Supporting Information

Silver-promoted oxidative sulfonylation and ring-expansion of vinylcyclopropanes with sodium sulfinates leading to dihydronaphthalene derivatives

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[†] These authors contributed equally to this work

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1. General Information

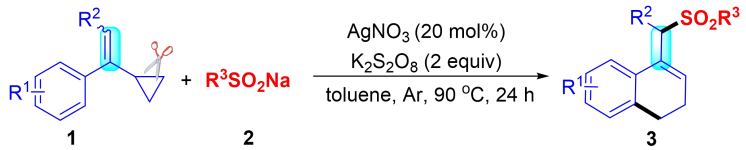
Unless otherwise stated, all commercial reagents were used as received. Potassium persulfate (MERYER, 99%), sodium trifluoromethanesulfinate (Ark Pharm, 95%), aldehydes (Innochem, >98%) and ketones (Innochem, >98%) were used without further treatment. All reagents and solvents were commercially available and used without any further purification unless specified. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (0.25mm, 300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25mm 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). All reactions were carried out with magnetic stirring and in dried glassware.Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quated in Hz. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, for ^{13}C NMR: $CDCl_3$ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experiment Section

2.1 General Procedure for the Synthesis of vinylcyclopropanes (1):

All vinylcyclopropanes **1** were synthesized according to the known methods.[1]

2.2 Typical Experimental Procedure for the Synthesis of 1-Sulfonylmethylated 3,4-Dihydronaphthalenes.



1 2 3

To a Schlenk tube were added vinylcyclopropanes **1** (0.2 mmol, 0.1 M), organosulfinates **2** (0.4 mmol, 2 equiv), $AgNO_3$ (6.8 mg, 20 mol%), $K_2S_2O_8$ (108.1

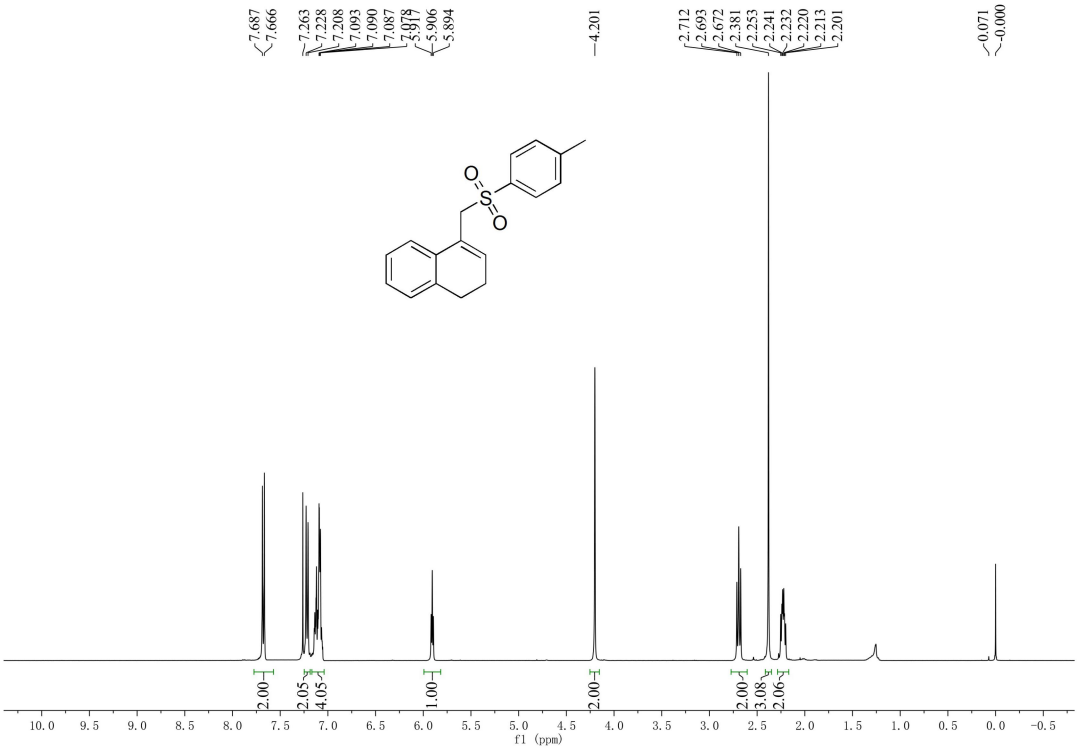
mg, 2 equiv) and toluene (2 mL). Then the tube was stirred at 90 °C (oil bath temperature) in argon atmosphere for 24 hour until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered, organic layer was dried over Na_2SO_4. Then removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 10 : 1) to provide the desired products **3**. A scaled-up experiment was carried in the presence of VCP **1a** (1 g, 6.94 mmol), sodium *p*-tolylsulfinate **2a** (13.86 mmol, 2 equiv), $AgNO_3$ (235.4 mg, 20 mol%), $K_2S_2O_8$ (3.75 g, 2 equiv) and toluene (40 mL) at 90 °C under argon atmosphere for 72 h successfully afforded the desired product **3aa** in 63% yield (1301.5 mg).

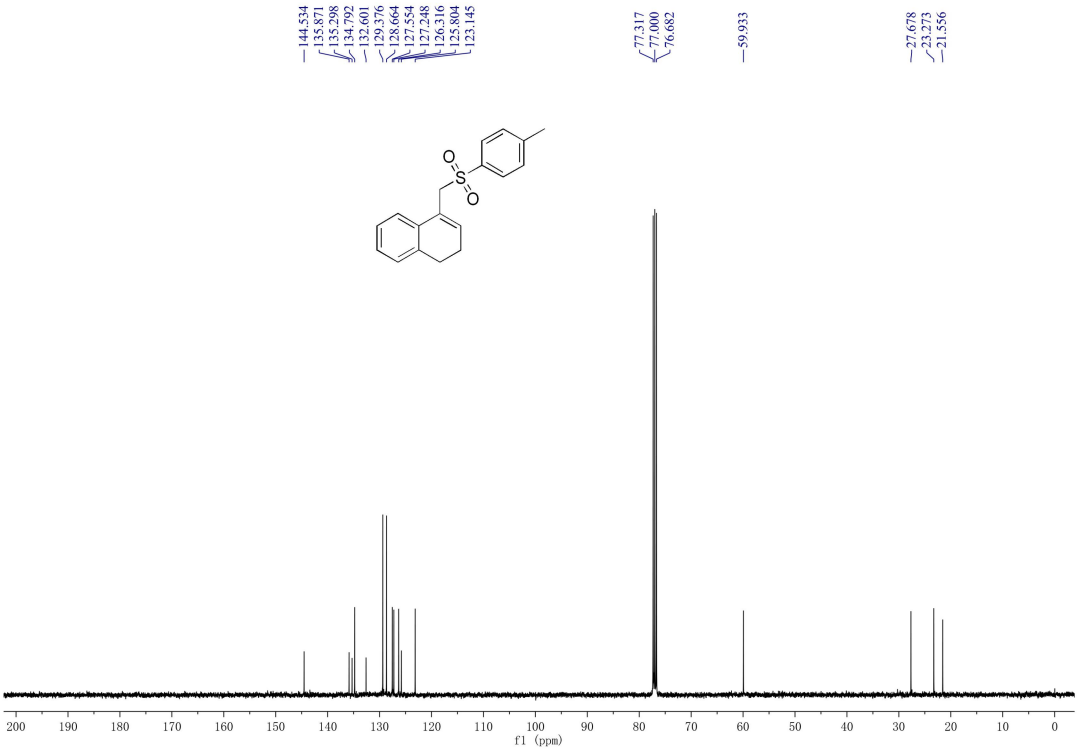
3. References

[1] J. Li, J.-Z. Chen, W. Jiao, G.-Q. Wang, Y. Li, X. Cheng and G.-G. Li, *J. Org. Chem.* **2016**, *81*, 9992-10001.

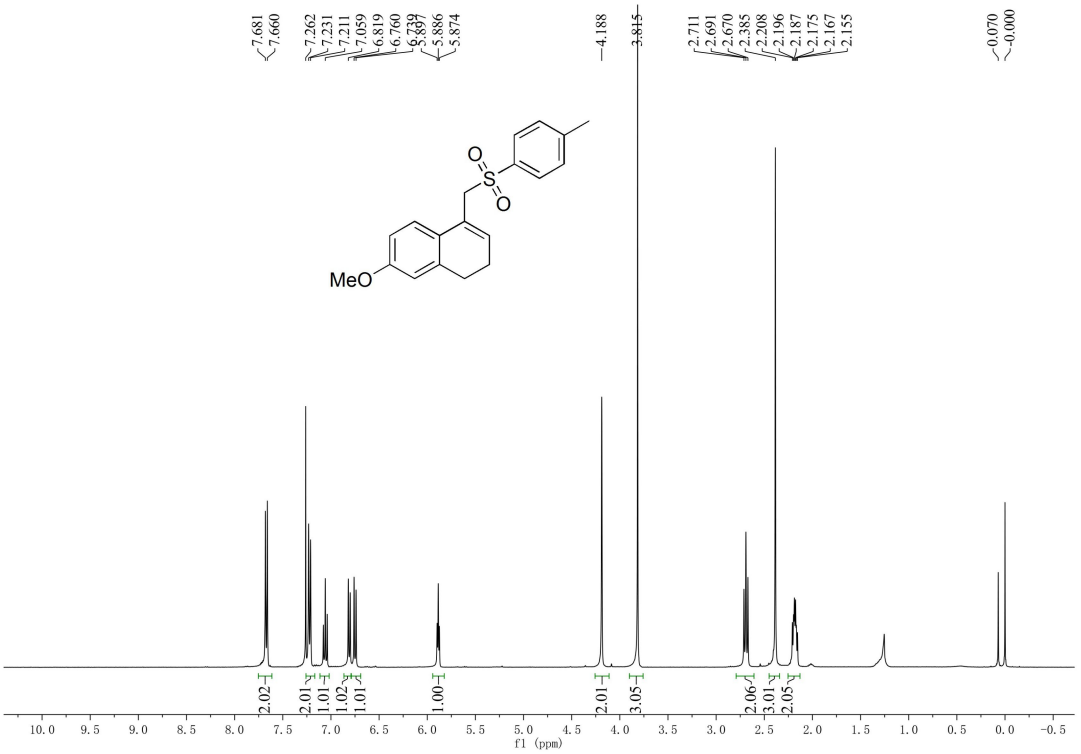
4. Spectra

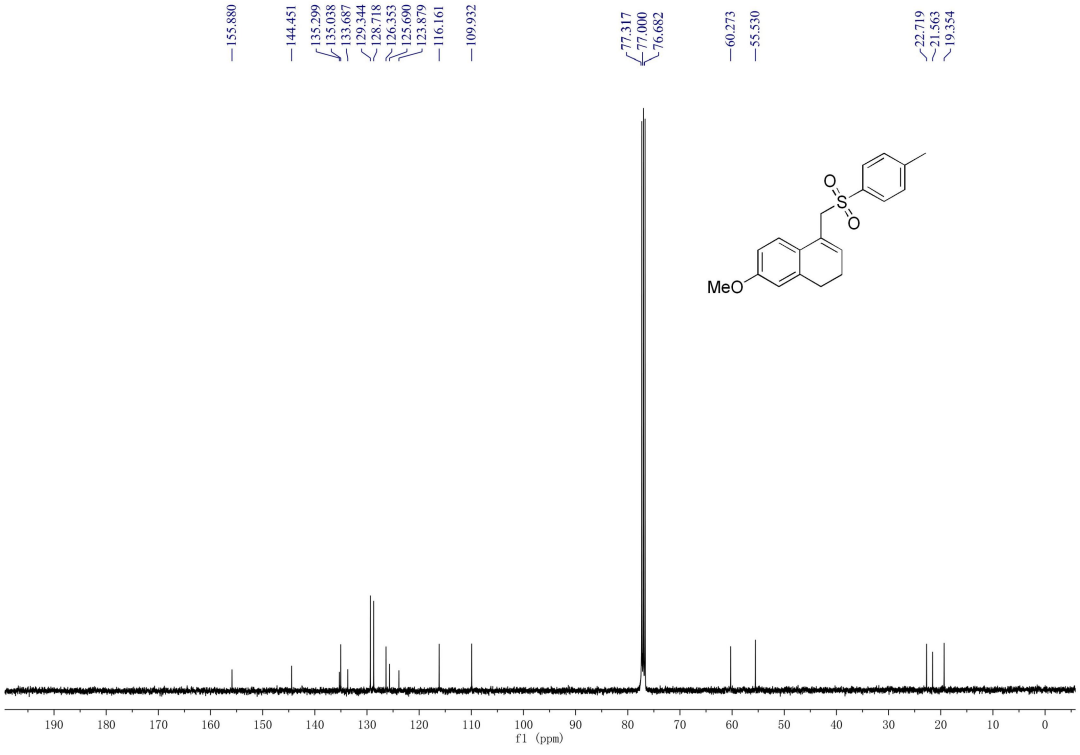
4-(Tosylmethyl)-1,2-dihydronaphthalene (3aa)





7-Methoxy-4-(tosylmethyl)-1,2-dihydronaphthalene (3ba)





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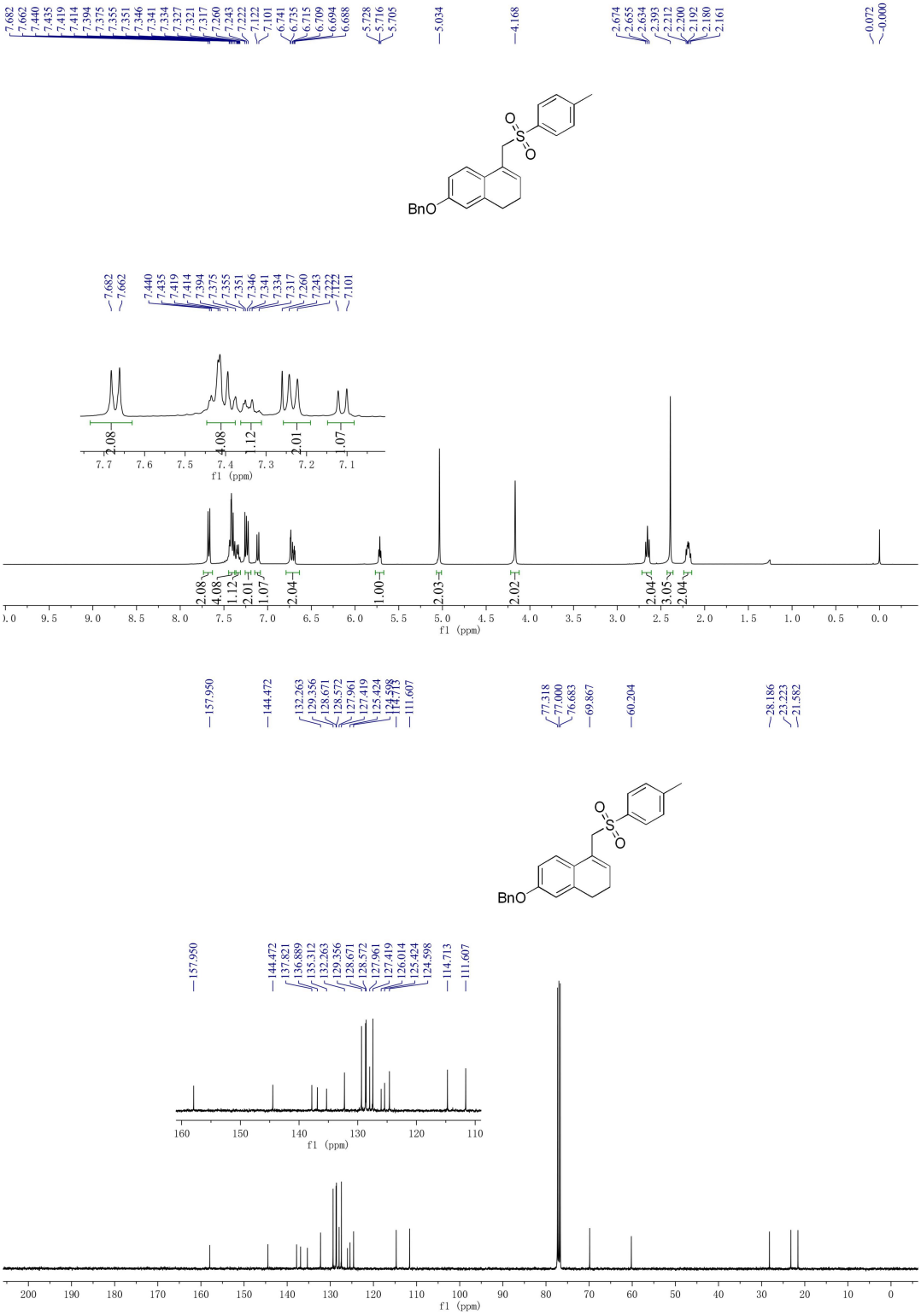

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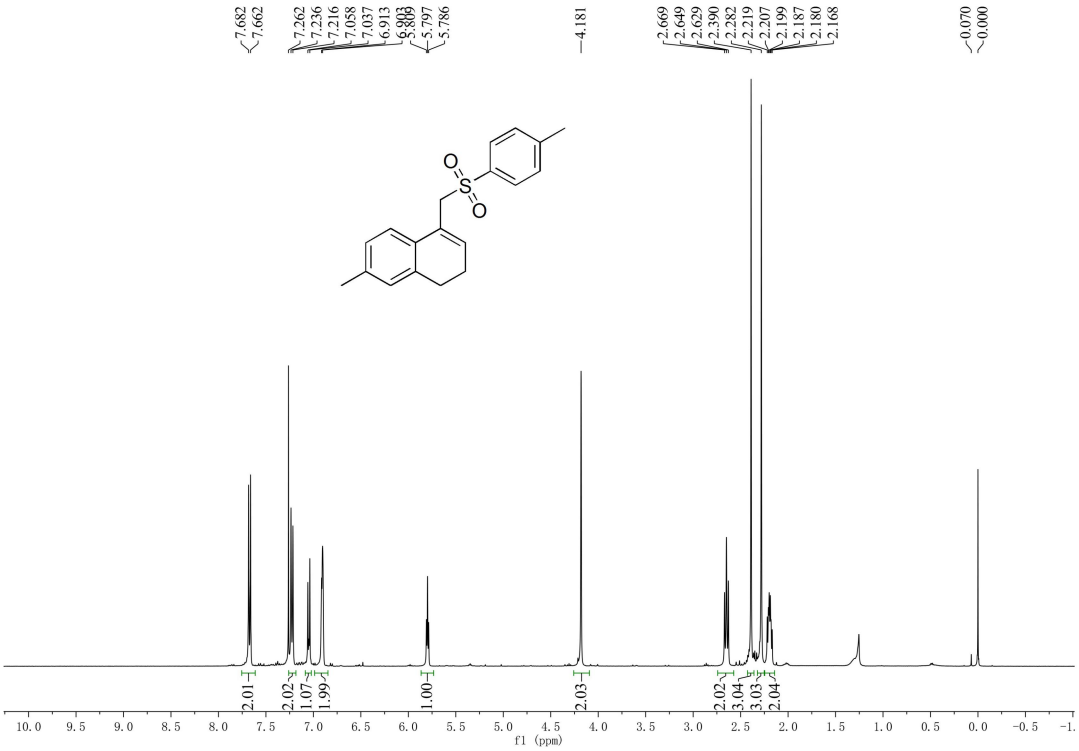

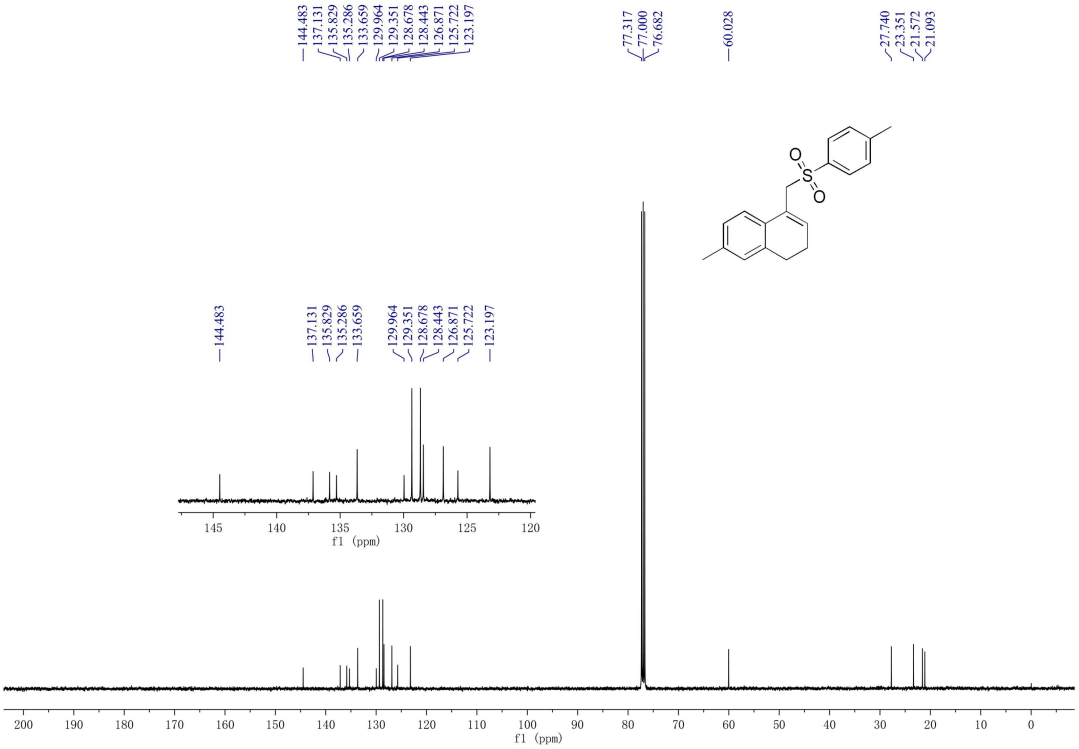

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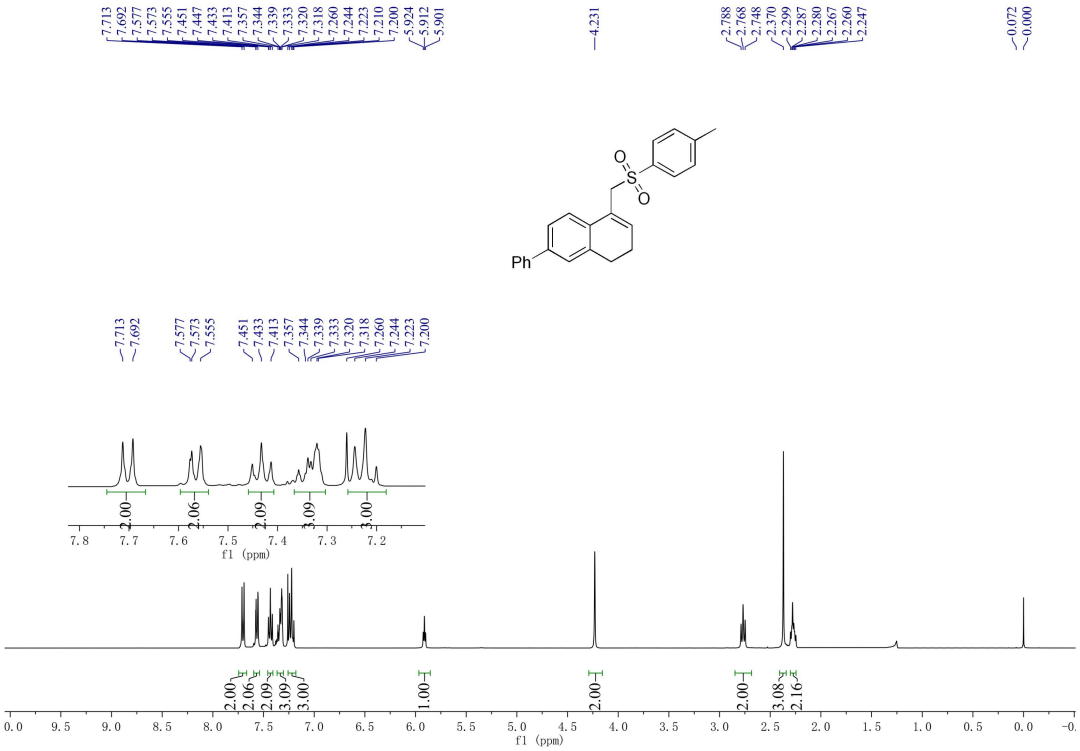

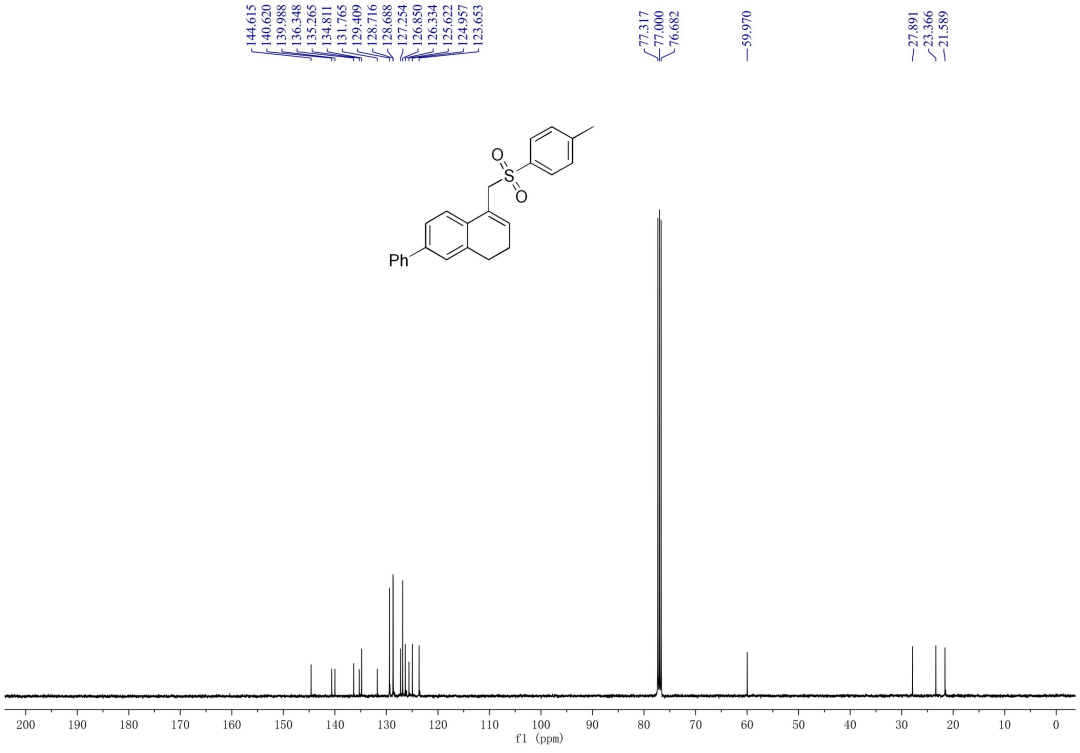

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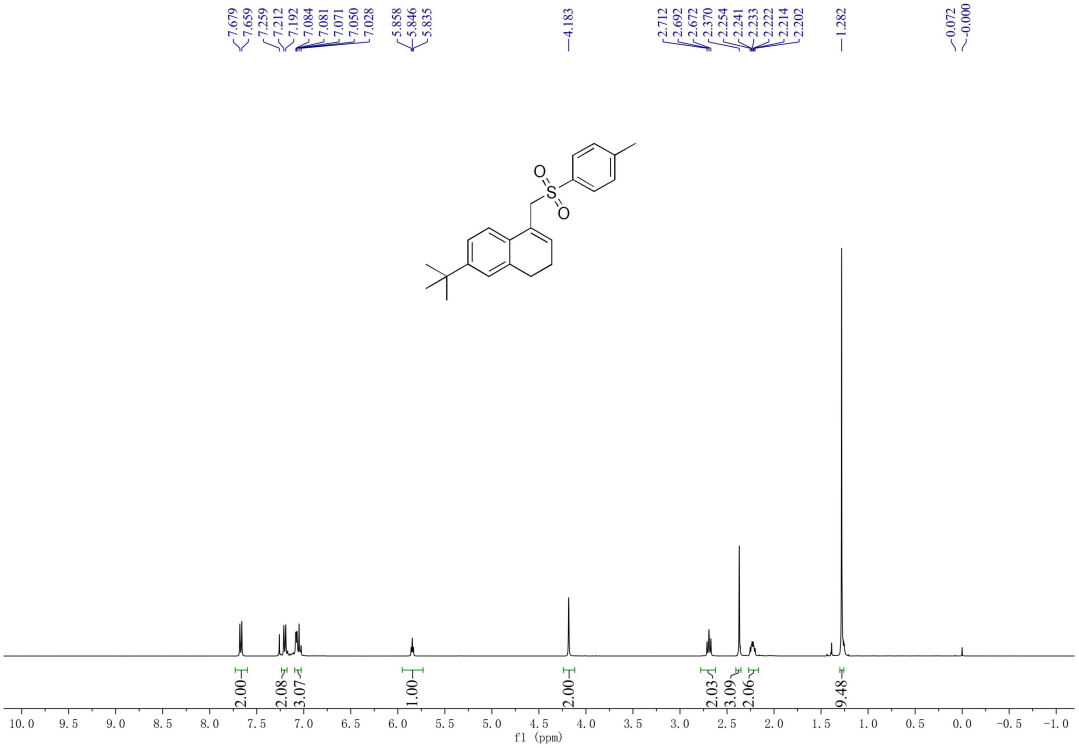

