

Palladium-Catalyzed Oxidative Carbonylation of Aryl Hydrazines with CO and O₂ at Atmospheric Pressure

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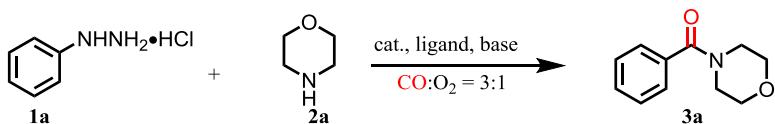
Supporting Information

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Optimization of reaction conditions:

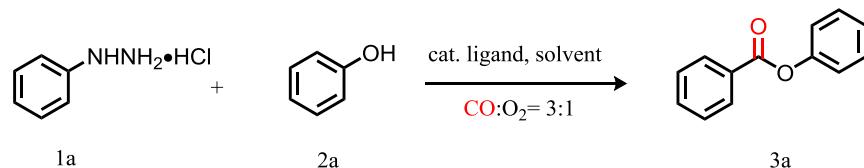
Table S1. Optimization of Reaction Conditions of Oxidative Aminocarbonylation^a



entry	Cat.	Ligand	Base (eq.)	Solvent	Yield (%) ^b
1 ^c	Pd(OAc) ₂	PPh ₃	-	PhMe	35
2	Pd(CH ₃ CN) ₂ Cl ₂	PPh ₃	Na ₂ CO ₃	PhMe	39
3	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	PhMe	42
4	Pd(PPh ₃) ₄	PPh ₃	Na ₂ CO ₃	PhMe	13
5	Pd(OAc) ₂	dppe	Na ₂ CO ₃	PhMe	2
6	Pd(OAc) ₂	2,2'-Dipyridyl	Na ₂ CO ₃	PhMe	17
7	Pd(OAc) ₂	1,10-o-Phenanthroline	Na ₂ CO ₃	PhMe	14
8	Pd(OAc) ₂	PPh ₃	K ₂ CO ₃	PhMe	37
9	Pd(OAc) ₂	PPh ₃	DABCO	PhMe	20
10	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	Dioxane	66
11	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	dmso:dioxane (1:9)	76
12 ^d	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	dmso:dioxane (1:9)	32
13 ^e	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	dmso:dioxane (1:9)	8
14 ^f	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	dmso:dioxane (1:9)	66
15 ^g	Pd(OAc) ₂	PPh ₃	Na ₂ CO ₃	dmso:dioxane (1:9)	64

^aReaction condition: **1a** (2 eq.), **2a** (0.2 mmol), cat. (3 mol%), ligand (20 mol%), base (1 eq.) solvent (1 mL), CO:O₂ (3:1), 100 °C, 12 h. ^b Isolated yield. ^c **1a** was replaced with phenylhydrazine. ^d 80 °C. ^e 120 °C. ^f 10 h. ^g 15 h.

Table S2. Optimization of Reaction Conditions of Oxidative Alkoxy carbonylation^a



Entry	Cat.	Ligand	Solvent	yield (%) ^b
1 ^c	Pd(OAc) ₂	PPh ₃	PhMe	6
2 ^c	Pd(PPh ₃) ₄	PPh ₃	PhMe	5
3 ^c	PdCl ₂	PPh ₃	PhMe	9
4 ^c	PdCl ₂ (dppp)	PPh ₃	PhMe	15
5 ^c	PdCl ₂ (dppp)	DPPF	PhMe	19
6 ^c	PdCl ₂ (dppp)	Xantphos	PhMe	20
7	PdCl ₂ (dppp)	TMDAP	PhMe	50
8	PdCl ₂ (dppp)	TMEDA	PhMe	39
9	PdCl ₂ (dppp)	DMAEA	PhMe	13
10	PdCl ₂ (dppp)	TMDAP	DMF	3
11	PdCl ₂ (dppp)	TMDAP	dioxane	28
12	PdCl ₂ (dppp)	TMDAP	4-CF ₃ -Ph	72
13 ^d	PdCl ₂ (dppp)	TMDAP	4-CF ₃ -Ph	60
14 ^e	PdCl ₂ (dppp)	TMDAP	4-CF ₃ -Ph	76
15 ^f	PdCl ₂ (dppp)	TMDAP	4-CF ₃ -Ph	79
16 ^g	PdCl ₂ (dppp)	TMDAP	4-CF ₃ -Ph	65

^aReaction condition: 1a (4.0 eq), 2a (0.2 mmol), cat. (3 mol %), ligand (2.0 eq), solvent (2.0 mL)

CO:O₂= 3:1, 100 °C, 12 h. ^b Isolated yield. ^c ligand (20 mol %). ^d CO:O₂= 1:1. ^e 24 h.

^f 2a was replaced with Ph-OH (0.2 mmol) and NaOH (1.2 eq). ^g 1a (3.0 eq).

Mechanistic study:

Scheme S1. A plausible reaction mechanism

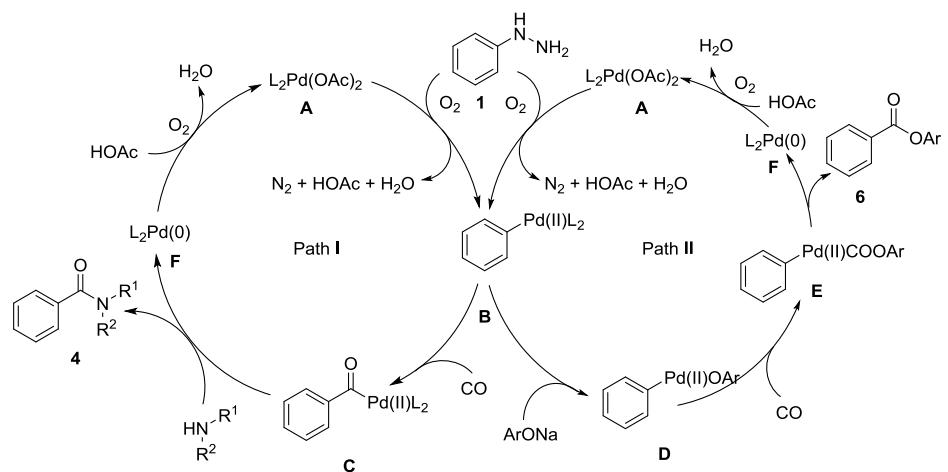
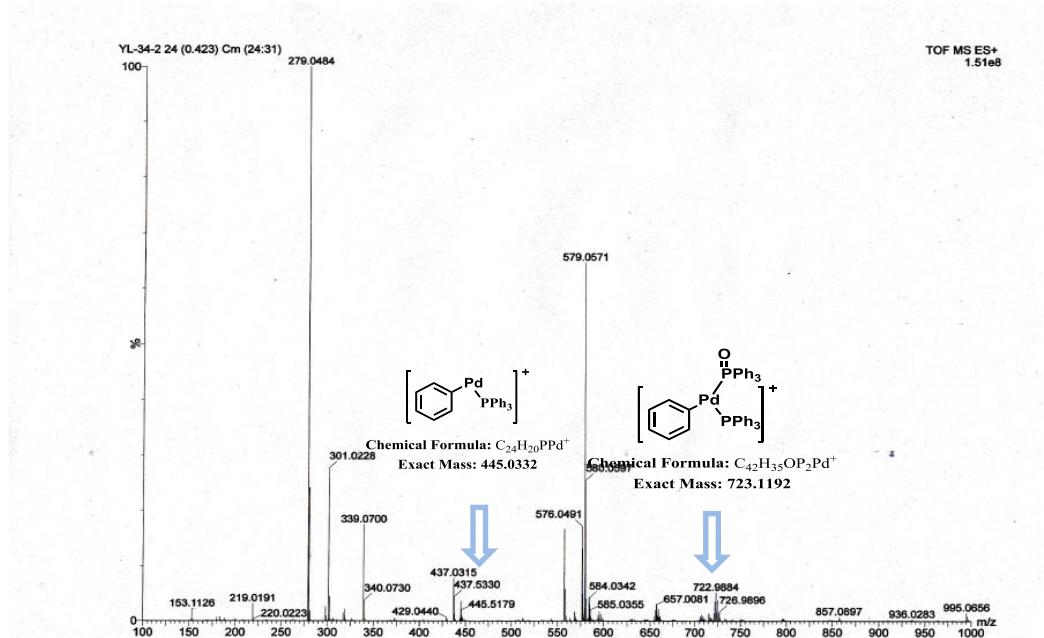
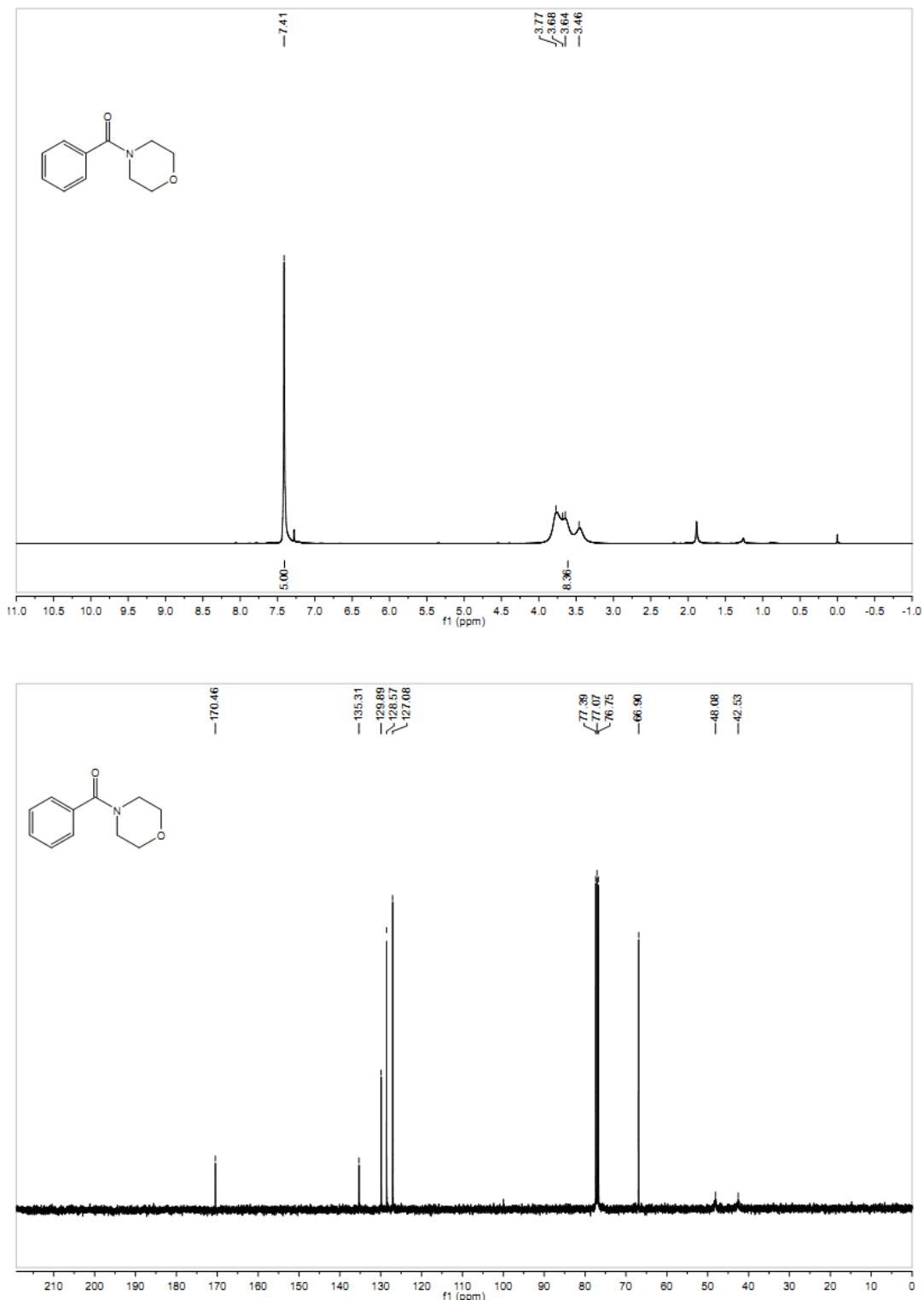


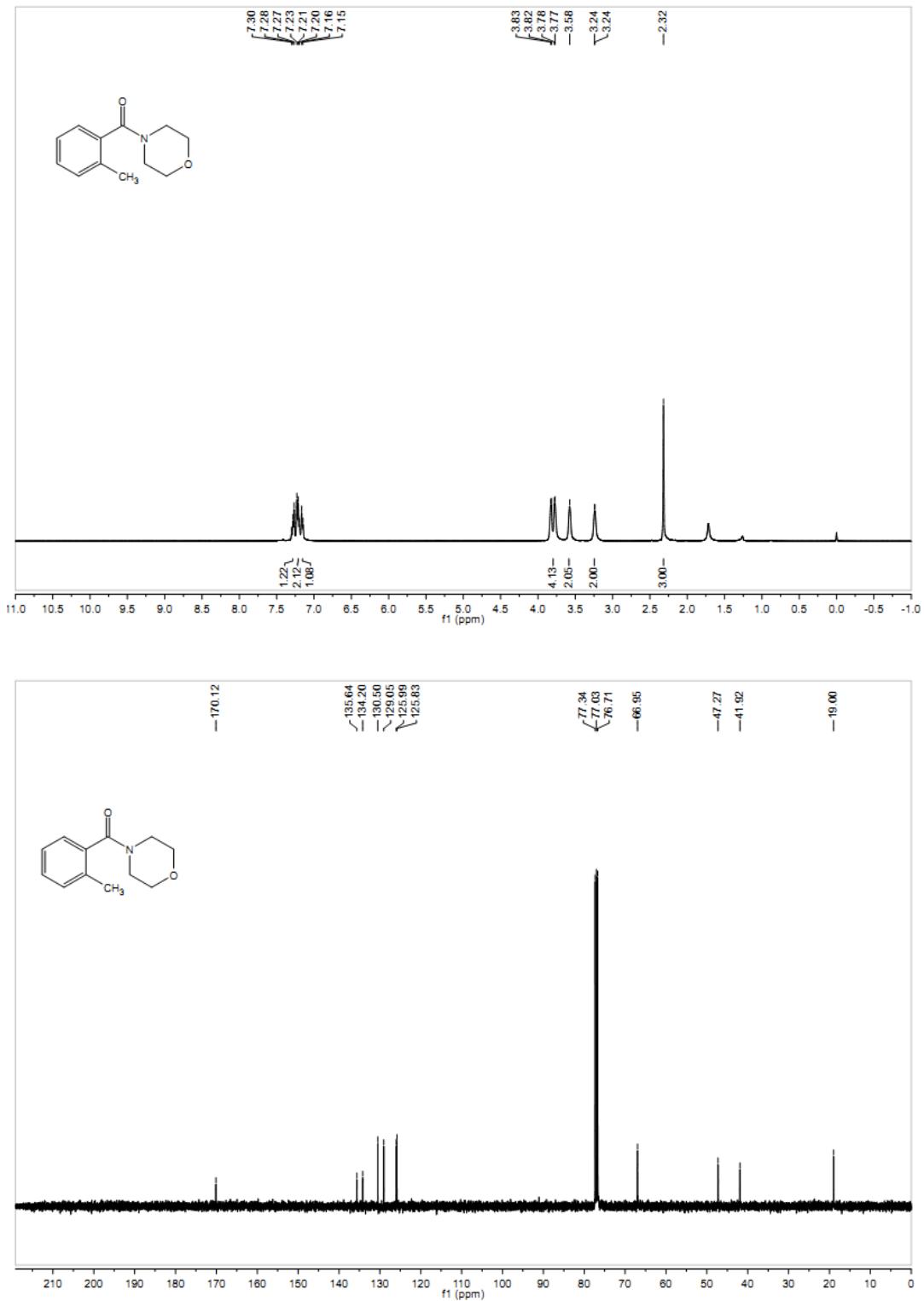
Figure S1. Palladium species **B** was detected by ESI-MS



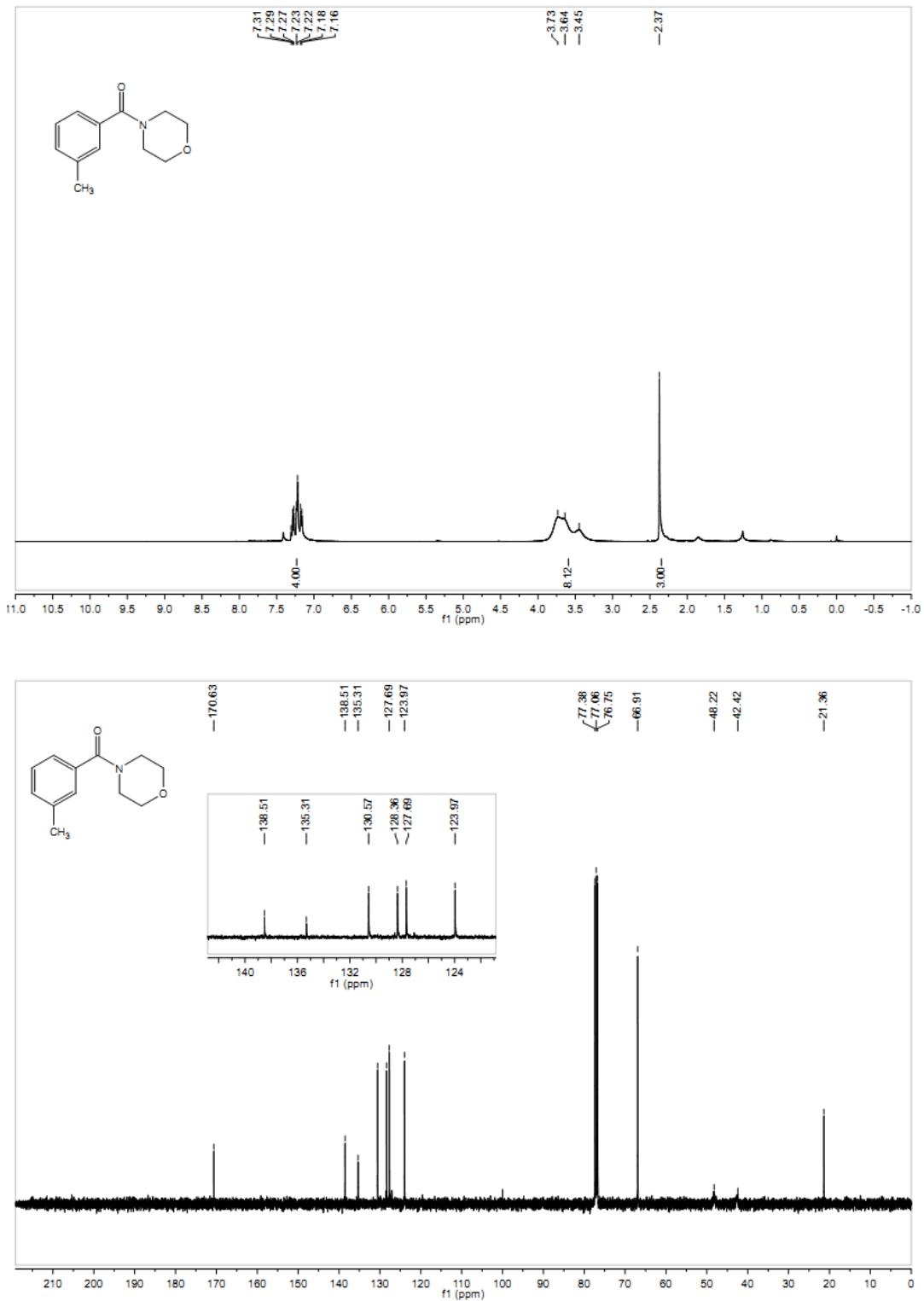
Copies of $^1\text{H-NMR}$ & $^{13}\text{C-NMR}$ spectrum



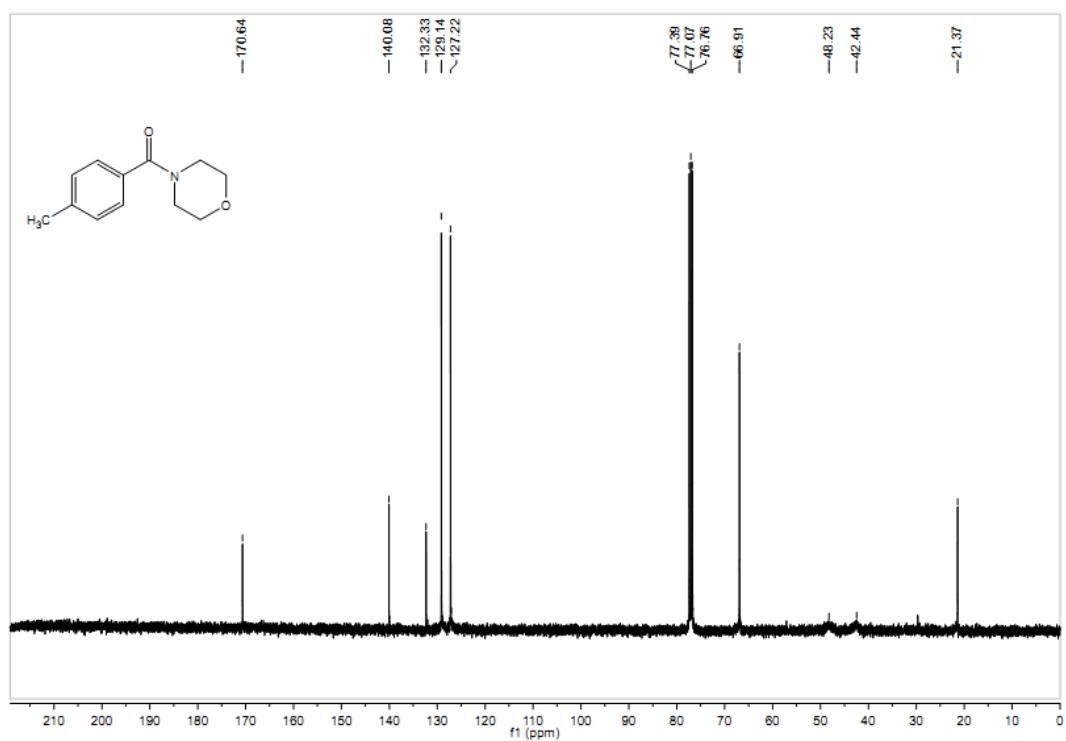
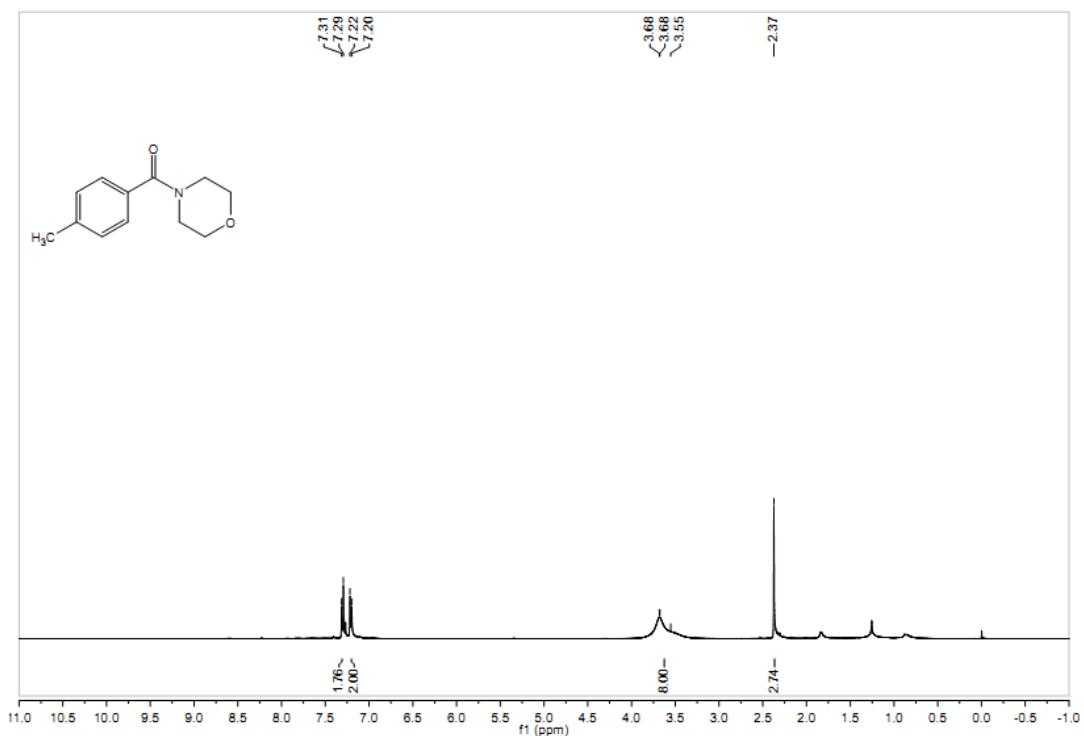
^1H NMR and ^{13}C NMR for compound 3a



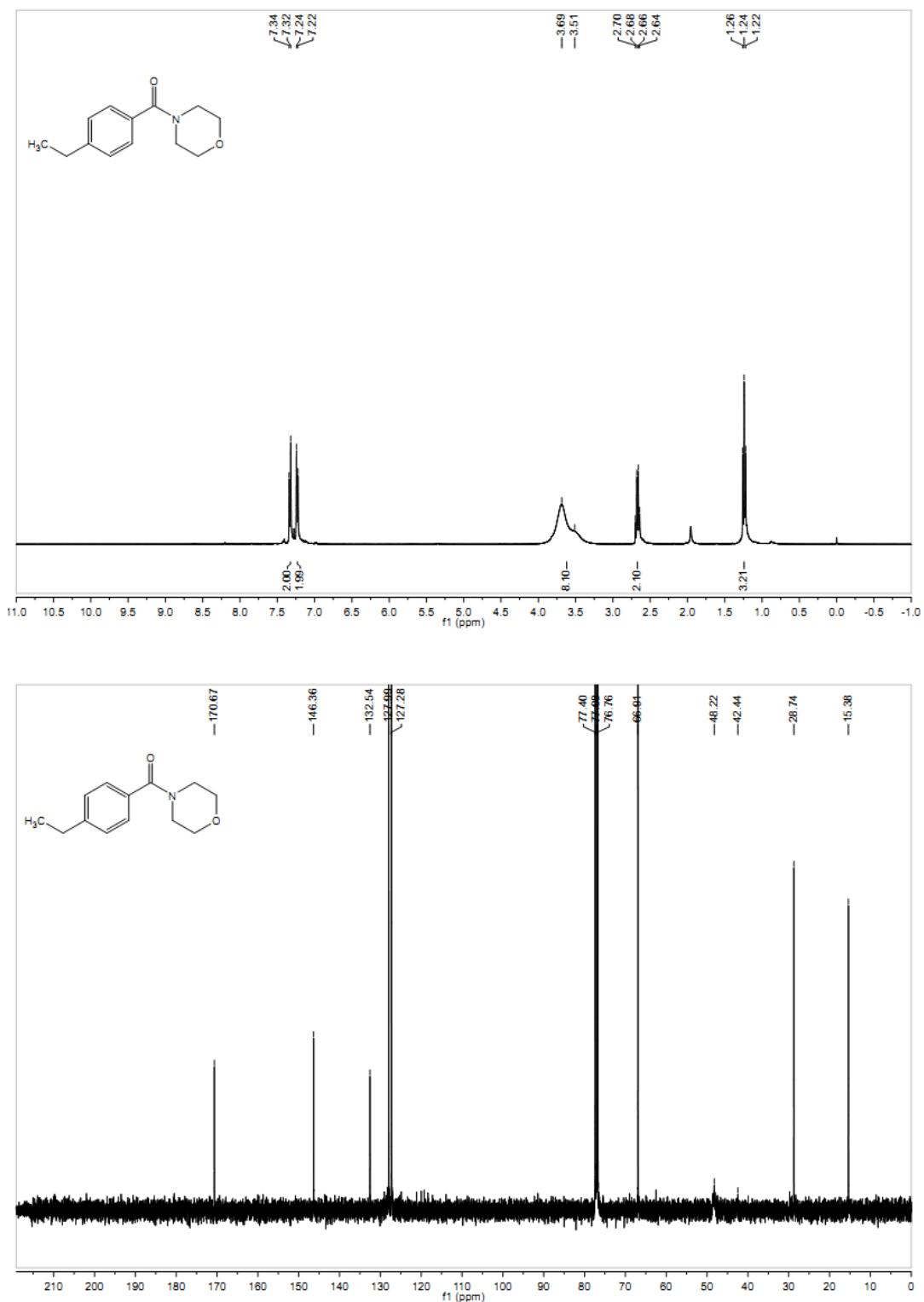
¹H NMR and ¹³C NMR for compound 3b



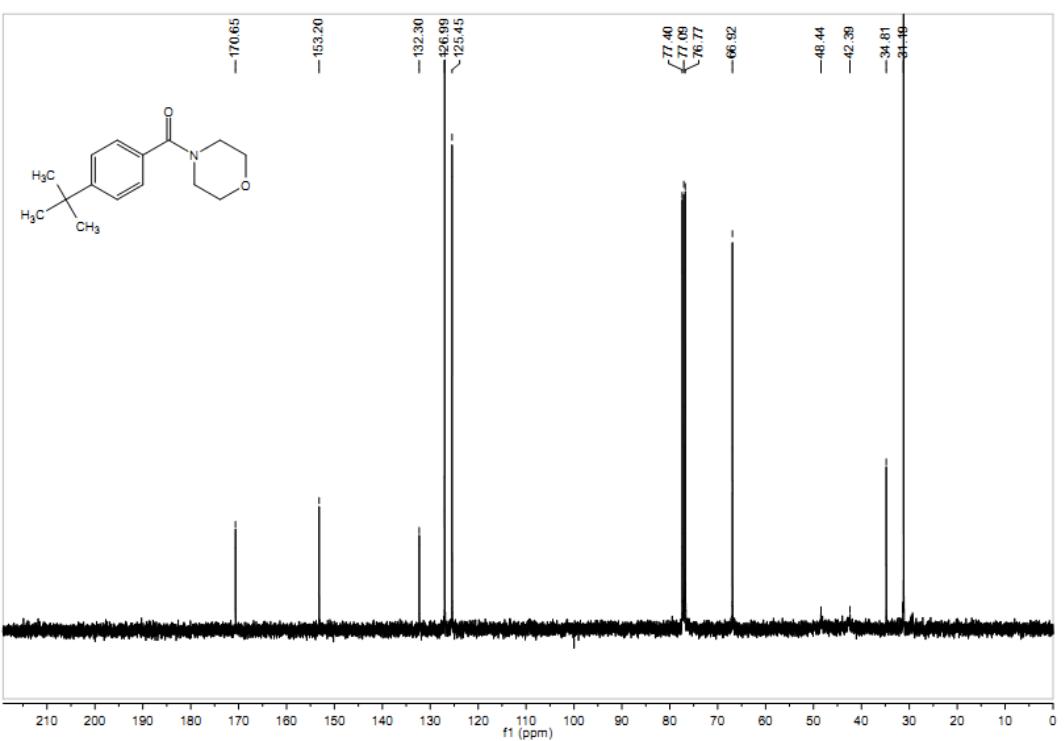
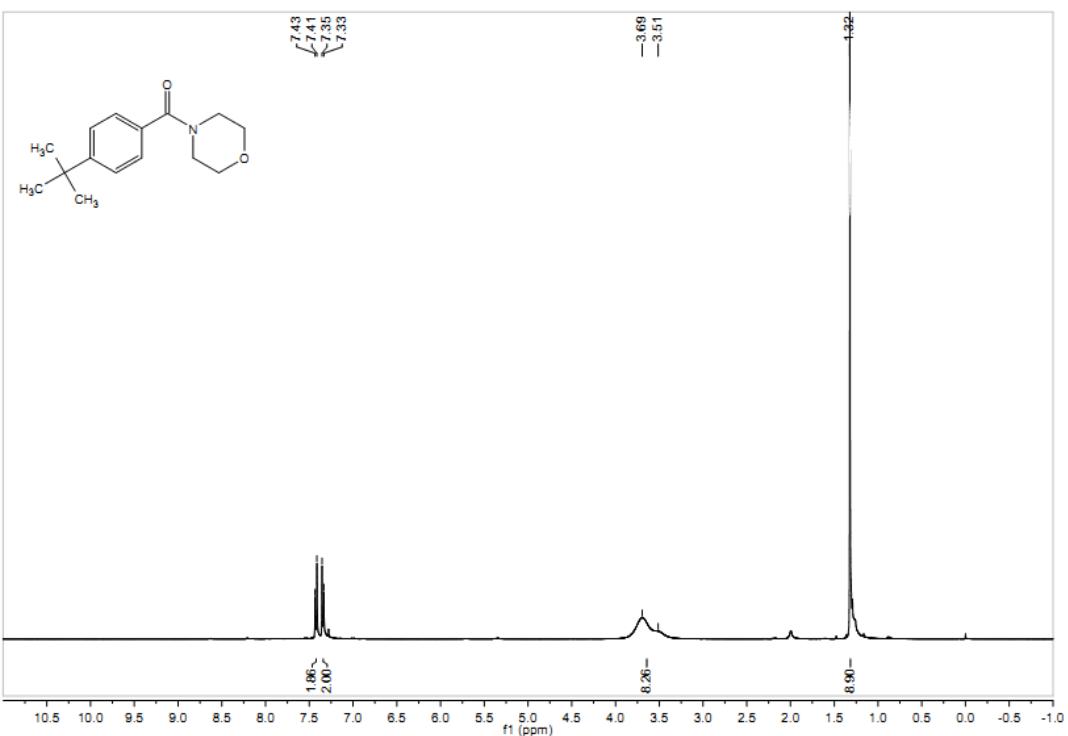
¹H NMR and ¹³C NMR for compound 3c



