Supporting Information for

Copper-catalyzed Perfluoroalkylation of Allyl Phosphates with Stable Perfluoroalkylzinc Reagents

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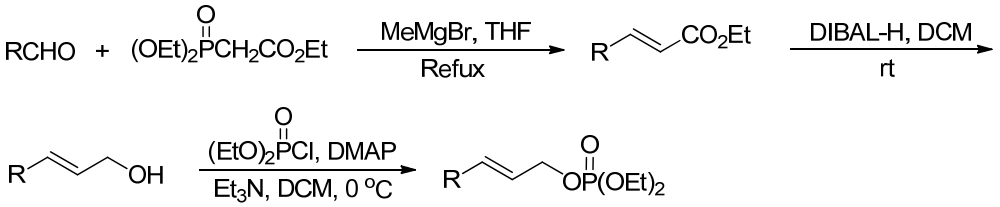
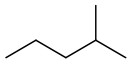
List of Content

Preparation of compounds (*E*)-(1l, 1j, 1o, 1h, 1m, 1a, 1n, 1g, 1i).



R = $CH_3(CH_2)_{10}$, (*E*)-**1a**, 74%

R =  (*E*)-**1g**,73%

R = Cy, (*E*)-**1h**, 76%

R = $PhCH_2$, (*E*)-**1i**, 84%

R = $Ph(CH_2)_2$, (*E*)-**1j**, 71%

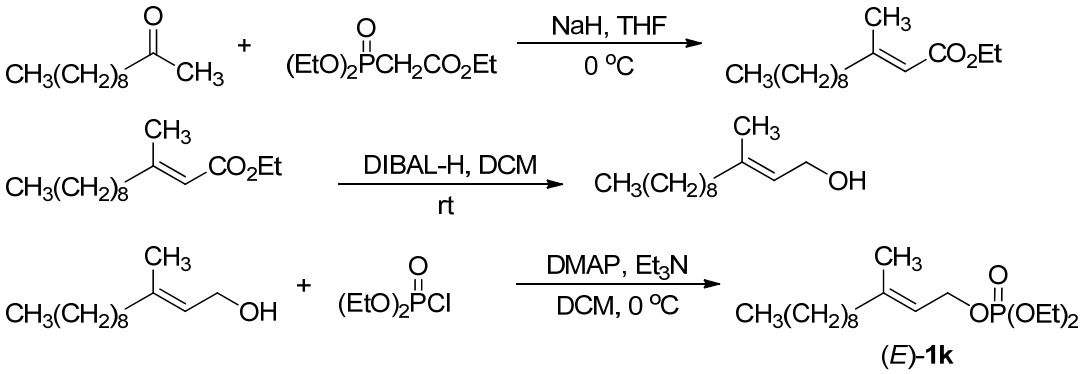
R = Ph, (*E*)-**1l**, 76%

R = pMePh, (*E*)-**1m**, 83%

R = p-*t*BuPh, (*E*)-**1n**, 73%

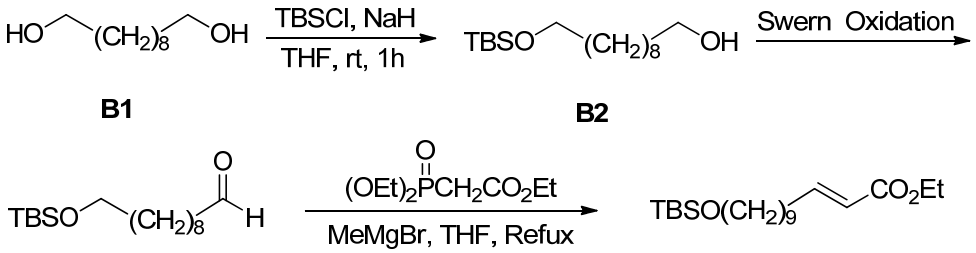
R = mMeOPh, (*E*)-**1o**, 82%

Preparation of compound (*E*)-1k.



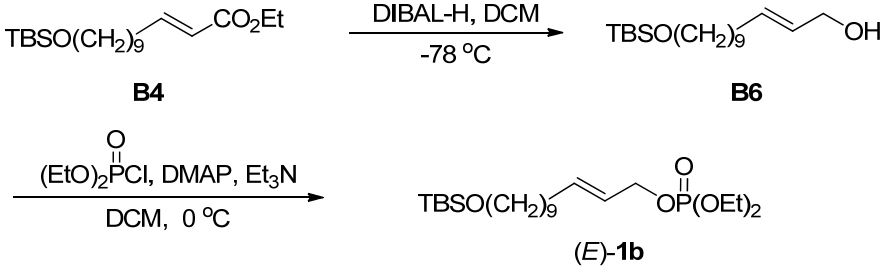
(*E*)-**1k**

Preparation of compound B4.



B1 **B2** **B3** **B4**

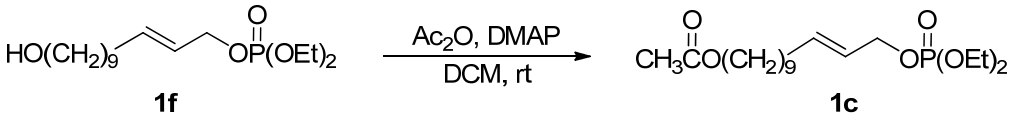
Preparation of compound (*E*)-1b



B4 **B6**

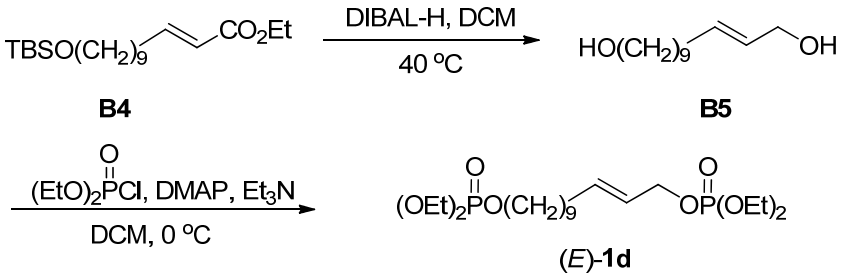
(*E*)-**1b**

Preparation of compound (*E*)-1c



1f **1c**

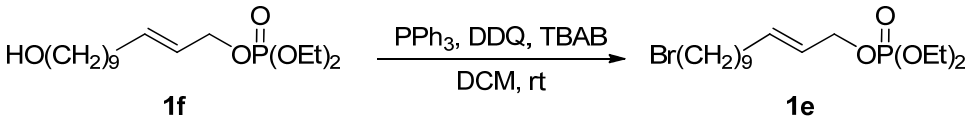
Preparation of compound (*E*)-1d



B4 **B5**

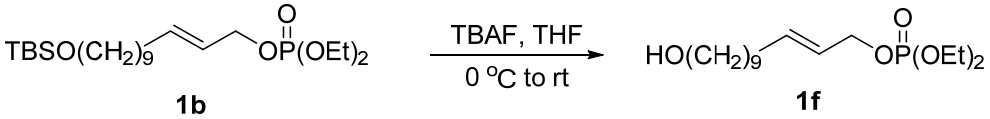
(*E*)-**1d**

Preparation of compound (*E*)-1e



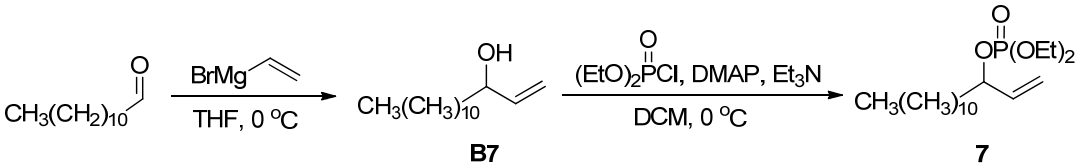
1f **1e**

Preparation of compound (*E*)-1f



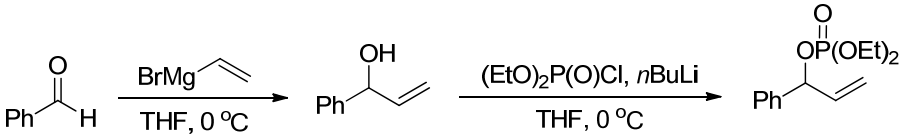
1b **1f**

Preparation of compound 7



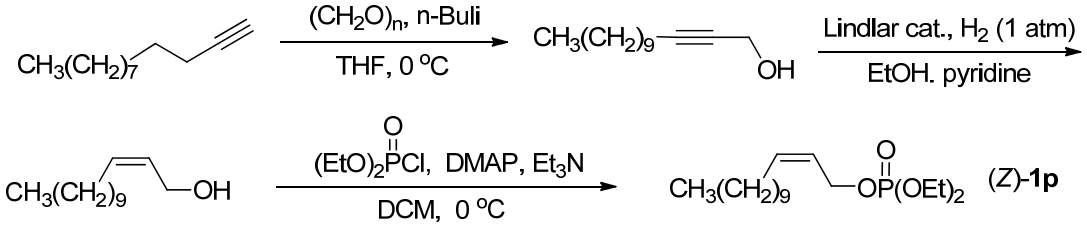
B7 **7**

Preparation of compound 8



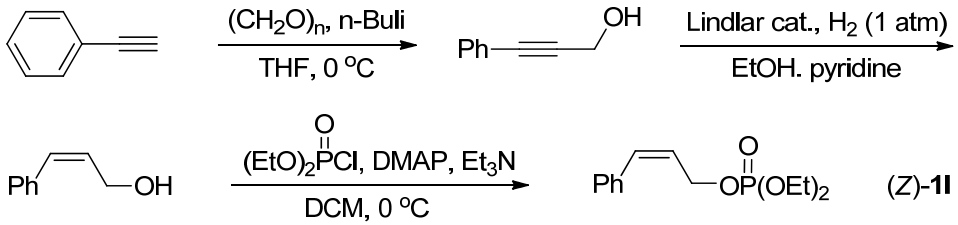
B8 **8**

Preparation of (Z)-diethyl tridec-2-en-1-yl phosphate (*Z*)-1p.



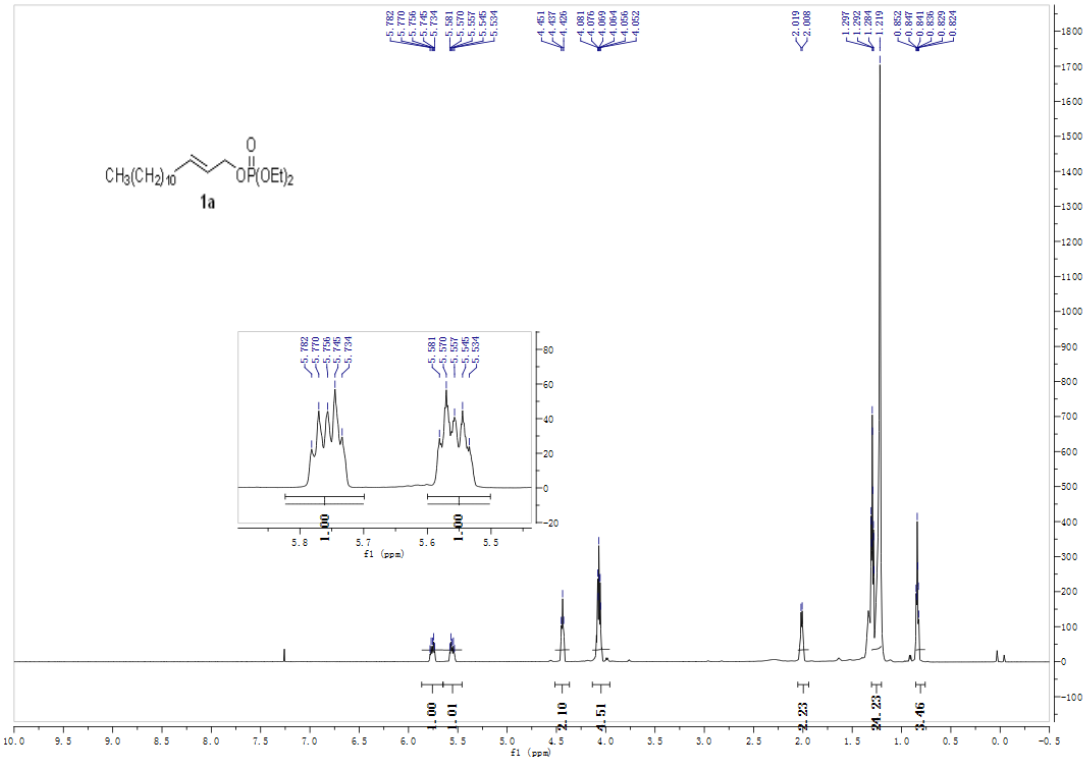
(*Z*)-**1p**

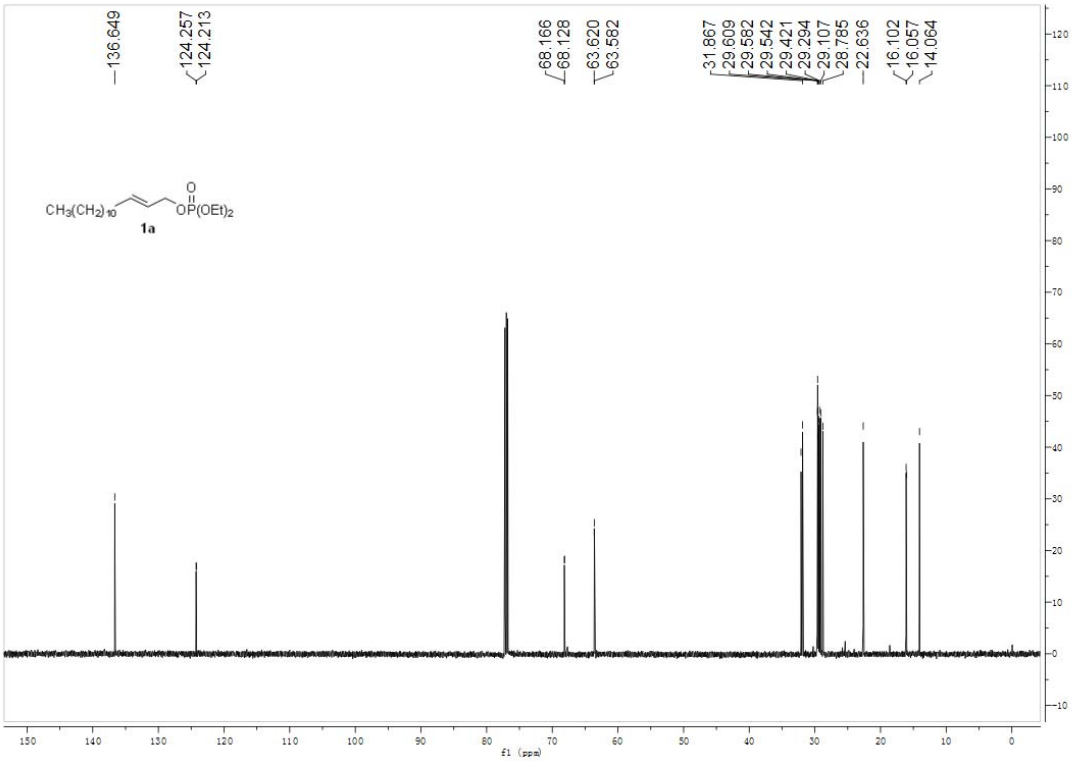
Preparation of compounds (*Z*)-diethyl (3-phenylallyl) phosphate (*Z*)-1l.



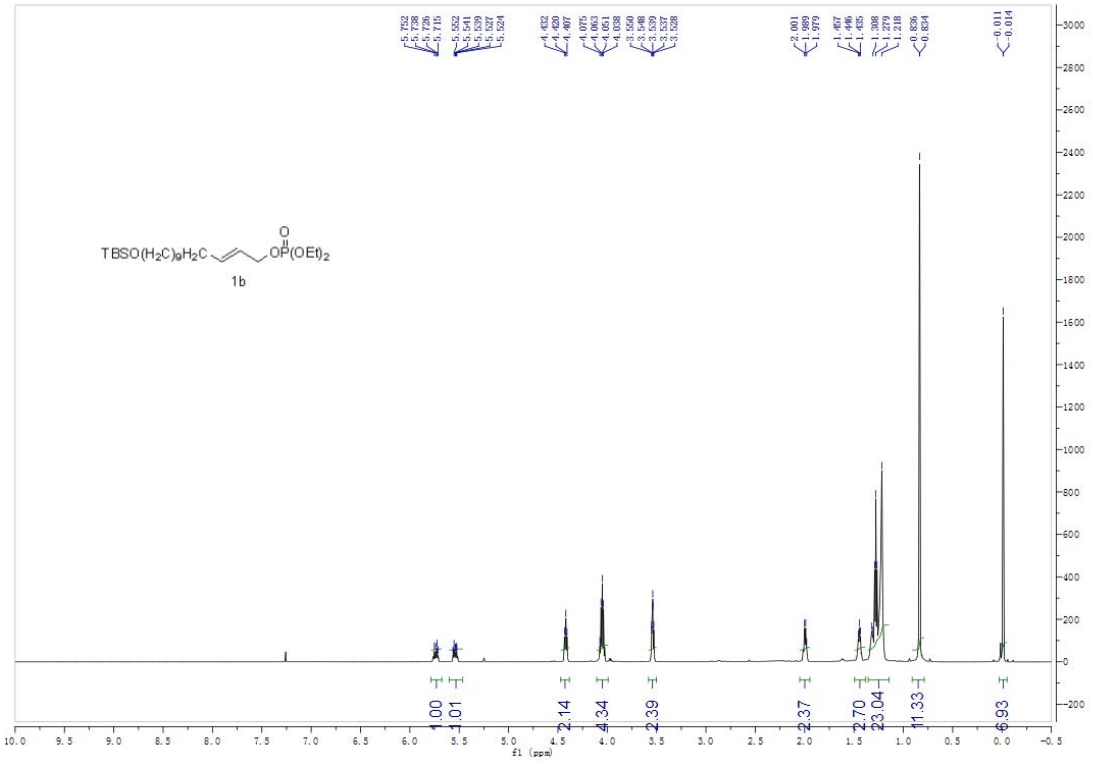
(*Z*)-**1l**

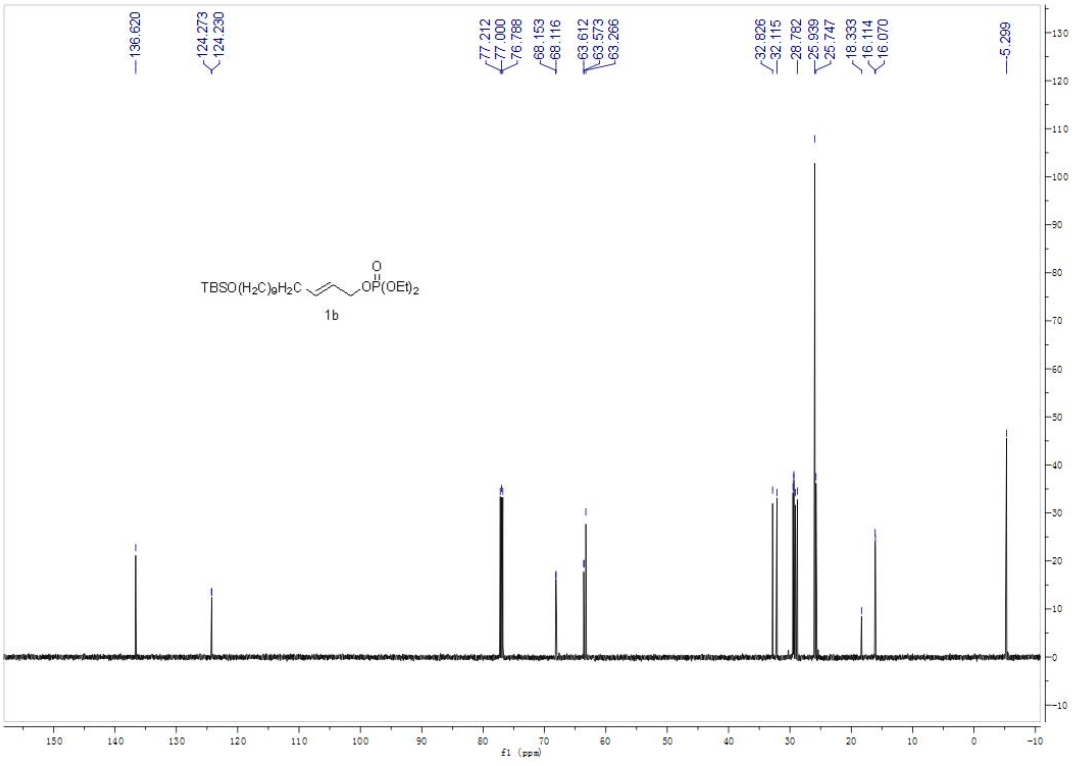
(*E*)-diethyl tetradec-2-en-1-yl phosphate ((*E*)-1a)



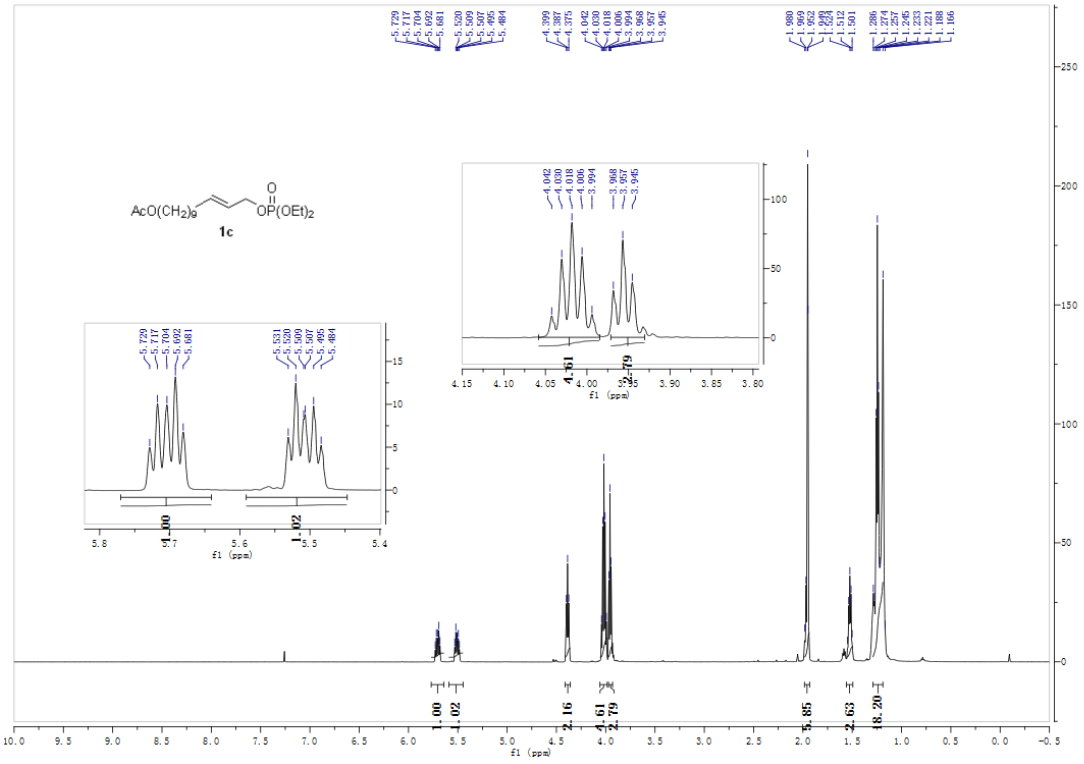


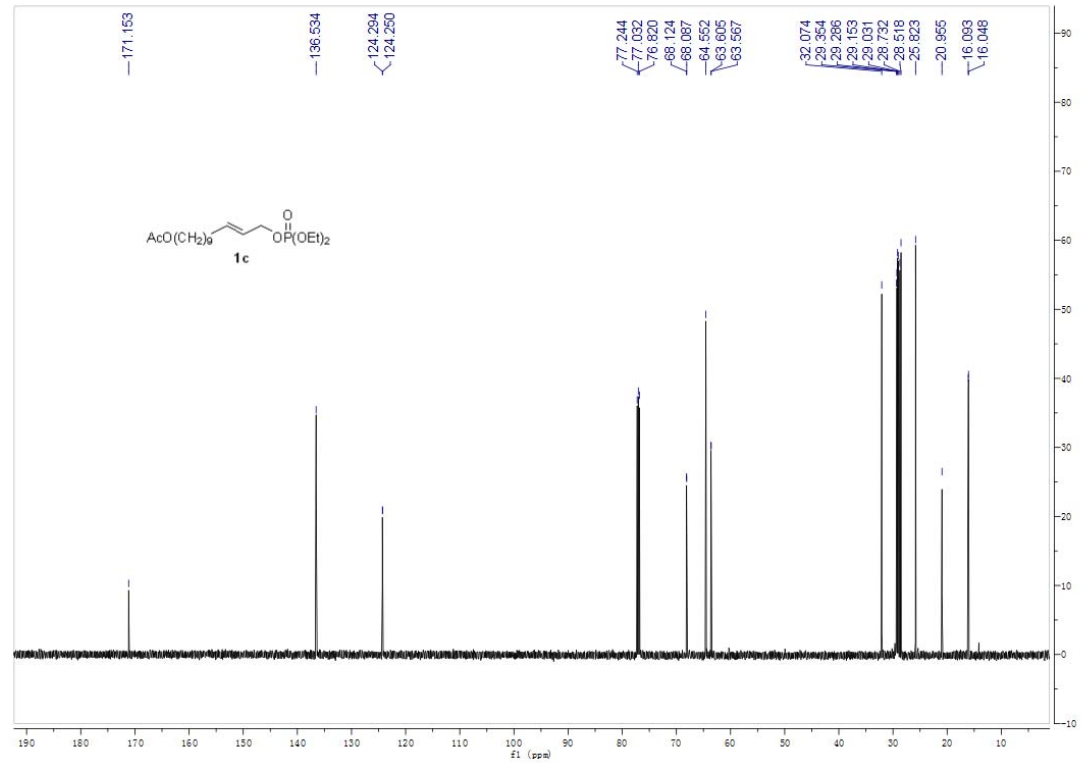
(*E*)-12-((tert-butyldimethylsilyl)oxy)dodec-2-en-1-yl diethyl phosphate ((*E*)-1b)



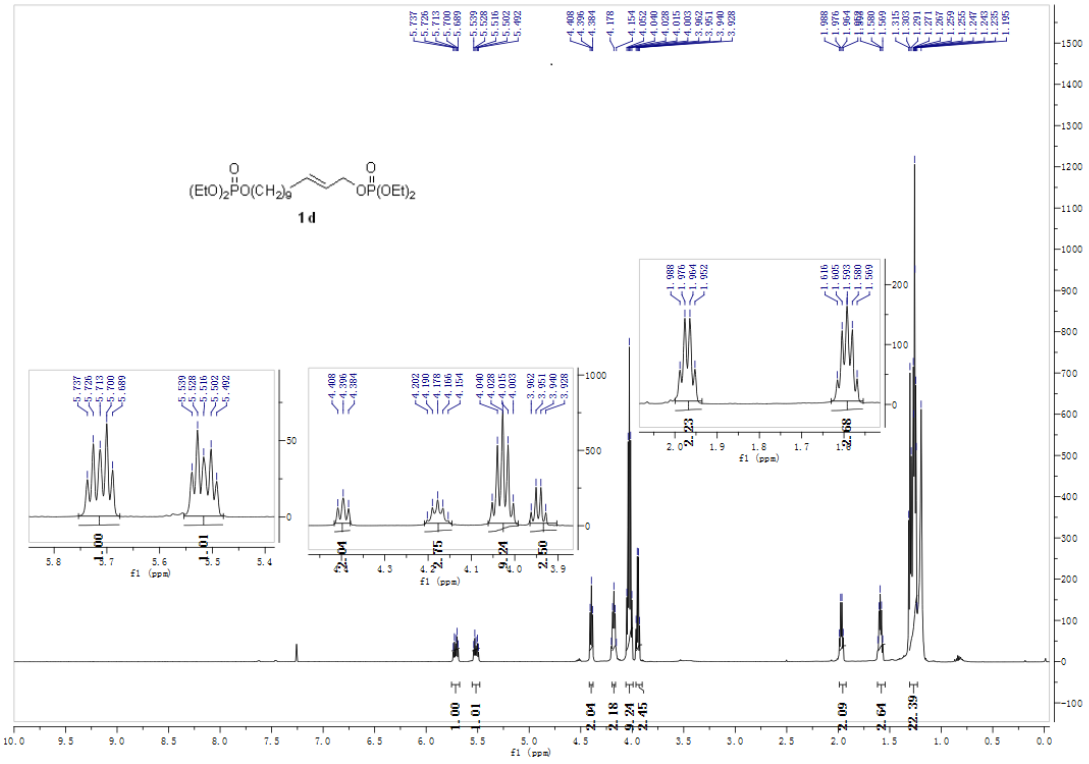


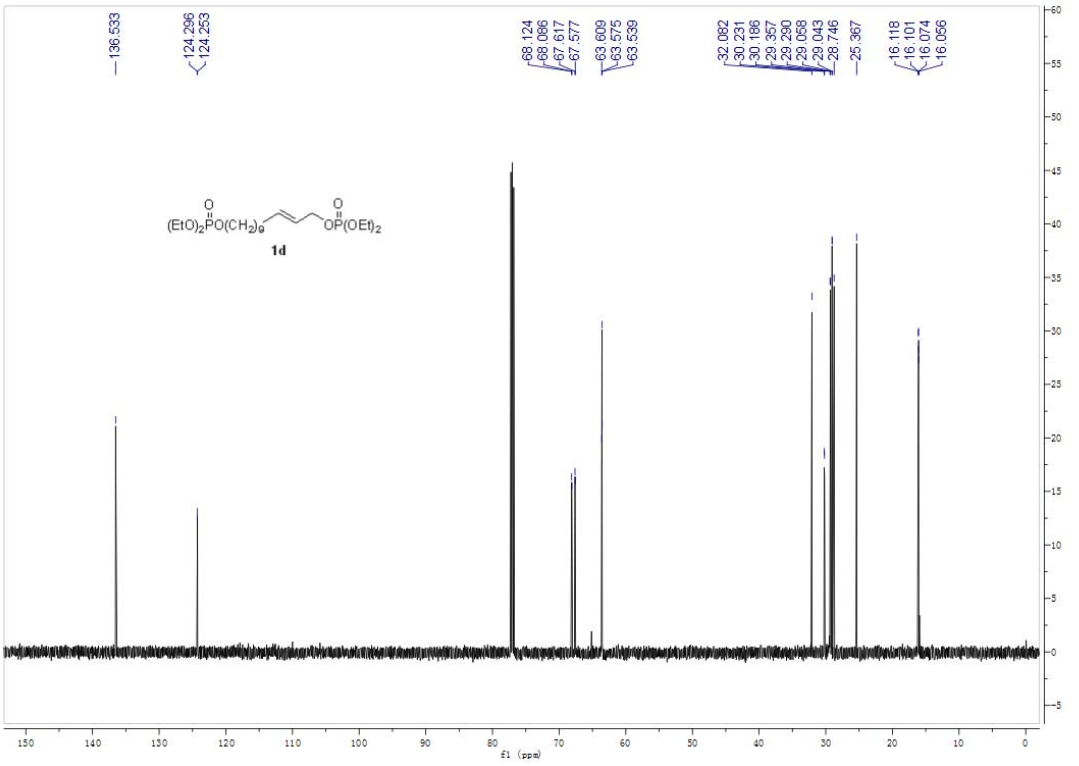
(*E*)-12-((diethoxyphosphoryl)oxy)dodec-10-en-1-yl acetate ((*E*)-1c)



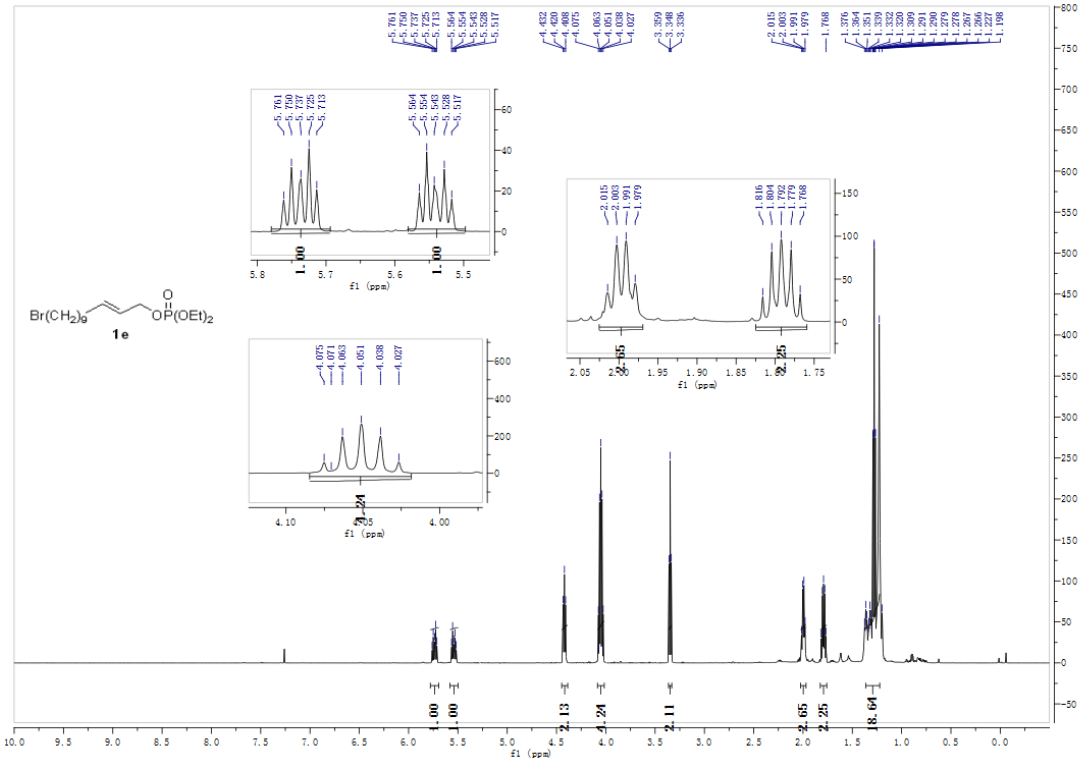


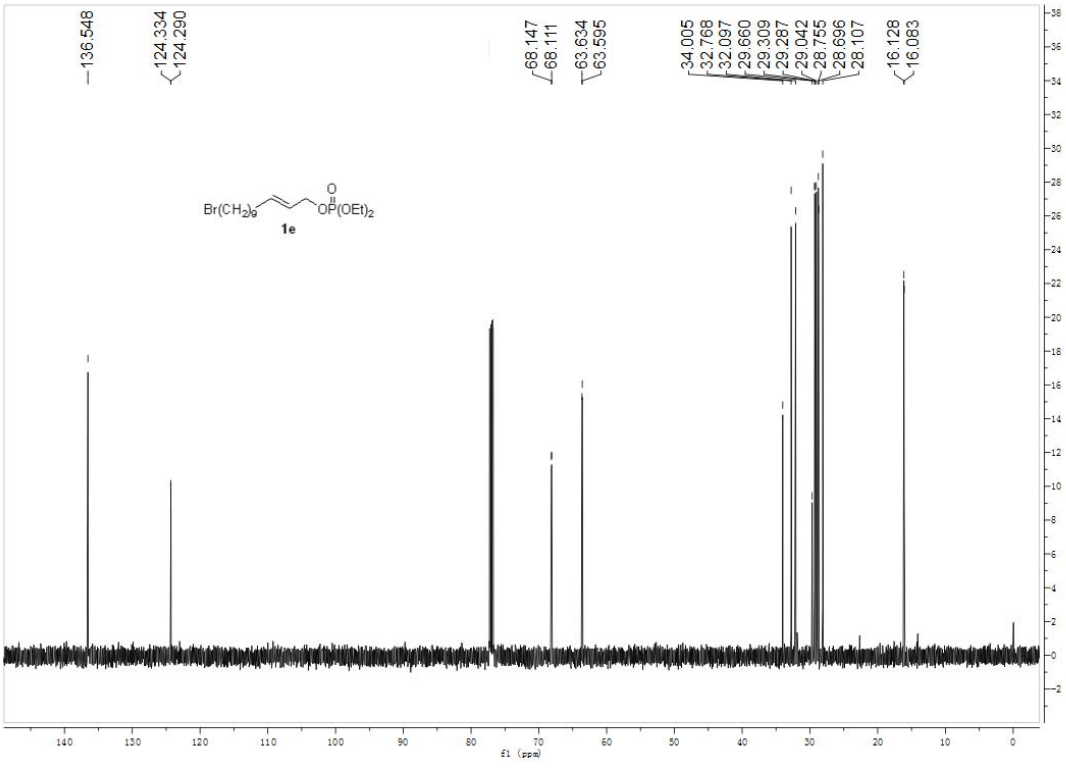
(*E*)-dodec-2-ene-1,12-diyl tetraethyl bis(phosphate) ((*E*)-1d)



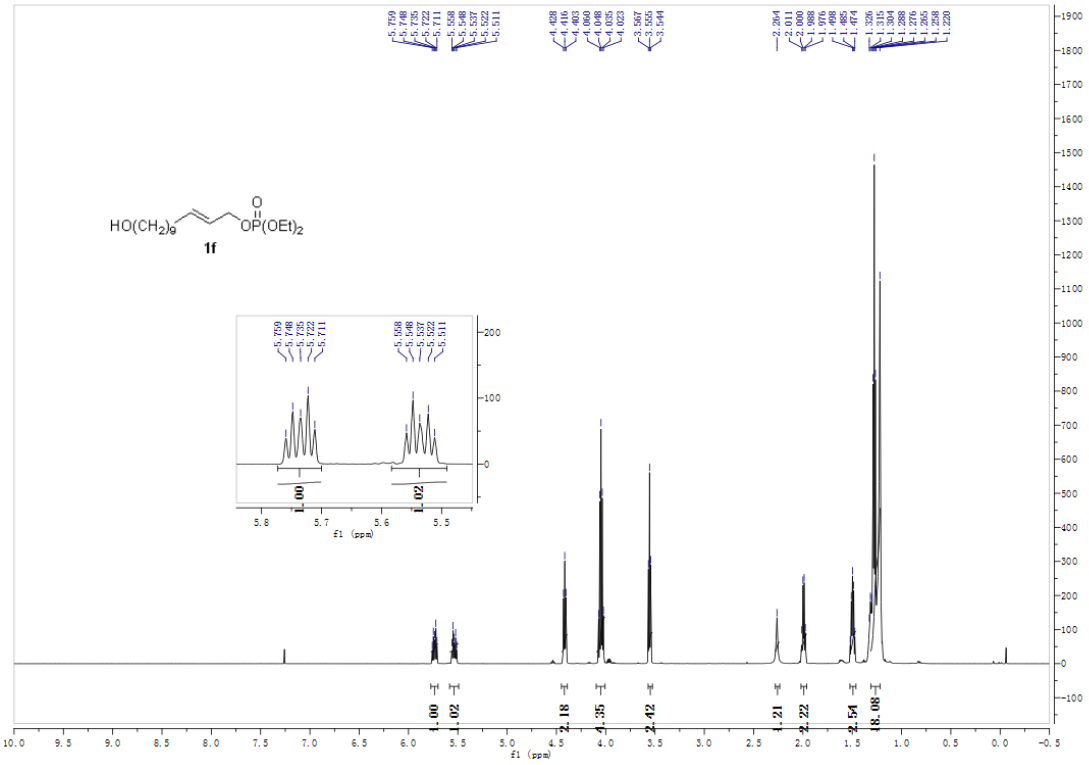


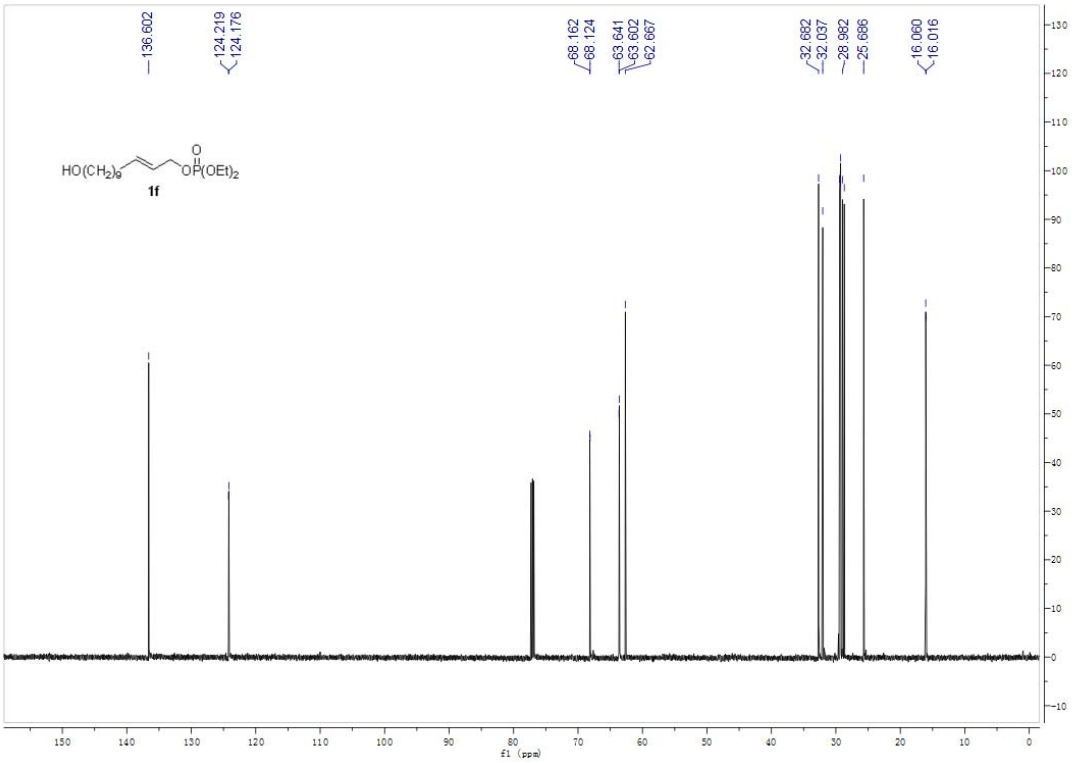
(*E*)-12-bromododec-2-en-1-yl diethyl phosphate ((*E*)-1e)