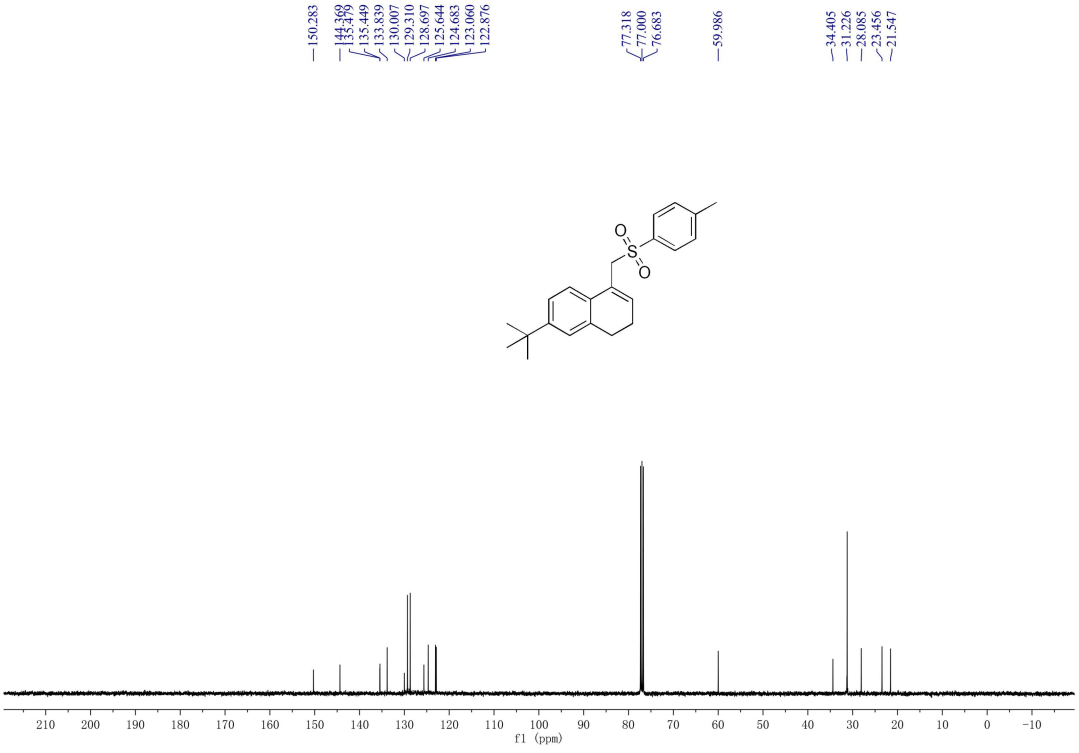

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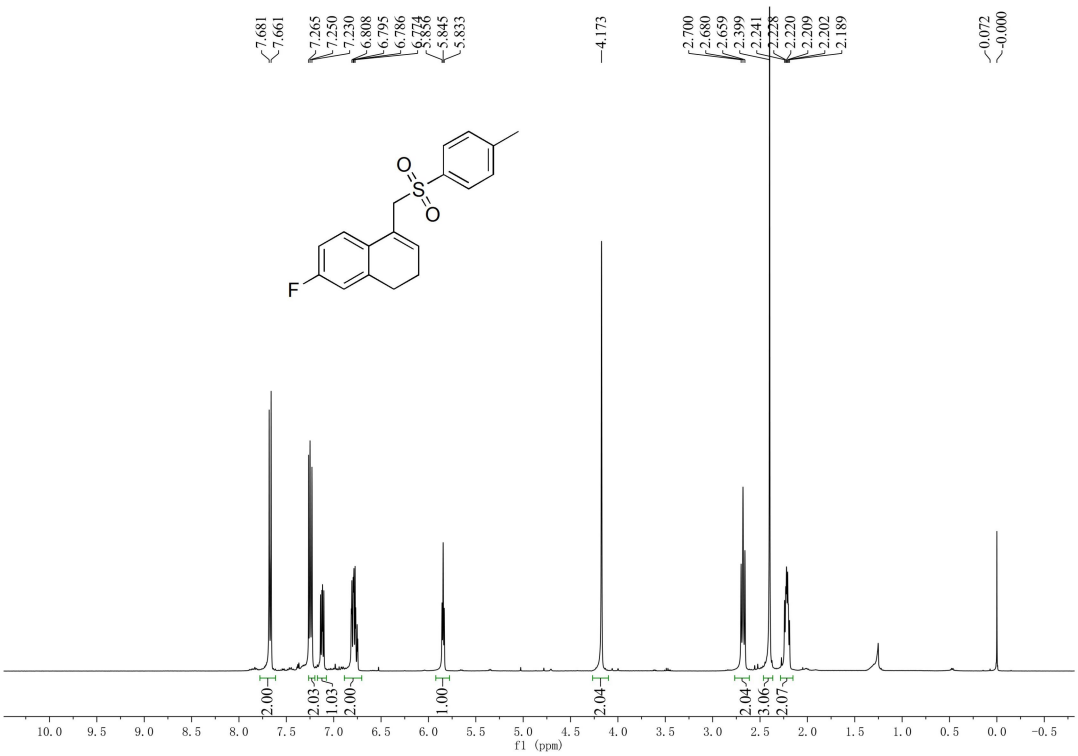

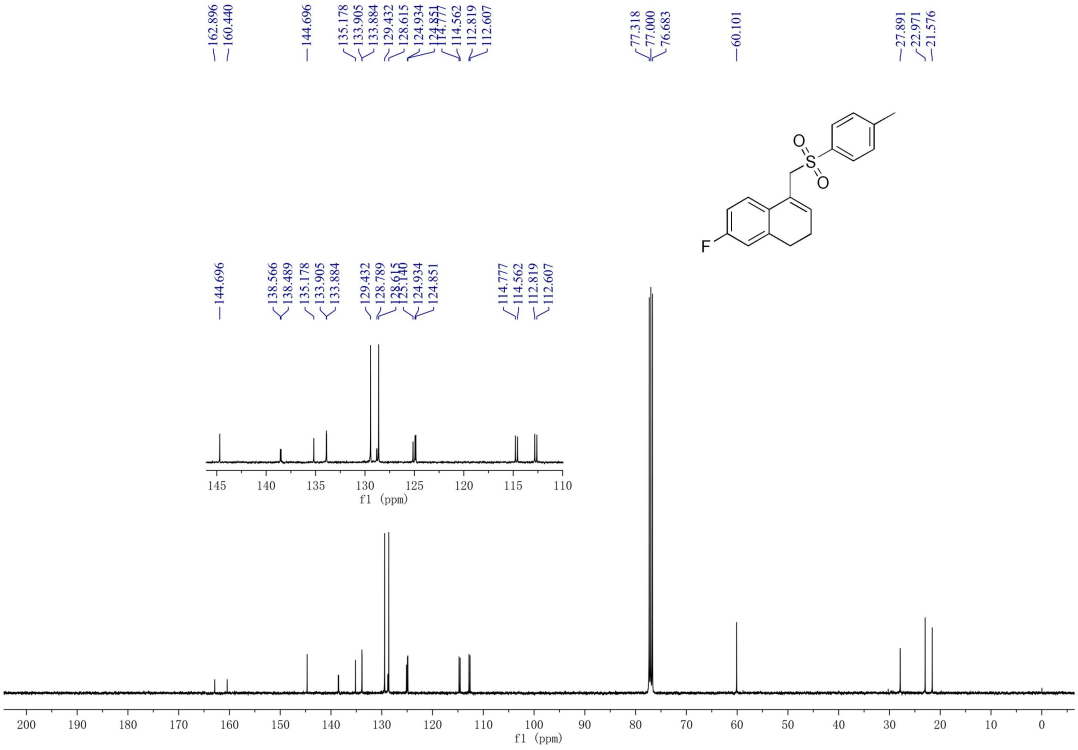

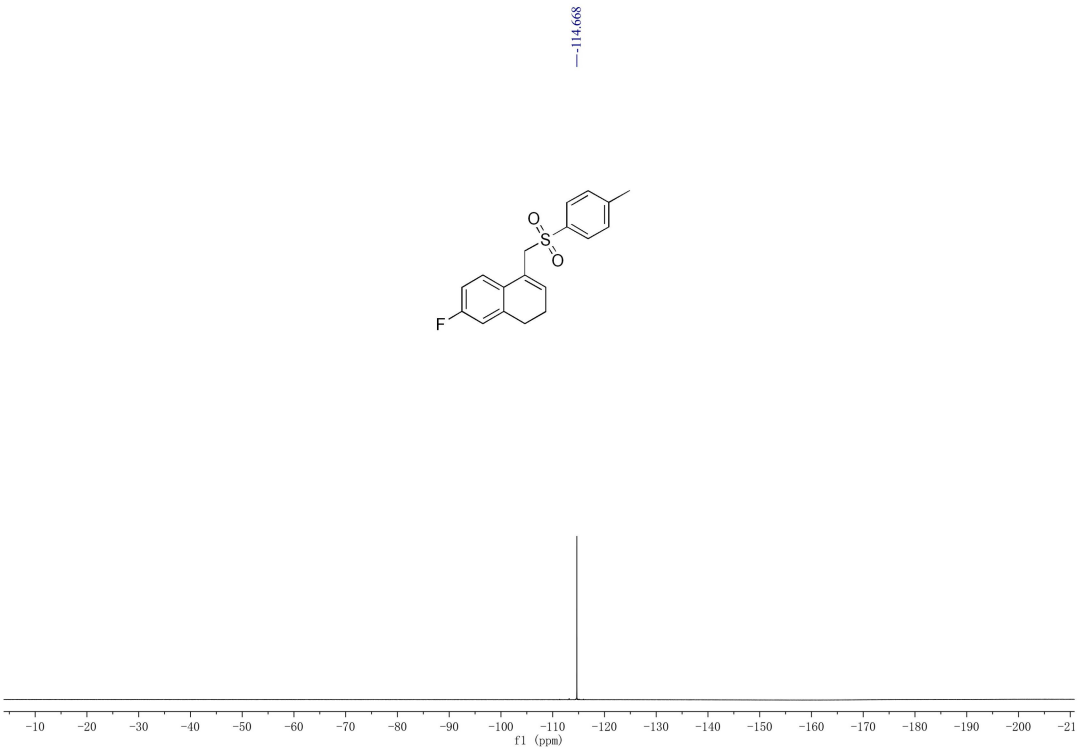
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S
O
F
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-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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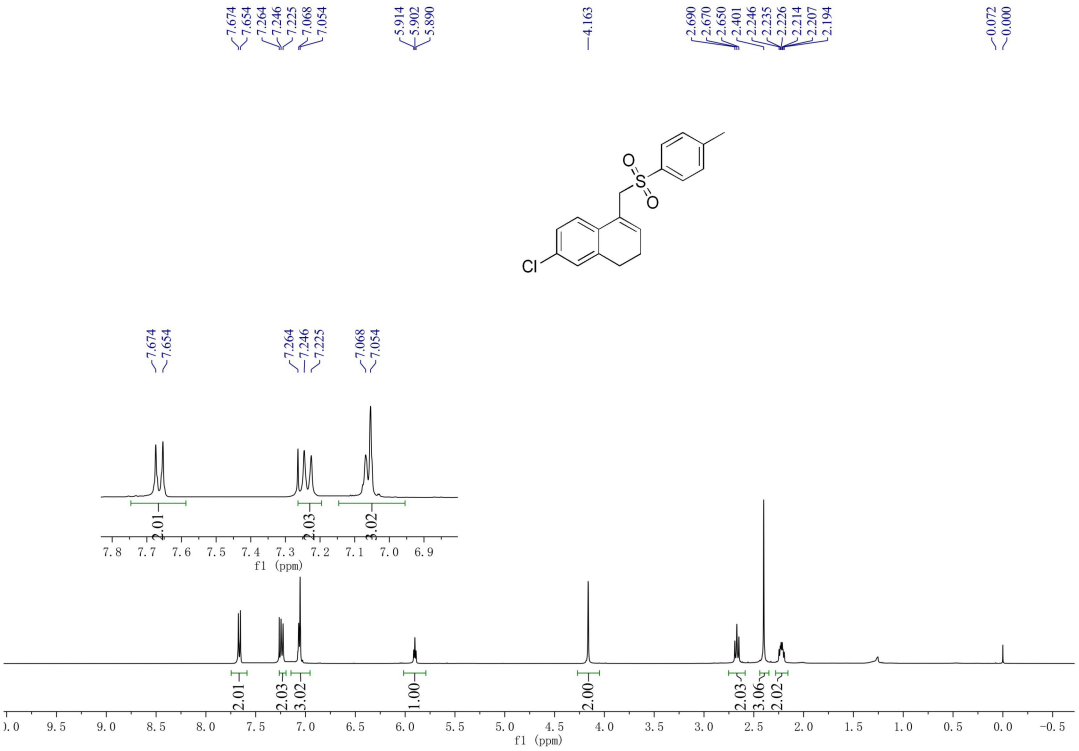
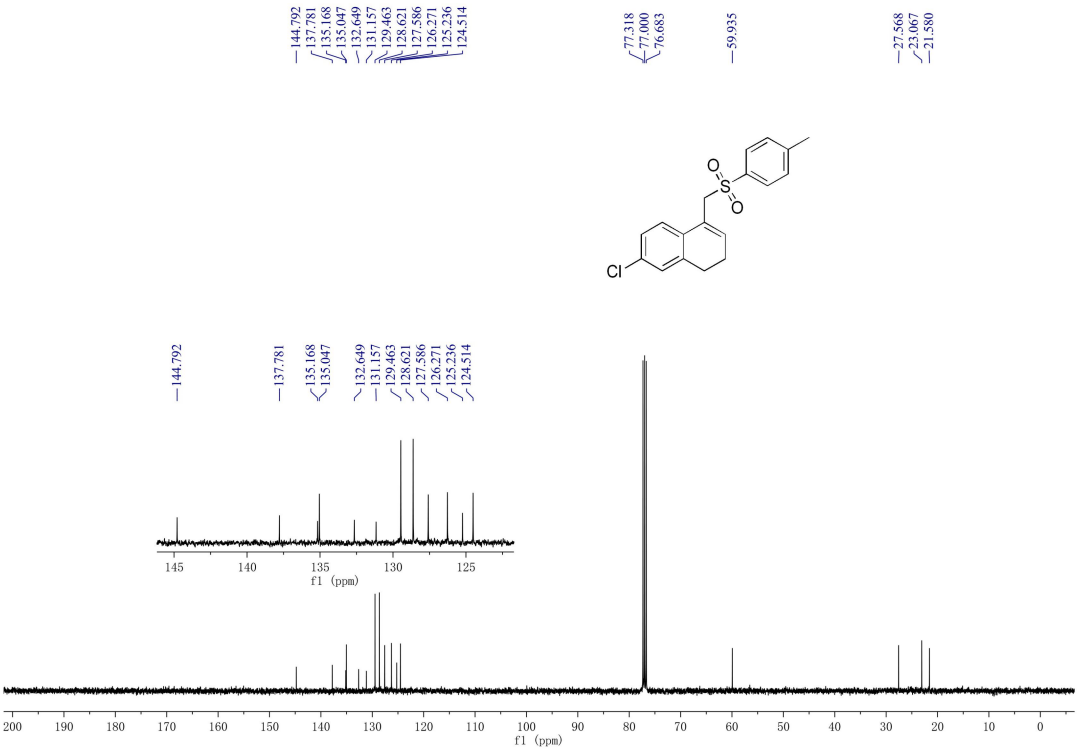
-180
-190
-200
-21
f1 (ppm)

7-Chloro-4-(tosylmethyl)-1,2-dihydronaphthalene (3ha)





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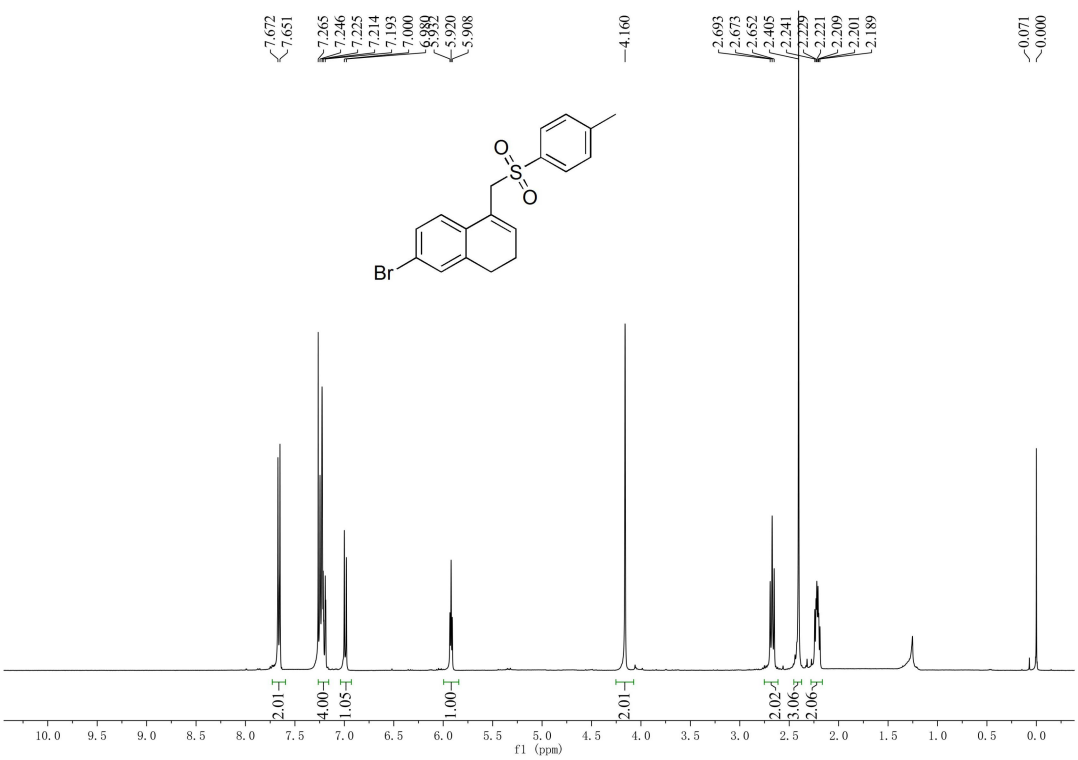

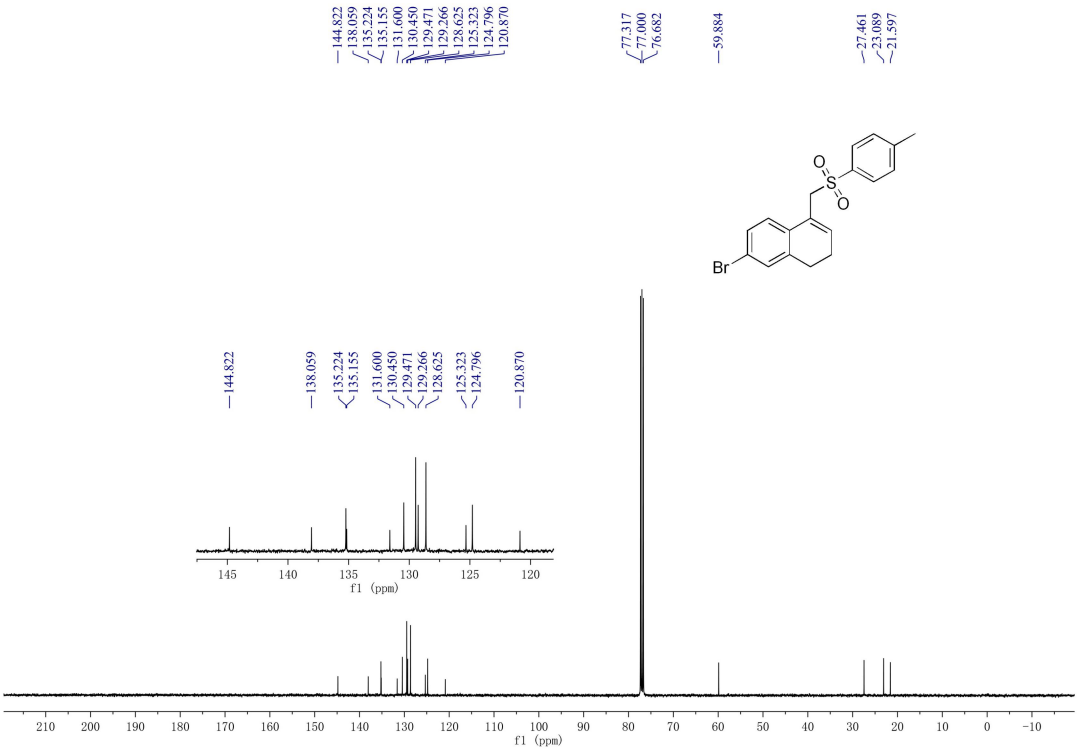

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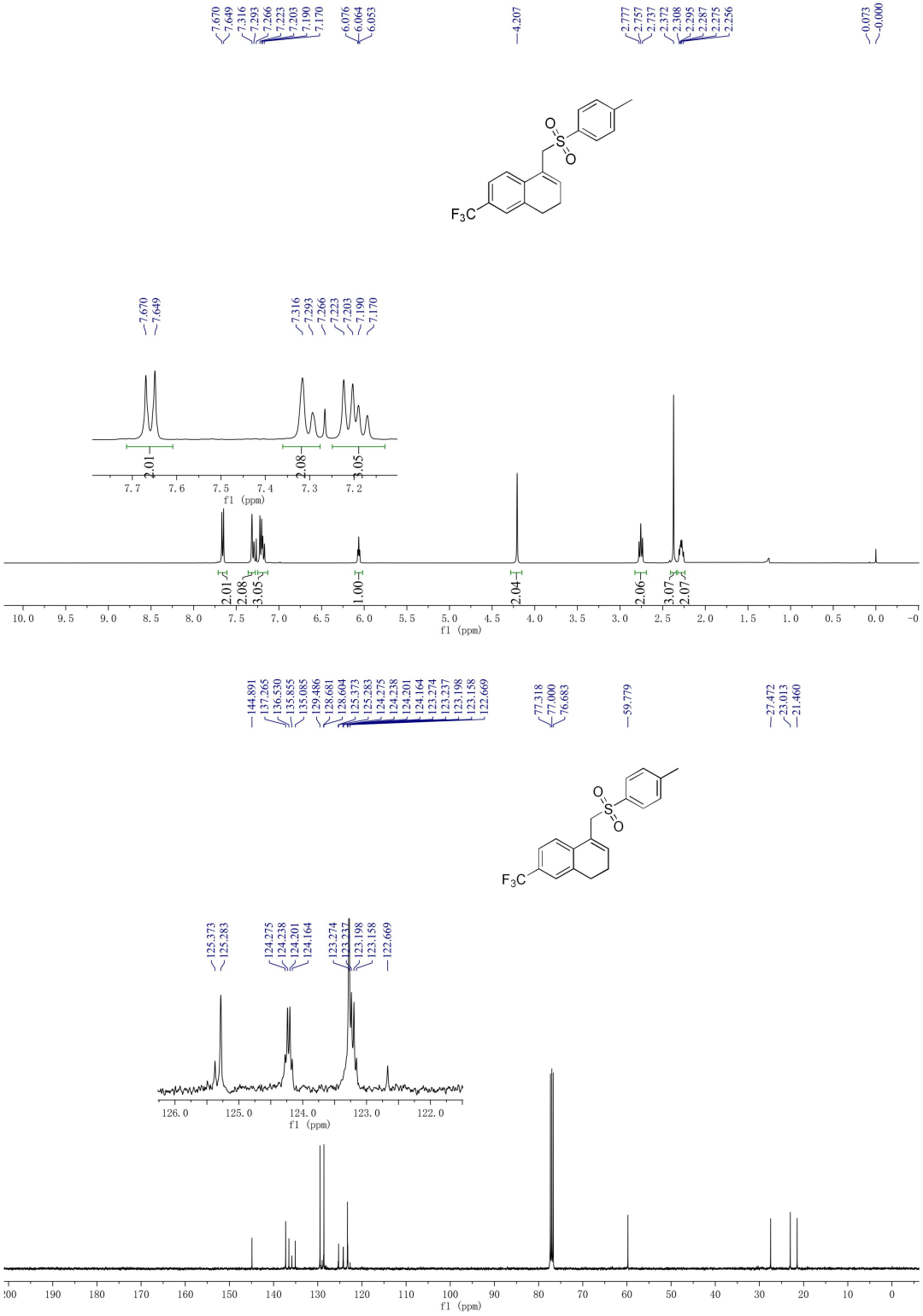

