Supporting Information

Fluoromethoxymethylation of Nitrogen Heterocyclic Compounds with Fluoromethyl Iodide

Rongkang Wang , Tianqi Ding, Lvqi Jiang*, Wujuan He, Wenbin Yi*

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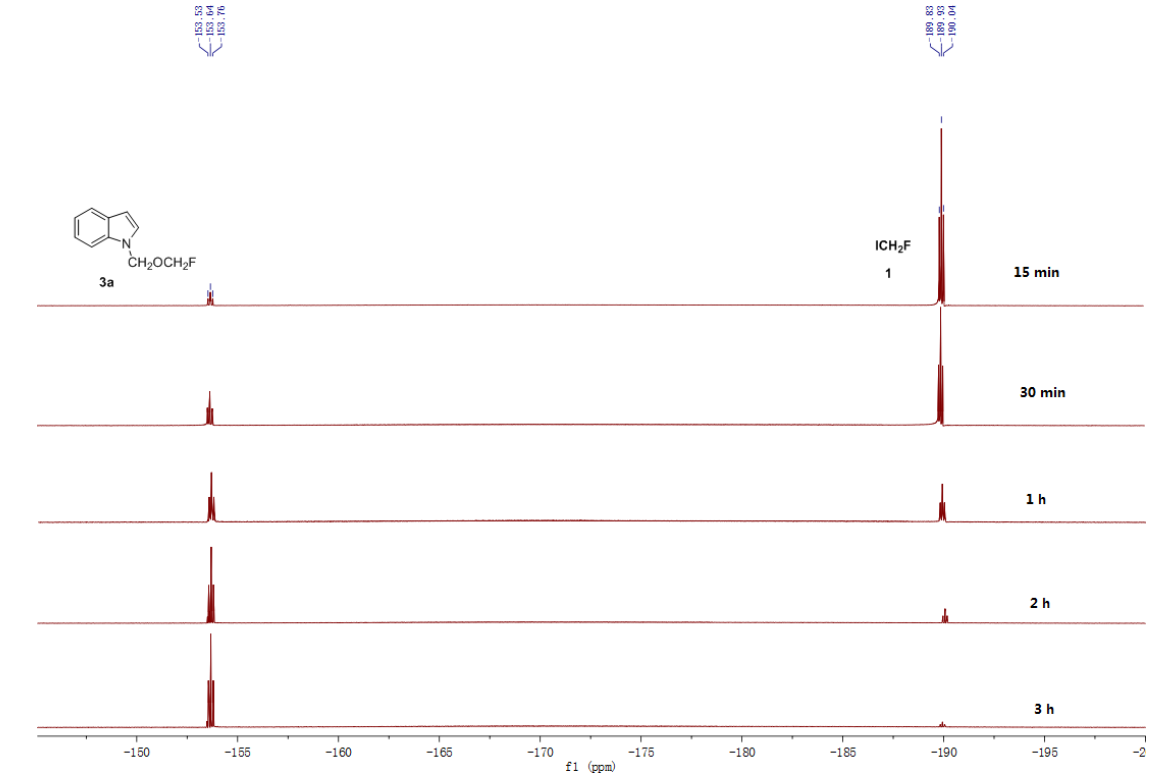
