

# Supplementary Information

## **Rhodium-Catalyzed Annulation of Primary Benzylamine with $\alpha$ -Diazo Ketone towards Isoquinoline**

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### **Table of Contents**

<b>1. Mechanism</b>	<b>S2</b>
<b>2. Copies of the <math>^1\text{H}</math> NMR and <math>^{13}\text{C}</math> NMR Spectra</b>	<b>S3</b>

## 1. Mechanism

### 1.1 Detection of H<sub>2</sub>

A piece of filter paper soaked with the solution of phosphomolybdic acid/PdCl<sub>2</sub> is a sensitive detector of reducing gas, such as H<sub>2</sub> and CO.

The wet test paper turned dark blue when absorbing purified H<sub>2</sub> (Entry 1).

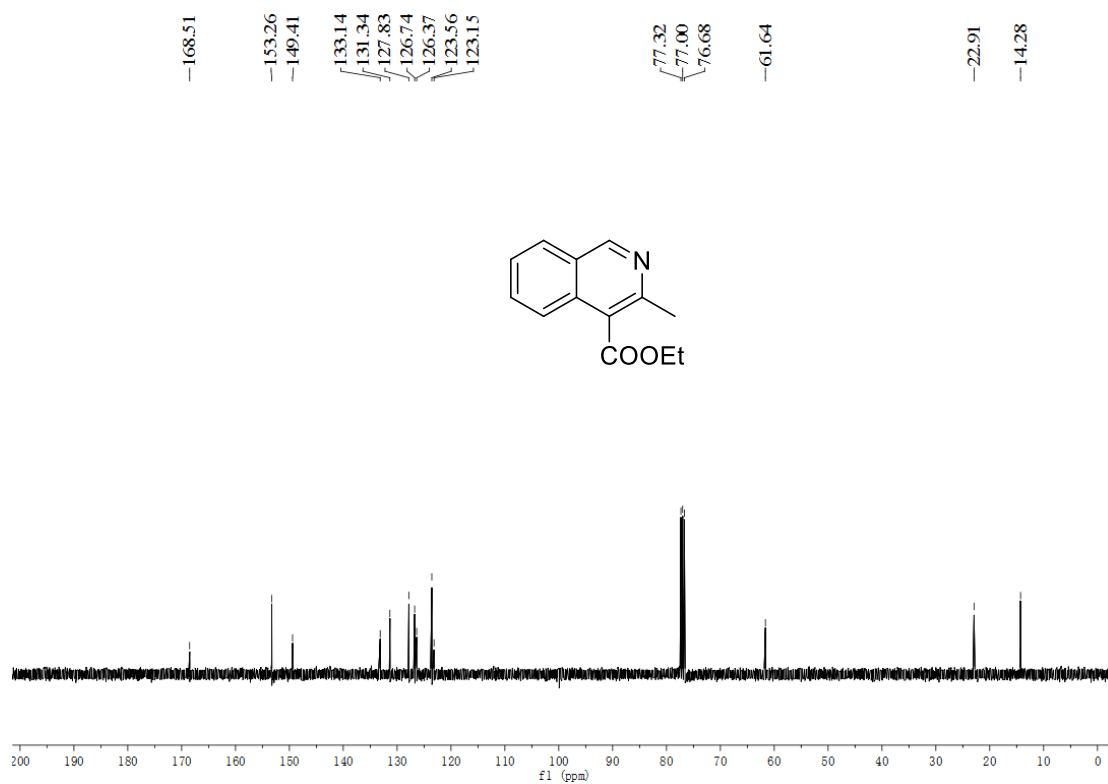
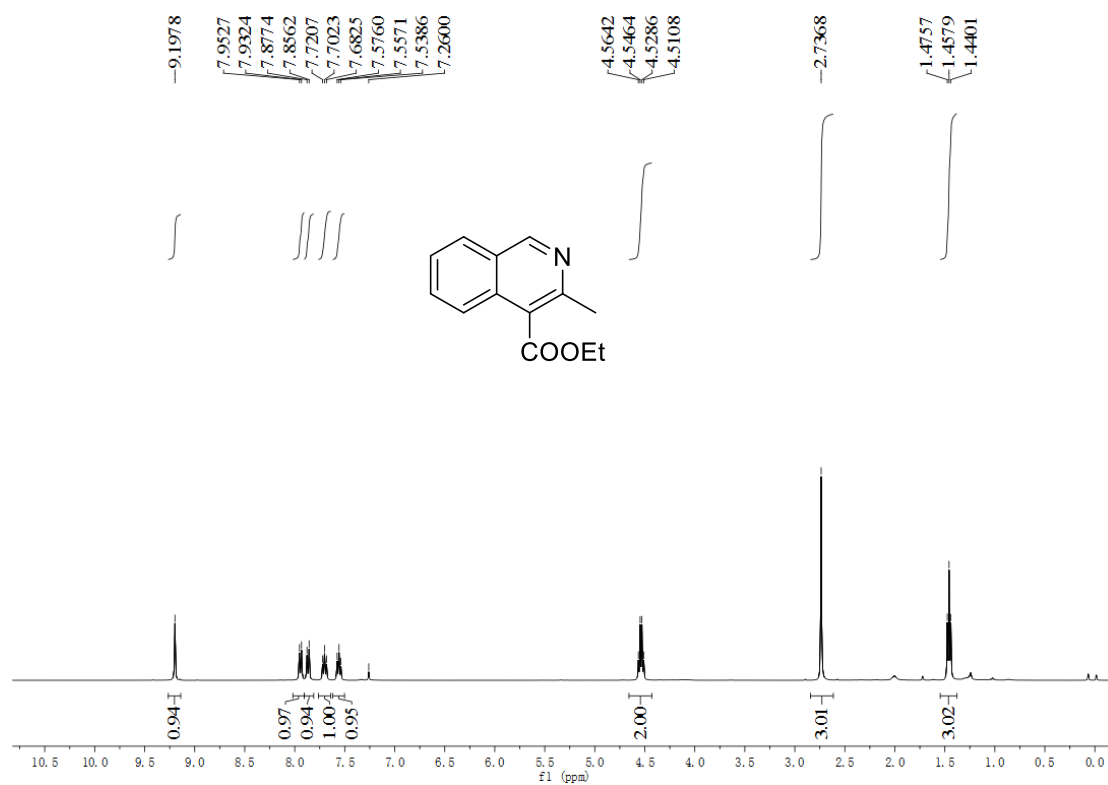


Entry	2	3	4	5
[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	√	√	×	√
AgSbF <sub>6</sub>	√	√	√	×
Atmosphere	Air	N <sub>2</sub>	Air	Air
Color of paper	+	+	-	+

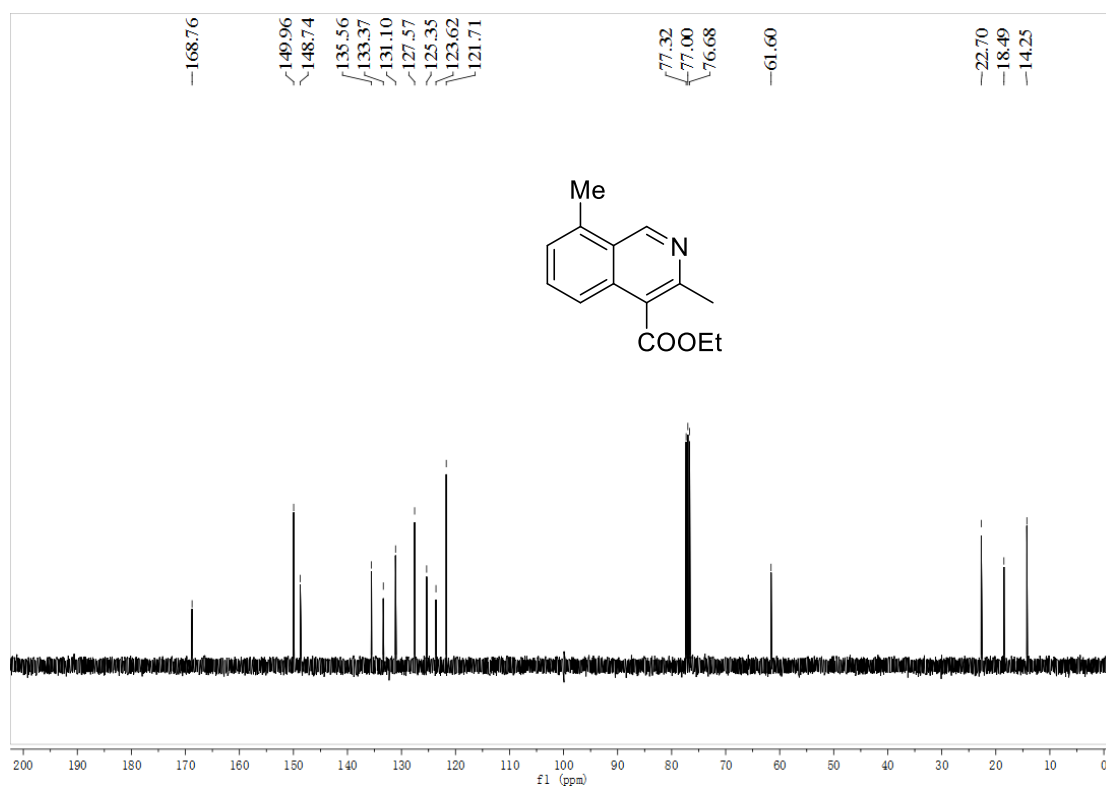
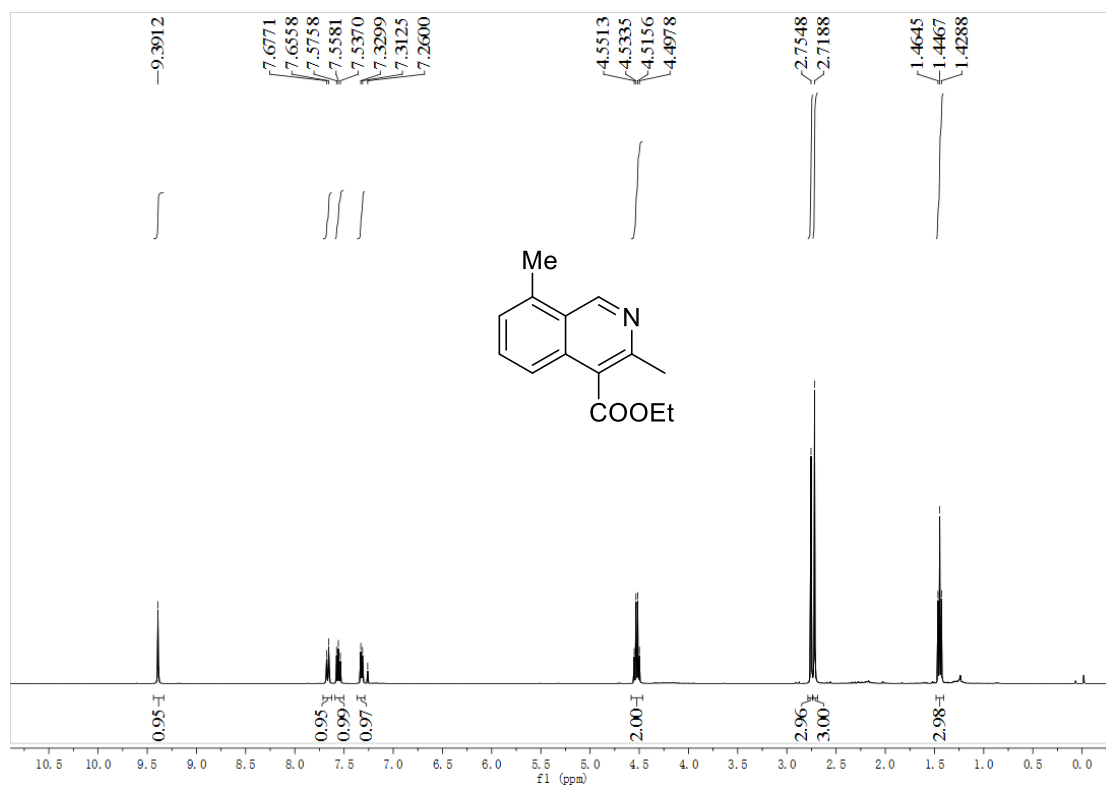
“-” means negative result; “+” means positive result.

## 2. Copies of the $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

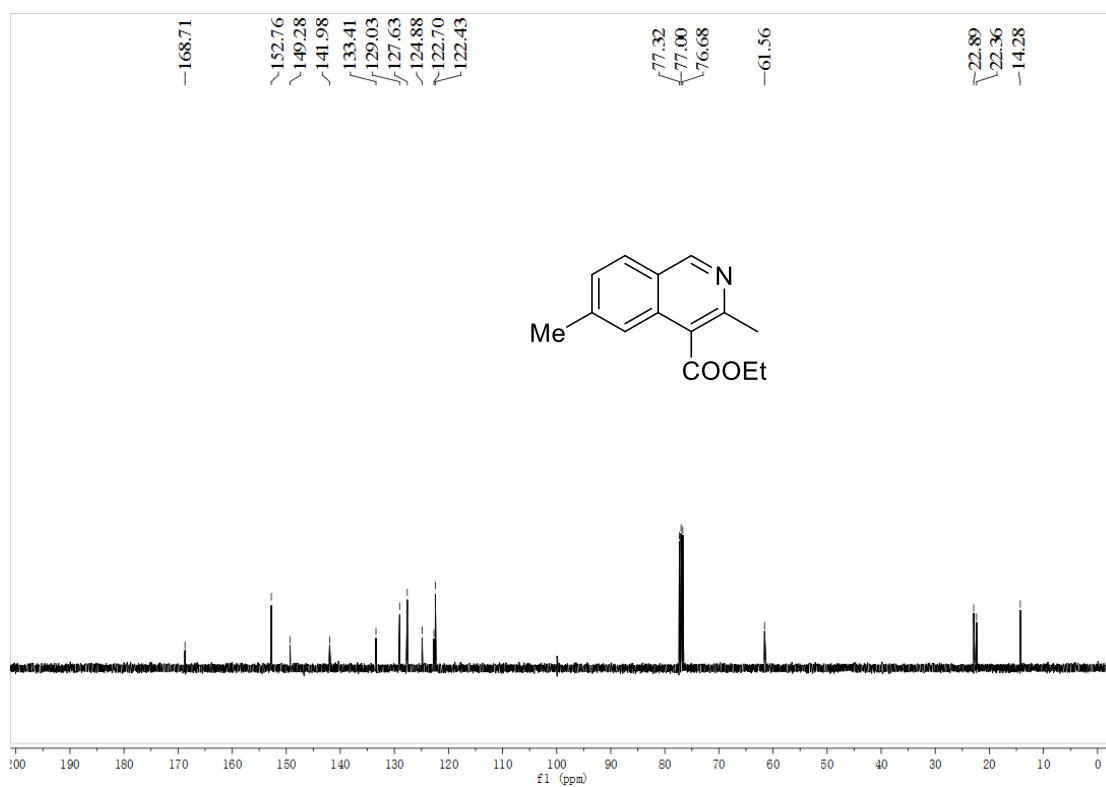
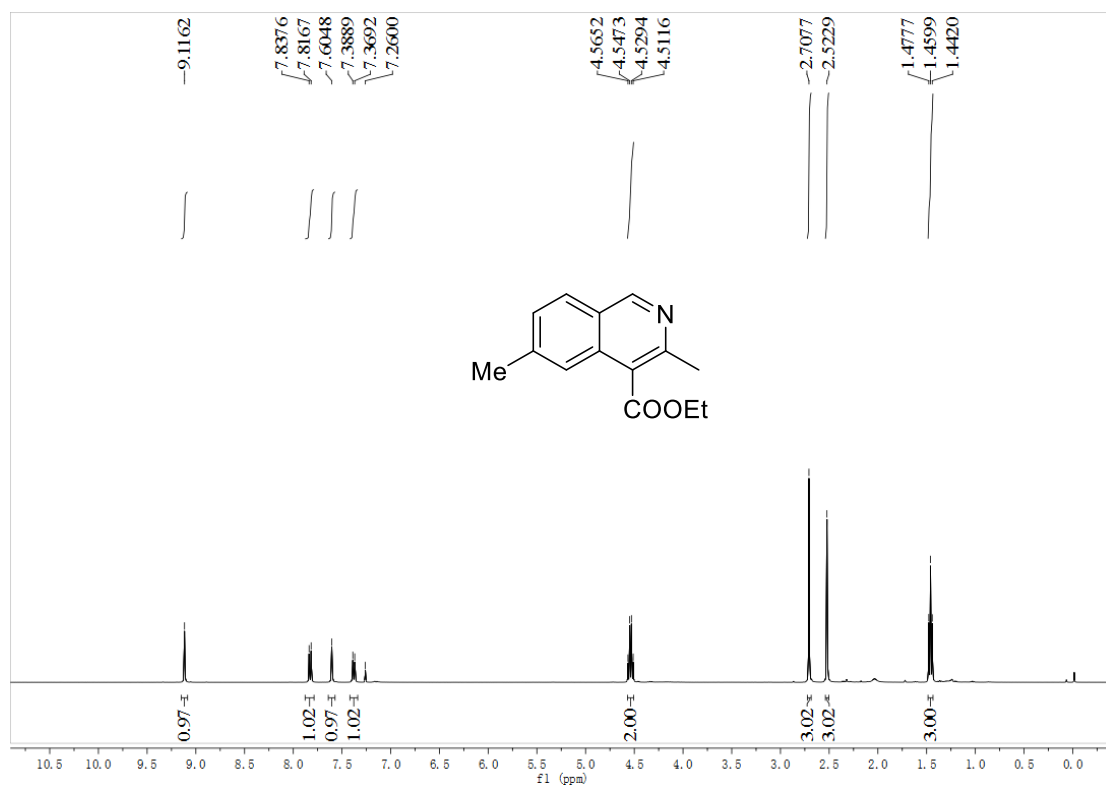
### Ethyl 3-methylisoquinoline-4-carboxylate (3aa)