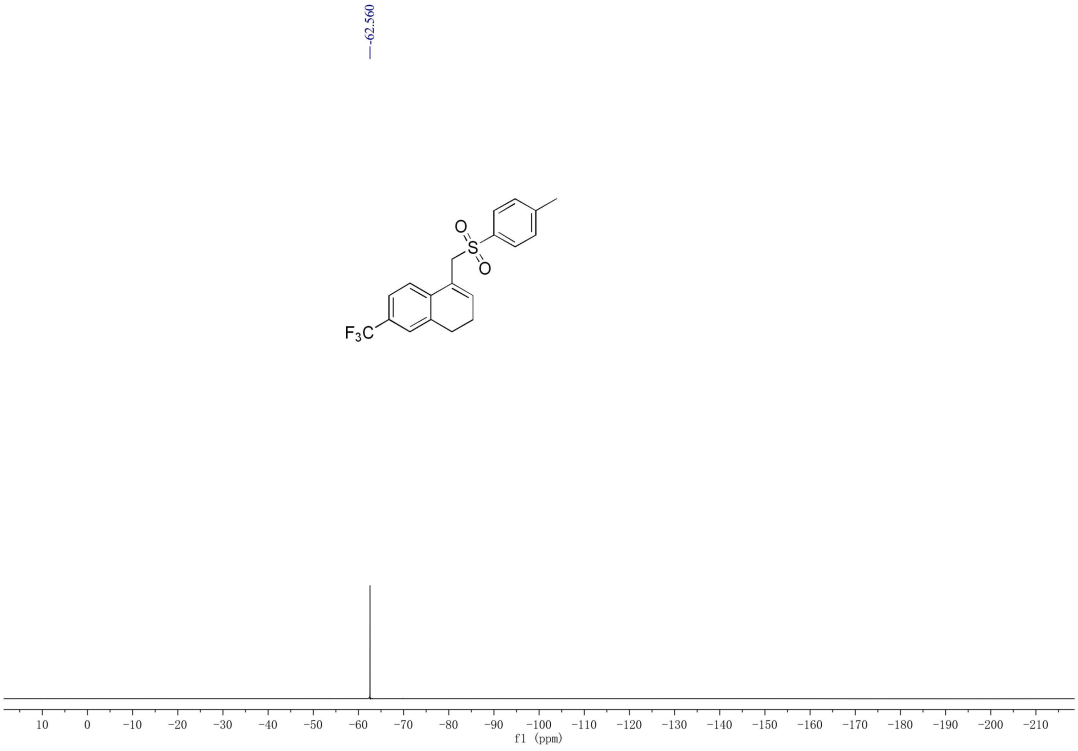
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F3C
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-110
-120
-130
-140
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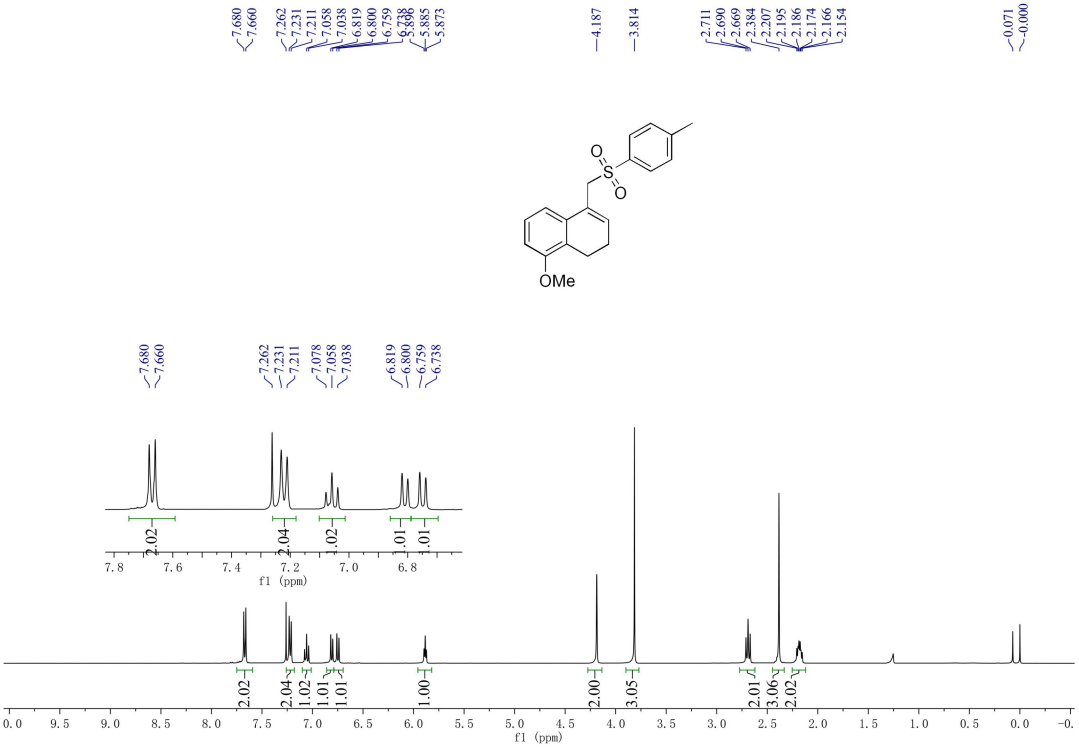
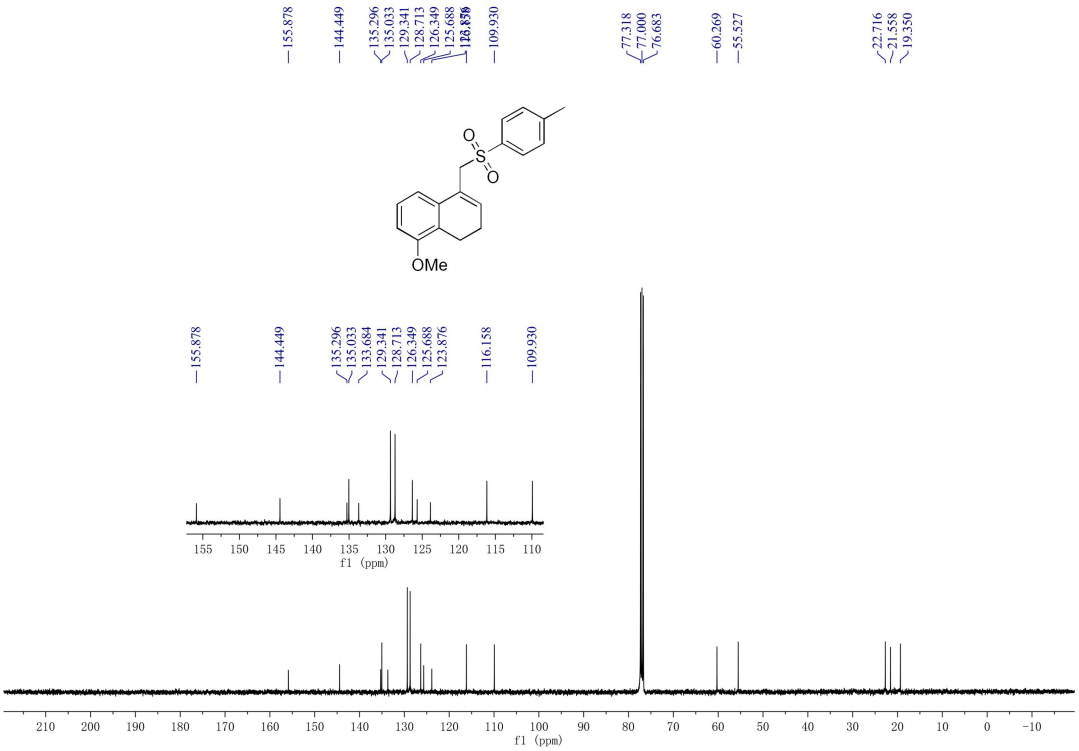
-200
-210
f1 (ppm)

8-Methoxy-4-(tosylmethyl)-1,2-dihydronaphthalene (3ka)





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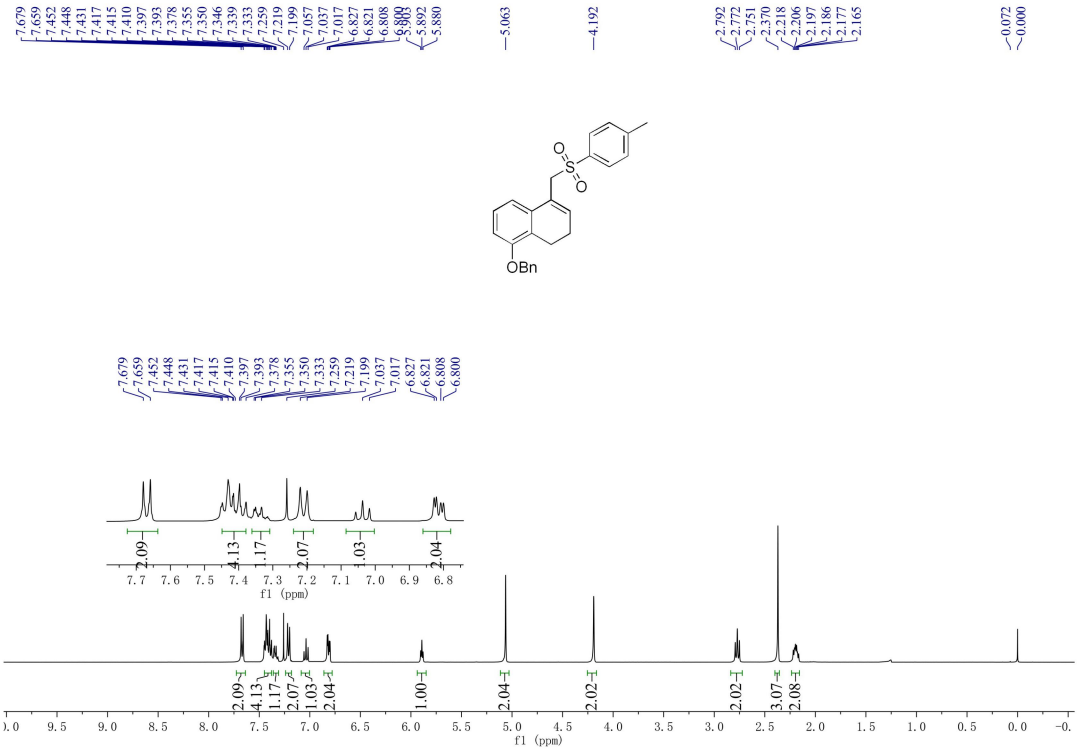
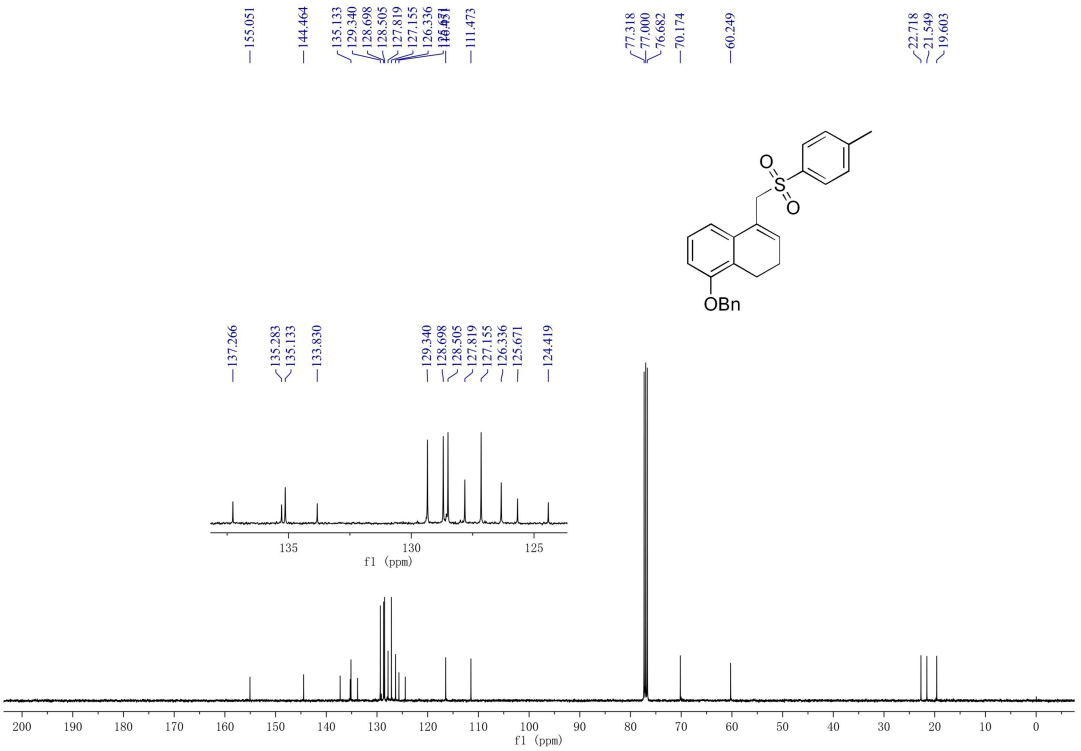
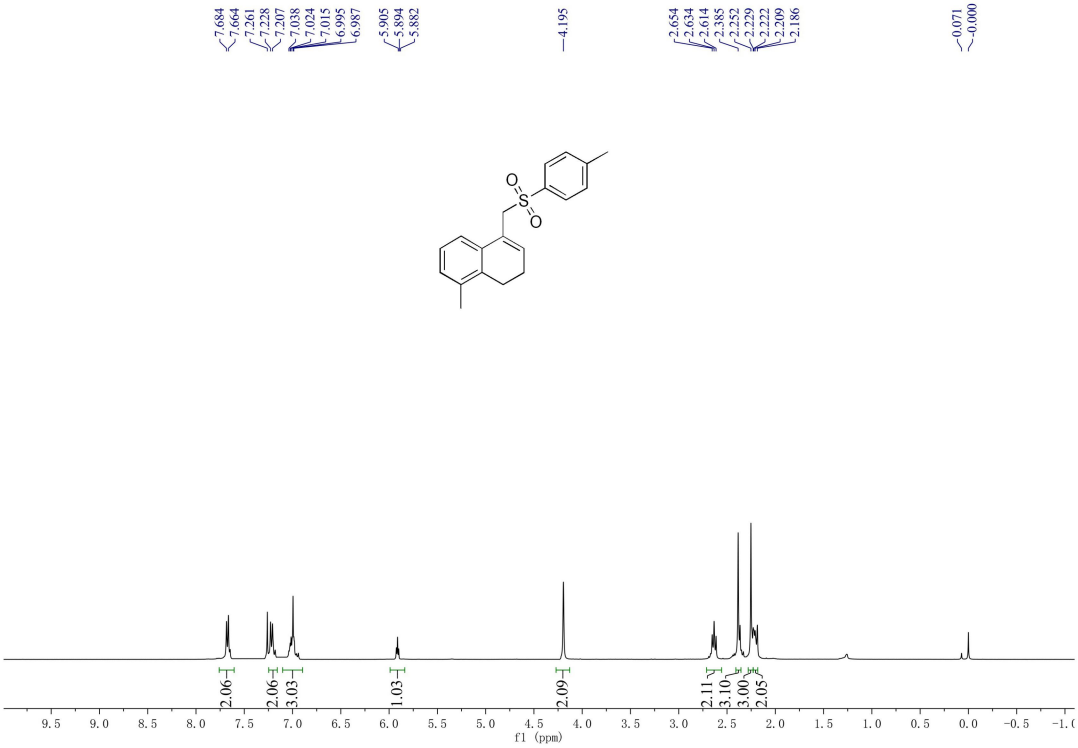
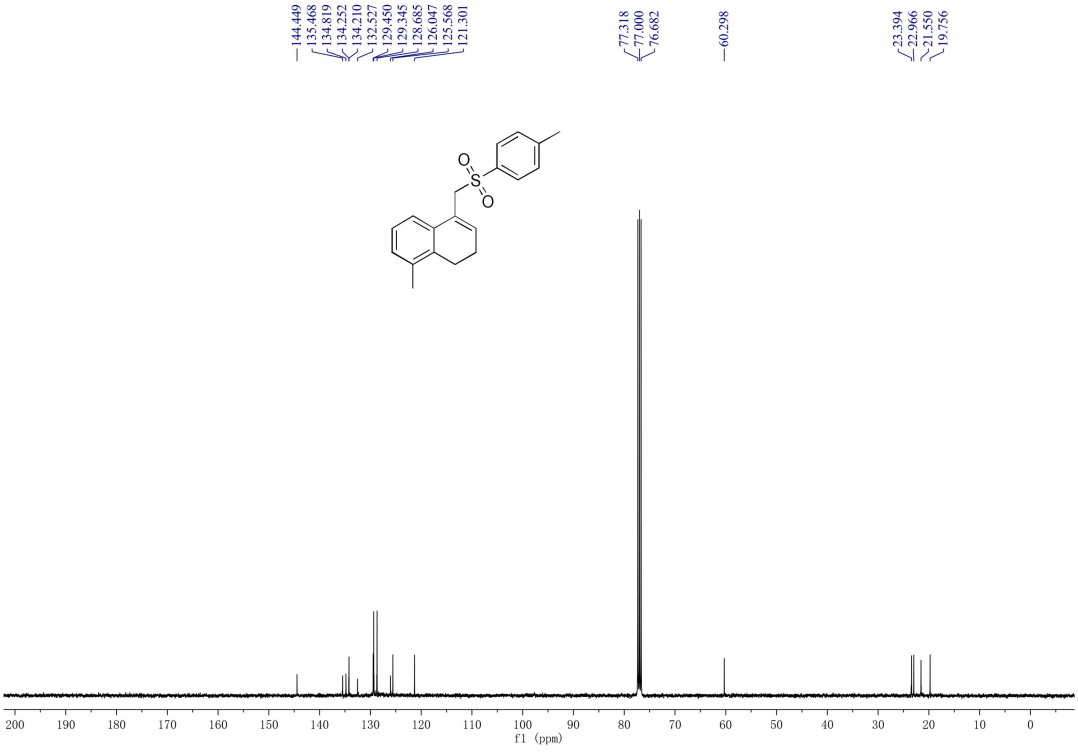




8-Methyl-4-(tosylmethyl)-1,2-dihydronaphthalene (3ma)

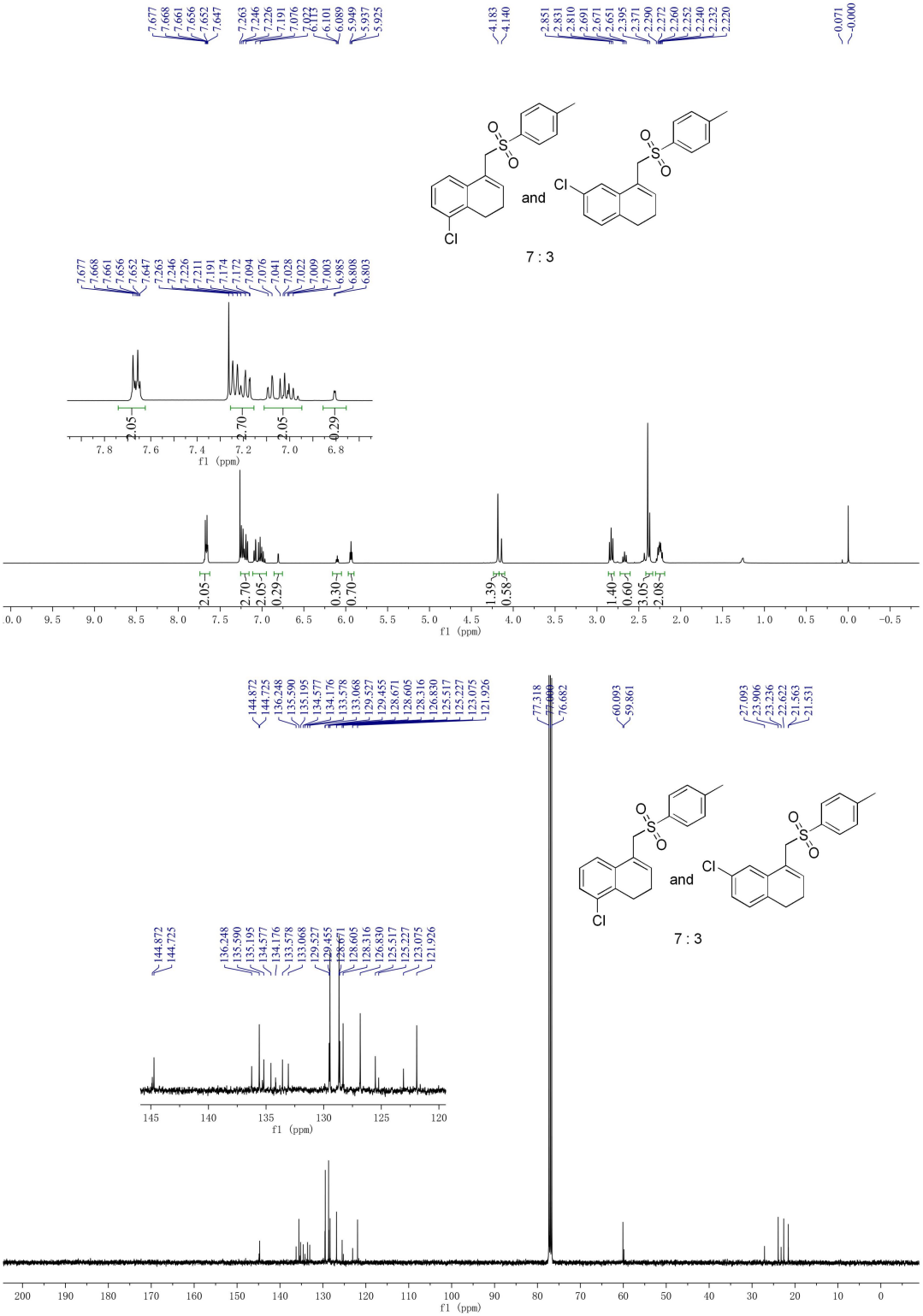




8-Chloro-4-(tosylmethyl)-1,2-dihydronaphthalene (3na) and

6-Chloro-4-(tosylmethyl)-1,2-dihydronaphthalene

(3na')



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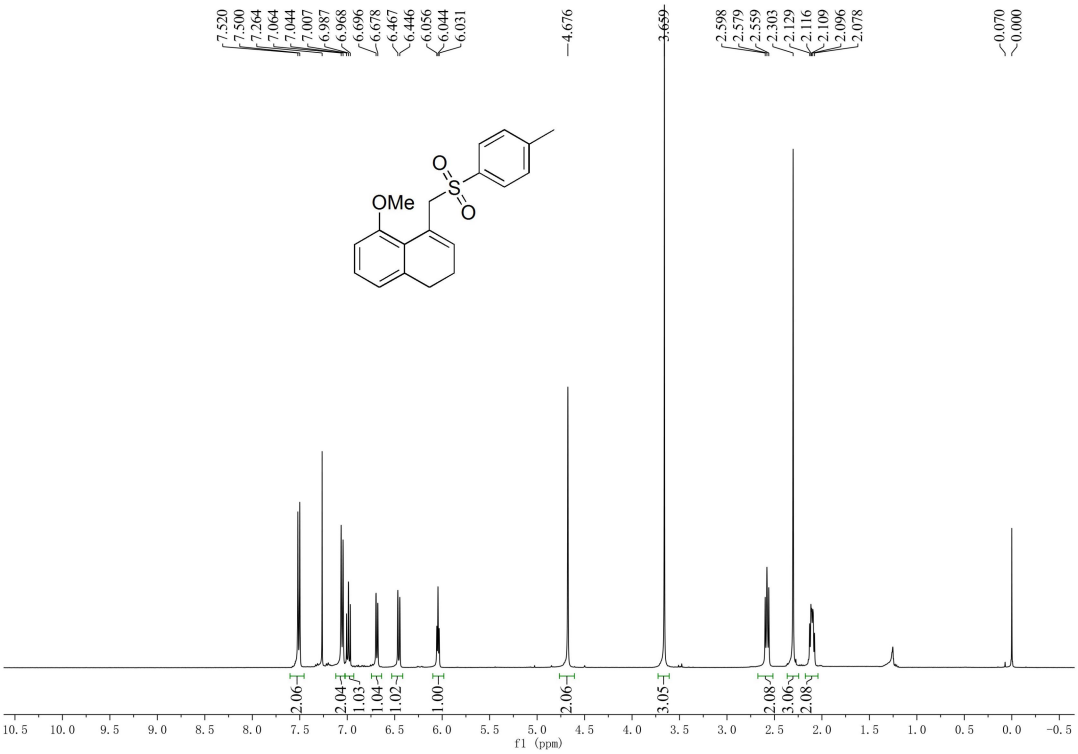

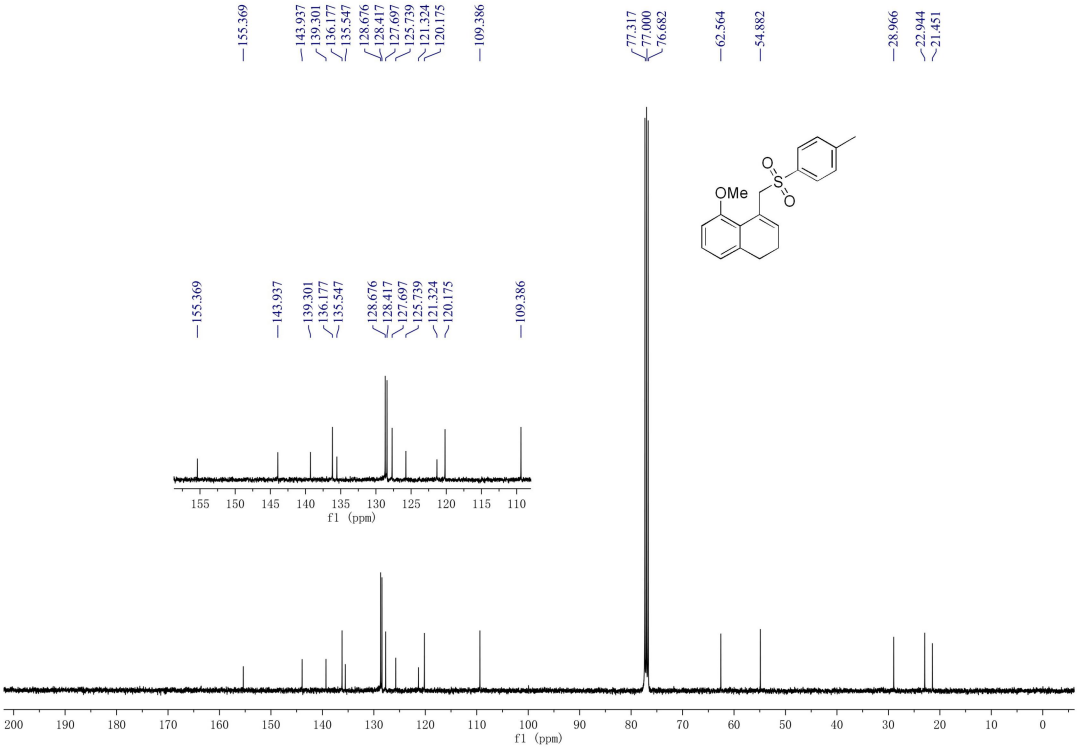

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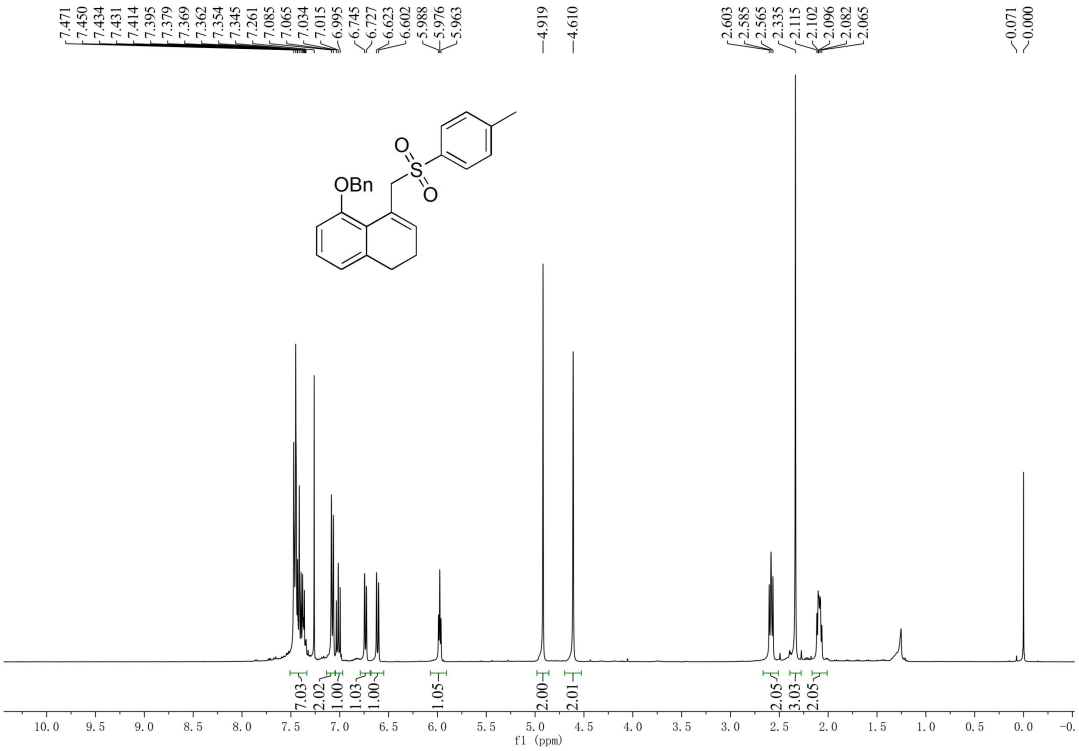

