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Supporting information

Soft detoxification of chemical warfare agent simulants and pesticides under pressure

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General information

All reagent and CWA simulants (CEES, CTEA), and 4-nitrophenyl dimethyl phosphate (Methyl Paraoxon) were purchased from Sigma Aldrich and used as provided; solvents were purchased from VWR and used without further purification.
High-pressure reactions were performed in piston−cylinder type devices: U16 (Unipress, Warsaw, Poland), designed for P = 16 kbar, and an Ollivaud/Lebas (France) for P = 14 kbar.

Figure 1. Pictures of piston−cylinder type apparatus U16 (Unipress, Warsaw, Poland): front (left) and side (right)

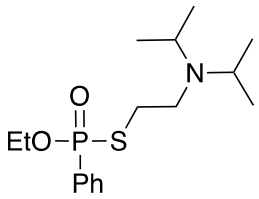
Figure 2. Piston−cylinder type apparatus Ollivaud/Lebas, France.

High field ^{1}H, ^{13}C, and ^{31}P NMR studies were performed on a 300 MHz Bruker Spectrospin spectrometer. Chemical shifts (δ) are given with regard to TMS using solvent as internal reference, *J* coupling constants are given in Hertz. Low resolution mass spectra and gas chromatograms were performed on a Shimadzu QP2010 hybrid ionization apparatus (HP5- MS stationary phase, l = 30 cm, d = 0.25 mm, film thickness = 0.25 µm).

All reactions were conducted at room temperature (23 °C) except if noted otherwise, with no particular precautions with regard to residual moisture and air. However due to the acute toxicity of CWA simulants, all reactions were carried out under closed atmosphere in a very well-ventilated fume hood. All glassware and materials in contact of simulants were immersed in a bleach bath under the fume hood for one day before further washing and/or disposal.

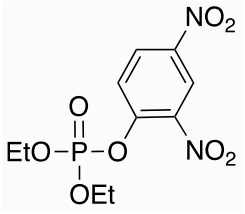
Preparation of starting materials

S-2-(Diisopropylamino)ethyl *O*-ethyl phenylphosphonothioate (PhX)



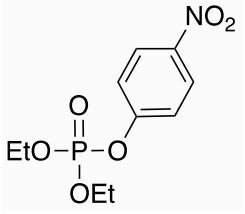
Prepared according to the literature,[1] pale yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.78 (m, 2H), 7.57 – 7.37 (m, 3H), 4.31 – 4.13 (m, 2H), 2.97 – 2.79 (m, 2H), 2.64 (dd, J = 13.3, 7.0 Hz, 2H), 2.58 – 2.49 (m, 2H), 1.37 (s, 3H), 0.90 (d, J = 6.5 Hz, 12H)
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 133.7 (d, J=148.8) 132.06 (d, *J* = 3.2 Hz), 130.89 (d, *J* = 10.8 Hz), 128.15 (d, *J* = 14.7 Hz), 61.67 (d, *J* = 6.8 Hz), 48.47 (s), 45.86 (d, *J* = 4.7 Hz), 30.98 (d, *J* = 2.1 Hz), 20.51 (t, *J* = 6.1 Hz), 16.08 (d, *J* = 6.7 Hz).
^{31}P NMR (121 MHz, $CDCl_3$) δ = 45.4 (m)
HRMS calc m/z: 330.1657 ($[M+H]^+$), found 330.1657 (0.0 ppm)

Diethyl 2,4-Dinitrophenyl phosphate (DEDNPP)



It was prepared according to the procedure described in literature, using THF as solvent instead benzene. The product was purified by flash chromatography (4:1 cyclohexane/ethyl acetate and 0.2% acetic acid; 56% yield (yellow solid), mp < 40 °C.[2]
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (td J_{HH} = 7.05 Hz, J_{HP} = 1.17 Hz, 6H), 4.22-4.37 (m, 4H), 7.85 (dd, J_{HH} = 9.15 Hz, J_{HH} = 1.05 Hz), 8.47 (ddd, J_{HH} = 9.15 Hz, J_{HH} = 2.77, J_{HP} = 0.39 Hz, 1H), 8.83 (dd, J_{HH} = 2.77 Hz, J_{HP} = 1.05 Hz, 1H)
^{13}C NMR (75 MHz, $CDCl_3$): 16.1 (d, J = 6.75), 65.2 (d, J = 6.26); 120.6 (d, J = 5.54); 125.7 (s); 144.7 (s); 155.6 (d, J = 6.34)
^{31}P NMR (121 MHz, $CDCl_3$): -7.5 (quint, 8.4 J_{PH})
HRMS calc m/z: 321.0488 Da ($[M+H]^+$), found 321.0488 (0.0 ppm)

Diethyl 4-nitrophenyl phosphate (Paraoxon)



It was prepared according to the procedure employed for the DEDNPP; see above. The product was purified by flash chromatography (3:2 cyclohexane/ethyl acetate and 0.2% acetic acid; 68% yield) (yellow liquid).[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ (td J_{HH} =7.05, JHP = 1.03, 6H), 4,27 (m, 4H), 7.73 and 8.17 (AA'BB', 4H).

^{13}C NMR (75 MHz, $CDCl_3$): 16.0 (d, J = 6.69), 66.1 (d, J = 6.66), 127.7 (s), 123.4 (d, J = 2.63), 128.8 (d, J = 0.90), 143.6 (s), 148.3 (d, J = 4.96).

^{31}P NMR (121 MHz, $CDCl_3$): -6.5 (qu, 8.5 J_{PH}).

HRMS calc m/z: 276.0637 Da ($[M+H]^+$), found 276.0616 (-7.6 ppm)

General Procedure for the neutralization of CWAs under high pressure

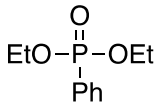
The mixture of CWAs (0.125 mmol for CTEA and DEAE and 0.044 mmol for PhX), and the nucleophile (0.375 mmol of pyrrolidine or EtOLi) were dissolved in dry ethanol (1 mL)[1] in a Teflon reaction vessel (0.9 mL) and submitted to a pressure of 14-16 kbar at room temperature. After 24 h, pressure was released, reaction medium was extracted (H_2O/diethyl ether, 3x2 mL) and volatiles were removed in vacuo before GC (decane is used as an internal standard, 0.125 mmol) and NMR analysis.

General Procedure for the neutralization of phosphate triesters under high pressure

Solvolysis reactions. A solution containing the phosphate triester (Paraoxon, Methyl Paraoxon or DEDNPP) (4.7 mmol L^{-1} in MeCN/H_2O, 99:1, v/v) was prepared and placed in a Teflon reaction vessel (2.5 or 2.7 mL). The reaction mixture was kept under 14 kbar or 16 kbar, at room temperature for 24 h. Then, the solvent was removed under reduced pressure, the residues were dissolved in $CDCl_3$ and analyzed by ^1H and ^{31}P NMR. The product ratio was calculated from ^{31}P NMR spectra.

Reactions with imidazole. A solution containing imidazole (28 mmol L^{-1}; 6 equivalents) and the phosphate triester (4.7 mmol L^{-1}; 1 equivalent) was prepared and placed in a Teflon reaction vessel (2.5 or 2.7 mL). The reaction mixture was kept under 14 kbar or 16 kbar, at room temperature for 24 h. Then, the solvent was removed under reduced pressure, the residues were dissolved in deuterium oxide and analyzed by ^1H and ^{31}P NMR. The product ratio was calculated from ^{31}P NMR spectra.

Diethyl phenylphosphonate (1)



Viscous colorless liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.63 (m, J = 13.3, 7.0 Hz, 2H), 7.53 – 7.10 (m, 3H), 4.21 – 3.80 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H)

^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 132.14 (d, J = 2.6 Hz), 131.44 (d, J = 9.9 Hz), 128.21 (d, J = 15.0 Hz), 128.04 (d), 61.83 (d, J = 5.4 Hz), 16.02 (d, J = 6.4 Hz).

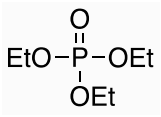
^{31}P{^1H} NMR (121 MHz, $CDCl_3$) δ = 18.74 (S)

HRMS calc m/z: 215.0837 Da ($[M+H]^+$), found 215.0833 (1.8 ppm)

Data in accordance to literature.[3]

[1] Commercial absolute ethanol > 99.7% was dried over molecular sieves before use.

Triethyl phosphate (2)

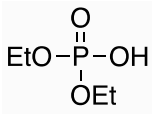


^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (td J_{HH} =7.1 Hz, J_{HP} = 0.89 Hz, 9H), 4.04 (dq, J_{HP} = 7.9 Hz, J_{HH} =7.1 Hz, 6H).0

^{31}P{^{1}H} NMR: -0.9 (s)

Data in accordance to literature.[3]

Diethyl phosphate (3b)

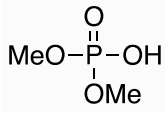


^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t J_{HH} =6.9 Hz, 6H), 3.95 - 4.06 (m, 4H).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): 0.6 (s)

Data in accordance to literature.[4]

Dimethyl phosphate (3c)

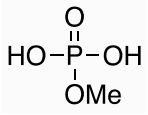


^{1}H NMR (300 MHz, D_2O) δ 3.55 (t J_{HP} =10.7 Hz, 6H)

^{31}P{^{1}H} NMR (121 MHz, D_2O): 3.6 (s)

Data in accordance to literature.[5]

Methyl phosphate (5c)

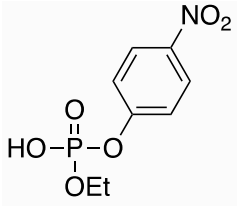


^{1}H NMR (300 MHz, D_2O) δ 3.44 (t J_{HP} =10.1 Hz, 3H)

^{31}P{^{1}H} NMR (121 MHz, D_2O): 4.7 (s)

Data in accordance to literature.[6]

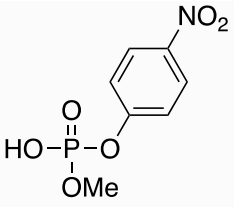
Ethyl 4-nitrophenyl hydrogen phosphate (4b)



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25(dt J_{HH}= 7.1 J_{HP} = 1.0 Hz, 3H), 4.01 (m, 2H), 7.28 and 8.12 (AA'BB', 4H).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): -7.1 (s)
Data in accordance to literature, slight shifted due to the solvent.[7]

Methyl 4-nitrophenyl hydrogen phosphate (4c)

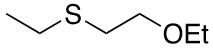


^1H NMR (300 MHz, $CDCl_3$) δ 3.91 (d, J_{HP} = 11.5 Hz 6H), 7.33 and 8.20 (AA'BB', 4H).
$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): -5.5 (bs)
4-Nitrophenol ($C_6H_5NO_3$)
^1H NMR (300 MHz, $CDCl_3$): 6. 89 and 8.14 (AA'BB', 4H).
Data in accordance to literature.[8]

2,4-Dinitrophenol
^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (d J = 9.3 Hz, 1H), 8.39 (d of d, J = 9.3, J = 2.7, 1H), 9.01 (d J = 2.7 Hz, 1H).
Data in accordance to literature.[9]

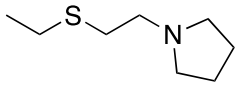
***N*-Methyl imidazole**
^1H NMR (300 MHz, D_2O):δ 3.73 (s, 3H), 7.10 (s, 1H), 7.17 (s, 1H), 7.89 (s, 1H).
Data in accordance to literature.[10]

1-Ethoxy-2-(ethylthio)ethane (6a)



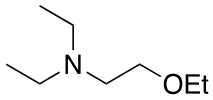
Viscous pale yellow liquid.
^1H NMR (300 MHz, $CDCl_3$) δ 3.65 – 3.37 (m, 4H), 2.76 – 2.48 (m, 4H), 1.20 (dt, J = 15.8, 7.2 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 77.58 (s), 77.16 (s), 76.74 (s), 70.30 (s), 66.39 (s), 31.23 (s), 26.48 (s), 15.24 (s), 14.94 (s).
HRMS calc m/z: 134.0765 Da (M), found 134.0767 (1.5 ppm)

1-[2-(Ethylthio)ethyl]-pyrrolidine (6b)



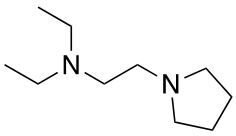
Viscous pale yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 4H), 2.35 (td, J = 7.0, 2.7 Hz, 6H), 1.67 – 1.50 (m, 4H), 1.07 (t, J = 7.4 Hz, 3H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 77.58 (s), 77.16 (s), 76.73 (s), 56.18 (s), 53.88 (s), 30.32 (s), 25.91 (s), 23.22 (s), 14.64 (s).
HRMS calc m/z: 160.1160 Da ($[M+H]^+$), found 160.1147 (8 ppm)

2-Ethoxy-*N*,*N*-diethylethanamine (7a)



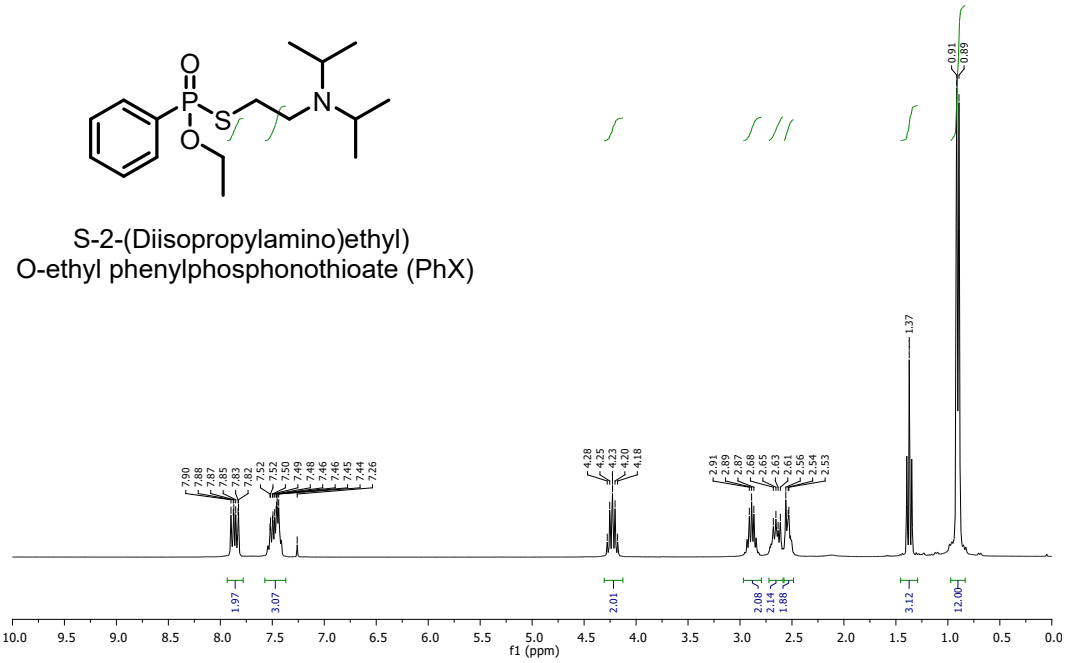
Viscous pale yellow liquid
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (q, J = 6.8 Hz, 4H), 2.64 – 2.44 (m, 6H), 1.14 (t, J = 7.0 Hz, 3H), 0.97 (t, J = 7.1 Hz, 6H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 77.58 (s), 77.16 (s), 76.74 (s), 69.09 (s), 66.49 (s), 52.39 (s), 47.71 (s), 15.22 (s), 11.71 (s).
HRMS calc m/z: 146.1545 Da ($[M+H]^+$), found 146.1538 (5 ppm)