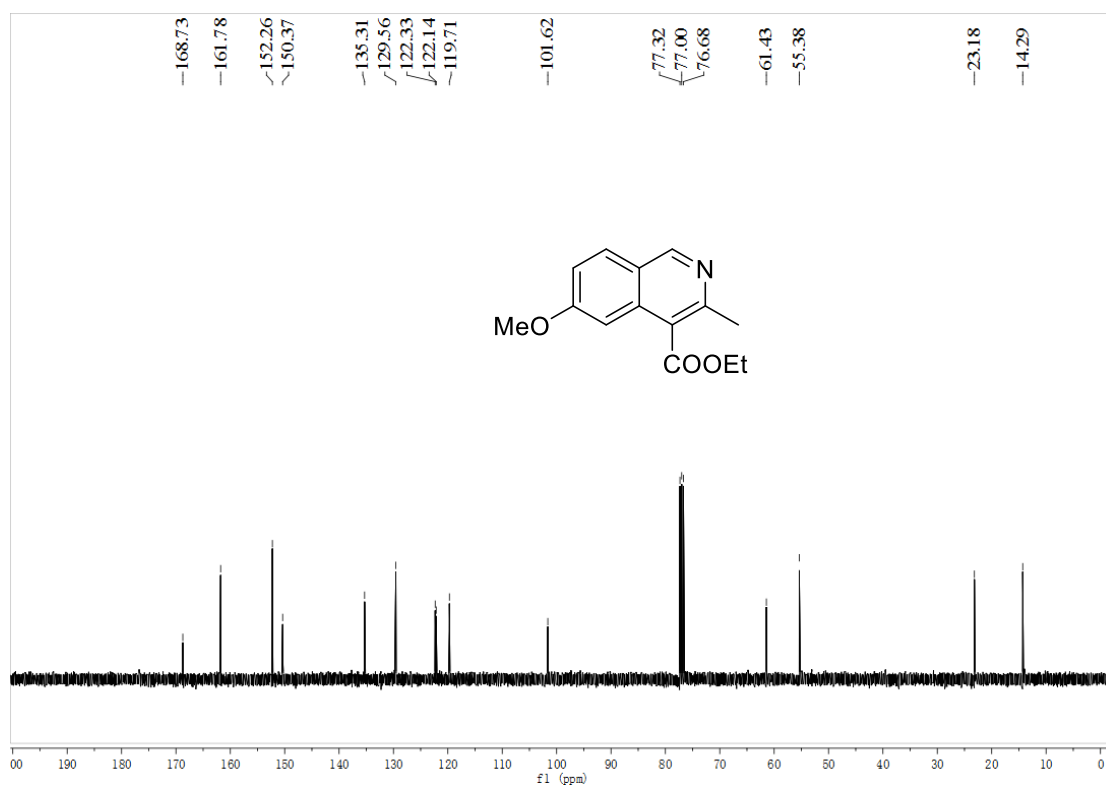
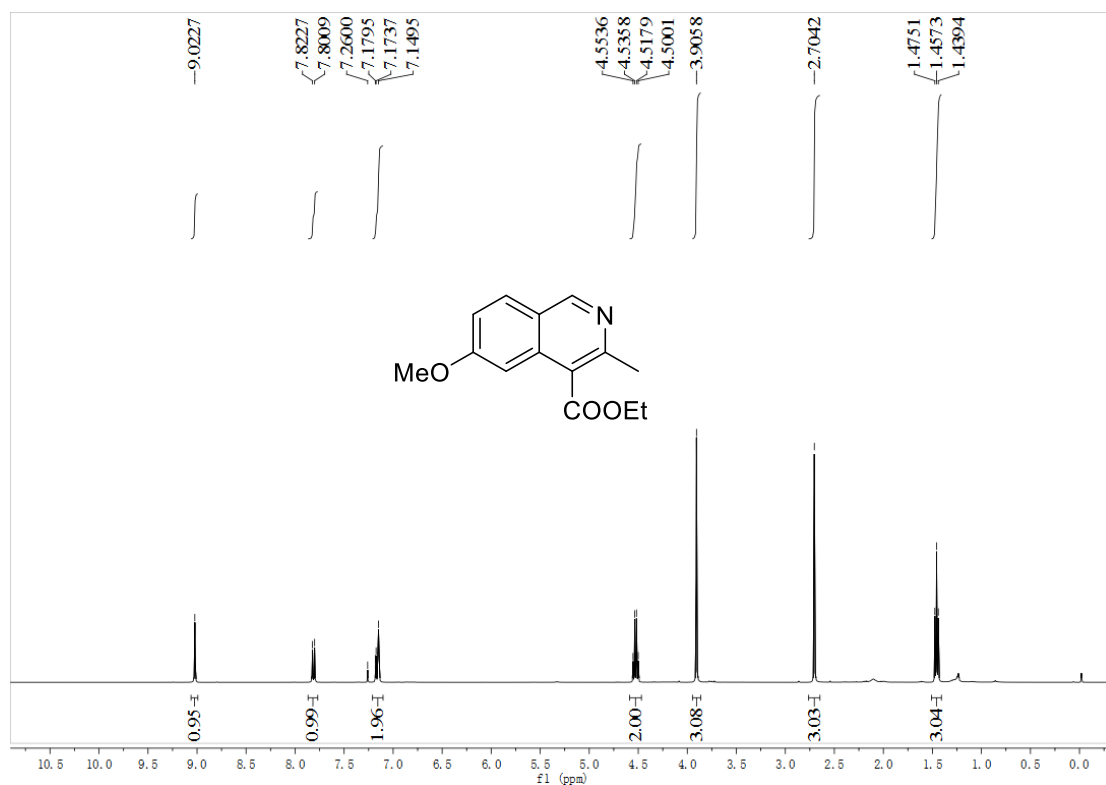
# **Ethyl 3,8-dimethylisoquinoline-4-carboxylate (3ba)**



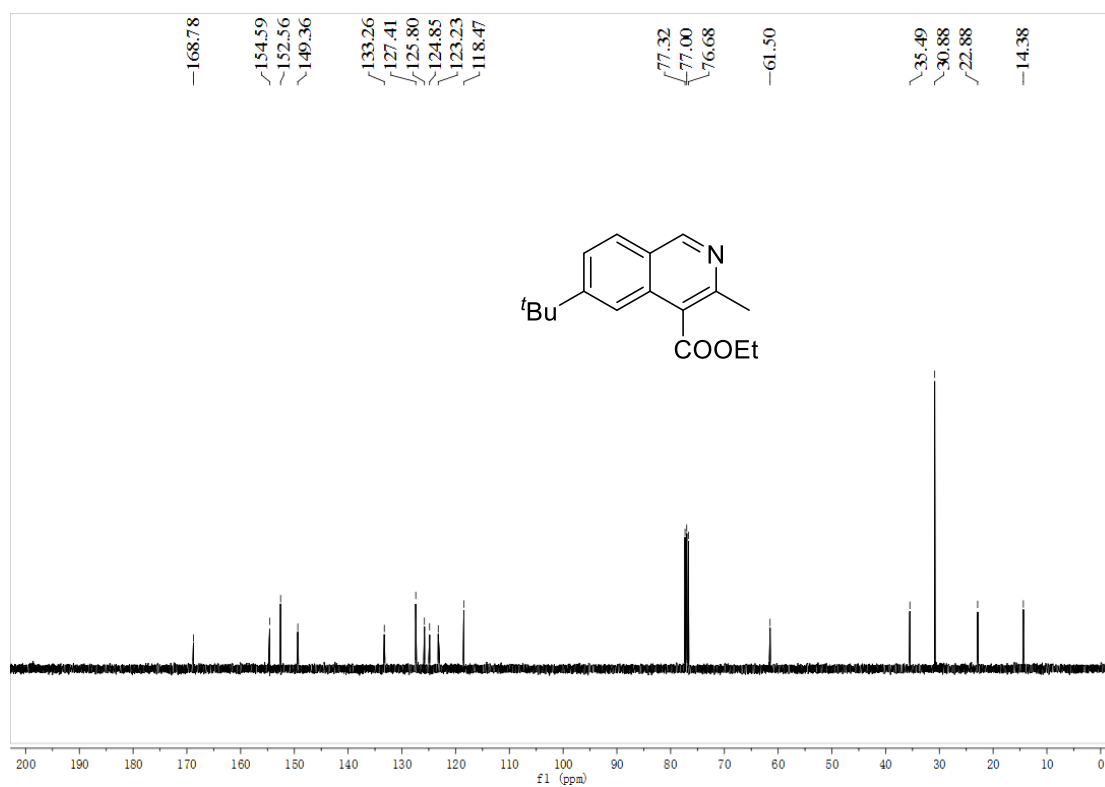
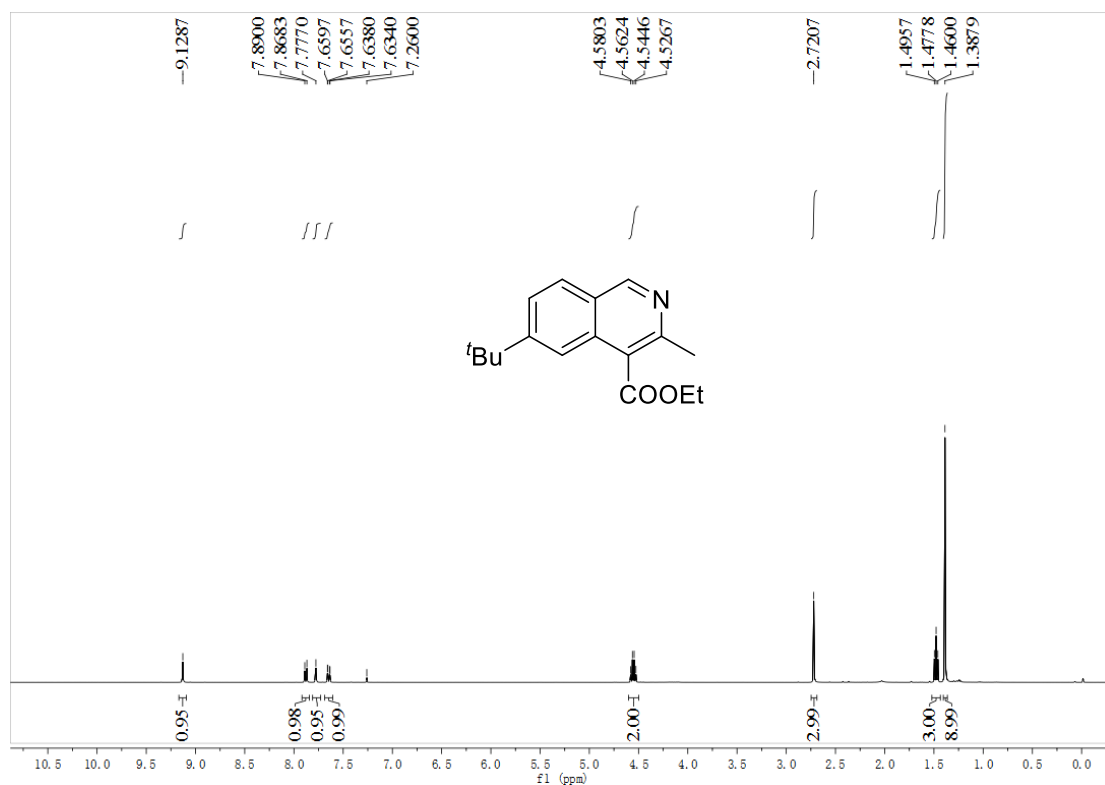
# **Ethyl 3,6-dimethyloisoquinoline-4-carboxylate (3ca)**



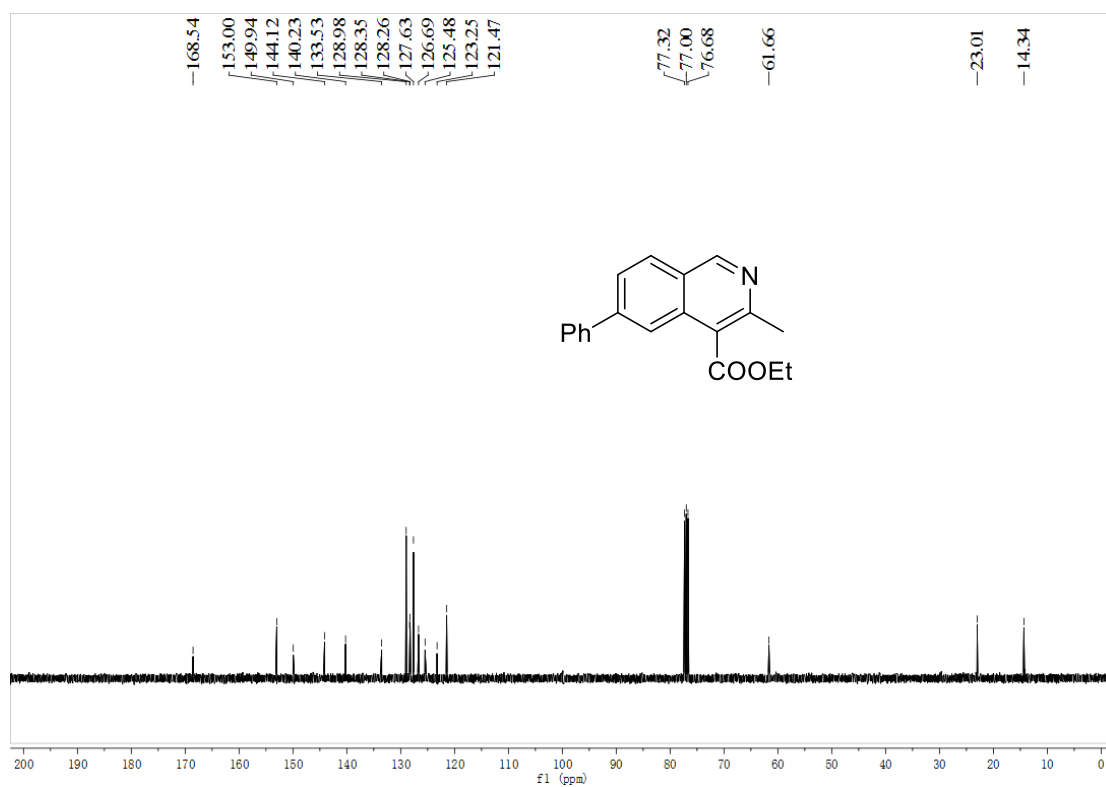
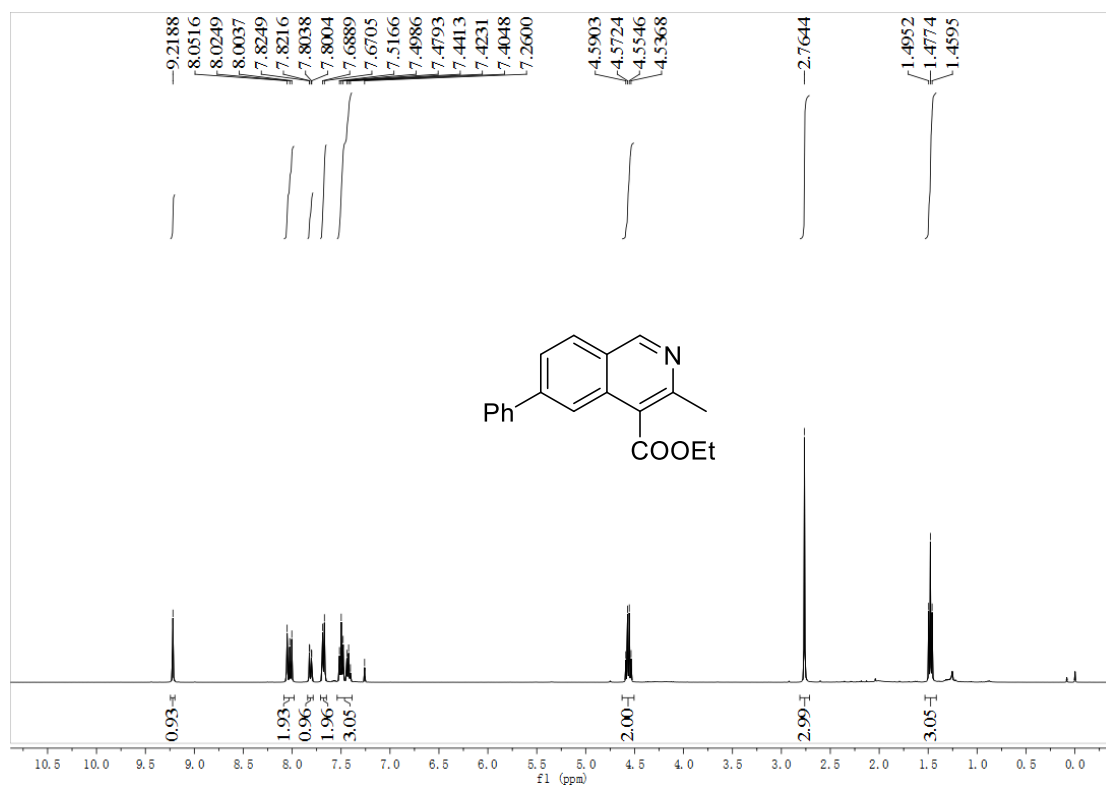
# **Ethyl 6-methoxy-3-methylisoquinoline-4-carboxylate (3da)**