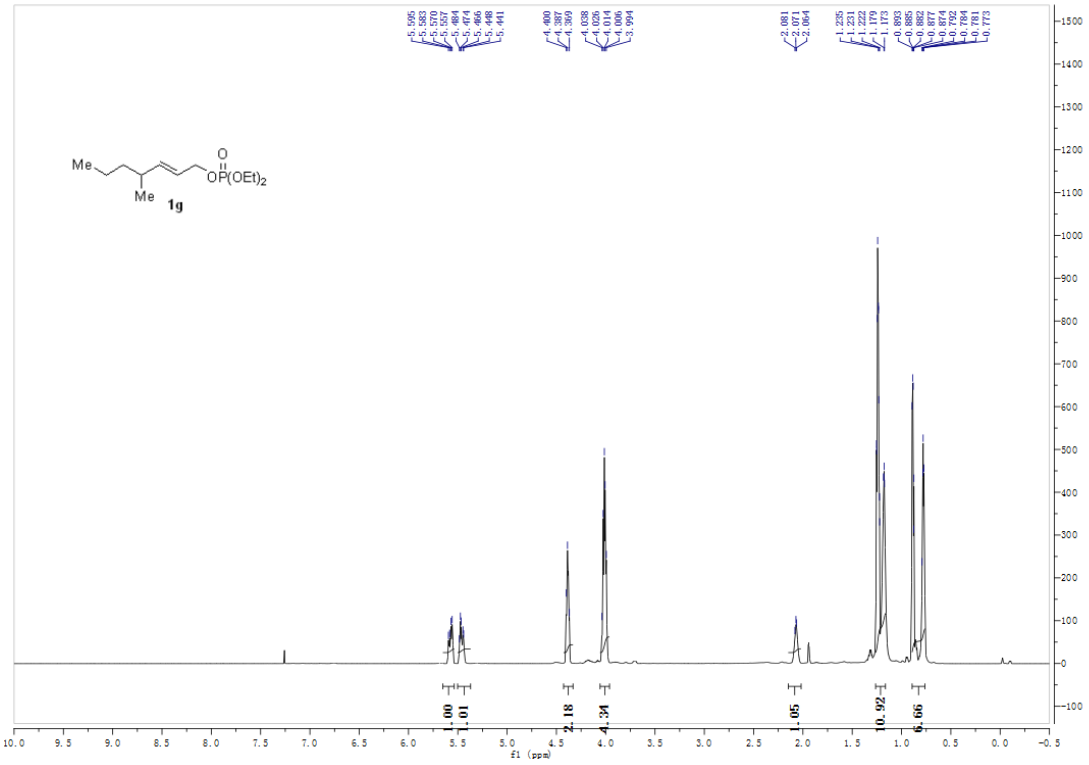


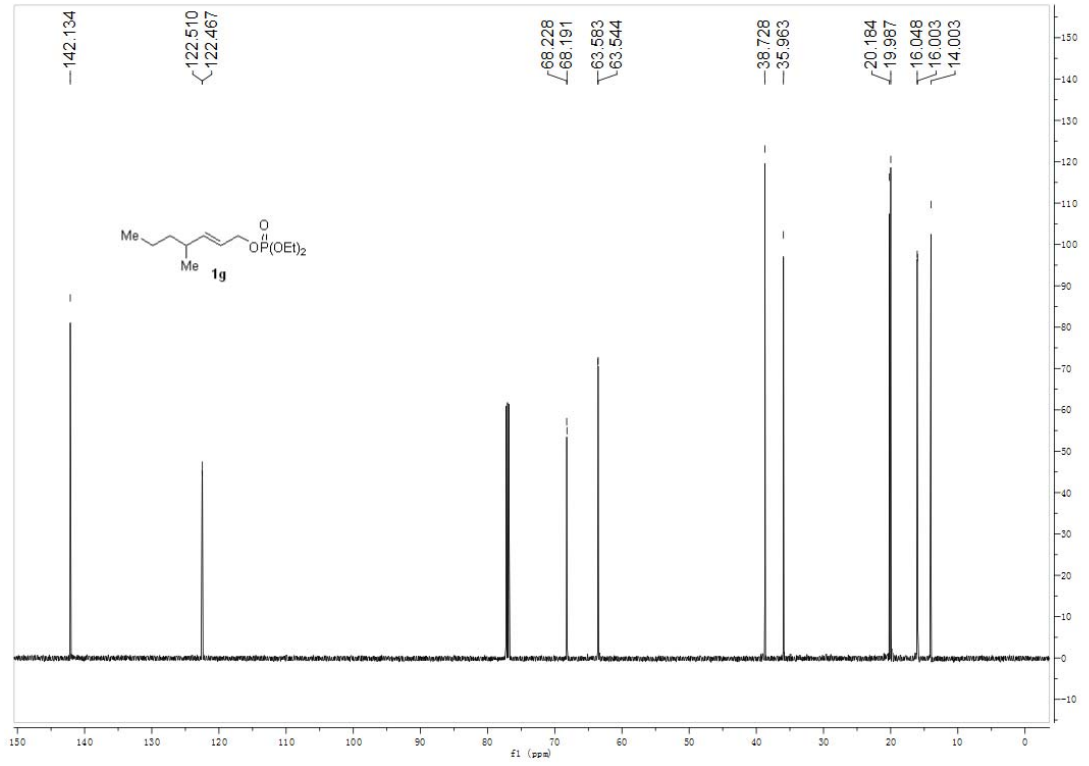
(*E*)-diethyl (12-hydroxydodec-2-en-1-yl) phosphate ((*E*)-1f)



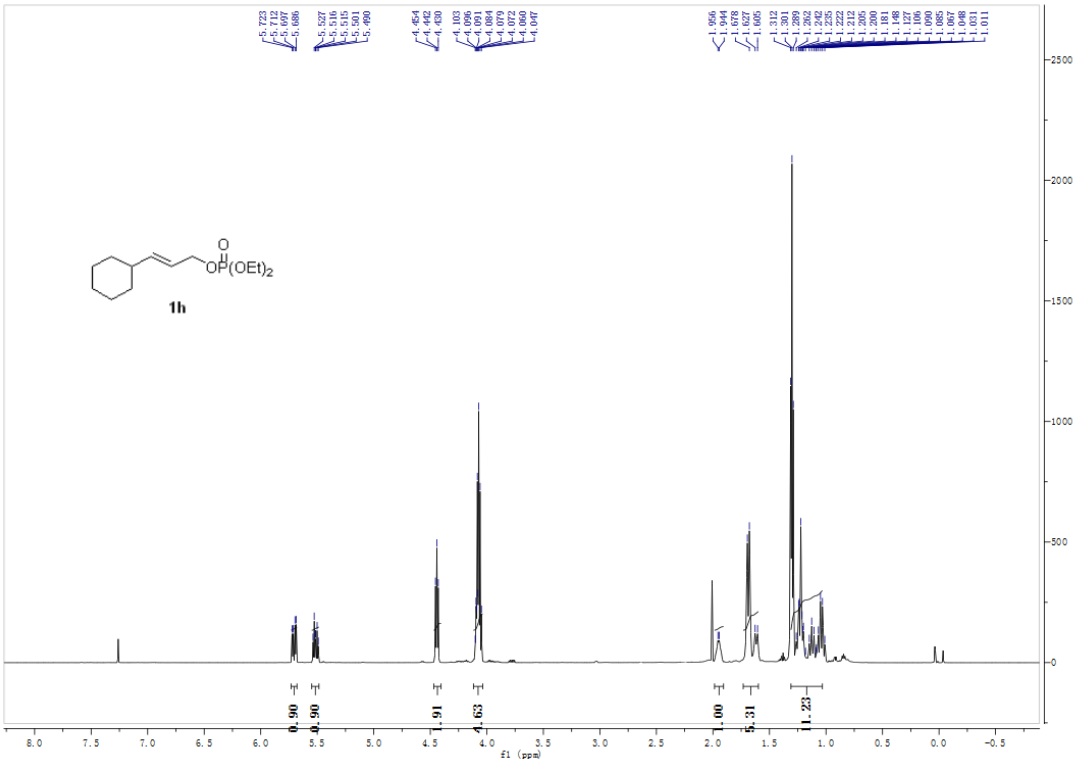


(*E*)-diethyl (4-methylhept-2-en-1-yl) phosphate ((*E*)-1g)

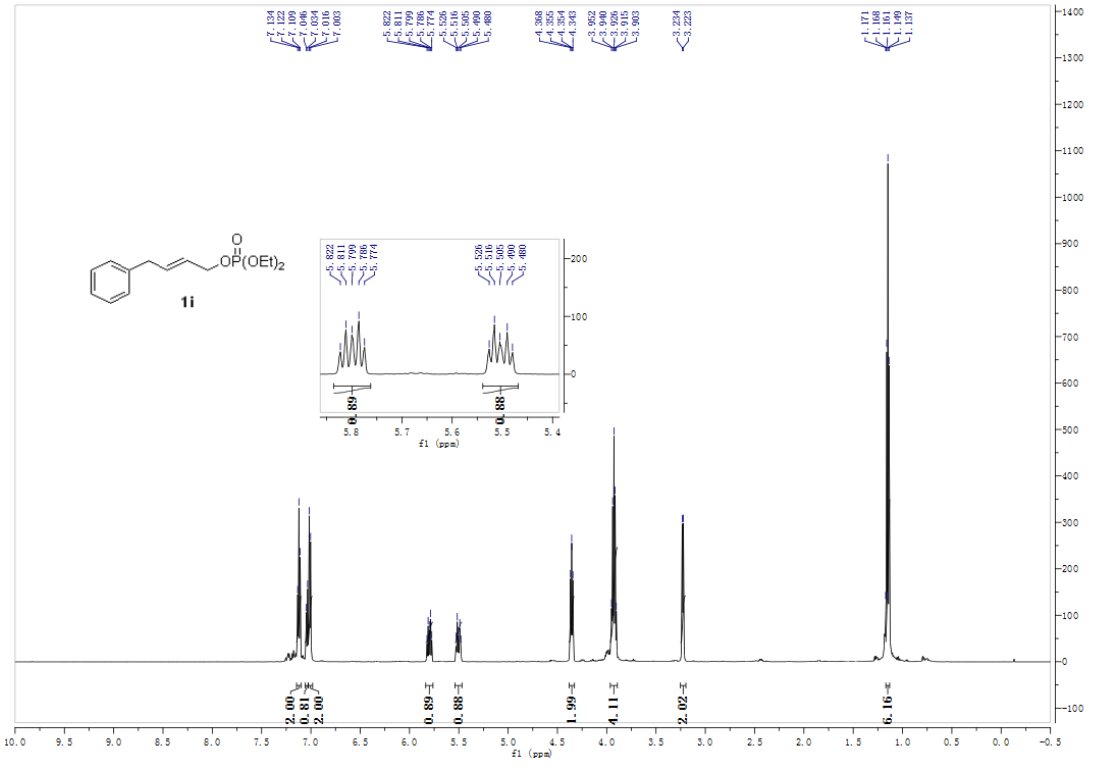




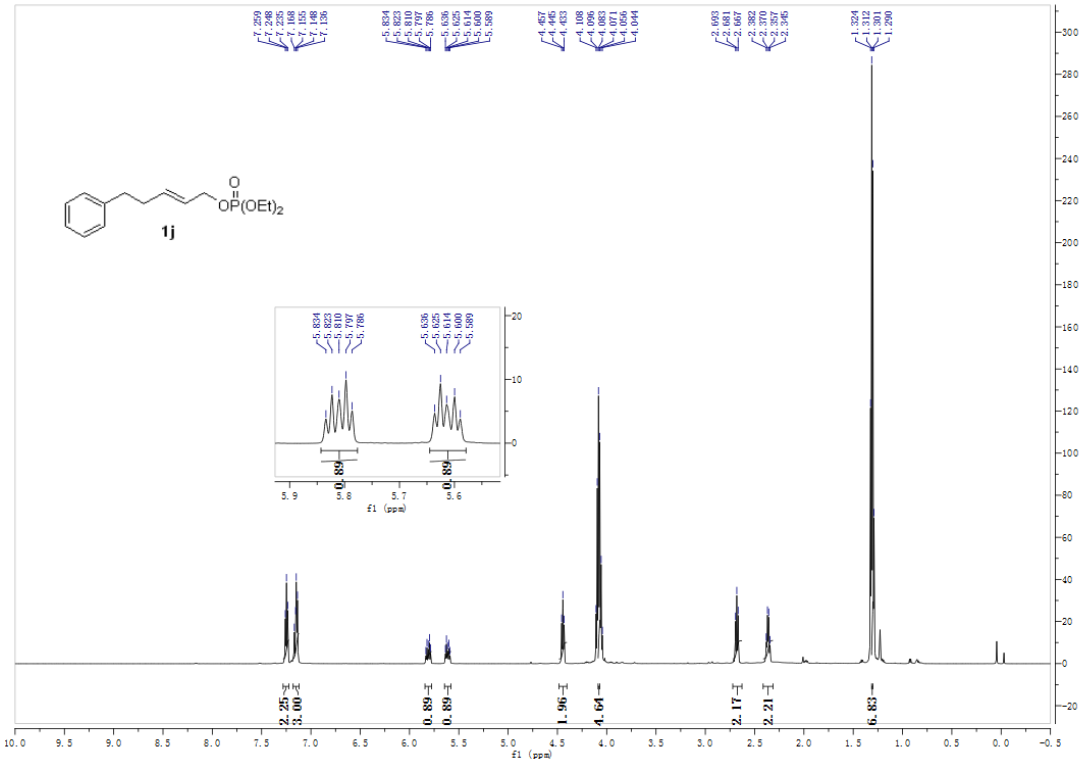
(*E*)-3-cyclohexylallyl diethyl phosphate ((*E*)-1h)



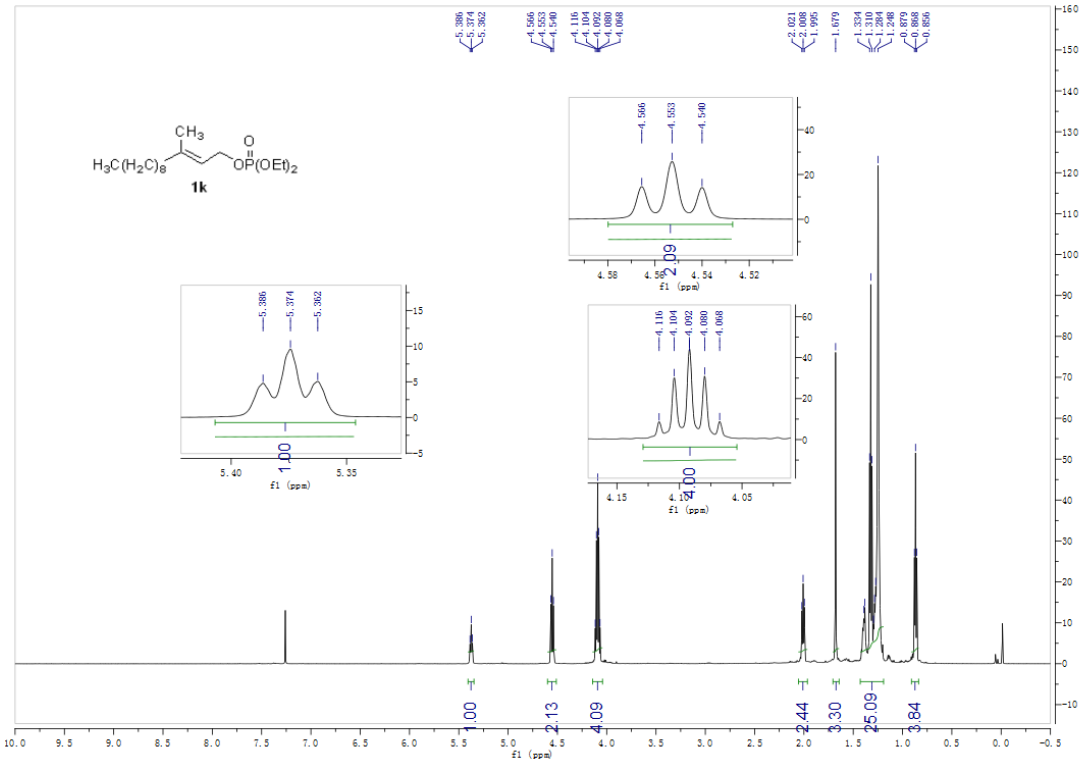
(*E*)-diethyl (4-phenylbut-2-en-1-yl) phosphate ((*E*)-1i)

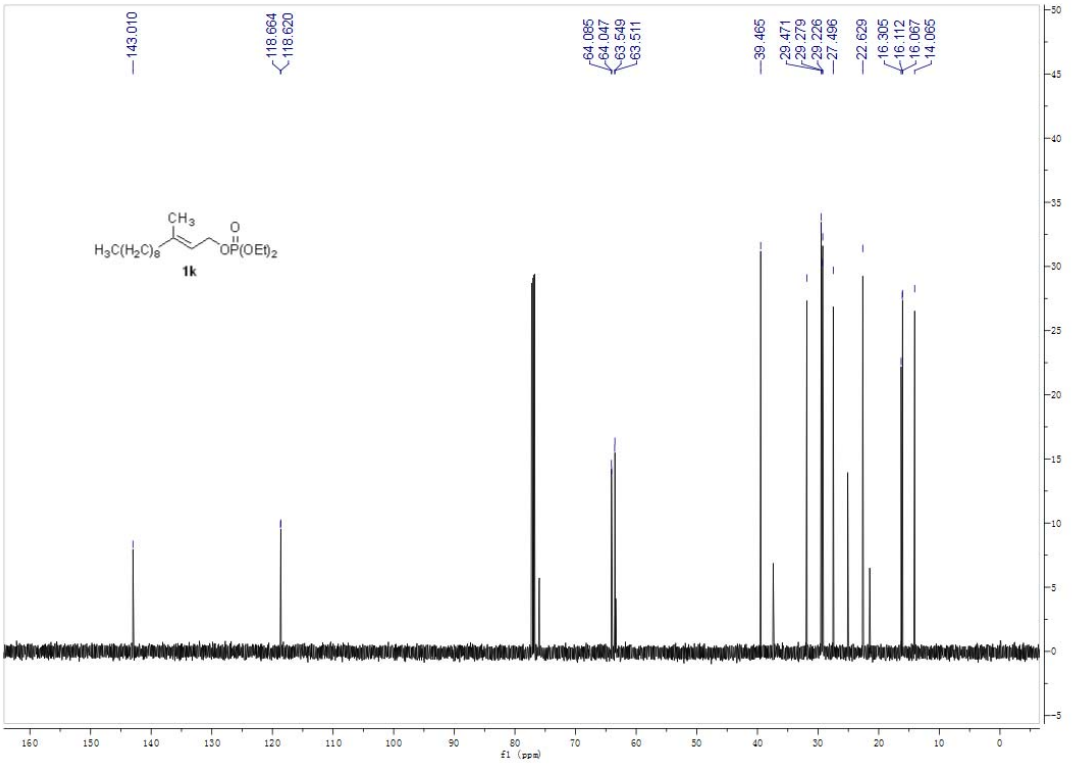


(*E*)-diethyl (5-phenylpent-2-en-1-yl) phosphate ((*E*)-1j)

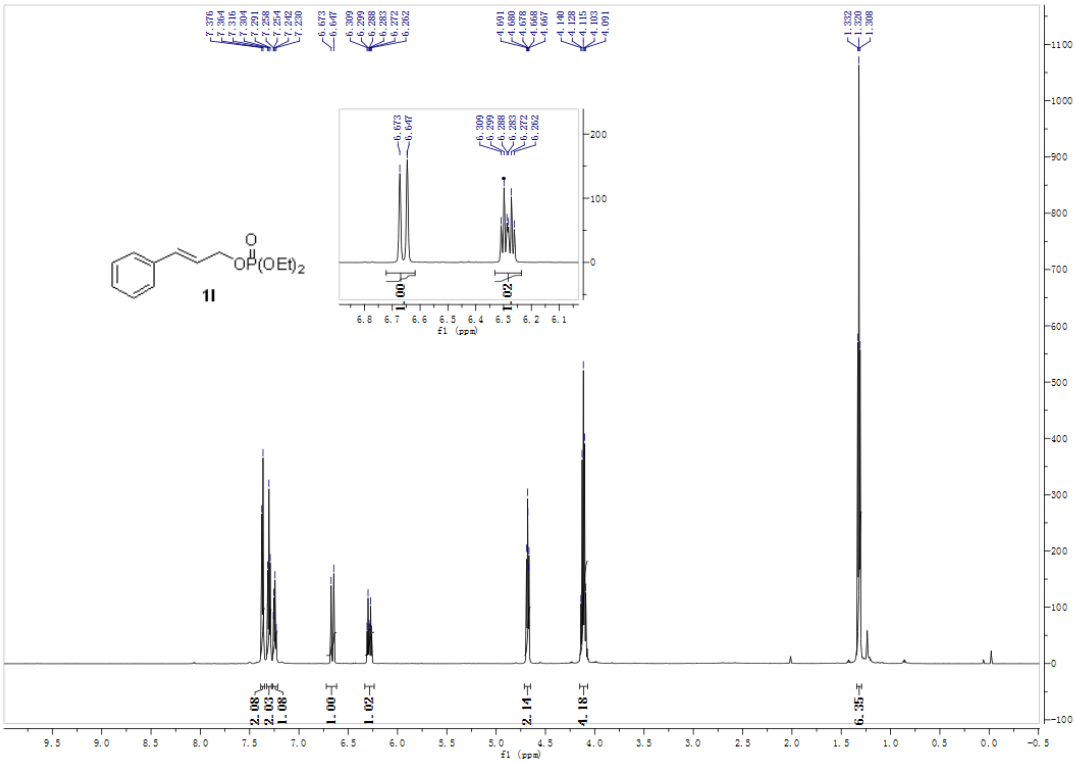


(*E*)-diethyl (2-methyldodec-2-en-1-yl) phosphate ((*E*)-1k)

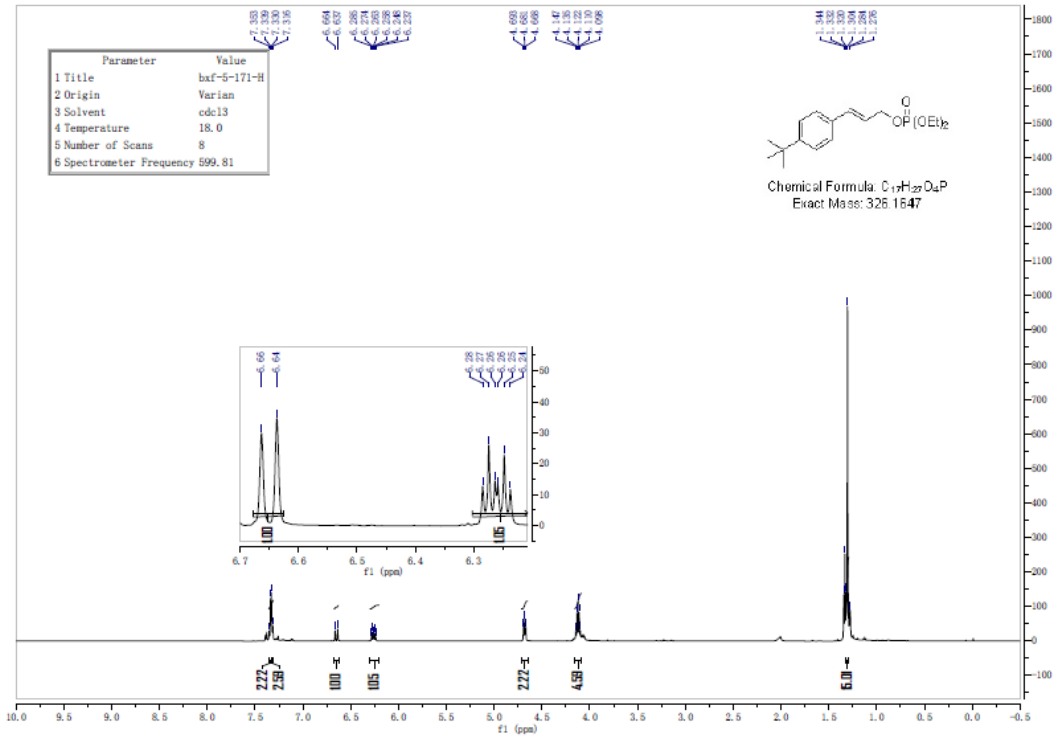


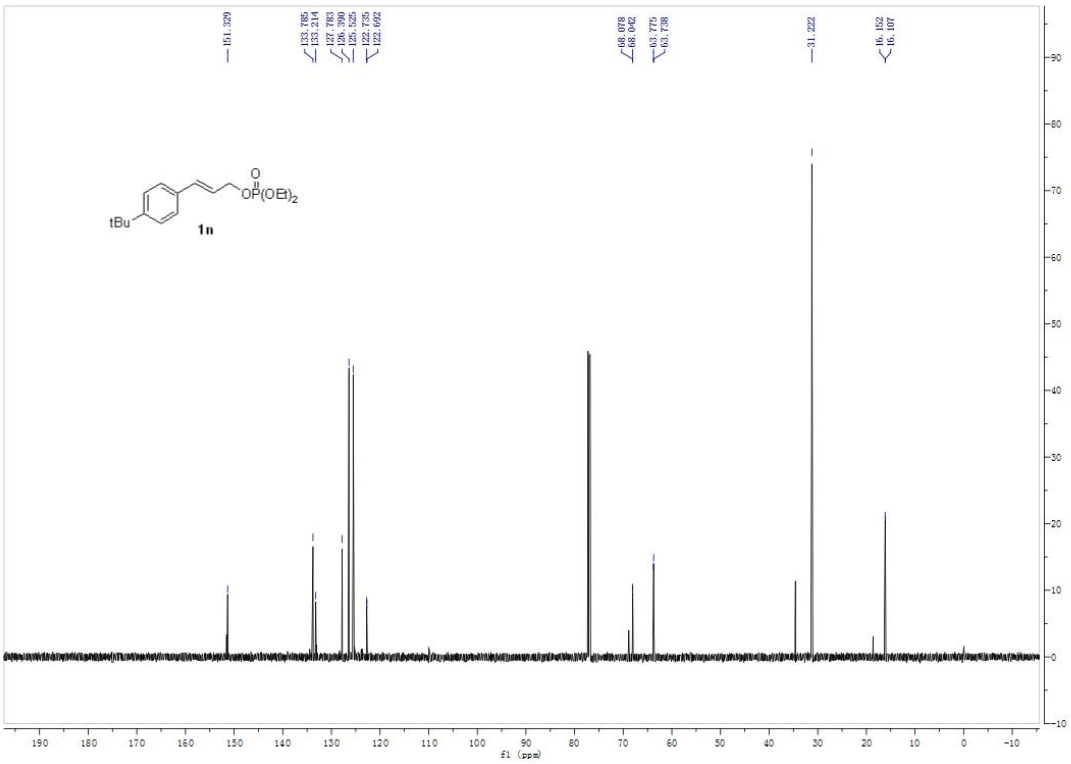


Cinnamyl diethyl phosphate ((*E*)-1l)

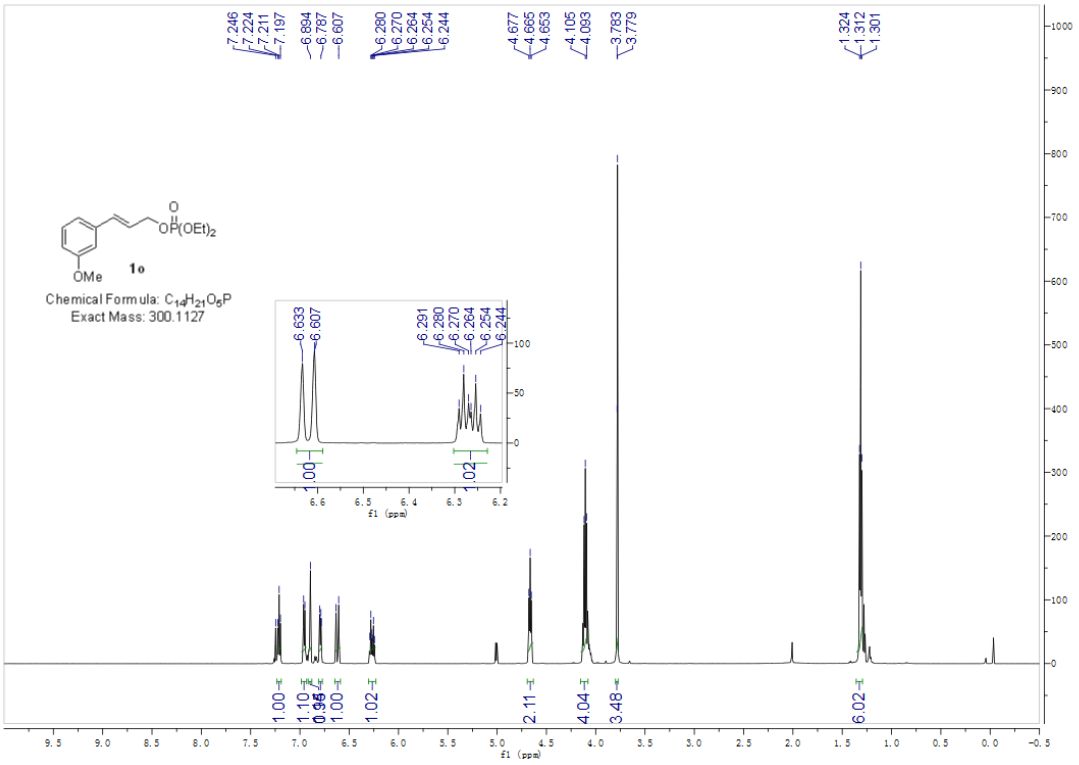


(*E*)-3-(4-(tert-butyl)phenyl)allyl diethyl phosphate ((*E*)-1n)

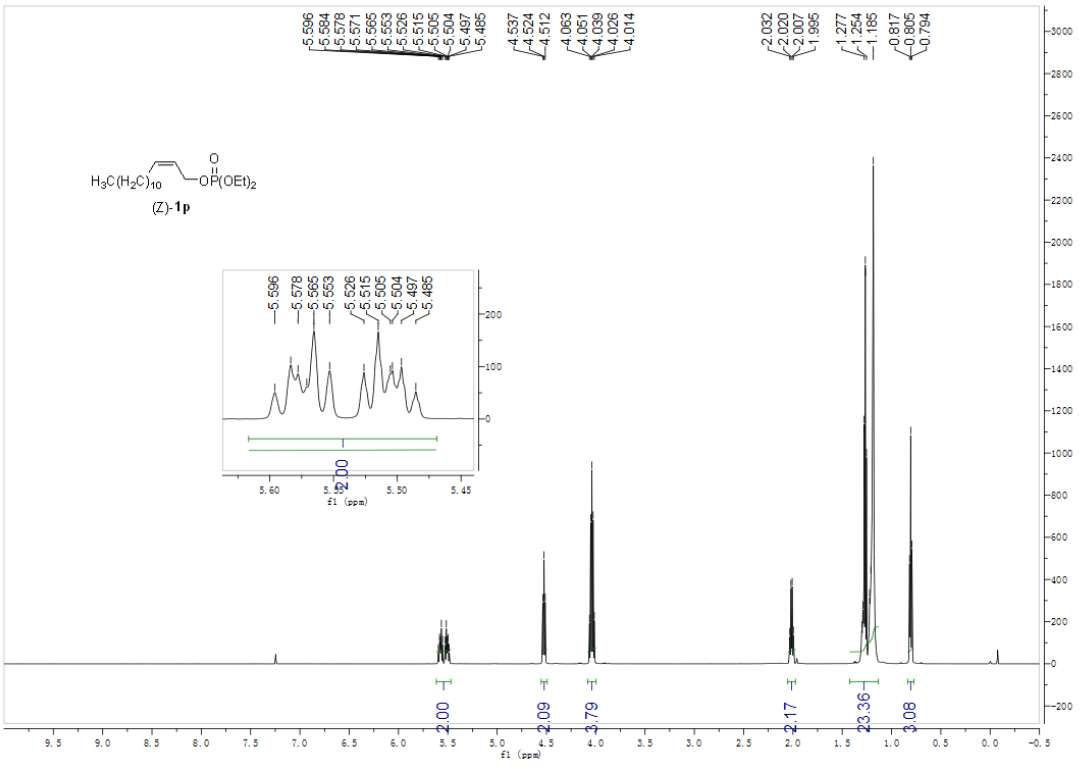


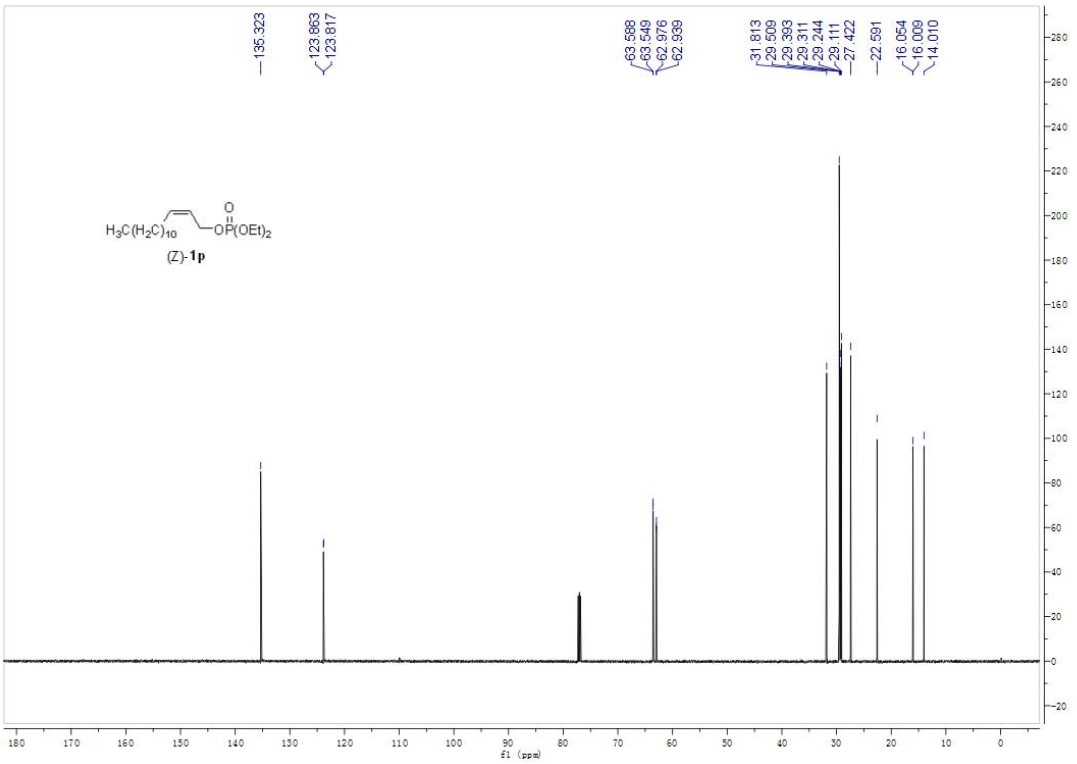


(*E*)-diethyl (3-(3-methoxyphenyl)allyl) phosphate ((*E*)-1o)

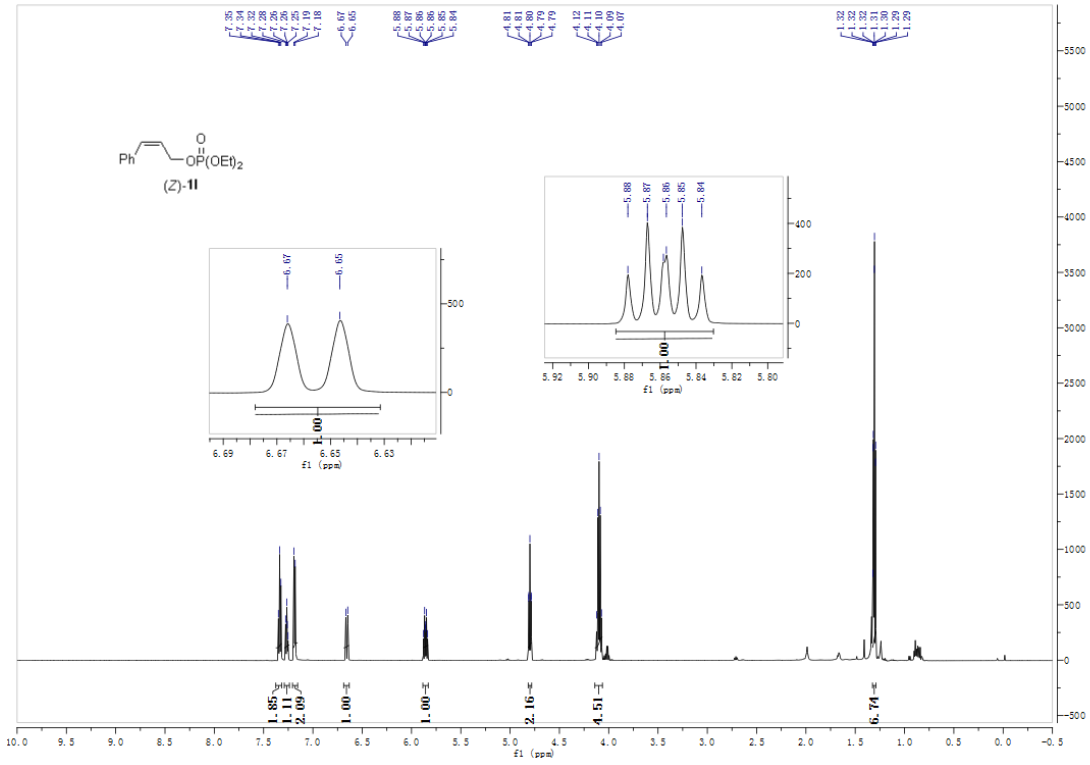


(*Z*)-diethyl tridec-2-en-1-yl phosphate ((*Z*)-1p)

