molecules

Supporting Information

Selective Esterification of Phosphonic Acids †

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† This work is dedicated to Professor Janusz Jurczak on the occasion of his 80th birthday.

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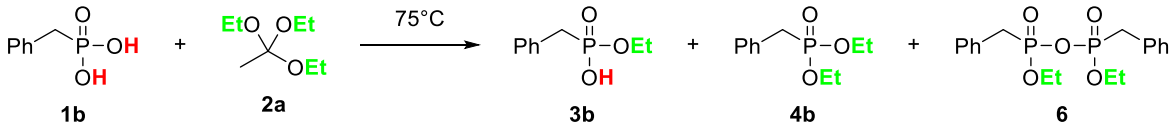
1. Results of additional experiments

1.1. *Studies on the reaction progress*

Table S1. Summarized data from the ^{31}P NMR measurements during the course of the esterification at elevated temperature. [1]



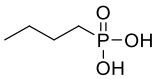
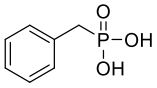
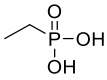
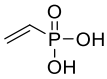
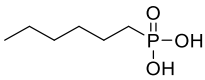
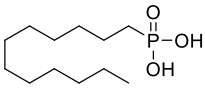
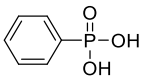
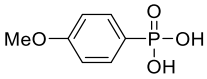
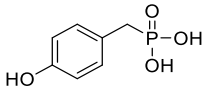
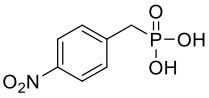
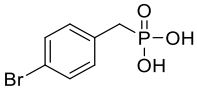
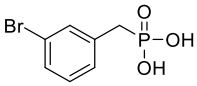
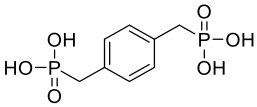
Entry	Time of reaction [h]	Substrate **1b** conversion [%]	Product yield [%] [2]		
			3b	**4b**	**6**
1	1	>99	21	46	34
2	2		13	53	34
3	4		8	60	32
4	6		4	64	31
5	8		0	74	26
6	24		0	99	0

[1] Reaction conditions: benzylphosphonic acid **1b** (1 equiv., 0.5 mmol), triethyl orthoacetate (30 equiv., 15 mmol). [2] The conversion of **1b** and product yields were determined on the basis of relative ^{31}P NMR integrals.

2. Analytical data for the studied compounds

2.1. *Structures and ^{31}P NMR chemical shifts for applied substrates*

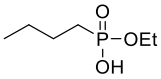
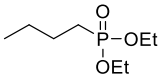
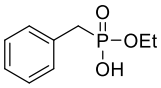
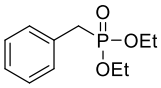
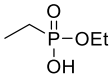
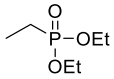
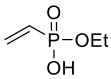
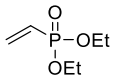
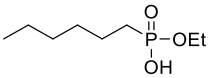
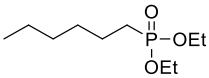
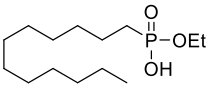
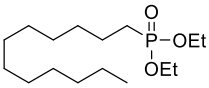
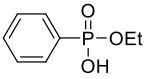
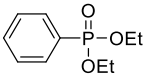
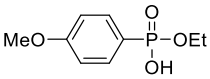
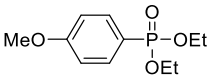
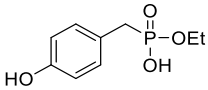
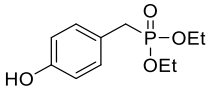
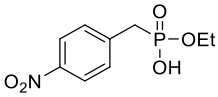
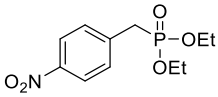
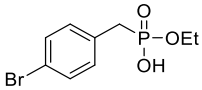
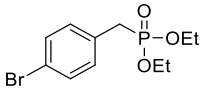
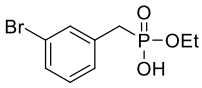
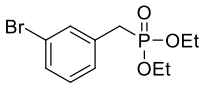
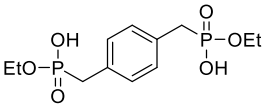
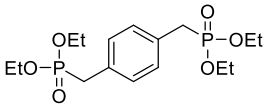
Table S2. Recorded ^{31}P NMR shifts for substrate phosphonic acids.

Symbol	Chemical Name	Structure	^{31}P NMR chemical shift [ppm] [1]
1a	*n*-butylphosphonic acid		27.8
1b	benzylphosphonic acid		21.3
1c	ethylphosphonic acid		29.1
1d	vinylphosphonic acid		12.0
1e	*n*-hexylphosphonic acid		27.4
1f	*n*-dodecylphosphonic acid		27.6
1g	phenylphosphonic acid		13.0
1h	(4-methoxyphenyl)phosphonic acid		13.7
1i	[(4-hydroxyphenyl)methyl]-phosphonic acid		22.4
1j	[(4-nitrophenyl)methyl]-phosphonic acid		24.9
1k	[(4-bromophenyl)methyl]-phosphonic acid		20.6
1l	[(3-bromophenyl)methyl]-phosphonic acid		20.5
1m	[1,4-phenylenebis(methylene)]-bis(phosphonic acid)		21.1

[1] Chemical shifts were measured for samples dissolved in dimethyl sulfoxide-d_6 (DMSO-d_6).

2.2. *Symbols, structures, and ^{31}P NMR chemical shifts of received products*

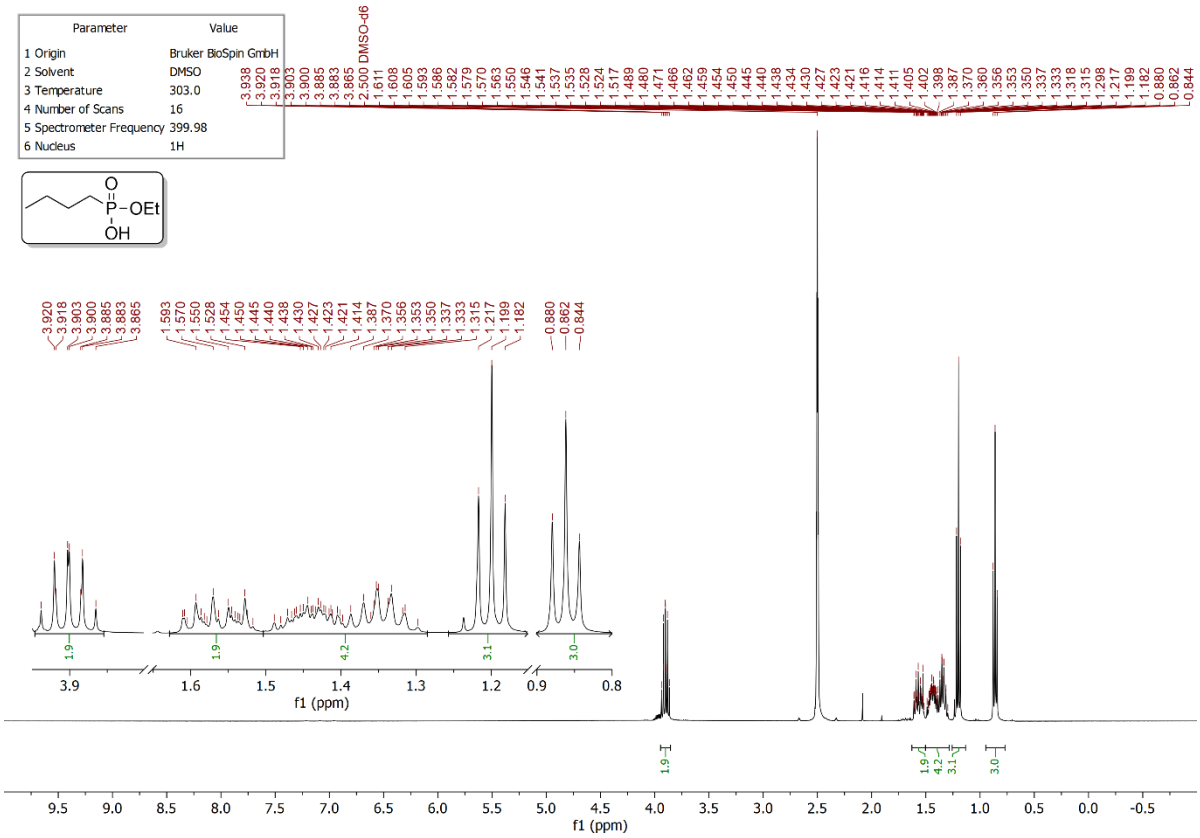
Table S3. Recorded ^{31}P NMR shifts for obtained mono- and diesters.

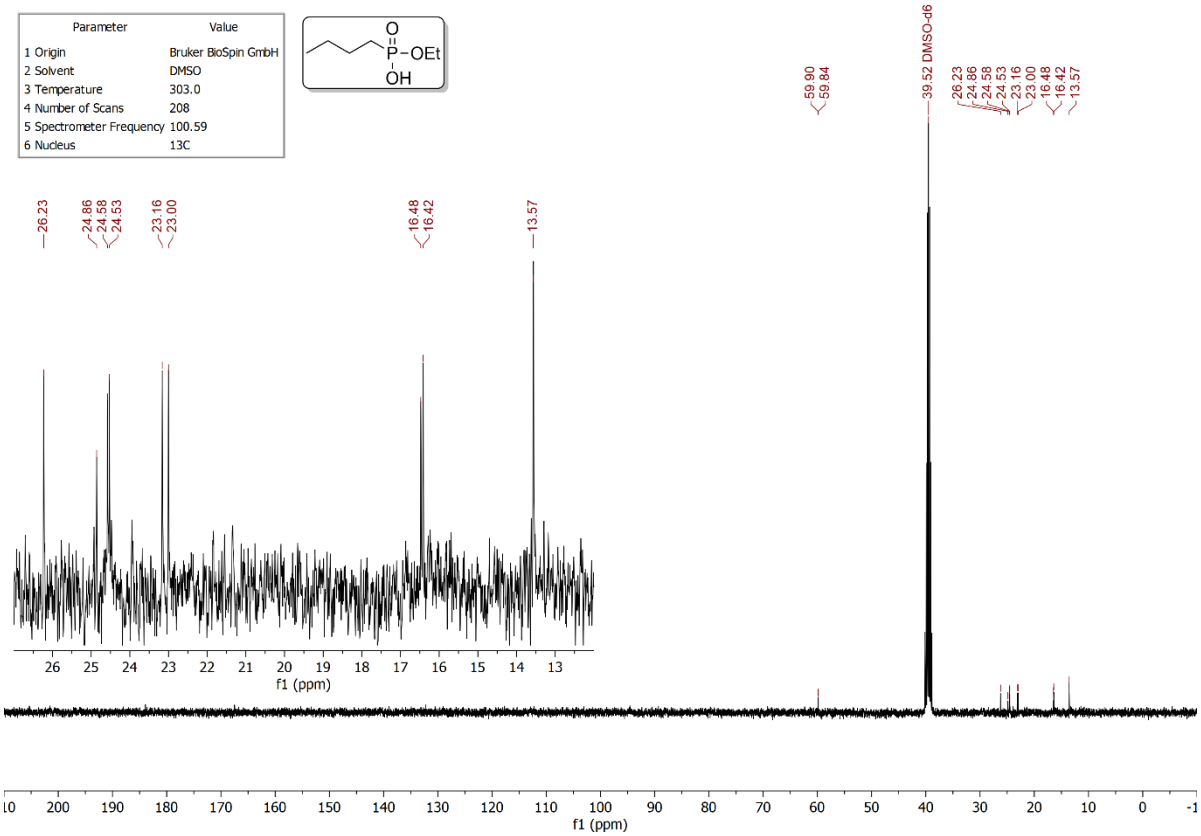
Symbol	Monoester structure	^{31}P NMR shift [ppm] [1]	Symbol	Diester structure	^{31}P NMR shift [ppm] [1]
3a		29.1	**4a**		32.0
3b		23.3	**4b**		26.5
3c		30.2	**4c**		33.1
3d		14.0	**4d**		16.9
3e		28.9	**4e**		31.9
3f		28.9	**4f**		31.9
3g		15.0	**4g**		17.8
3h		15.5	**4h**		18.8
3i		24.2	**4i**		27.1
3j		21.4	**4j**		24.9
3k		22.4	**4k**		25.8
3l		22.7	**4l**		25.9
3m		-	**4m**		26.5

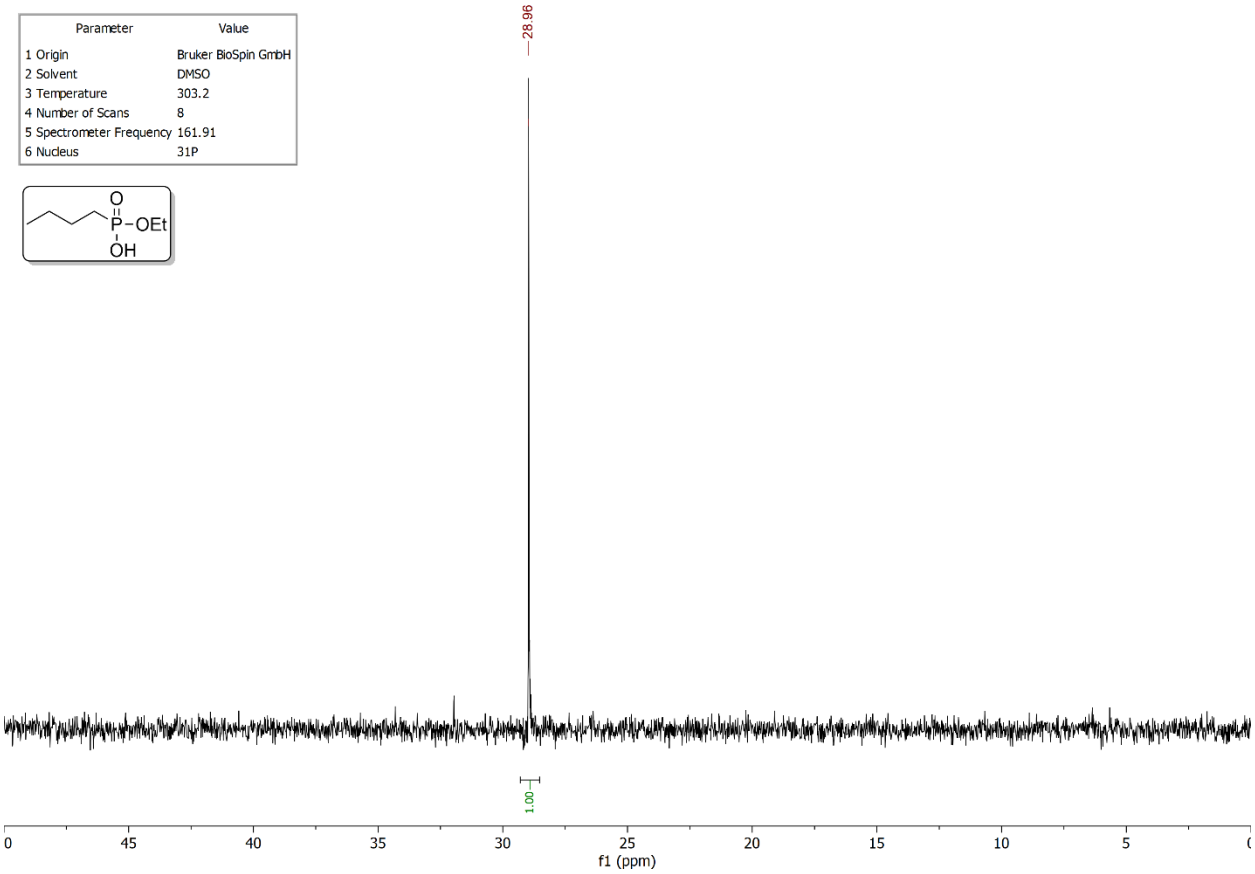
[1] Chemical shifts were measured for samples also dissolved in DMSO-d_6.

2.3. *^{1}H, ^{13}C, and ^{31}P NMR spectra of the monoesters*

Ethyl hydrogen butylphosphonate (**3a**)




Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 208
5 Spectrometer Frequency 100.59
6 Nucleus 13C
O
P-OEt
OH
26.23
24.86
24.58
24.53
23.16
23.00
16.48
16.42
13.57
59.90
59.84
39.52 DMSO-d6
f1 (ppm)


Parameter Value
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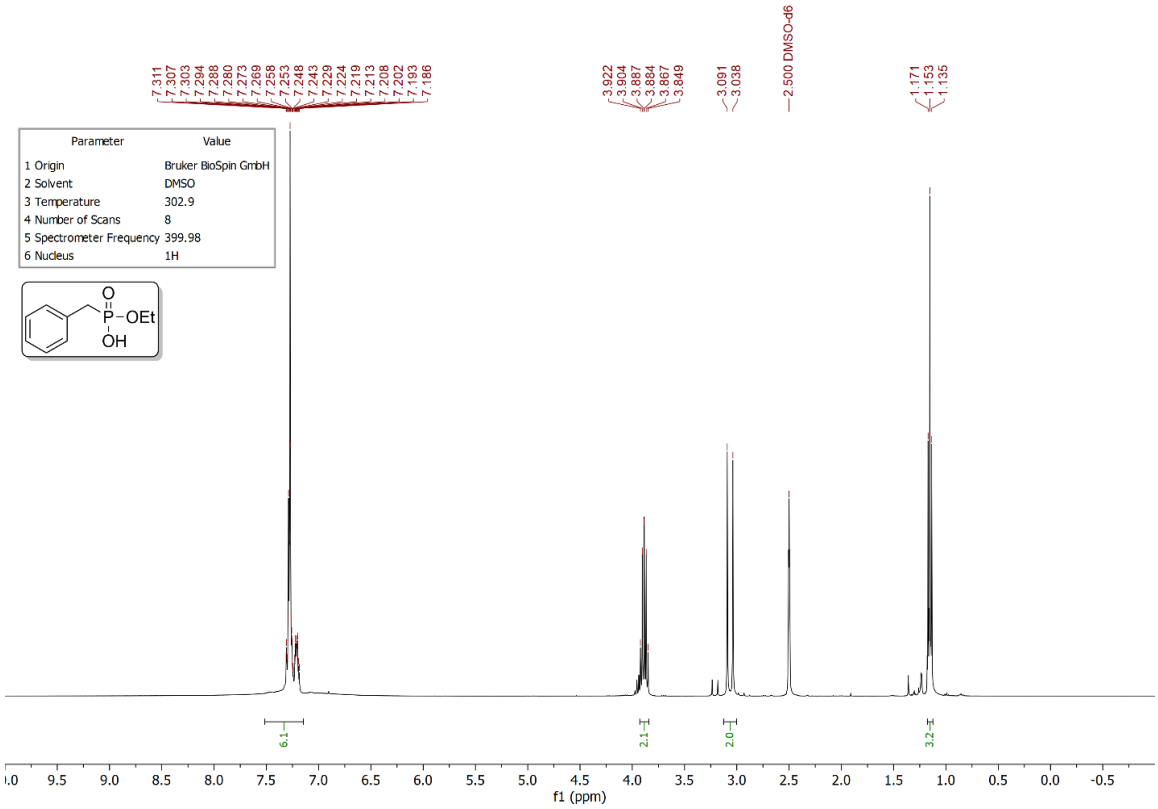
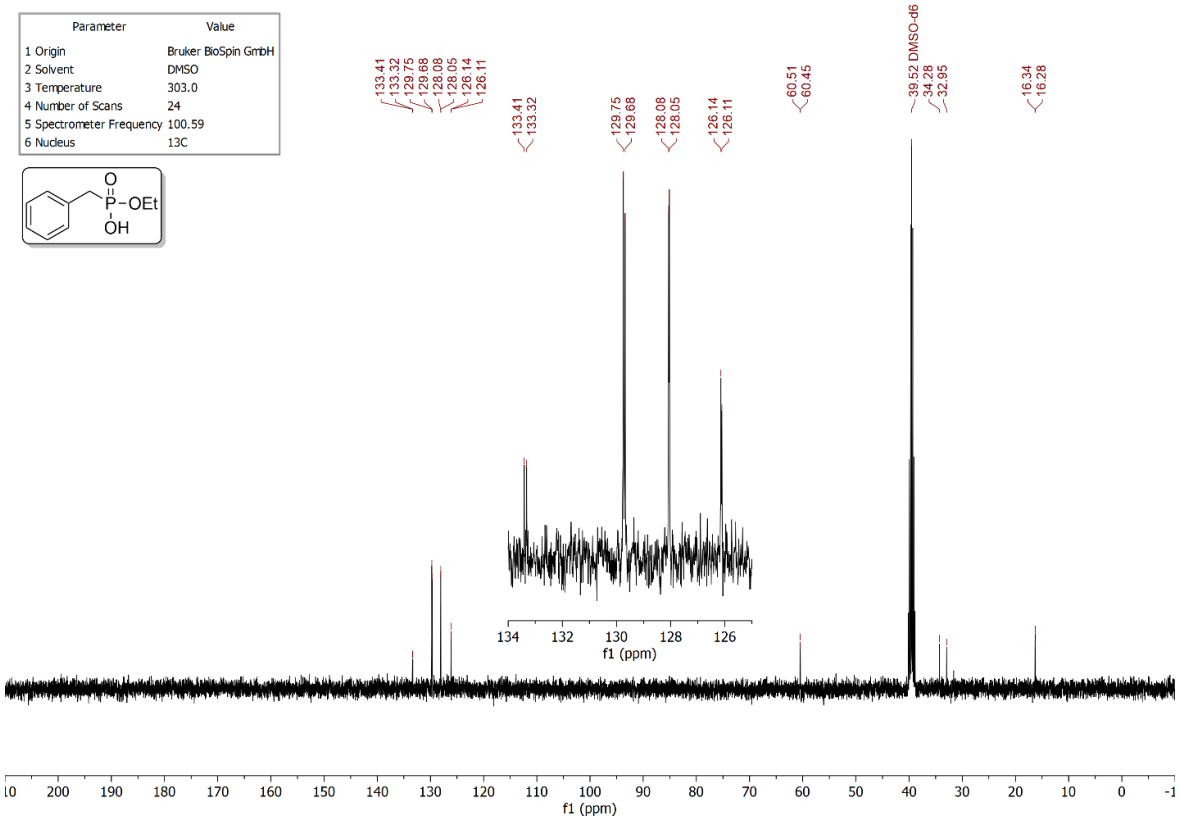
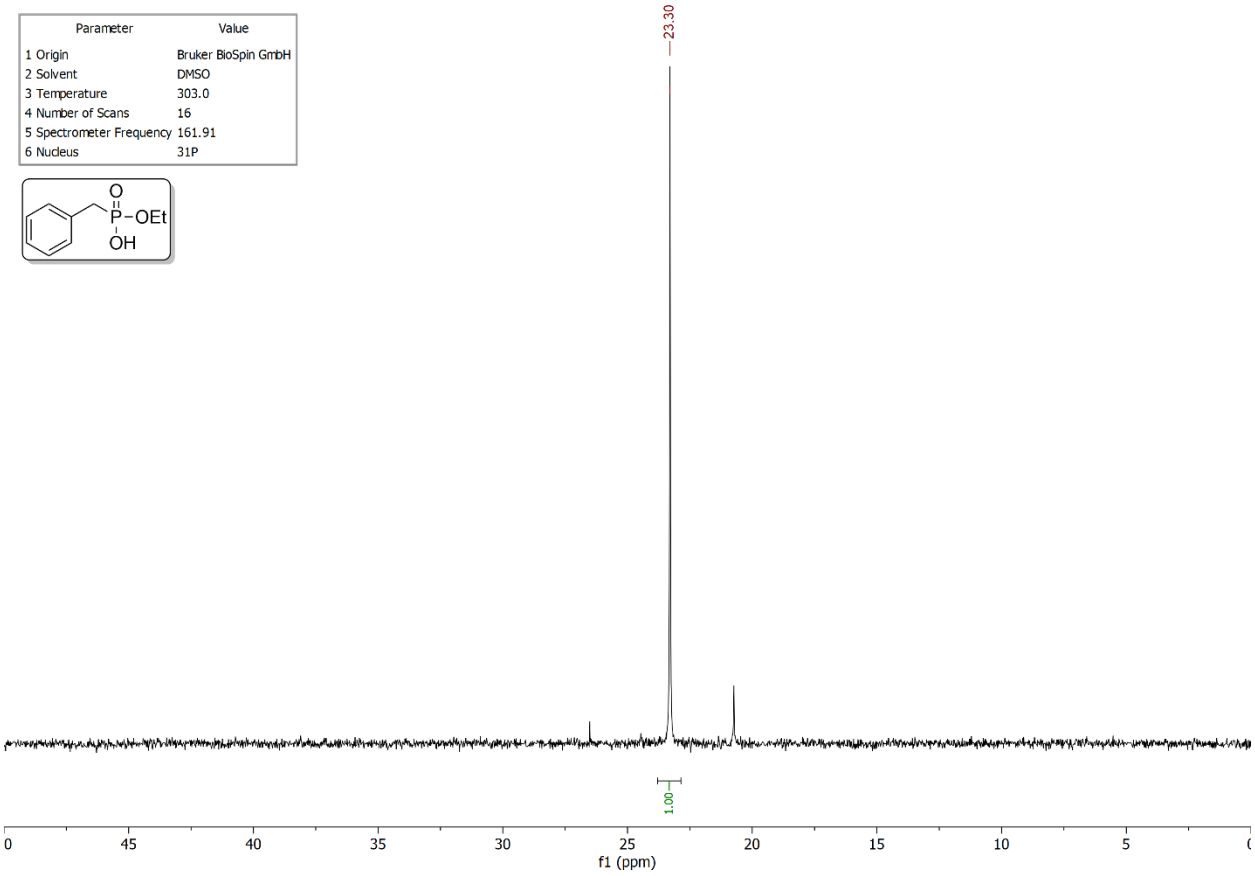
2 Solvent DMSO
3 Temperature 303.2
4 Number of Scans 8
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P-OEt
OH
28.96
1.00
f1 (ppm)

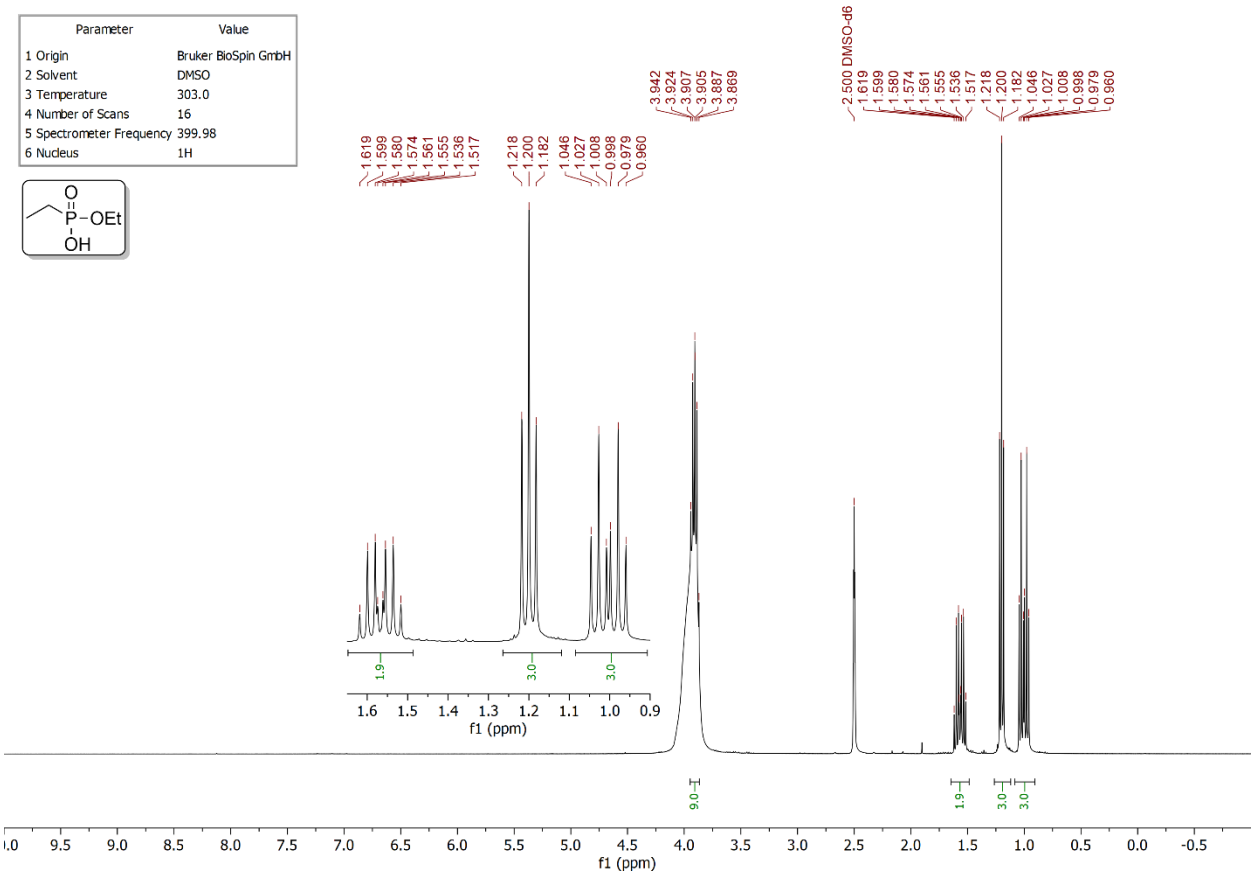
Ethyl hydrogen benzylphosphonate (**3b**)

