Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Domino Reaction Involving the Bestmann-Ohira Reagent and α,β-Unsaturated Aldehydes: Efficient Synthesis of Functionalized Pyrazoles

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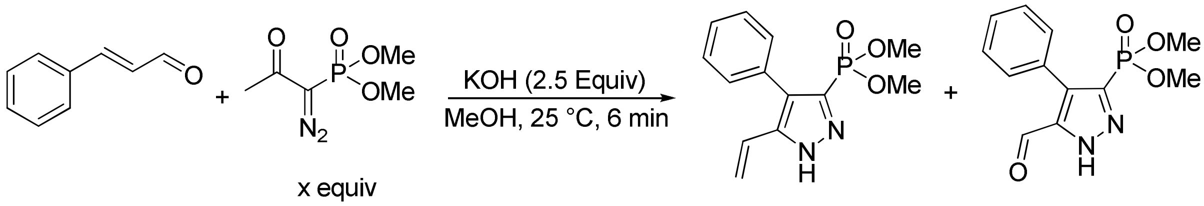
SUPPORTING INFORMATION

Content:

Optimization studies

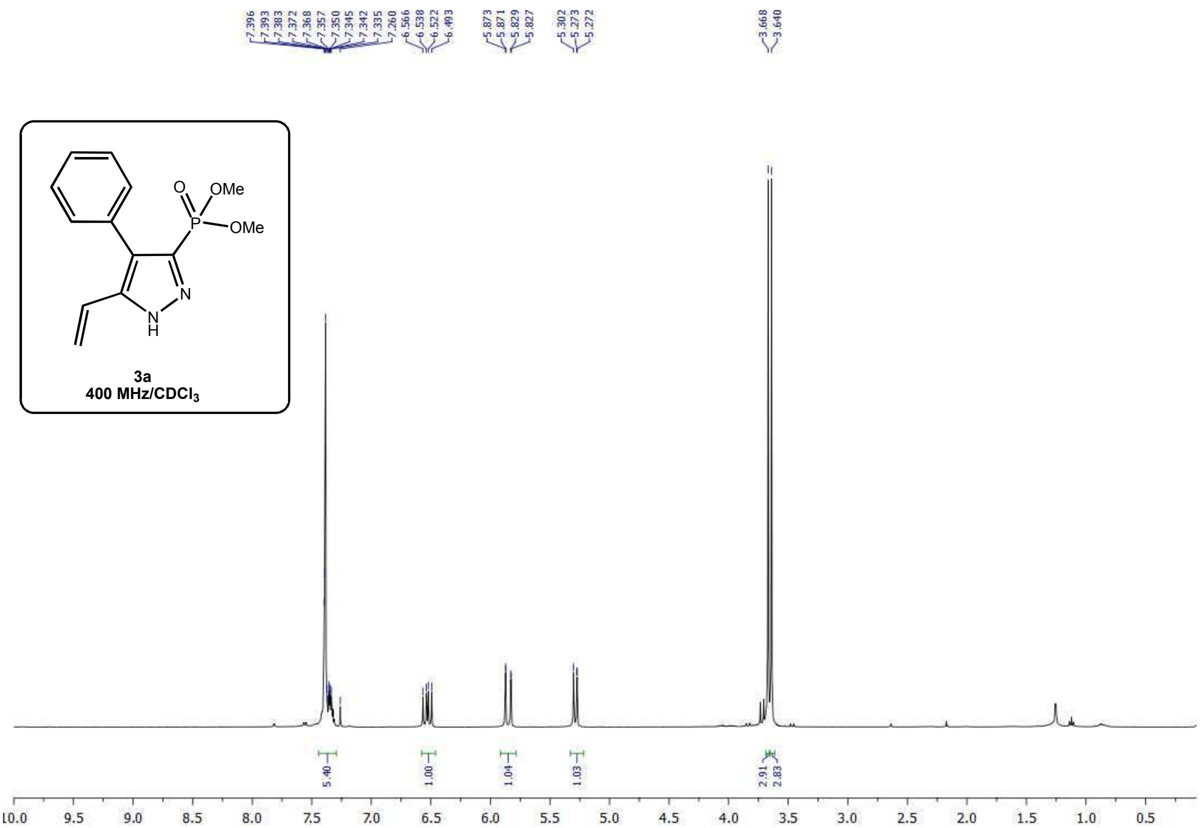
Our optimization studies commenced with the reaction of *trans*-cinnamaldehyde with 2.5 equiv of BOR in the presence of KOH. The reaction afforded the product in a reasonably good yield. A systematic optimization study using different bases revealed that KOH/MeOH system works best for the present reaction. In the next phase of our study, the stoichiometry of BOR was varied and interestingly, it was found that the reaction gets completed by the use of 2.5 equiv of BOR.

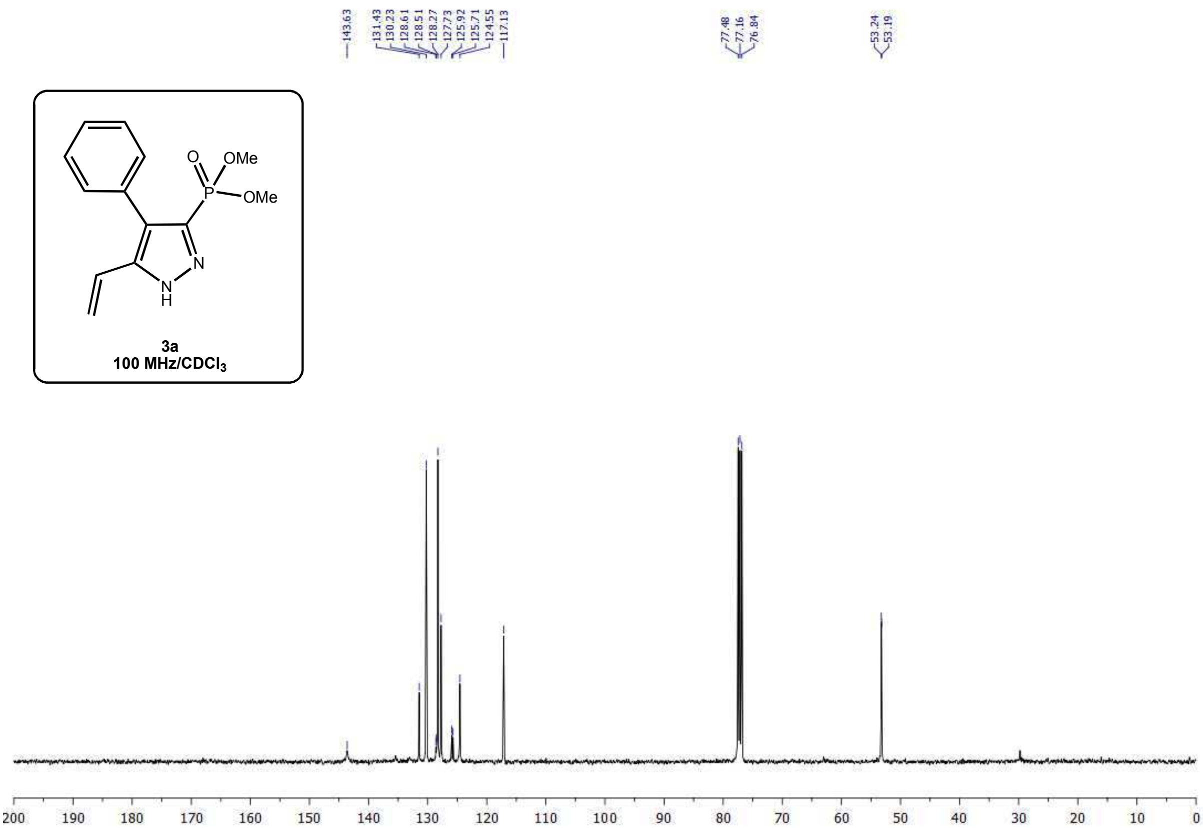
Table 1. Optimization with BOR

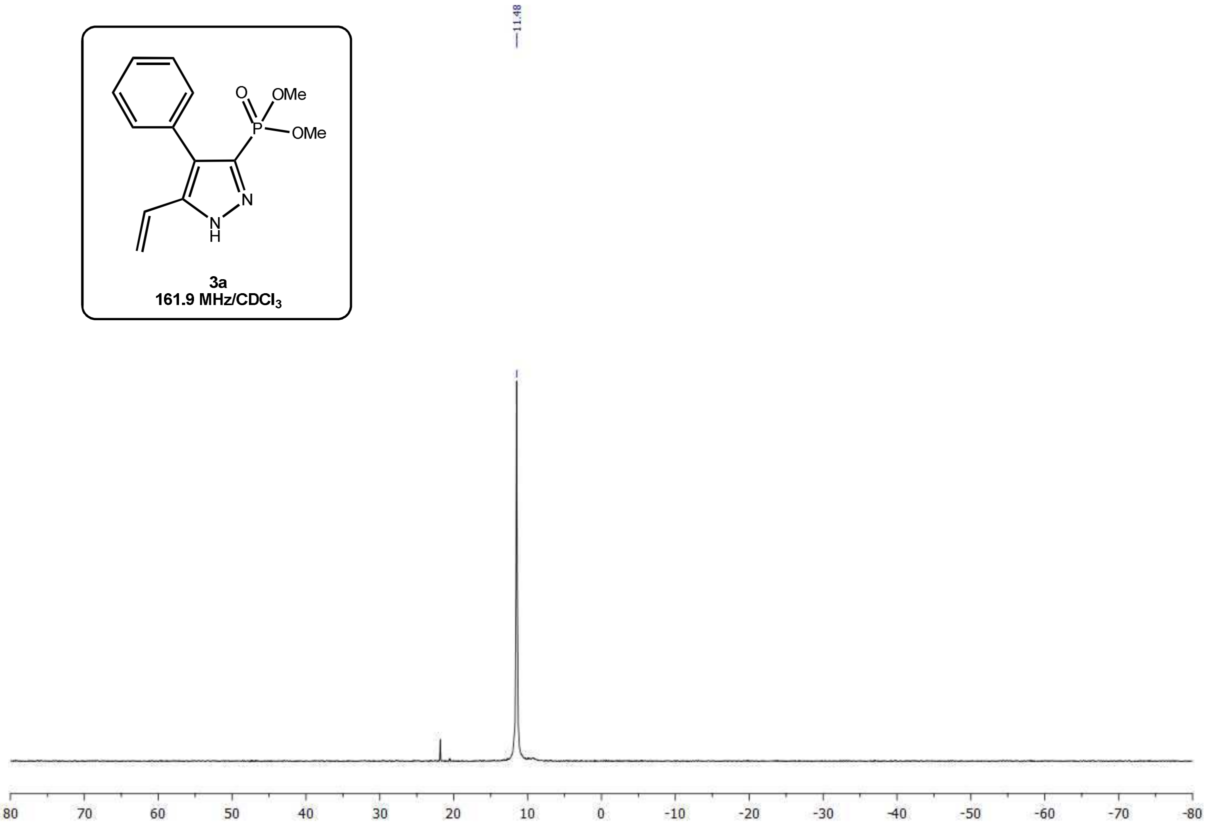


1a **2** **3a** **4**

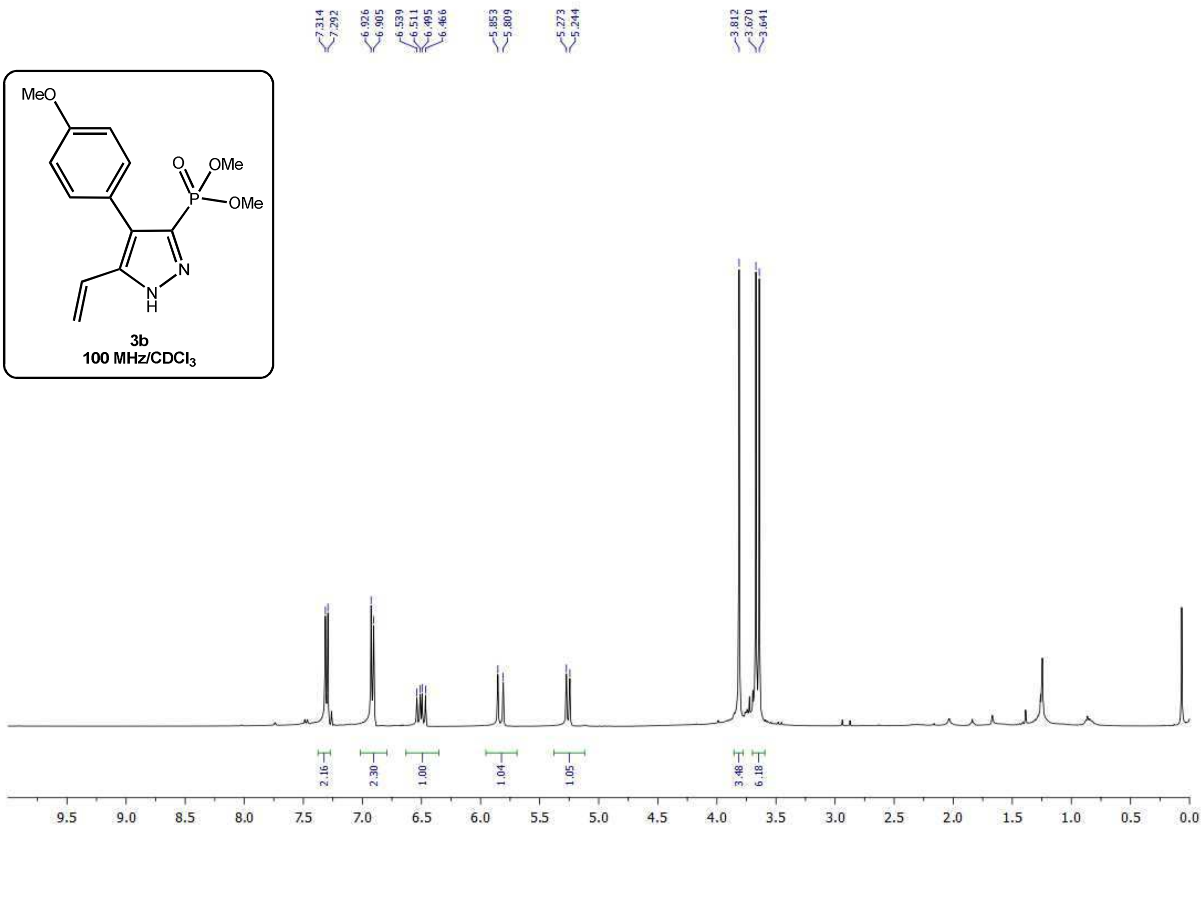
entry	BOR (equiv)	Base (equiv)	Yield (%) **3a**	**4**
1	1	2.5	33	16
2	1.5	2.5	51	21
3	2	2.5	60	10
4	2.5	2.5	69	trace
5	3	2.5	69	trace
6	3	3	69	trace


7.396
7.393
7.383
7.372
7.368
7.357
7.350
7.345
7.342
7.335
7.260
6.566
6.538
6.522
6.493
5.873
5.871
5.829
5.827
5.302
5.273
5.272
3.668
3.640
OMe
O
P
OMe
N
N
H
3a
400 MHz/CDCl3
5.40
1.00
1.04
1.03
2.91
2.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

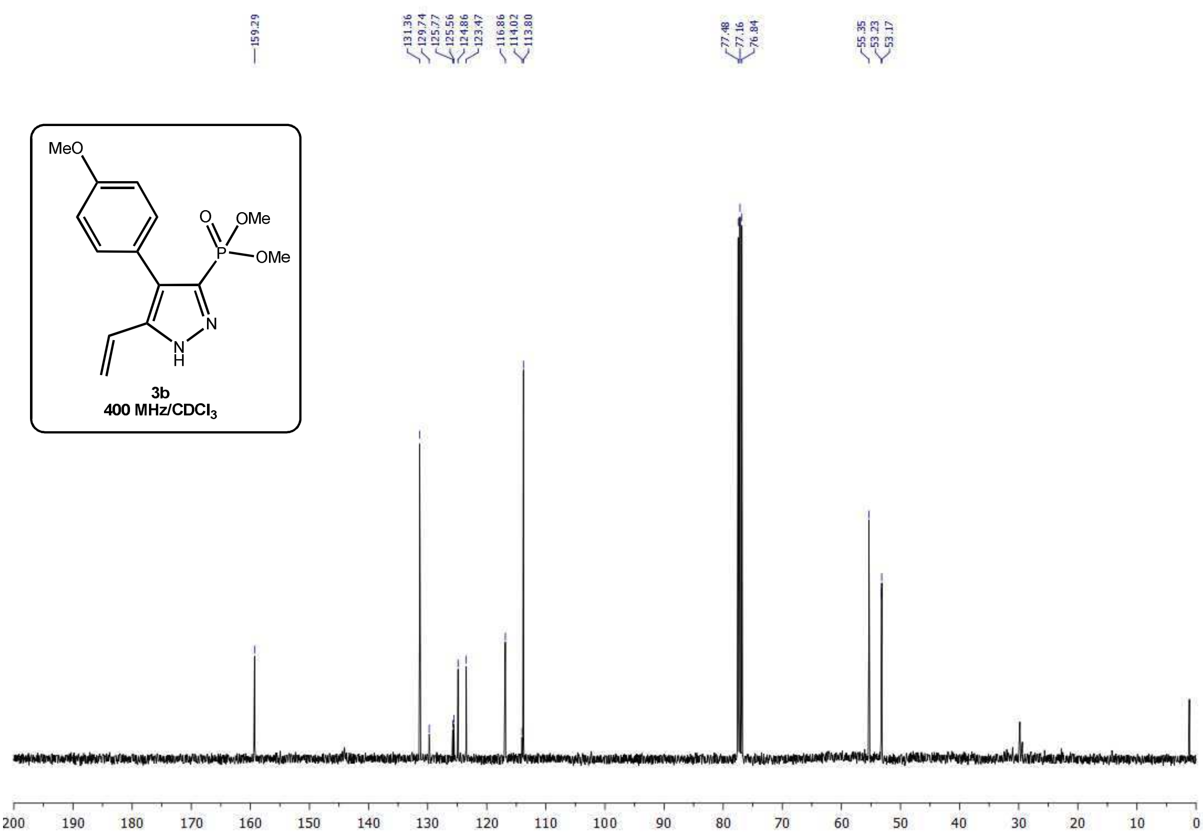

143.63
131.43
130.23
128.61
128.51
128.27
127.73
125.92
125.71
124.55
117.13
77.48
77.16
76.84
53.24
53.19
OMe
O
P
OMe
N
N
H
3a
100 MHz/CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

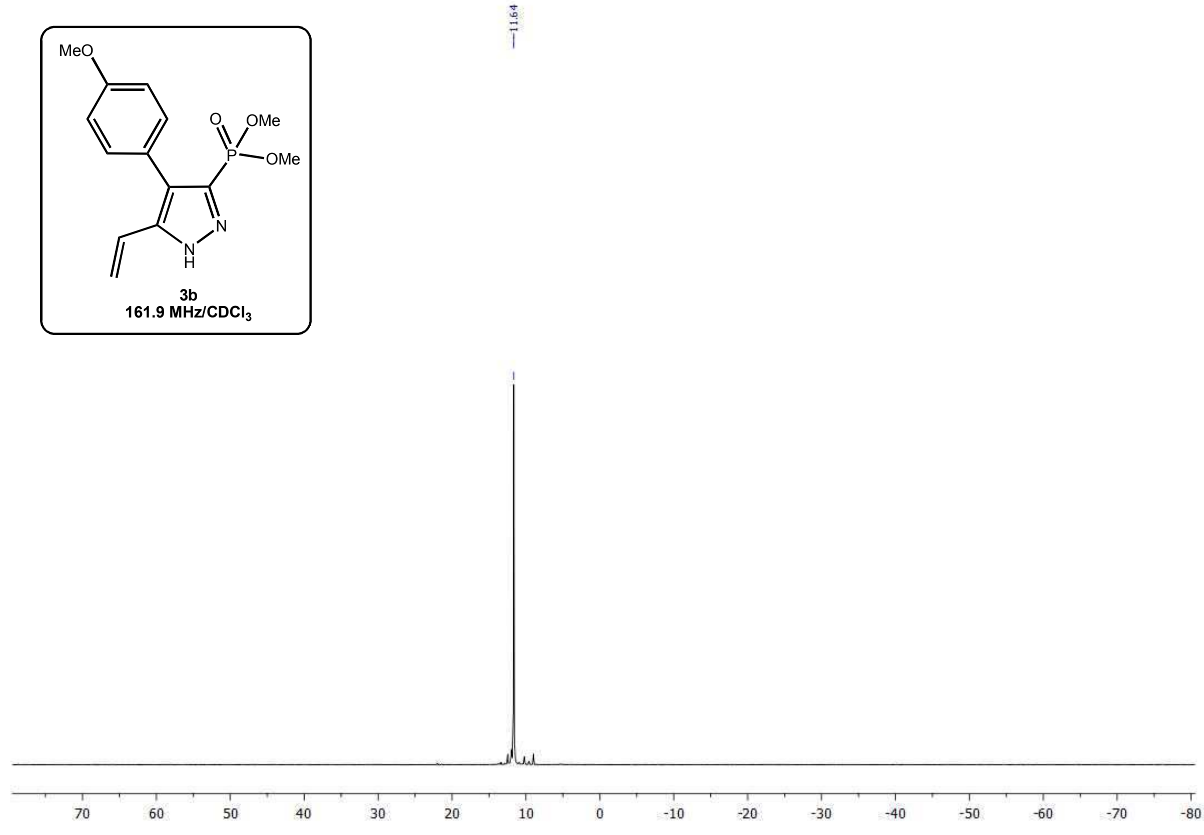


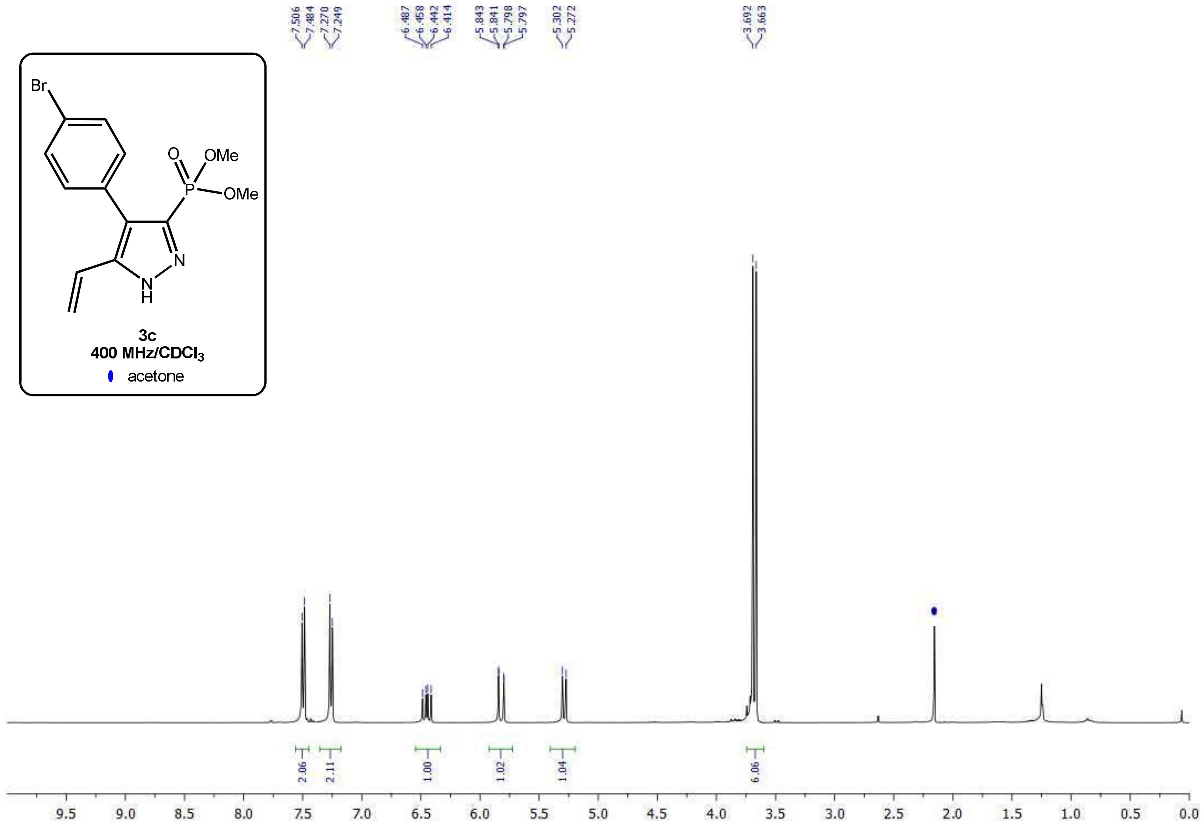
OMe
OMe
O
P
N
N
H
3a
161.9 MHz/CDCl3
11.48

