

Synthesis of 2-oxophosphorindolines *via* the copper-catalyzed intramolecular aromatic C-H insertion of diazophosphonamidates

Peipei Huang and Jiaxi Xu*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, P. R. China

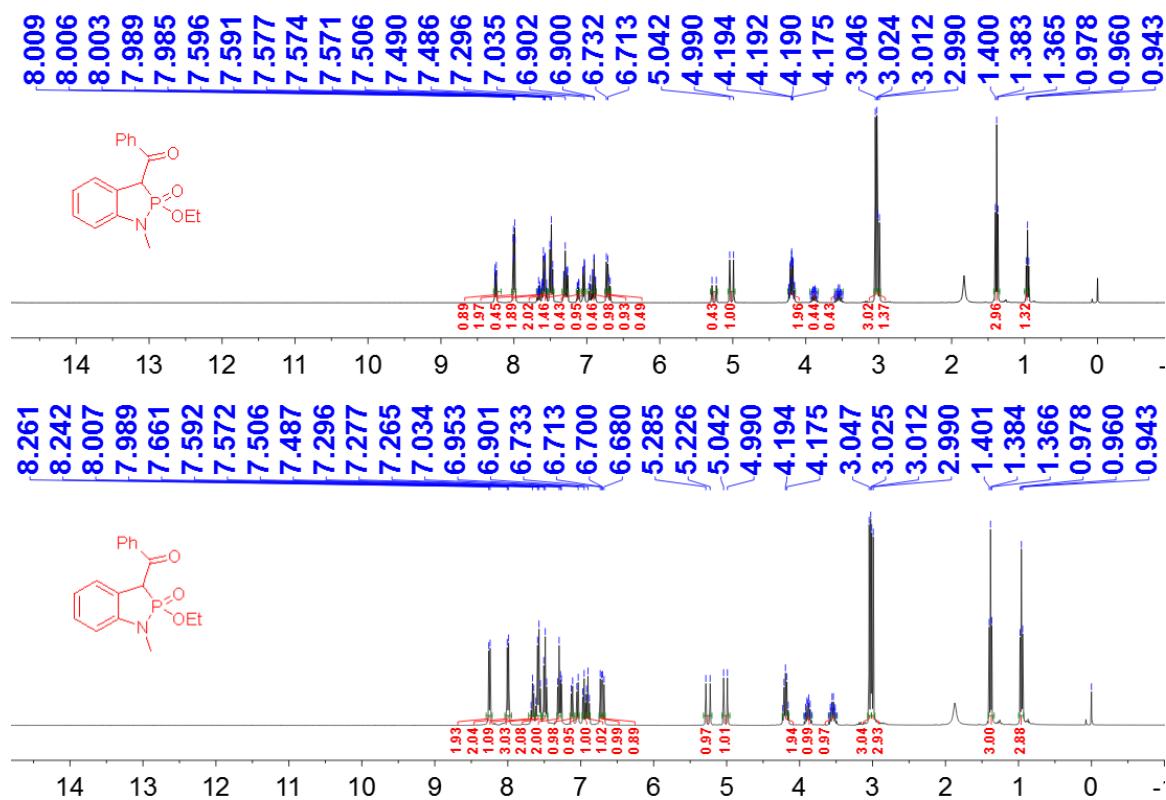
Fax: +86 10 64435565

E-mail: jxxu@mail.buct.edu.cn

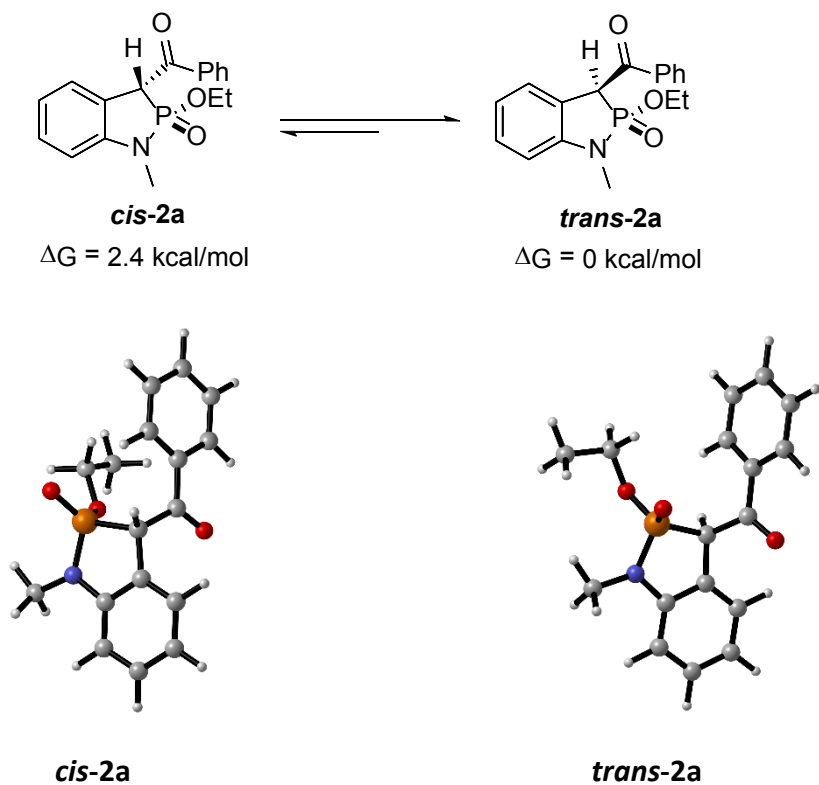
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1. Figure S1. ^1H NMR spectra of diastereomeric 2a after standing for a period of time



2. Figure S2. Structures and free energies (ΔG) calculated at the M06-2X/6-311++G(d,p)/SMD(Toluene)//M06-2X/6-31G(d)/SMD(Toluene) level.



<i>trans-2a</i>			
C	-4.525796	-1.529742	-0.209498
C	-4.028126	-0.246878	0.025054
H	-4.697068	0.567997	0.281351
H	-5.595438	-1.701897	-0.136829
C	-3.675045	-2.584098	-0.525034
H	-4.076868	-3.577226	-0.695852
C	-2.297819	-2.365760	-0.613364
H	-1.624304	-3.185368	-0.843247
C	-1.787091	-1.097093	-0.393372
C	-2.655771	-0.039502	-0.071855
N	-2.010794	1.189799	0.125182
C	-2.726750	2.371400	0.565785
H	-3.515609	2.617937	-0.151441
H	-3.169481	2.228937	1.558012
H	-2.031815	3.213534	0.608044
P	-0.345700	1.019849	0.252673
O	0.297051	1.179747	1.579319
O	0.227556	2.045370	-0.849165
C	1.362668	2.880743	-0.526674
H	2.048124	2.332781	0.125296
H	1.855442	3.066495	-1.484448

C	0.908691	4.169902	0.123036
H	0.184612	4.687925	-0.512644
H	0.455352	3.965037	1.097437
H	1.767129	4.830810	0.278894
C	-0.340719	-0.671622	-0.487738
H	-0.046092	-0.563188	-1.538934
C	0.663412	-1.571505	0.229706
O	0.291539	-2.468944	0.952794
C	2.121902	-1.299573	0.019116
C	3.036323	-2.045503	0.770400
H	2.653864	-2.785642	1.465478
C	4.400542	-1.830876	0.628234
H	5.104575	-2.410174	1.217295
C	4.865245	-0.867986	-0.267820
H	5.932064	-0.698278	-0.377752
C	3.961878	-0.123516	-1.021372
H	4.320203	0.624729	-1.721610
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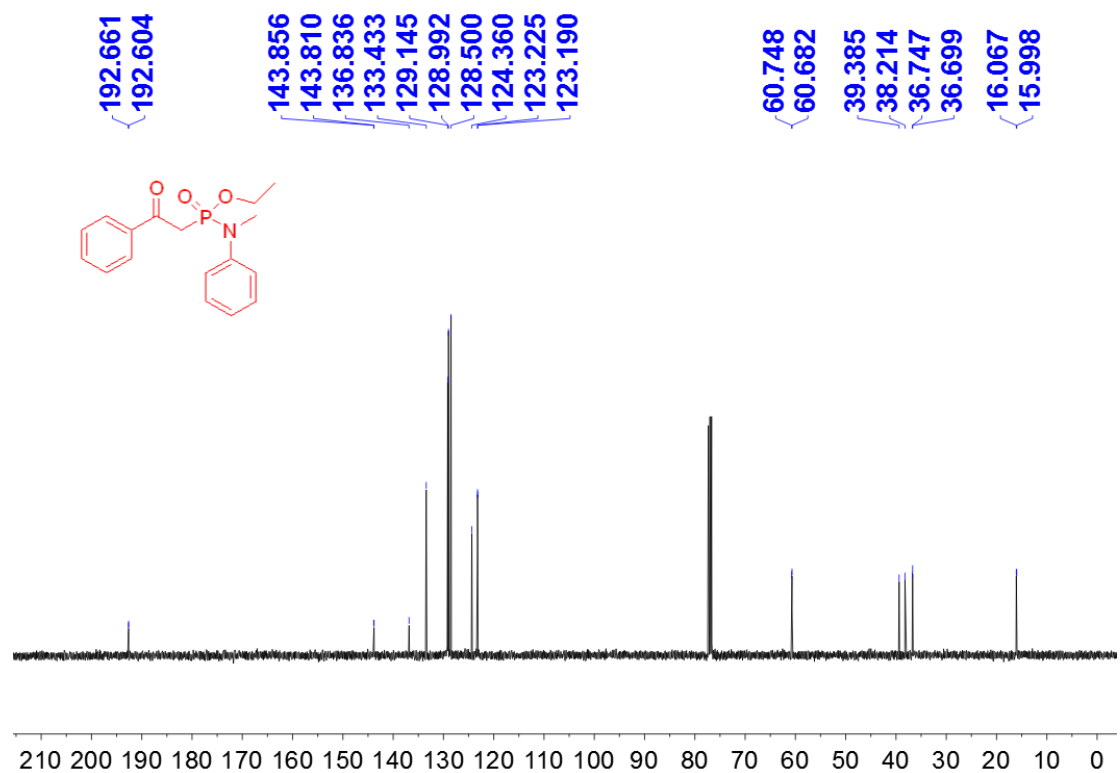
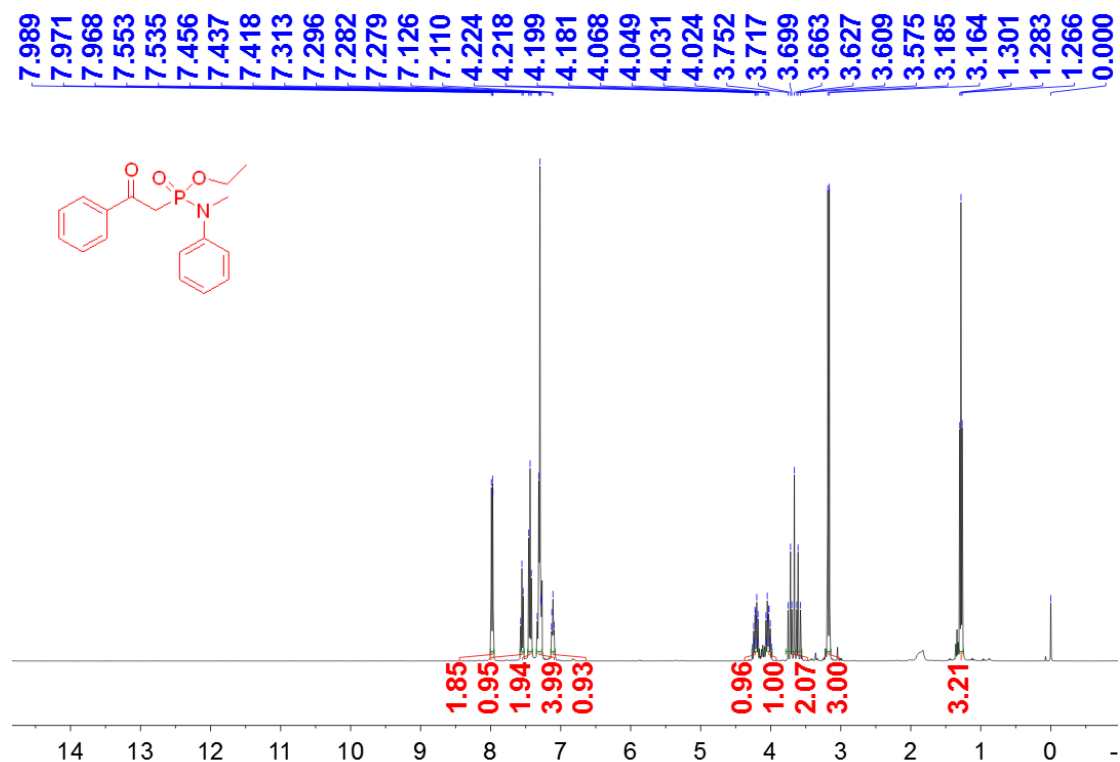
cis-2a

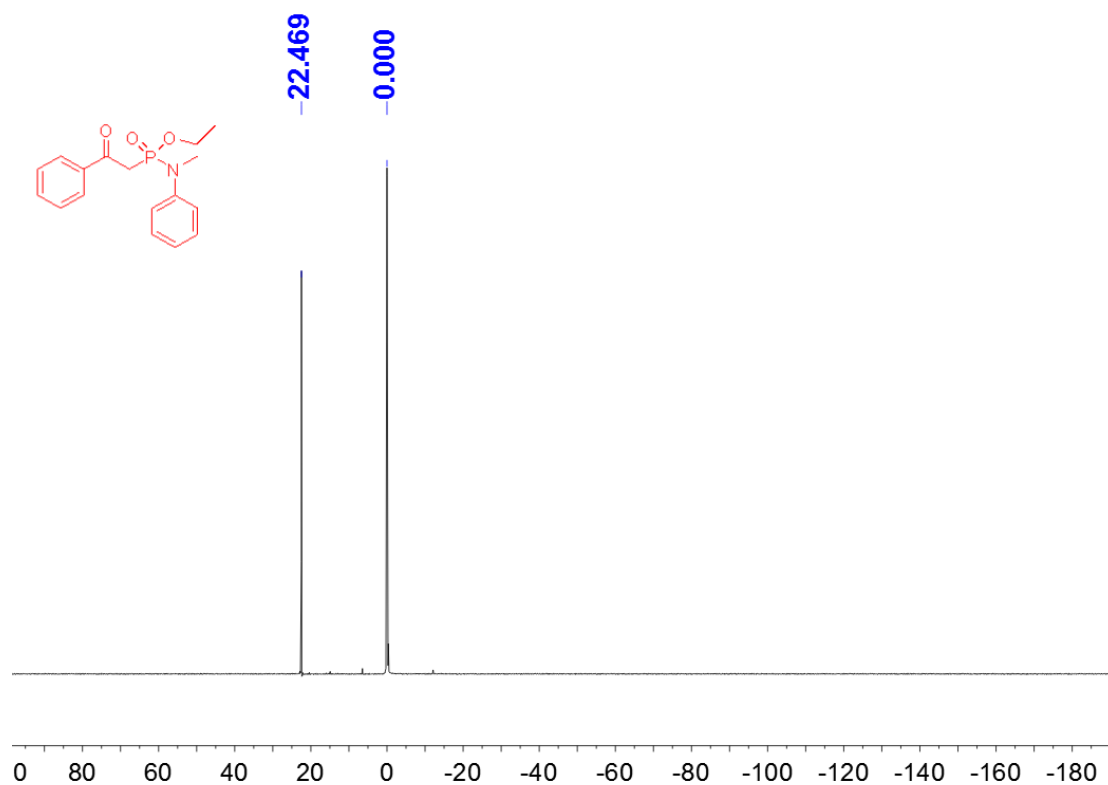
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H	-2.907556	2.226832	2.655938
C	-1.451540	2.122869	1.082540
H	-1.319512	3.202469	0.965310
H	-2.149742	1.778602	0.314172
O	-0.164978	1.490342	0.898478
P	0.412021	1.177663	-0.571119
O	-0.252274	1.956814	-1.642713
N	2.071713	1.336103	-0.412035
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H	2.040109	3.415098	-0.455305
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C	4.061464	-0.031146	0.144818
H	4.701187	0.837508	0.259996
C	4.568117	-1.318202	0.331679
H	5.615738	-1.439788	0.590271
C	3.752555	-2.437283	0.199355
H	4.159150	-3.430832	0.355754
C	2.403196	-2.280676	-0.126783

H	1.754507	-3.146552	-0.215405
C	1.884552	-1.011255	-0.323588
C	0.462501	-0.666164	-0.695993
H	0.258679	-0.913409	-1.745697
C	-0.607374	-1.305156	0.189978
O	-0.304558	-1.960037	1.162883
C	-2.044075	-1.073363	-0.167748
C	-3.013843	-1.512009	0.742420
H	-2.685407	-2.013878	1.647006
C	-4.361623	-1.300064	0.487235
H	-5.108143	-1.637852	1.199194
C	-4.753960	-0.652184	-0.685111
H	-5.807945	-0.484875	-0.885687
C	-3.796366	-0.219832	-1.598225
H	-4.098720	0.284871	-2.510118
C	-2.442515	-0.428024	-1.343782
H	-1.712524	-0.061916	-2.058319

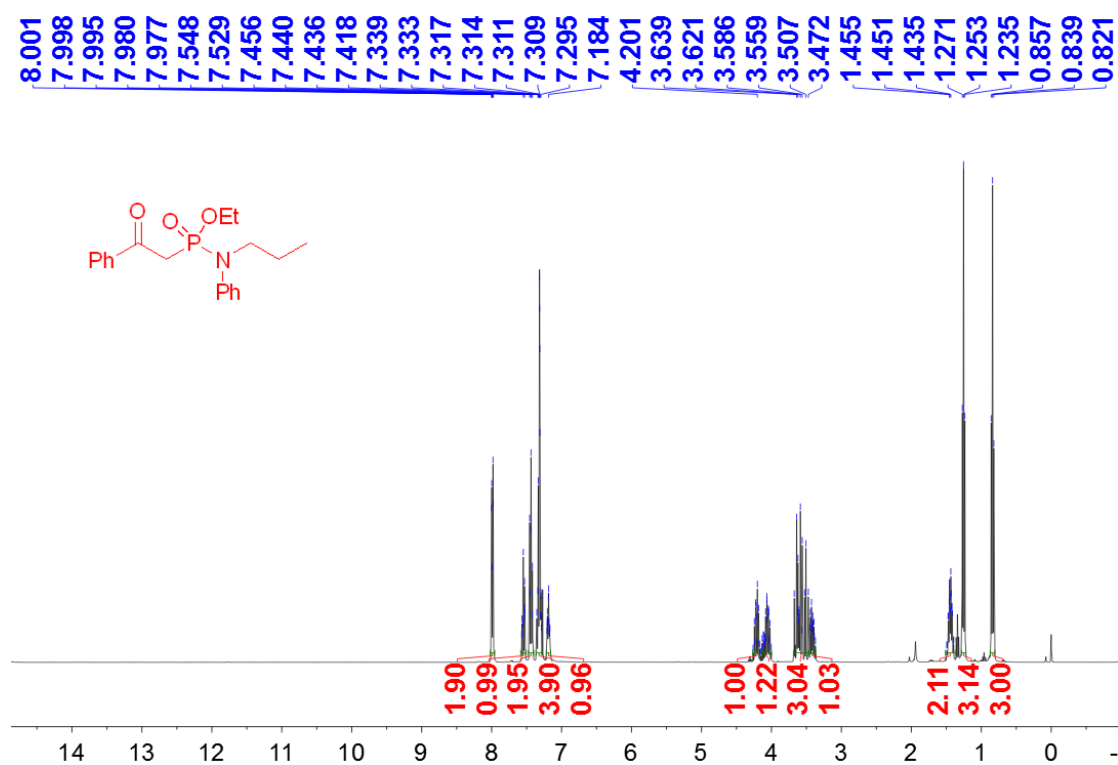
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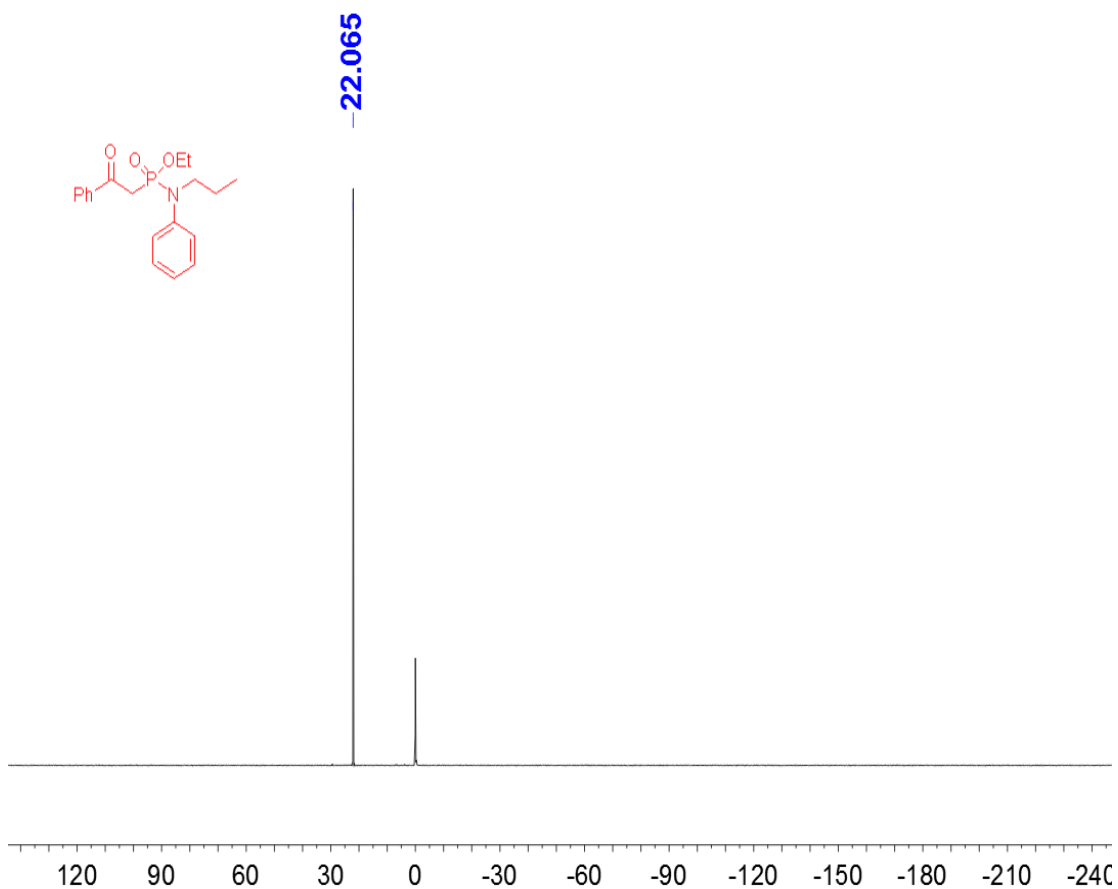
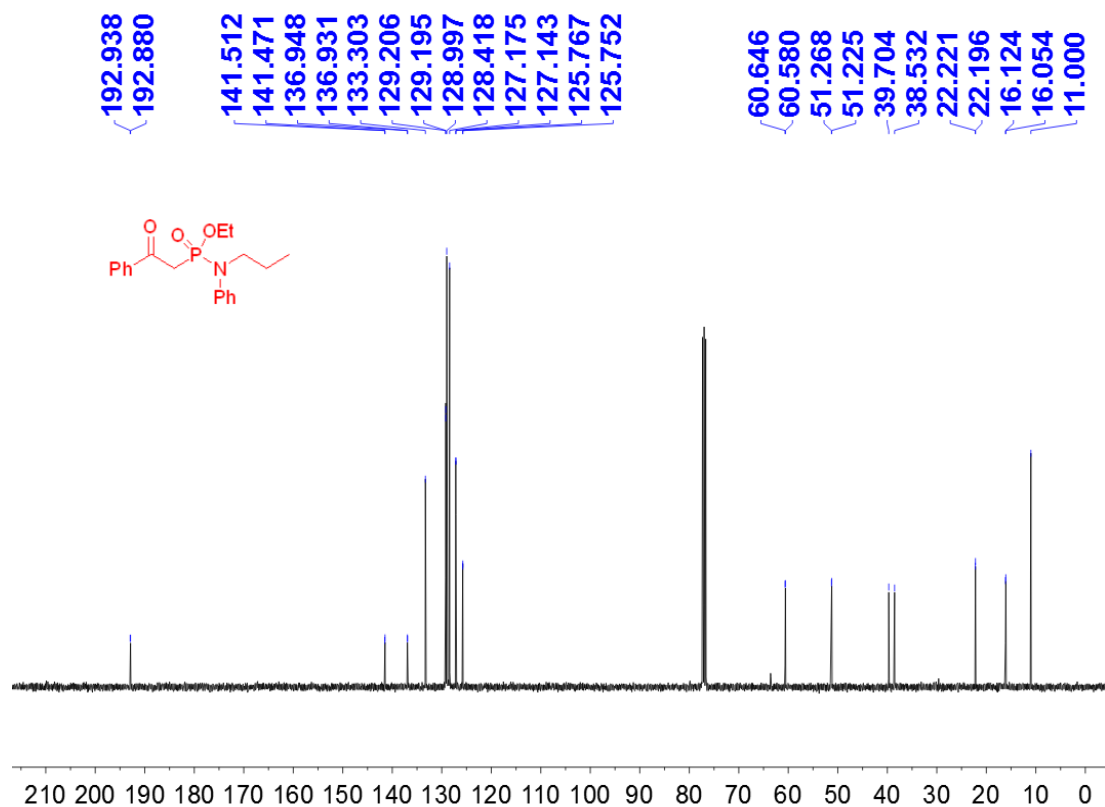
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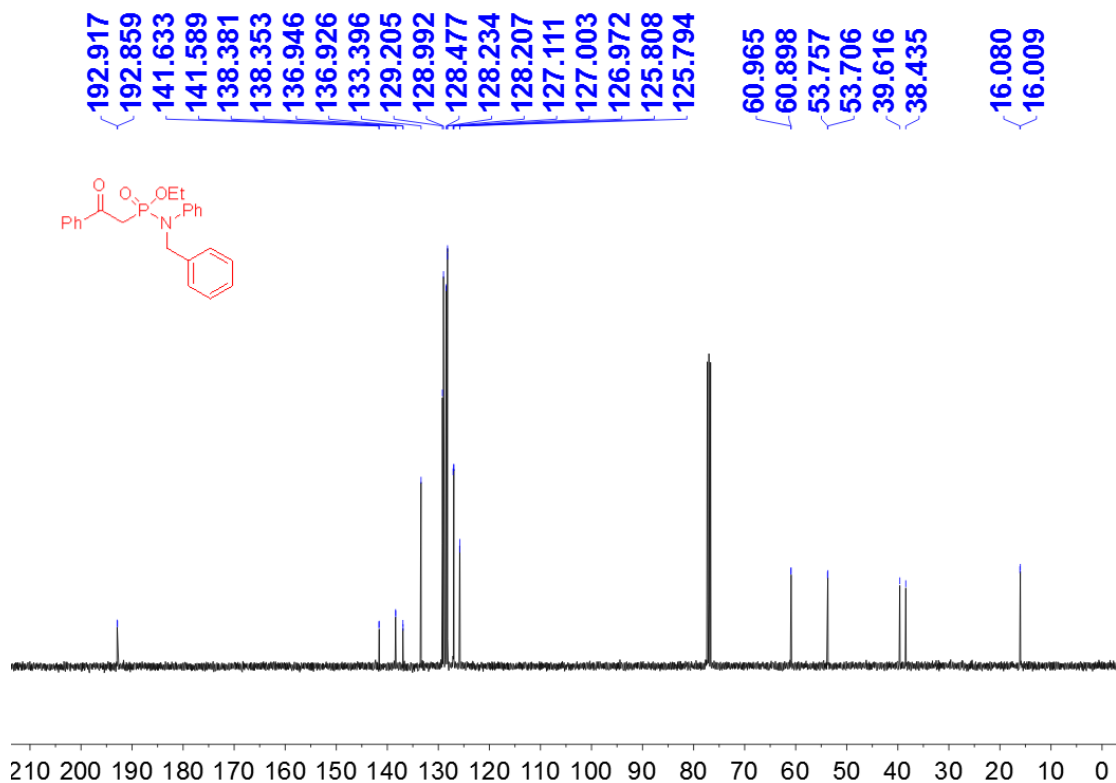
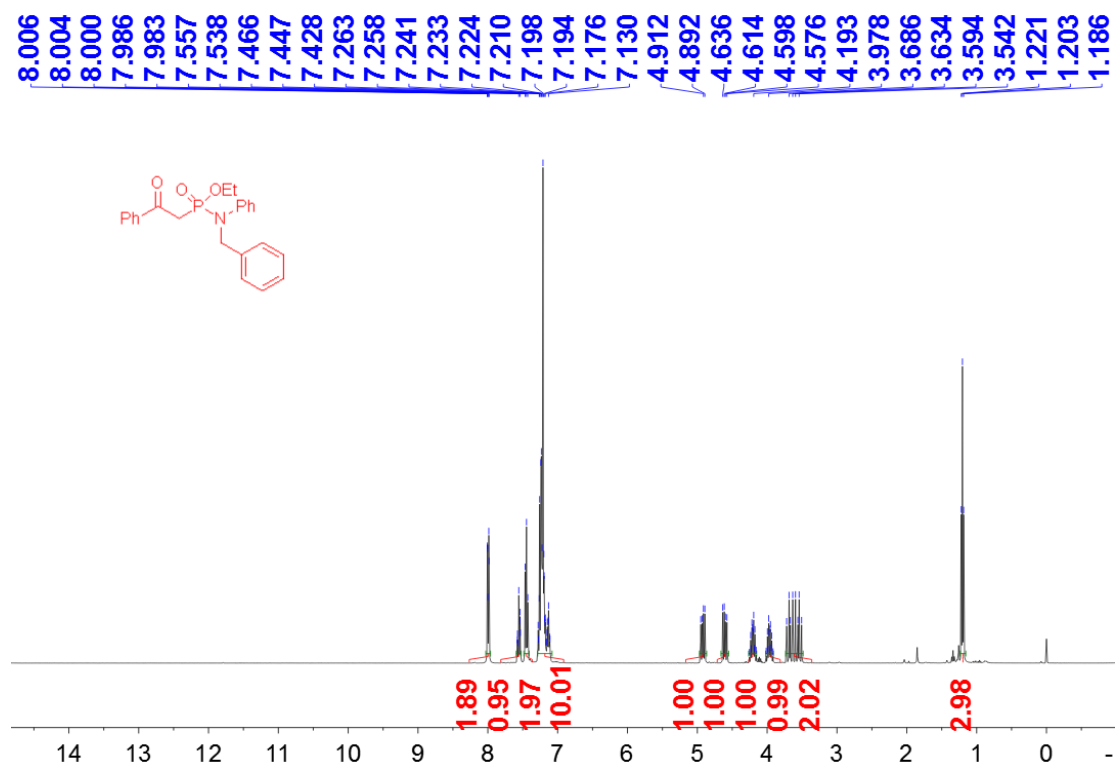


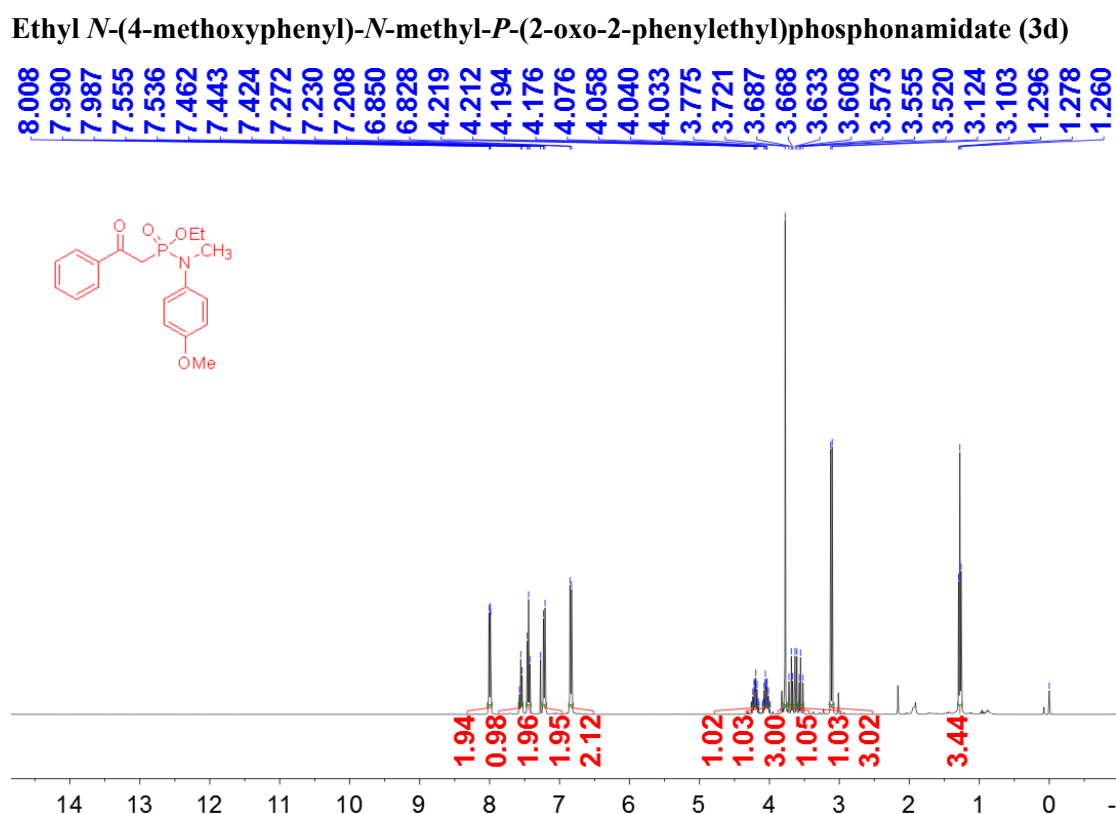
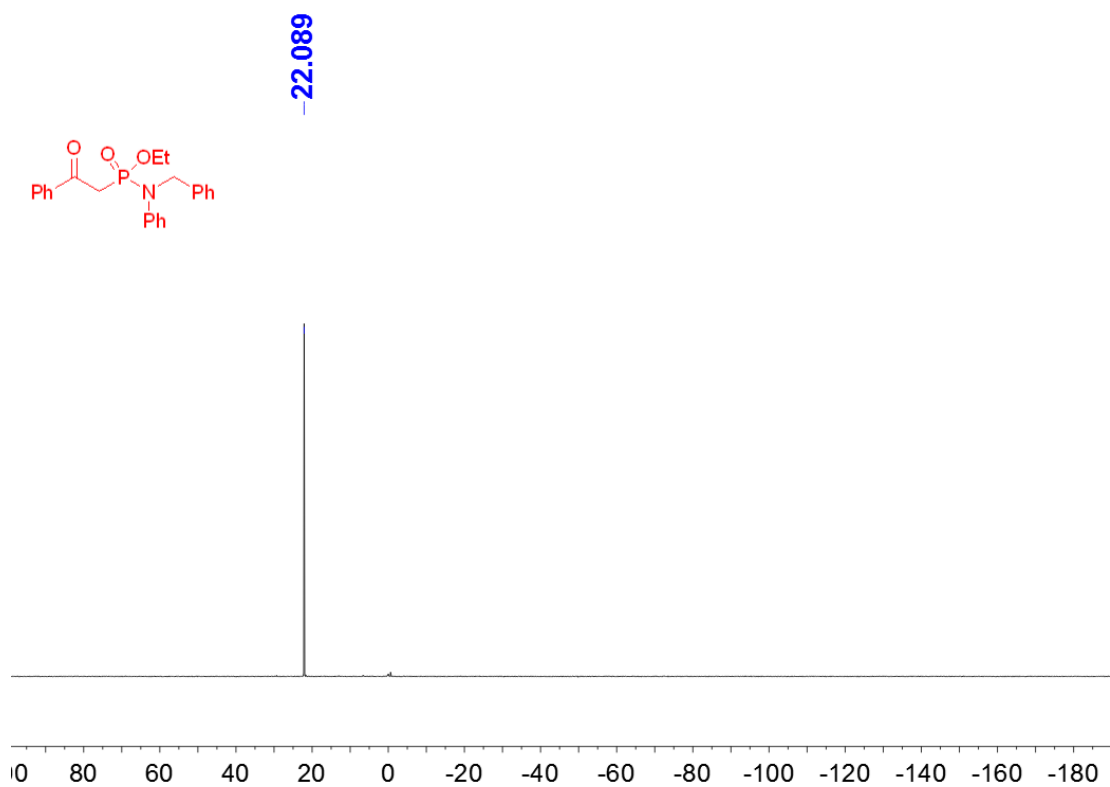
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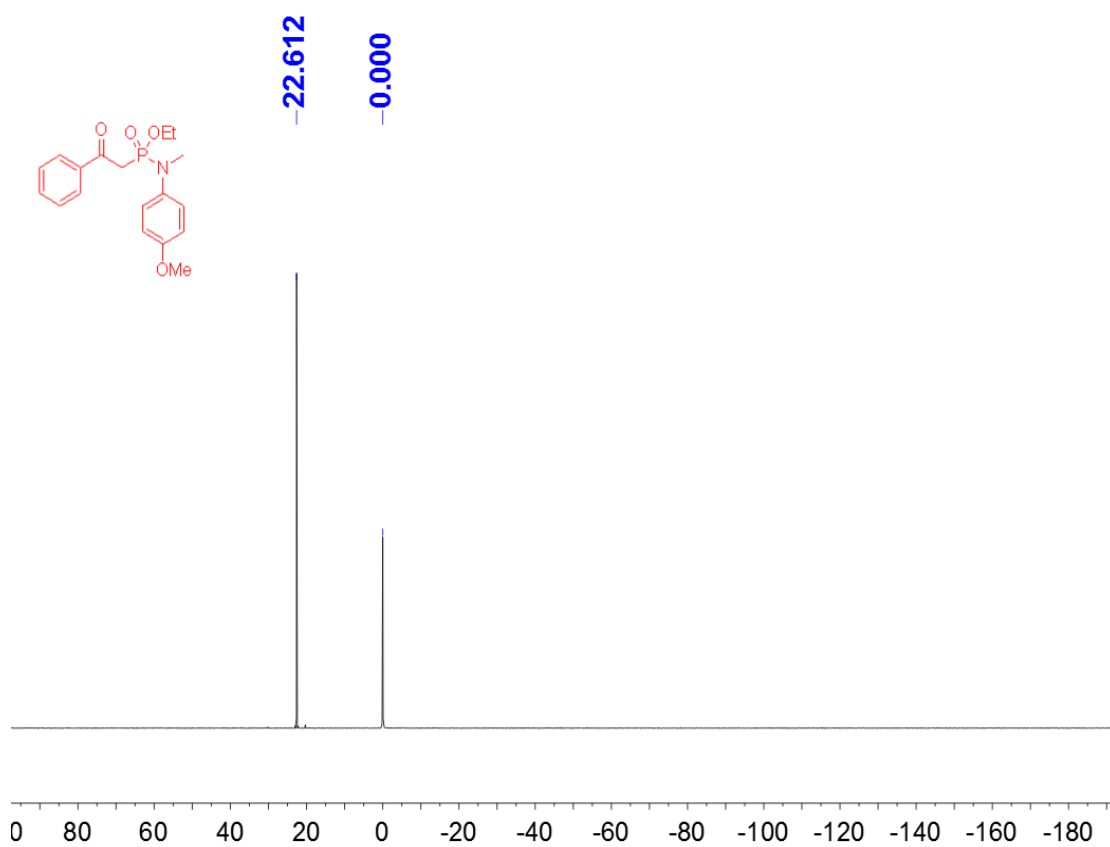
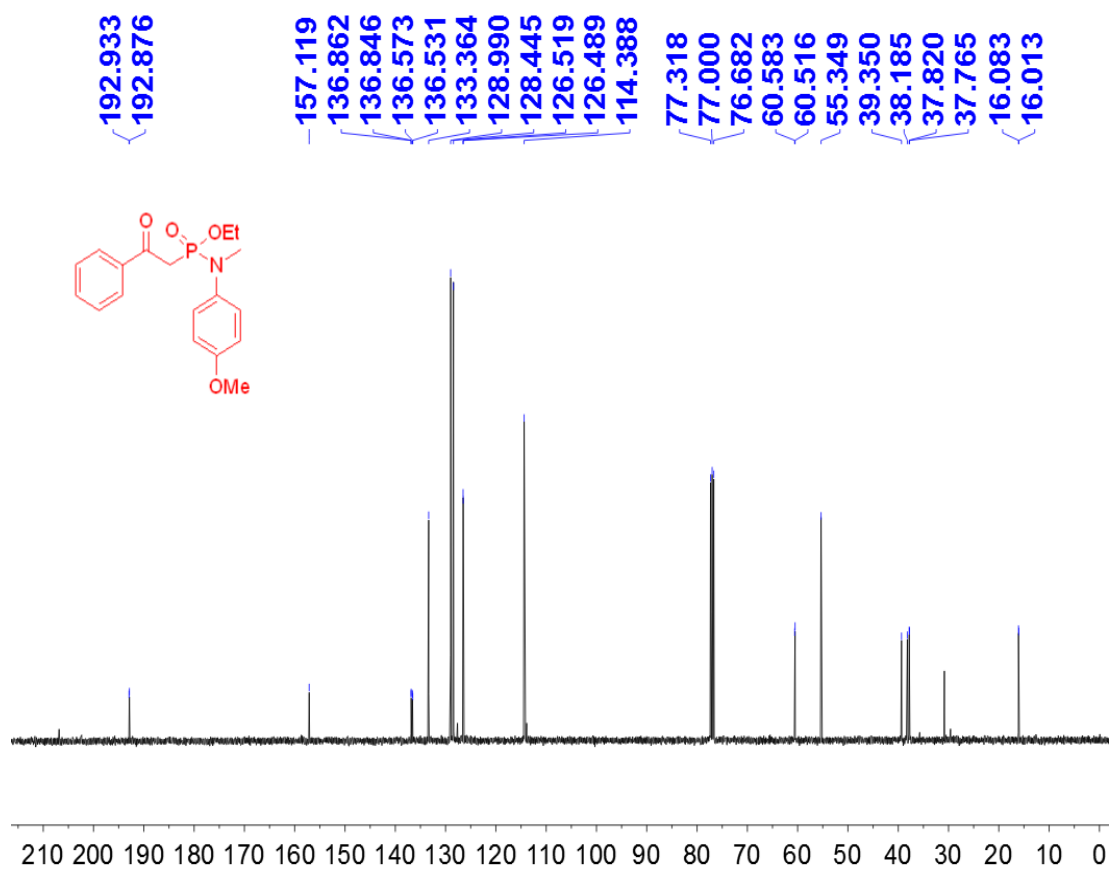




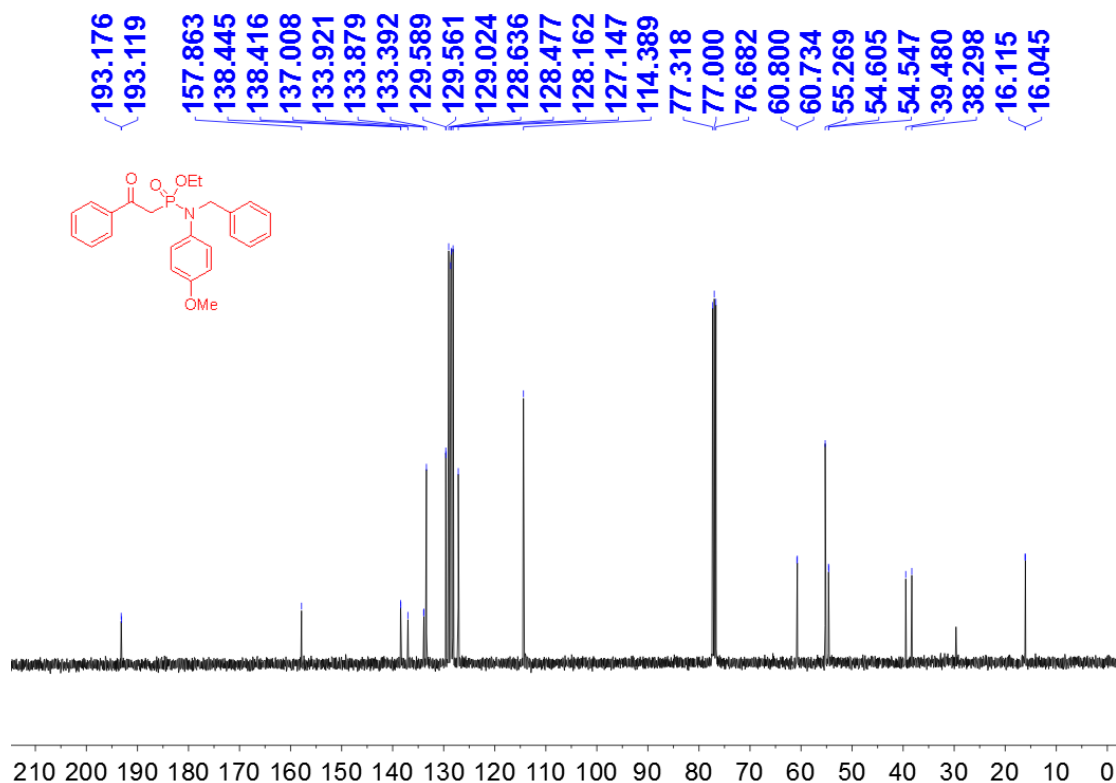
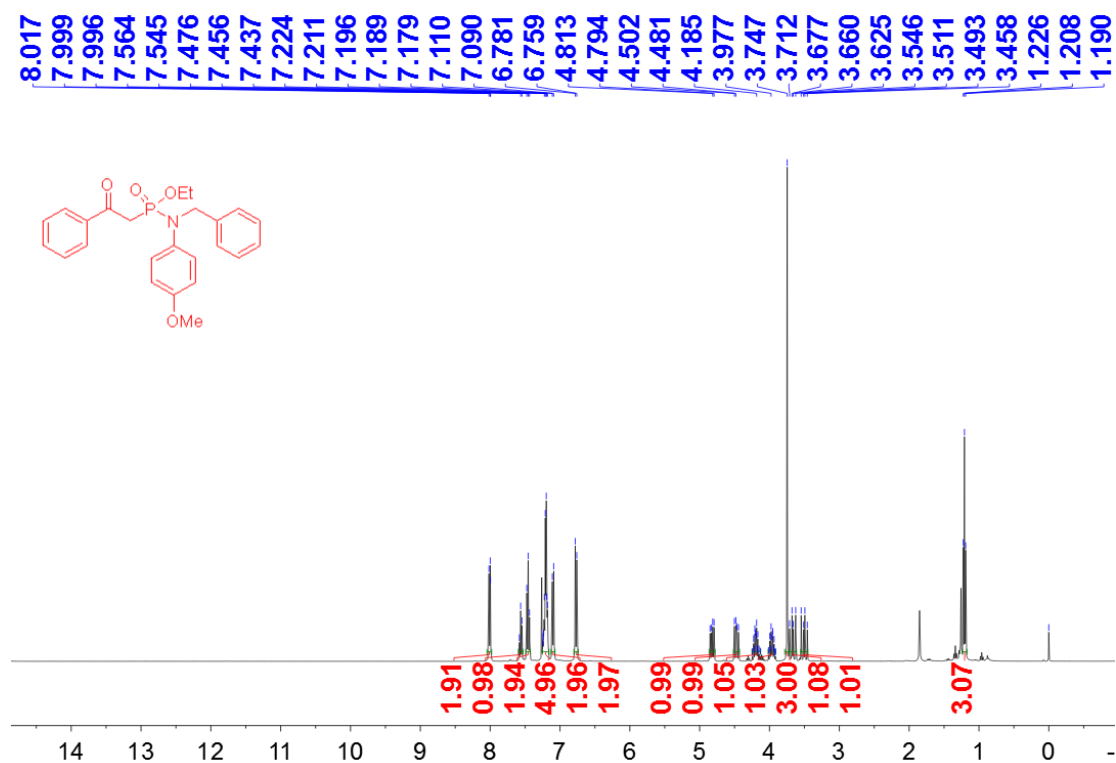
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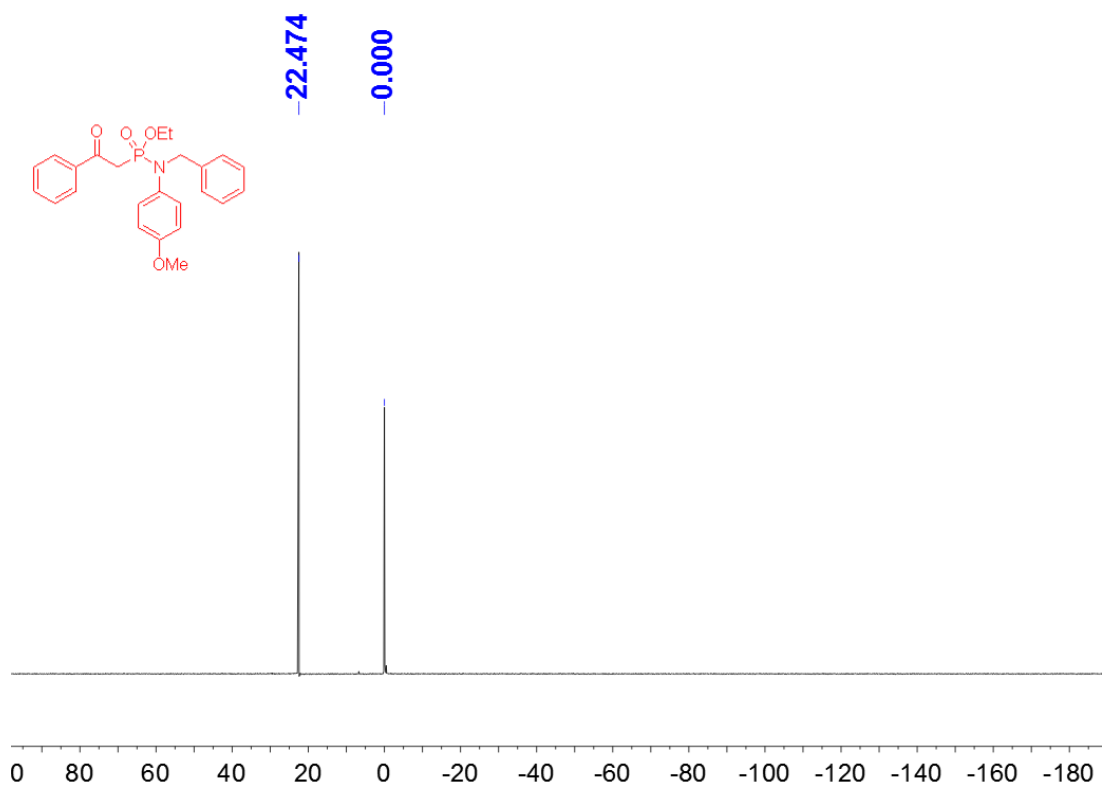




