

# Supporting Information

## Synthesis of 3-Substituted 2-Arylpyridines *via* Cu/Pd-Catalyzed Decarboxylative Cross-Coupling of Picolinic Acids with (Hetero)Aryl Halides

Dagmar Hackenberger,<sup>†</sup> Philip Weber,<sup>†</sup> David C. Blakemore,<sup>‡</sup> and Lukas J. Goossen\*<sup>†</sup>

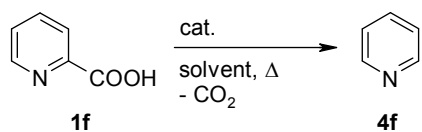
<sup>†</sup>Fakultät für Chemie und Biochemie, Ruhr Universität Bochum, Universitätsstr. 150, 44801  
Bochum (Germany)

<sup>‡</sup>Pfizer Inc., Eastern Point Road, Groton, CT 06340 (USA)

lukas.goossen@rub.de

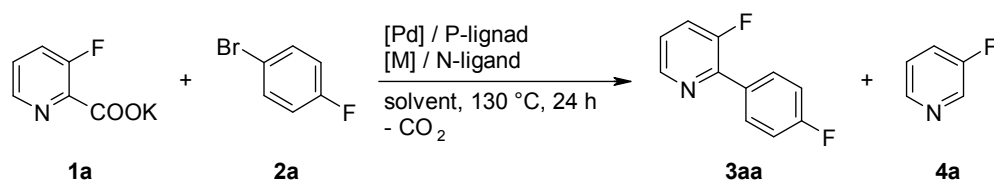
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**Table S1. Protodecarboxylation studies**

Entry	T (°C)	cat.	Yield (%) <b>4f</b>
1	190	Cu <sub>2</sub> O / phen	92
2	180	"	75
3	160	"	87
4	140	"	36
5	120	"	n.d.
6 <sup>a</sup>	"	"	11
7	190	-	69
8	180	-	43
9	160	-	50
10	140	-	21
11	120	-	n.d.
12 <sup>a</sup>	"	-	21

Reaction conditions: 0.5 mmol **1f**, Cu<sub>2</sub>O (5 mol%), Phen (10 mol%), NMP (1 mL), 24 h; GC yield with *n*-dodecane as internal standard. <sup>a</sup> In DMSO (1 mL), 16 h.

**Table S2. Optimization of the reaction conditions**

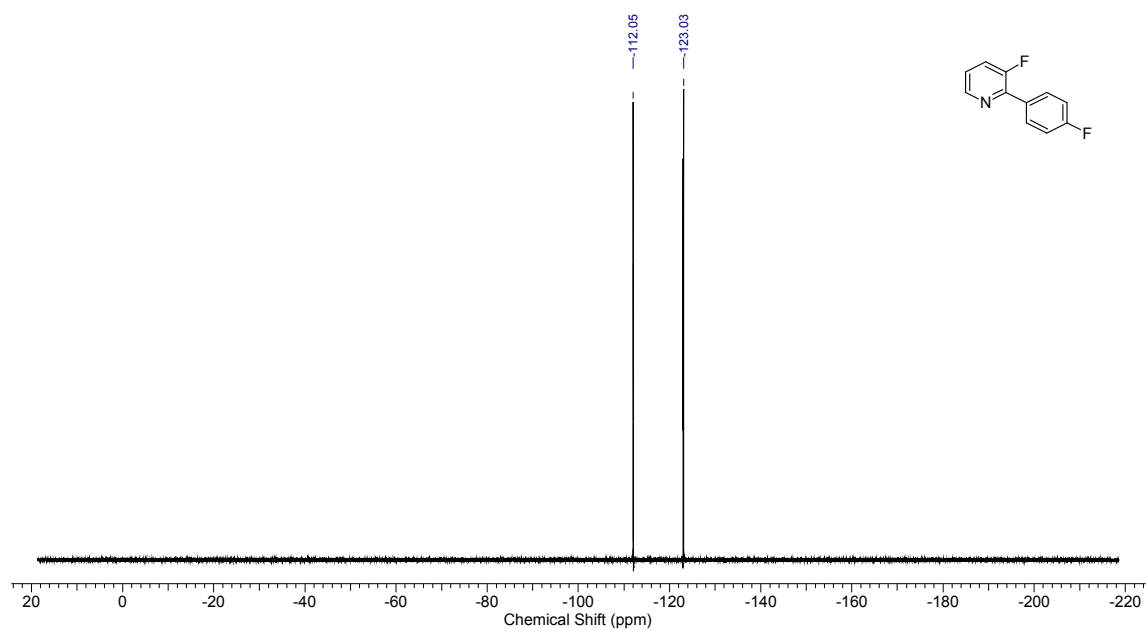
Entry	[M]	N-ligand	[Pd]	P-ligand	solvent	Yield (%)	
						3aa	4a
1	Cu <sub>2</sub> O	Phen	PdCl <sub>2</sub>	PPh <sub>3</sub>	NMP/Mes	49	n.d.
2	"	"	"	"	NMP	19	trace
3	"	"	"	"	Mes	5	n.d.
4	"	"	"	"	DMF	35	trace
5	"	"	"	"	DMAc	36	9
6	"	"	"	"	DMSO	60	7
7	"	"	Pd(COD)Cl <sub>2</sub>	"	"	74	8
8	"	"	PdBr <sub>2</sub>	"	"	51	14
9	"	"	PdI <sub>2</sub>	"	"	54	11
10	"	"	Pd(OAc) <sub>2</sub>	"	"	49	23
11	"	"	Pd(TFA) <sub>2</sub>	"	"	53	6
12	"	"	Pd(acac) <sub>2</sub>	"	"	67	9
13	"	"	Pd(F <sub>6</sub> -acac) <sub>2</sub>	"	"	30	31
14 <sup>a</sup>	CuCl	"	Pd(COD)Cl <sub>2</sub>	"	"	66	n.d.
15 <sup>a</sup>	CuBr	"	"	"	"	58	n.d.
16 <sup>a</sup>	CuI	"	"	"	"	71	8
17	Ag <sub>2</sub> CO <sub>3</sub>	"	"	"	"	66	10
18	Ag <sub>2</sub> O	"	"	"	"	52	30
19	Cu <sub>2</sub> O	Me <sub>2</sub> -phen	"	"	"	62	n.d.
20	"	Me <sub>4</sub> -phen	"	"	"	83	n.d.
21	"	Ph <sub>2</sub> -phen	"	"	"	79	9
22	"	NO <sub>2</sub> -phen	"	"	"	49	17
23	"	2,2'-bipy	"	"	"	70	7
24	"	pyridine	"	"	"	72	6
25	"	Me <sub>4</sub> -phen	"	P( <i>p</i> -Tol) <sub>3</sub>	"	84	trace
26	"	"	"	P( <i>o</i> -Tol) <sub>3</sub>	"	78	7
27	"	"	"	PCy <sub>3</sub>	"	28	trace

28	"	"	"	P(2-Furyl) <sub>3</sub>	"	74	7
29	"	"	"	BINAP	"	75	n.d.
30	"	"	"	JohnPhos	"	41	8
31	"	"	"	SPhos	"	80	6
32	"	"	"	XPhos	"	74	11
33	"	"	"	CyJohnPhos	"	82	10
34	"	"	"	DavePhos	"	92	7
35	"	-	"	"	"	93	trace
36 <sup>b</sup>	"	-	"	"	"	64	12
37 <sup>c</sup>	"	-	"	"	"	23	7
38 <sup>d</sup>	"	-	"	"	"	18	5
39	-	-	"	"	"	7	32
40	Cu <sub>2</sub> O	-	"	-	"	12	trace
41	"	-	-	-	"	n.d.	n.d.

Reaction conditions: 0.5 mmol **1a**, 1.0 mmol **2a**, [M] (5 mol%), N-ligand (10 mol%), [Pd] (5 mol%), P-ligand (15 mol%), solvent (2 mL), 130 °C, 24 h; <sup>19</sup>F-NMR yield with 1,4-difluorobenzene as internal standard. <sup>a</sup> 10 mol% [M] was used; <sup>b</sup> 120 °C; <sup>c</sup> 110°C; <sup>d</sup> 100 °C.

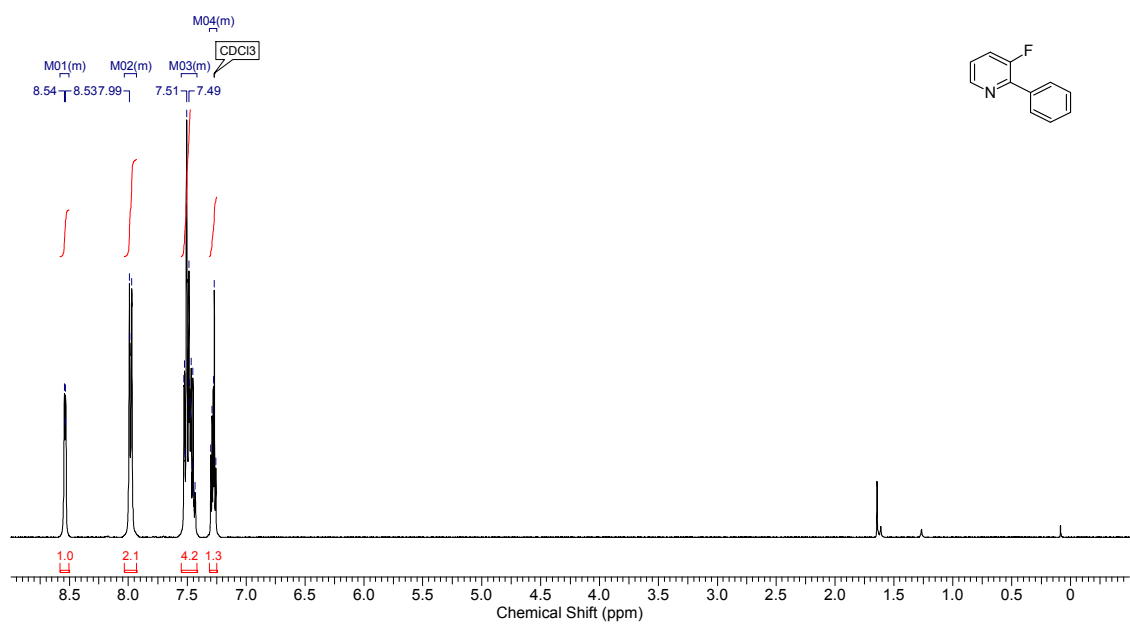


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

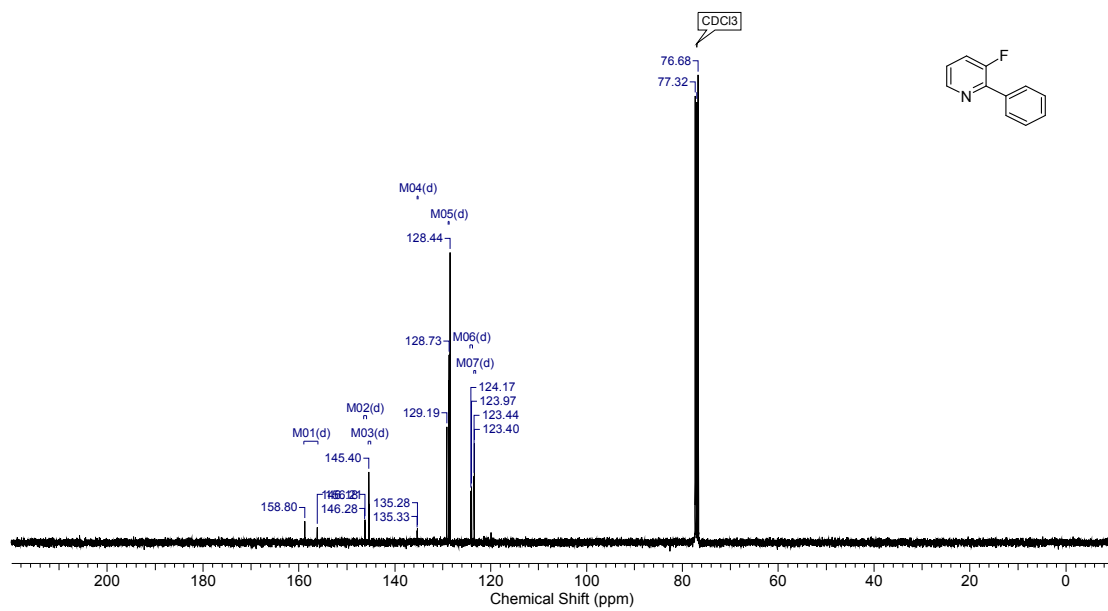


3-Fluoro-2-phenylpyridine (**3ab**)

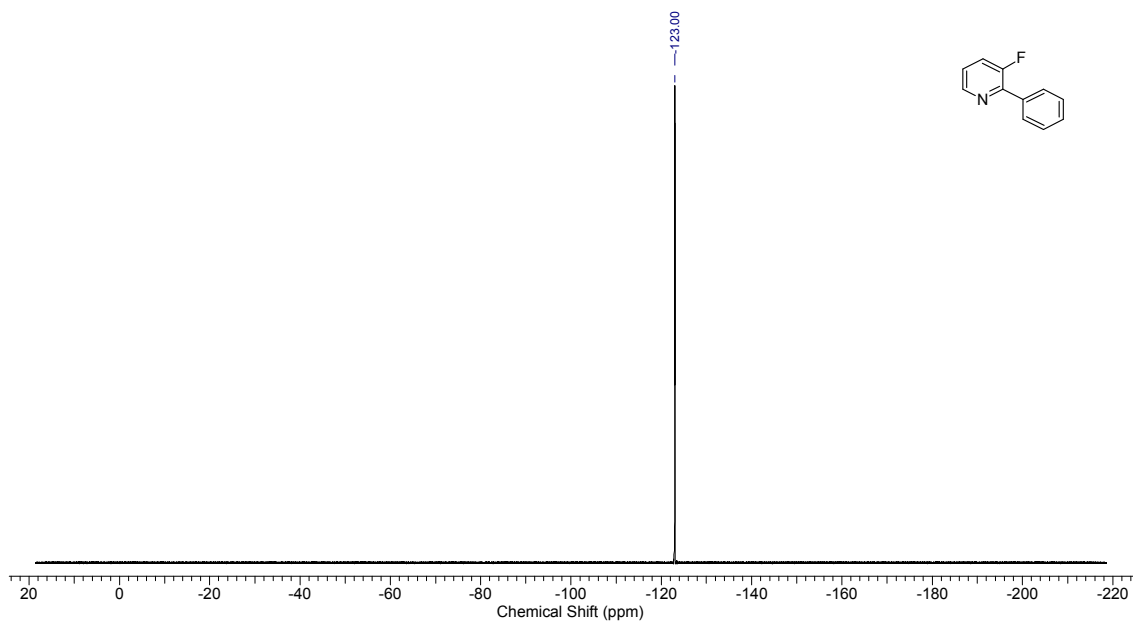
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

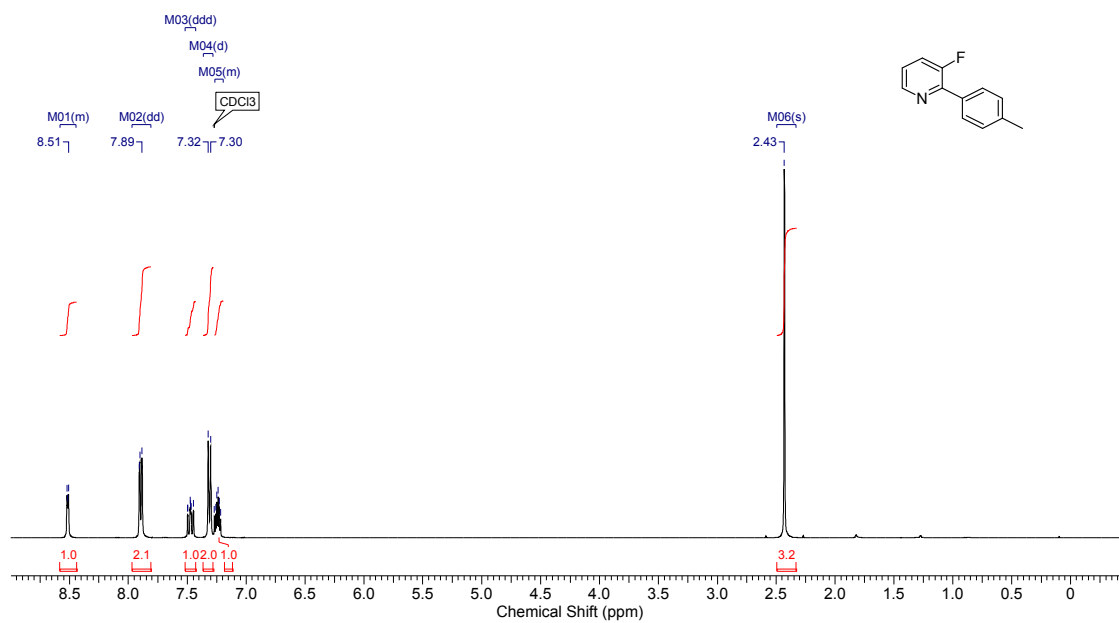


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

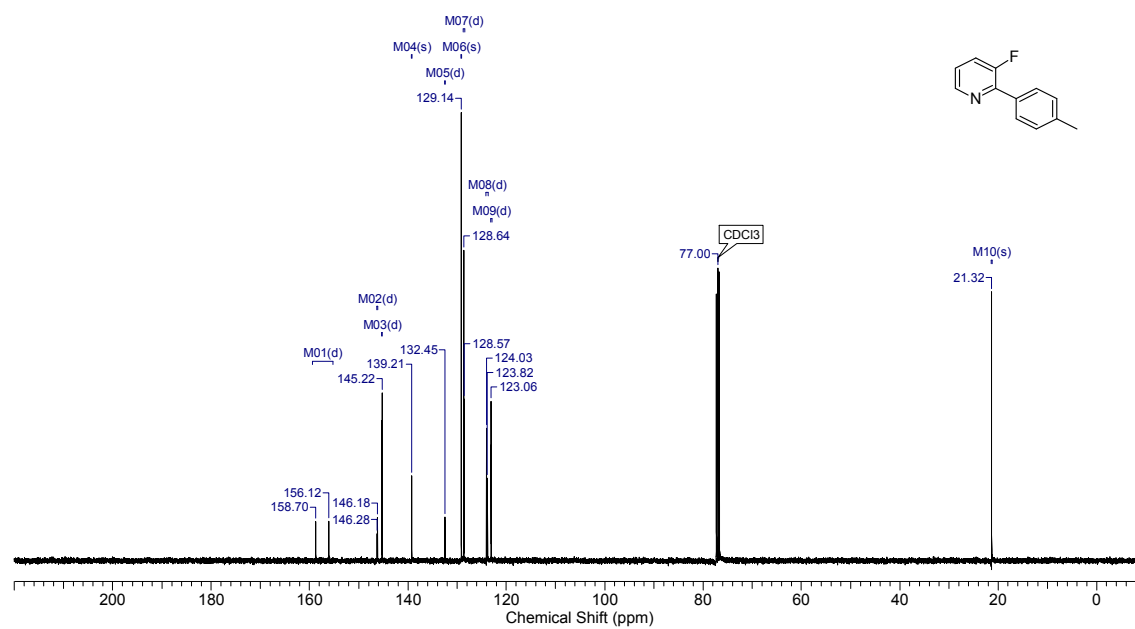


### 3-Fluoro-2-(4-methylphenyl)pyridine (**3ac**)

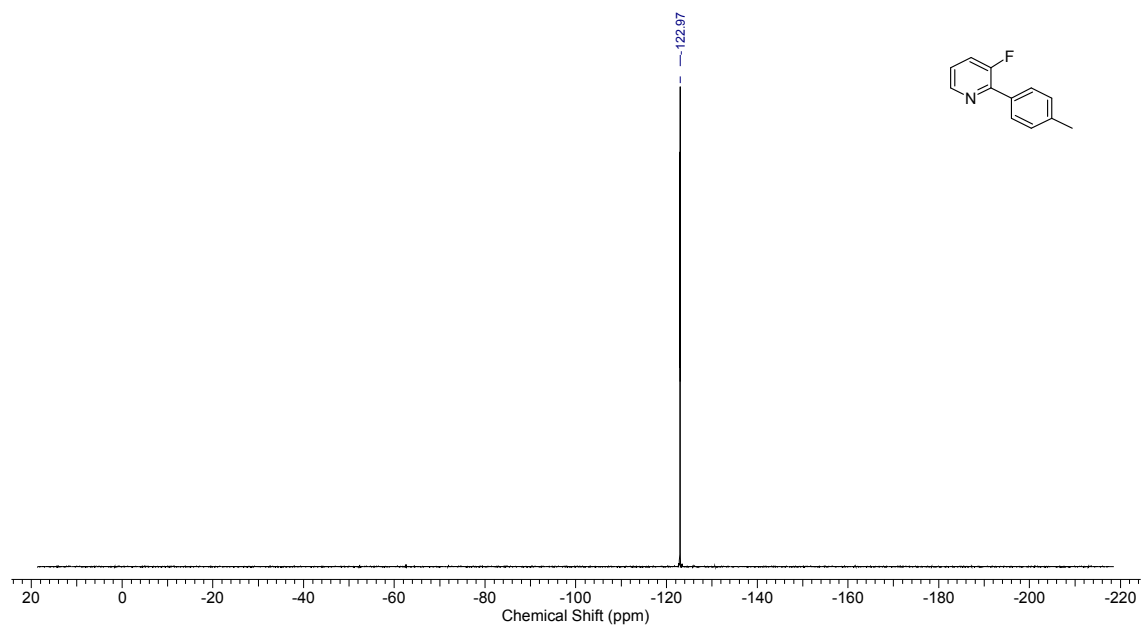
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (from method B)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

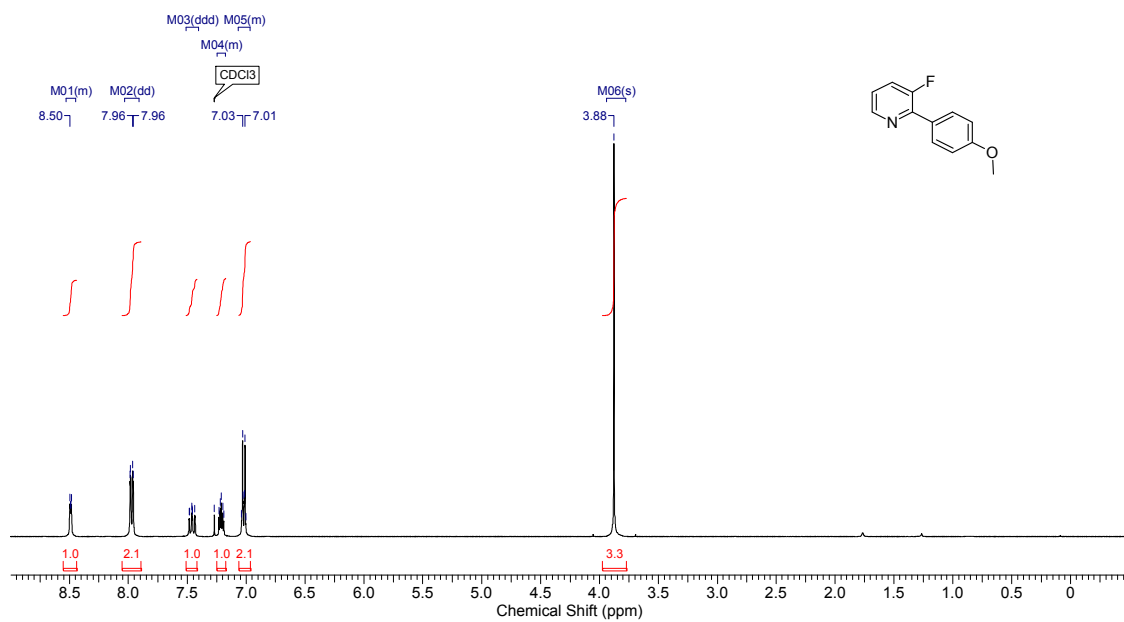


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

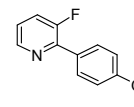
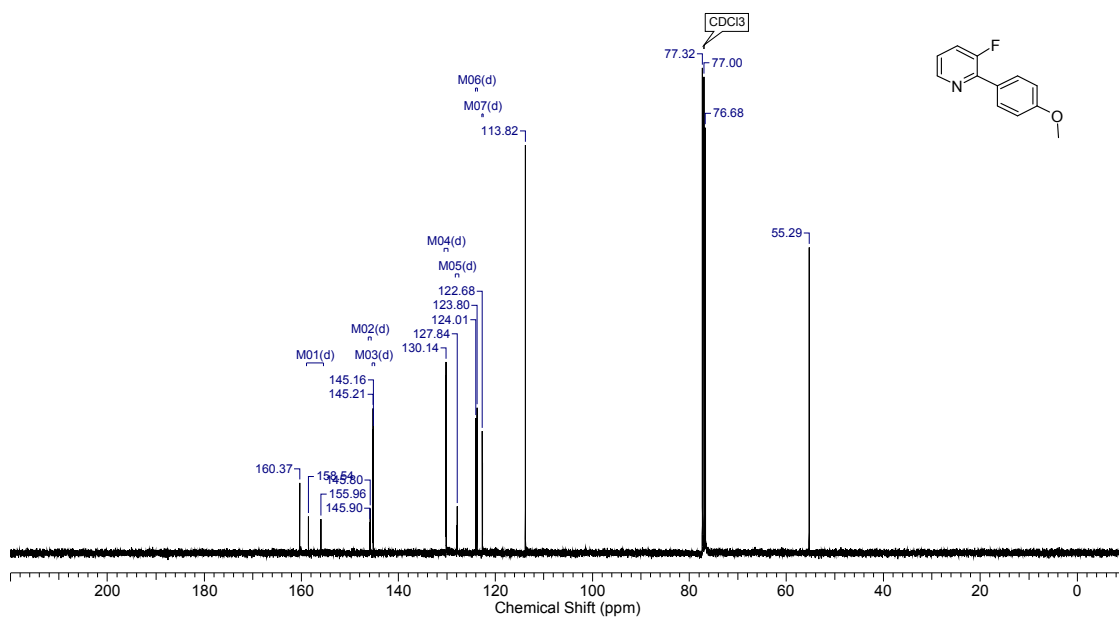


3-Fluoro-2-(4-methoxyphenyl)pyridine (**3ad**)

