Photoredox-Enabled Synthesis of β-Substituted Pyrroles from Pyrrolidines

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Supporting Information

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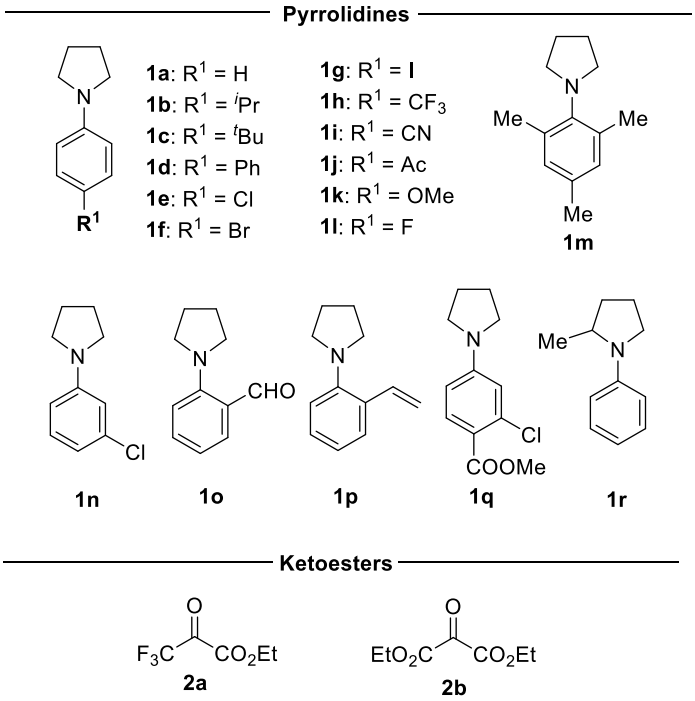
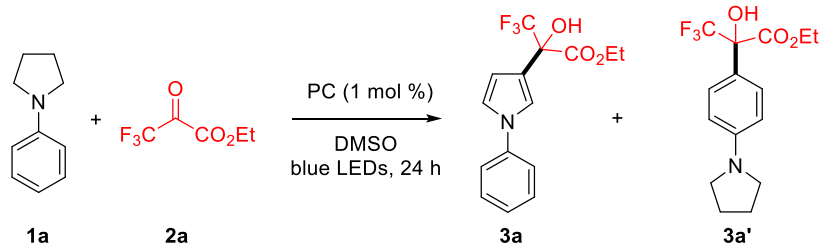
1. Scheme S1. List of the Starting Materials



2. Table S1. Optimization of Photocatalysts.[a]



entry	photocatalysts	yield of **3a** (%)[b]	yield of **3a'** (%)[b]
1	Eosin Y	29	trace
2	Rhodamine B	19	trace
3	$Ru(bpy)_3(PF_6)_2$	33	trace
4	$Ru(bpy)_3Cl_2{\cdot}H_2O$	36	trace
5	$Ir(ppy)_2(dtbbpy)PF_6$	53	trace
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	53	trace
7	$Ir(ppy)_3$	27	trace
8	-	-	66%

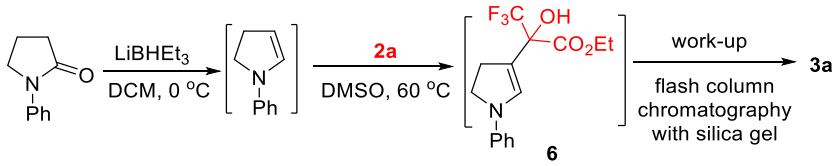
[a]Reaction conditions: a solution of **1a** (0.1 mmol), **2a** (0.25 mmol), PC (0.001 mmol) in the DMSO (1.0 mL) was irradiated by blue LED strips for 24 h under an air atmosphere. [b]^{1}H NMR yield.

3. Scheme S2. Reaction Set-up for Synthesis of β-Substituted Pyrroles.

Reaction set-up

The LED light Strips (OPPLE 12-LE-38465, 4.5 W, 435 nm) are used as light source. The distance between the light source and the irradiation vessel is about 7 cm.

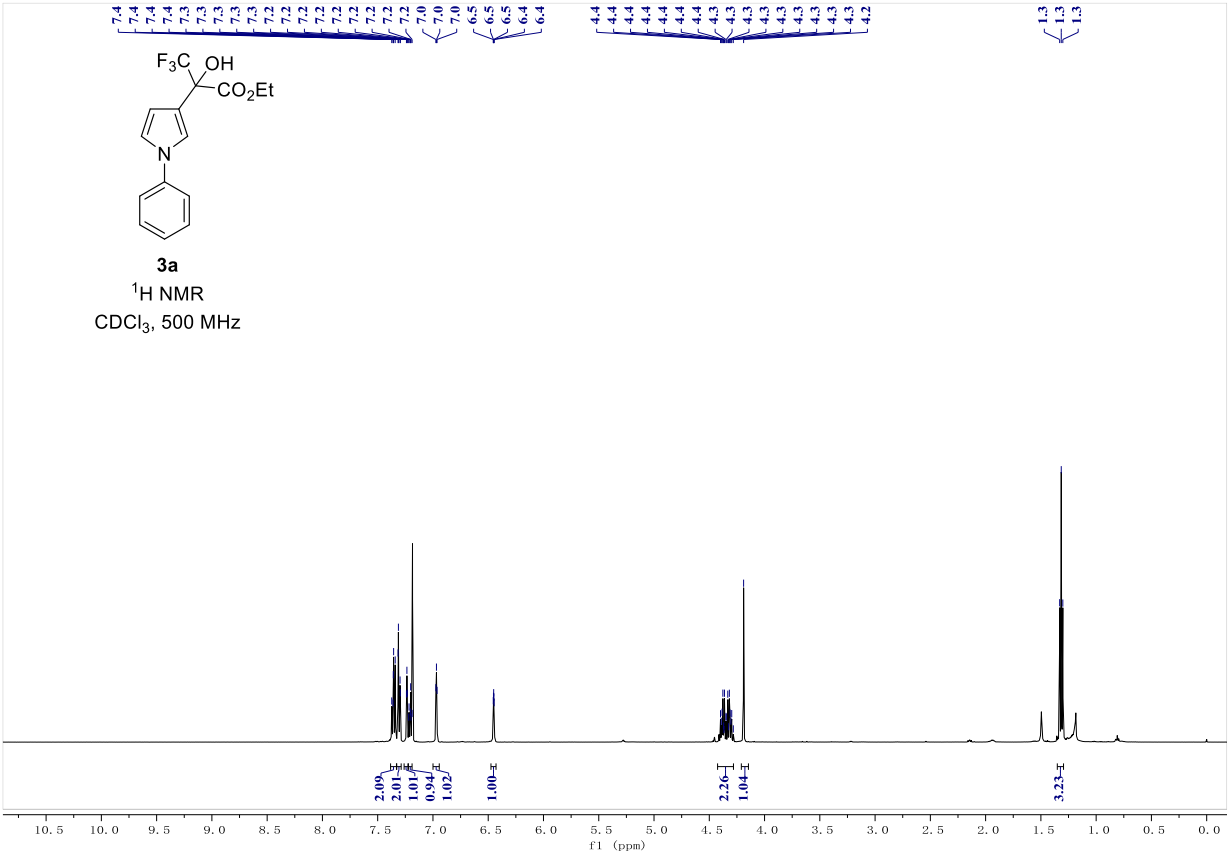
4. Mechanistic Study of Aromatization

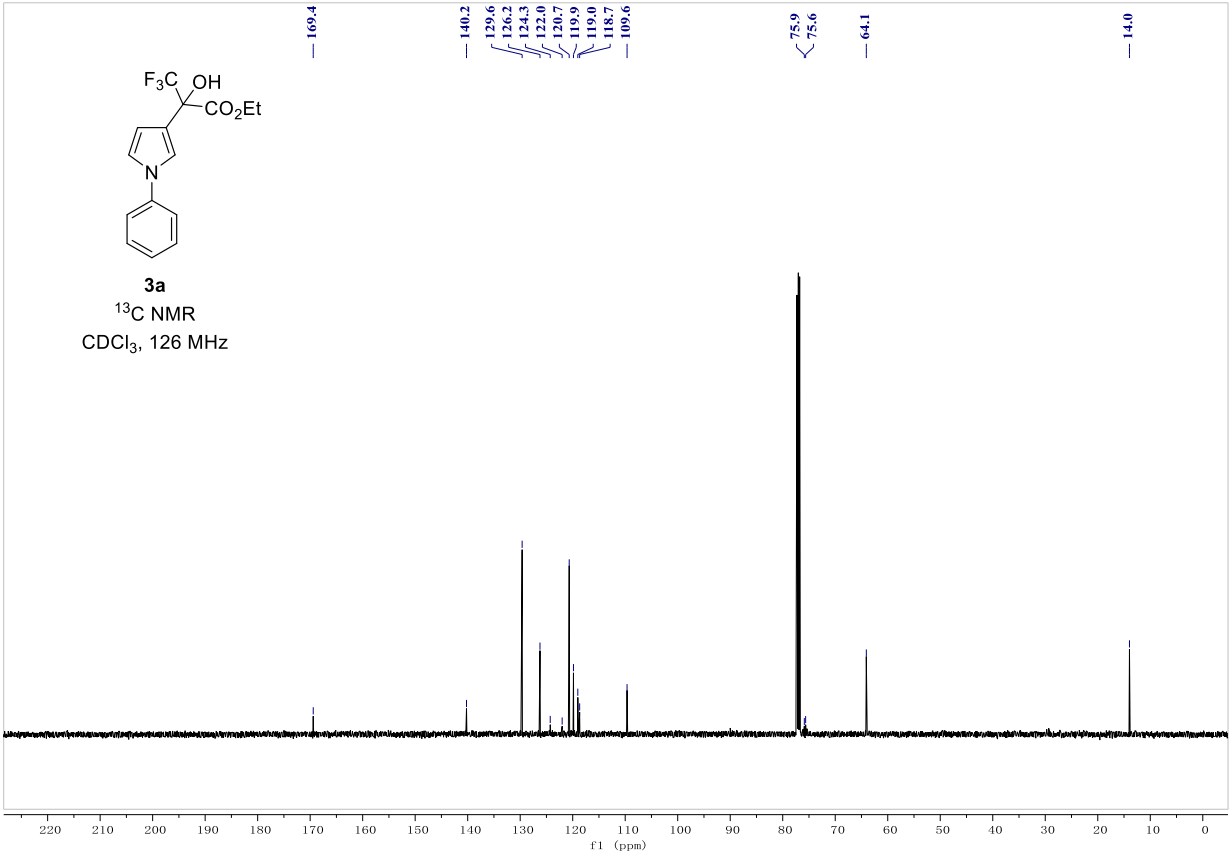


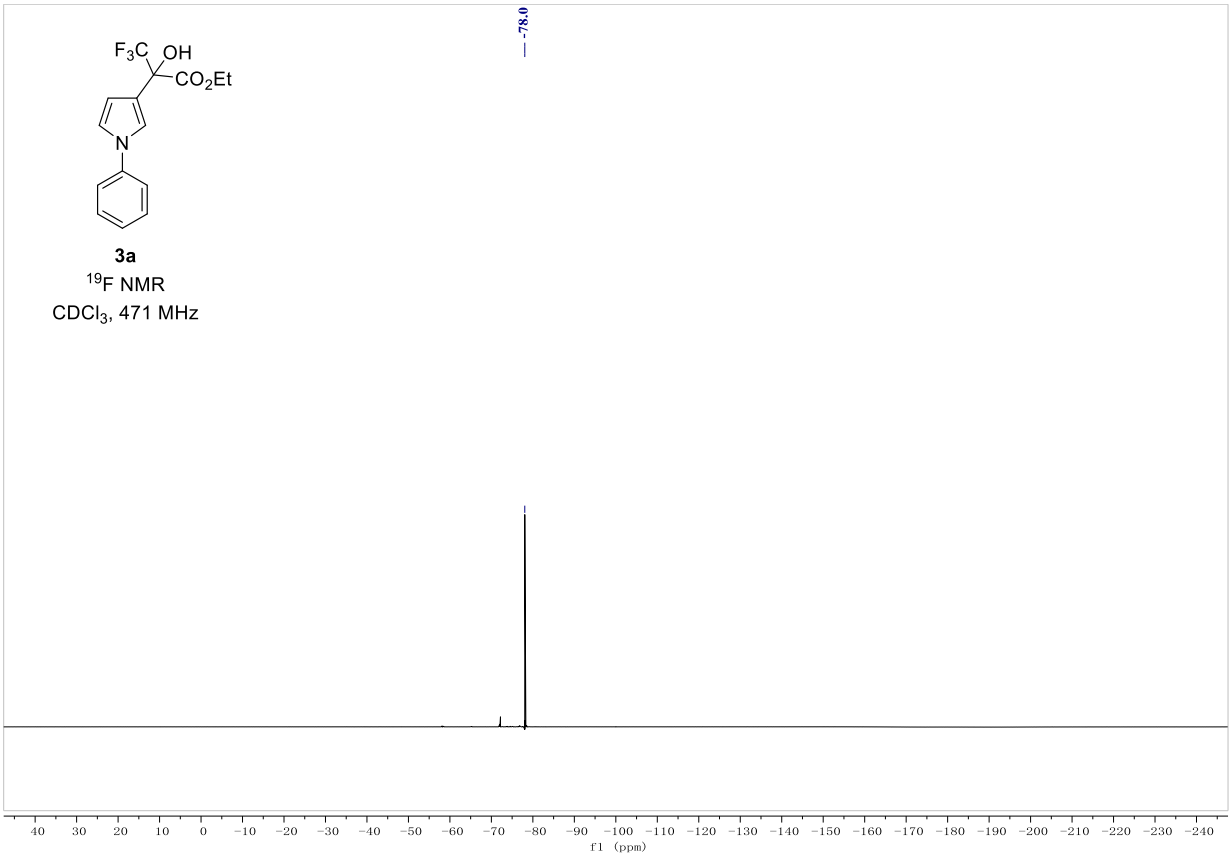
1-phenylpyrrolidin-2-one (806.0 mg, 1.0 mmol) was added into an oven-dried 100 mL reaction tube which was equipped with a rubber stopper and magnetic stir. The flask was evacuated and backfilled with N_2 for 3 times. Then, DCM (25 mL) was added. The reaction mixture was stirred at 0 °C for 30 min, and then $LiBHEt_3$ (1.1 mmol, 1.1equiv.) was added into this system via a syringe. After stirring at 0 °C for 10 min, **2a** (1.1 mmol, 1.1equiv.) was then added and the reaction mixture was stirred at 60 °C for 10 h. The progress of the reaction was monitored by TLC, and a new spot **A** appeared. After the reaction was completed, the solvent was evaporated and the residue was subjected to a flash silica gel chromatography (EtOAc : hexane = 1:20). Finally, the isolated product was **3a**, which is different from the above spot **A** on

TLC. This result suggested that the aromatization of the α,β-unsaturated amine **6** could be achieved by the atmospheric oxygen involved oxidation.

5. NMR Spectra for All Compounds



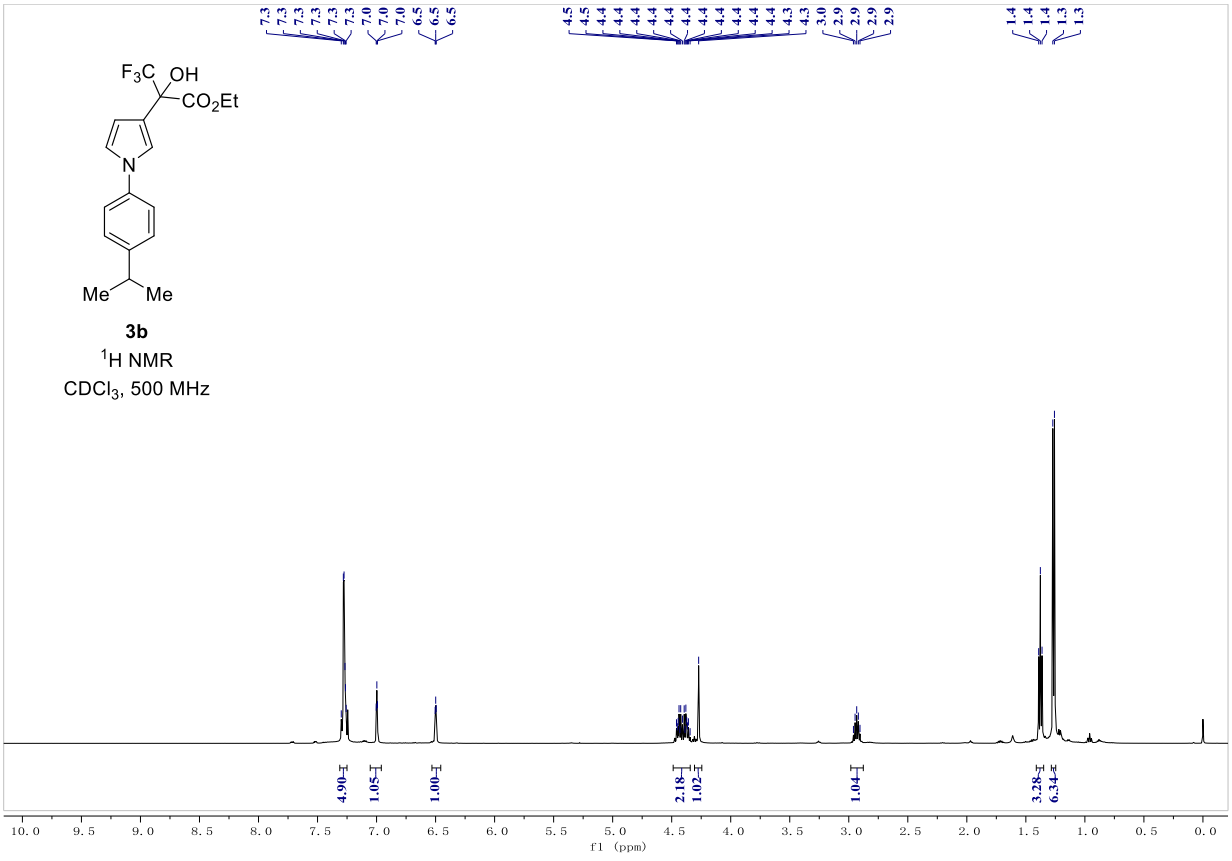




3a

^{19}F NMR

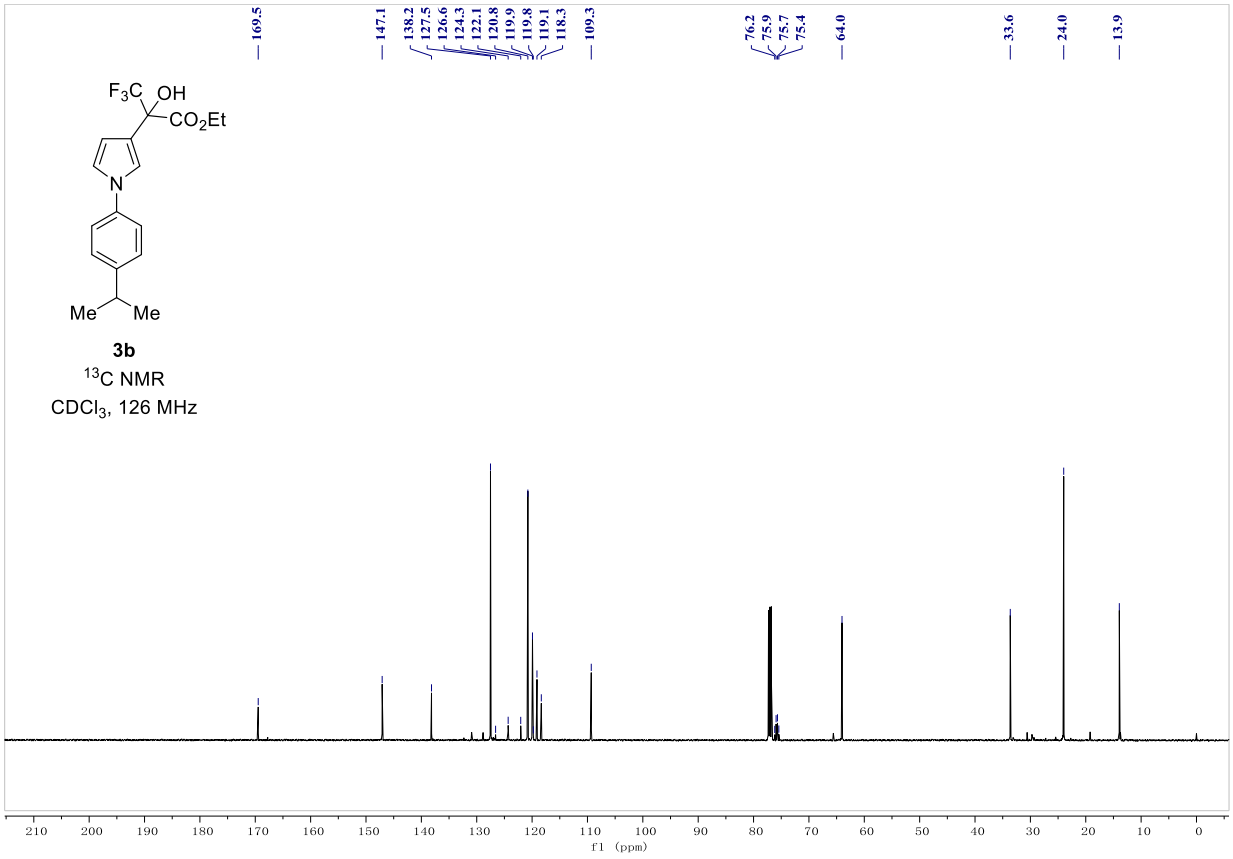
$CDCl_3$, 471 MHz



3b

^{1}H NMR

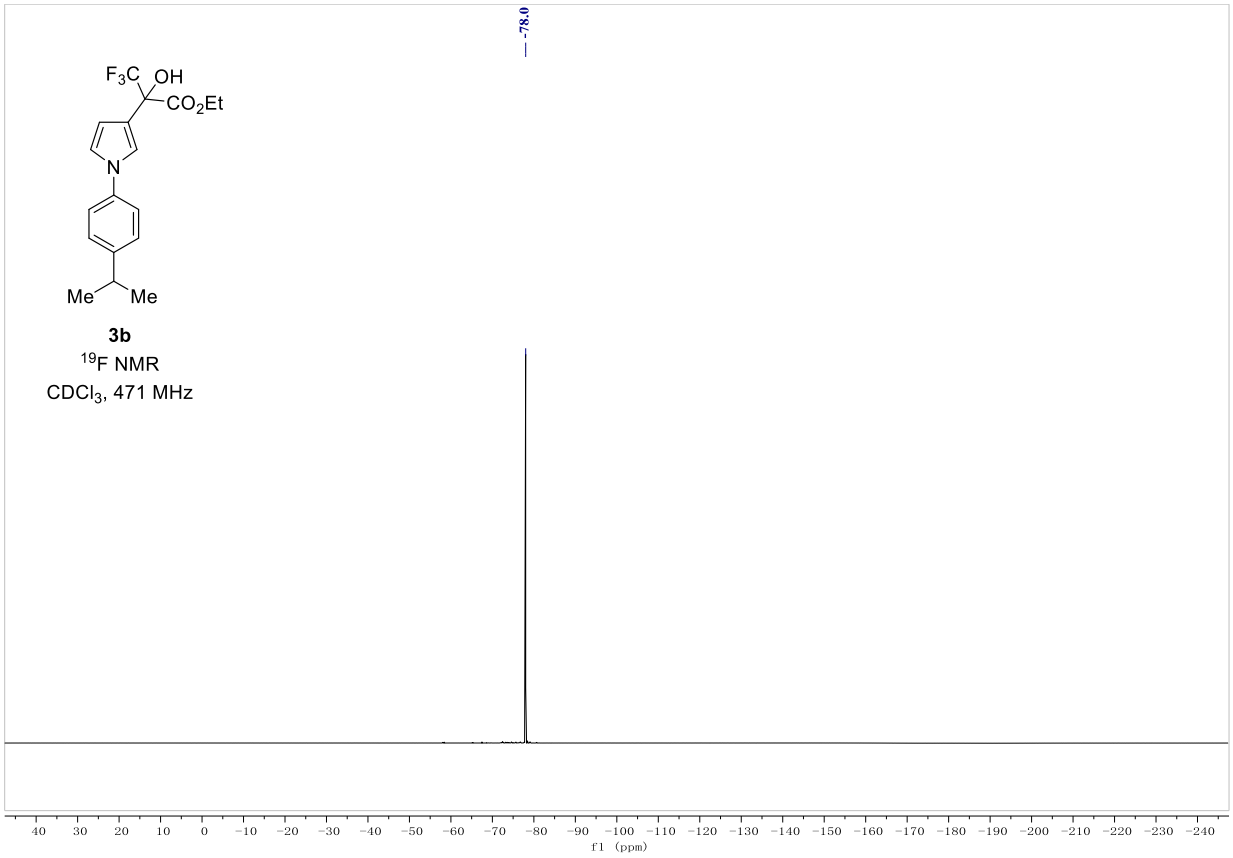
$CDCl_3$, 500 MHz



3b

^{13}C NMR

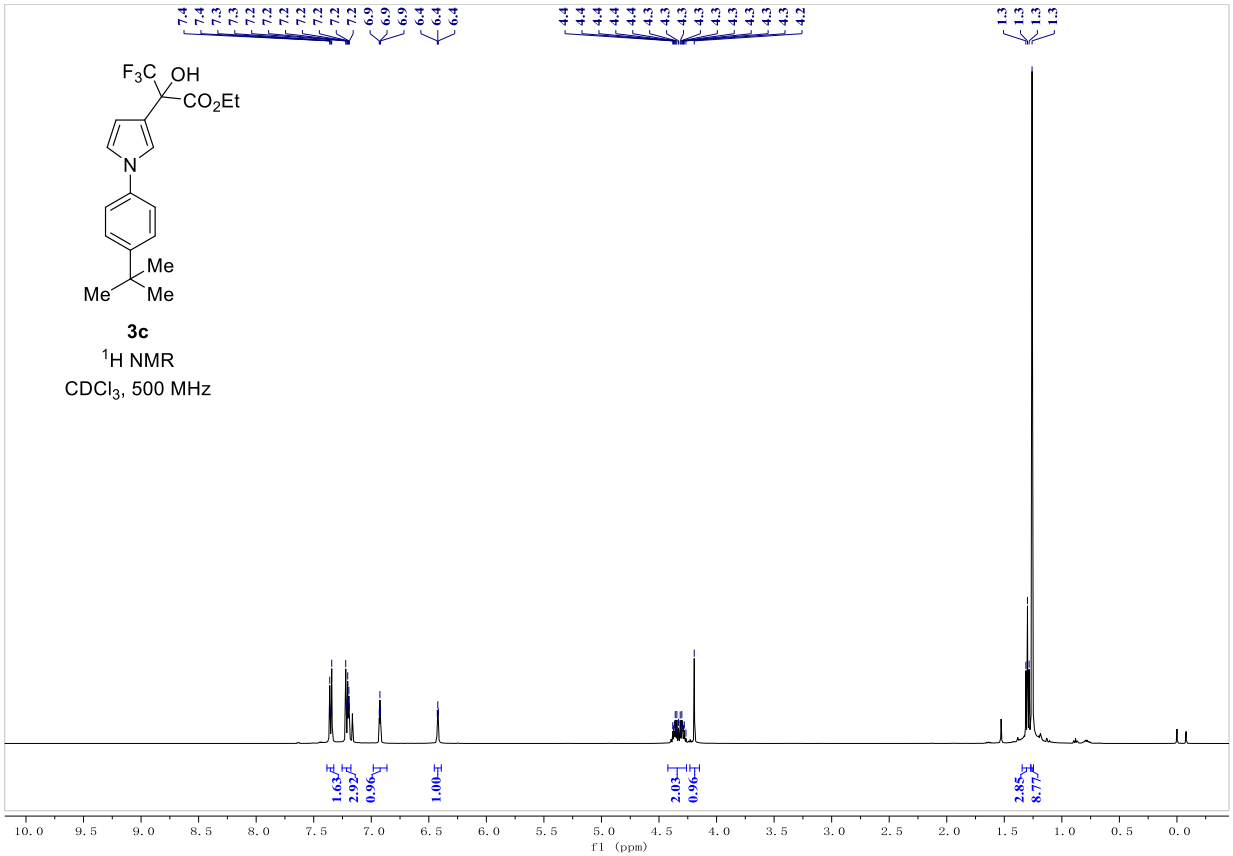
$CDCl_3$, 126 MHz



3b

^{19}F NMR

$CDCl_3$, 471 MHz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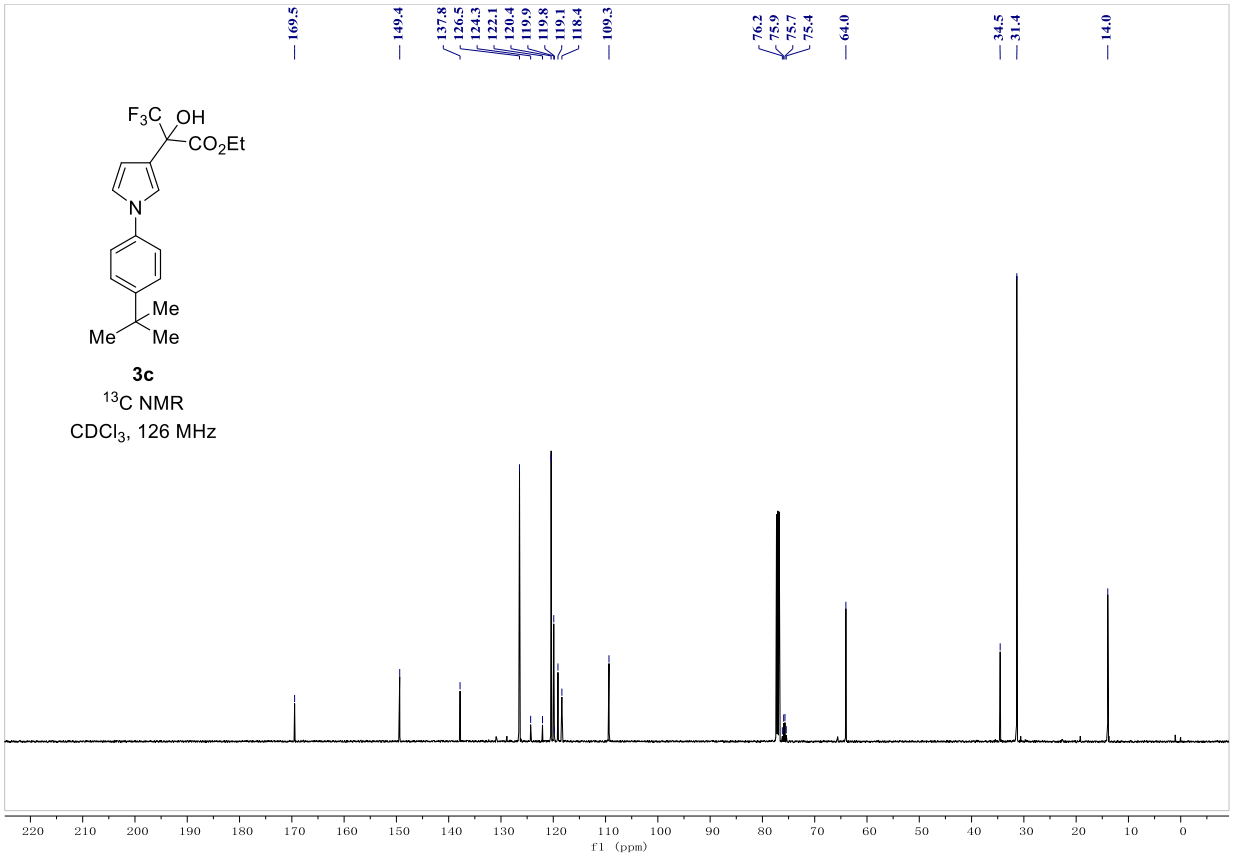
N
Me
Me Me
3c
1H NMR
CDCl3, 500 MHz
f1 (ppm)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CO2Et
N
Me
Me Me
3c
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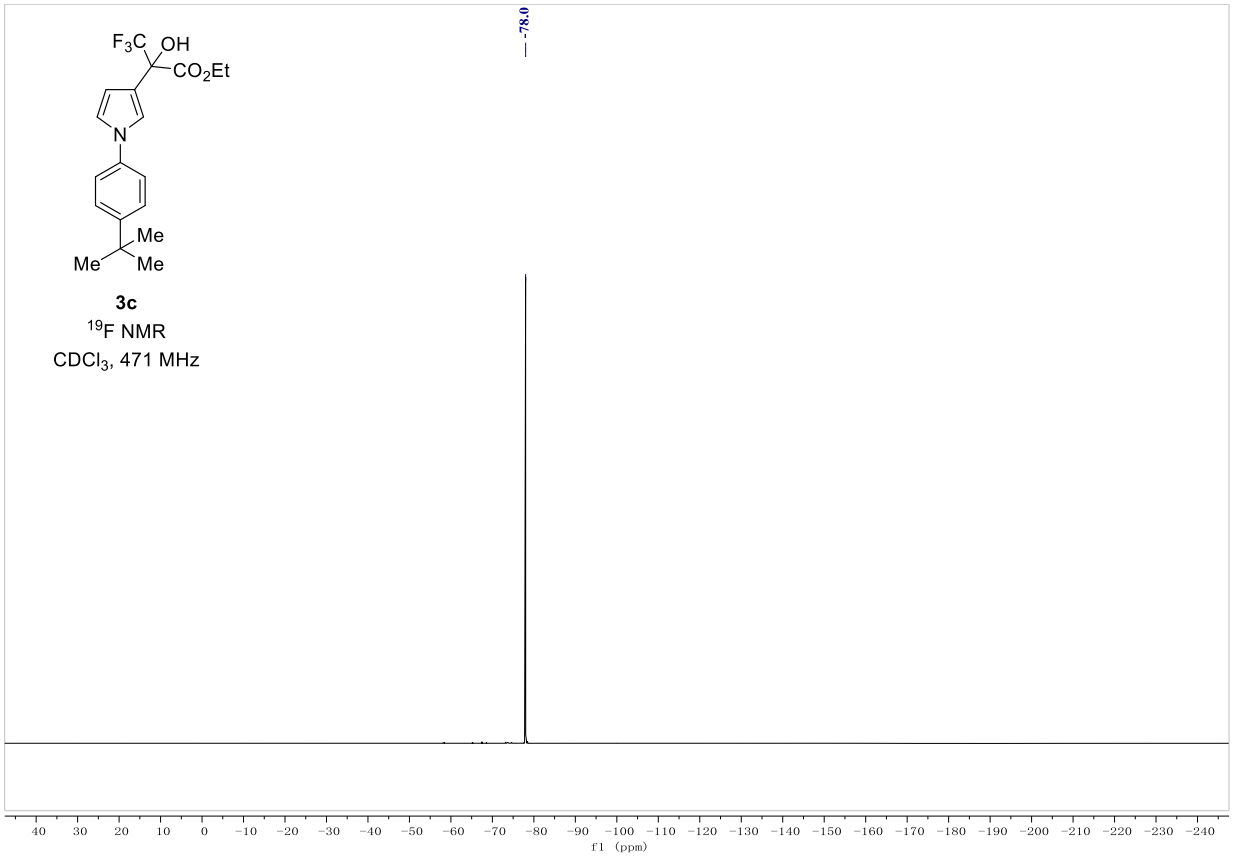
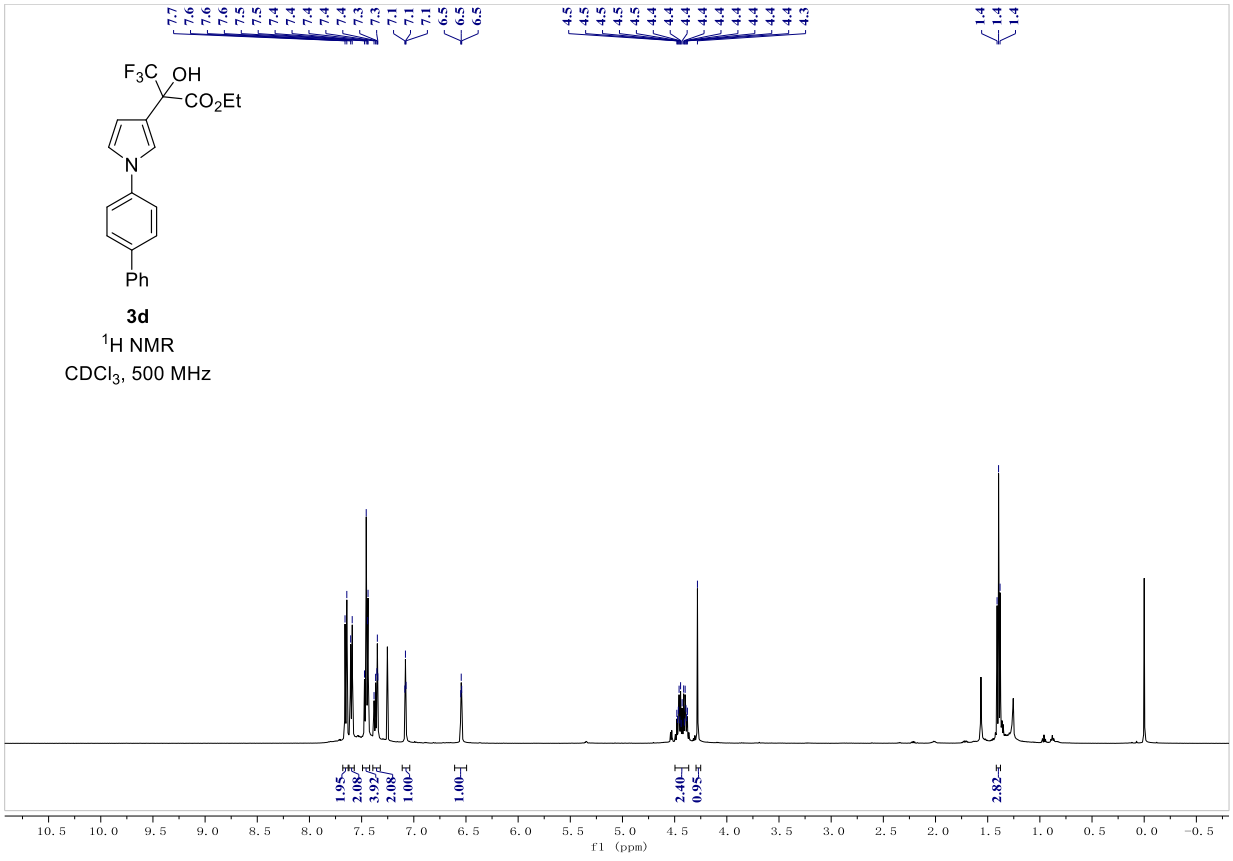
CDCl3, 126 MHz
f1 (ppm)