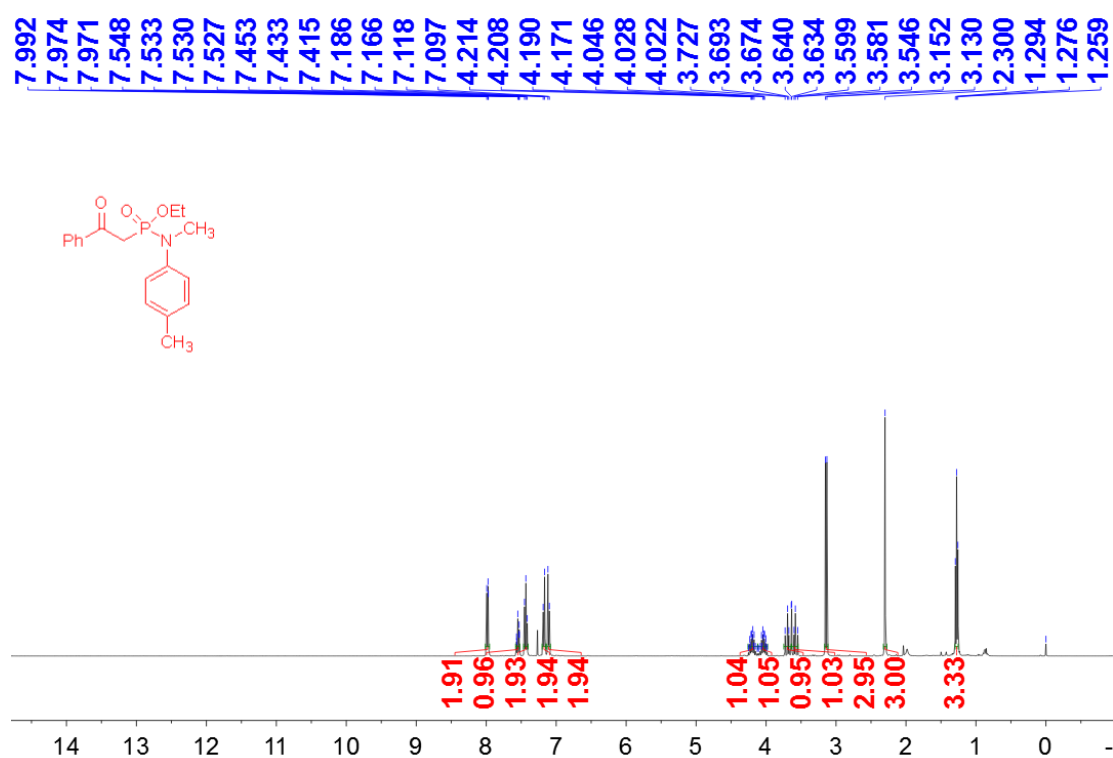


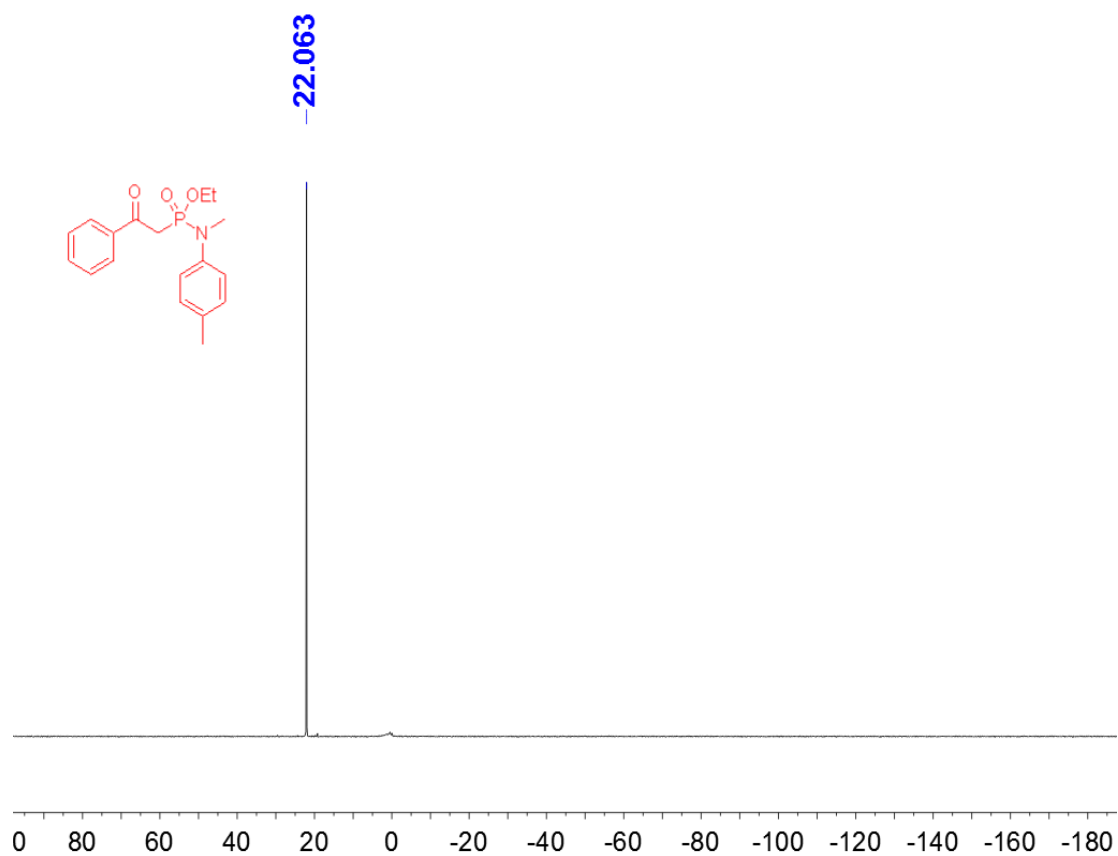
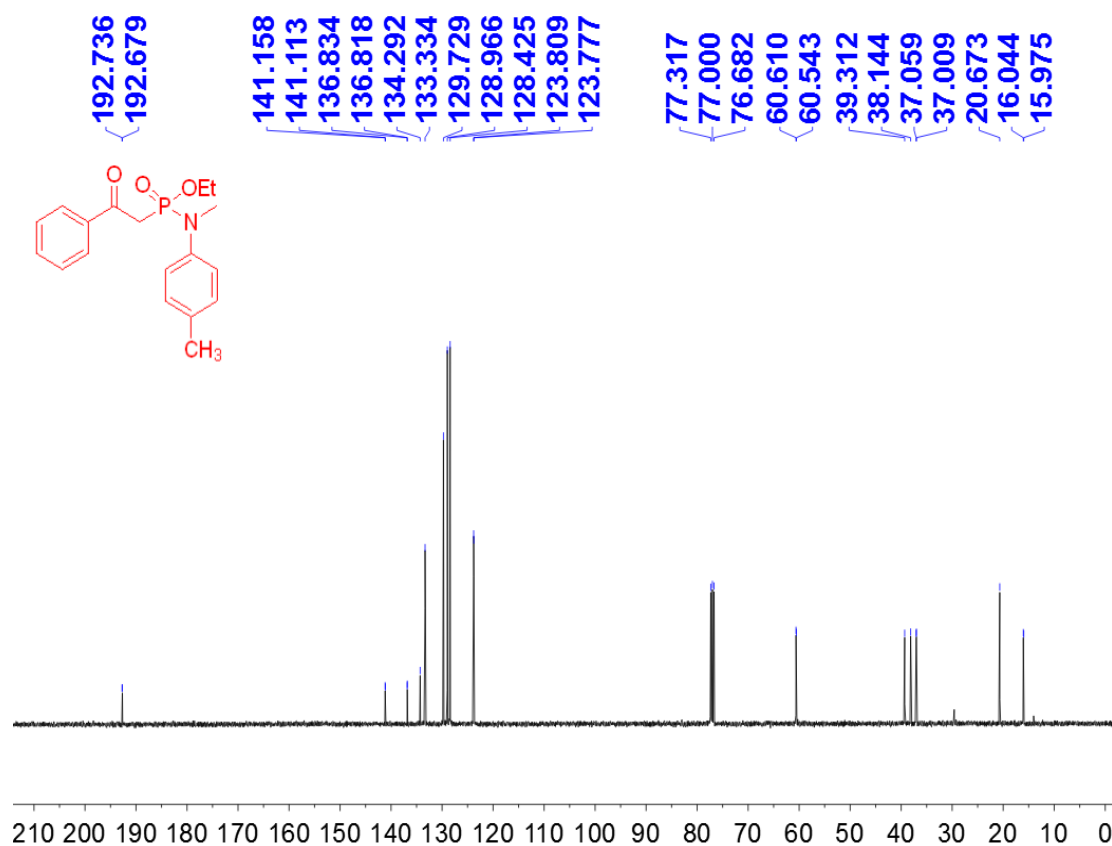
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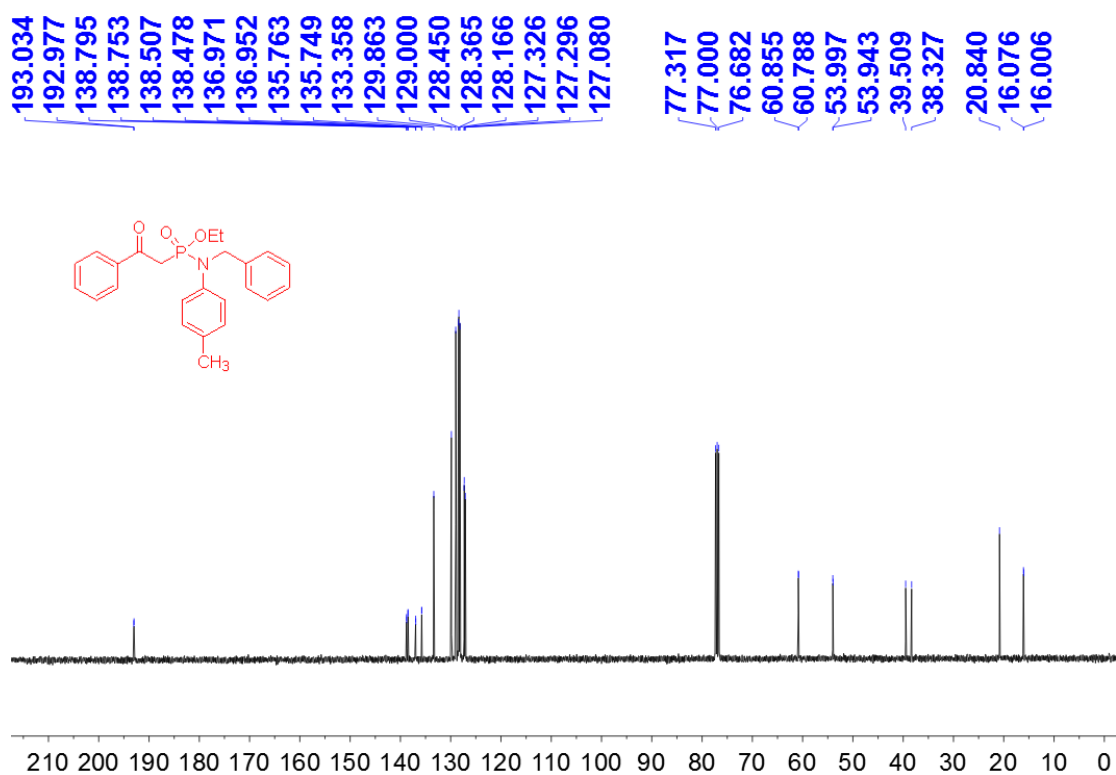
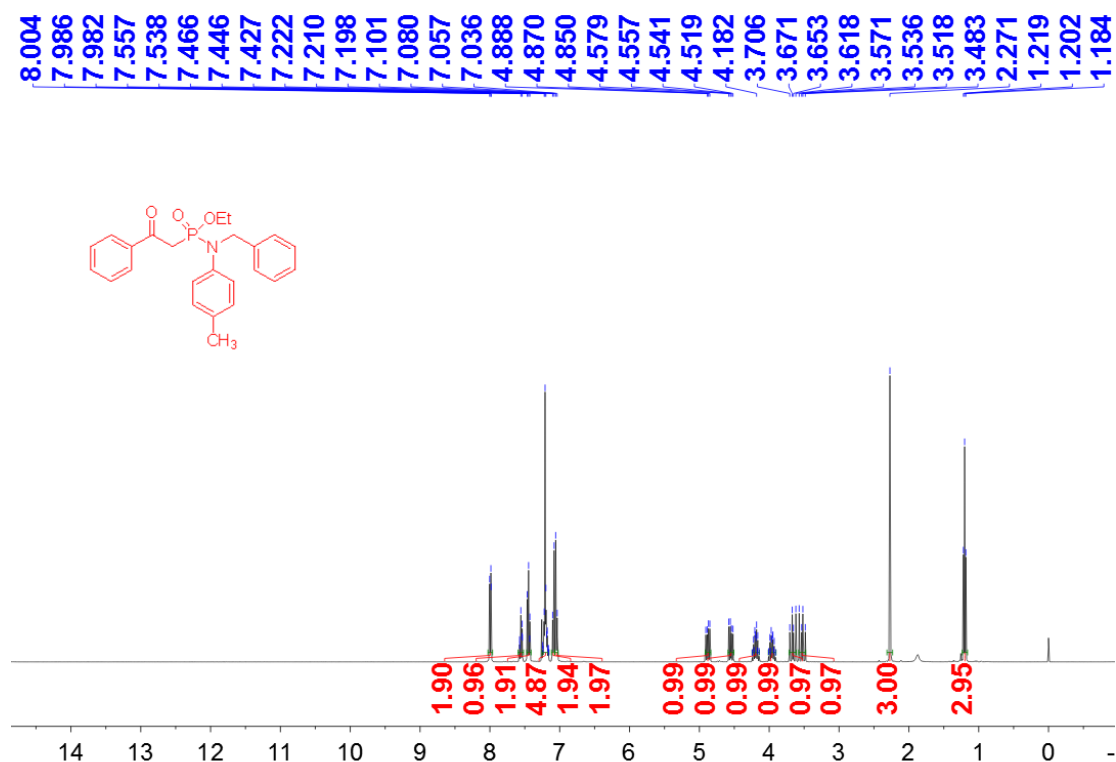


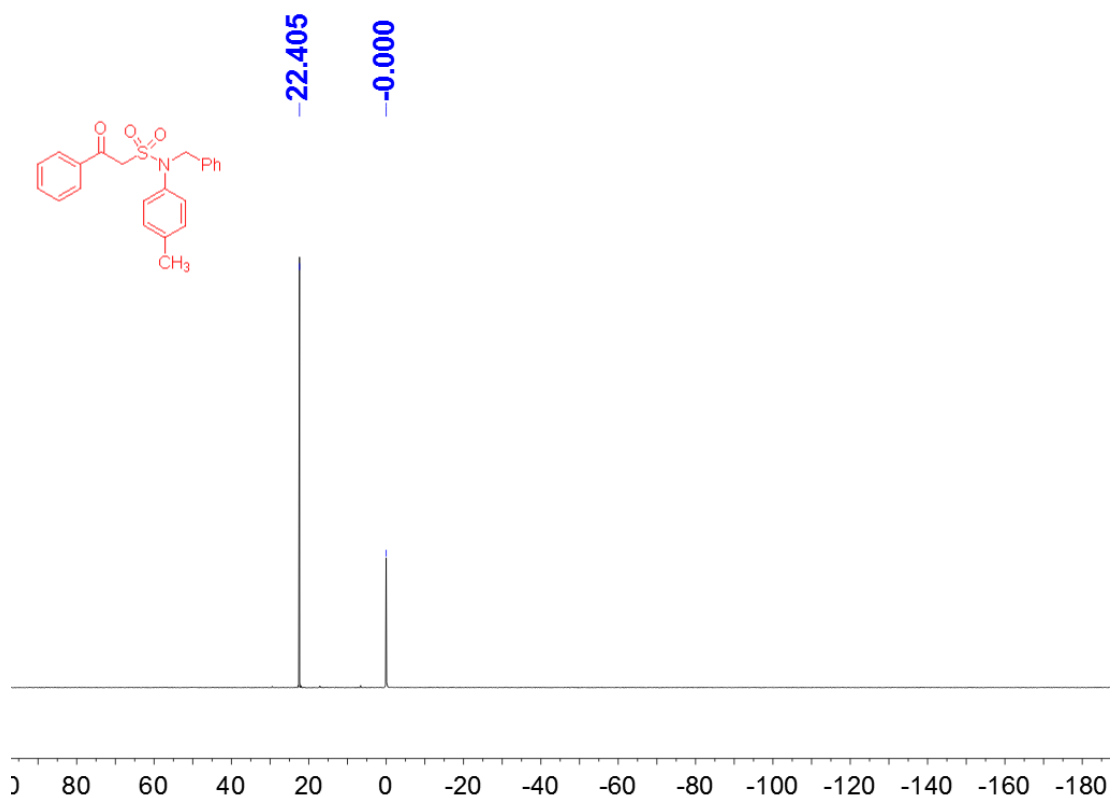
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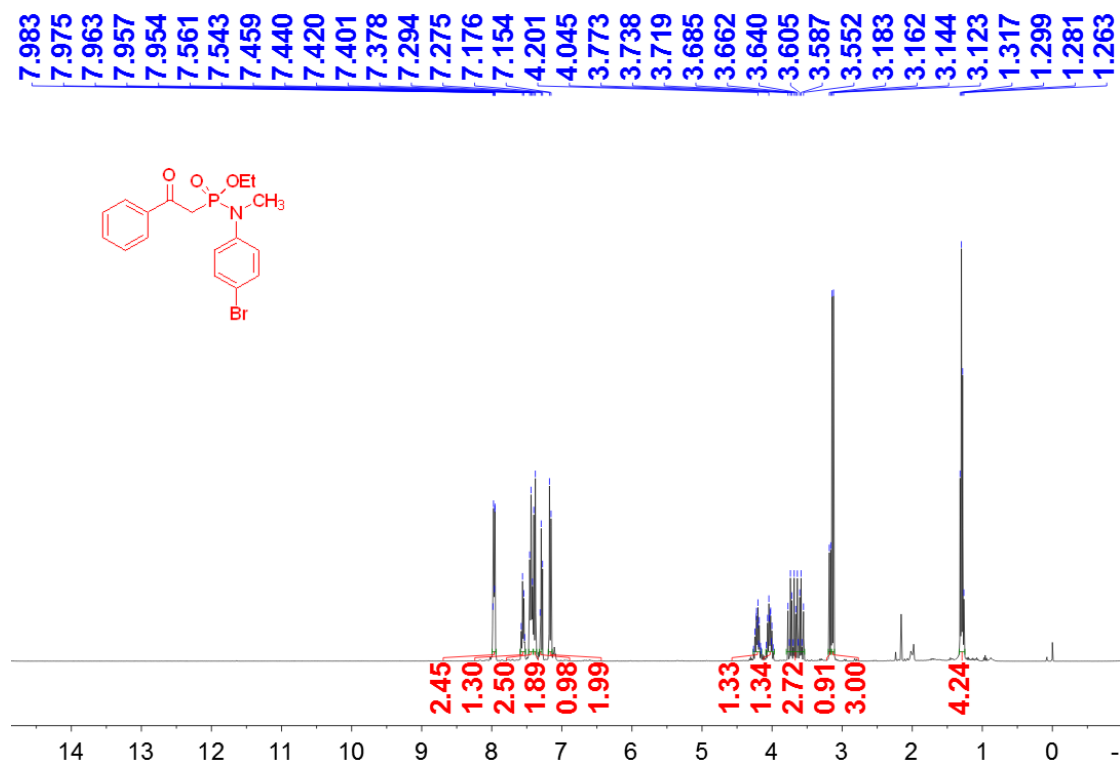


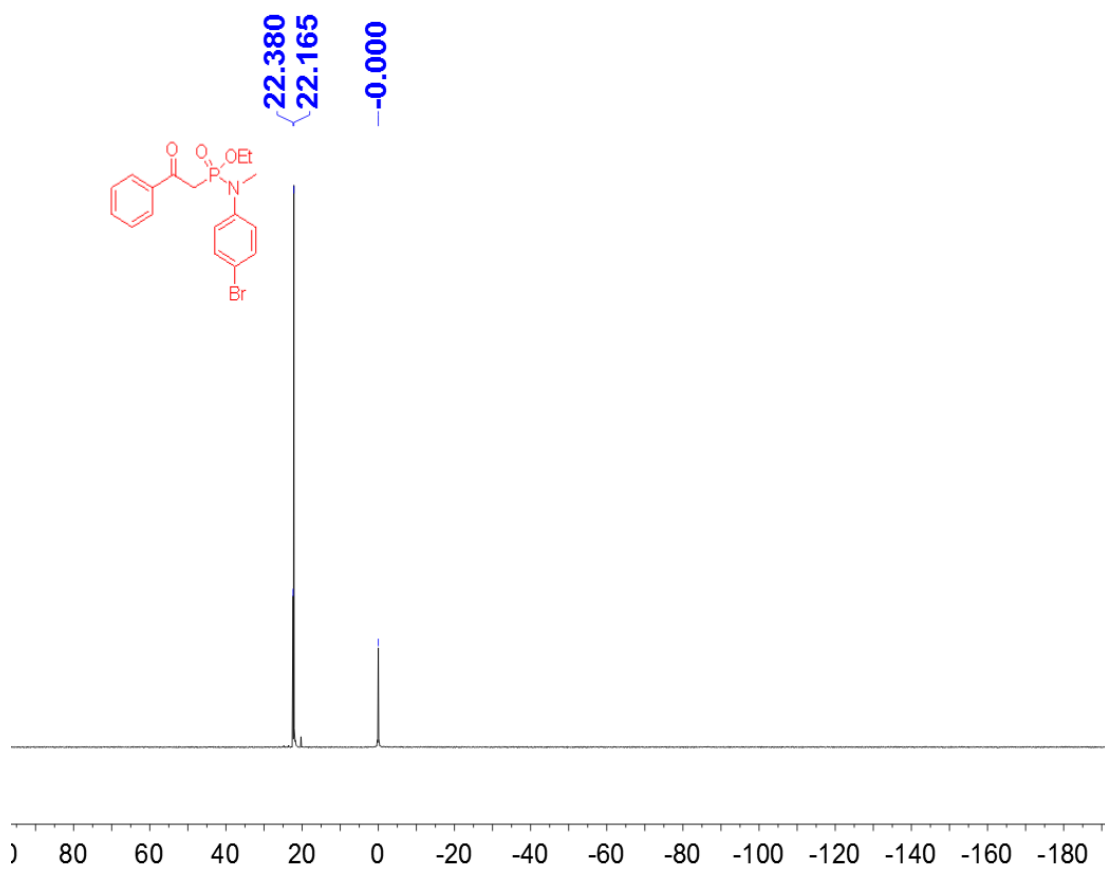
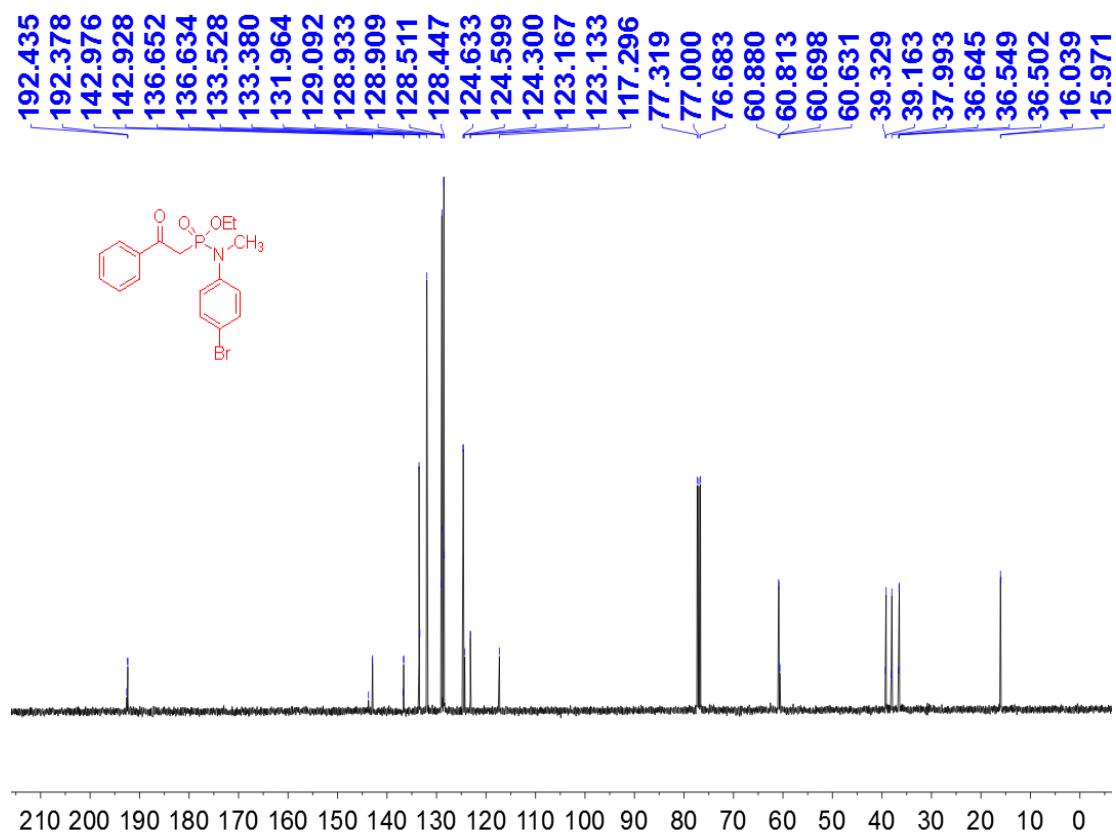
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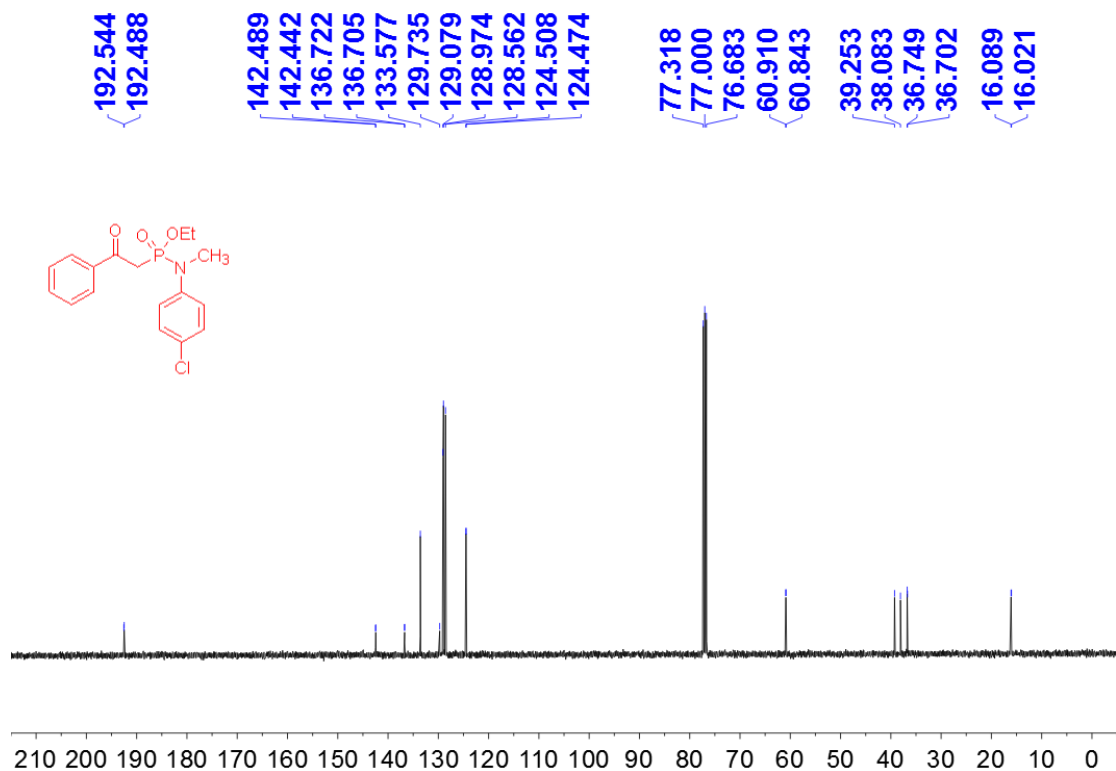
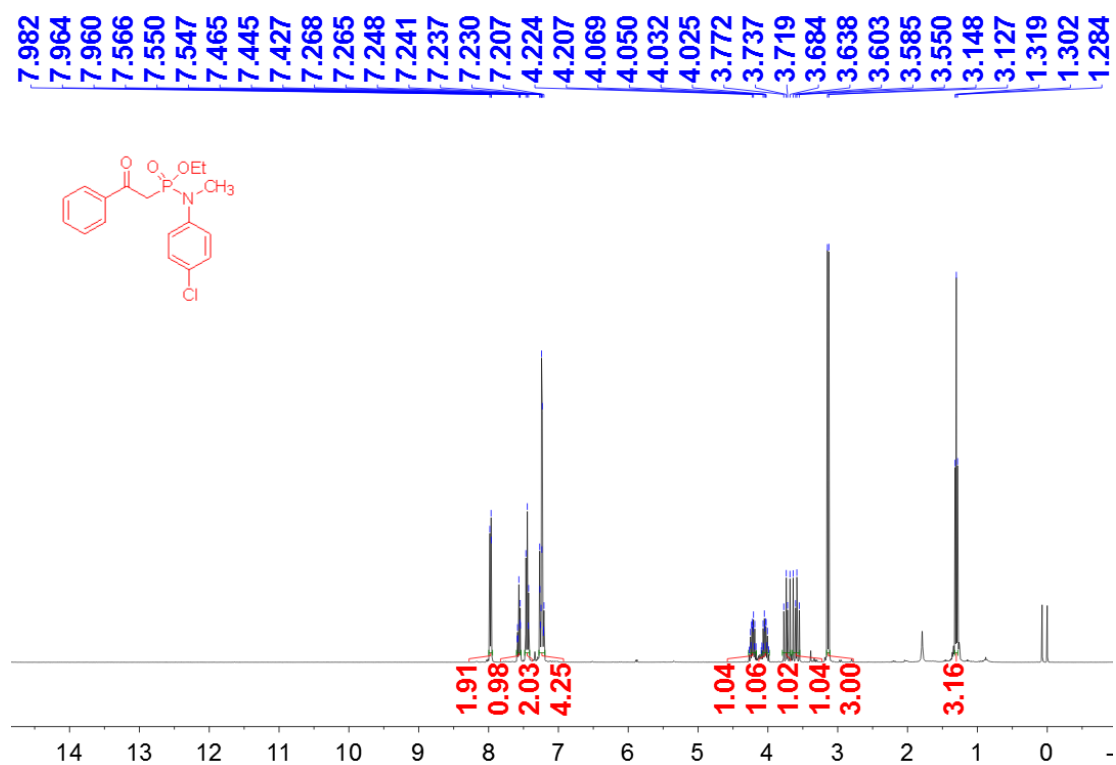


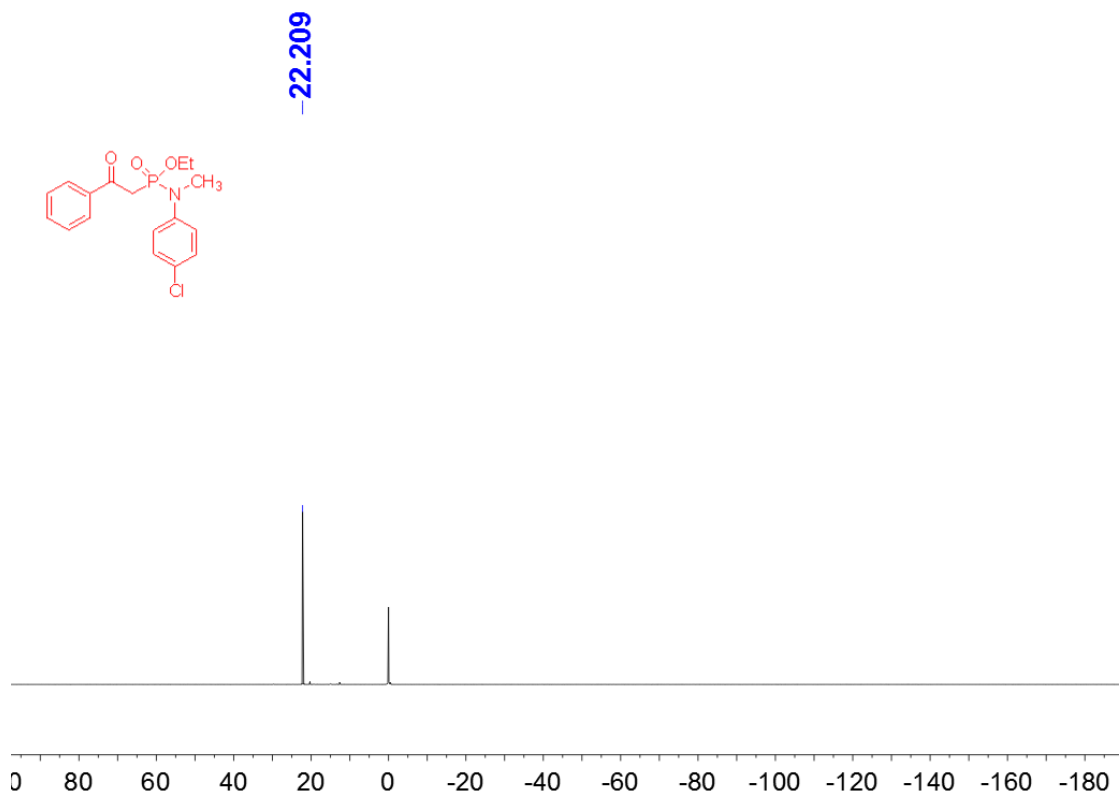
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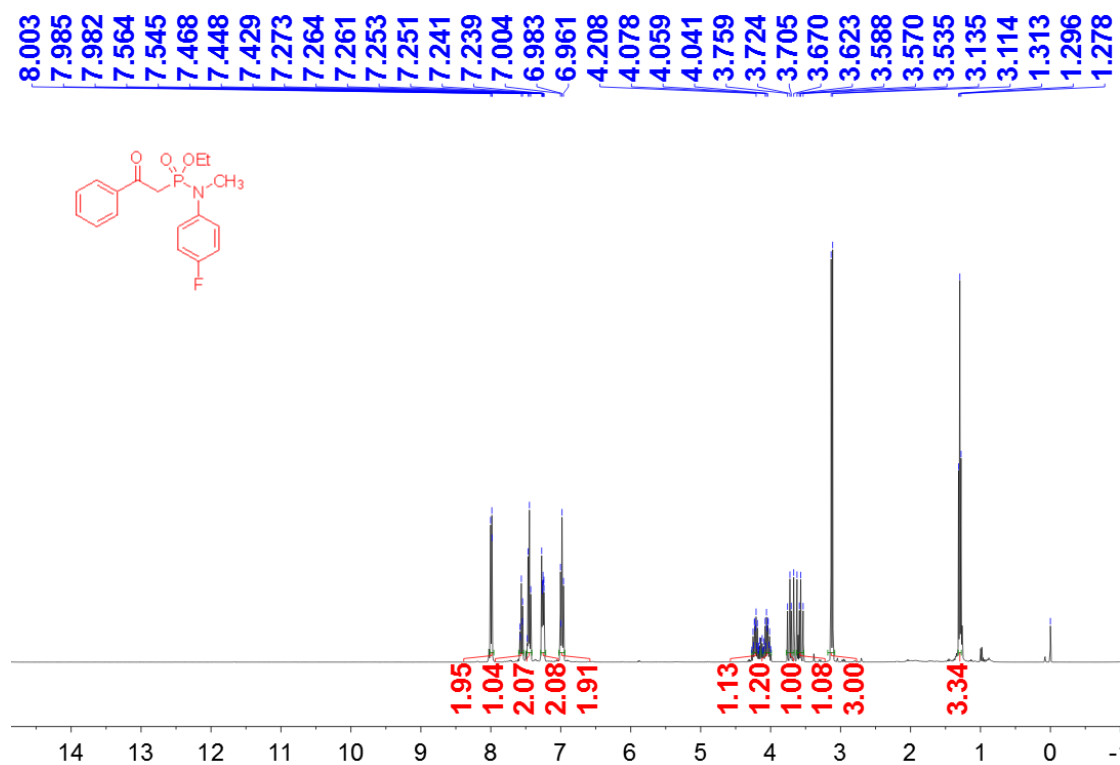


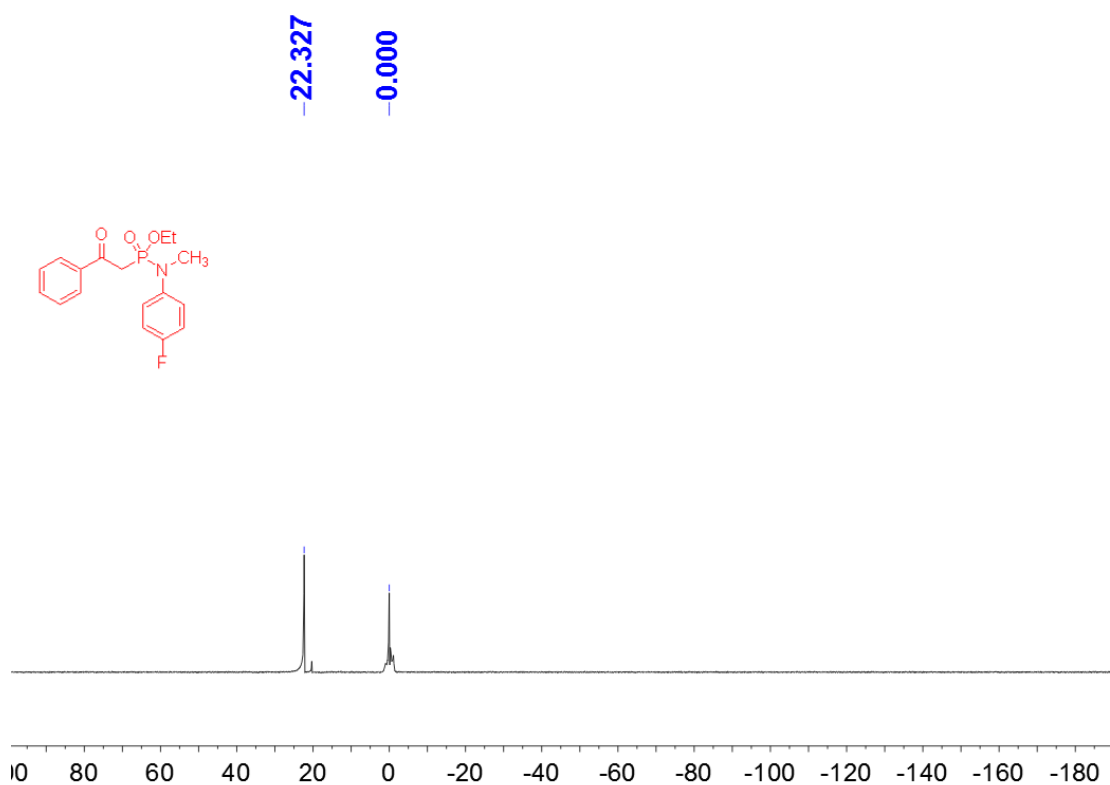
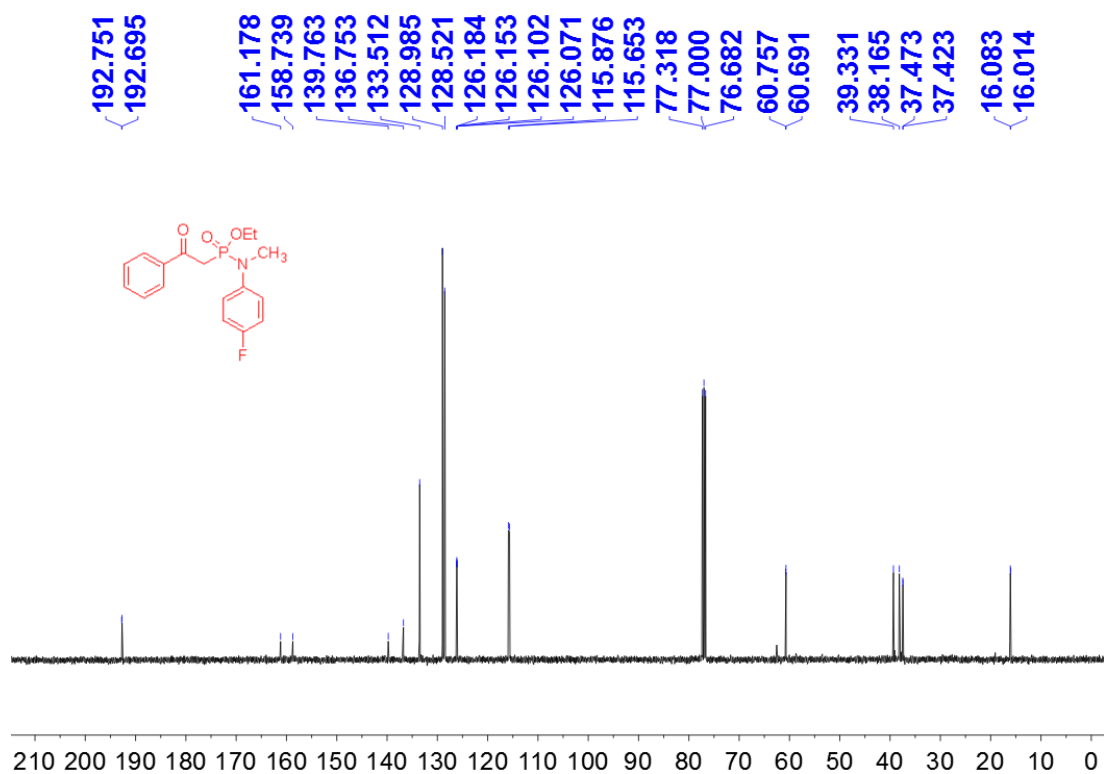
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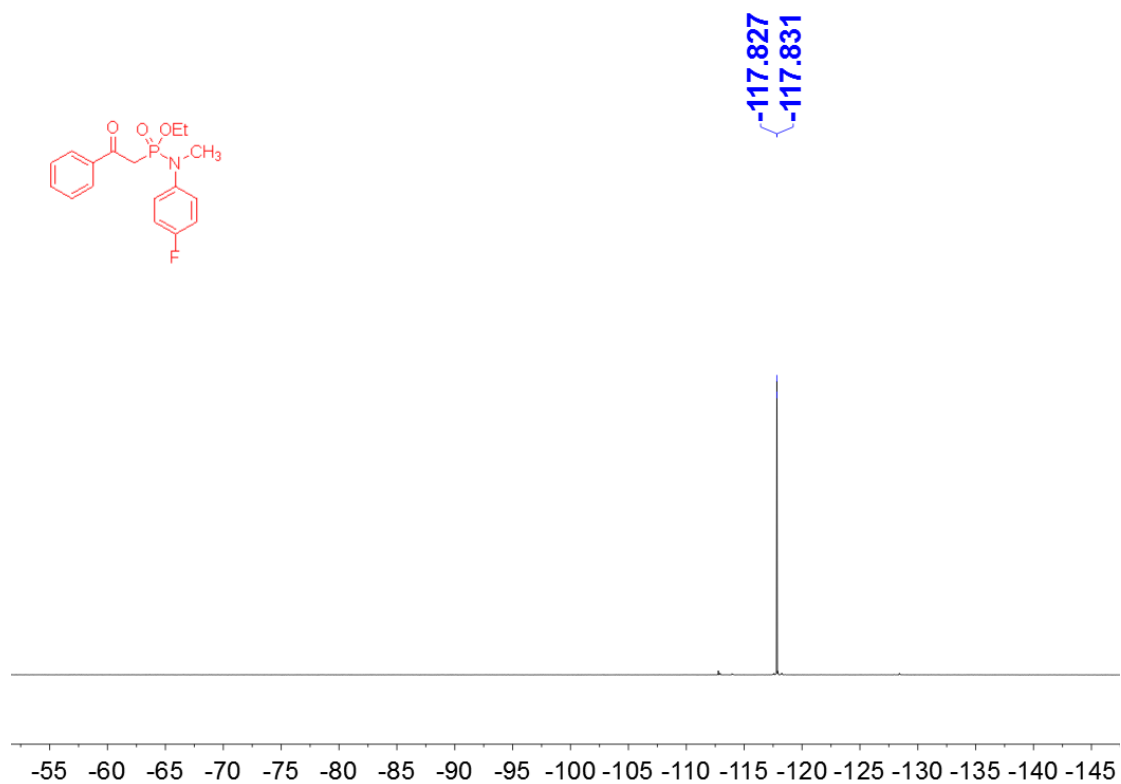




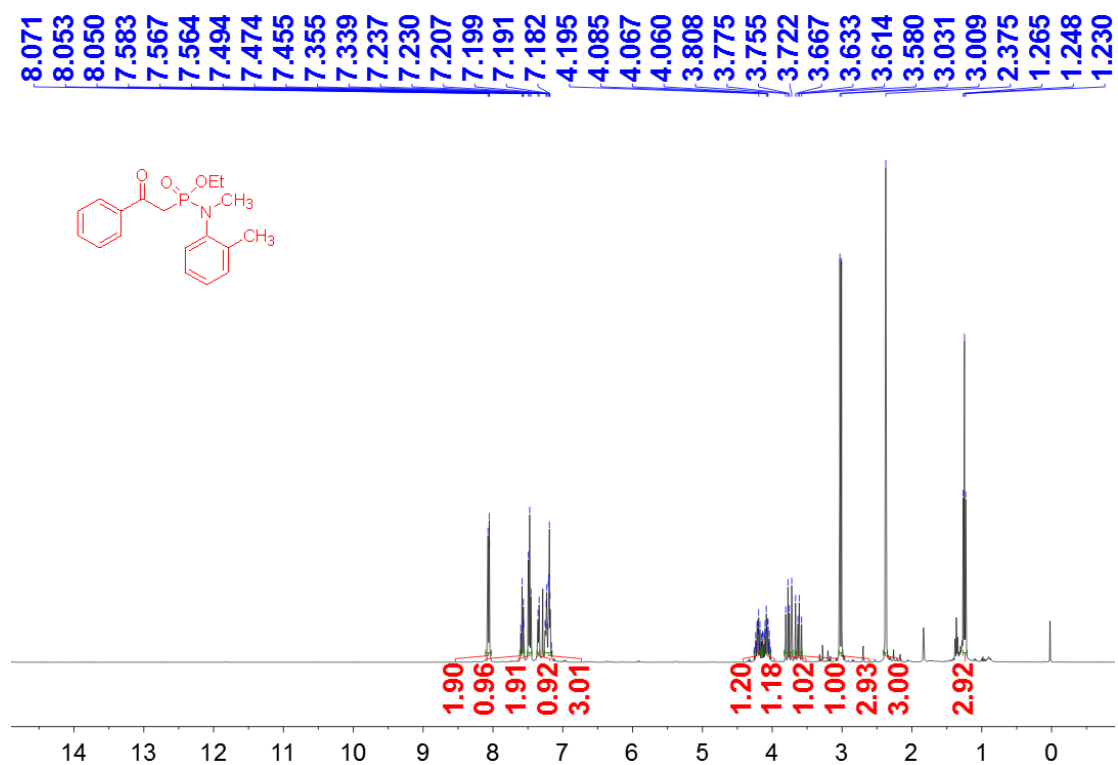
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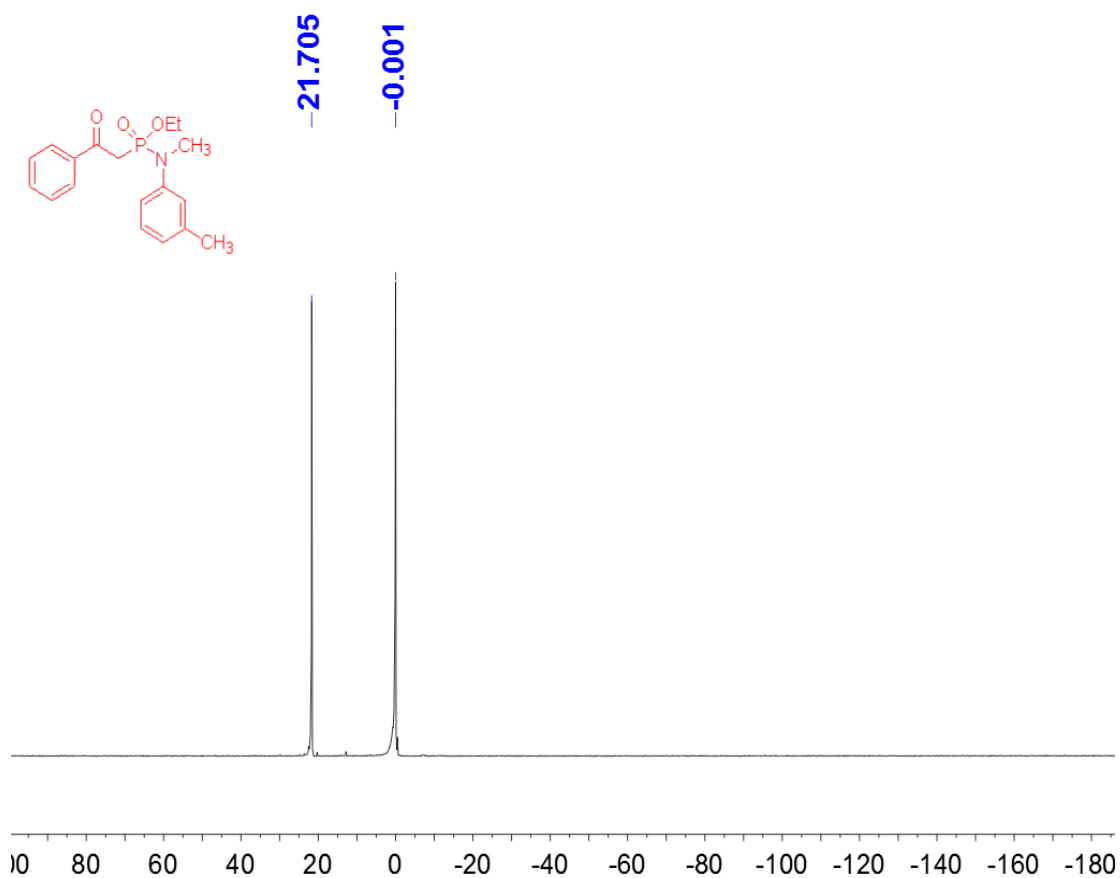
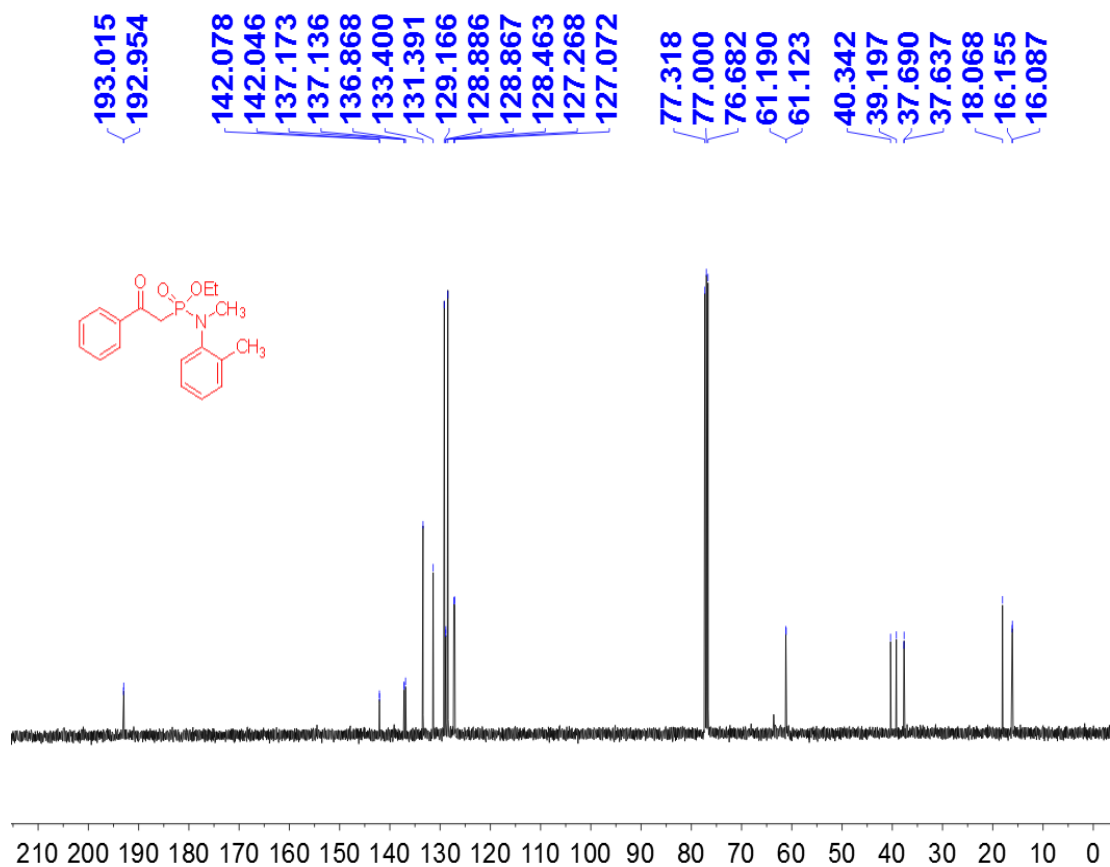




