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Supporting Information

Selectively Catalytic Hydrodefluorination of Perfluoroarenes by $Co(PMe_3)_4$ with Sodium Formate as Reducing Agent and Mechanism Study

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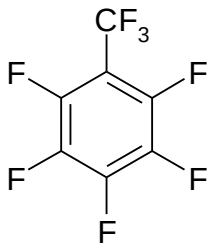
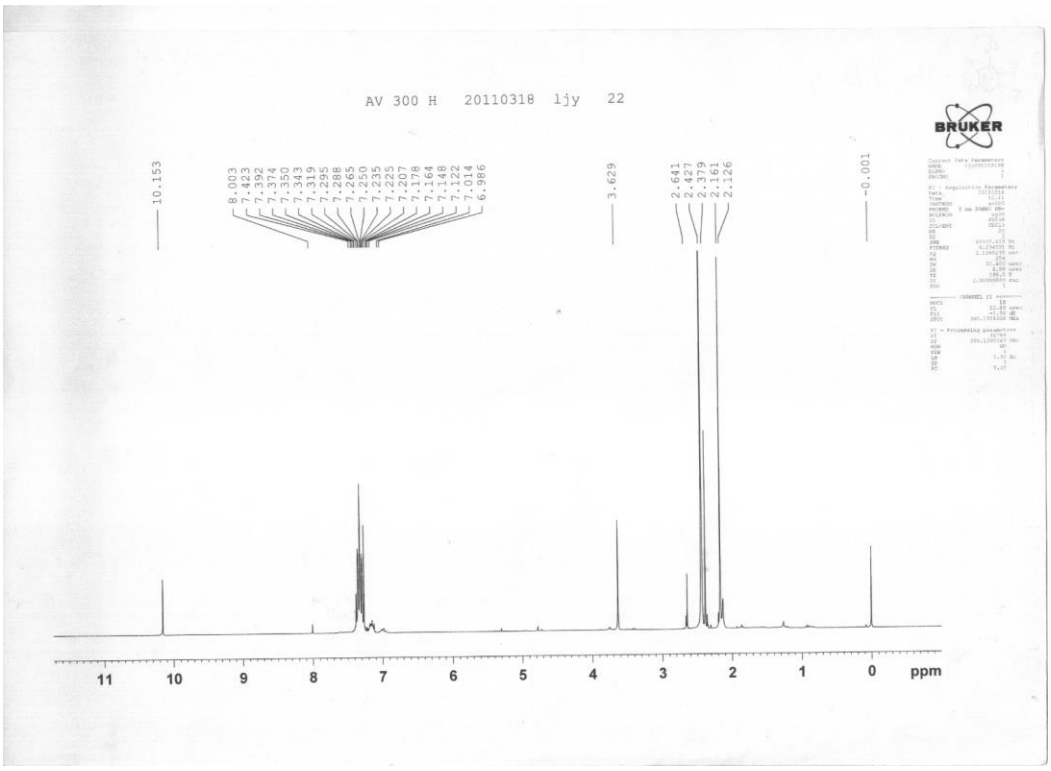
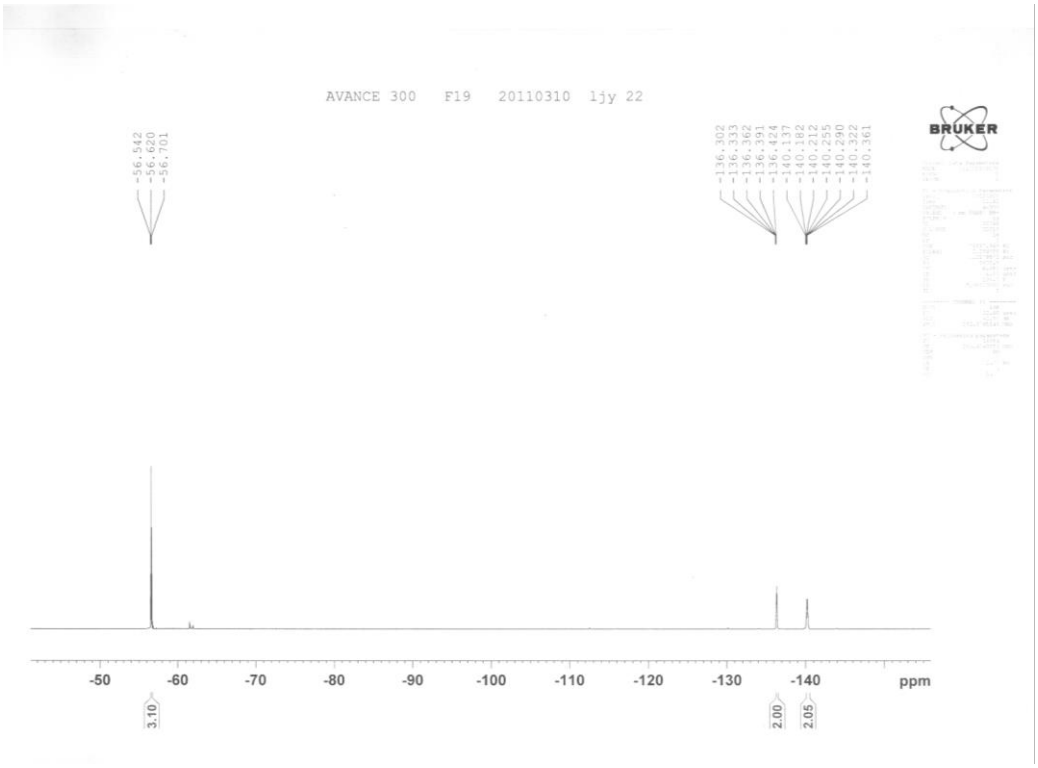
1. Spectra of 1a - 4a and 4b