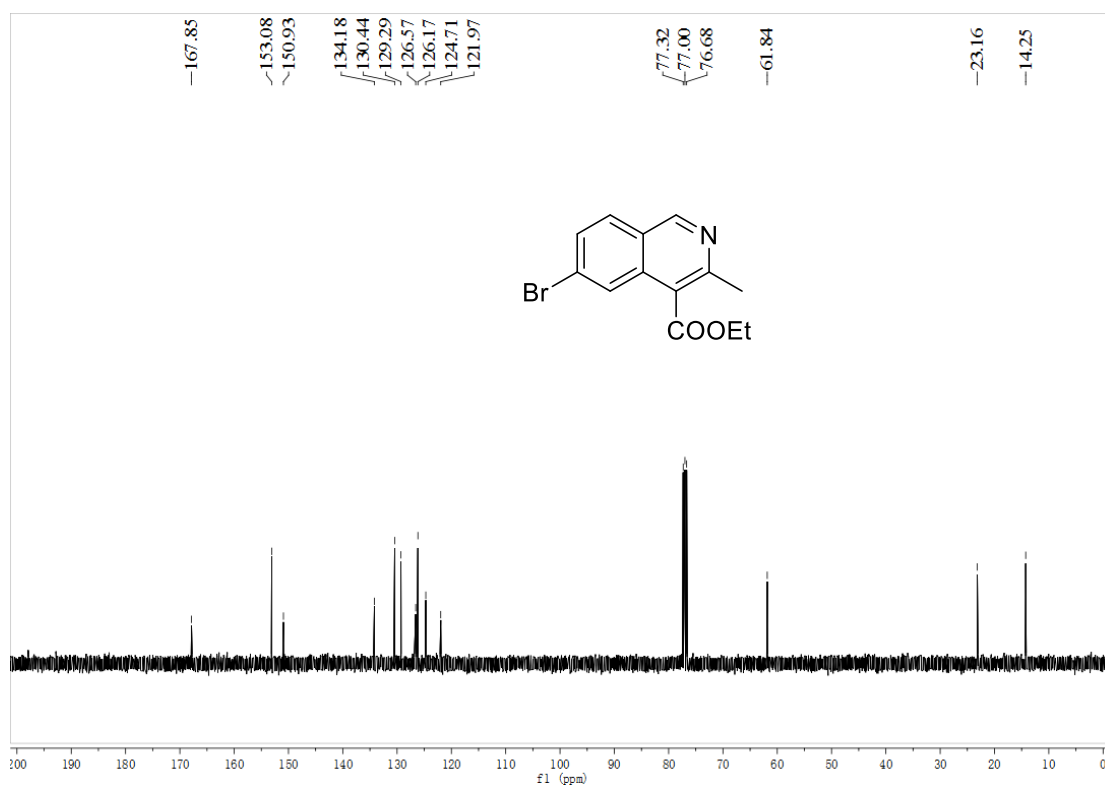
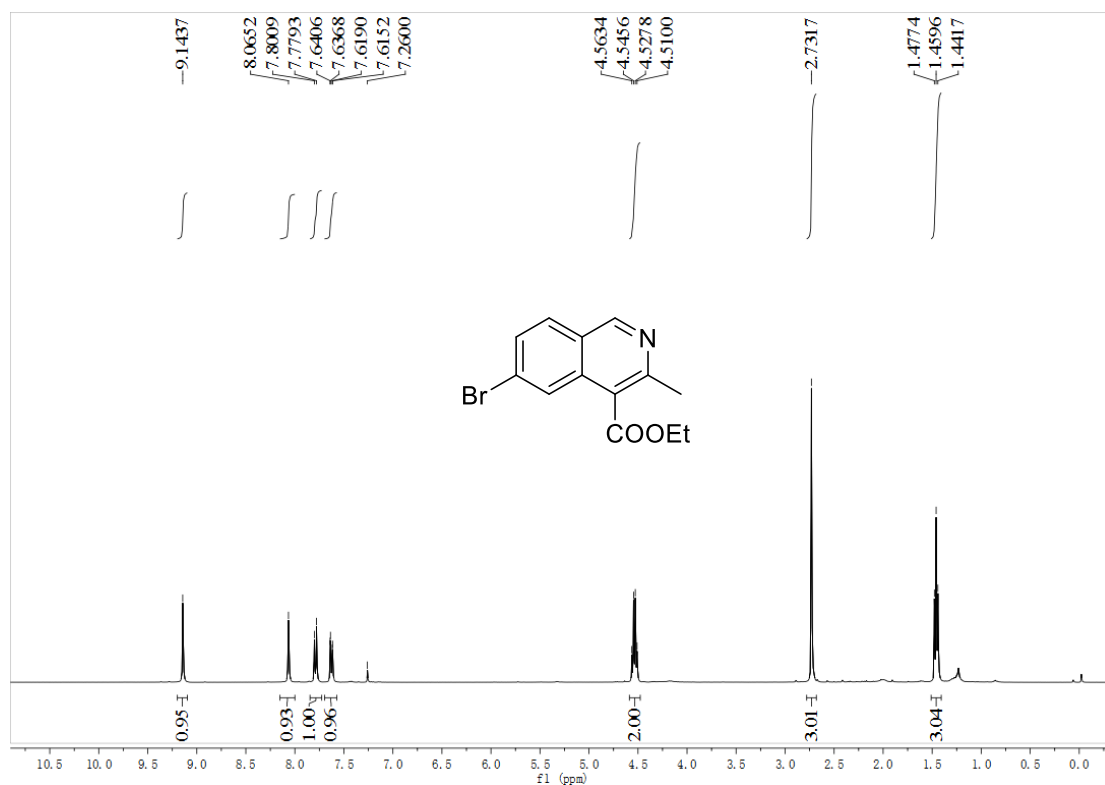
# **Ethyl 6-(tert-butyl)-3-methylisoquinoline-4-carboxylate (3ea)**



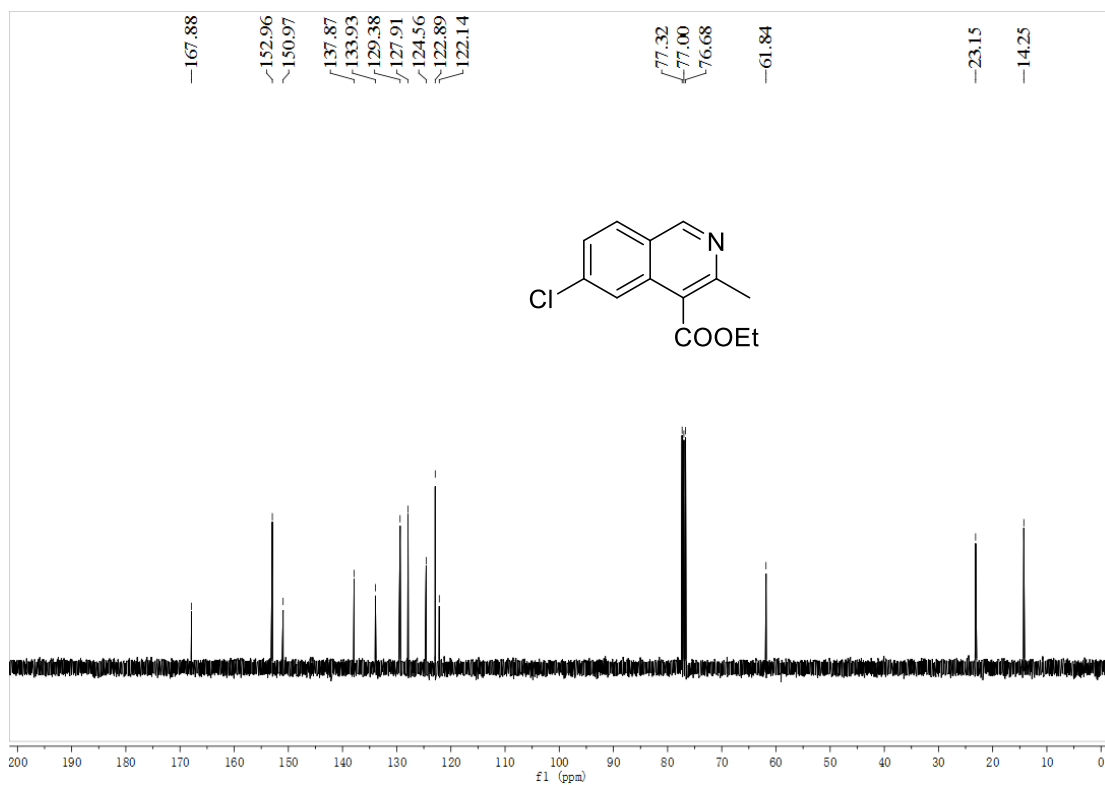
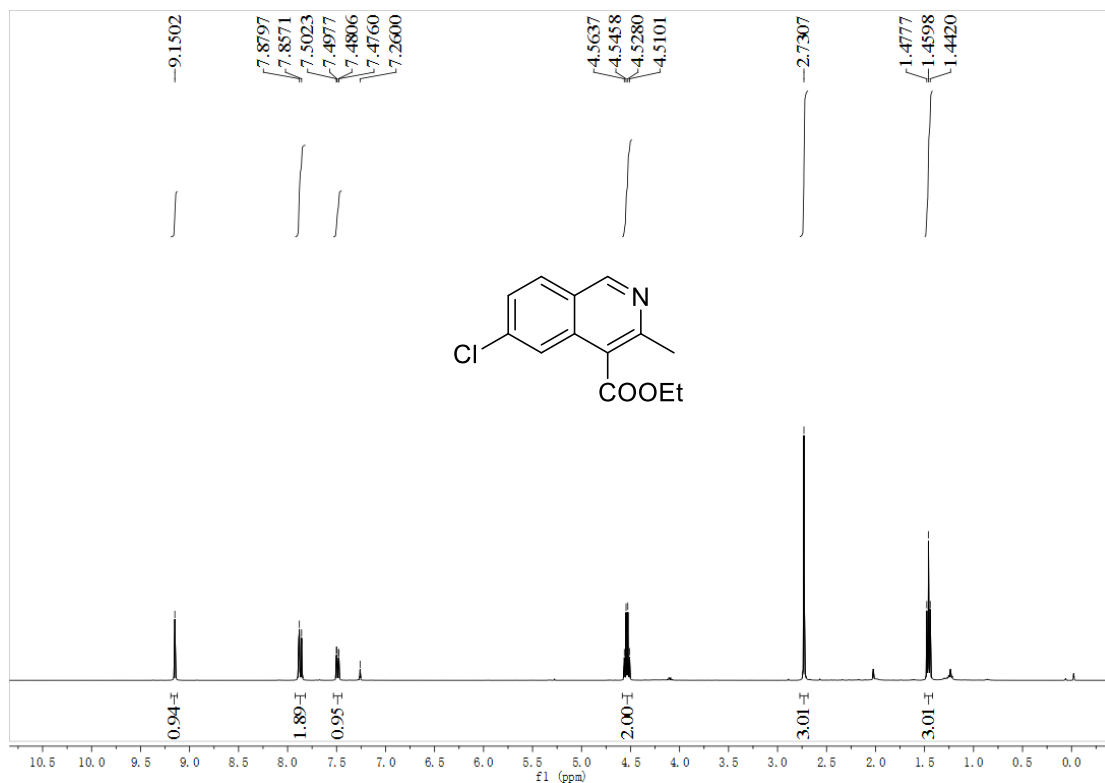
# **Ethyl 3-methyl-6-phenylisoquinoline-4-carboxylate (3fa)**



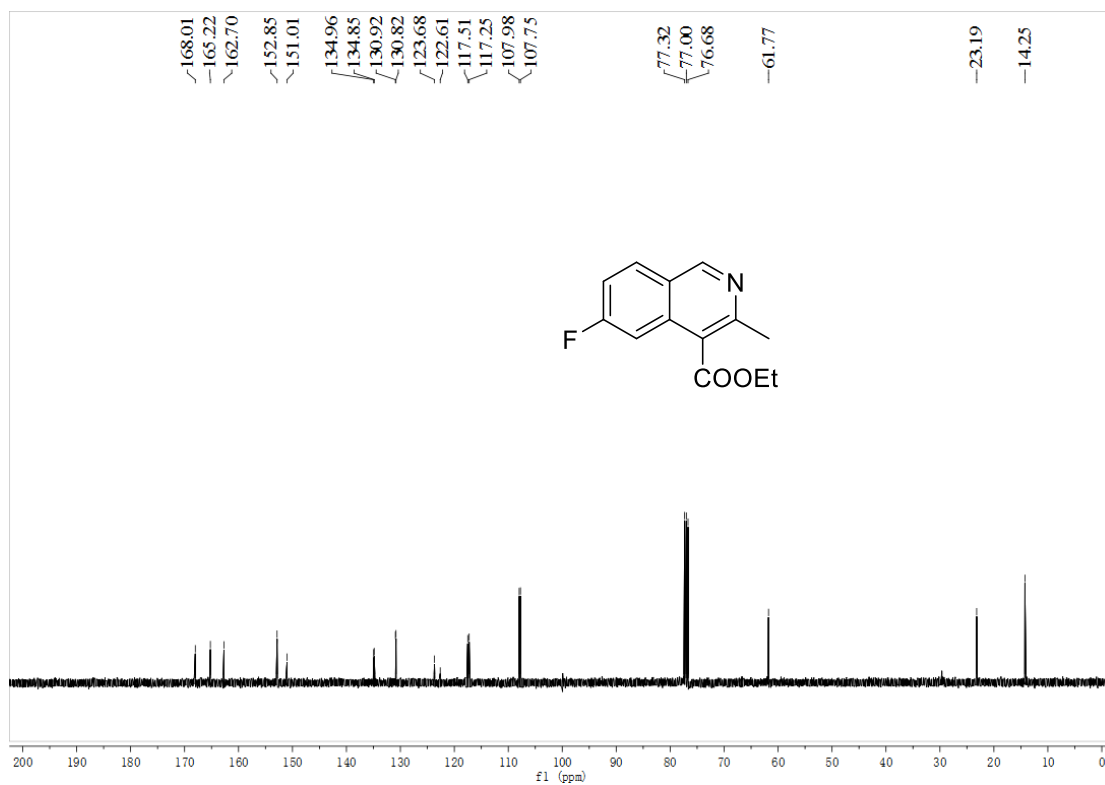
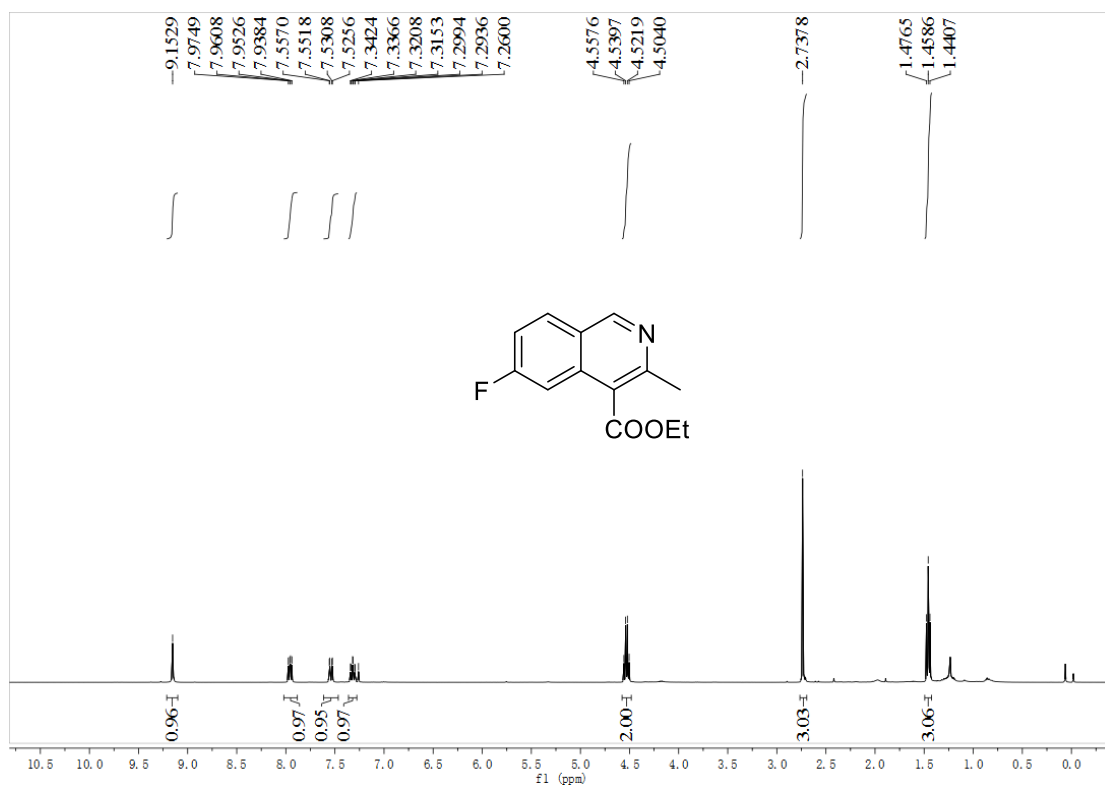
**Ethyl 6-bromo-3-methylisoquinoline-4-carboxylate (3ga):**