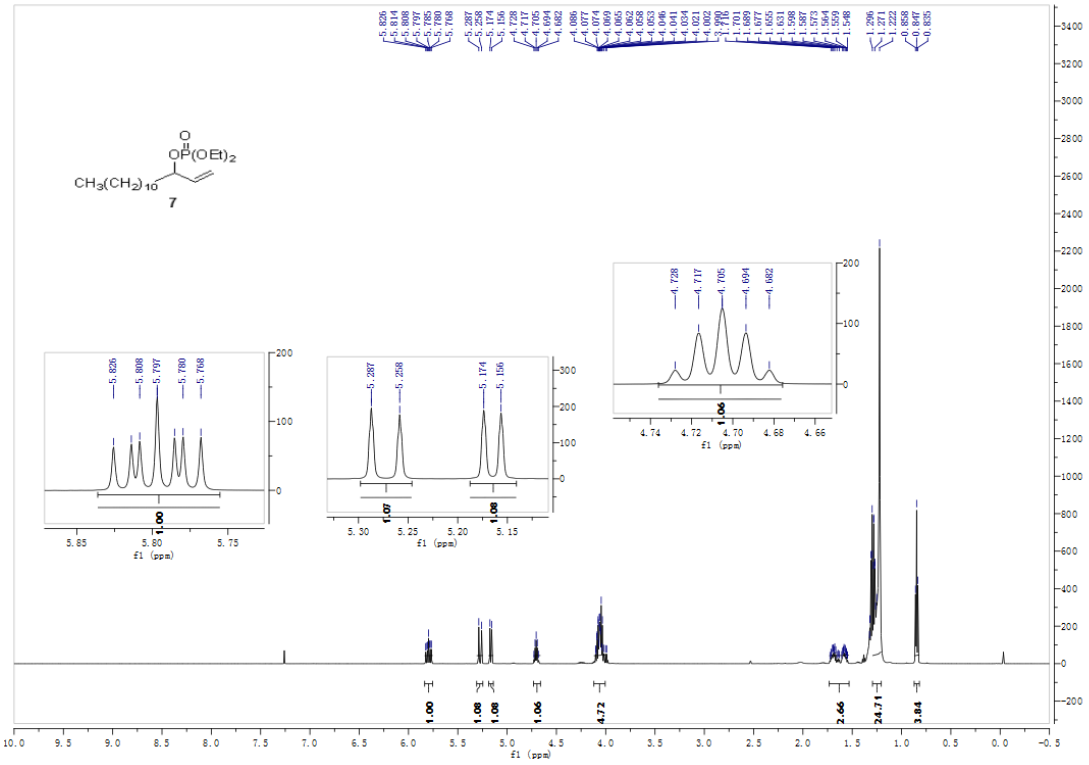


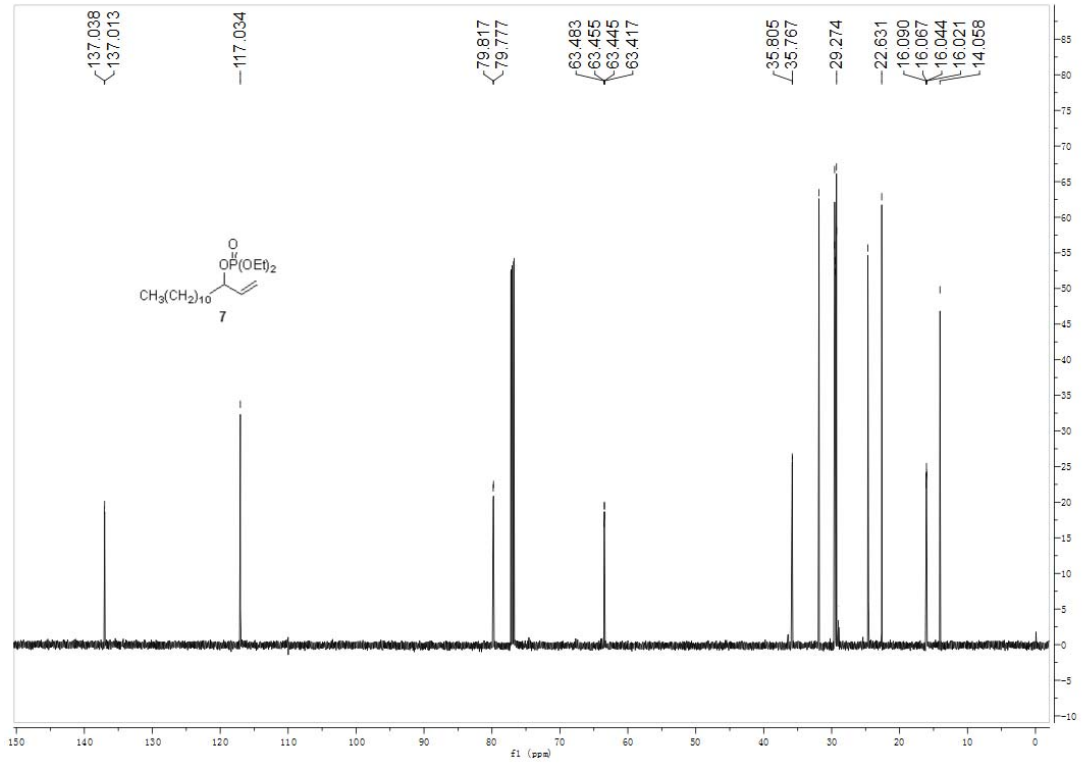


(Z)-diethyl tridec-2-en-1-yl phosphate ((Z)-1l)

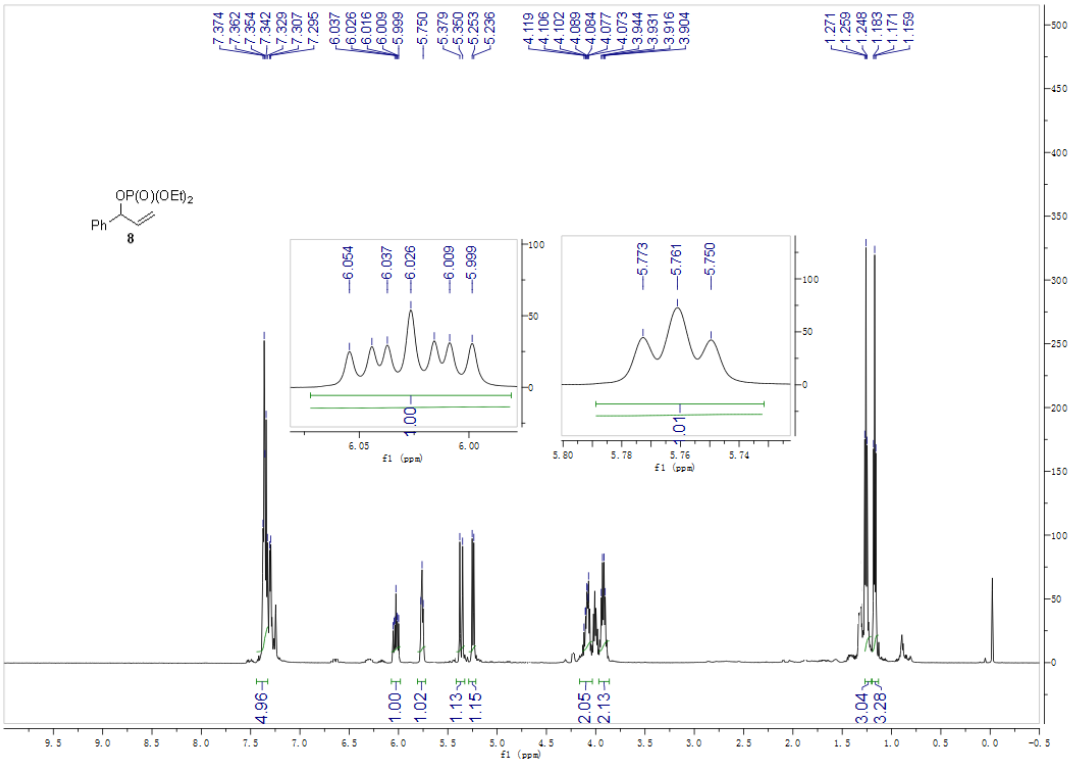


Diethyl tetradec-1-en-3-yl phosphate (7)

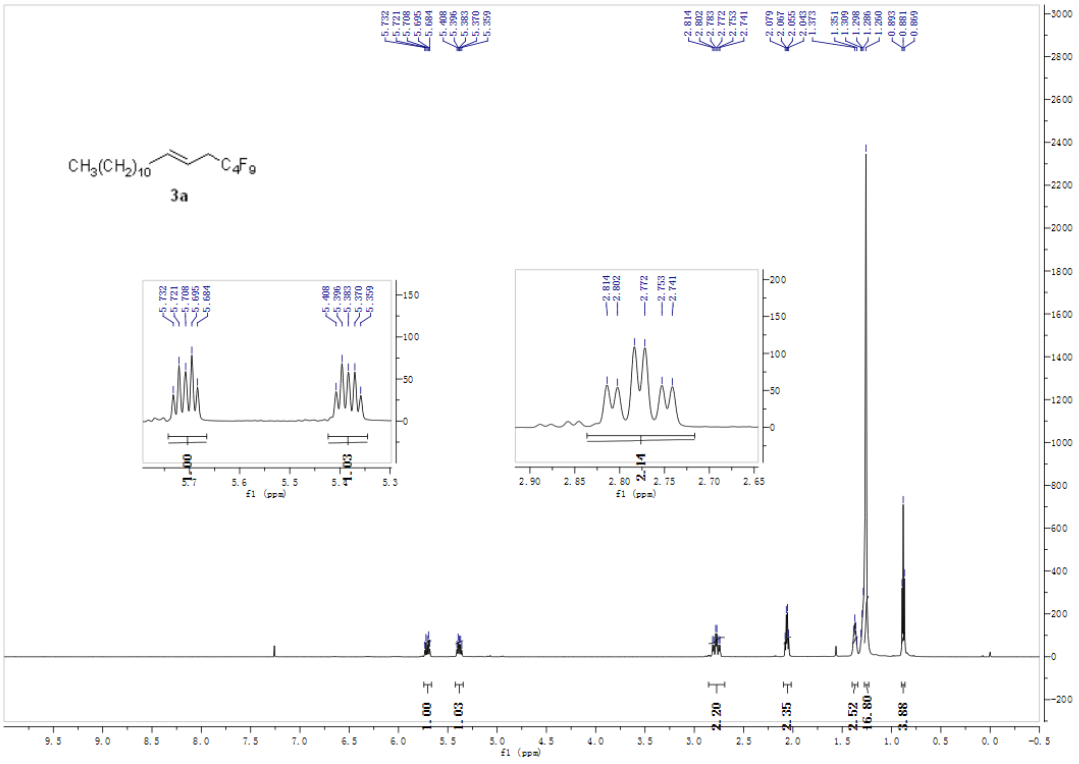


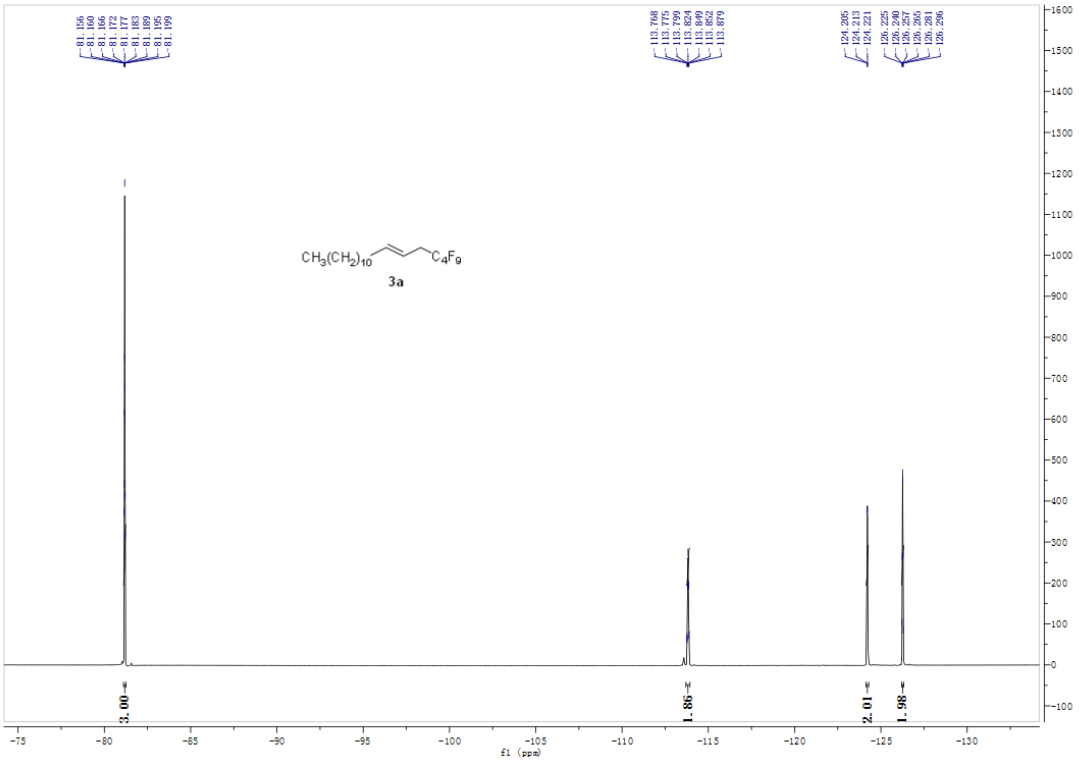


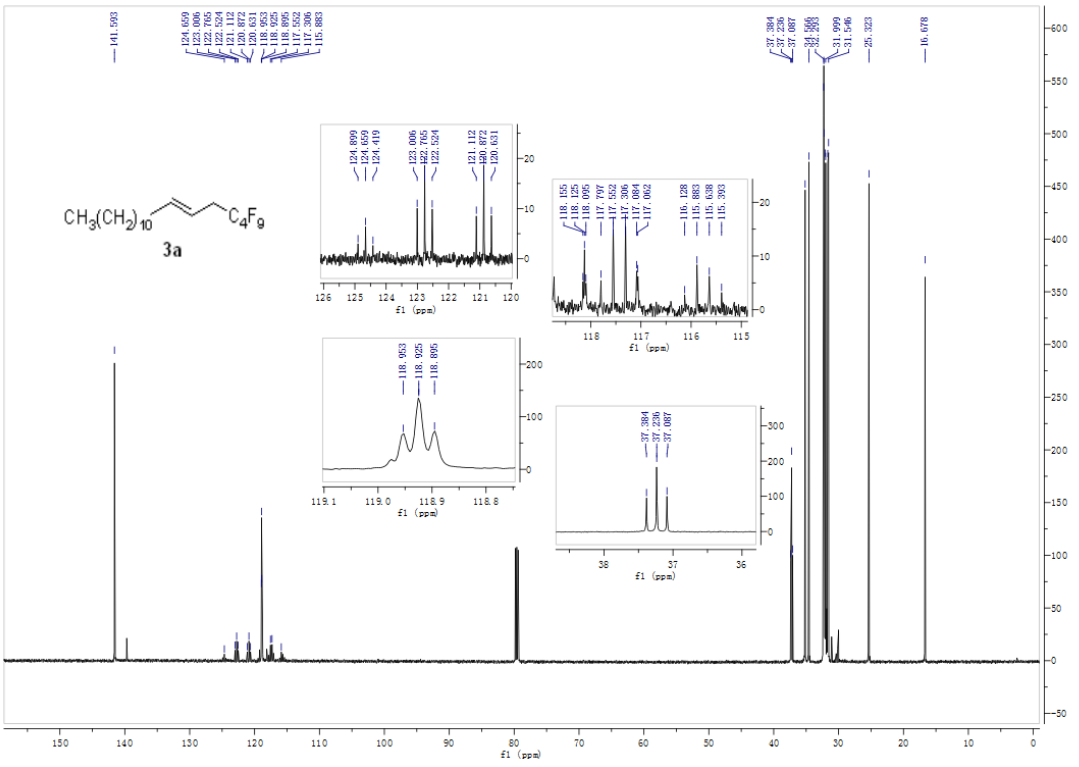
Diethyl (1-phenylallyl) phosphate (**8**)



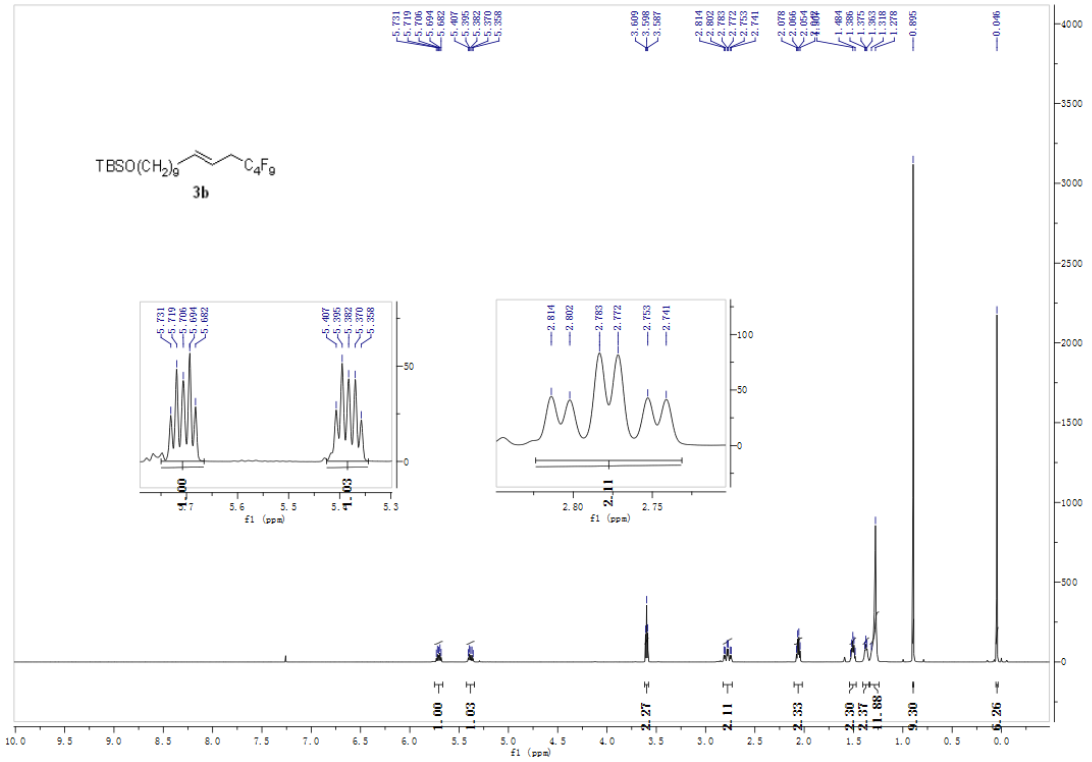
(*E*)-1,1,1,2,2,3,3,4,4-nonafluorooctadec-6-ene (3a)

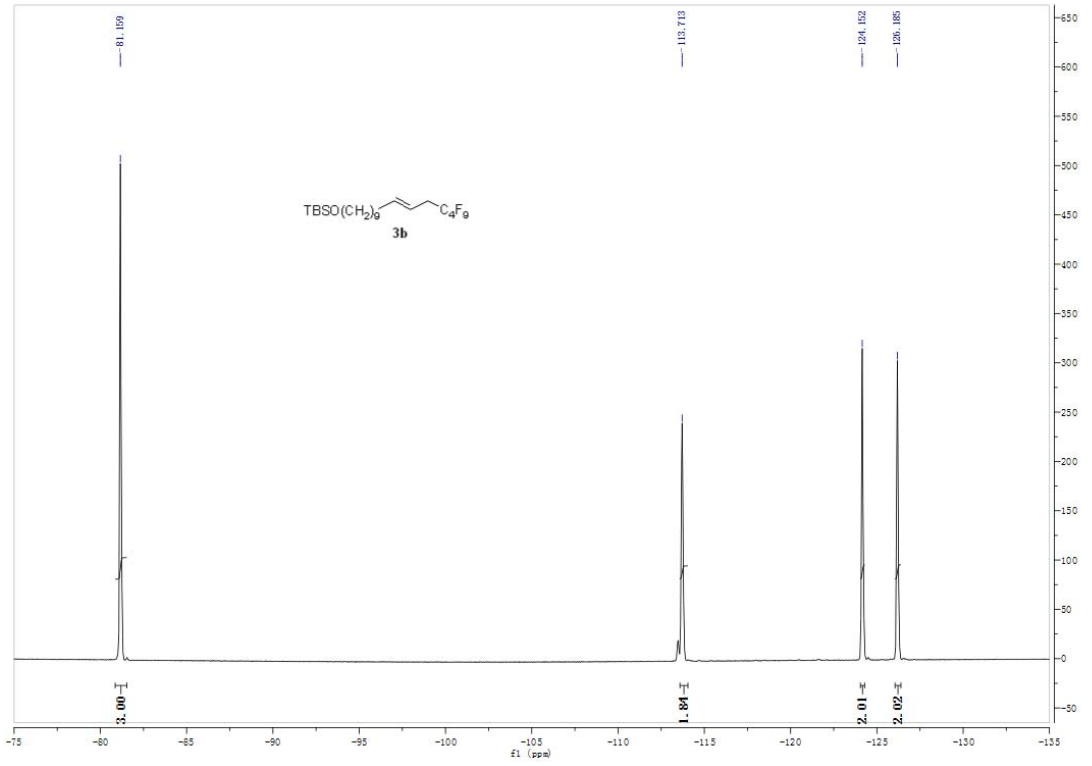


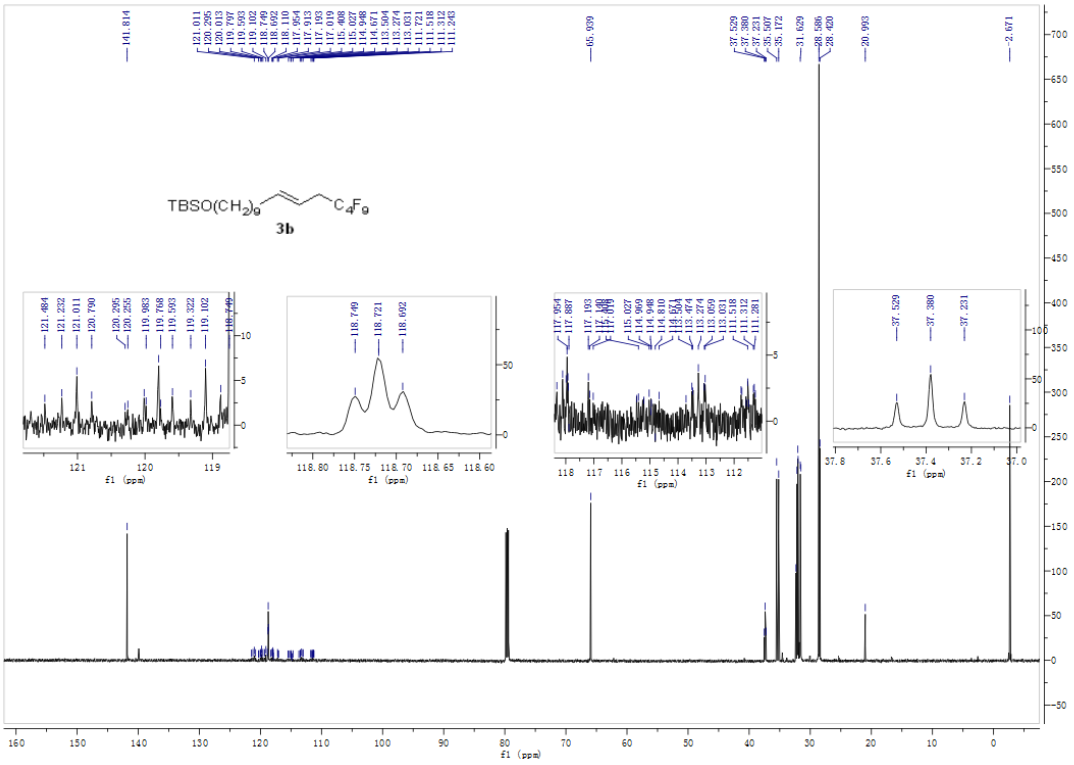

CH3(CH2)10
C4F9
3a
f1 (ppm)


CH3(CH2)10
C4F9
3a
f1 (ppm)

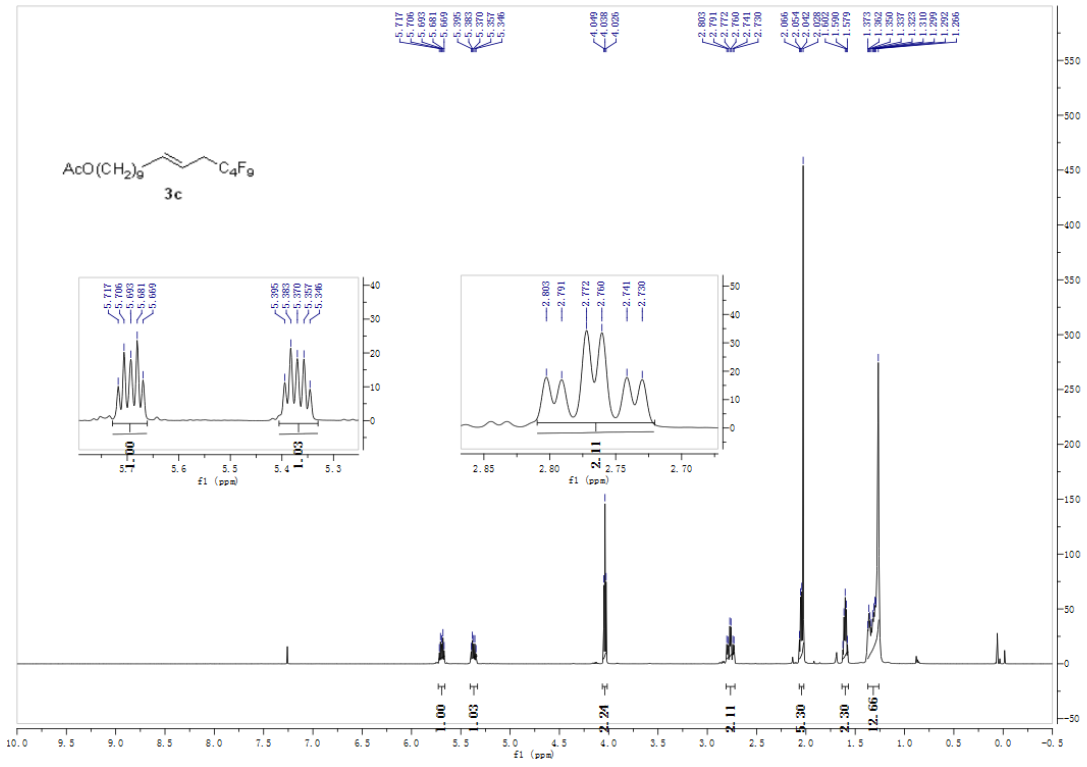
(*E*)-tert-butyldimethyl((13,13,14,14,15,15,16,16,16-nonafluorohexadec-10-en-1-yl)oxy)silane (3b)

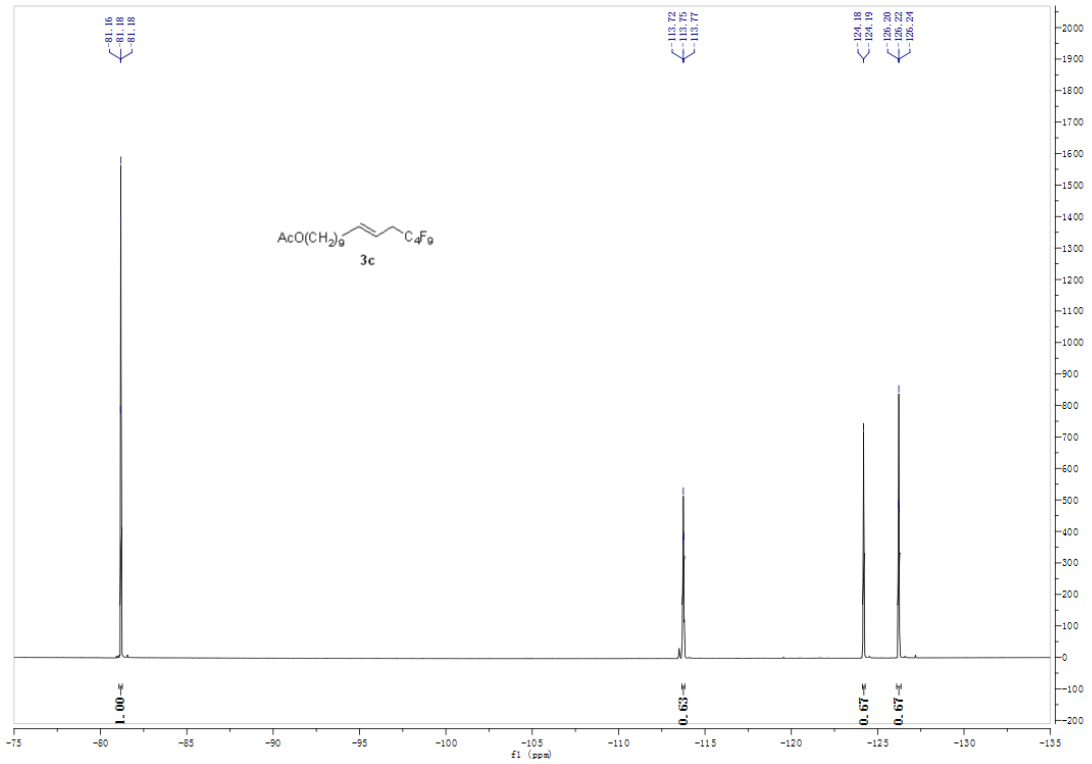


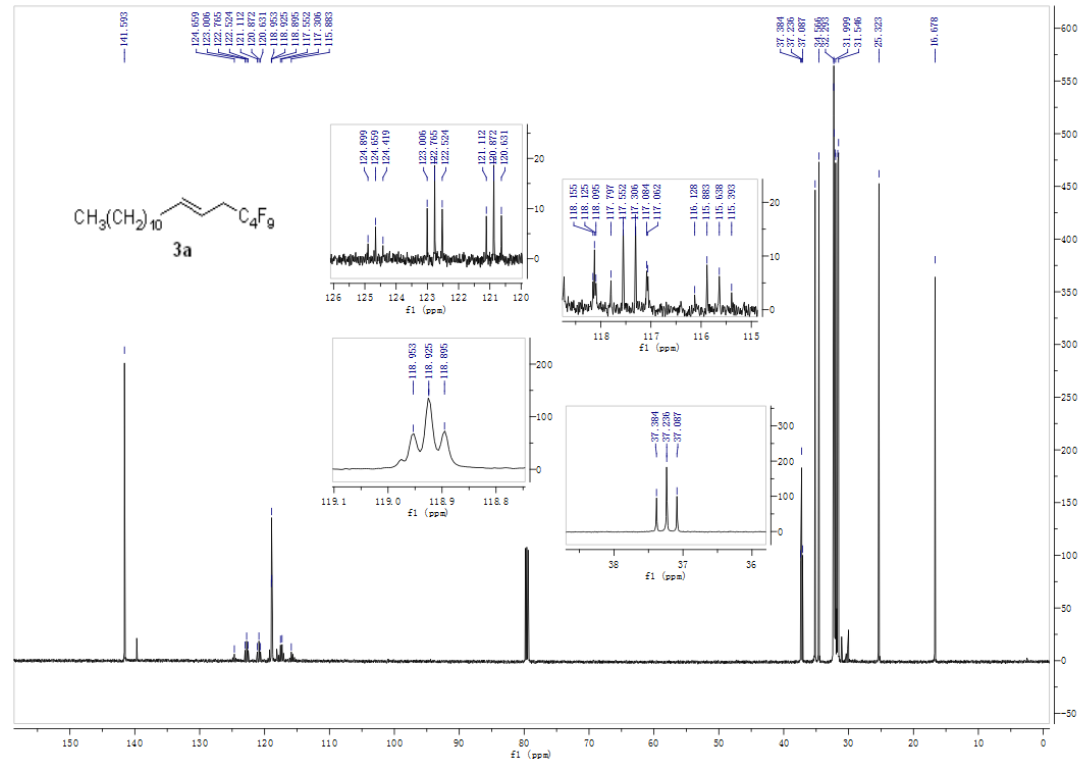




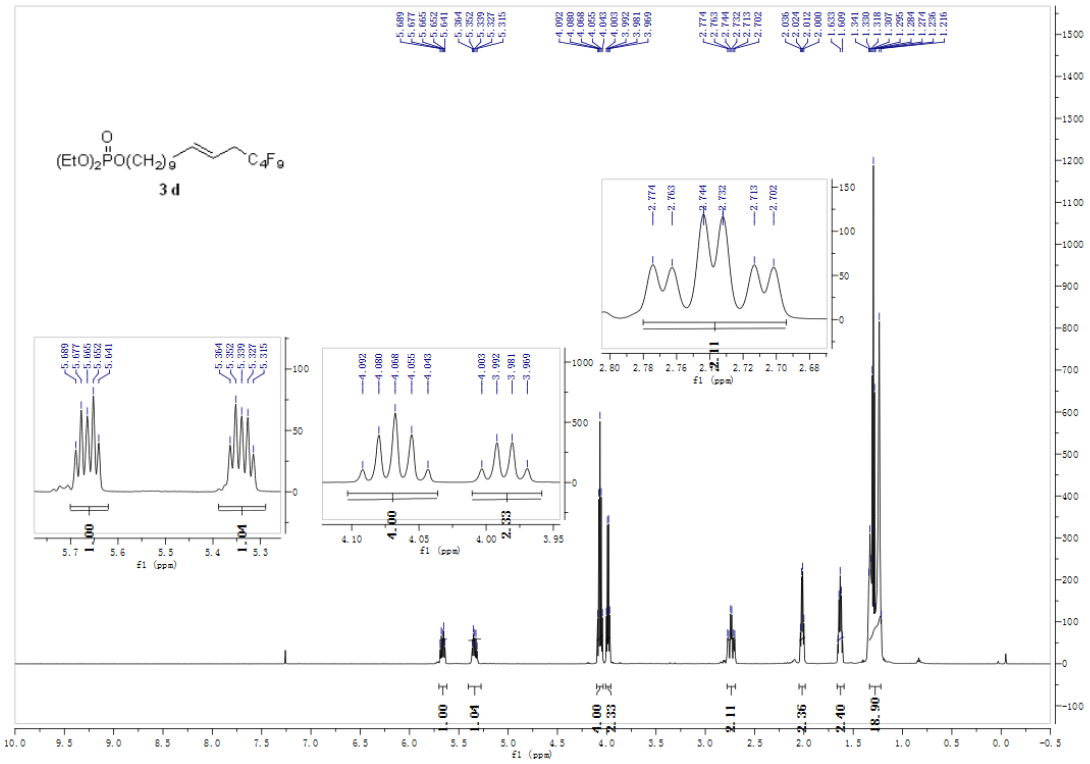
(*E*)-13,13,14,14,15,15,16,16-octafluorohexadec-10-en-1-yl acetate (3c)

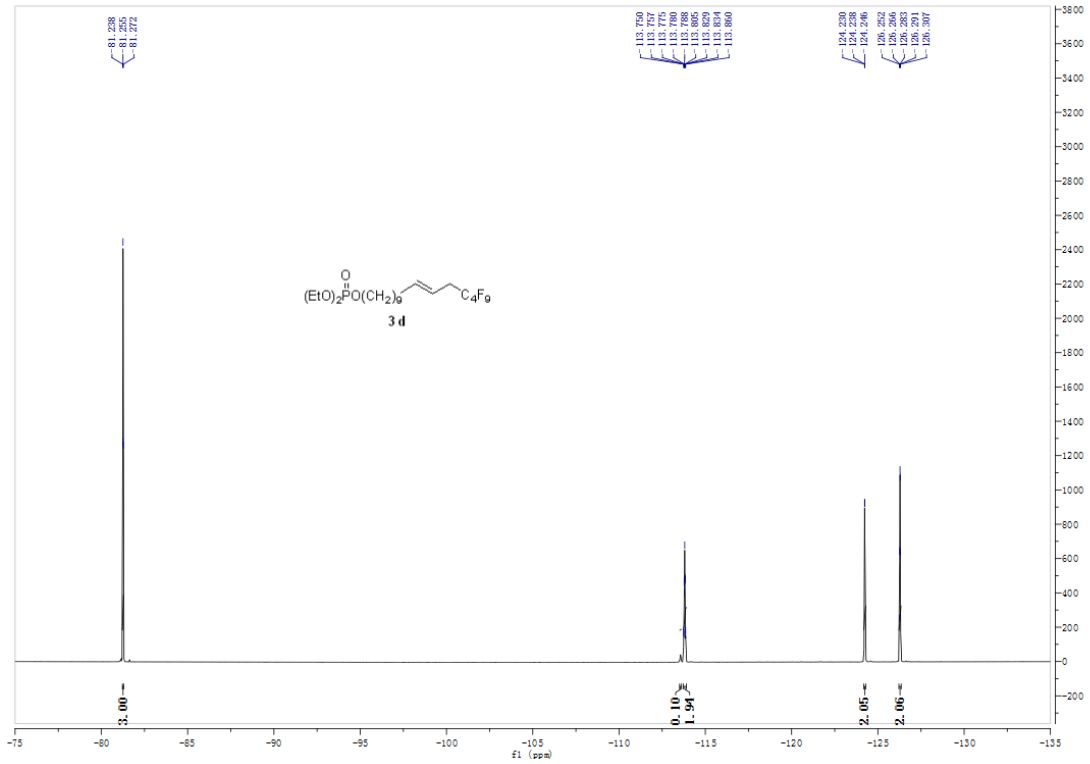


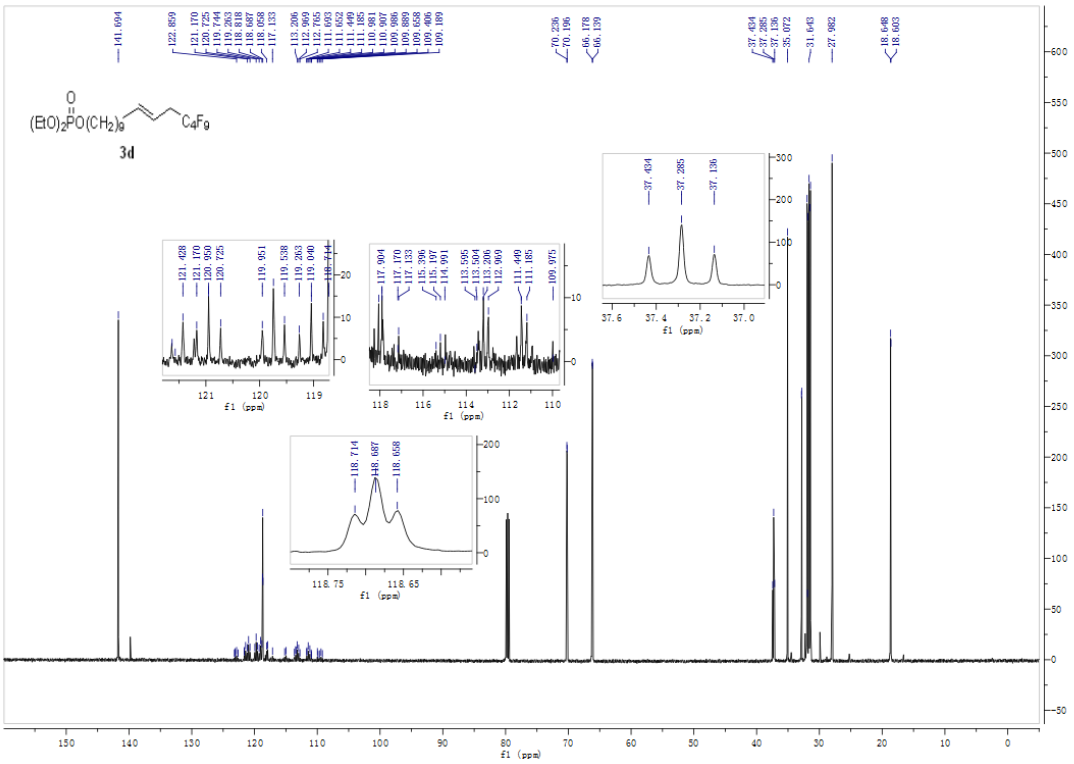

81.16
81.18
81.18
113.72
113.75
113.77
124.18
124.19
126.20
126.22
126.24
AcO(CH2)9
C4F9
3c
1.00
0.63
0.67
0.67
f1 (ppm)