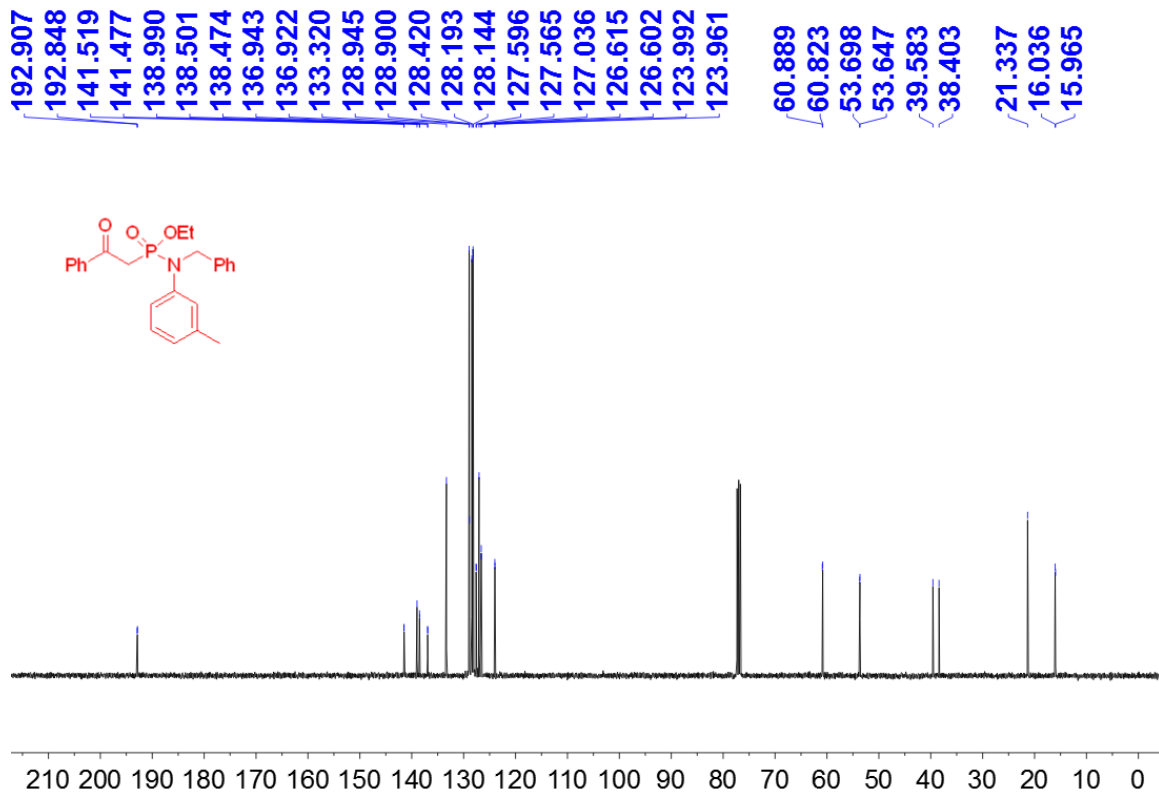
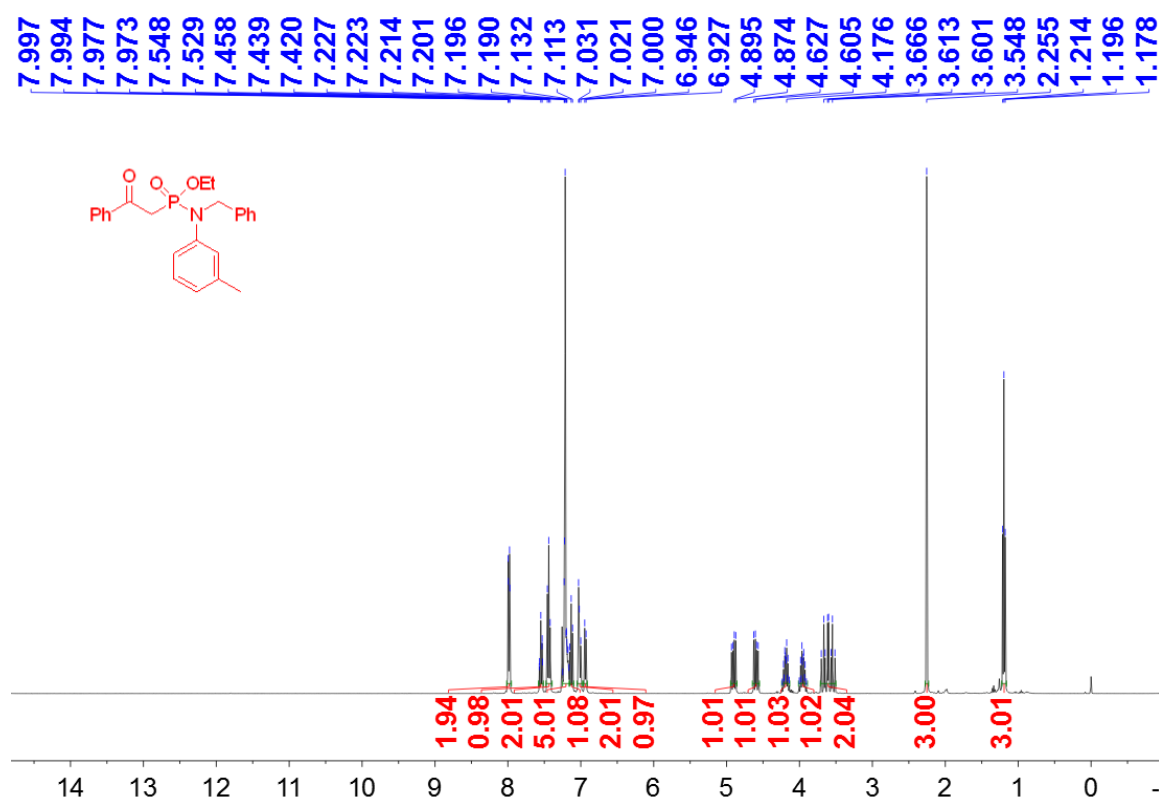


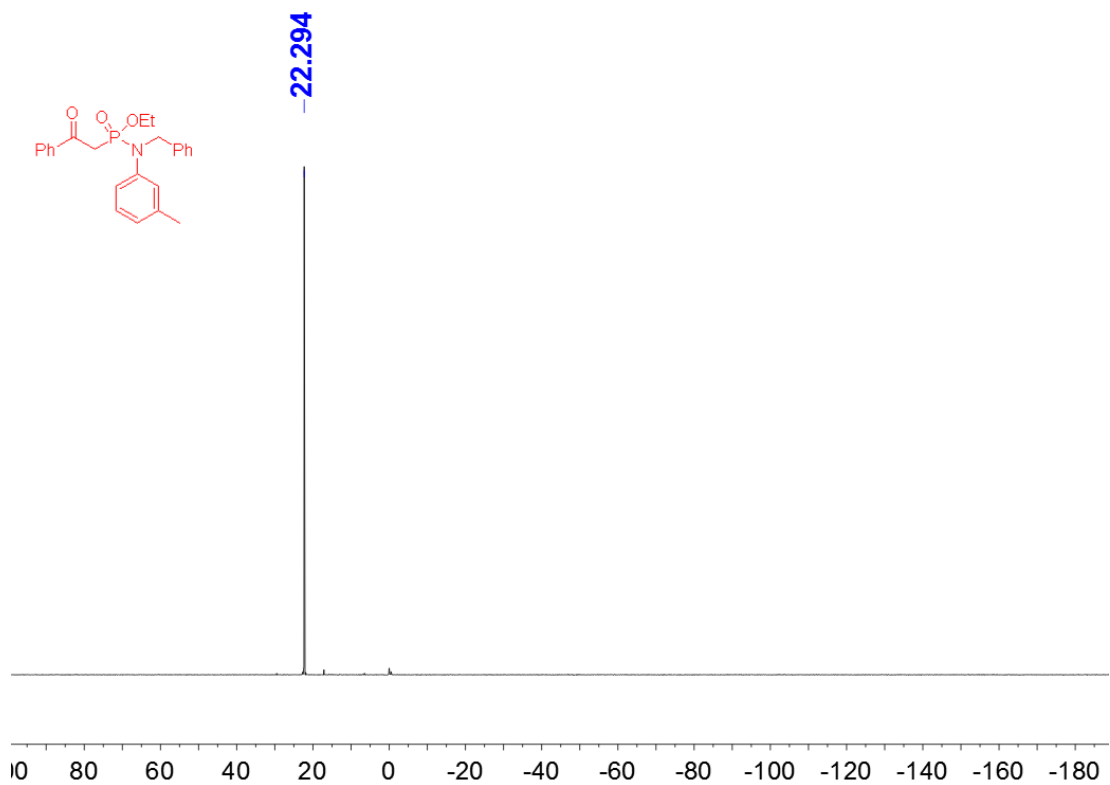
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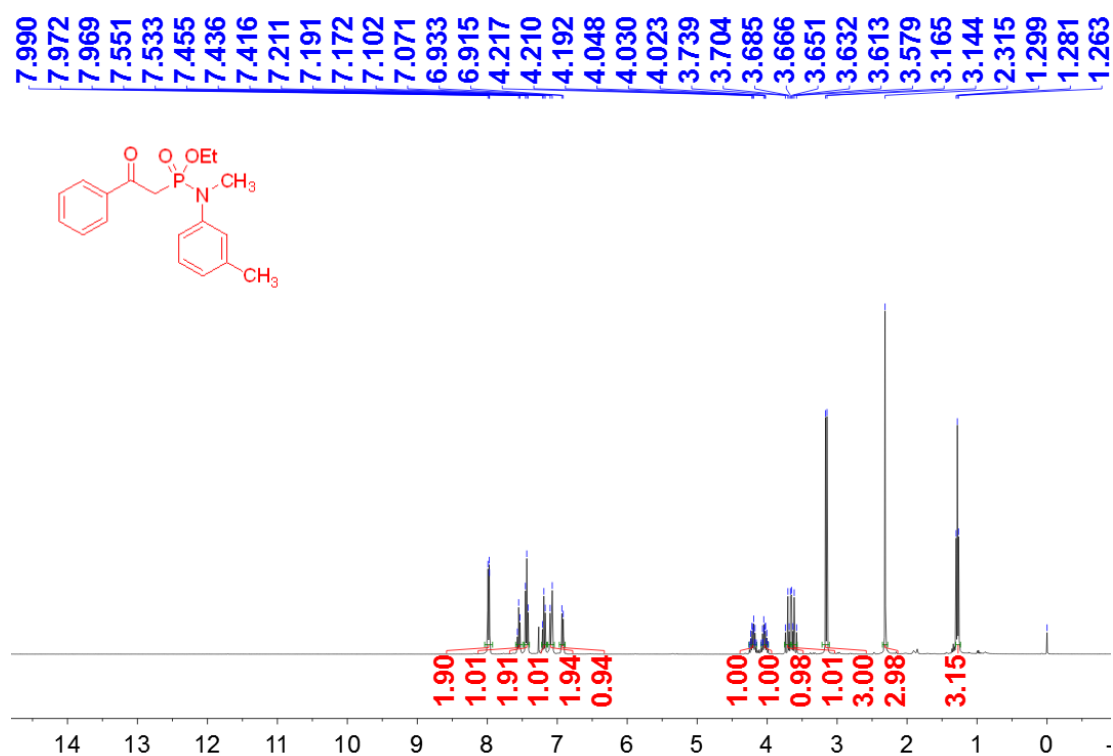


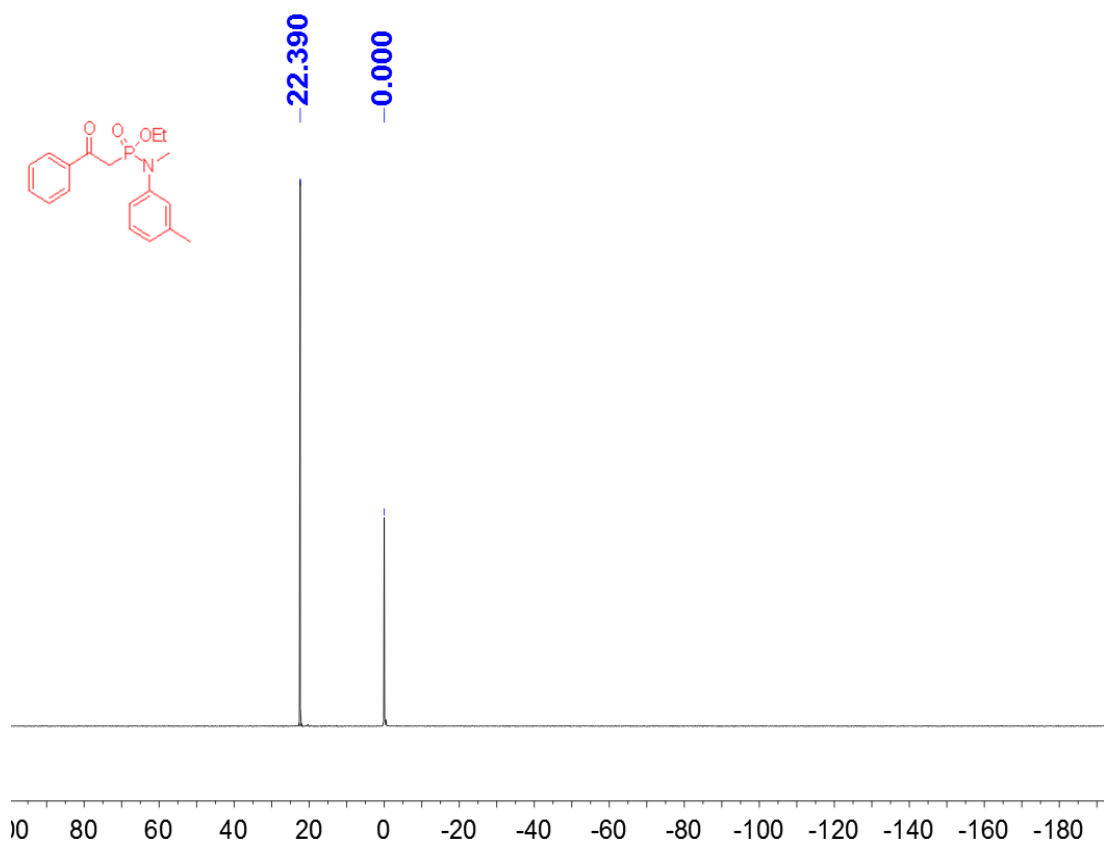
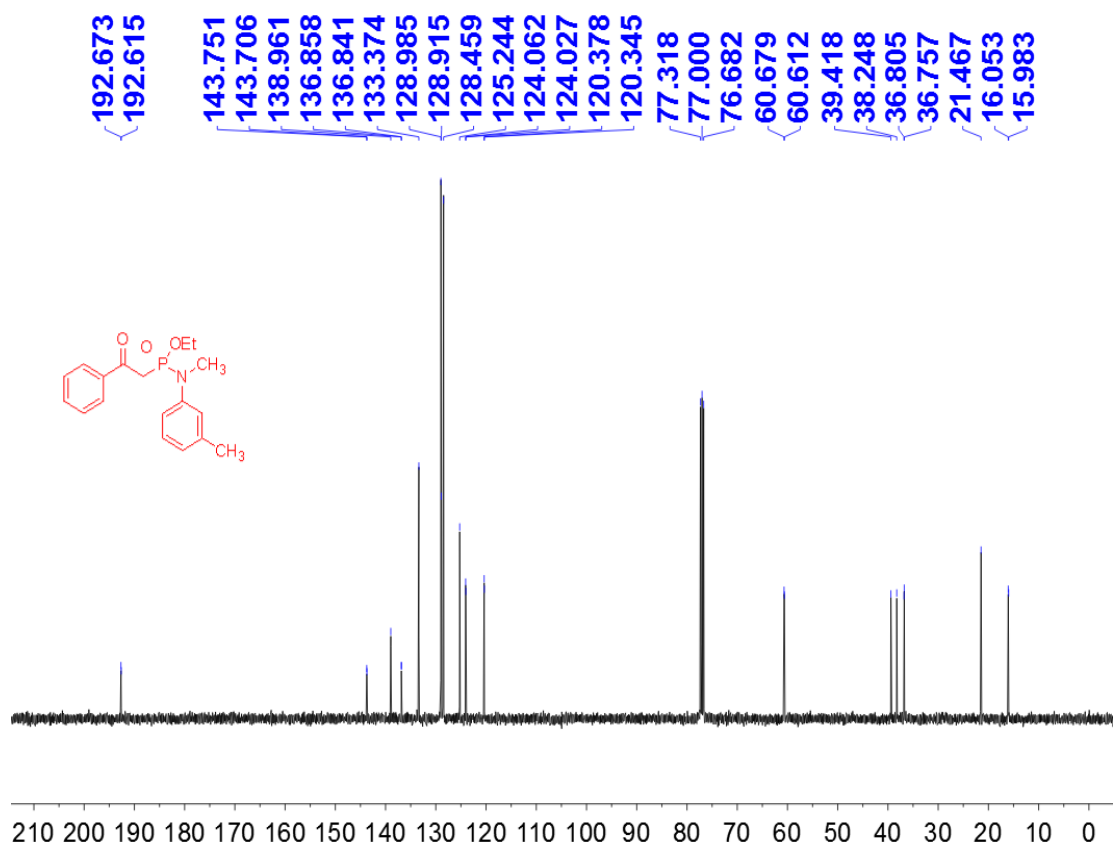
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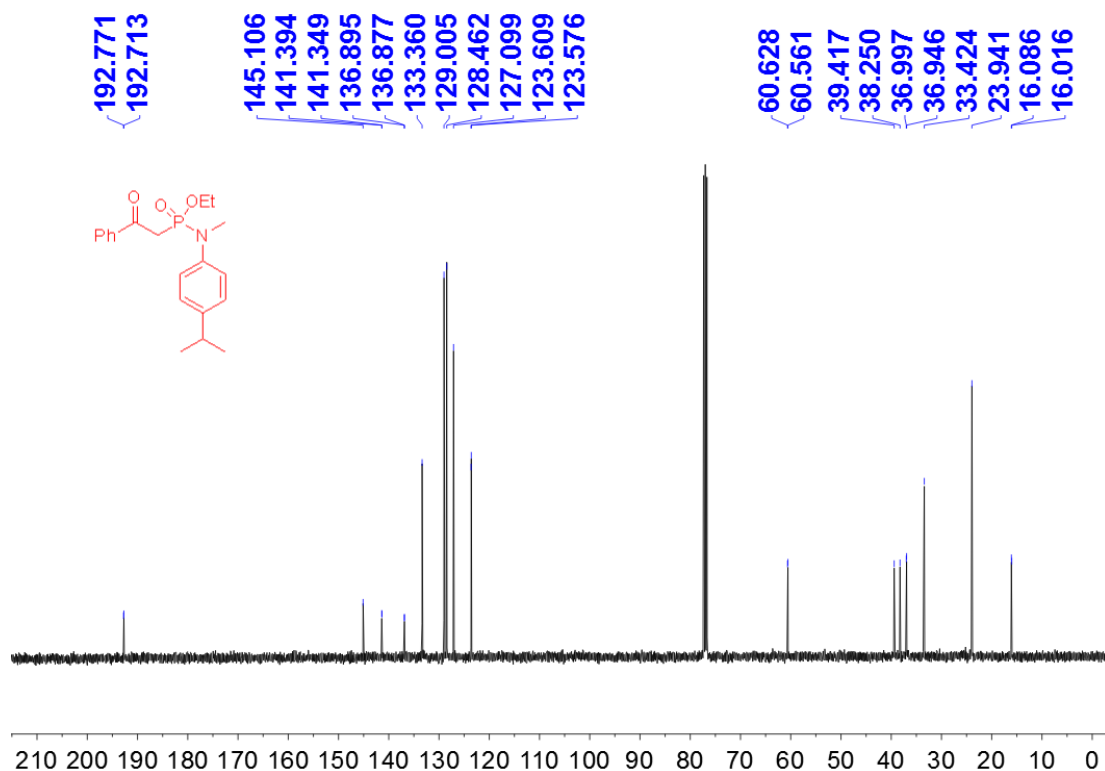
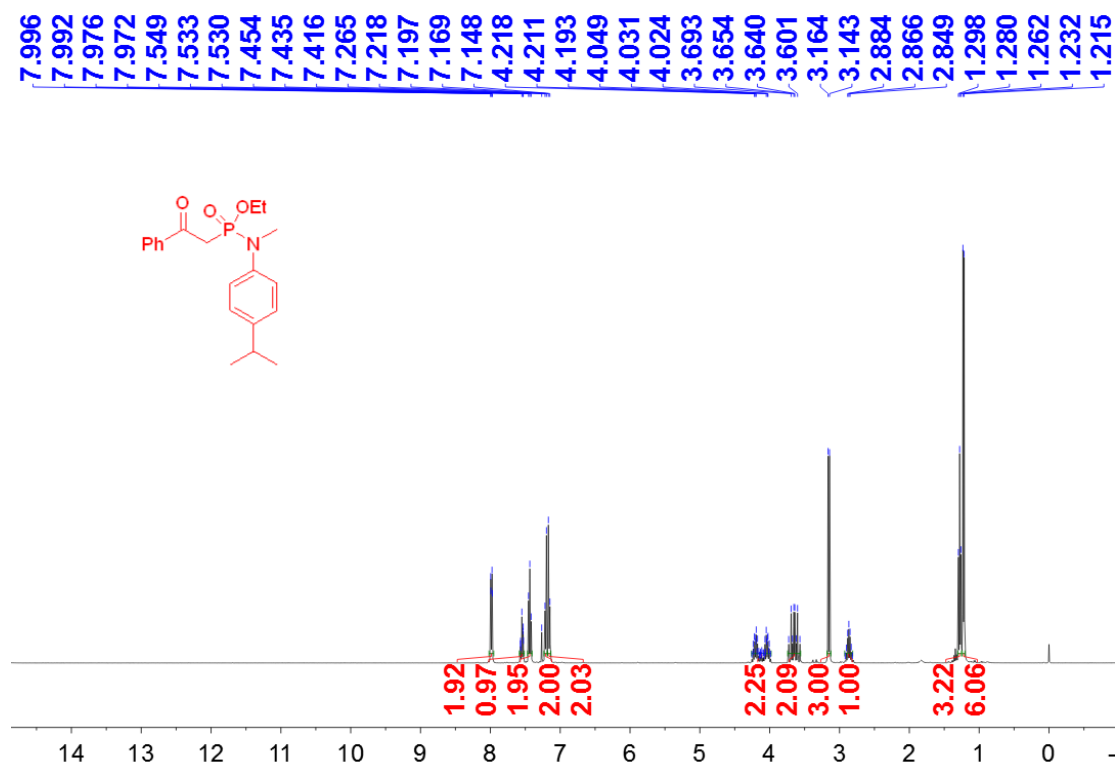


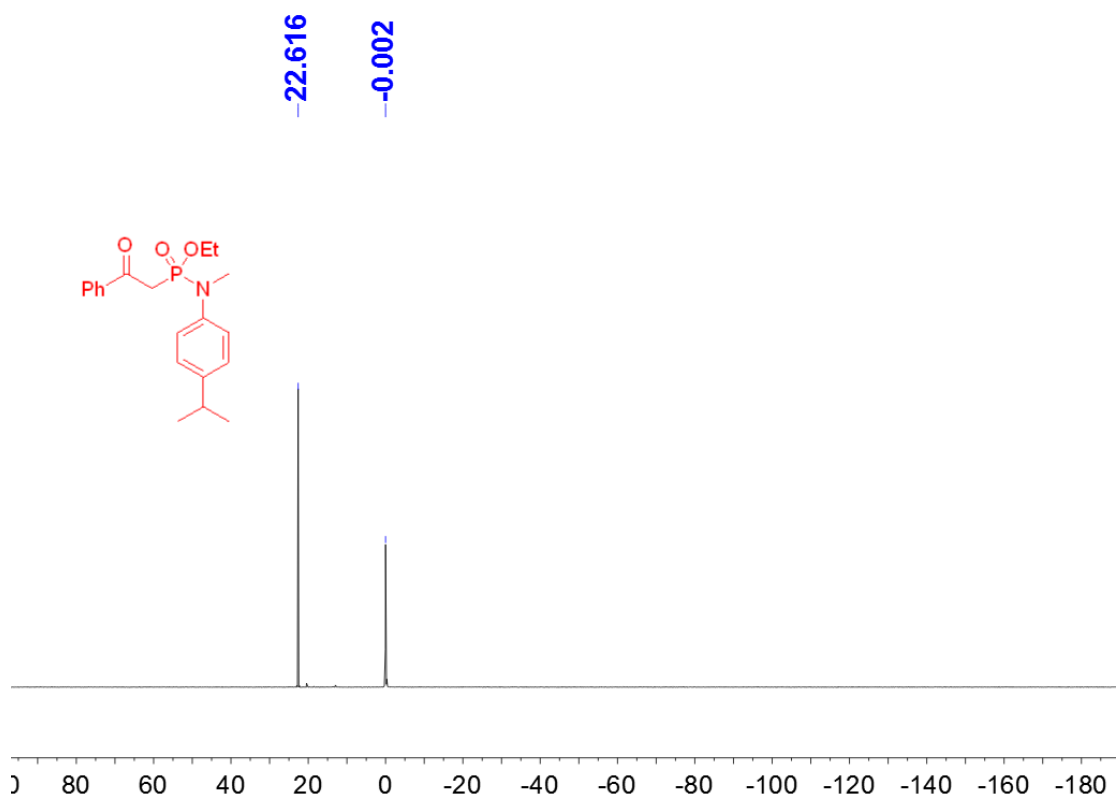
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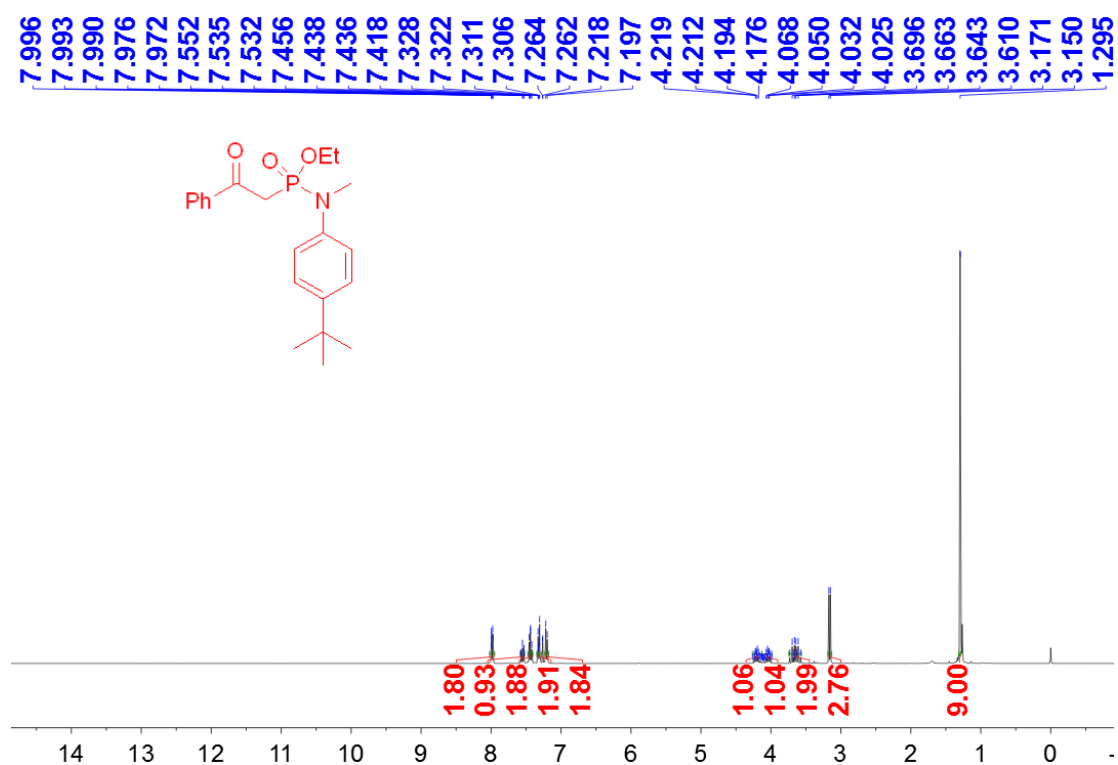


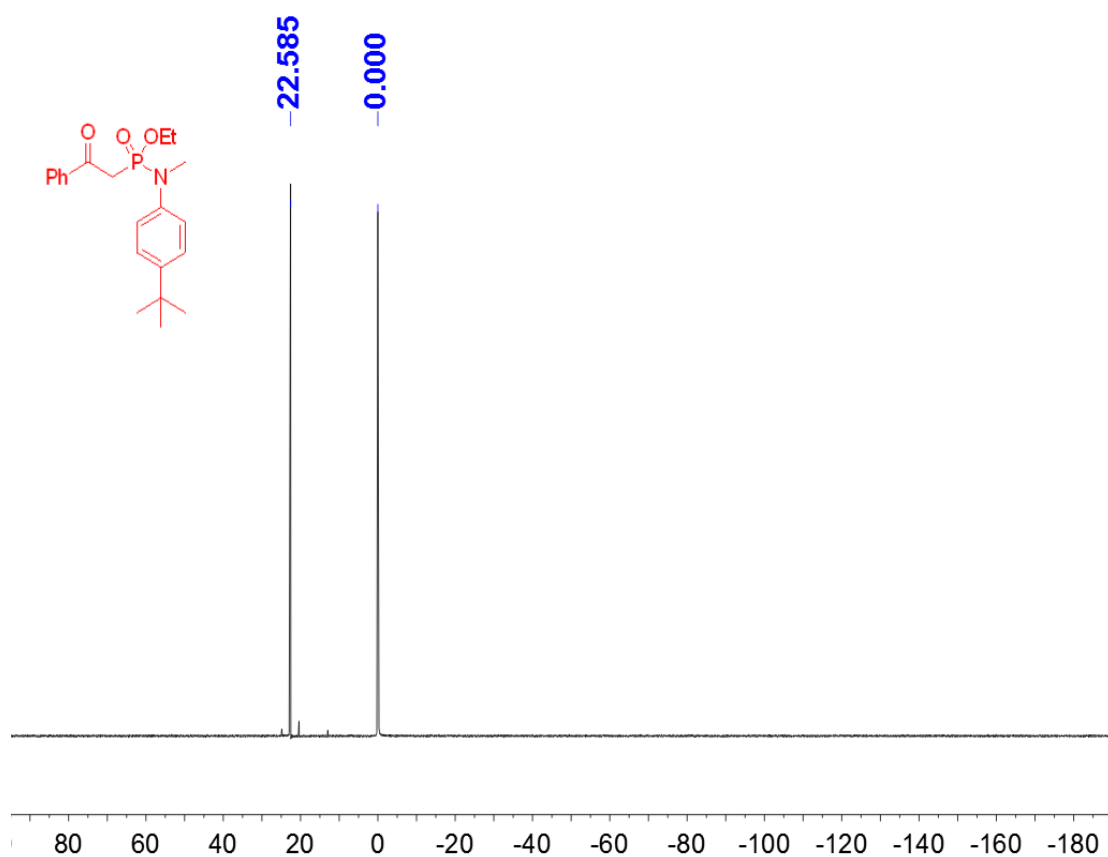
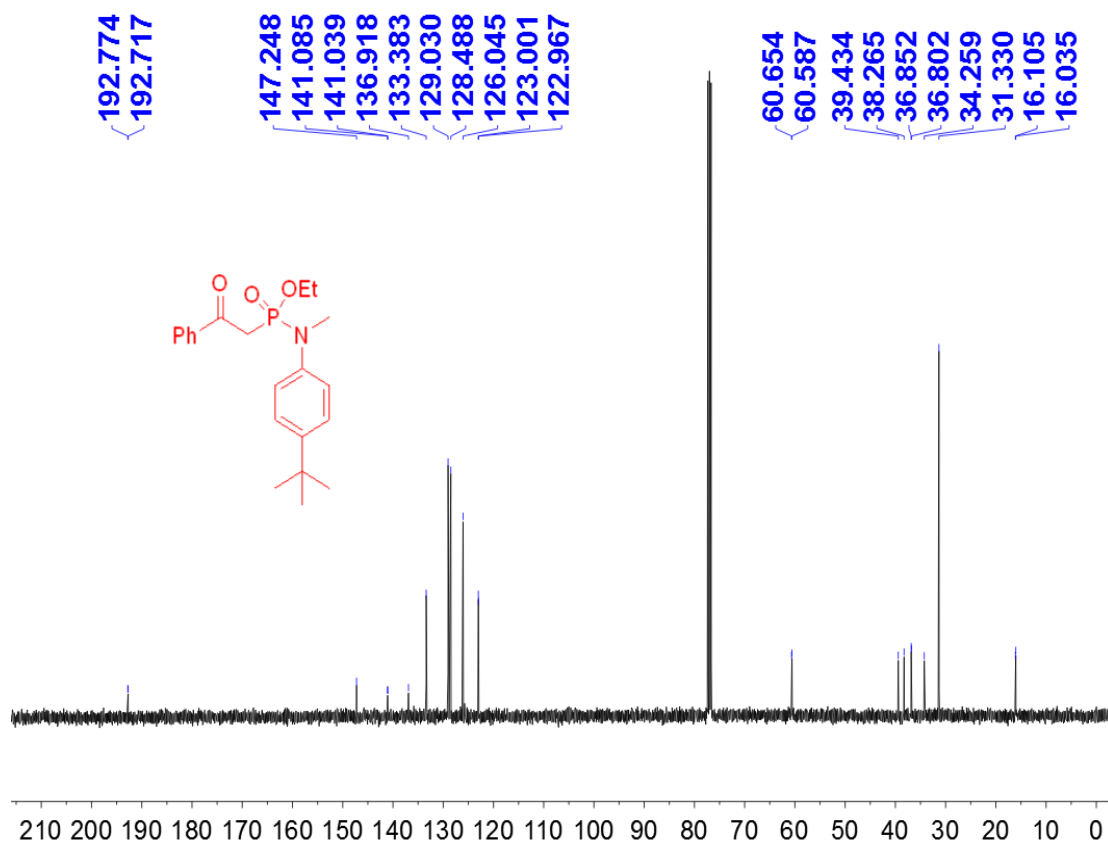
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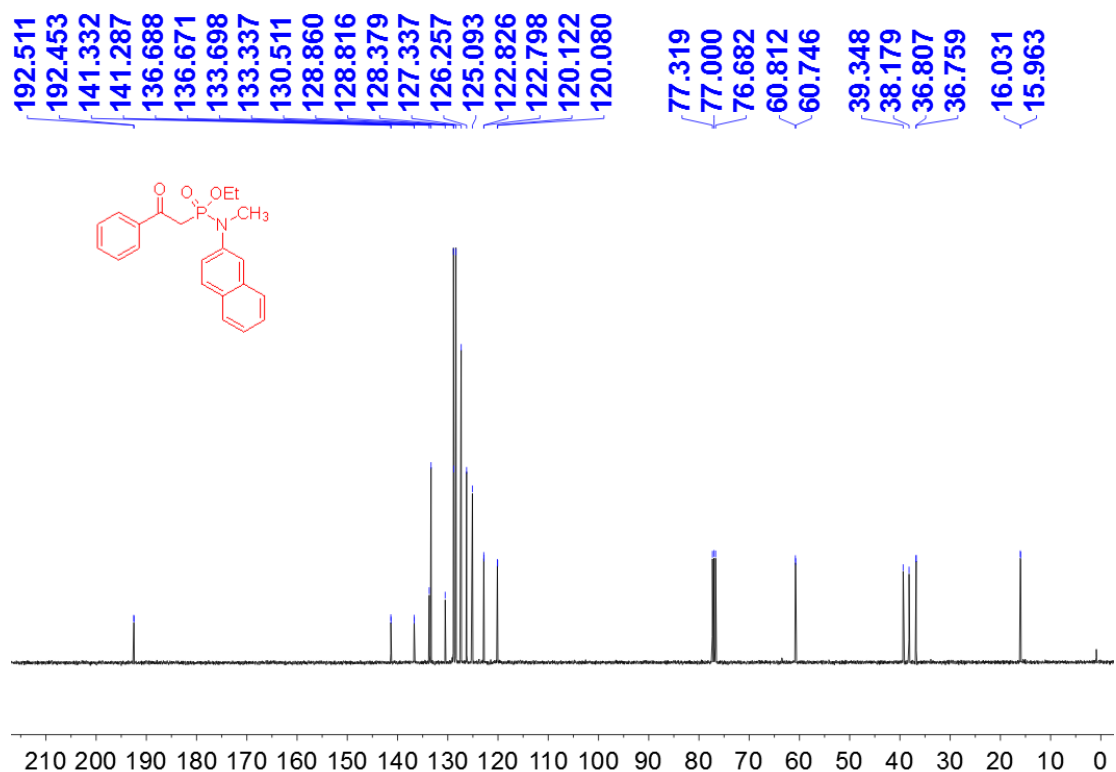
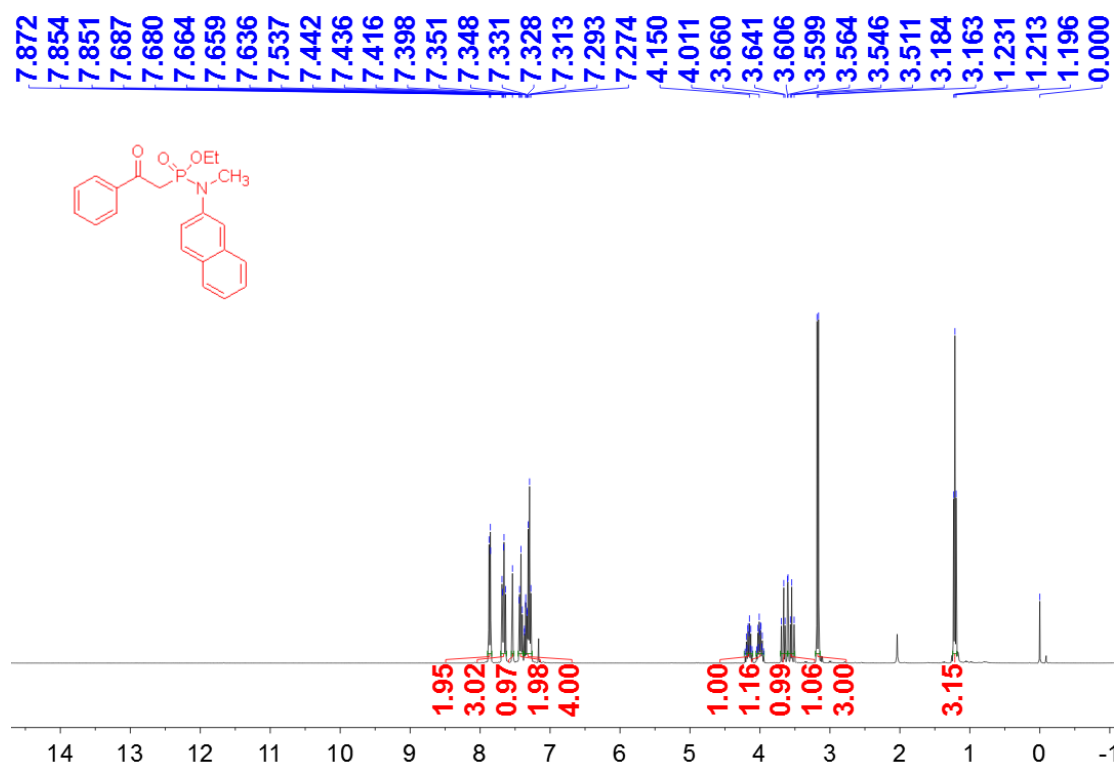


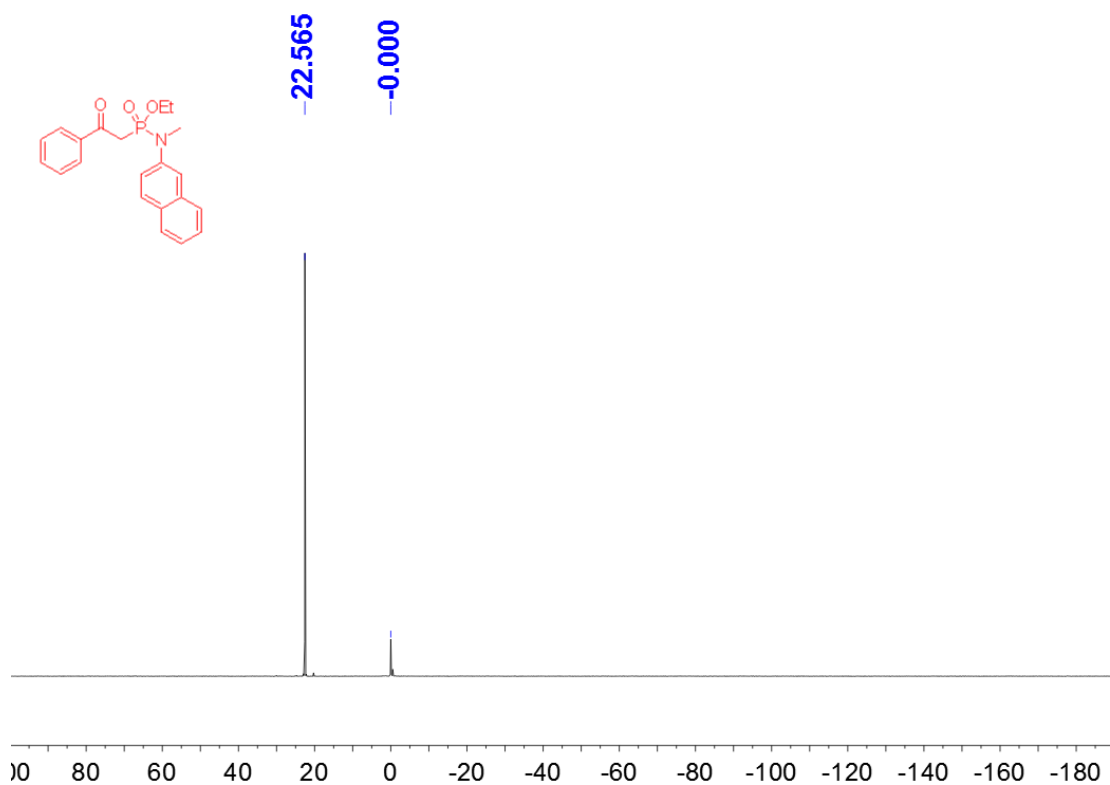
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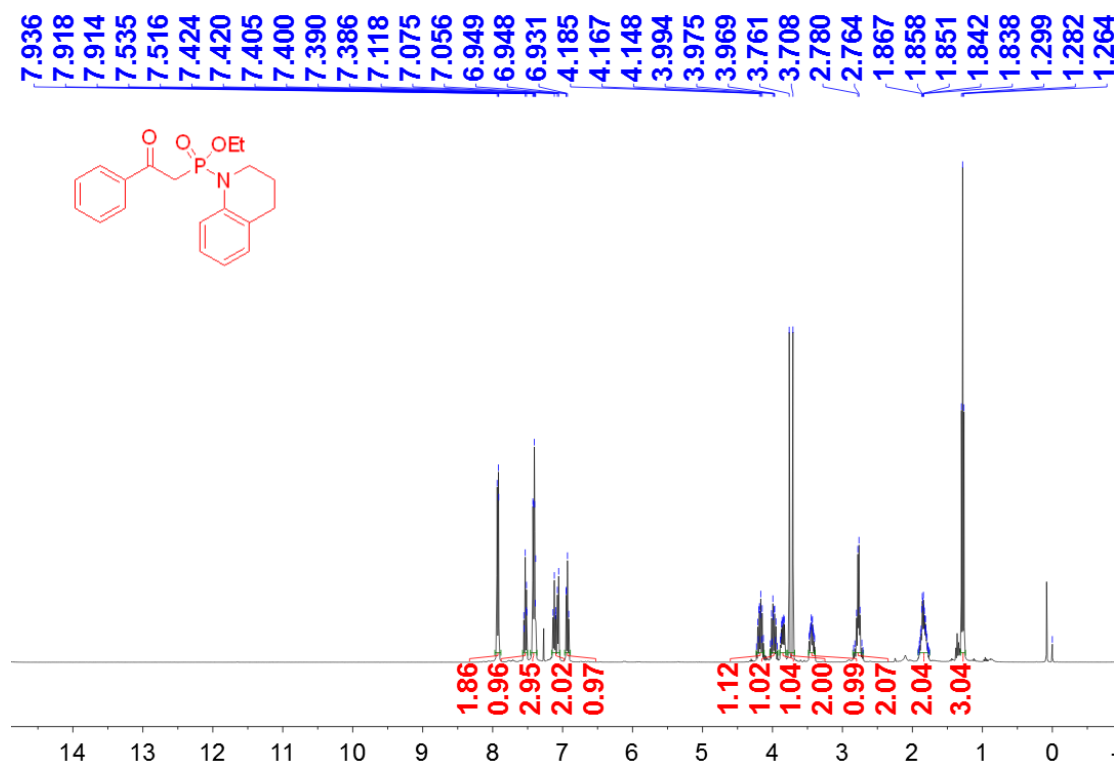


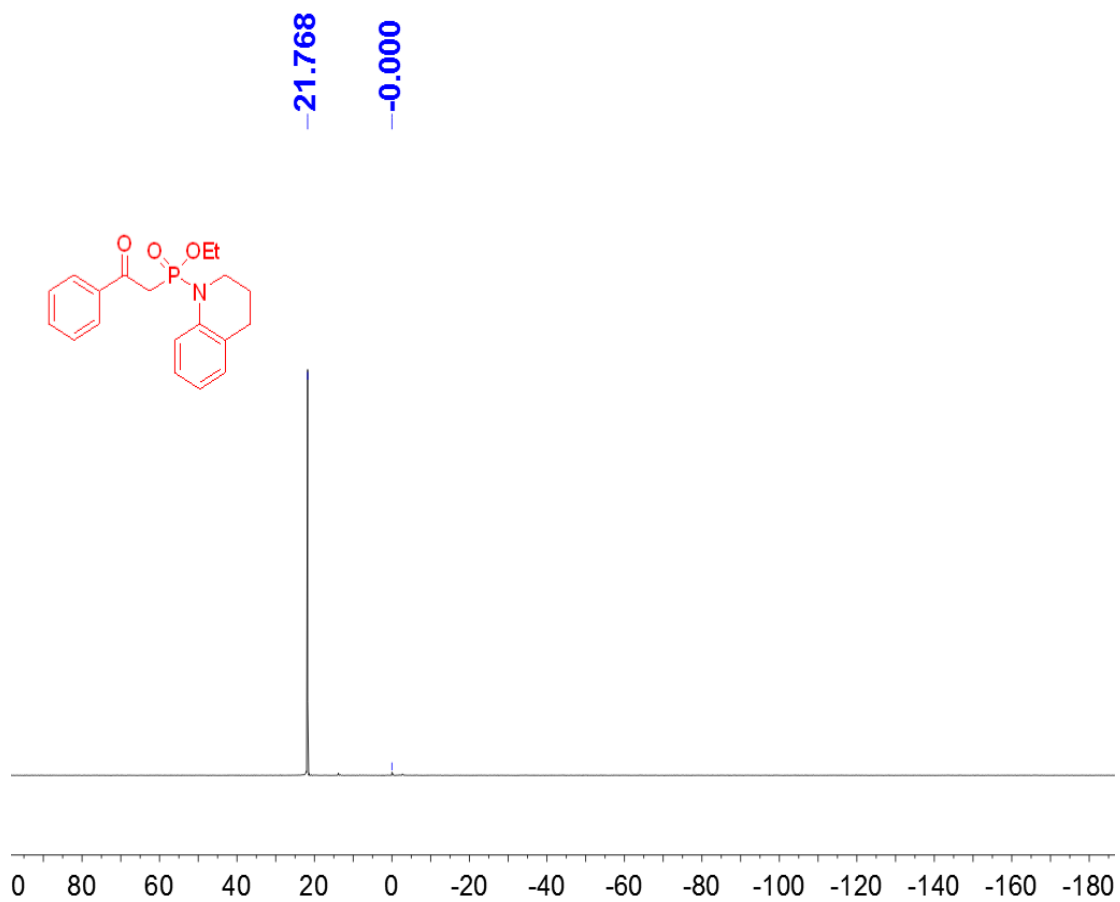
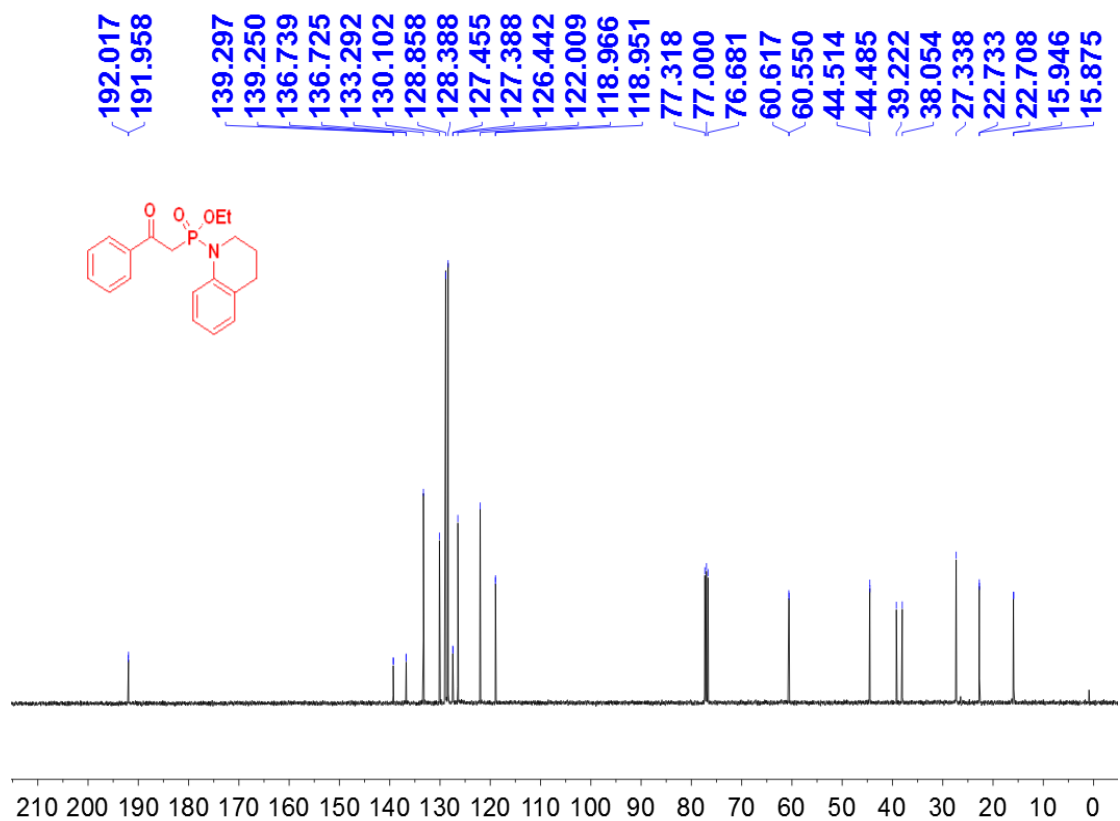
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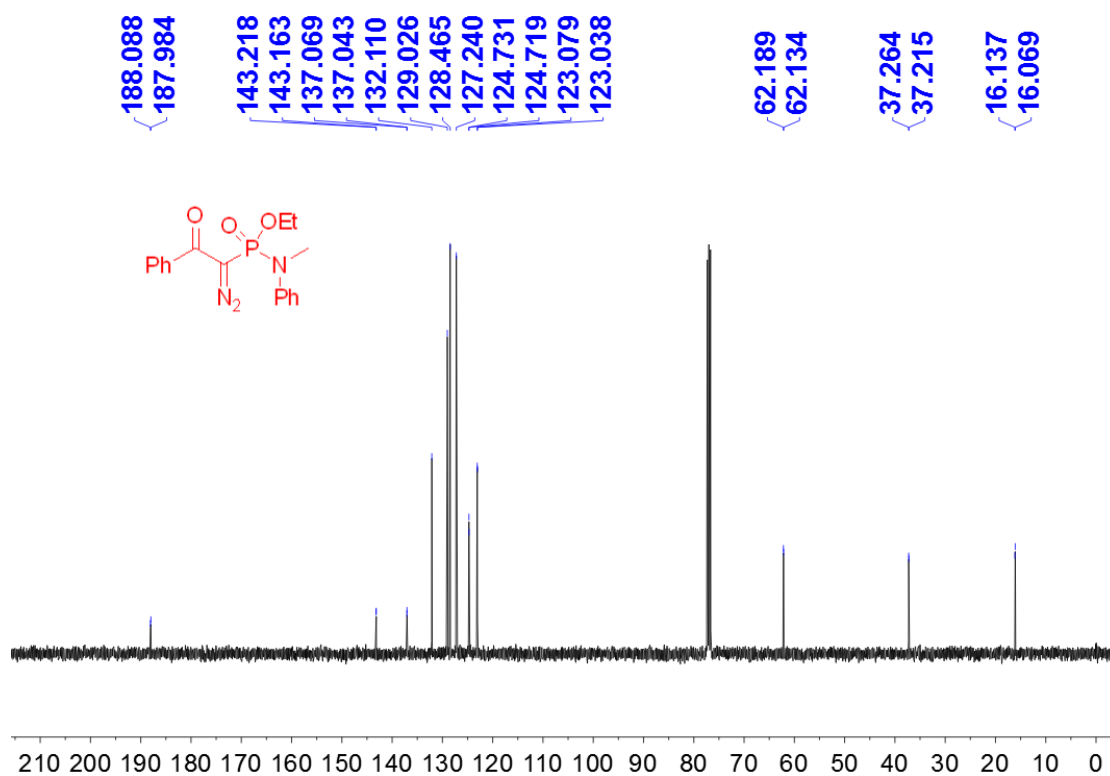
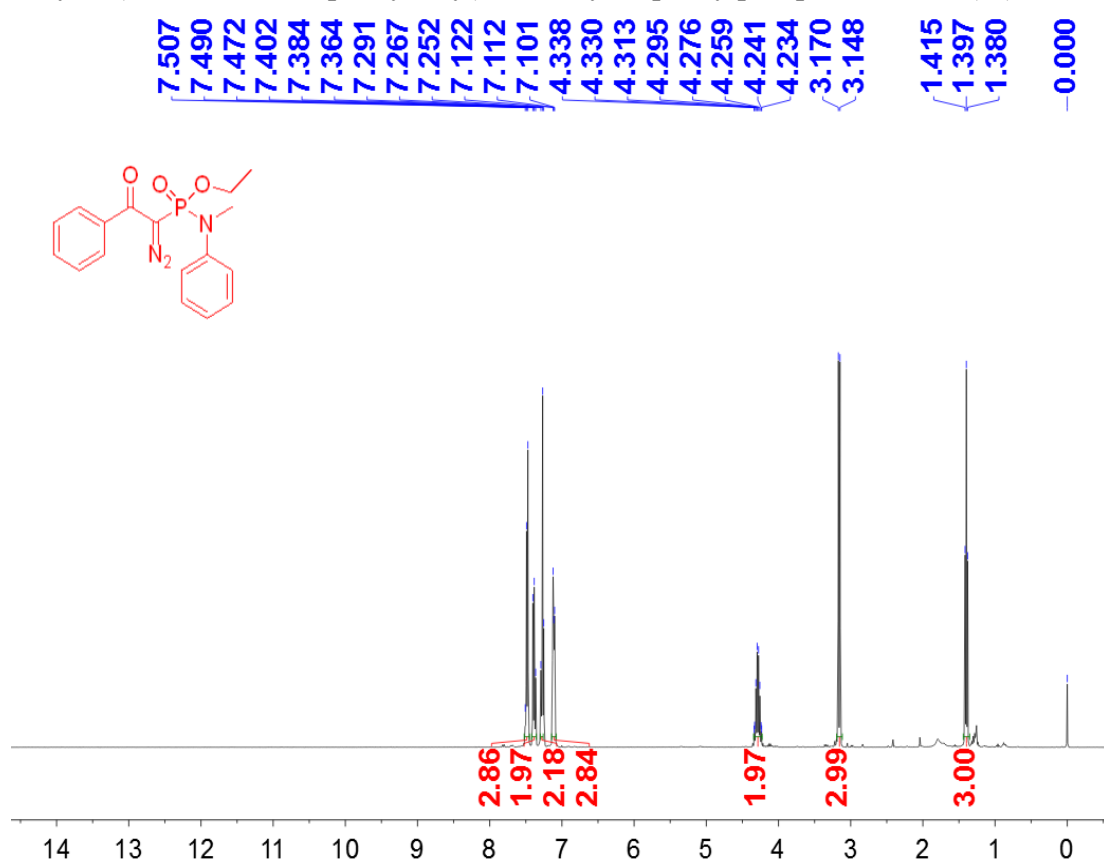