3c

^{19}F NMR

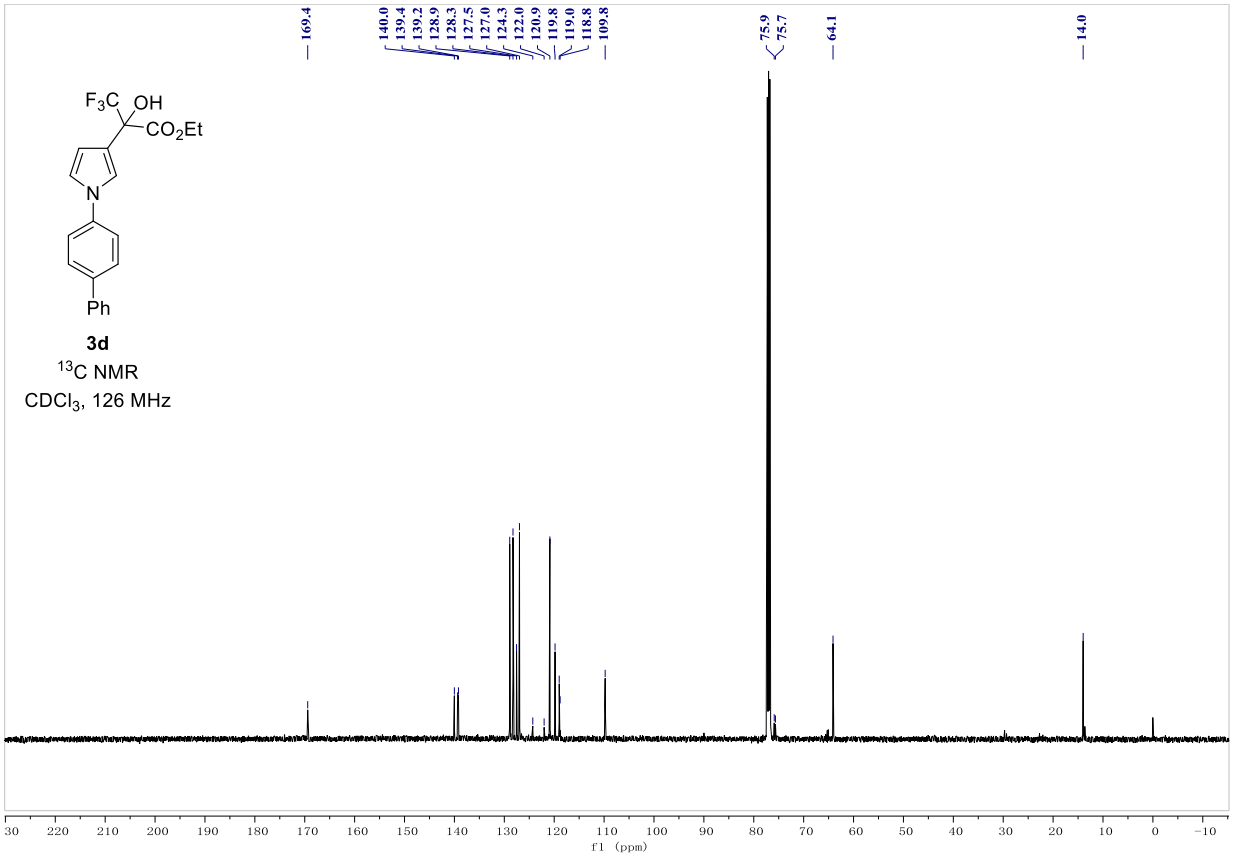
$CDCl_3$, 471 MHz



3d

^{1}H NMR

$CDCl_3$, 500 MHz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118.8
109.8
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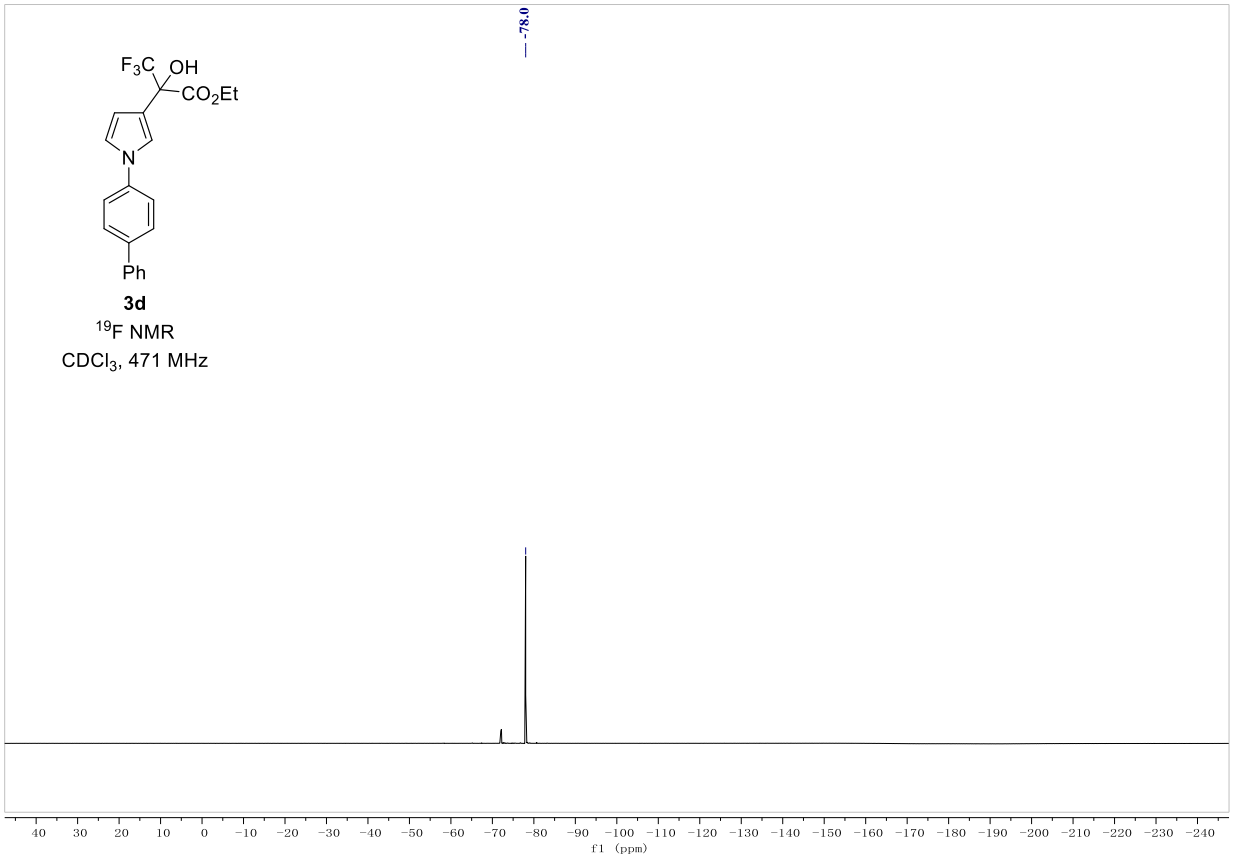
Ph
3d
13C NMR
CDCl3, 126 MHz
f1 (ppm)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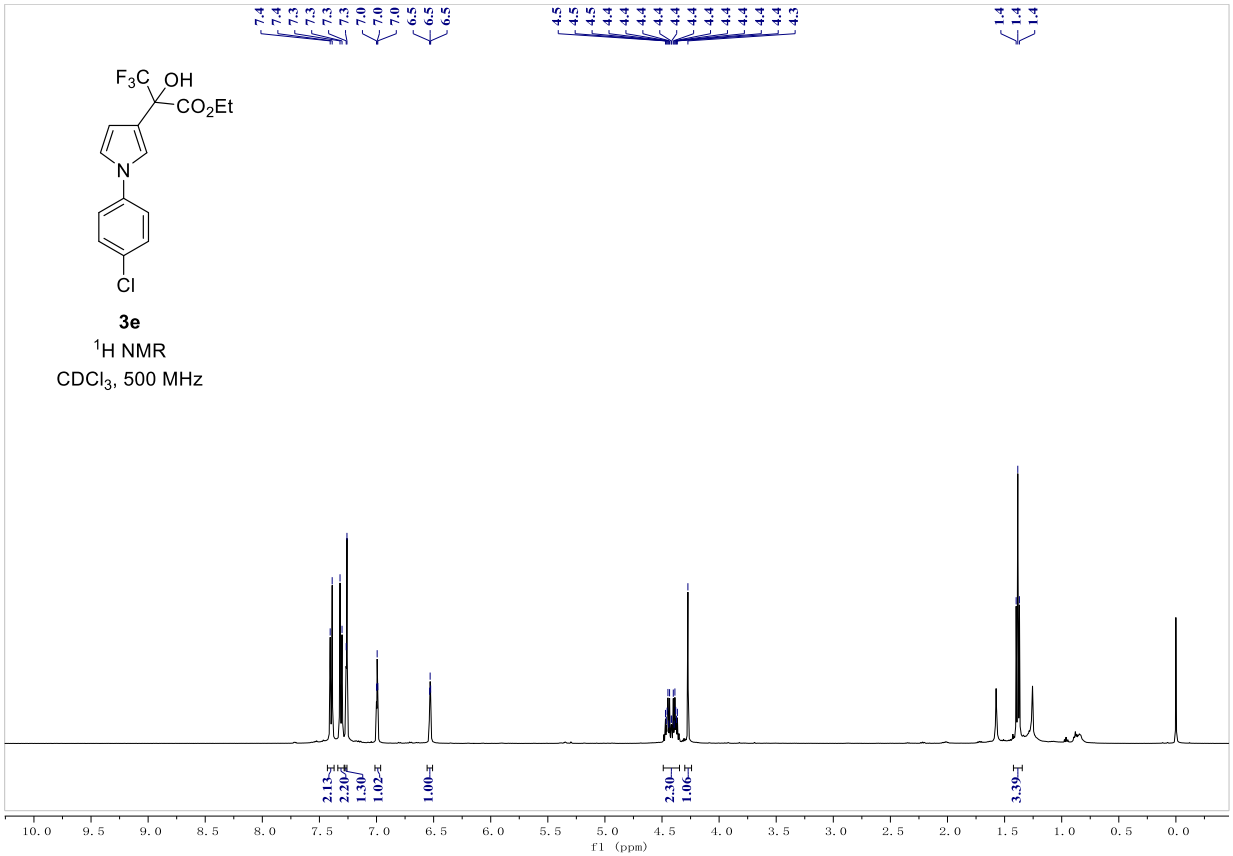
CDCl3, 471 MHz
f1 (ppm)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Cl
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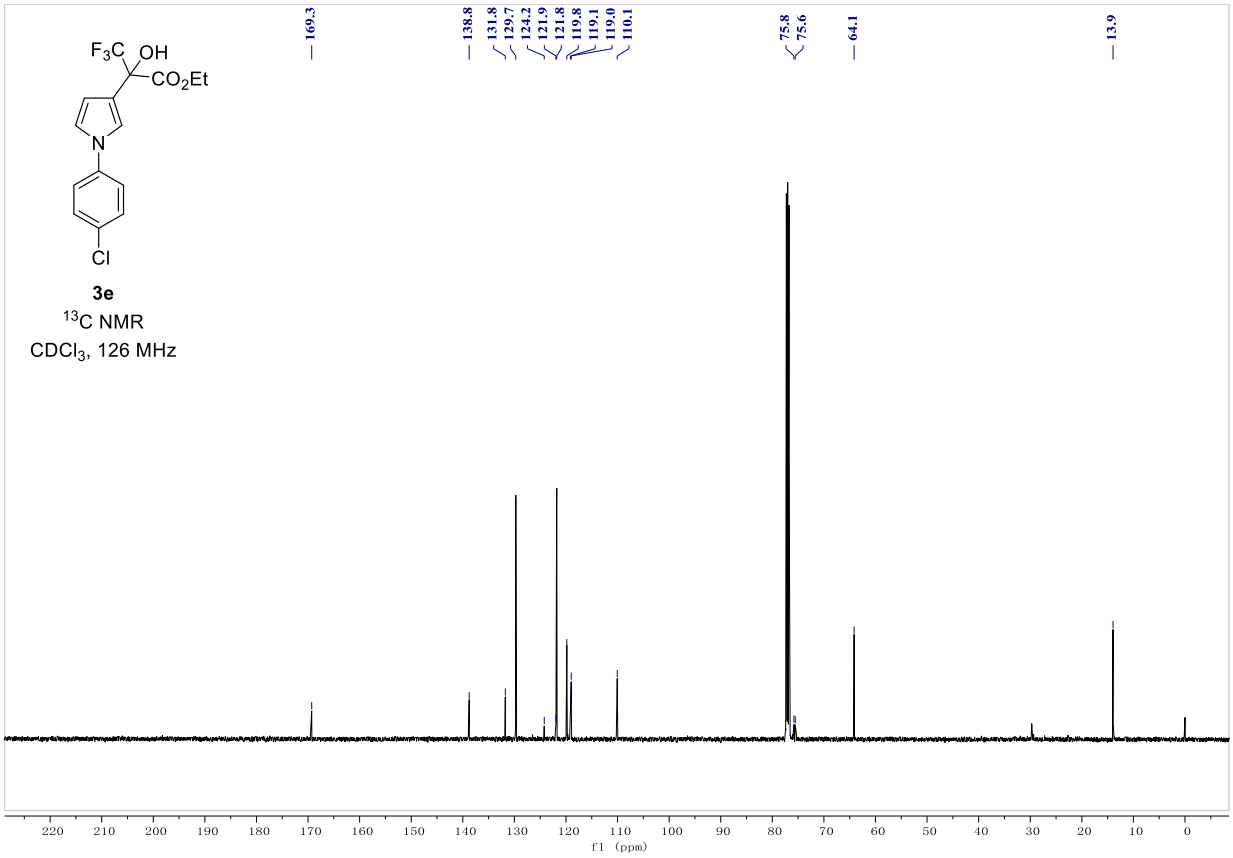
CDCl3, 500 MHz
f1 (ppm)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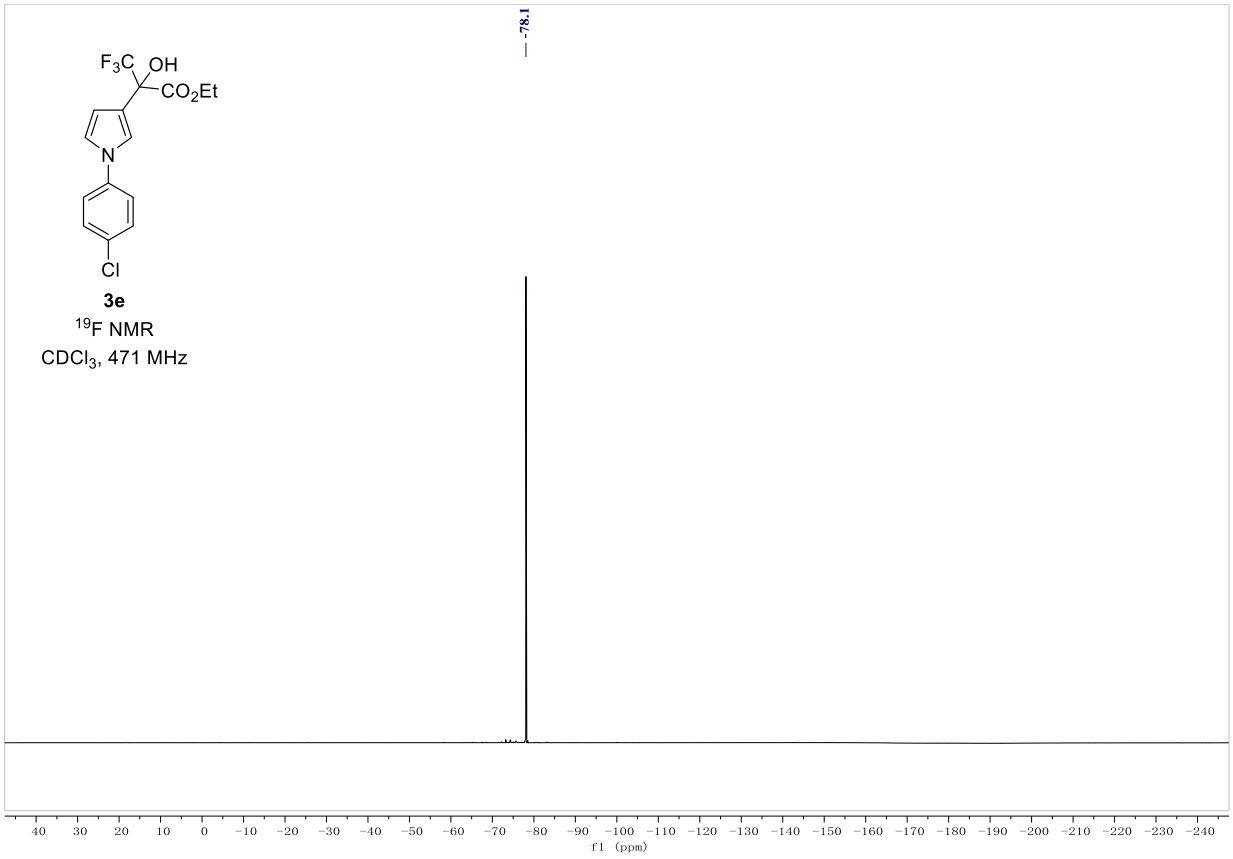
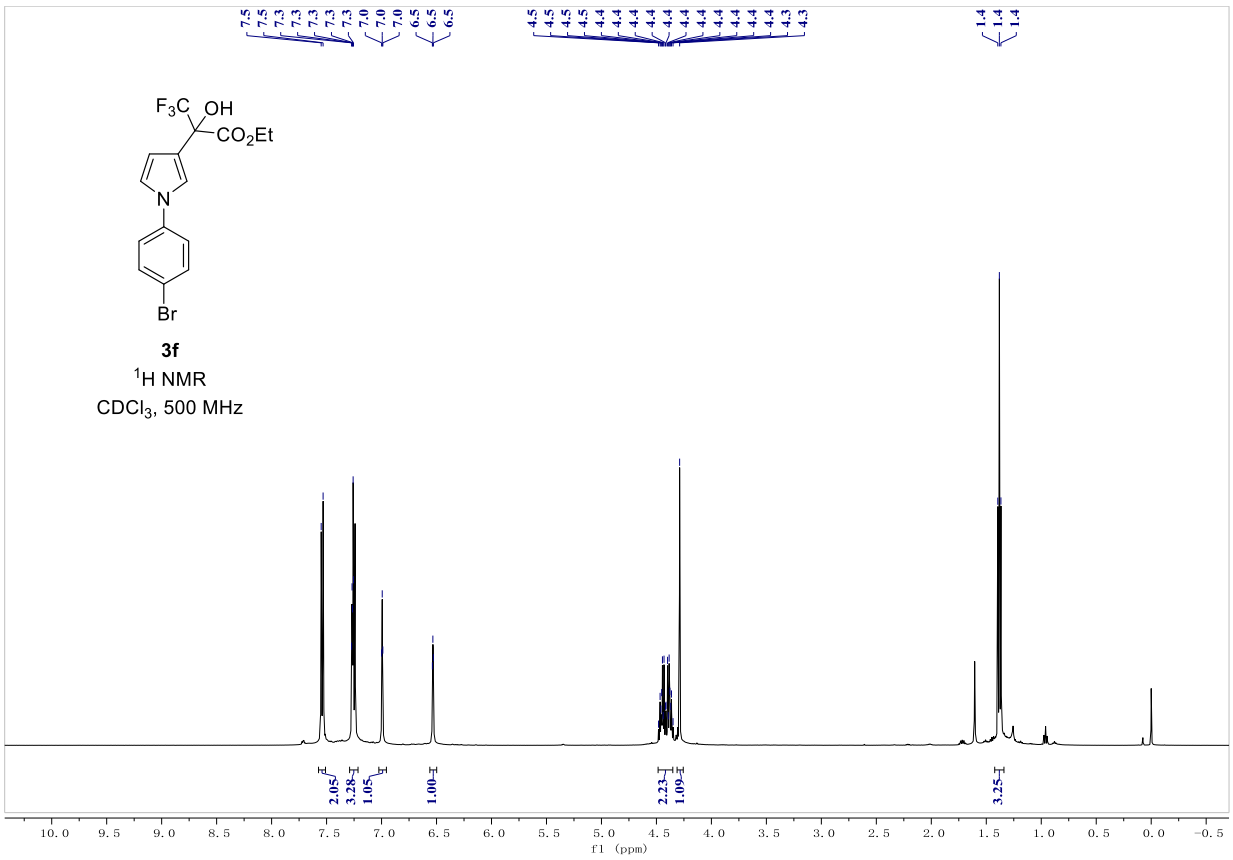


