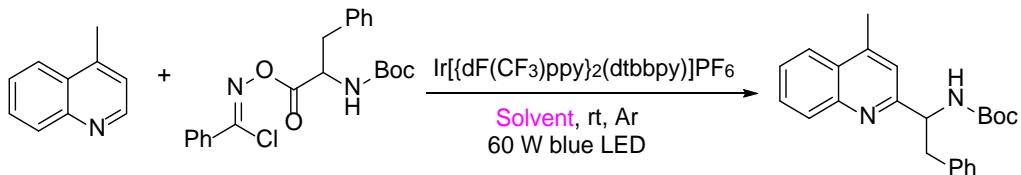


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## I. Optimizations of the Reaction Conditions

**Table S1: Optimization of different solvents<sup>[a]</sup>**



Entry	Solvent	Yield <sup>[b]</sup>
1	DCM	78%
2	DMF	46%
3	THF	32%
4	Acetone	75%
5	MeCN	82%
6	Toluene	71%

[a]All reactions were carried out with 4-methylquinoline (57.2 mg, 0.40 mmol), NHBC esters (0.20 mmol, 1eq.), Photocatalyst (2 mol%) in solvent (2.0 mL) at rt under Ar and 60W blue LEDs. [b] Isolated yield.

**Table S2: Optimization of Photocatalysts<sup>[a]</sup>**



Entry	PC	Yield <sup>[b]</sup>
1	4CzIPN	20%
2	Ir(ppy) <sub>3</sub>	45%
3	Ir(mppy) <sub>3</sub>	30%

4	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (bpy)]PF <sub>6</sub>	50%
5	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	70%
6	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> .6H <sub>2</sub> O	n.d.
7	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	n.d.
8	Eosin B	n.d.
9	Eosin Y	n.d.

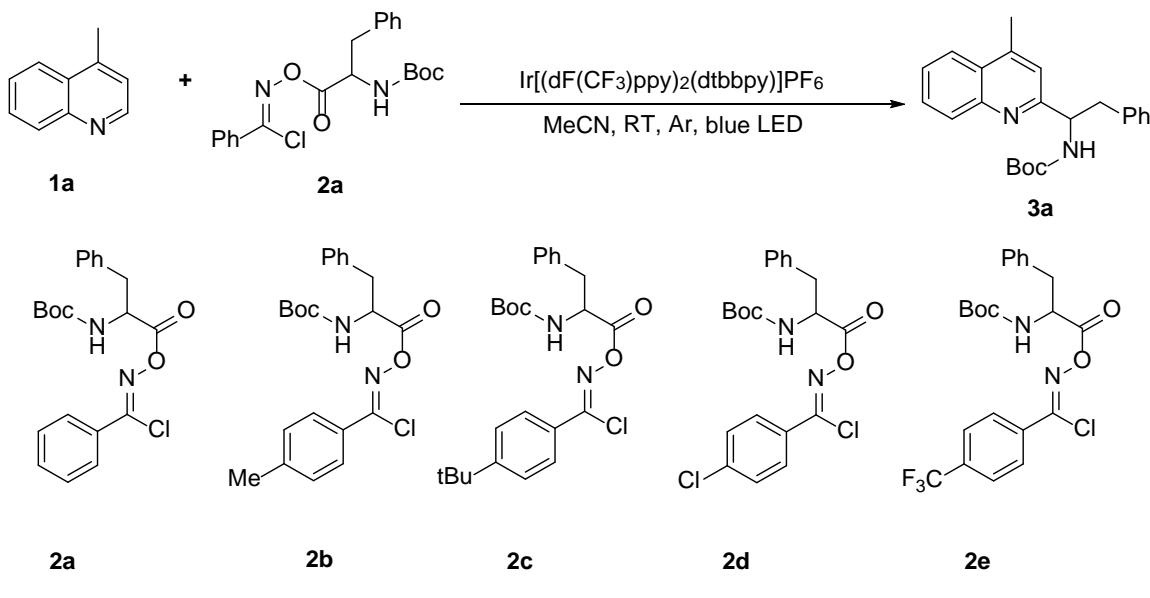
[a]All reactions were carried out with 4-methylquinoline (57.2 mg, 0.40 mmol), NHBC esters (0.20 mmol, 1eq.), Photocatalyst (2 mol%) in solvent (2.0 mL) at rt under Ar and 10W blue LEDs. [b] Isolated yield.

**Table S3: Optimization of Light<sup>[a]</sup>**



Entry	Light	Yield <sup>b</sup>
1	10W Blue LED	70%
2	30W Blue LED	70%
3	60W Blue LED	82%
4	90W Blue LED	75%
5	CFL	62%
6	White LED	51%

[a]All reactions were carried out with 4-methylquinoline (57.2 mg, 0.40 mmol), NHBC esters (0.20 mmol, 1eq.), Photocatalyst (2 mol%) in solvent (2.0 mL) at rt under Ar and 60W blue LEDs. [b] Isolated yield.

**Table S4: Optimization of R-NHBC<sup>[a]</sup>**

Entry	2	Yield <sup>b</sup>
1	<b>2a</b>	82%
2	<b>2b</b>	75%
3	<b>2c</b>	76%
4	<b>2d</b>	72%
5	<b>2e</b>	34%

[a]All reactions were carried out with 4-methylquinoline (57.2 mg, 0.40 mmol), NHBC esters (0.20 mmol, 1eq.), Photocatalyst (2 mol%) in solvent (2.0 mL) at rt under Ar and 60W blue LEDs. [b] Isolated yield.

**Table S5: Optimization of Reaction time<sup>[a]</sup>**

	<b>Entry</b>  <b>Time</b>  <b>Yield<sup>[b]</sup></b>	
1	4h	51%
2	8h	63%
3	12h	82%
4	16h	81%
5	20h	82%
6	24h	80%

[a]All reactions were carried out with 4-methylquinoline (57.2 mg, 0.40 mmol), NHBC esters (0.20 mmol, 1eq.), Photocatalyst (2 mol%) in solvent (2.0 mL) at rt under Ar and 60W blue LEDs. [b] Isolated yield.

**Table S6: Control Experiments<sup>[a]</sup>**

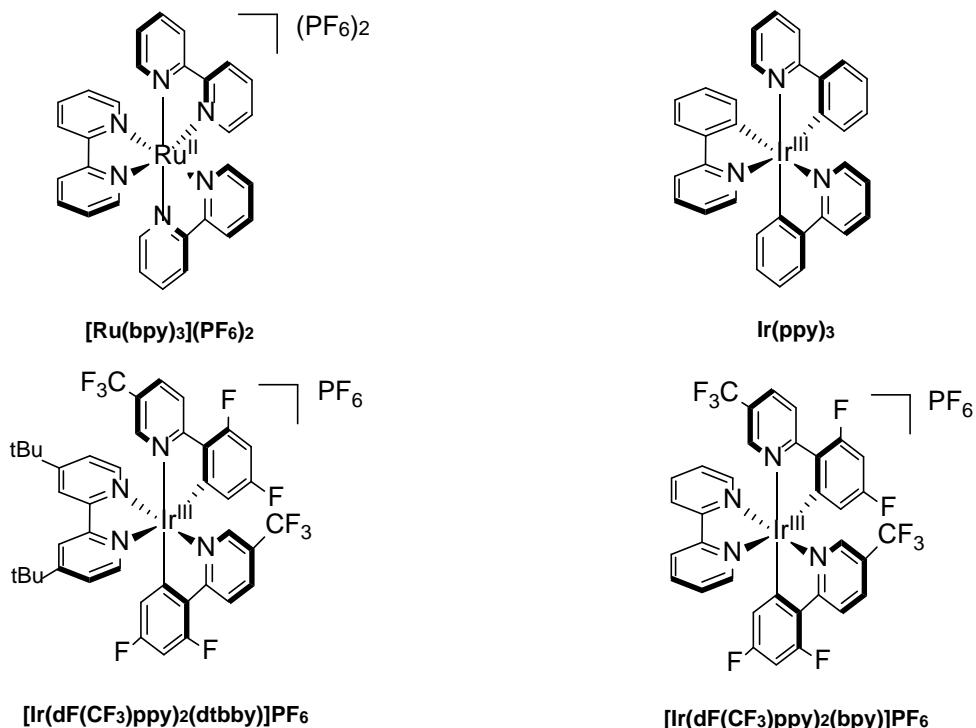
	<b>Entry</b>  <b>Variations from conditions</b>  <b>Yield<sup>[b]</sup></b>	
1	none	82%
2	without photocatalyst	n.d.
3	without light	n.d
4	In the air	67%
5	TEMPO	n.d

[a]All reactions were carried out with 4-methylquinoline (57.2 mg, 0.40 mmol), NHBC esters (0.20 mmol, 1eq.), Photocatalyst (2 mol%) in solvent (2.0 mL) at rt under Ar and 60W blue LEDs. [b] Isolated yield.

## II. Preliminary quenching studies

The preliminary quenching studies were all performed under oxygen-free conditions in an argon-filled glovebox. All photocatalysts and the substrates were weighed in vials and placed inside the glovebox. Acetonitrile was degassed by argon sparging for 1 h and placed inside the glovebox. The photocatalyst/substrate samples were dissolved in acetonitrile. In a cuvette solutions of substrate (25 mM) and the respective photocatalyst (10  $\mu$ M) or solutions of only photocatalyst (10  $\mu$ M) were prepared. This equates 2500 equivalents of the potential quencher compared to the photocatalyst. The cuvette was capped with a PTFE stopper, sealed with parafilm and moved to the fluorescence spectrometer. After the measurement, the cuvette was emptied, rinsed with acetonitrile and dried inside a glovebox. The next sample was subsequently transferred to the same cuvette.

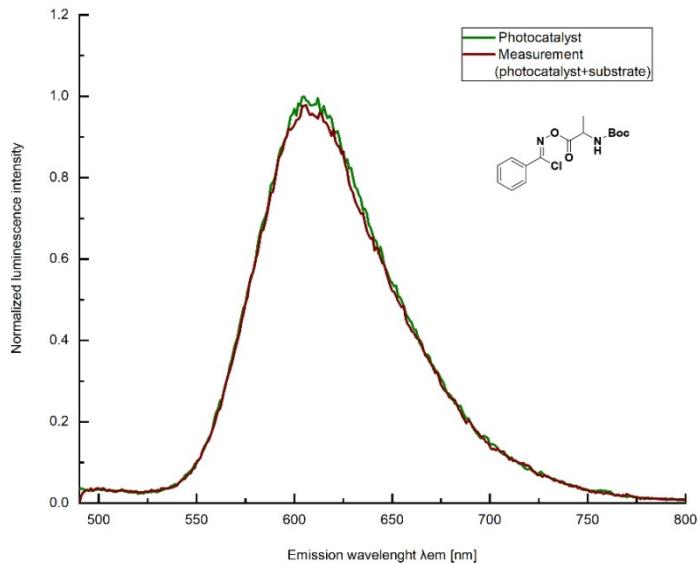
The structures of the photocatalysts employed in this study are shown in figure S1. The wavelength used to calculate the quenching percentage are shown below.



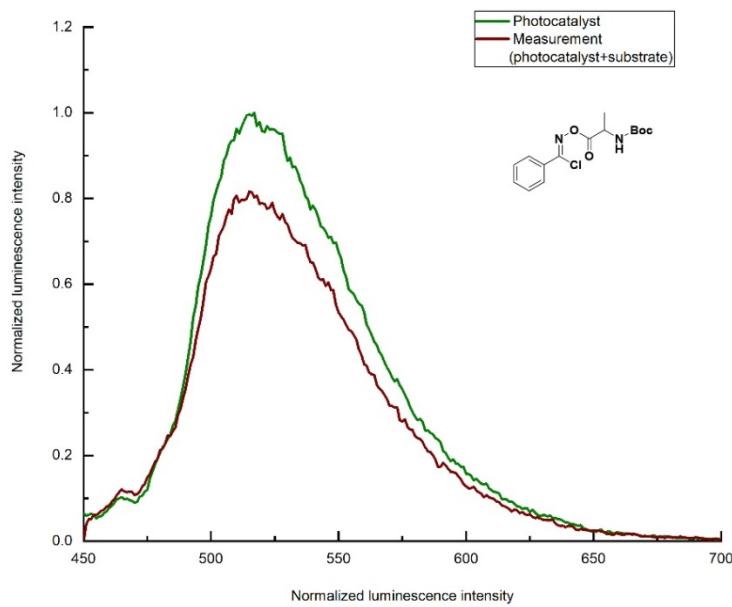
**Figure S1.** Photocatalysts employed in the quenching studies.

The resulting quenching percentage with the different photocatalysts and *tert*-butyl (Z)-(1-(((chlorophenyl)methylene)amino)oxy)-1-oxopropan-2-yl)carbamate (b) are shown below.

**[Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and *ert*-butyl (Z)-(1-(((chlorophenyl)methylene)amino)oxy)-1-oxopropan-2-yl)carbamate (b)**

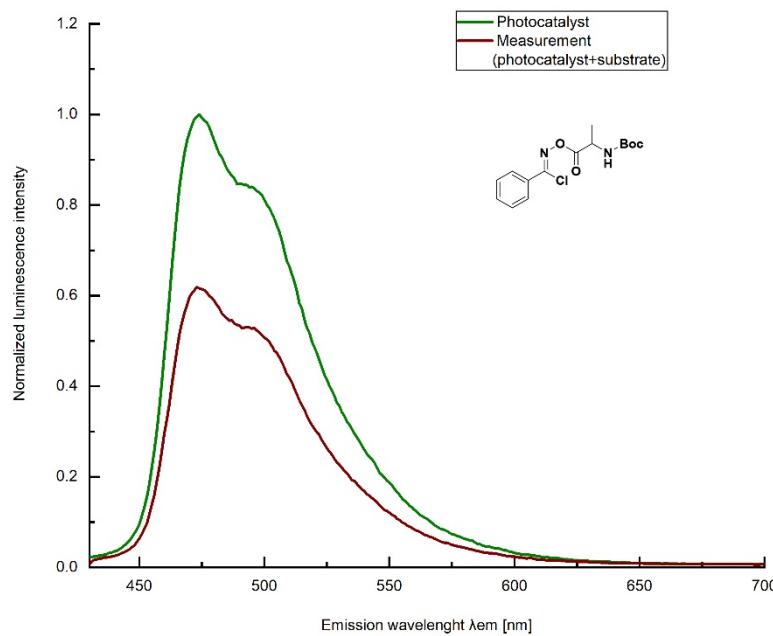


**fac-Ir(ppy)<sub>3</sub> and *ert*-butyl (Z)-(1-(((chlorophenyl)methylene)amino)oxy)-1-oxopropan-2-yl)carbamate (b)**



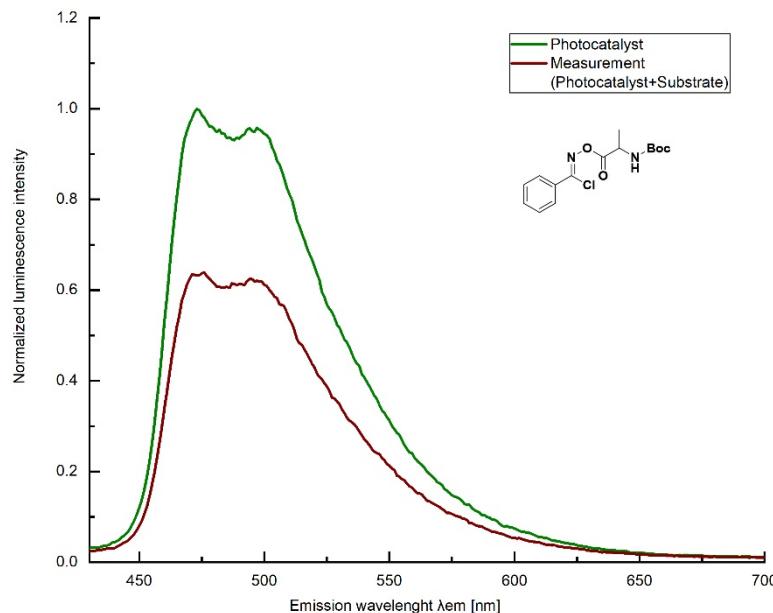
**[Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> and *ert*-butyl**

**(Z)-(1-(((chlorophenyl)methylene)amino)oxy)-1-oxopropan-2-yl)carbamate (b)**



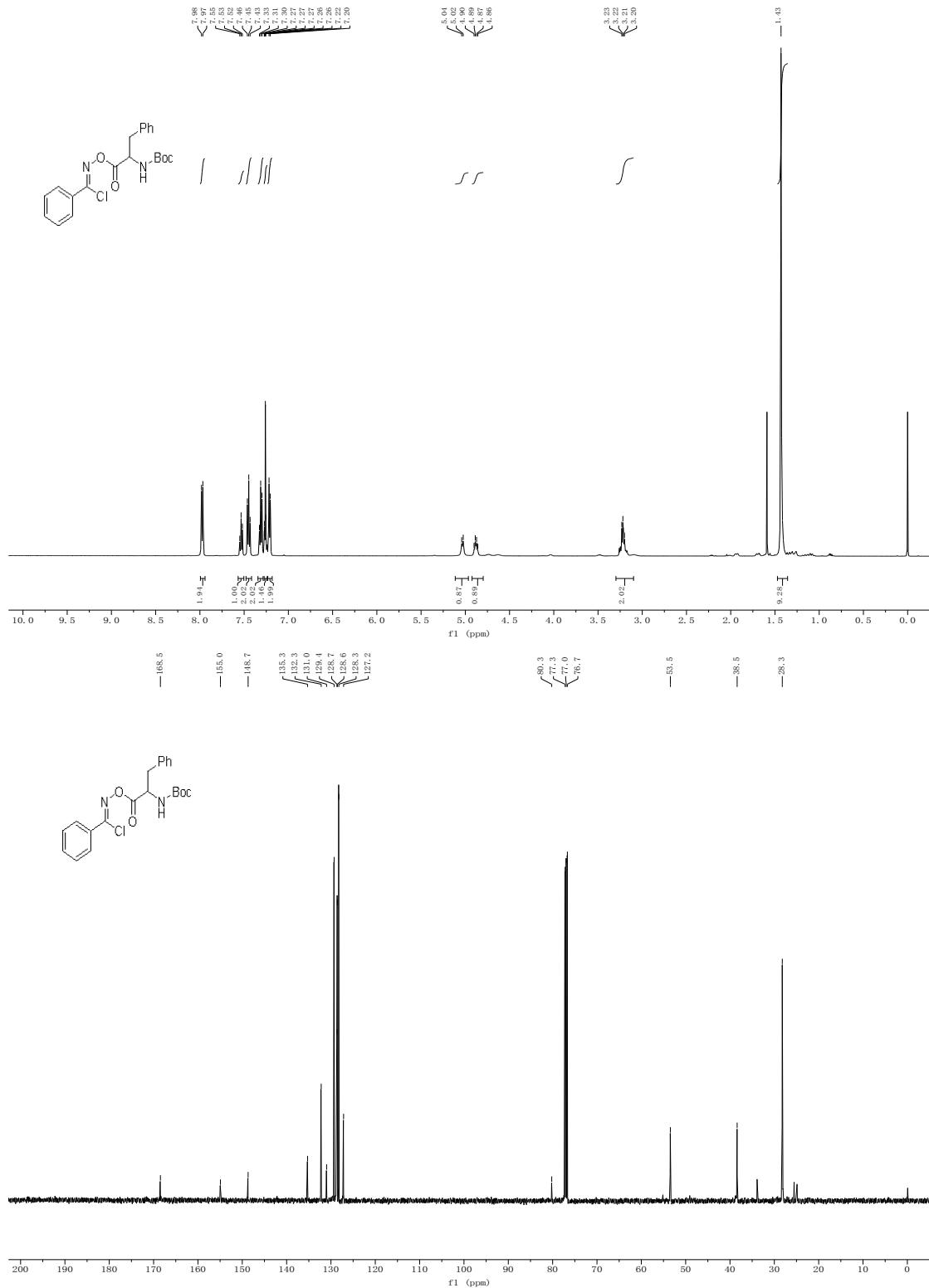
**[Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> and *ert*-butyl**

**(Z)-(1-(((chlorophenyl)methylene)amino)oxy)-1-oxopropan-2-yl)carbamate (b)**

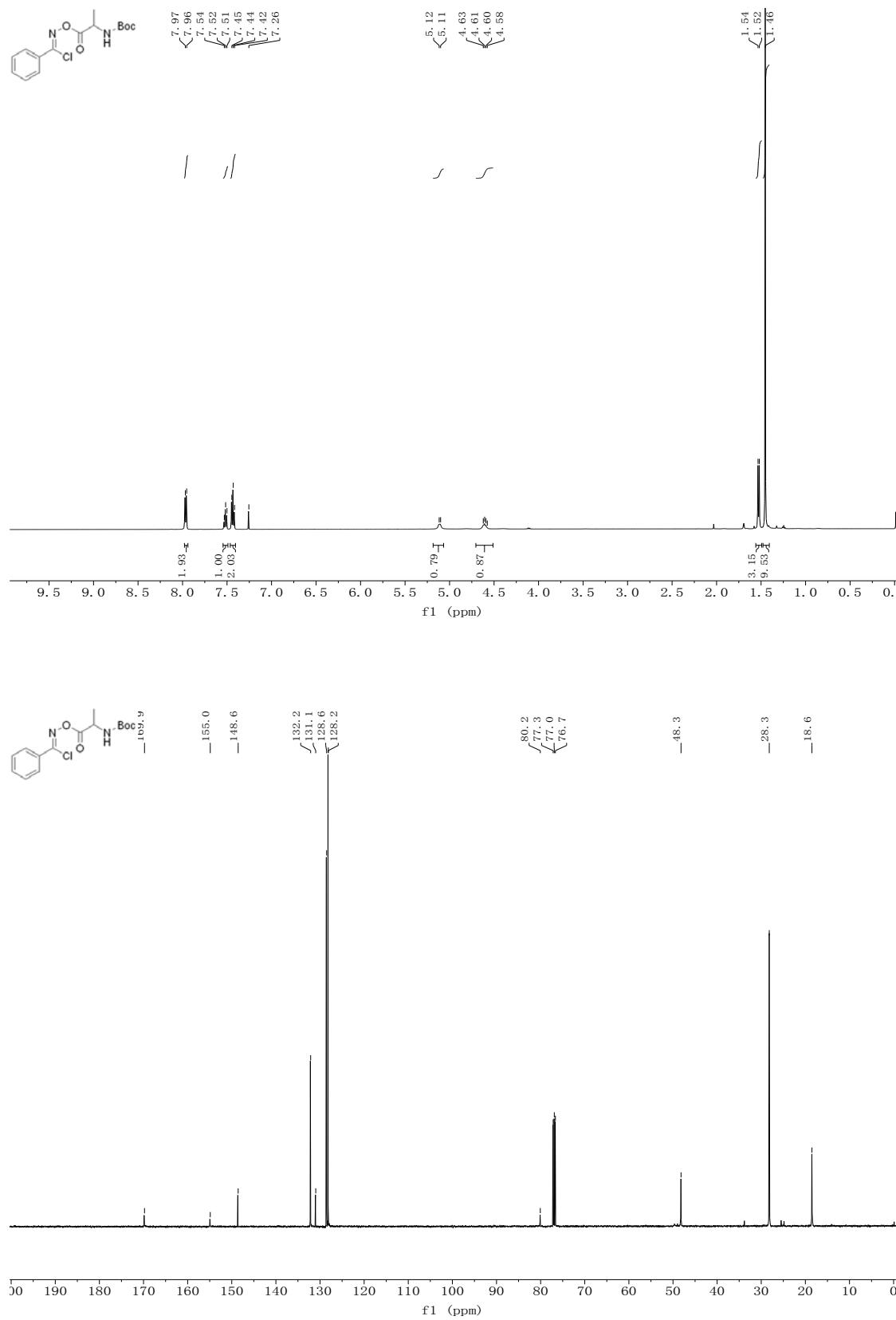


### III. NMR Spectra

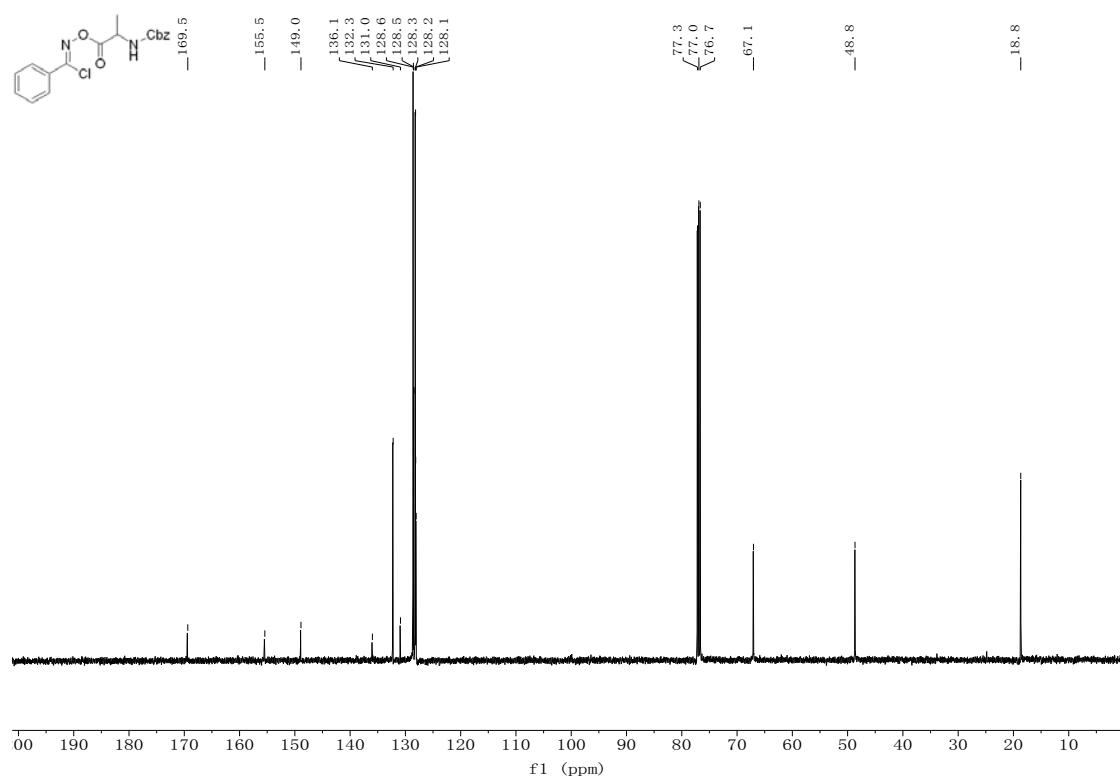
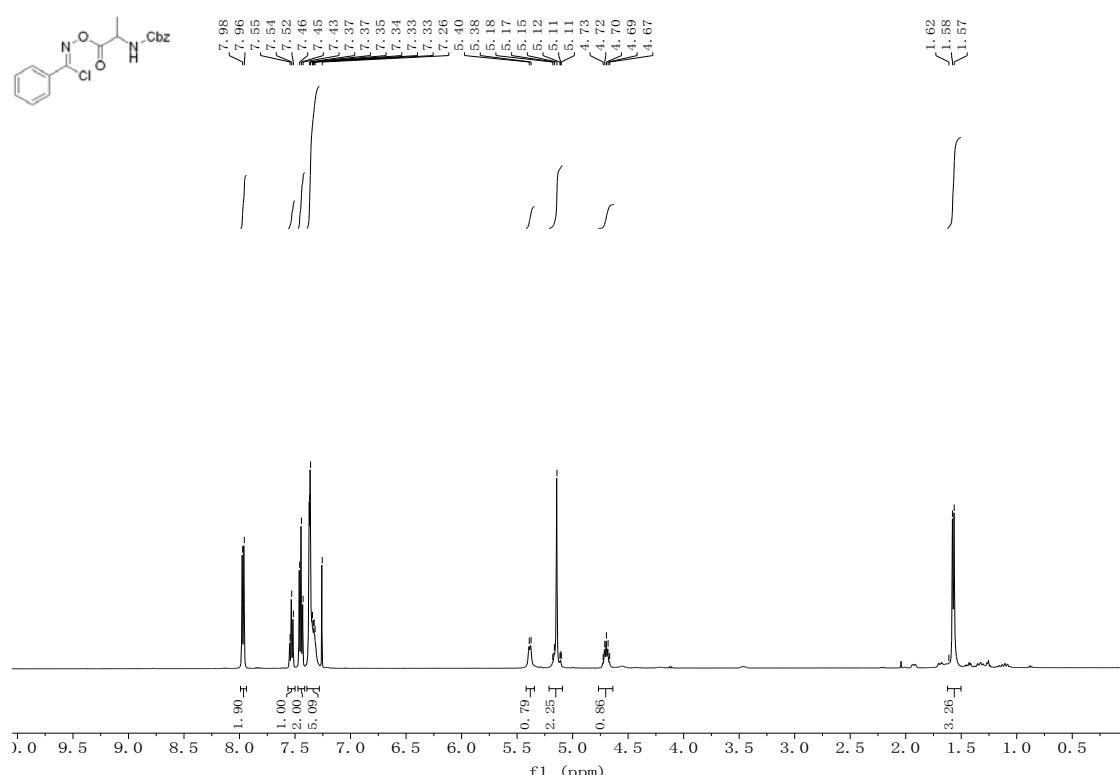
**tert-butyl (Z)-(1-(((chlorophenyl)methylene)amino)oxy)-1-oxo-3-phenylpropan-2-yl)carbamate (a)**