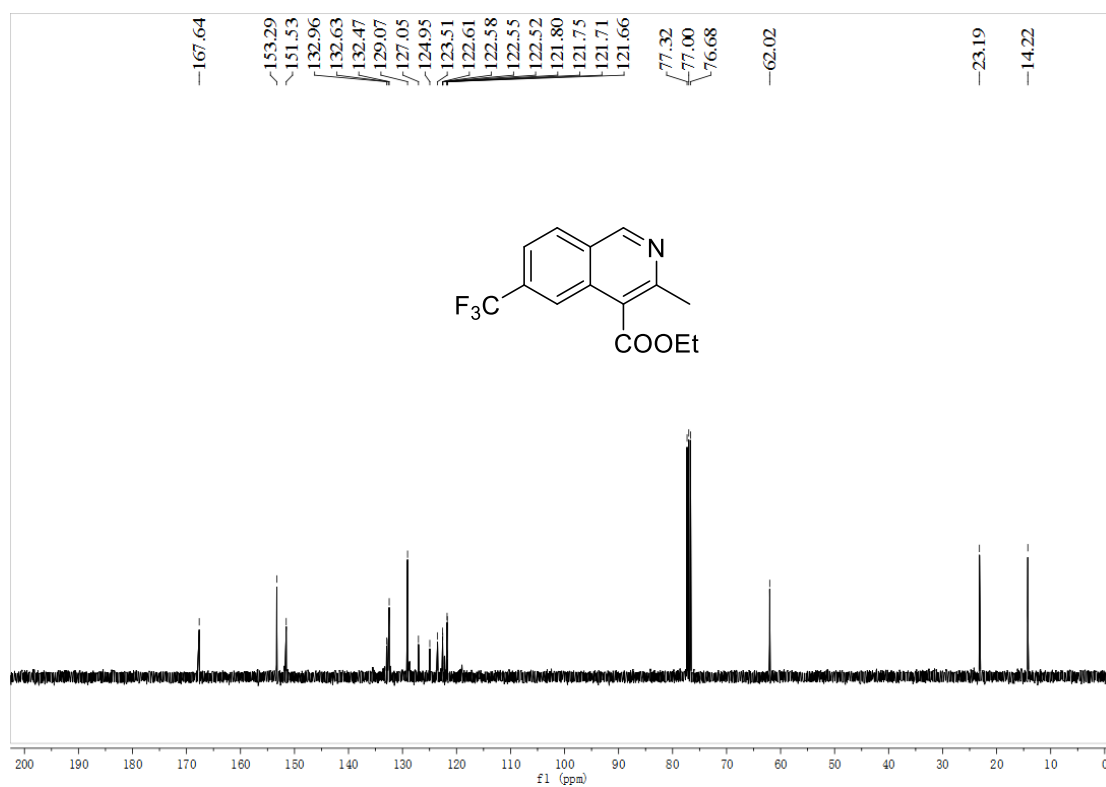
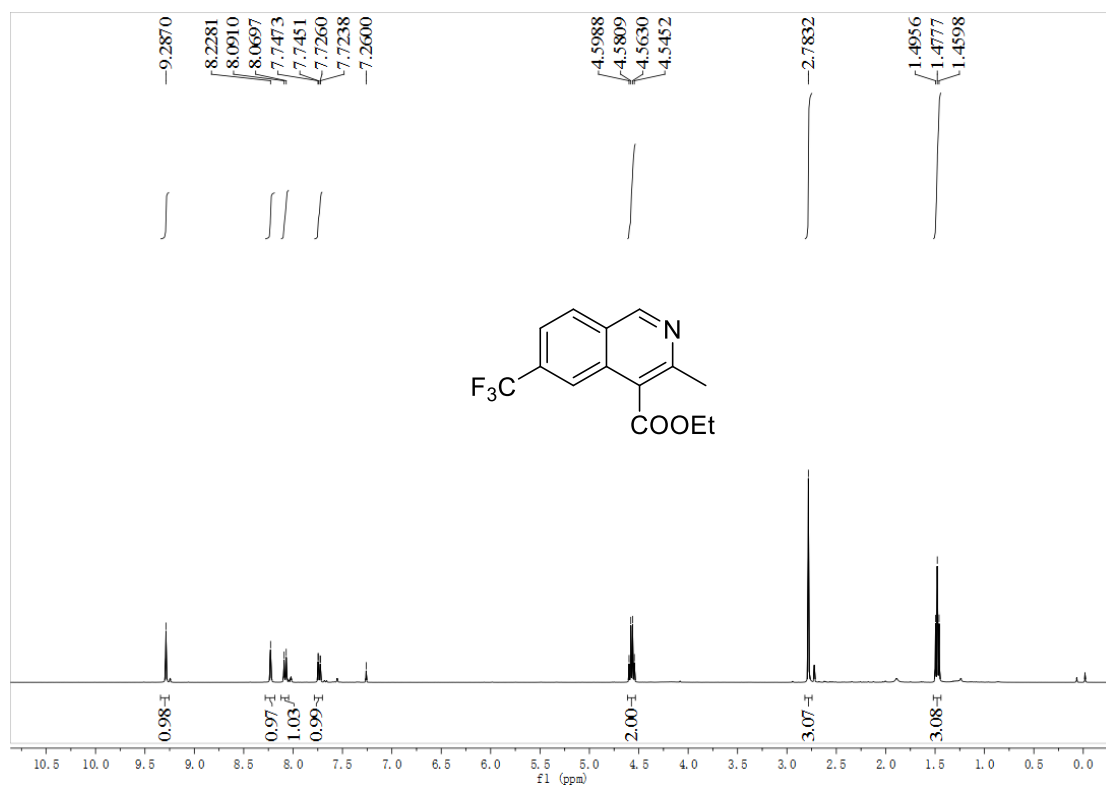
# **Ethyl 6-chloro-3-methylisoquinoline-4-carboxylate (3ha)**



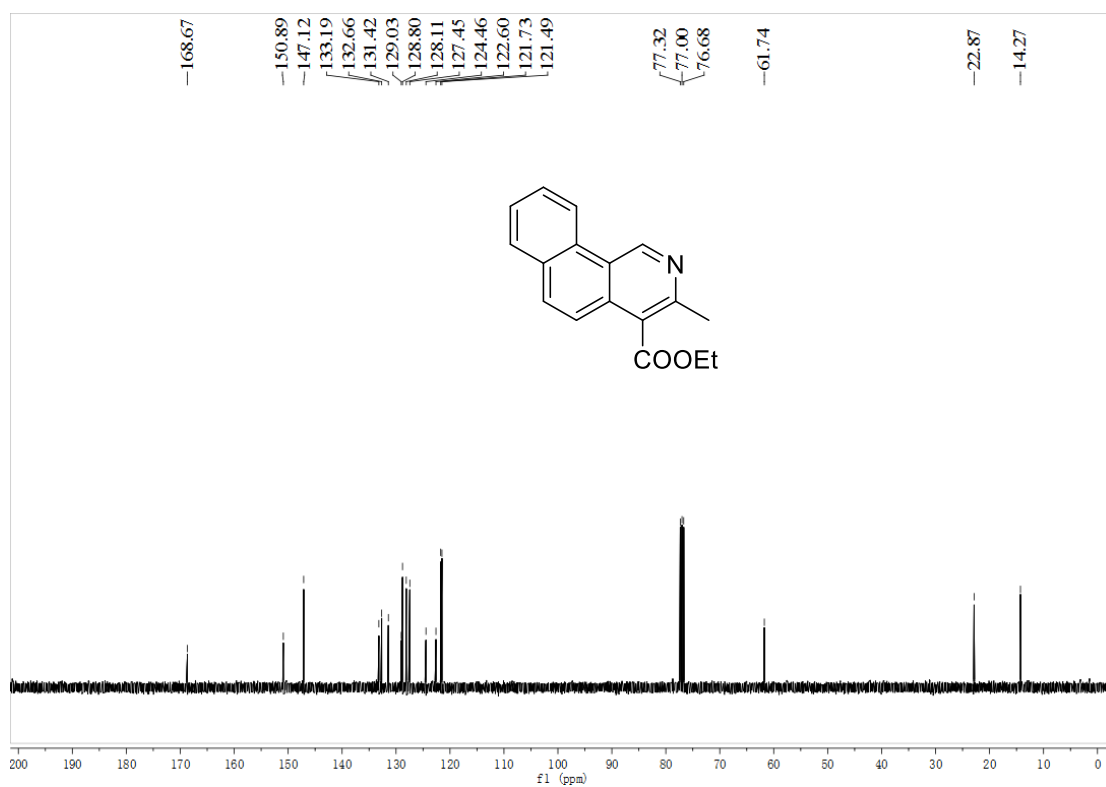
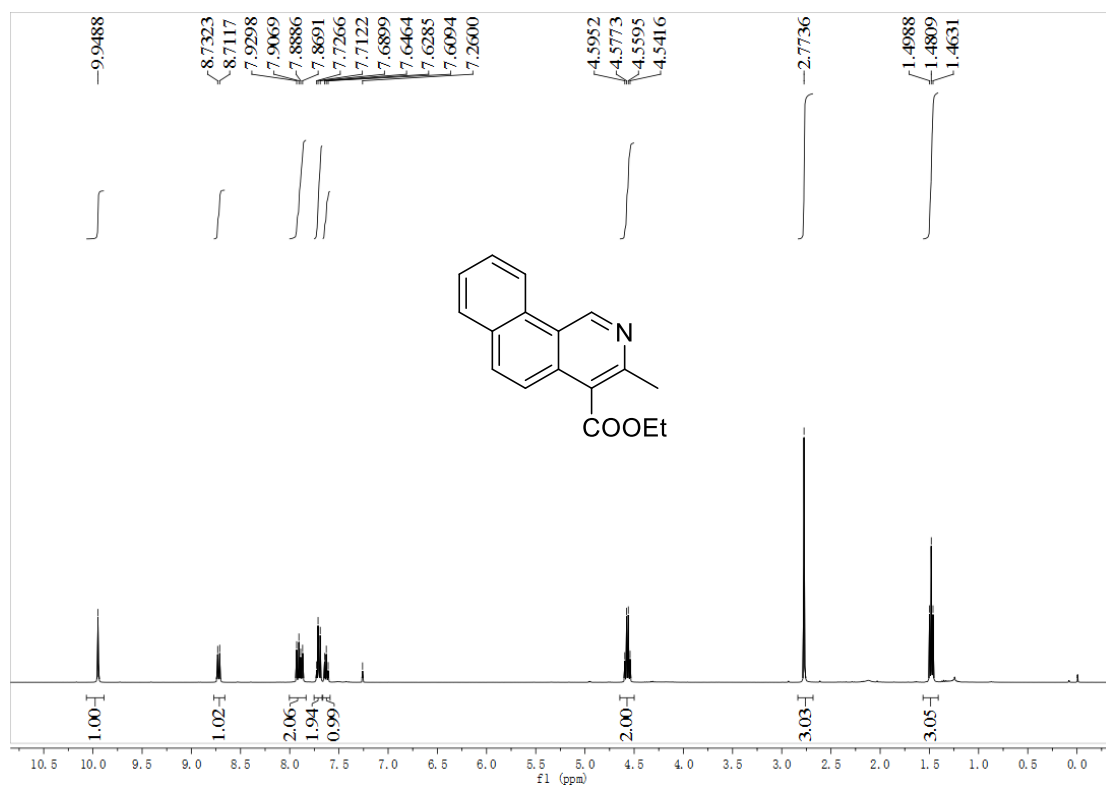
# **Ethyl 6-fluoro-3-methylisoquinoline-4-carboxylate (3ia)**



