

Supporting Information for

**Geminal Difunctionalization of α -Diazo
Arylmethylphosphonates: Synthesis of Fluorinated
Phosphonates**

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of Chemistry, Peking University, Beijing 100871, China*

*^bState Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences,
Shanghai 200032, China*

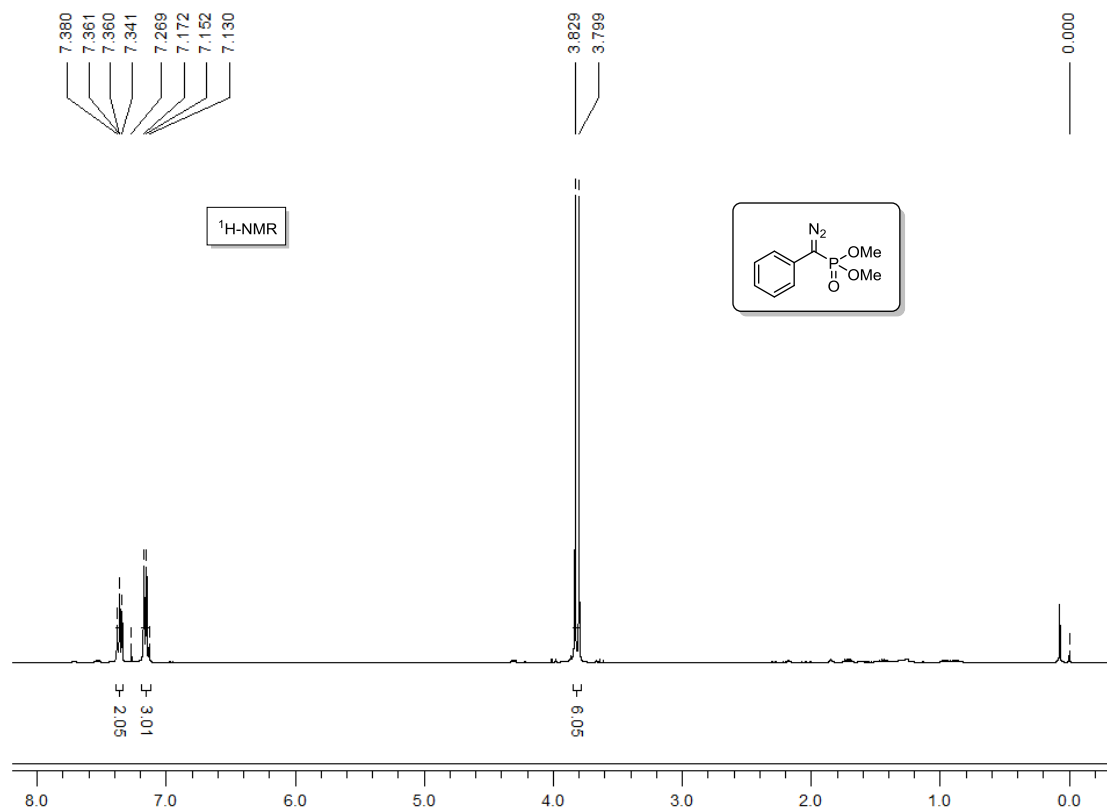
Email: wangjb@pku.edu.cn

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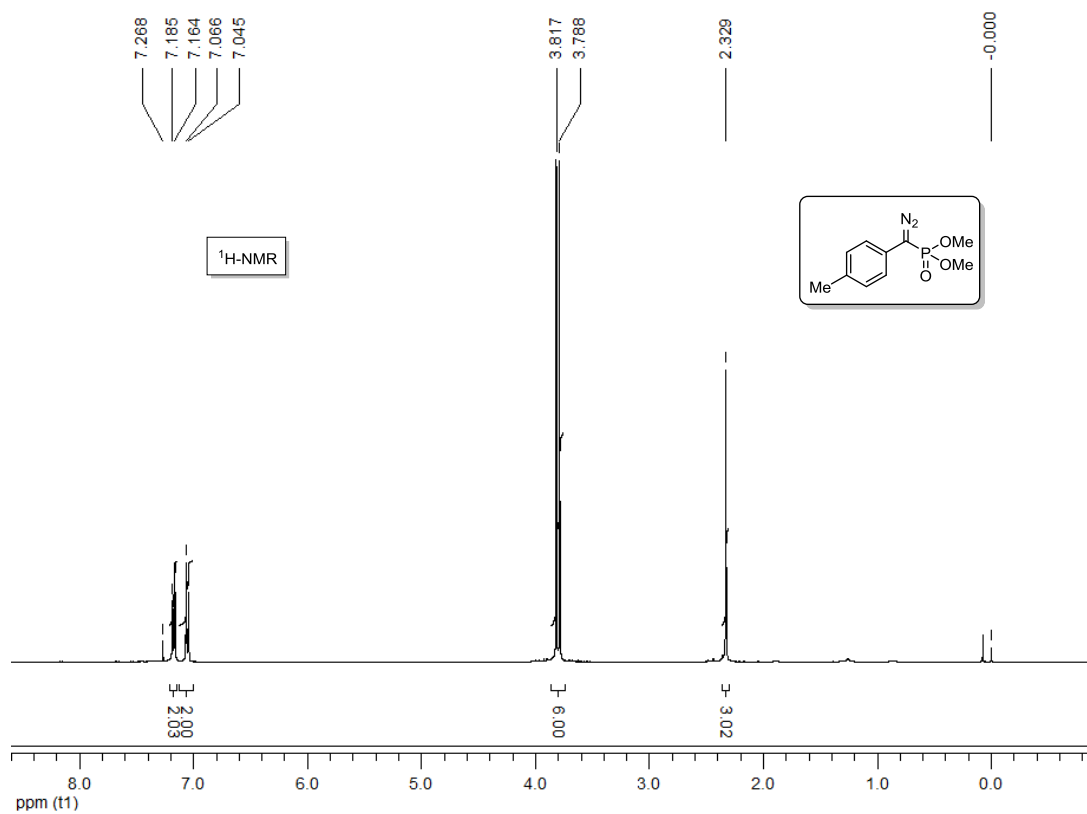
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1. ^1H NMR spectra of diazo substrates 1a-m

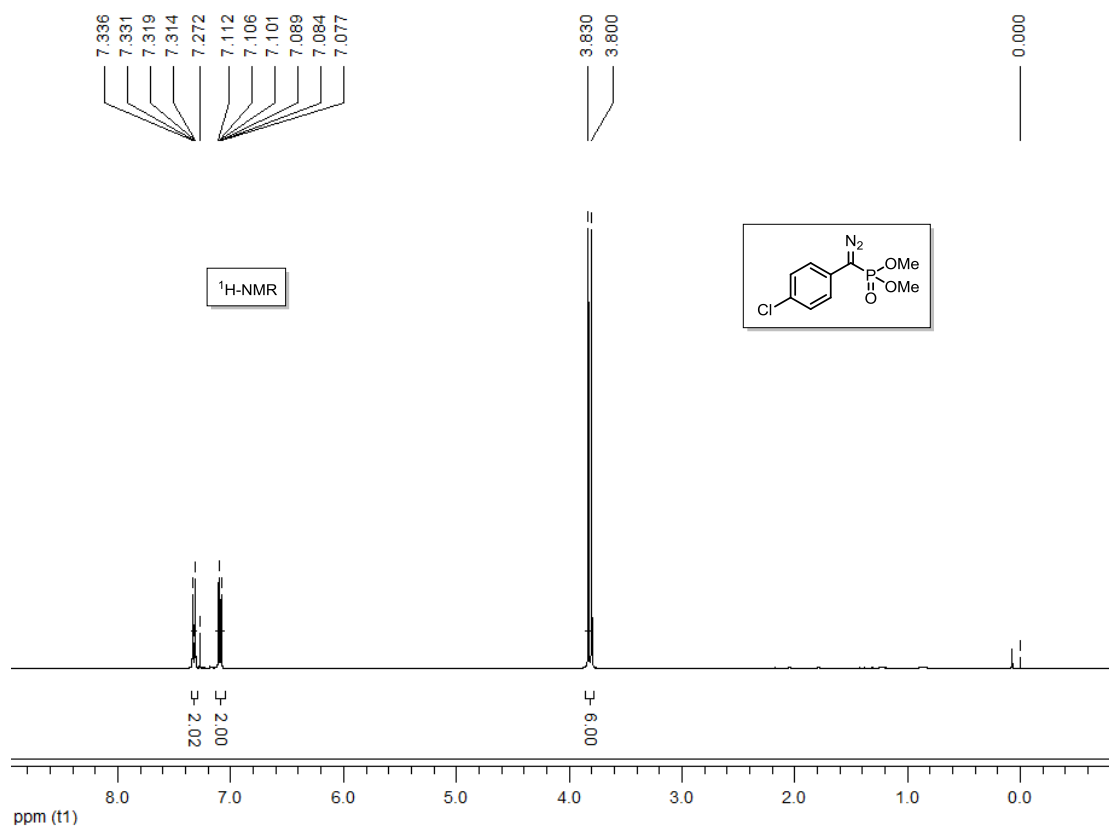
Dimethyl (diazo(phenyl)methyl)phosphonate (**1a**)



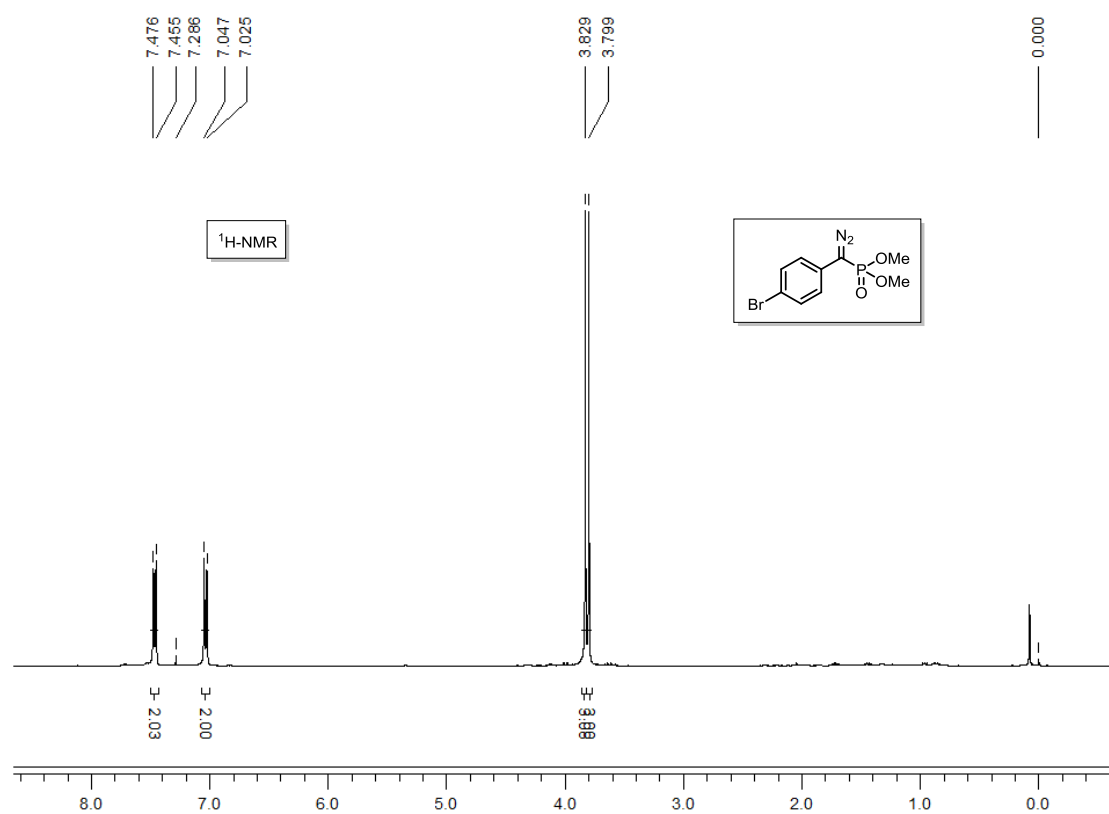
Dimethyl (Diazo(p-tolyl)methyl)phosphonate (**1b**)



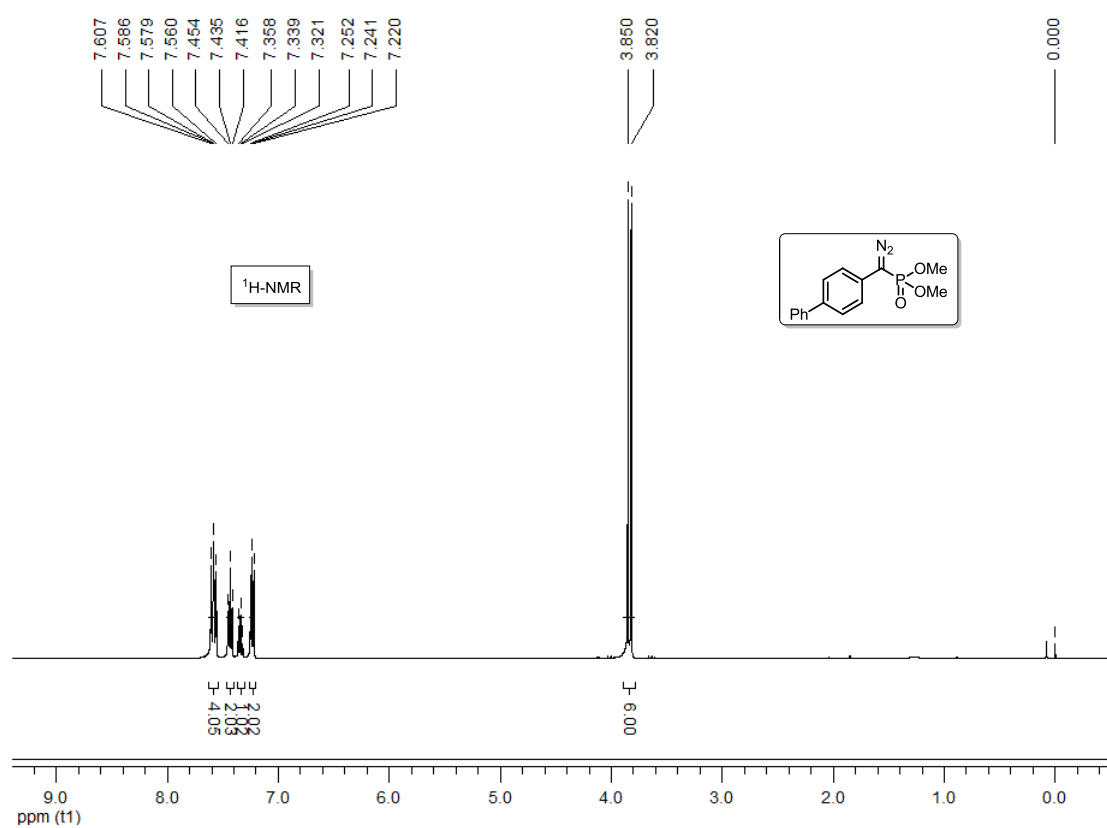
Dimethyl ((4-chlorophenyl)(diazo)methyl)phosphonate (**1c**)



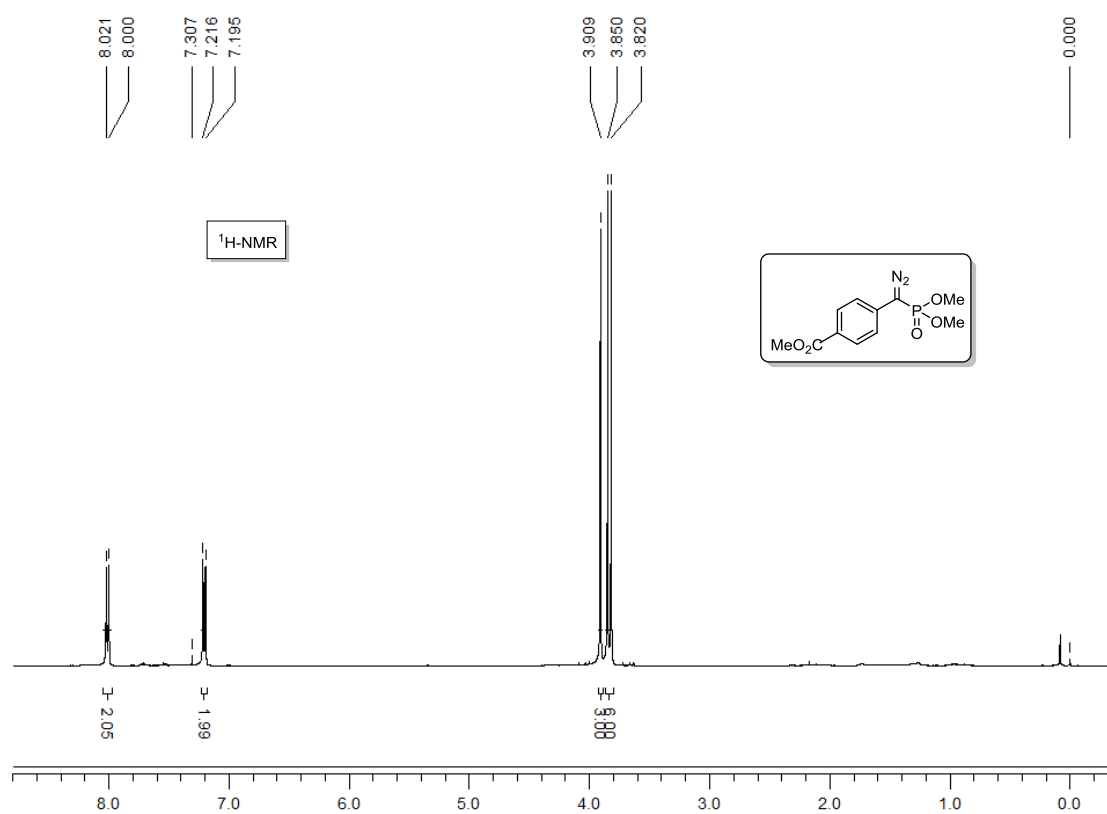
Dimethyl ((4-bromophenyl)(diazo)methyl)phosphonate (**1d**)



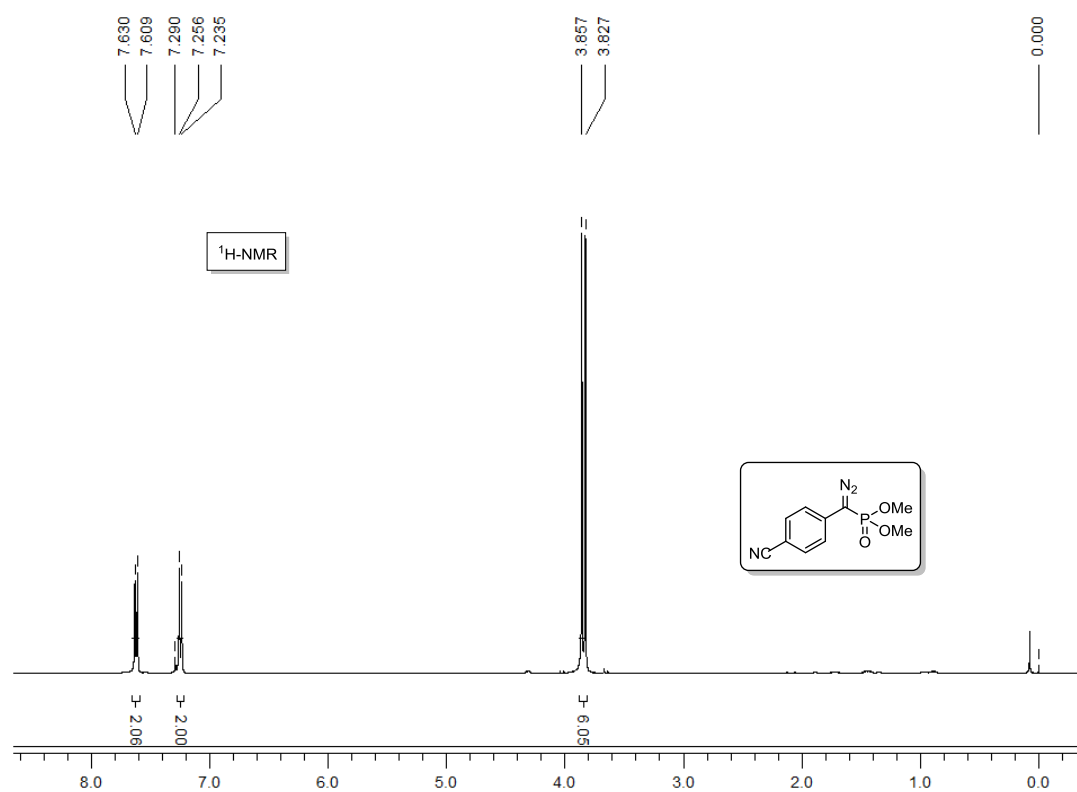
Dimethyl ([1,1'-biphenyl]-4-yl(diazo)methyl)phosphonate (**1e**)



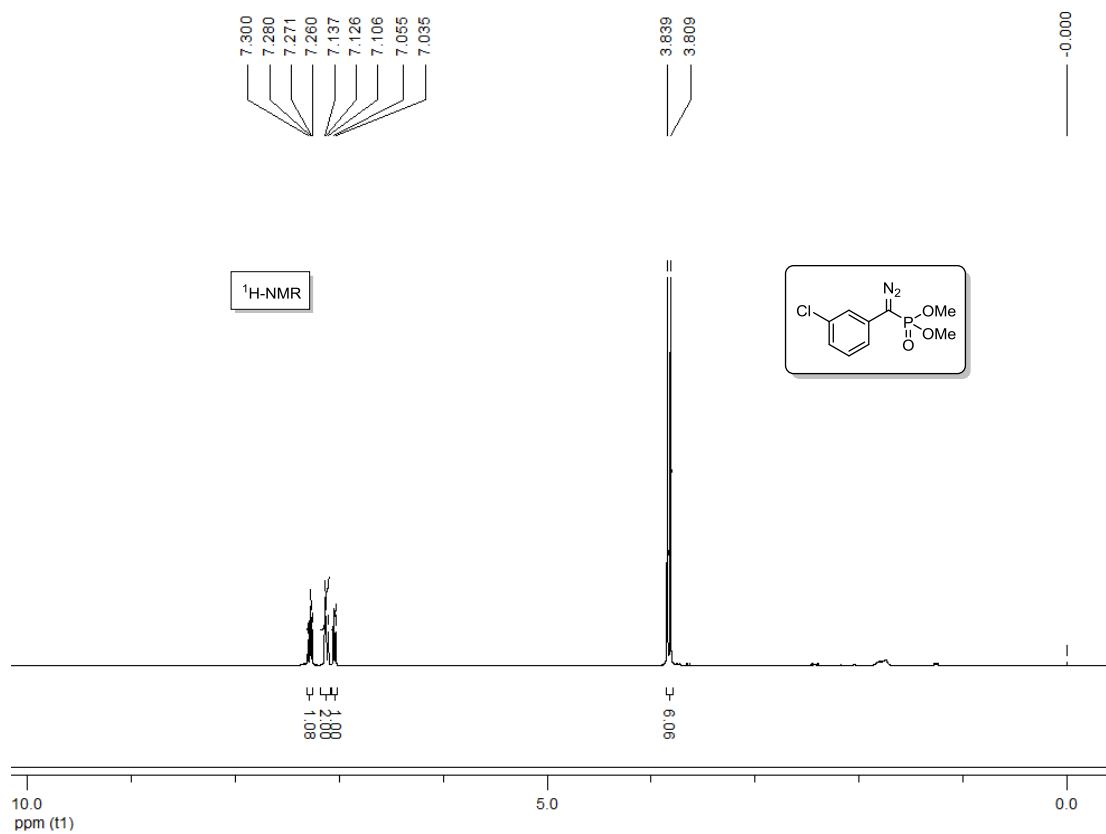
Methyl 4-(diazo(dimethoxyphosphoryl)methyl)benzoate (**1f**)



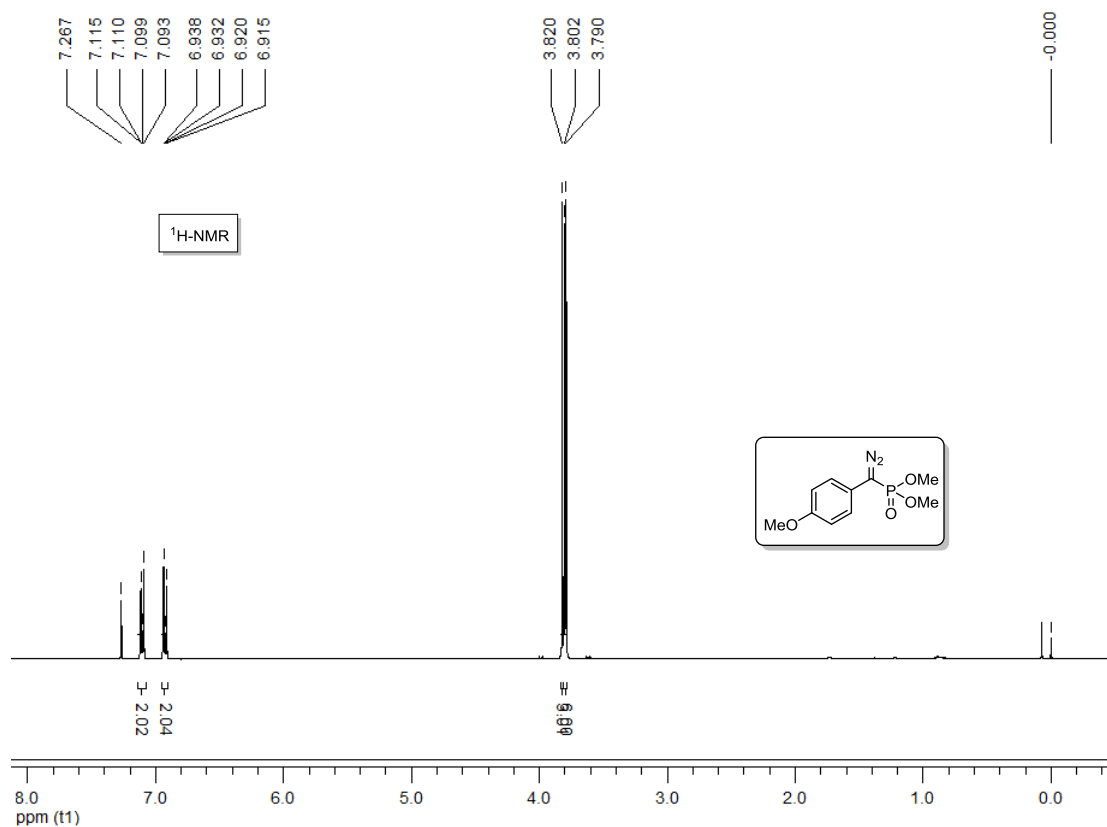
Dimethyl ((4-cyanophenyl)(diazo)methyl)phosphonate (**1g**)



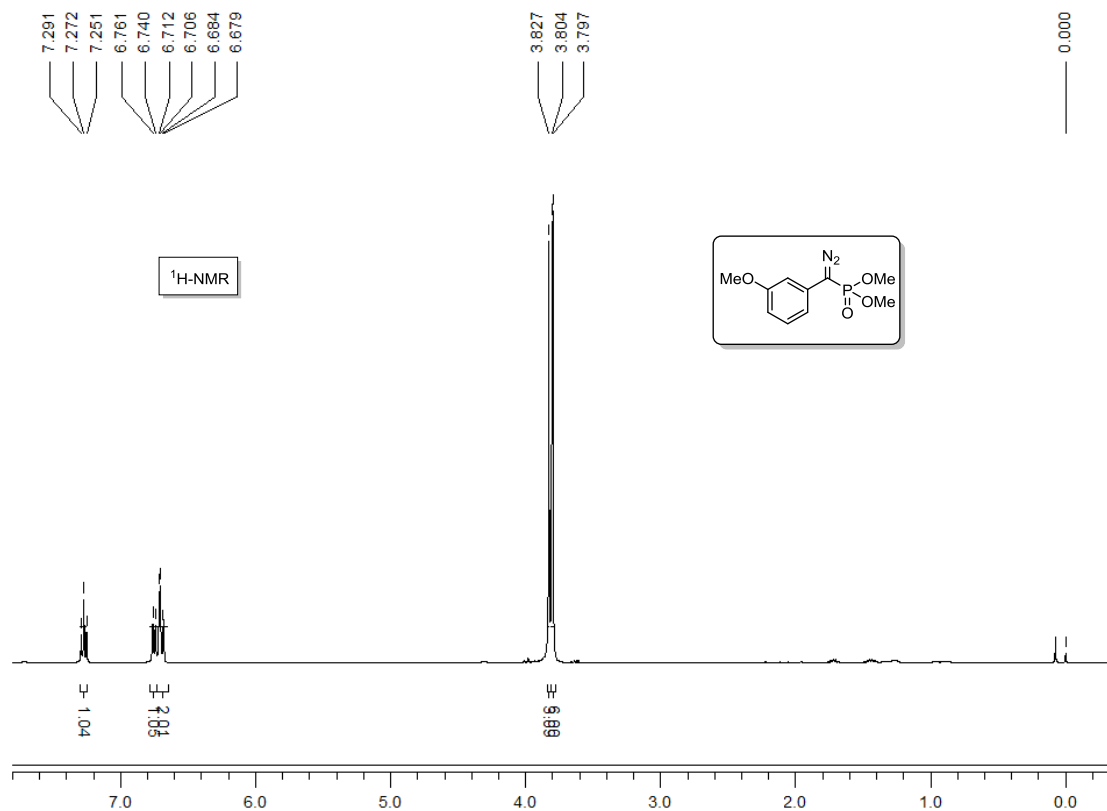
Dimethyl ((3-chlorophenyl)(diazo)methyl)phosphonate (**1h**)



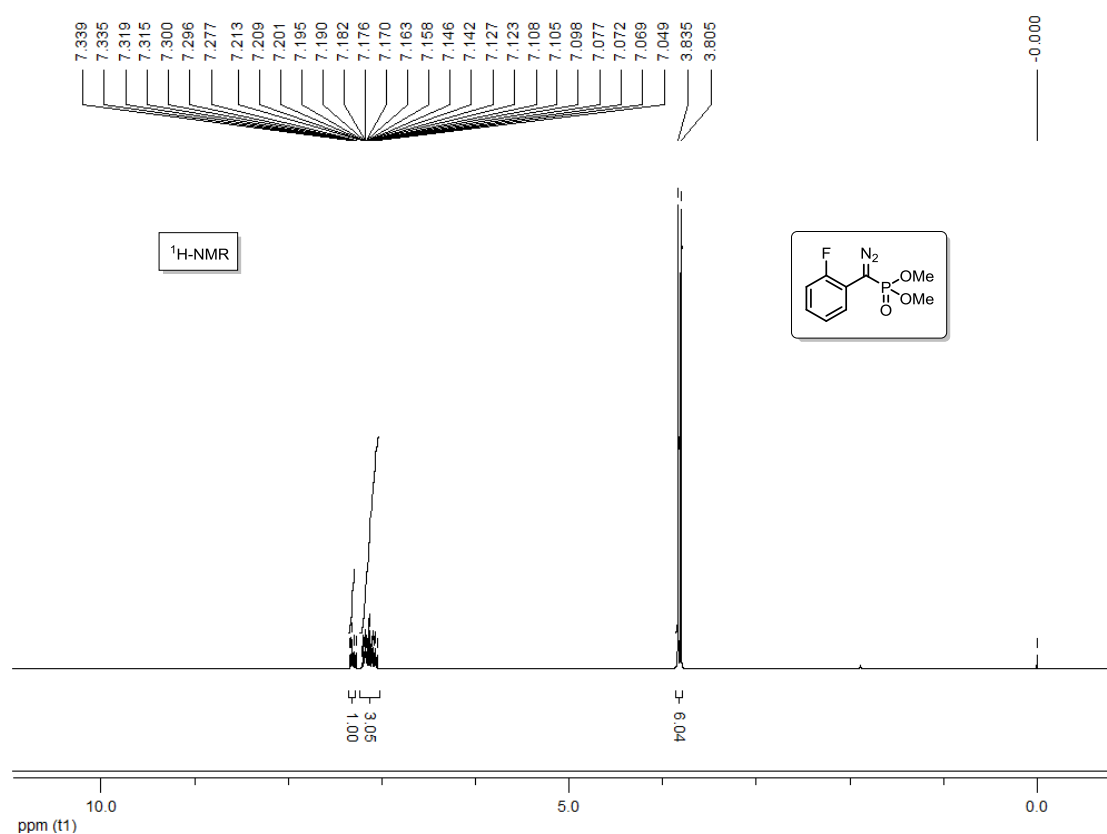
Dimethyl (diazo(4-methoxyphenyl)methyl)phosphonate (**1i**)



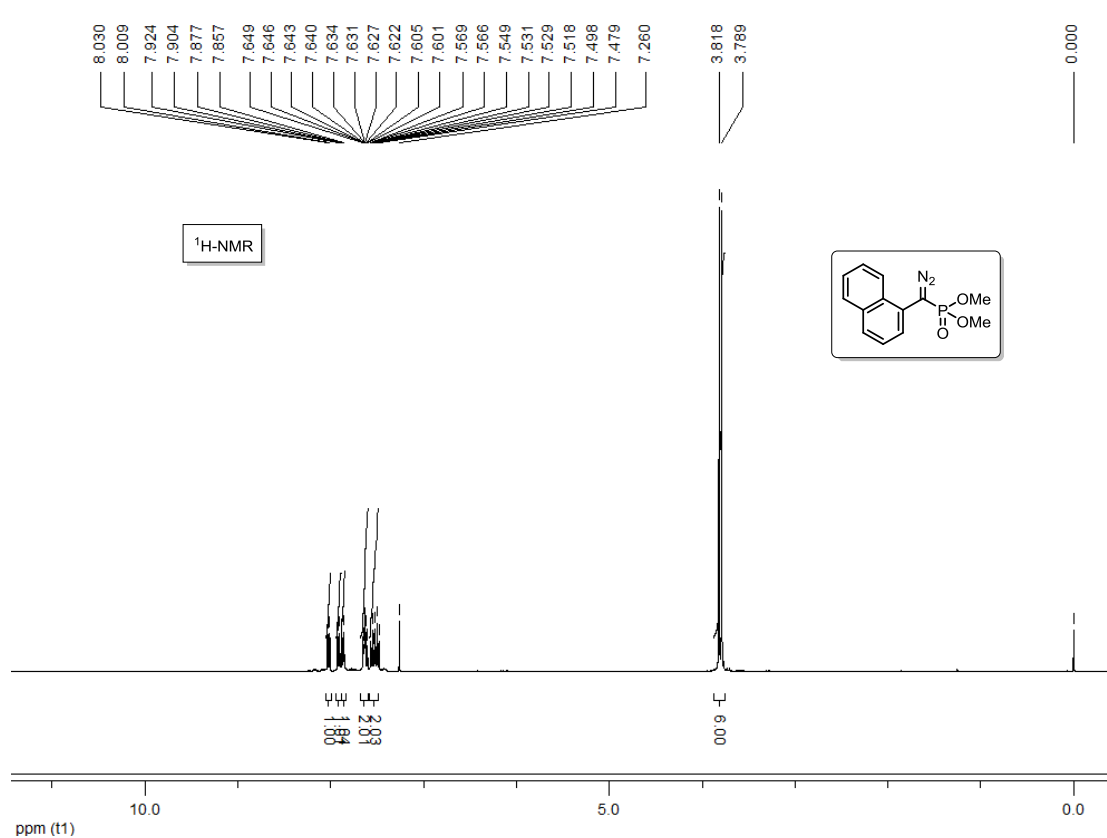
Dimethyl (diazo(3-methoxyphenyl)methyl)phosphonate (**1j**)



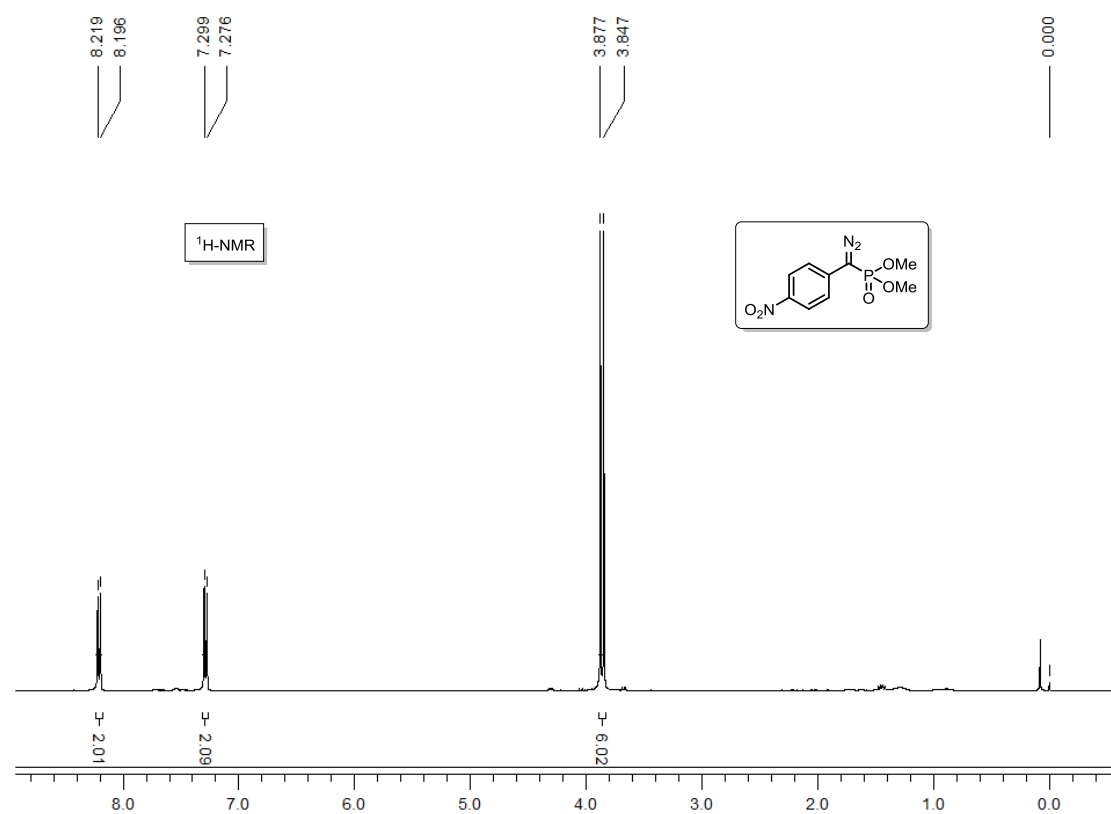
Dimethyl (diazo(2-fluorophenyl)methyl)phosphonate (**1k**)



Dimethyl (diazo(naphthalen-1-yl)methyl)phosphonate (**1l**)

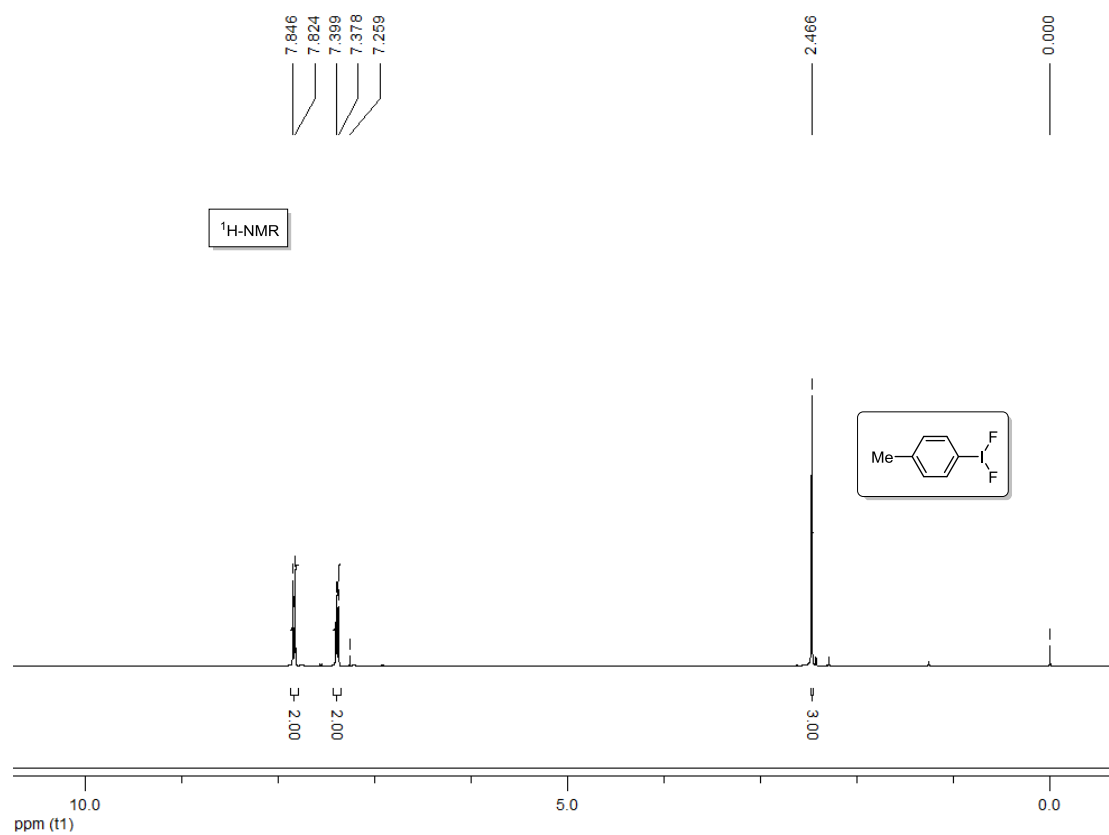


Dimethyl (diazo(4-nitrophenyl)methyl)phosphonate (**1m**)