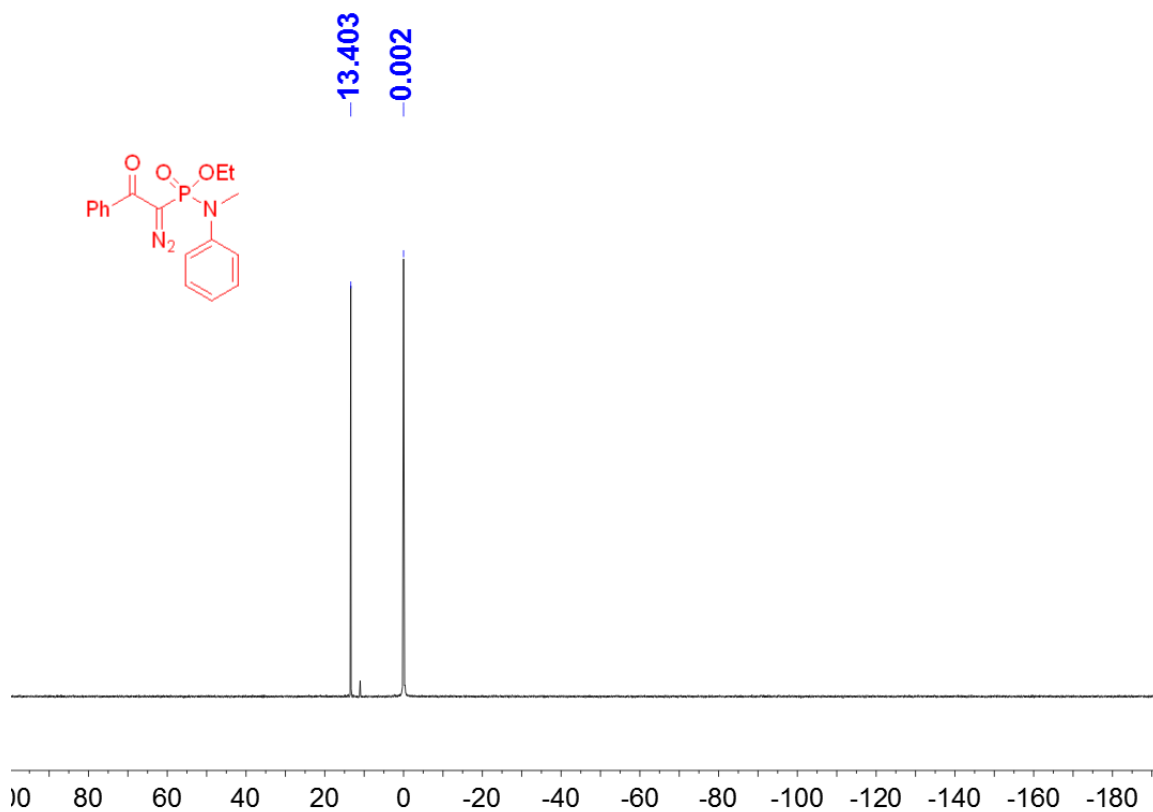
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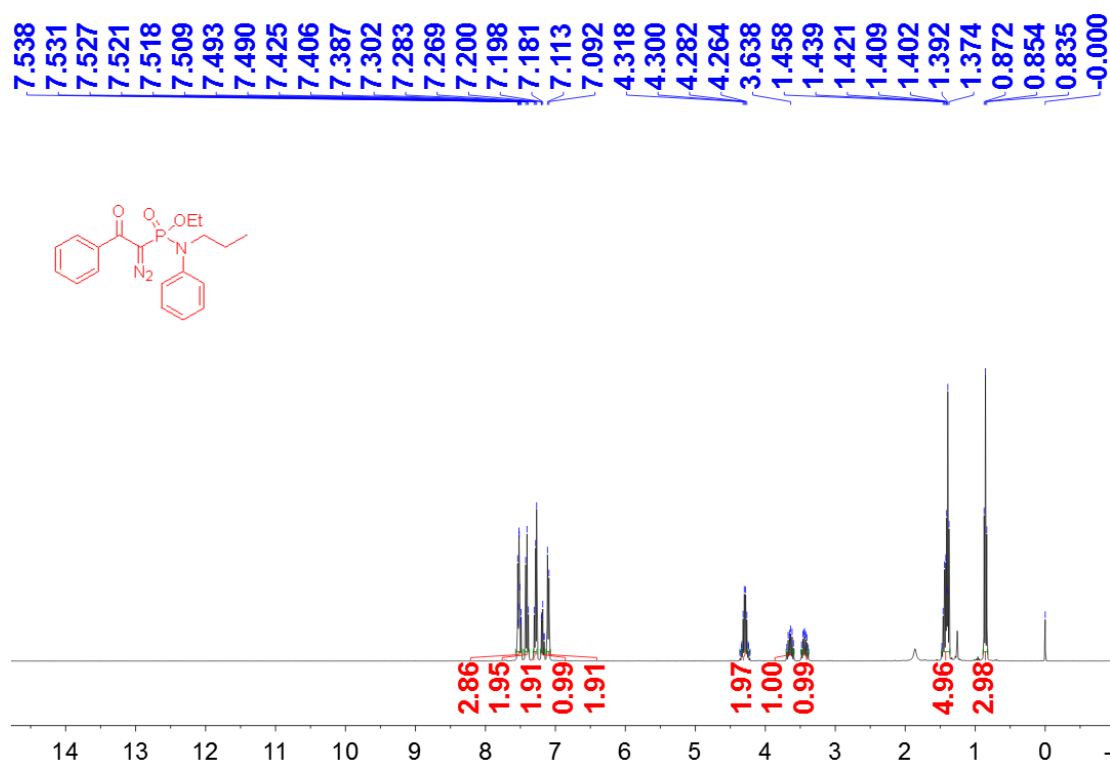


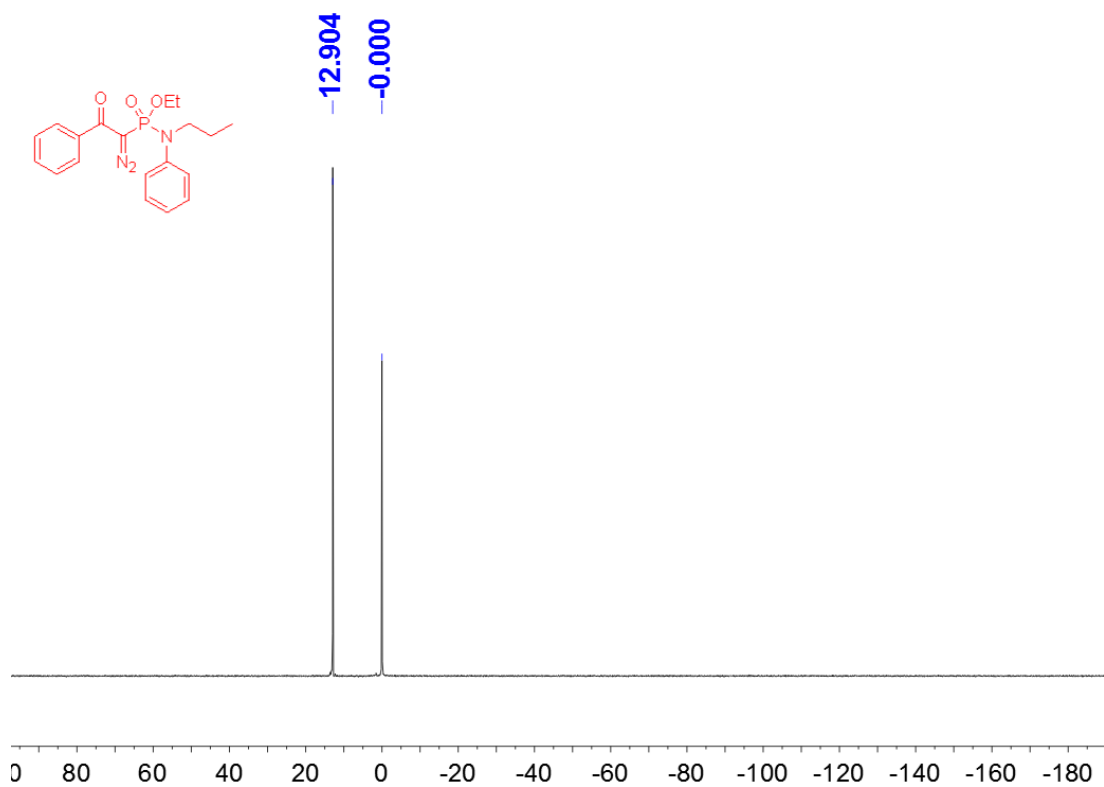
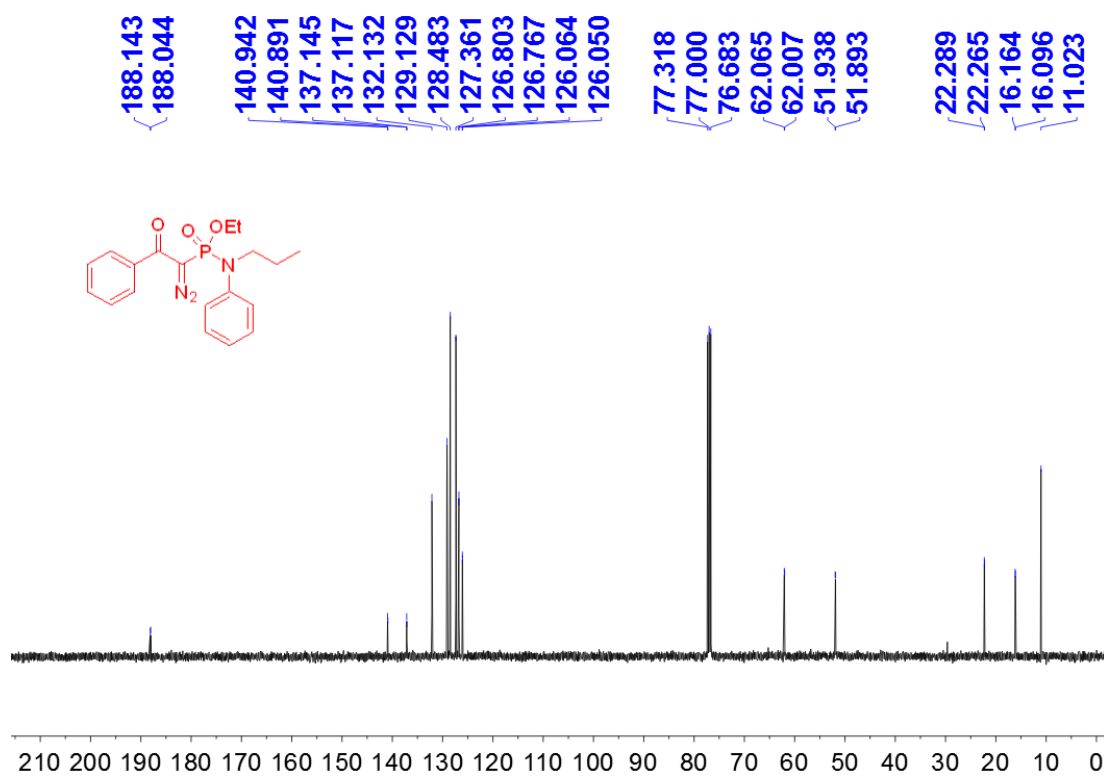
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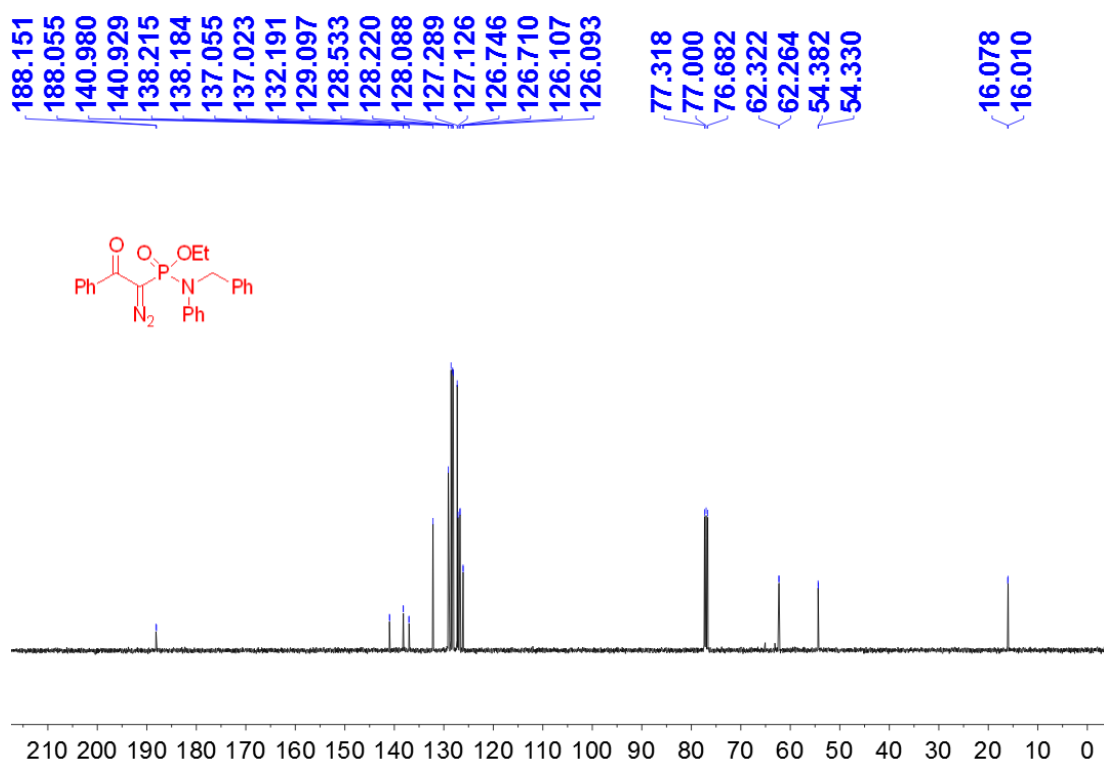
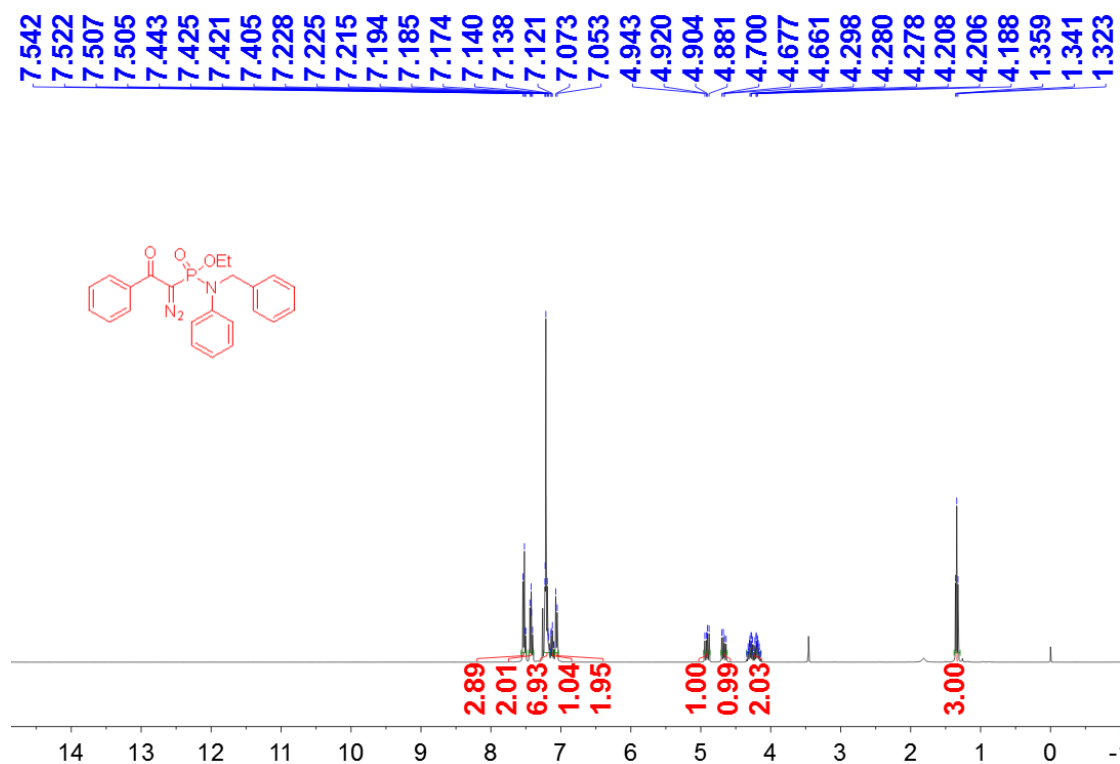


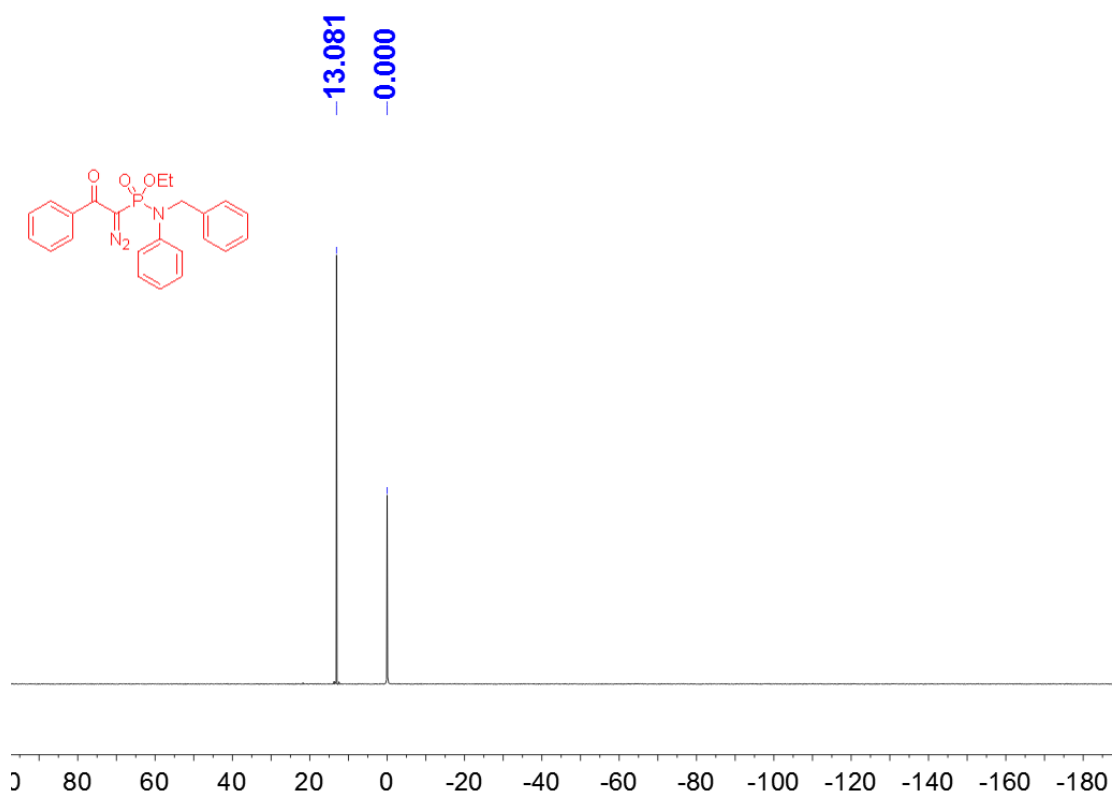
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-phenyl-*N*-propylphosphonamidate (1b)



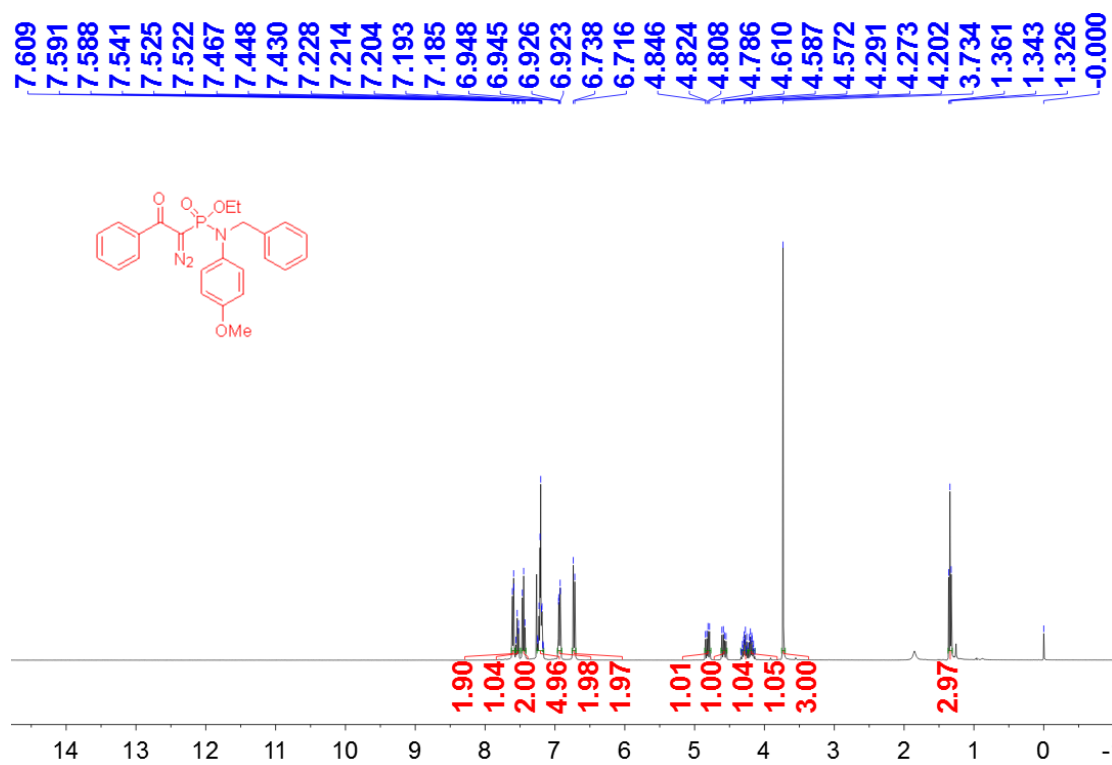


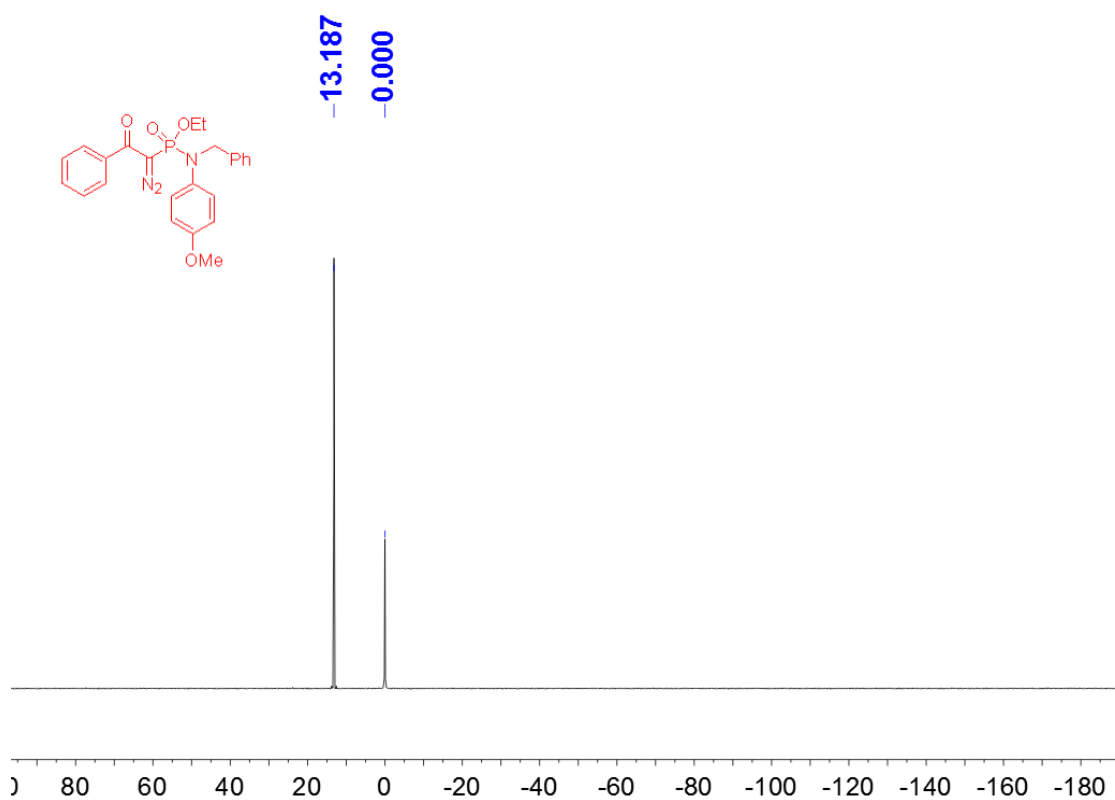
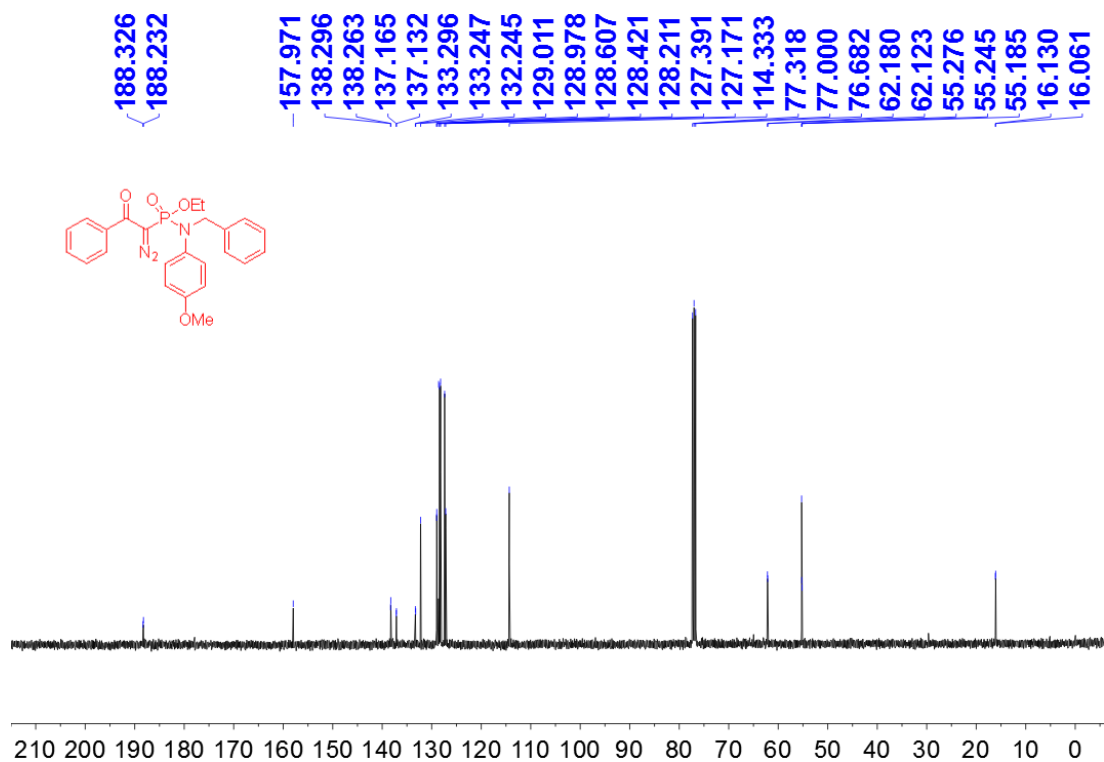
Ethyl *N*-benzyl-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-phenylphosphonamidate (1c)



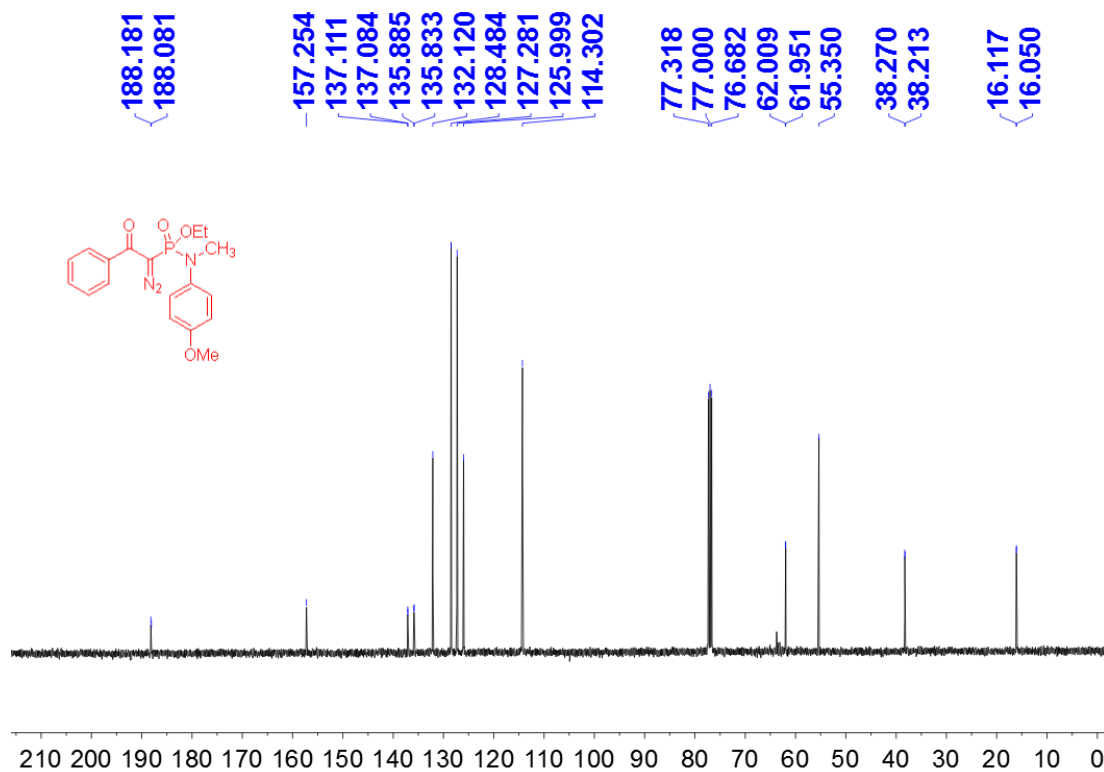
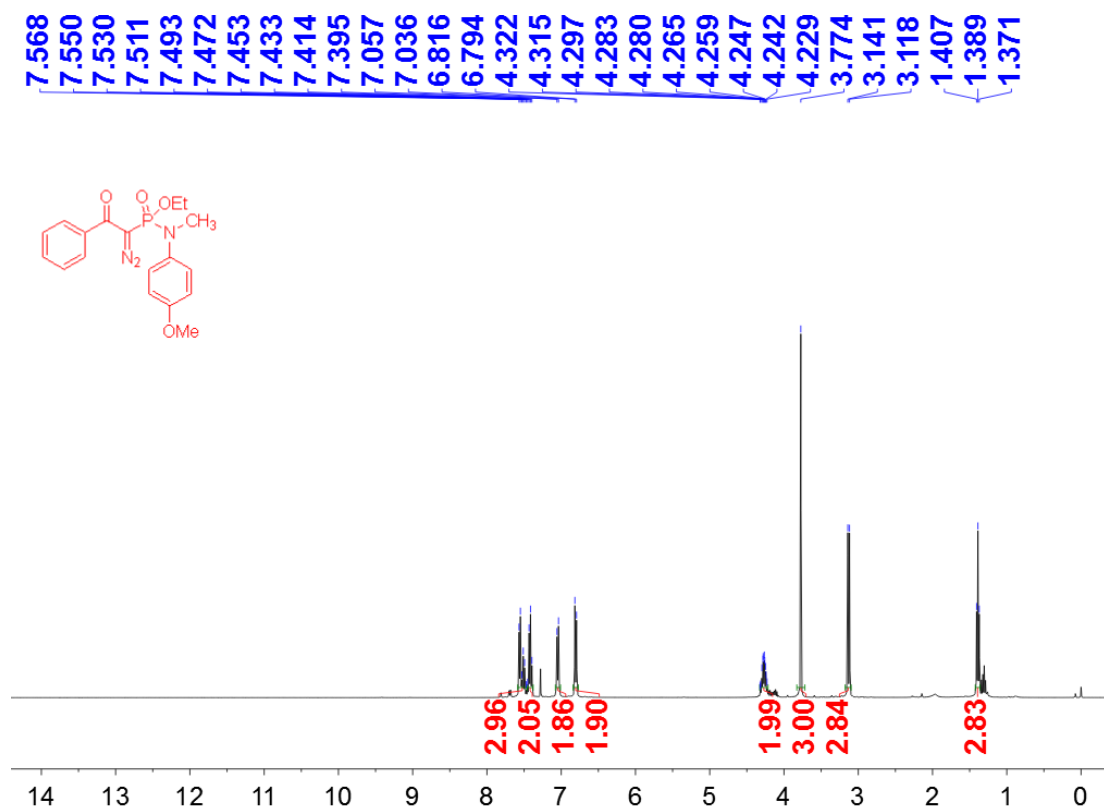


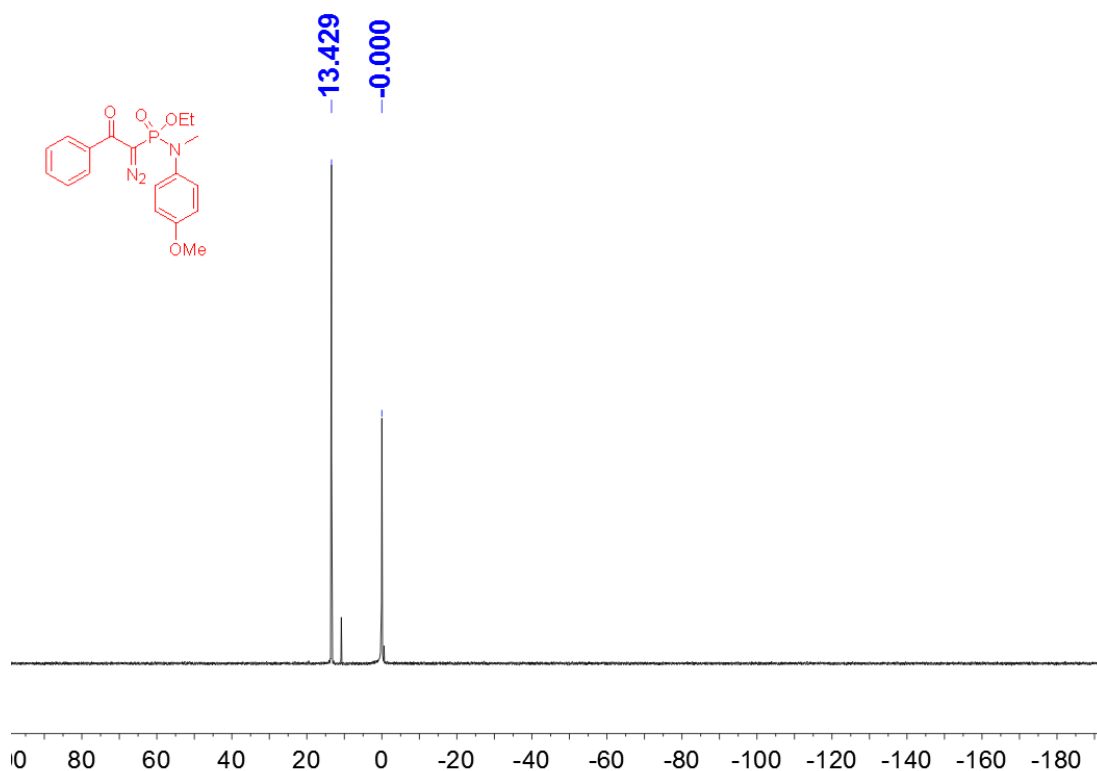
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-(4-methoxyphenyl)-*N*-methylphosphonamidate (1d)



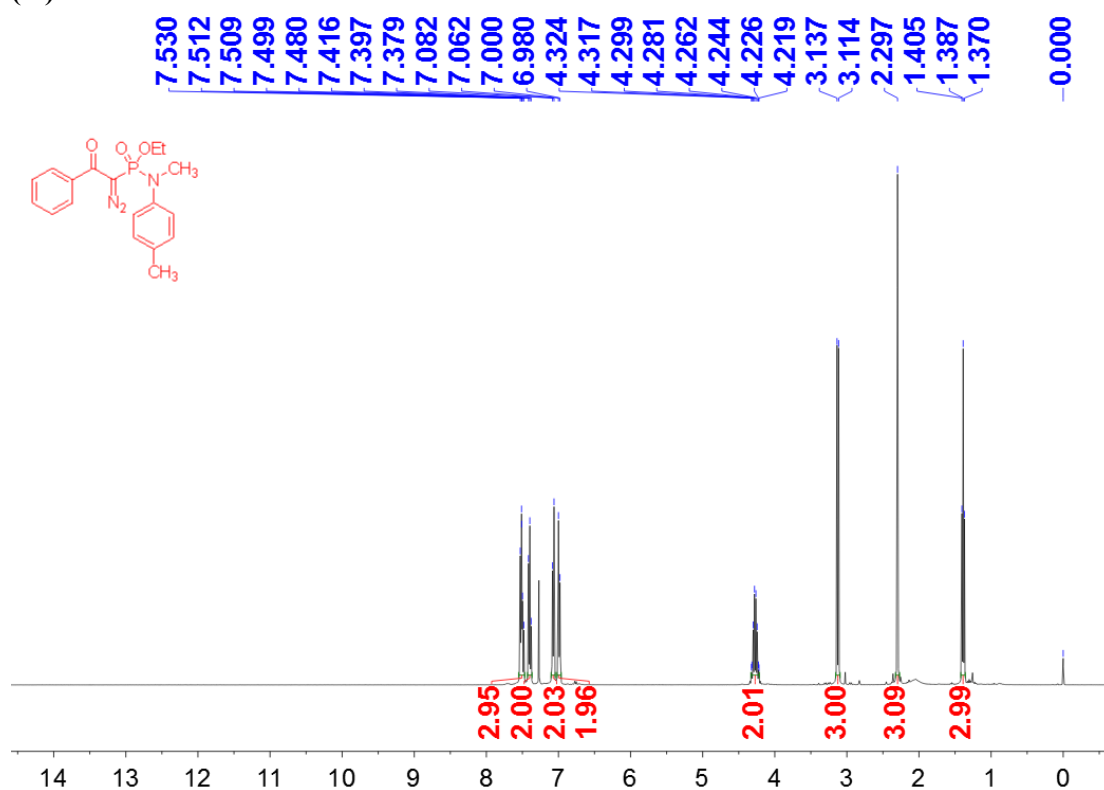


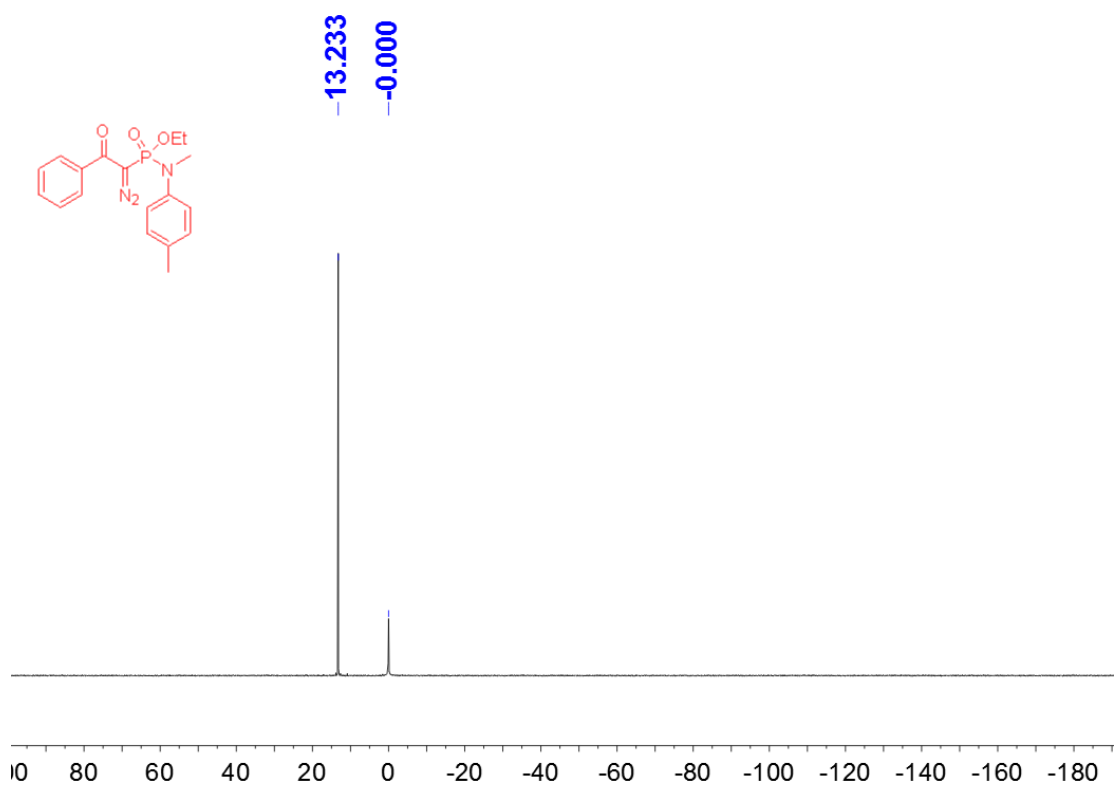
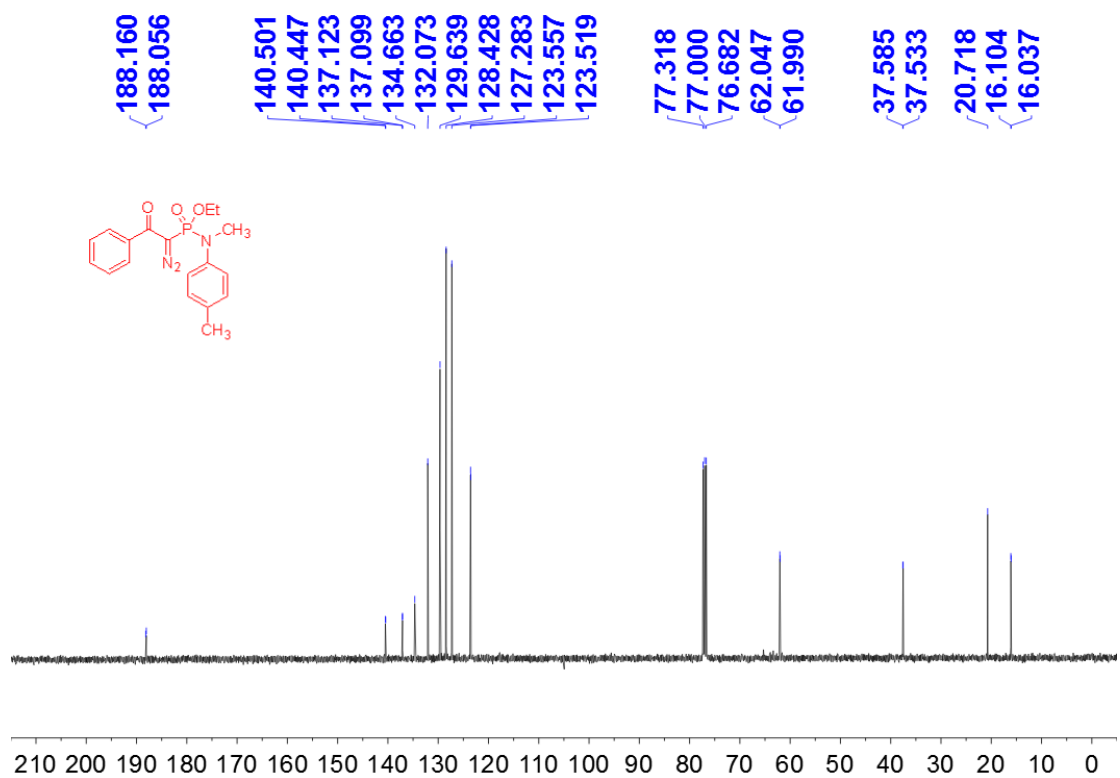
Ethyl *N*-benzyl-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-(4-methoxyphenyl)phosphonamidate (1e)



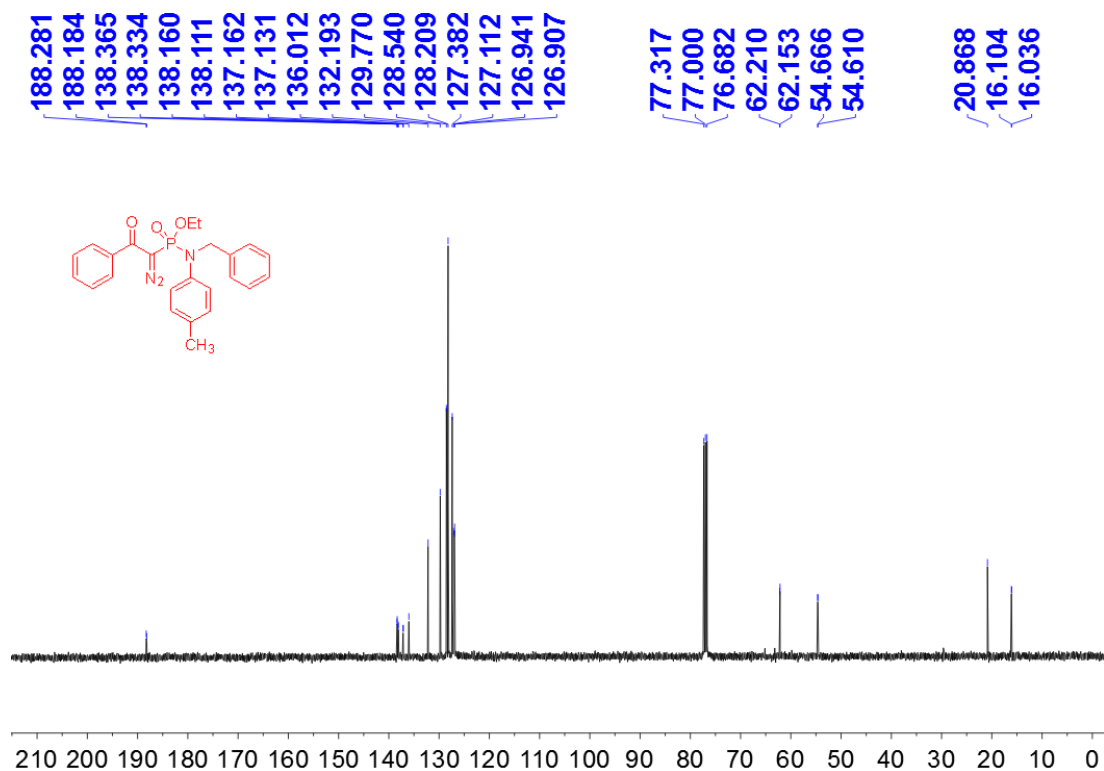
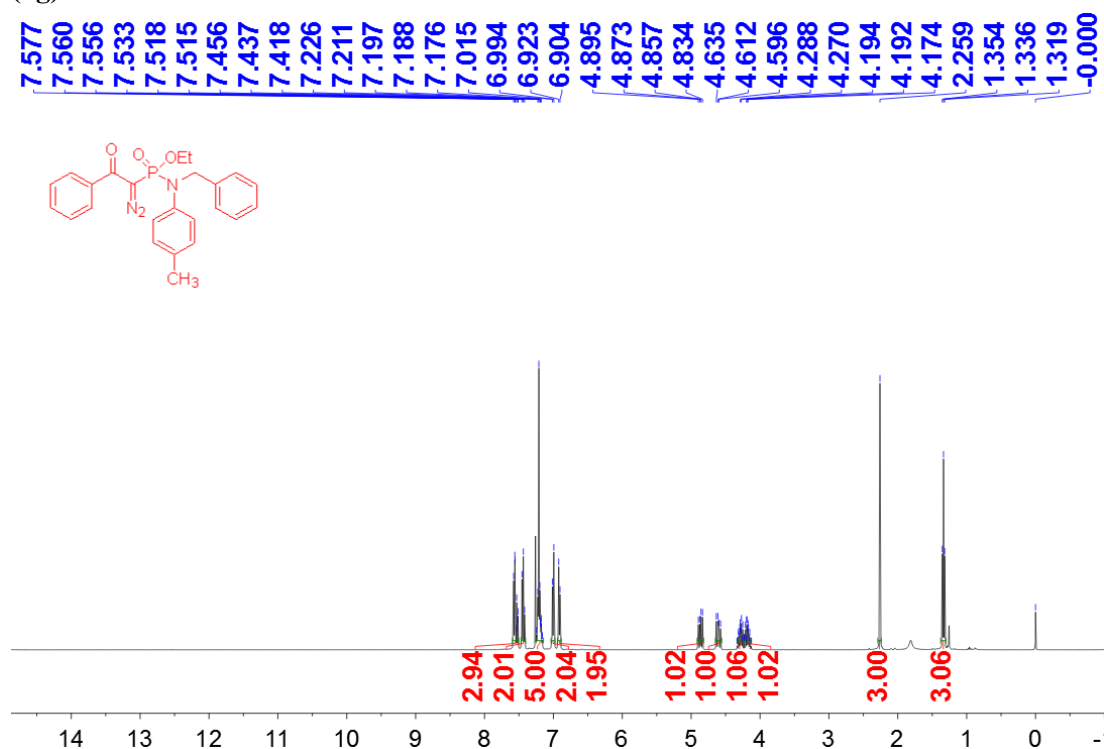