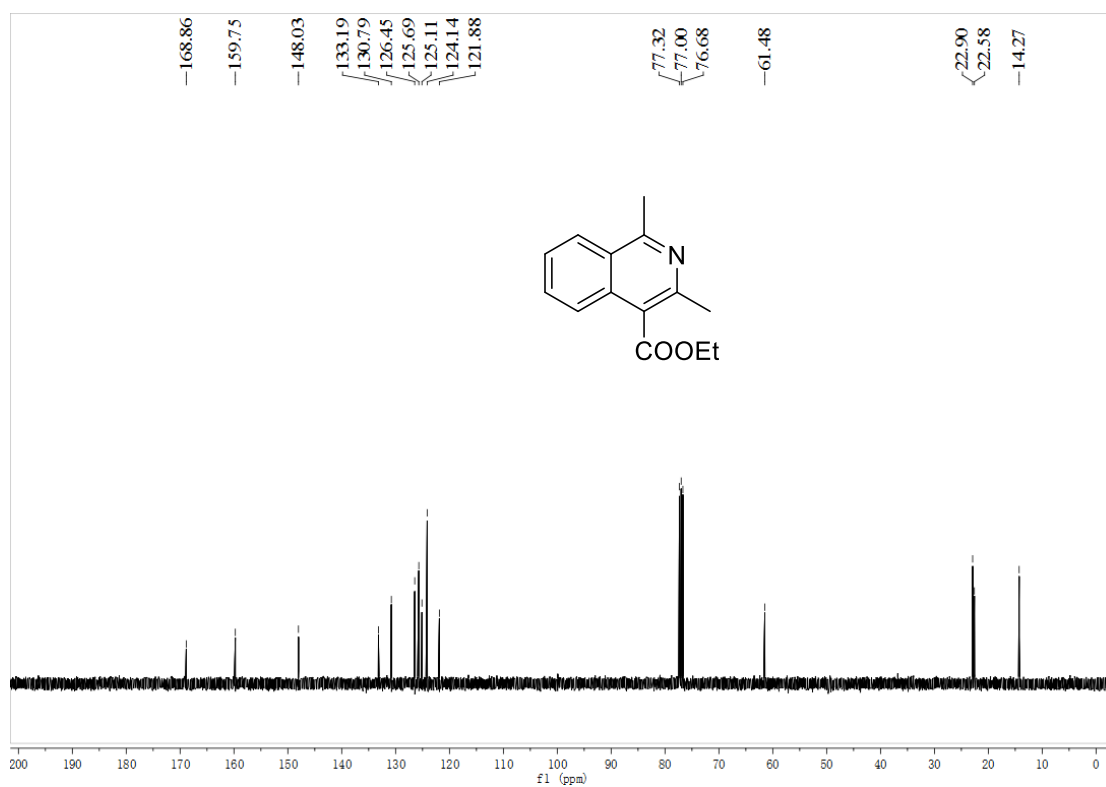
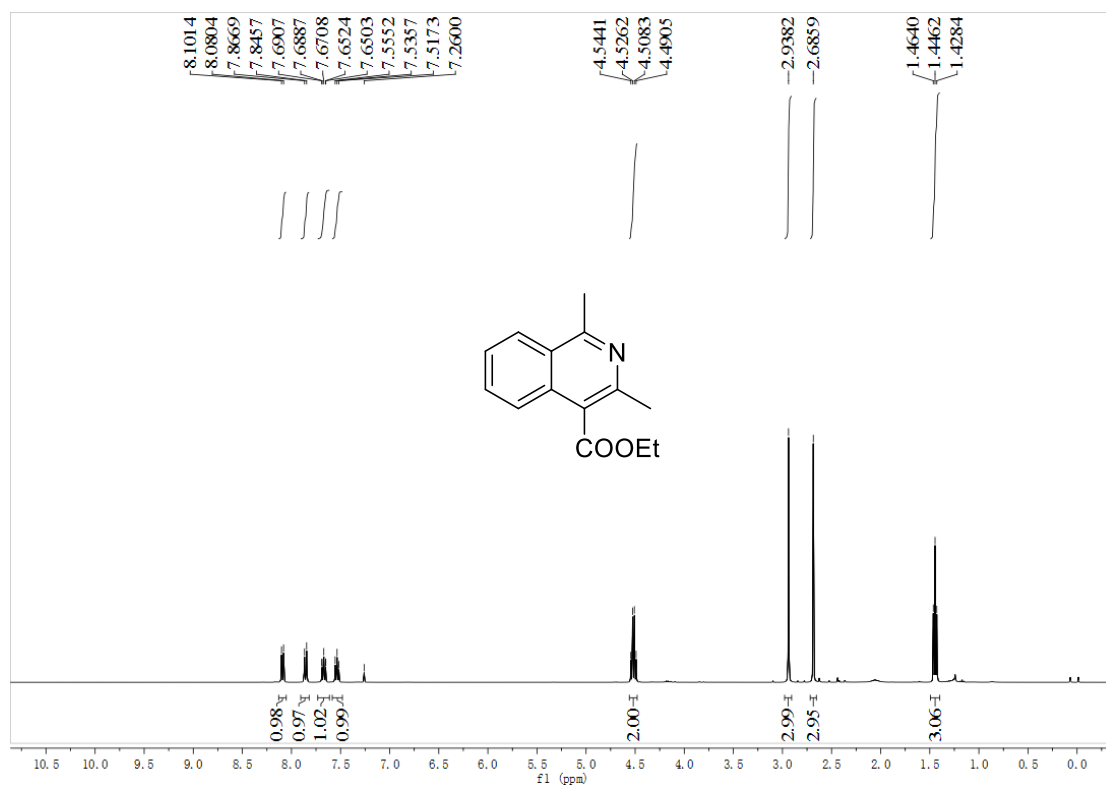
# **Ethyl 3-methyl-6-(trifluoromethyl)isoquinoline-4-carboxylate (3ja)**



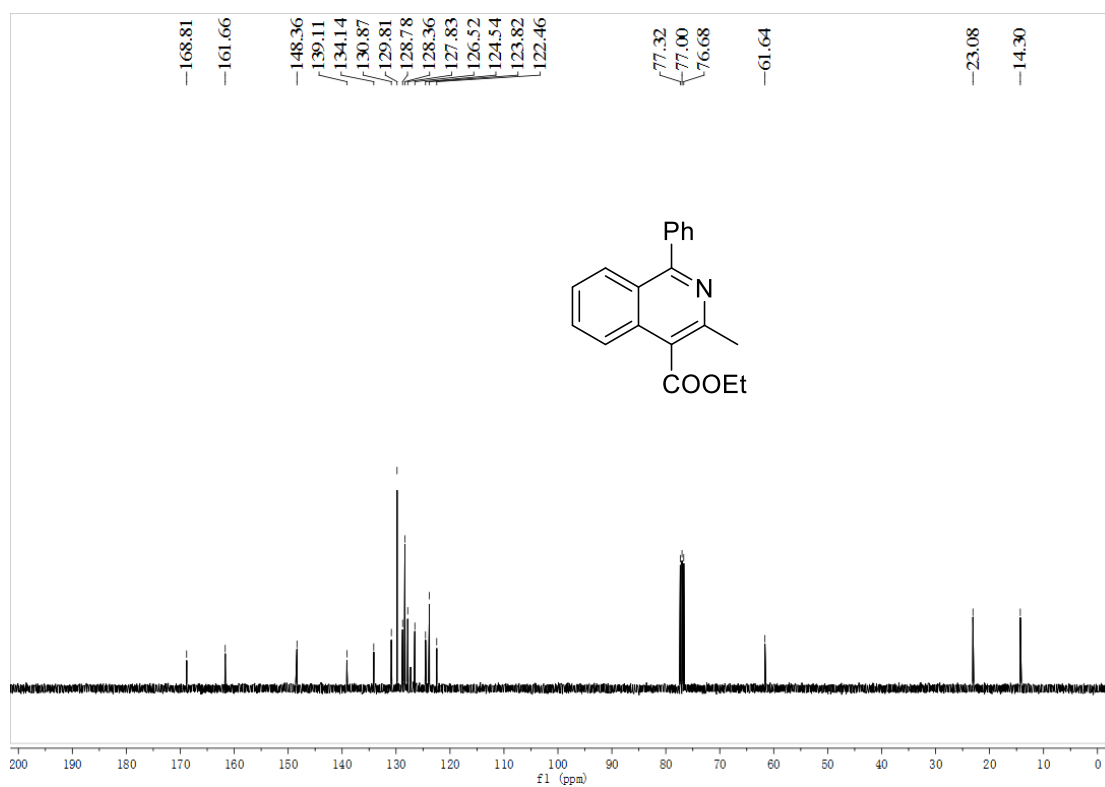
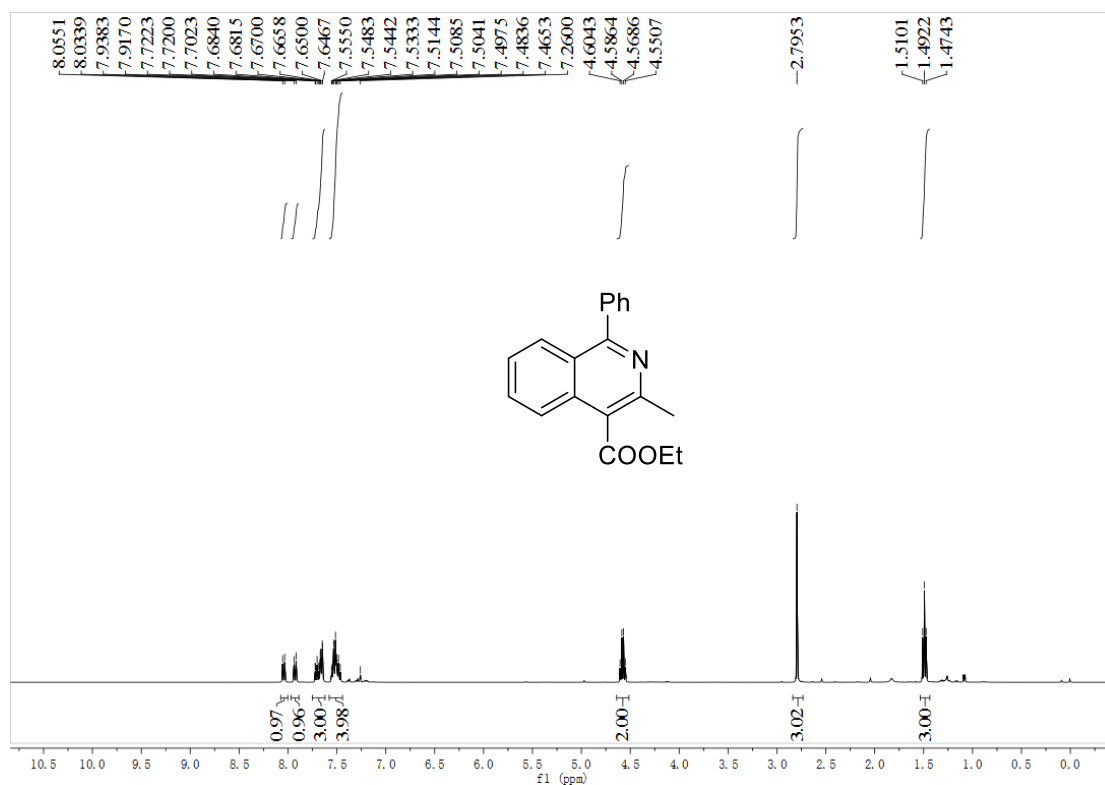
# **Ethyl 3-methylbenzo[h]isoquinoline-4-carboxylate (3ka)**



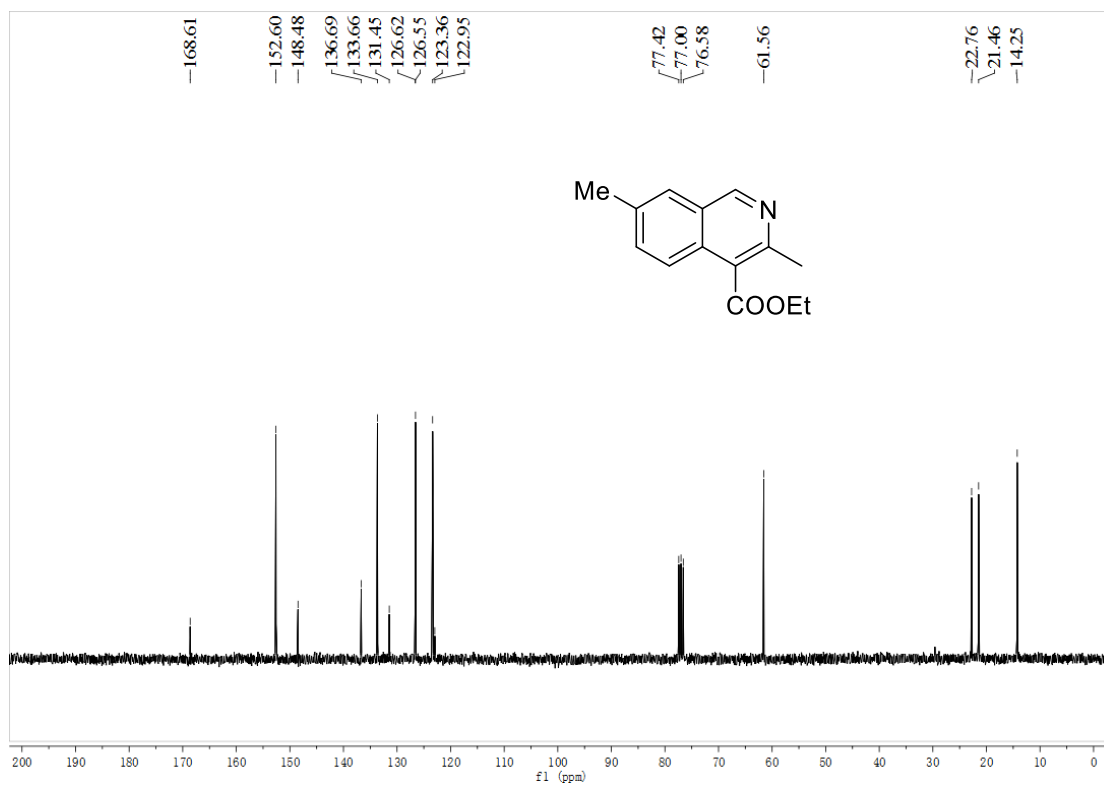
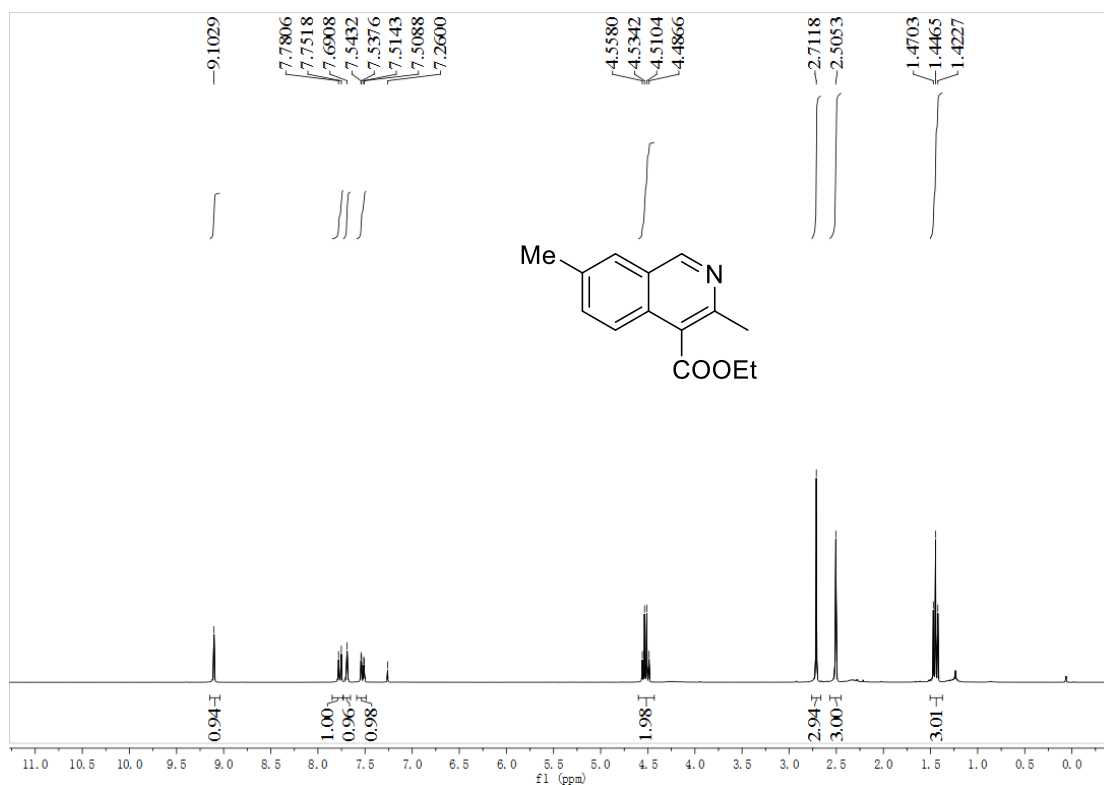
# **Ethyl 1,3-dimethylisoquinoline-4-carboxylate (3la)**