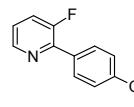
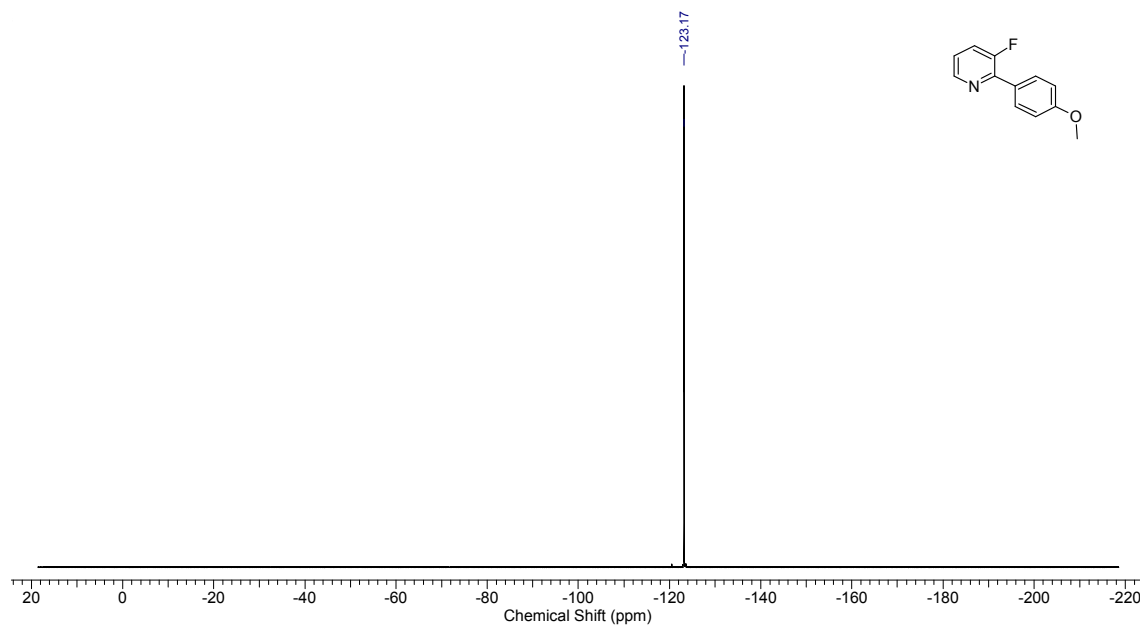
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

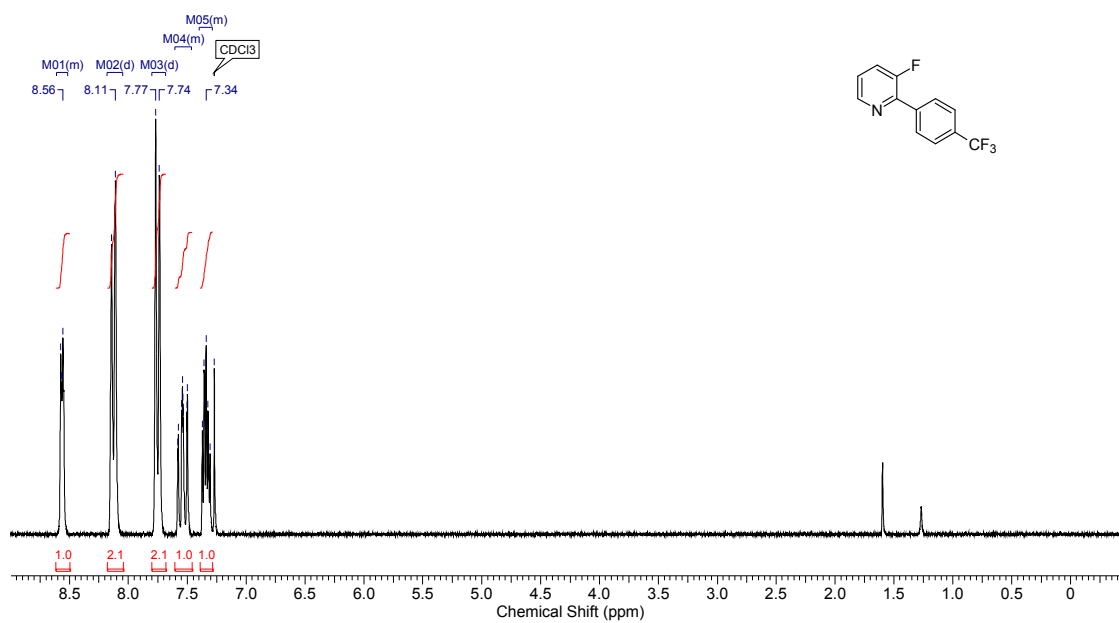


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

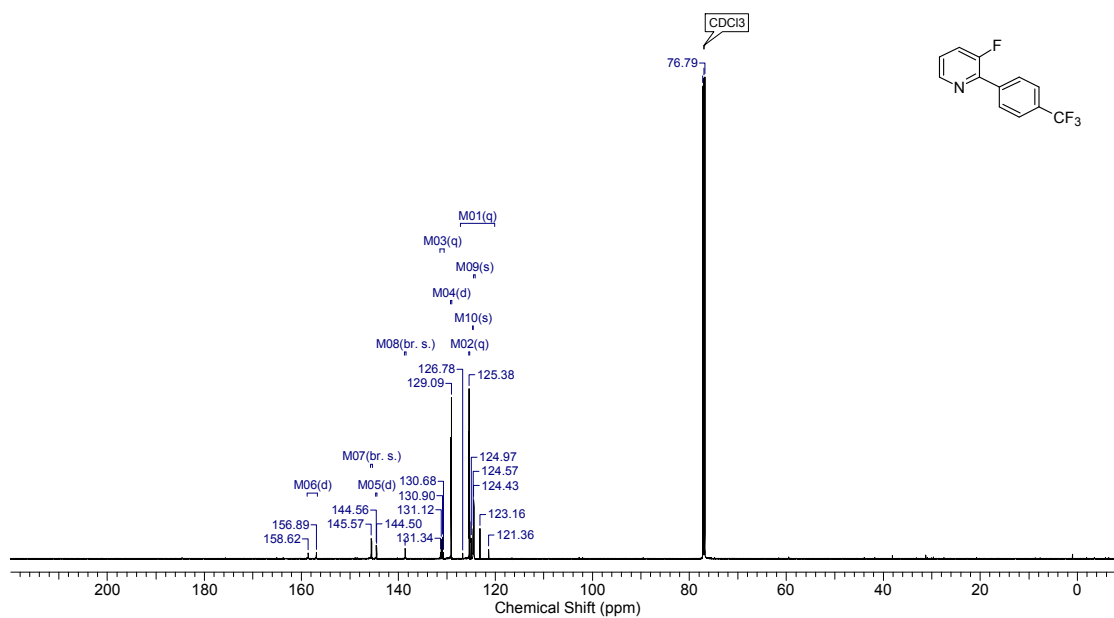


### 3-Fluoro-2-[4-(trifluoromethyl)phenyl]pyridine (**3ae**)

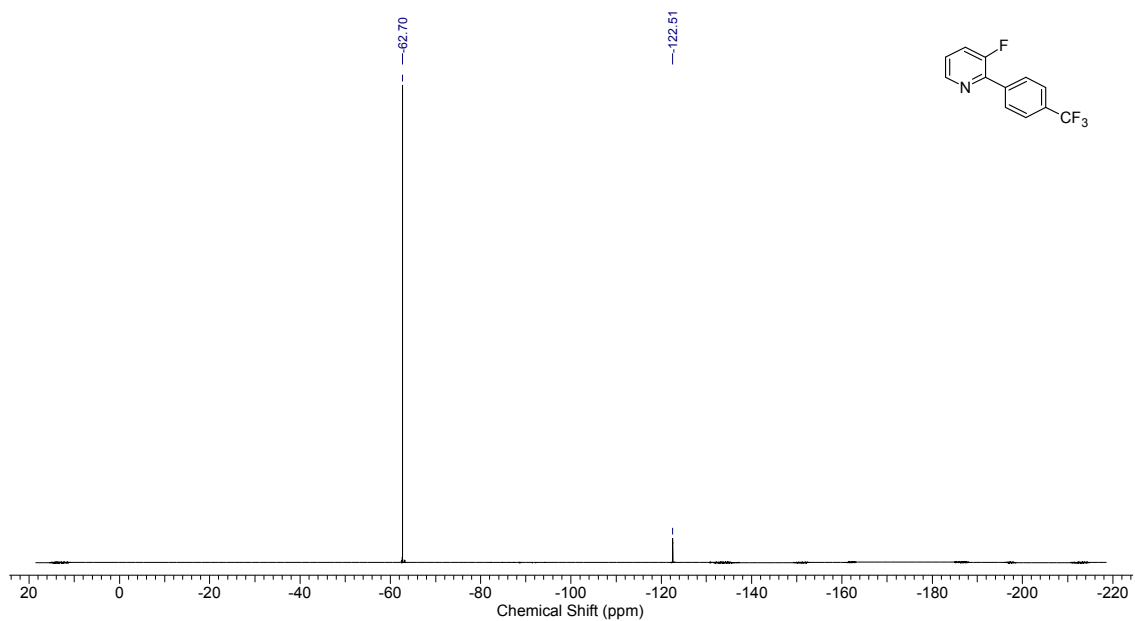
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$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 151 MHz)

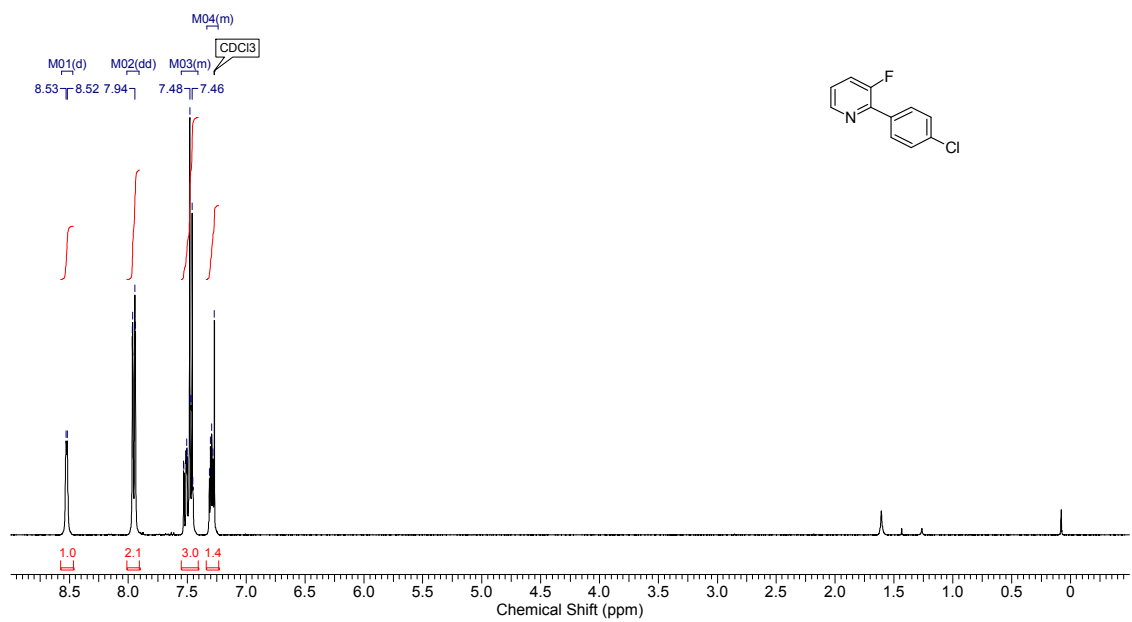


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

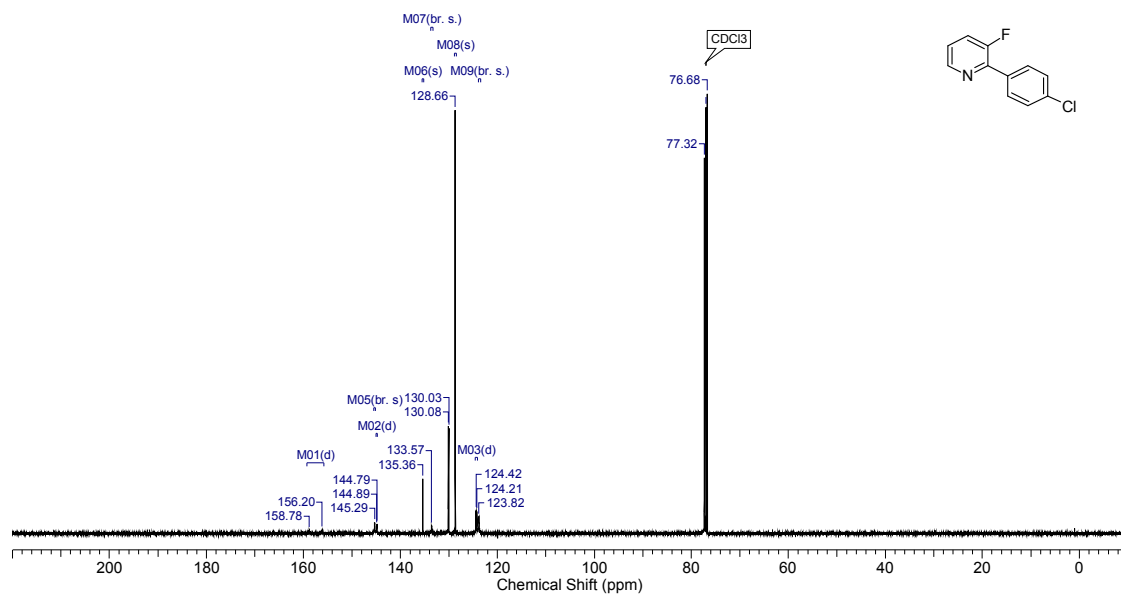


2-(4-Chlorophenyl)-3-fluoropyridine (**3af**)

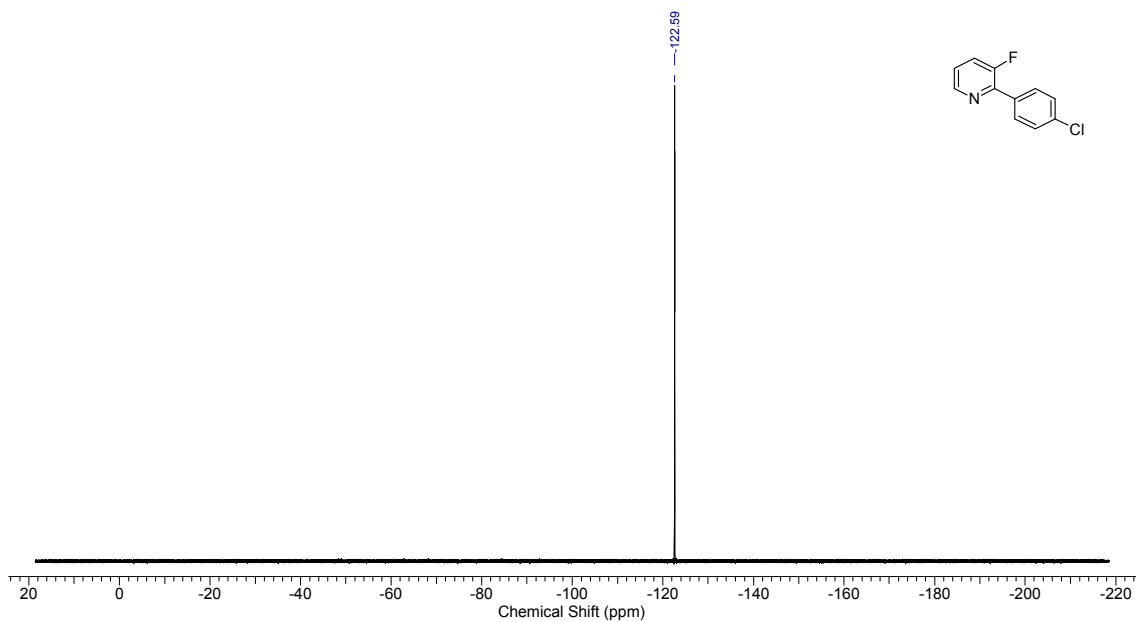
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

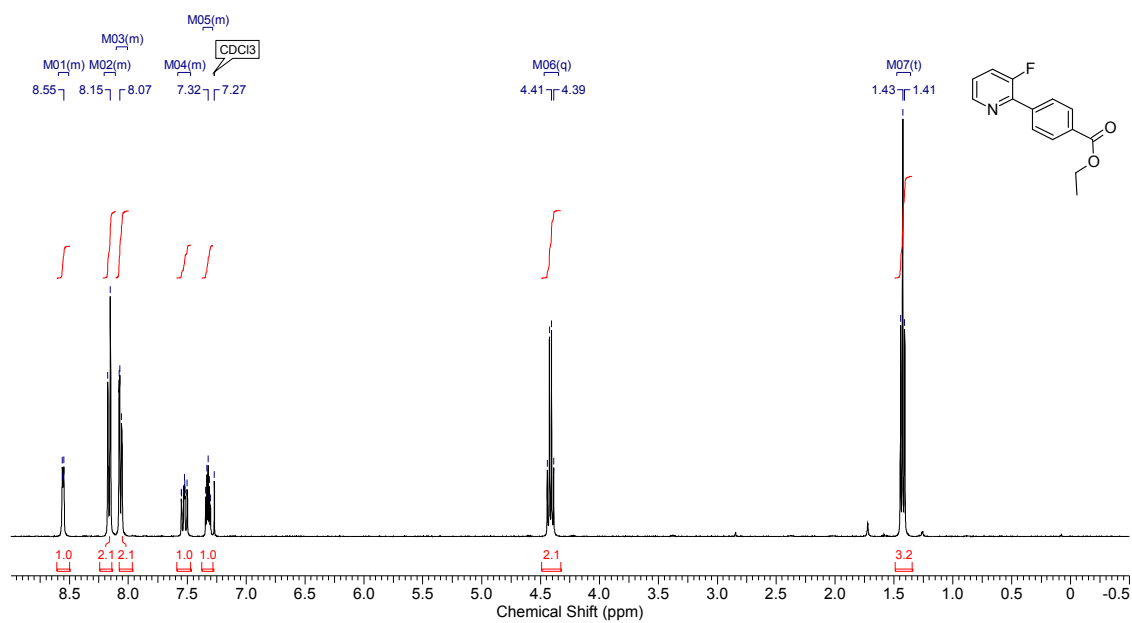


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

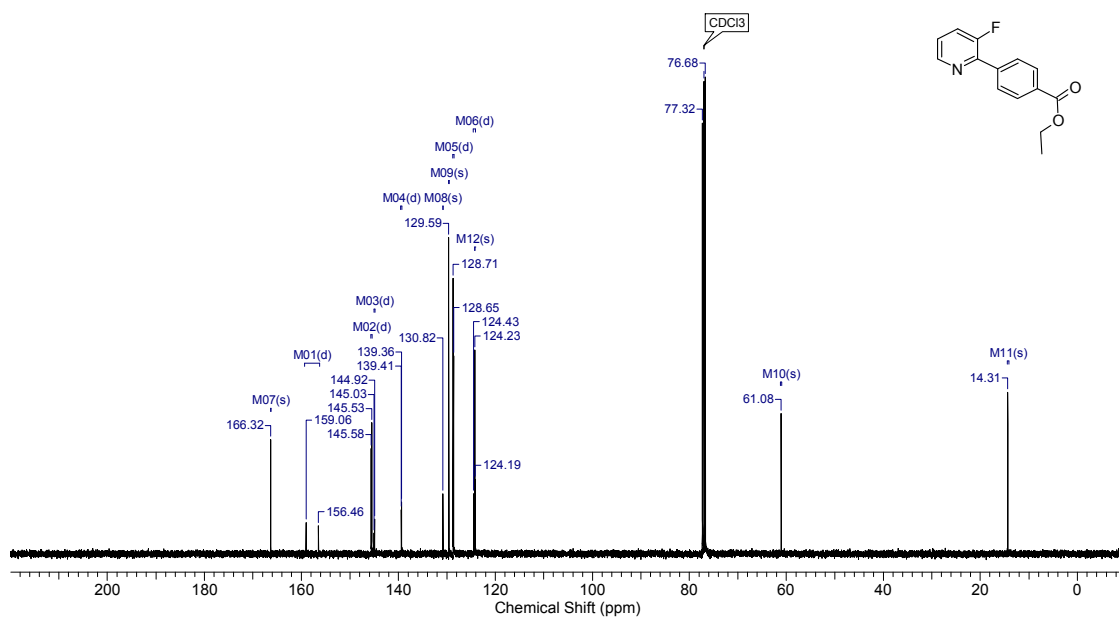


# 4-(3-Fluoro-2-pyridinyl)benzoic acid ethyl ester (**3ag**)

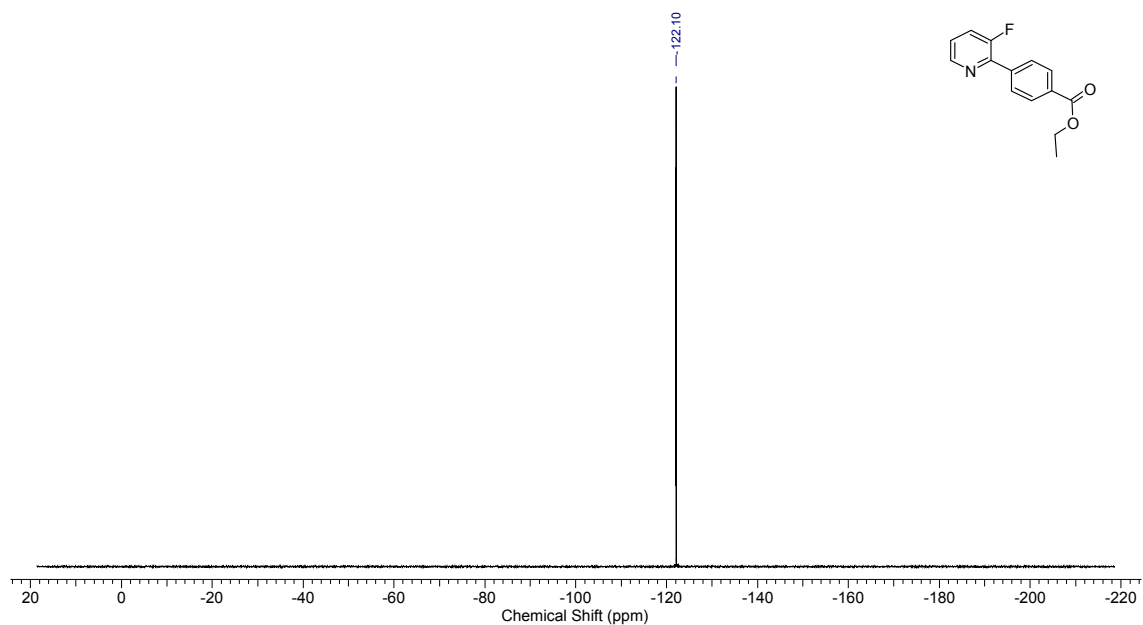
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$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

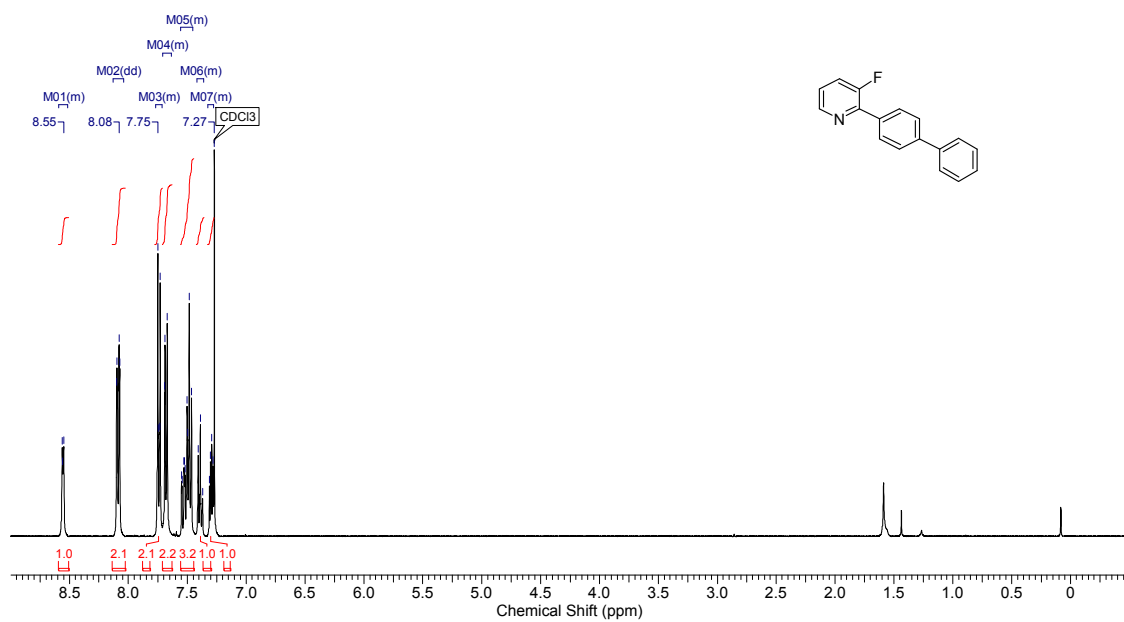


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

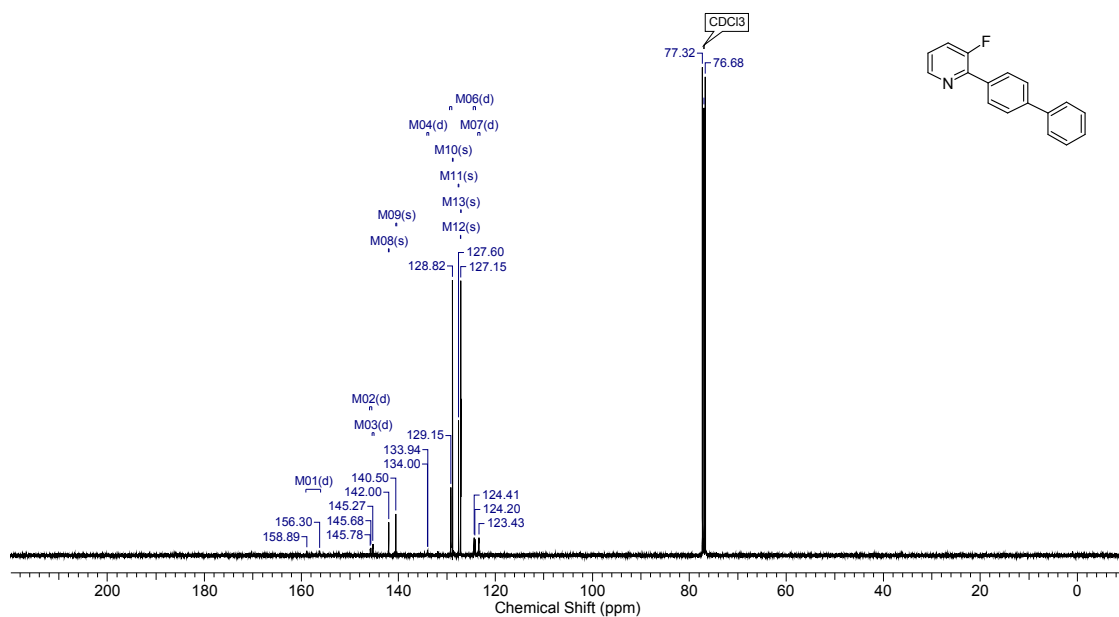


2-[1,1'-Biphenyl]-4-yl-3-fluoropyridine (**3ah**)