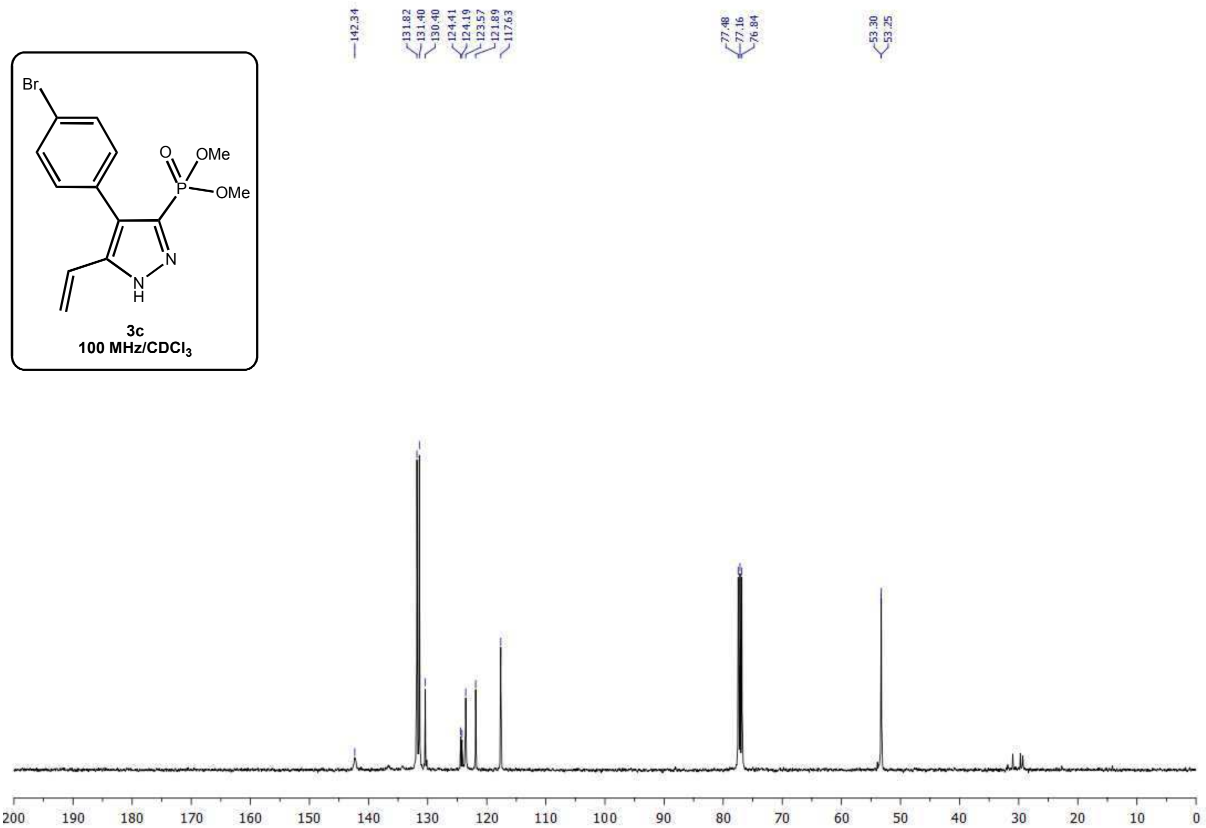


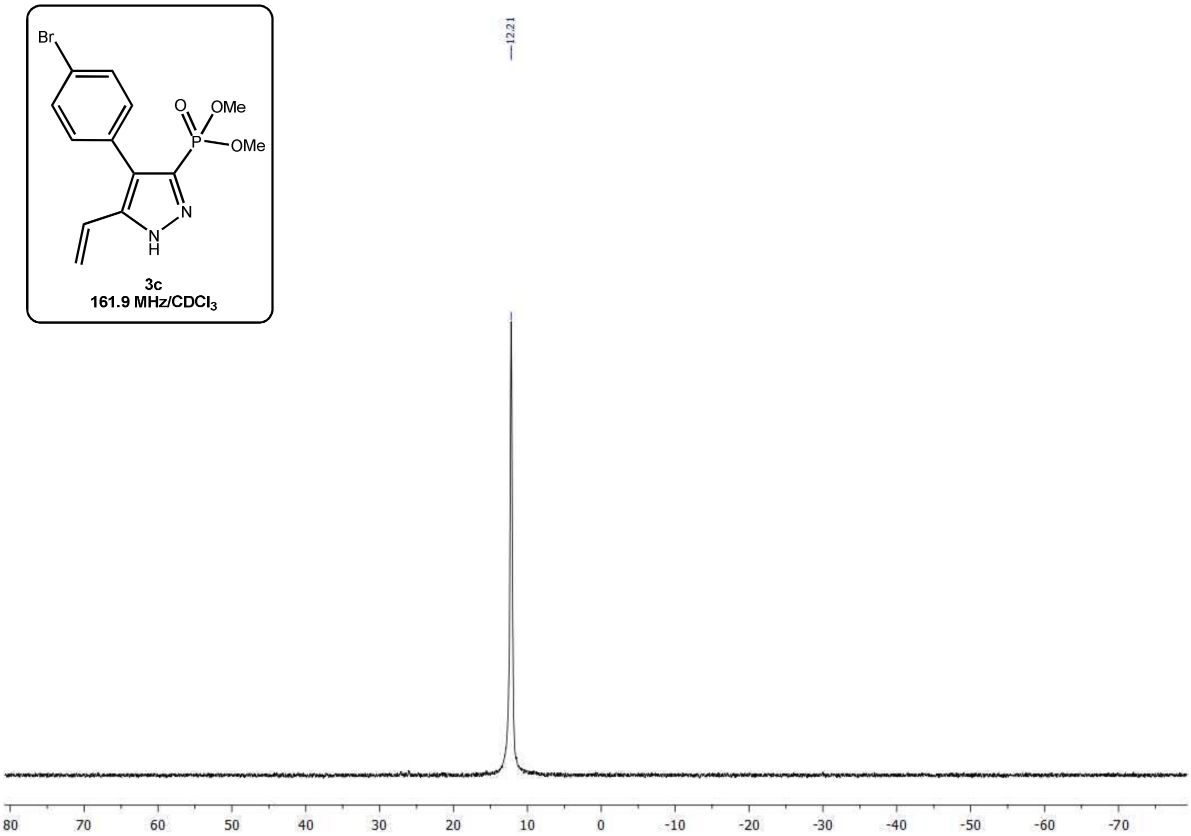
MeO
OMe
OMe
O
P
N
N
H
3b
100 MHz/CDCl3
7.314
7.292
6.926
6.905
6.539
6.511
6.495
6.466
5.853
5.809
5.273
5.244
3.812
3.670
3.641
2.16
2.30
1.00
1.04
1.05
3.48
6.18

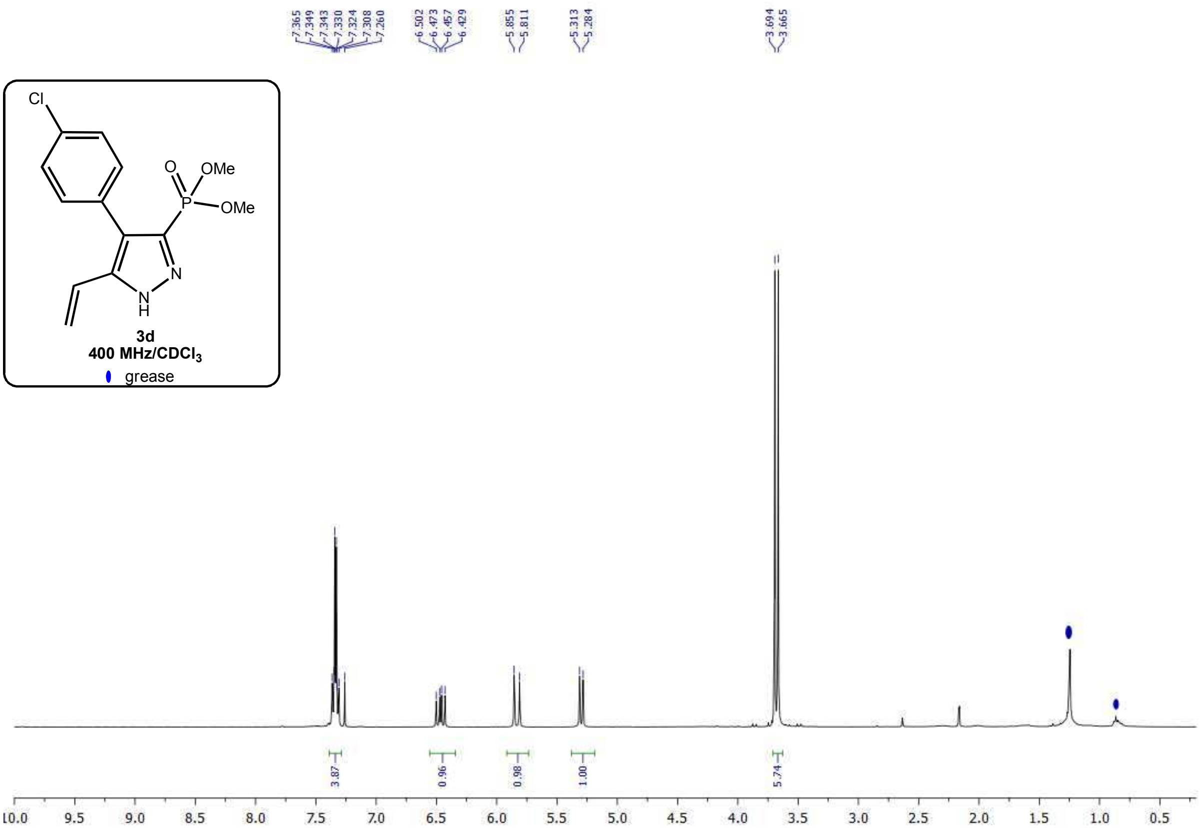

3b
400 MHz/CDCl3

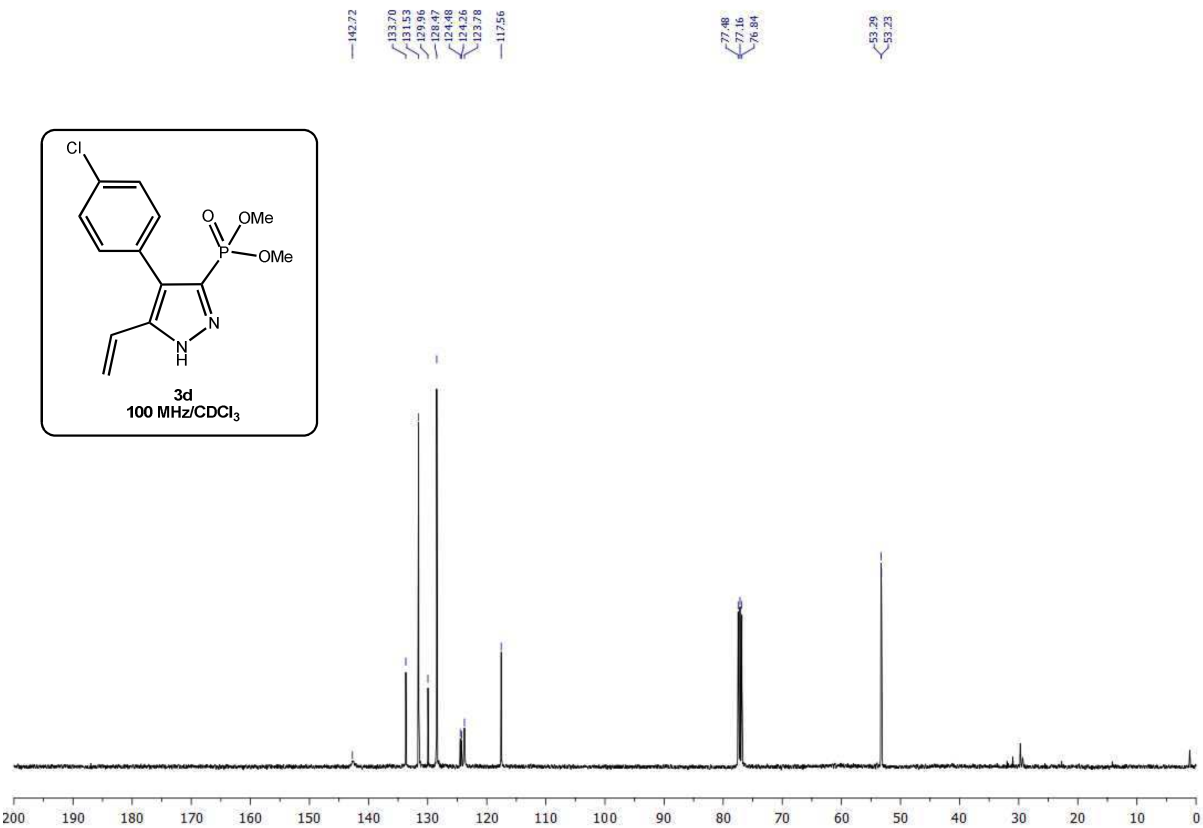

3b
161.9 MHz/CDCl3

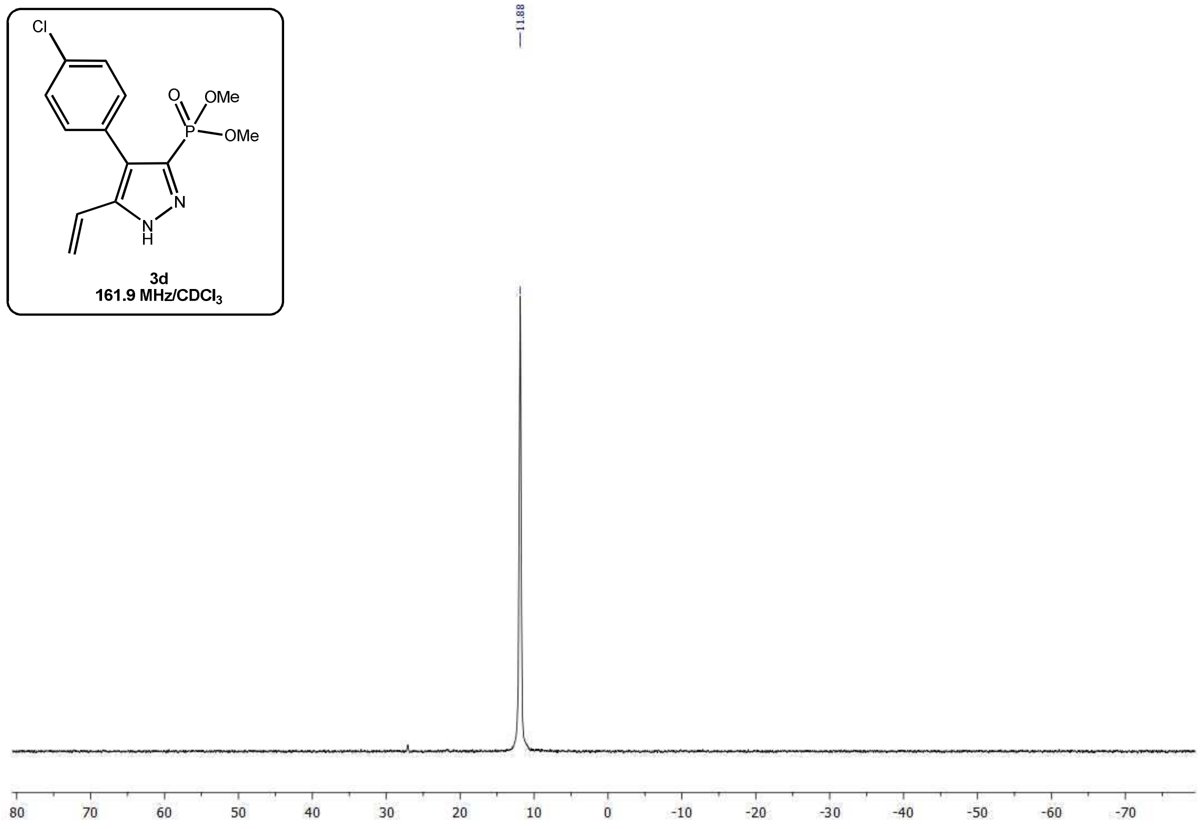

Br
OMe
O
P
OMe
N
N
H
3c
400 MHz/CDCl$_3$
acetone
7.506
7.484
7.270
7.249
6.487
6.458
6.442
6.414
5.843
5.841
5.798
5.797
5.302
5.272
3.692
3.663
2.06
2.11
1.00
1.02
1.04
6.06

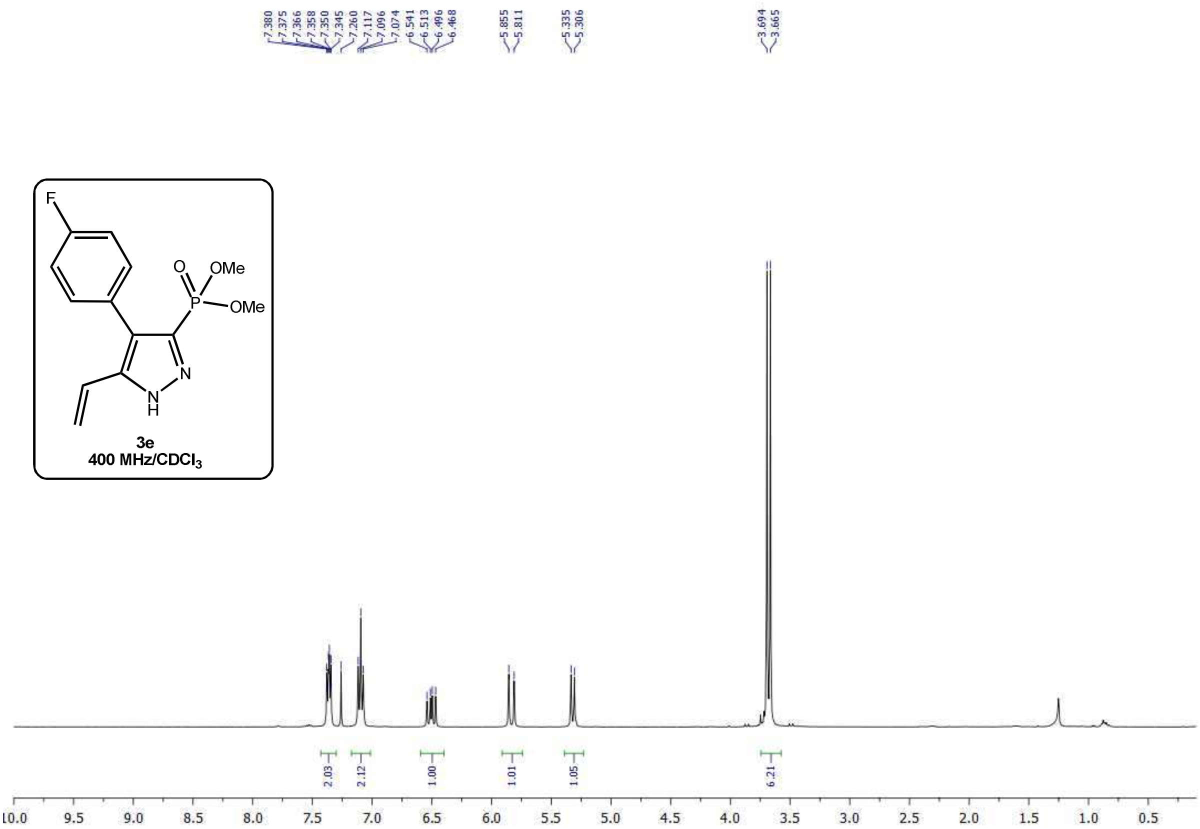

Br
OMe
O
P
OMe
N
N
H
3c
100 MHz/CDCl$_3$
142.34
131.82
131.40
130.40
124.41
124.19
123.57
121.89
117.63
77.48
77.16
76.84
53.30
53.25


12.21
Br
O
OMe
P
OMe
N
N
H
3c
161.9 MHz/CDCl3
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70

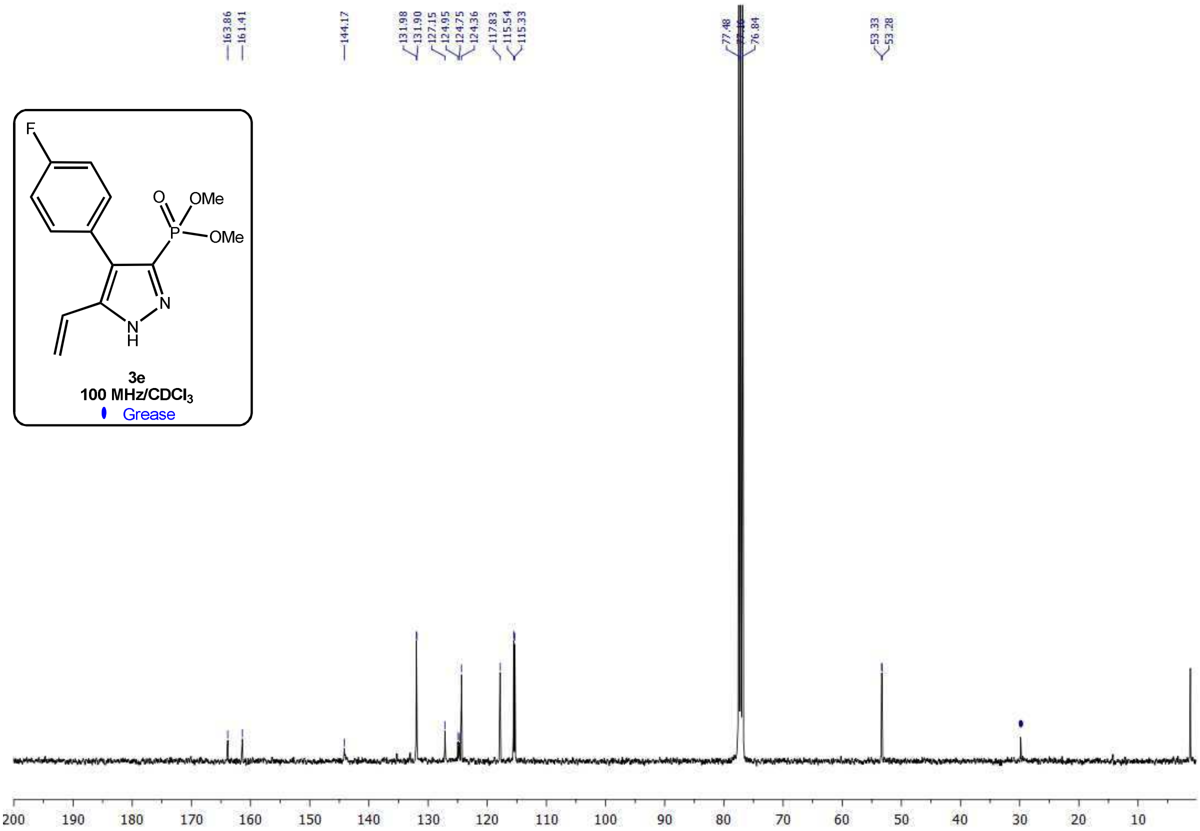

7.365
7.349
7.343
7.330
7.324
7.308
7.260
6.502
6.473
6.457
6.429
5.855
5.811
5.313
5.284
3.694
3.665
Cl
O
OMe
P
OMe
N
N
H
3d
400 MHz/CDCl3
grease
3.87
0.96
0.98
1.00
5.74
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


142.72
133.70
131.53
129.96
128.47
124.48
124.26
123.78
117.56
77.48
77.16
76.84
53.29
53.23
Cl
O
OMe
P
OMe
N
N
H
3d
100 MHz/CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


11.88
Cl
O
OMe
P
OMe
N
N
H
3d
161.9 MHz/CDCl3
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70



7.380
7.375
7.366
7.358
7.350
7.345
7.260
7.117
7.096
7.074
6.541
6.513
6.496
6.468
5.855
5.811
5.335
5.306
3.694
3.665
F
O
OMe
P
OMe
N
N
H
3e
400 MHz/CDCl3
2.03
2.12
1.00
1.01
1.05
6.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



163.86
161.41
144.17
131.98
131.90
127.15
124.95
124.75
124.36
117.83
115.54
115.33
77.48
76.84
53.33
53.28
F
O
OMe
P
OMe
N
N
H
3e
100 MHz/CDCl3
Grease
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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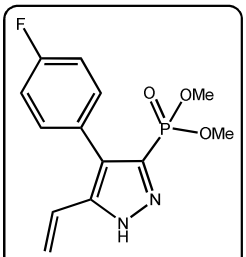
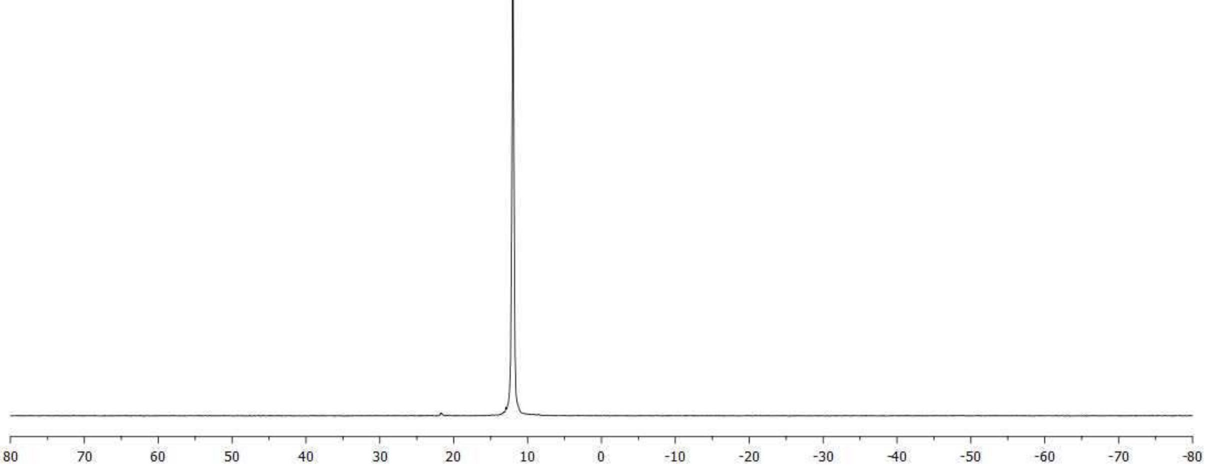
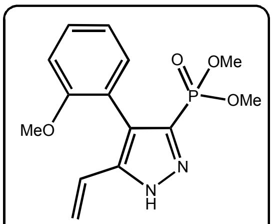
50
40
30
20
10