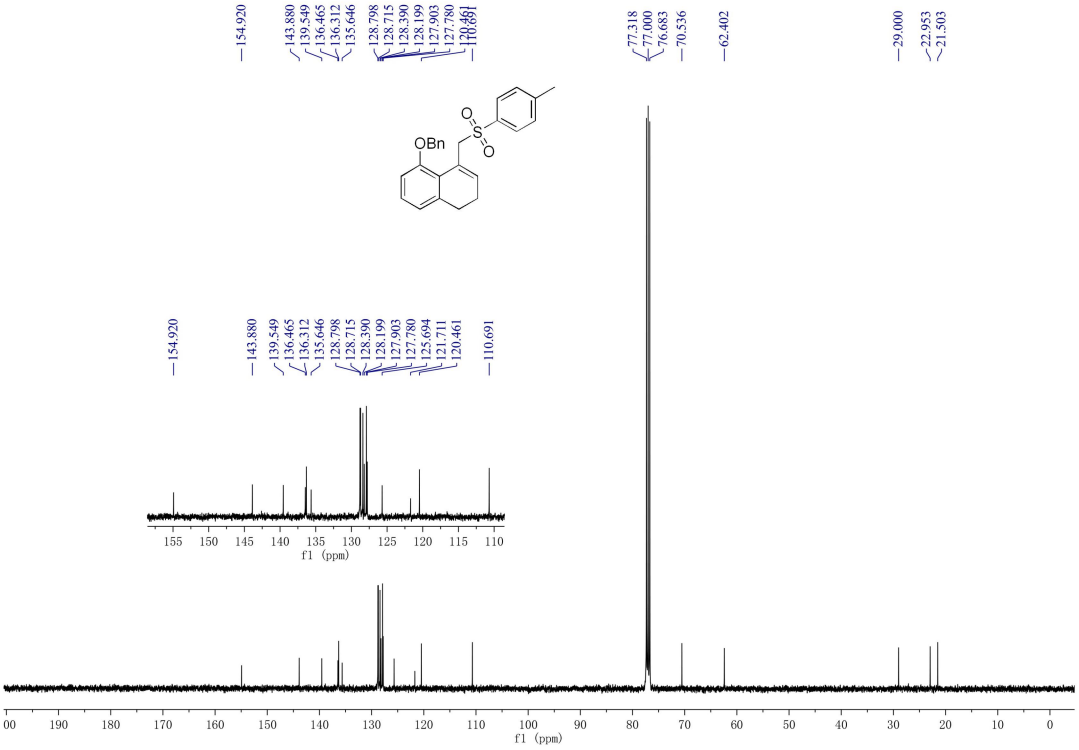

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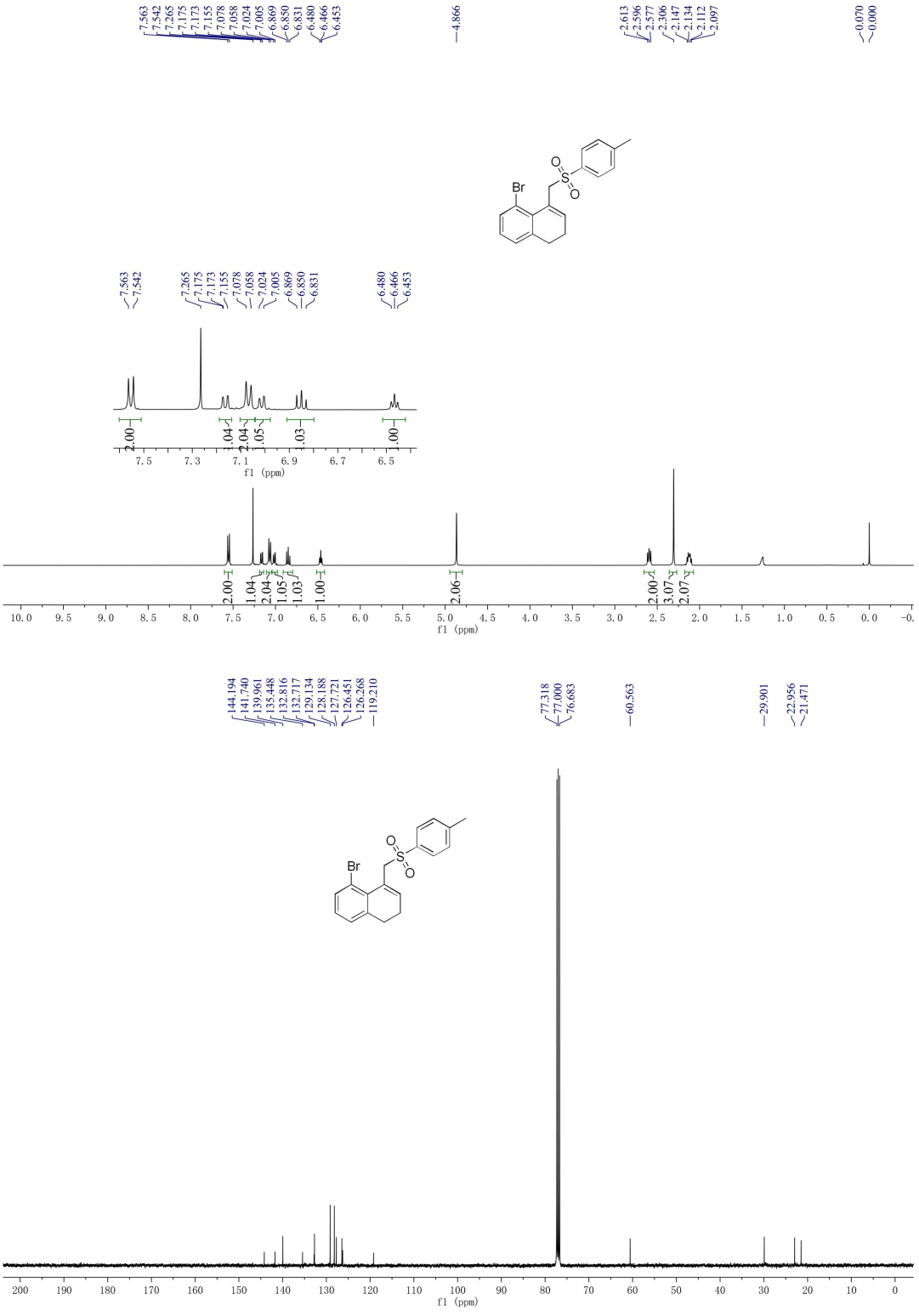

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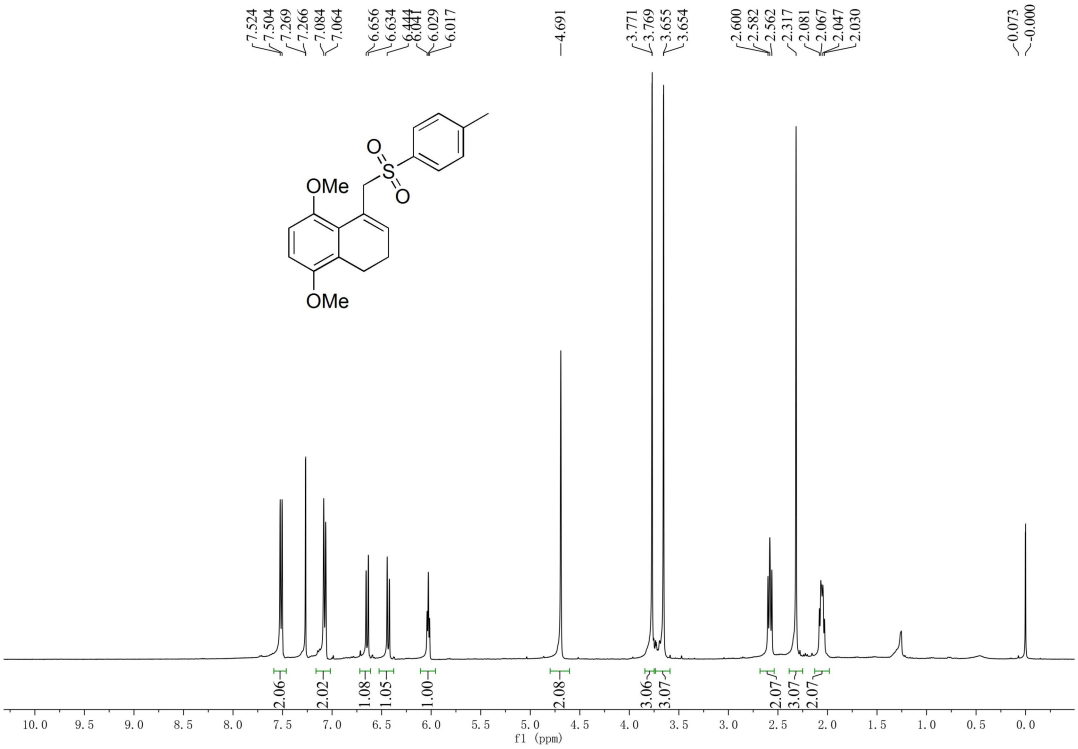

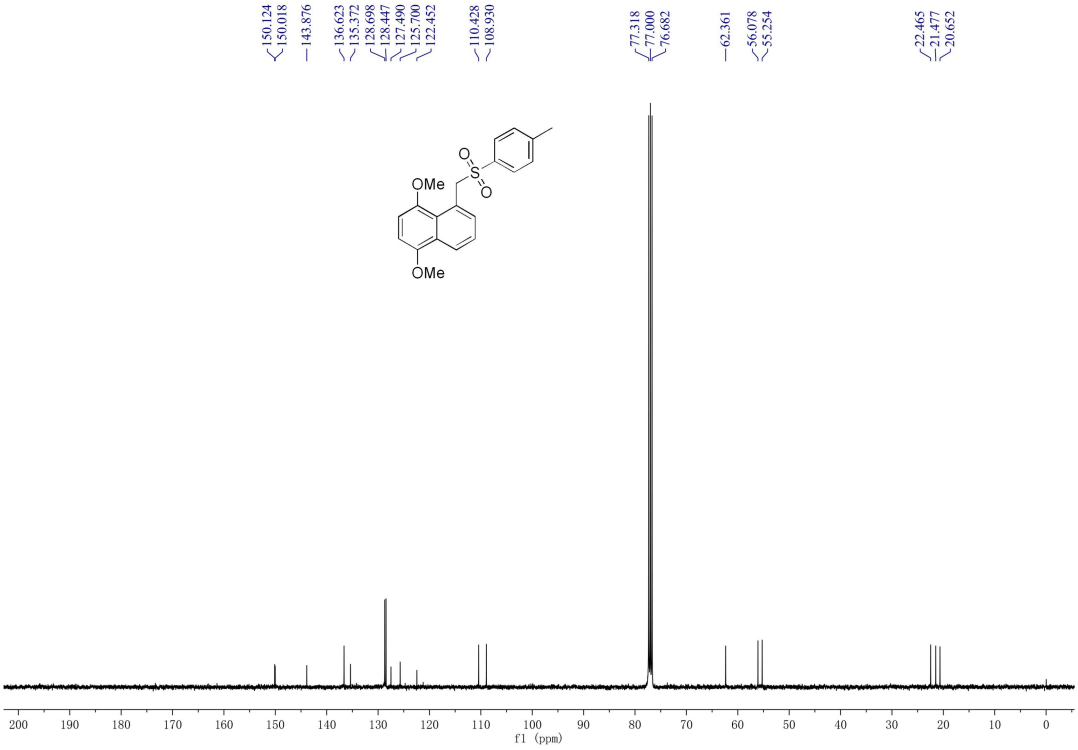

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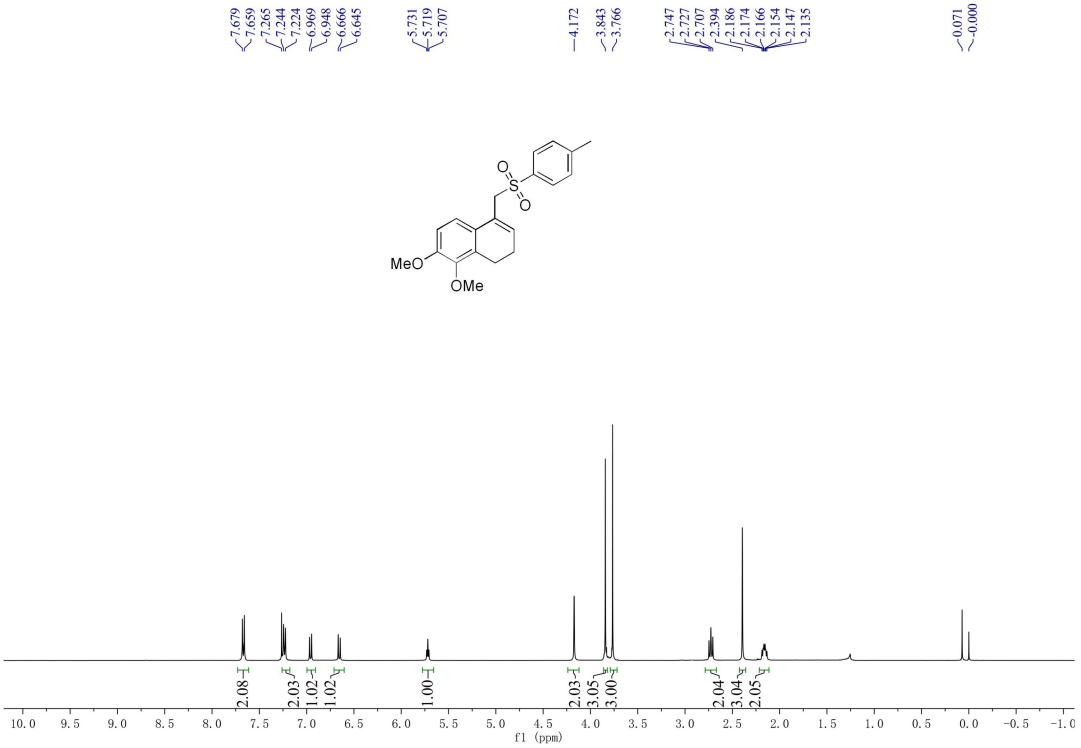

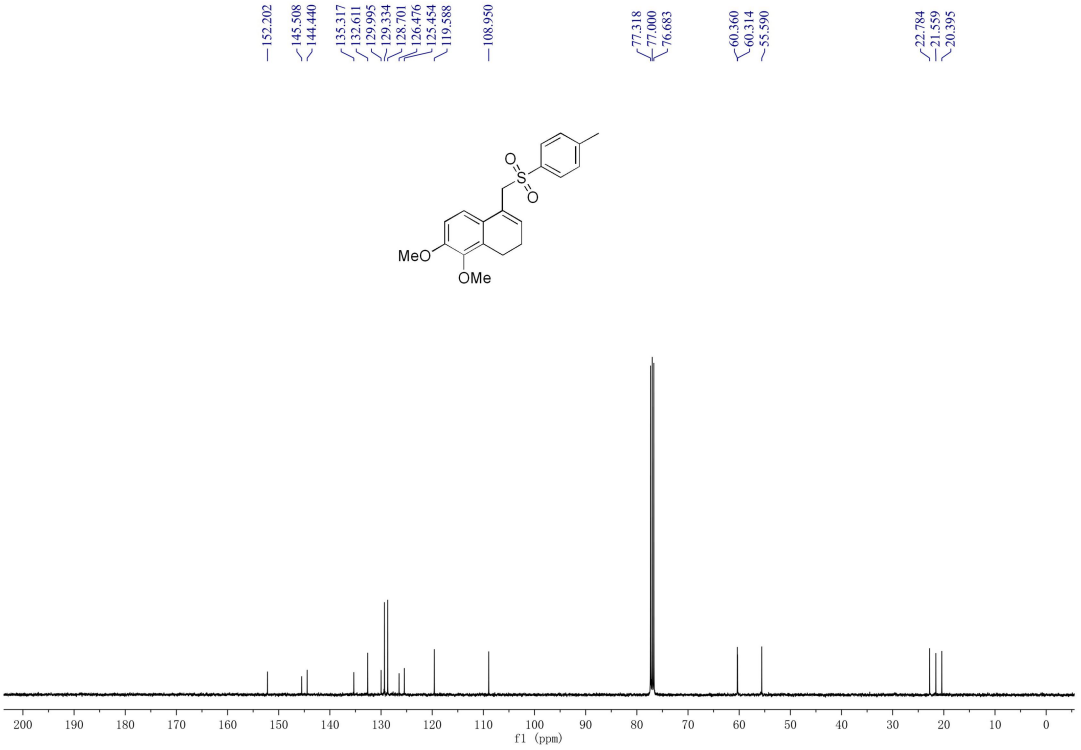

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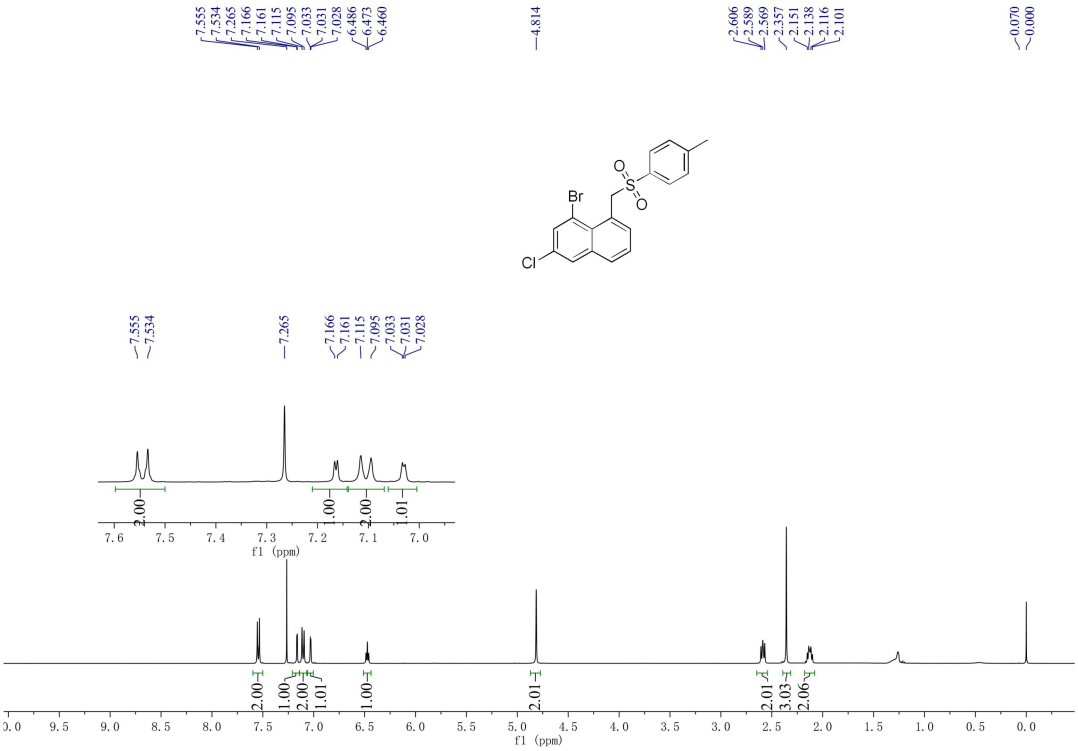

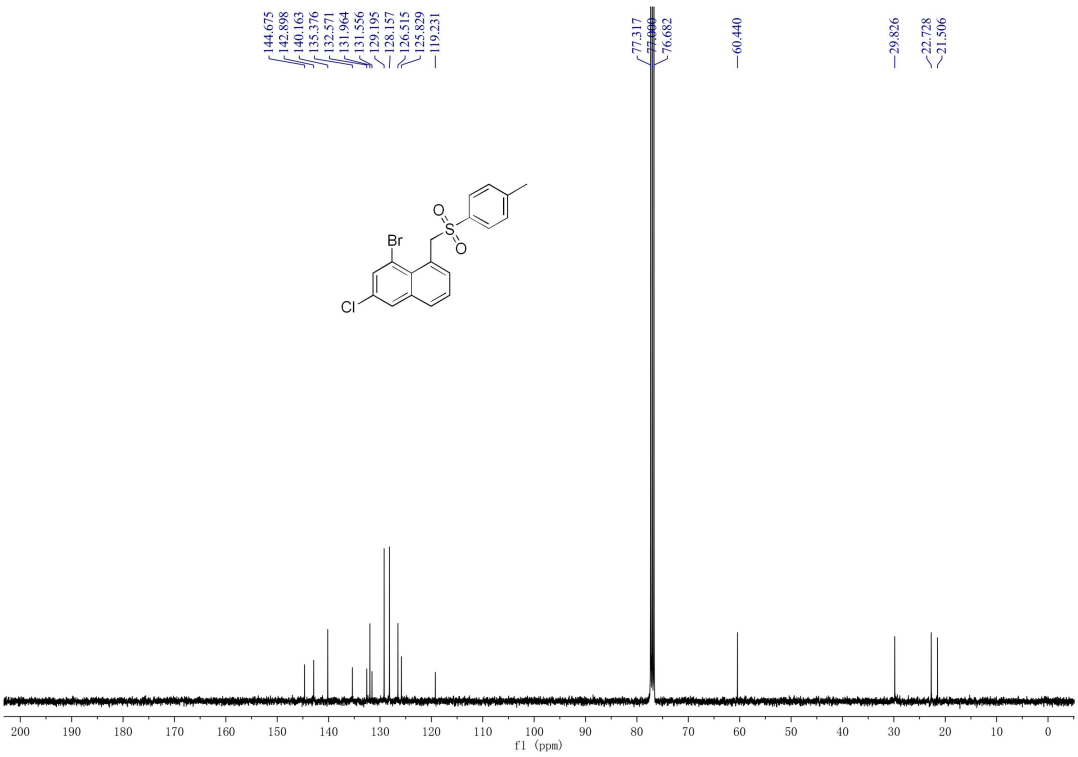

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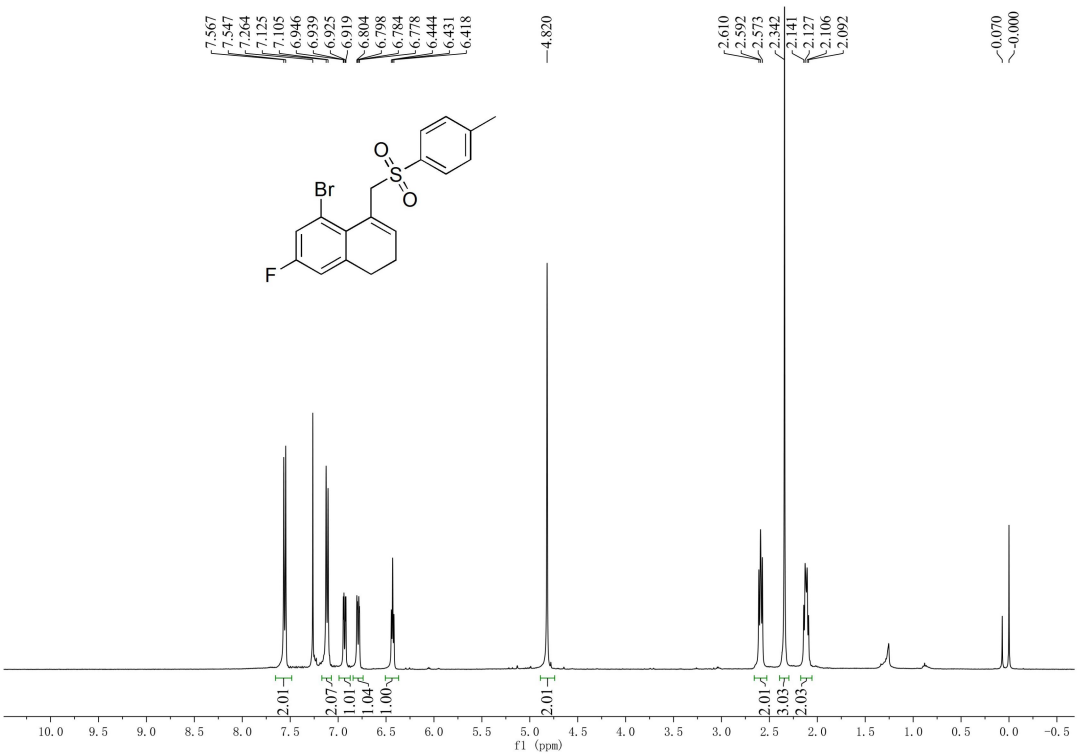