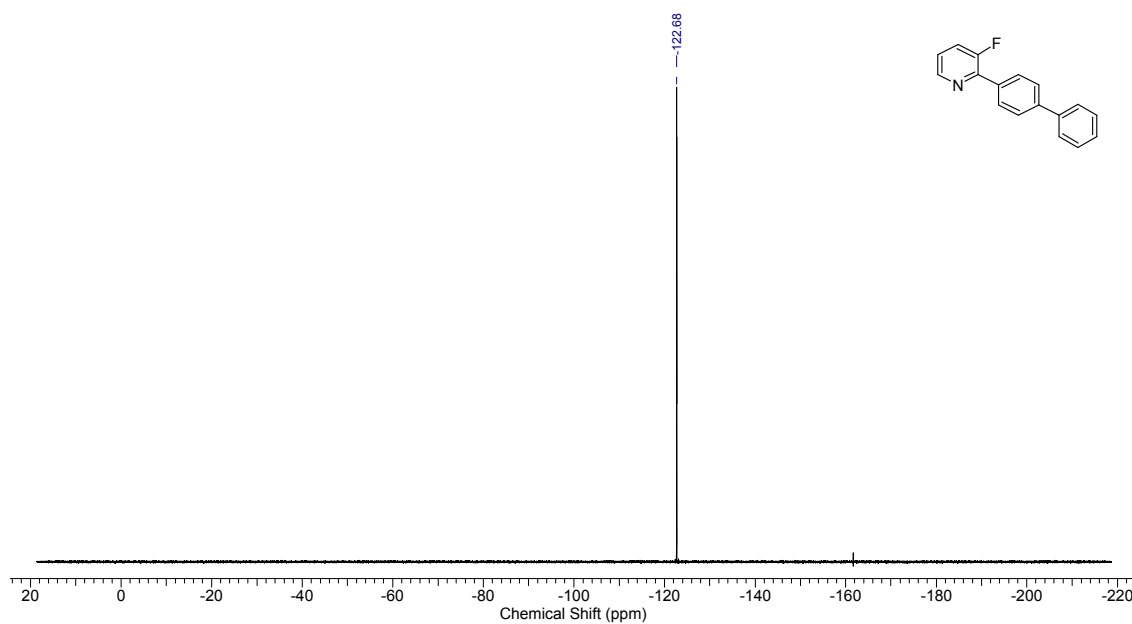
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$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

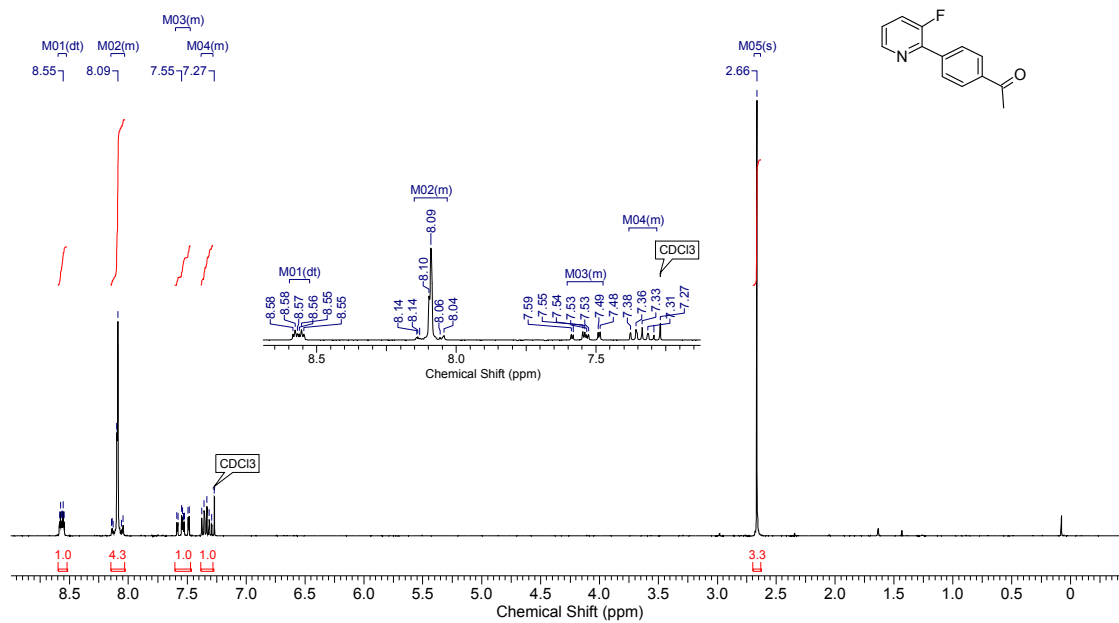


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

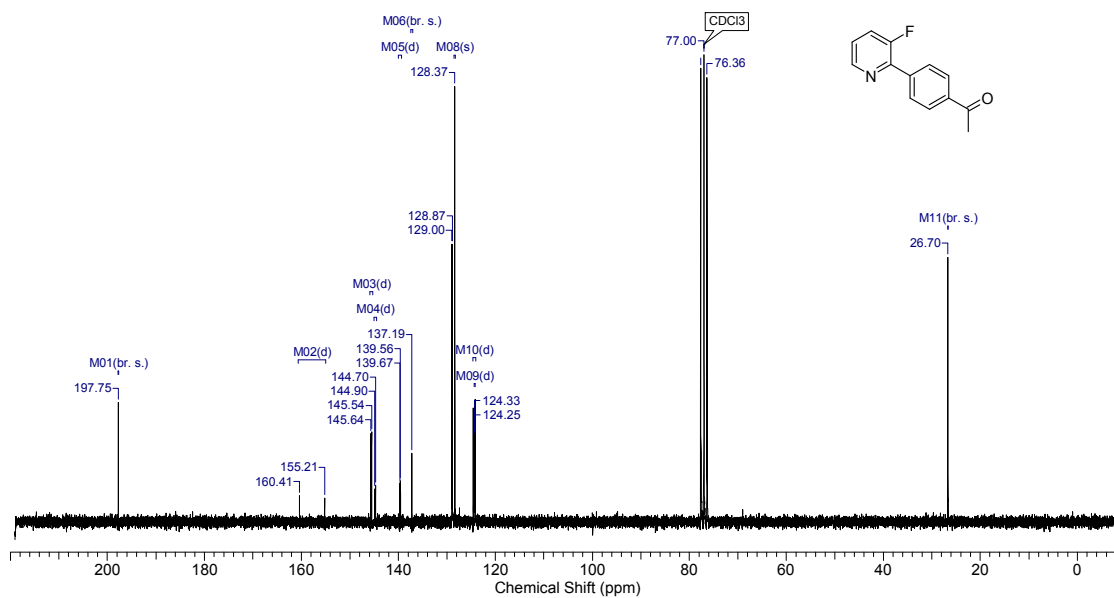


# 1-[4-(3-Fluoro-2-pyridinyl)phenyl]ethanone (**3ai**)

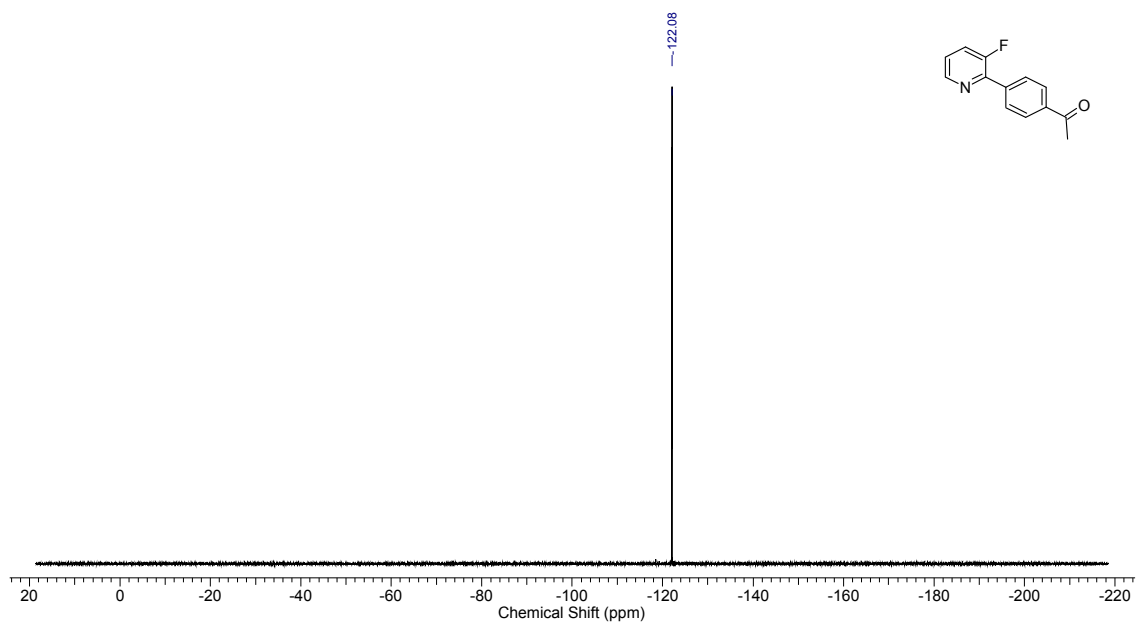
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

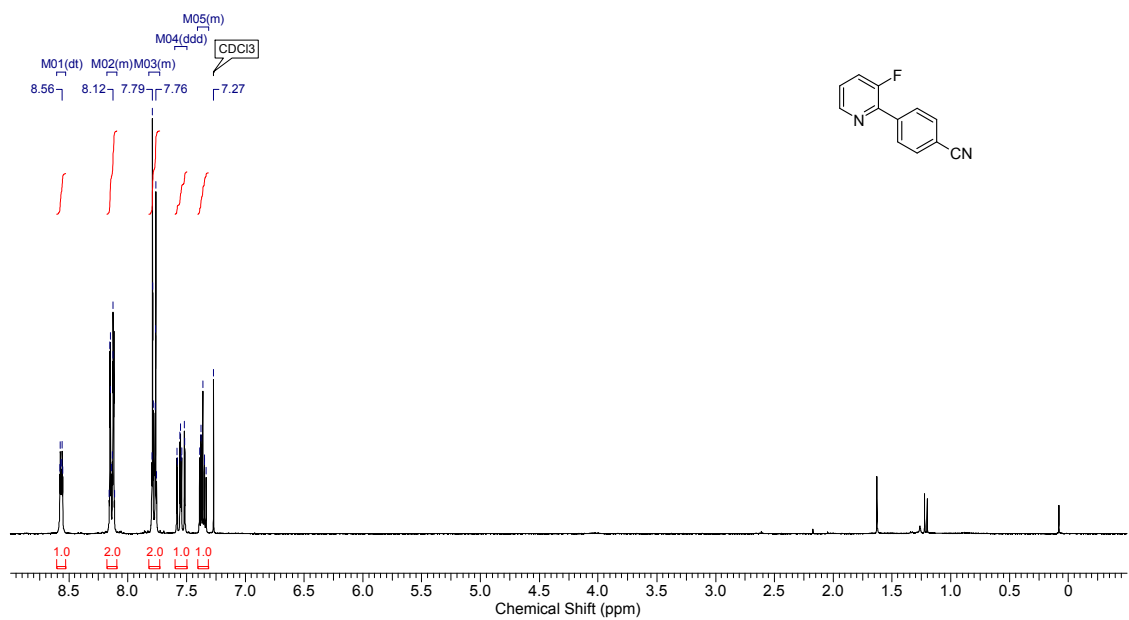


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

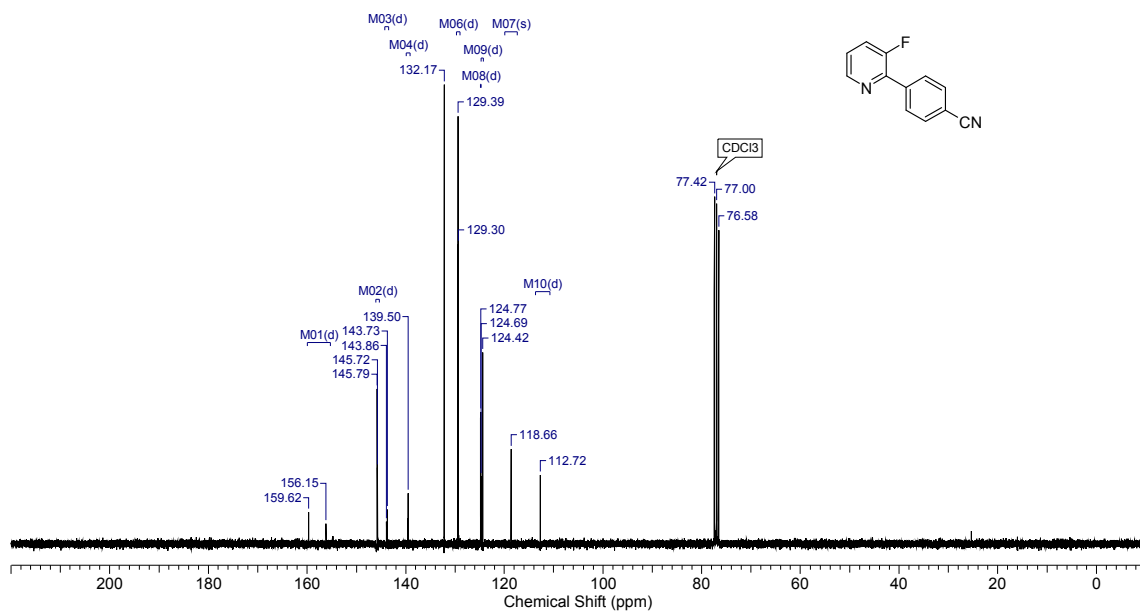


4-(3-Fluoro-2-pyridinyl)benzonitrile (**3aj**)

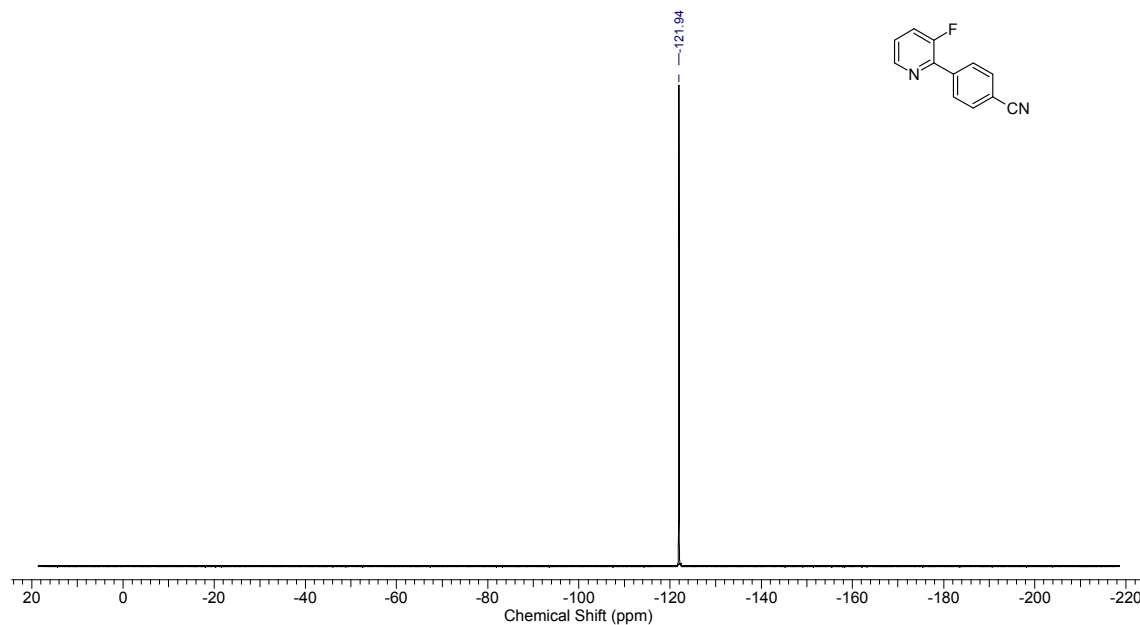
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$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)

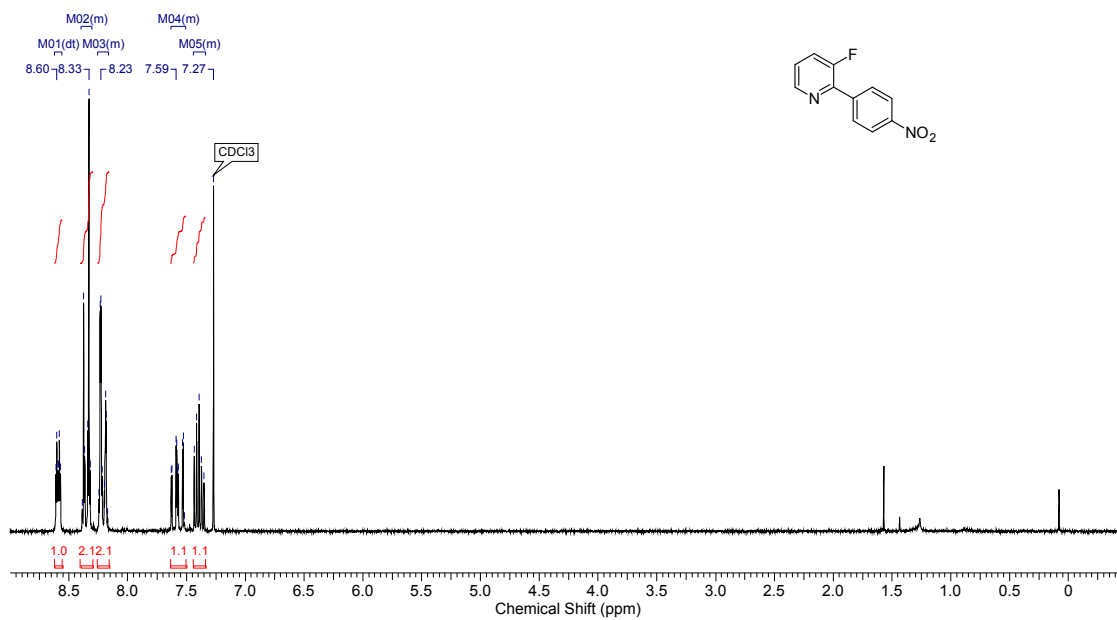


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

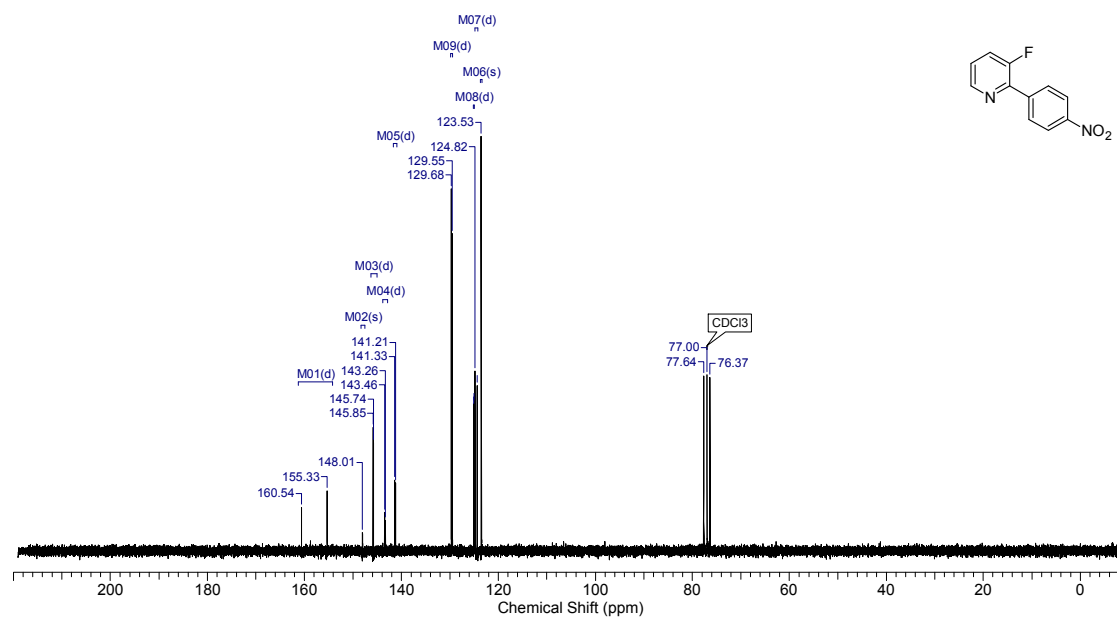


### 3-Fluoro-2-(4-nitrophenyl)pyridine (**3ak**)

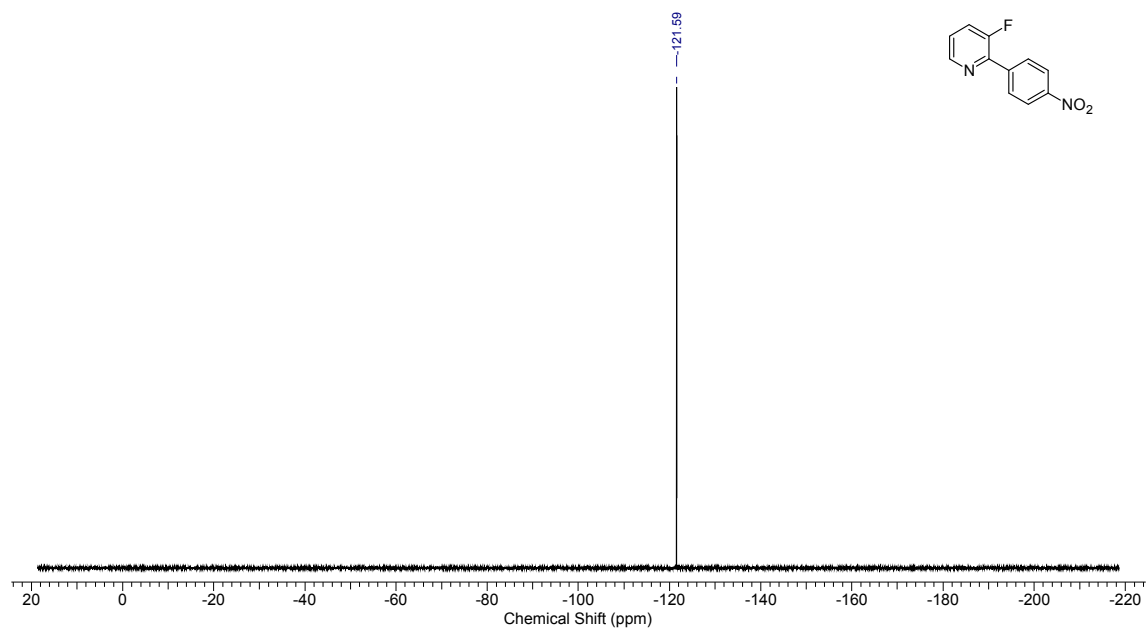
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

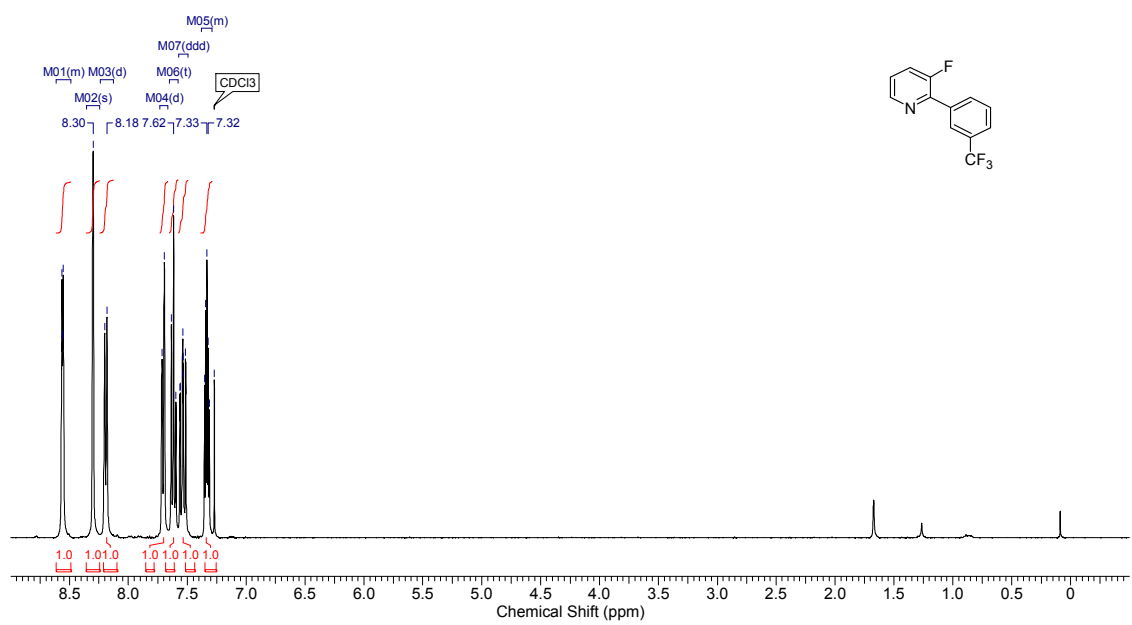


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

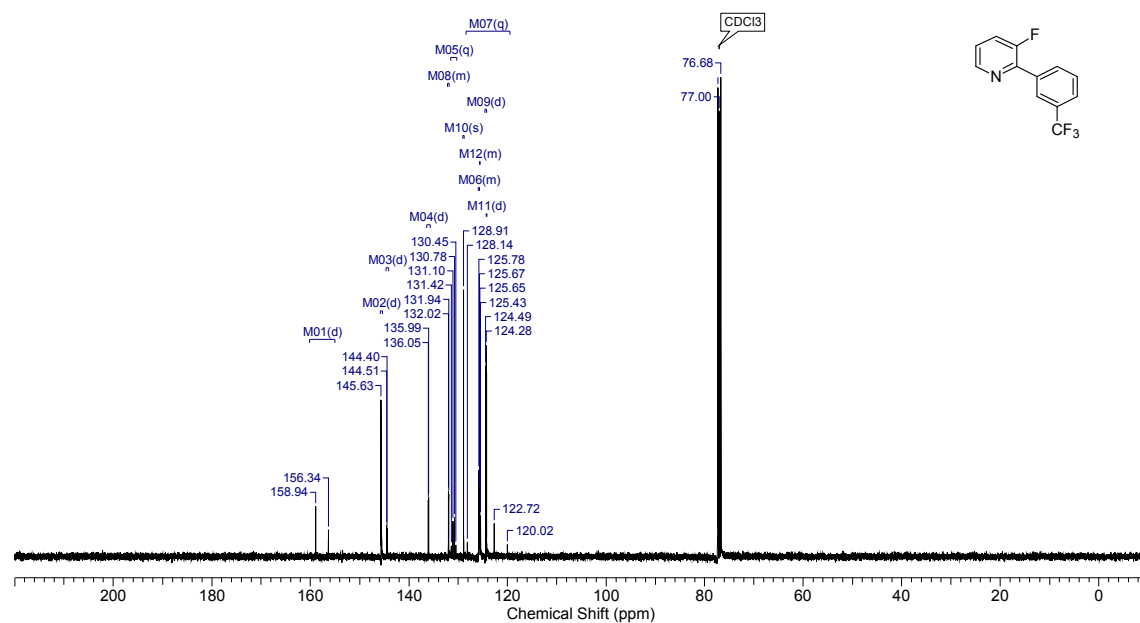


3-Fluoro-2-[3-(trifluoromethyl)phenyl]pyridine (**3a1**)