141.593
124.659
123.006
122.765
122.524
121.112
120.872
120.631
118.953
118.925
118.895
117.552
117.308
115.883
37.384
37.236
37.087
32.353
31.999
31.546
25.323
16.678
CH3(CH2)10
C4F9
3a
f1 (ppm)

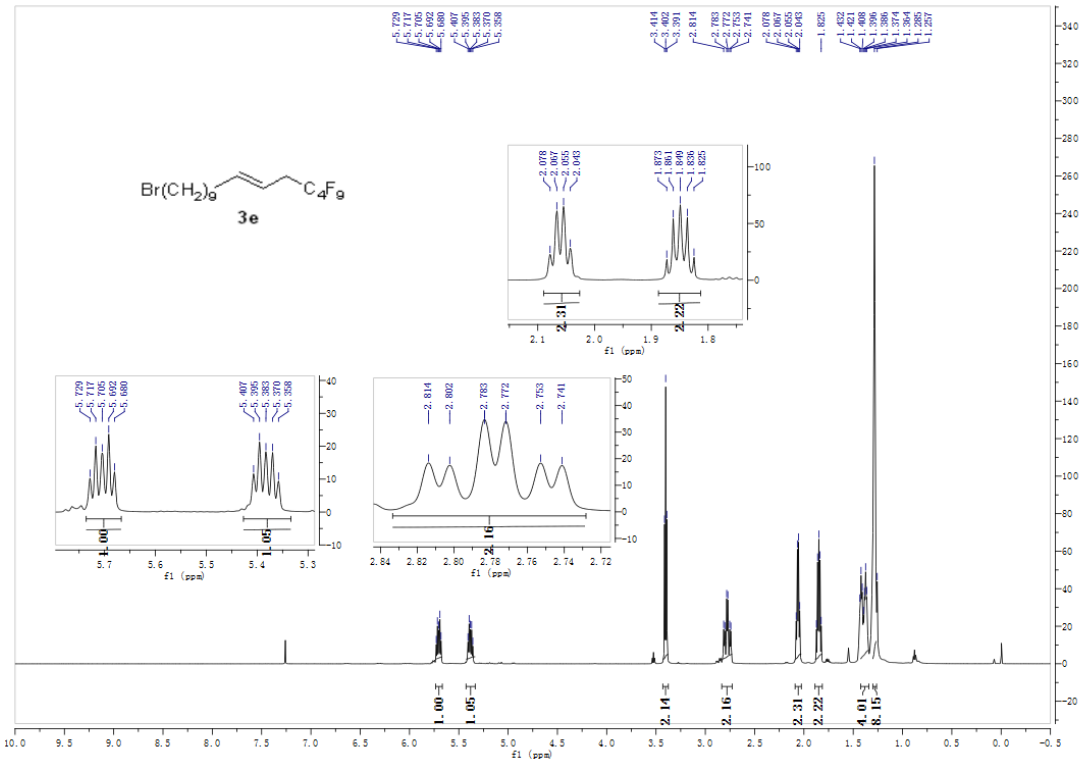
(*E*)-diethyl (13,13,14,14,15,15,16,16,16-nonafluorohexadec-10-en-1-yl) phosphate (3d)

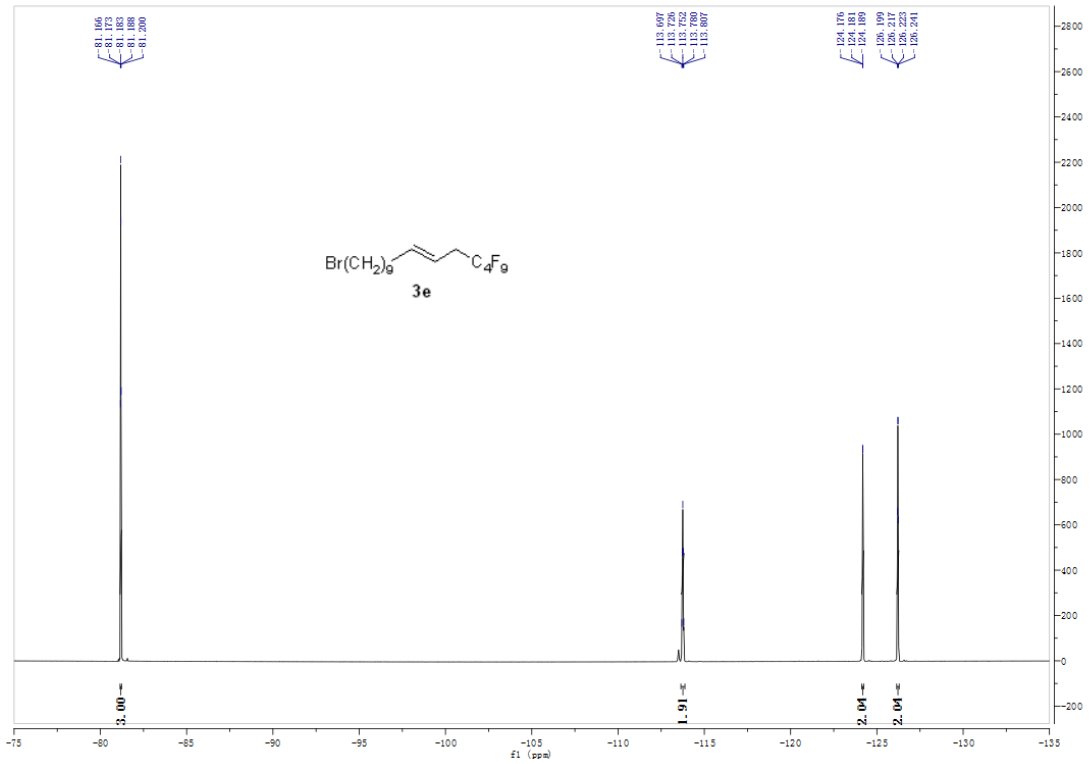


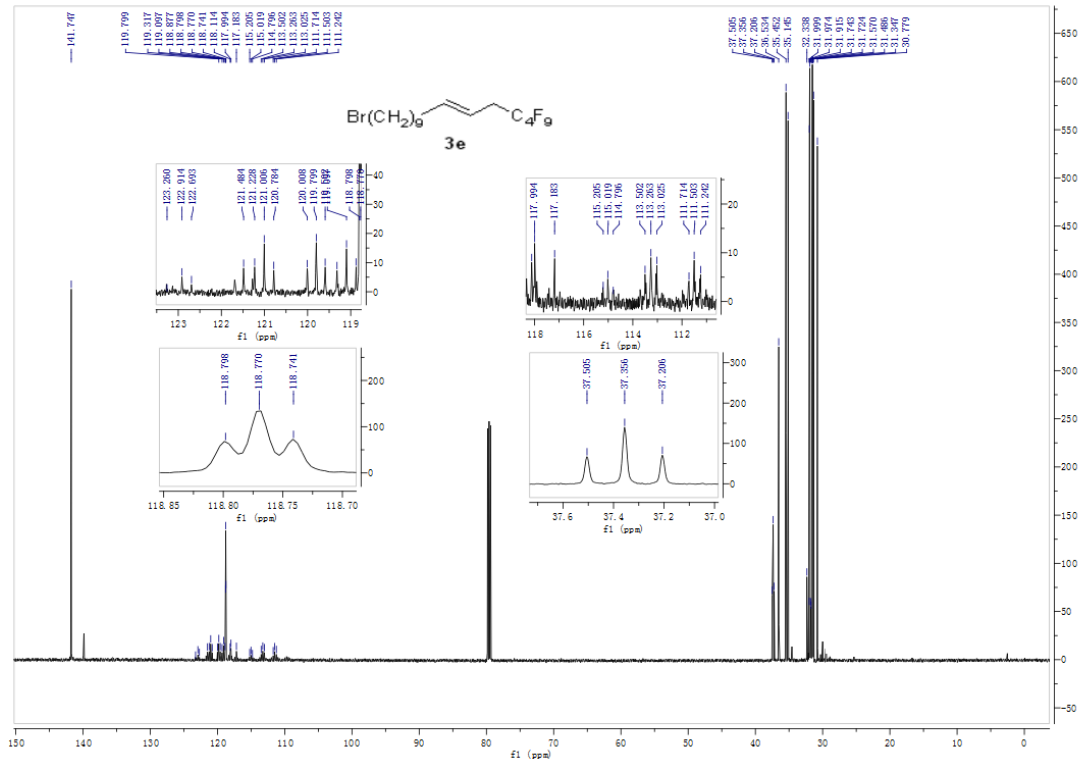




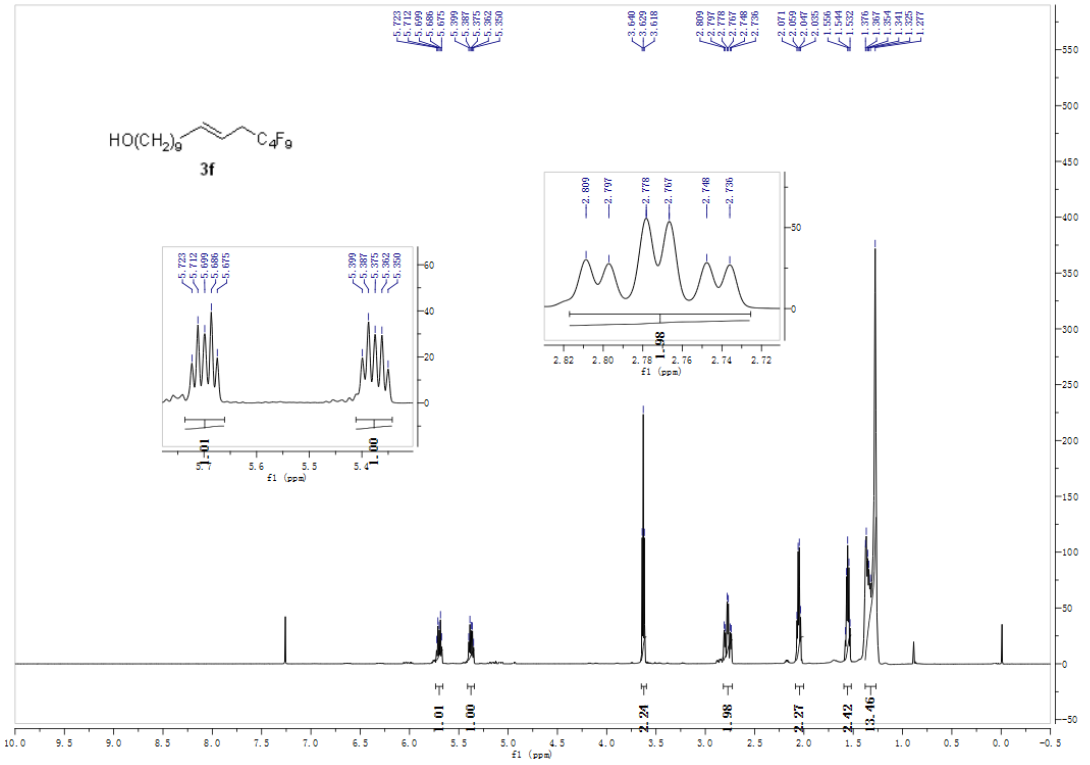
(*E*)-16-bromo-1,1,1,2,2,3,3,4,4-nonafluorohexadec-6-ene (3e)

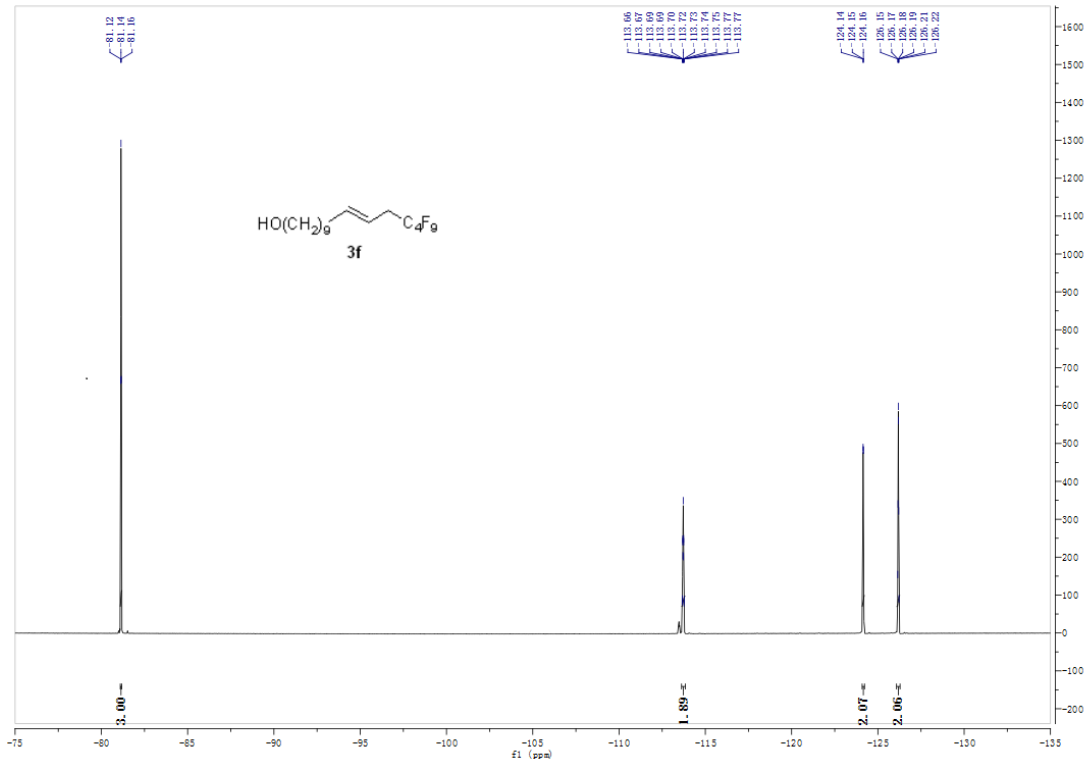


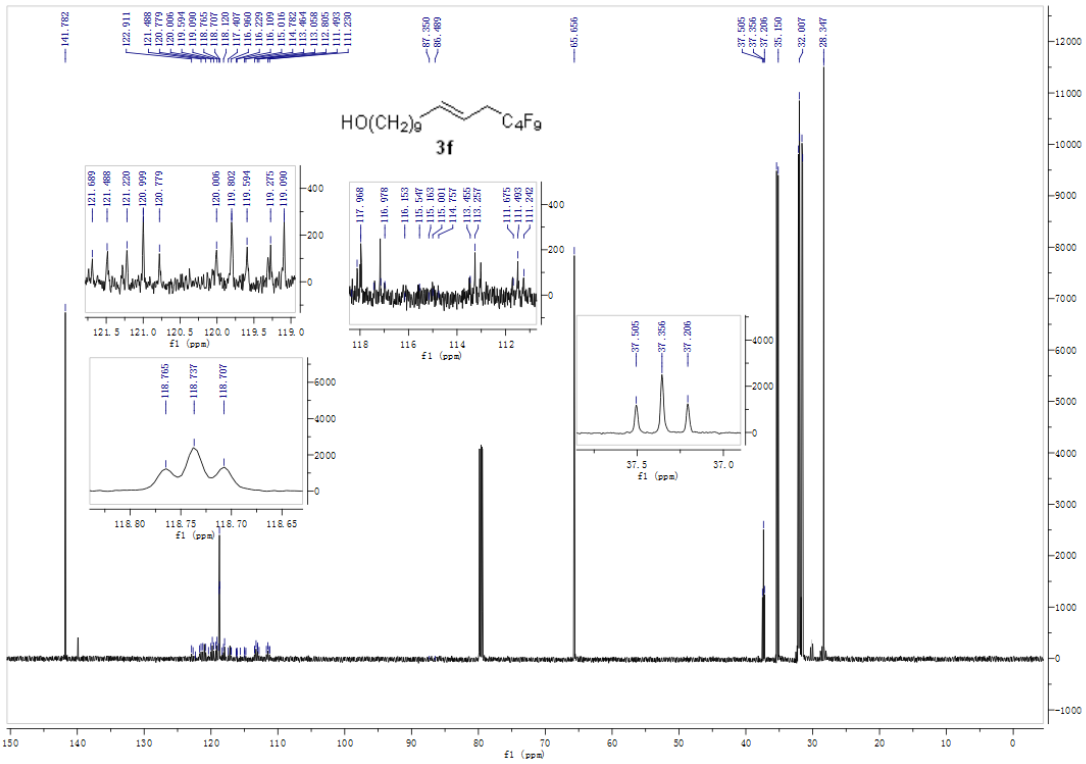

Br(CH2)9
C4F9
3e
3.00
1.91
2.04
2.04
f1 (ppm)


Br(CH2)9
C4F9
3e
f1 (ppm)

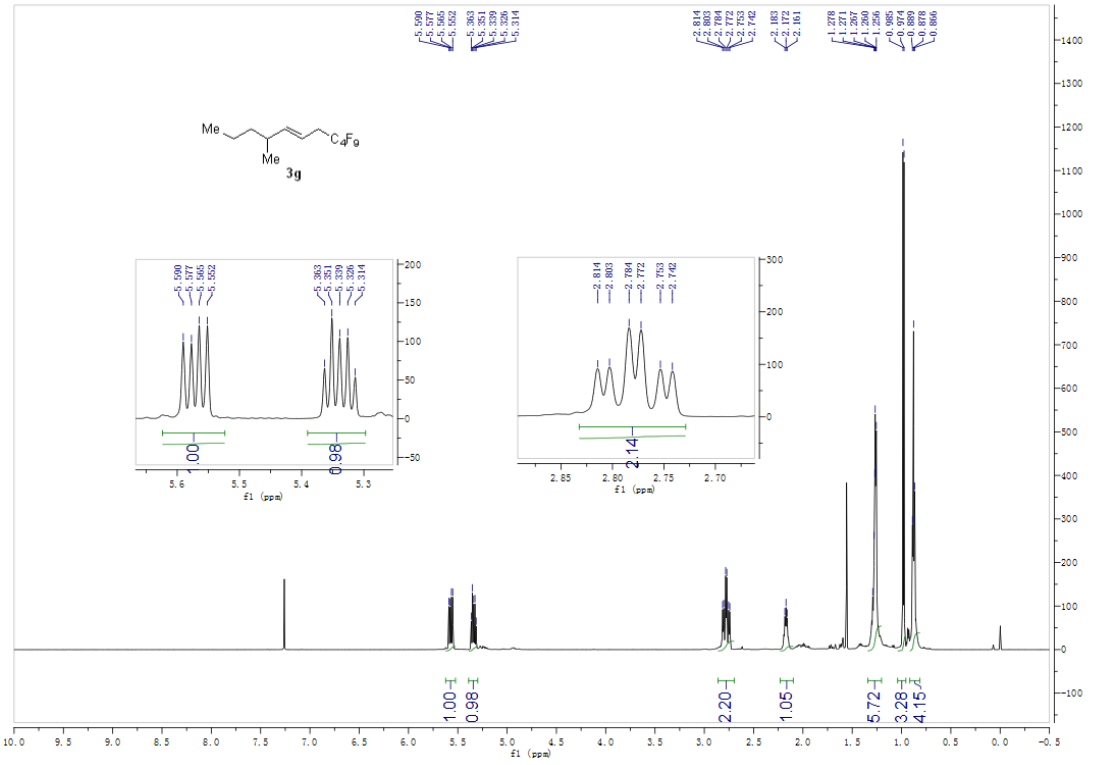
(*E*)-13,13,14,14,15,15,16,16,16-nonafluorohexadec-10-en-1-ol (3f)

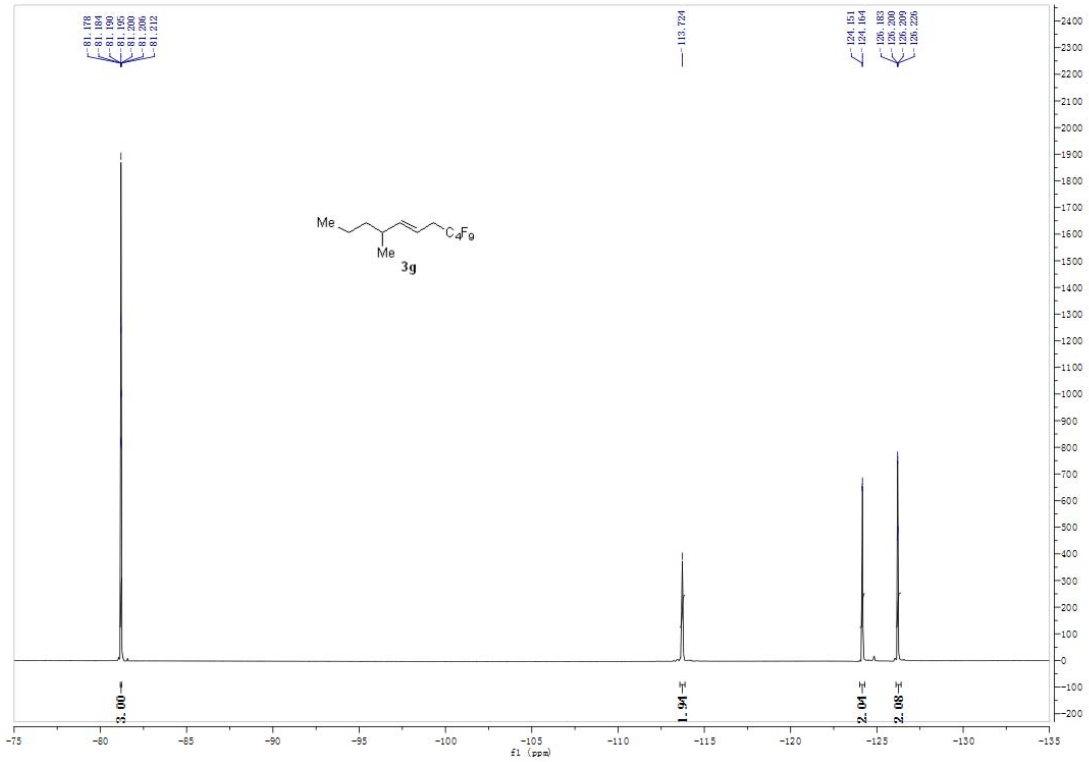


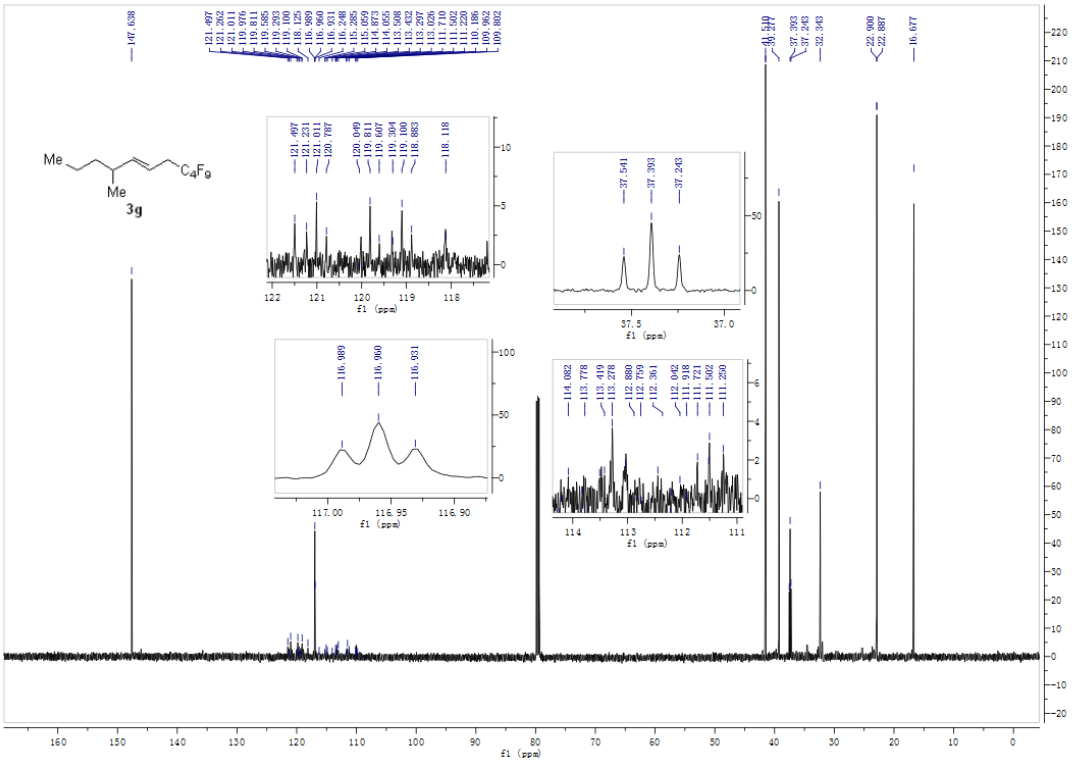




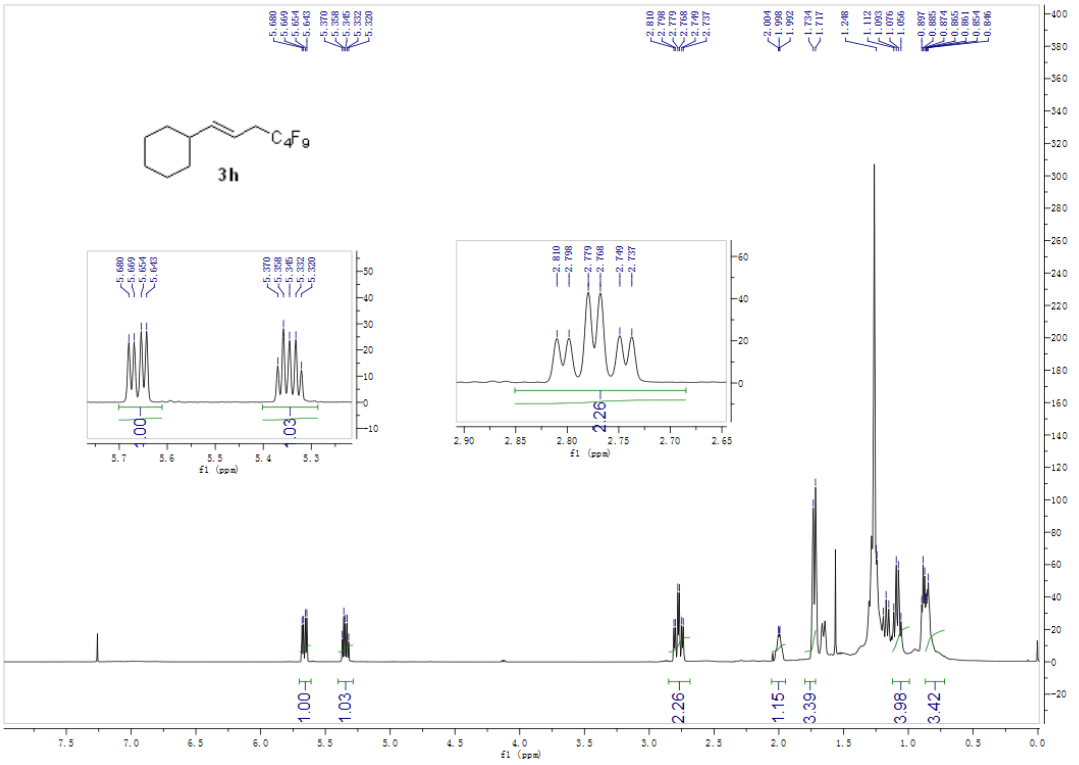
(*E*)-8,8,9,9,10,10,11,11,11-nonafluoro-4-methylundec-5-ene (3g)

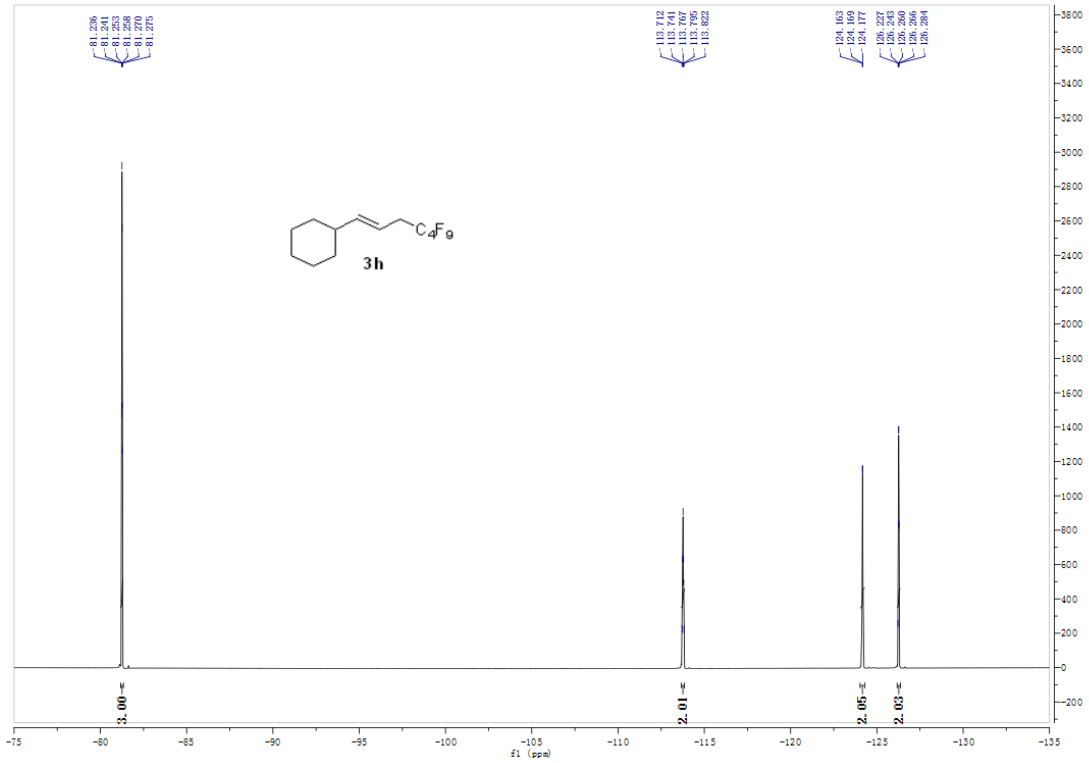


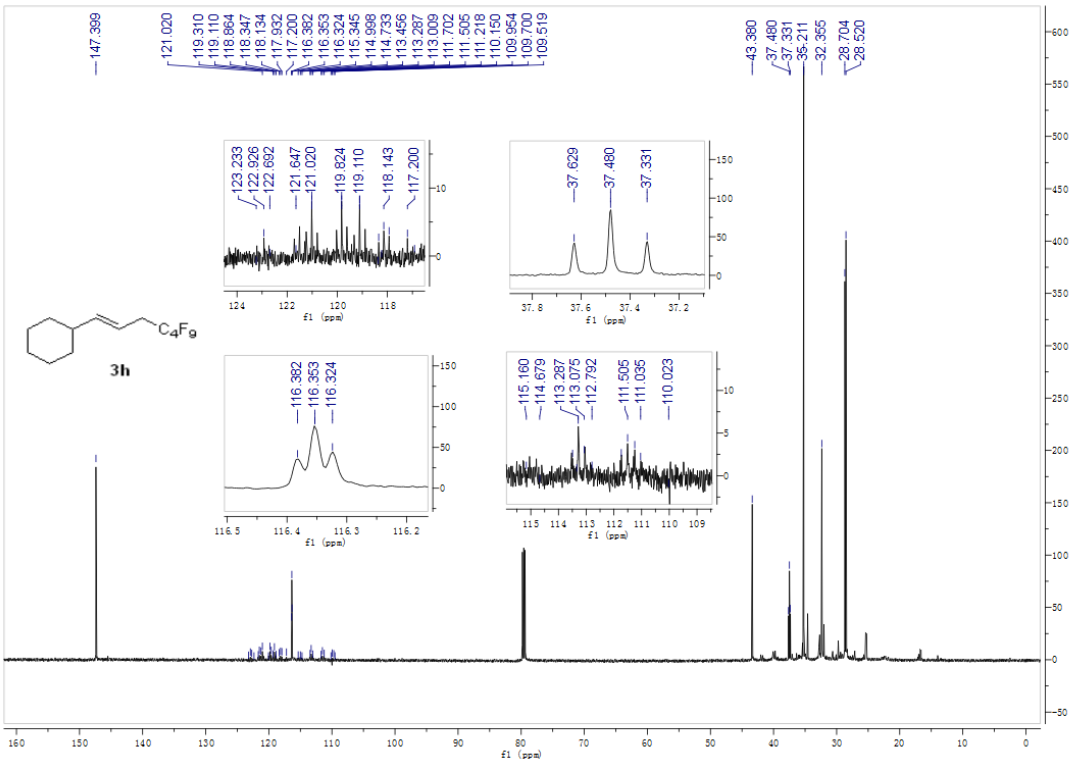

Me
Me
C4F9
3g
f1 (ppm)


Me
Me
C4F9
3g
f1 (ppm)

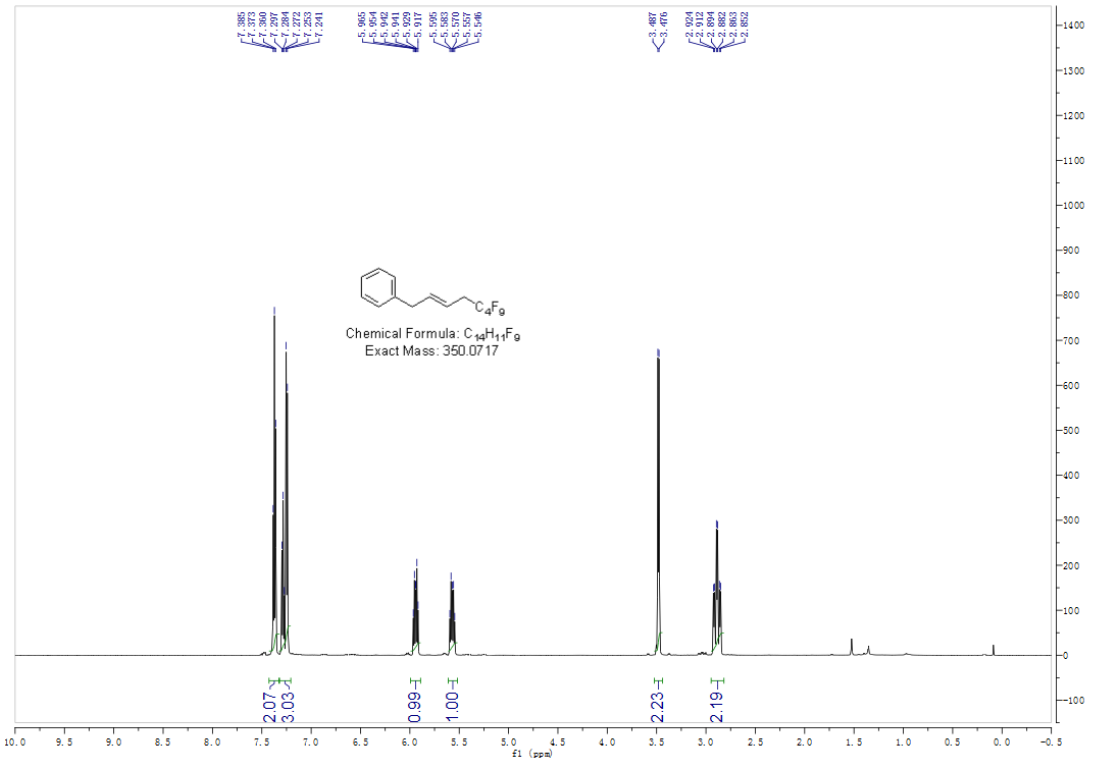
(*E*)-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl)cyclohexane (3h)

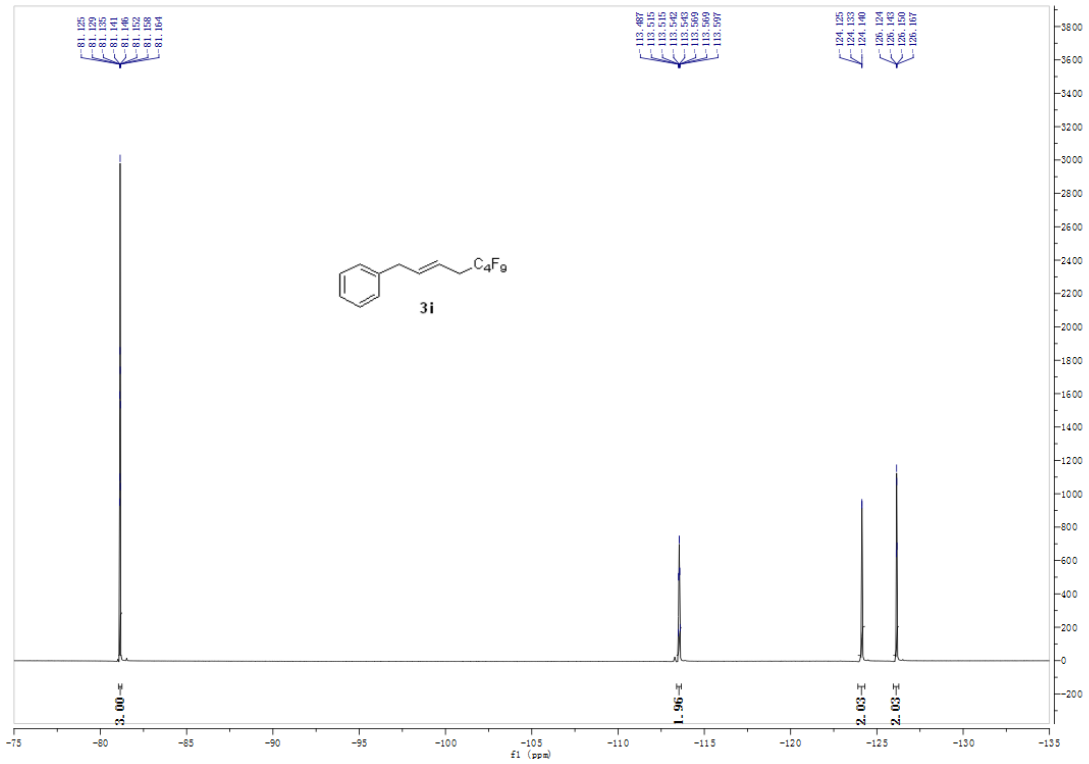


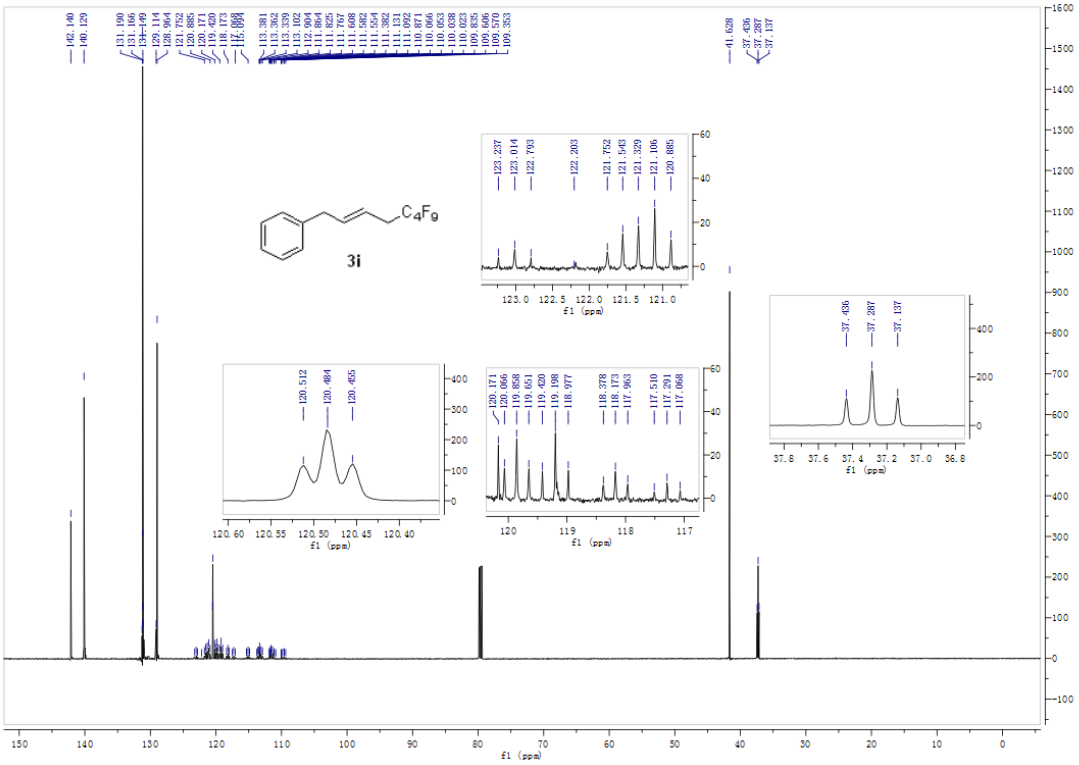




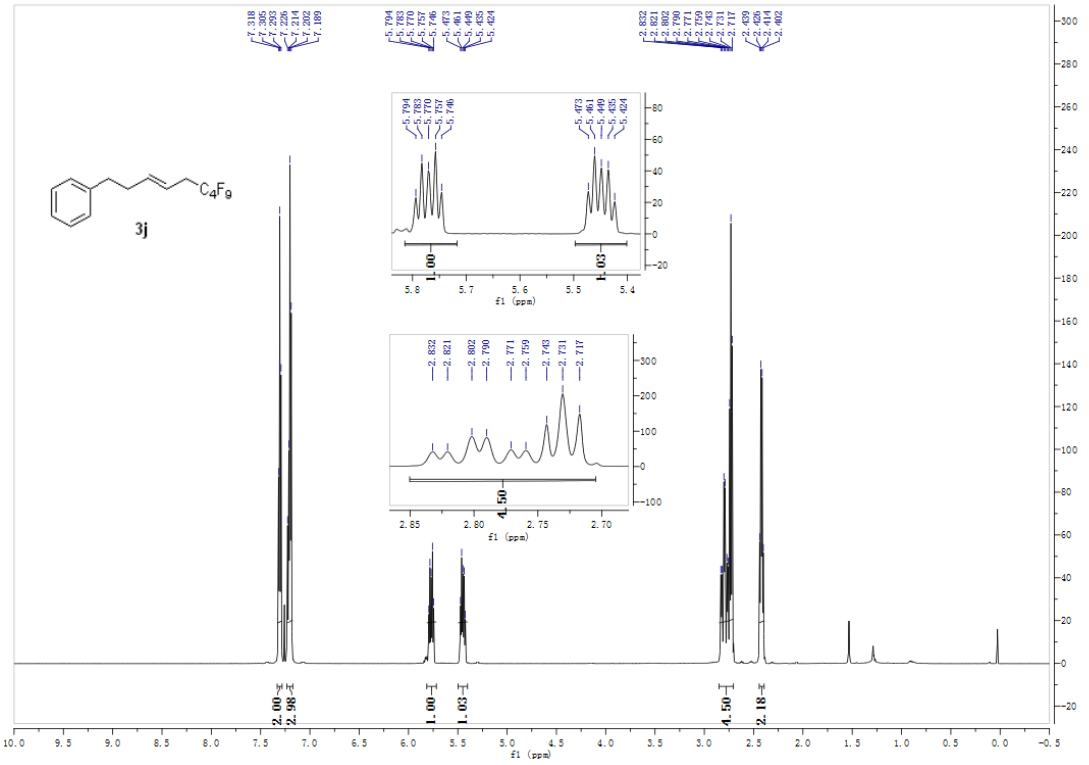
(*E*)-(5,5,6,6,7,7,8,8,8-nonafluorooct-2-en-1-yl)benzene (3i)