1) **1a**

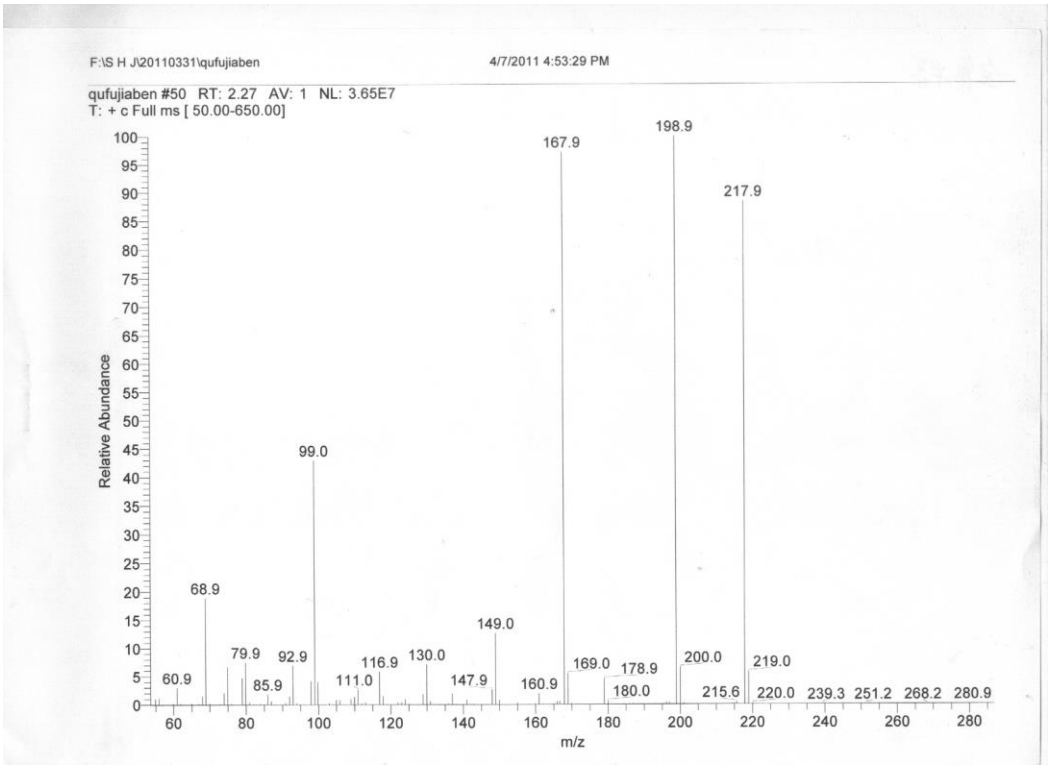




^{1}H NMR (300 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, $CDCl_3$)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4/7/2011 4:53:29 PM
qufujiaben #50 RT: 2.27 AV: 1 NL: 3.65E7
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
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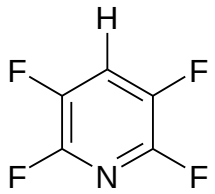
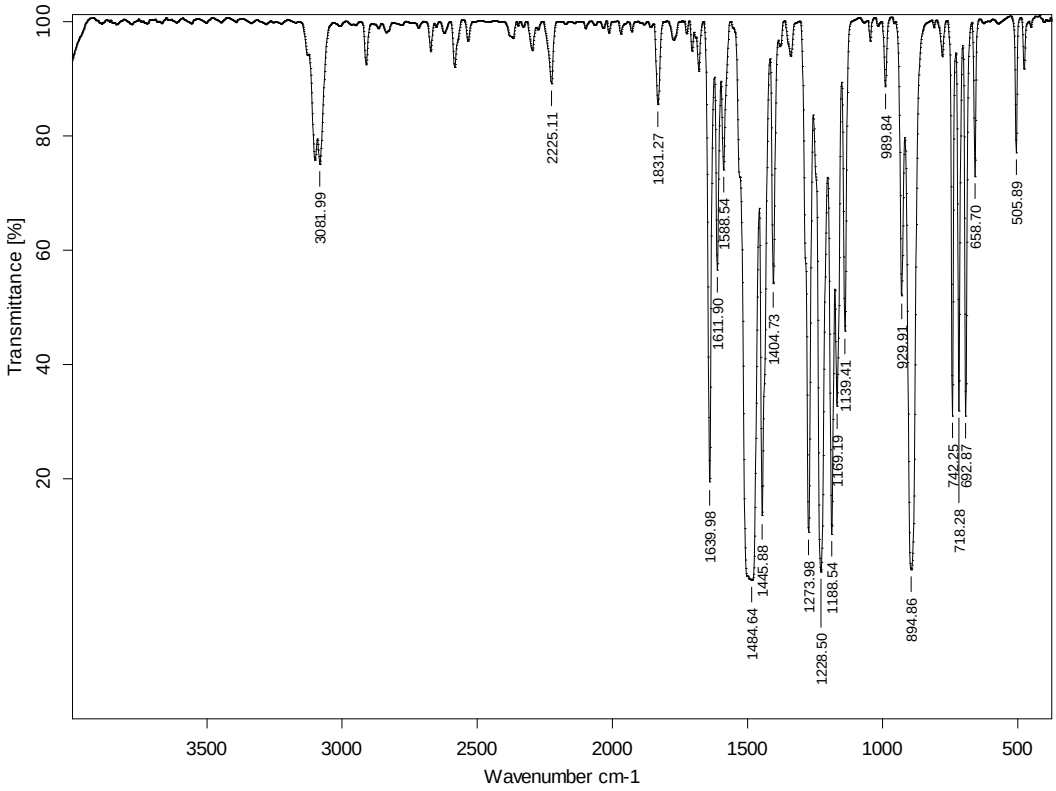
198.9
217.9
99.0
68.9
149.0
79.9
92.9
116.9
130.0
169.0
178.9
200.0
219.0
60.9
85.9
111.0
147.9
160.9
180.0
215.6
220.0
239.3
251.2
268.2
280.9

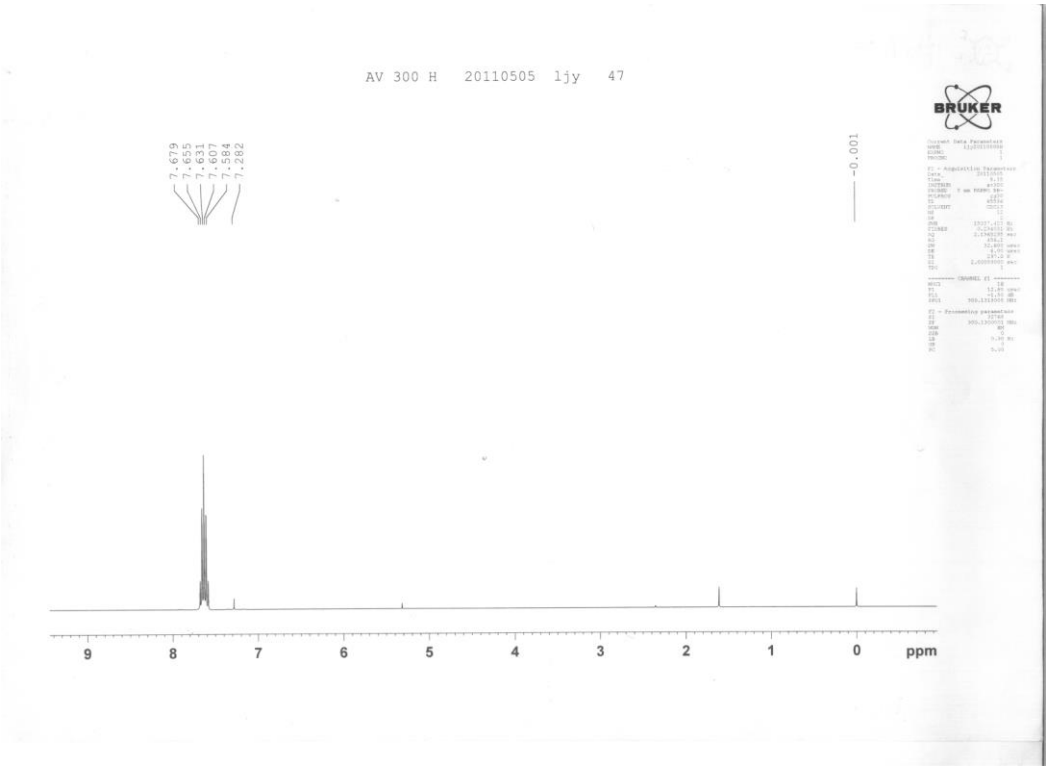
GC-MS (m/z)