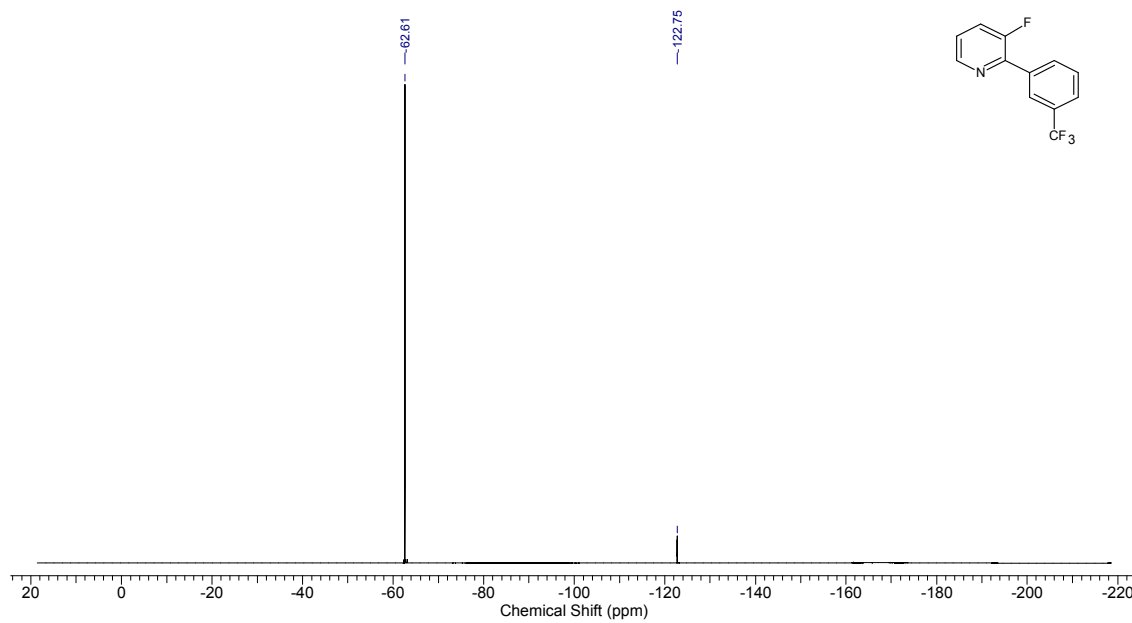
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

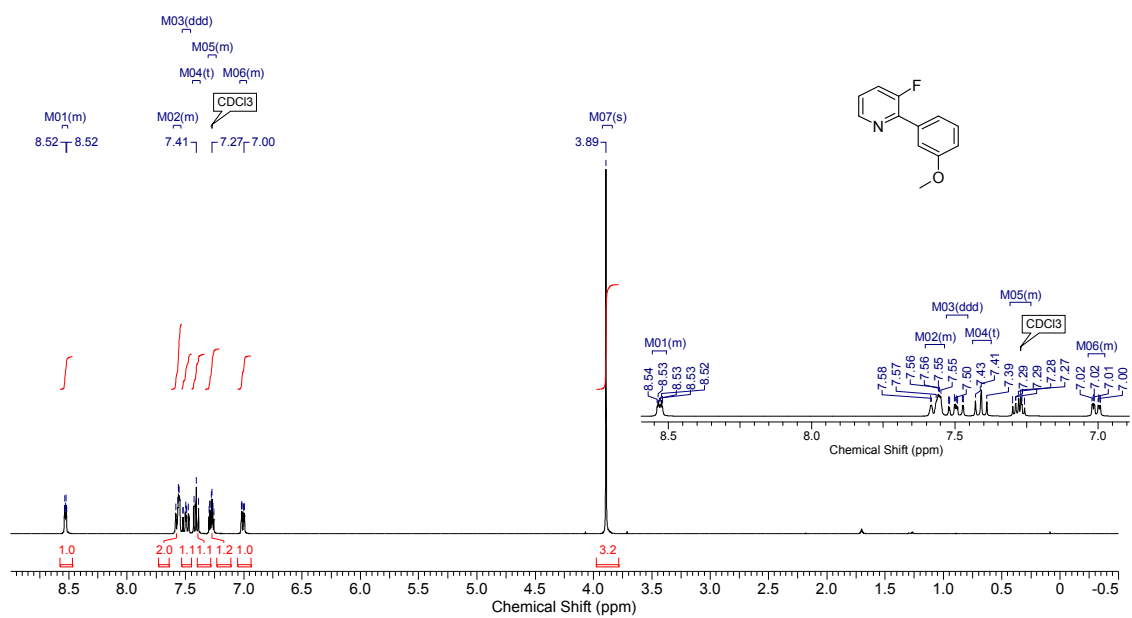


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

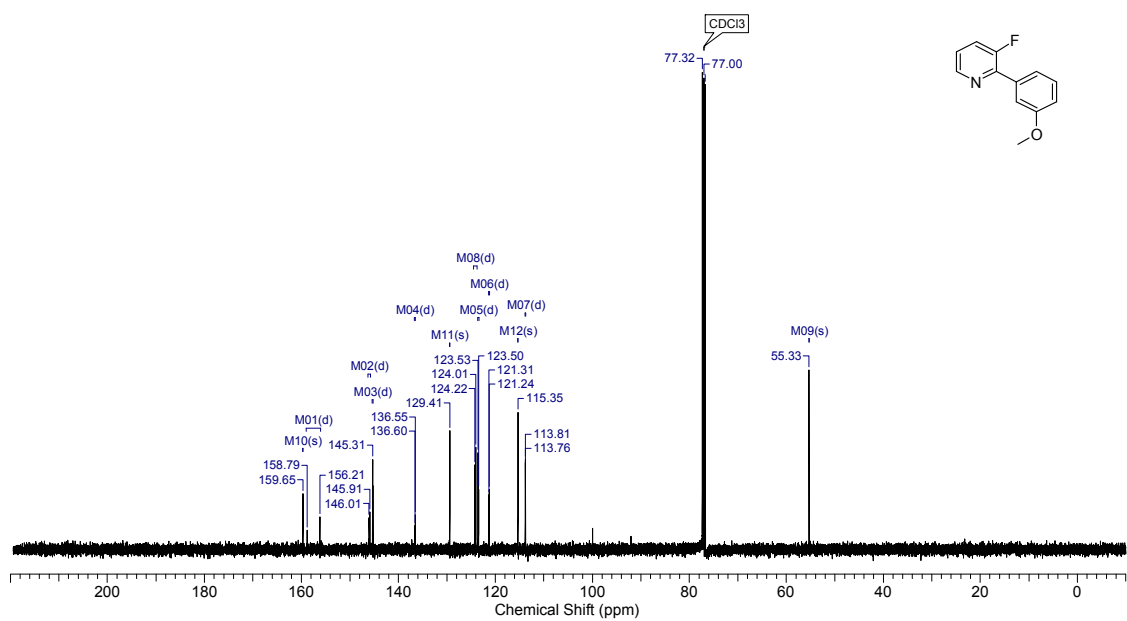


### 3-Fluoro-2-(3-methoxyphenyl)pyridine (**3am**)

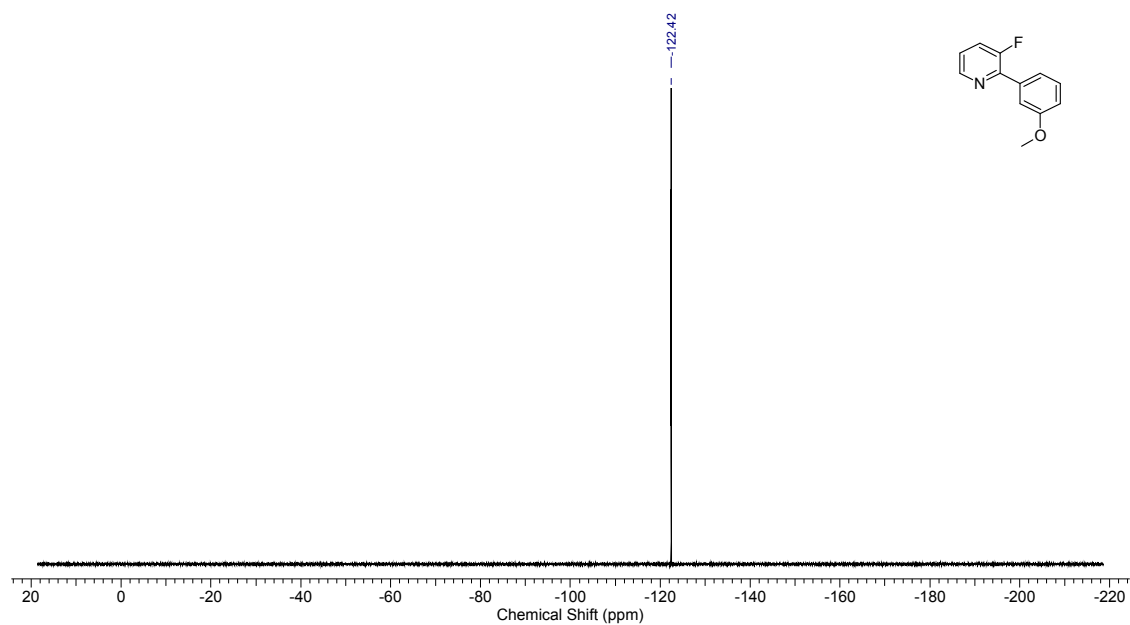
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$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

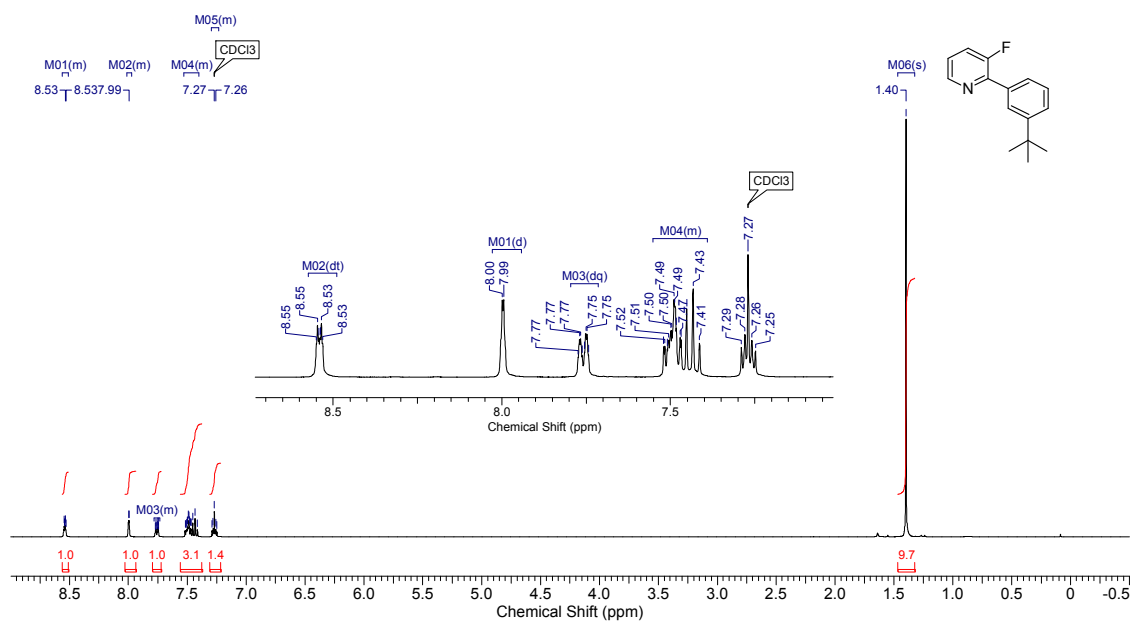


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)



2-[3-(*tert*-Butyl)phenyl]-3-fluoropyridine (**3an**)

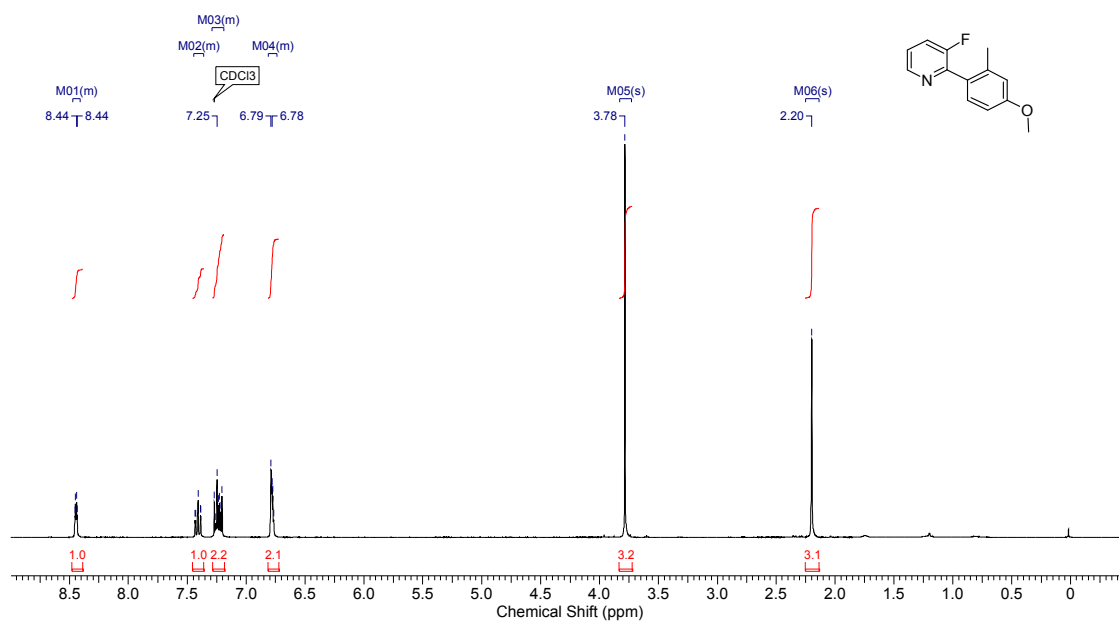
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) (from method B)



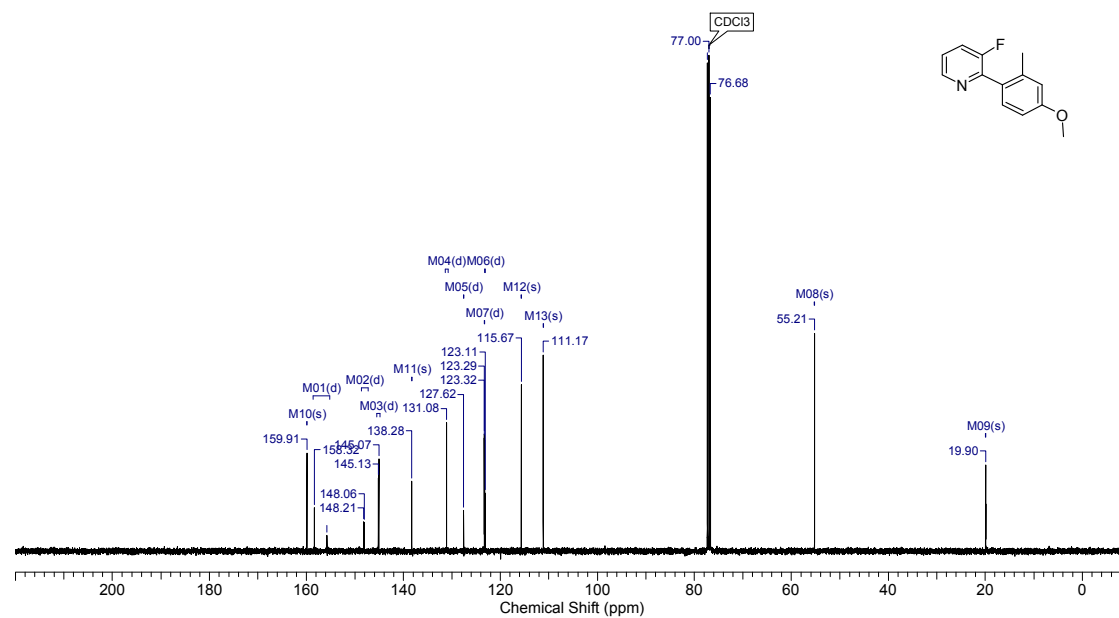


### 3-Fluoro-2-(5-methoxy-2-methylphenyl)pyridine (**3ao**)

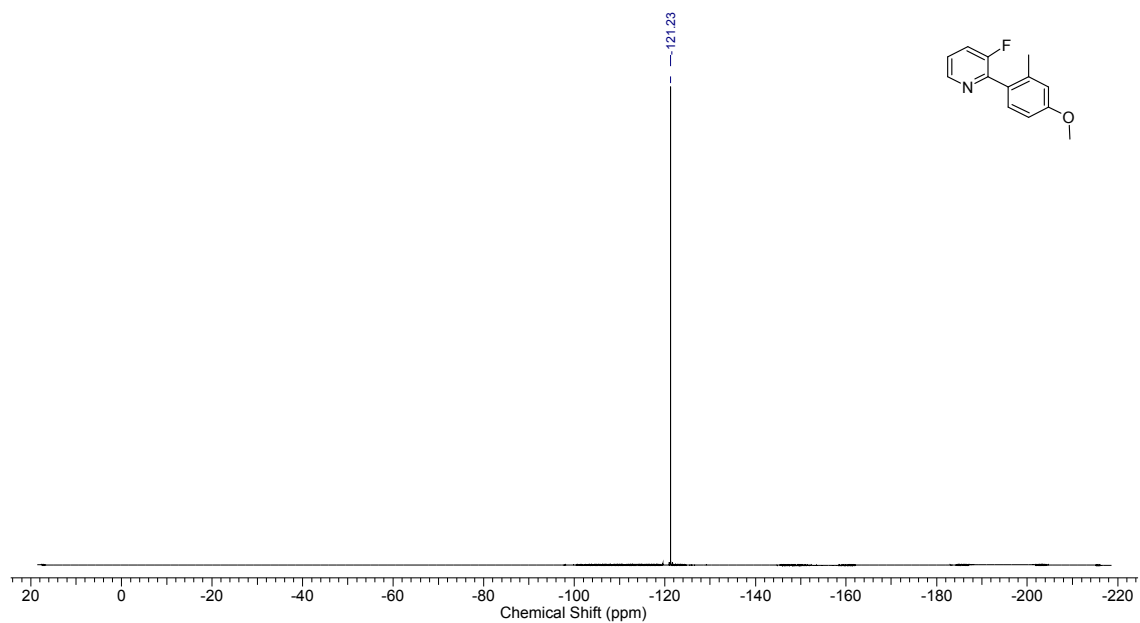
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

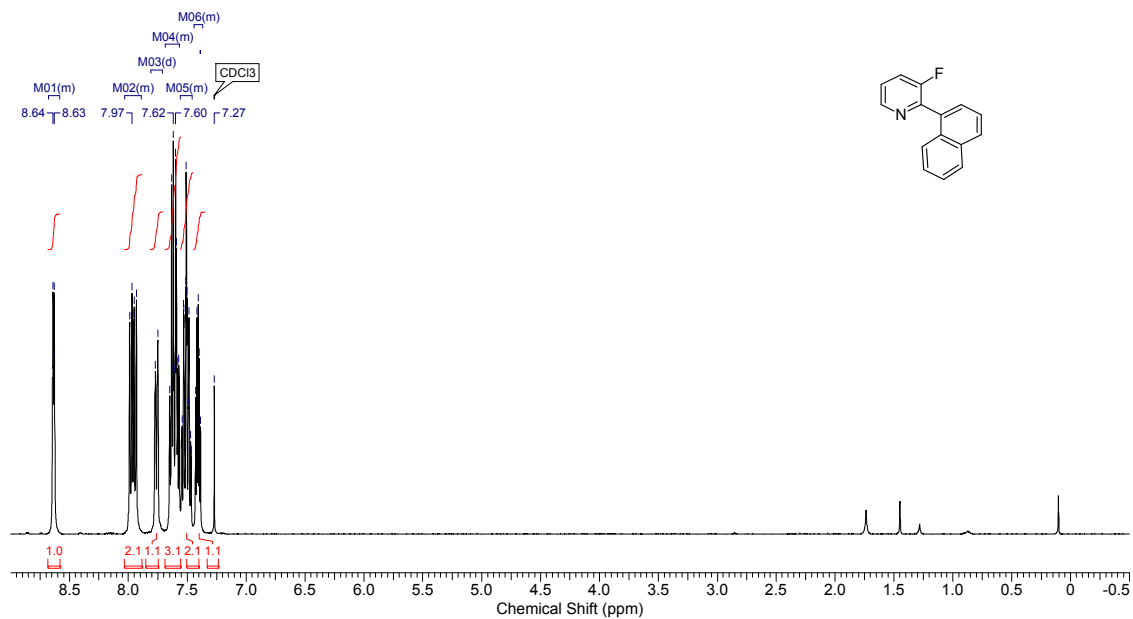


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

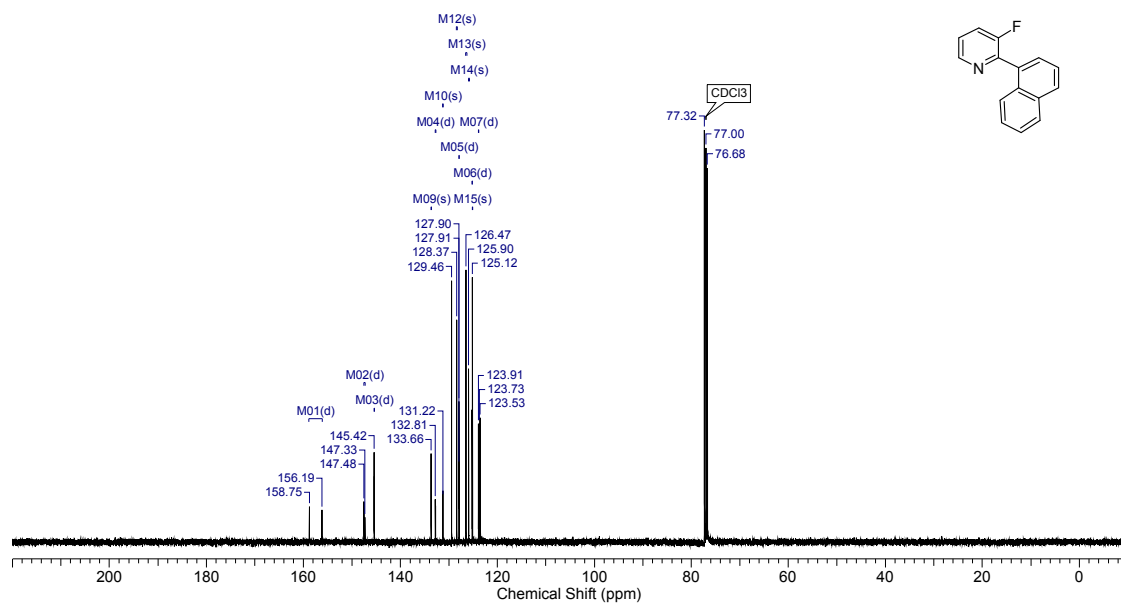


3-Fluoro-2-(1-naphthalenyl)pyridine (**3ap**)

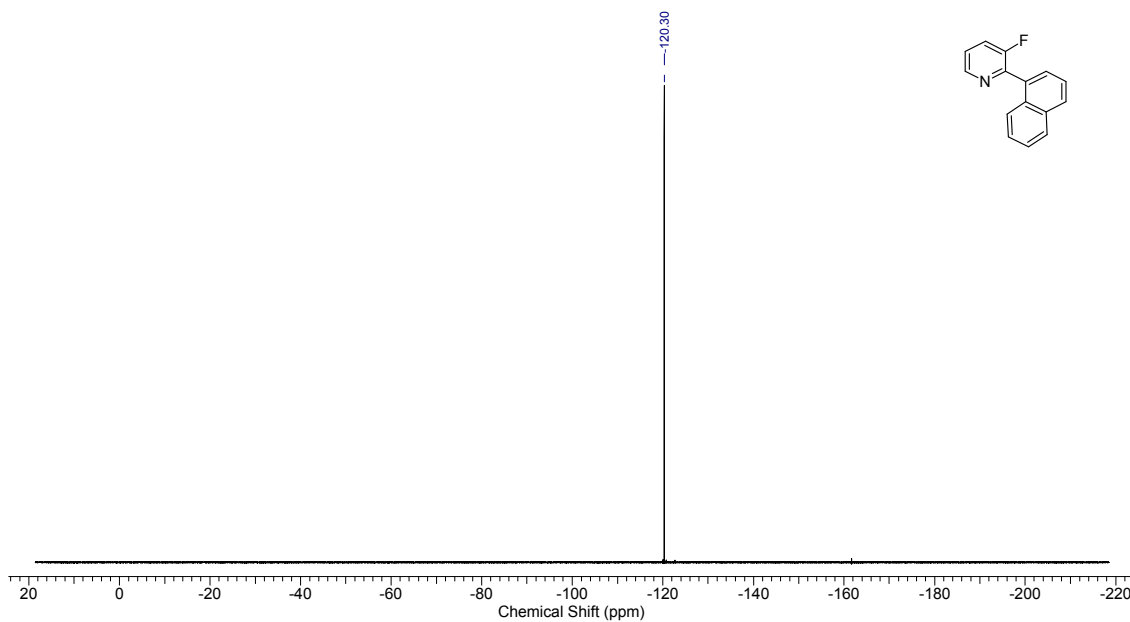
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

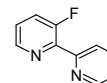
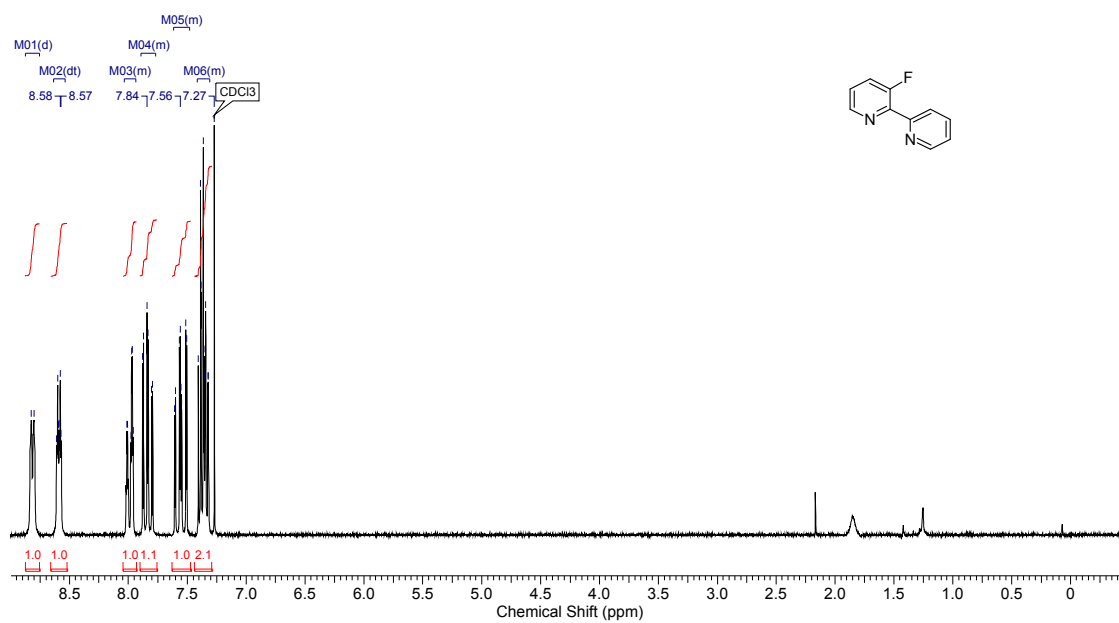


