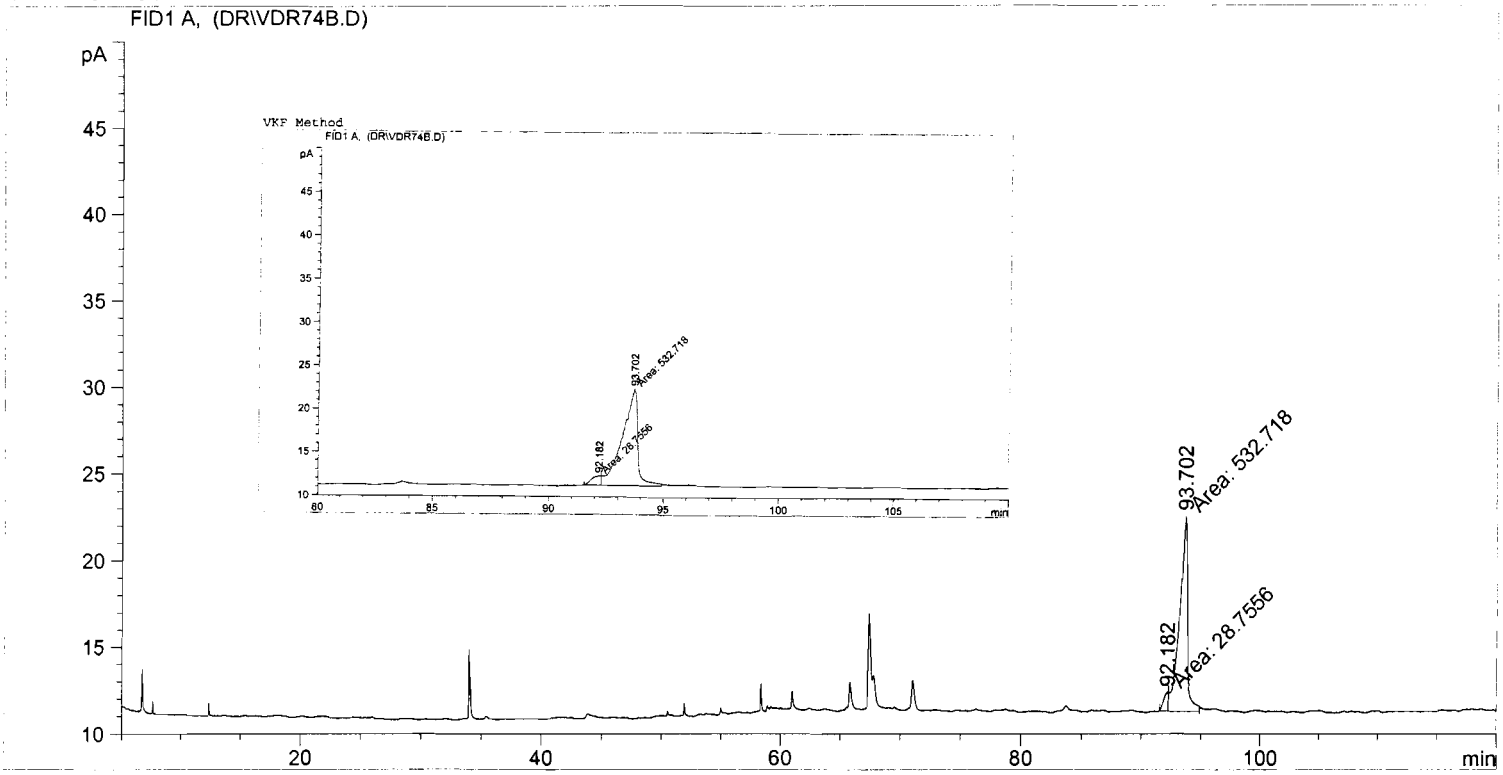
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	70.753	MF	0.2608	23.90595	1.52766	2.41994
2	71.050	FM	0.2406	24.45295	1.69411	2.47531
3	93.091	MF	1.0078	471.01038	7.78916	47.67915
4	94.012	FM	0.6618	468.50565	11.79805	47.42560
Totals :				987.87492	22.80898	

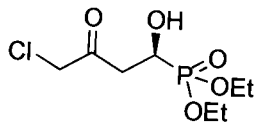
```
 Results obtained with standard integrator!
==========================================================================
```

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE

```
==========================================================================
Injection Date  : 6/1/2006 1:29:56 PM
Sample Name     : V-DR-74-B                        Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/1/2006 1:20:54 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/5/2006 9:38:01 AM by dodda
                  (modified after loading)
VKF Method
```



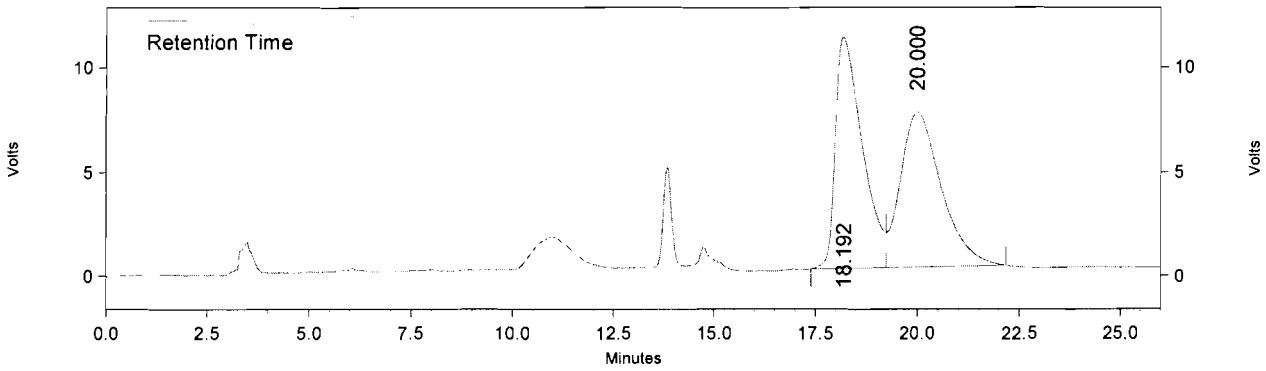

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  92.182 MF    0.4497   28.75555    1.06568  5.12144
   2  93.702 FM    0.7911  532.71796   11.22378 94.87856