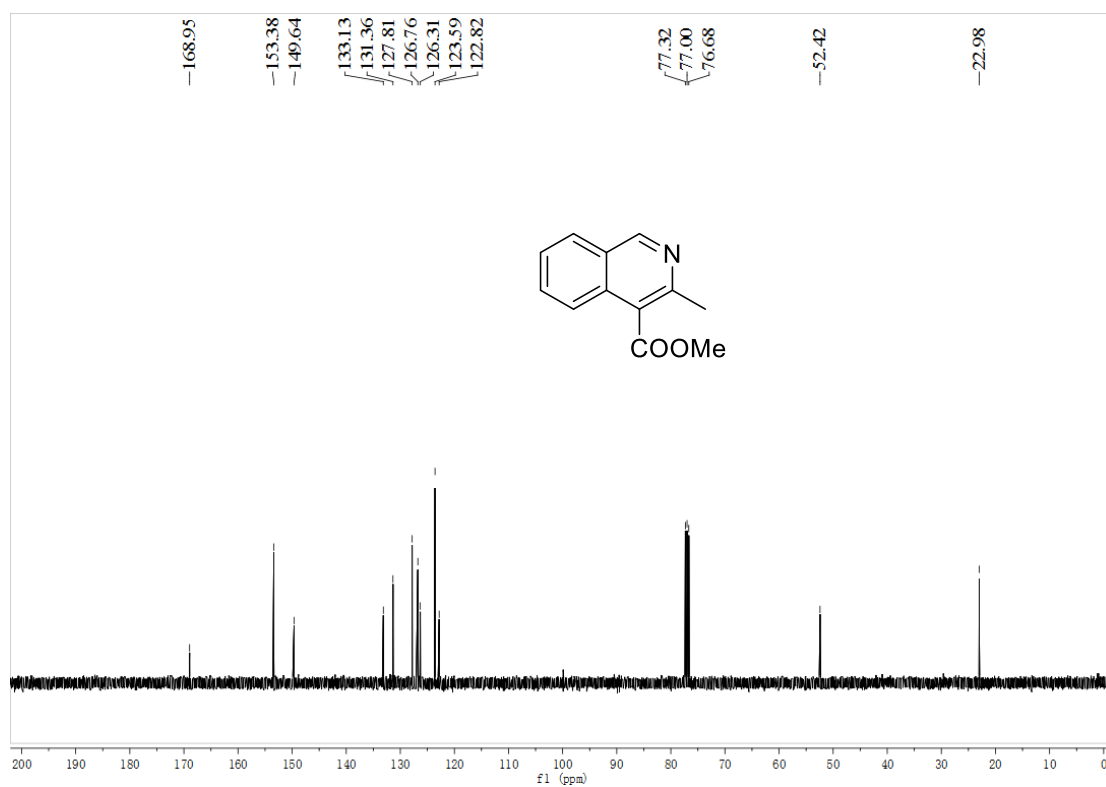
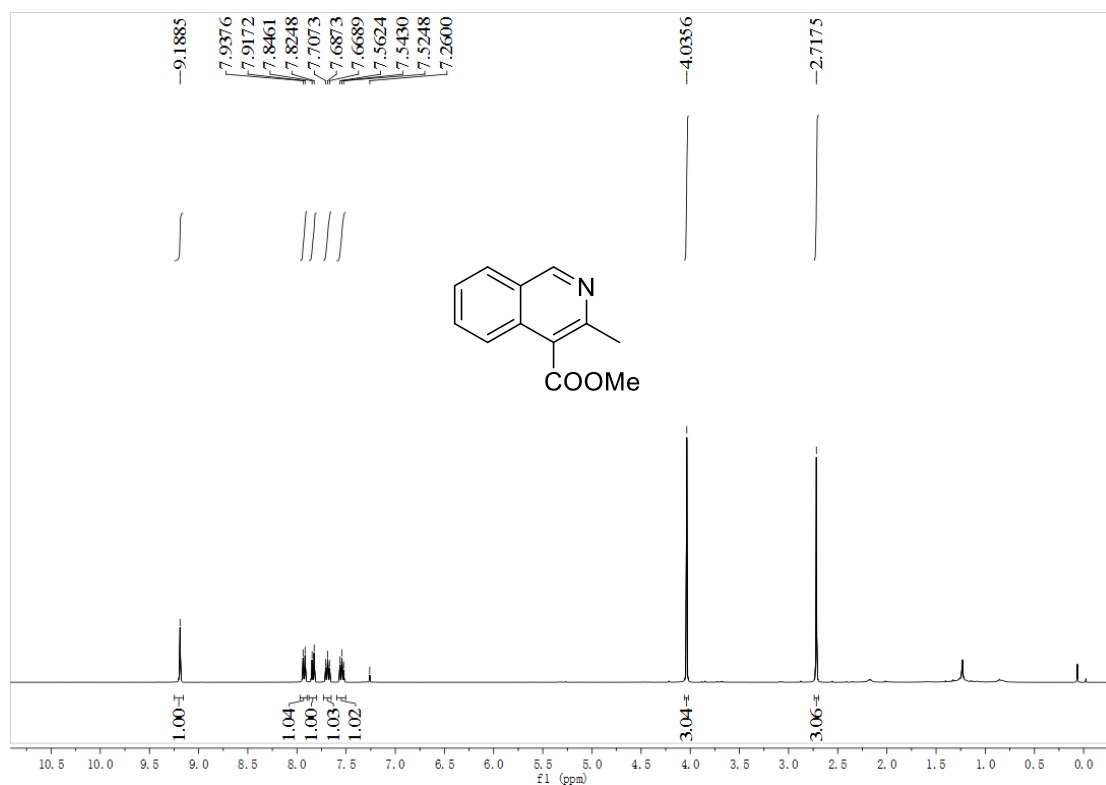
# **Ethyl 3-methyl-1-phenylisoquinoline-4-carboxylate (3ma)**



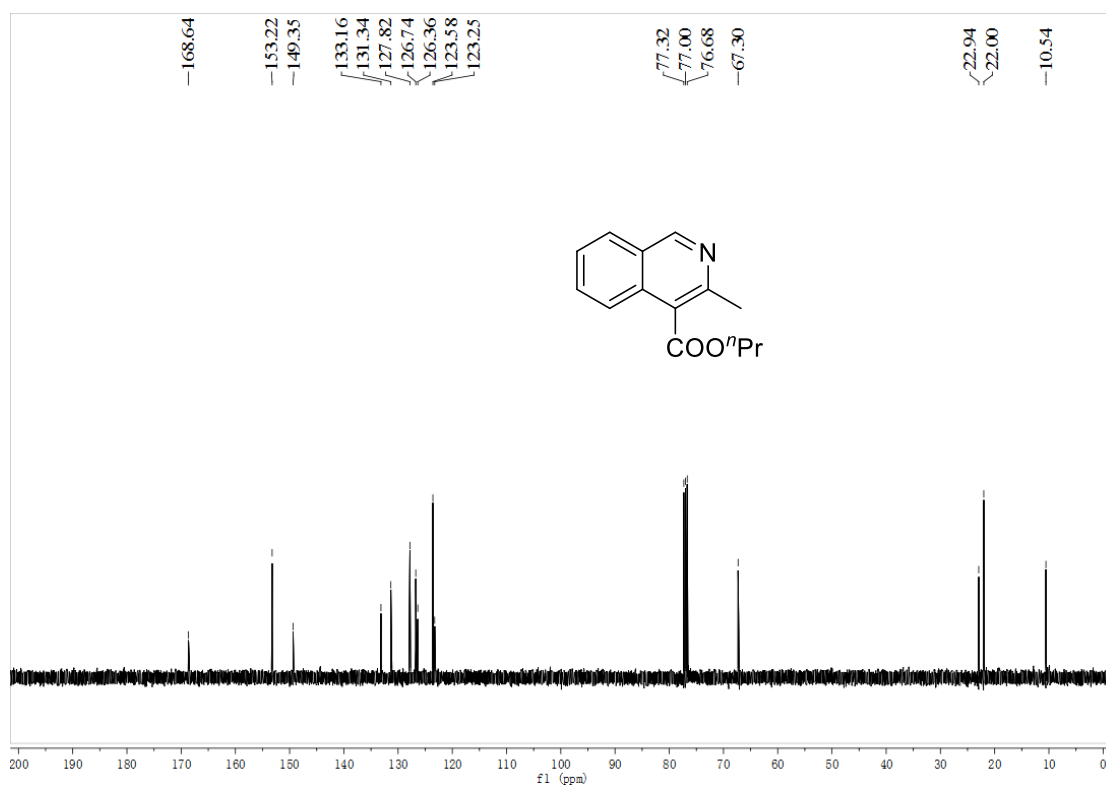
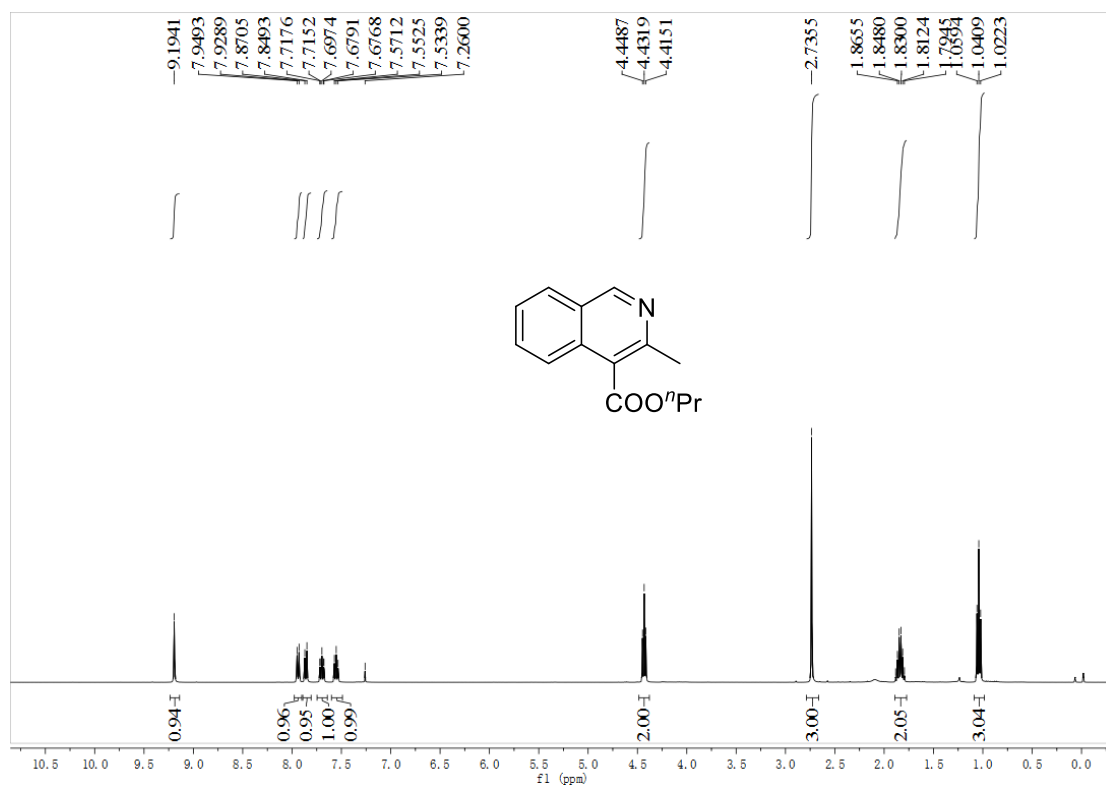
# **Ethyl 3,7-dimethylisoquinoline-4-carboxylate (3na)**



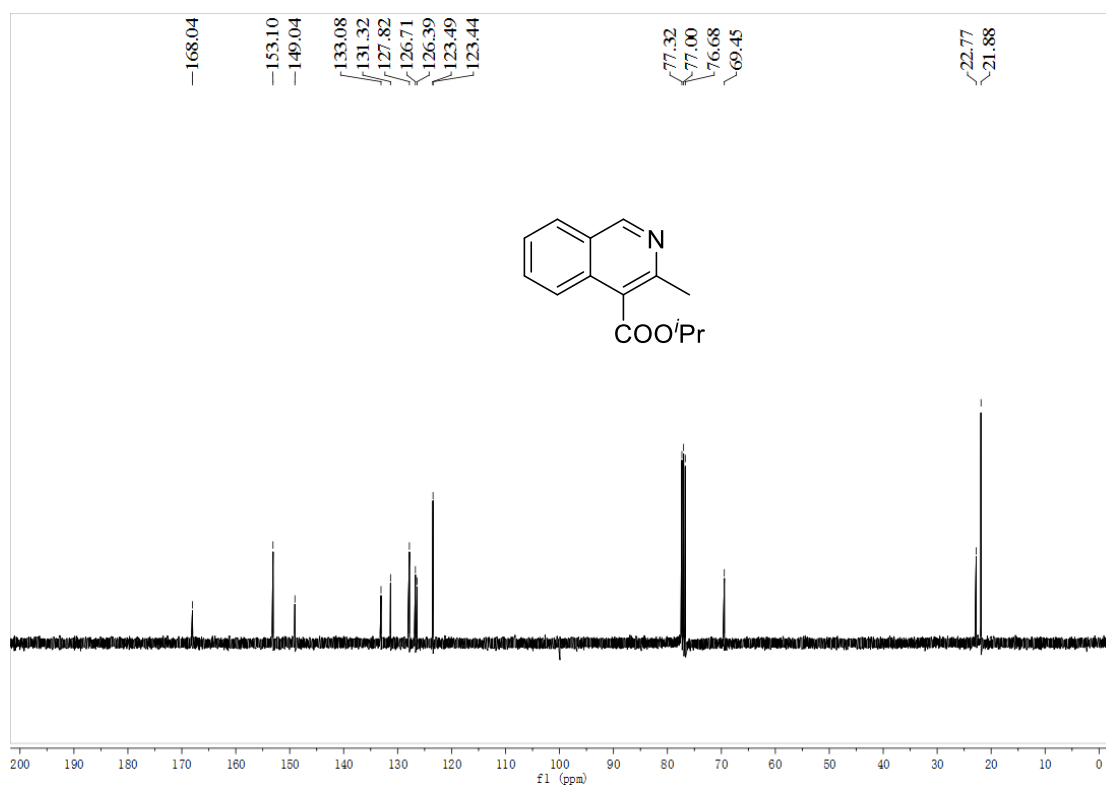
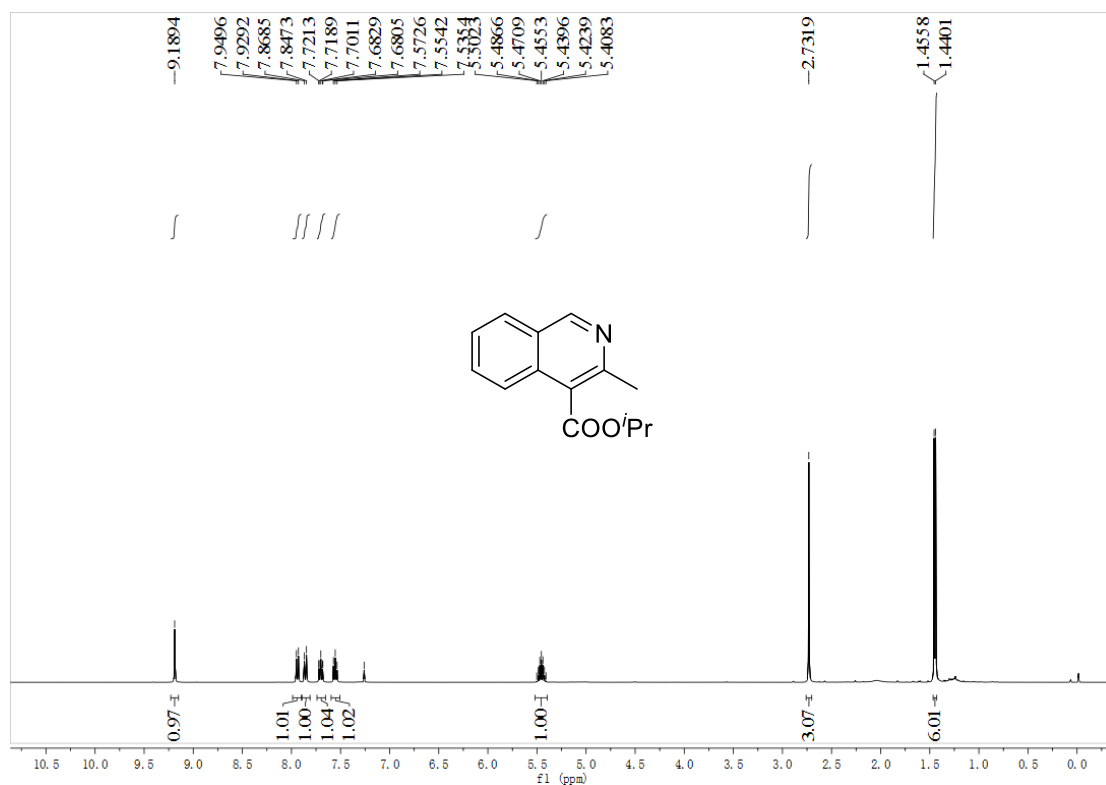
# **Methyl 3-methylisoquinoline-4-carboxylate (3ab)**