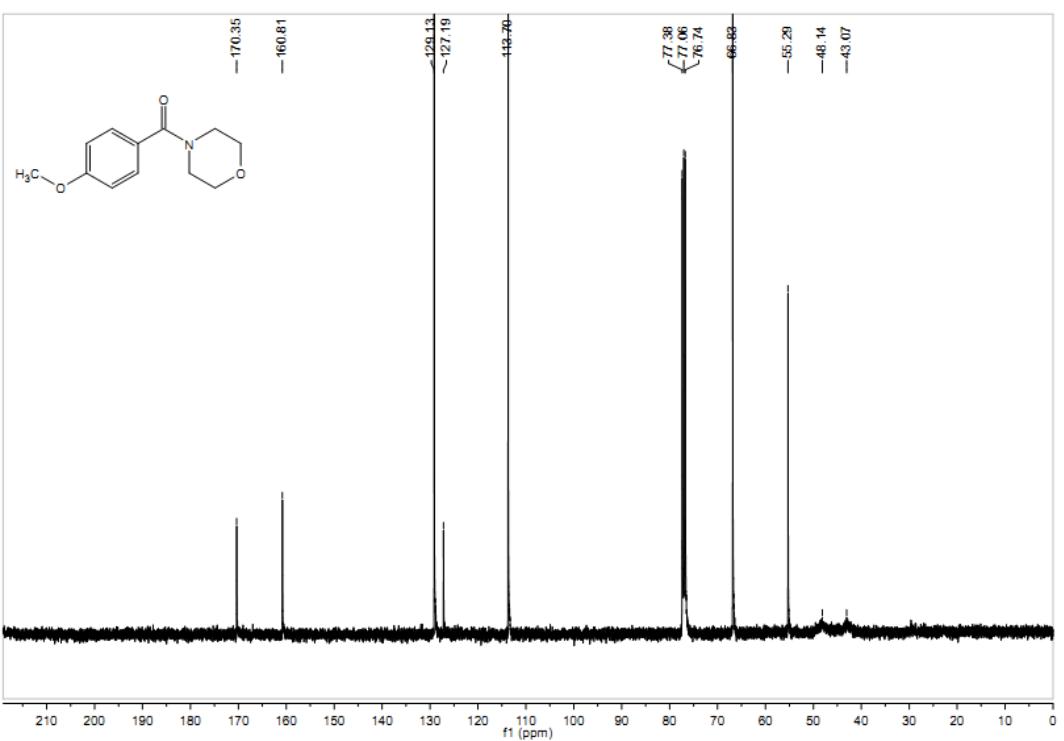
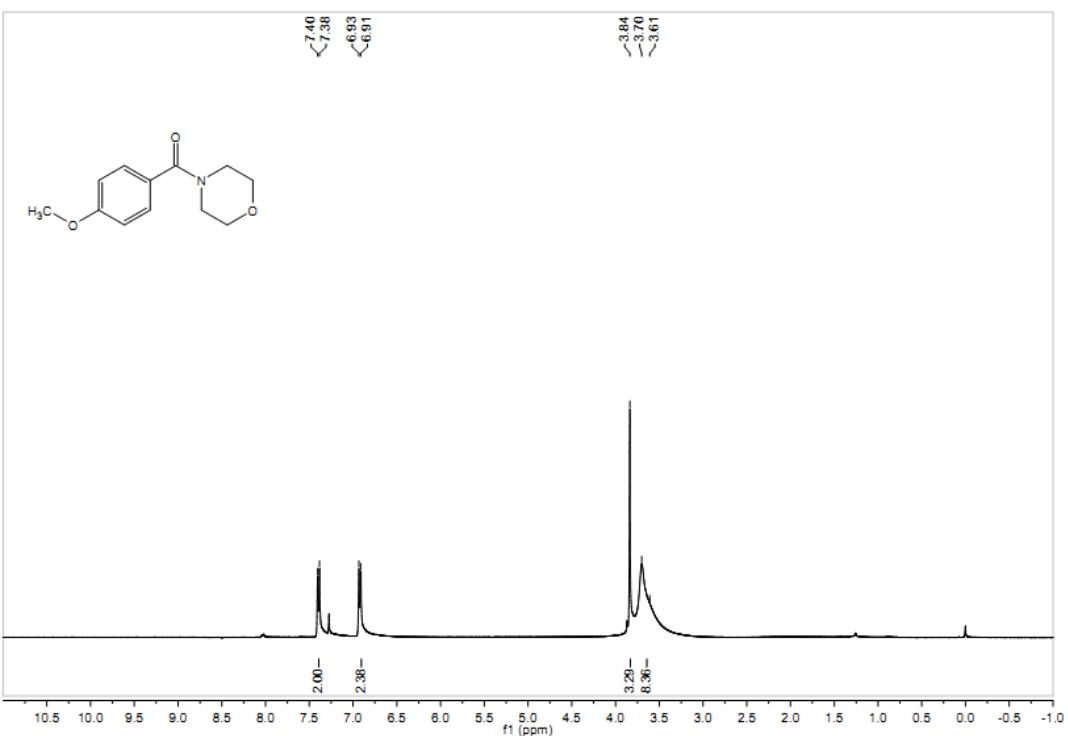
¹H NMR and ¹³C NMR for compound 3d



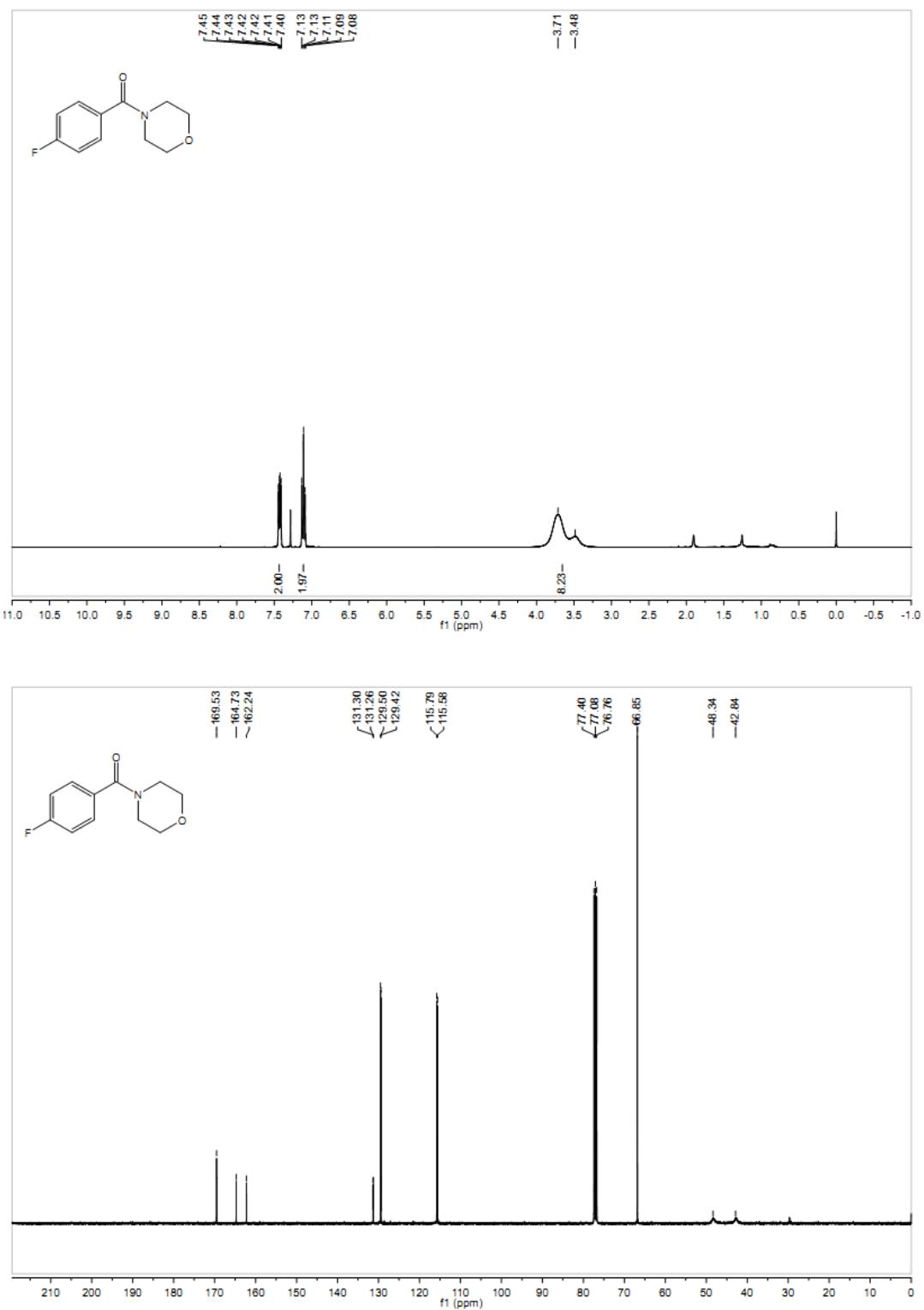
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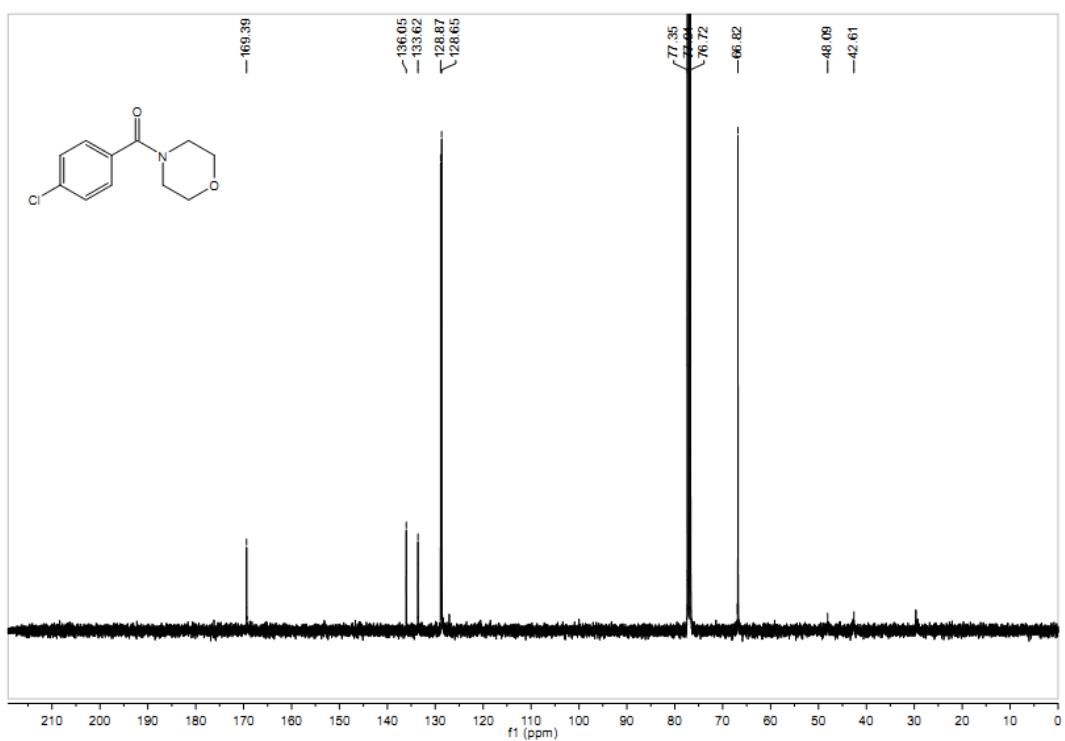
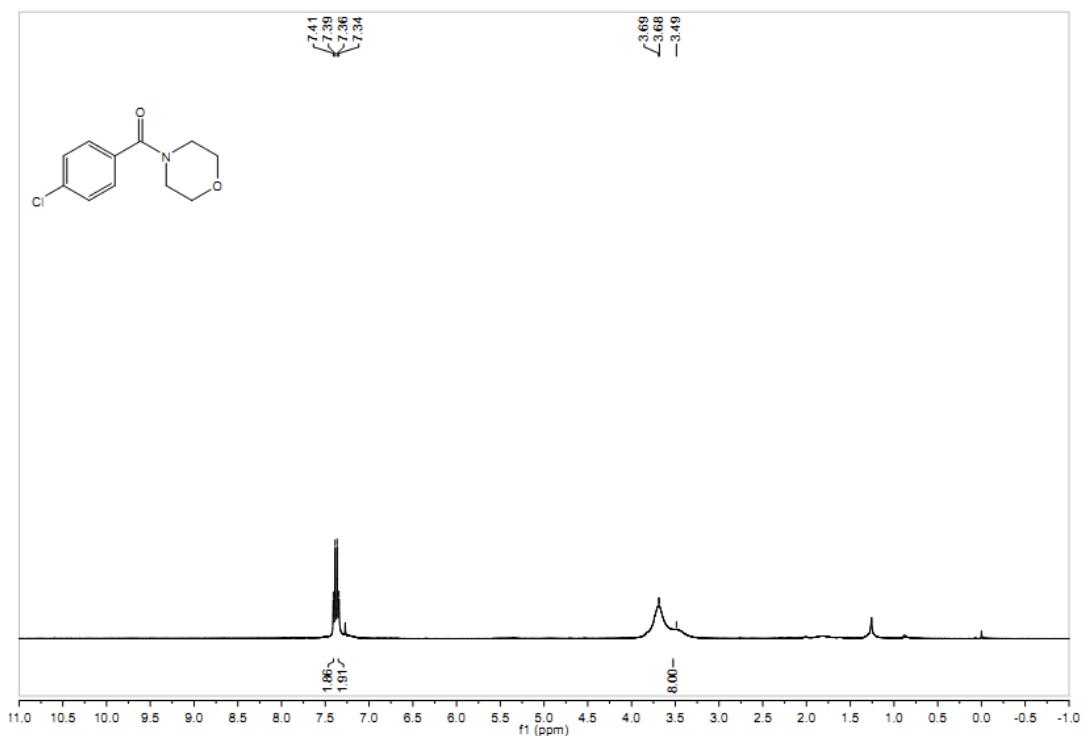
¹H NMR and ¹³C NMR for compound 3f



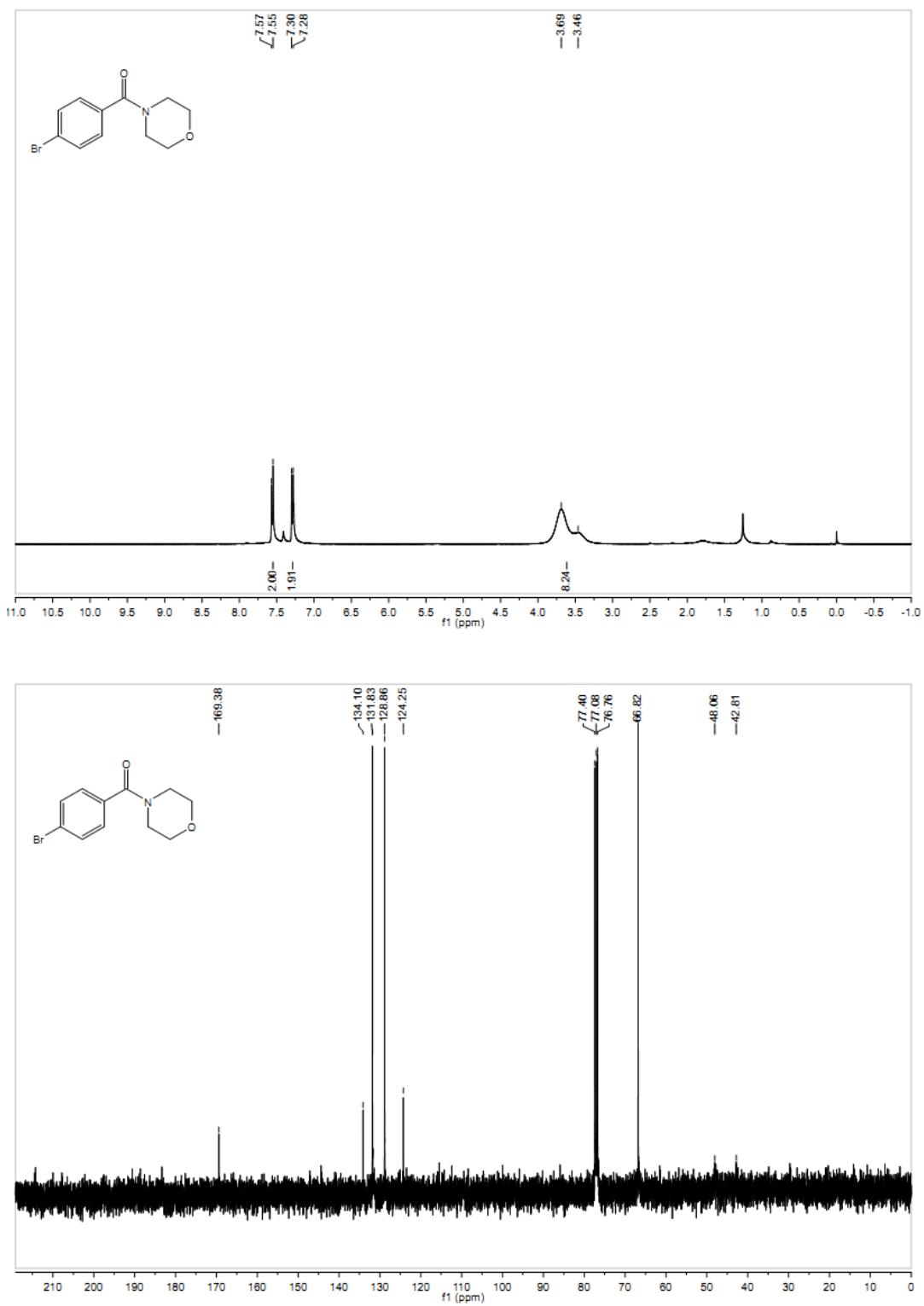
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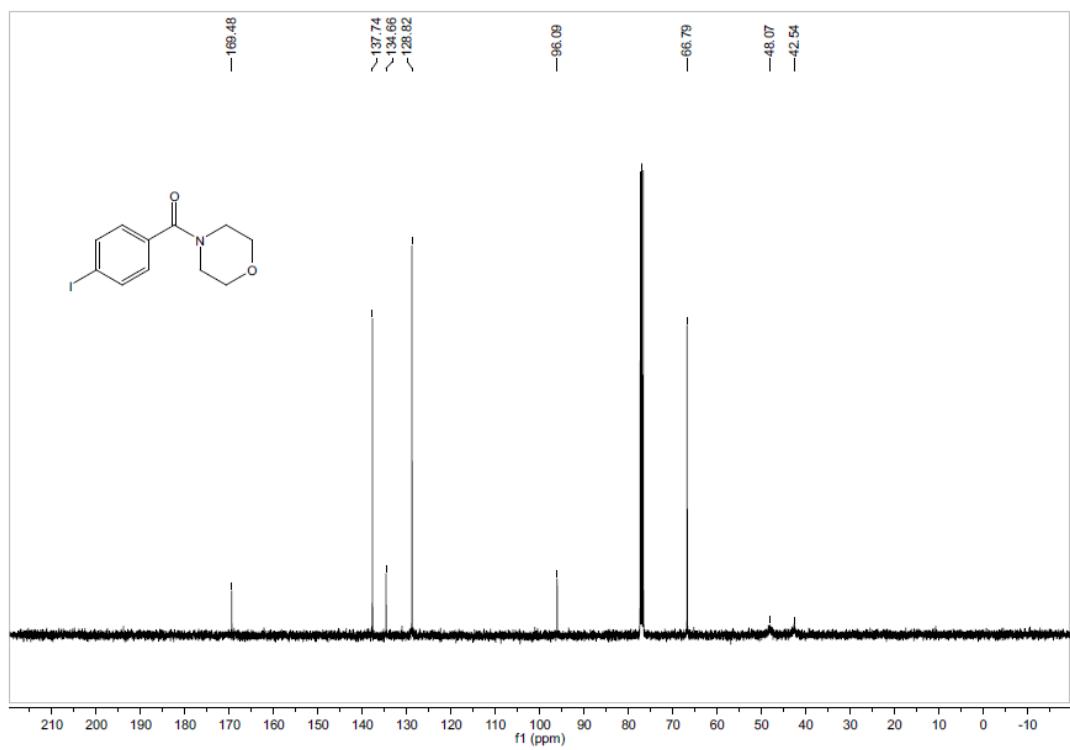
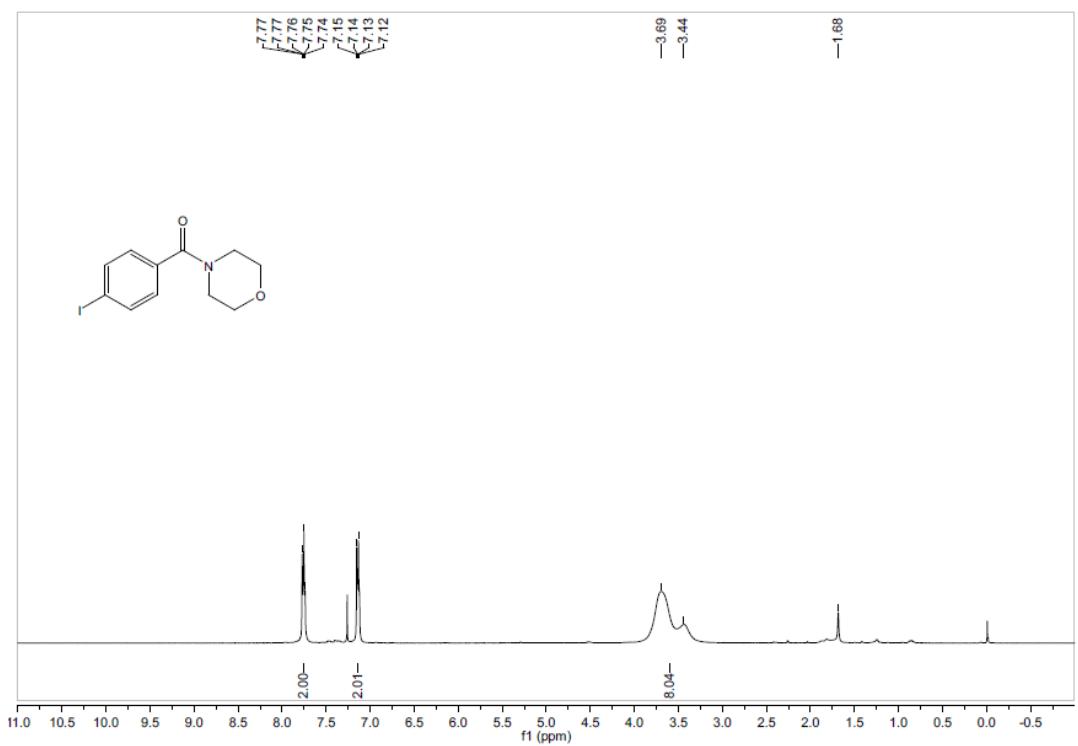
¹H NMR and ¹³C NMR for compound 3h



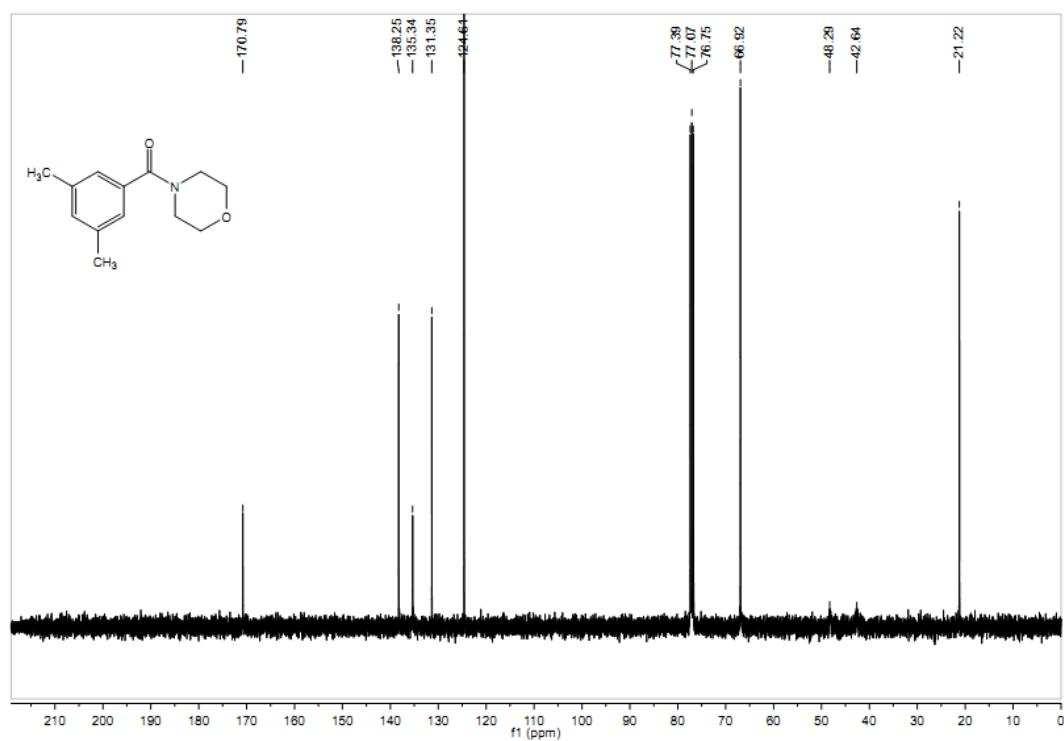
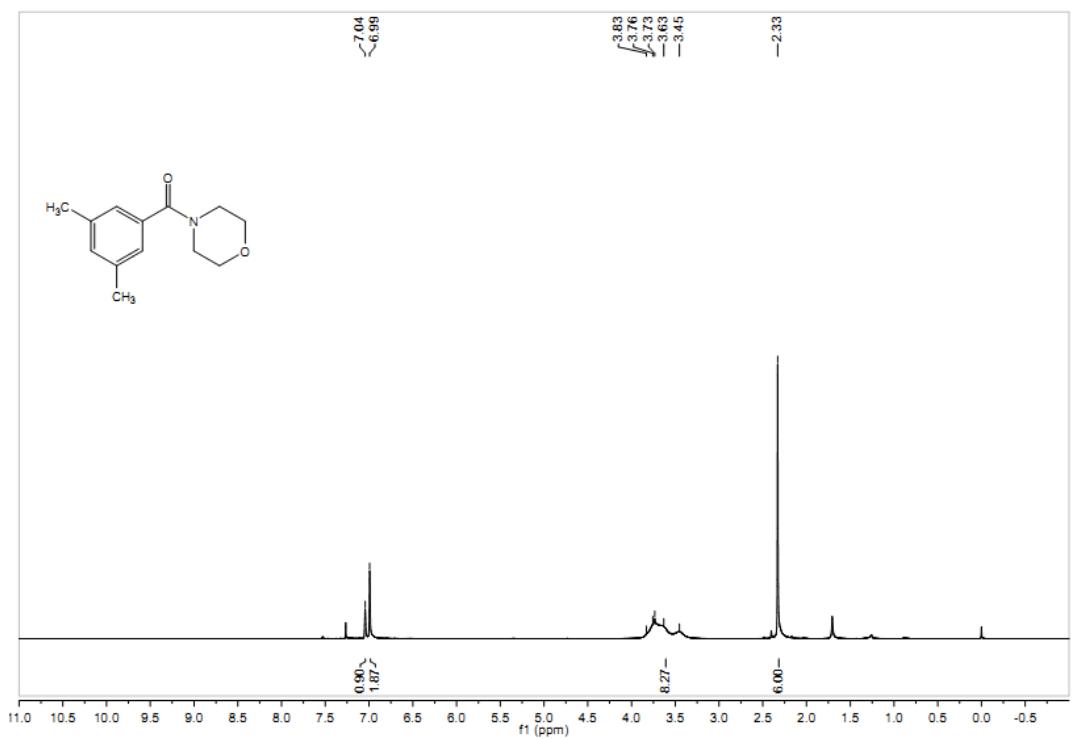
¹H NMR and ¹³C NMR for compound 3i



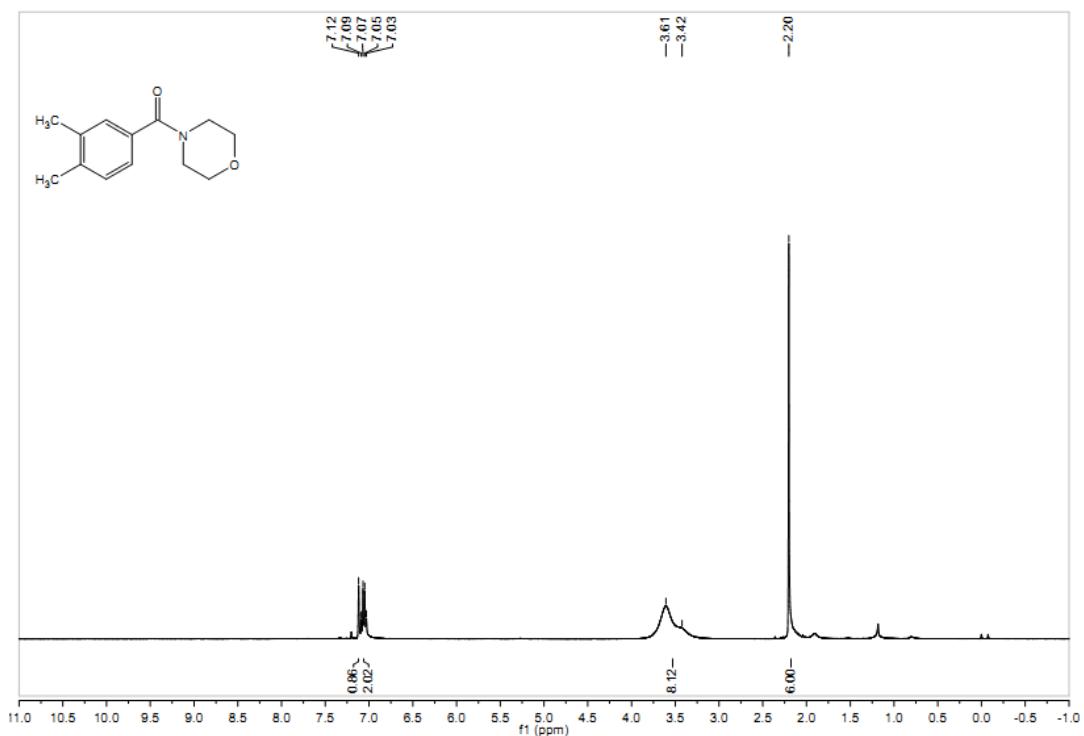
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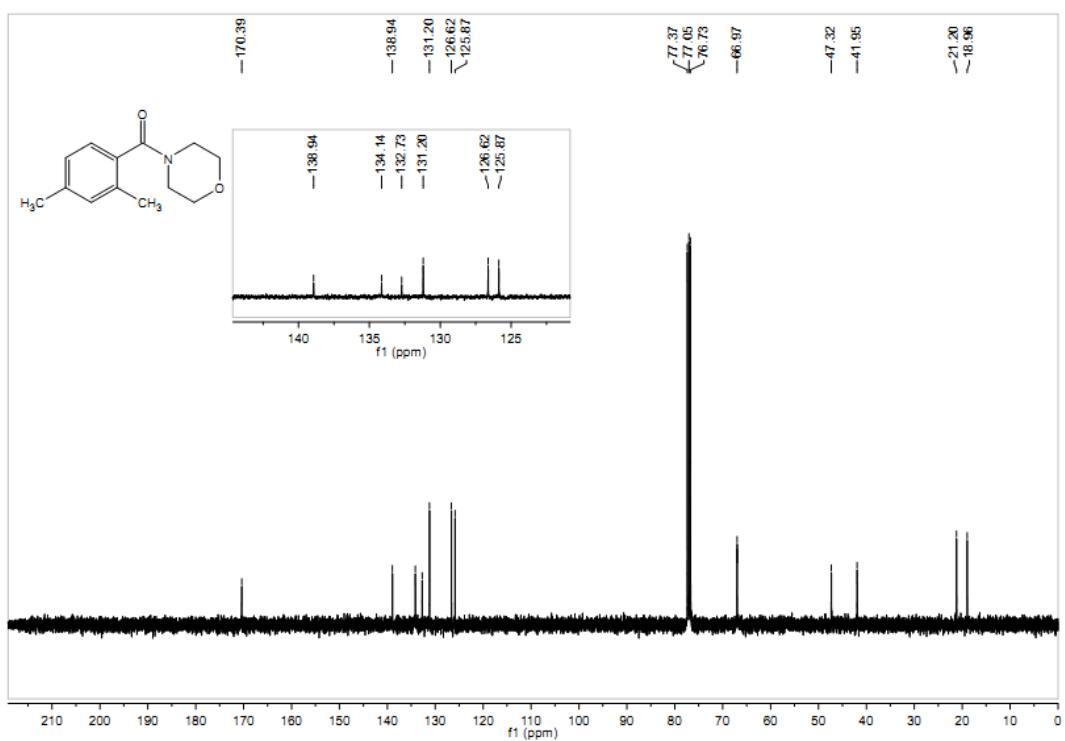
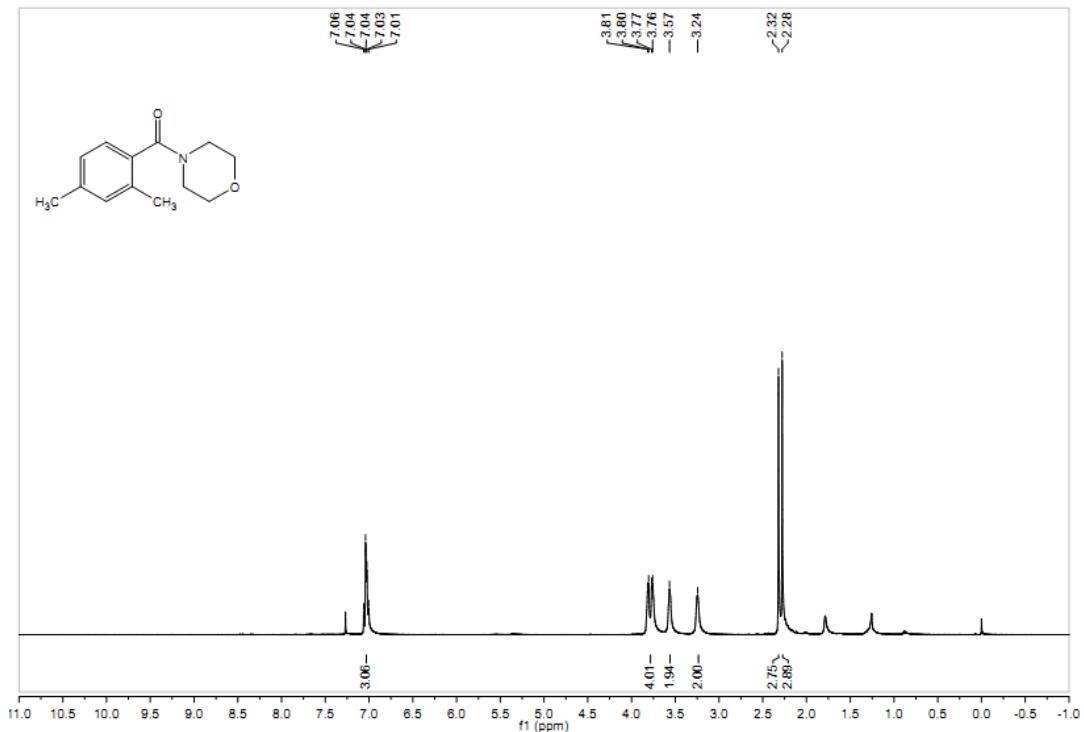
¹H NMR and ¹³C NMR for compound 3k