3e

^{19}F NMR

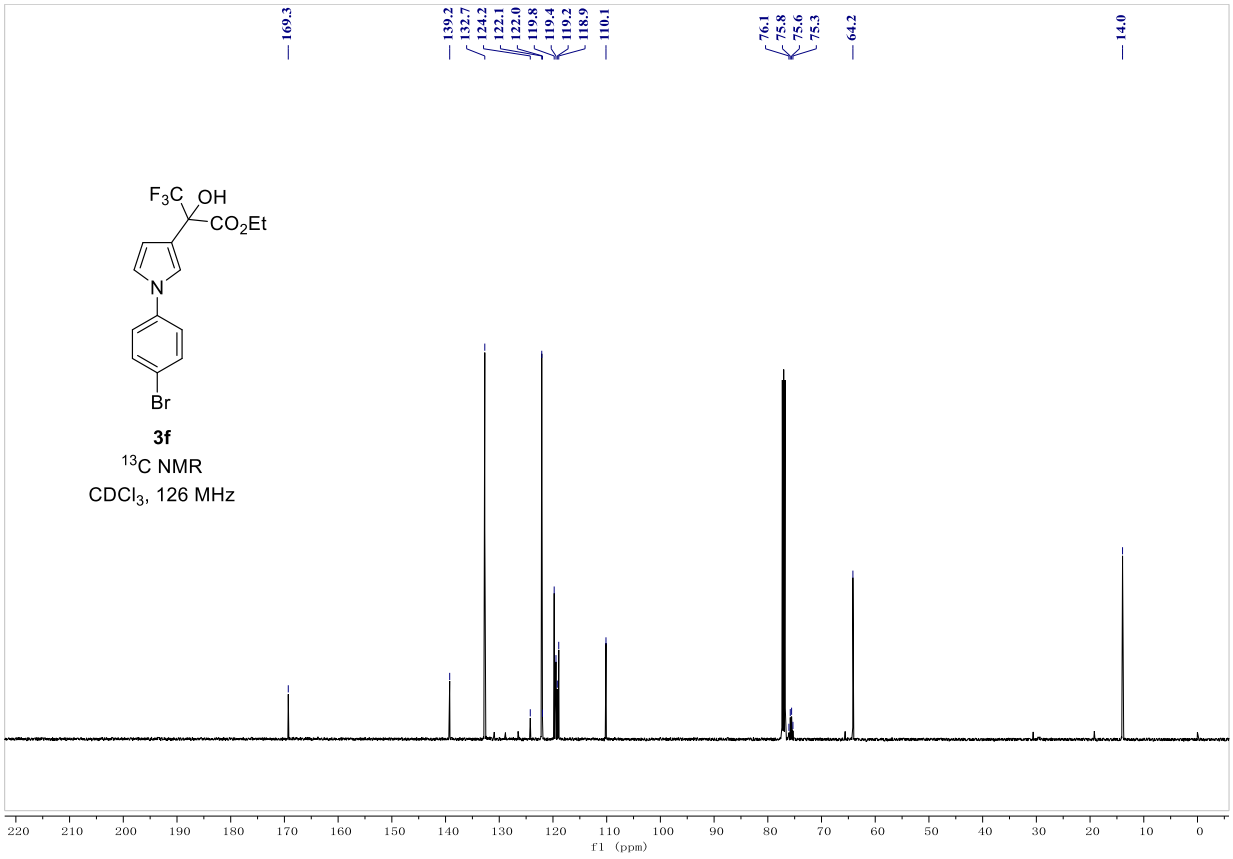
$CDCl_3$, 471 MHz



3f

^{1}H NMR

$CDCl_3$, 500 MHz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75.8
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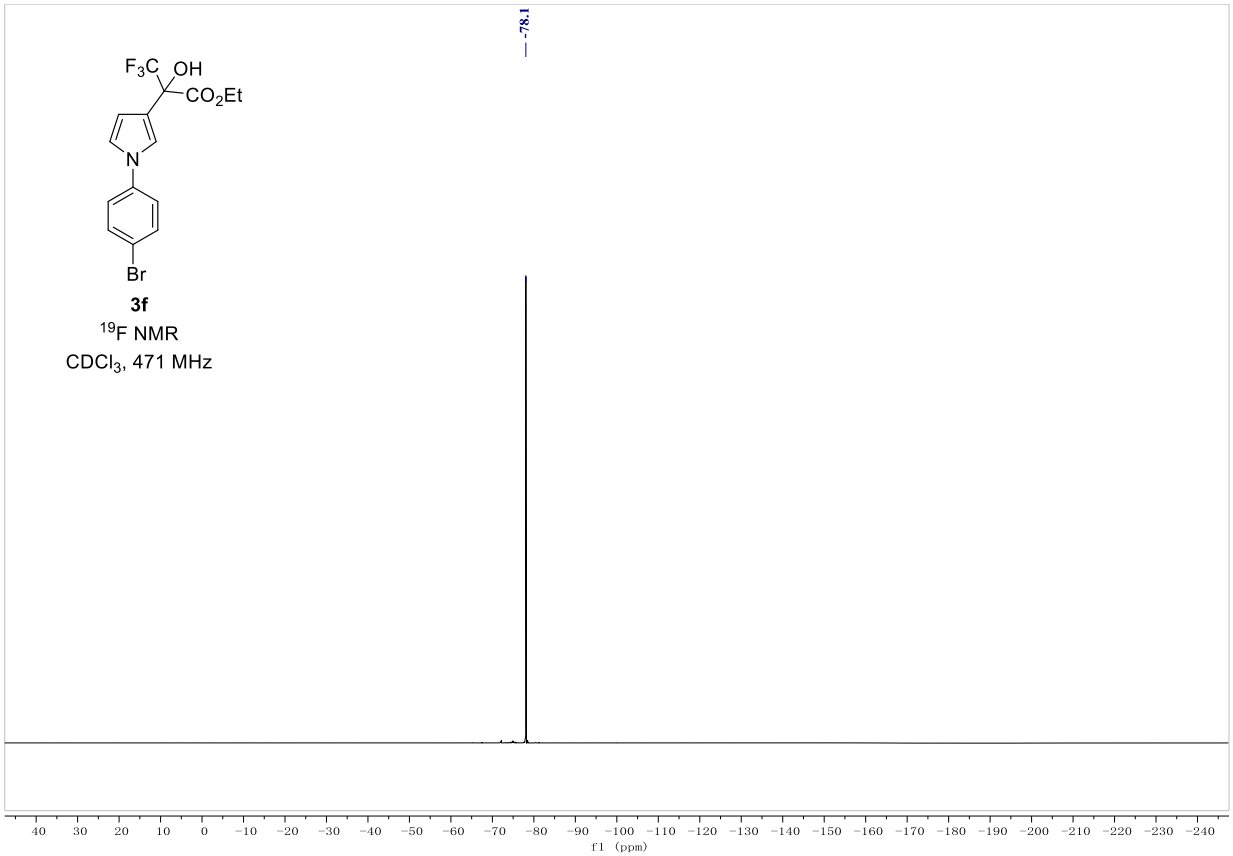
Br
3f
13C NMR
CDCl3, 126 MHz
f1 (ppm)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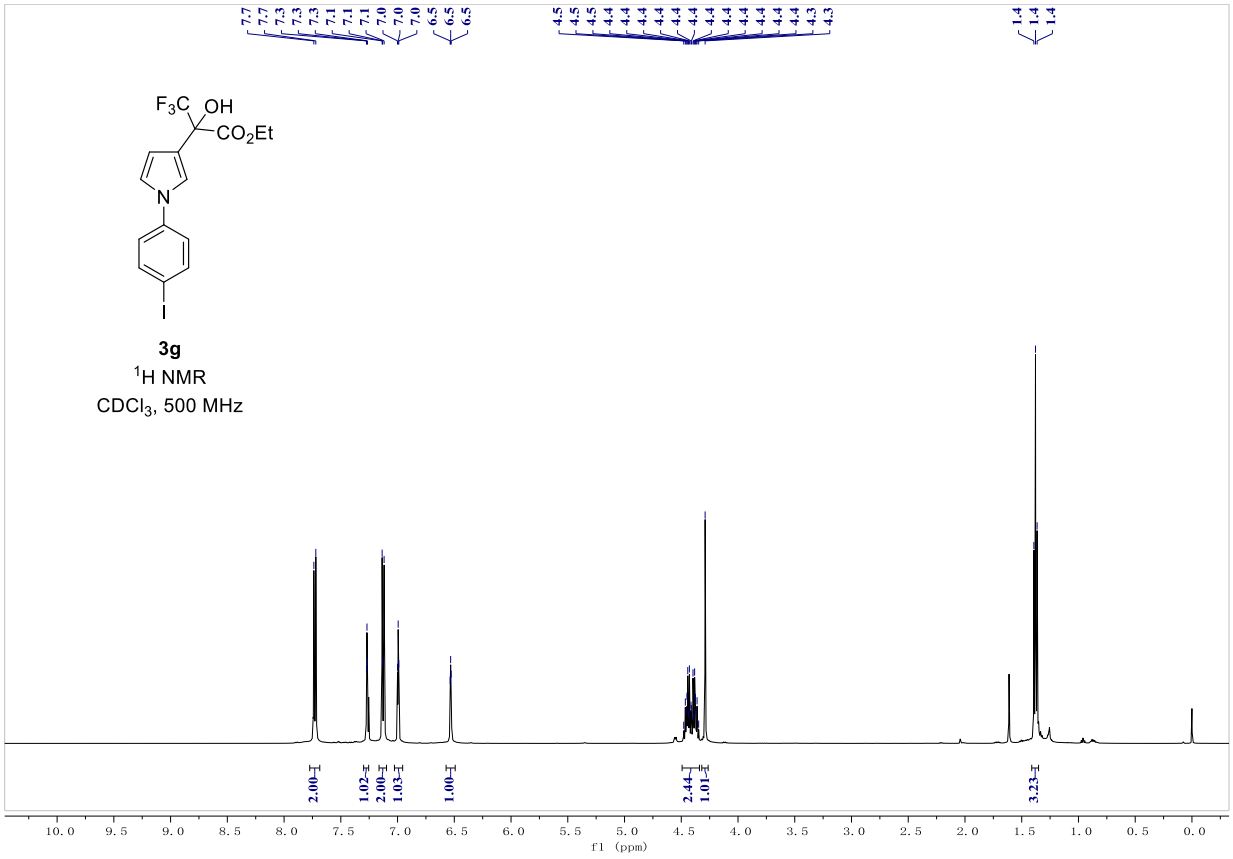
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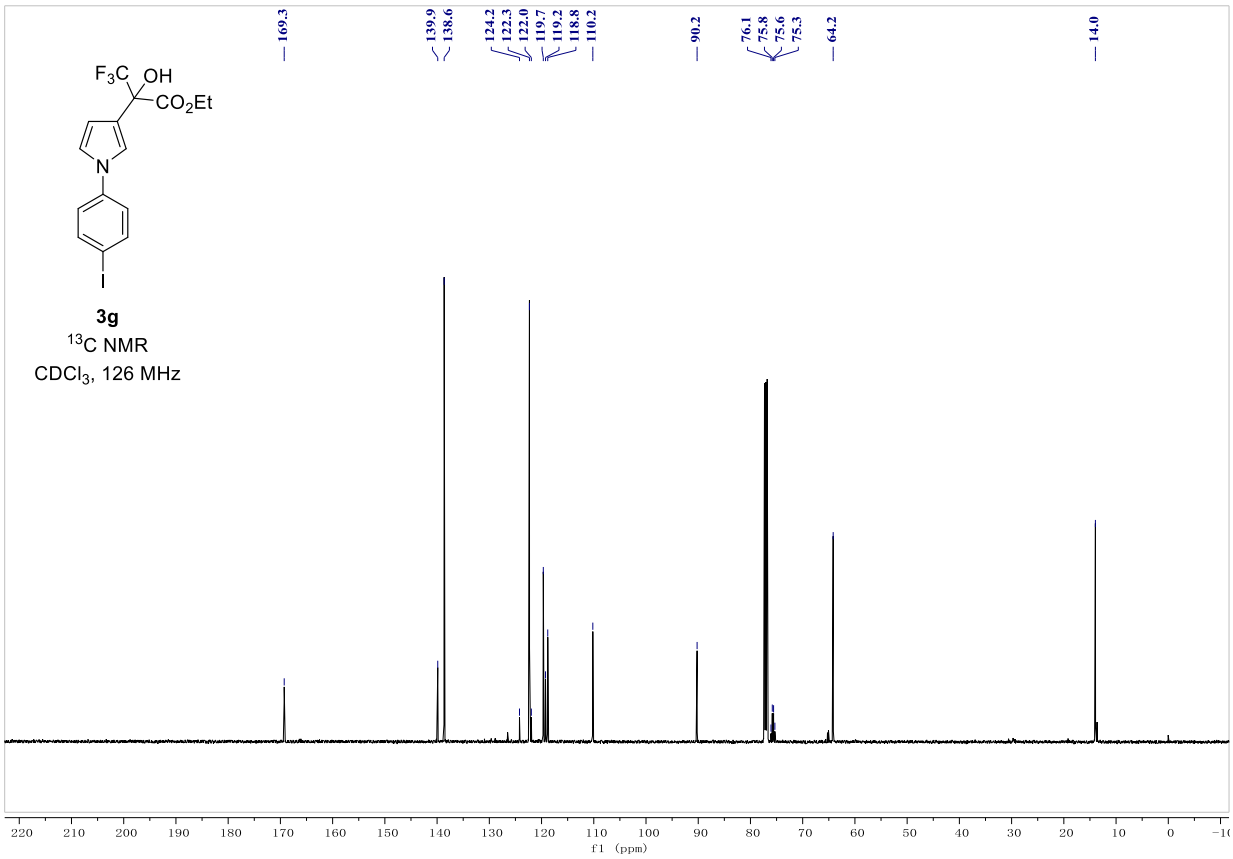
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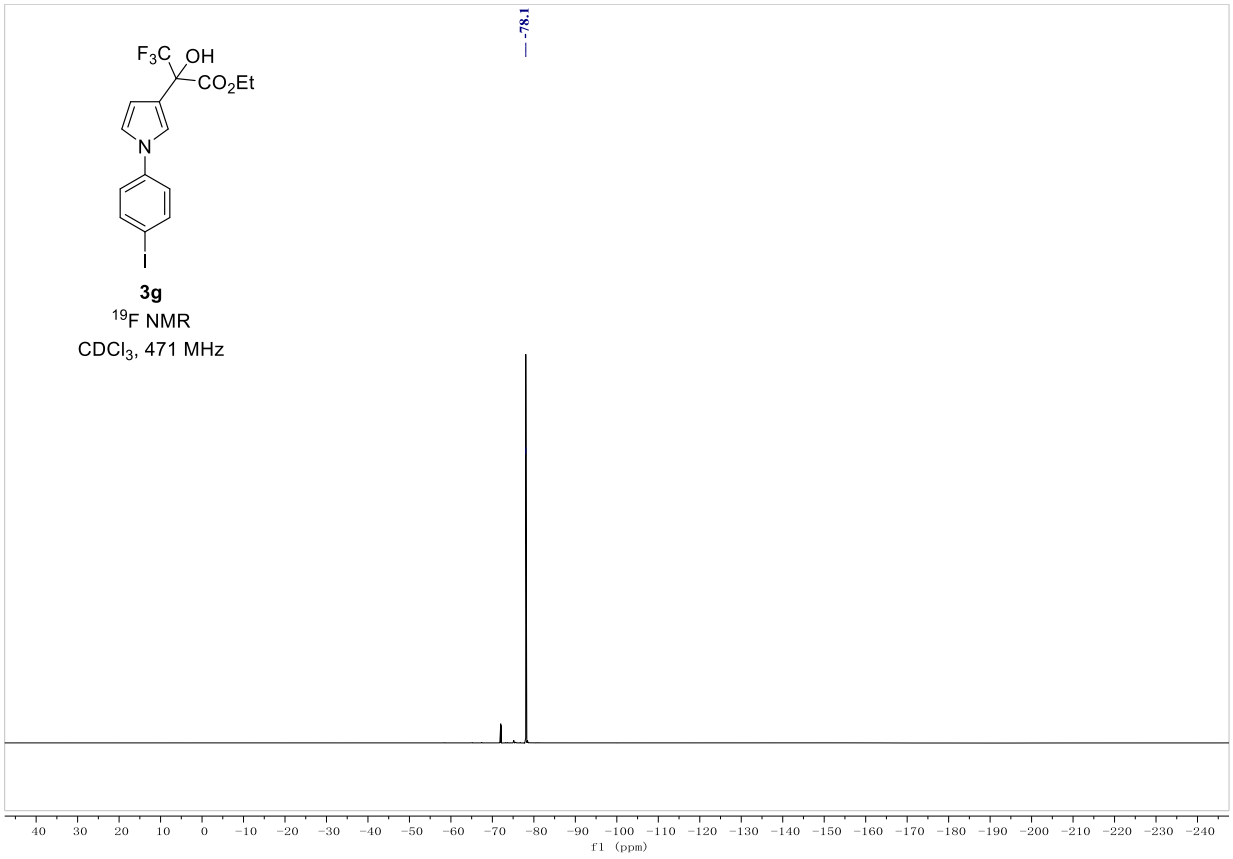
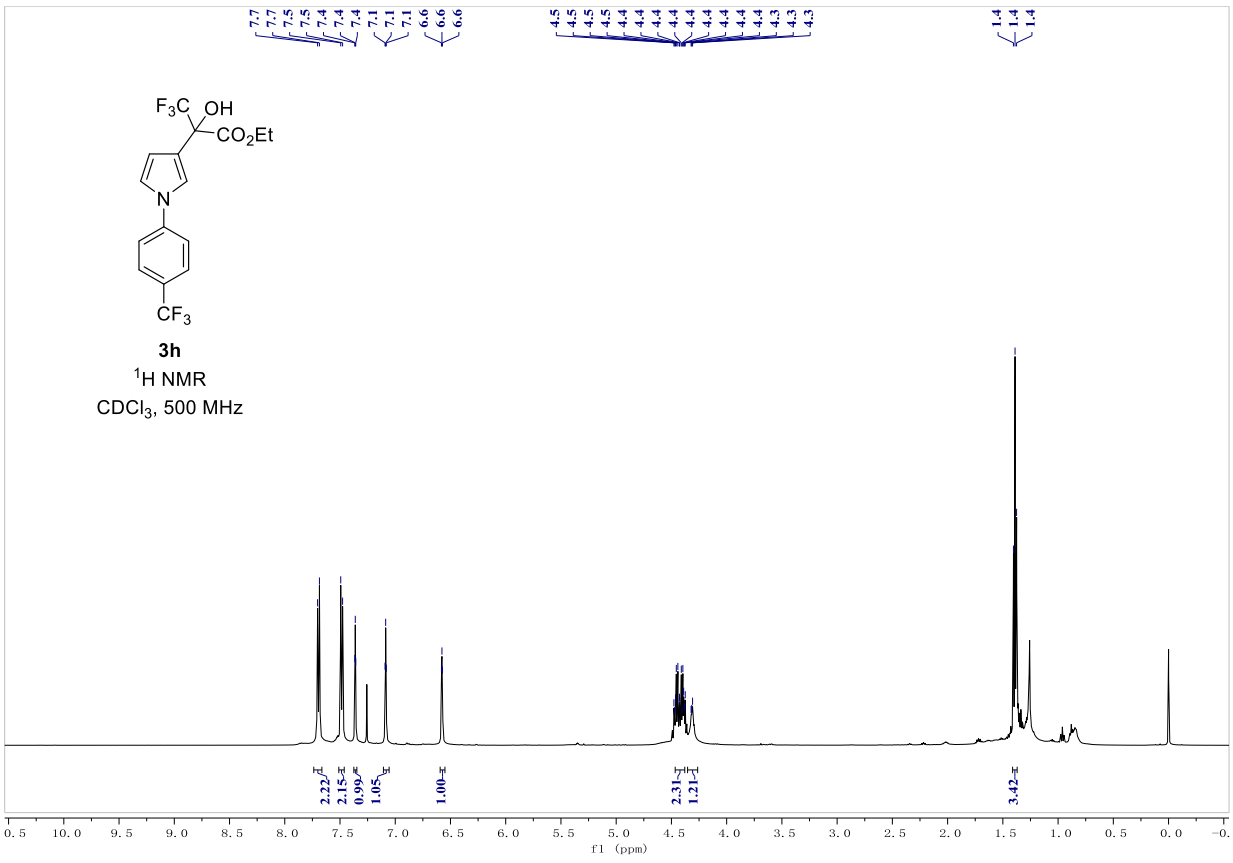
f1 (ppm)



3g

^{19}F NMR

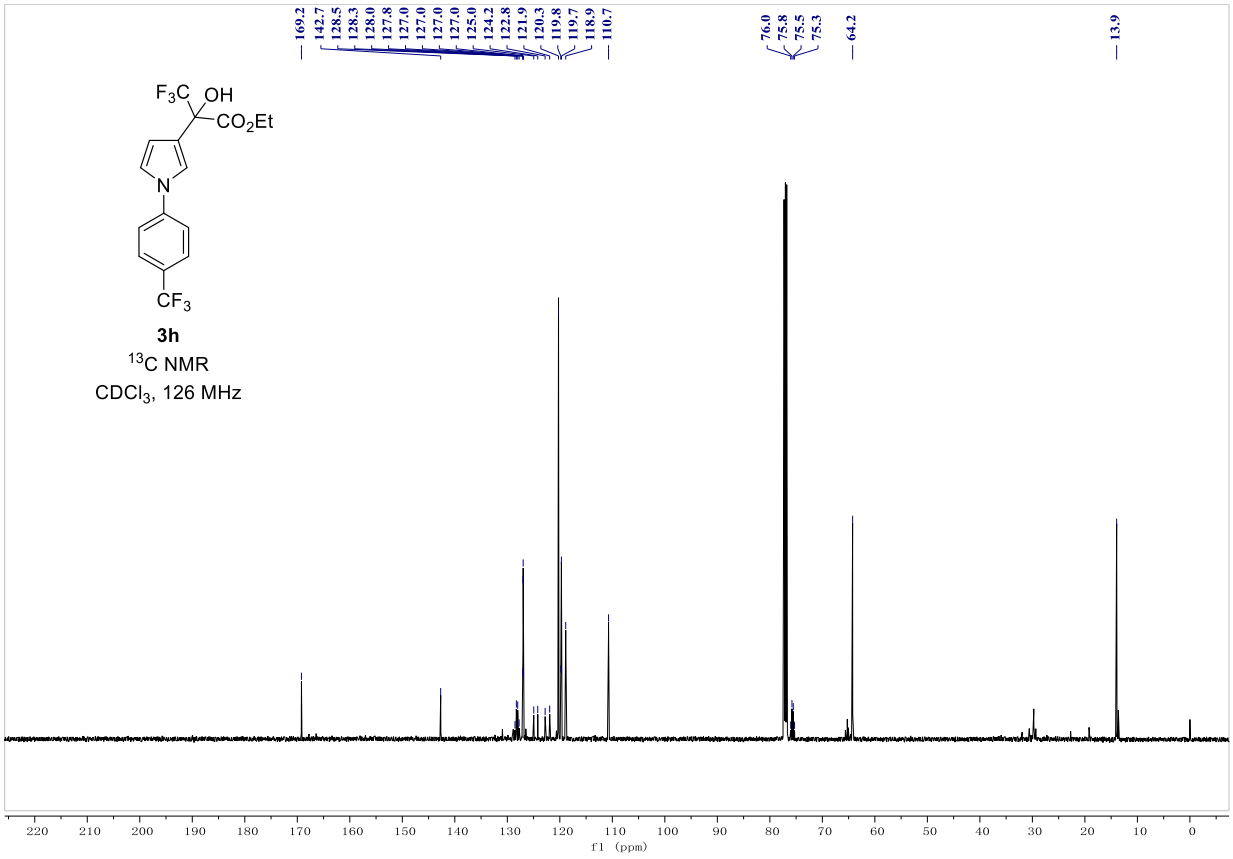
$CDCl_3$, 471 MHz



3h

^{1}H NMR

$CDCl_3$, 500 MHz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121.9
120.3
119.8
119.7
118.9
110.7
76.0
75.8
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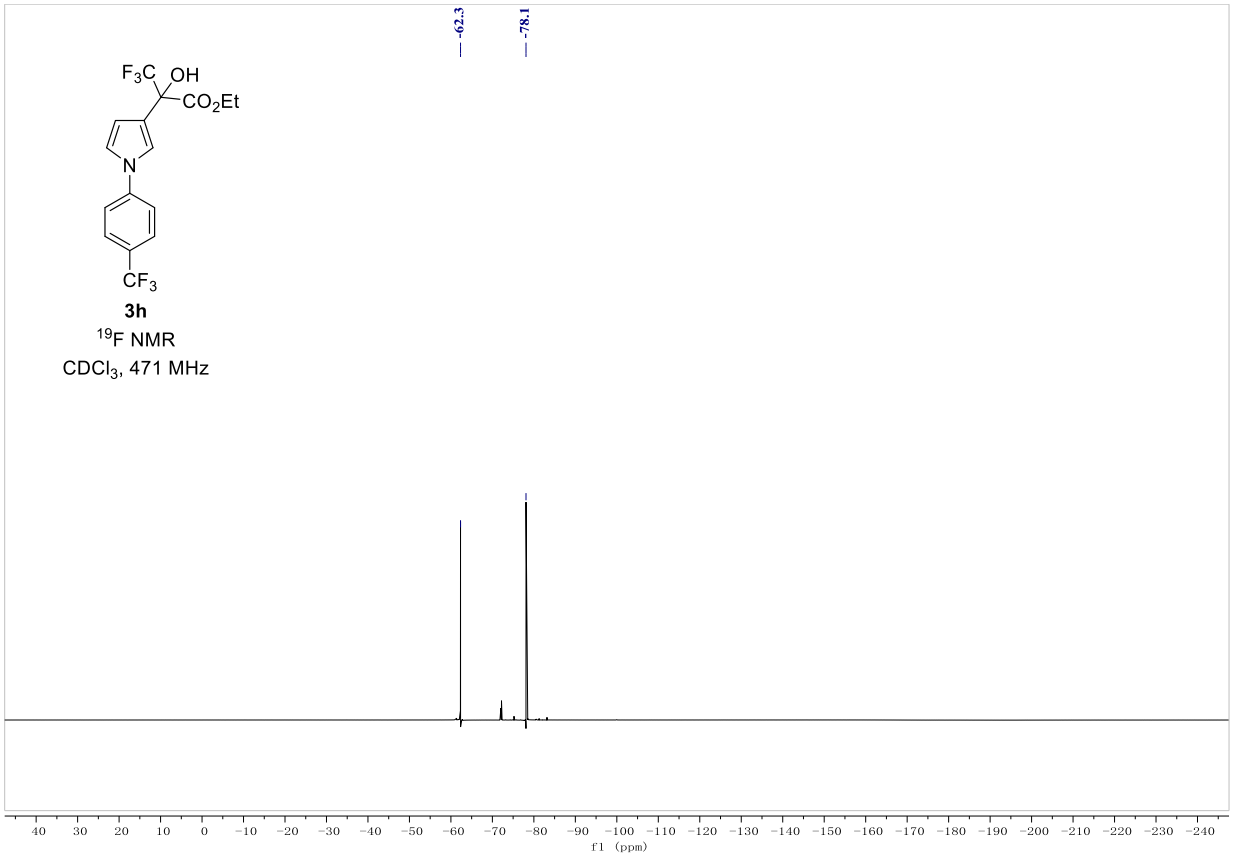
N
CF3
3h
13C NMR
CDCl3, 126 MHz
f1 (ppm)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CF3
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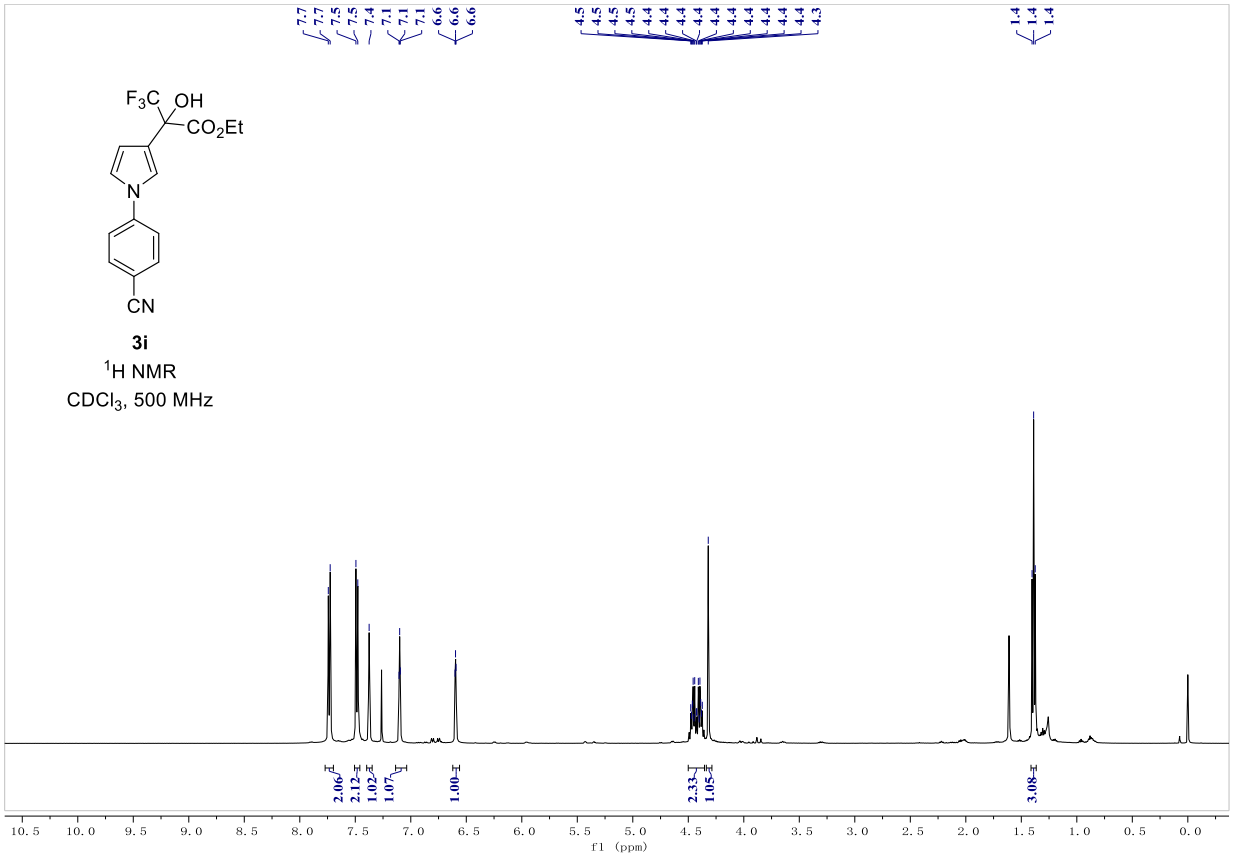
19F NMR
CDCl3, 471 MHz
f1 (ppm)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1H NMR
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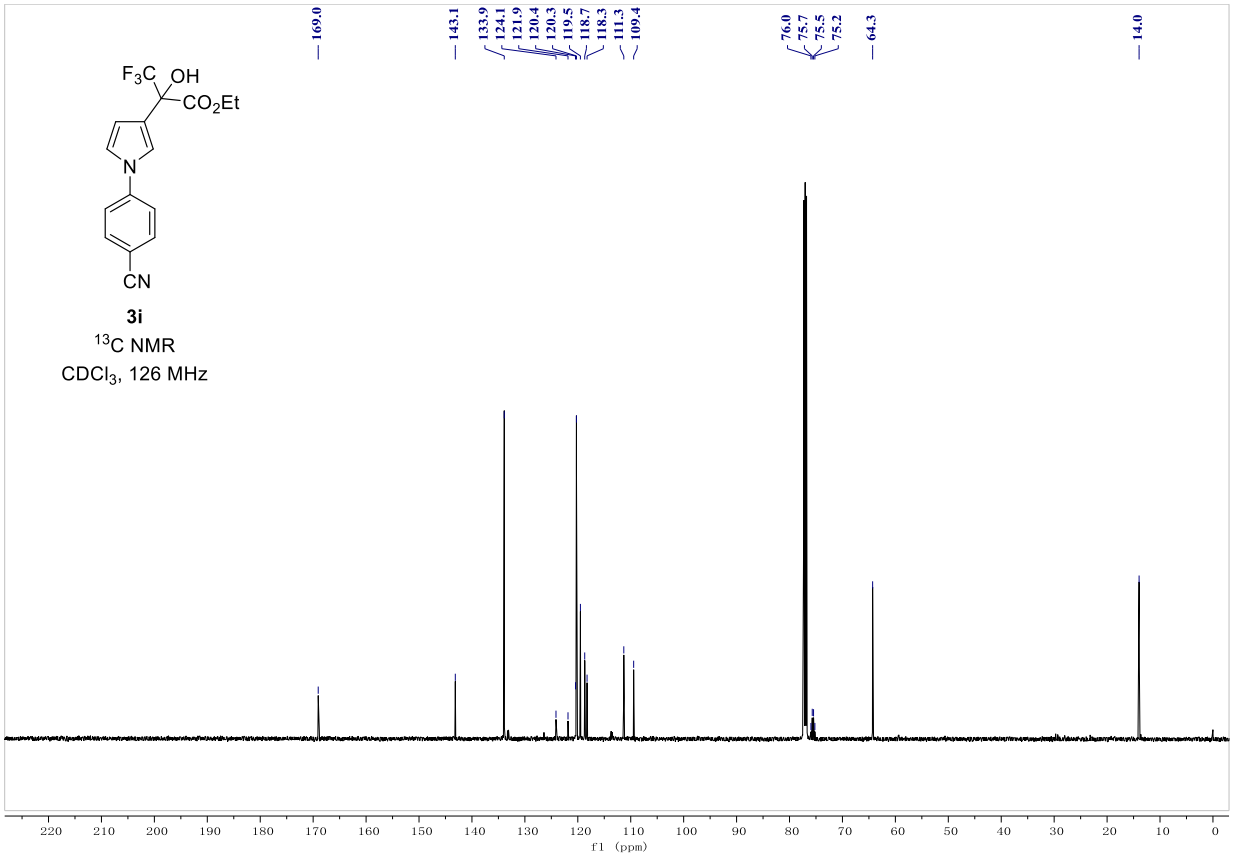
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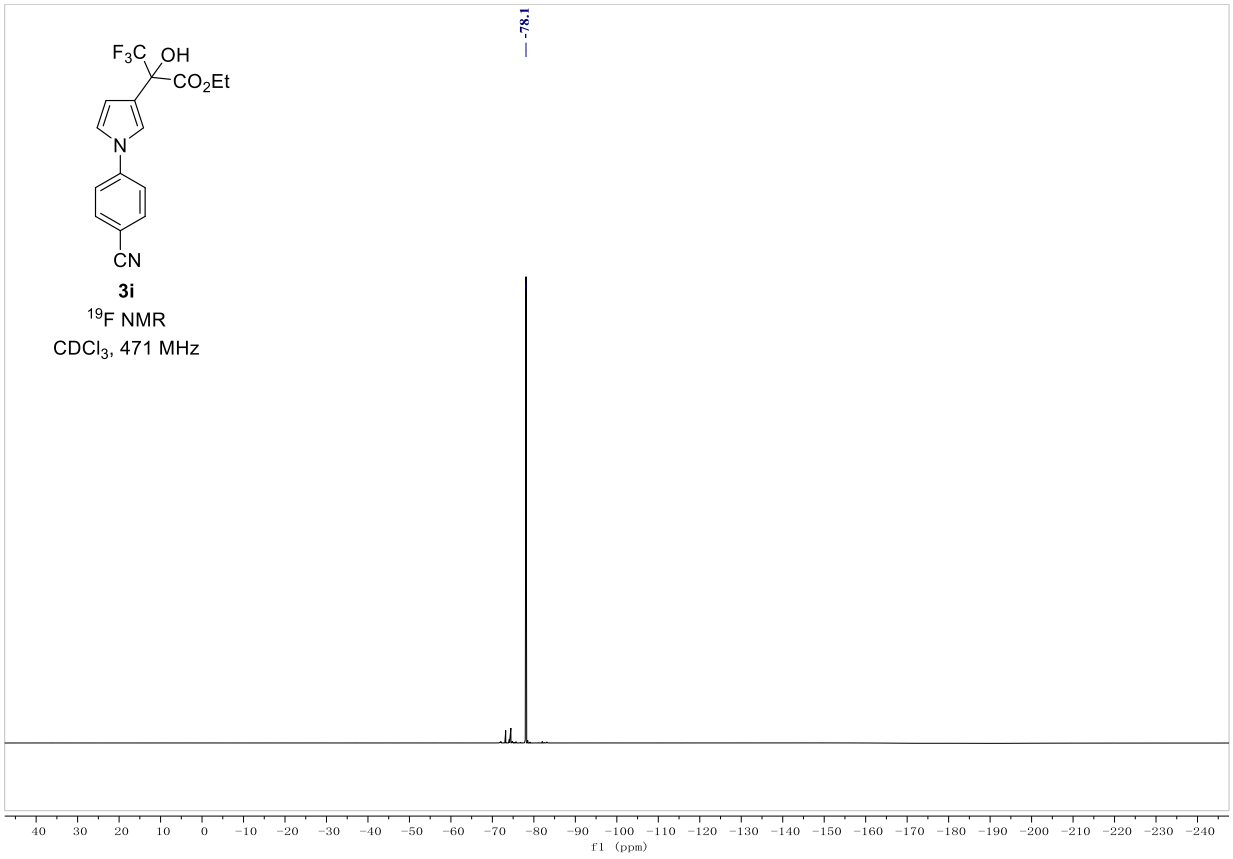
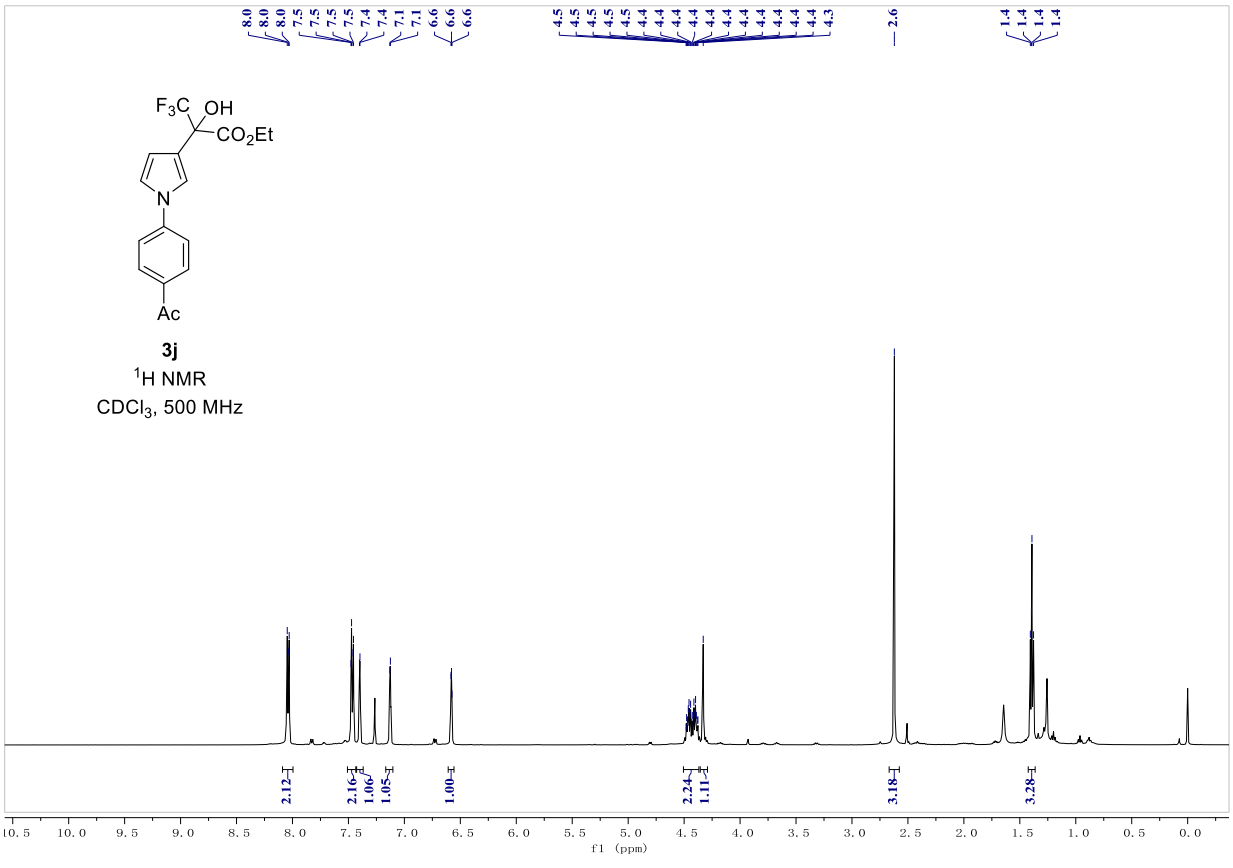


