Electronic Supplementary Information (ESI)

Highly Shape- and Regio-selective Peroxy-trifluoromethylation of Styrene by Metal-Organic Framework $Cu_3(BTC)_2$

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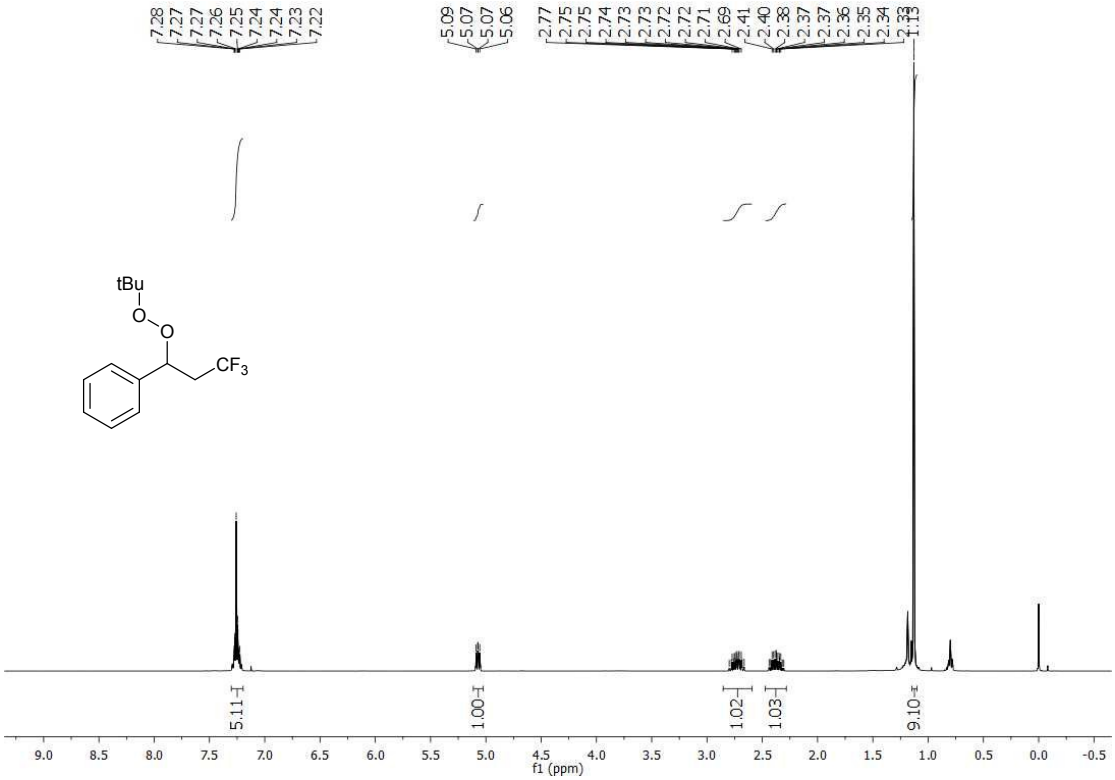
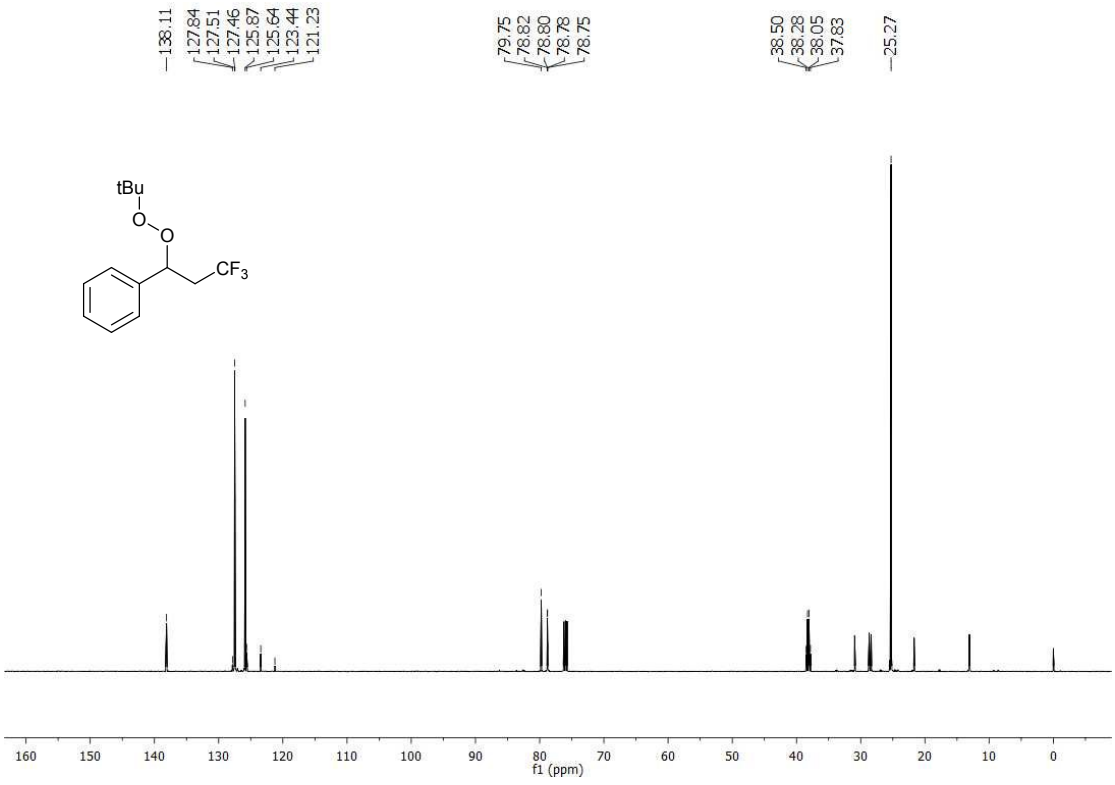
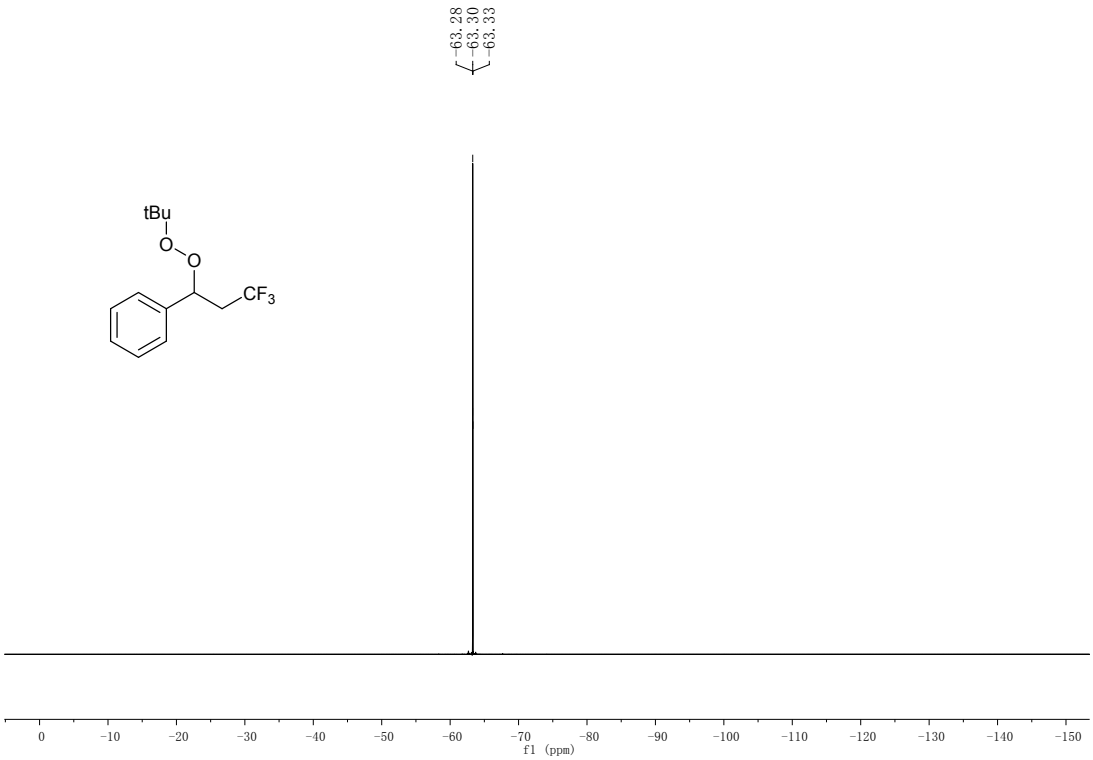
(1-(*tert*-butylperoxy)-3,3,3-trifluoropropyl)benzene (2a)







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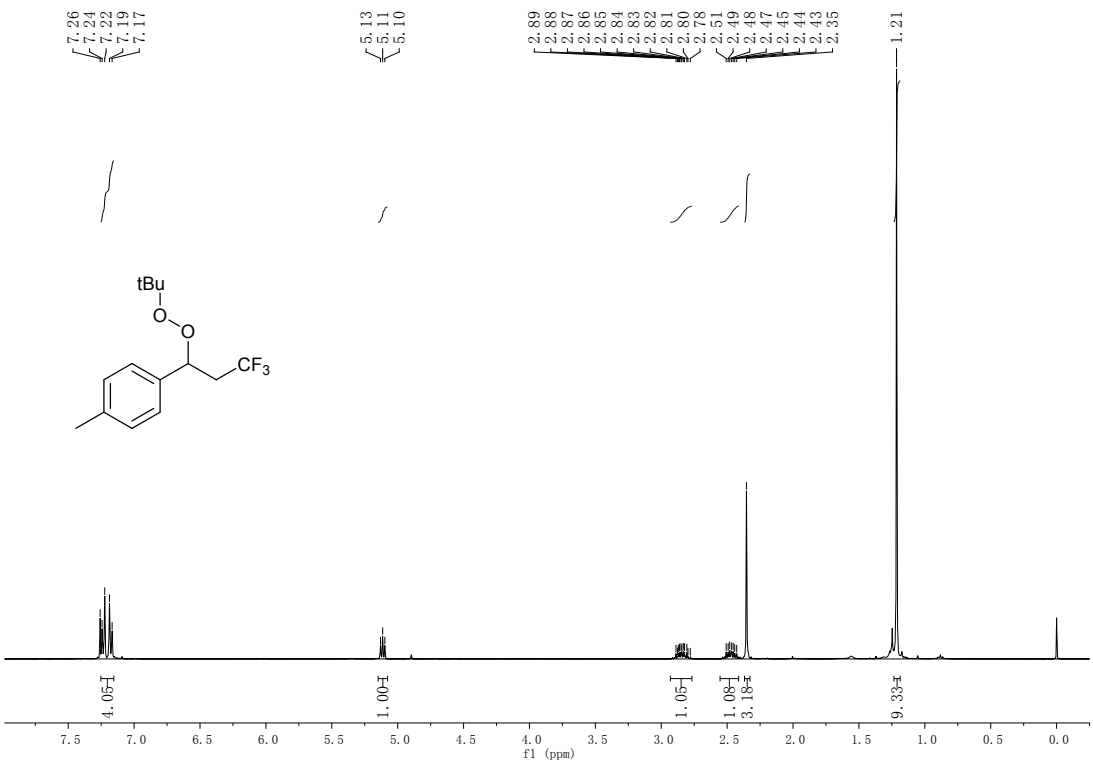

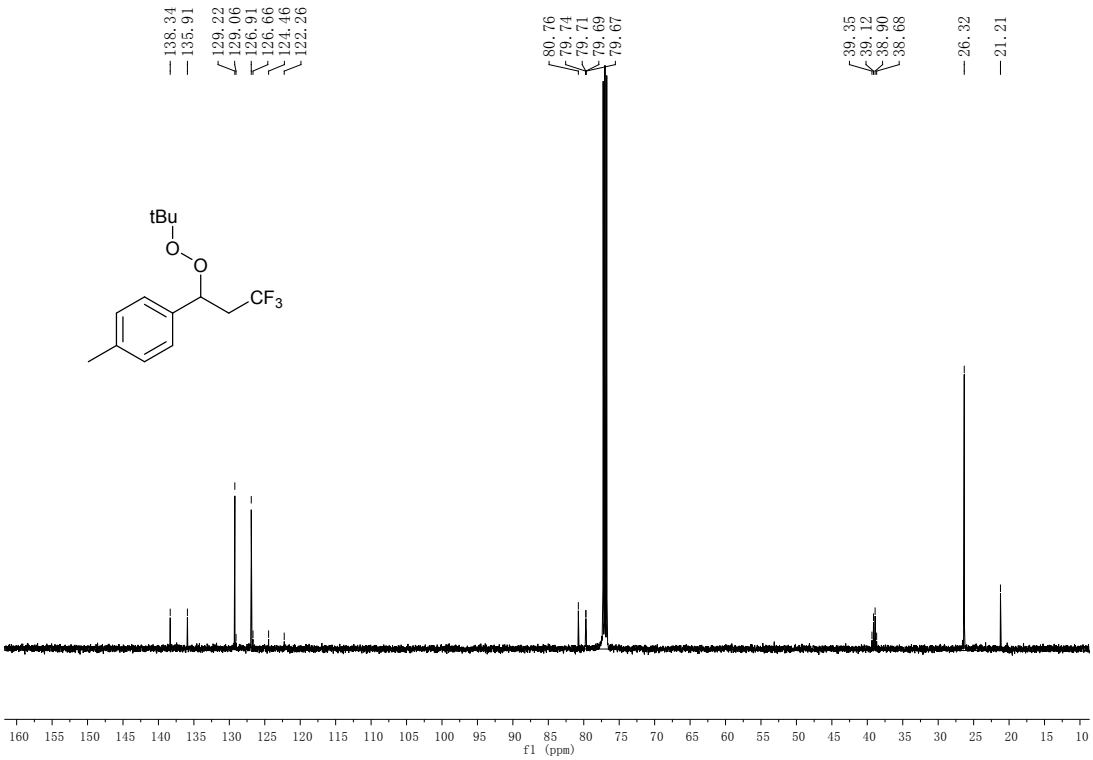
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26.32
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CF3
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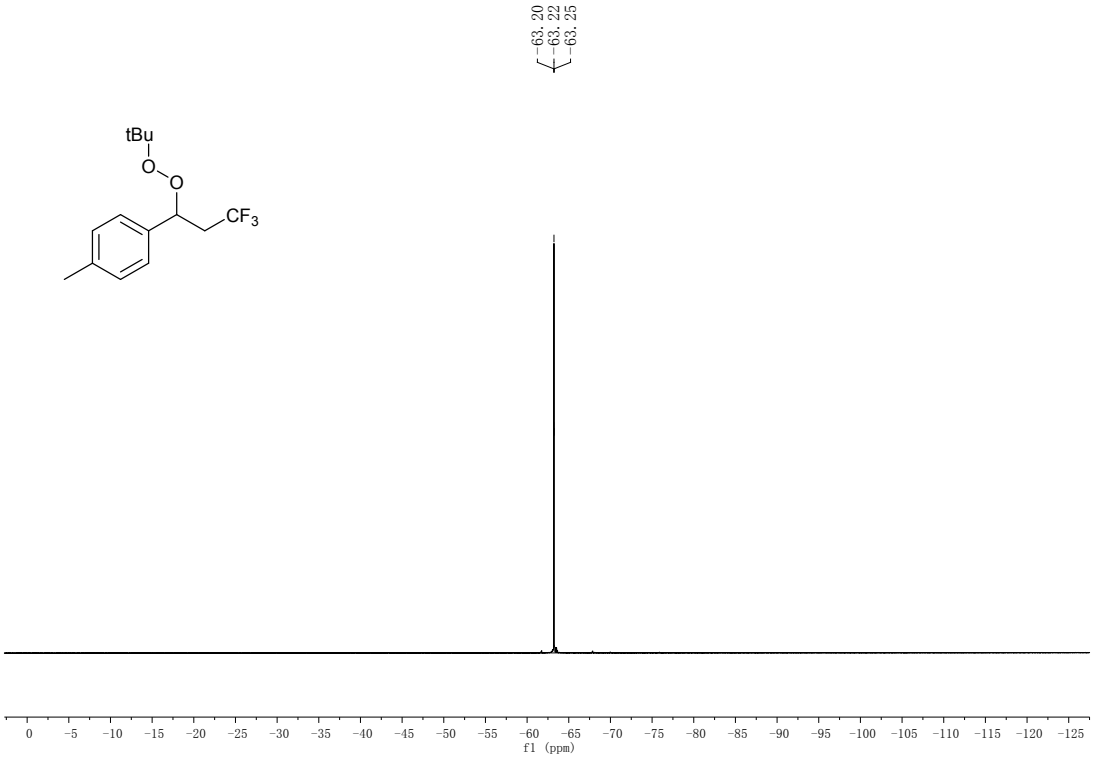
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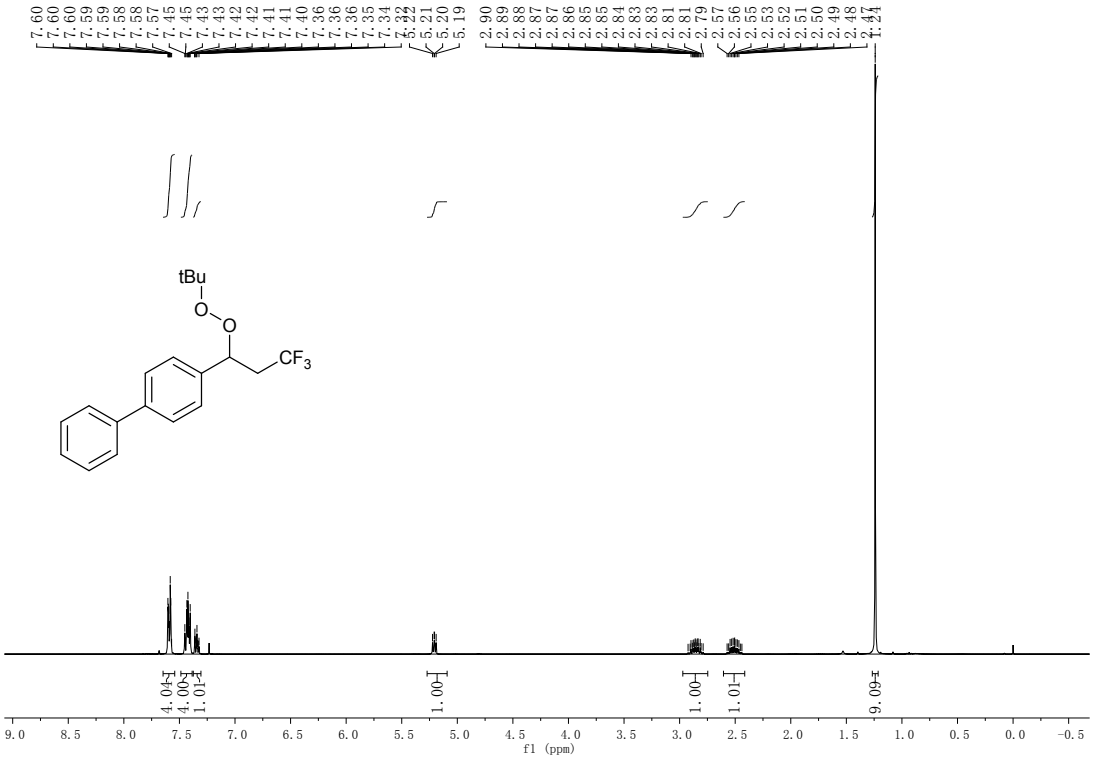