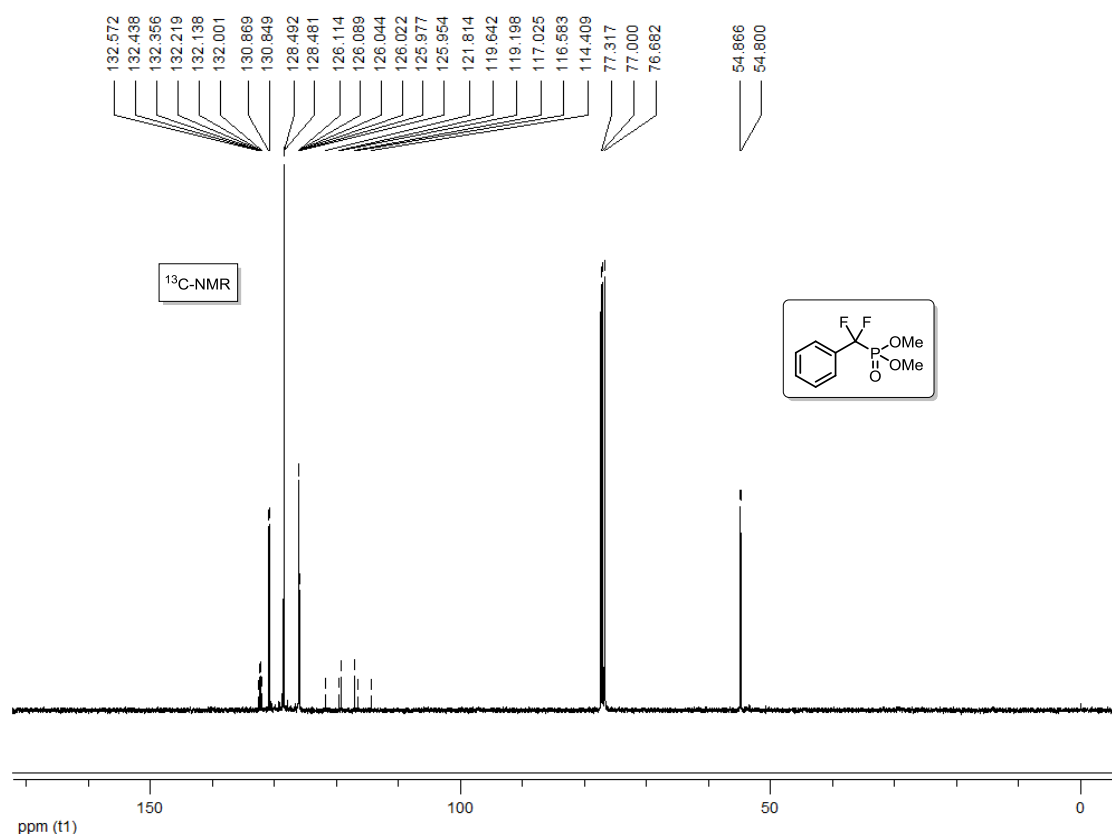
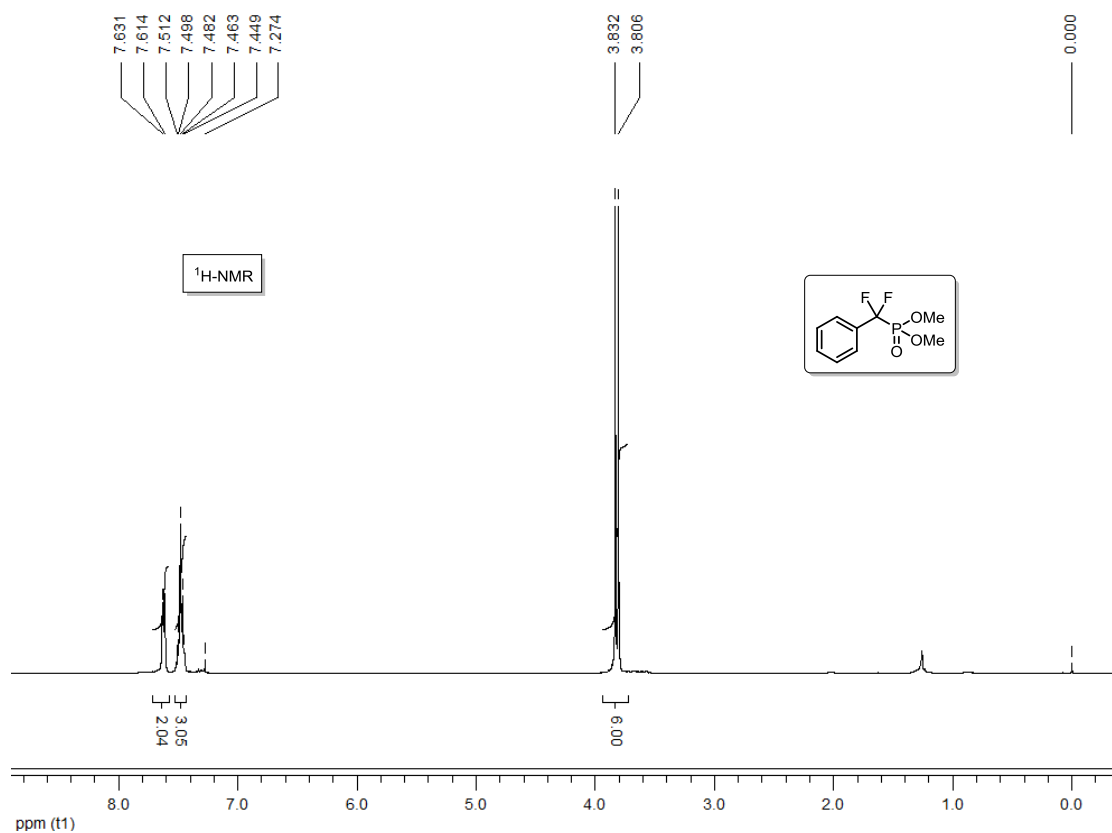
2. ^1H NMR spectra of (difluoroiodo)toluene 2

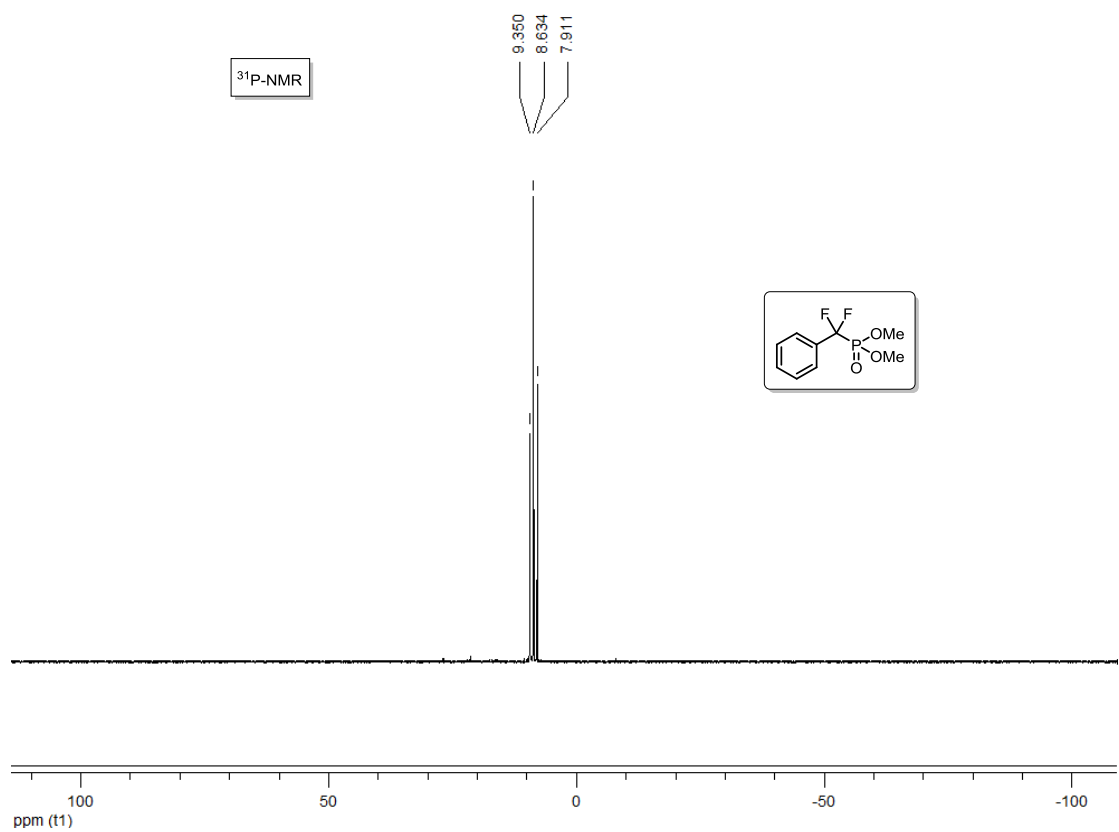
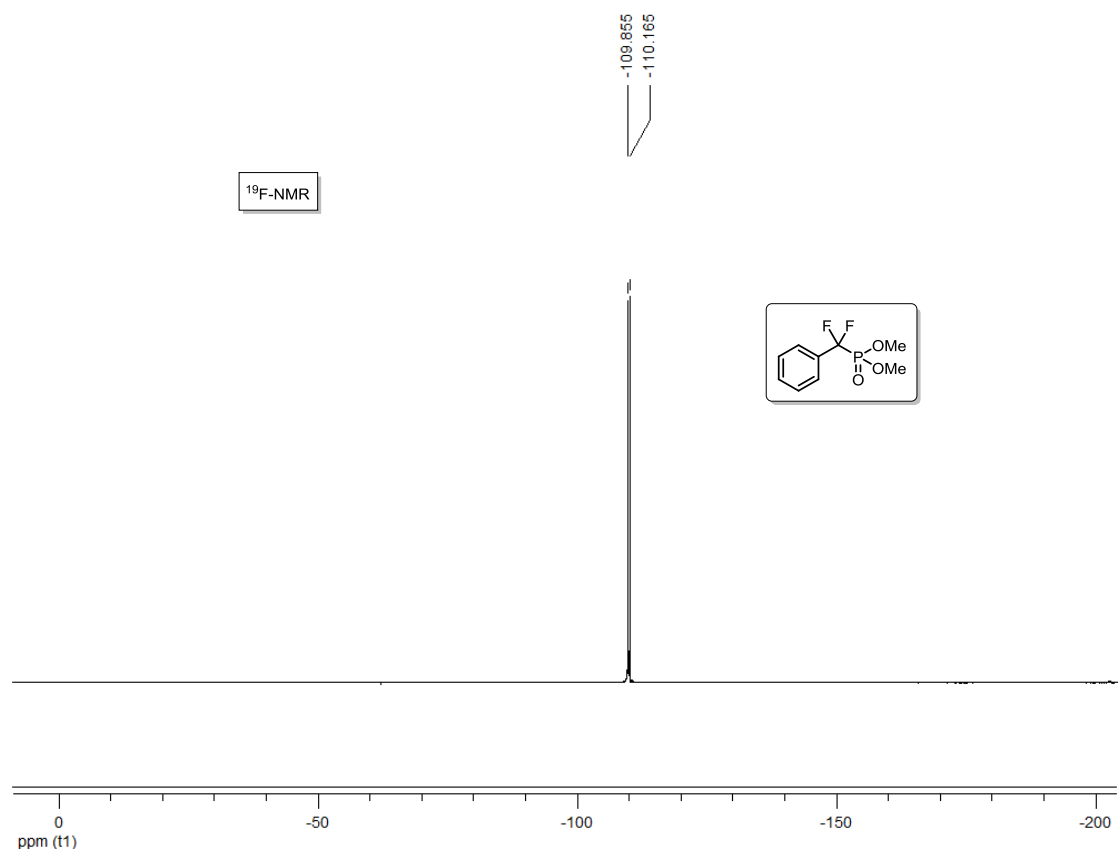
(Difluoroiodo)toluene (2)



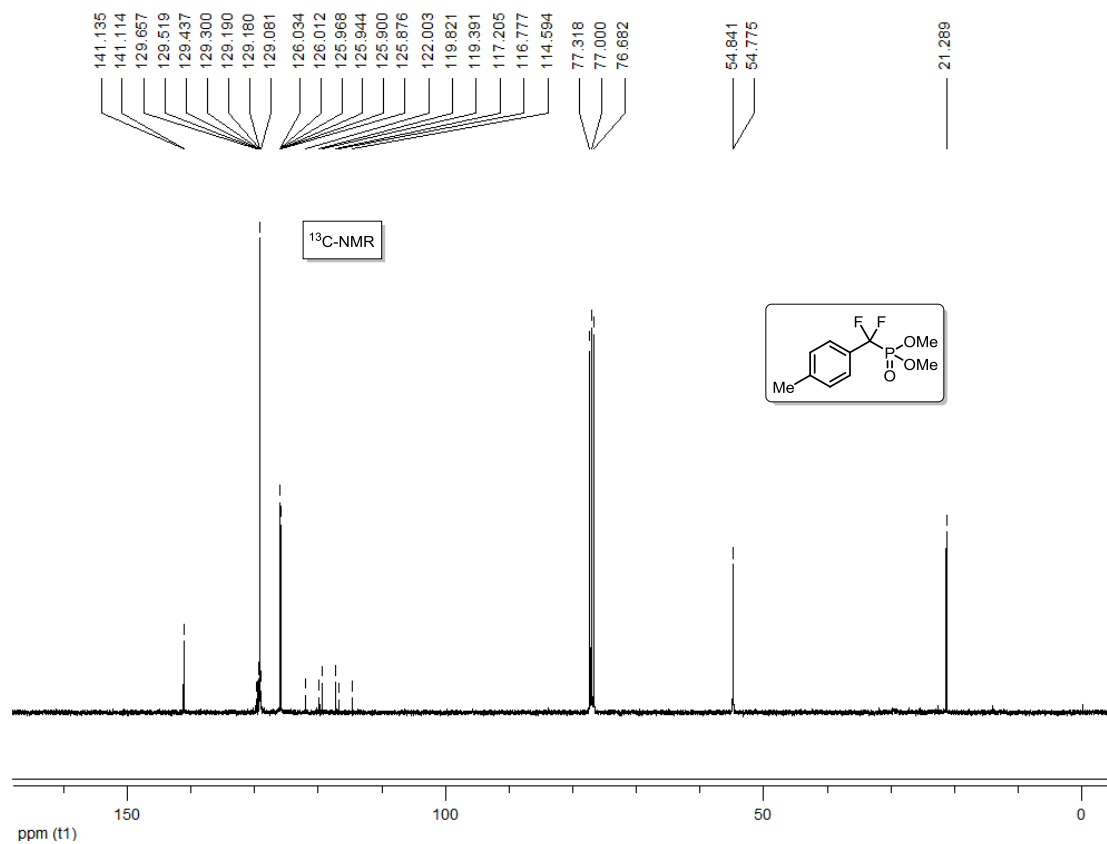
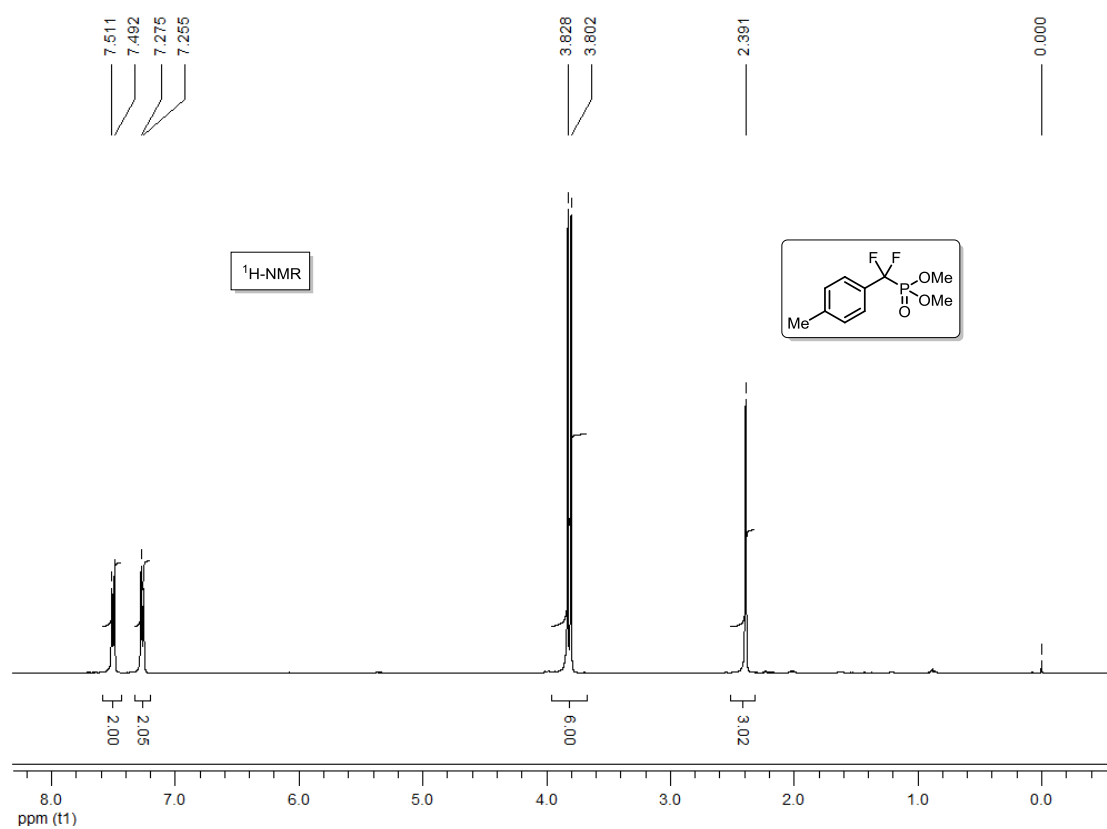
3. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra for the products 3a-h

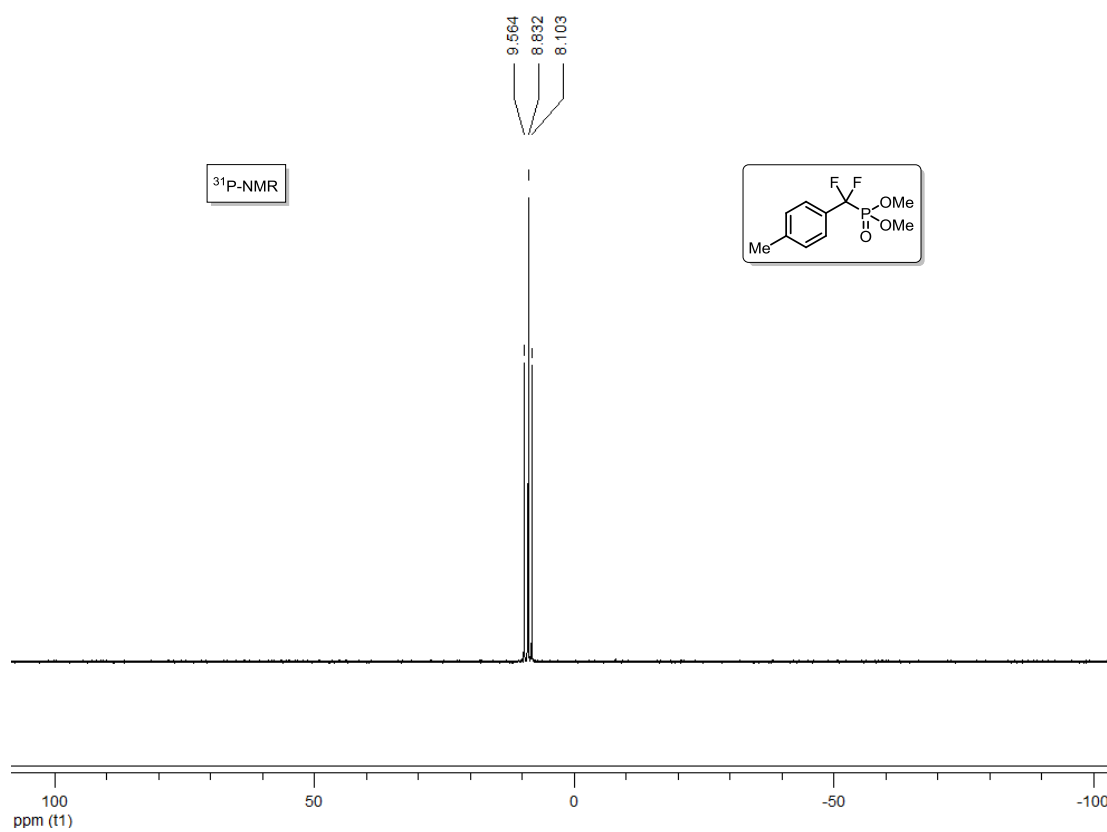
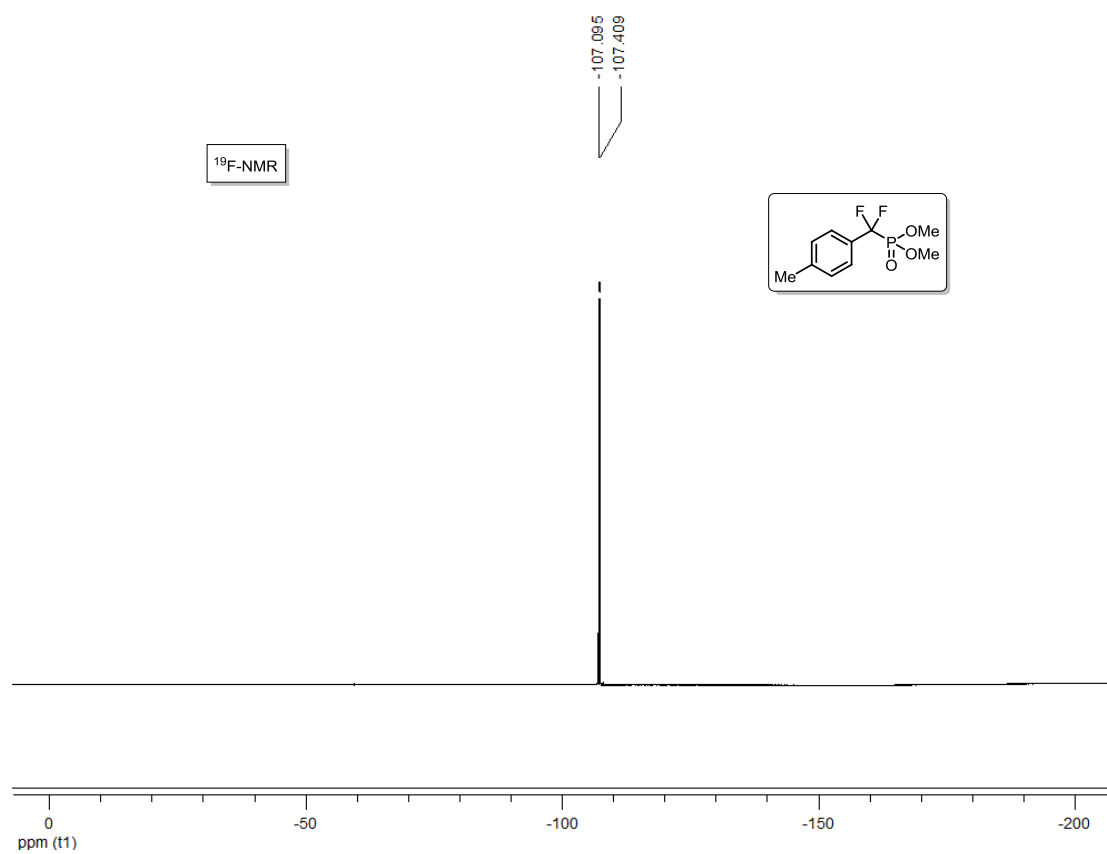
Dimethyl (difluoro(phenyl)methyl)phosphonate (**3a**)



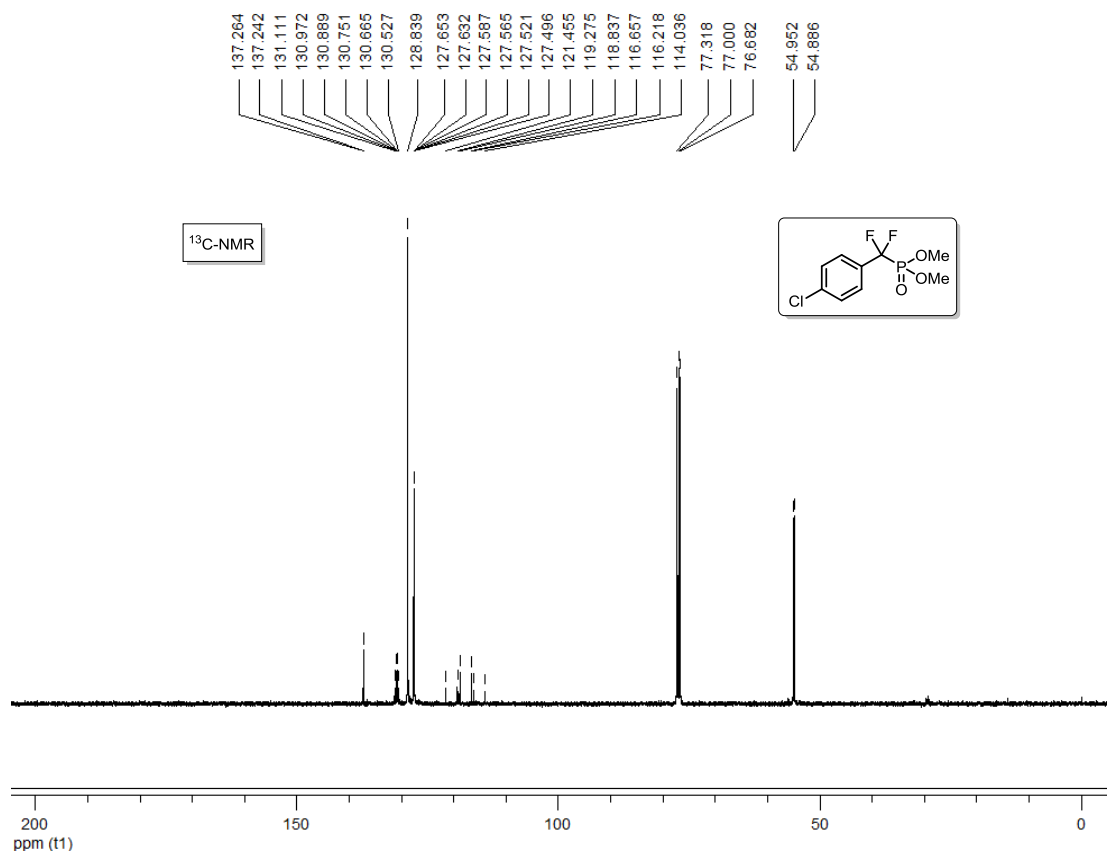
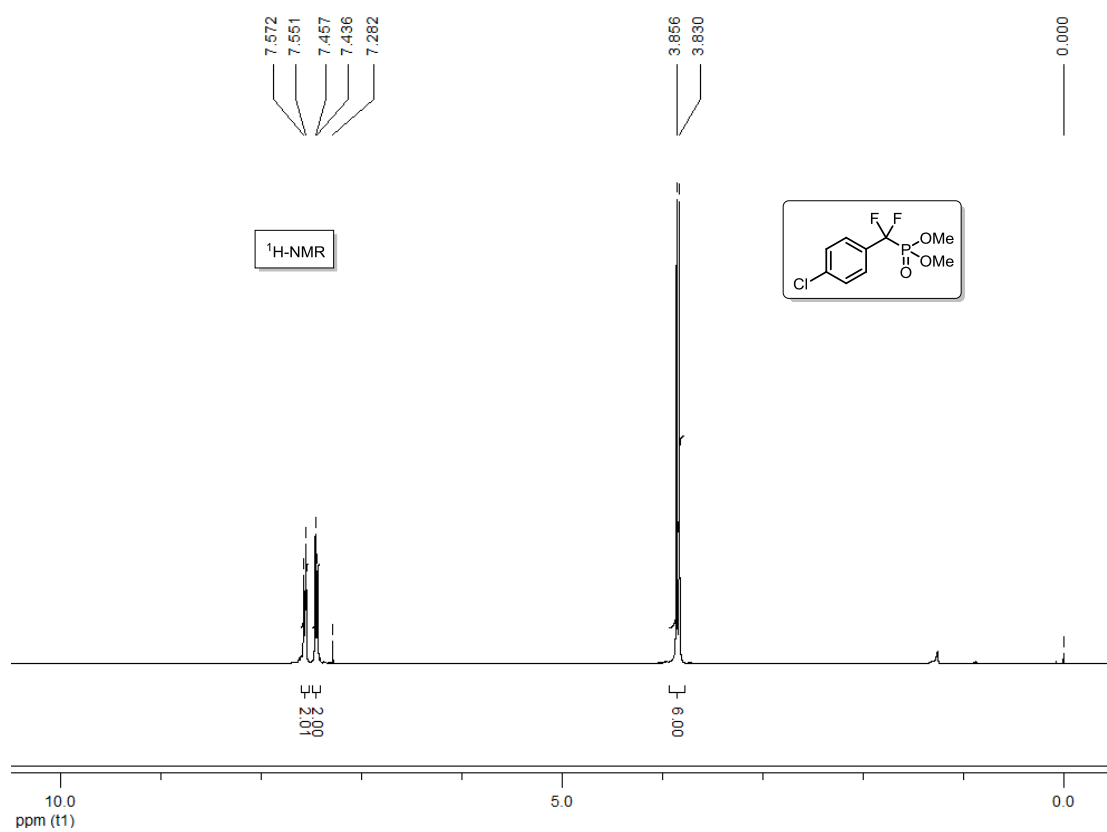


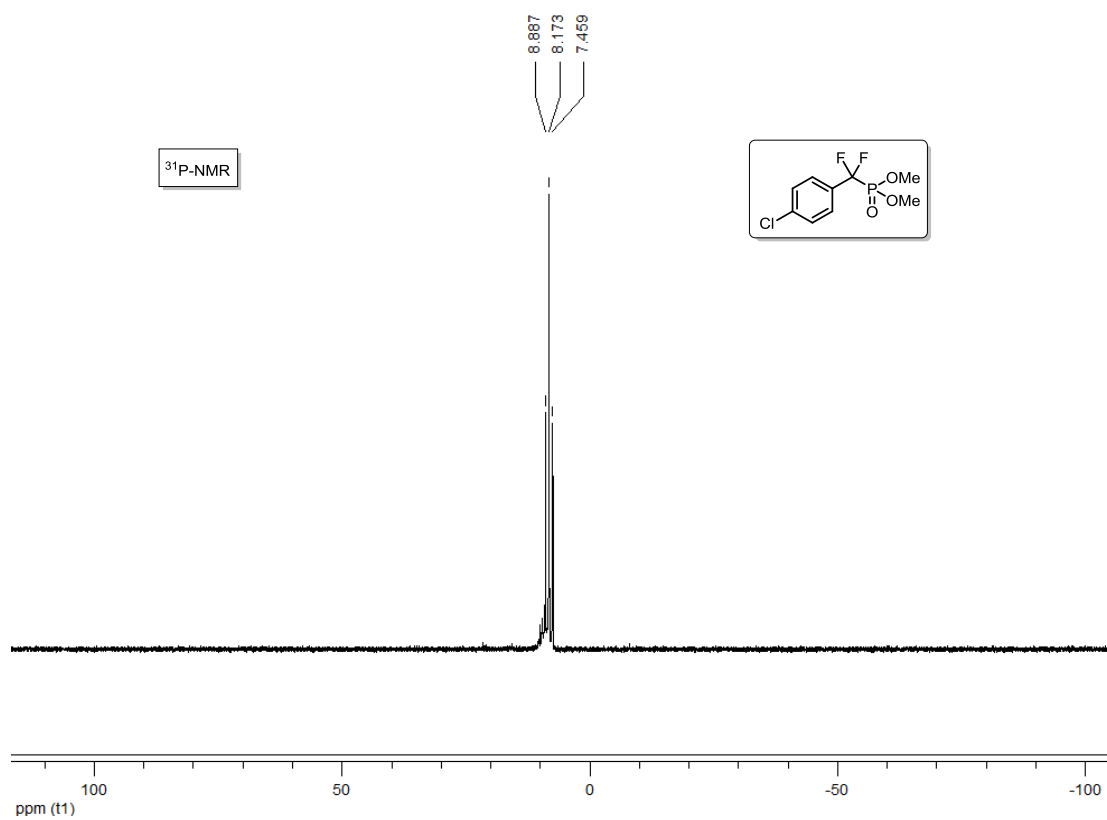
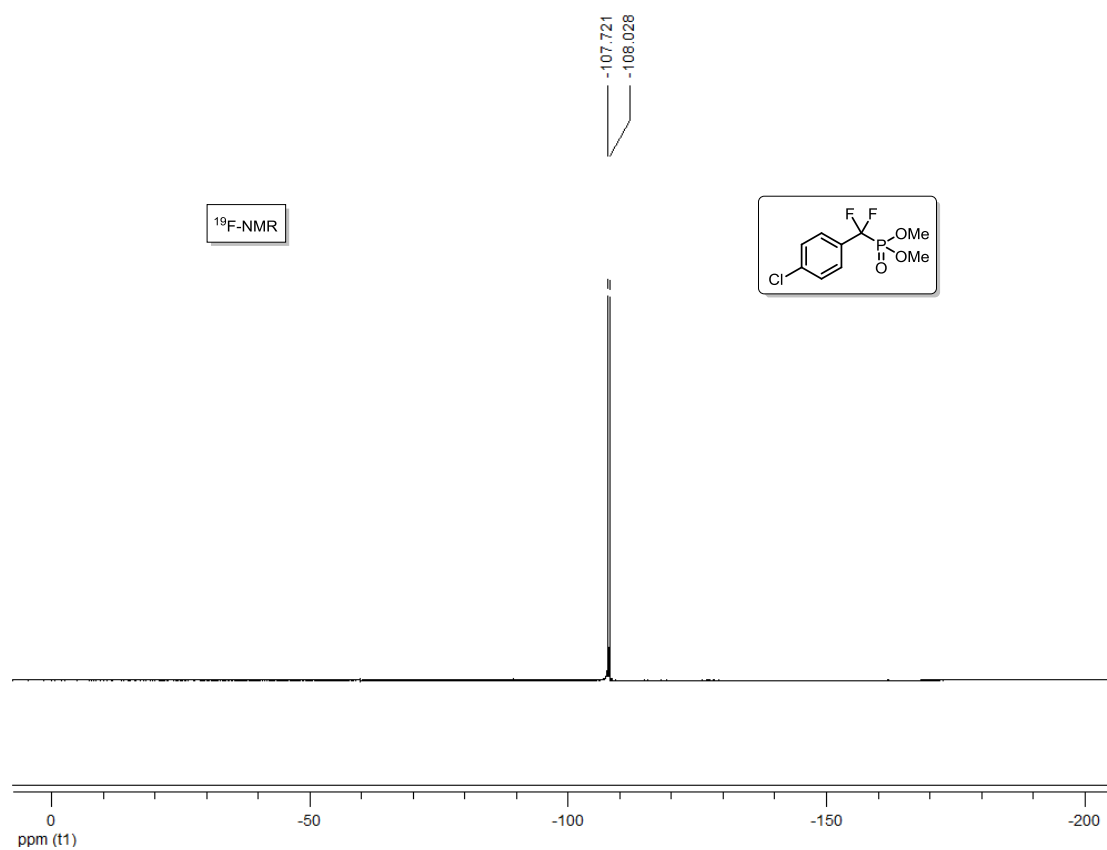
Dimethyl (difluoro(p-tolyl)methyl)phosphonate (**2b**)



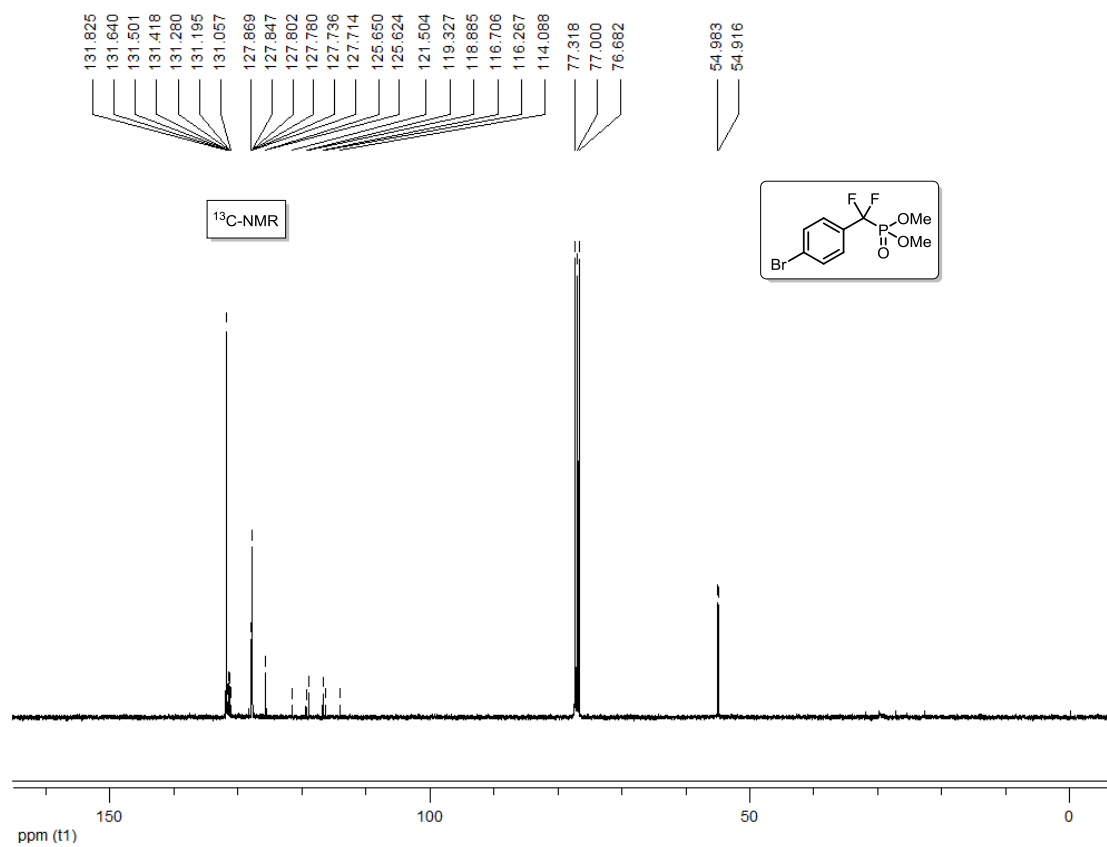
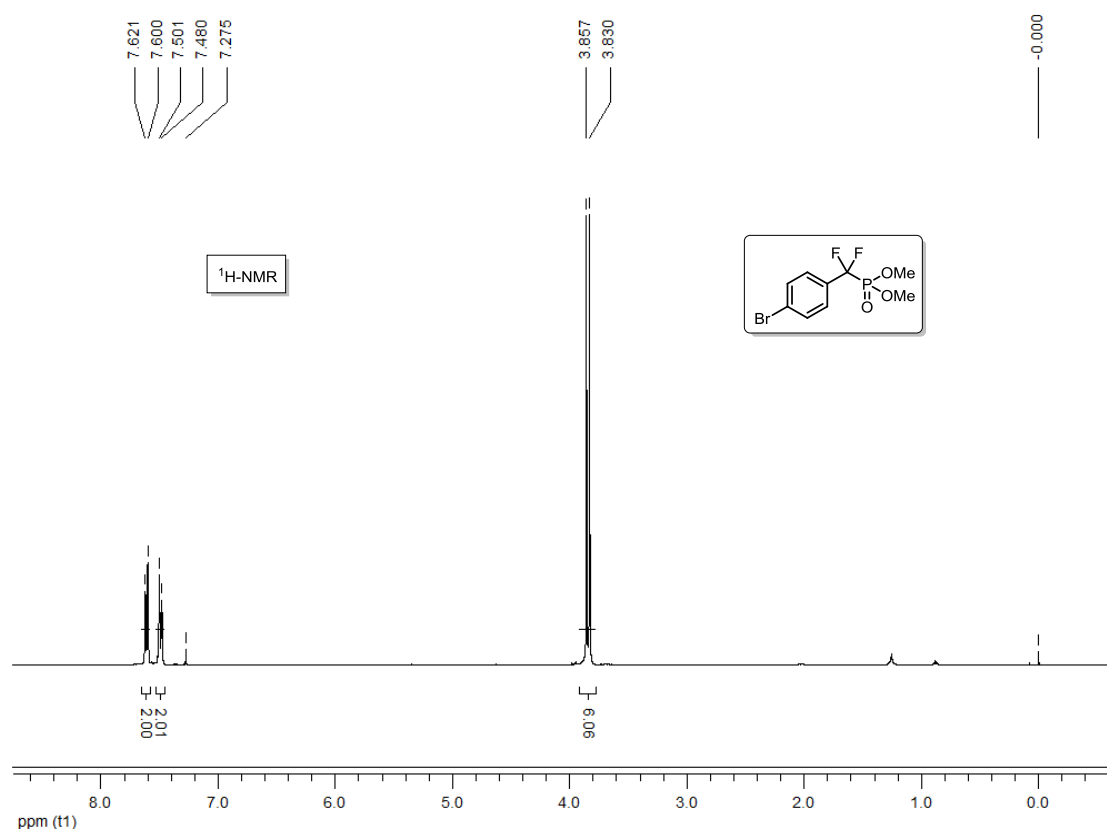


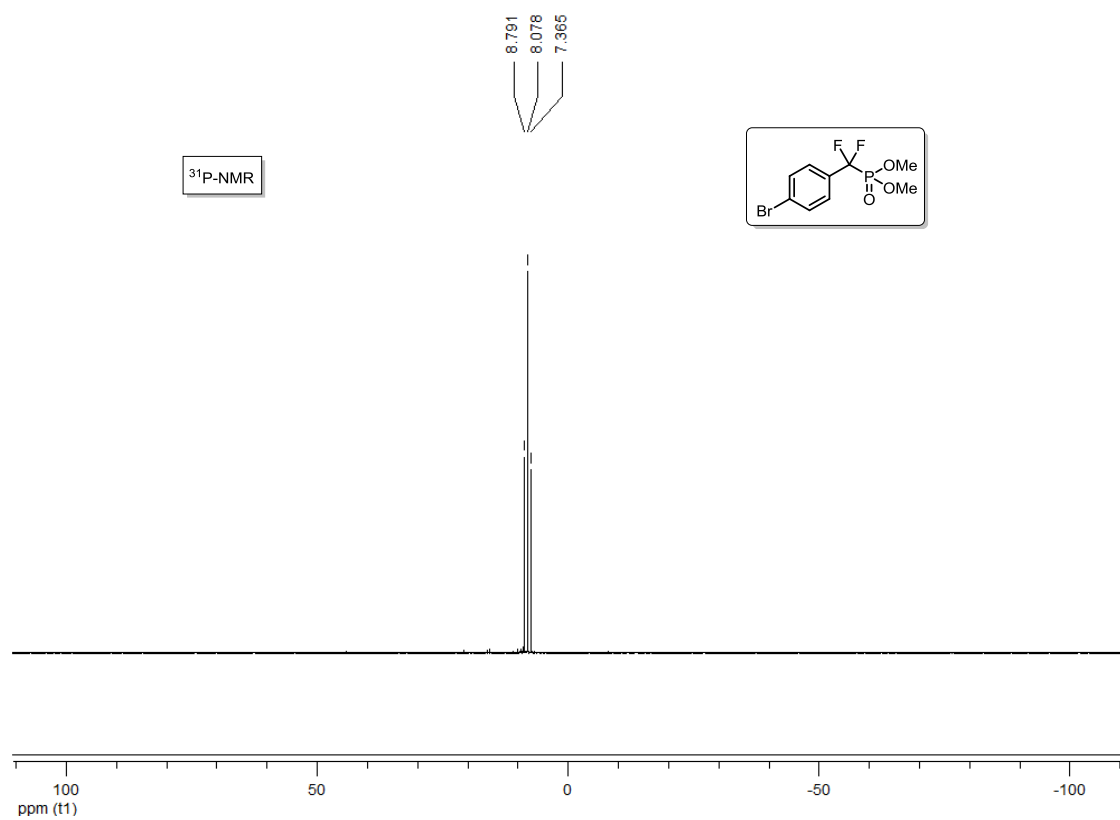
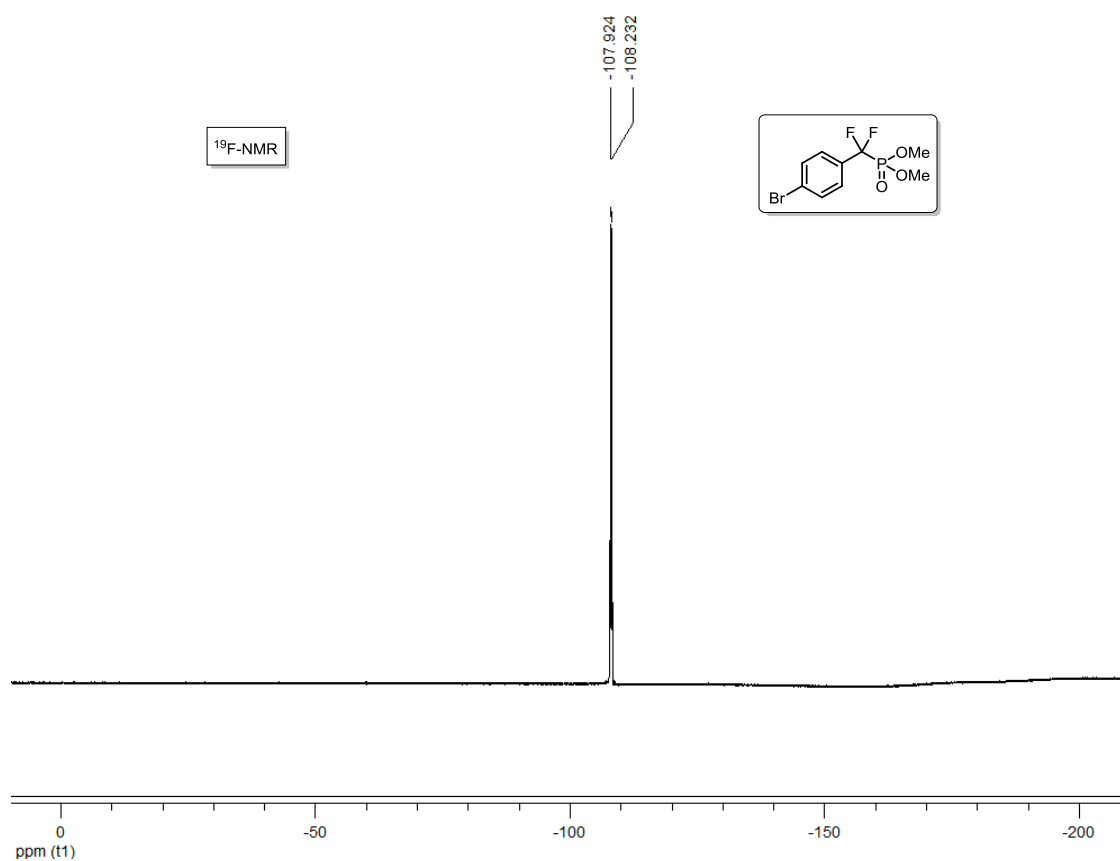
Dimethyl ((4-chlorophenyl)difluoromethyl)phosphonate (**3c**)