3i

^{19}F NMR

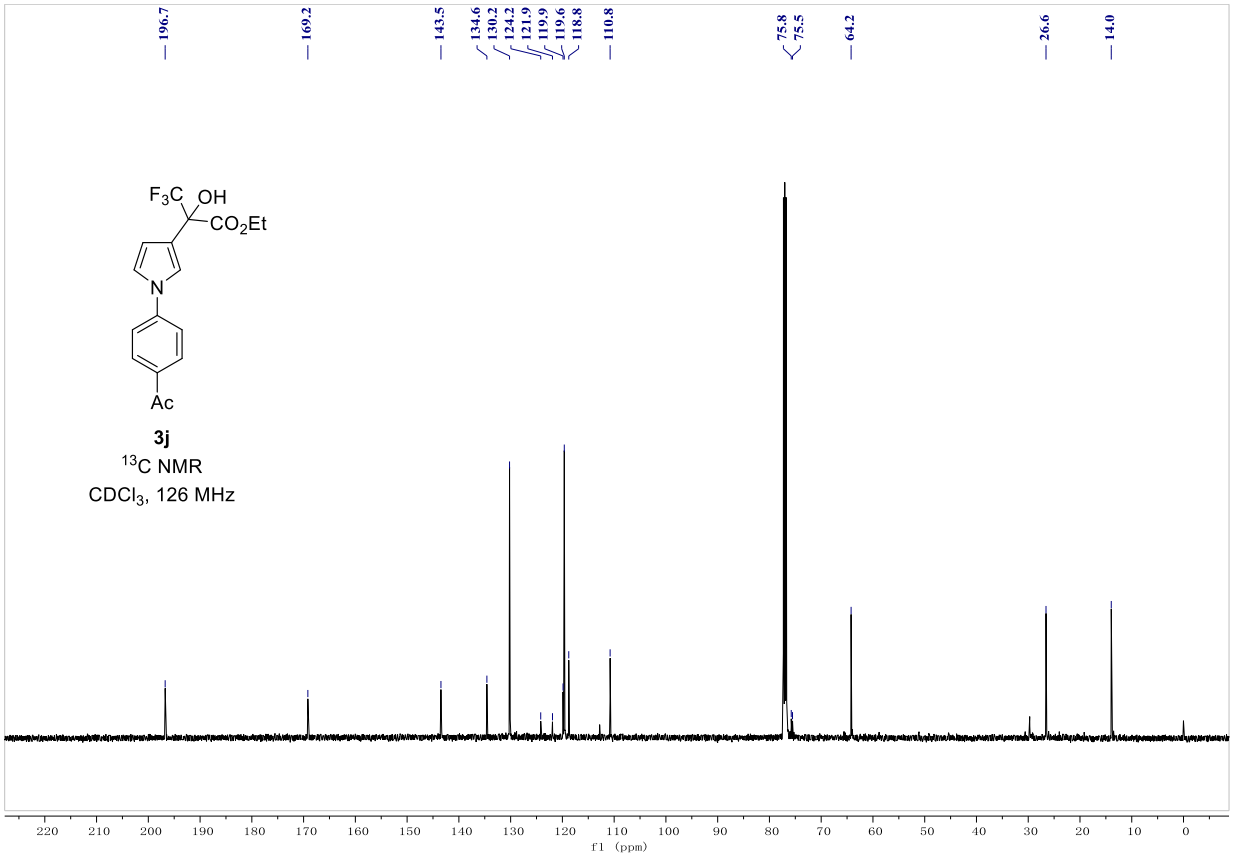
$CDCl_3$, 471 MHz



3j

^{1}H NMR

$CDCl_3$, 500 MHz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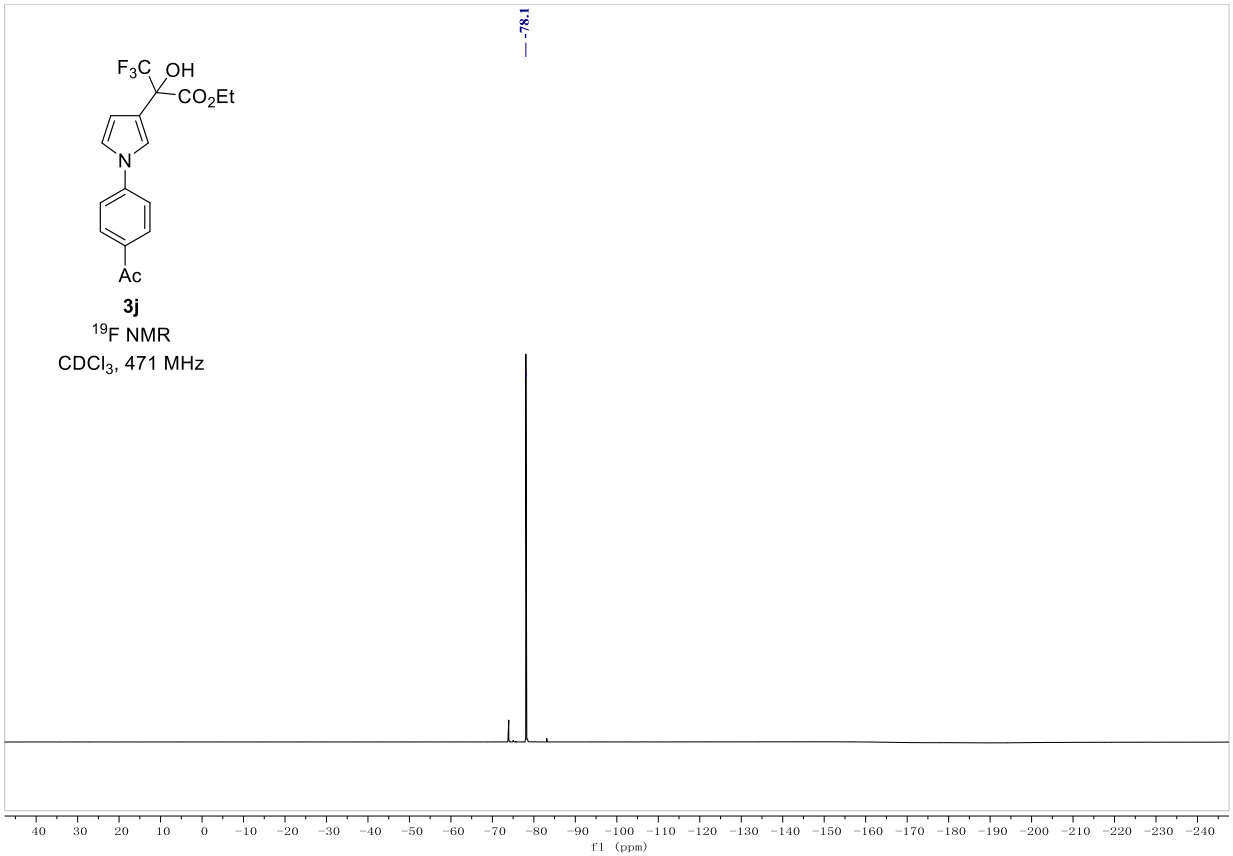
N
Ac
3j
13C NMR
CDCl3, 126 MHz
f1 (ppm)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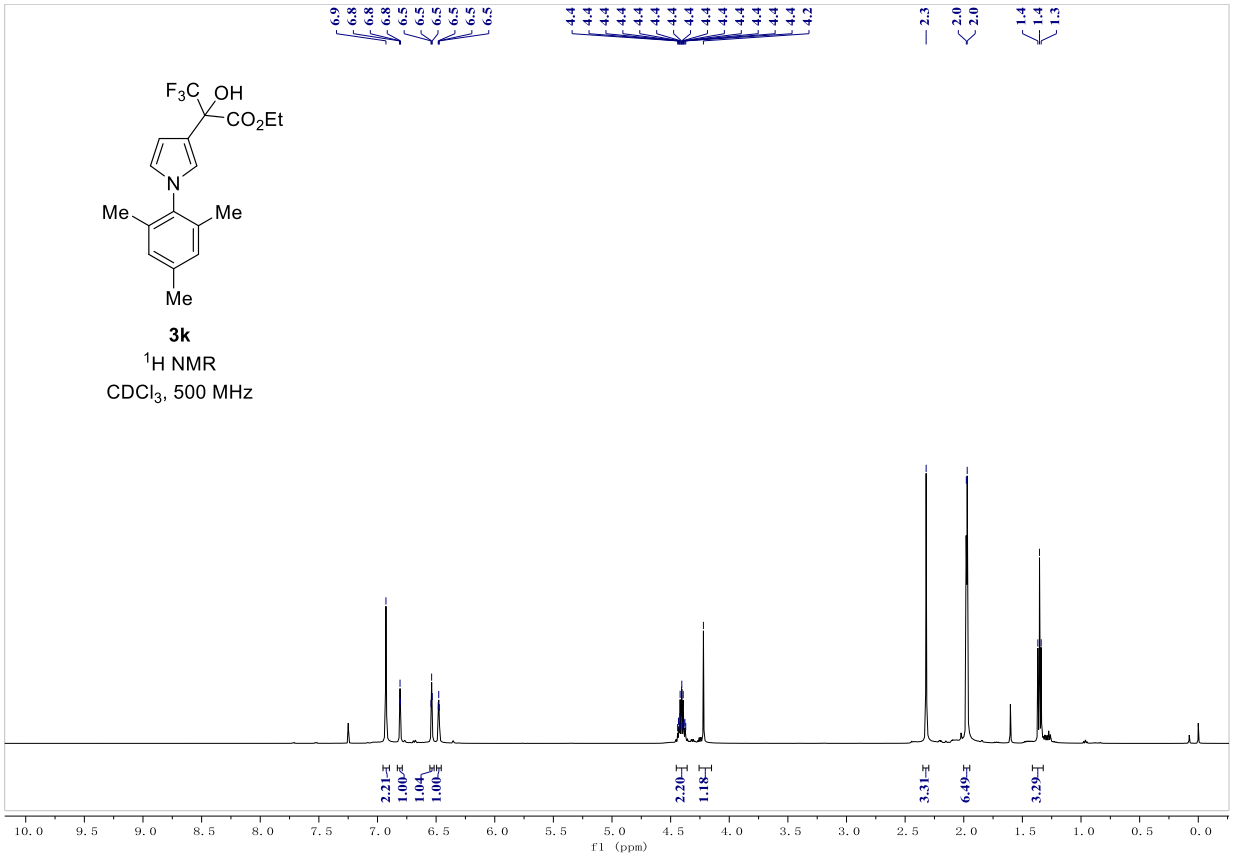
N
Ac
3j
19F NMR
CDCl3, 471 MHz
f1 (ppm)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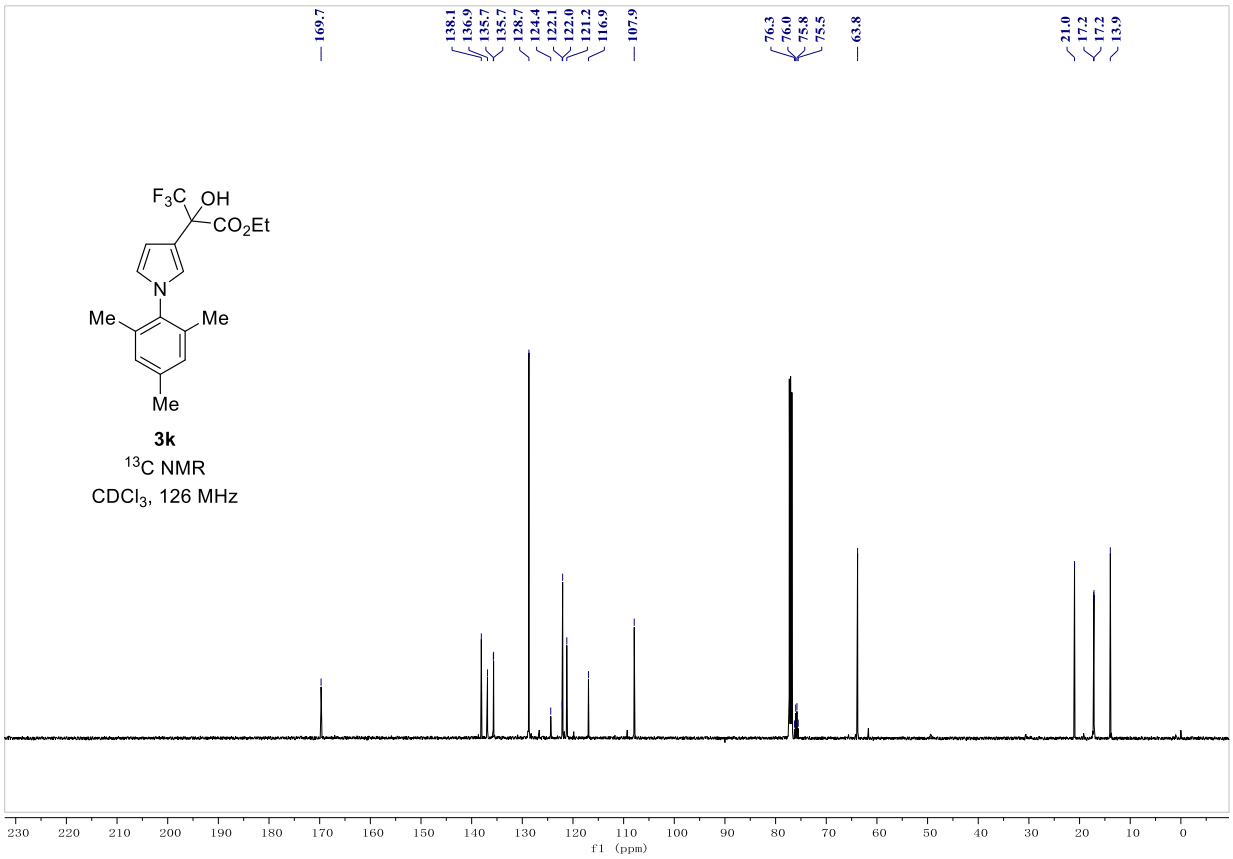
Me
Me
Me
3k
1H NMR
CDCl3, 500 MHz
f1 (ppm)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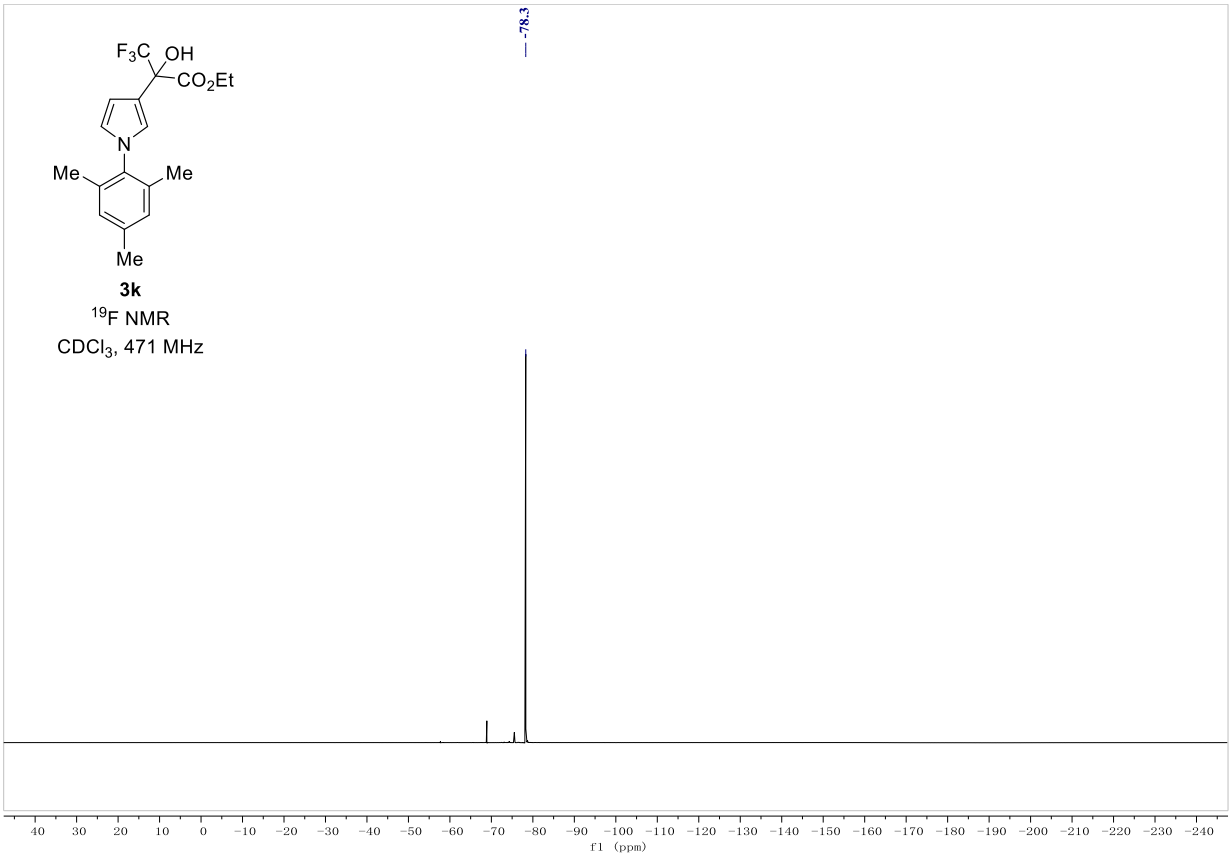
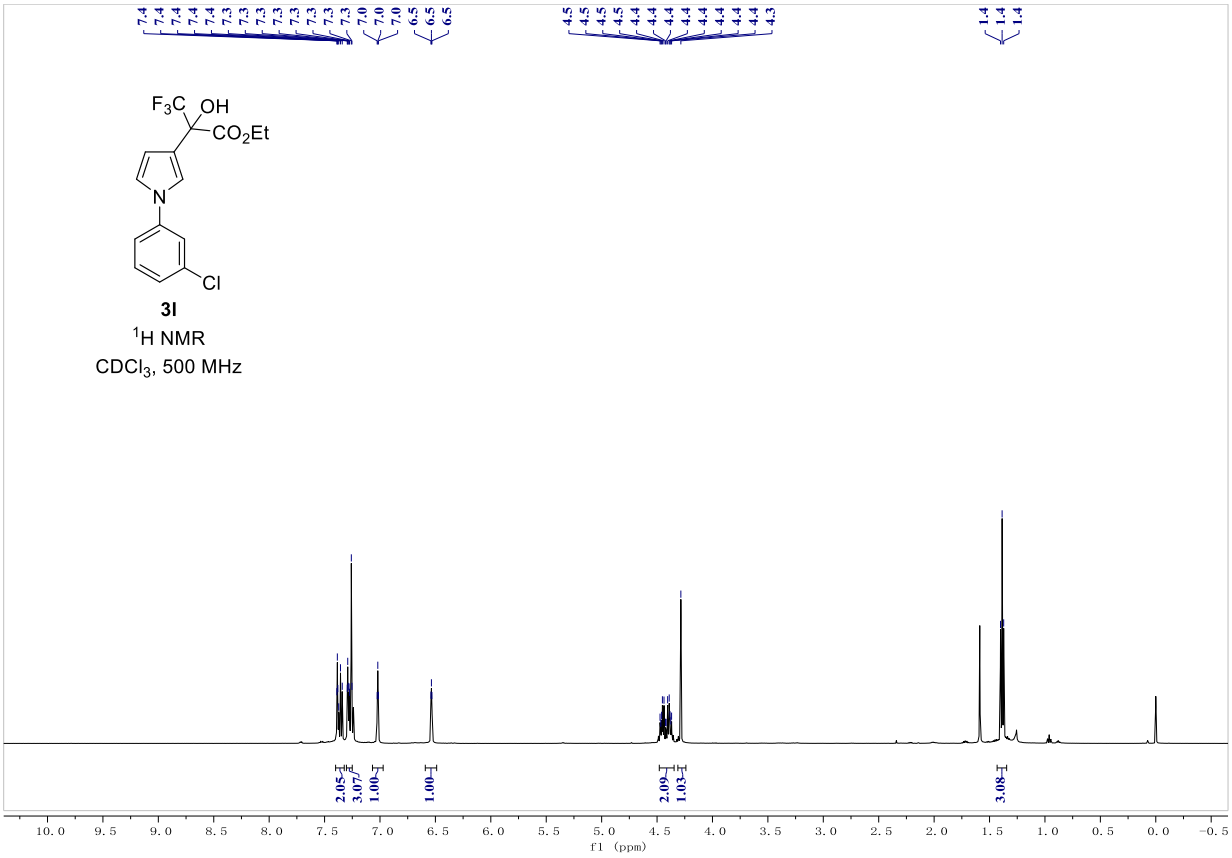
N
Me
Me
Me
3k
13C NMR
CDCl3, 126 MHz
f1 (ppm)



