

## SUPPORTING INFORMATION

### **Straightforward Access to Enantioenriched *cis*-3-Fluoro-Dihydroquinolin-4-ols Derivatives *via* Ru(II)-Catalyzed-Asymmetric Transfer Hydrogenation/Dynamic Kinetic Resolution**

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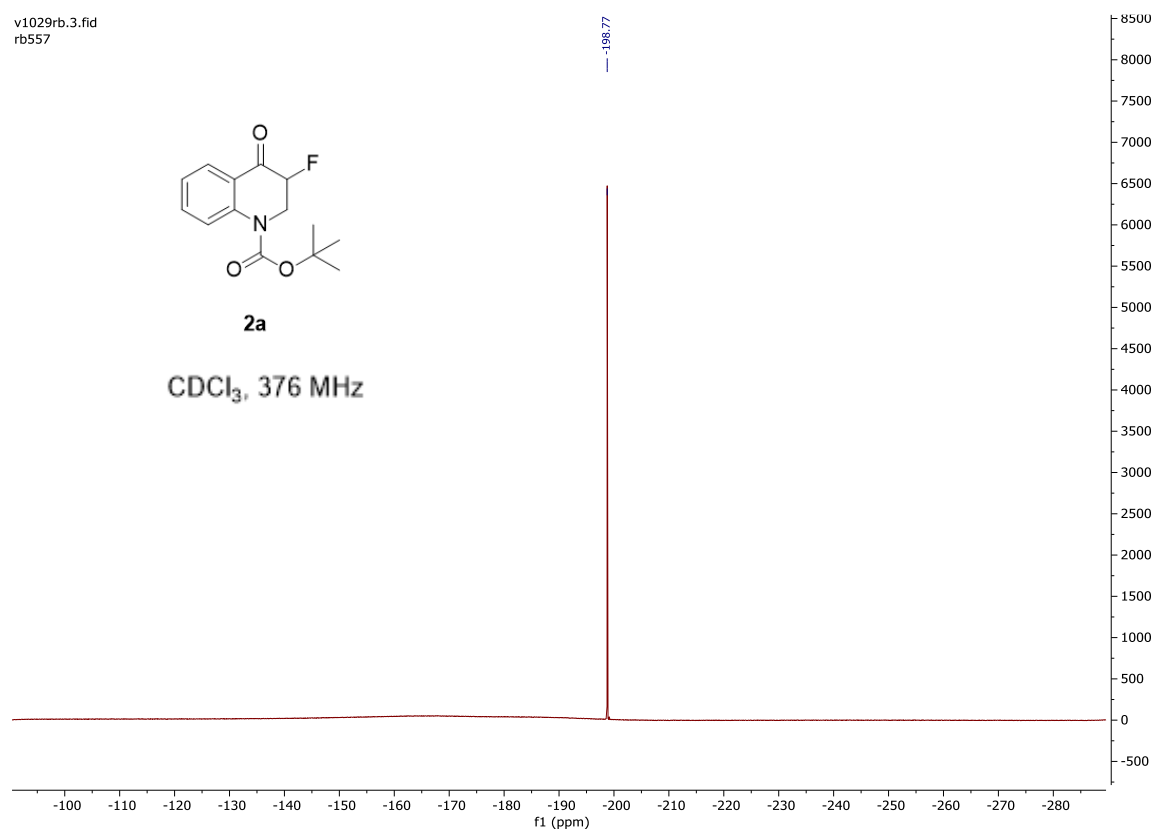
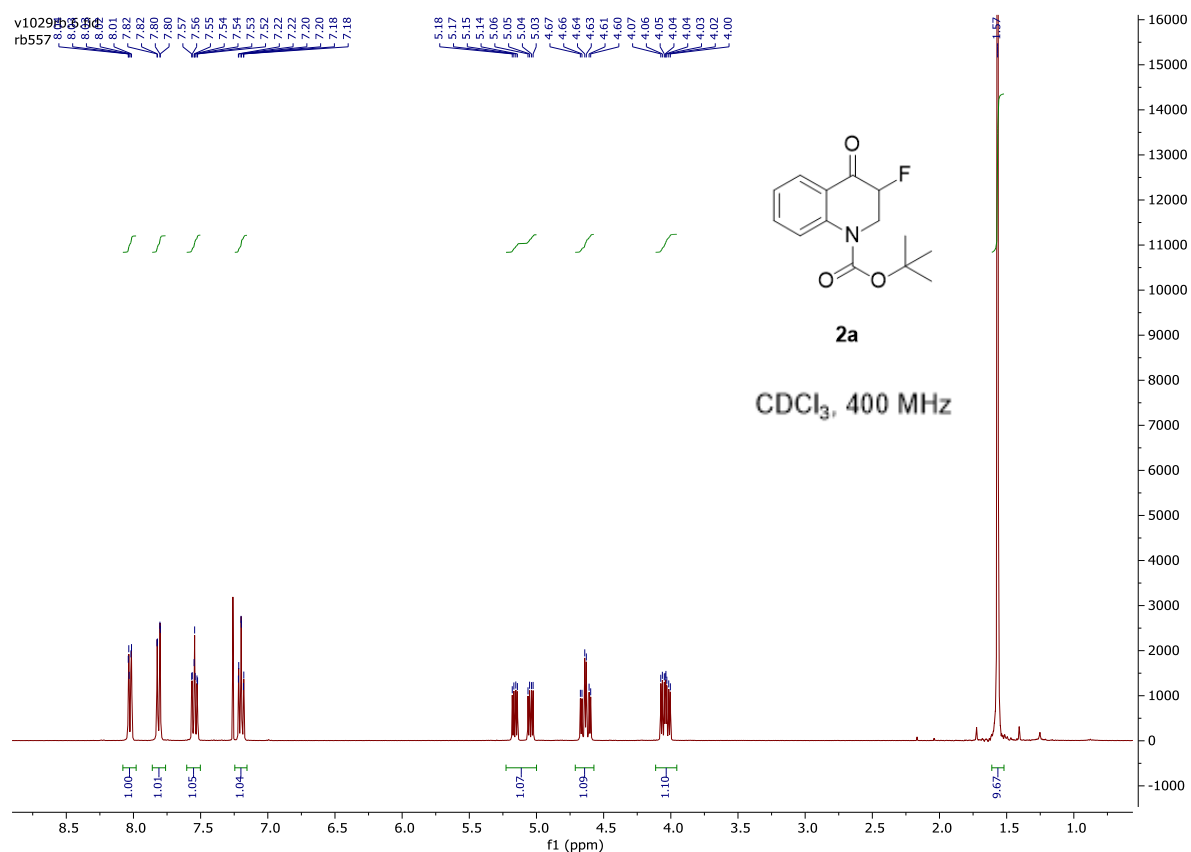
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### **1) General Information**

All air and/or water sensitive reactions were carried out under an argon atmosphere. THF, CH<sub>2</sub>Cl<sub>2</sub> and toluene were dried over alumina columns in a solvent purification apparatus (Innovative technology). Methanol, isopropanol, chlorobenzene, trifluoromethylbenzene, ethyl acetate and acetonitrile from Sigma-Aldrich were used without further purification. Hexafluoroisopropanol (HFIP) was purchased from TCI and was used without further purification. Formic acid/triethylamine (1:1) mixture was purchased from Fluka or Alfa Aesar and was used without further purification. Reactions were monitored by thin layer chromatography carried out on precoated silica gel plates (Merck 60F254) and revealed with either an ultra-violet lamp ( $\lambda = 254$  nm) or a potassium permanganate solution. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded using a Bruker AC 400 (400 MHz). The chemical shifts are expressed in parts per million (ppm) referenced to residual chloroform (7.26 ppm). Data are reported as follows: chemical shifts ( $\delta$ ), multiplicity (recorded as s, singlet; d, doublet; t, triplet; q, quadruplet; quint, quintuplet; sext, sextuplet; hept, heptuplet; m, multiplet and br, broad), coupling constants and integration. Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded using a Bruker AC 400 (101 MHz). The chemical shifts are expressed in parts per million (ppm) relative to the centre line of the triplet at 77.16 ppm for CDCl<sub>3</sub>. Melting points (m. p.) were determined on a K f ler melting point apparatus. Optical rotations were measured on a Jasco P-1010 polarimeter. High resolution mass spectrometric (HRMS) analyses were measured on LTQ-Orbitrap (Thermo Fisher Scientific) at Sorbonne Universit .

## 2) NMR Spectra



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189.69  
188.55

152.77

144.06

135.00

128.08

124.61

123.85

123.19

88.10

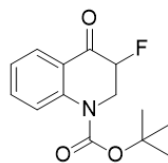
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83.19

48.76

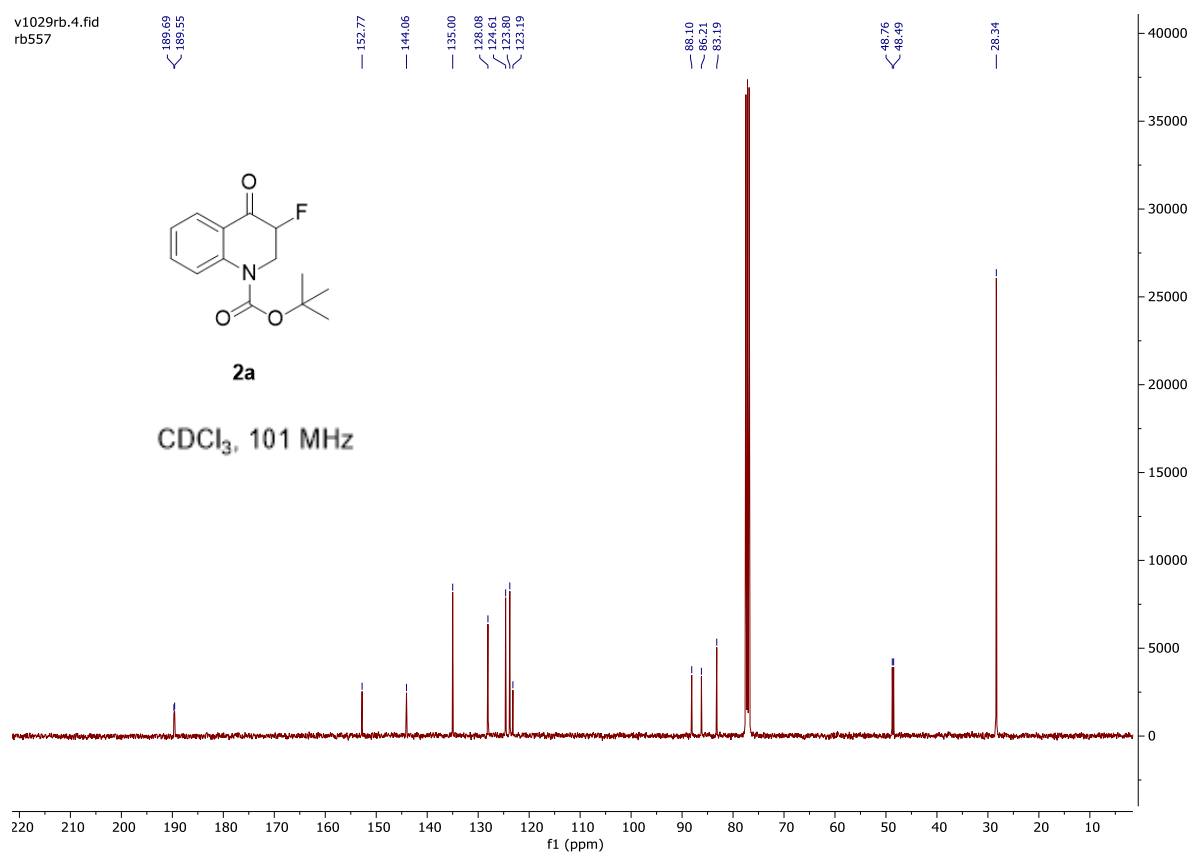
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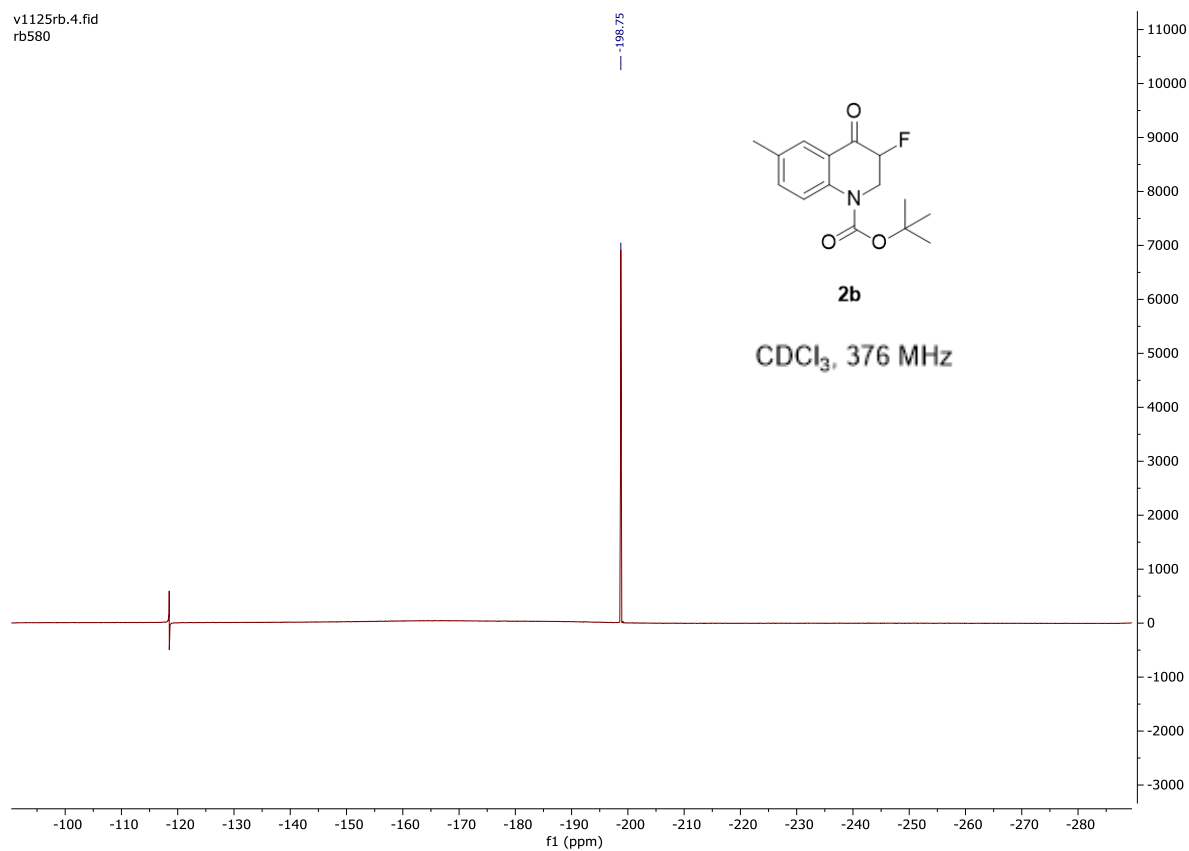
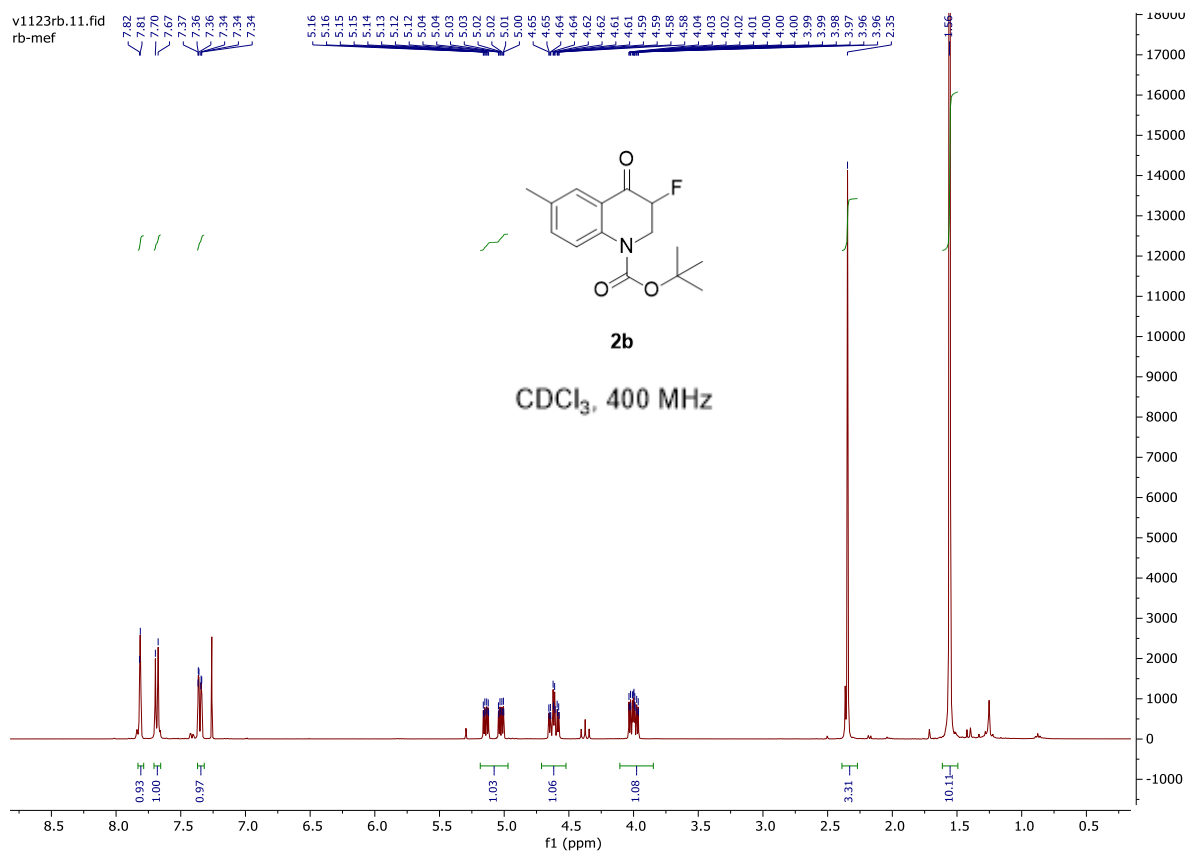
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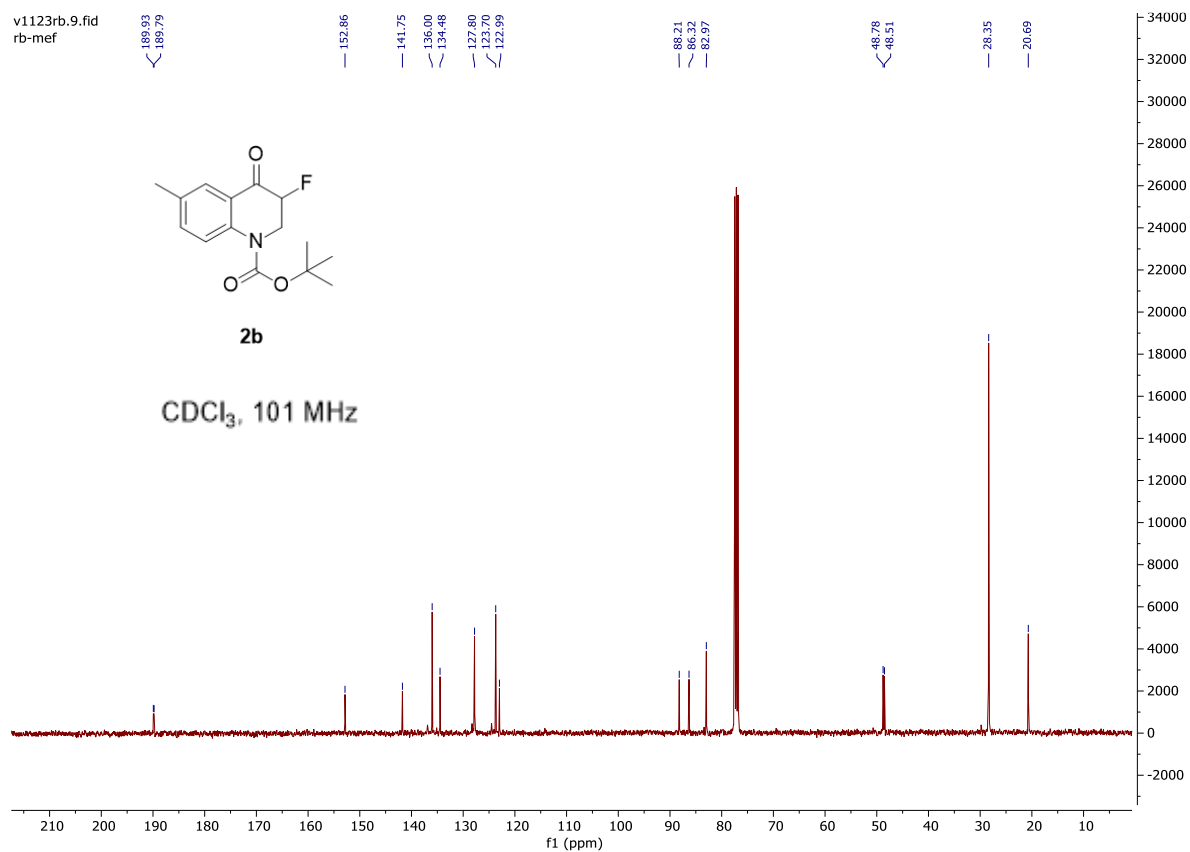
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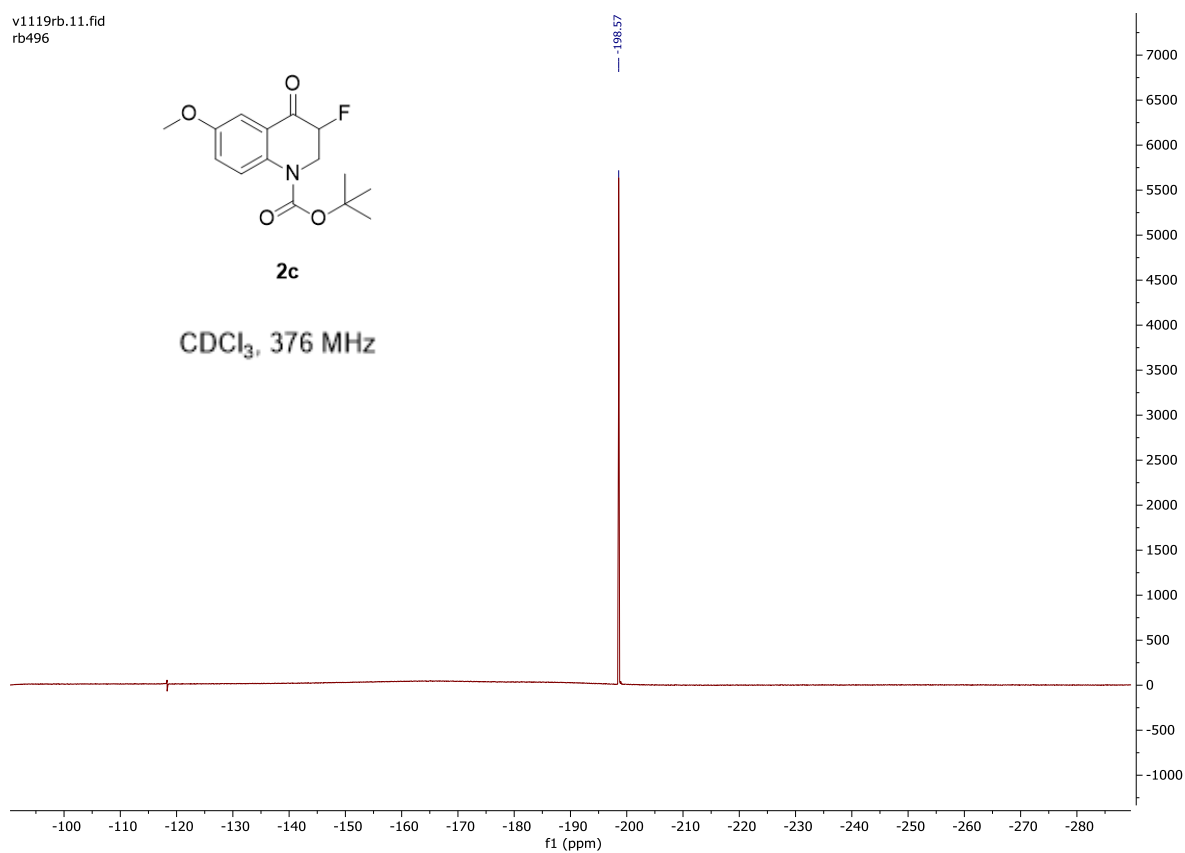
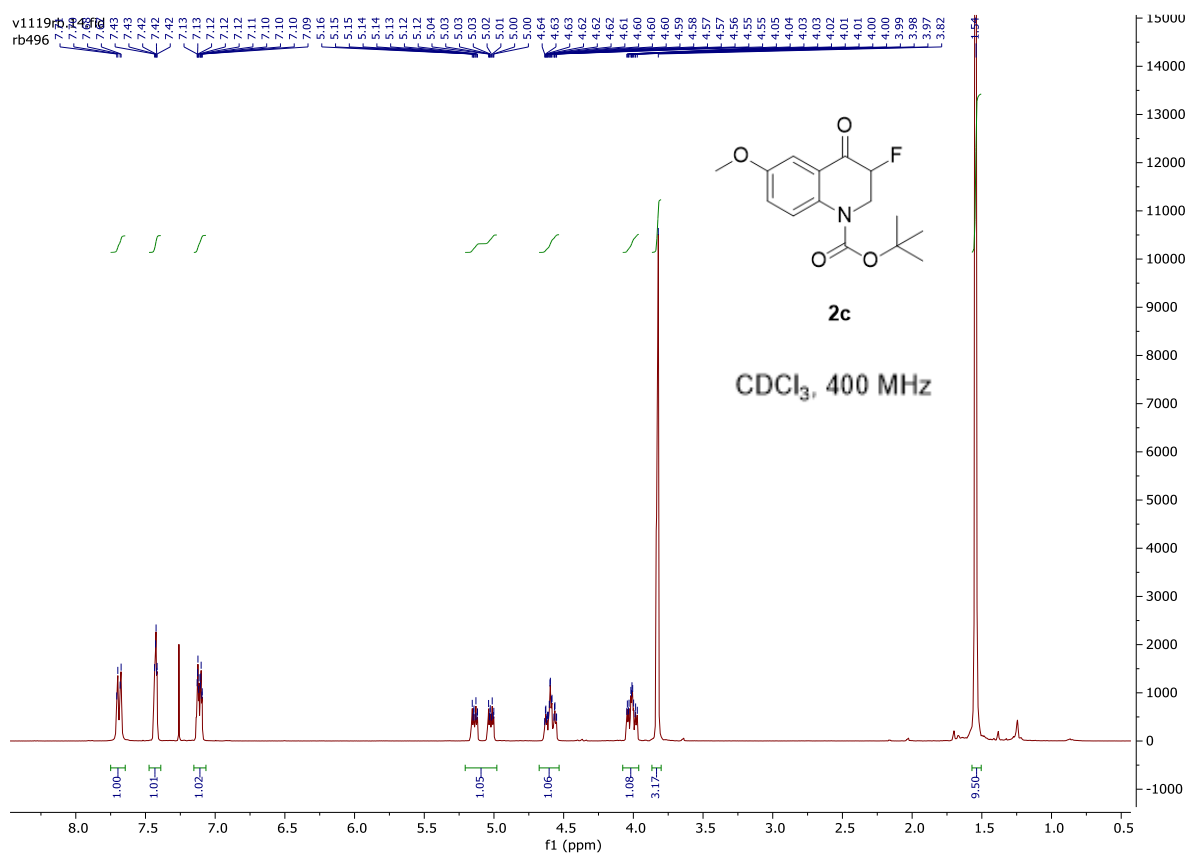
CDCl<sub>3</sub>, 101 MHz