Totals :                   561.47351   12.28946

 Results obtained with standard integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================
```



6d (90% ee)

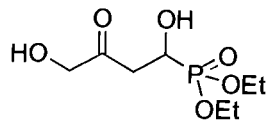
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-53-K
User: System
Acquired: 5/23/2006 12:38:31 PM
Printed: 6/15/2006 9:43:45 AM



SPD-10AVvp
Ch1-271nm
Results

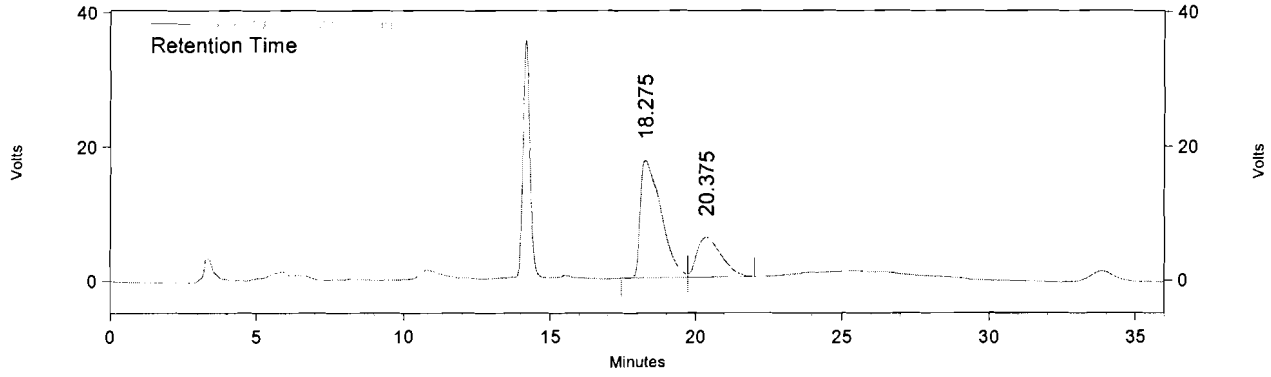
Retention Time	Area	Area %	Height	Height %
18.192	510847	49.70	11073	59.83
20.000	517050	50.30	7434	40.17
Totals	1027897	100.00	18507	100.00



racemic

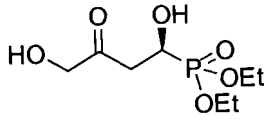
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-59-F
User: System
Acquired: 5/25/2006 4:03:51 PM
Printed: 5/25/2006 4:43:05 PM



SPD-10AVvp
Ch1-271nm
Results

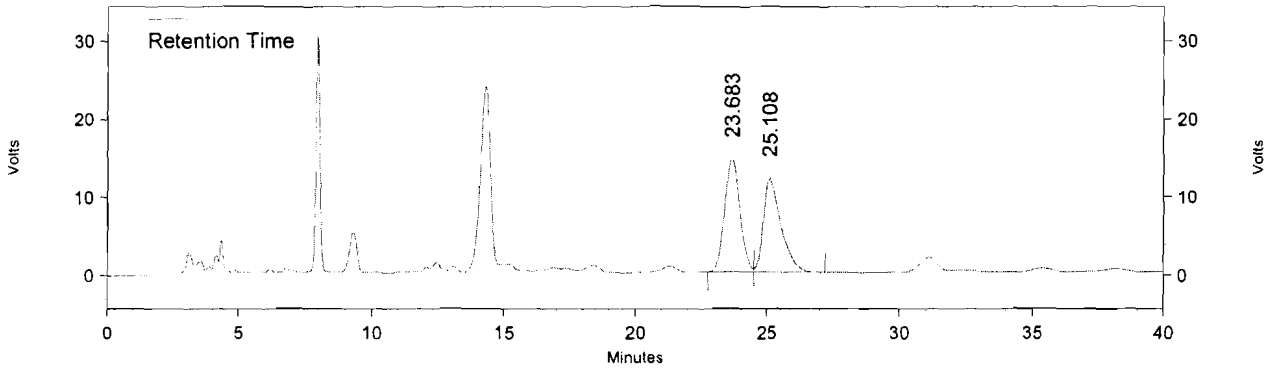
Retention Time	Area	Area %	Height	Height %
18.275	865342	71.70	17473	74.67
20.375	341631	28.30	5926	25.33
Totals	1206973	100.00	23399	100.00



6e (43% ee)

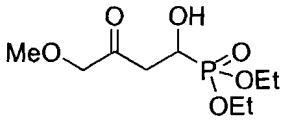
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-54-A
User: System
Acquired: 5/25/2006 9:00:03 AM
Printed: 6/15/2006 9:43:17 AM



SPD-10AVvp
Ch1-278nm
Results

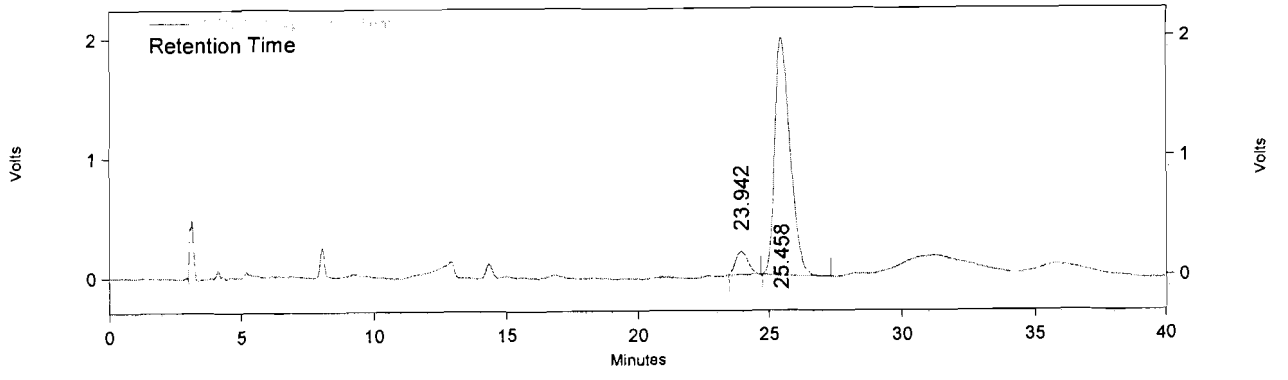
Retention Time	Area	Area %	Height	Height %
23.683	578924	50.84	14441	54.56