3k

^{19}F NMR

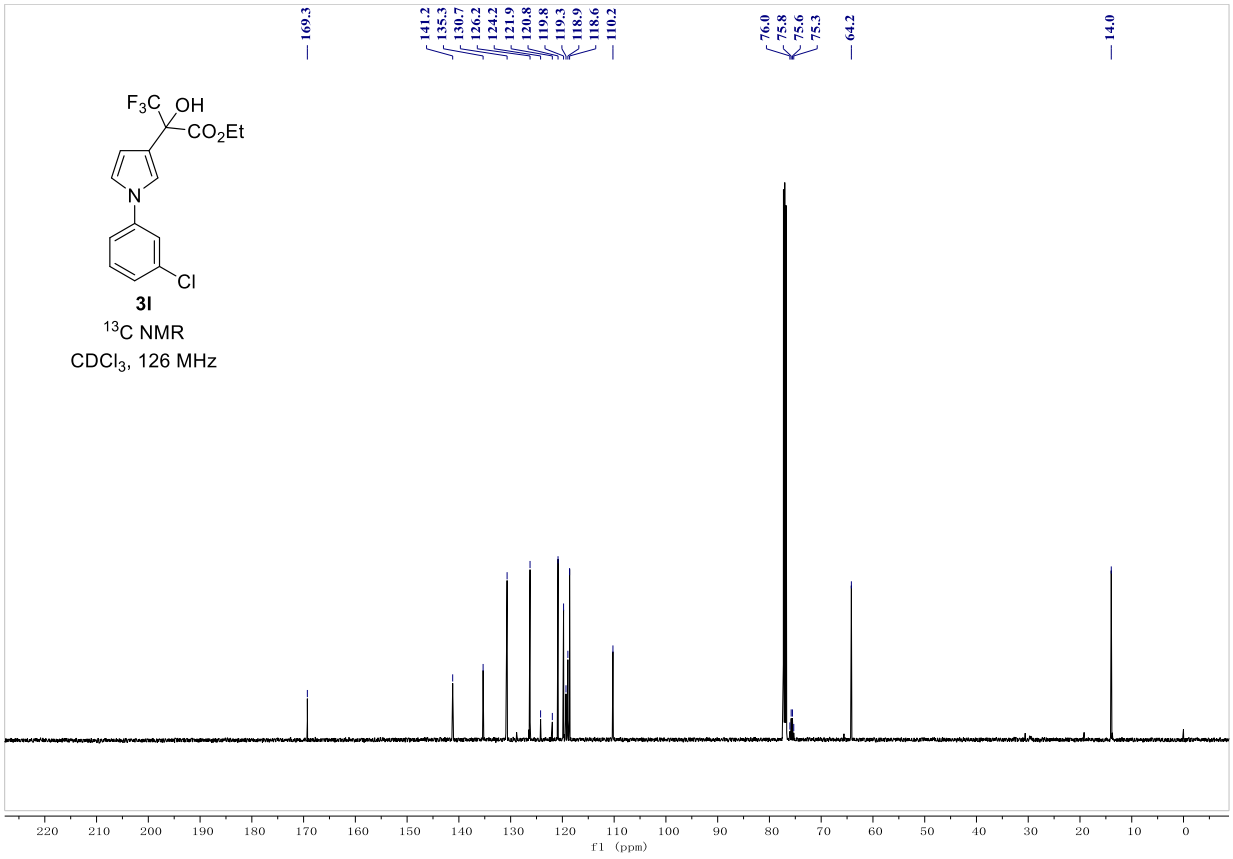
$CDCl_3$, 471 MHz



3l

^{1}H NMR

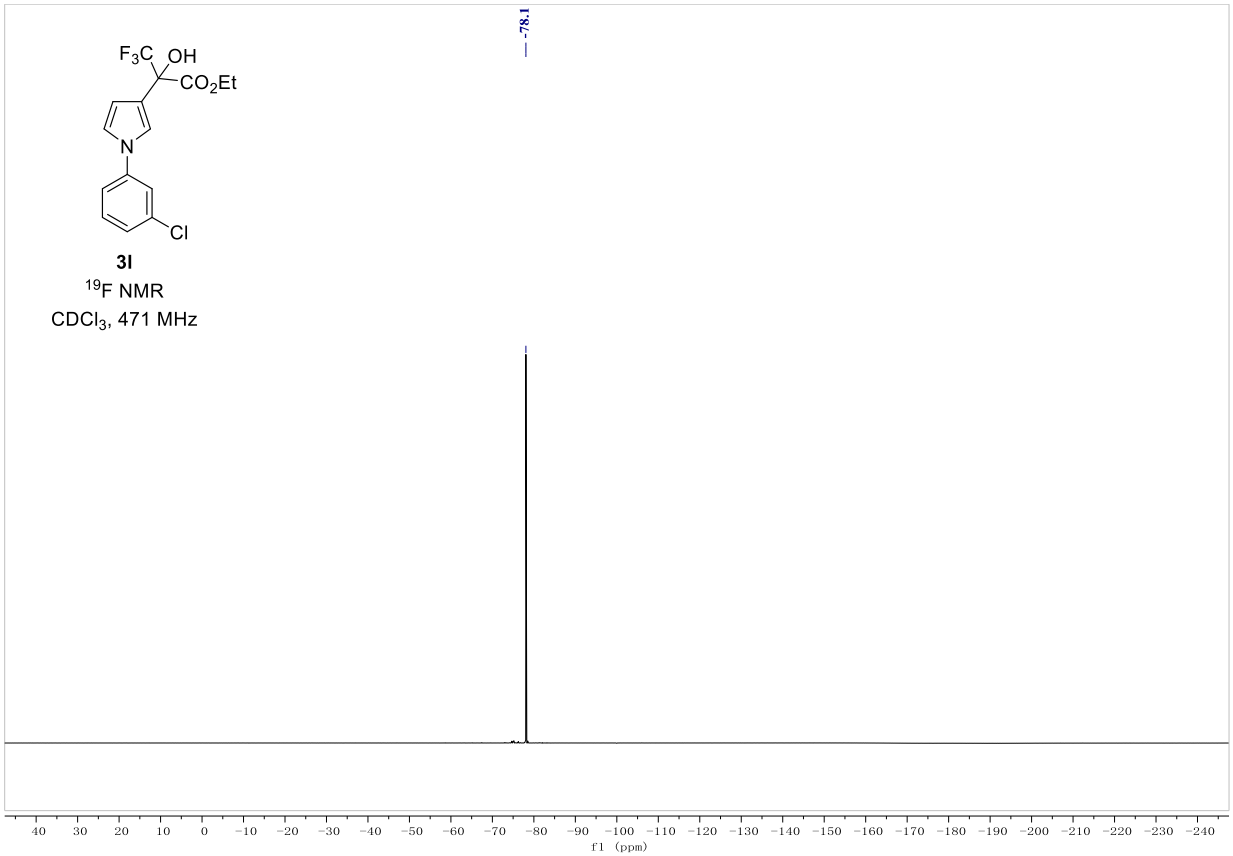
$CDCl_3$, 500 MHz



3l

^{13}C NMR

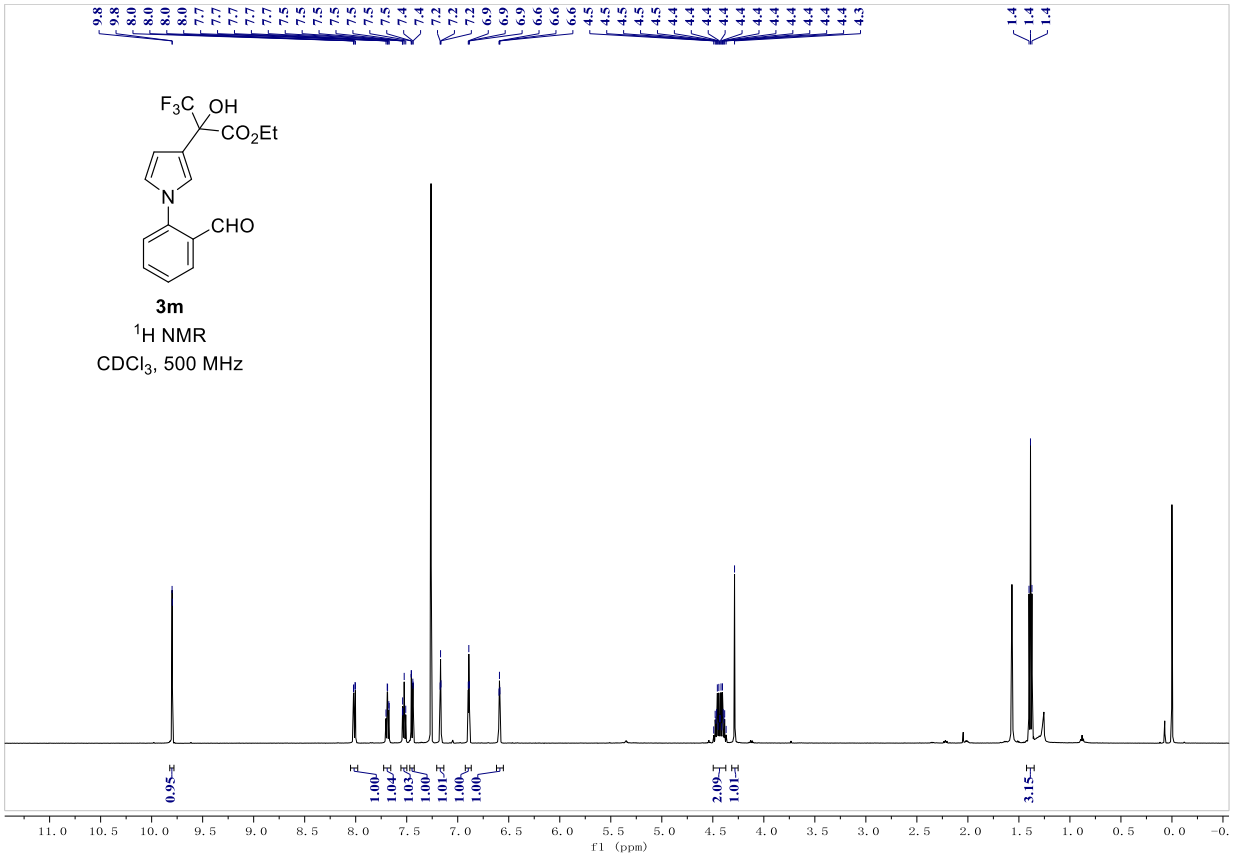
$CDCl_3$, 126 MHz



3l

^{19}F NMR

$CDCl_3$, 471 MHz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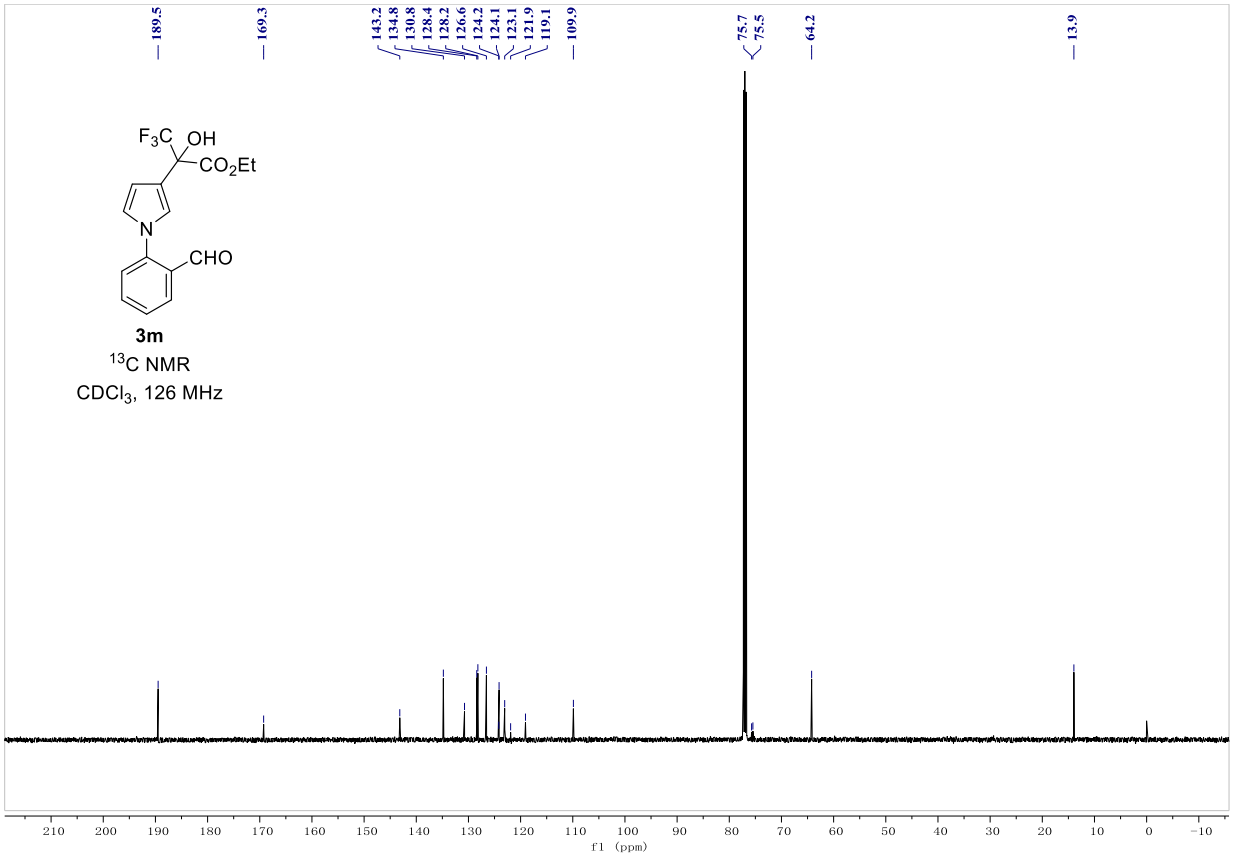
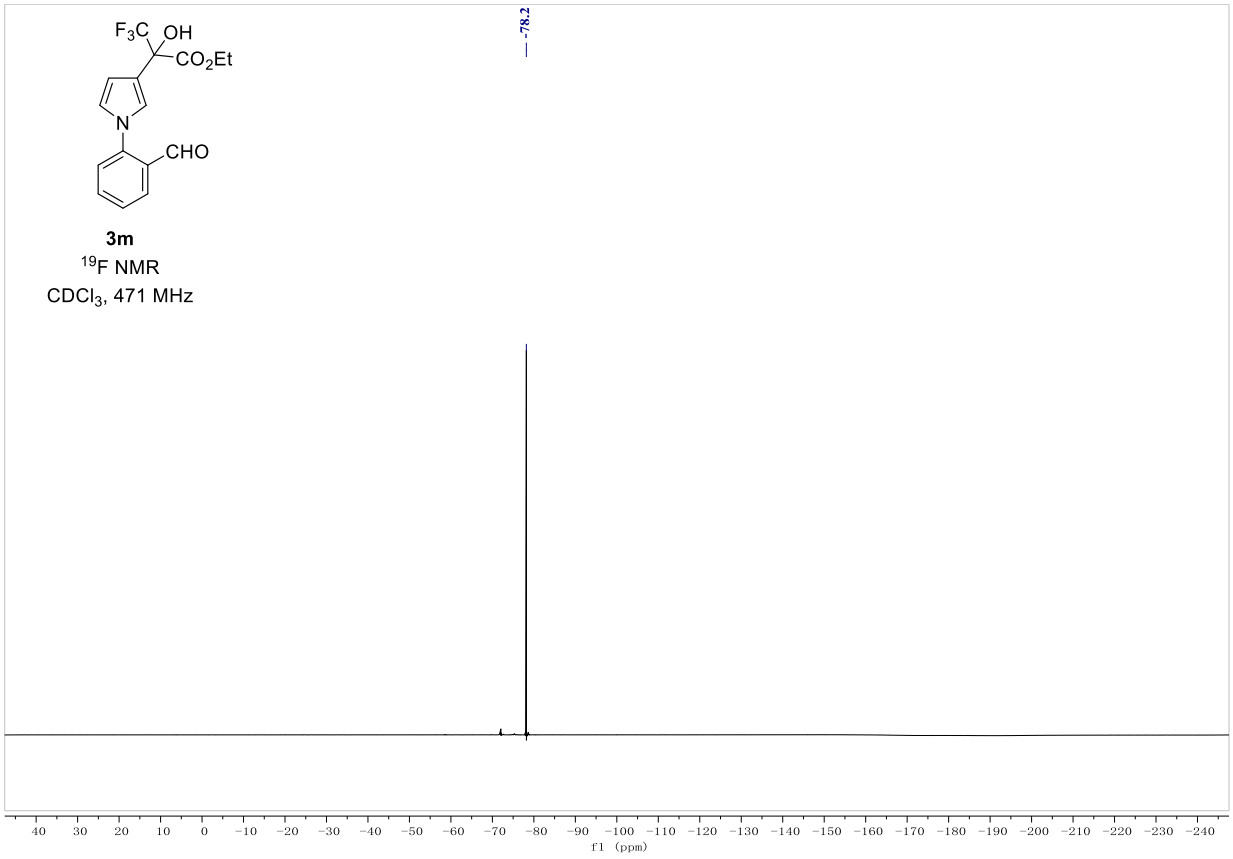
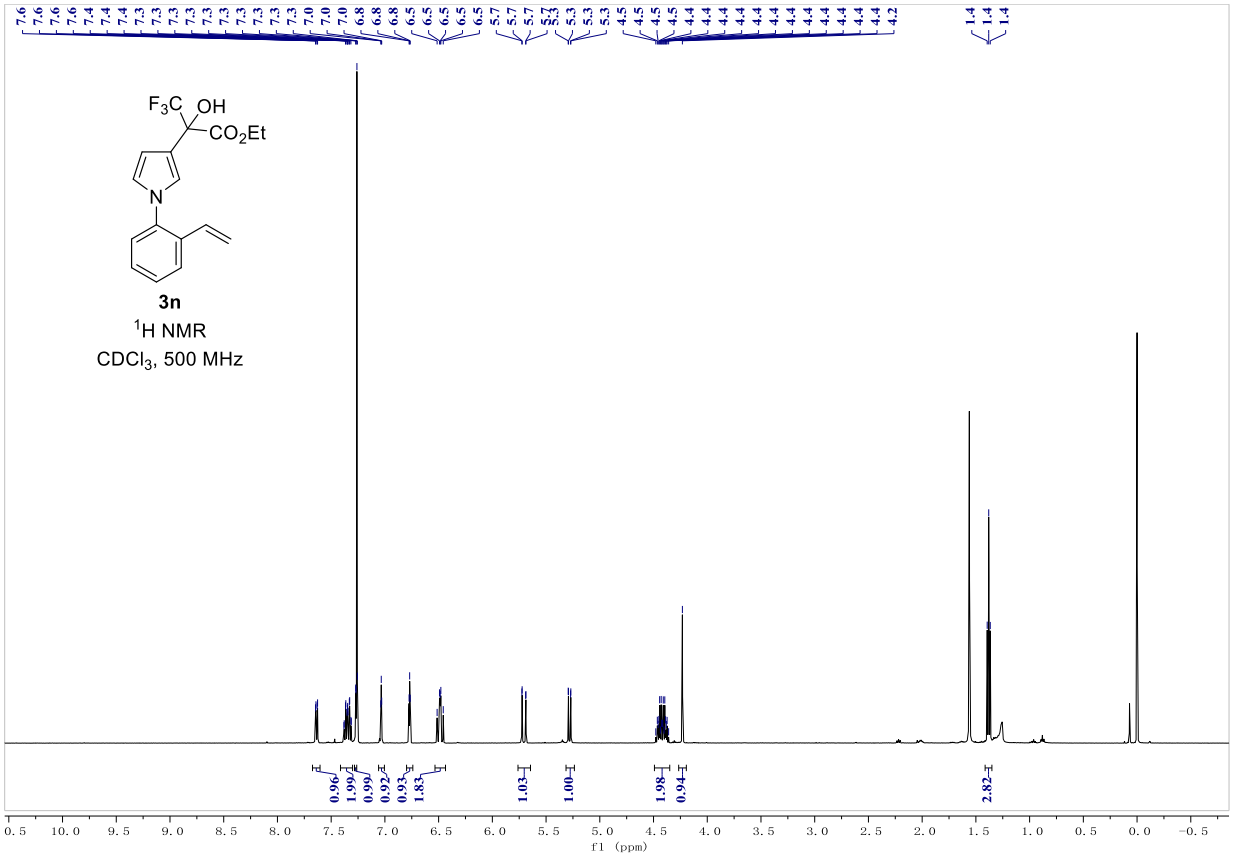
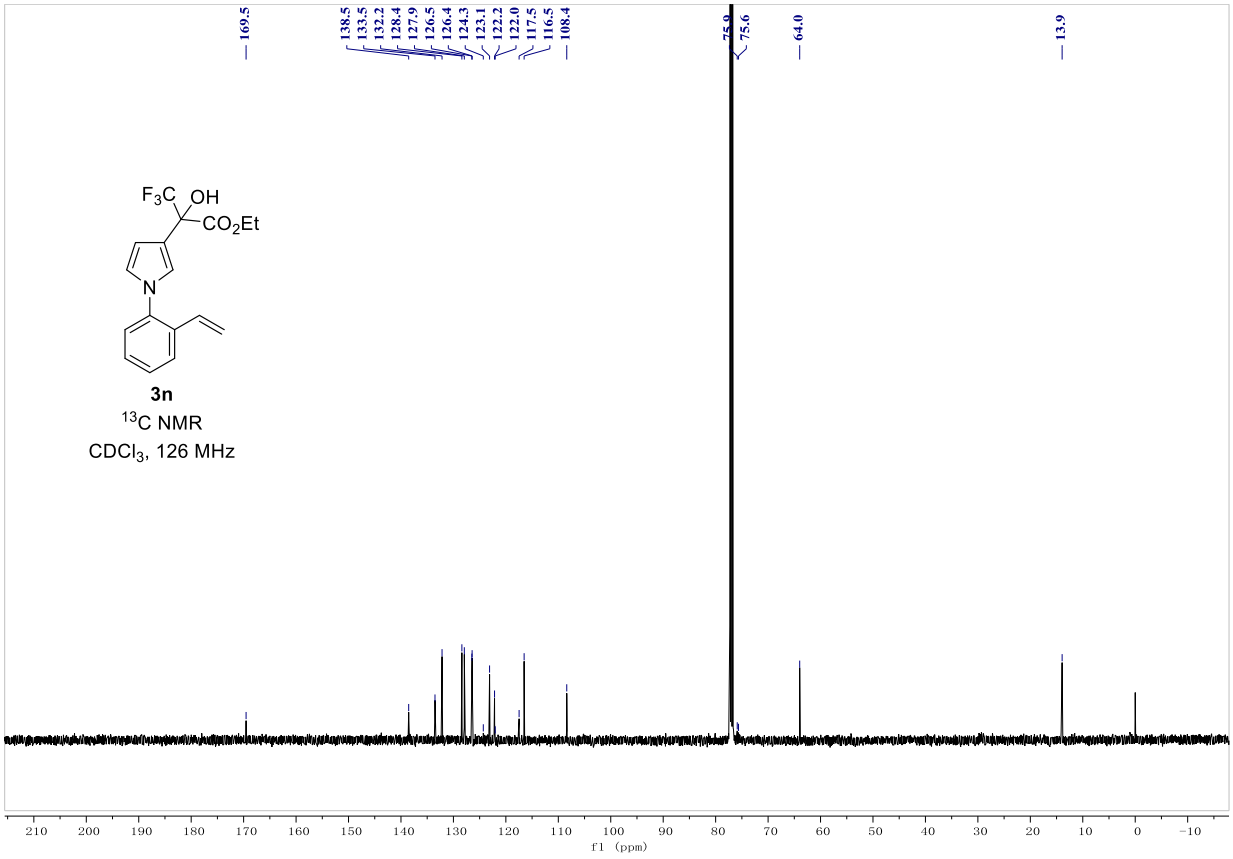
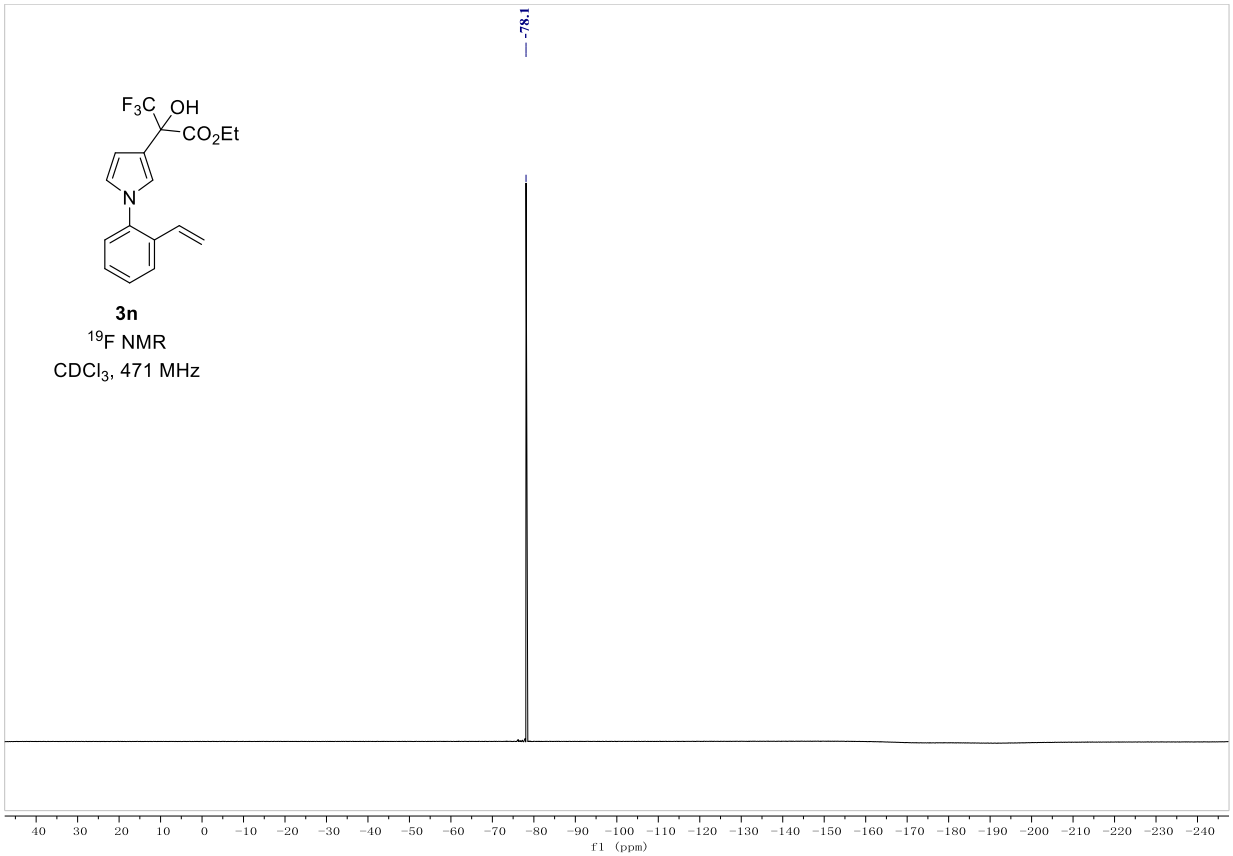
CO2Et
N
CHO
3m
1H NMR
CDCl3, 500 MHz
f1 (ppm)

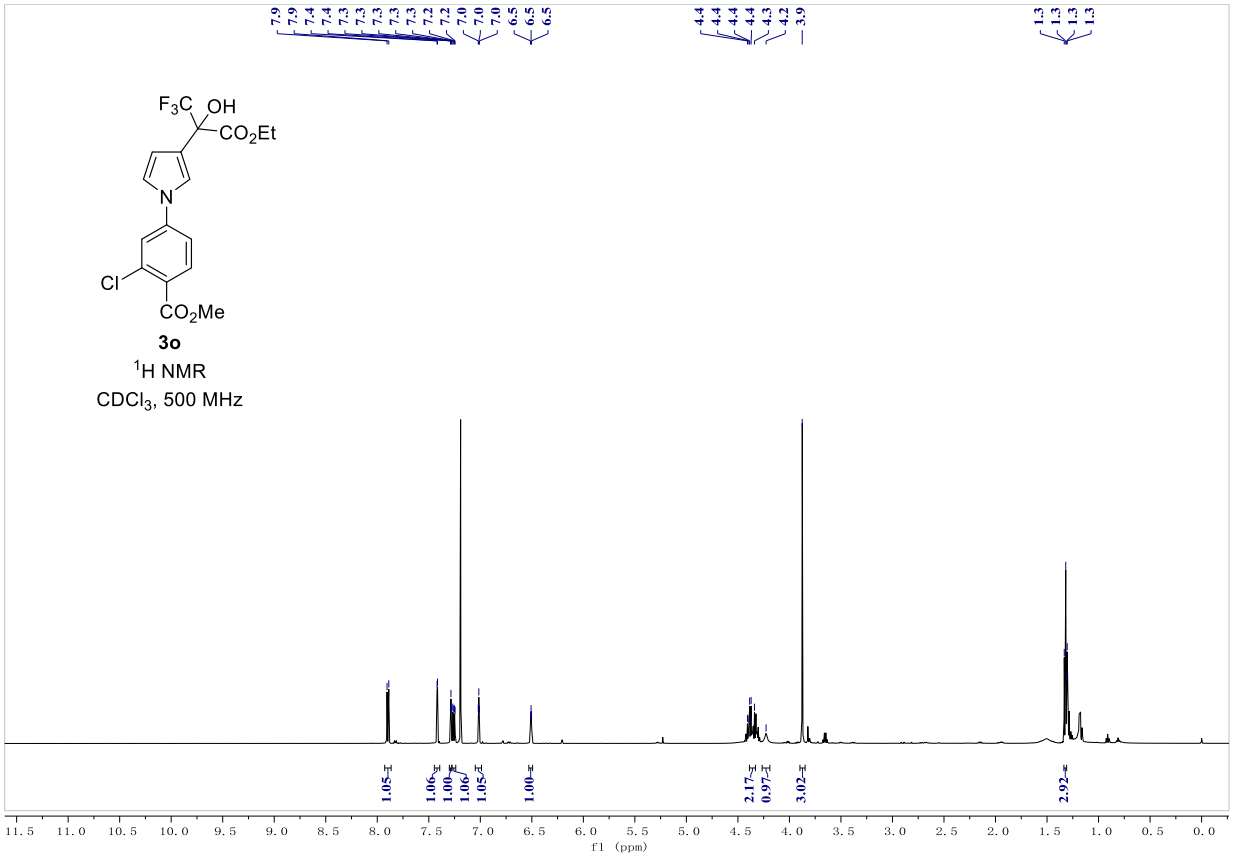

F3C OH
CO2Et
N
CHO
3m
13C NMR
CDCl3, 126 MHz
f1 (ppm)

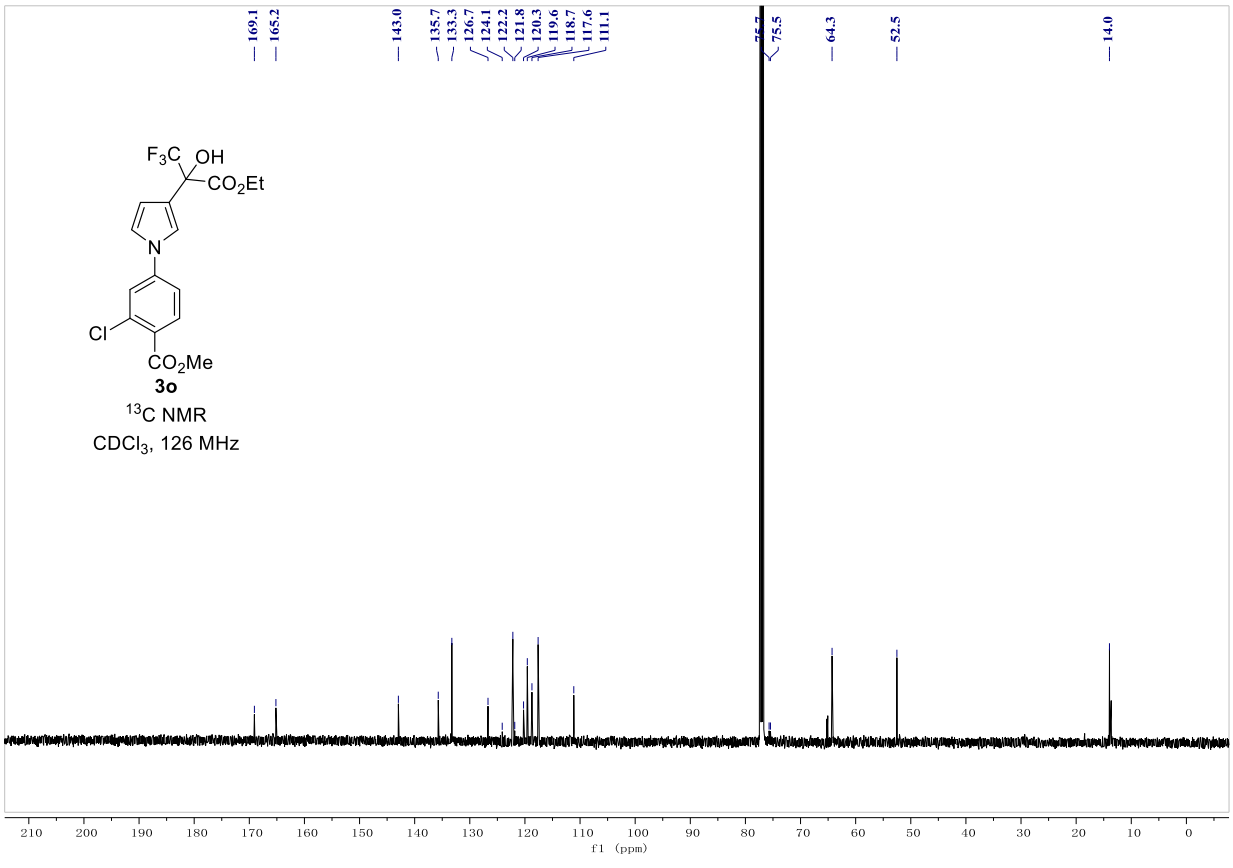

F3C OH
CO2Et
N
CHO
-78.2
3m
19F NMR
CDCl3, 471 MHz
f1 (ppm)

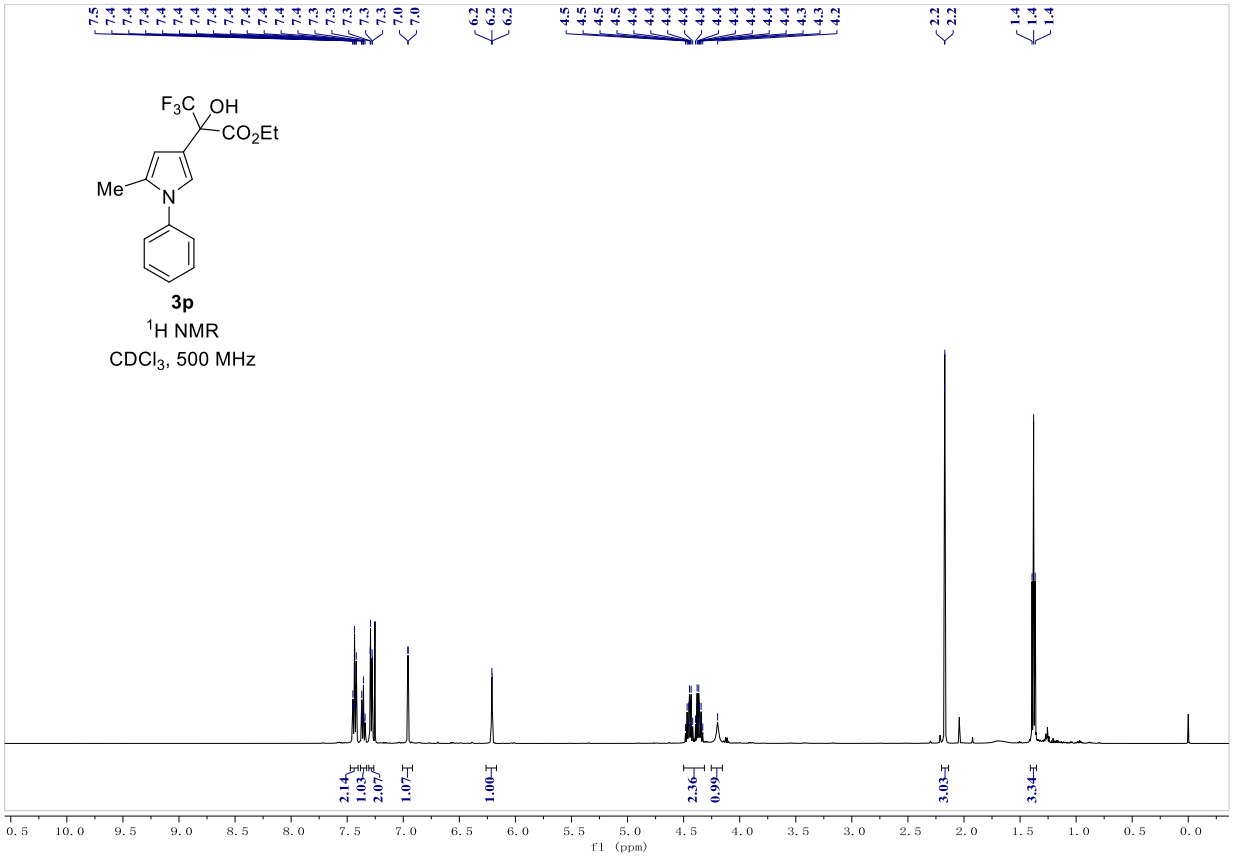

F3C OH
CO2Et
N
3n
1H NMR
CDCl3, 500 MHz
0.96
1.99
0.99
0.92
0.93
1.83
1.03
1.00
1.98
0.94
2.82
f1 (ppm)

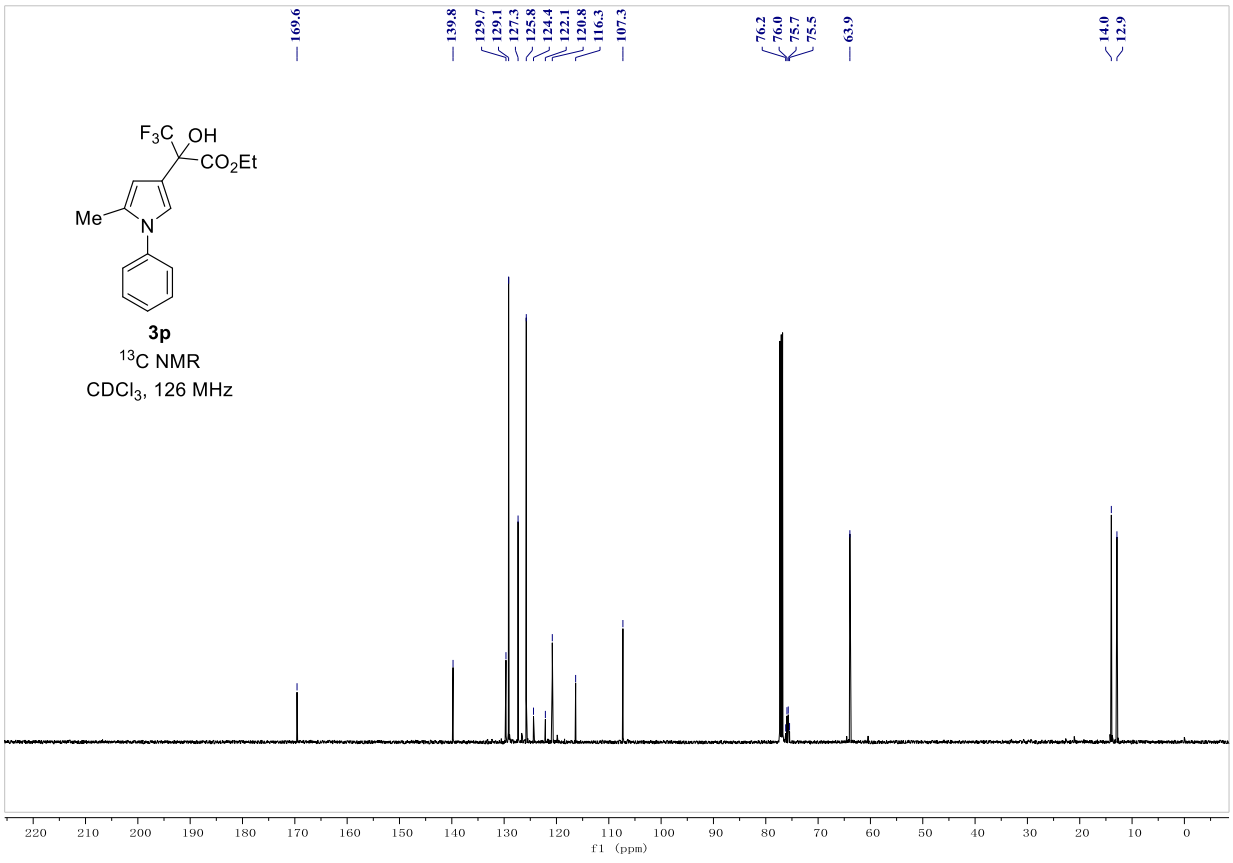

169.5
138.5
133.5
132.2
128.4
127.9
126.5
126.4
124.3
123.1
122.2
122.0
117.5
116.5
108.4
75.9
75.6
64.0
13.9
F3C OH
CO2Et
N
3n
13C NMR
CDCl3, 126 MHz
f1 (ppm)

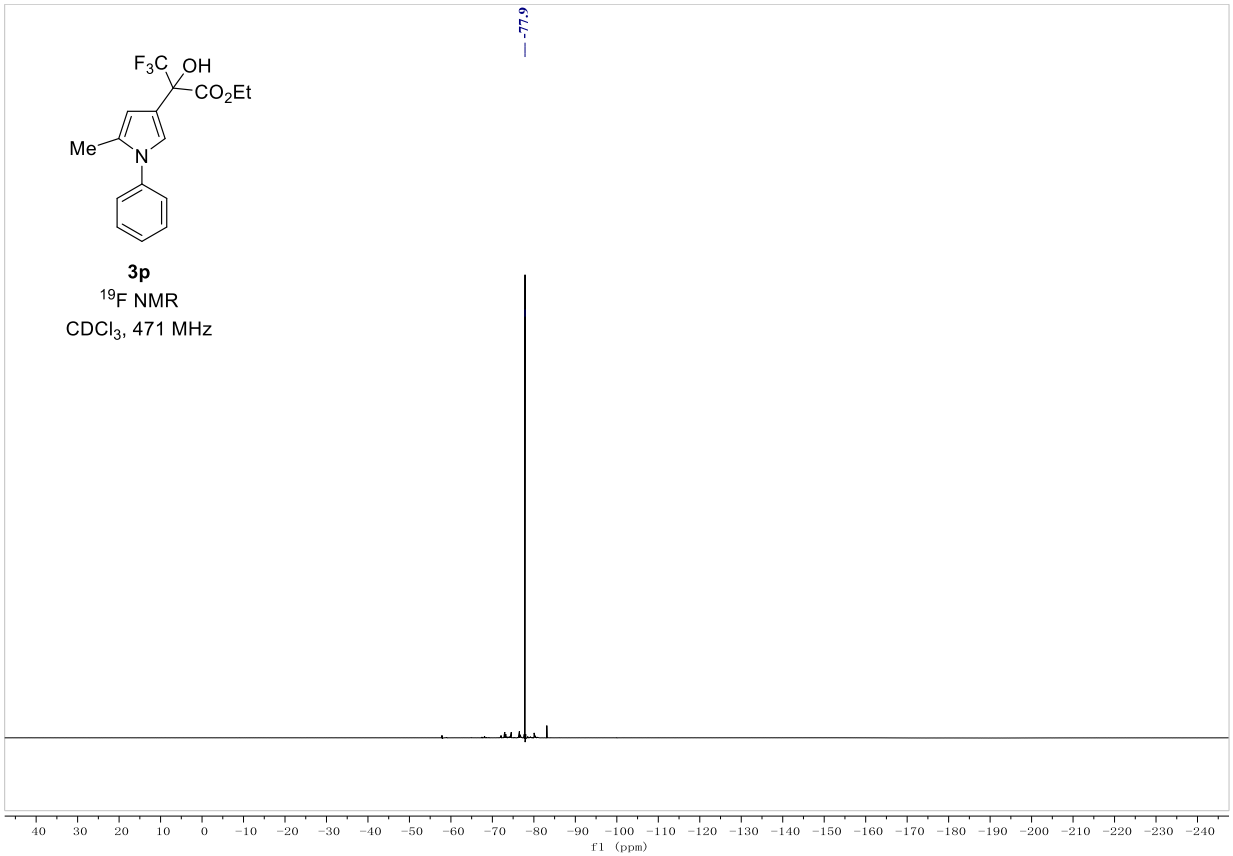

-78.1
F3C OH
CO2Et
N
3n
19F NMR
CDCl3, 471 MHz
f1 (ppm)


F3C OH
CO2Et
N
Cl
CO2Me
3o
1H NMR
CDCl3, 500 MHz
f1 (ppm)


F3C OH
CO2Et
N
Cl
CO2Me
3o
13C NMR
CDCl3, 126 MHz
f1 (ppm)


F3C OH
CO2Et
Me
N
3p
1H NMR
CDCl3, 500 MHz
f1 (ppm)


F3C OH
CO2Et
Me
N
3p
13C NMR
CDCl3, 126 MHz
f1 (ppm)