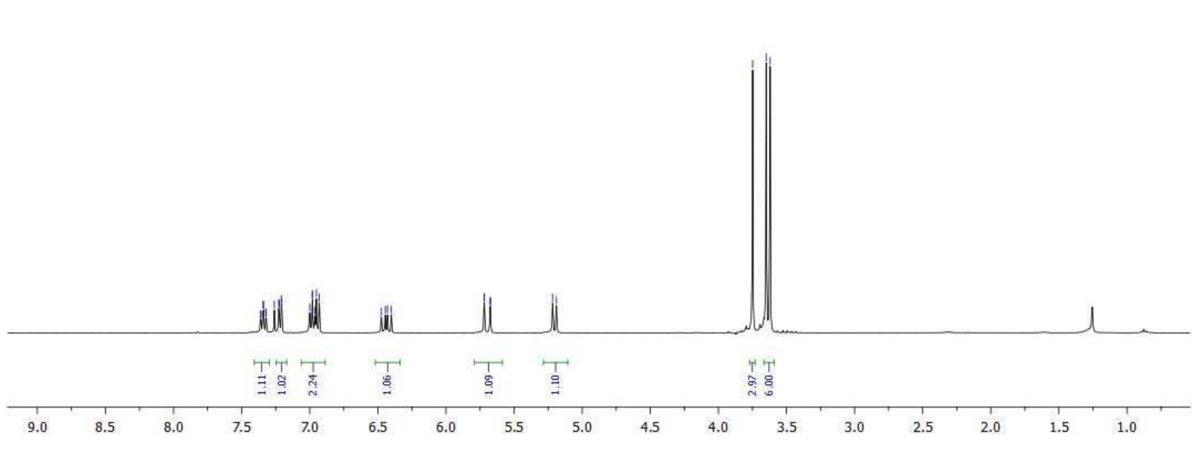


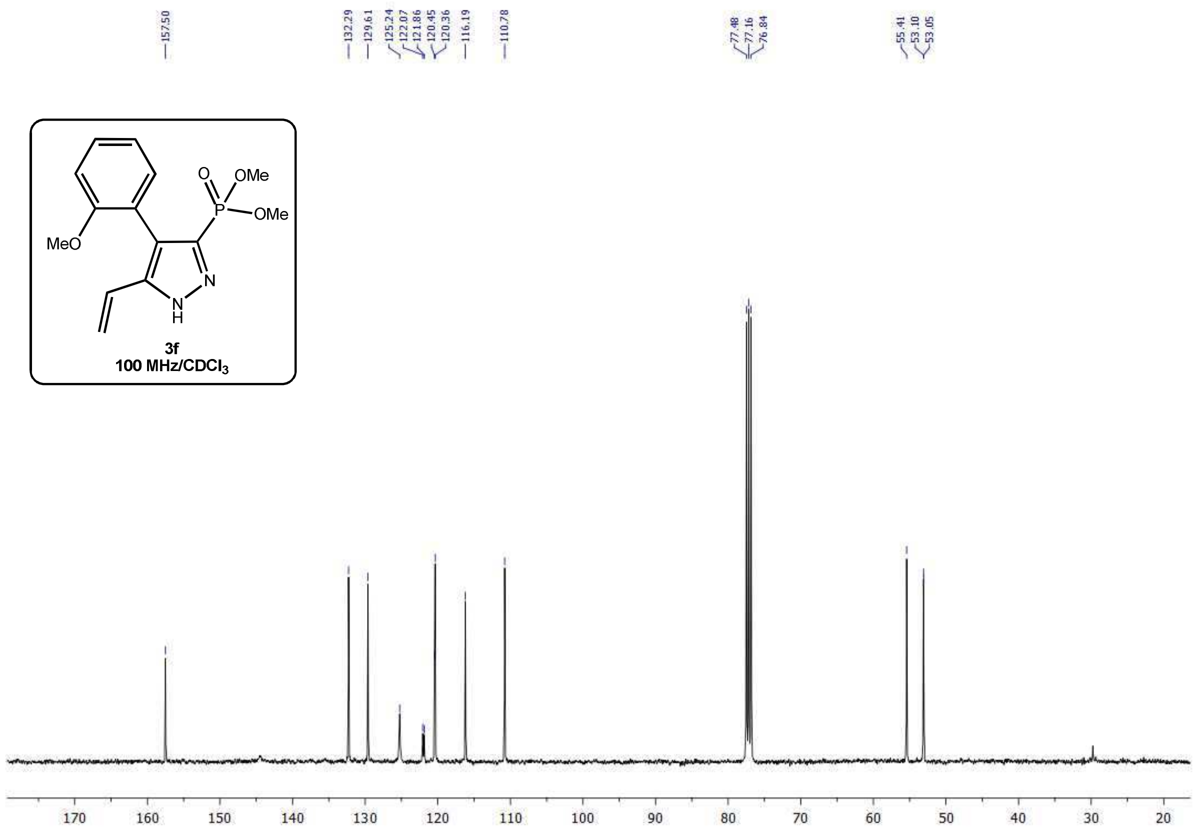
3e
161.9 MHz/$CDCl_3$



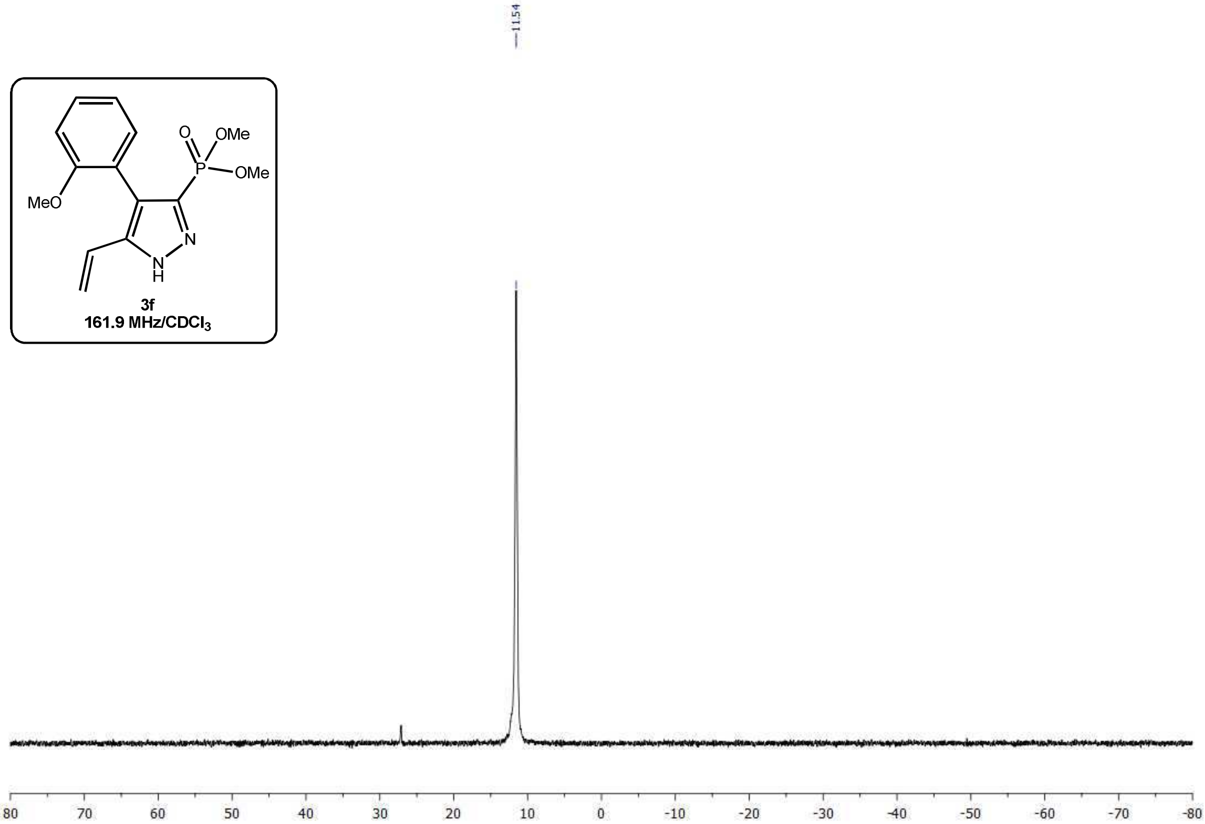


3f
400 MHz/$CDCl_3$

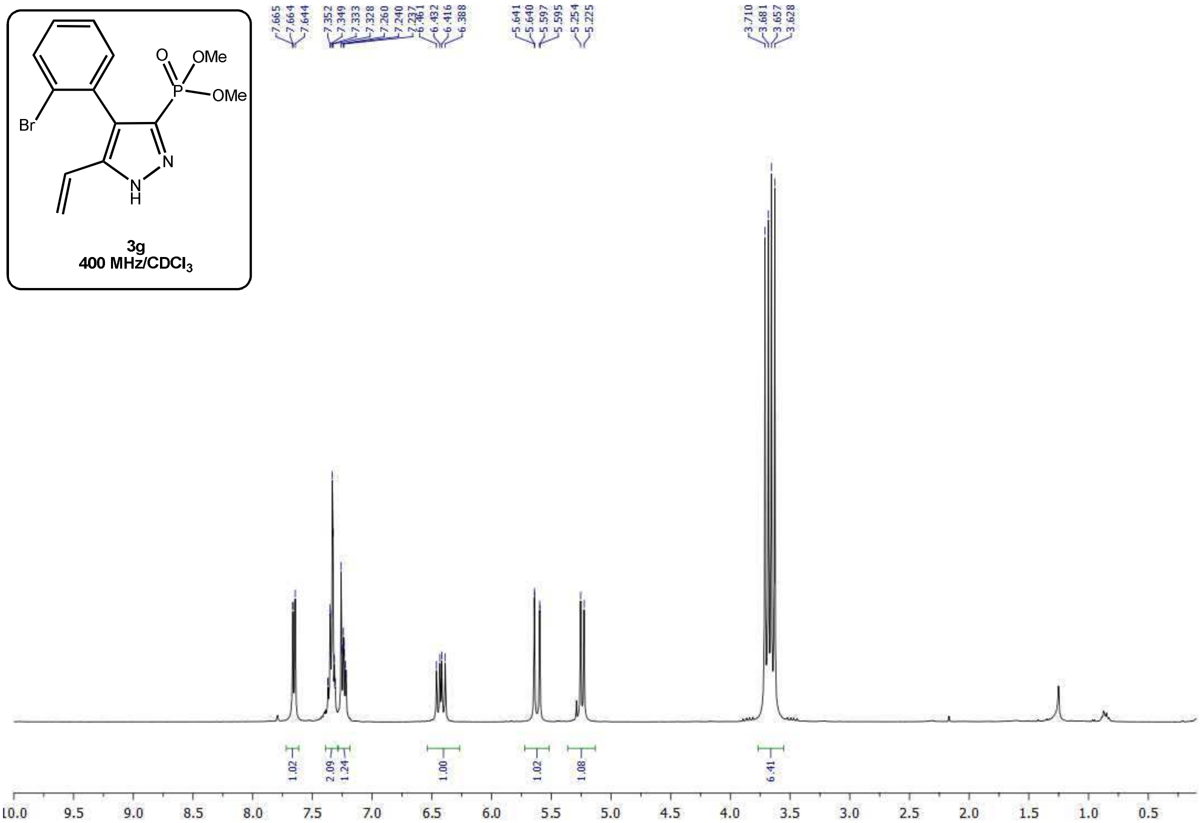




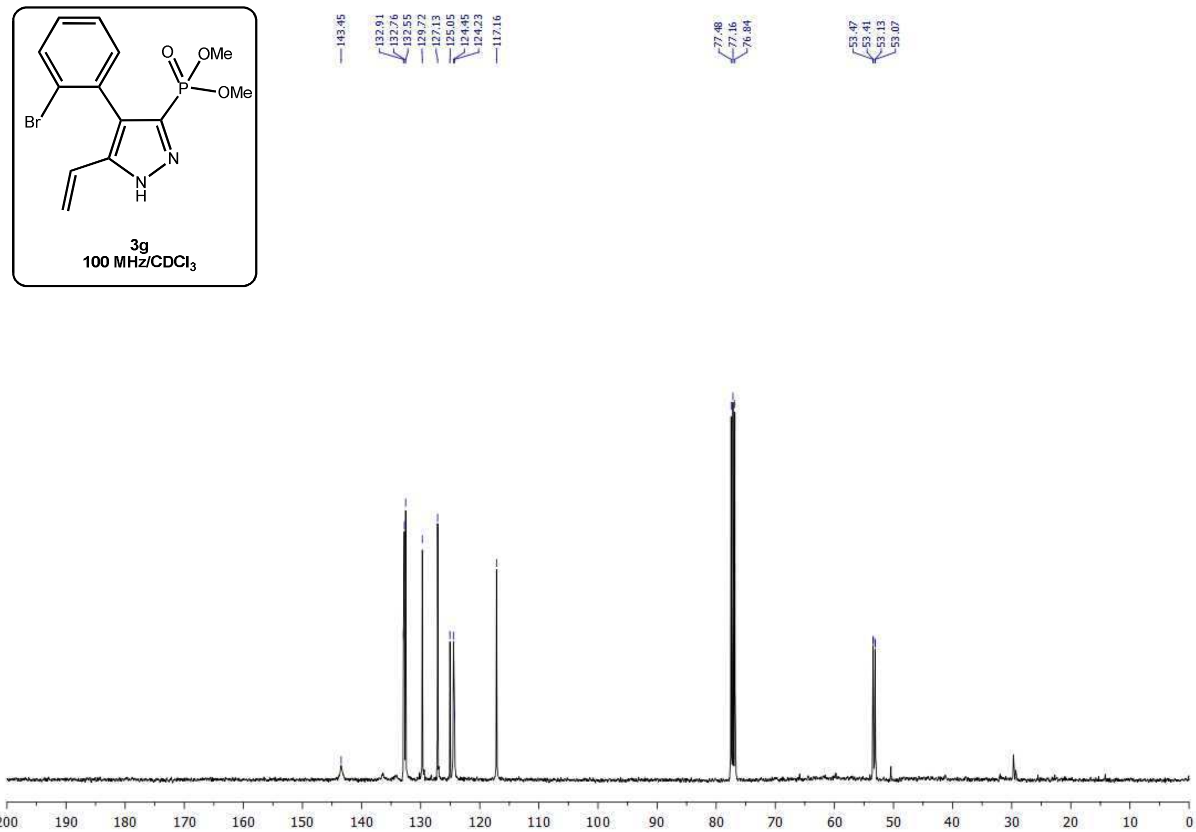
3f
100 MHz/CDCl$_3$



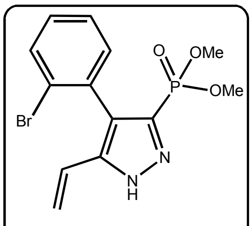
3f
161.9 MHz/CDCl$_3$



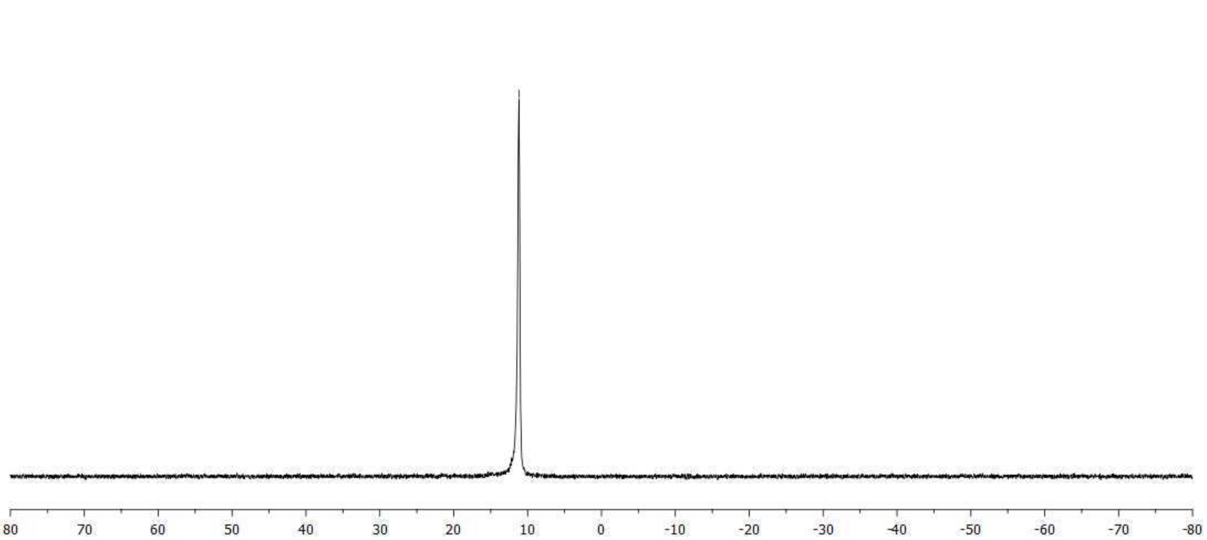
OMe
OMe
Br
N
H
3g
400 MHz/CDCl3

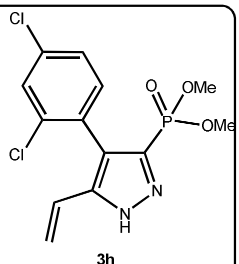


OMe
OMe
Br
N
H
3g
100 MHz/CDCl3
143.45
132.91
132.76
132.55
129.72
127.13
125.05
124.45
124.23
117.16
77.48
77.16
76.84
53.47
53.41
53.13
53.07