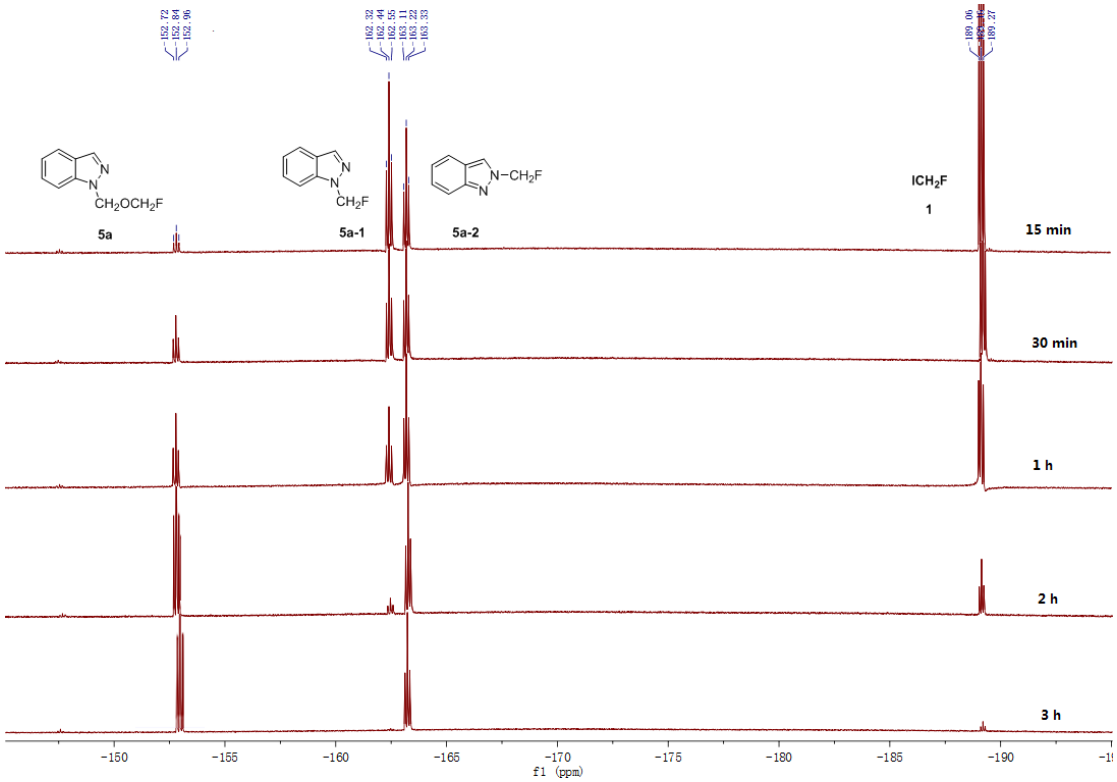
1. Mechanistic Studies





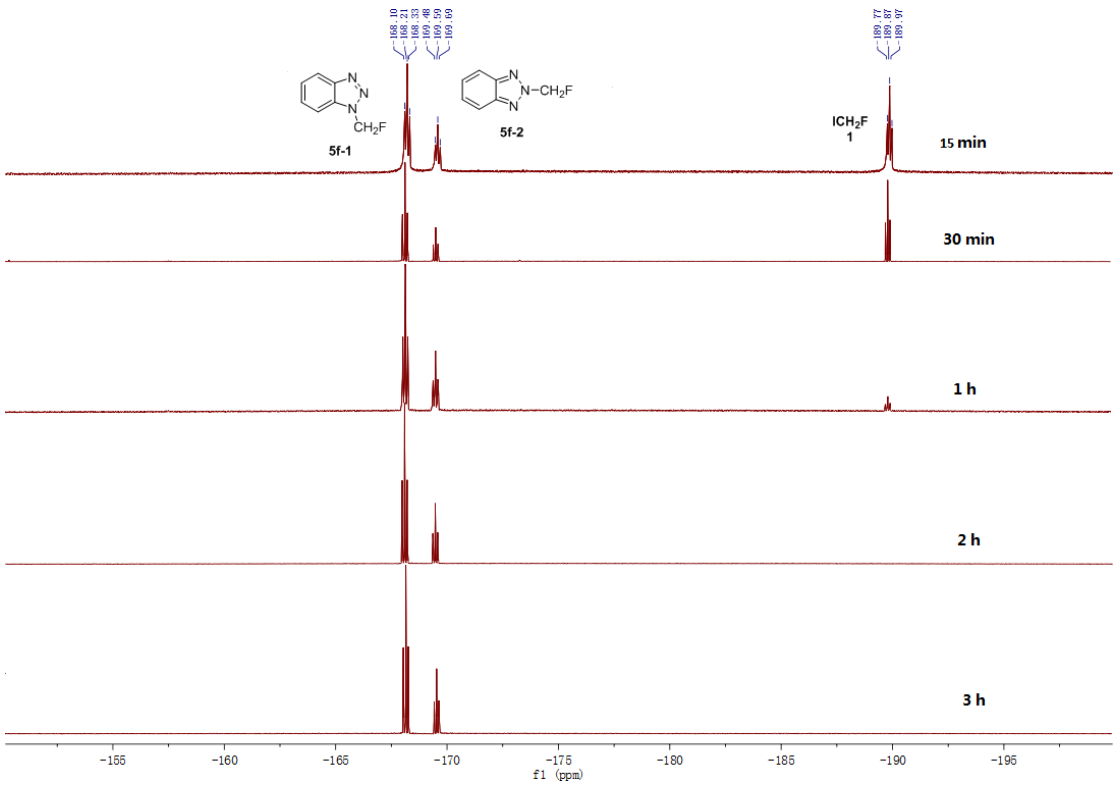


Figure S1. Progress of the reaction of **2a**, **4a** and **4f**, for up to 3 h, by ^{19}F NMR spectroscopy.