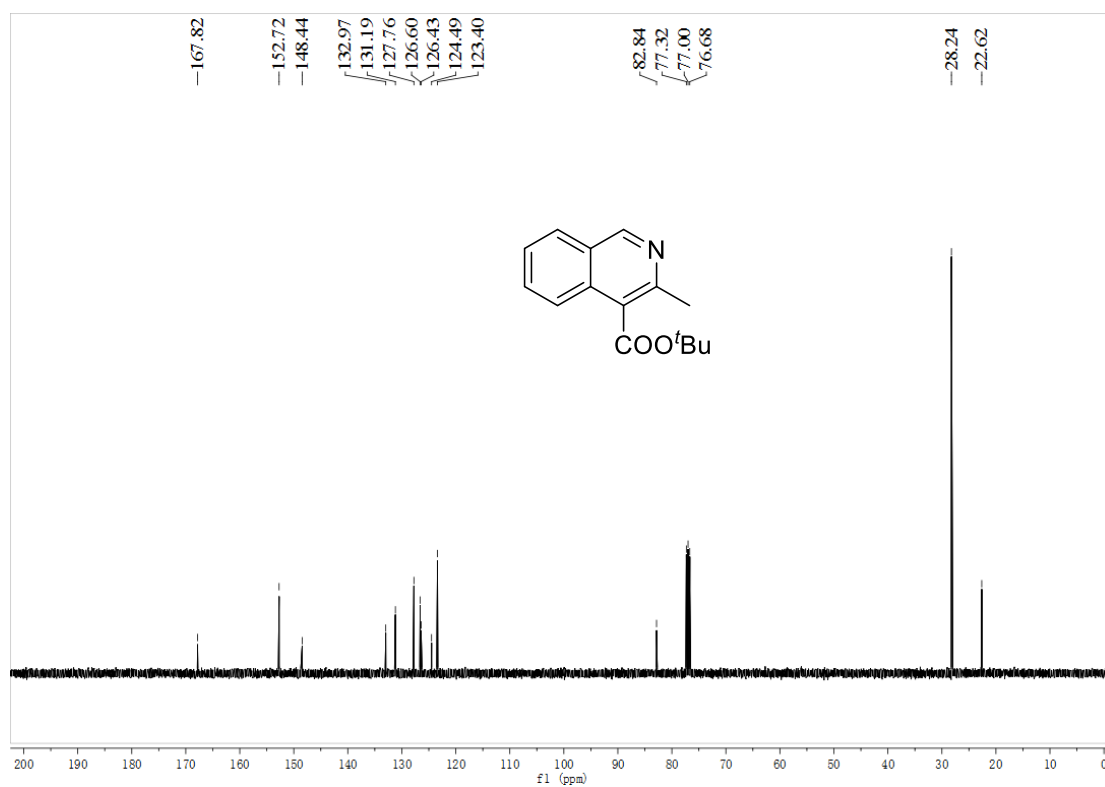
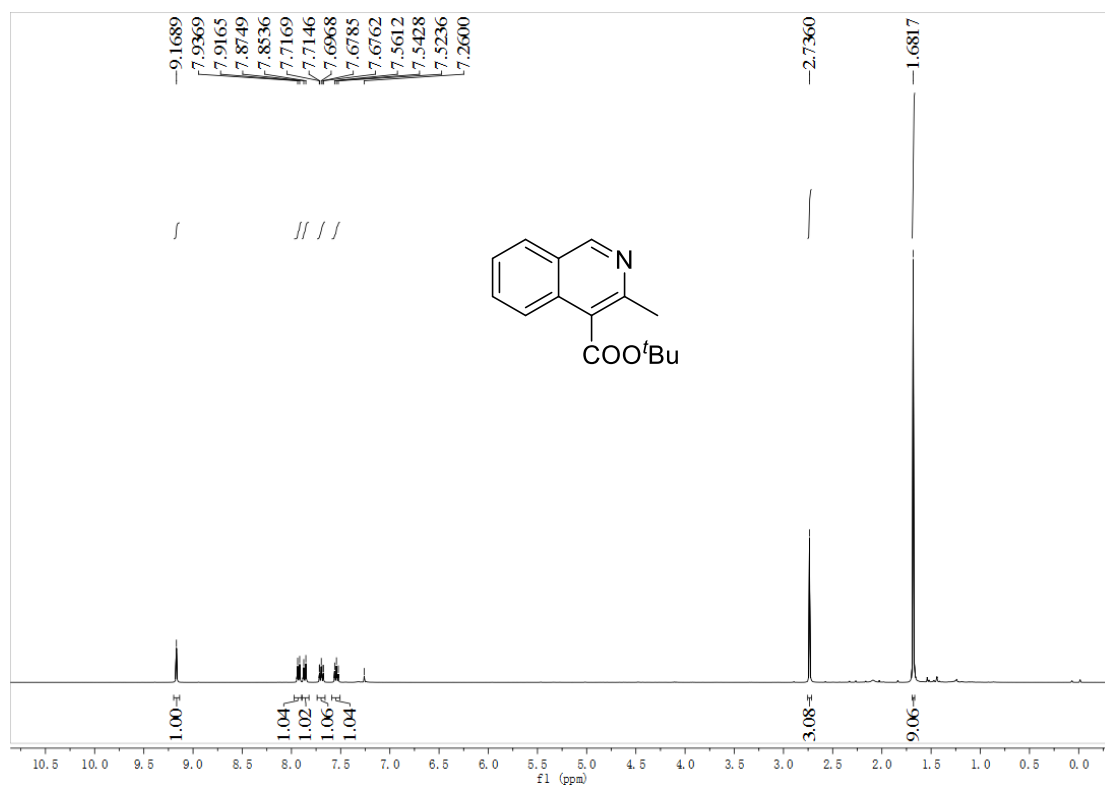
**n-Propyl 3-methylisoquinoline-4-carboxylate (3ac)**



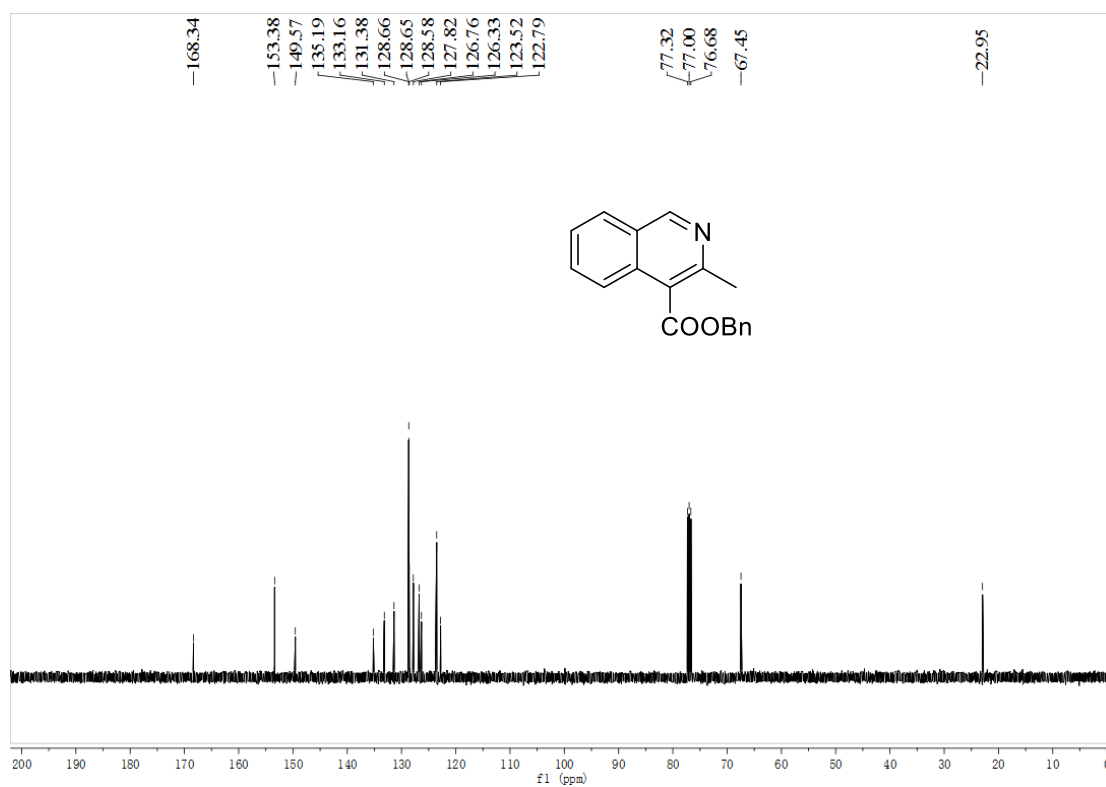
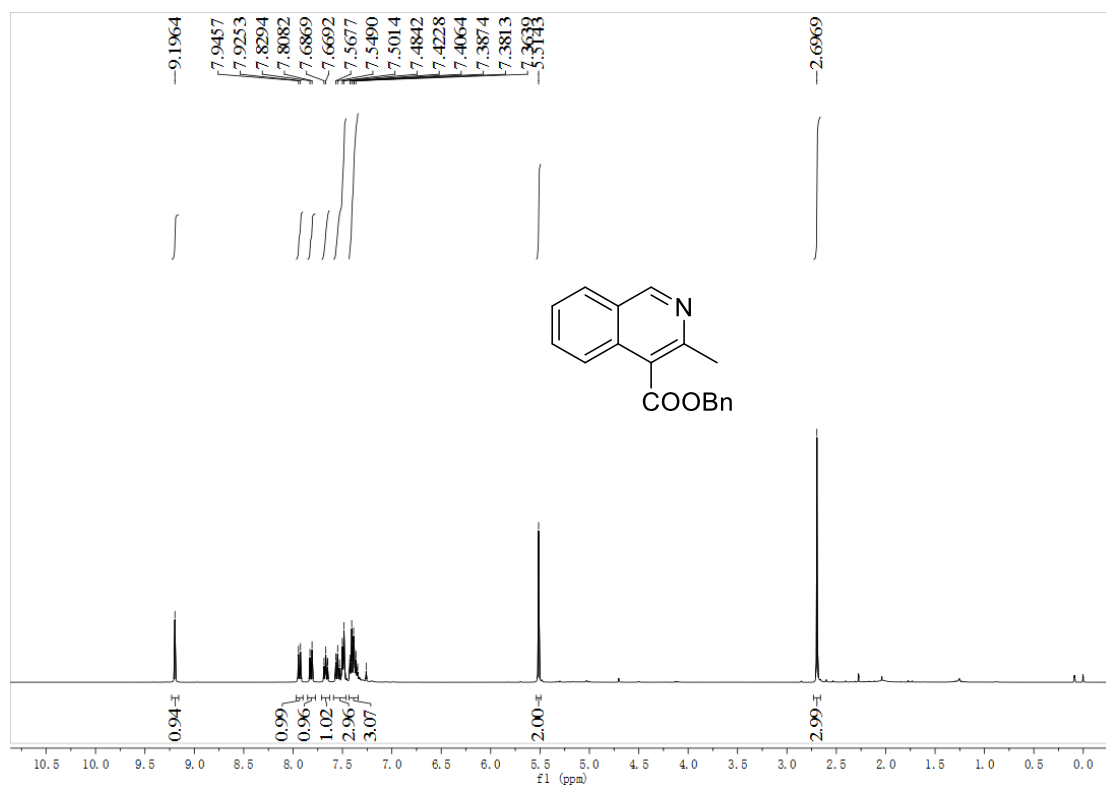
**i-Propyl 3-methylisoquinoline-4-carboxylate (3ad)**



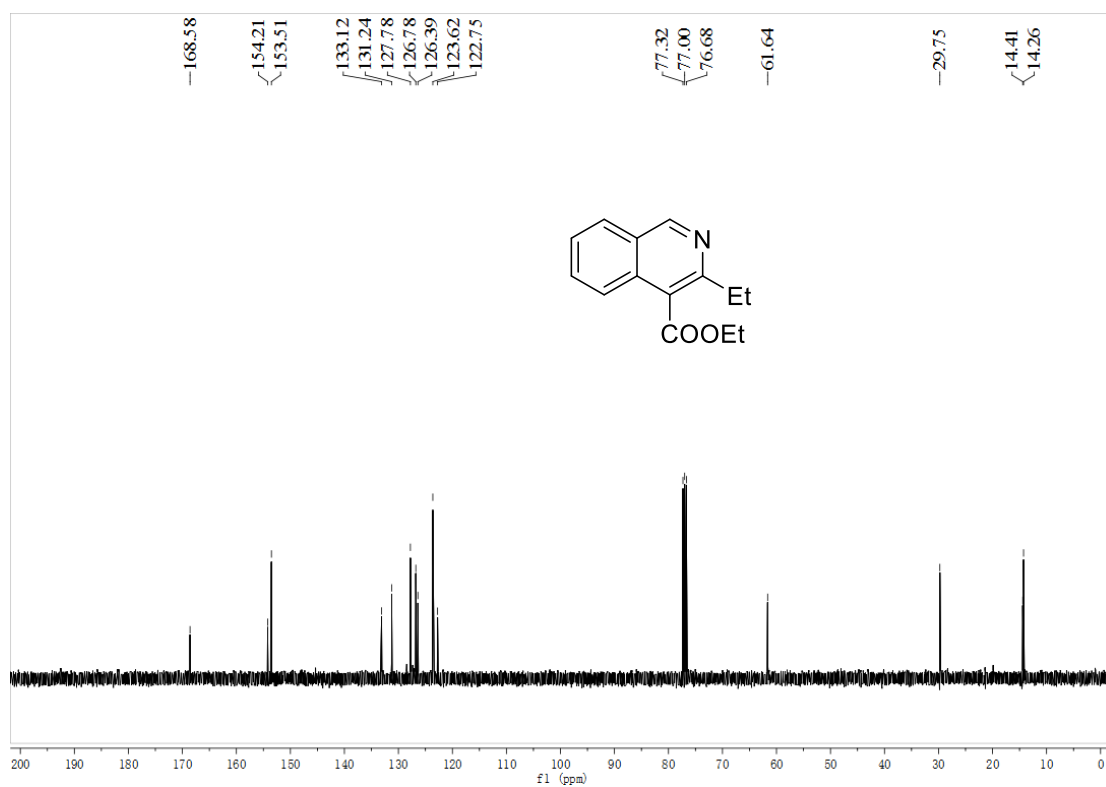
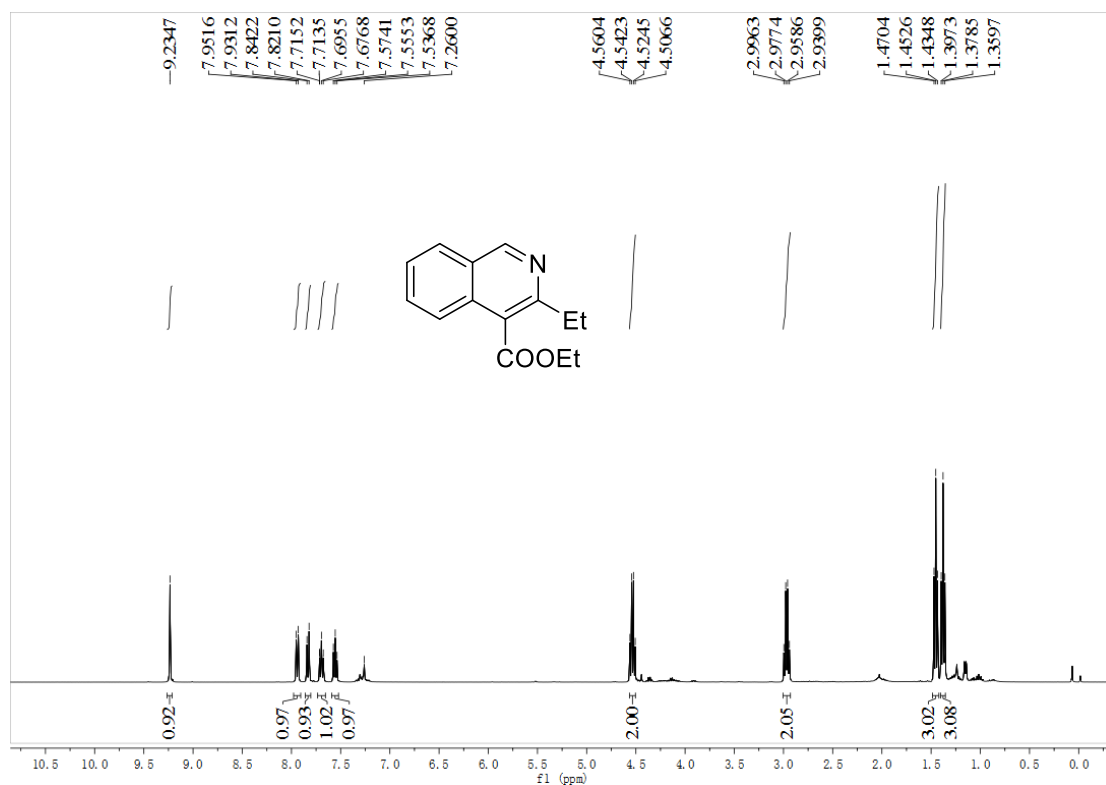
**tert-Butyl 3-methylisoquinoline-4-carboxylate (3ae)**