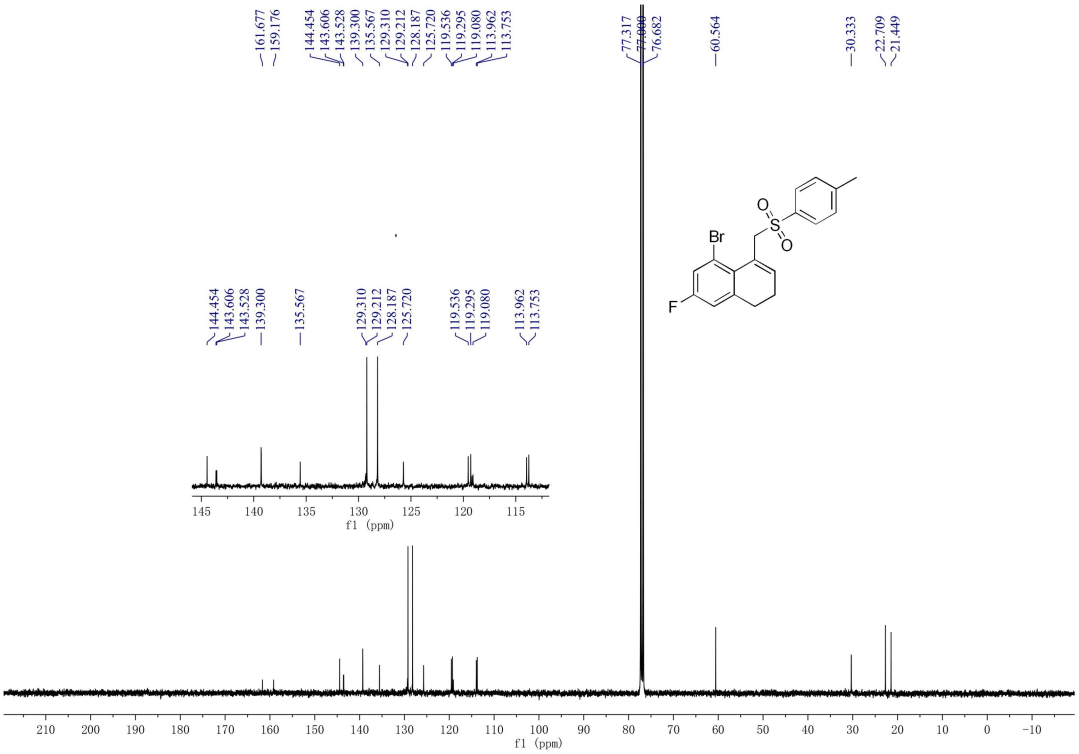

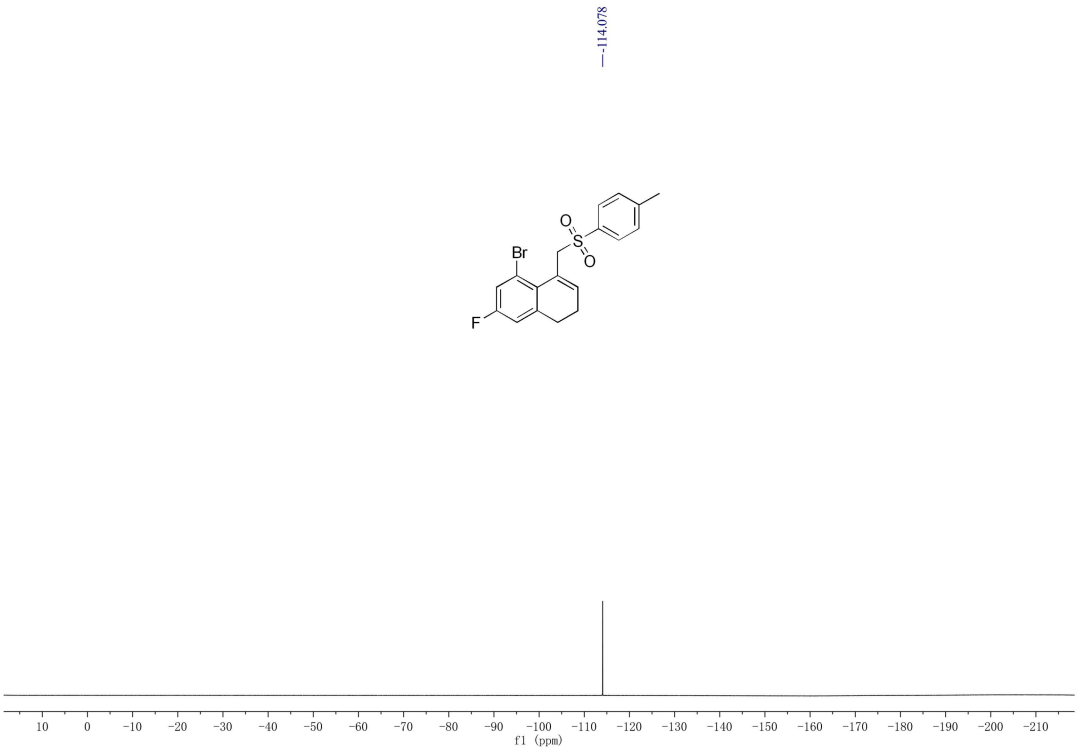
-114.078
O
S
O
Br
F
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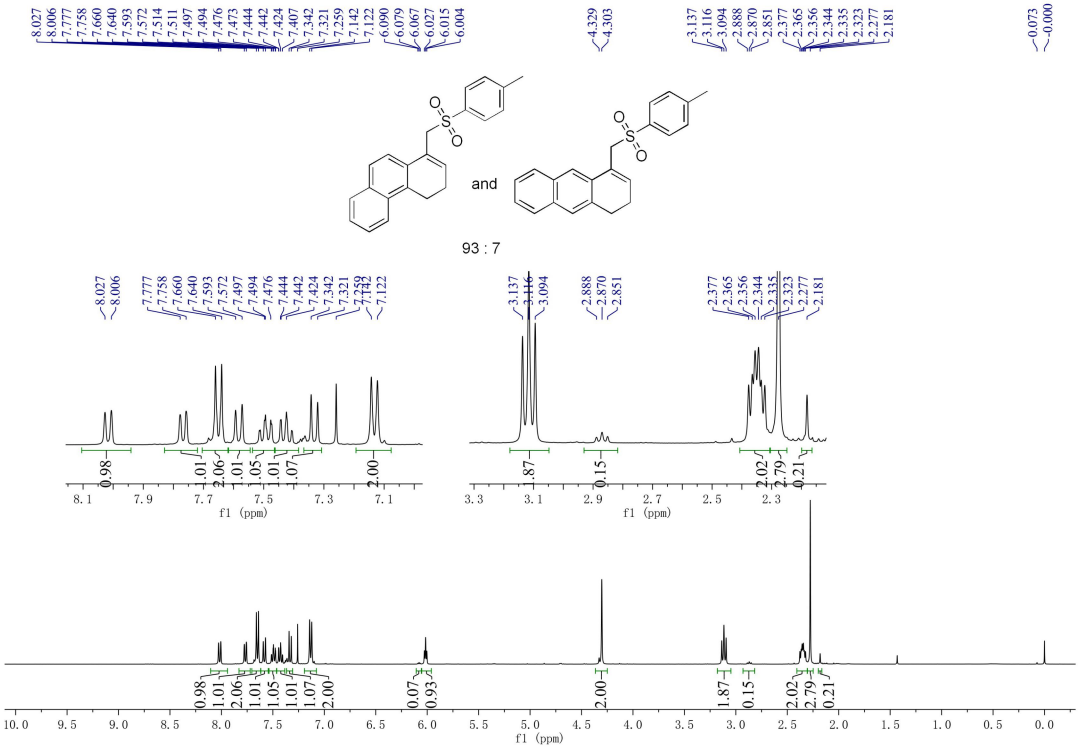
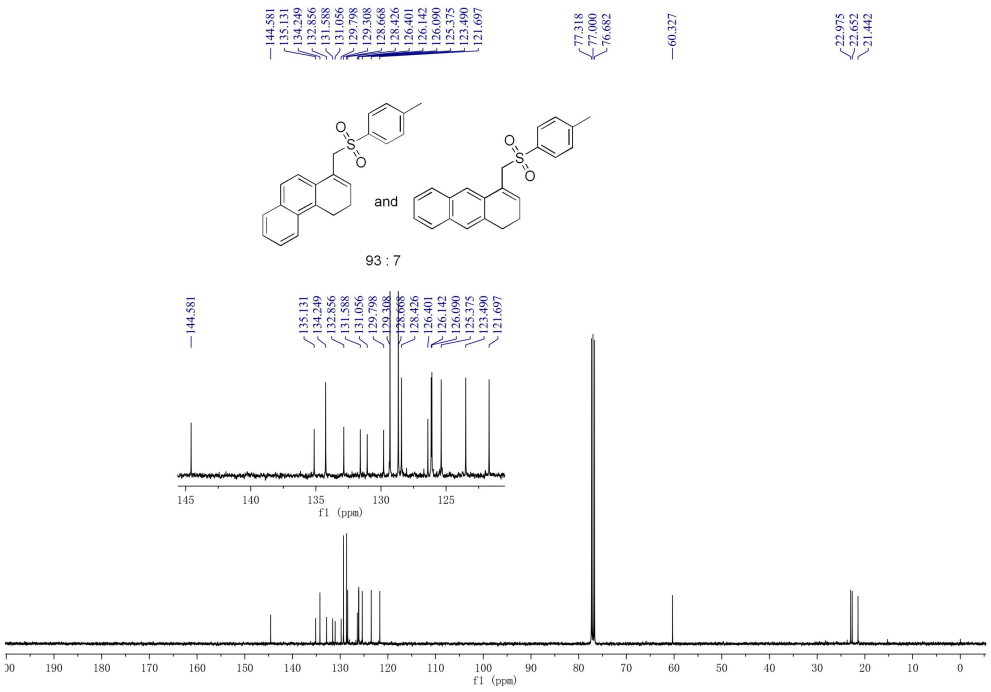
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

1-(Tosylmethyl)-3,4-dihydrophenanthrene (3va) and

4-(Tosylmethyl)-1,2-dihydroanthracene

(3va')





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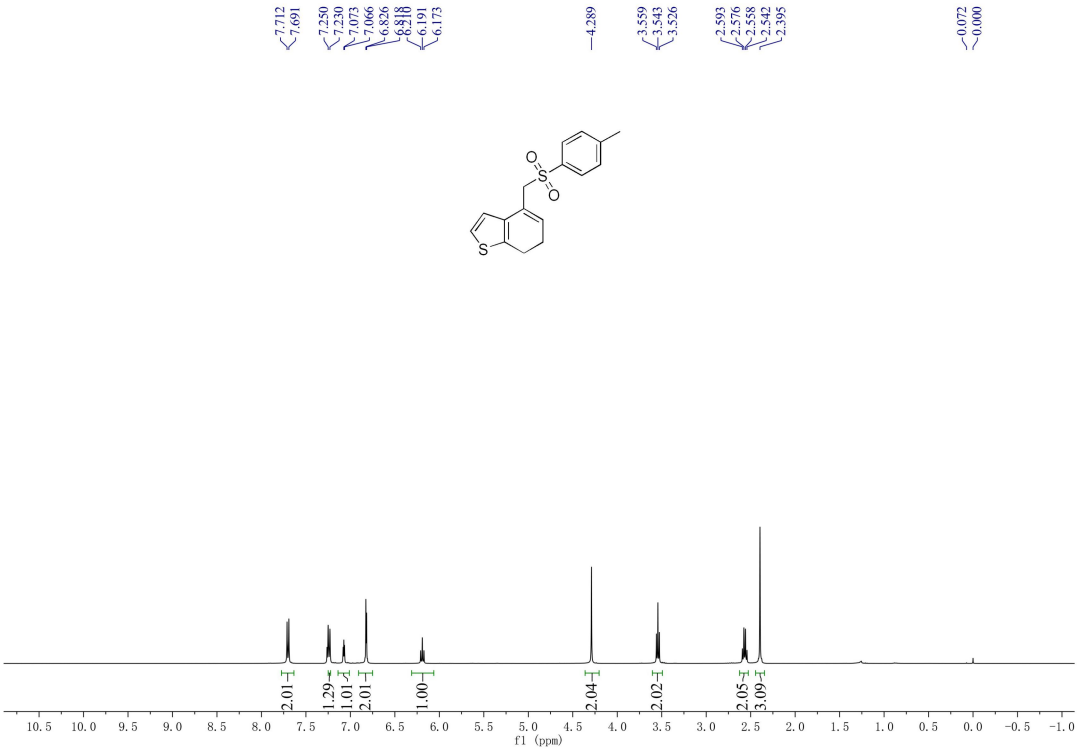
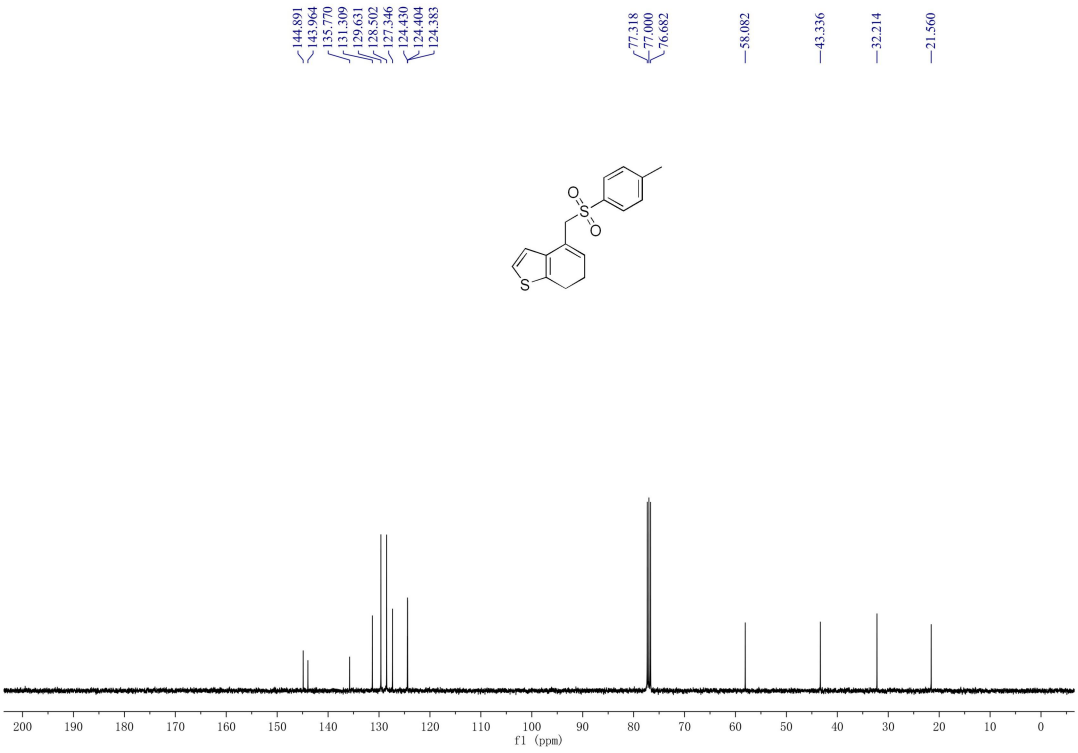
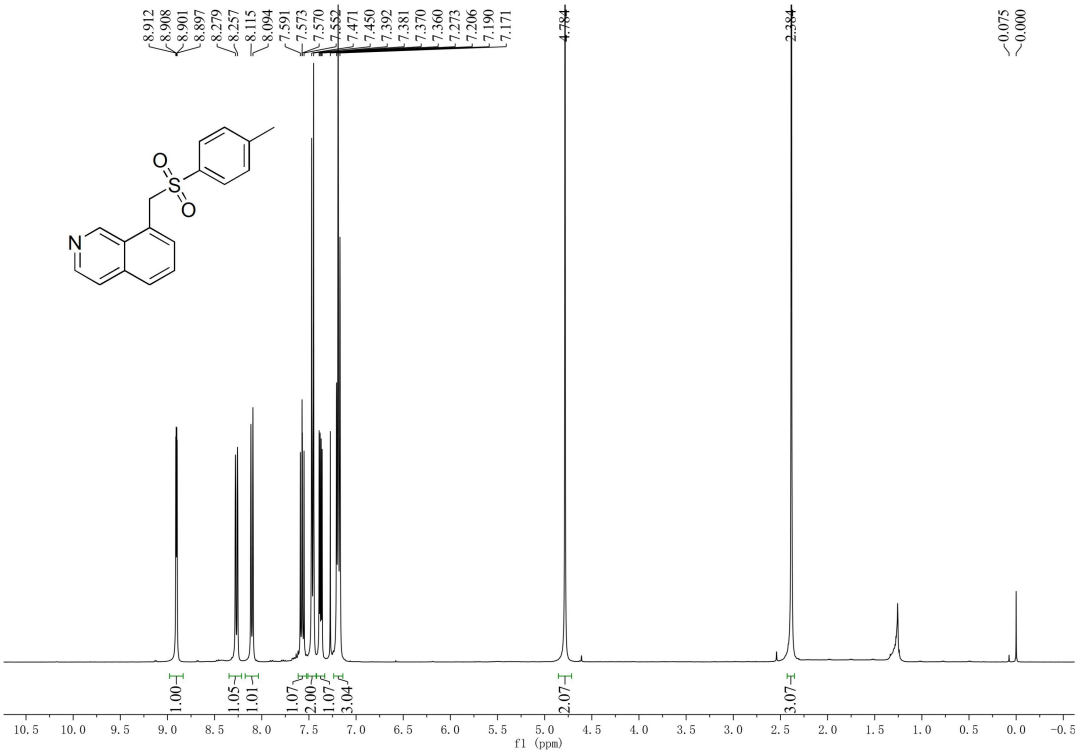
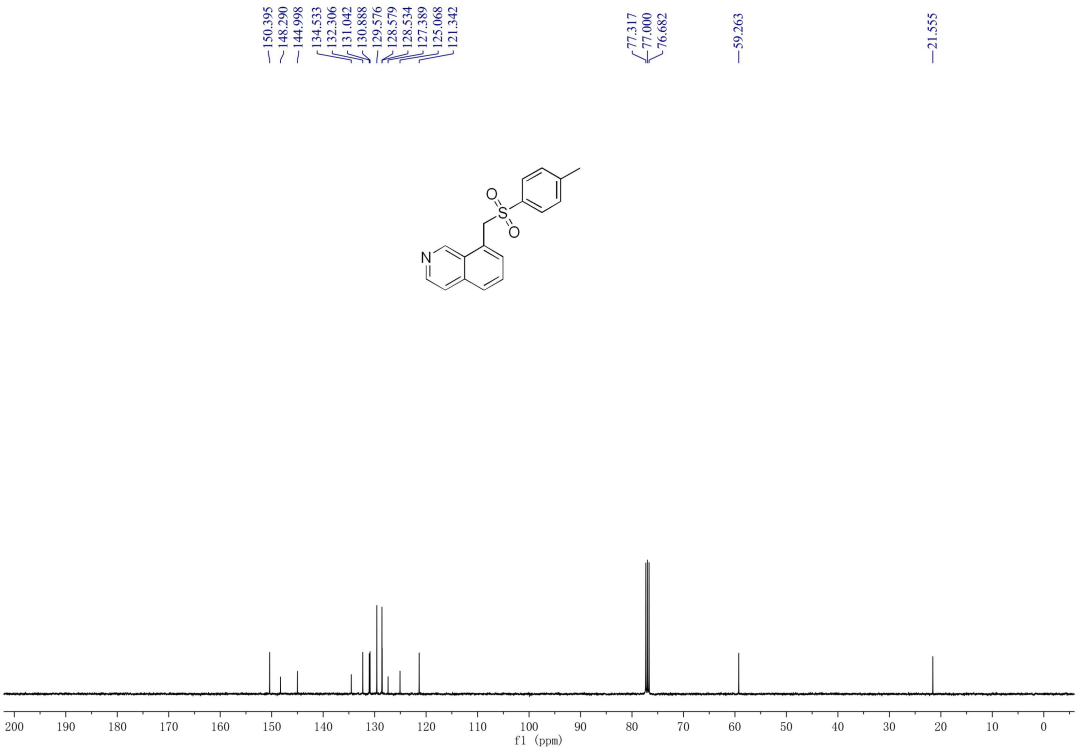


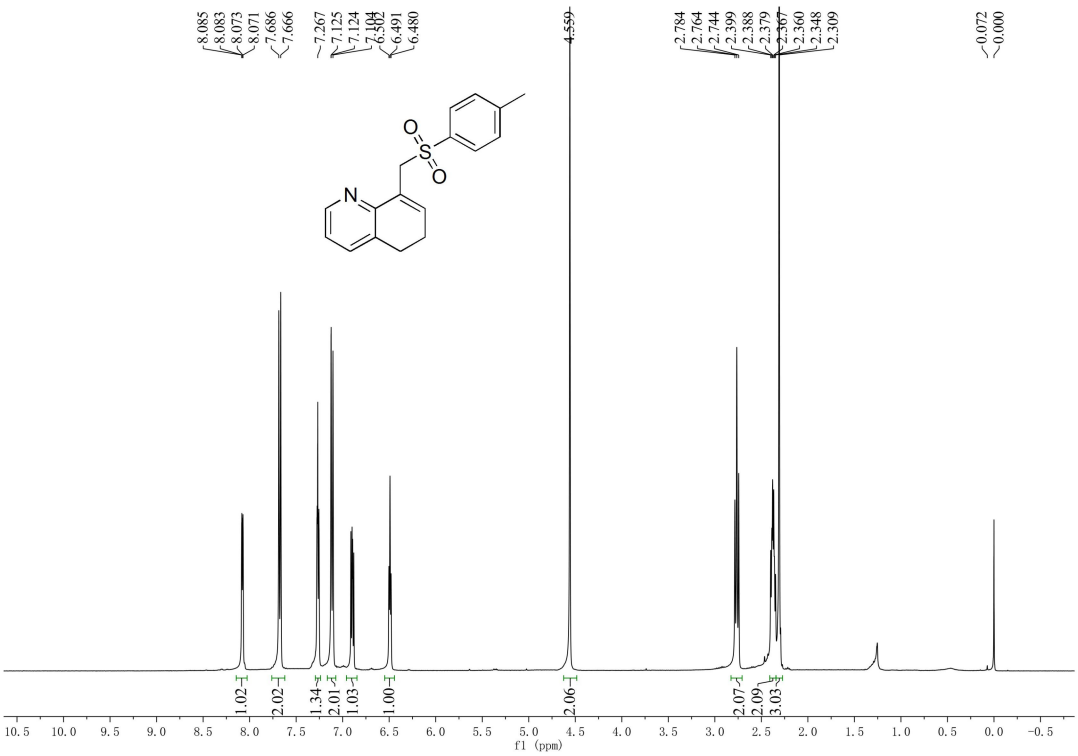


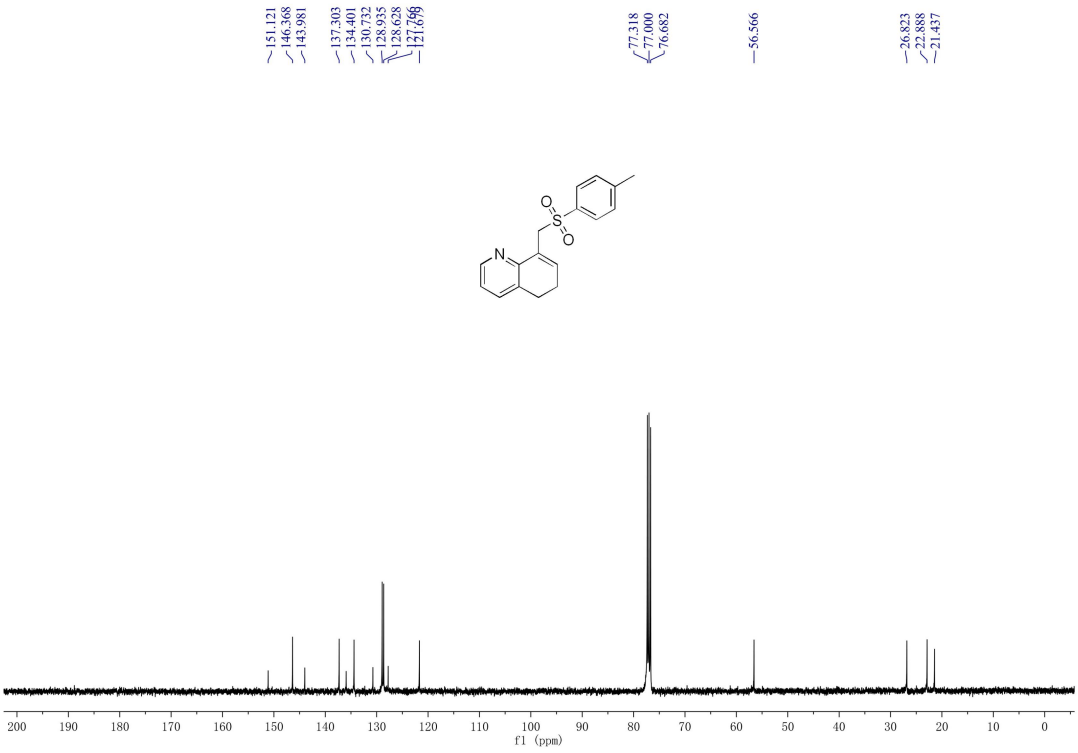
8-(Tosylmethyl)isoquinoline (3xa)



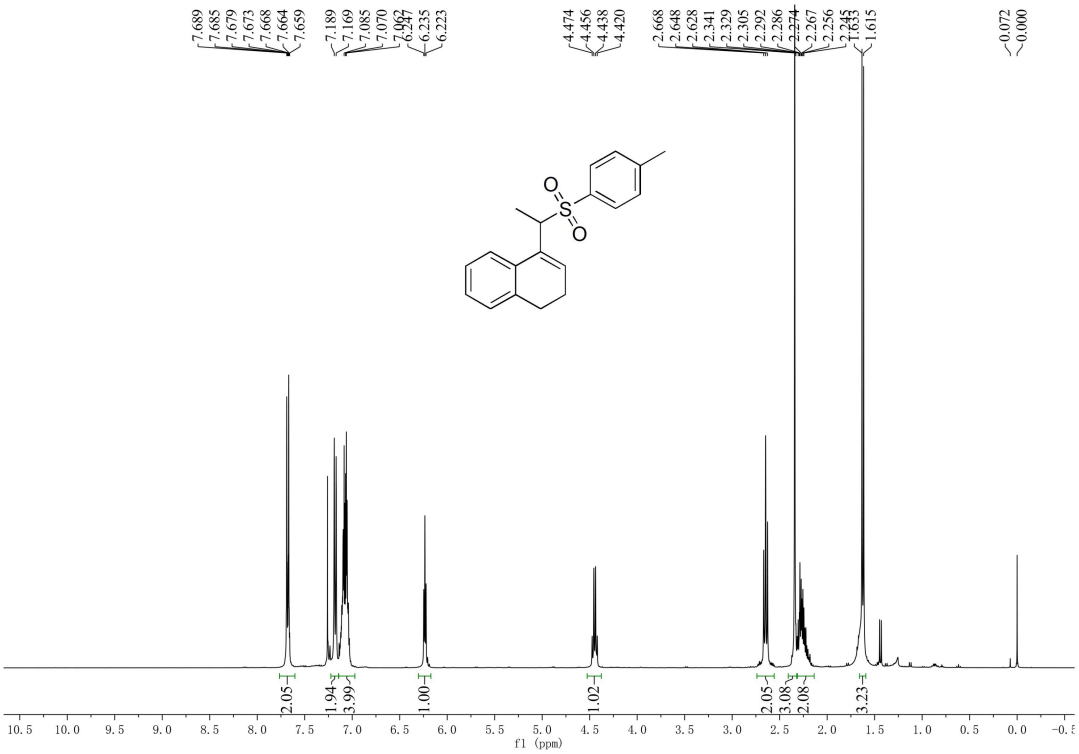


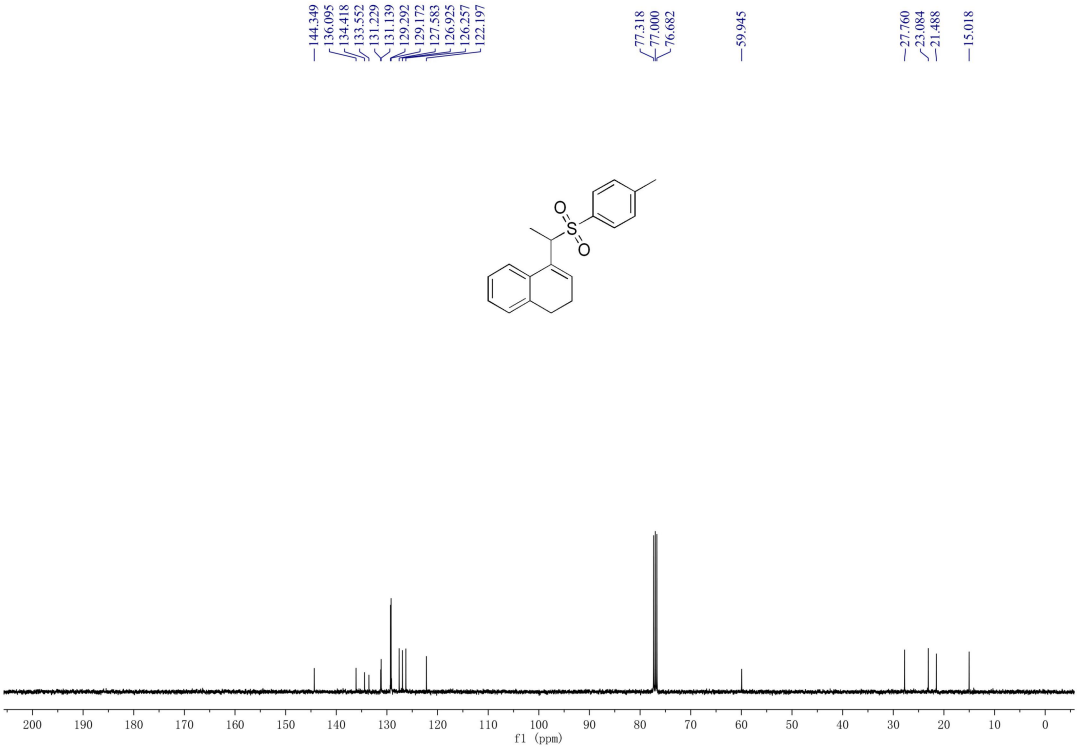
8-(Tosylmethyl)-5,6-dihydroquinoline (3ya)