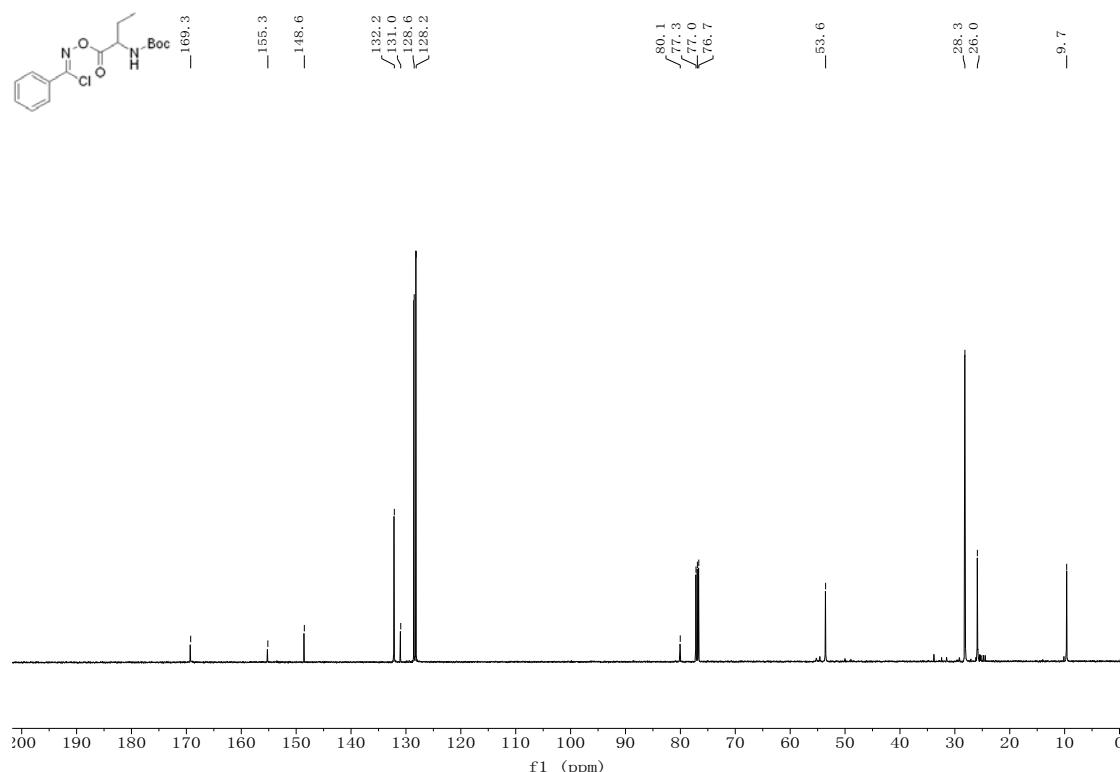
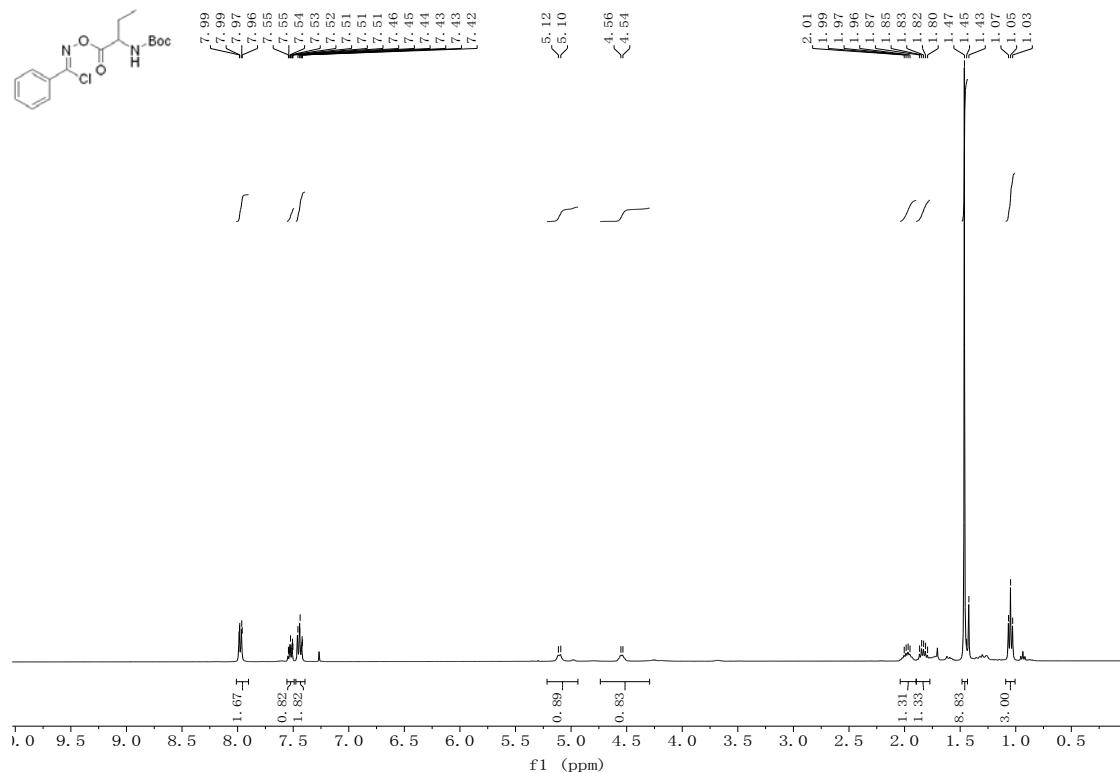


**tert-butyl(Z)-((chlorophenyl)methyleneamino)oxy-1-oxopropan-2-ylcarbamate (b)**



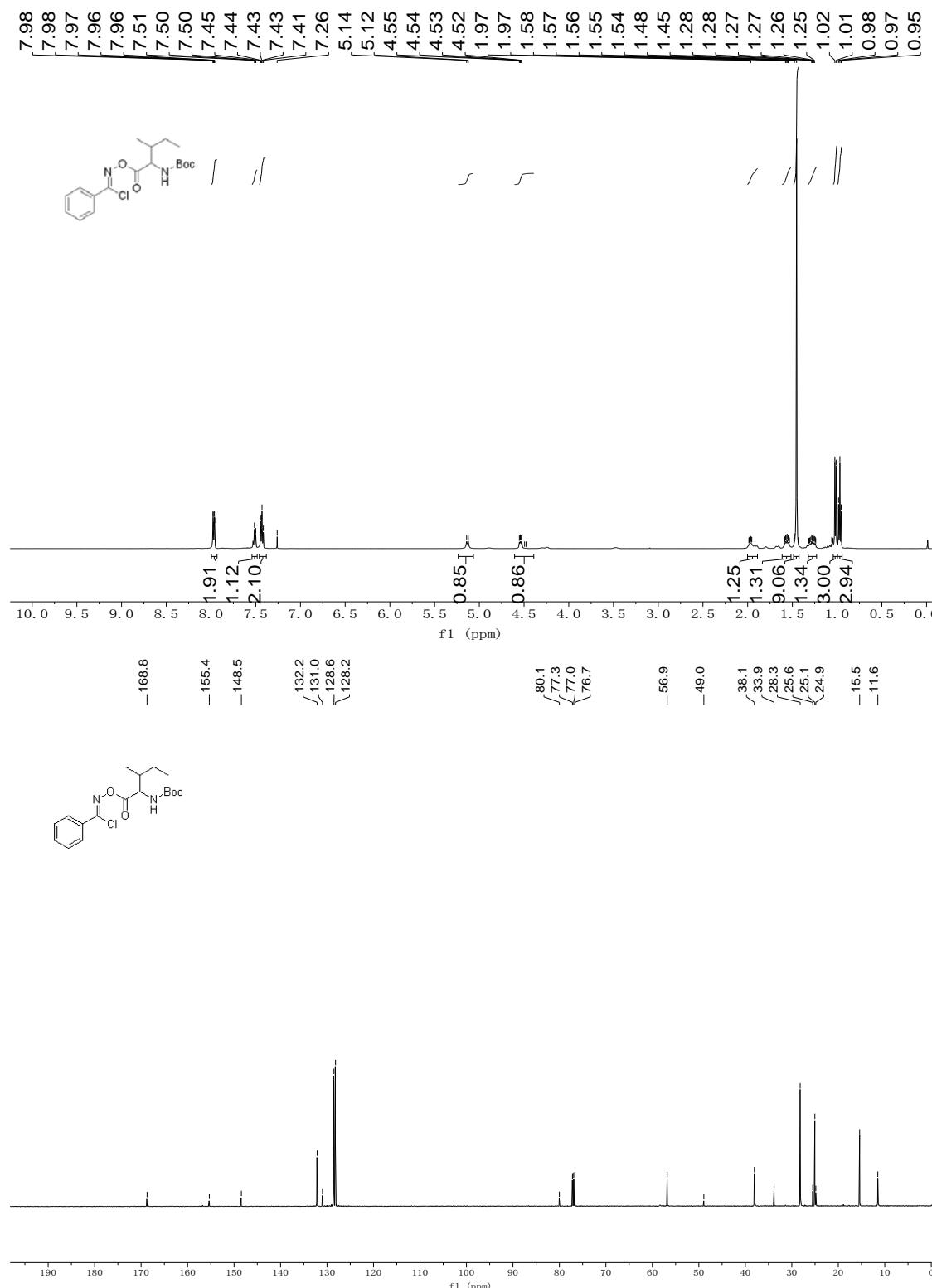
**Benzyl(Z)-((chlorophenyl)methylene)aminooxy)-1-oxopropan-2-yl)carbamate (c)**



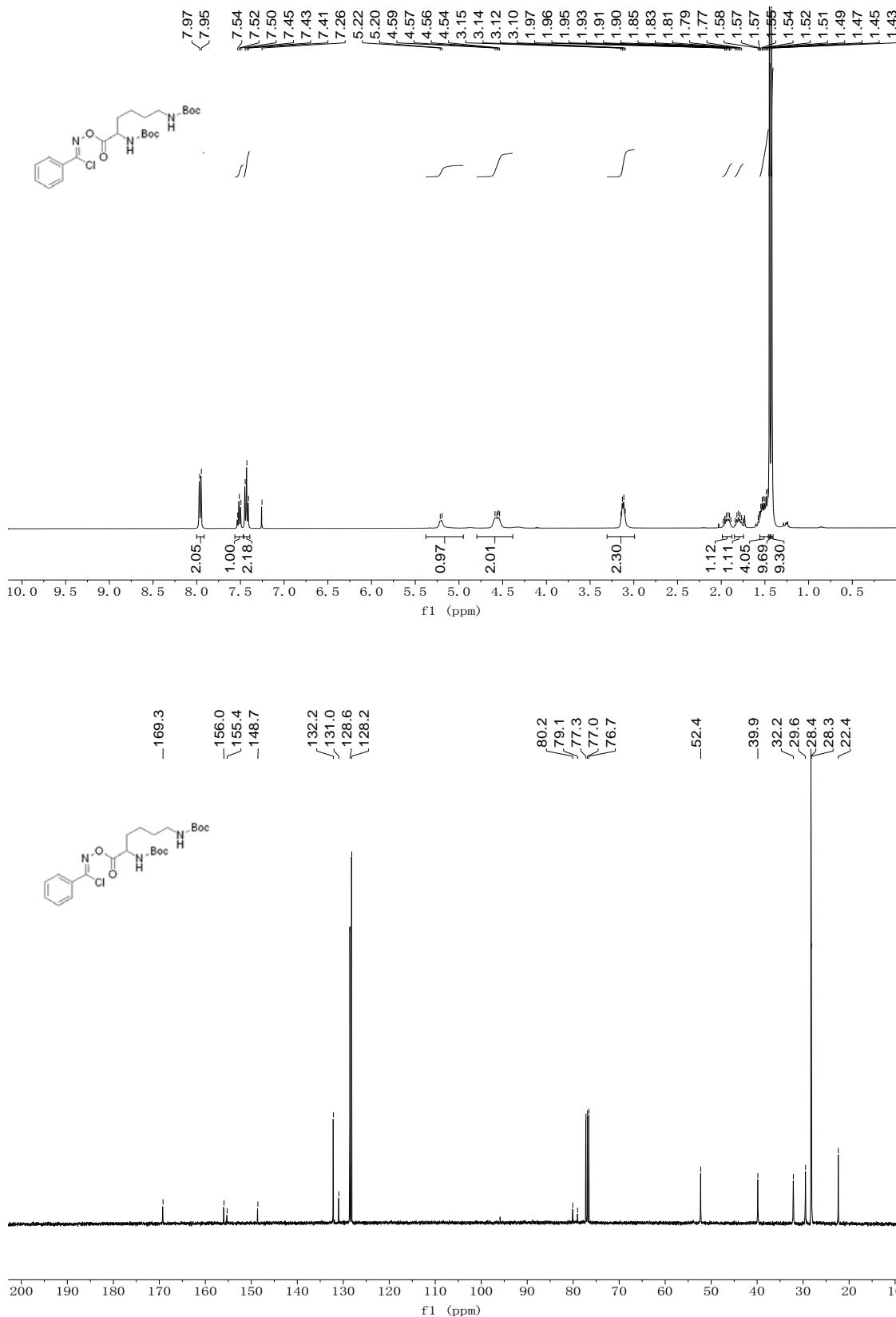
**tert-butyl****(Z)-(1-((chlorophenyl)methylene)amino)oxy)-1-oxobutan-2-yl)carbamate(d)**

### **tert-butyl**

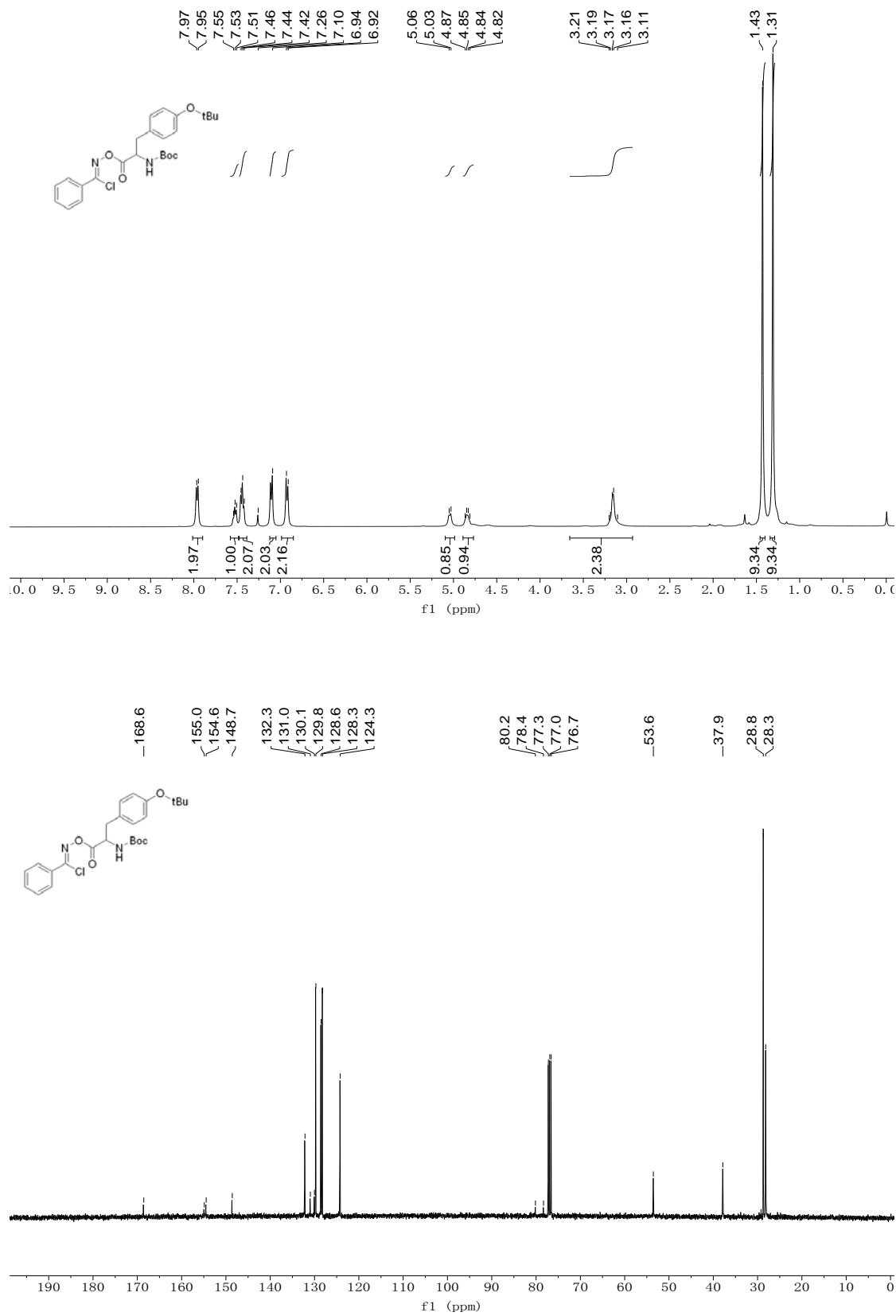
**(Z)-(1-(((chloro(phenyl)methylene)amino)oxy)-3-methyl-1-oxopentan-2-yl)carbamate (e)**



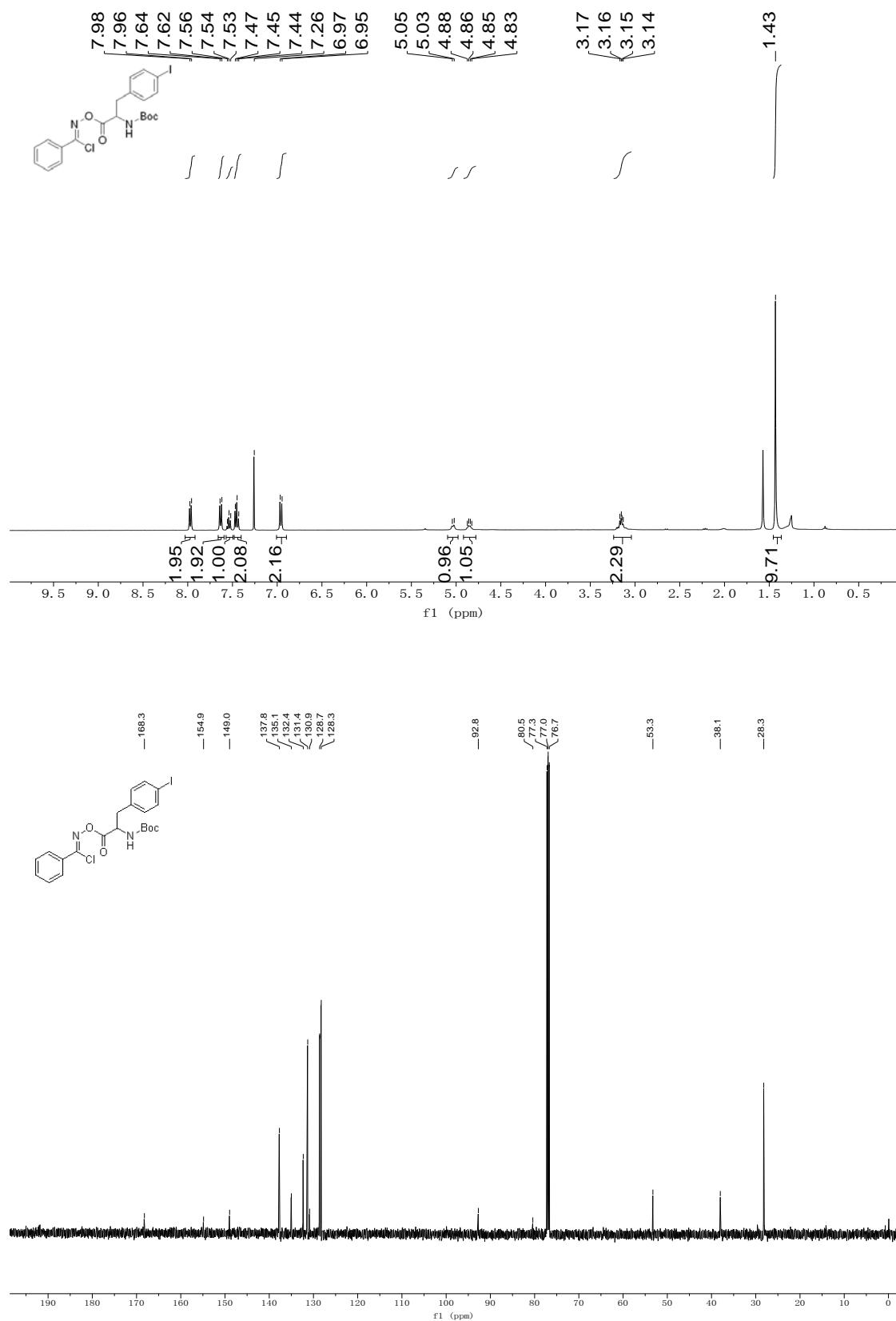
**di-tert-butyl ((6-(((chlorophenyl)methylene)amino)oxy)-6-oxohexane-1,5-diyl)  
(Z)-dicarbamate (f)**