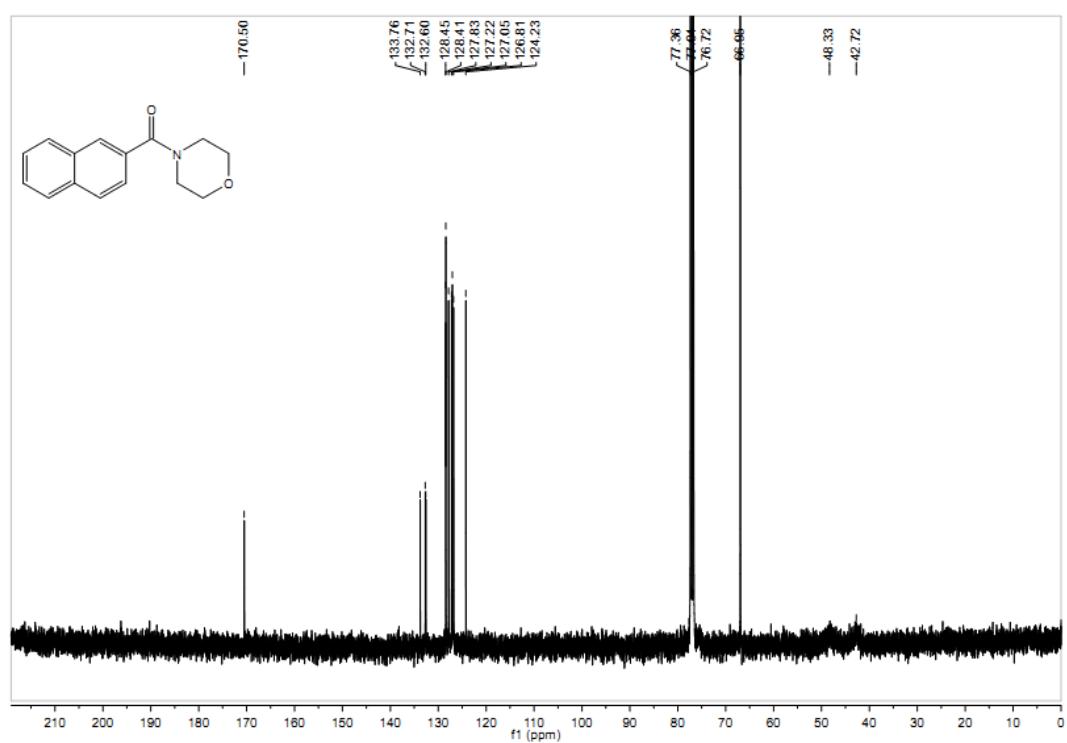
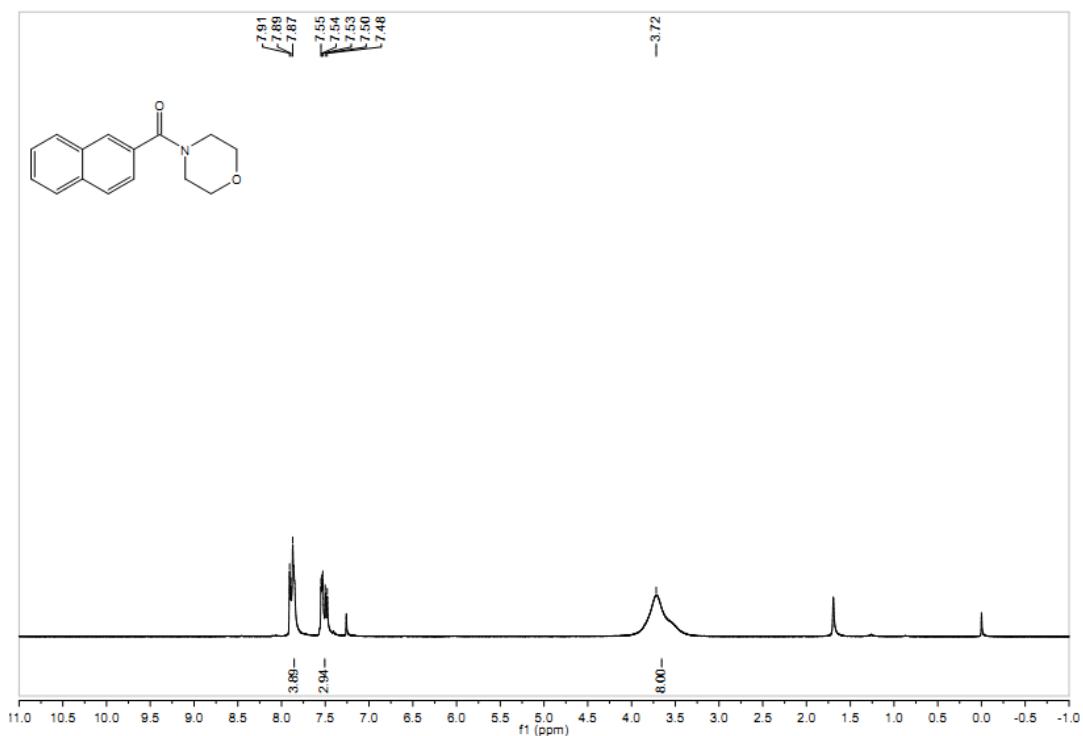
^1H NMR and ^{13}C NMR for compound 31



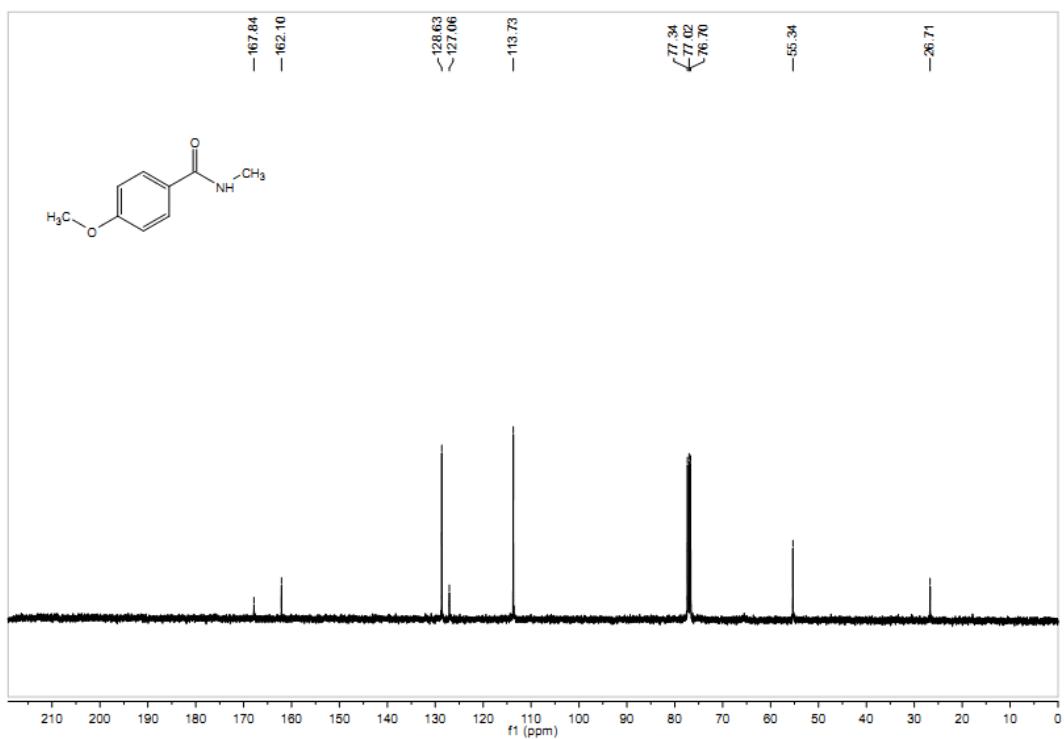
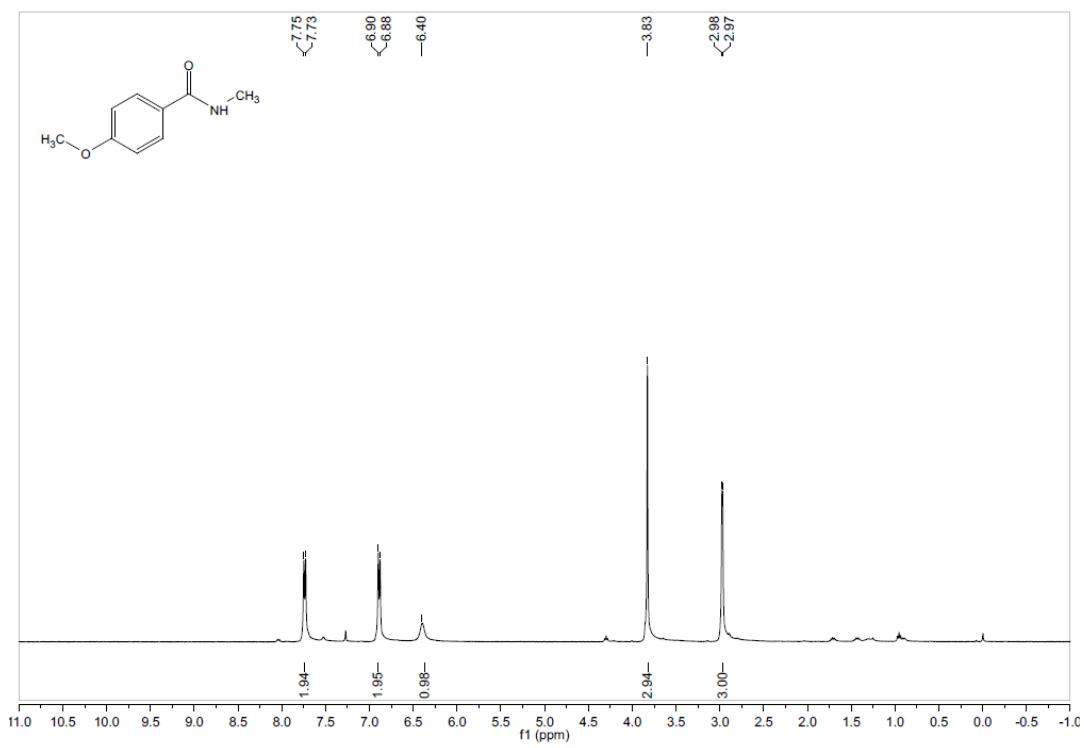
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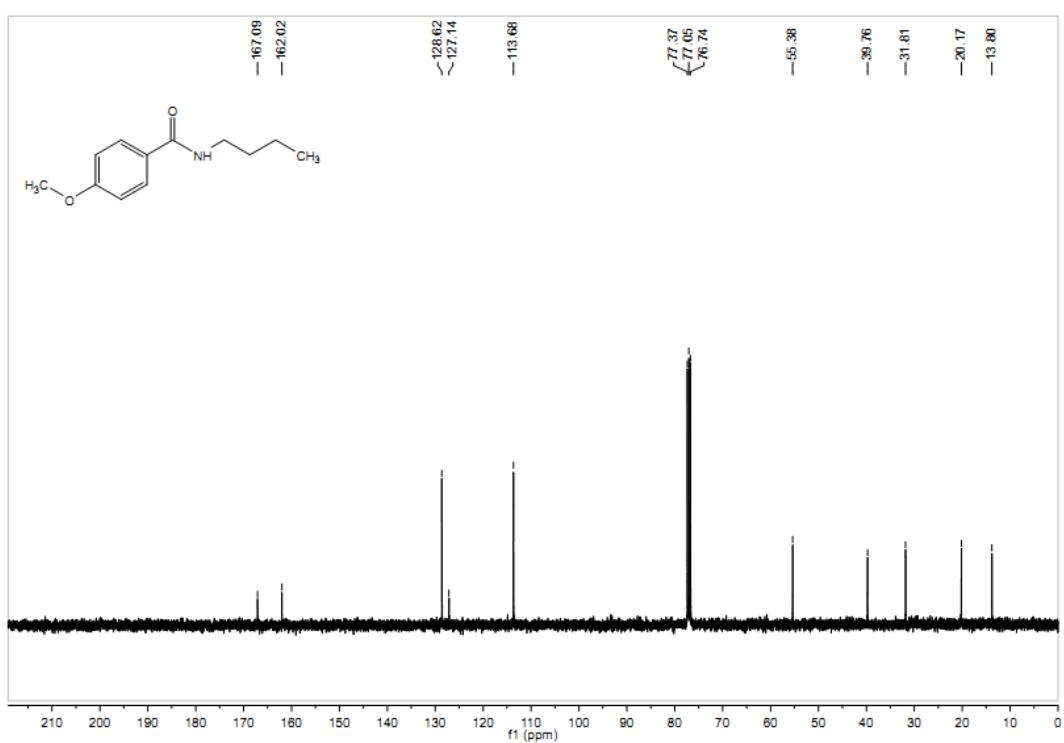
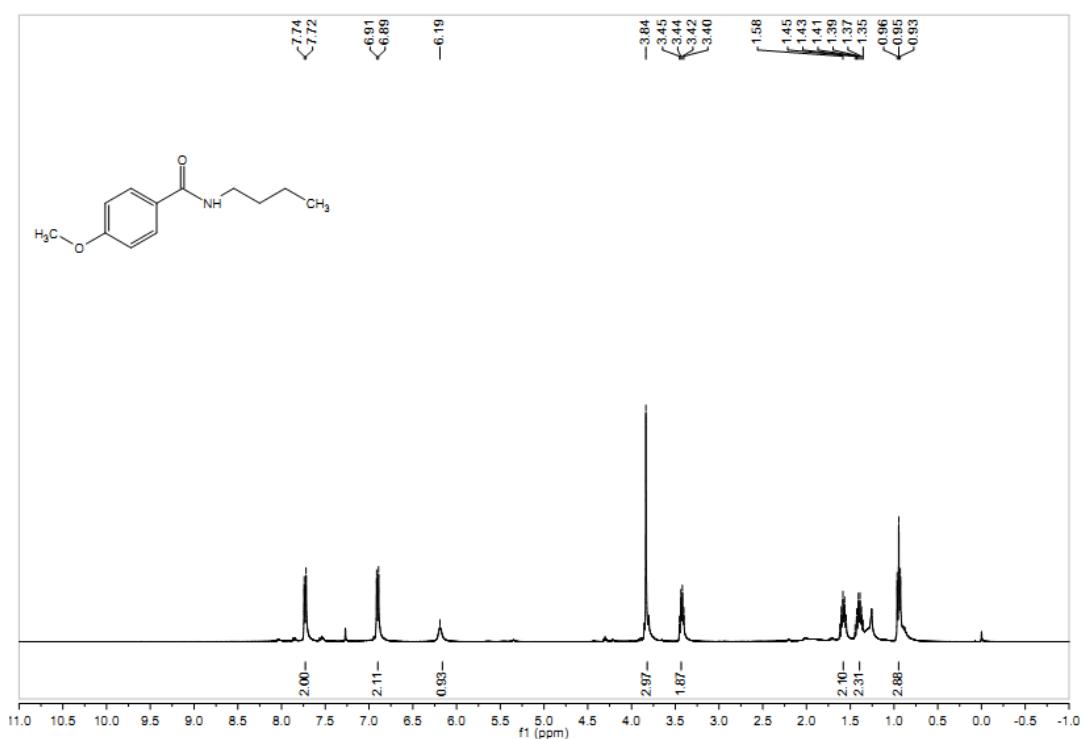
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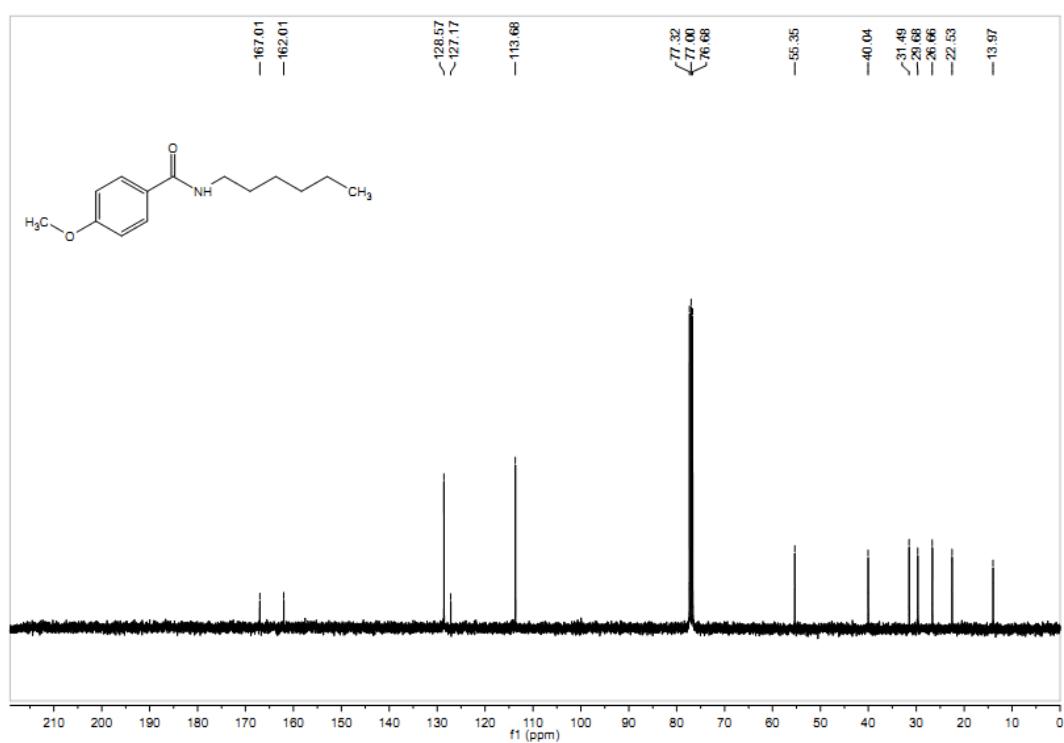
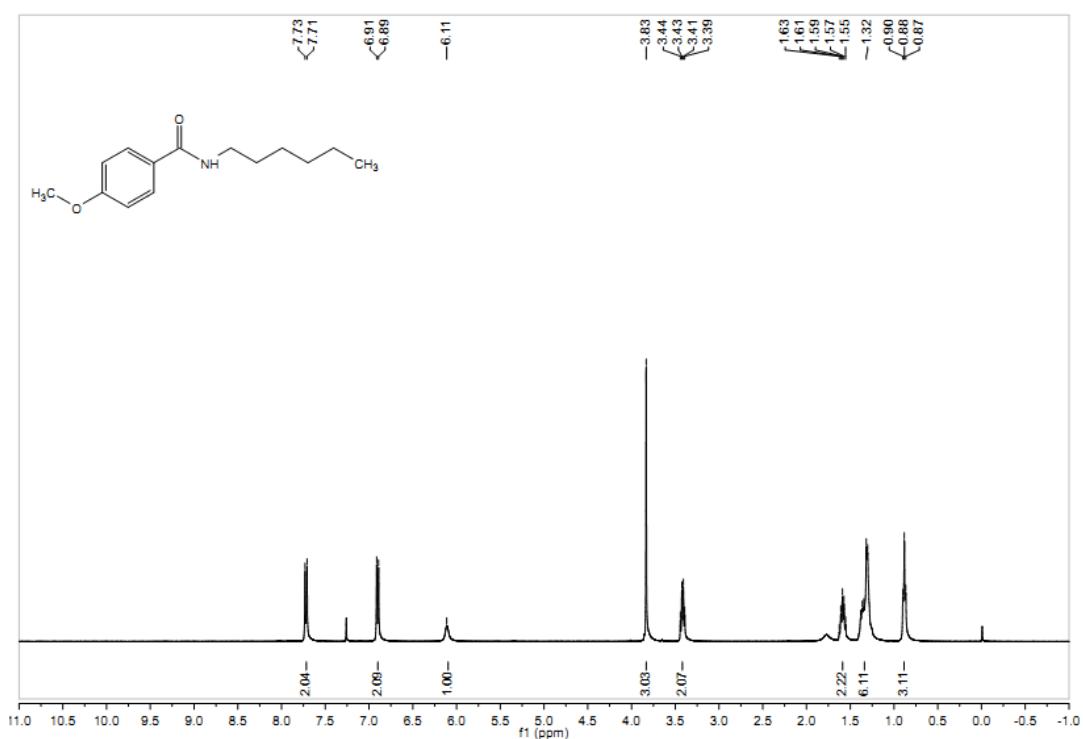
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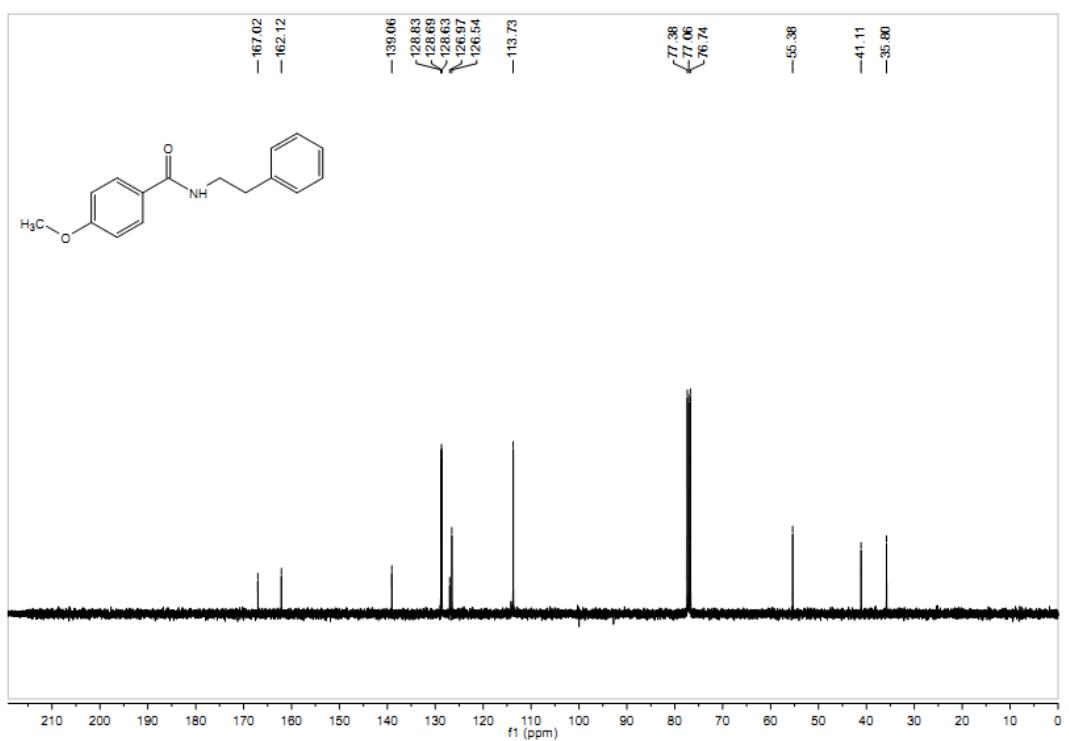
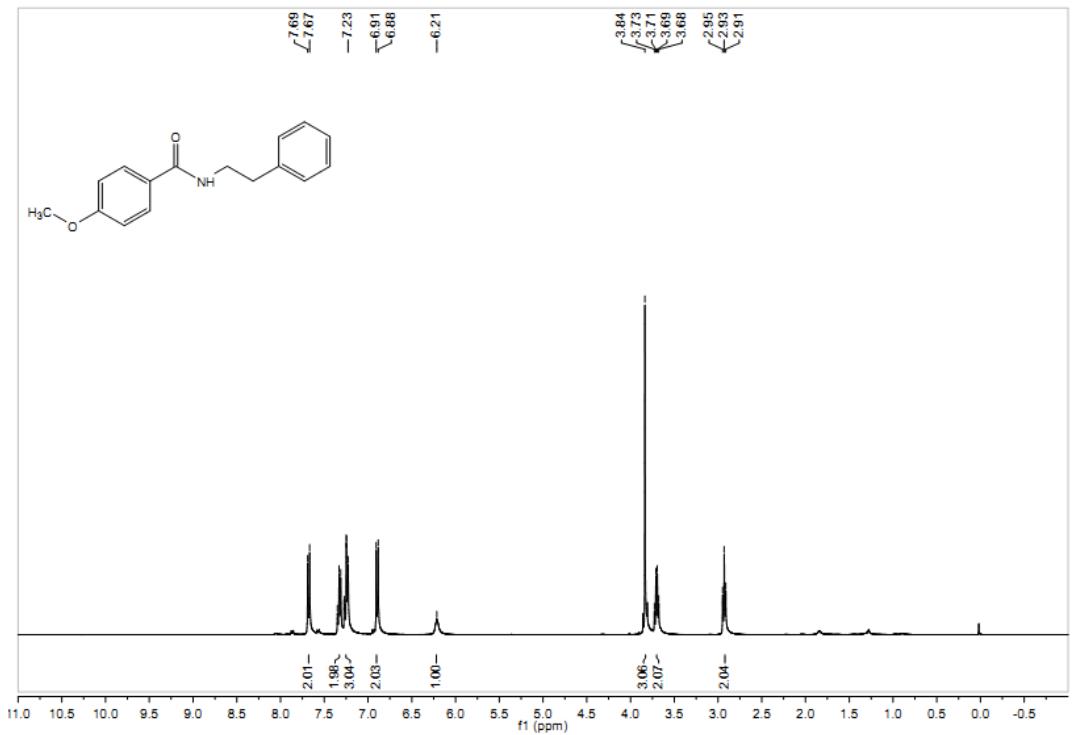
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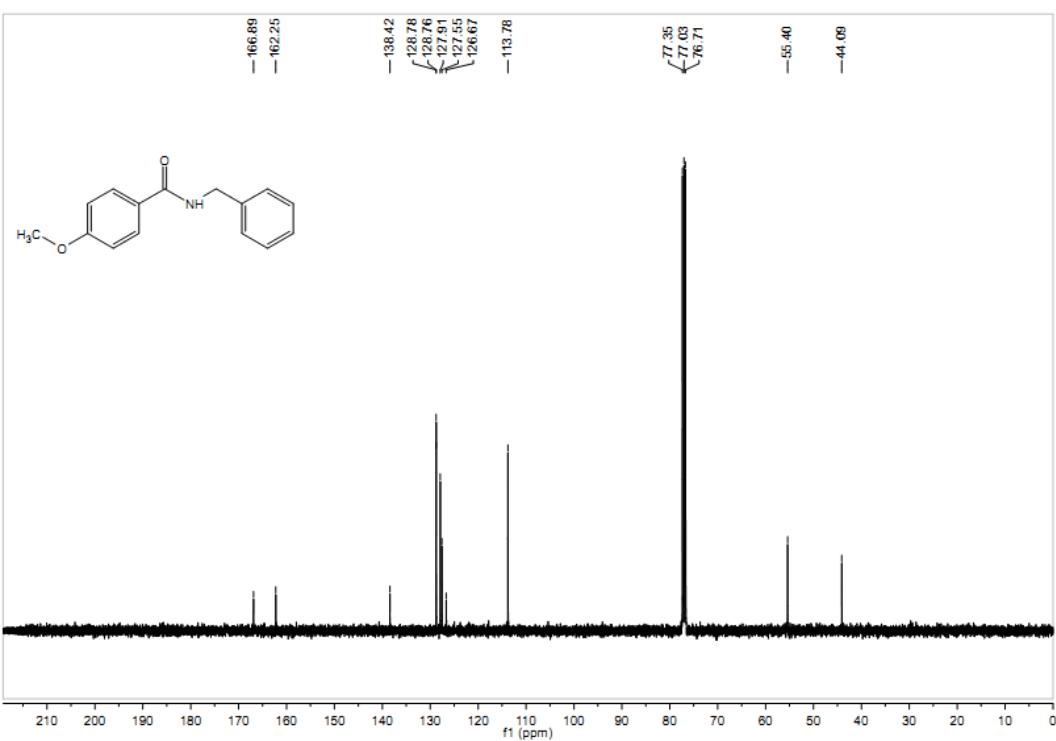
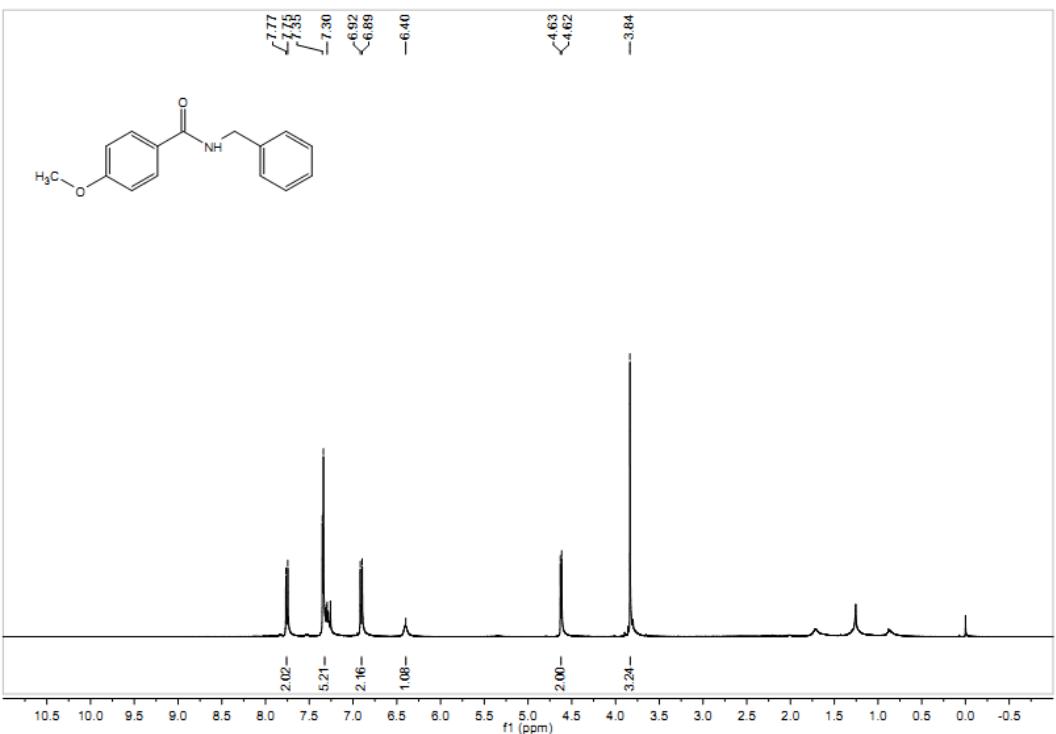
^1H NMR and ^{13}C NMR for compound 4b