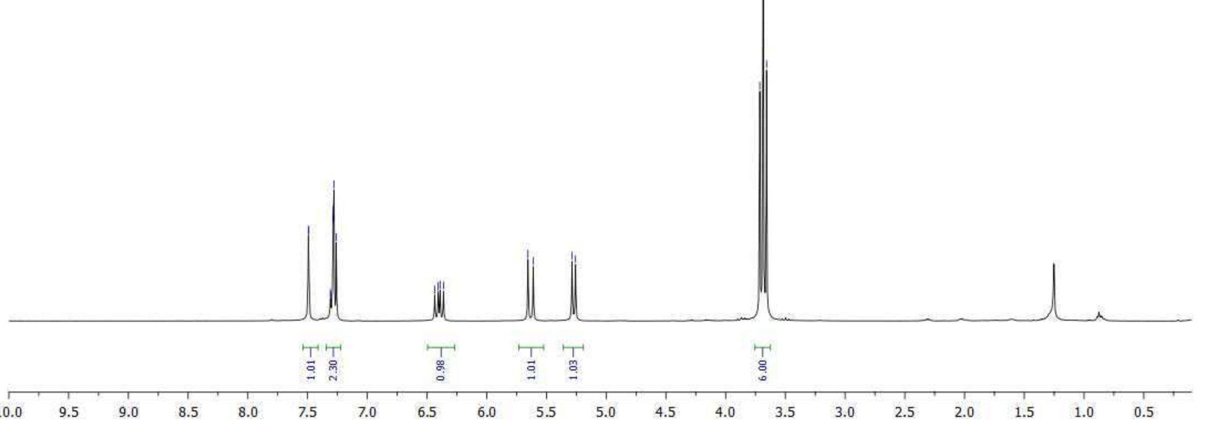


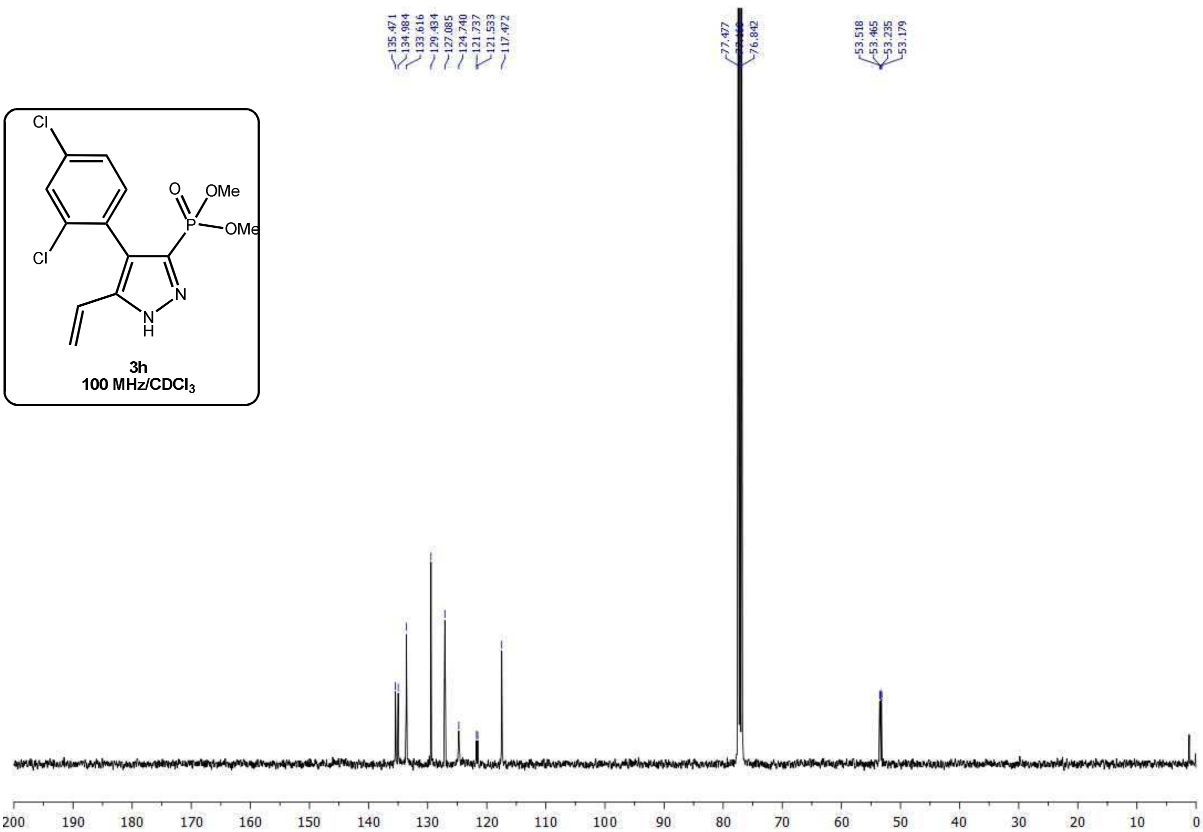
3g
161.9 MHz/CDCl$_3$

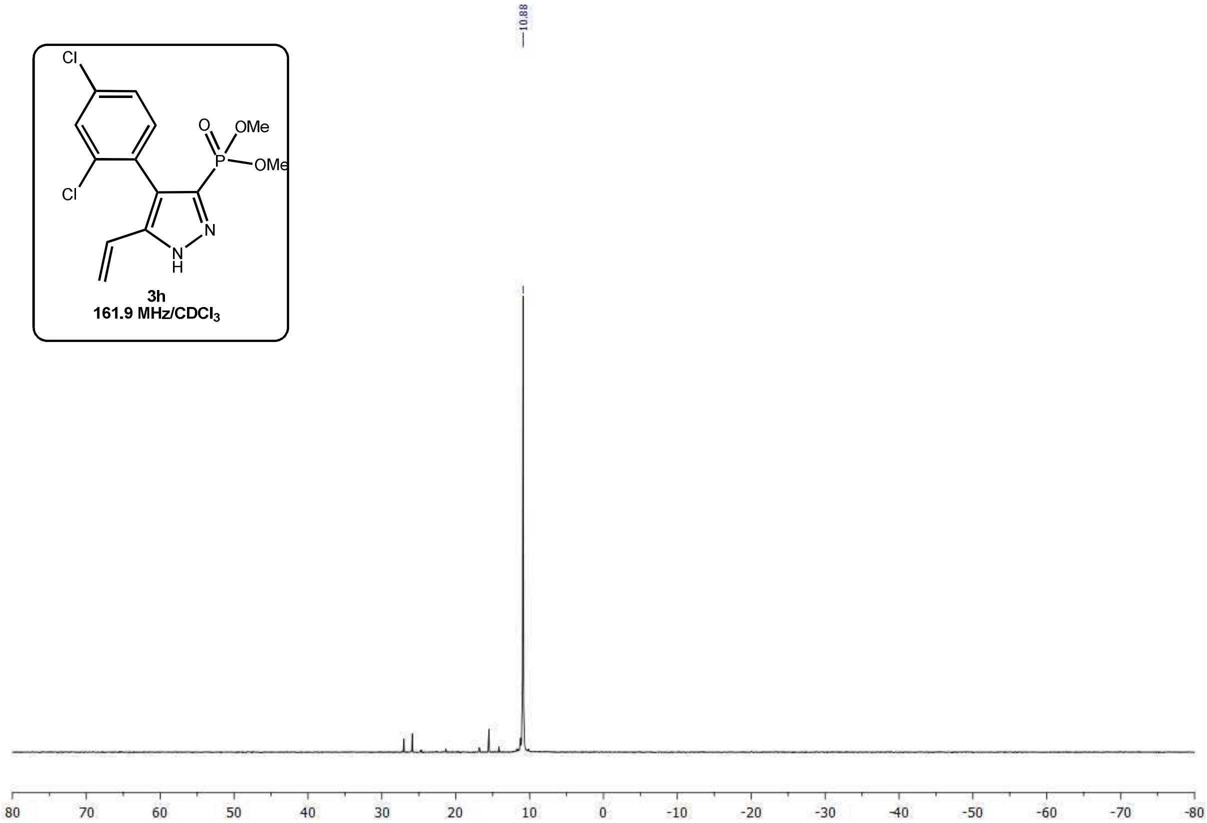


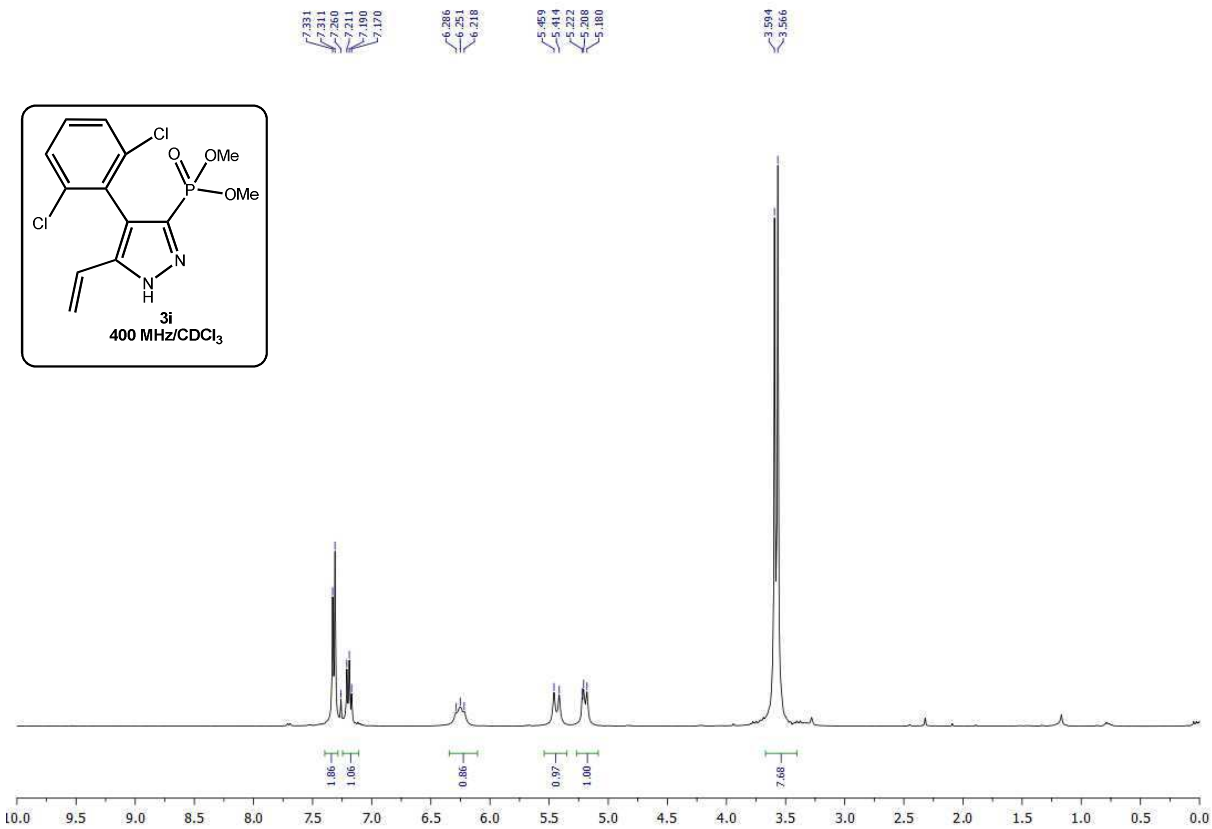


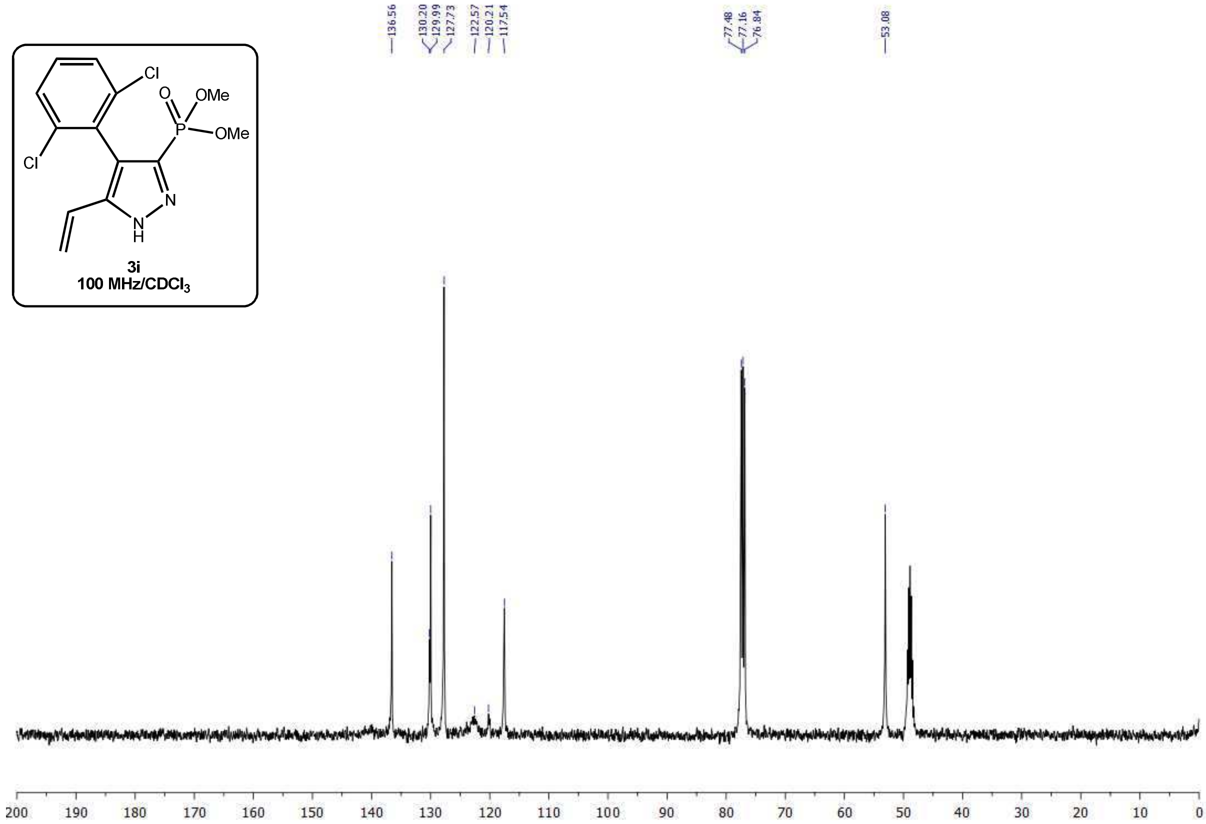
3h
400 MHz/CDCl$_3$

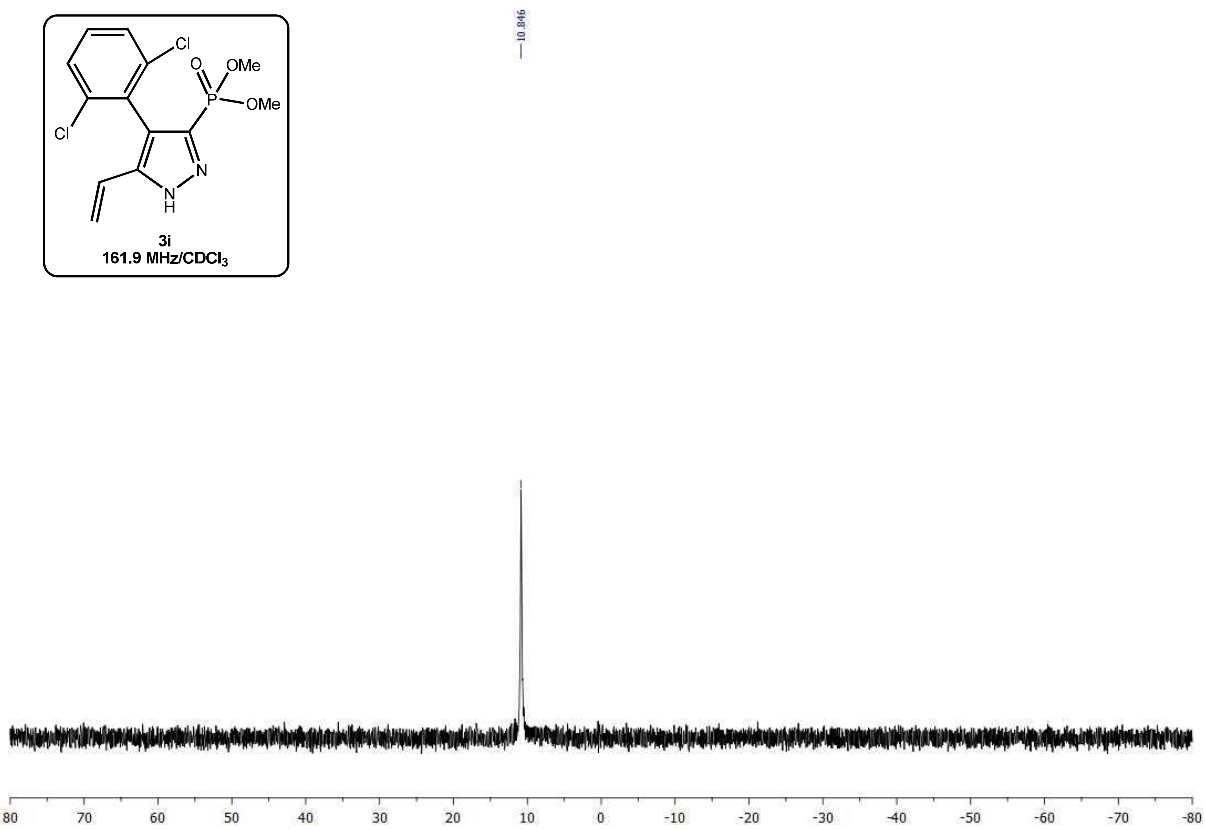



135.471
134.984
133.616
129.434
127.085
124.740
121.737
121.533
117.472
77.477
76.842
53.518
53.465
53.235
53.179
Cl
Cl
O
OMe
P
OMe
N
N
H
3h
100 MHz/CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

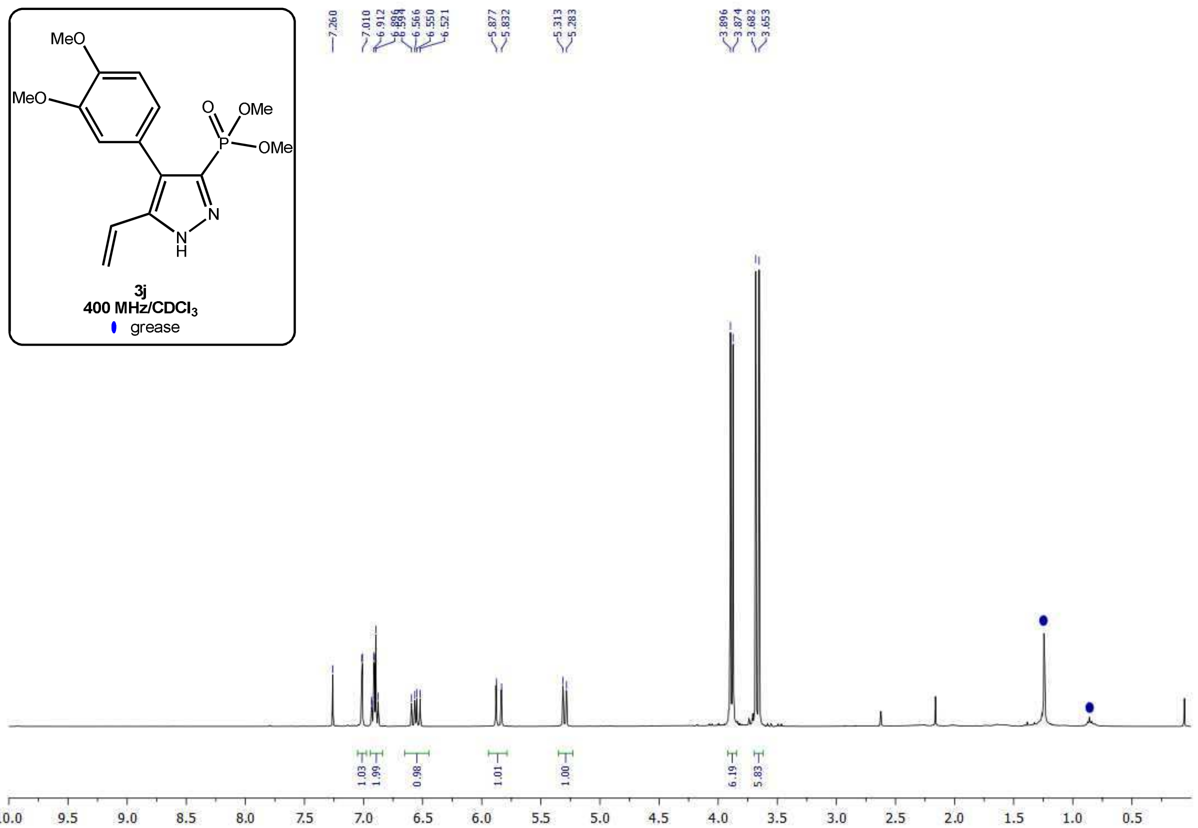

10.88
Cl
Cl
O
OMe
P
OMe
N
N
H
3h
161.9 MHz/CDCl3
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80



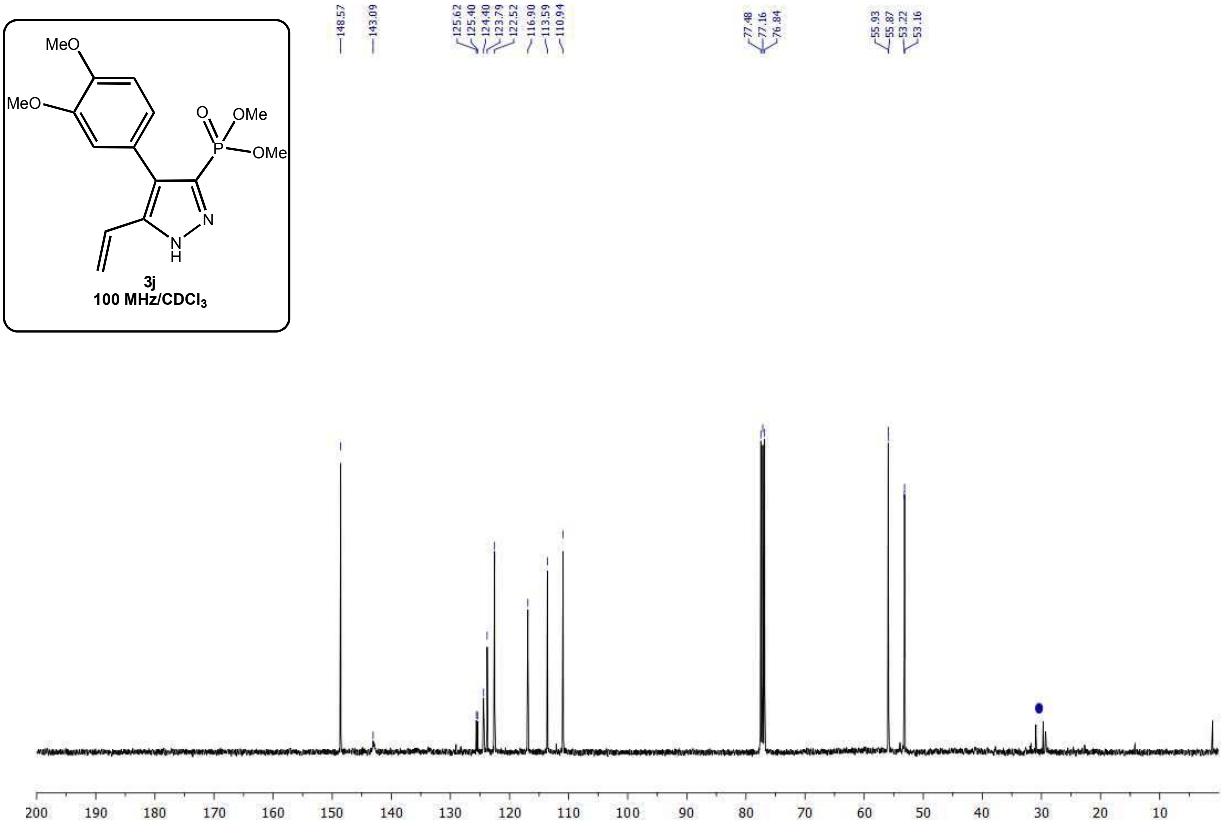


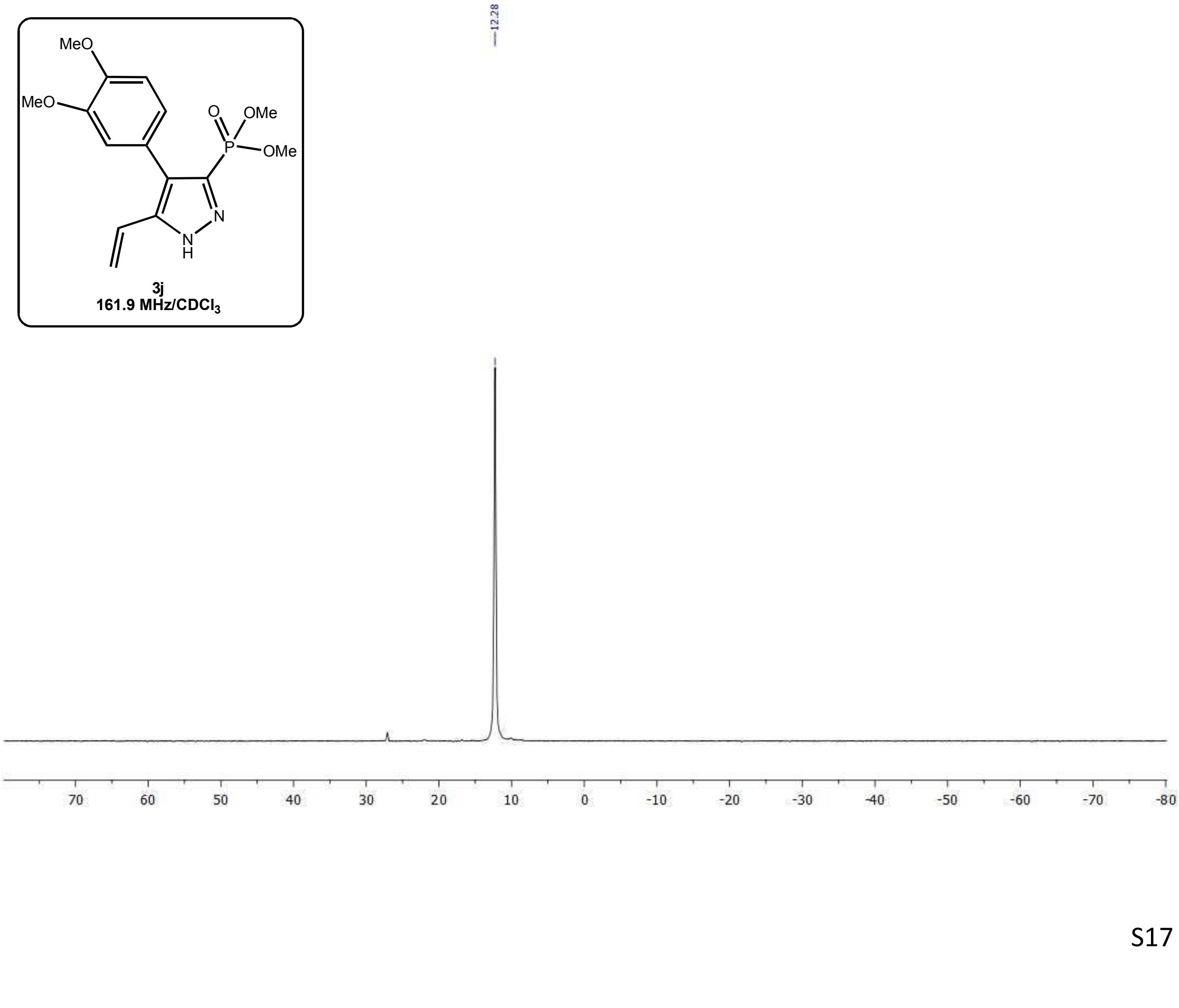


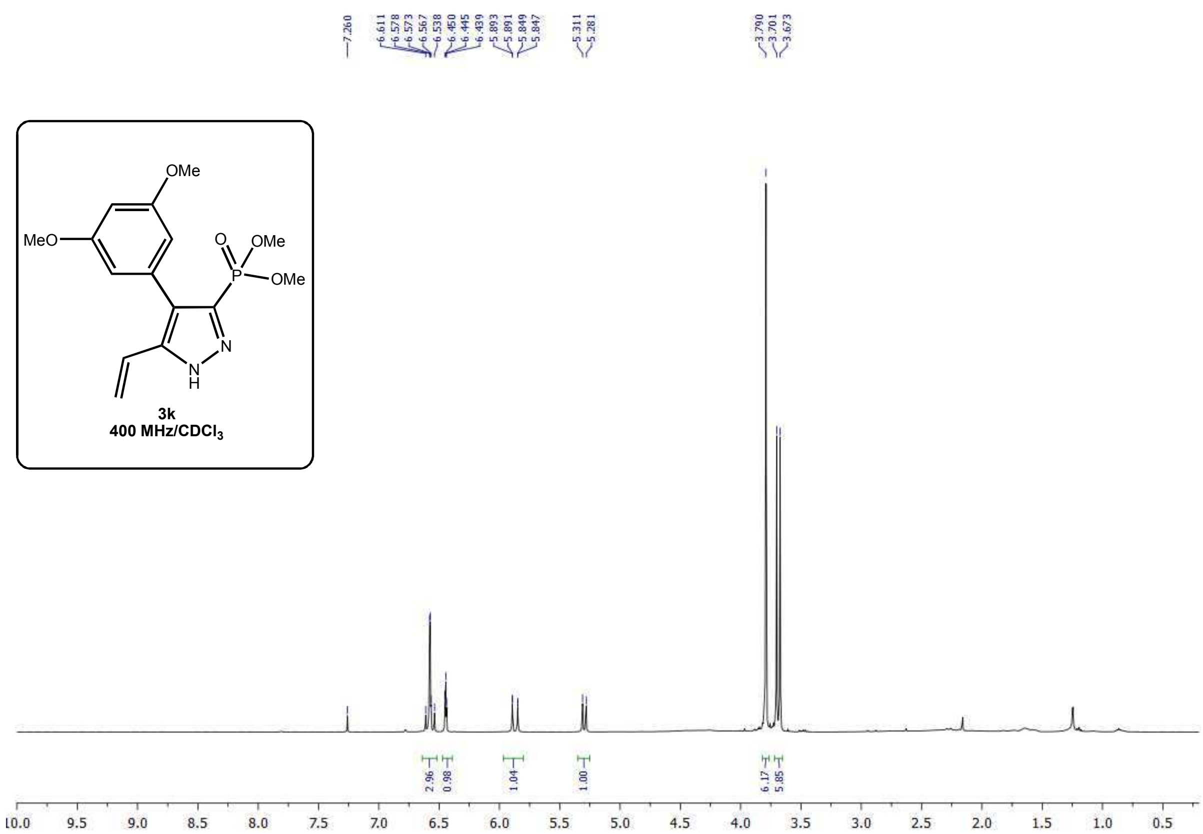
Cl
O
OMe
P
OMe
Cl
N
N
H
3i
161.9 MHz/CDCl3
10.846
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80



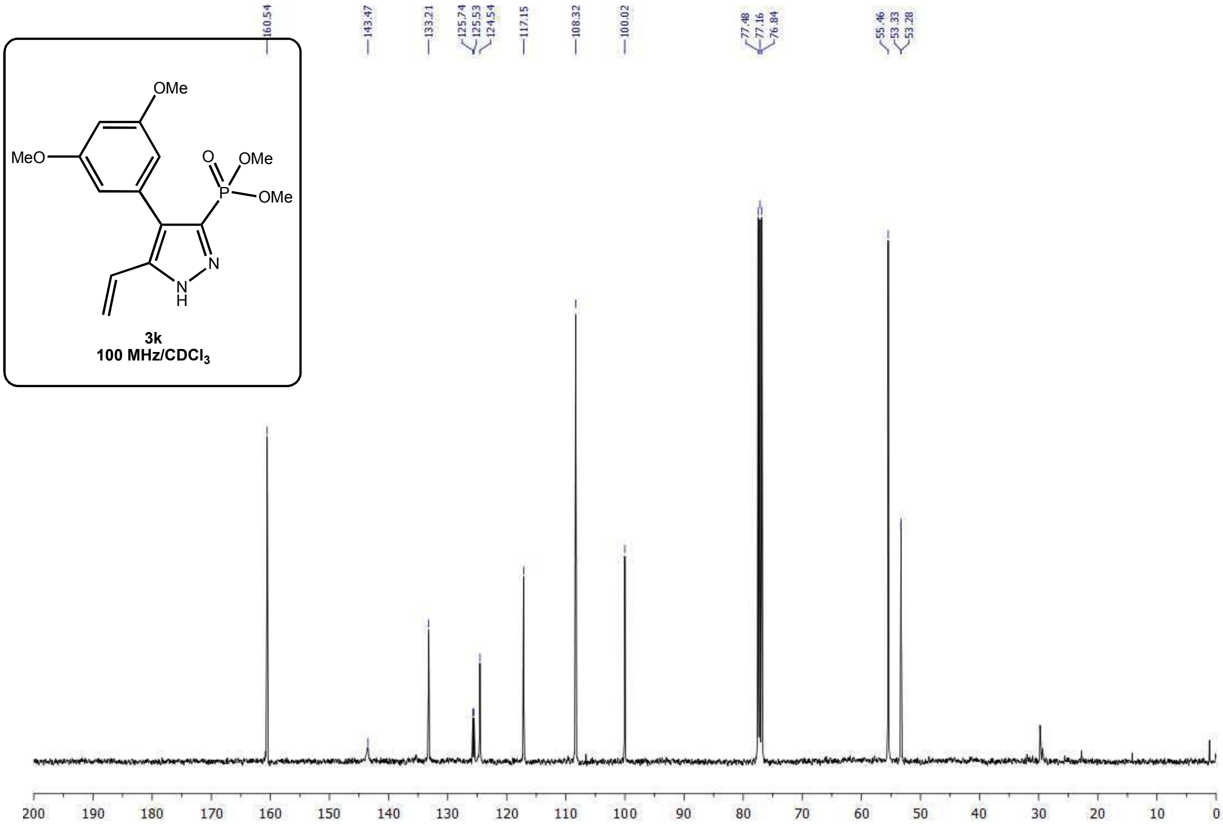
MeO
MeO
O
OMe
P
OMe
N
N
H
3j
400 MHz/CDCl3
grease
7.260
7.010
6.912
6.896
6.891
6.566
6.550
6.521
5.877
5.832
5.313
5.283
3.896
3.874
3.682
3.653
1.03
1.99
0.98
1.01
1.00
6.19
5.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


MeO
MeO
O
OMe
P
OMe
N
N
H
3j
100 MHz/CDCl$_3$
148.57
143.09
125.62
125.40
124.40
123.79
122.52
116.90
113.59
110.94
77.48
77.16
76.84
55.93
55.87
53.22
53.16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