2) **2a**

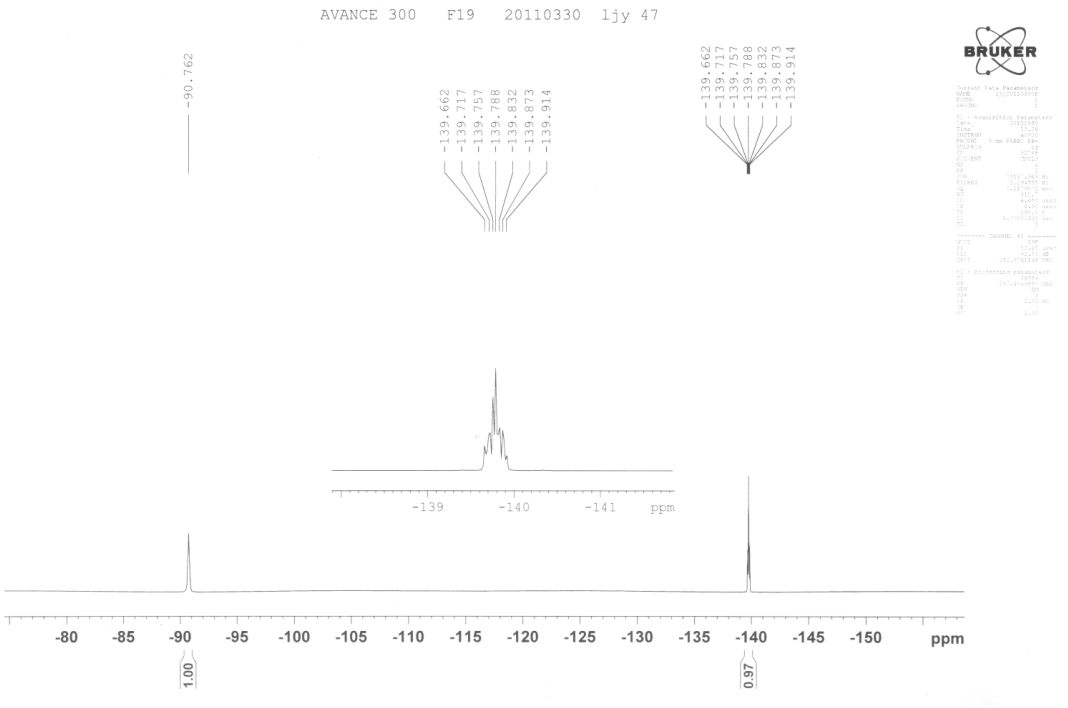

H
F
F
F
N
F



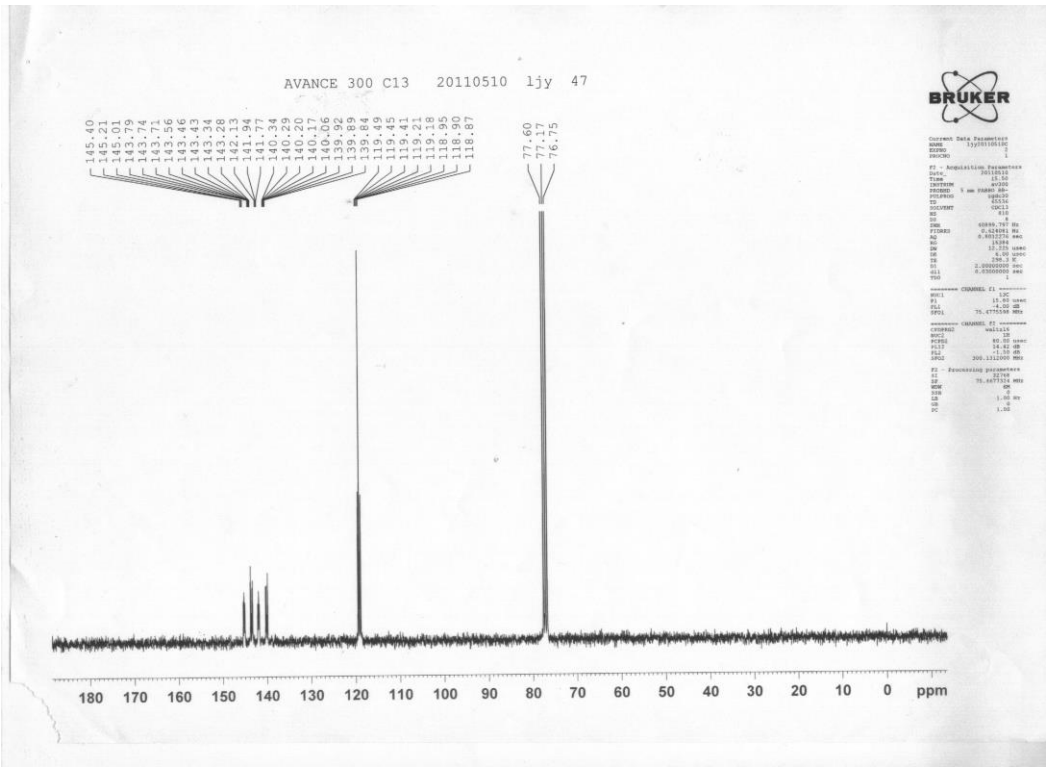
IR spectroscopy

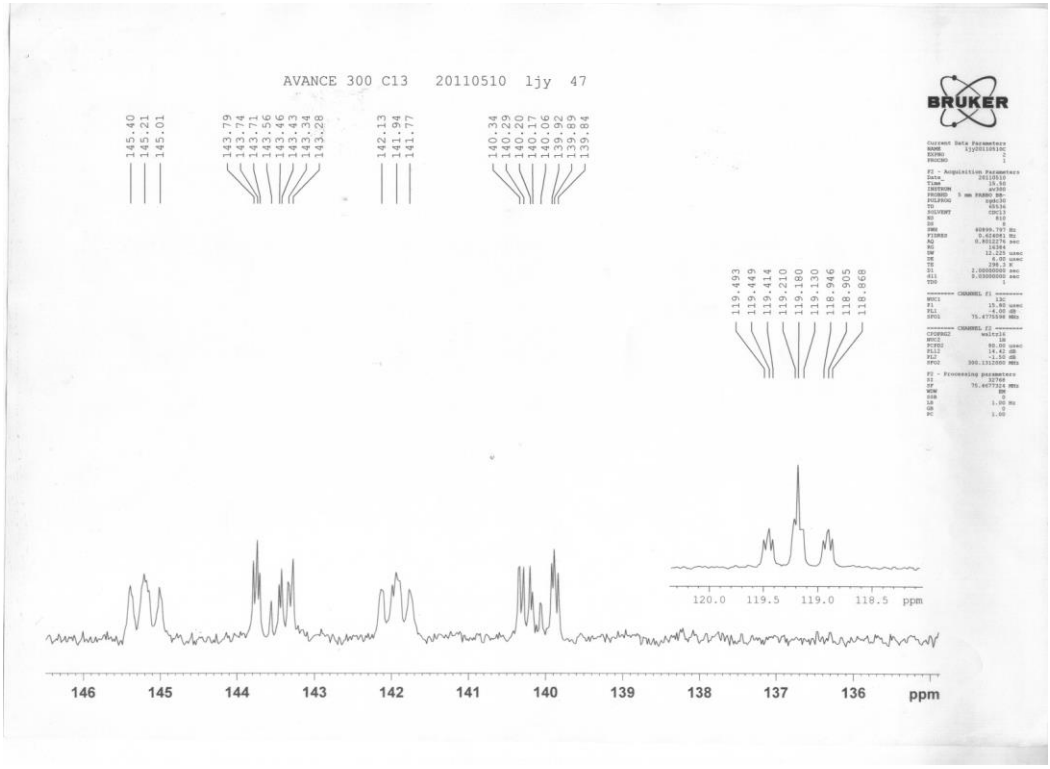


^{1}H NMR (300 MHz, $CDCl_3$)

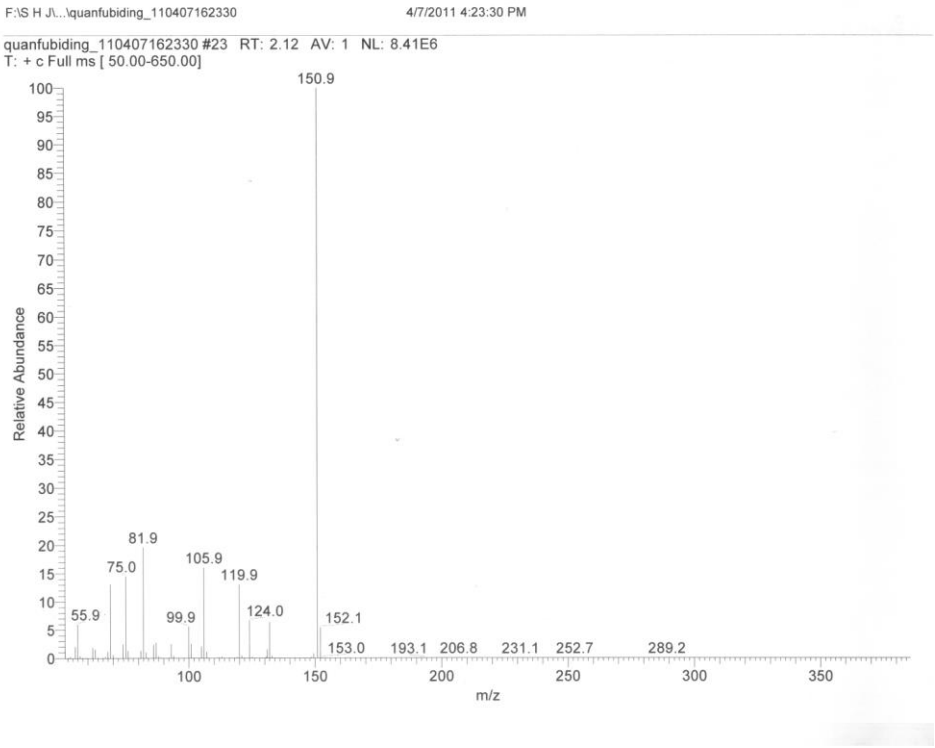


^{19}F NMR (282 MHz, $CDCl_3$)