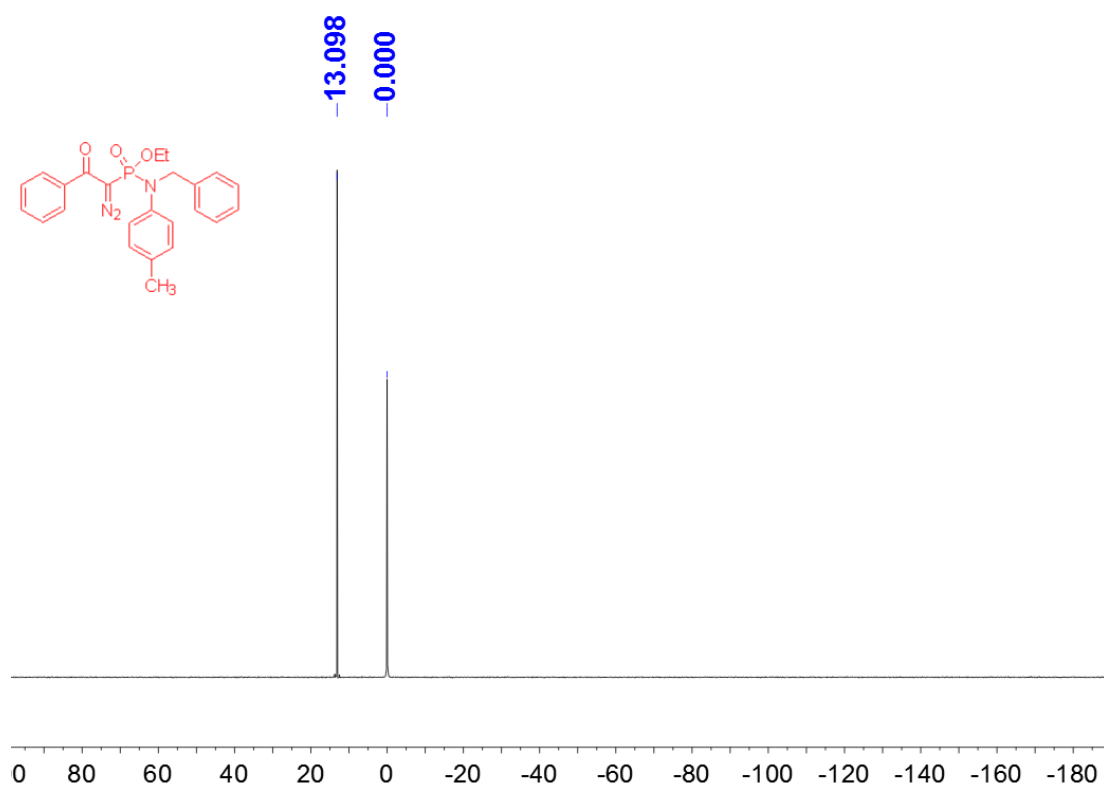
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methyl-*N*-(4-methylphenyl)phosphonamidate (1f)



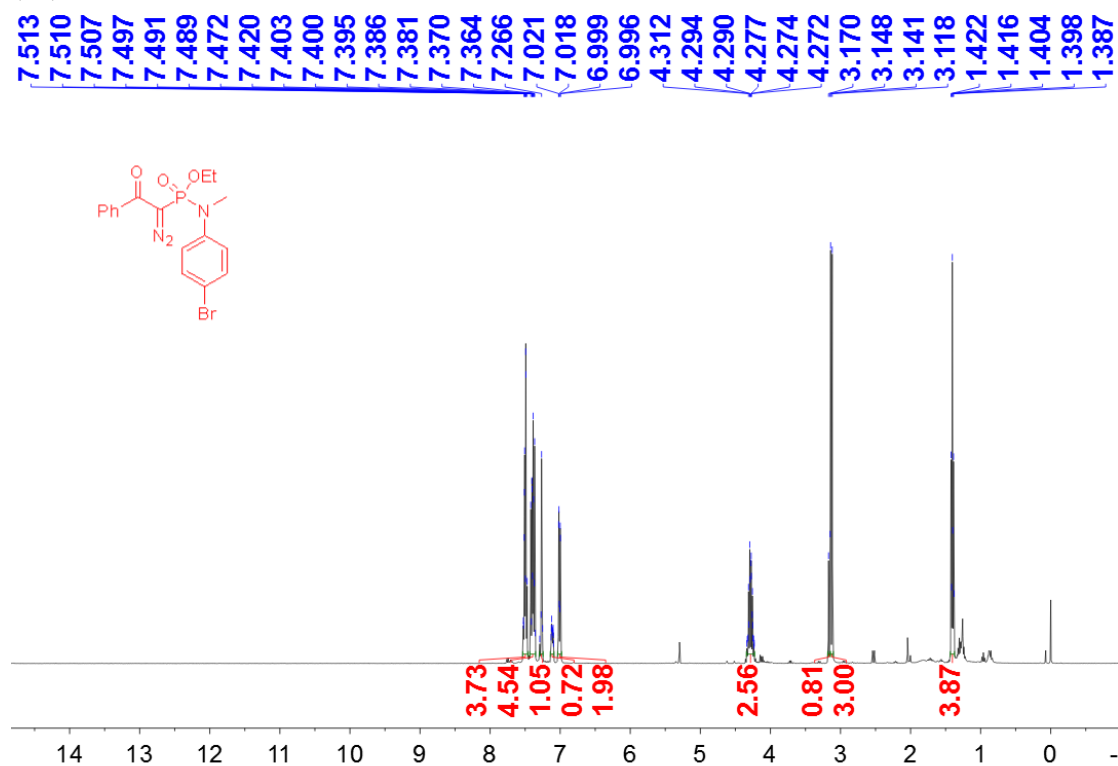


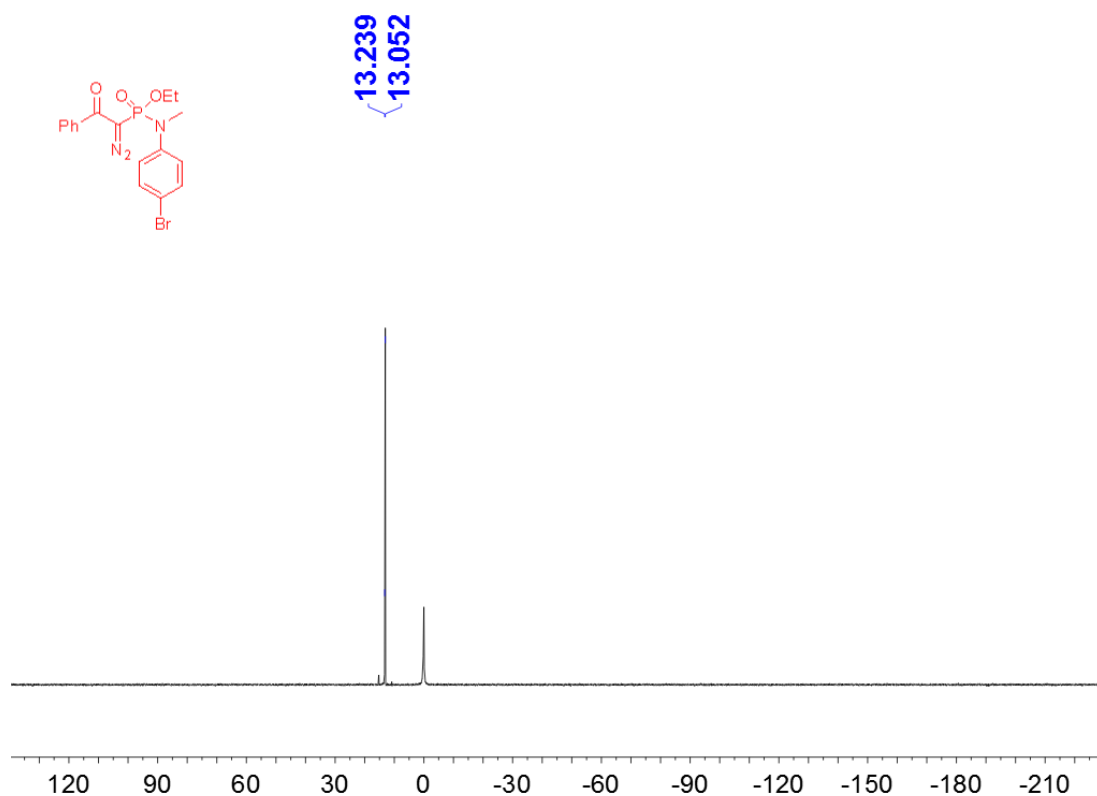
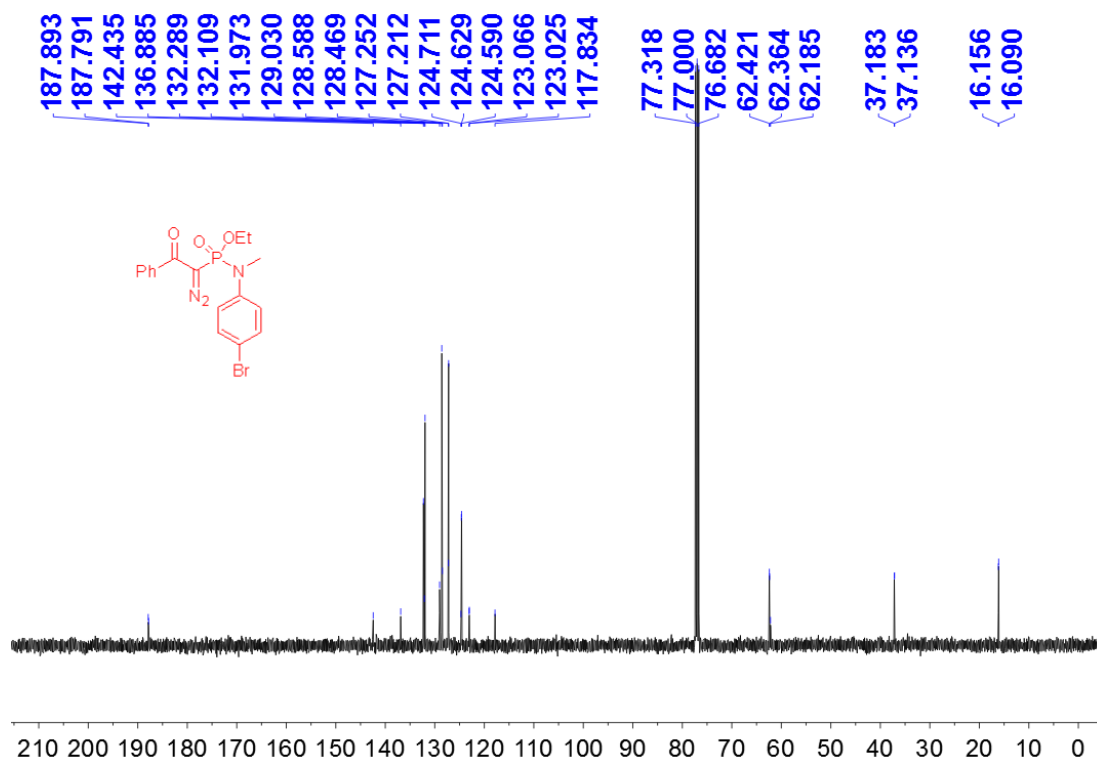
Ethyl *N*-benzyl-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-(4-methylphenyl)phosphonamidate (1g)



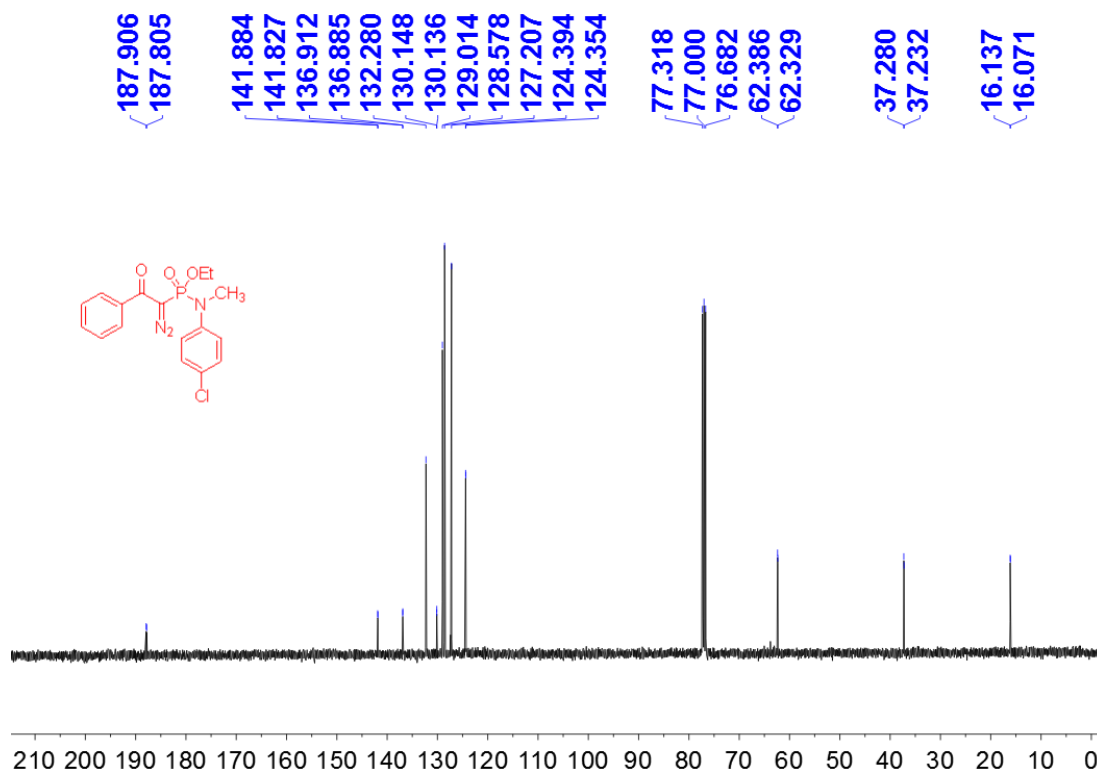
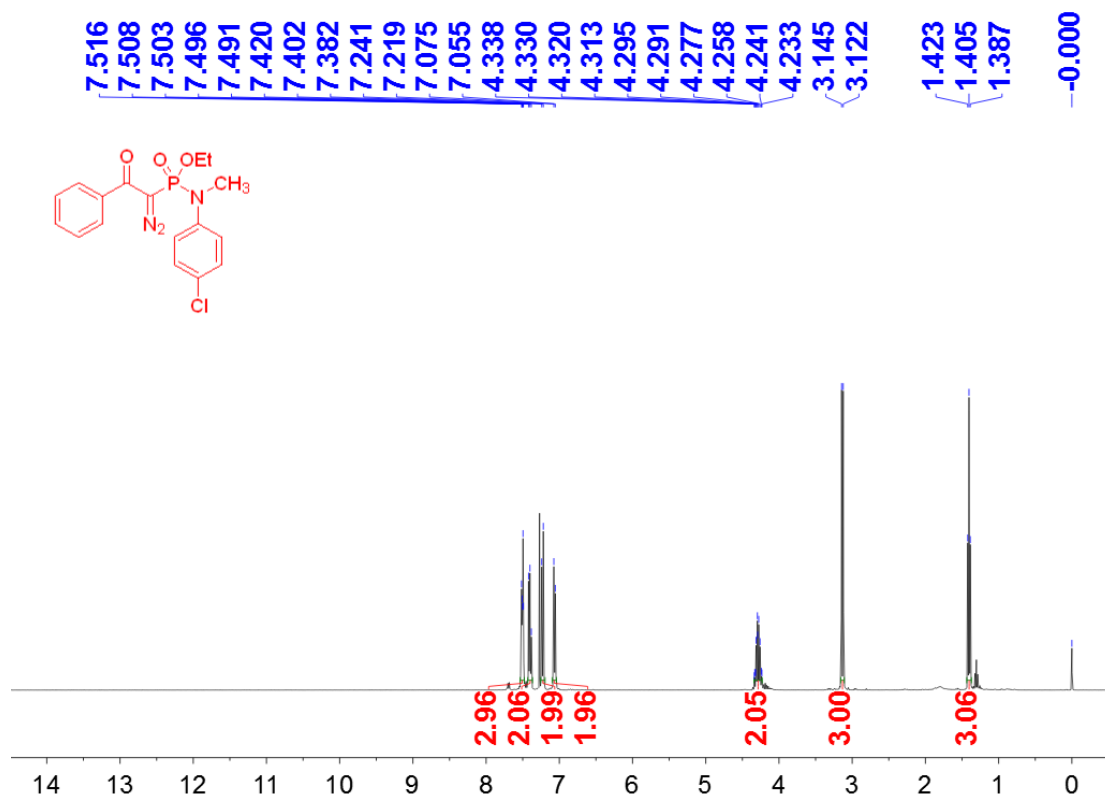


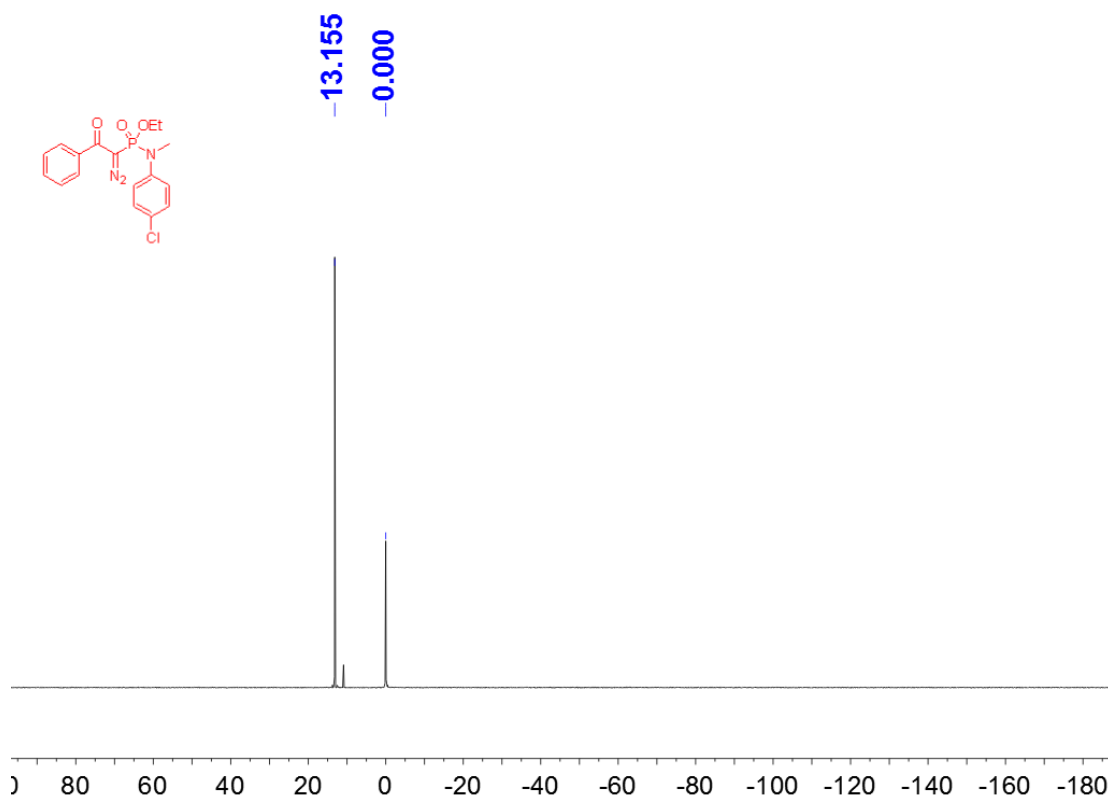
Ethyl *N*-(4-bromophenyl)-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methylphosphonamidate (1h)



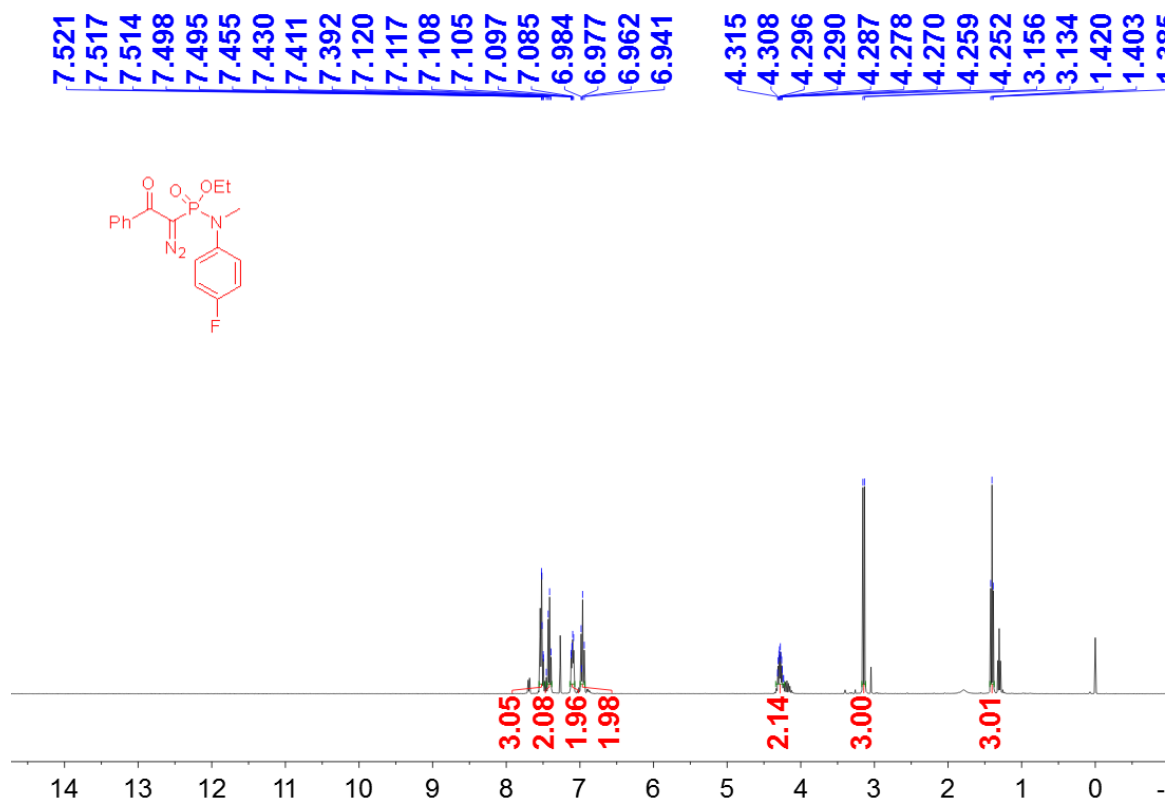


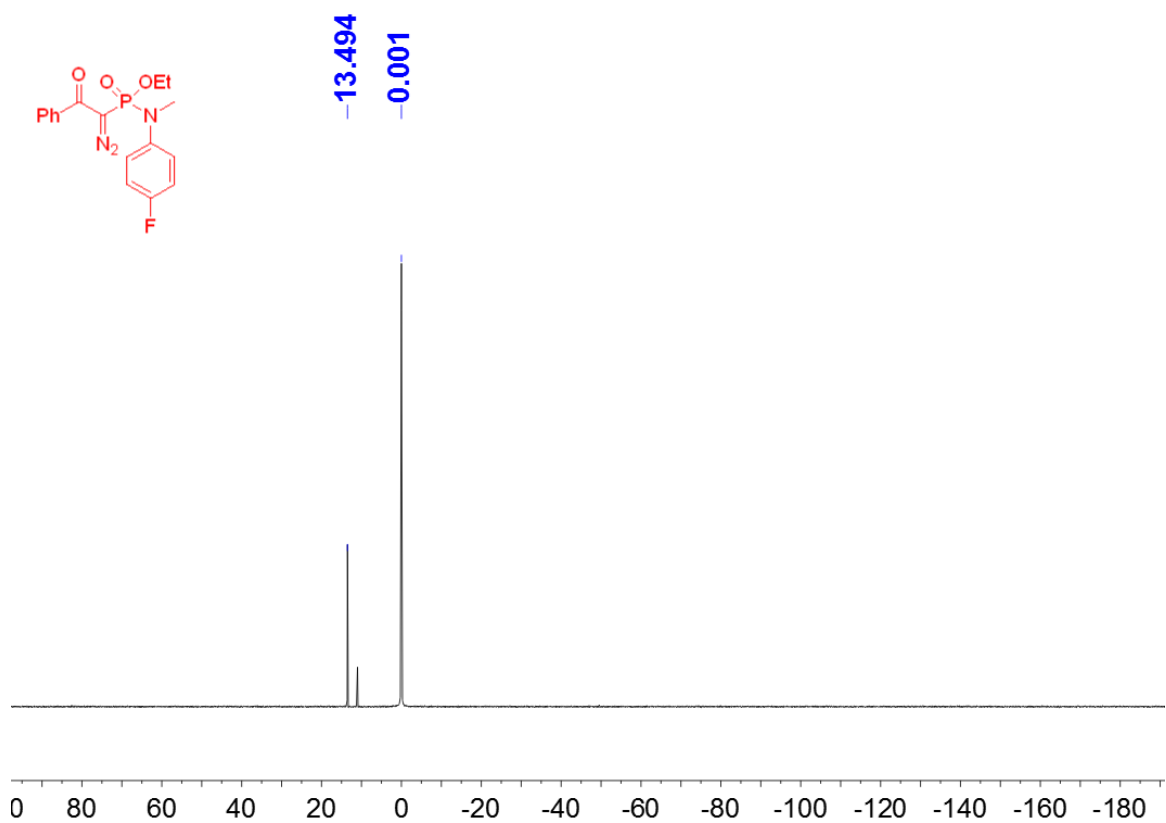
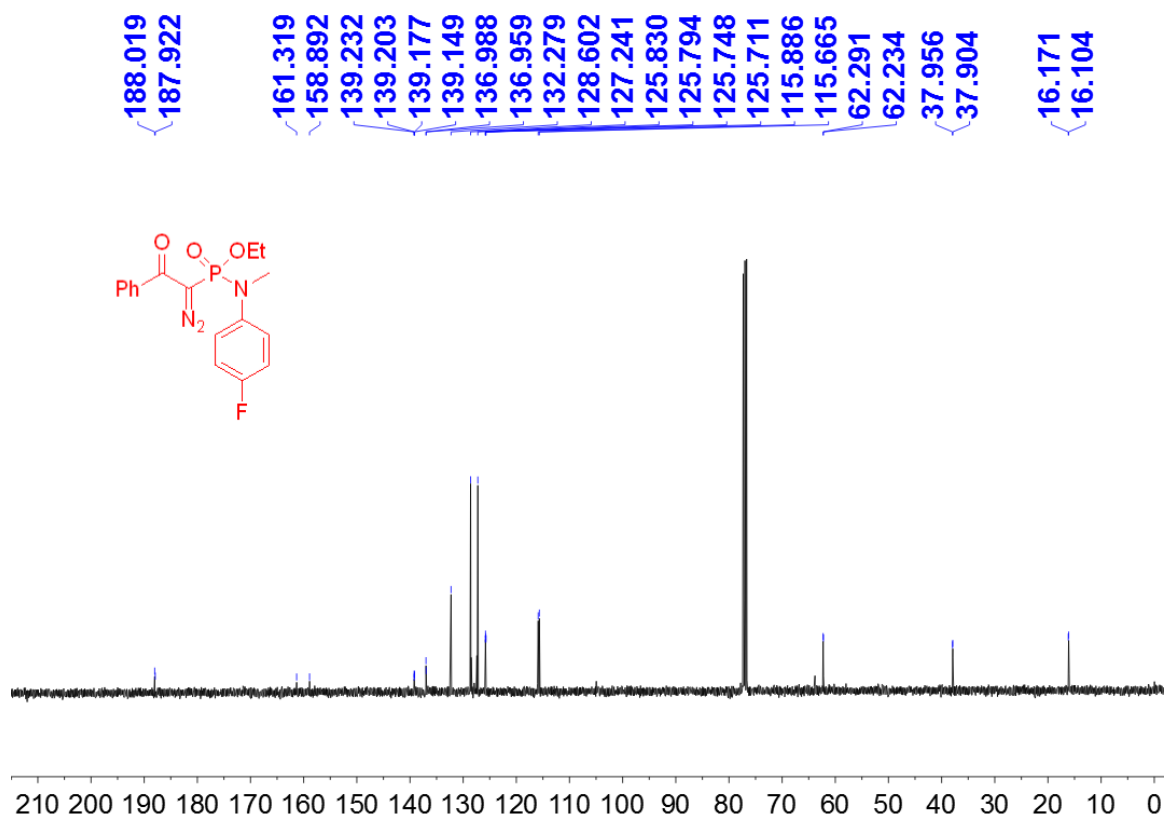
Ethyl *N*-(4-chlorophenyl)-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methylphosphonamidate (1i)

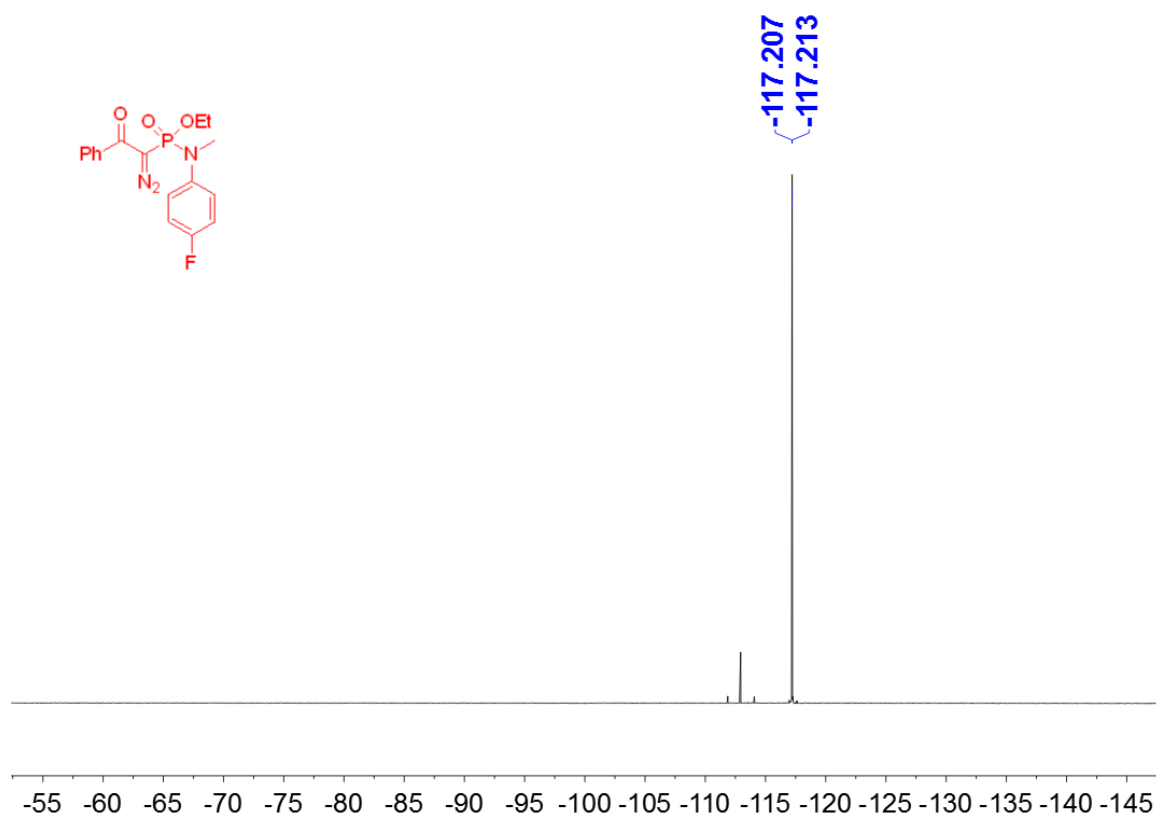




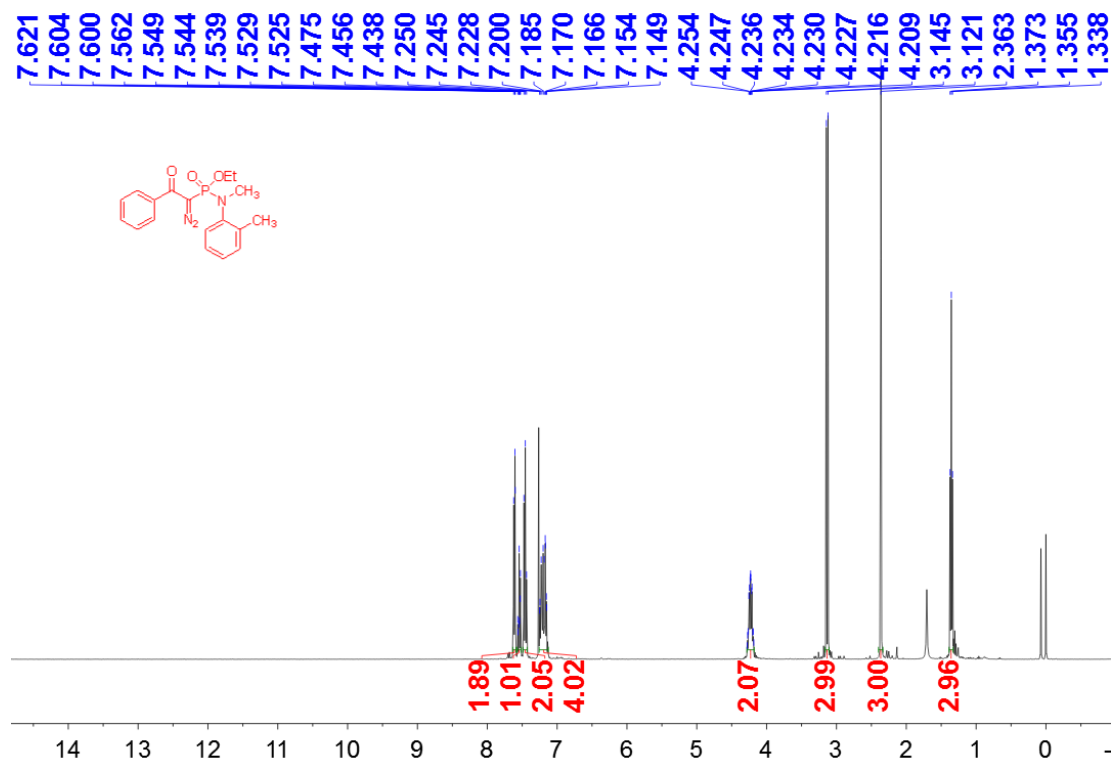
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-(4-fluorophenyl)-*N*-methylphosphonamidate (1j)

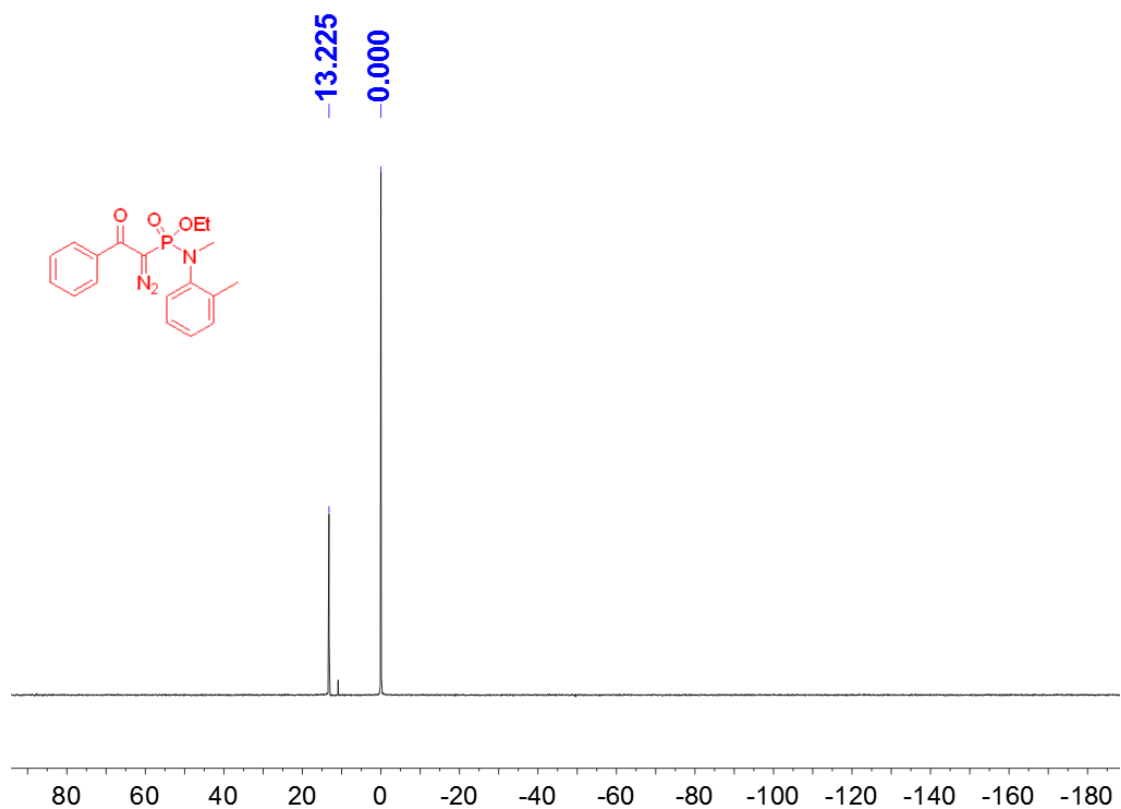
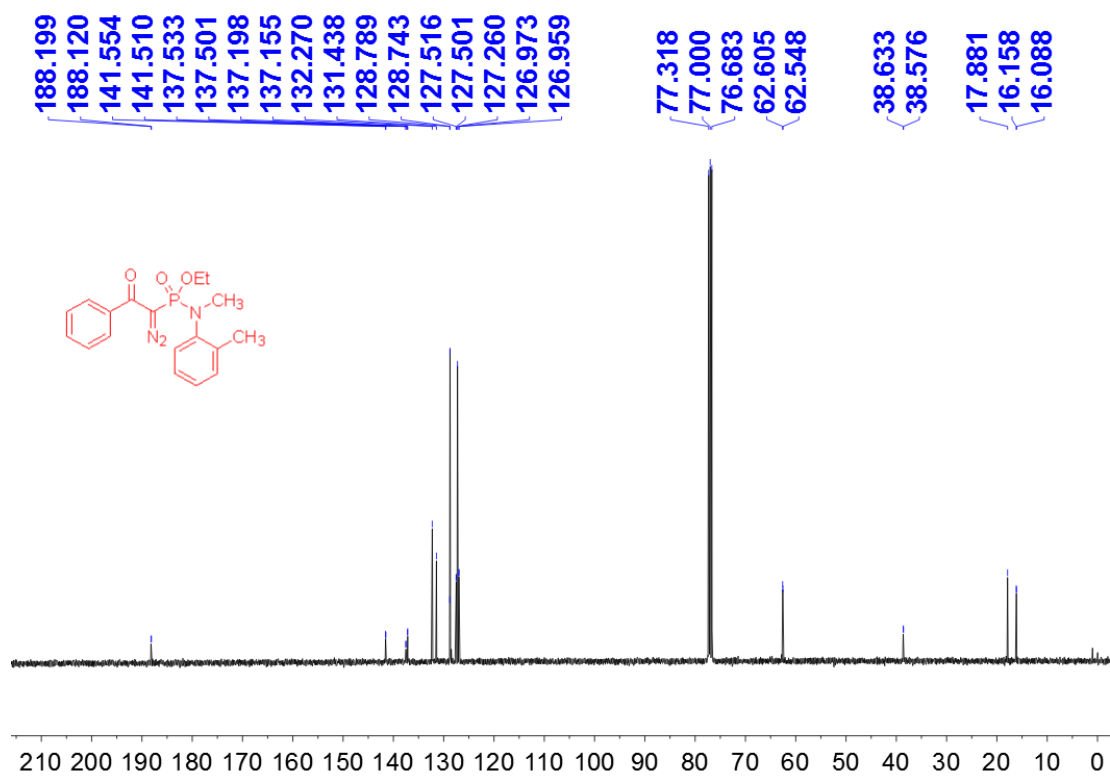




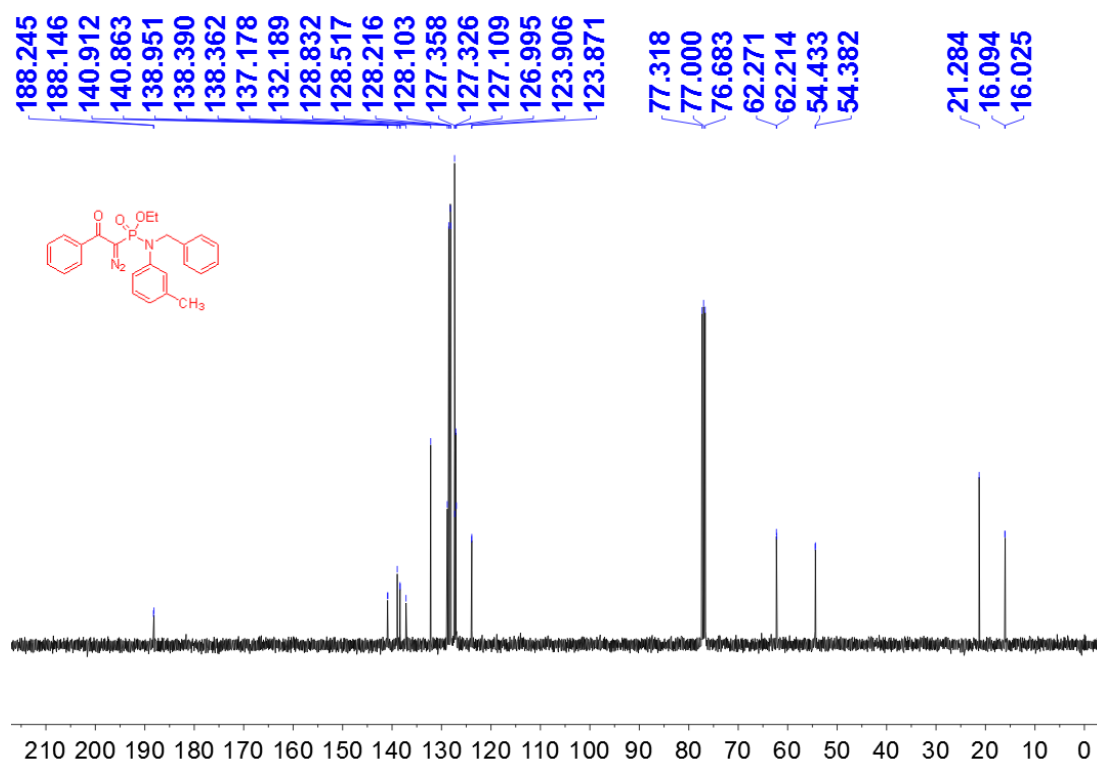
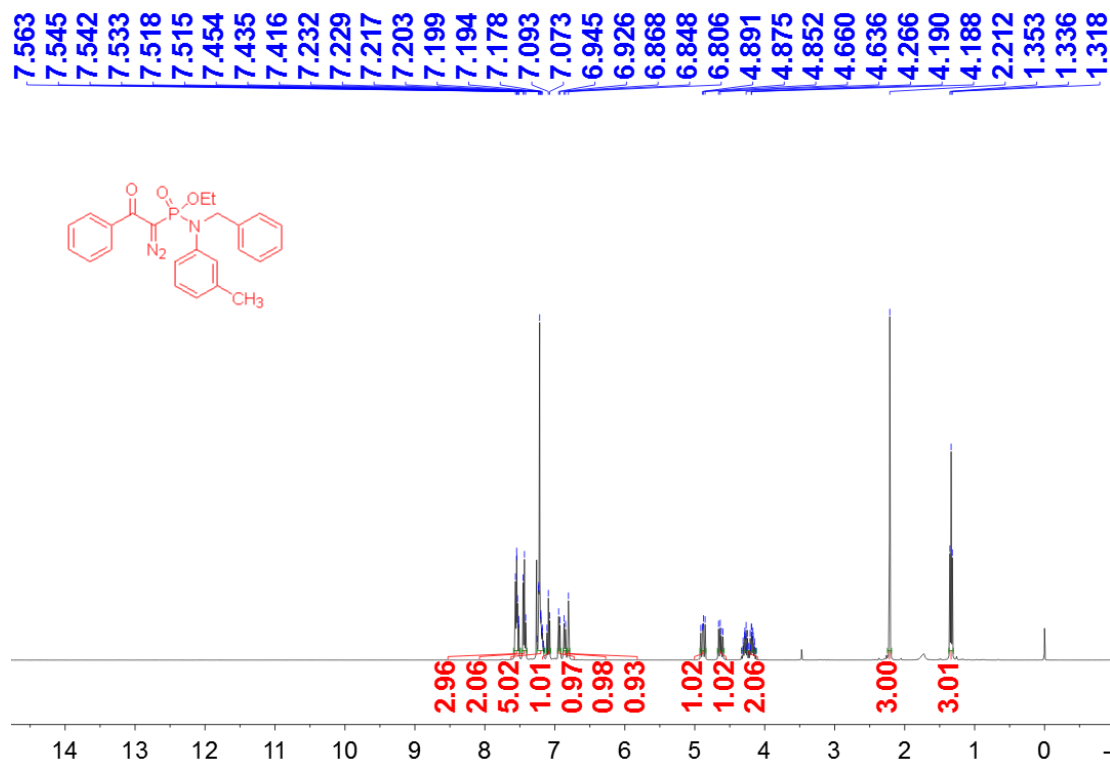


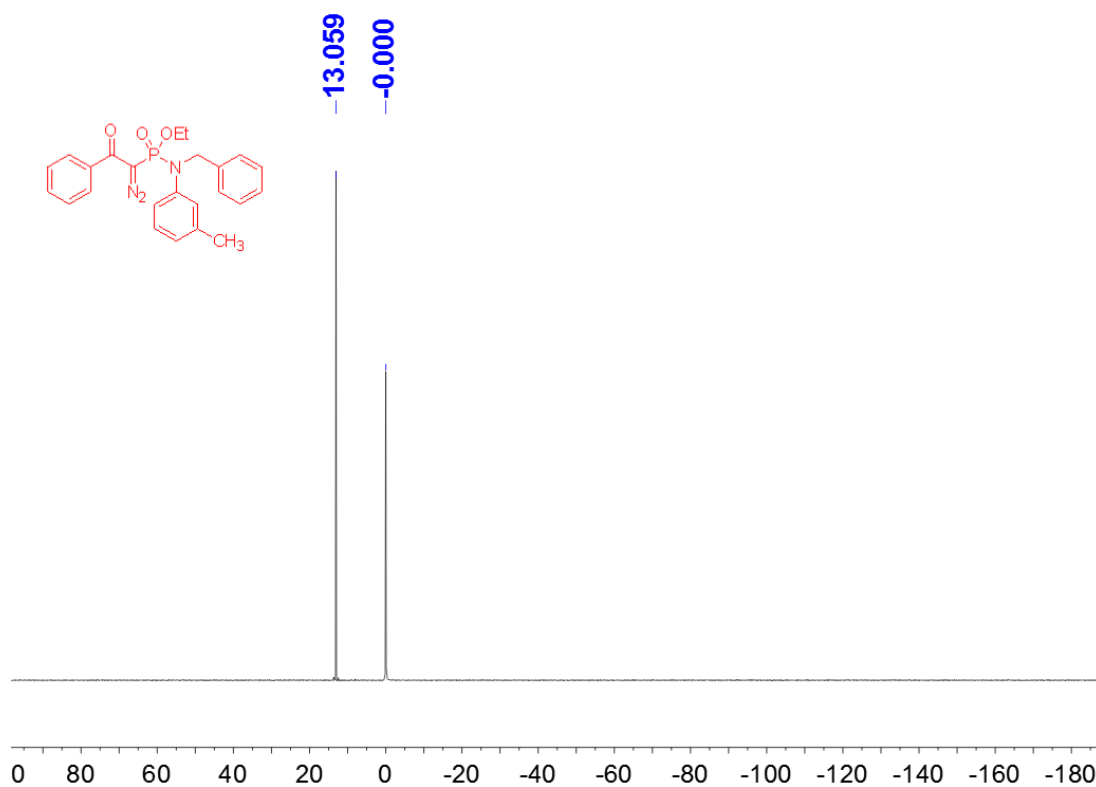
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methyl-*N*-(2-methylphenyl)phosphonamidate (1k)



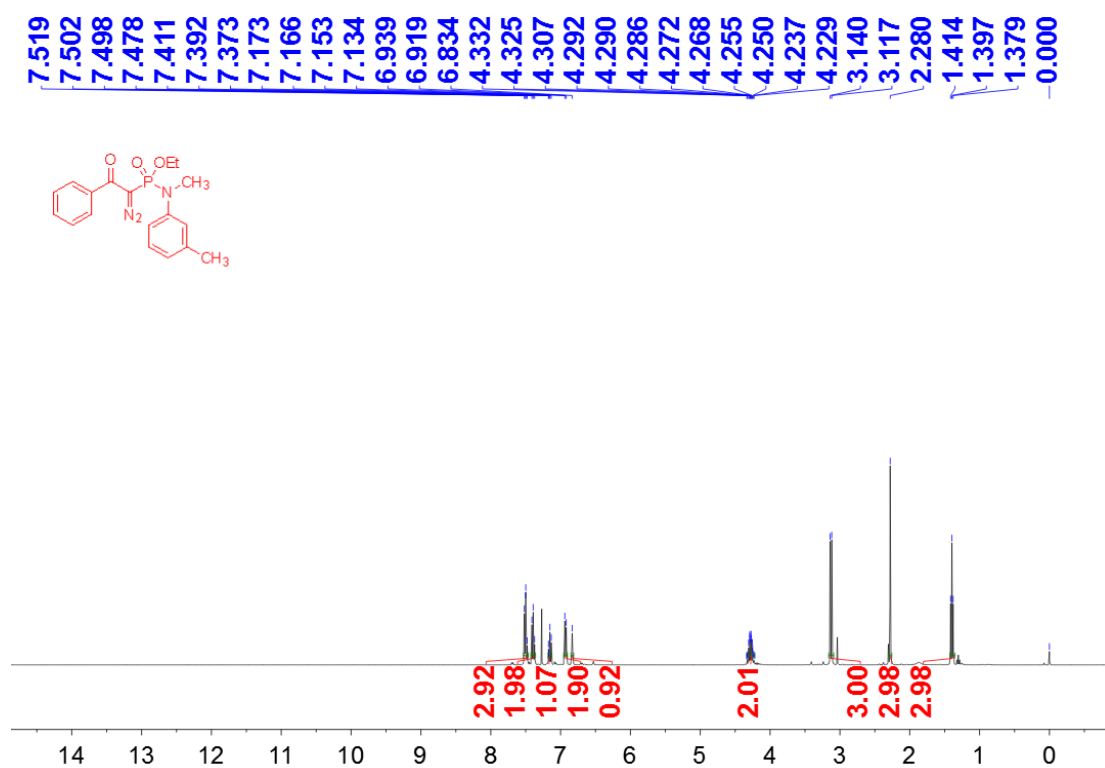


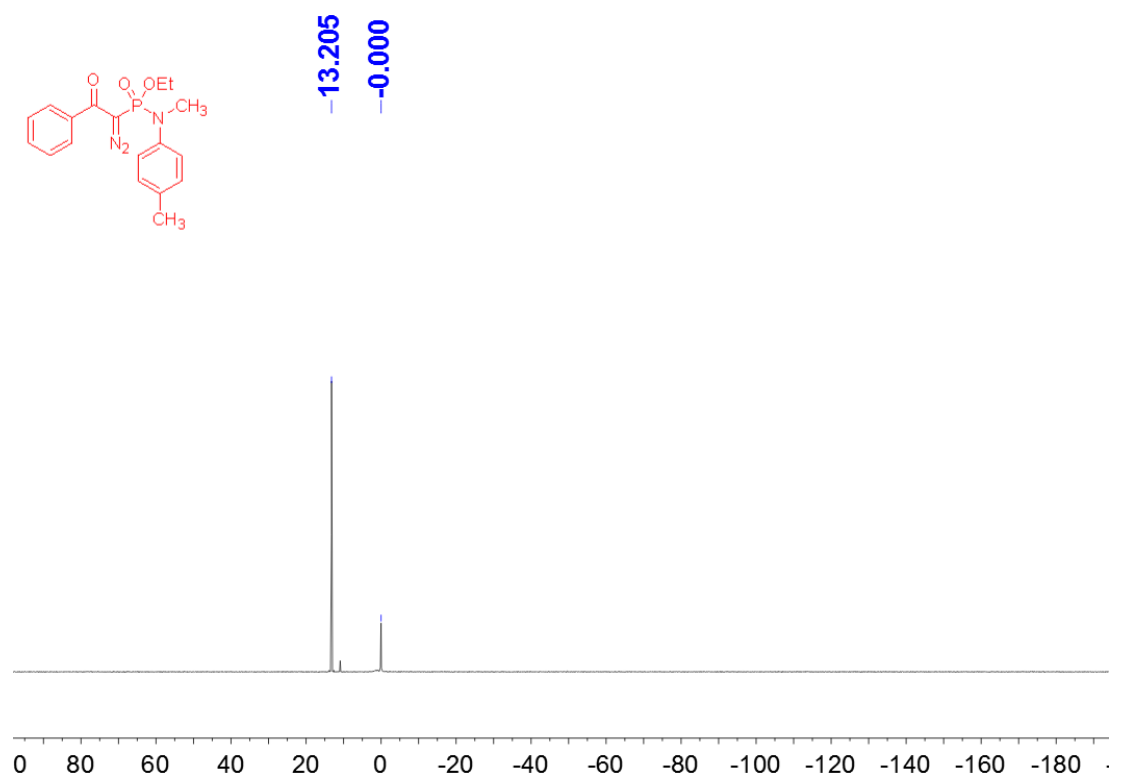
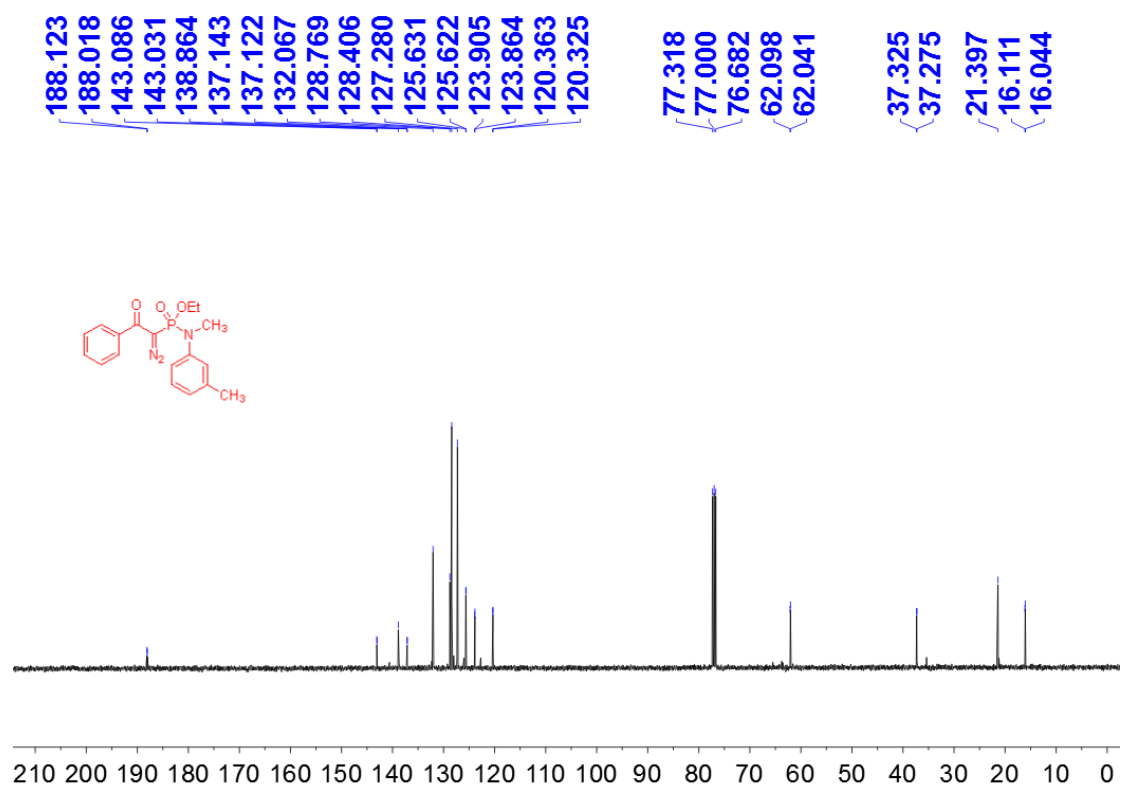
Ethyl *N*-benzyl-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-(3-methylphenyl)phosphonamidate (11)