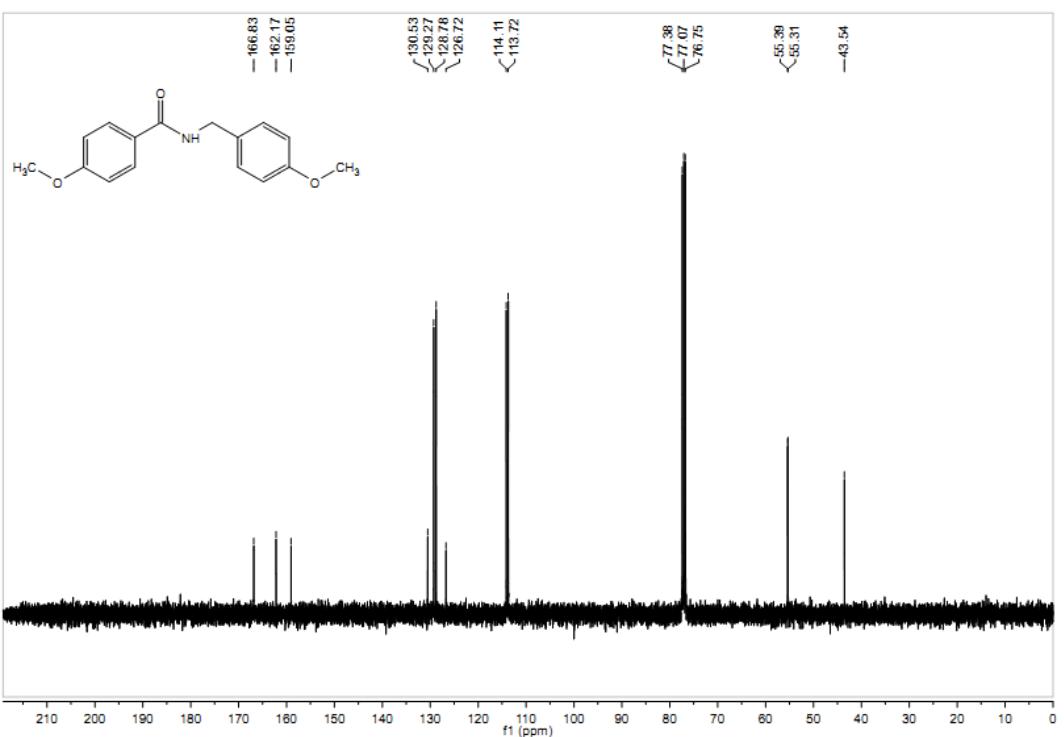
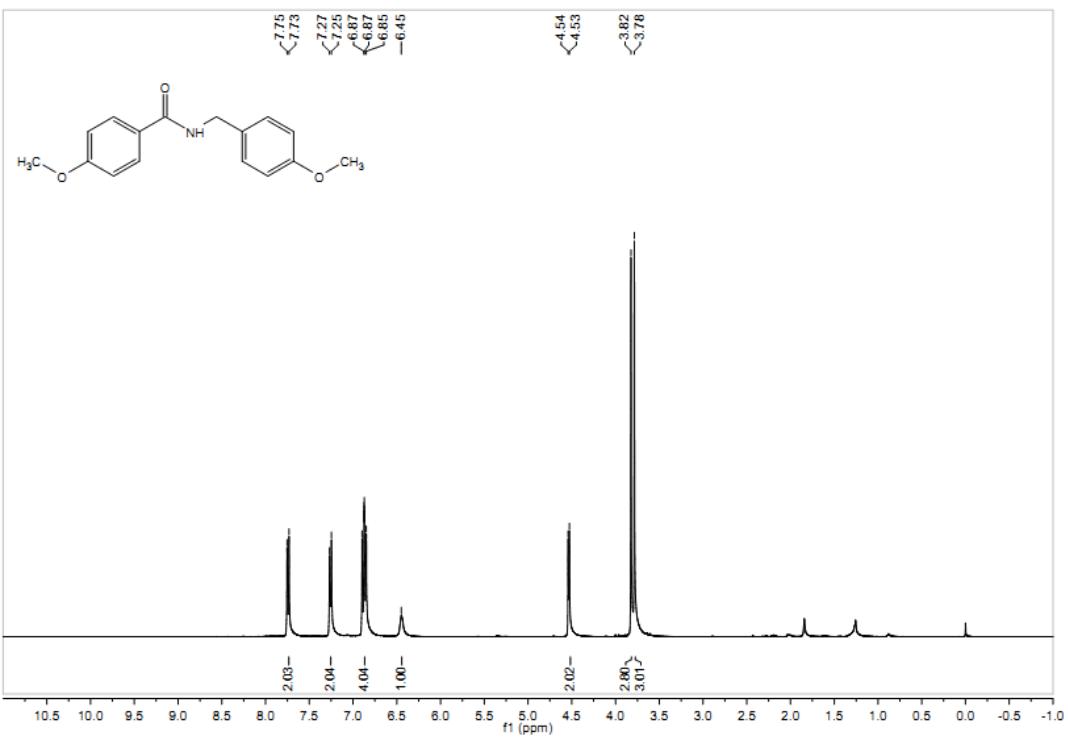
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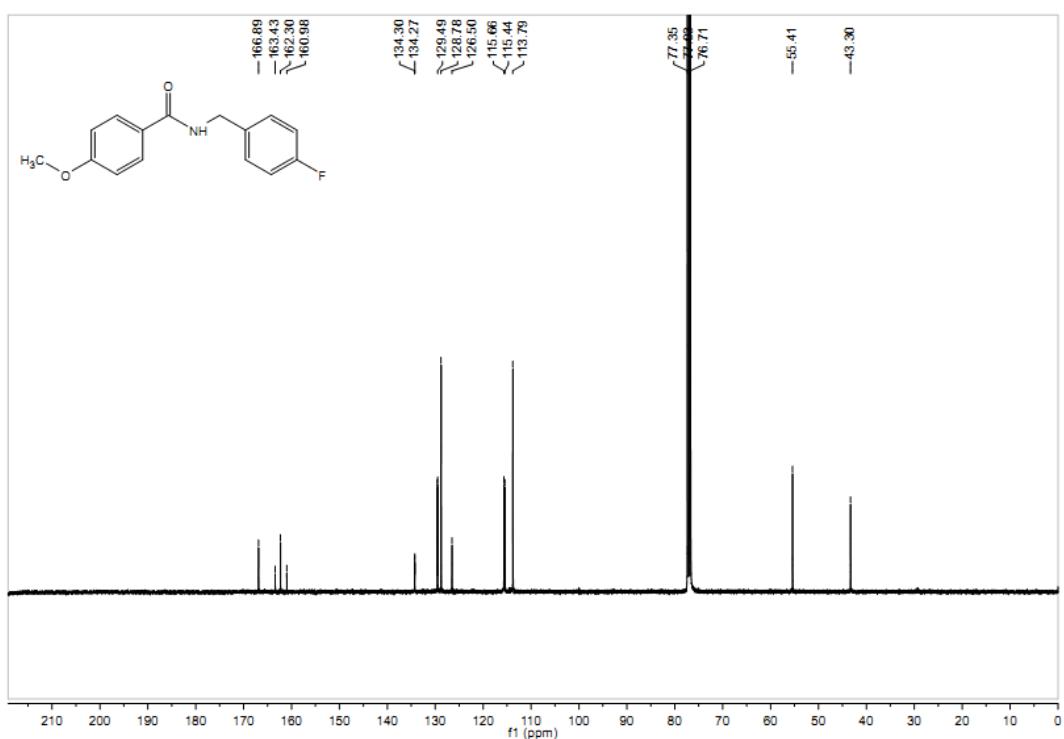
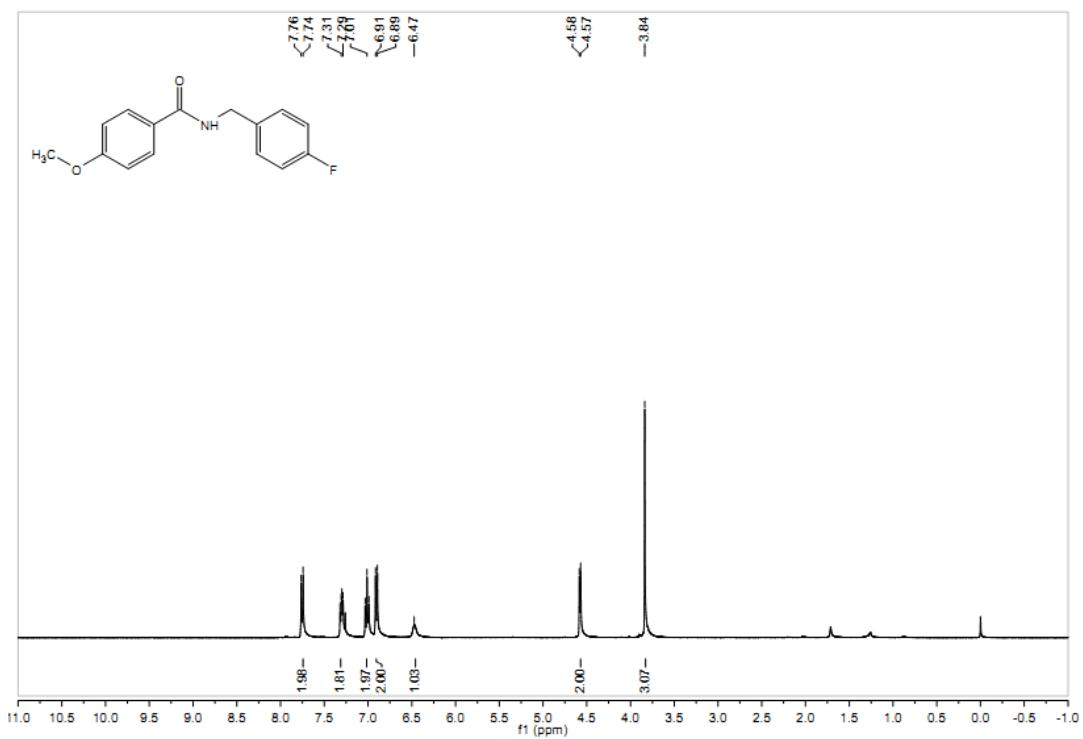
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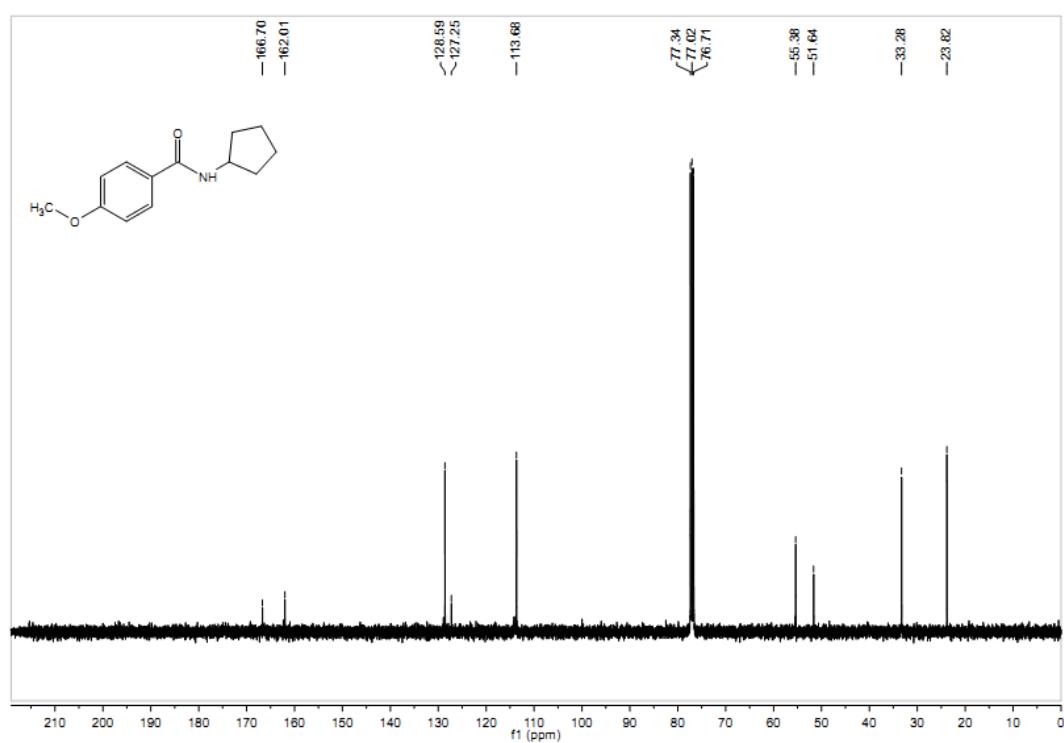
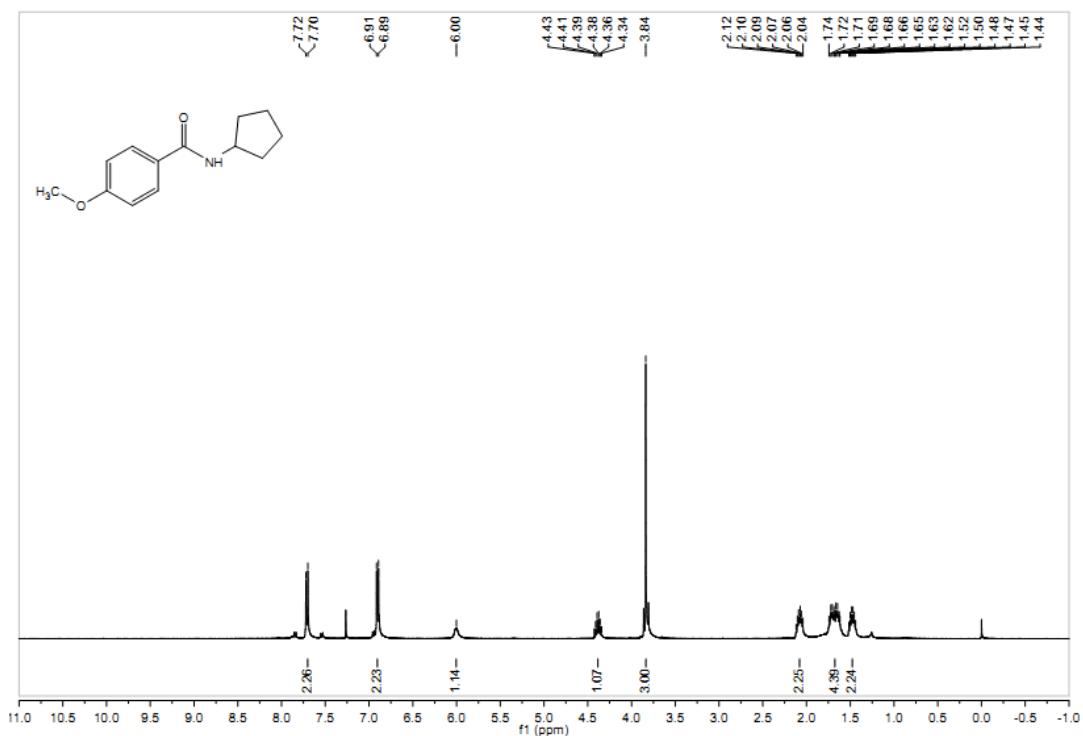
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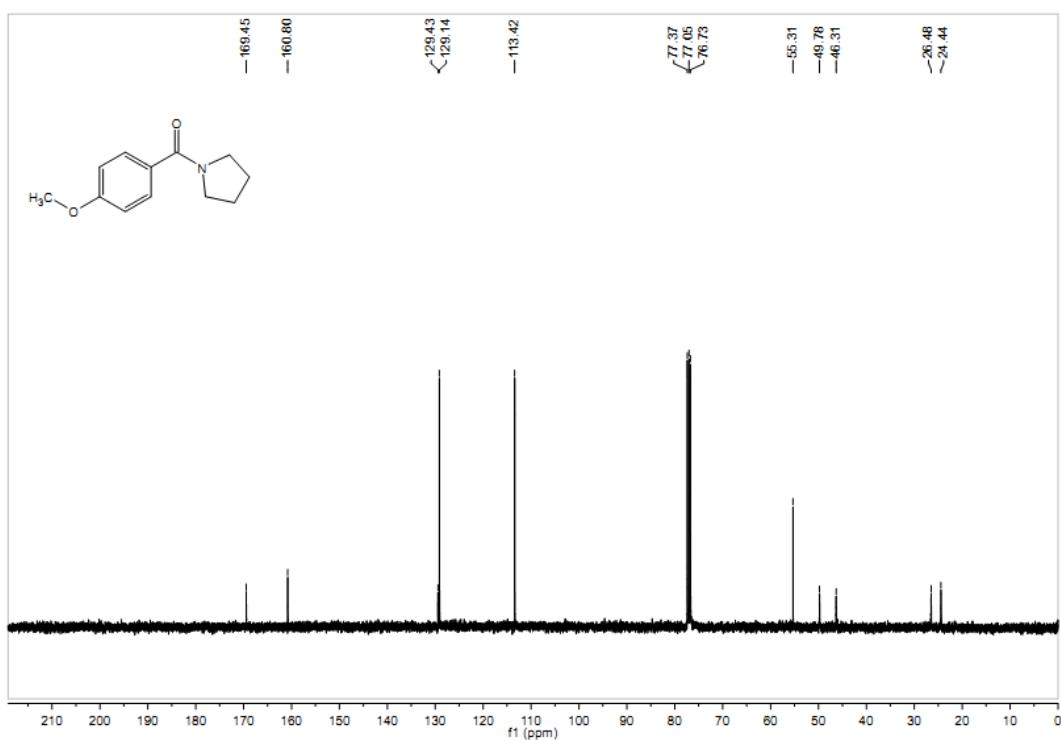
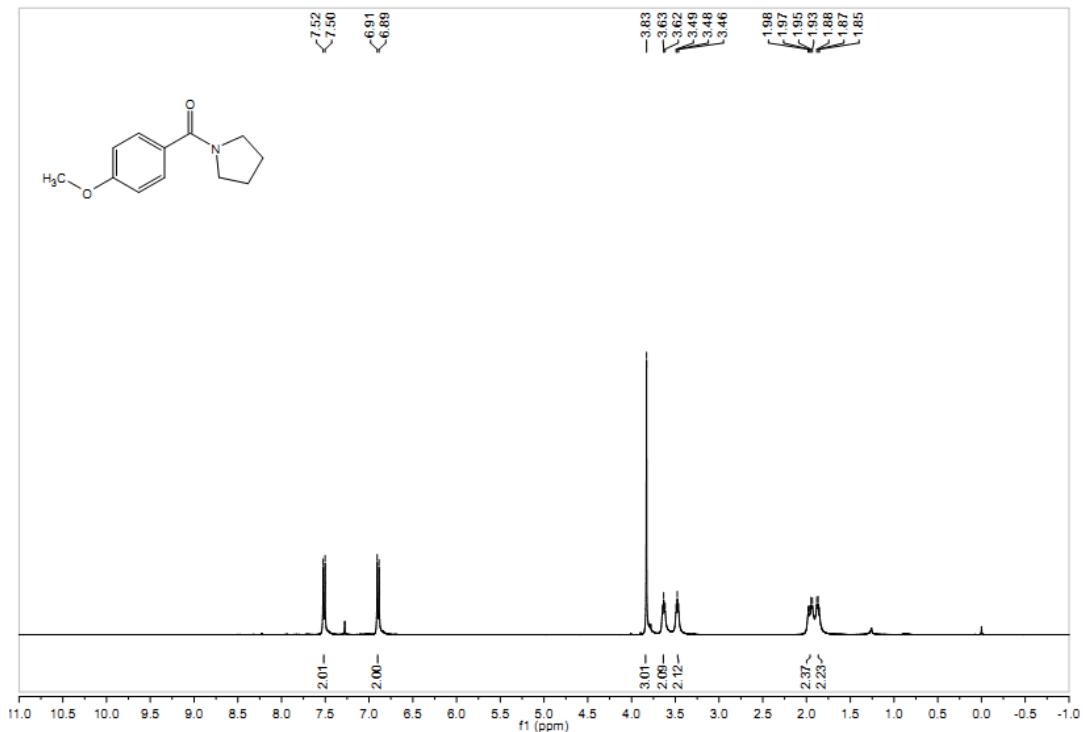
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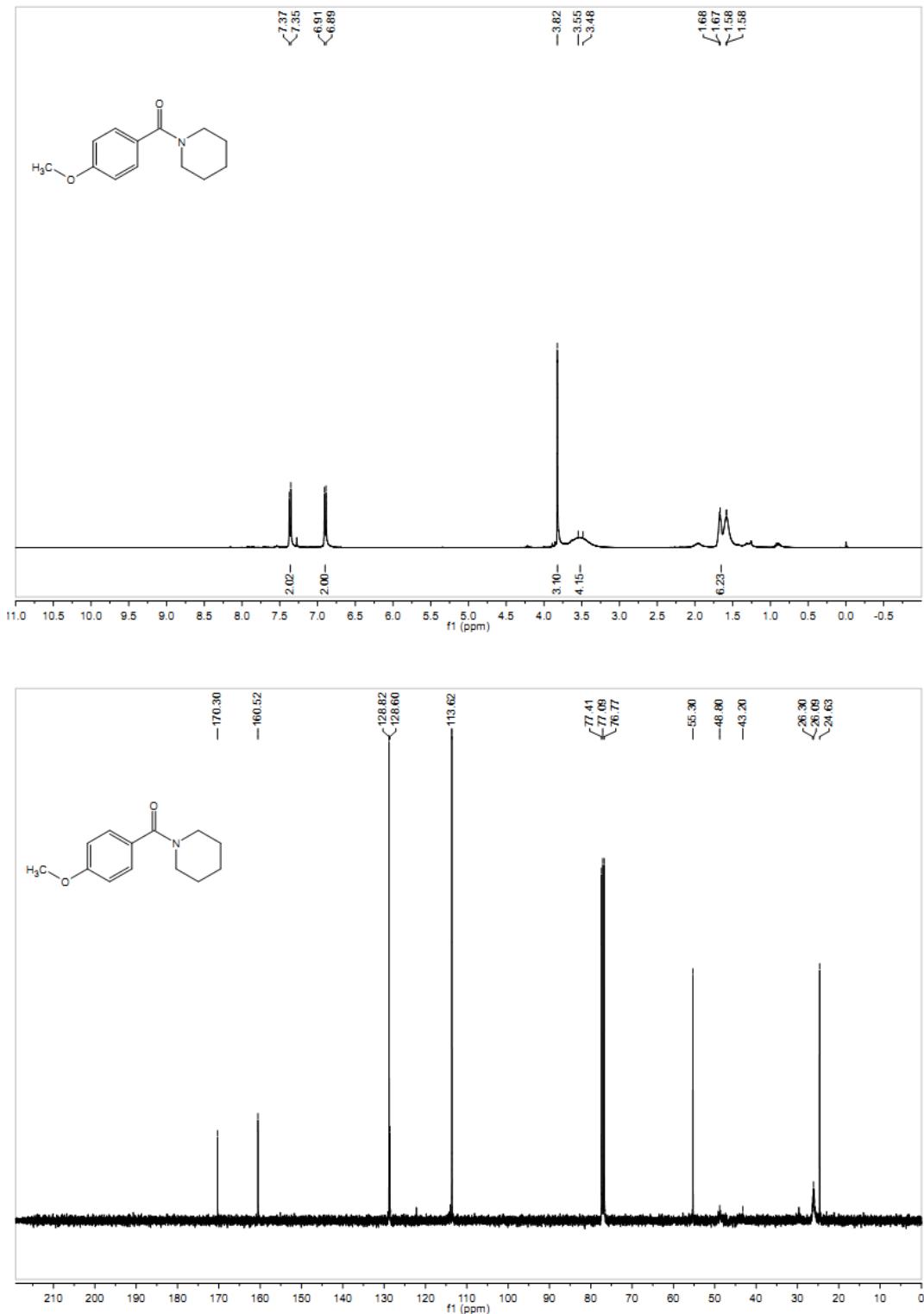
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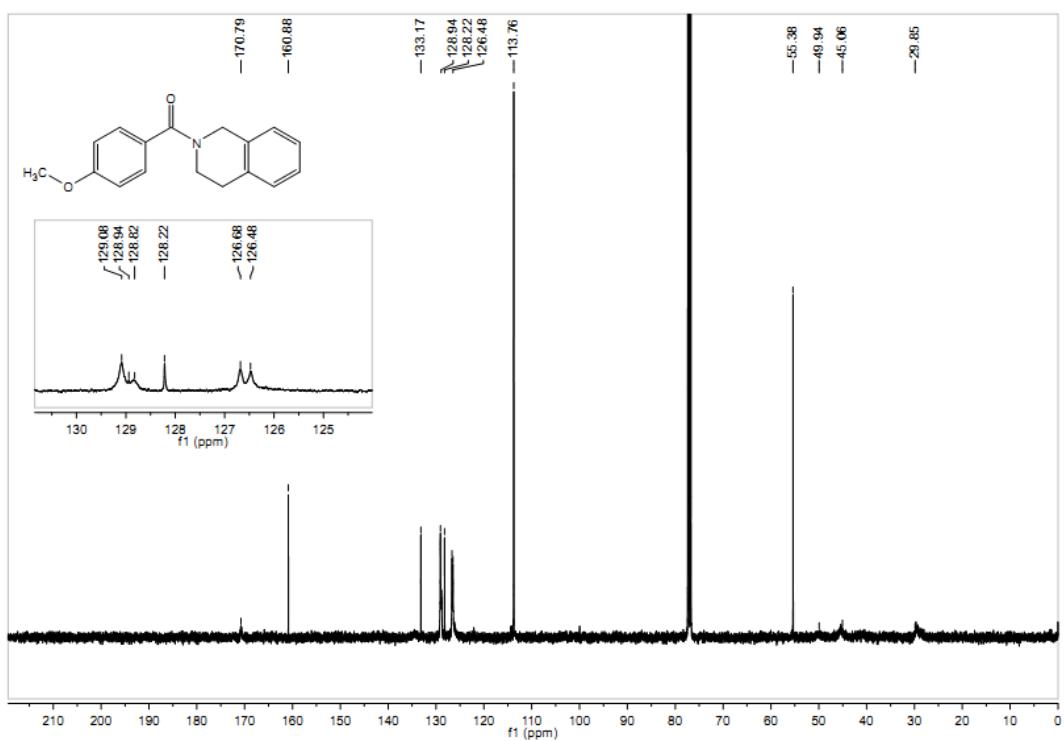
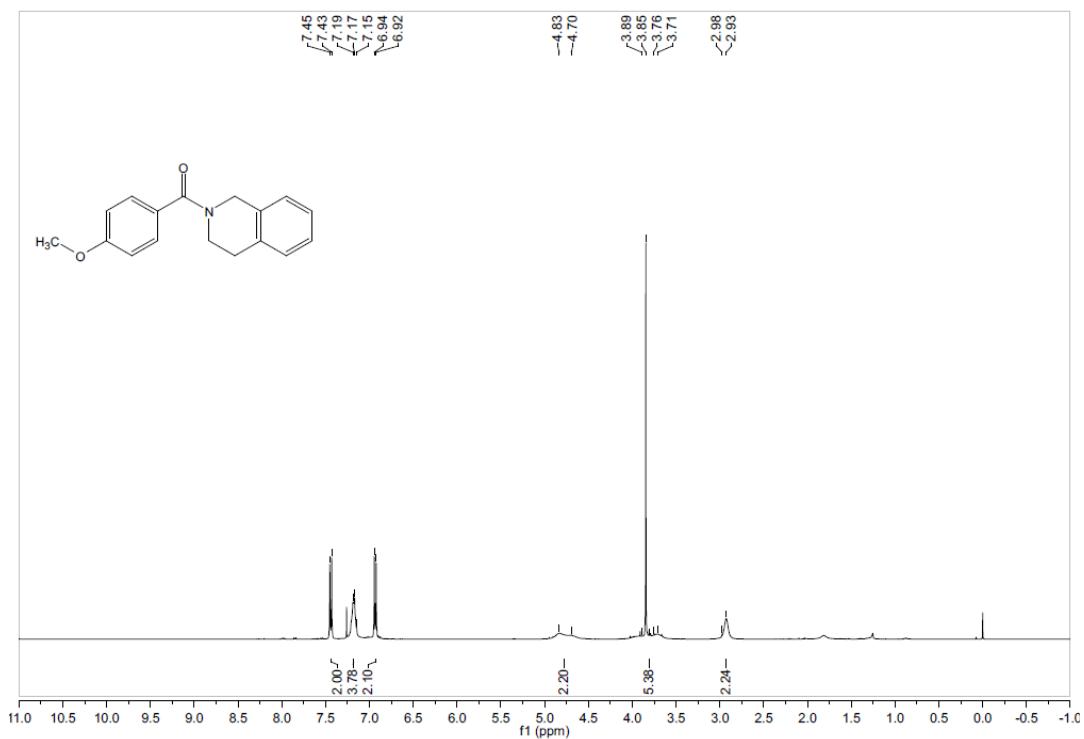
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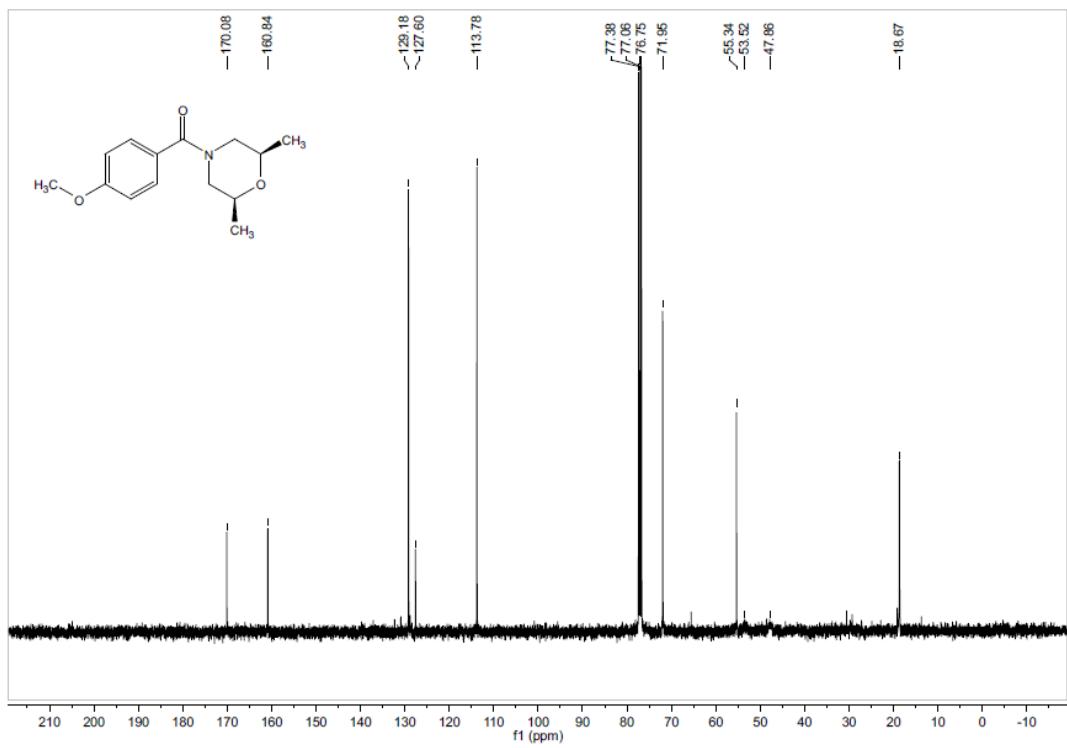
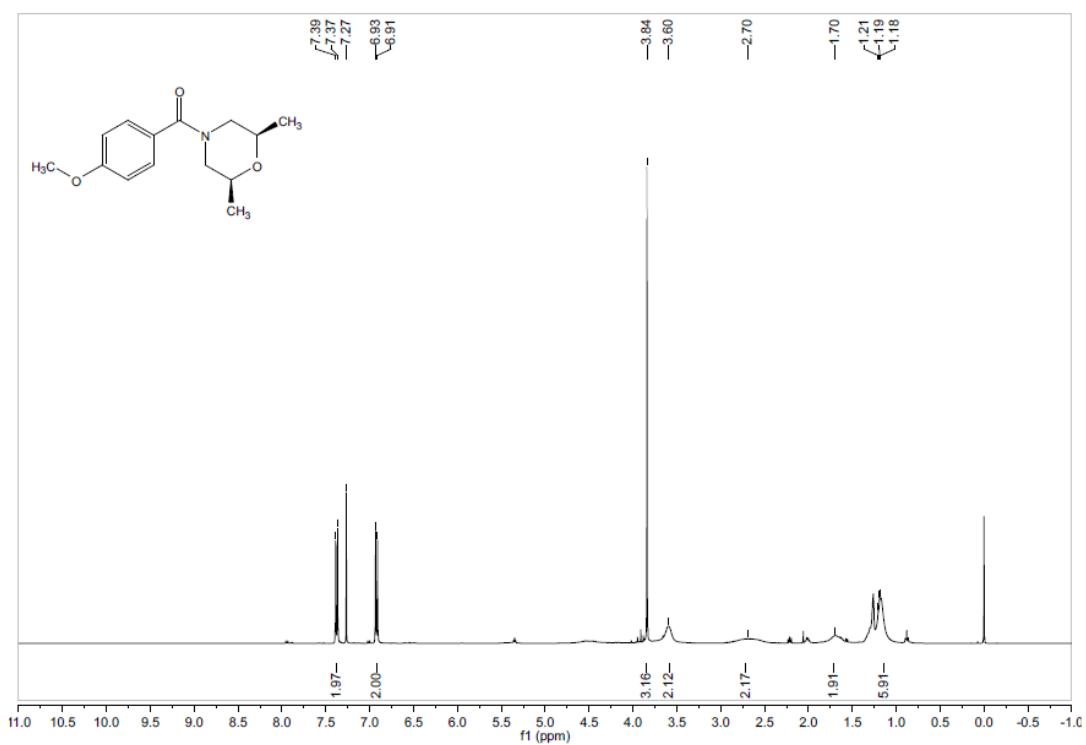
¹H NMR and ¹³C NMR for compound 4i