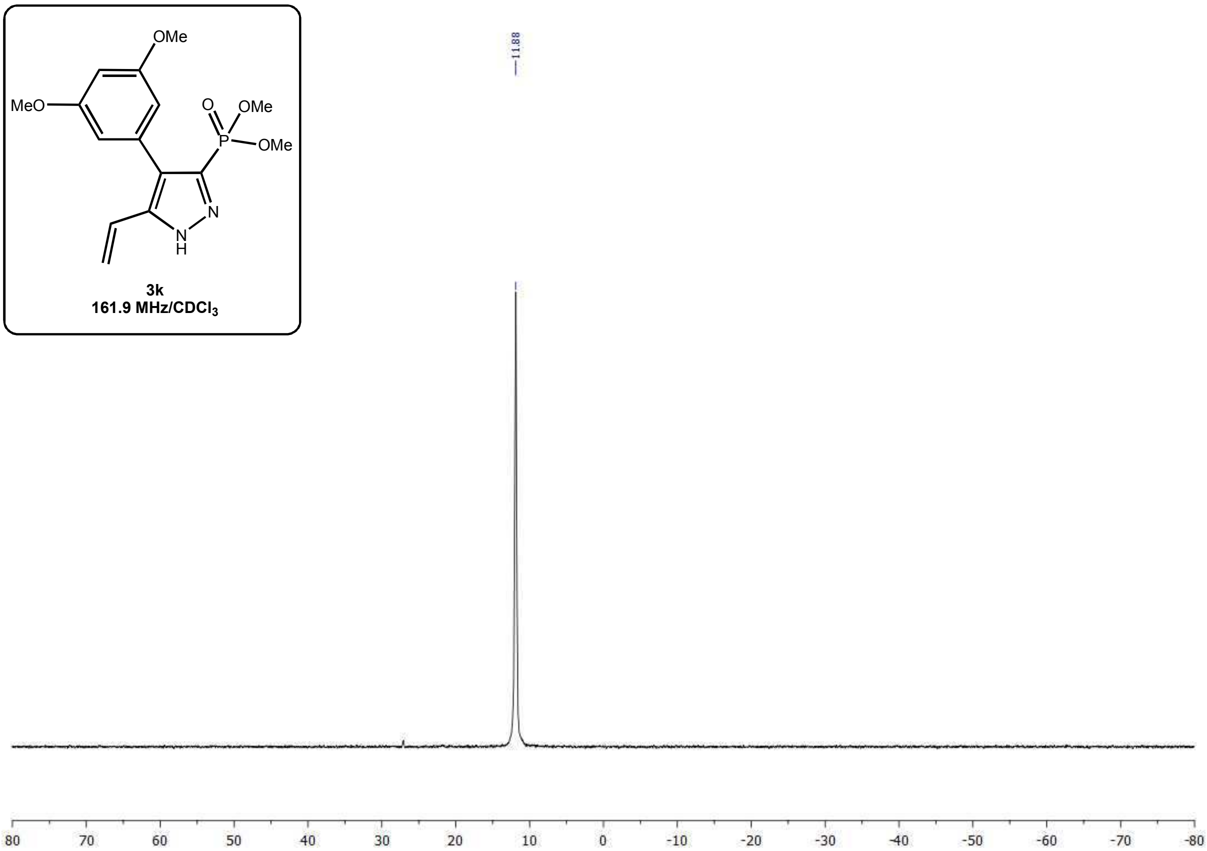

MeO
MeO
O
OMe
P
OMe
N
N
H
3j
161.9 MHz/CDCl$_3$
12.28
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80

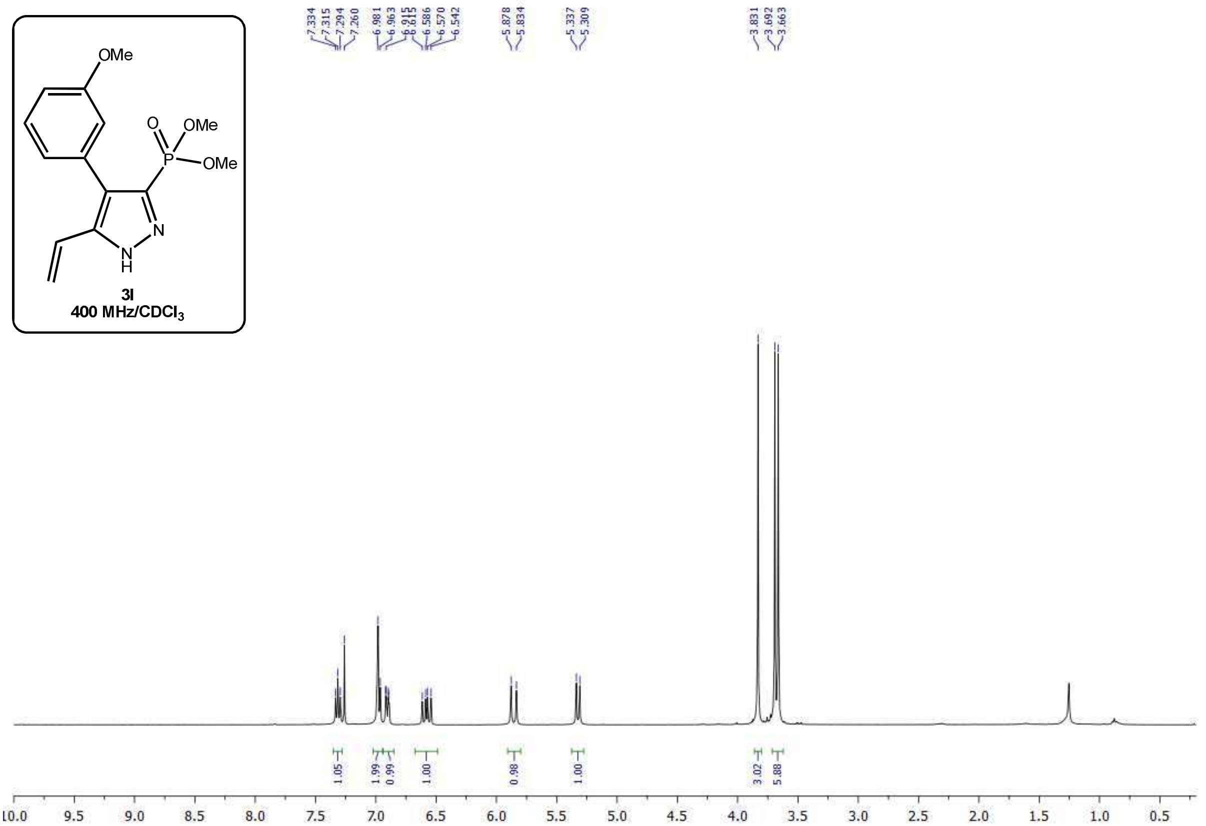


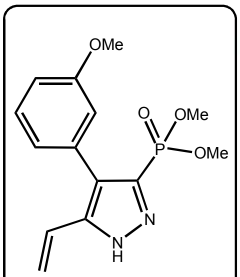
OMe
MeO
O
OMe
P
OMe
N
N
H
3k
400 MHz/CDCl3
7.260
6.611
6.578
6.573
6.567
6.538
6.450
6.445
6.439
5.893
5.891
5.849
5.847
5.311
5.281
3.790
3.701
3.673
2.96
0.98
1.04
1.00
6.17
5.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5



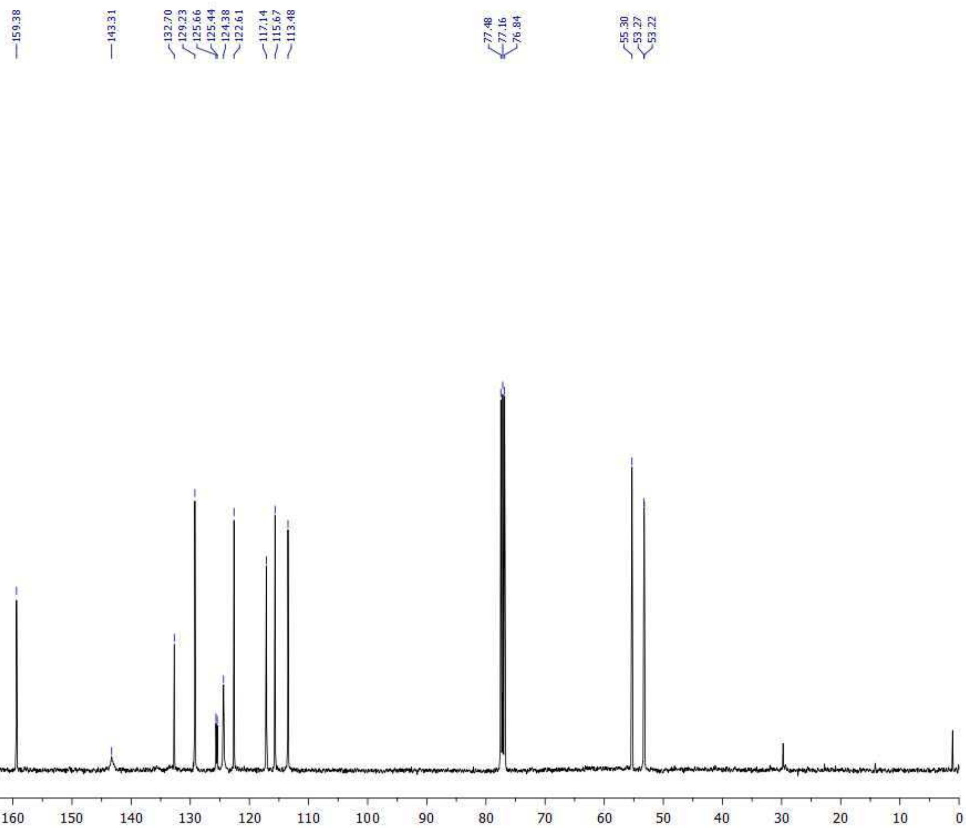
OMe
MeO
O
OMe
P
OMe
N
N
H
3k
100 MHz/CDCl3
160.54
143.47
133.21
125.74
125.53
124.54
117.15
108.32
100.02
77.48
77.16
76.84
55.46
53.33
53.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

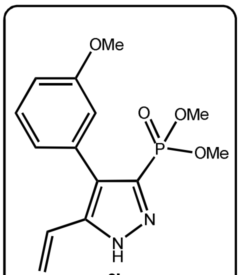

OMe
MeO
O
OMe
P
OMe
N
N
H
3k
161.9 MHz/CDCl3
11.88
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80


OMe
O
OMe
P
OMe
N
N
H
3l
400 MHz/CDCl3
7.334 7.315 7.294 7.260 6.981 6.963 6.915 6.615 6.586 6.570 6.542 5.878 5.834 5.337 5.309 3.831 3.692 3.663
1.05 1.99 0.99 1.00 0.98 1.00 3.02 5.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