***N*,*N*-Diethyl-1-pyrrolidineethanamine (7b)**

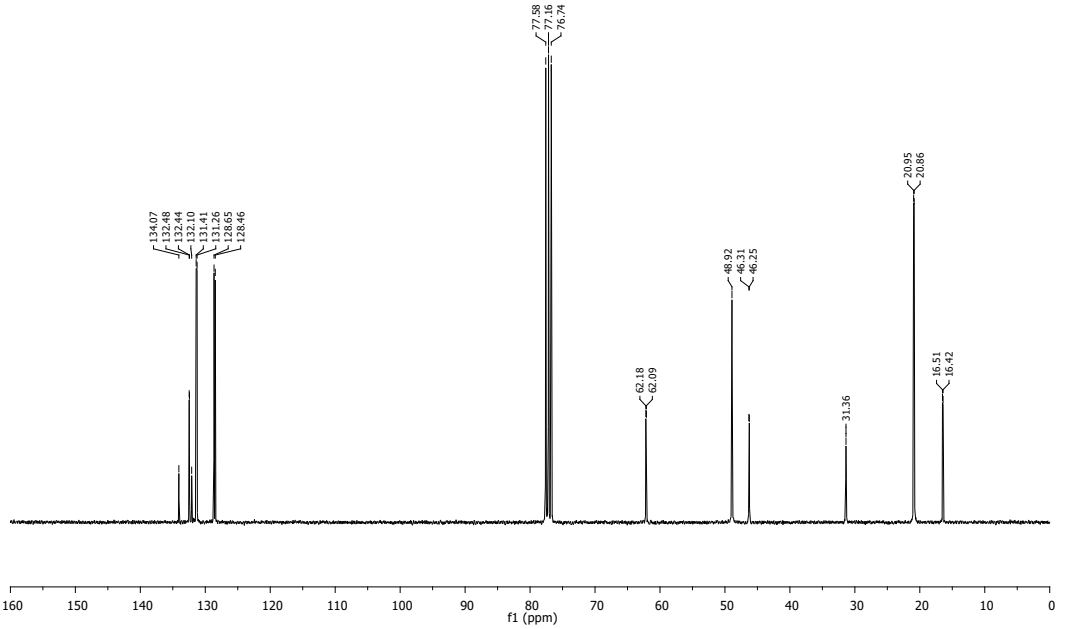


Viscous yellow pale liquid
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 – 2.27 (m, 12H), 1.62 (t, J = 3.4 Hz, 4H), 0.88 (t, J = 7.2 Hz, 6H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 77.59 (s), 77.16 (s), 76.74 (s), 54.52 (s), 54.46 (s), 51.86 (s), 47.41 (s), 23.27 (s), 11.66 (s).
HRMS calc m/z: 171.1861 Da ($[M+H]^+$), found 171.1858 (1.7 ppm)

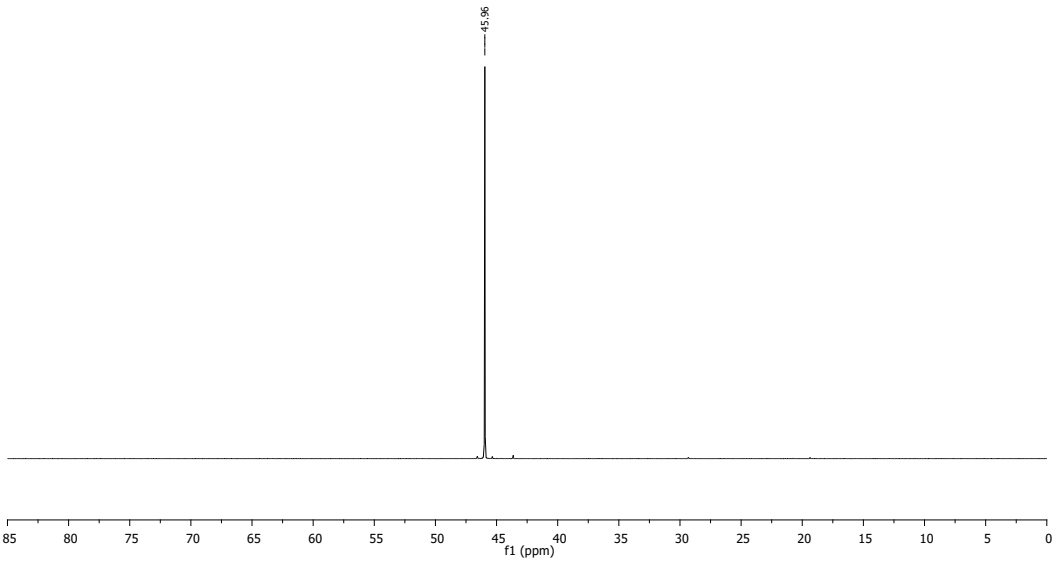
High field NMR Spectra



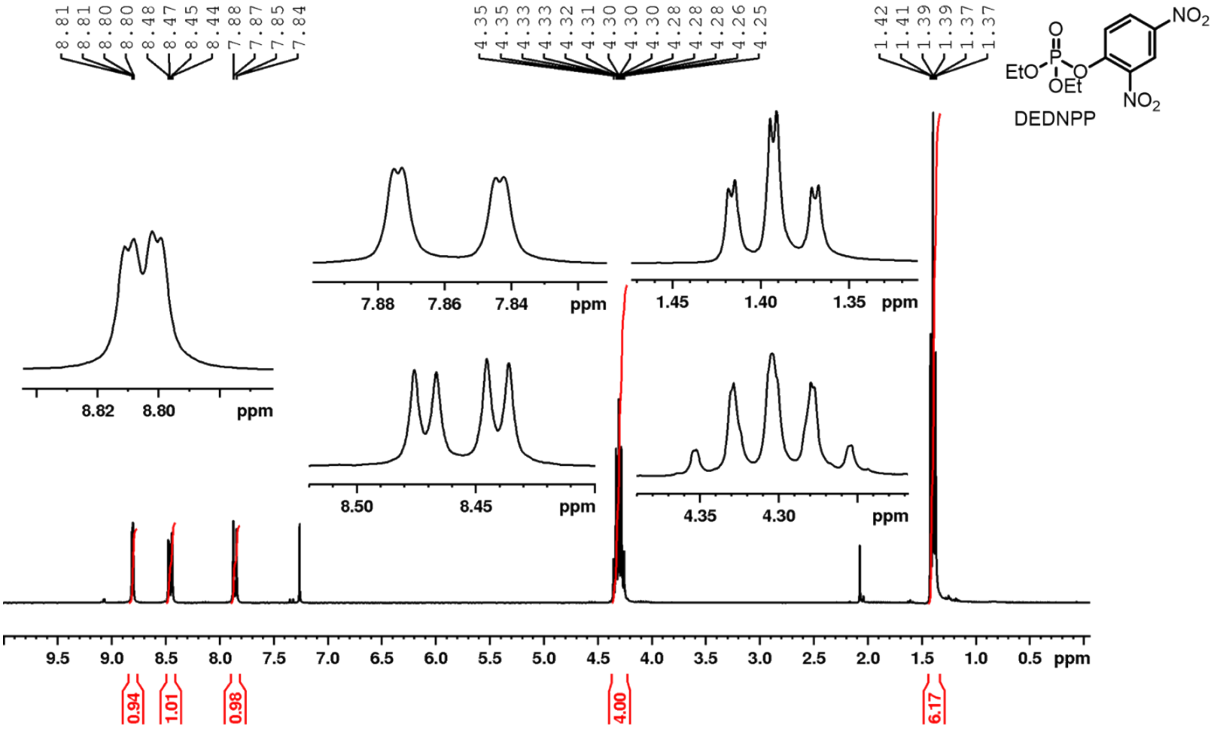
^{1}H NMR (300 MHz, $CDCl_3$) of *S*-2-(Diisopropylamino)ethyl) *O*-ethyl phenylphosphonothioate (PhX)



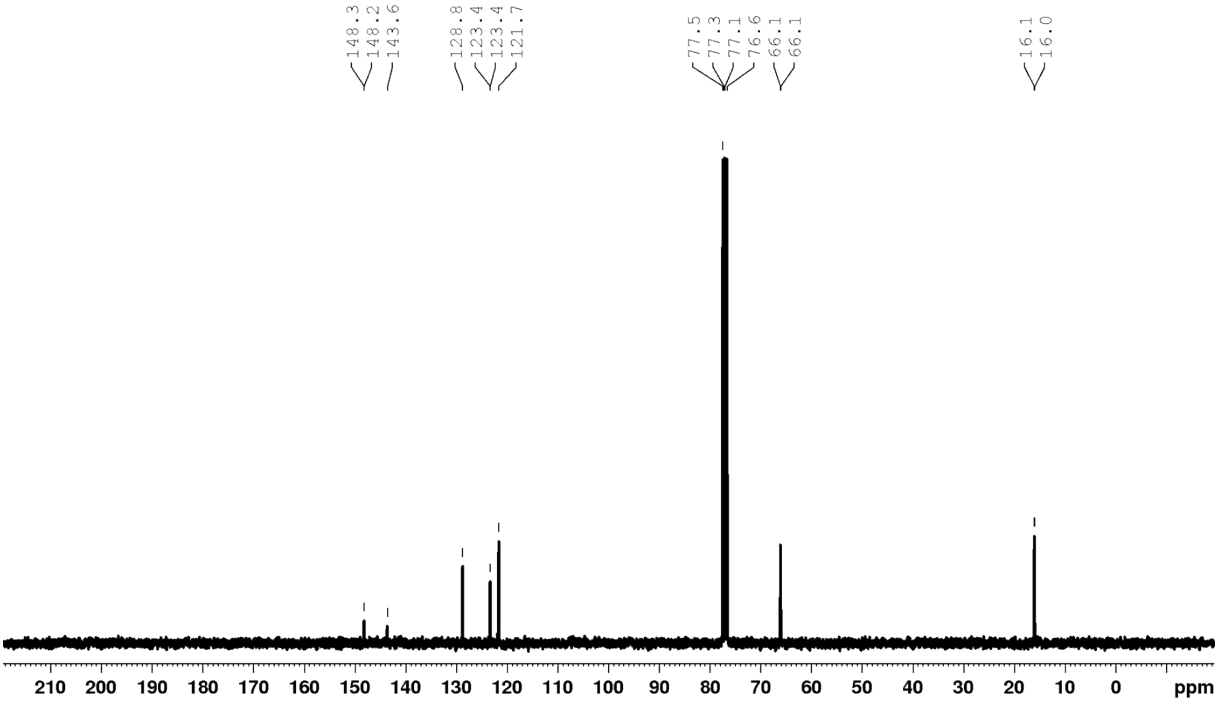
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of *S*-2-(Diisopropylamino)ethyl) *O*-ethyl phenylphosphonothioate (PhX)



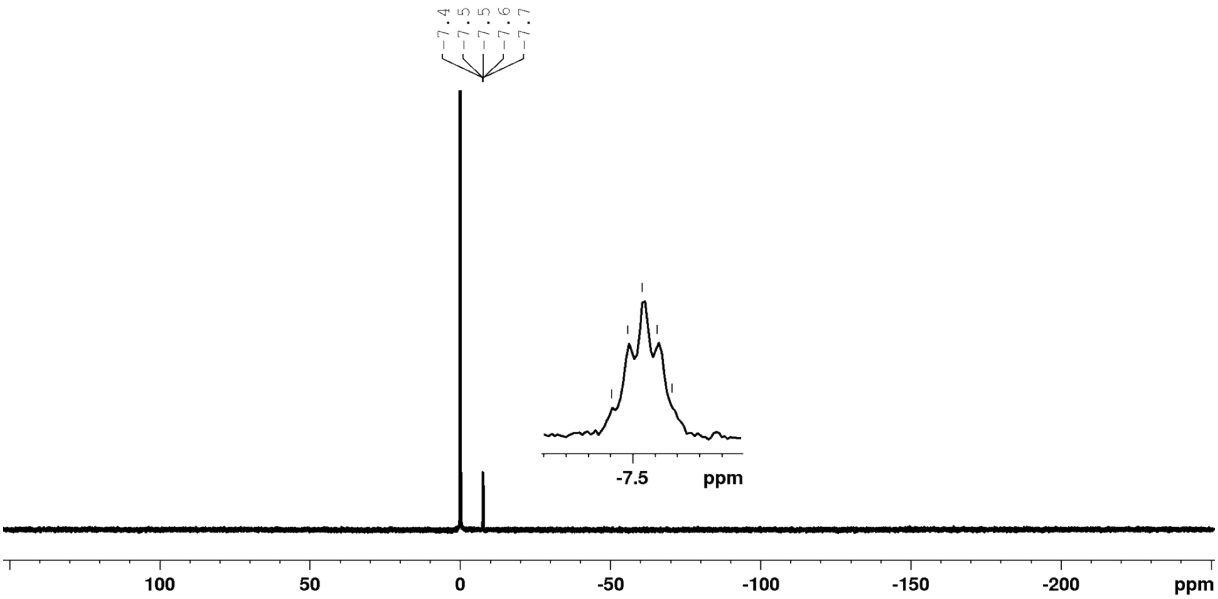
^{31}P NMR (121 MHz, $CDCl_3$) of *S*-2-(Diisopropylamino)ethyl) *O*-ethyl phenylphosphonothioate (PhX)



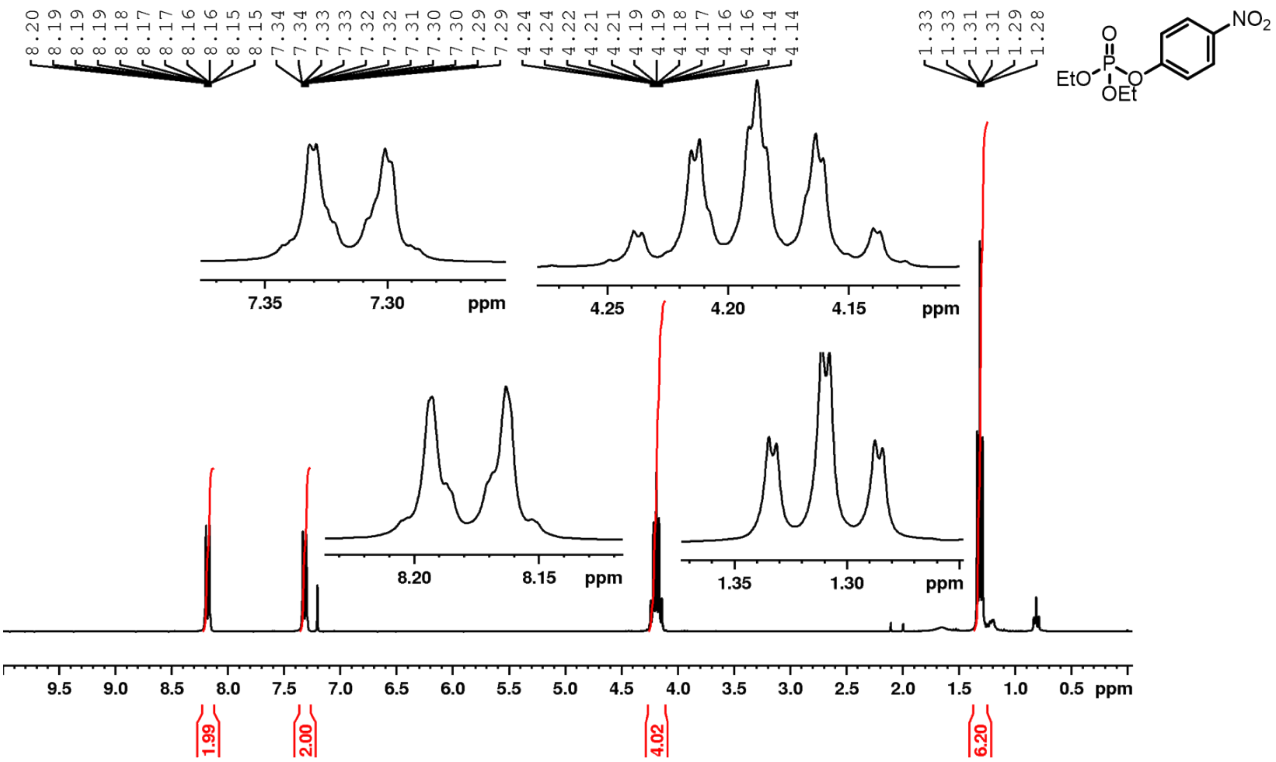
^{1}H NMR (300 MHz, $CDCl_3$) of diethyl 2,4-dinitrophenyl phosphate (DEDNPP)



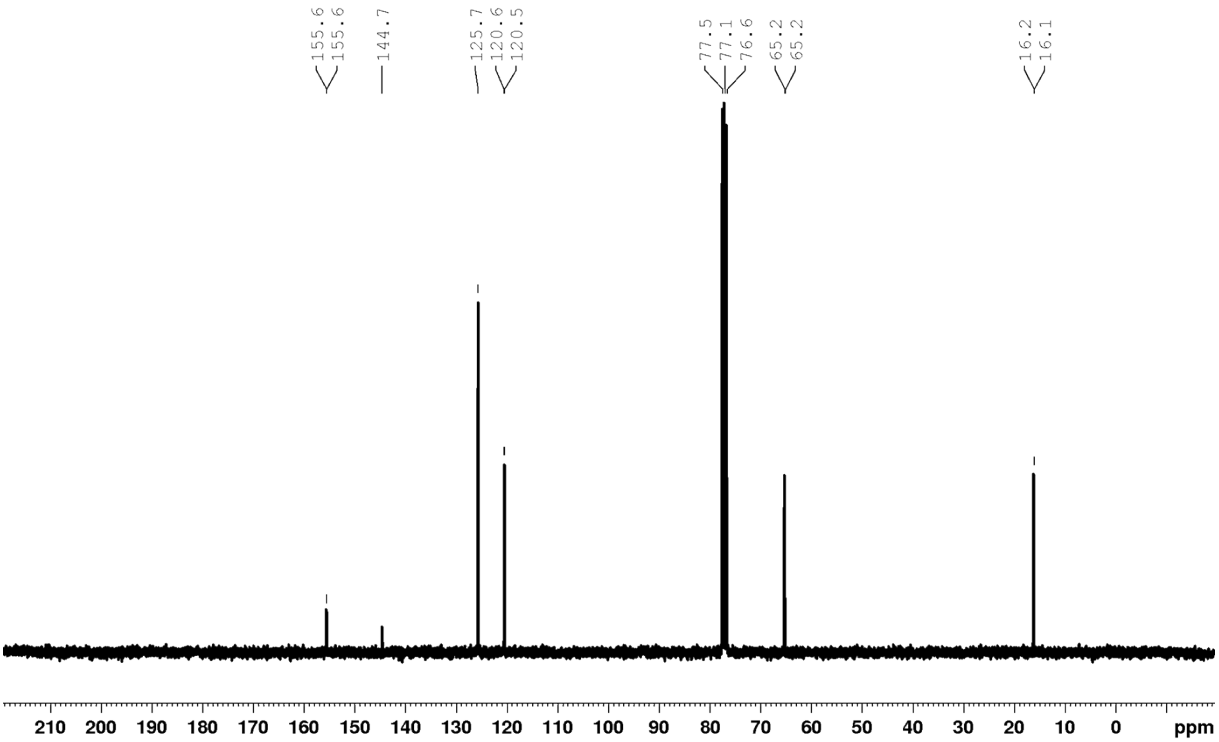
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of diethyl 2,4-dinitrophenyl phosphate (DEDNPP)