25.108	559883	49.16	12025	45.44
Totals	1138807	100.00	26466	100.00



racemic

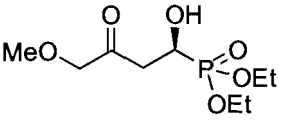
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-62-F
User: System
Acquired: 5/26/2006 9:57:59 PM
Printed: 5/26/2006 10:41:56 PM



SPD-10AVvp
Ch1-278nm
Results

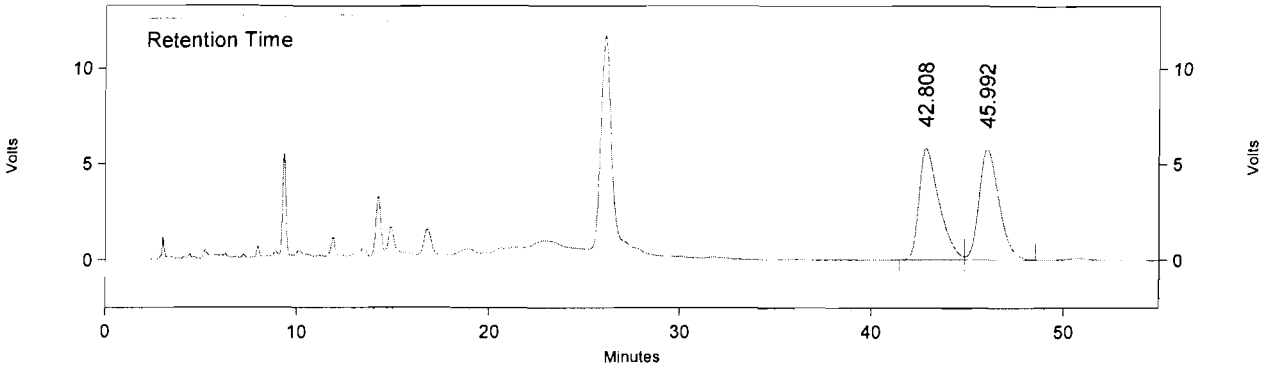
Retention Time	Area	Area %	Height	Height %
23.942	6412	7.41	194	8.91
25.458	80151	92.59	1984	91.09
Totals	86563	100.00	2178	100.00



6f (85% ee)

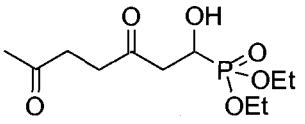
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-32-A
User: System
Acquired: 5/5/2006 5:15:27 PM
Printed: 6/15/2006 9:42:55 AM



SPD-10AVvp
Ch1-271nm
Results

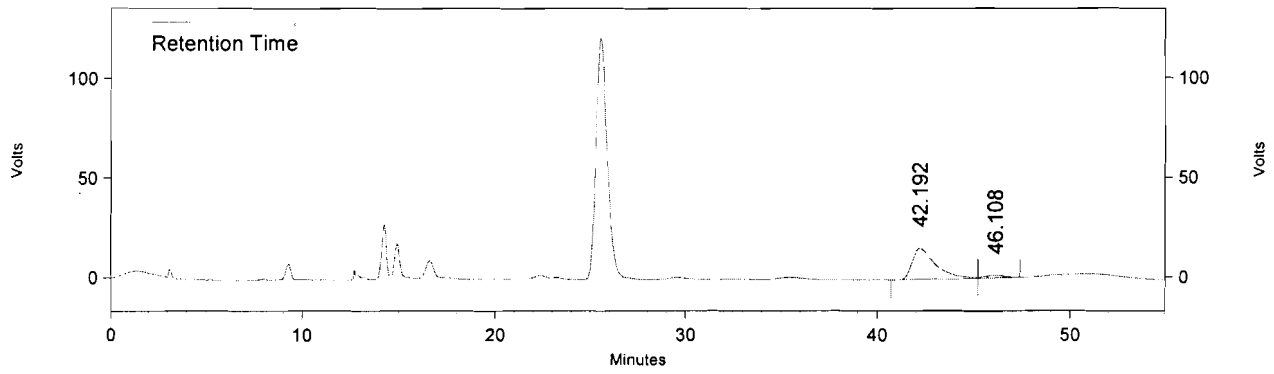
Retention Time	Area	Area %	Height	Height %
42.808	418244	50.01	5830	50.22
45.992	418136	49.99	5780	49.78
Totals	836380	100.00	11610	100.00



racemic

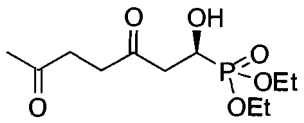
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-31-D
User: System
Acquired: 5/5/2006 7:33:22 PM
Printed: 6/15/2006 9:42:29 AM



SPD-10AVvp
Ch1-276nm
Results

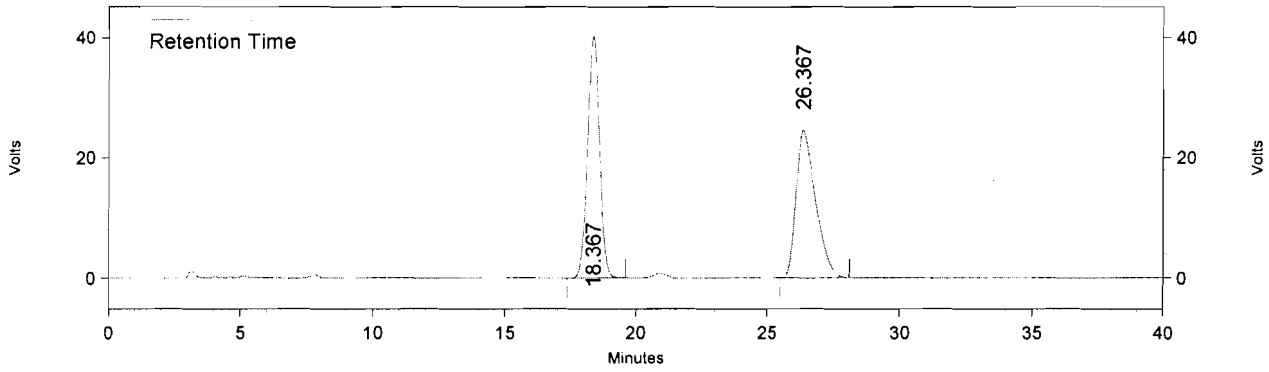
Retention Time	Area	Area %	Height	Height %
42.192	1300373	92.95	15641	92.05
46.108	98573	7.05	1350	7.95
Totals	1398946	100.00	16991	100.00



6g (86% ee)

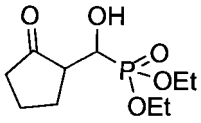