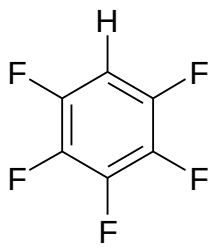


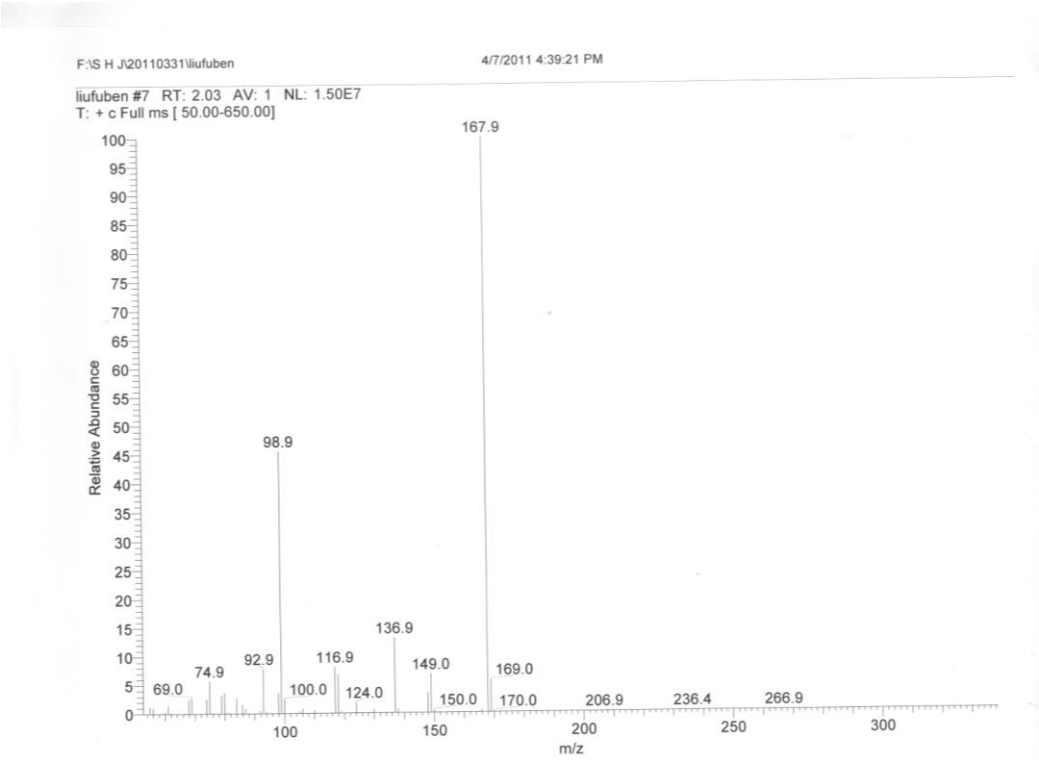
^{13}C NMR (74.5 MHz, $CDCl_3$)



GC-MS (m/z)

3) **3a**

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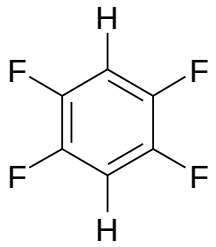
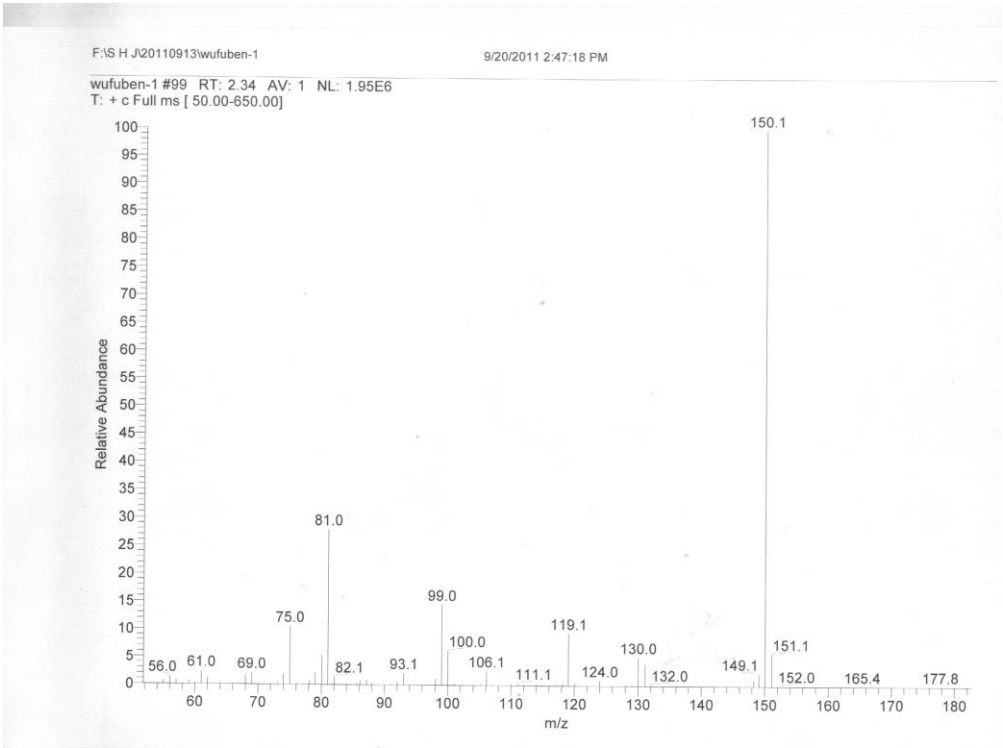
4/7/2011 4:39:21 PM
liufuben #7 RT: 2.03 AV: 1 NL: 1.50E7
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
167.9
98.9
136.9
92.9
116.9
149.0
169.0
74.9
69.0
100.0
124.0
150.0
170.0
206.9
236.4
266.9

GC-MS (m/z)

4) **3b**

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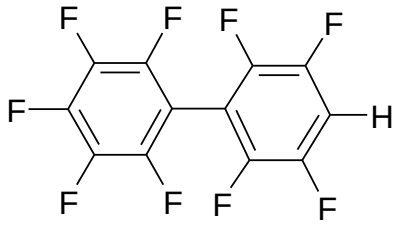
9/20/2011 2:47:18 PM
wufuben-1 #99 RT: 2.34 AV: 1 NL: 1.95E6
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
150.1
81.0
99.0
75.0
119.1
100.0
130.0
151.1
56.0
61.0
69.0
82.1
93.1
106.1
111.1
124.0
132.0
149.1
152.0
165.4
177.8

GC-MS (m/z)