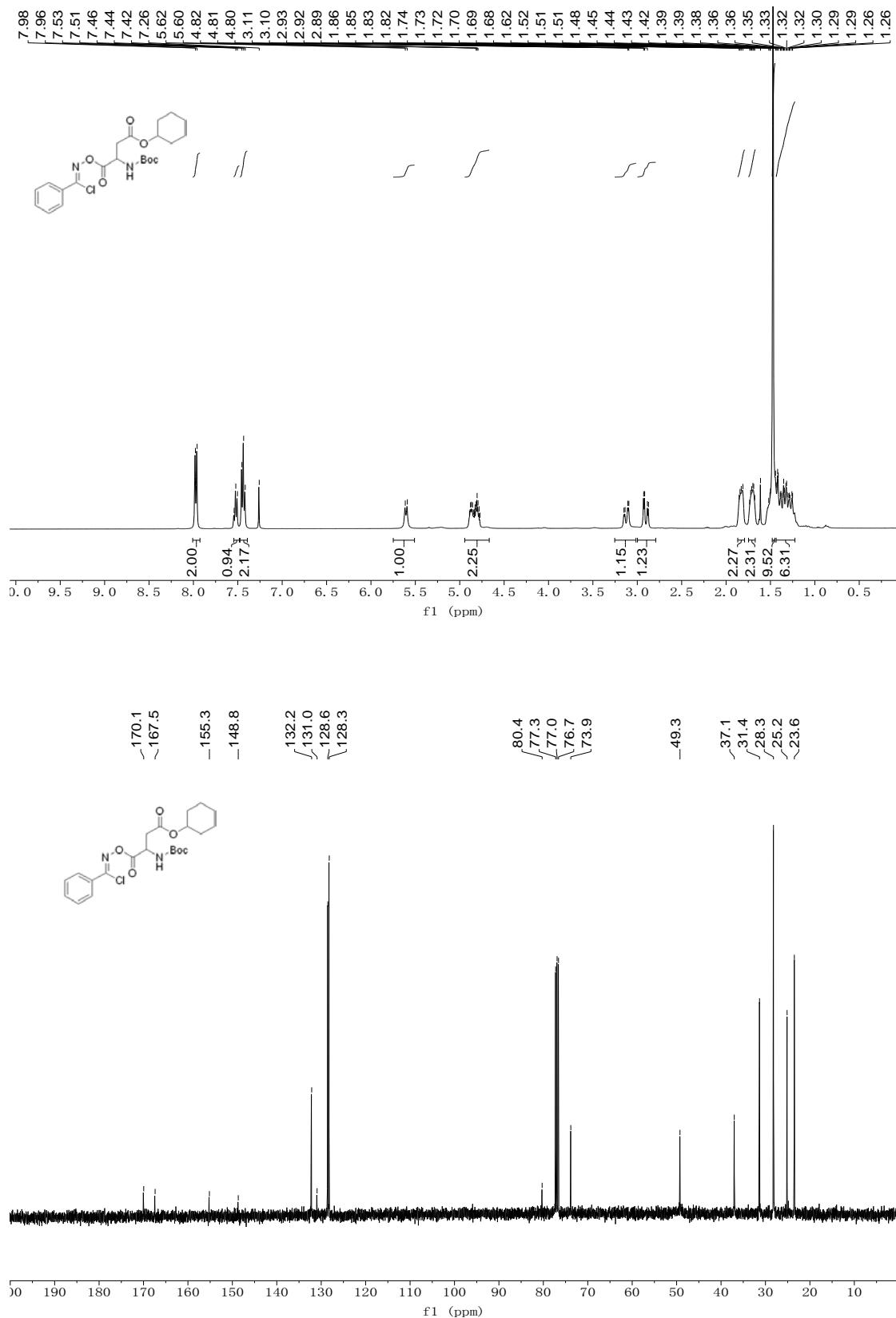
**tert-butyl (Z)-(3-(4-(tert-butoxy)phenyl)-1-((chlorophenyl)methylene)amino)oxy)-1-oxopropan-2-yl)carbamate (g)**



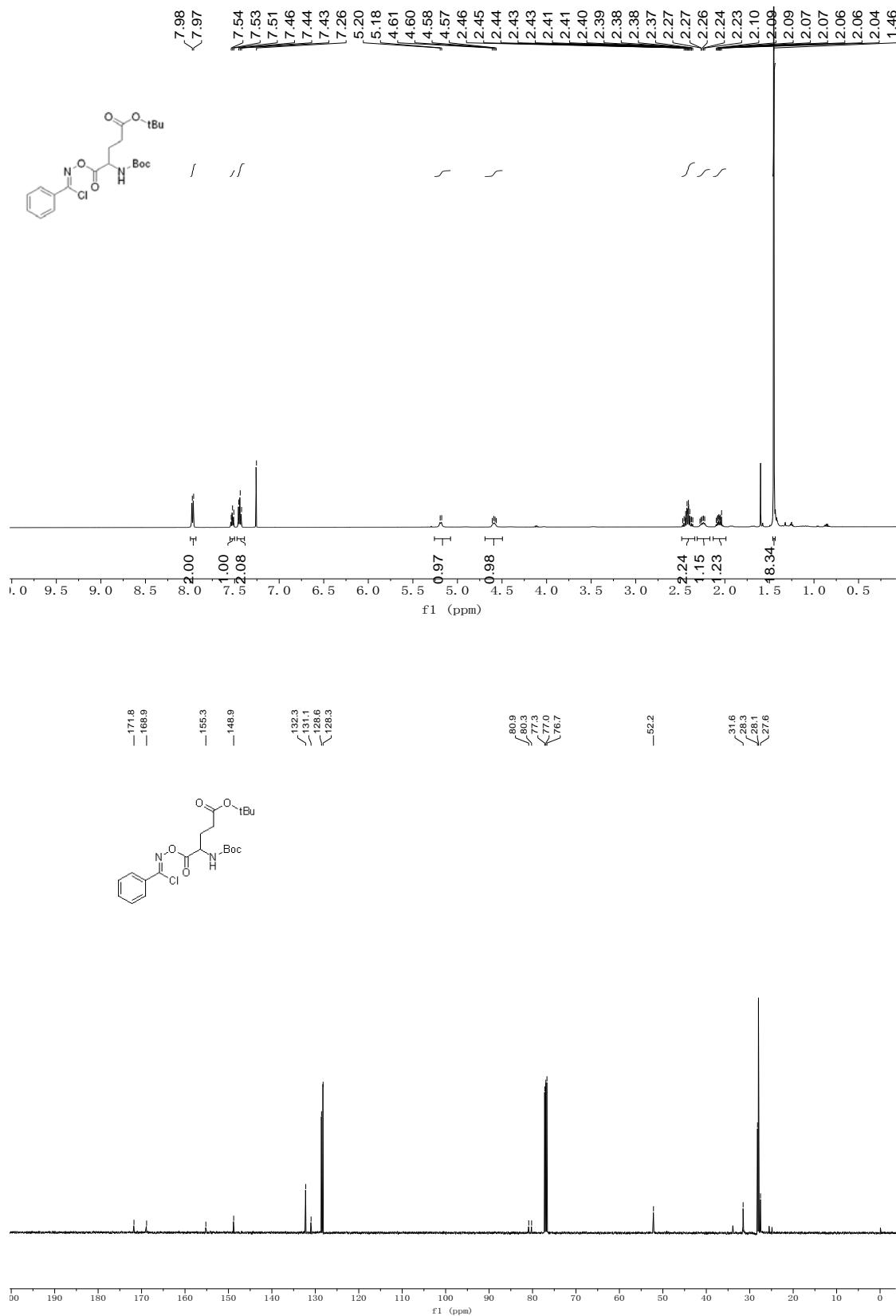
**tert-butyl (Z)-(1-((chlorophenyl)methylene)amino)oxy)-3-(4-iodophenyl)-1-oxopropan-2-yl)carbamate (h)**

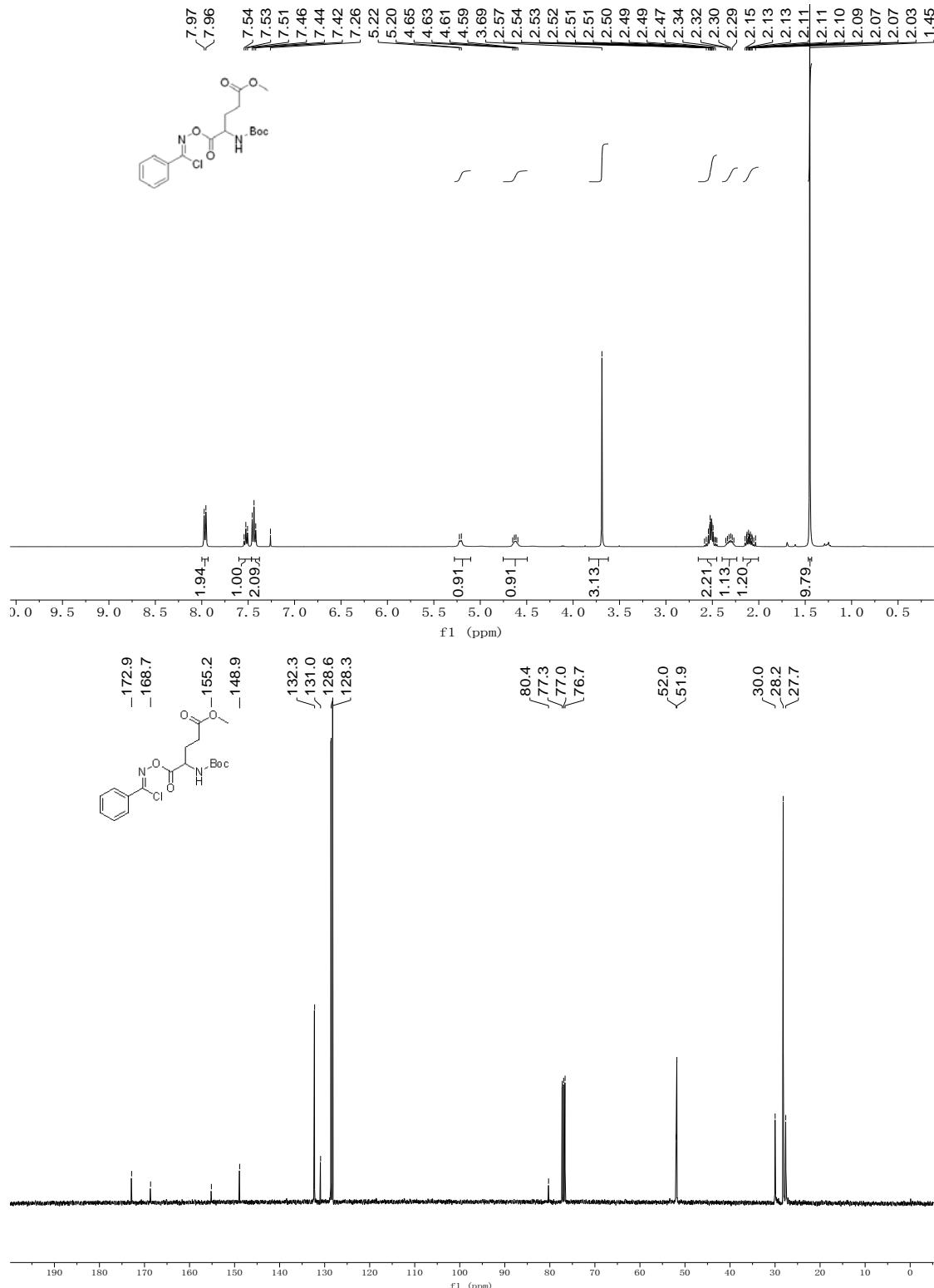


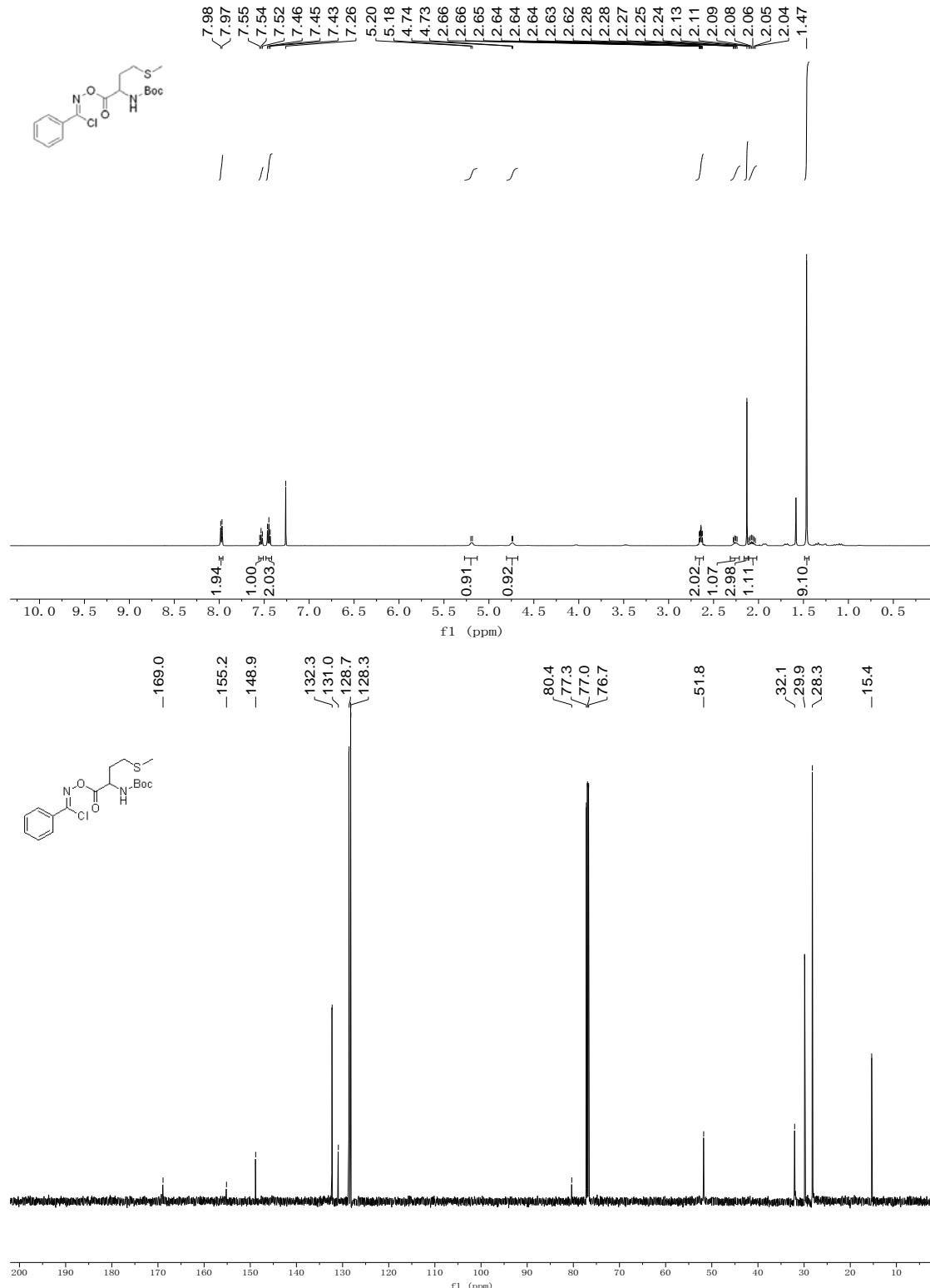
**cyclohexyl (Z)-3-((tert-butoxycarbonyl)amino)-4-(((chlorophenyl)methylene) amino)oxy)-4-oxobutanoate (i)**



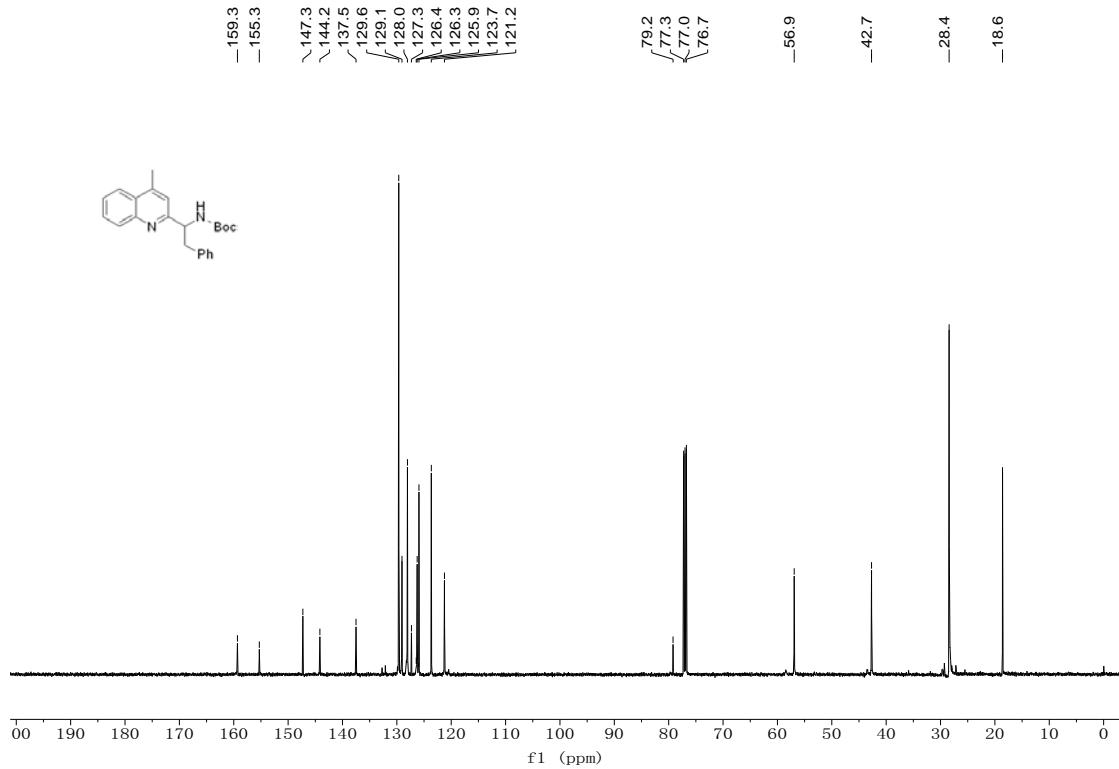
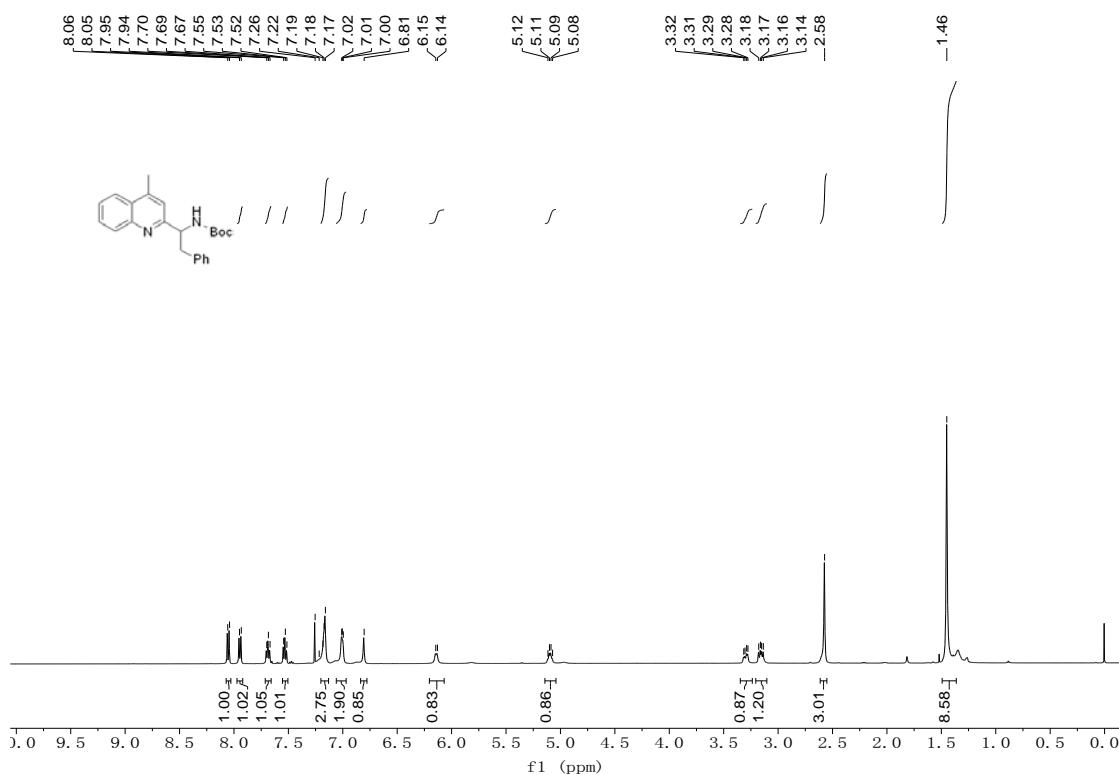
**tert-butyl (Z)-4-((tert-butoxycarbonyl)amino)-5-(((chlorophenyl)methylene)amino)oxy)-5-oxopentanoate (j)**



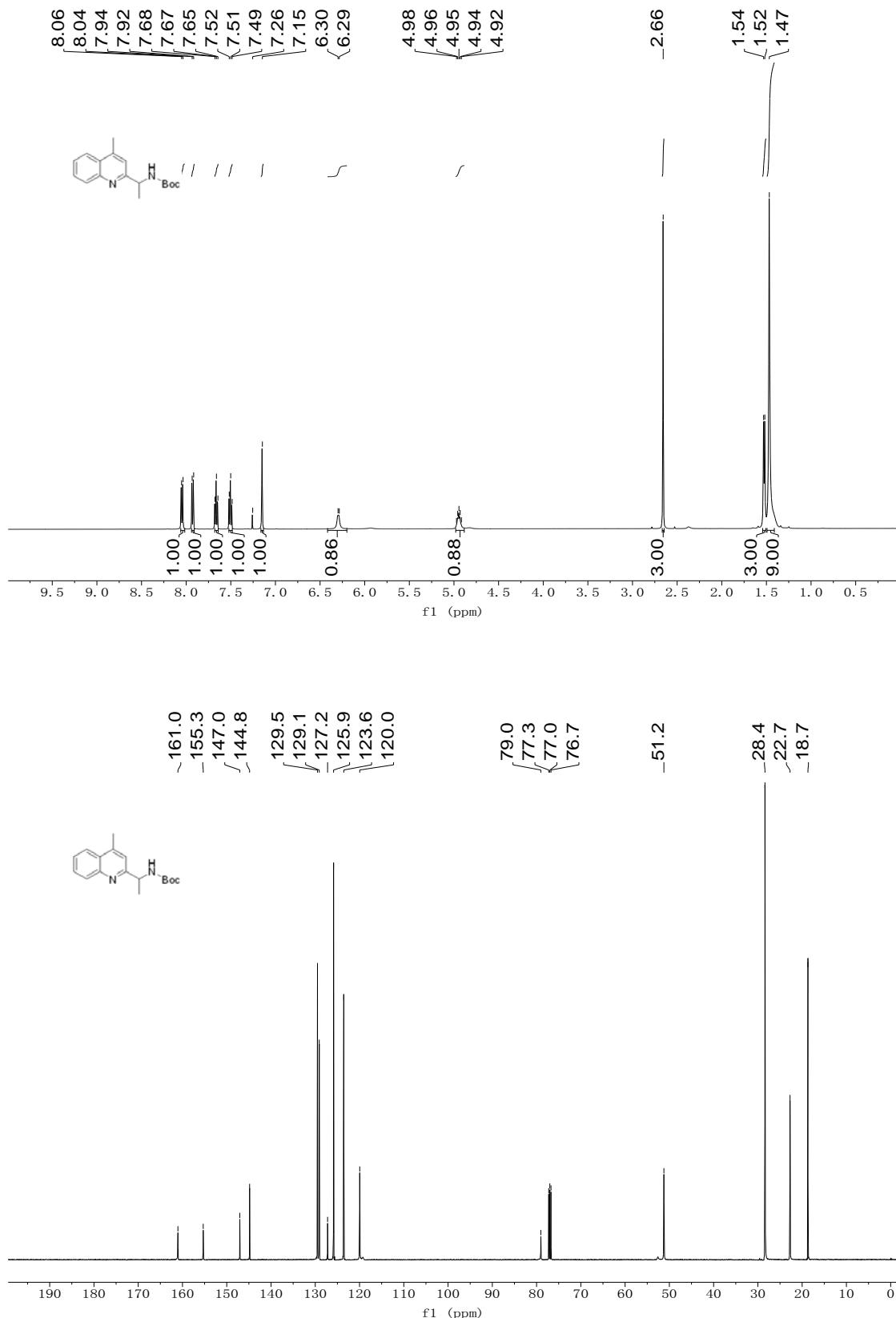
**methyl****(Z)-4-((tert-butoxycarbonyl)amino)-5-(((chlorophenyl)methylene)amino)oxy)-5-oxopentanoate (k)**