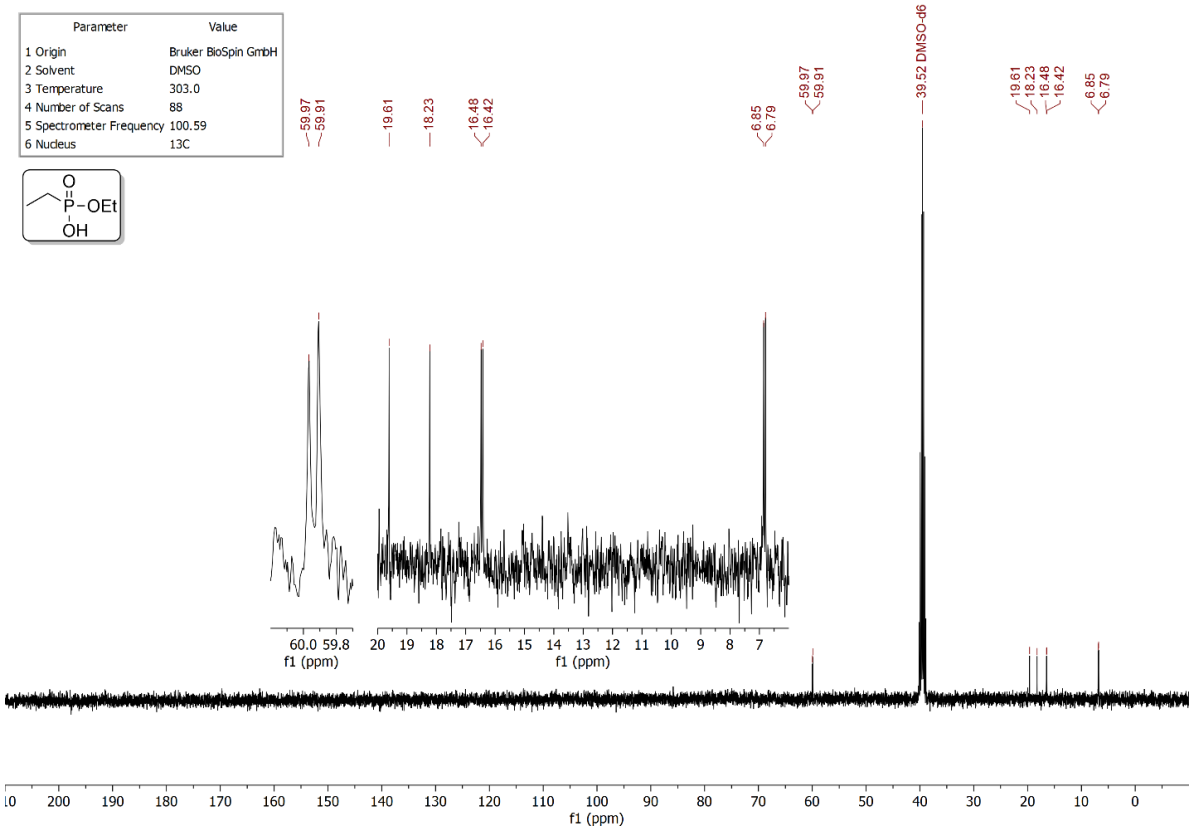



Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 24
5 Spectrometer Frequency 100.59
6 Nucleus 13C
O
P-OEt
OH
133.41
133.32
129.75
129.68
128.08
128.05
126.14
126.11
60.51
60.45
39.52 DMSO-d6
34.28
32.95
16.34
16.28
134 132 130 128 126
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P-OEt
OH
23.30
1.00
0 45 40 35 30 25 20 15 10 5
f1 (ppm)

Ethyl hydrogen ethylphosphonate (**3c**)




Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 88
5 Spectrometer Frequency 100.59
6 Nucleus 13C
59.97
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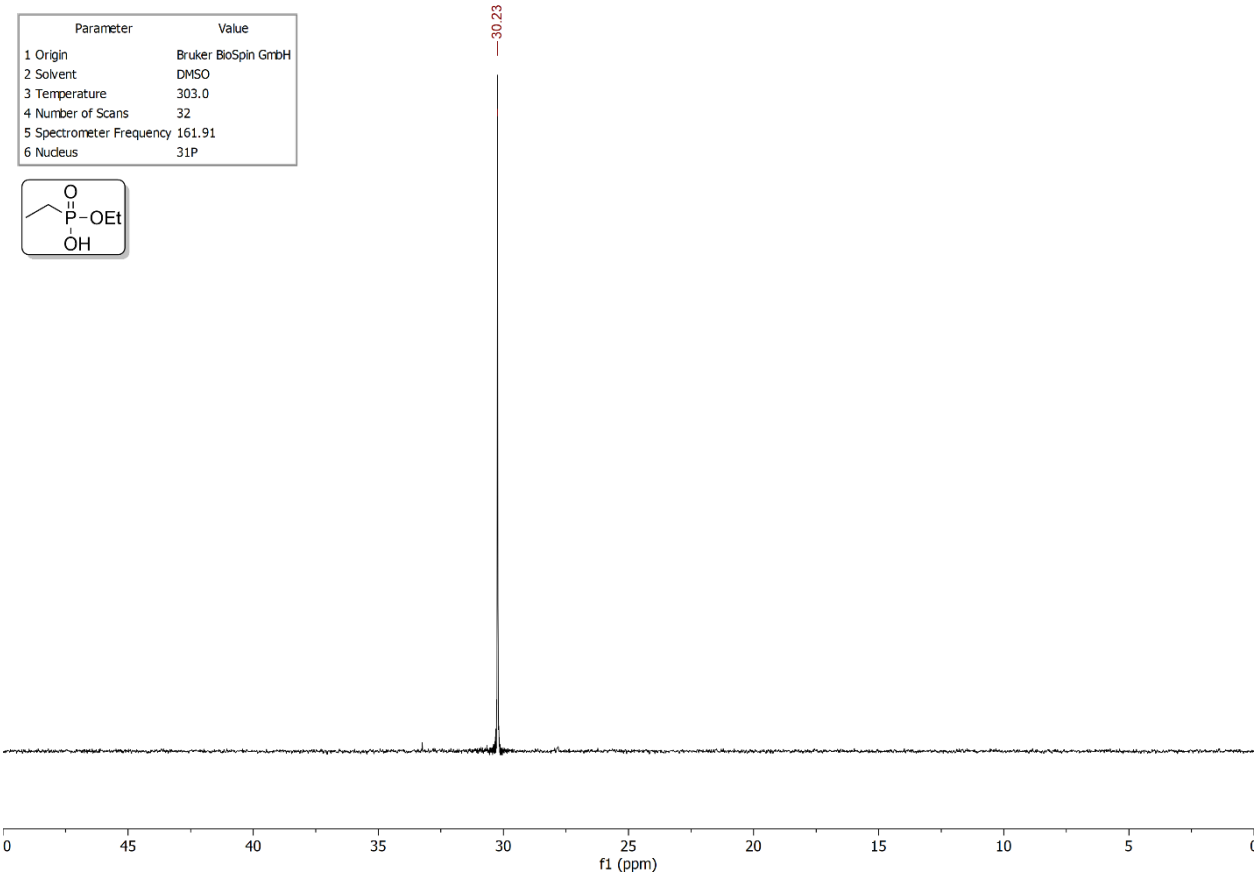
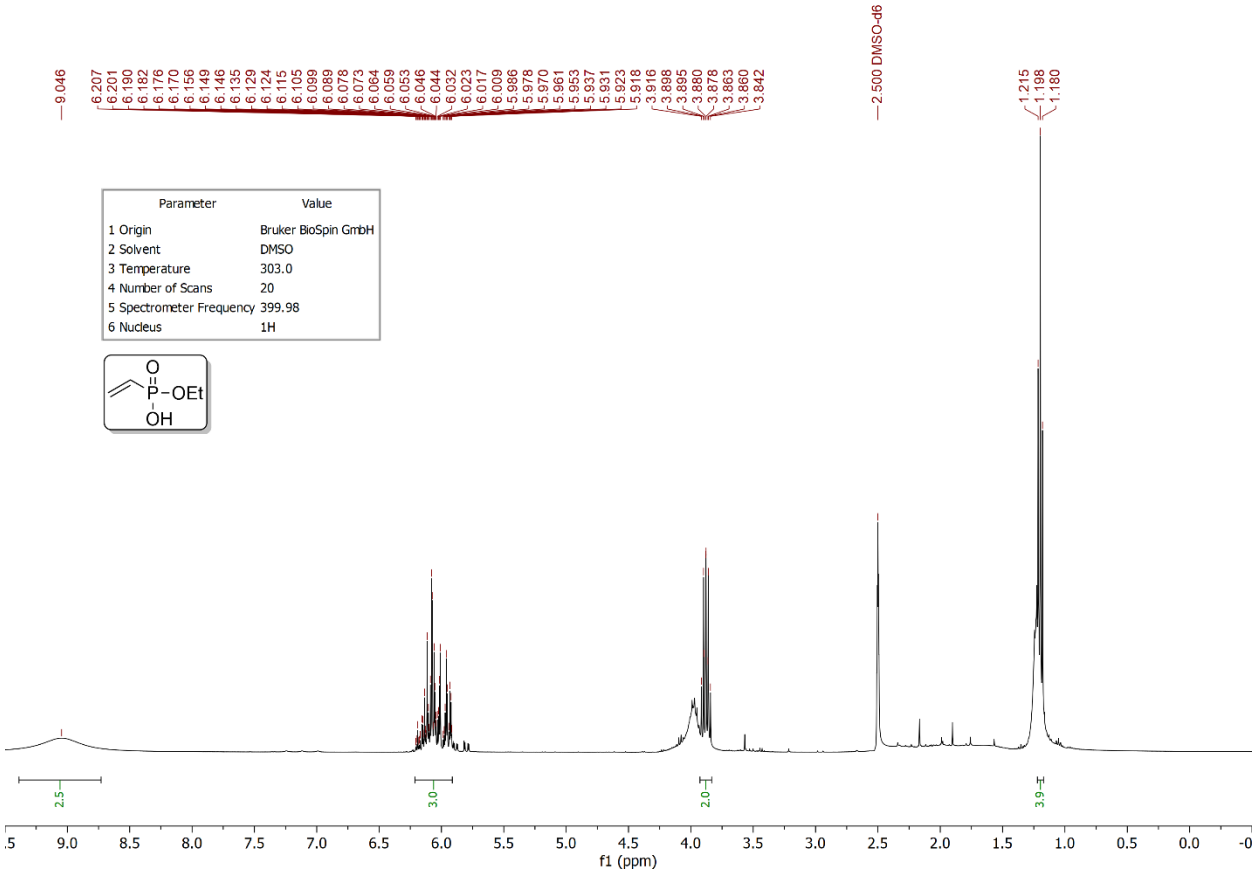
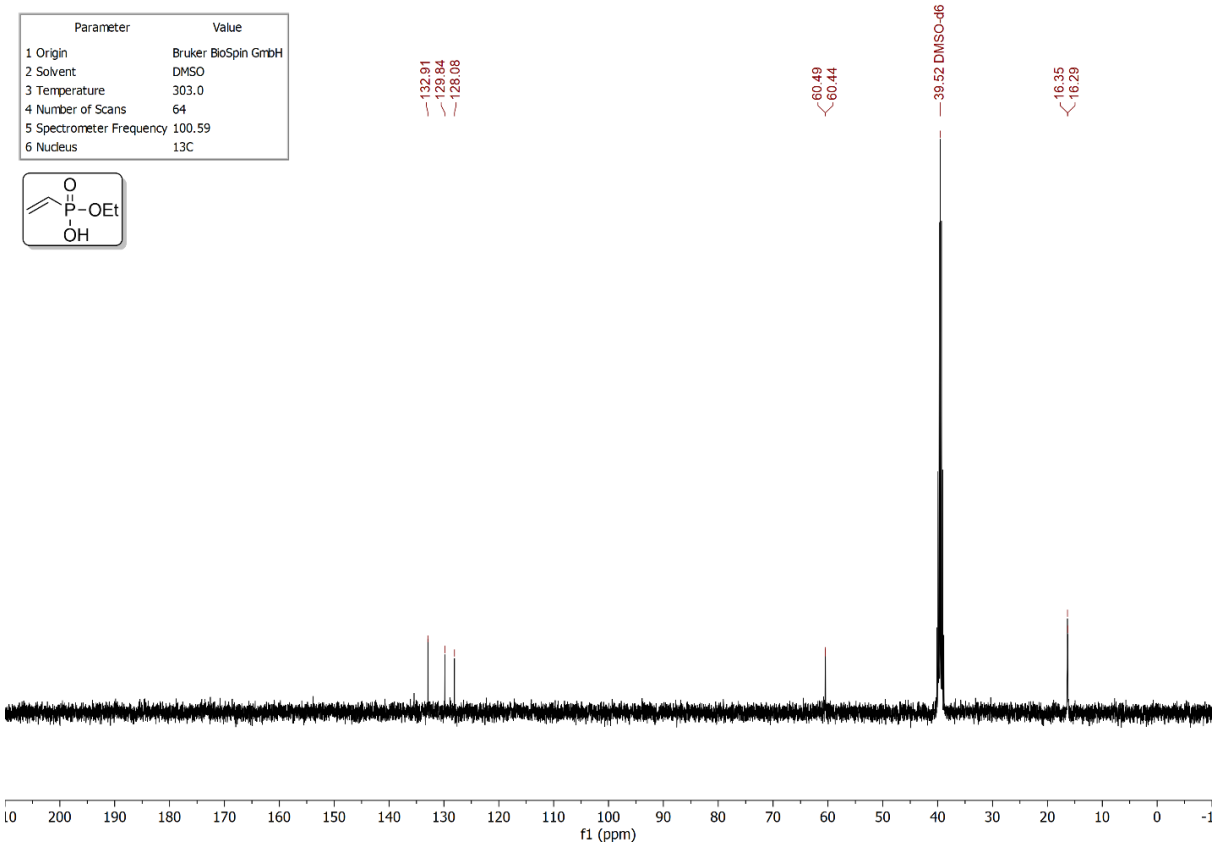
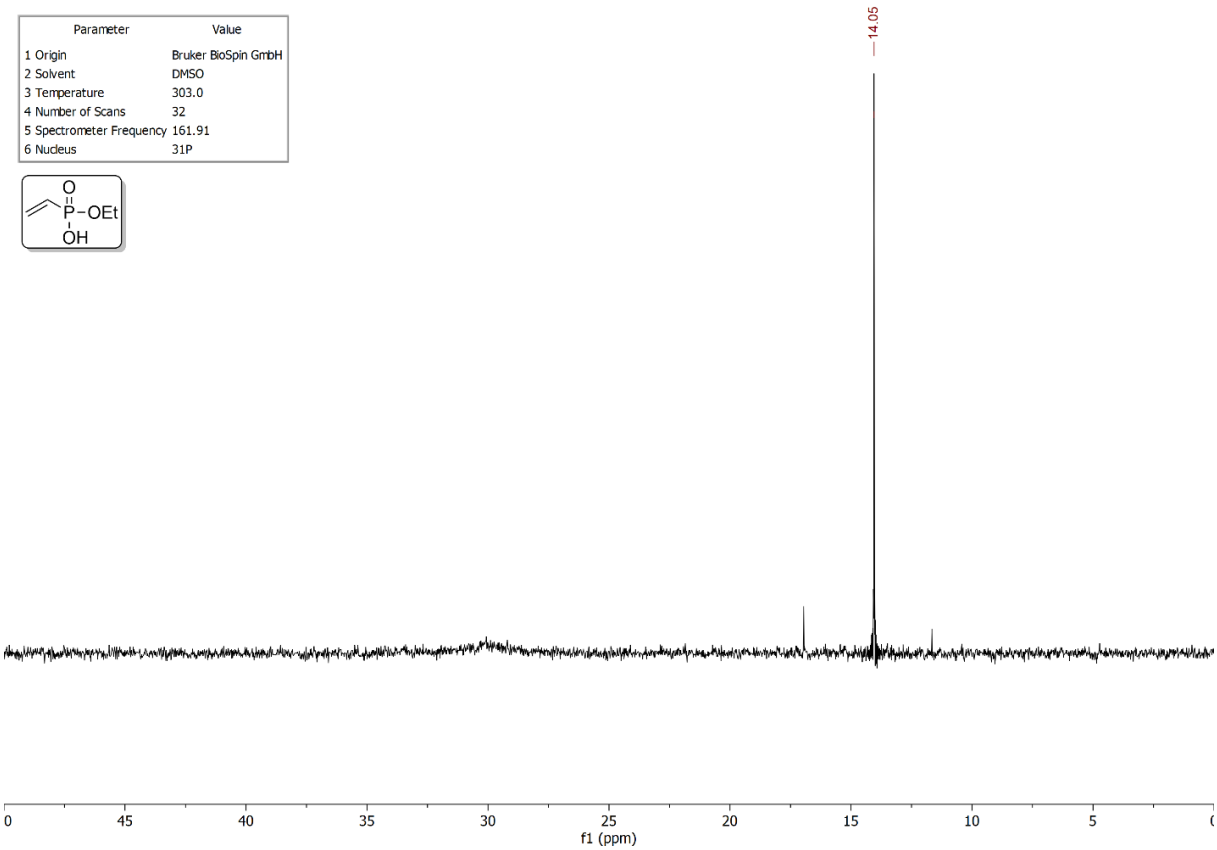
6.85
6.79
39.52 DMSO-d6
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 32
5 Spectrometer Frequency 161.91
6 Nucleus 31P
30.23
f1 (ppm)

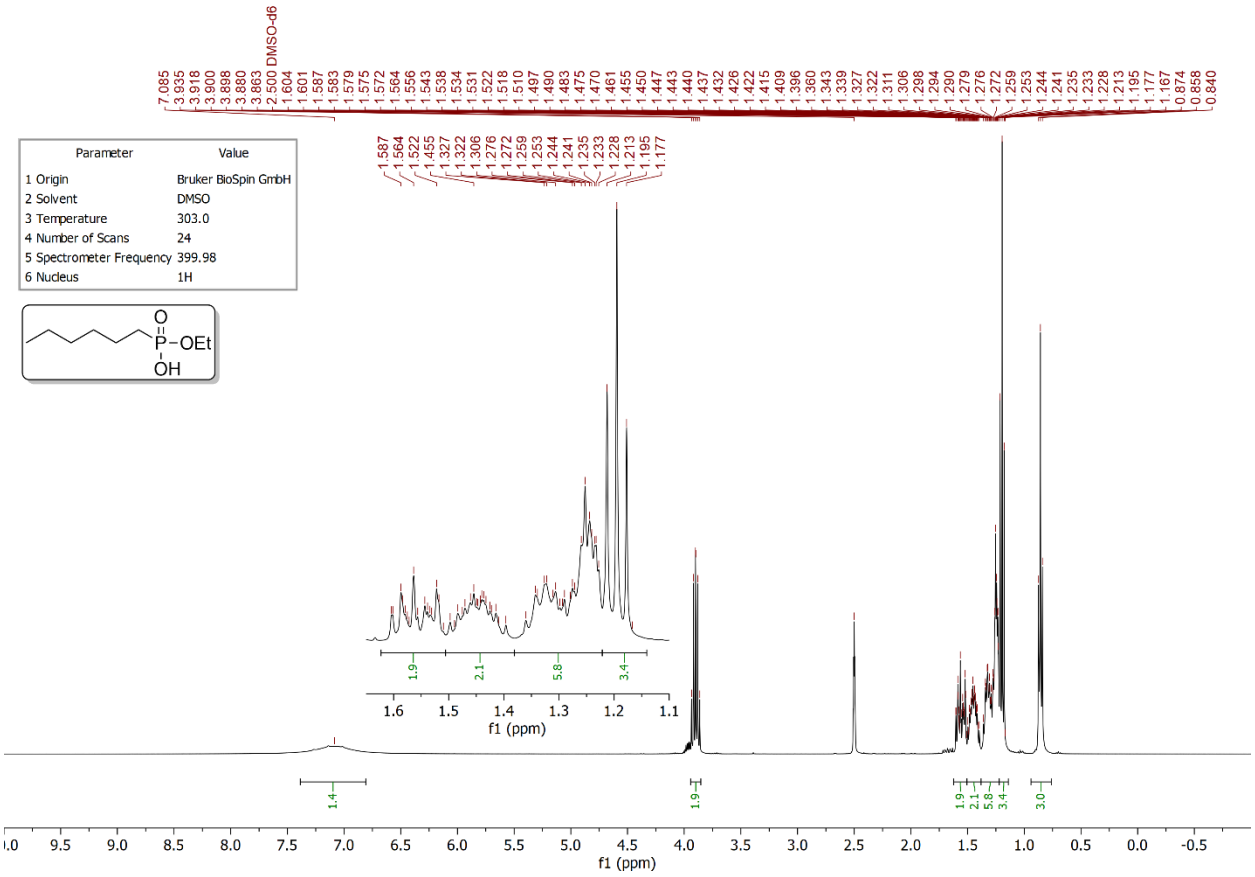
Ethyl hydrogen vinylphosphonate (**3d**)

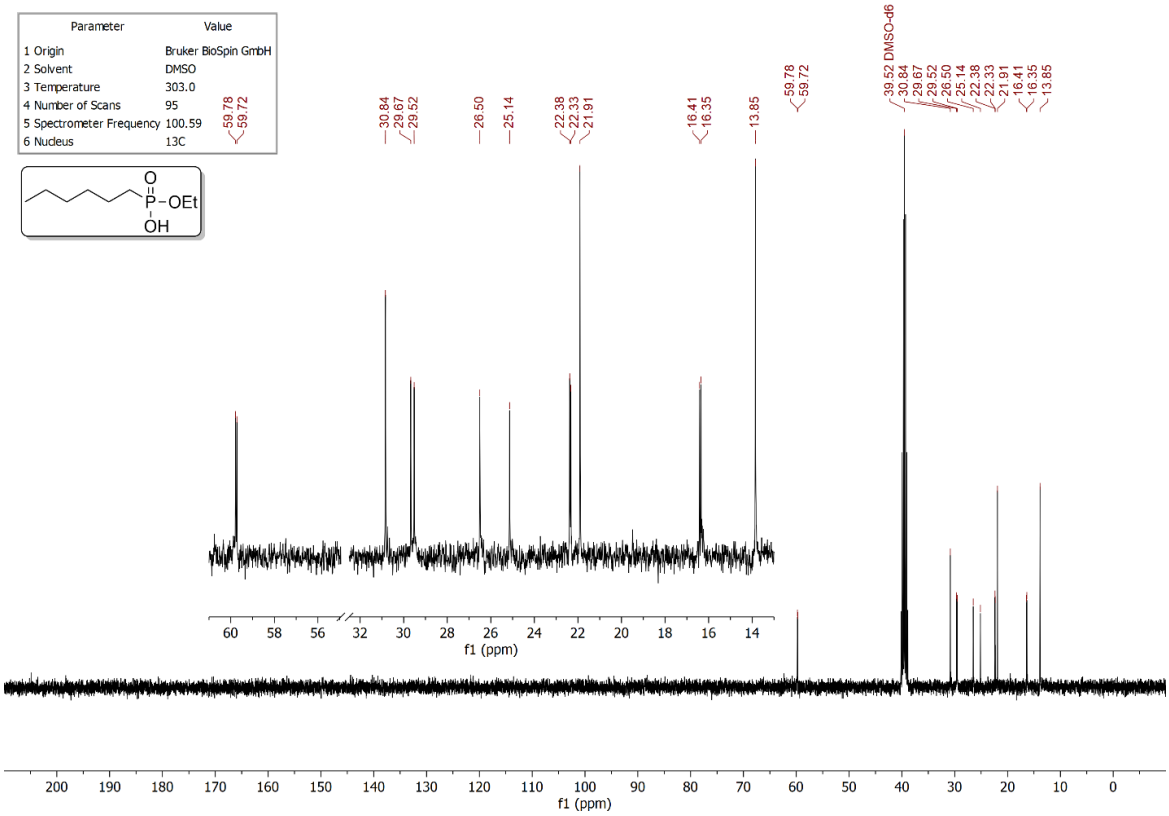


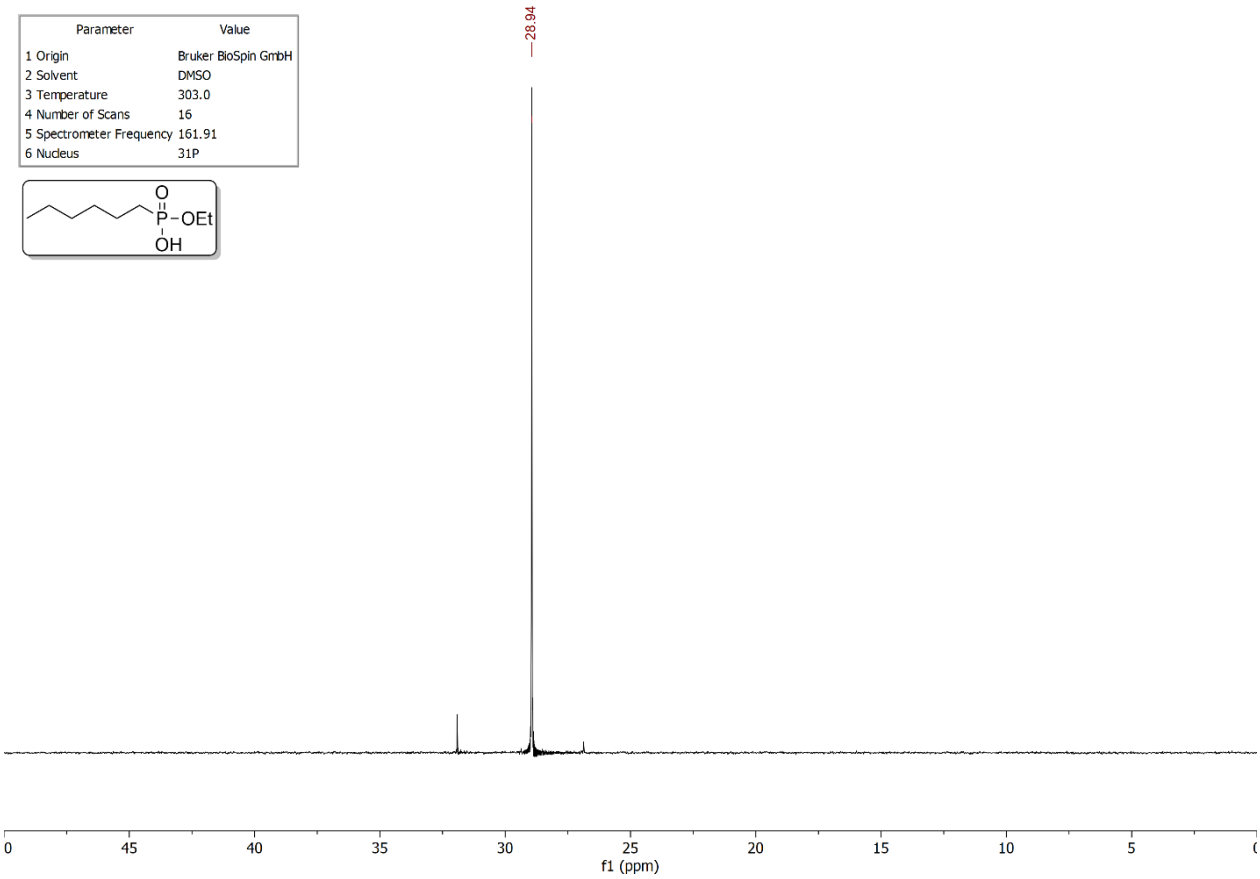

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 64
5 Spectrometer Frequency 100.59
6 Nucleus 13C
132.91
129.84
128.08
60.49
60.44
39.52 DMSO-d6
16.35
16.29
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 32
5 Spectrometer Frequency 161.91
6 Nucleus 31P
14.05
f1 (ppm)