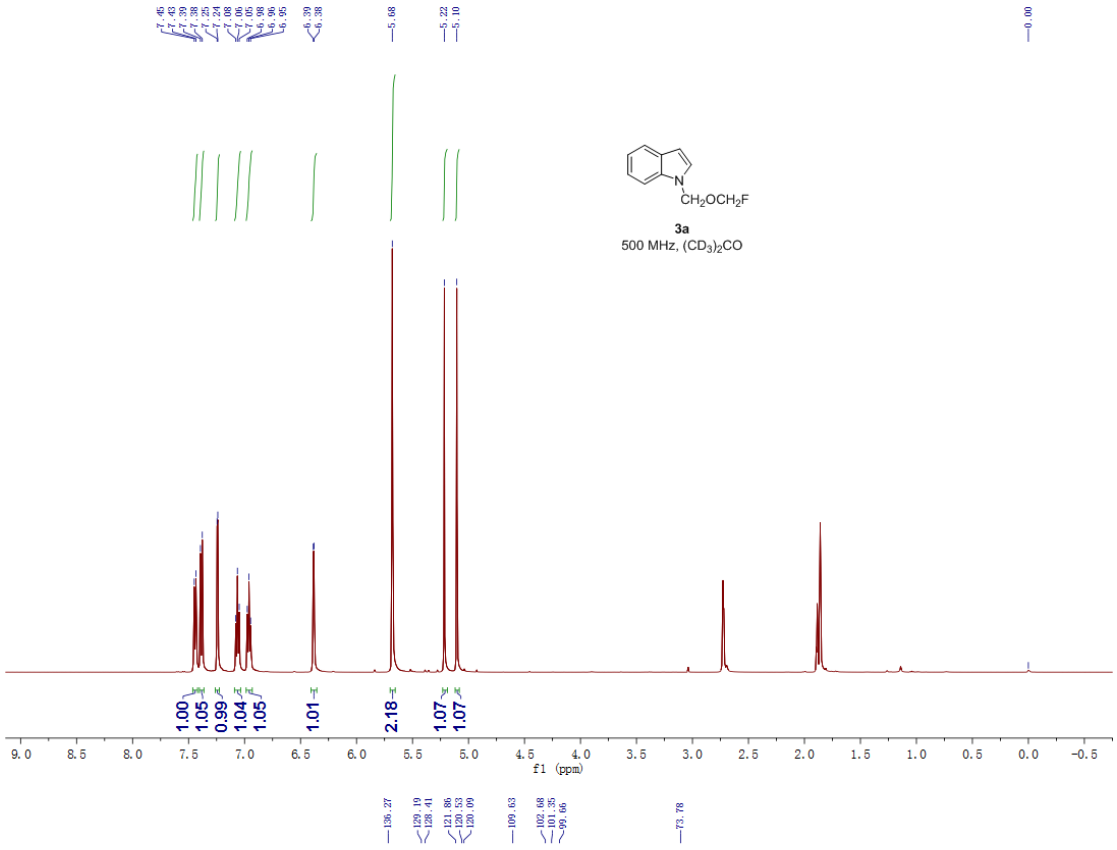
To understand the mechanism of this fluoromethoxymethyl reaction, we decided to trace the reactions by ^{19}F NMR in three cases (**2a**, **4a** and **4f**). The results were displayed in Figure S1. During the 3 hours reaction process of reaction with **2a**, only two singals including those for the reagent **1** (δ -189.9 ppm) and product **3a** (δ -153.6 ppm) were observed. The amount of ICH_2F decreased and the desired product **3a** increased during the reaction process. For 1*H*-indazole **4a**, the signals were very different. In spite of reagent **1** and product **5a**, two new singals were obtained: δ −162.5 ppm (**5a-1**) and δ −163.2 ppm (**5a-2**), which were two CH_2F-substituted products[1]. It was obvious that **5a-1** decreased accompanied by the increase of product **5a,** while another signal of δ −163.2 ppm (**5a-2**) was observed with no significant change. This indicated that only one CH_2F-substituted intermediate (**5a-1**) could convert to the final product **5a**.