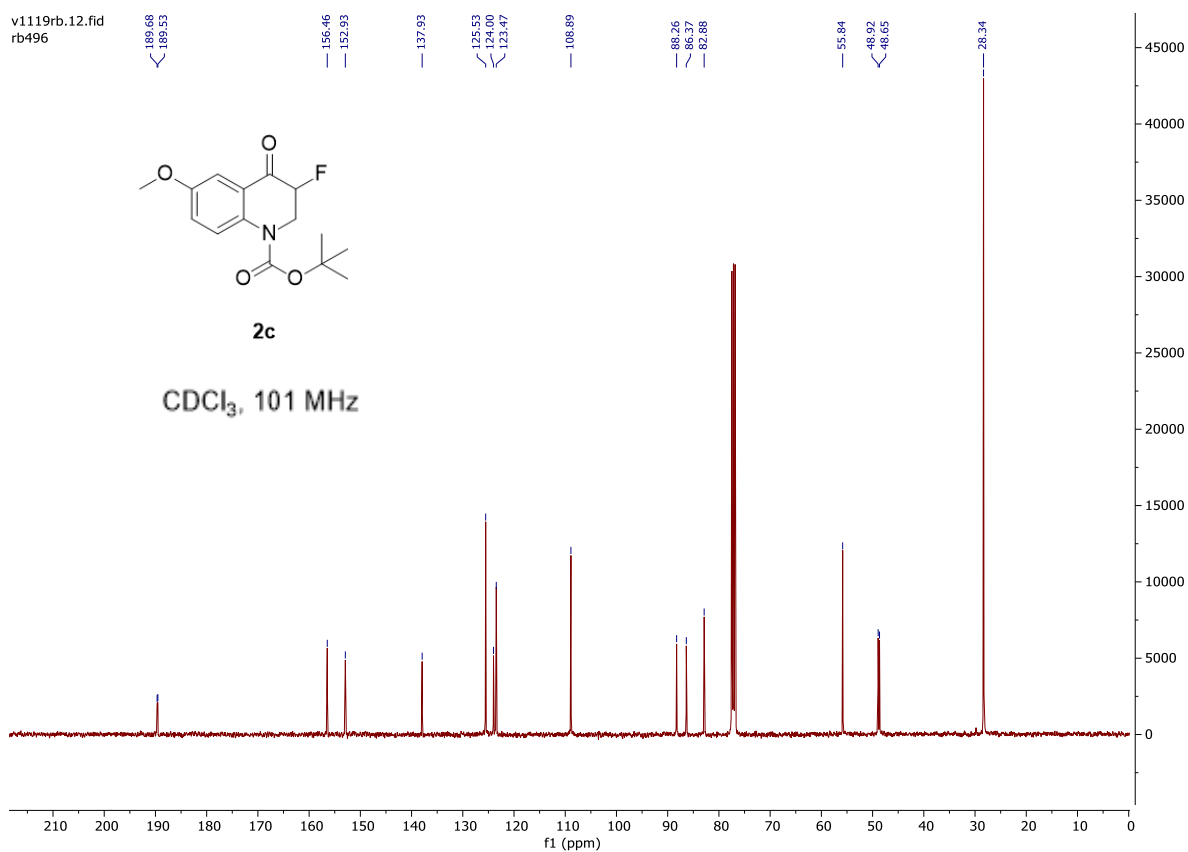


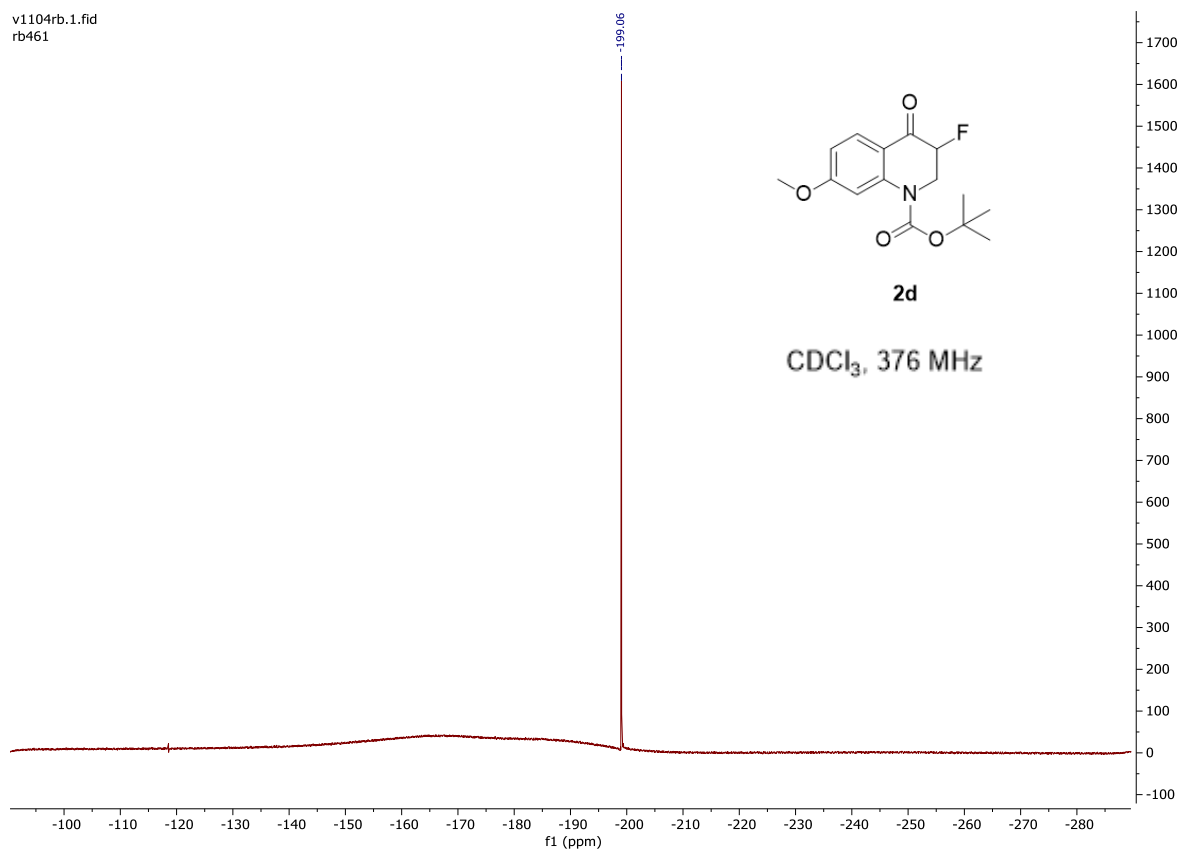
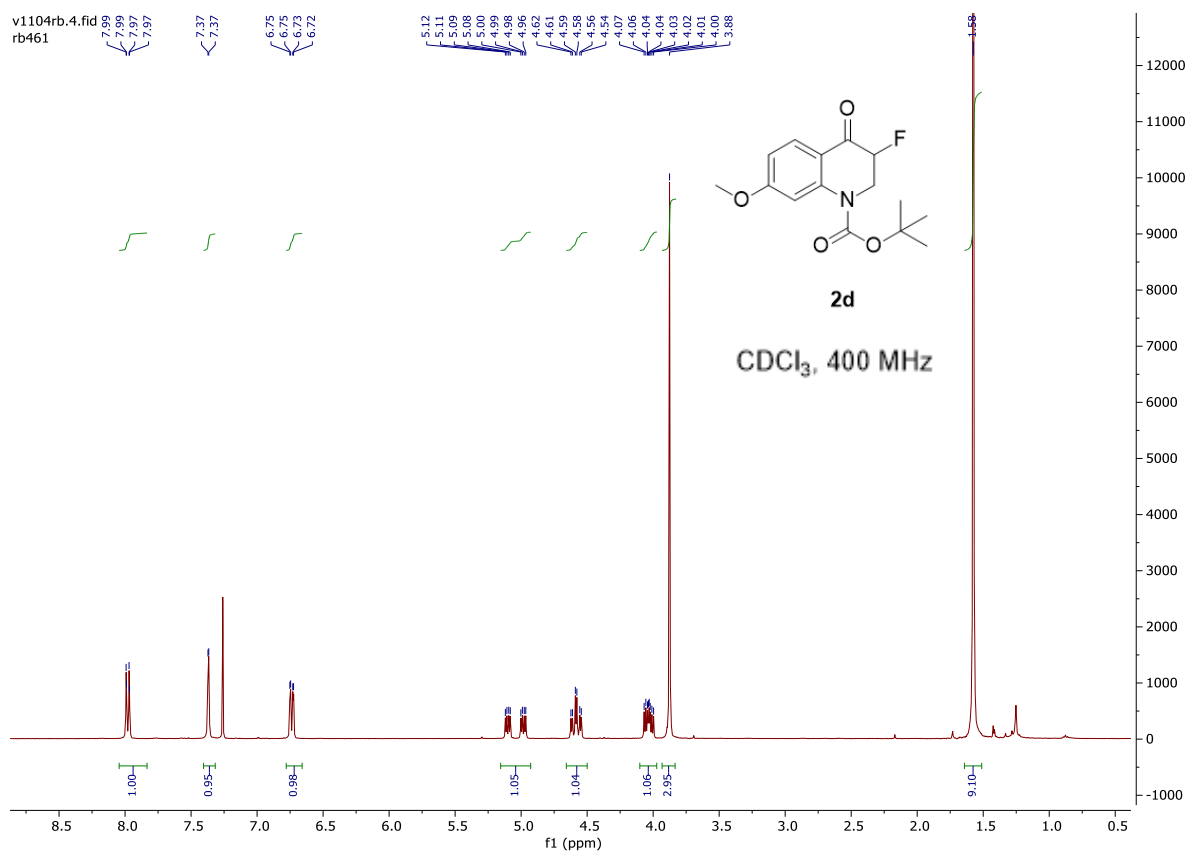
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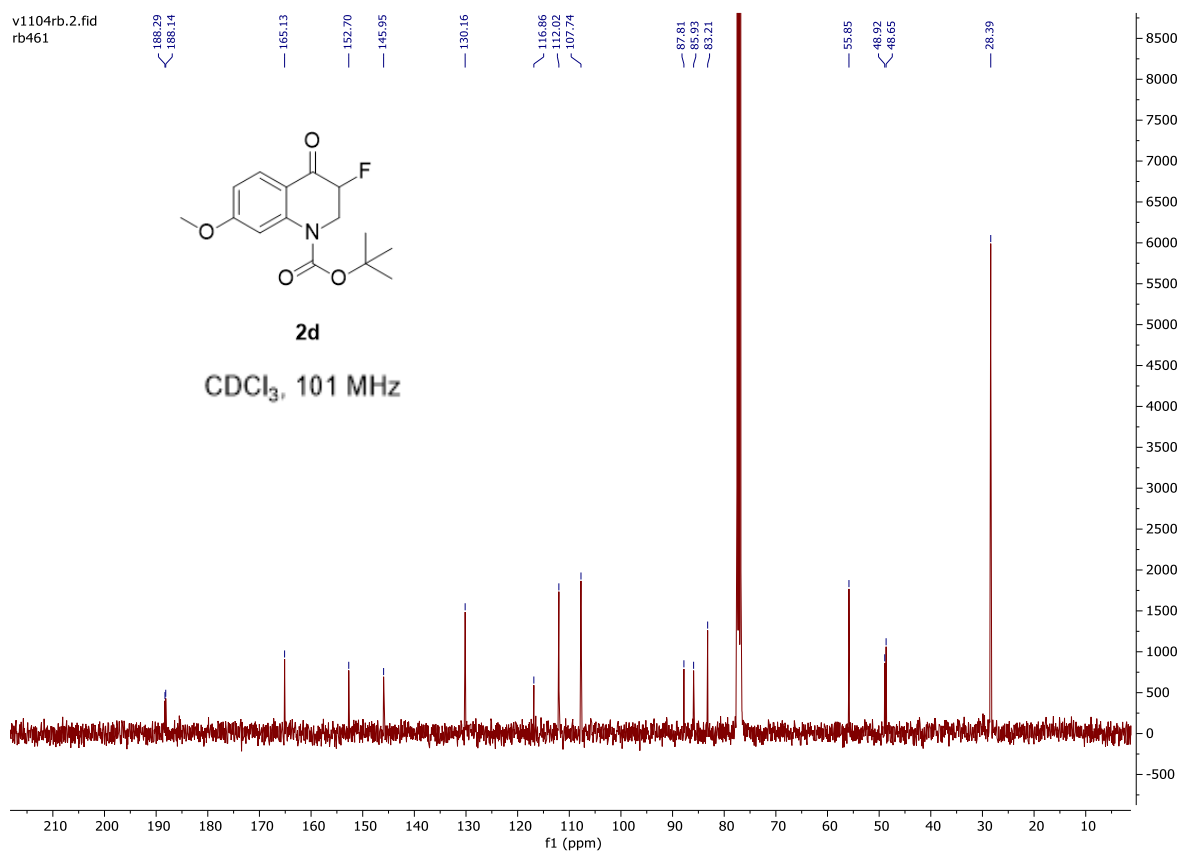


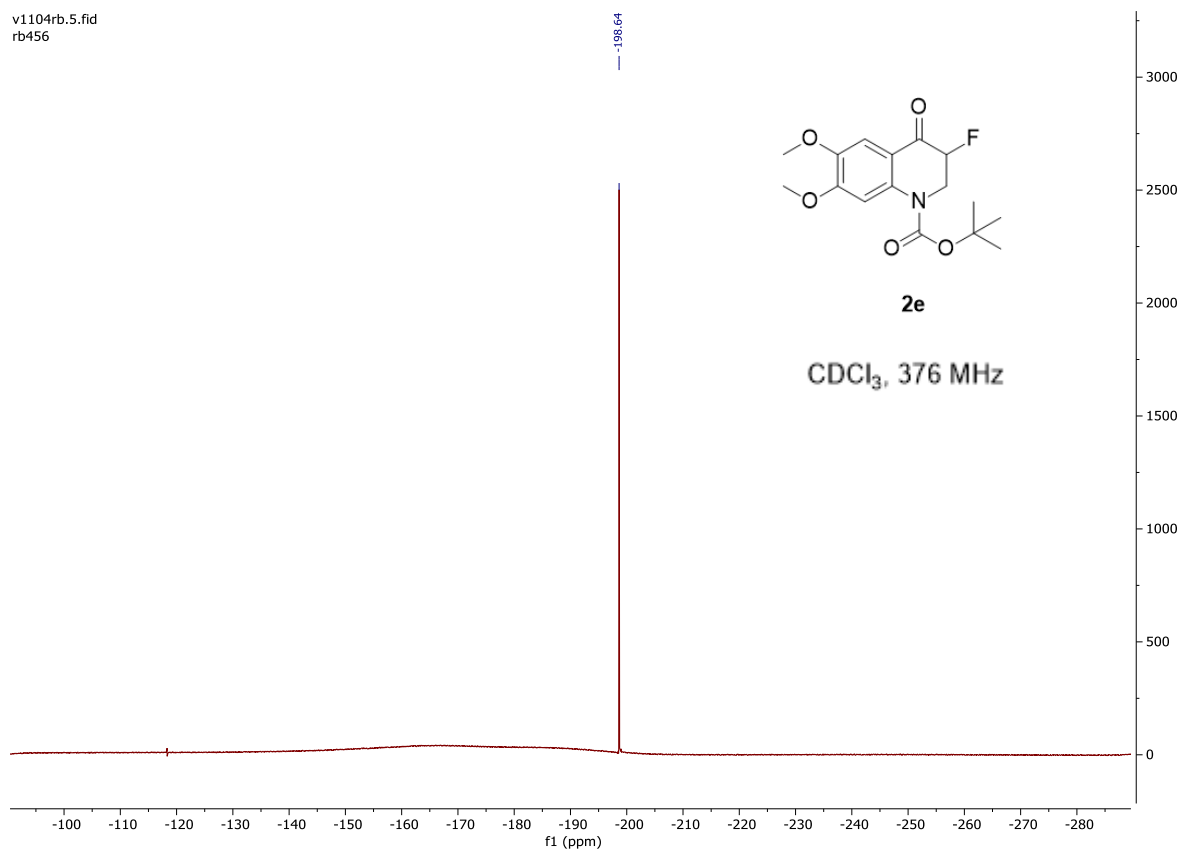
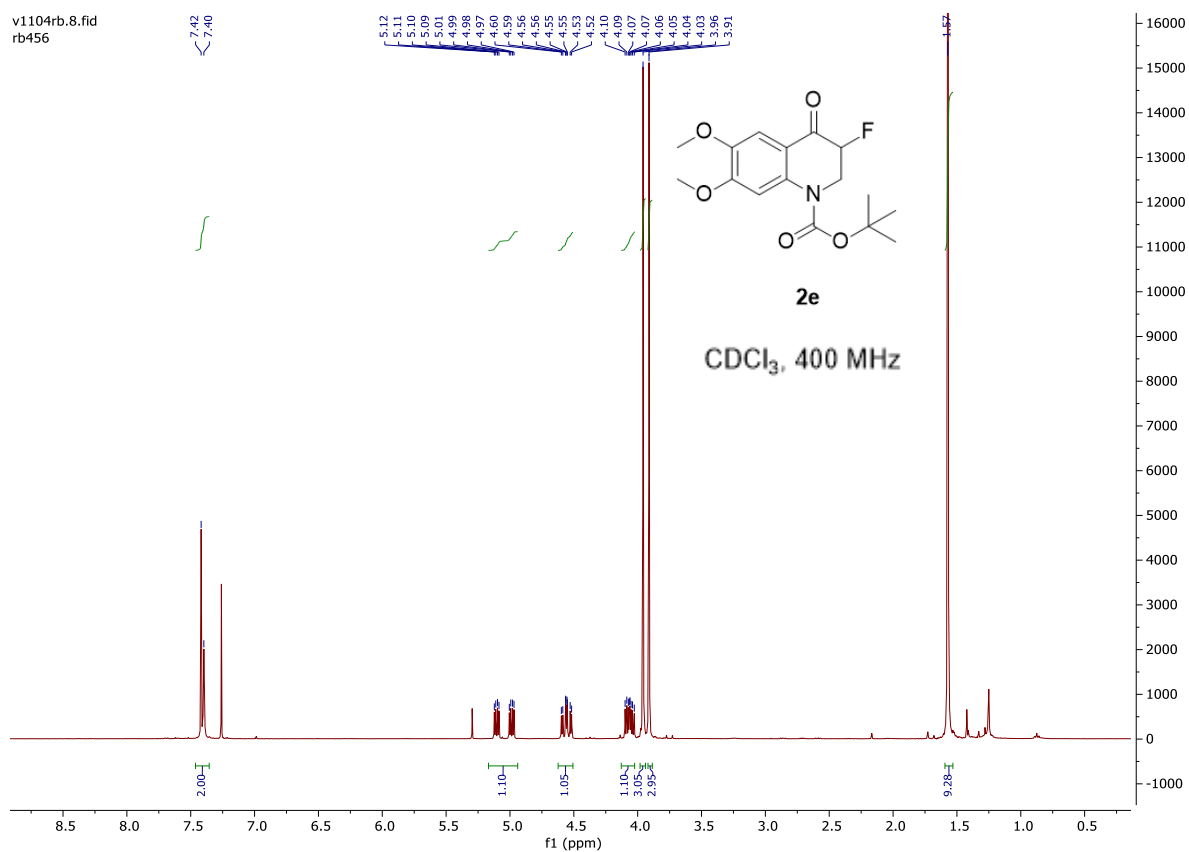
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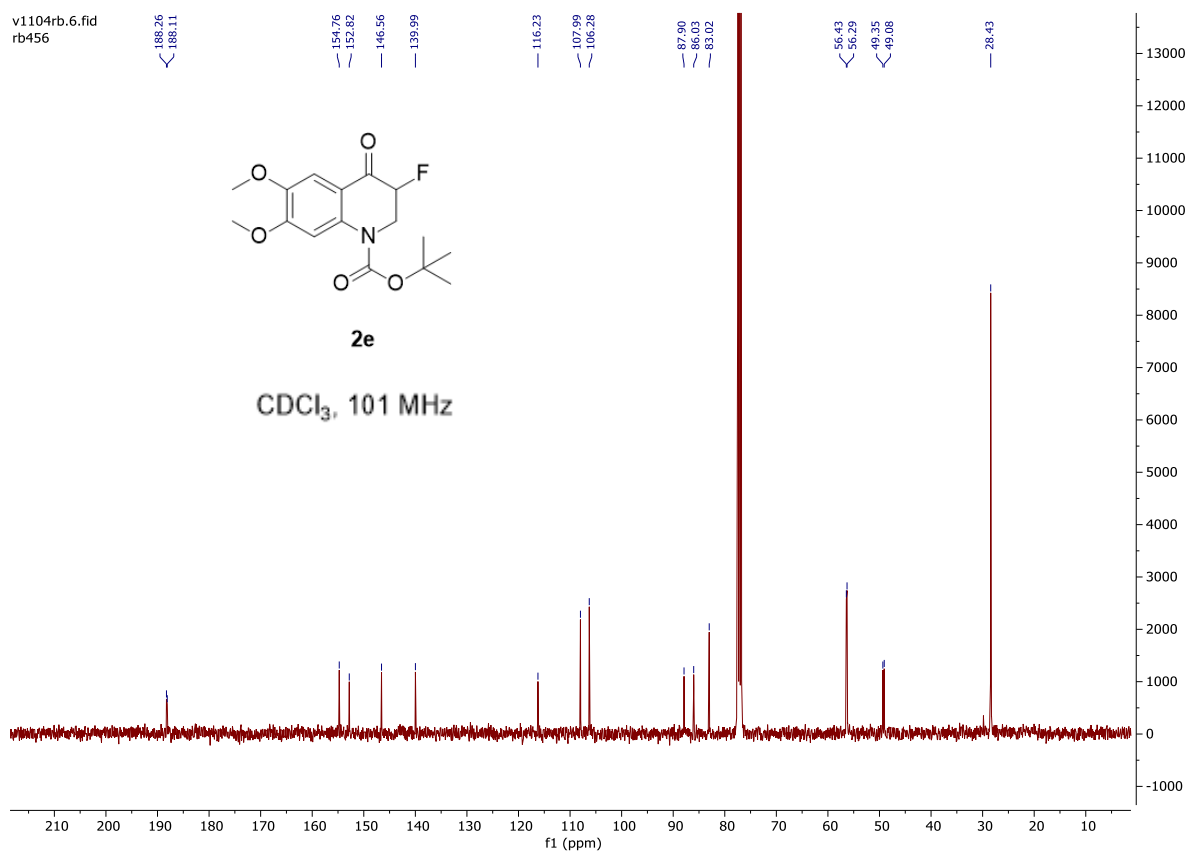


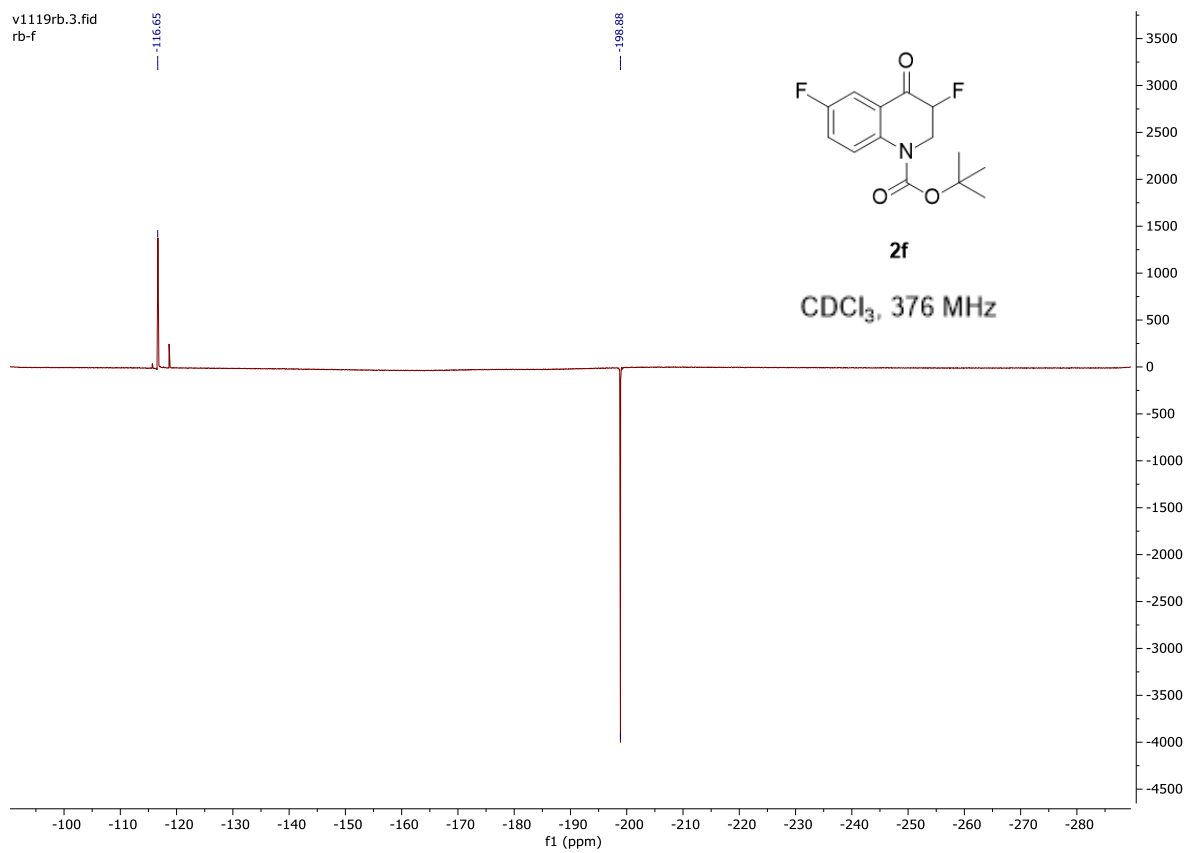
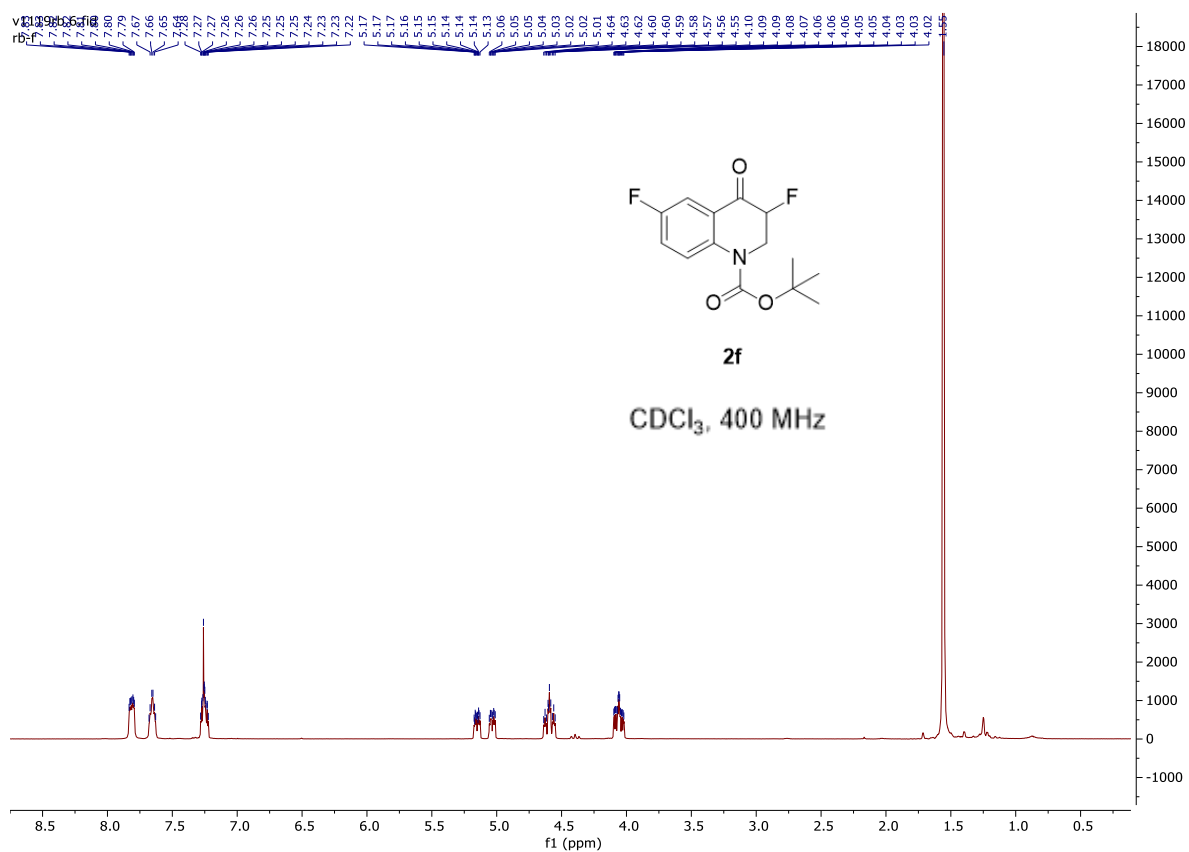