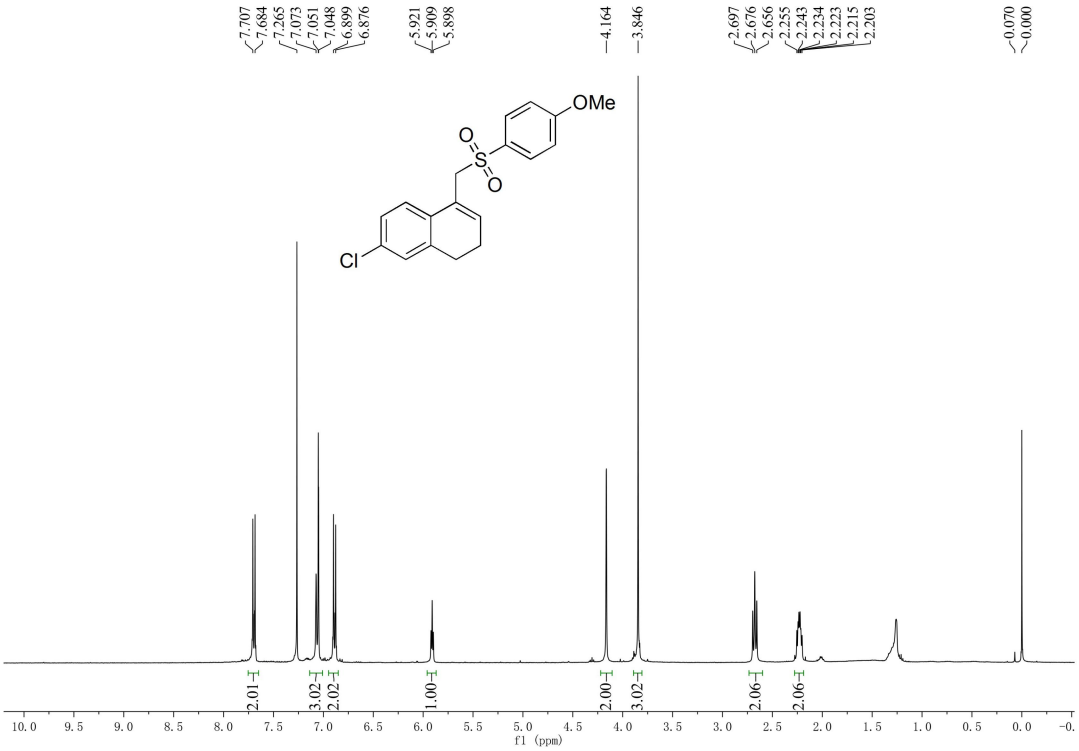


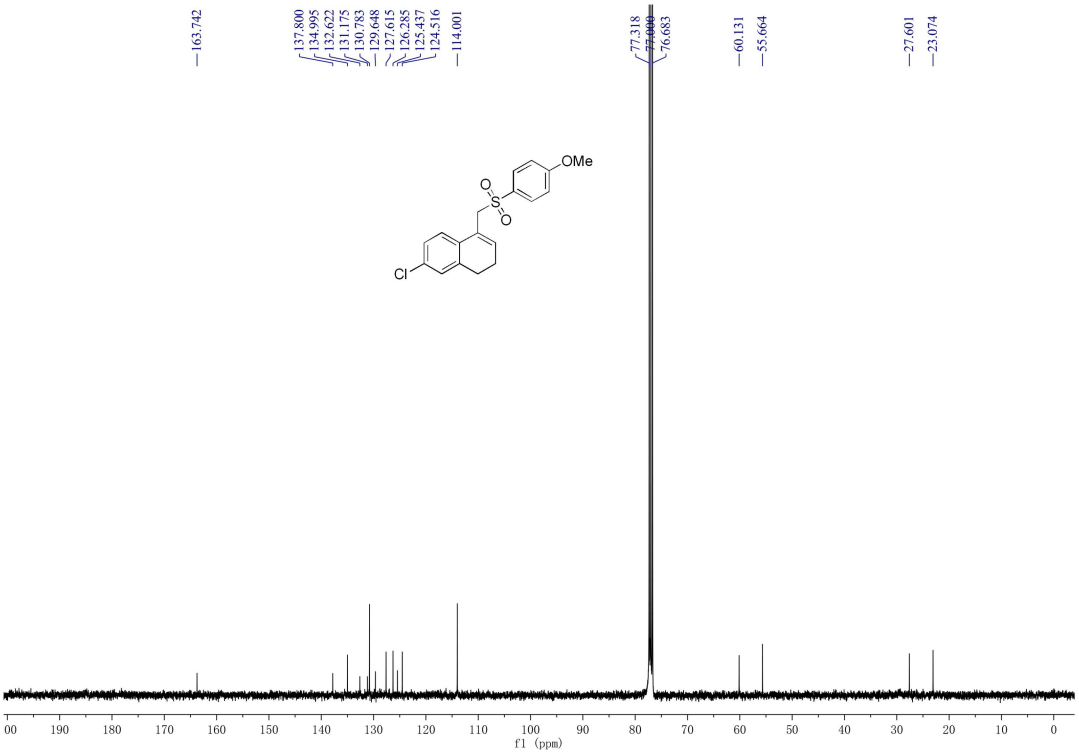
4-(1-Tosylethyl)-1,2-dihydronaphthalene (3za)



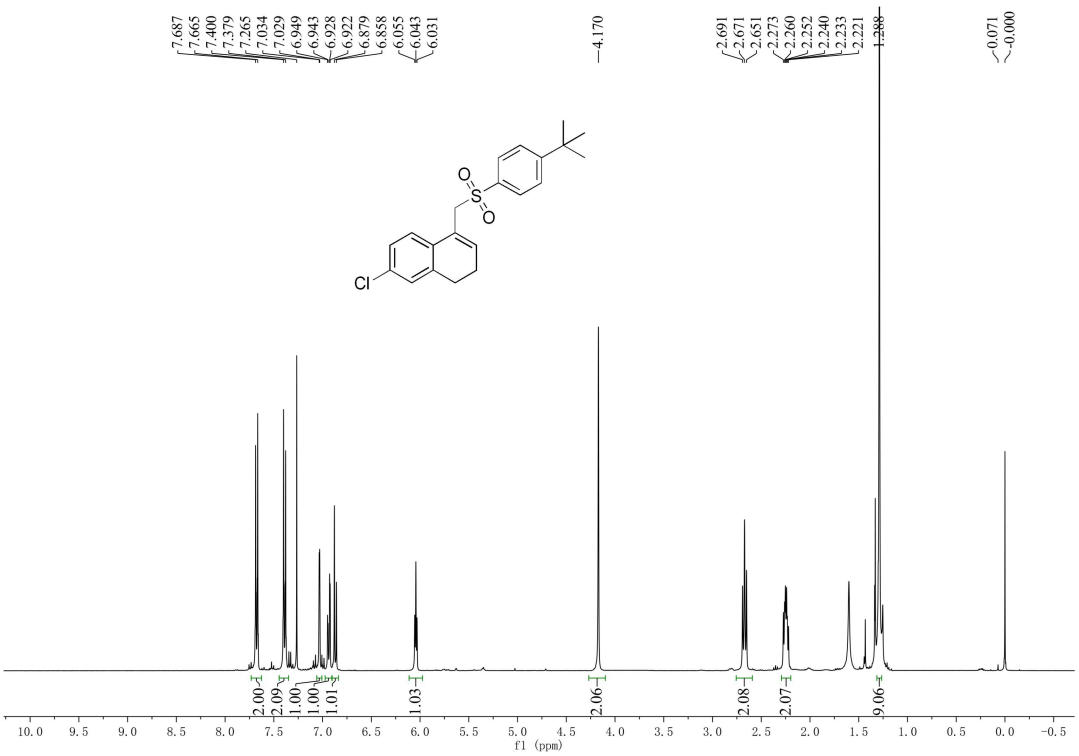


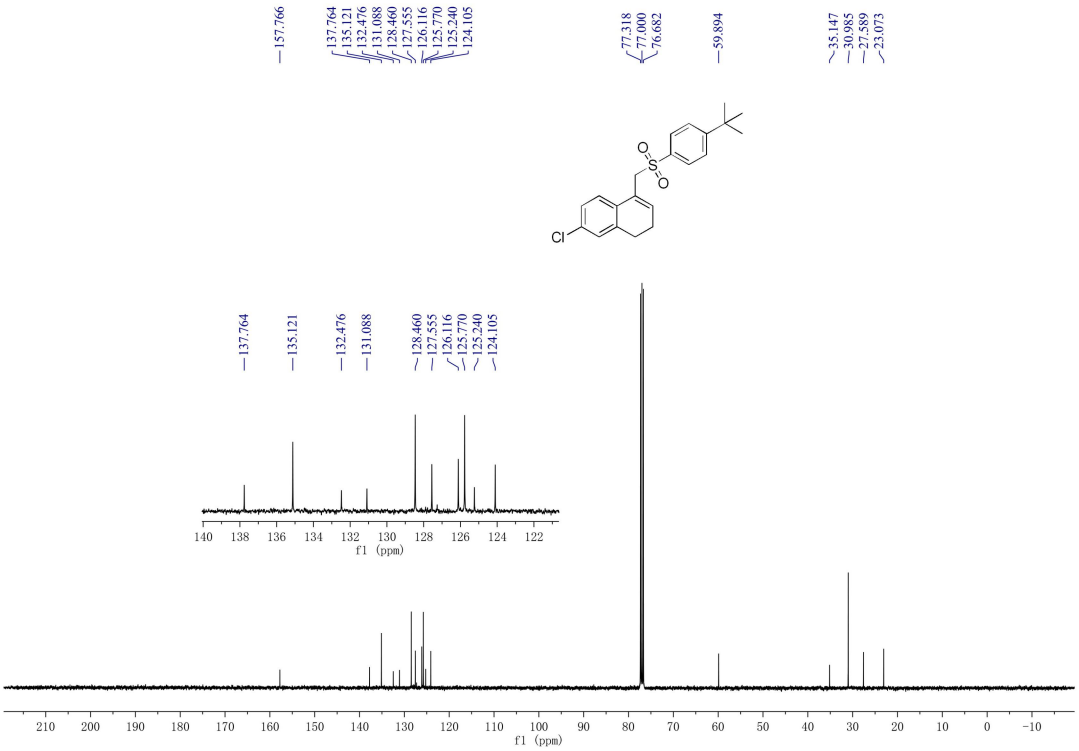
7-Chloro-4-(((4-methoxyphenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3hb)



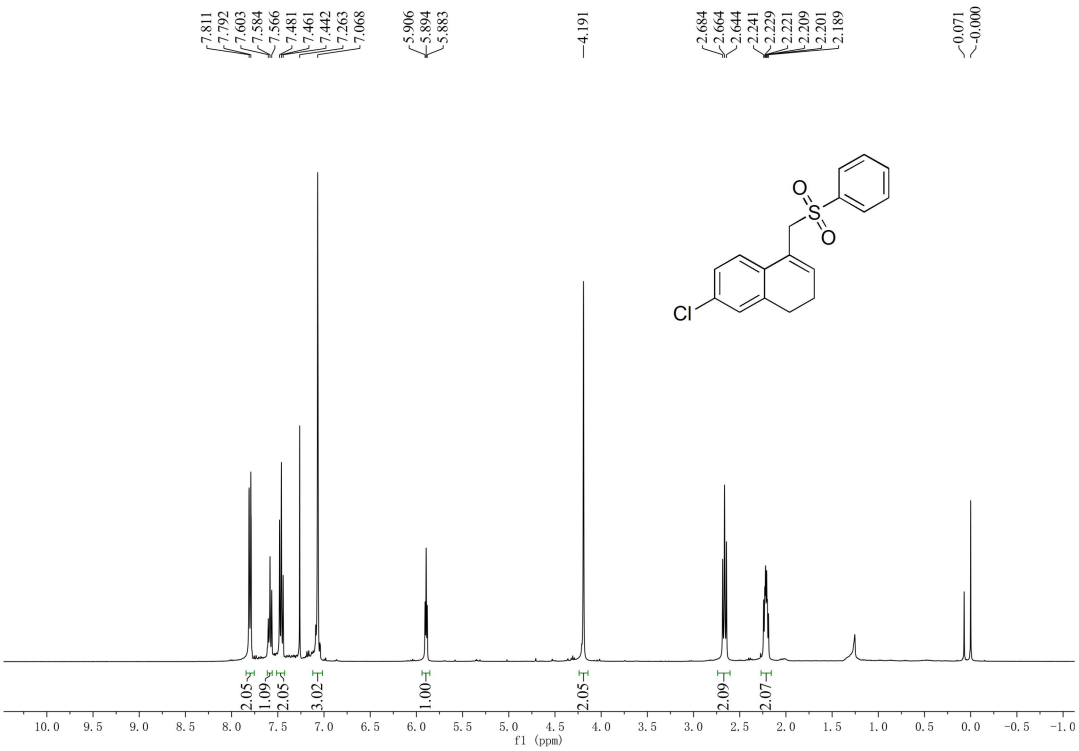


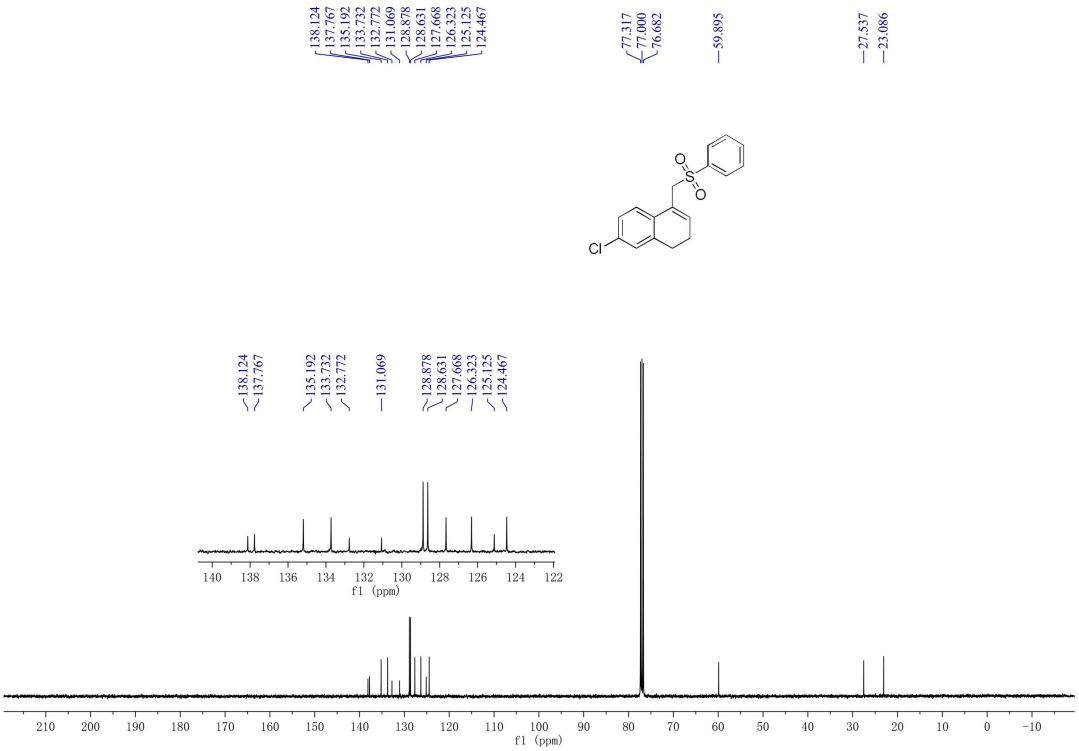
4-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-7-chloro-1,2-dihydronaphthalene (3hc)



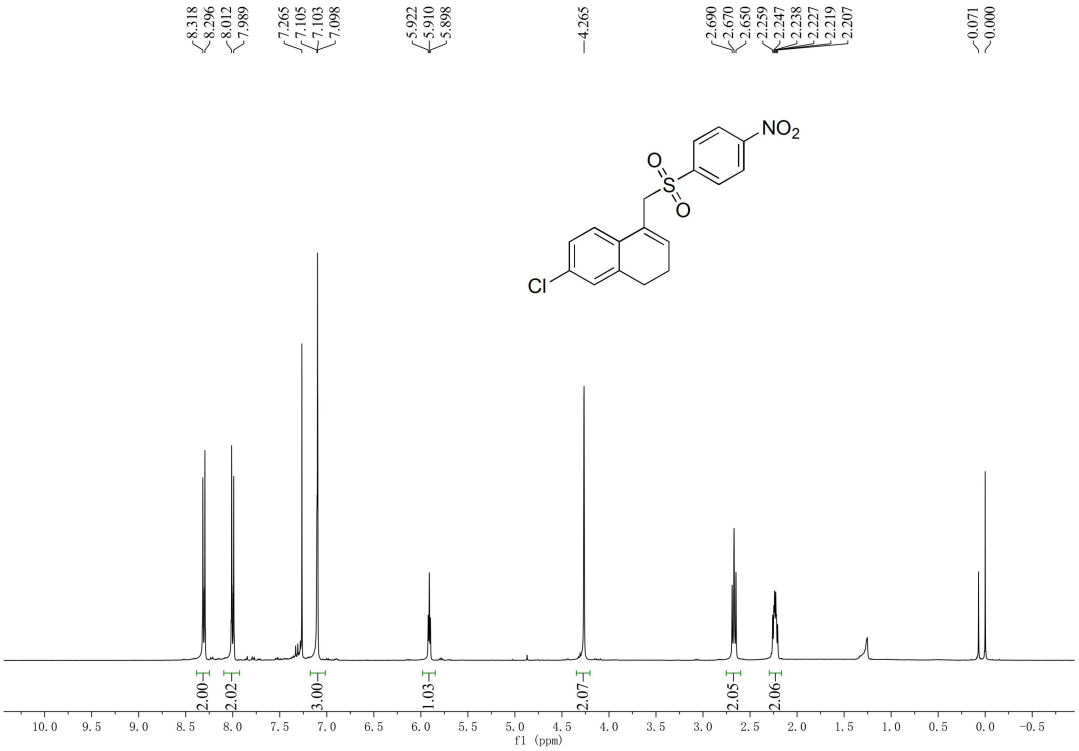


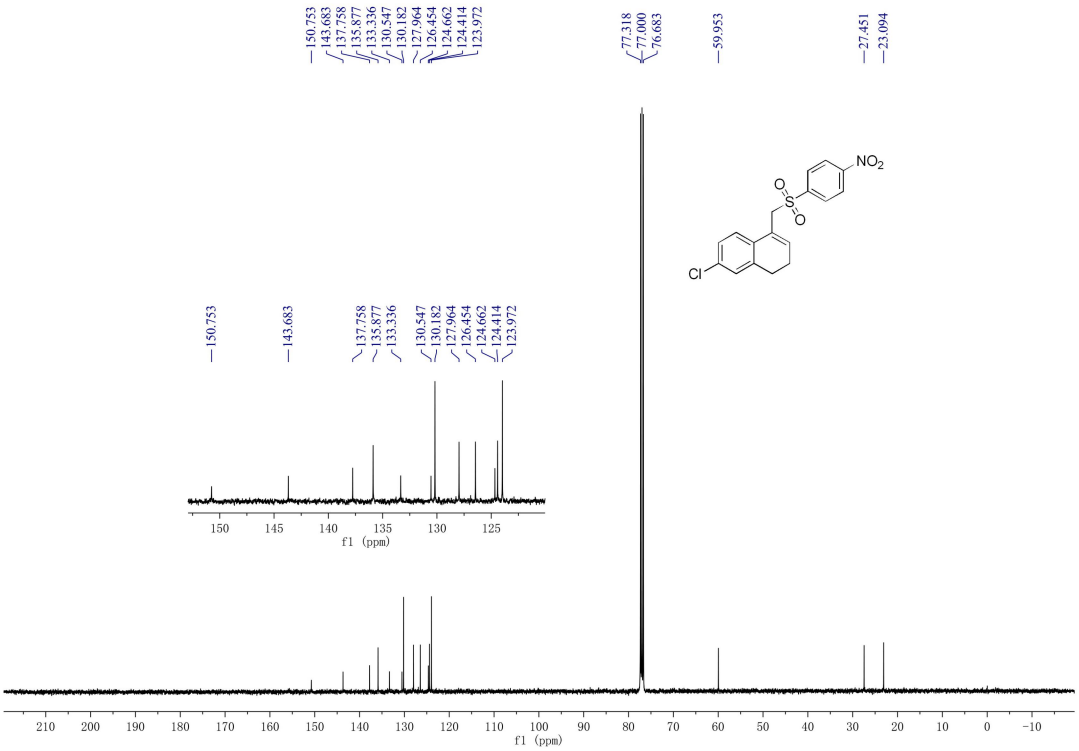
7-Chloro-4-((phenylsulfonyl)methyl)-1,2-dihydronaphthalene (3hd)



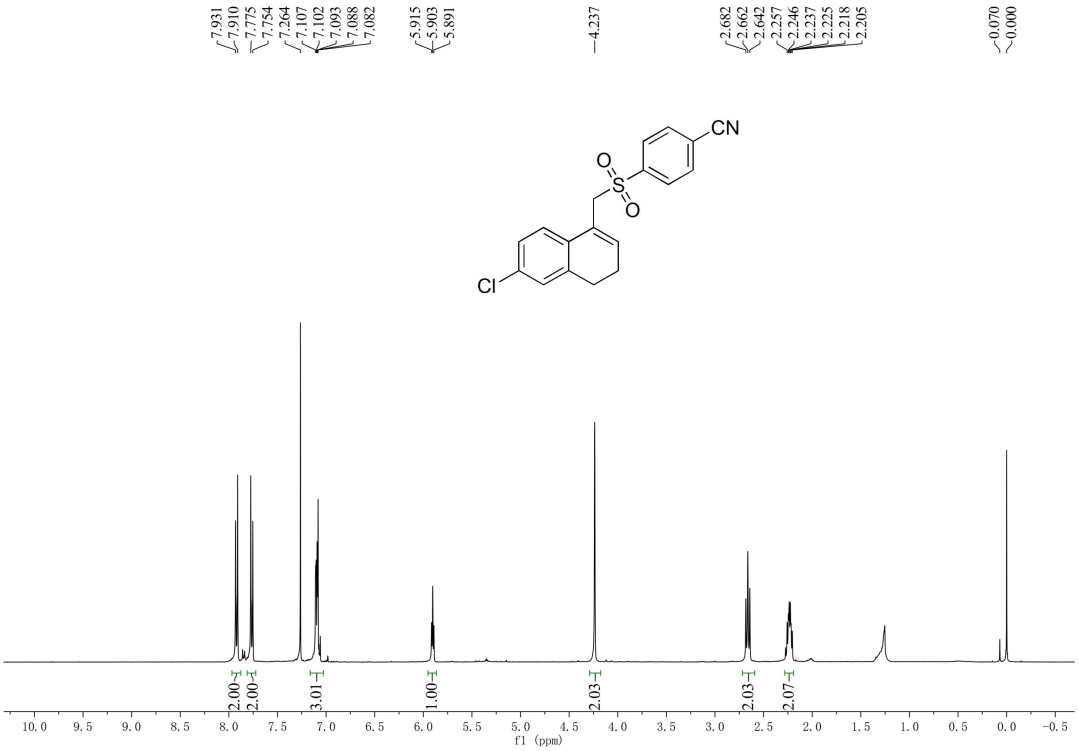


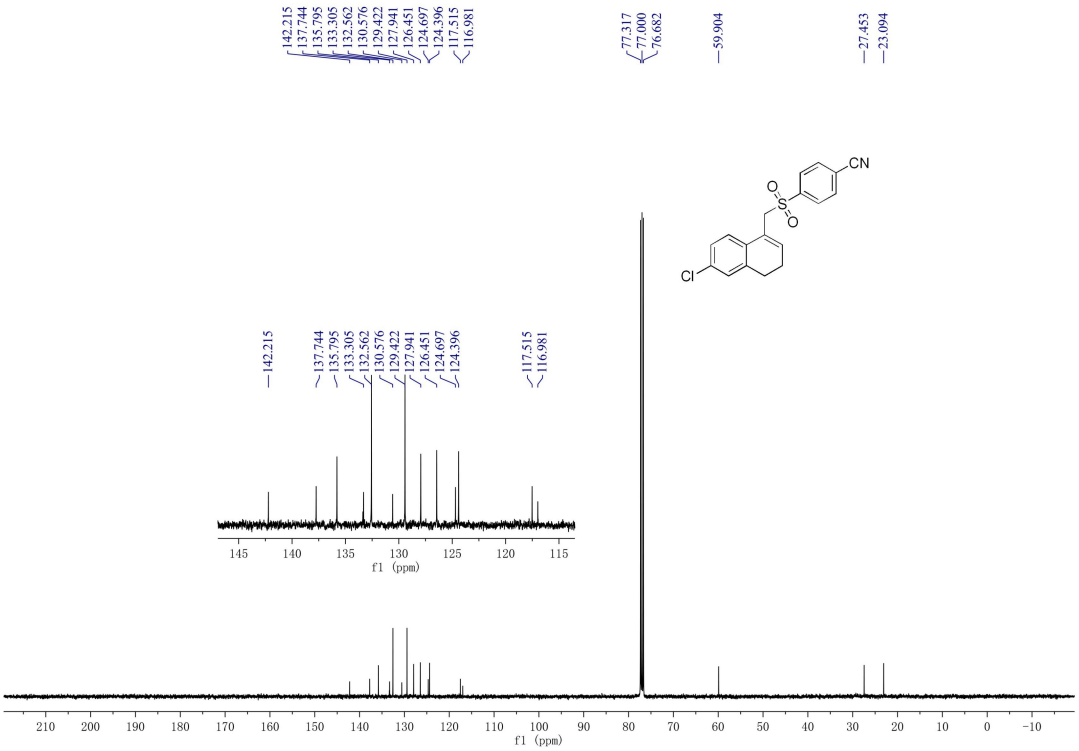
7-Chloro-4-(((4-nitrophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3he)





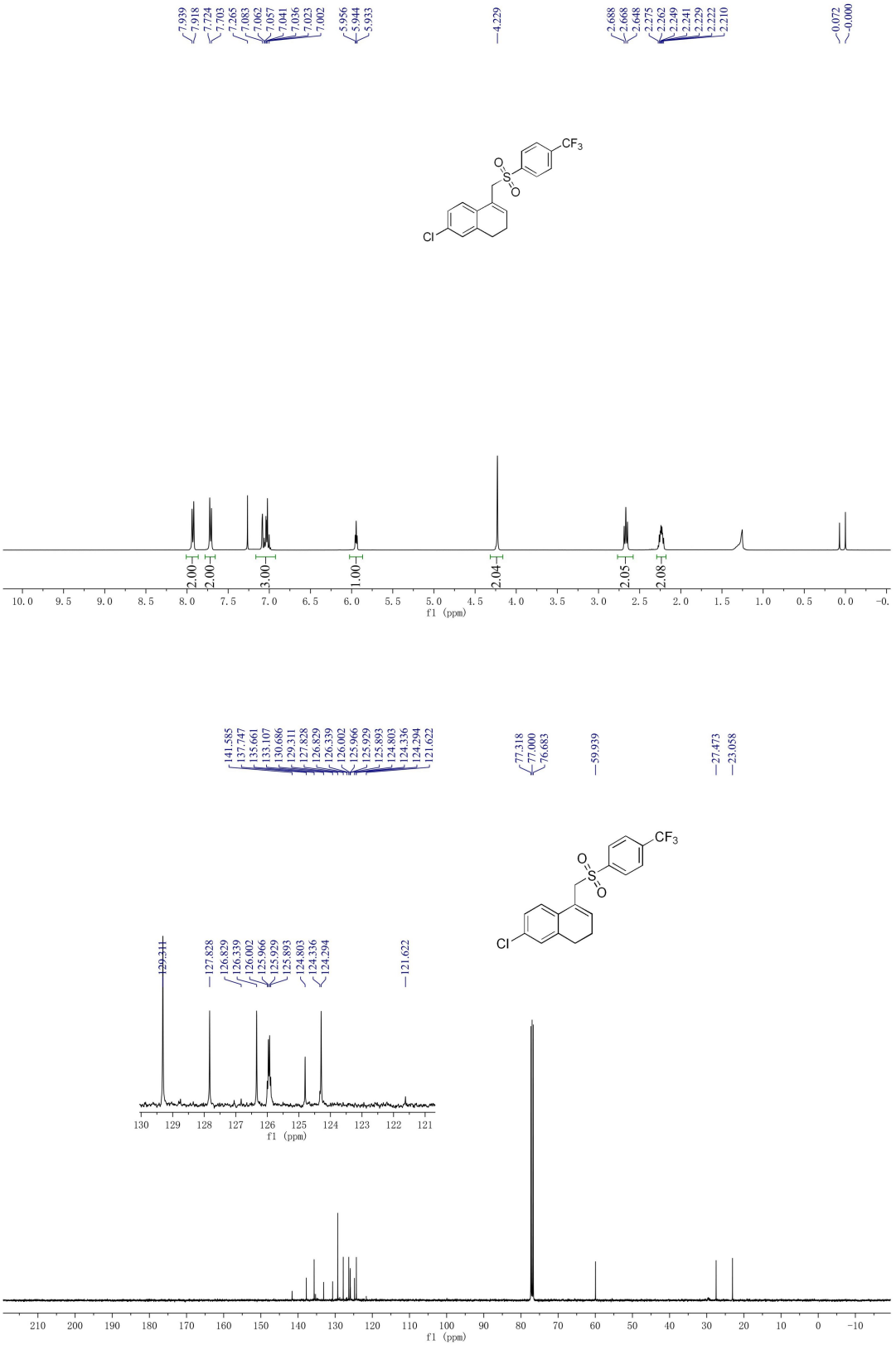
4-(((6-Chloro-3,4-dihydronaphthalen-1-yl)methyl)sulfonyl)benzonitrile (3hf)