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-26
User: System
Acquired: 5/2/2006 6:16:48 PM
Printed: 6/15/2006 9:41:51 AM



SPD-10AVvp
Ch1-292nm
Results

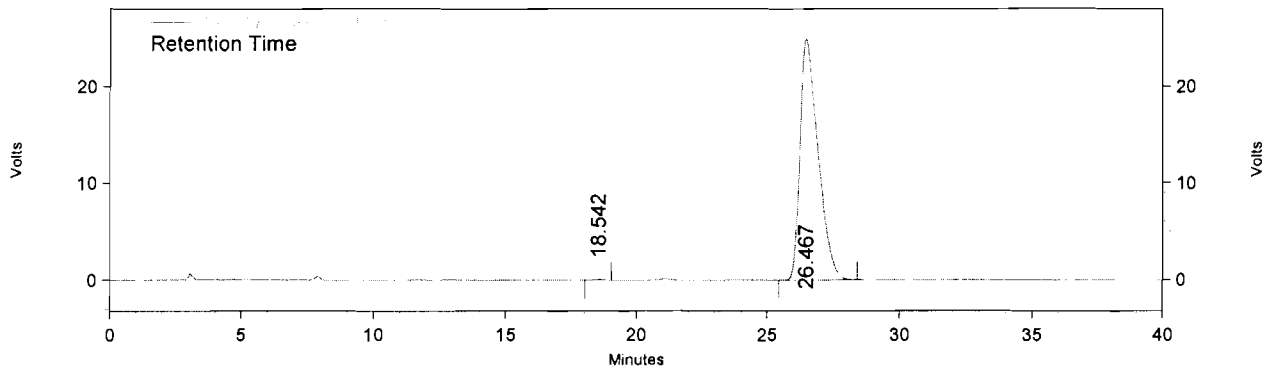
Retention Time	Area	Area %	Height	Height %
18.367	1277041	50.53	40121	62.13
26.367	1250334	49.47	24460	37.87
Totals	2527375	100.00	64581	100.00



racemic (syn)

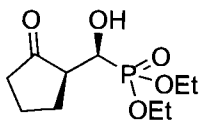
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-27A
User: System
Acquired: 5/2/2006 5:33:33 PM
Printed: 6/15/2006 9:40:47 AM



SPD-10AVvp
Ch1-292nm
Results

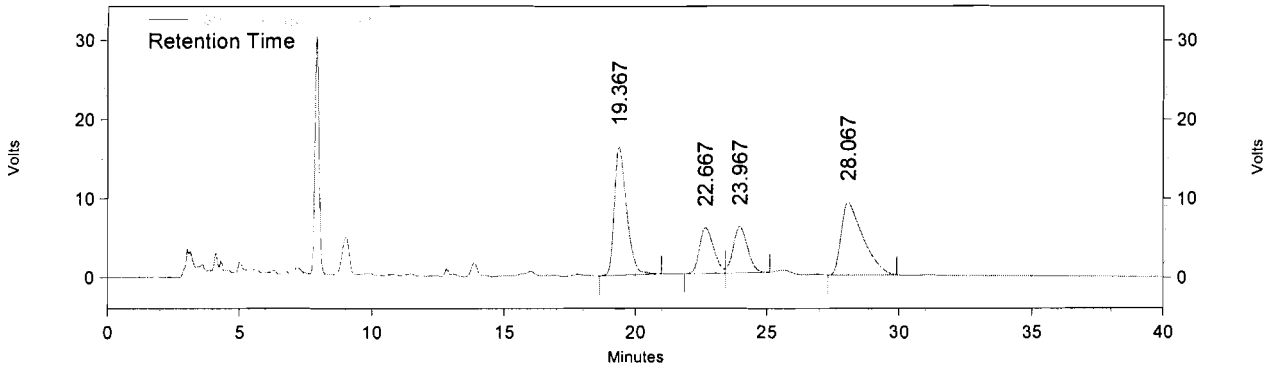
Retention Time	Area	Area %	Height	Height %
18.542	1933	0.16	79	0.32
26.467	1184478	99.84	24969	99.68
Totals	1186411	100.00	25048	100.00



6h (> 99% ee)

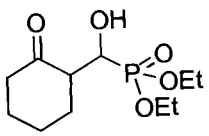
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-21(CYCLOHEXANONE-PHOSPHONATE)
User: System
Acquired: 4/28/2006 4:15:32 PM
Printed: 5/16/2006 9:43:54 PM



SPD-10AVvp
Ch1-280nm
Results

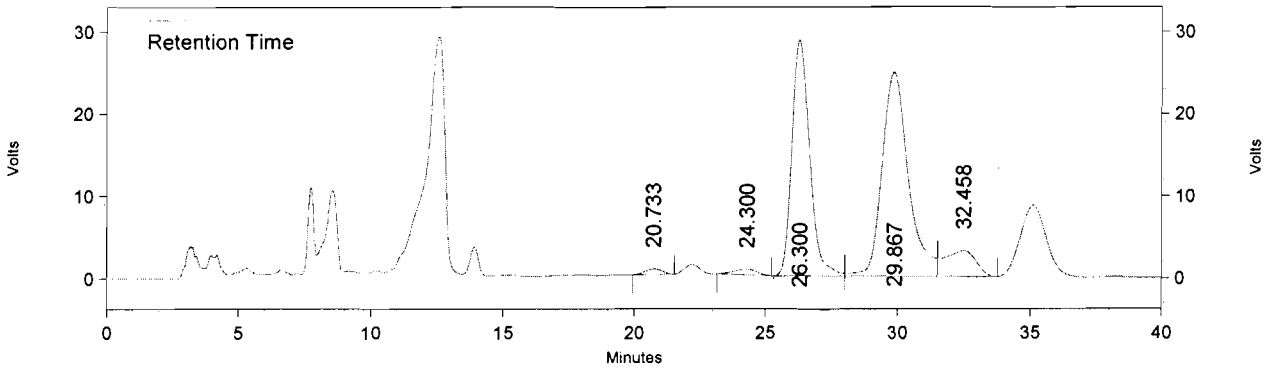
Retention Time	Area	Area %	Height	Height %
19.367	524830	35.14	16255	43.62
22.667	222025	14.86	5873	15.76
23.967	222963	14.93	5914	15.87
28.067	523821	35.07	9221	24.75
Totals	1493639	100.00	37263	100.00



racemic

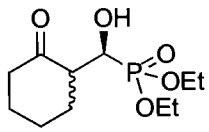