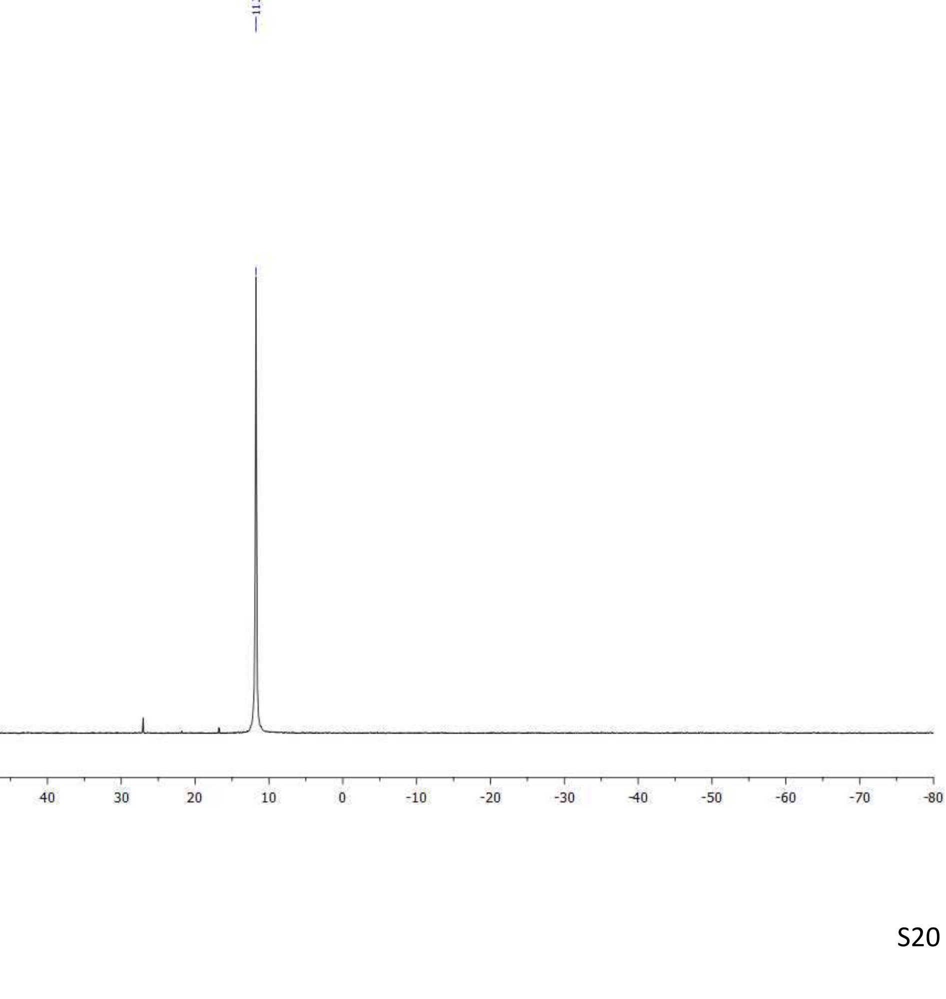


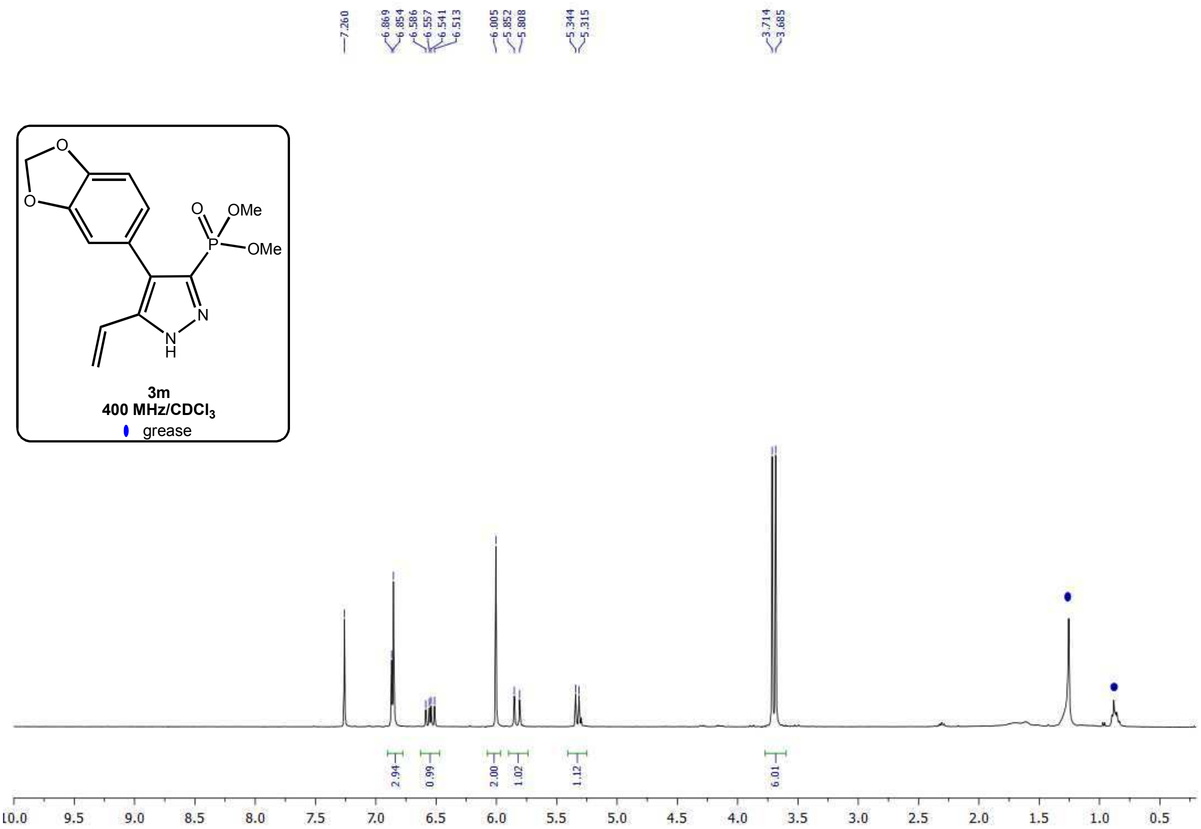
3l
100 MHz/CDCl$_3$

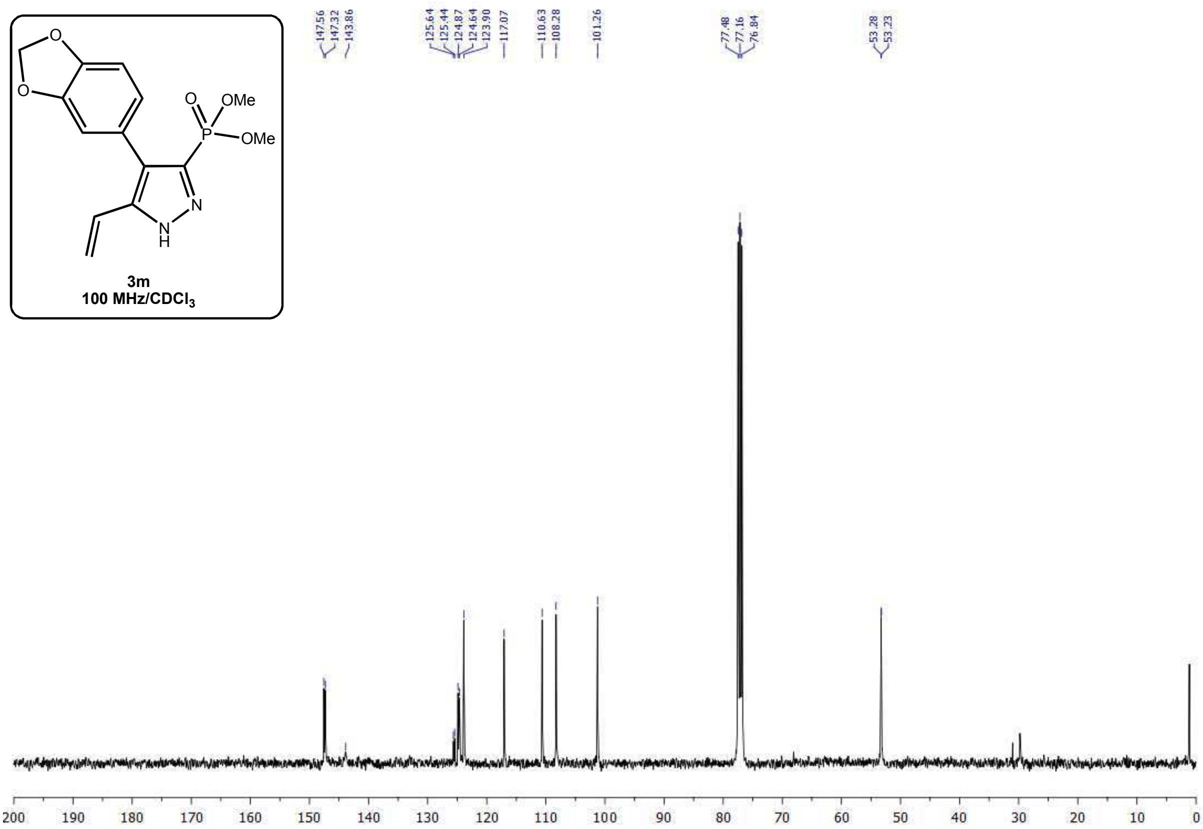


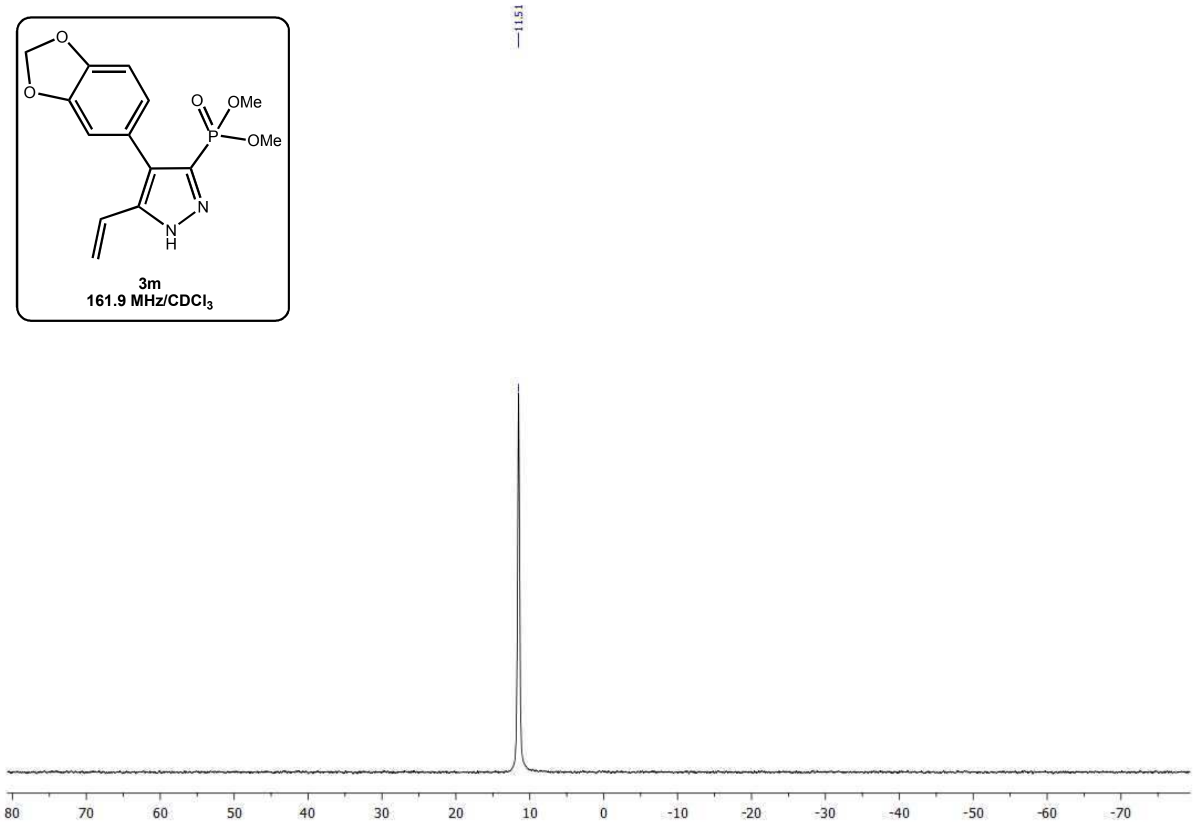


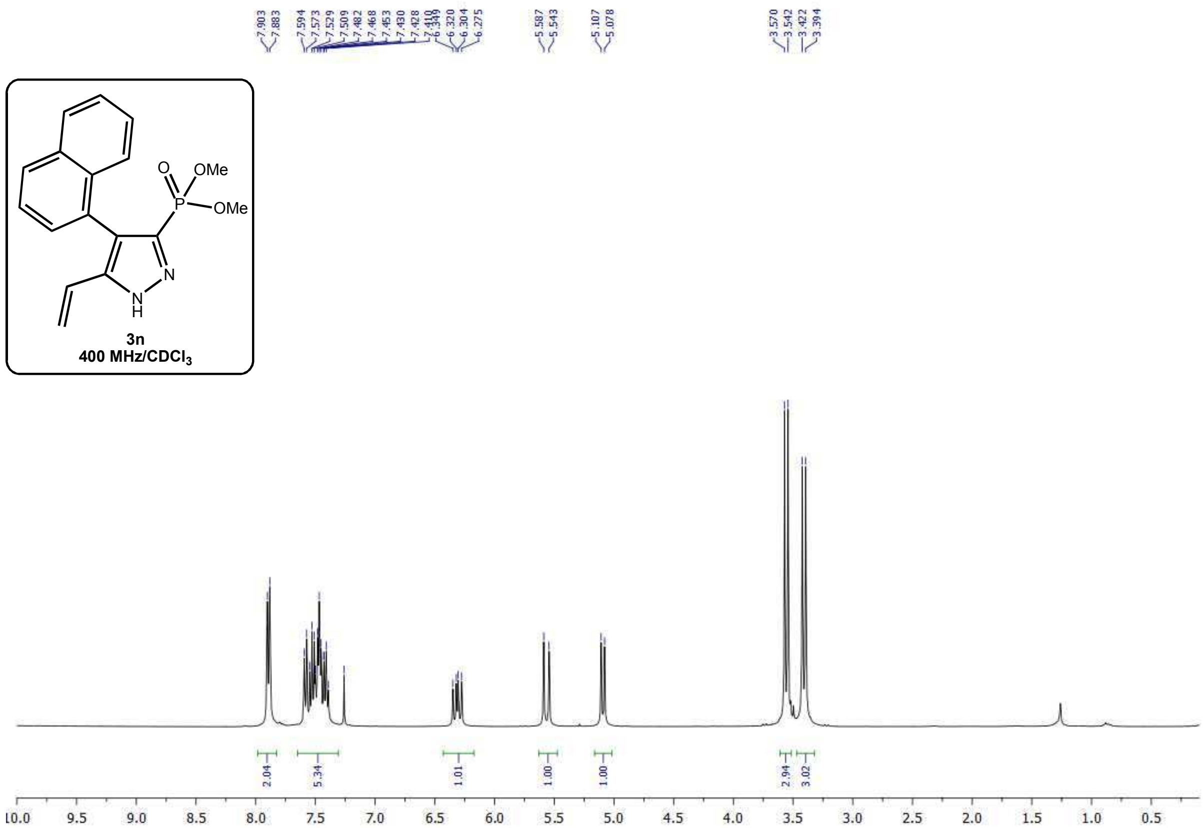
3l
161.9 MHz/CDCl$_3$

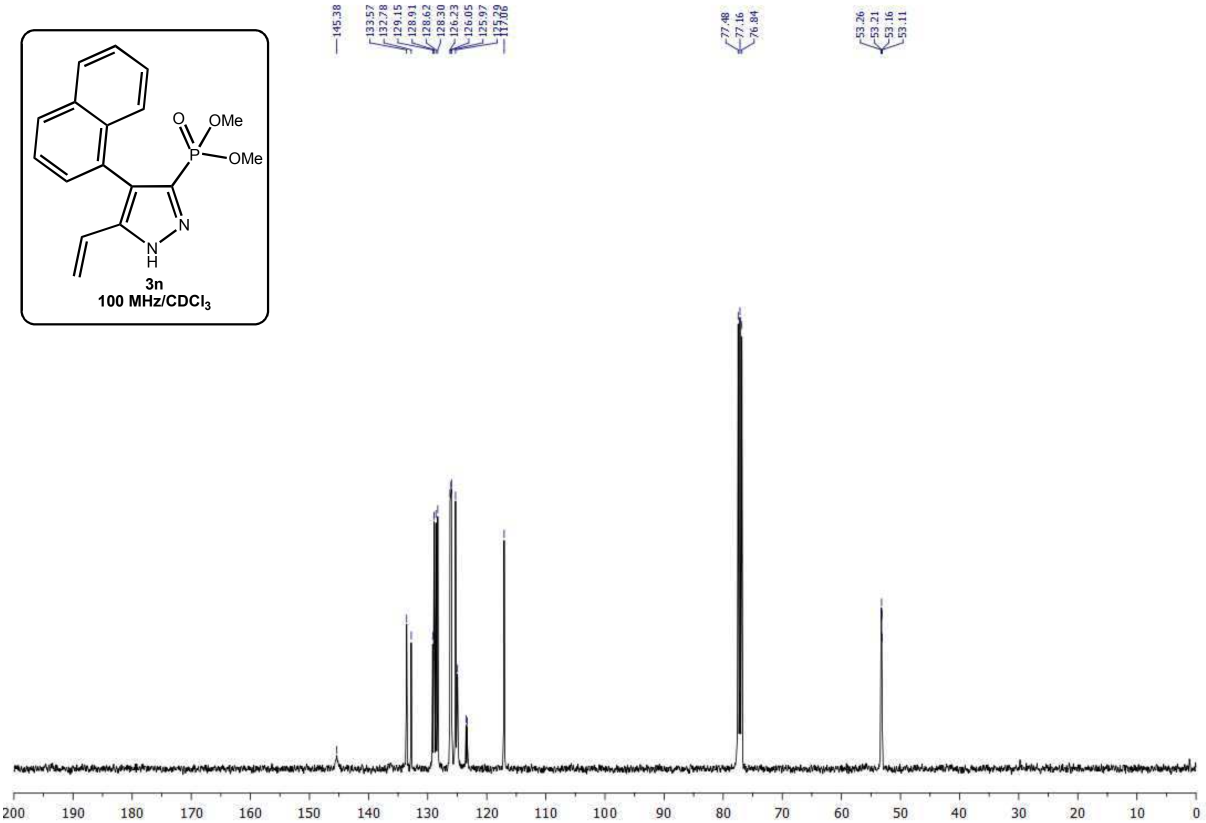


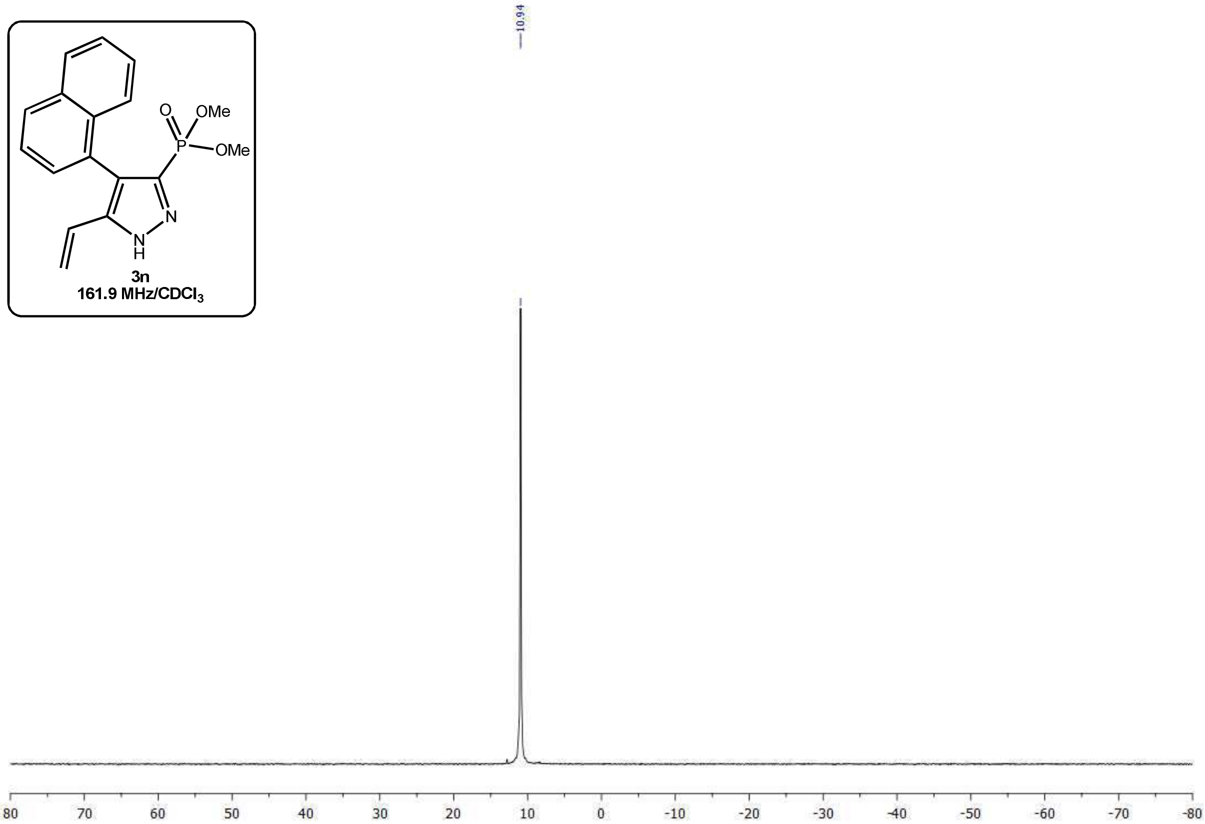

7.260
6.869
6.854
6.586
6.557
6.541
6.513
6.005
5.852
5.808
5.344
5.315
3.714
3.685
OMe
OMe
O
P
N
H
3m
400 MHz/CDCl3
grease
2.94
0.99
2.00
1.02
1.12
6.01

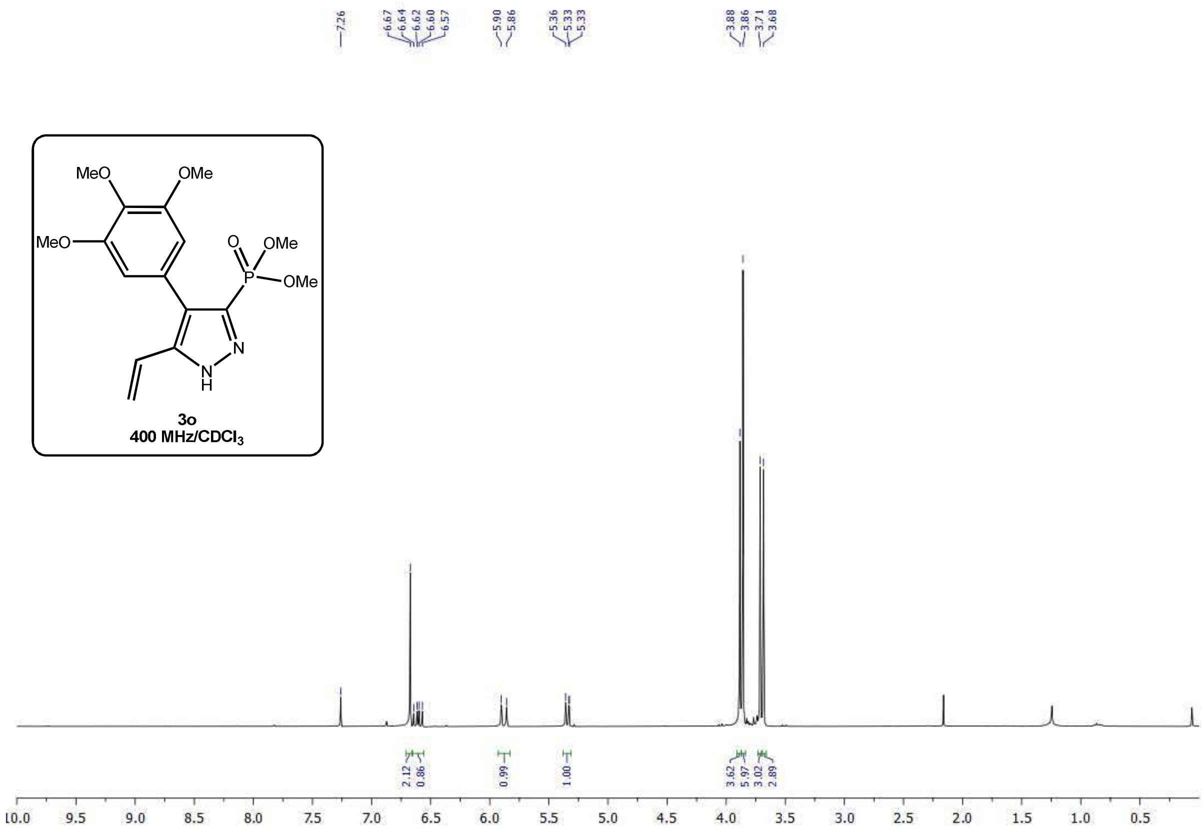

147.56
147.32
143.86
125.64
125.44
124.87
124.64
123.90
117.07
110.63
108.28
101.26
77.48
77.16
76.84
53.28
53.23
OMe
OMe
3m
100 MHz/CDCl3

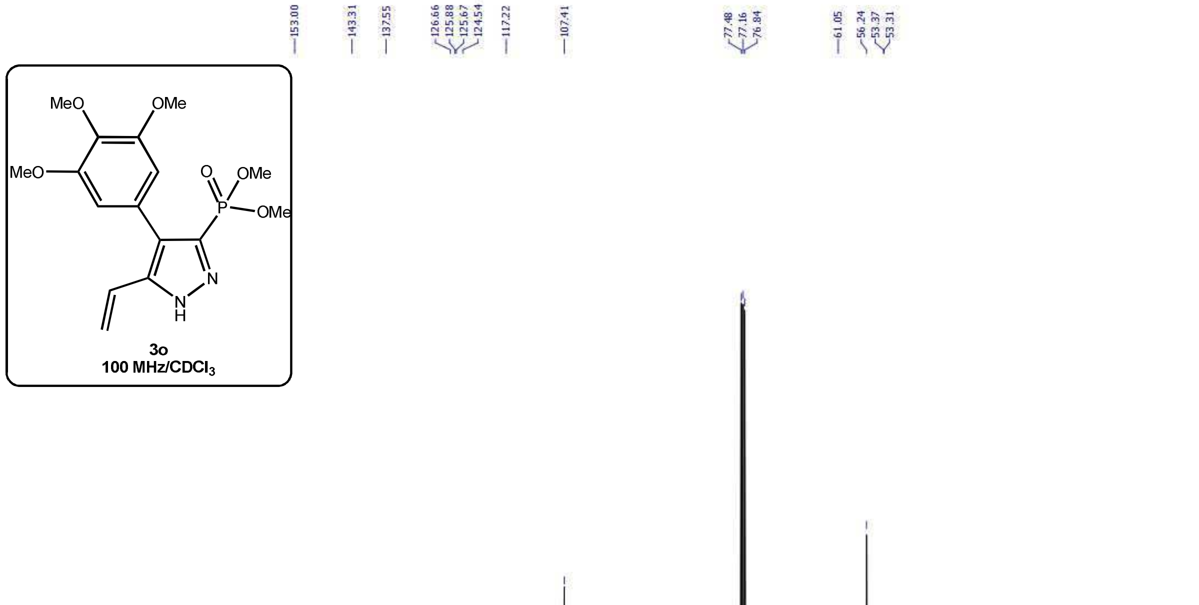

3m
161.9 MHz/CDCl3
OMe
OMe
11.51
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70

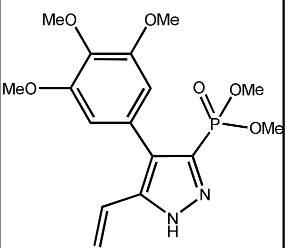

3n
400 MHz/CDCl3
OMe
OMe
7.903 7.883 7.594 7.573 7.529 7.509 7.482 7.468 7.453 7.430 7.428 7.410 6.349 6.320 6.304 6.275 5.587 5.543 5.107 5.078 3.570 3.542 3.422 3.394
2.04 5.34 1.01 1.00 1.00 2.94 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


OMe
OMe
O
P
N
N
H
3n
100 MHz/CDCl3
145.38
133.57
132.78
129.15
128.91
128.62
128.30
126.23
126.05
125.97
77.48
77.16
76.84
53.26
53.21
53.16
53.11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

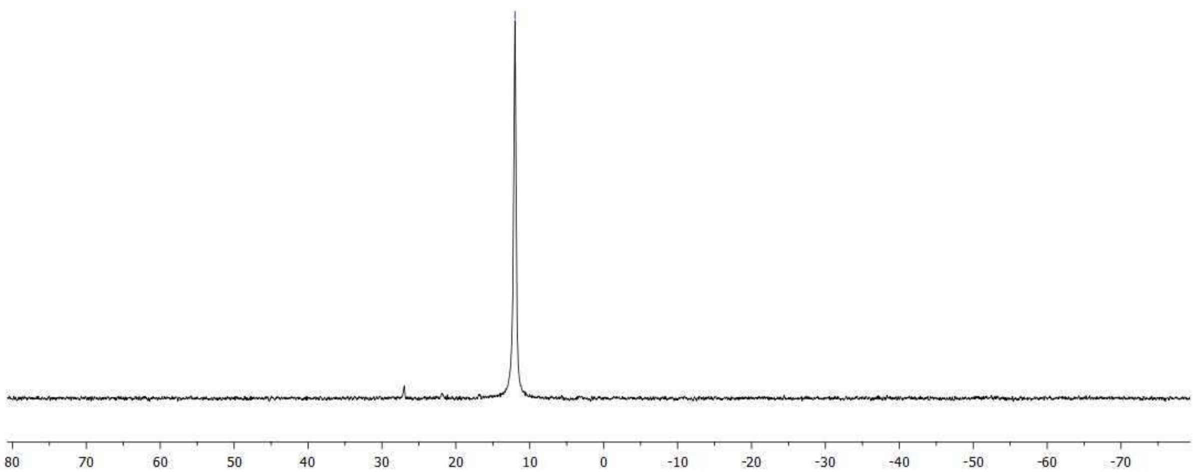

OMe
OMe
O
P
N
N
H
3n
161.9 MHz/CDCl3
10.94
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80

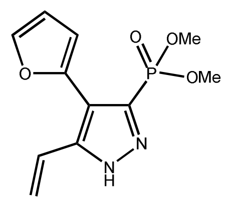

7.26
6.67
6.64
6.62
6.60
6.57
5.90
5.86
5.36
5.33
5.33
3.88
3.86
3.71
3.68
MeO
OMe
MeO
O
OMe
P
OMe
N
N
H
3o
400 MHz/CDCl$_3$
2.12
0.86
0.99
1.00
3.62
5.97
3.02
2.89


153.00
143.31
137.55
126.66
125.88
125.67
124.54
117.22
107.41
77.48
77.16
76.84
61.05
56.24
53.37
53.31
MeO
OMe
MeO
O
OMe
P
OMe
N
N
H
3o
100 MHz/CDCl$_3$