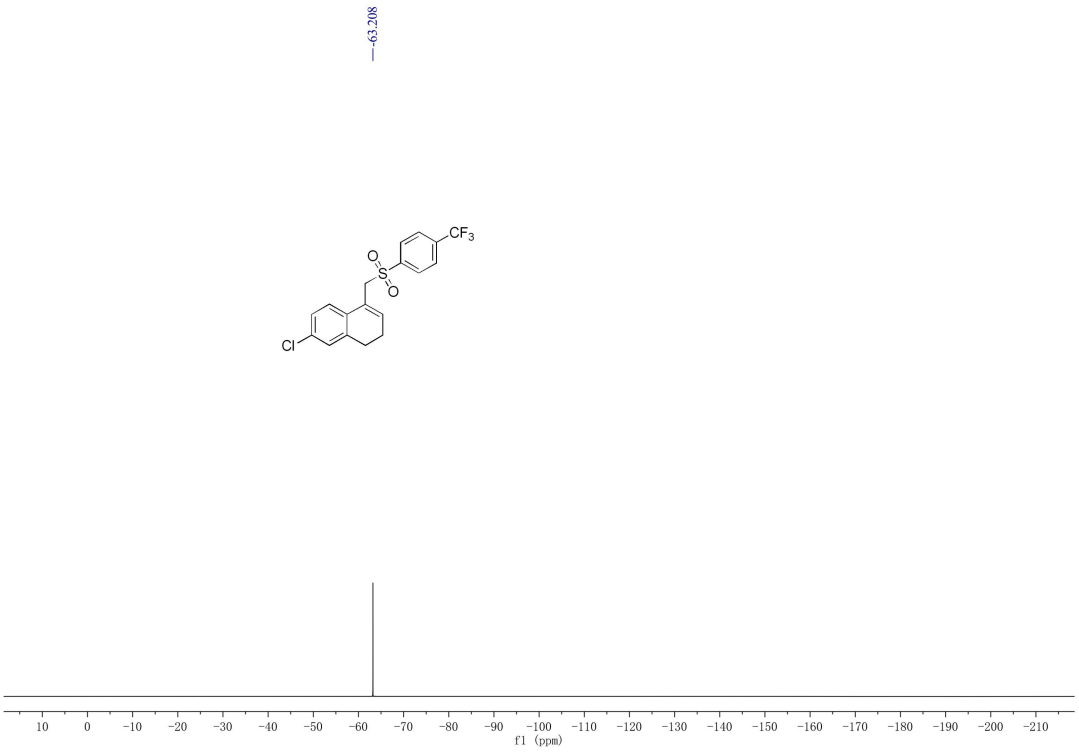




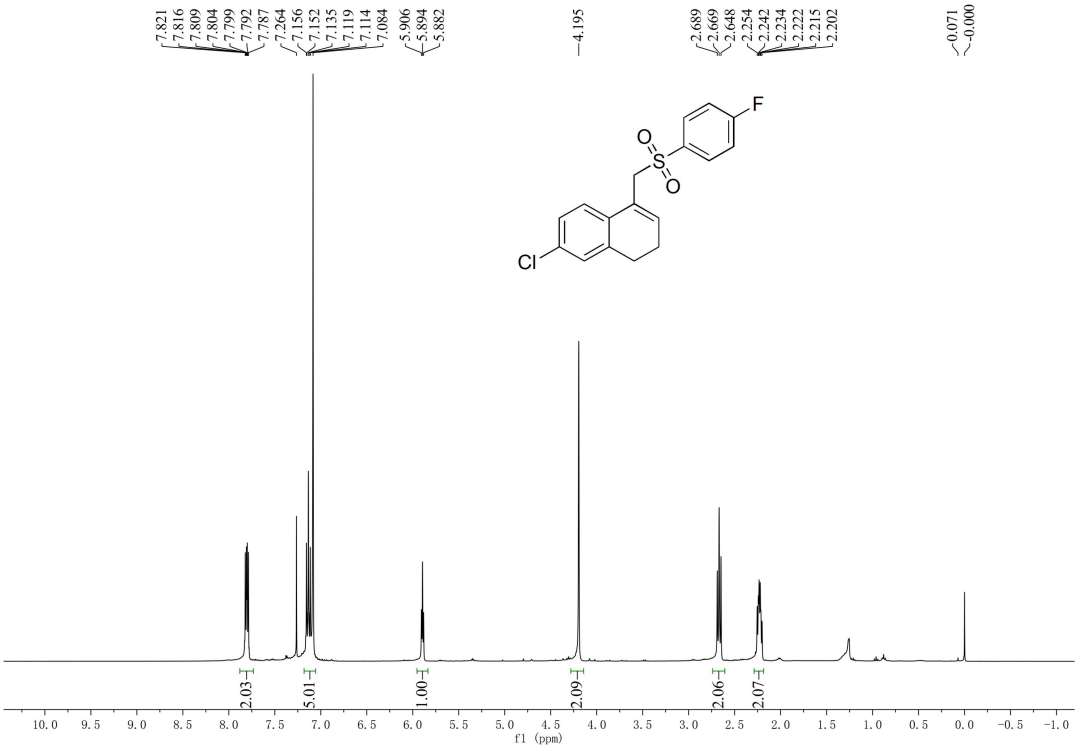
7-Chloro-4-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)-1,2-dihydronaphthalen

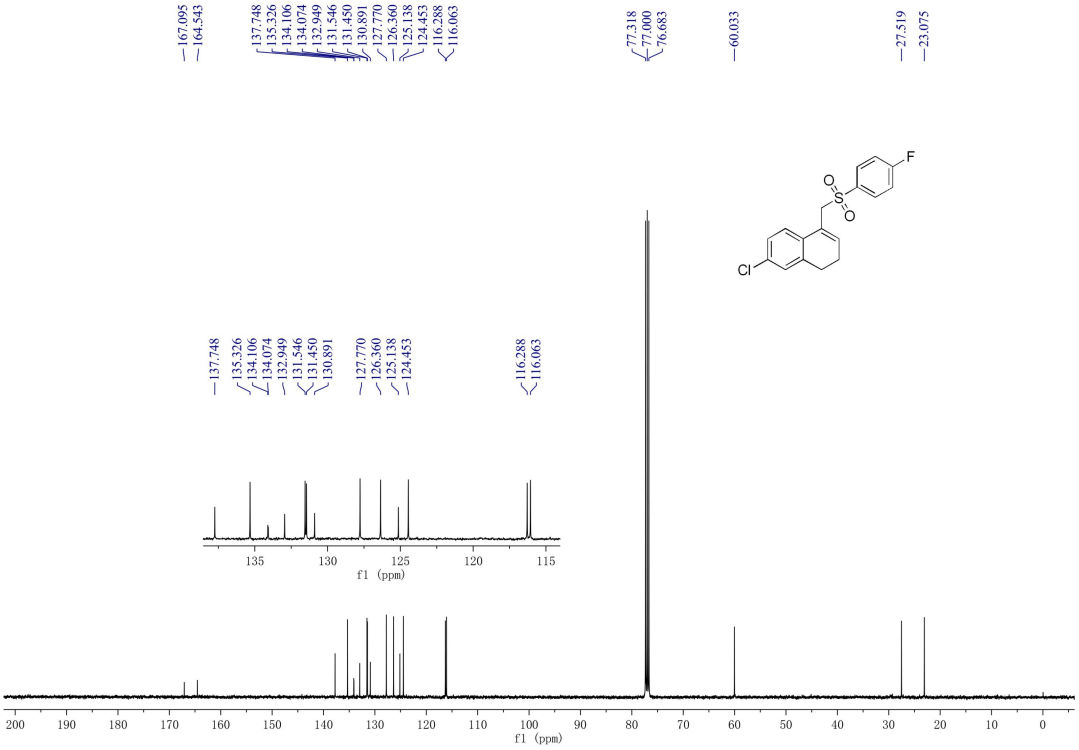
e (3hg)

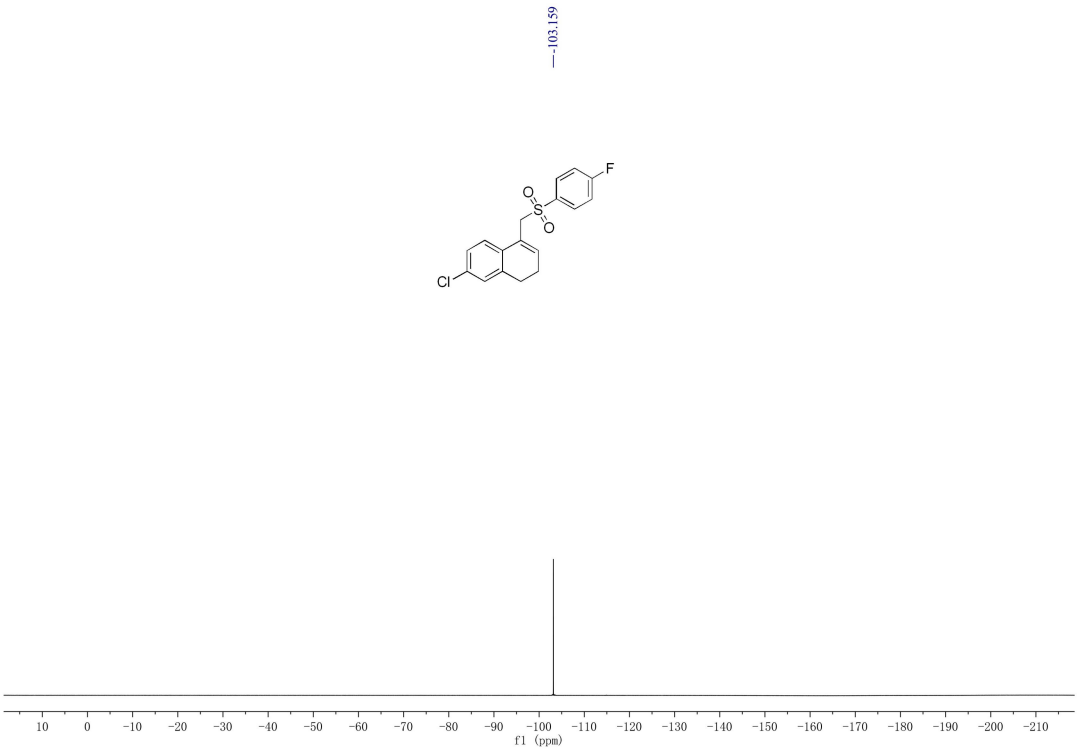



-63.208
CF3
O
S
O
Cl
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

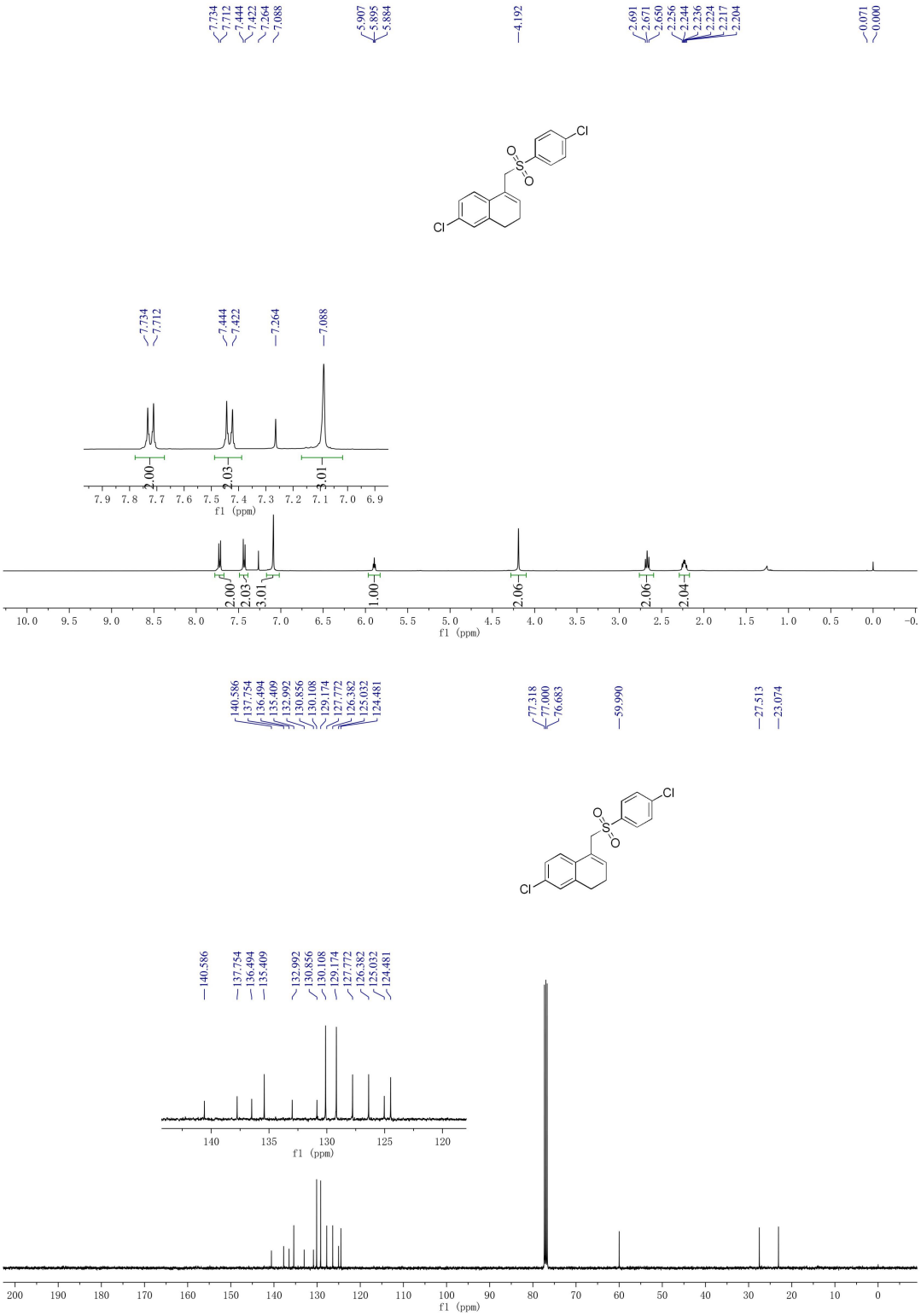
7-Chloro-4-(((4-fluorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3hh)



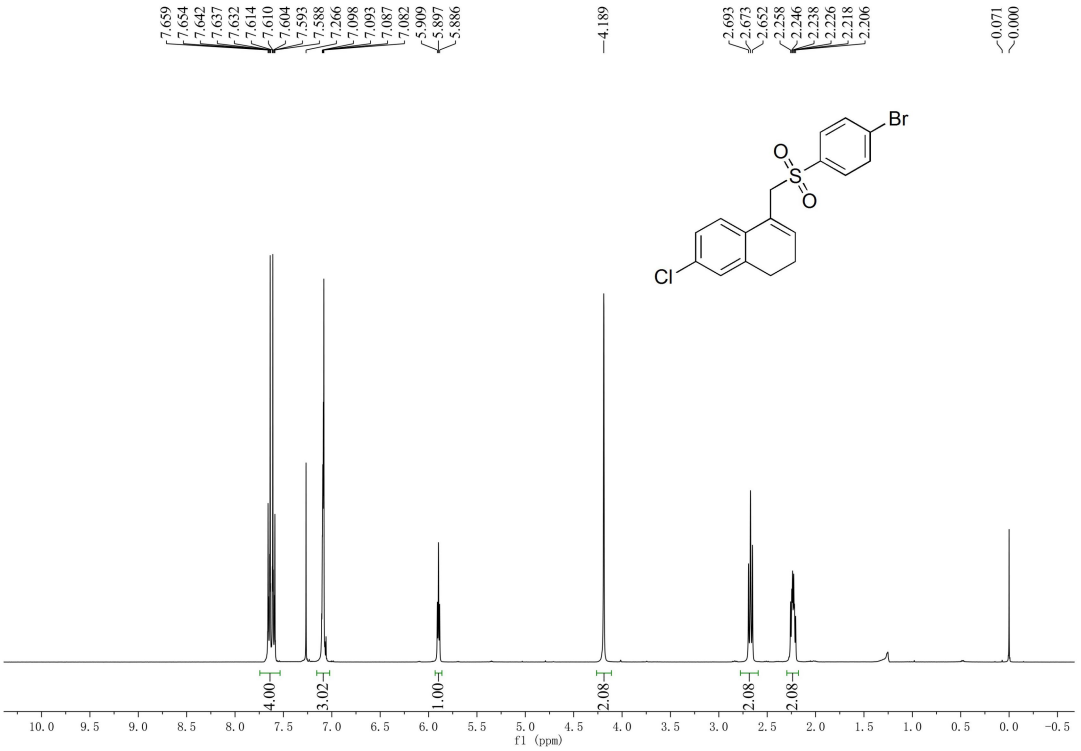


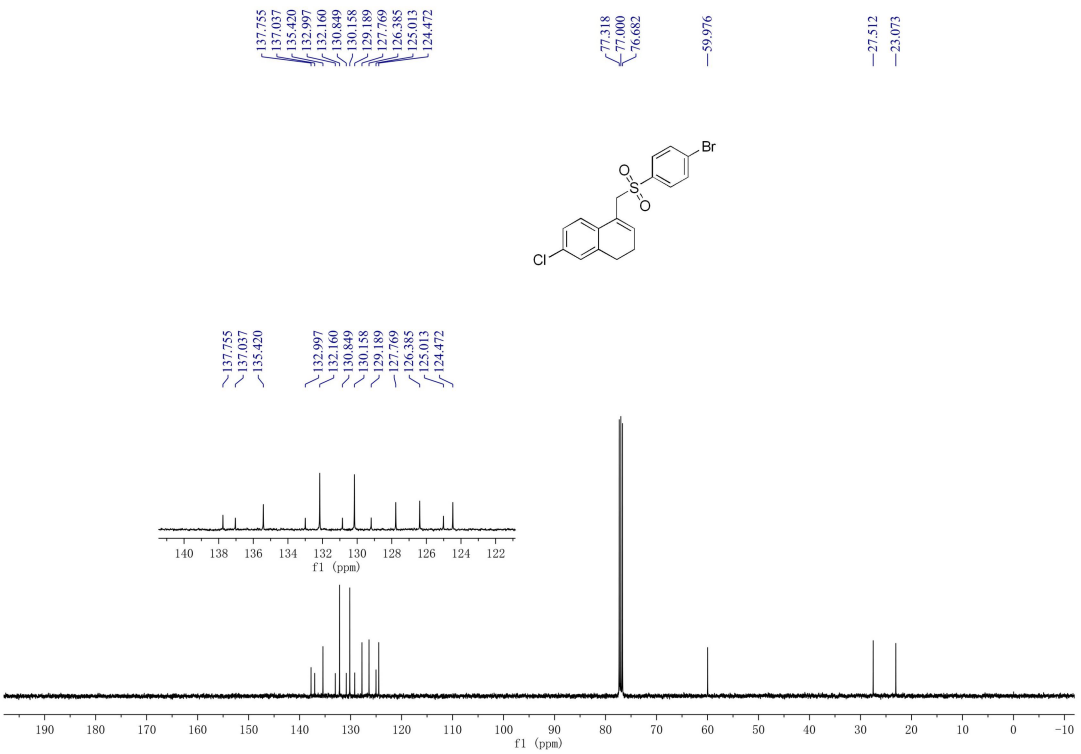

-103.159
F
O
S
O
Cl
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

7-Chloro-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3hi)

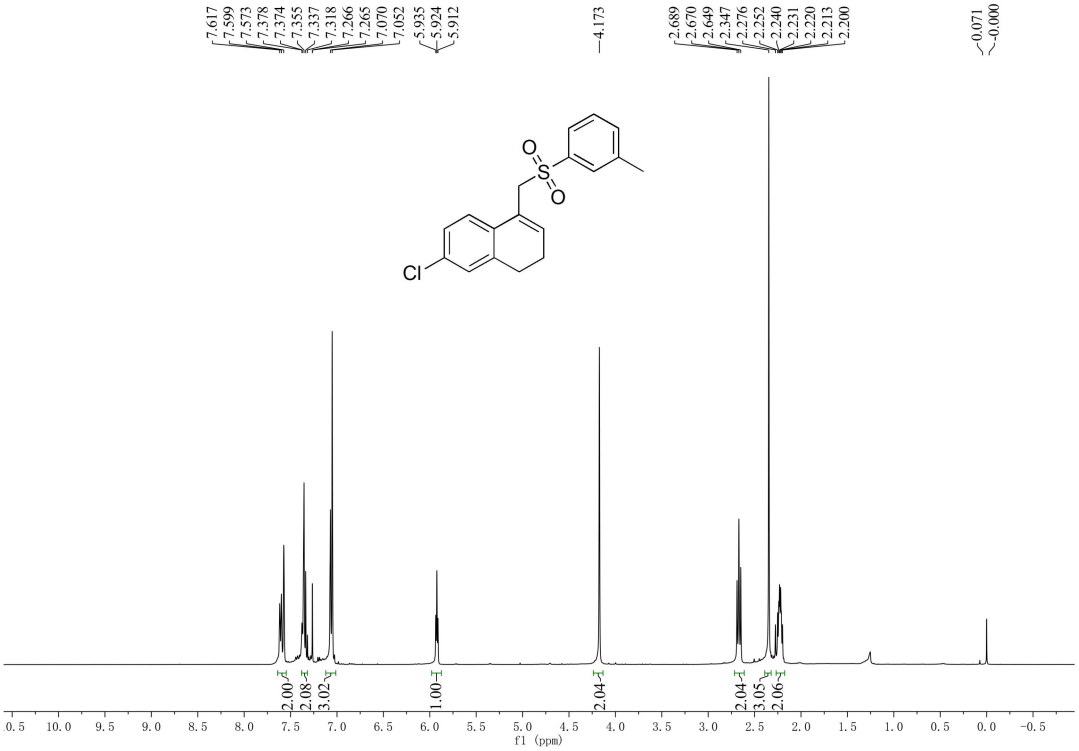


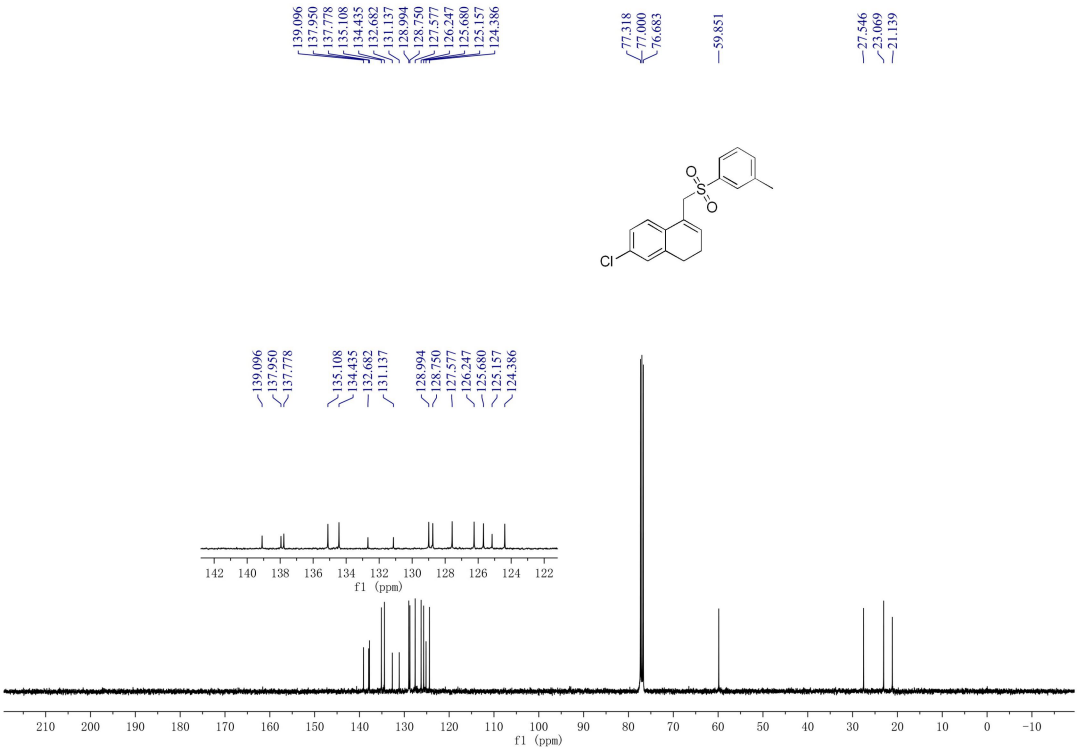
4-(((4-Bromophenyl)sulfonyl)methyl)-7-chloro-1,2-dihydronaphthalene (3hj)



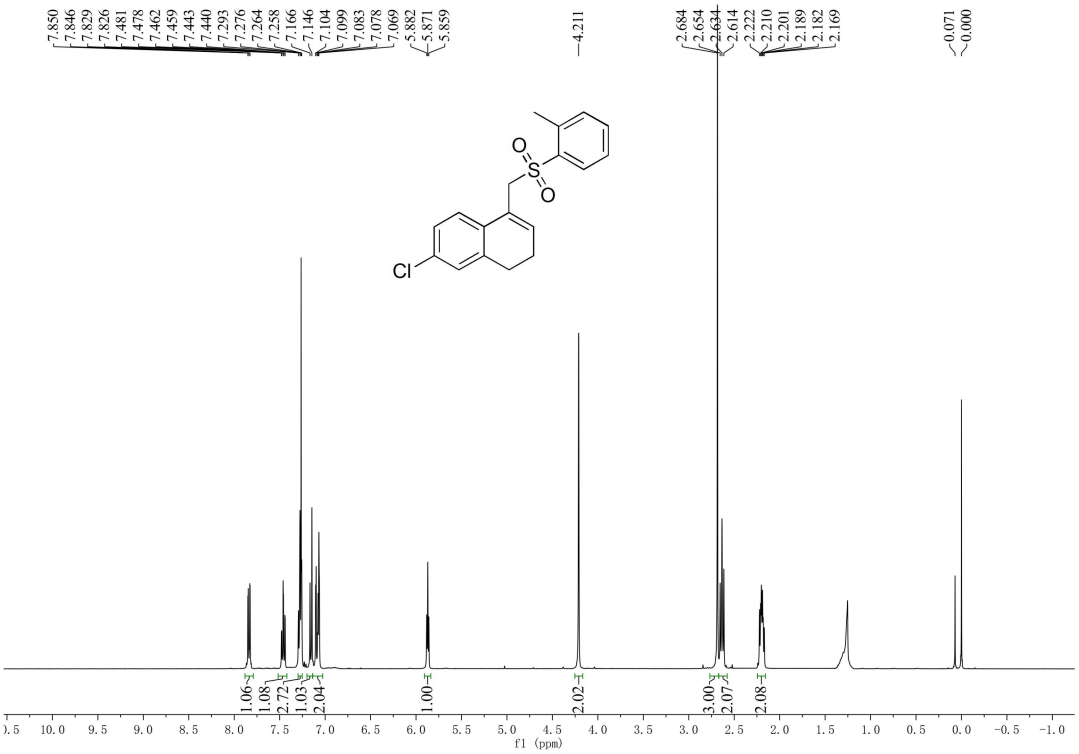


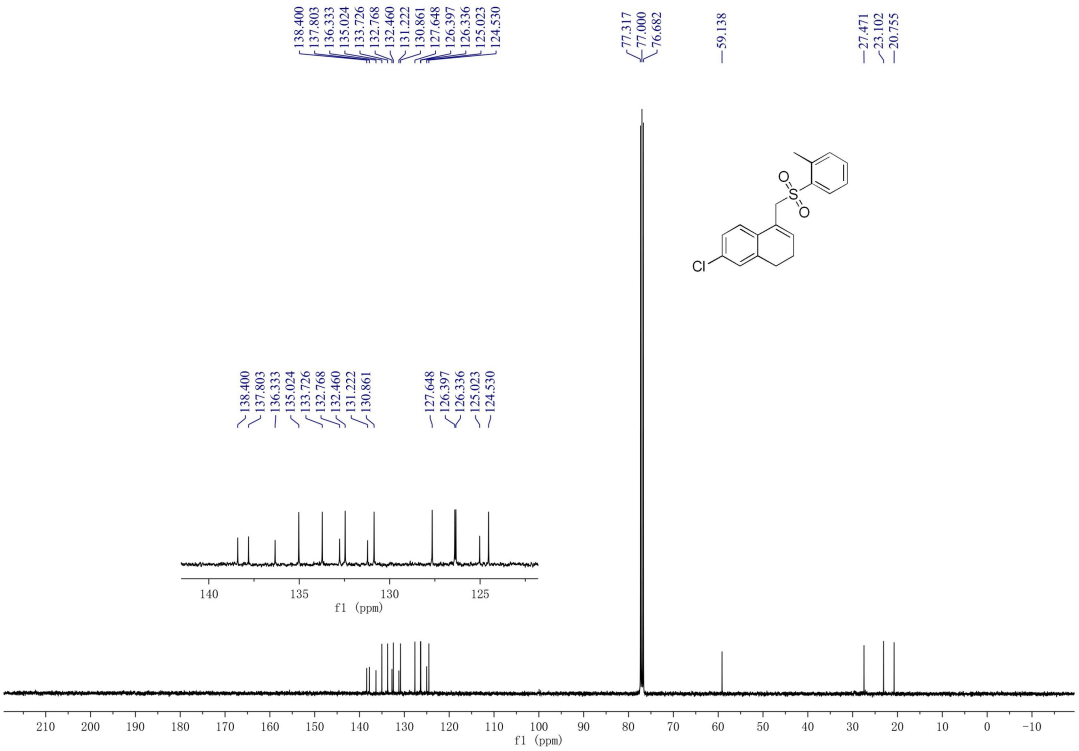
7-Chloro-4-((*m*-tolylsulfonyl)methyl)-1,2-dihydronaphthalene (3hk)