Dimethyl ((4-bromophenyl)difluoromethyl)phosphonate (**3d**)

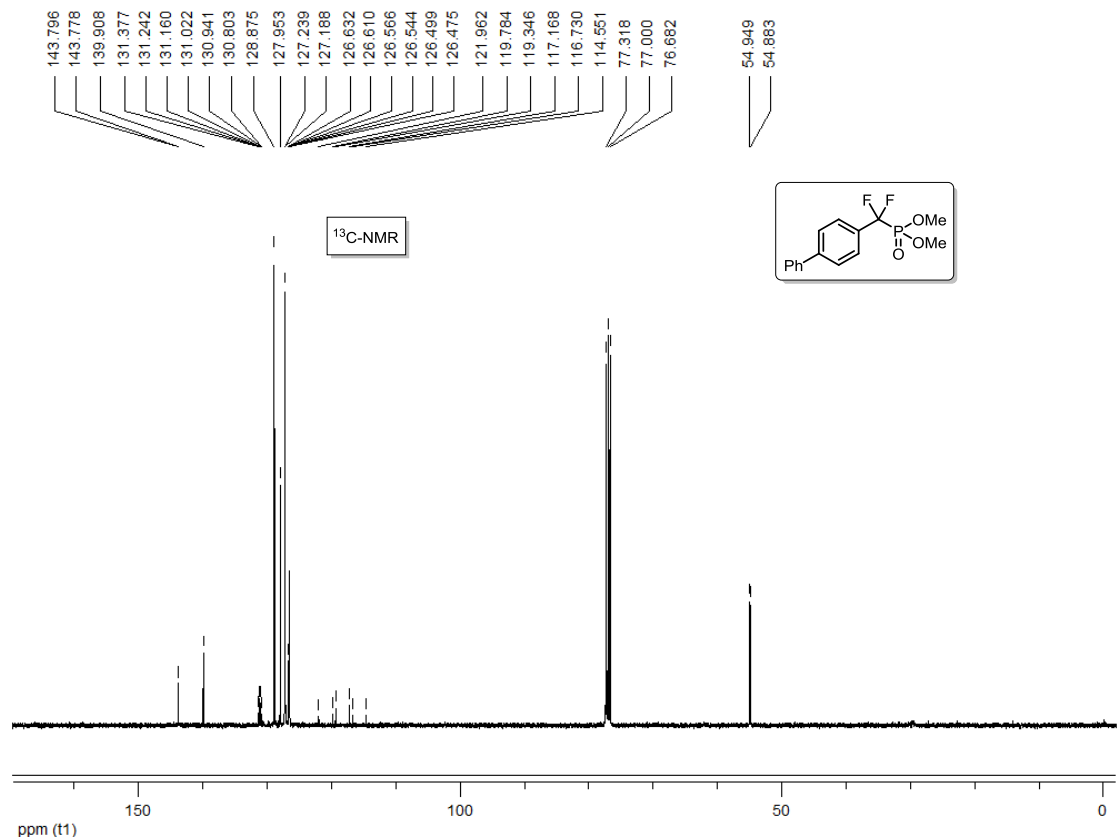


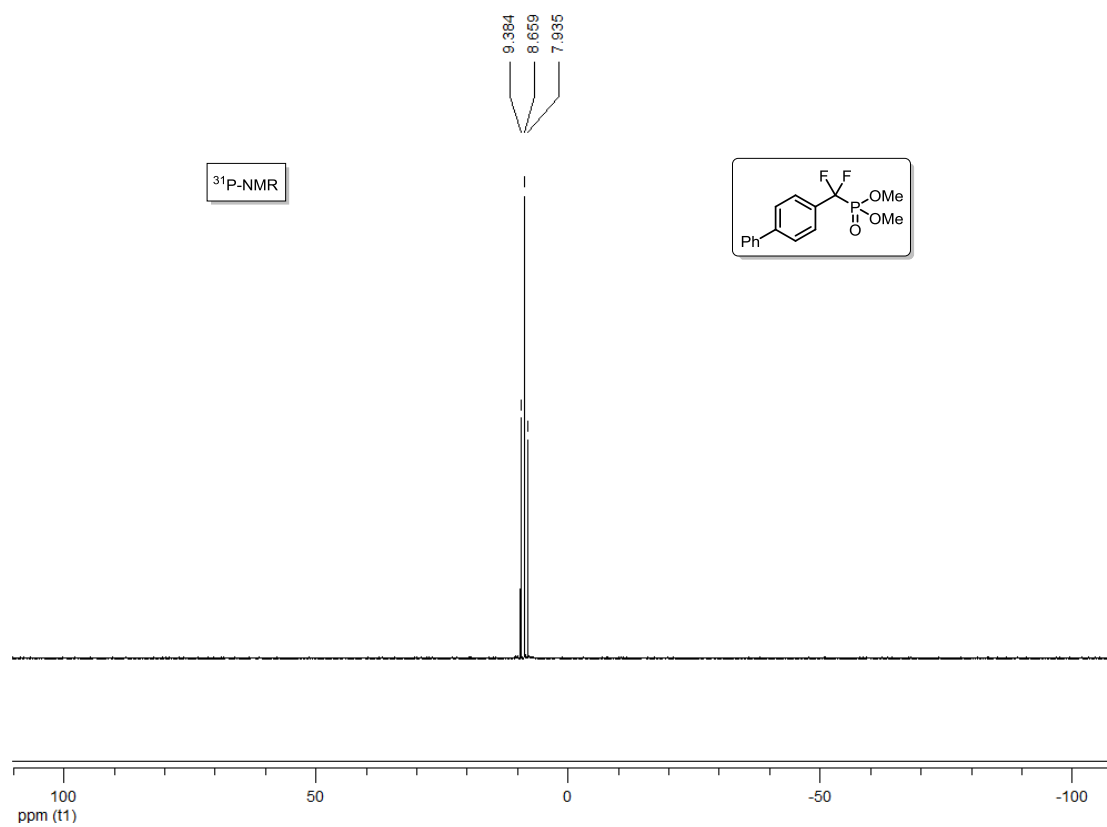
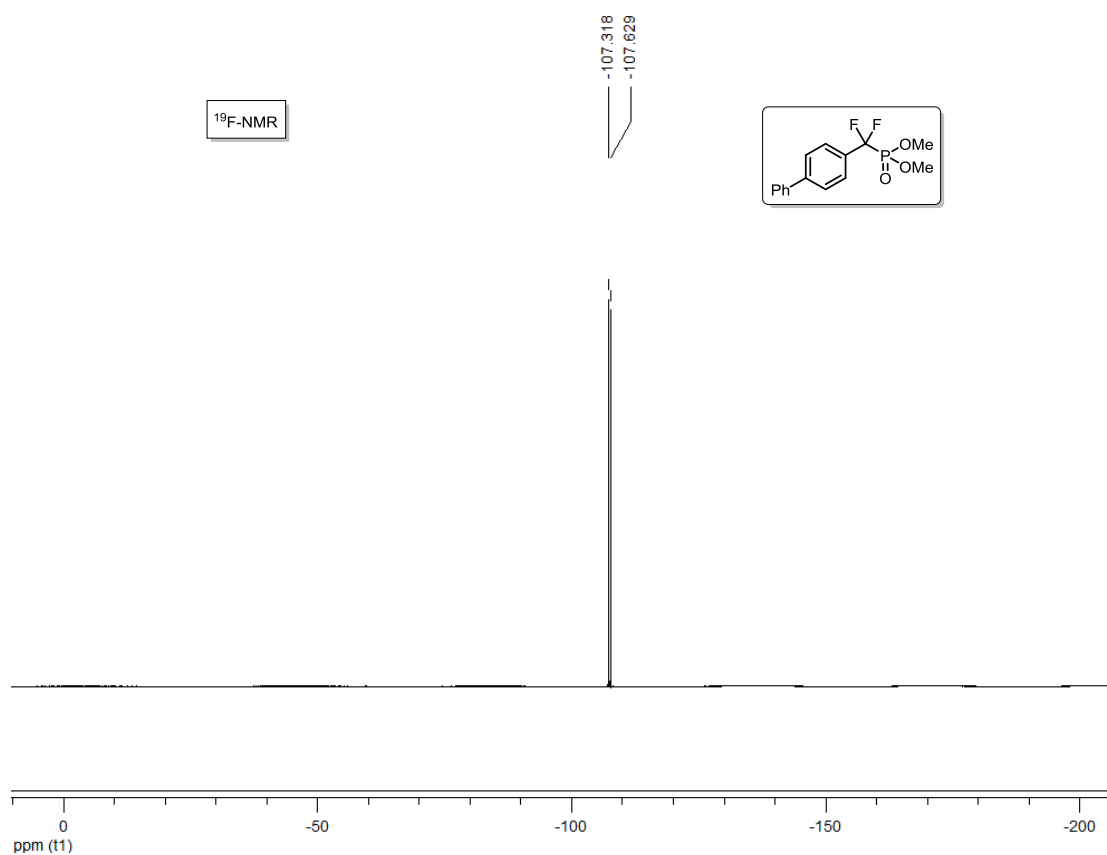


¹H-NMR

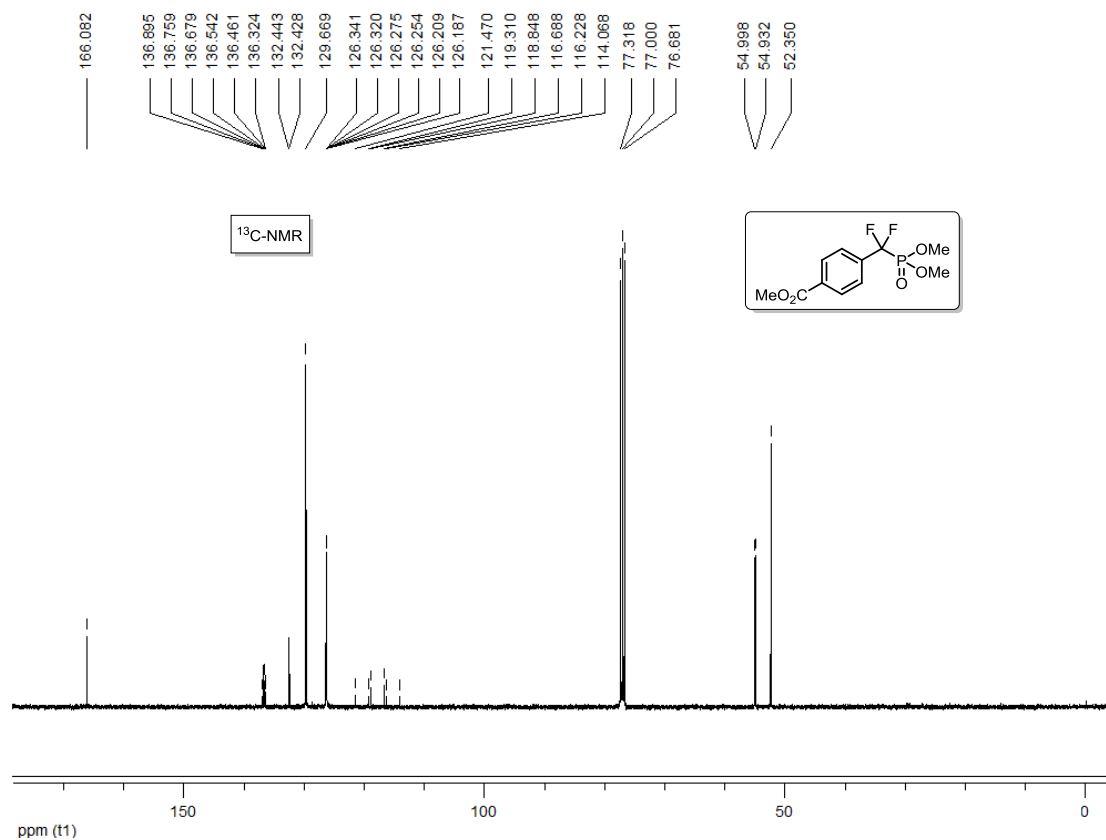
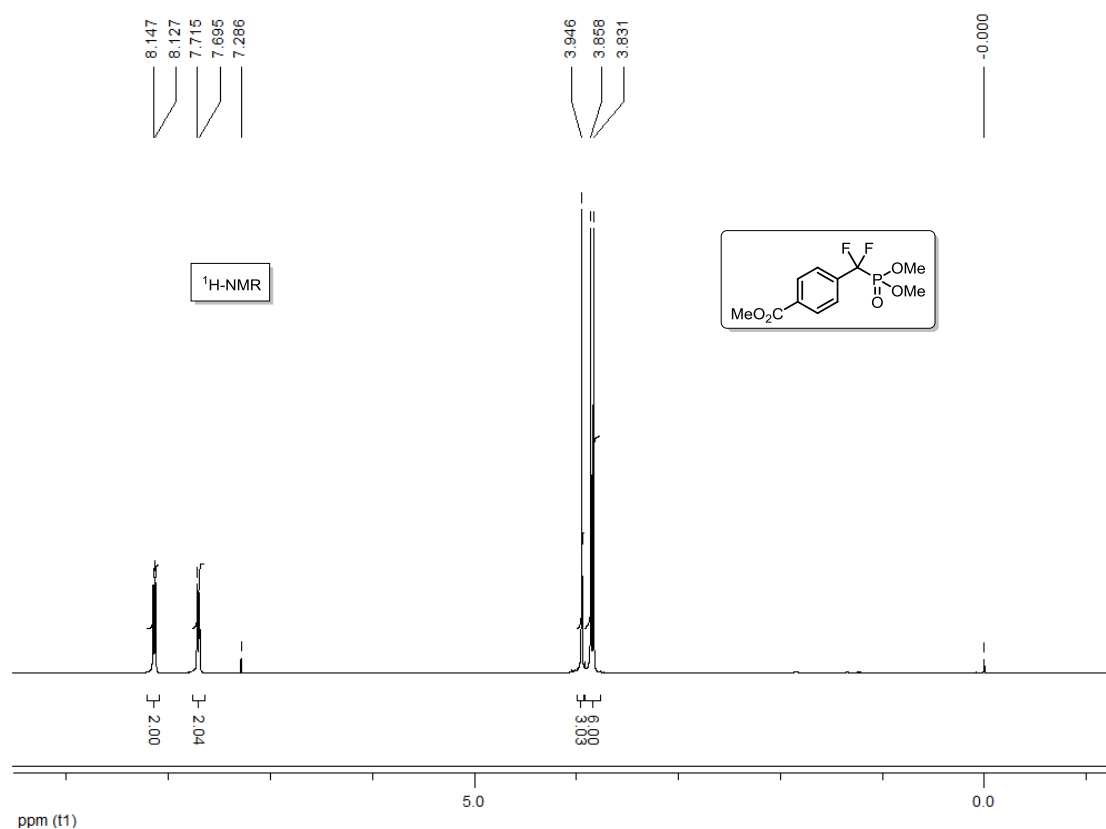
Chemical structure: COOP(=O)(OC)C(F)(F)c1ccc(Sc2ccccc2)cc1

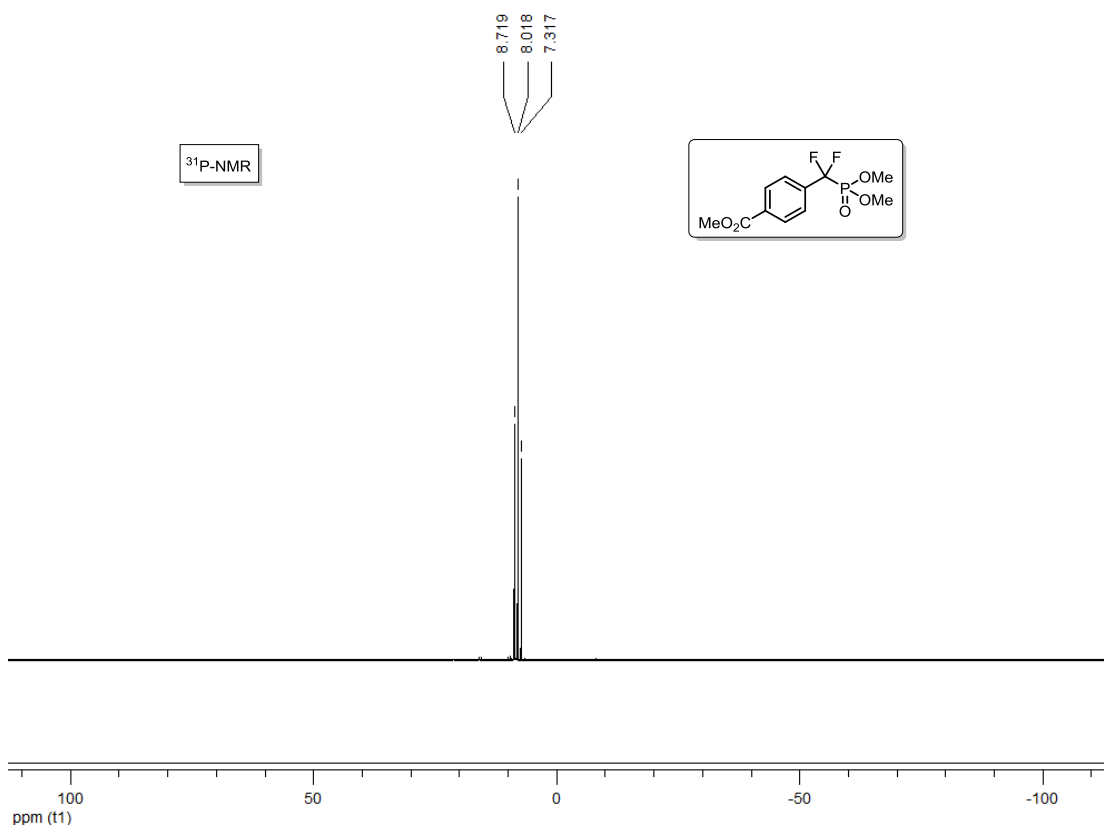
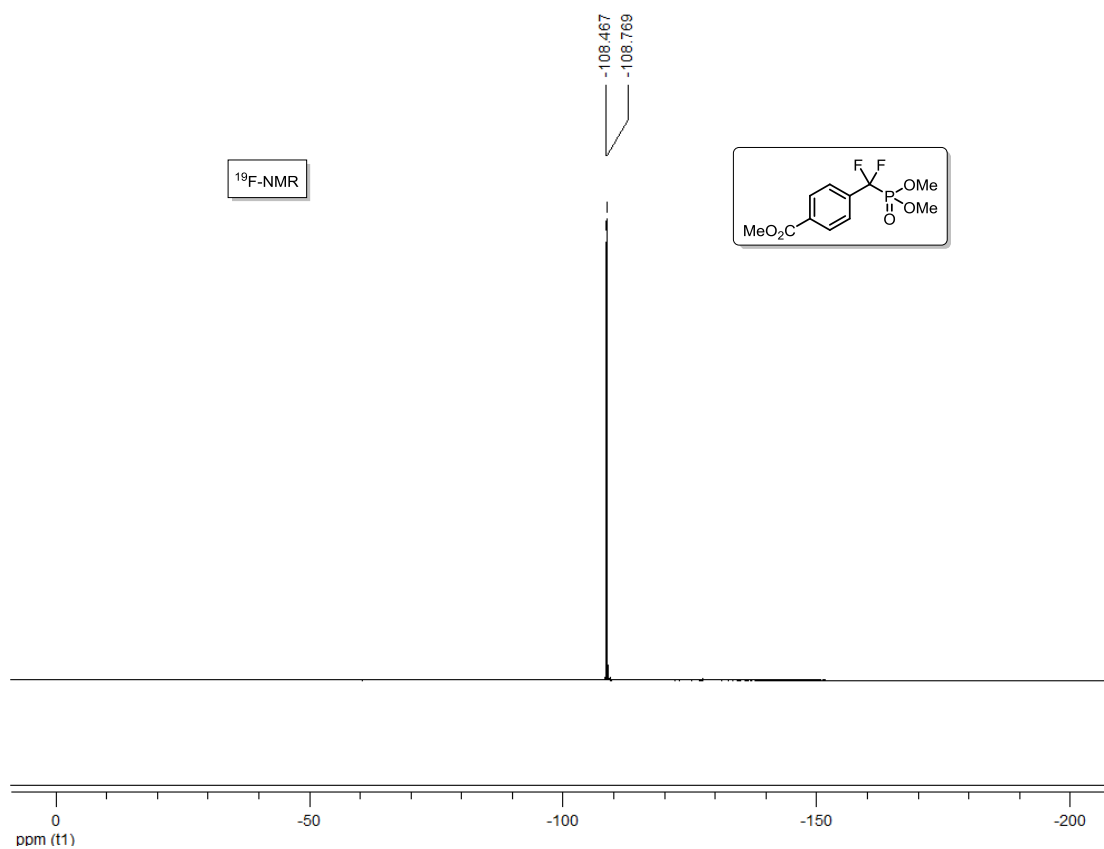
Chemical Shift (ppm)	Integration
7.708, 7.686, 7.665, 7.607, 7.589, 7.477, 7.458, 7.439, 7.401, 7.383, 7.364, 7.254	4.01, 1.09, 2.09, 2.91
3.870, 3.844	6.00
0.000	-



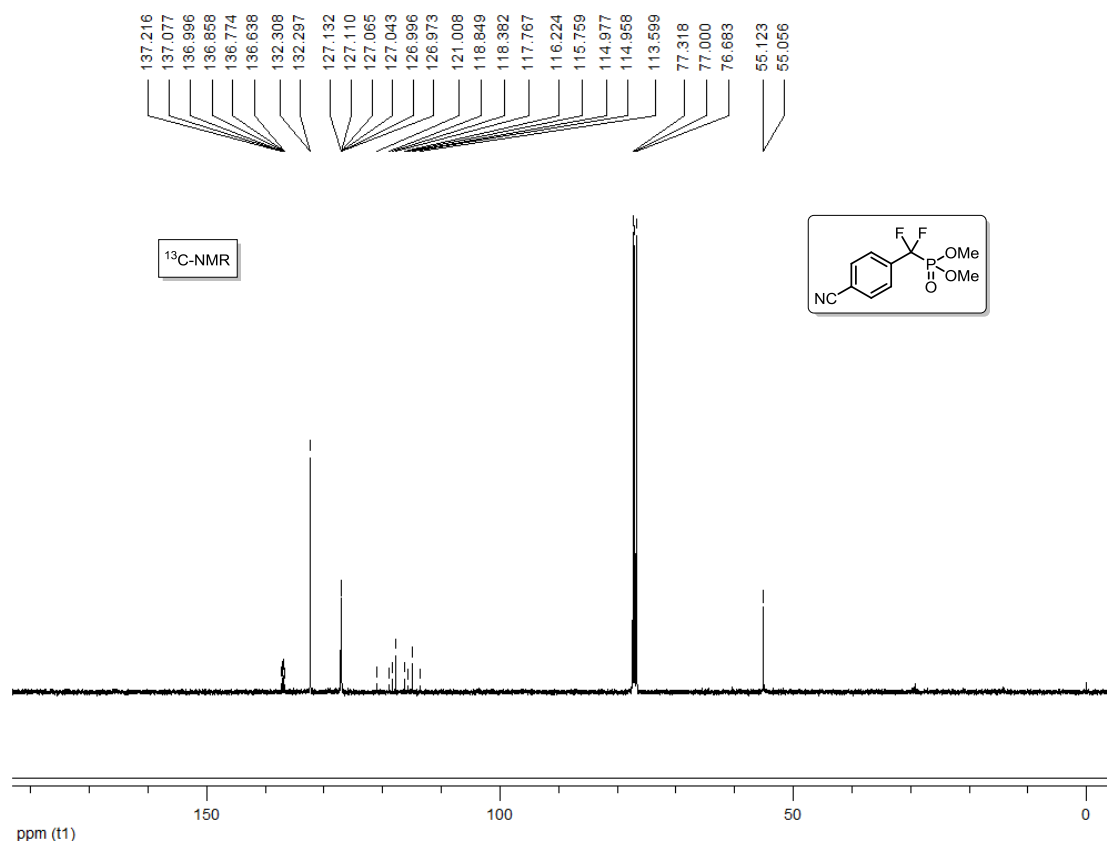
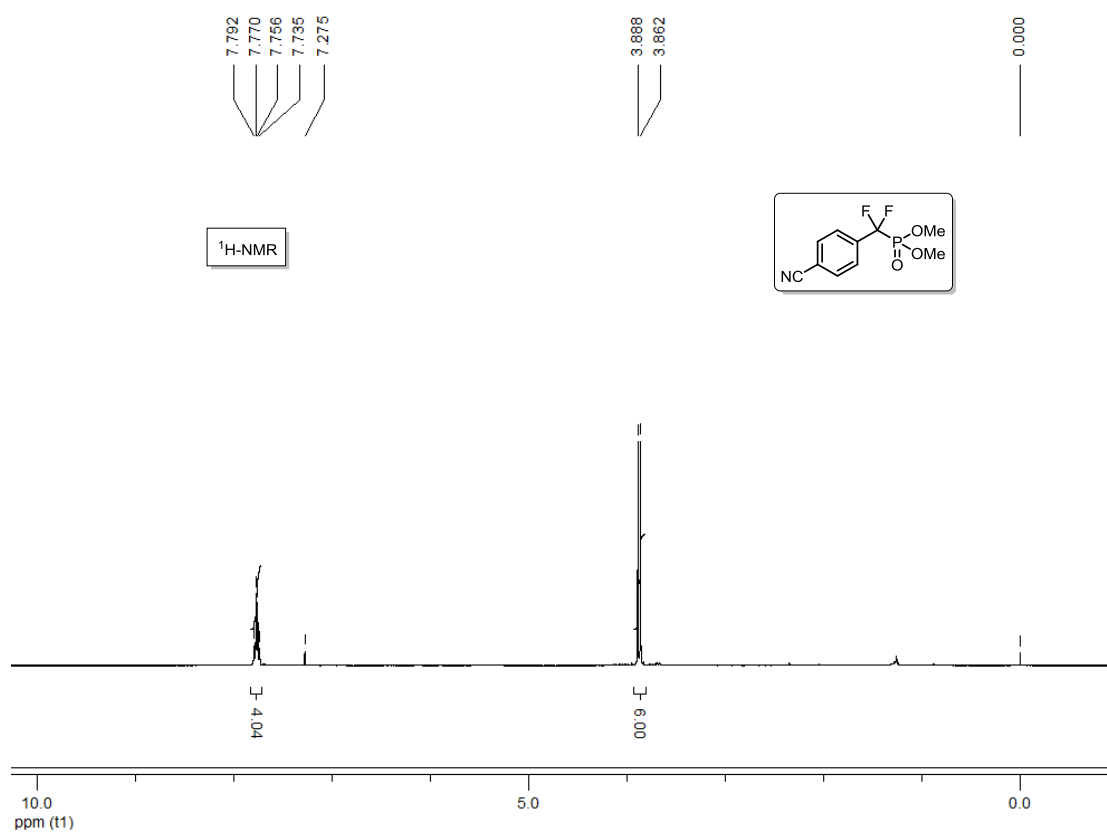


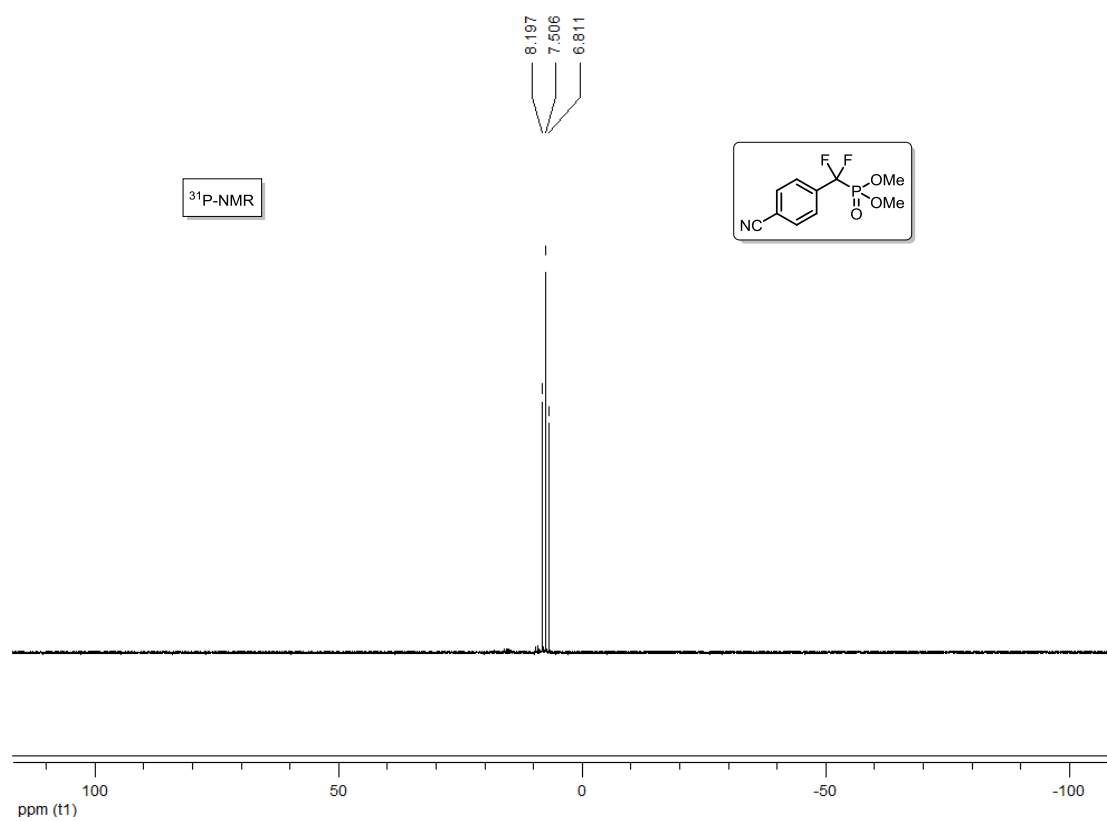
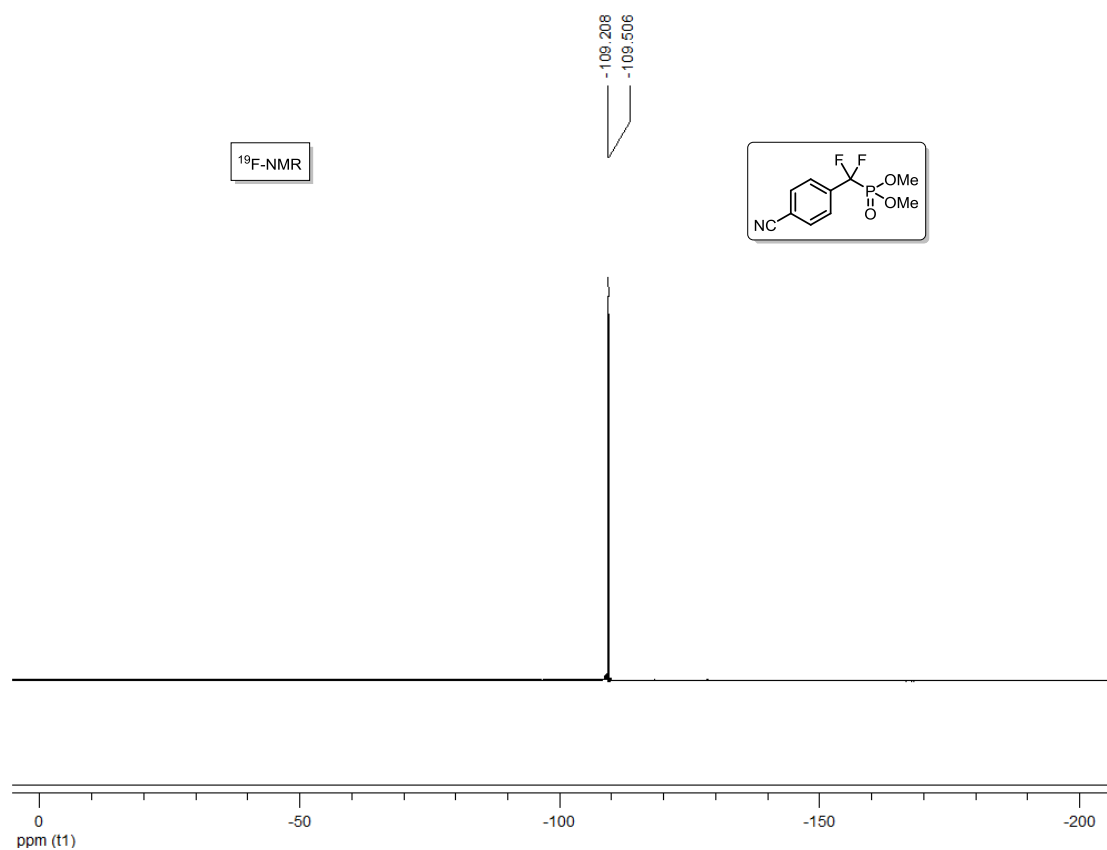
Methyl 4-((dimethoxyphosphoryl)difluoromethyl)benzoate (**3f**)



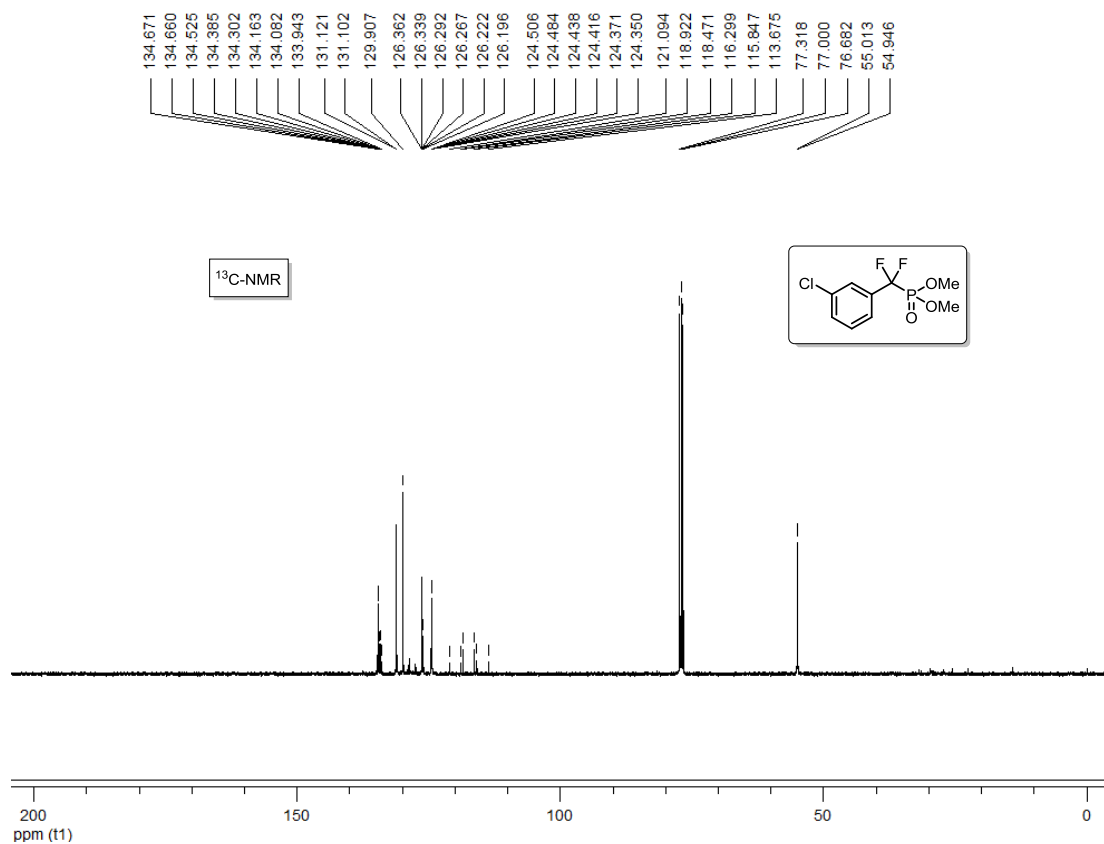
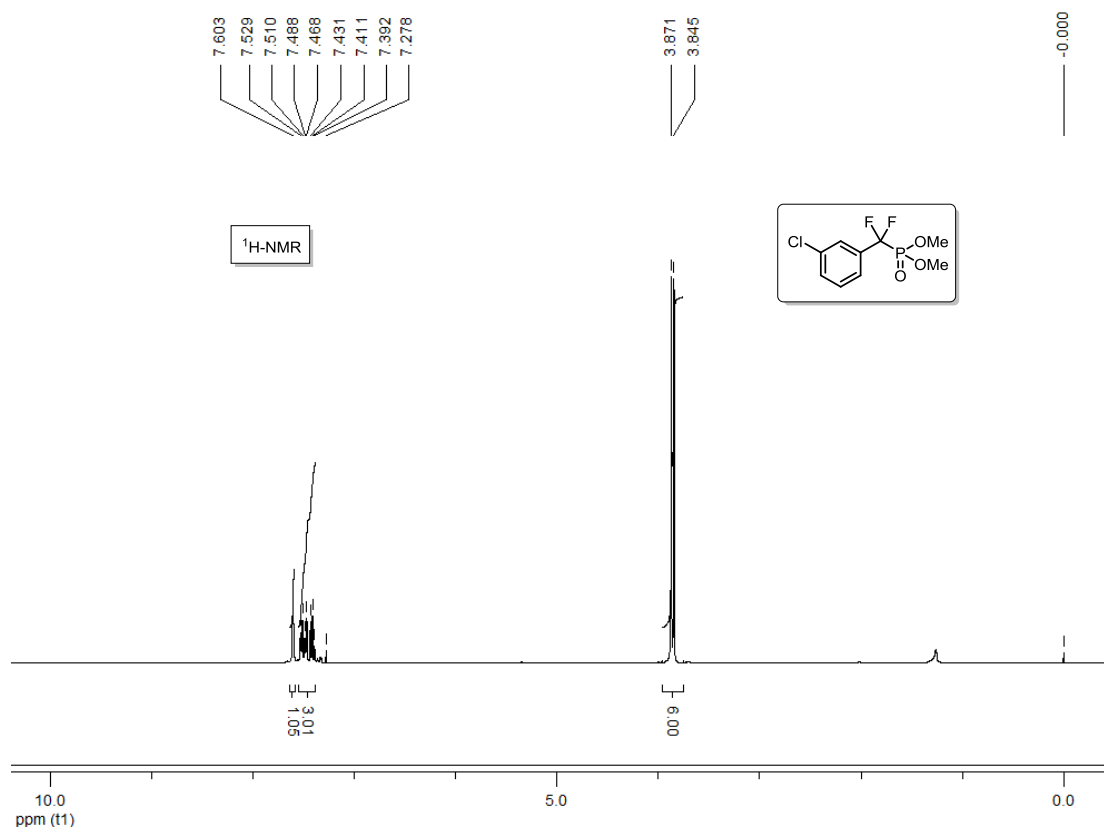


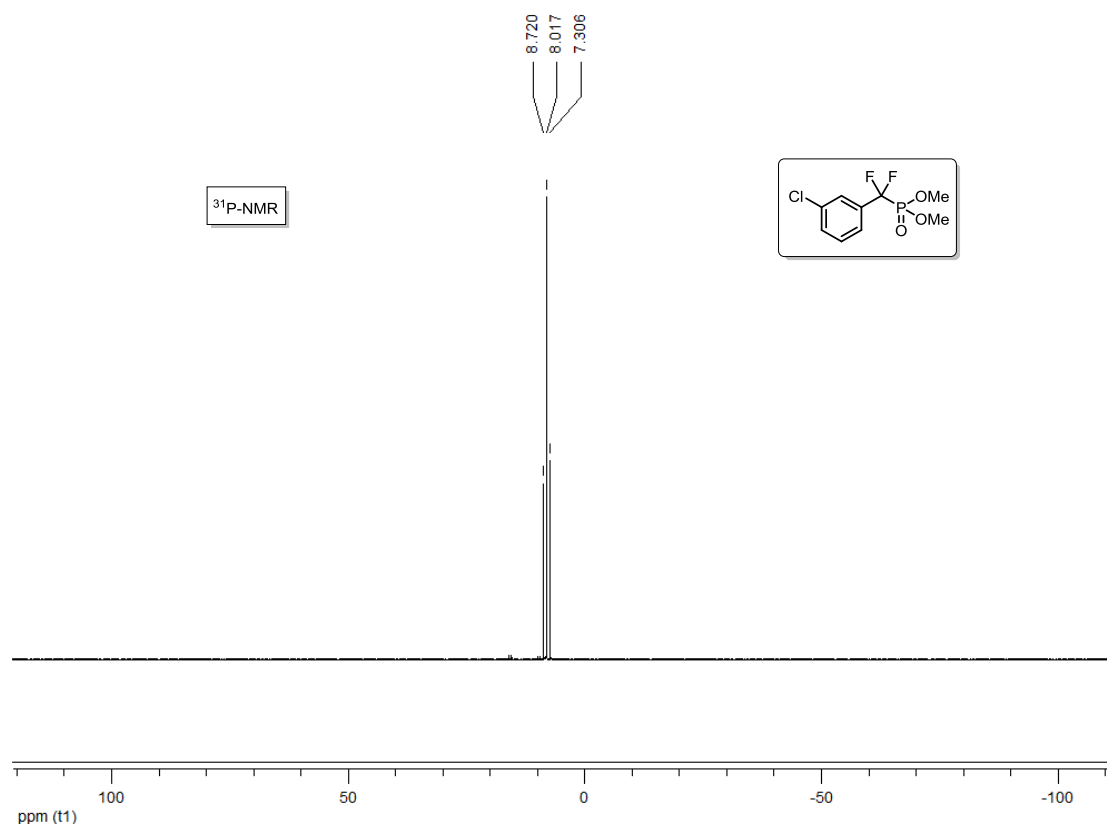
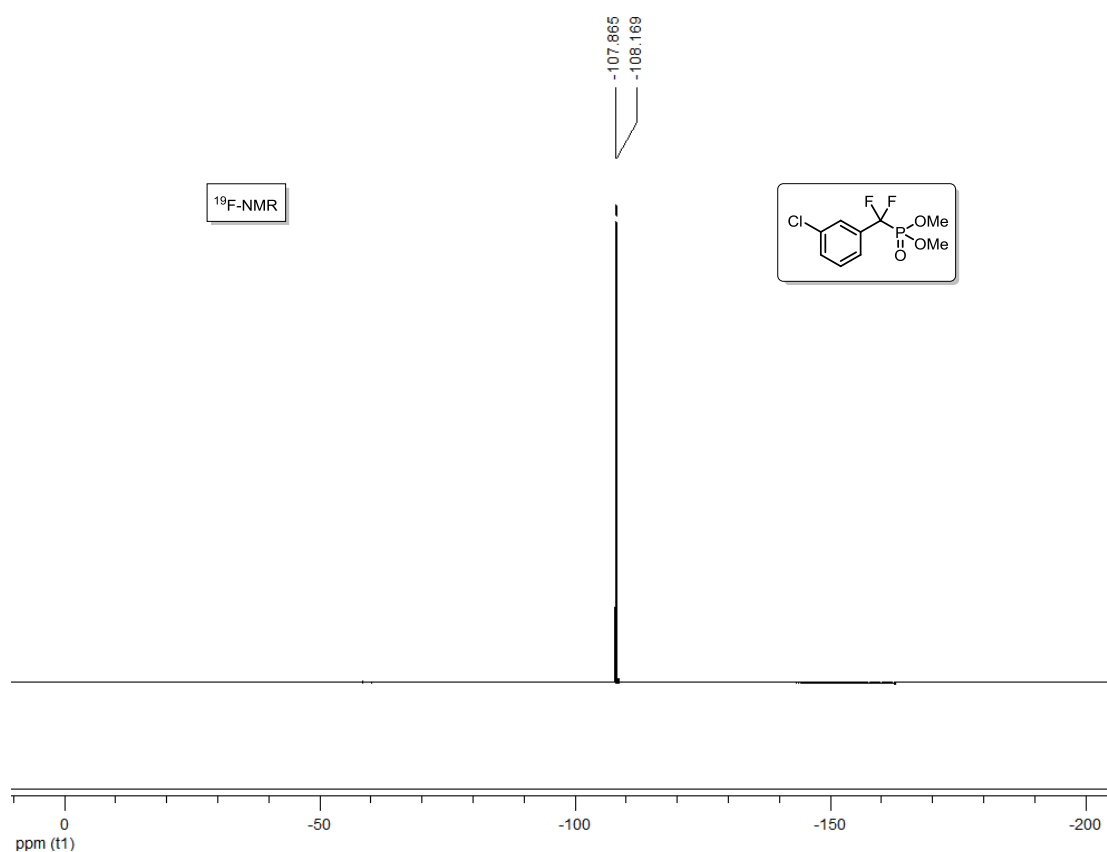
Dimethyl ((4-cyanophenyl)difluoromethyl)phosphonate (**3g**)