[2] For the case of 1*H*-benzotriazole **4f**, it was similar that two CH_2F-substituted products **5f-1** (δ −168.2 ppm) and **5f-2** (δ −169.6 ppm) were observed, but neither could transfer to the CH_2OCH_2F product.

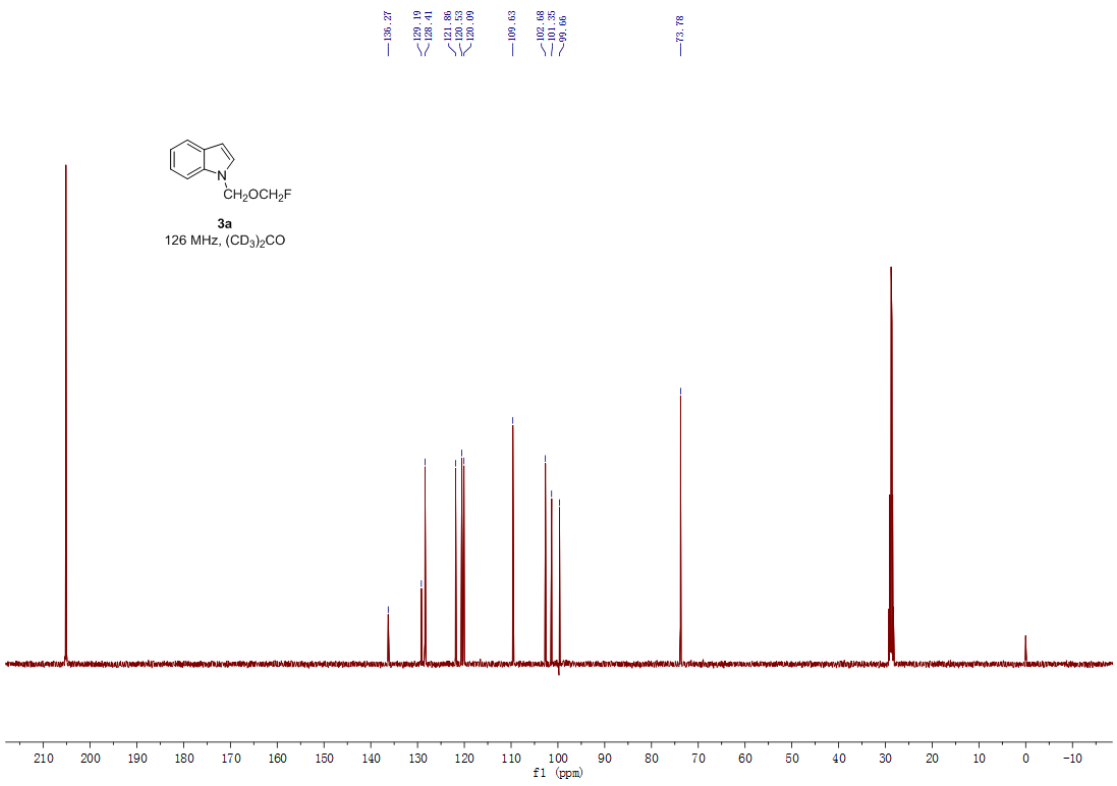
References:

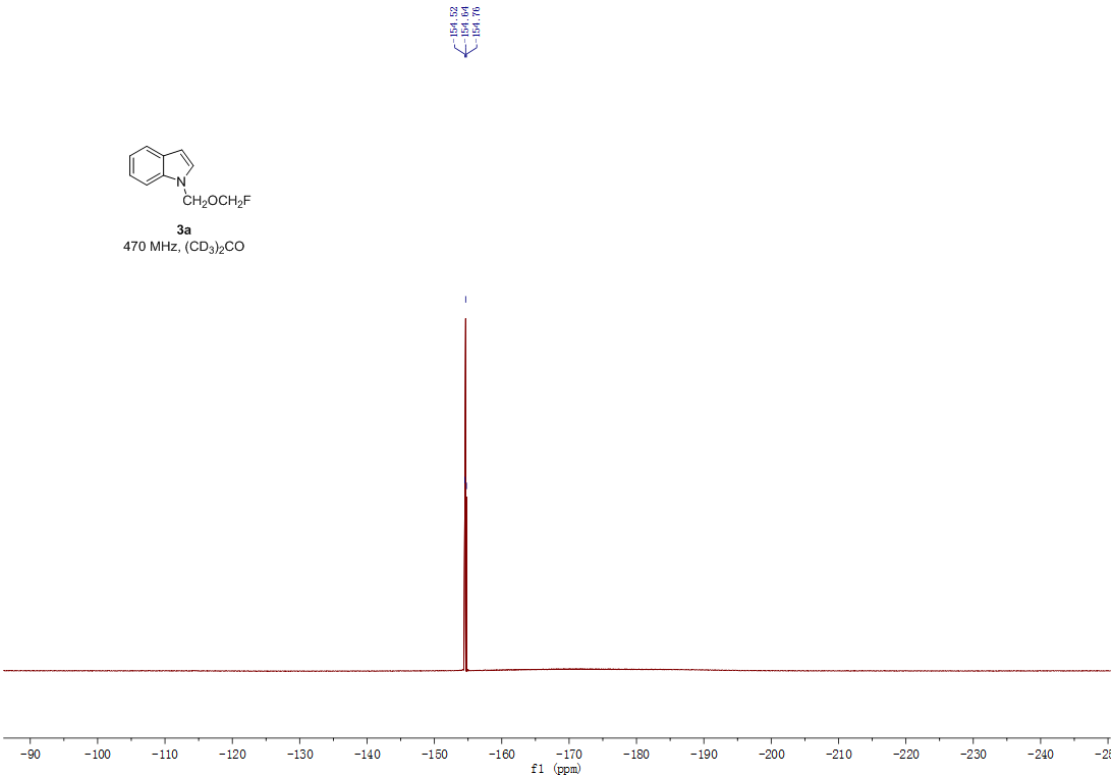
1. Zhang, W.; Zhu, L.; Hu, J. Electrophilic monofluoromethylation of O-, S-, and N-nucleophiles with chlorofluoromethane. *Tetrahedron.* **2007**, *63*, 10569-10575.

2. The structure of CH_2F-substituted intermediates **5a-1** and **5a-2** were confirmed by comparing ^{13}C NMR spectra with the similar CH_3-substituted compounds: a) Cheung, M.; Boloor, A.; Stafford, J. A. Efficient and Regioselective Synthesis of 2-Alkyl-2*H*-indazoles. *J. Org. Chem.* **2003**, *68*, 4093-4095; b) Liu, H.-J.; Hung, S.-F.; Chen, C.-L.; Lin, M.-H. A method for the regioselective synthesis of 1-alkyl-1*H*-indazoles. *Tetrahedron.* **2013**, *69*, 3907-3912.