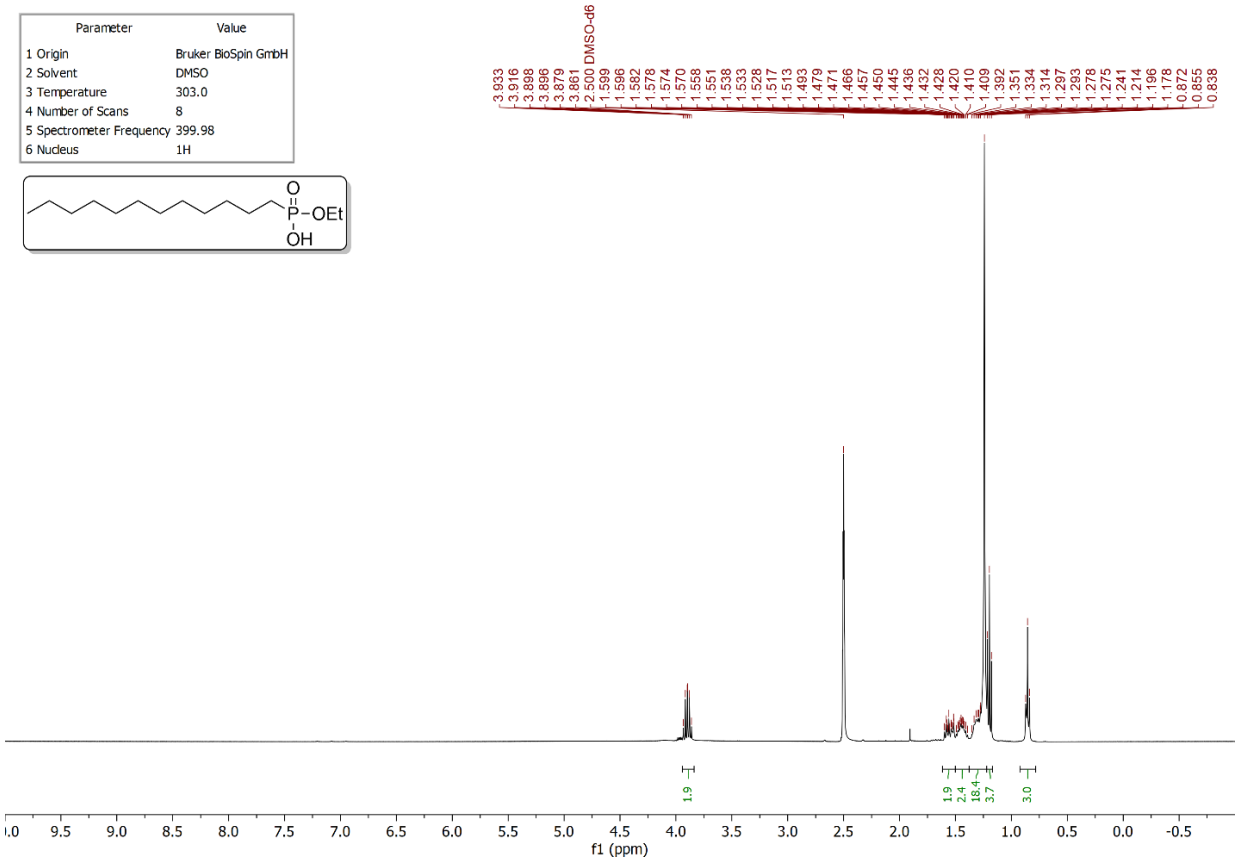
Ethyl hydrogen hexylphosphonate (**3e**)

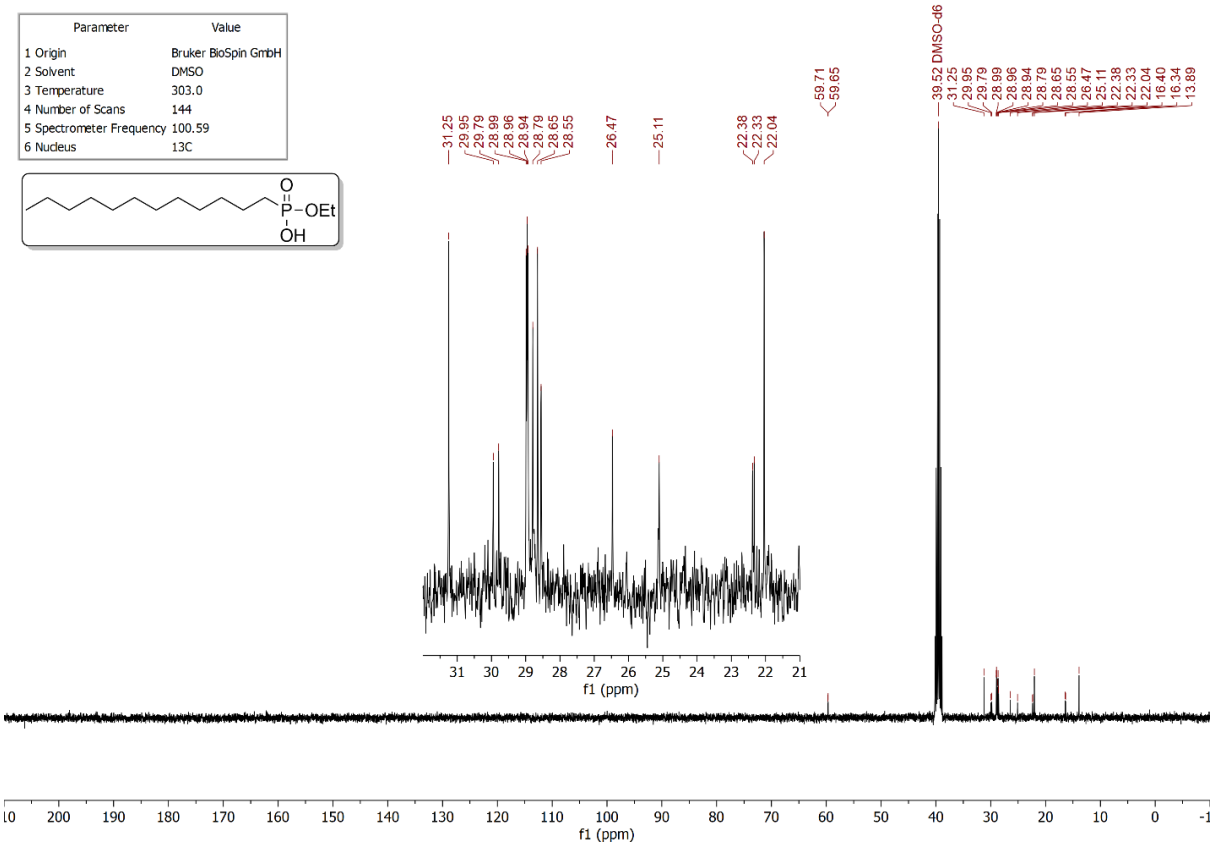


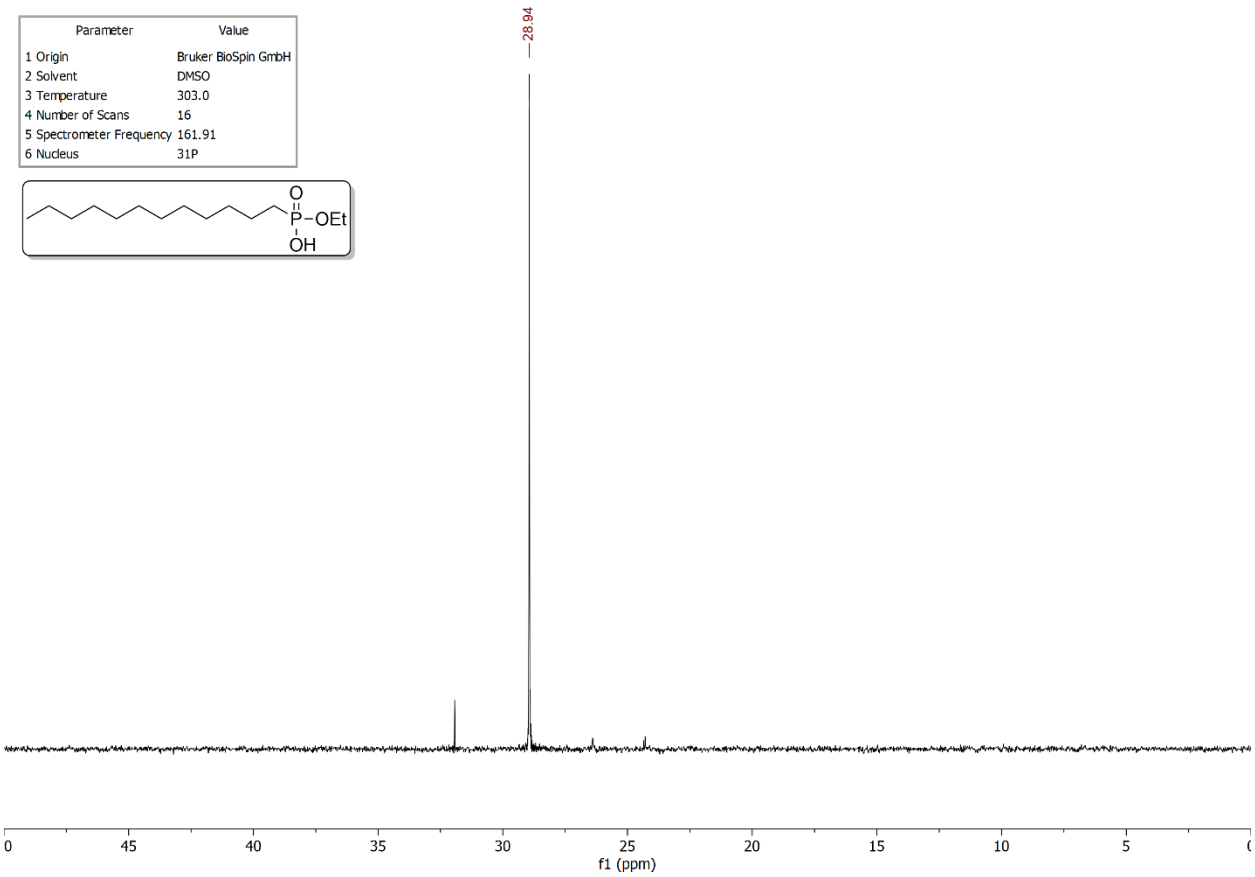

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 95
5 Spectrometer Frequency 100.59
6 Nucleus 13C
59.78
59.72
30.84
29.67
29.52
28.50
25.14
22.38
22.33
21.91
16.41
16.35
13.85
39.52 DMSO-d6
O
P-OEt
OH
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
28.94
O
P-OEt
OH
f1 (ppm)

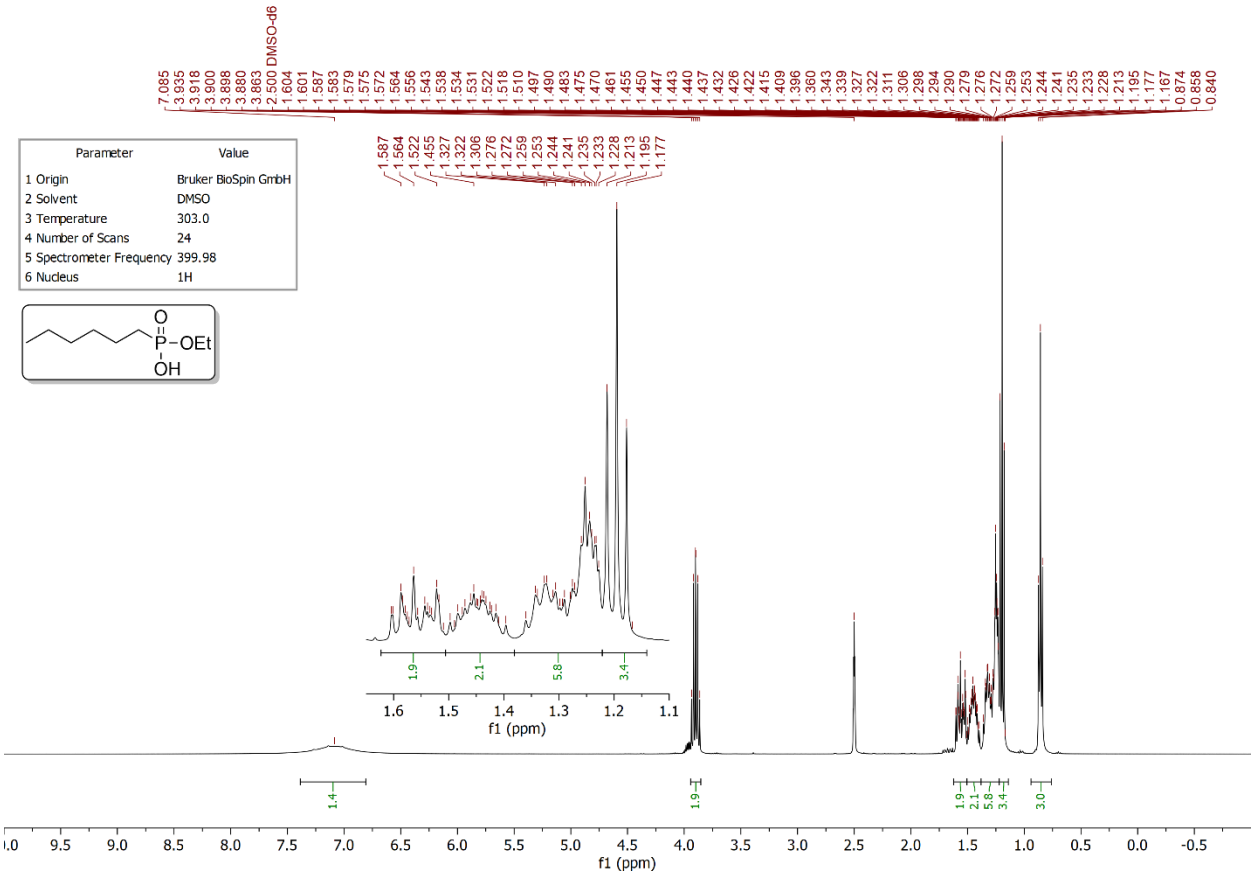
Ethyl hydrogen dodecylphosphonate (**3f**)

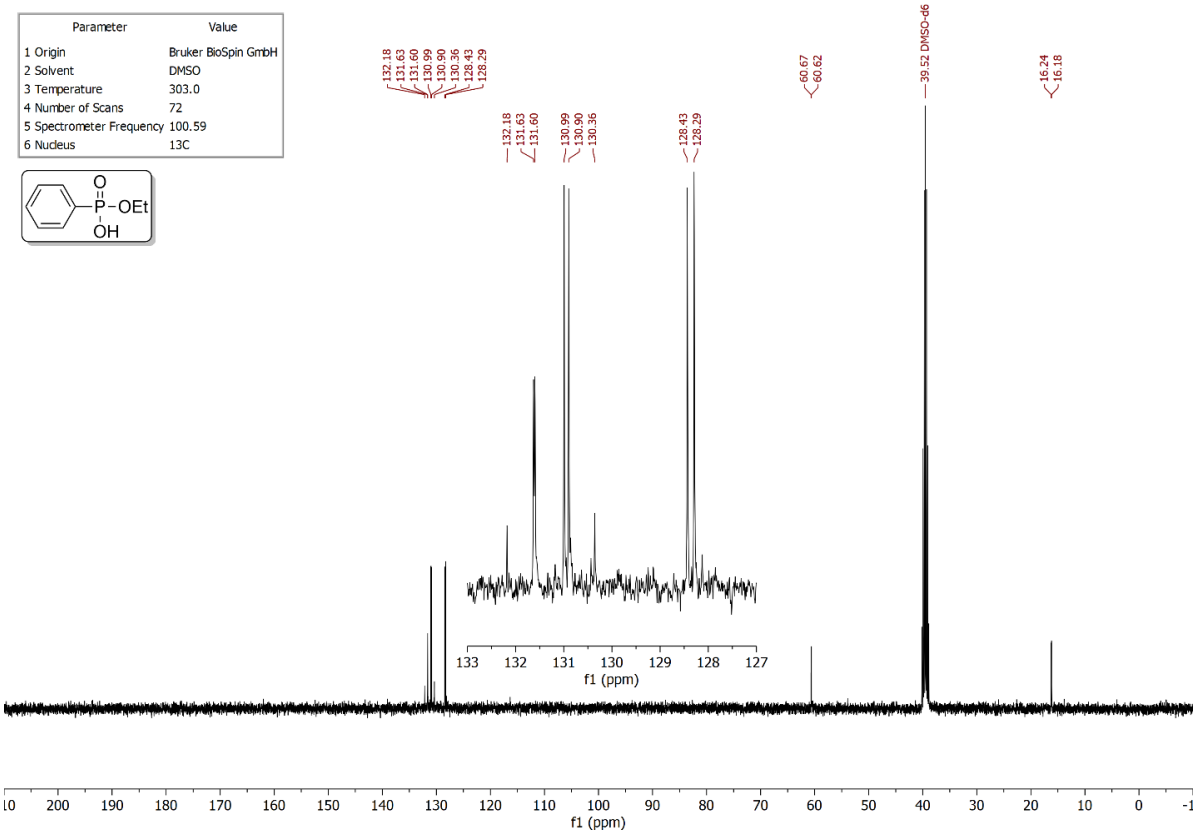


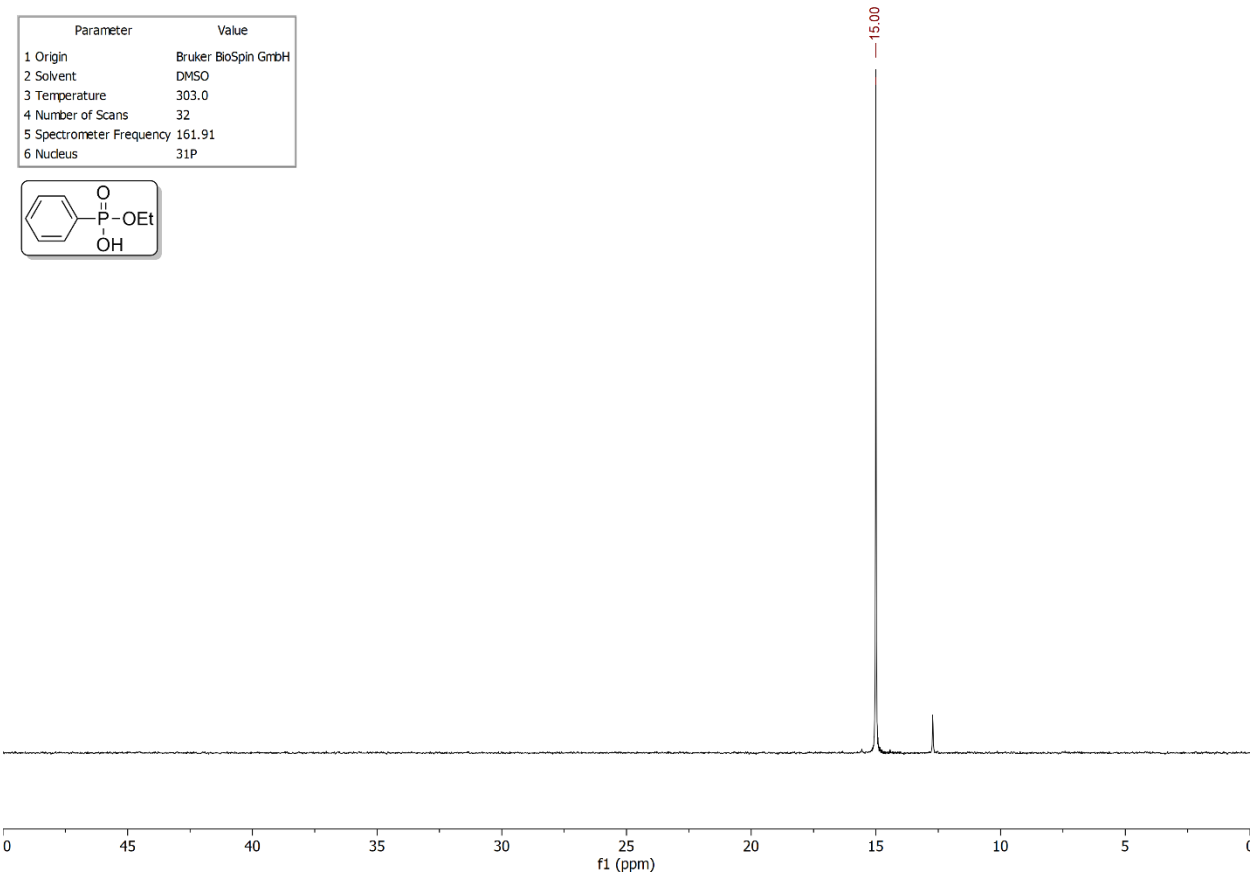

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 144
5 Spectrometer Frequency 100.59
6 Nucleus 13C
O
P–OEt
OH
31.25
29.95
29.79
28.99
28.96
28.94
28.79
28.65
28.55
26.47
25.11
22.38
22.33
22.04
59.71
59.65
39.52 DMSO-d6
31.25
29.95
29.79
28.99
28.96
28.94
28.79
28.65
28.55
26.47
25.11
22.38
22.33
22.04
16.40
16.34
13.89
31 30 29 28 27 26 25 24 23 22 21
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P–OEt
OH
28.94
0 45 40 35 30 25 20 15 10 5
f1 (ppm)

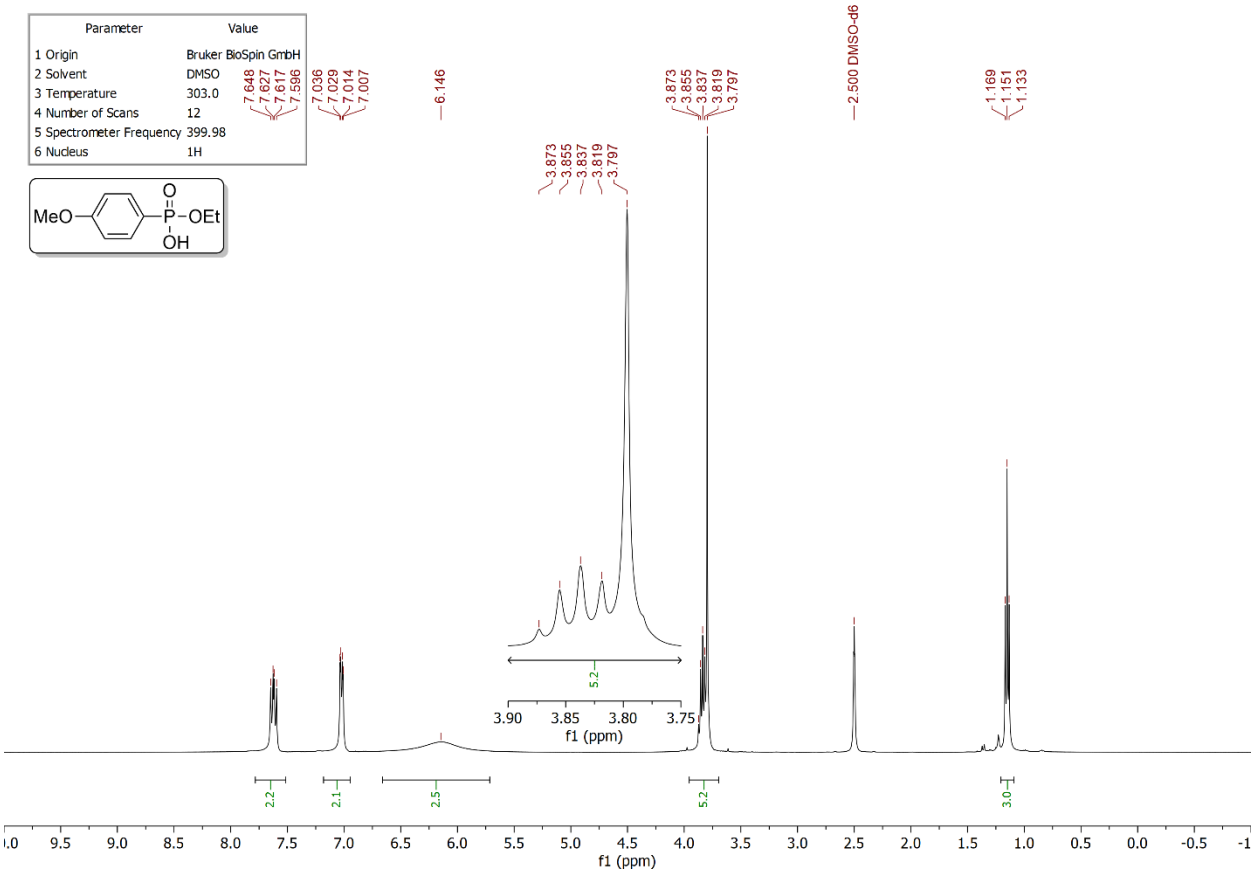
Ethyl hydrogen phenylphosphonate (**3g**)

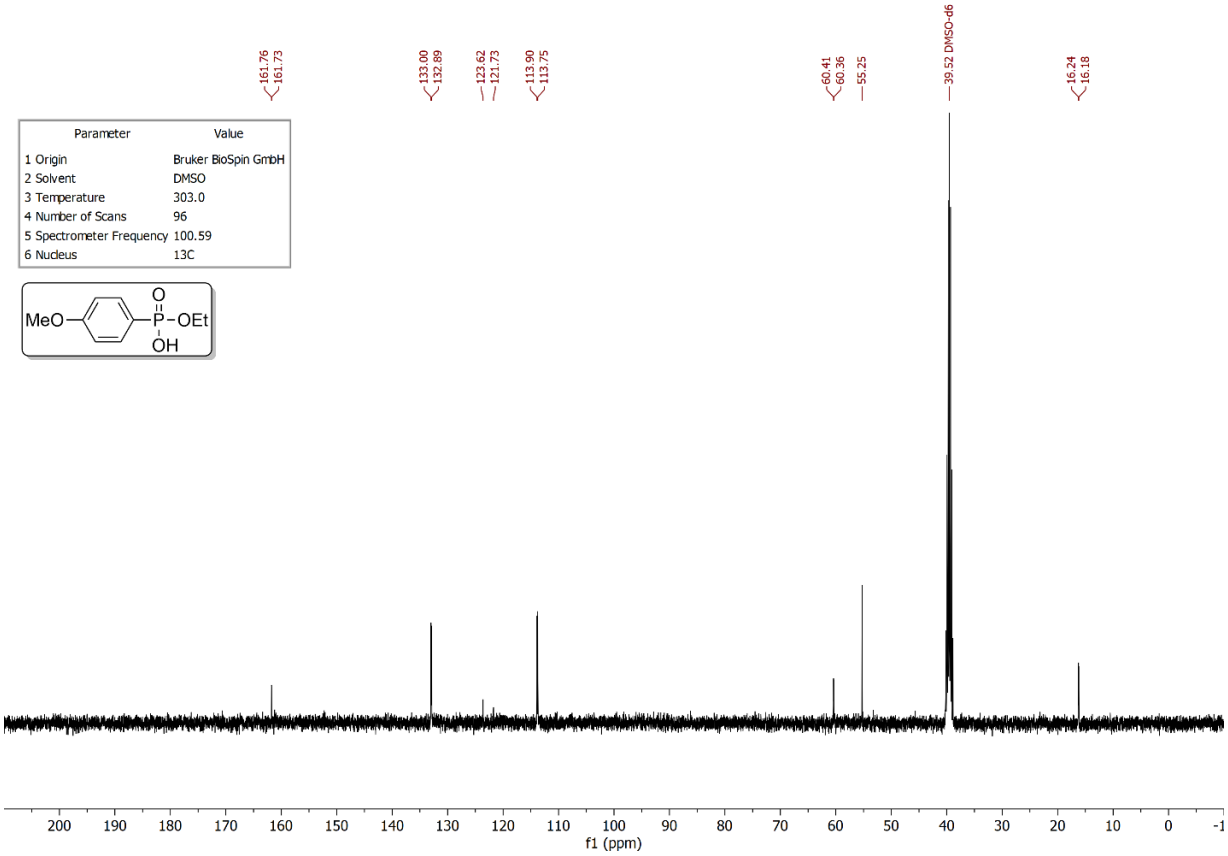


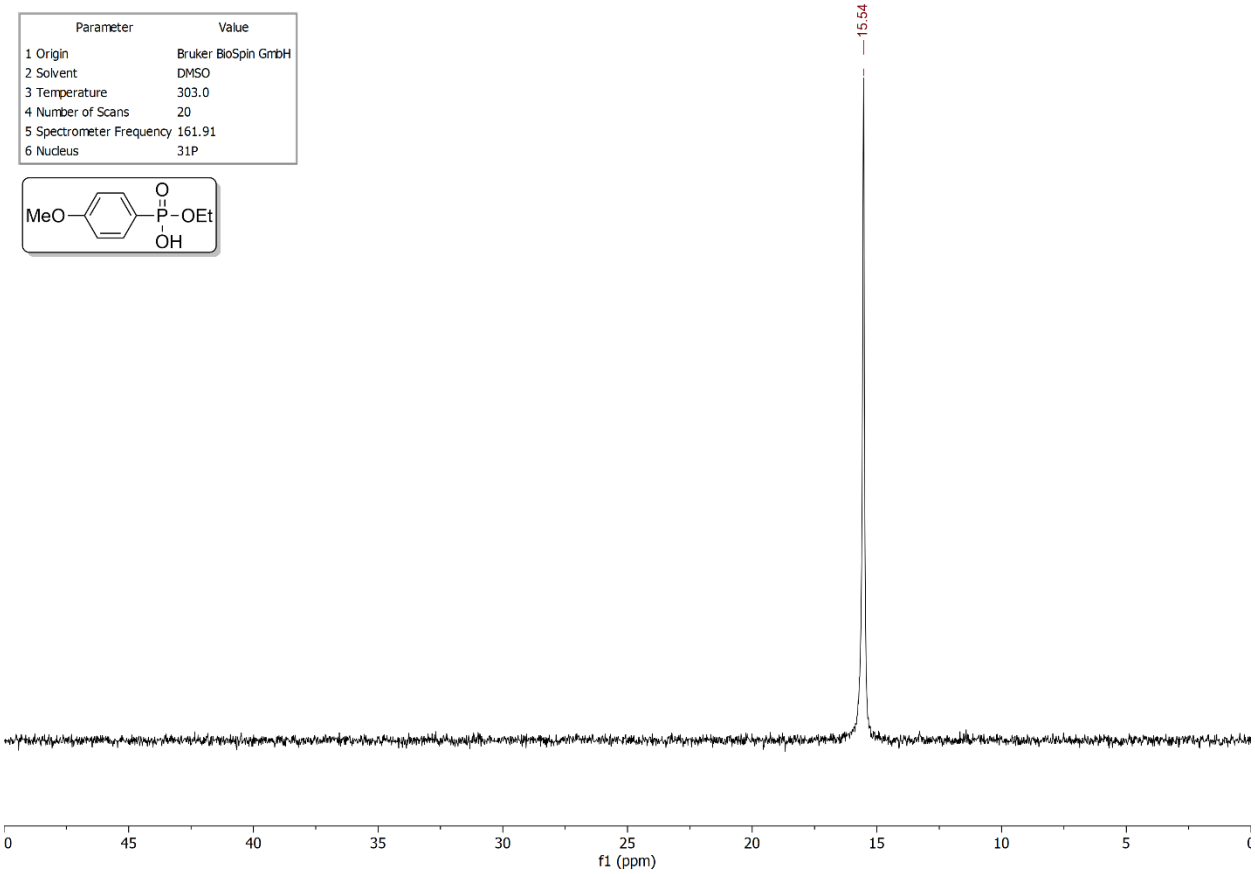

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 72
5 Spectrometer Frequency 100.59
6 Nucleus 13C
O
P-OEt
OH
132.18
131.63
131.60
130.99
130.90
130.36
128.43
128.29
60.67
60.62
39.52 DMSO-d6
16.24
16.18
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 32
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P-OEt
OH
15.00
f1 (ppm)