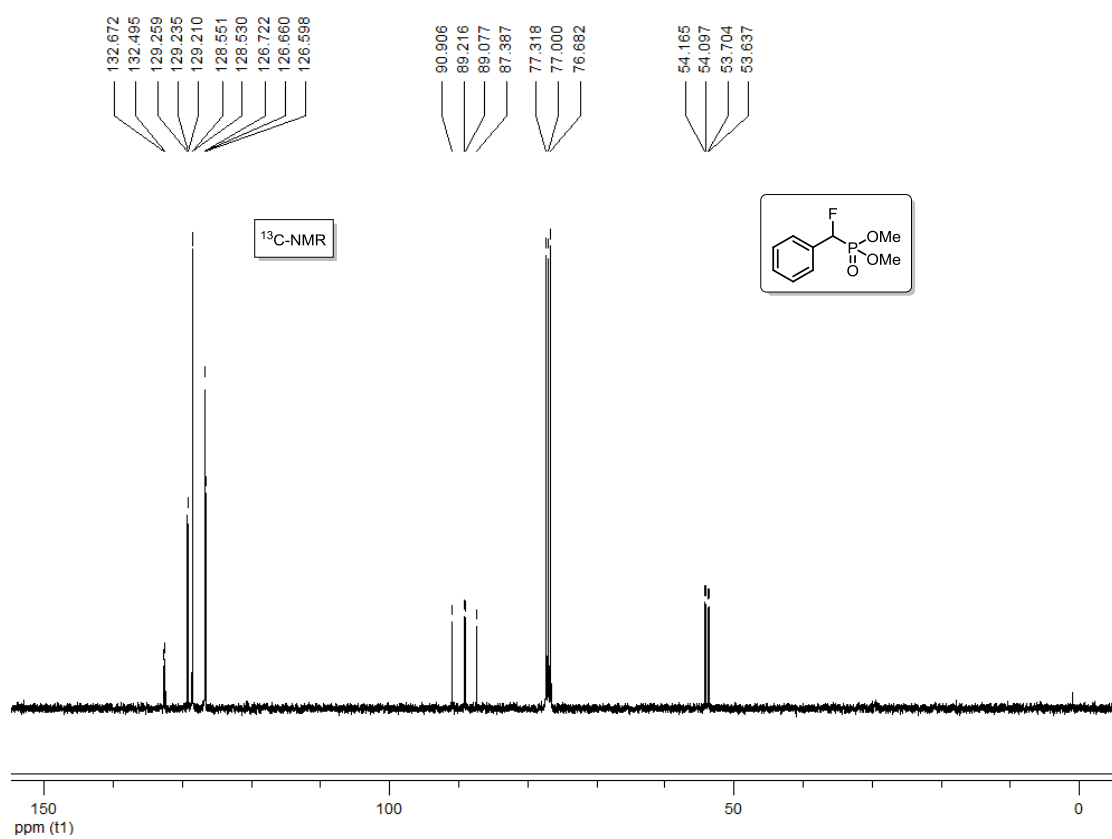
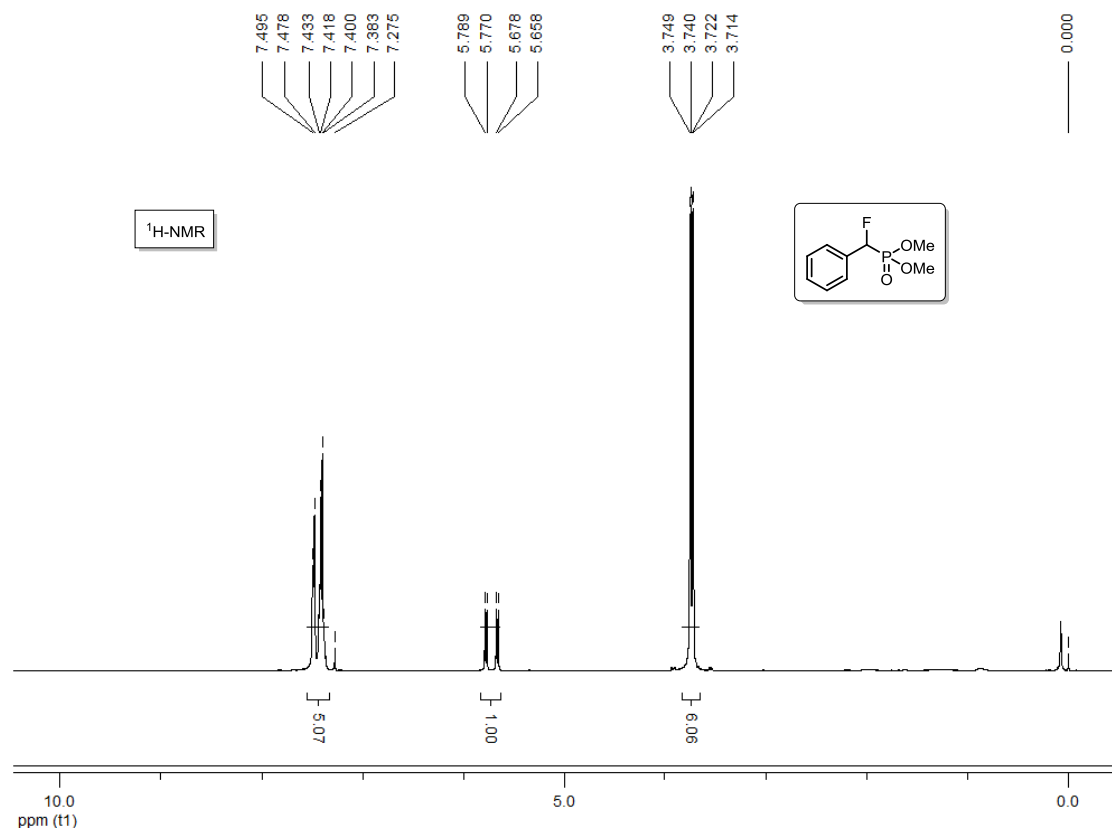
Dimethyl ((3-chlorophenyl)difluoromethyl)phosphonate (**3h**)

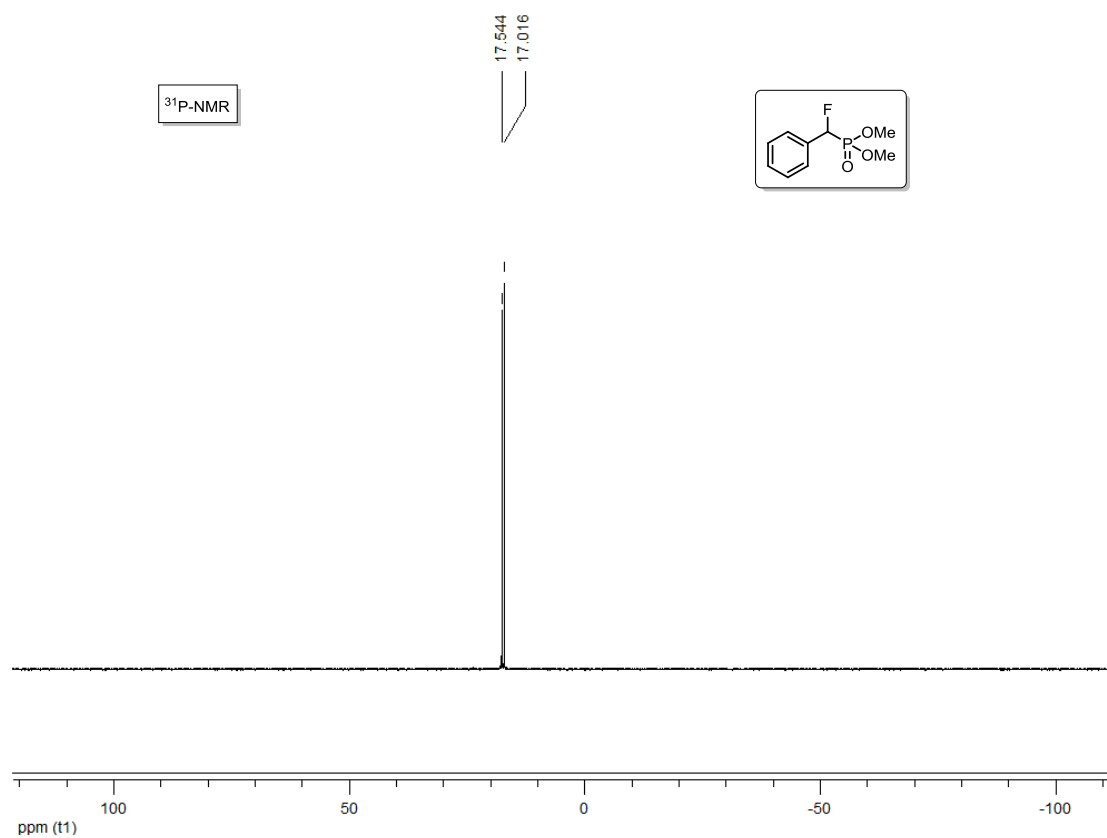
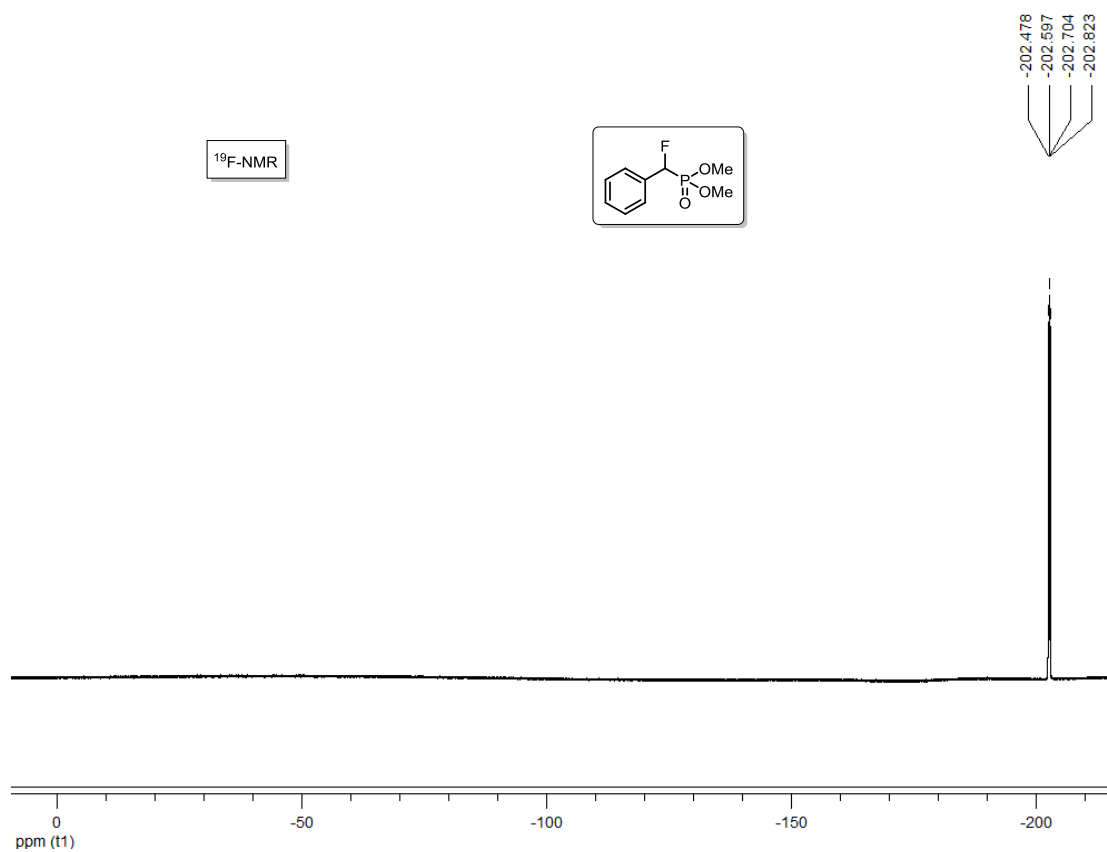




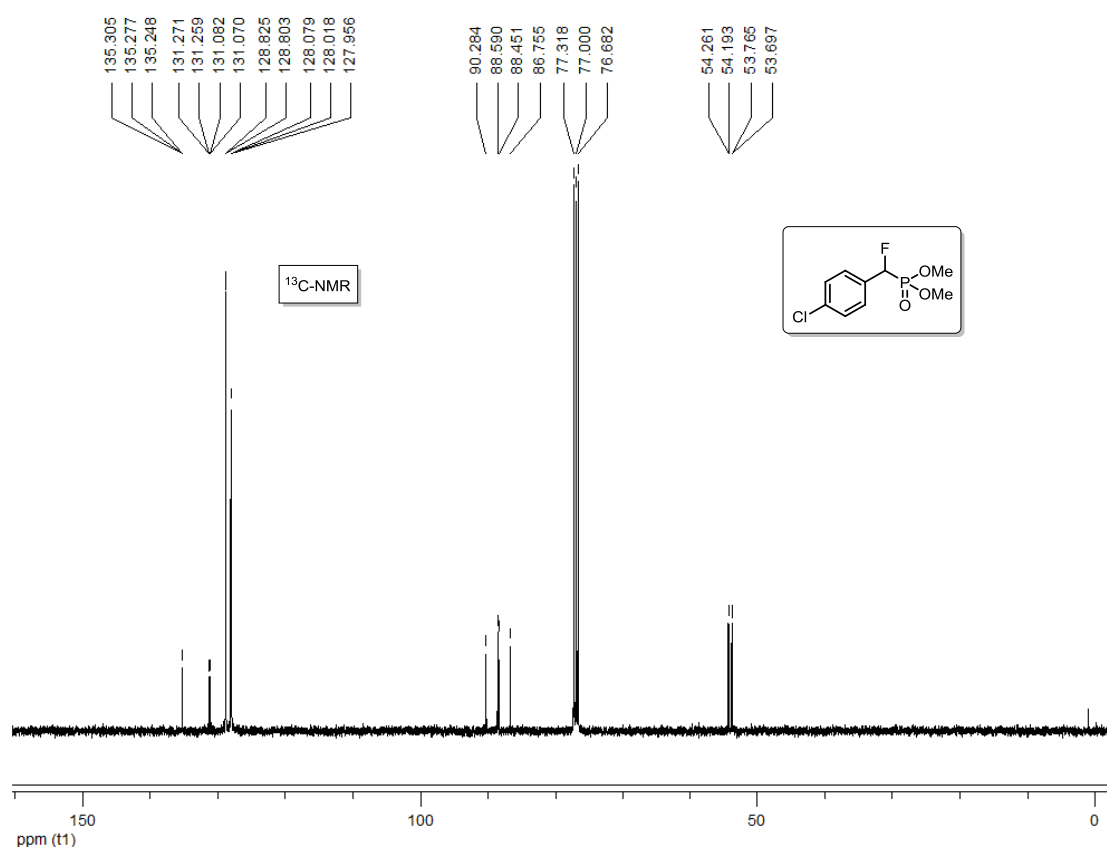
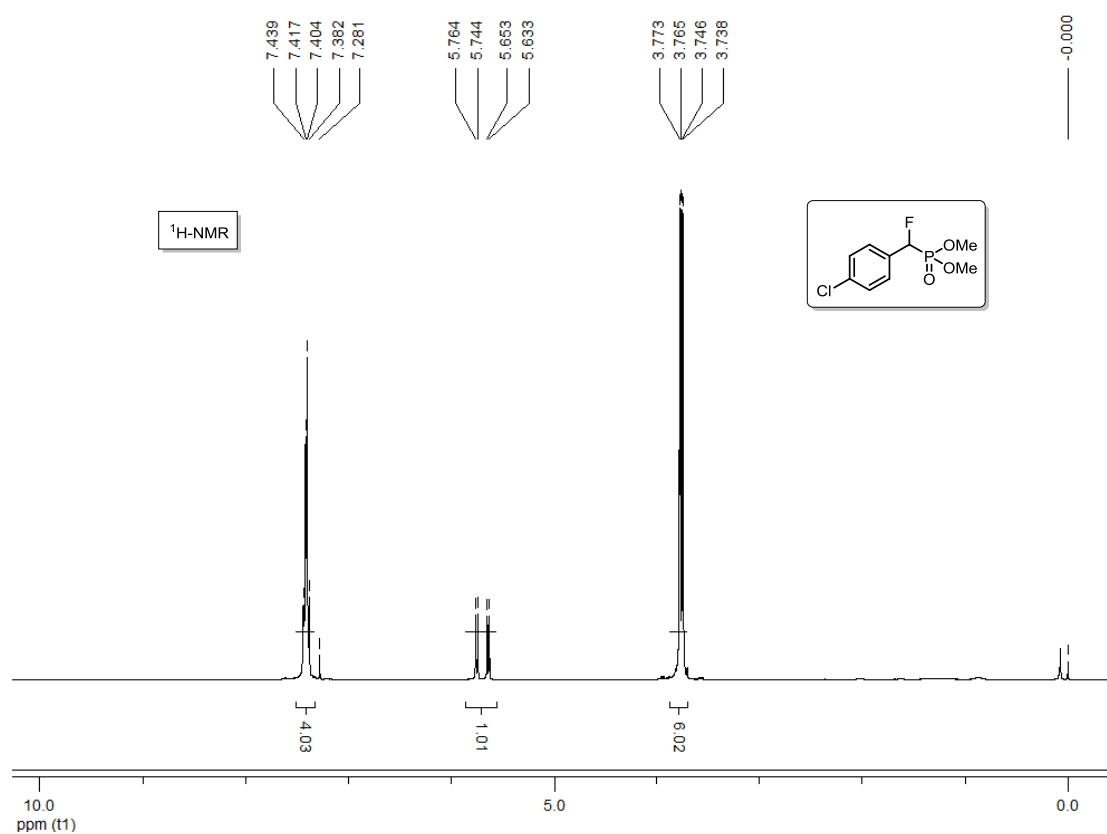
4. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra for the products 4a-g

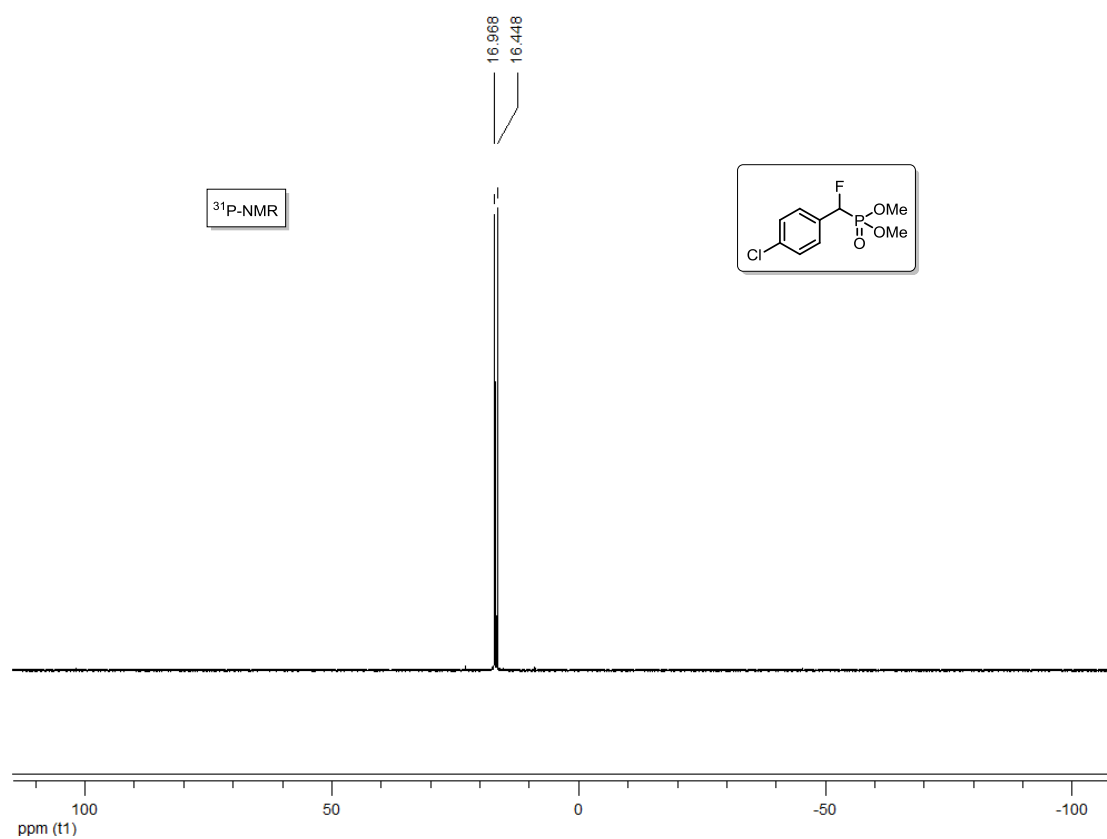
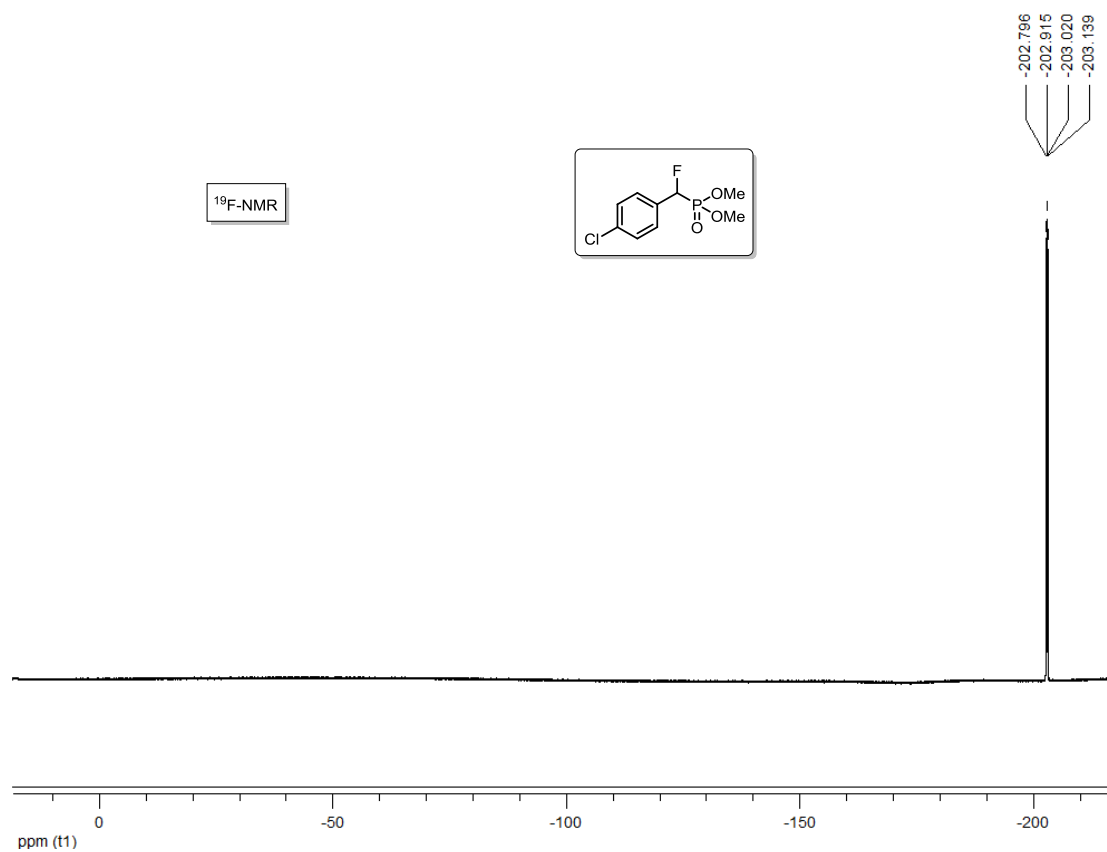
Dimethyl(fluoro(phenyl)methyl)phosphonate (**4a**)



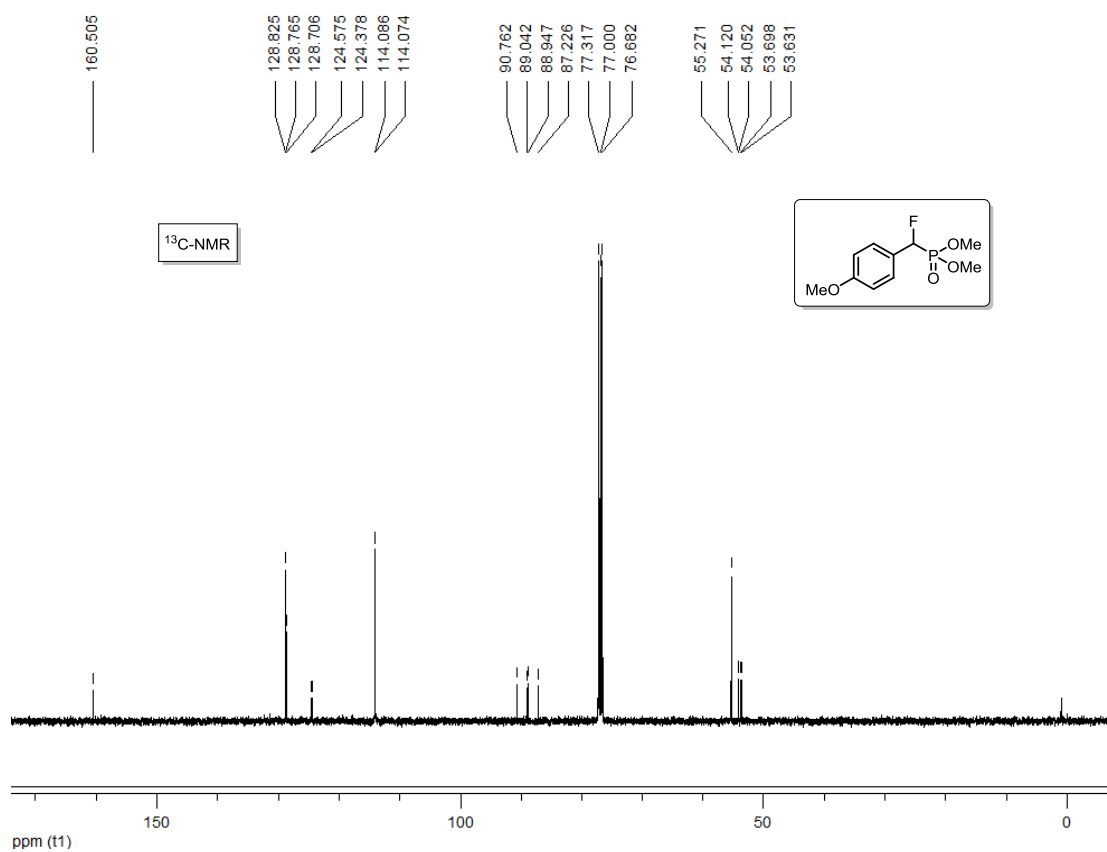
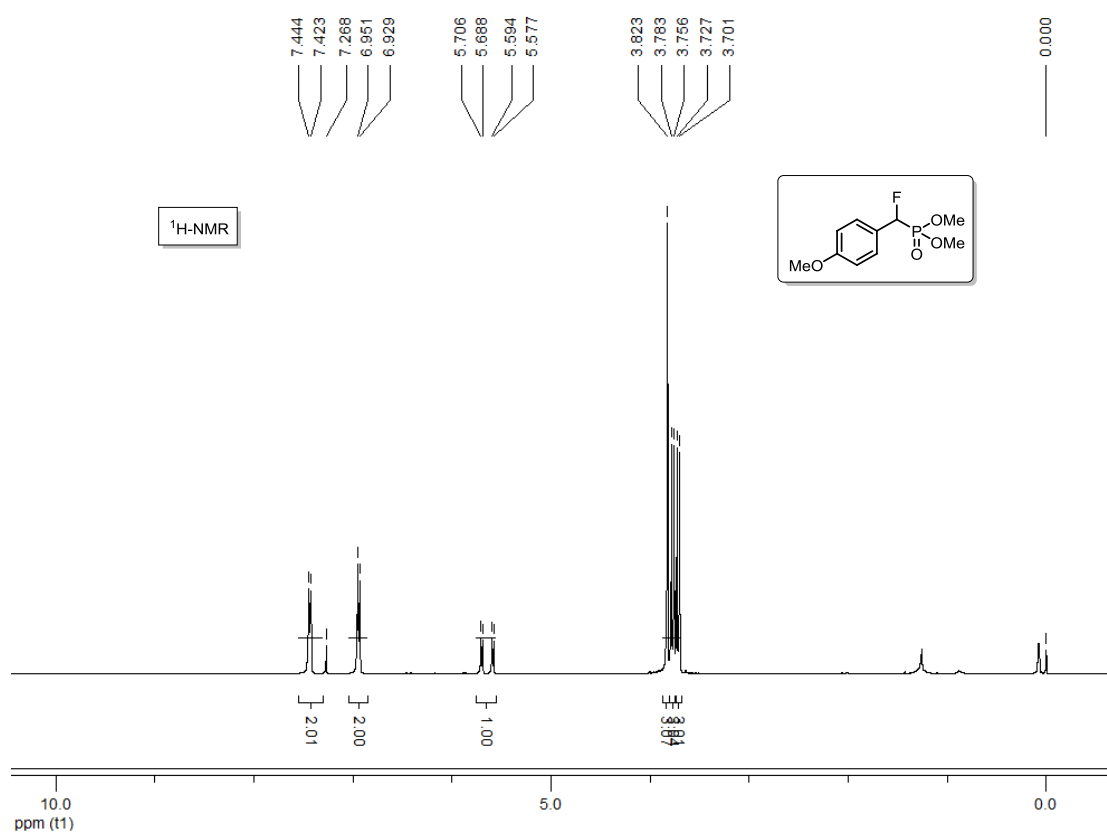


Dimethyl ((4-chlorophenyl)fluoromethyl)phosphonate (**4b**)

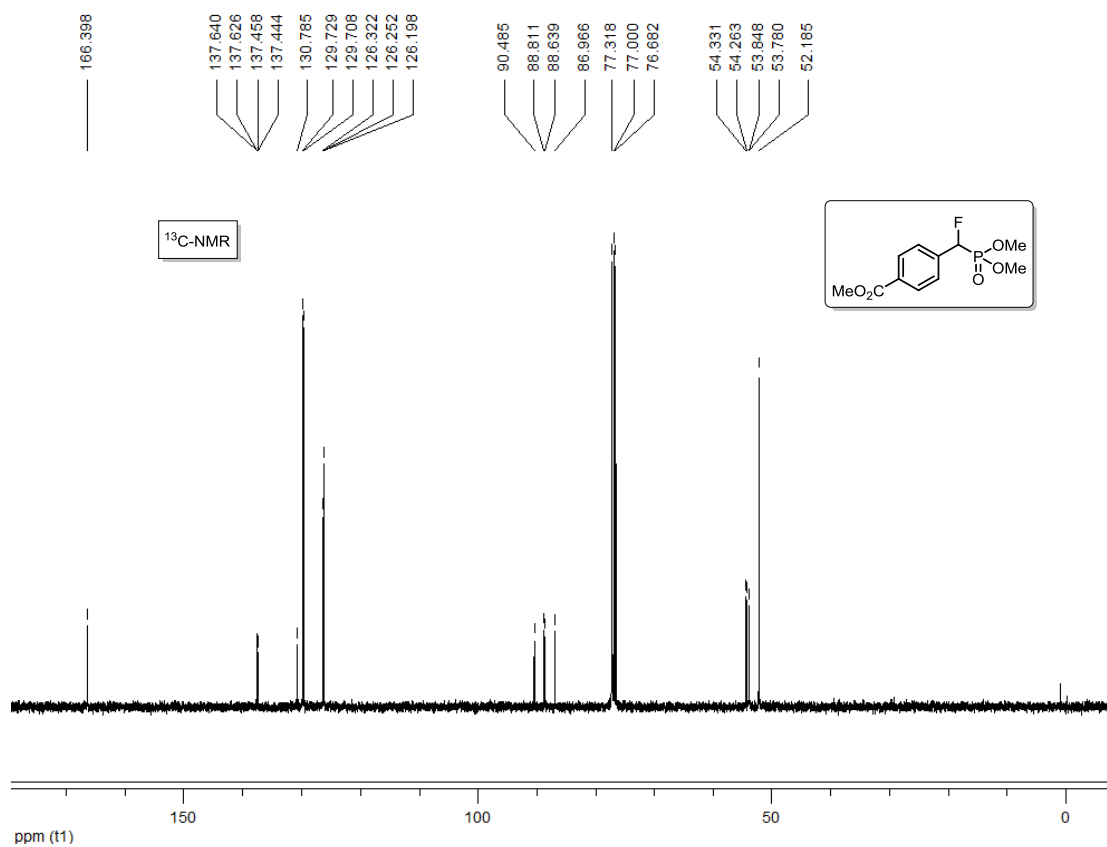
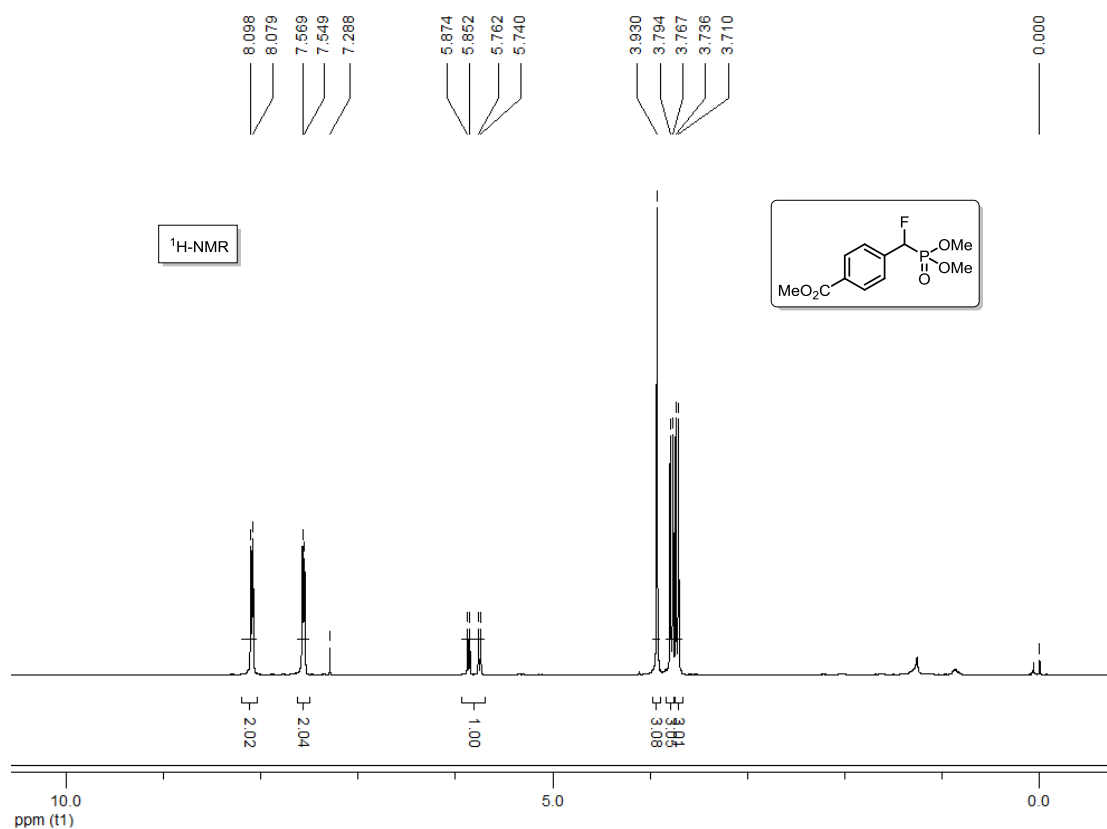


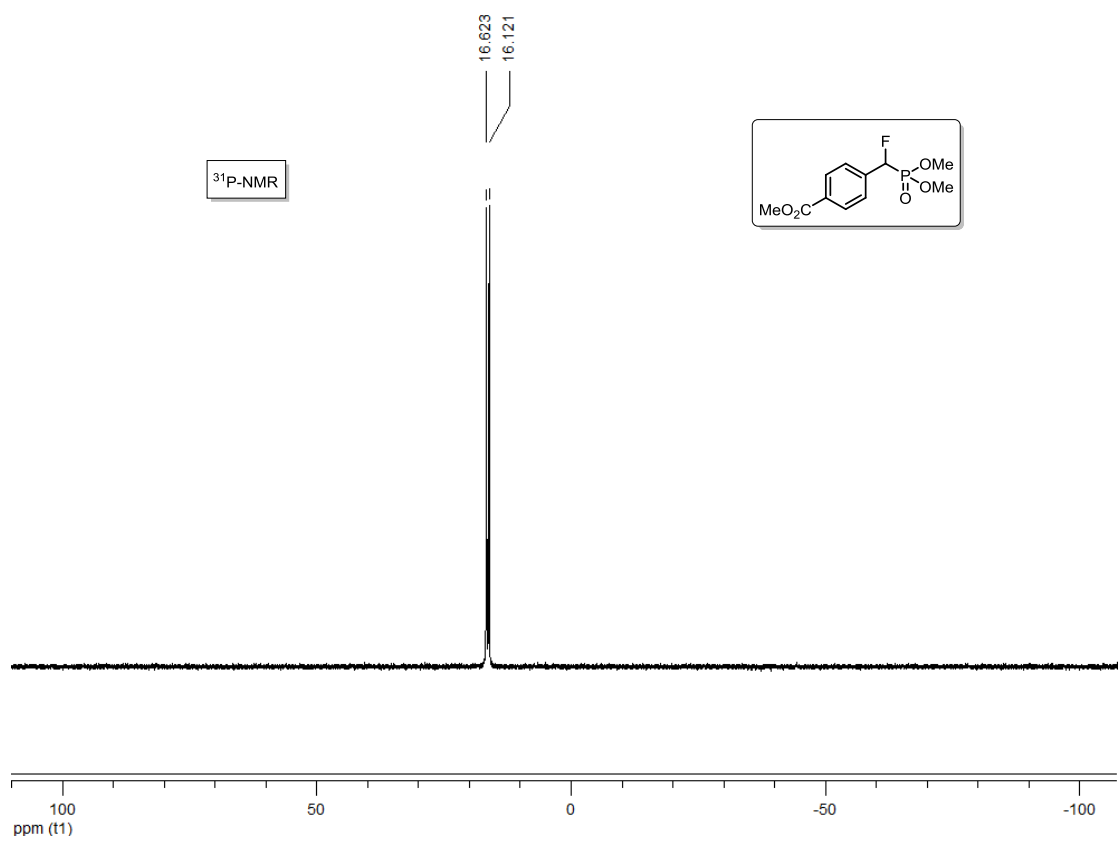
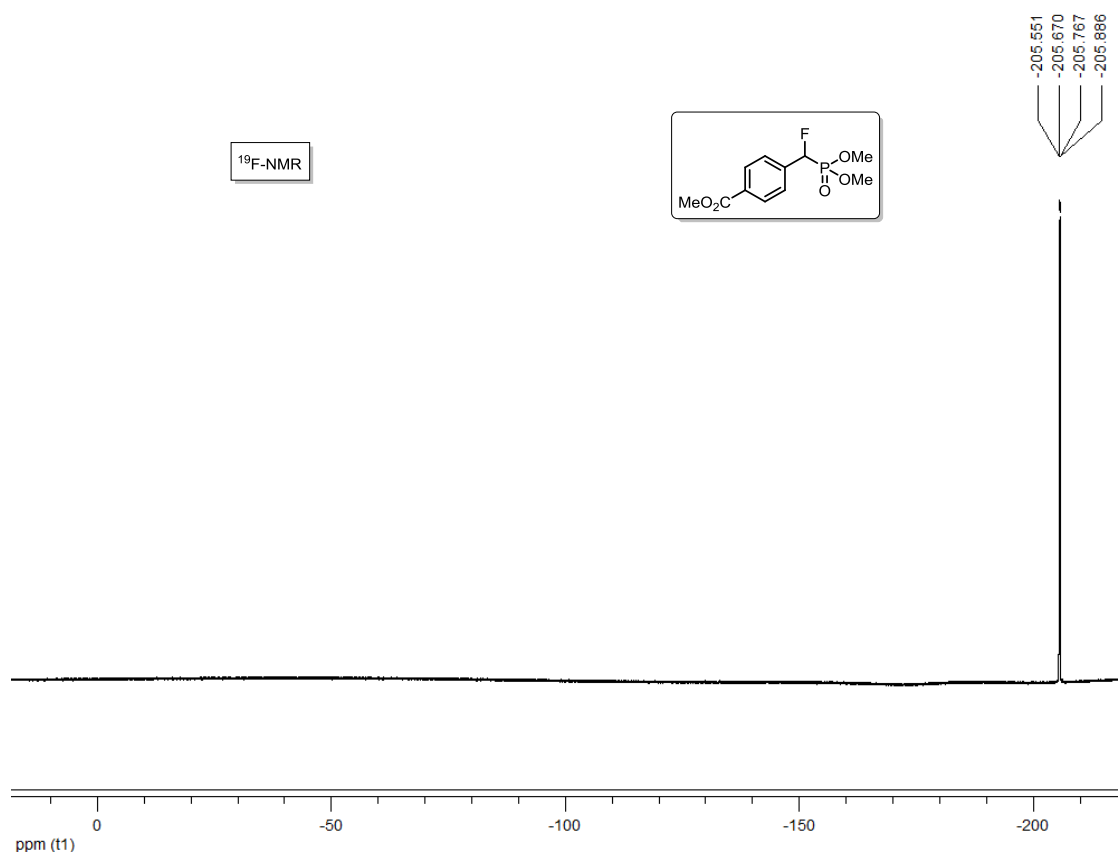


Dimethyl (fluoro(4-methoxyphenyl)methyl)phosphonate (**4c**)