5) **4a**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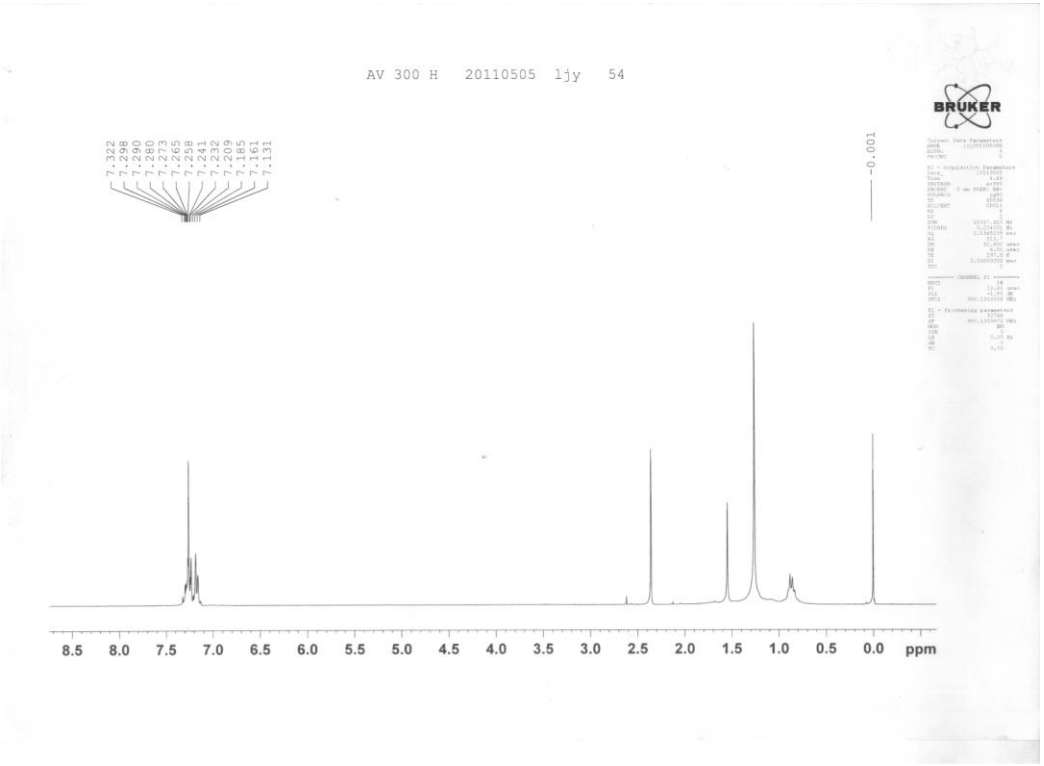
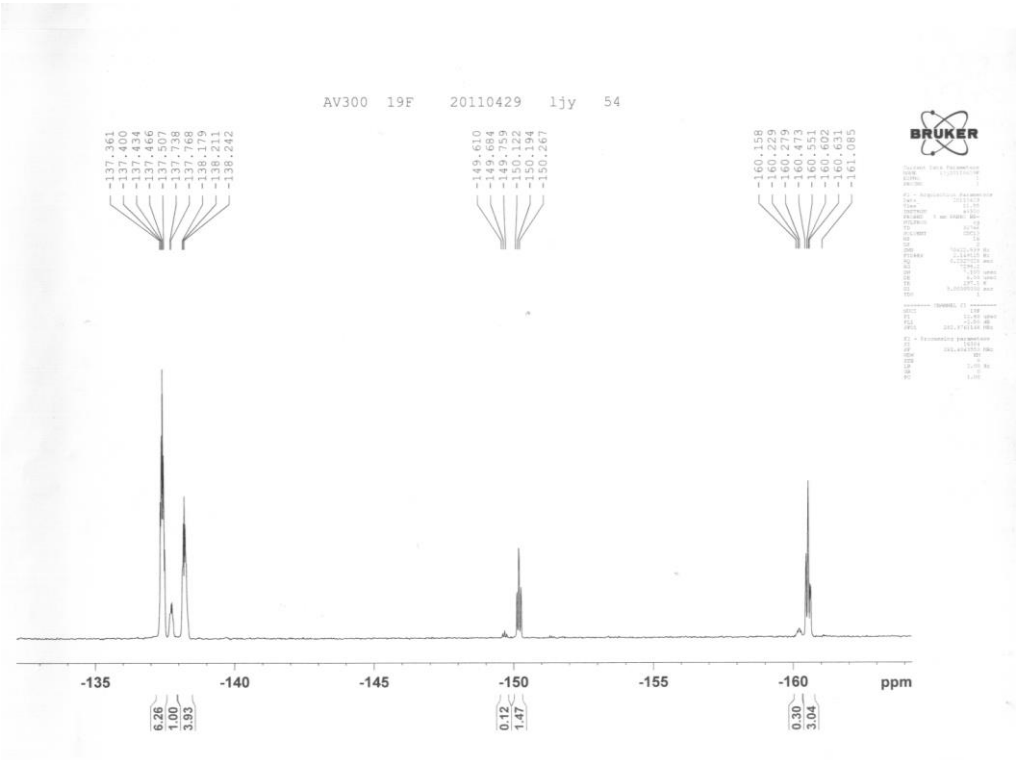
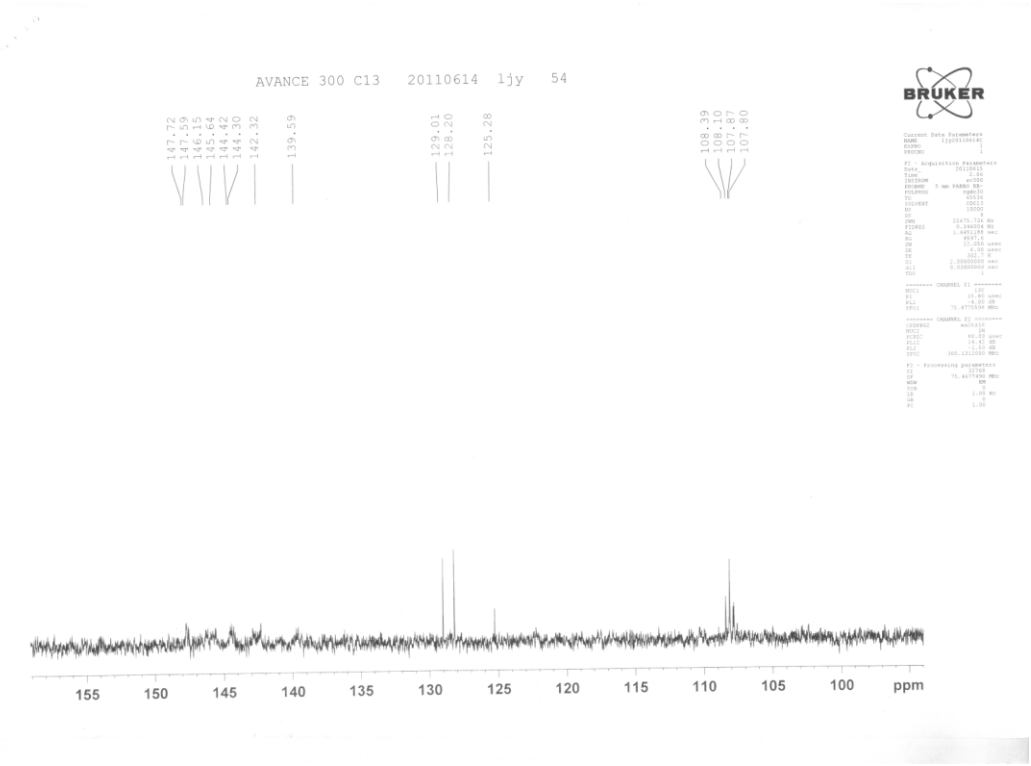
F
F



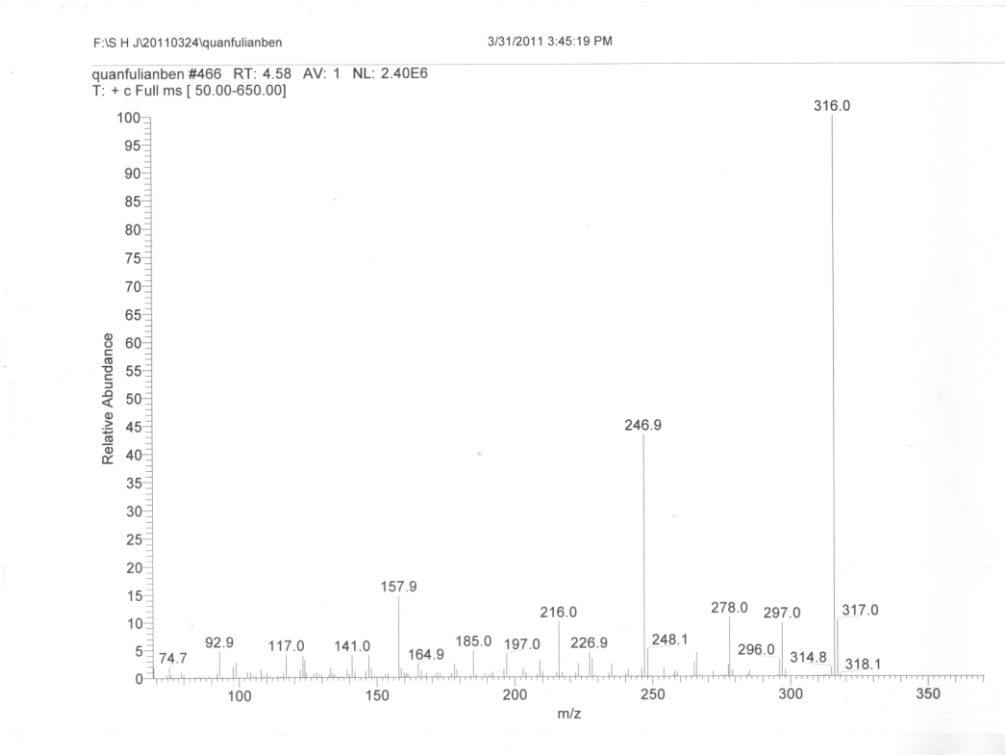
^{1}H NMR (300 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, $CDCl_3$)