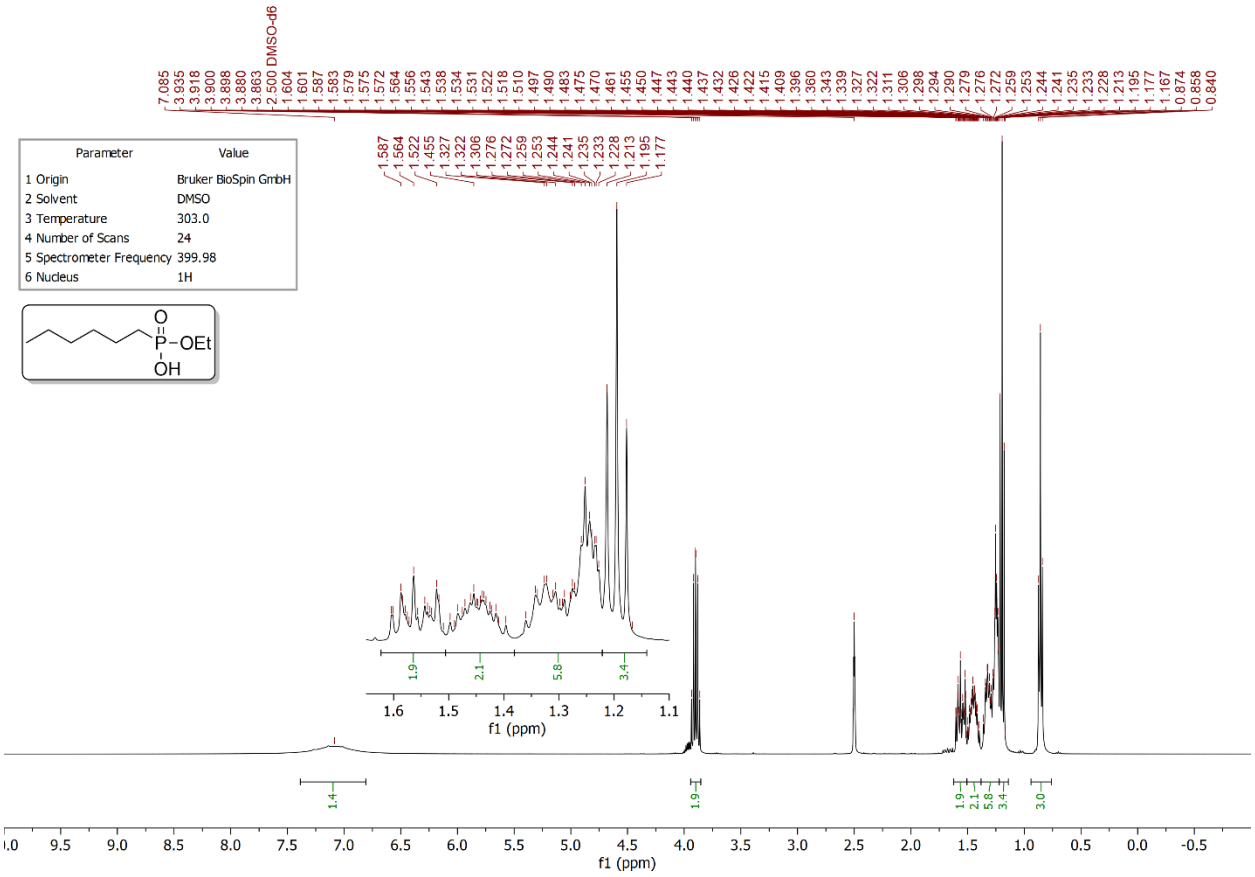
Ethyl hydrogen (4-methoxyphenyl)phosphonate (**3h**)

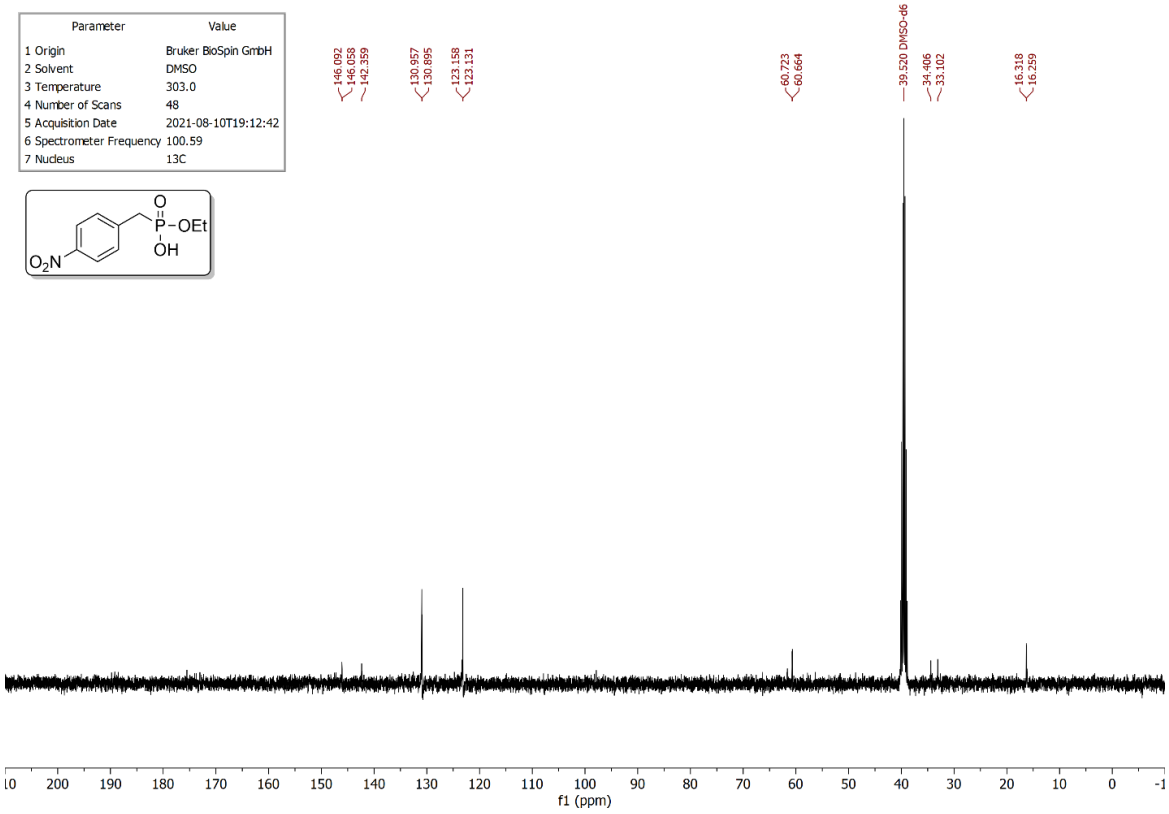


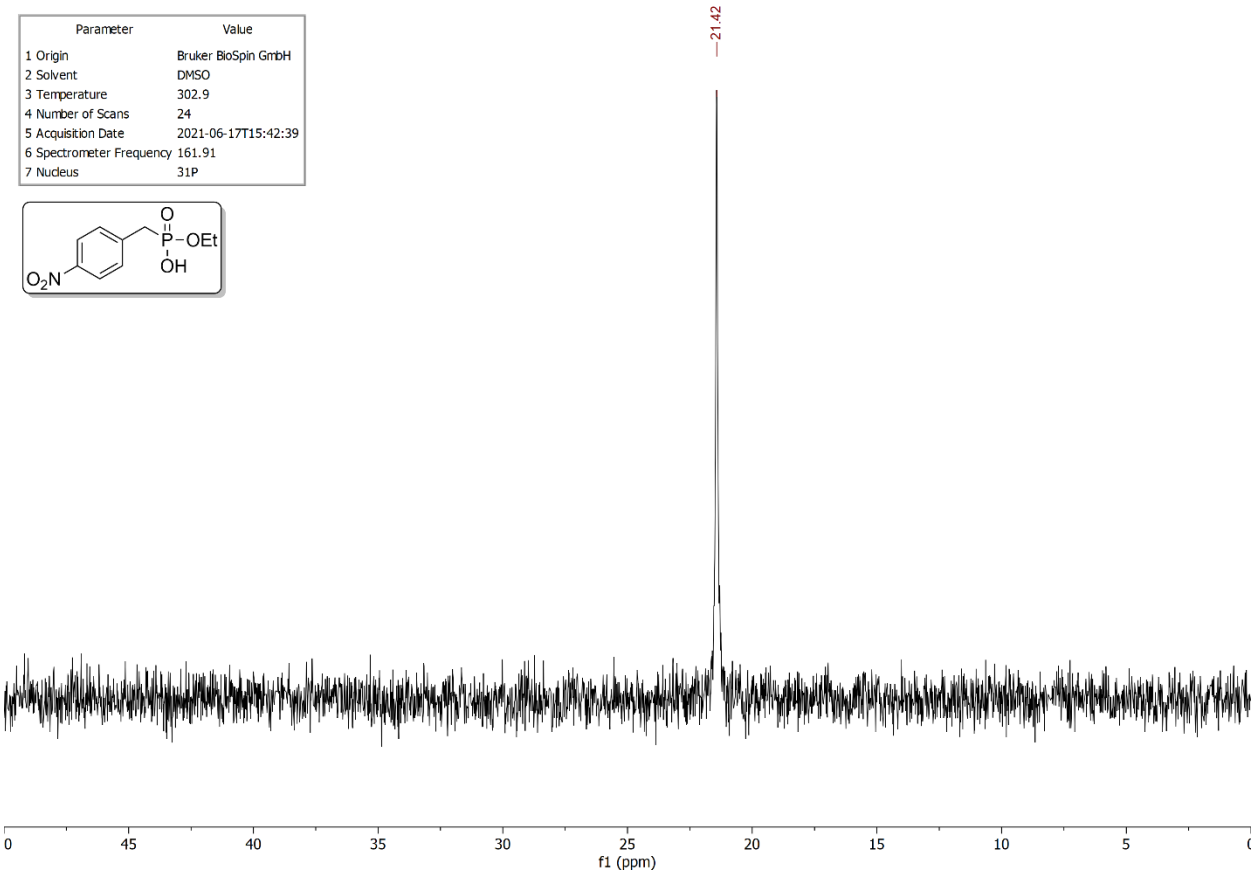

161.76
161.73
133.00
132.89
123.62
121.73
113.90
113.75
60.41
60.36
55.25
39.52 DMSO-d6
16.24
16.18
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 96
5 Spectrometer Frequency 100.59
6 Nucleus 13C
MeO
O
P
OEt
OH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


15.54
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 20
5 Spectrometer Frequency 161.91
6 Nucleus 31P
MeO
O
P
OEt
OH
0 45 40 35 30 25 20 15 10 5
f1 (ppm)

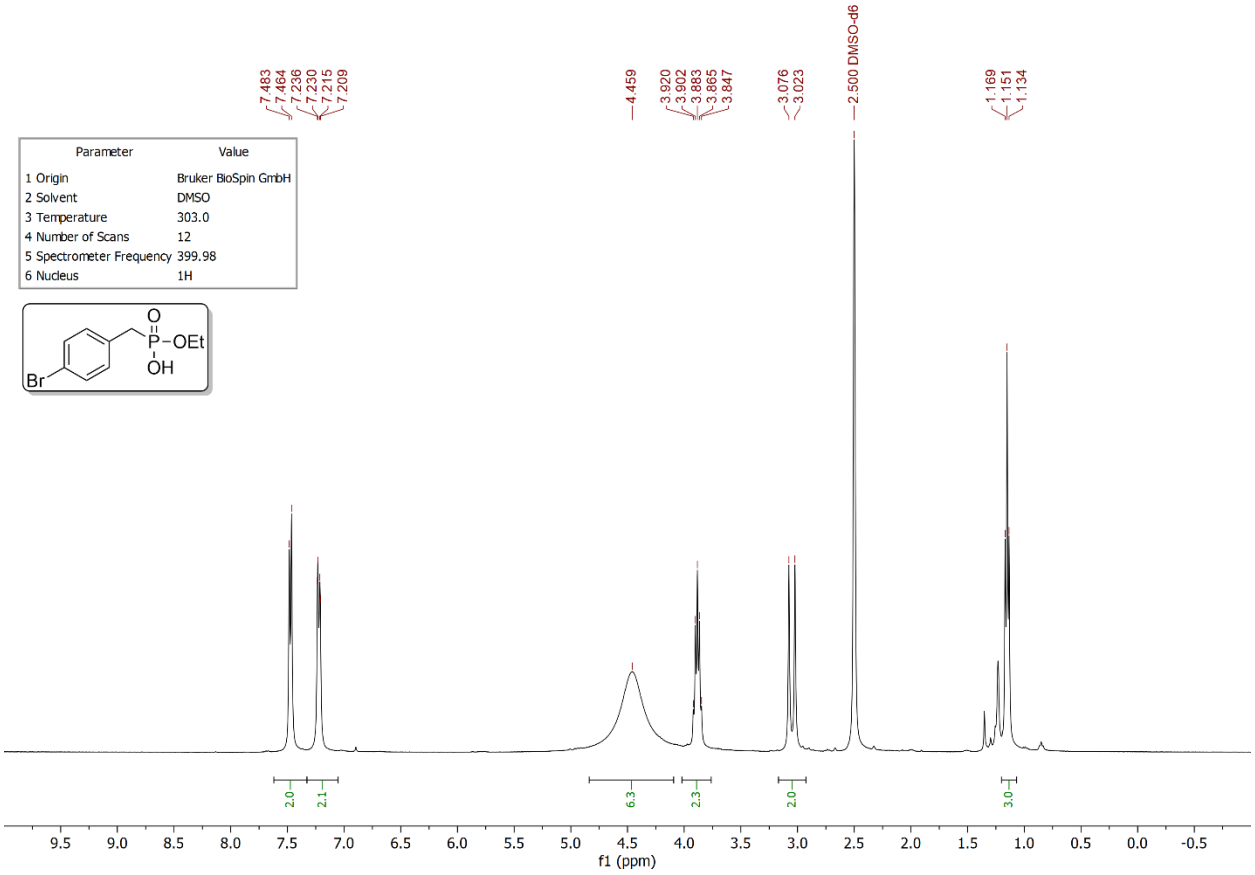
Ethyl hydrogen [(4-nitrophenyl)methyl]phosphonate (**3j**)

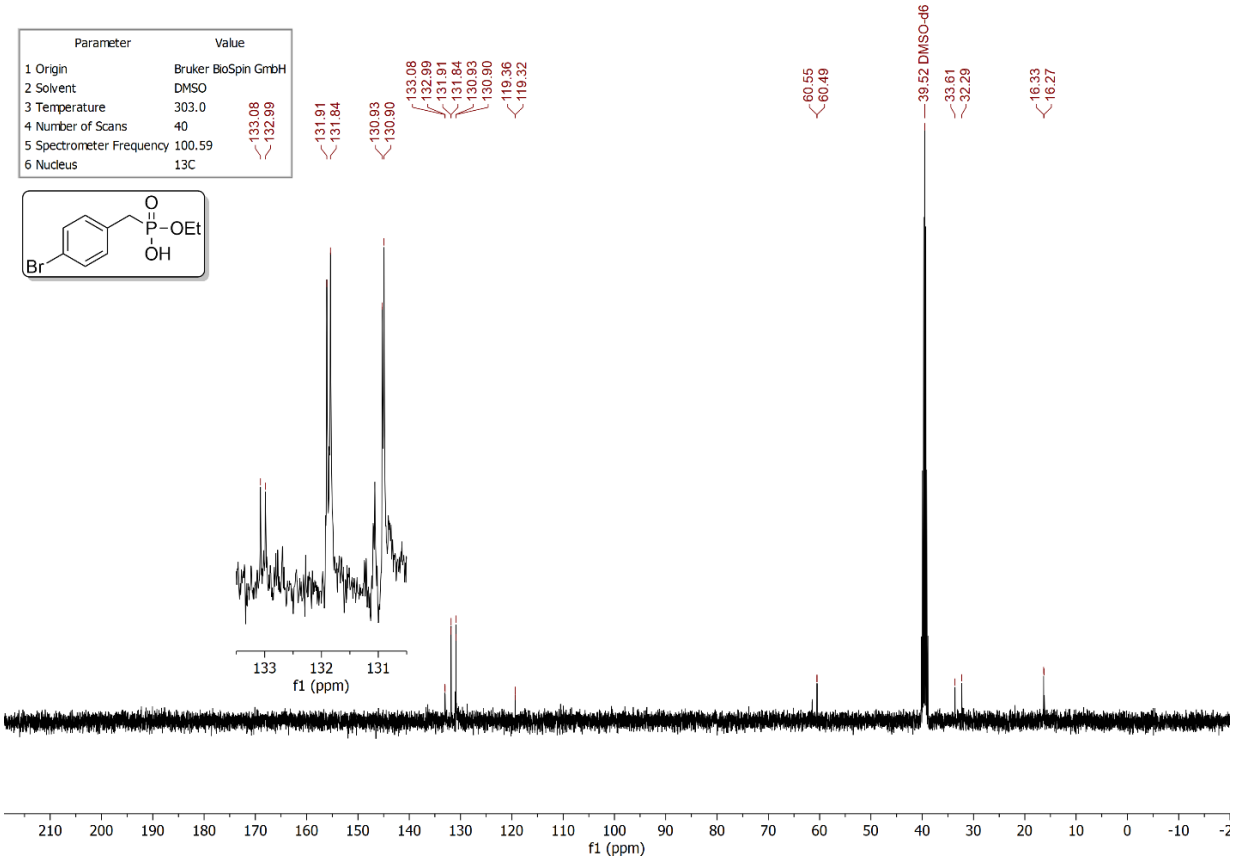


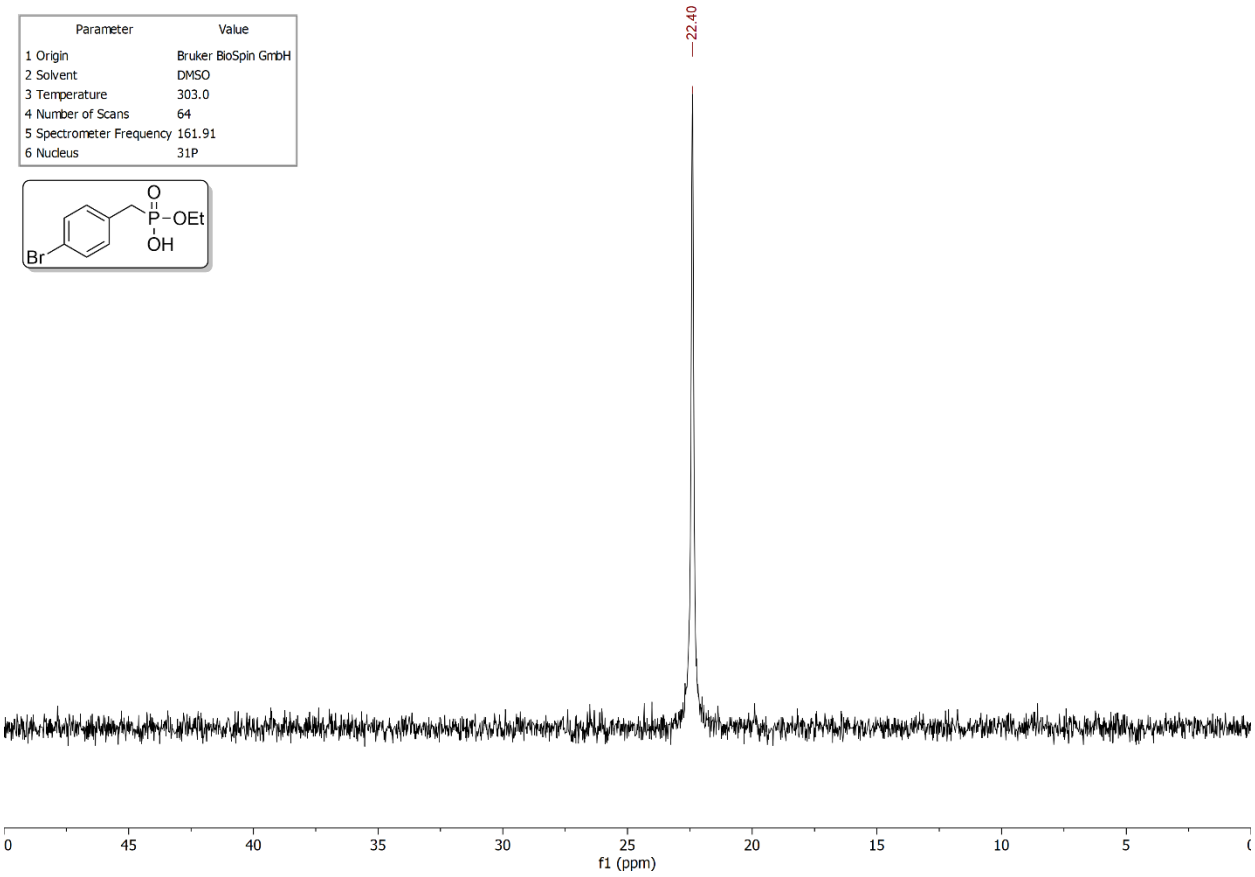

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 48
5 Acquisition Date 2021-08-10T19:12:42
6 Spectrometer Frequency 100.59
7 Nucleus 13C
146.092
145.058
142.359
130.957
130.895
123.158
123.131
60.723
60.664
39.520 DMSO-d6
34.406
33.102
16.318
16.259
O
P–OEt
OH
O2N
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 302.9
4 Number of Scans 24
5 Acquisition Date 2021-06-17T15:42:39
6 Spectrometer Frequency 161.91
7 Nucleus 31P
21.42
O
P–OEt
OH
O2N
f1 (ppm)

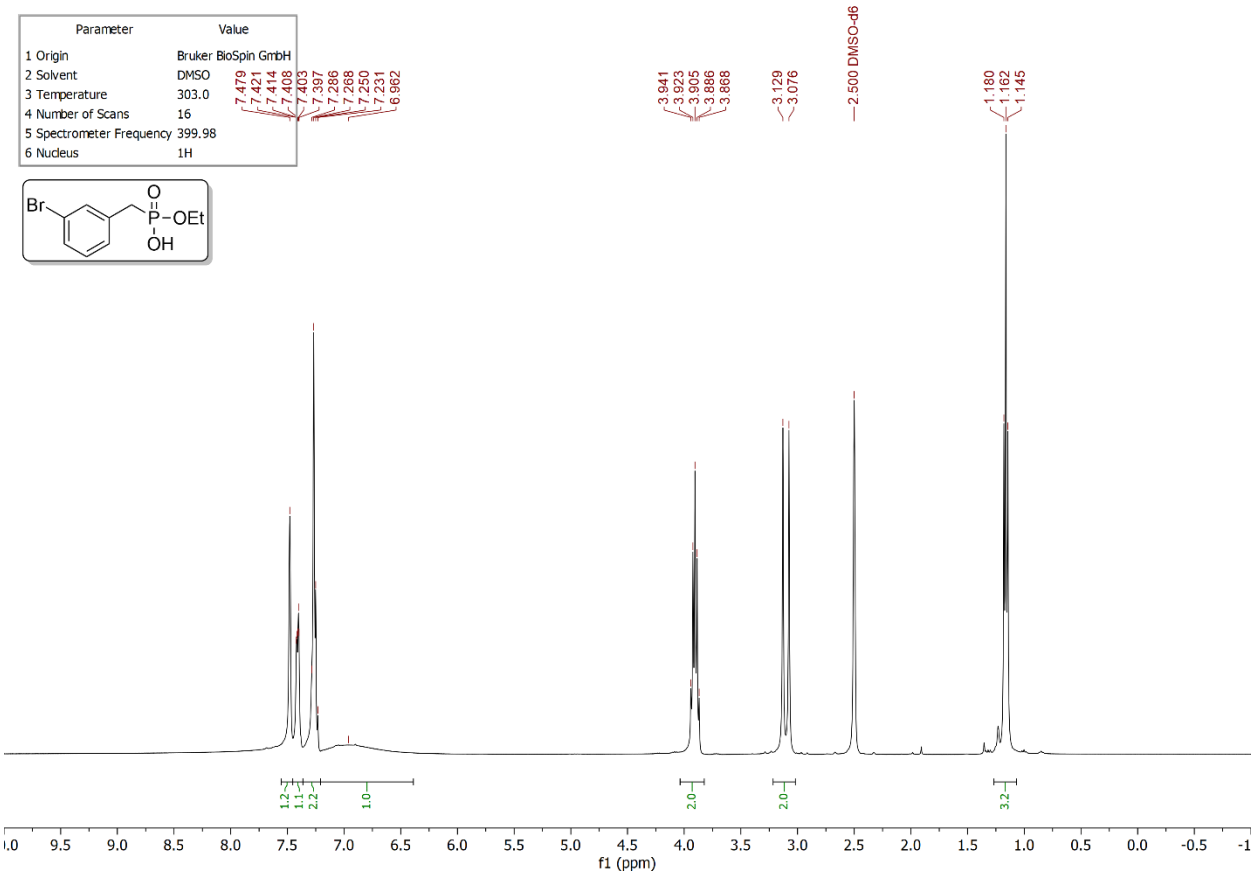
Ethyl hydrogen [(4-bromophenyl)methyl]phosphonate (**3k**)