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

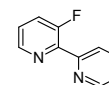
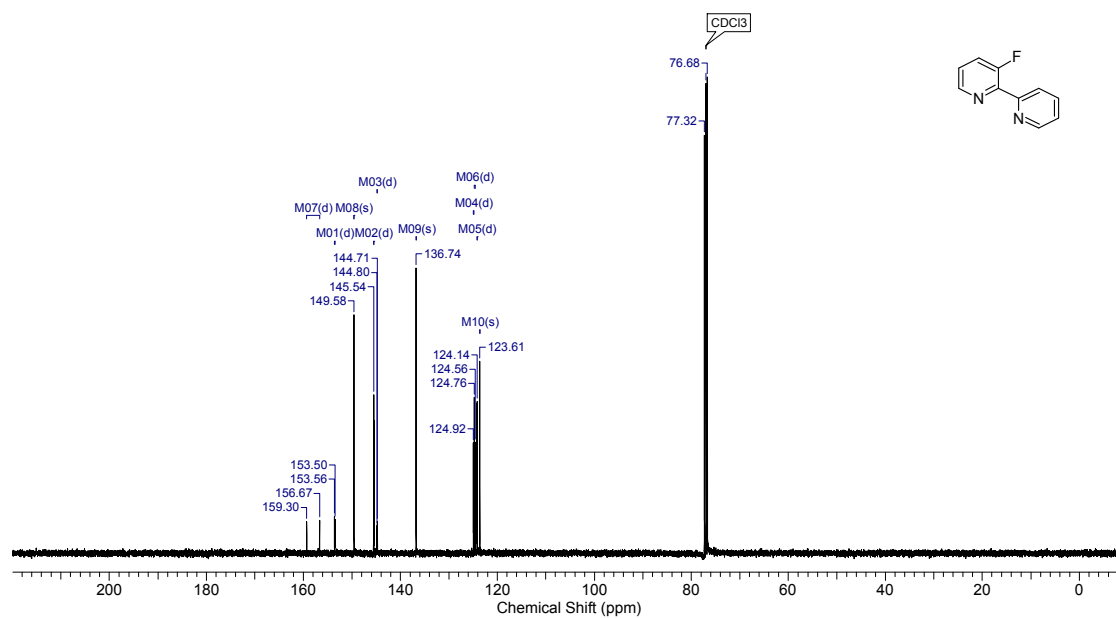


### 3-Fluoro-2,2'-bipyridine (**3aq**)

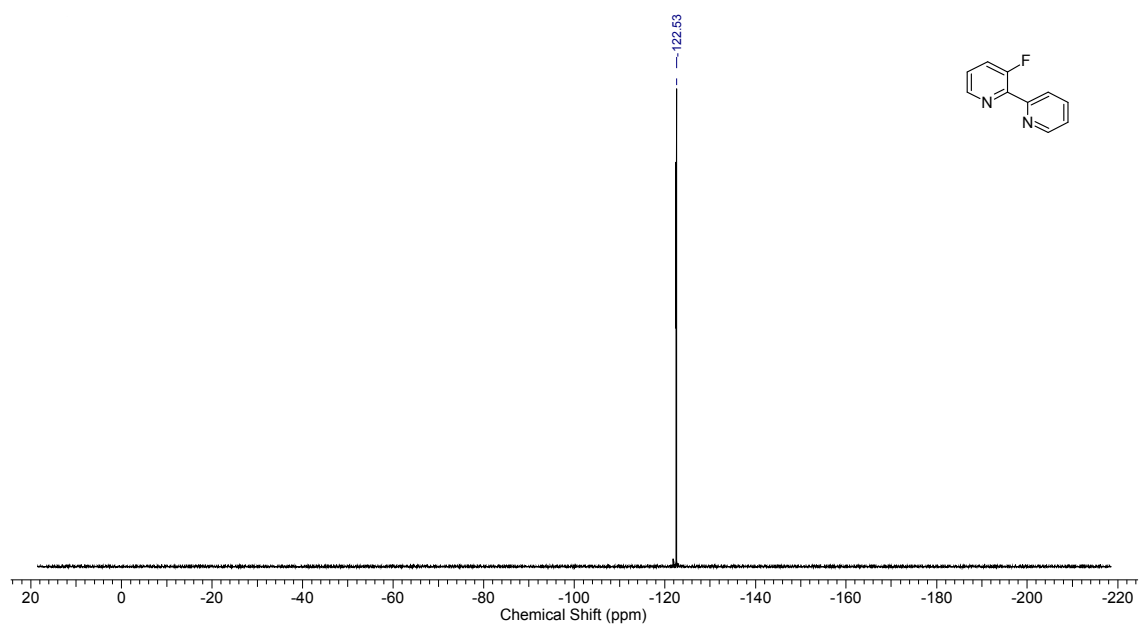
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

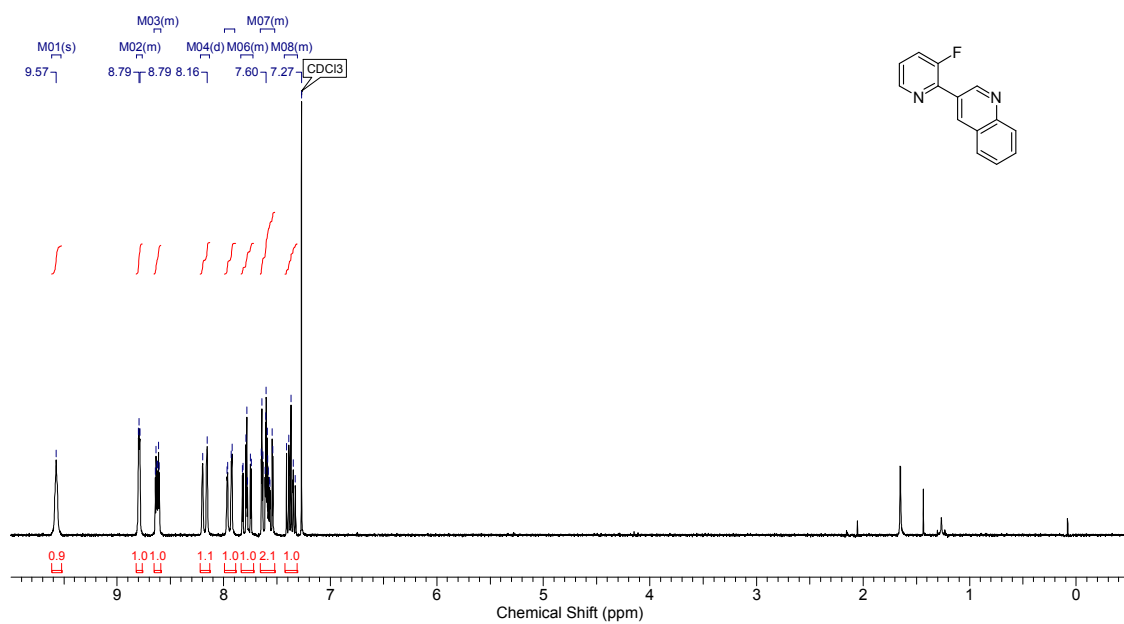


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

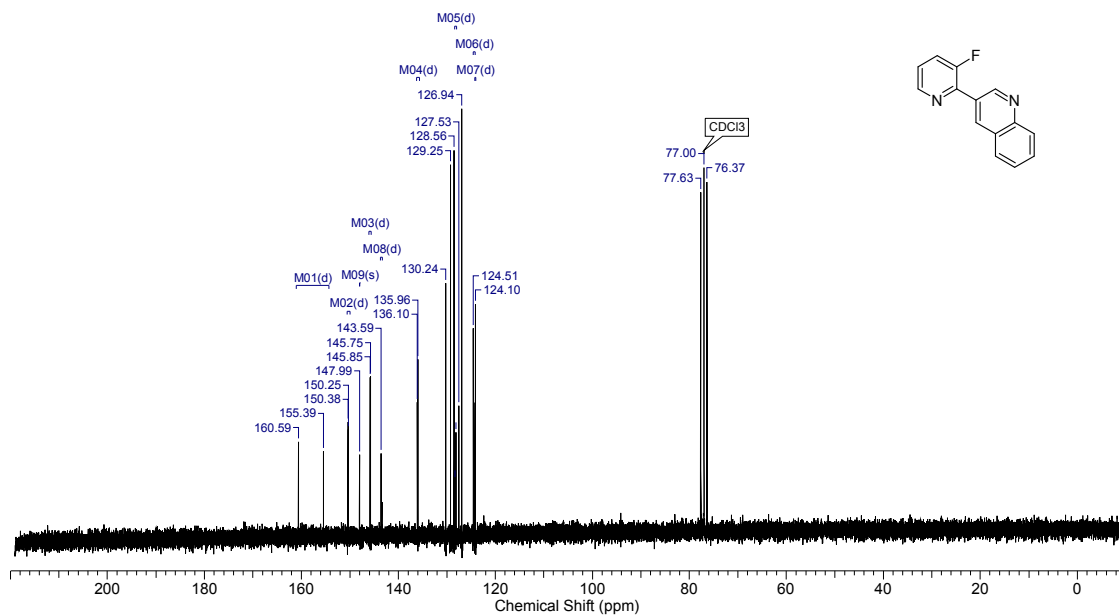


3-(3-Fluoro-2-pyridinyl)quinolone (**3ar**)

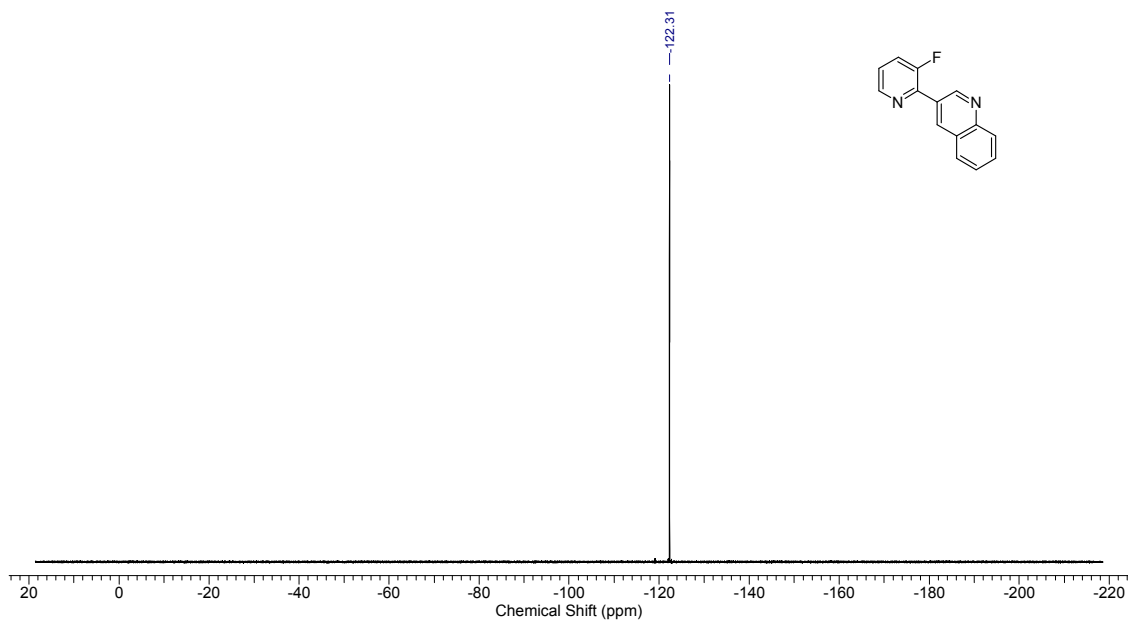
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

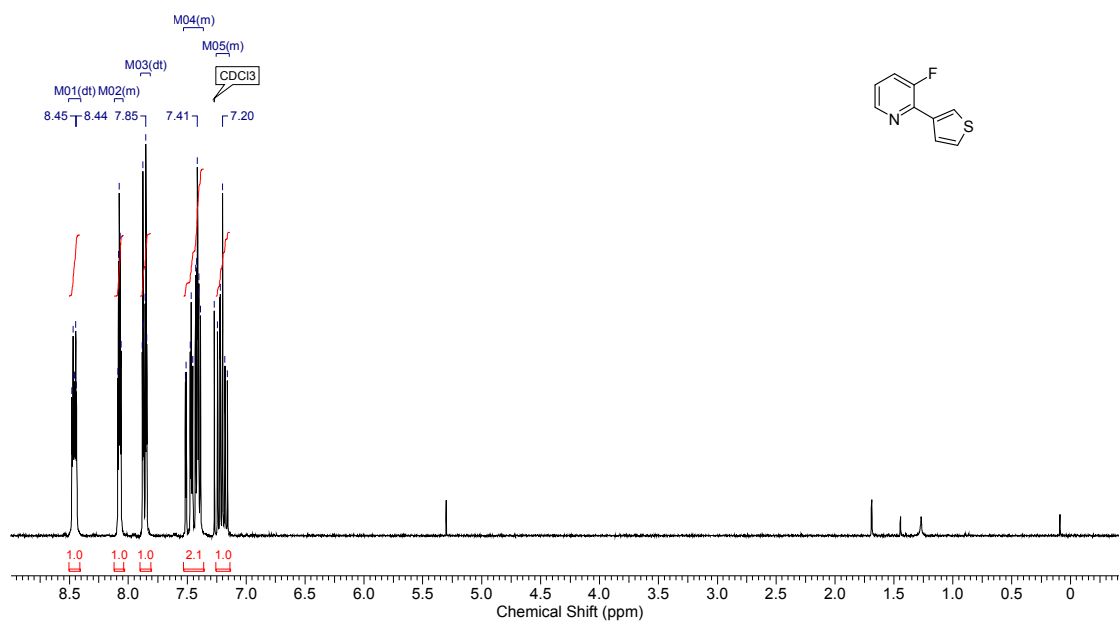


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

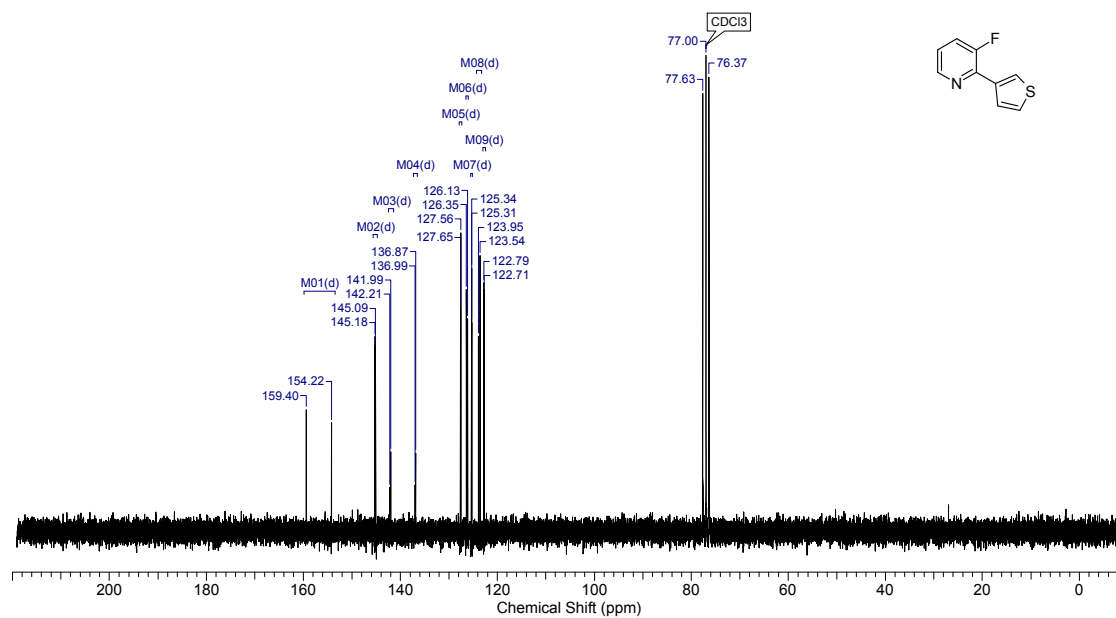


### 3-Fluoro-2-(3-thienyl)pyridine (**3as**)

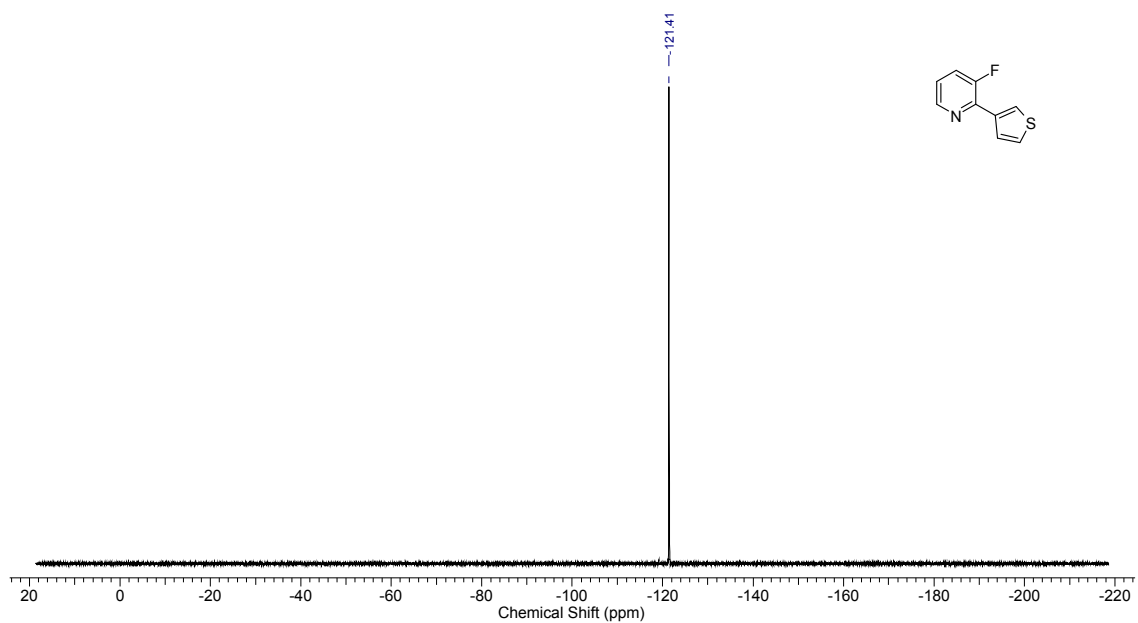
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

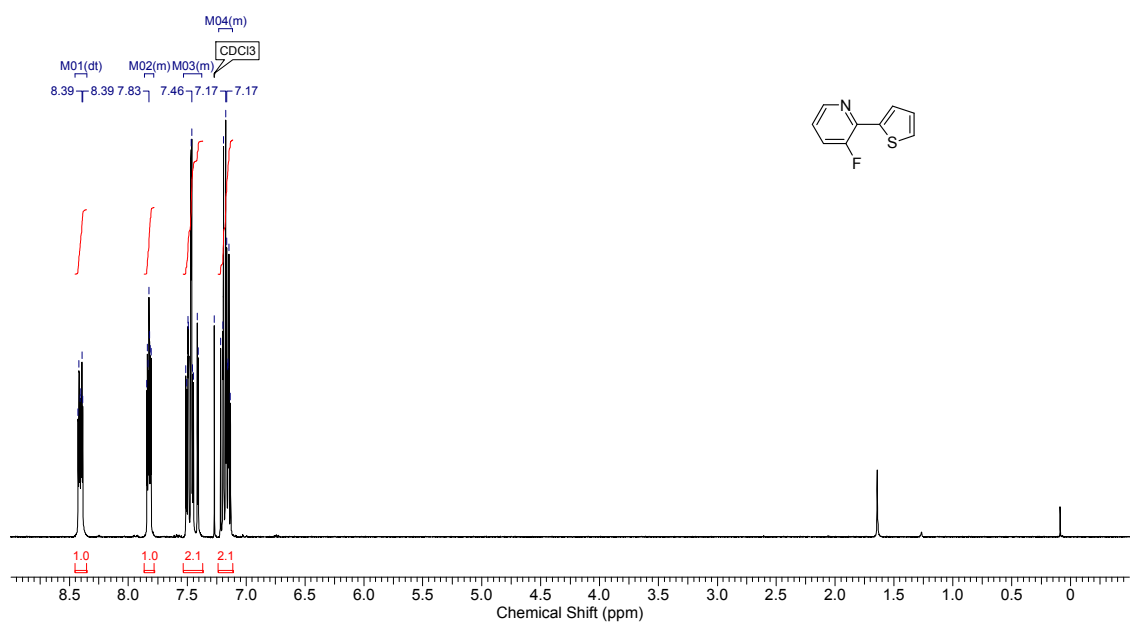


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

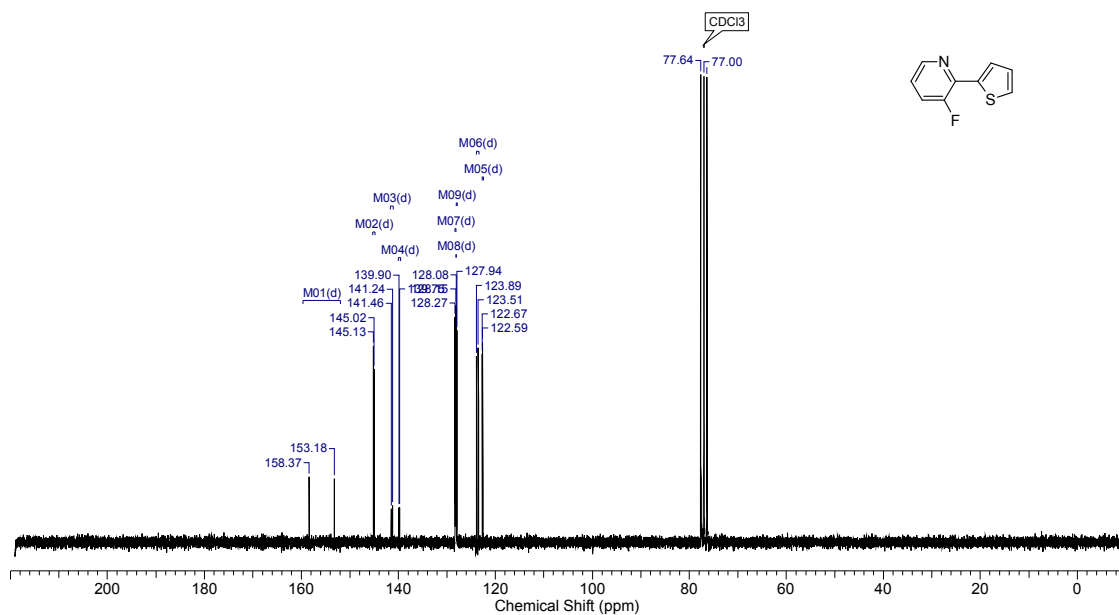


3-Fluoro-2-(2-thienyl)pyridine (**3at**)

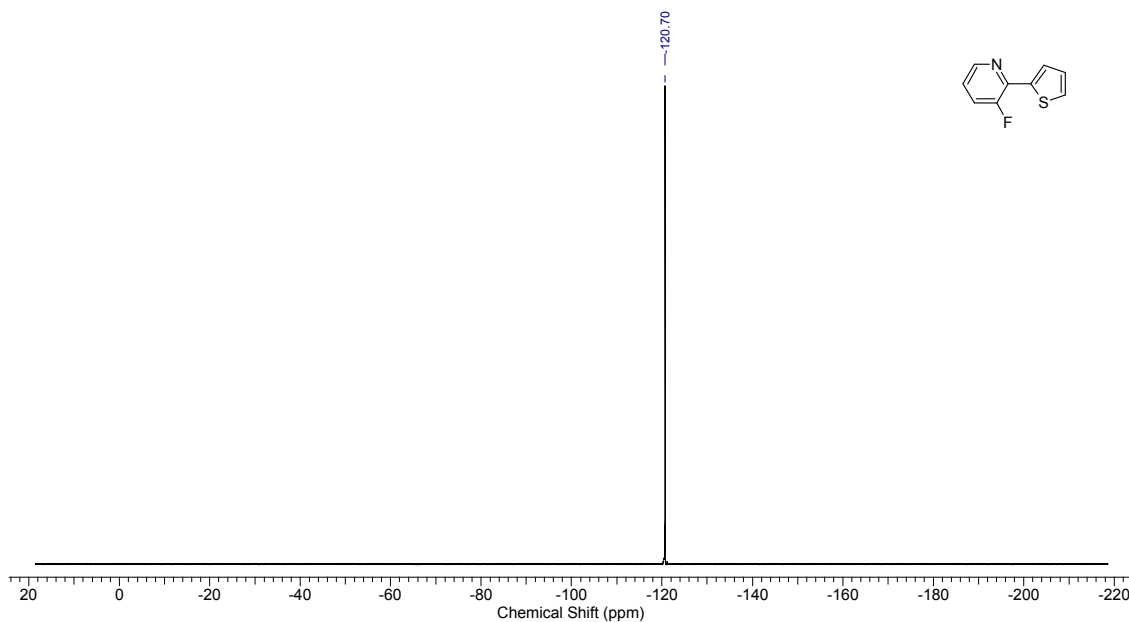
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