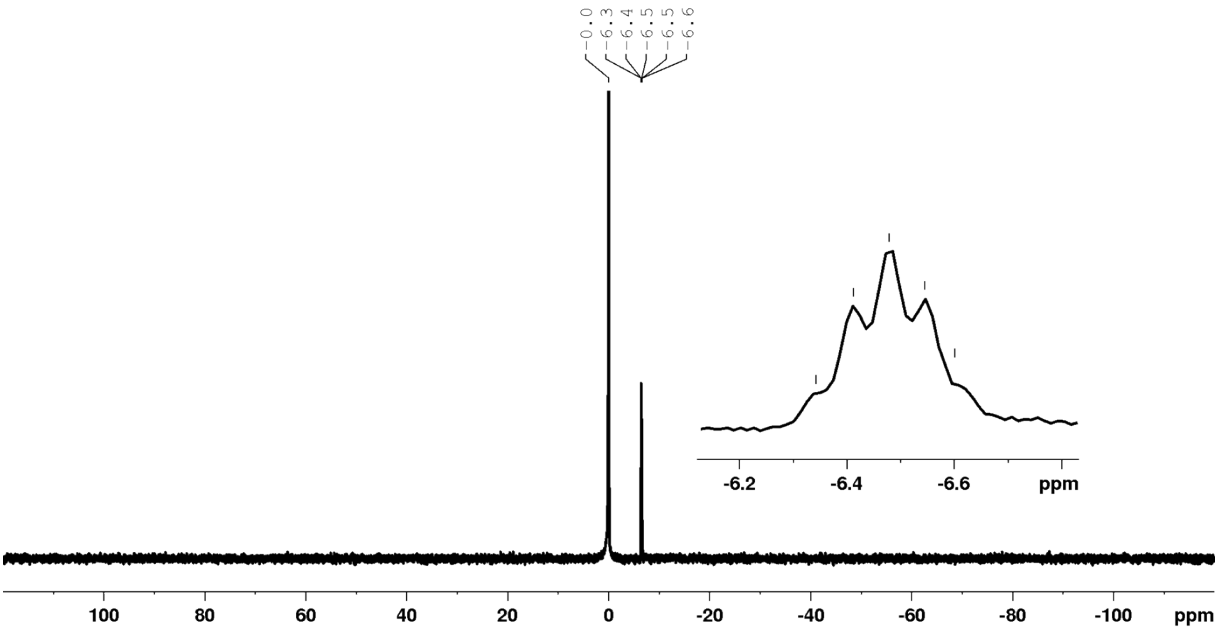
^{31}P NMR (121 MHz, $CDCl_3$) of diethyl 2,4-dinitrophenyl phosphate (DEDNPP) (with H_3PO_4 as reference, δ = 0 ppm)



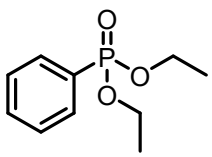
^{1}H NMR (300 MHz, $CDCl_3$) of diethyl 4-nitrophenyl phosphate (Paraoxon)



^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of diethyl 4-nitrophenyl phosphate (Paraoxon)

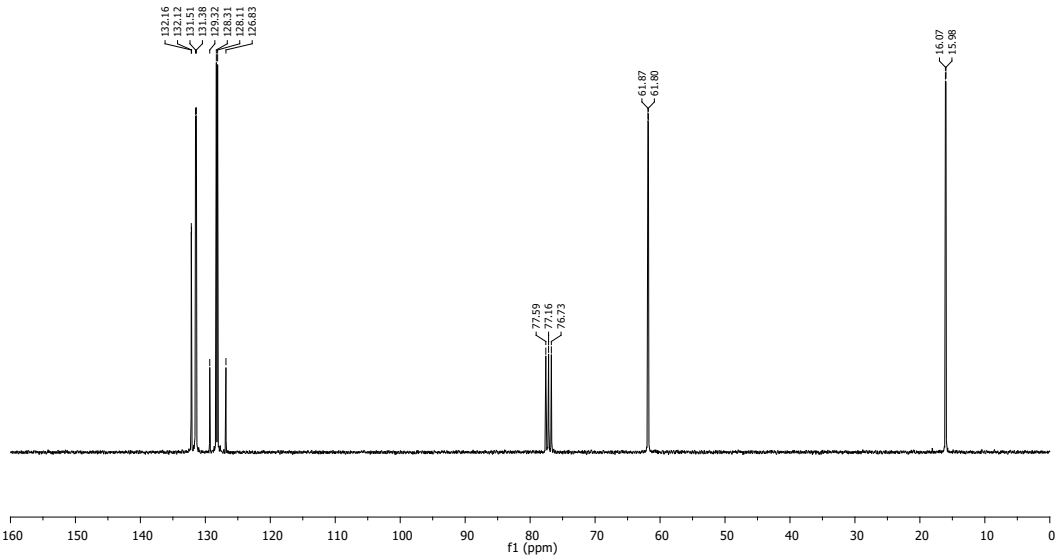


^{31}P NMR (121 MHz, $CDCl_3$) of diethyl 4-nitrophenyl phosphate (Paraoxon) (with H_3PO_4 as reference, δ = 0 ppm)

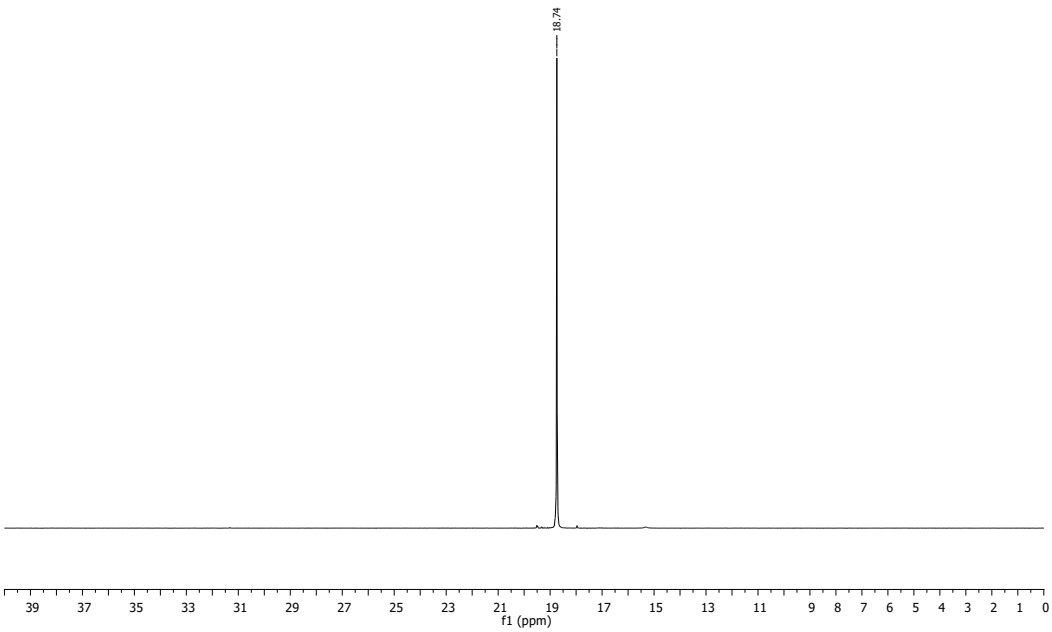


Diethyl phenylphosphonate

^{1}H NMR (300 MHz, $CDCl_3$) of diethyl phenylphosphonate

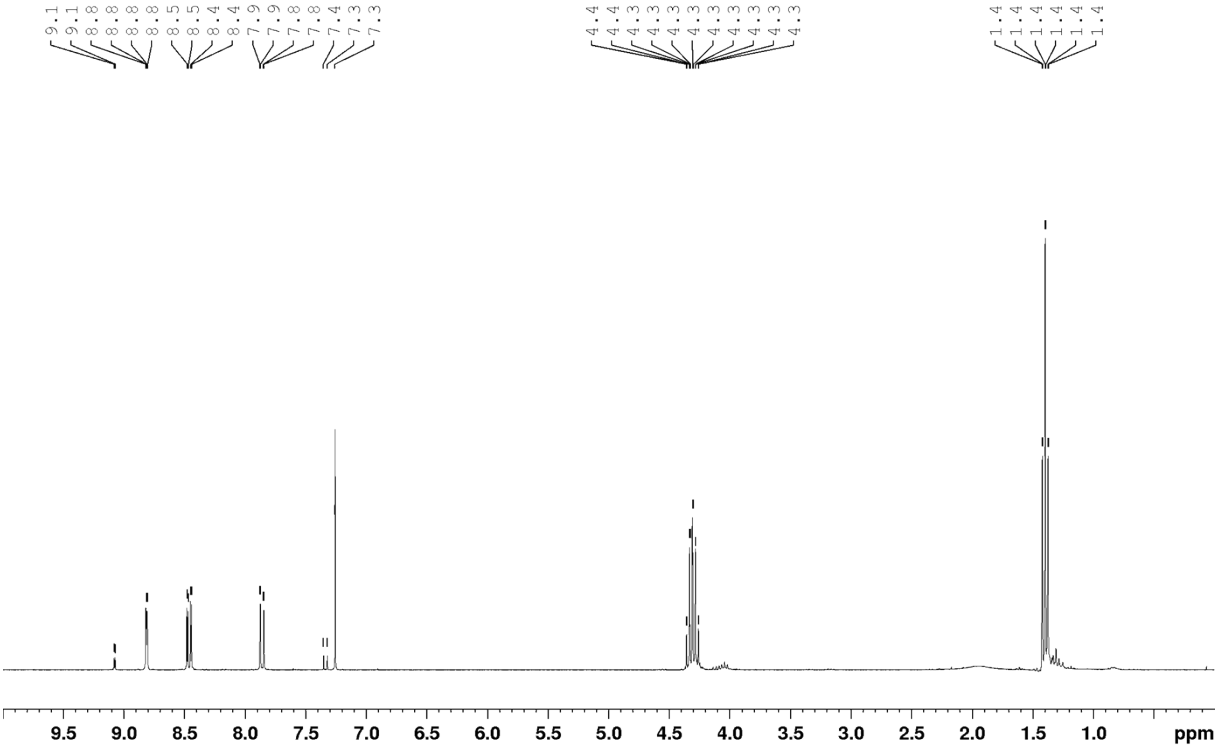


^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of diethyl phenylphosphonate

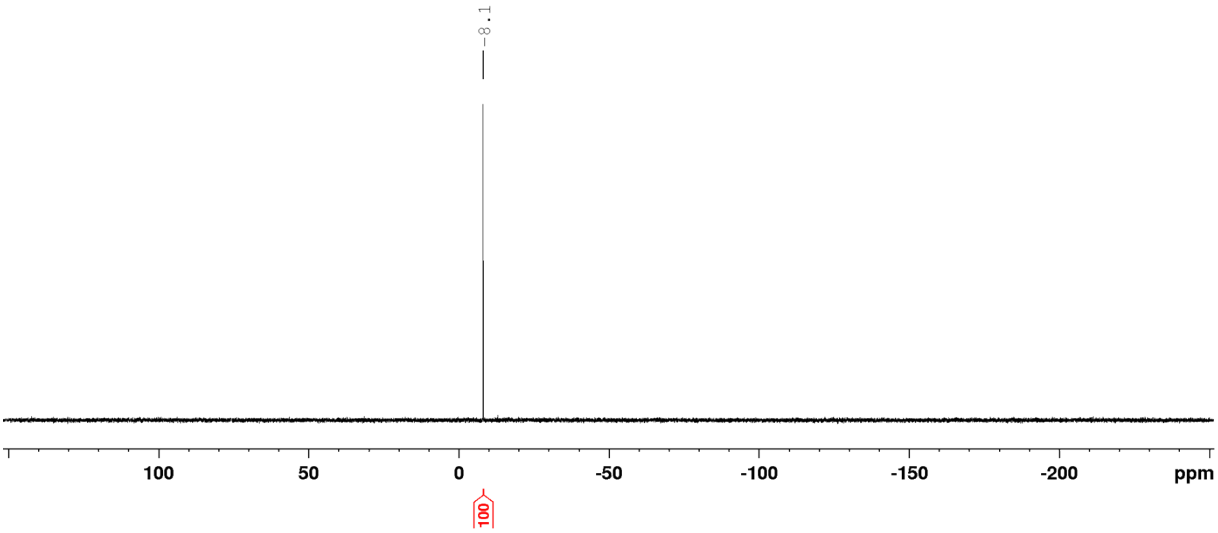


^{31}P NMR (121 MHz, $CDCl_3$) of diethyl phenylphosphonate

DEDNPP in EtOH 96% at 10^{-3} kbar (NMR in $CDCl_3$, 300 MHz): Table 1, entry 5

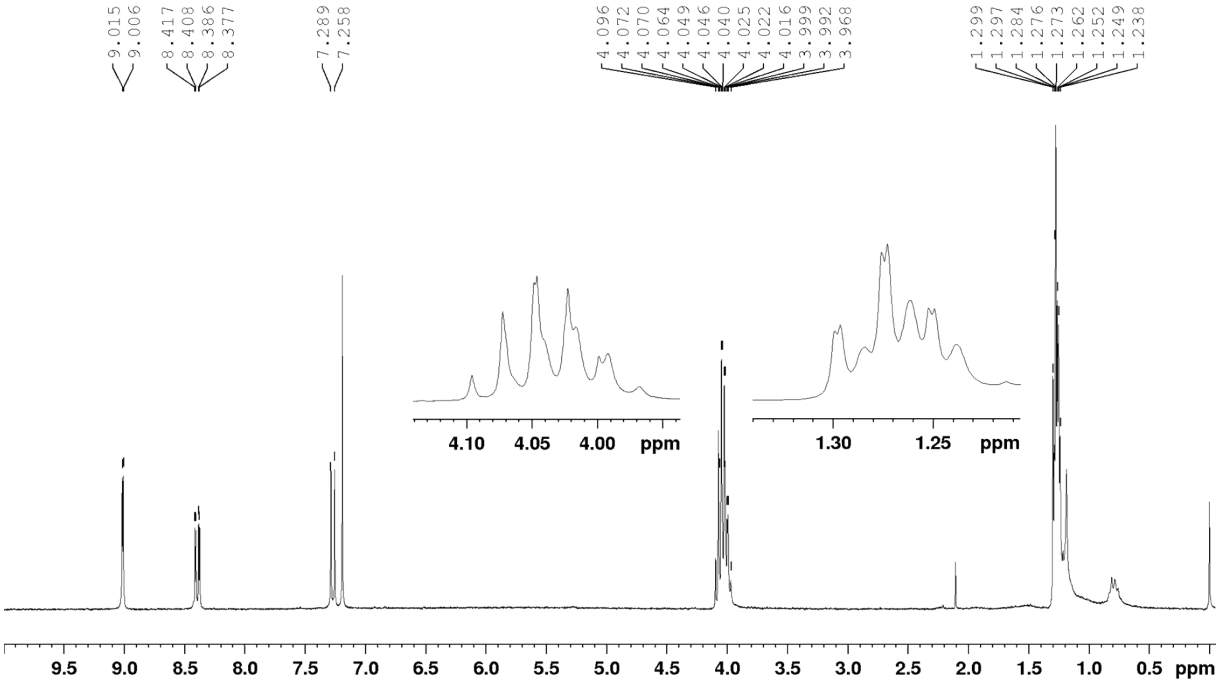


^{1}H NMR (300 MHz, $CDCl_3$) DEDNPP in EtOH 96% at 10^{-3} kbar

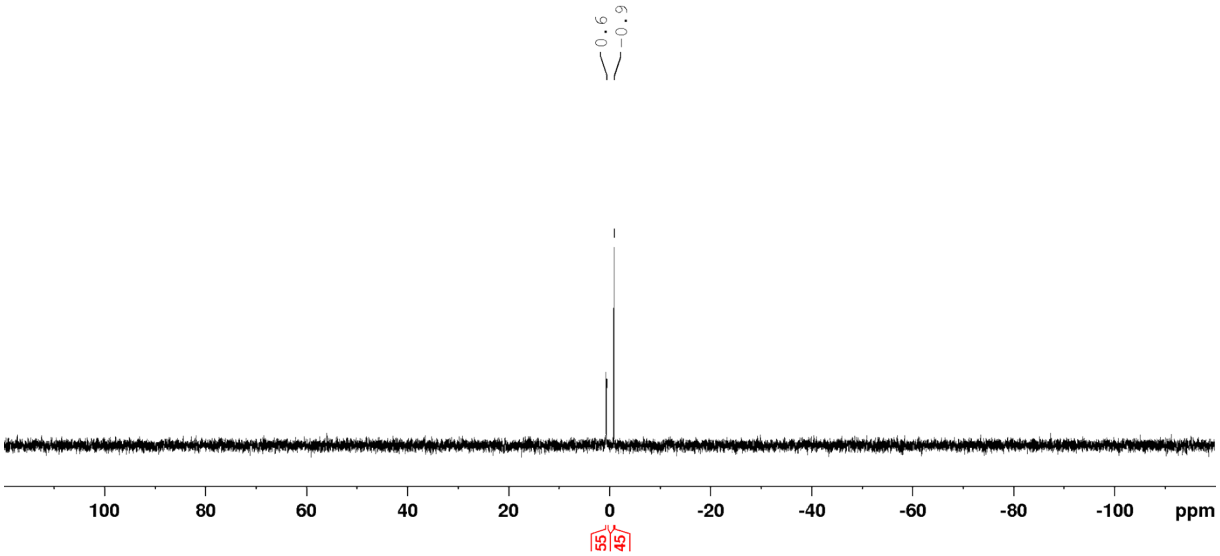


^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) DEDNPP in EtOH 96% at 10^{-3} kbar