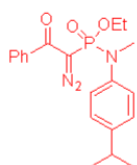
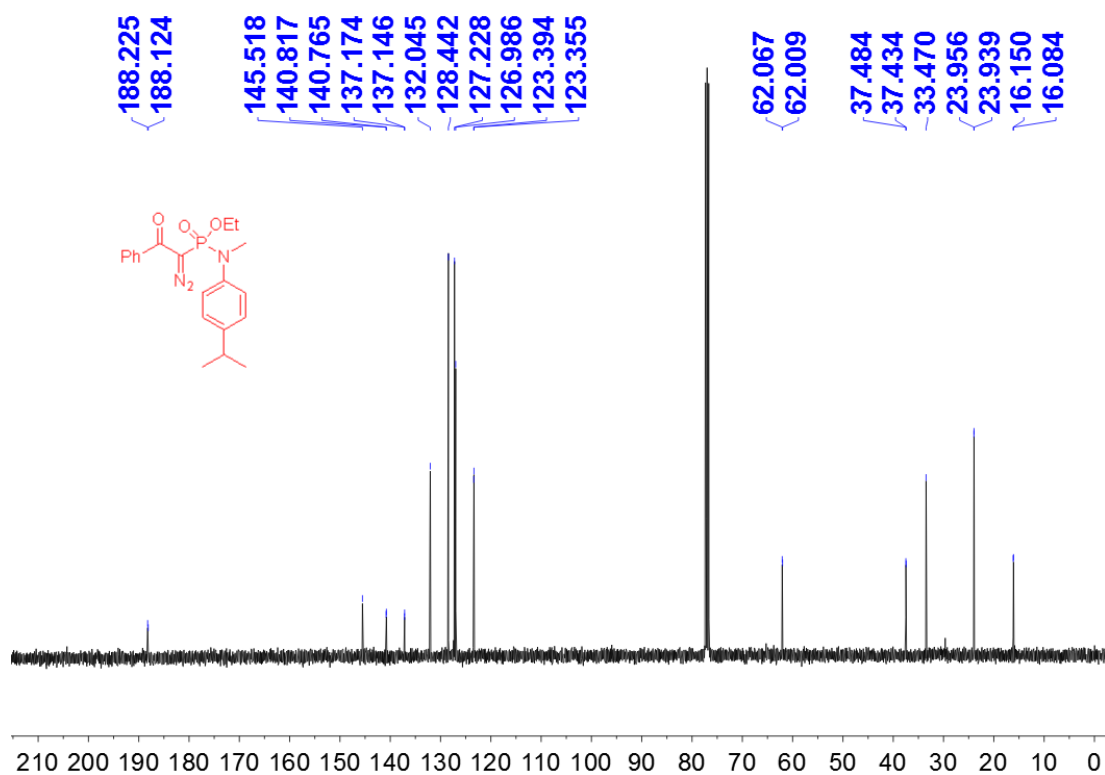
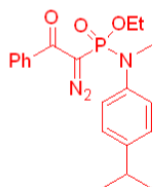
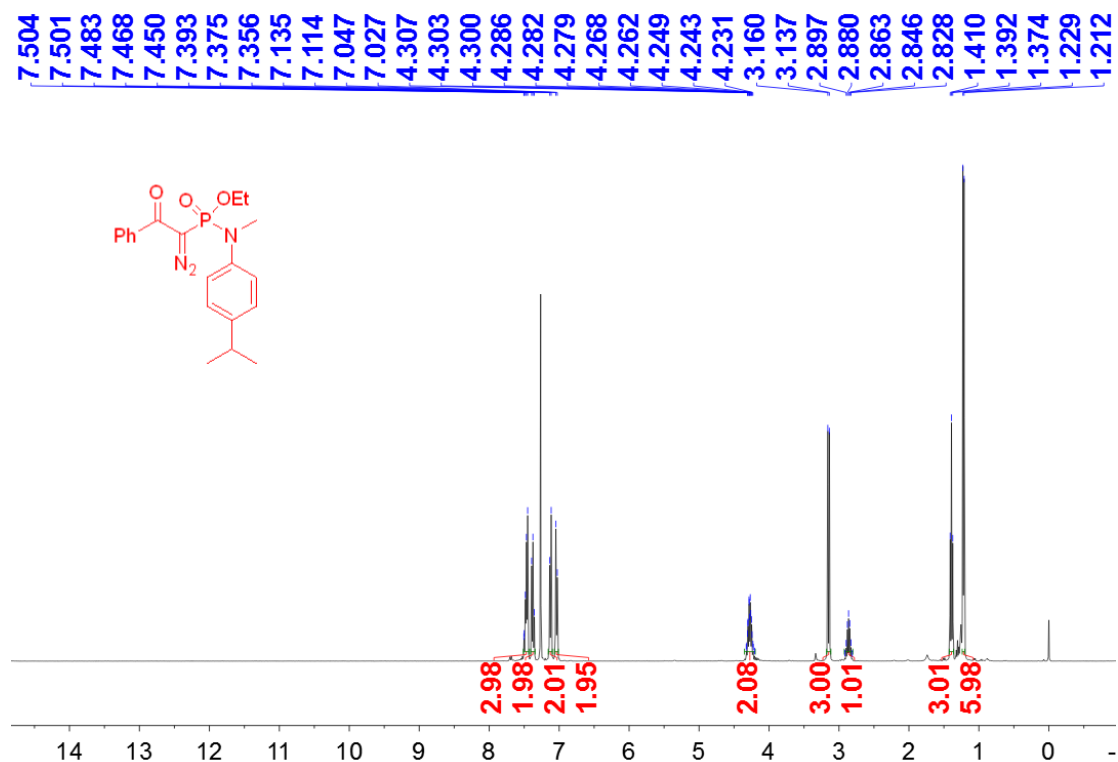


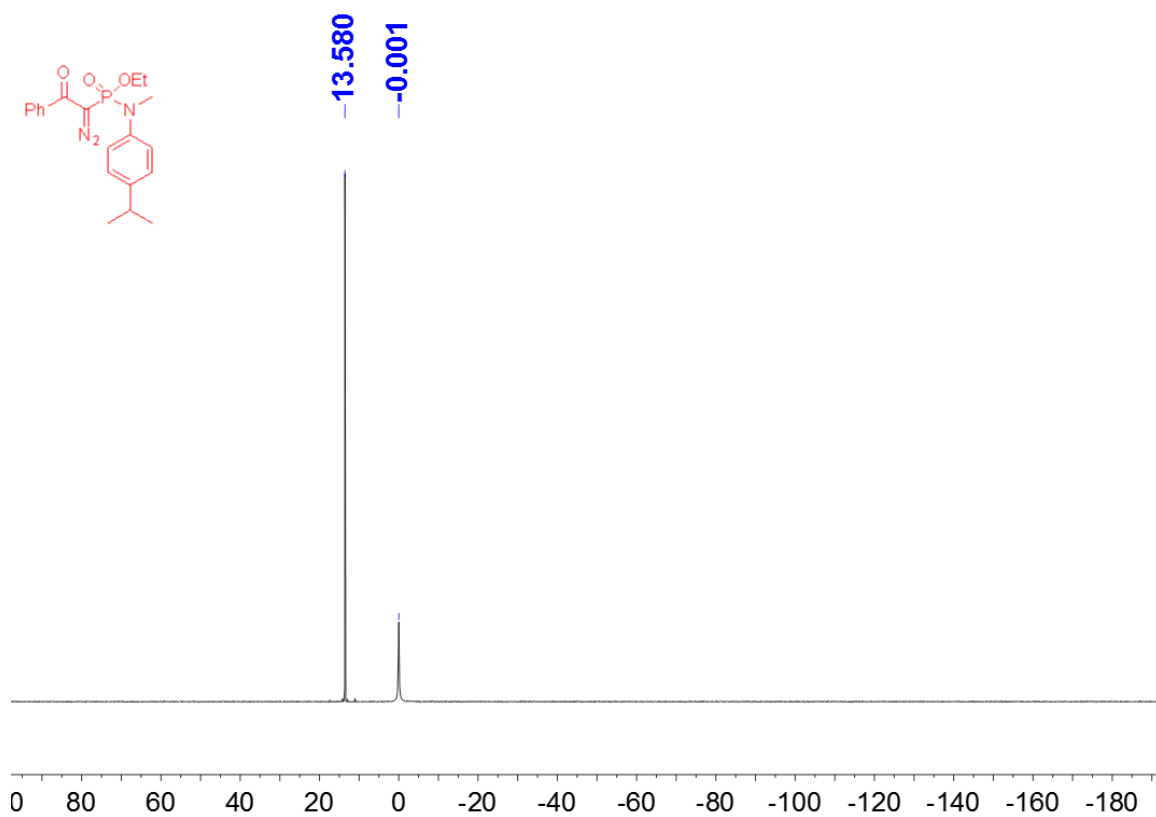
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methyl-*N*-(3-methylphenyl)phosphonamidate (1m)



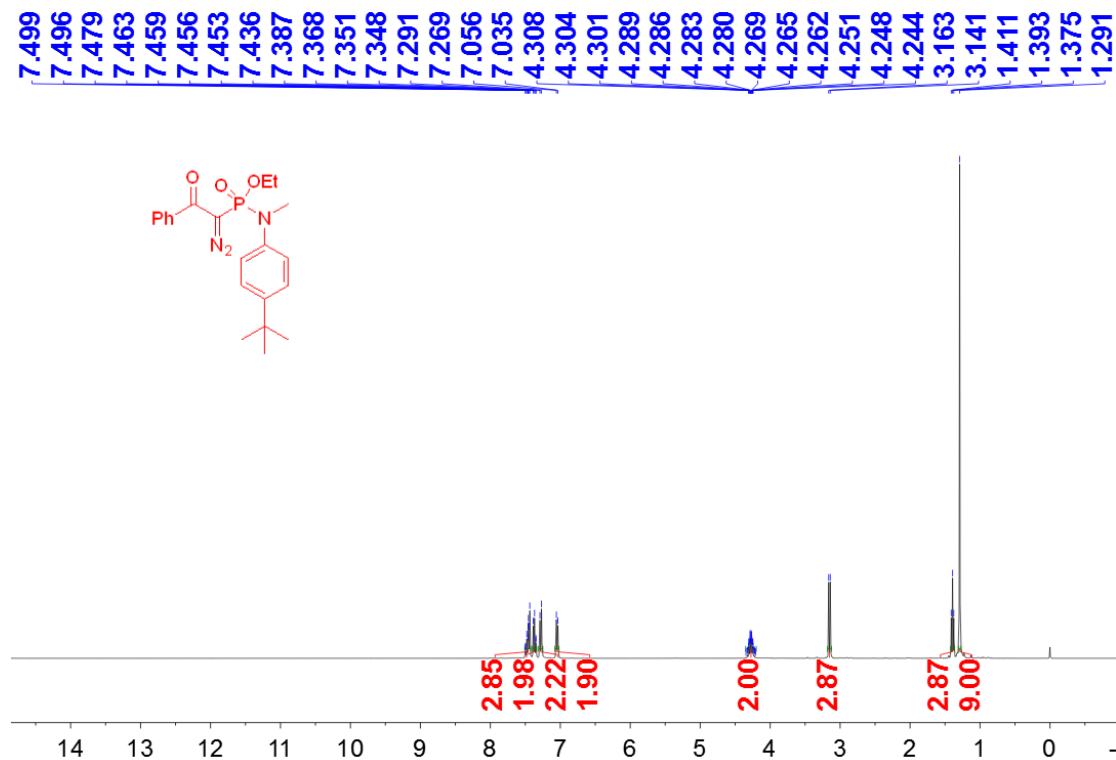


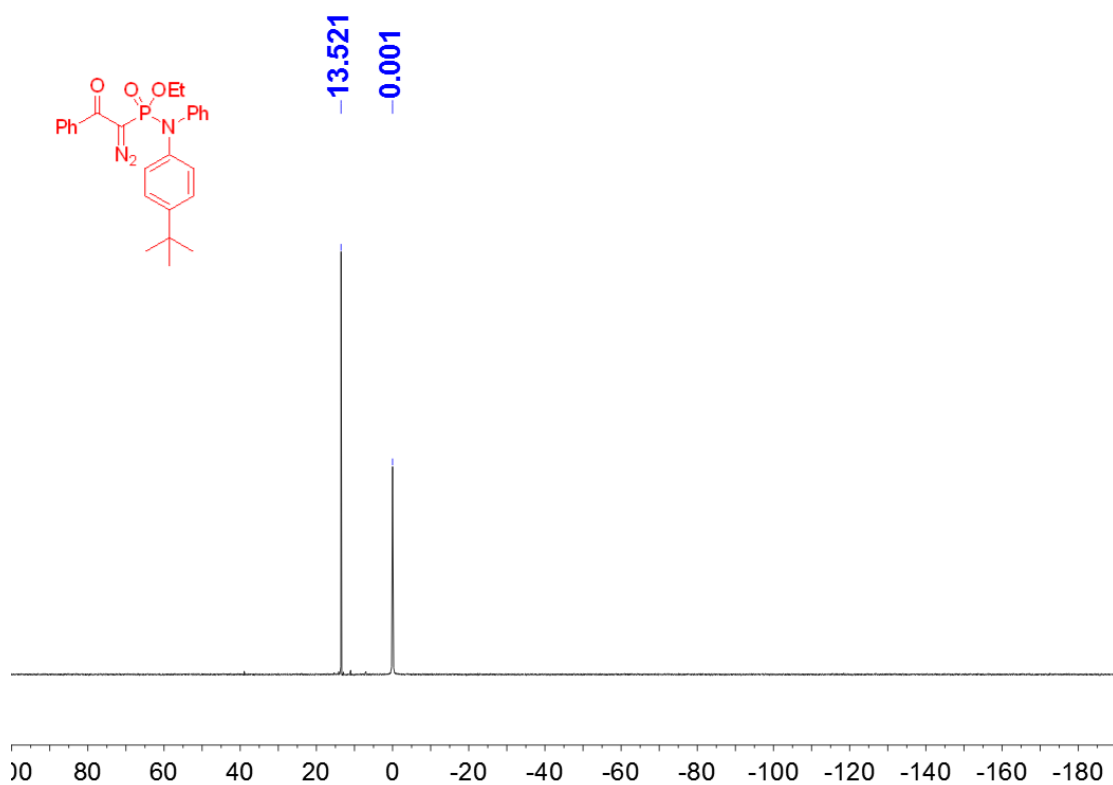
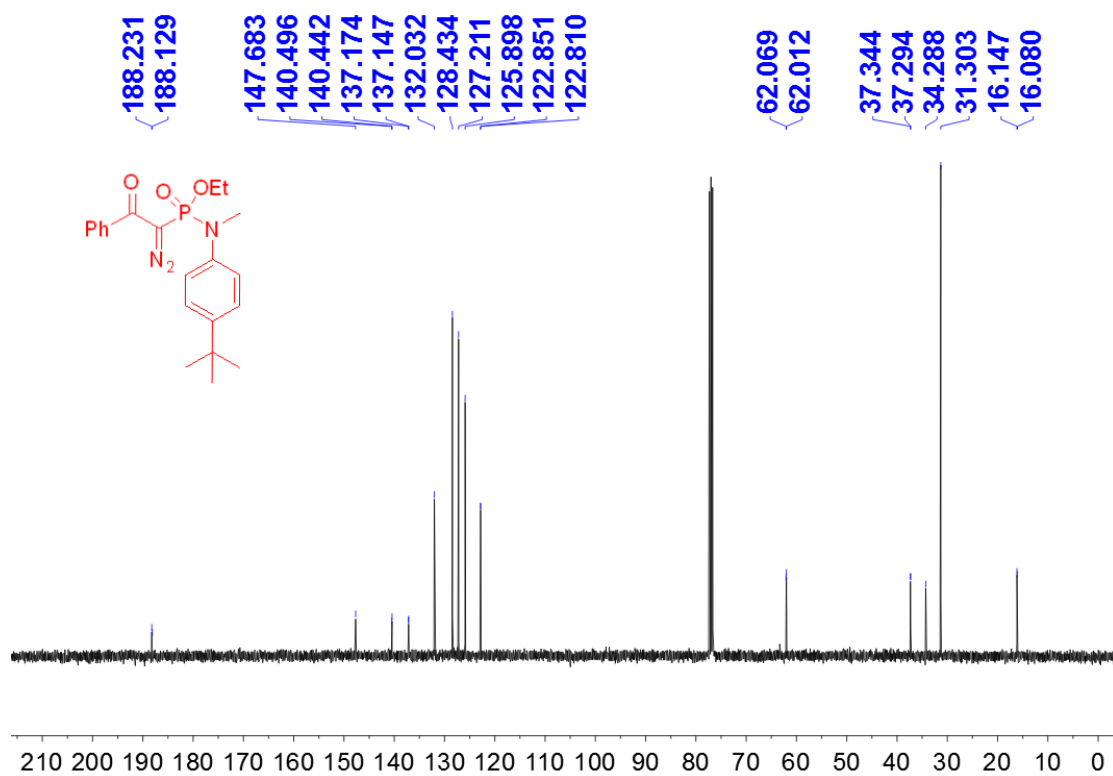
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-(4-isopropylphenyl)-*N*-methylphosphonamidate (**1n**)



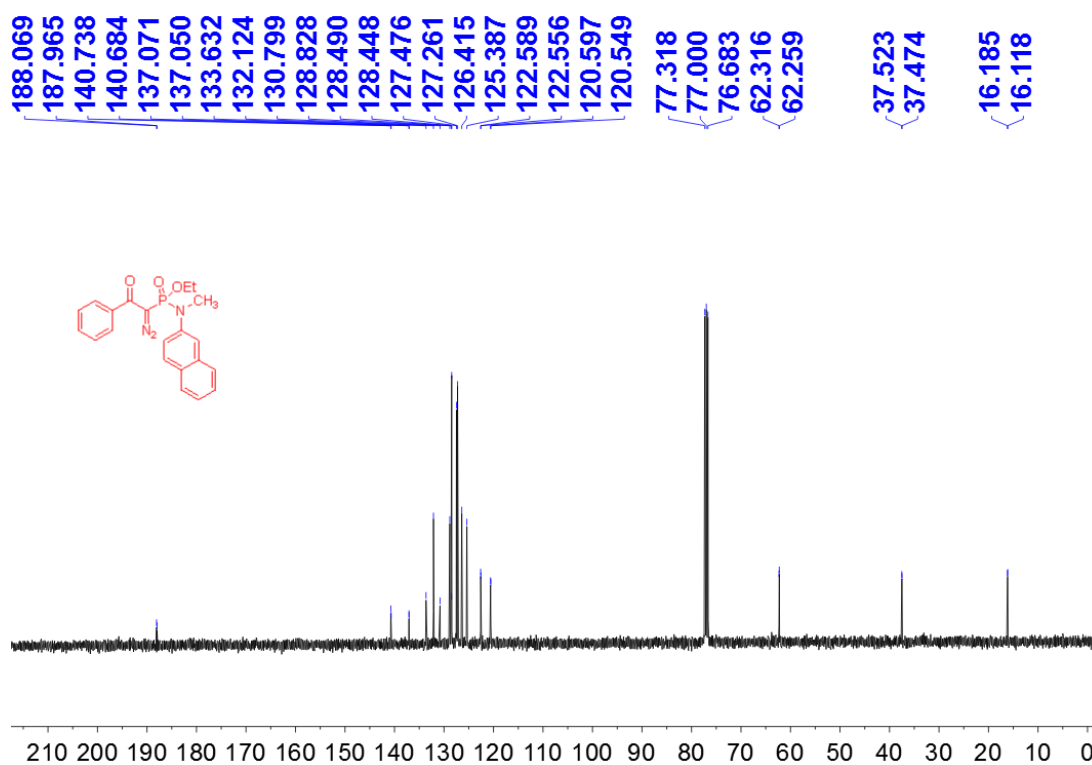
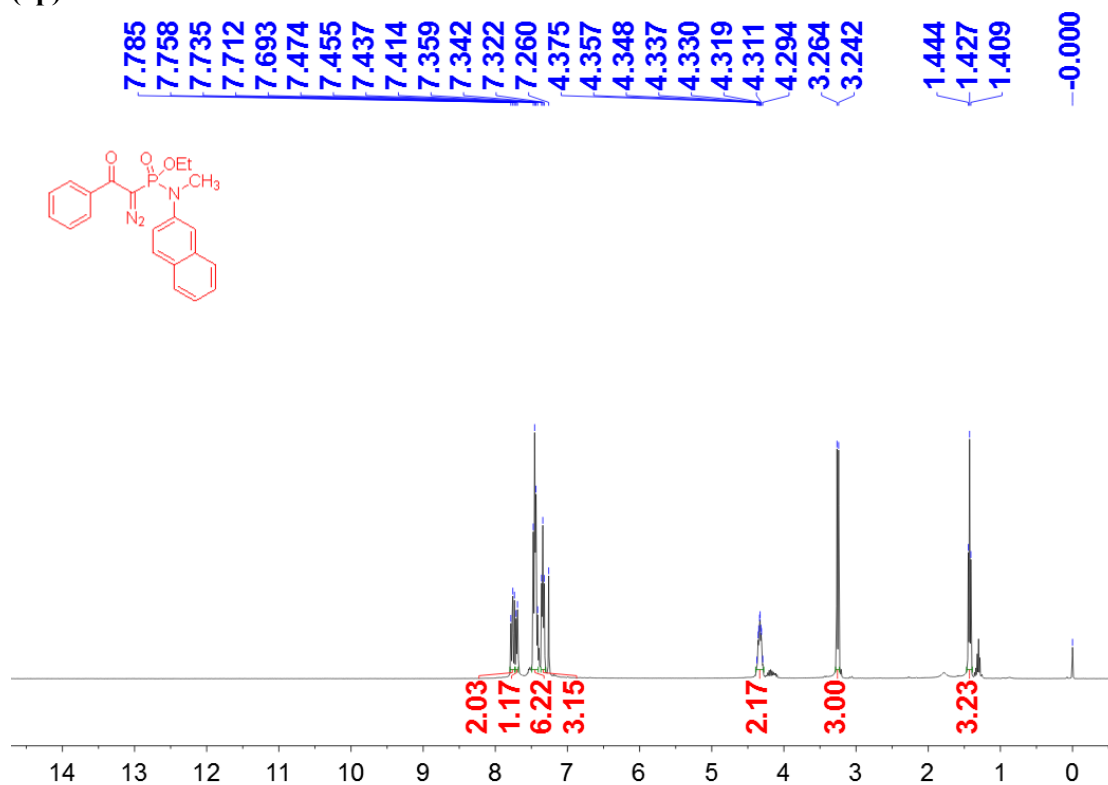


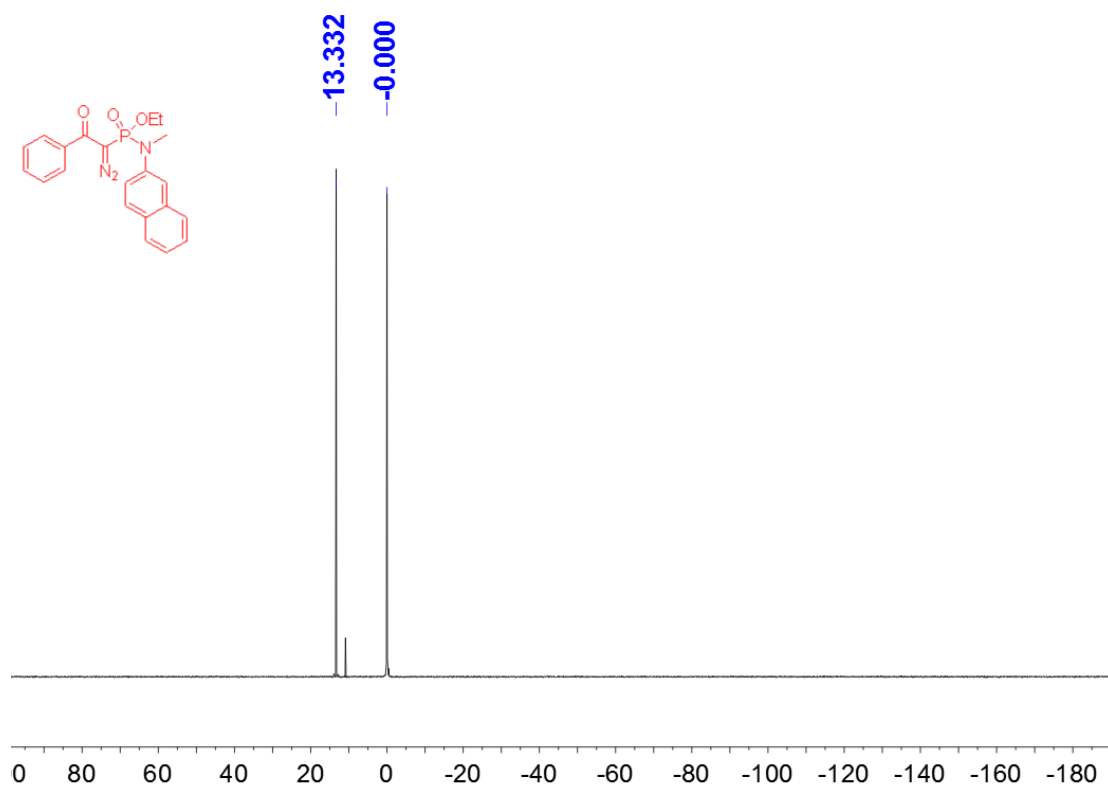
Ethyl *N*-[4-(*tert*-butyl)phenyl]-*P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methylphosphonamidate (10)



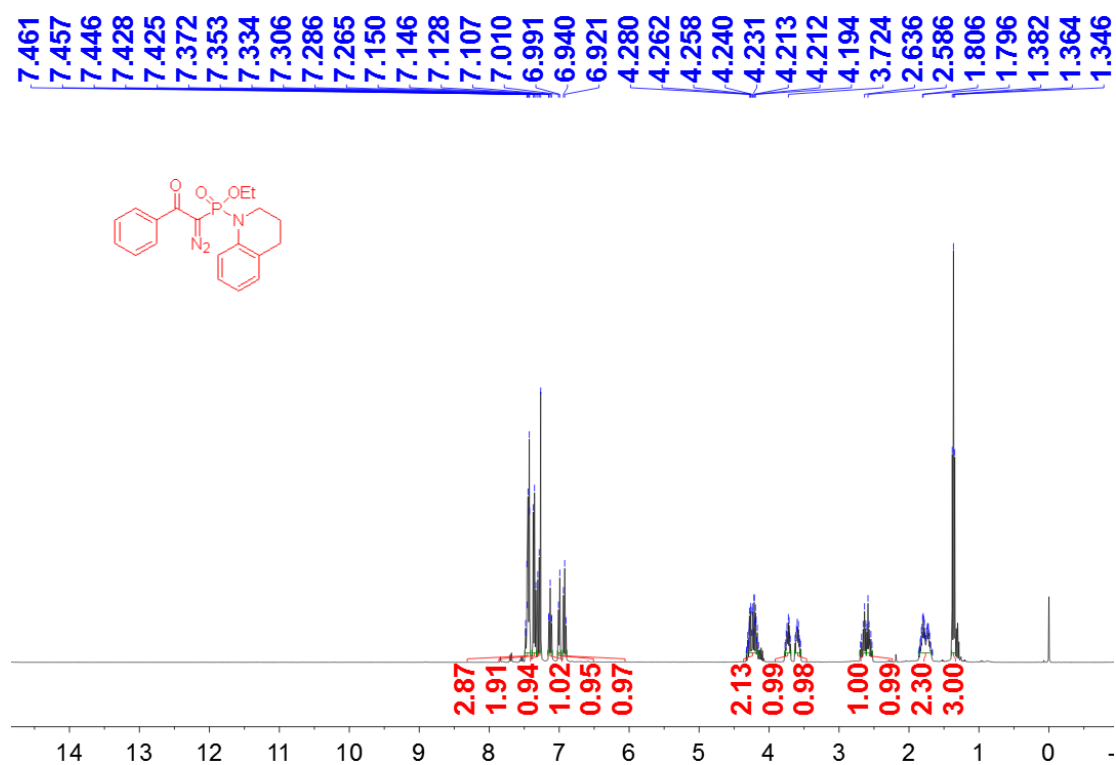


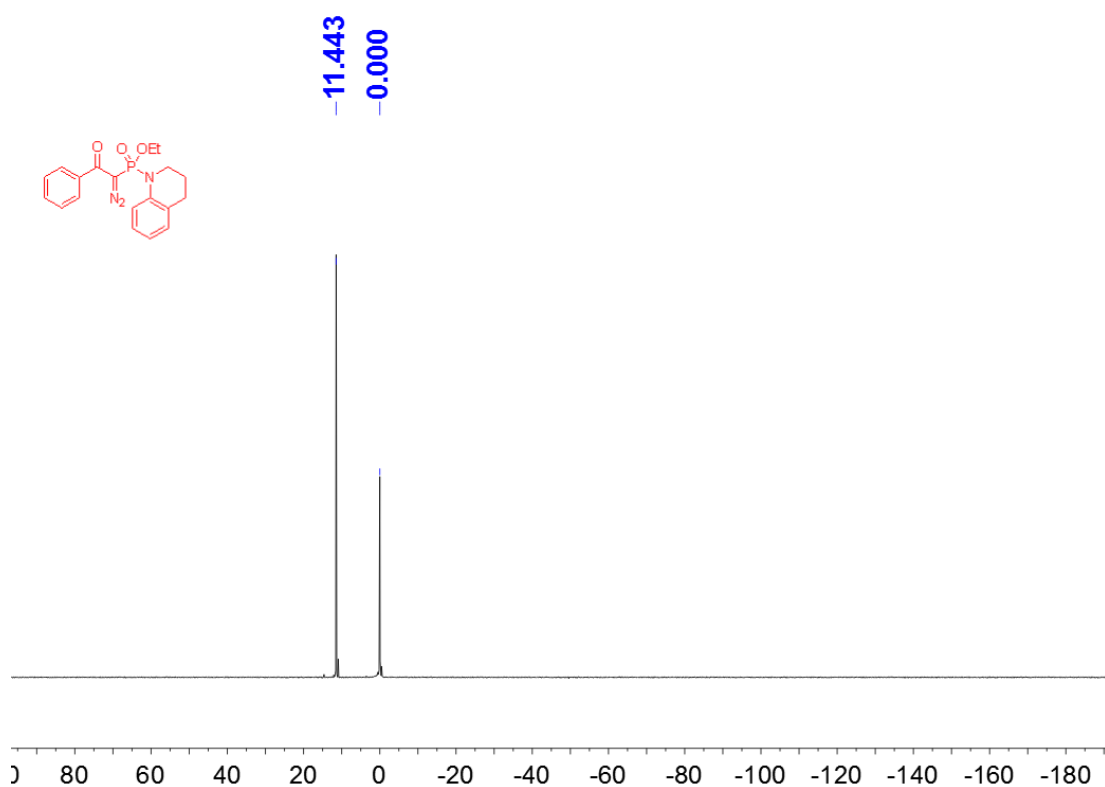
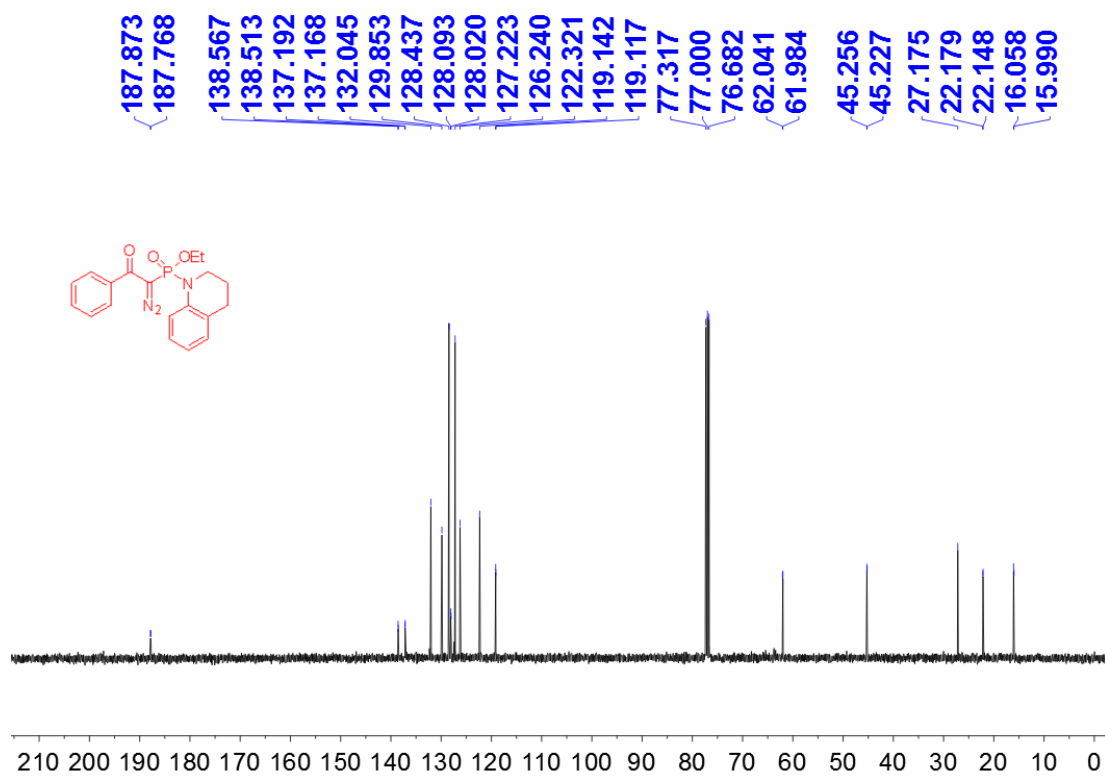
Ethyl *P*-(1-diazo-2-oxo-2-phenylethyl)-*N*-methyl-*N*-(naphthalen-2-yl)phosphonamidate (1p)



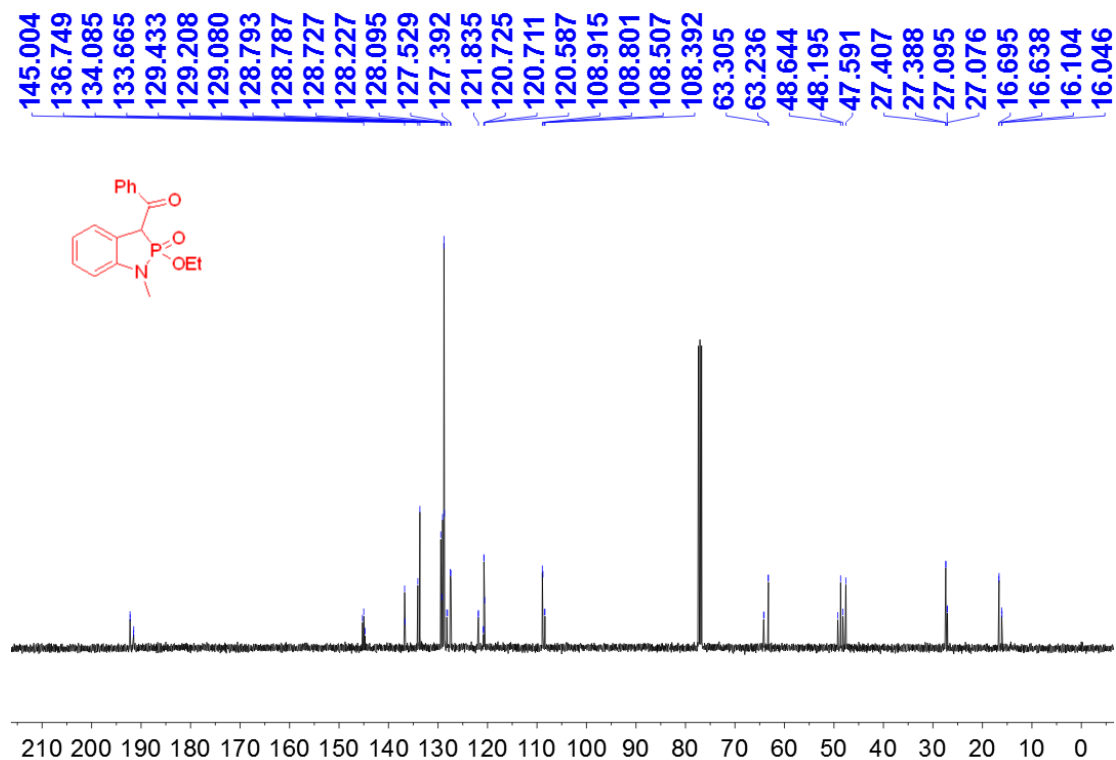
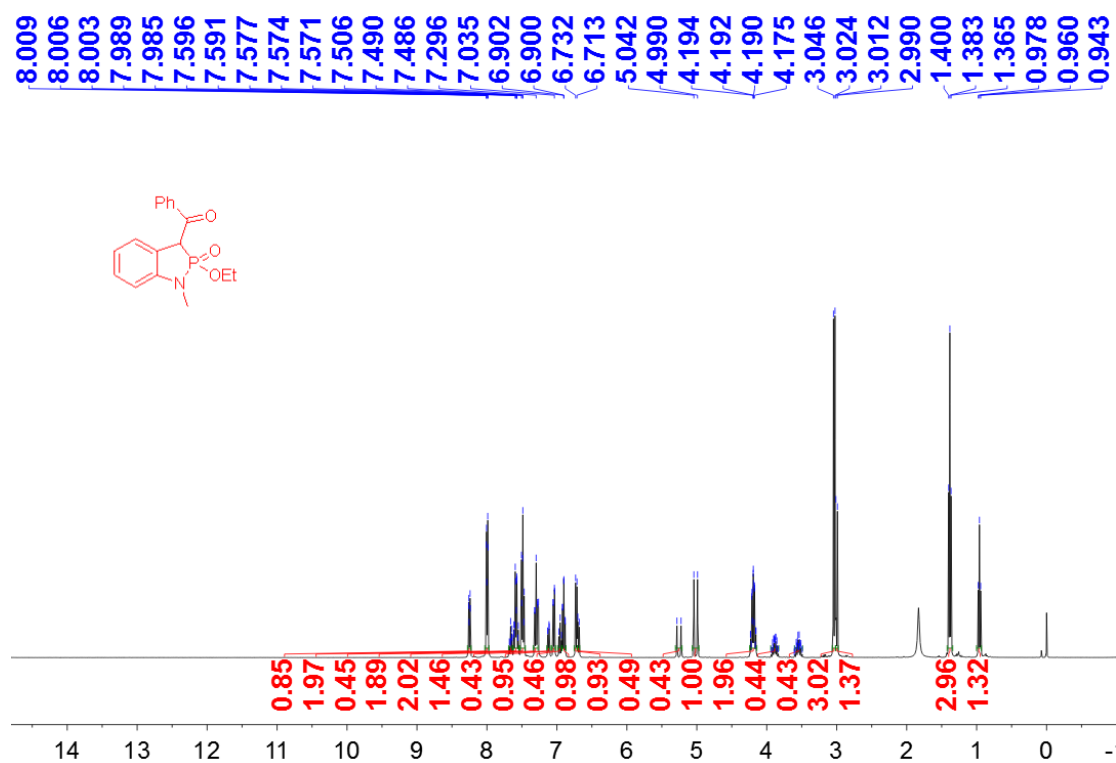


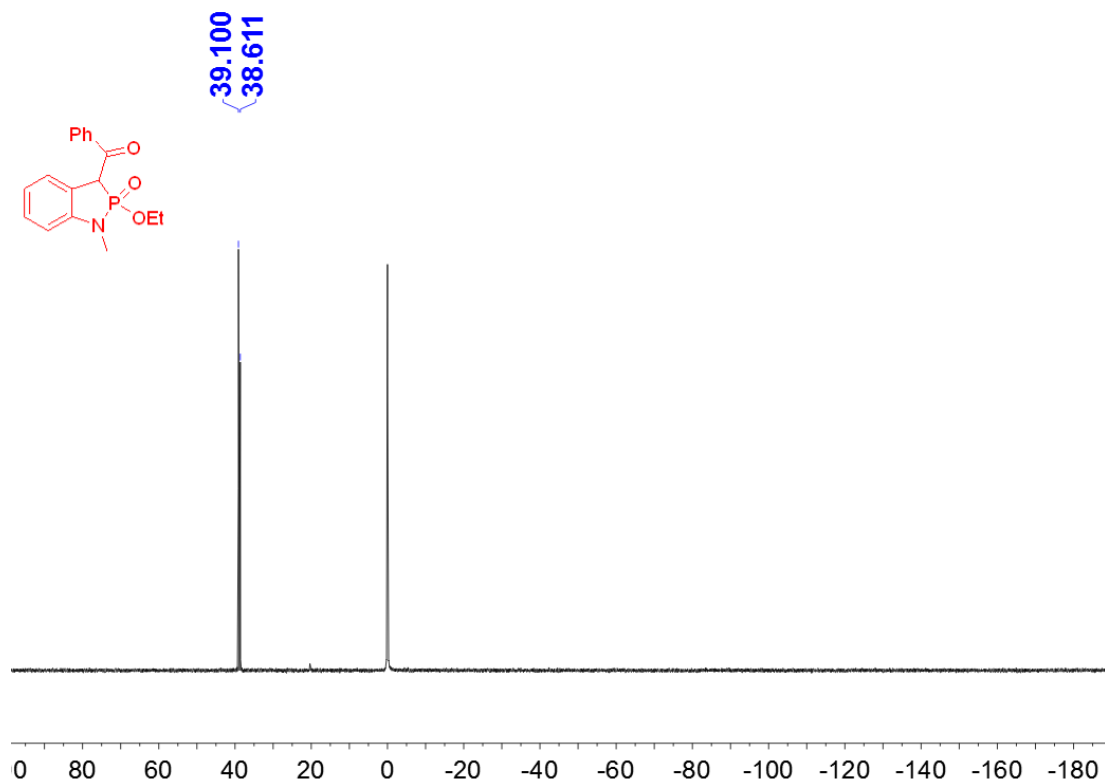
Ethyl (1-diazo-2-oxo-2-phenylethyl)(3,4-dihydroquinolin-1(2H)-yl)phosphinate (1q)



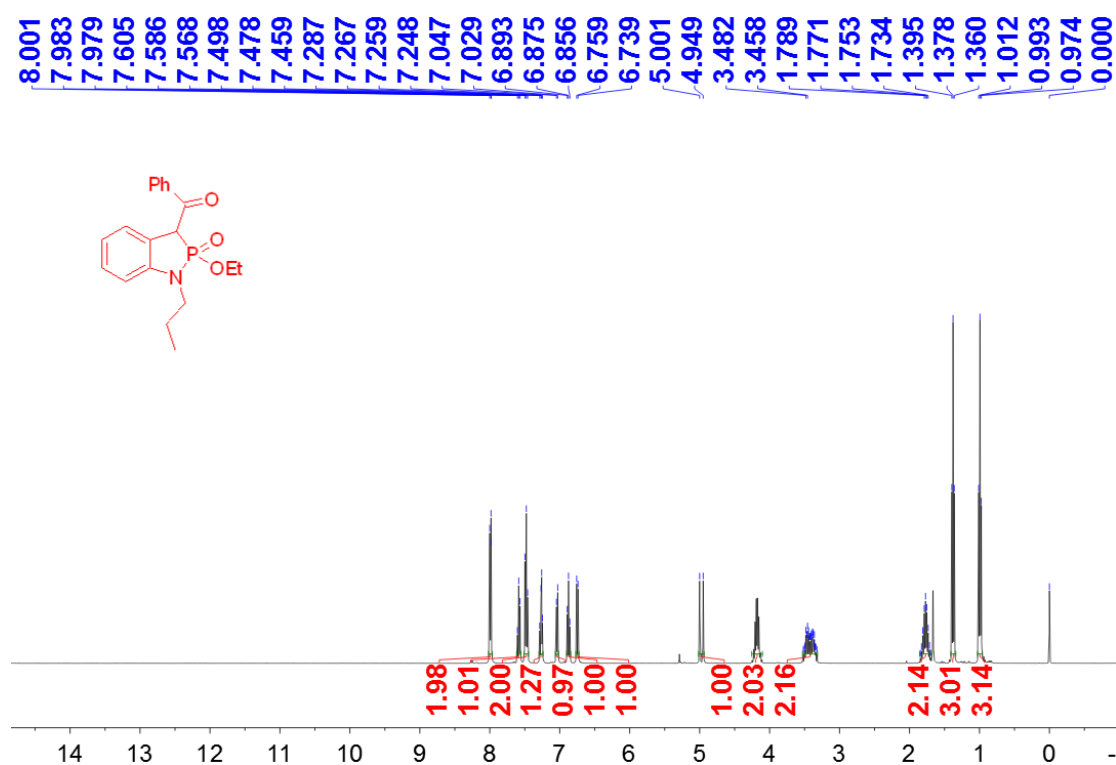


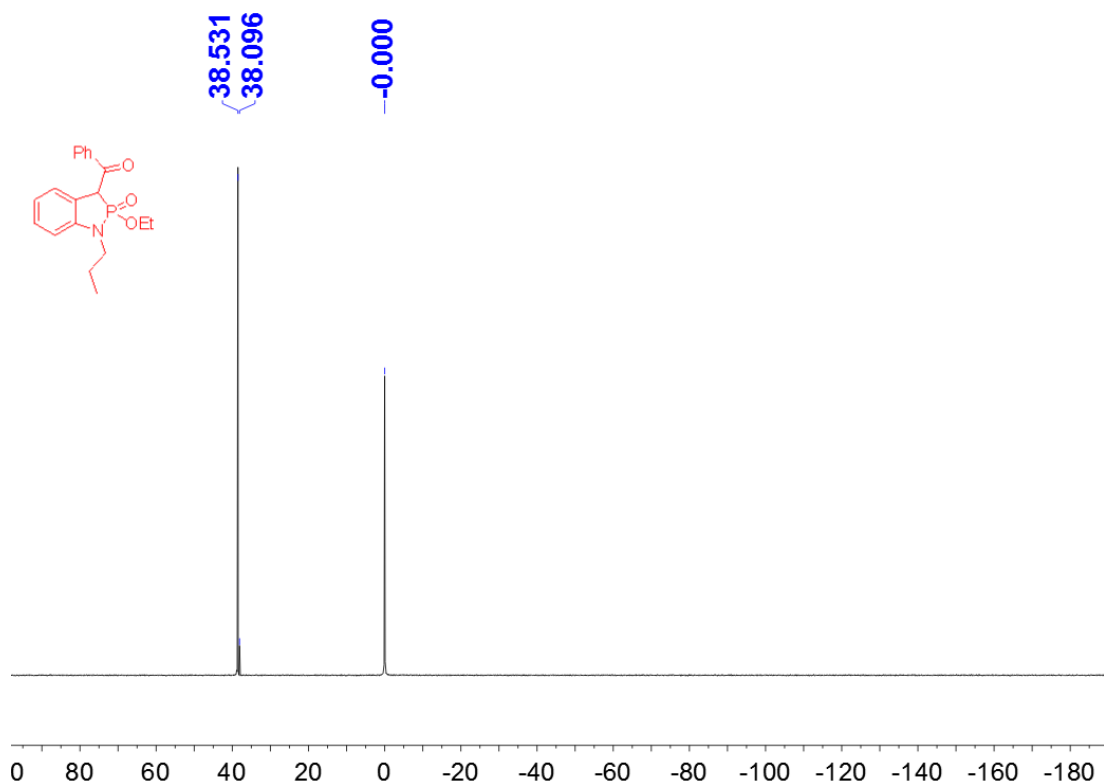
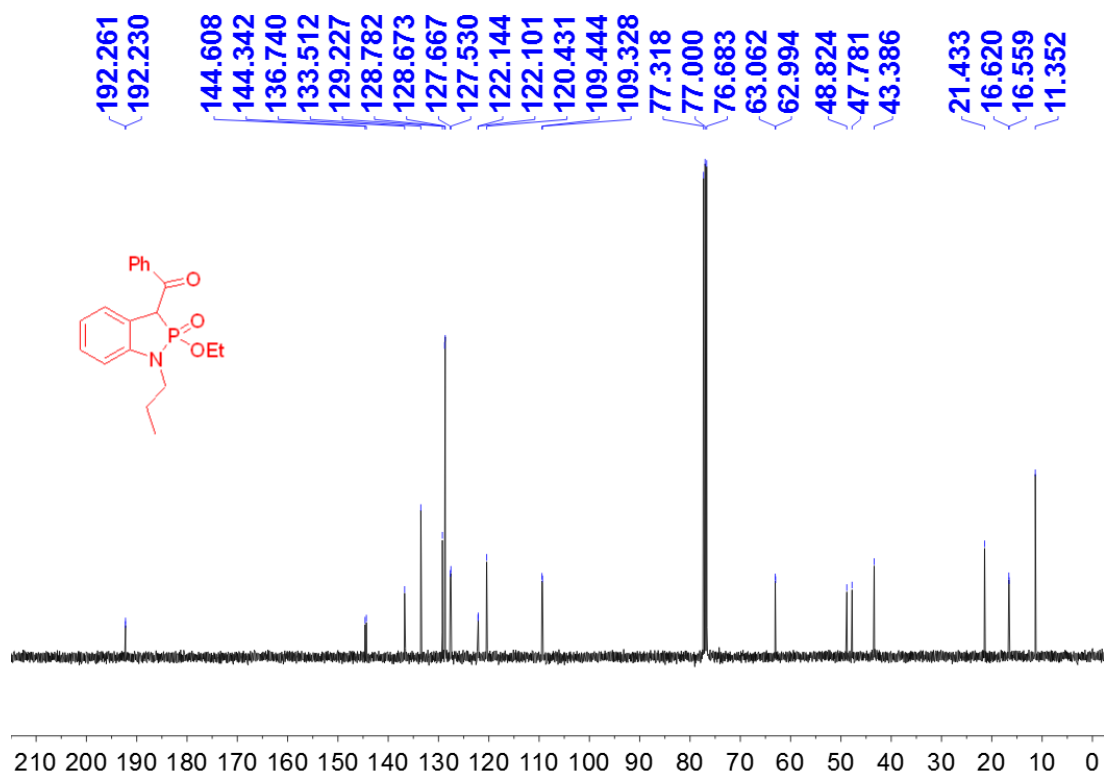
3-Benzoyl-2-ethoxy-1-methyl-2-oxophosphorindoline (2a)