-77.9
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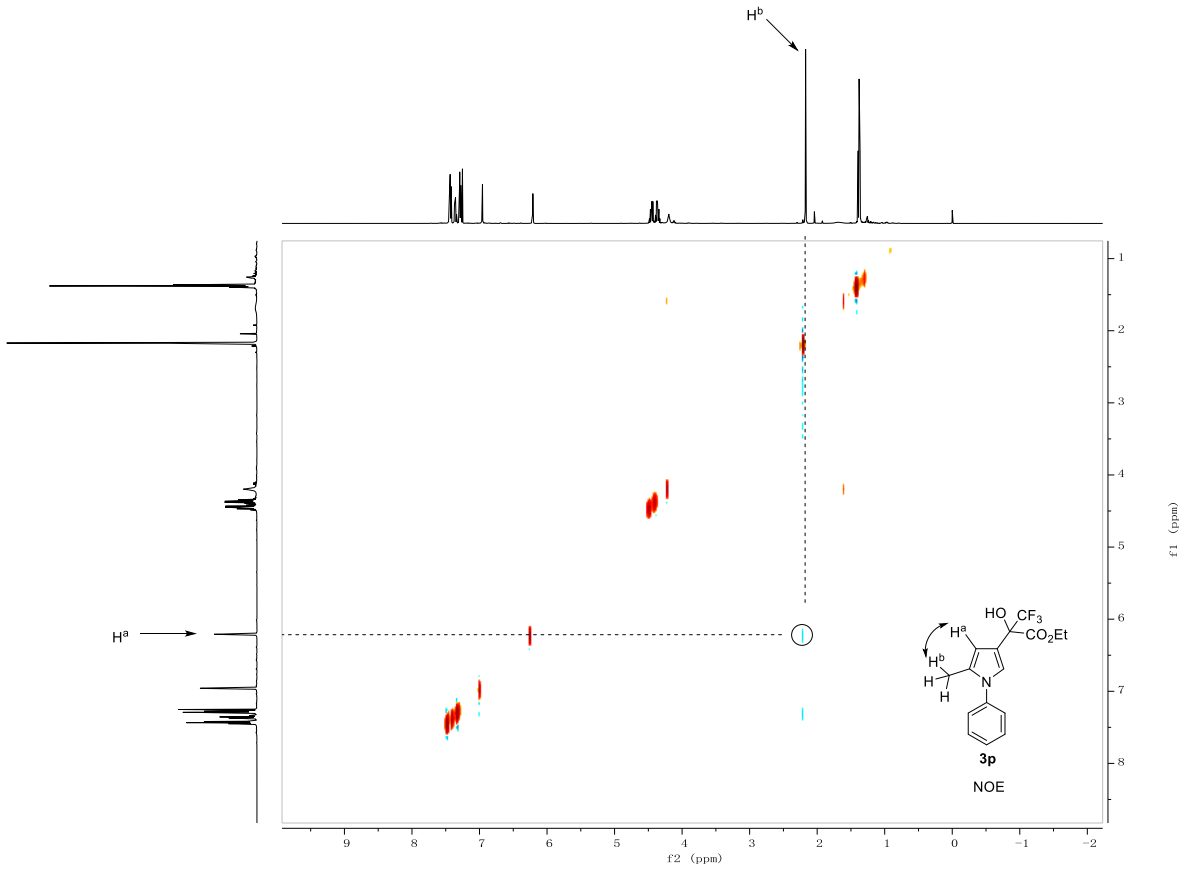
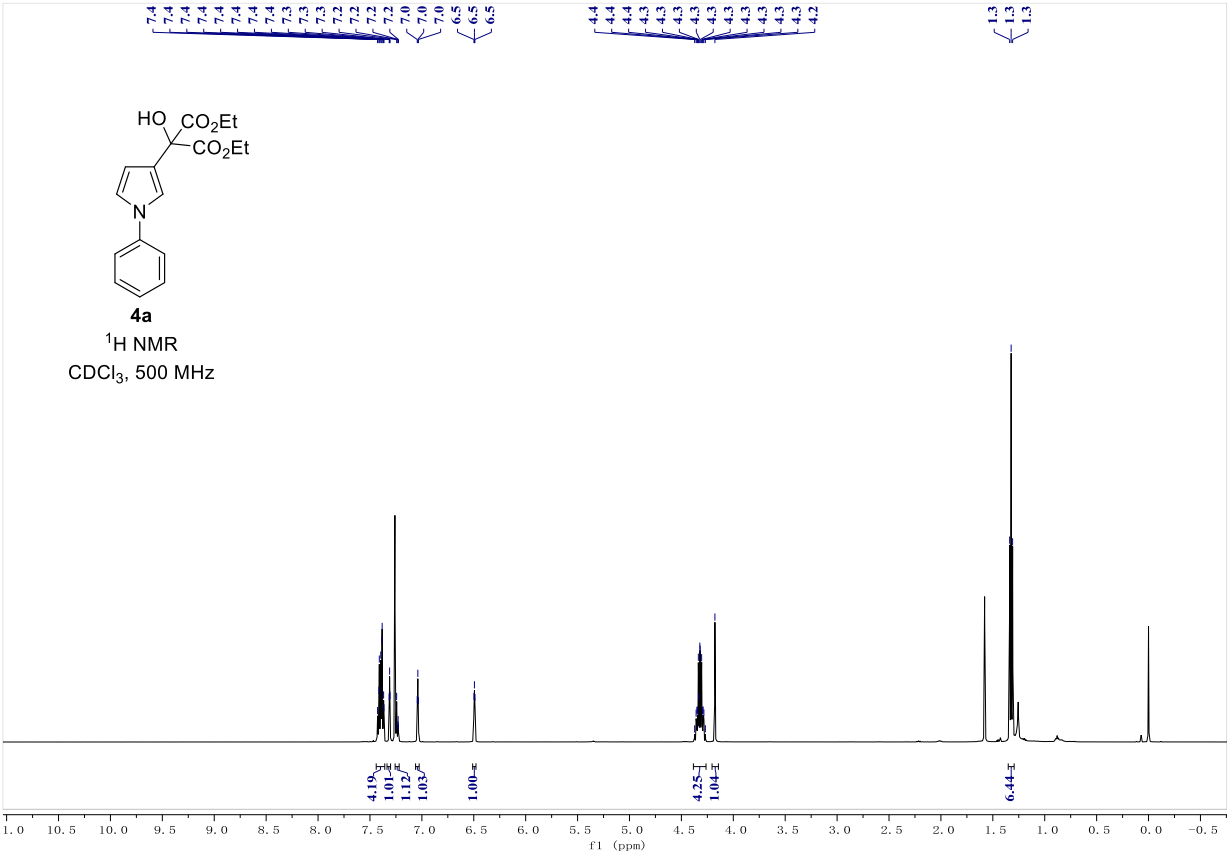
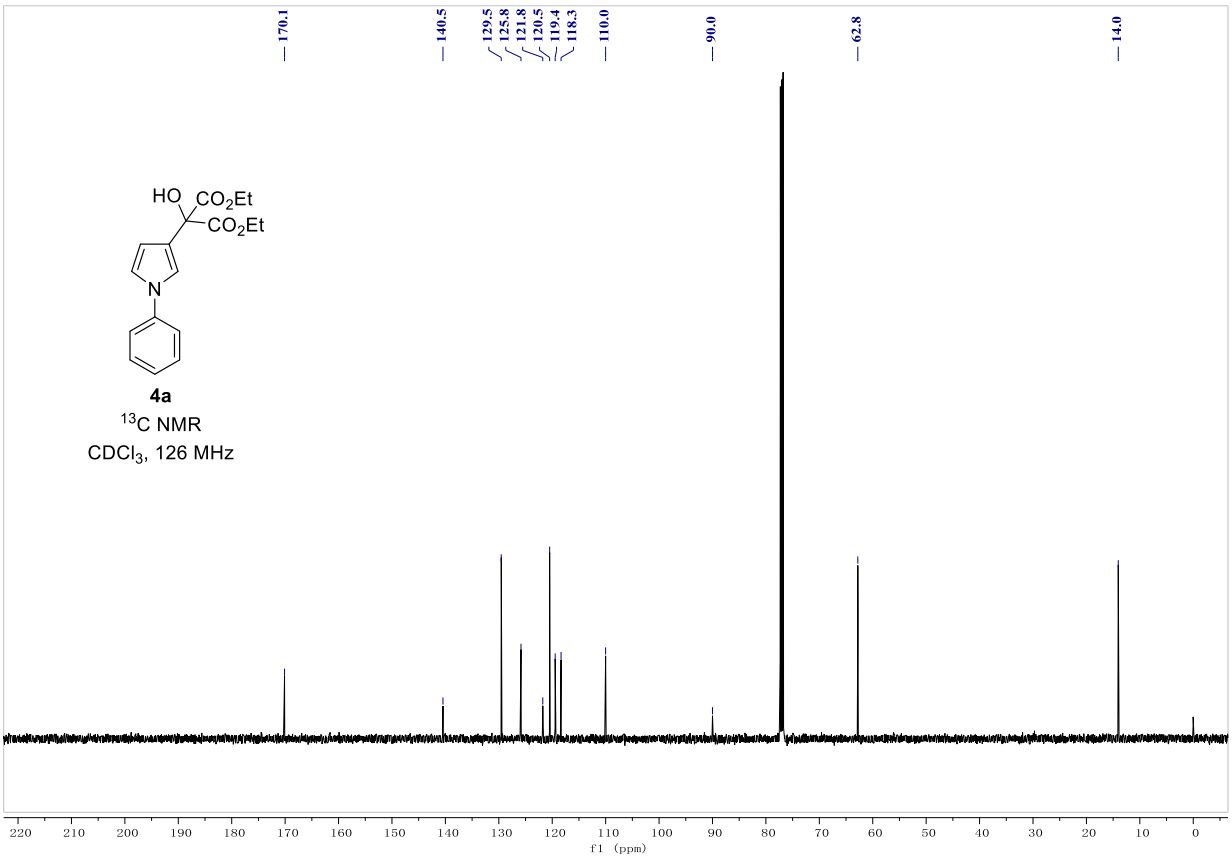
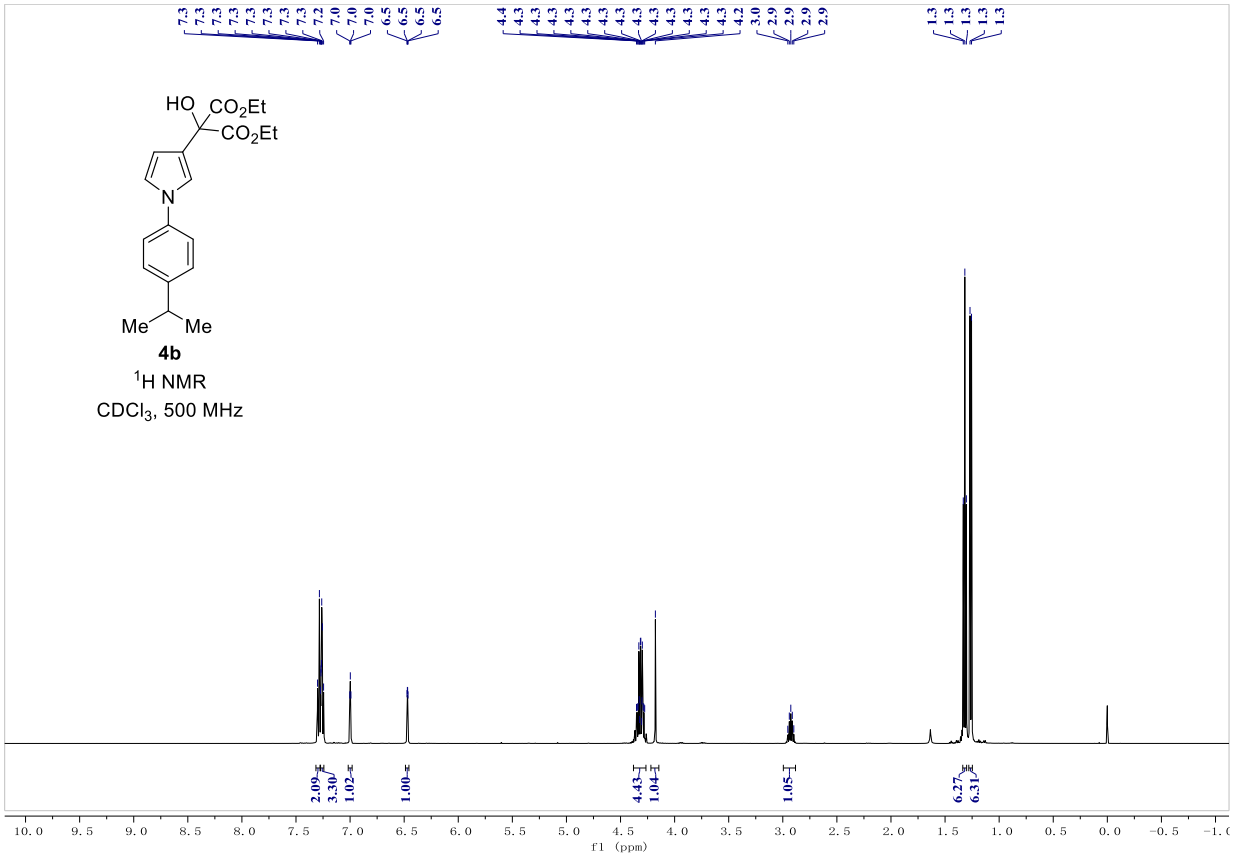
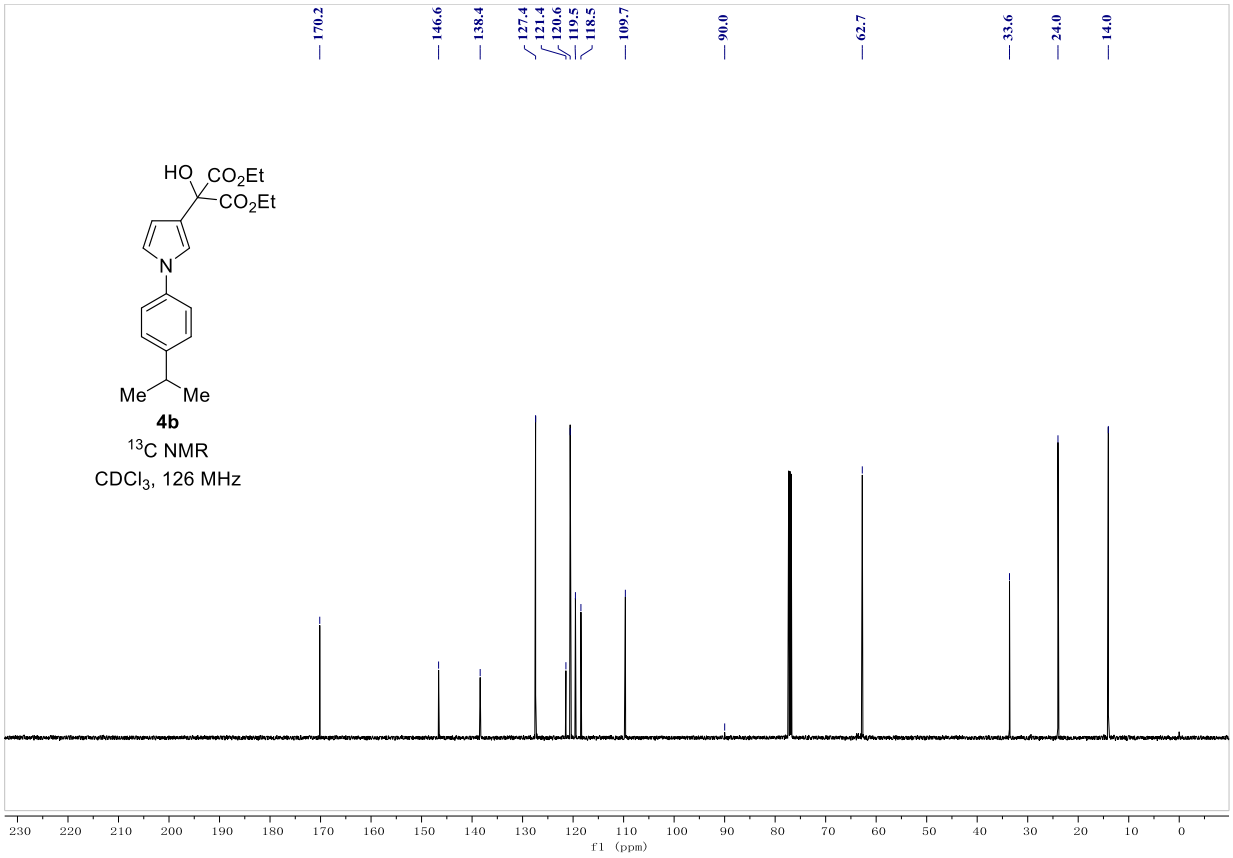
CO2Et
Me
N
3p
19F NMR
CDCl3, 471 MHz
f1 (ppm)


Hb
Ha
HO CF3
CO2Et
Ha
Hb
H
H
N
3p
NOE
f2 (ppm)
f1 (ppm)