DEDNPP in EtOH 96% at 14 kbar (NMR in $CDCl_3$, 300 MHz): Table 1, entry 6

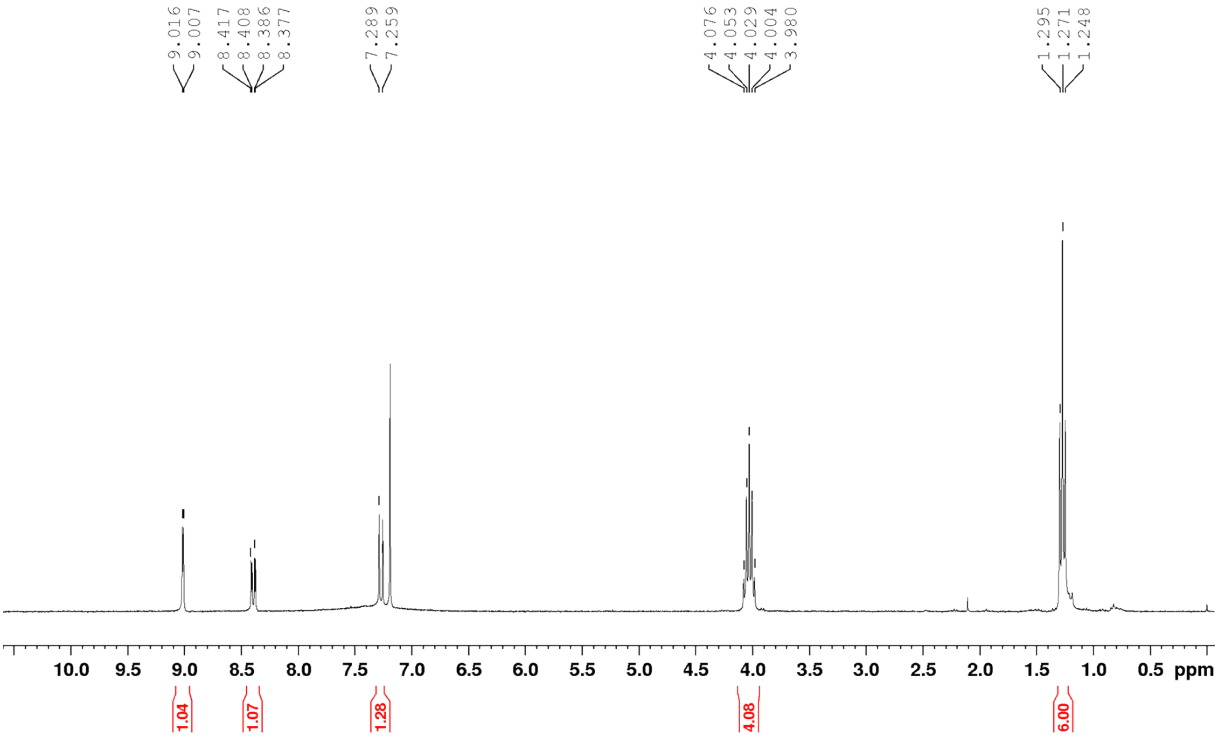


^{1}H NMR (300 MHz, $CDCl_3$) DEDNPP in EtOH 96% at 14 kbar

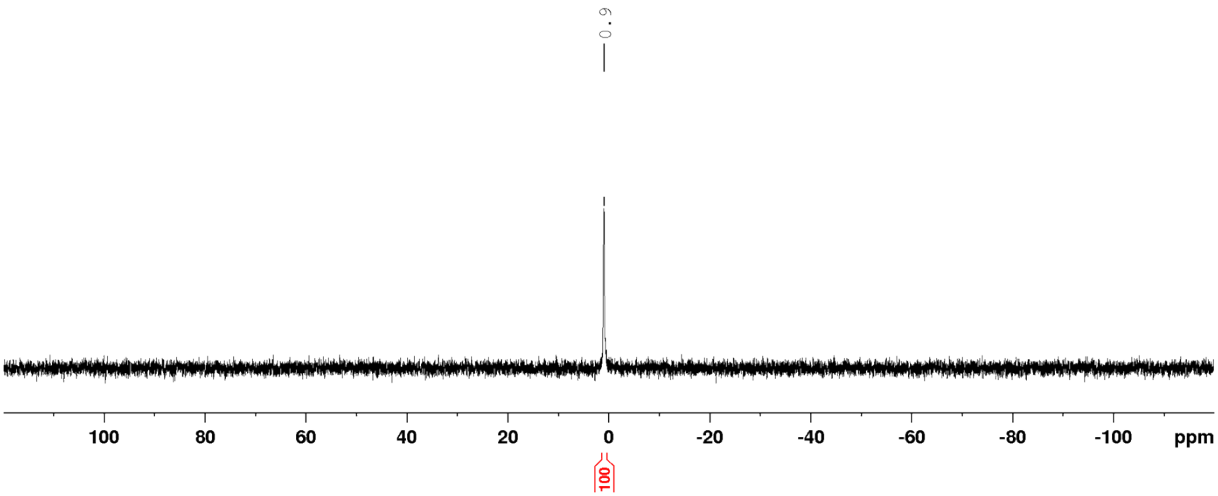


^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) DEDNPP in EtOH 96% at 14 kbar

DEDNPP in MeCN/H_2O (99:1) at 14 kbar (NMR in $CDCl_3$, 300 MHz): Table 1, entry 7

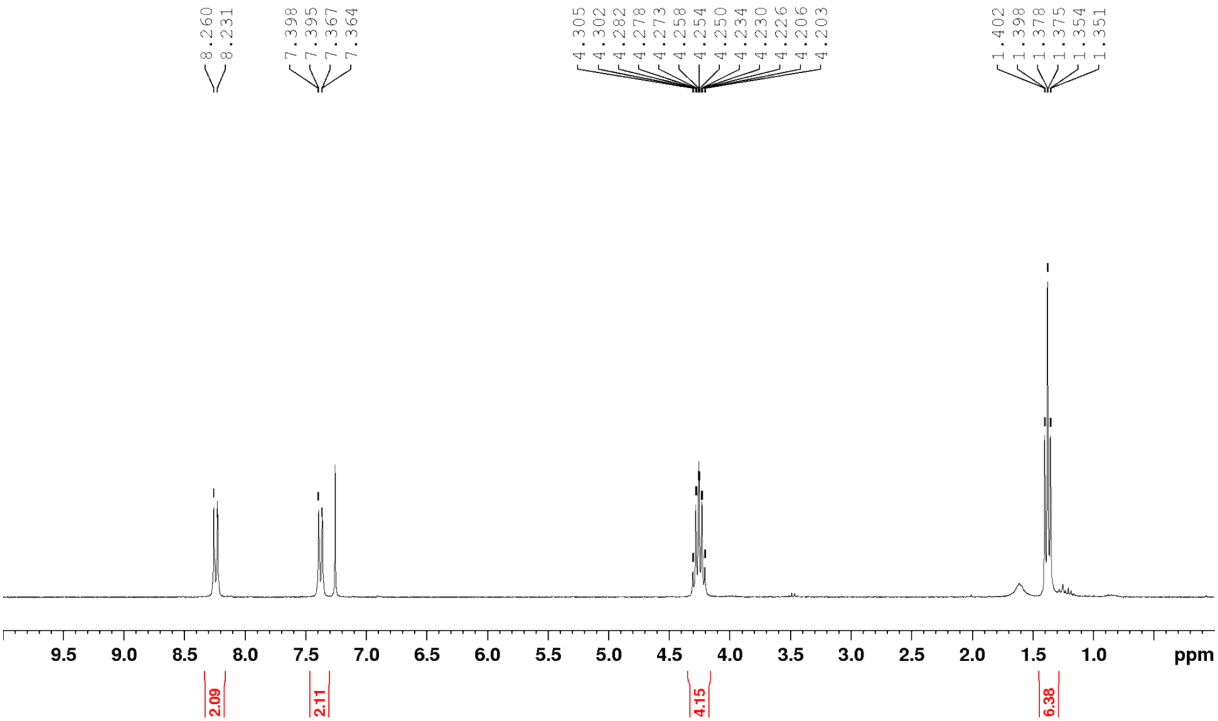


^{1}H NMR (300 MHz, $CDCl_3$) DEDNPP in MeCN/H_2O (99:1) at 14 kbar

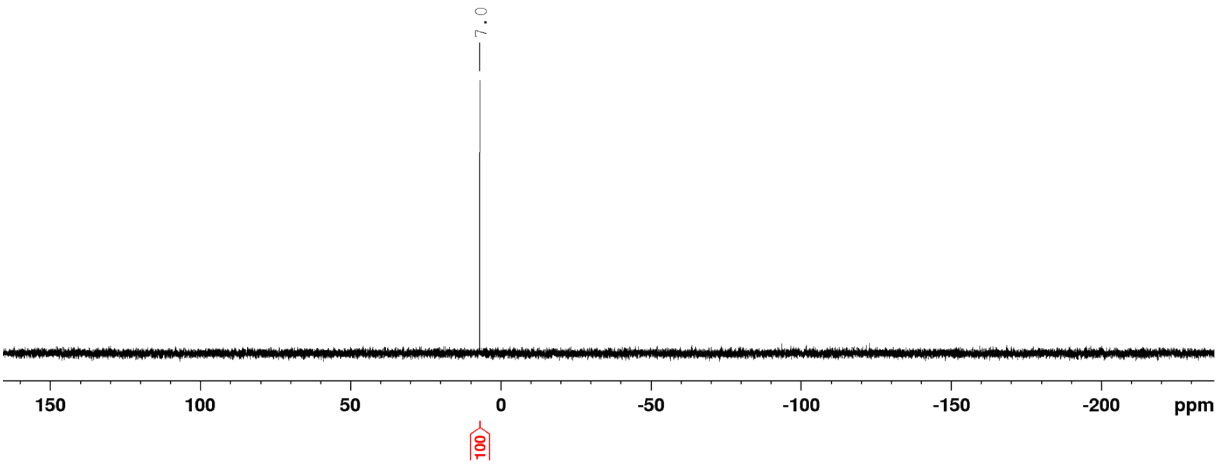


^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) DEDNPP in MeCN/H_2O (99:1) at 14 kbar

Paraoxon in MeCN/H_2O (99:1) at 14 kbar (NMR in $CDCl_3$, 300 MHz): Table 1, entry 8

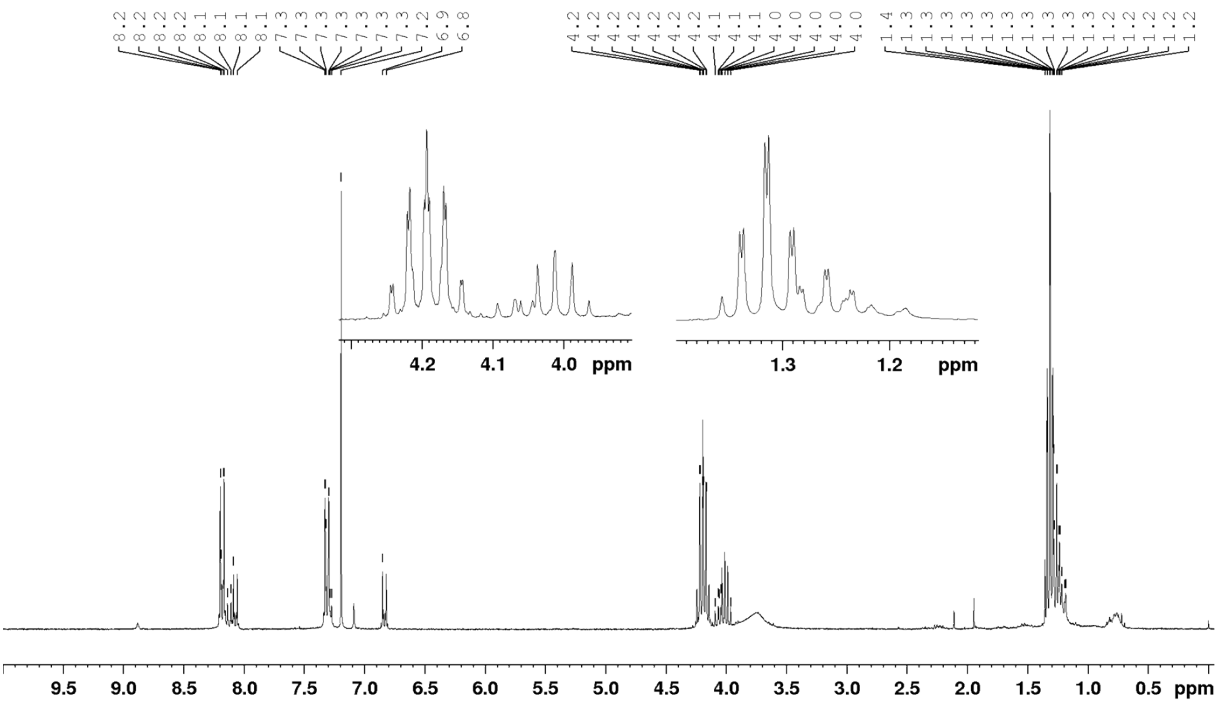


^{1}H NMR (300 MHz, $CDCl_3$) Paraoxon in MeCN/H_2O (99:1) at 14 kbar

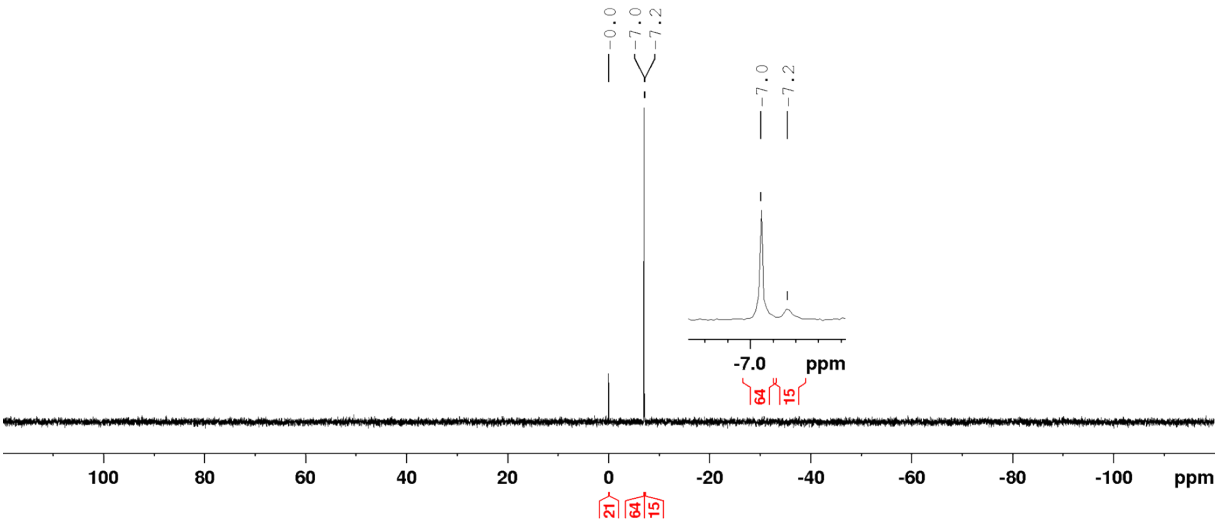


^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) Paraoxon in MeCN/H_2O (99:1) at 14 kbar