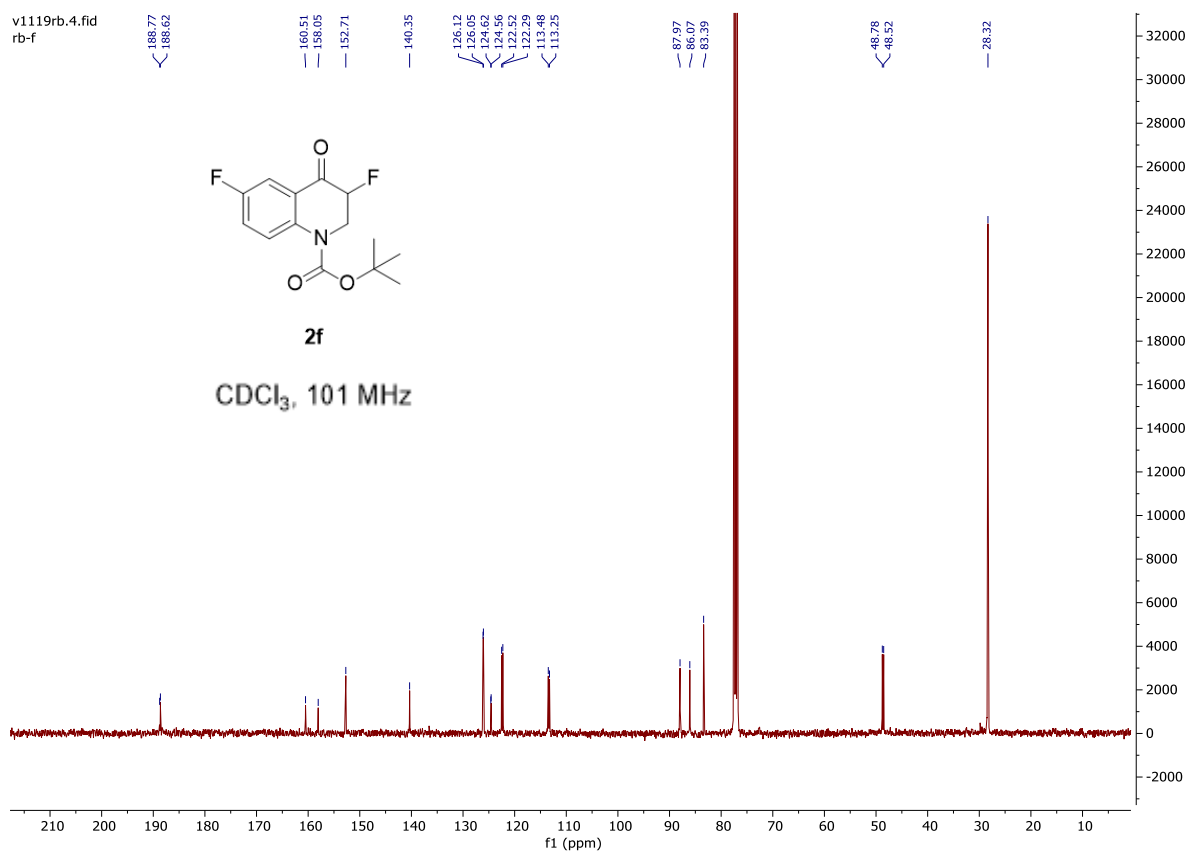


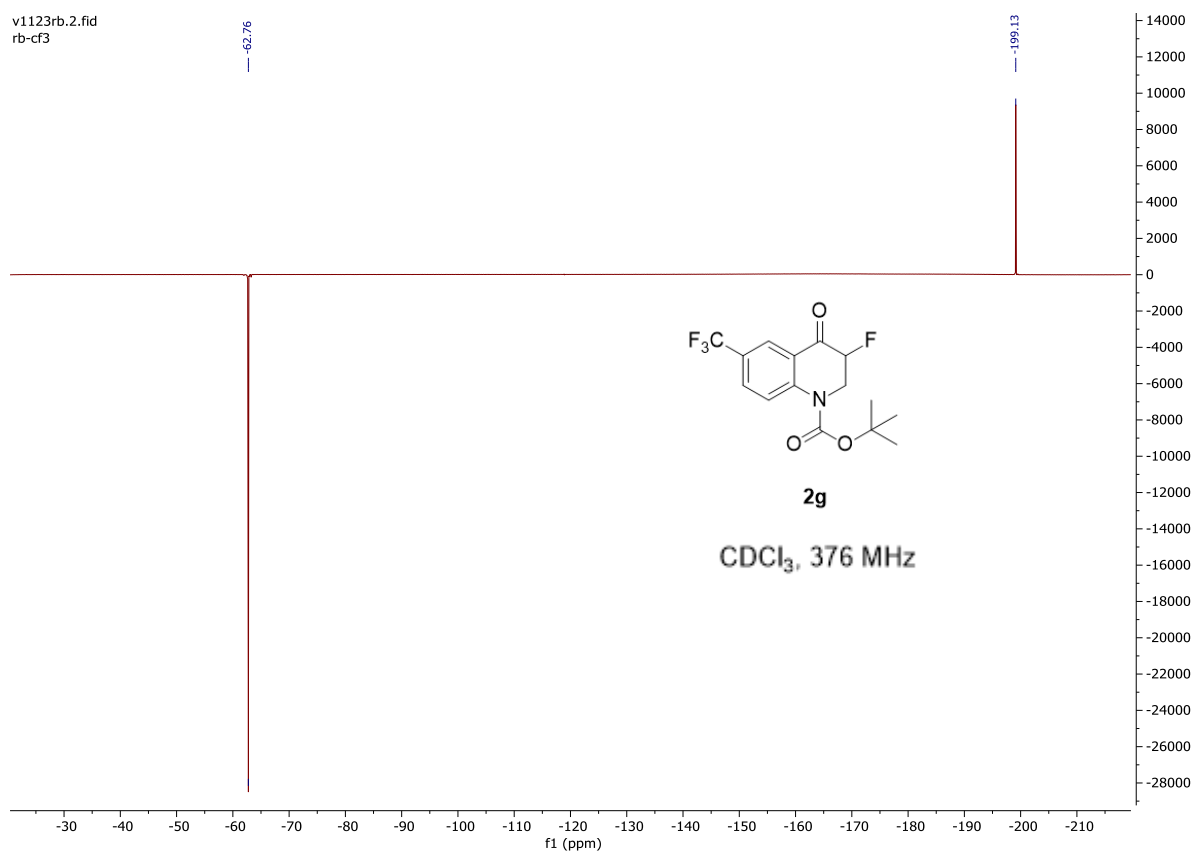
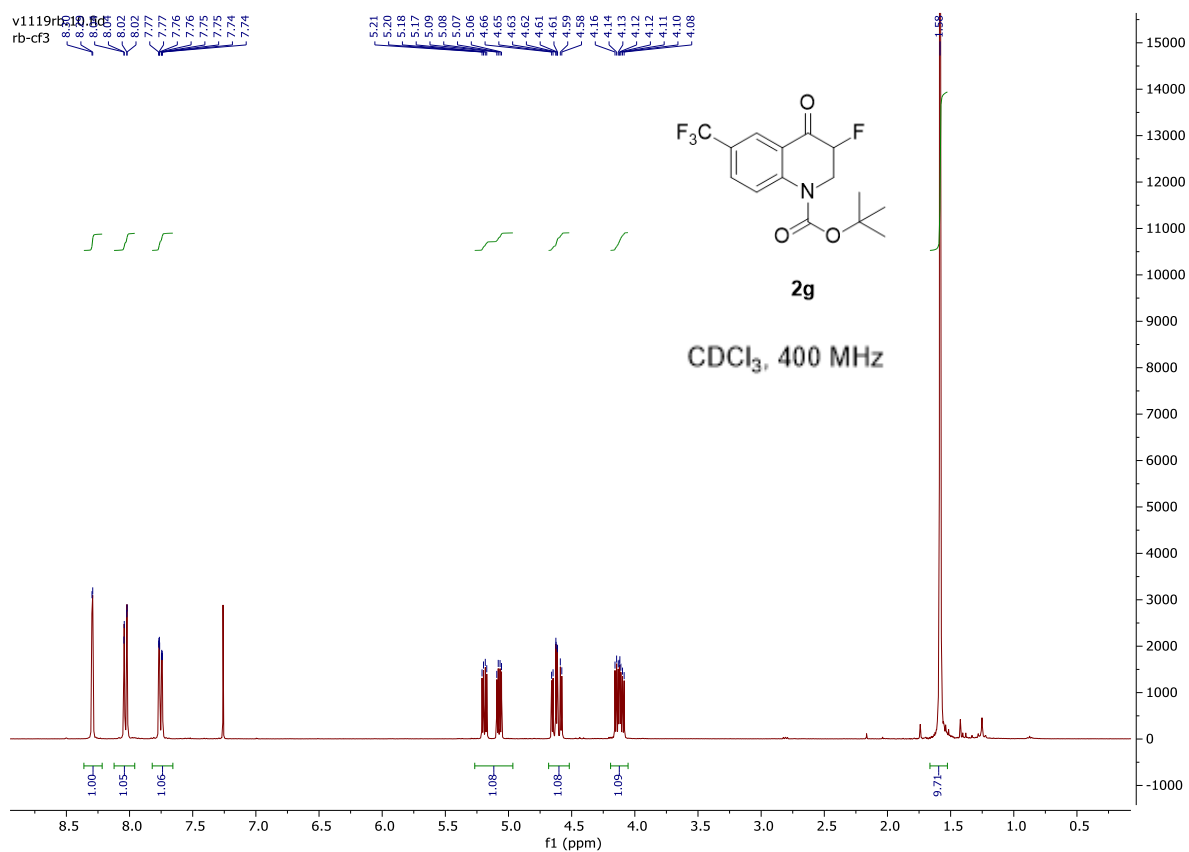


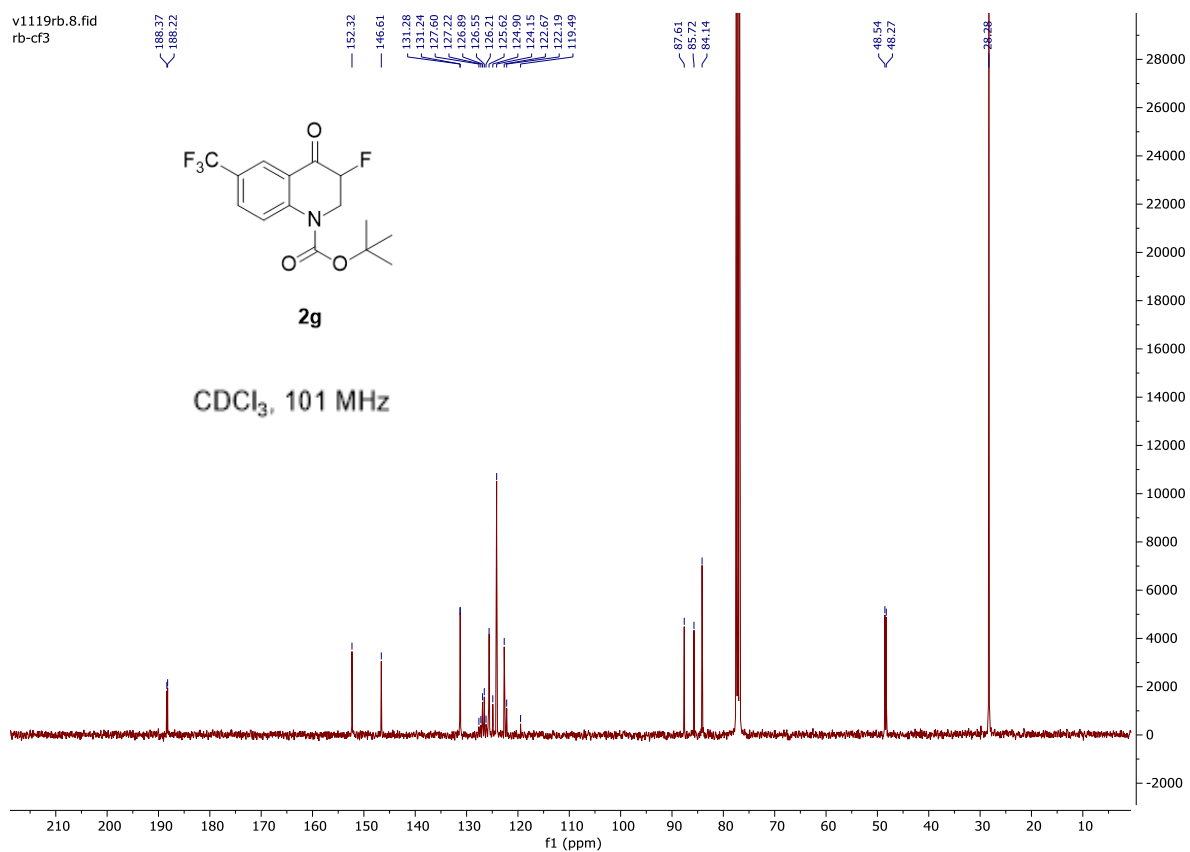
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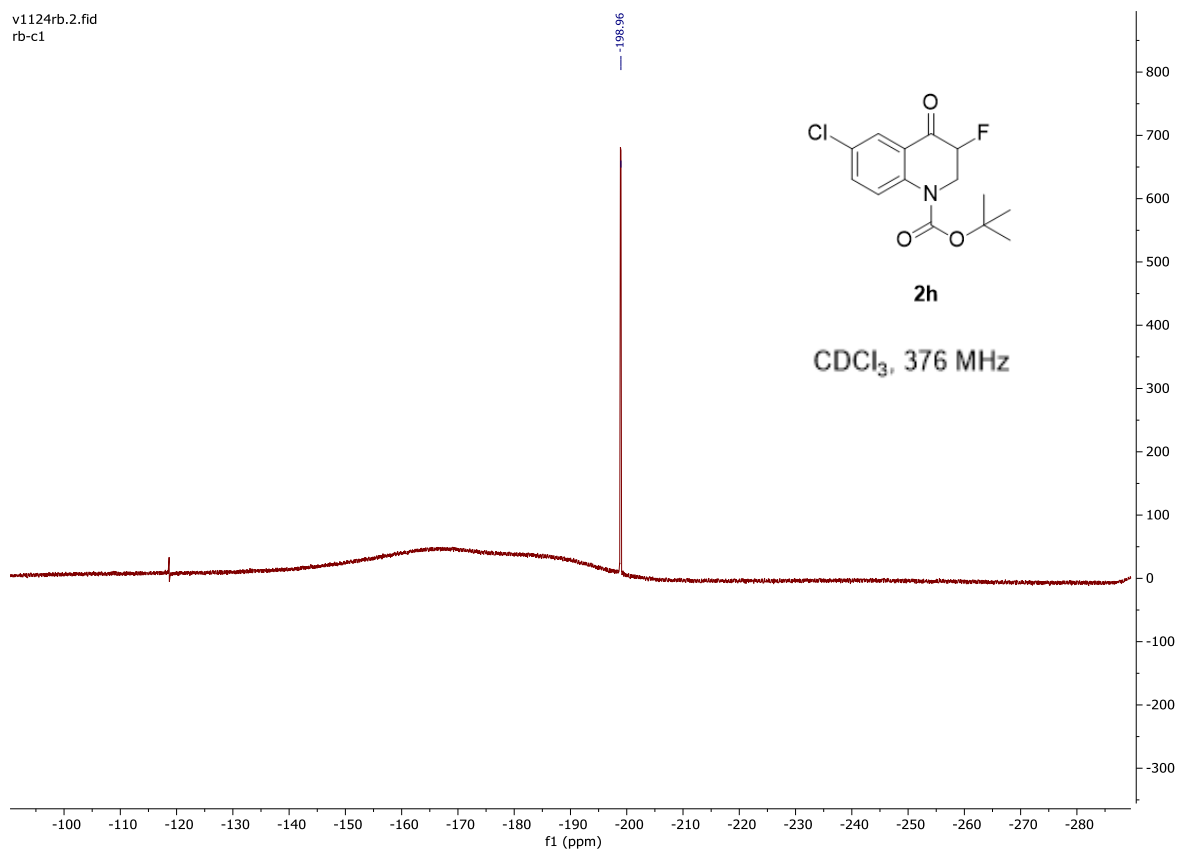
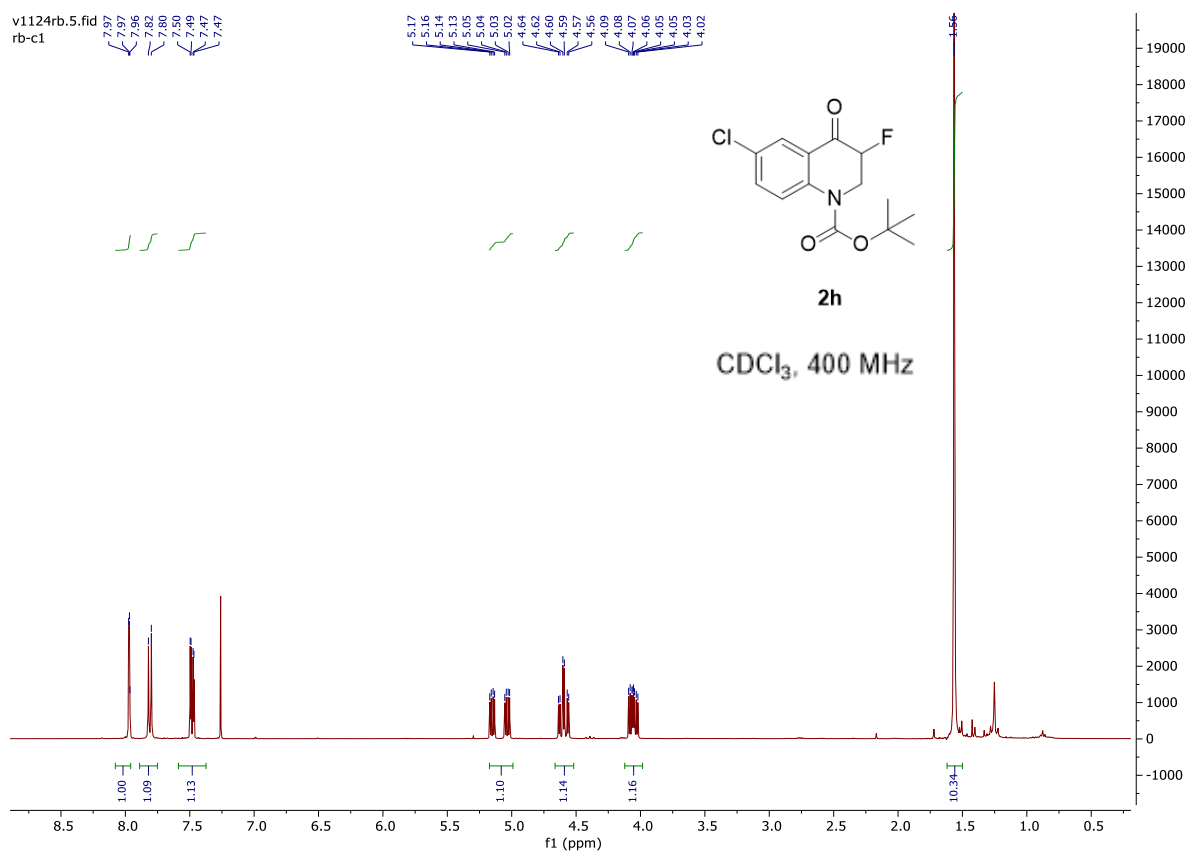






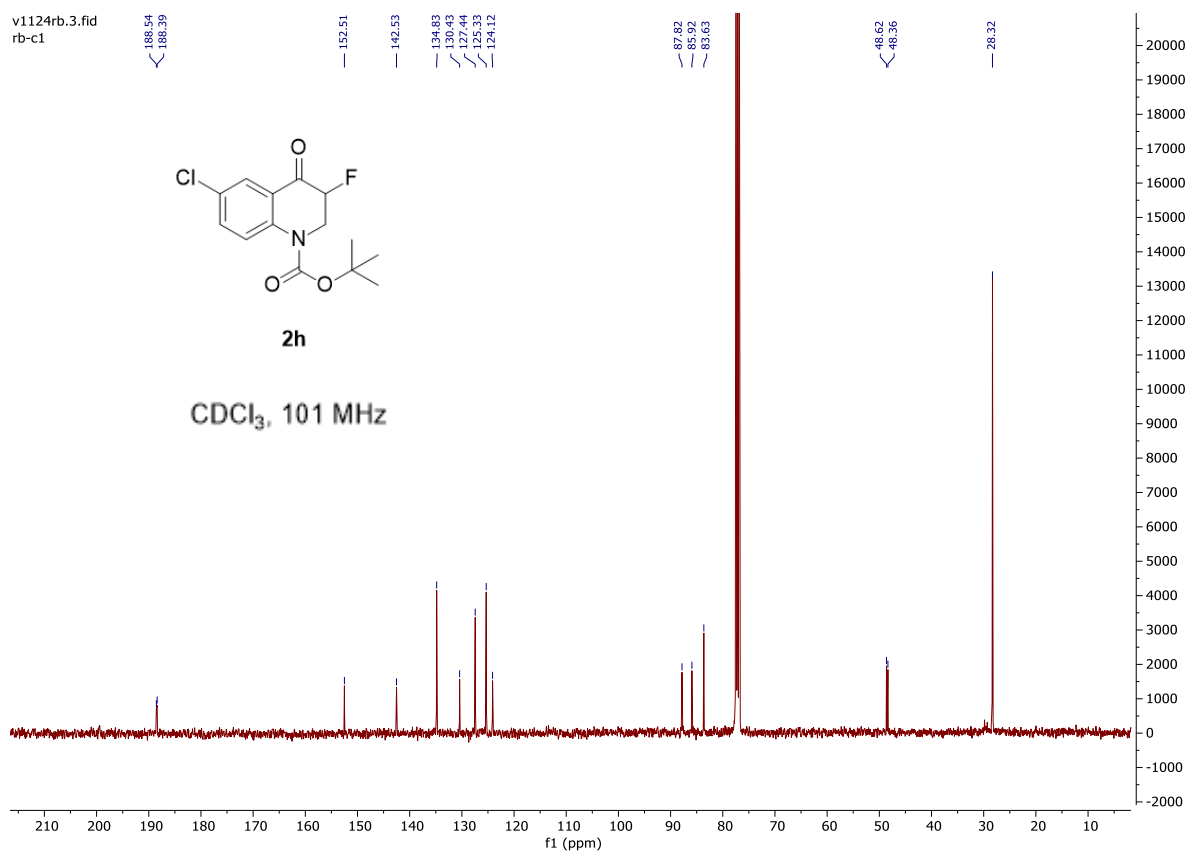


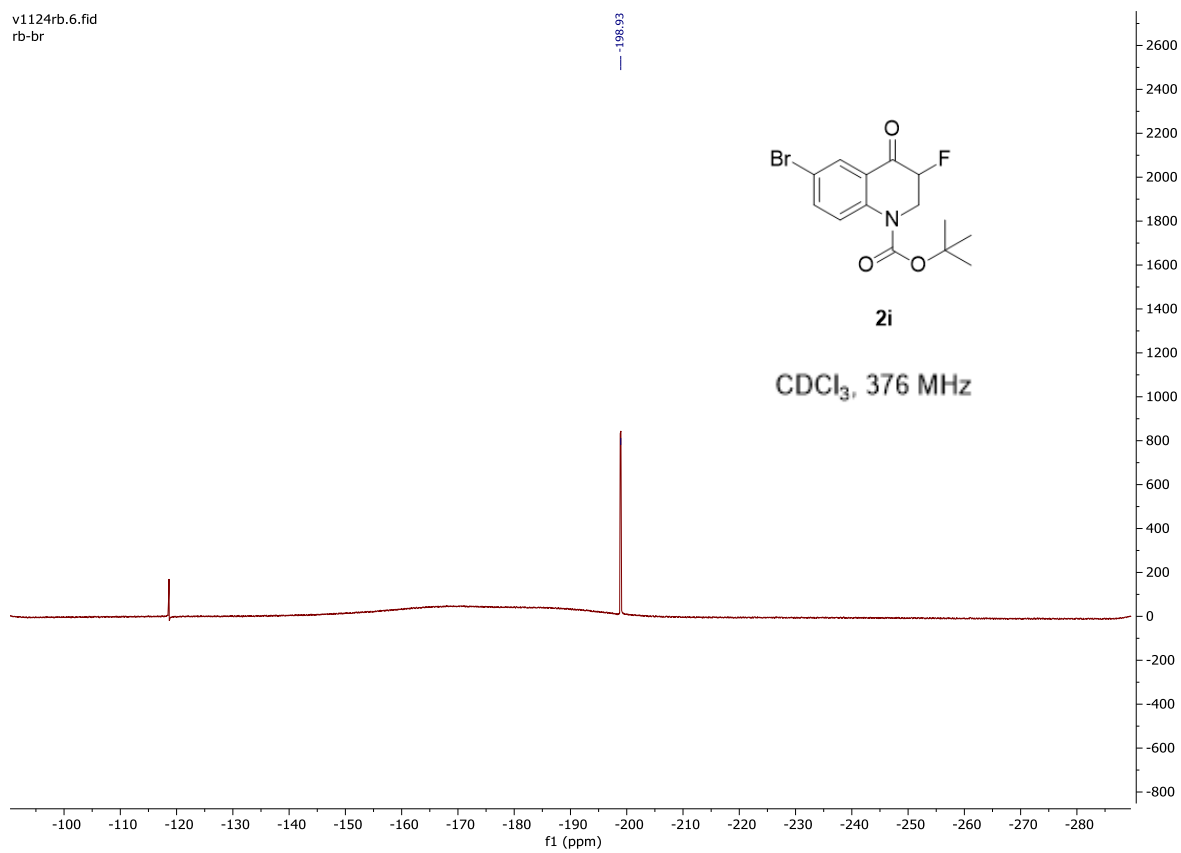
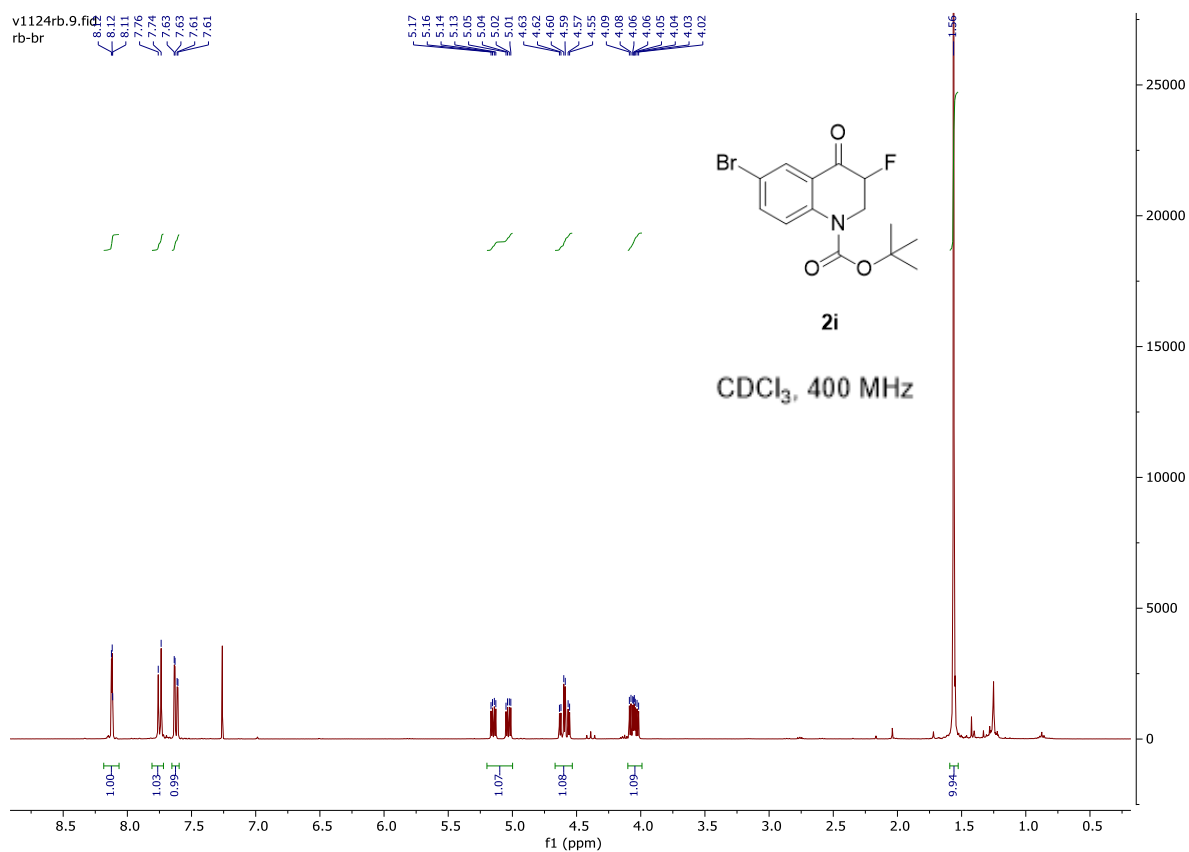