HO
CO2Et
CO2Et
N
4a
1H NMR
CDCl3, 500 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
4a
13C NMR
CDCl3, 126 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
Me
Me
4b
1H NMR
CDCl3, 500 MHz
f1 (ppm)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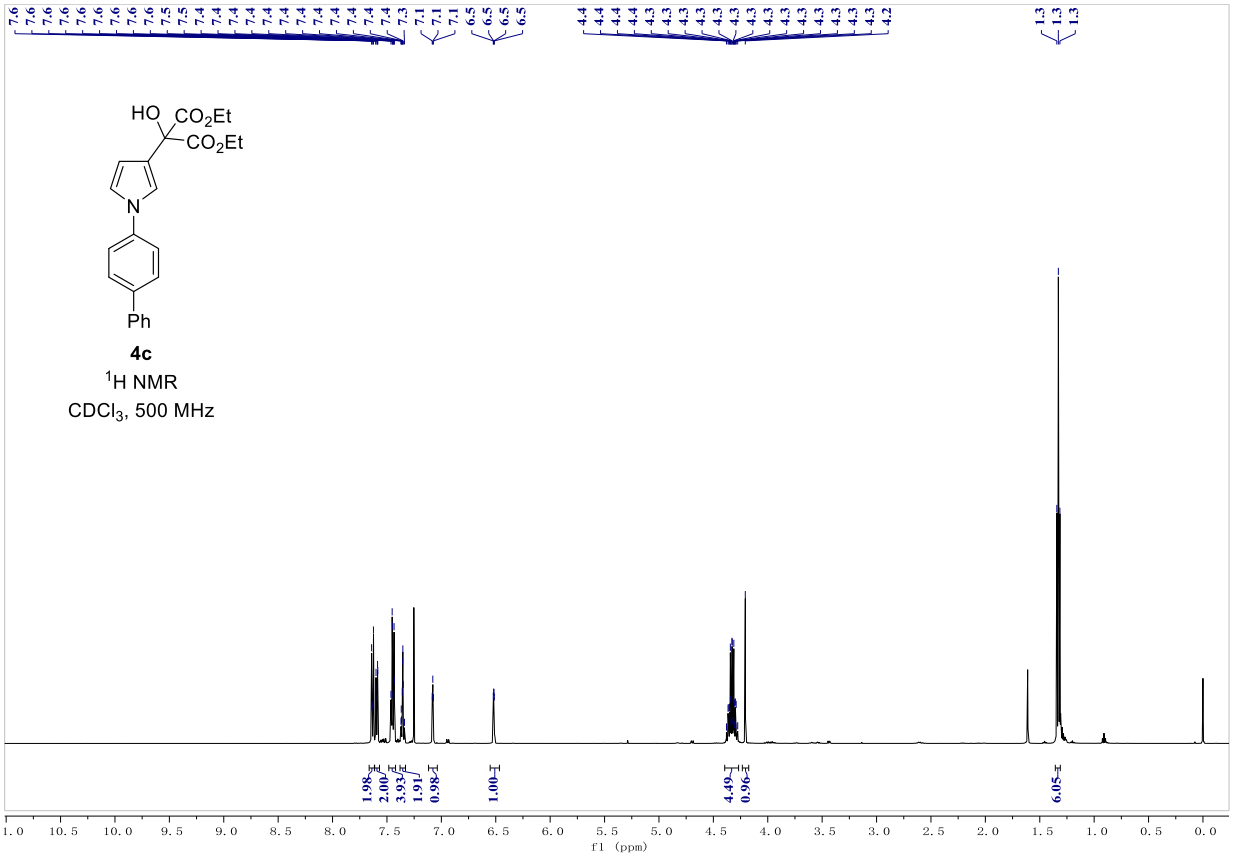
CO2Et
CO2Et
N
Me
Me
4b
13C NMR
CDCl3, 126 MHz
f1 (ppm)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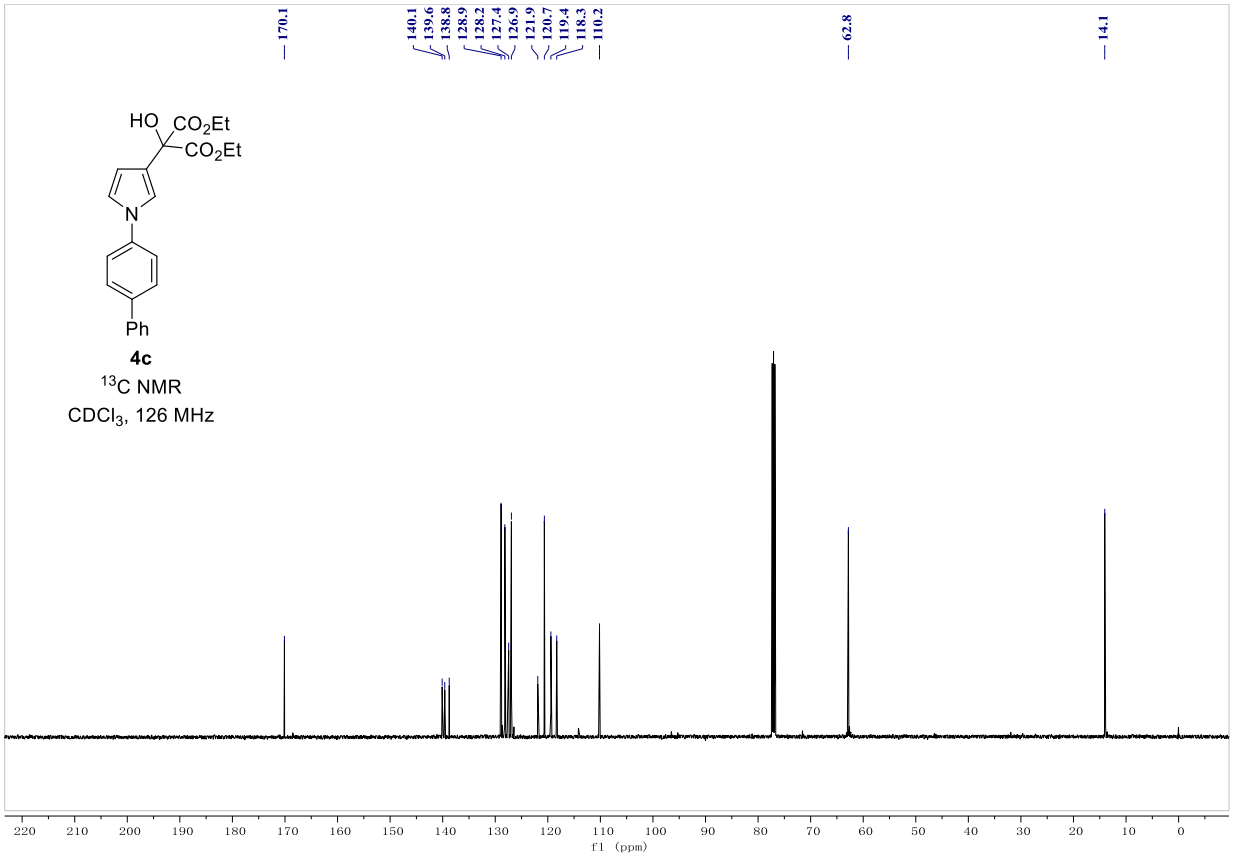
CO2Et
CO2Et
N
Ph
4c
1H NMR
CDCl3, 500 MHz
f1 (ppm)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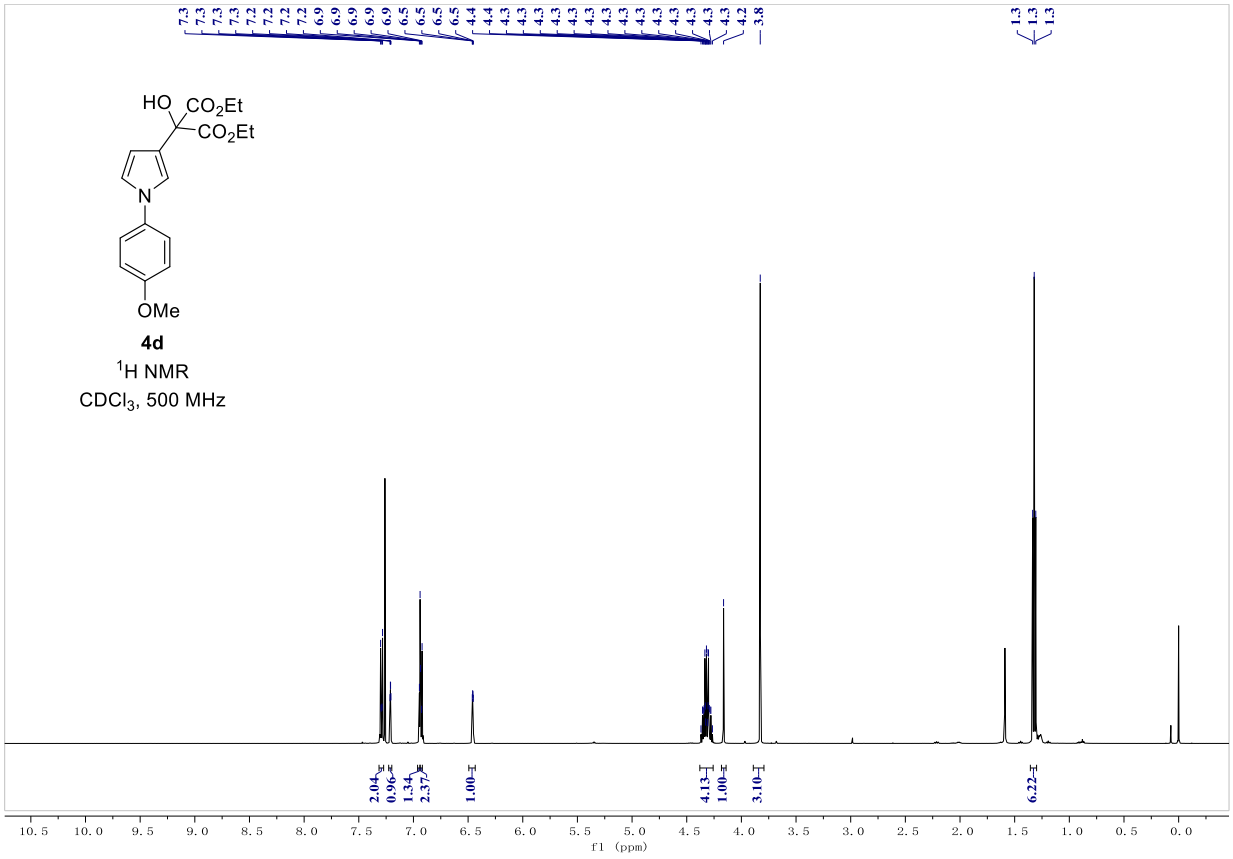
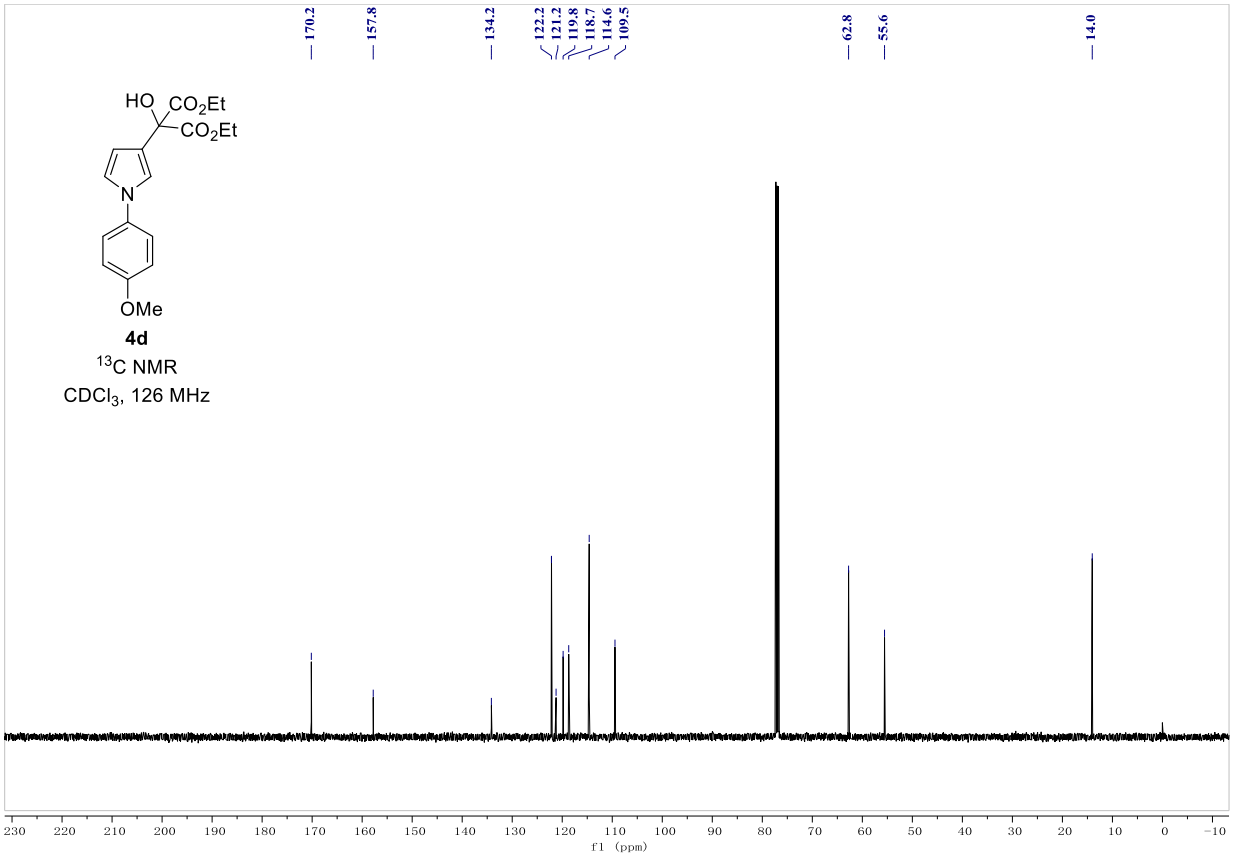
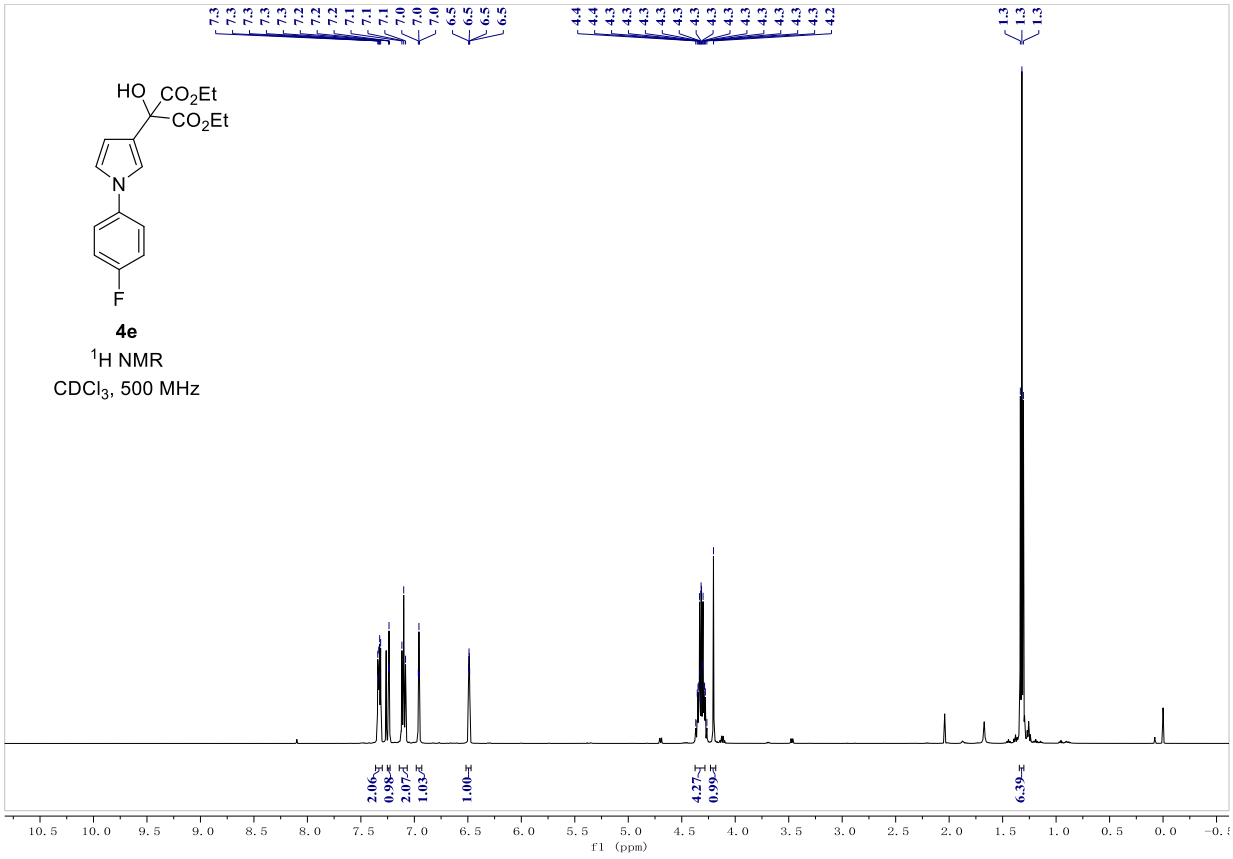
CO2Et
CO2Et
N
Ph
4c
13C NMR
CDCl3, 126 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
OMe
4d
1H NMR
CDCl3, 500 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
OMe
4d
13C NMR
CDCl3, 126 MHz
f1 (ppm)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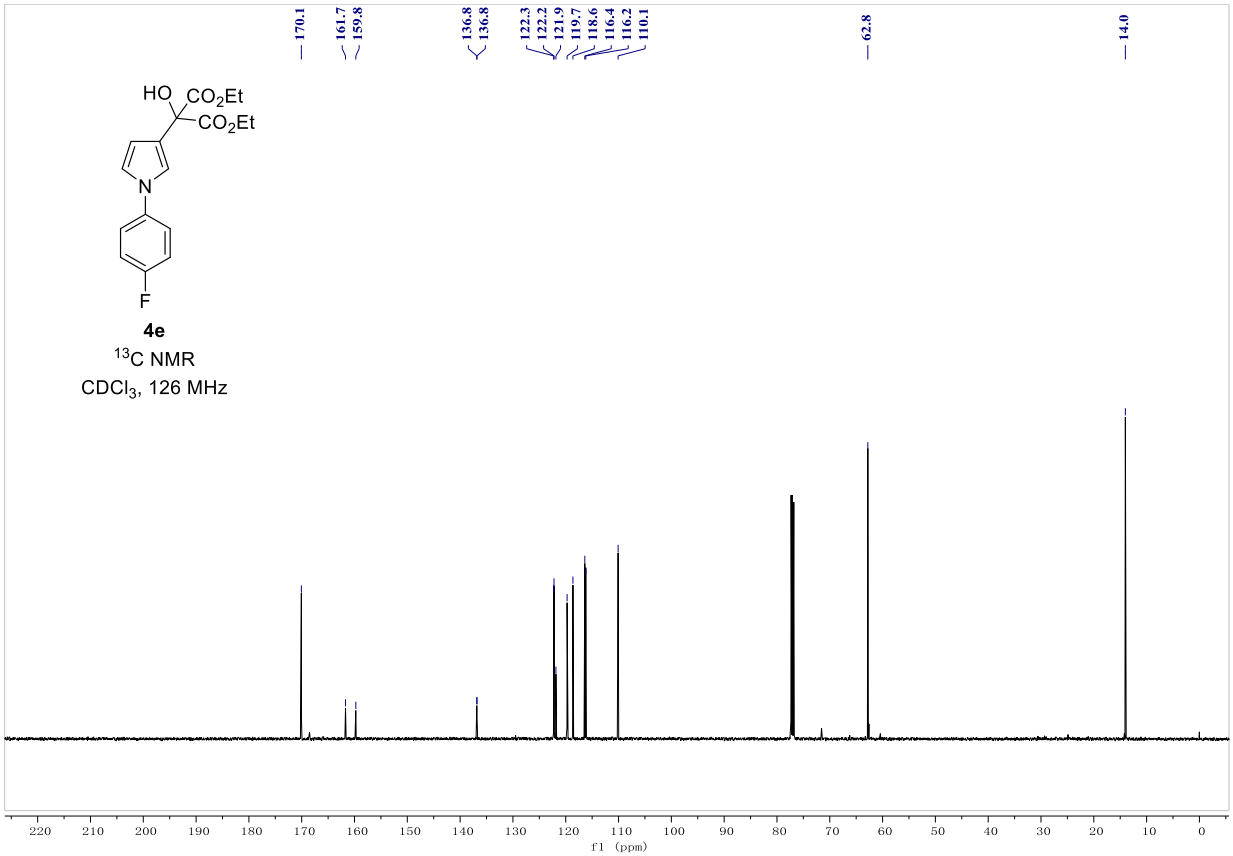
CO2Et
CO2Et
N
F
4e
1H NMR
CDCl3, 500 MHz
f1 (ppm)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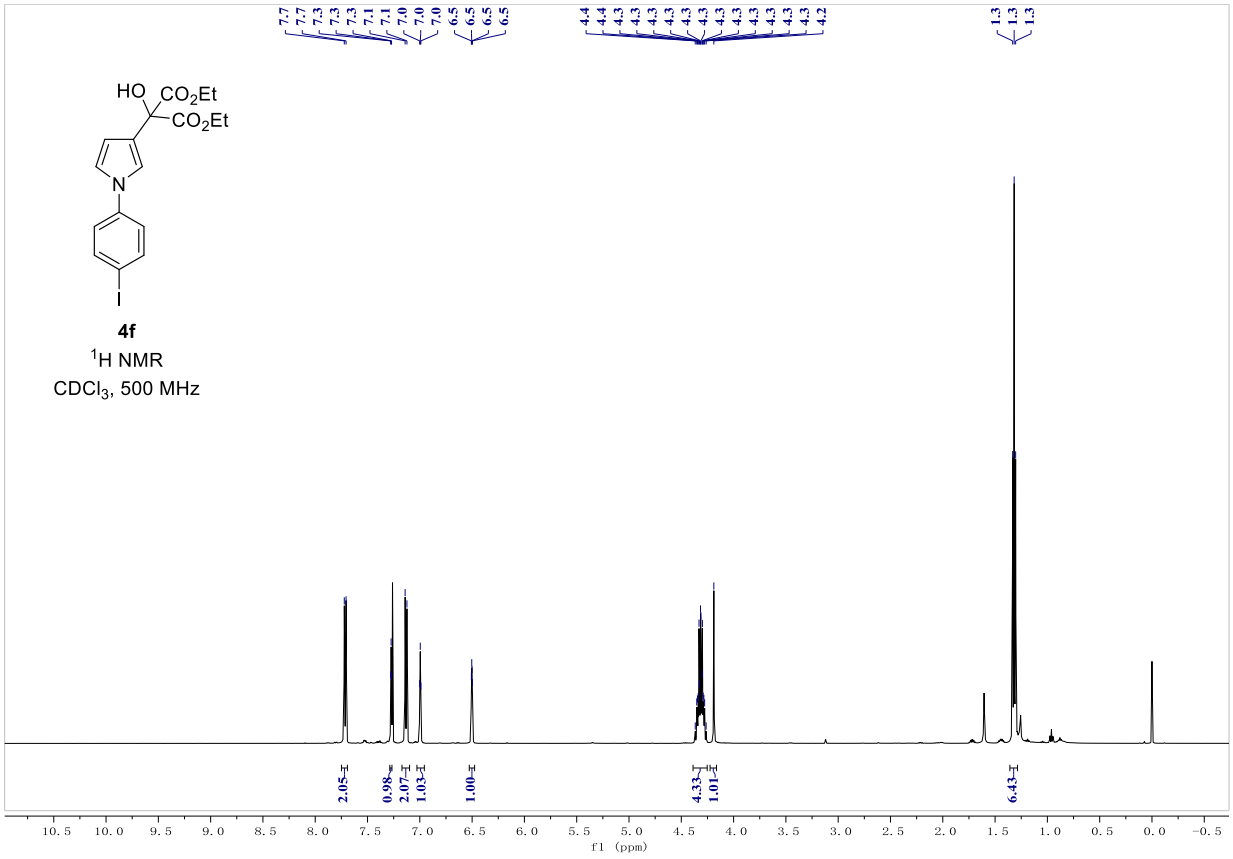
CO2Et
CO2Et
N
F
4e
13C NMR
CDCl3, 126 MHz
f1 (ppm)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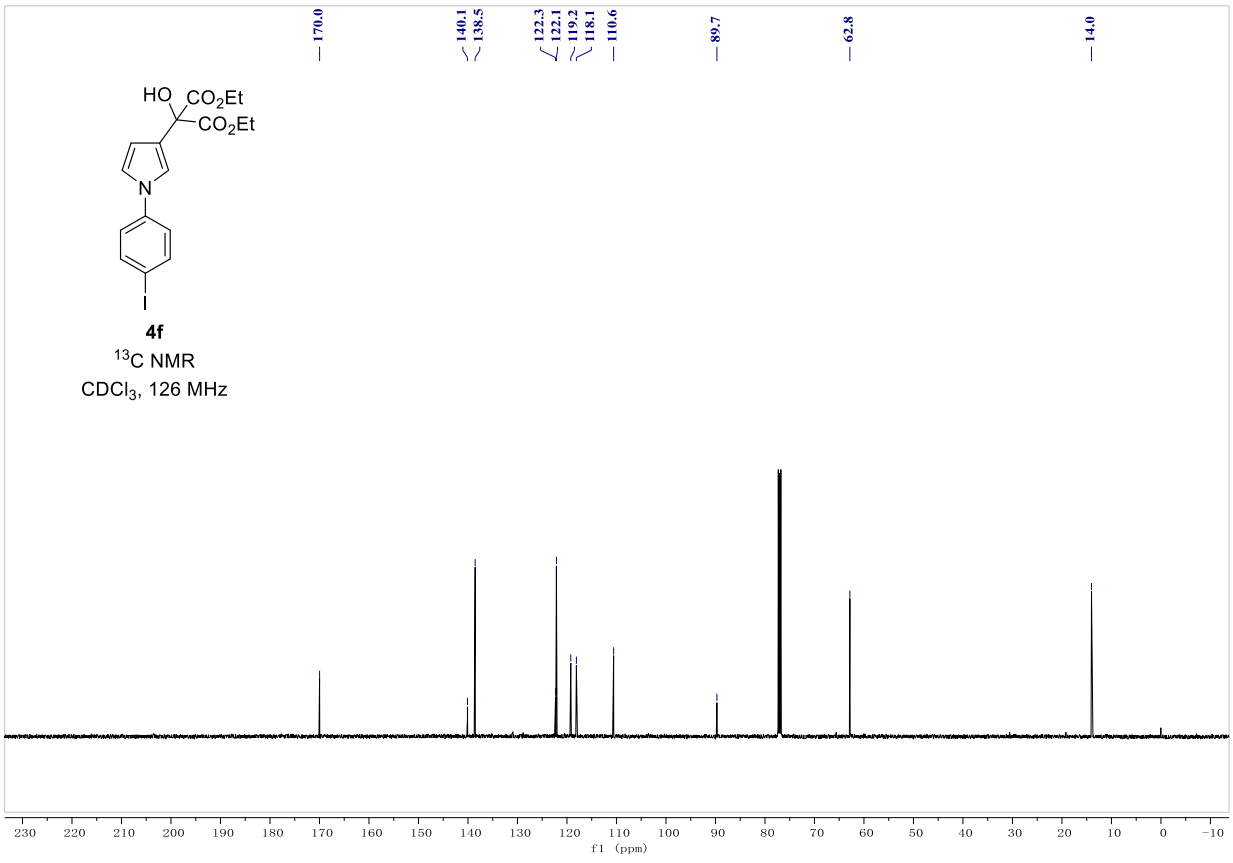
CO2Et
CO2Et
N
I
4f
1H NMR
CDCl3, 500 MHz
f1 (ppm)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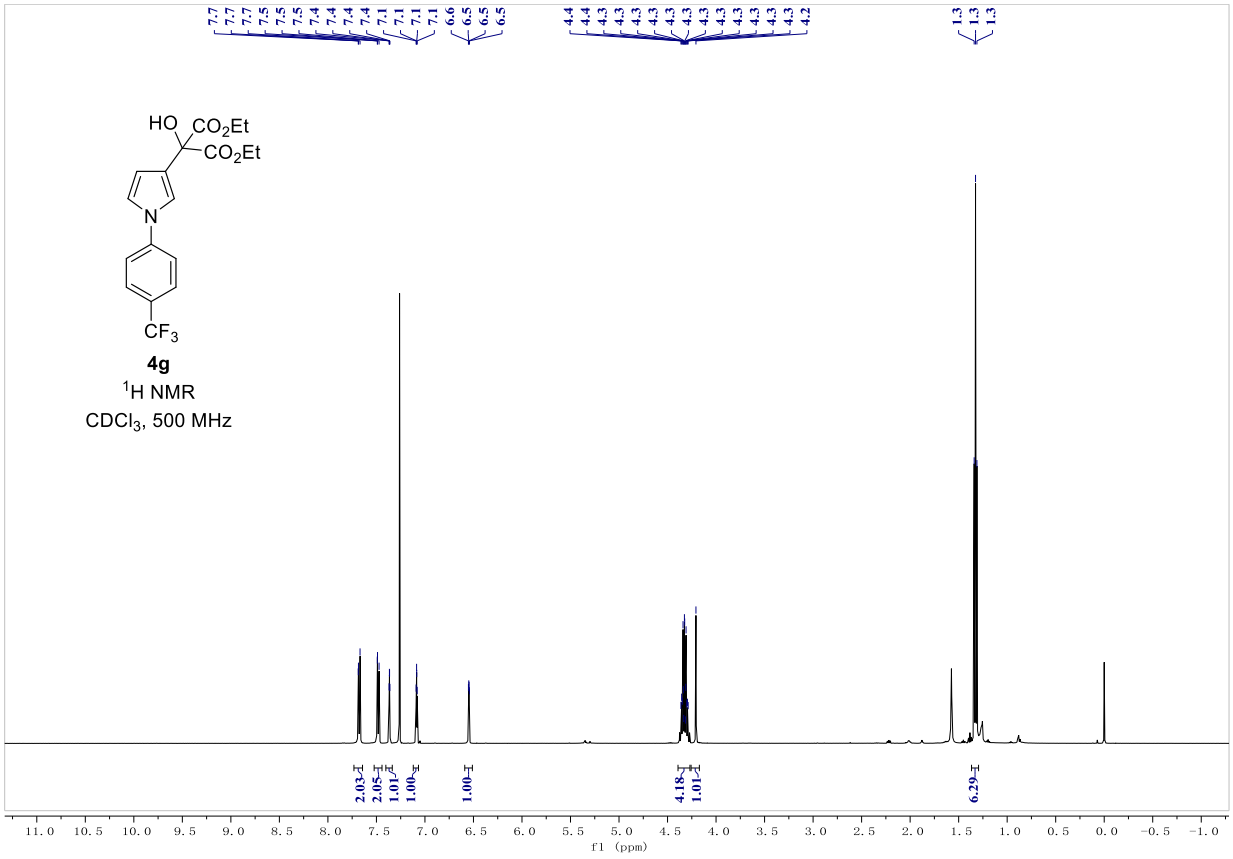
CO2Et
CO2Et
N
I
4f
13C NMR
CDCl3, 126 MHz
f1 (ppm)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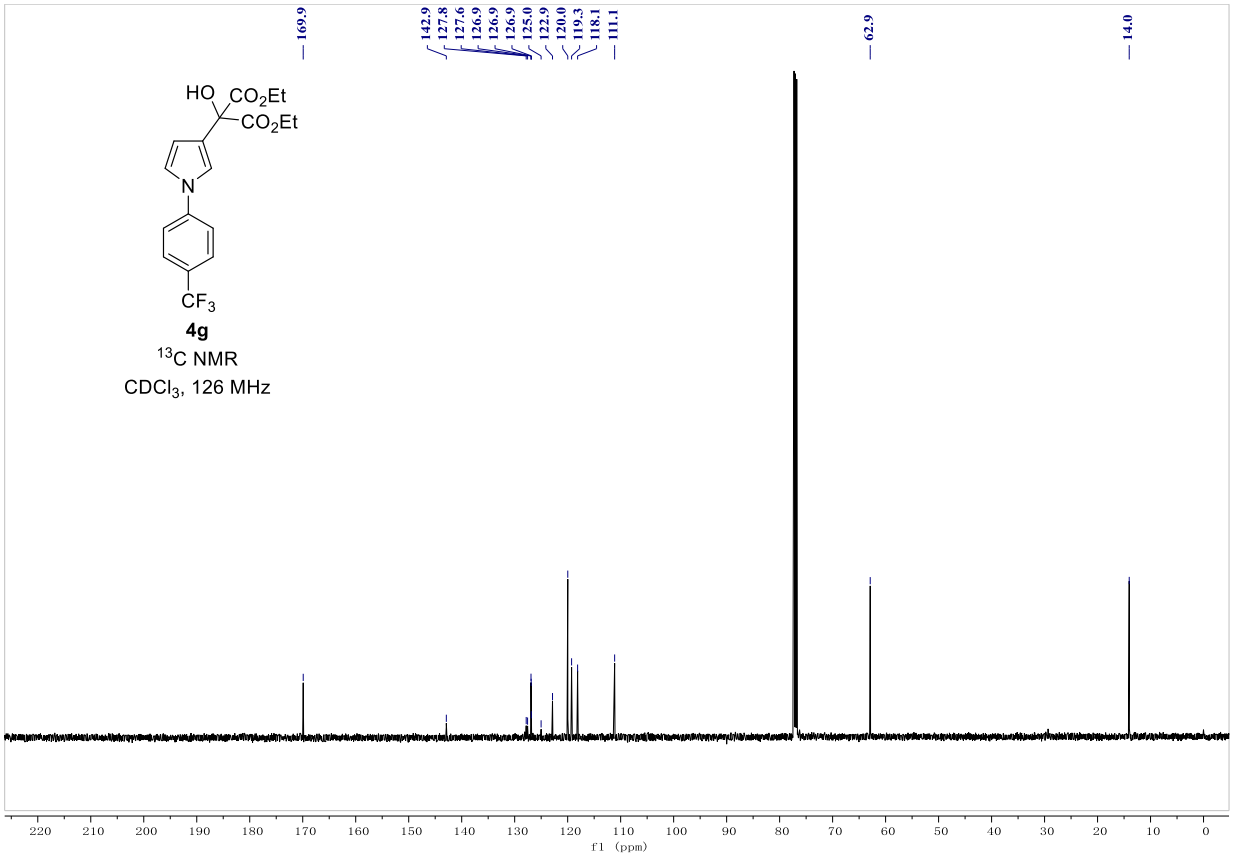
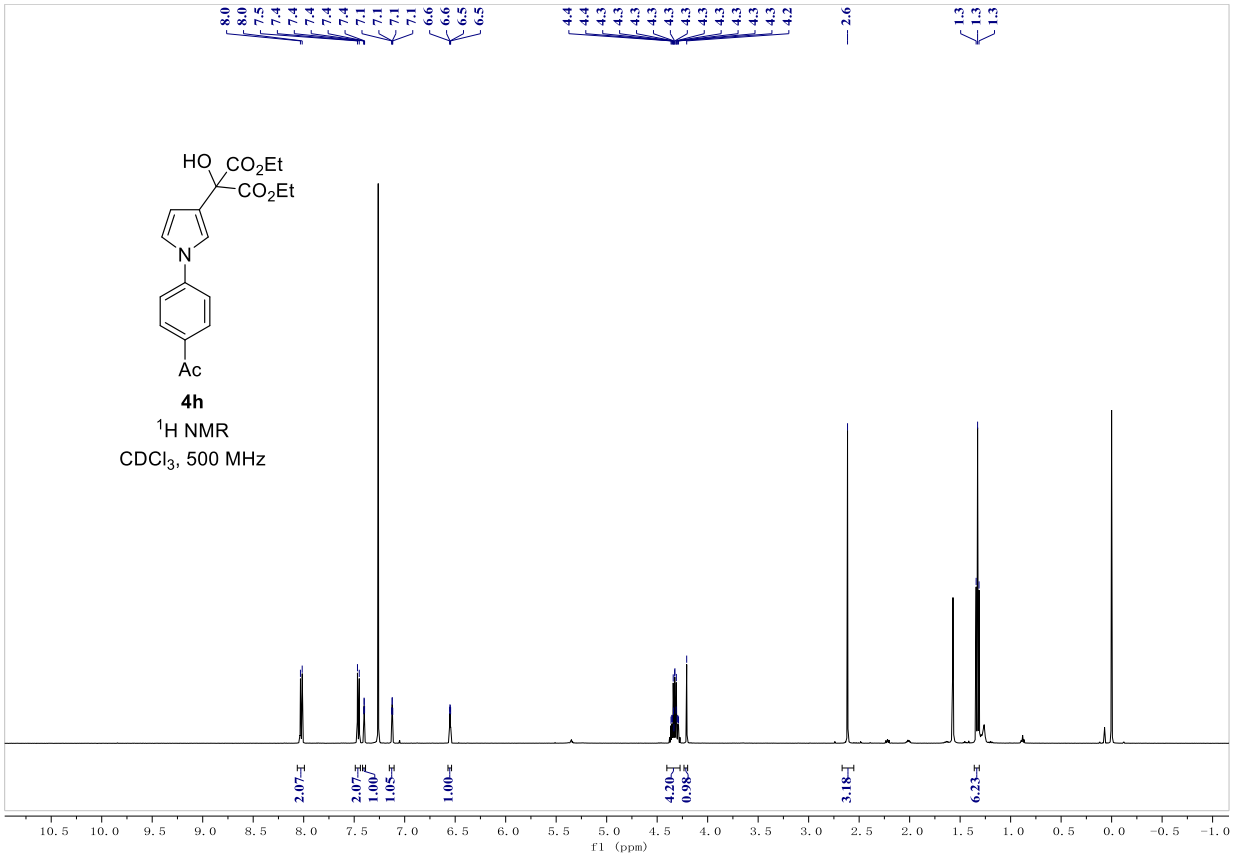
CO2Et
CO2Et
N
CF3
4g
1H NMR
CDCl3, 500 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
CF3
4g
13C NMR
CDCl3, 126 MHz
f1 (ppm)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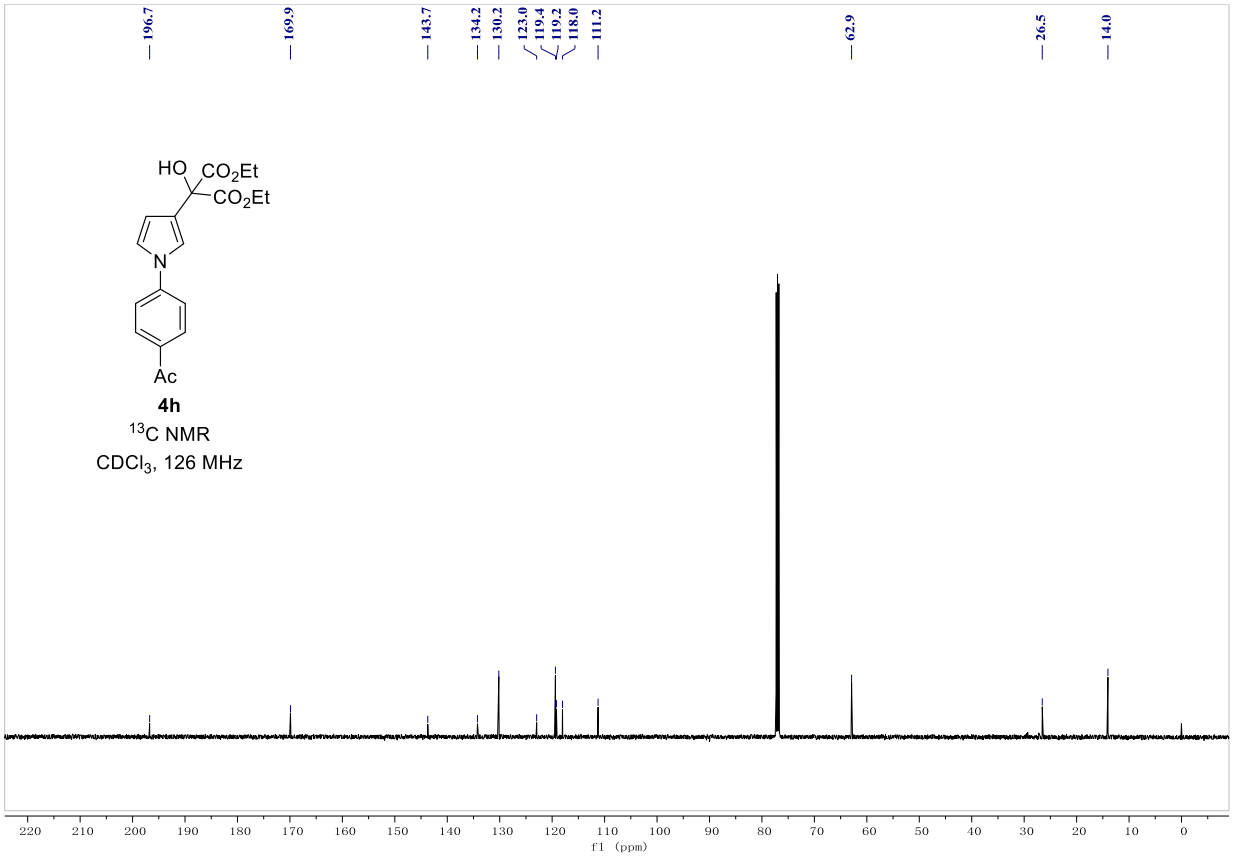
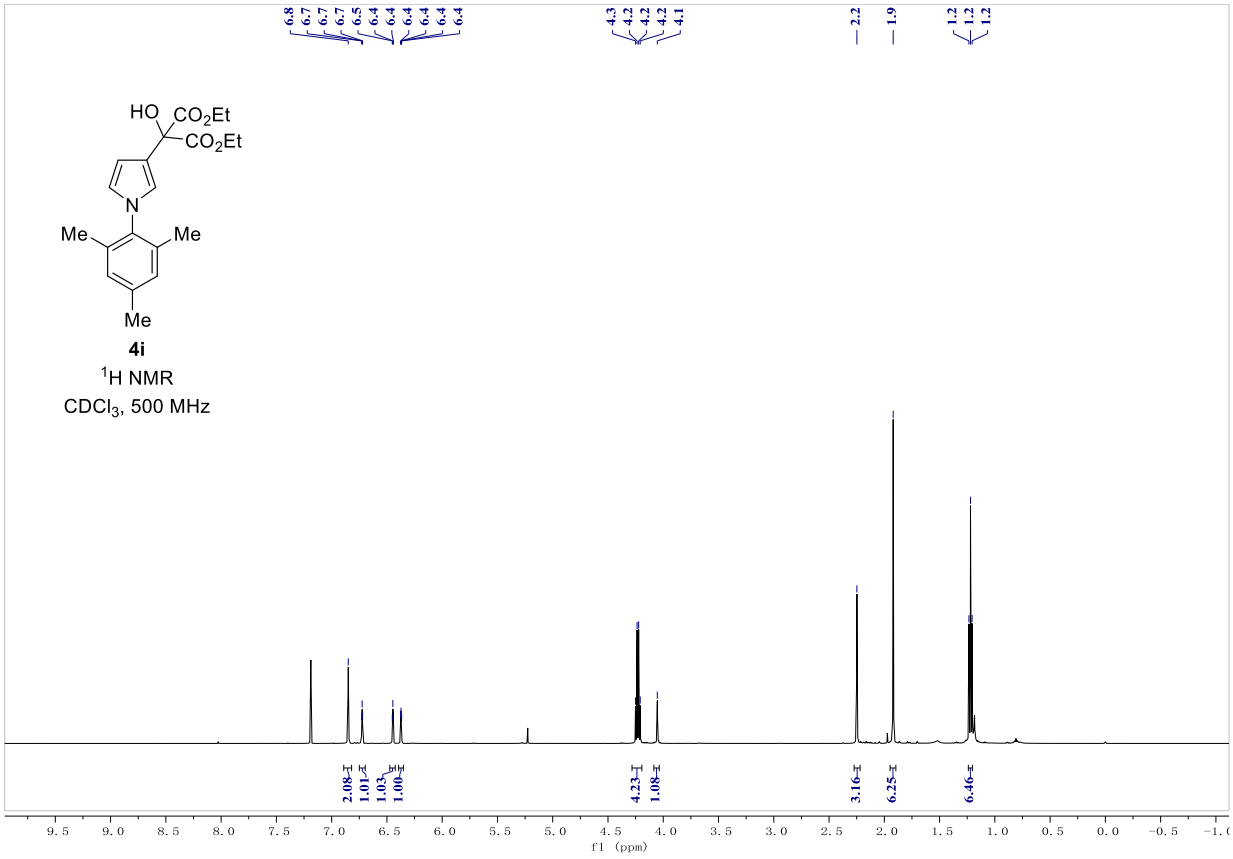
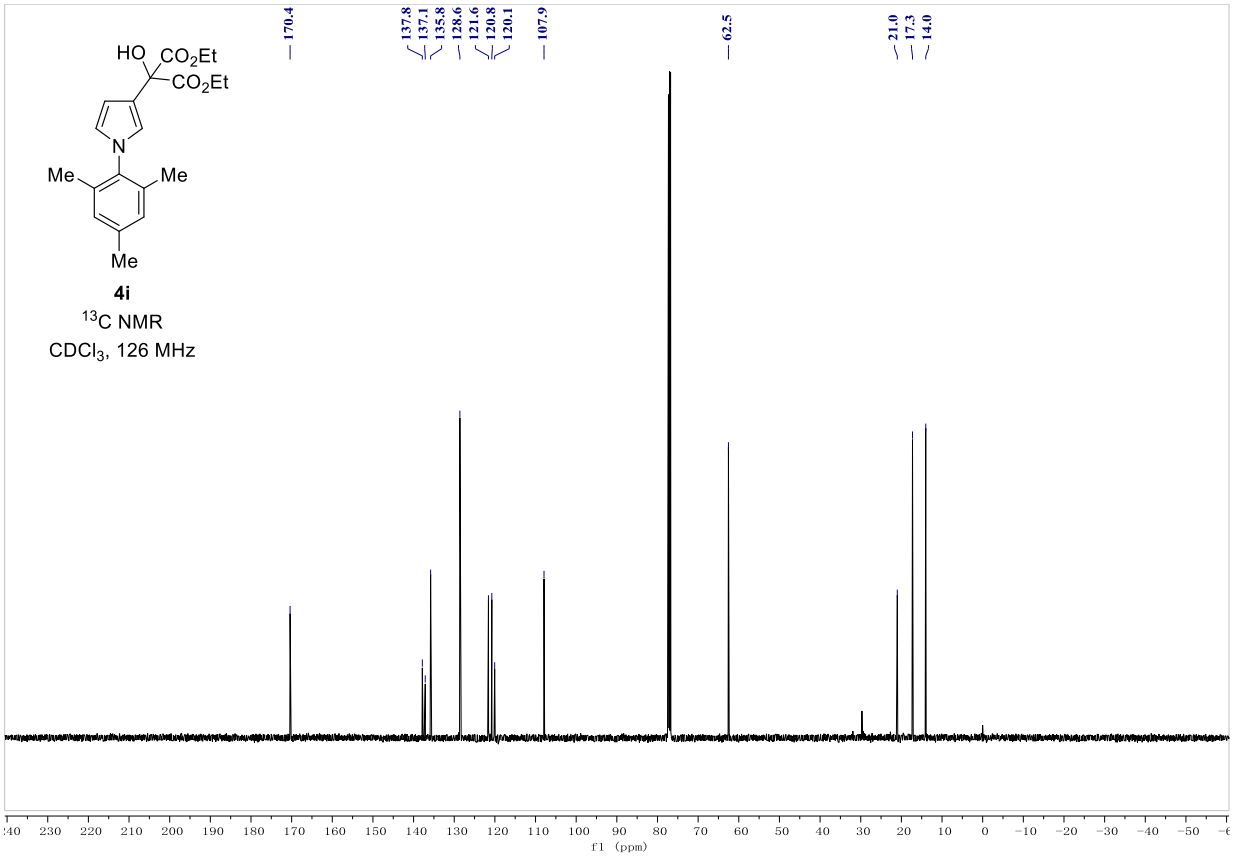
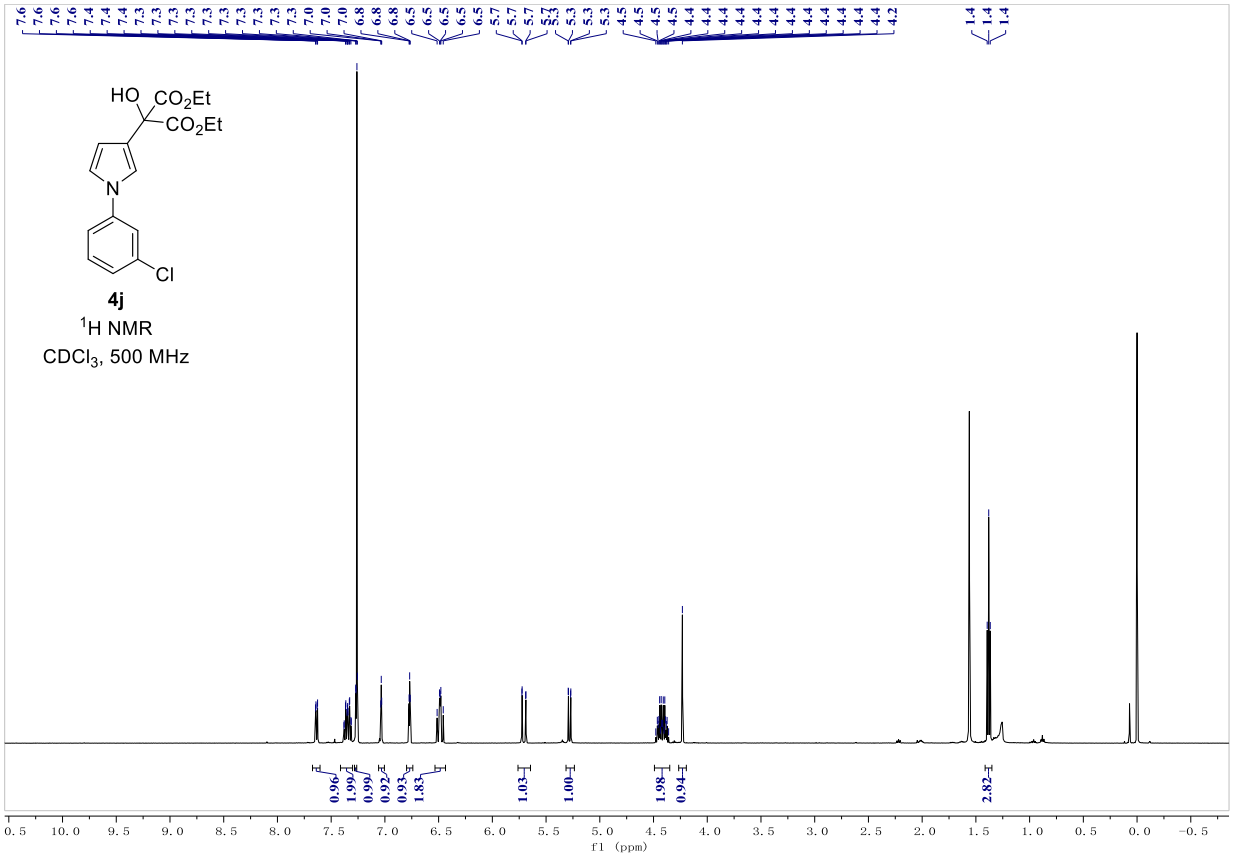
CO2Et
CO2Et
N
Ac
4h
1H NMR
CDCl3, 500 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
Ac
4h
13C NMR
CDCl3, 126 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
Me
Me
Me
4i
1H NMR
CDCl3, 500 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
Me
Me
Me
4i
13C NMR
CDCl3, 126 MHz
f1 (ppm)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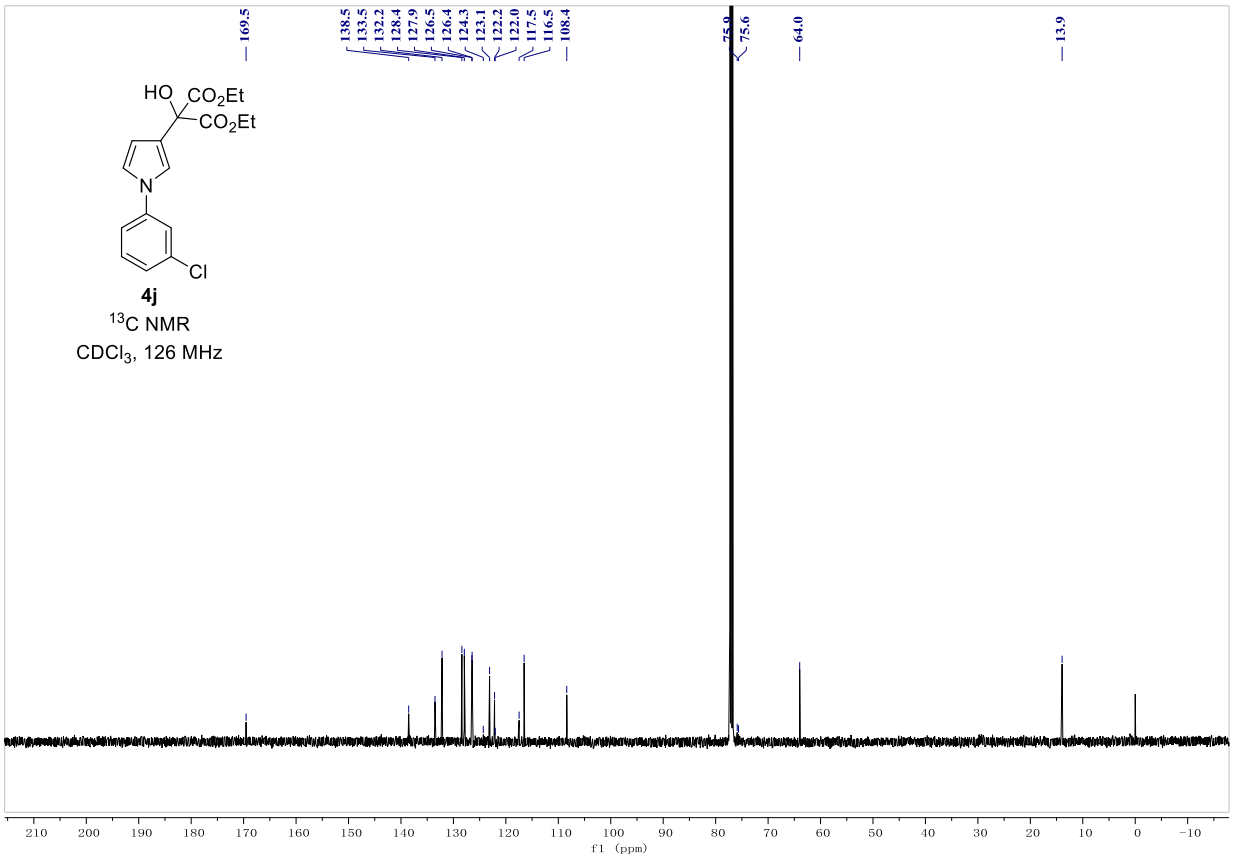
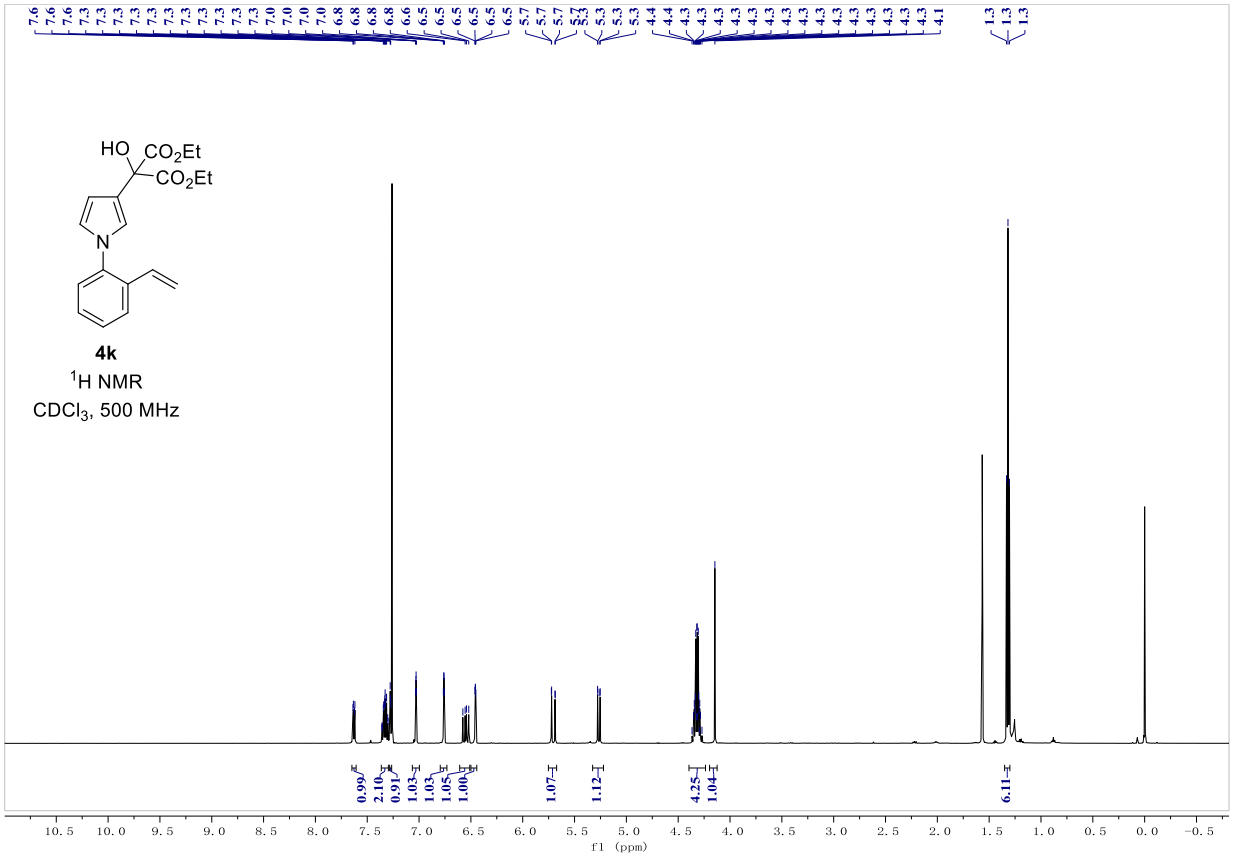
CO2Et
CO2Et
N
Cl
4j
1H NMR
CDCl3, 500 MHz
f1 (ppm)