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-46C
User: System
Acquired: 5/17/2006 11:09:02 AM
Printed: 6/15/2006 9:40:18 AM



SPD-10AVvp
Ch1-277nm
Results

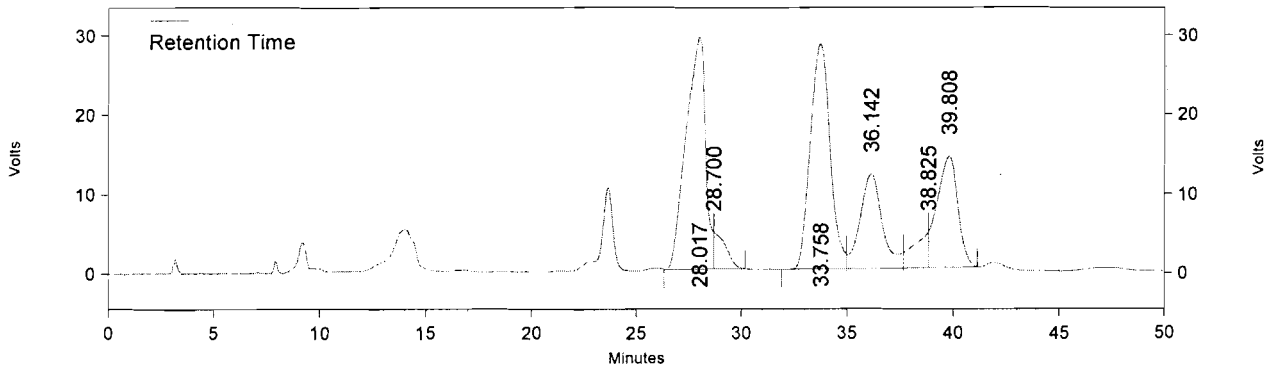
Retention Time	Area	Area %	Height	Height %
20.733	30368	0.90	663	1.14
24.300	40892	1.22	677	1.17
26.300	1337537	39.76	28685	49.54
29.867	1700270	50.54	24789	42.81
32.458	254990	7.58	3094	5.34
Totals	3364057	100.00	57908	100.00



6i
(*anti* 96 % ee; *syn* 95 % ee)

Area % Report

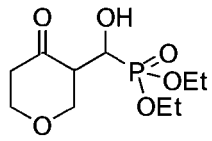
Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-39C
User: System
Acquired: 5/11/2006 8:30:58 PM
Printed: 5/16/2006 8:54:19 PM



SPD-10AVvp
Ch1-275nm
Results

Retention Time	Area	Area %	Height	Height %
28.017	1888189	31.65	29199	31.51
28.700	180522	3.03	4613	4.98
33.758	1846321	30.95	28362	30.60
36.142	876489	14.69	11952	12.90
38.825	218872	3.67	4542	4.90
39.808	955850	16.02	14008	15.12

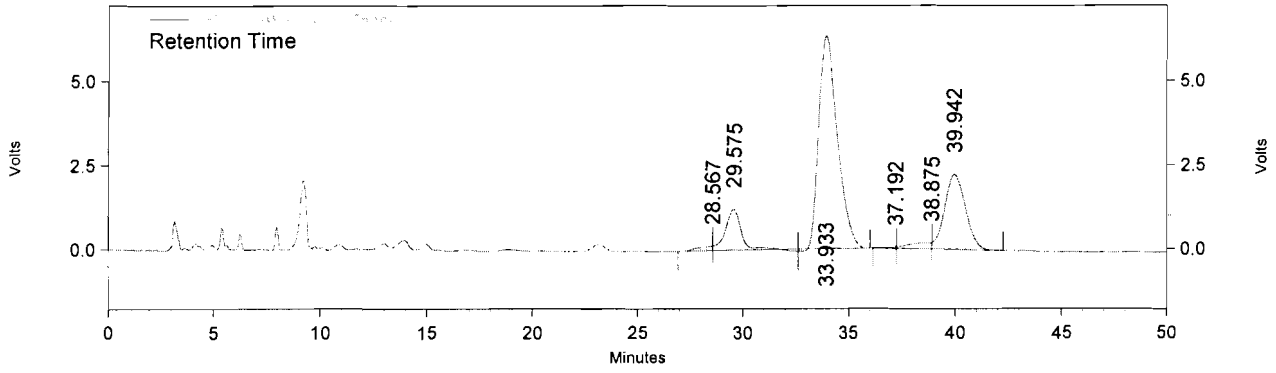
Totals	5966243	100.00	92676	100.00



racemic

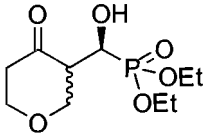
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-45-A
User: System
Acquired: 5/16/2006 8:00:55 PM
Printed: 5/16/2006 8:52:15 PM



SPD-10AVvp
Ch1-276nm
Results

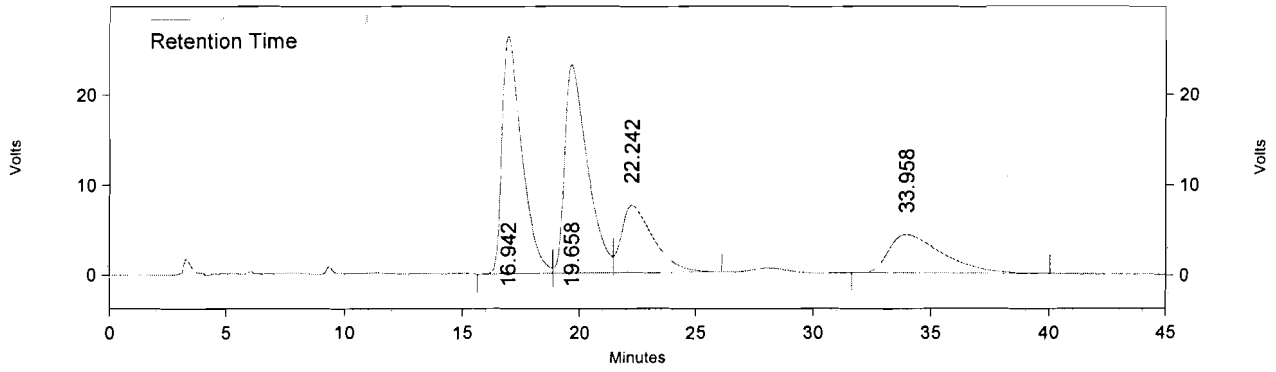
Retention Time	Area	Area %	Height	Height %