Paraoxon in MeCN/H_2O (99:1) at 16 kbar (NMR in $CDCl_3$, 300 MHz): Table 1, entry 9

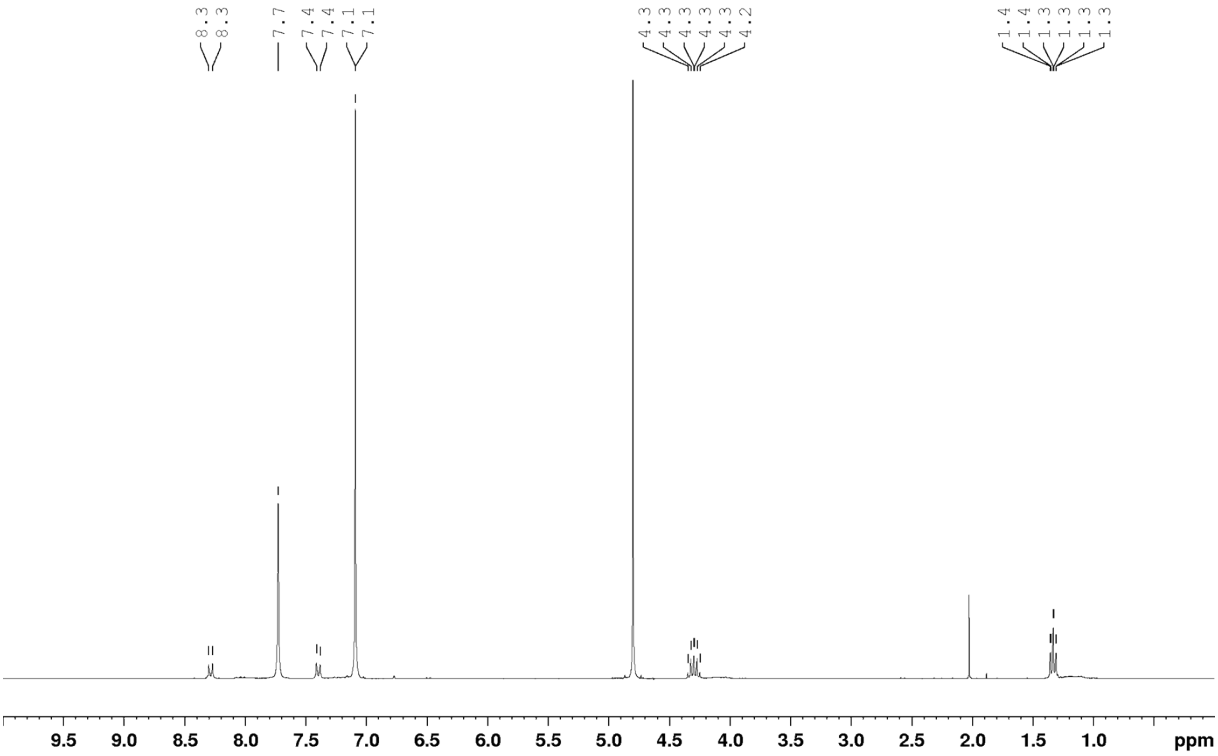


^{1}H NMR (300 MHz, $CDCl_3$) Paraoxon in MeCN/H_2O (99:1) at 16 kbar

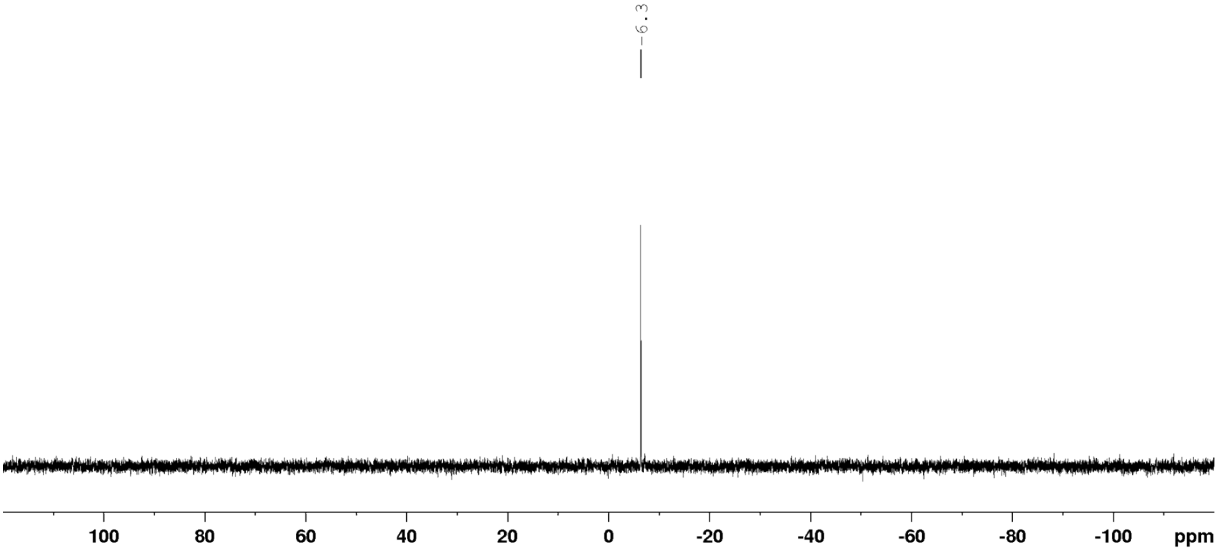


^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) Paraoxon in MeCN/H_2O (99:1) at 16 kbar

Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar (^1H and ^{31}P NMR in D_2O): Table 2, entry 1

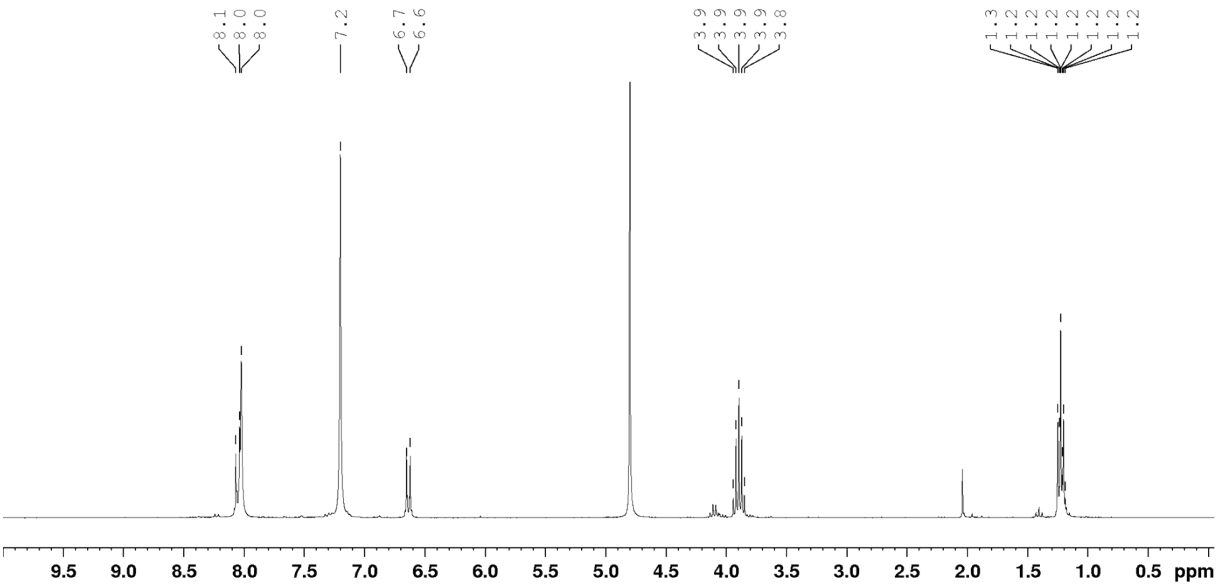


^1H NMR (300 MHz, D_2O) Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar

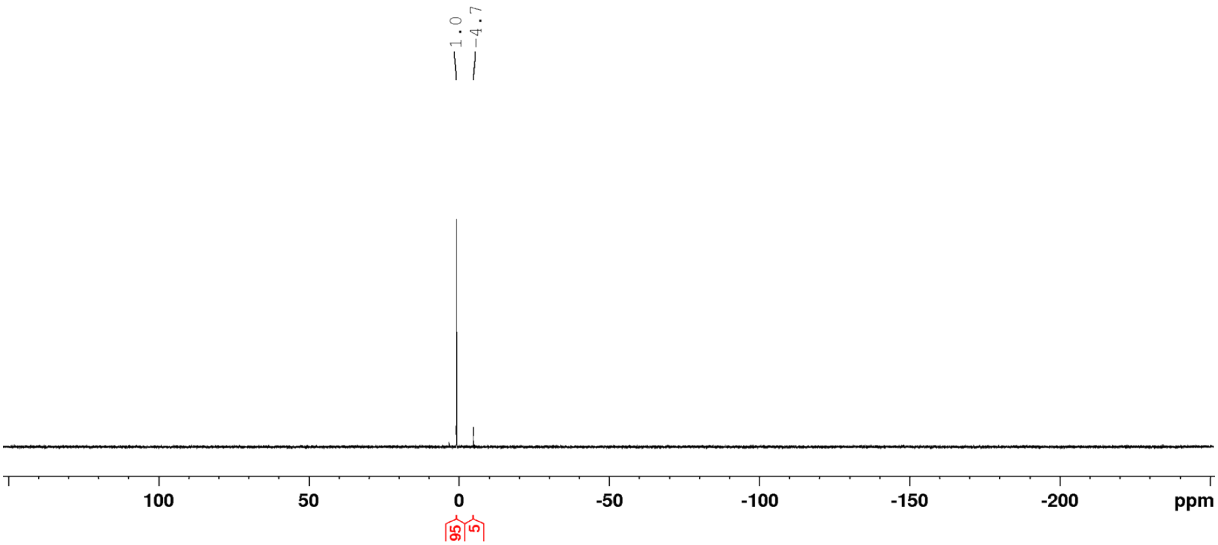


^{31}P {^1H} NMR (121 MHz, D_2O) Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar

Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar (^1H and ^{31}P NMR in D_2O): Table 2, entry 2

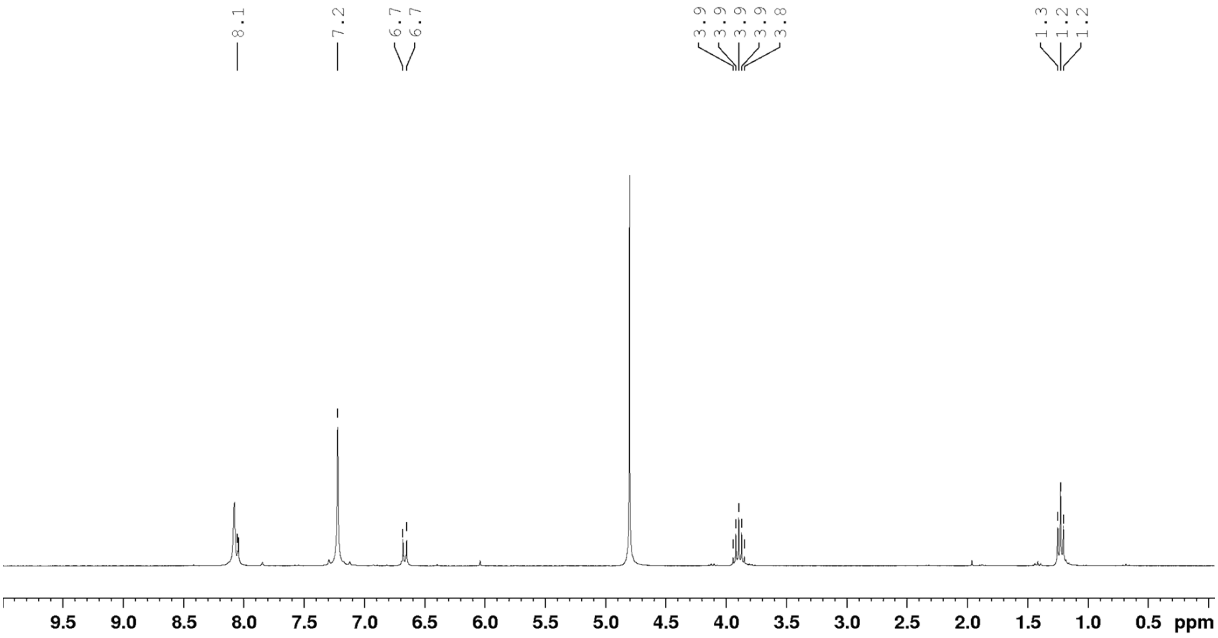


^1H NMR (300 MHz, D_2O) Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar

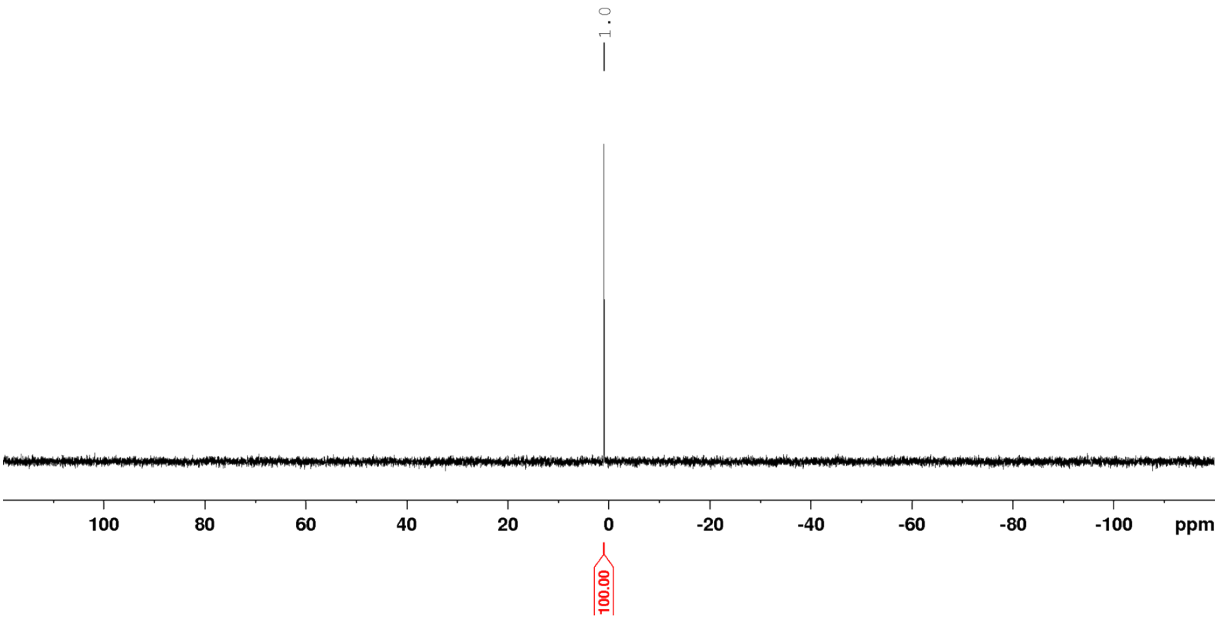


^{31}P {^1H} NMR (121 MHz, D_2O) Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar

Paraoxon in MeCN/H_2O (99:1) with imidazole at 16 kbar (^1H and ^{31}P NMR in D_2O): Table 2, entry 3