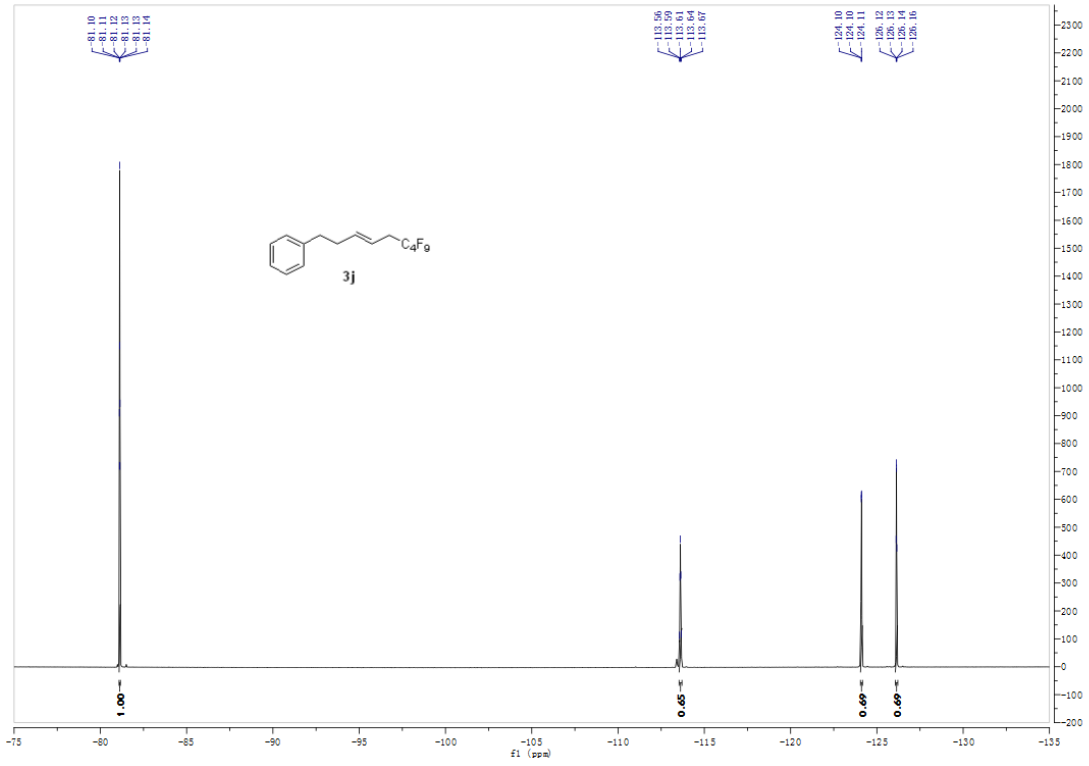


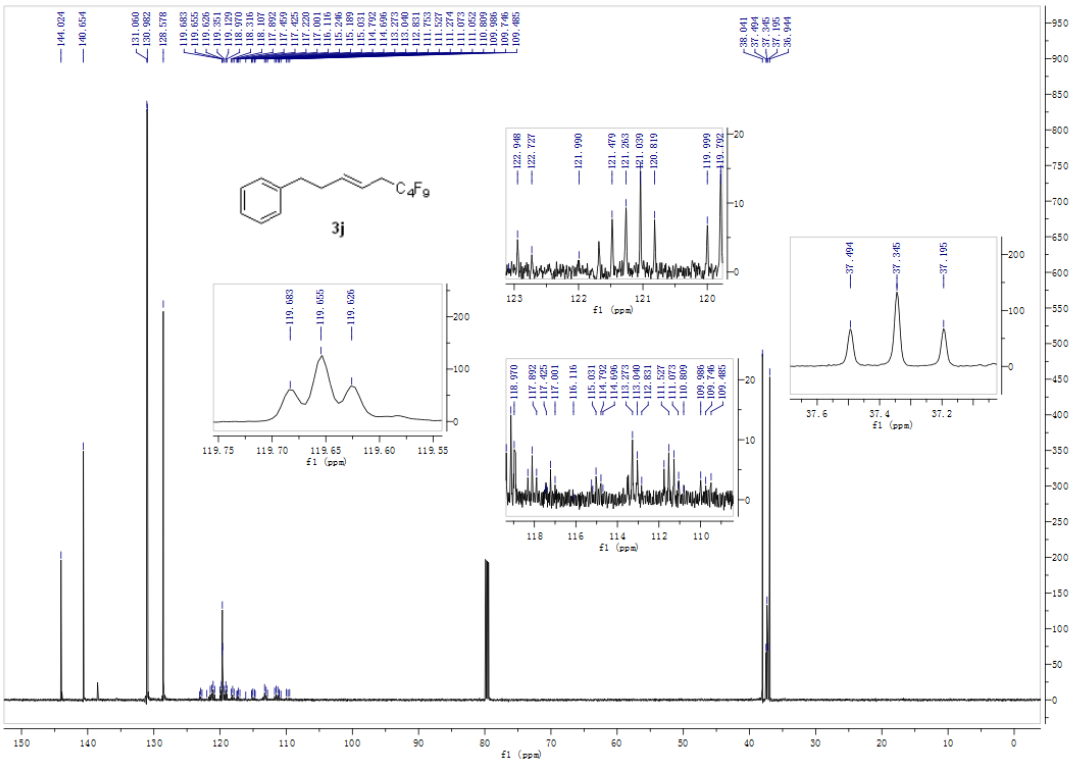

3i
3.00
1.96
2.03
2.03
f1 (ppm)


3i
f1 (ppm)

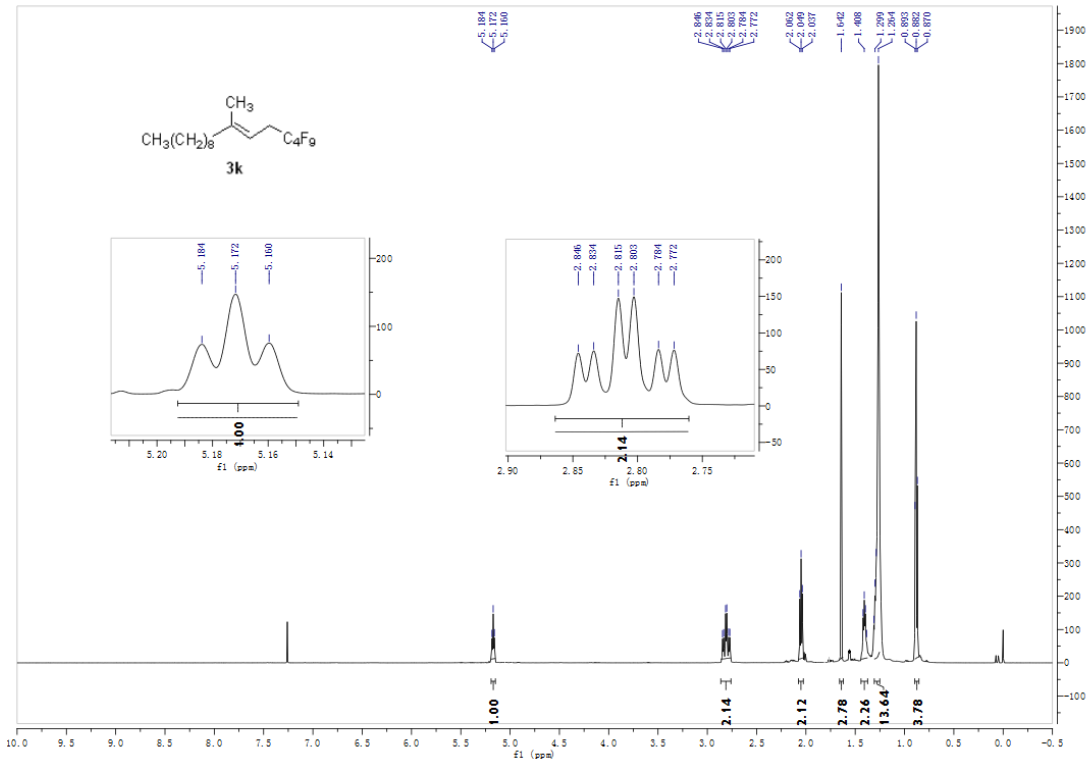
(*E*)-(6,6,7,7,8,8,9,9,9-nonafluorononon-3-en-1-yl)benzene (3j)

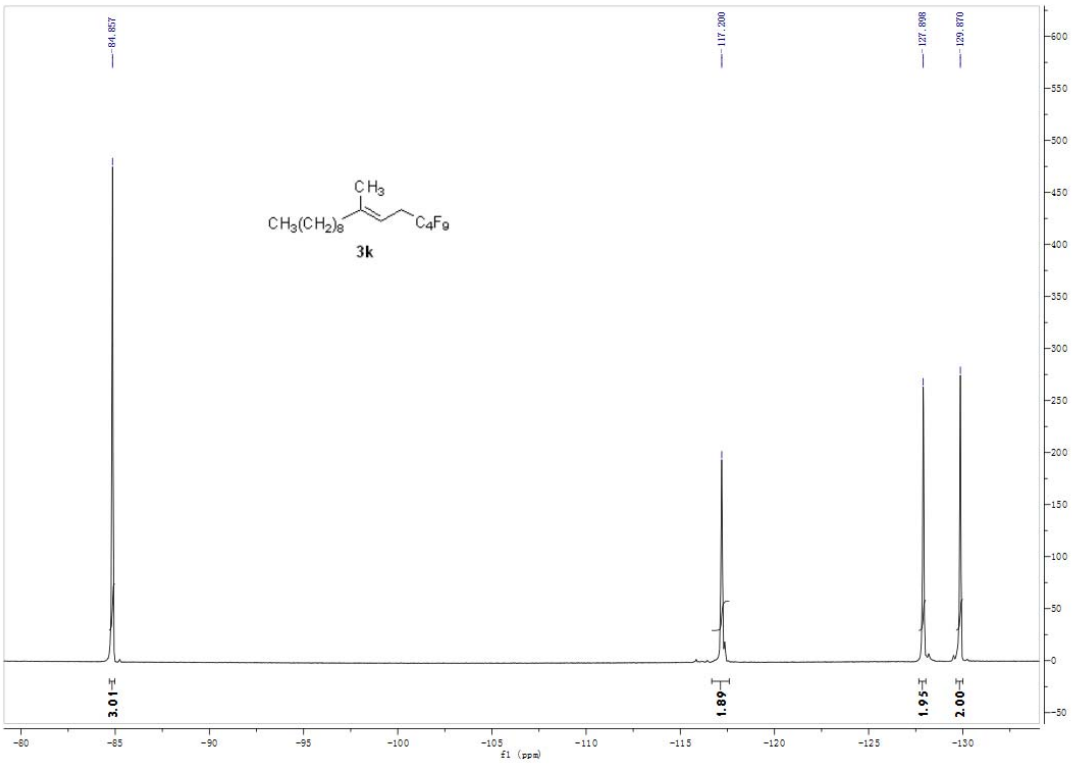


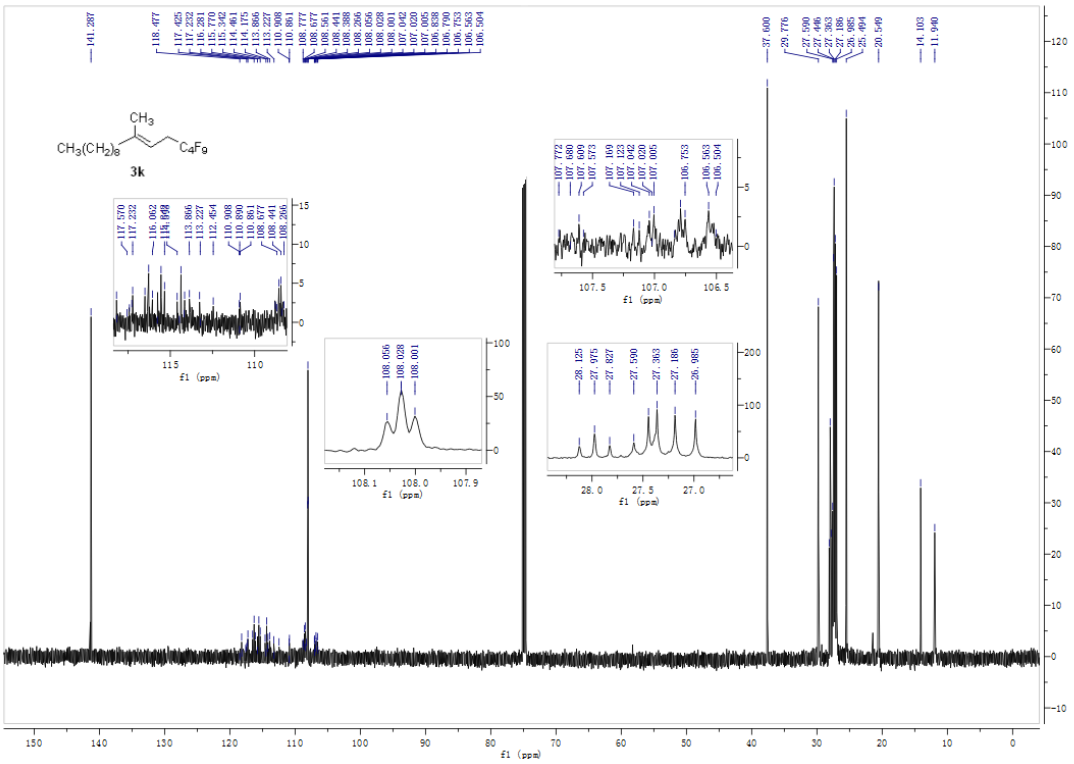




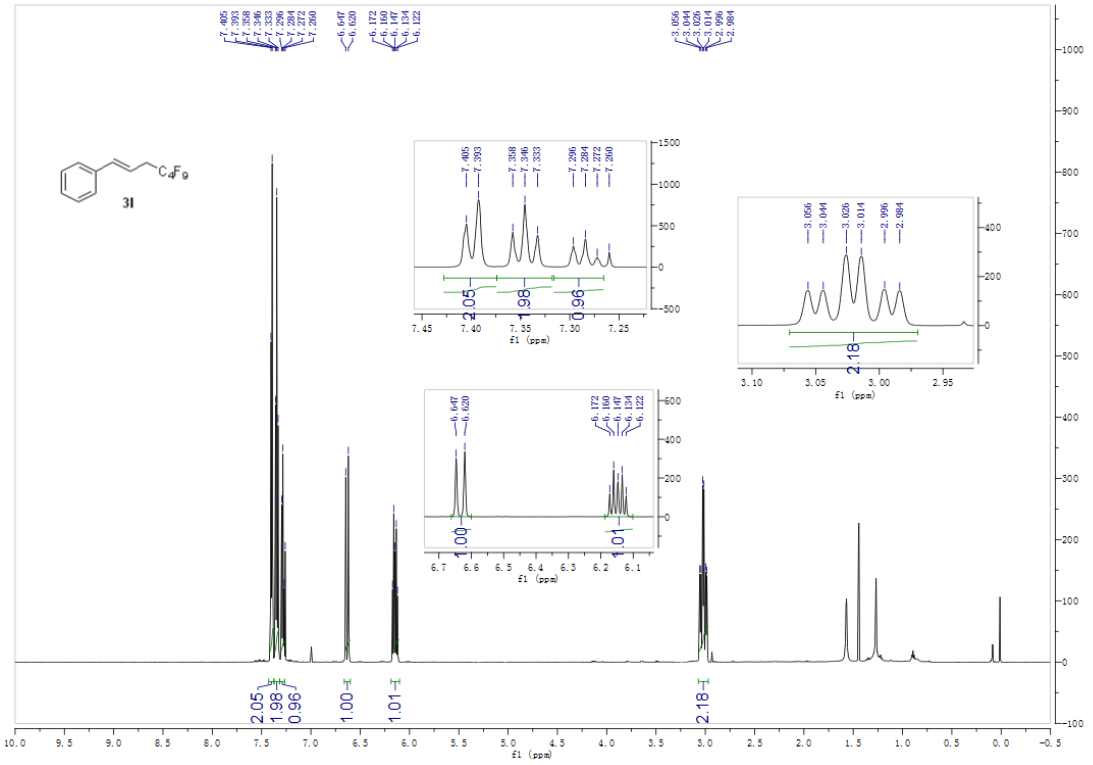
(*E*)-1,1,1,2,2,3,3,4,4-nonafluoro-6-methylhexadec-6-ene (3k)



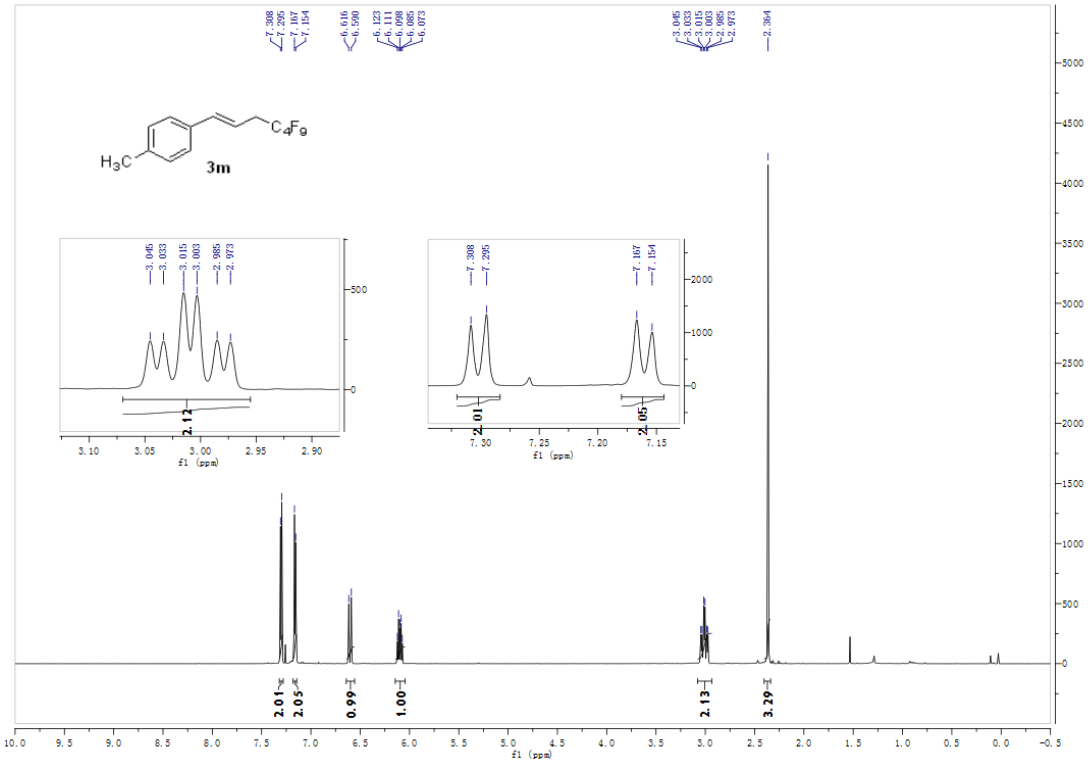

-84.857
-117.200
-127.898
-129.870
CH3
CH3(CH2)8
C4F9
3k
3.01
1.89
1.95
2.00
f1 (ppm)

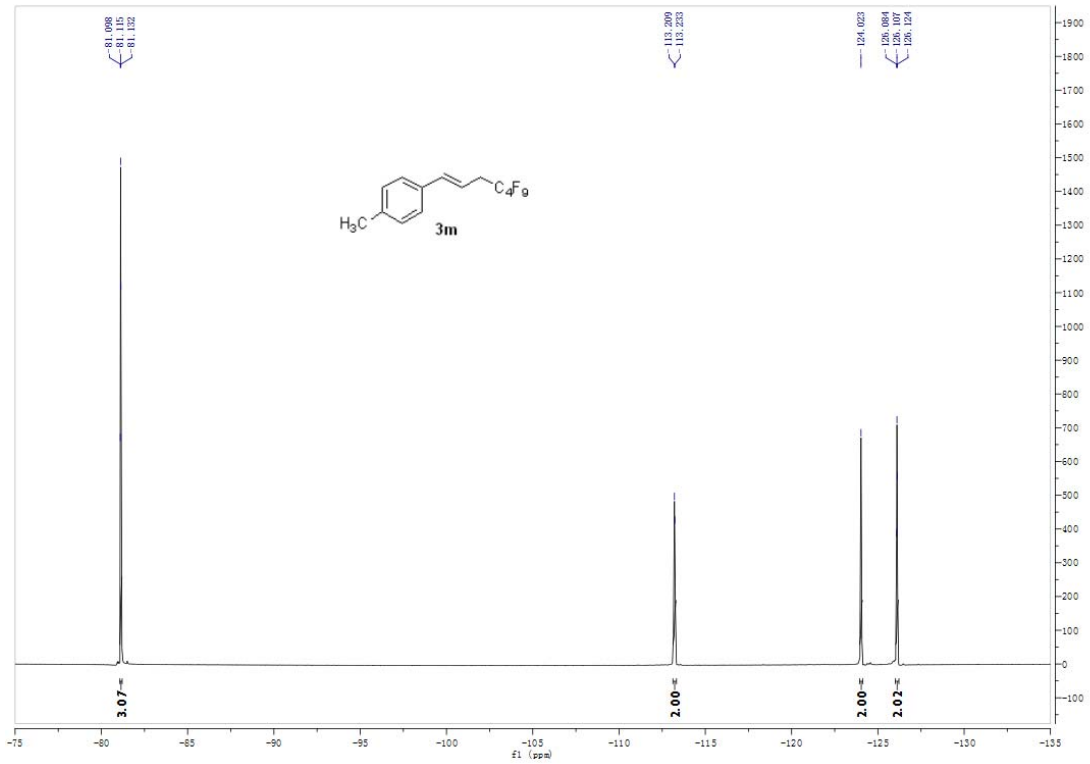

141.287
118.477
117.425
117.232
116.281
115.770
115.342
114.461
114.175
113.366
113.227
110.908
110.861
108.777
108.677
108.561
108.441
108.388
108.266
108.056
108.028
108.001
107.042
107.020
107.005
106.795
106.753
106.563
106.504
37.600
29.776
27.590
27.496
27.383
27.186
26.985
25.494
20.549
14.103
11.940
CH3
CH3(CH2)8
C4F9
3k
f1 (ppm)

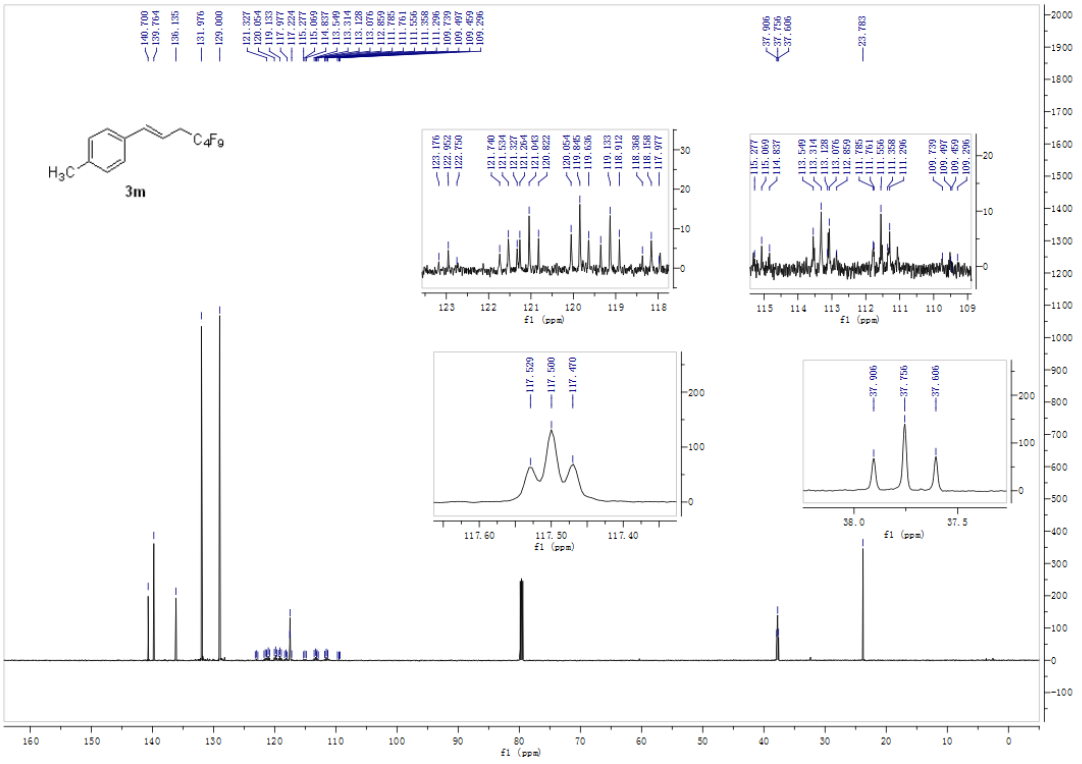
(*E*)-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl)benzene (3l)



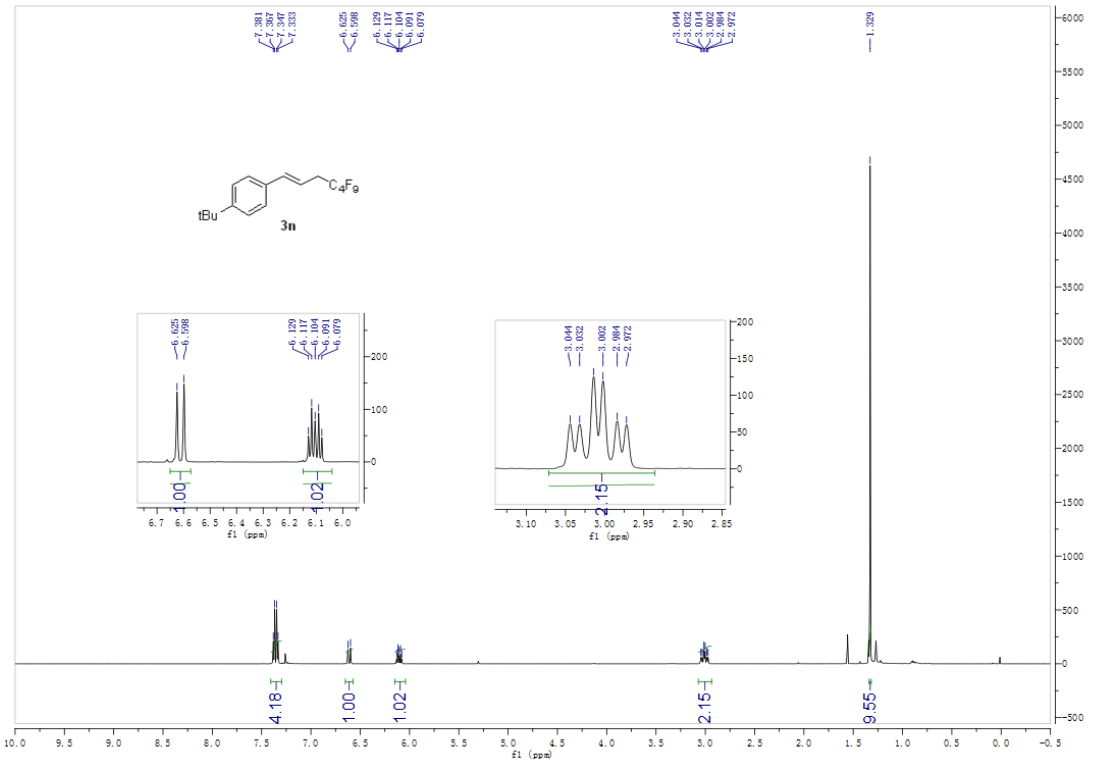
(*E*)-1-methyl-4-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl)benzene (3m)

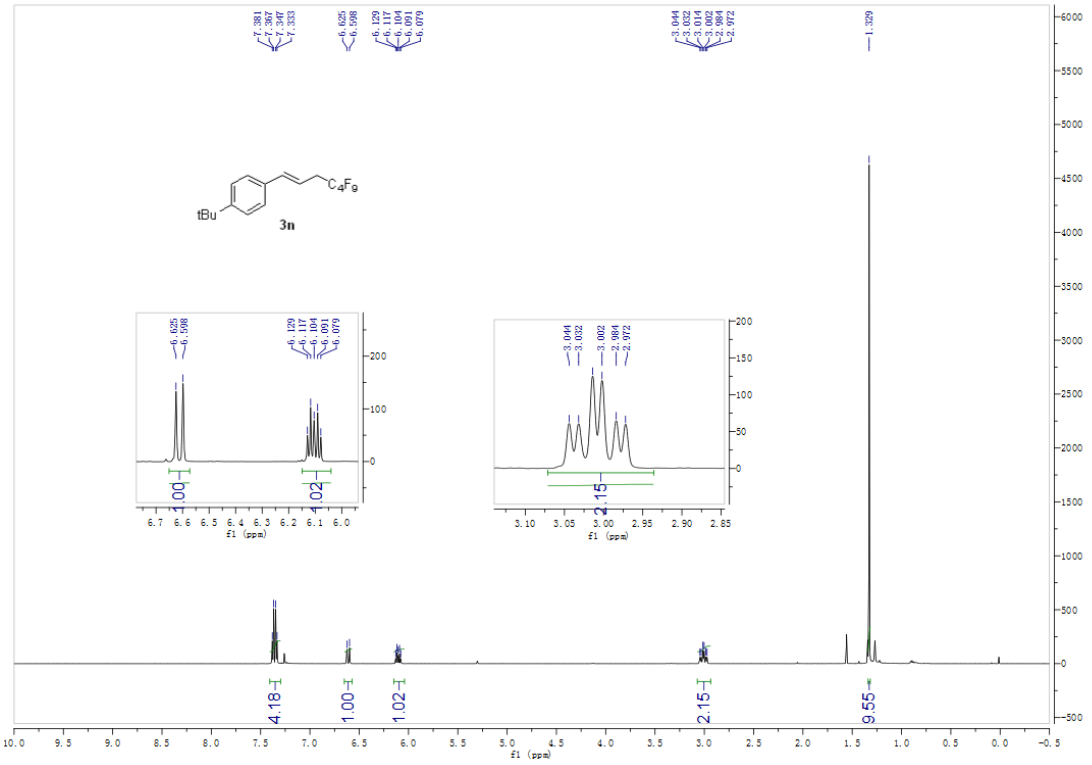


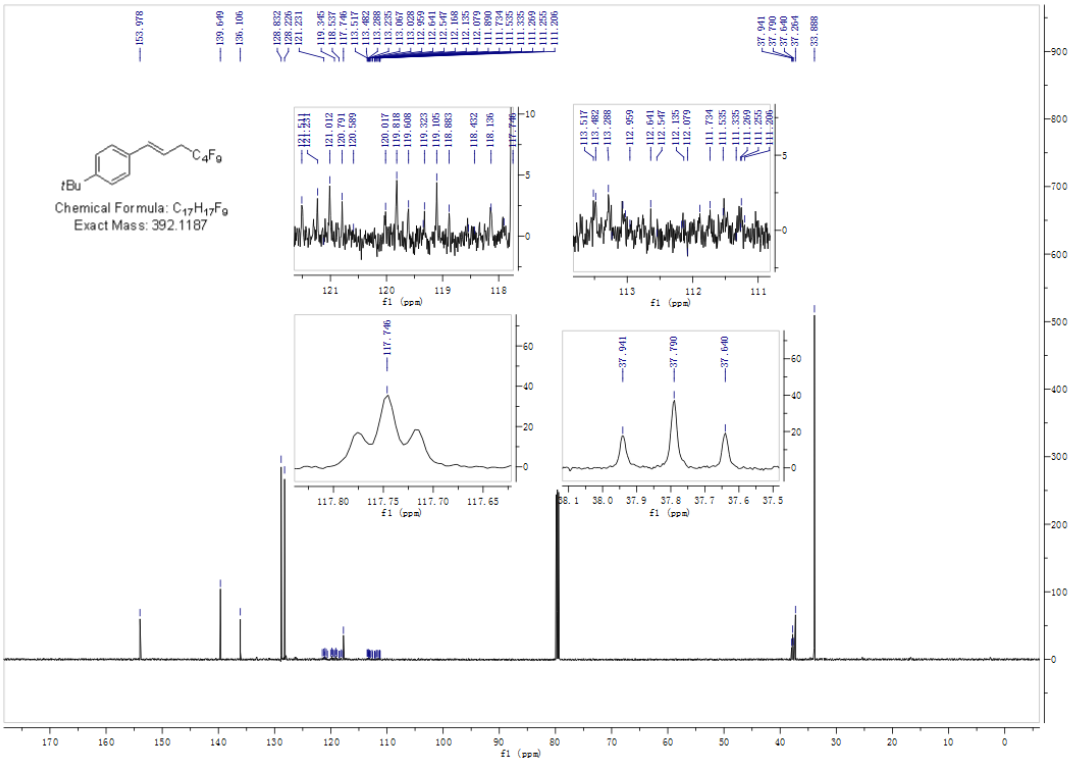




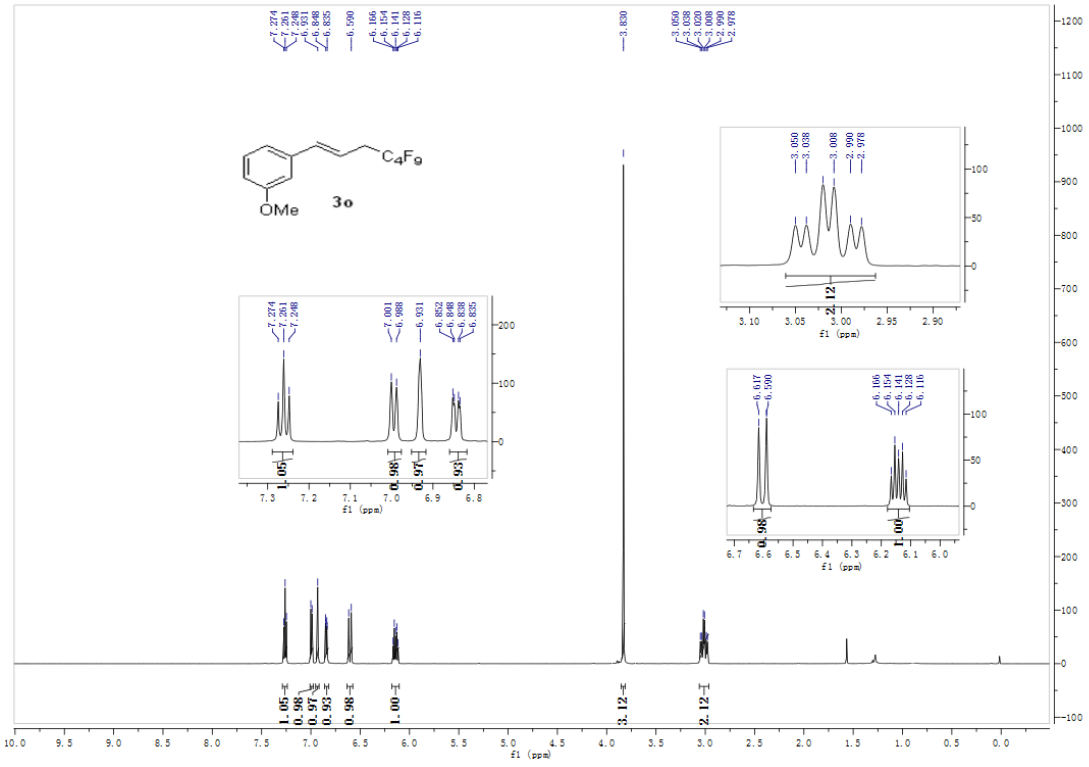
(*E*)-1-methyl-3-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl)benzene (3n)