28.567	6289	1.02	140	1.38
29.575	61415	9.94	1218	12.01
33.933	384552	62.21	6340	62.50
37.192	798	0.13	30	0.30
38.875	12273	1.99	184	1.81
39.942	152809	24.72	2232	22.00
Totals	618136	100.00	10144	100.00



6j
(*anti* 97 % ee; *syn* 99 % ee)

Area % Report

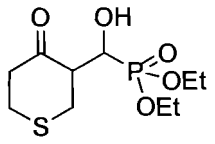
Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-40C
User: System
Acquired: 5/13/2006 10:19:40 PM
Printed: 5/15/2006 11:16:51 PM



SPD-10AVvp
Ch1-256nm
Results

Retention Time	Area	Area %	Height	Height %
16.942	1543746	34.46	26298	43.05
19.658	1565690	34.95	23118	37.84
22.242	707536	15.79	7475	12.24
33.958	662581	14.79	4203	6.88

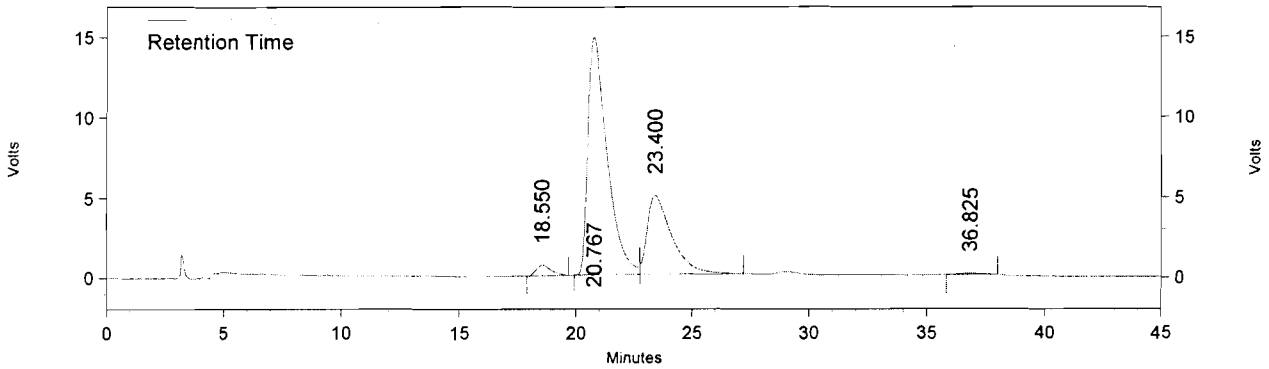
Totals	4479553	100.00	61094	100.00



racemic

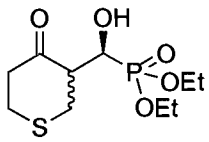
Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\V-DR-44-B
User: System
Acquired: 5/15/2006 10:27:39 PM
Printed: 5/15/2006 11:13:00 PM



SPD-10AVvp
Ch1-254nm
Results

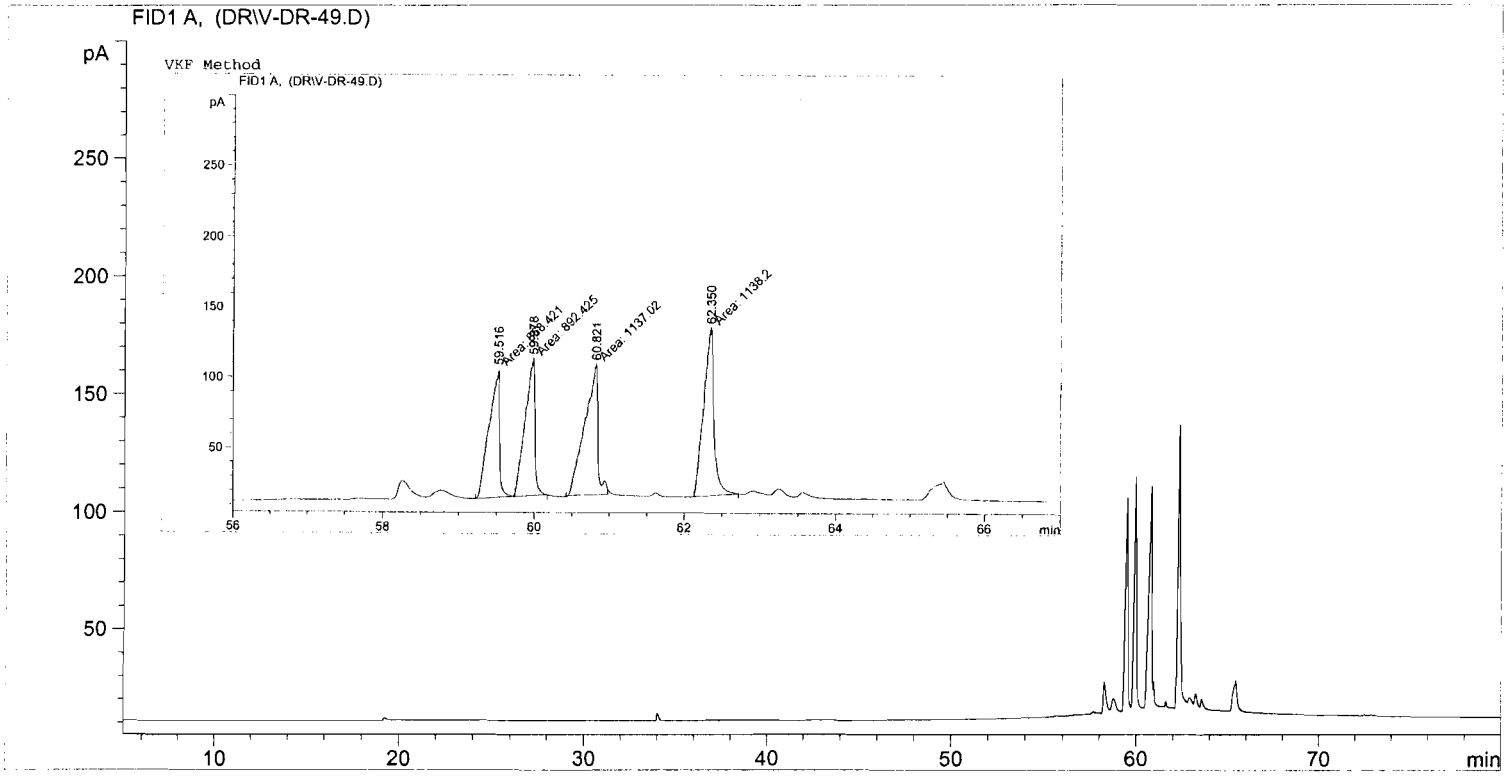
Retention Time	Area	Area %	Height	Height %
18.550	29215	2.33	658	3.20
20.767	852525	68.12	14856	72.25
23.400	363565	29.05	4962	24.13
36.825	6185	0.49	87	0.42
Totals	1251490	100.00	20563	100.00



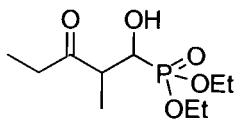
6k
(*anti* 93 % ee; *syn* 97 % ee)

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE