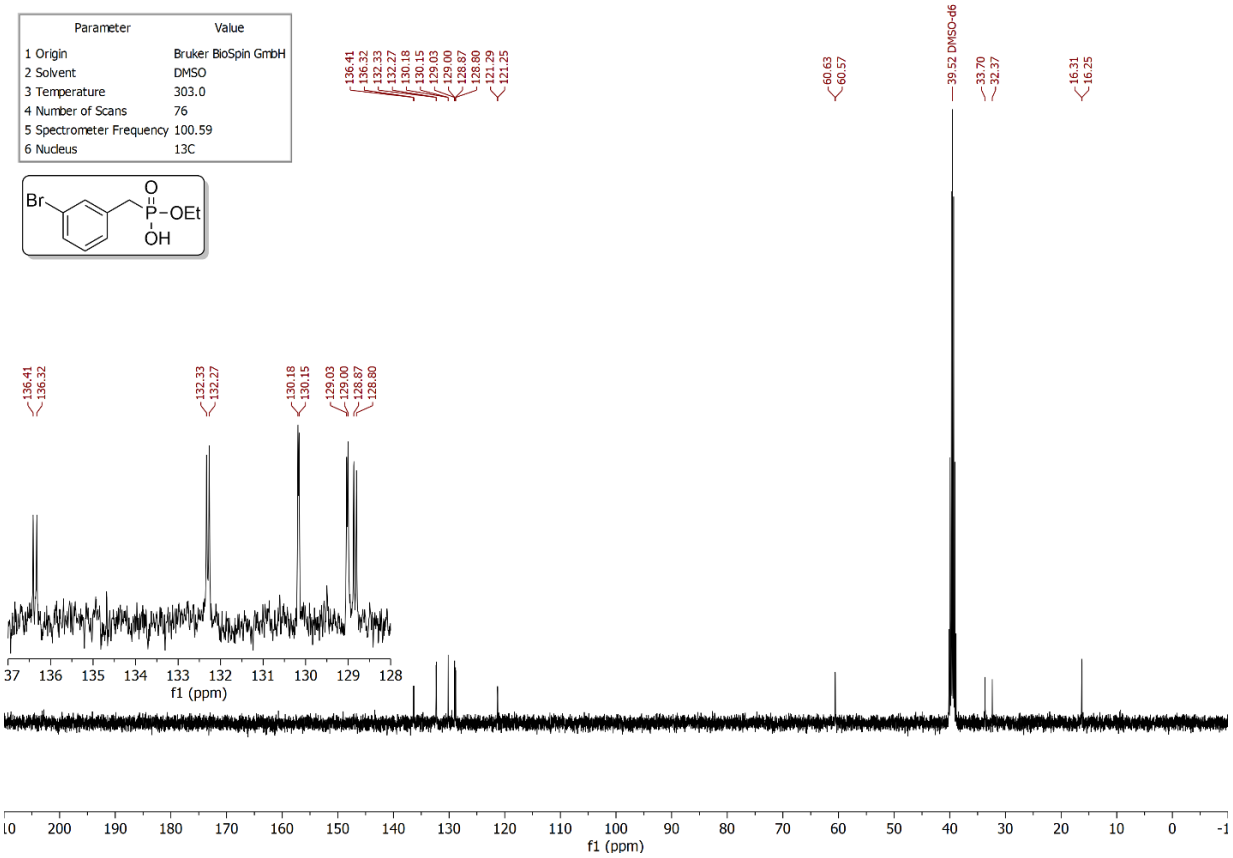


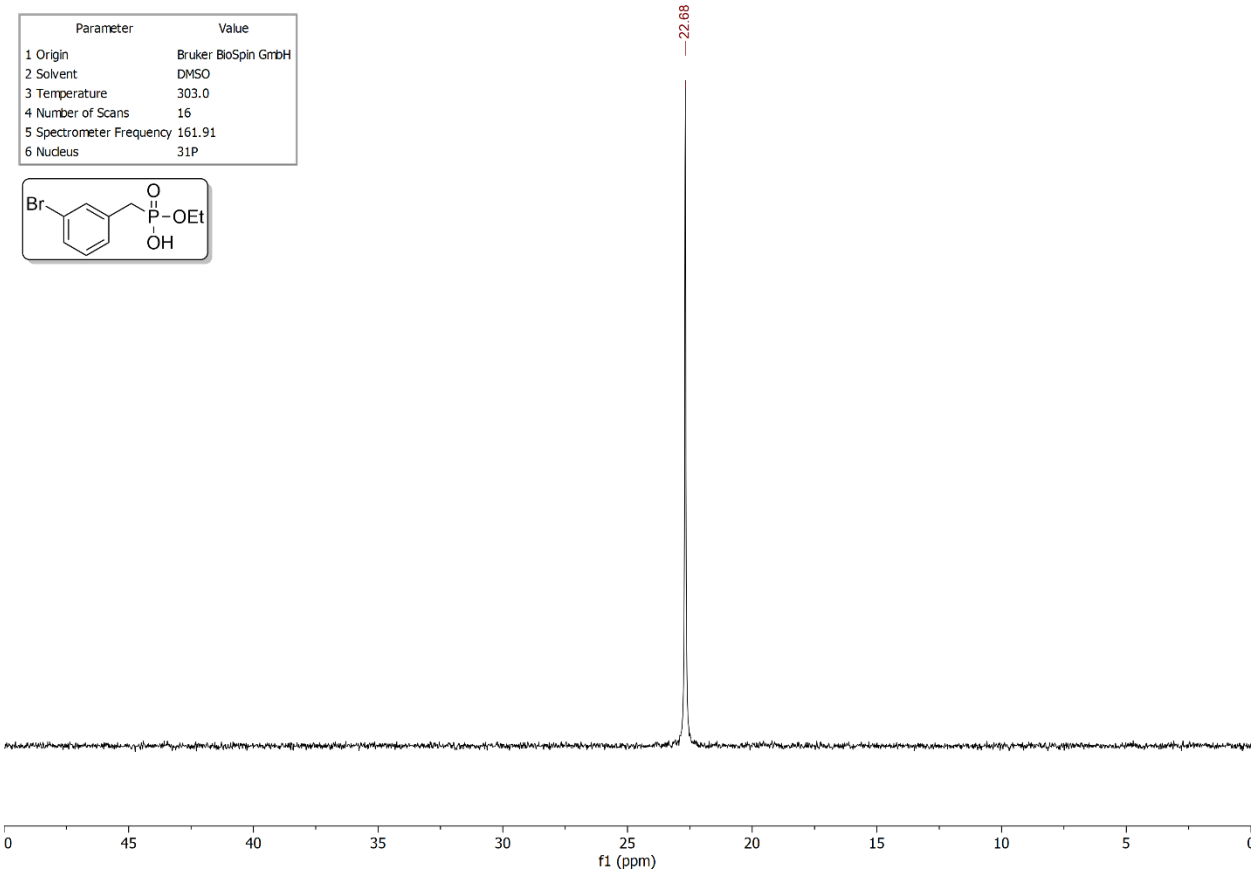

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 40
5 Spectrometer Frequency 100.59
6 Nucleus 13C
133.08
132.99
131.91
131.84
130.93
130.90
133.08
132.99
131.91
131.84
130.93
130.90
119.36
119.32
60.55
60.49
39.52 DMSO-d6
33.61
32.29
16.33
16.27
O
P–OEt
OH
Br
133 132 131
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 64
5 Spectrometer Frequency 161.91
6 Nucleus 31P
22.40
O
P–OEt
OH
Br
0 45 40 35 30 25 20 15 10 5
f1 (ppm)

Ethyl hydrogen [(3-bromophenyl)methyl]phosphonate (**3l**)

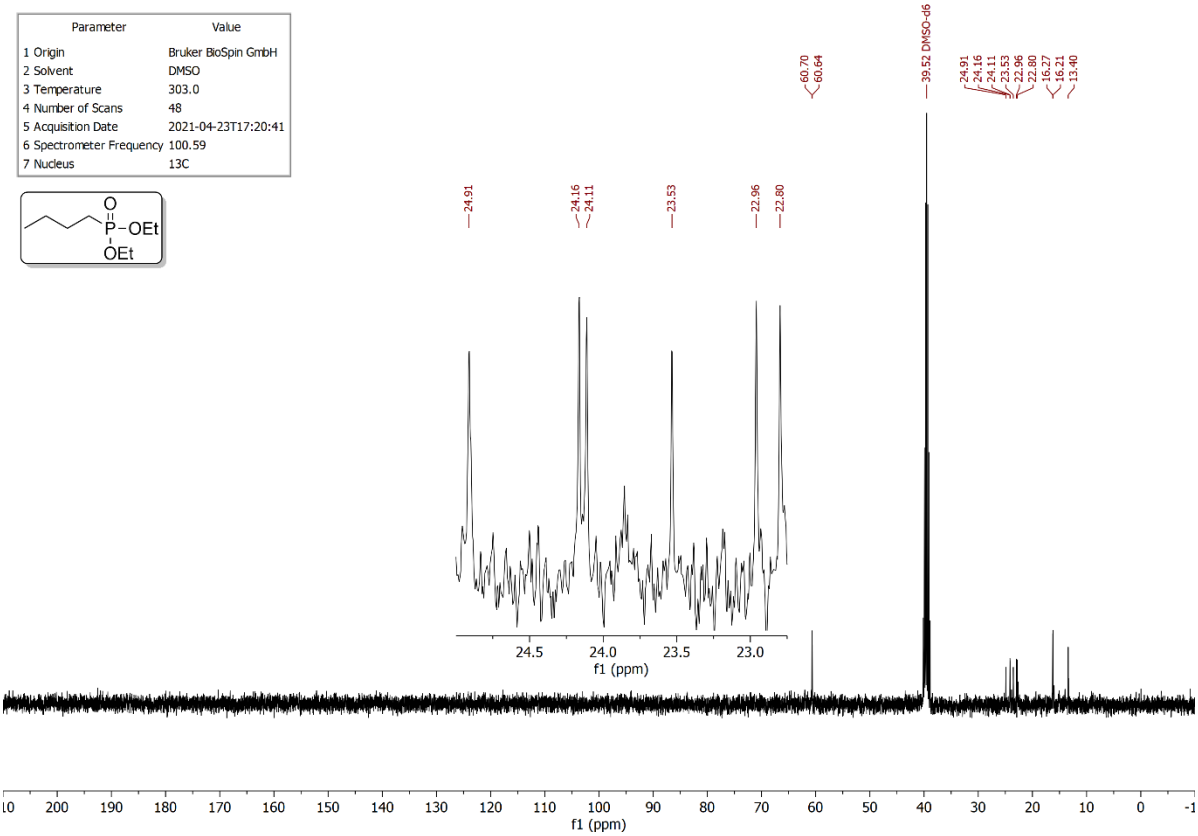


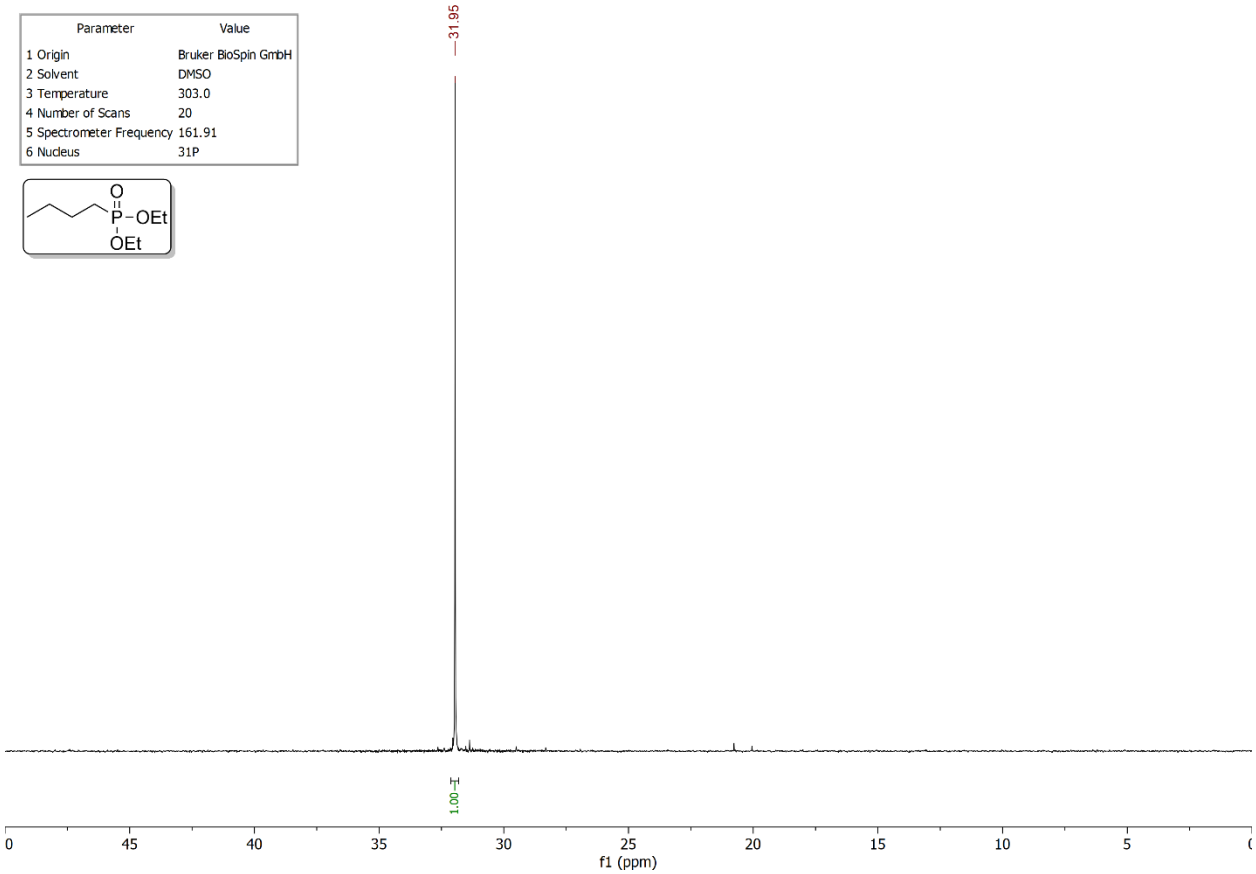

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 76
5 Spectrometer Frequency 100.59
6 Nucleus 13C
Br
O
P–OEt
OH
136.41
136.32
132.33
132.27
130.18
130.15
129.03
129.00
128.87
128.80
121.29
121.25
60.63
60.57
39.52 DMSO-d6
33.70
32.37
16.31
16.25
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
Br
O
P–OEt
OH
22.68
f1 (ppm)

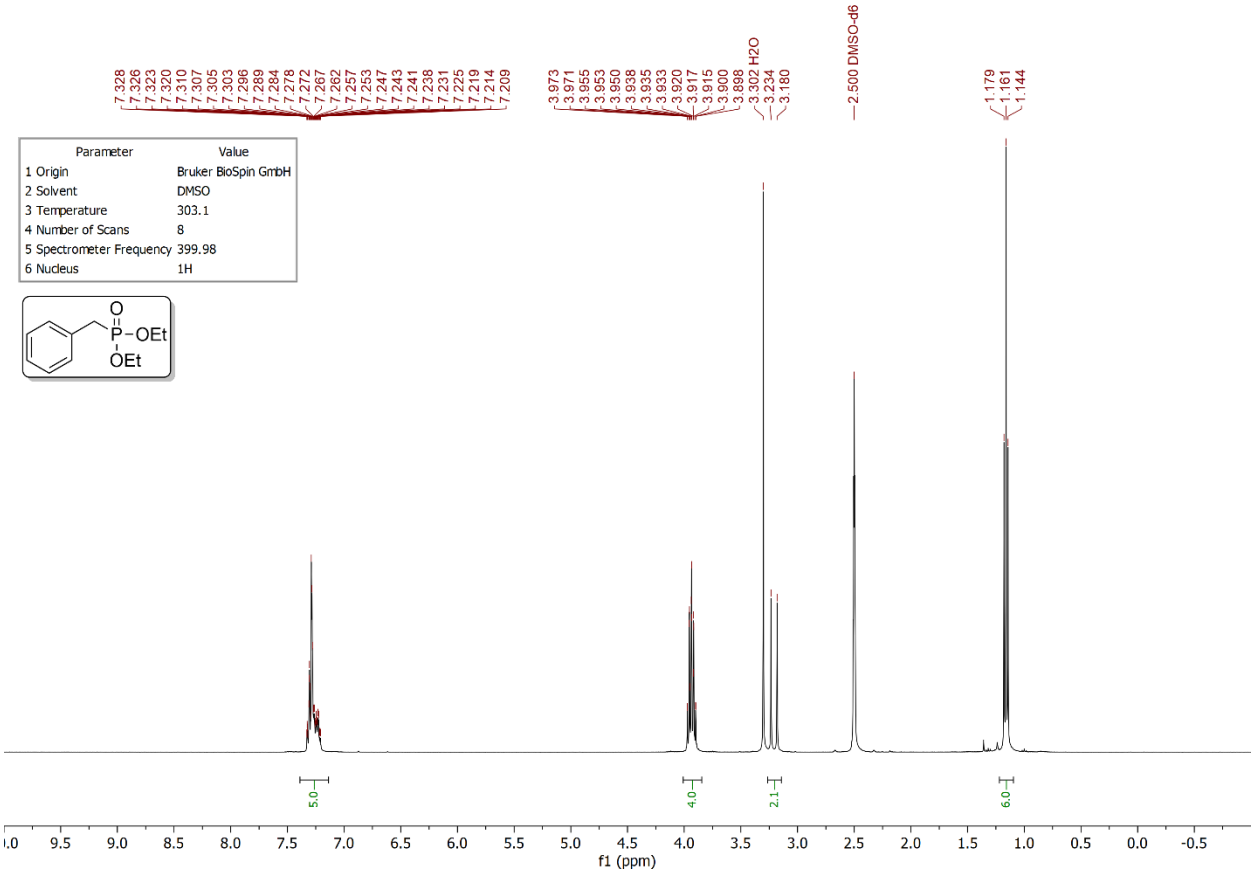
2.4. *^{1}H, ^{13}C and ^{31}P NMR spectra of the diesters*

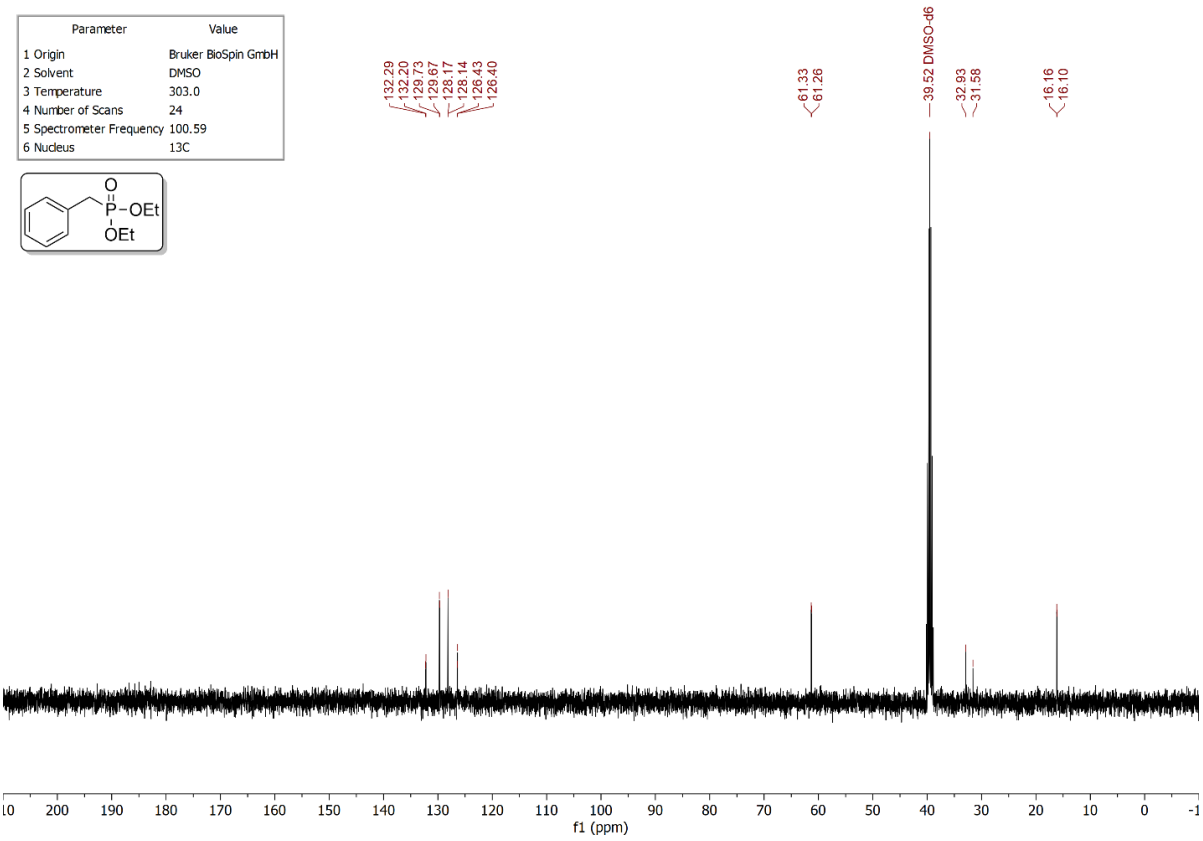
Diethyl butylphosphonate (**4a**)

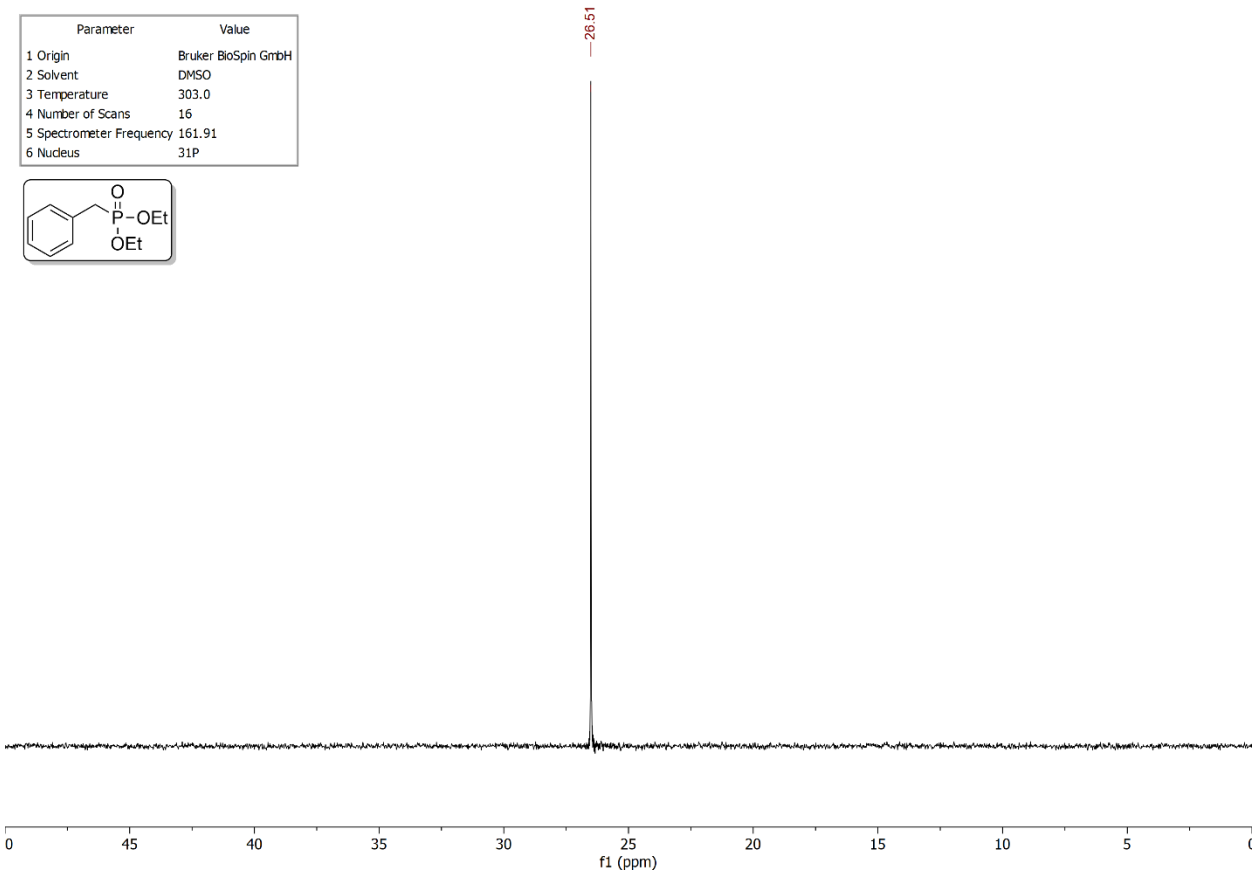



Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 20
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P-OEt
OEt
31.95
1.00
0
45
40
35
30
25
20
15
10
5
f1 (ppm)

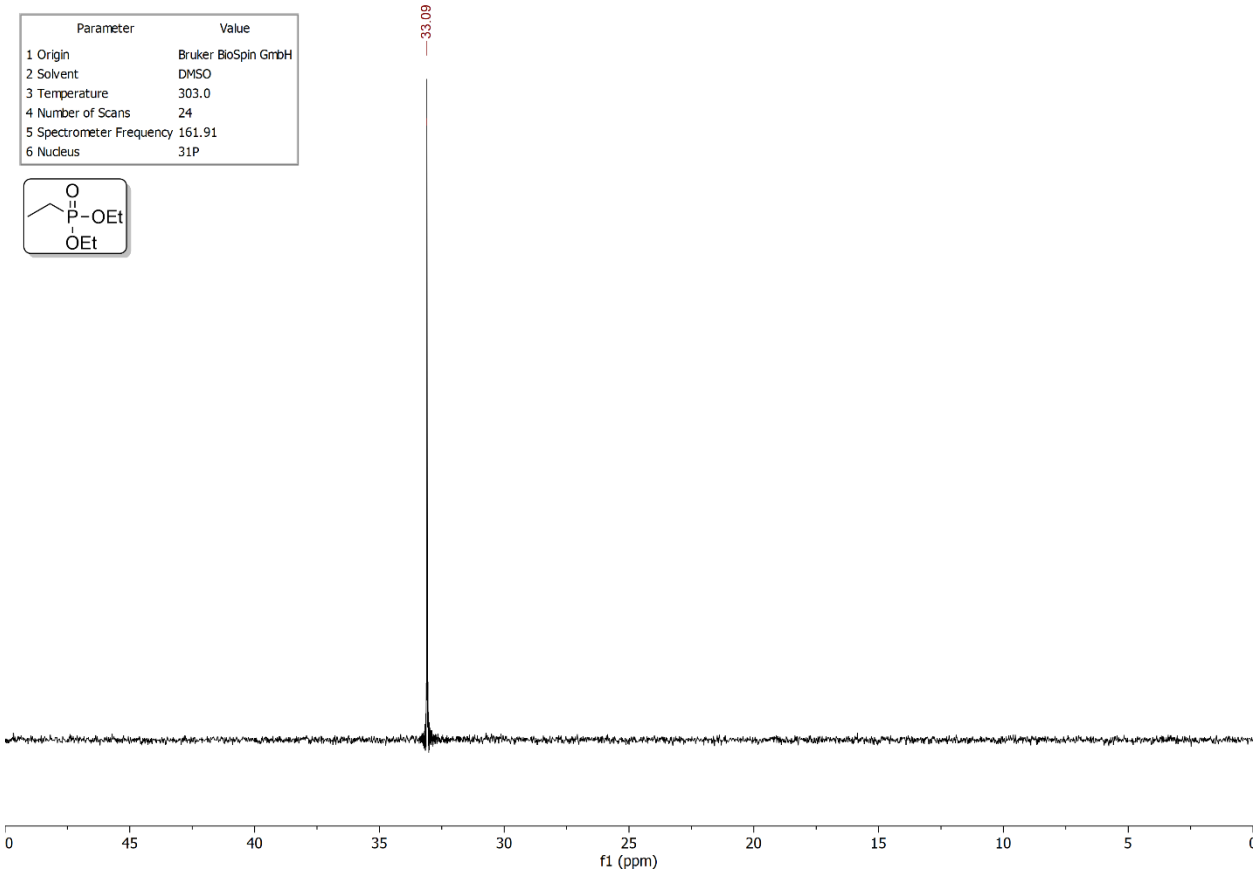
Diethyl benzylphosphonate (**4b**)