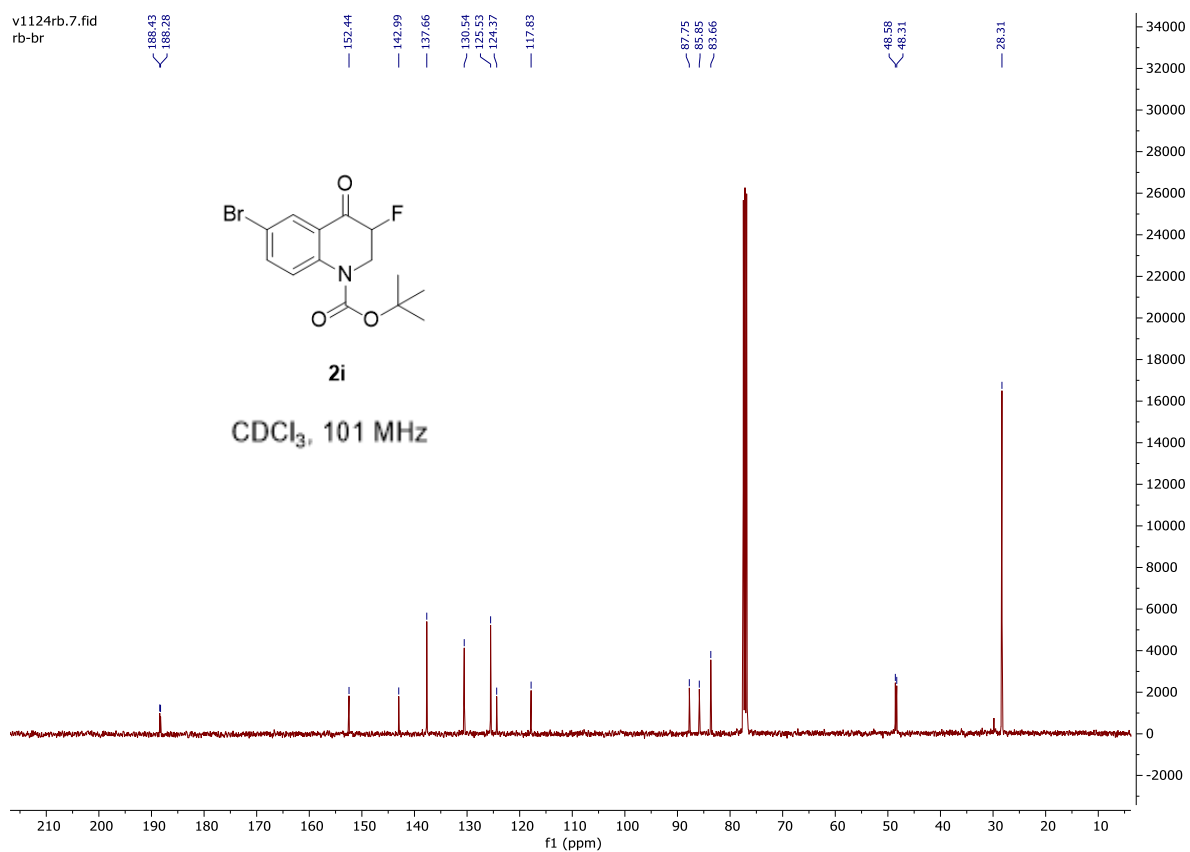


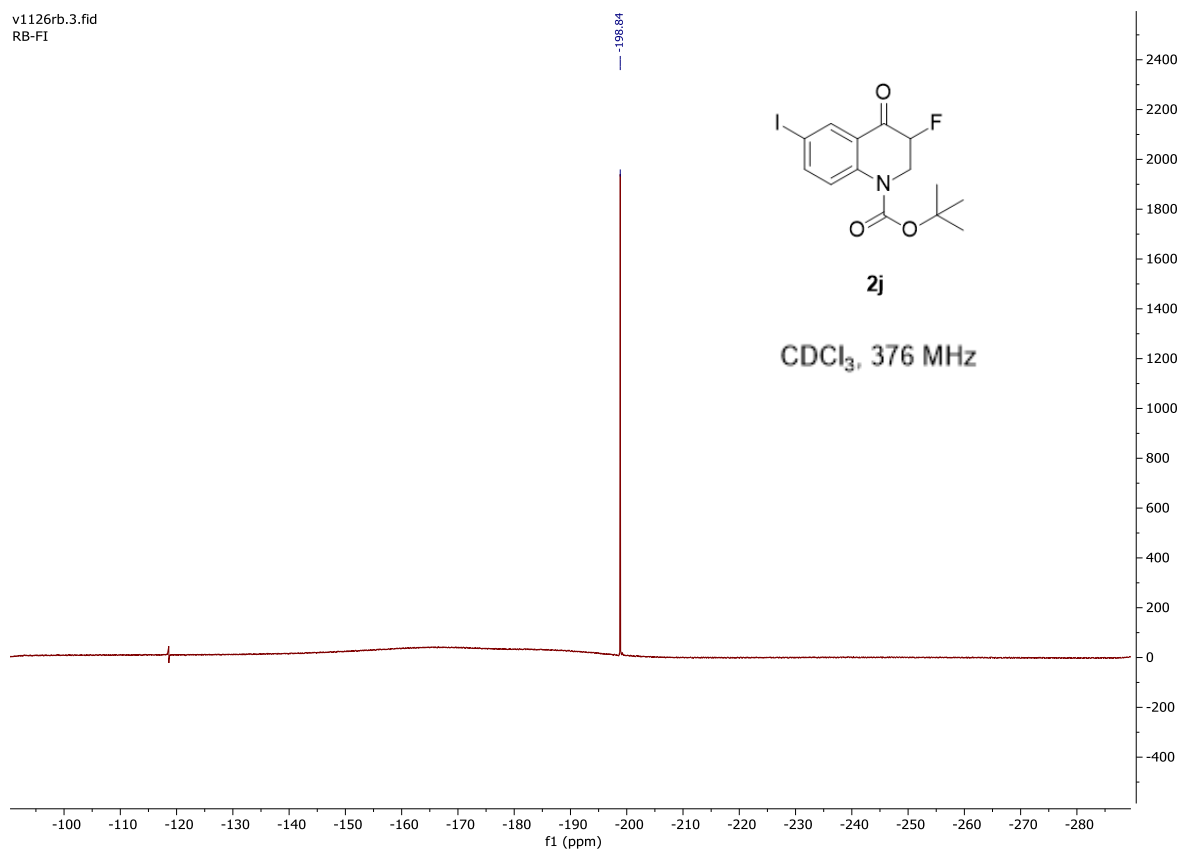
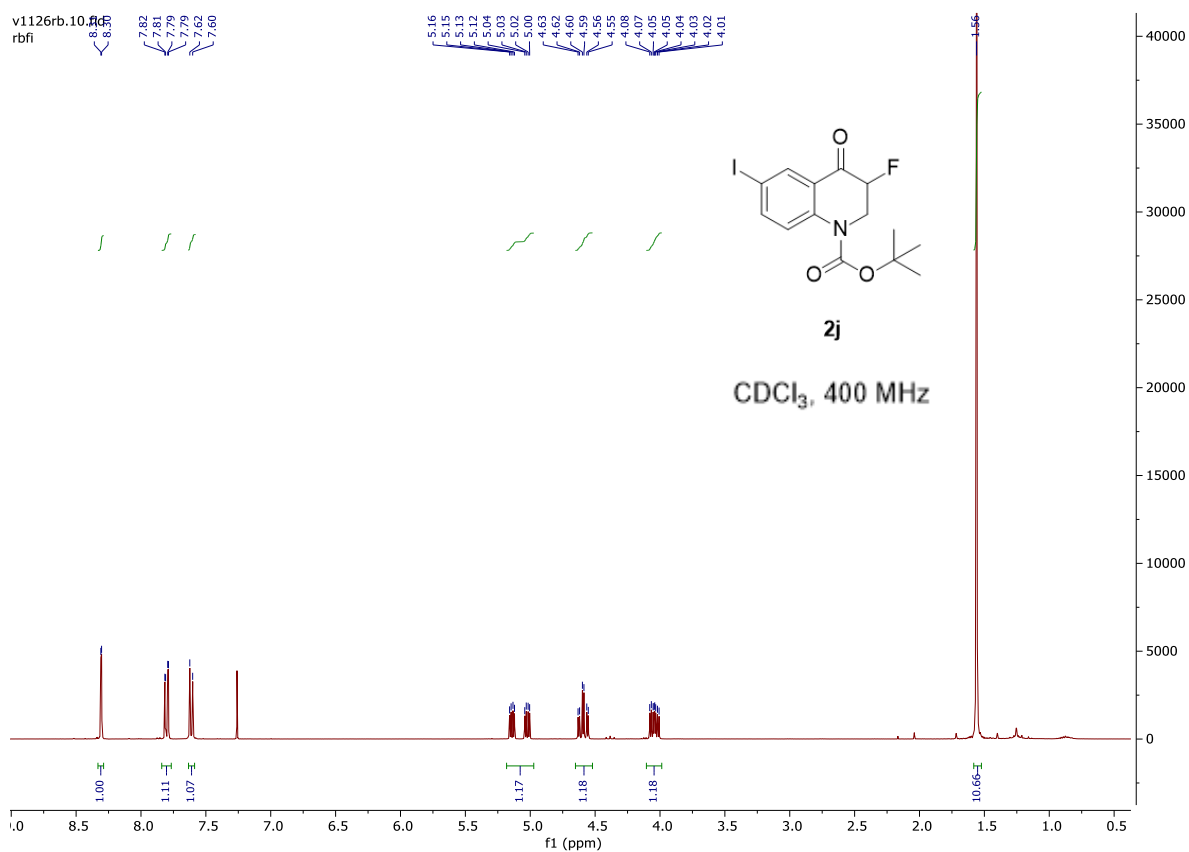


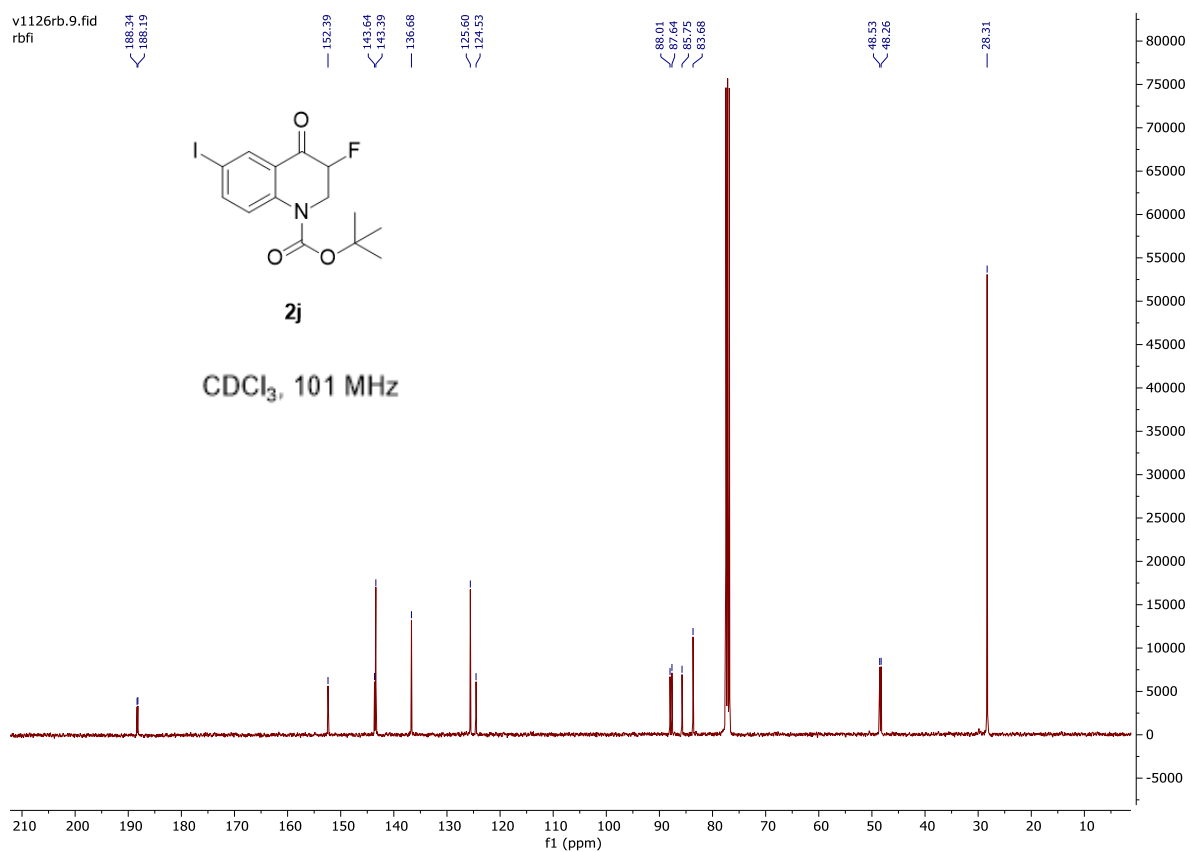
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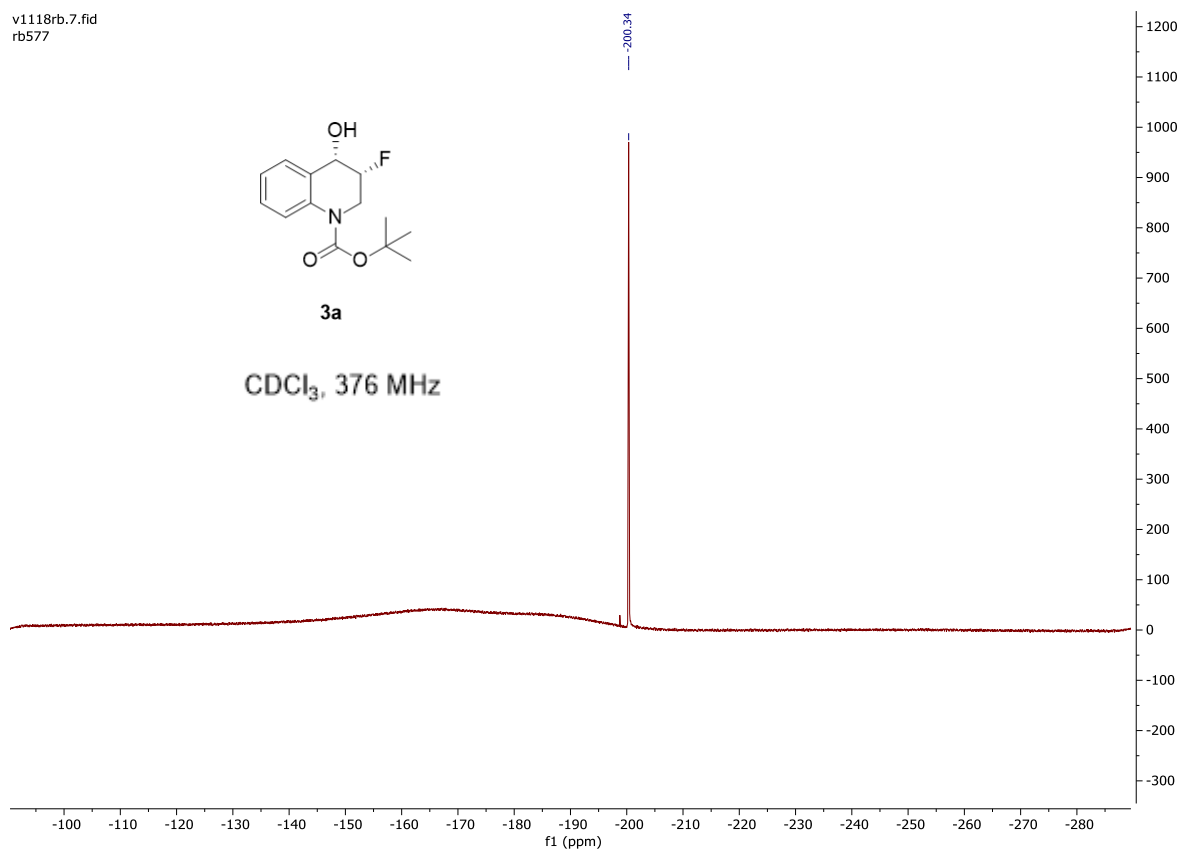
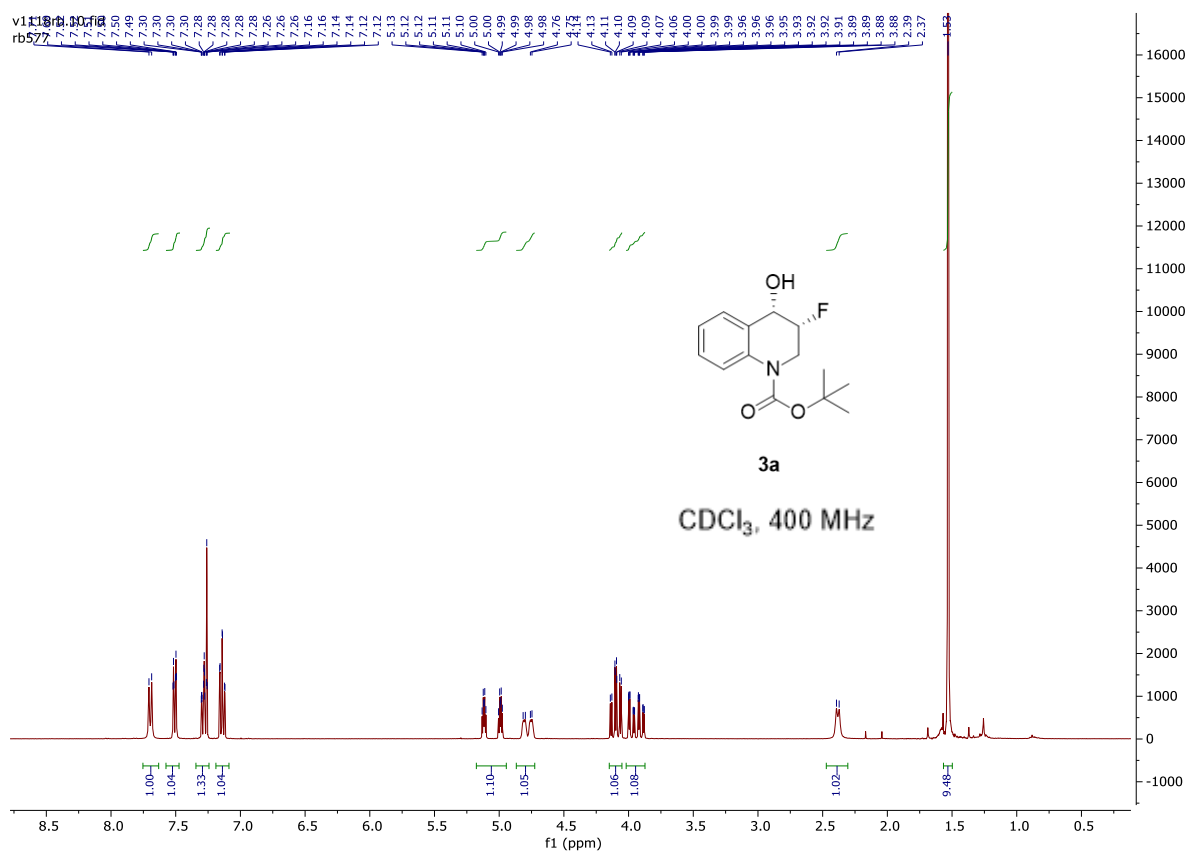




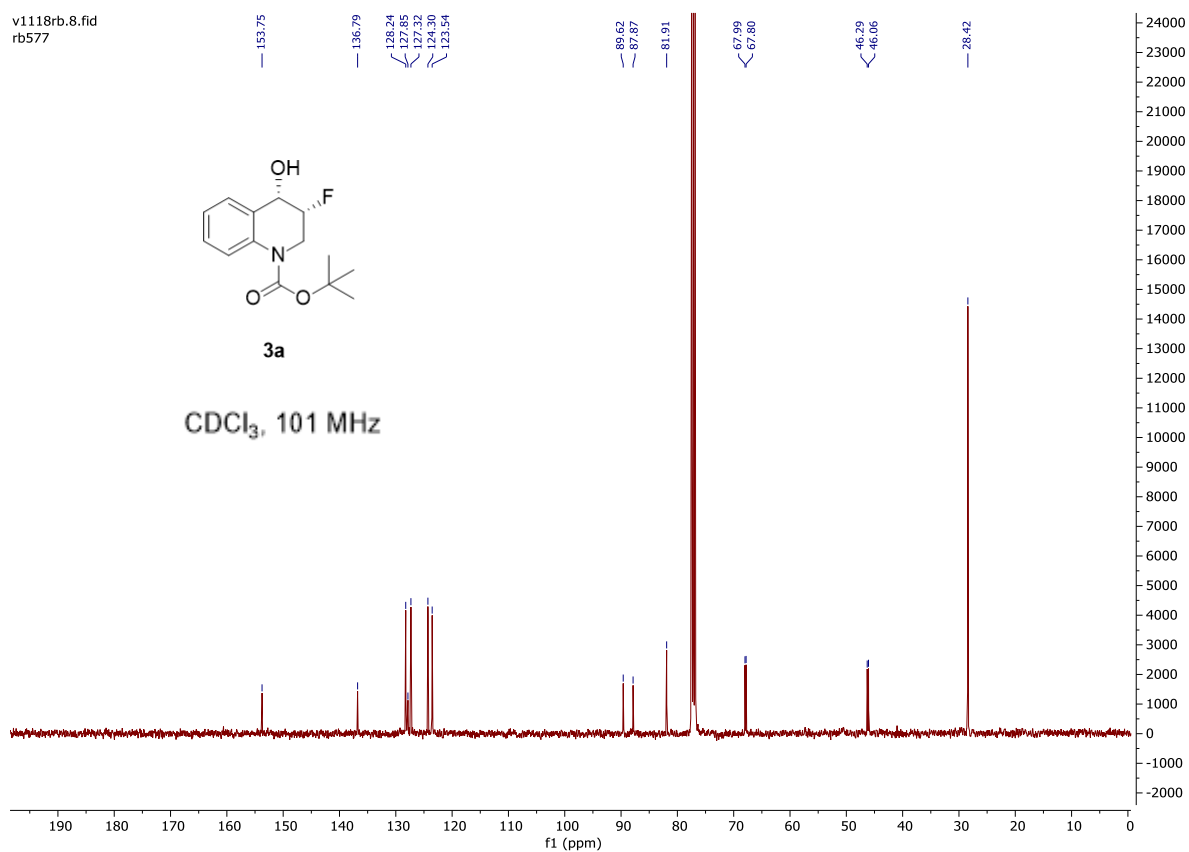


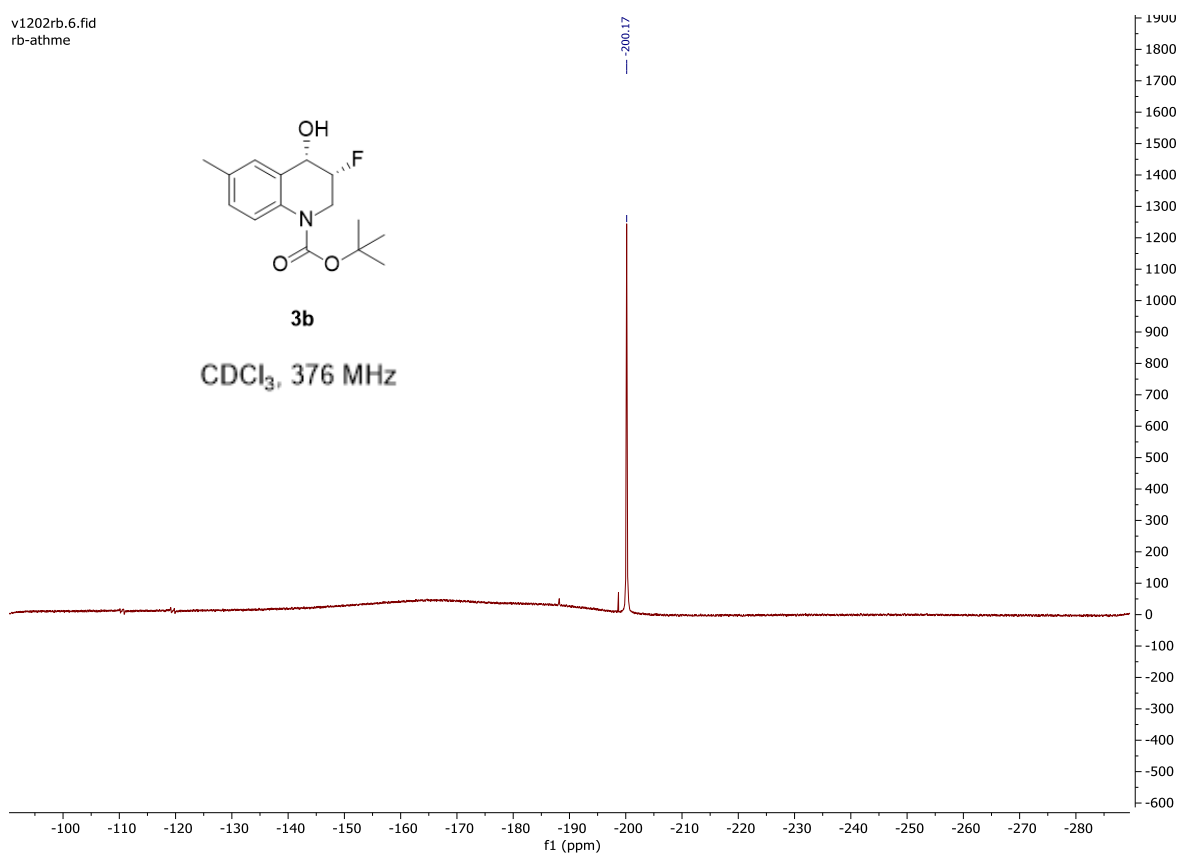
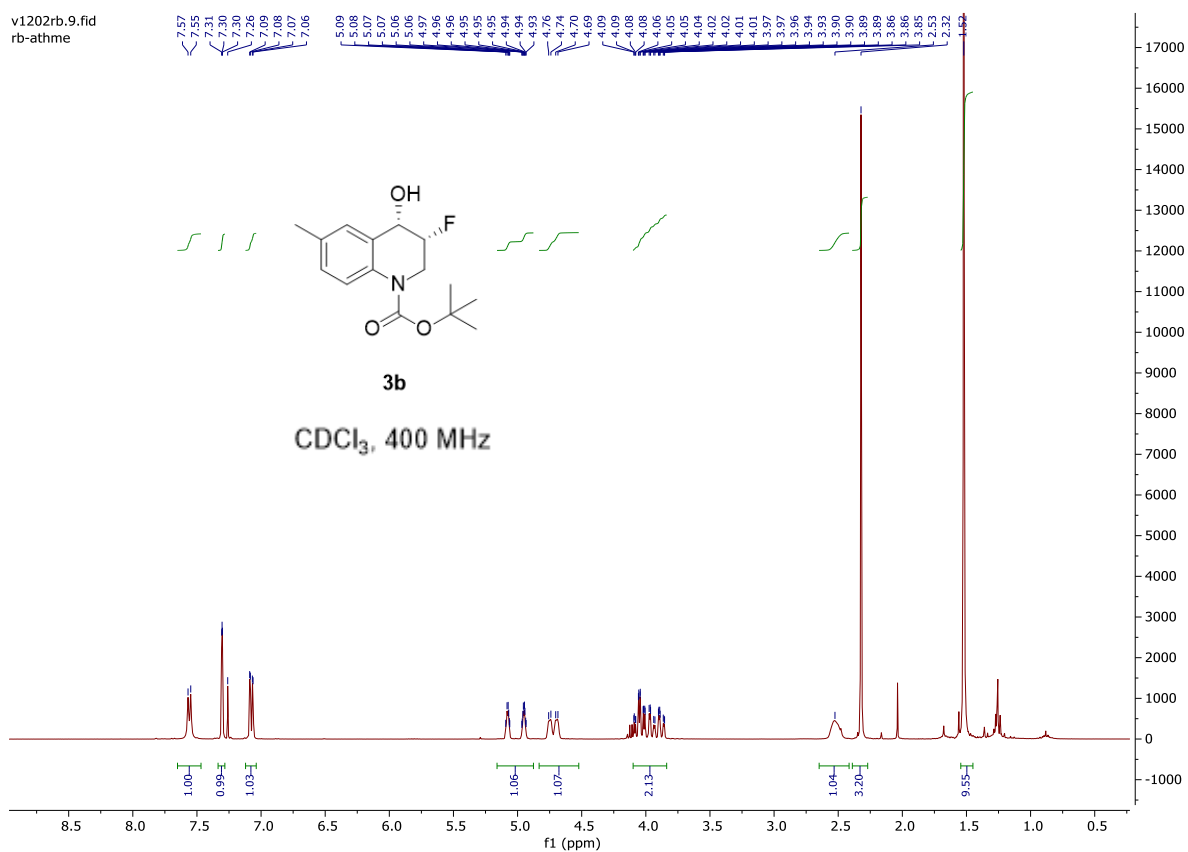






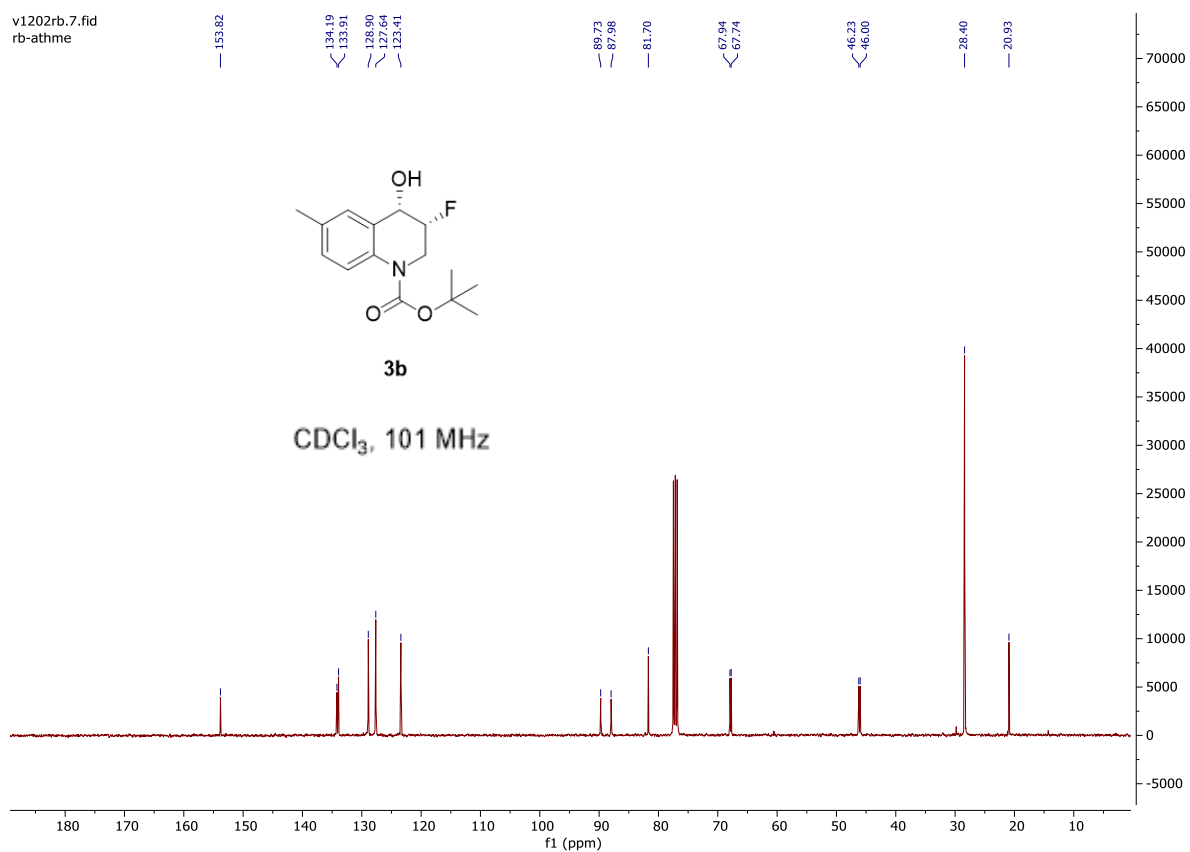
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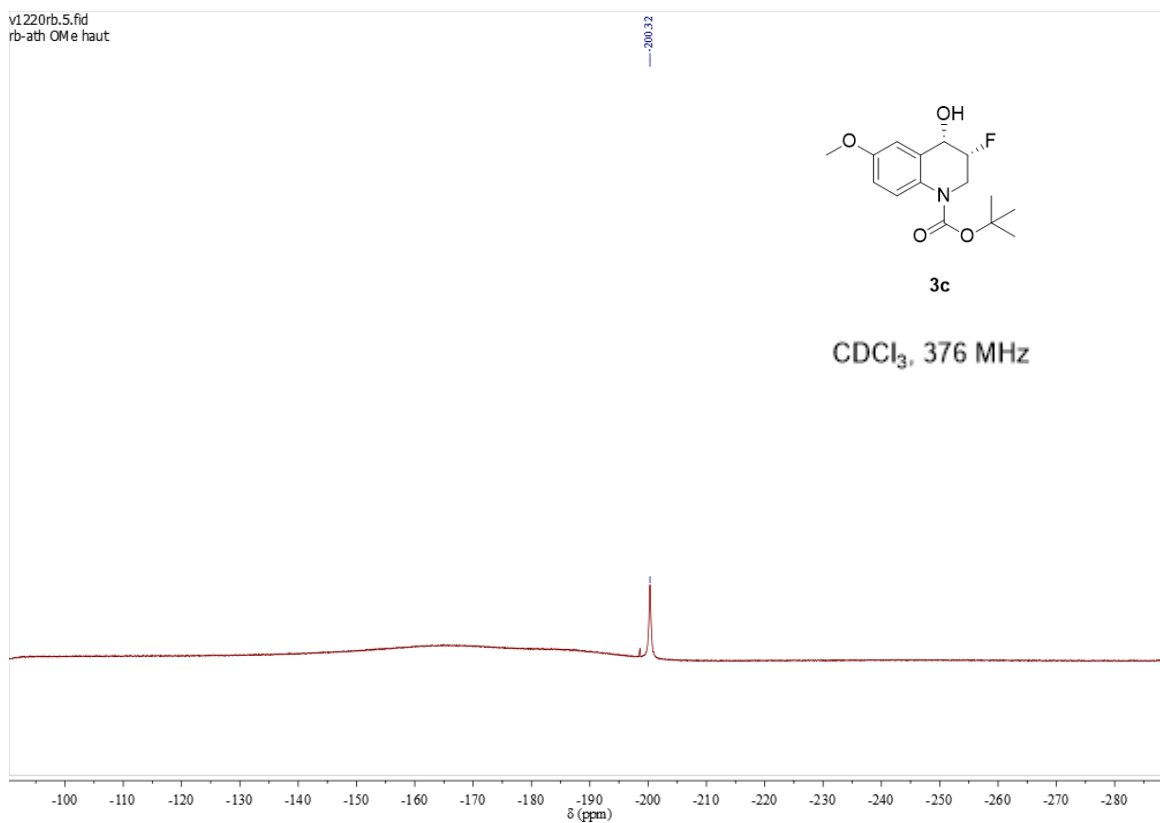
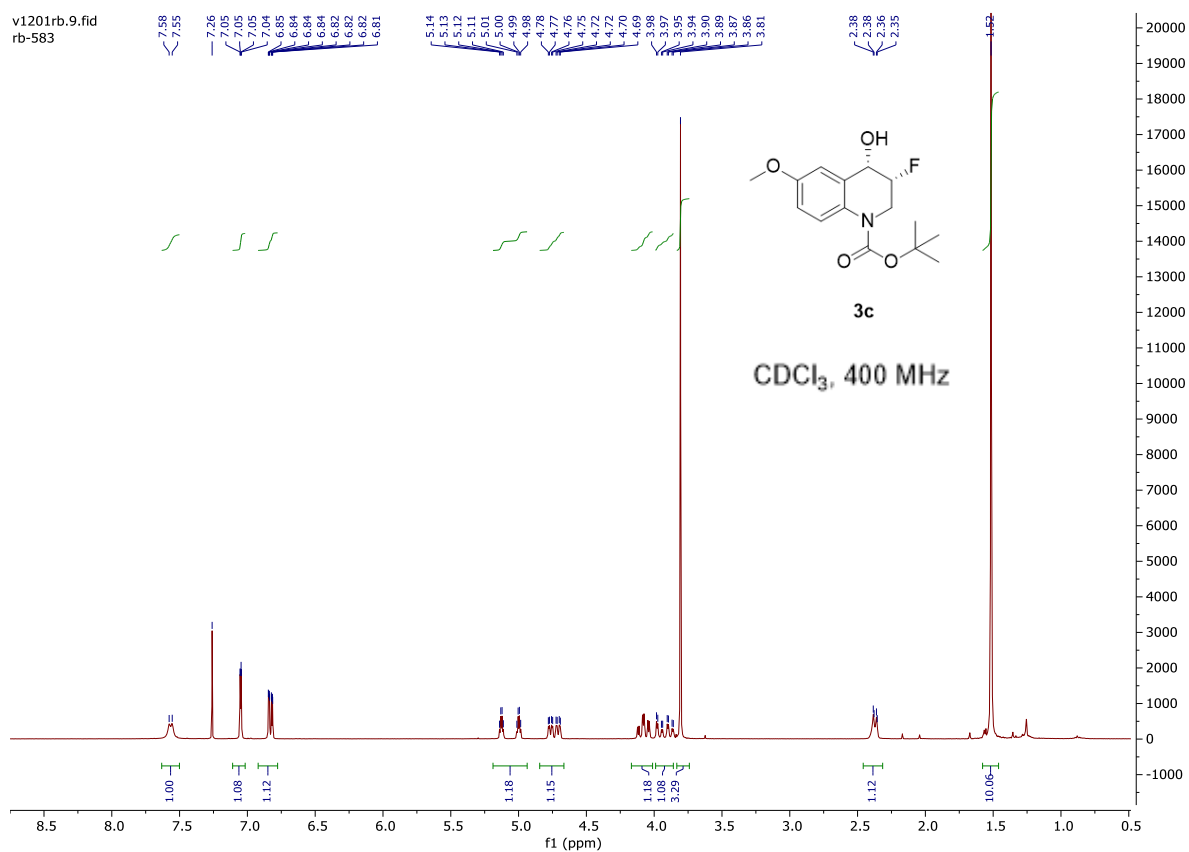