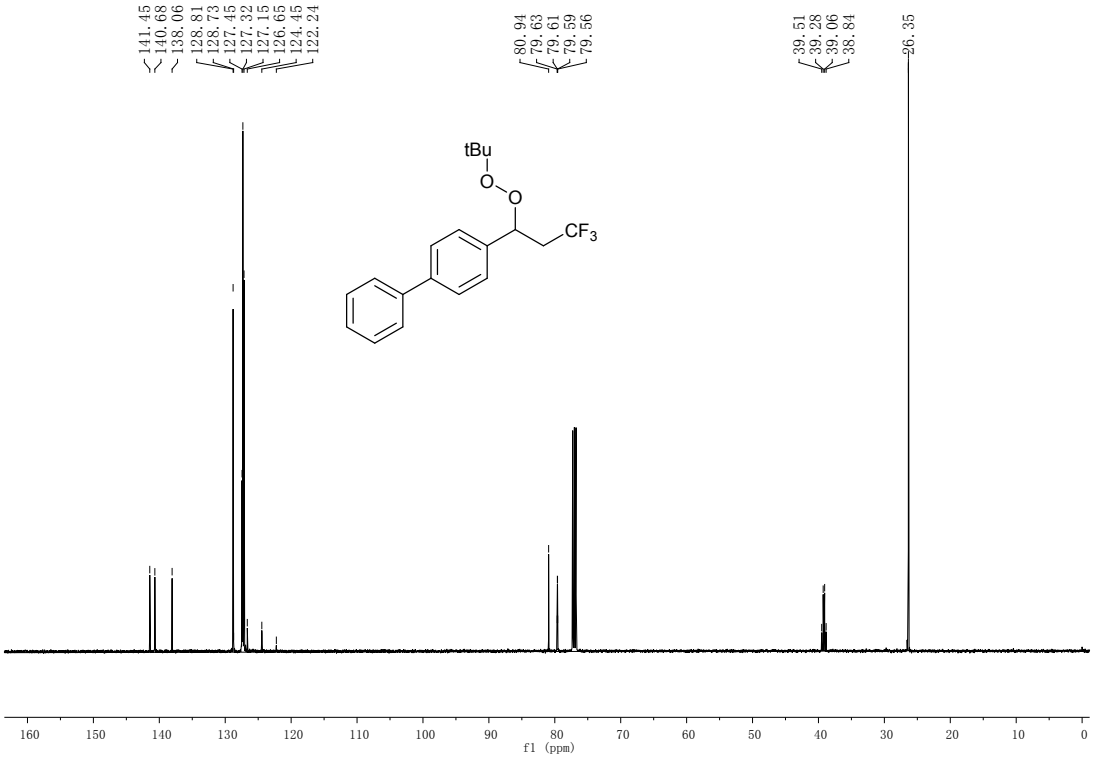

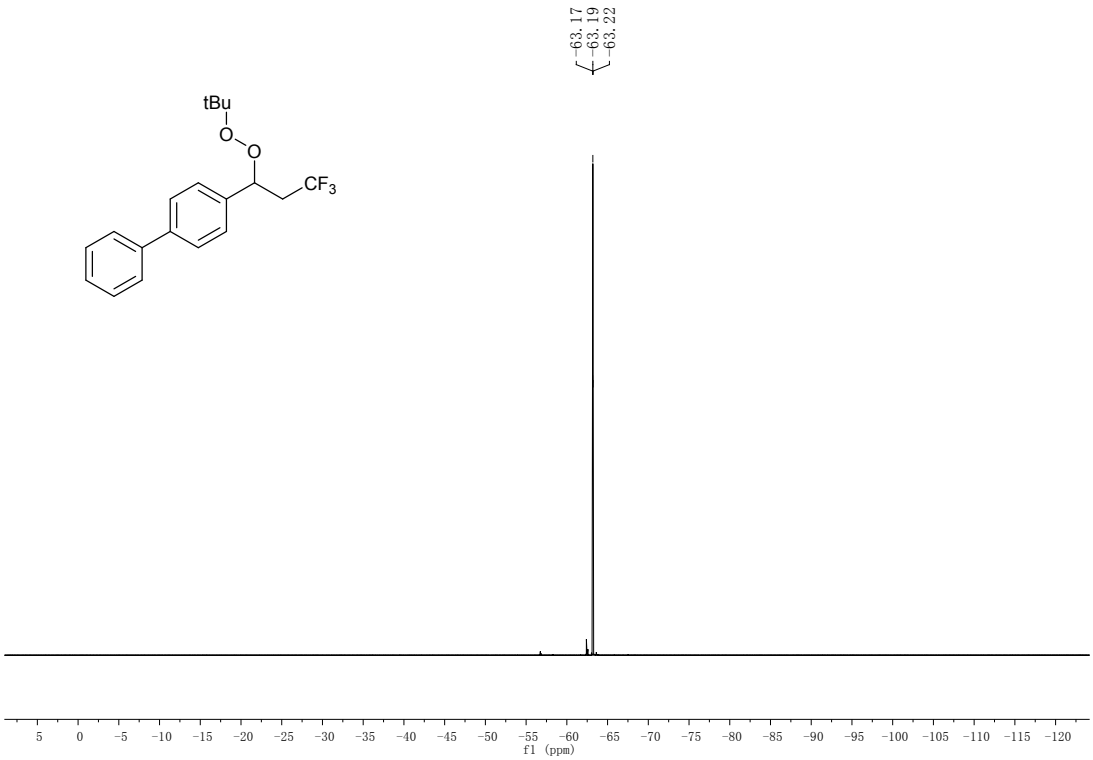

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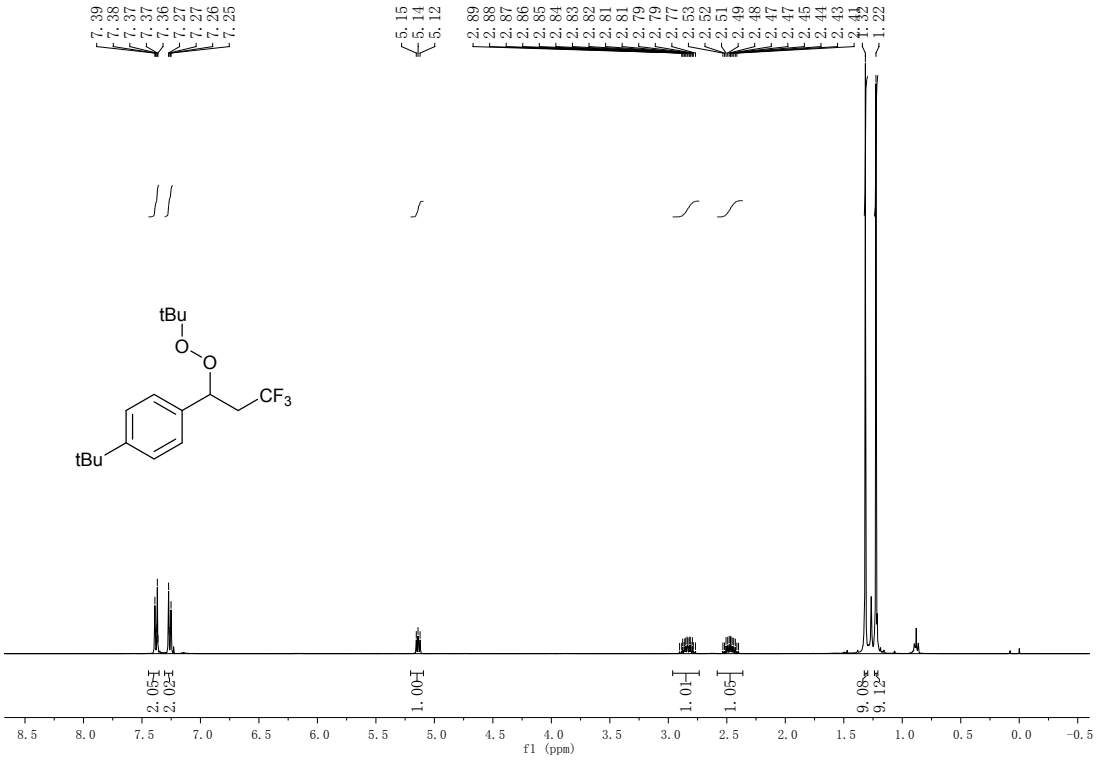

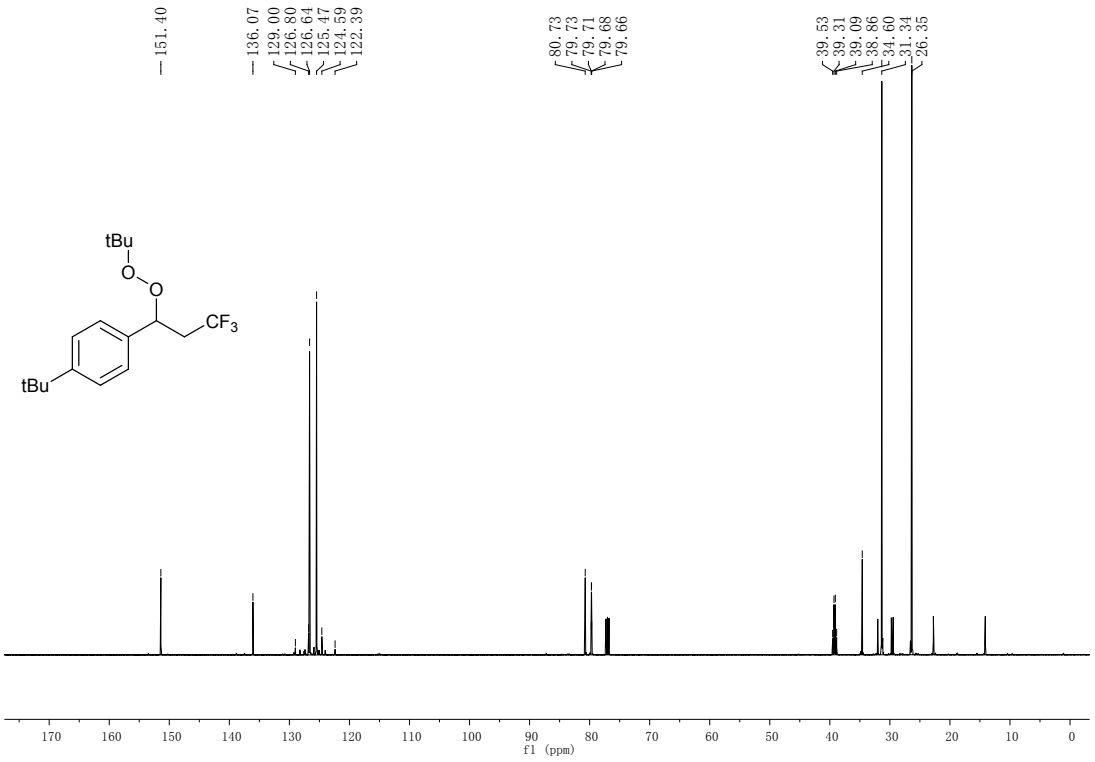
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39.53
39.31
39.09
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34.60
31.34
26.35
tBu
O
O
CF3
tBu
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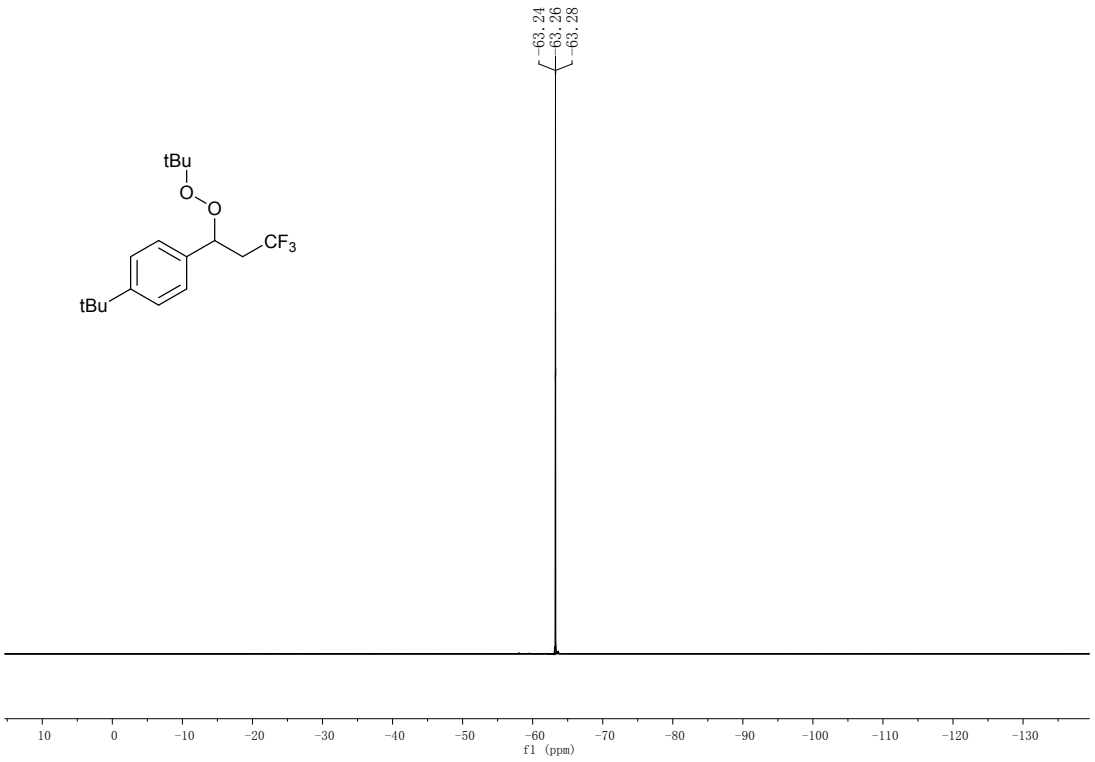
f1 (ppm)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−30
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−50
−60
−70
−80
−90
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−120
−130
f1 (ppm)

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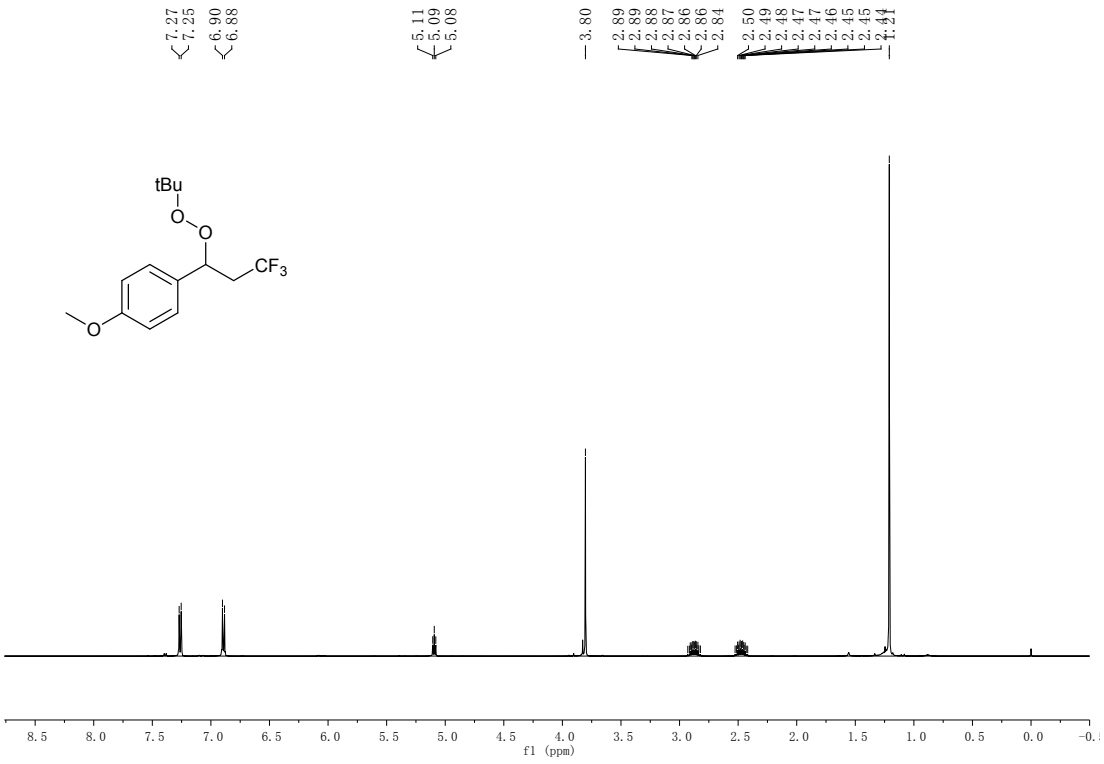