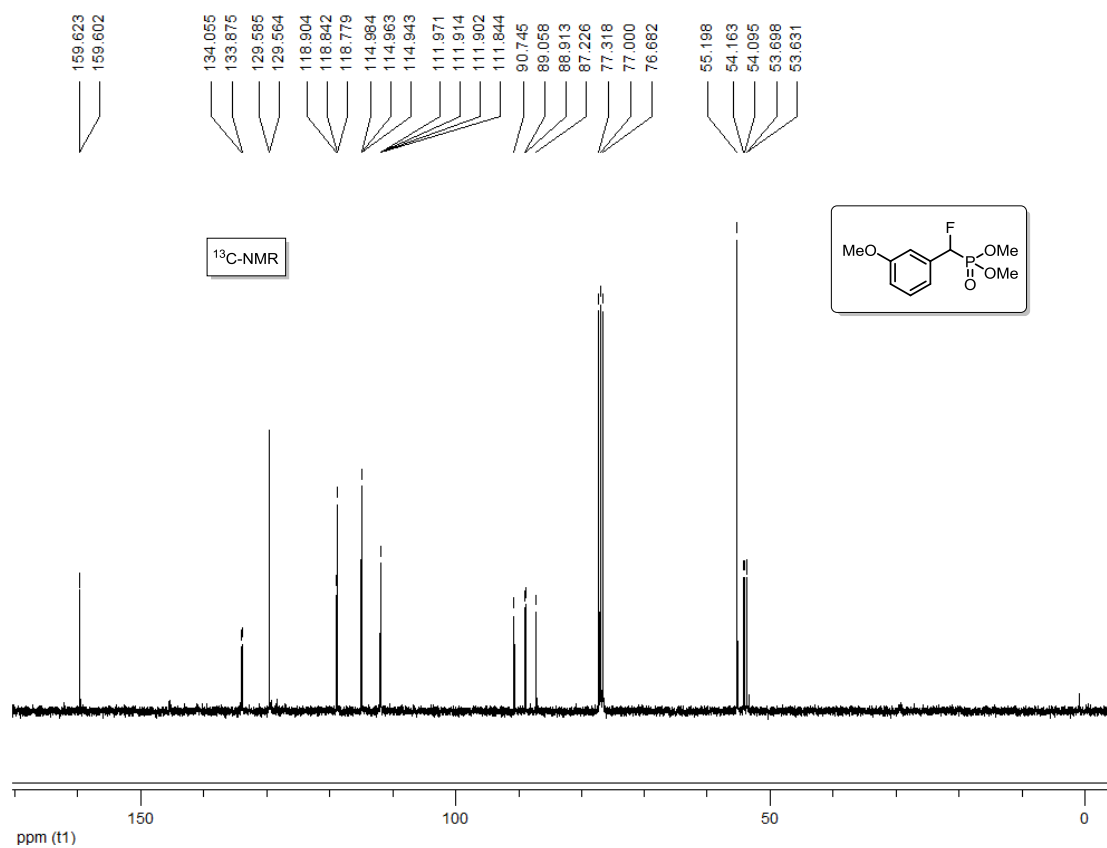
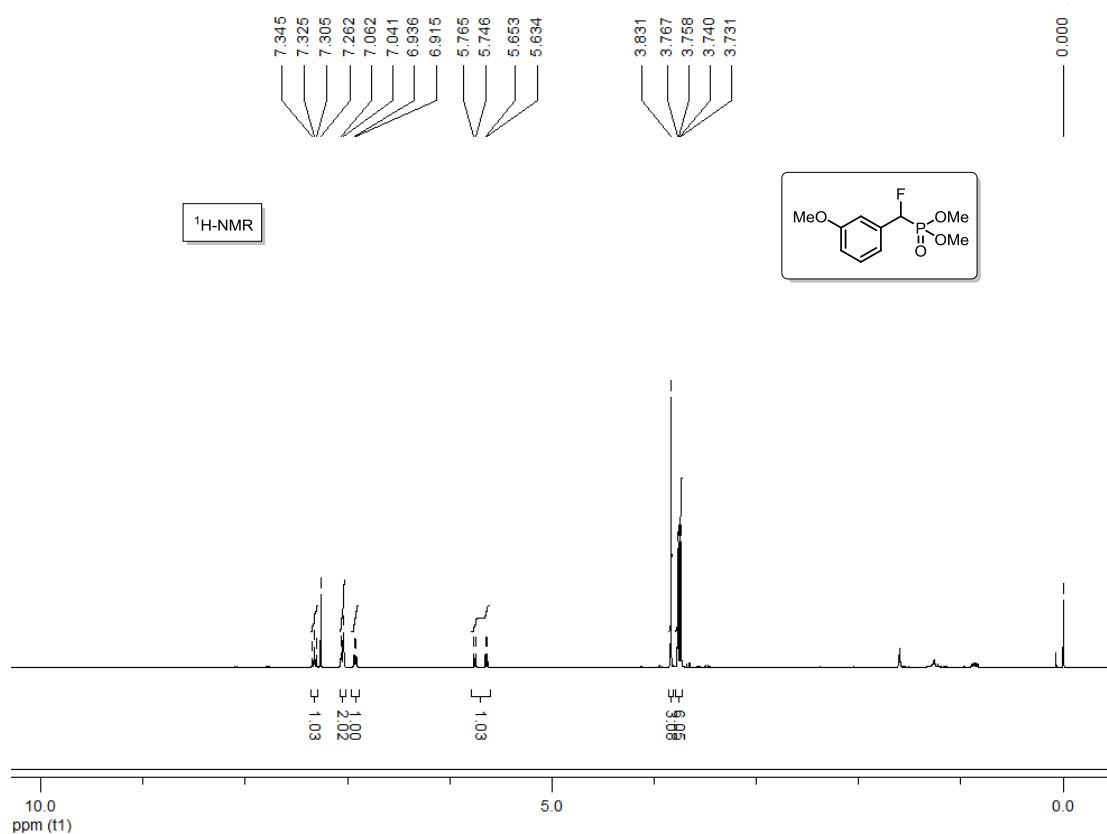


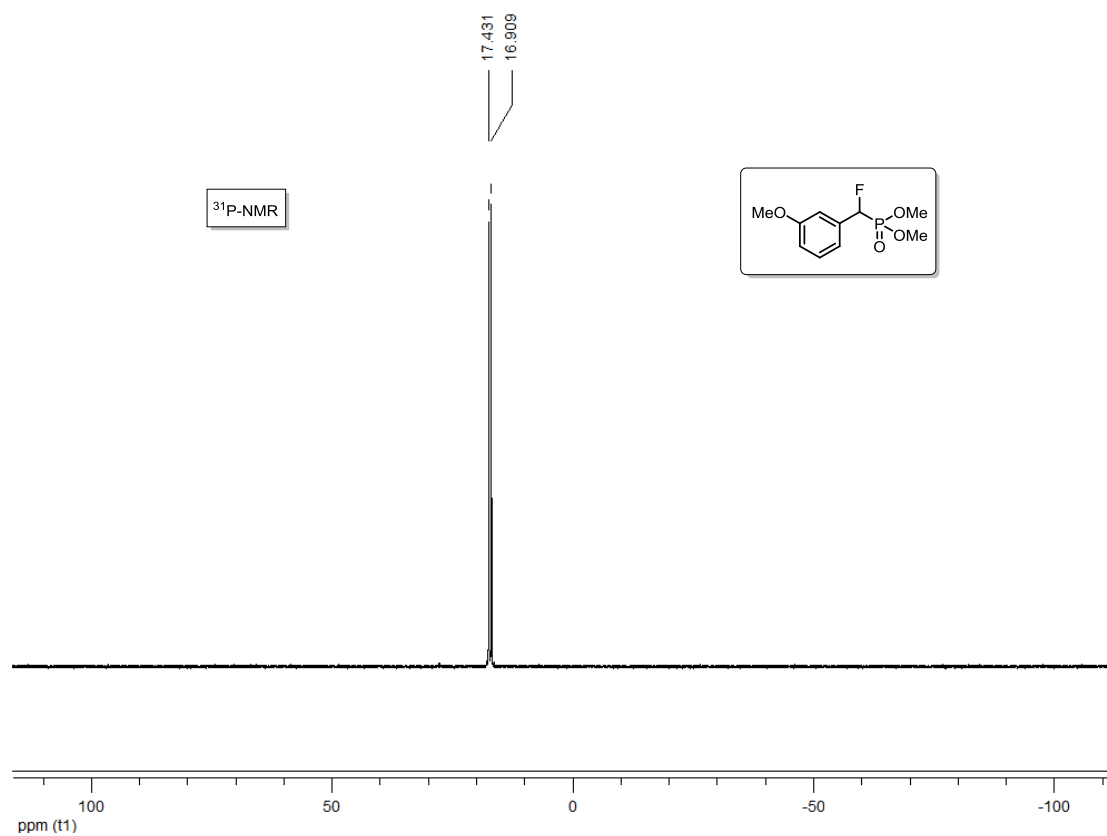
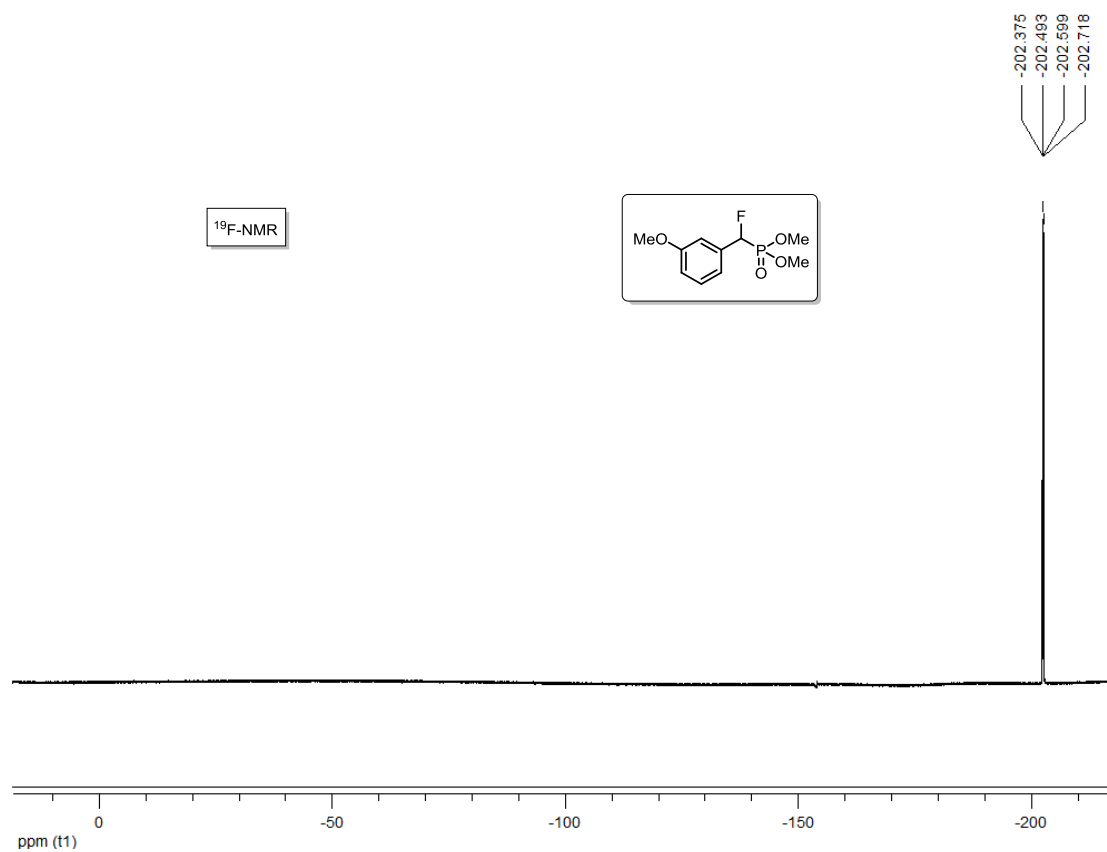
Methyl 4-((dimethoxyphosphoryl)fluoromethyl)benzoate (**4d**)



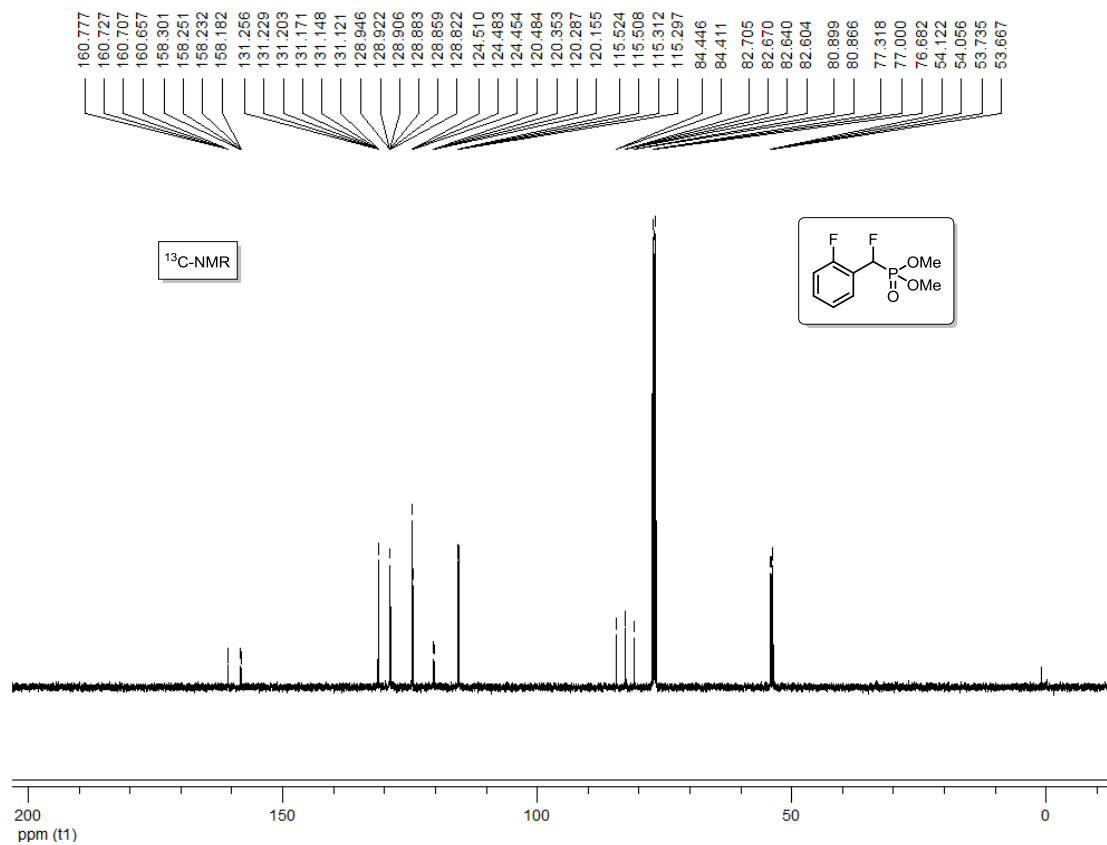
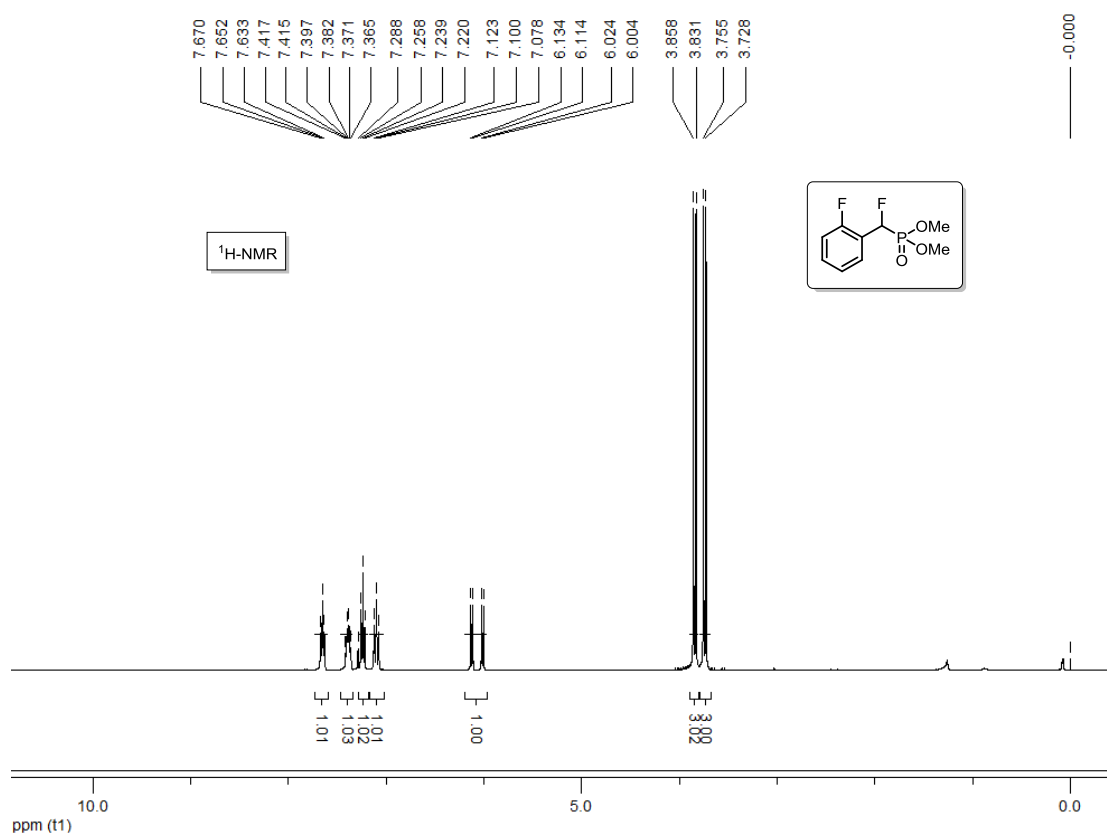


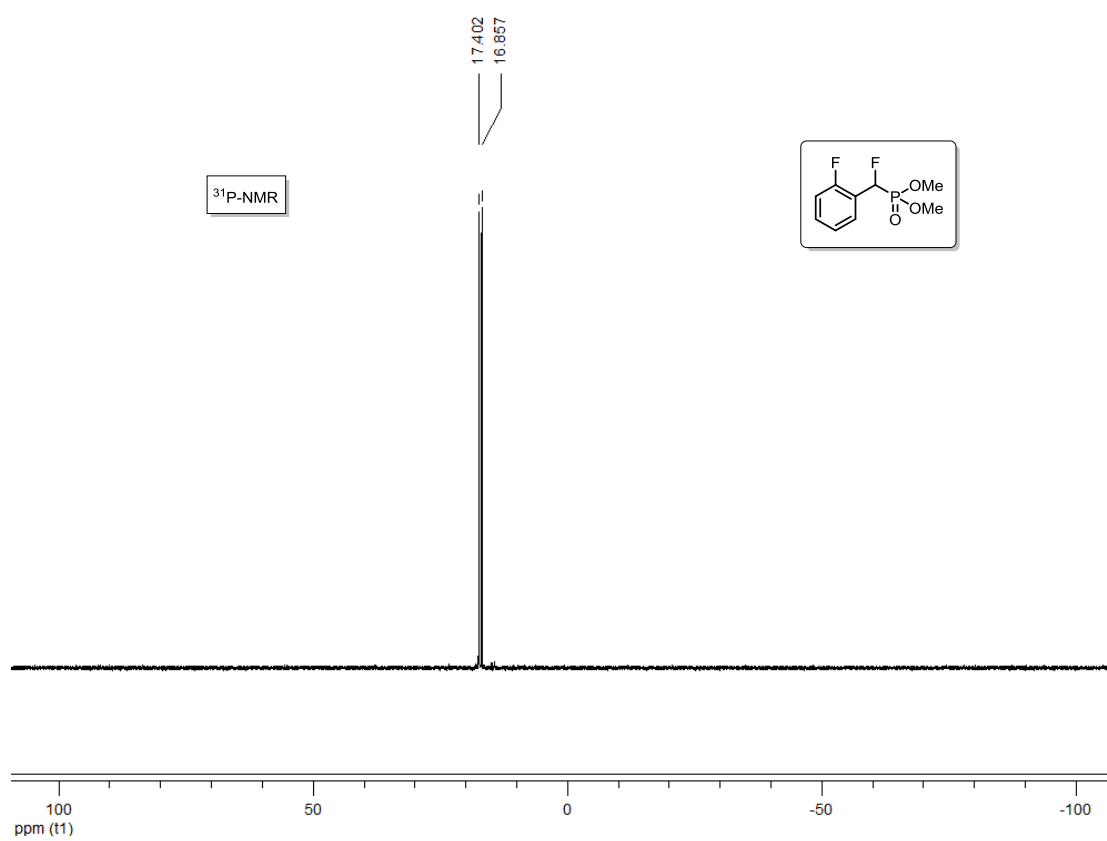
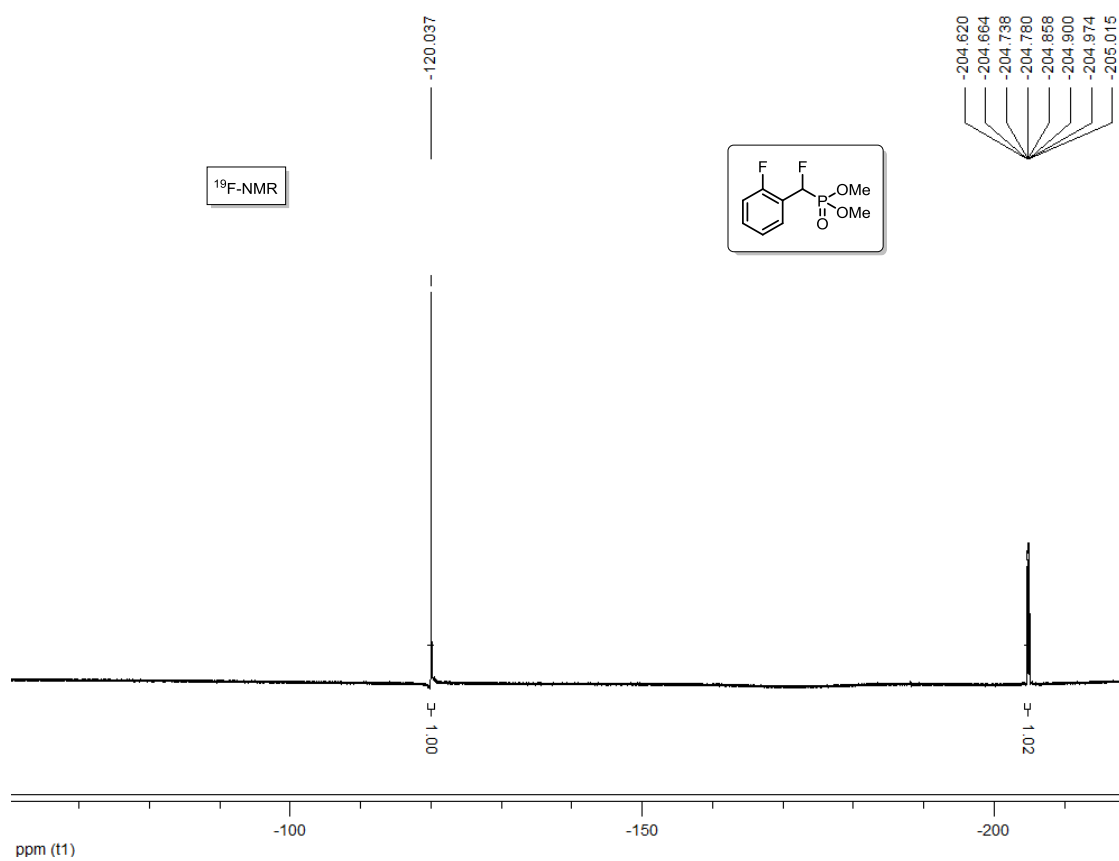
Dimethyl (fluoro(3-methoxyphenyl)methyl)phosphonate (**4e**)



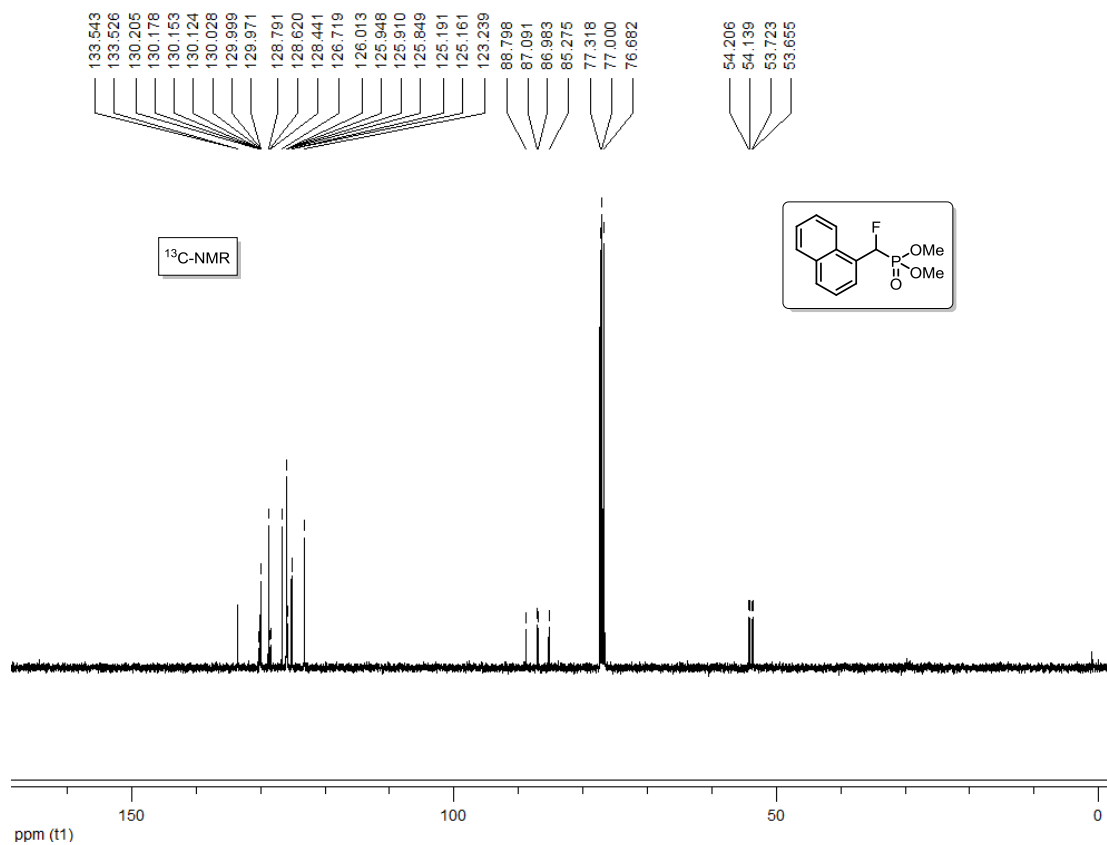
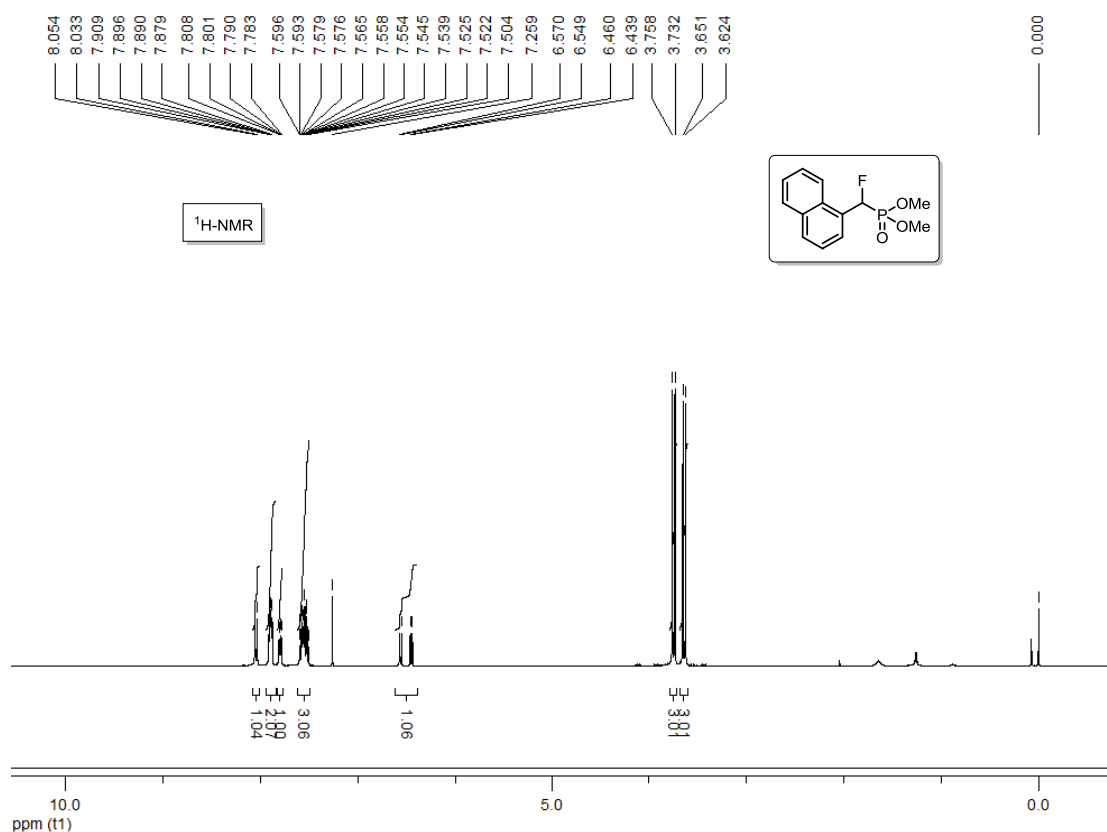


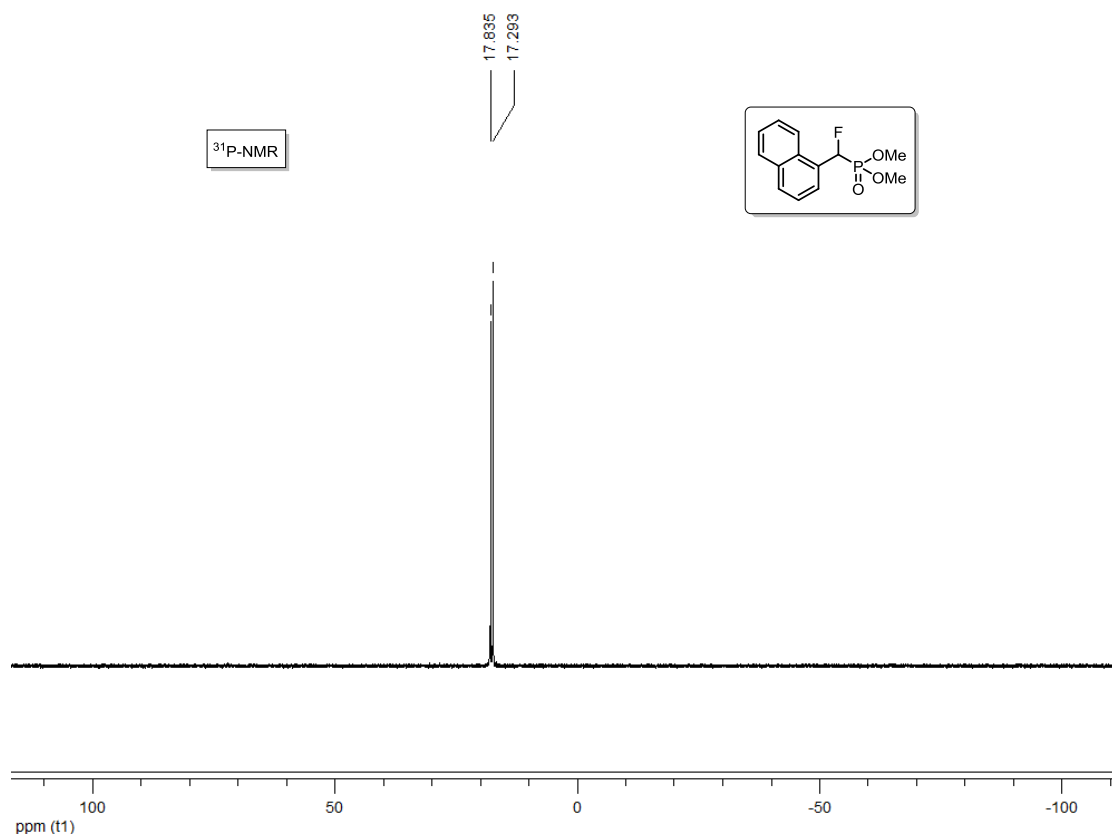
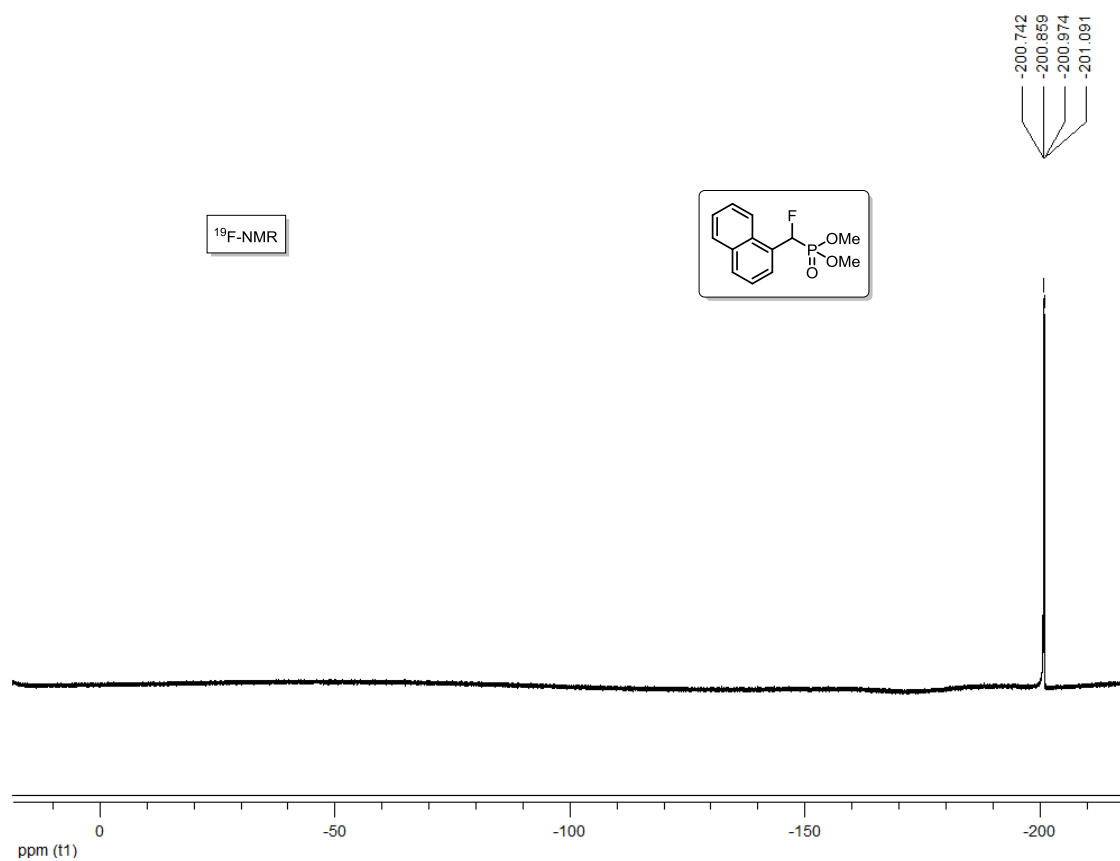
Dimethyl (fluoro(2-fluorophenyl)methyl)phosphonate (**4f**)





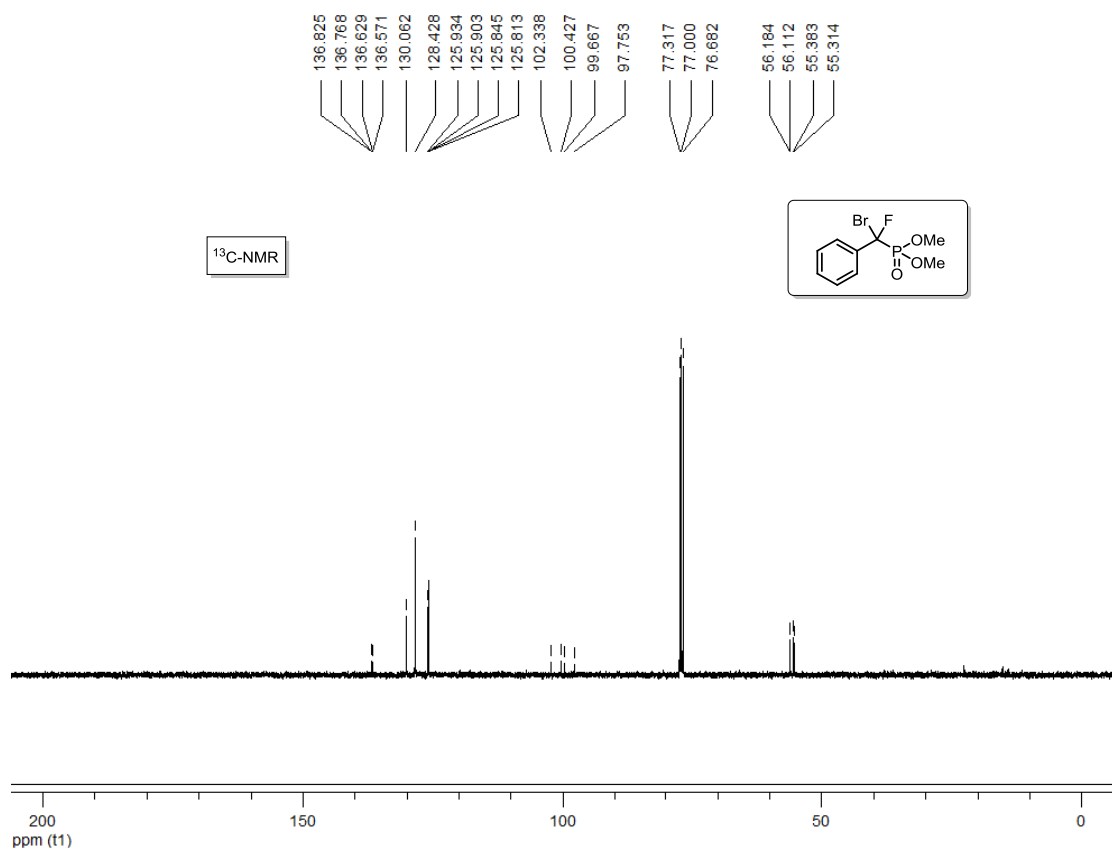
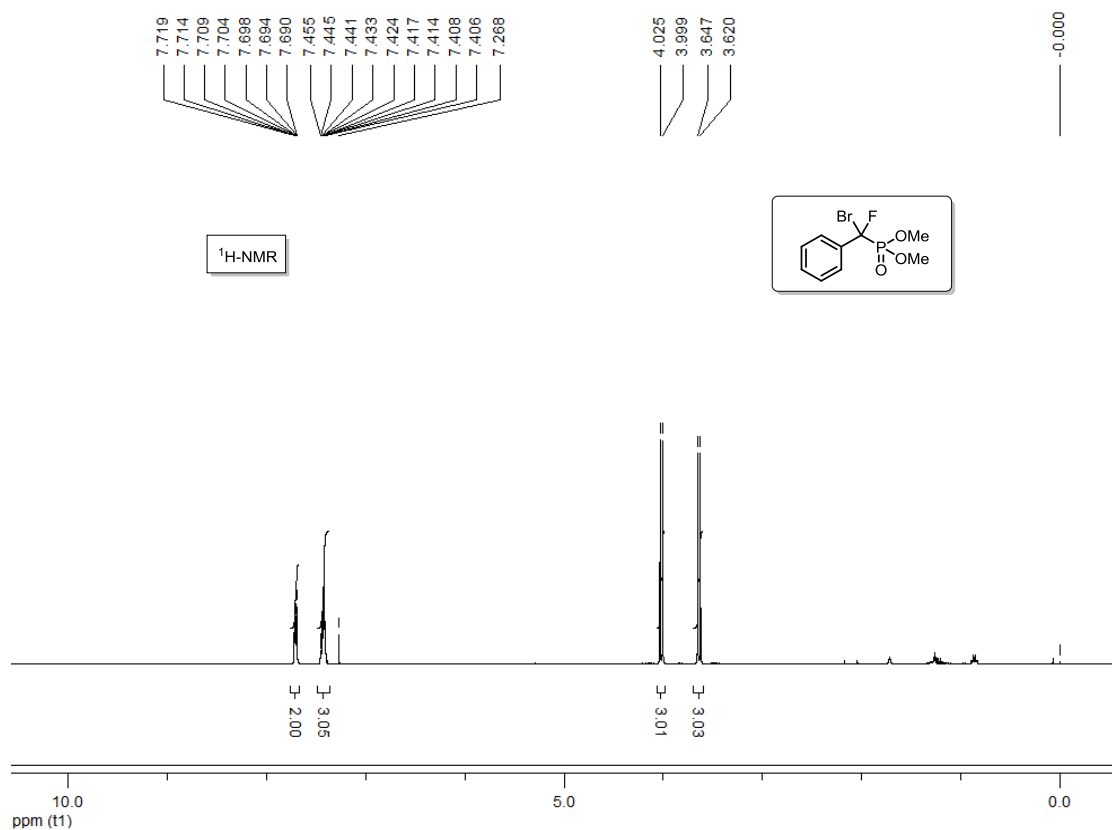
Dimethyl (fluoro(naphthalen-1-yl)methyl)phosphonate (**4g**)

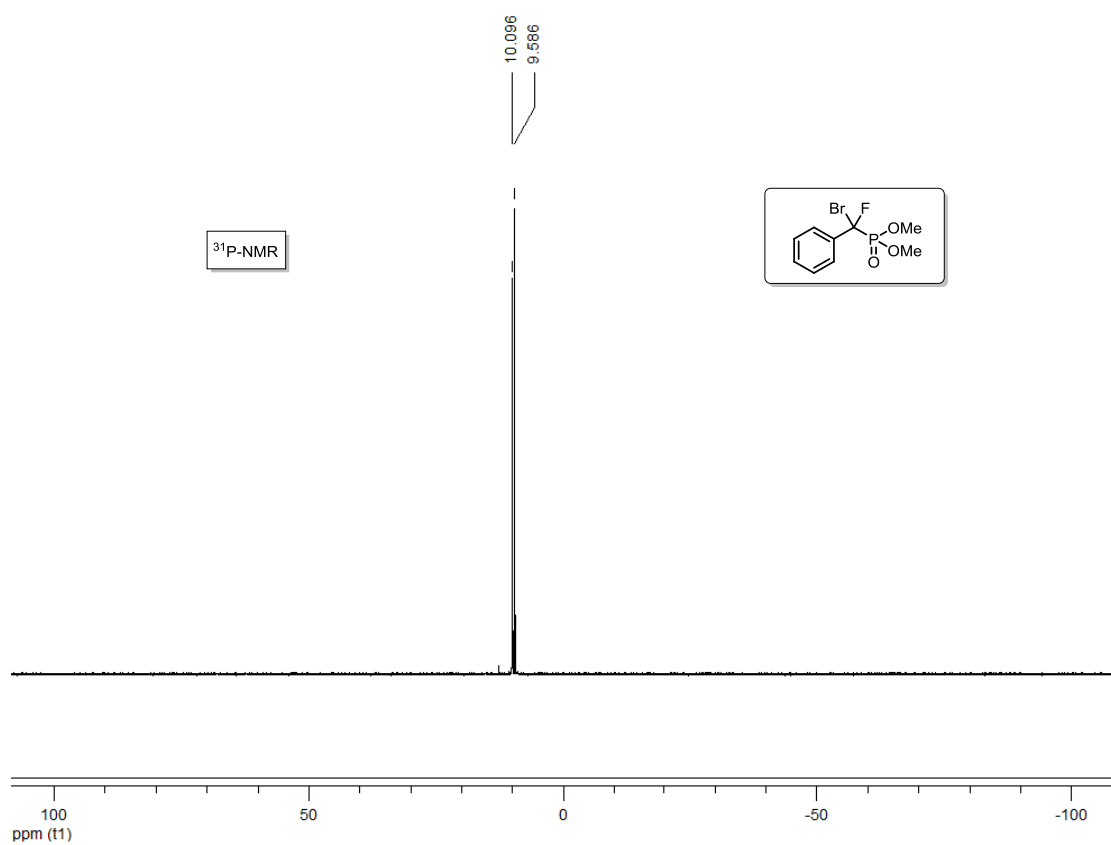
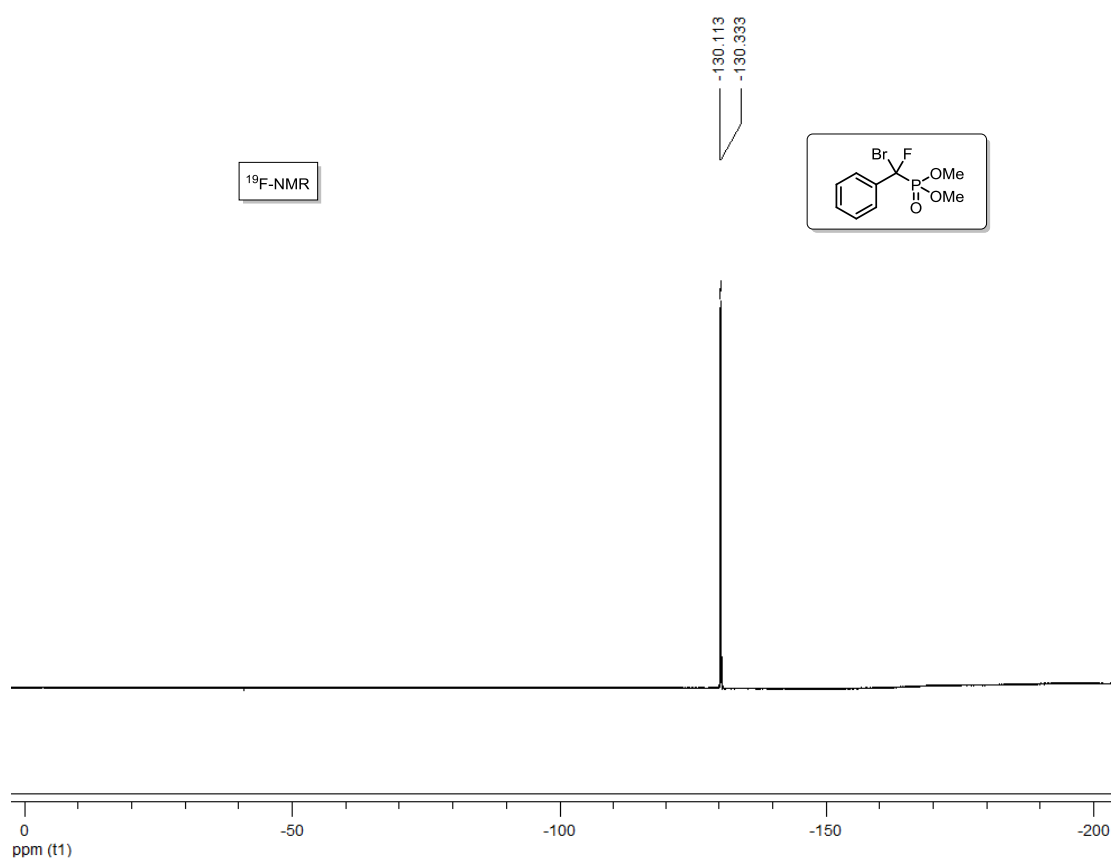