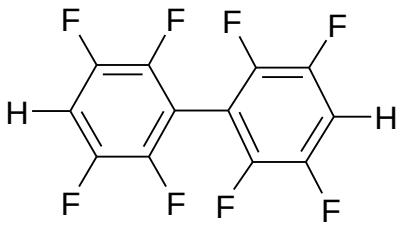


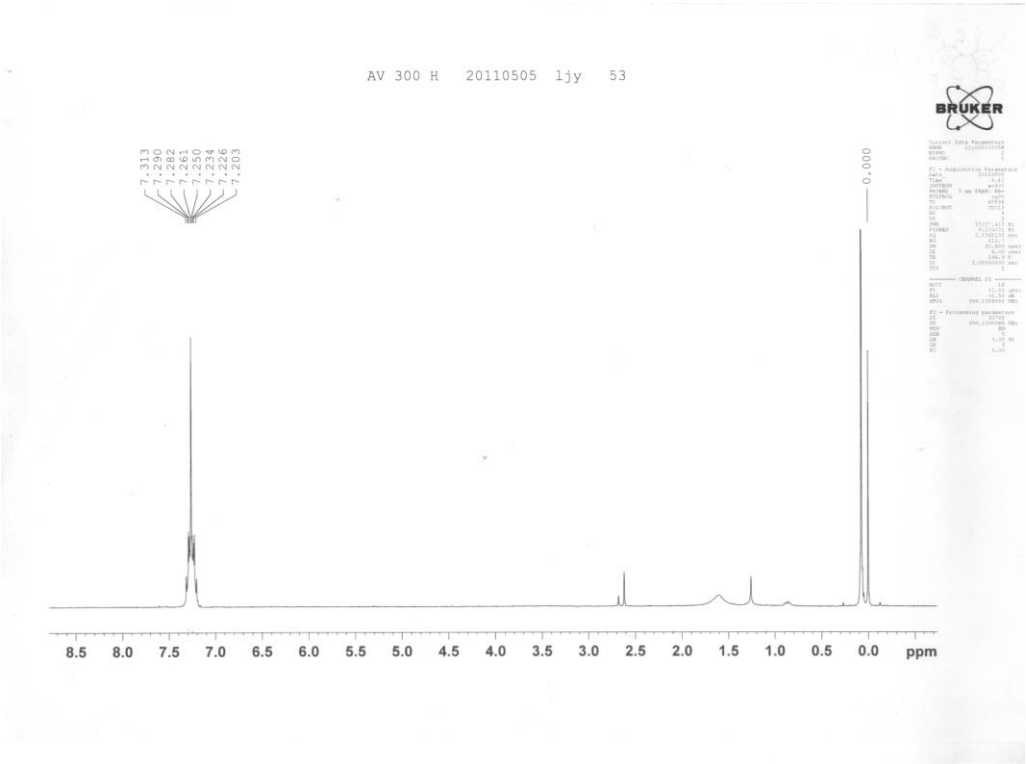
^{13}C NMR (74.5 MHz, $CDCl_3$)



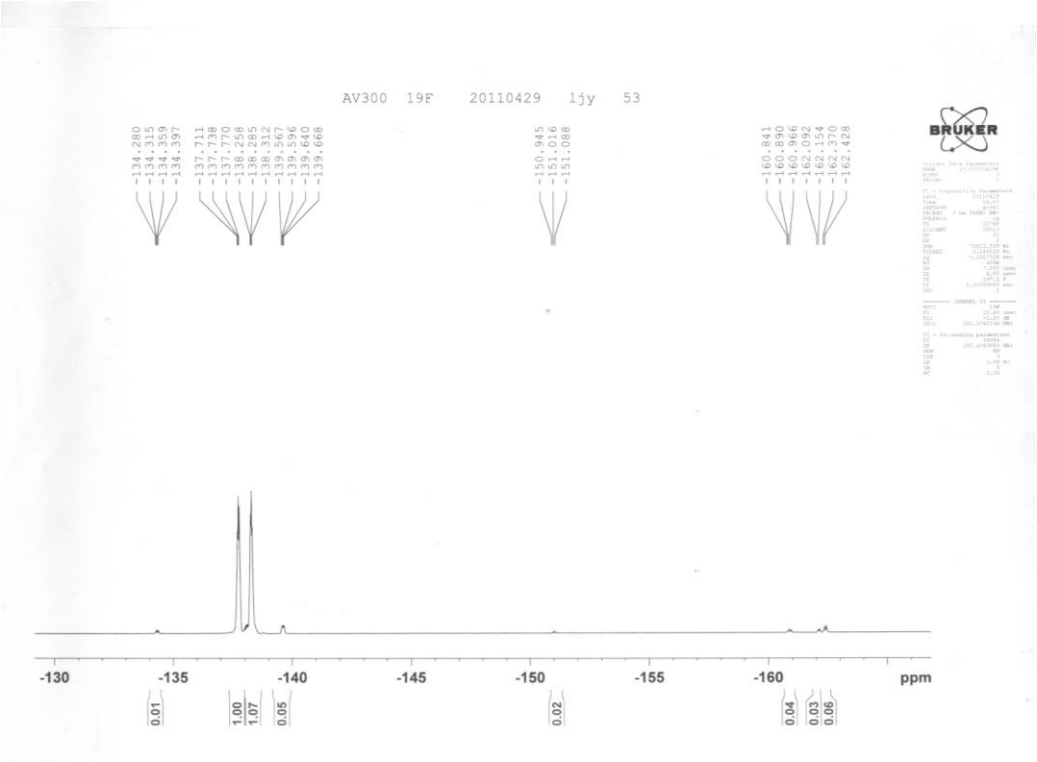
GC-MS (m/z)