HO
CO2Et
CO2Et
N
Cl
4j
13C NMR
CDCl3, 126 MHz
f1 (ppm)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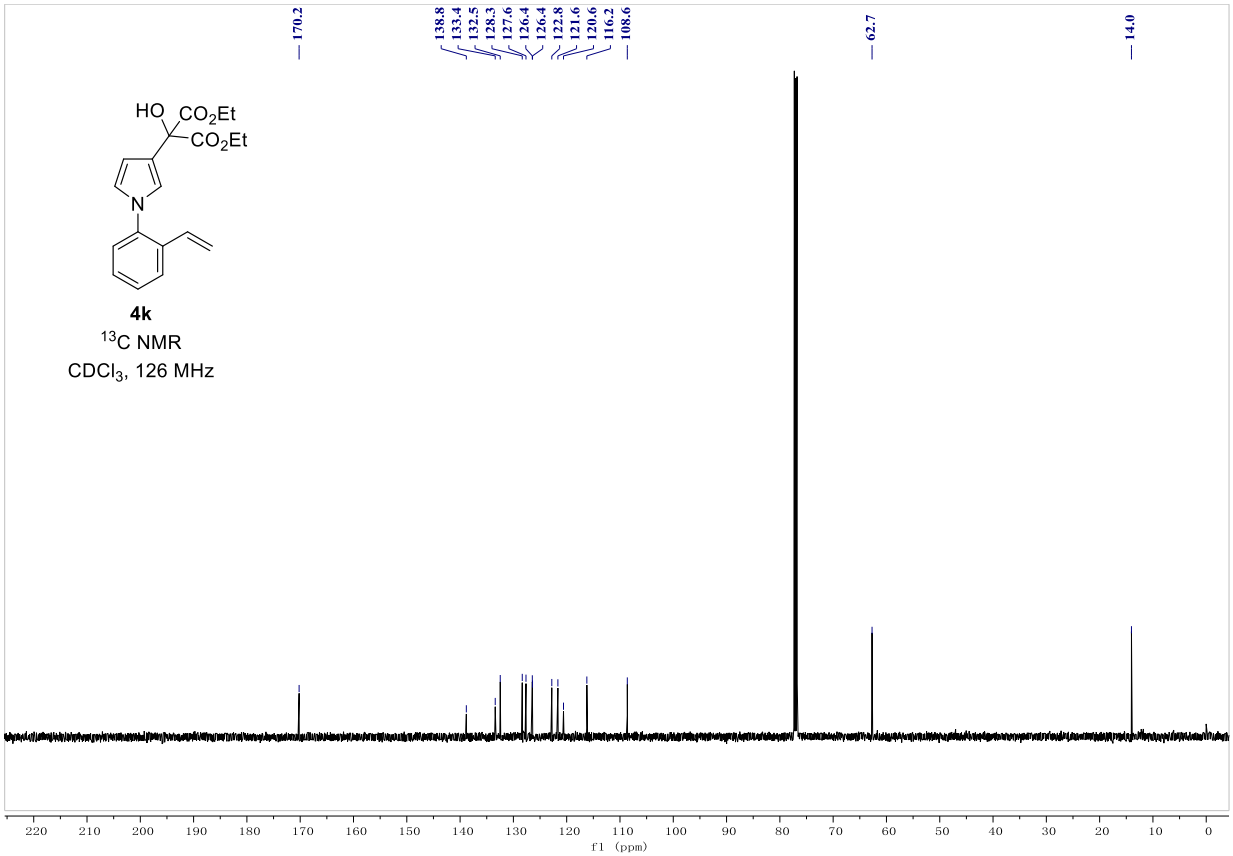
CO2Et
CO2Et
N
4k
1H NMR
CDCl3, 500 MHz
f1 (ppm)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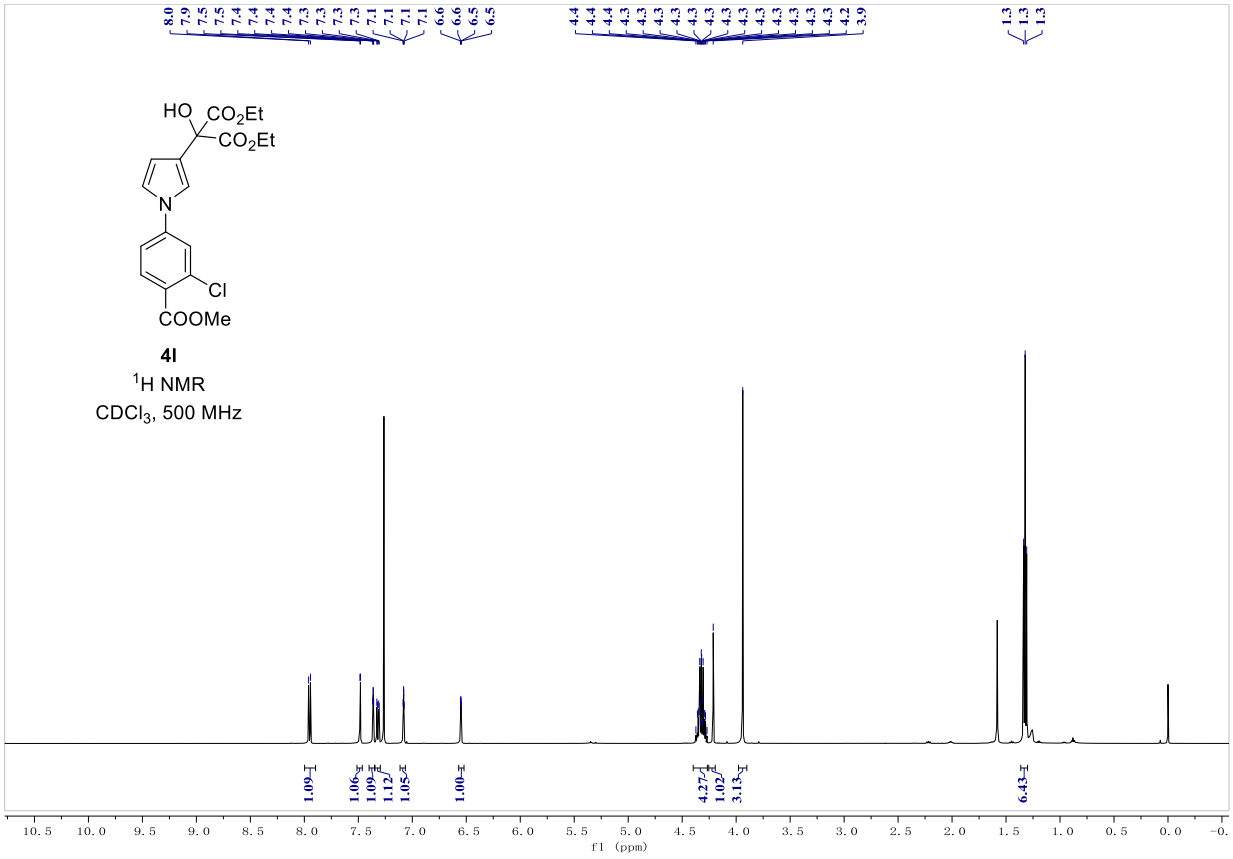
CO2Et
CO2Et
N
4k
13C NMR
CDCl3, 126 MHz
f1 (ppm)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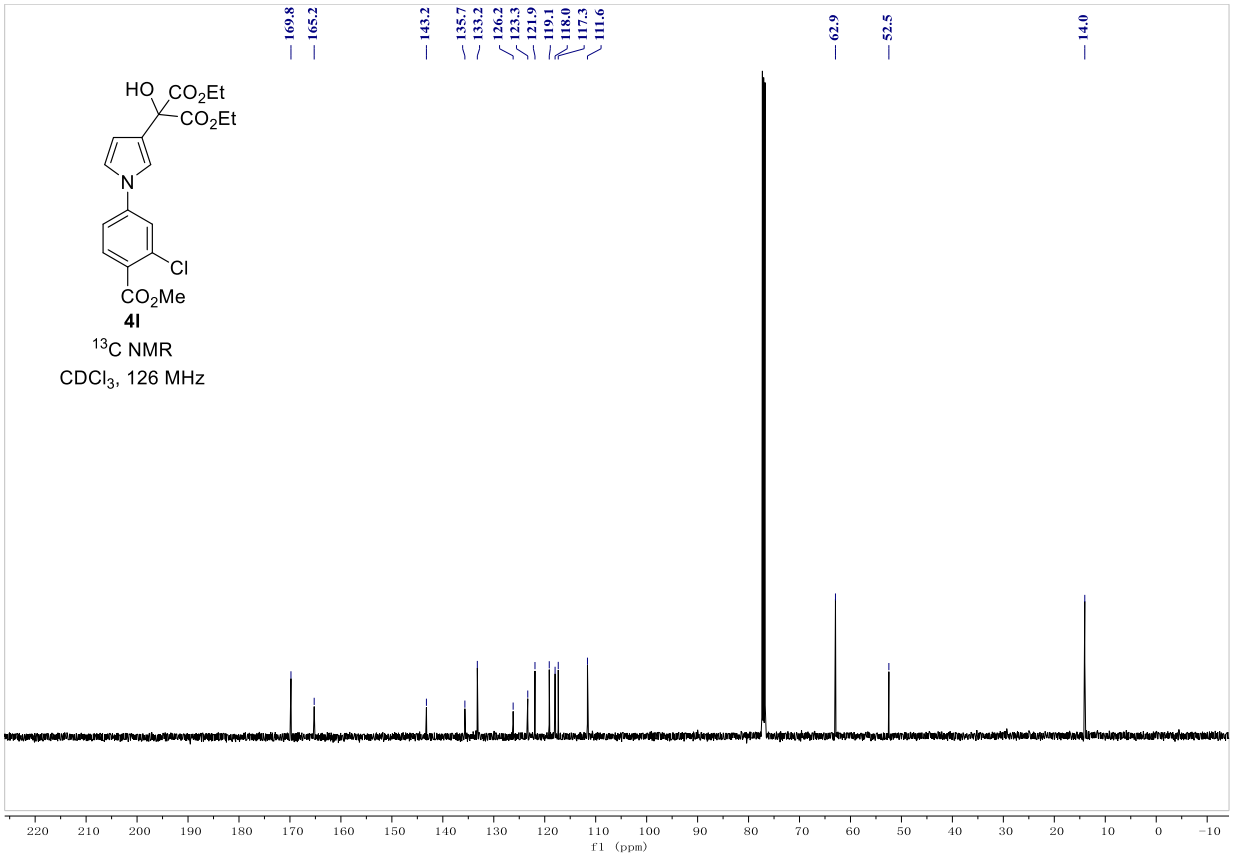
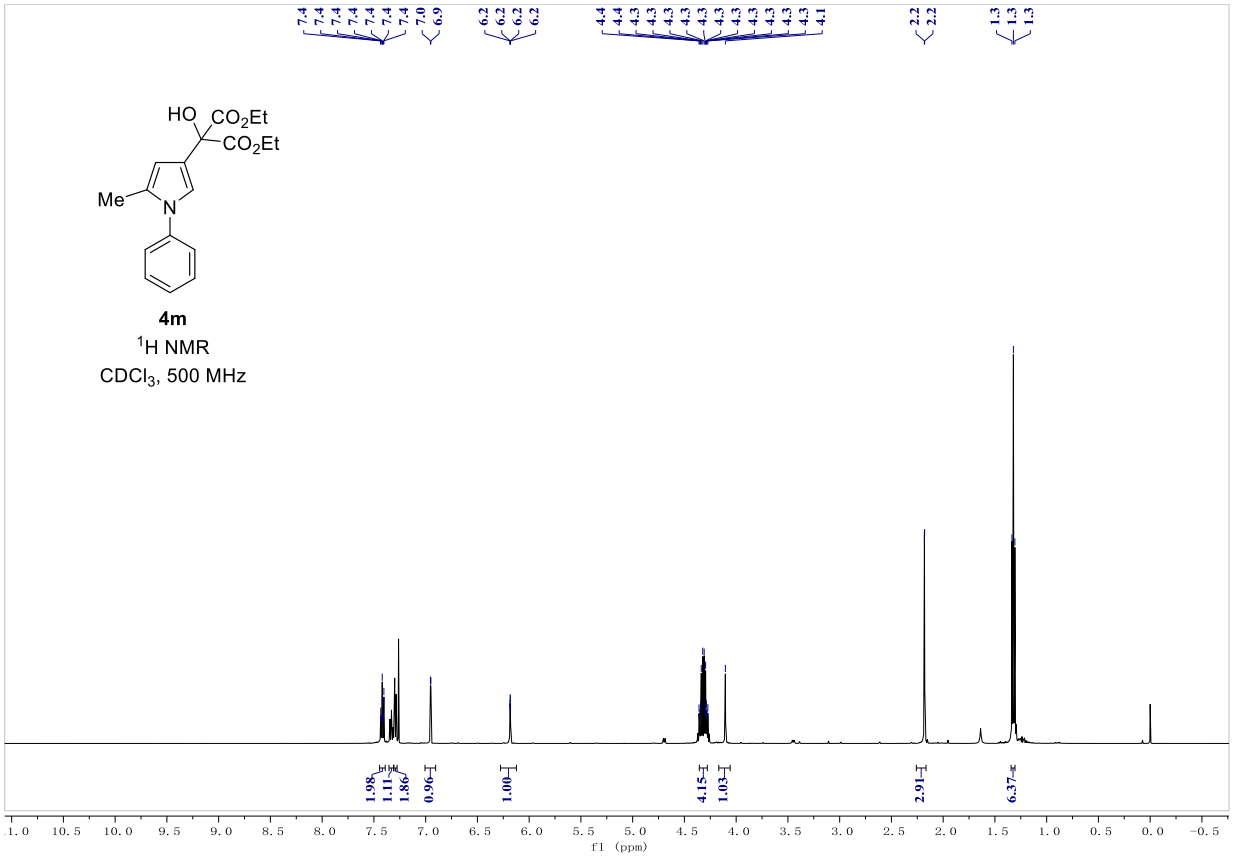
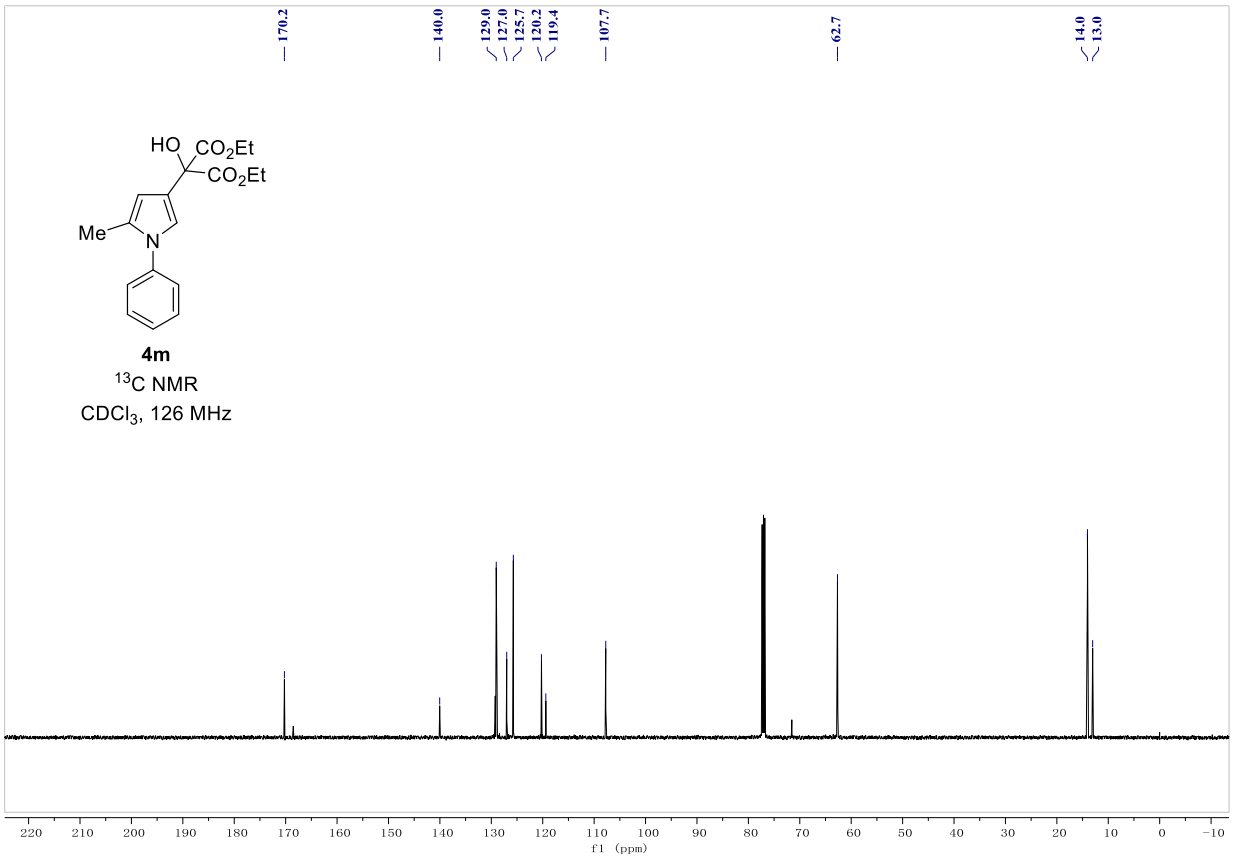
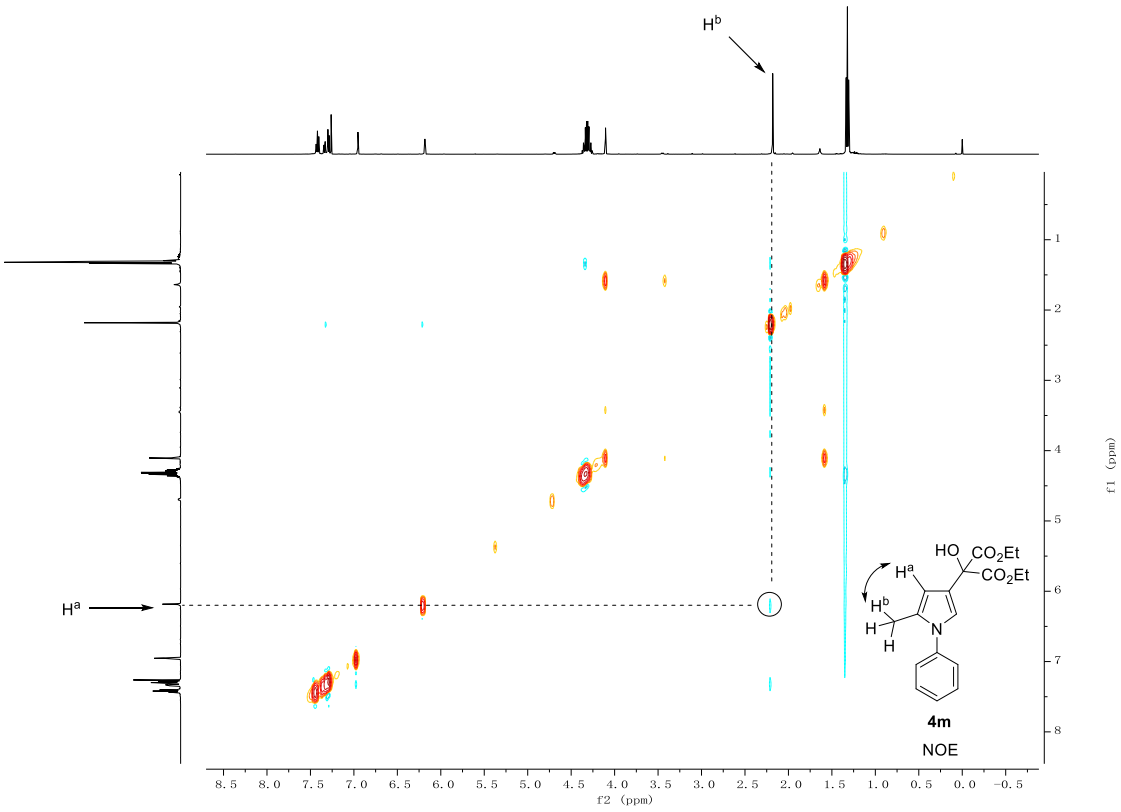
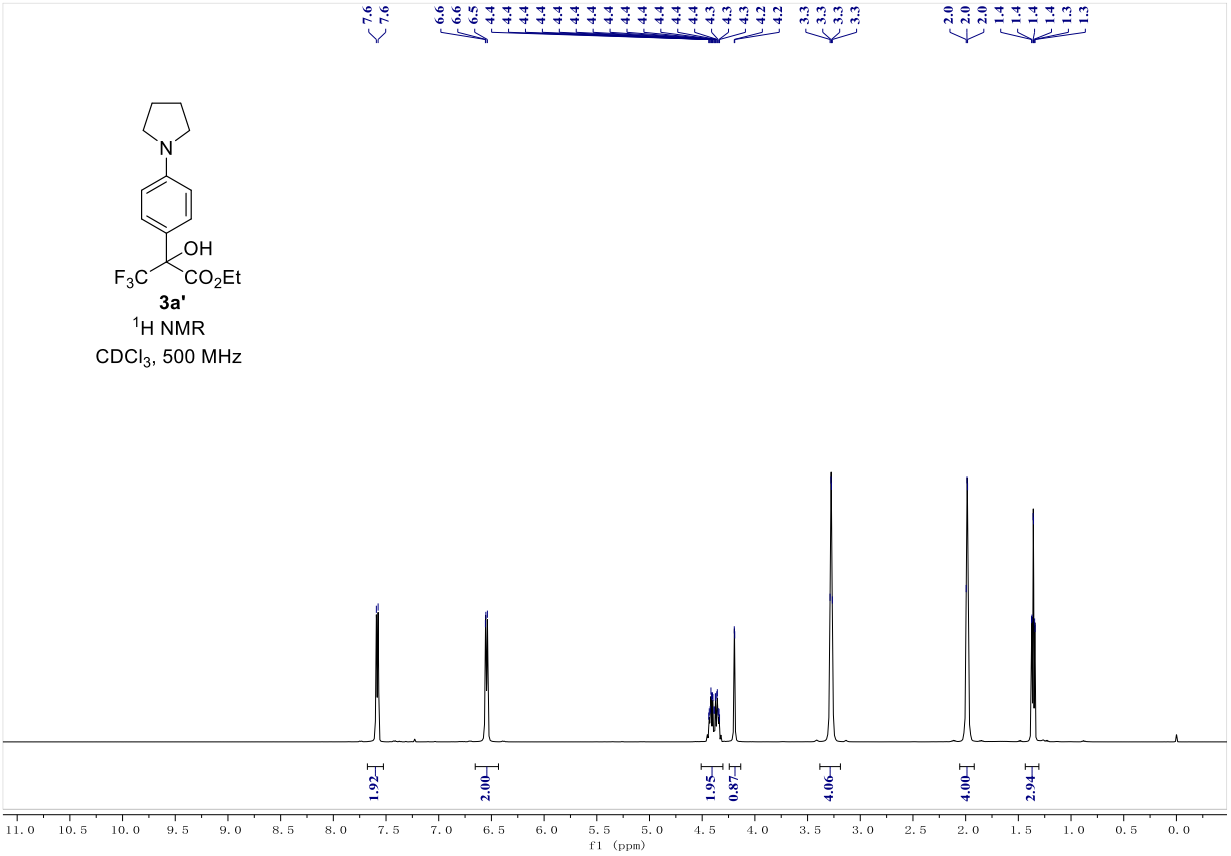
CO2Et
CO2Et
N
Cl
COOMe
4l
1H NMR
CDCl3, 500 MHz
f1 (ppm)

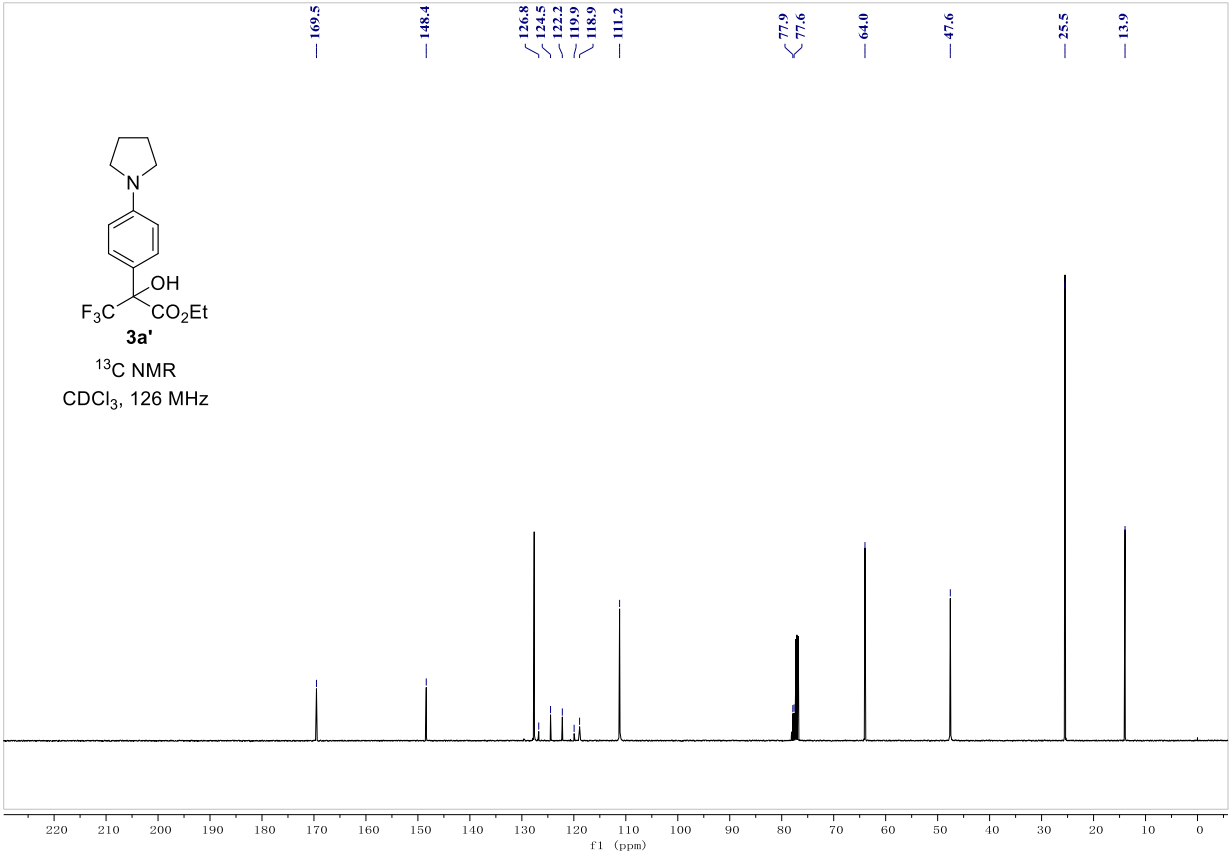

HO
CO2Et
CO2Et
N
Cl
CO2Me
4l
13C NMR
CDCl3, 126 MHz
f1 (ppm)

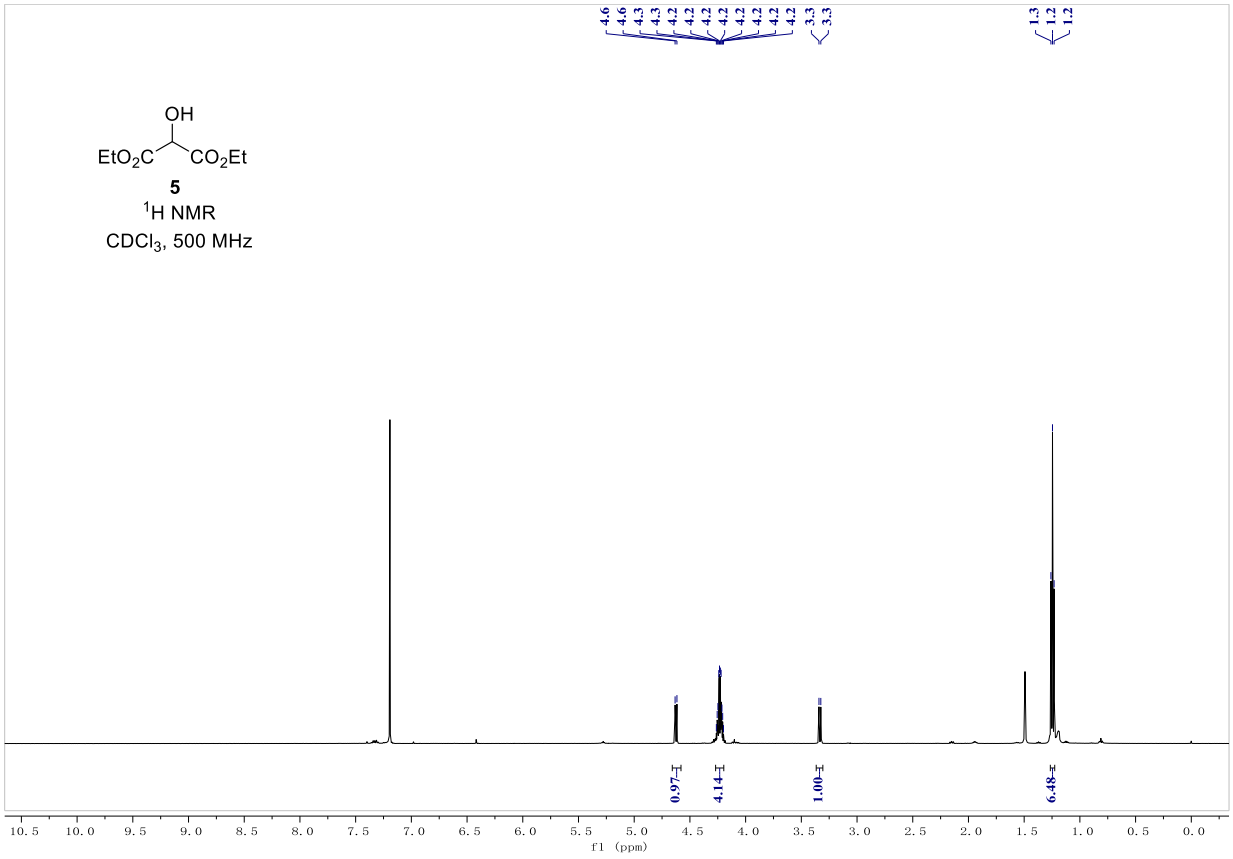

HO
CO2Et
CO2Et
Me
N
4m
1H NMR
CDCl3, 500 MHz
f1 (ppm)

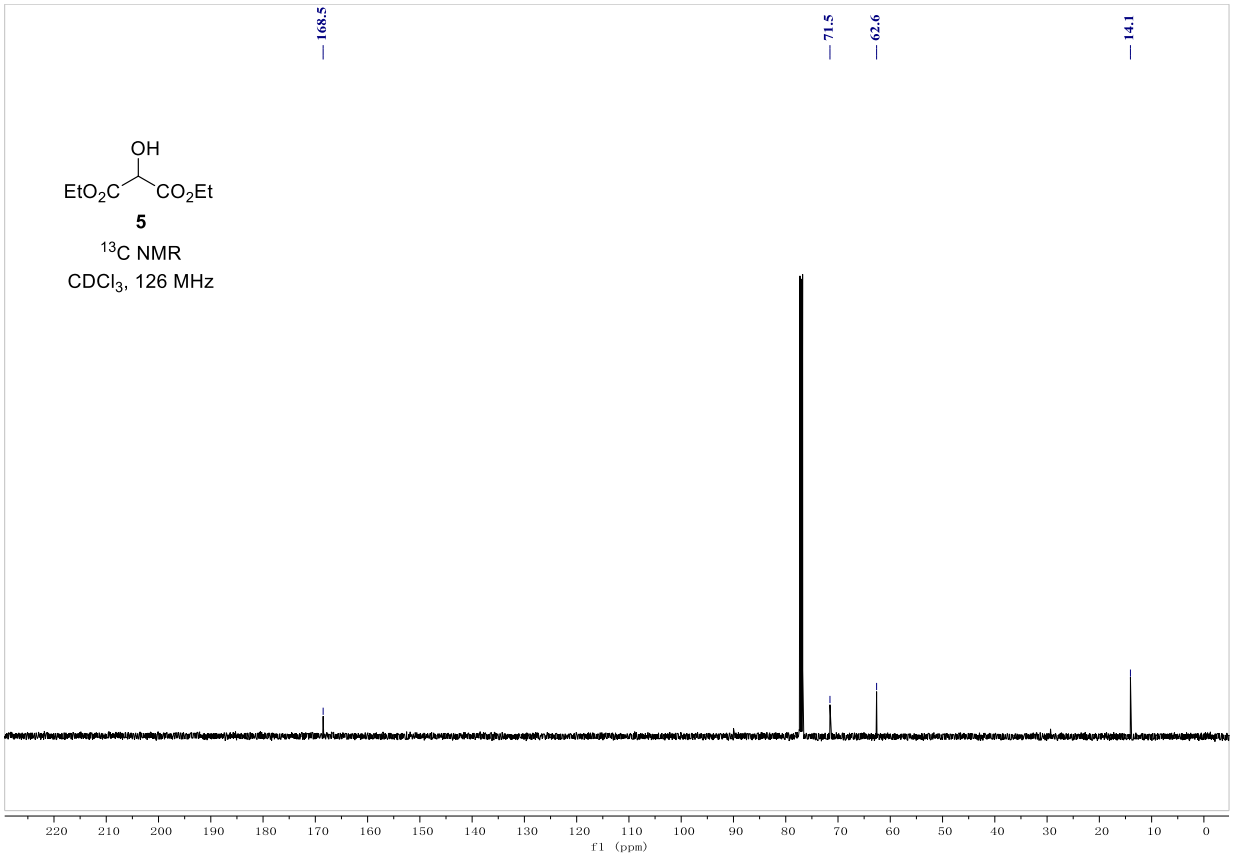

HO
CO2Et
CO2Et
Me
N
4m
13C NMR
CDCl3, 126 MHz
f1 (ppm)


H^b
H^a
HO
CO2Et
CO2Et
H^a
H^b
H
H
N
4m
NOE
f2 (ppm)
f1 (ppm)


7.6
7.6
6.6
6.6
6.5
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.4
4.3
4.3
4.3
4.2
4.2
3.3
3.3
3.3
3.3
2.0
2.0
2.0
1.4
1.4
1.4
1.4
1.3
1.3
N
OH
F3C
CO2Et
3a'
1H NMR
CDCl3, 500 MHz
1.92
2.00
1.95
0.87
4.06
4.00
2.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.5
148.4
126.8
124.5
122.2
119.9
118.9
111.2
77.9
77.6
64.0
47.6
25.5
13.9
N
OH
F3C
CO2Et
3a'
13C NMR
CDCl3, 126 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
EtO2C
CO2Et
5
1H NMR
CDCl3, 500 MHz
4.6
4.6
4.3
4.3
4.2
4.2
4.2
4.2
4.2
4.2
4.2
4.2
3.3
3.3
1.3
1.2
1.2
0.97
4.14
1.00
6.48
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.5
71.5
62.6
14.1
OH
EtO2C
CO2Et
5
13C NMR
CDCl3, 126 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)