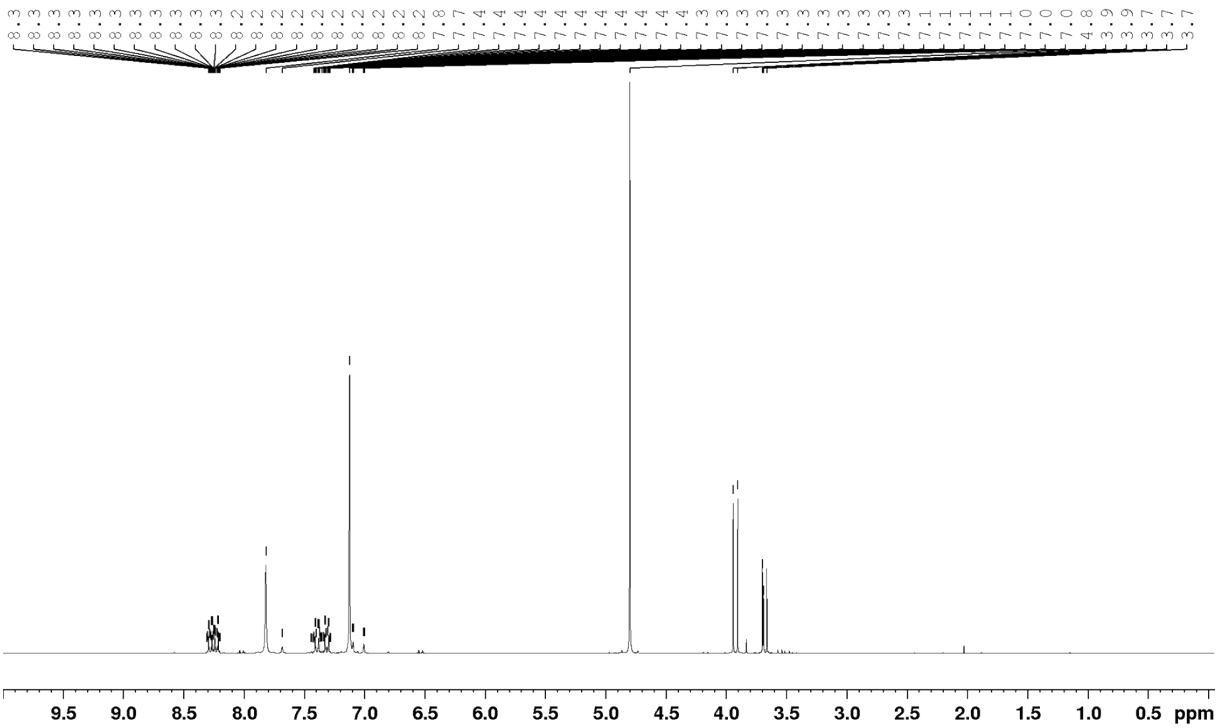


^1H NMR (300 MHz, D_2O) Paraoxon in MeCN/H_2O (99:1) with imidazole at 16 kbar

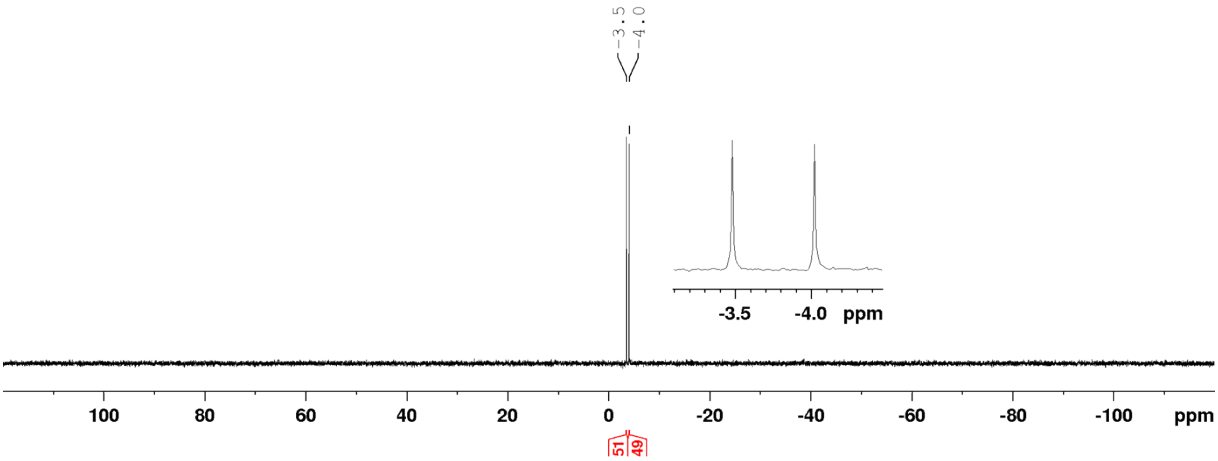


^{31}P {^1H} NMR (121 MHz, D_2O) Paraoxon in MeCN/H_2O (99:1) with imidazole at 16 kbar

Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 1 bar (^1H and ^{31}P NMR in D_2O): Table 2, entry 4

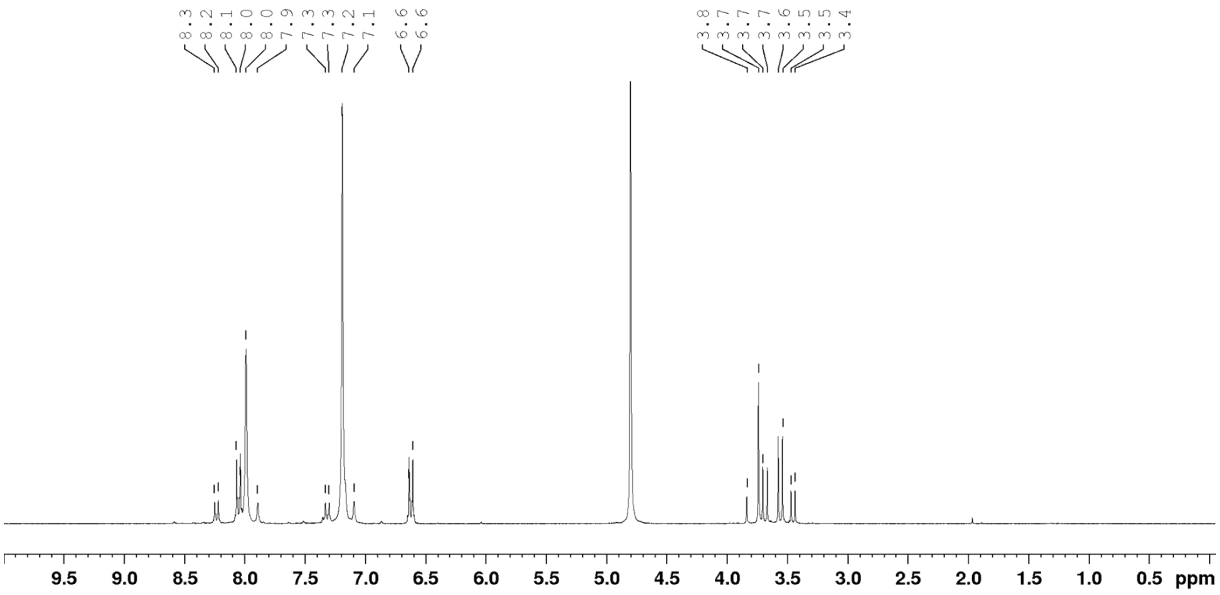


^1H NMR (300 MHz, D_2O) Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 1 bar

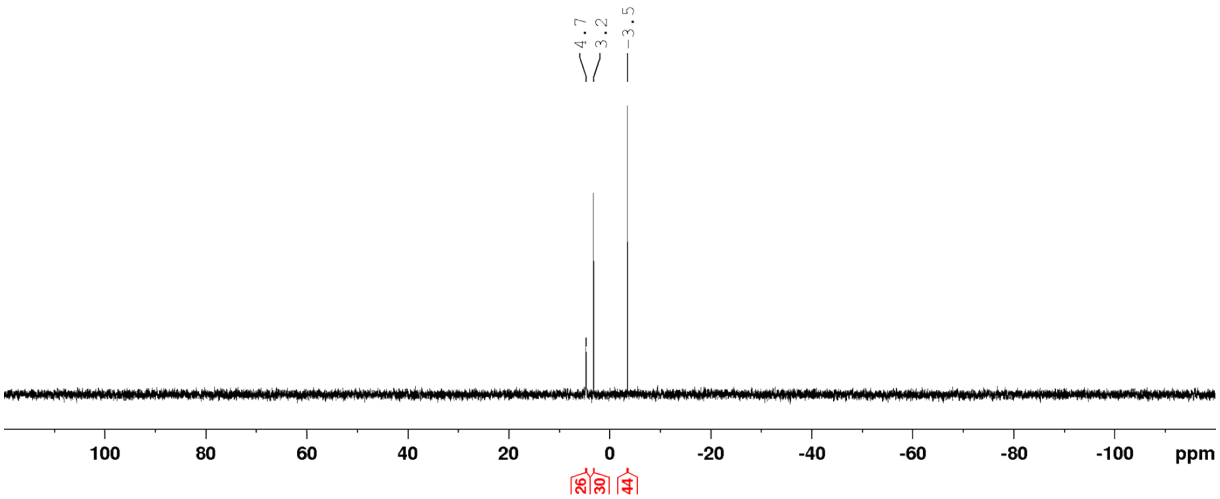


^{31}P {^1H} NMR (121 MHz, D_2O) Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 1 bar

Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar (^1H and ^{31}P NMR in D_2O): Table 2, entry 5

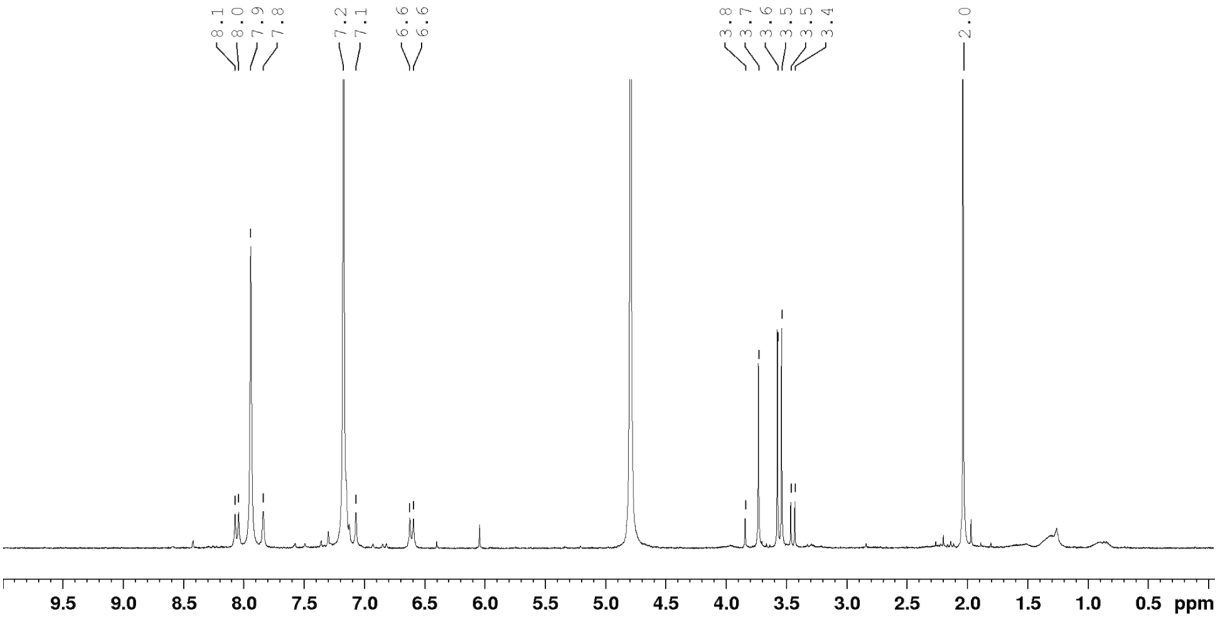


^1H NMR (300 MHz, D_2O) Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar

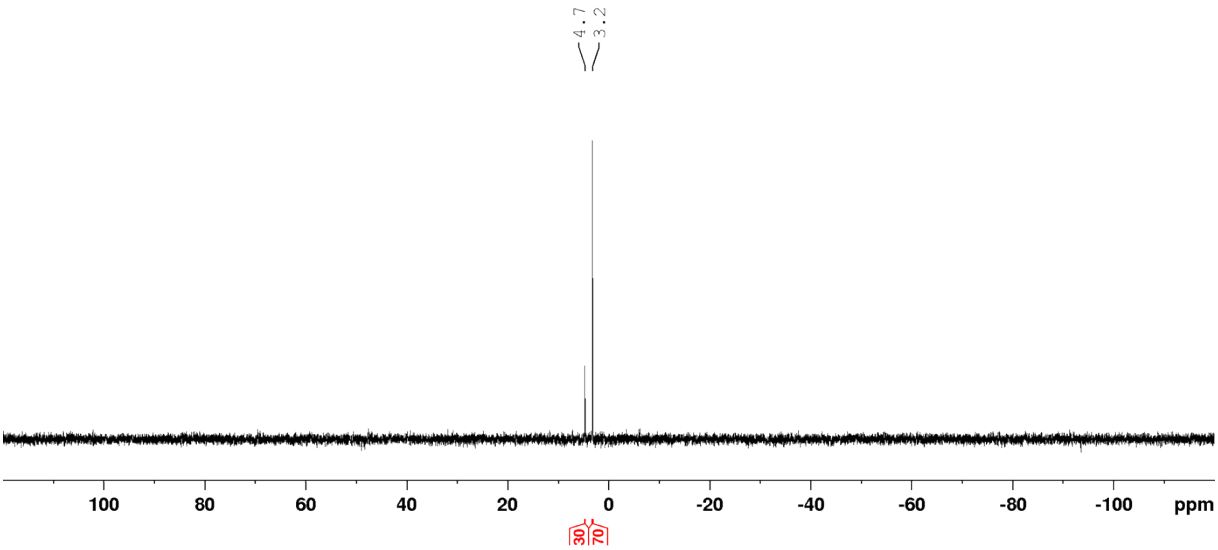


^{31}P {^1H} NMR (121 MHz, D_2O) Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 14 kbar

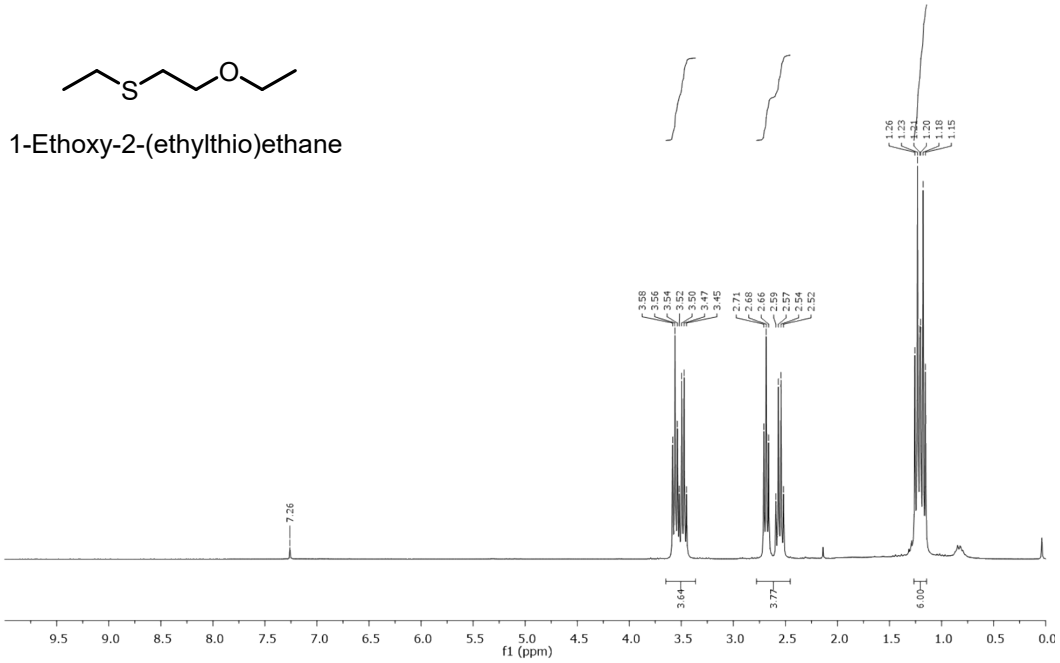
Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 16 kbar (^1H and ^{31}P NMR in D_2O): Table 2, entry 6



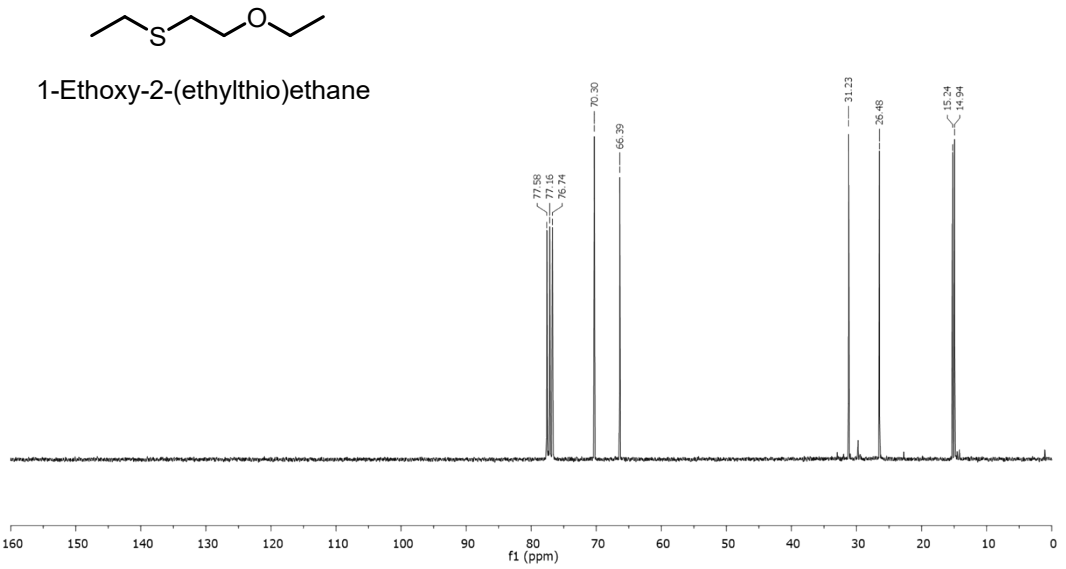
^1H NMR (300 MHz, D_2O) Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 16 kbar