**tert-butyl****(Z)-(1-(((chlorophenyl)methylene)amino)oxy)-4-(methylthio)-1-oxobutan-2-ylcarbamate (I)**

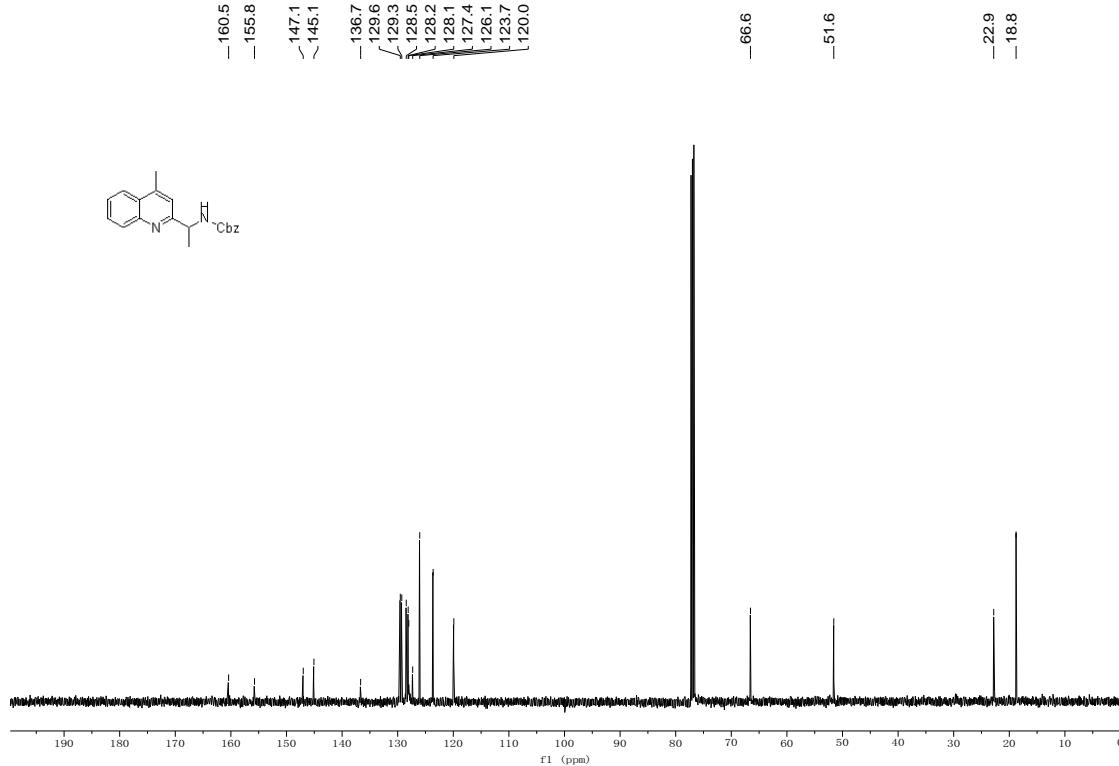
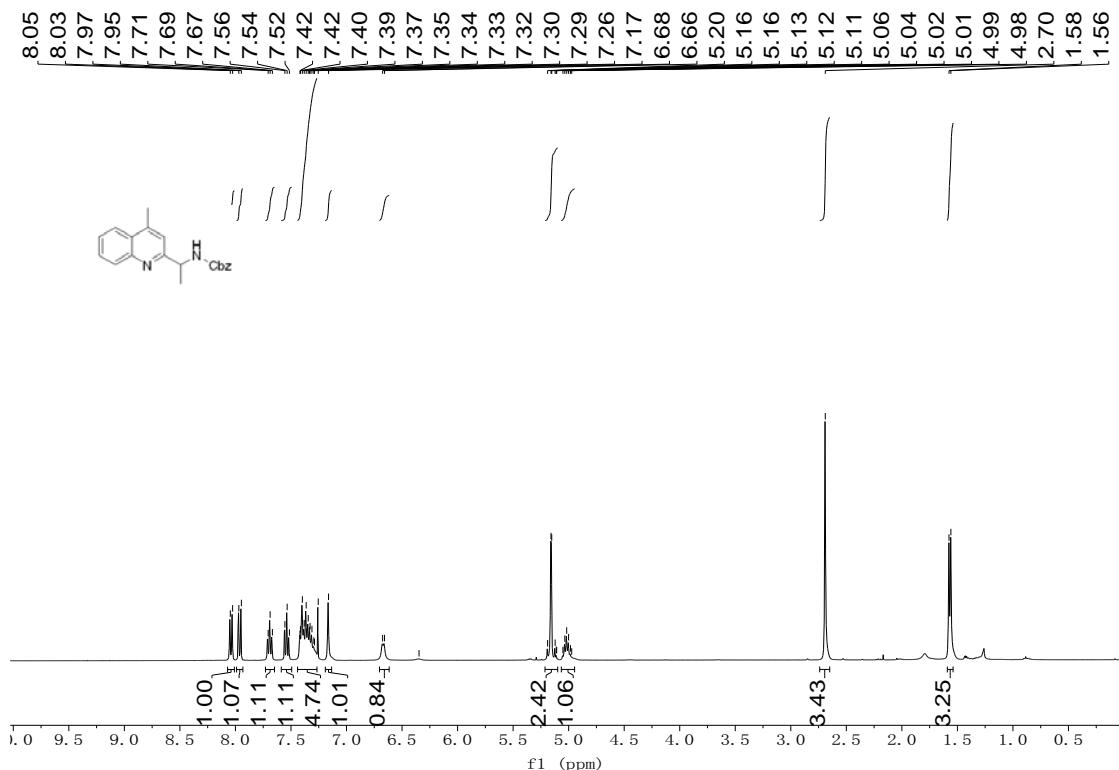
**tert-butyl (1-(4-methylquinolin-2-yl)-2phenylethy)carbamate (1)**



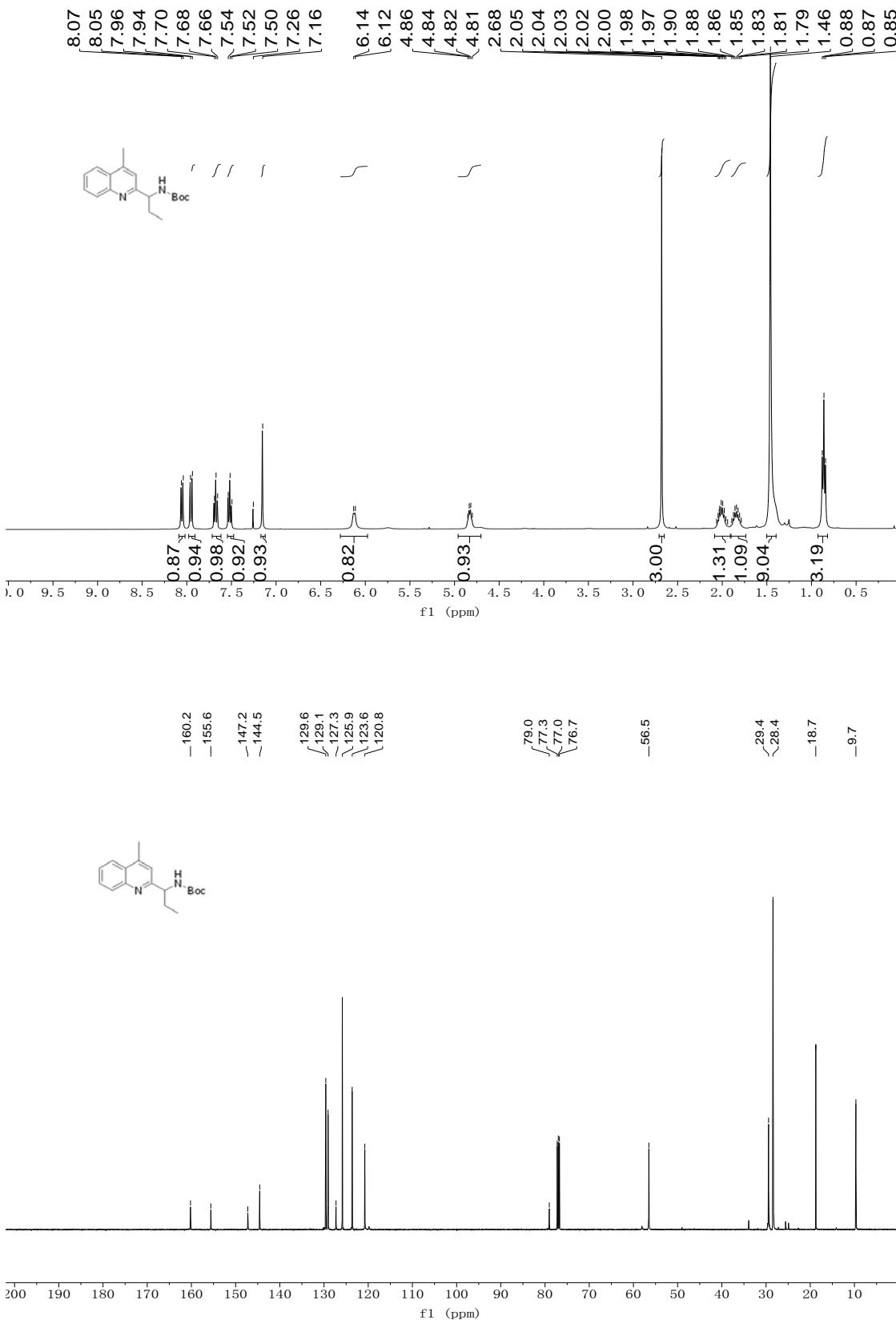
**tert-butyl (1-(4-methylquinolin-2-yl)ethyl)carbamate (2)**



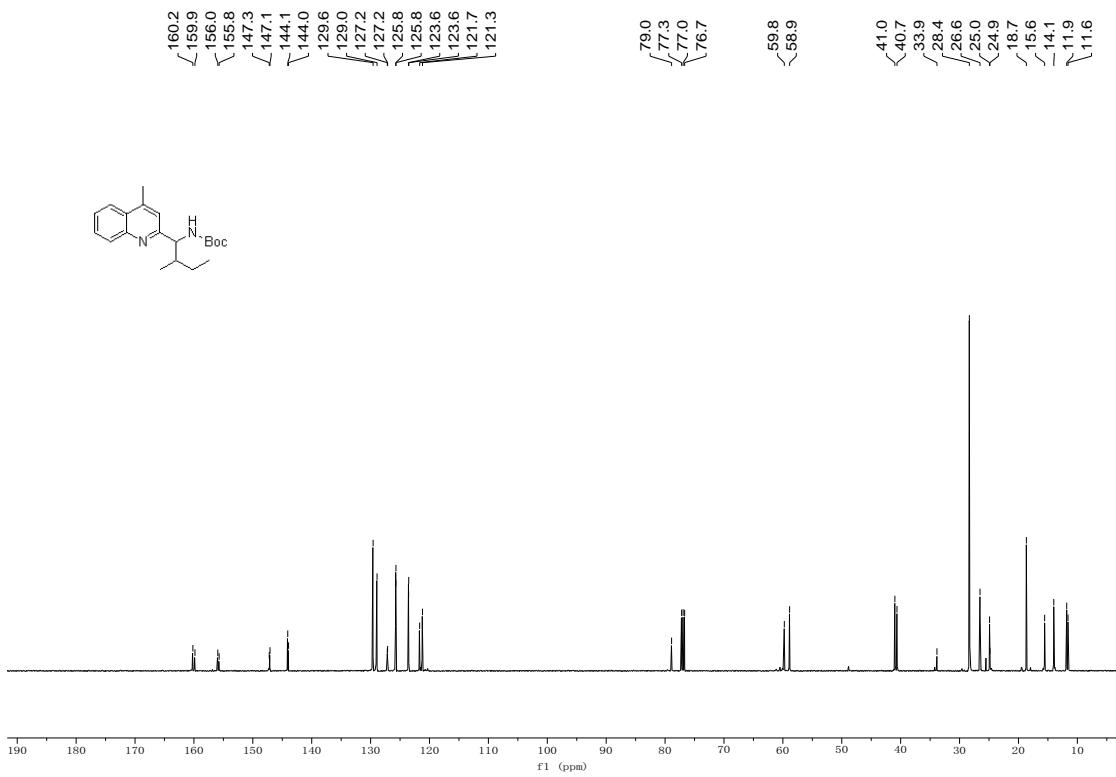
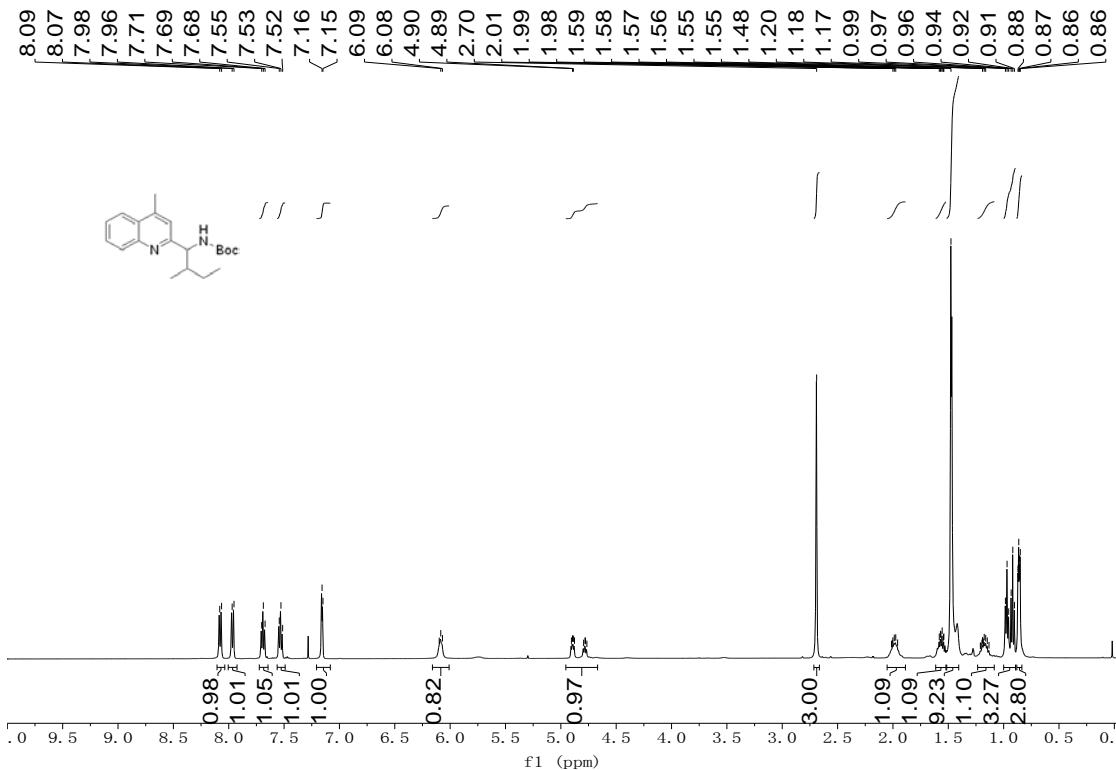
**benzyl (2-phenyl-1-(4-methylquinolin-2-yl)ethyl) carbamate (3)**



**tert-butyl (1-(4-methylquinolin-2-yl)propyl)carbamate (4)**



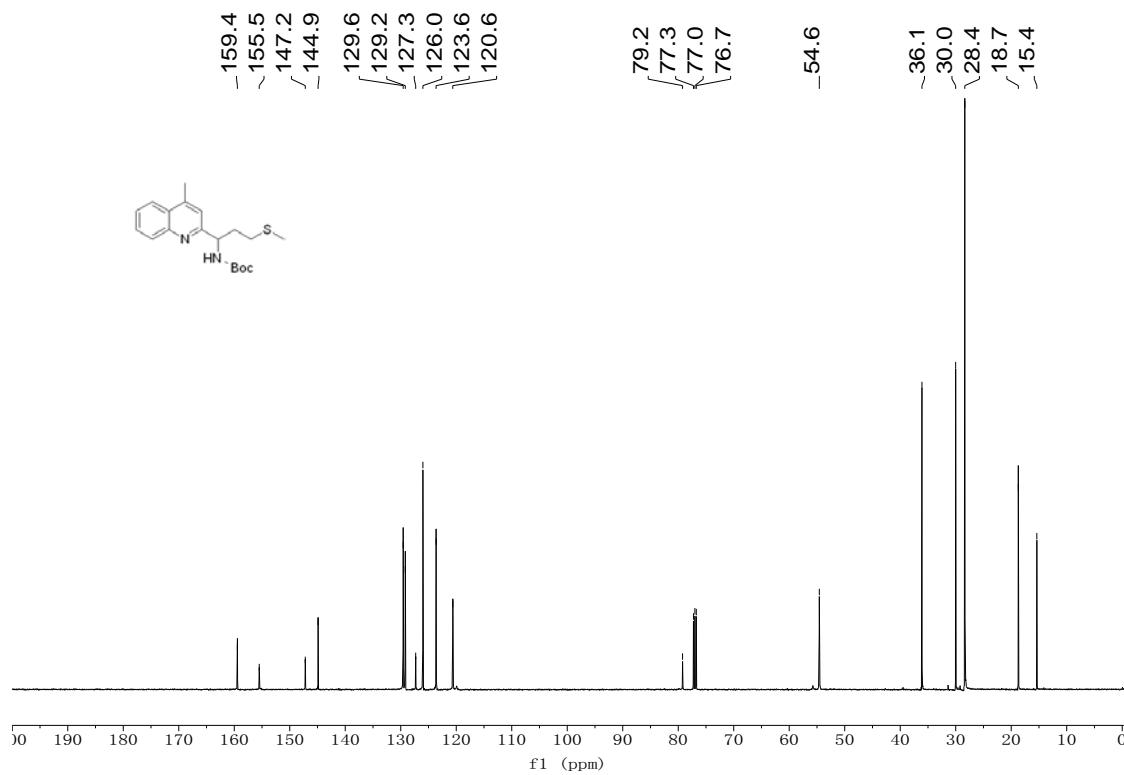
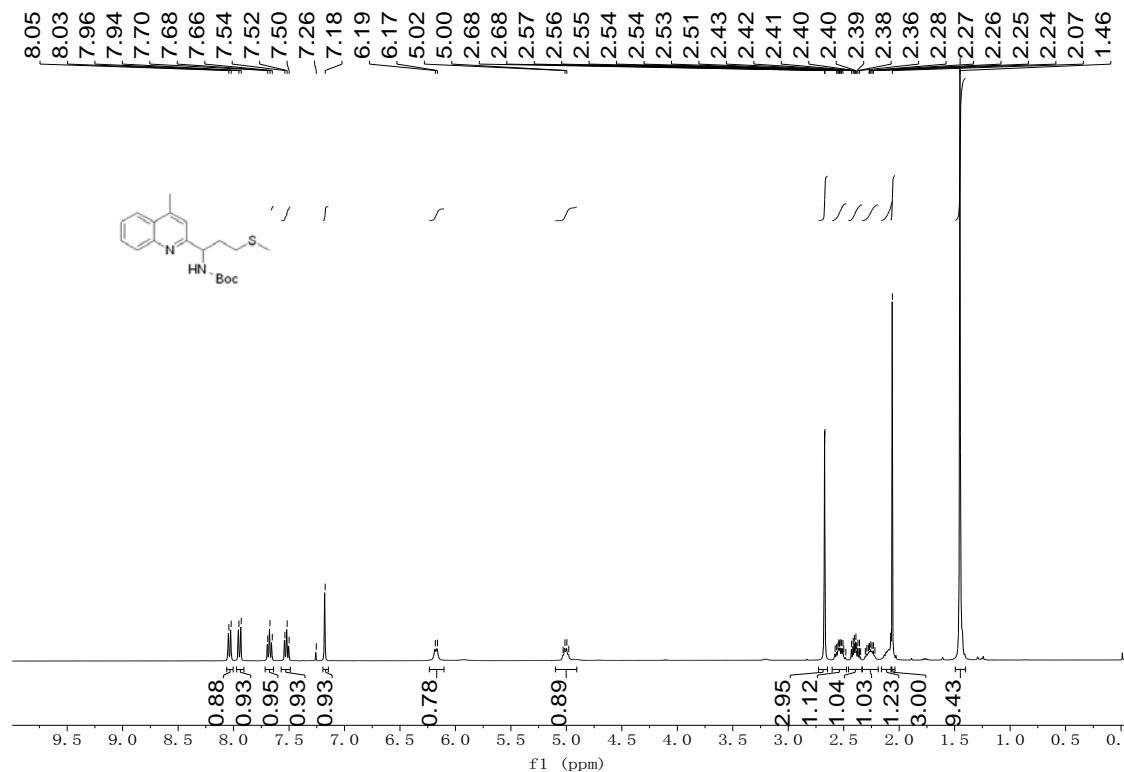
**tert-butyl (2-methyl-1-(4-methylquinolin-2-yl)-2-butyl)carbamate (5)**



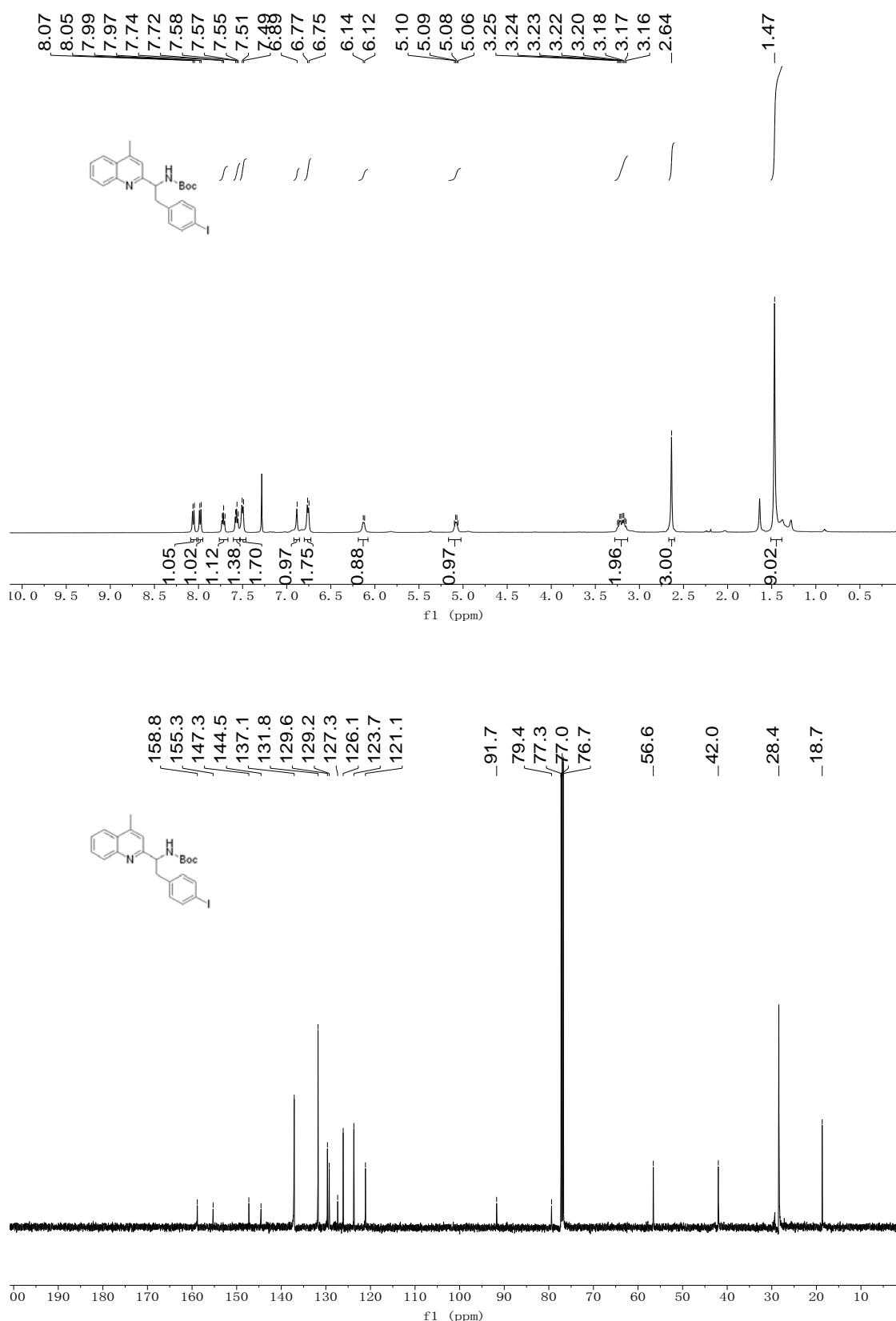
**tert-butyl 4-((tert-butoxycarbonyl)amino)-4-(4-methylquinolin-2-yl)butanoate  
(6)**



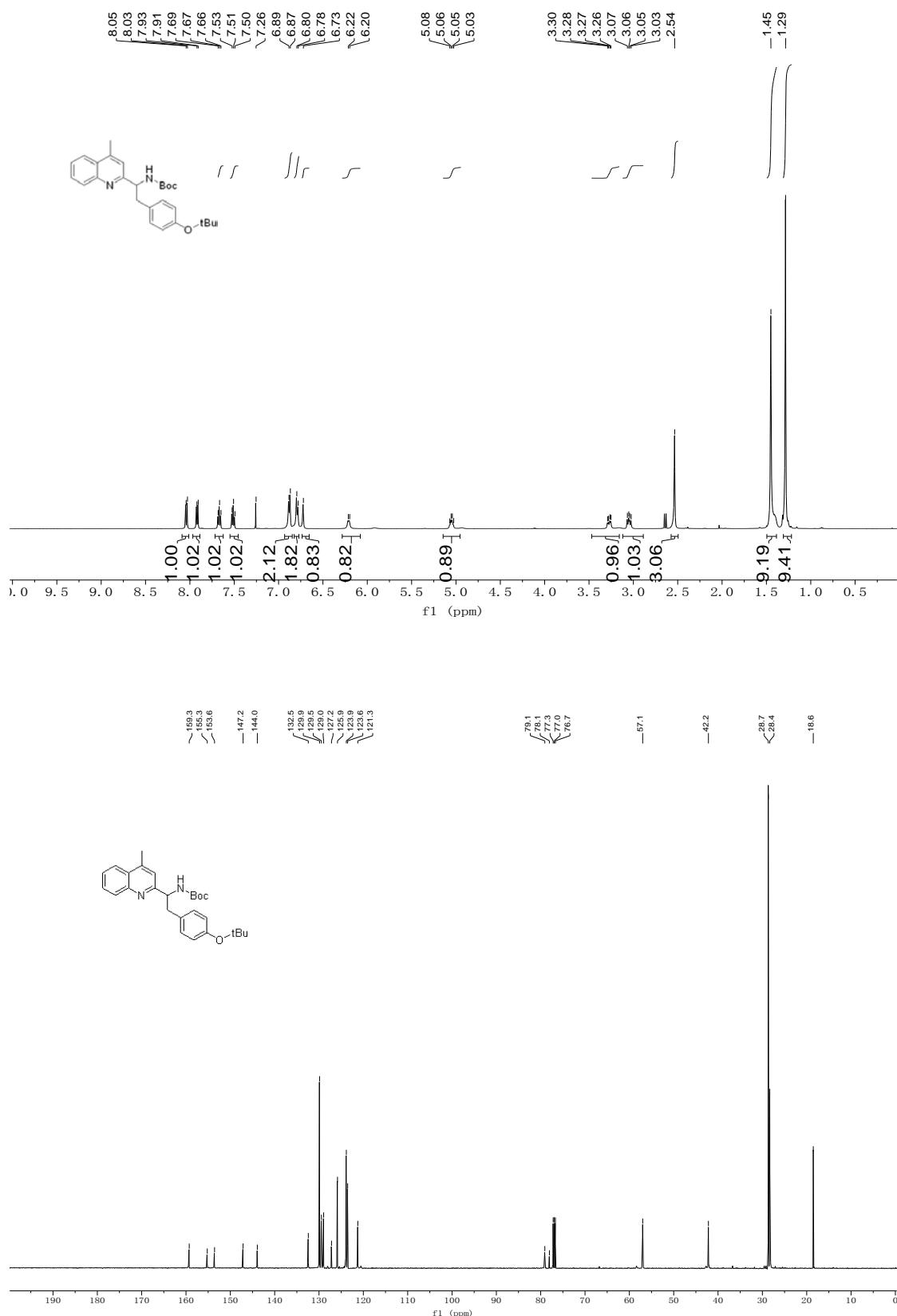
**tert-butyl (1-(4-methylquinolin-2-yl)-3-(methylthio)propyl)carbamate (7)**