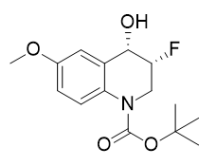


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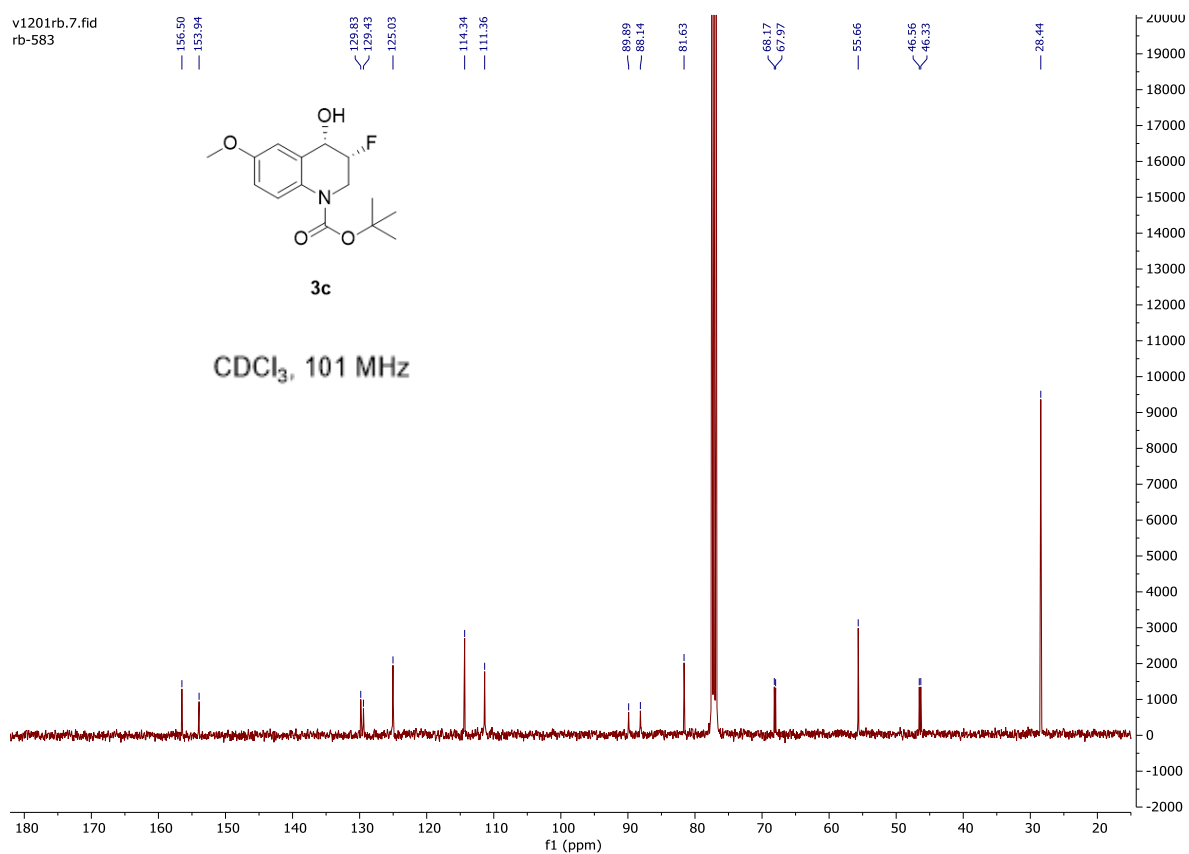


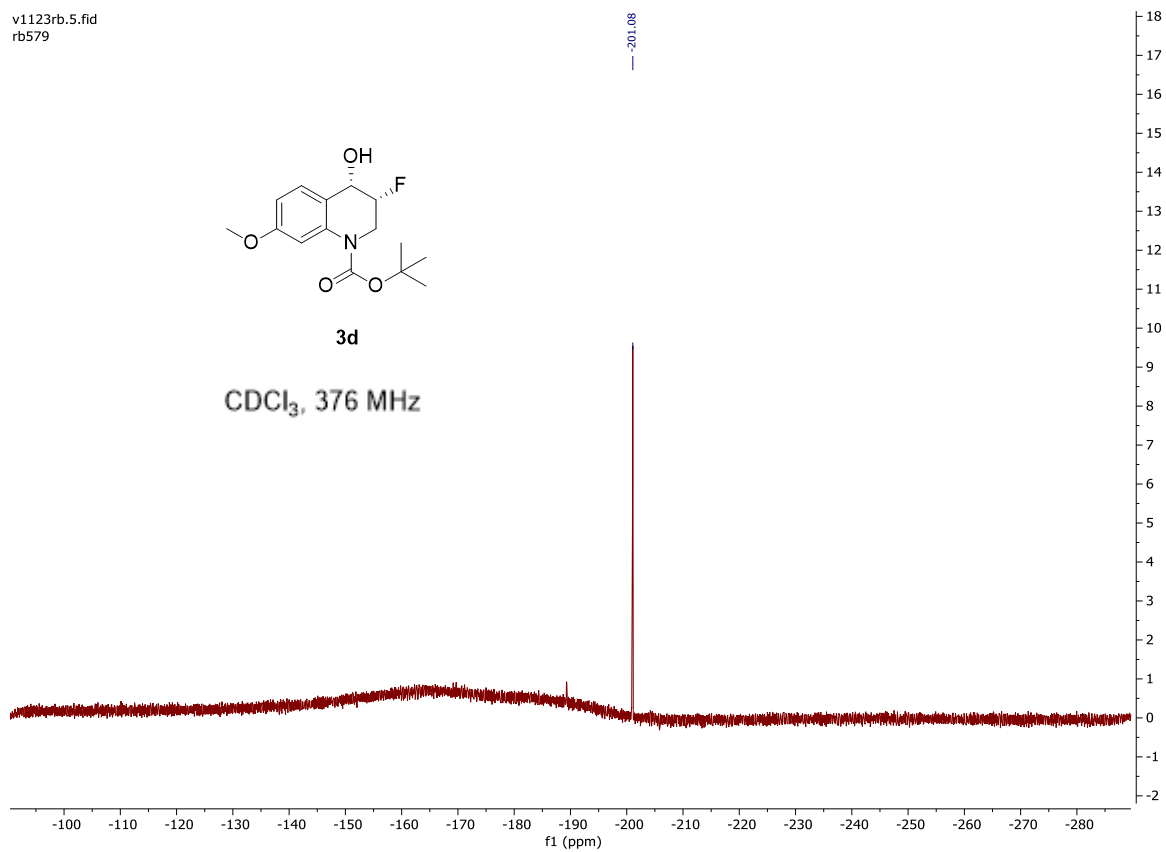
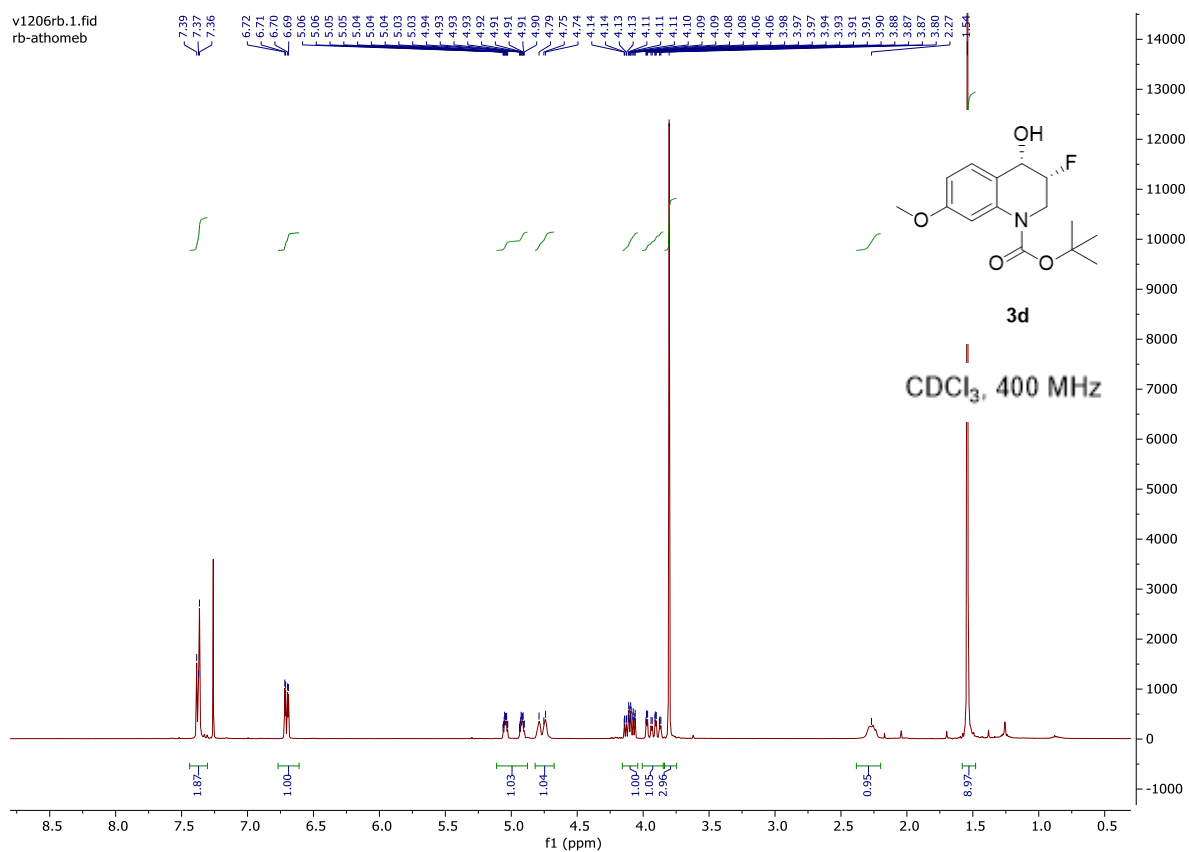
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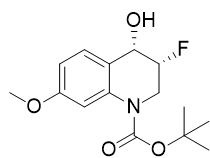
3c

CDCl<sub>3</sub>, 101 MHz



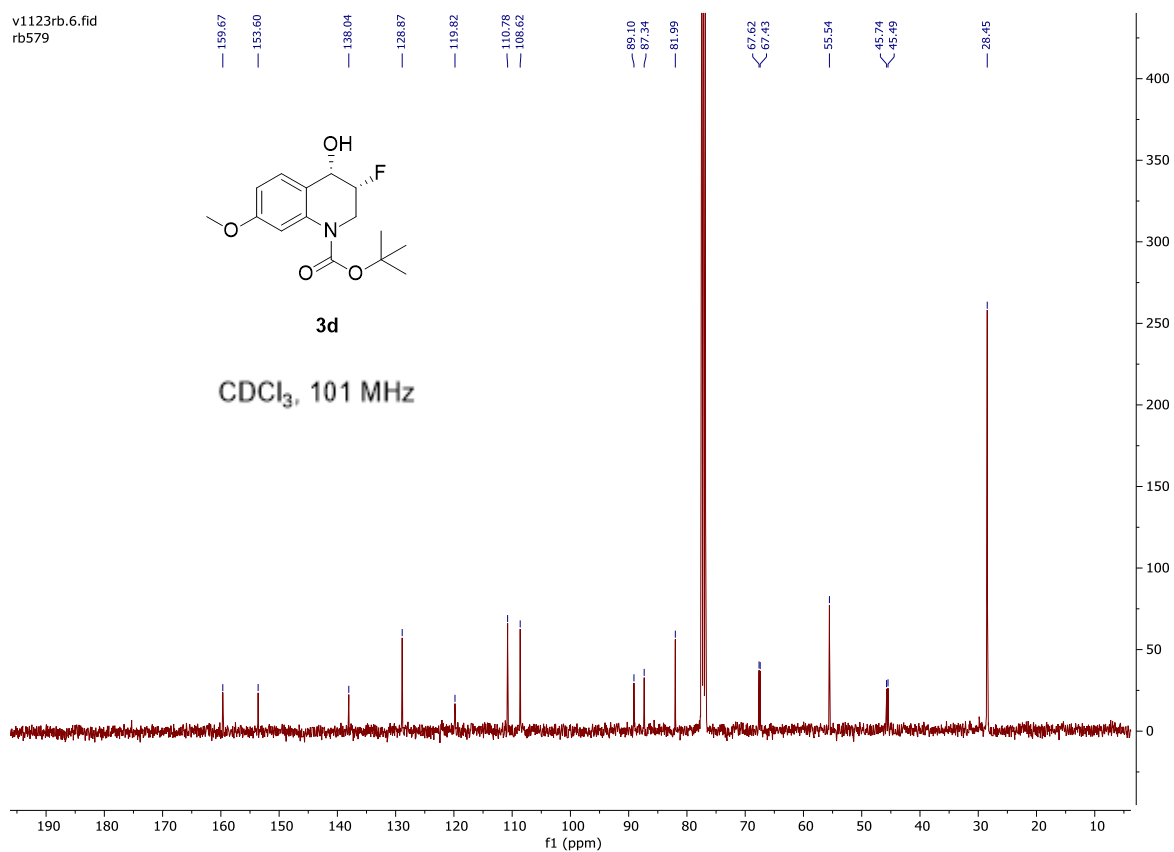


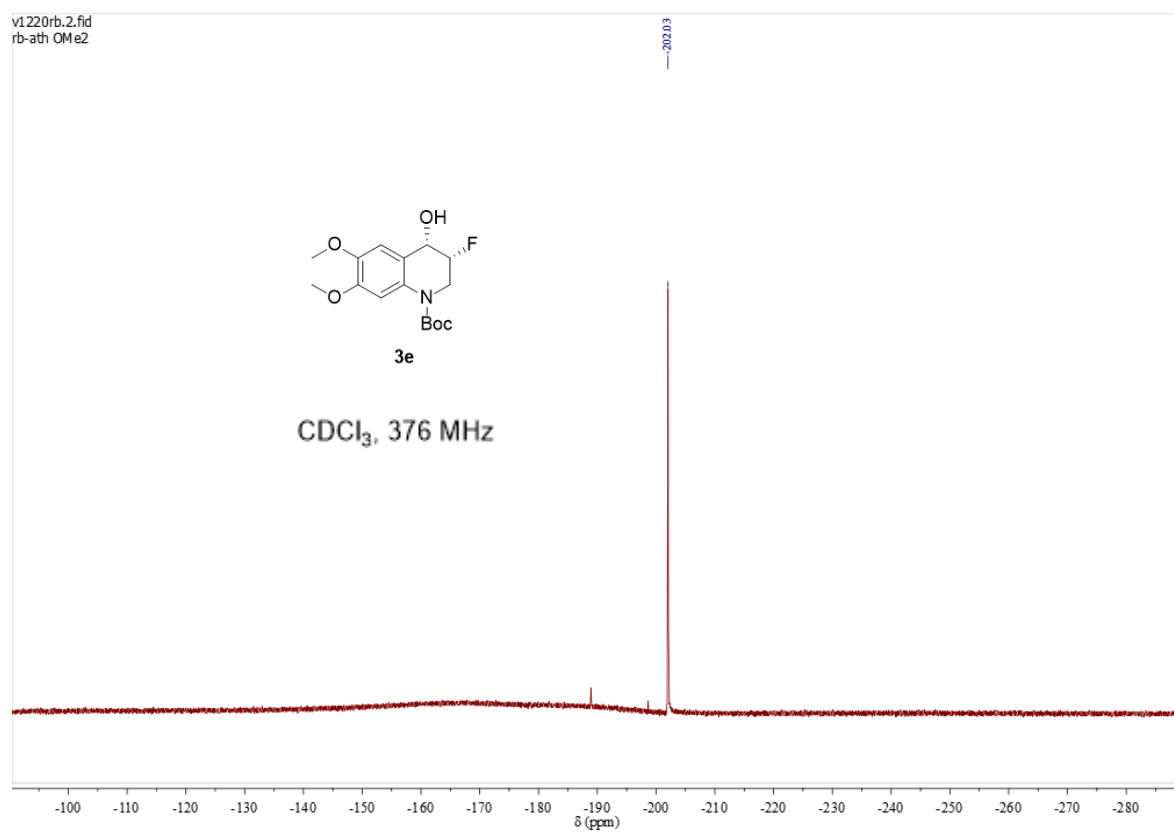
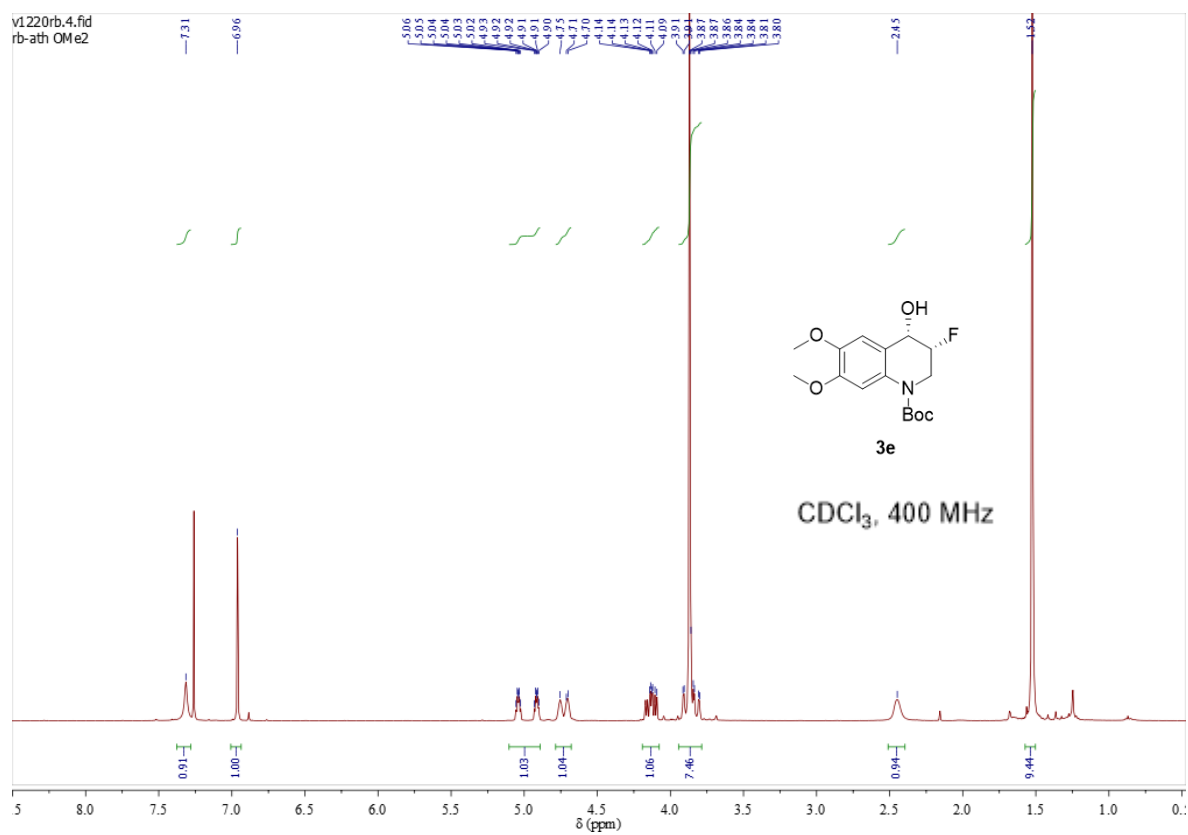
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**3d**

CDCl<sub>3</sub>, 101 MHz





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— 153.80  
— 146.49  
— 146.15

— 130.40

— 119.59

— 109.97  
— 107.48

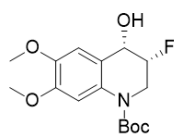
— 89.05  
— 87.30  
— 81.72

— 67.67  
— 67.47

— 56.19  
— 56.09

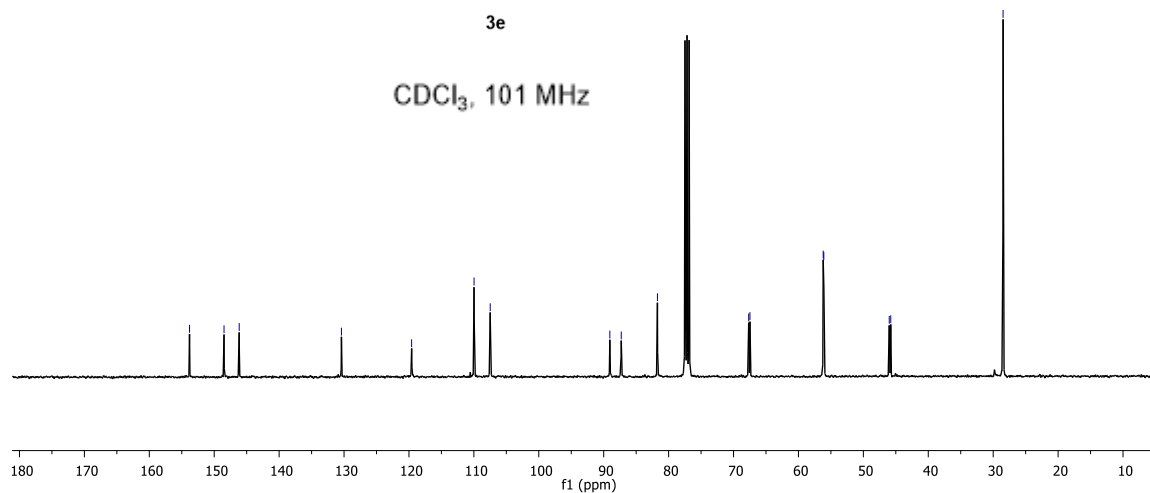
— 46.01  
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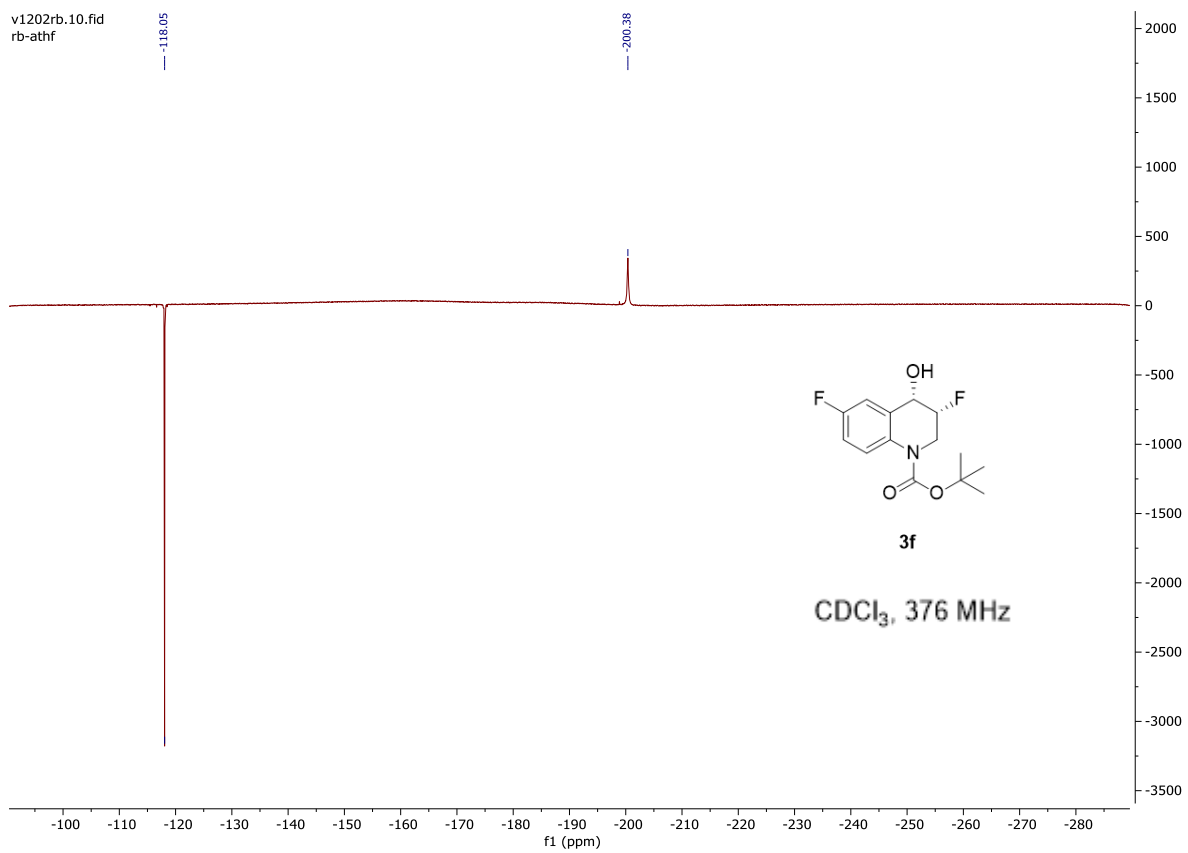
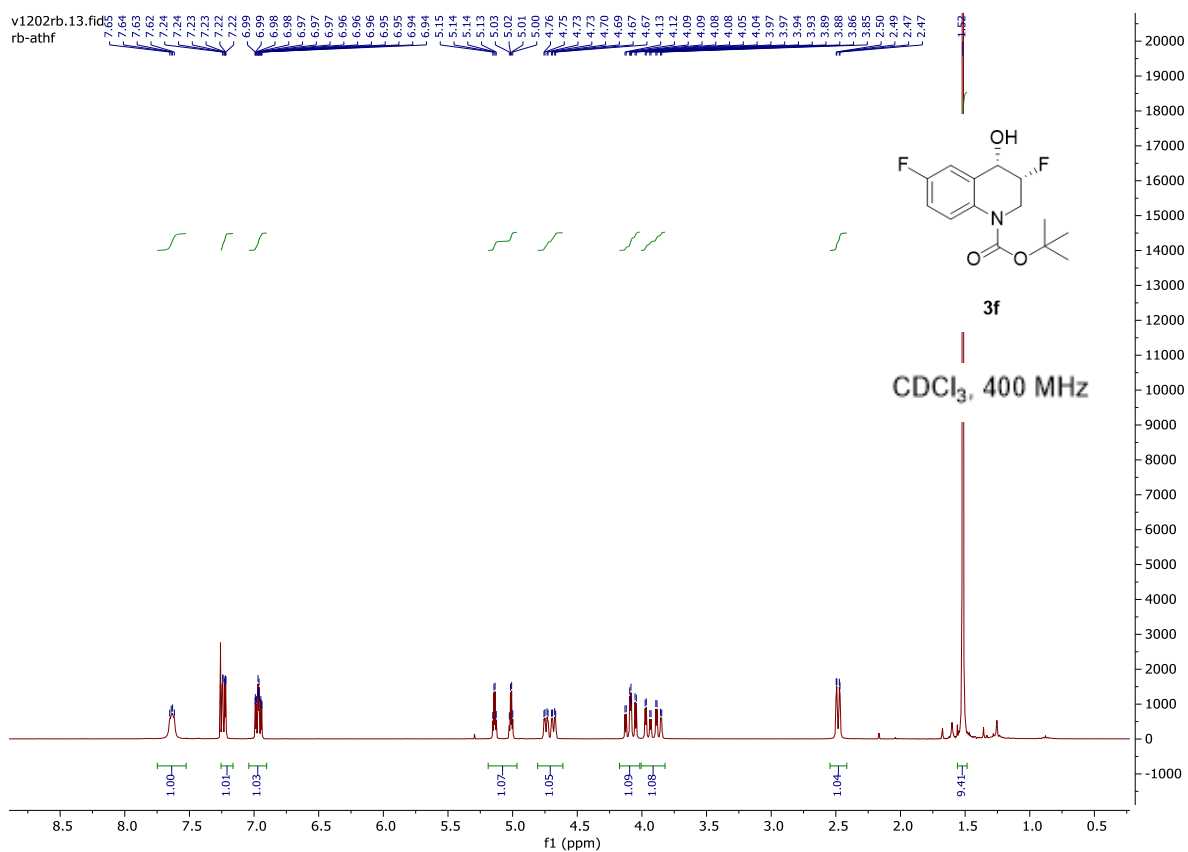
— 28.48