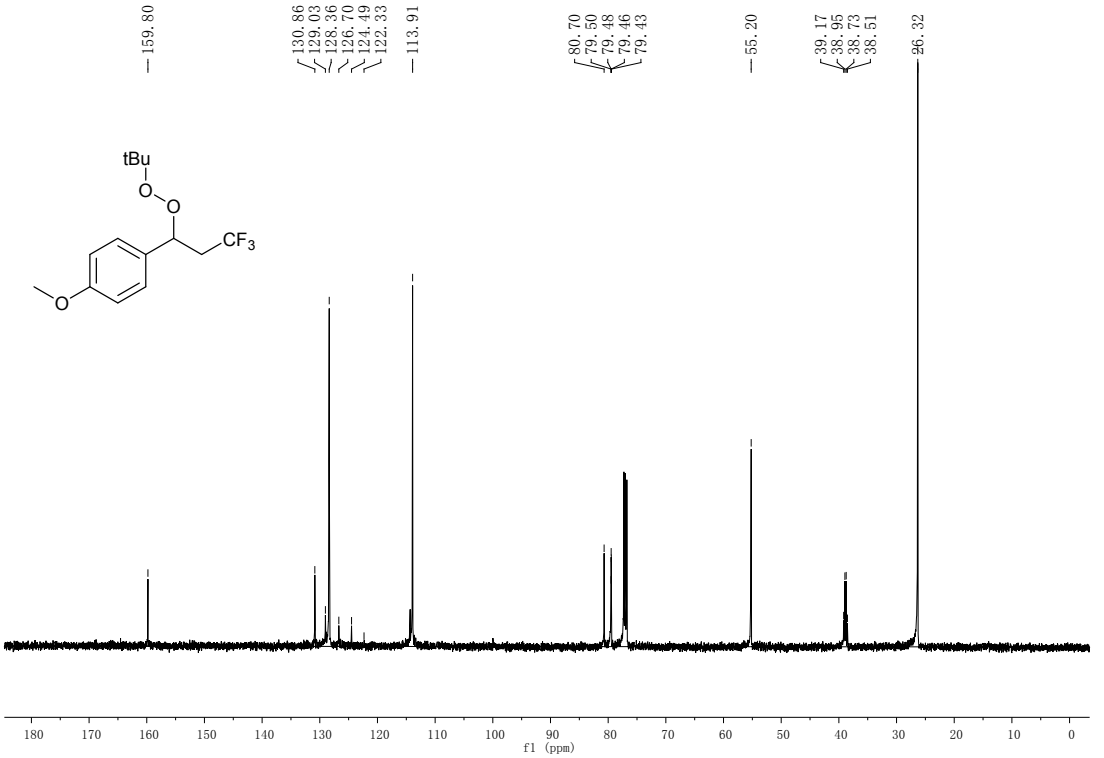

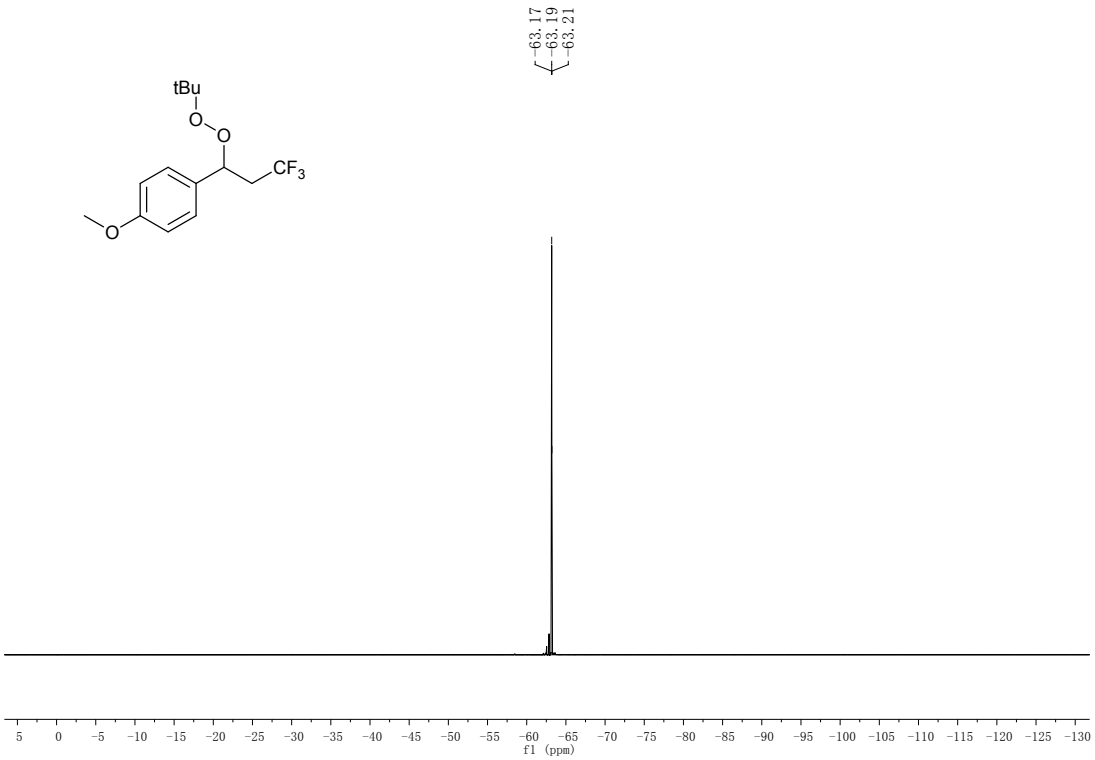

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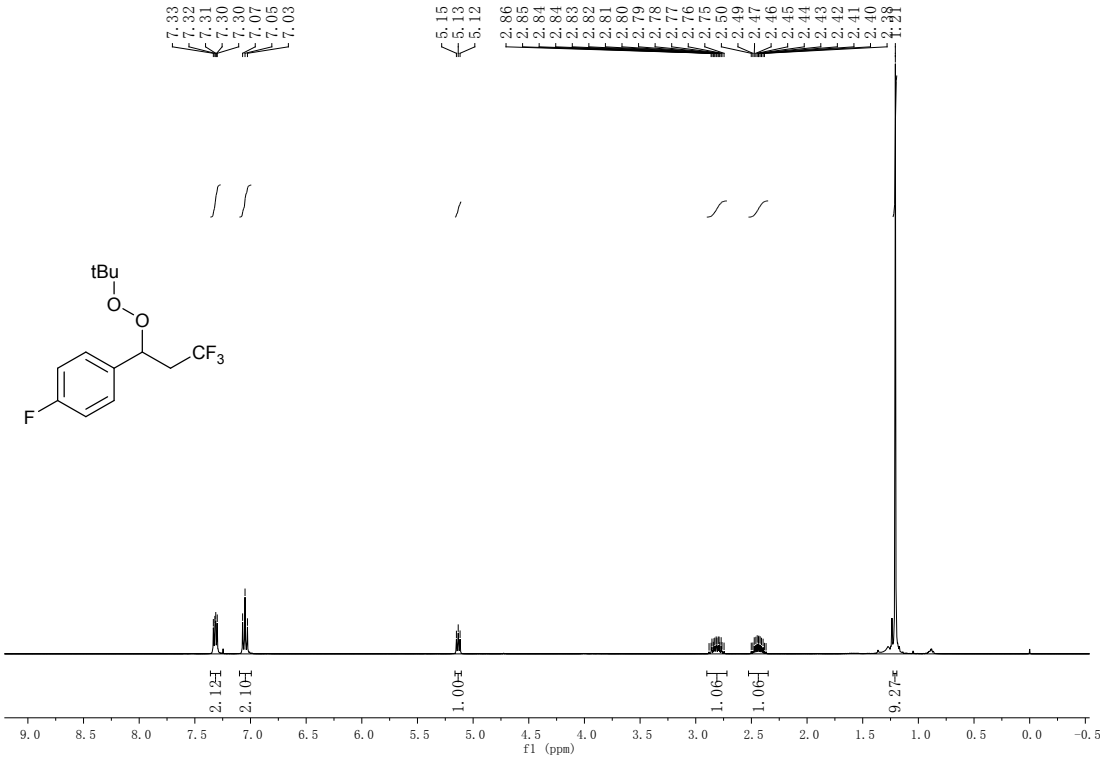

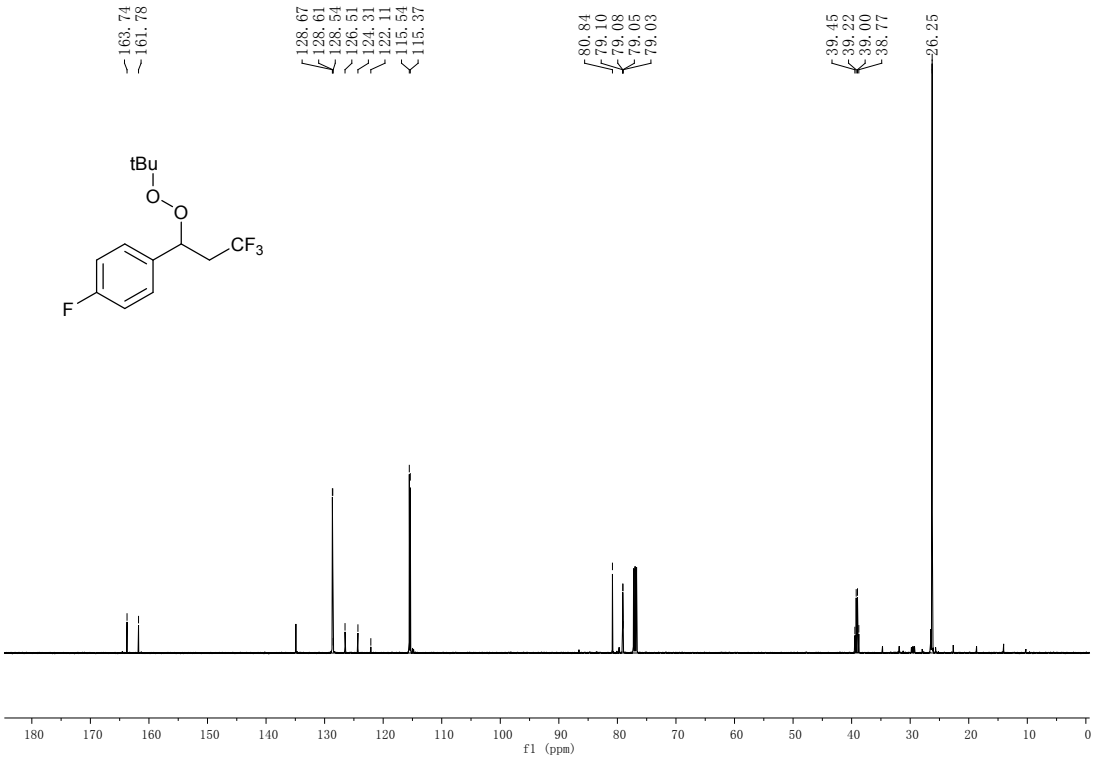
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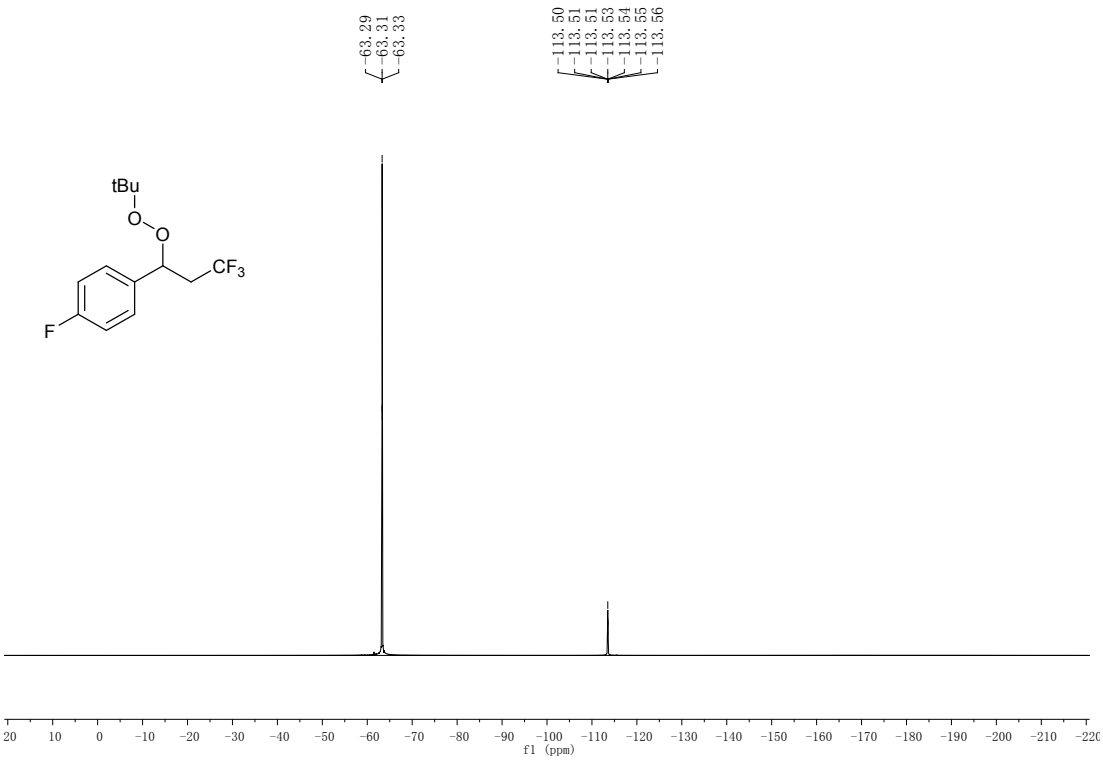
tBu
O
O
CF3
F
f1 (ppm)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-113.51
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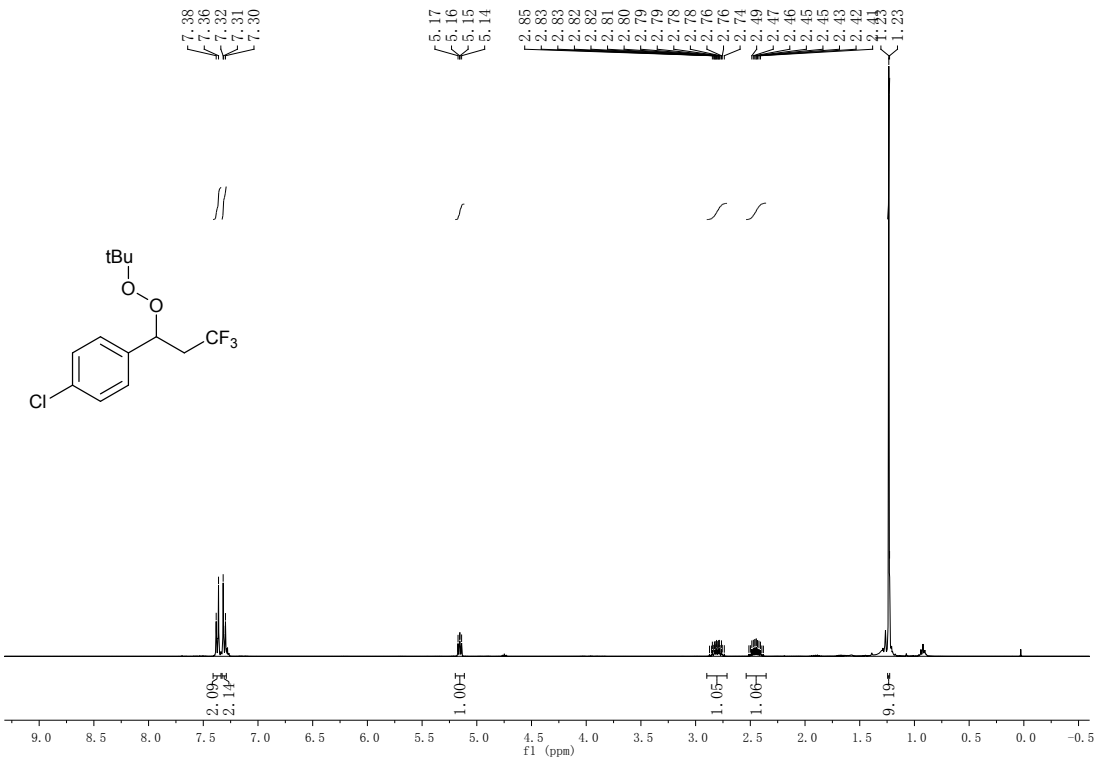
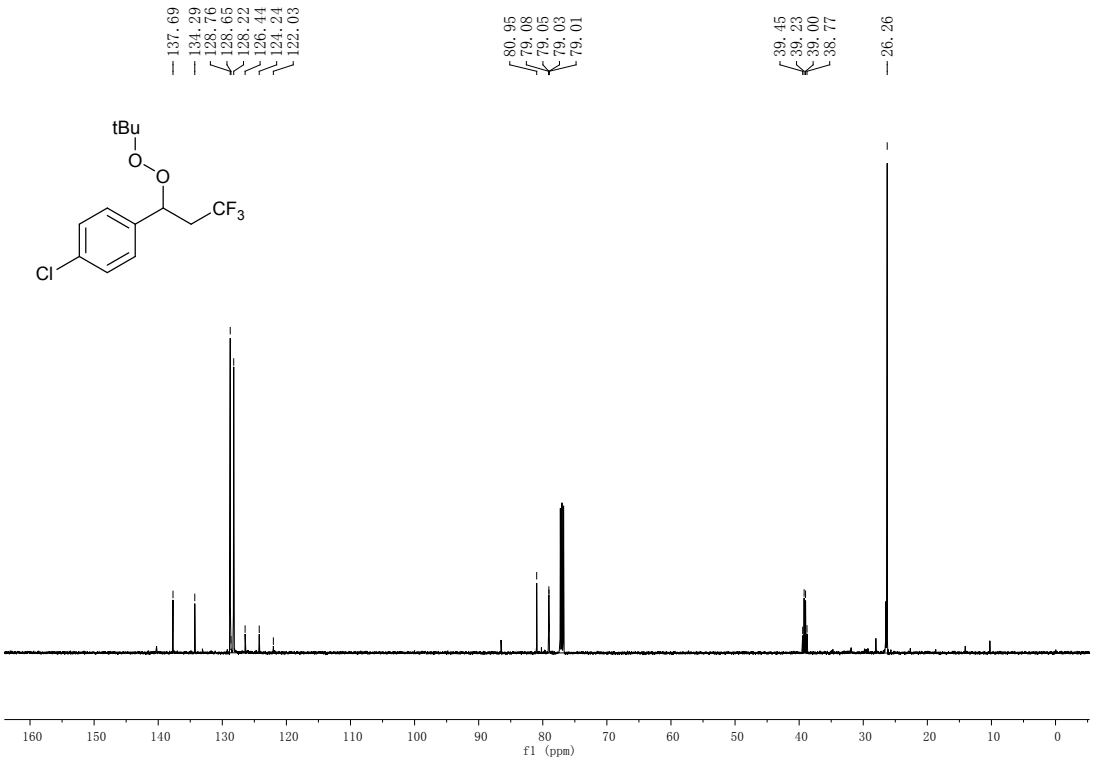
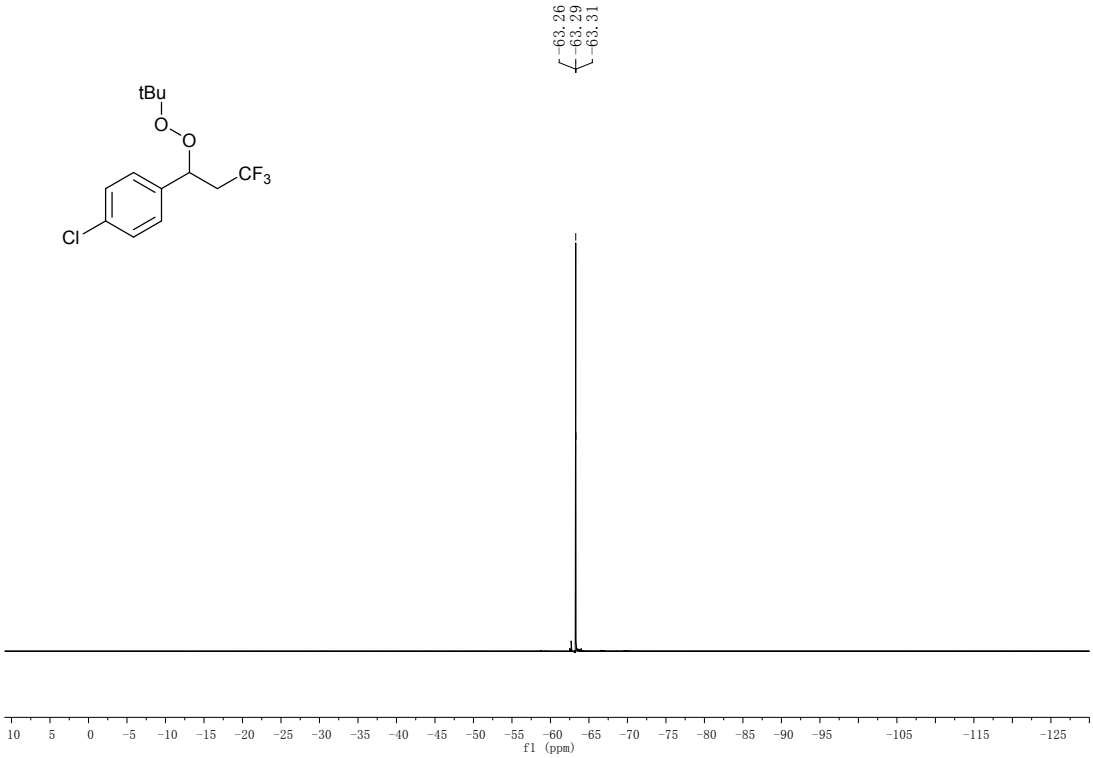
-113.54
-113.55
-113.56
tBu
O
O
CF3
F
f1 (ppm)