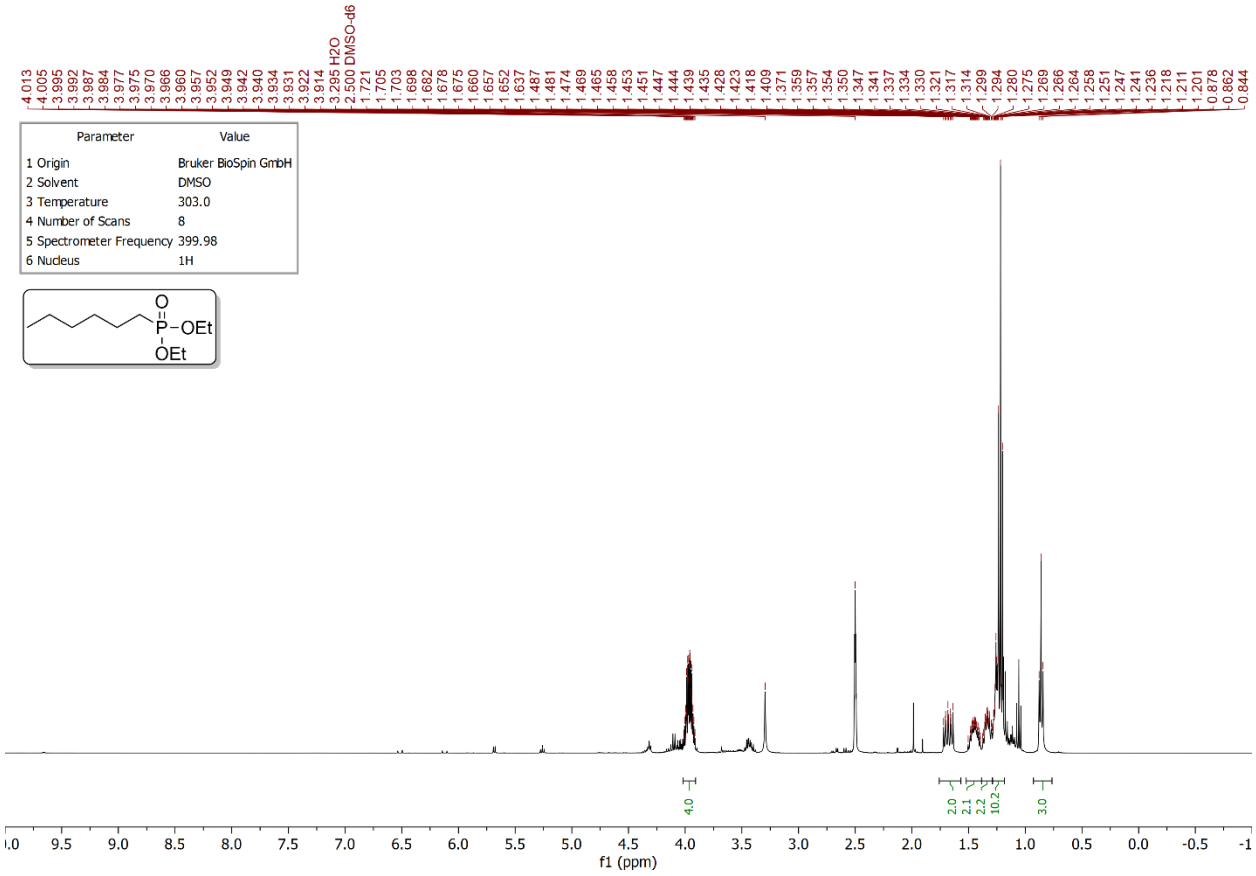

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 24
5 Spectrometer Frequency 100.59
6 Nucleus 13C
132.29
132.20
129.73
129.67
128.17
128.14
126.43
126.40
61.33
61.26
39.52 DMSO-d6
32.93
31.58
16.16
16.10
f1 (ppm)

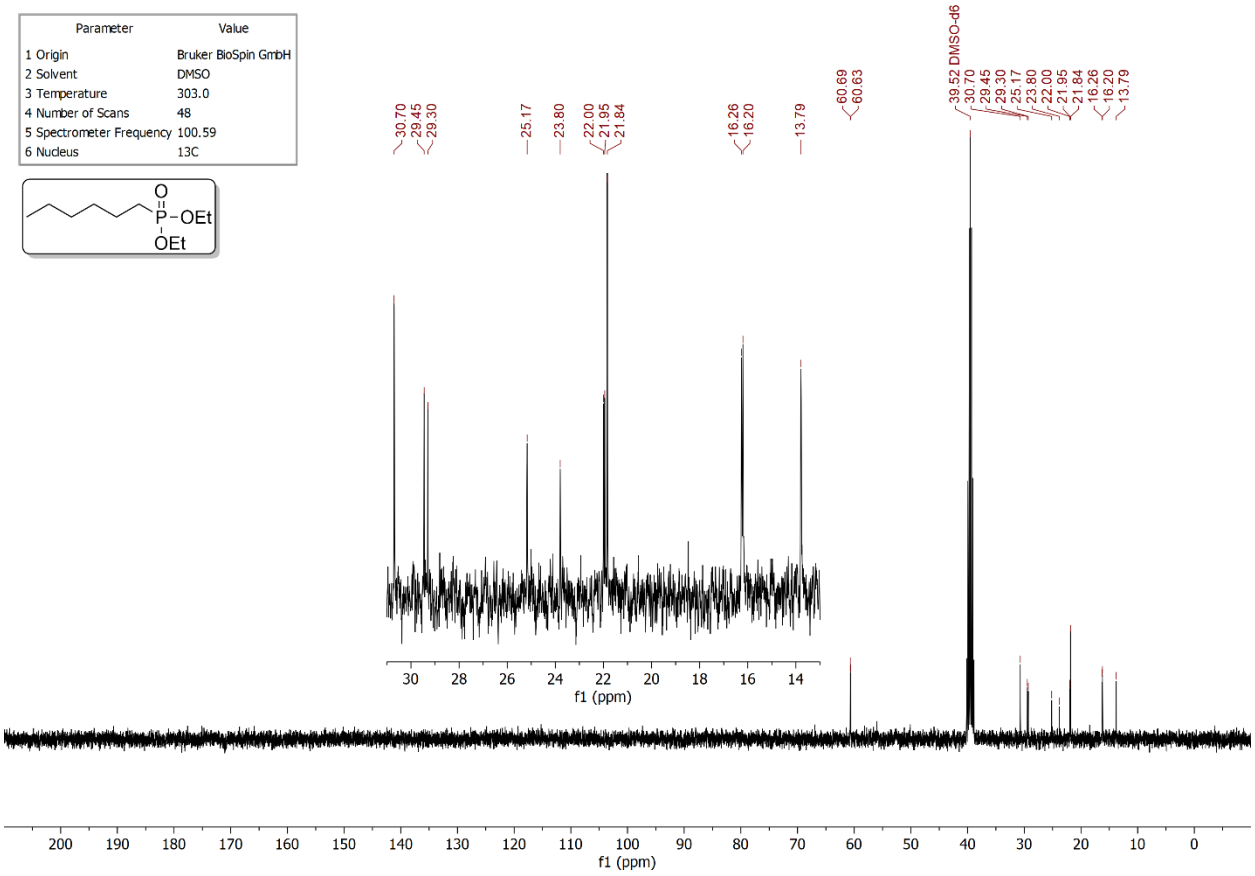

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
28.51
f1 (ppm)

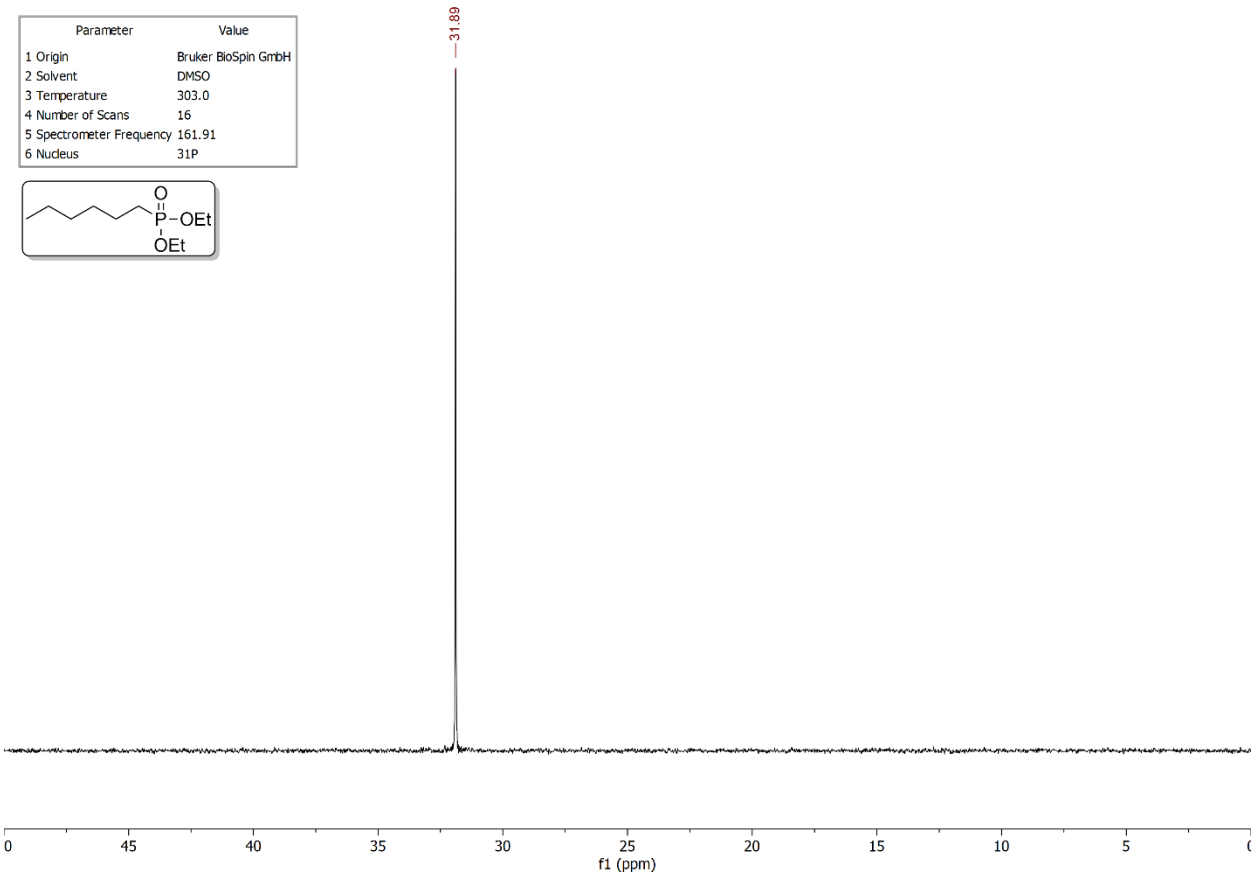
Diethyl ethylphosphonate (**4c**)



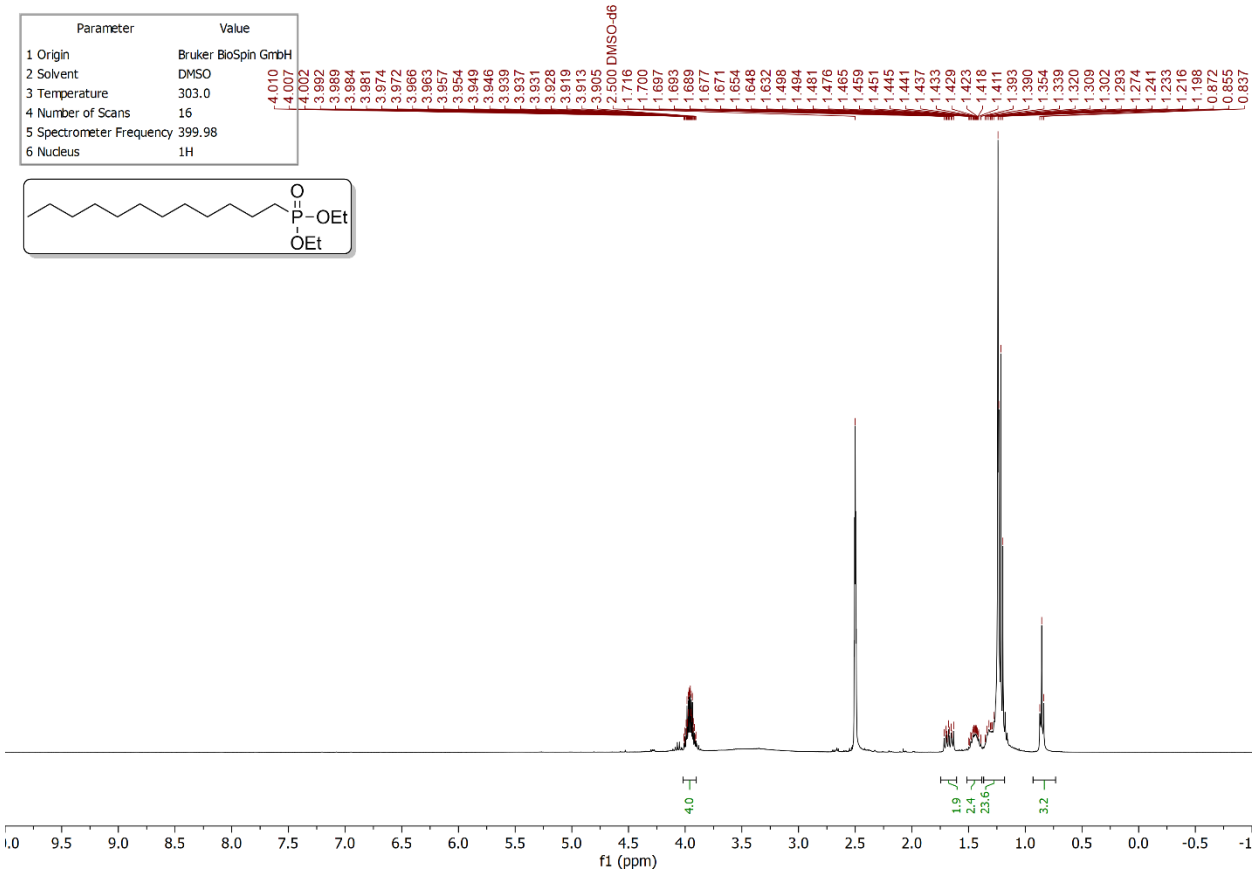
Diethyl hexylphosphonate (**4e**)

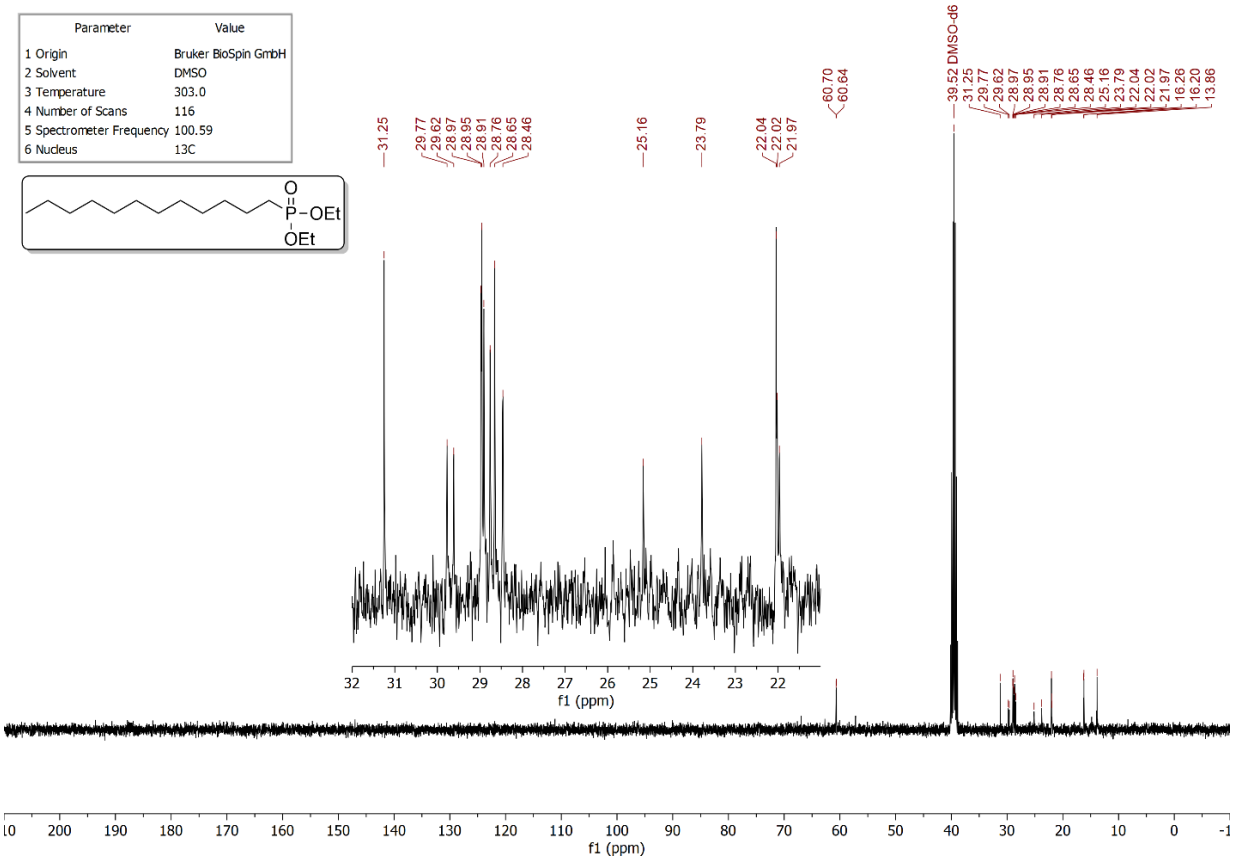

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 8
5 Spectrometer Frequency 399.98
6 Nucleus 1H
O
P–OEt
OEt
3.295 H2O
2.500 DMSO-d6
4.0
2.0
2.1
2.2
10.2
3.0
f1 (ppm)

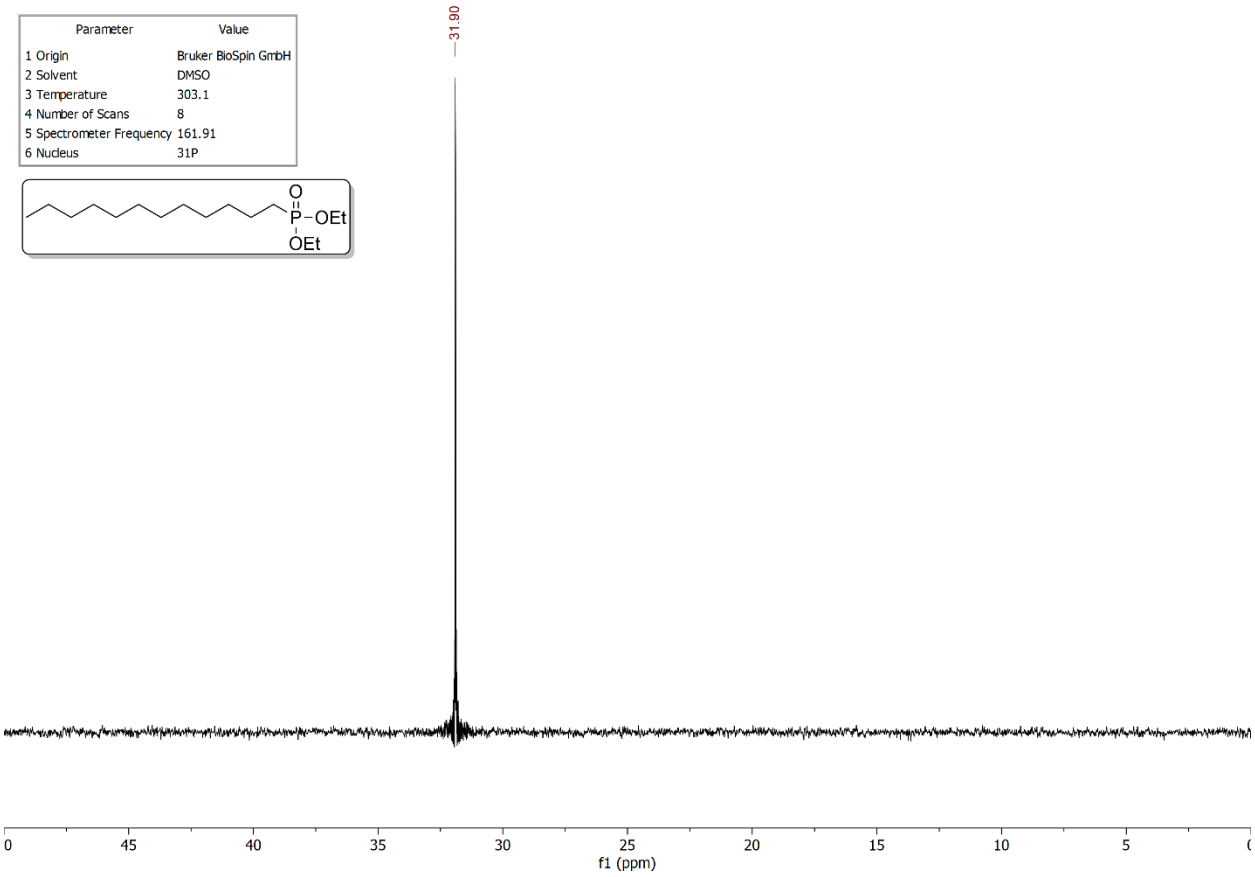

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 48
5 Spectrometer Frequency 100.59
6 Nucleus 13C
O
P-OEt
OEt
30.70
29.45
29.30
25.17
23.80
22.00
21.95
21.84
16.26
16.20
13.79
60.69
60.63
39.52 DMSO-d6
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P-OEt
OEt
31.89
f1 (ppm)

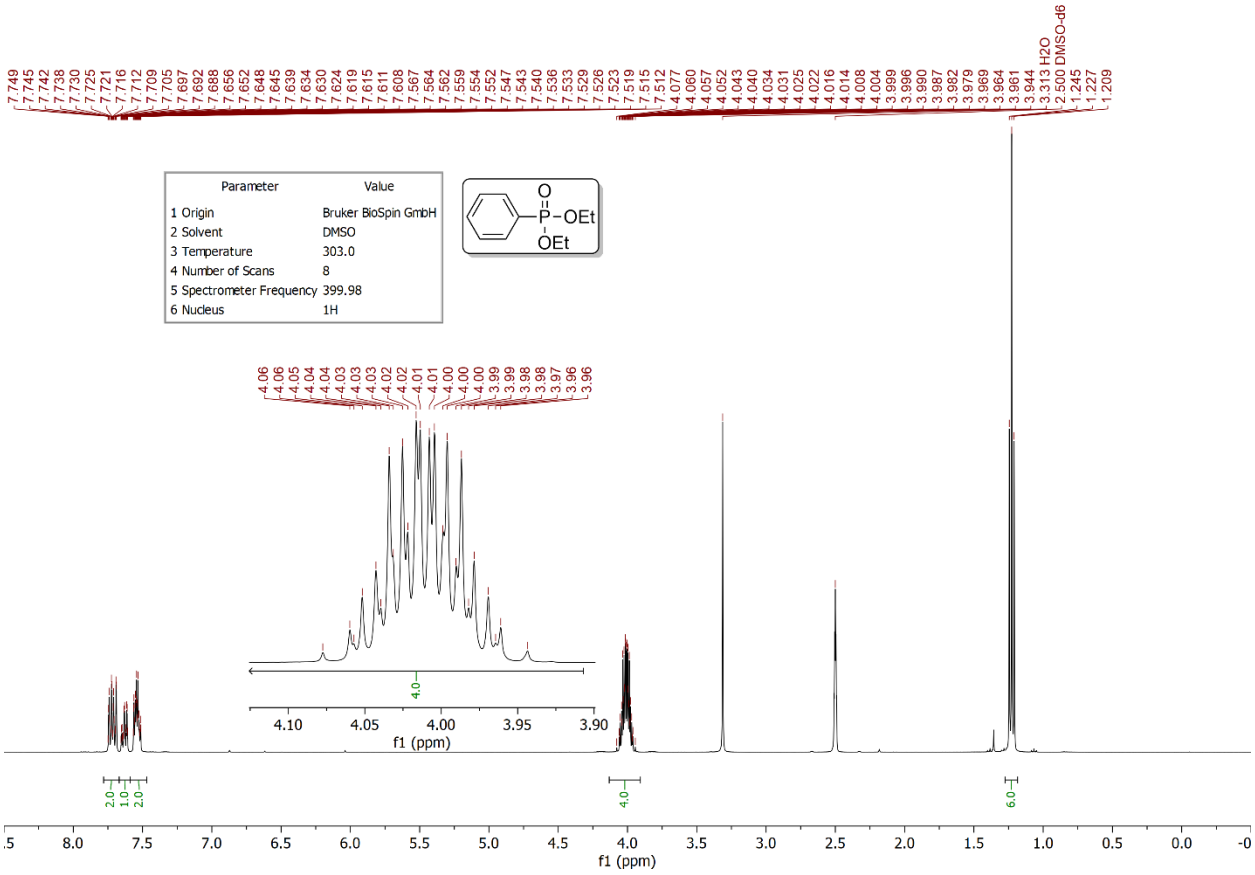
Diethyl dodecylphosphonate (**4f**)

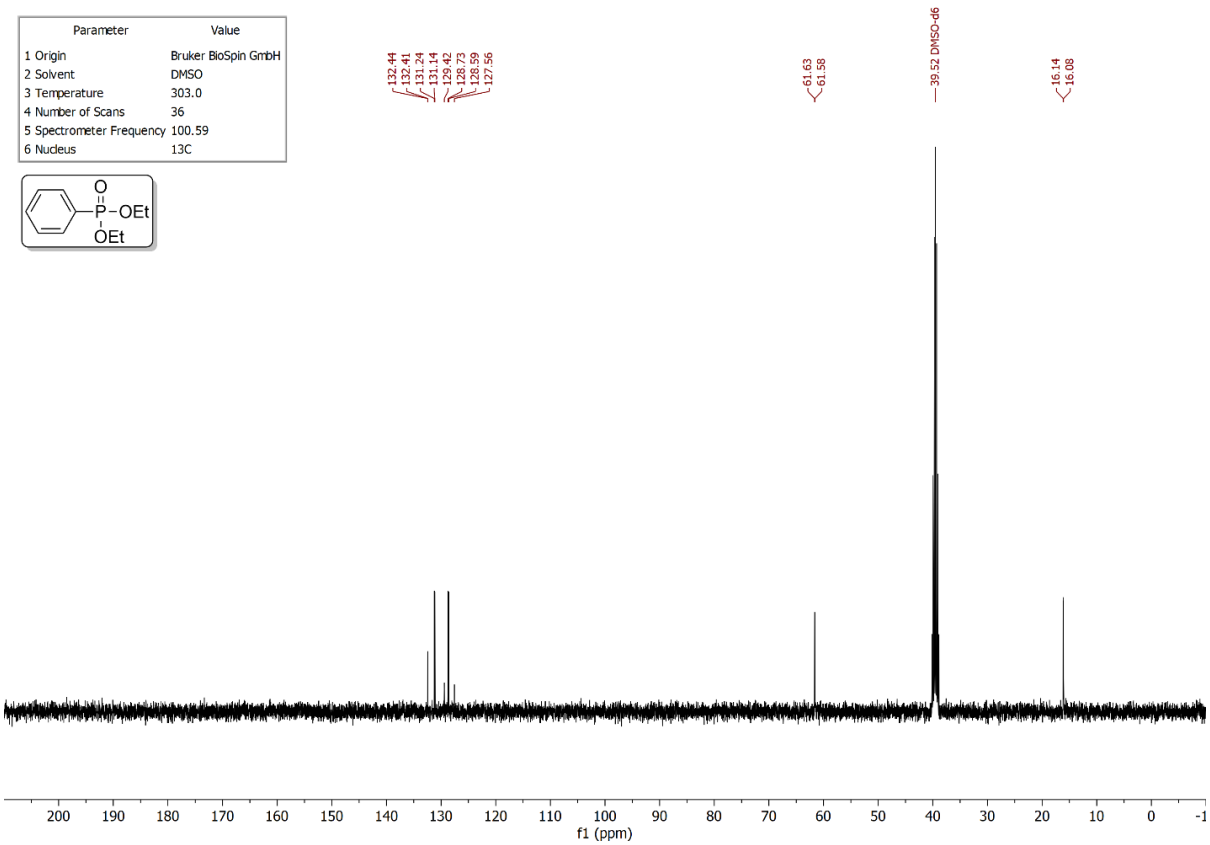


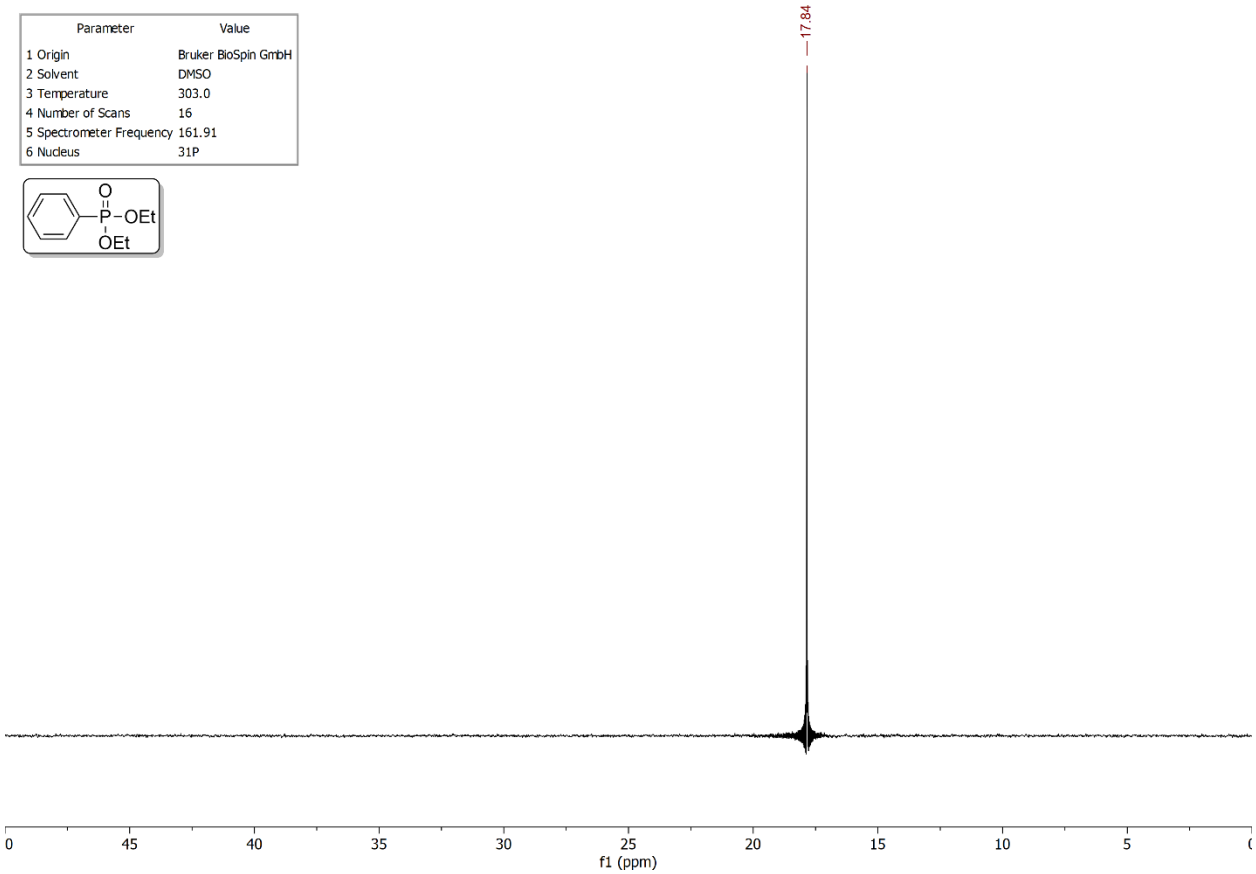

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 116
5 Spectrometer Frequency 100.59
6 Nucleus 13C
O
P–OEt
OEt
31.25
29.77
29.62
28.97
28.95
28.91
28.76
28.65
28.46
25.16
23.79
22.04
22.02
21.97
60.70
60.64
39.52 DMSO-d6
31.25
29.77
29.62
28.97
28.95
28.91
28.76
28.65
28.46
25.16
23.79
22.04
22.02
21.97
16.20
13.86
f1 (ppm)
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.1
4 Number of Scans 8
5 Spectrometer Frequency 161.91
6 Nucleus 31P
O
P–OEt
OEt
31.90
f1 (ppm)