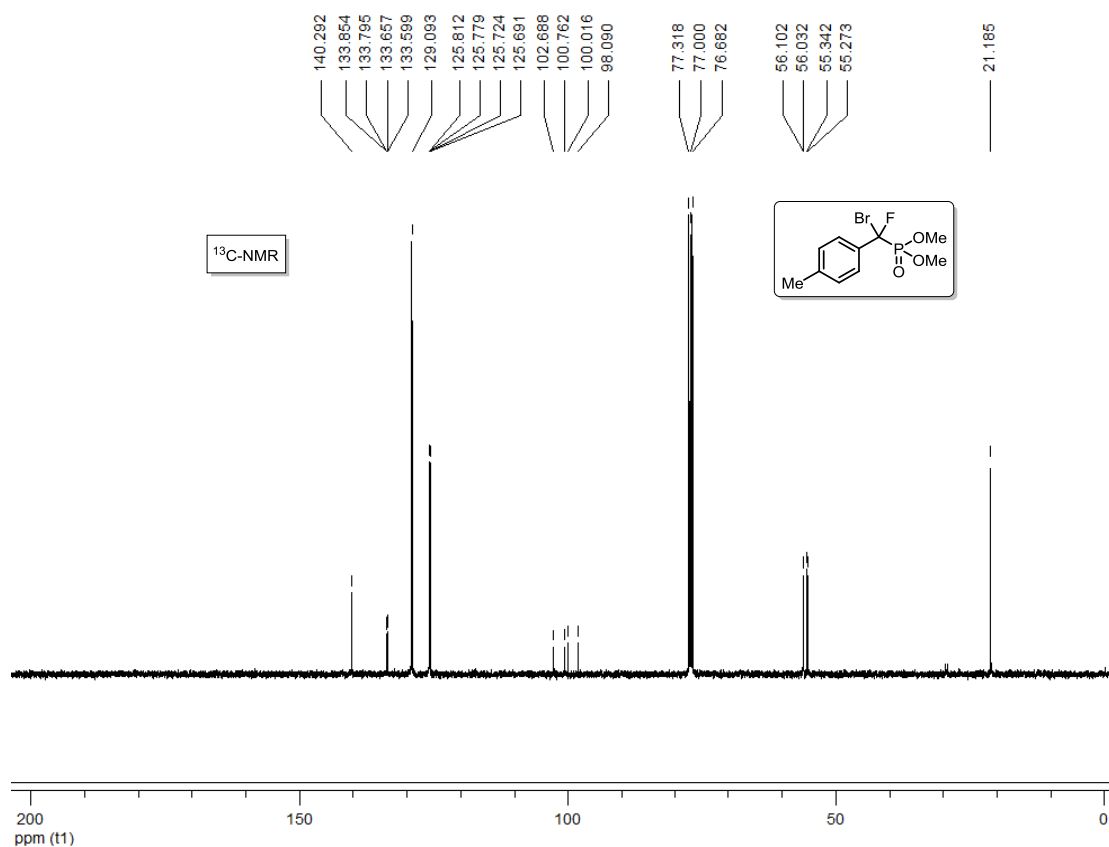
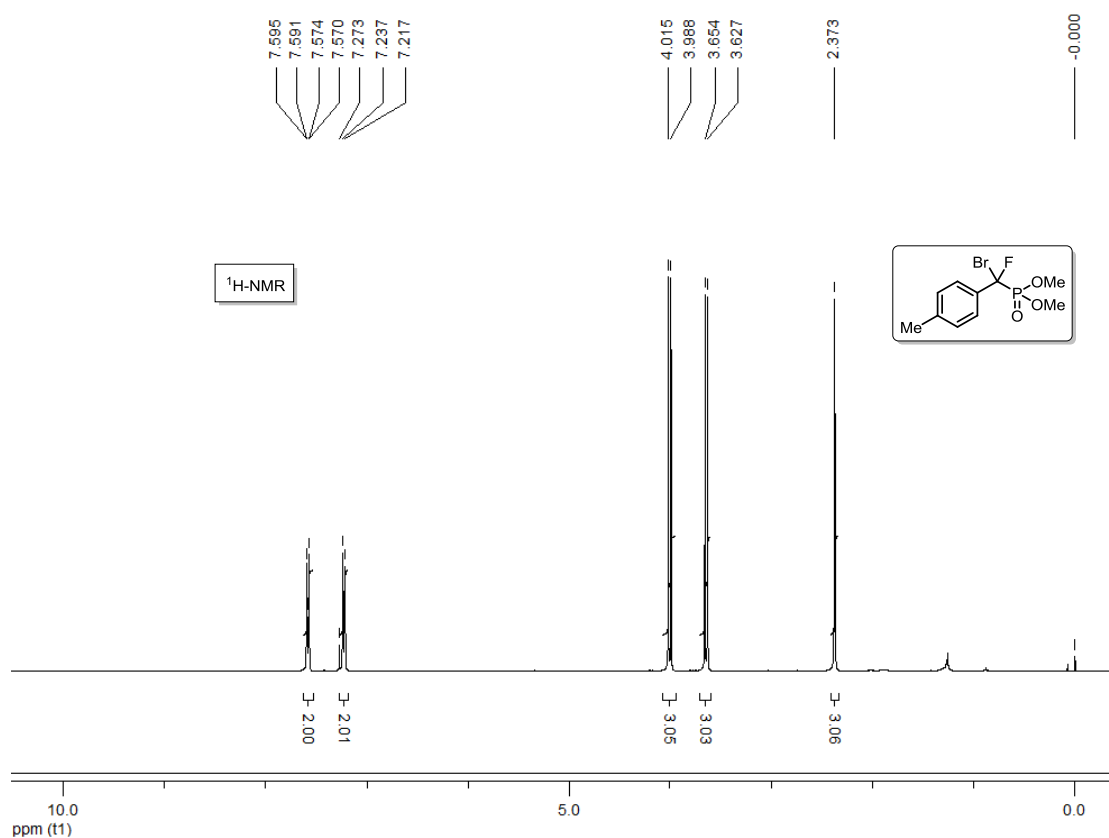
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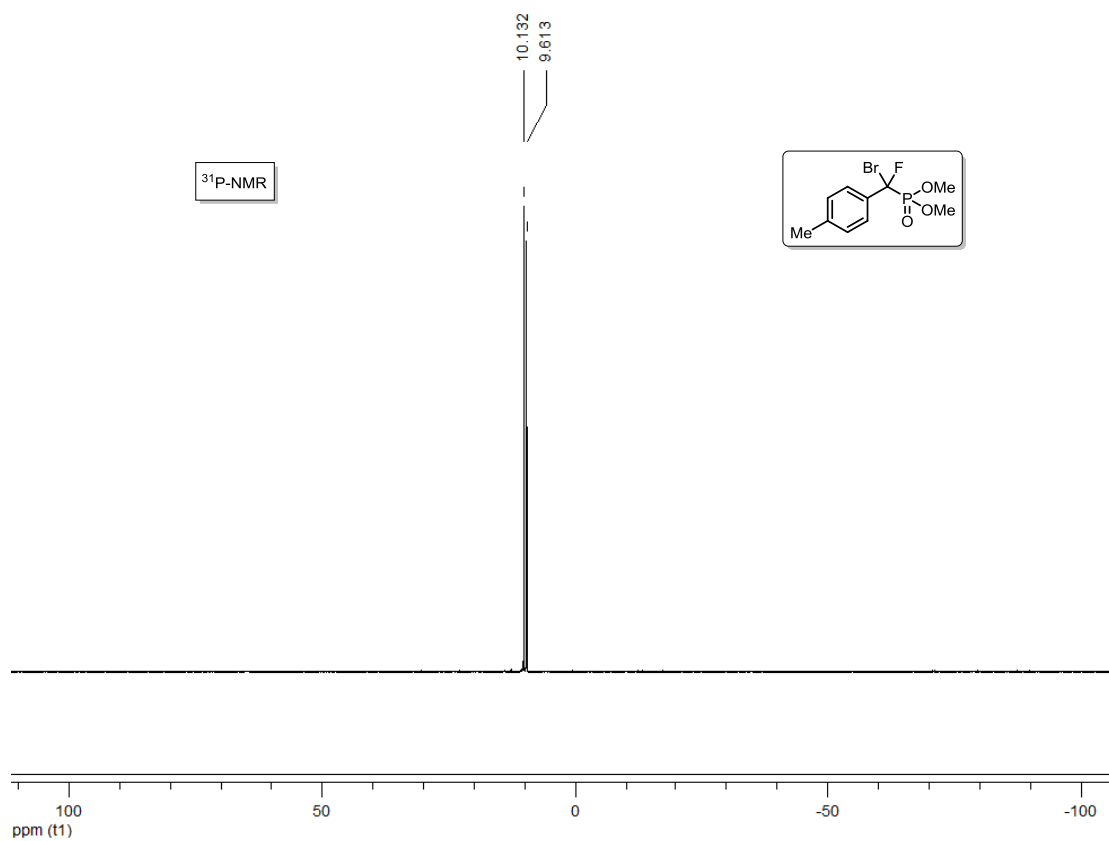
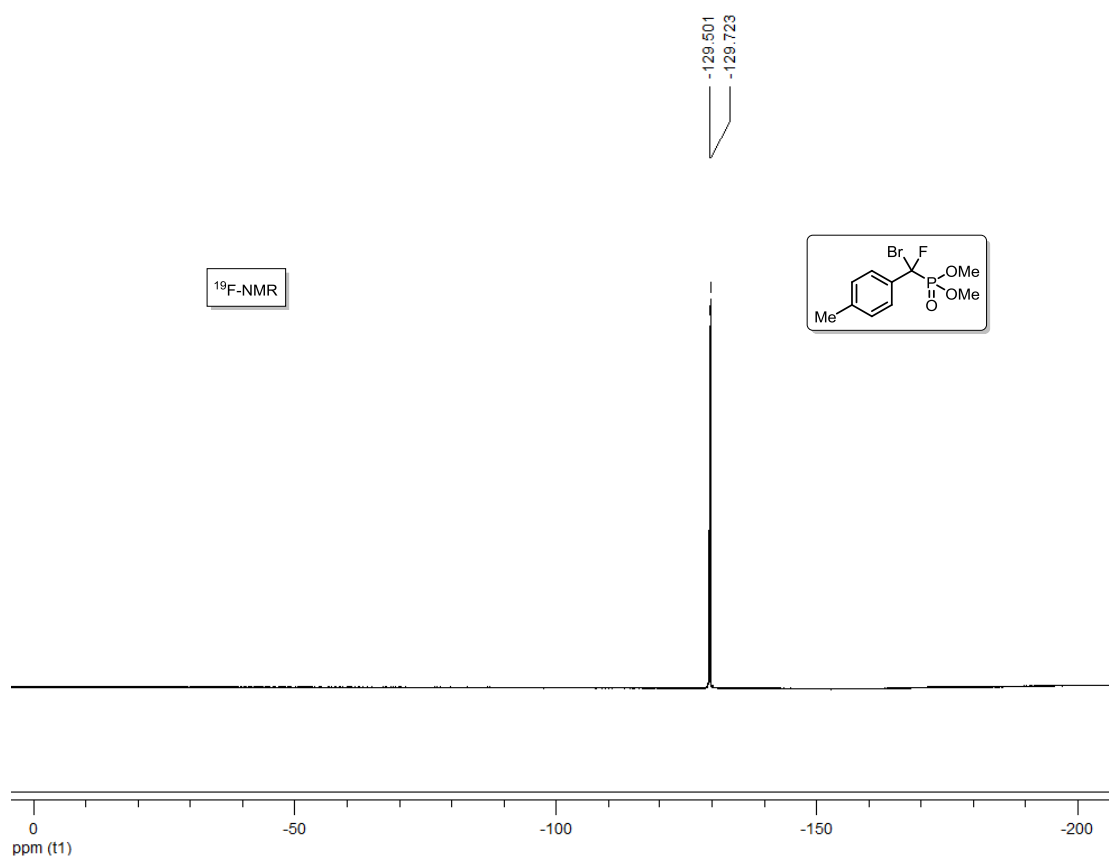
Dimethyl (bromofluoro(phenyl)methyl)phosphonate (5a)



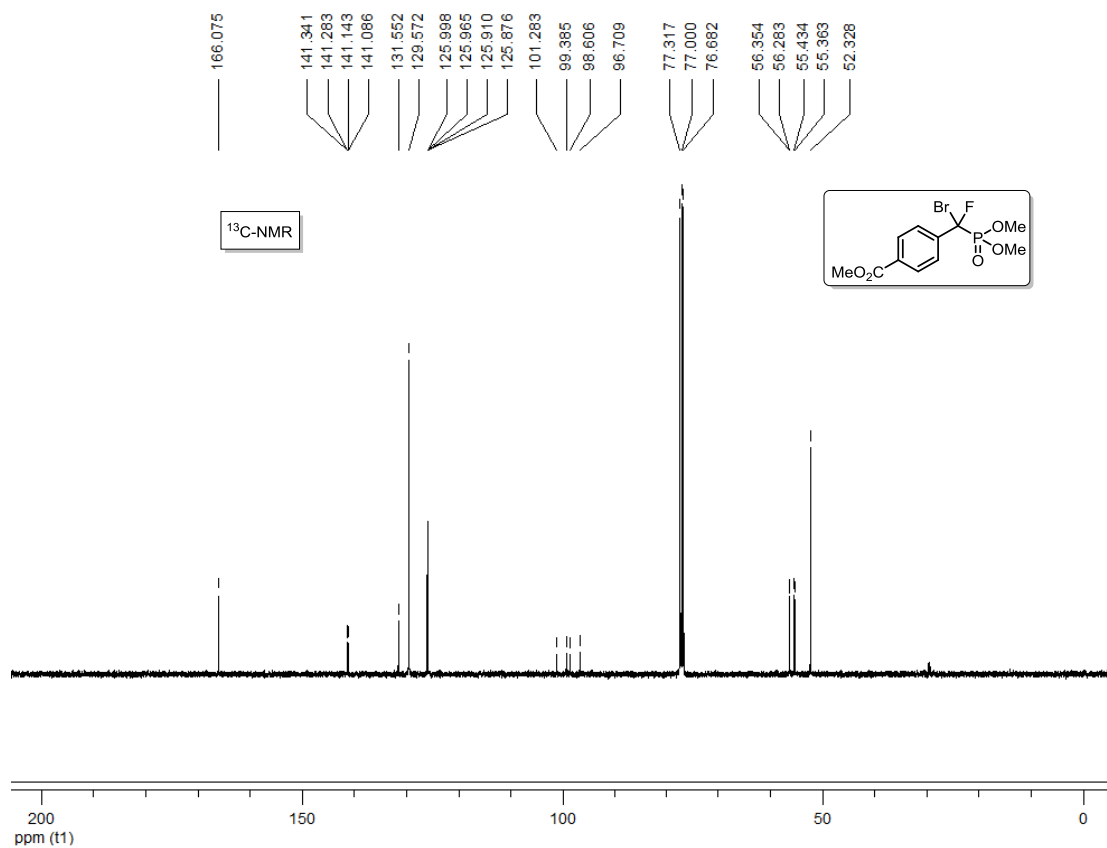
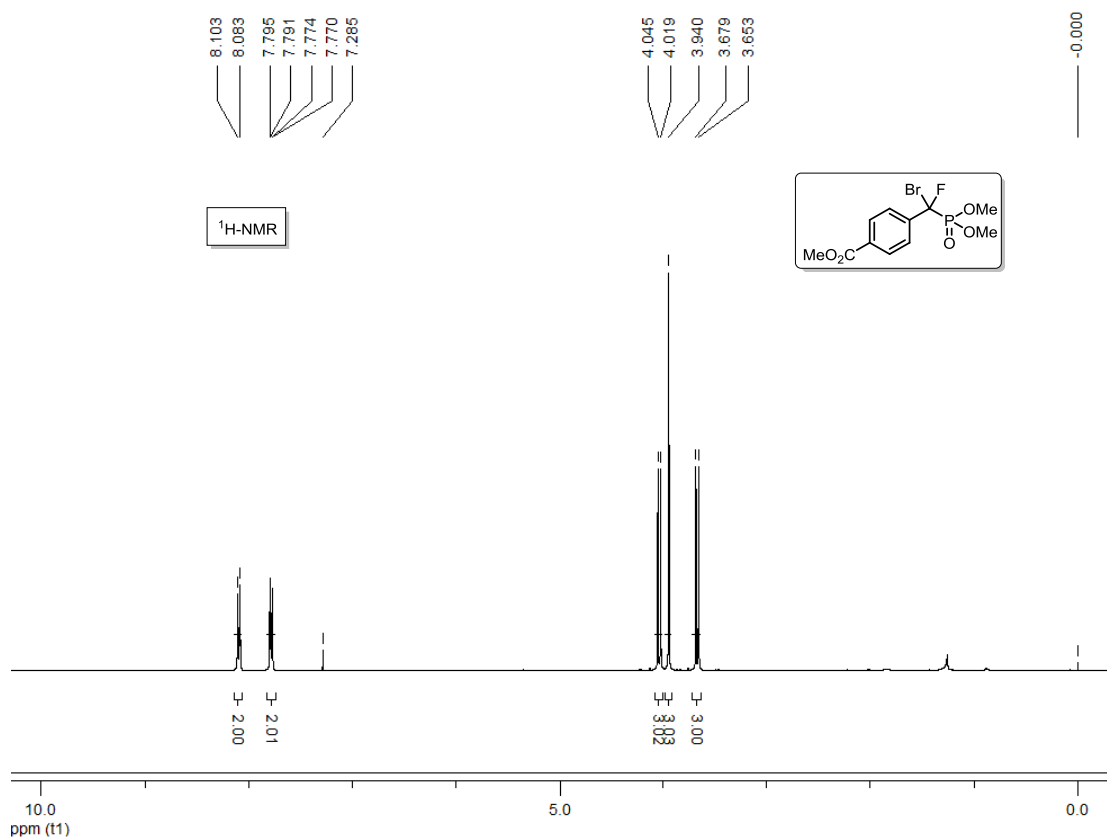


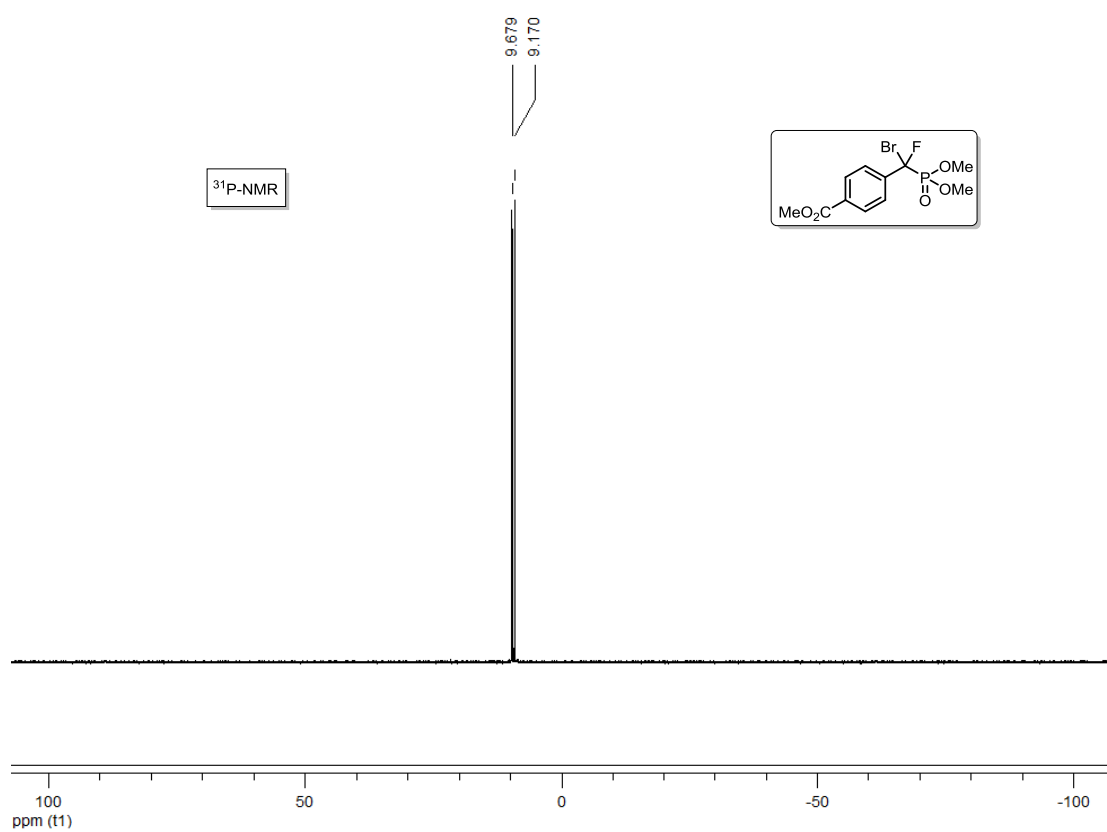
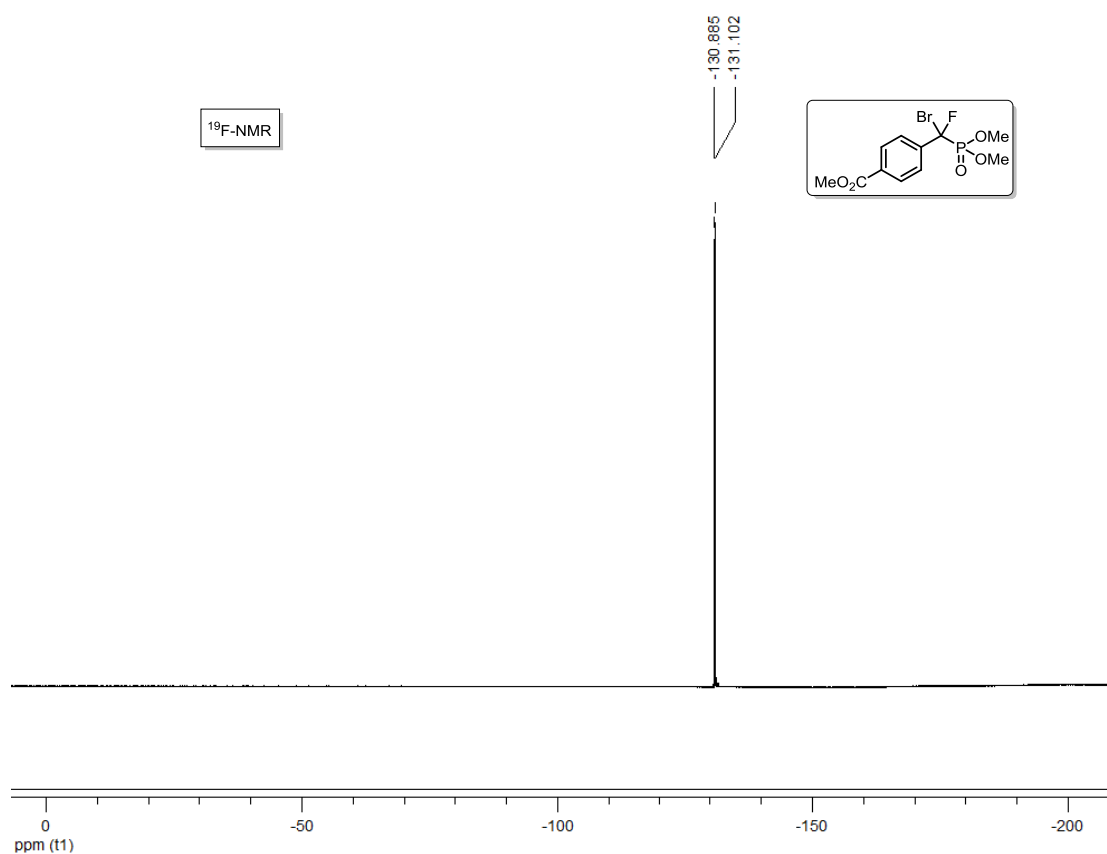
Dimethyl (bromofluoro(*p*-tolyl)methyl)phosphonate (**5b**)



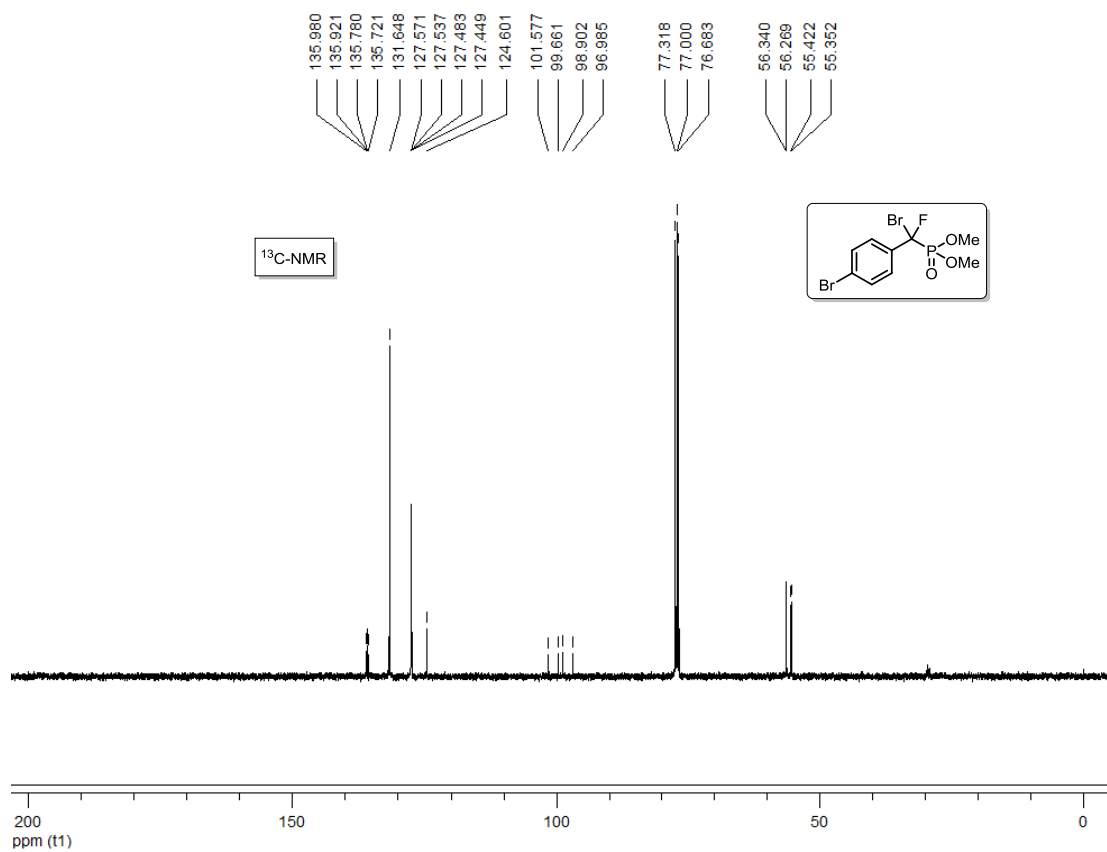
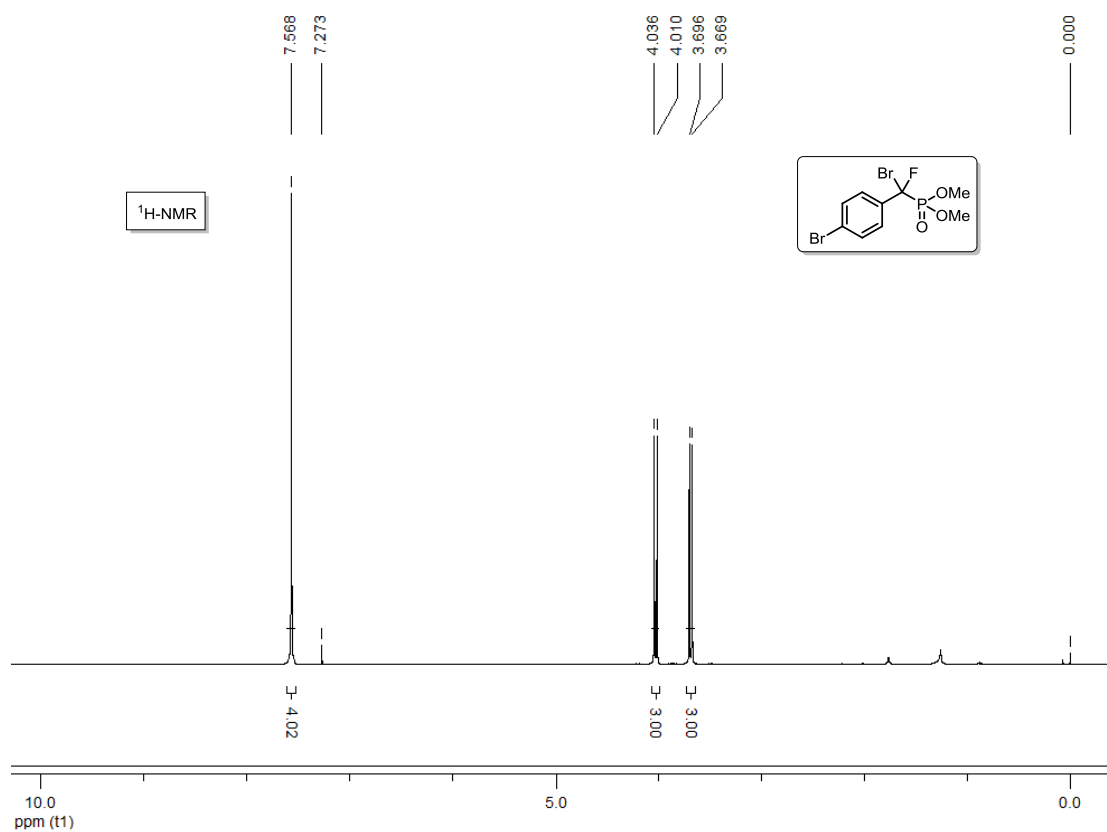


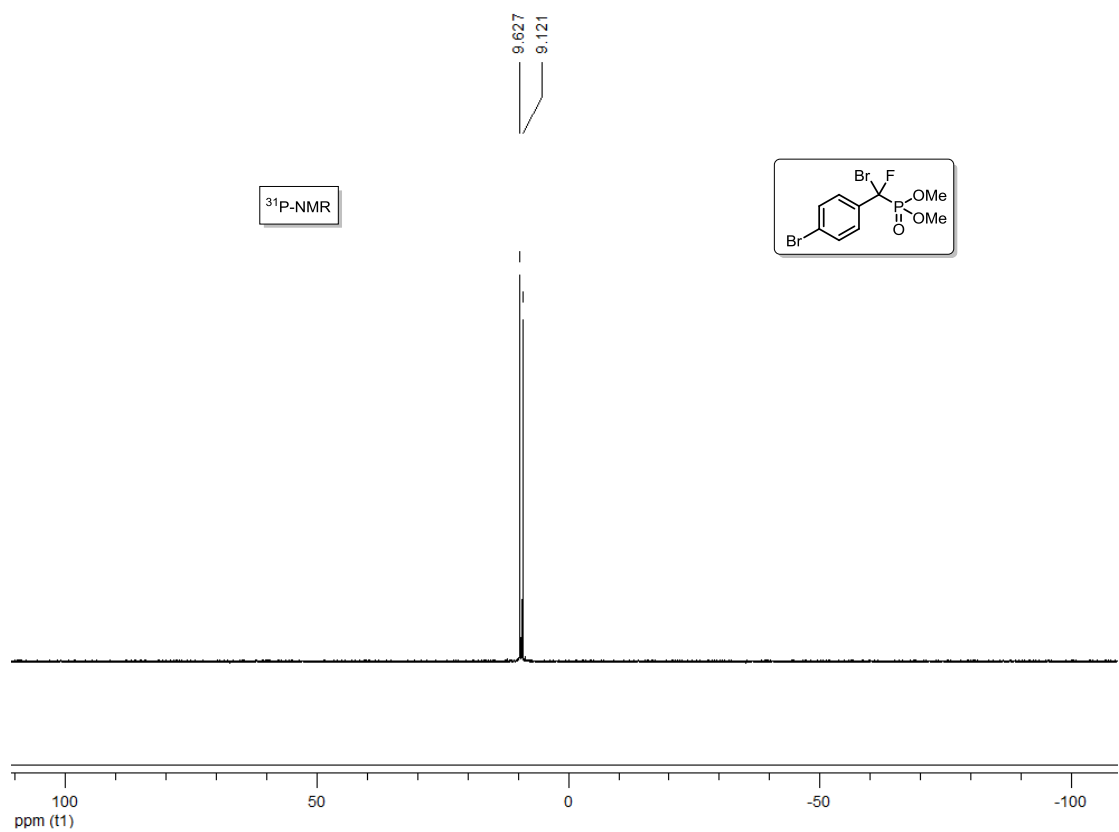
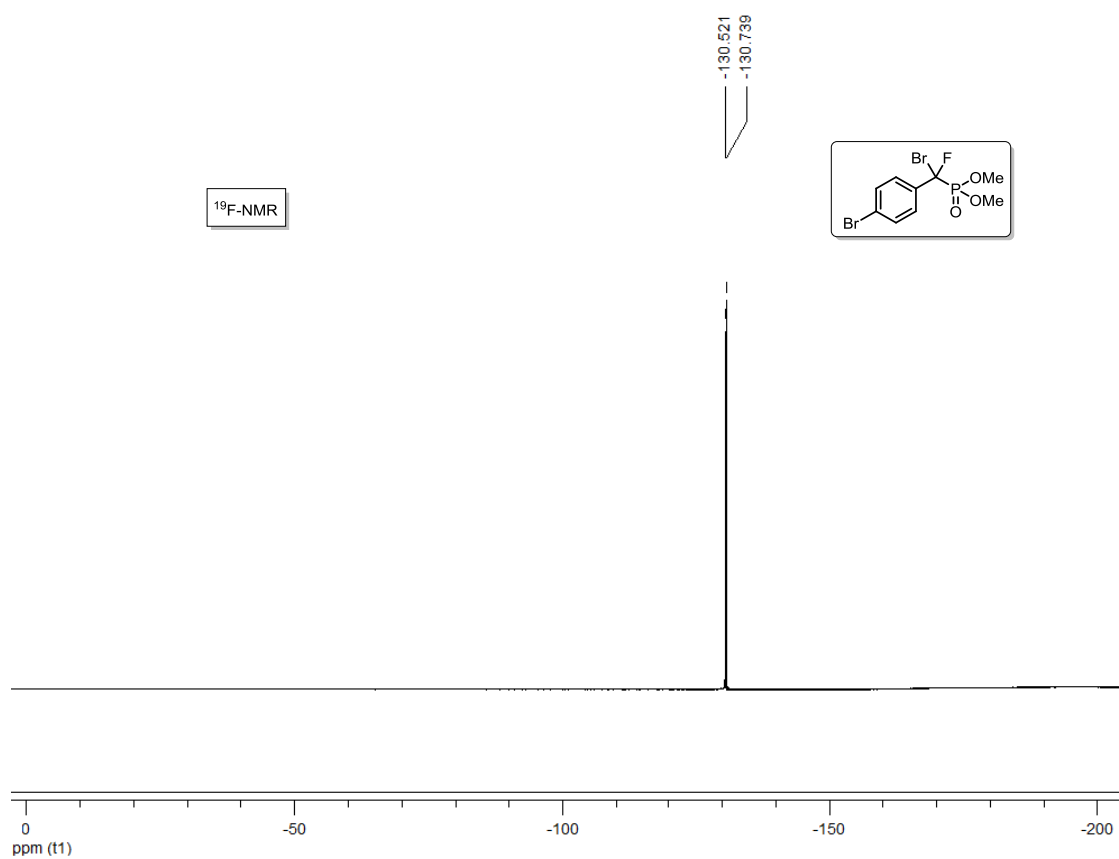
Methyl 4-(bromo(dimethoxyphosphoryl)fluoromethyl)benzoate (**5c**)



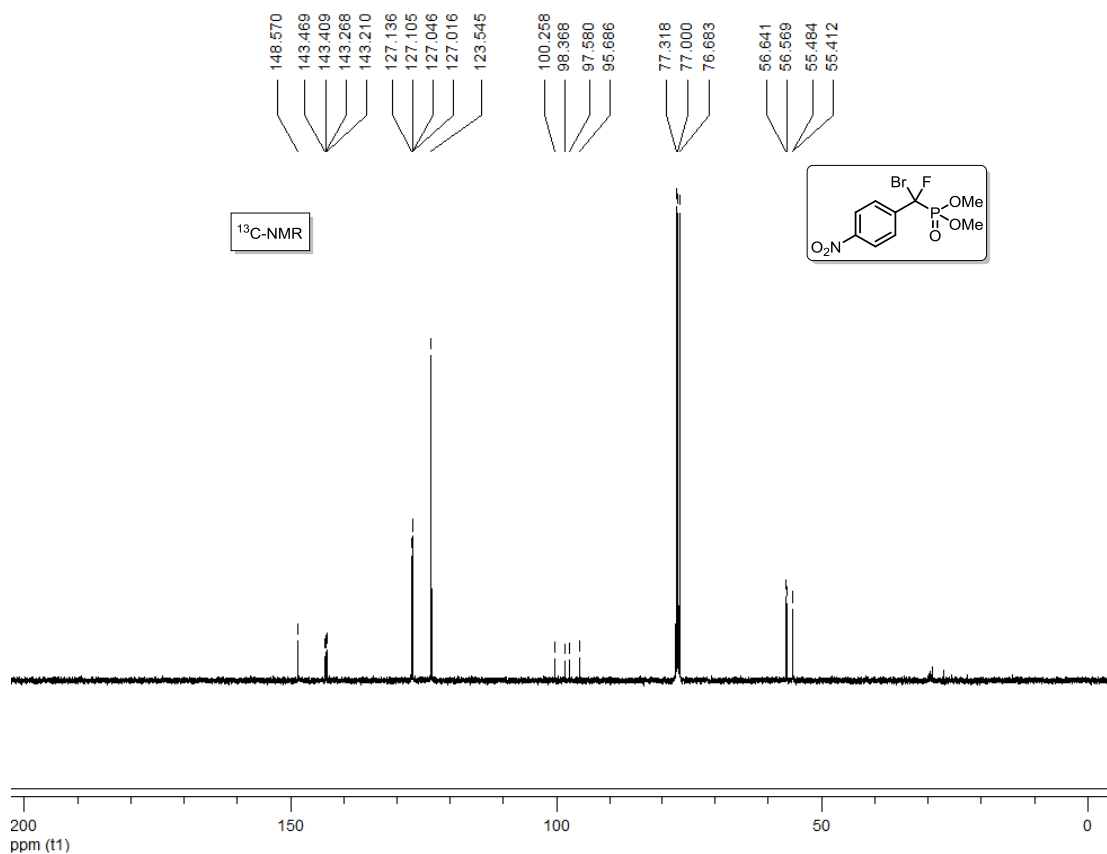
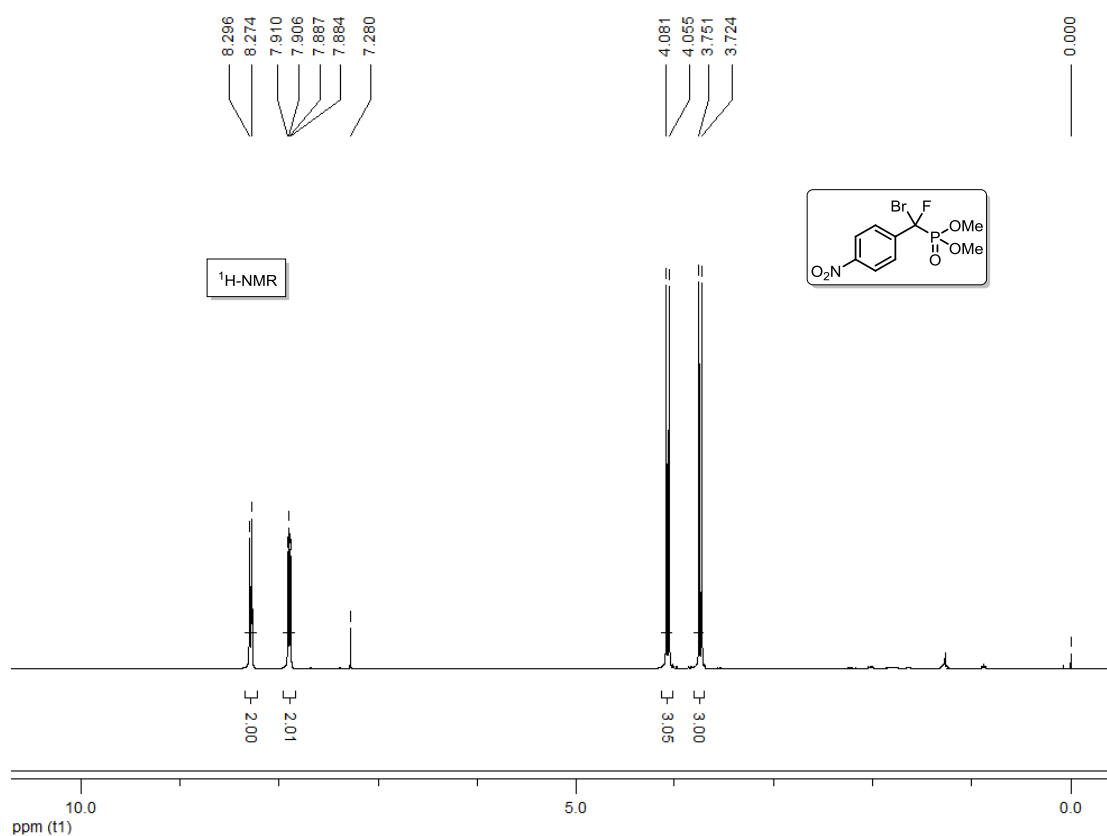