2. NMR Spectra



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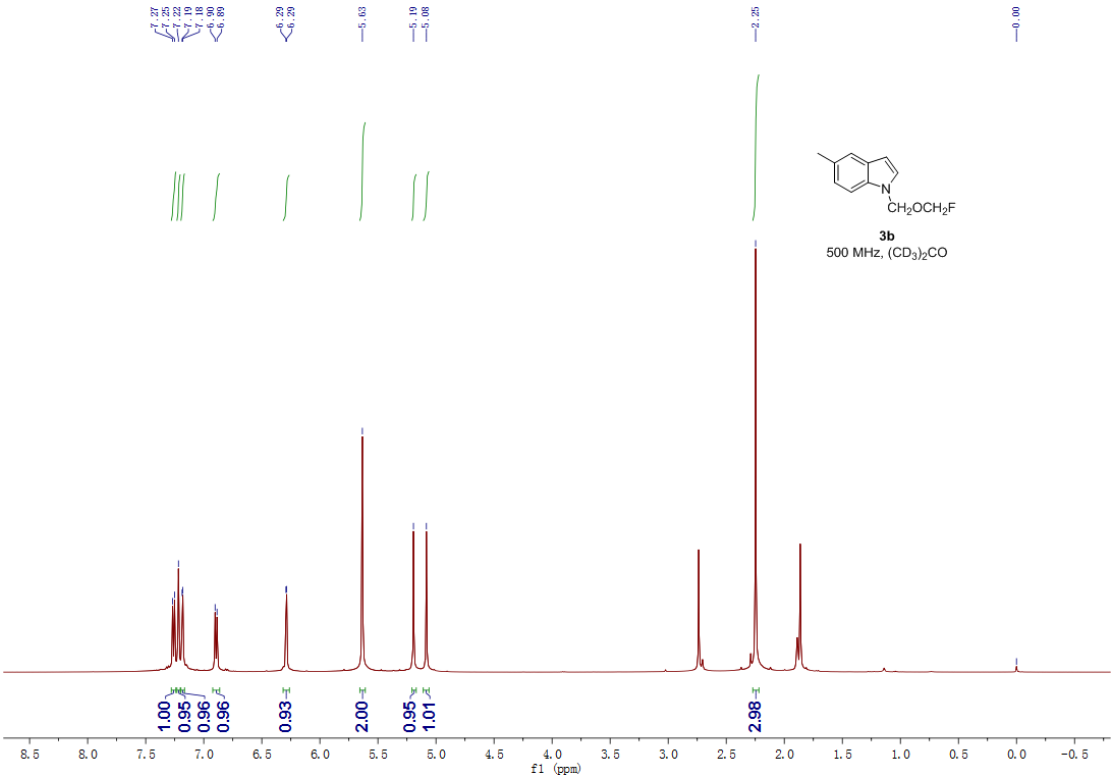
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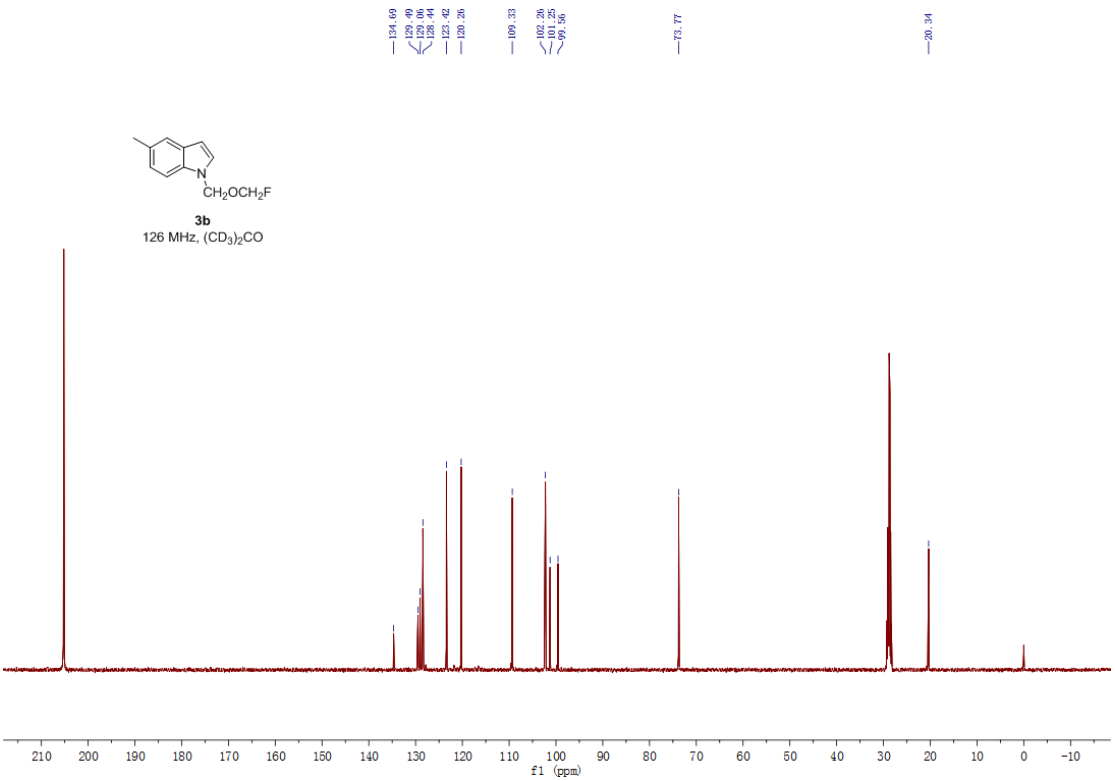