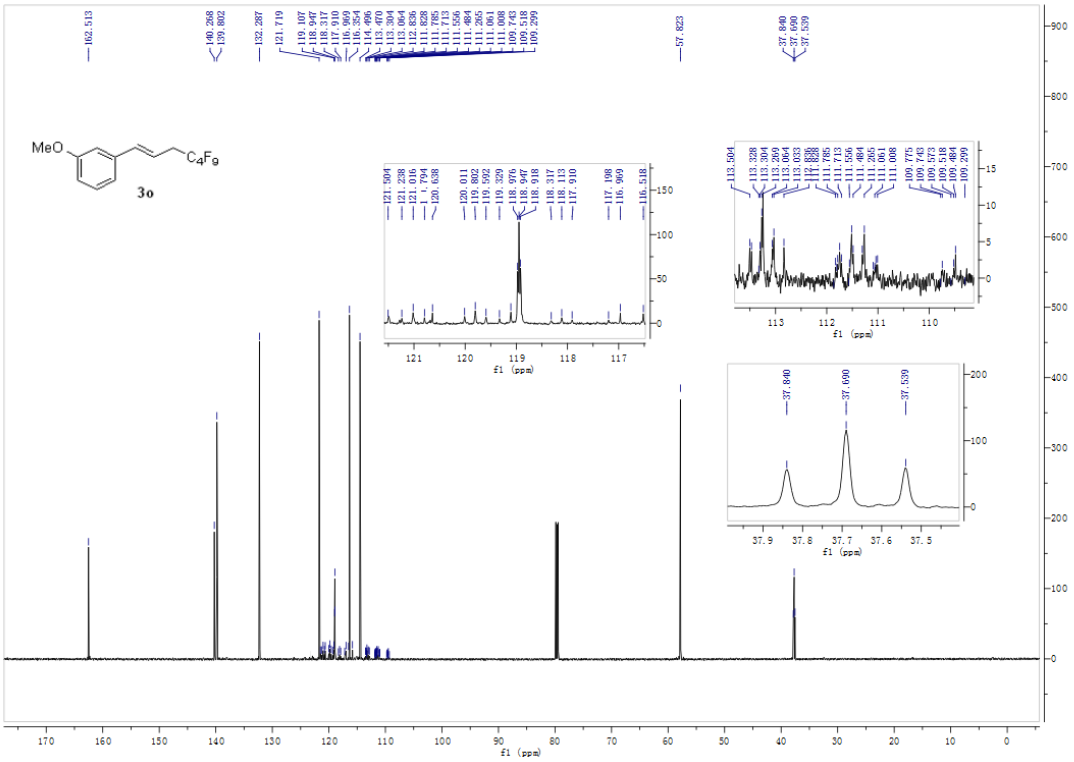



tBu
C4F9
3n

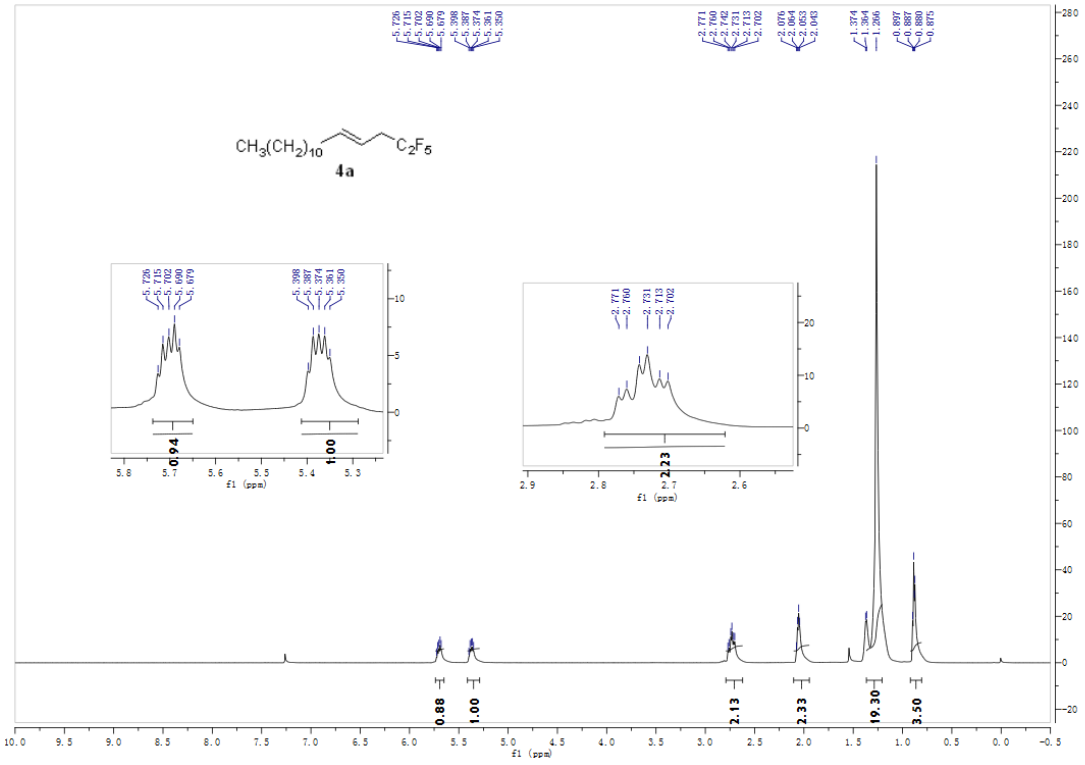

tBu
C4F9
Chemical Formula: C17H17F9
Exact Mass: 392.1187

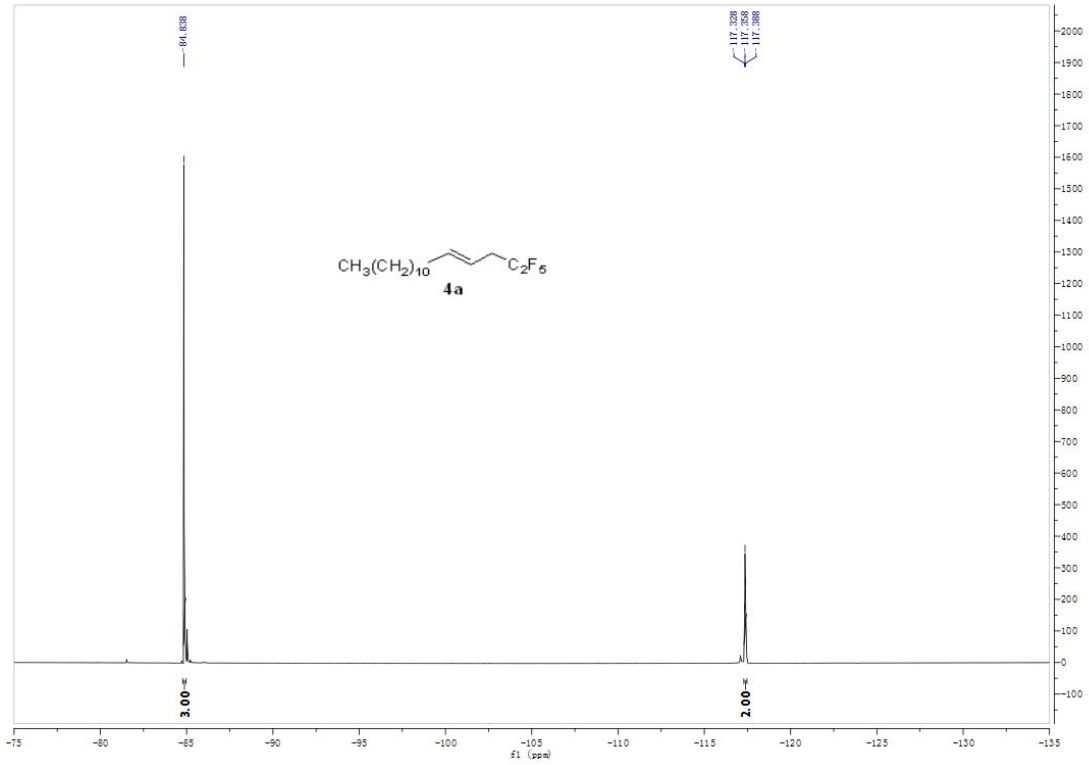
(*E*)-1-methoxy-3-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl)benzene (3o)

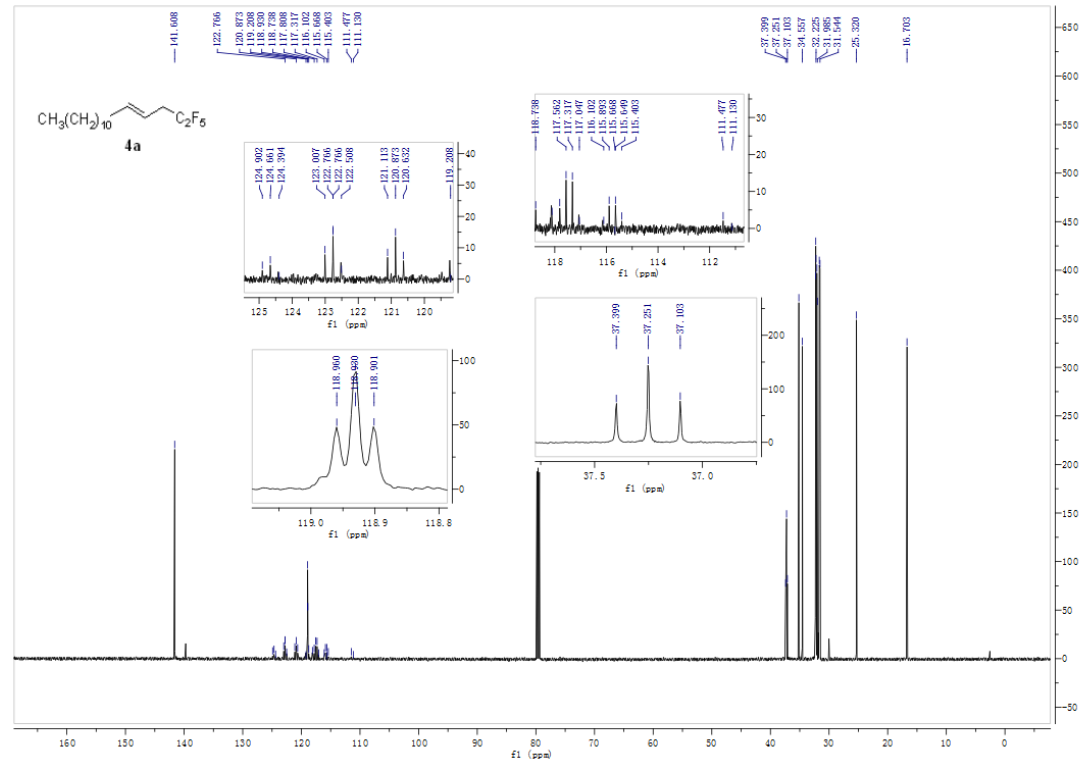




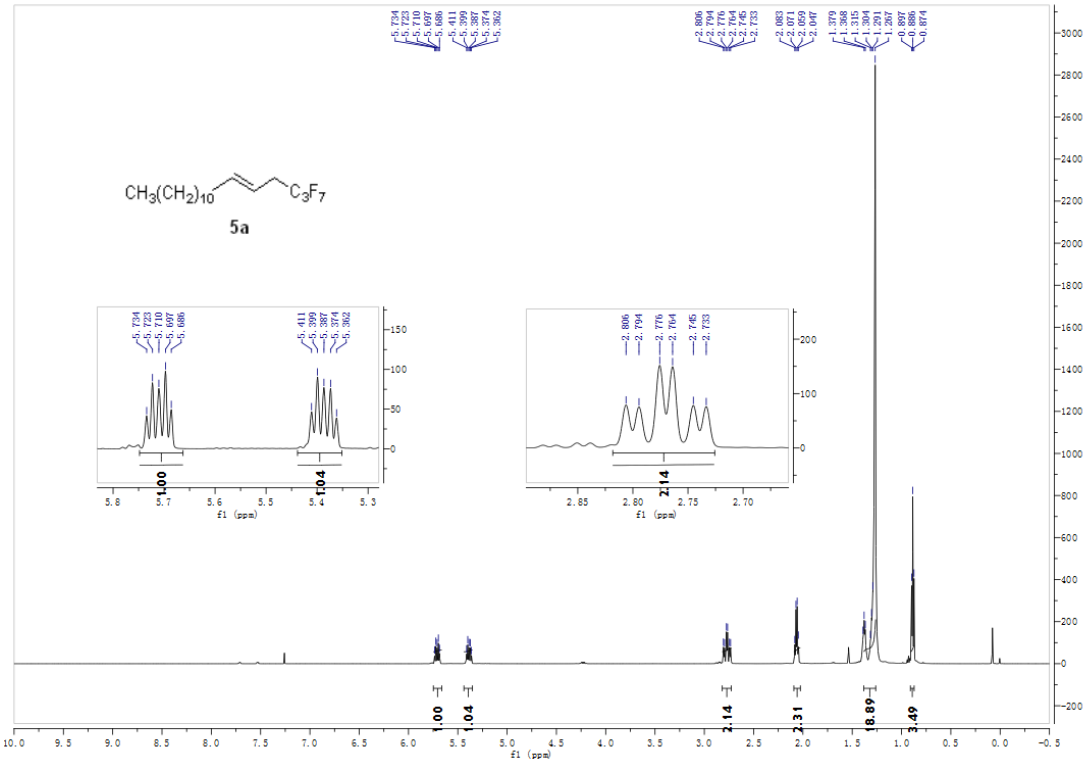
(*E*)-1,1,1,2,2-pentafluorohexadec-4-ene (4a)

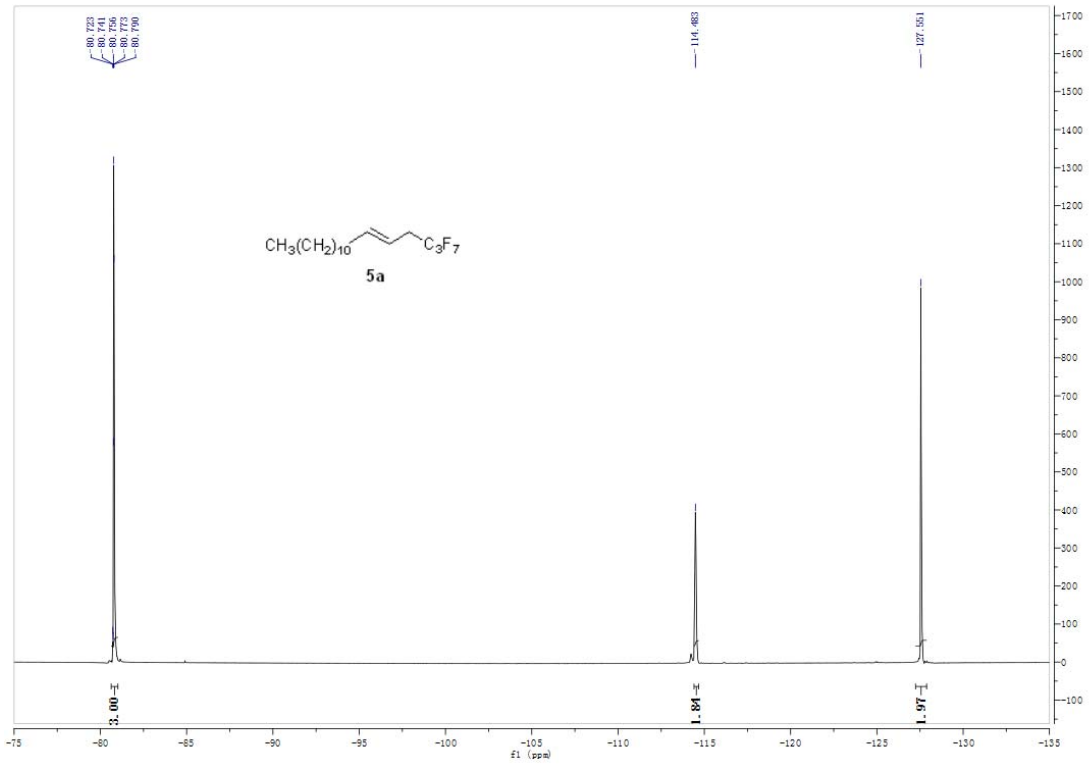


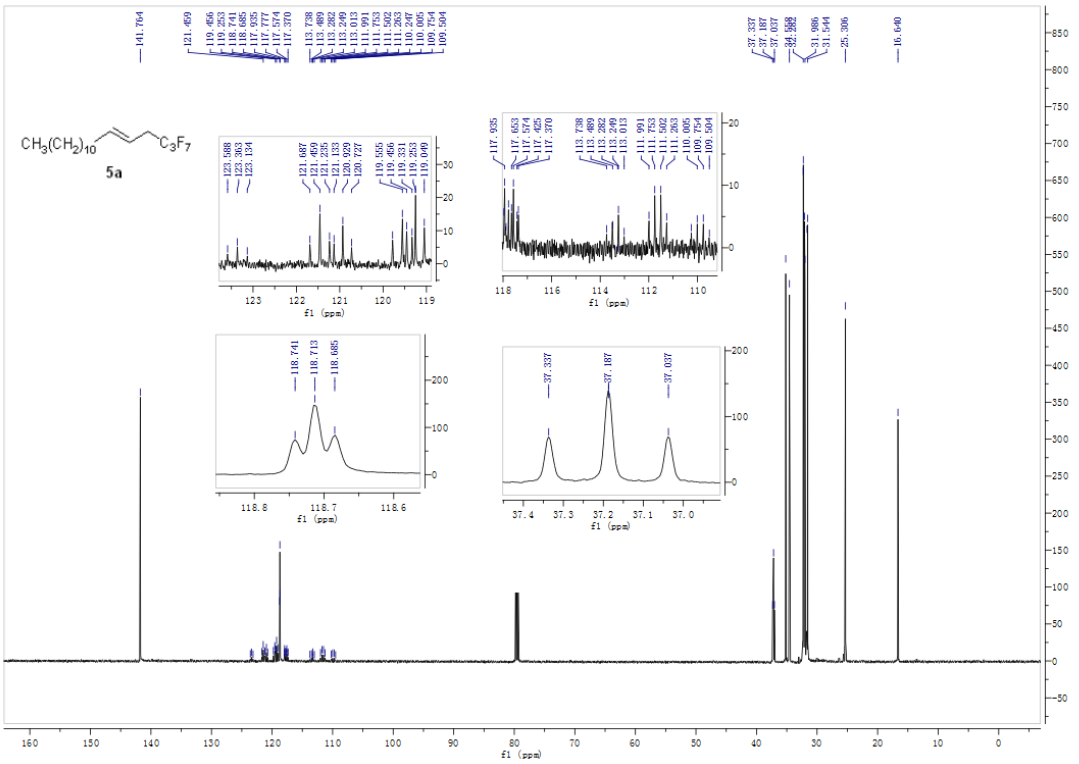

-84.838
-117.328
-117.358
-117.388
CH3(CH2)10
C2F5
4a
3.00
2.00
f1 (ppm)


141.608
122.766
120.873
119.208
118.738
117.808
117.317
116.102
115.668
115.403
111.477
111.130
37.399
37.251
37.103
34.557
32.225
31.985
31.544
25.320
16.703
CH3(CH2)10
C2F5
4a
124.902
124.661
124.394
123.007
122.766
122.525
122.508
121.113
120.873
120.632
119.208
118.960
118.930
118.901
118.798
117.562
117.317
117.047
116.102
115.893
115.668
115.649
115.403
111.477
111.130
37.399
37.251
37.103
f1 (ppm)

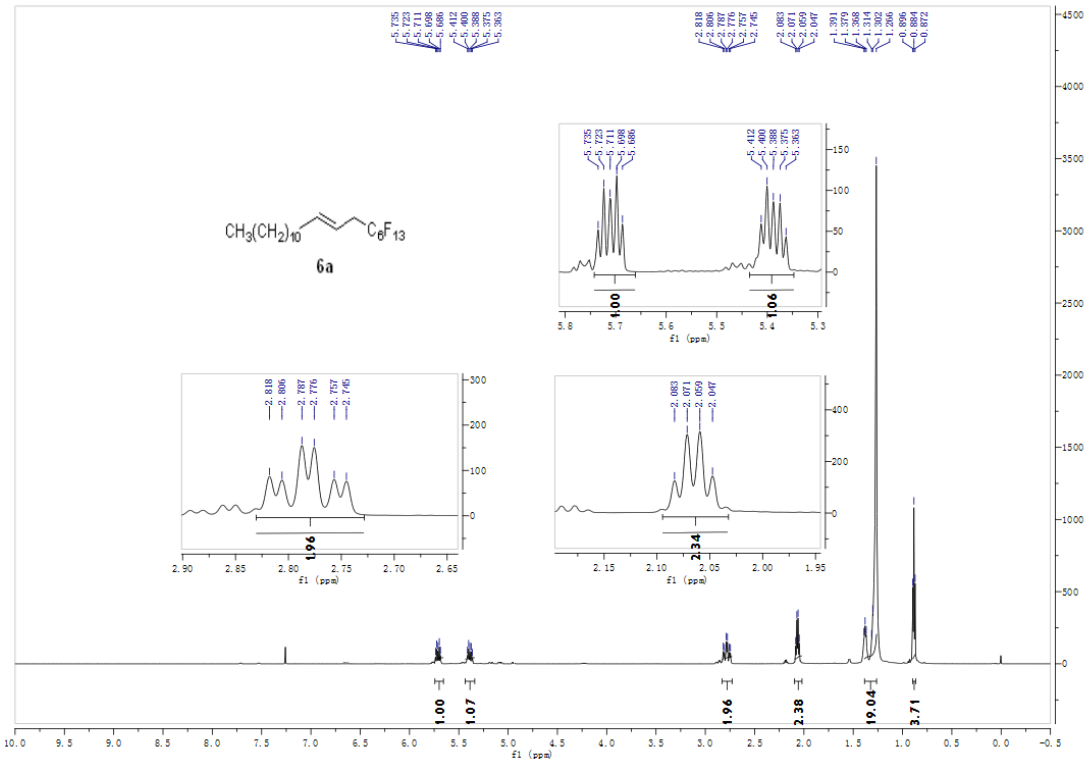
(*E*)-1,1,1,2,2,3,3-heptafluoroheptadec-5-ene (5a)

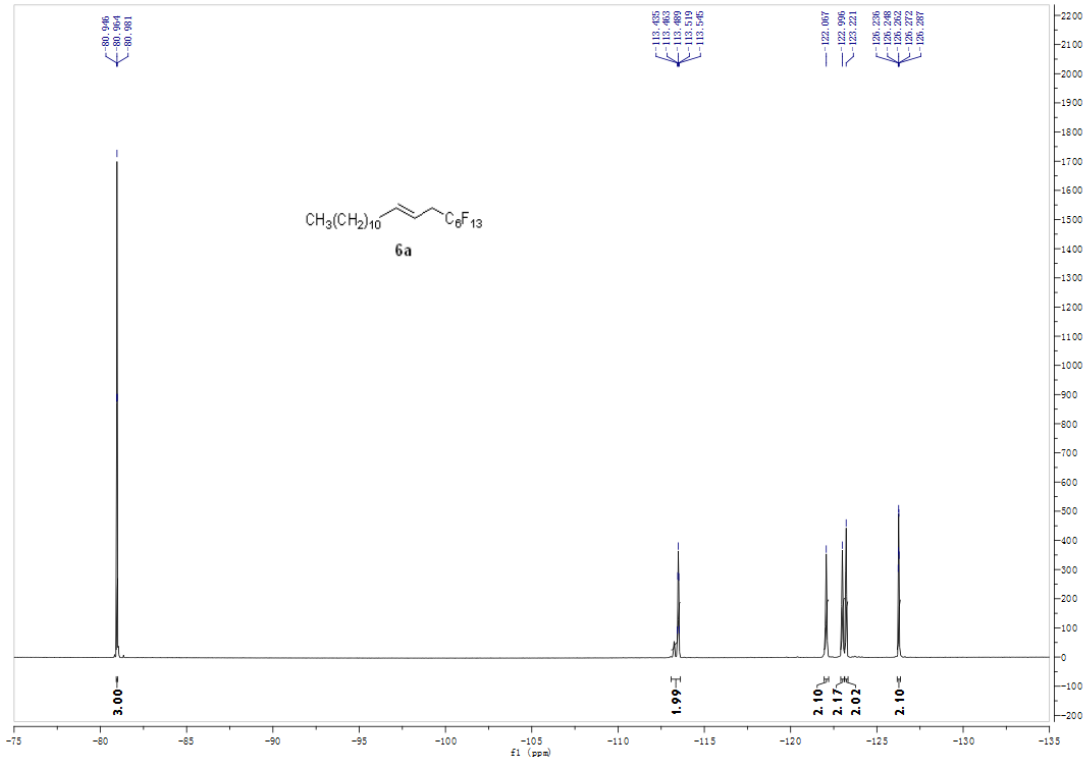


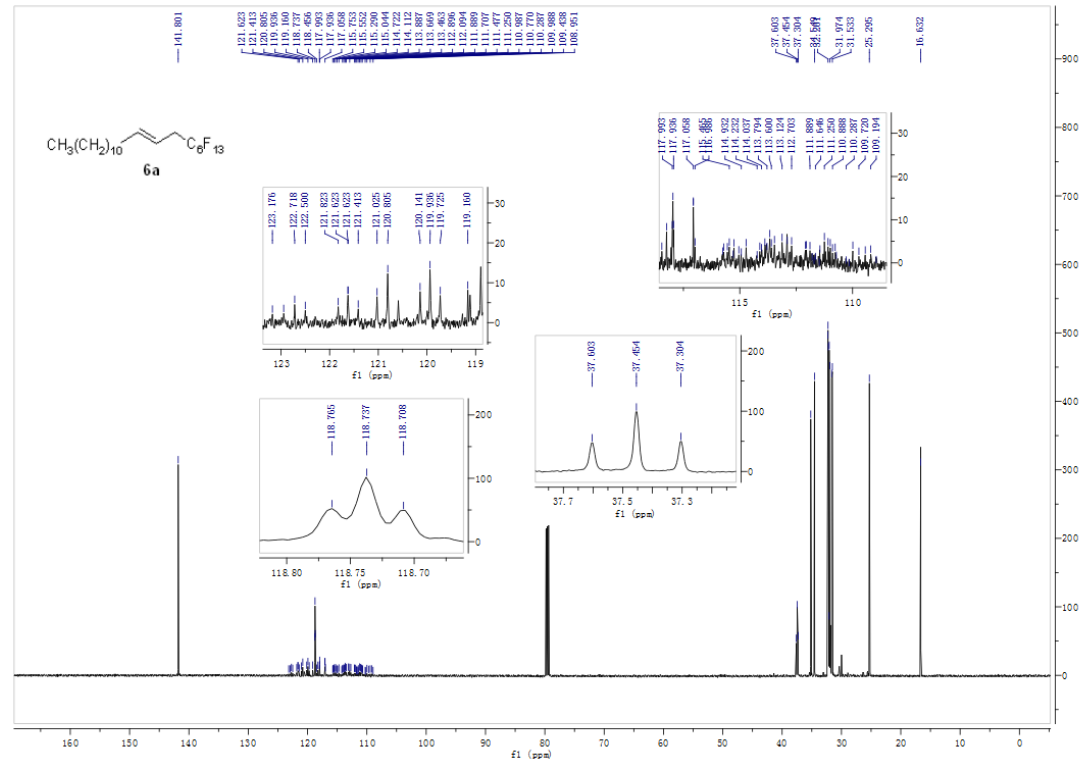




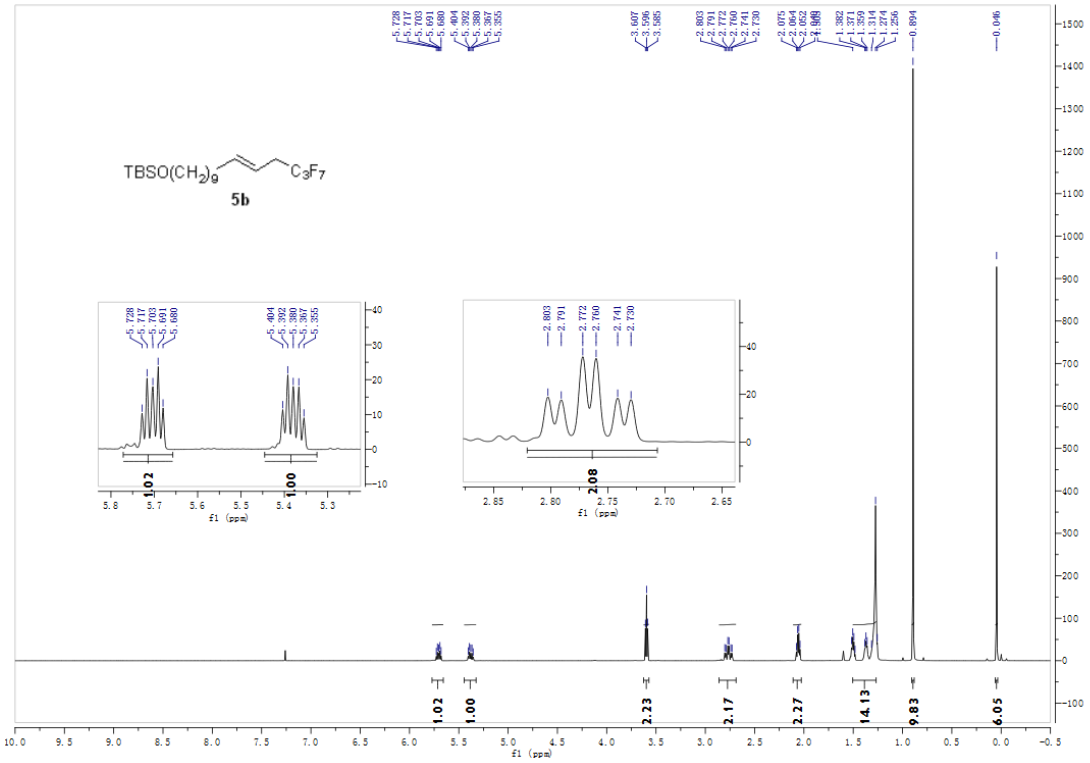
(*E*)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoroicos-8-ene (6a)

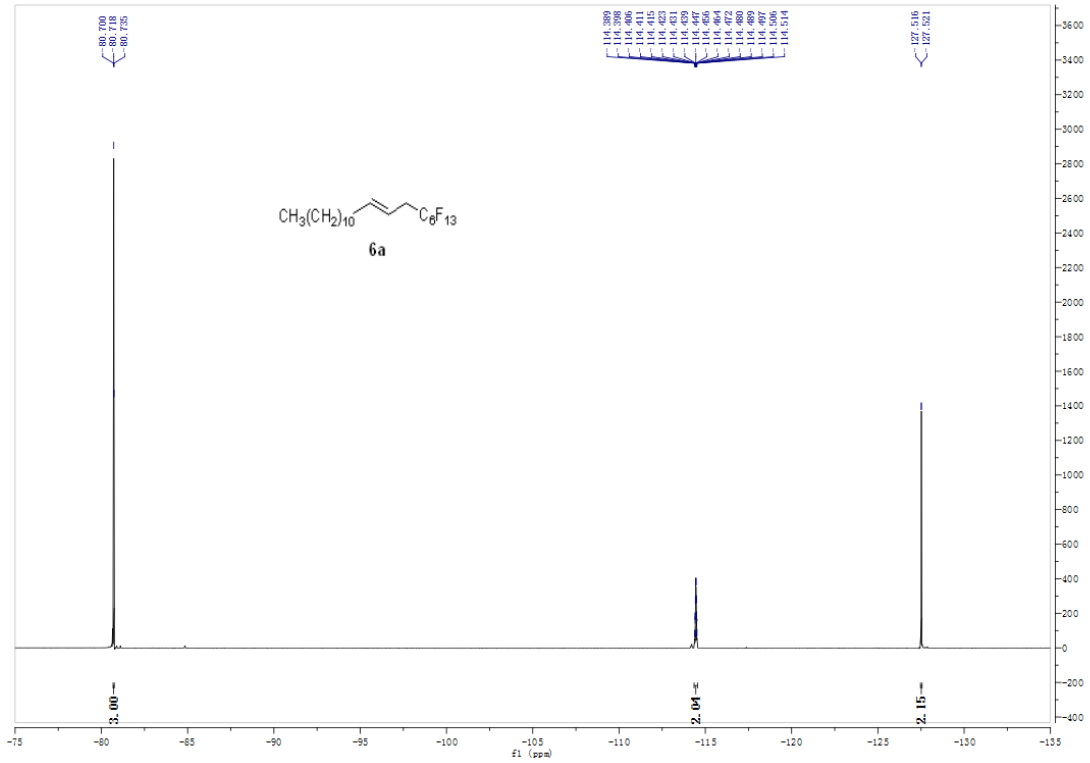


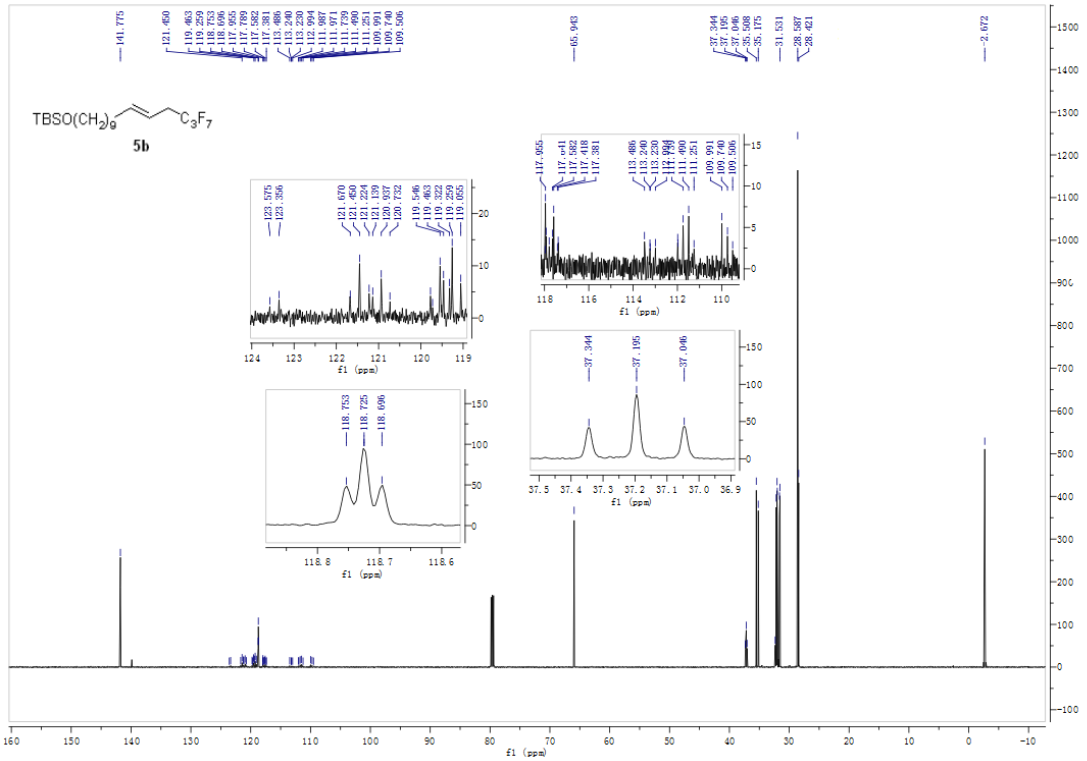

CH3(CH2)10
C6F13
6a
f1 (ppm)


CH3(CH2)10
C6F13
6a
f1 (ppm)

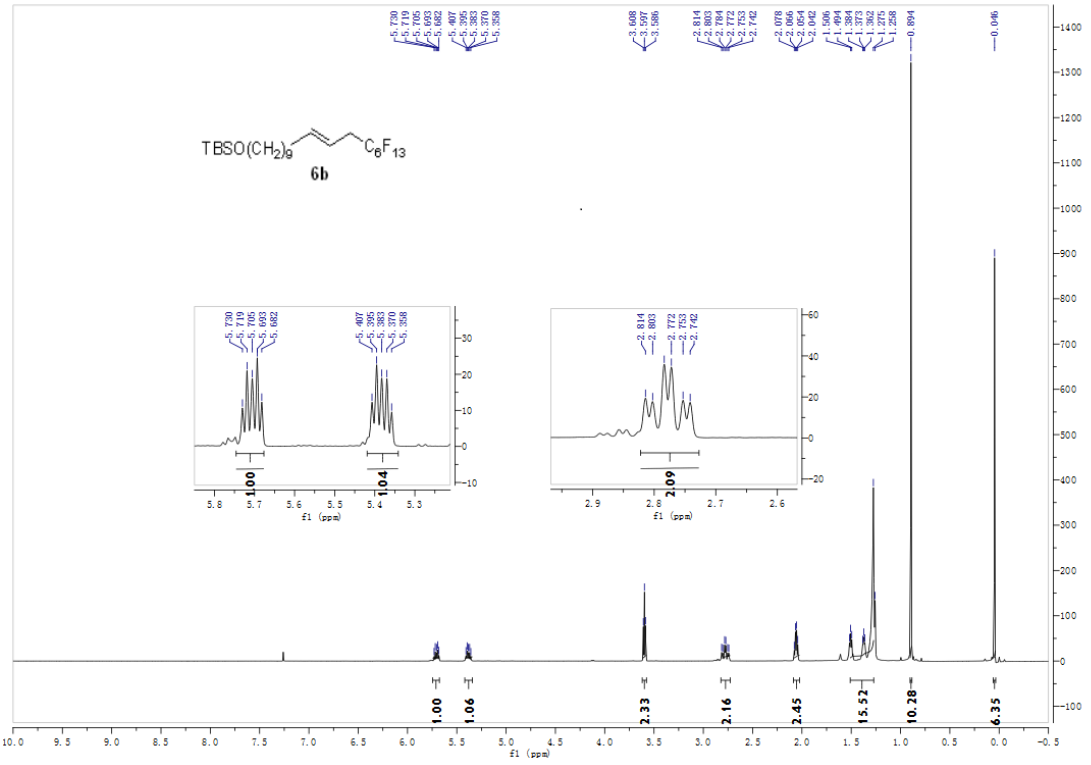
(*E*)-tert-butyl((15,15,16,16,17,17,17-heptafluoroheptadec-12-en-1-yl)oxy)dimethylsilane (5b)