**3e**

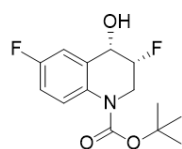
CDCl<sub>3</sub>, 101 MHz





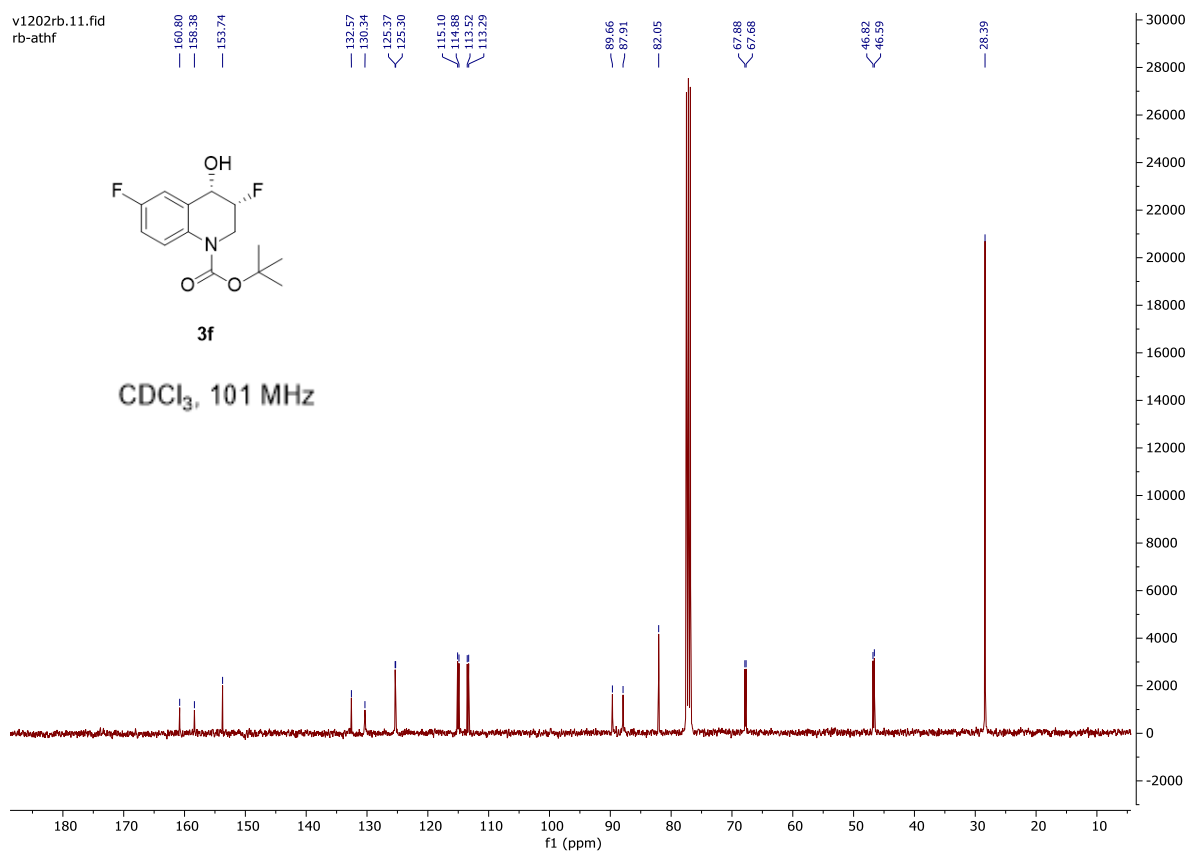


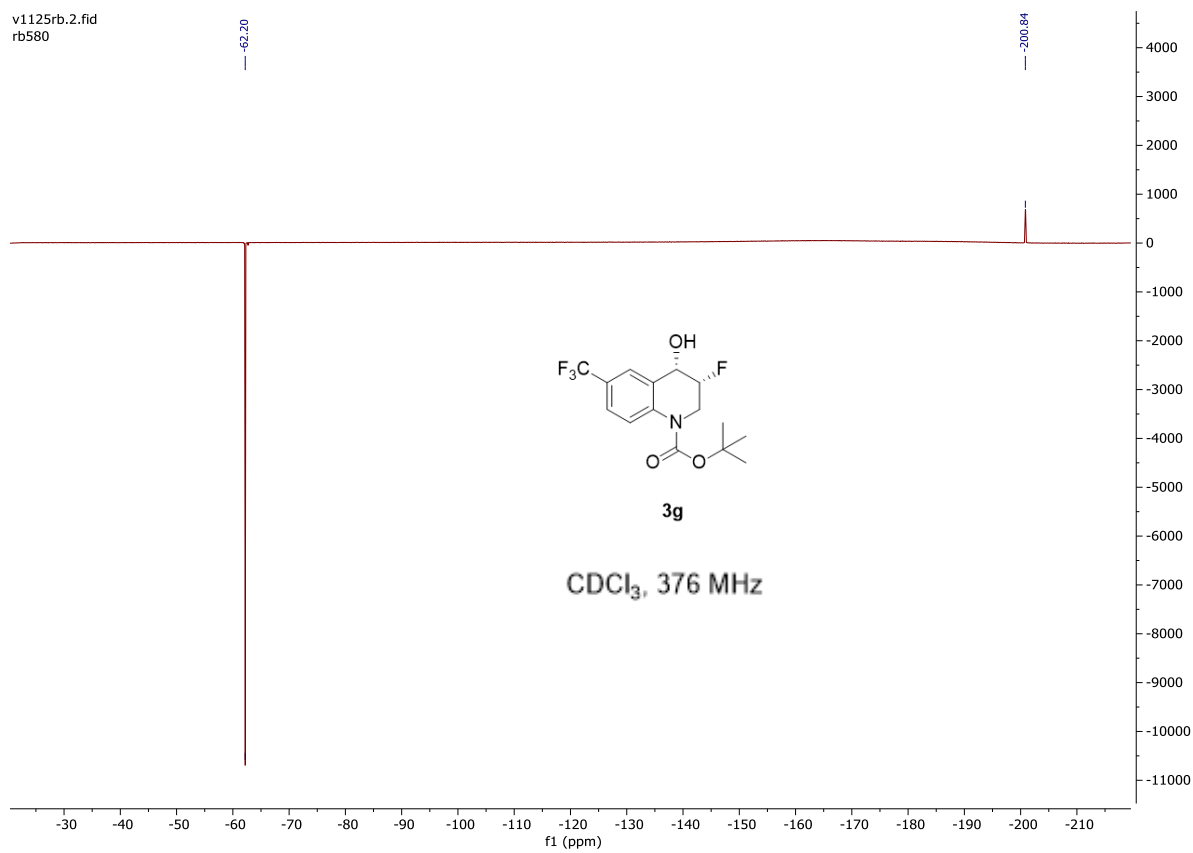
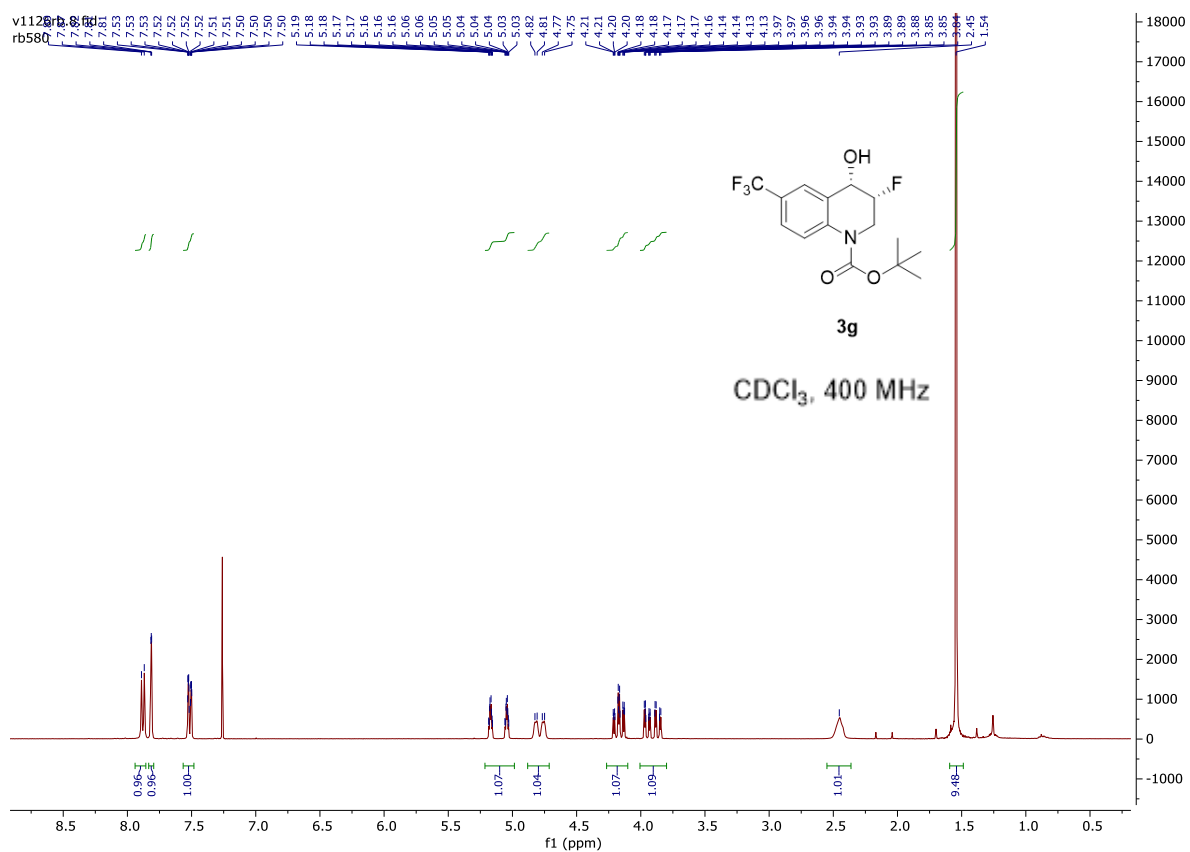
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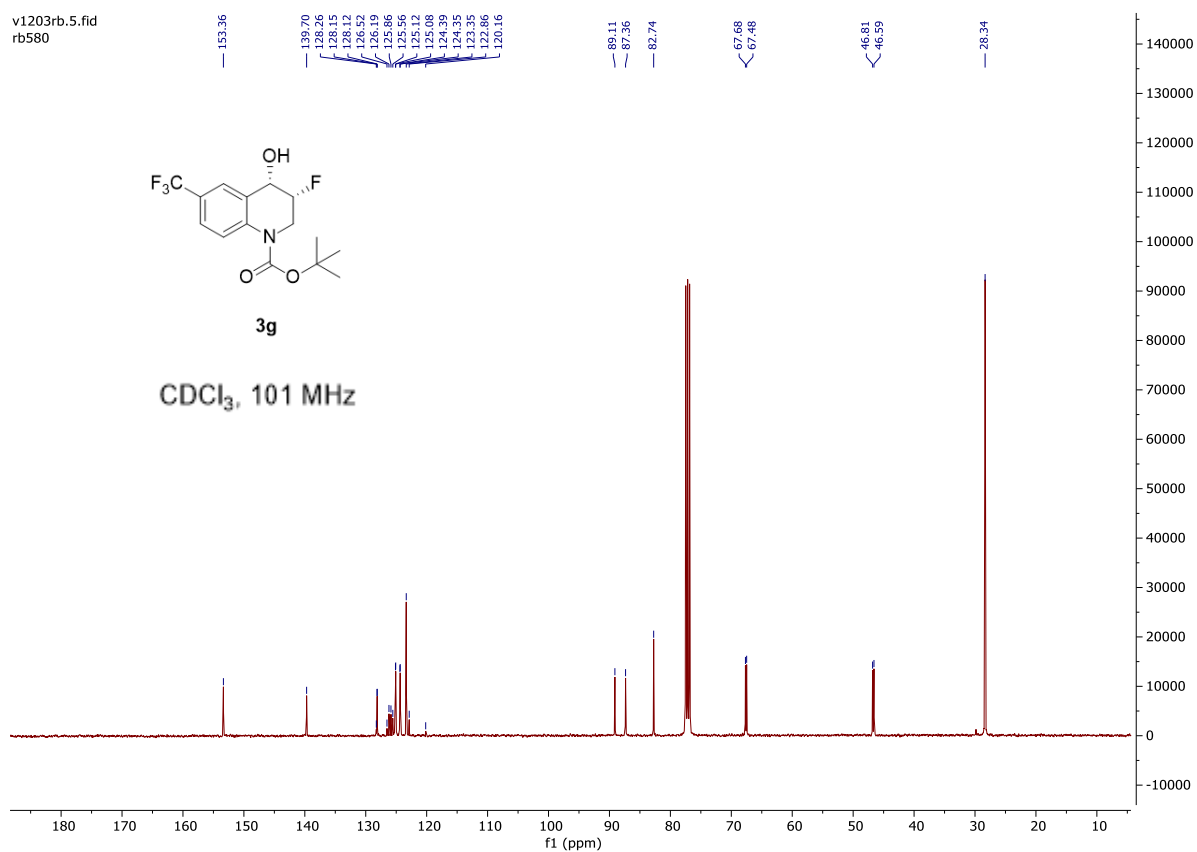
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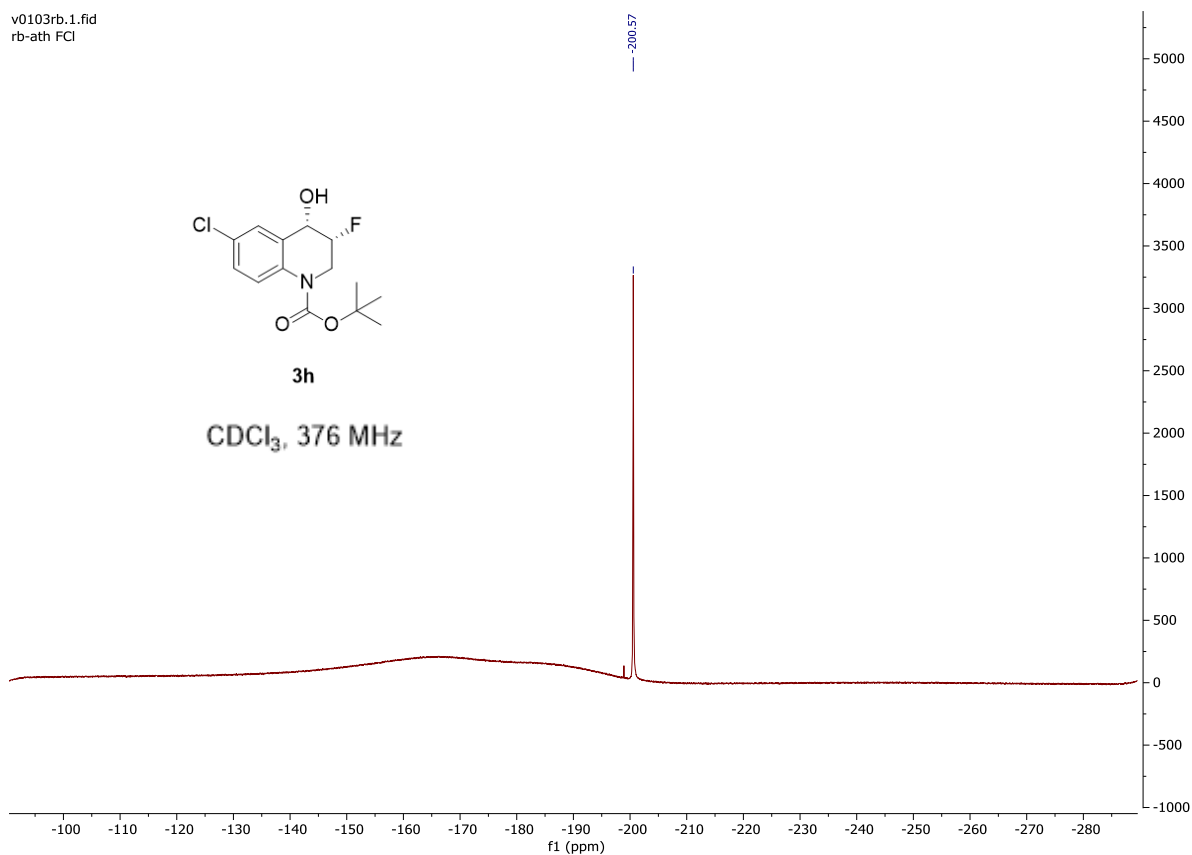
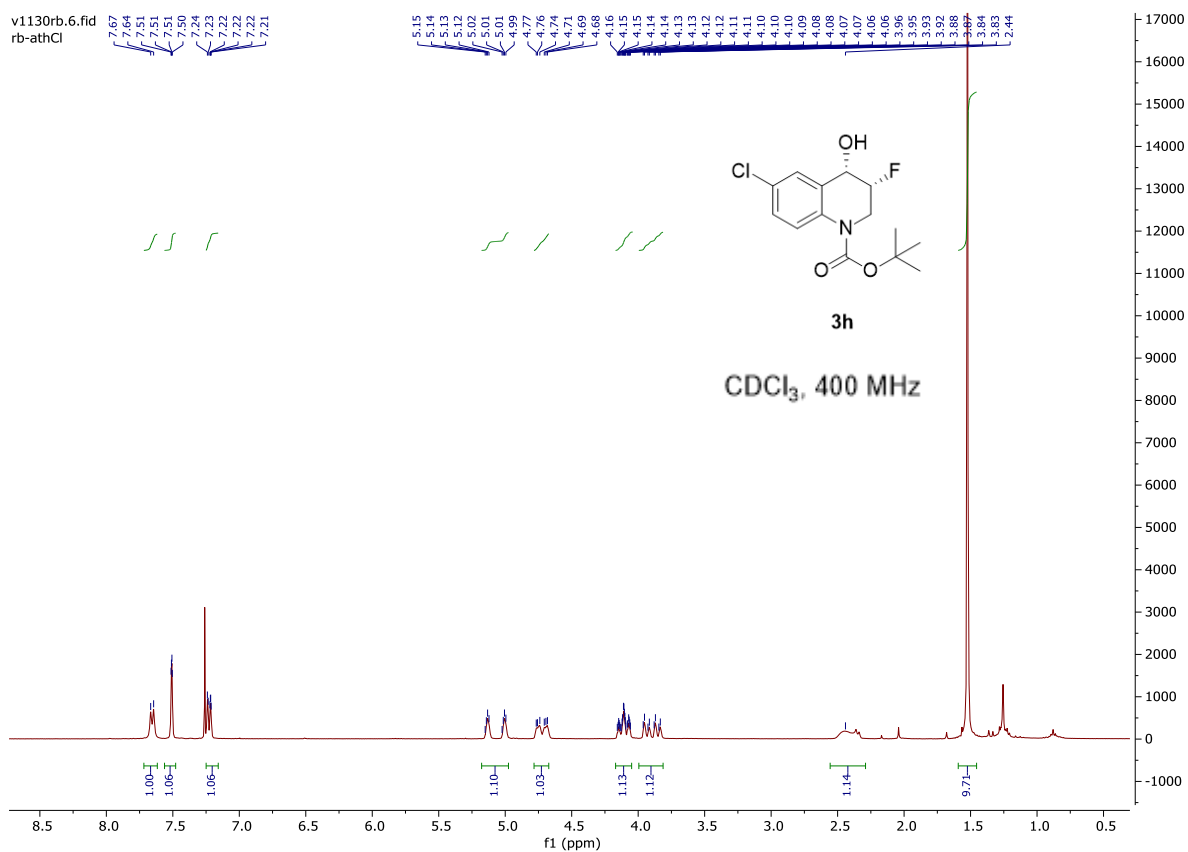
CDCl<sub>3</sub>, 101 MHz



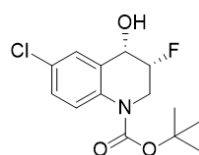


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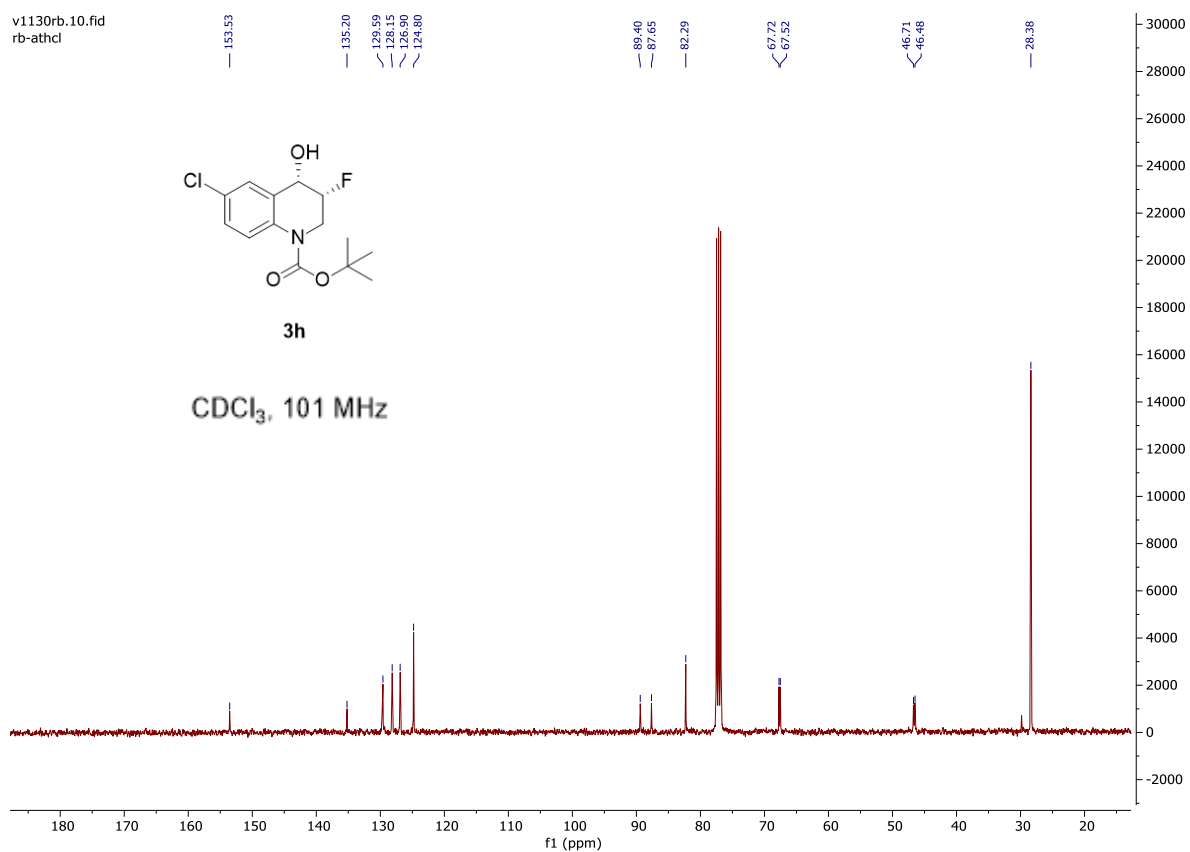


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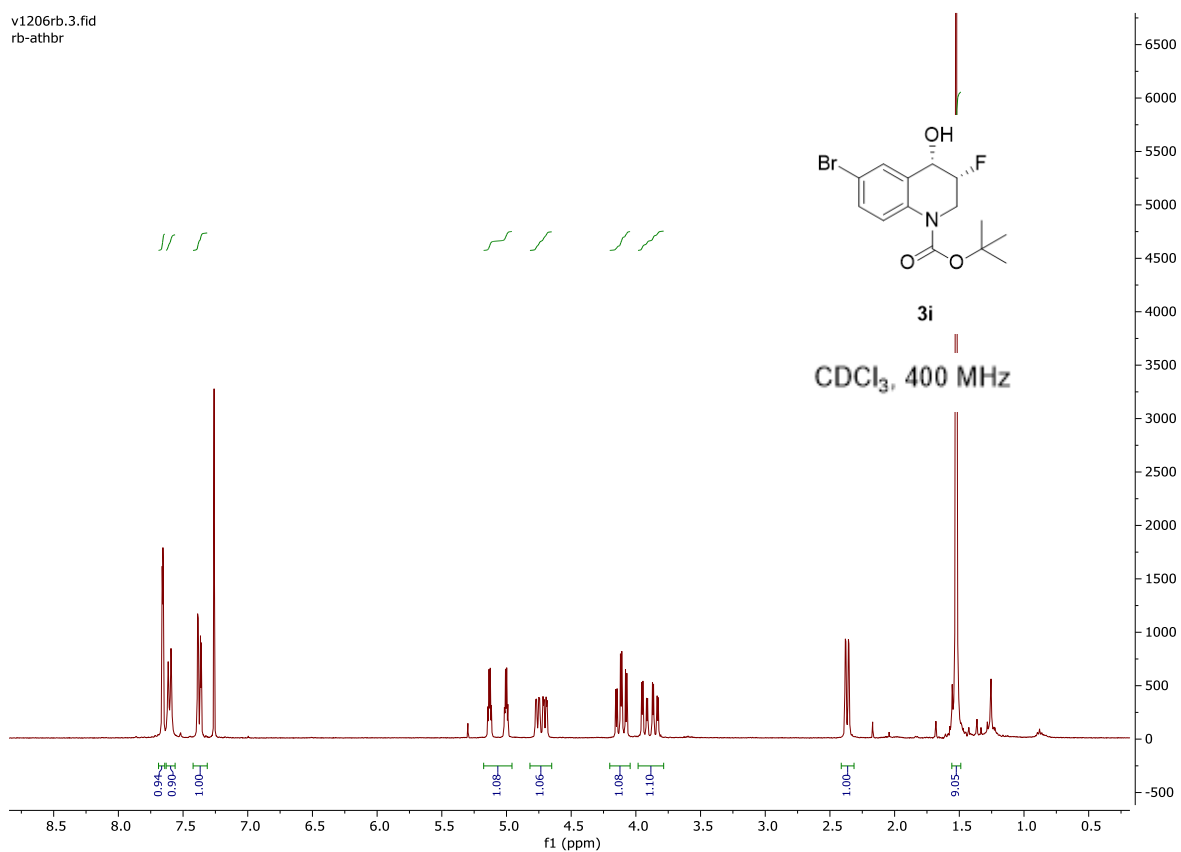