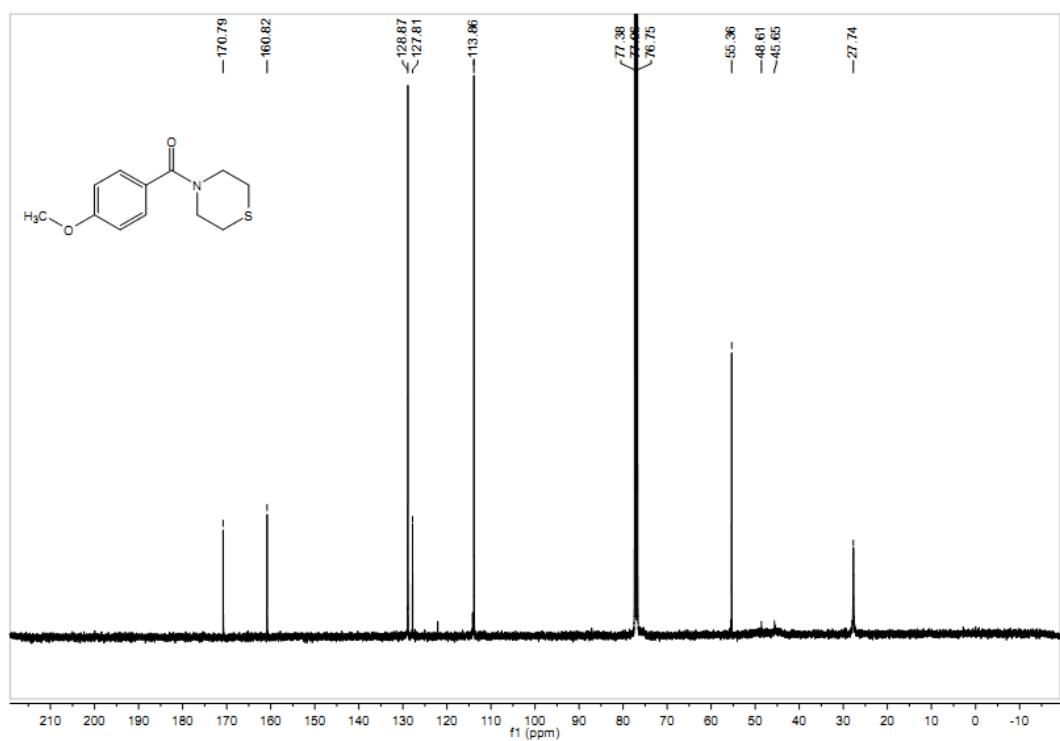
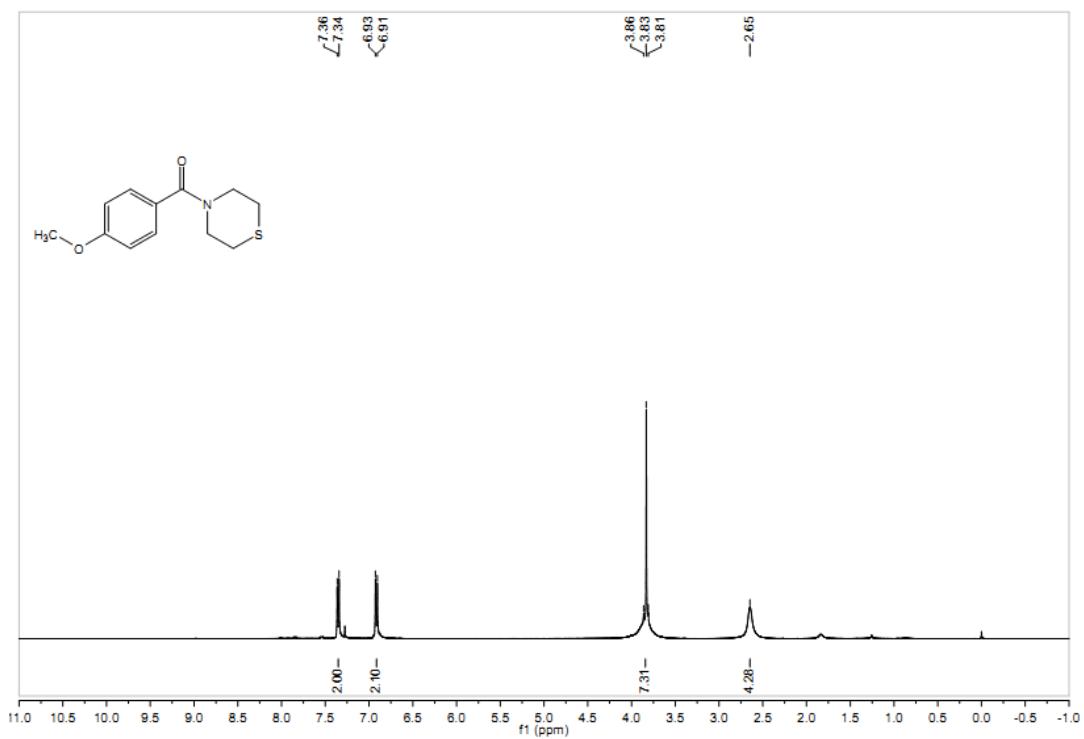
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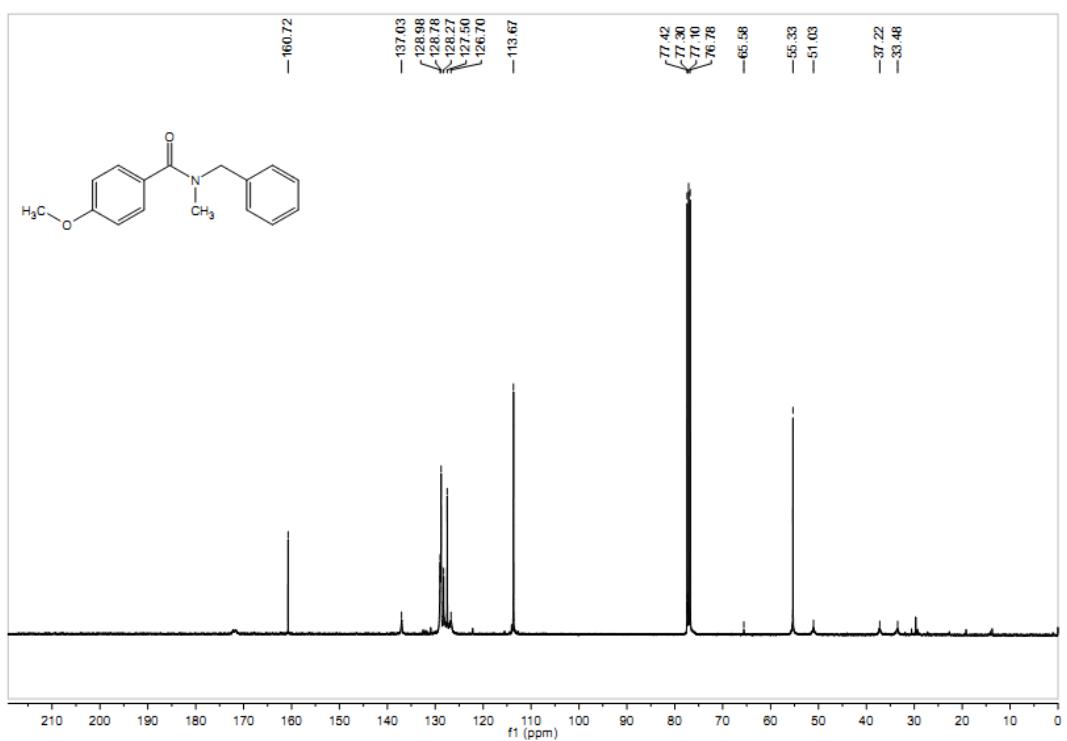
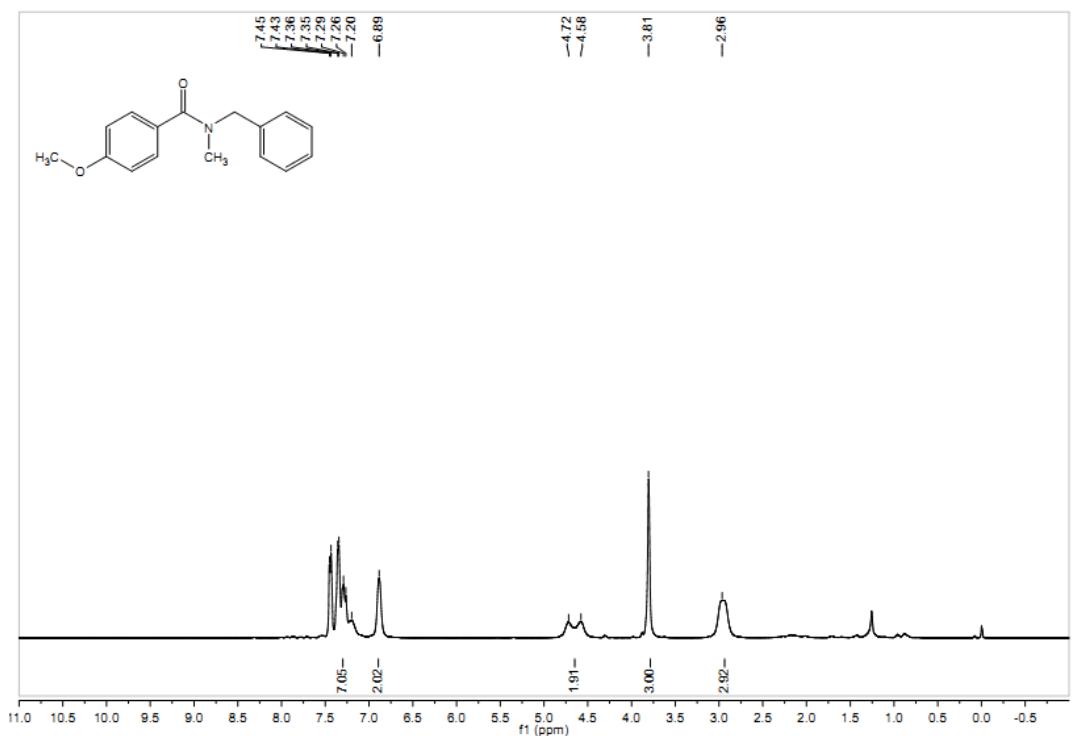
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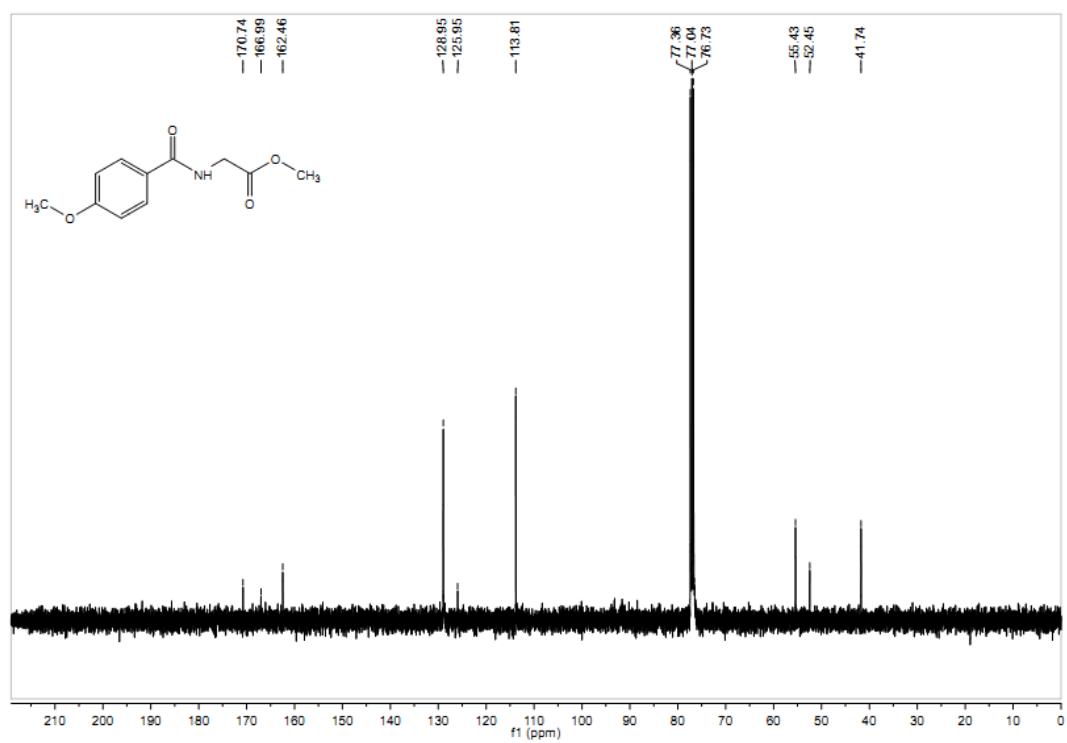
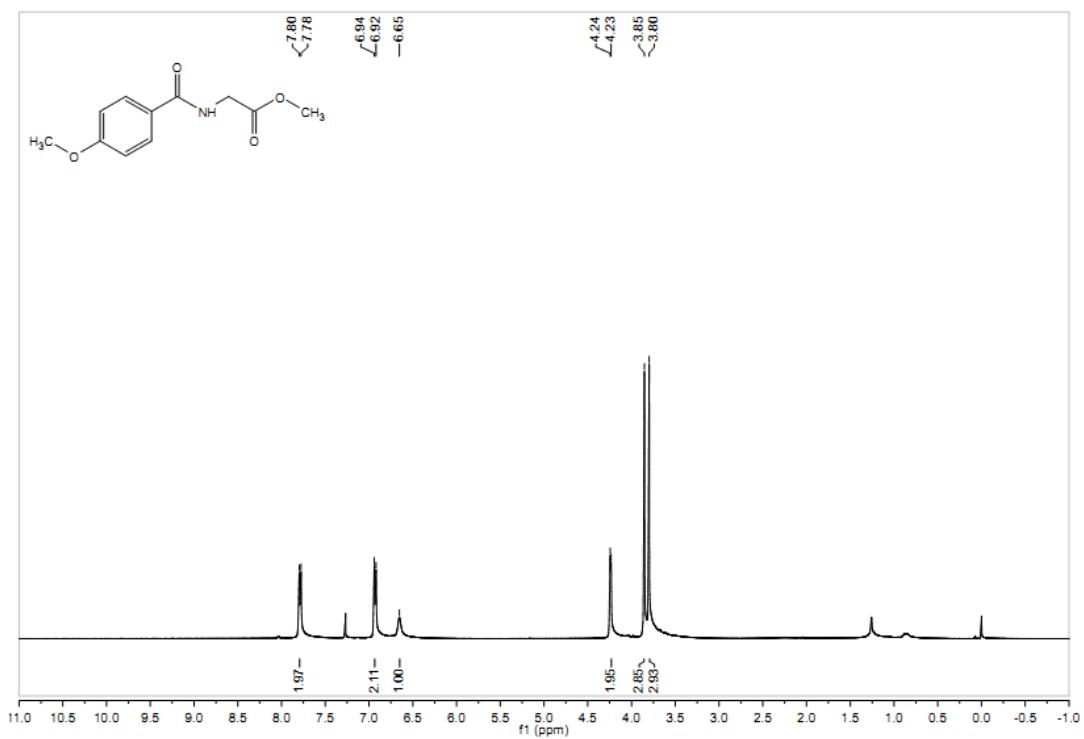
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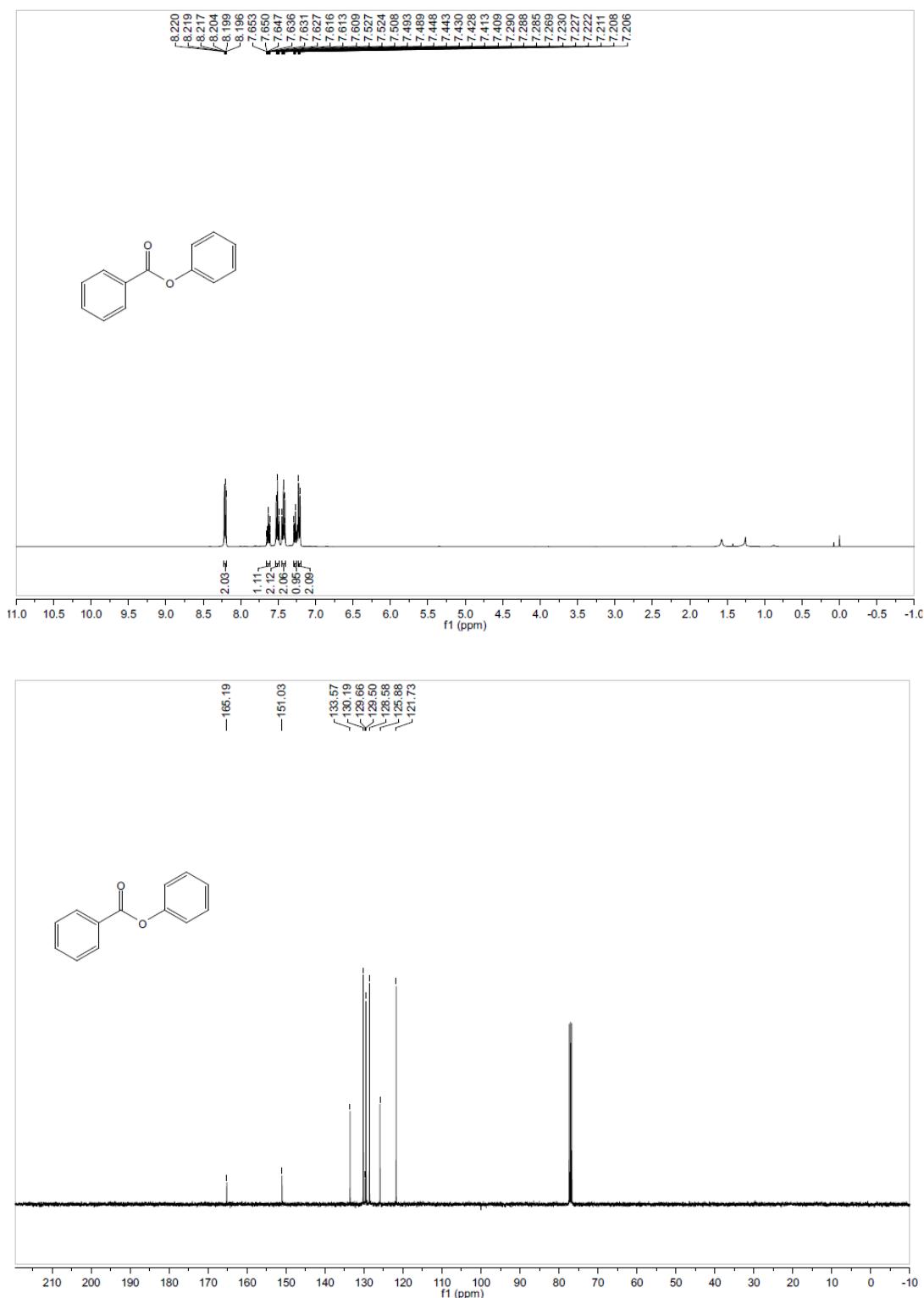
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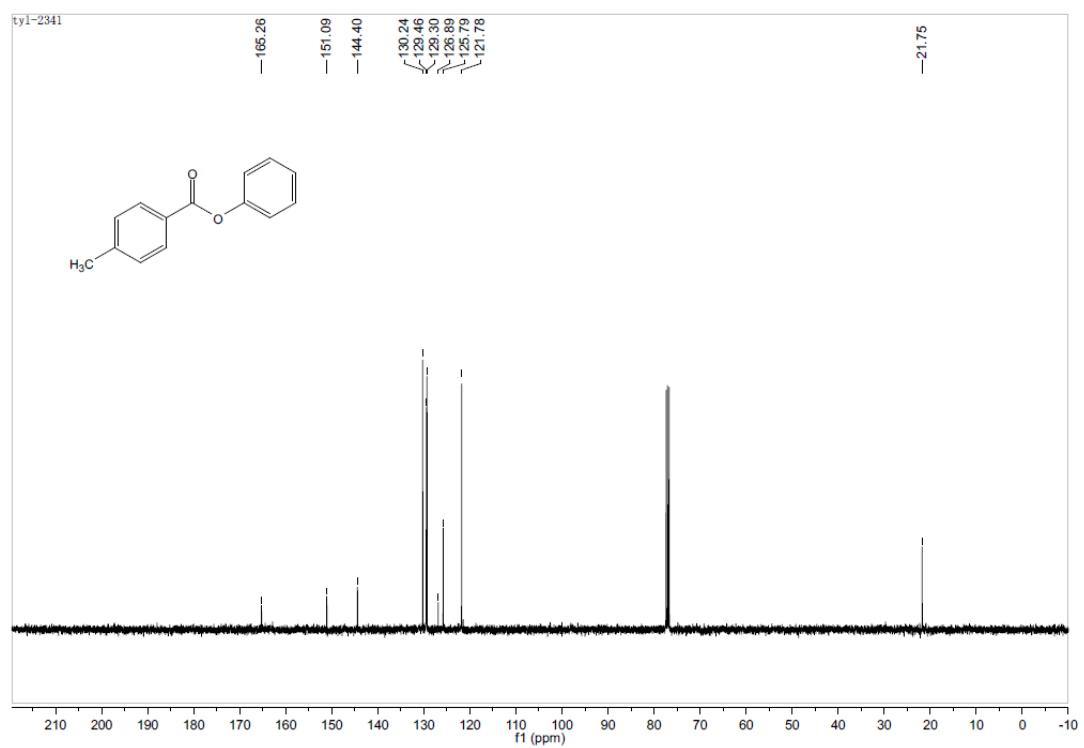
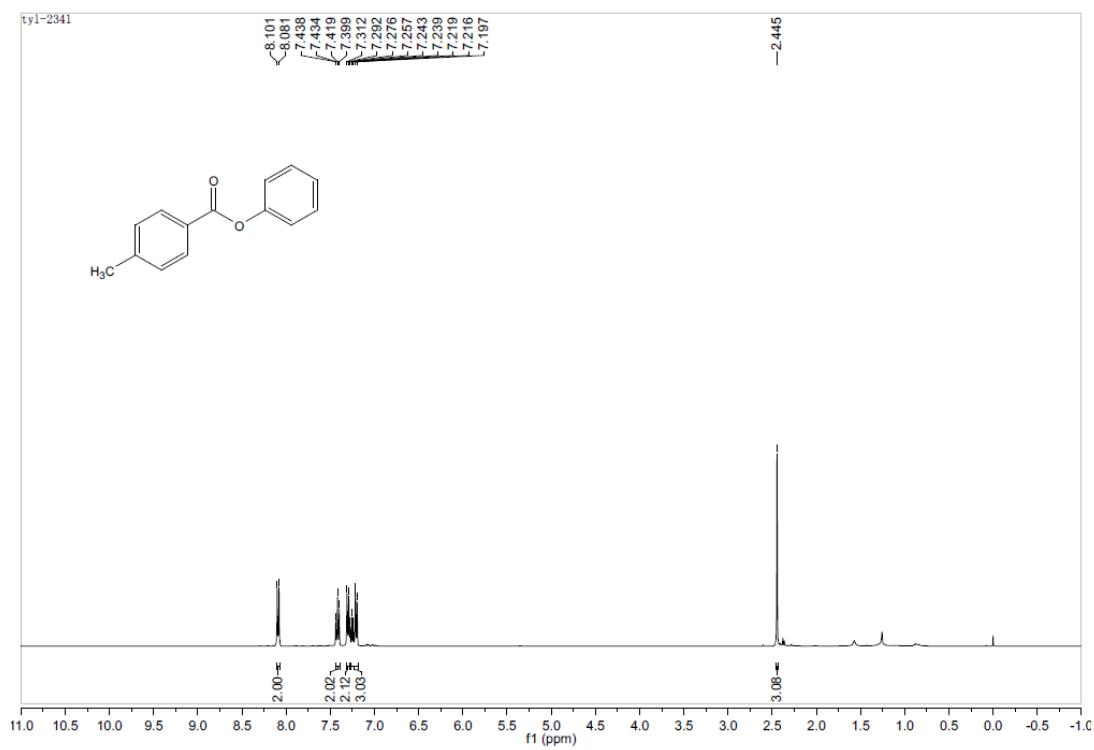
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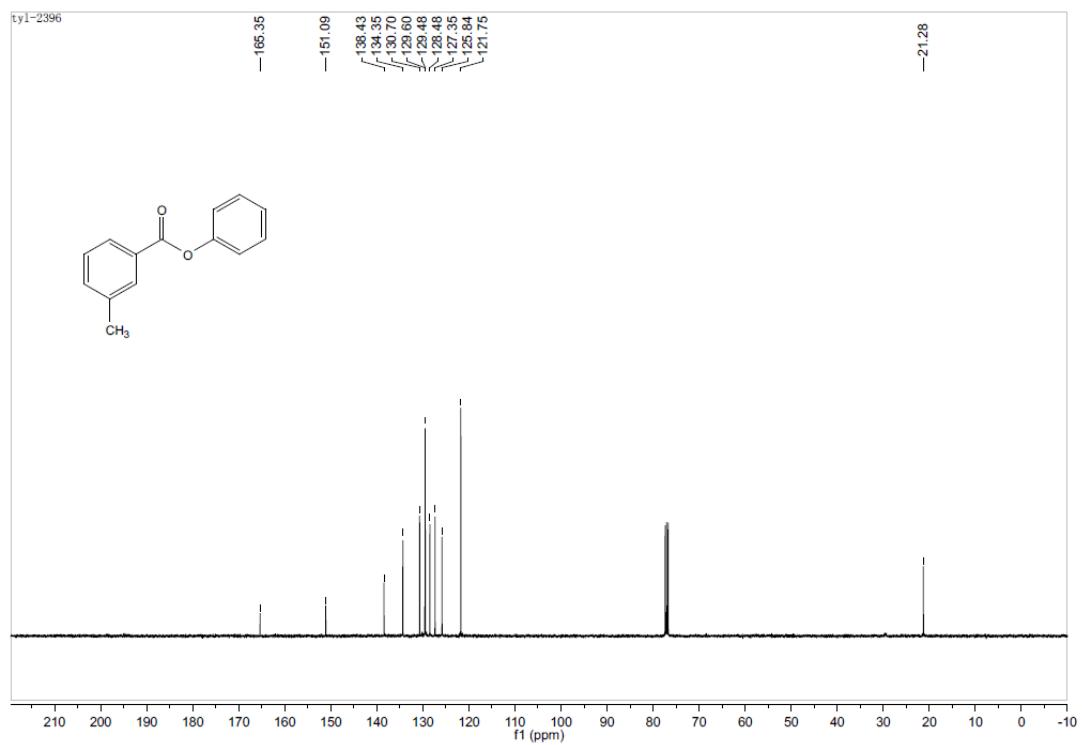
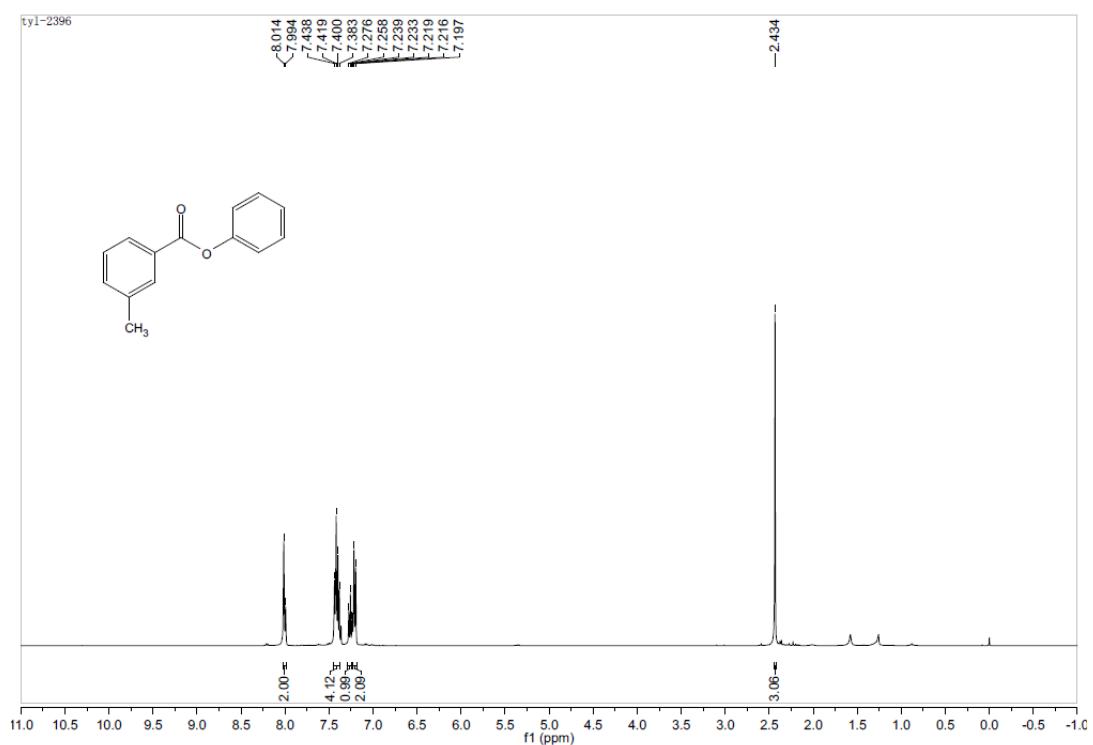
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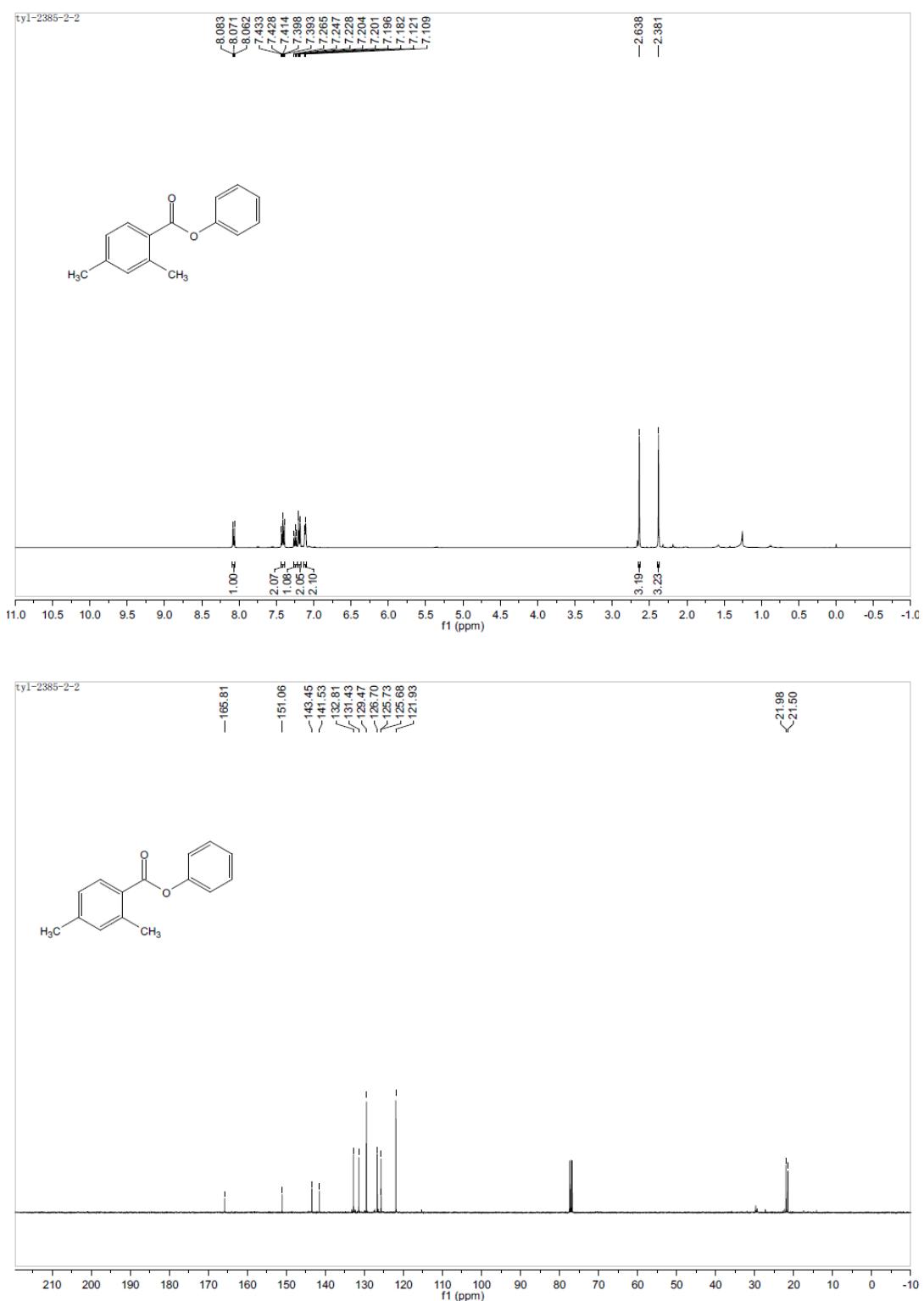
^1H NMR and ^{13}C NMR for compound 6a