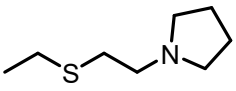
^{31}P {^1H} NMR (121 MHz, D_2O) Methyl Paraoxon in MeCN/H_2O (99:1) with imidazole at 16 kbar



^{1}H NMR (300 MHz, $CDCl_3$) of 1-ethoxy-2-(ethylthio)ethane

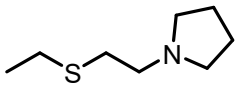


^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of 1-ethoxy-2-(ethylthio)ethane



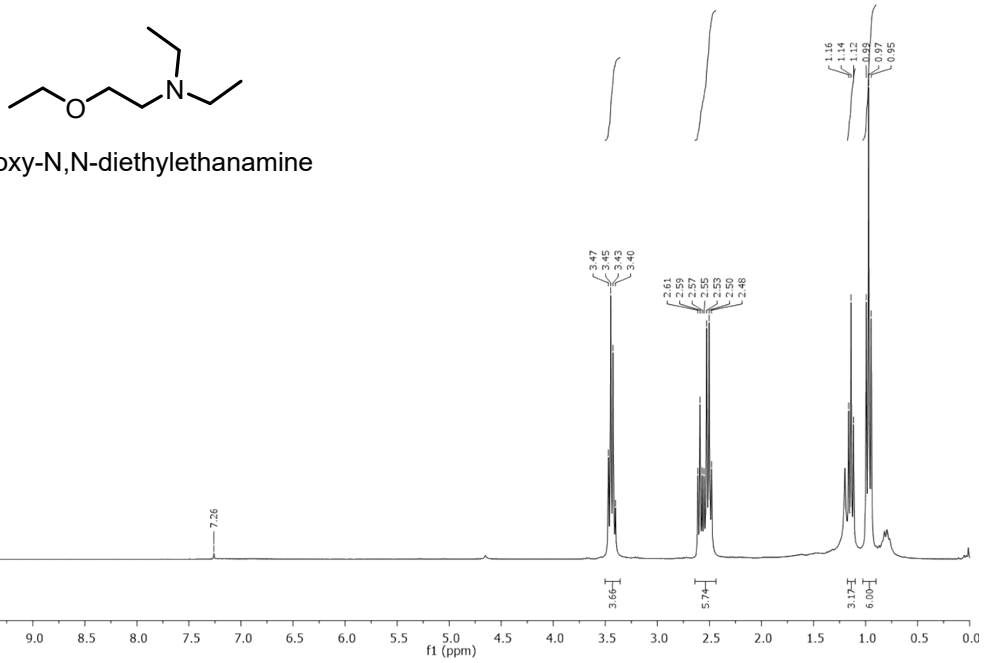
1-[2-(Ethylthio)ethyl]-pyrrolidine

^{1}H NMR (300 MHz, CDCl3) of 1-[2-(ethylthio)ethyl]-pyrrolidine

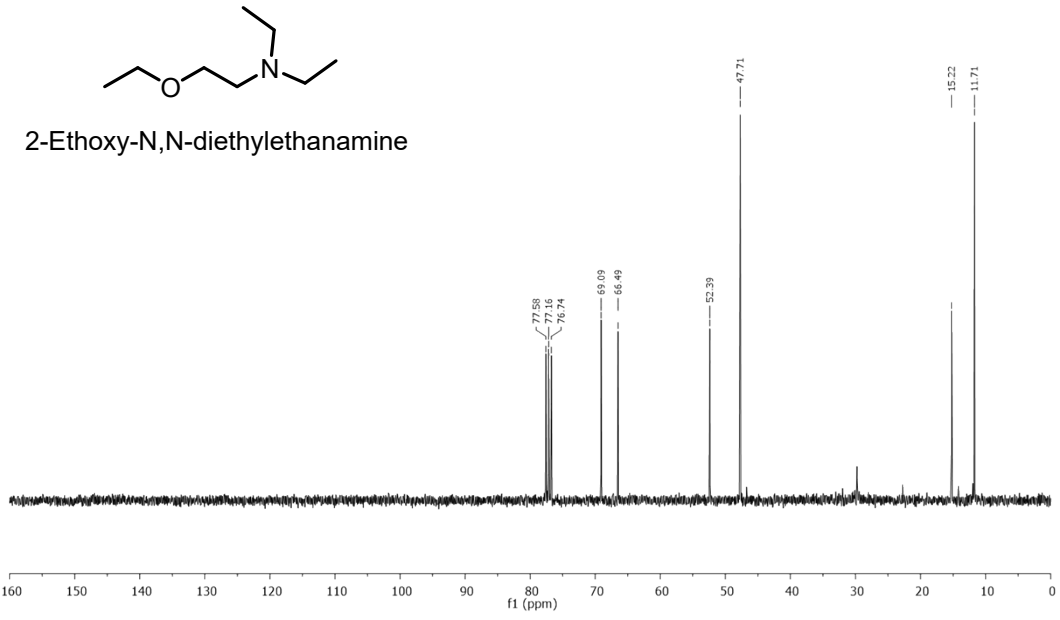


1-[2-(Ethylthio)ethyl]-pyrrolidine

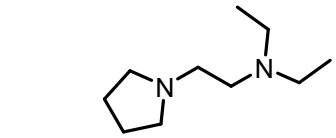
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of 1-[2-(ethylthio)ethyl]-pyrrolidine



^{1}H NMR (300 MHz, $CDCl_3$) of 2-ethoxy-N,N-diethylethanamine

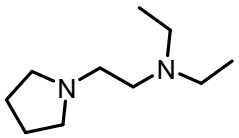


^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of 2-ethoxy-N,N-diethylethanamine

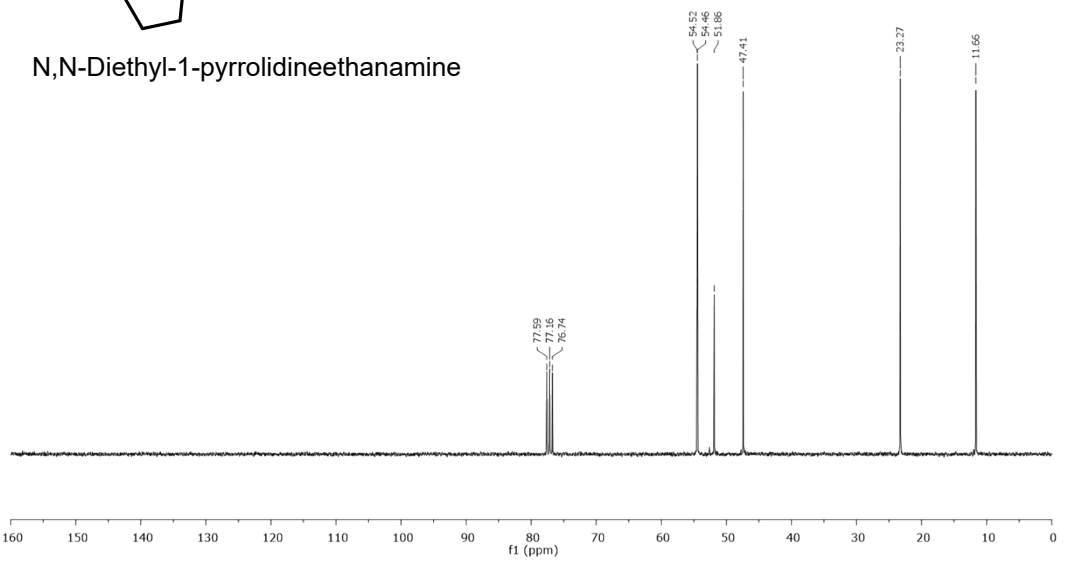


N,N-Diethyl-1-pyrrolidineethanamine

^{1}H NMR (300 MHz, $CDCl_3$) of N,N-Diethyl-1-pyrrolidine ethanamine



N,N-Diethyl-1-pyrrolidineethanamine



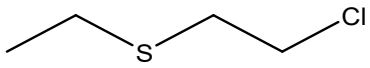
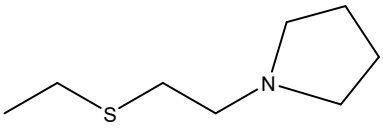
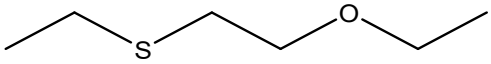
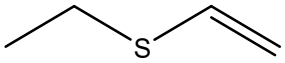
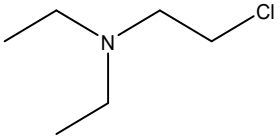
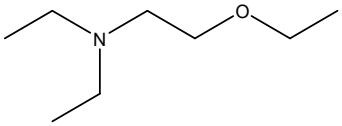
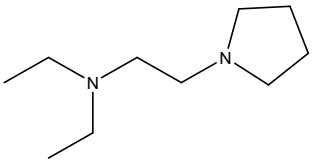
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of N,N-Diethyl-1-pyrrolidine ethanamine

GC-MS results

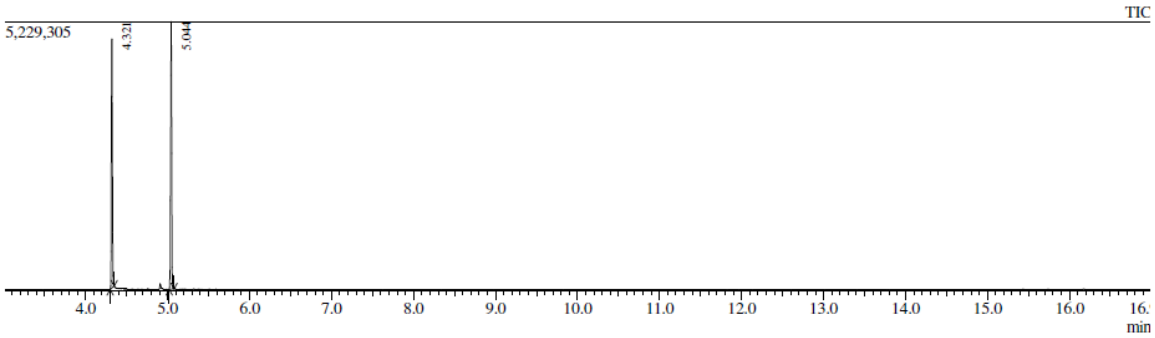
Results table

Entry	Substrate	Scavenger	P (kbar)	Temp. (°C)	Time (h)	Conv. (%)
1	CEES	Ethanol	$1 \cdot 10^{-3}$	20 °C	24	0
2	CEES	Ethanol	$1 \cdot 10^{-3}$	50 °C	24	69
3	CEES	Ethanol	14		24	32
4	CEES	Ethanol	16		24	14
5	CTEA	Ethanol*	4		24	0
6	CTEA	Ethanol*	16		24	0
7	CEES	EtOLi	1	20 °C	24	37
8	CEES	EtOLi	14		24	100
9	CTEA	EtOLi	14		24	100
10	CEES	Pyrrolidine	$1 \cdot 10^{-3}$	20 °C	24	15
11	CEES	Pyrrolidine	14		24	100
12	CTEA	Pyrrolidine	14		24	100

The results are obtained by low resolution GC-MS (Shimadzu QP2010 hybrid ionization apparatus (HP5- MS stationary phase, l = 30 cm, d = 0.25 mm, film thickness = 0.25 µm) following the method A (Starting temperature is set at 50 °C, hold for 2 min then the temperature is increased by 20 °C/min to reach 250 °C and hold for 5 min). The ethyl vinyl sulfide formation was detected following method B (starting temperature is set at 40°C, hold at 5 min, then increasing by 15 °C/min to reach 150 °C and hold for 2 min. The latest analysis was performed by low resolution GC-MS (Thermo scientific, TRACE 1310 gas chromatography and ISQ 7000 single Quadrupole Mass spectrometer) (HP5- MS stationary phase, l = 30 cm, d = 0.25 mm, film thickness = 0.25 µm).

Compounds	Retention times (min)	
	Method A	Method B
Decane	5.08	9.842
	4.348	8.712
	7.303	
	4.947	9.586
		3.179
	4.179	
	4.617	
	6.896	

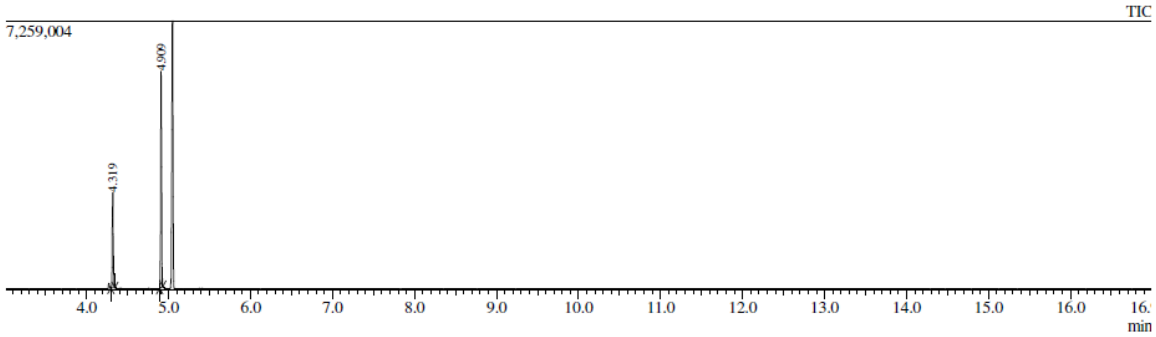
Entry 1 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.321	4.300	4.350	4090182	48.20	4846974	48.22	0.84	MI	
2	5.044	5.020	5.080	4396281	51.80	5204523	51.78	0.84	MI	
				8486463	100.00	10051497	100.00			

Entry 2 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.319	4.295	4.345	2126612	30.89	2567739	30.54	0.83	MI	
2	4.909	4.890	4.930	4757619	69.11	5841279	69.46	0.81	MI	
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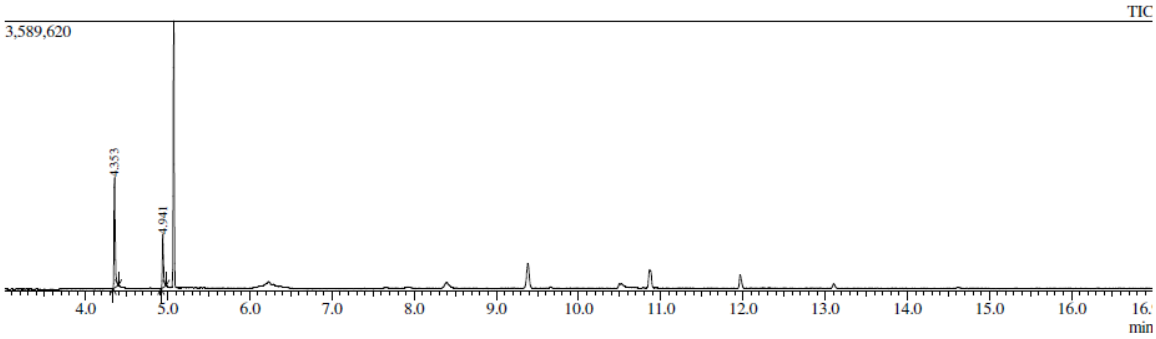
Entry 3 (method A)



Peak Report TIC

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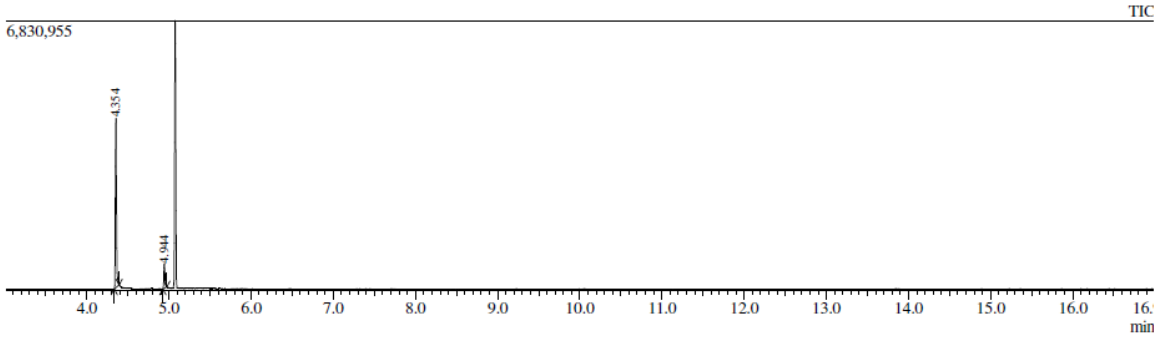
2	4.941	4.920	4.980	713164	31.99	708021	32.55	1.01	MI	
				2229671	100.00	2175411	100.00			