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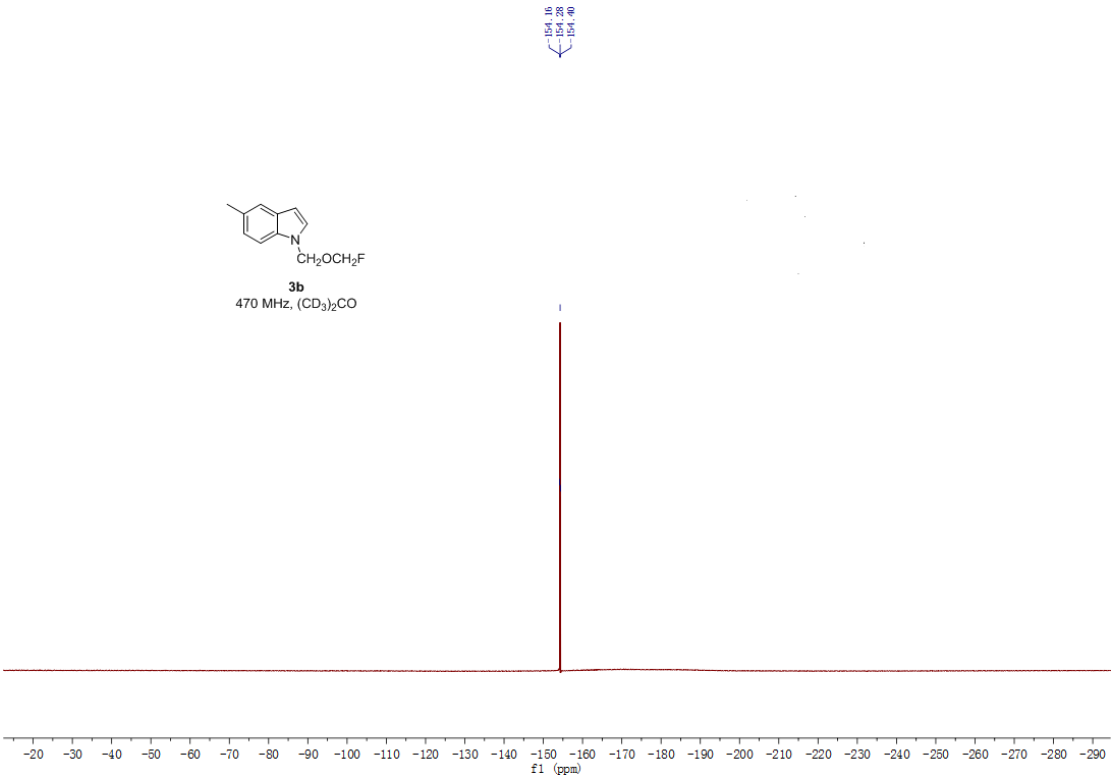
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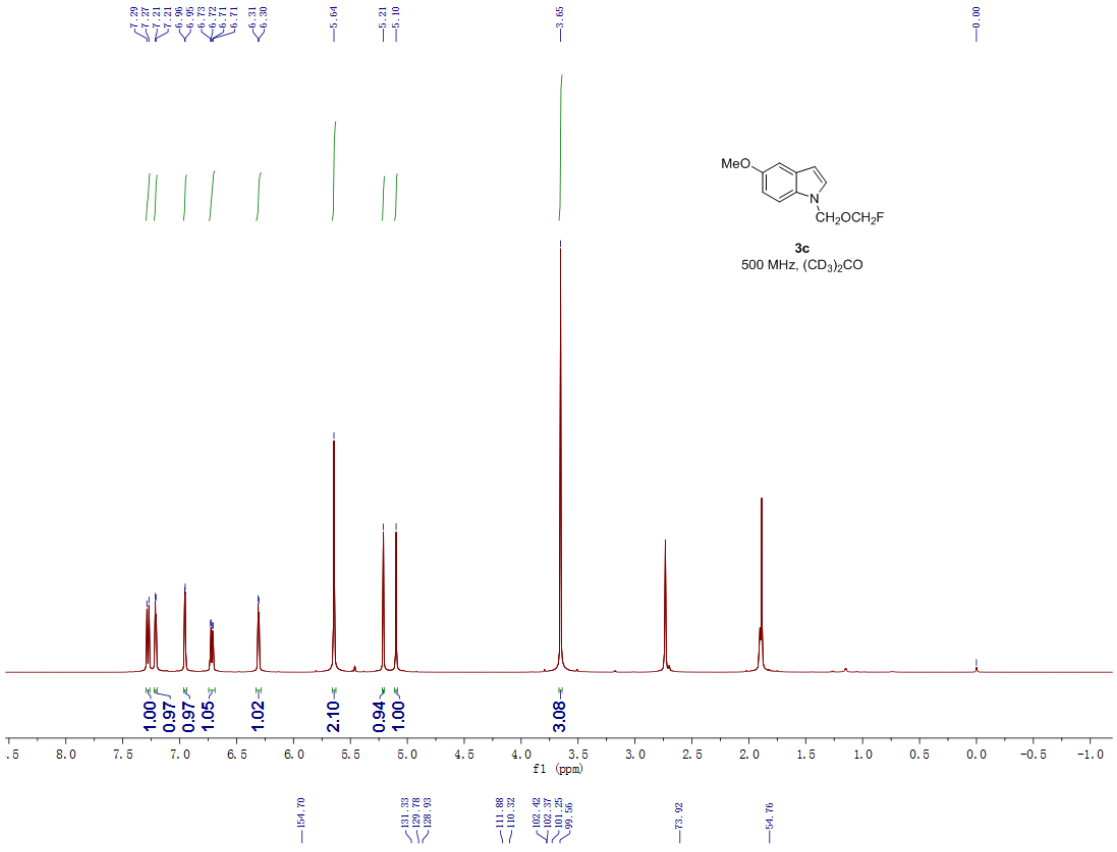
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5.21