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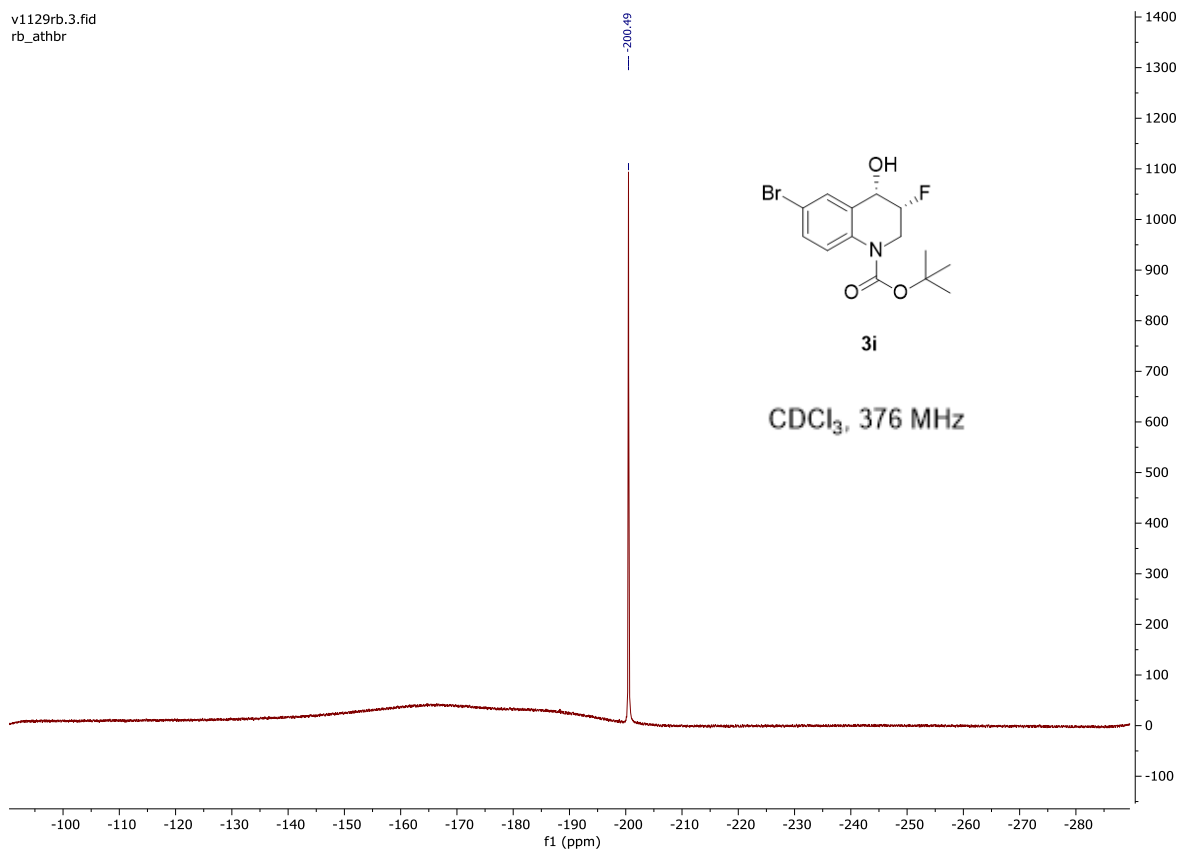
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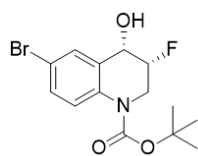
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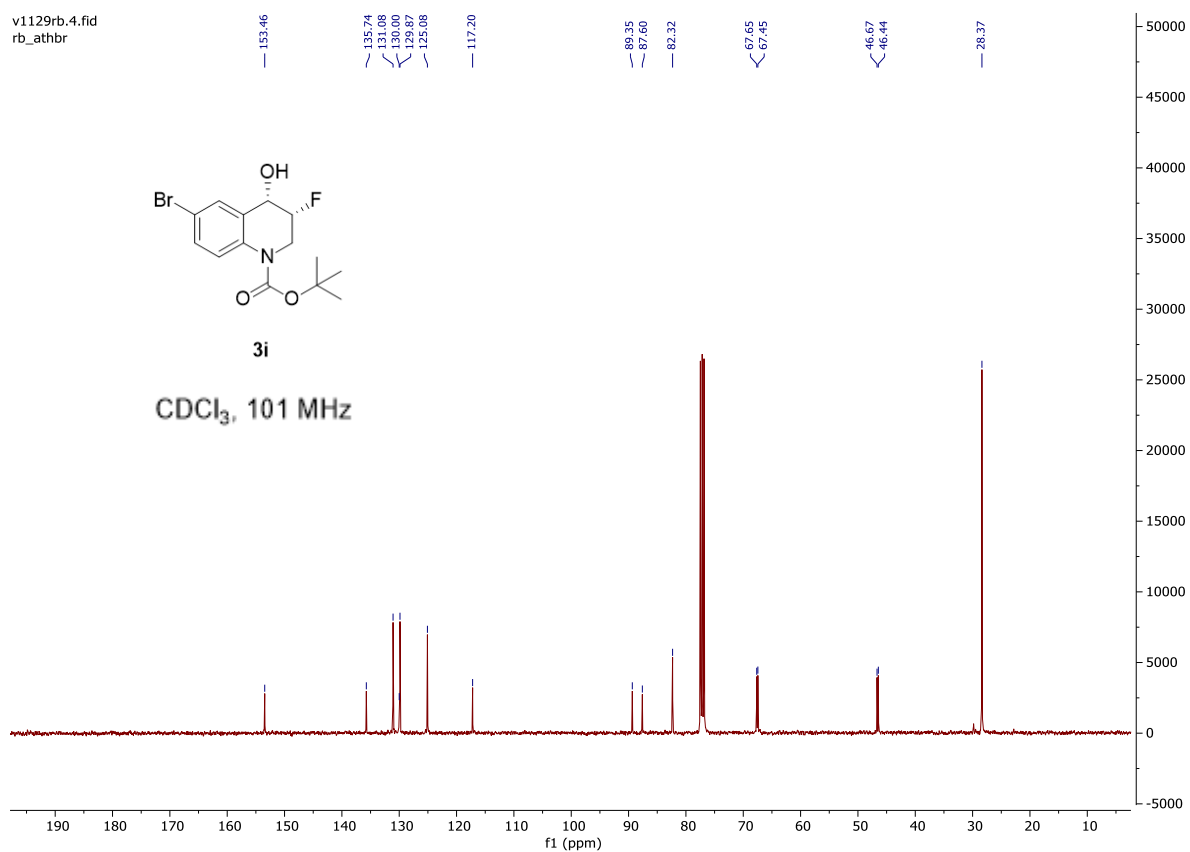


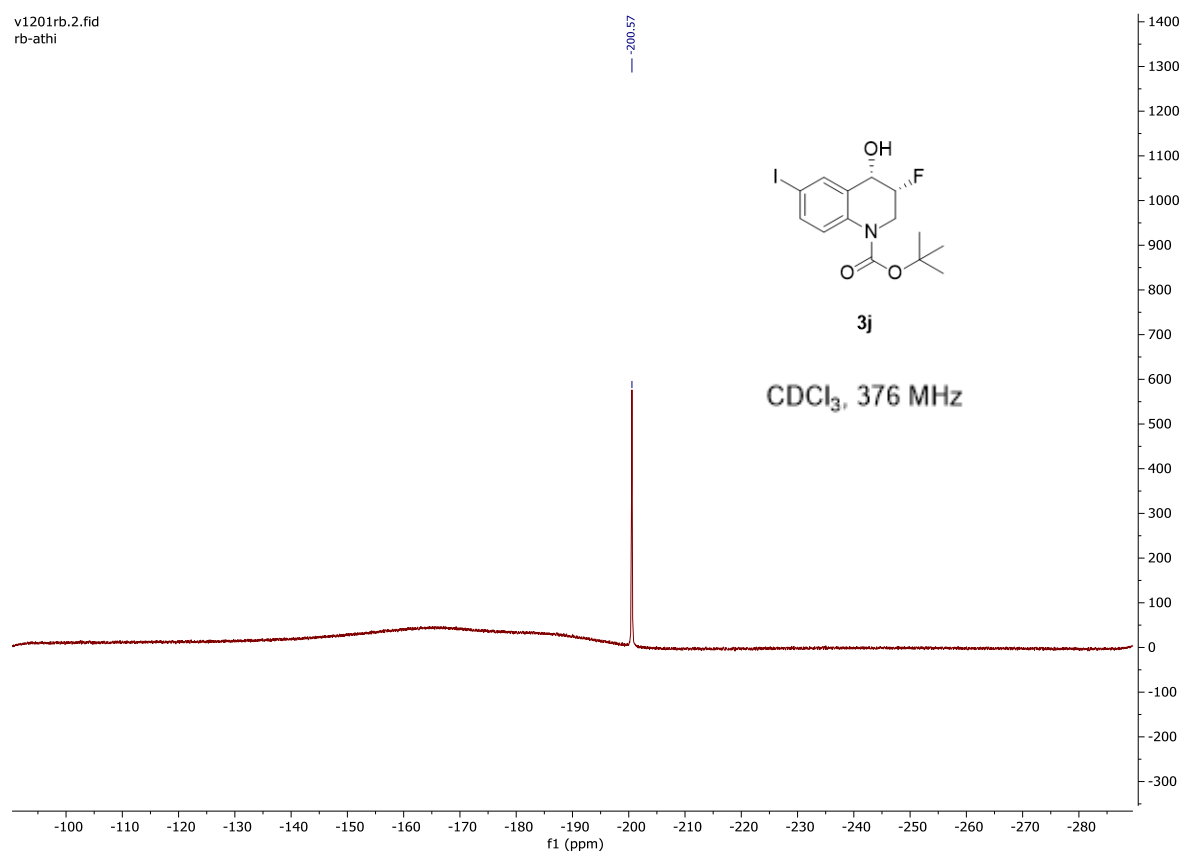
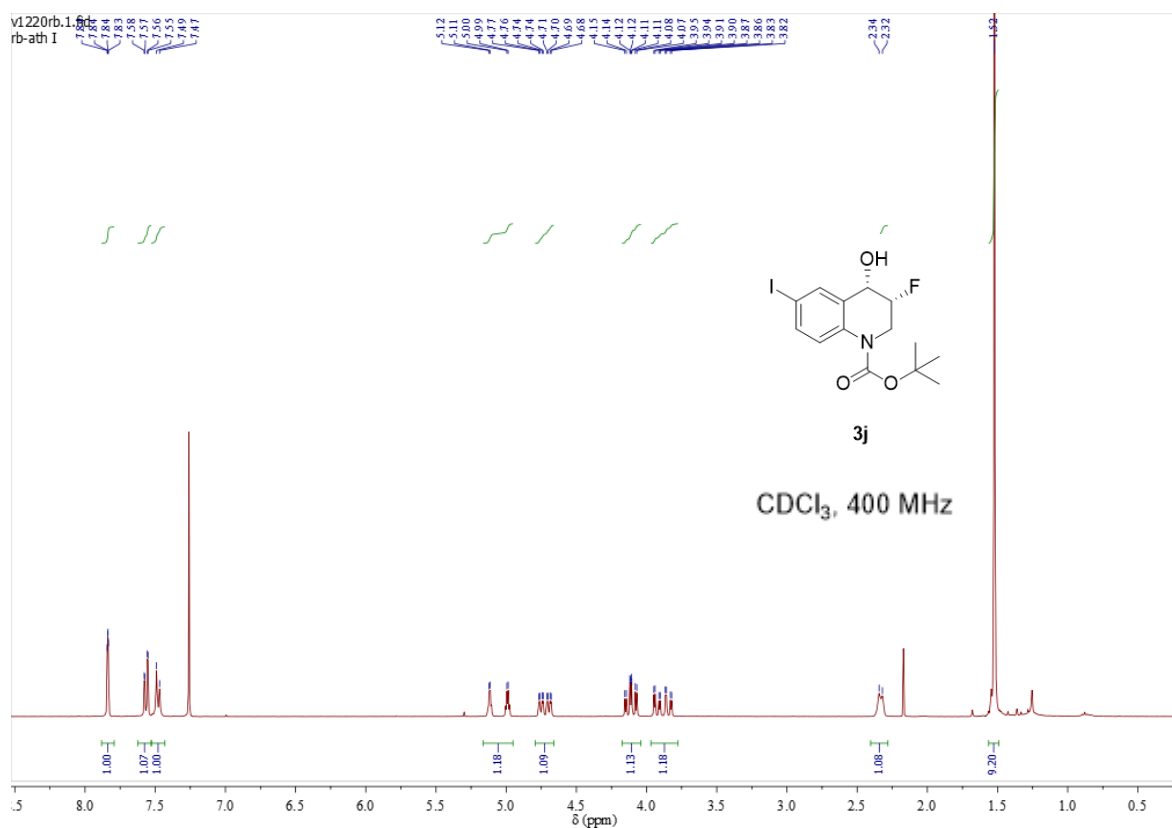
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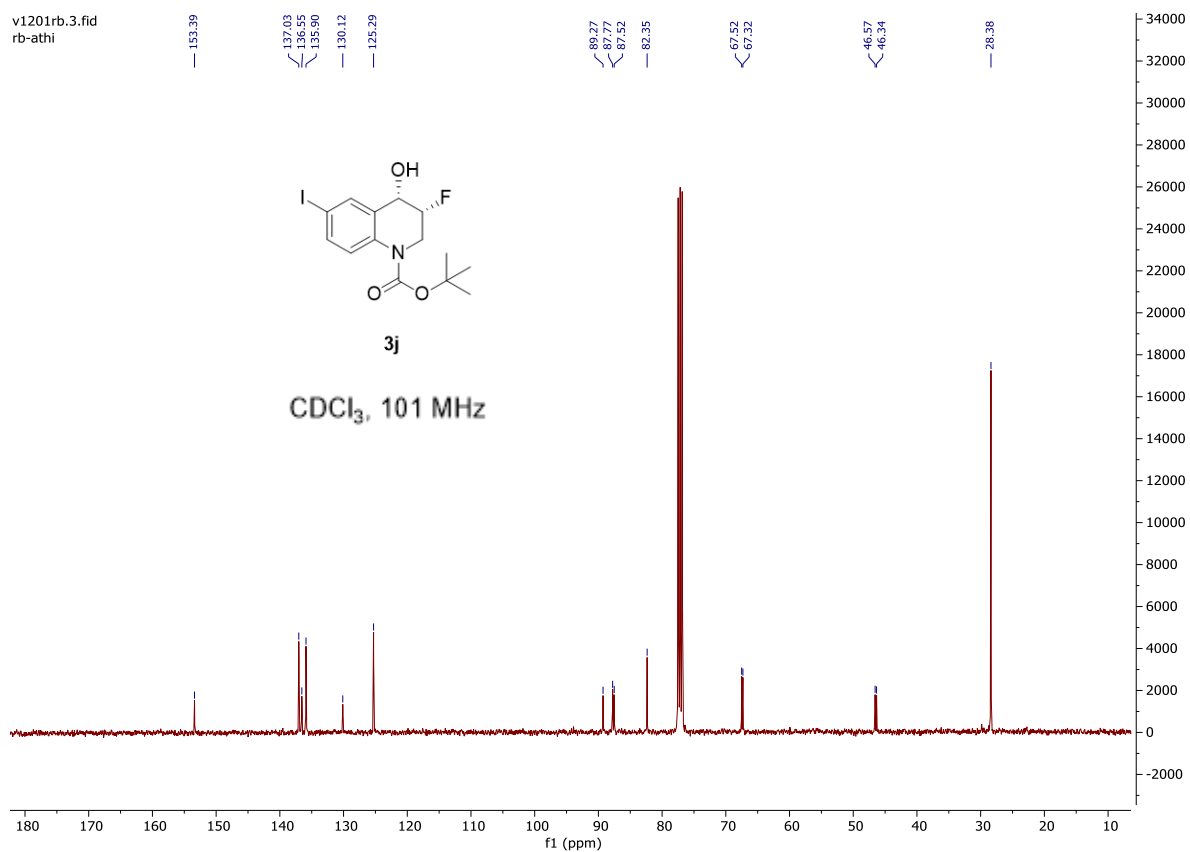
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CDCl<sub>3</sub>, 101 MHz



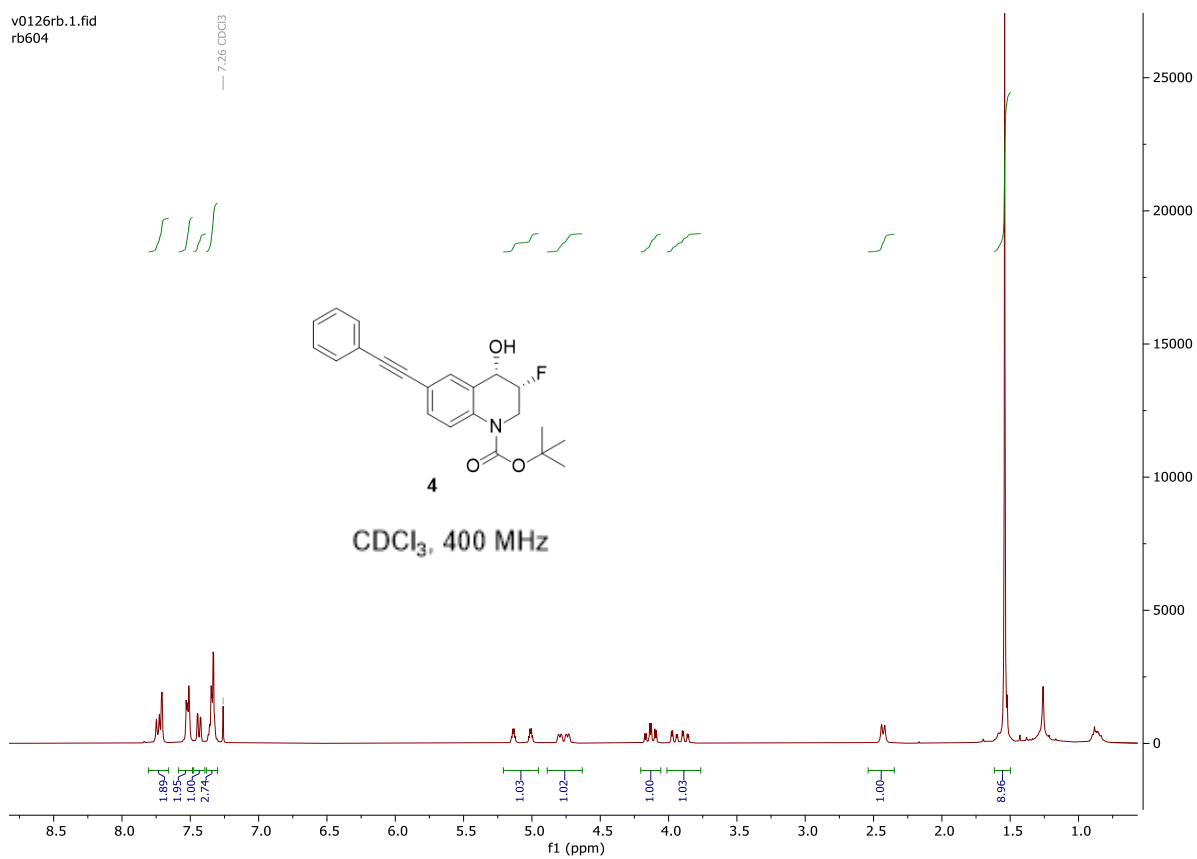






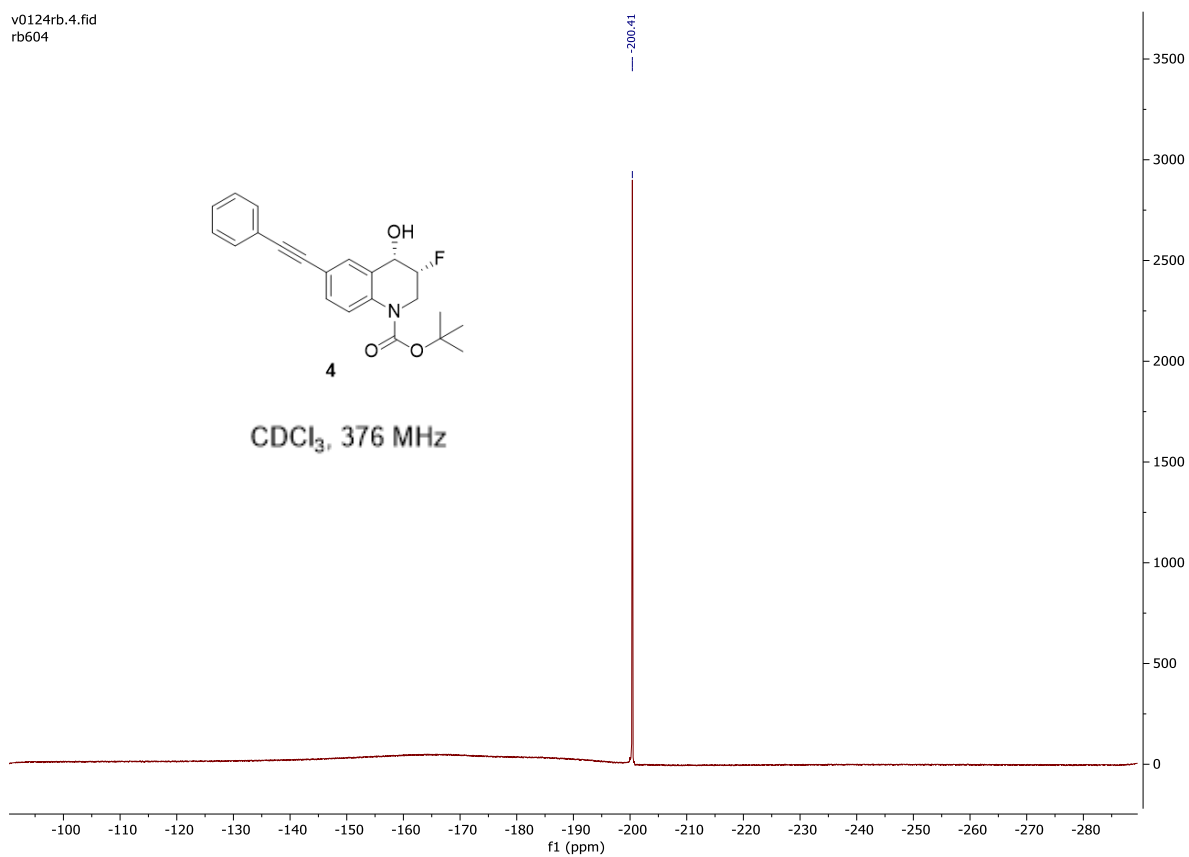
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— 7.26 CDCl<sub>3</sub>

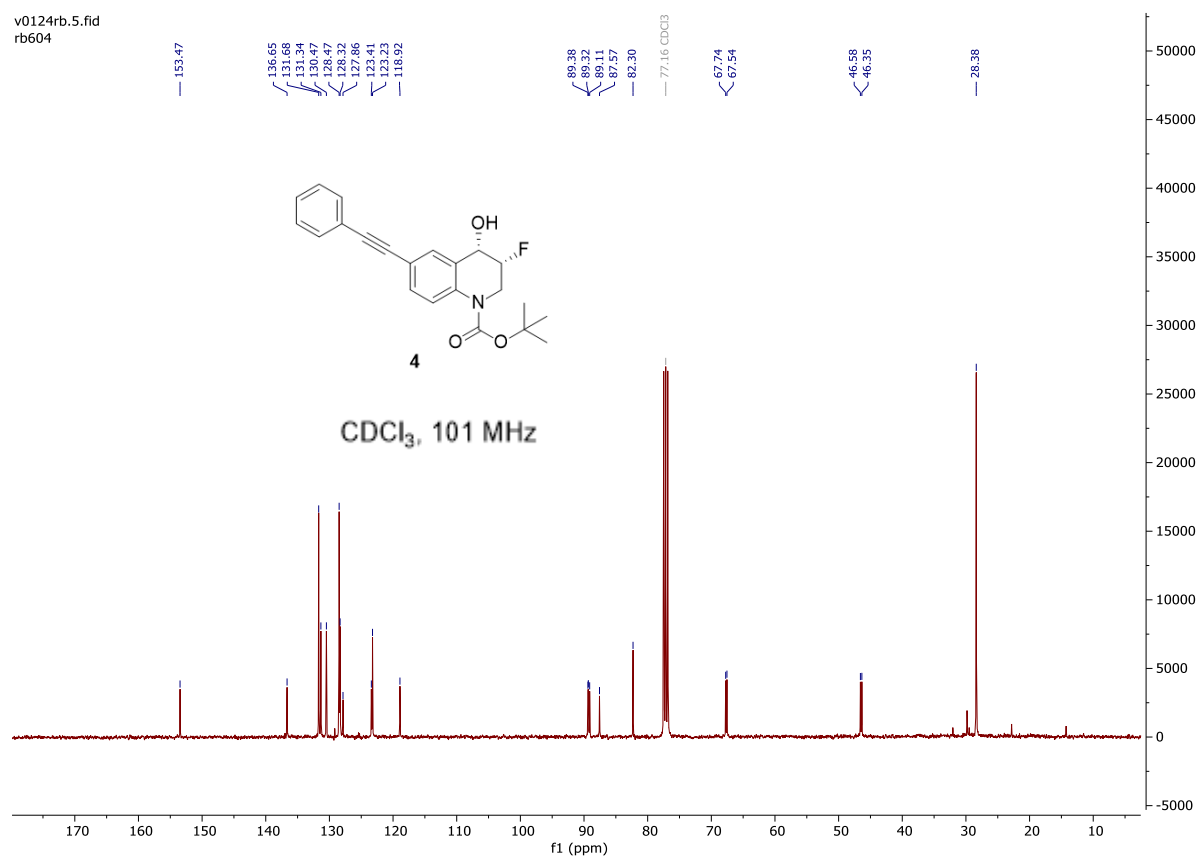


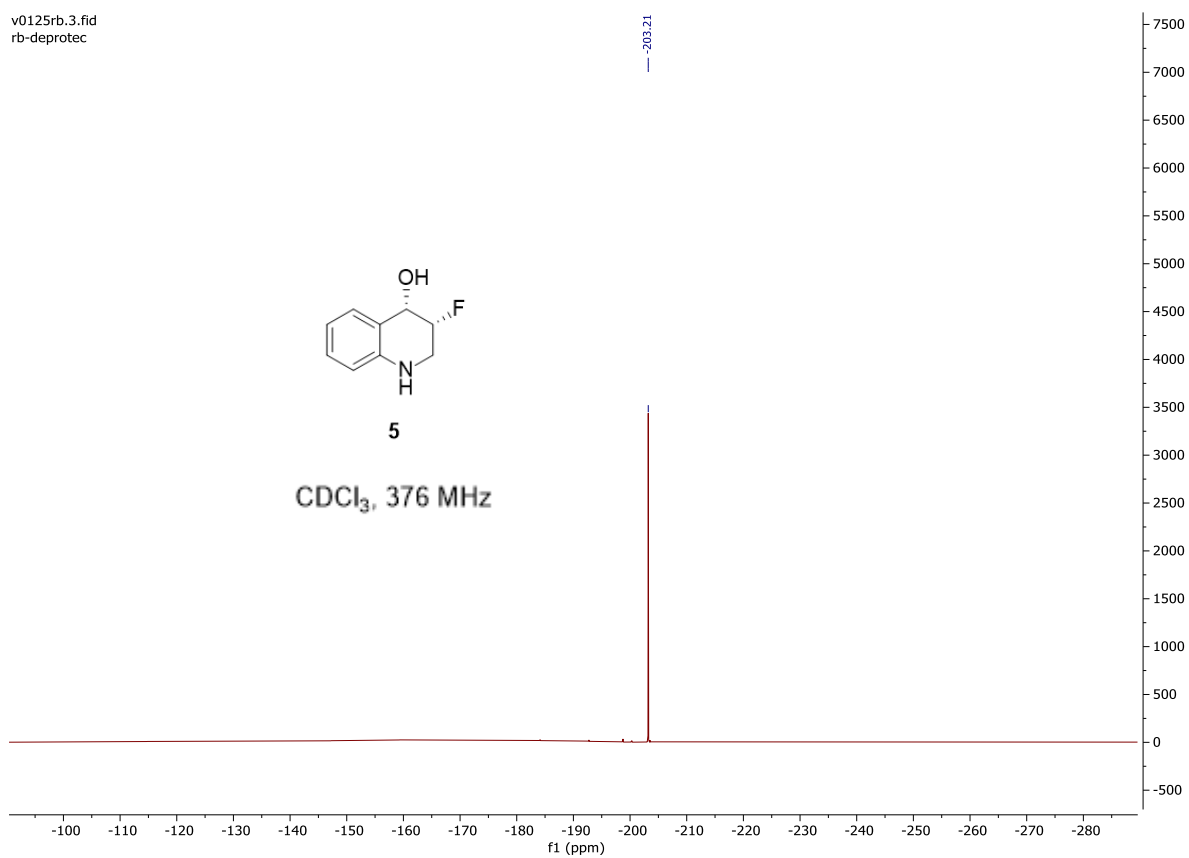
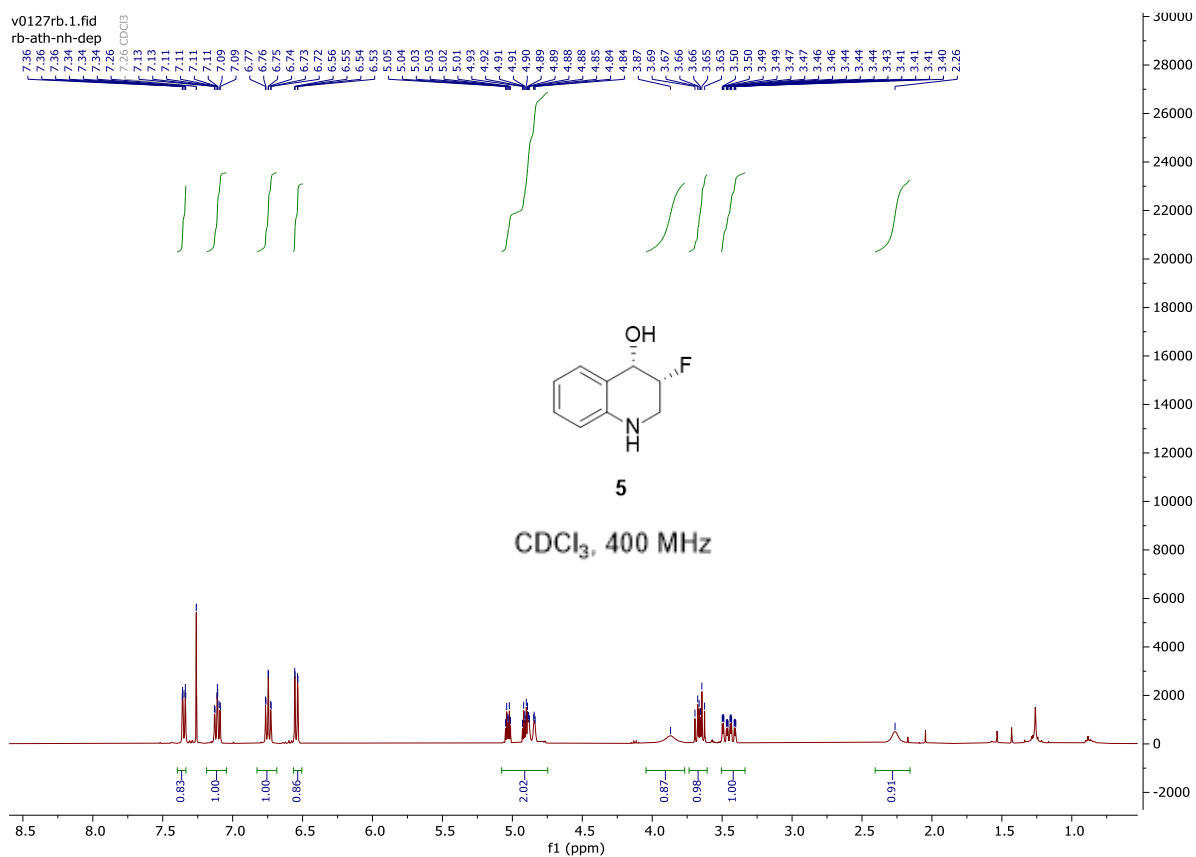
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— -200.41