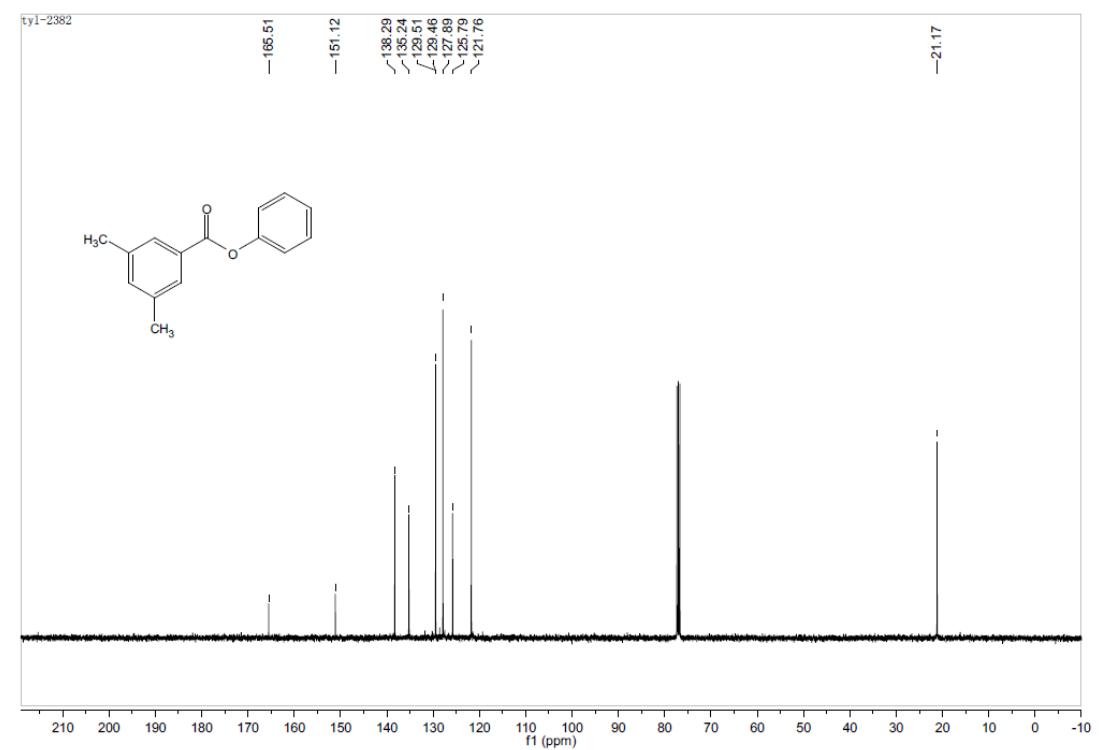
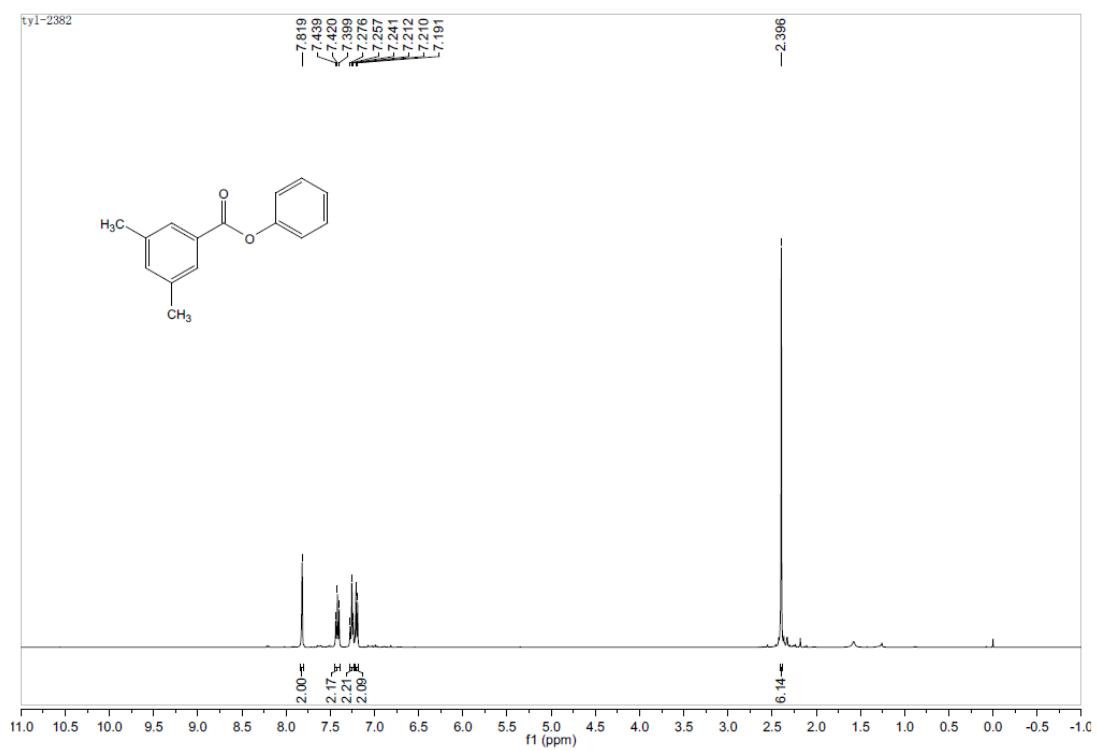
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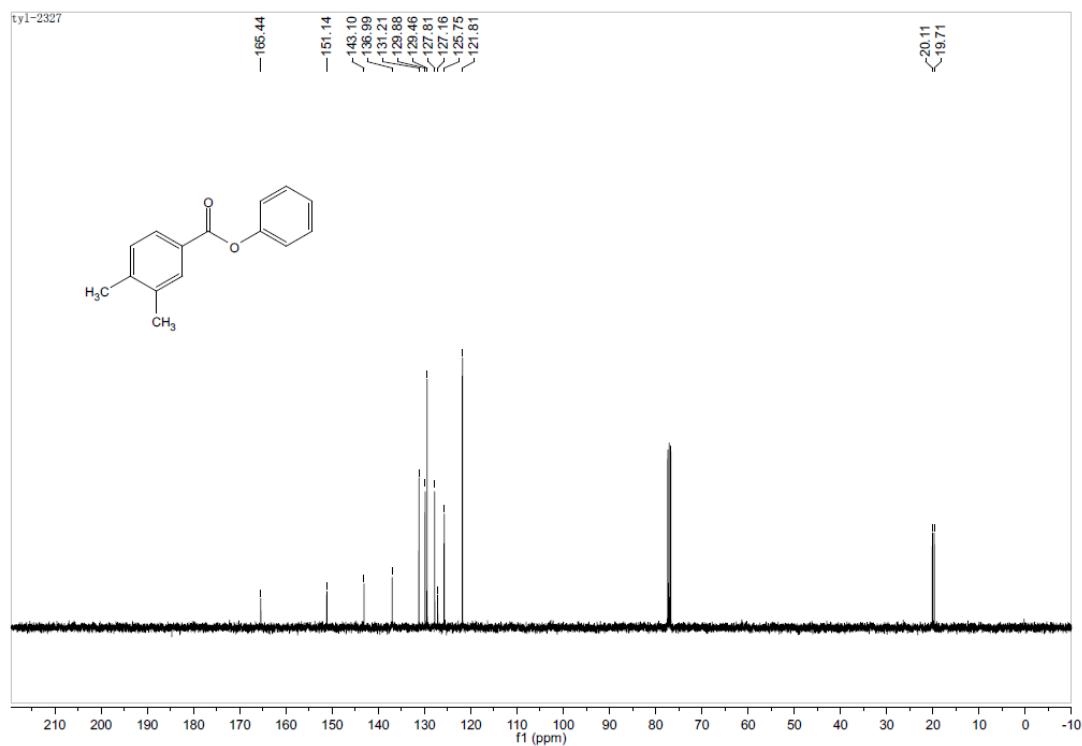
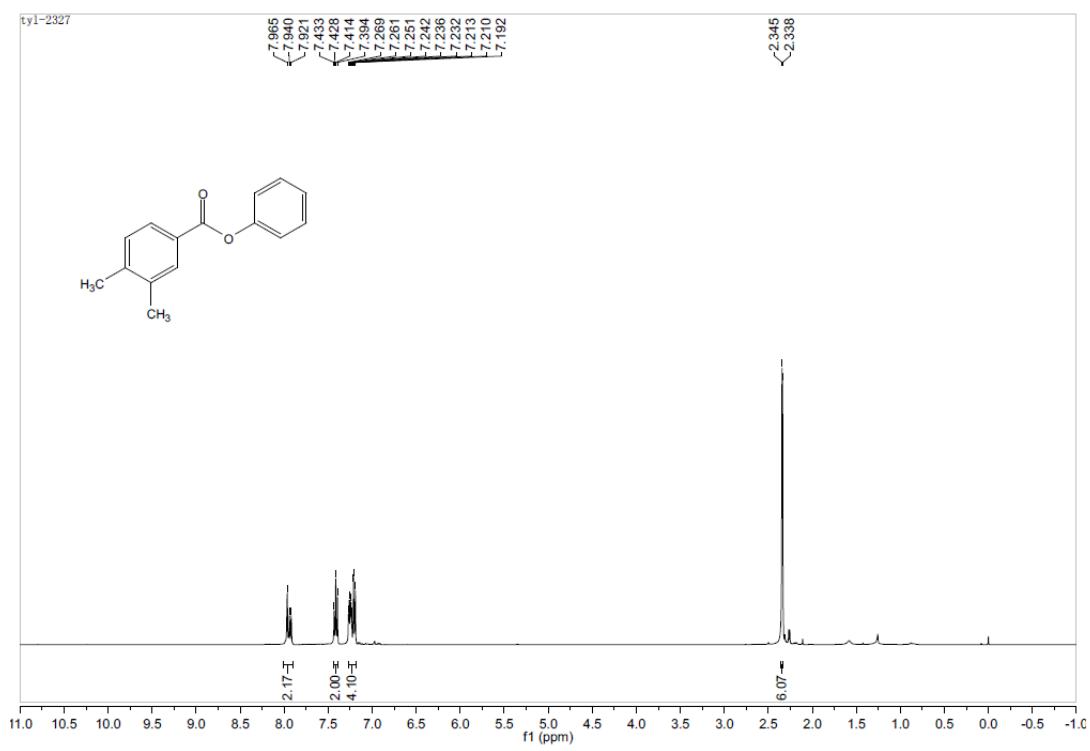
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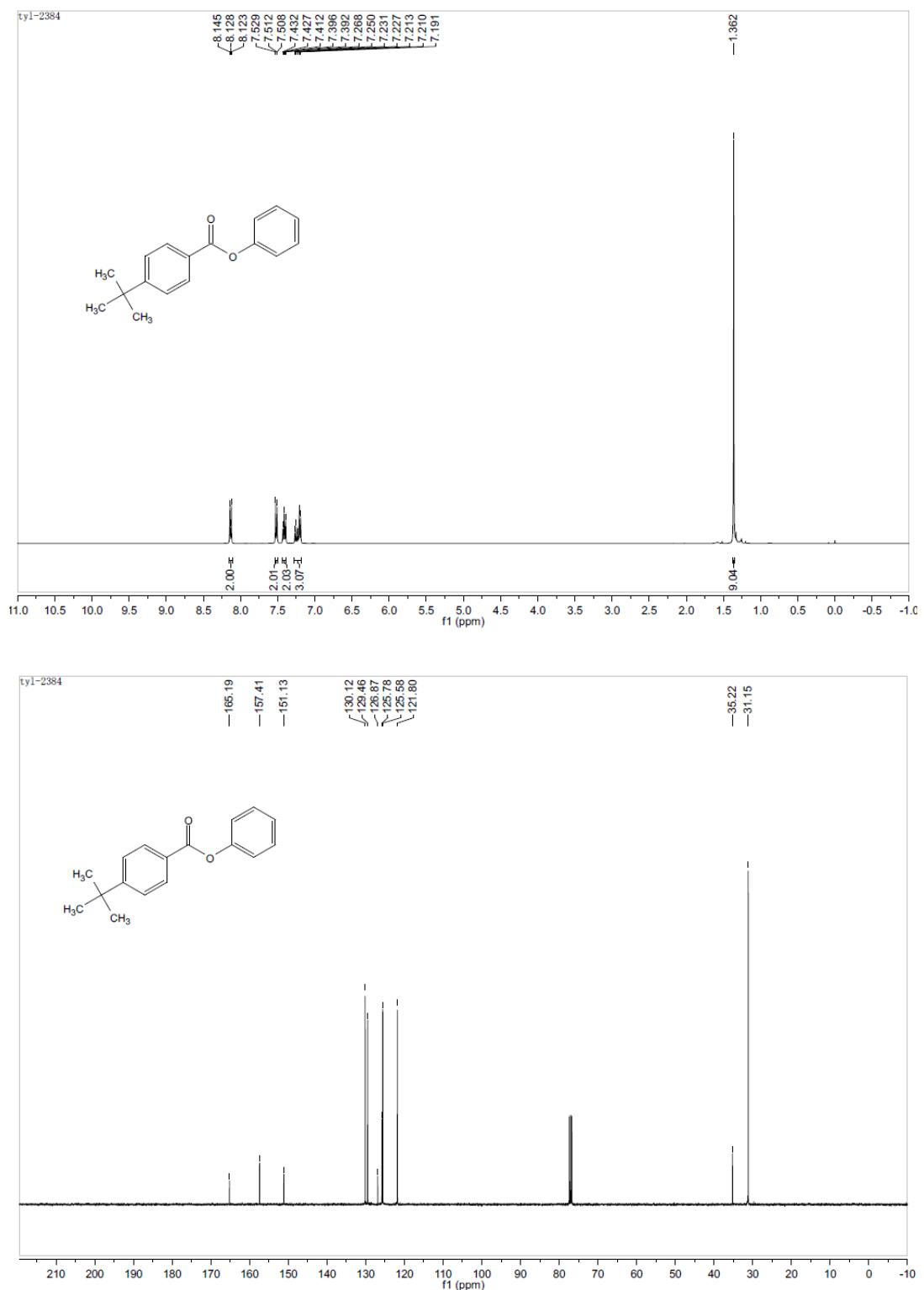
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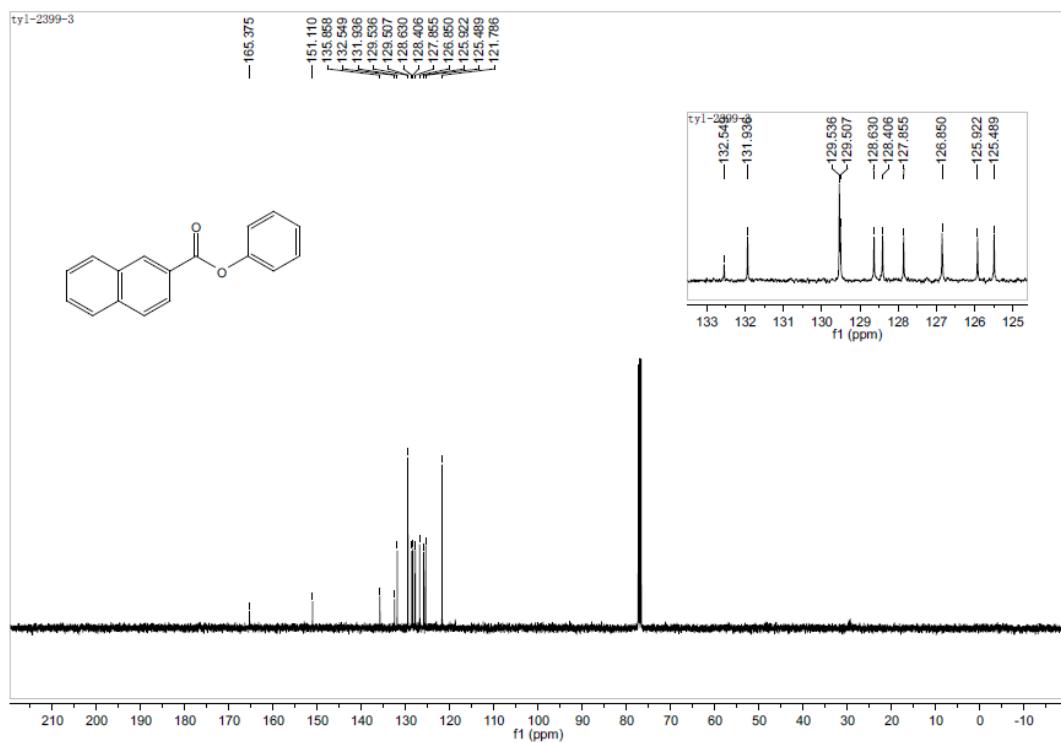
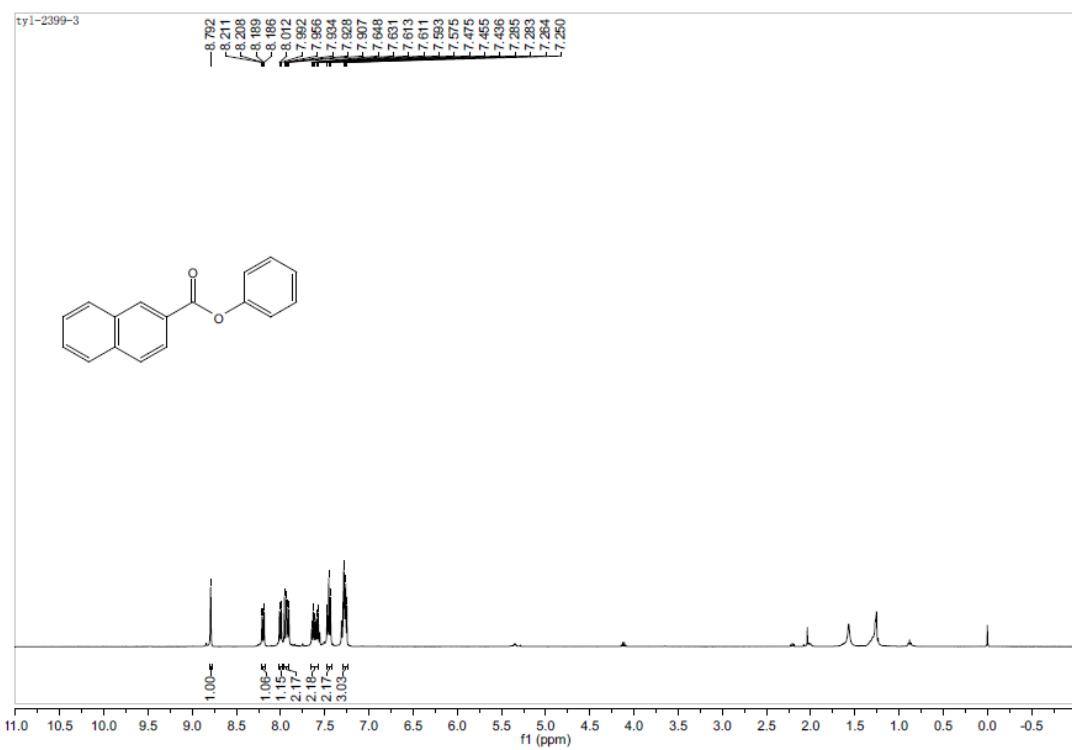
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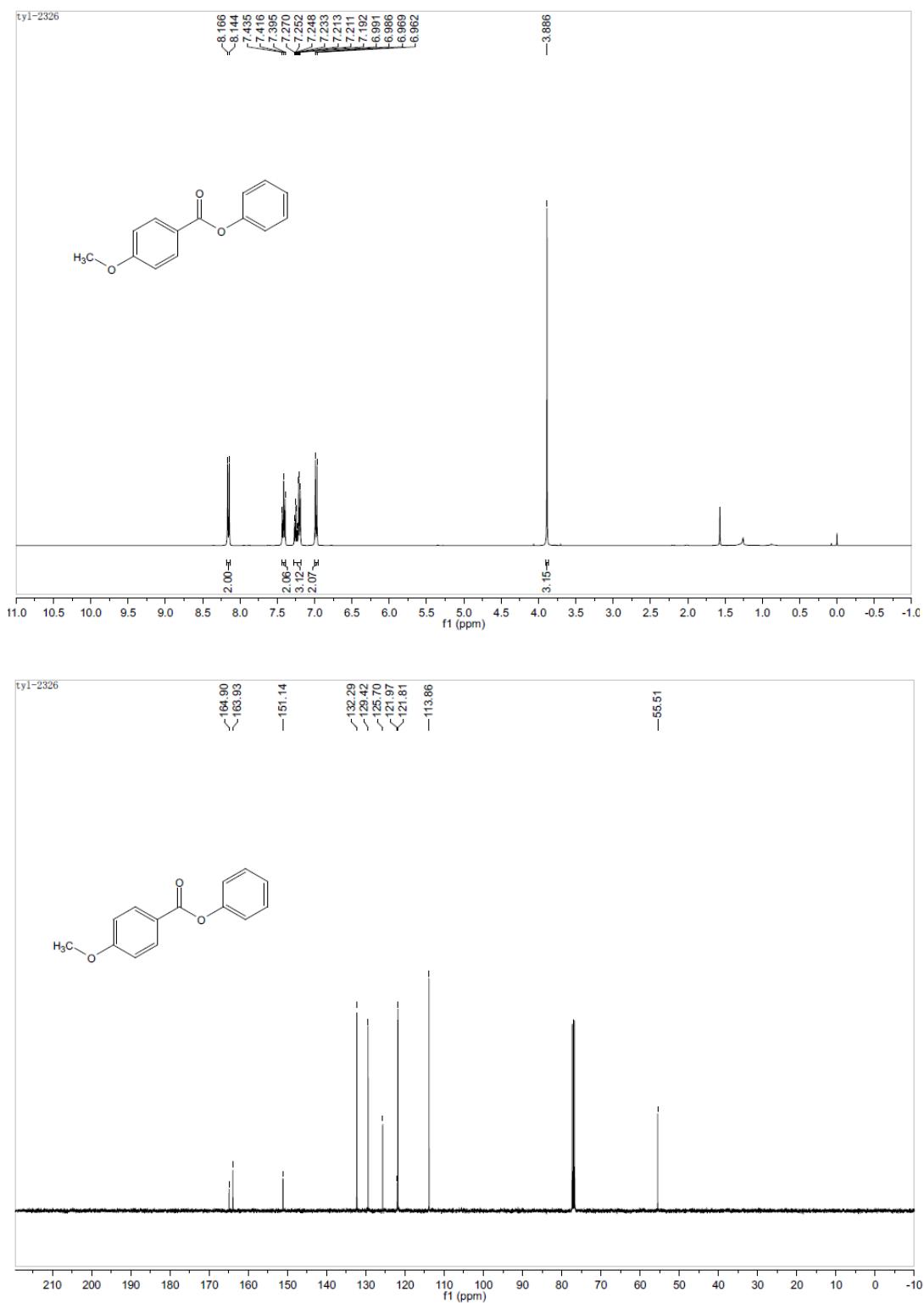
¹H NMR and ¹³C NMR for compound 6f



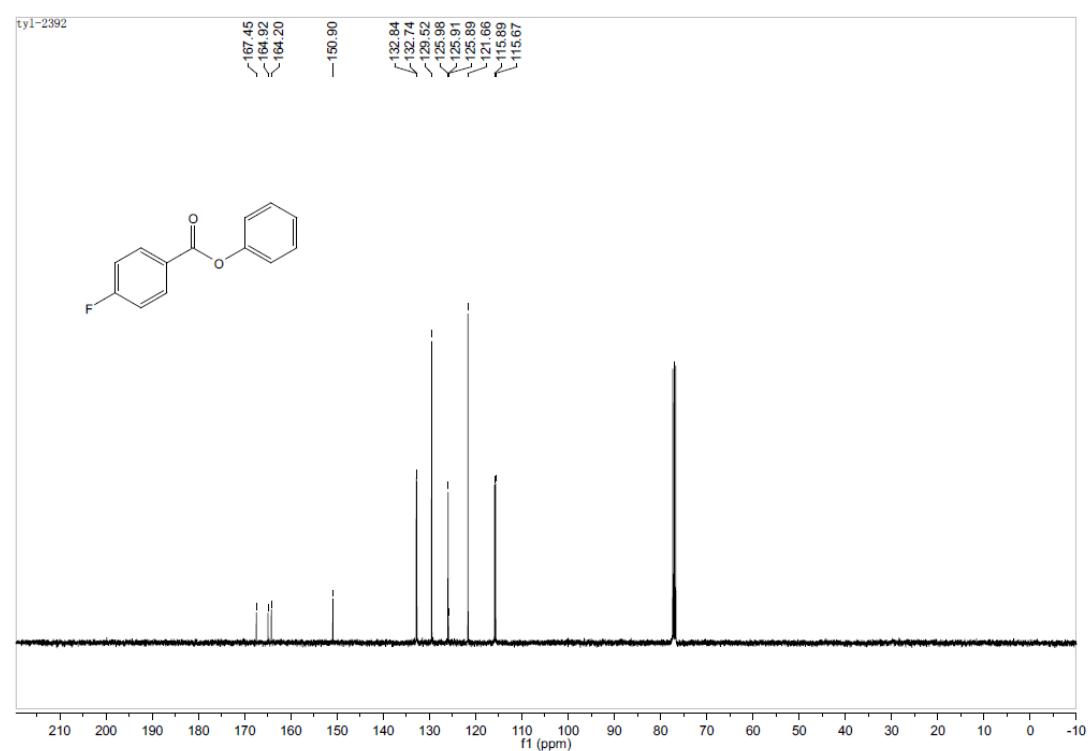
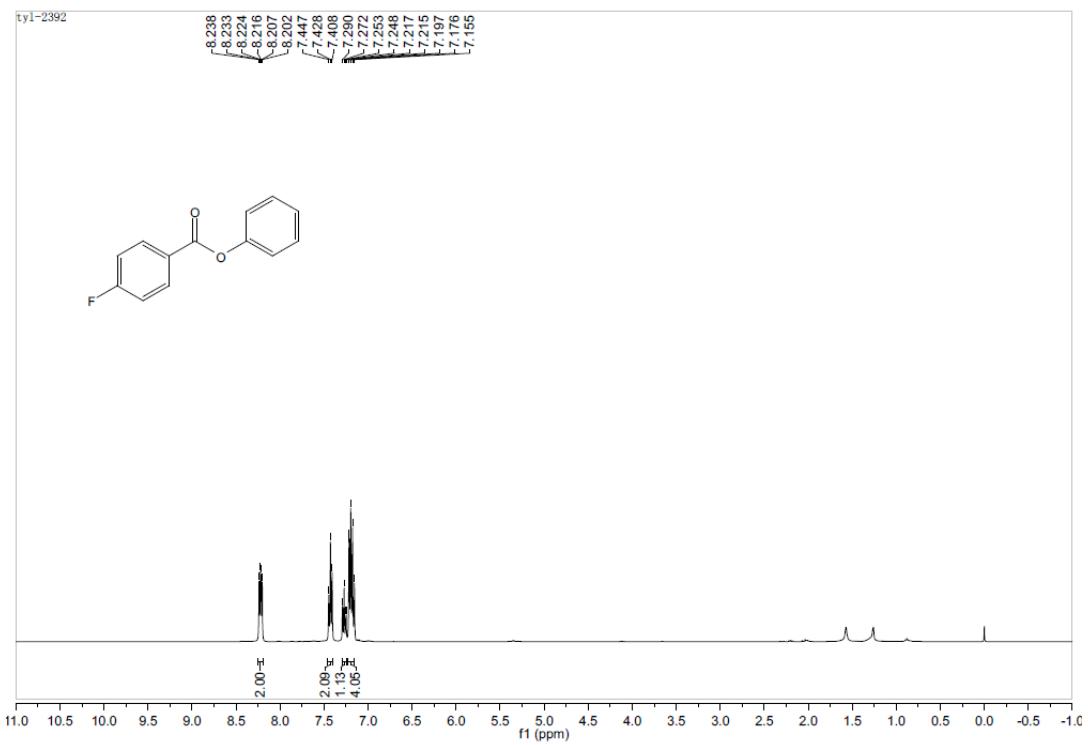
^1H NMR and ^{13}C NMR for compound 6g