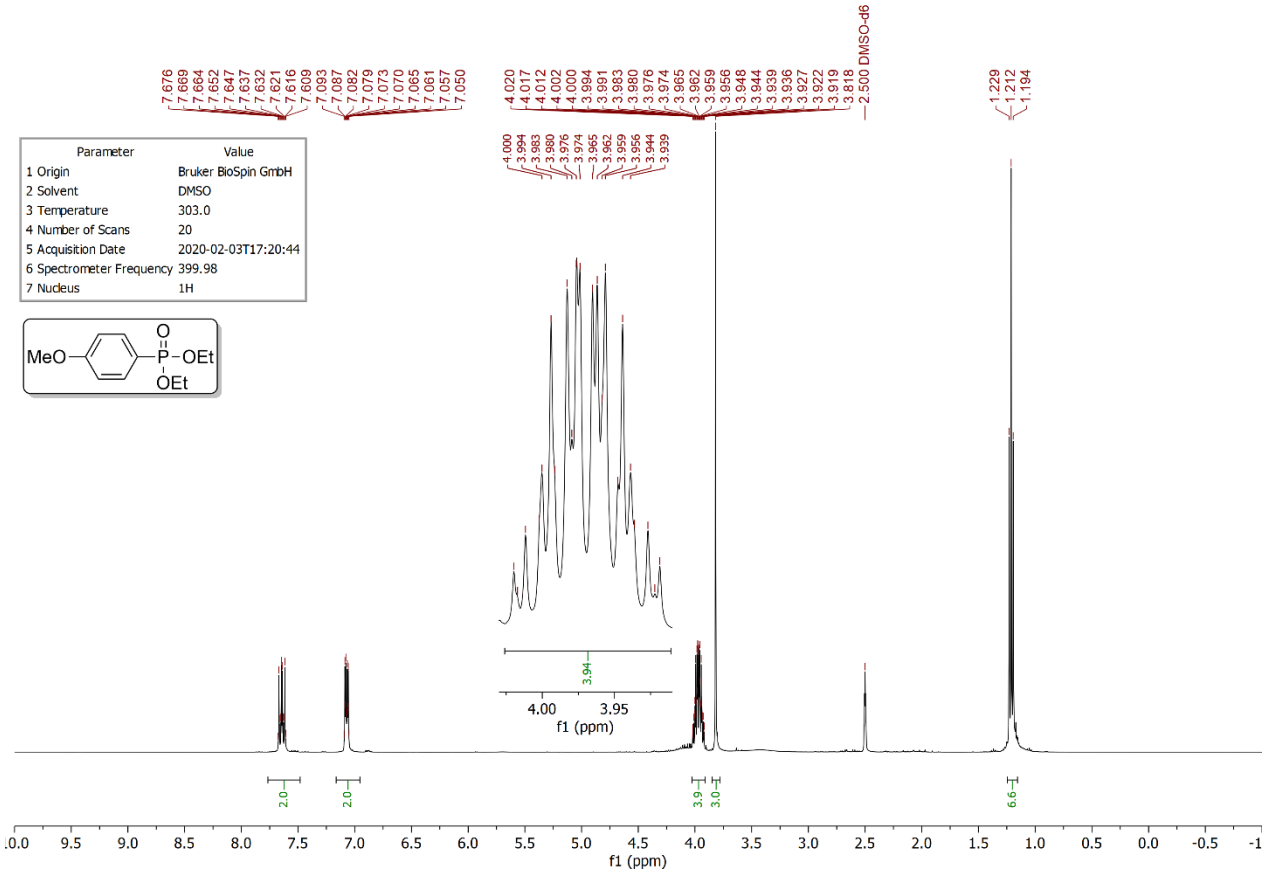
Diethyl phenylphosphonate (**4g**)

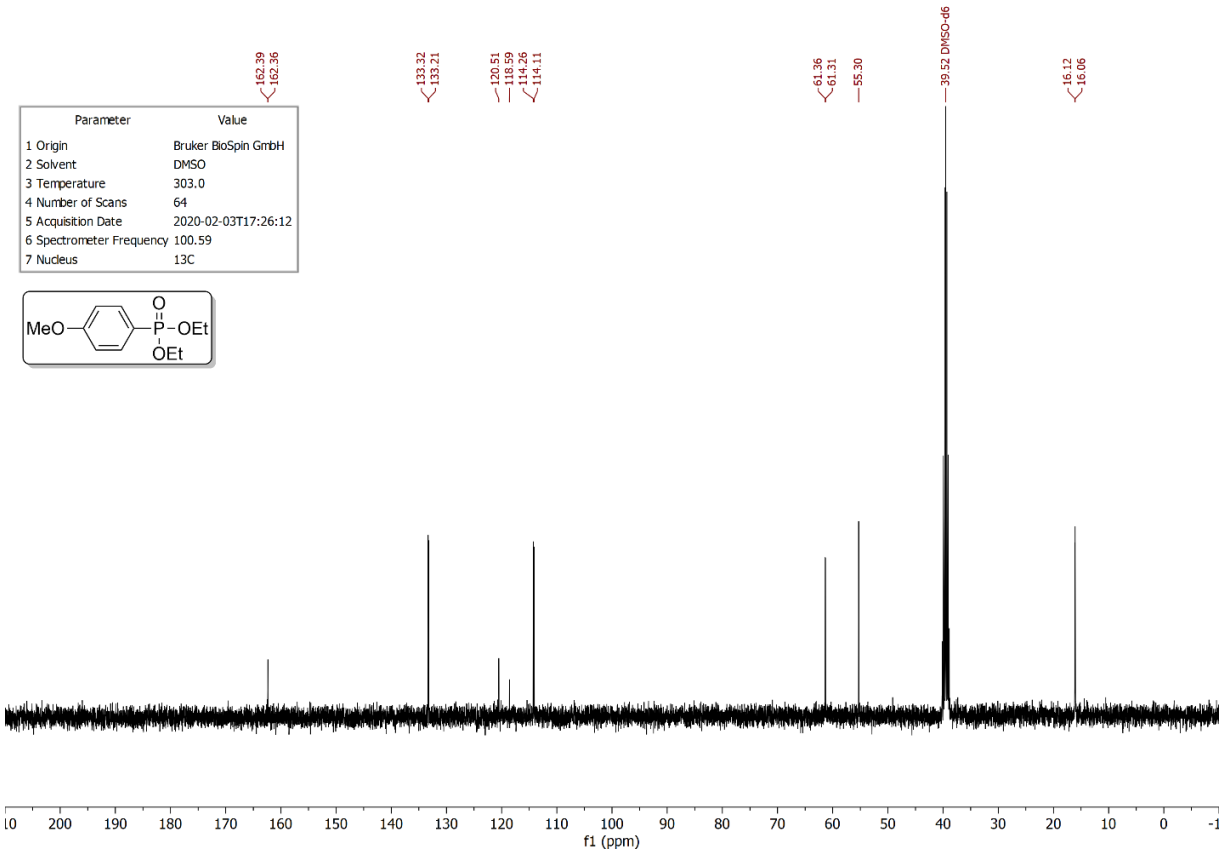


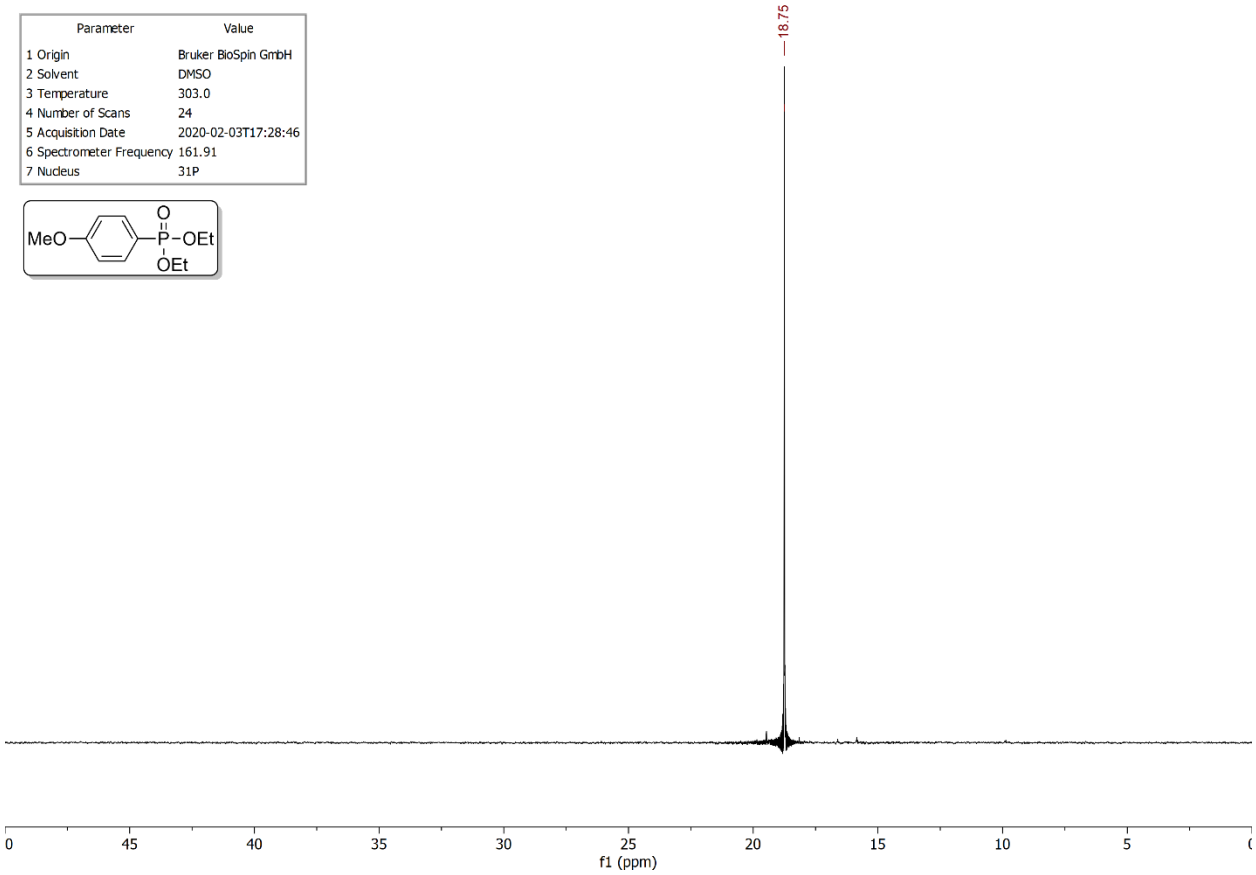

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 36
5 Spectrometer Frequency 100.59
6 Nucleus 13C
132.44
132.41
131.24
131.14
129.42
128.73
128.59
127.56
61.63
61.58
39.52 DMSO-d6
16.14
16.08
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
17.84
f1 (ppm)

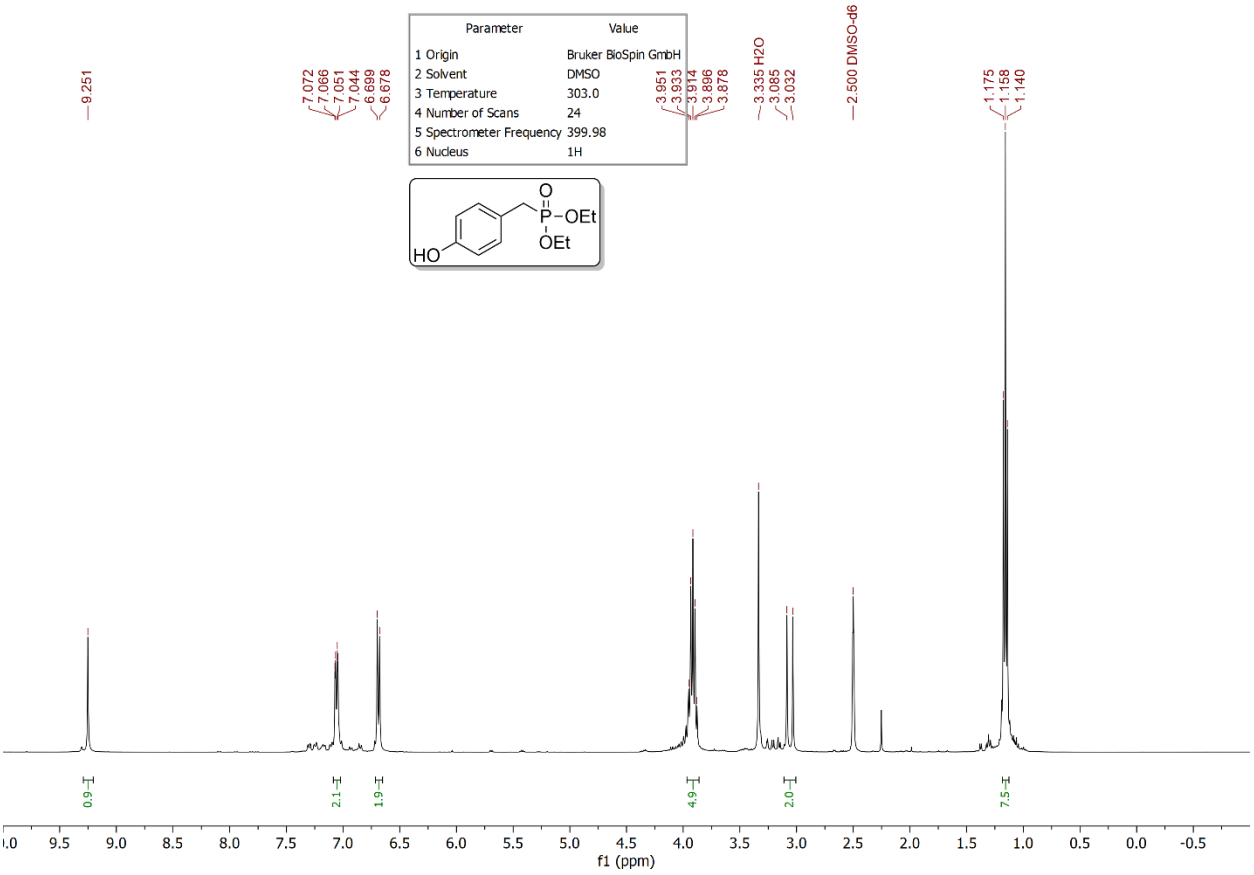
Diethyl (4-methoxyphenyl)phosphonate (**4h**)

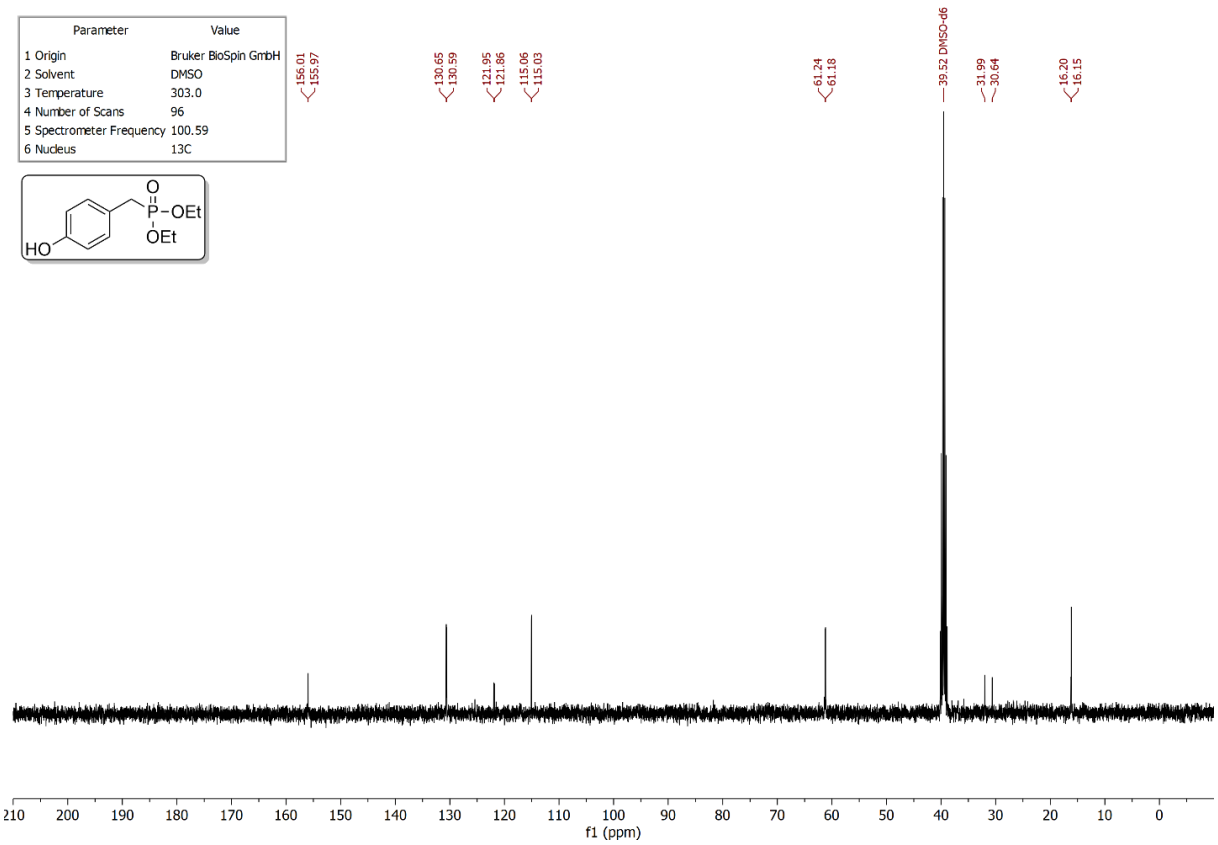


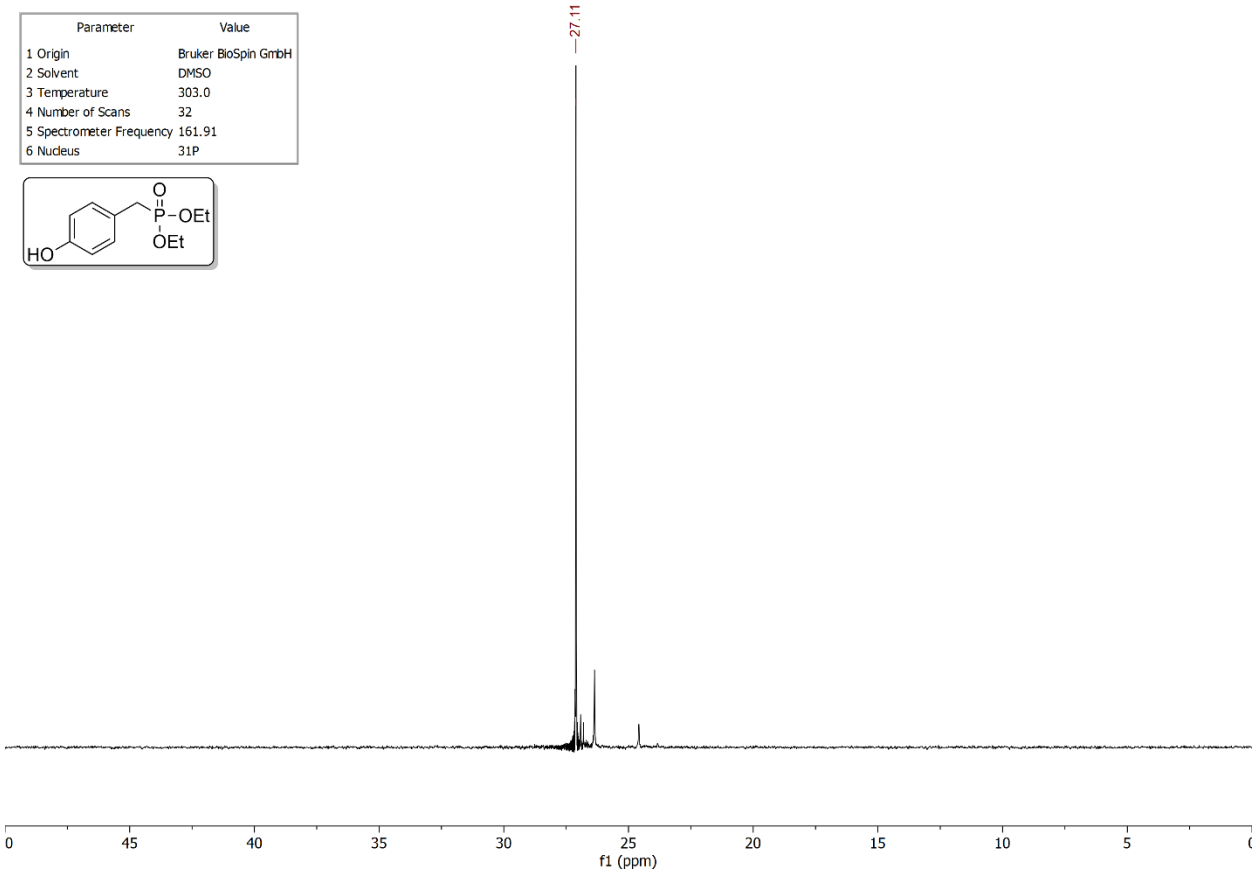

162.39
162.36
133.32
133.21
120.51
118.59
114.26
114.11
61.36
61.31
55.30
39.52 DMSO-d6
16.12
16.06
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 64
5 Acquisition Date 2020-02-03T17:26:12
6 Spectrometer Frequency 100.59
7 Nucleus 13C
MeO
O
P
OEt
OEt
f1 (ppm)


18.75
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 24
5 Acquisition Date 2020-02-03T17:28:46
6 Spectrometer Frequency 161.91
7 Nucleus 31P
MeO
O
P
OEt
OEt
f1 (ppm)

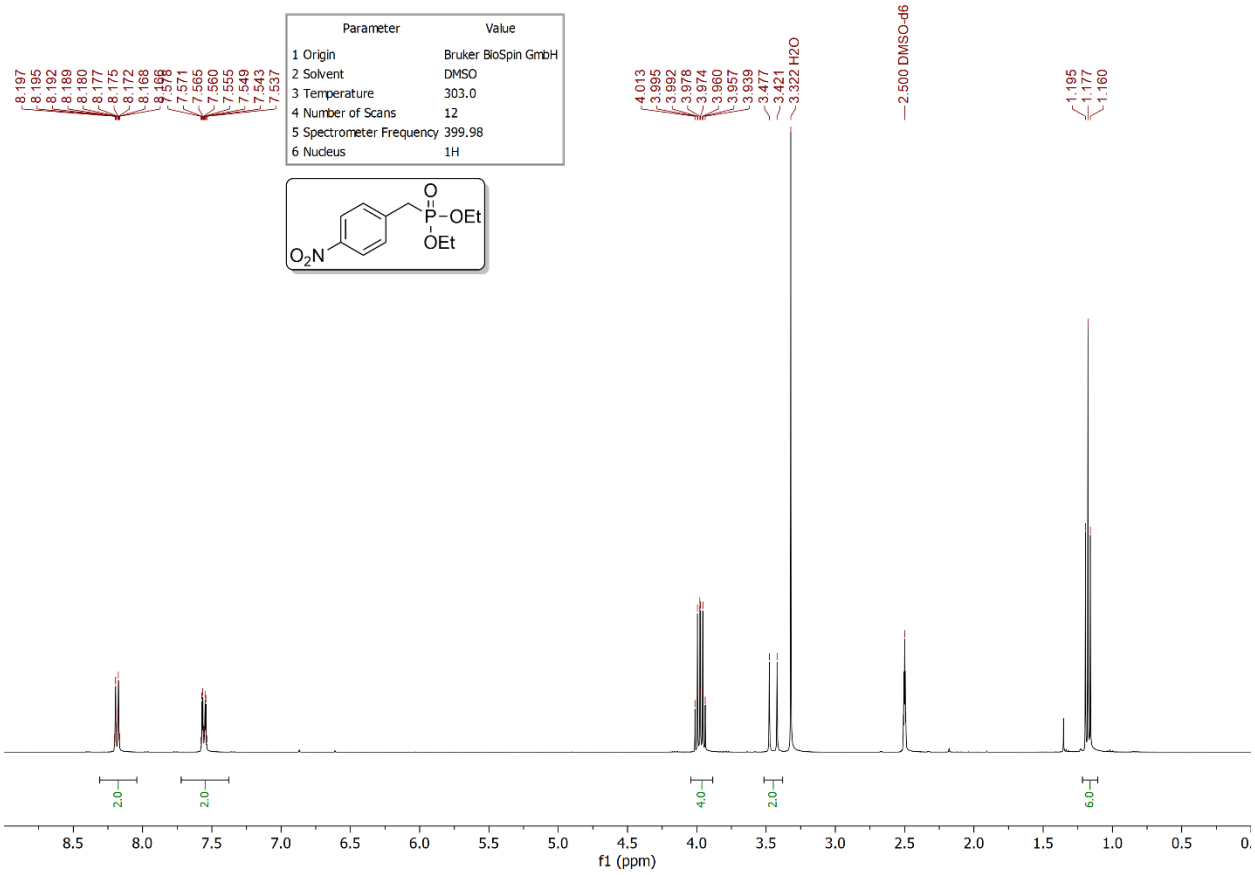
Diethyl [(4-hydroxyphenyl)methyl]phosphonate (**4i**)