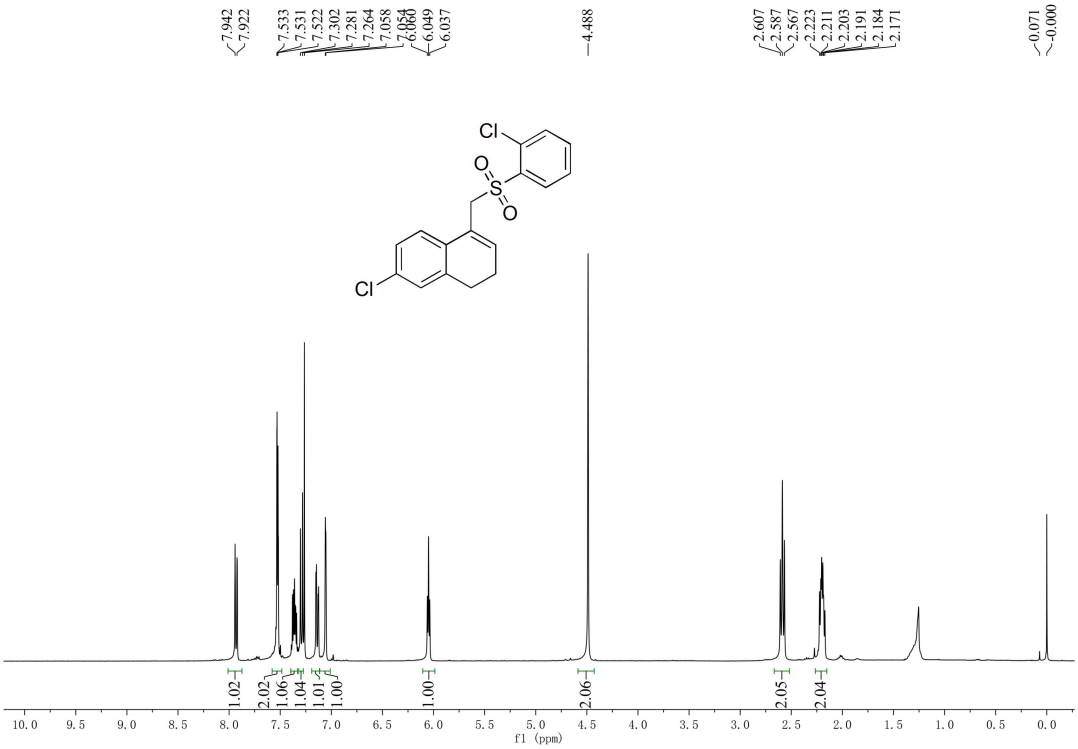


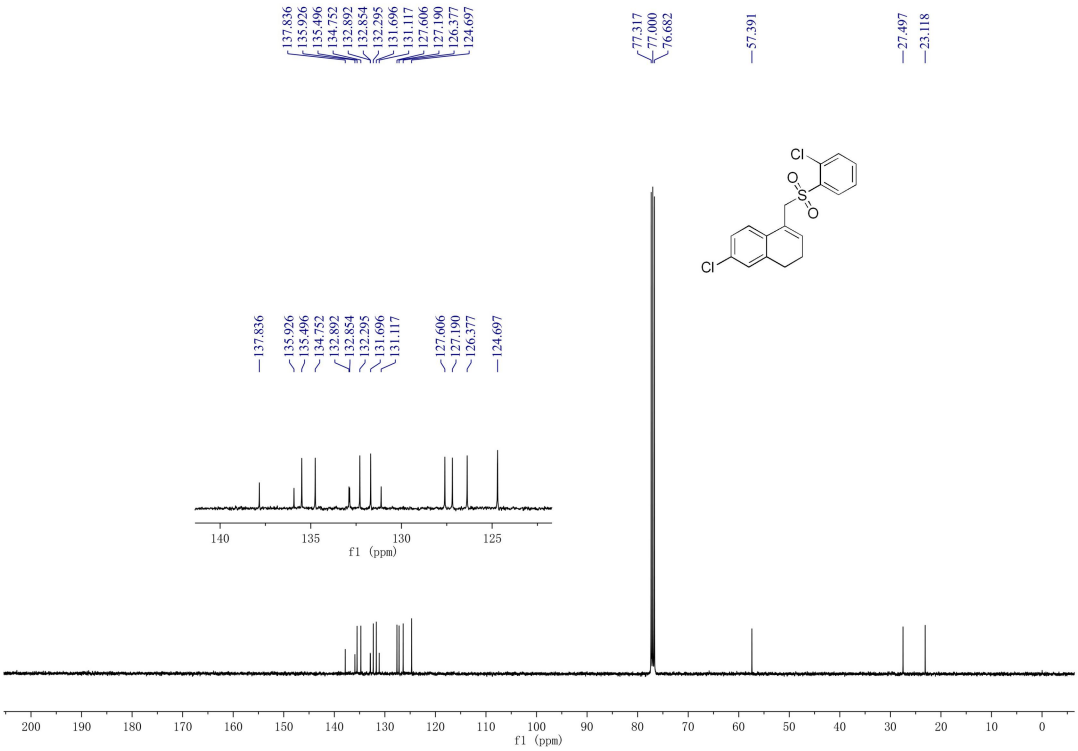
7-Chloro-4-((*o*-tolylsulfonyl)methyl)-1,2-dihydronaphthalene (3hl)



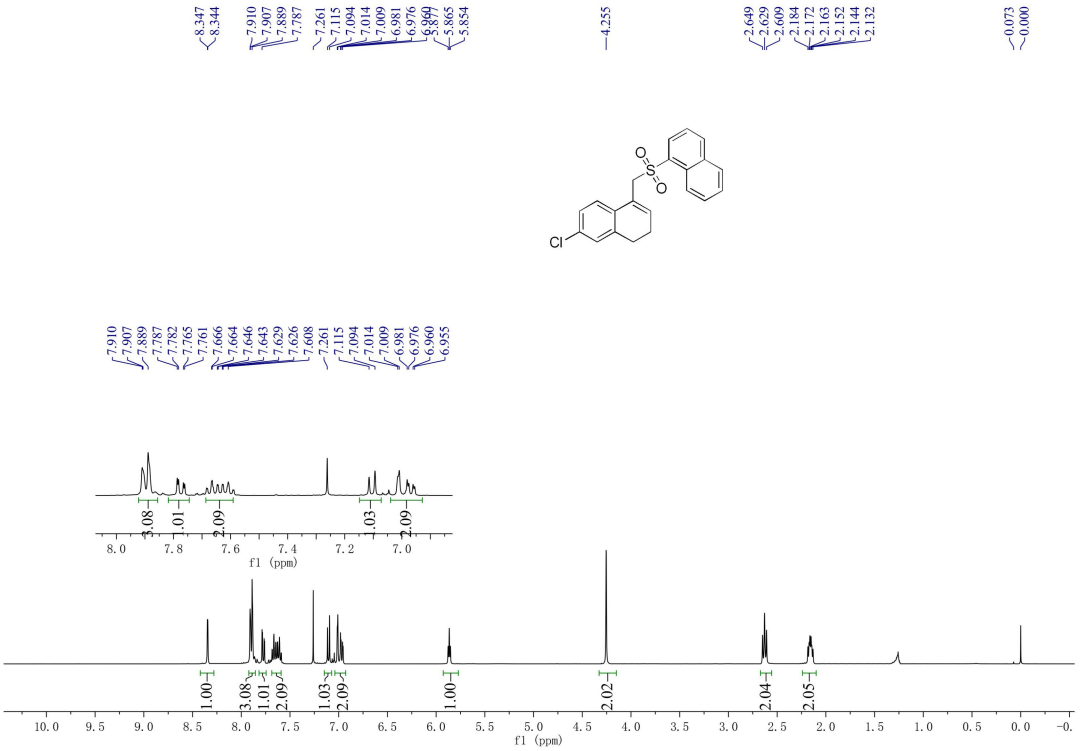


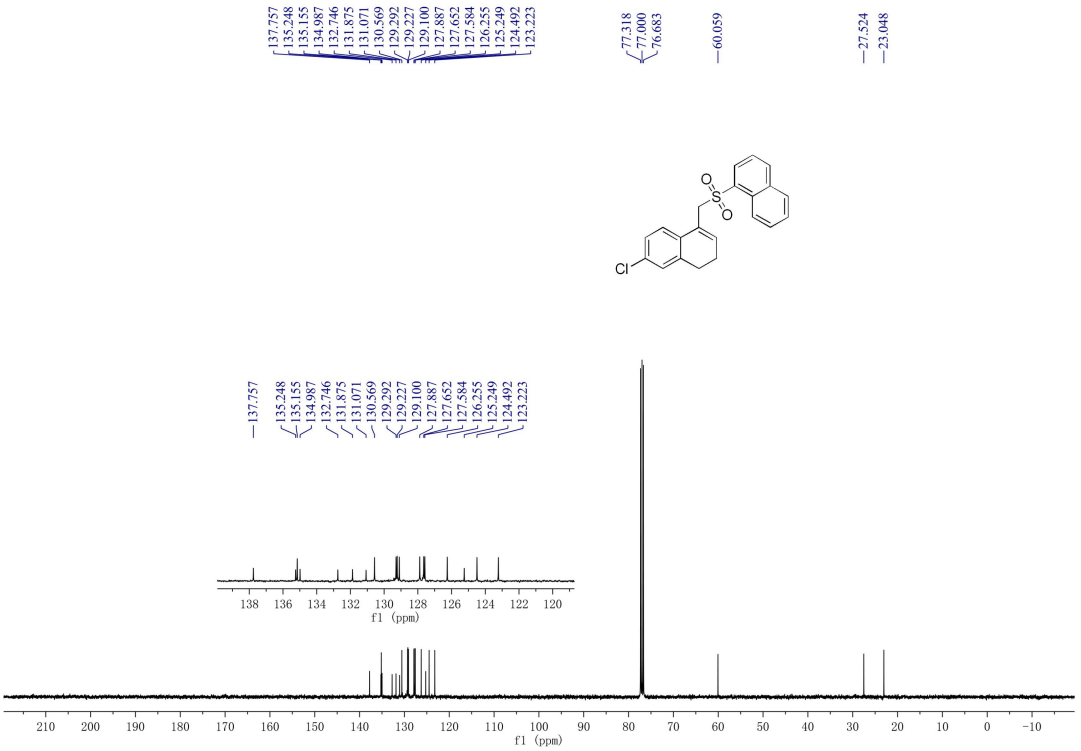
7-Chloro-4-(((2-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3hm)



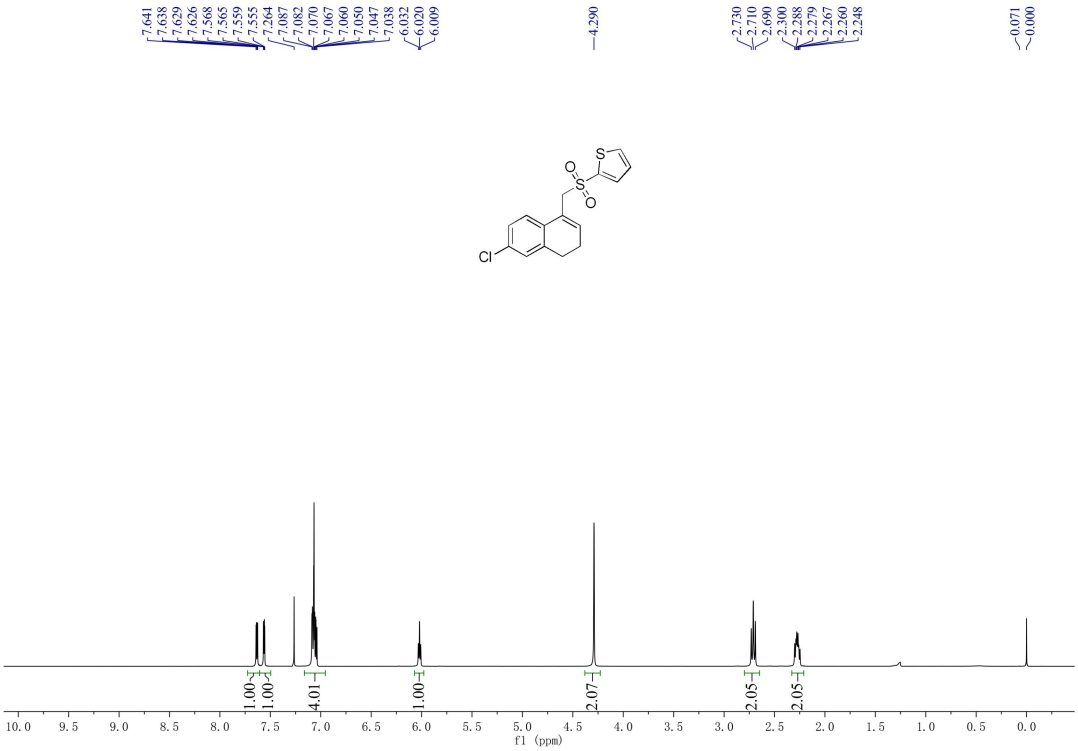


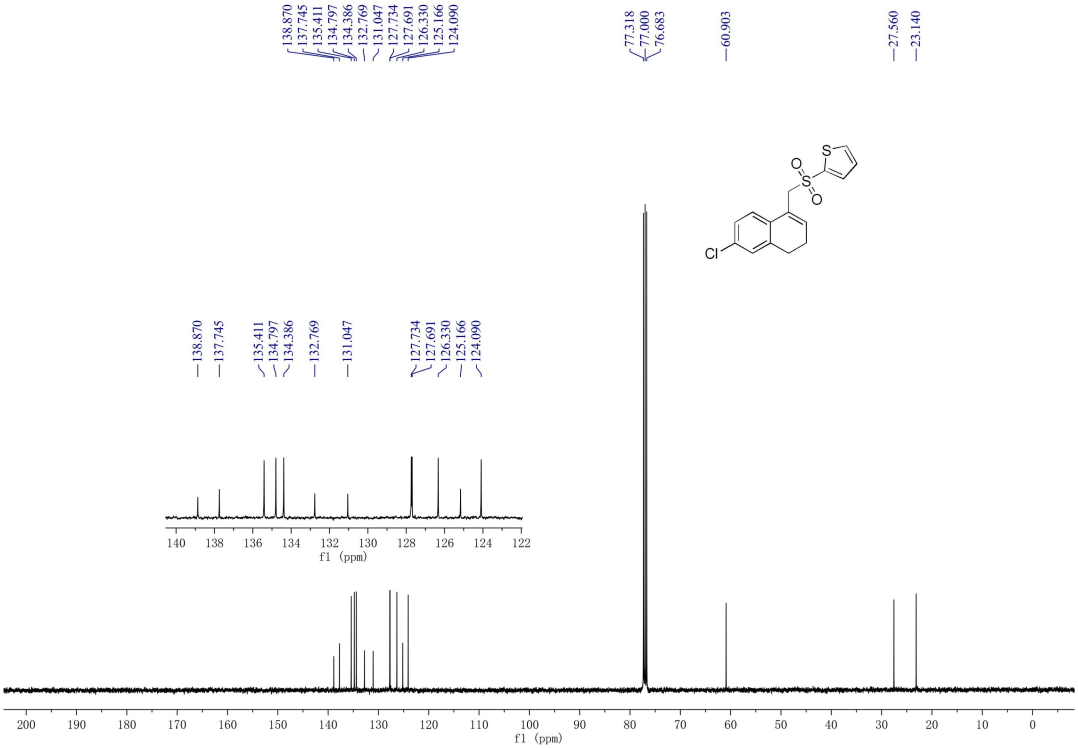
1-(((6-Chloro-3,4-dihydronaphthalen-1-yl)methyl)sulfonyl)naphthalene (3hn)



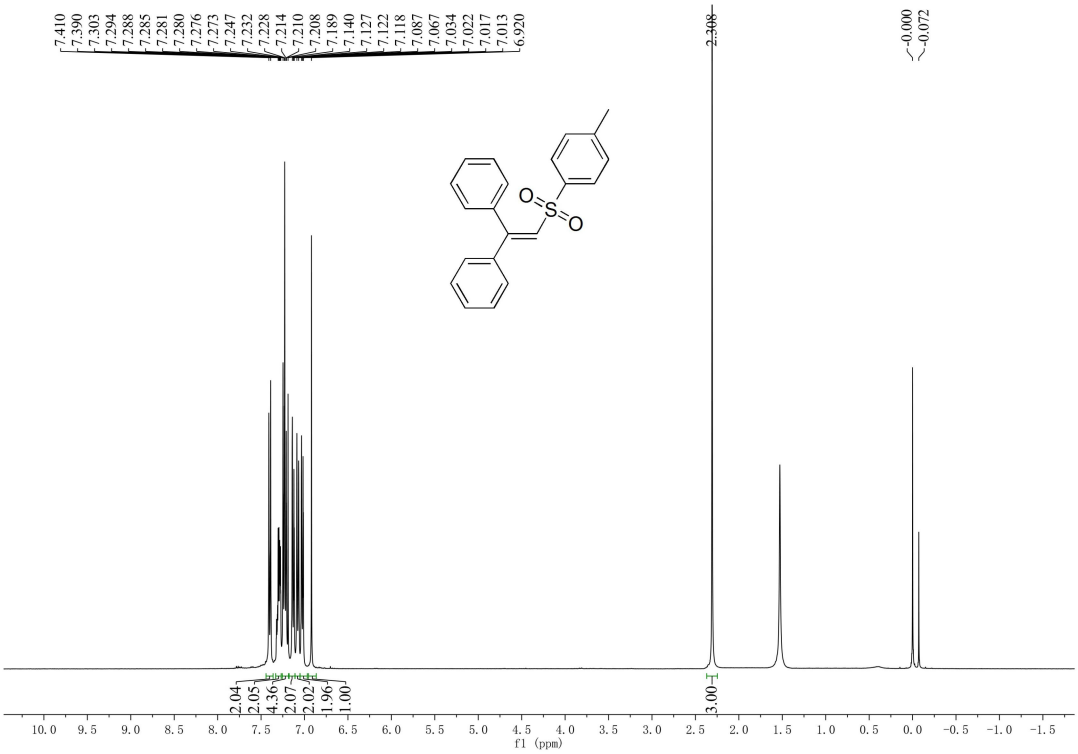


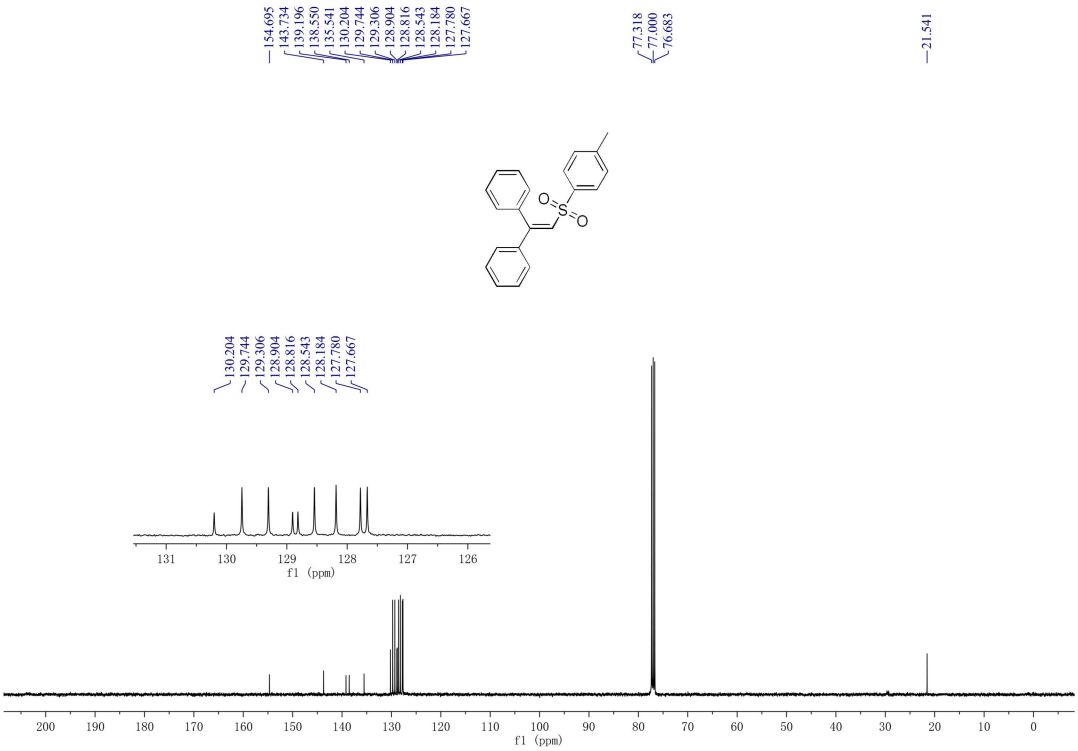
2-(((6-Chloro-3,4-dihydronaphthalen-1-yl)methyl)sulfonyl)thiophene (3ho)



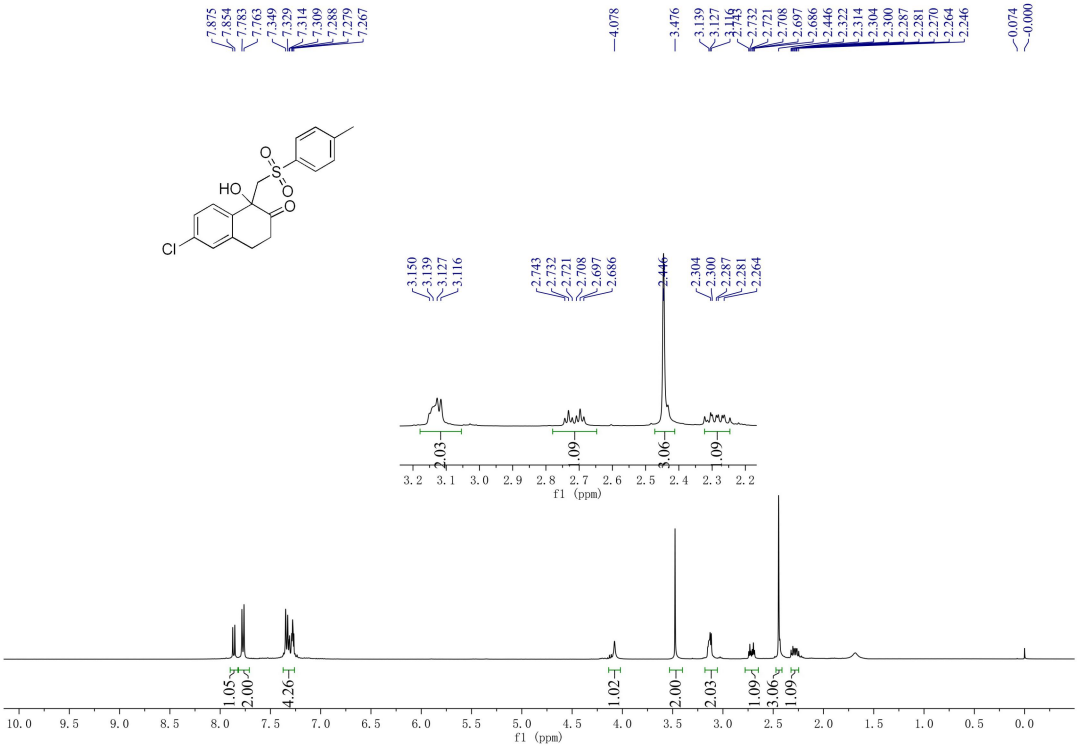


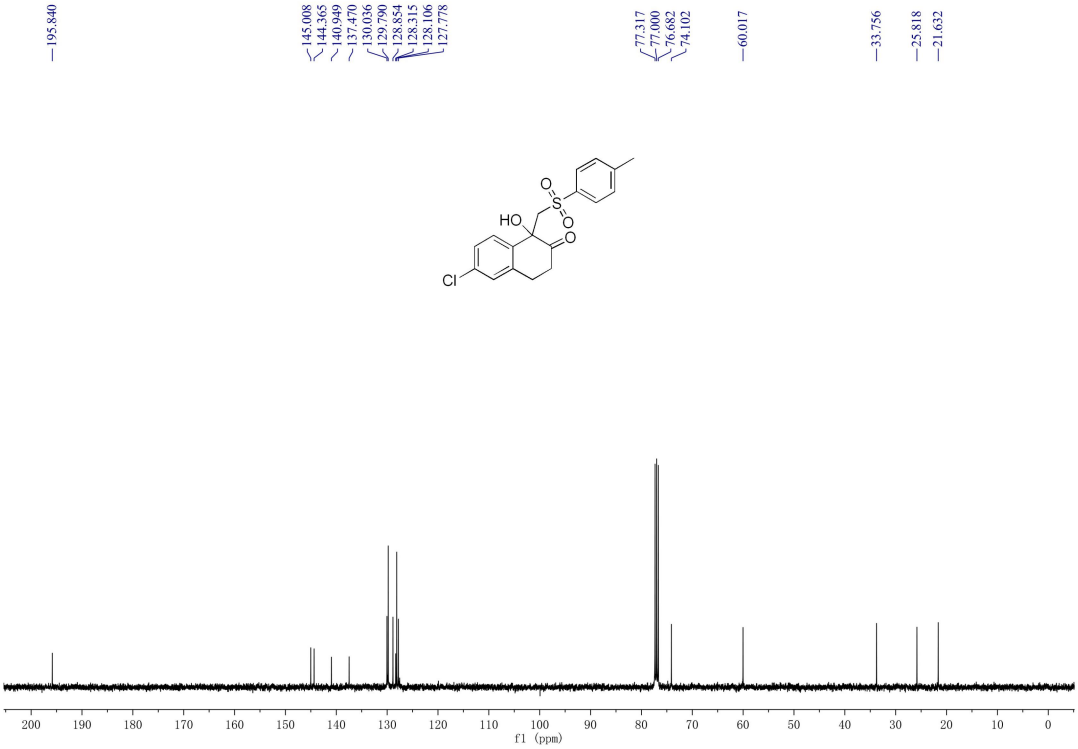
(2-Tosylethene-1,1-diyl)dibenzene (5)





6-Chloro-1-hydroxy-1-(tosylmethyl)-3,4-dihydronaphthalen-2(*1H*)-one (6)





6-Chloro-1-(tosylmethyl)naphthalene (7)