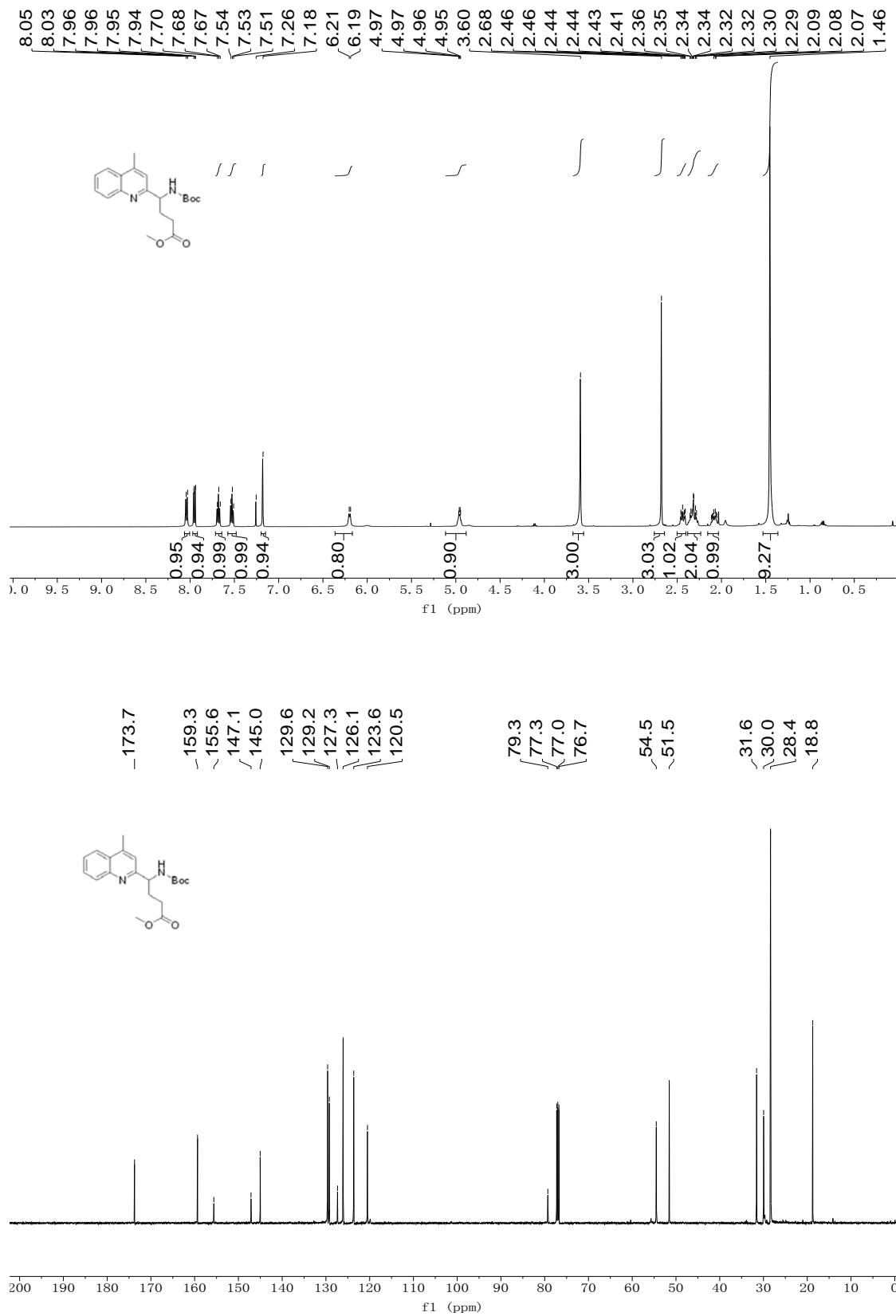
**tert-butyl (2-(4-iodophenyl)-1-(4-methylquinolin-2-yl)ethyl)carbamate (8)**



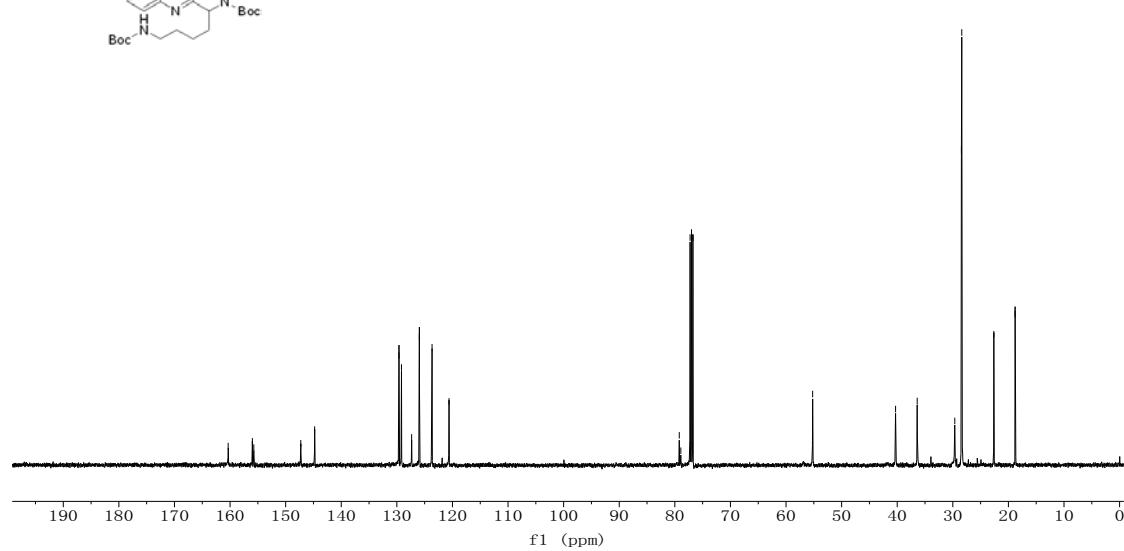
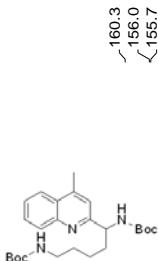
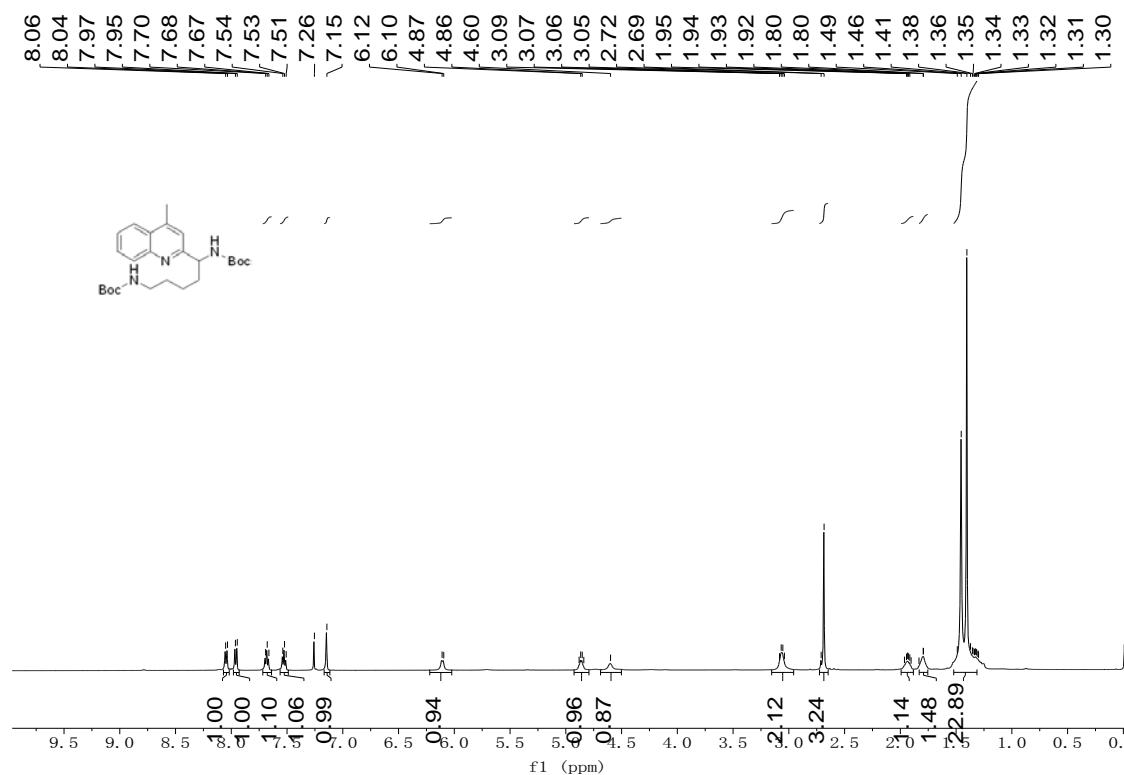
**tert-butyl (2-(4-(tert-butoxy)phenyl)-1-(4-methylquinolin-2-yl)ethyl)carbamate (9)**



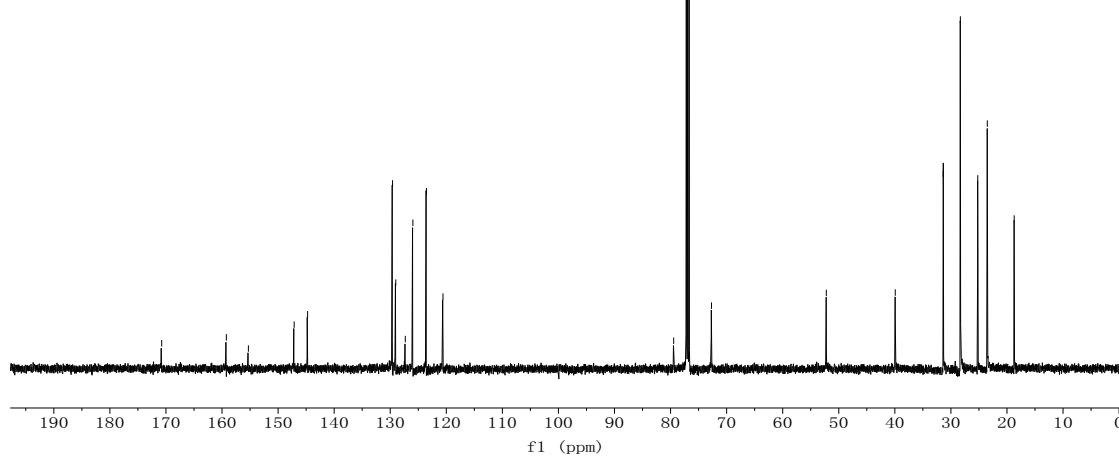
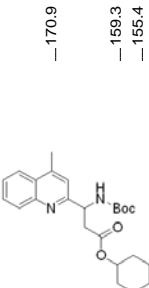
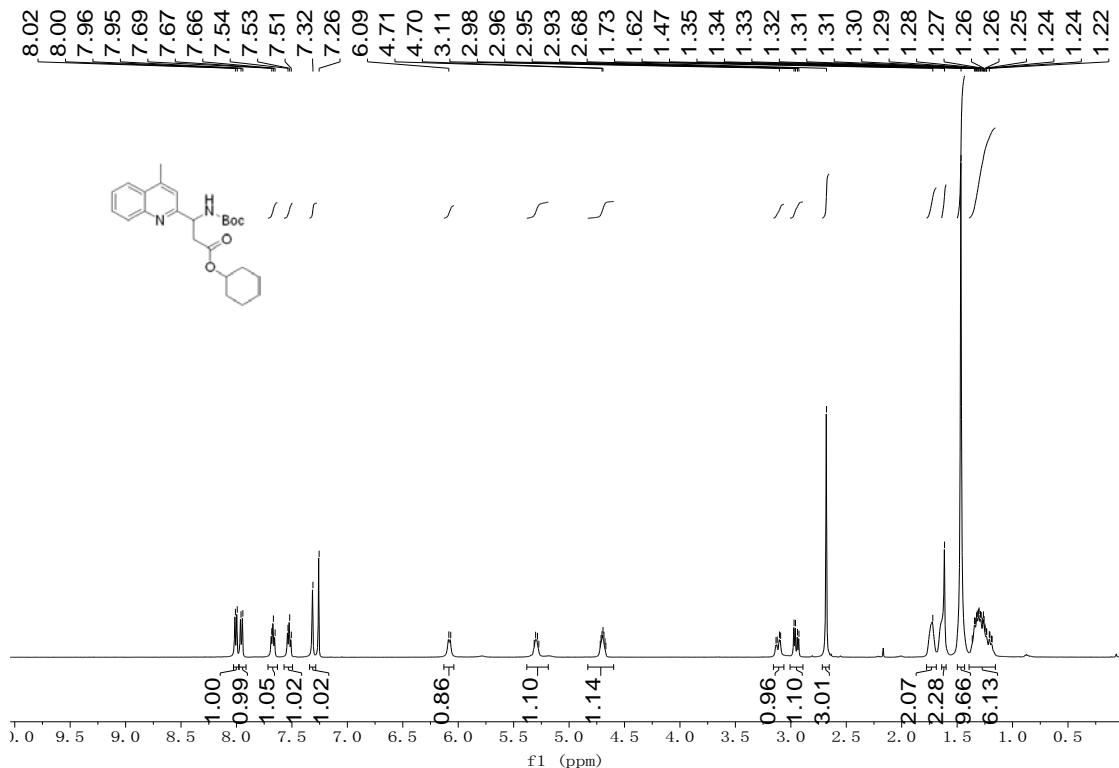
#### **methyl 4-((tert-butoxycarbonyl)amino)-4-(4-methylquinolin-2-yl)butanoate (10)**



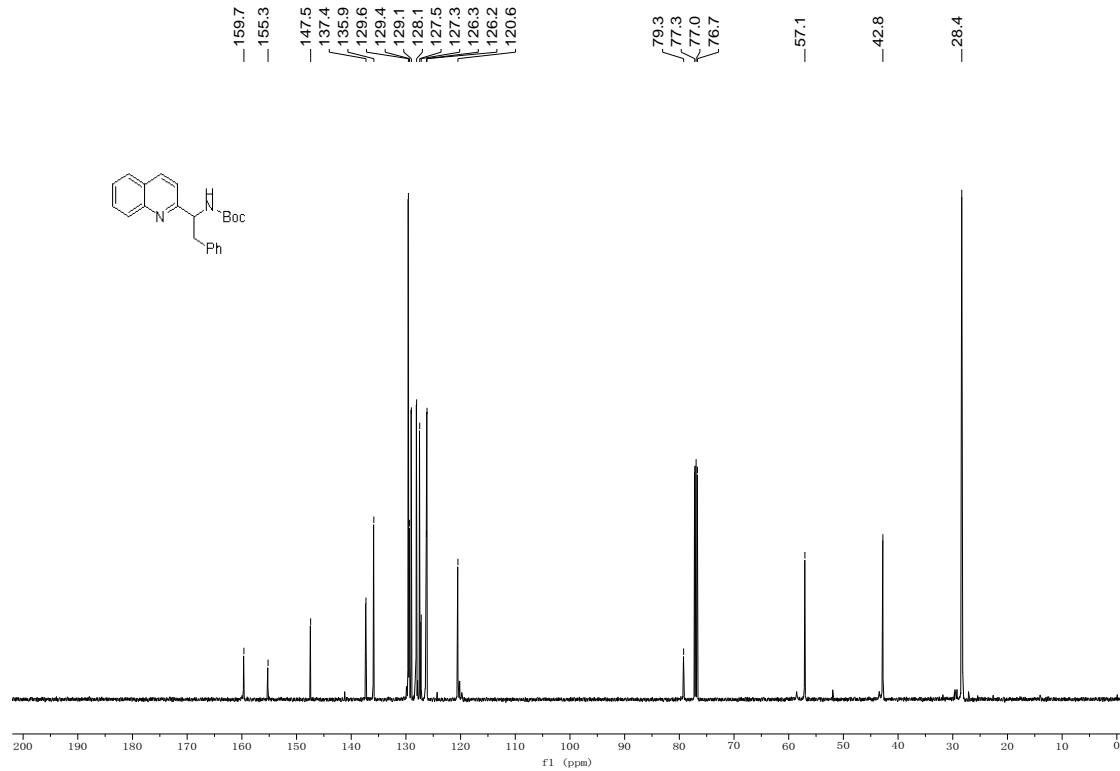
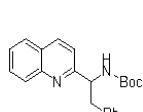
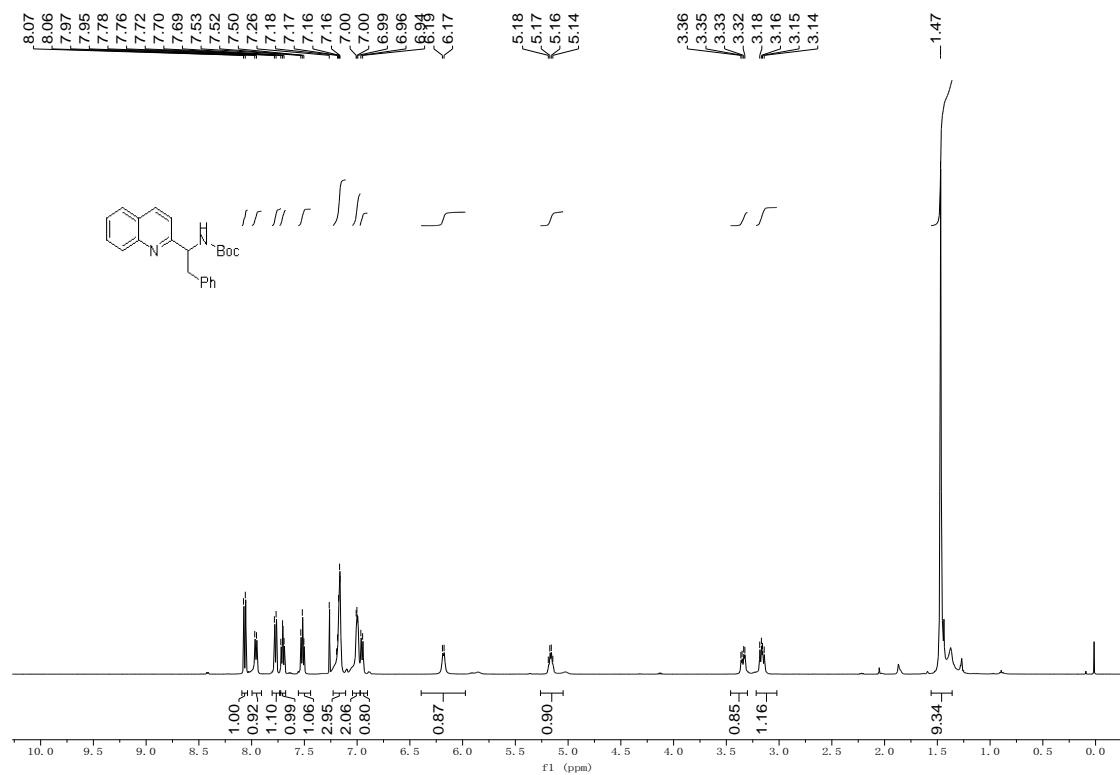
#### **Di-*tert*-butyl (1-(4-methylquinolin-2-yl)pentane-1,5-diyl)dicarbamate (11)**



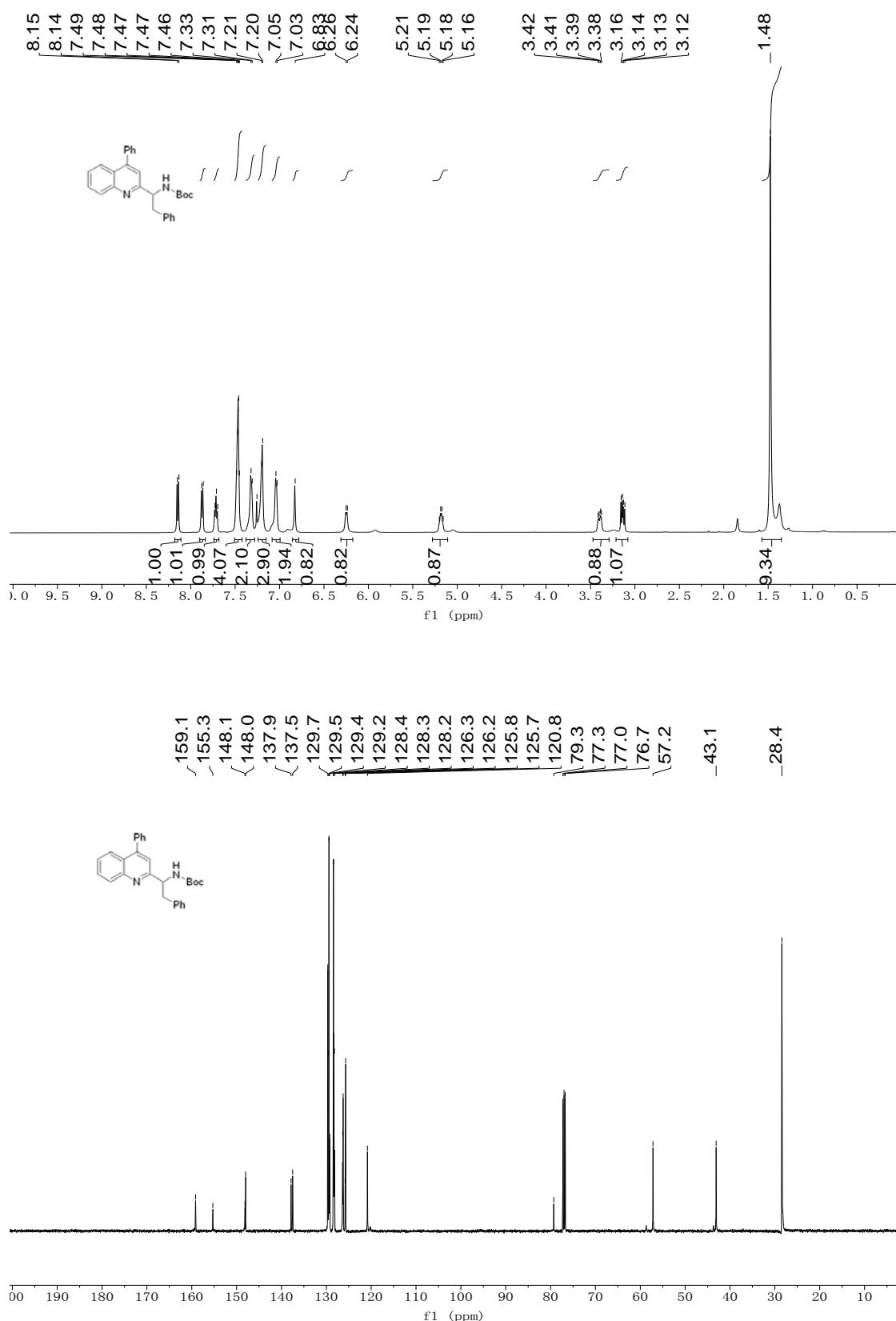
### Cyclohexyl 3-((tert-butoxycarbonyl)amino)-3-(4-methylquinolin-2-yl)propanoate (12)



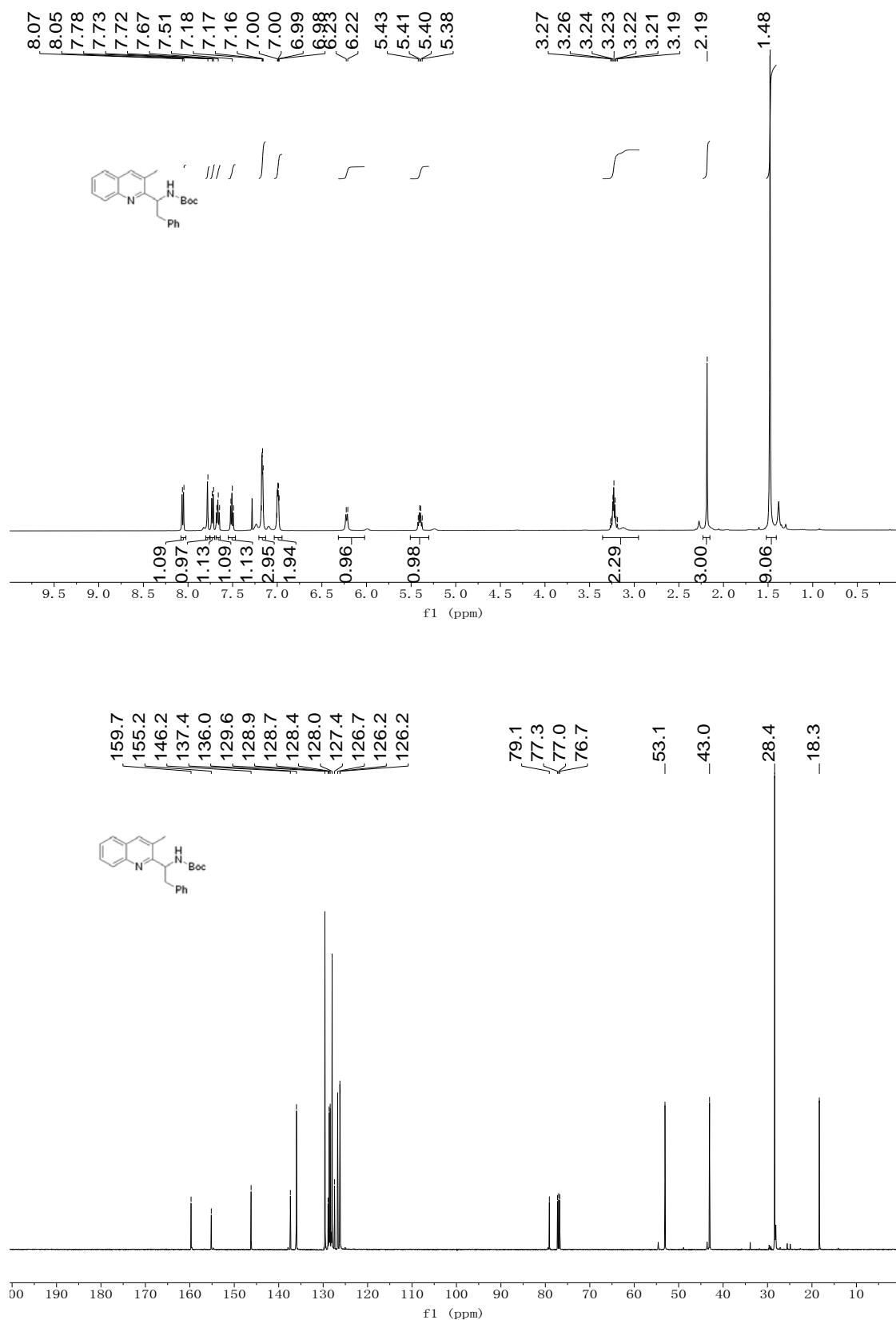
***tert*-butyl (2-phenyl-1-(quinolin-2-yl)ethyl)carbamate (13)**