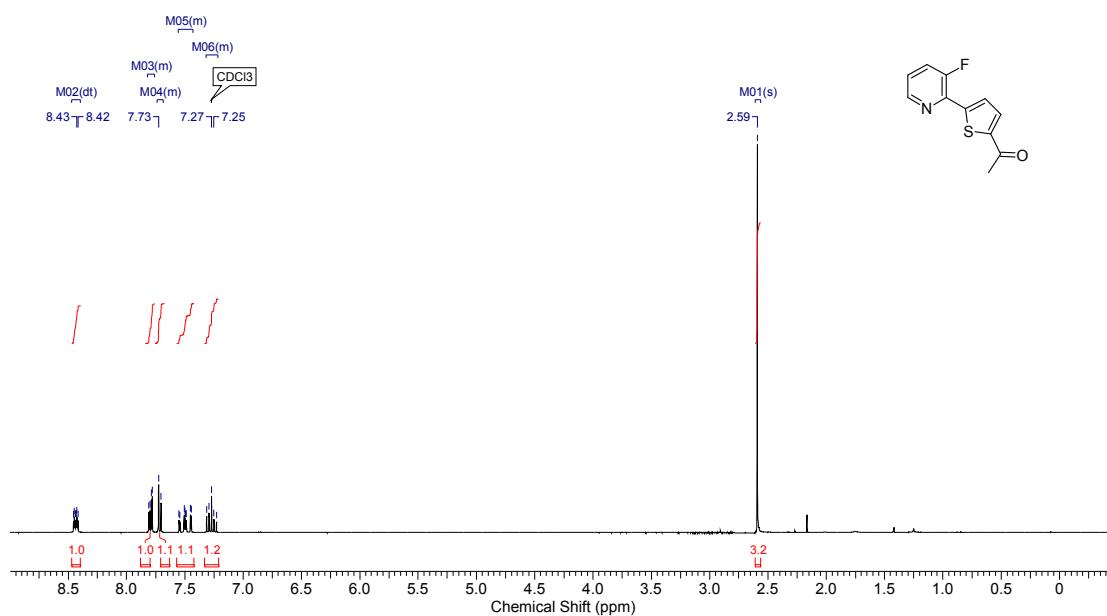


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

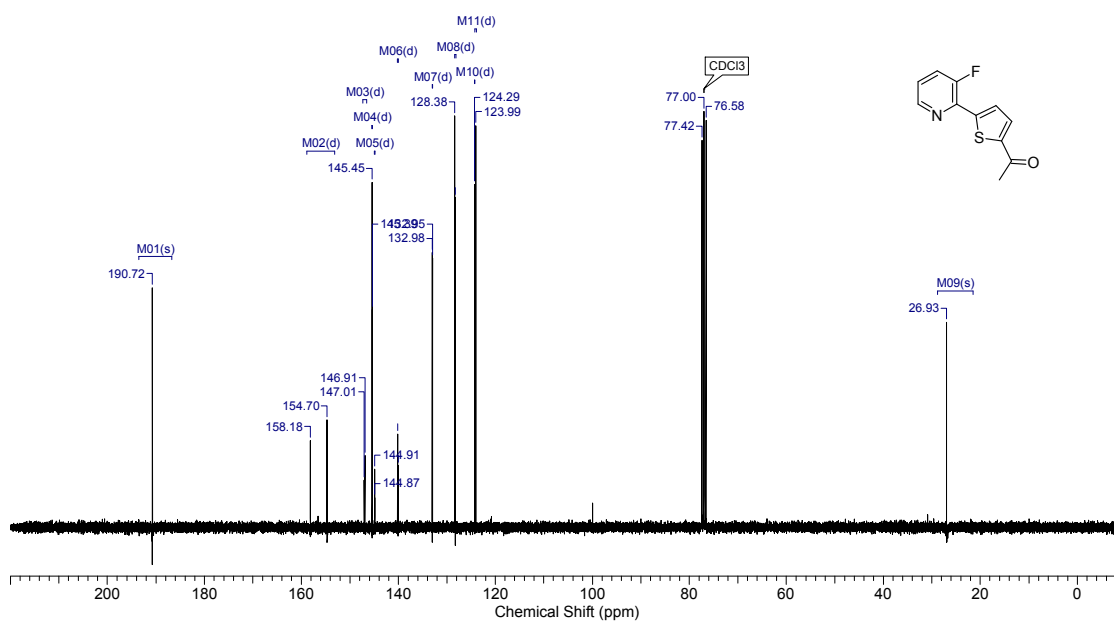


# 1-[5-(3-Fluoro-2-pyridinyl)-2-thienyl]ethanone (**3au**)

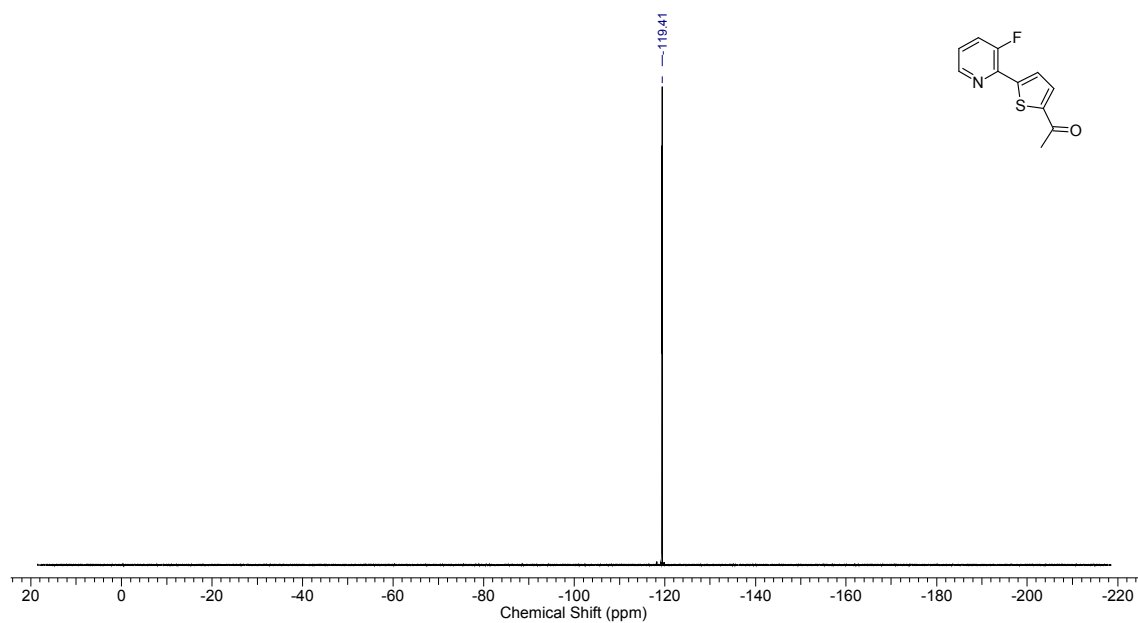
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)

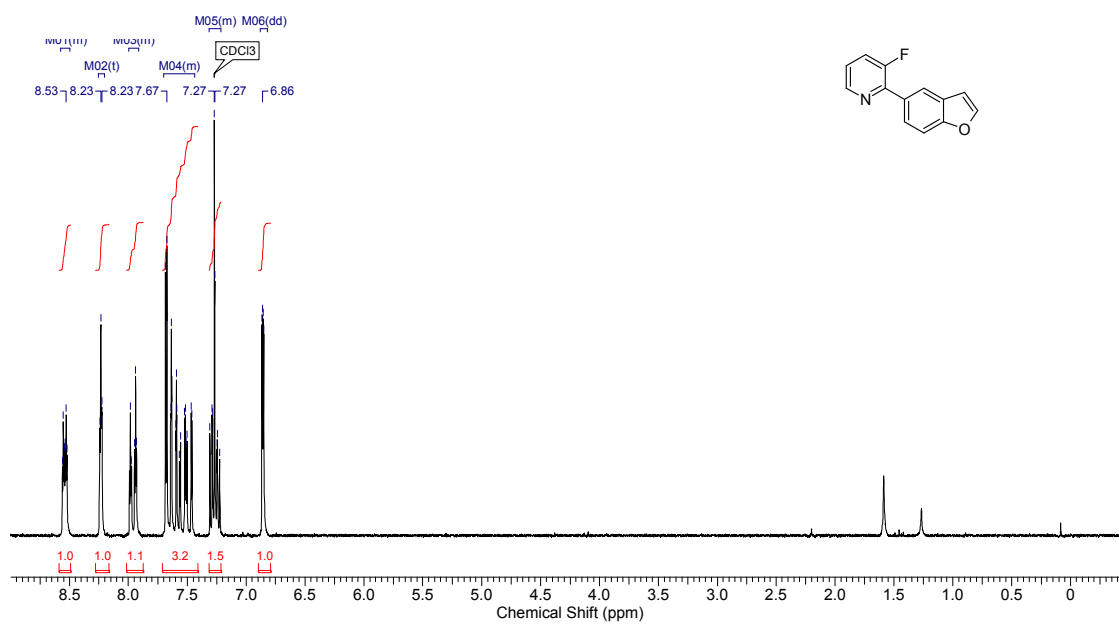


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

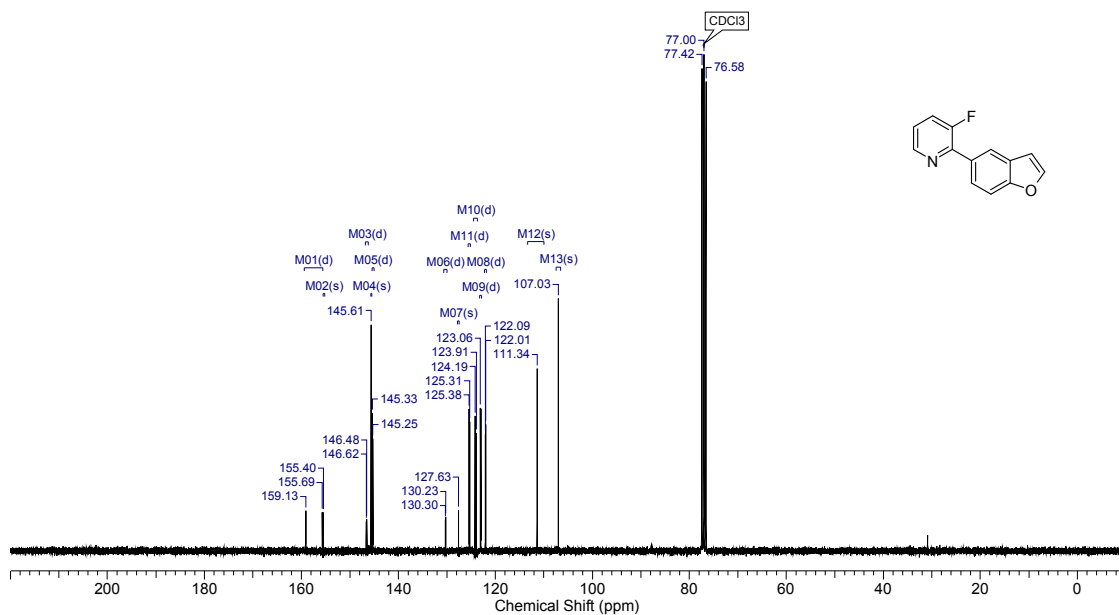


3-Fuoro-2-(5-benzofuranyl)pyridine (**3av**)

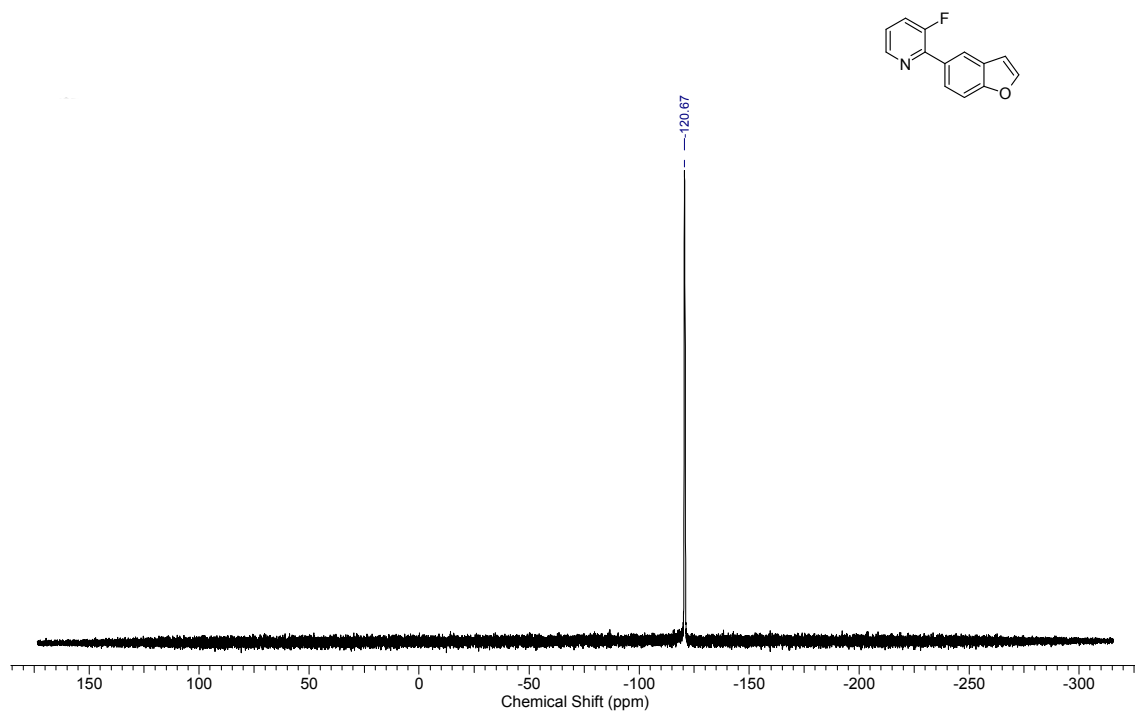
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)

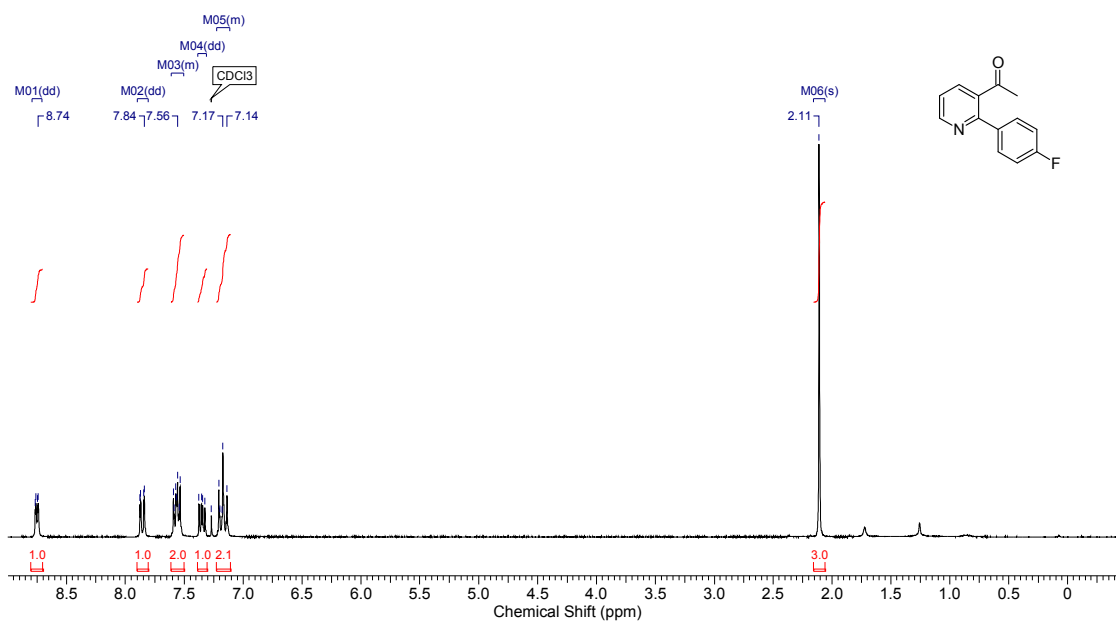


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 41 MHz)

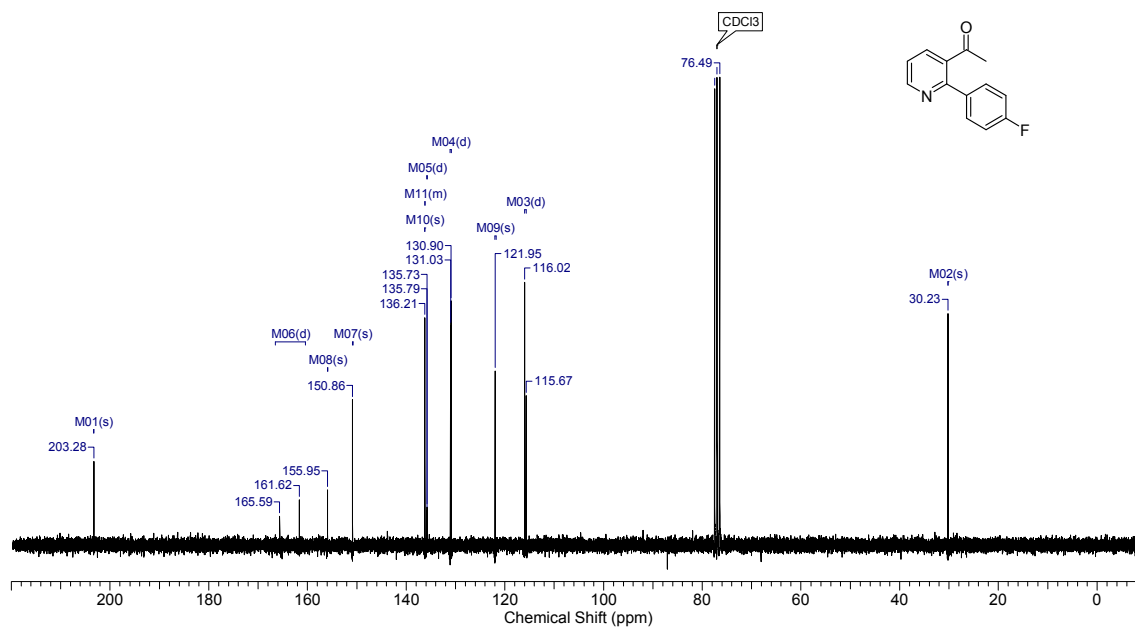


# 1-[2-(4-Fluorophenyl)-3-pyridinyl]ethanone (**3ba**)

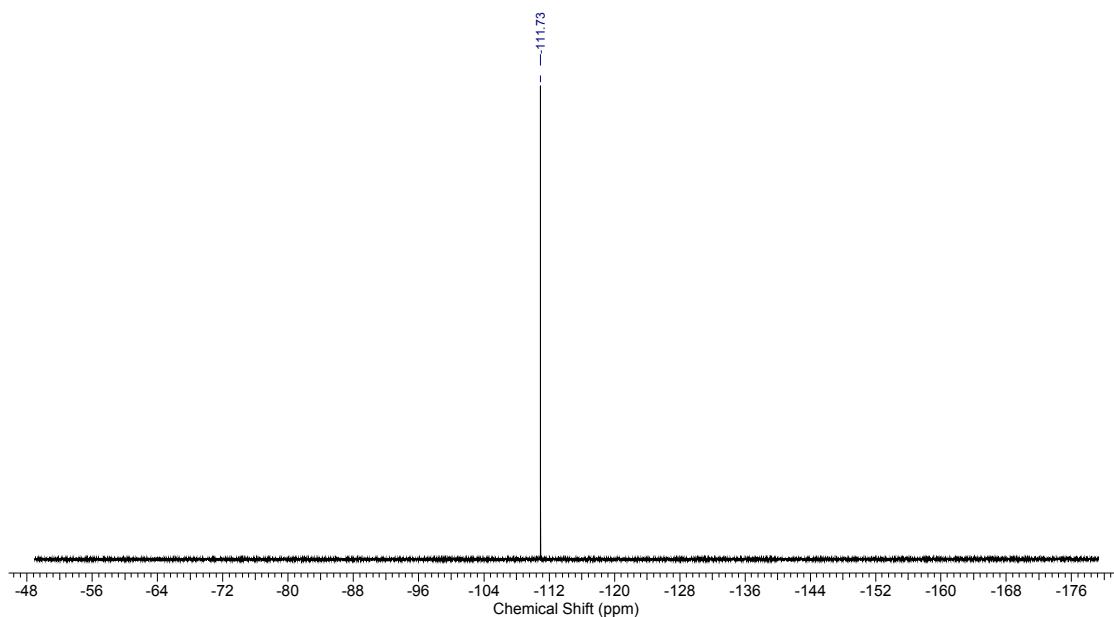
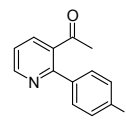
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 63 MHz)

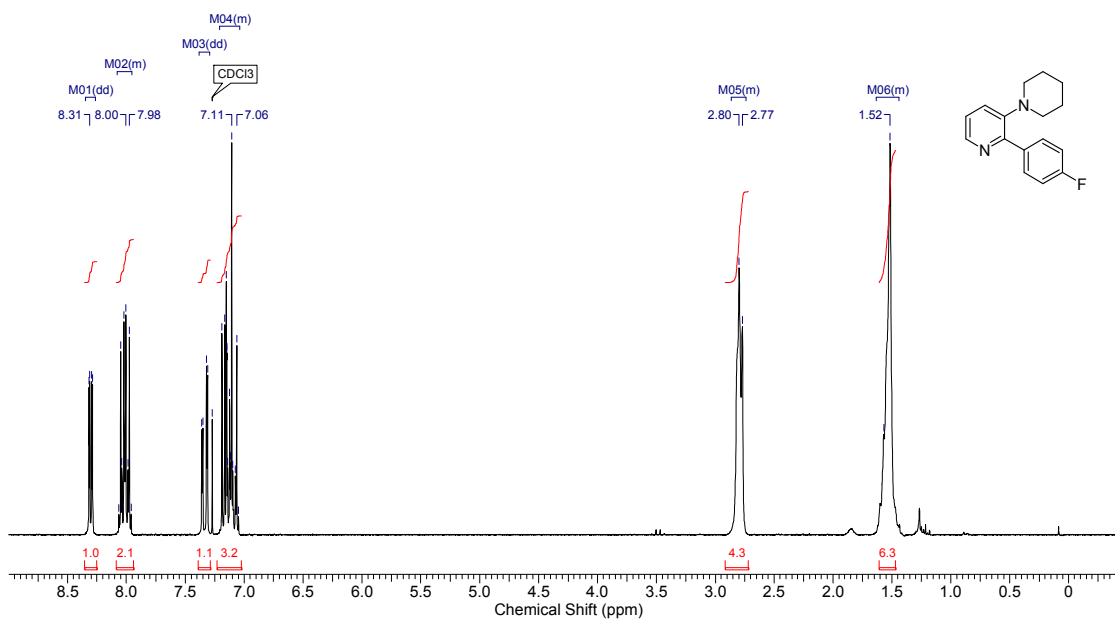


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 235 MHz)

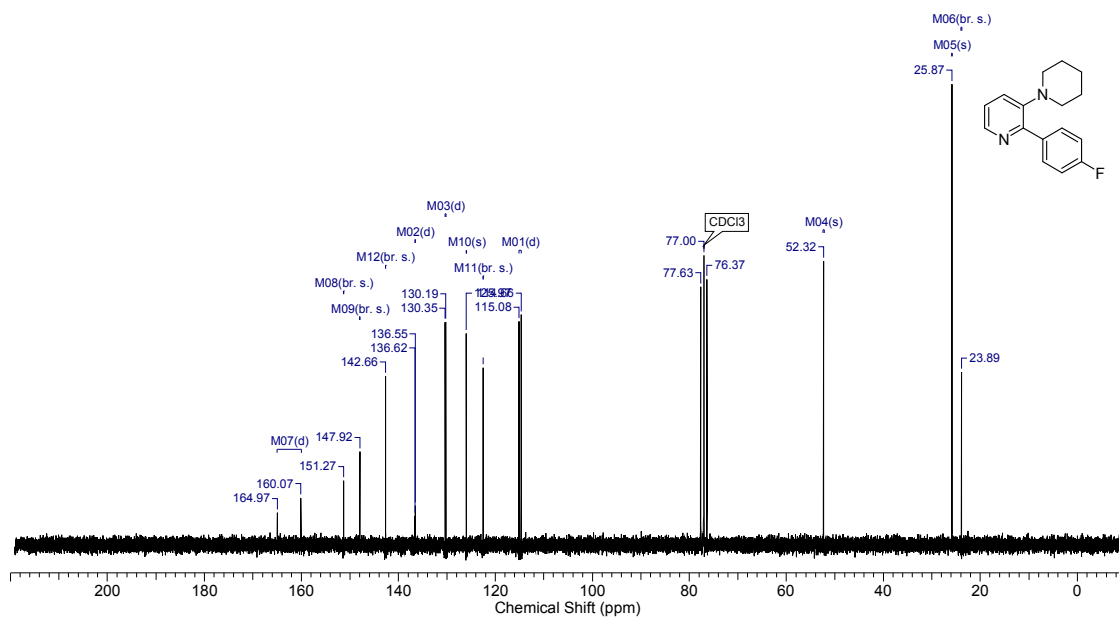


3-(1-Piperidiny)-2-(4-fluorophenyl)pyridine (**3ca**)

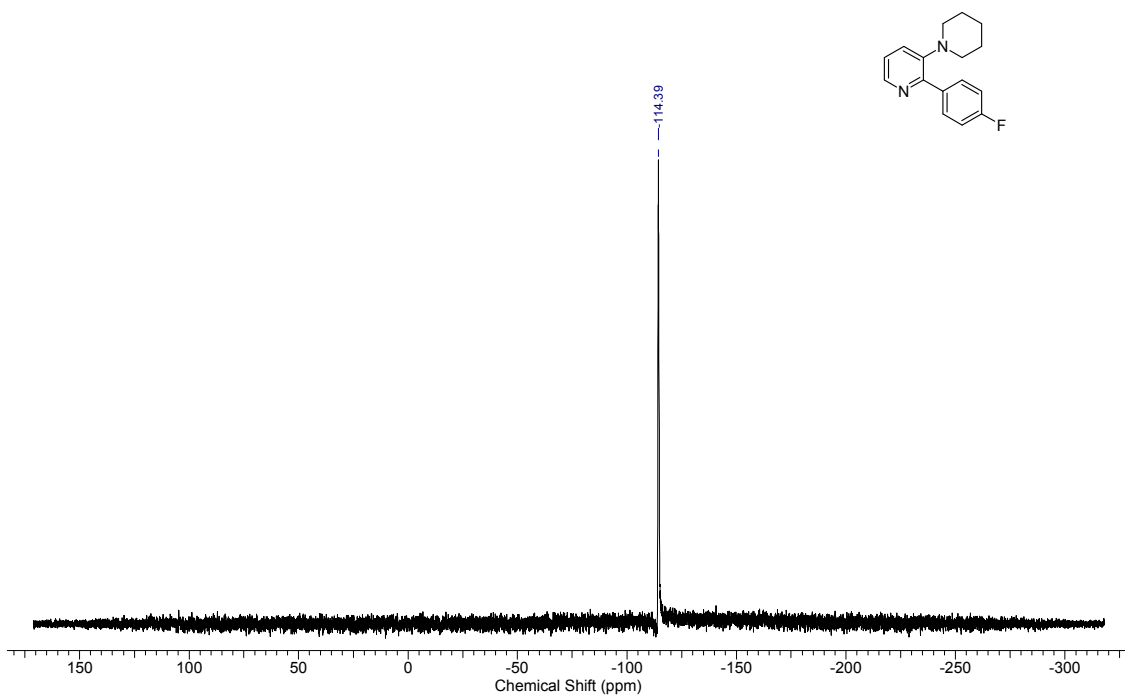
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

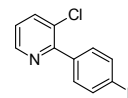
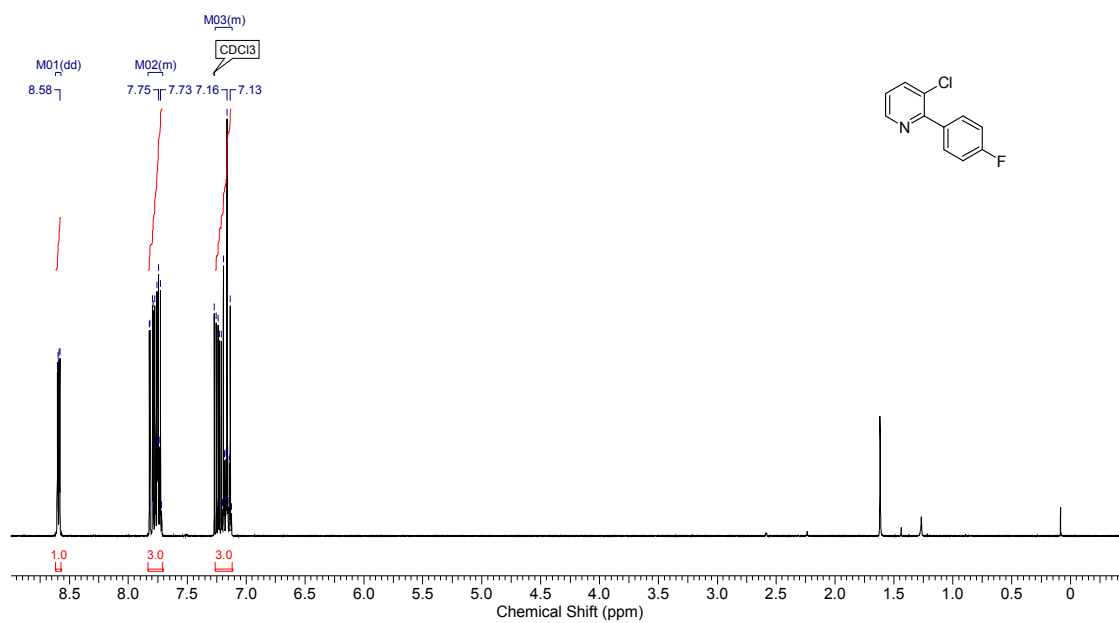


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 41 MHz)