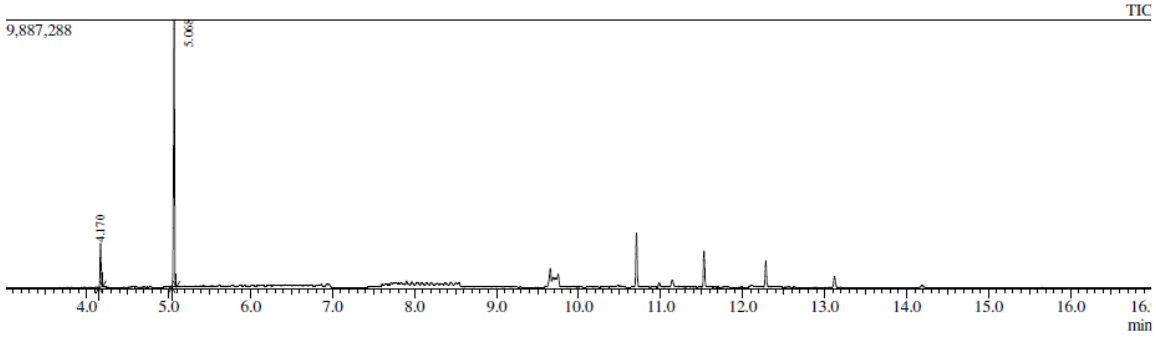
Entry 4 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.354	4.335	4.395	3875381	86.24	4296373	87.52	0.90	MI	
2	4.944	4.925	4.975	618595	13.76	612608	12.48	1.01	MI	
				4493976	100.00	4908981	100.00			

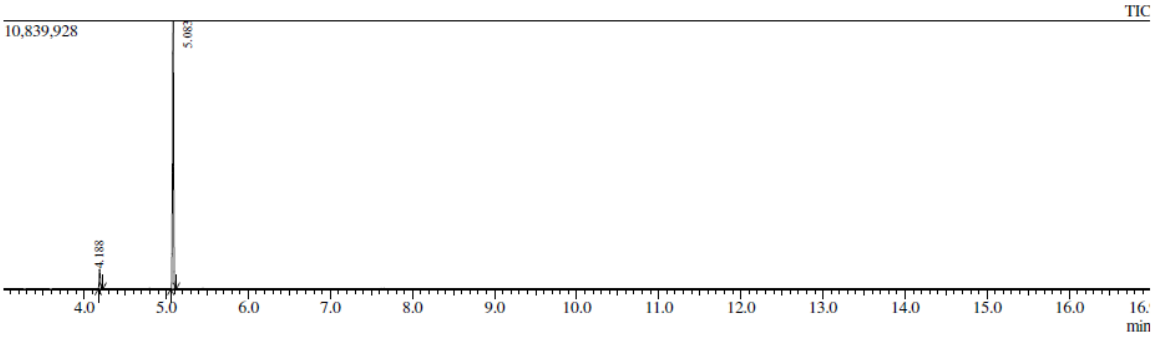
Entry 5 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.170	4.155	4.200	1364174	12.70	1608141	14.06	0.85	MI	
2	5.068	5.040	5.095	9379236	87.30	9826906	85.94	0.95	MI	
				10743410	100.00	11435047	100.00			

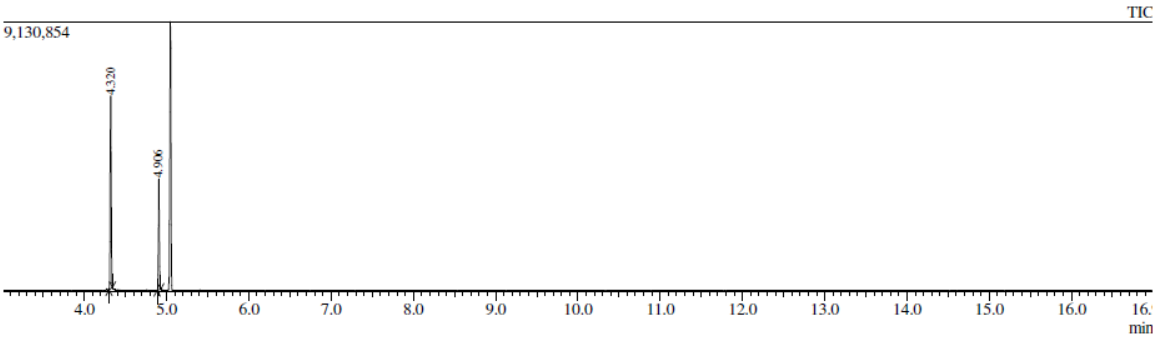
Entry 6 (method A)



Peak Report TIC

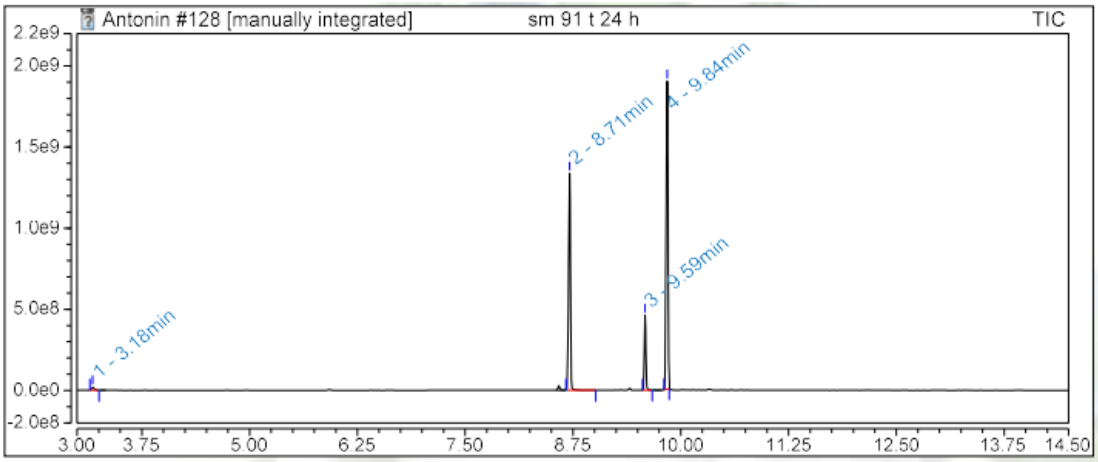
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.188	4.170	4.230	787024	7.49	784689	6.77	1.00	MI	
2	5.083	5.055	5.125	9724270	92.51	10813128	93.23	0.90	MI	
				10511294	100.00	11597817	100.00			

Entry 7 (methods A and B)



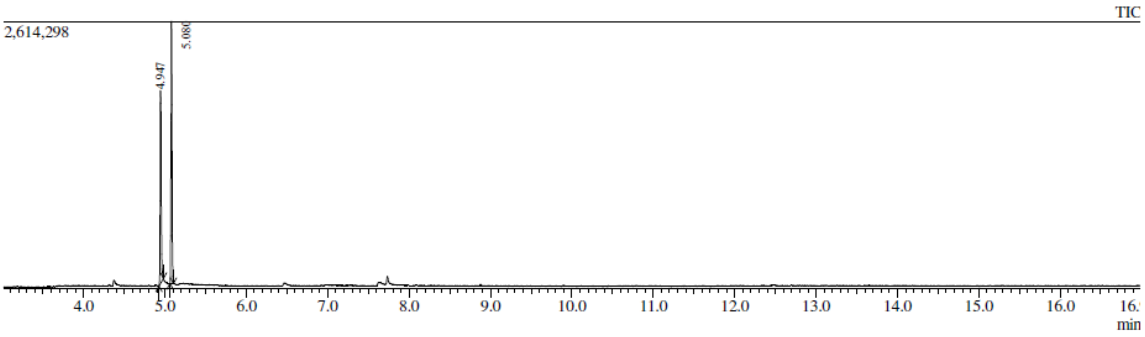
Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.320	4.300	4.340	5745742	64.97	6523729	63.46	0.88	MI	
2	4.906	4.885	4.930	3097914	35.03	3756181	36.54	0.82	MI	
				8843656	100.00	10279910	100.00			



No.	Peak Name	Retention Time min	Area counts*min	Relative Area %
1		3.179	629065.407	0.70
2		8.712	33686750.636	37.28
3		9.586	9346715.987	10.34
4		9.842	46704276.172	51.68
Total:			**90366808.202**	**100.00**

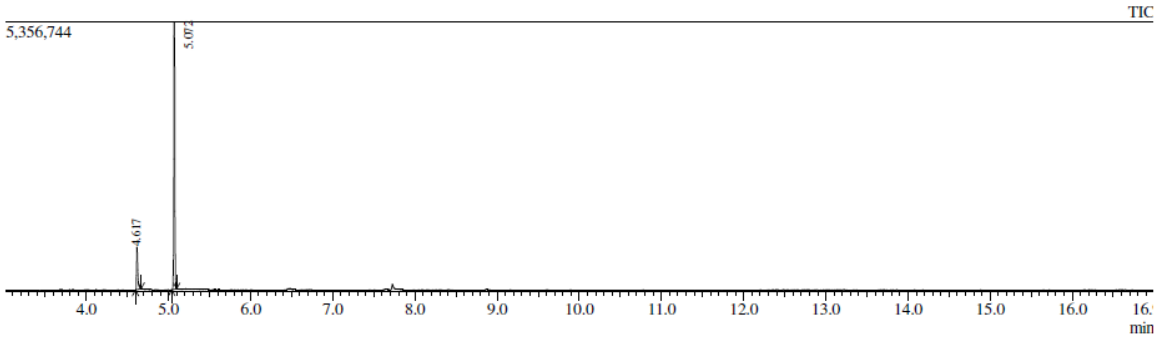
Entry 8 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.947	4.925	4.980	1749613	45.38	1884185	42.32	0.93	MI	
2	5.080	5.060	5.105	2105816	54.62	2567614	57.68	0.82	MI	
				3855429	100.00	4451799	100.00			

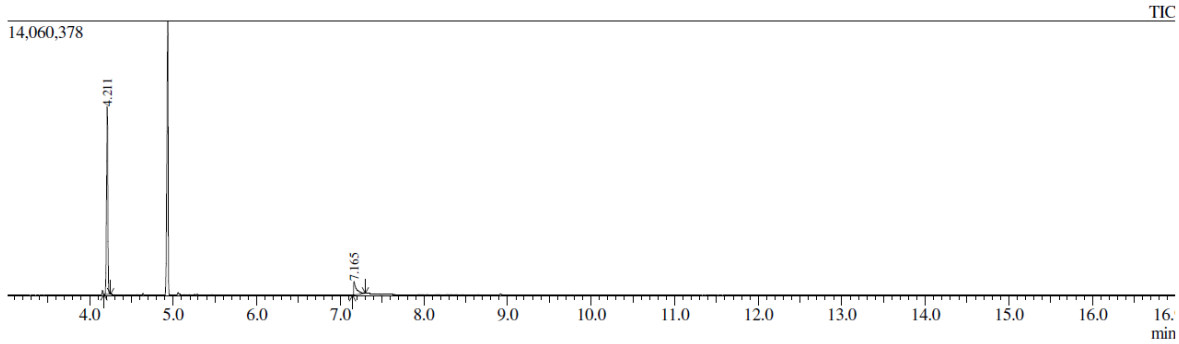
Entry 9 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.617	4.600	4.670	862701	15.92	846989	13.73	1.02	MI	
2	5.072	5.040	5.100	4556290	84.08	5320098	86.27	0.86	MI	
				5418991	100.00	6167087	100.00			

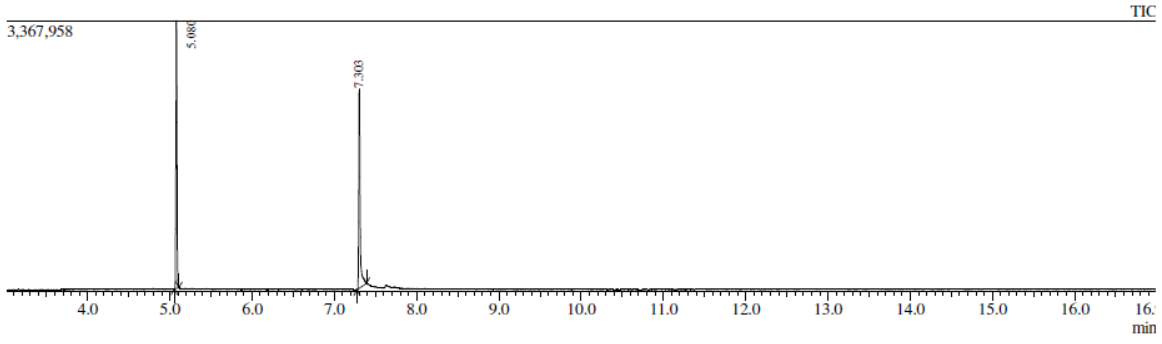
Entry 10 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.211	4.170	4.250	9899906	85.44	9605216	93.33	1.03	MI	
2	7.165	7.145	7.300	1686852	14.56	686983	6.67	2.46	MI	
				11586758	100.00	10292199	100.00			

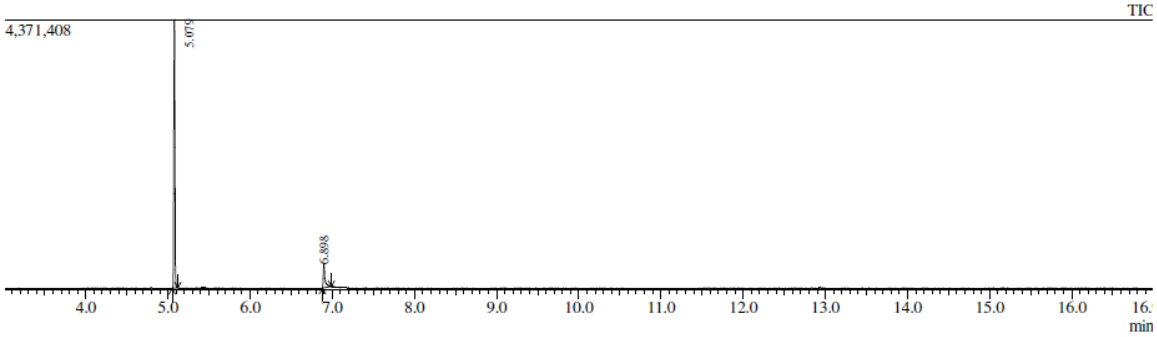
Entry 11 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.080	5.055	5.110	2763233	49.26	3334468	57.32	0.83	MI	
2	7.303	7.275	7.390	2846577	50.74	2482569	42.68	1.15	MI	
				5609810	100.00	5817037	100.00			

Entry 12 (method A)



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.079	5.050	5.120	3806120	86.93	4351276	91.89	0.87	MI	
2	6.898	6.880	6.990	572044	13.07	383988	8.11	1.49	MI	
				4378164	100.00	4735264	100.00			

References

1 P.-Y. Renard, H. Schwebel, P. Vayron, L. Josien, A. Valleix and C. Mioskowski, *Chem. – Eur. J.*, 2002, **8**, 2910–2916.

2 R. A. Moss and Y. Ihara, *J. Org. Chem.*, 1983, **48**, 588–592.

3 T. Yoshino, S. Imori and H. Togo, *Tetrahedron*, 2006, **62**, 1309–1317.

4 R. J. P. Corriu, G. F. Lanneau and D. Leclercq, *Tetrahedron*, 1986, **42**, 5591–5600.

5 K. Khulbe, P. Roy, A. Radhakrishnan and G. Mugesh, *ChemCatChem*, 2018, **10**, 4826–4831.

6 J.-P. Biron and R. Pascal, *J. Am. Chem. Soc.*, 2004, **126**, 9198–9199.

7 P. Hendry and A. M. Sargeson, *J. Am. Chem. Soc.*, 1989, **111**, 2521–2527.

8 B. van Loo, C. D. Bayer, G. Fischer, S. Jonas, E. Valkov, M. F. Mohamed, A. Vorobieva, C. Dutruel, M. Hyvönen and F. Hollfelder, *J. Am. Chem. Soc.*, 2019, **141**, 370–387.

9 M. S. Kumar, K. C. Rajanna, M. Venkateswarlu and K. L. Rao, *Int. J. Chem. Kinet.*, 2016, **48**, 171–196.

10 R. A. Gagliano, R. C. Knowlton and L. D. Byers, *J. Org. Chem.*, 1989, **54**, 5247–5250.