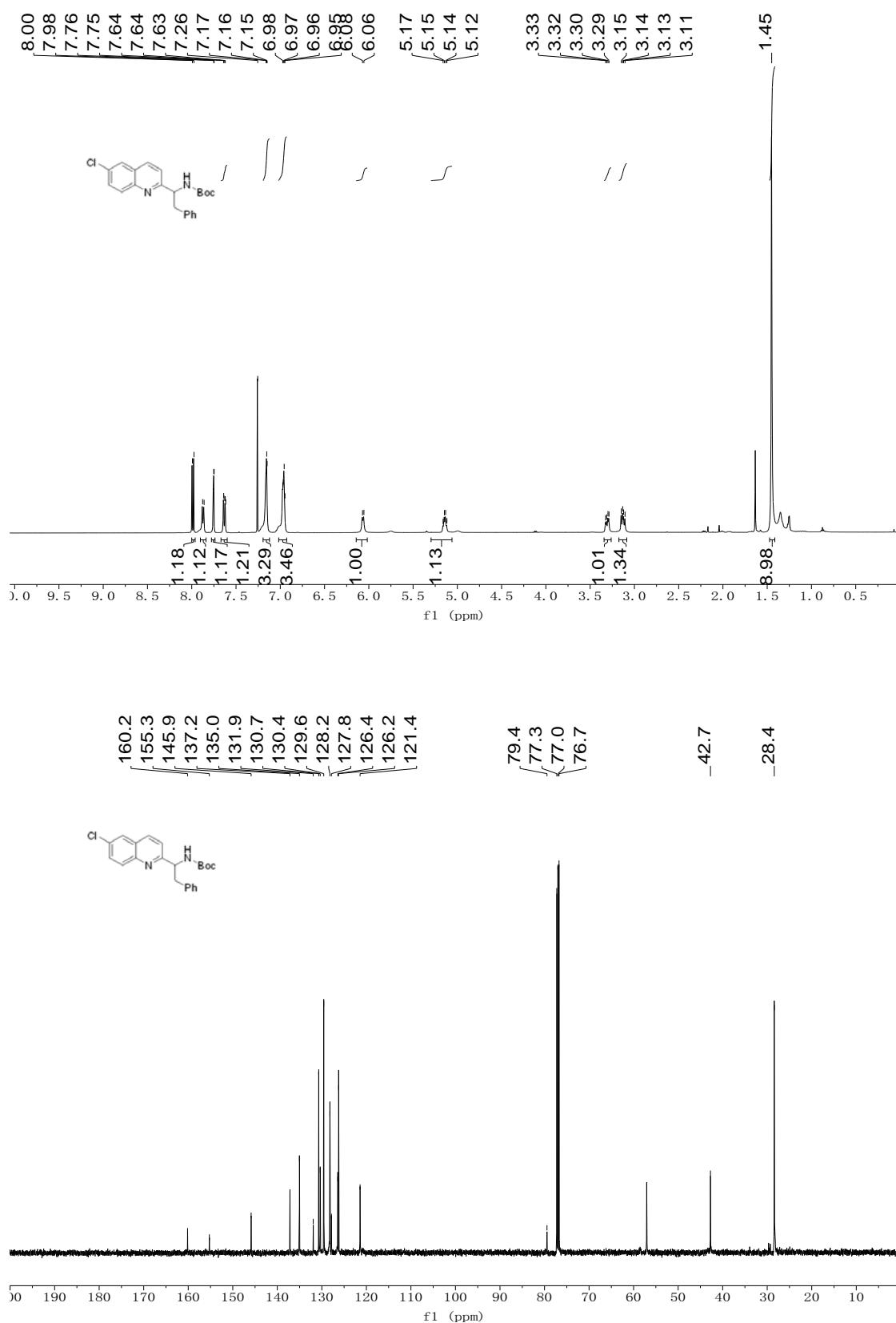
**tert-butyl (2-phenyl-1-(4-phenylquinolin-2-yl)ethyl)carbamate (14)**



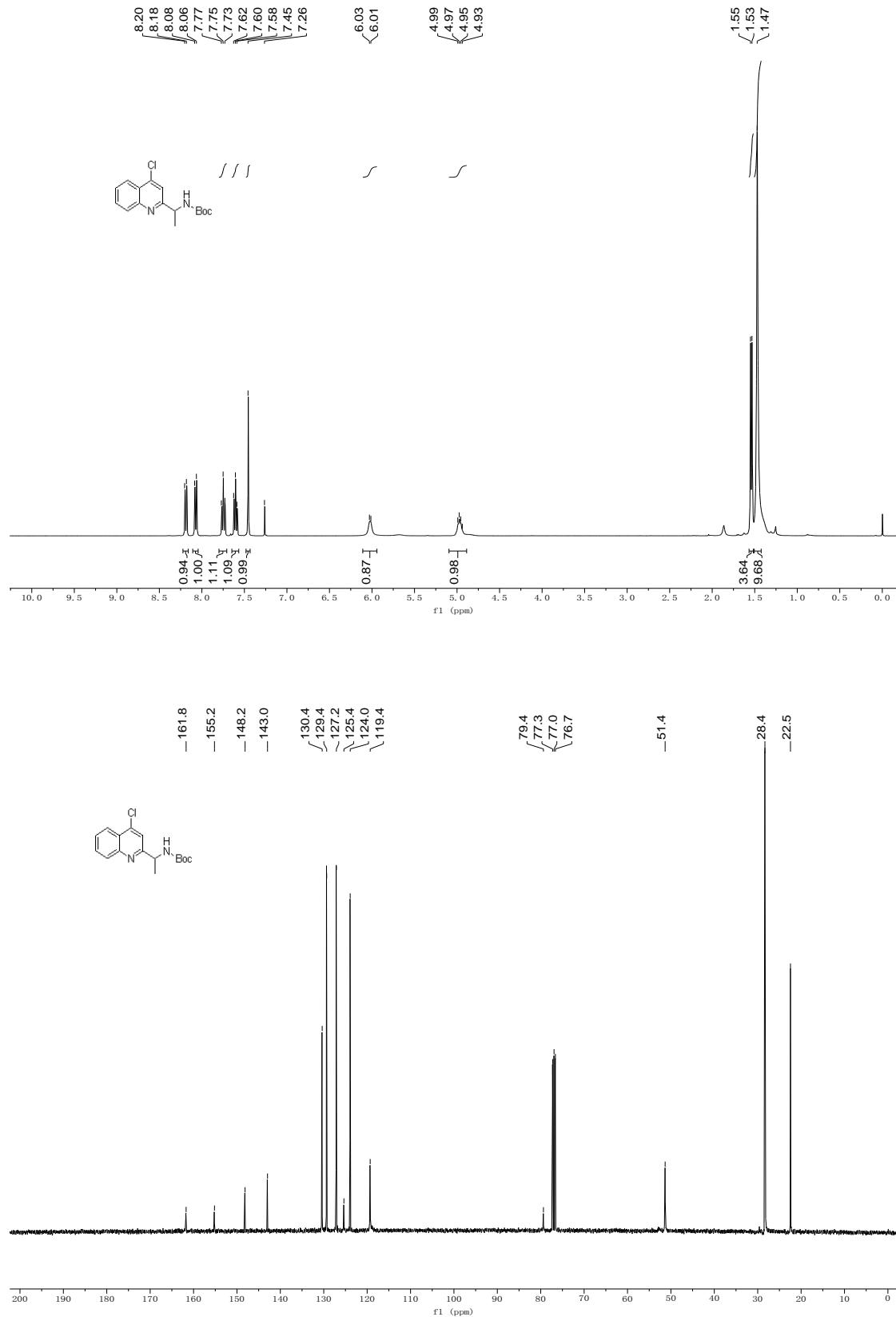
***tert*-butyl (1-(3-methylquinolin-2-yl)-2-phenylethyl)carbamate (15)**



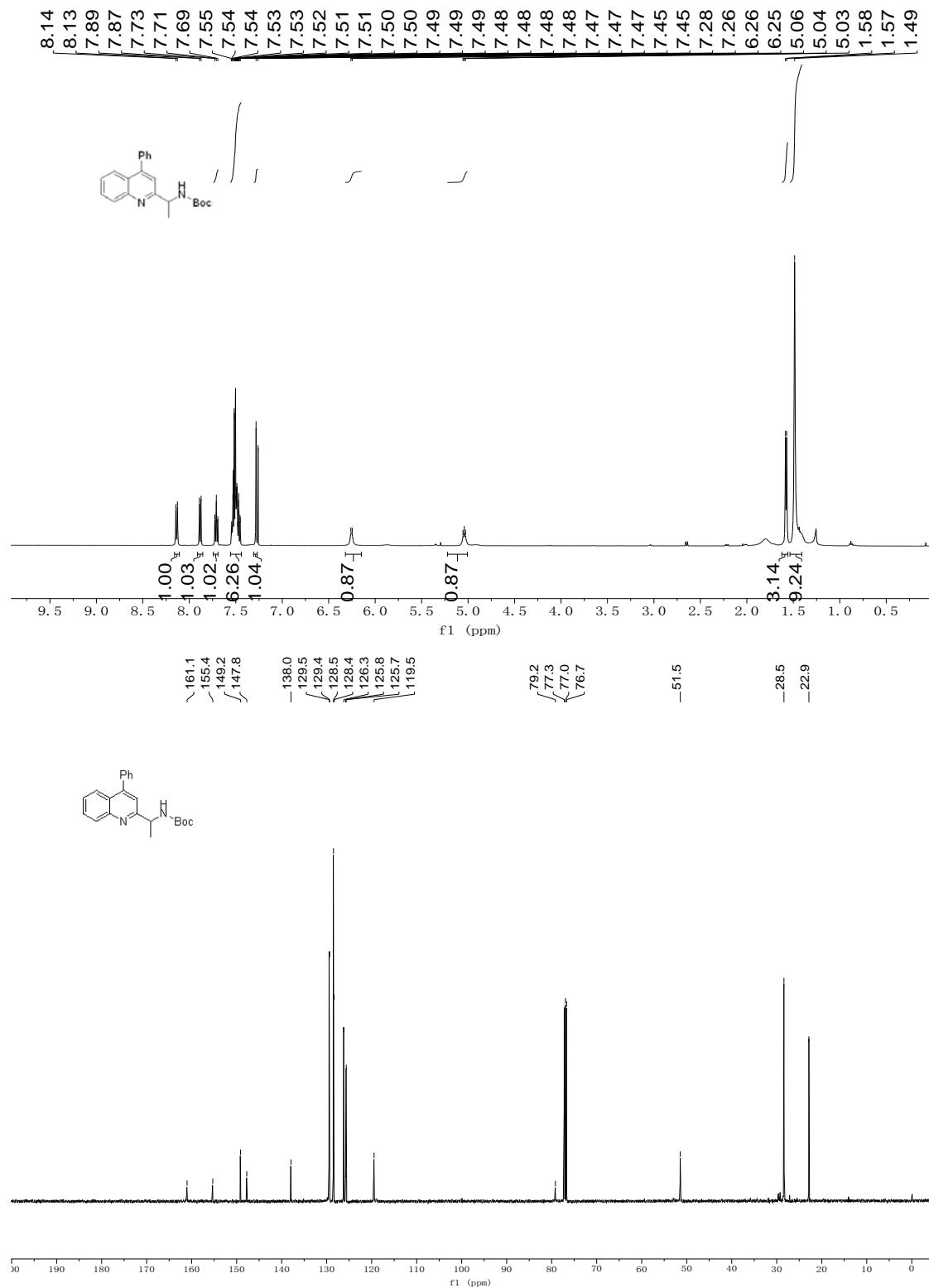
**tert-butyl (1-(6-chloroquinolin-2-yl)-2-phenylethyl)carbamate (16)**



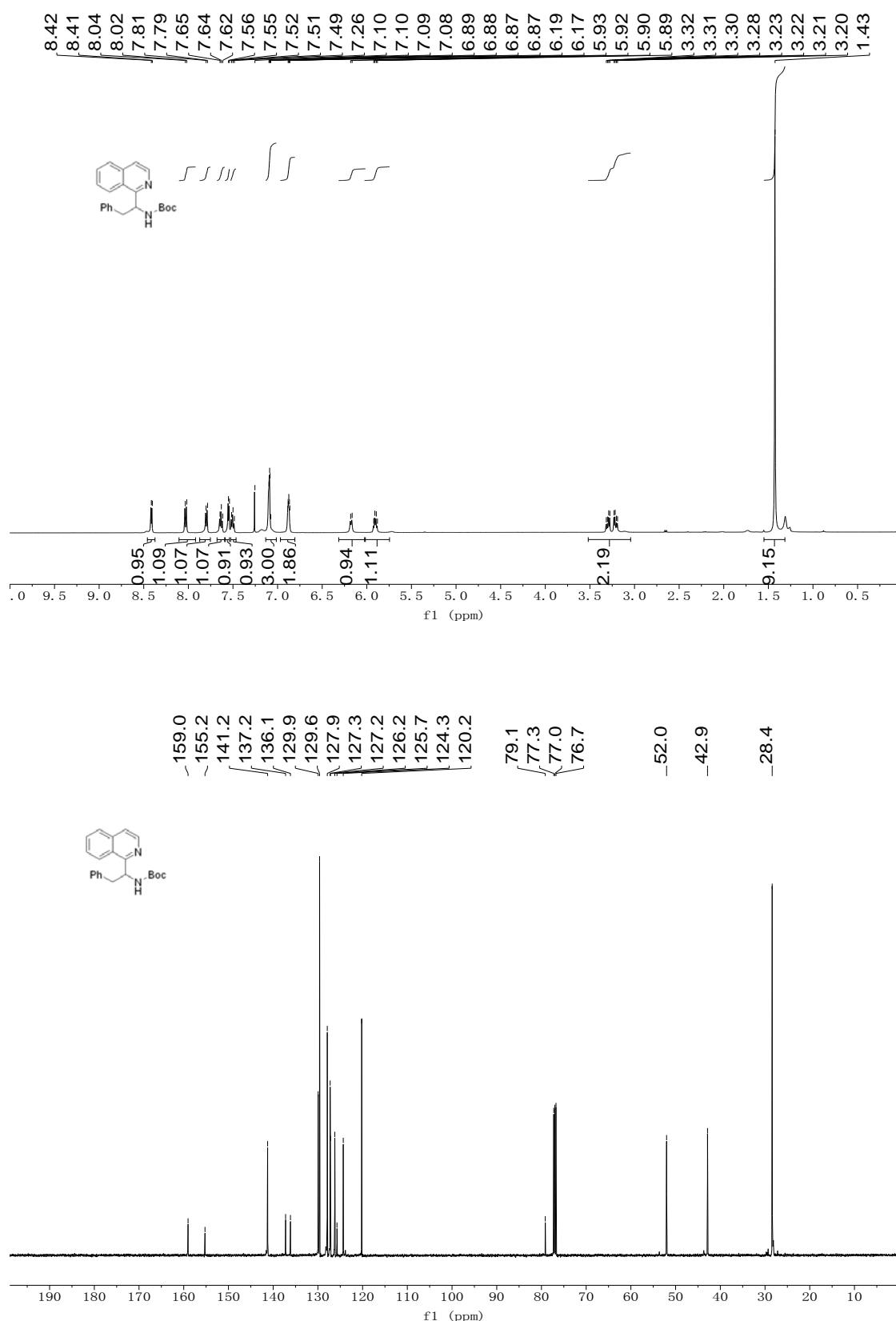
**tert-butyl (1-(4-chloroquinolin-2-yl)ethyl)carbamate (17)**



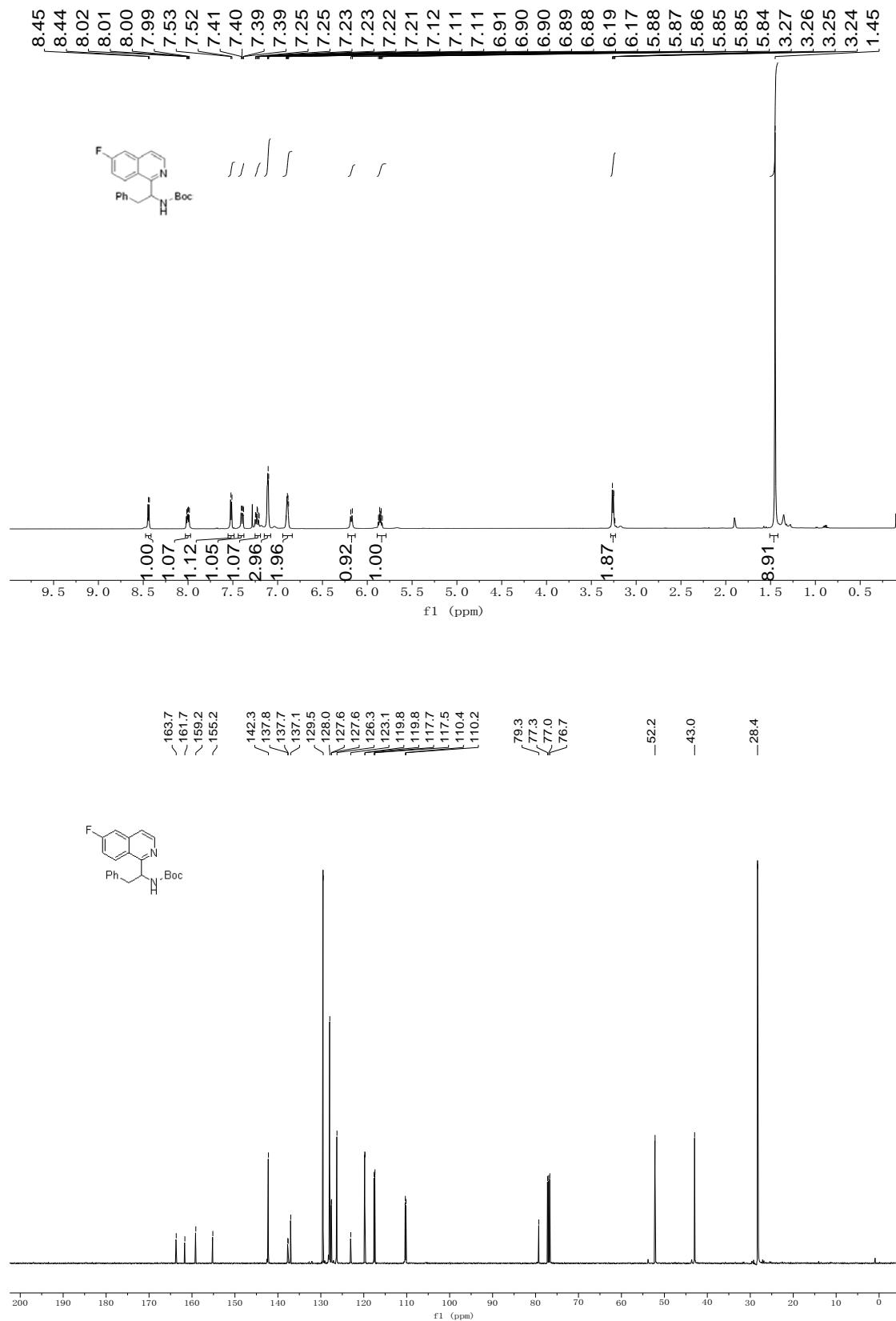
***tert*-butyl (1-(4-phenylquinolin-2-yl)ethyl)carbamate (18)**



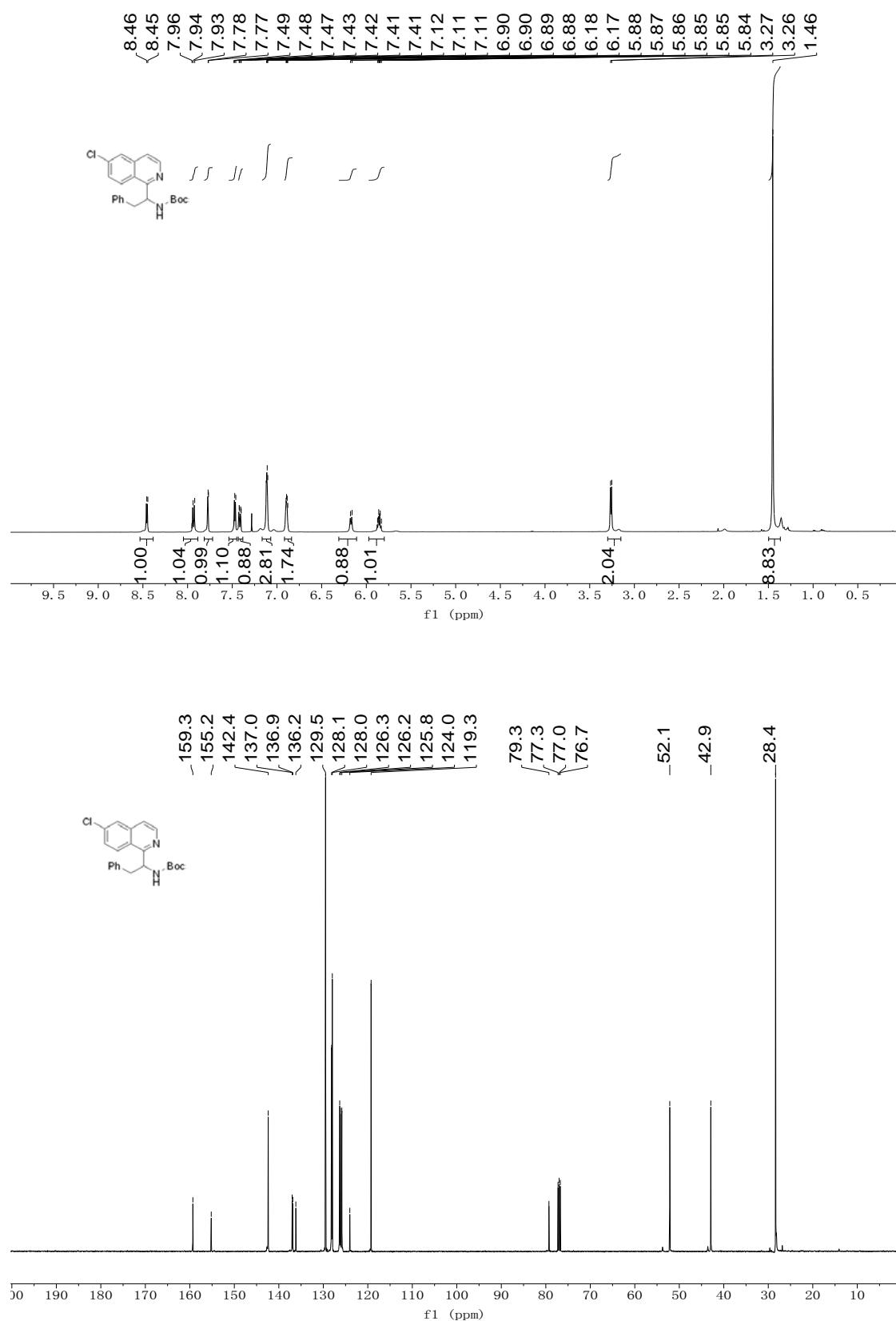
**tert-butyl (1-(isoquinolin-1-yl)-2-phenylethyl)carbamate (19)**



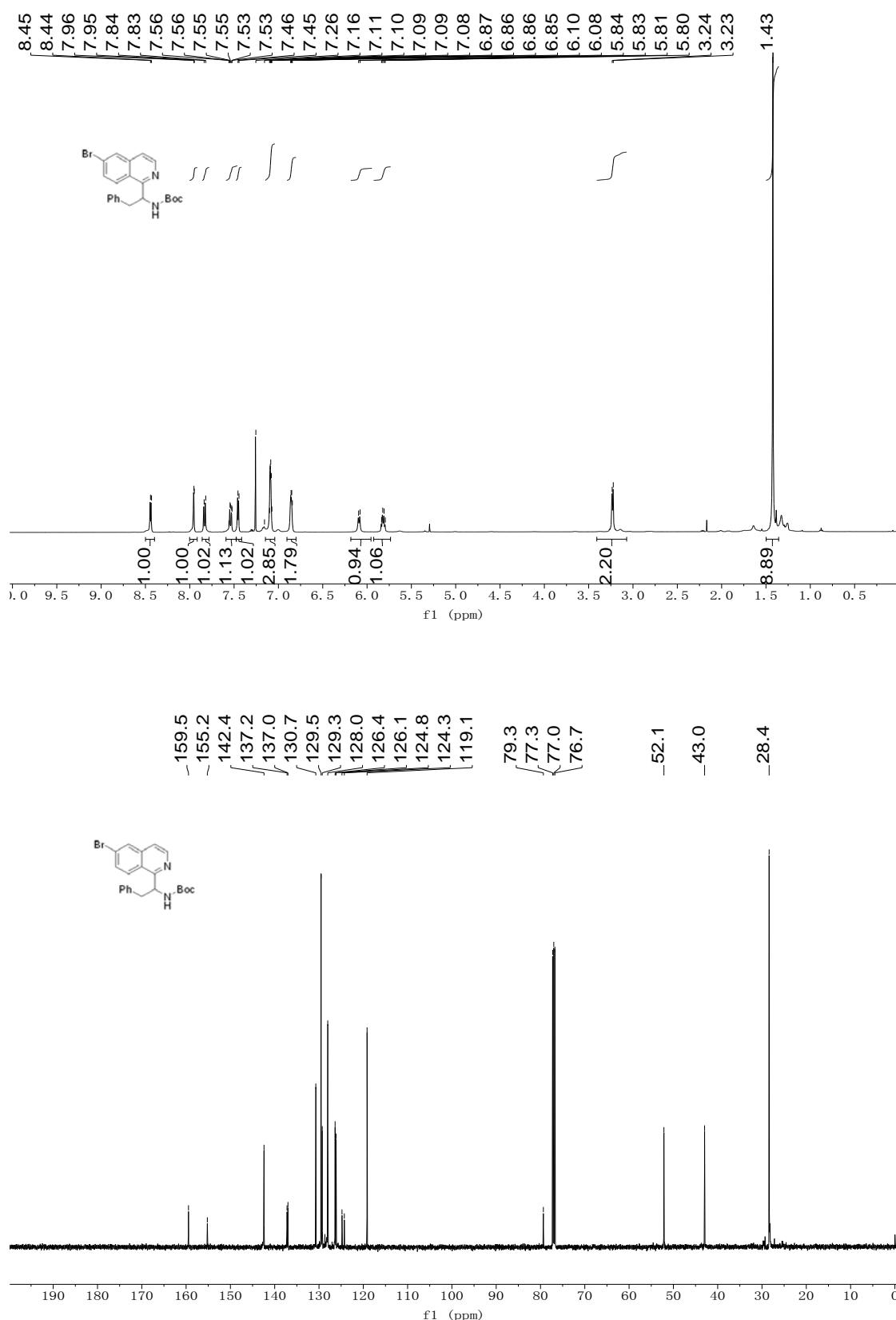
**tert-butyl (1-(6-fluoroisoquinolin-1-yl)-2-phenylethyl)carbamate (20)**