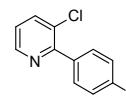
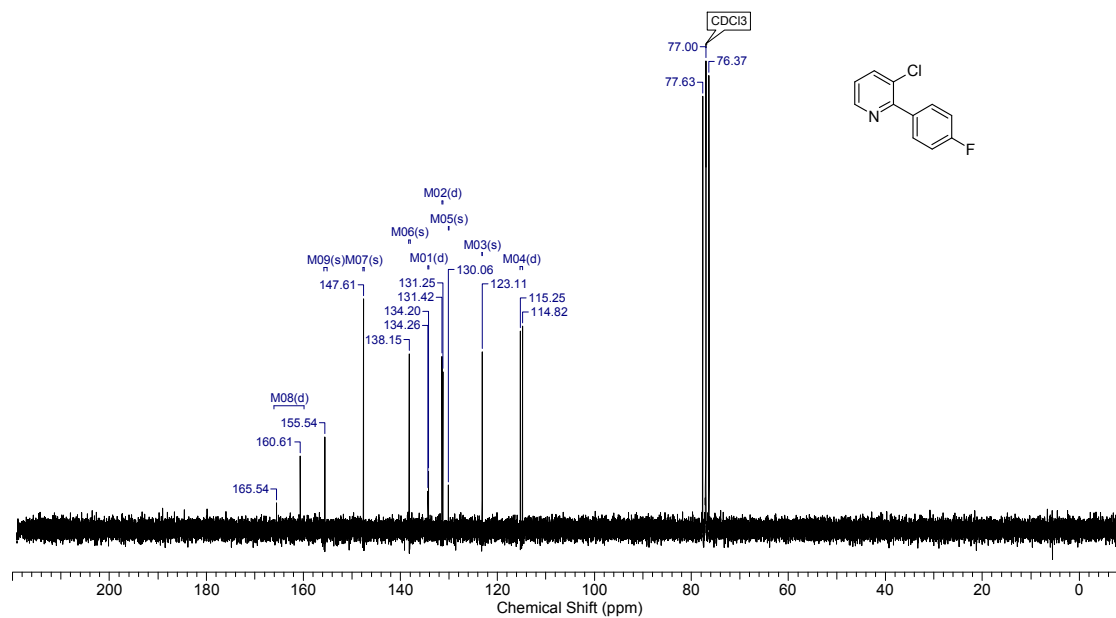


### 3-Chloro-2-(4-fluorophenyl)pyridine (**3da**)

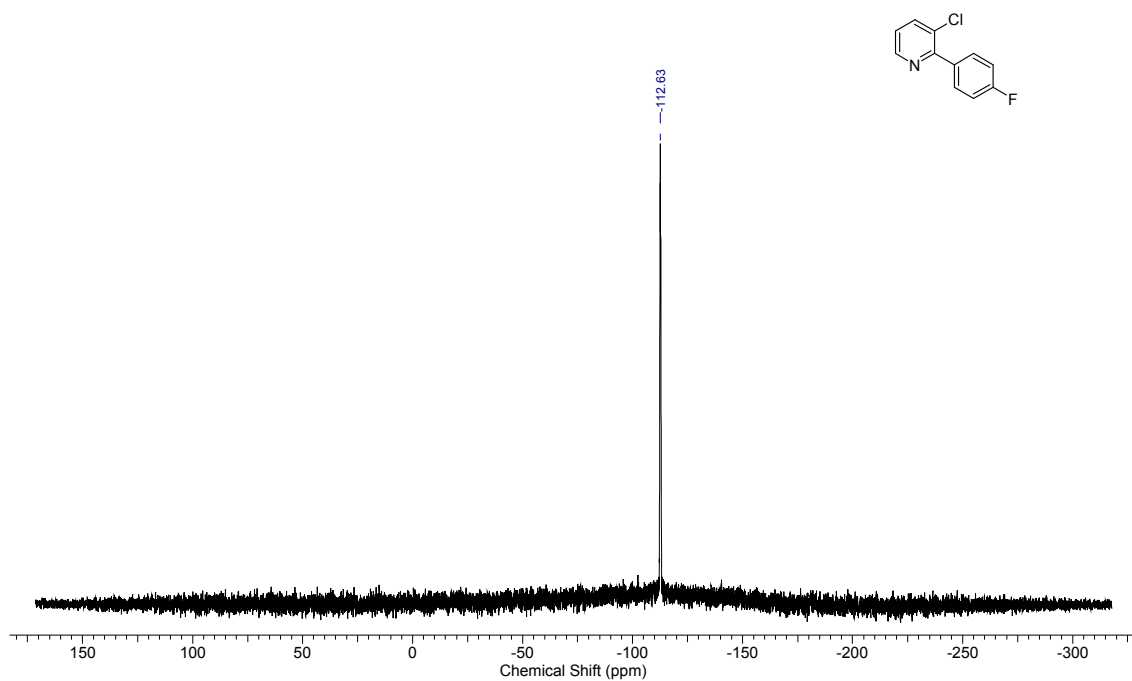
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

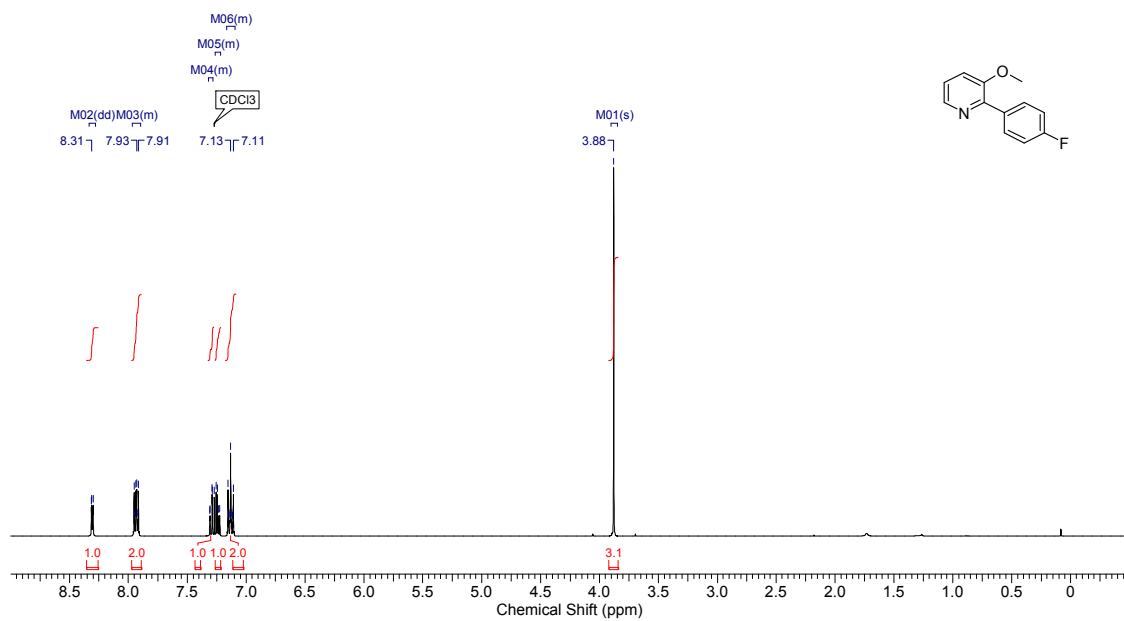


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 41 MHz)

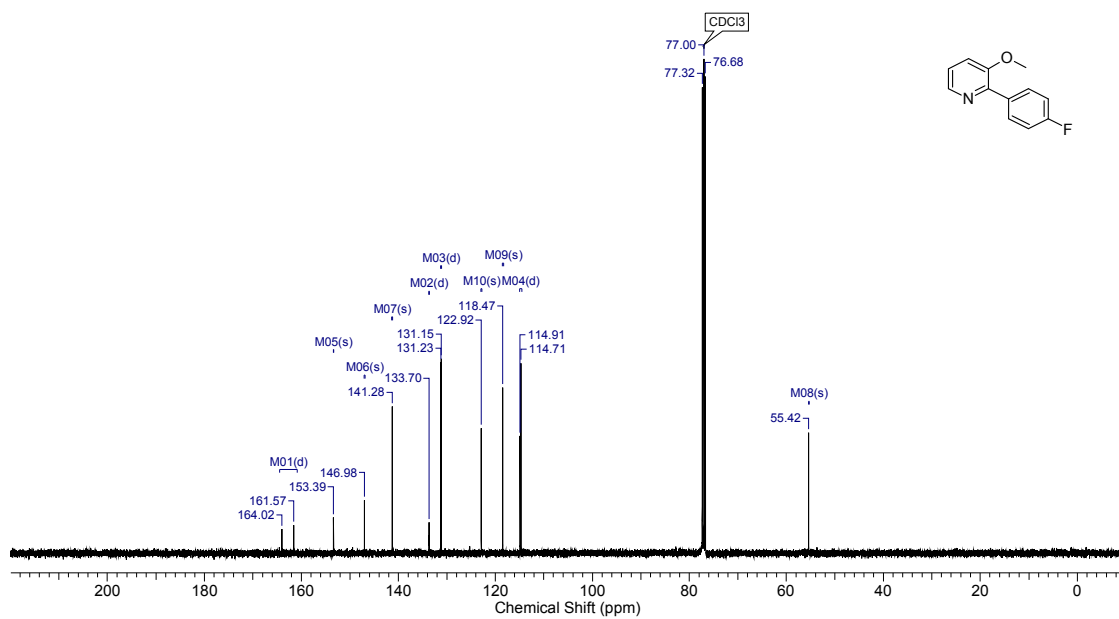


2-(4-fluorophenyl)-3-methoxypyridine (**3ea**)

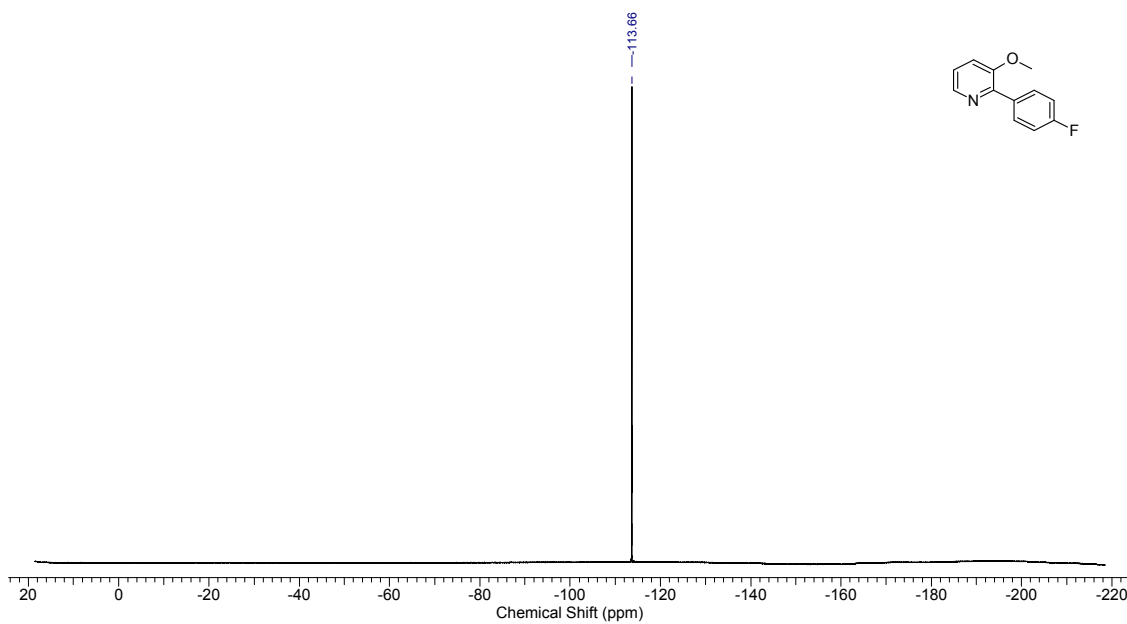
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

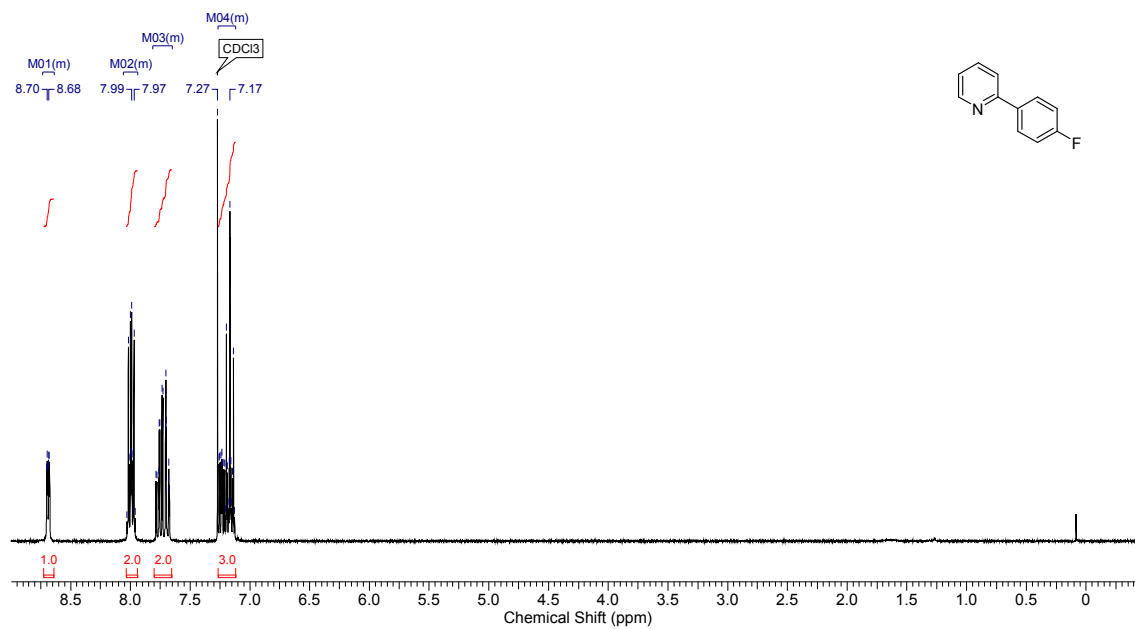


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 377 MHz)

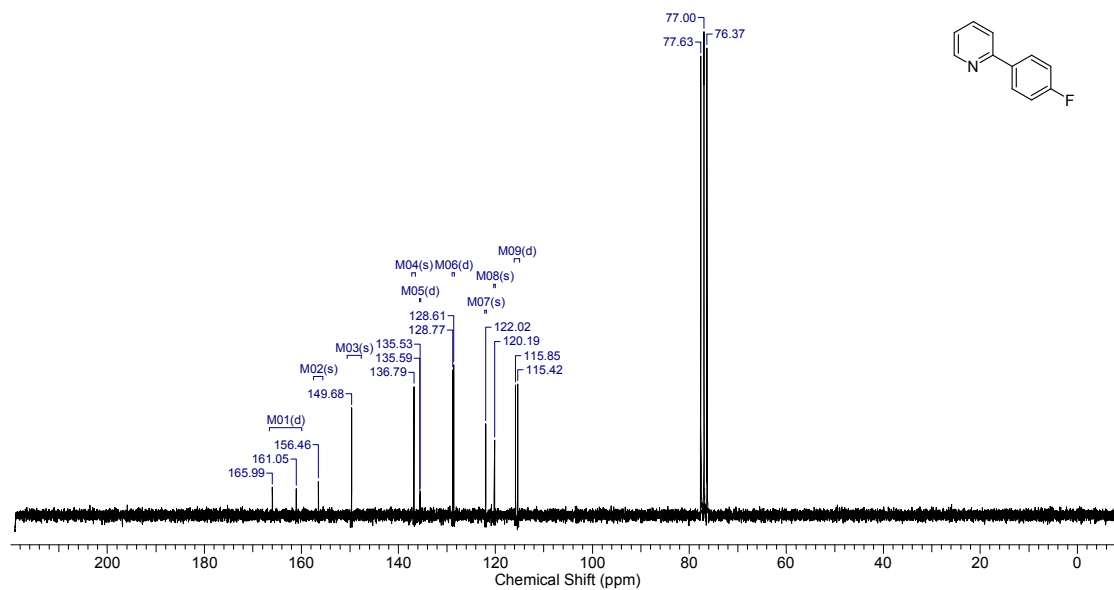


# 2-(4-Fluorophenyl)-pyridine (**3fa**)

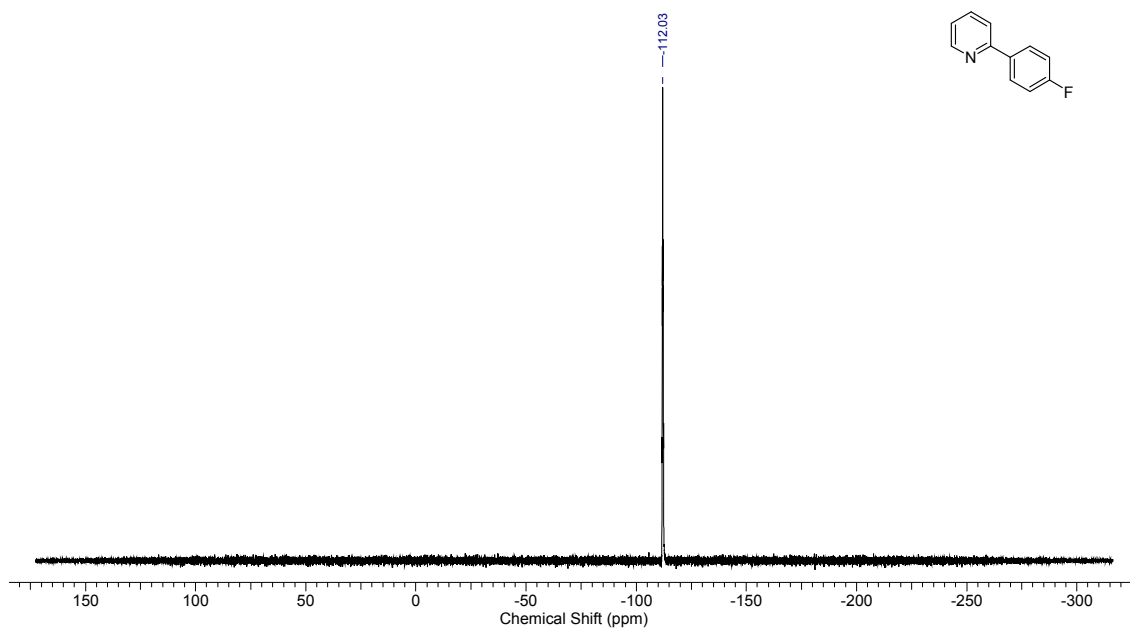
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)

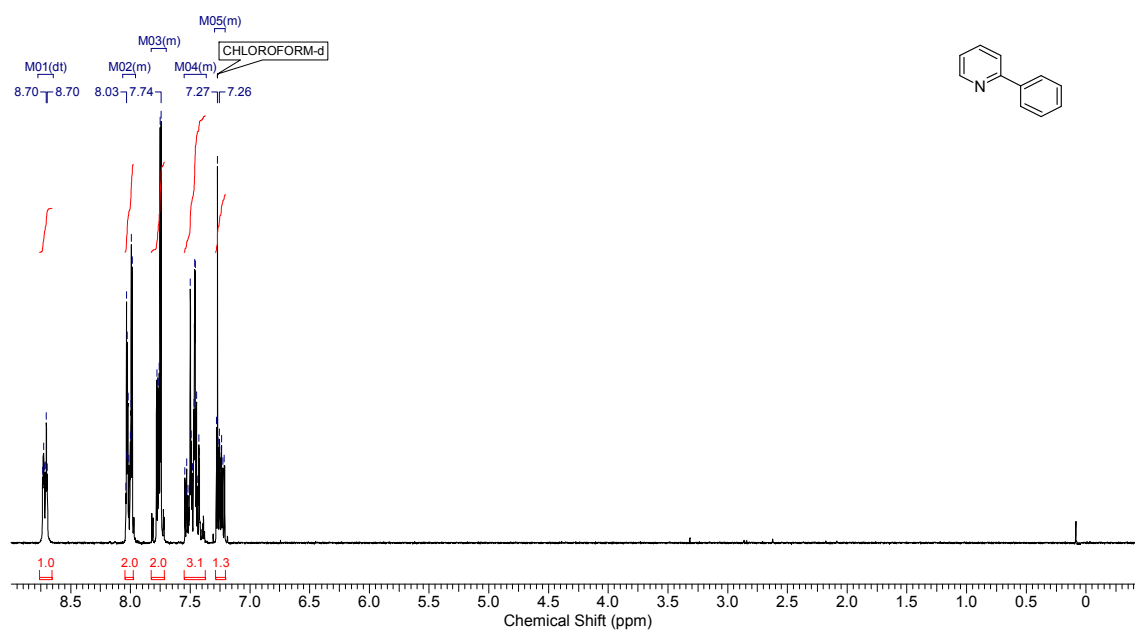


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 41 MHz)

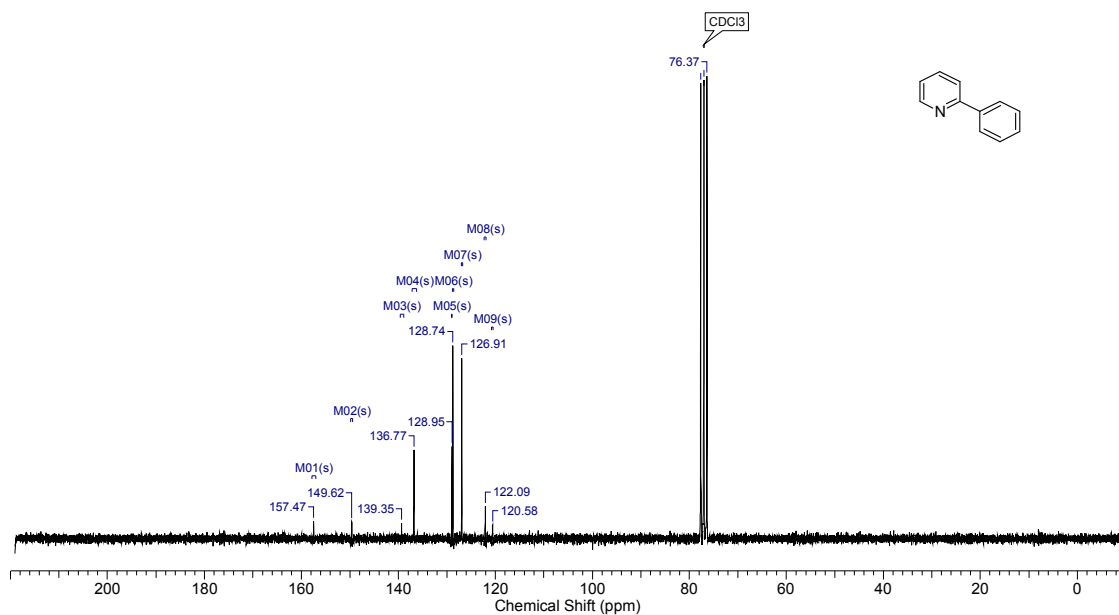


2-Phenylpyridine (**3fb**)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)

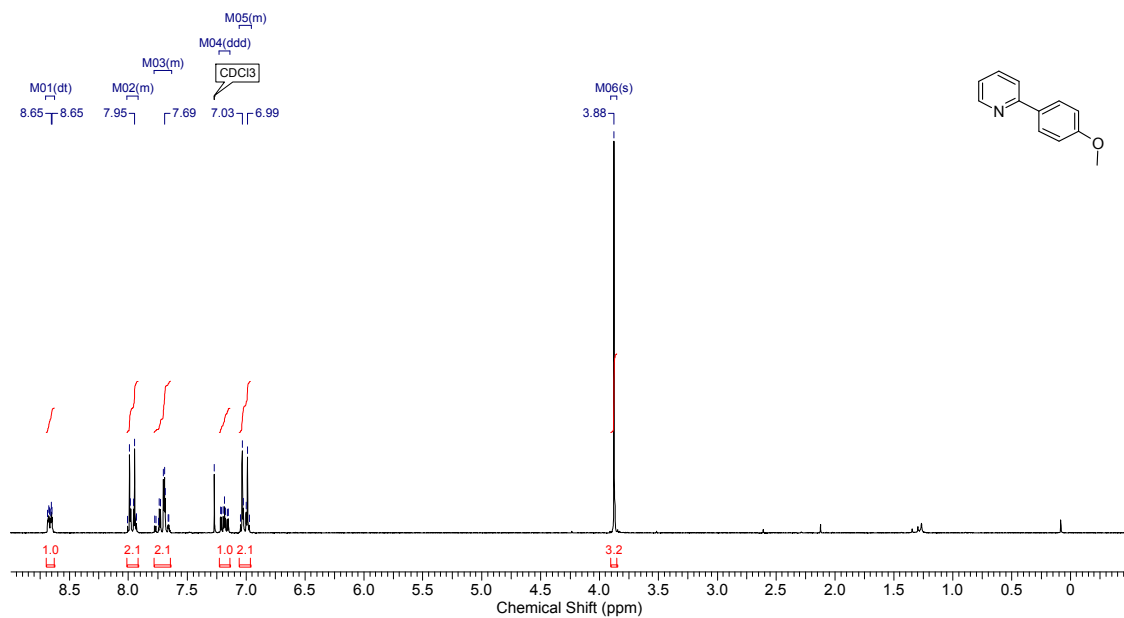


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

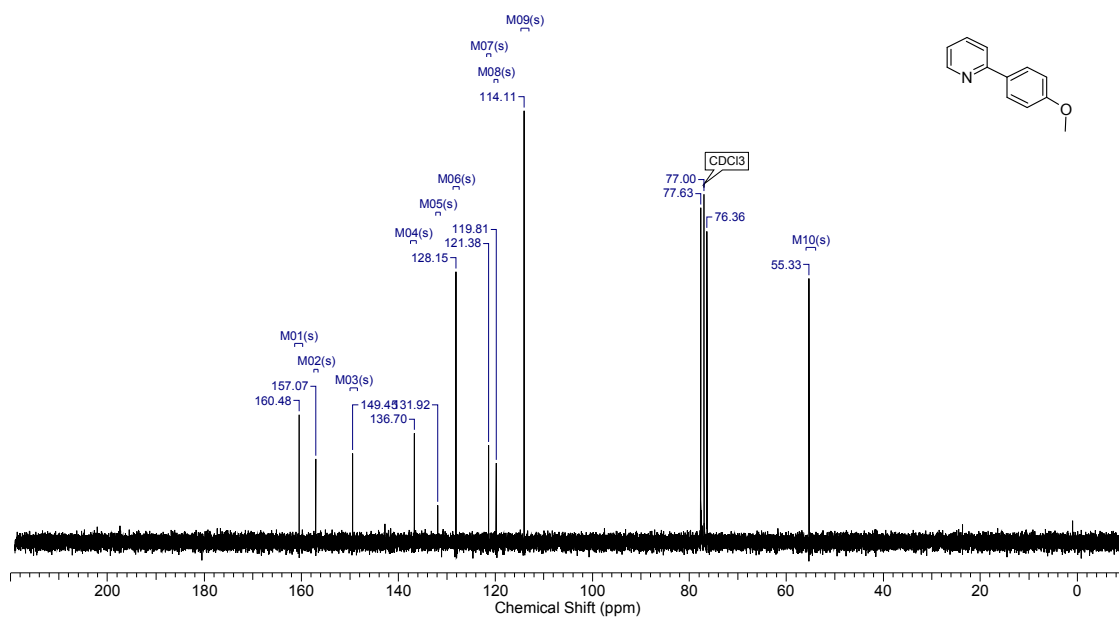


2-(4-Methoxyphenyl)-pyridine (**3fd**)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)