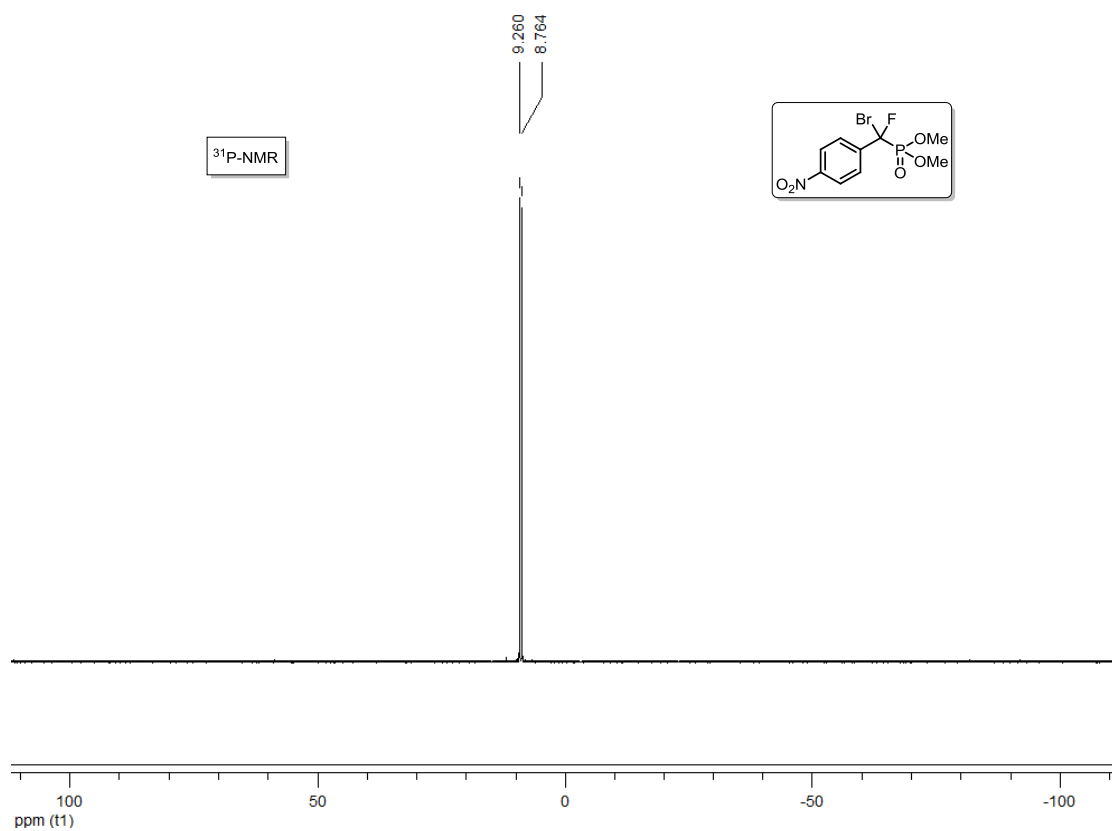
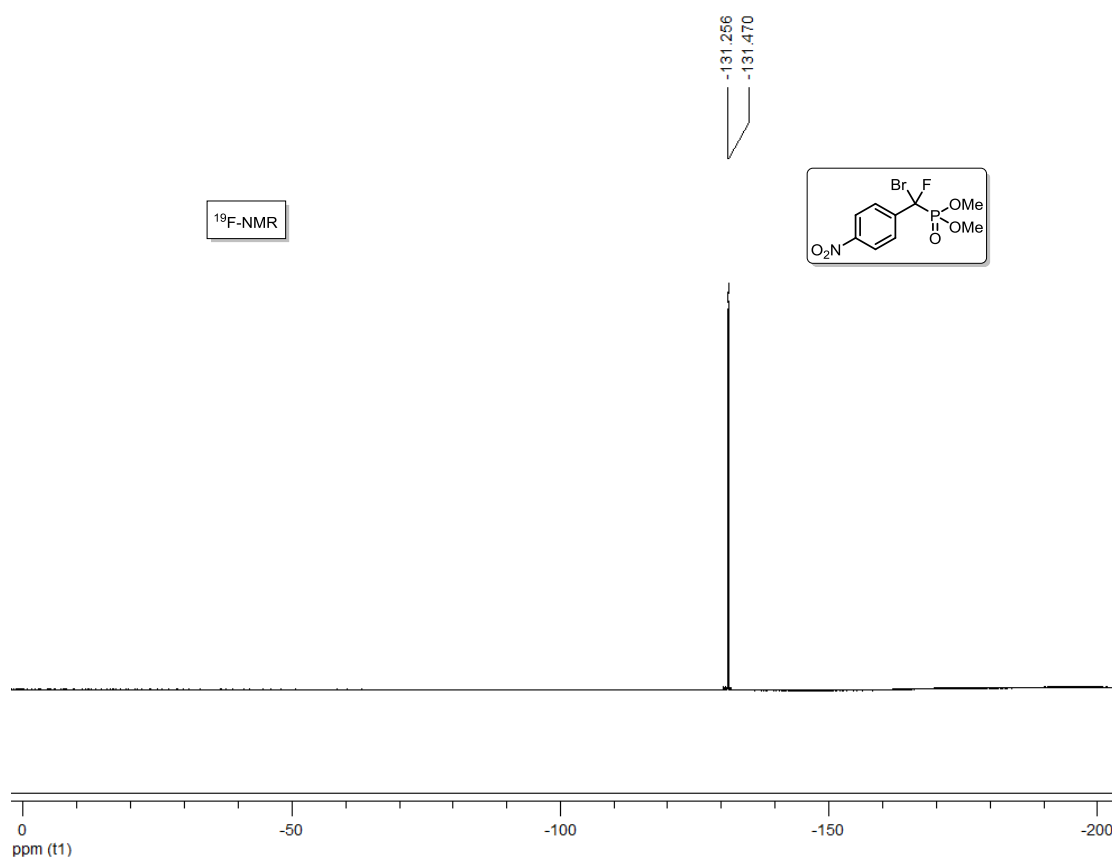
Dimethyl (bromo(4-bromophenyl)fluoromethyl)phosphonate (**5d**)



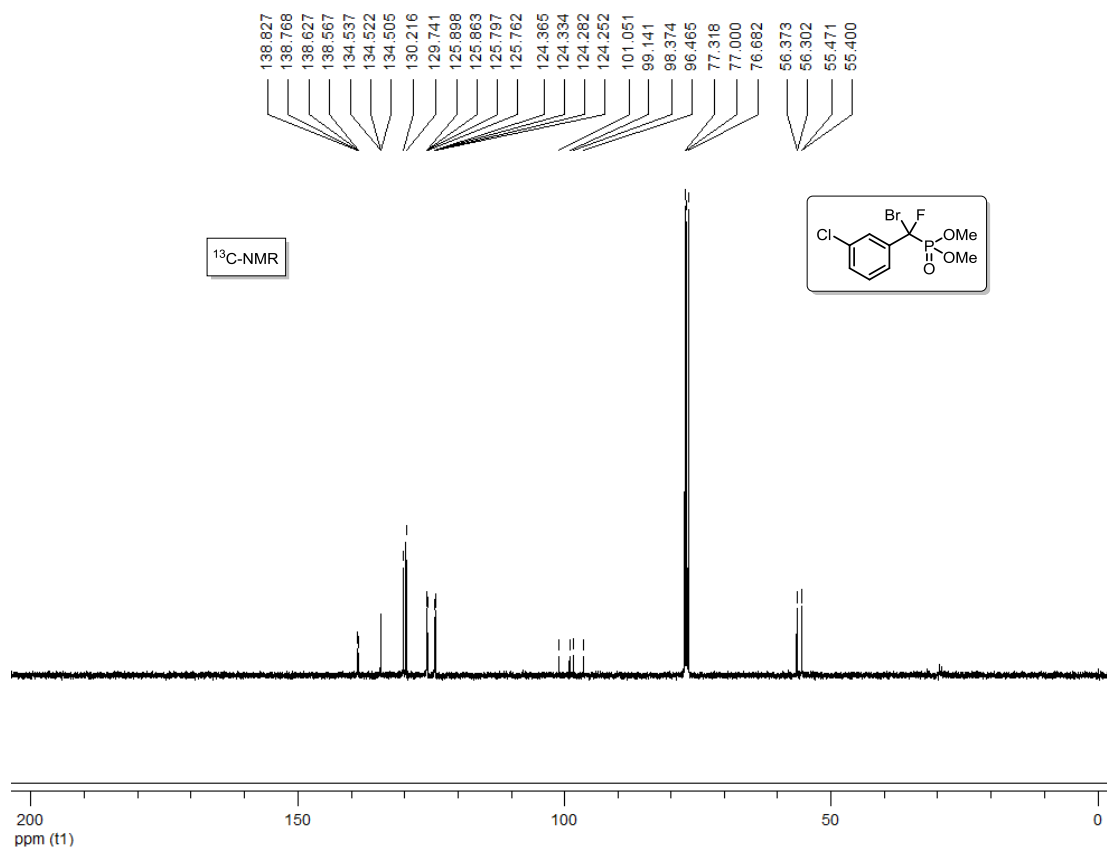
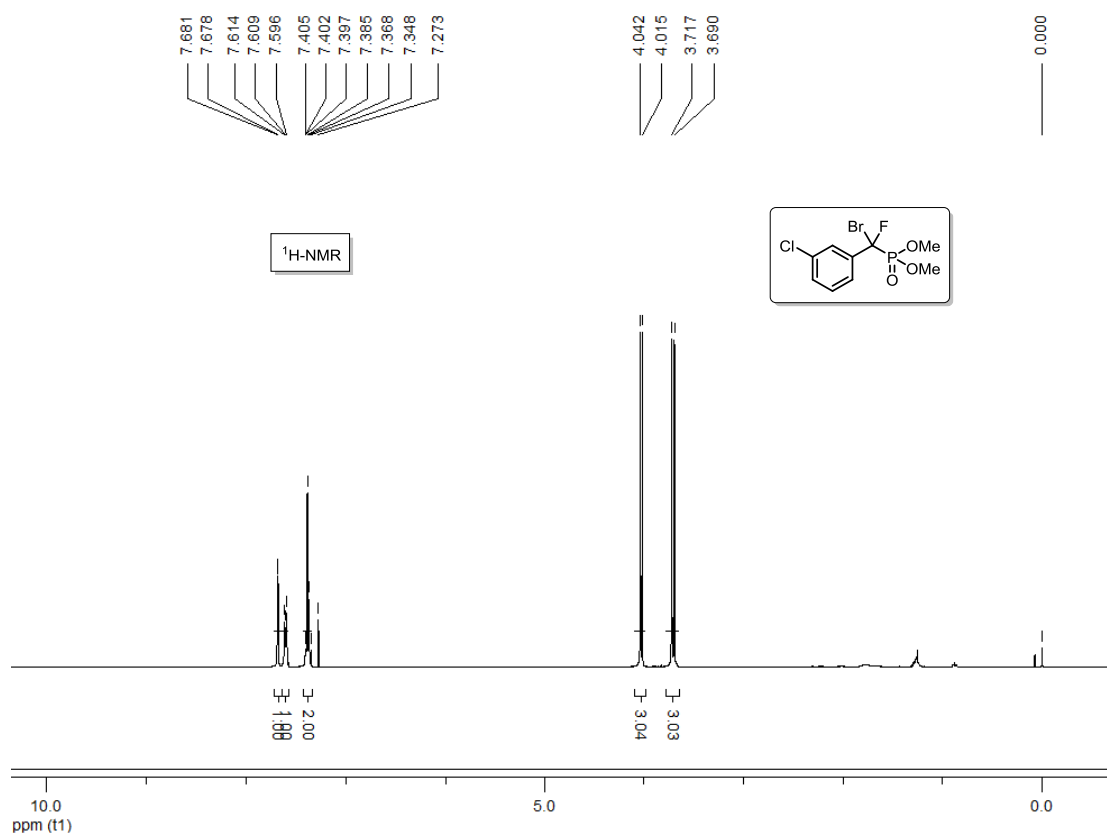


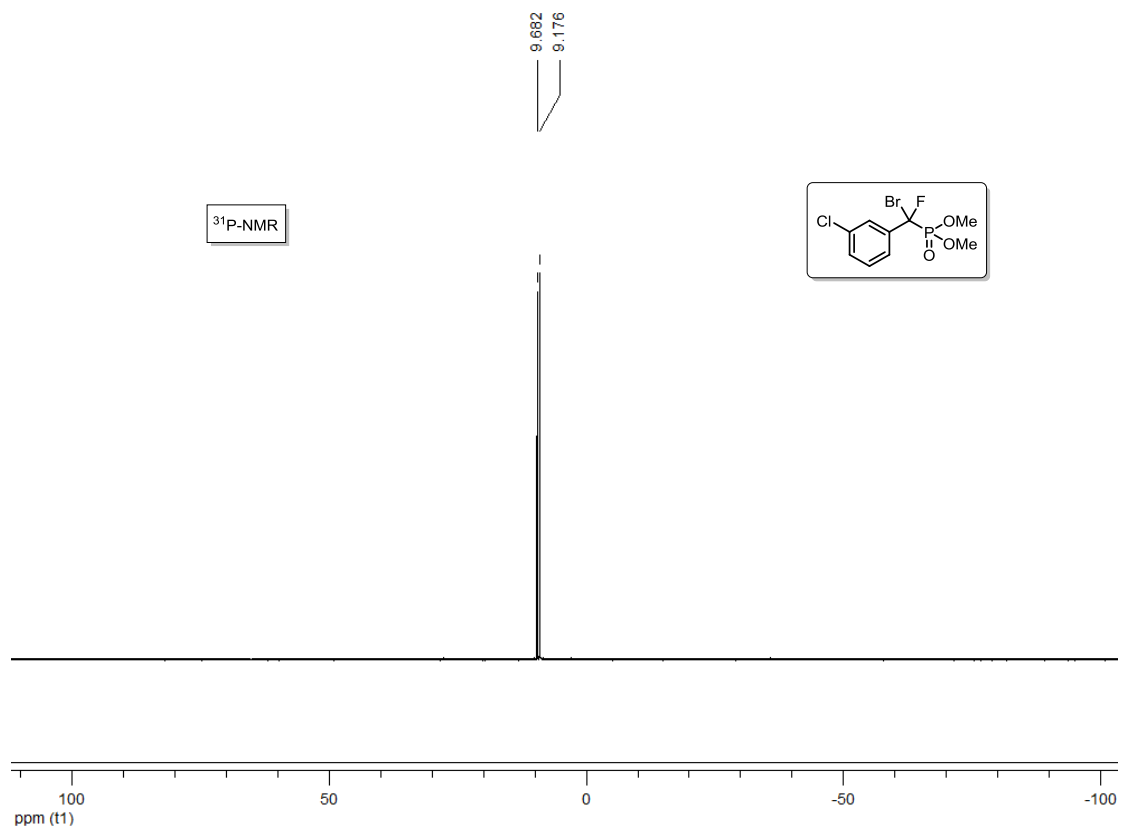
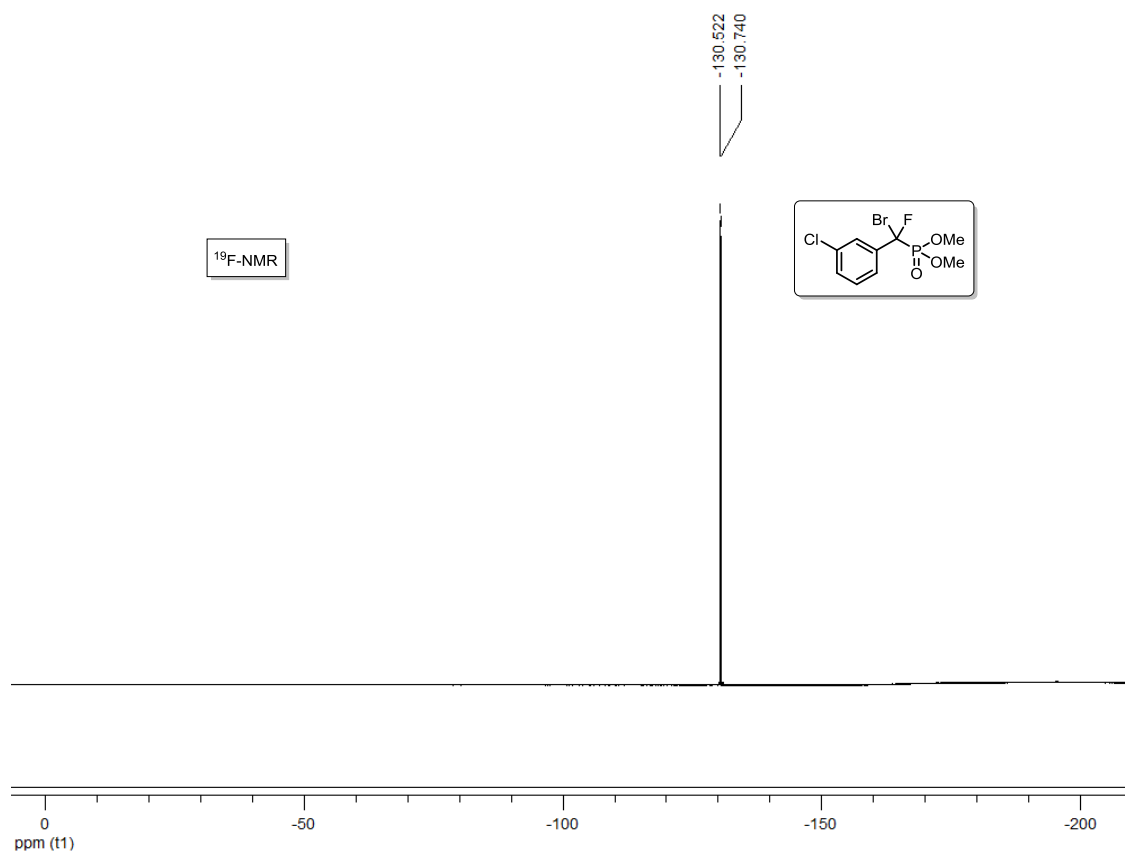
Dimethyl (bromofluoro(4-nitrophenyl)methyl)phosphonate (**5e**)





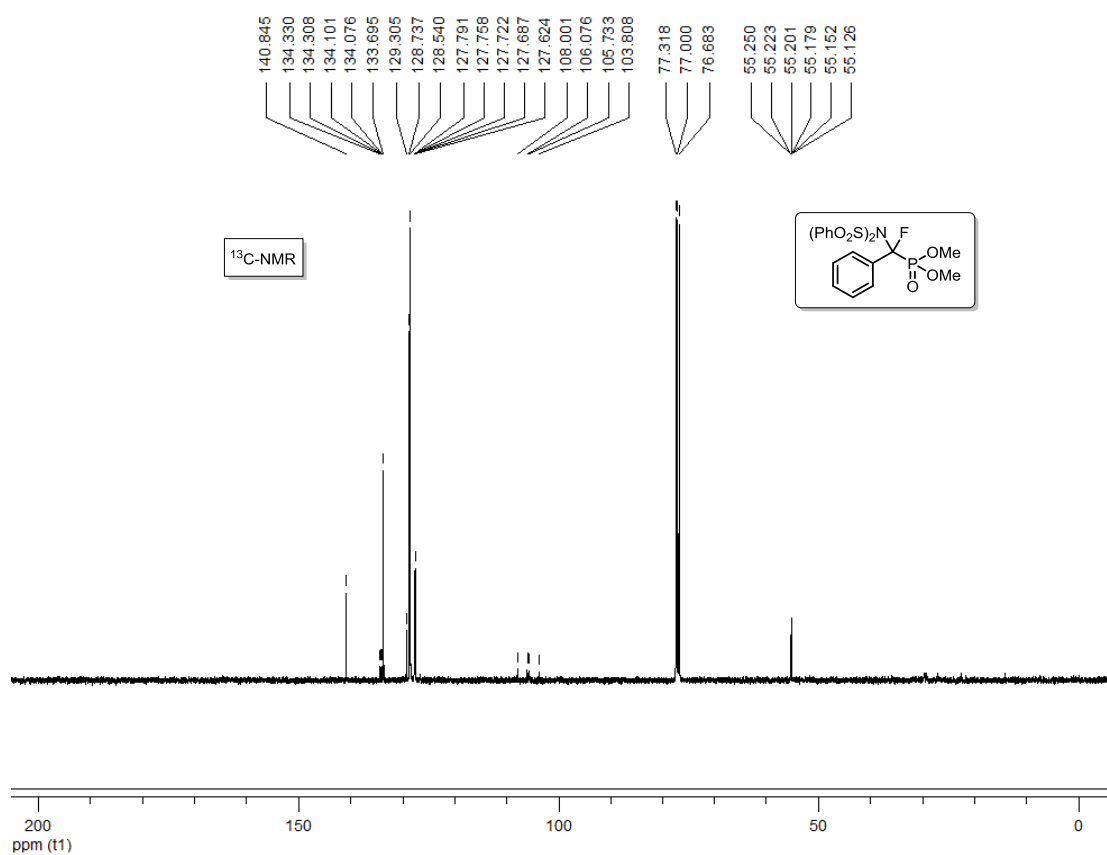
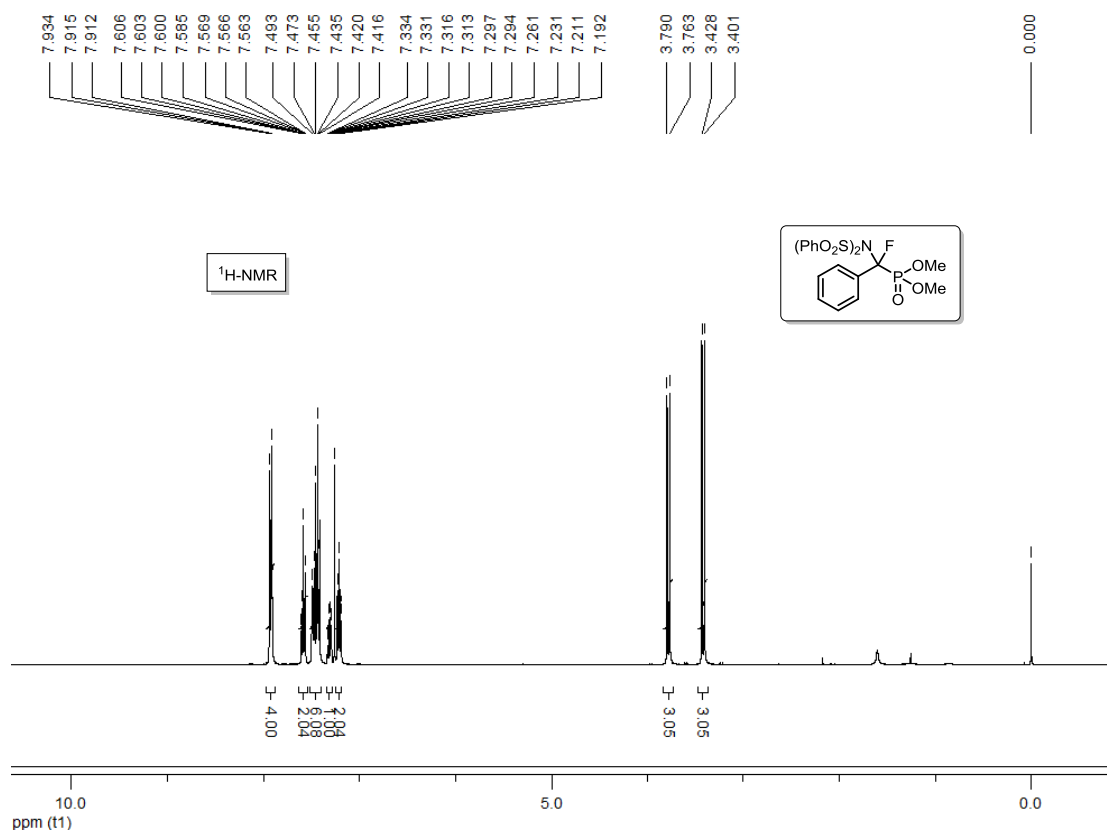
Dimethyl (bromo(3-chlorophenyl)fluoromethyl)phosphonate (**5f**)

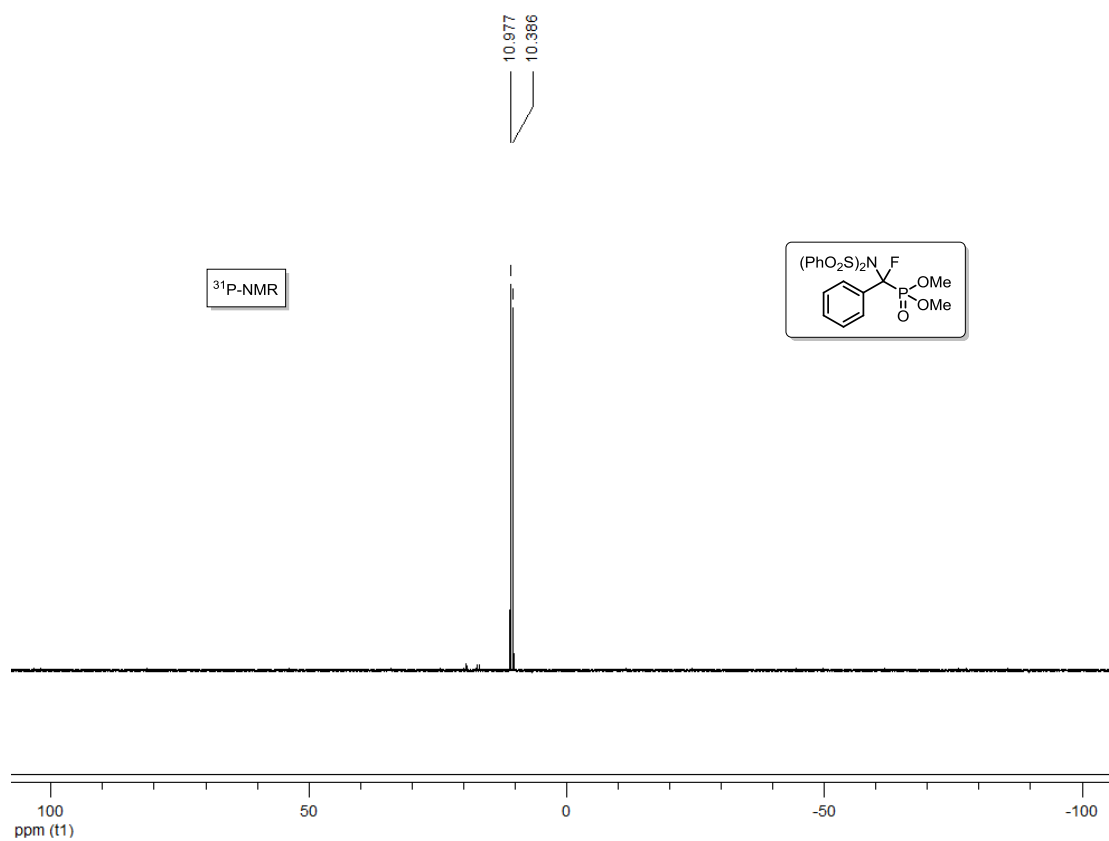
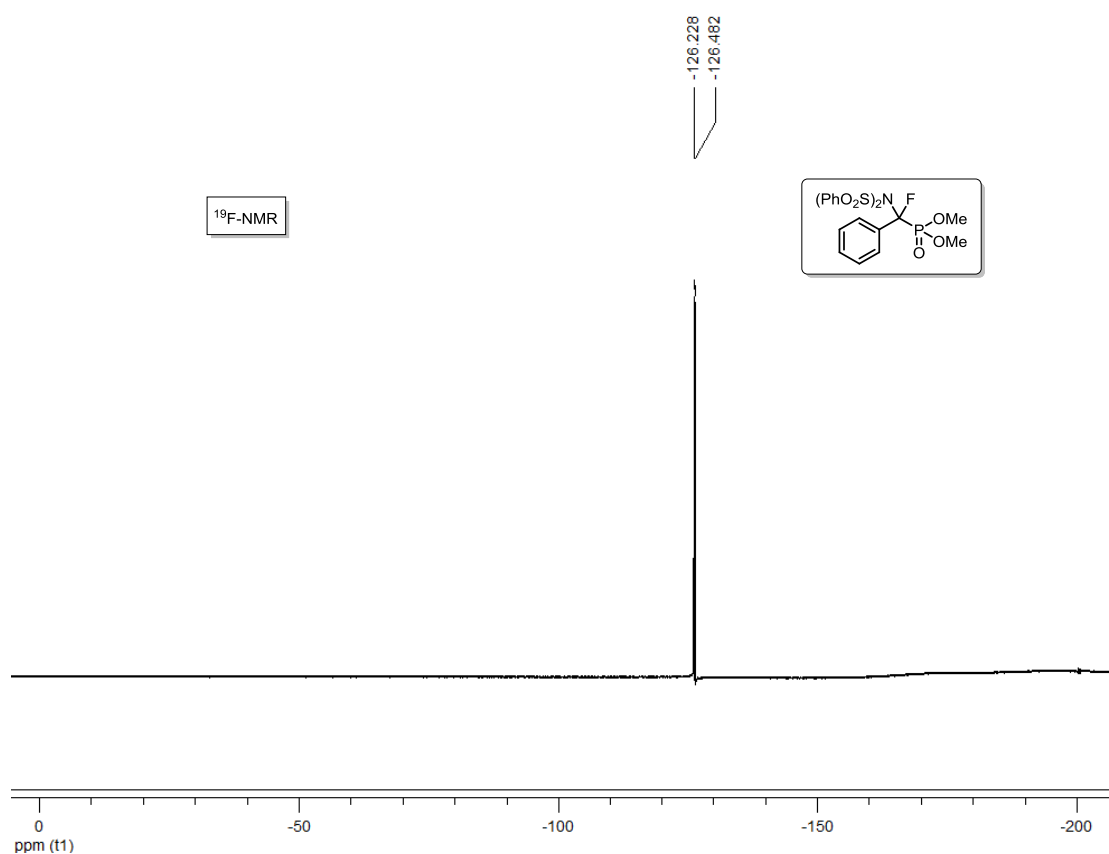




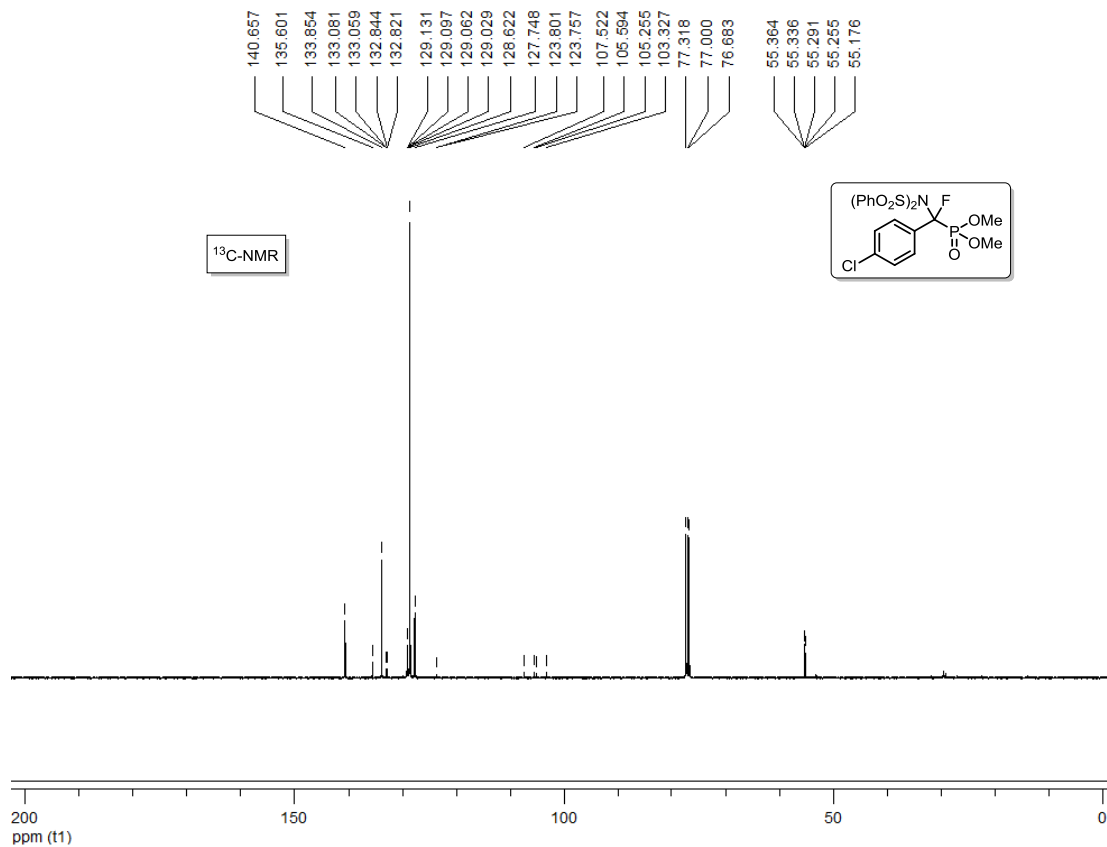
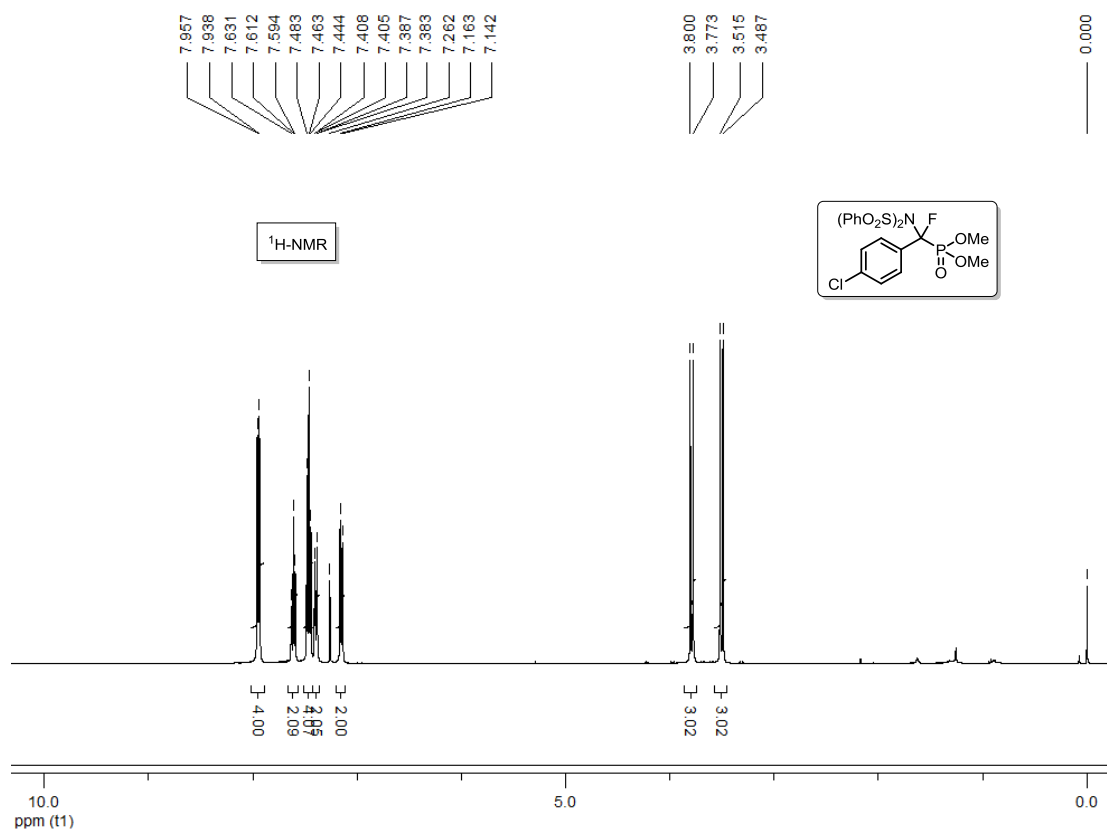
6. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra for the products 6a-c

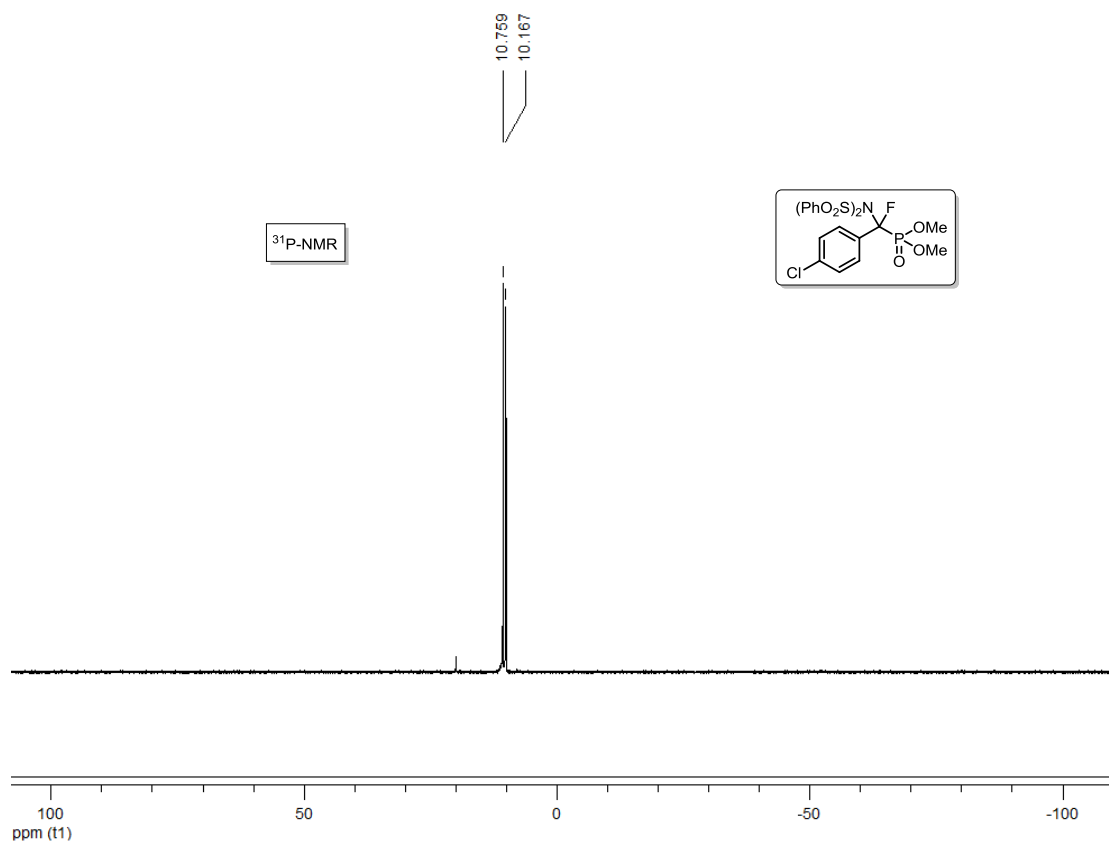
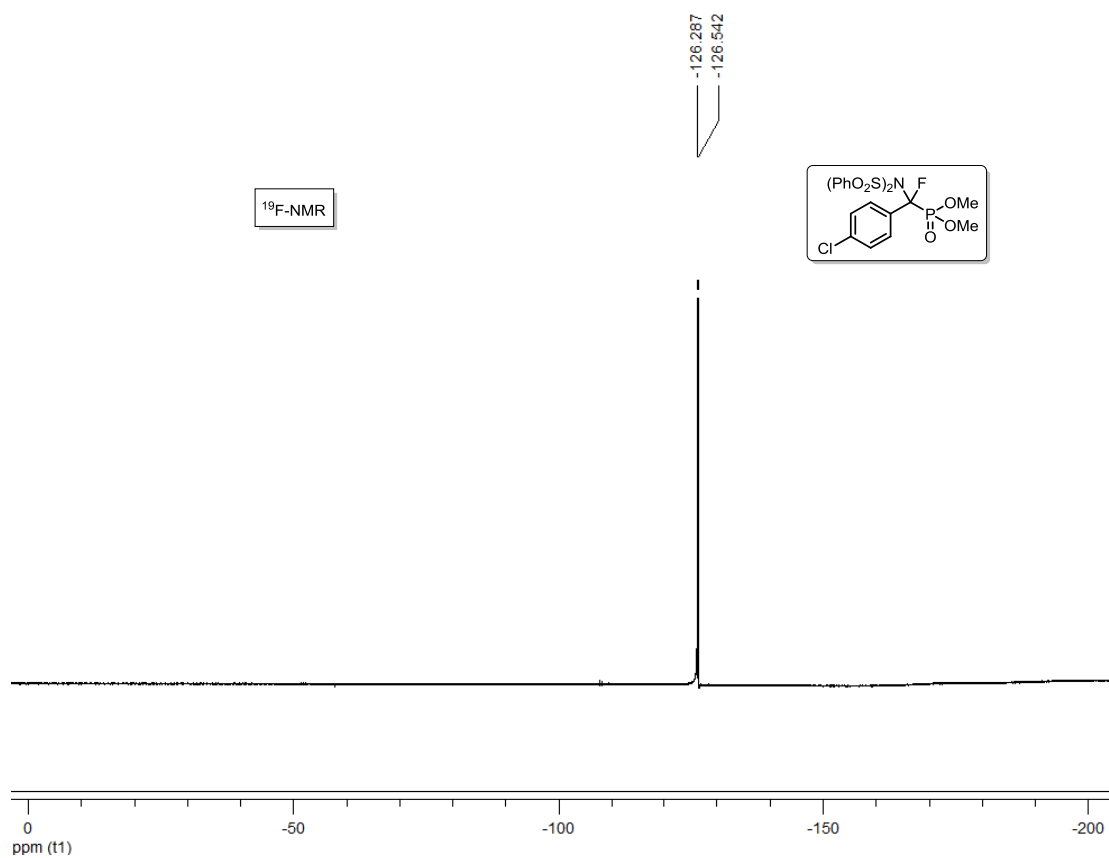
Dimethyl (fluoro(phenyl)(*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phosphonate (**6a**)





Dimethyl ((4-chlorophenyl)fluoro(*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phosphonate (**6b**)