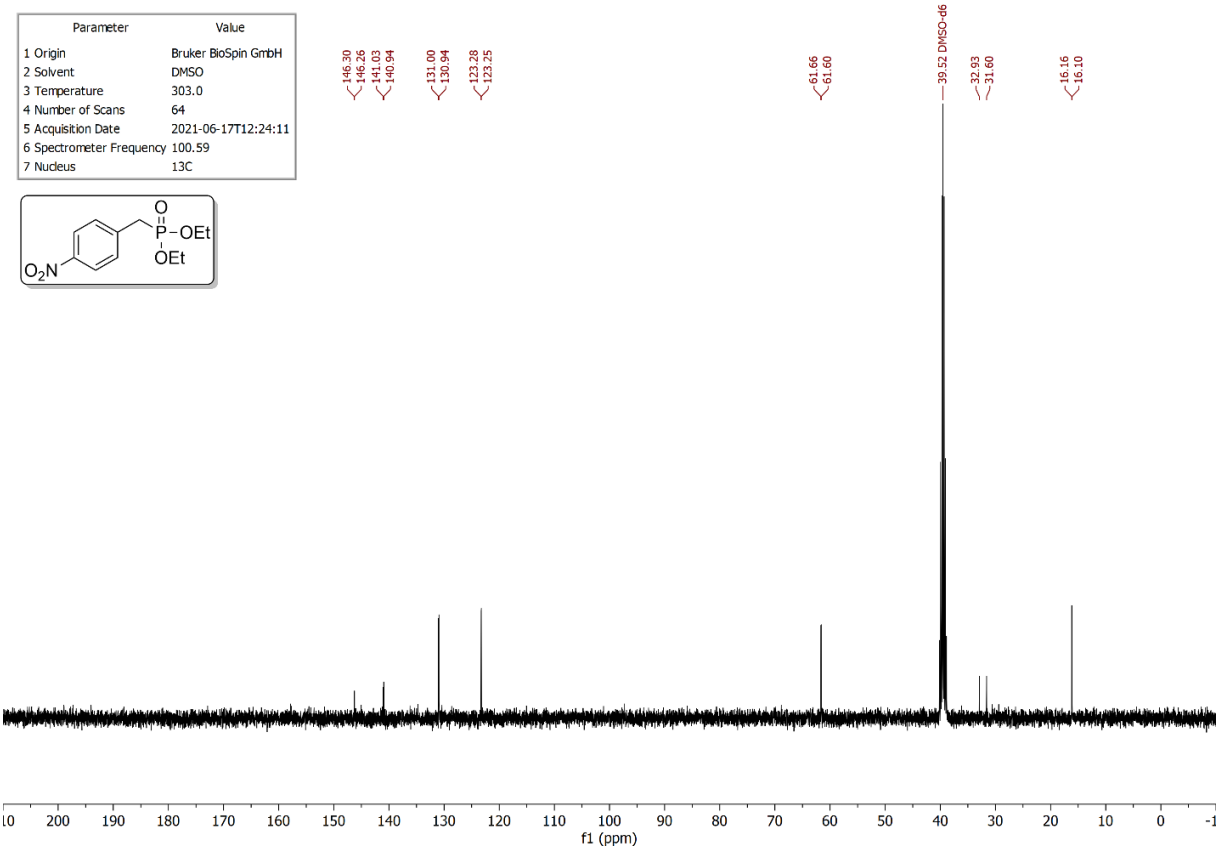


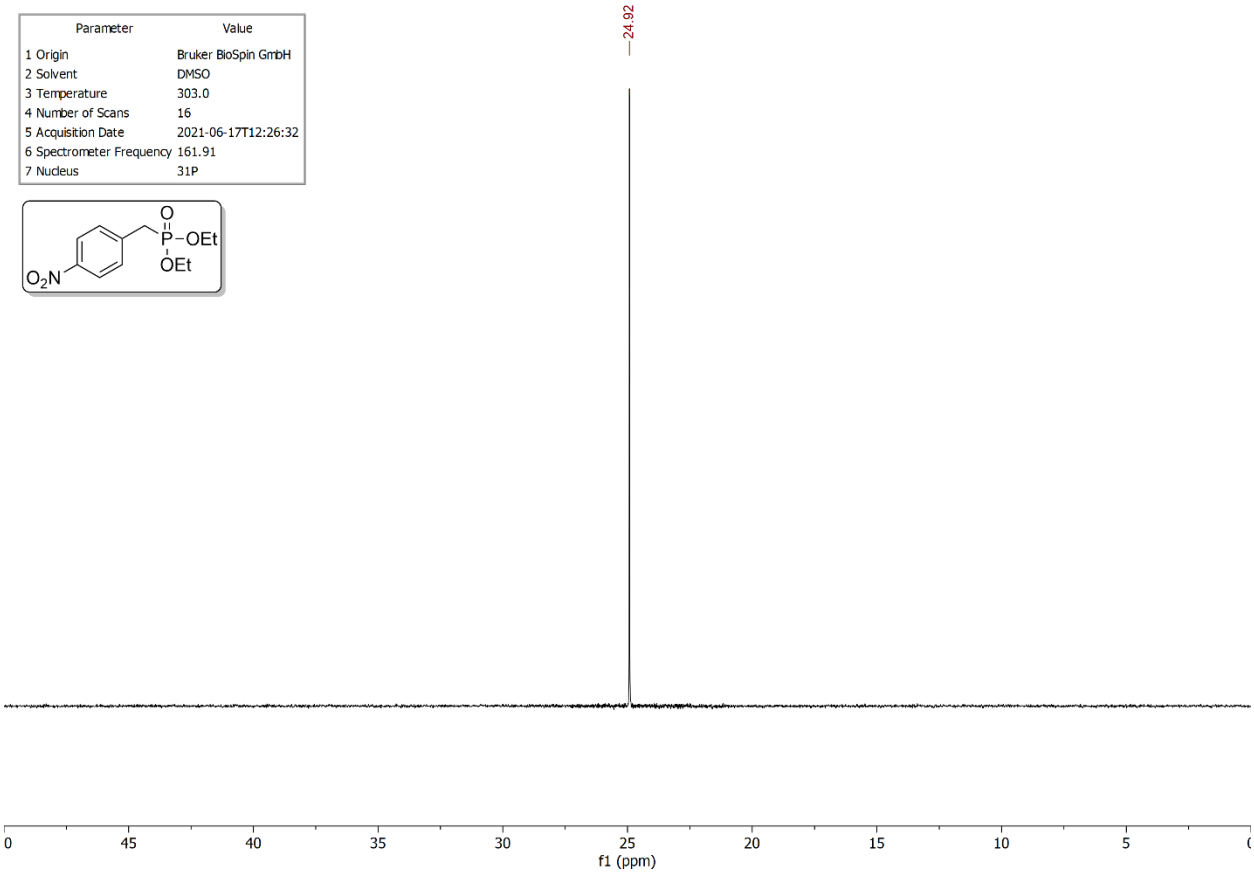

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 96
5 Spectrometer Frequency 100.59
6 Nucleus 13C
155.01
155.97
130.65
130.59
121.95
121.86
115.06
115.03
61.24
61.18
39.52 DMSO-d6
31.99
30.64
16.20
16.15
HO
O
P-OEt
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 32
5 Spectrometer Frequency 161.91
6 Nucleus 31P
27.11
HO
O
P-OEt
OEt
0 45 40 35 30 25 20 15 10 5
f1 (ppm)

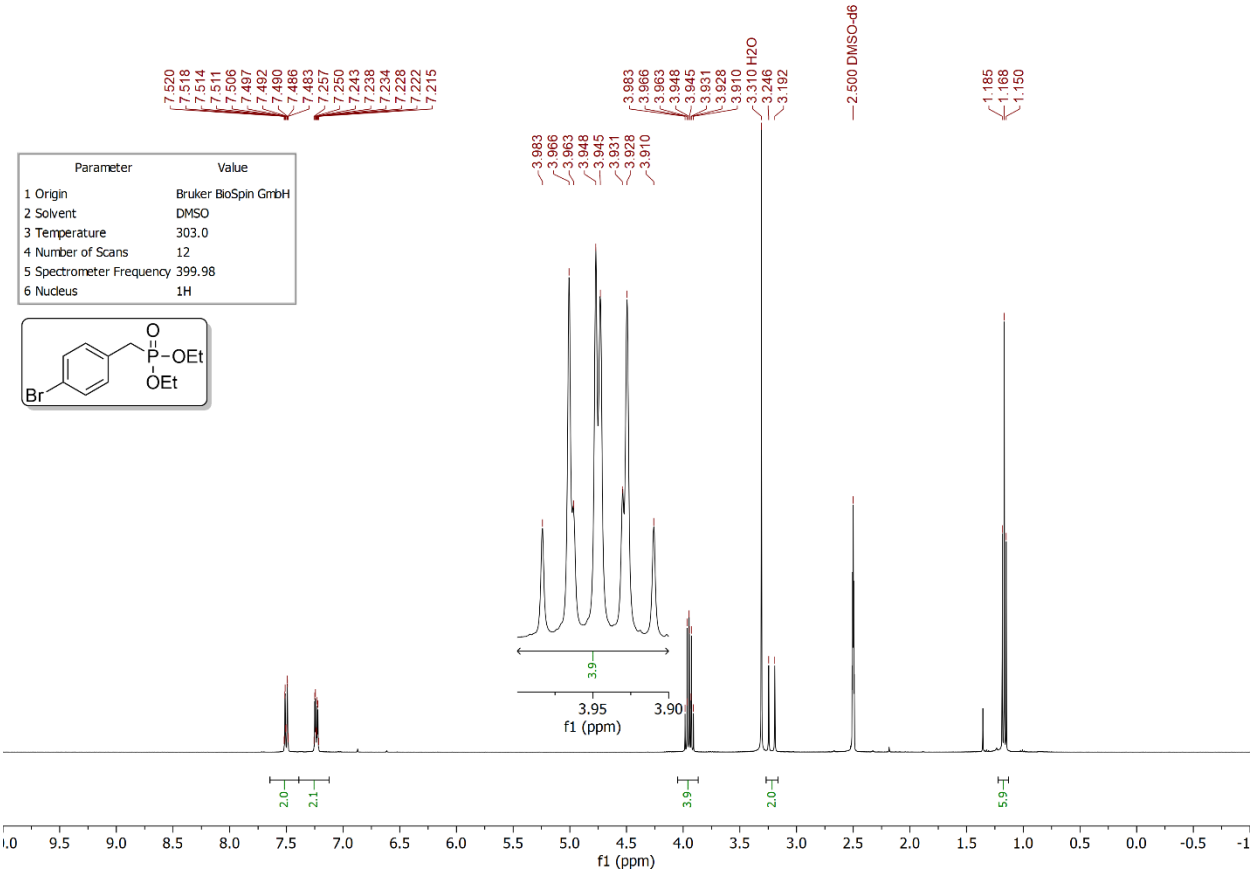
Diethyl [(4-nitrophenyl)methyl]phosphonate (**4j**)

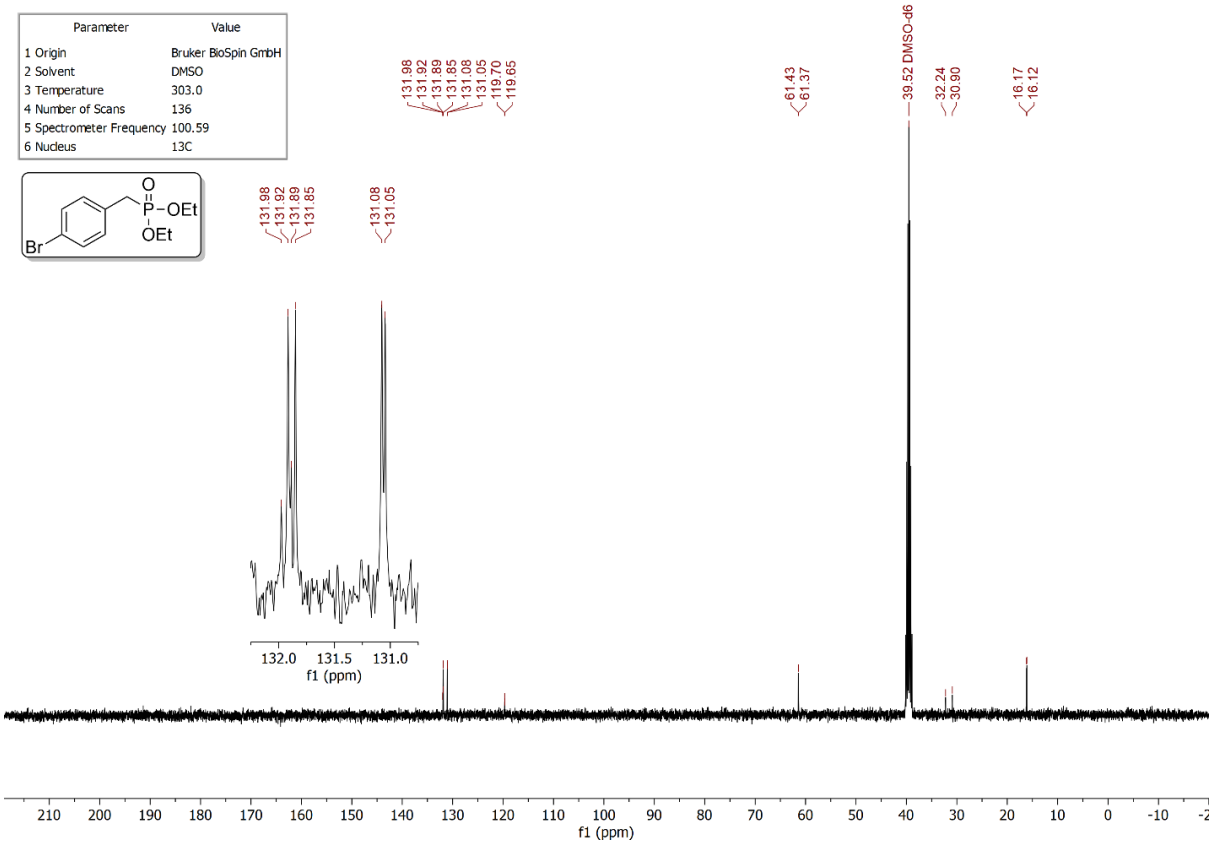


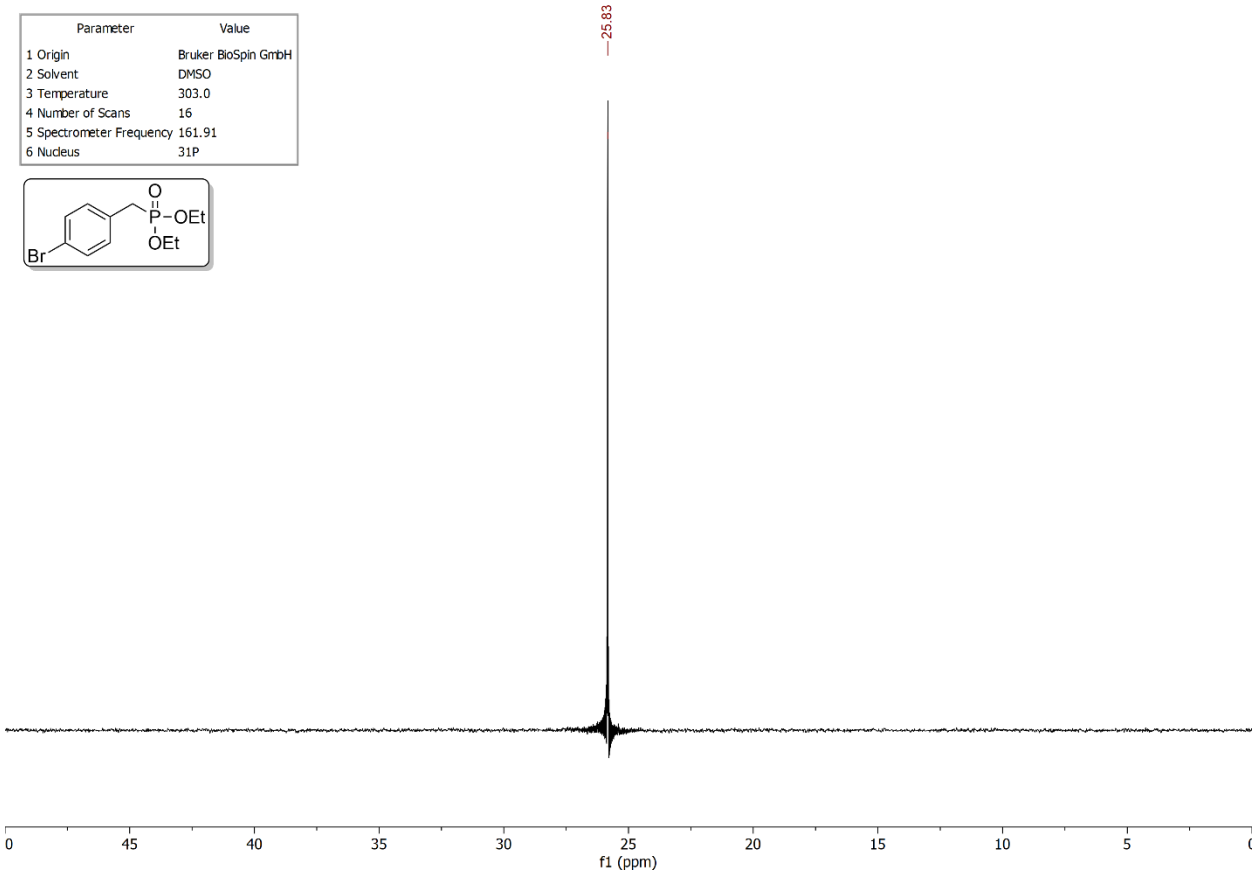

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 64
5 Acquisition Date 2021-06-17T12:24:11
6 Spectrometer Frequency 100.59
7 Nucleus 13C
146.30
146.26
141.03
140.94
131.00
130.94
123.28
123.25
61.66
61.60
39.52 DMSO-d6
32.93
31.60
16.16
16.10
O
P–OEt
OEt
O2N
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Acquisition Date 2021-06-17T12:26:32
6 Spectrometer Frequency 161.91
7 Nucleus 31P
24.92
O
P–OEt
OEt
O2N
f1 (ppm)

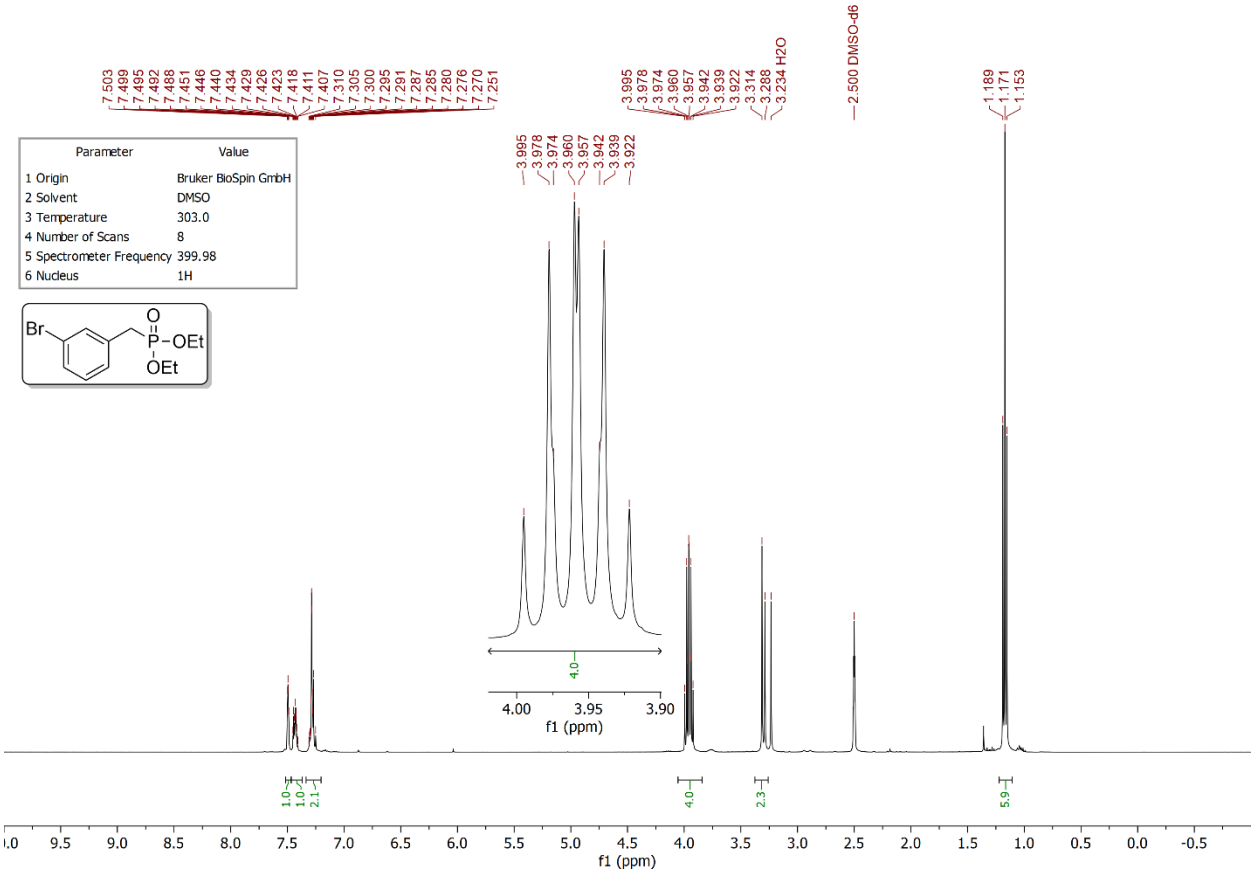
Diethyl [(4-bromophenyl)methyl]phosphonate (**4k**)

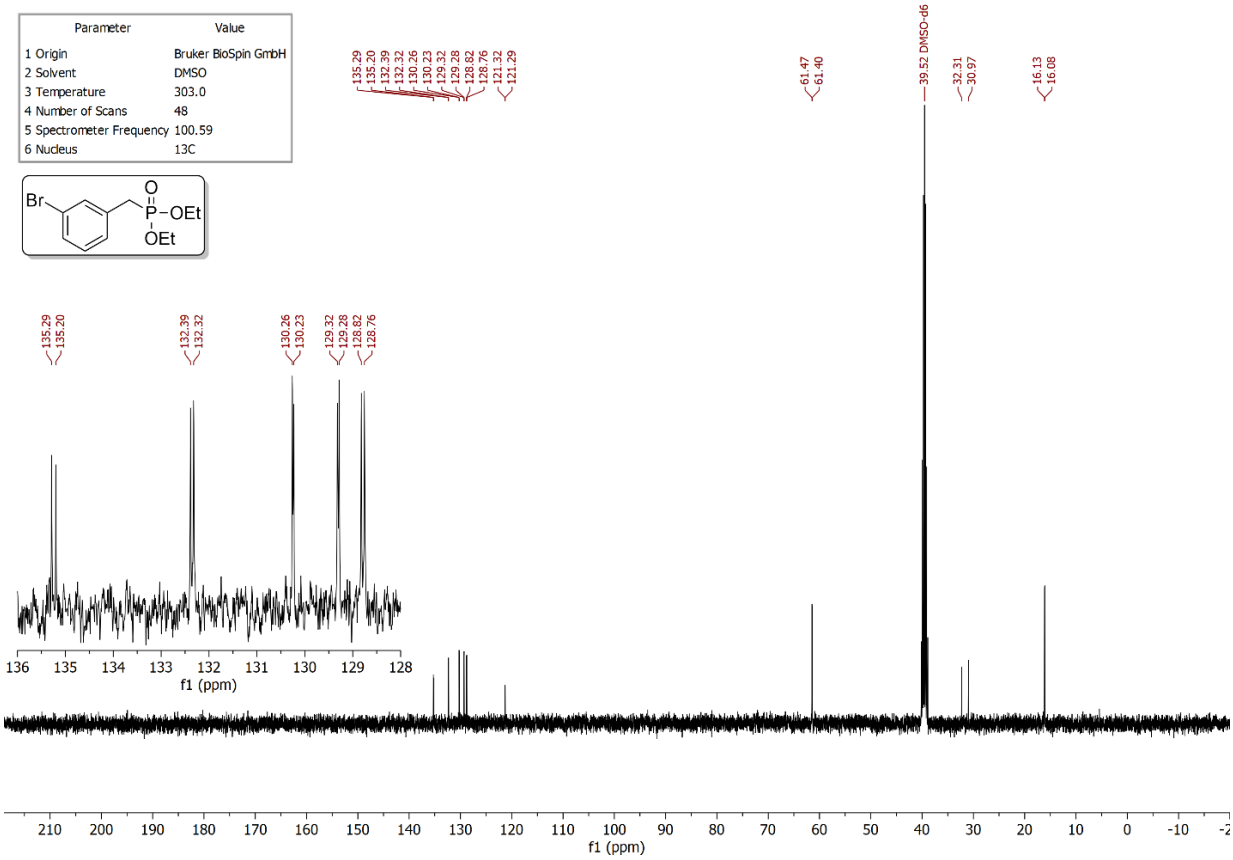


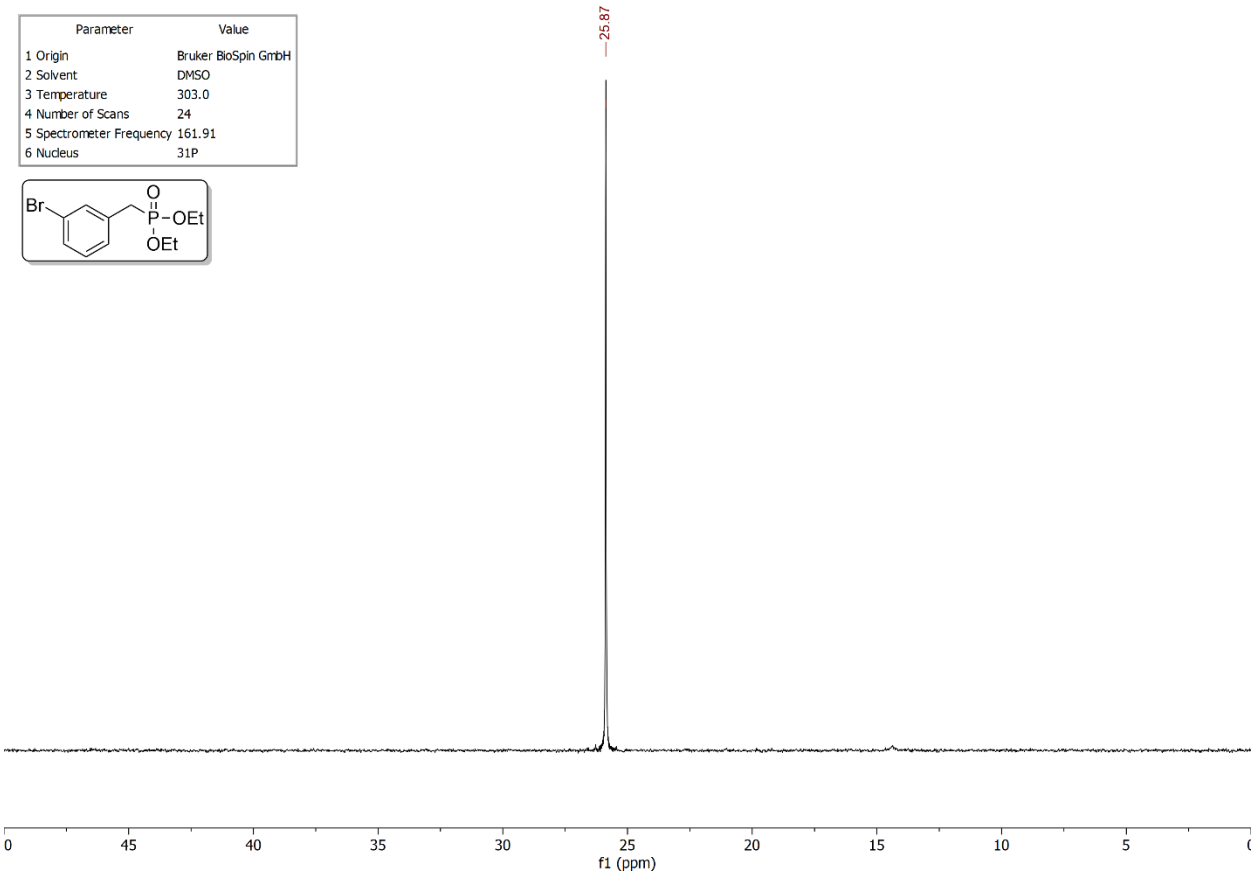

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 136
5 Spectrometer Frequency 100.59
6 Nucleus 13C
131.98
131.92
131.89
131.85
131.08
131.05
119.70
119.65
61.43
61.37
39.52 DMSO-d6
32.24
30.90
16.17
16.12
132.0 131.5 131.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 16
5 Spectrometer Frequency 161.91
6 Nucleus 31P
25.83
0 45 40 35 30 25 20 15 10 5
f1 (ppm)

Diethyl [(3-bromophenyl)methyl]phosphonate (**4l**)




Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 48
5 Spectrometer Frequency 100.59
6 Nucleus 13C
Br
O
P–OEt
OEt
135.29
135.20
132.39
132.32
130.26
130.23
129.32
129.28
128.82
128.76
121.32
121.29
61.47
61.40
39.52 DMSO-d6
32.31
30.97
16.13
16.08
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent DMSO
3 Temperature 303.0
4 Number of Scans 24
5 Spectrometer Frequency 161.91
6 Nucleus 31P
Br
O
P–OEt
OEt
25.87
f1 (ppm)