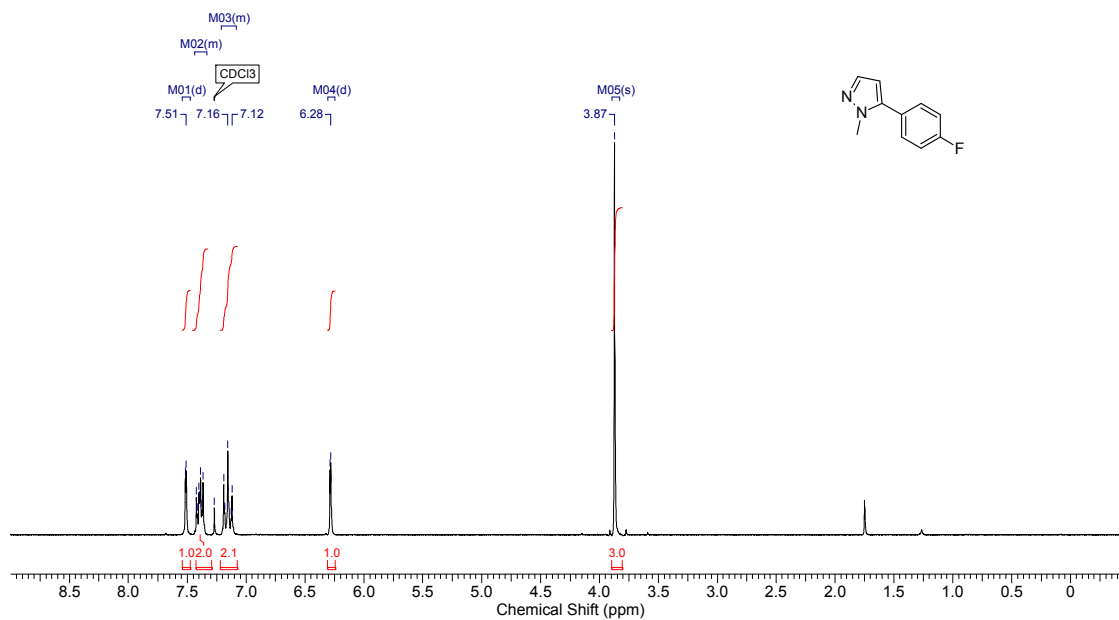


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

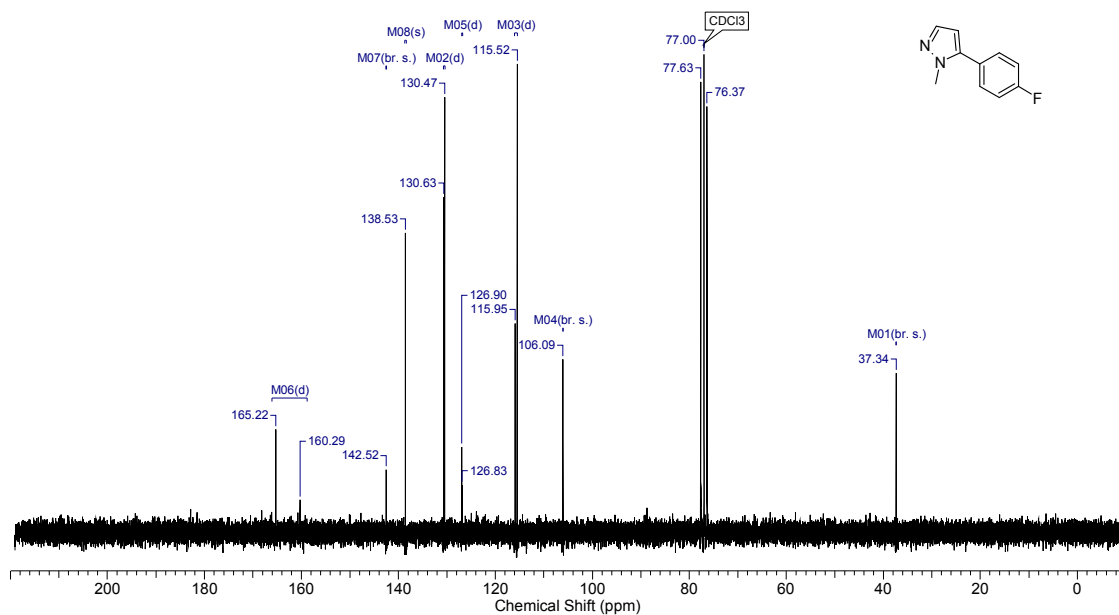


5-(4-Fluorophenyl)-1-methyl-1H-pyrazole (**3ga**)

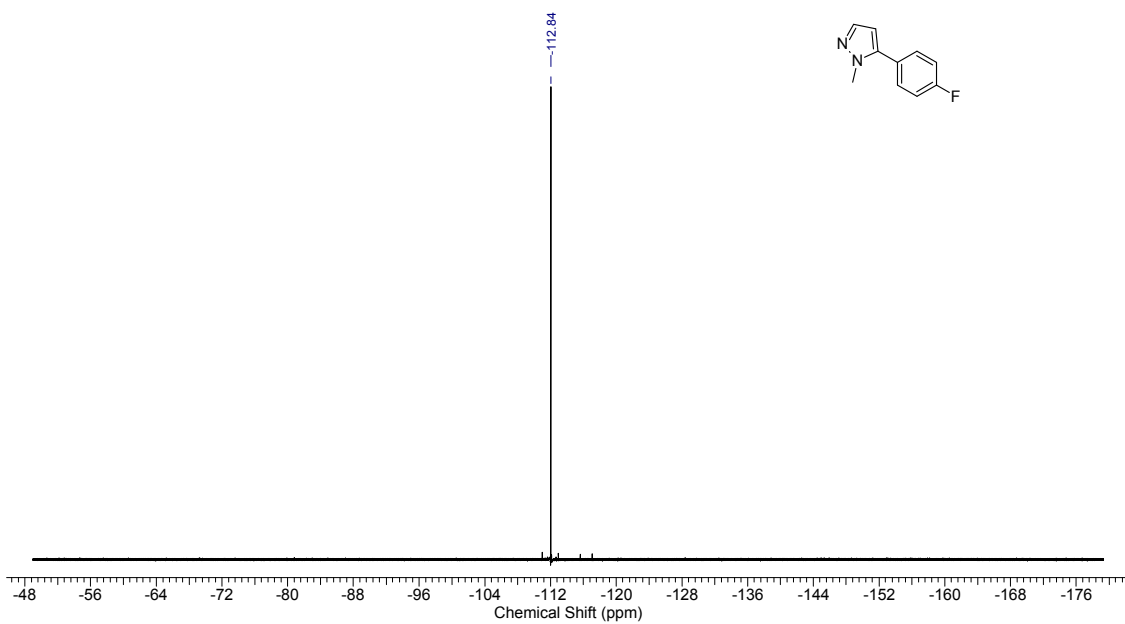
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

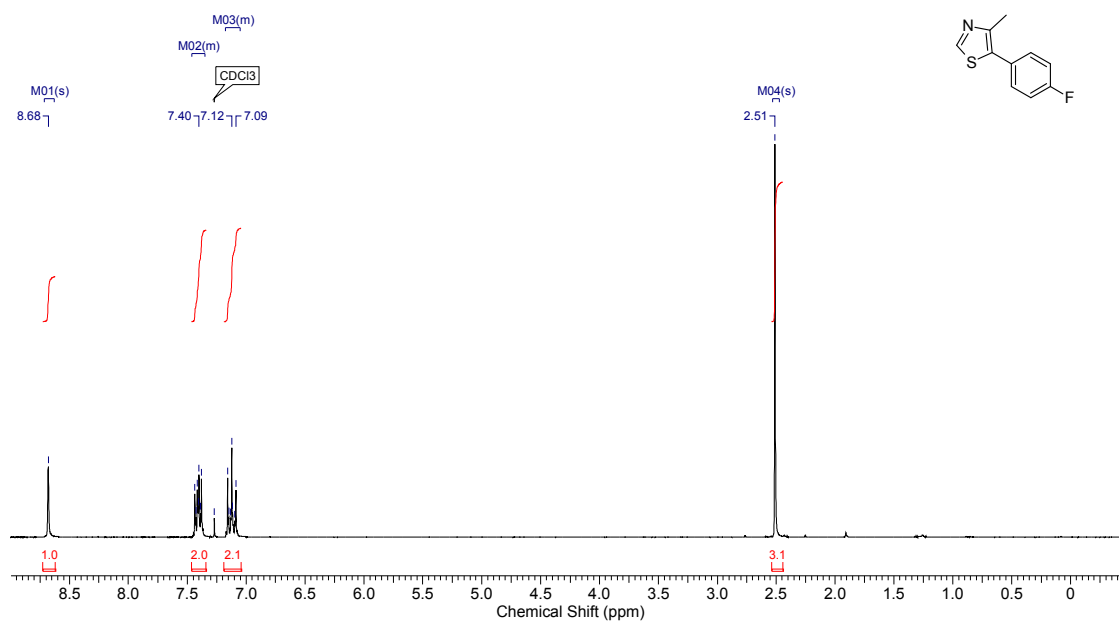


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 235 MHz)

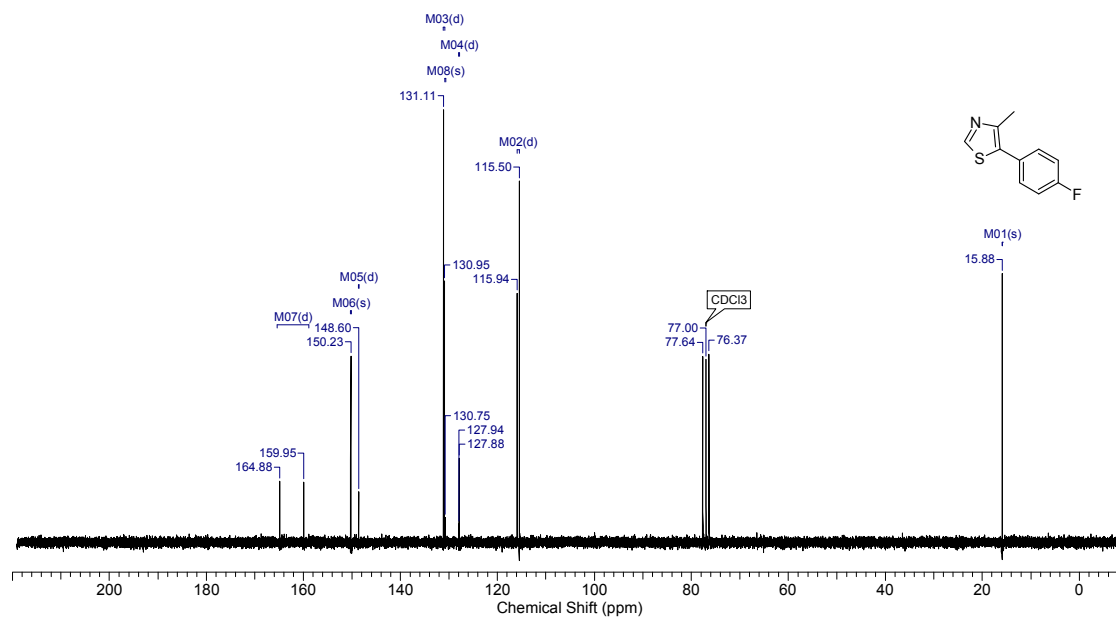


### 5-(4-Fluorophenyl)-4-methyl-thiazole (**3ha**)

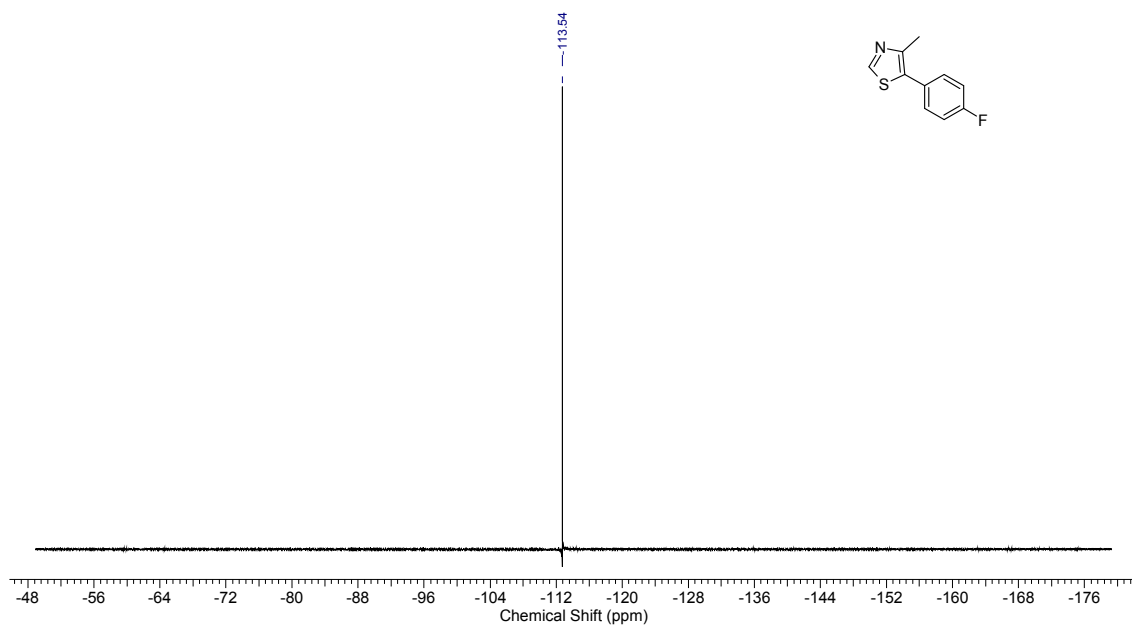
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz) (from method B)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

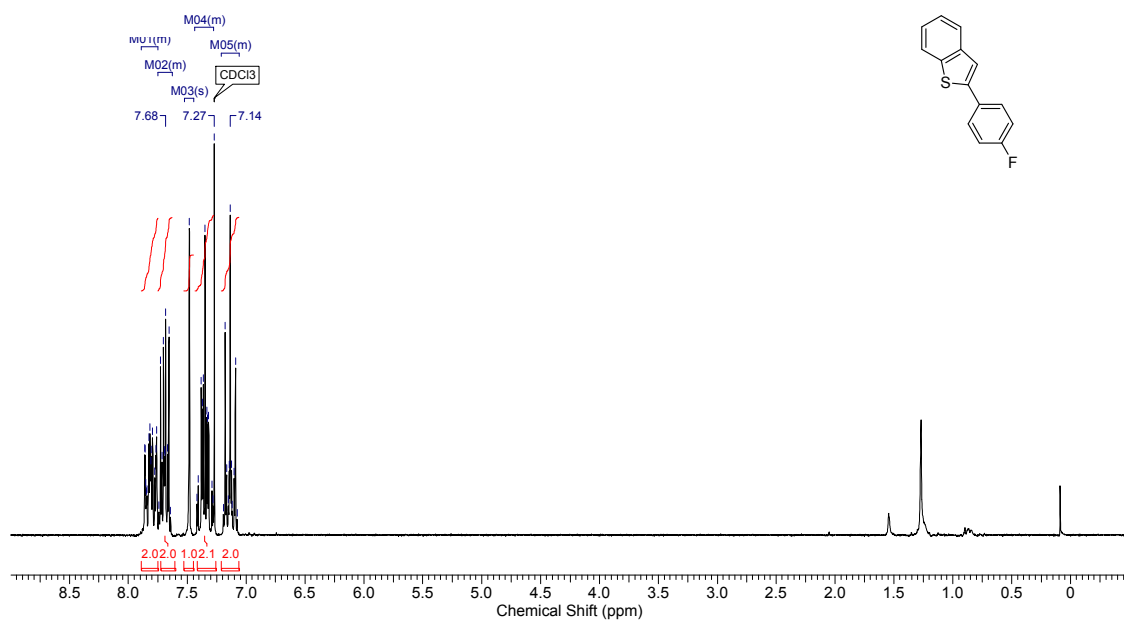


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 235 MHz)

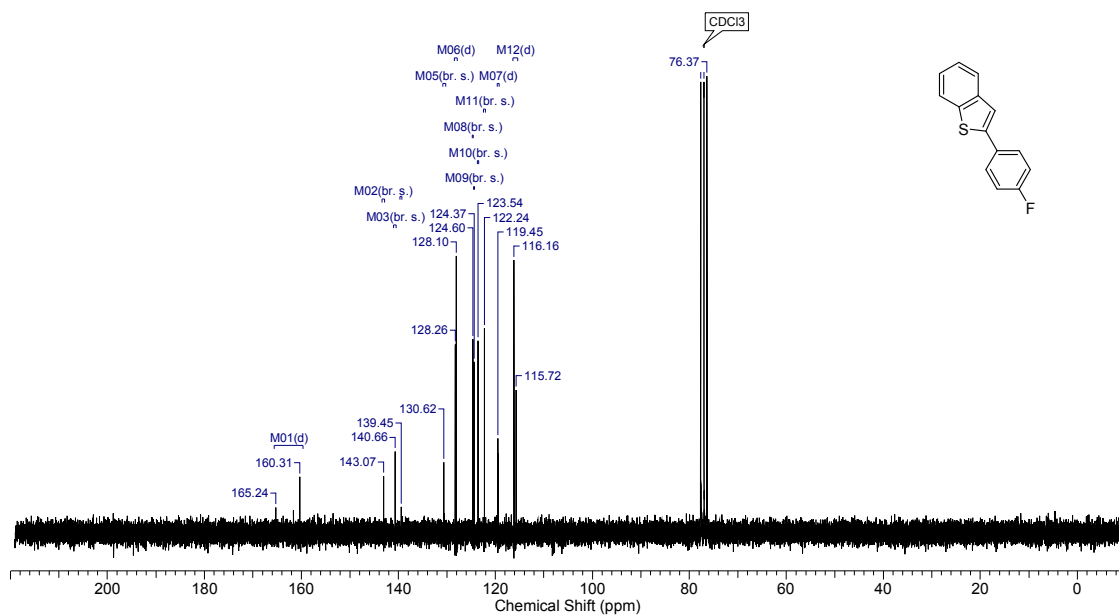


2-(4-Fluorophenyl)-benzo[b]thiophene (**3ia**)

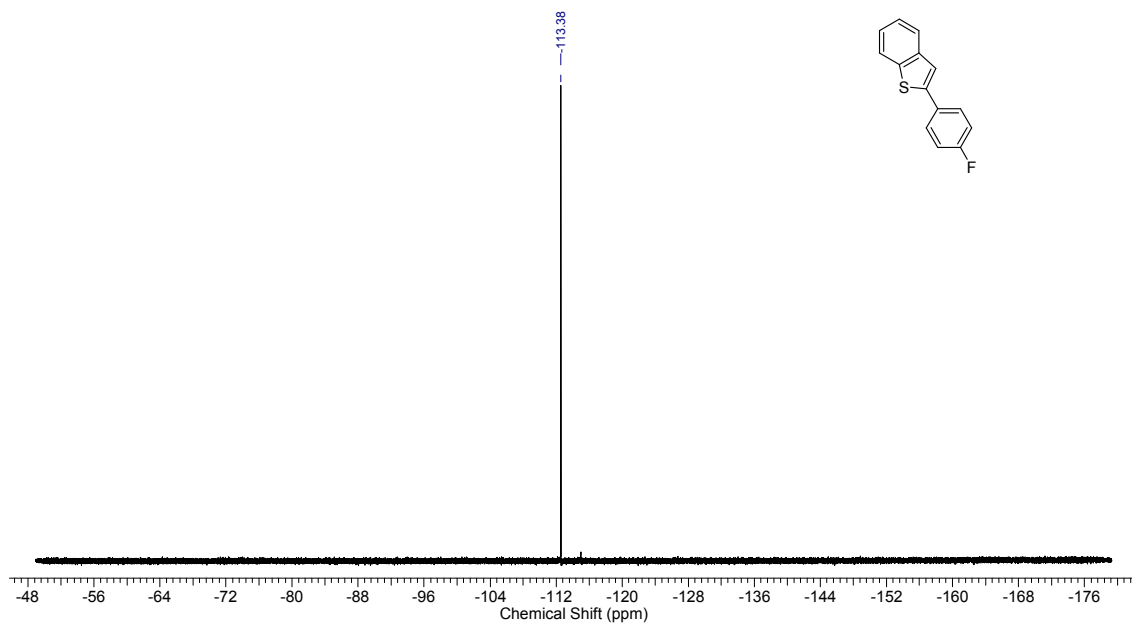
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

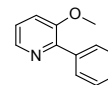
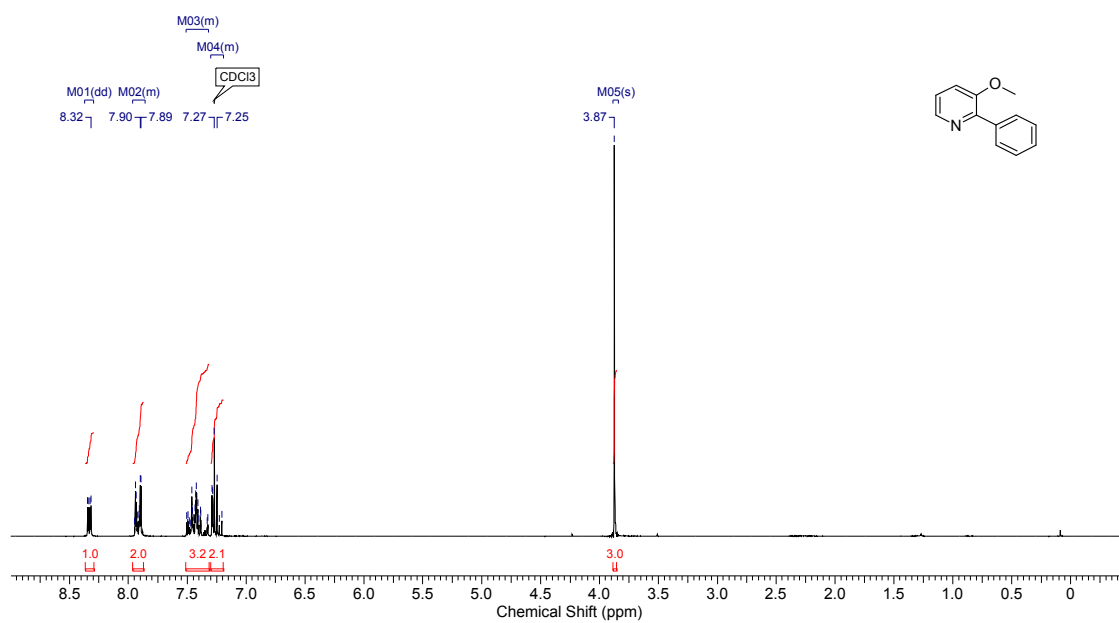


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 235 MHz)

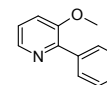
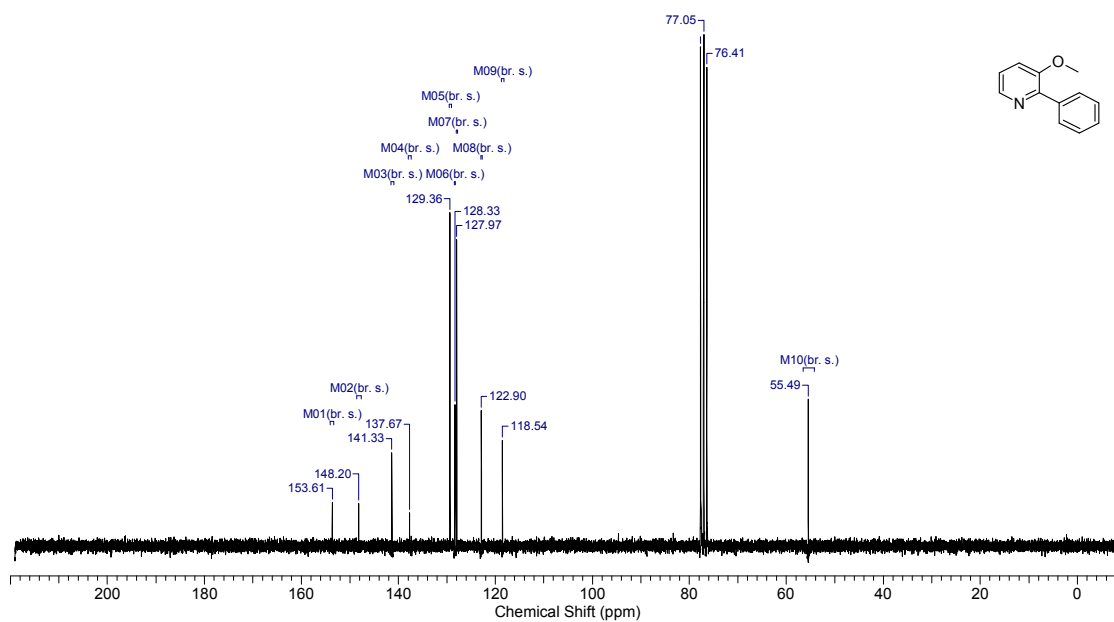


### 3-Methoxy-2-phenylpyridine (4)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)

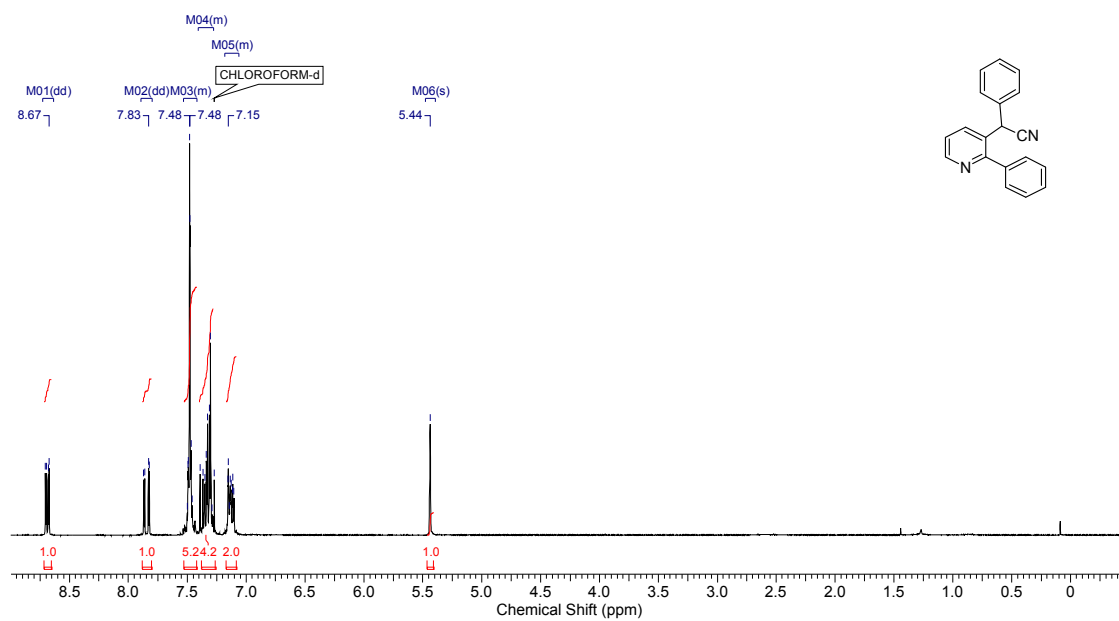


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)



## 2-Phenyl-2-(3-(2-phenyl)pyridyl)acetonitrile (6)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)