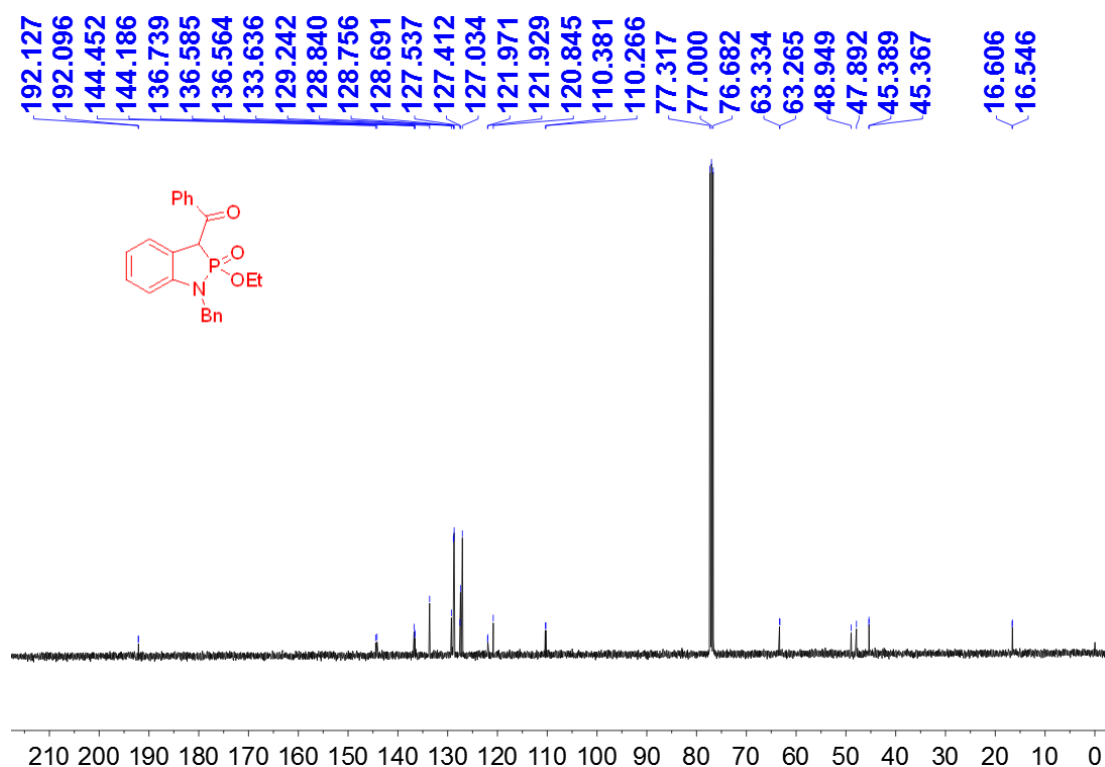
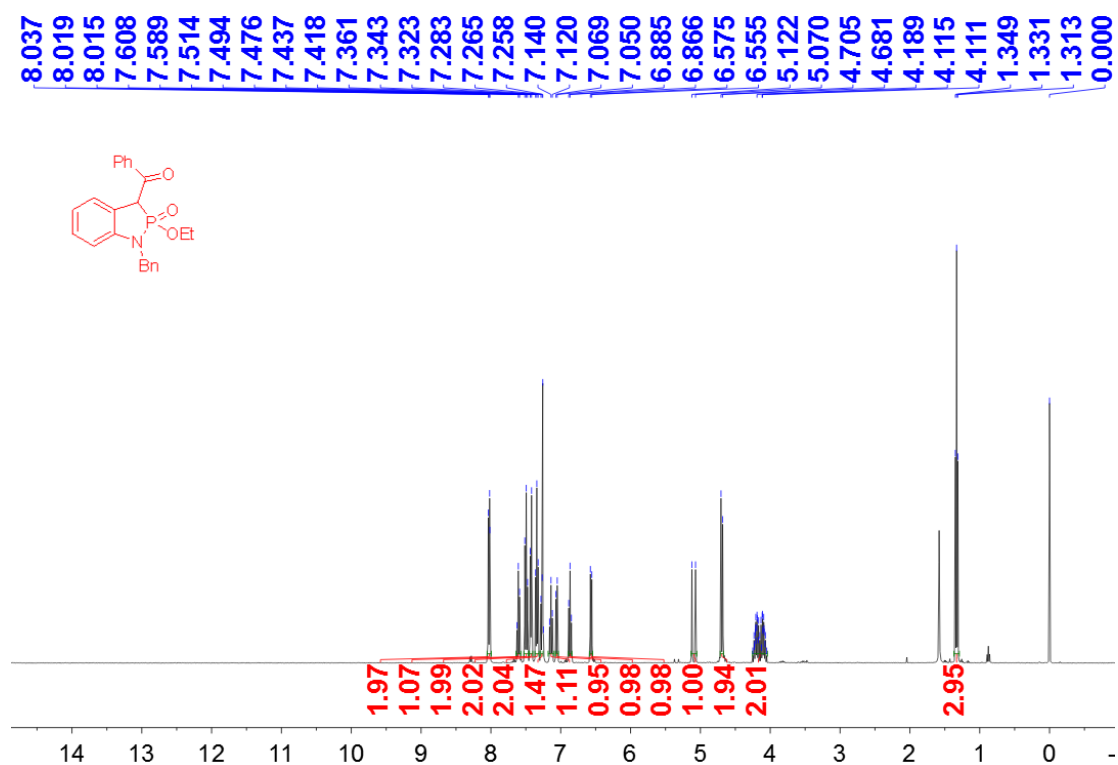


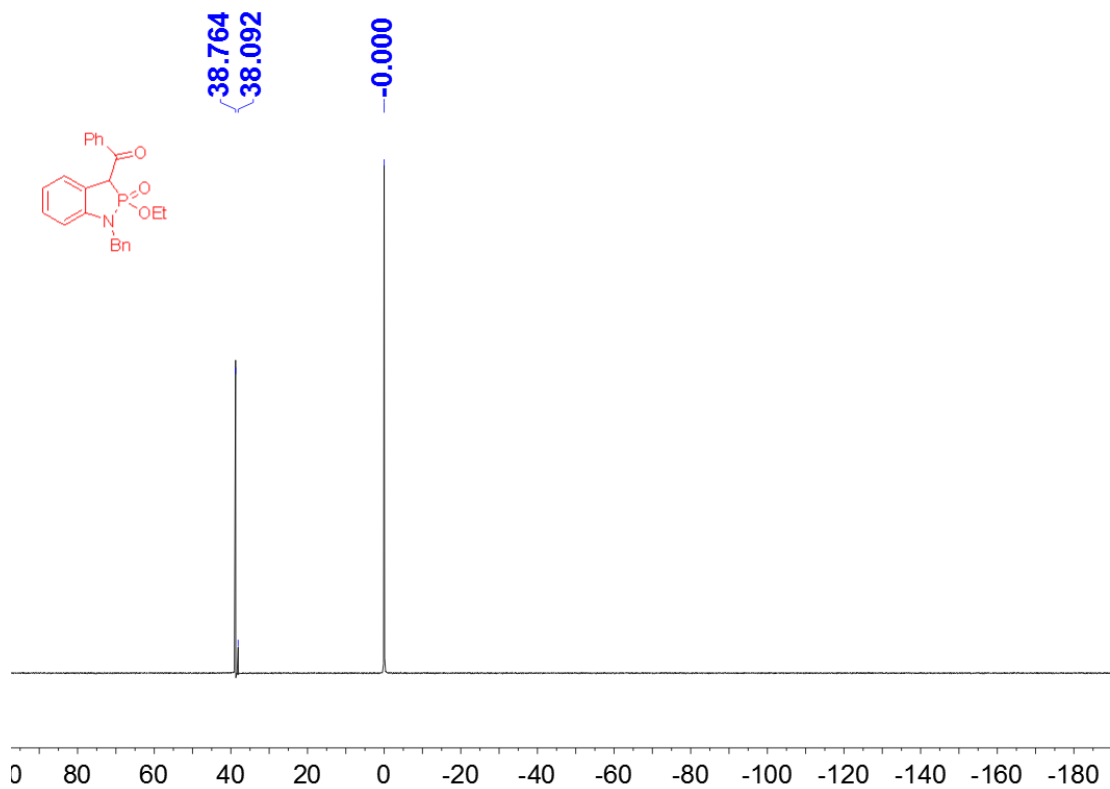
3-Benzoyl-2-ethoxy-2-oxo-1-propylphosphorindoline (2b)



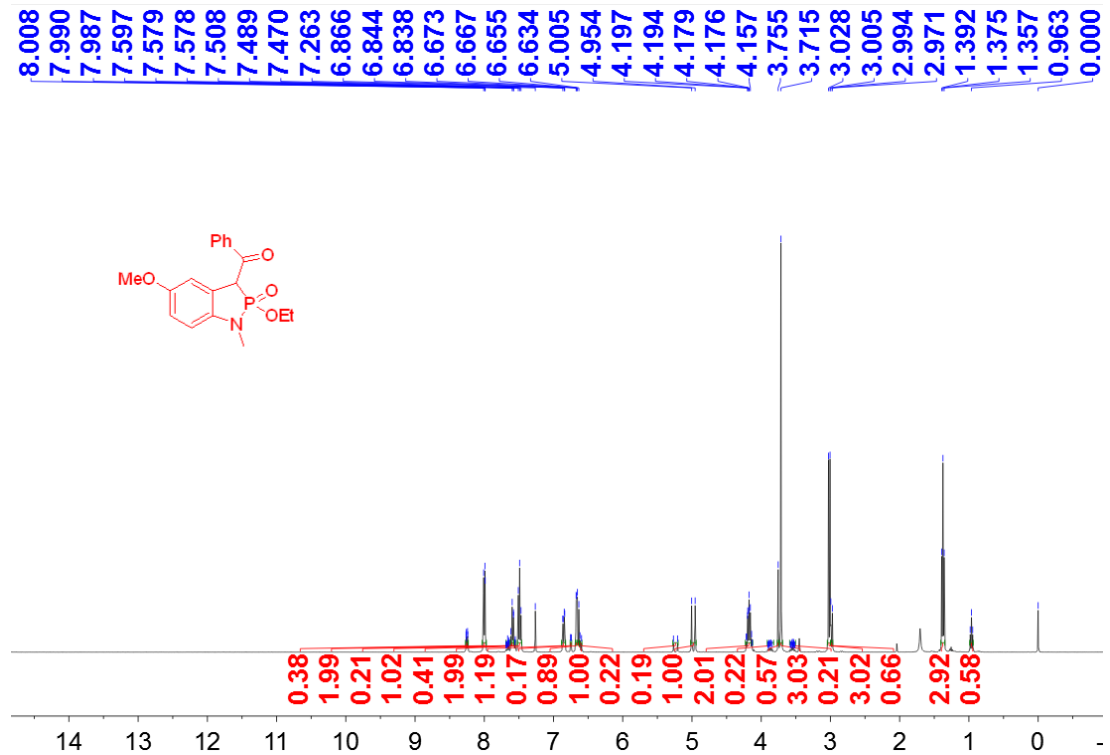


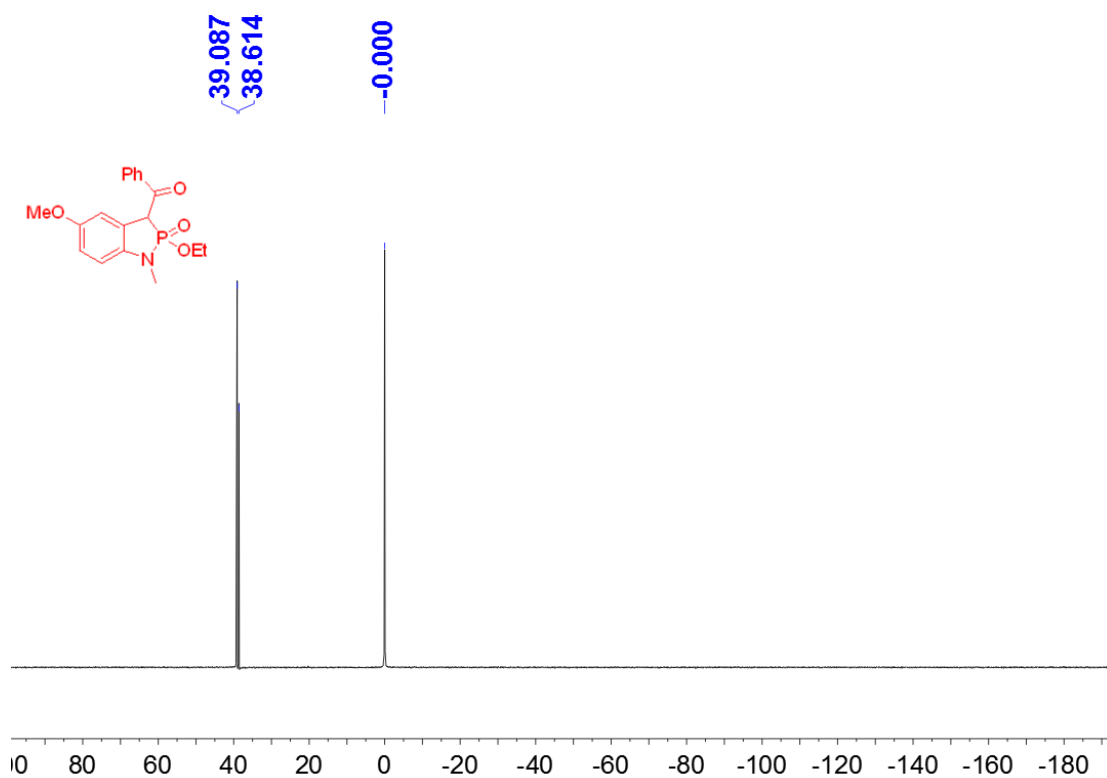
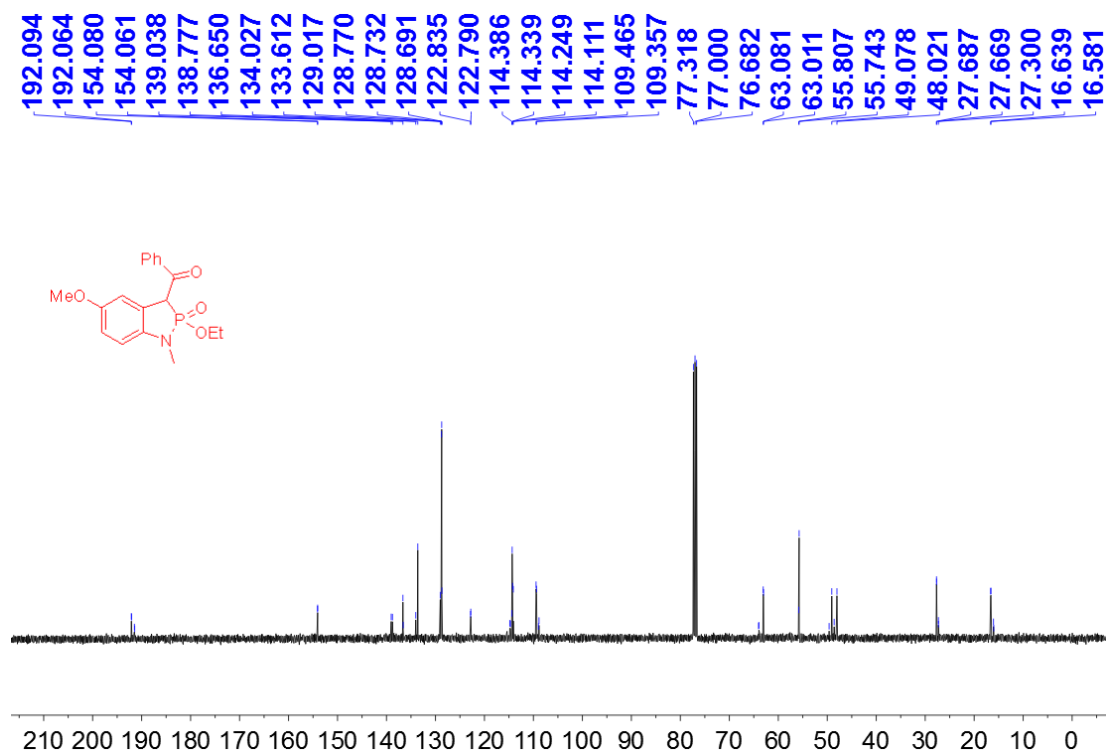
3-Benzoyl-1-benzyl-2-ethoxy-2-oxophosphorindoline (2c)



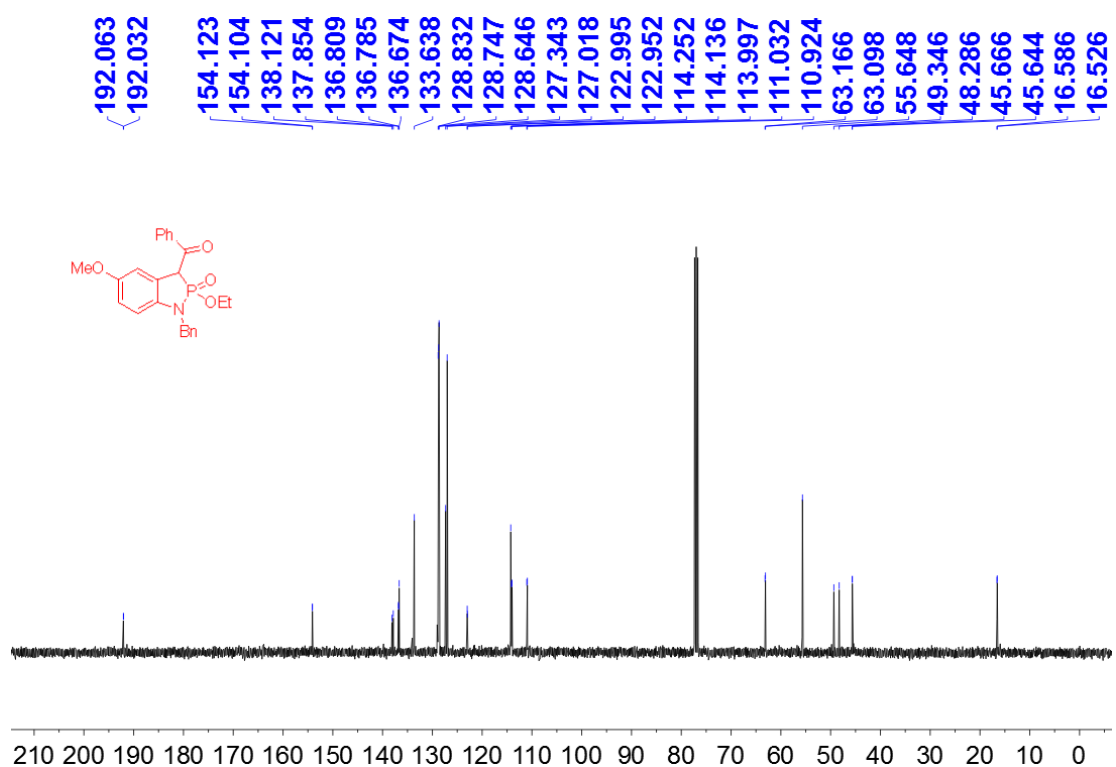
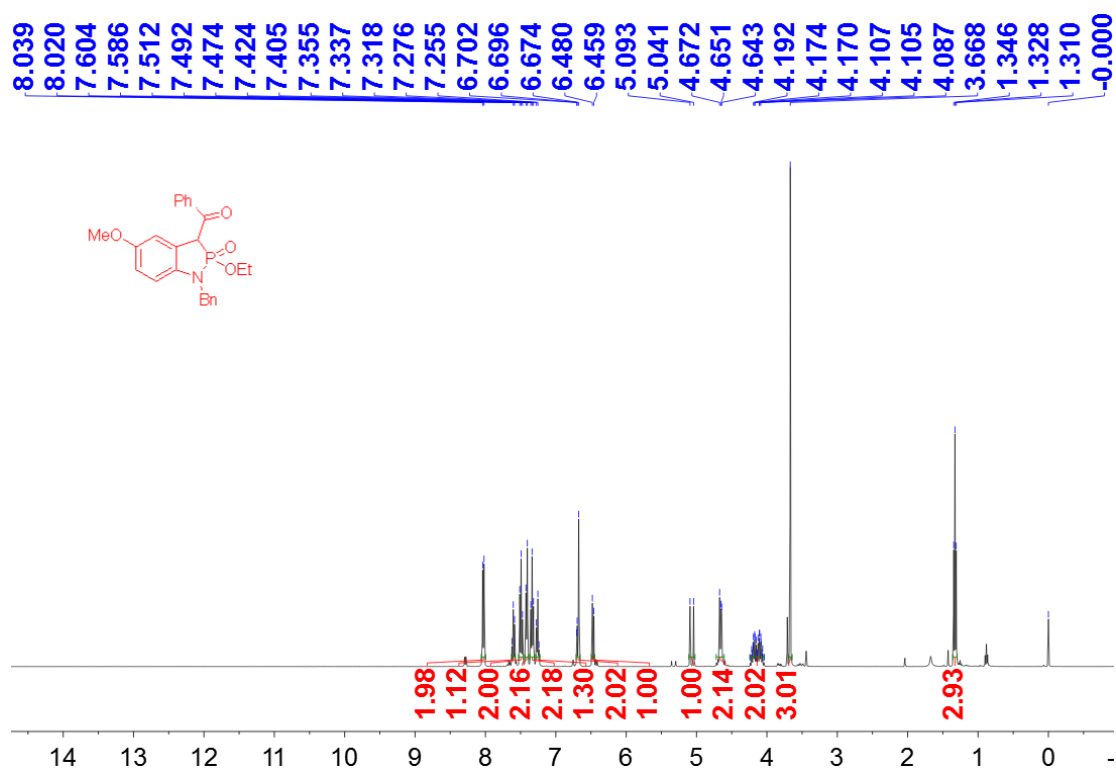


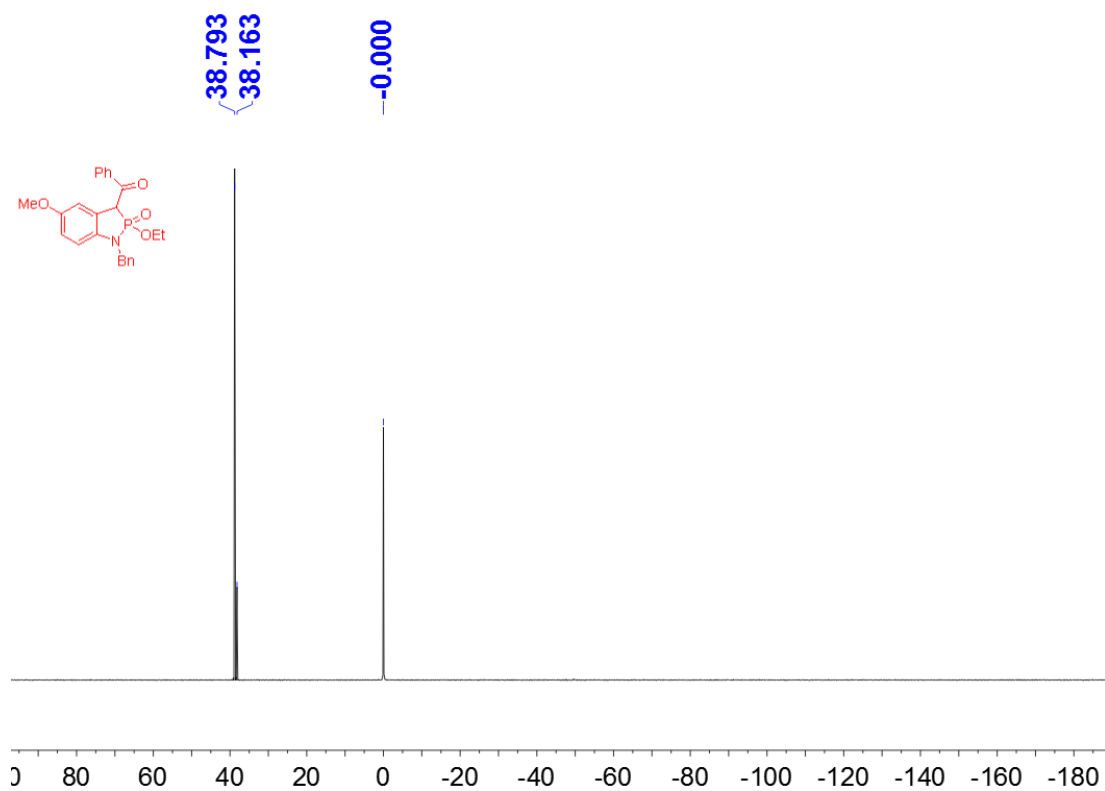
3-Benzoyl-2-ethoxy-5-methoxy-1-methyl-2-oxophosphorindoline (2d)



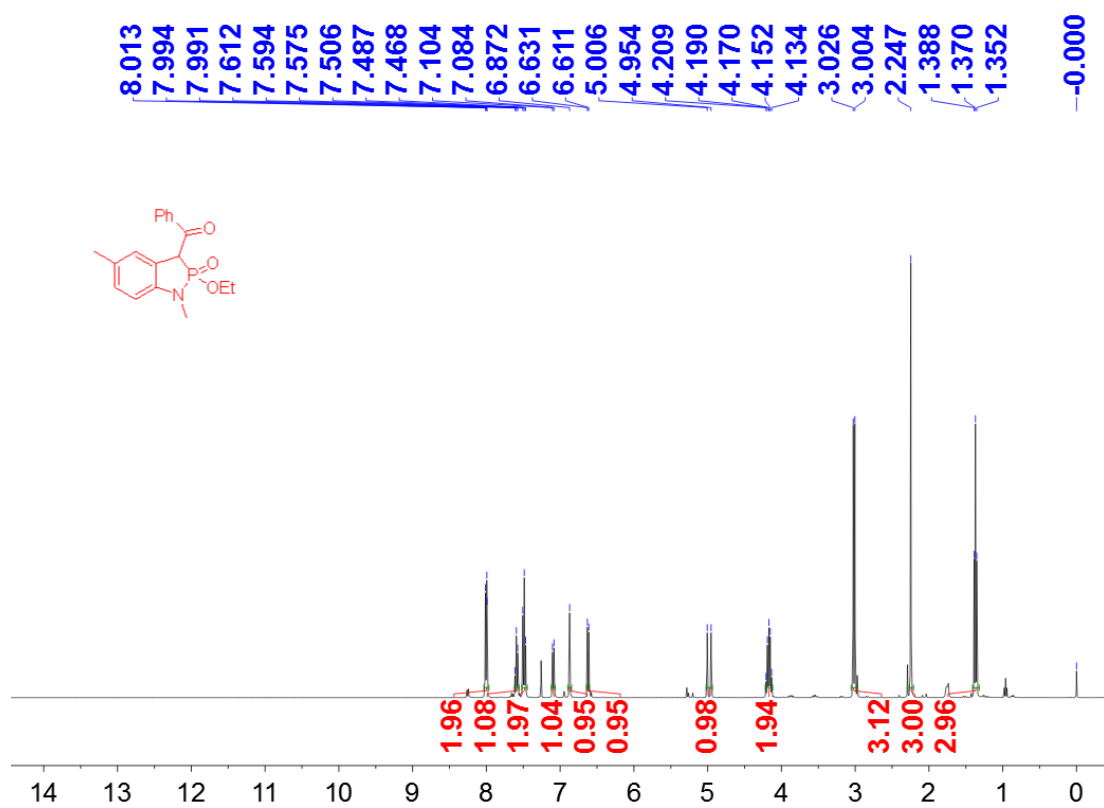


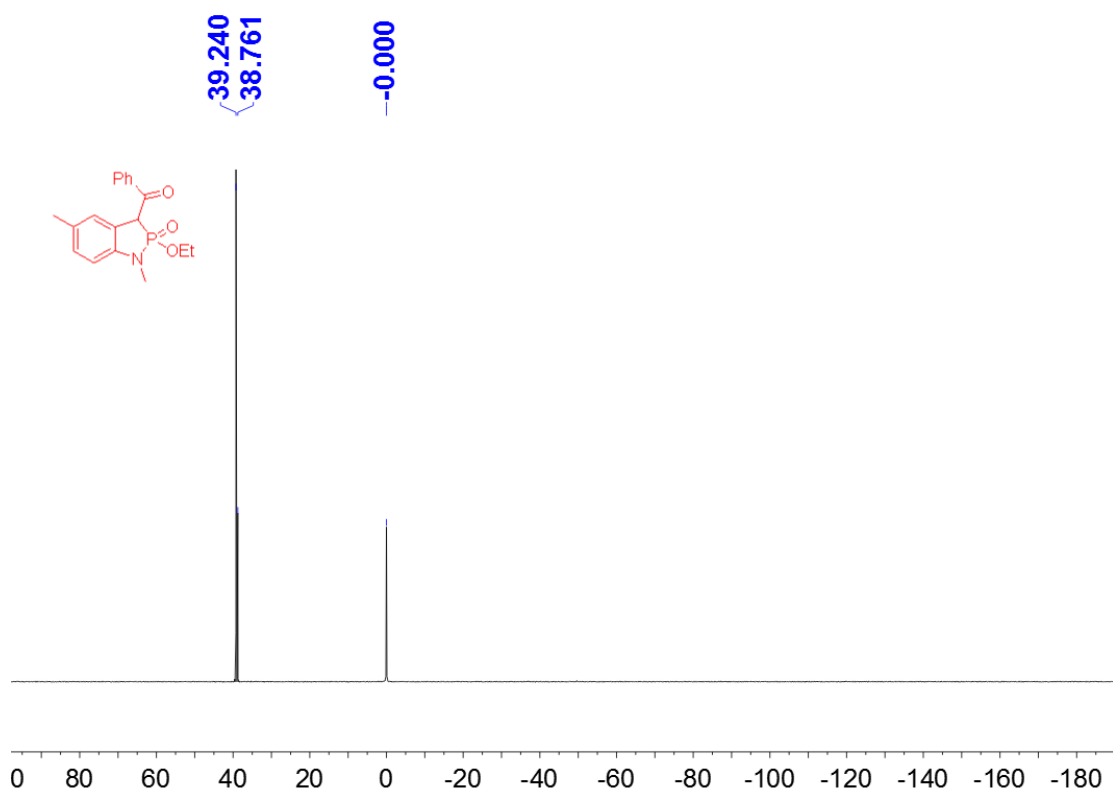
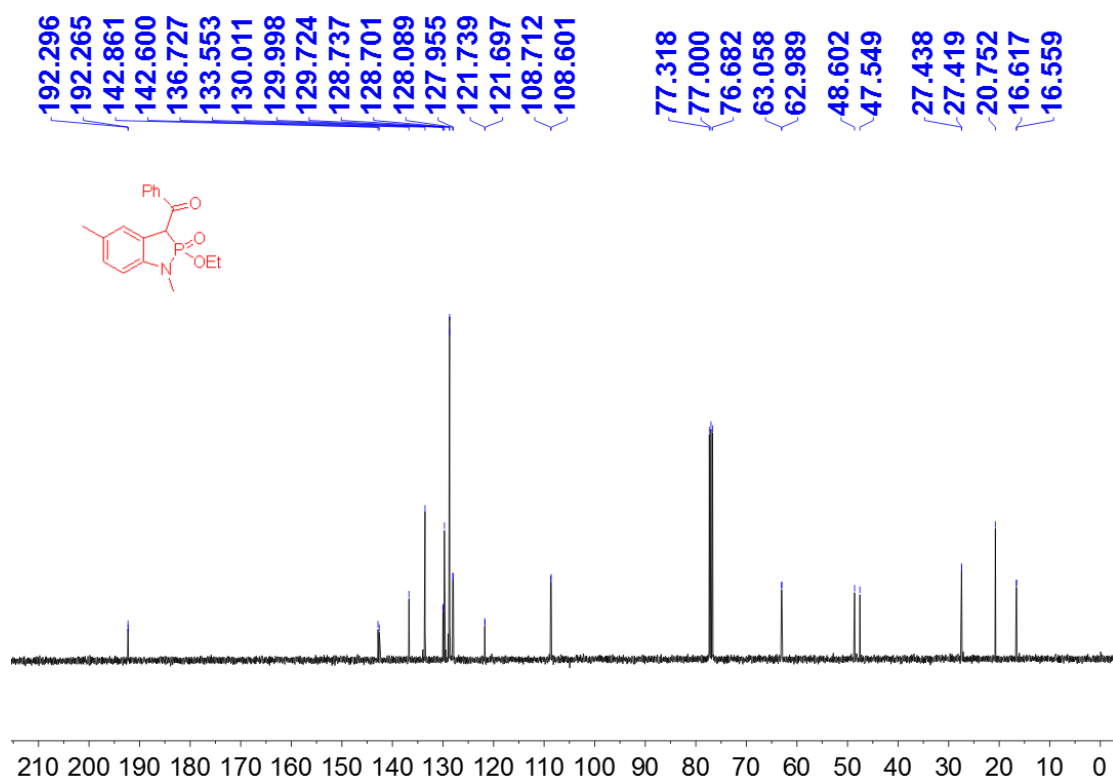
3-Benzoyl-1-benzyl-2-ethoxy-5-methoxy-2-oxophosphorindoline (2e)



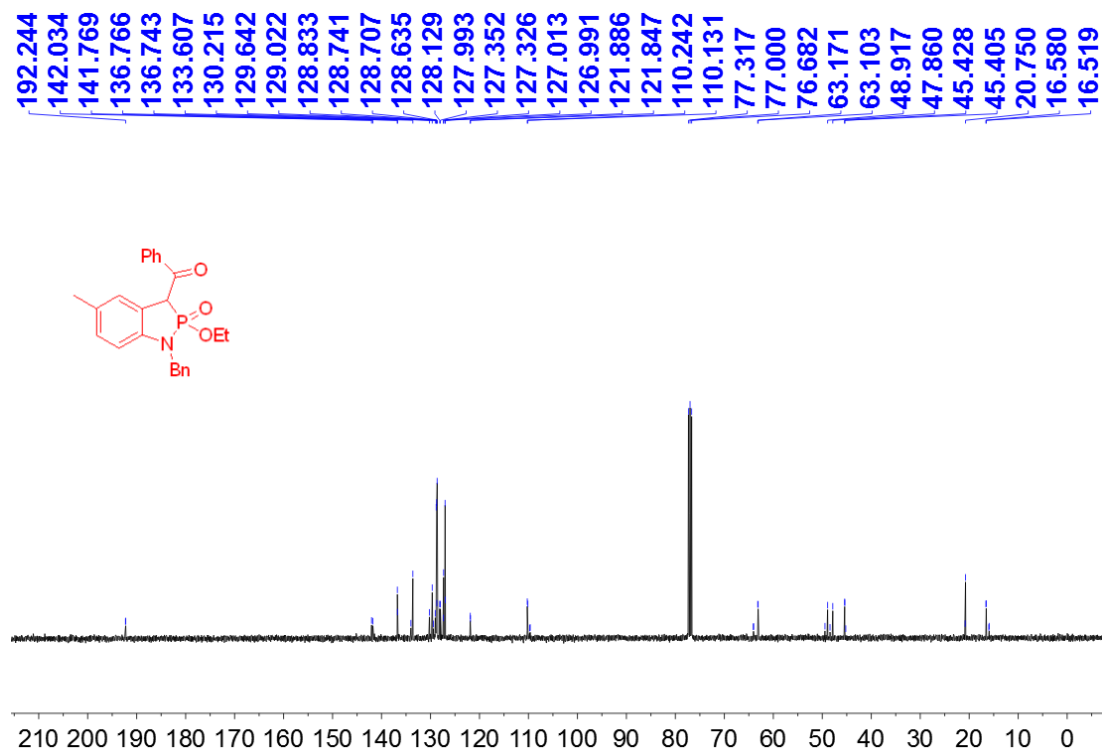
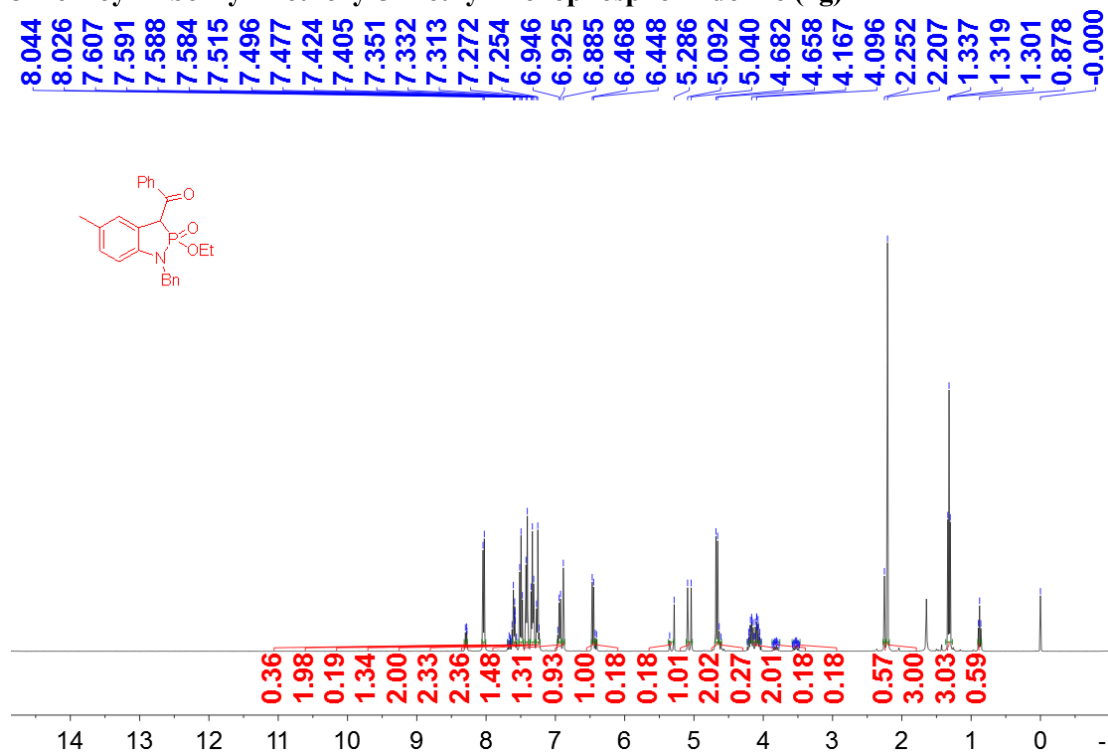


3-Benzoyl-2-ethoxy-1,5-dimethyl-2-oxophosphorindoline (2f)



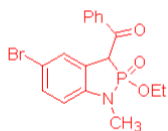


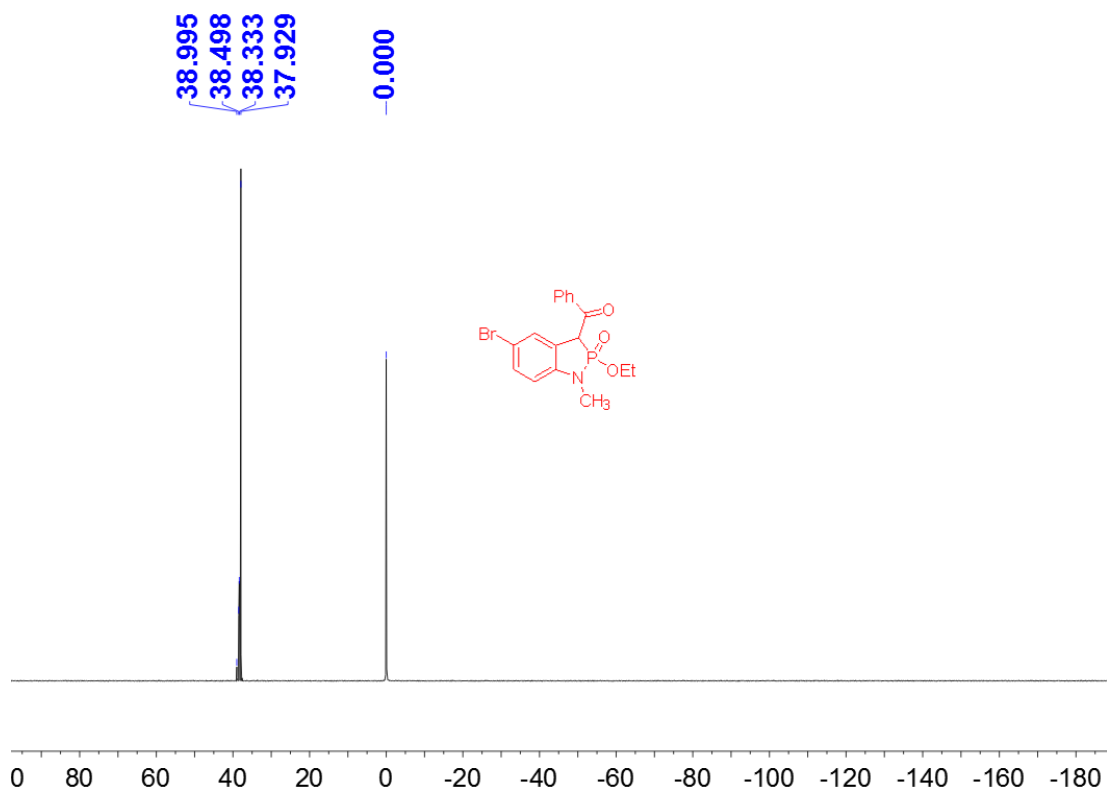
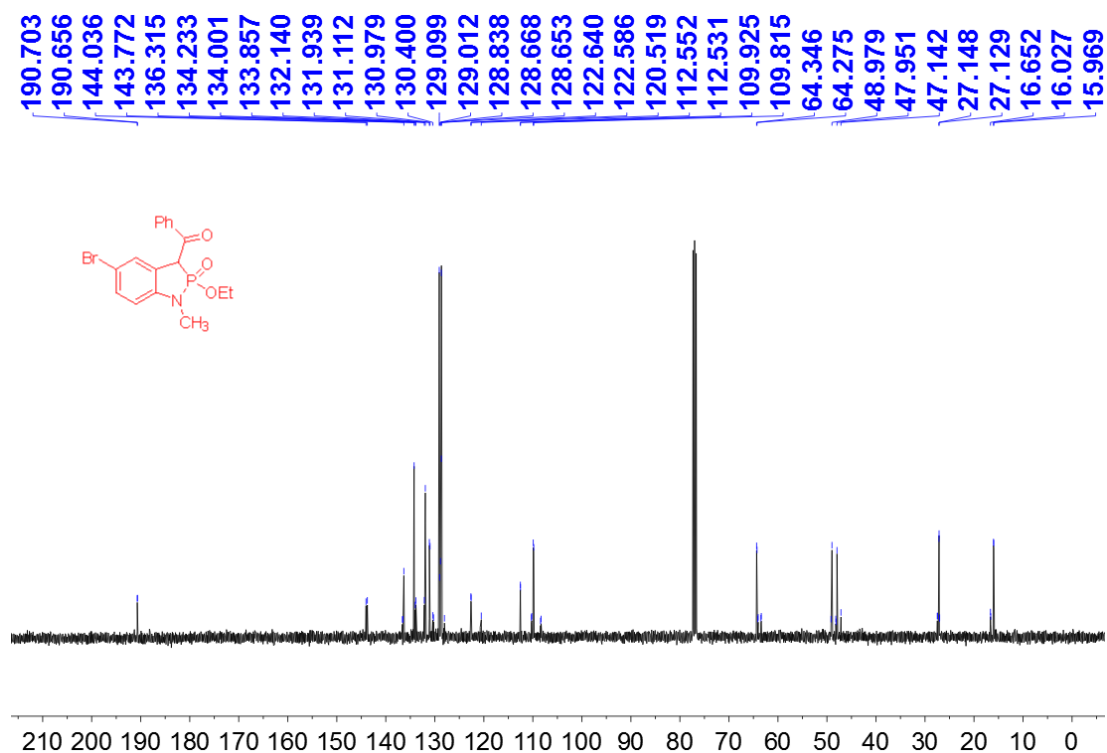
3-Benzoyl-1-benzyl-2-ethoxy-5-methyl-2-oxophosphorindoline (2g)



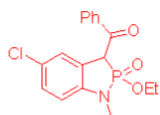
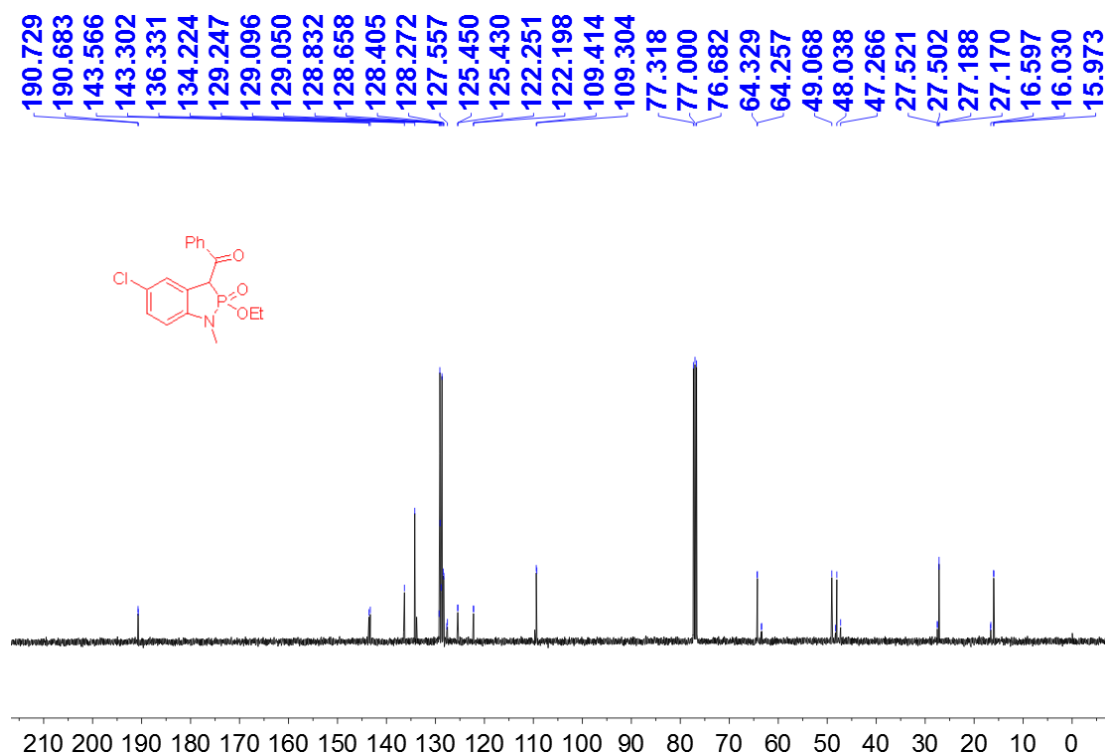
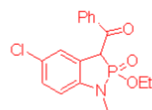
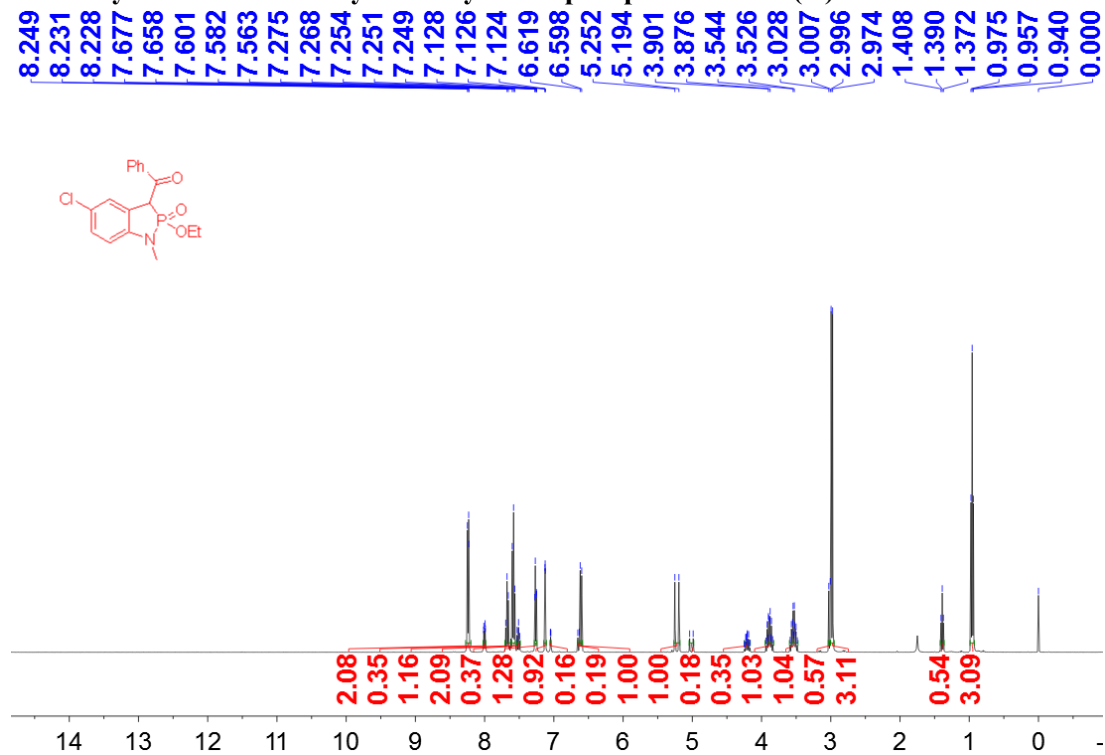


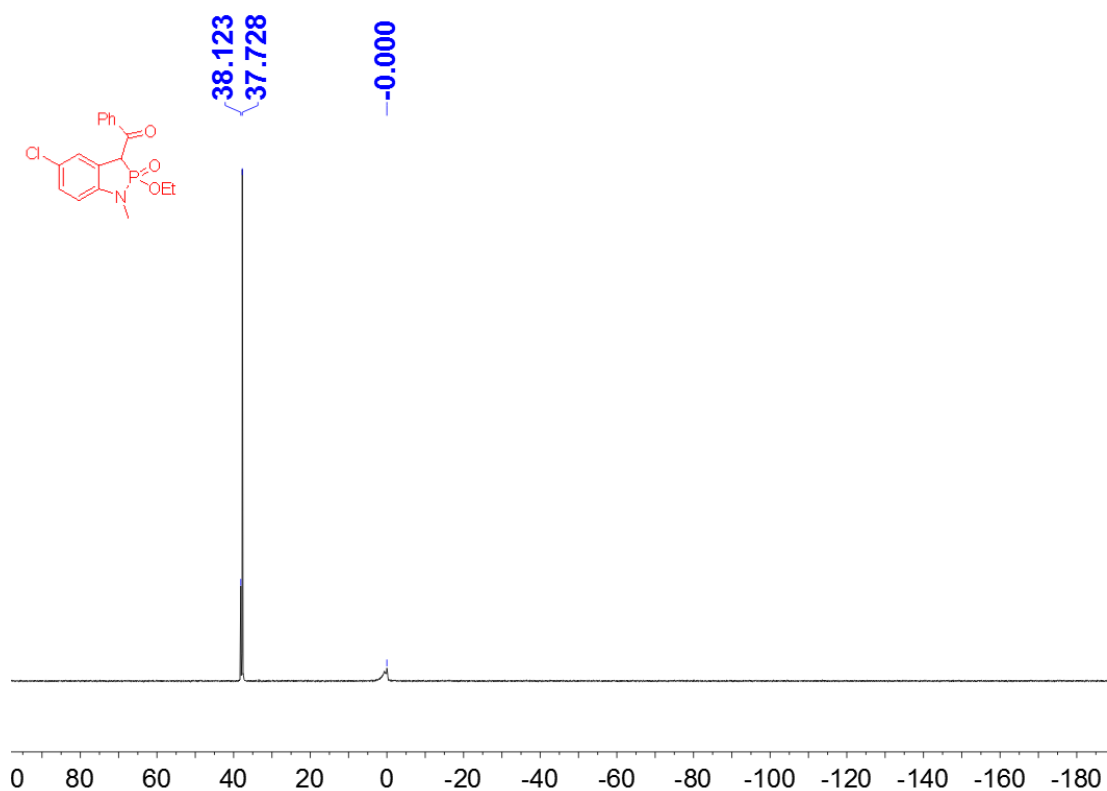
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8.228
8.224
7.676
7.658
7.601
7.585
7.581
7.562
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7.396
7.393
7.268
7.259
7.257
7.254
6.577
6.574
6.555
6.553
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0.975
0.962
0.957
0.939