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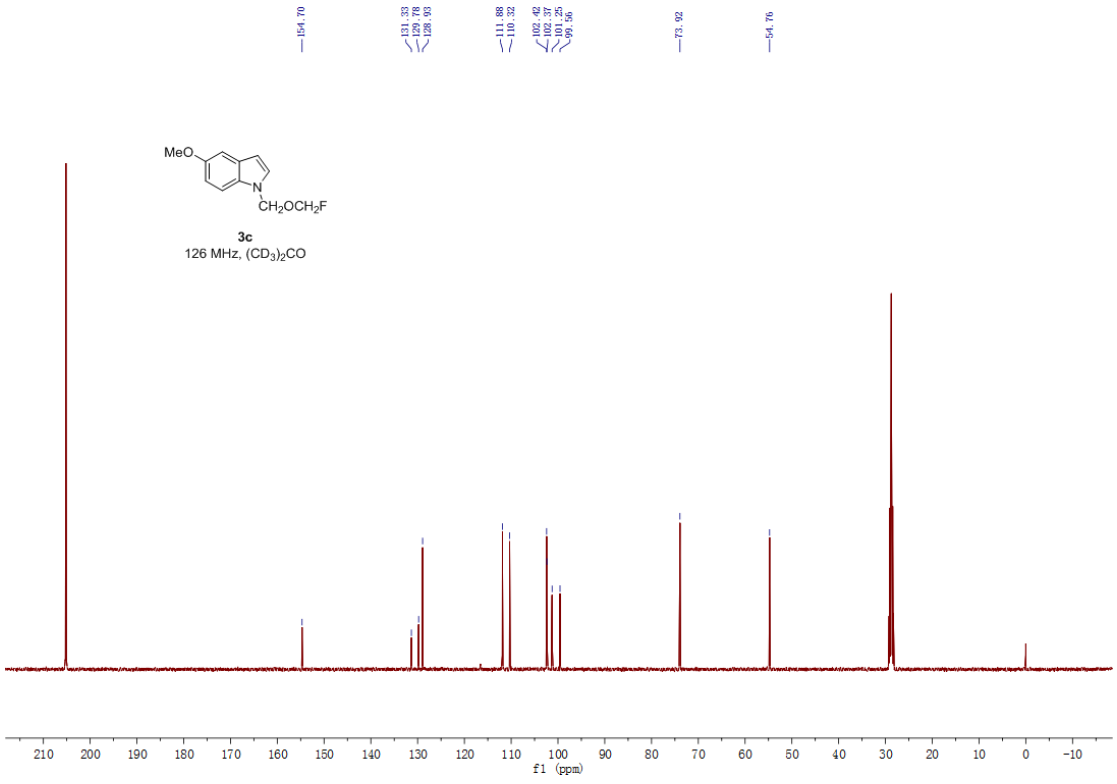
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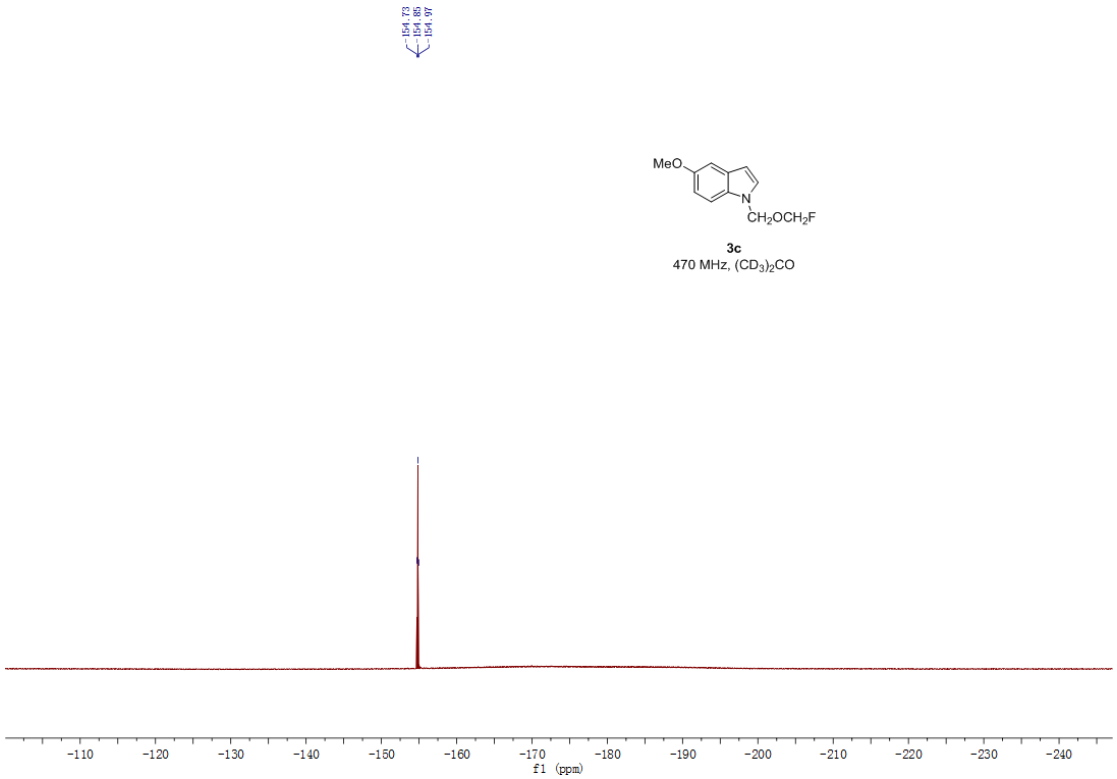