1-(1-(*tert*-butylperoxy)-3,3,3-trifluoropropyl)-4-chlorobenzene (2g)







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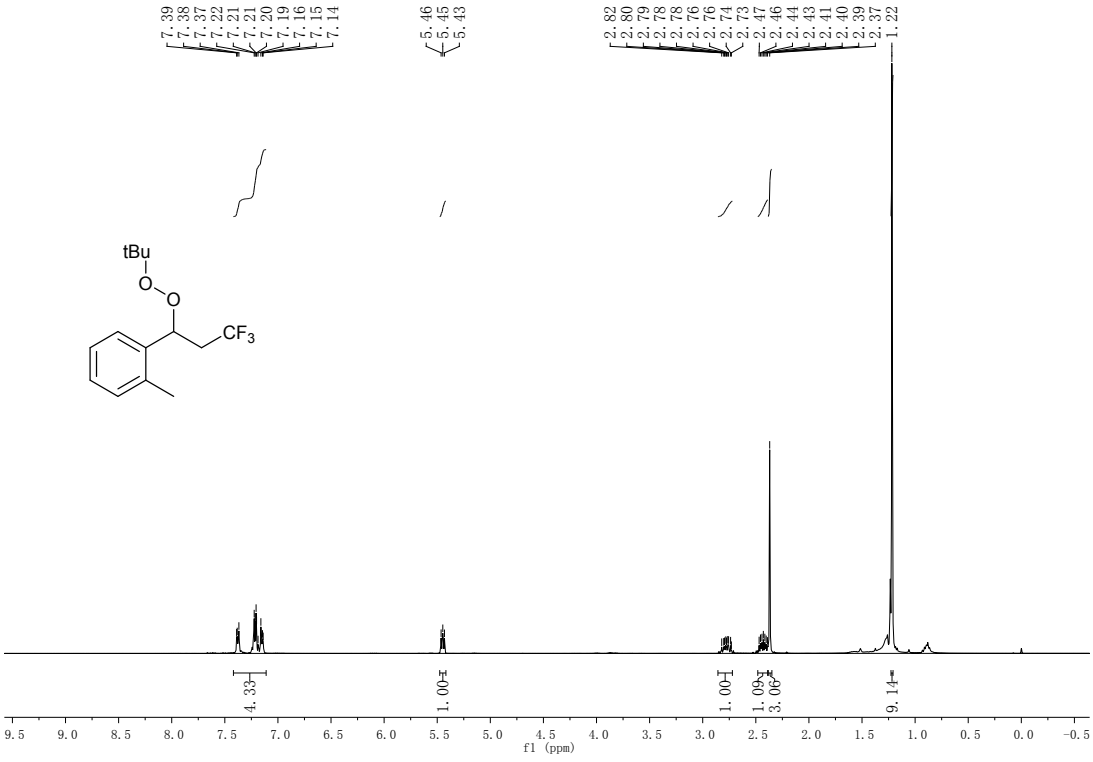

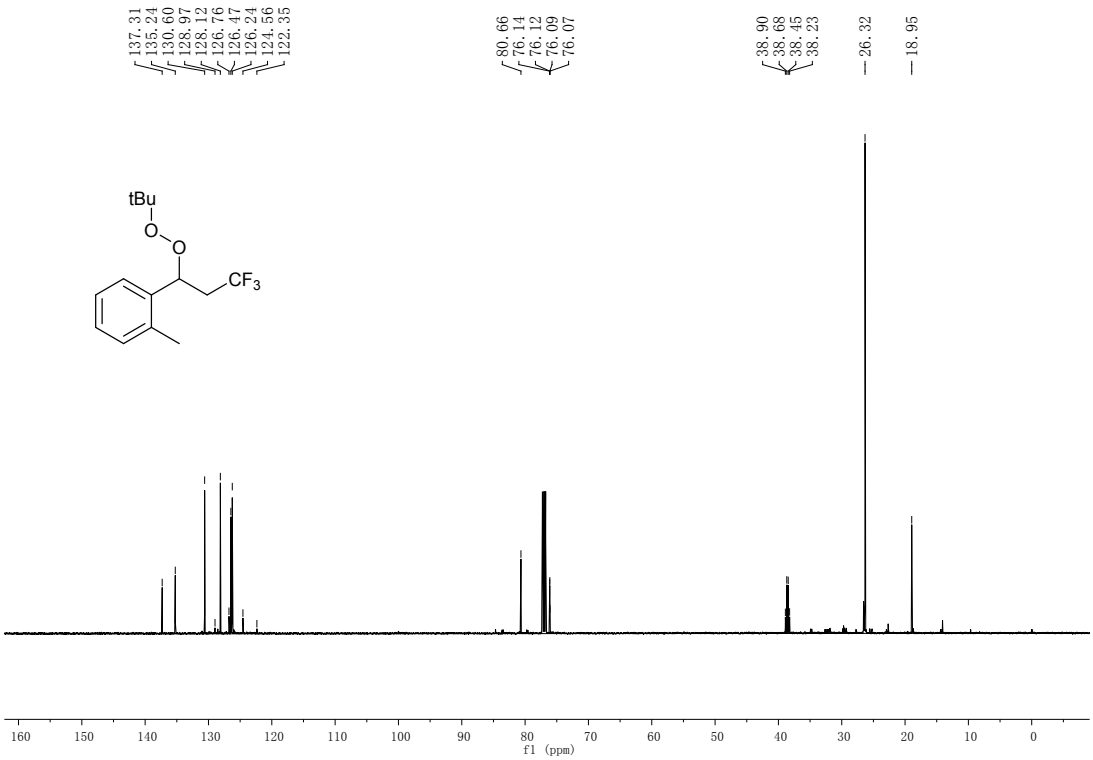
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18.95
tBu
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O
CF3
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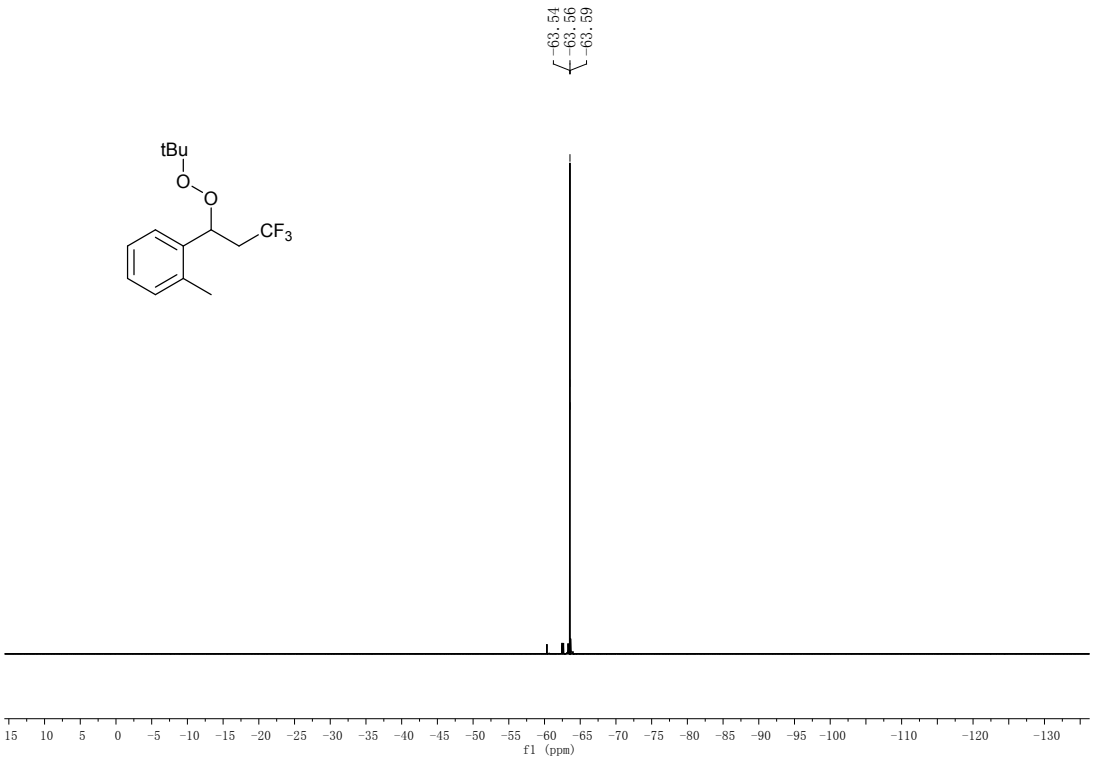
f1 (ppm)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CF3
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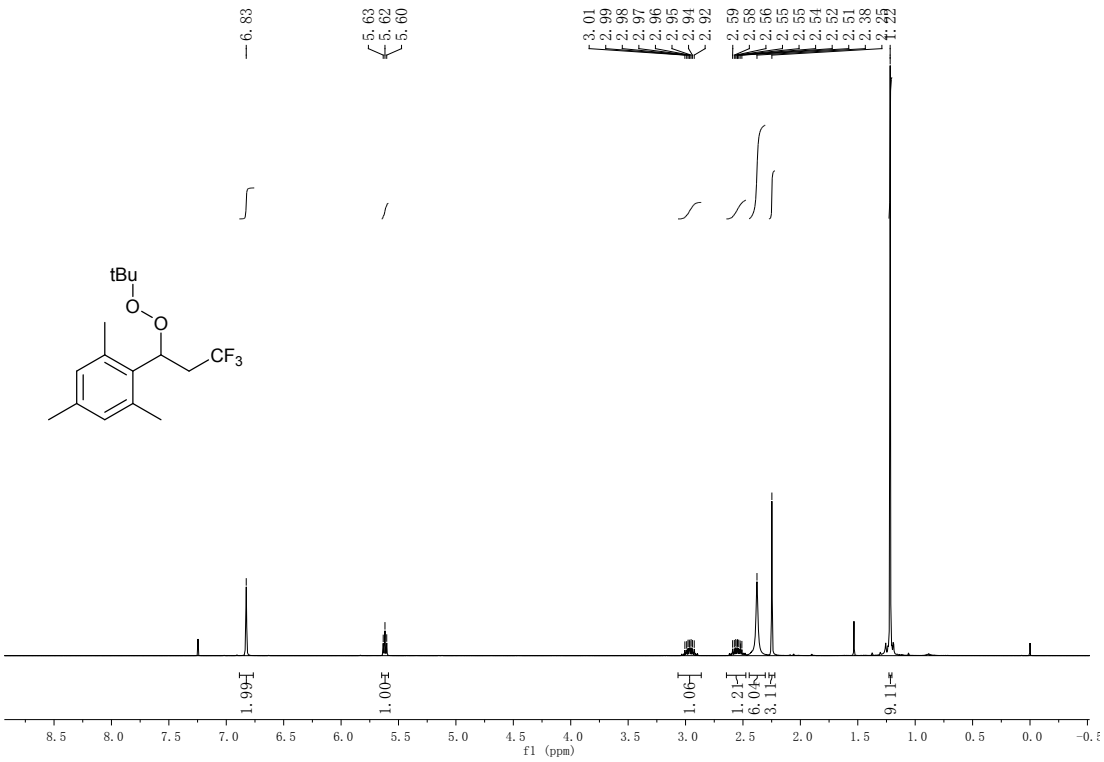
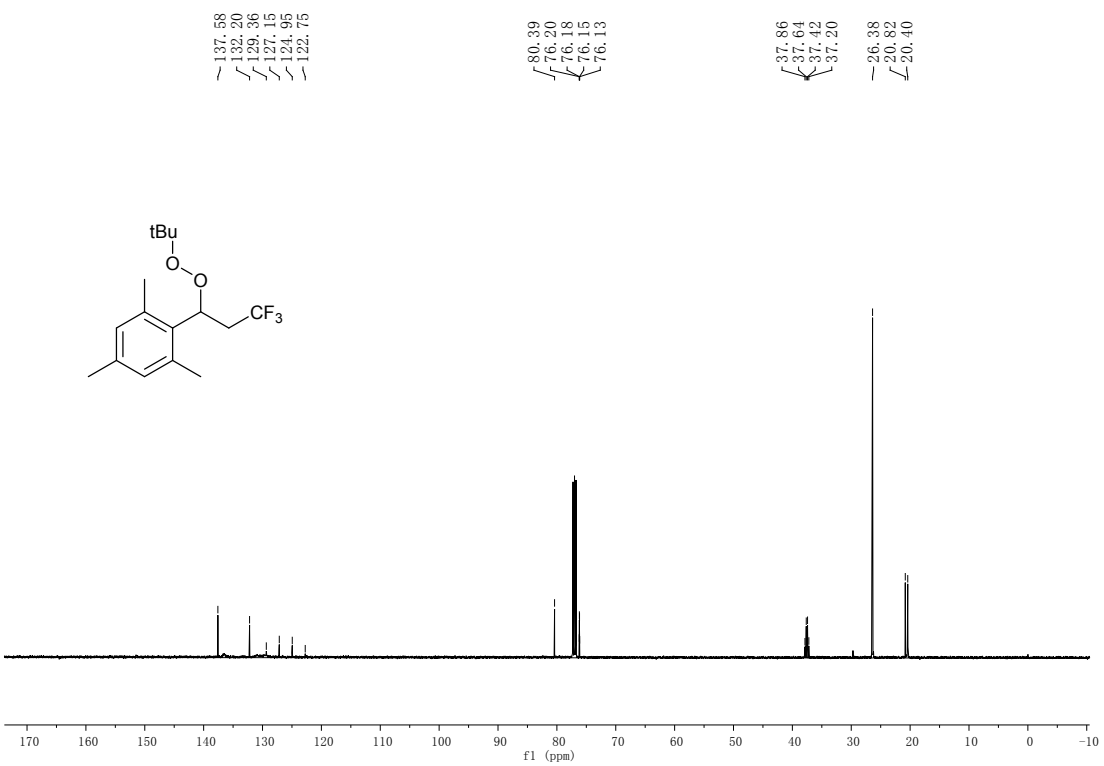
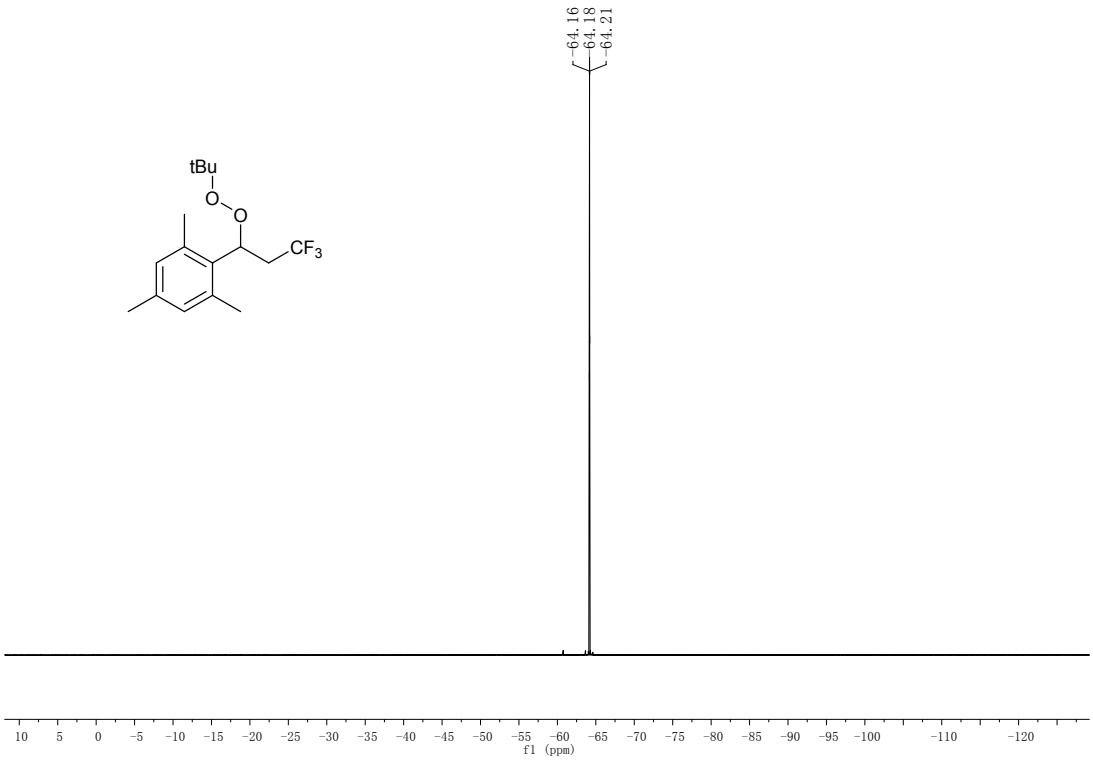
f1 (ppm)