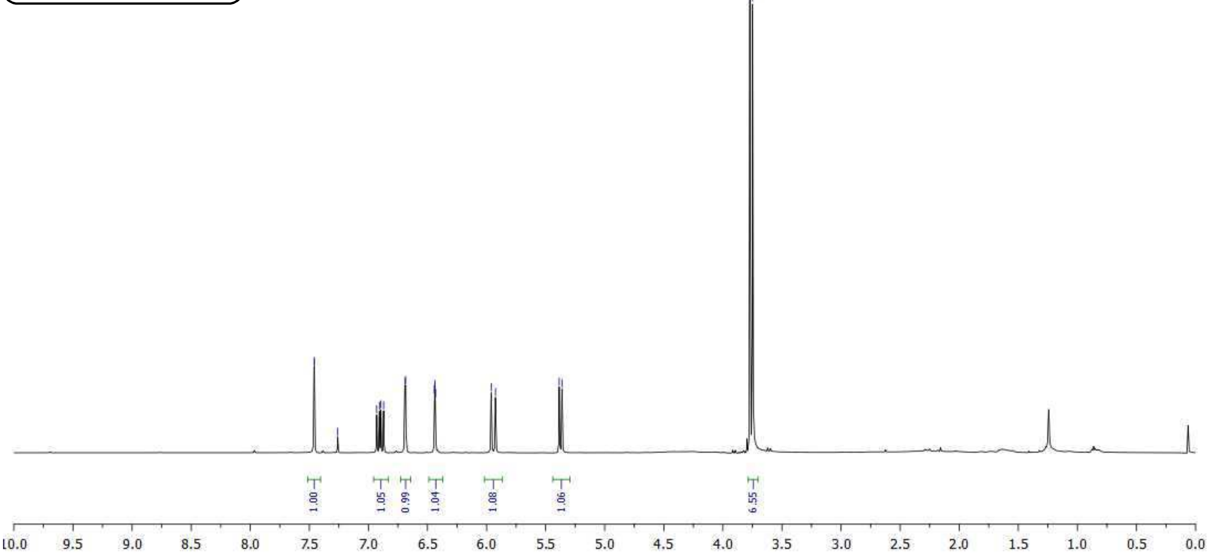


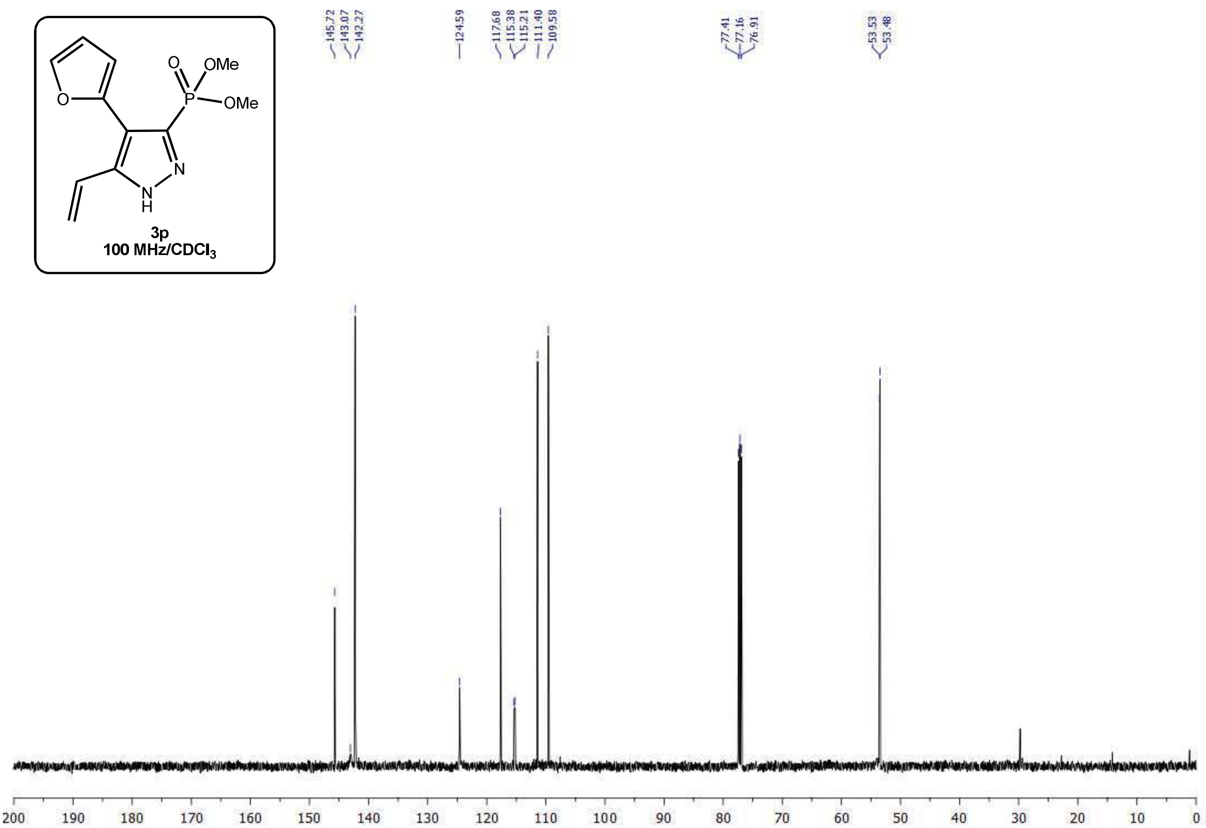
3o
161.9 MHz/CDCl$_3$



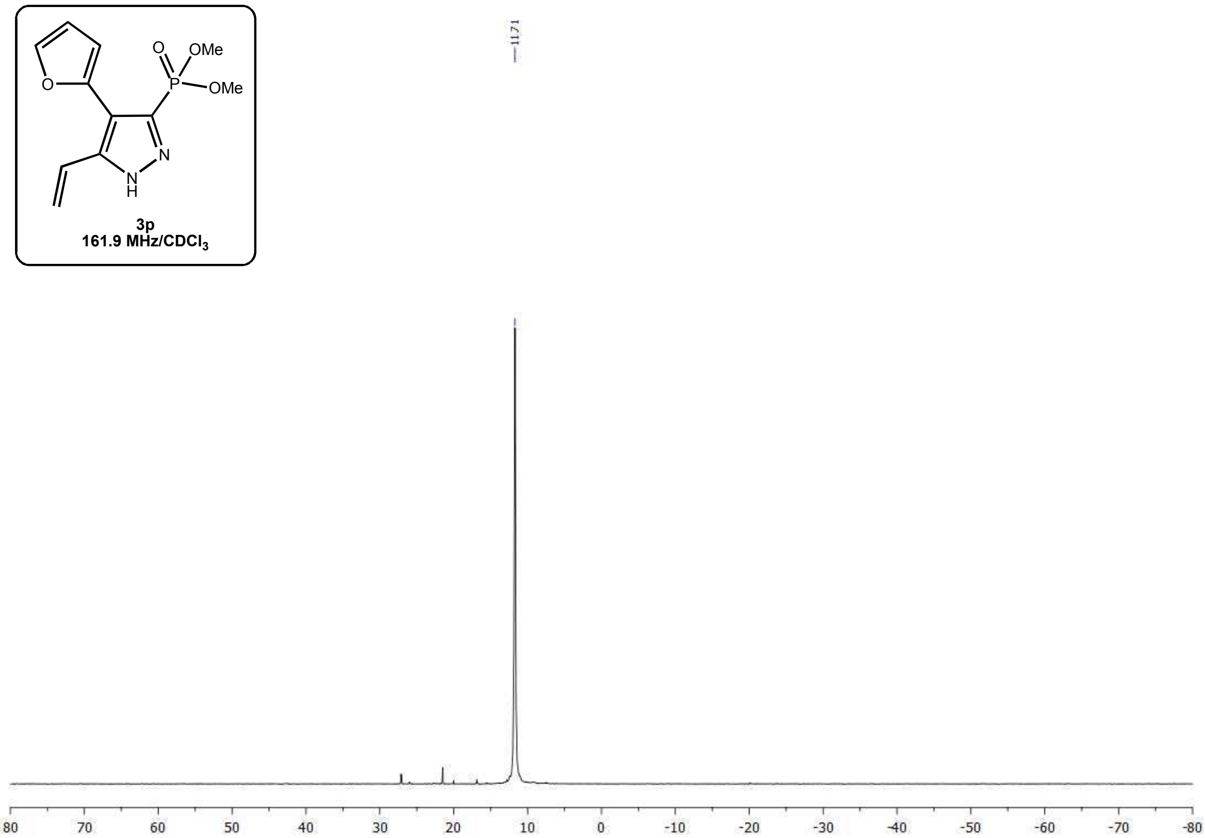


3p
400 MHz/CDCl$_3$

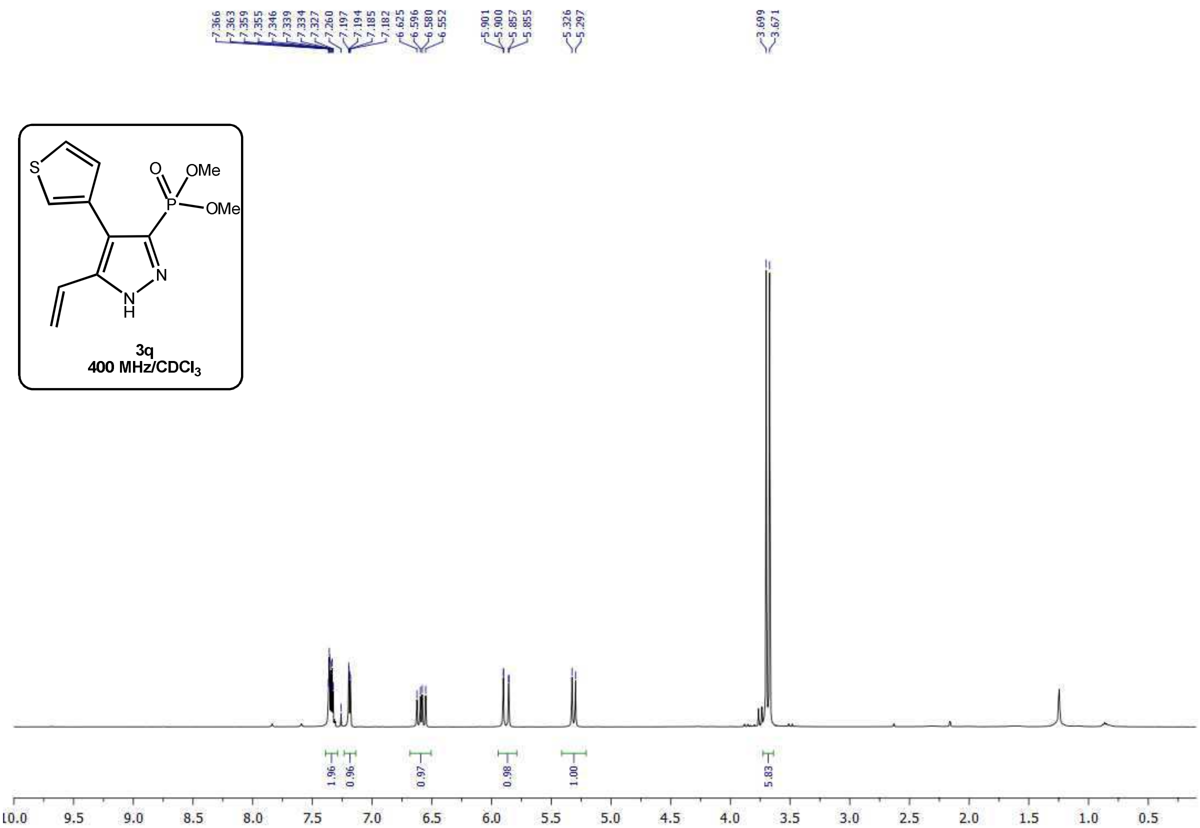


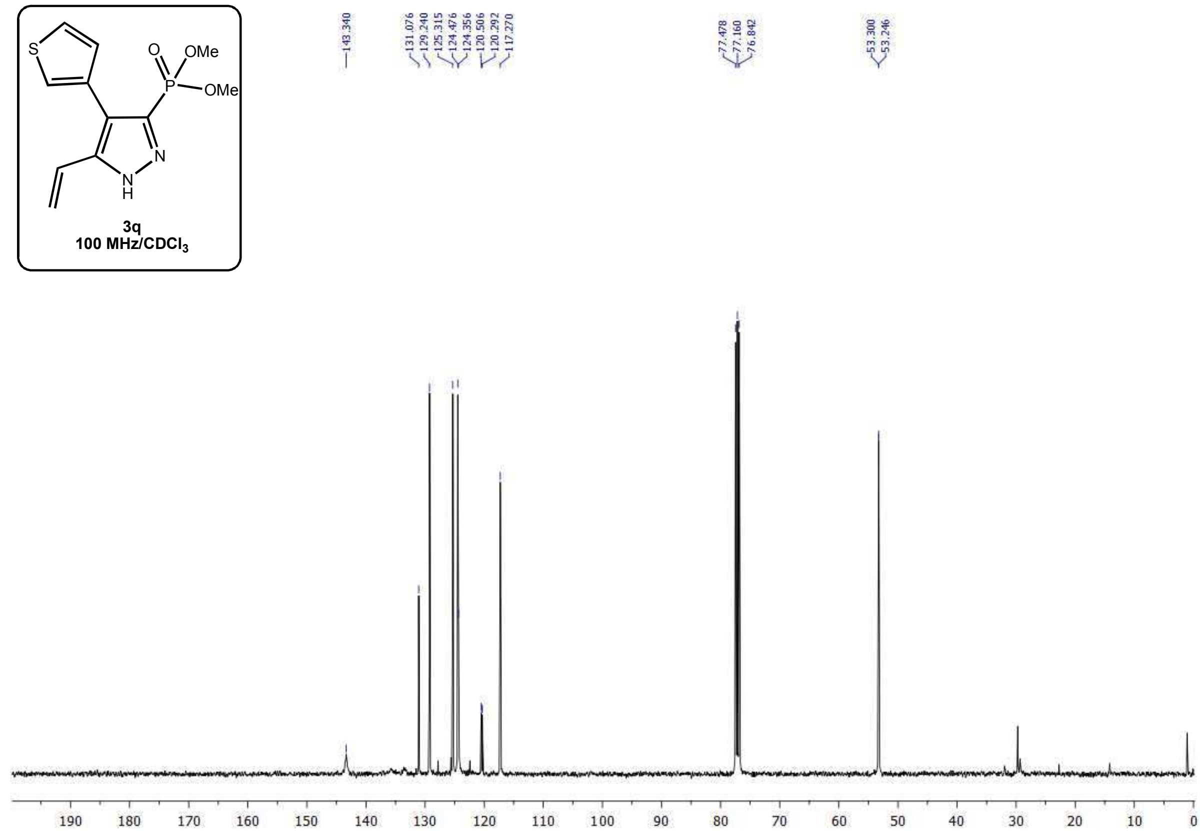


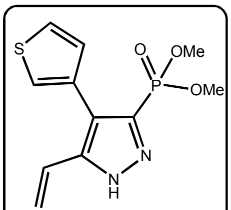
3p
100 MHz/CDCl$_3$



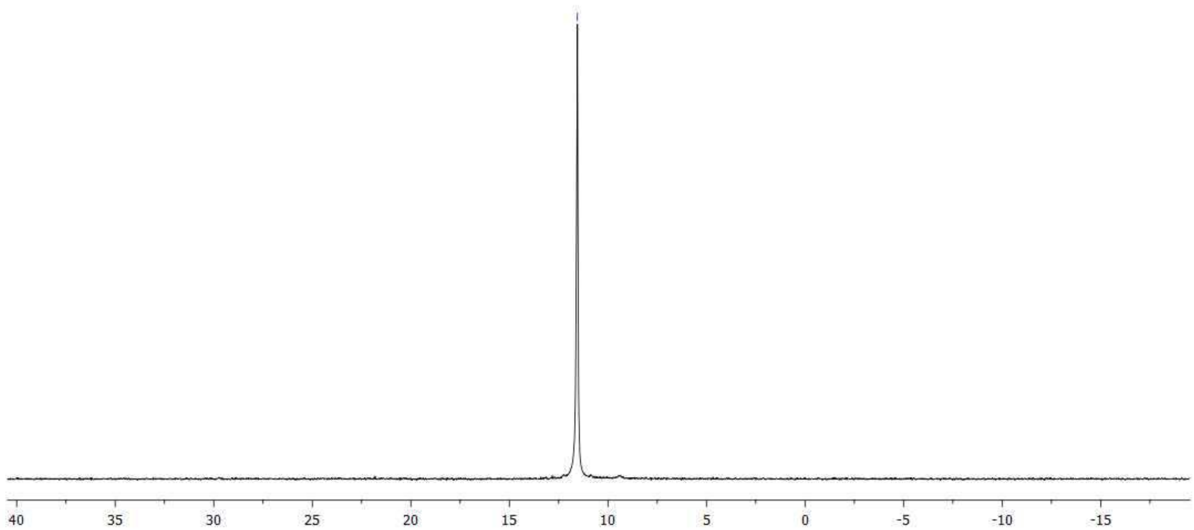
3p
161.9 MHz/CDCl$_3$

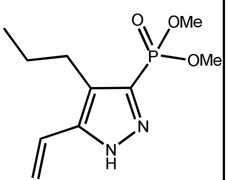

OMe
OMe
3q
400 MHz/CDCl3
7.366
7.363
7.359
7.355
7.346
7.339
7.334
7.327
7.260
7.197
7.194
7.185
7.182
6.625
6.596
6.580
6.552
5.901
5.900
5.857
5.855
5.326
5.297
3.699
3.671
1.96
0.96
0.97
0.98
1.00
5.83


OMe
OMe
3q
100 MHz/CDCl3
143.340
131.076
129.240
125.315
124.476
124.356
120.506
120.292
117.270
77.478
77.160
76.842
53.300
53.246

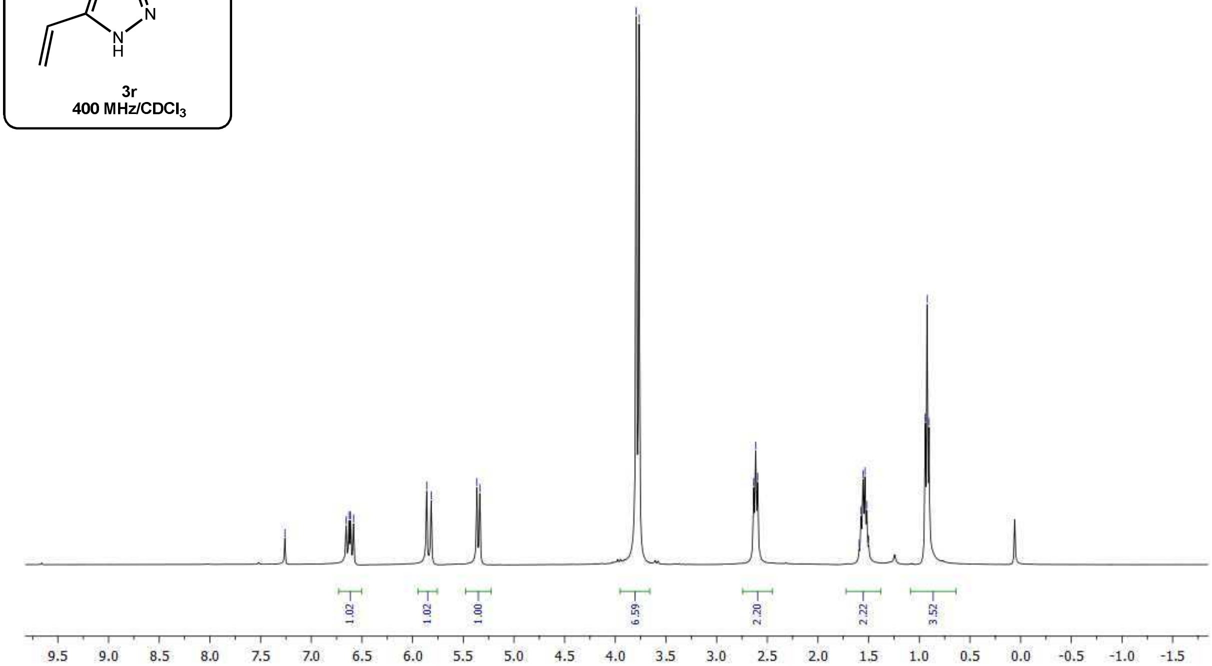


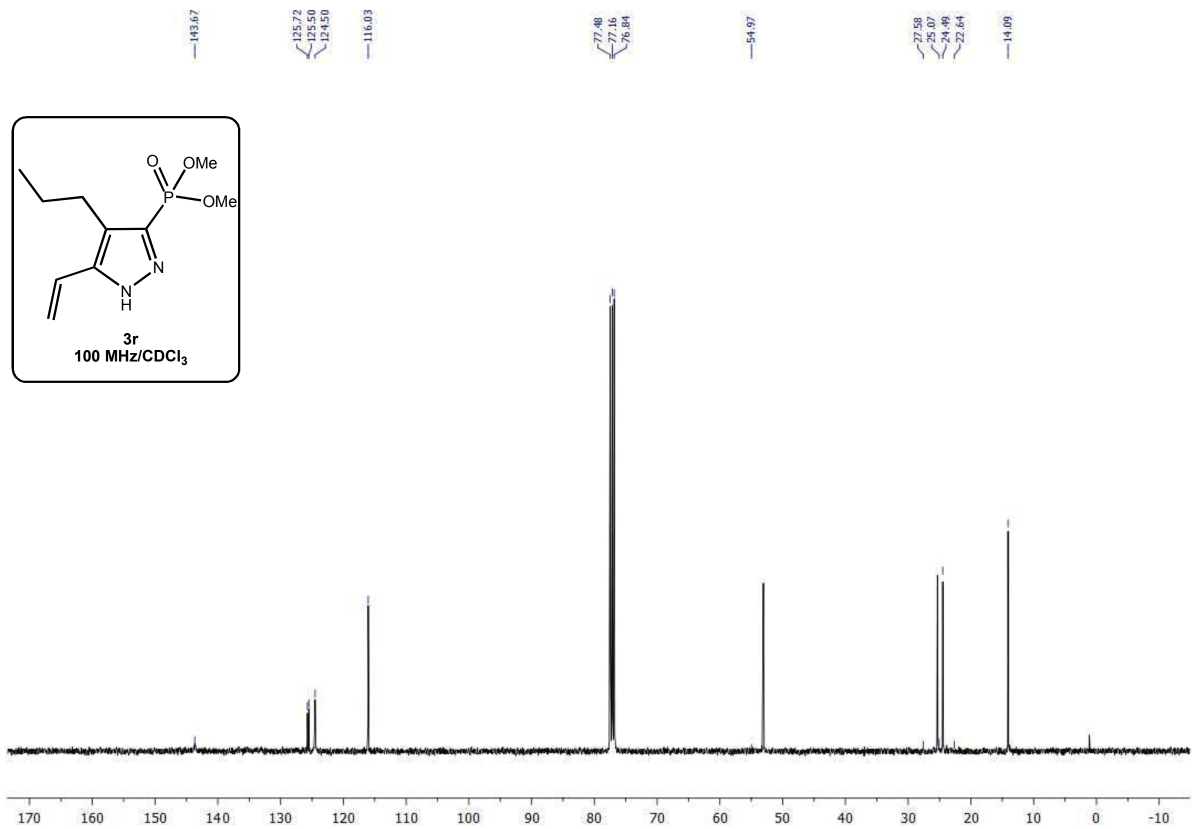
3q
161.9 MHz/$CDCl_3$

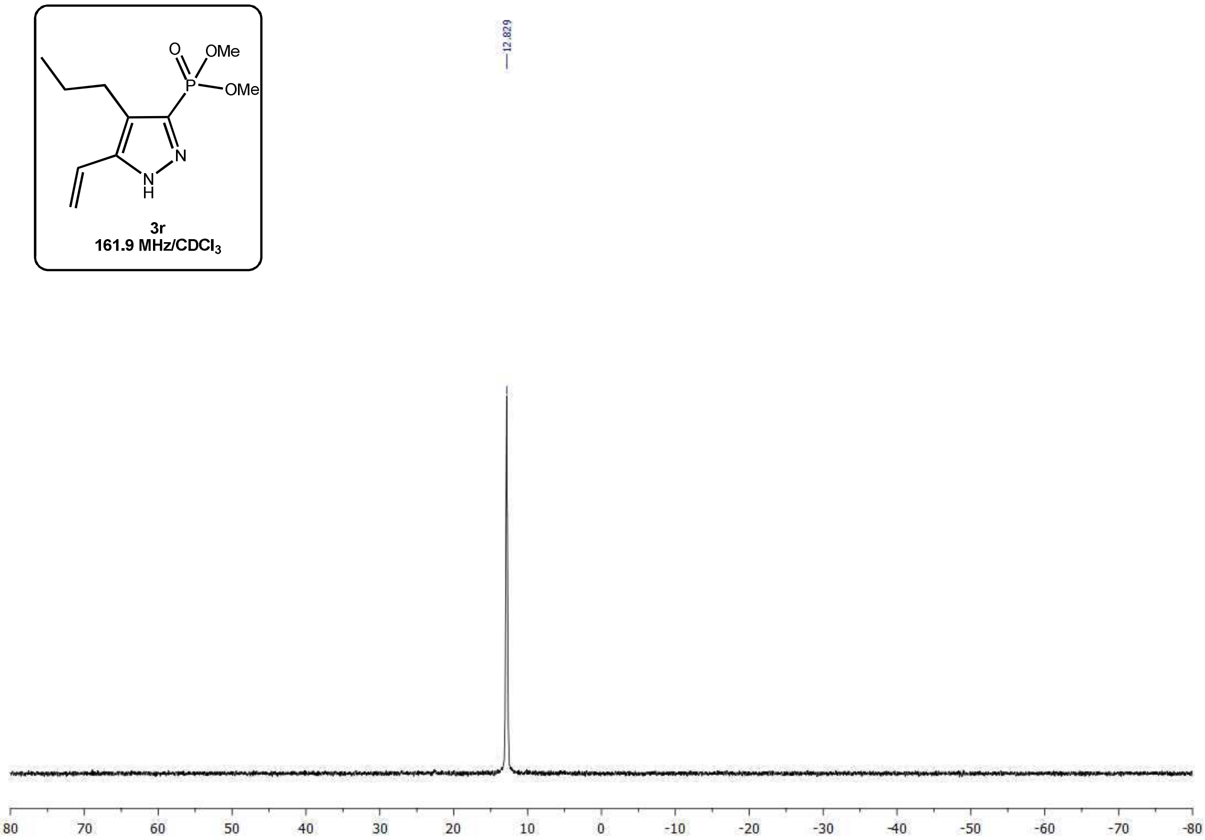


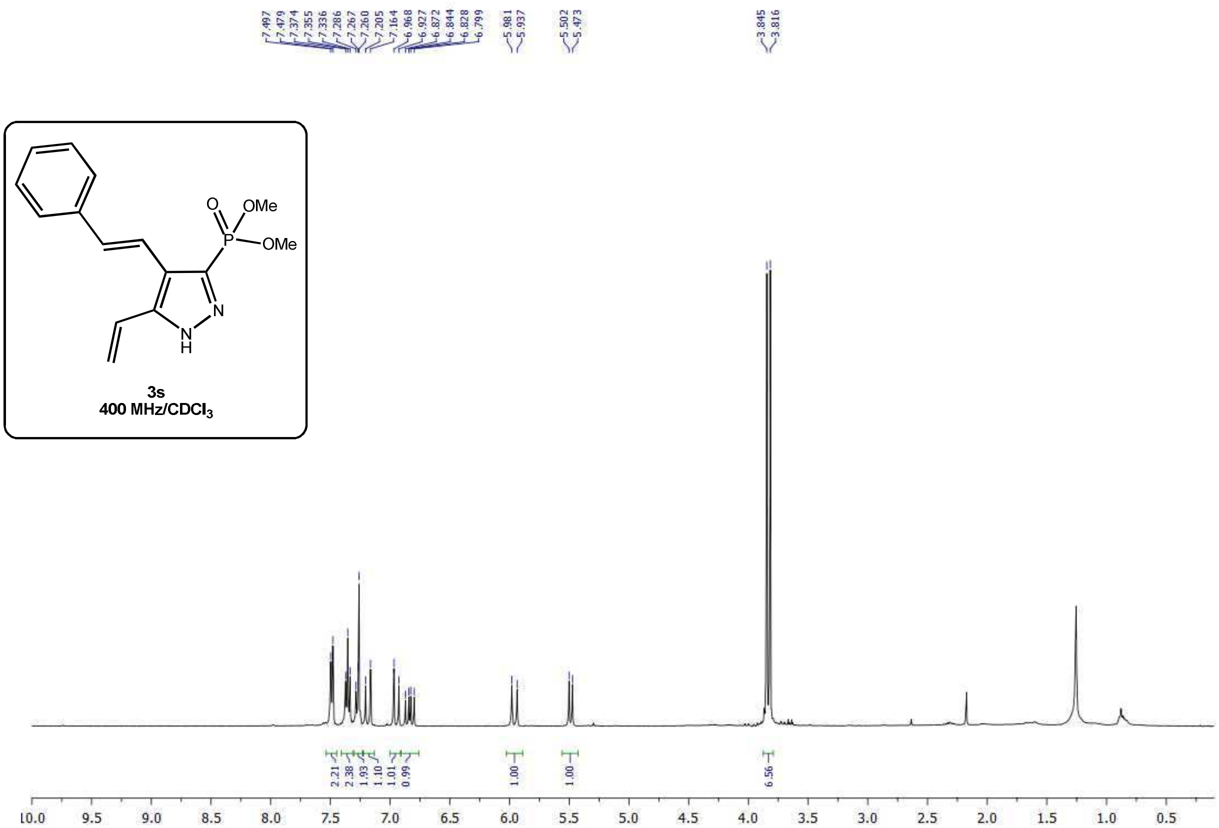


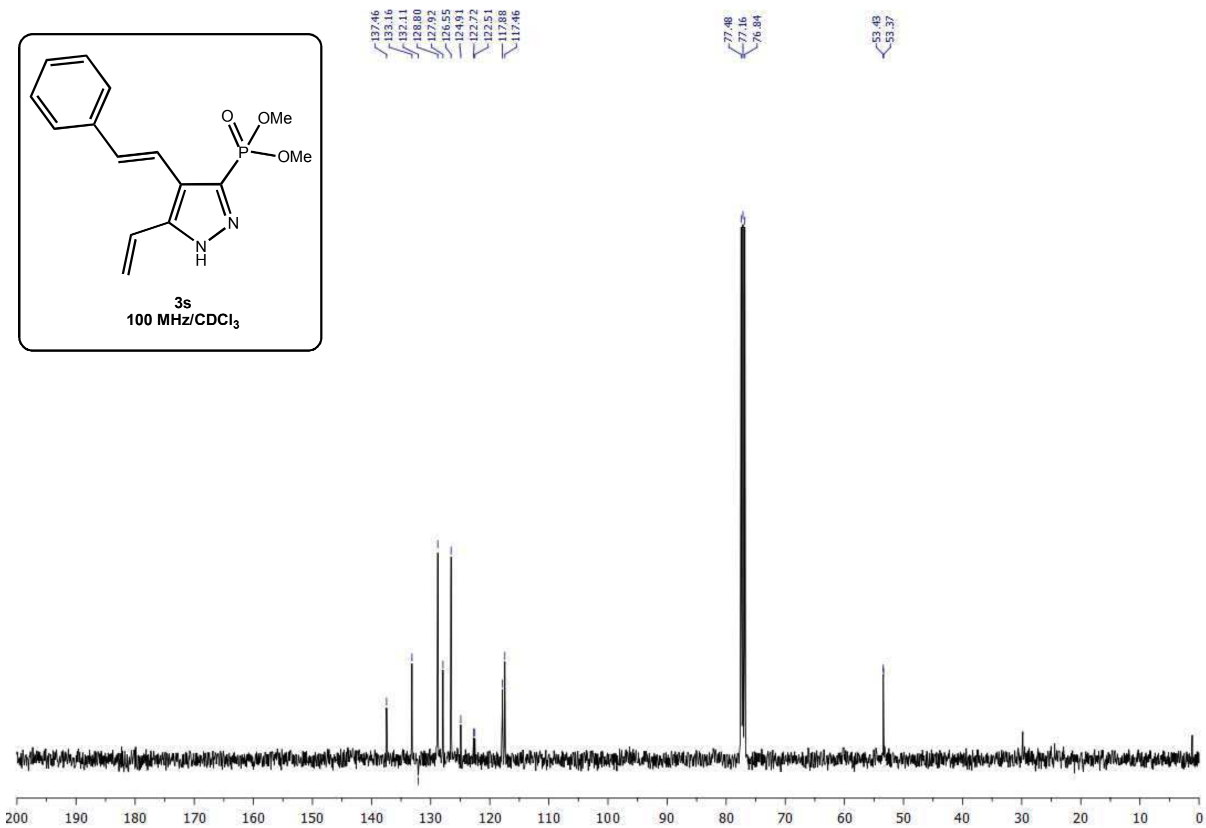
3r
400 MHz/$CDCl_3$

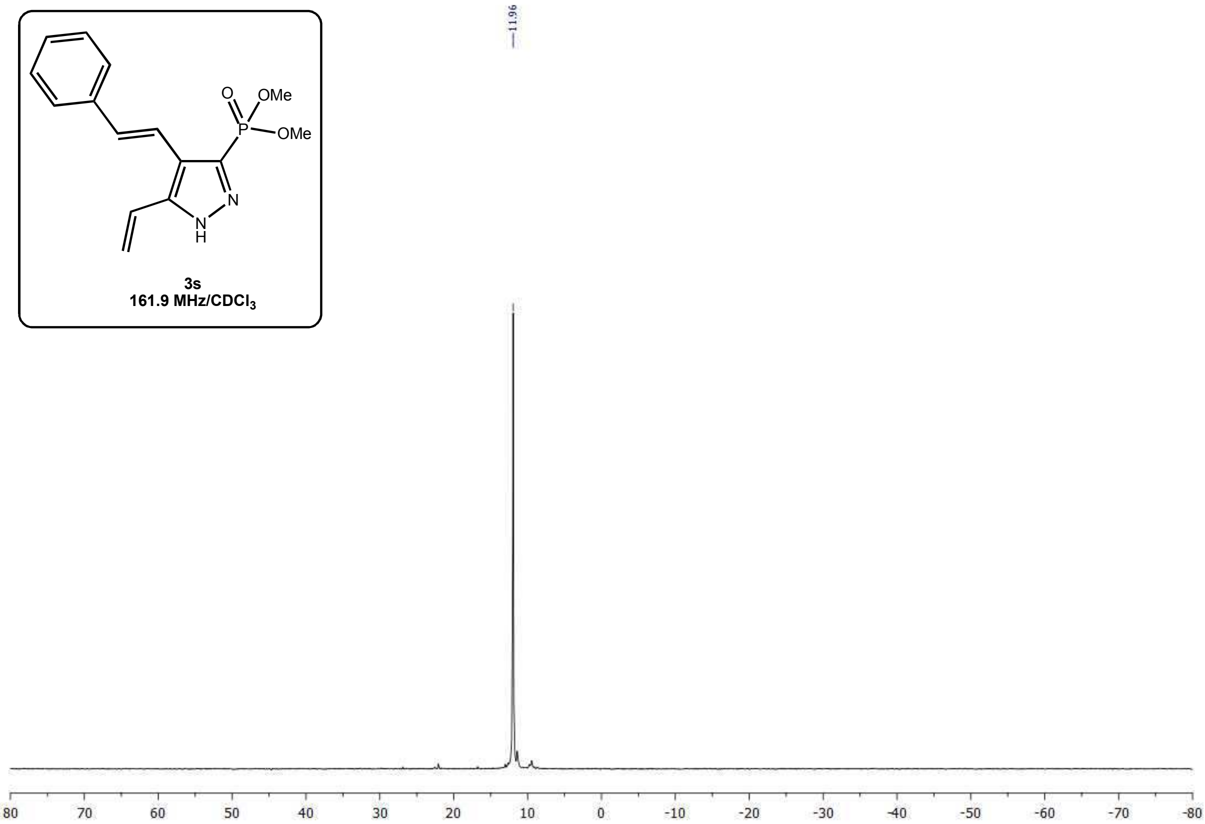



143.67
125.72
125.50
124.50
116.03
77.48
77.16
76.84
54.97
27.58
25.07
24.49
22.64
14.09
O
OMe
P
OMe
N
N
H
3r
100 MHz/CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

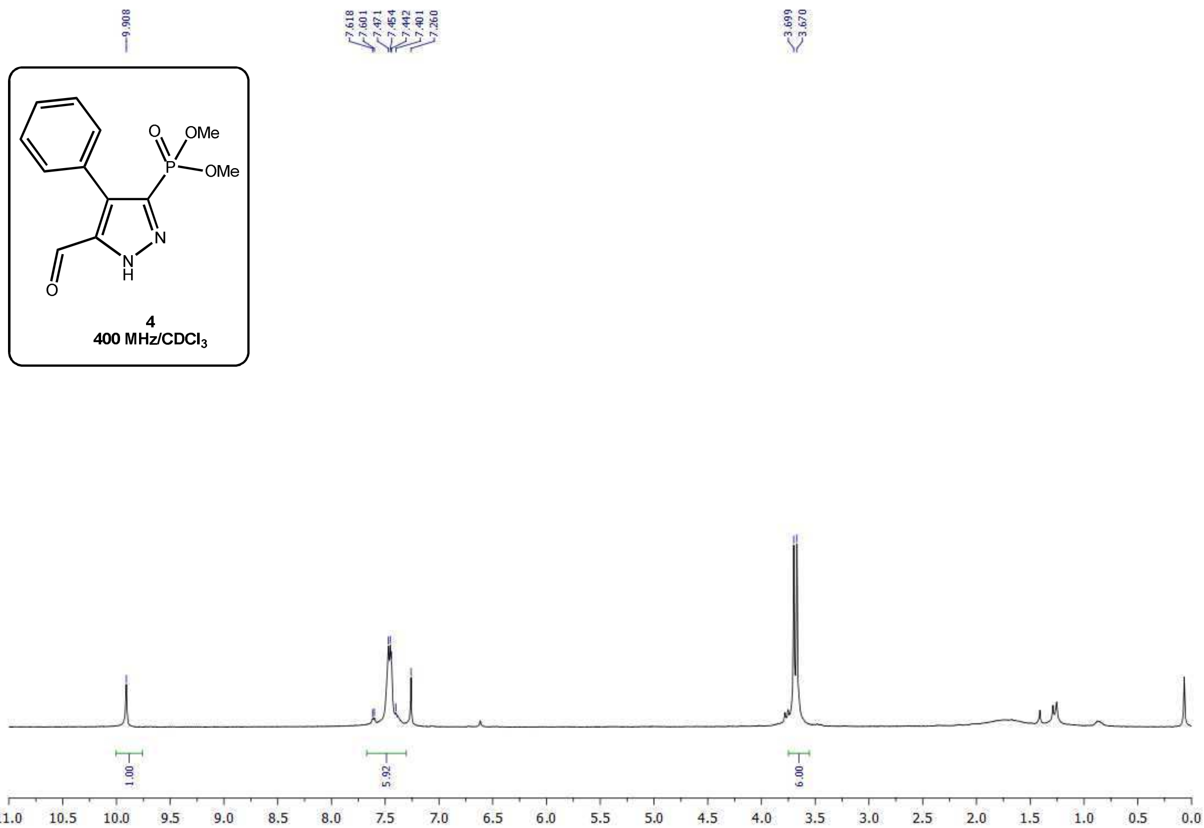

12.829
O
OMe
P
OMe
N
N
H
3r
161.9 MHz/CDCl3
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80


7.497
7.479
7.374
7.355
7.336
7.286
7.267
7.260
7.205
7.164
6.968
6.927
6.872
6.844
6.828
6.799
5.981
5.937
5.502
5.473
3.845
3.816
O
OMe
P
OMe
N
N
H
3s
400 MHz/CDCl$_3$
2.21
2.38
1.93
1.10
1.01
0.99
1.00
1.00
6.56