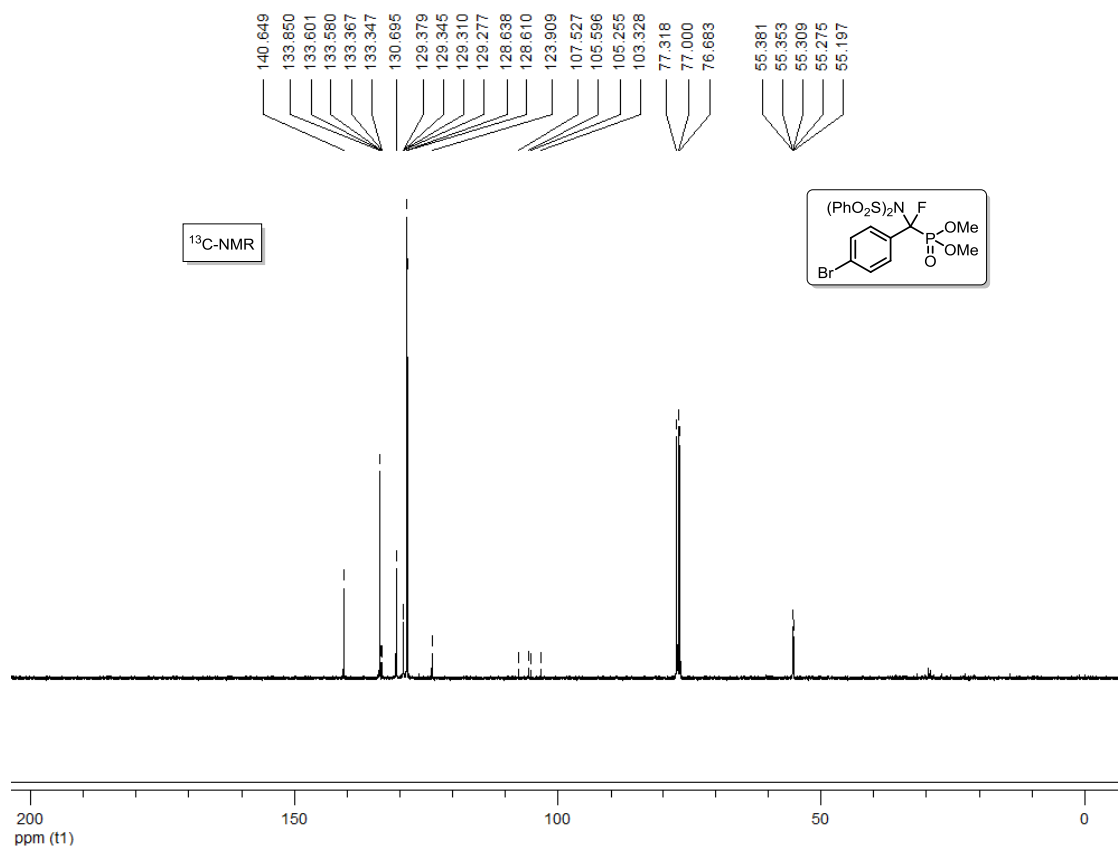


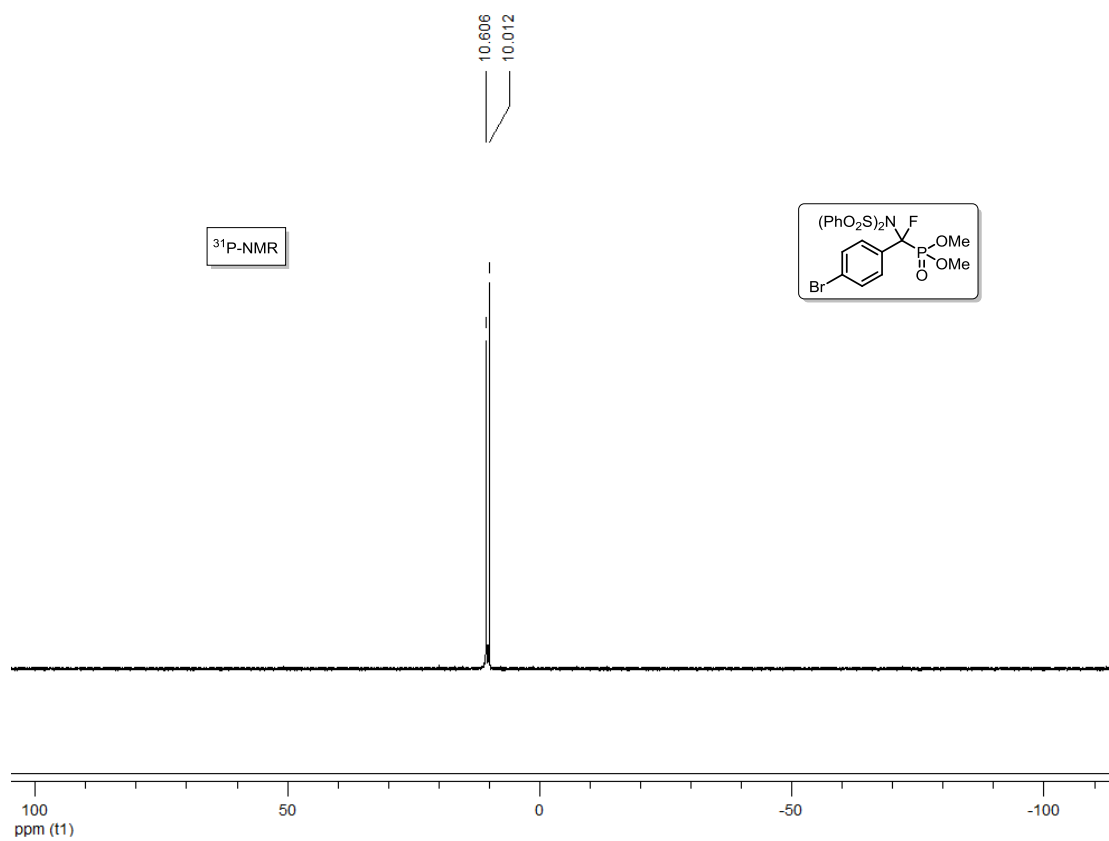
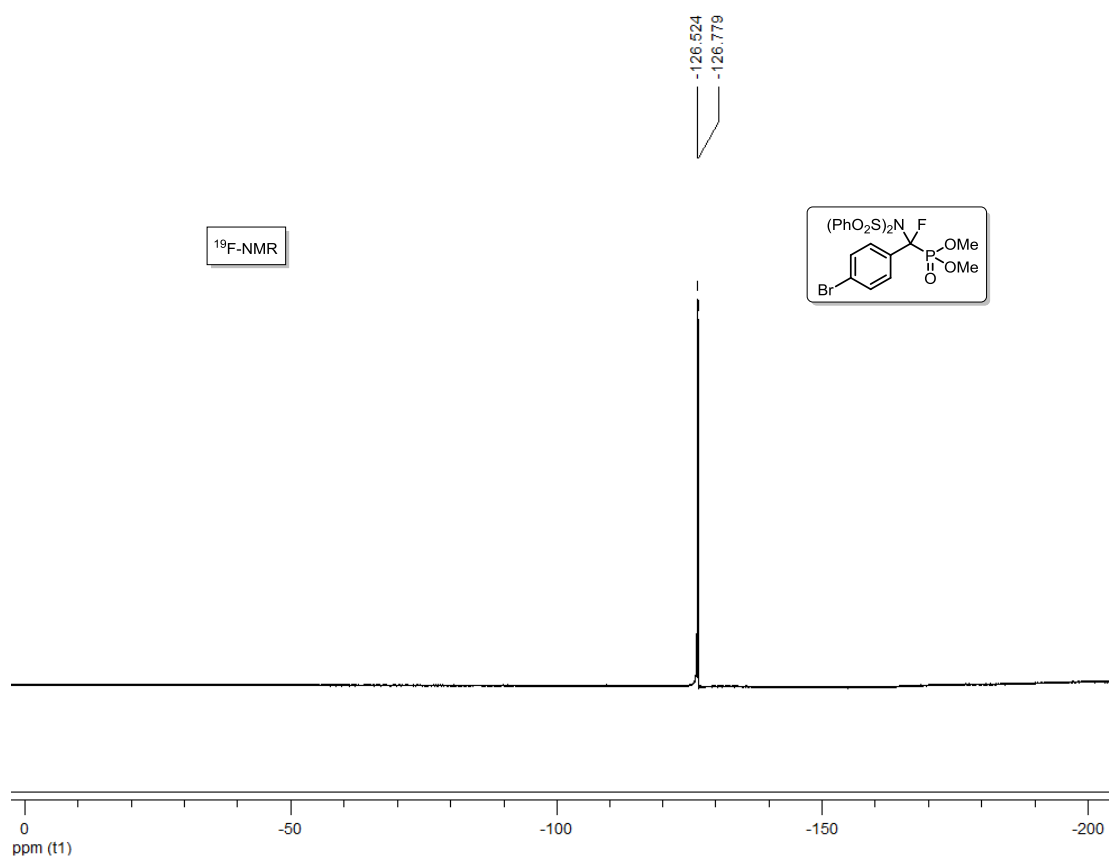


¹H-NMR

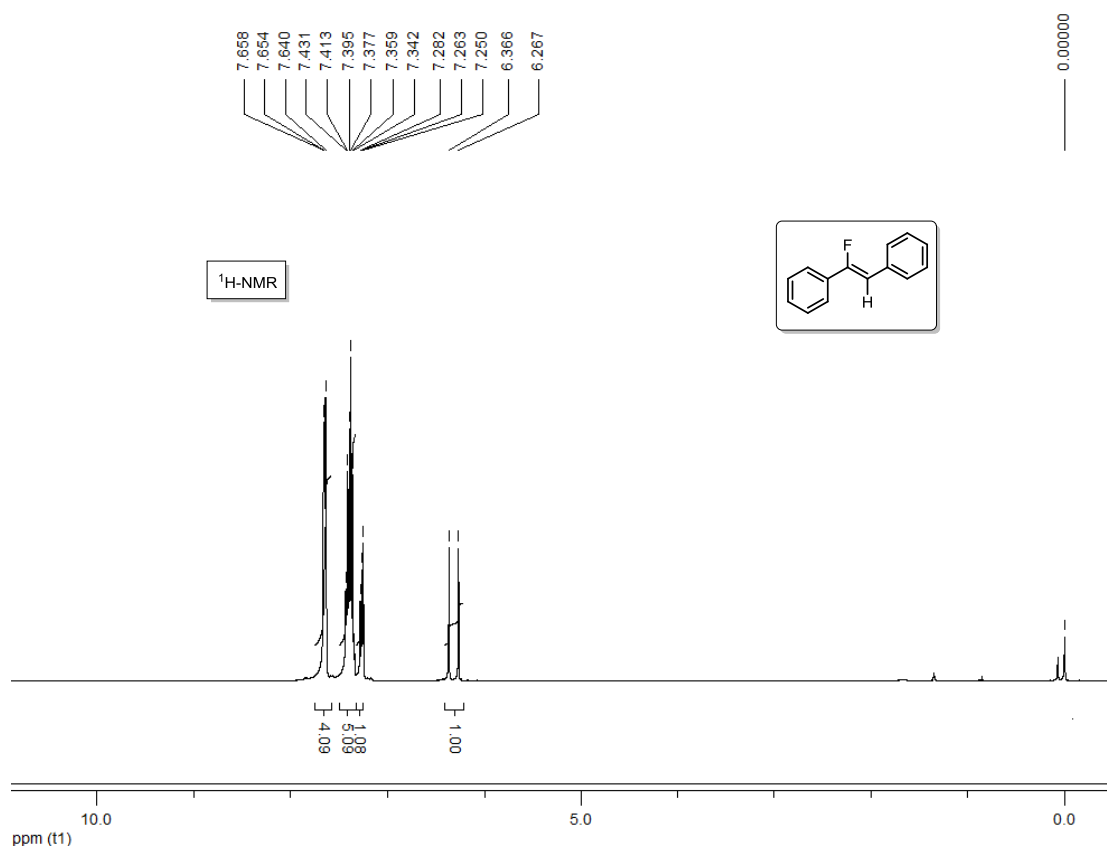
Chemical structure: COOP(=O)(F)C(c1ccc(Br)cc1)N(S(=O)(=O)c2ccccc2)S(=O)(=O)c3ccccc3

Chemical Shift (ppm)	Integration
7.954, 7.935, 7.633, 7.615, 7.596, 7.485, 7.465, 7.446, 7.338, 7.313, 7.309, 7.292, 7.286, 7.262	4.00, 2.04, 4.06, 4.07
3.801, 3.774, 3.516, 3.489	3.03, 3.03

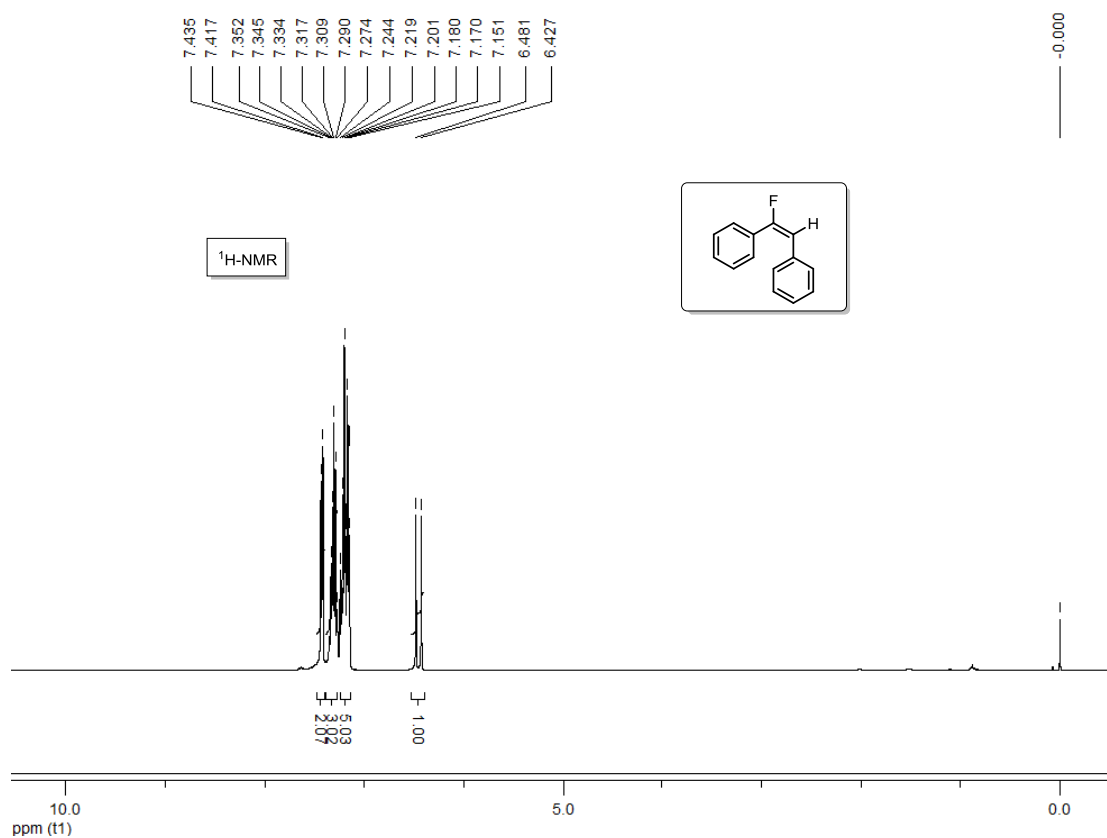




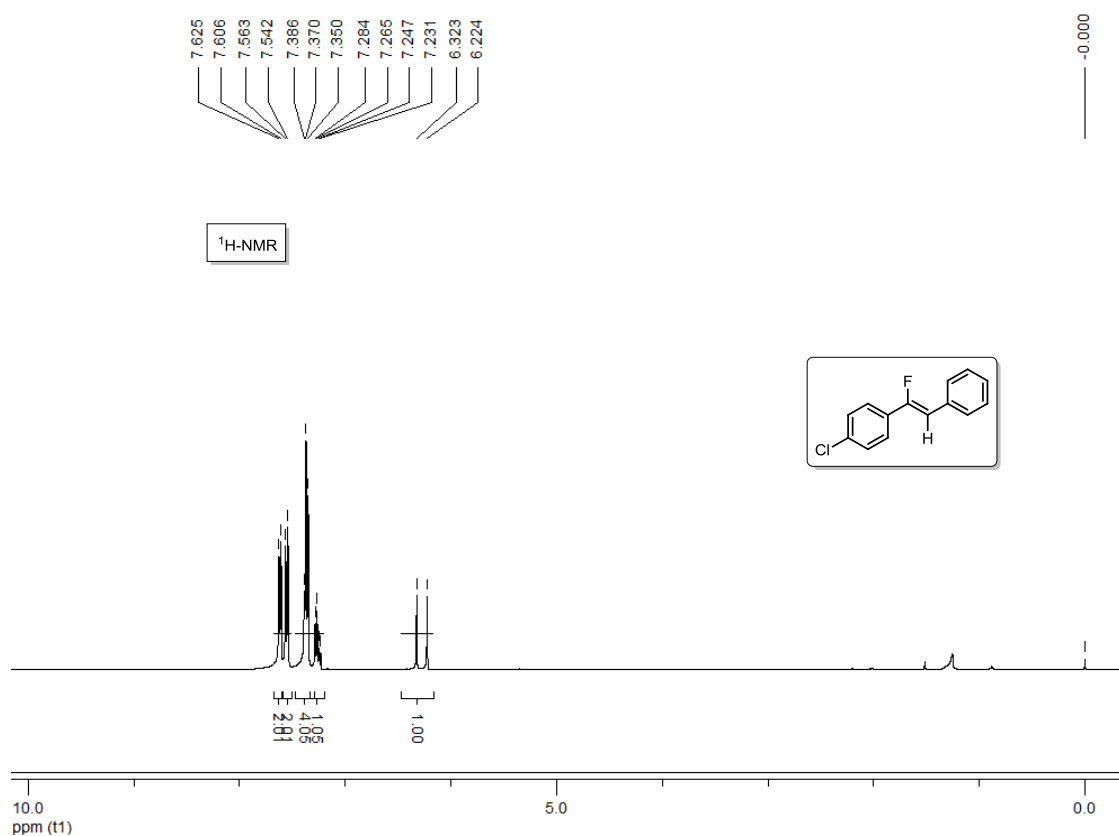
7. ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra for the products 7a-d and 7a'-d'
 (Z)-(1-Fluoroethene-1,2-diyl)dibenzene (7a)



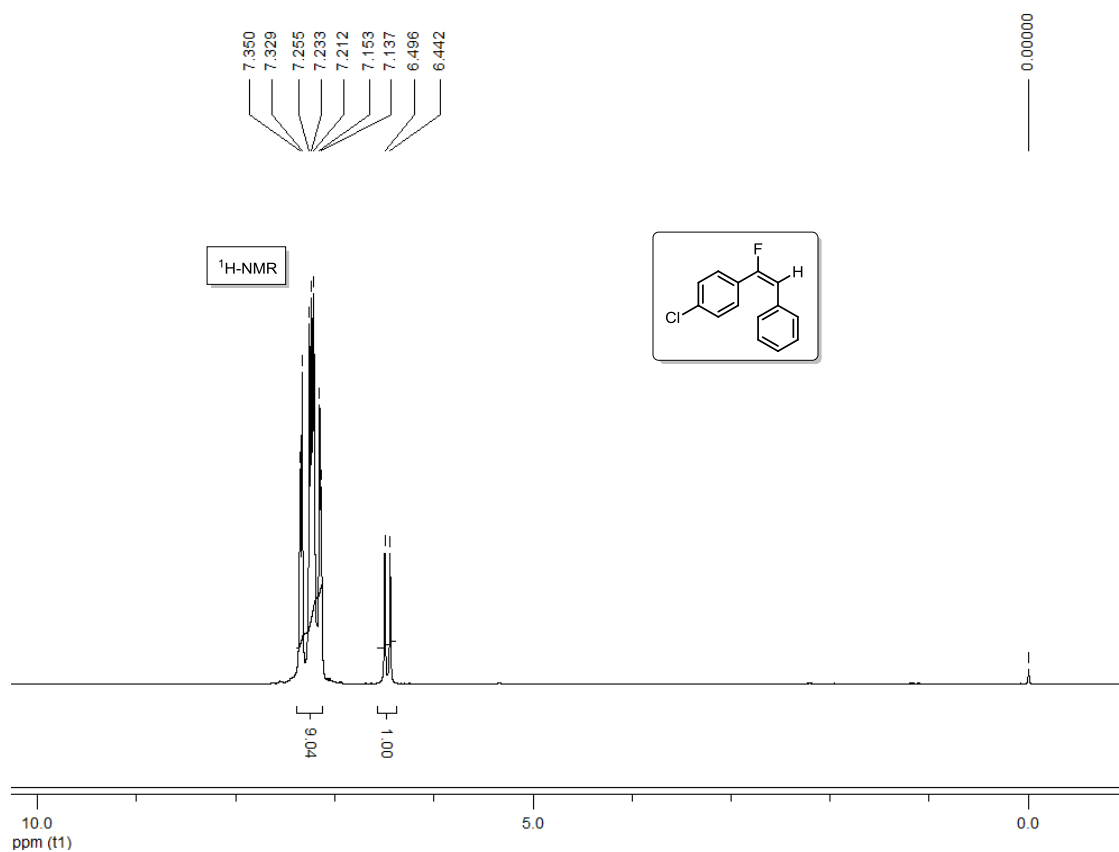
(E)-(1-Fluoroethene-1,2-diyl)dibenzene (7a')



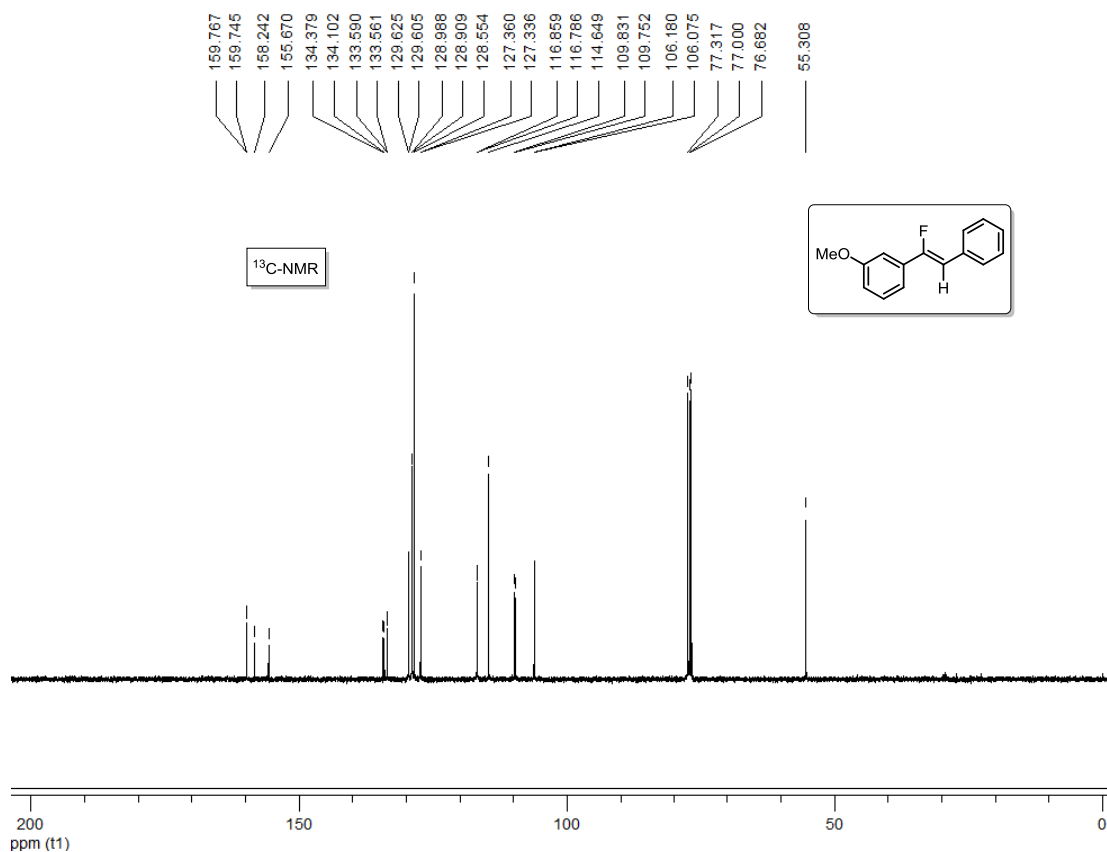
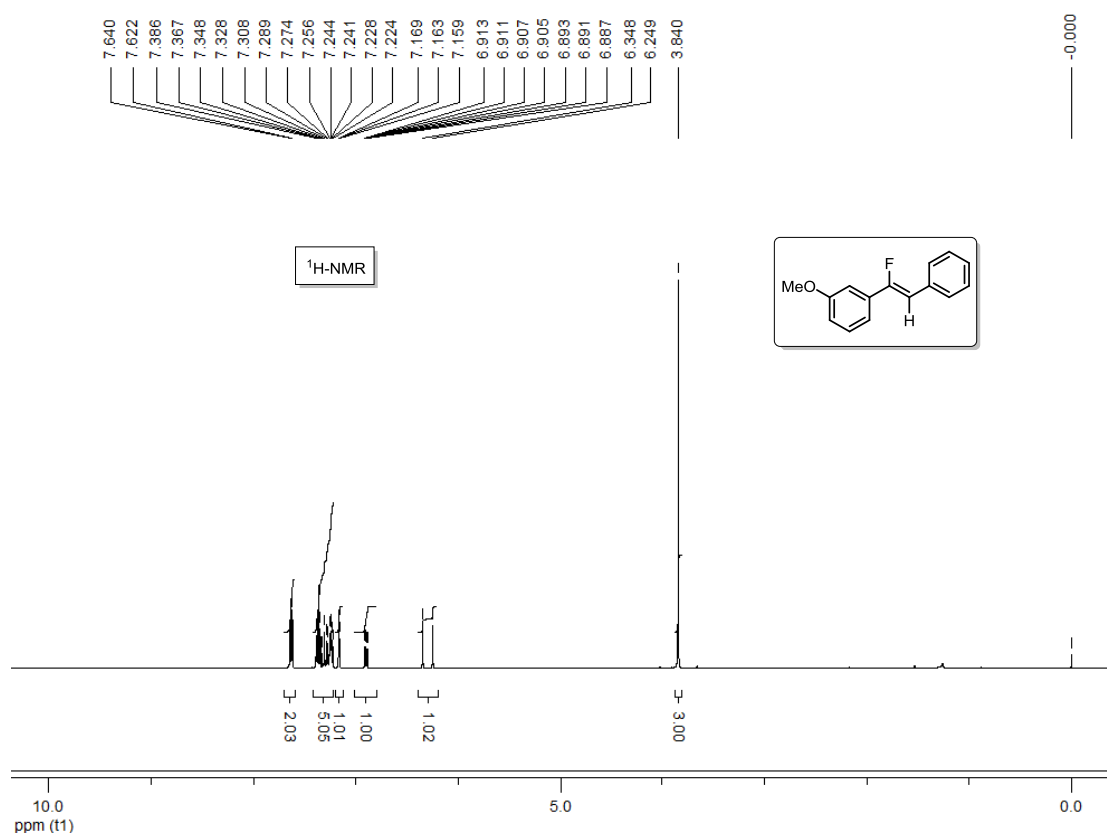
(Z)-1-Chloro-4-(1-fluoro-2-phenylvinyl)benzene (**7b**)

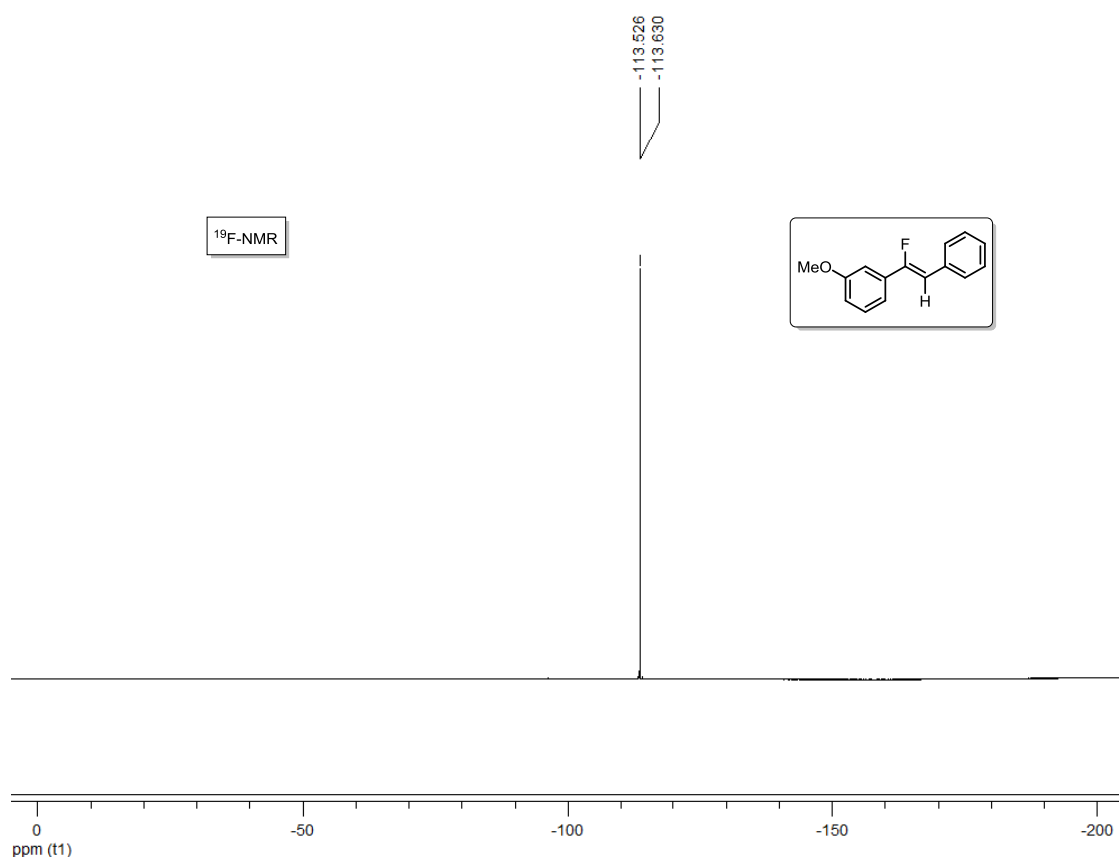


(E)-1-Chloro-4-(1-fluoro-2-phenylvinyl)benzene (**7b'**)

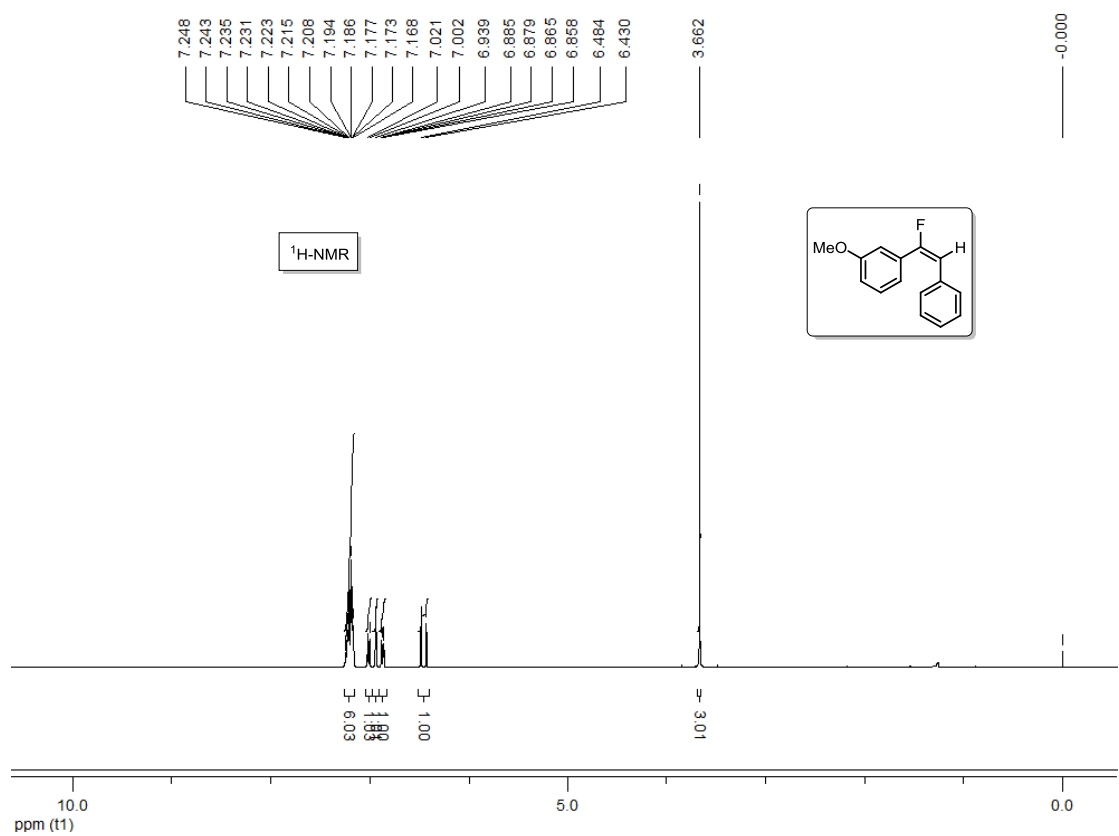


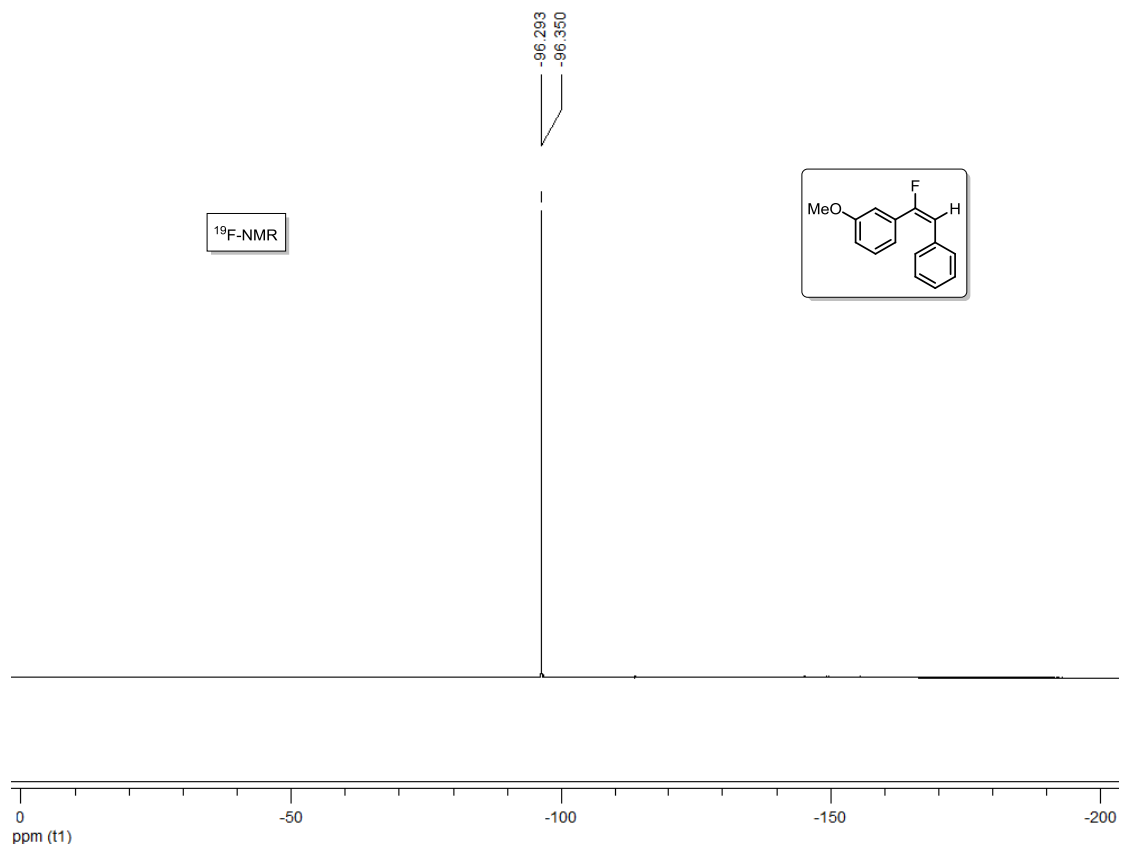
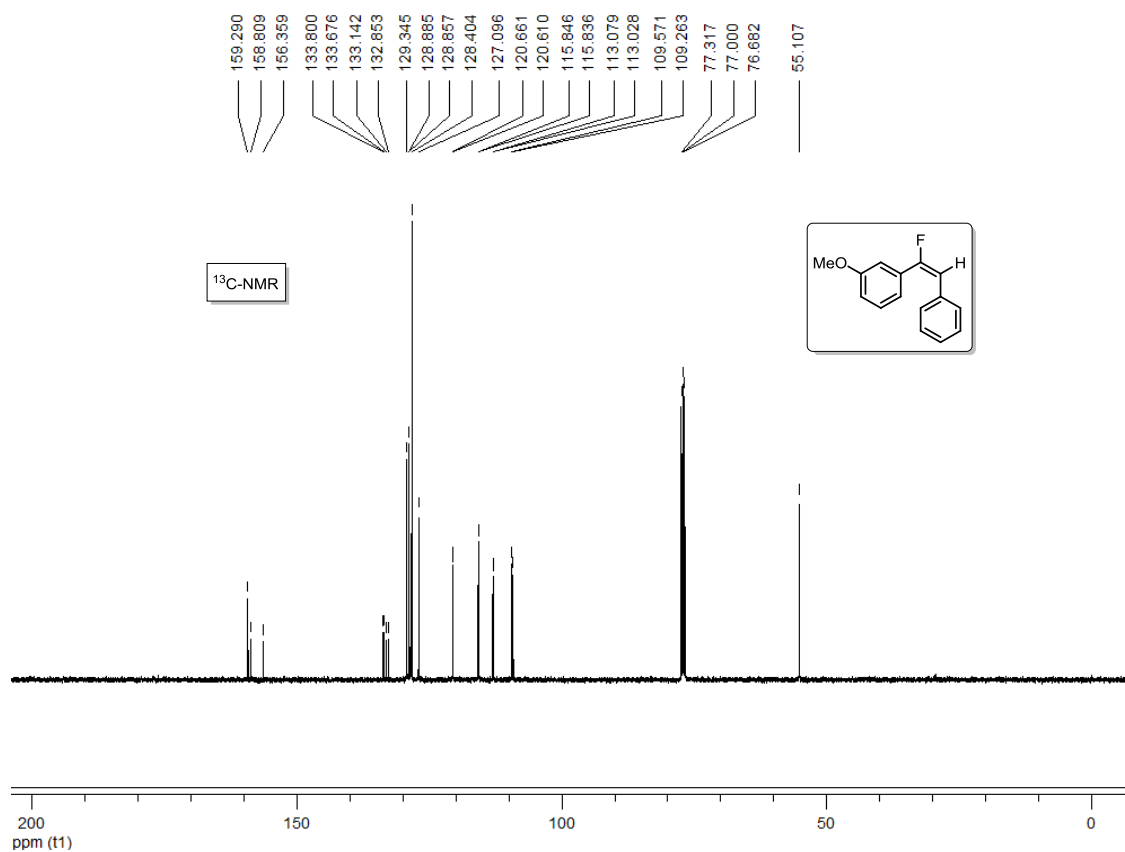
(Z)-1-(1-Fluoro-2-phenylvinyl)-3-methoxybenzene (7c)



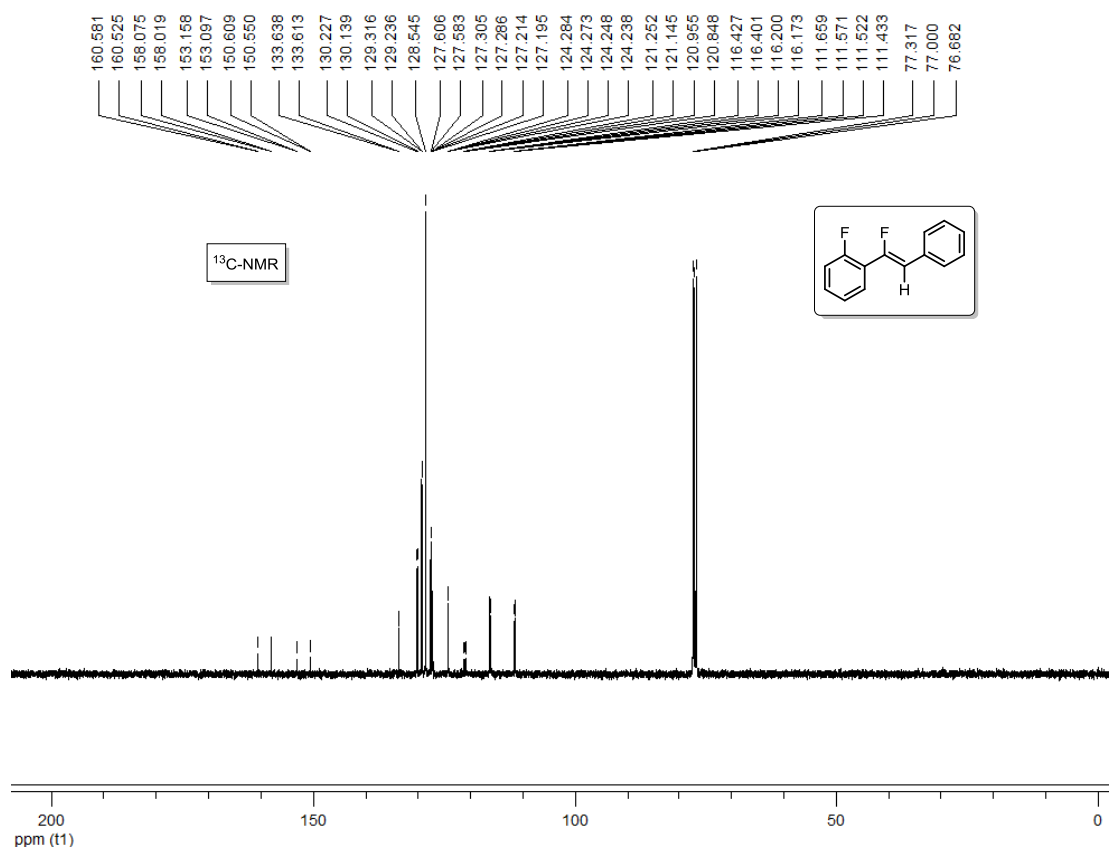
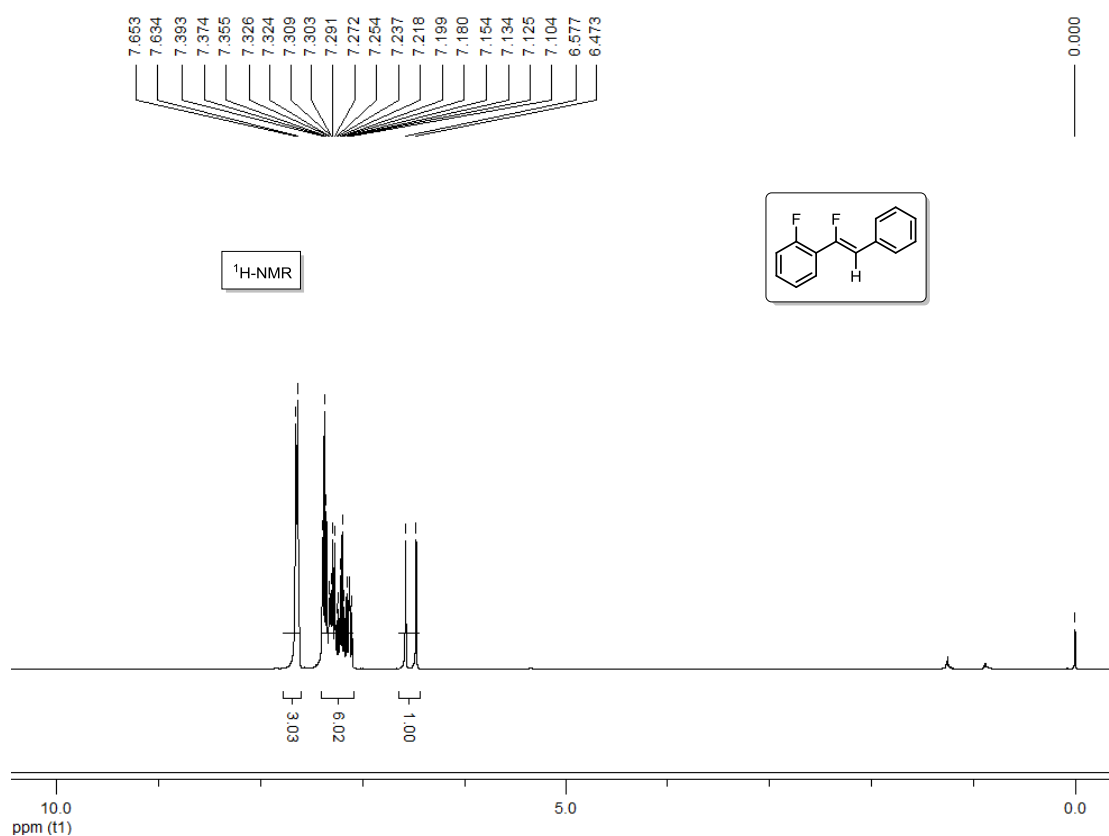


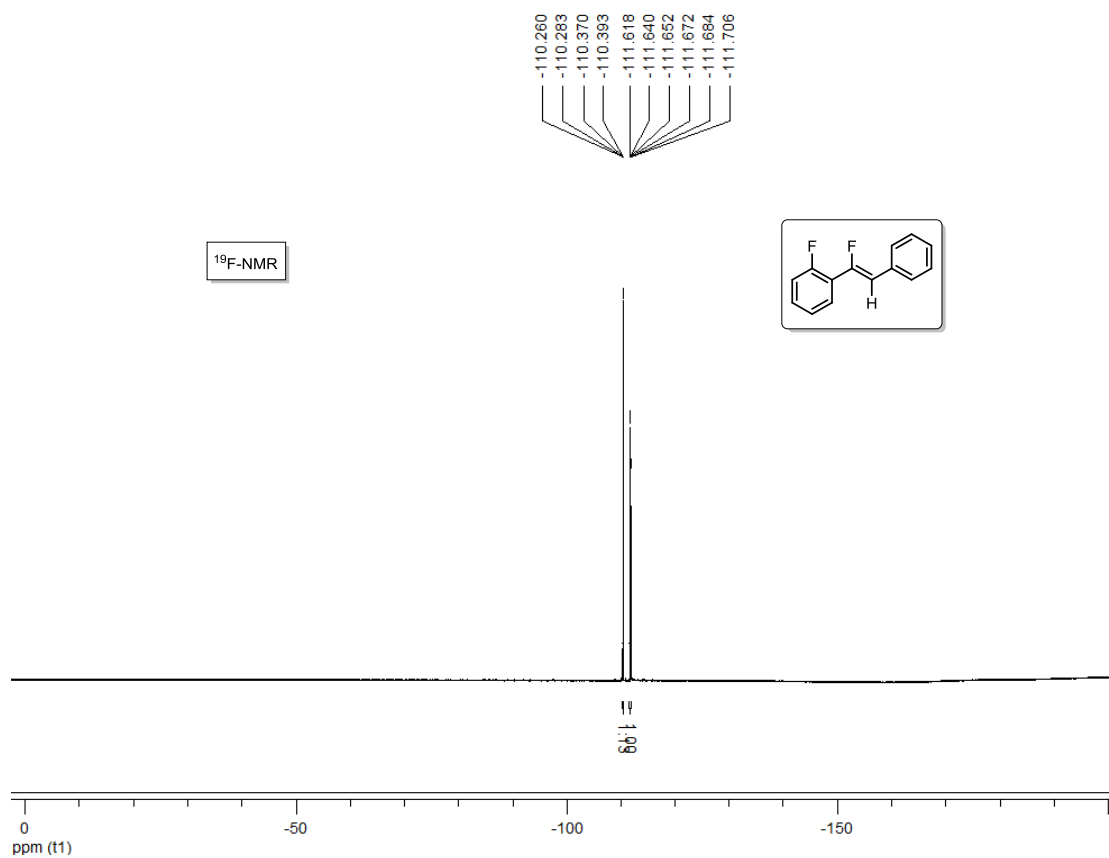
(*E*)-1-(1-Fluoro-2-phenylvinyl)-3-methoxybenzene (**7c'**)





(Z)-1-Fluoro-2-(1-fluoro-2-phenylvinyl)benzene (**7d**)





(*E*)-1-Fluoro-2-(1-fluoro-2-phenylvinyl)benzene (**7d'**)