2-(1-(*tert*-butylperoxy)-3,3,3-trifluoropropyl)-1,3,5-trimethylbenzene (2i)







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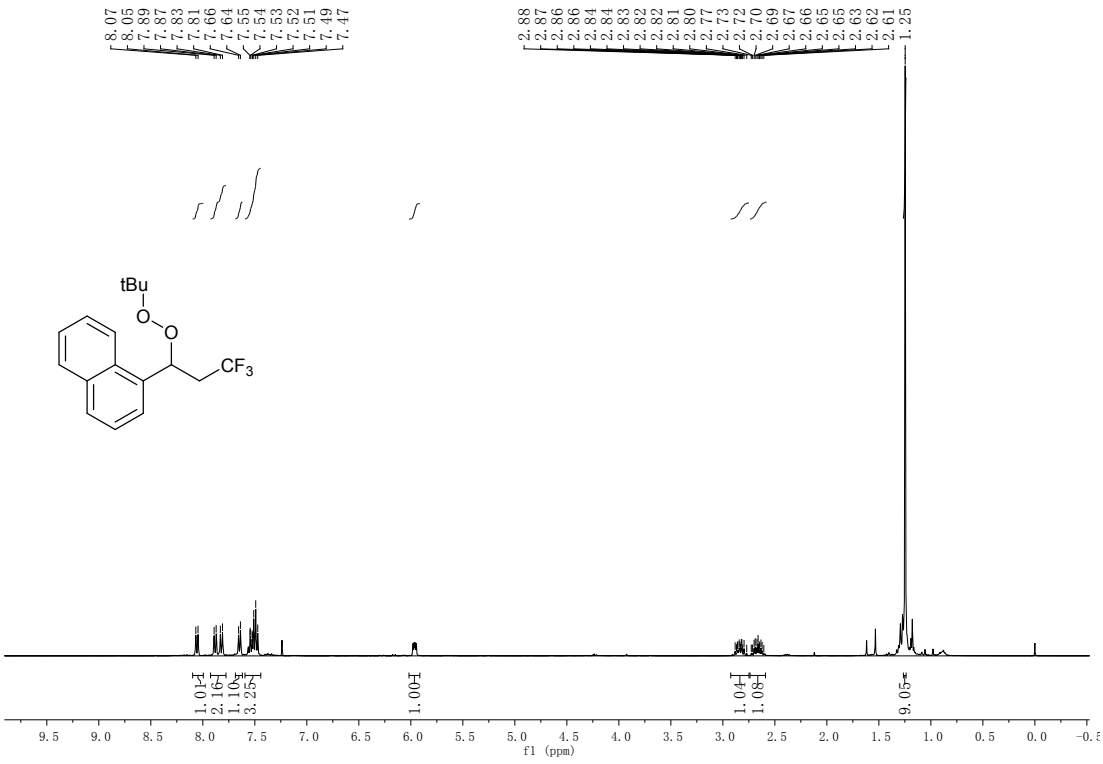

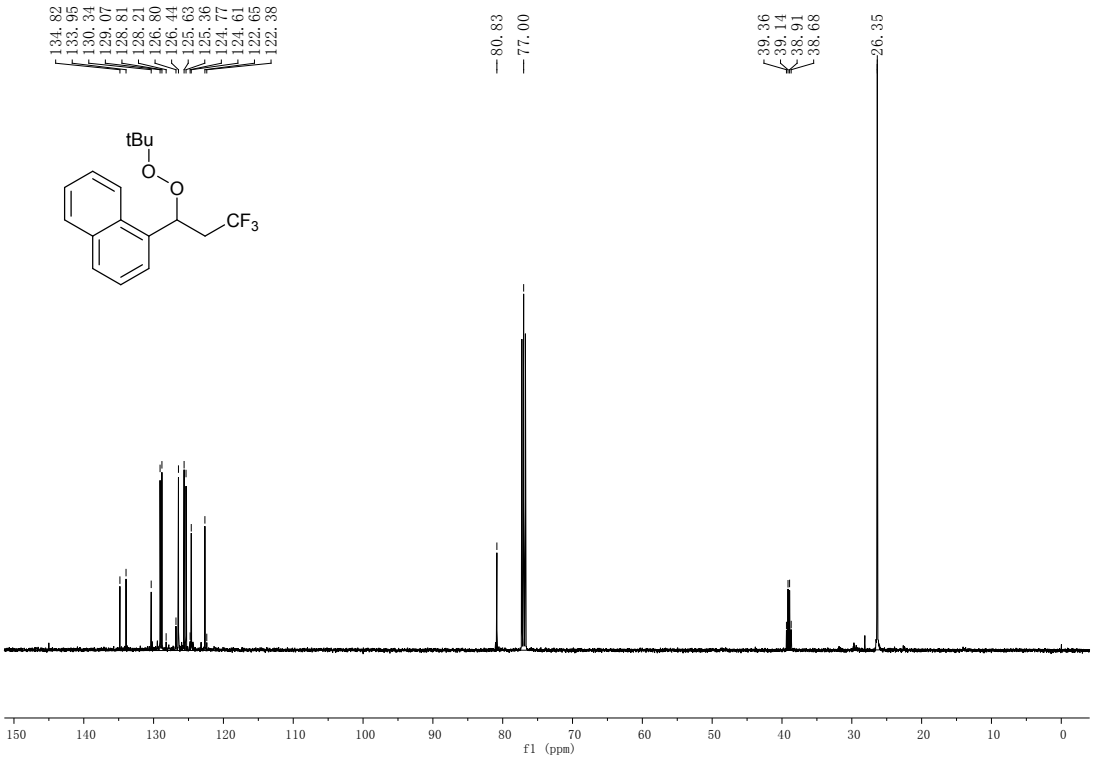
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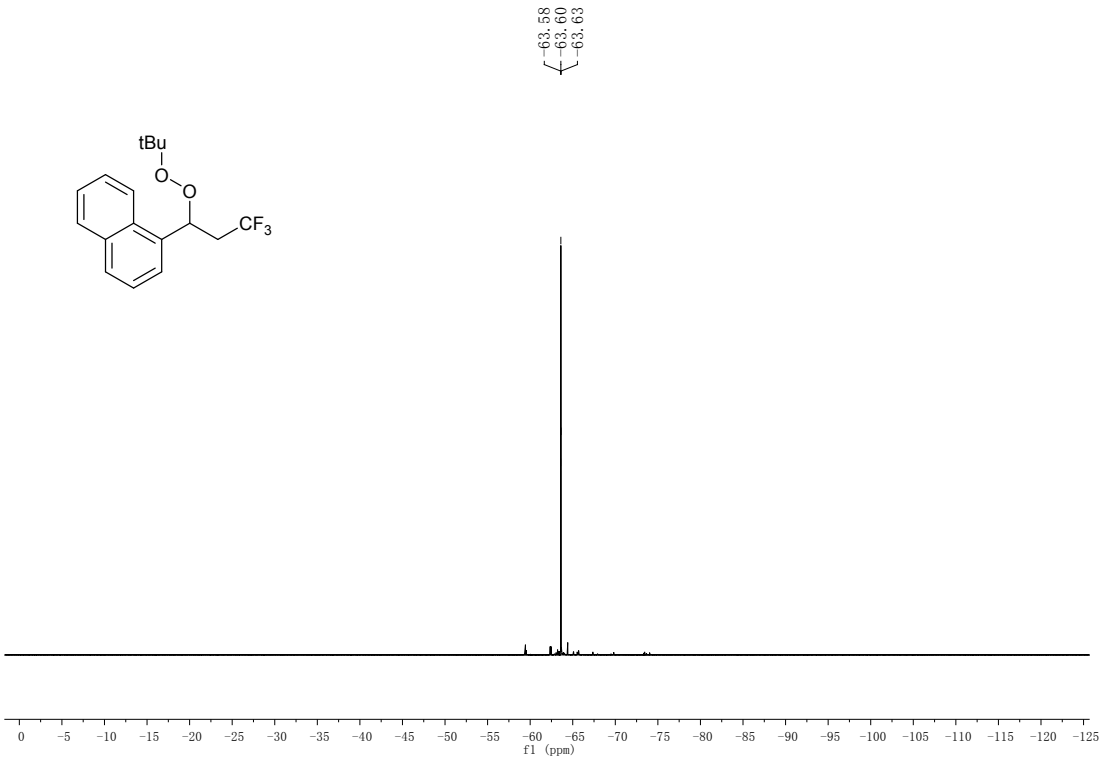
f1 (ppm)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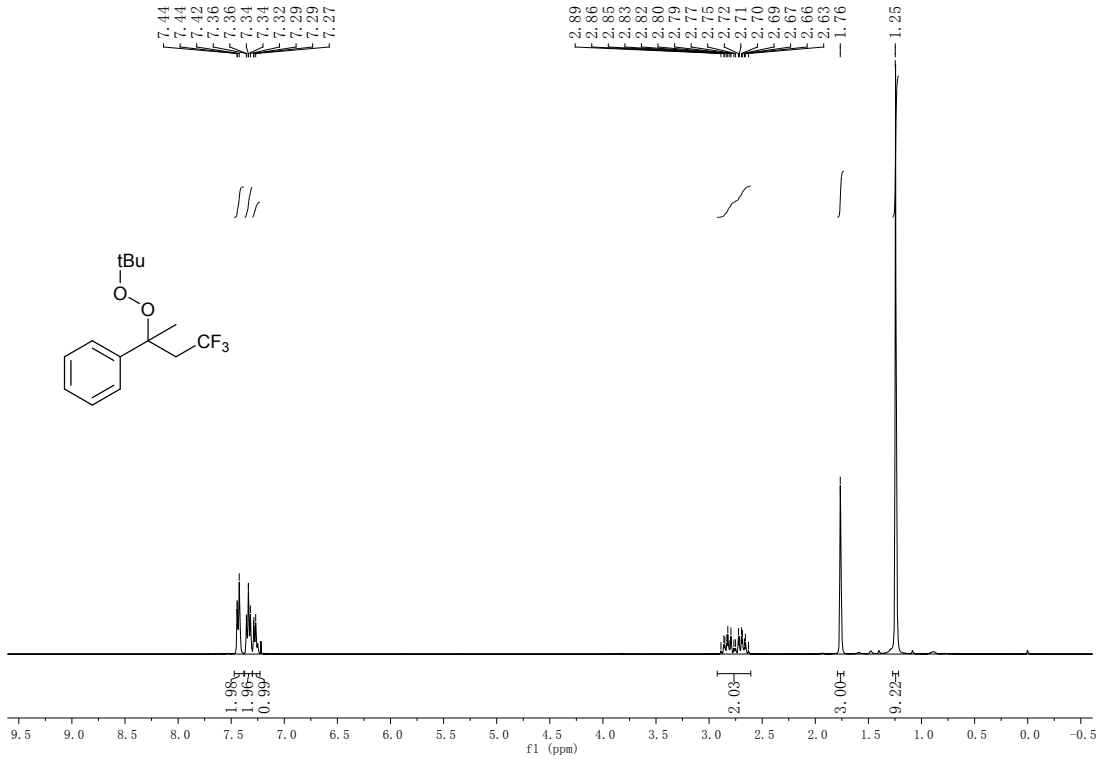
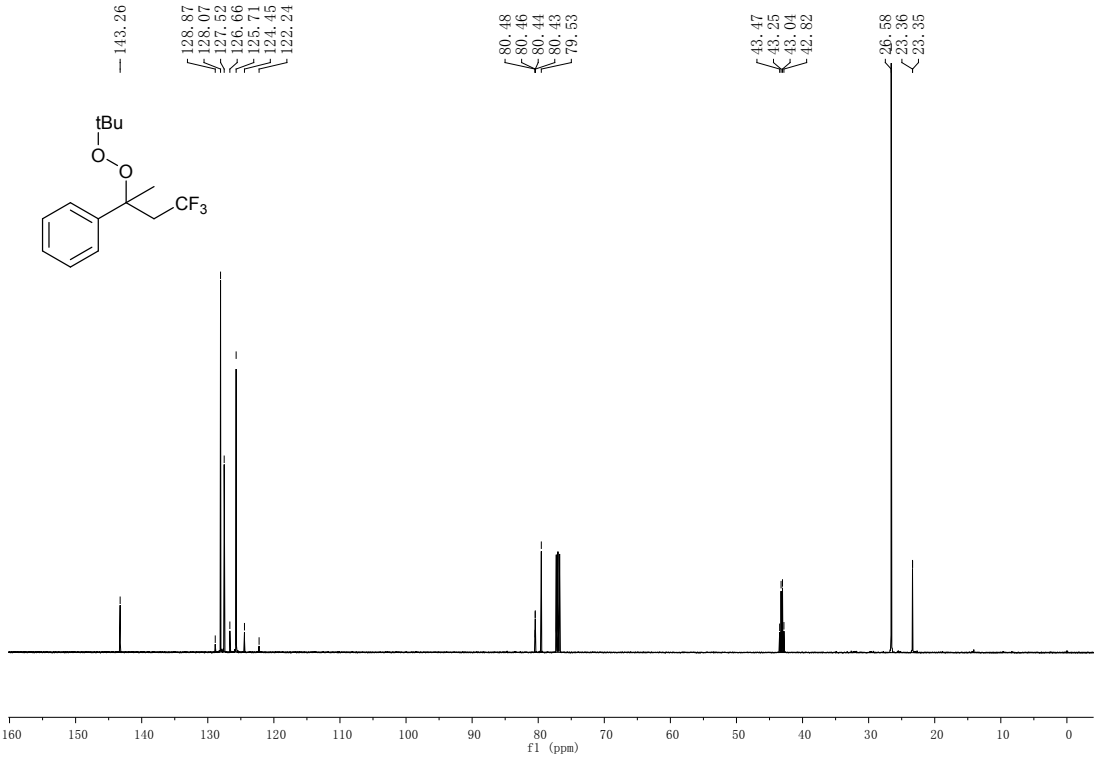
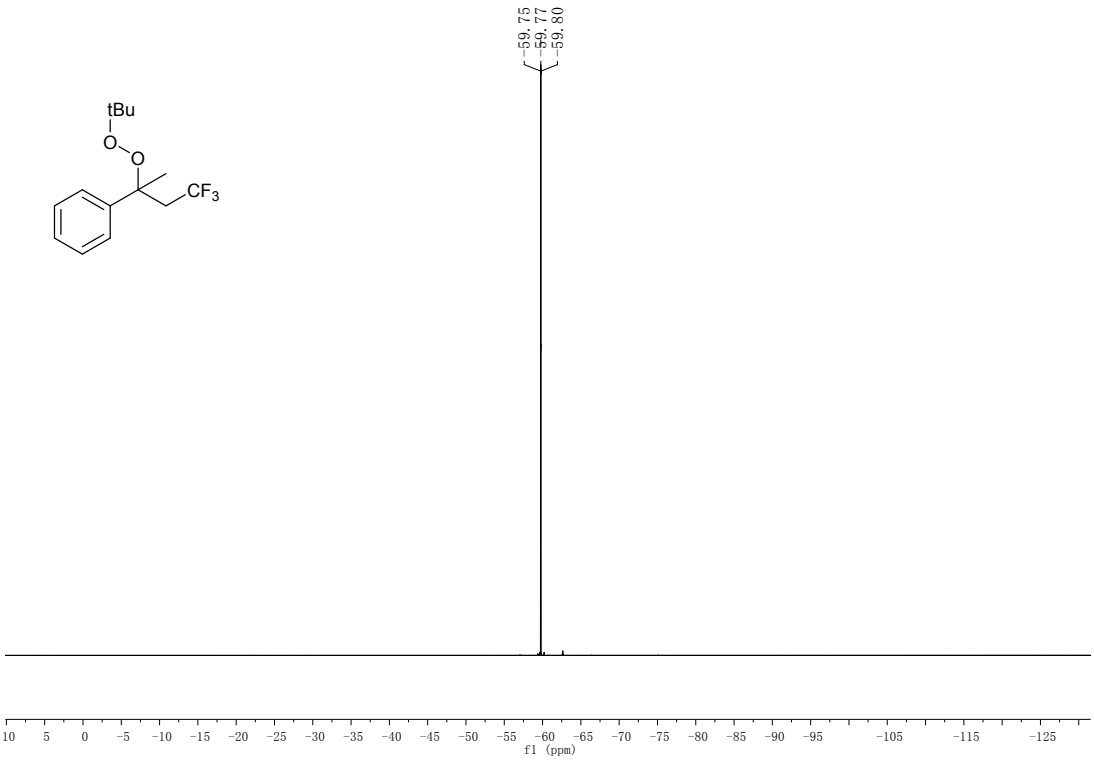
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

(2-(*tert*-butylperoxy)-4,4,4-trifluorobutan-2-yl)benzene (2k)