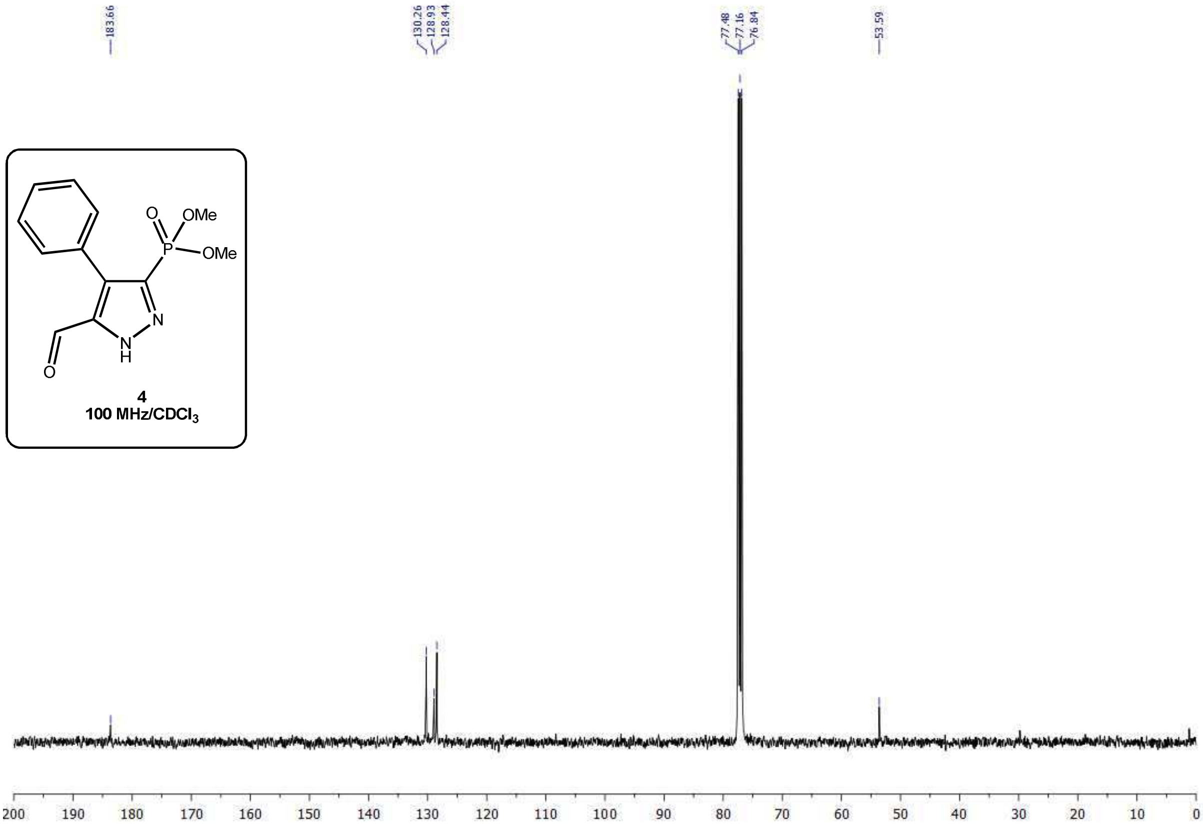

137.46
133.16
132.11
128.80
127.92
126.55
124.91
122.72
122.51
117.88
117.46
77.48
77.16
76.84
53.43
53.37
O
OMe
P
OMe
N
N
H
3s
100 MHz/CDCl$_3$



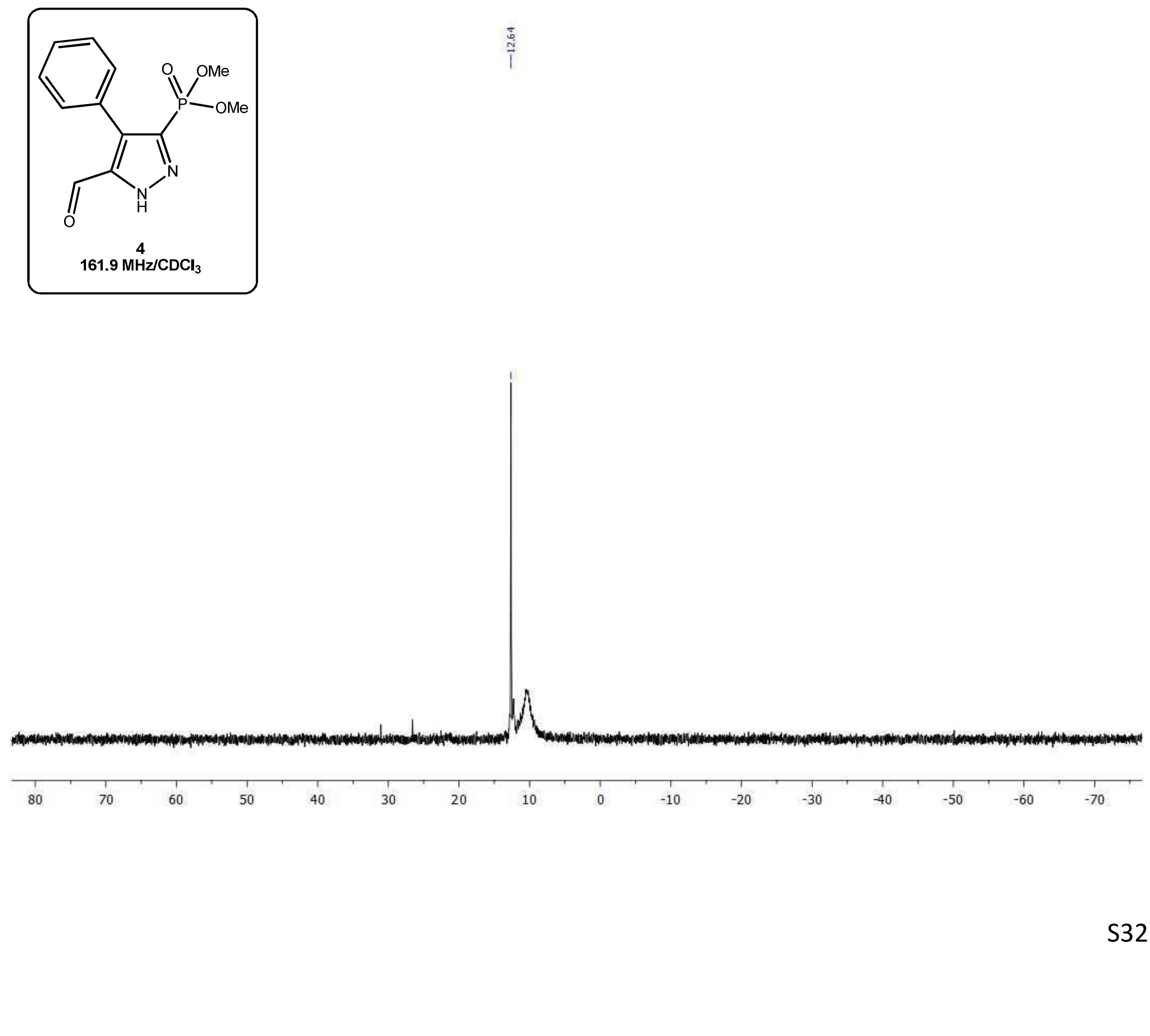
11.96
O
OMe
P
OMe
N
N
H
3s
161.9 MHz/CDCl3
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80



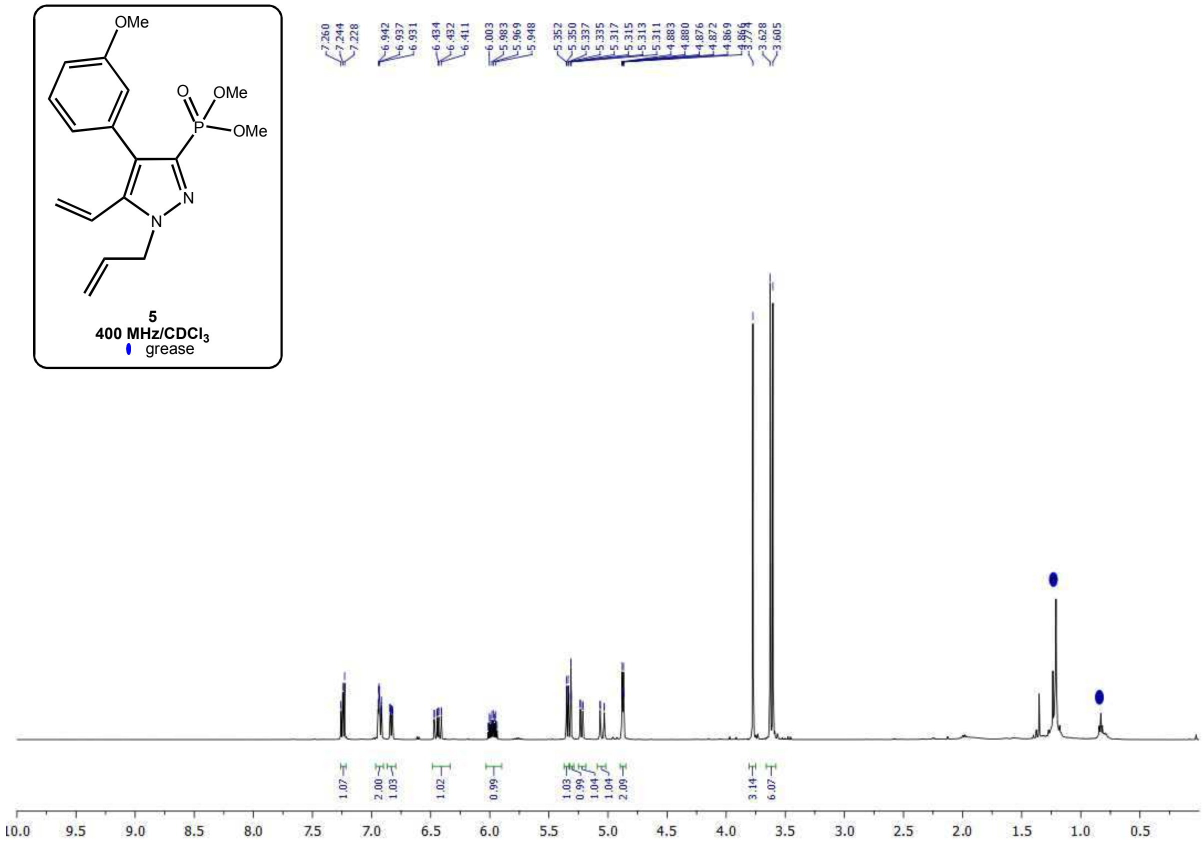
9.908
7.618 7.601 7.471 7.454 7.442 7.401 7.260
3.699 3.670
O
OMe
P
OMe
N
N
H
O
4
400 MHz/CDCl3
1.00
5.92
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

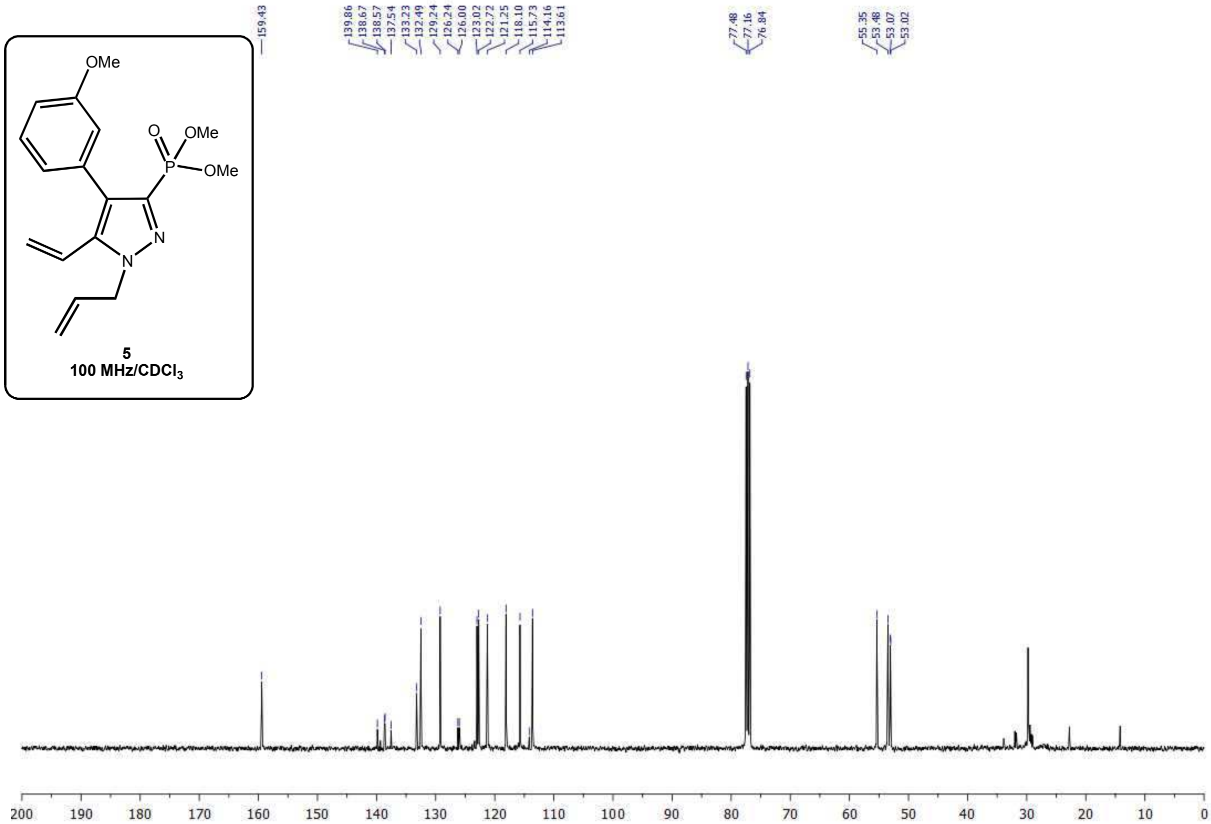


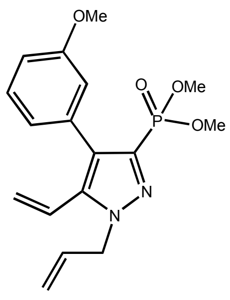
183.66
130.26
128.93
128.44
77.48
77.16
76.84
53.59
OMe
OMe
P
O
N
N
H
O
4
100 MHz/CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



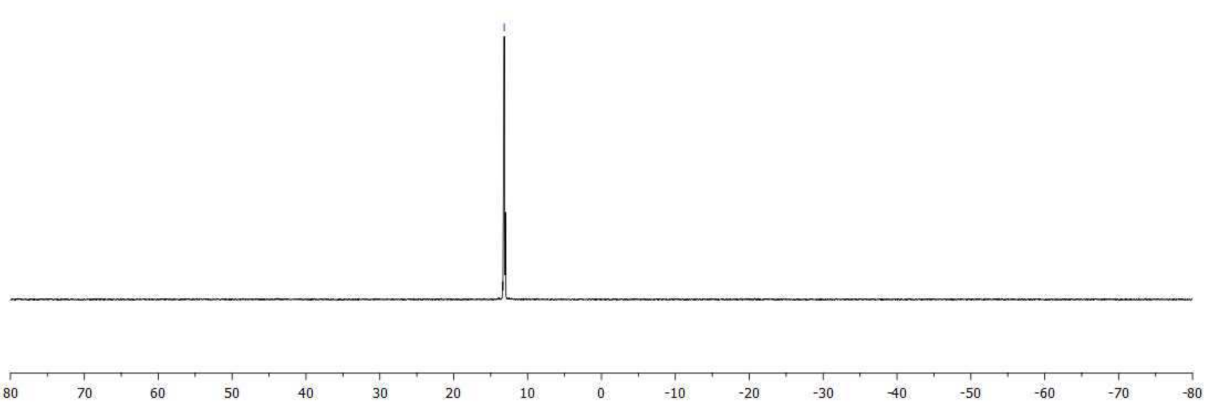
12.64
OMe
OMe
P
O
N
N
H
O
4
161.9 MHz/CDCl$_3$
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70

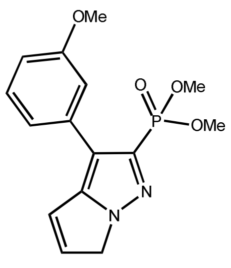

OMe
O
P
OMe
OMe
N
N
5
400 MHz/CDCl$_3$
grease


OMe
O
P
OMe
OMe
N
N
5
100 MHz/CDCl$_3$

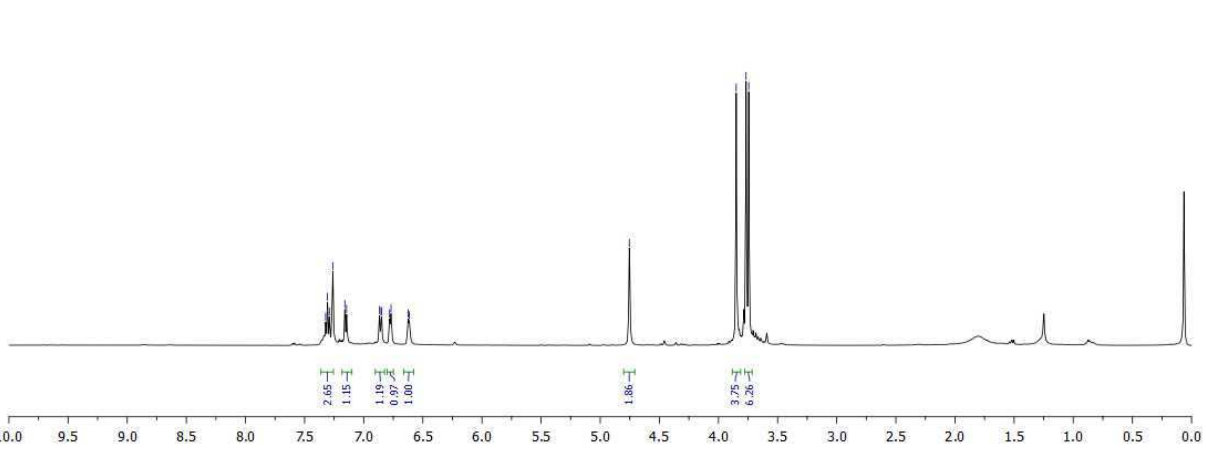


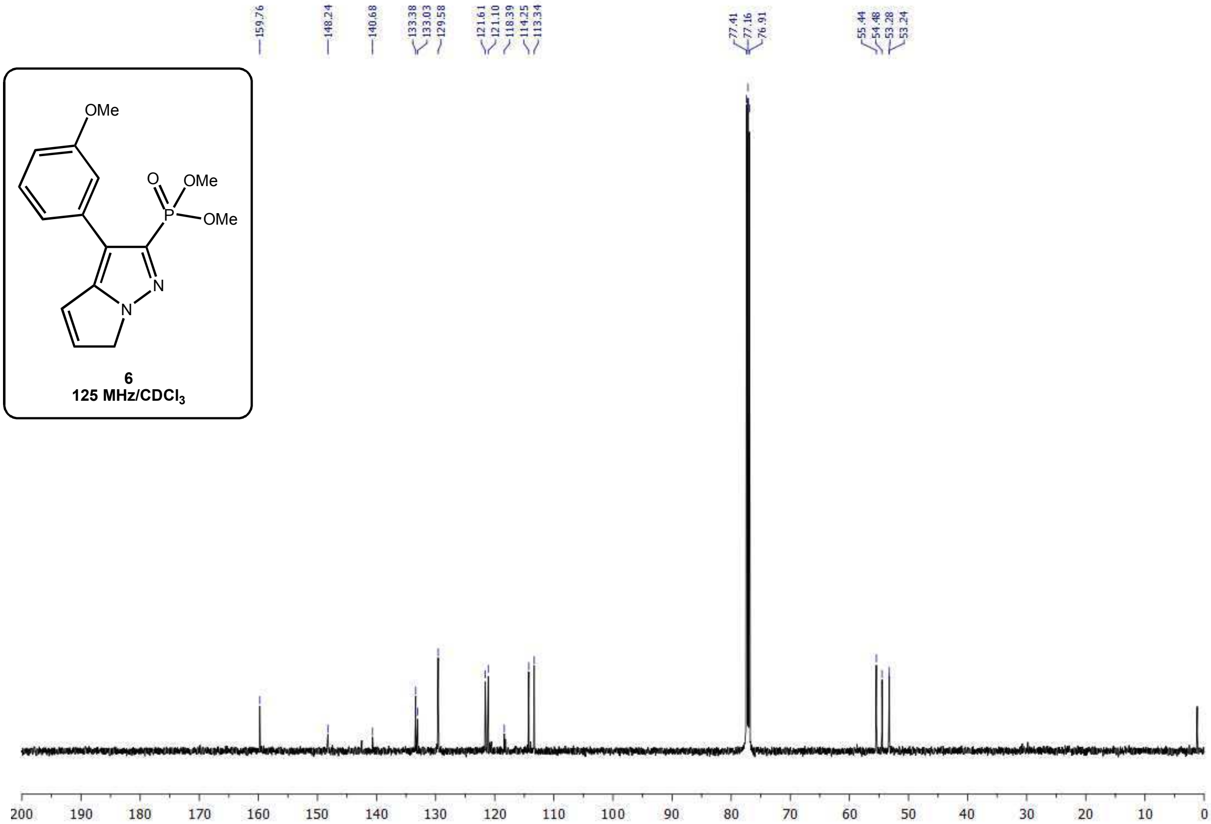
5
161.9 MHz/$CDCl_3$

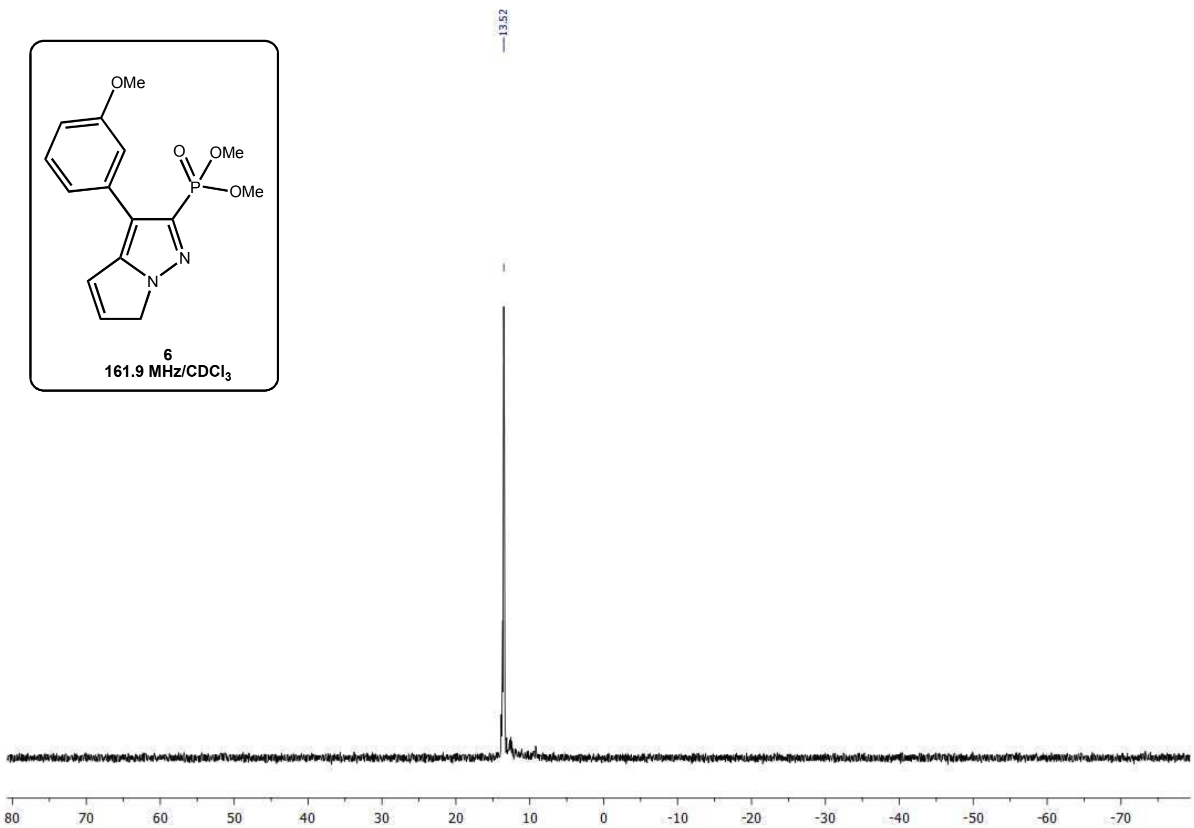




6
500 MHz/$CDCl_3$




6
125 MHz/CDCl3


6
161.9 MHz/CDCl3