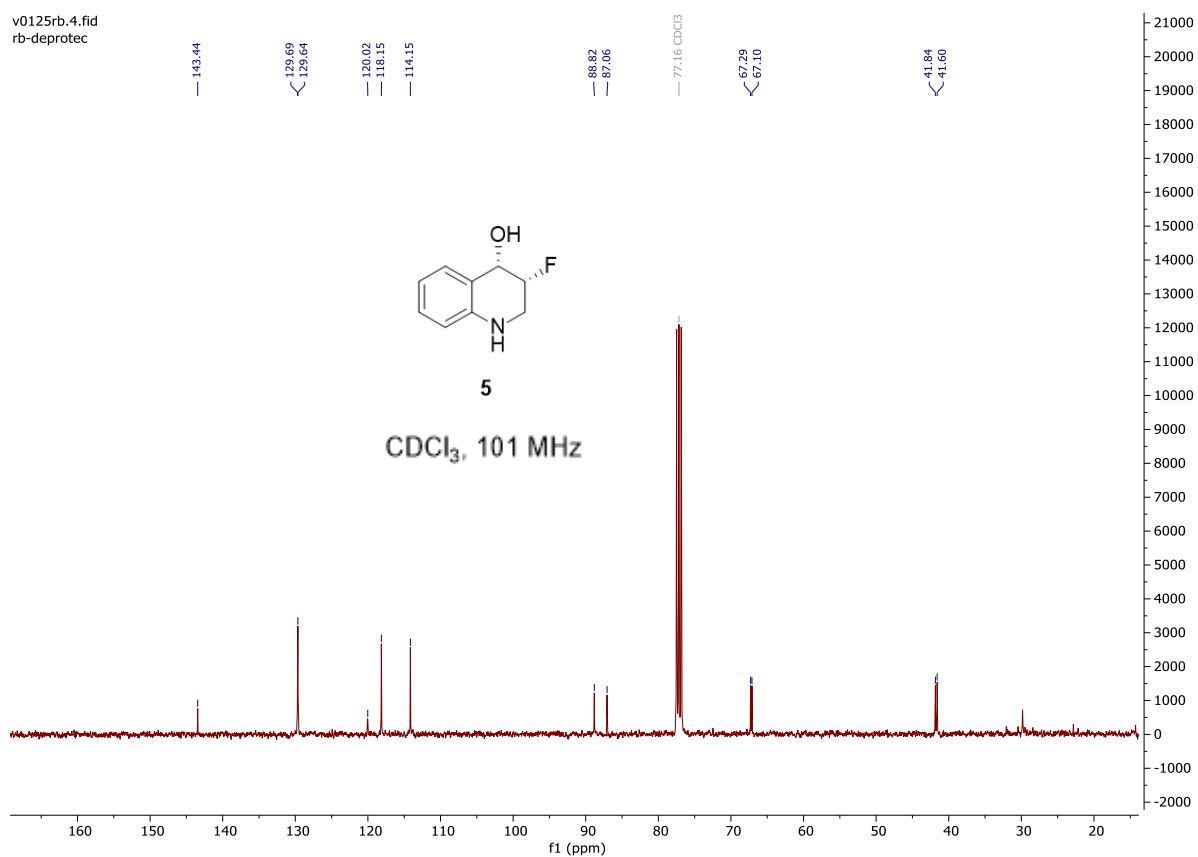


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### 3) SFC Spectra

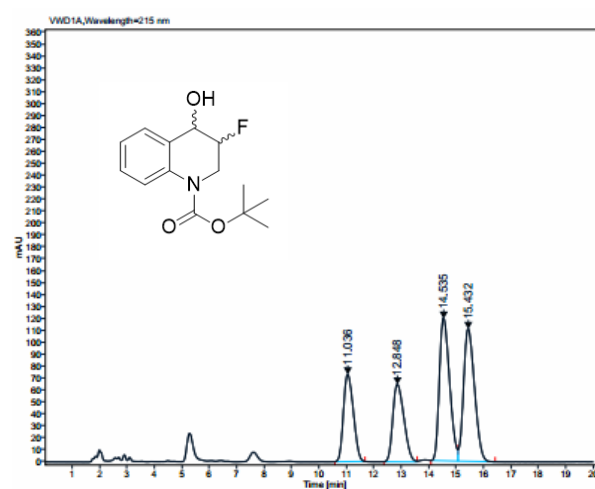
Sample Name

**RB rac  
NBocF Ph  
bis**

Injection Acq Method Name IE - 100 bars - 2 mL.min<sup>-1</sup> - 4% EtOH.amx

Injection Acquired Date 2021-12-08 15:21:40+01:00

RT	Peak Area %
11.036	18.63
12.848	18.59
14.535	31.45
15.432	31.33



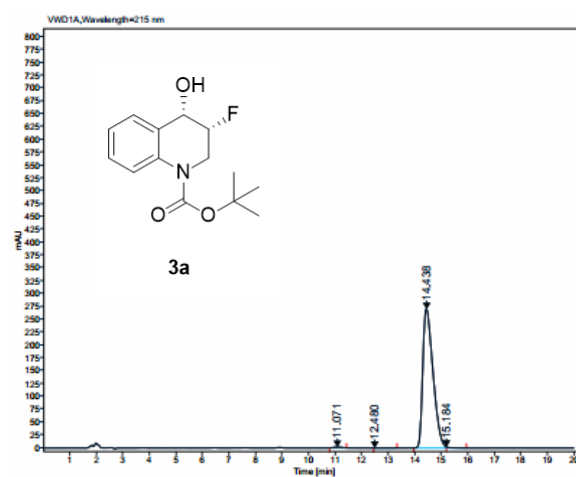
Sample Name

**RB ATH  
NBocF Ph**

Injection Acq Method Name IE - 100 bars - 2 mL.min<sup>-1</sup> - 4% EtOH.amx

Injection Acquired Date 2021-12-08 15:50:09+01:00

RT	Peak Area %
11.071	0.45
12.480	0.00
14.438	99.28
15.184	0.27



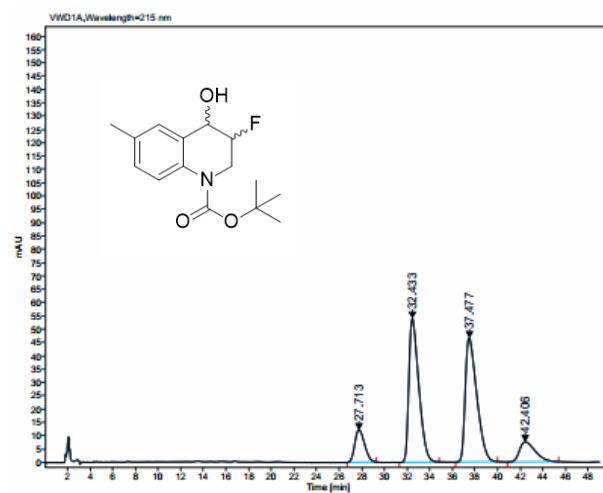
Sample Name

**RB rac  
NBoc F  
Me bis**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 2.5% EtOH.amx

Injection Acquired Date 2021-12-09 14:48:04+01:00

RT	Peak Area %
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32.433	40.92
37.477	40.98
42.406	9.03



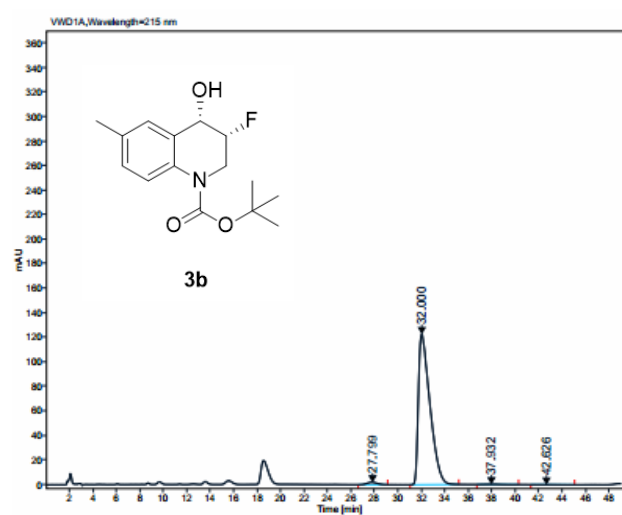
Sample Name

**RB ATH  
NBoc F  
Me**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 2.5% EtOH.amx

Injection Acquired Date 2021-12-09 16:00:08+01:00

RT	Peak Area %
27.799	1.40
32.000	98.40
37.932	0.18
42.626	0.01

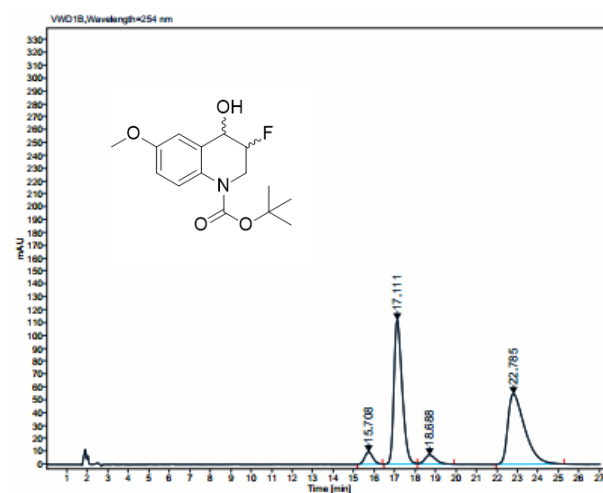


Sample Name **RB rac  
NBoc F  
OMe haut**

Injection Acq Method Name IF - 100 bars - 2 mL.min-1 - 4.5% EtOH.amx

Injection Acquired Date 2021-12-10 15:44:50+01:00

RT	Peak Area %
15.708	3.91
17.111	46.09
18.688	3.92
22.785	46.08

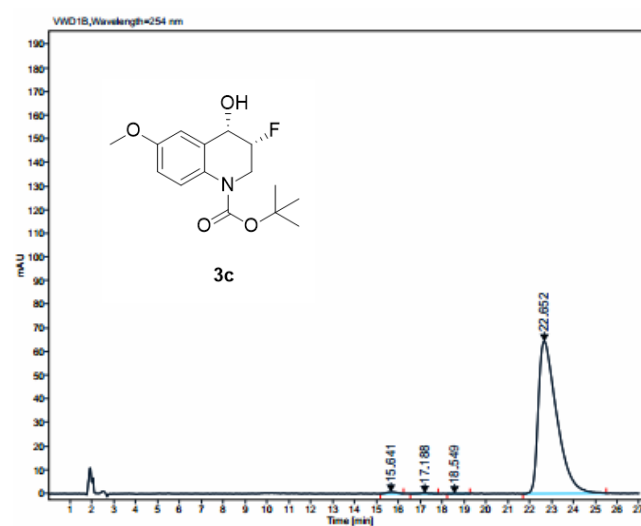


Sample Name **RB ATH  
NBoc F  
OMe haut**

Injection Acq Method Name IF - 100 bars - 2 mL.min-1 - 4.5% EtOH.amx

Injection Acquired Date 2021-12-10 16:21:59+01:00

RT	Peak Area %
15.641	0.57
17.188	0.18
18.549	0.00
22.652	99.25





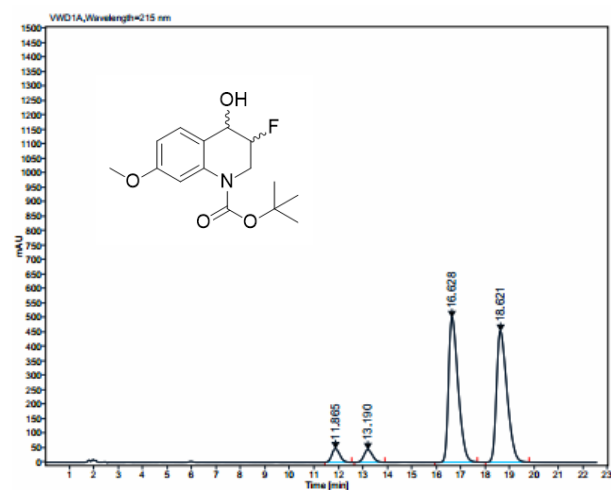
Sample Name

**RB rac**  
**NBoc F**  
**OMe bas**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 5% EtOH.amx

Injection Acquired Date 2021-12-13 15:53:19+01:00

RT	Peak Area %
11.865	3.60
13.190	3.59
16.628	46.44
18.621	46.37



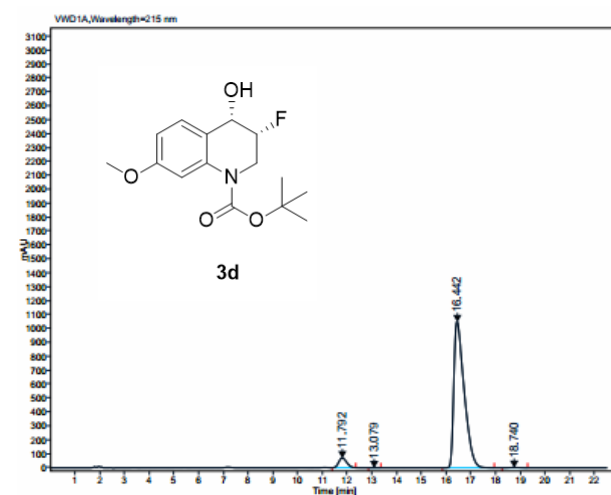
Sample Name

**RB ATH**  
**NBoc F**  
**OMe bas**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 5% EtOH.amx

Injection Acquired Date 2021-12-13 18:46:24+01:00

RT	Peak Area %
11.792	4.92
13.079	0.01
16.442	94.88
18.740	0.20



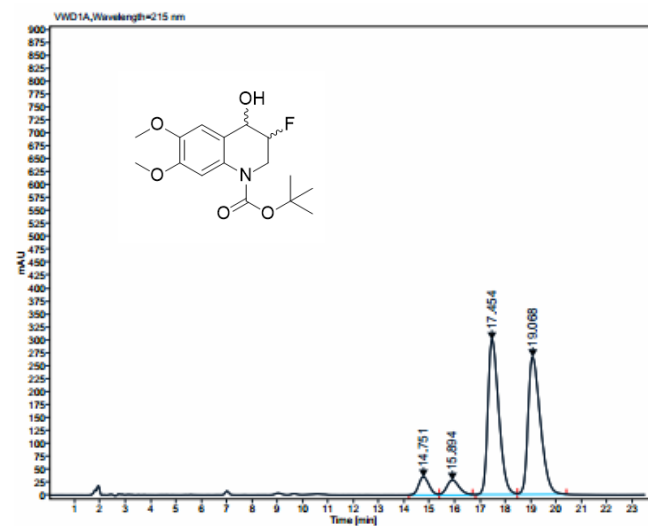
Sample Name

**RB rac  
NBoc F  
OMe2 bis**

Injection Acq Method Name IF - 100 bars - 2 mL.min-1 - 5% EtOH.amx

Injection Acquired Date 2021-12-13 13:32:06+01:00

RT	Peak Area %
14.751	5.02
15.894	5.01
17.454	44.97
19.068	44.99



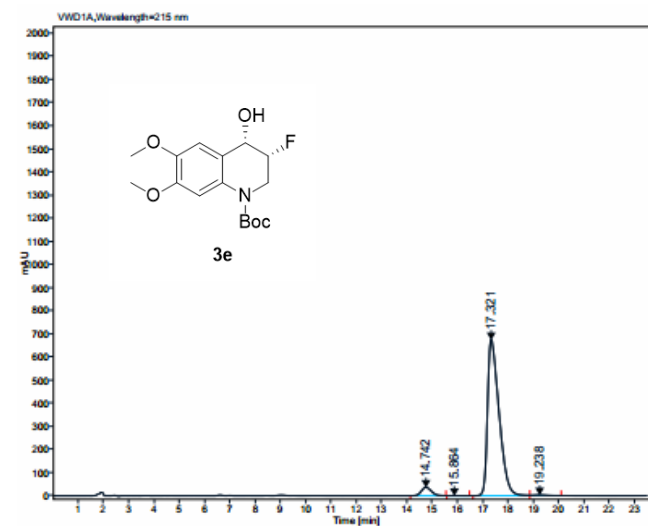
Sample Name

**RB ATH  
NBoc F  
OMe2**

Injection Acq Method Name IF - 100 bars - 2 mL.min-1 - 5% EtOH.amx

Injection Acquired Date 2021-12-13 14:15:27+01:00

RT	Peak Area %
14.742	4.50
15.864	0.16
17.321	94.90
19.238	0.45



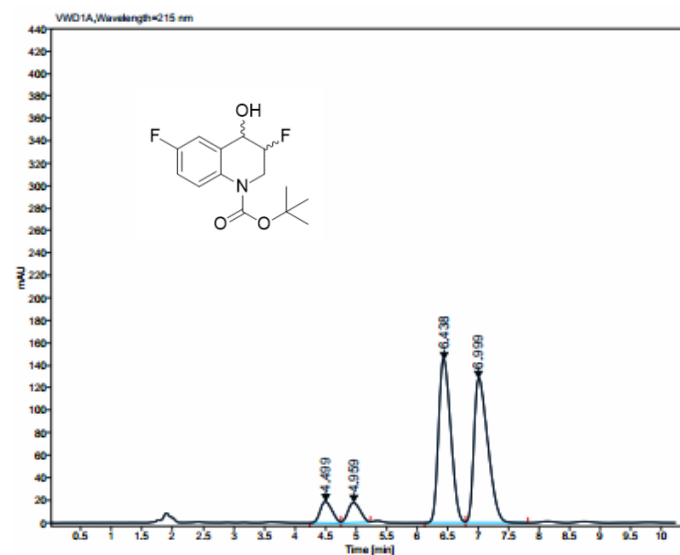
Sample Name

**RB rac  
NBocF F**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 6% MeOH.amx

Injection Acquired Date 2021-12-07 13:07:33+01:00

RT	Peak Area %
4.499	5.69
4.959	5.58
6.438	44.30
6.999	44.43



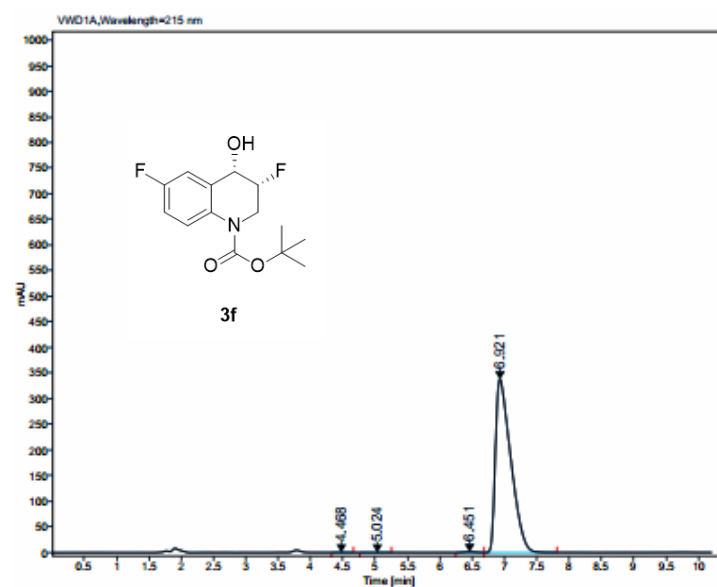
Sample Name

**RB ATH  
NBocF F**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 6% MeOH.amx

Injection Acquired Date 2021-12-07 13:42:07+01:00

RT	Peak Area %
4.468	0.04
5.024	0.00
6.451	0.25
6.921	99.70



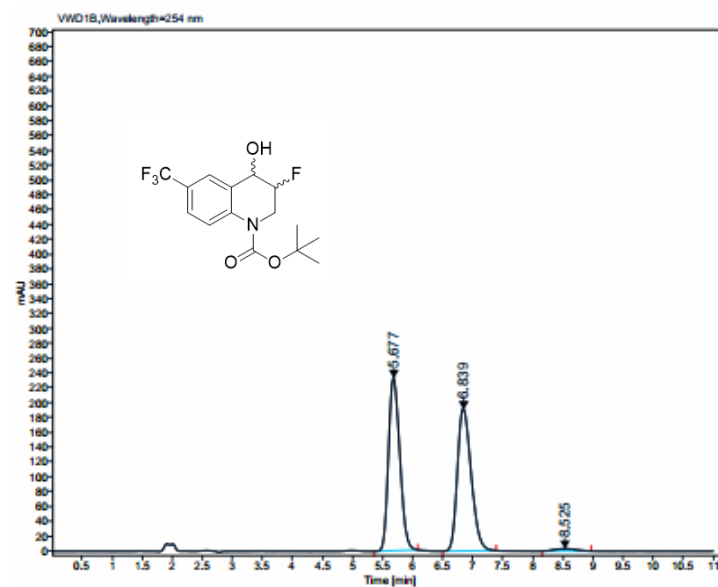
Sample Name

**RB rac  
NBoc F  
CF3 2**

Injection Acq Method Name IF - 100 bars - 2 mL.min-1 - 4% EtOH.amx

Injection Acquired Date 2021-12-10 17:44:38+01:00

RT	Peak Area %
5.677	49.32
6.839	49.36
8.525	1.33



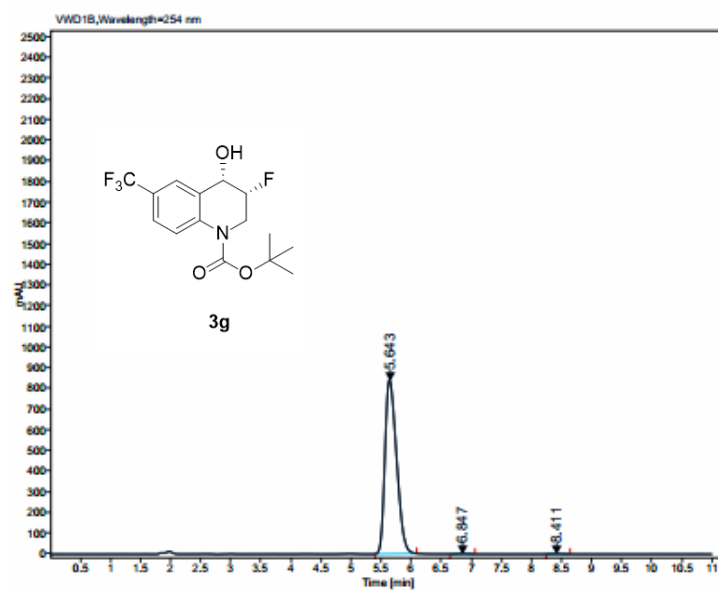
Sample Name

**RB ATH  
NBoc F  
CF3**

Injection Acq Method Name IF - 100 bars - 2 mL.min-1 - 4% EtOH.amx

Injection Acquired Date 2021-12-10 18:17:50+01:00

RT	Peak Area %
5.643	99.75
6.847	0.14
8.411	0.10



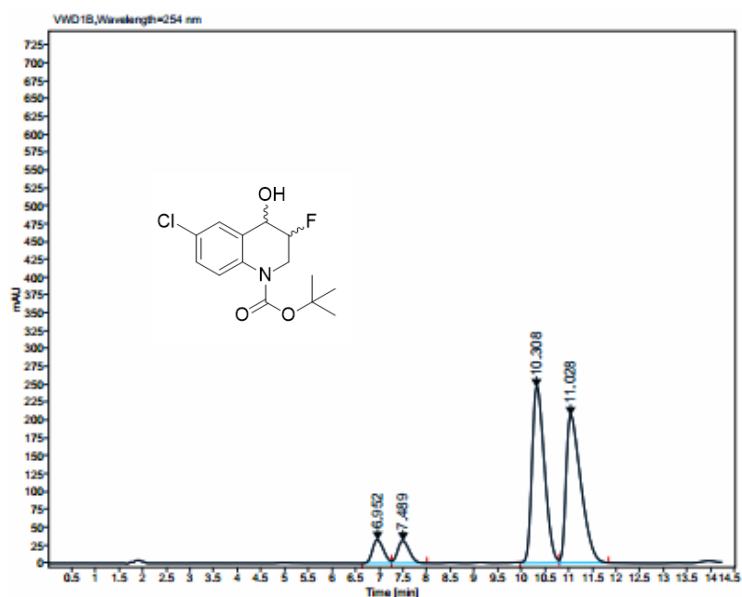
Sample Name

**RB rac  
NBocF Cl**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 6% MeOH.amx

Injection Acquired Date 2021-12-07 10:39:45+01:00

RT	Peak Area %
6.952	5.27
7.489	5.32
10.308	44.65
11.028	44.76



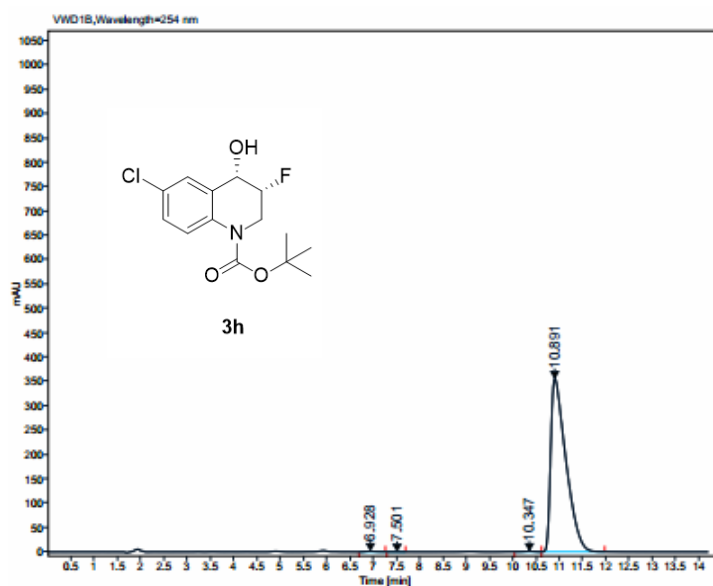
Sample Name

**RB ATH  
NBocF Cl**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 6% MeOH.amx

Injection Acquired Date 2021-12-07 11:10:45+01:00

RT	Peak Area %
6.928	0.23
7.501	0.00
10.347	0.16
10.891	99.60



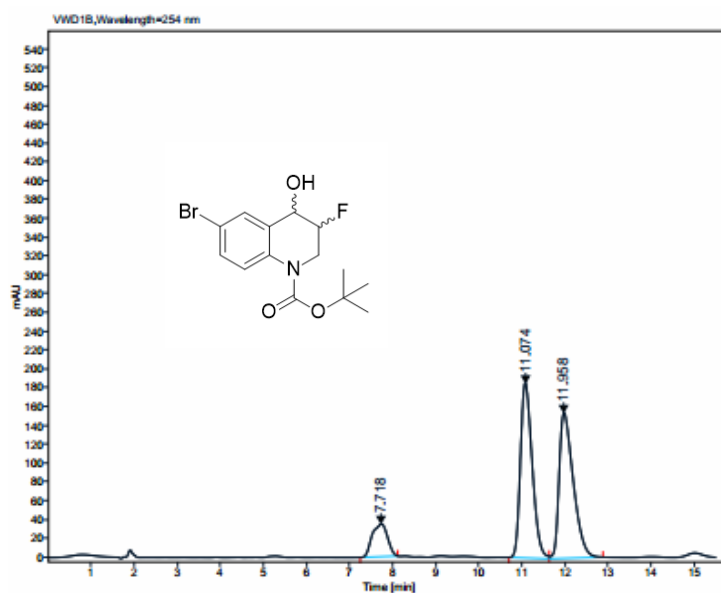
Sample Name

**RB rac  
NBocF Br  
tris**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 7% MeOH.amx

Injection Acquired Date 2021-12-07 17:47:22+01:00

RT	Peak Area %
7.718	10.82
11.074	44.61
11.958	44.57



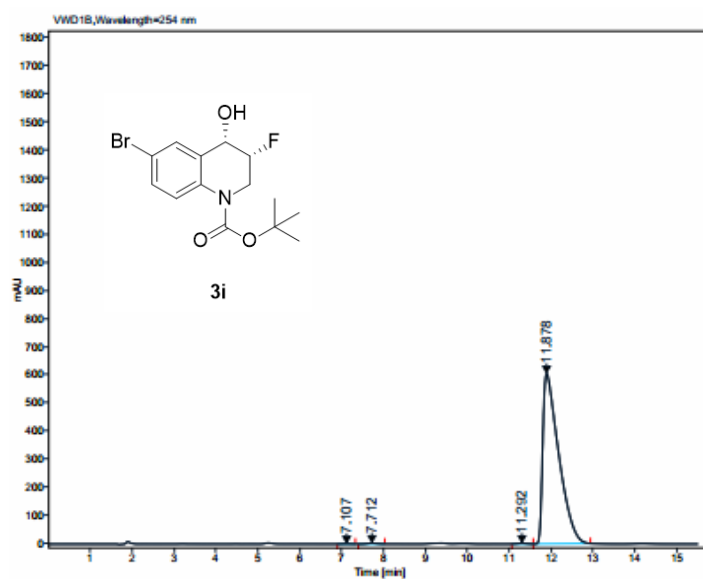
Sample Name

**RB ATH  
NBocF Br**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 7% MeOH.amx

Injection Acquired Date 2021-12-07 17:09:53+01:00

RT	Peak Area %
7.107	0.05
7.712	0.26
11.292	0.22
11.878	99.47



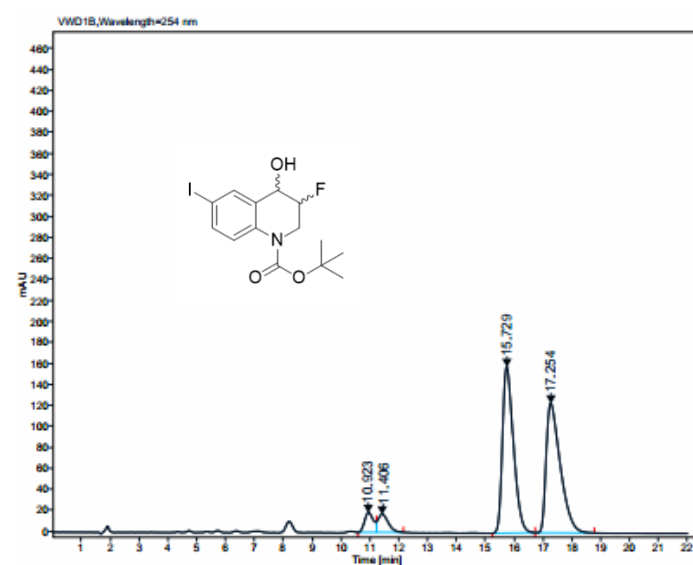
Sample Name

**RB rac  
NBocF I  
bis**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 7% MeOH.amx

Injection Acquired Date 2021-12-08 09:14:27+01:00

RT	Peak Area %
10.923	4.42
11.406	4.59
15.729	45.49
17.254	45.49



Sample Name

**RB ATH  
NBocF I**

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 7% MeOH.amx

Injection Acquired Date 2021-12-08 09:42:09+01:00

RT	Peak Area %
10.488	0.02
11.285	0.40
15.814	0.22
16.690	99.35