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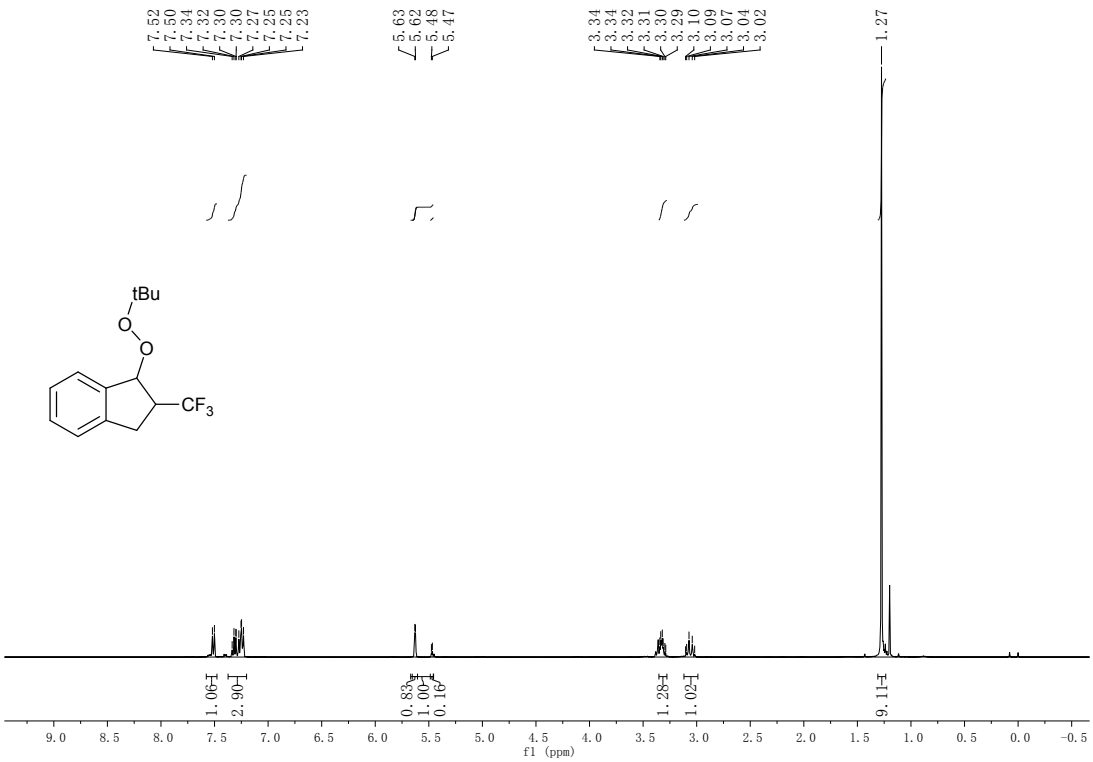

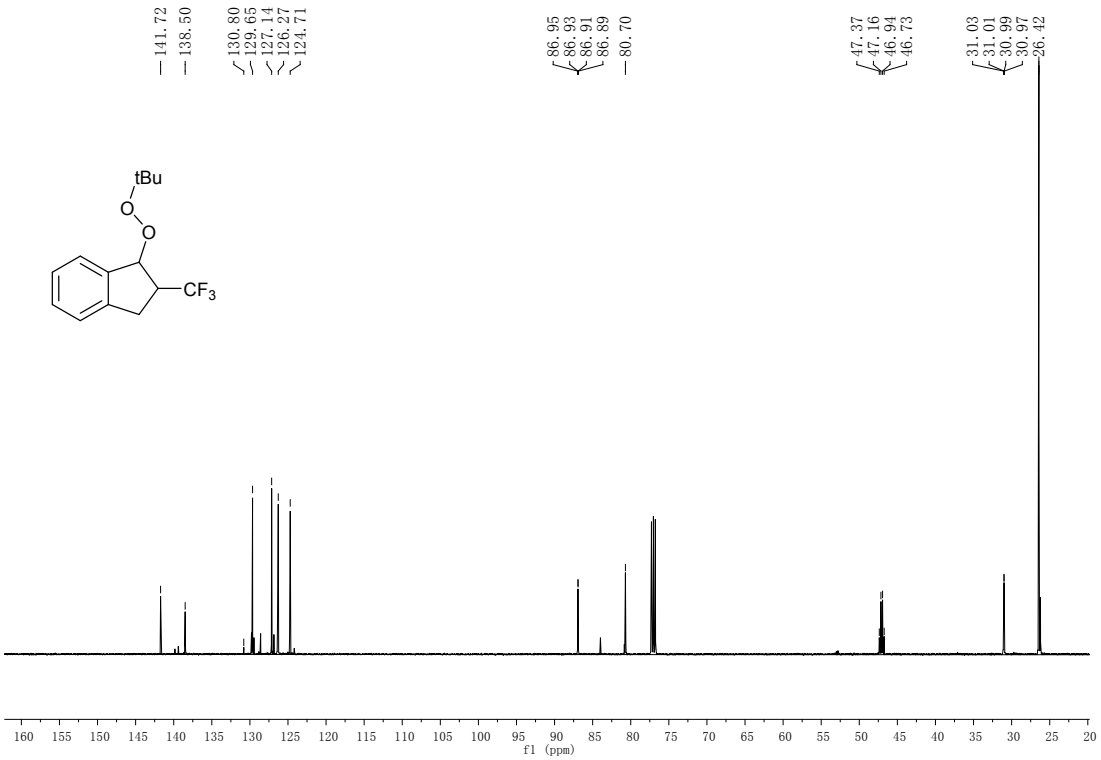
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47.16
46.94
46.73
31.03
31.01
30.99
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26.42
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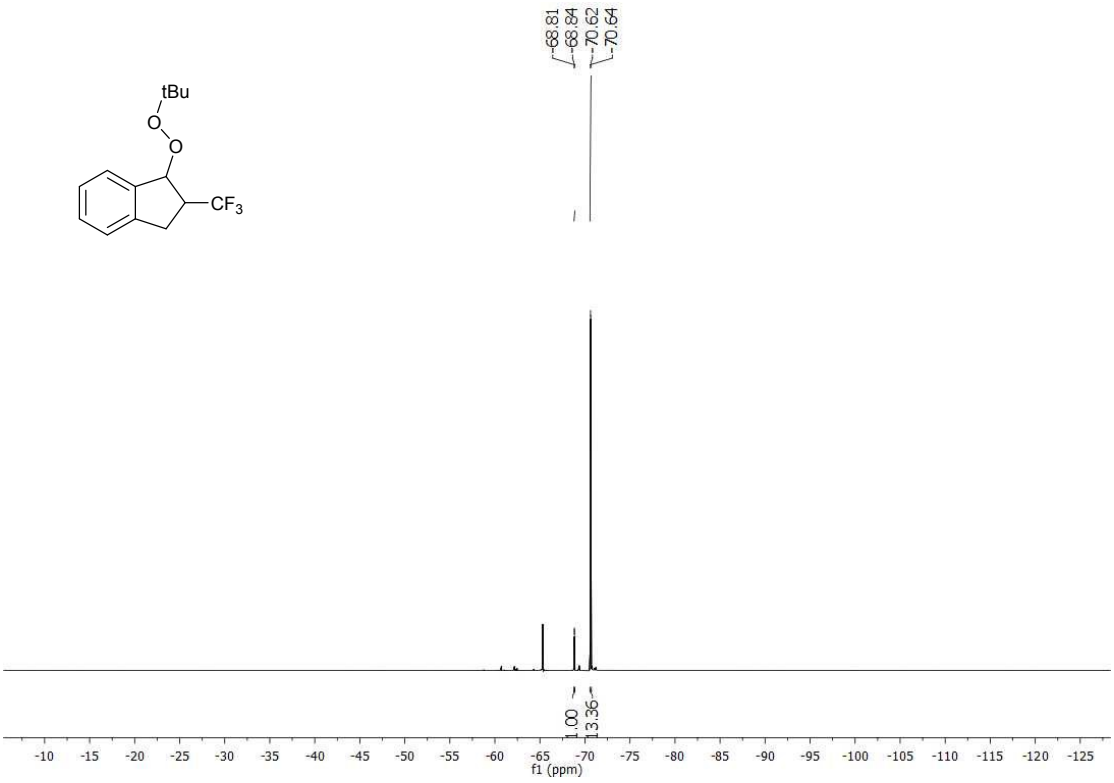
O
CF3
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)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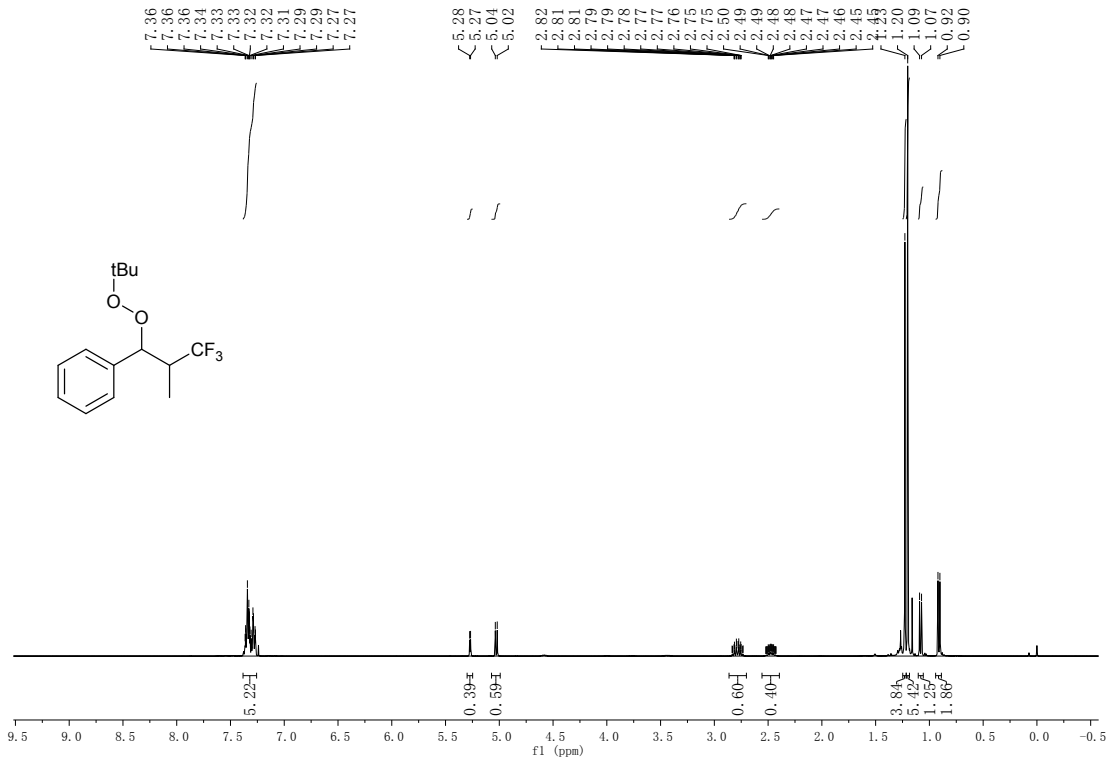
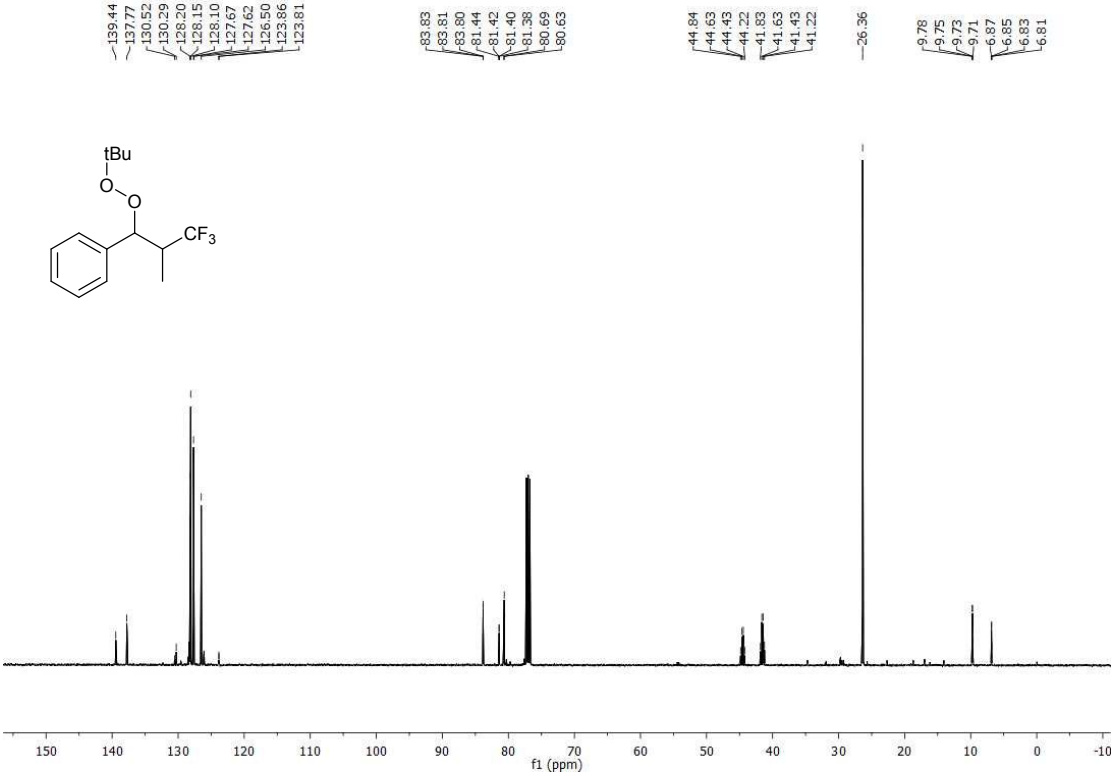
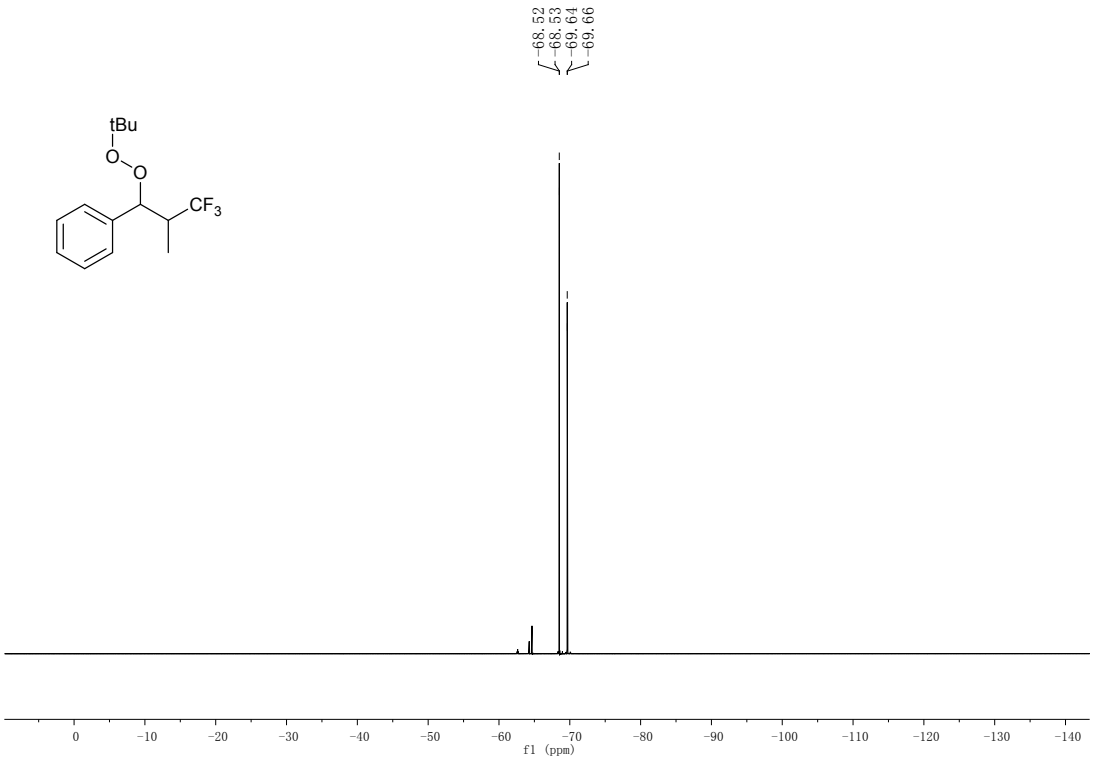
13.36
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

(1-(*tert*-butylperoxy)-3,3,3-trifluoro-2-methylpropyl)benzene (2m)







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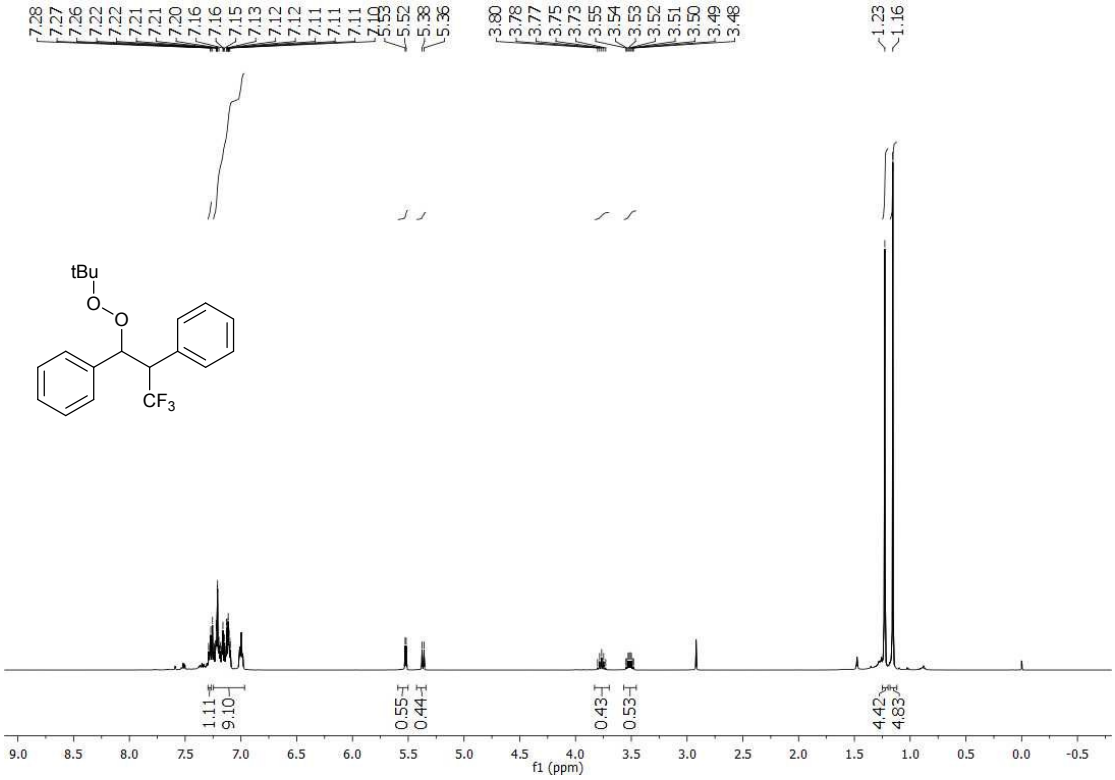