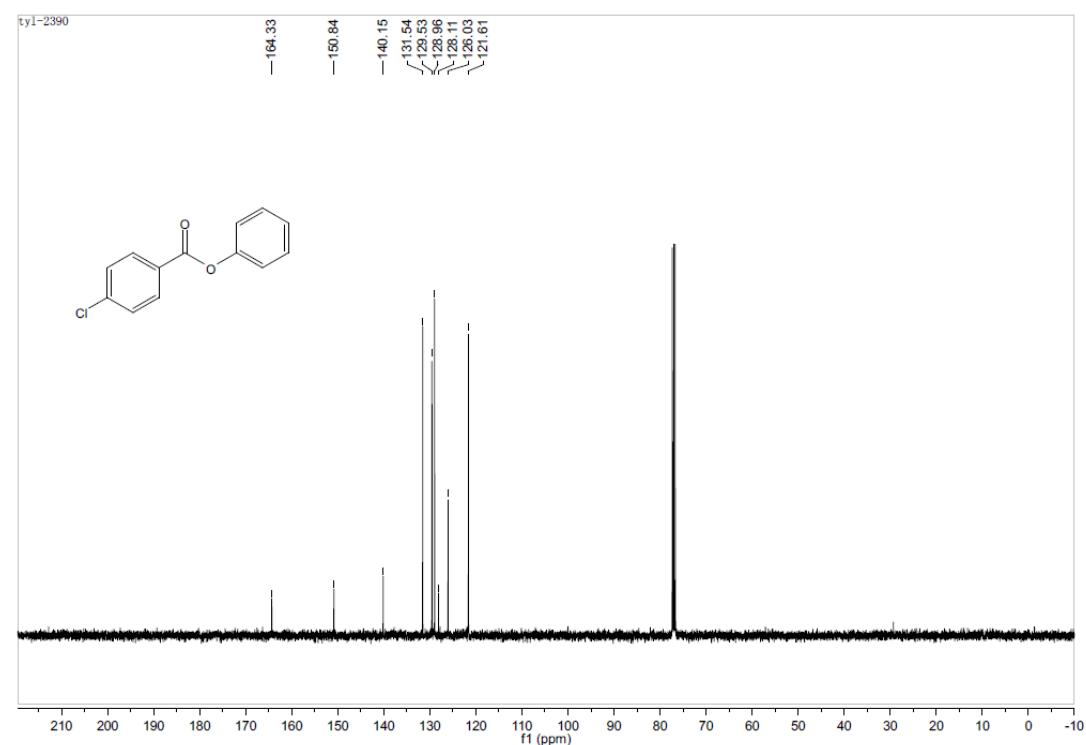
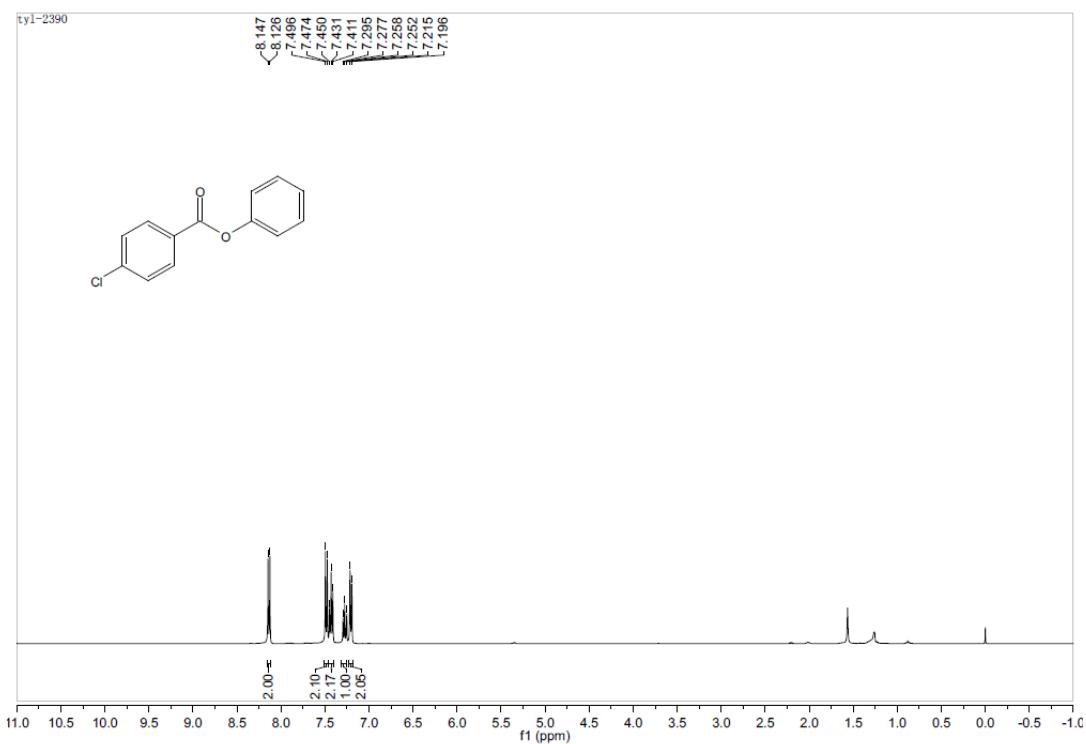
^1H NMR and ^{13}C NMR for compound 6h



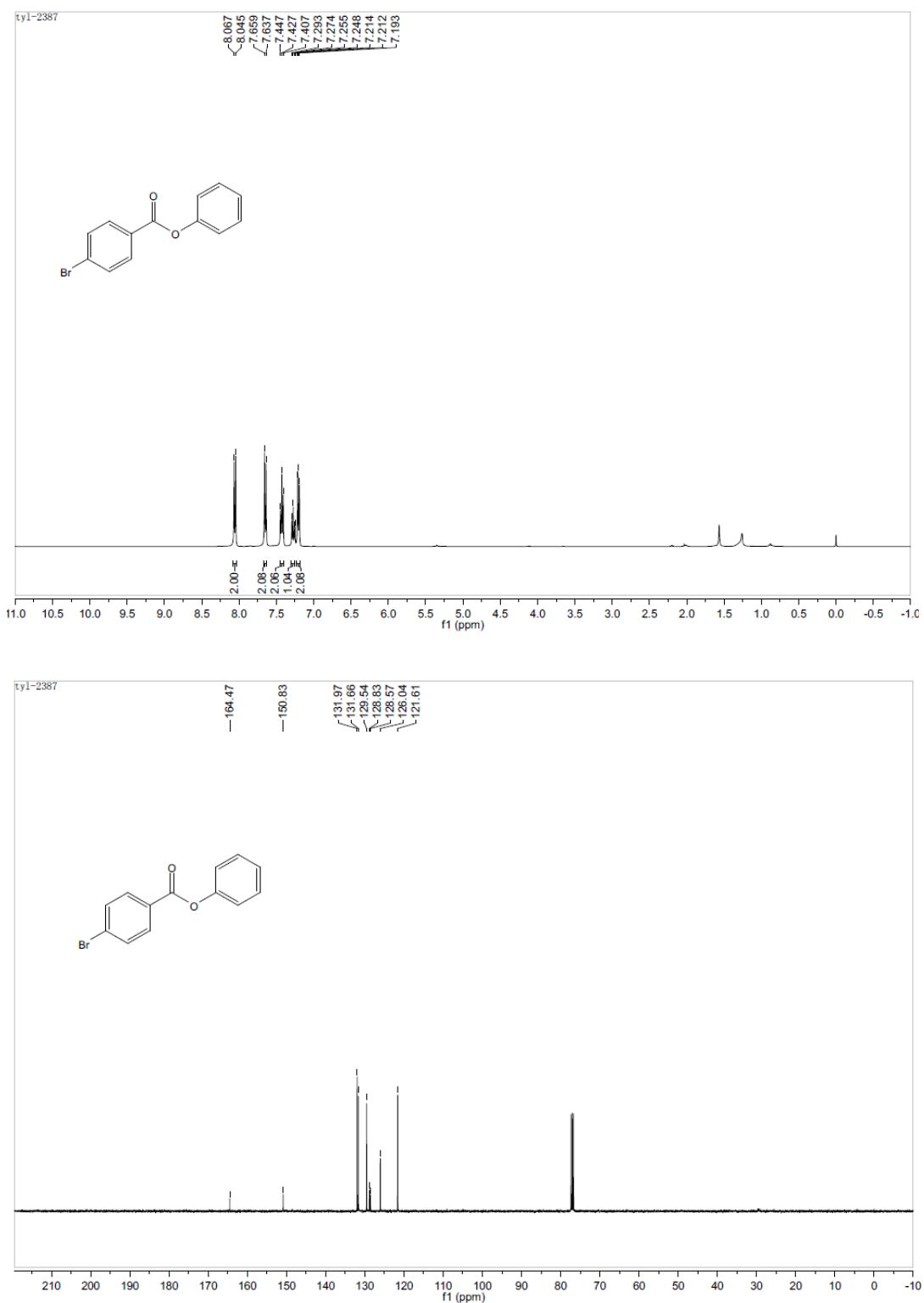
^1H NMR and ^{13}C NMR for compound 6i

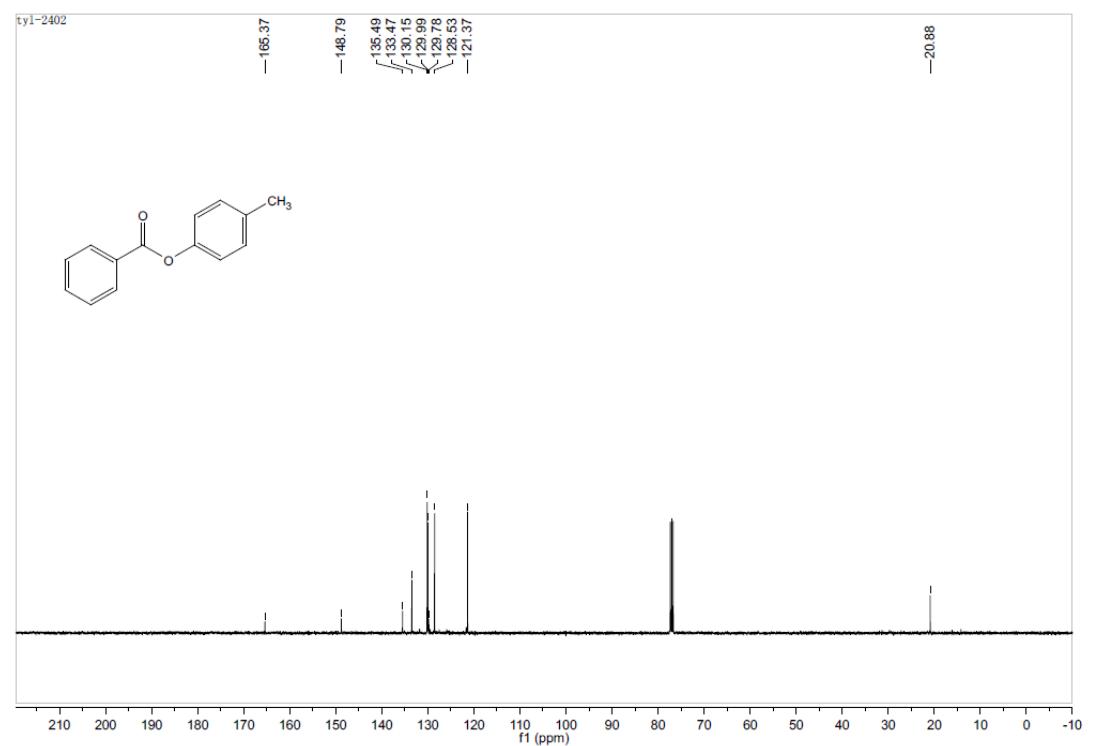
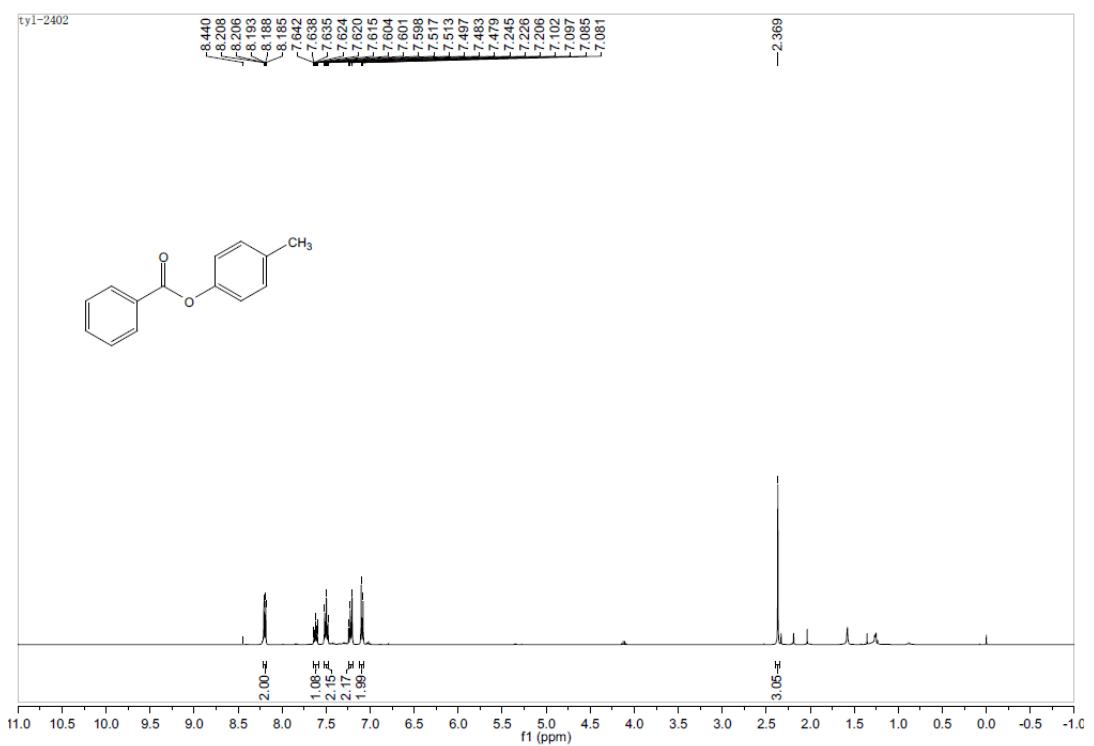


¹H NMR and ¹³C NMR for compound 6j

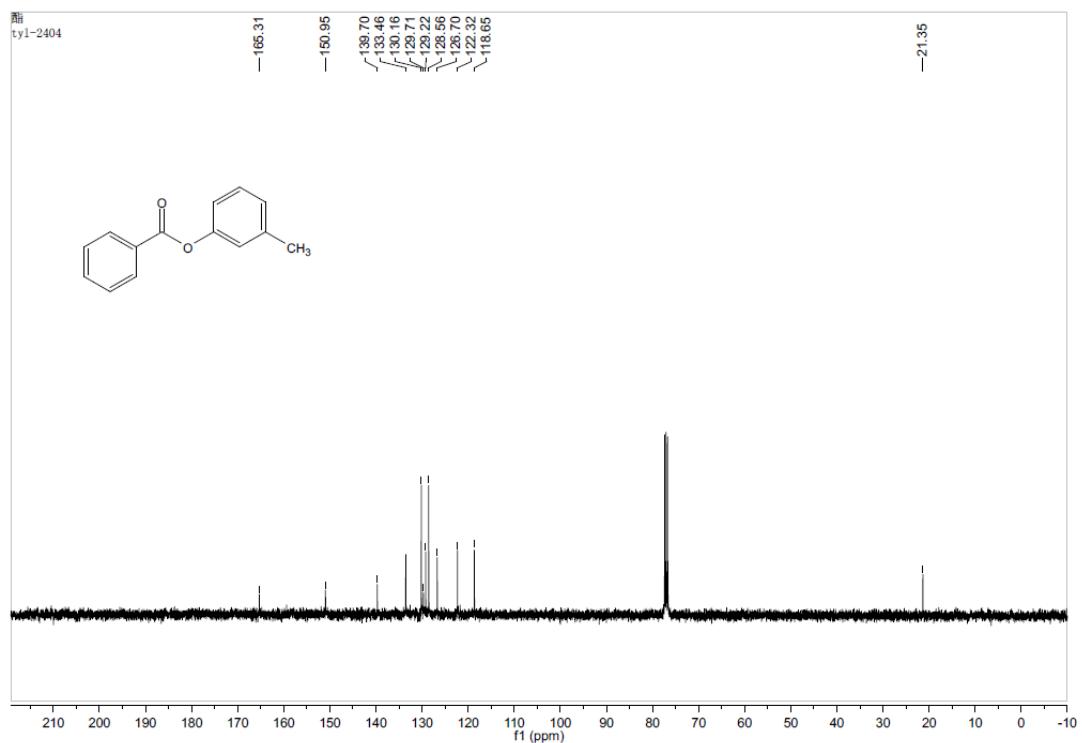
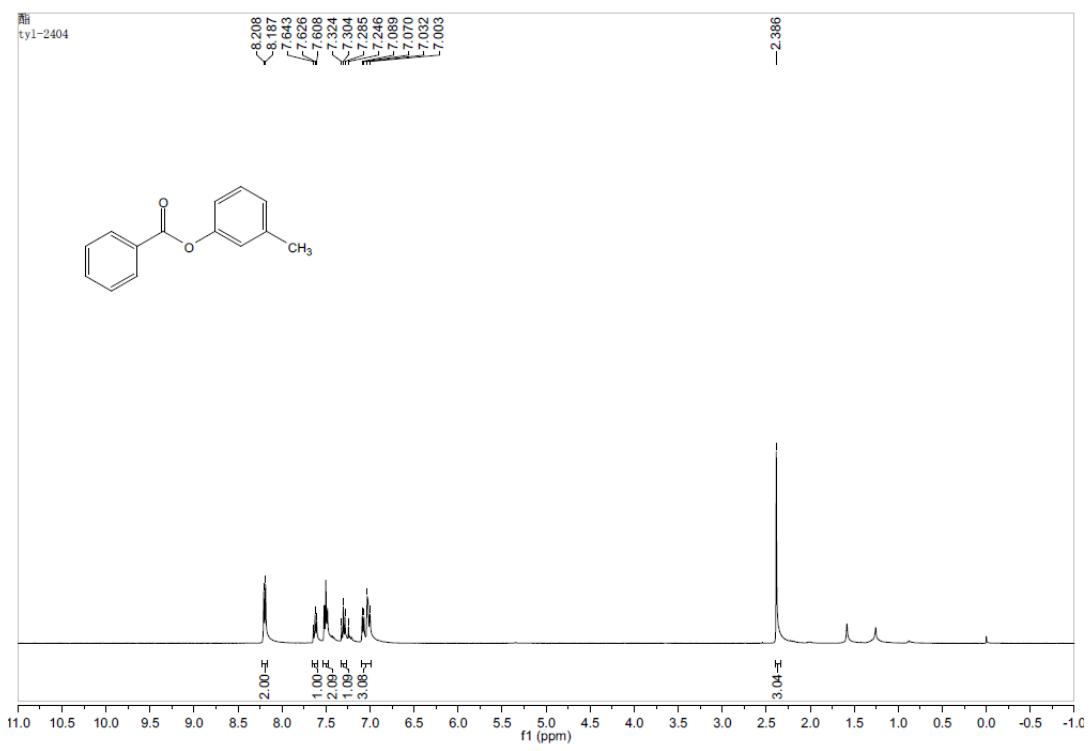


¹H NMR and ¹³C NMR for compound 6k

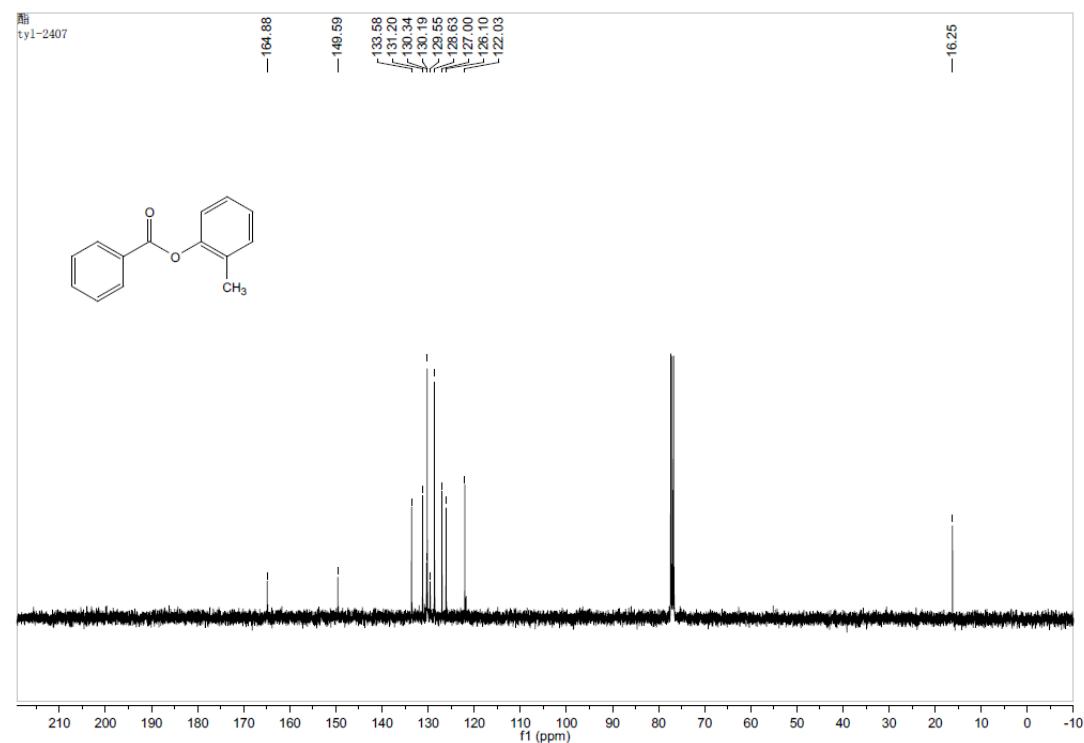
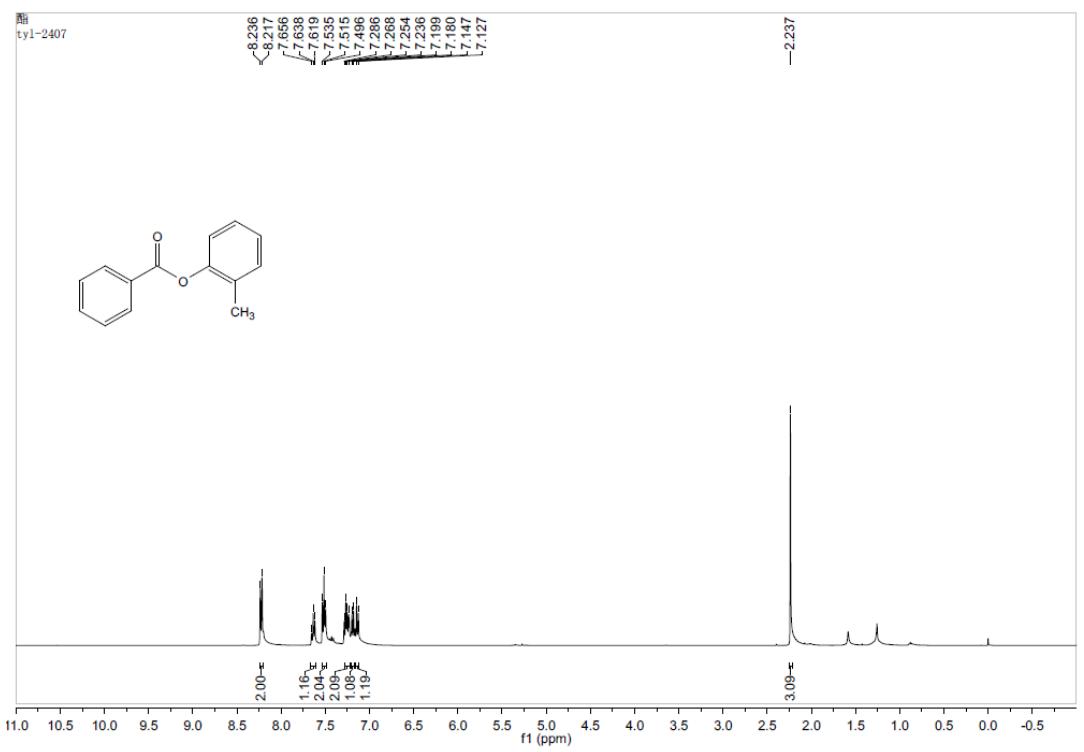




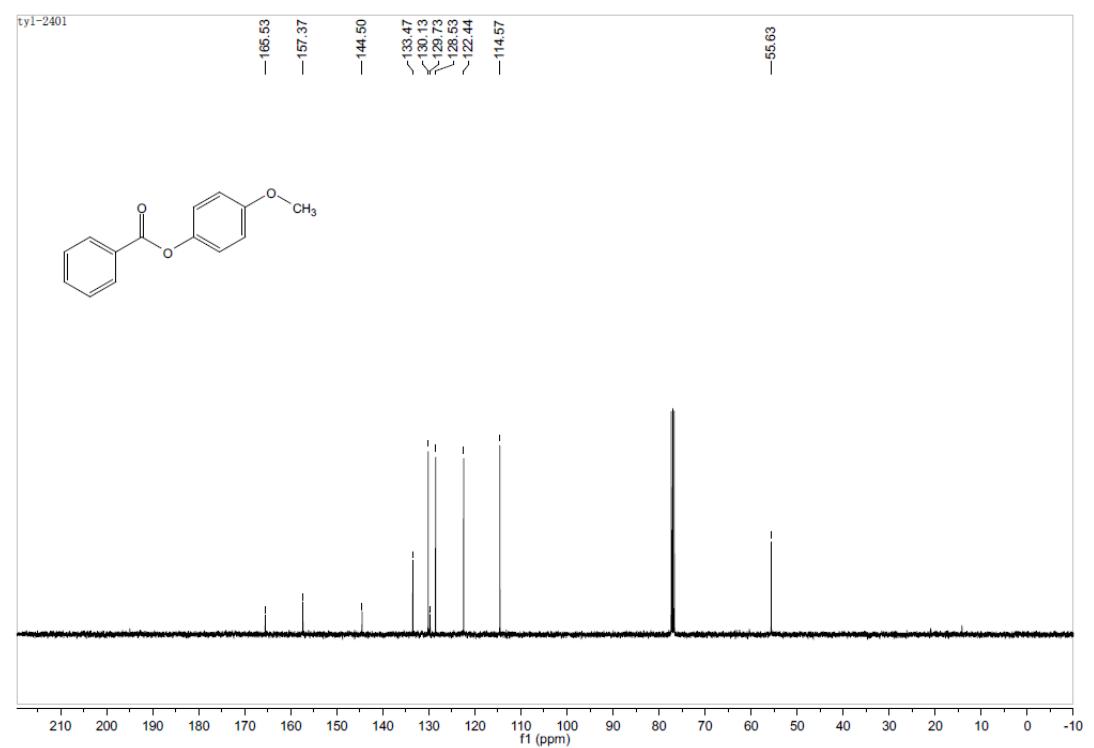
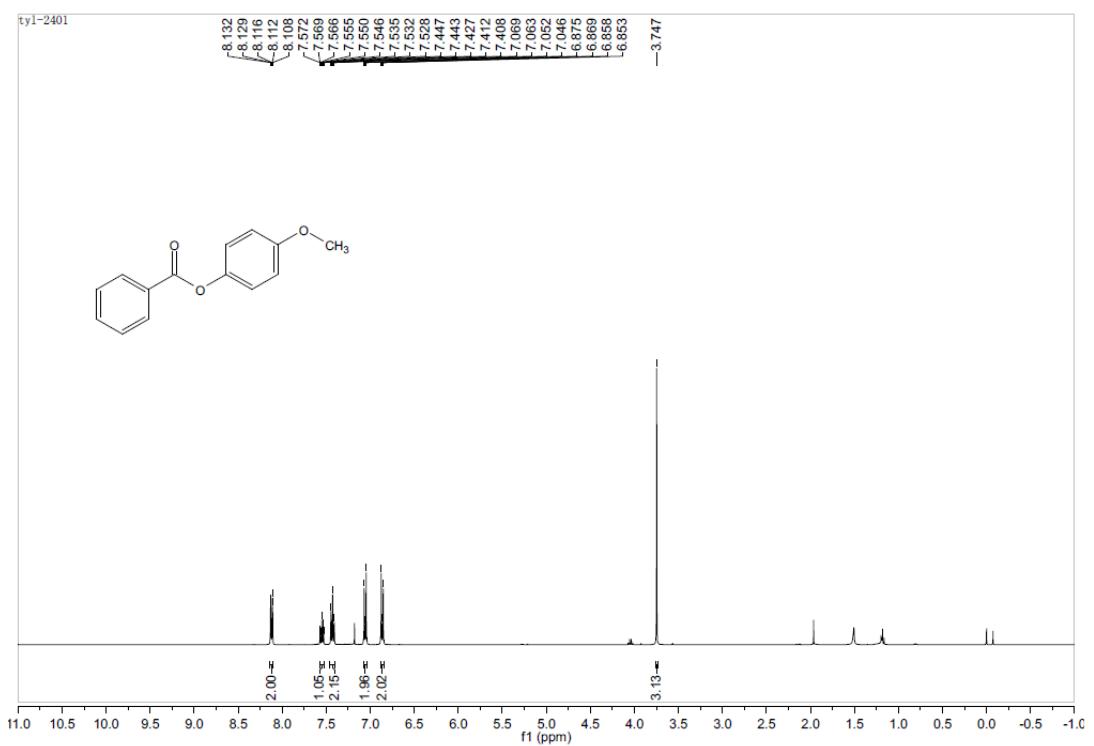
^1H NMR and ^{13}C NMR for compound 6m



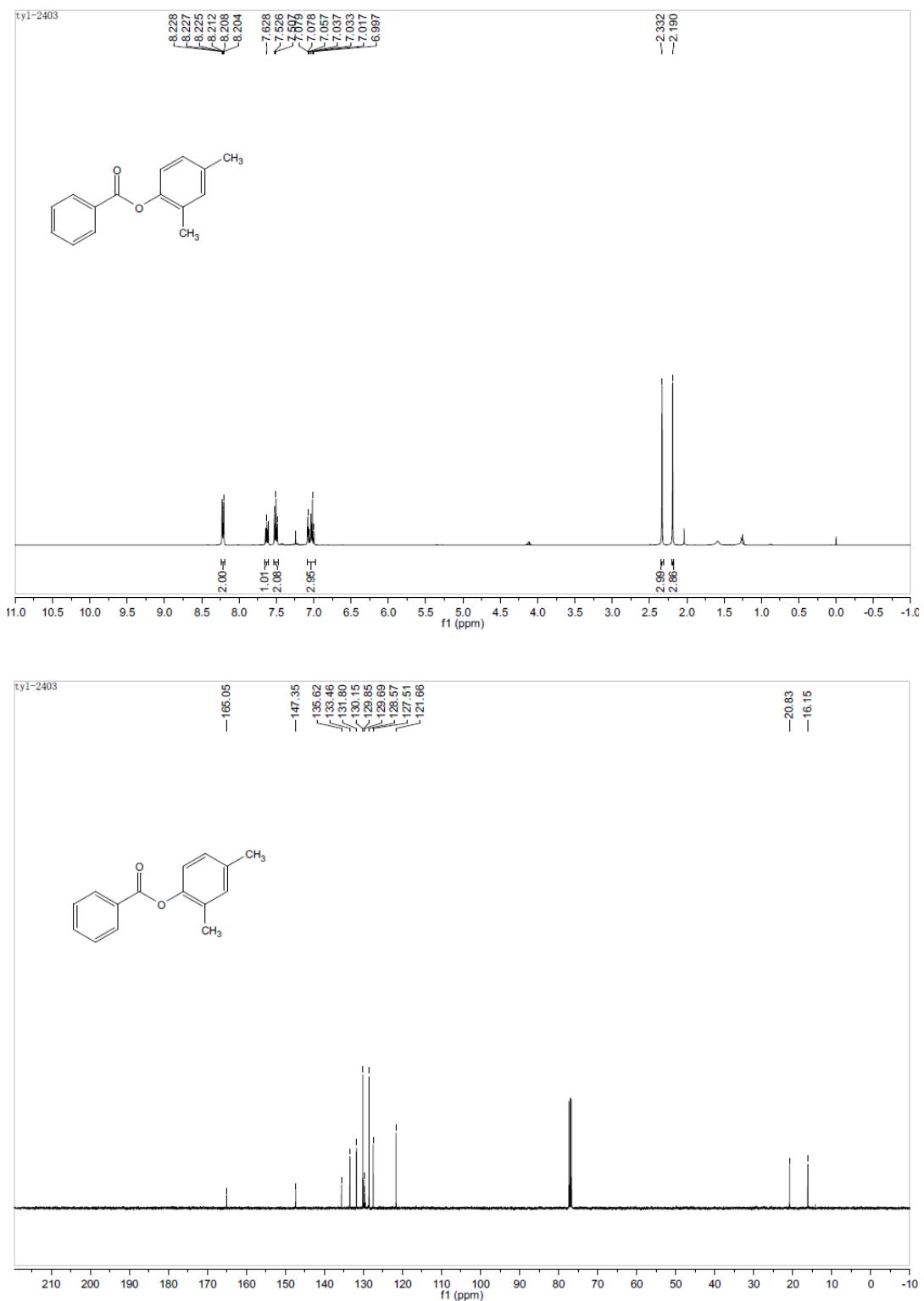
^1H NMR and ^{13}C NMR for compound 6n



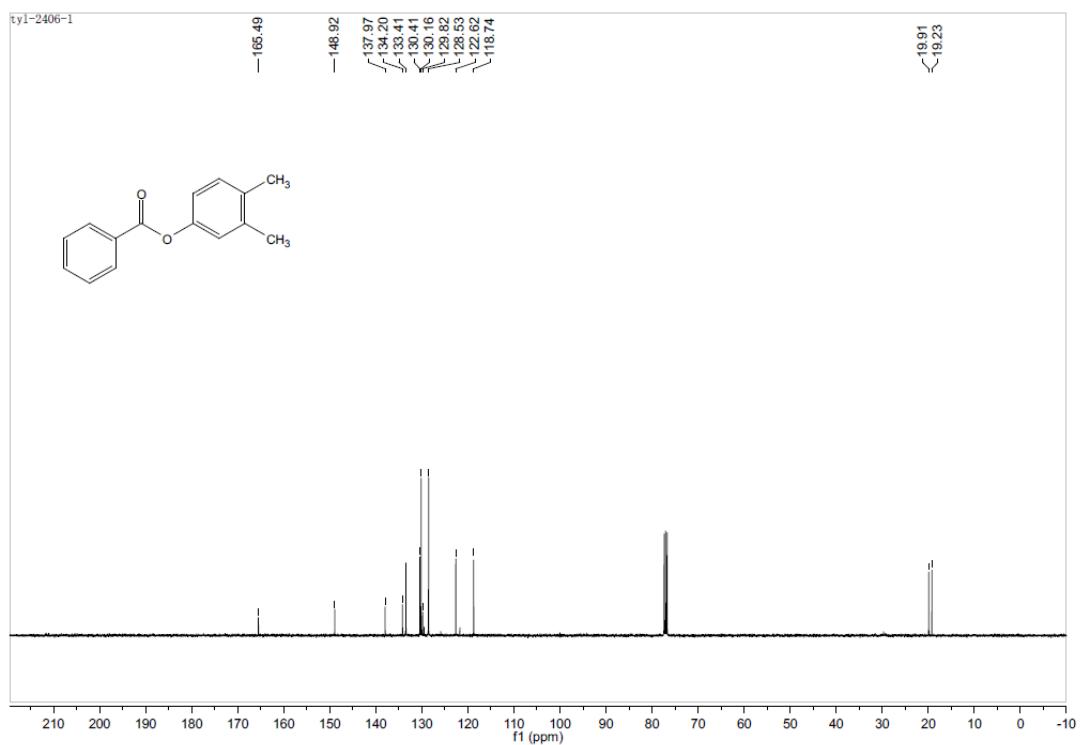
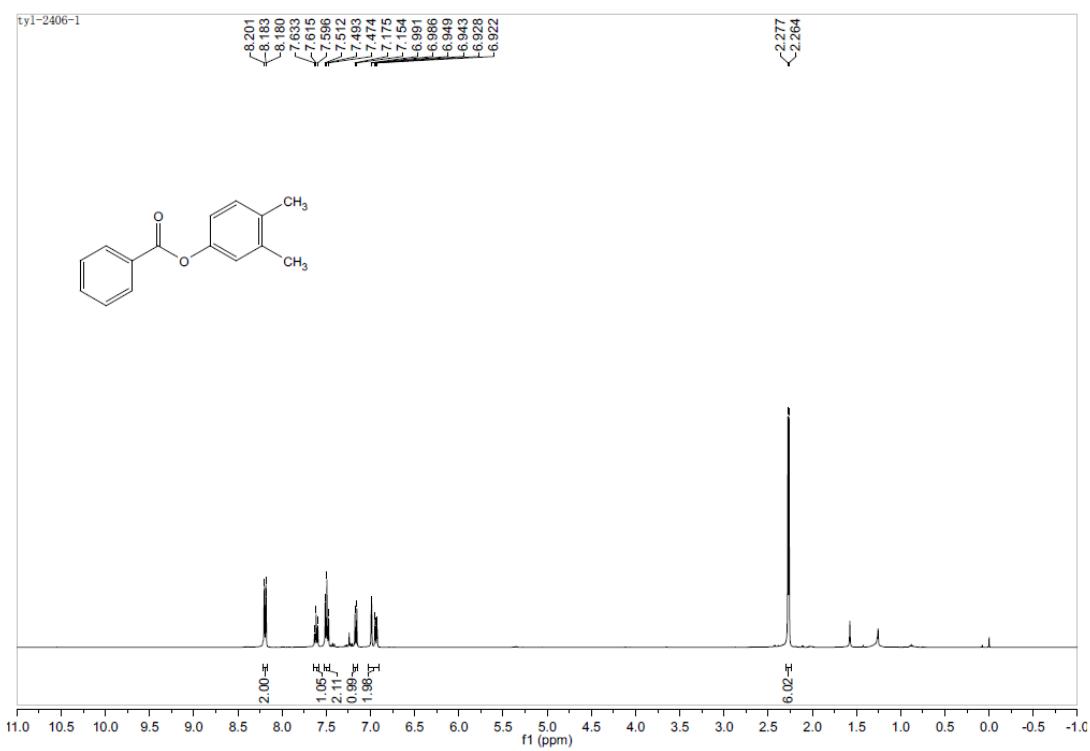
^1H NMR and ^{13}C NMR for compound 6o