```
==========================================================================
Injection Date  : 5/25/2006 8:39:00 AM
Sample Name     : V-DR-49-D                        Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 5/25/2006 8:33:16 AM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 9/6/2006 4:10:54 PM by dodda
                  (modified after loading)
VKF Method
```



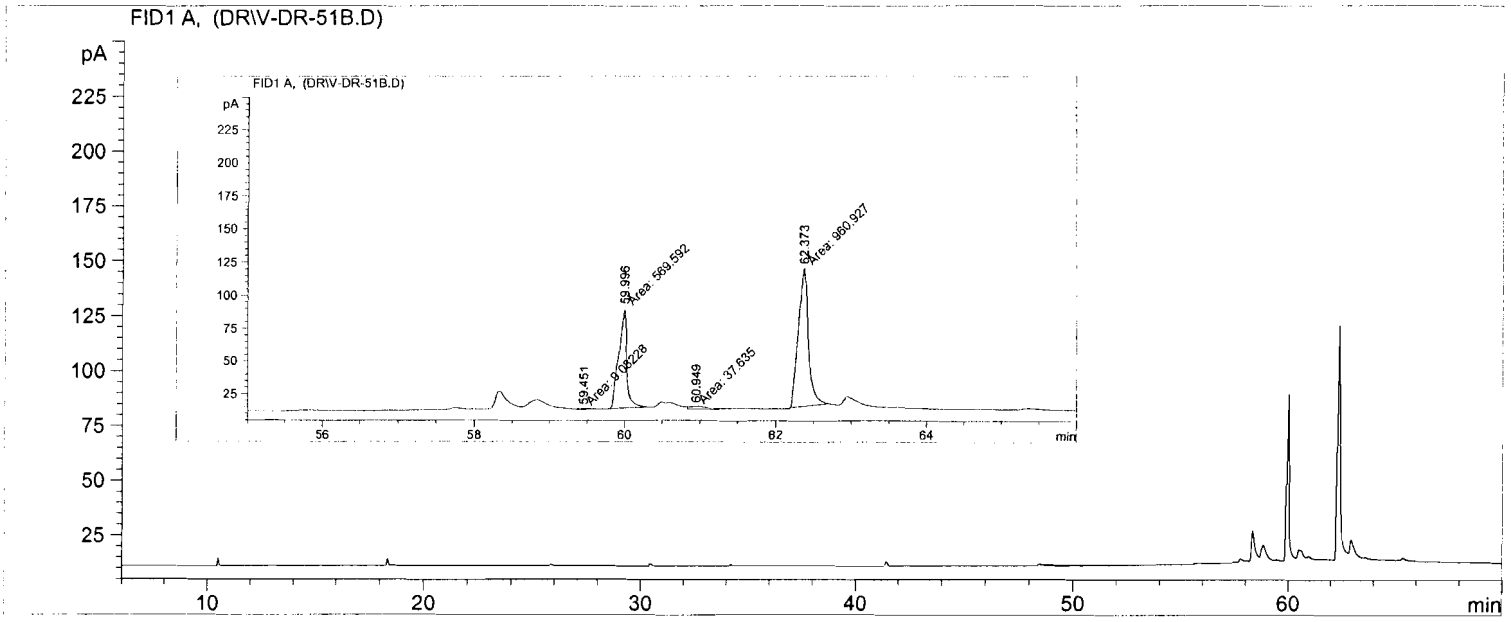

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  59.516 MF    0.1588  868.42090   91.14473 21.51653
   2  59.978 FM    0.1530  892.42474   97.23463 22.11126
   3  60.821 MM    0.2042 1137.01575   92.78307 28.17140
   4  62.350 MM    0.1594 1138.20337  119.00426 28.20082

Totals :                  4036.06476  400.16670

 Results obtained with standard integrator!
==========================================================================
```