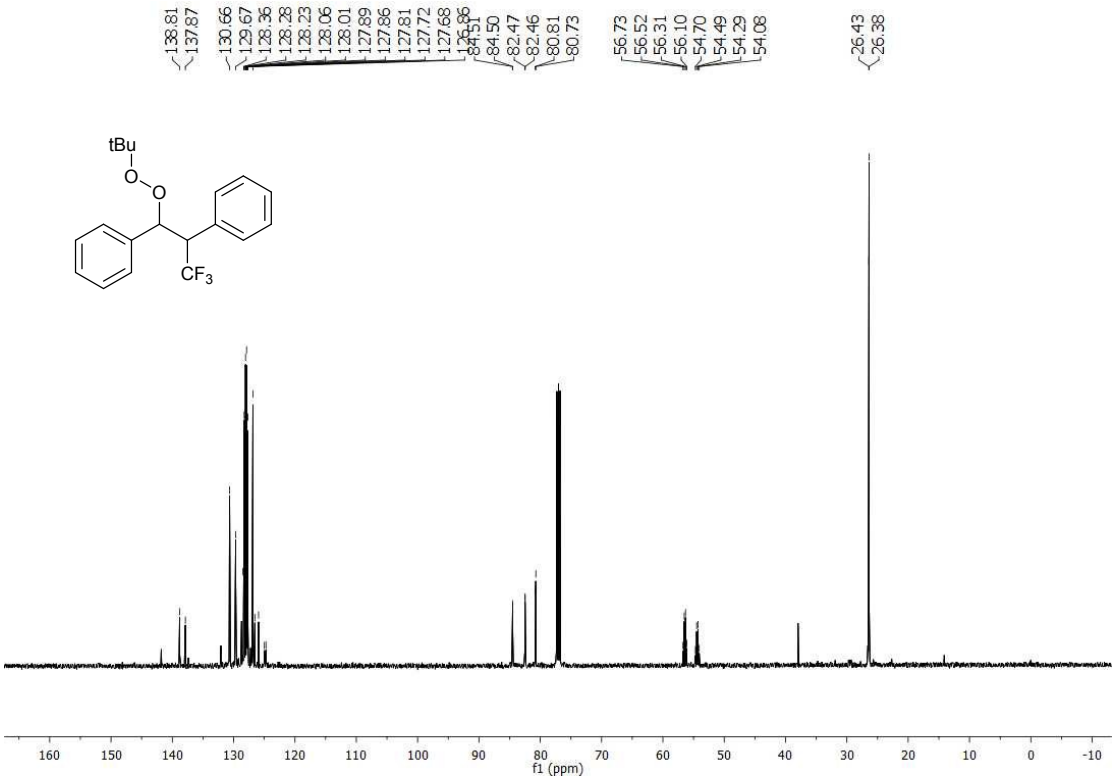
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tBu
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O
CF3
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10
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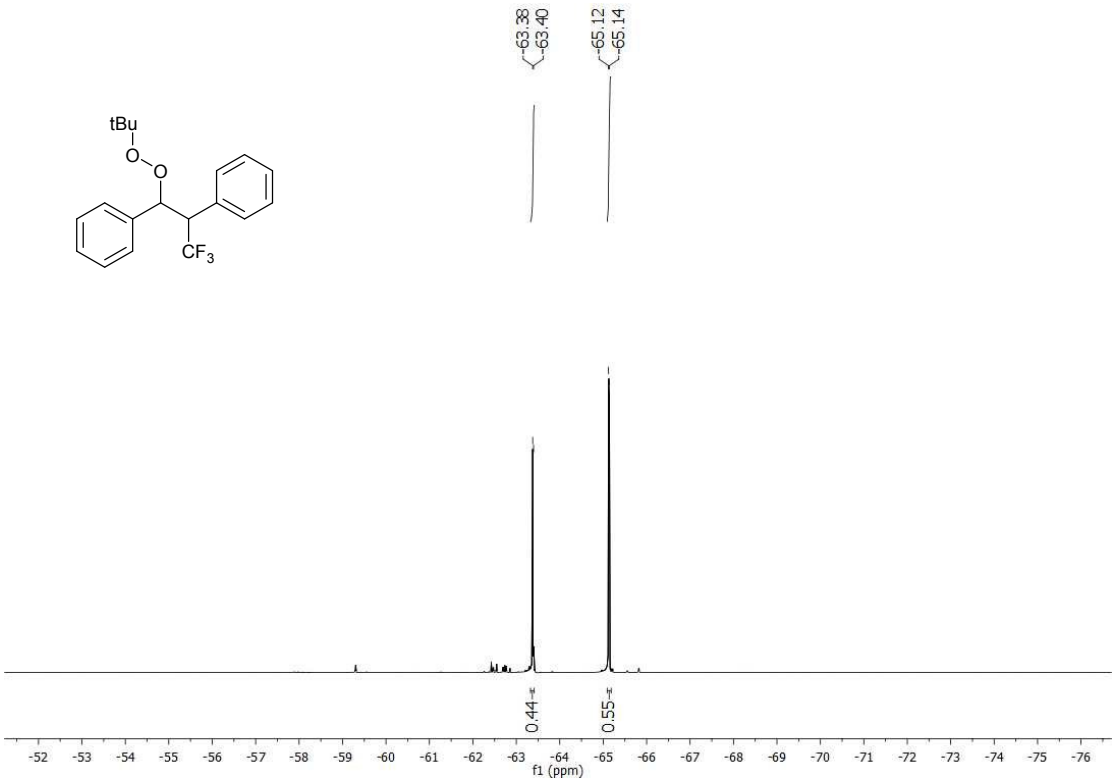
-10
f1 (ppm)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-56
-57
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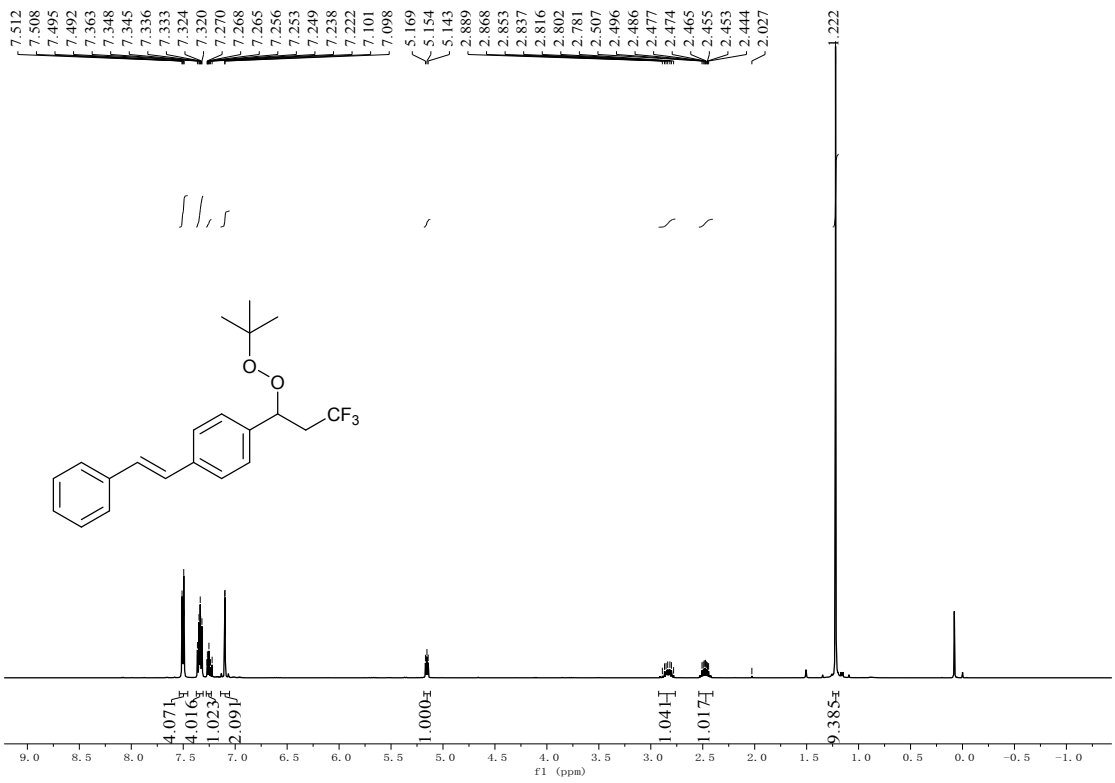
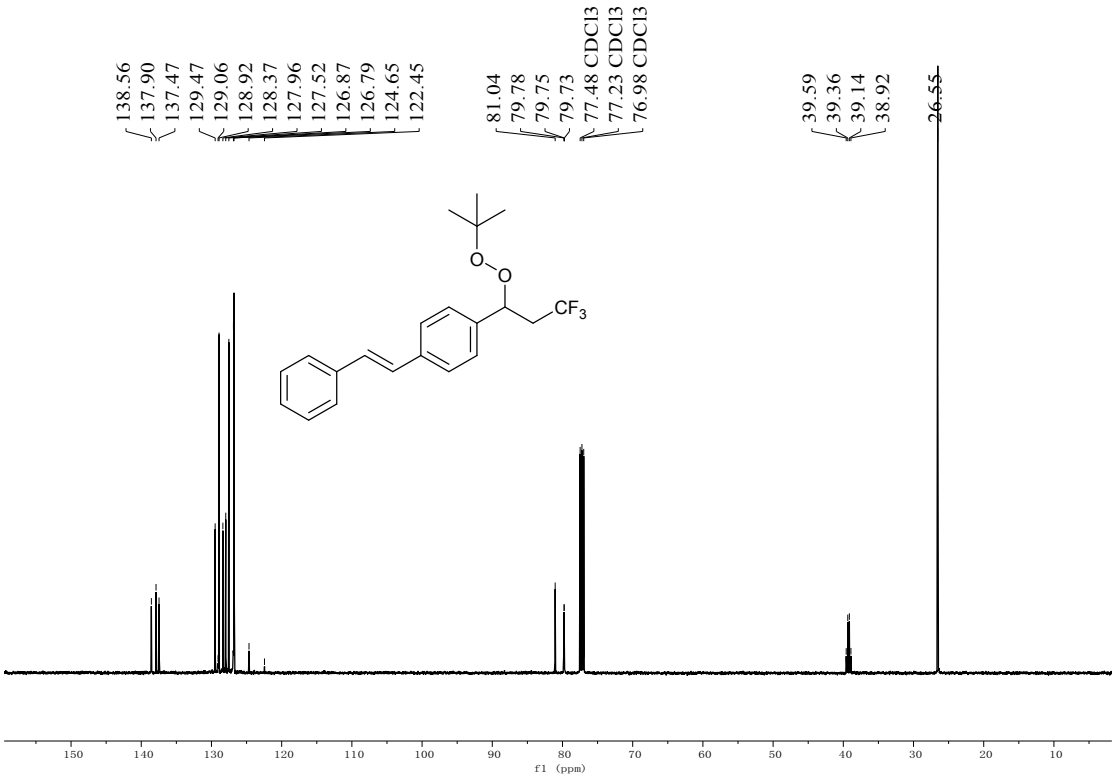
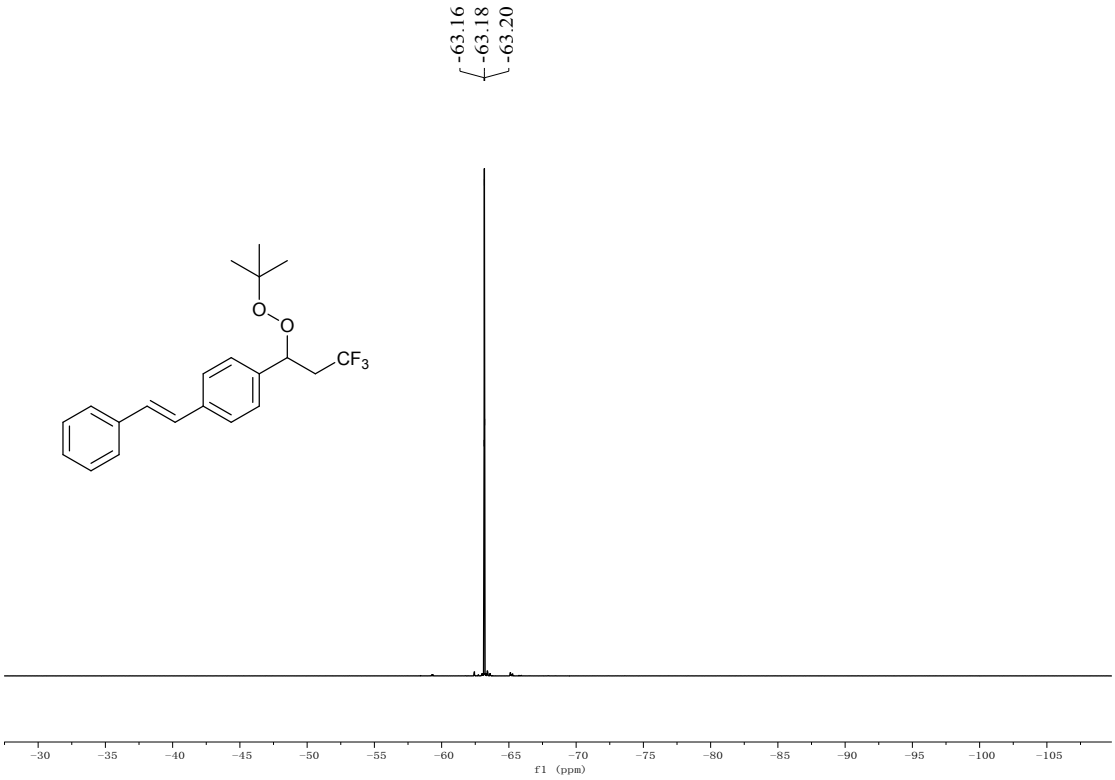
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
f1 (ppm)

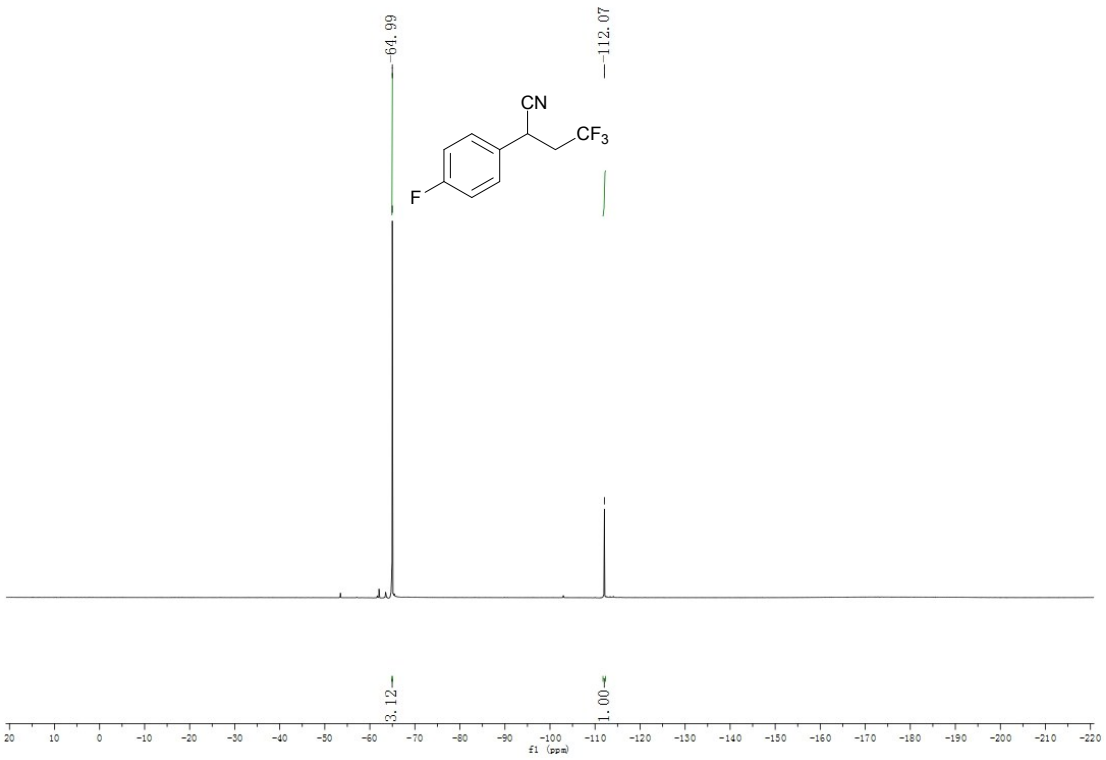
(*E*)-1-(1-(*tert*-butylperoxy)-3,3,3-trifluoropropyl)-4-styrylbenzene (2o)