6) **4b**

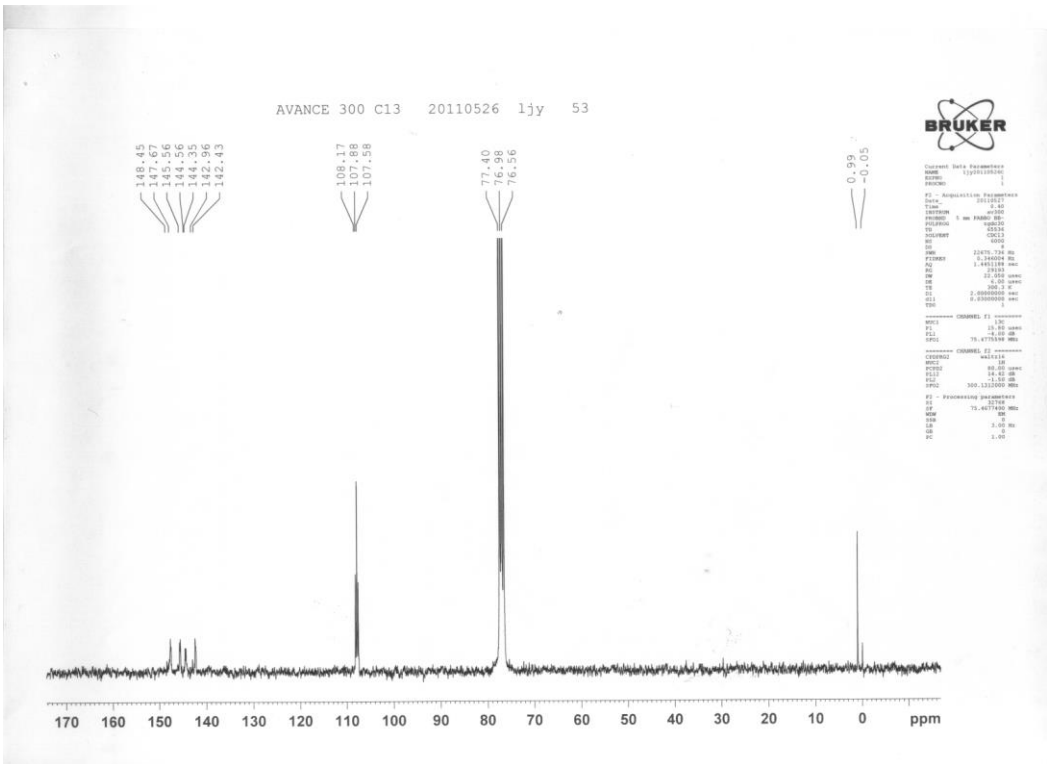


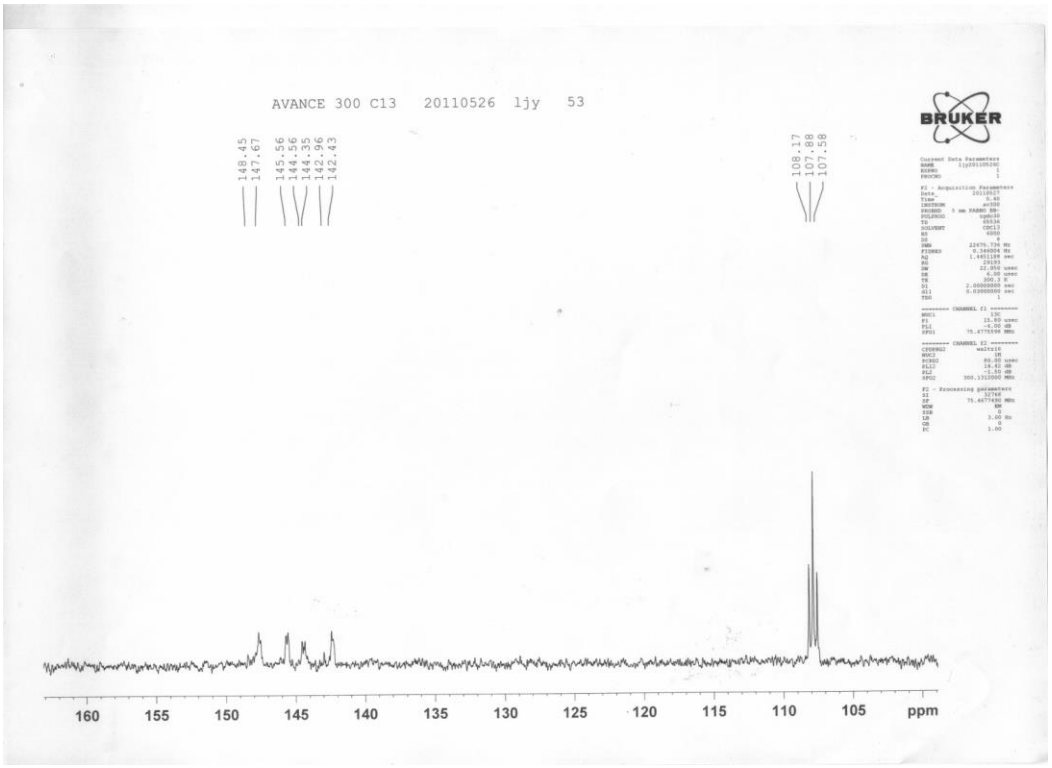


^{1}H NMR (300 MHz, $CDCl_3$)

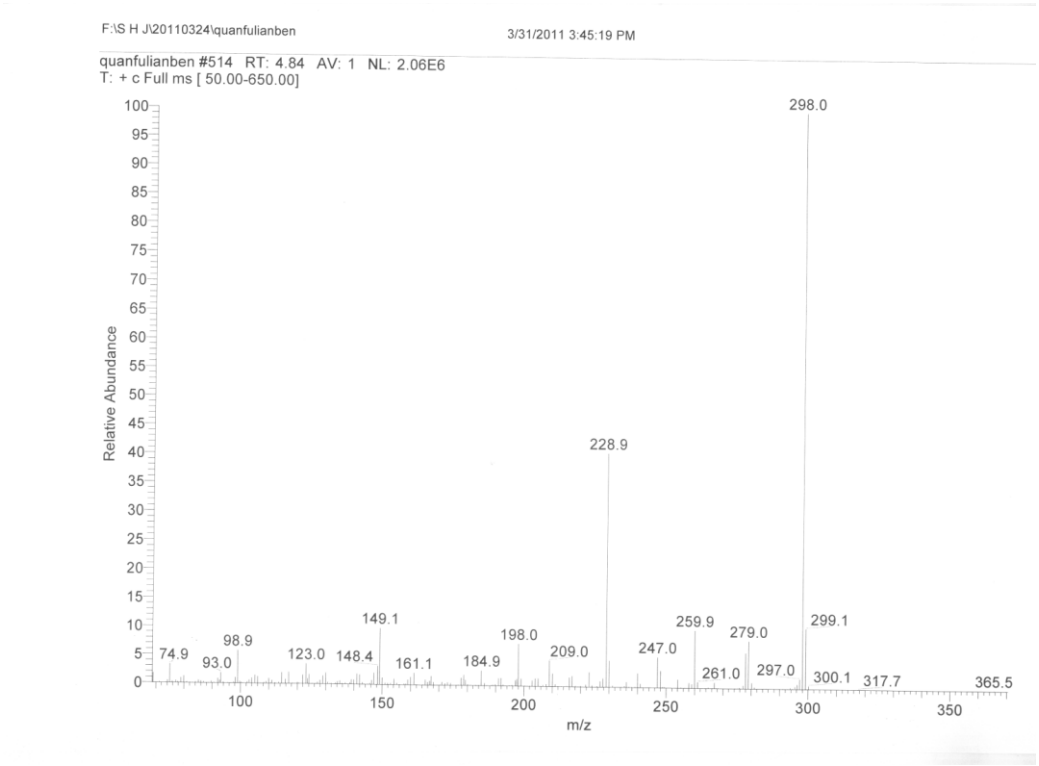


^{19}F NMR (282 MHz, $CDCl_3$)



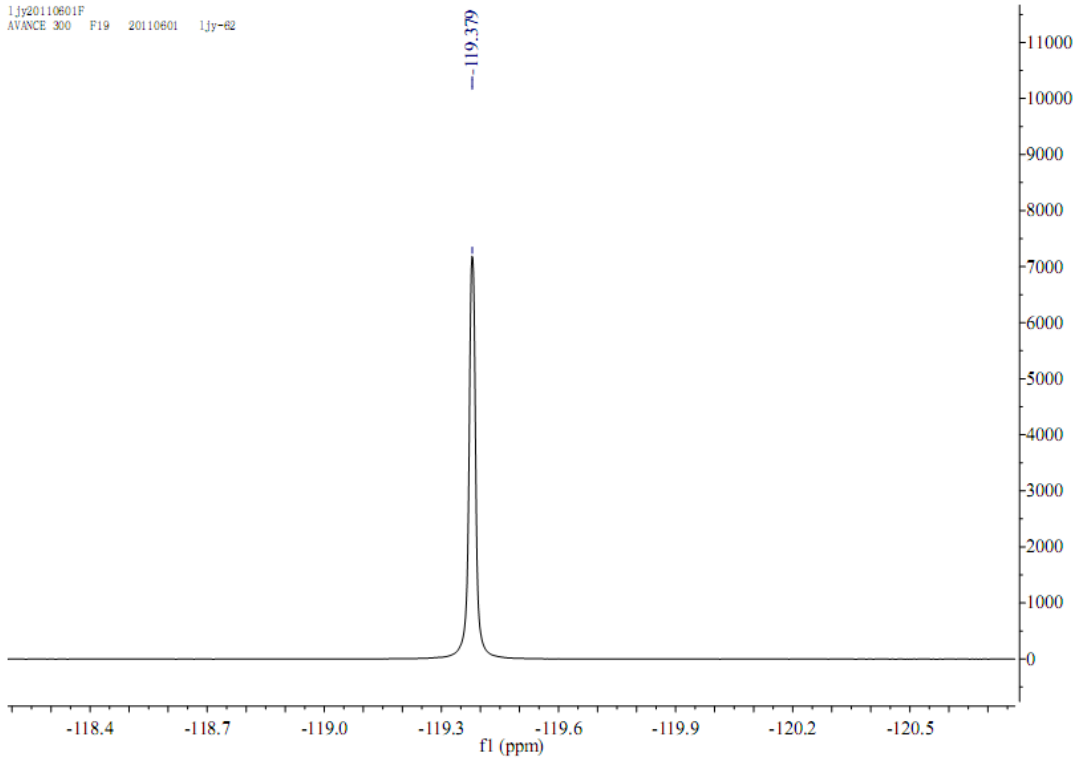


^{13}C NMR (74.5 MHz, $CDCl_3$)