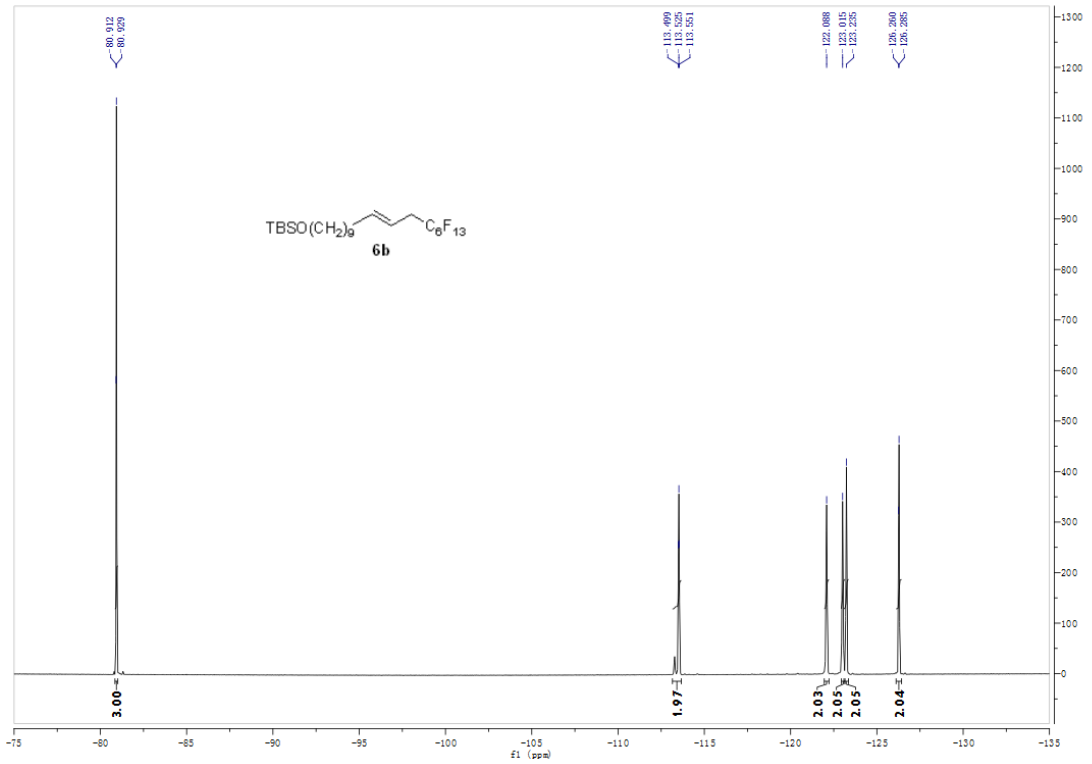


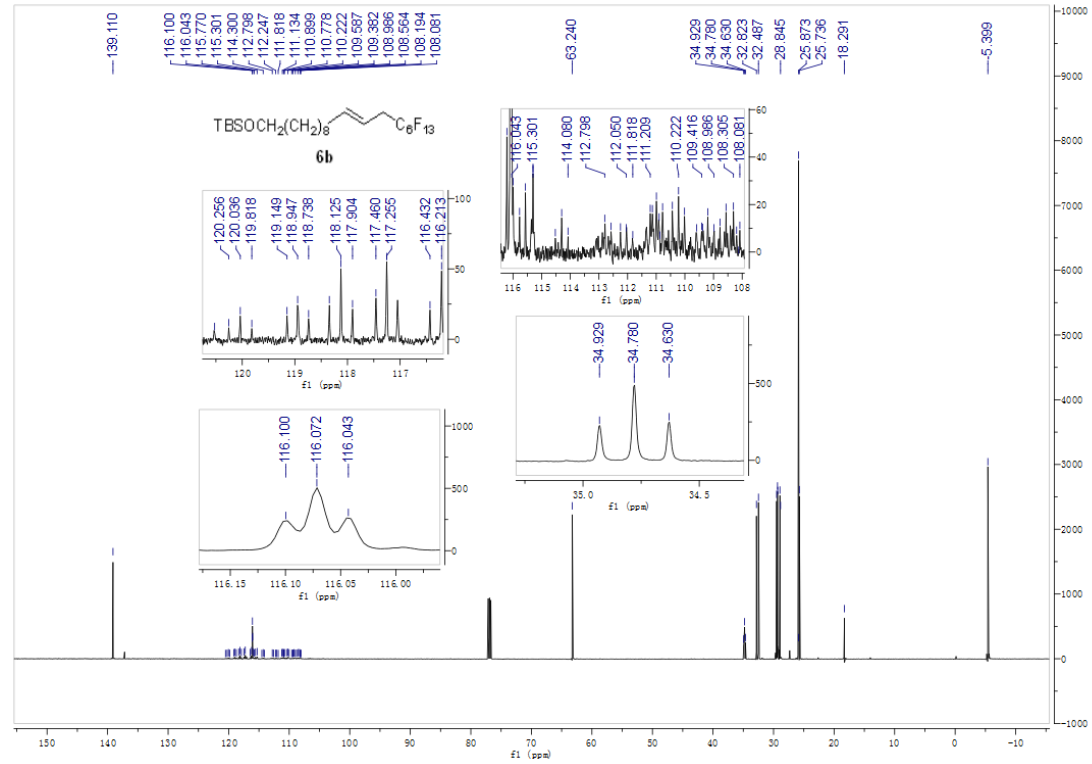




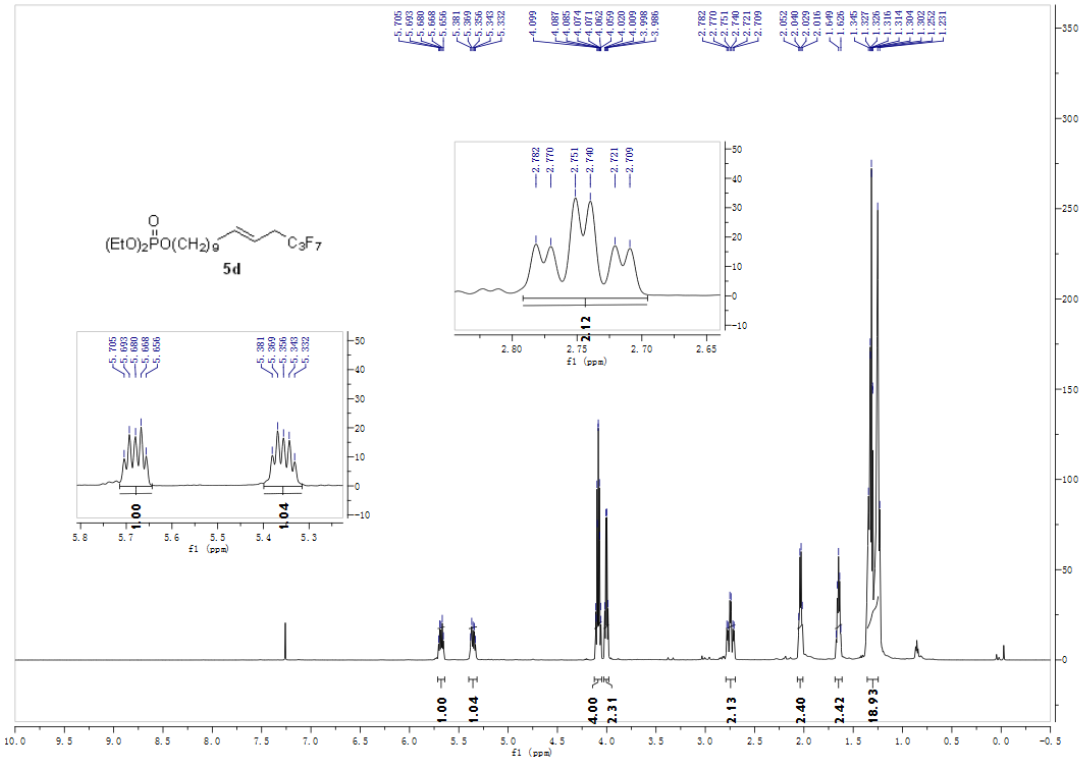
(*E*)-tert-butyldimethyl((15,15,16,16,17,17,18,18,19,19,20,20,20-tridecafluoroicos-12-en-1-yl)oxy)silane (6b)

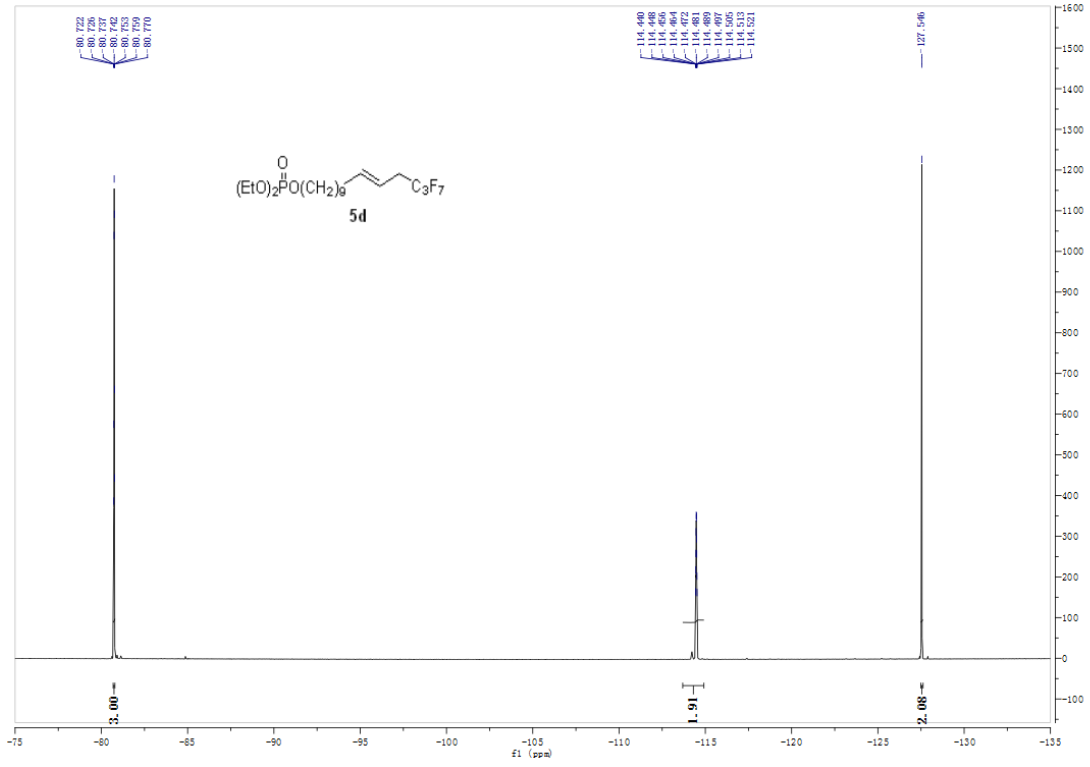


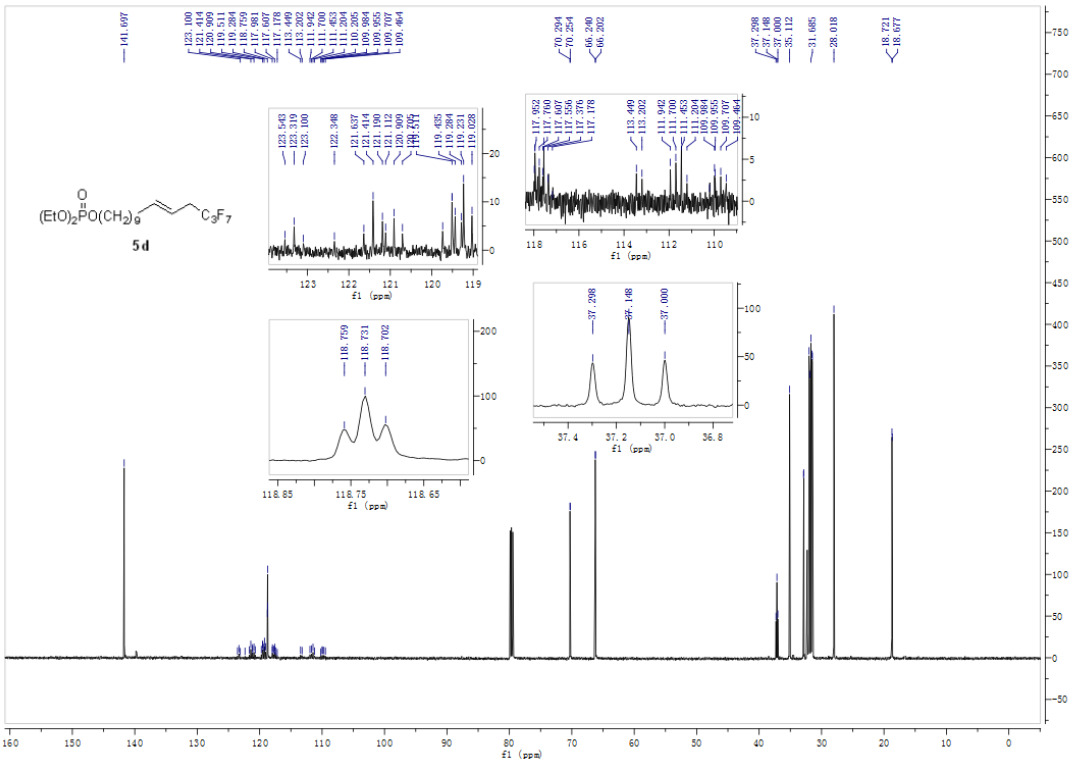

TBSO(CH2)9
C6F13
6b
f1 (ppm)


TBSOCH2(CH2)8
C6F13
6b
f1 (ppm)

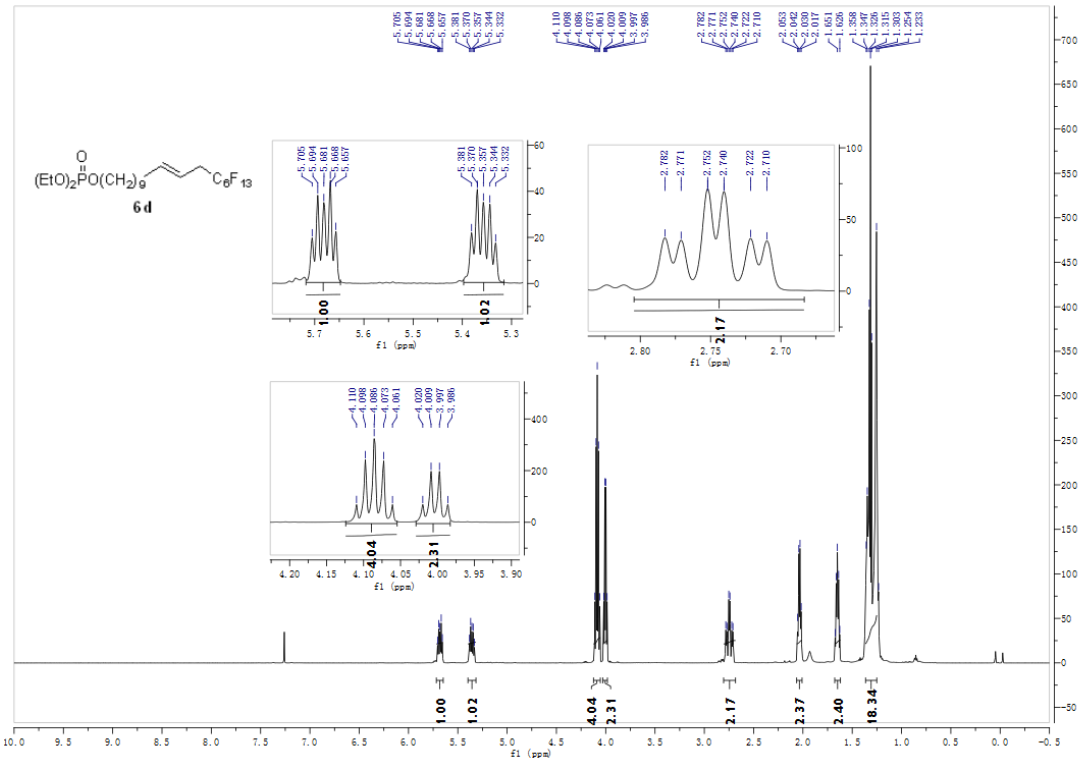
(*E*)-diethyl (13,13,14,14,15,15,15-heptafluoropentadec-10-en-1-yl) phosphate (5d).

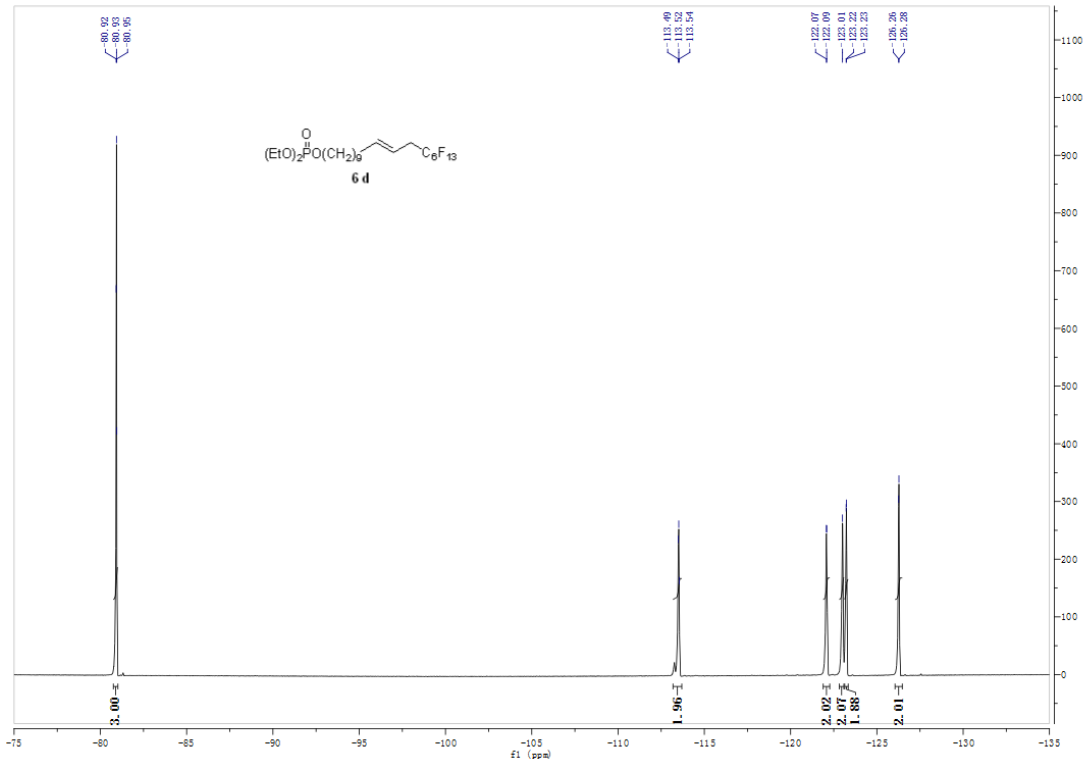


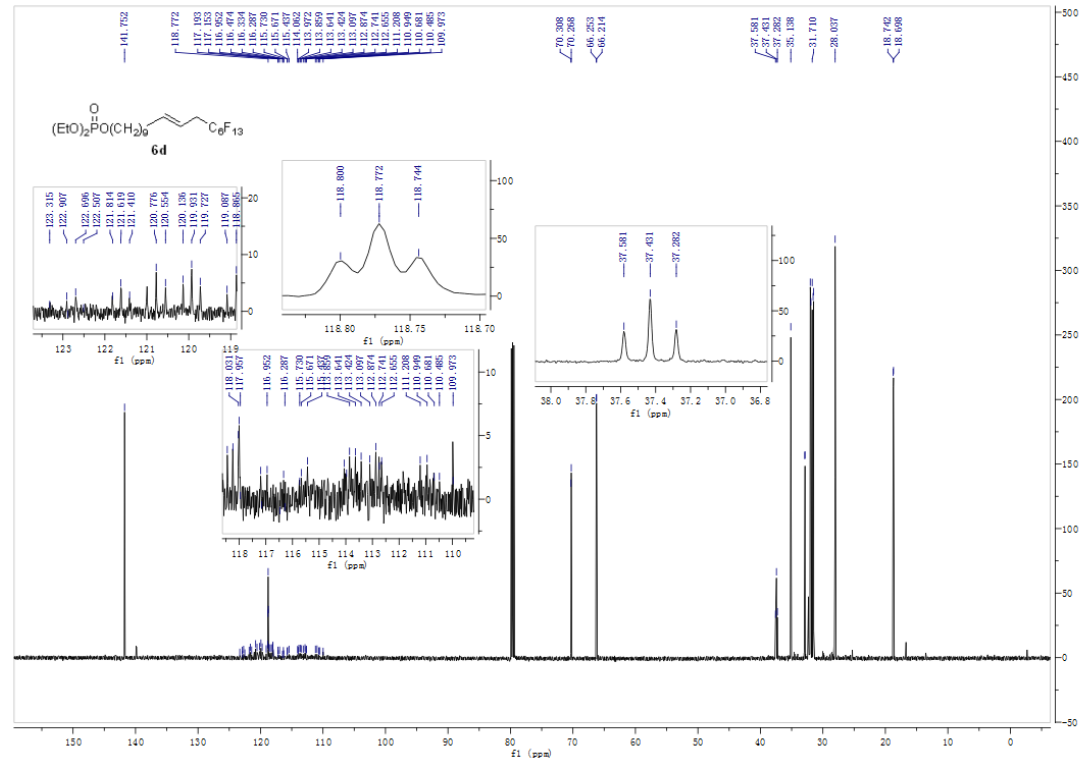




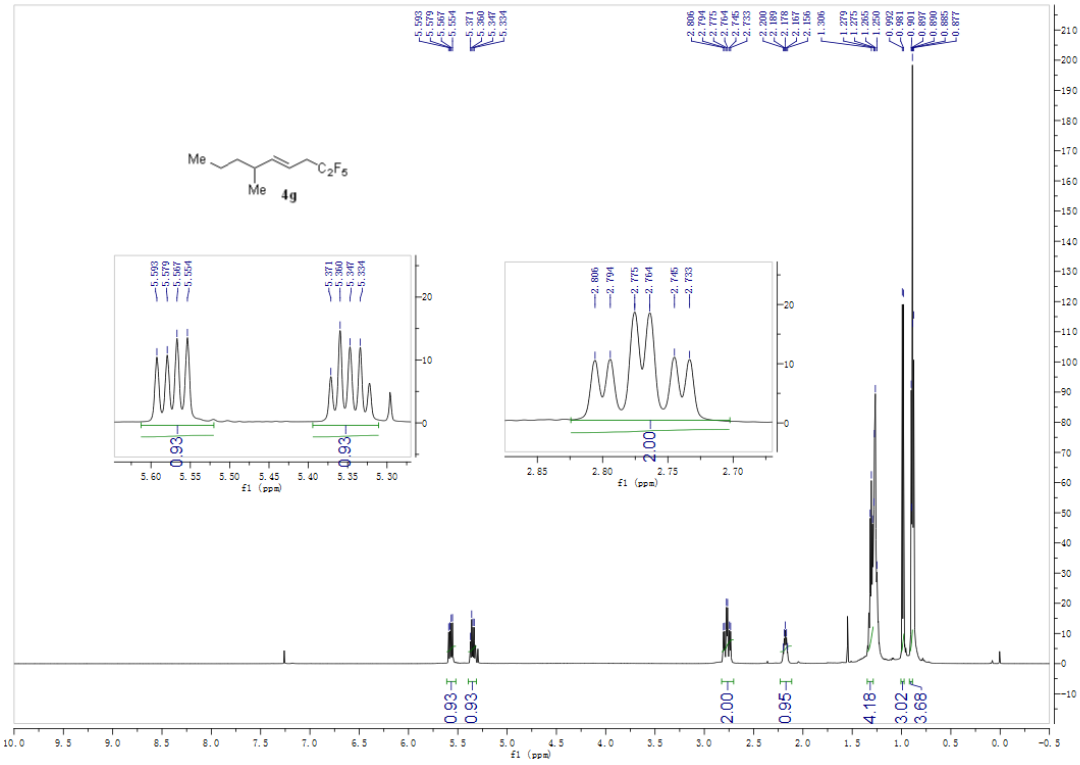
(*E*)-diethyl (13,13,14,14,15,15,16,16,17,17,18,18,18-tridecafluorooctadec-10-en-1-yl) phosphate (6d)

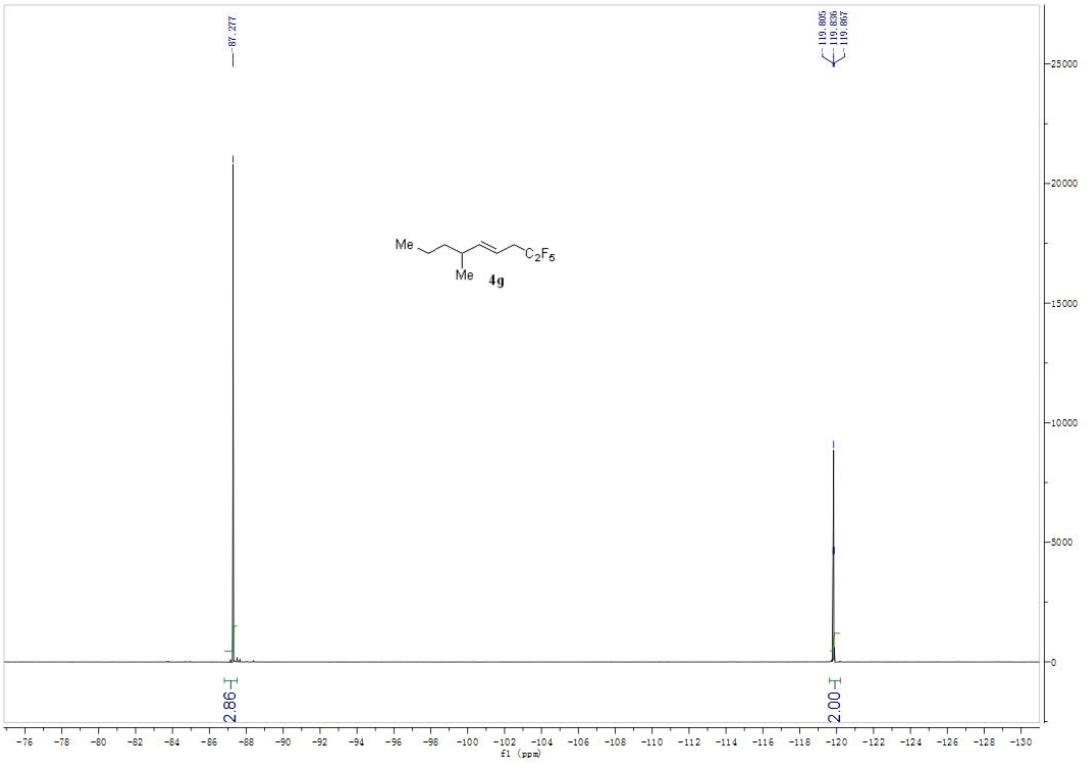


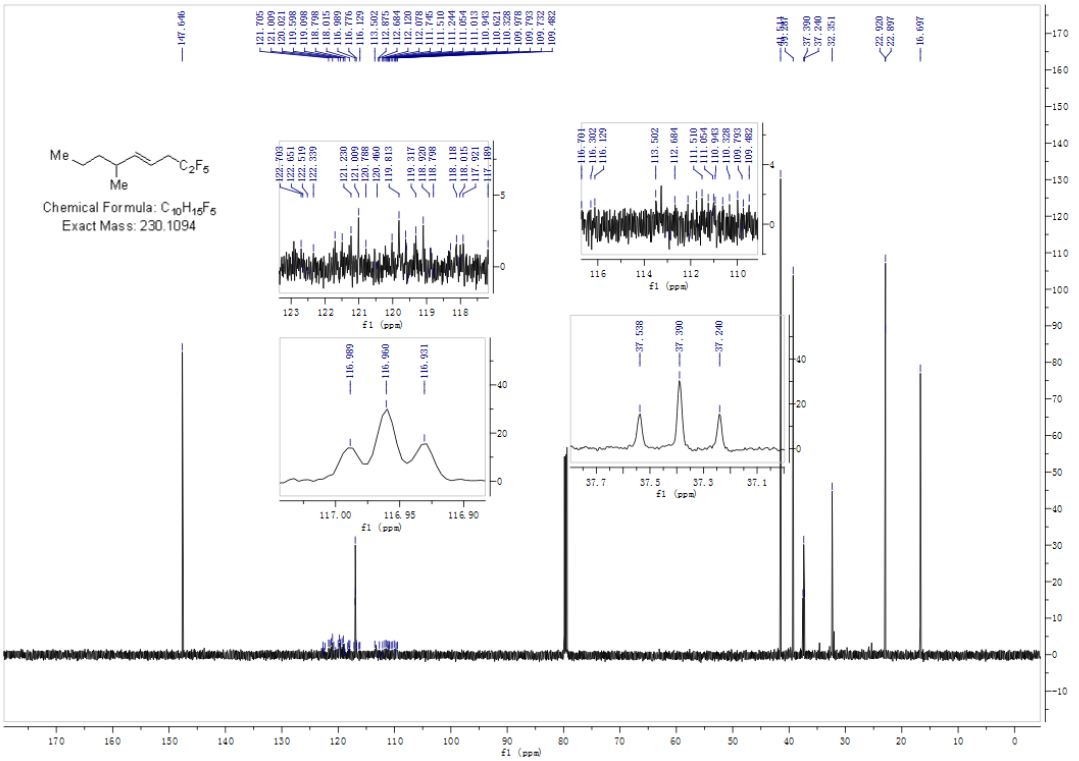

6 d
3.00
1.96
2.02
2.07
1.88
2.01
f1 (ppm)


6d
f1 (ppm)

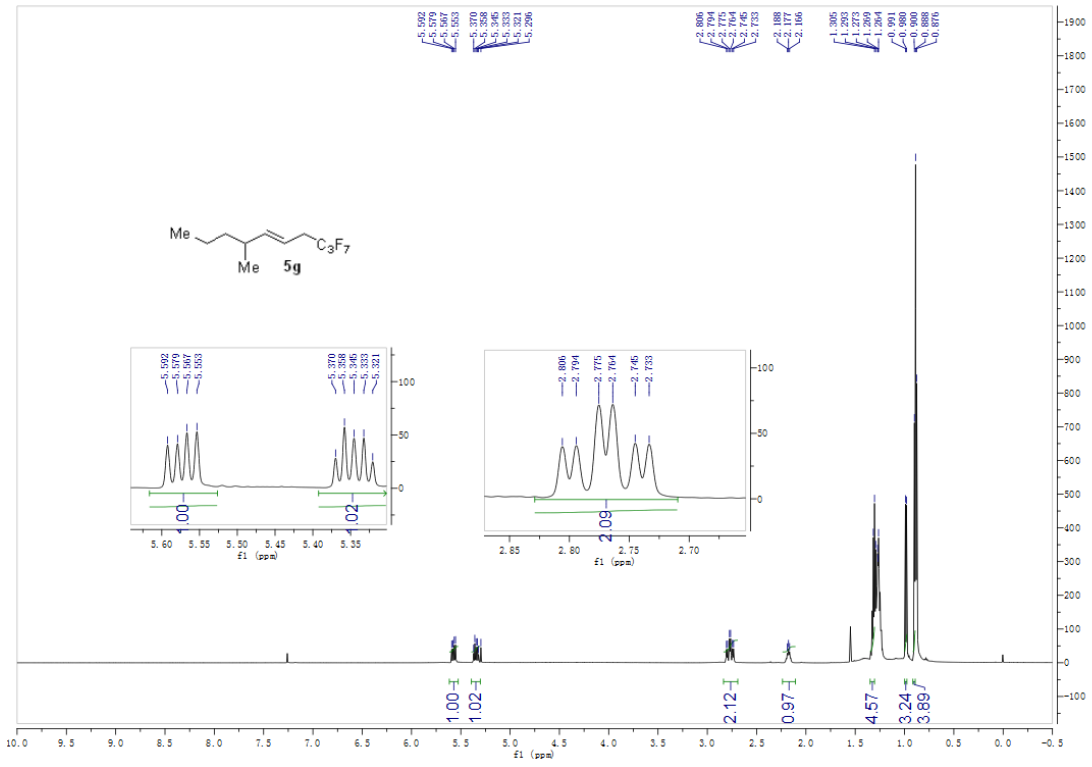
(*E*)-1,1,1,2,2-pentafluoro-6-methylnon-4-ene (4g)

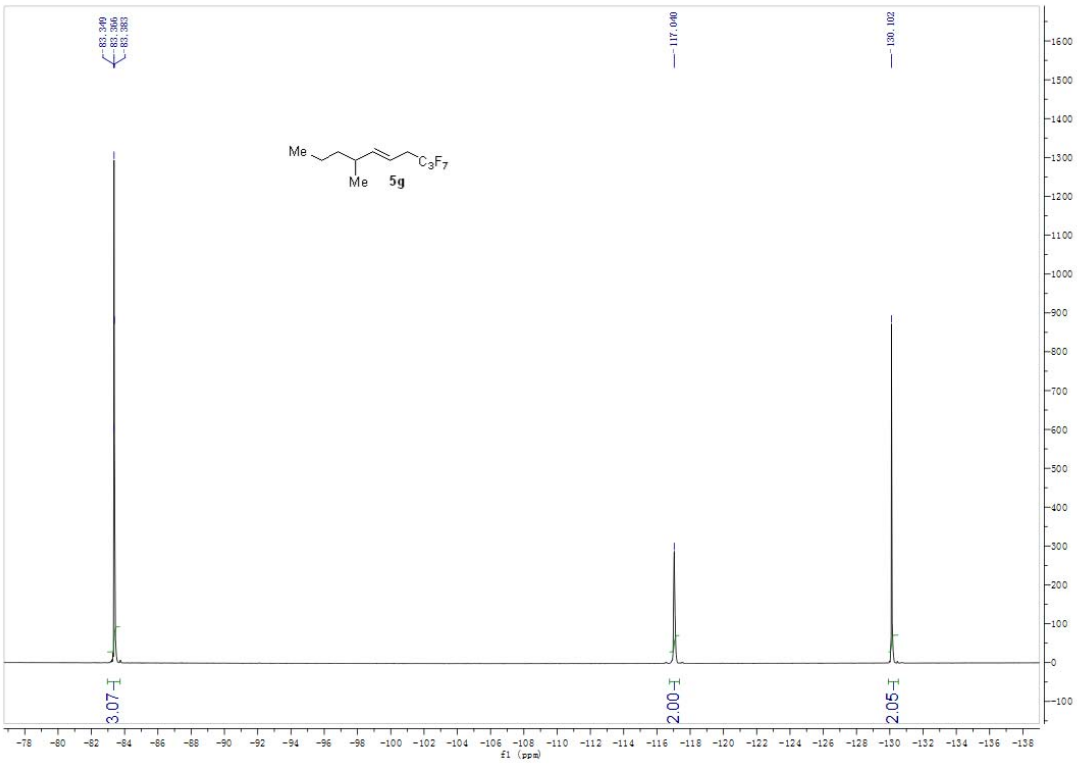


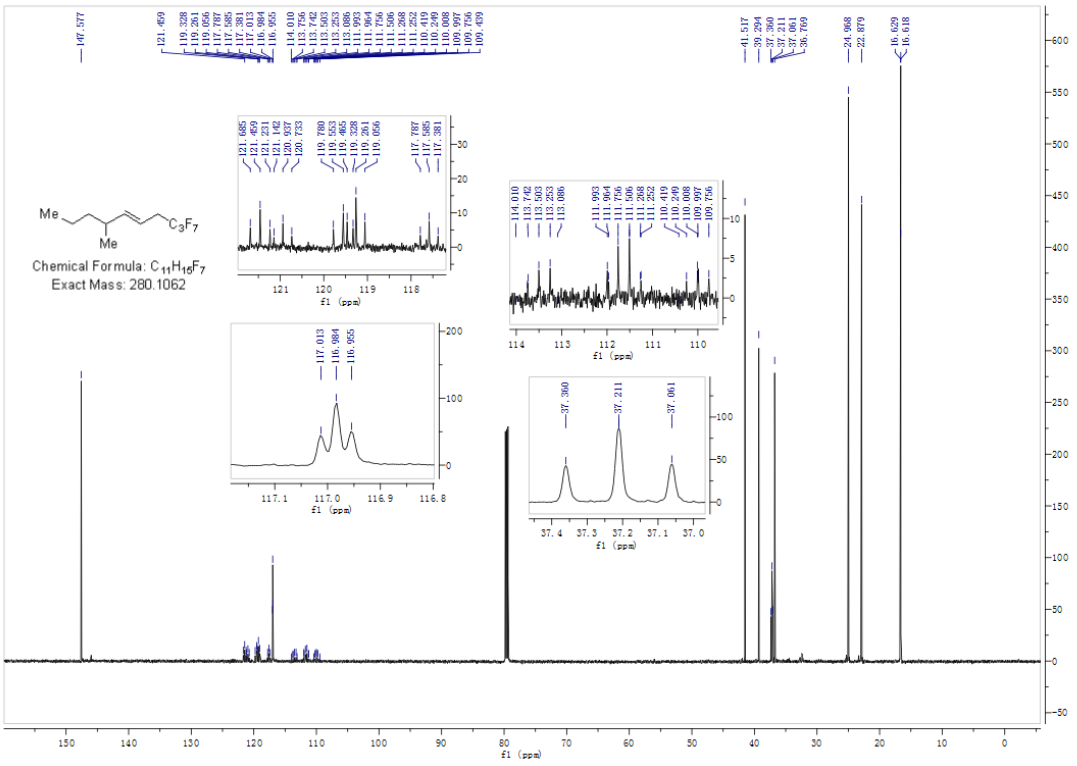




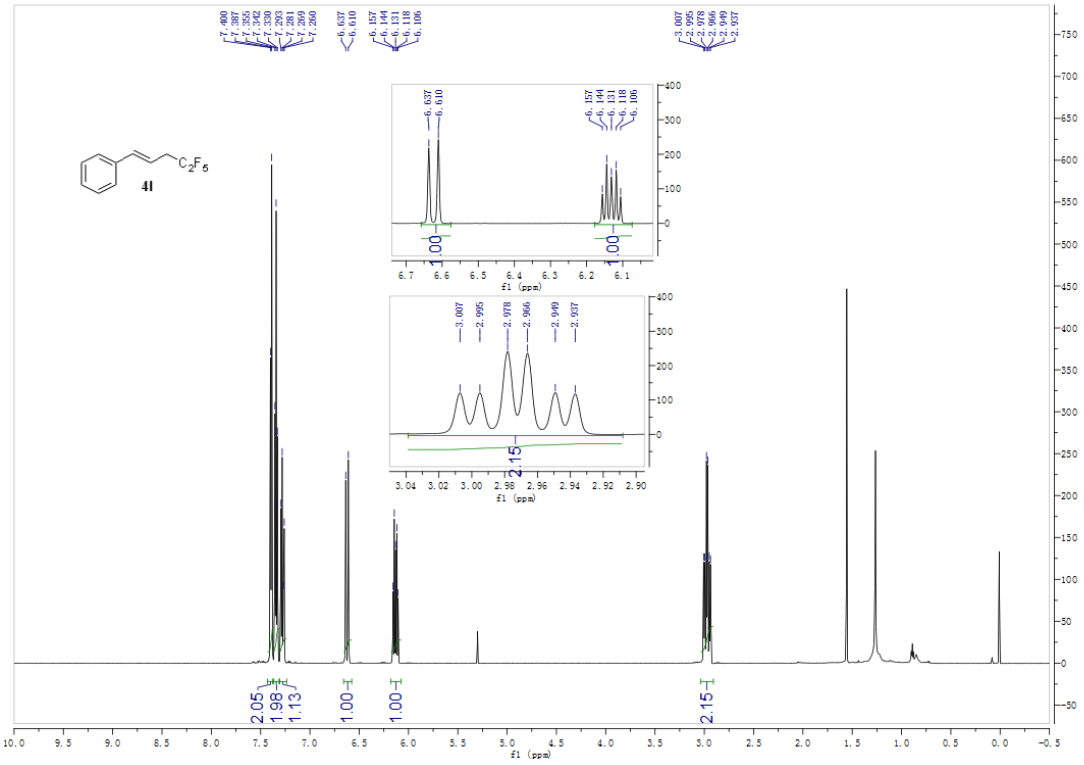
(*E*)-1,1,1,2,2,3,3-heptafluoro-7-methyldec-5-ene (5g)

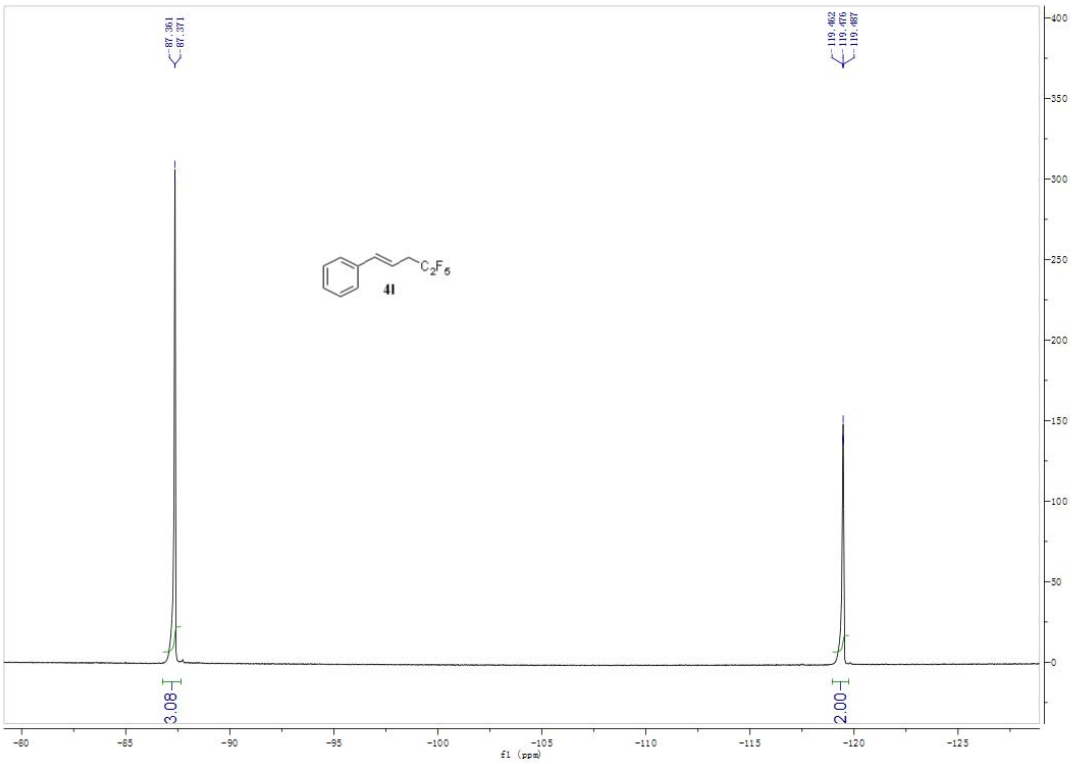



Me
Me
C_3F_7
5g
3.07
2.00
2.05
f1 (ppm)