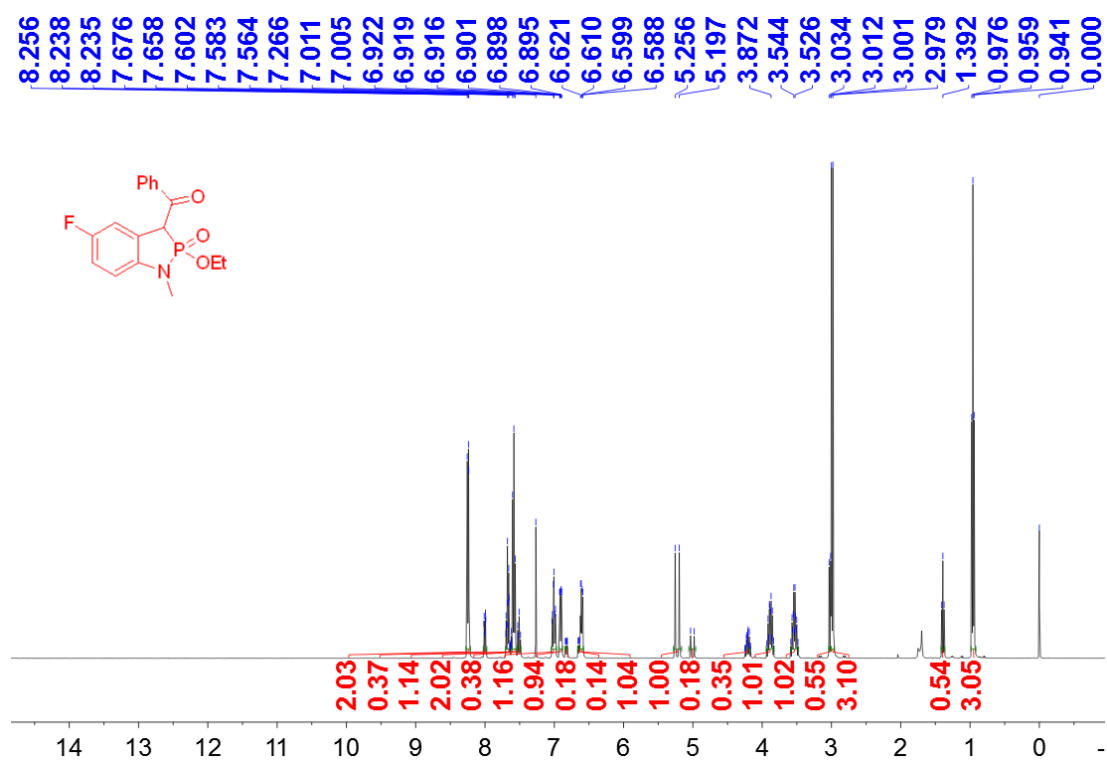


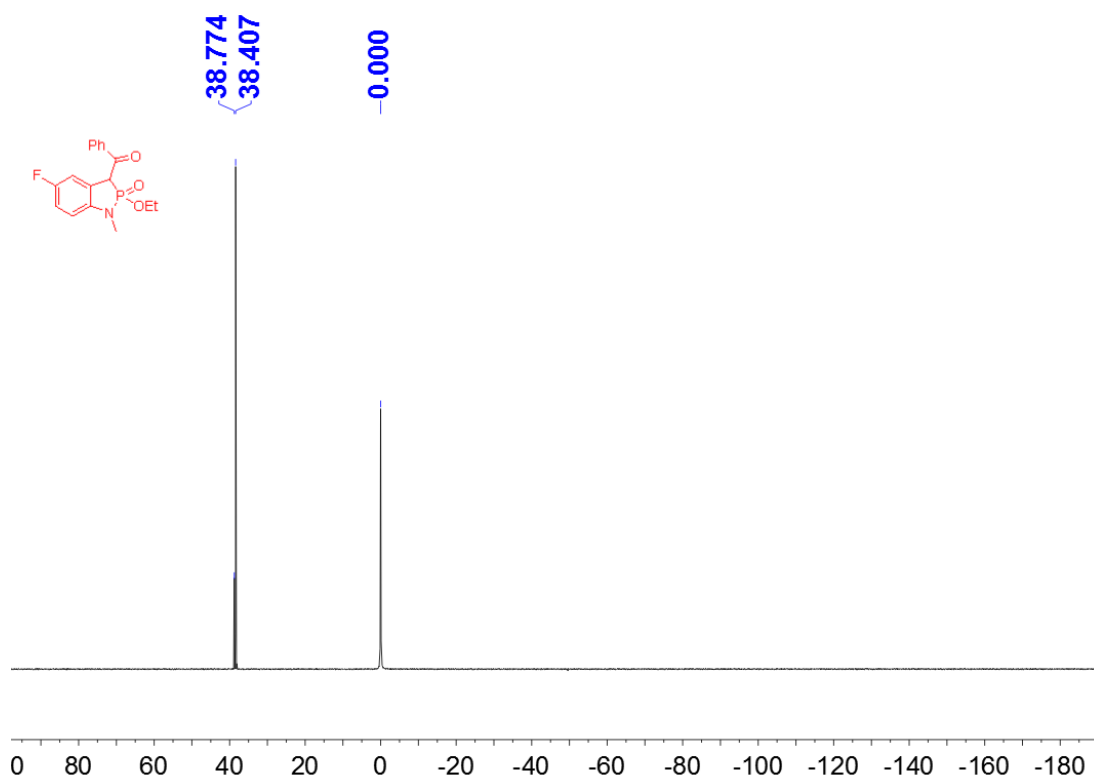
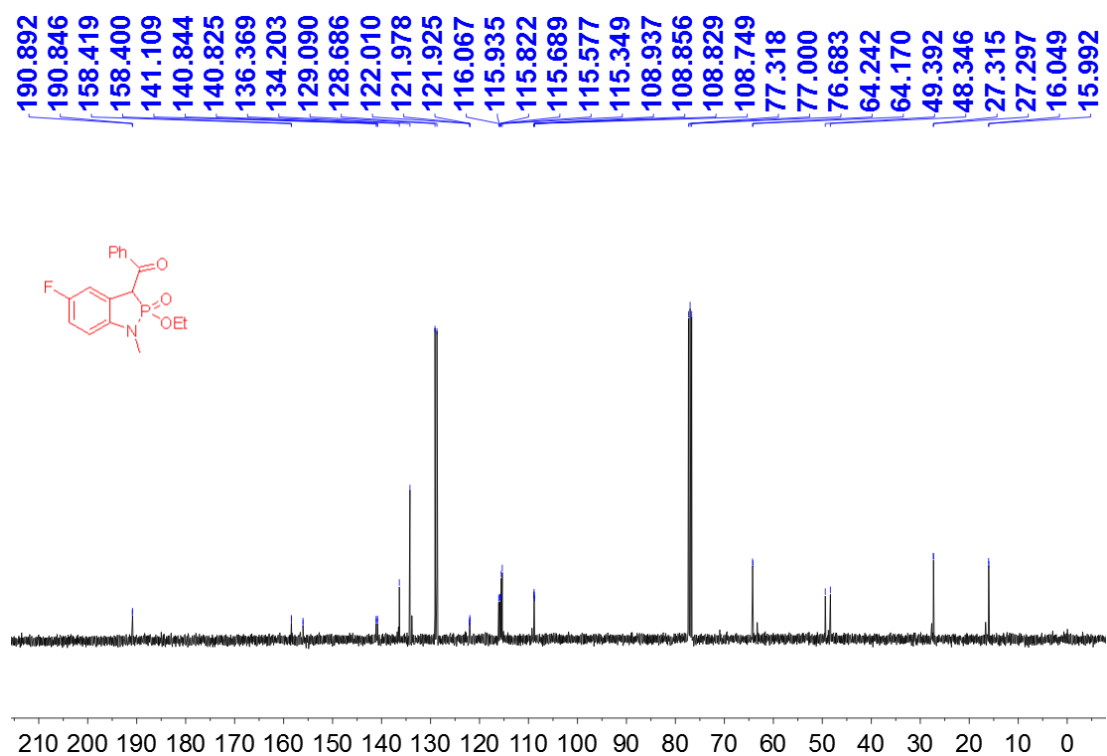
3-Benzoyl-5-chloro-2-ethoxy-1-methyl-2-oxophosphorindoline (2i)

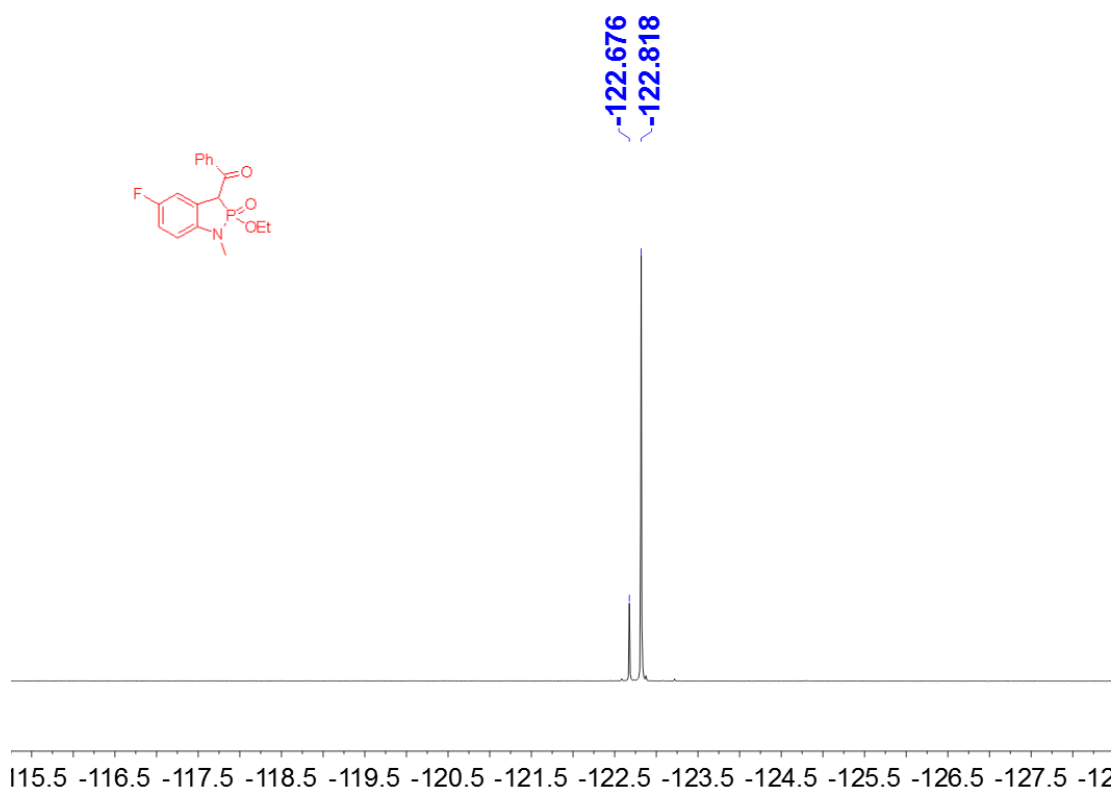




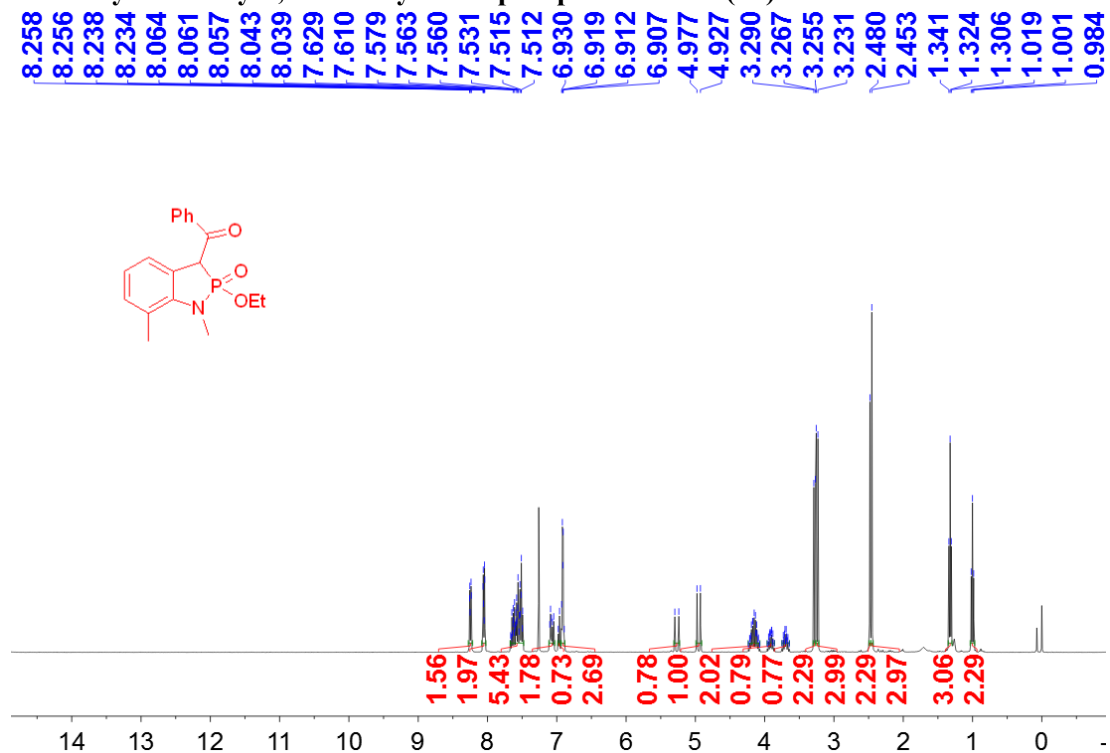
3-Benzoyl-2-ethoxy-5-fluoro-1-methyl-2-oxophosphorindoline (2j)

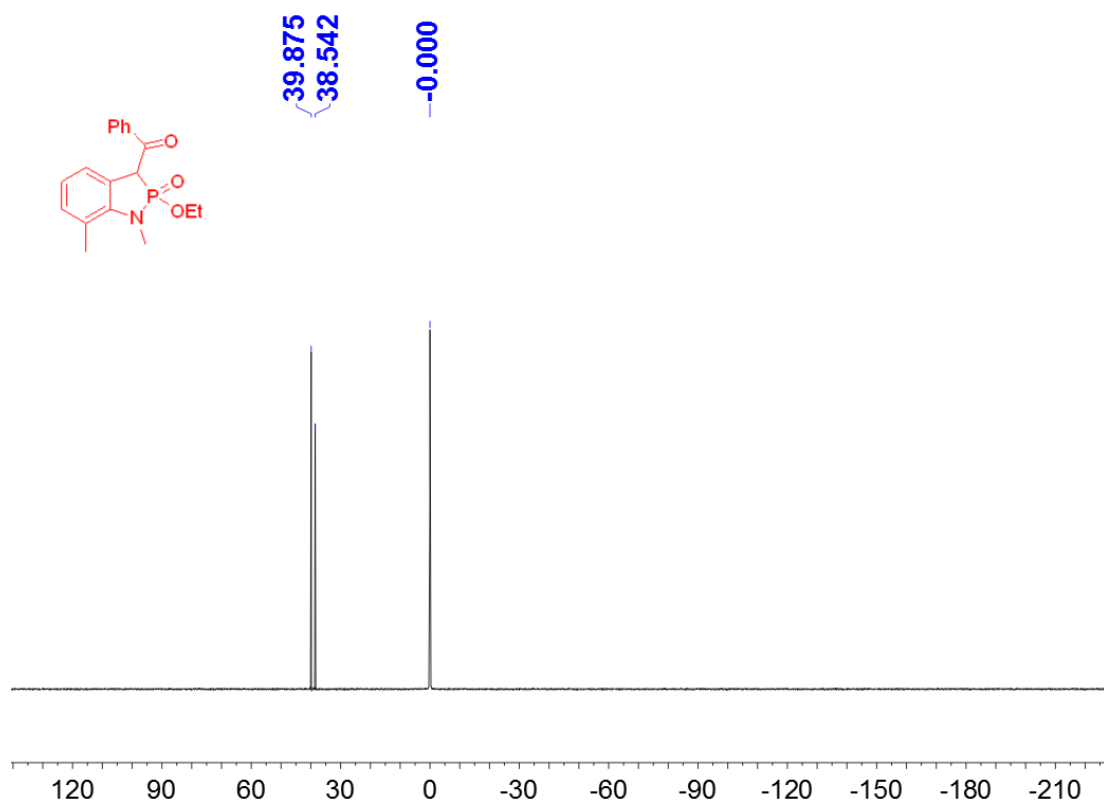
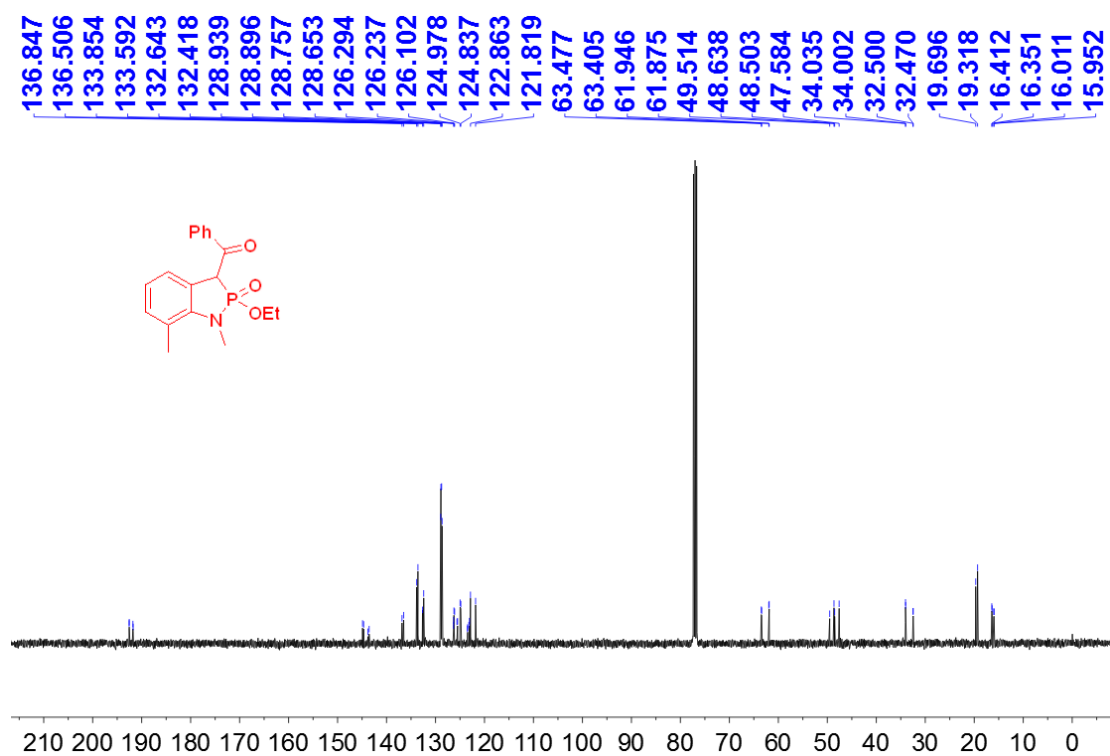




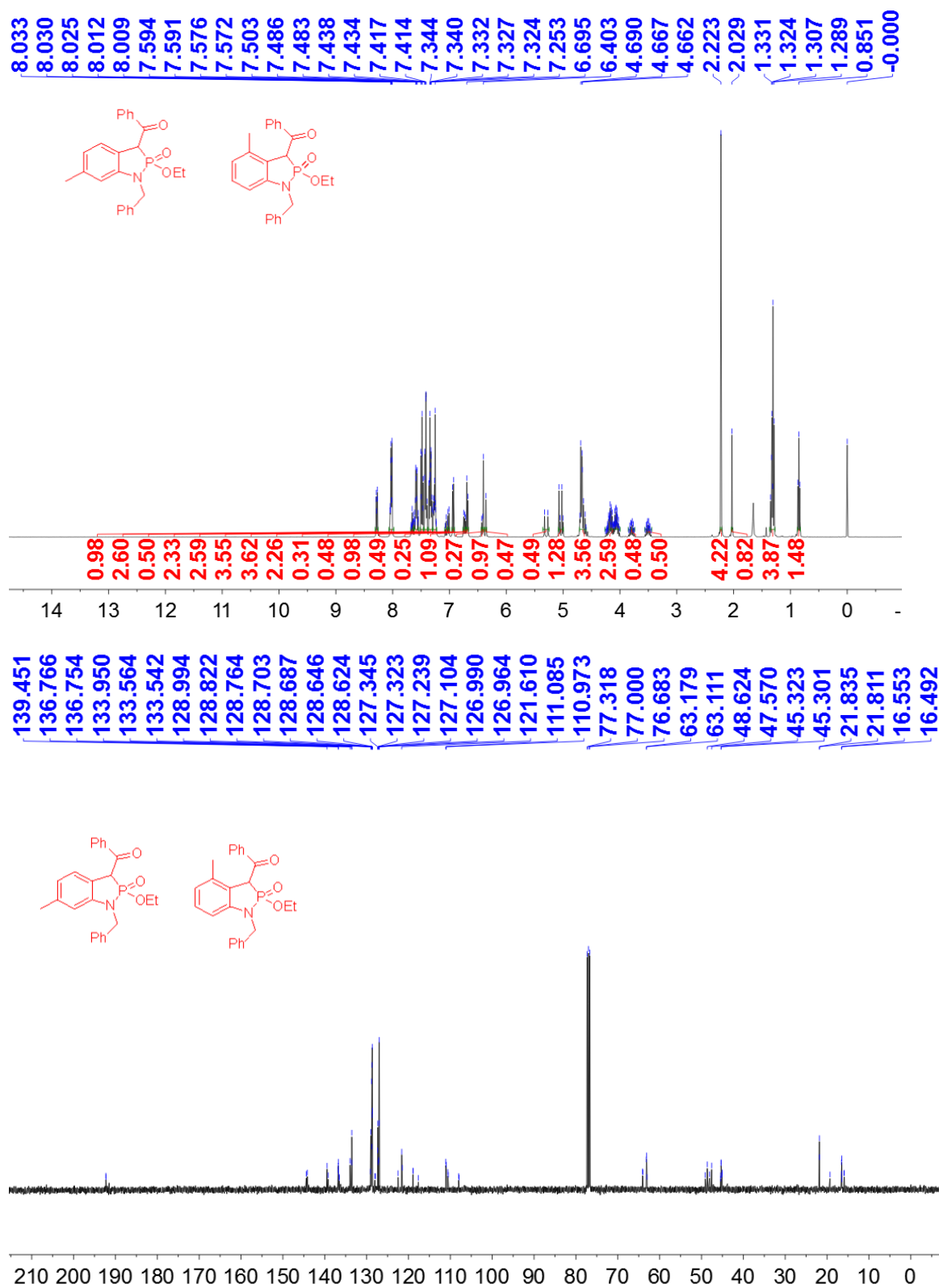


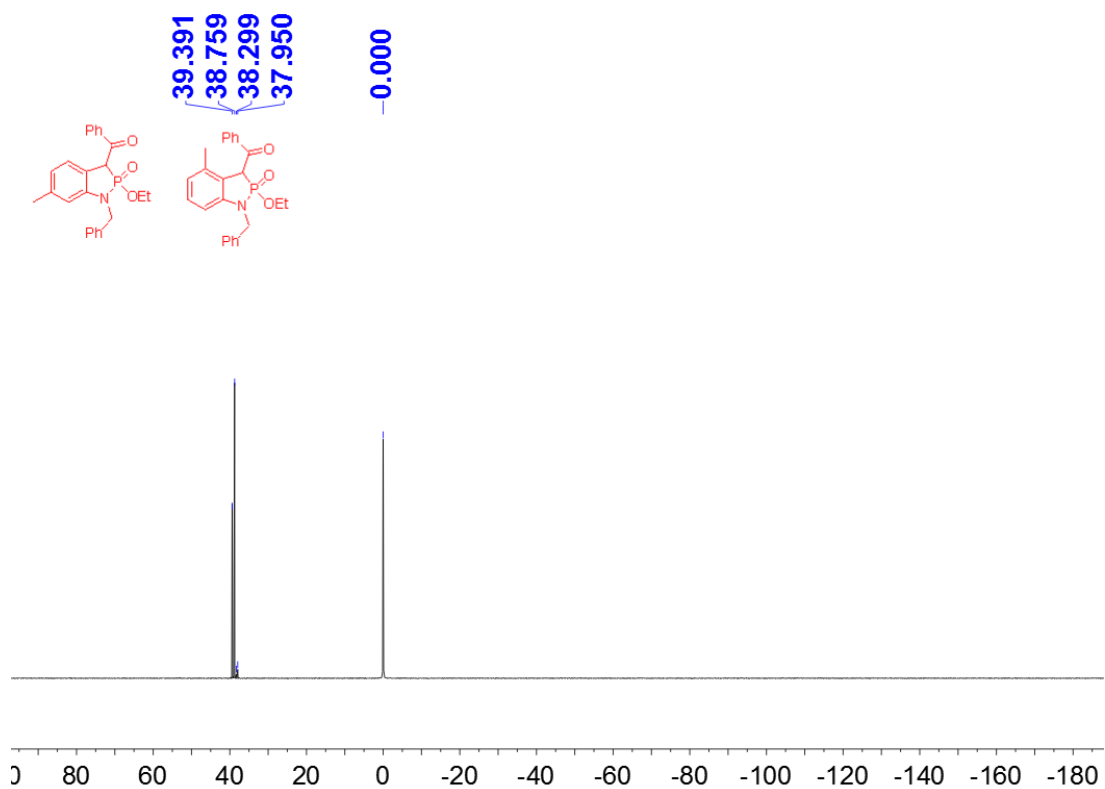
3-Benzoyl-2-ethoxy-1,7-dimethyl-2-oxophosphorindoline (2k)



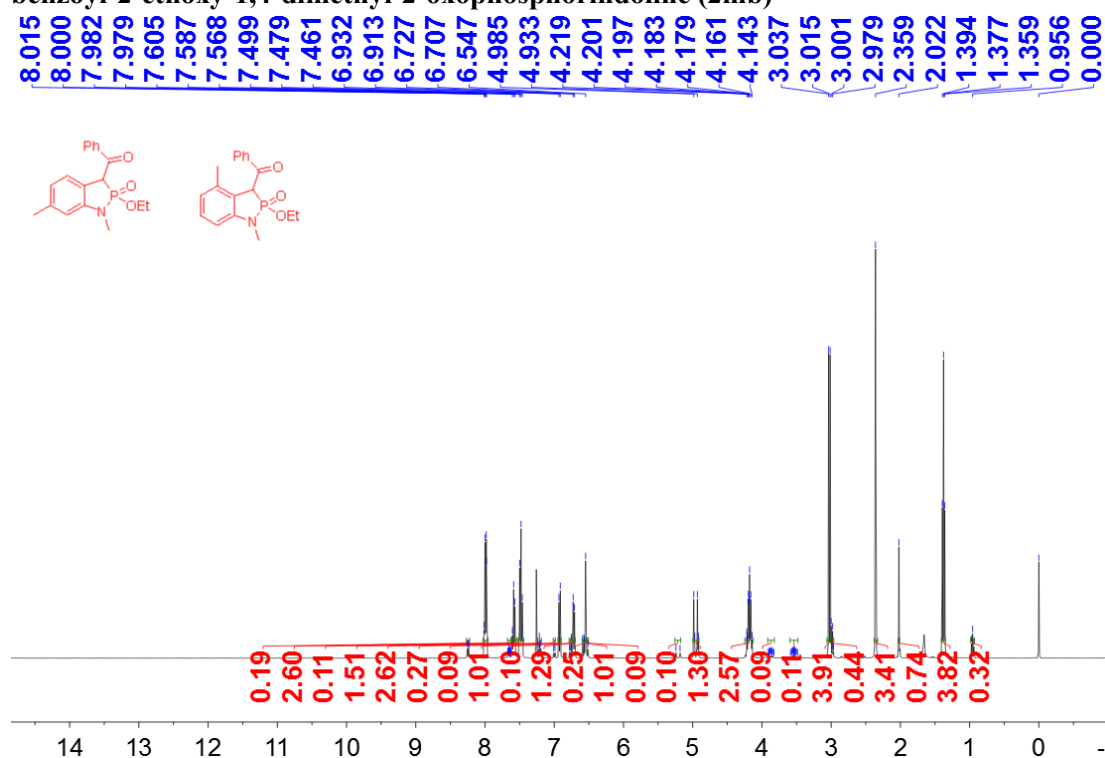


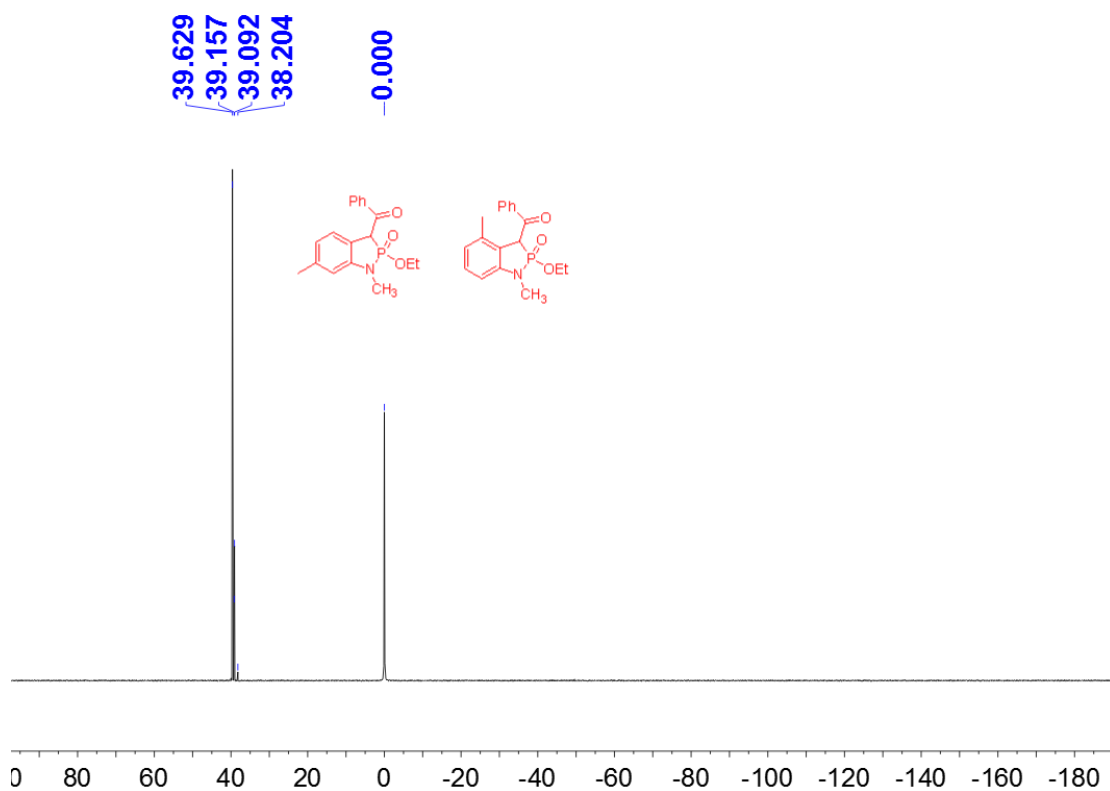
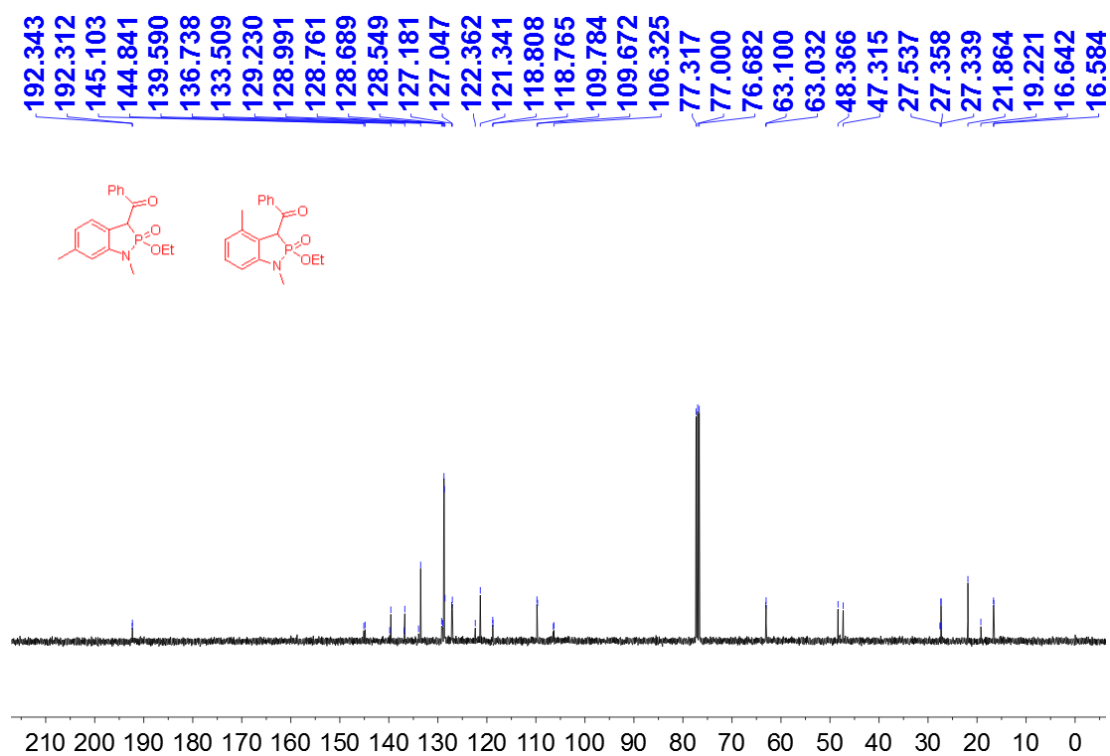
Mixture of 3-benzoyl-1-benzyl-2-ethoxy-6-methyl-2-oxophosphorindoline (2la) and 3-benzoyl-1-benzyl-2-ethoxy-4-methyl-2-oxophosphorindoline (2lb)



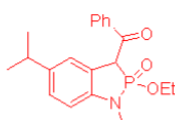
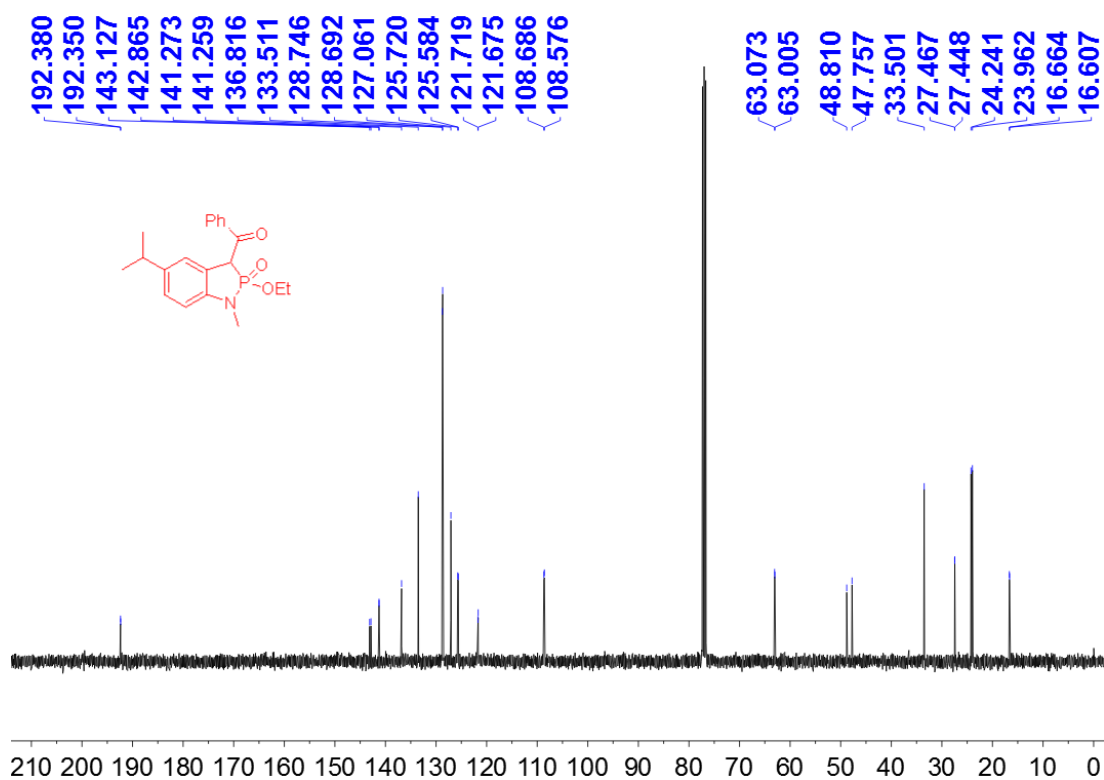
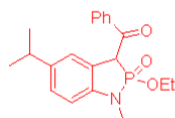
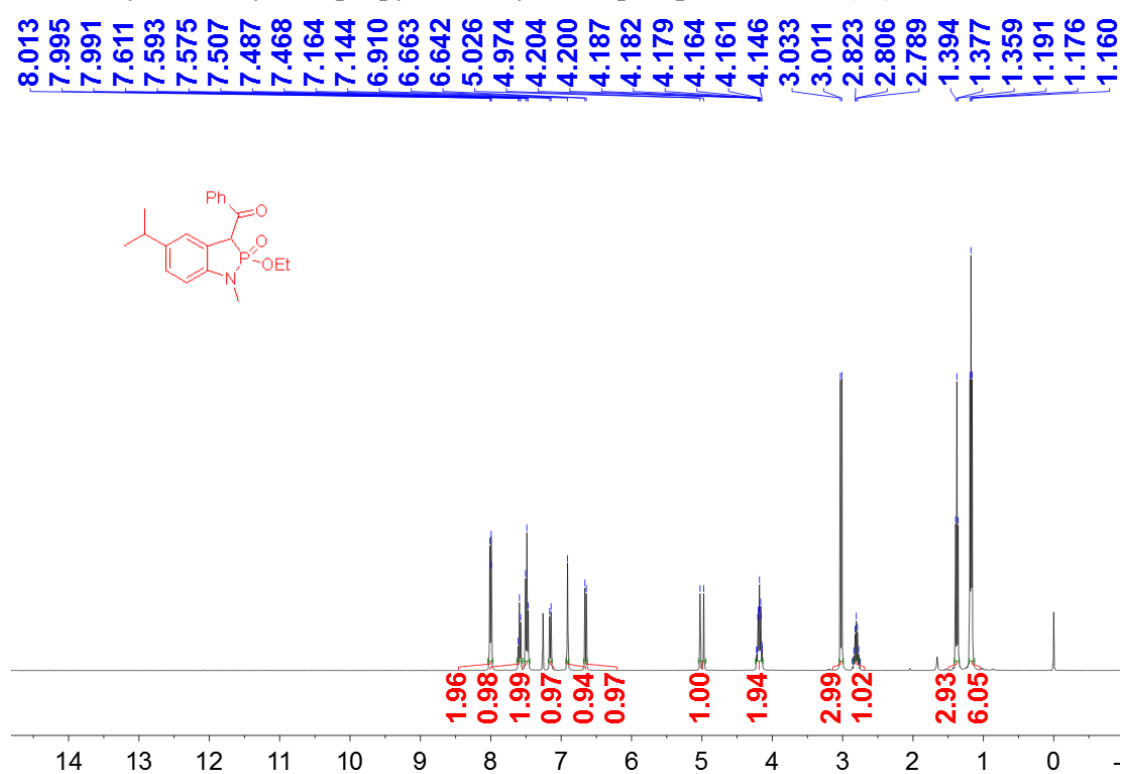


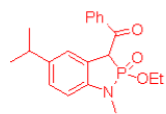
Mixture of 3-benzoyl-2-ethoxy-1,6-dimethyl-2-oxophosphorindoline (2ma) and 3-benzoyl-2-ethoxy-1,4-dimethyl-2-oxophosphorindoline (2mb)



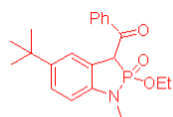


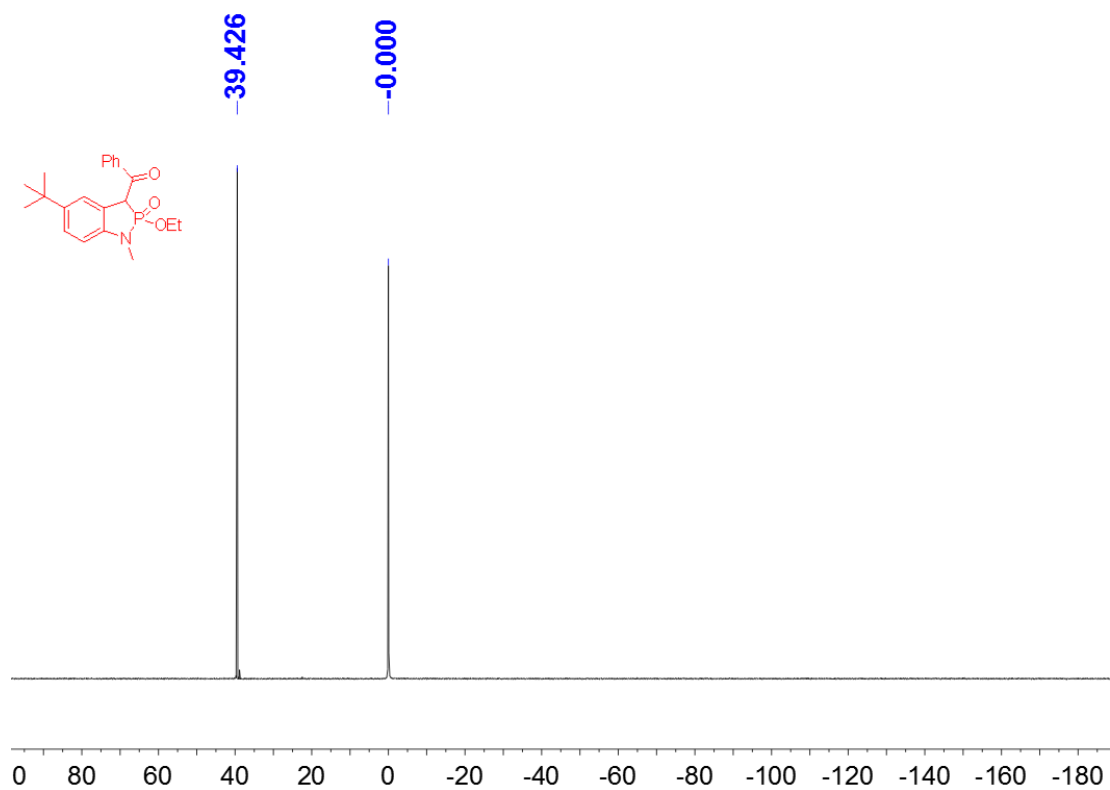
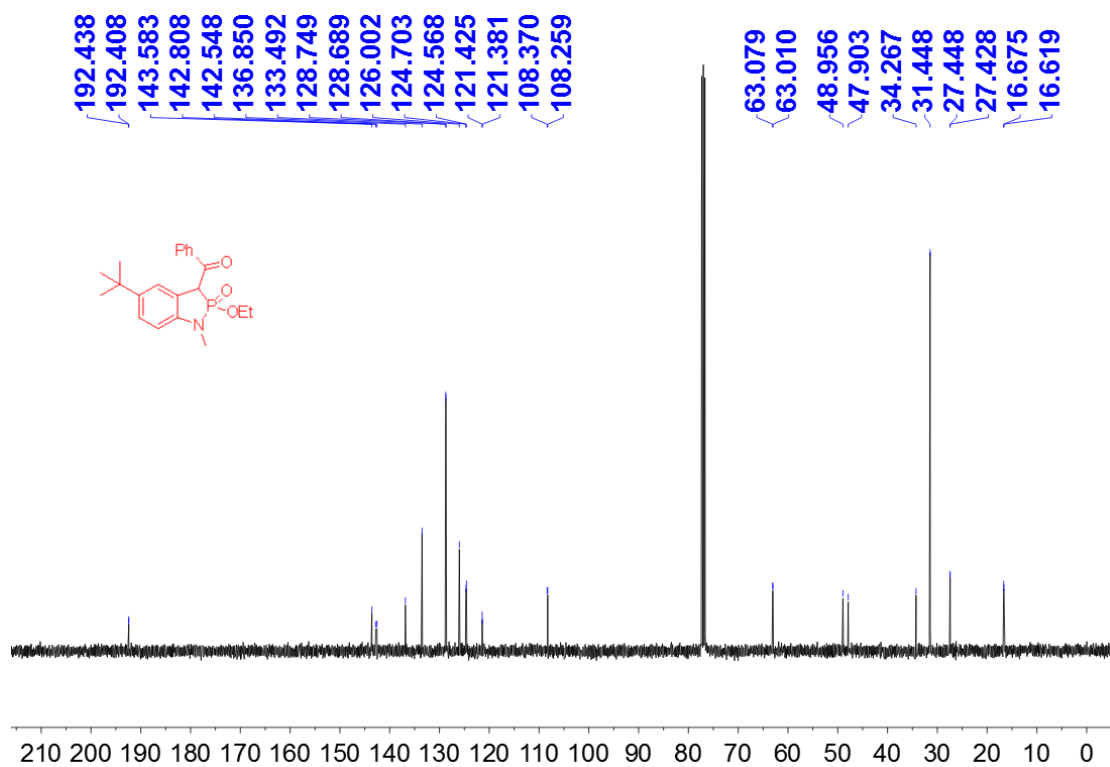
3-Benzoyl-2-ethoxy-5-isopropyl-1-methyl-2-oxophosphorindoline (2n)



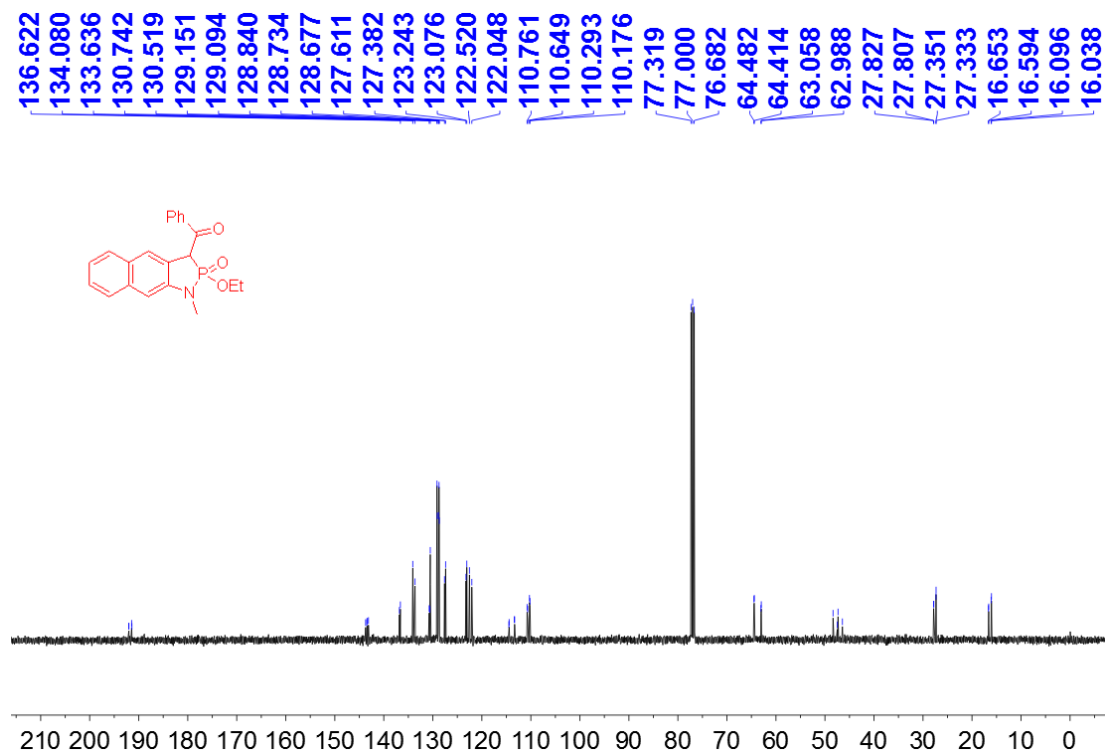
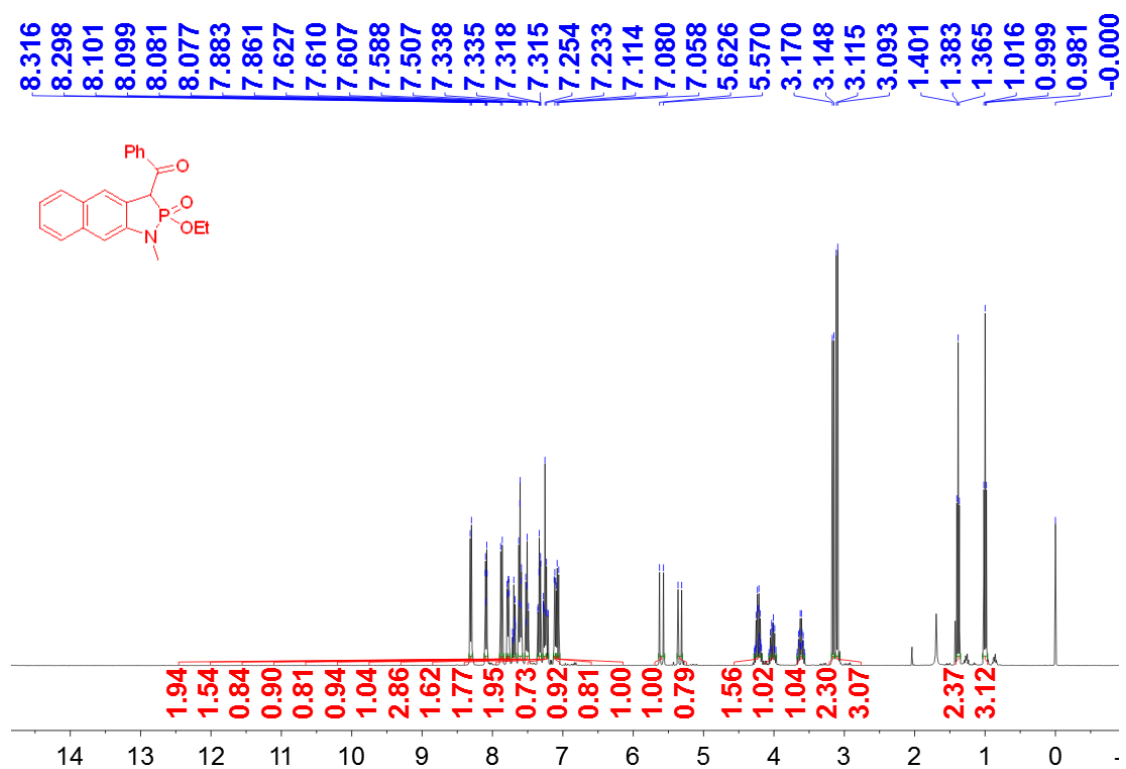


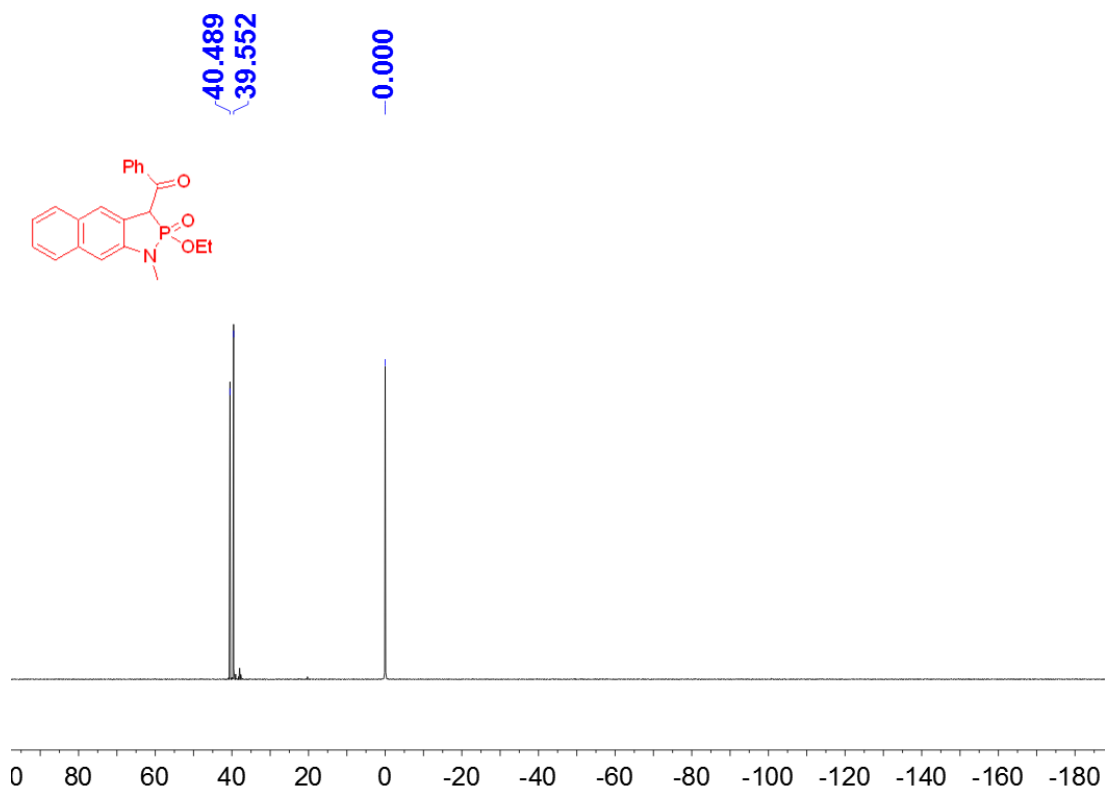
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8.009
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7.593
7.577
7.574
7.570
7.507
7.488
7.469
7.324
7.304
7.056
6.668
6.648
5.034
4.982
4.208
4.203
4.190
4.185
4.181
4.168
4.164
4.149
3.035
3.014
1.396
1.379
1.361
1.243





3-Benzoyl-2-ethoxy-1-methyl-2-oxobenzo[f]phosphorindoline (2p)





2-Benzoyl-1-ethoxy-1-oxoazacyclohexano[3,2,1-*h,i*]phosphorindoline (2q)