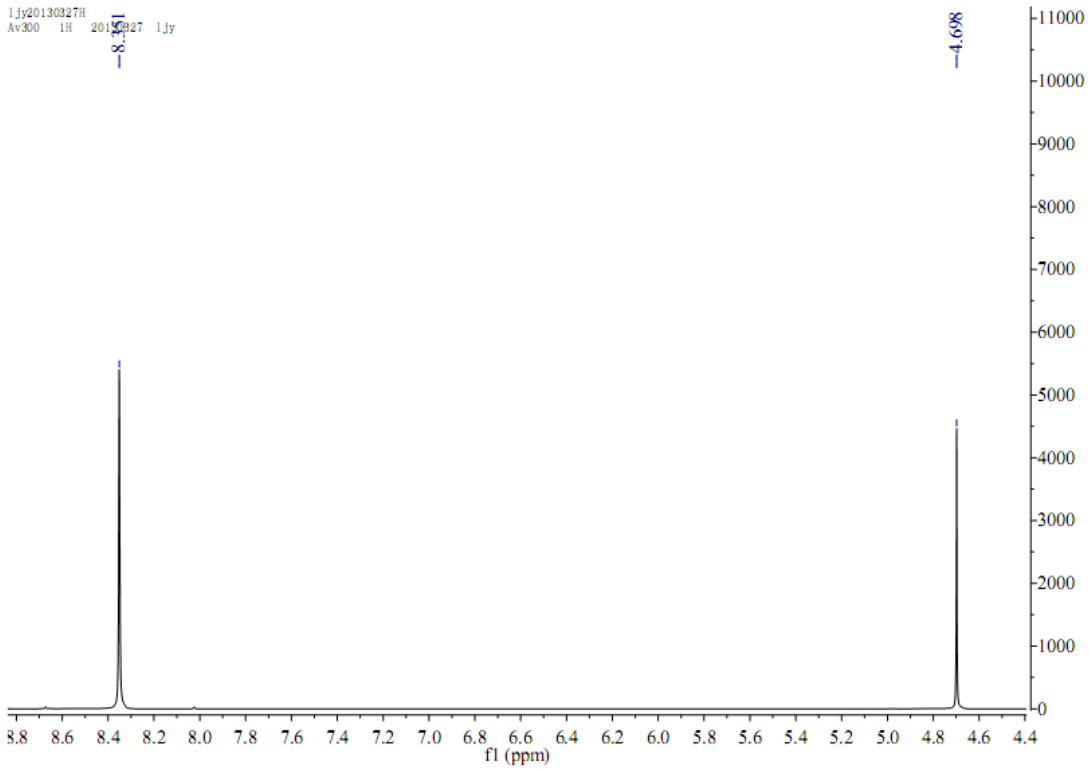
GC-MS (m/z)

7) NaF



^{19}F NMR (282 MHz, H_2O)

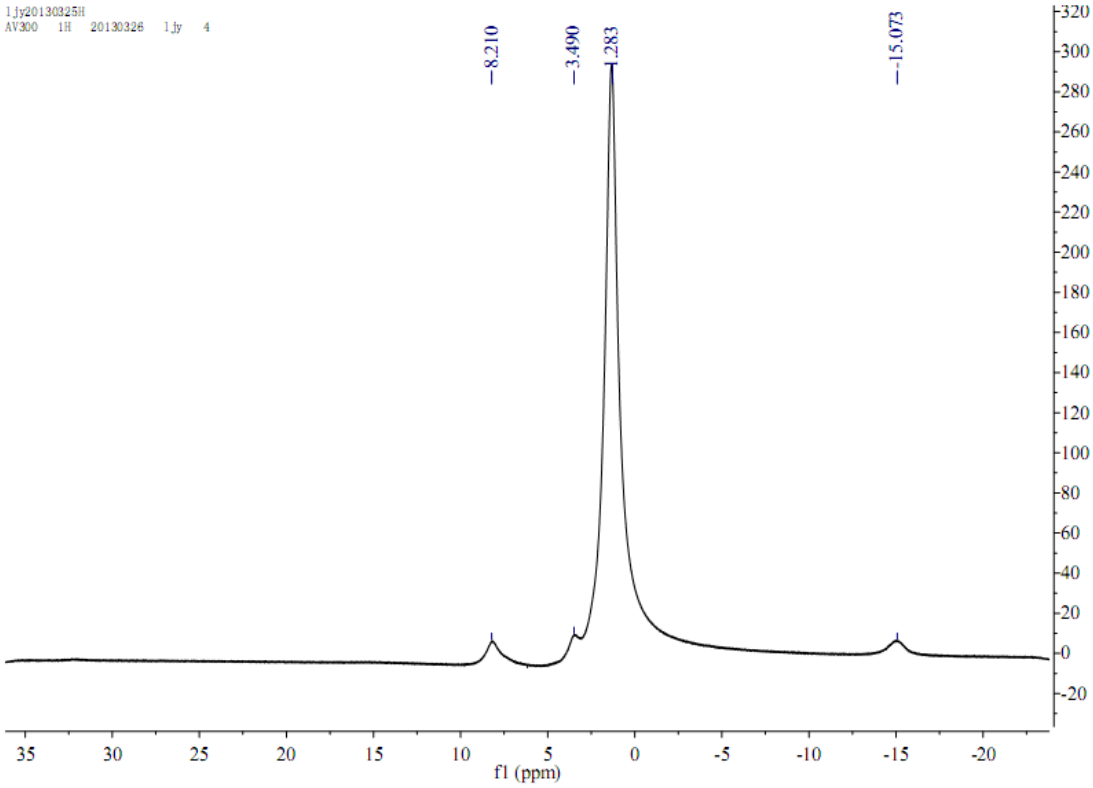
8) HCOONa



^{1}H NMR (300 MHz, D_2O)

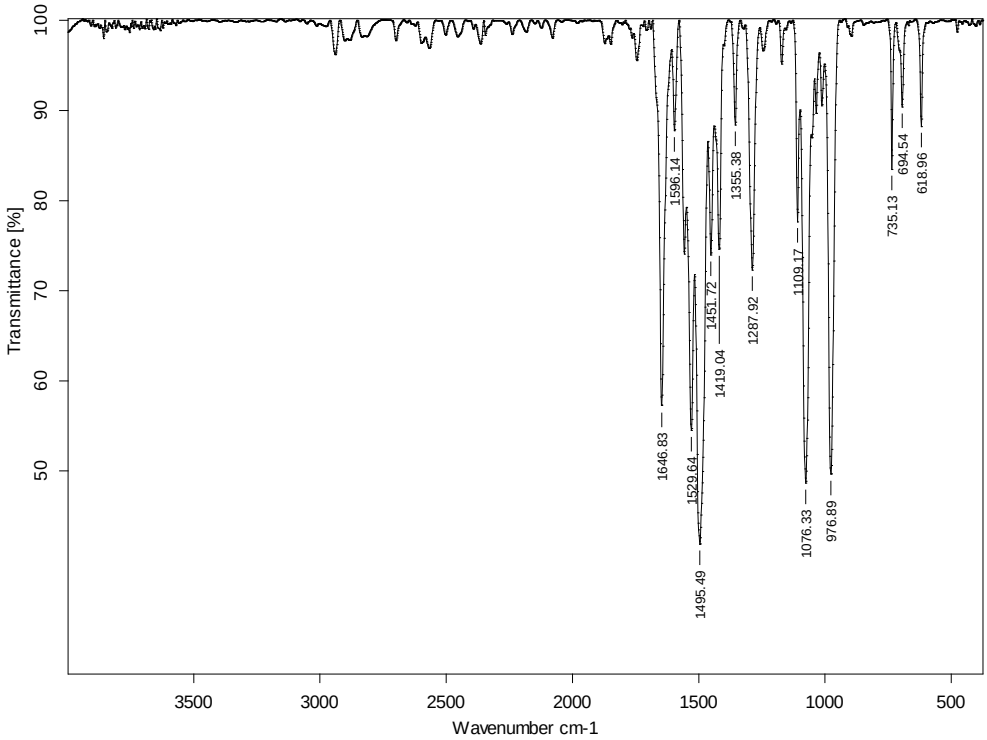
9) the *in situ* ^{1}H NMR

The sample of $C_{12}F_{10}$ (0.020 g, 0.060 mmol) was added in a solution of 0.6 mL of DMSO-D_6 with $Co(PMe_3)_4$ (0.021 g, 0.060 mmol), HCOONa (0.012, 0.180 mmol) in a NMR tube at -80℃, This mixture was allowed to warm to 80 ℃ and the color of the reaction solution turned to orange from brown.



^{1}H NMR (300 MHz, DMSO-D_6)

10) IR spectroscopy of pentafluoropyridine


Transmittance [%]
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80
70
60
50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
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1596.14
1529.64
1495.49
1451.72
1419.04
1355.38
1287.92
1109.17
1076.33
976.89
735.13
694.54
618.96