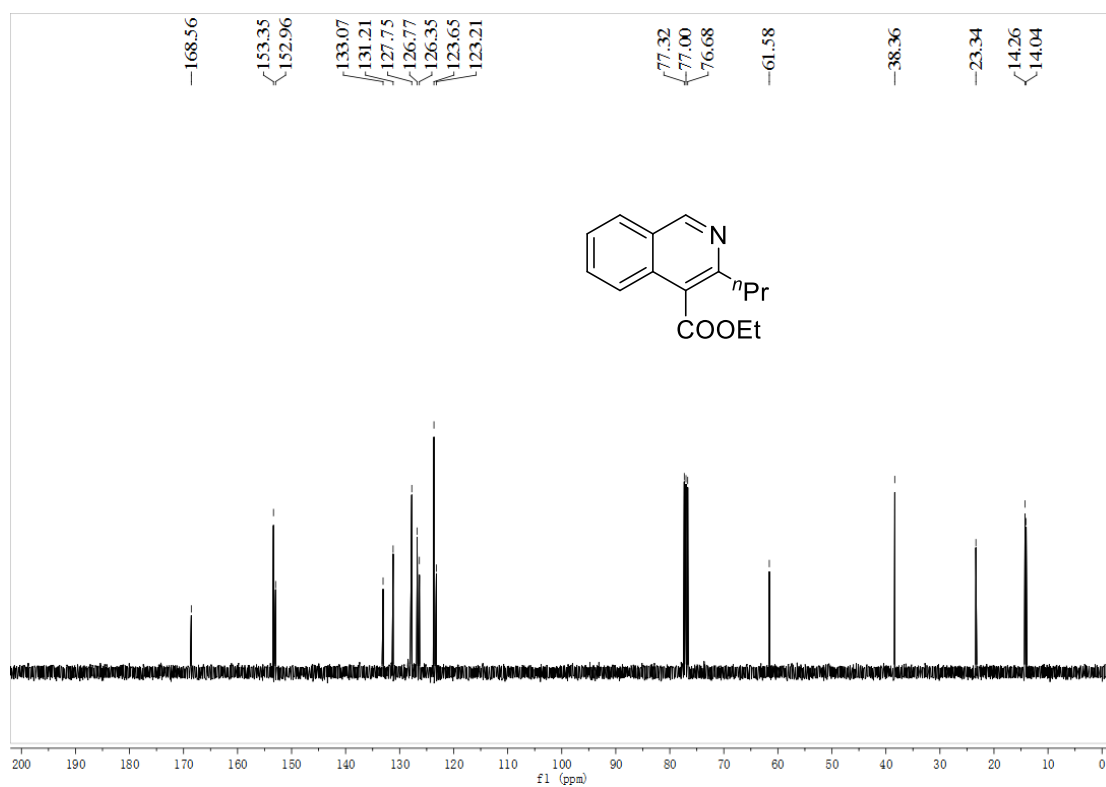
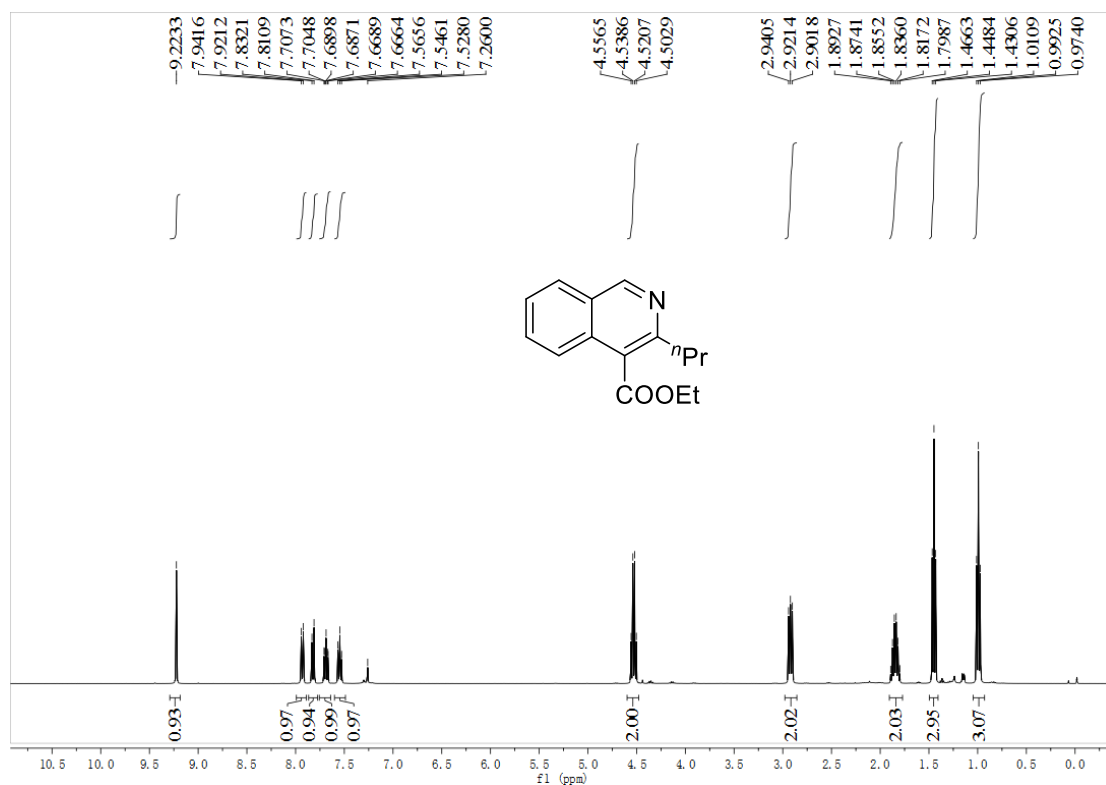
# **Benzyl 3-methyloquinoline-4-carboxylate (3af)**



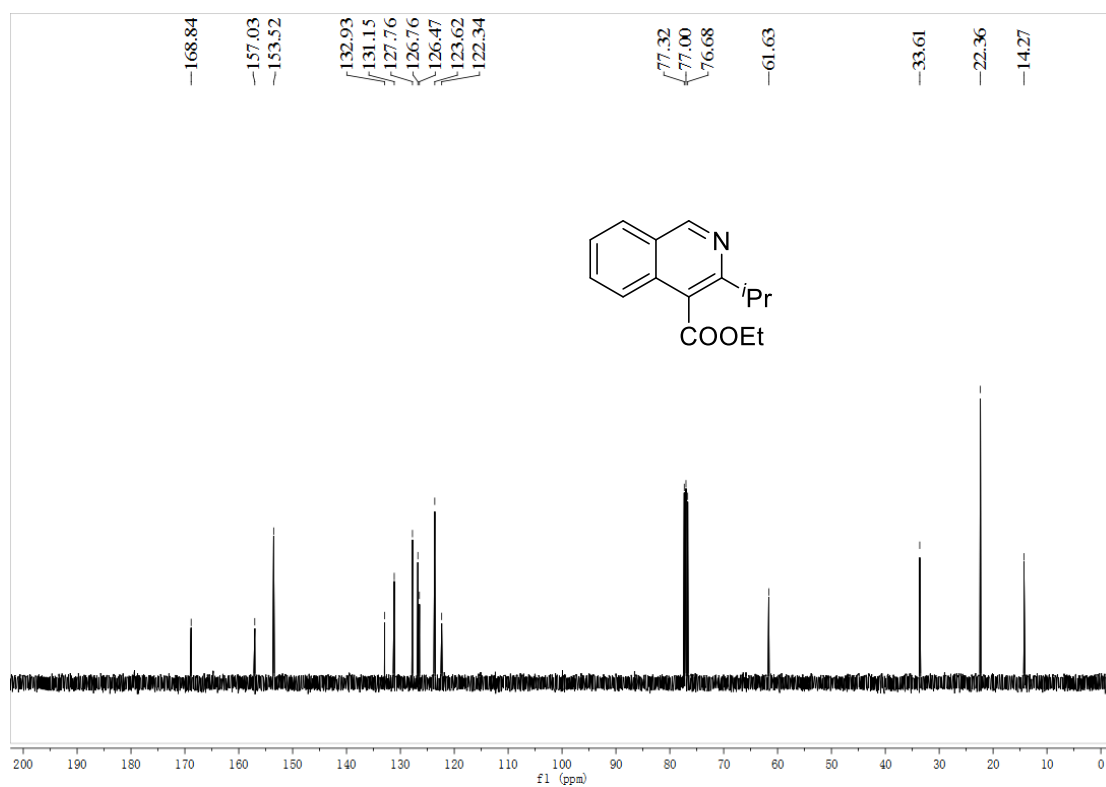
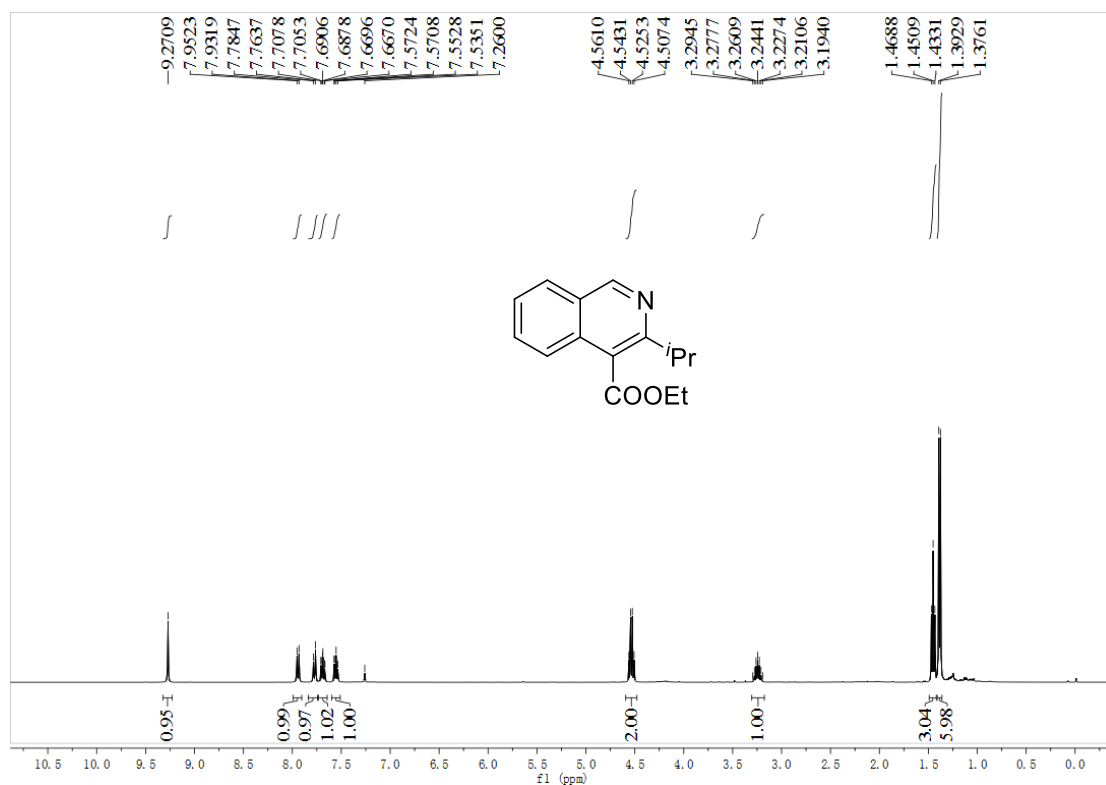
# **Ethyl 3-ethylisoquinoline-4-carboxylate (3ag)**



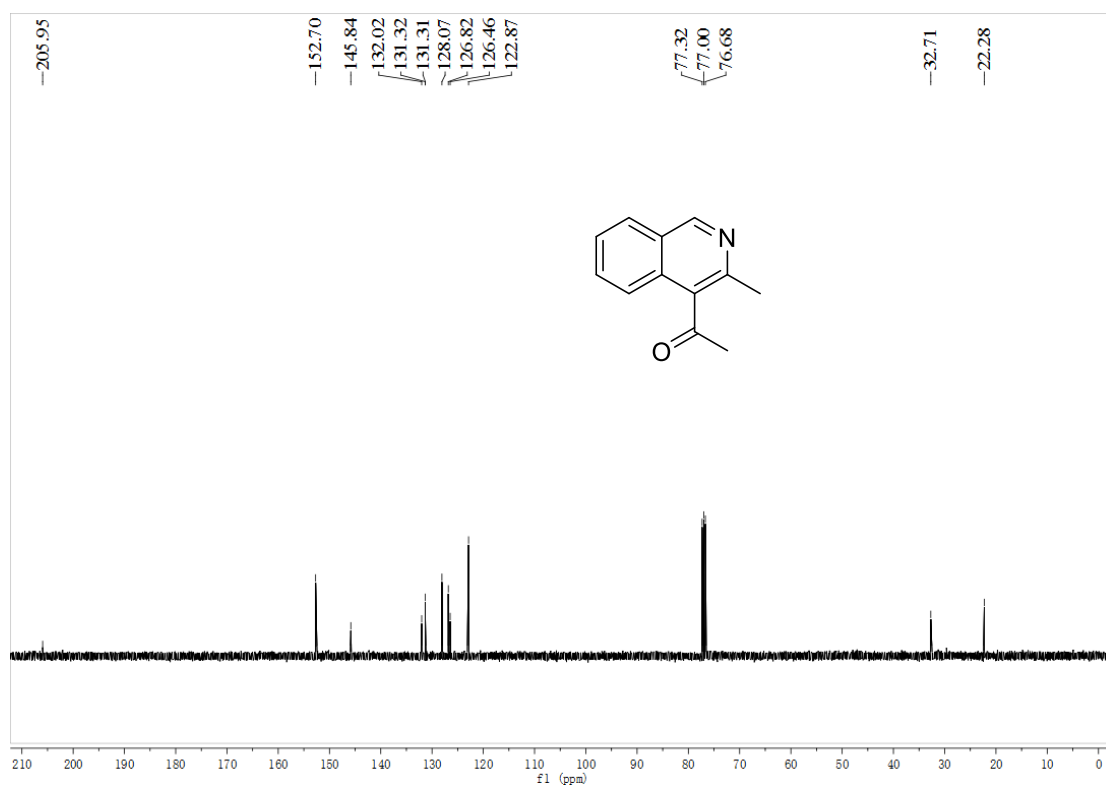
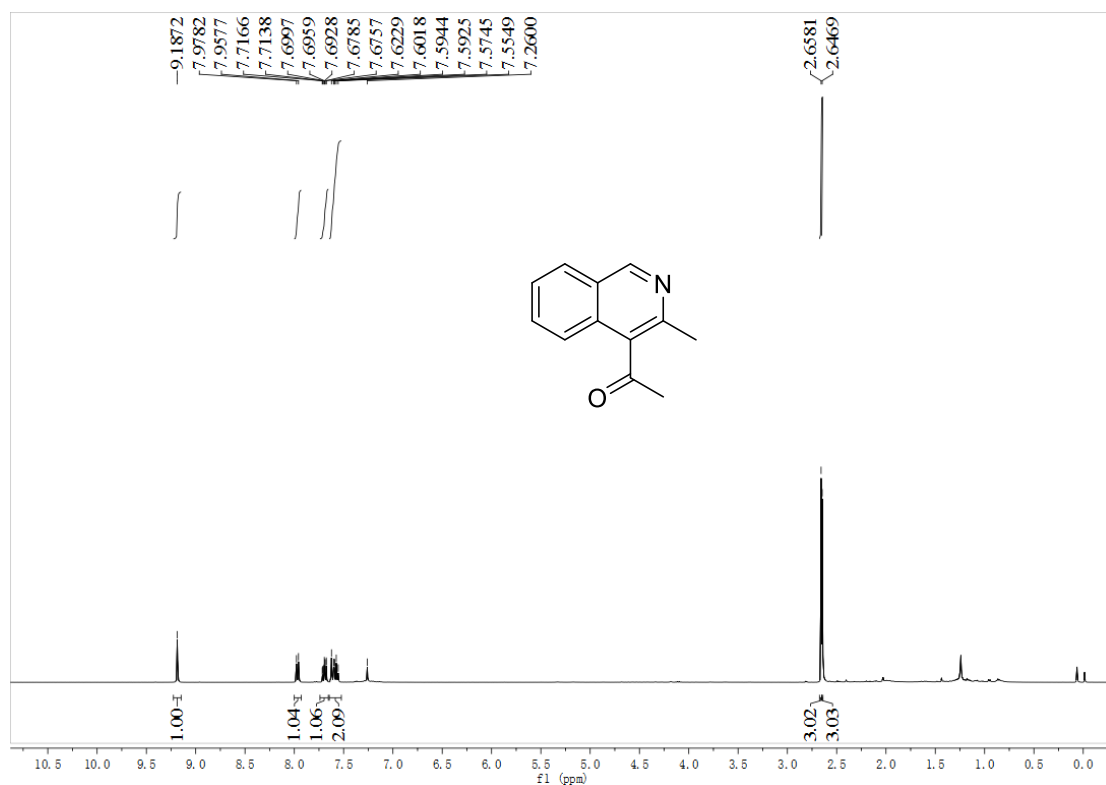
# **Ethyl 3-propylisoquinoline-4-carboxylate (3ah)**



# **Ethyl 3-isopropylisoquinoline-4-carboxylate (3ai)**



# **1-(3-Methyloquinolin-4-yl)ethan-1-one (3ak)**



### 3,3-Dimethyl-3,4-dihydrophenanthridin-1(2H)-one (3al)