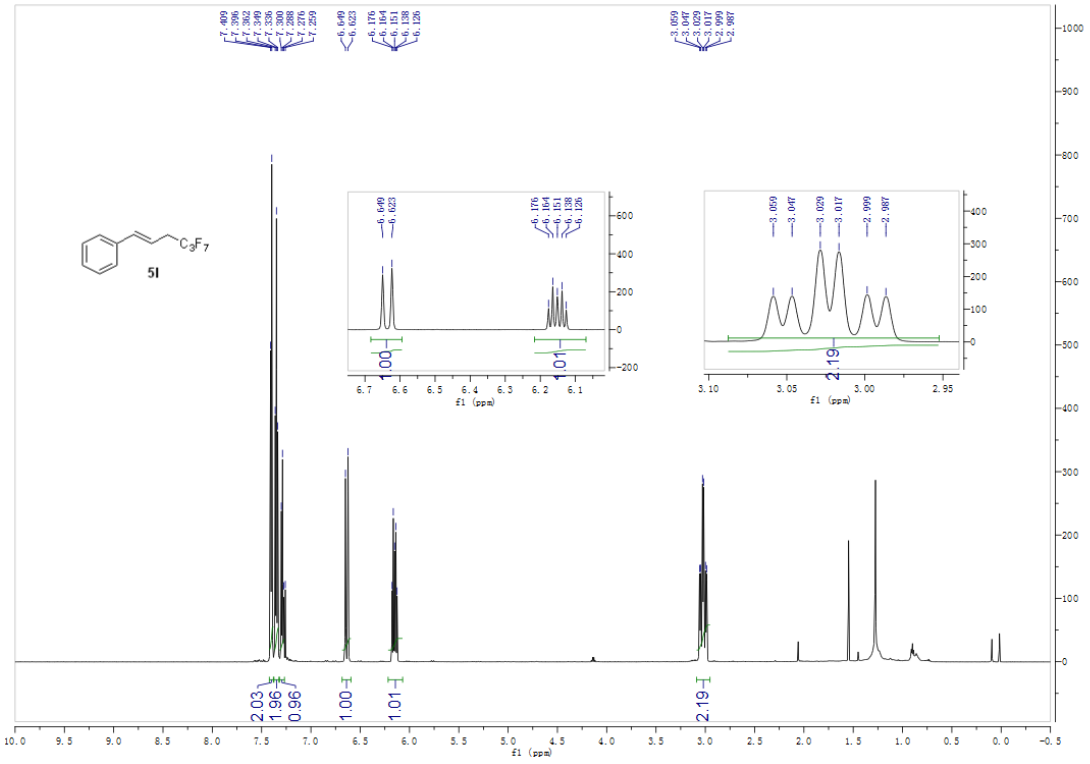

Me
Me
C_3F_7
Chemical Formula: $C_{11}H_{16}F_7$
Exact Mass: 280.1062
f1 (ppm)

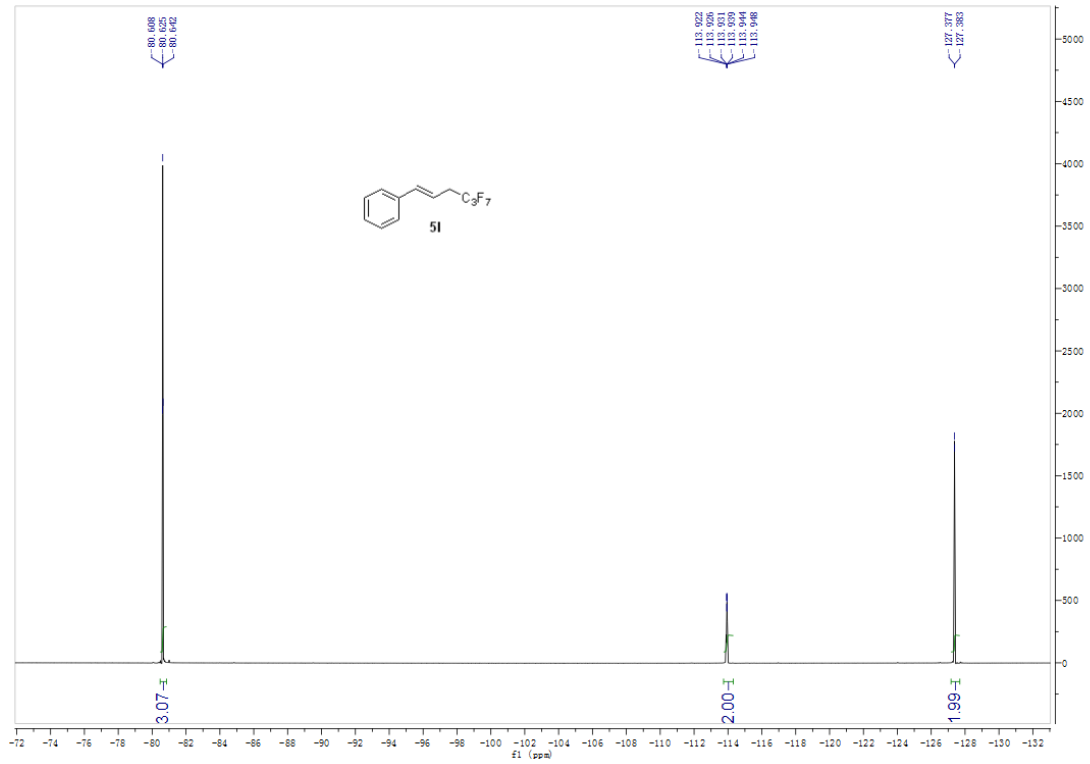
(*E*)-(4,4,5,5,5-pentafluoropent-1-en-1-yl)benzene (4l)



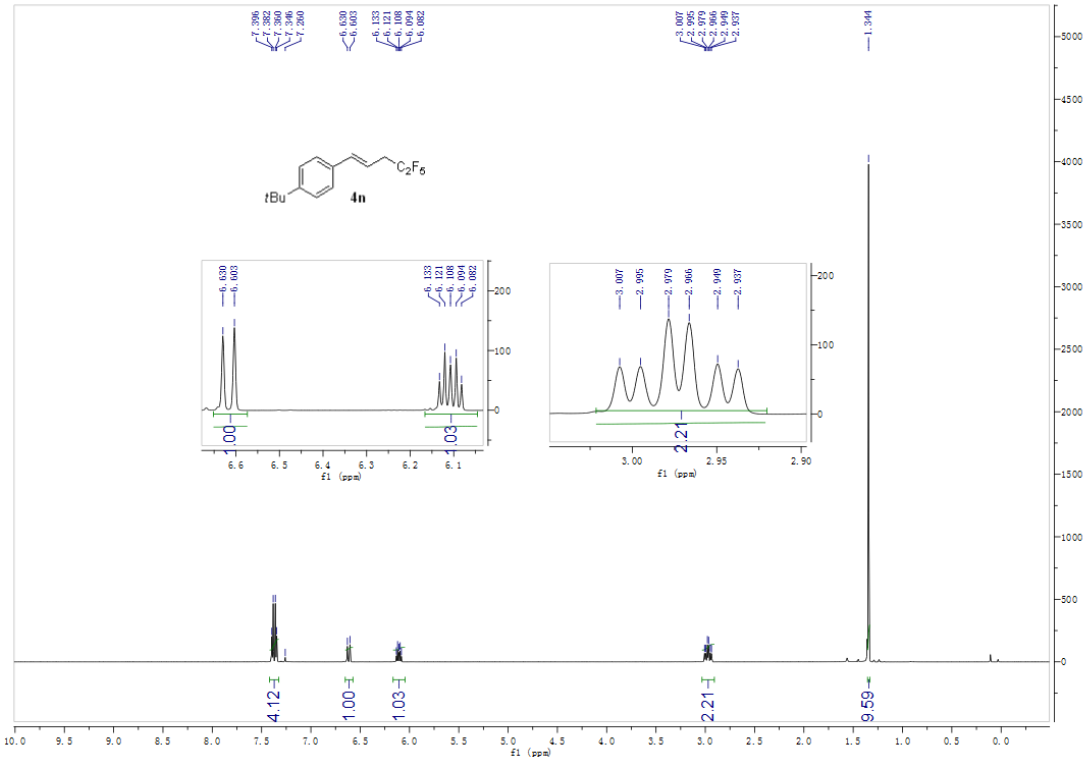


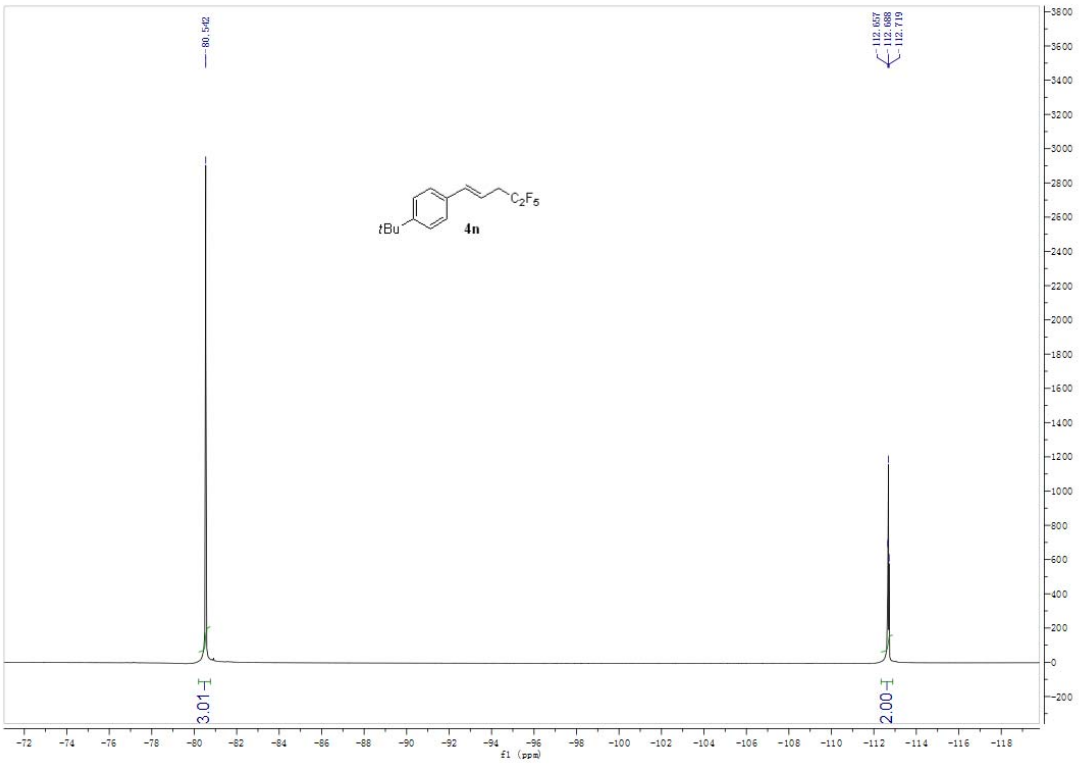
(*E*)-(4,4,5,5,6,6,6-heptafluorohex-1-en-1-yl)benzene (5l)

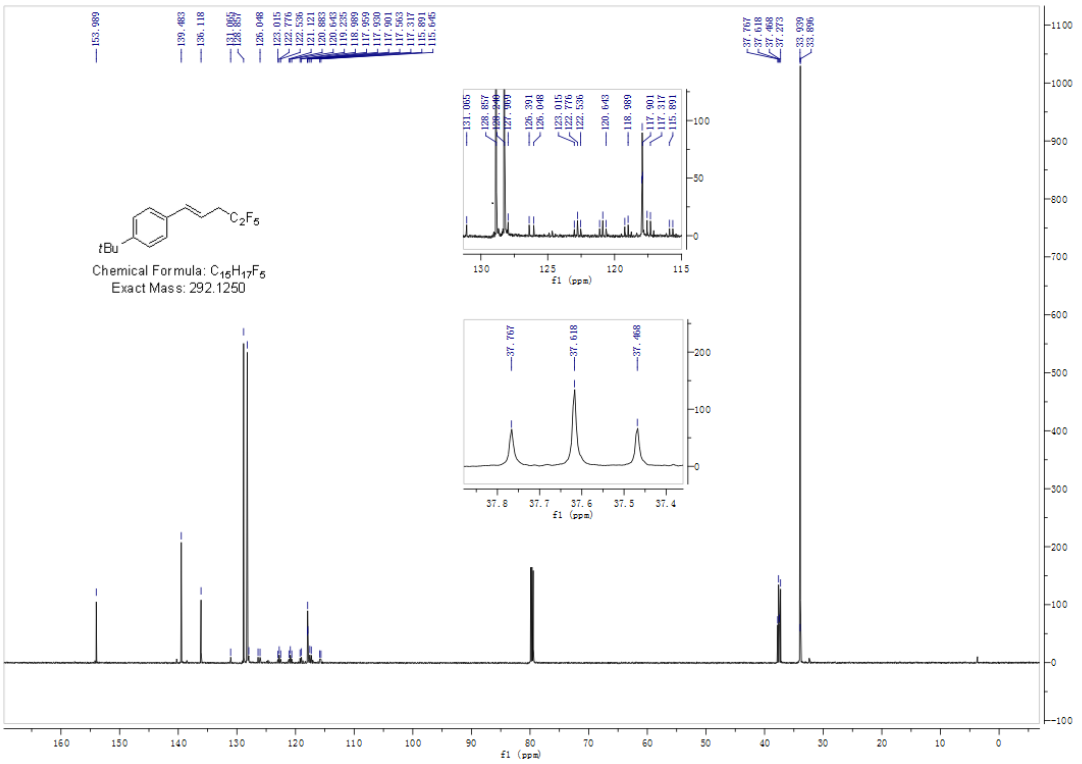




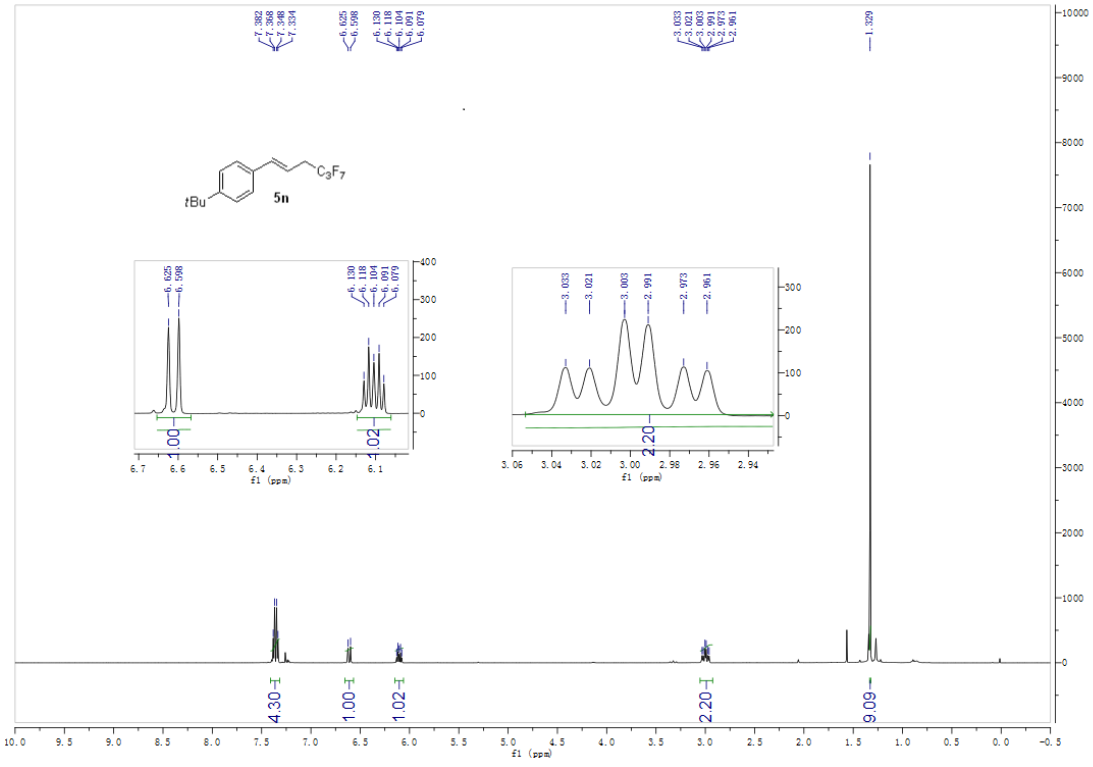
(*E*)-1-(tert-butyl)-4-(4,4,5,5,5-pentafluoropent-1-en-1-yl)benzene (4n)

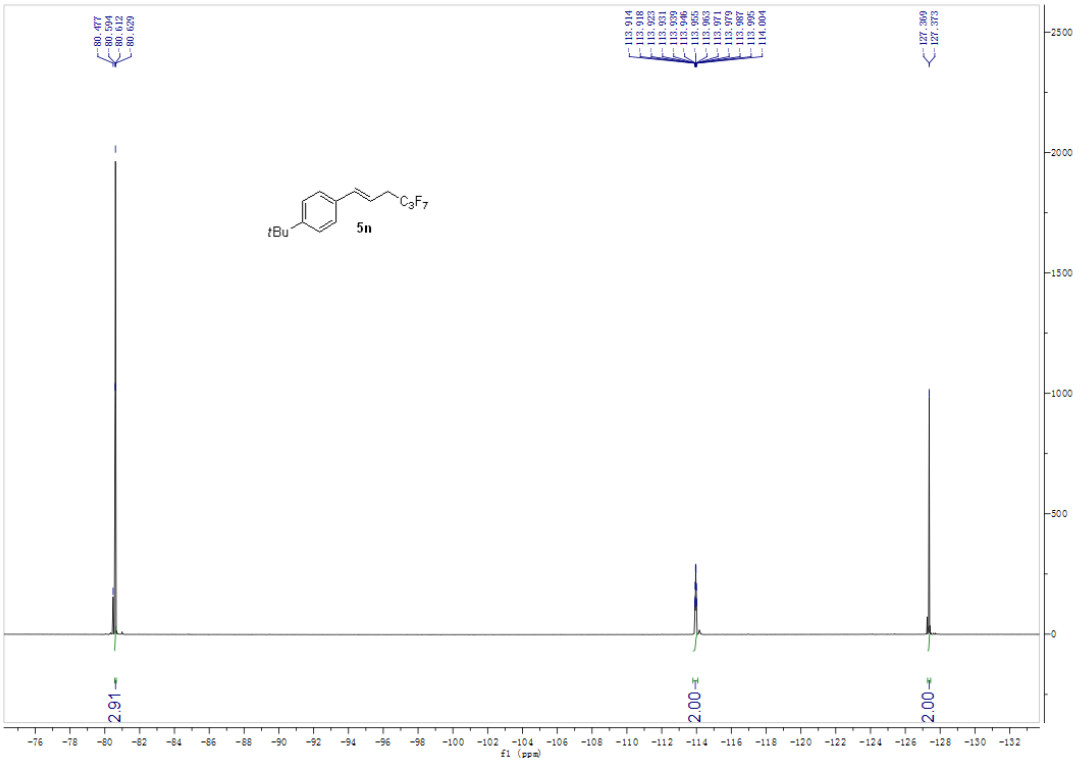


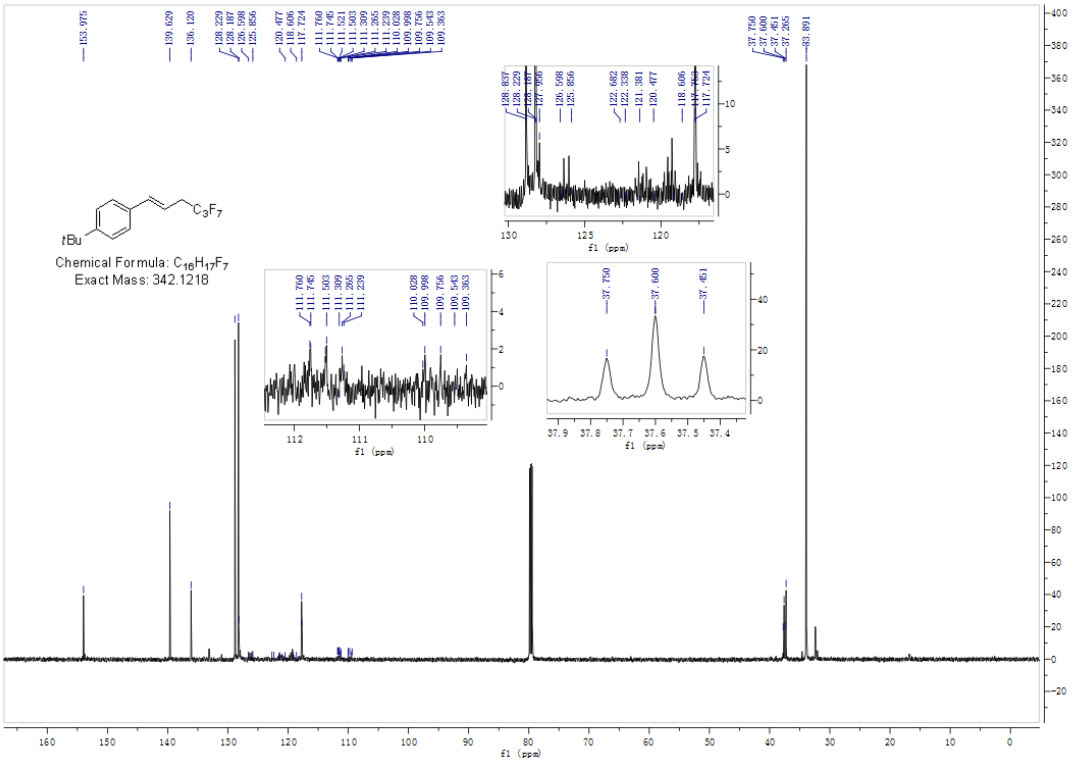




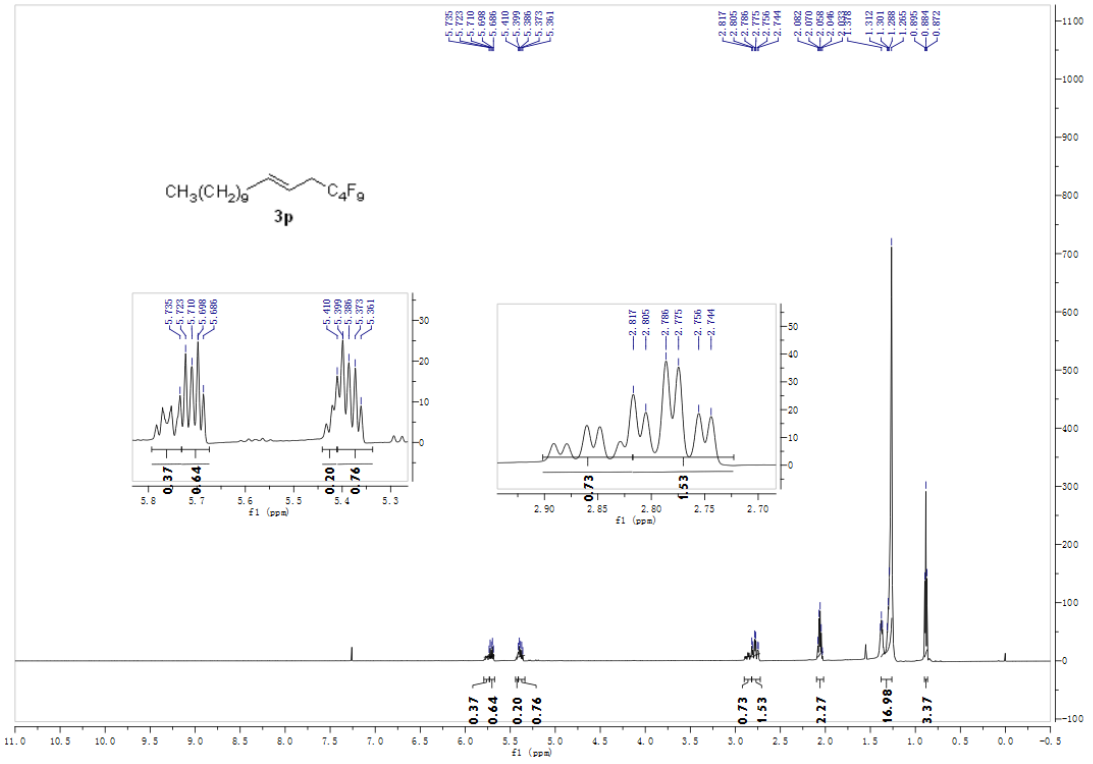
(*E*)-1-(tert-butyl)-4-(4,4,5,5,6,6,6-heptafluorohex-1-en-1-yl)benzene (5n).

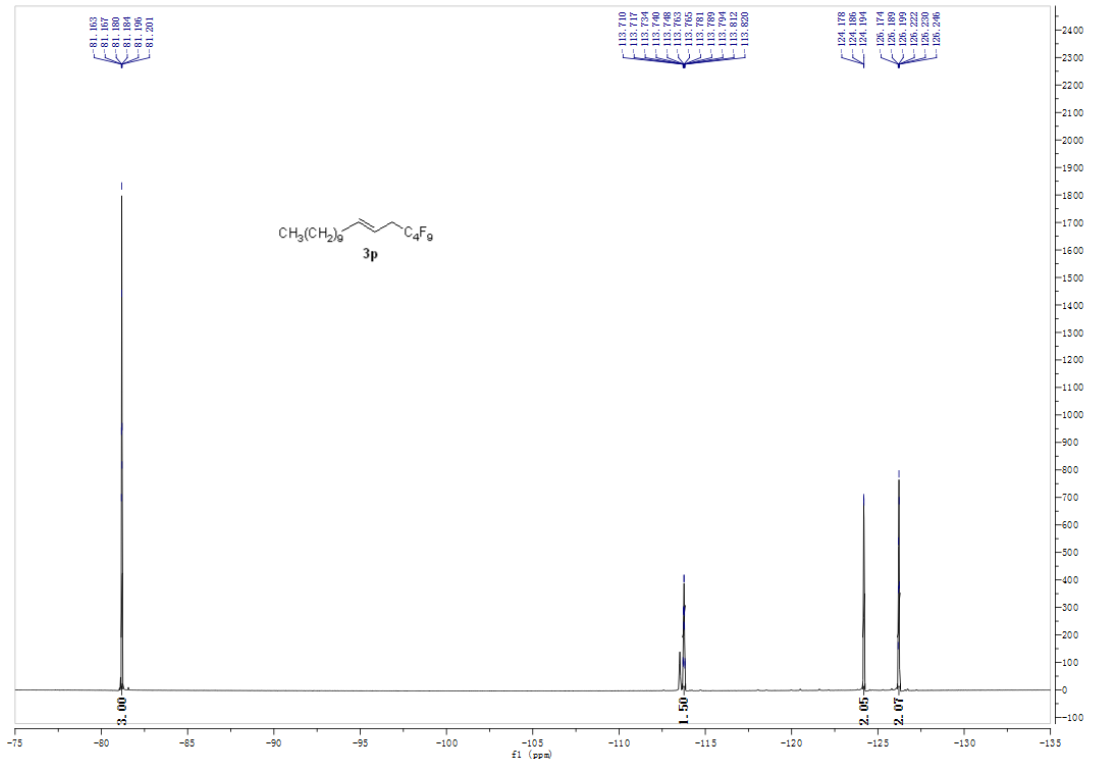


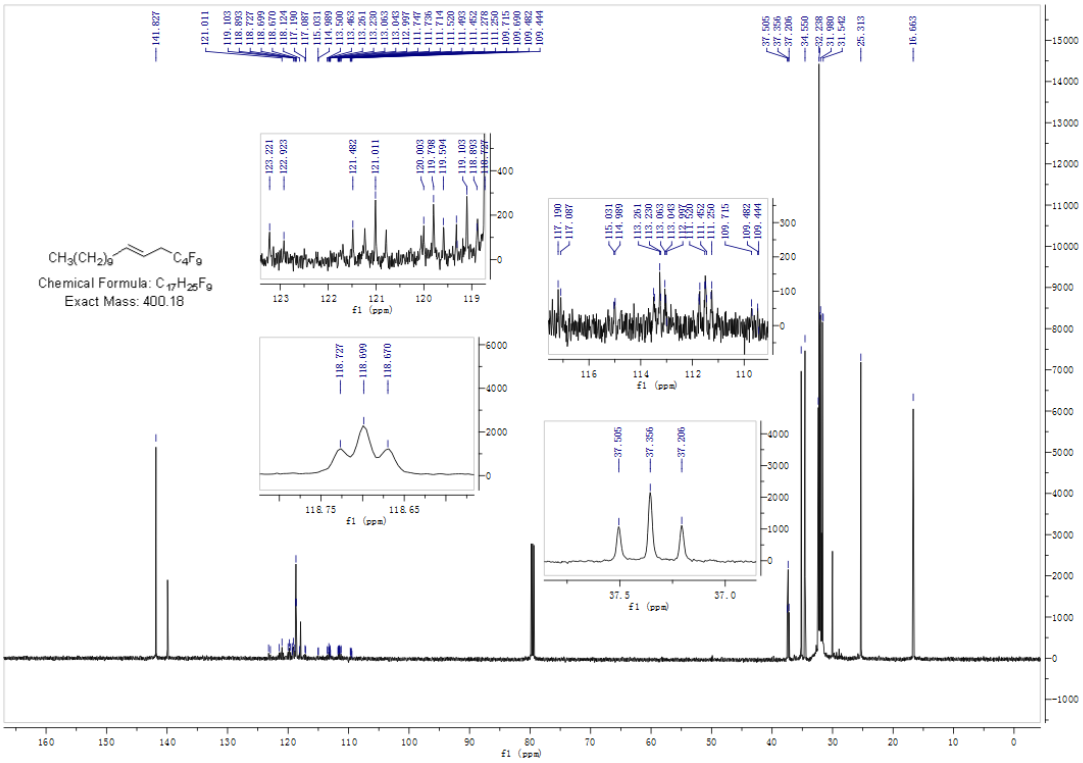

80.477
80.594
80.612
80.629
113.914
113.918
113.923
113.931
113.939
113.946
113.955
113.963
113.971
113.979
113.987
113.995
114.004
127.369
127.373
tBu
C3F7
5n
2.91
2.00
2.00
f1 (ppm)


153.975
139.629
136.120
128.229
128.187
126.598
125.856
120.477
118.606
117.724
111.760
111.745
111.521
111.503
111.399
111.265
111.239
110.028
109.998
109.736
109.543
109.363
37.750
37.600
37.461
37.255
83.891
tBu
C3F7
Chemical Formula: C16H17F7
Exact Mass: 342.1218
f1 (ppm)

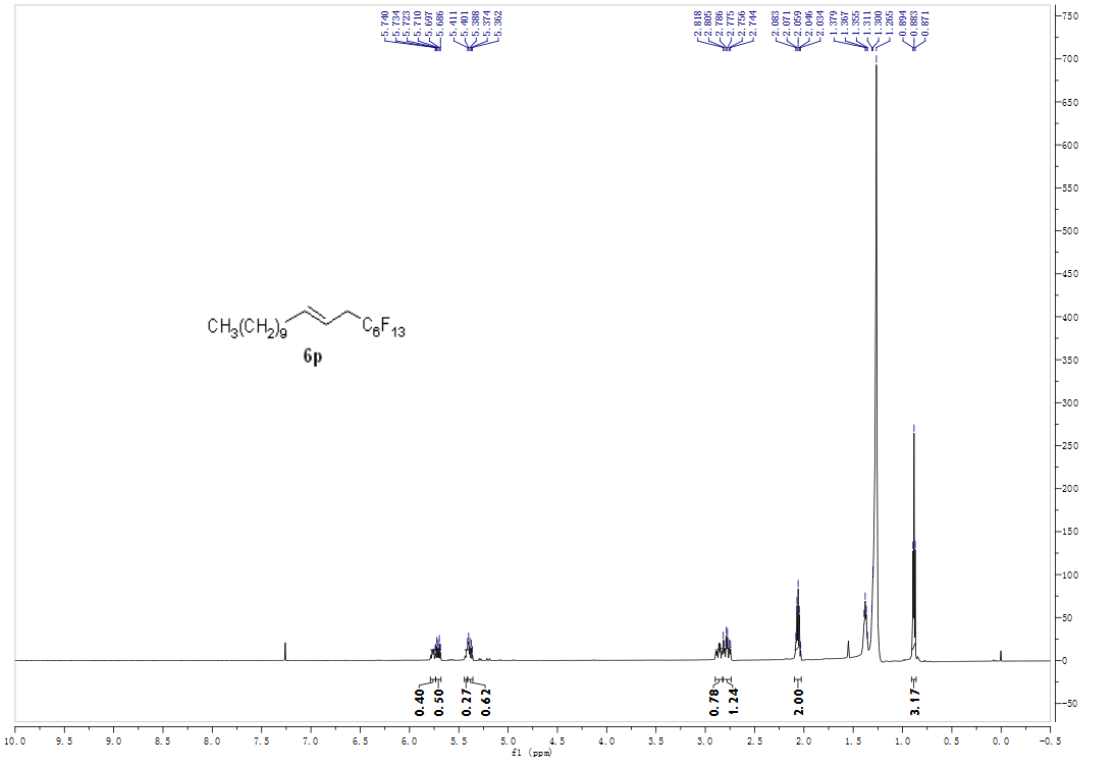
(*E*)-1,1,1,2,2,3,3,4,4-nonafluoroheptadec-6-ene (3p)

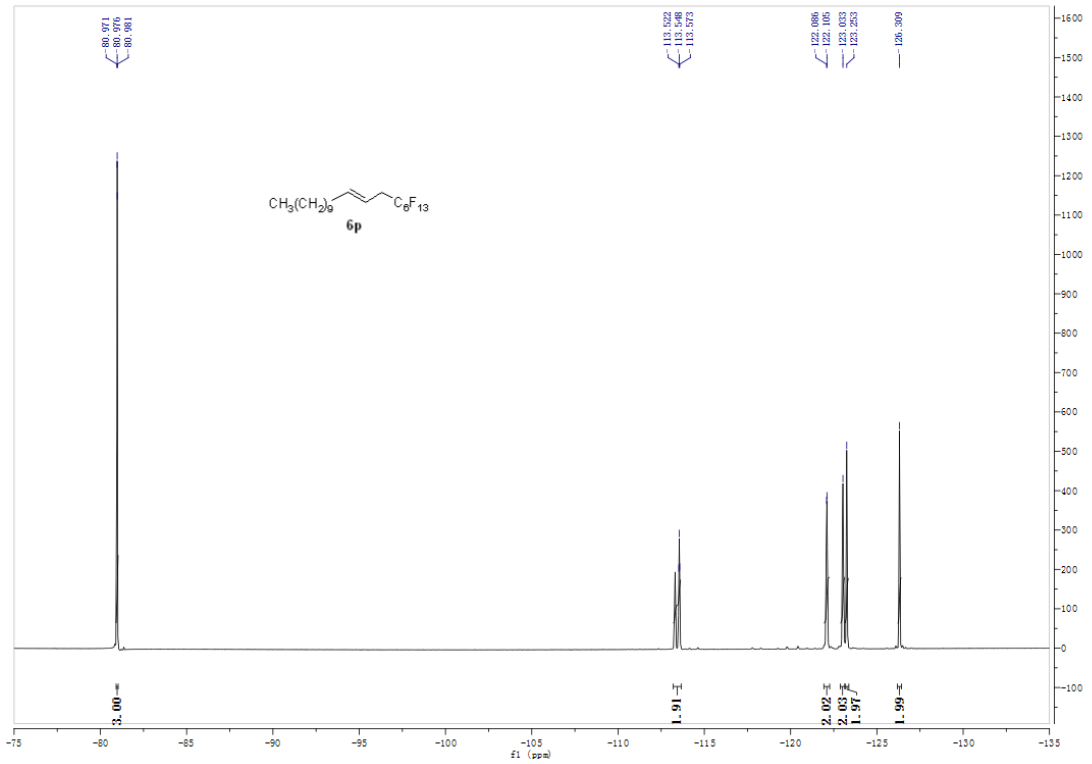


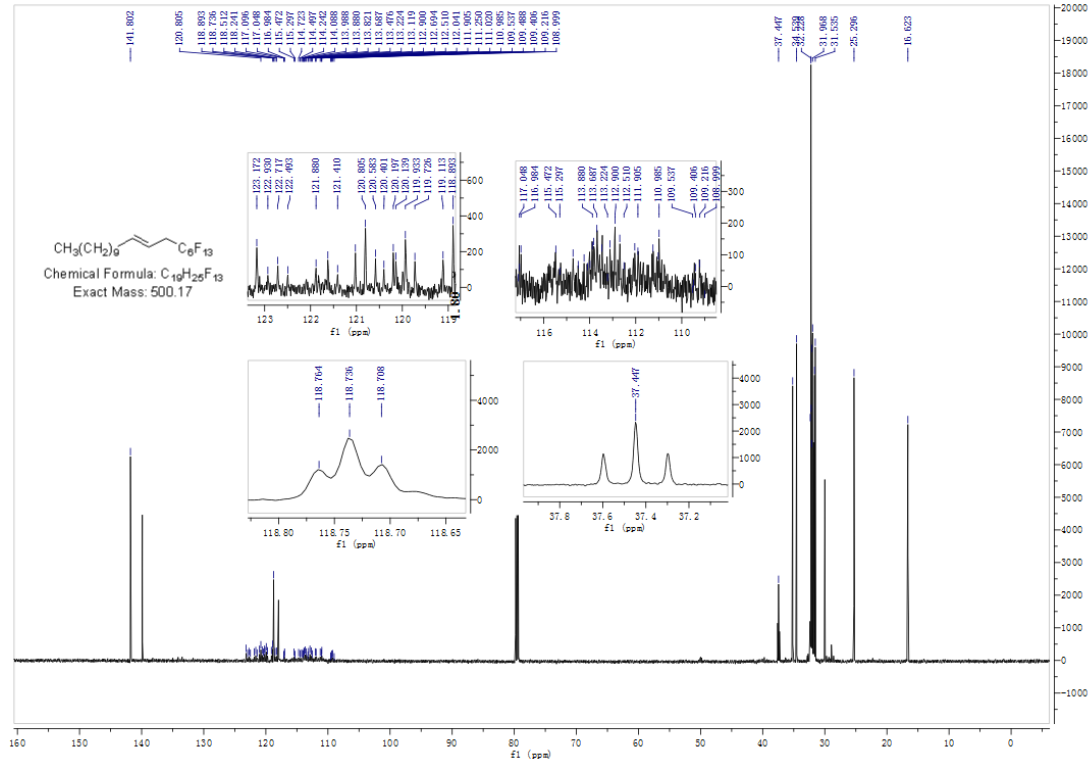




(*E*)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononadec-8-ene (6p)




80.971
80.976
80.981
113.522
113.548
113.573
122.086
122.105
123.033
123.253
126.309
CH3(CH2)9
C6F13
6p
3.00
1.91
2.02
2.03
1.97
1.99
f1 (ppm)


141.802
120.805
118.893
118.736
118.512
118.341
117.096
117.048
116.984
115.472
115.297
114.723
114.497
114.282
114.088
113.988
113.880
113.821
113.687
113.476
113.224
113.119
112.900
112.694
112.510
112.041
111.905
111.250
111.050
110.985
109.537
109.488
109.406
109.216
108.999
37.447
32.538
32.228
31.968
31.535
25.296
16.623
CH3(CH2)9
C6F13
Chemical Formula: C19H25F13
Exact Mass: 500.17
118.764
118.736
118.708
37.447
f1 (ppm)