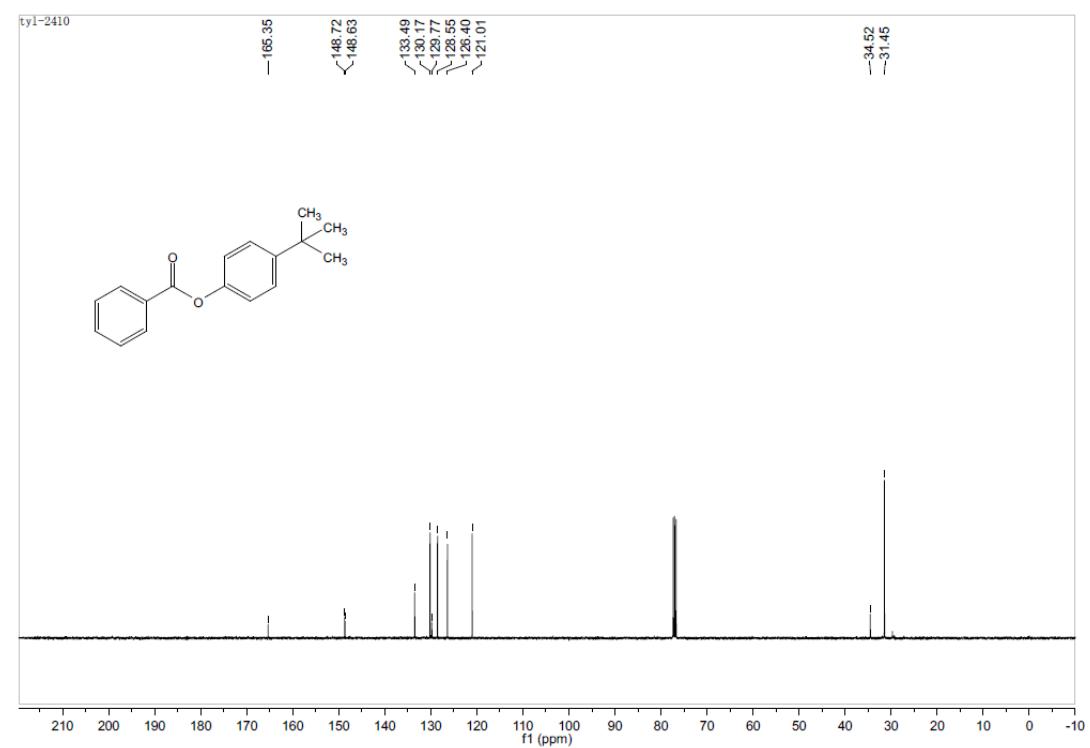
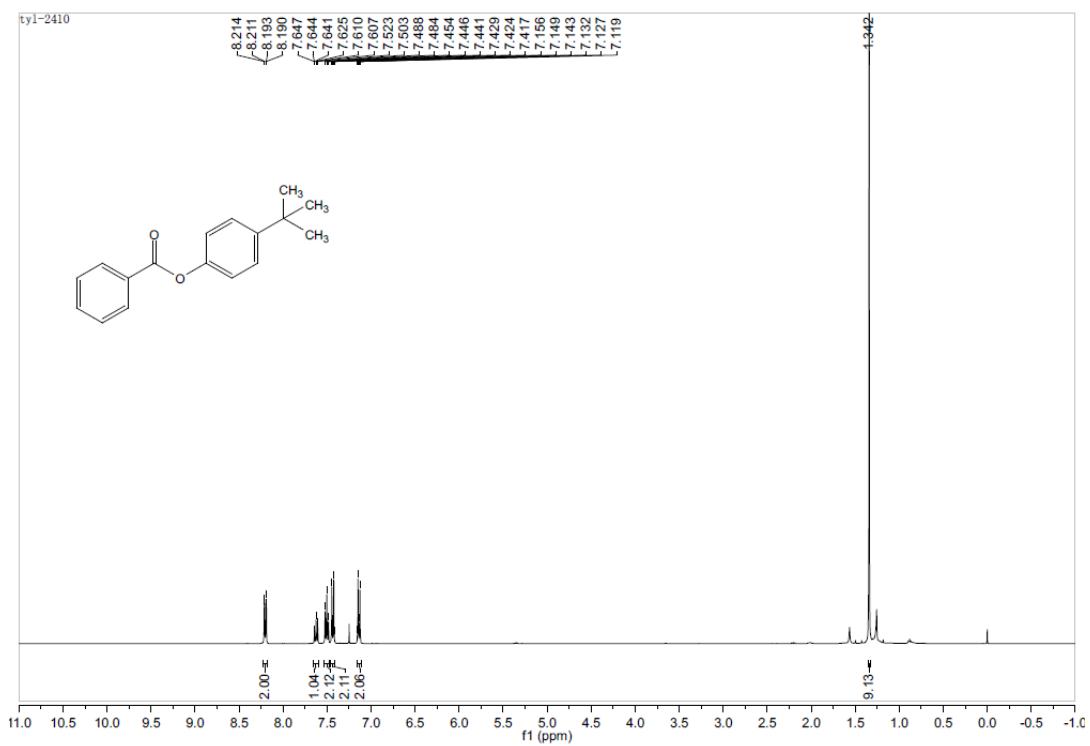
¹H NMR and ¹³C NMR for compound 6p



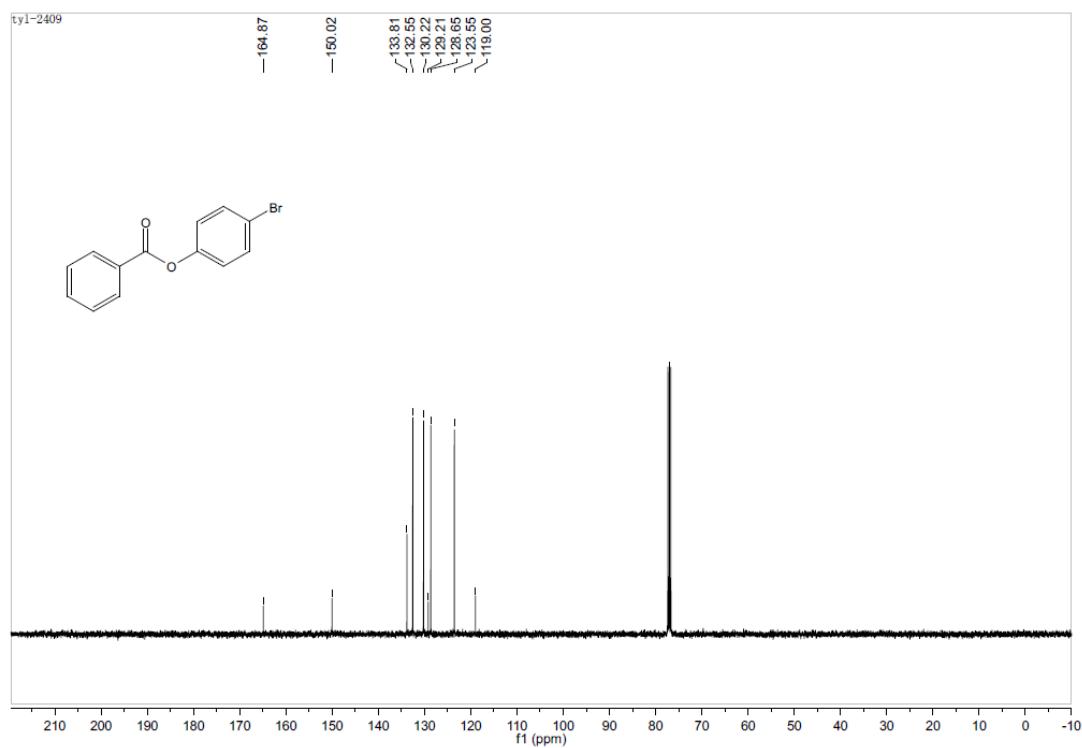
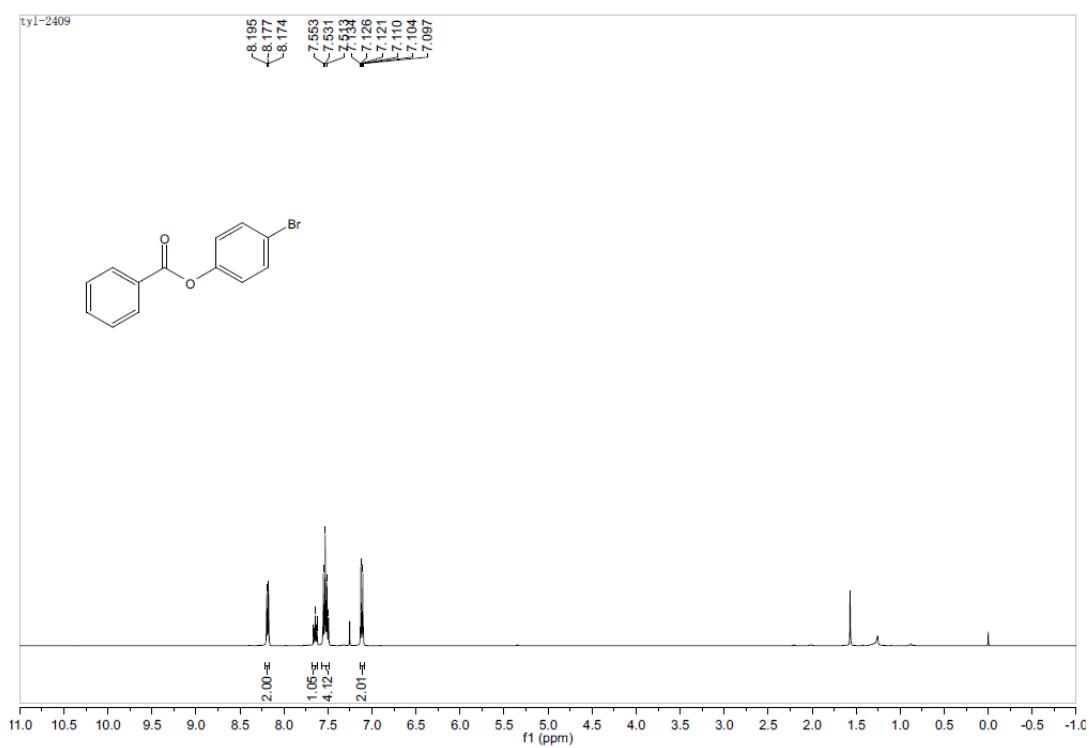
¹H NMR and ¹³C NMR for compound 6q



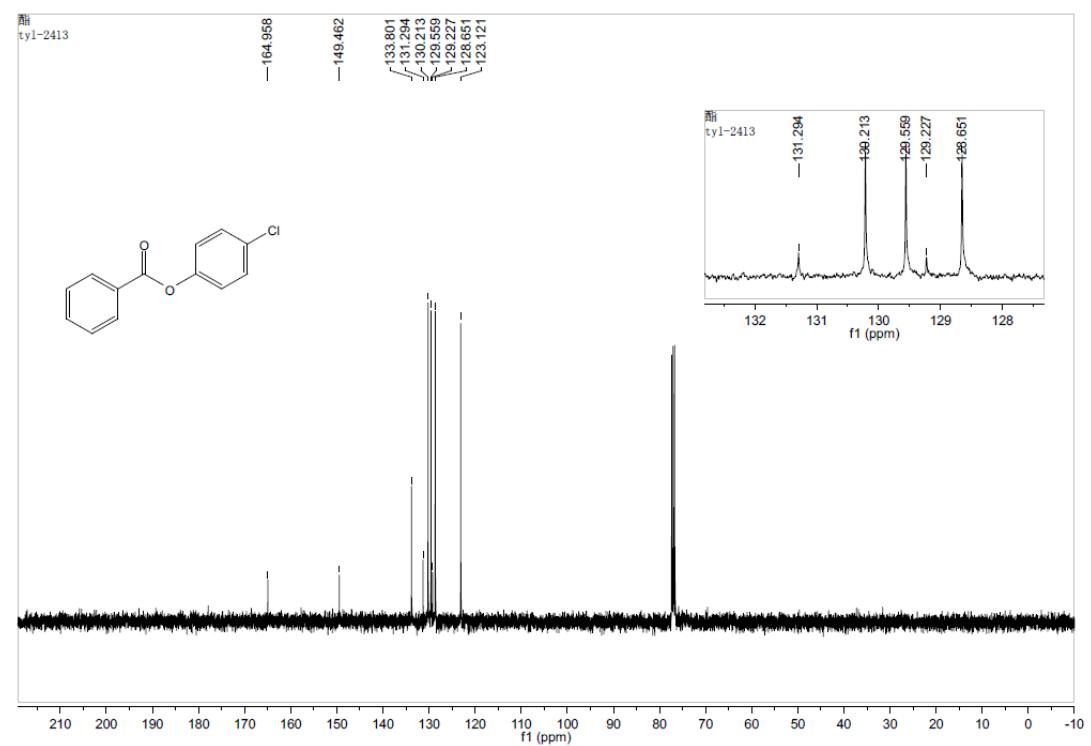
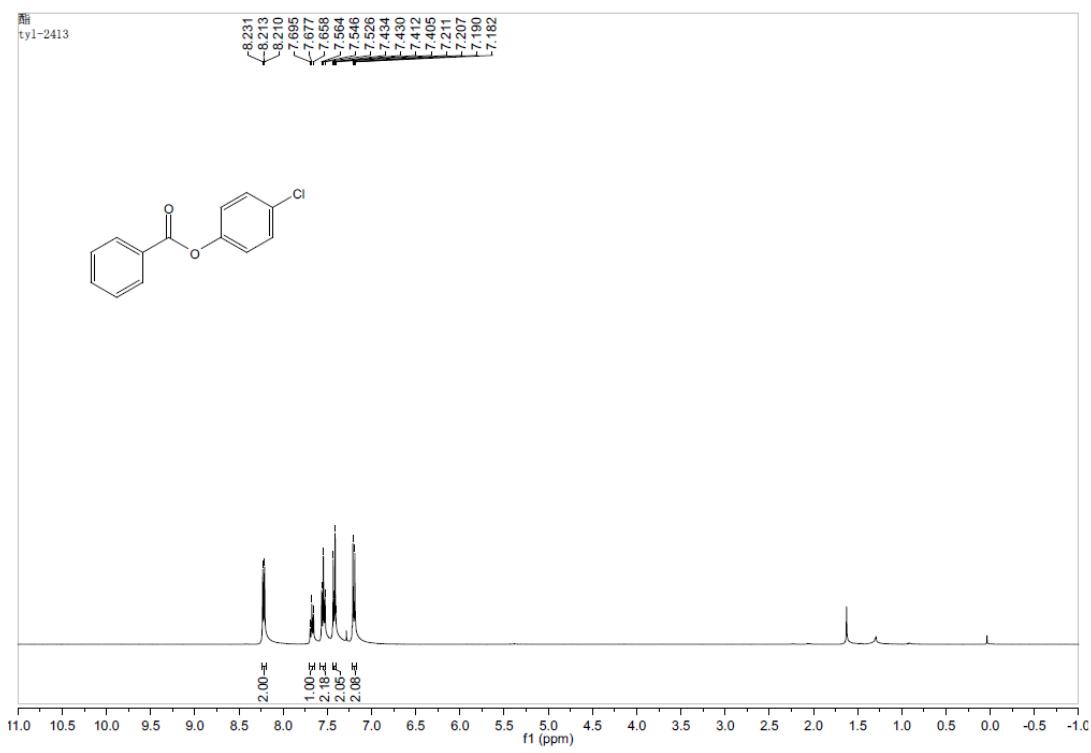
¹H NMR and ¹³C NMR for compound 6r



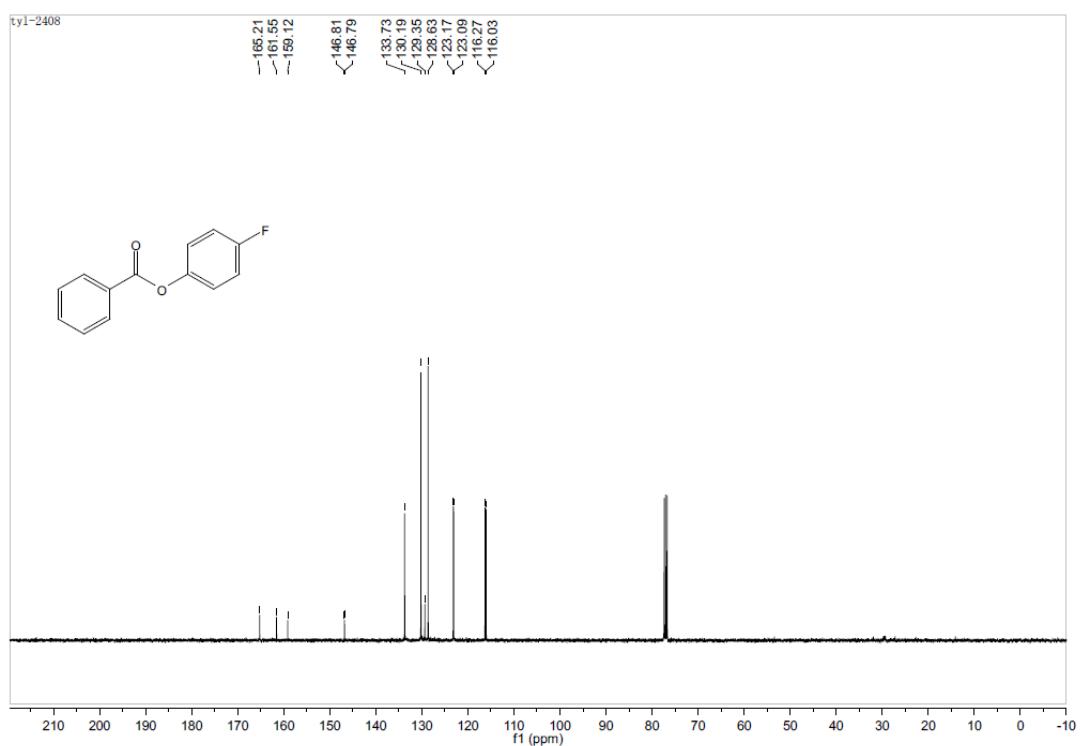
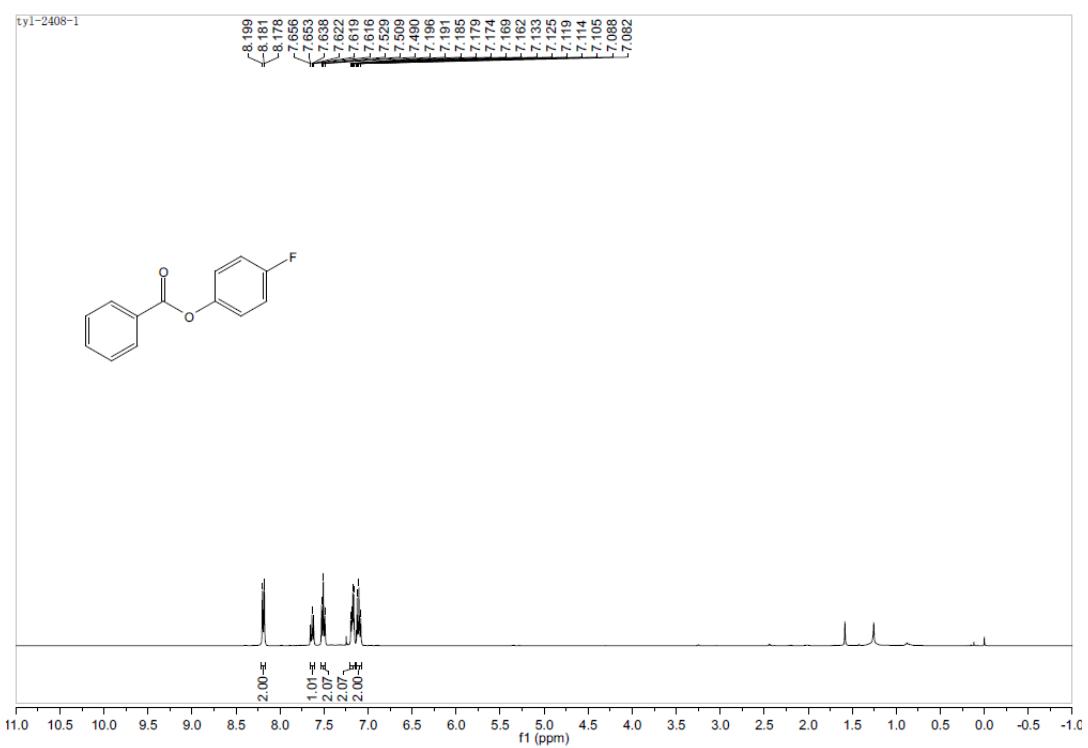
^1H NMR and ^{13}C NMR for compound 6s



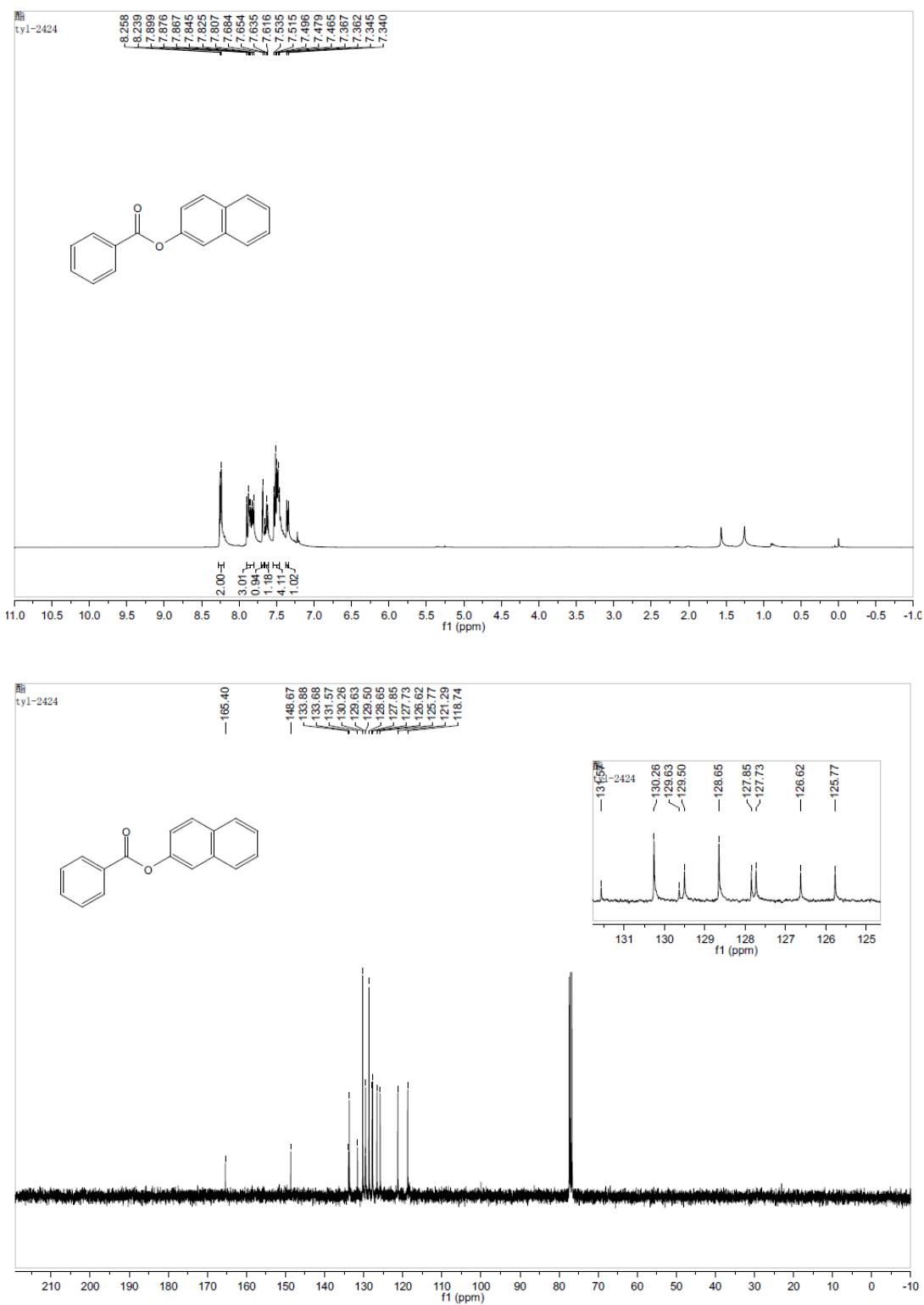
^1H NMR and ^{13}C NMR for compound 6t



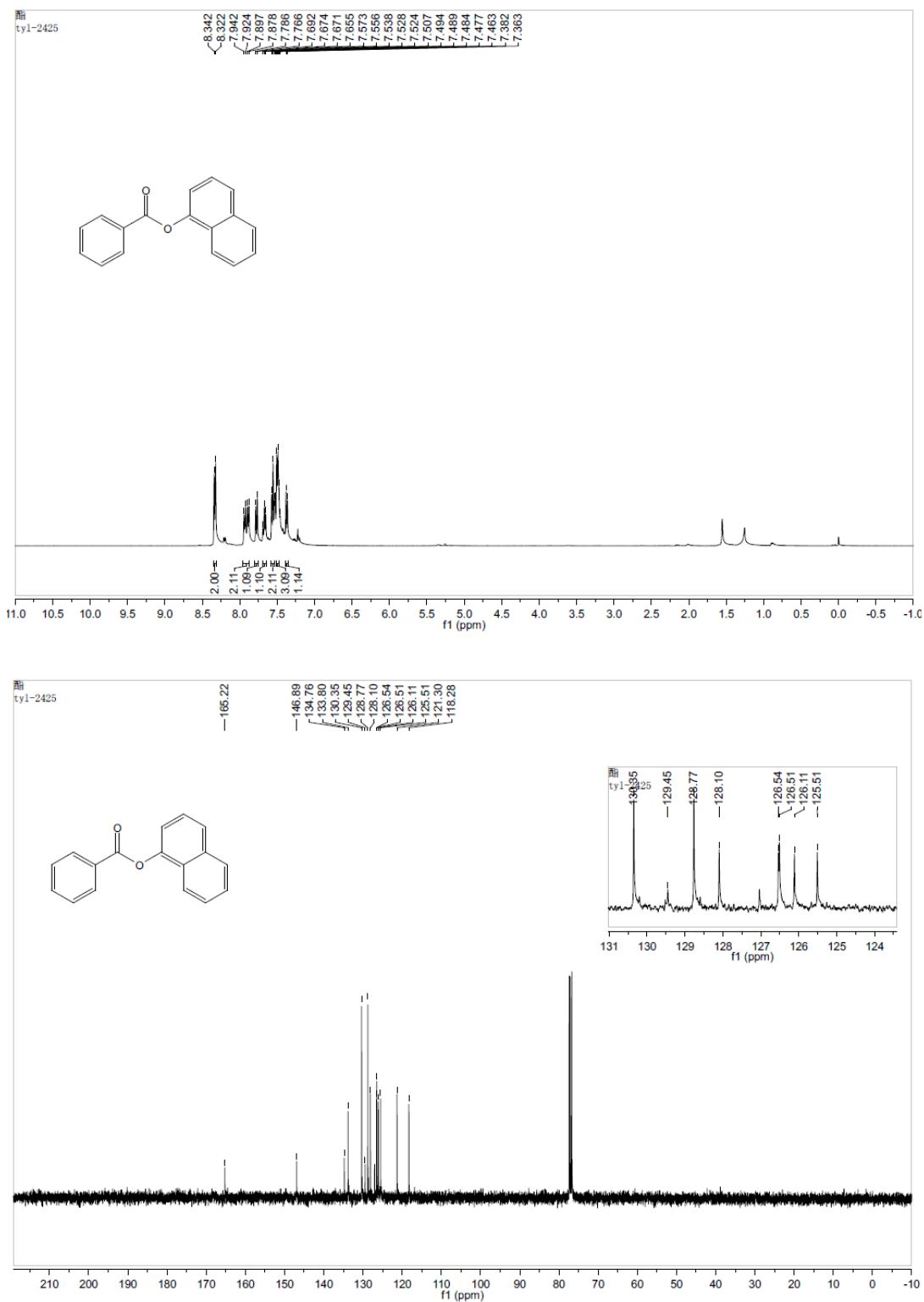
¹H NMR and ¹³C NMR for compound 6u



¹H NMR and ¹³C NMR for compound 6v



^1H NMR and ^{13}C NMR for compound 6w



¹H NMR and ¹³C NMR for compound 6x