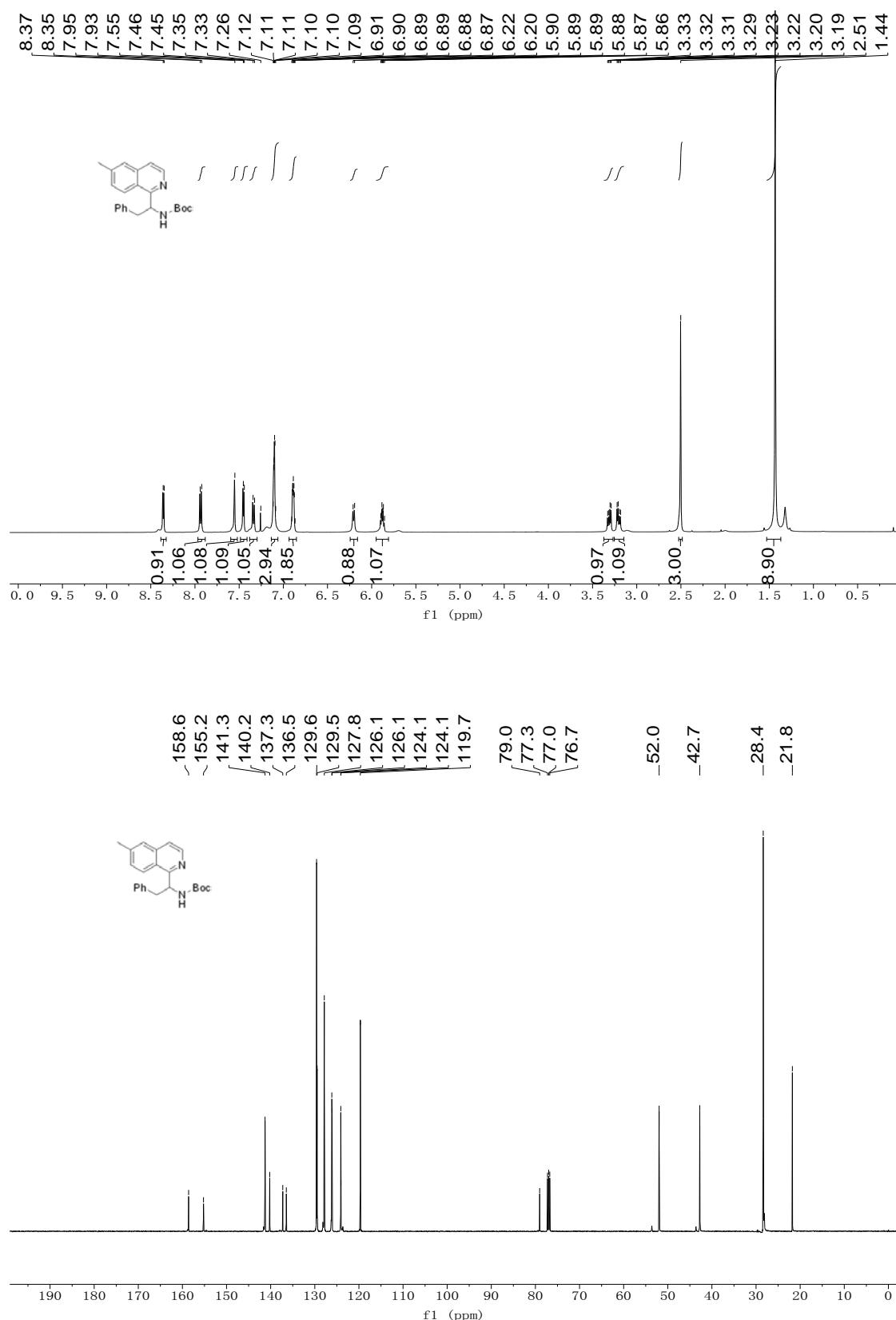
*tert*-butyl (1-(6-chloroisoquinolin-1-yl)-2-phenylethyl)carbamate (21)



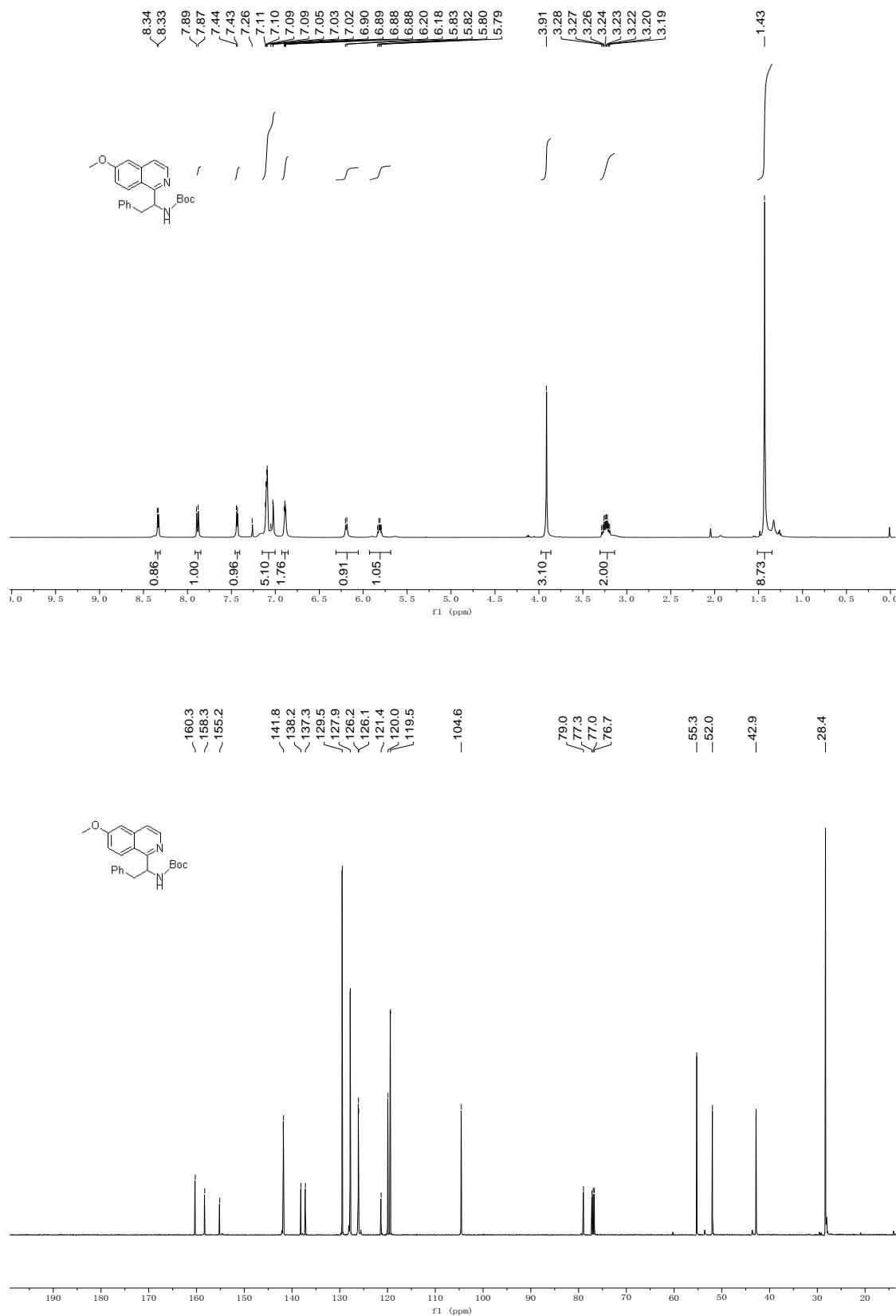
**tert-butyl (1-(6-bromoisoquinolin-1-yl)-2-phenylethyl)carbamate (22)**



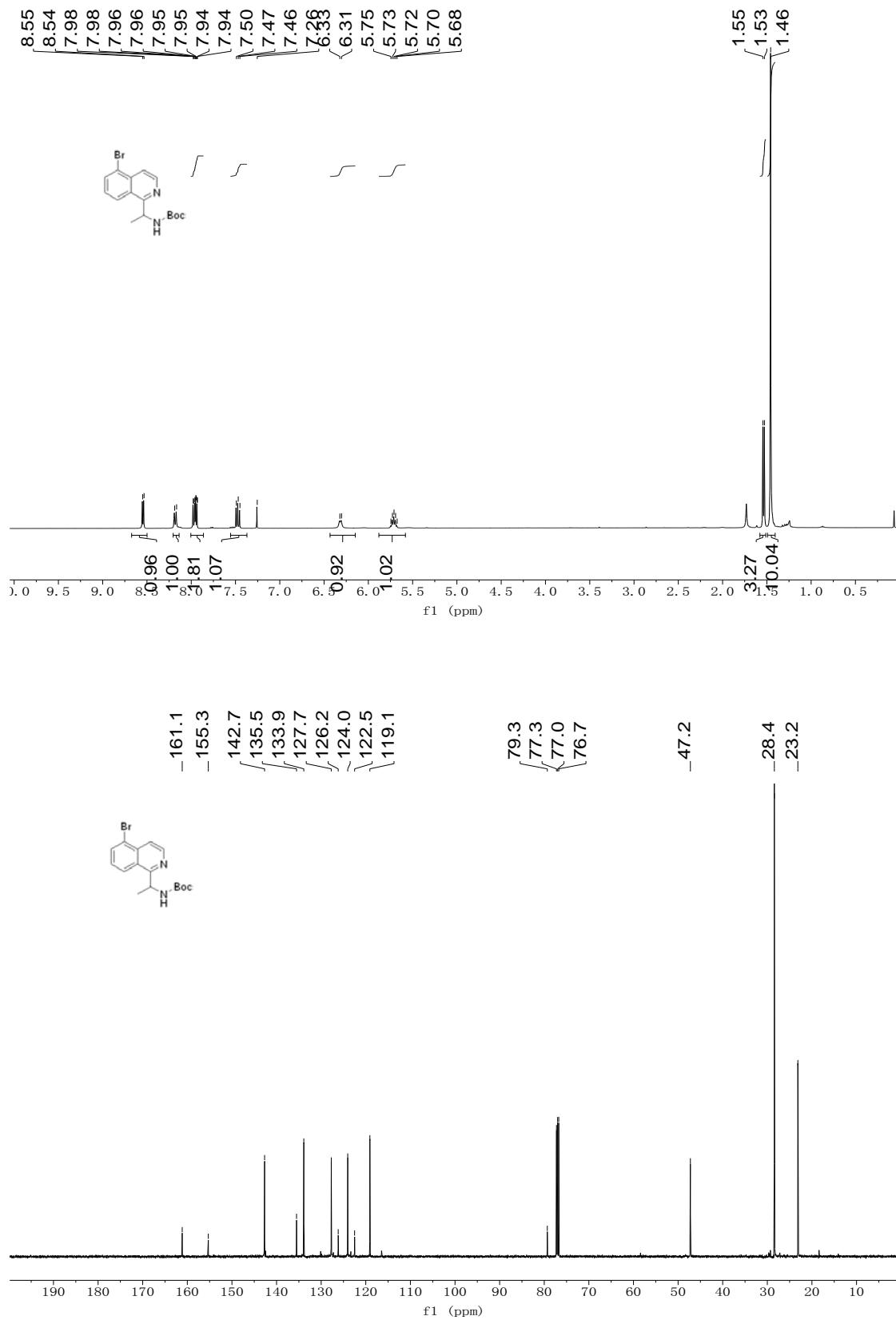
**tert-butyl (1-(6-methylisoquinolin-1-yl)-2-phenylethyl)carbamate (23)**



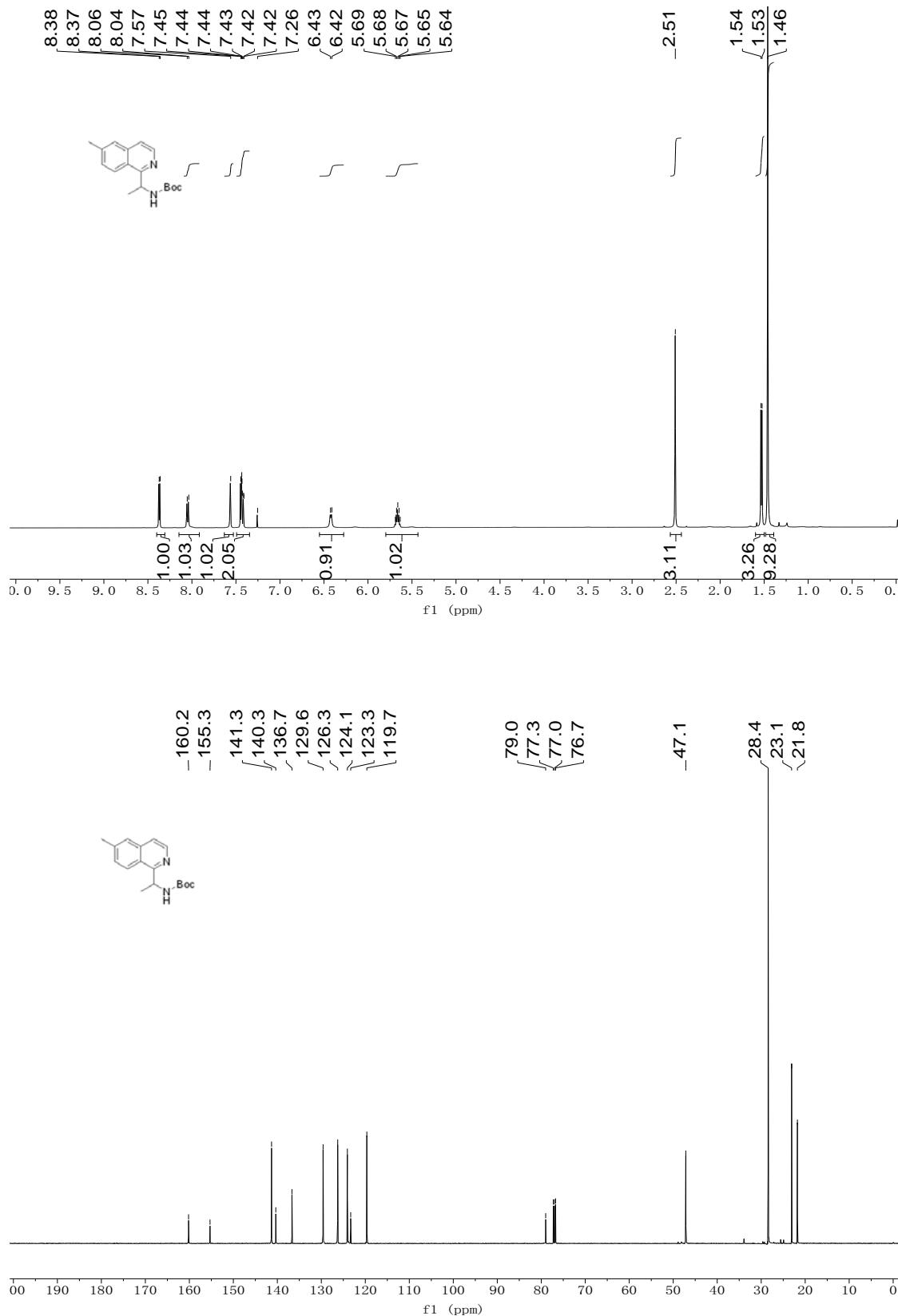
**tert-butyl (1-(6-methoxyisoquinolin-1-yl)-2-phenylethyl)carbamate (24)**



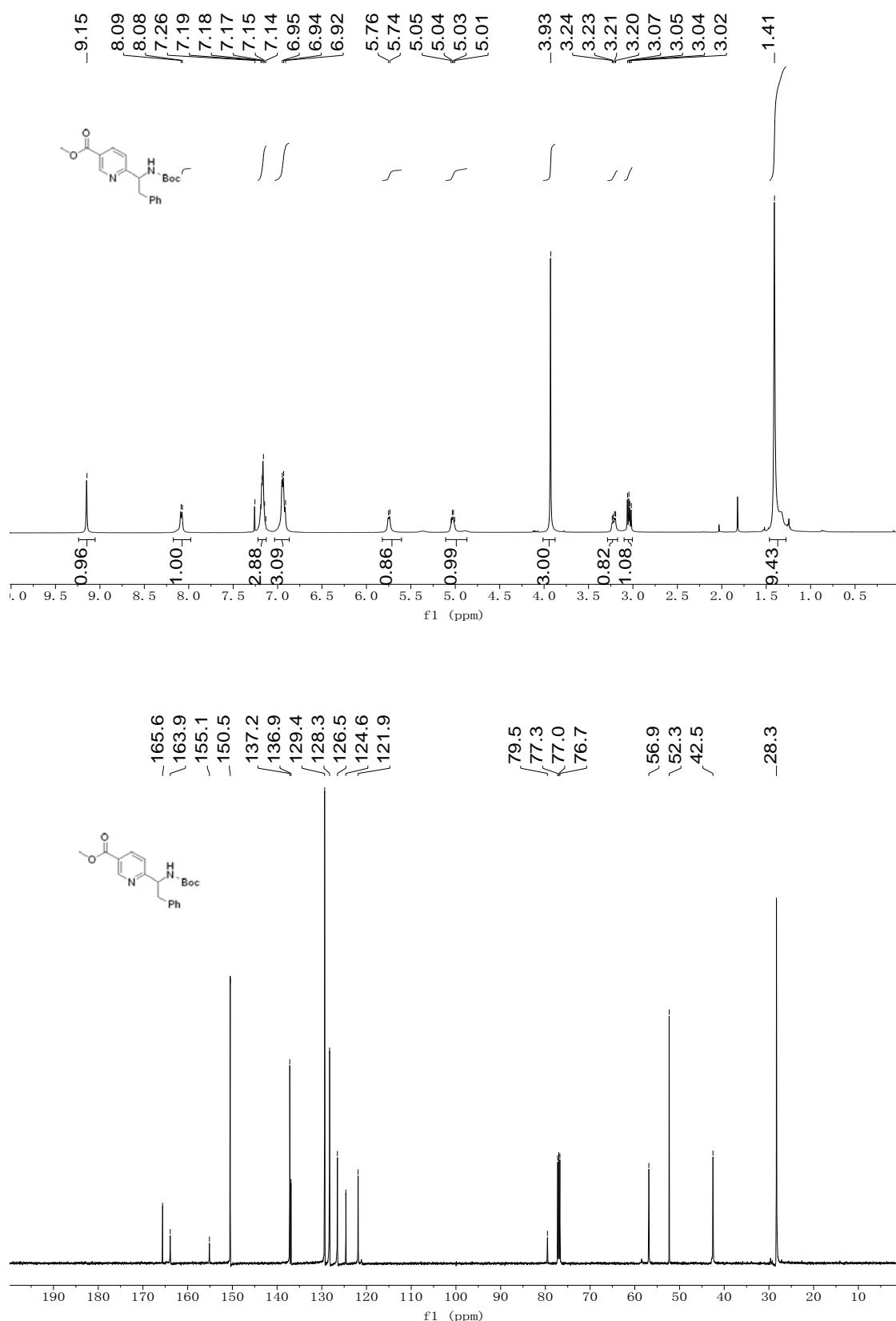
***tert*-butyl (1-(5-bromoisoquinolin-1-yl)ethyl)carbamate (25)**



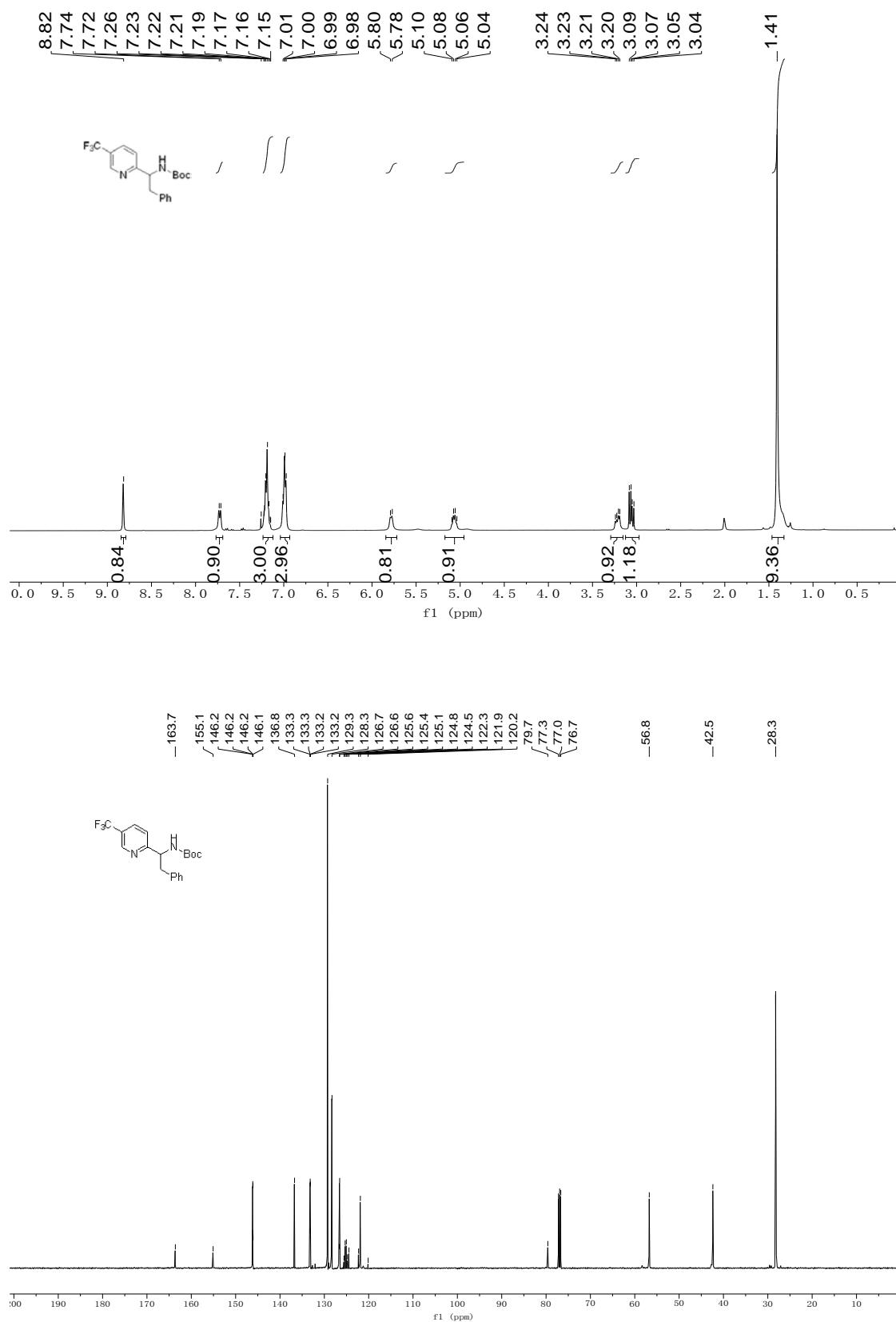
**tert-butyl (1-(3-methylquinolin-2-yl)ethyl)carbamate (26)**