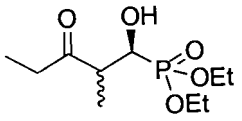
racemic

DIETHYL ALPHAHYDROXYKETOPHOSPHONATE

```
==========================================================================
Injection Date  : 5/19/2006 5:59:25 PM
Sample Name     : V-DR-51-B                        Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 5/18/2006 9:51:19 PM by dodda
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 9/6/2006 5:14:11 PM by dodda
                  (modified after loading)
VKF Method
==========================================================================
```



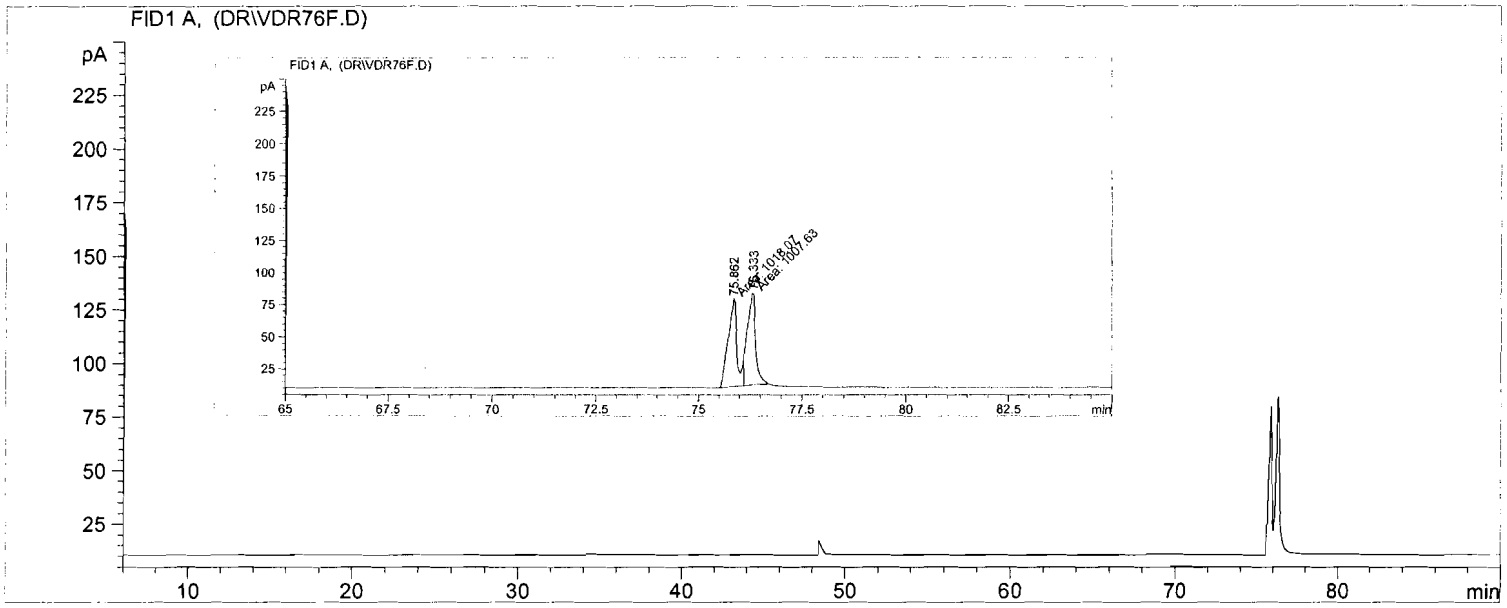

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  59.451 MM    0.1561    9.08228 9.69993e-1  0.57584
   2  59.996 MM    0.1246  569.59198   76.19481 36.11330
   3  60.949 MM    0.2809   37.63504    2.23303  2.38614
   4  62.373 MM    0.1524  960.92694  105.06031 60.92473

Totals :                  1577.23624  184.45814

 Results obtained with standard integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================

Signal 1: FID1 A,
```



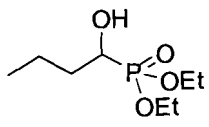
6l
(anti 92% ee; syn 97% ee)

DIETHYL ALPHAHYDROXYPHOSPHONATE

```
==========================================================================
Injection Date  : 6/5/2006 8:11:49 PM
Sample Name     : V-DR-76-F                        Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/5/2006 8:10:45 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 9/6/2006 5:18:00 PM by dodda
                  (modified after loading)
VKF Method
==========================================================================
```



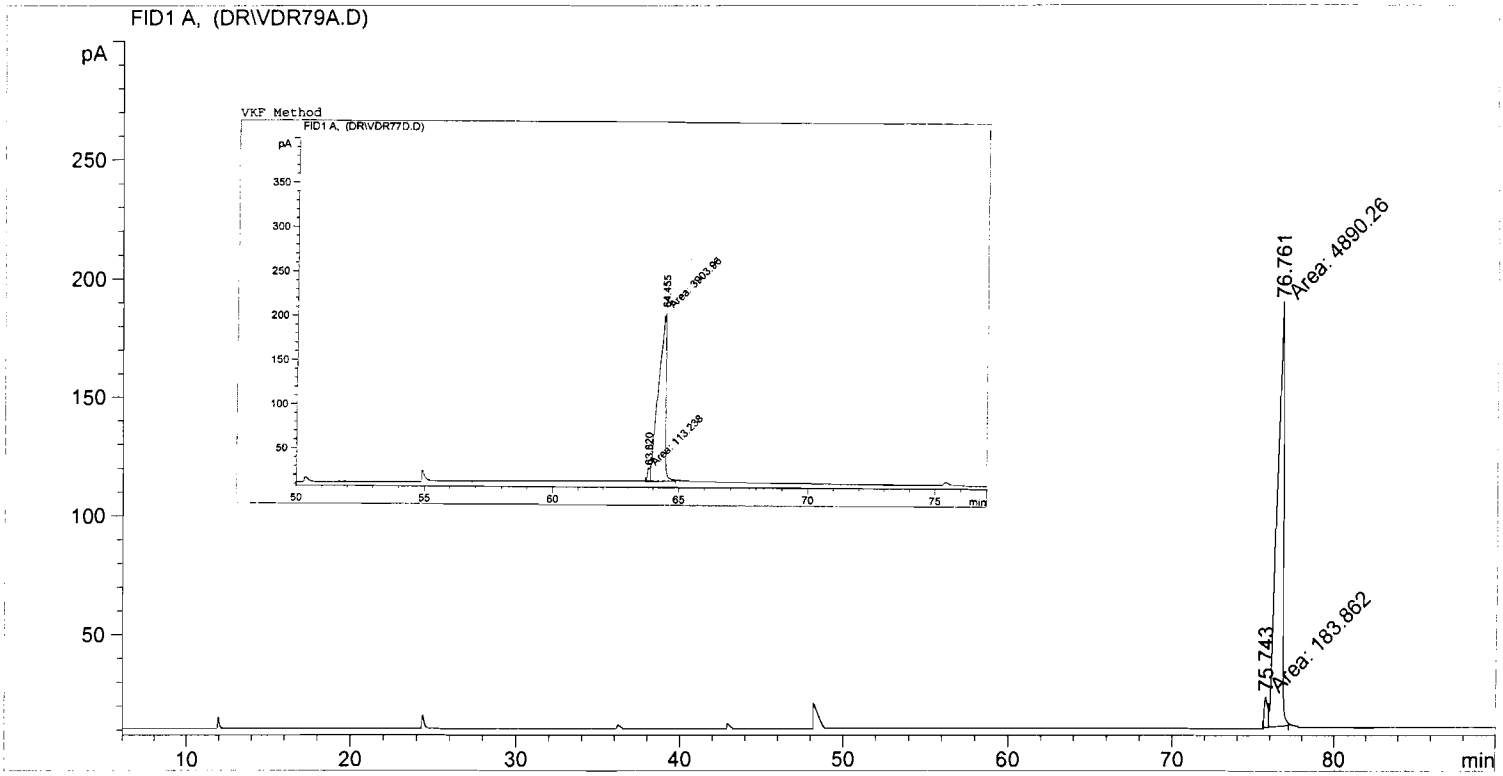

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  75.862 MF    0.2502 1018.07349   67.81412 50.25768
   2  76.333 FM    0.2346 1007.63361   71.57278 49.74232

Totals :                  2025.70709  139.38689

 Results obtained with standard integrator!
==========================================================================
                        Summed Peaks Report
==========================================================================

Signal 1: FID1 A,
```



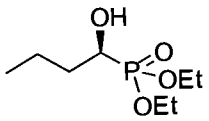
racemic

DIETHYL ALPHAHYDROXYPHOSPHONATE

```
==========================================================================
Injection Date  : 6/5/2006 6:07:21 PM
Sample Name     : V-DR-79-A                        Location : Vial 1
Acq. Operator   : dodda                               Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/5/2006 6:07:51 PM by dodda
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\28-11-05.M
Last changed    : 6/5/2006 8:09:55 PM by dodda
                  (modified after loading)
VKF Method
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      2.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  75.743 MF    0.2451  183.86171   12.50261  3.62352
   2  76.761 FM    0.4599 4890.26318  177.23874 96.37648

Totals :                  5074.12489  189.74135

 Results obtained with standard integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================
```



7 (93% ee)