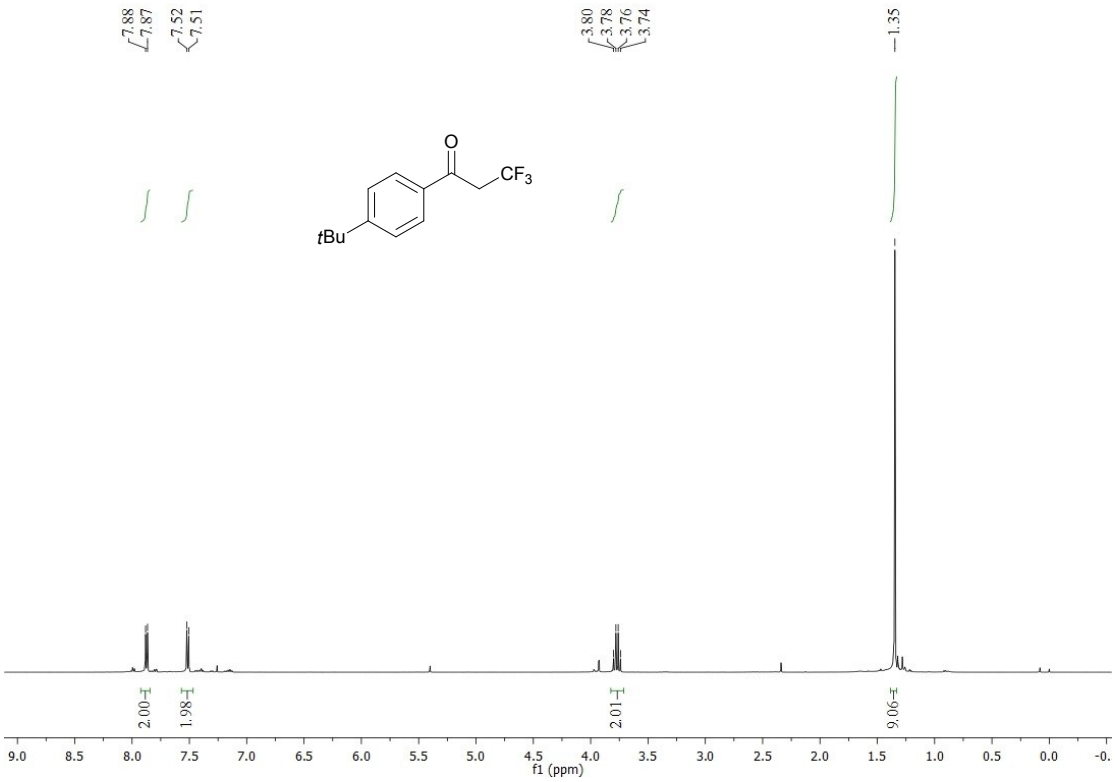


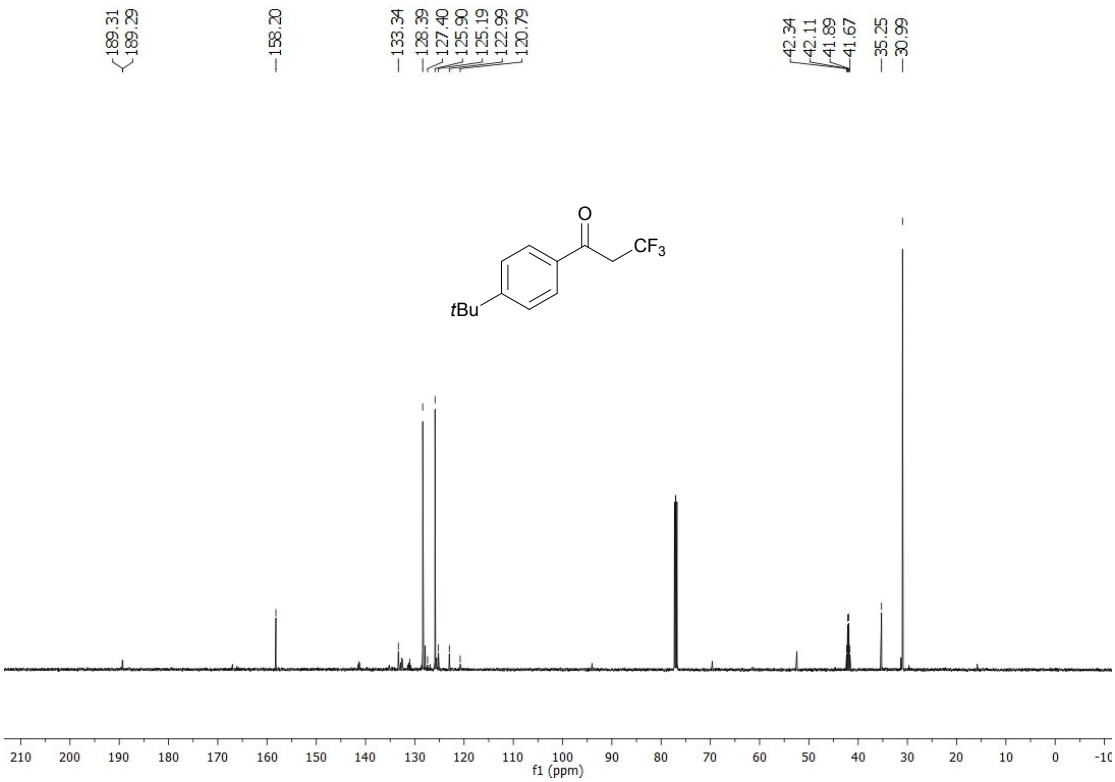


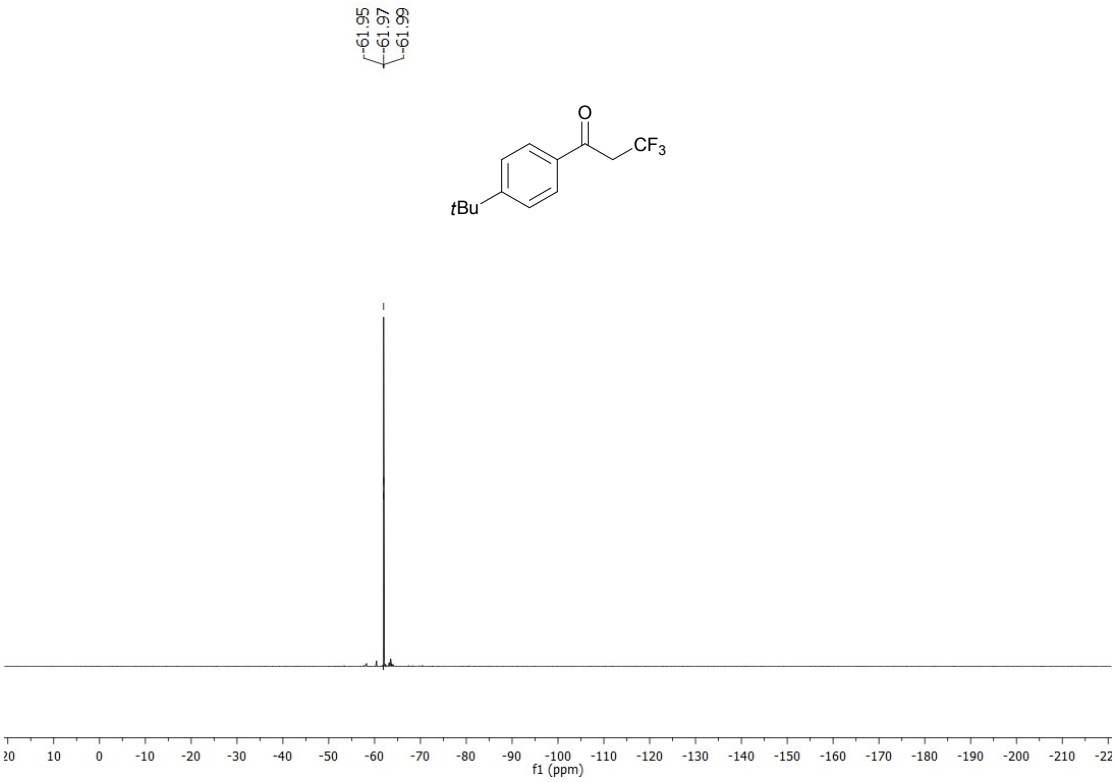
4,4,4-trifluoro-2-(4-fluorophenyl)butanenitrile (3)



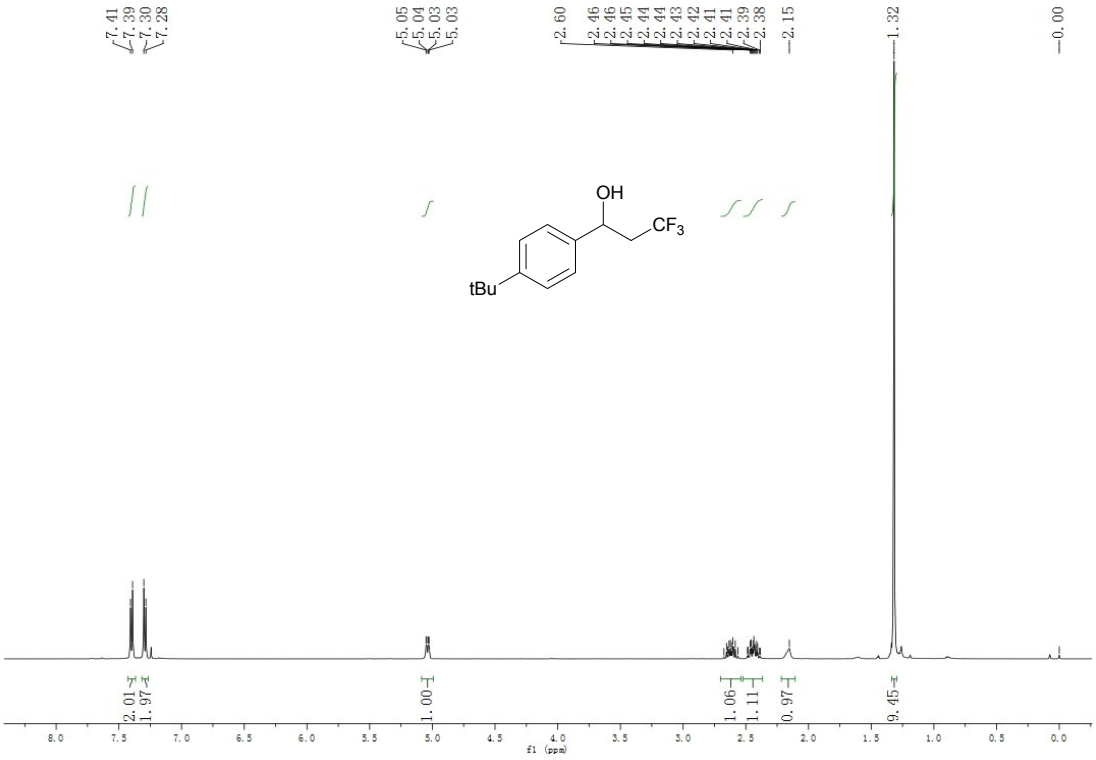
1-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoropropan-1-one (4)

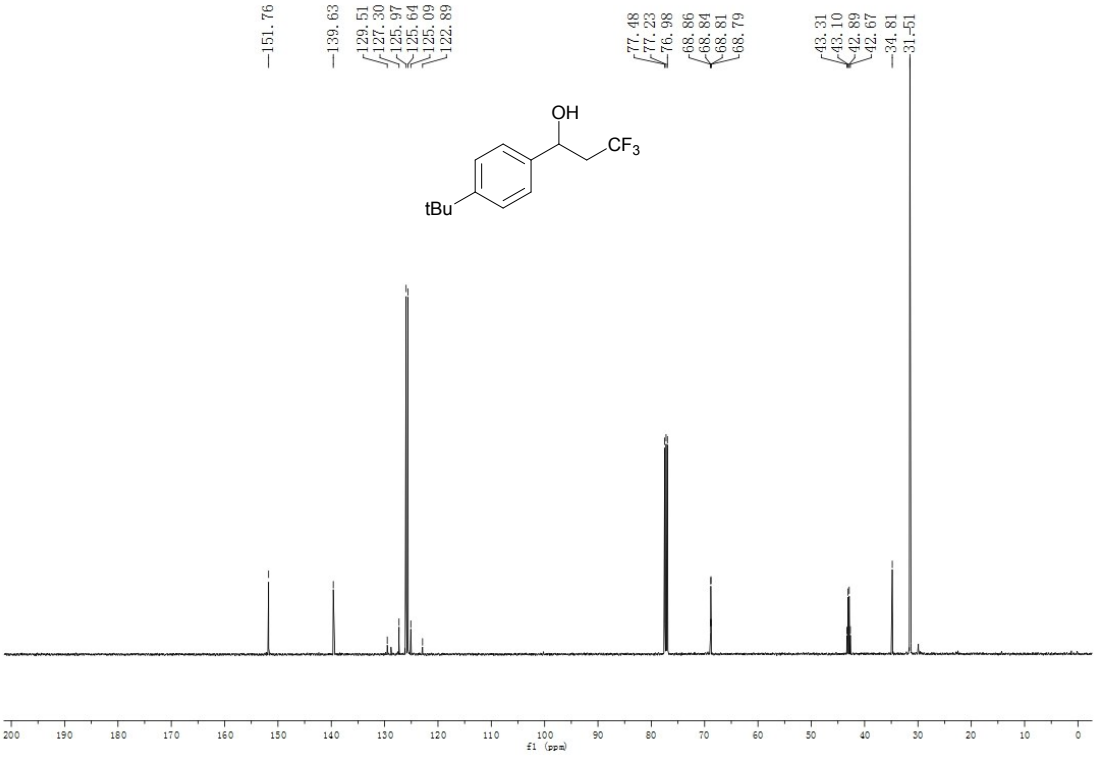



189.31
189.29
158.20
133.34
128.39
127.40
125.90
125.19
122.99
120.79
42.34
42.11
41.89
41.67
35.25
30.99
O
CF3
tBu
f1 (ppm)


-61.95
-61.97
-61.99
O
CF3
tBu
f1 (ppm)

1-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoropropan-1-ol (5)





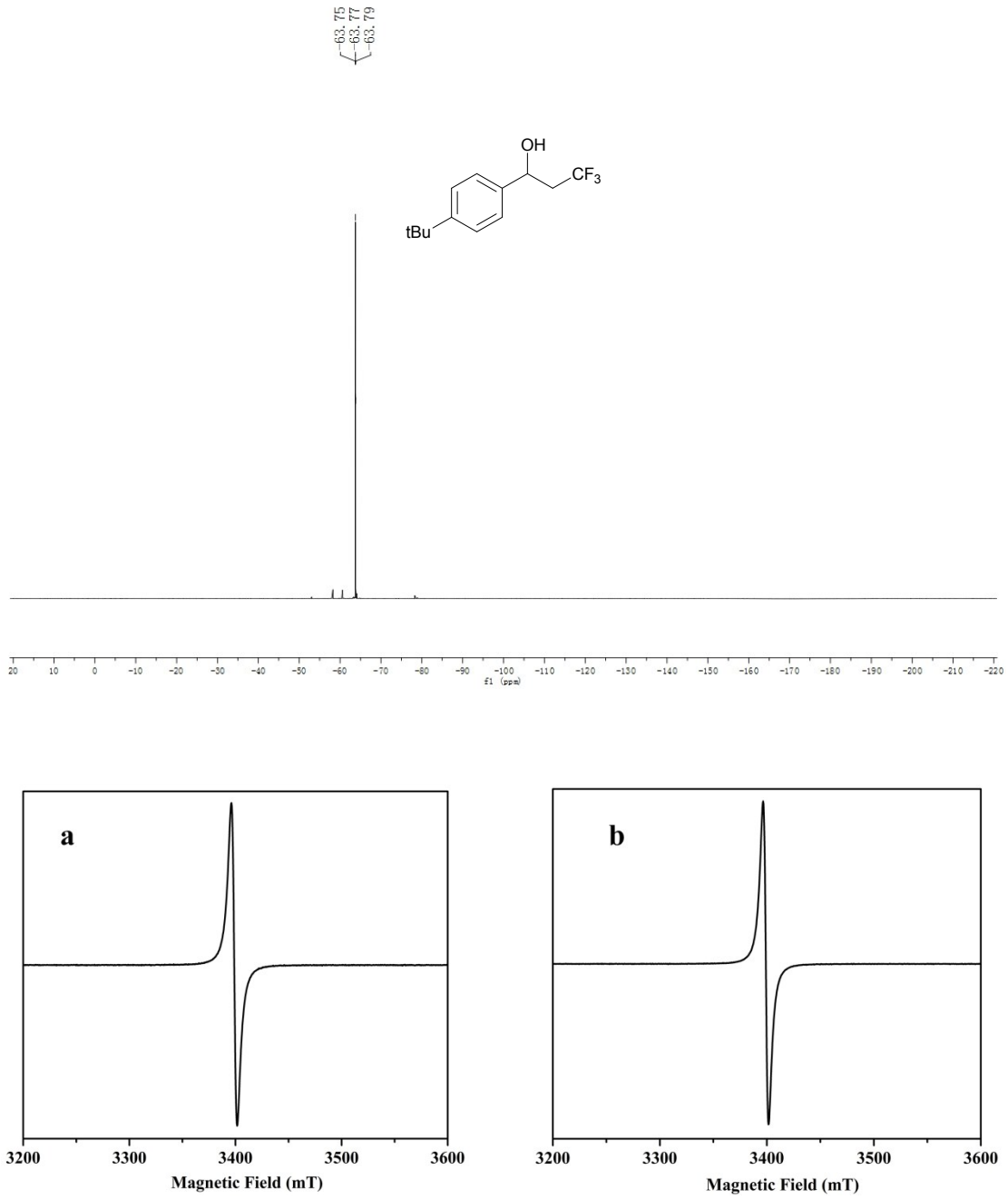
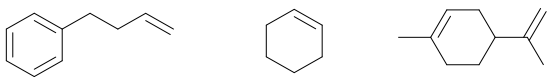


Figure S1. EPR Spectra of TEMPO (a) before reaction (g = 2.0544) and (b) a recovery after reaction (g = 2.0547). Reaction condition: 2.4 mmol TEMPO was added to the suspension of 0.02 mmol Cu_3(**BTC**)$_2$ in 2 mL of anhydrous CH_3CN and the reaction mixture was stirred under 60 ^oC. After 24 hrs, the Cu_3(**BTC**)$_2$ was removed out through centrifugation and TEMPO was recovered by evaporating the solvent. EPR spectra were applied to TEMPO before reaction and after reaction. The same g value suggested that the TEMPO was functionally compatible with the Cu_3(**BTC**)$_2$ during this procedure.



1o 4-Phenyl-1-butene

1p cyclohexene

1q (±)-limonene

Figure S2. Substrates with negligible conversions.