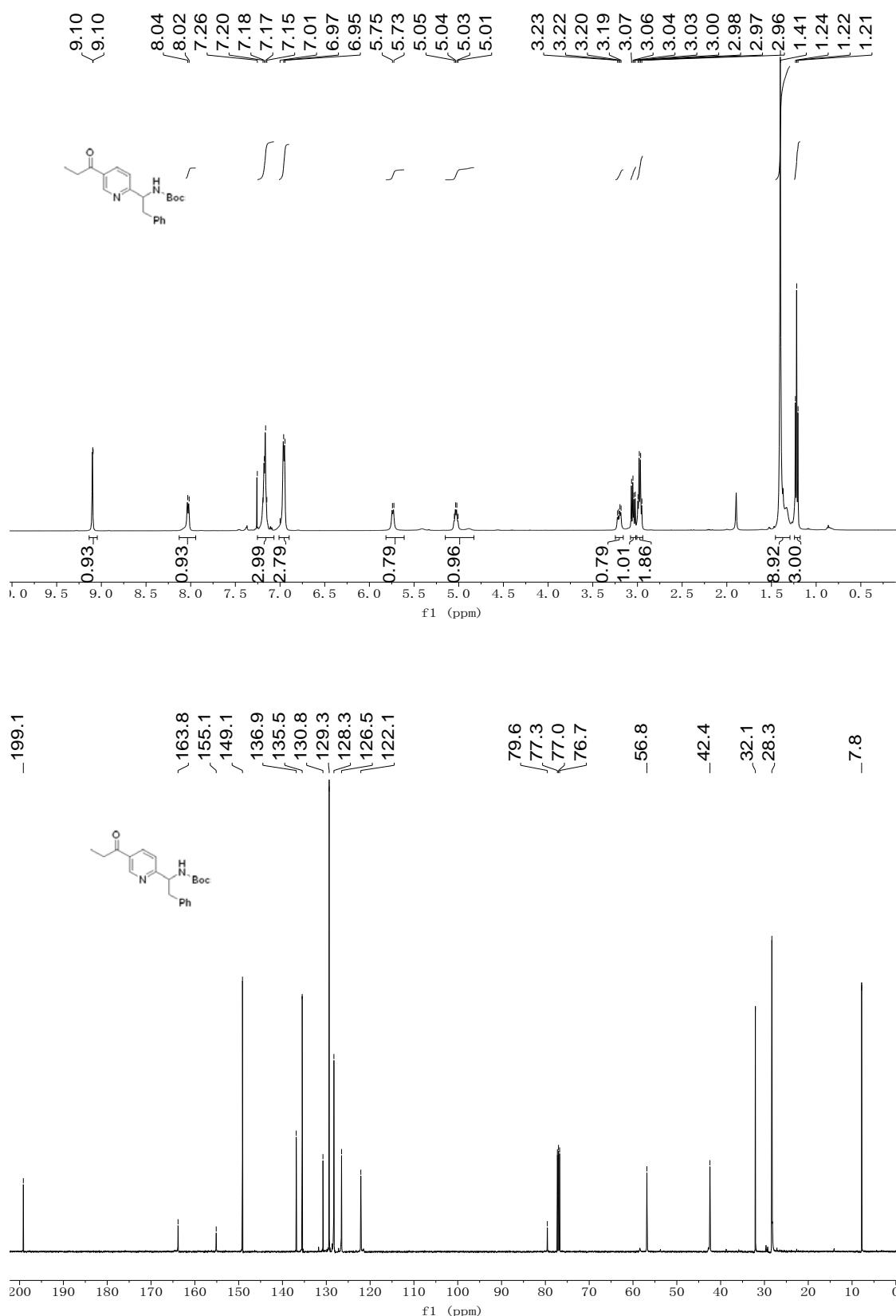
**methyl 6-((tert-butoxycarbonyl)amino)-2-phenylethyl)nicotinate (27)**



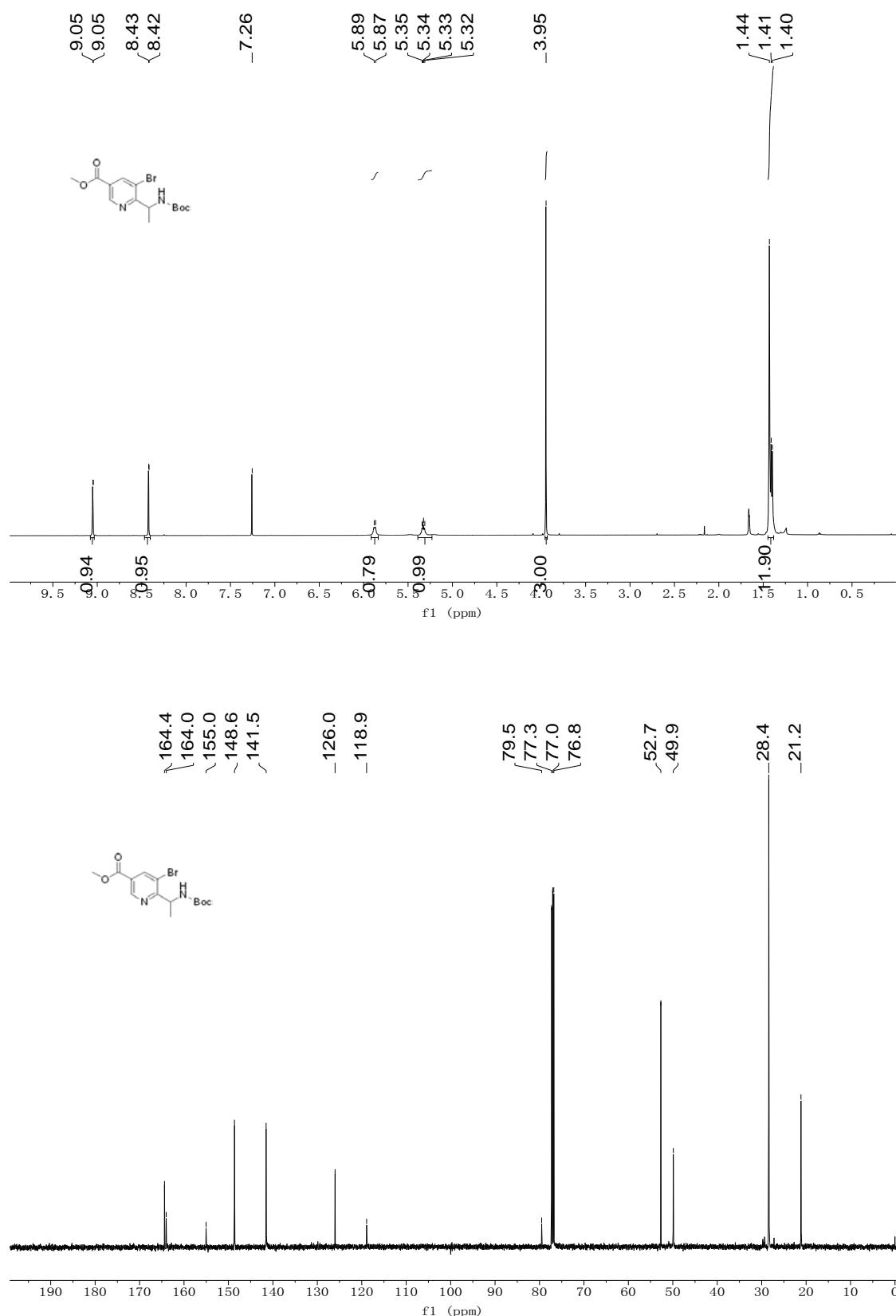
***tert*-butyl (2-phenyl-1-(5-(trifluoromethyl)pyridin-2-yl)ethyl)carbamate (28)**



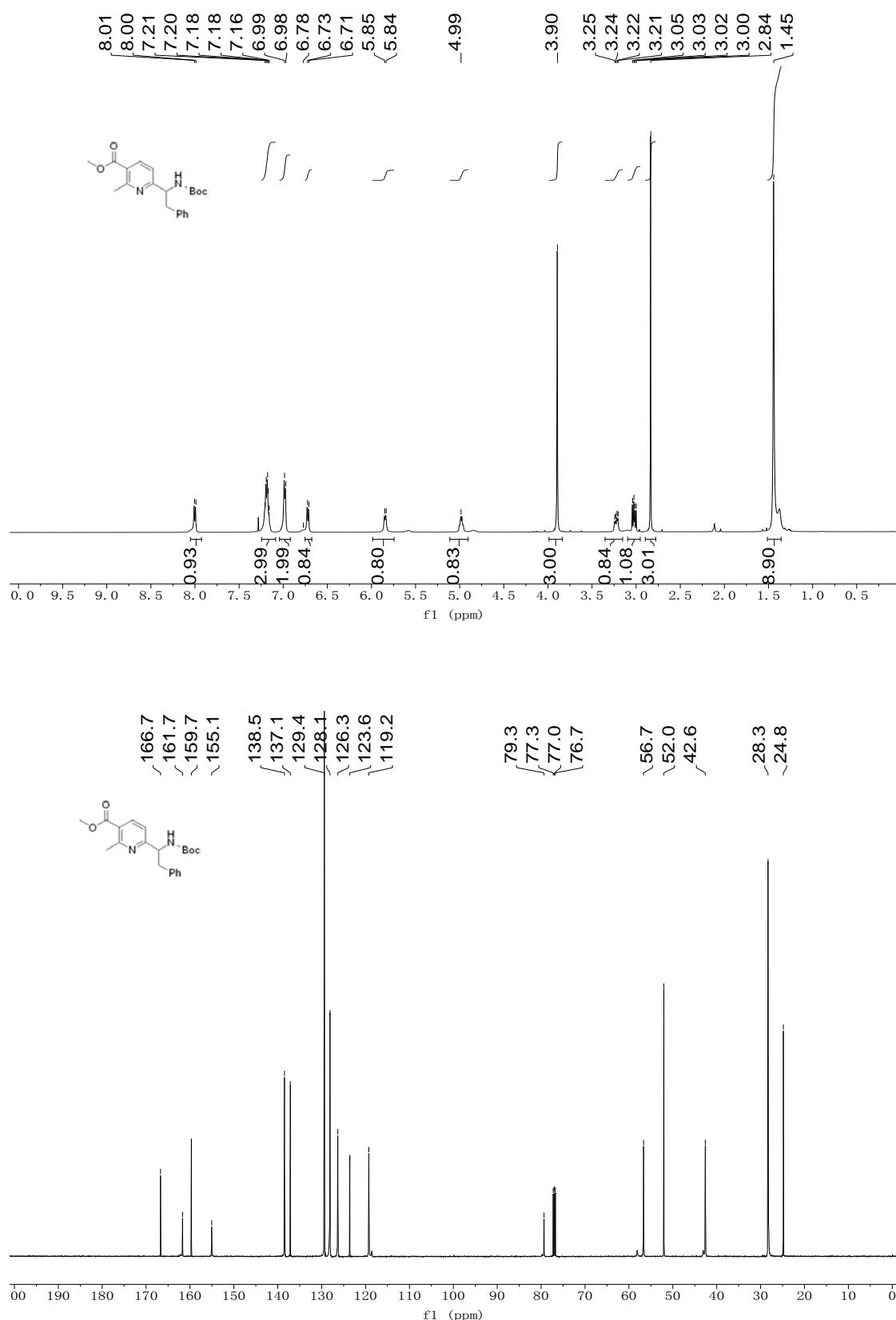
**tert-butyl (2-phenyl-1-(5-propionylpyridin-2-yl)ethyl)carbamate (29)**



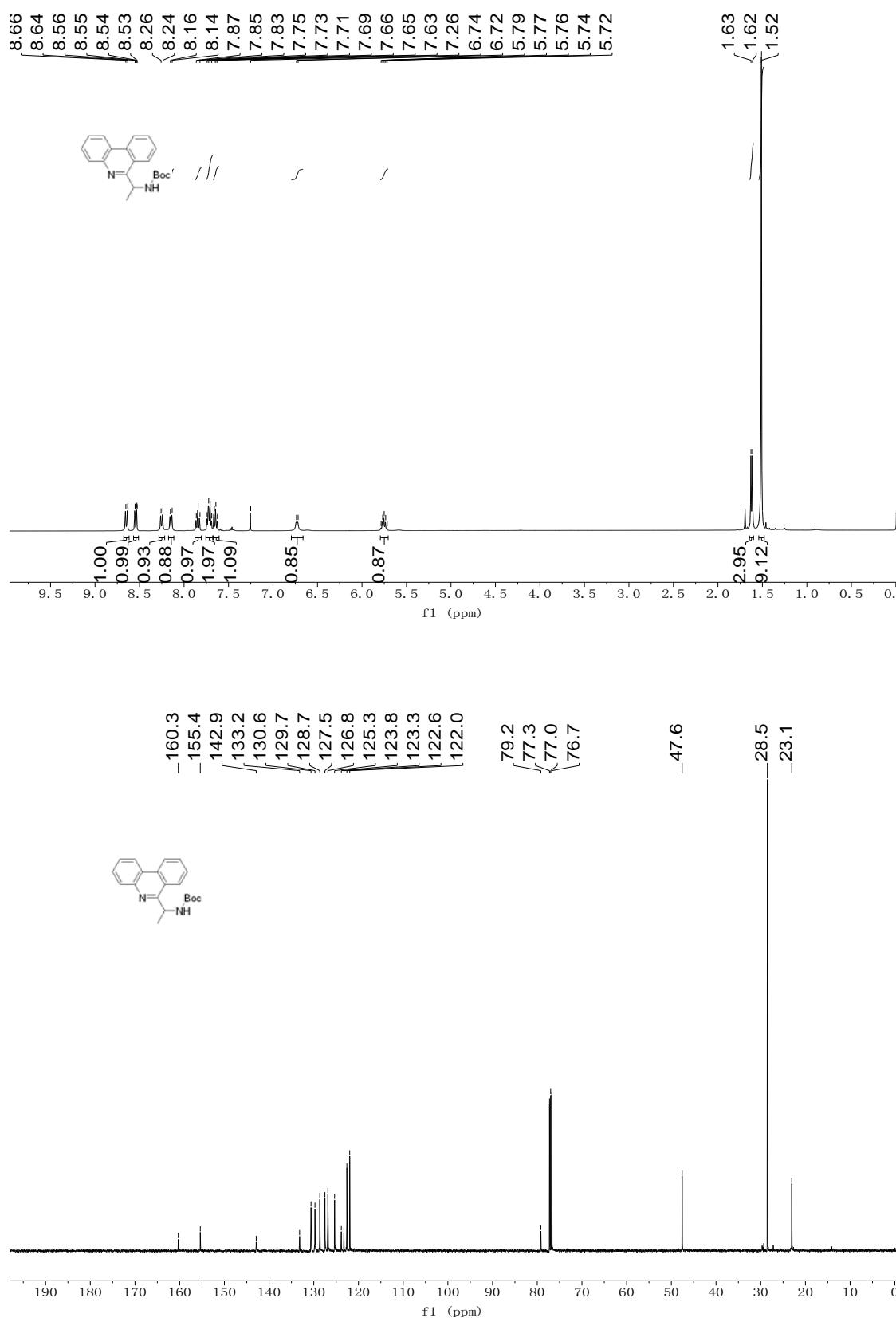
**methyl 5-bromo-6-((tert-butoxycarbonyl)amino)ethyl)nicotinate (30)**



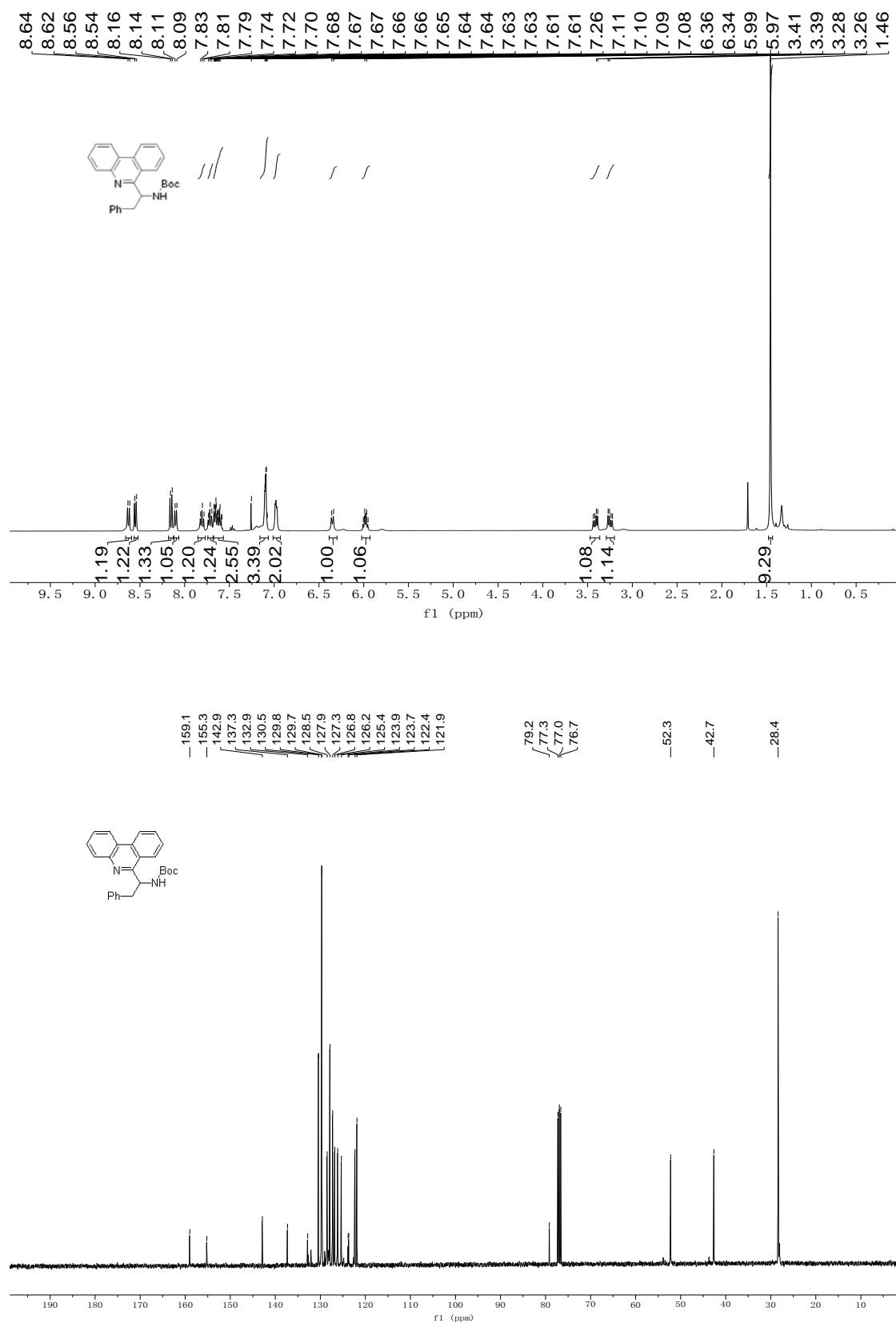
**methyl 6-((tert-butoxycarbonyl)amino)-2-phenylethyl)-2-methylnicotinate (31)**



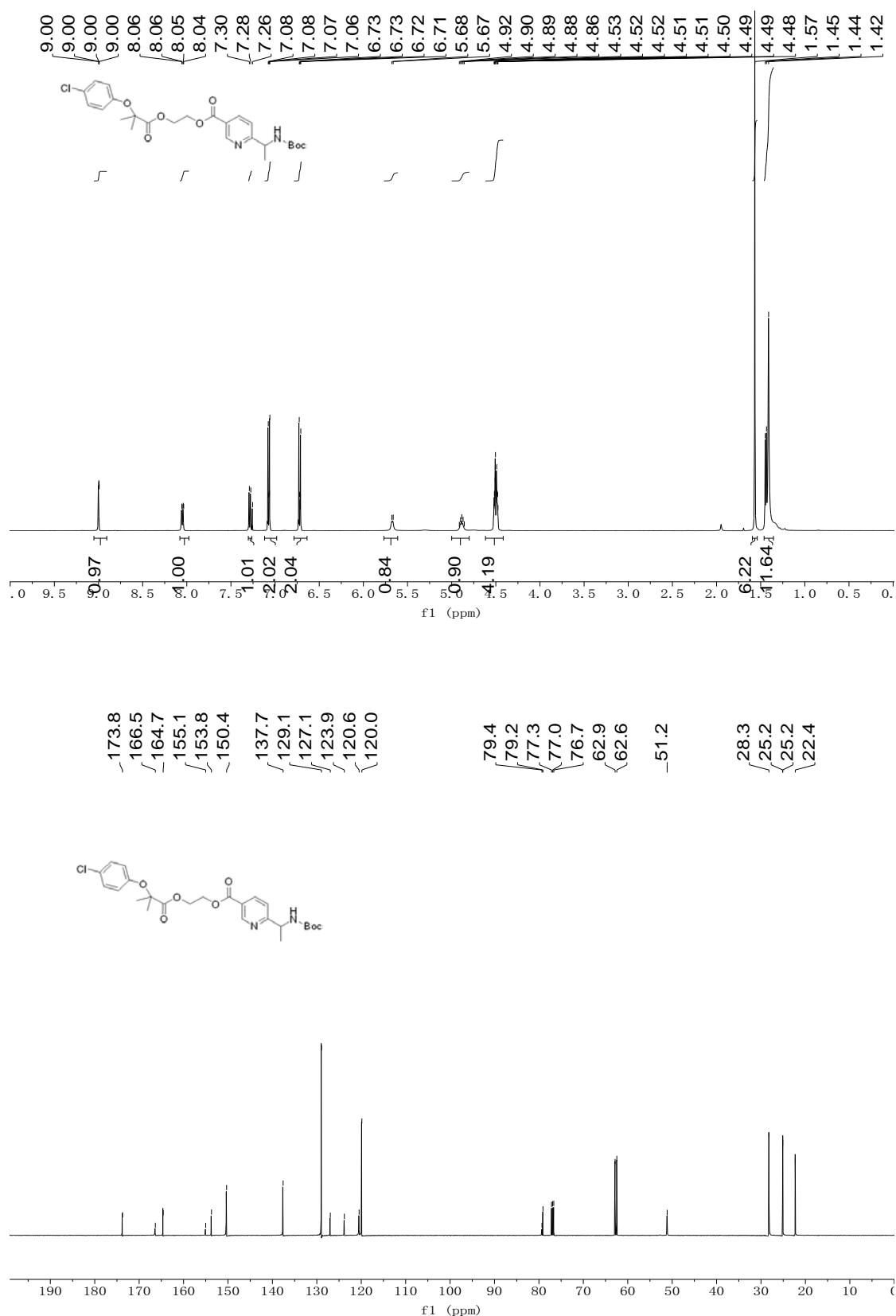
**tert-butyl (1-(phenanthridin-6-yl)ethyl)carbamate (32)**



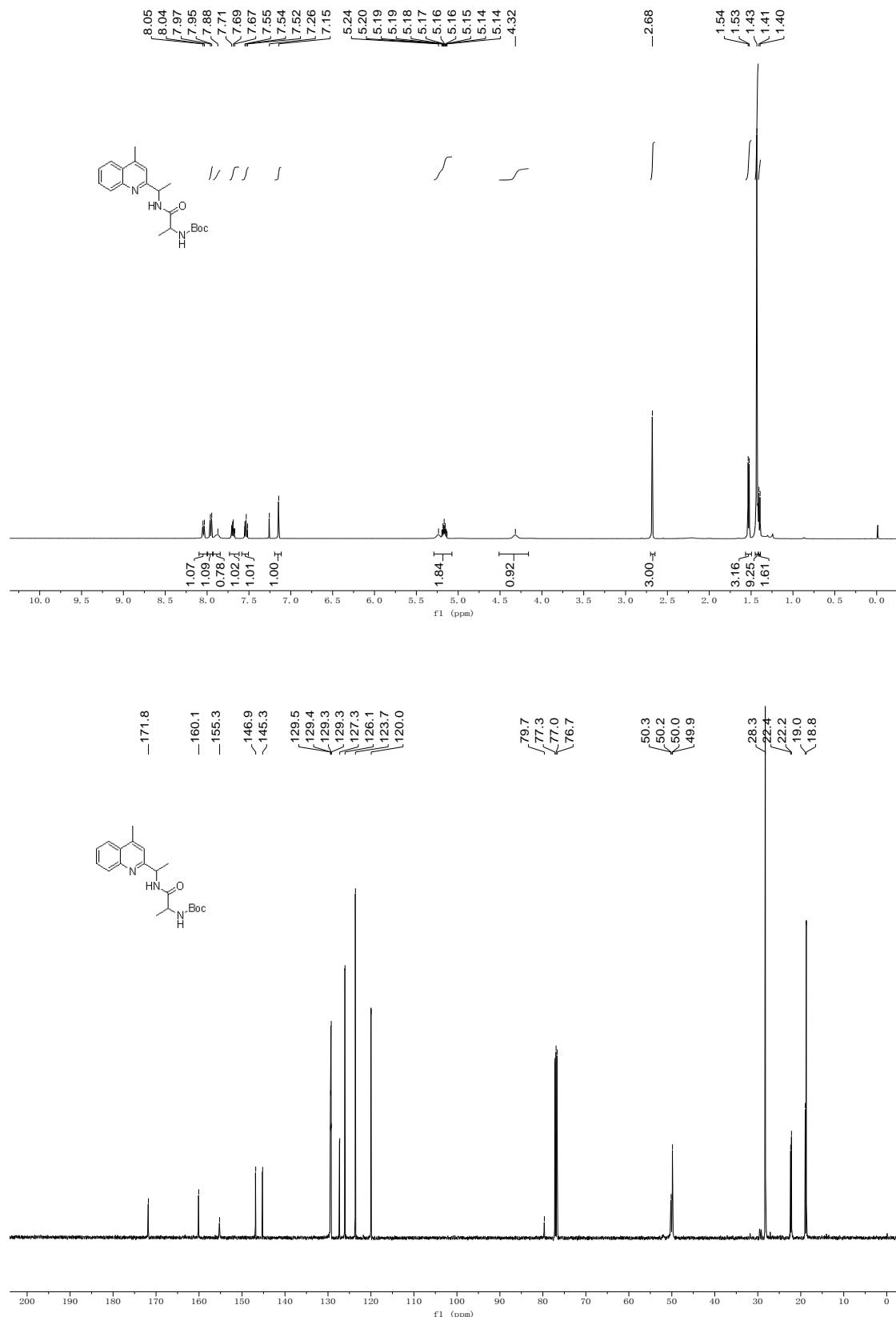
***tert*-butyl (1-(phenanthridin-6-yl)-2-phenylethyl)carbamate (33)**



**2-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)ethyl 6-((tert-butoxycarbonyl)amino)ethyl)nicotinate (34)**



***tert*-butyl (1-((1-(4-methylquinolin-2-yl)ethyl)amino)-1-oxopropan-2-yl)carbamate (35)**



**tert-butyl**

**12-((1-((2-(4-(tert-butoxy)phenyl)-1-(4-methylquinolin-2-yl)ethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamoyl)-9-((tert-butoxycarbonyl)amino)butyl)-2,2-dimethyl-4,7,10-trioxo-6-(3-((2,2,4,6,7-pentamethyl-2,3-dihydrobenzofuran-5-yl)sulfonyl)guanidino)propyl)-3-oxa-5,8,11-triazatetradecan-14-oate (36)**