f1 (ppm)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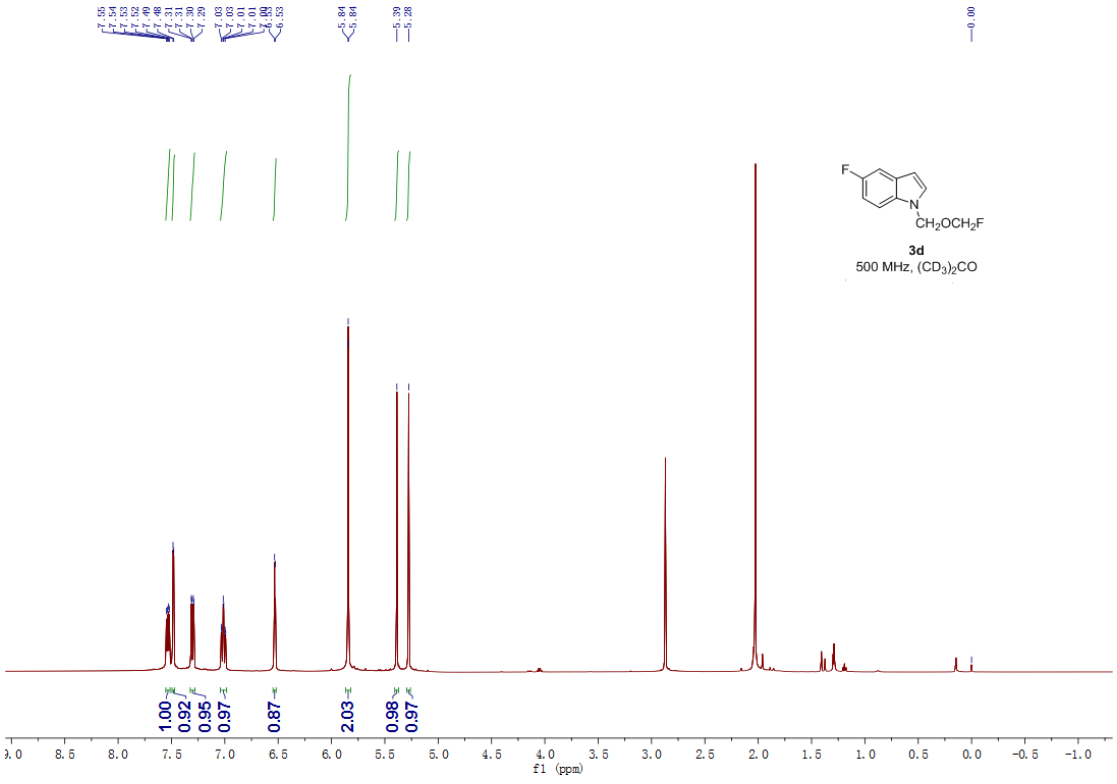
f1 (ppm)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5.39
5.28
0.00
F
N
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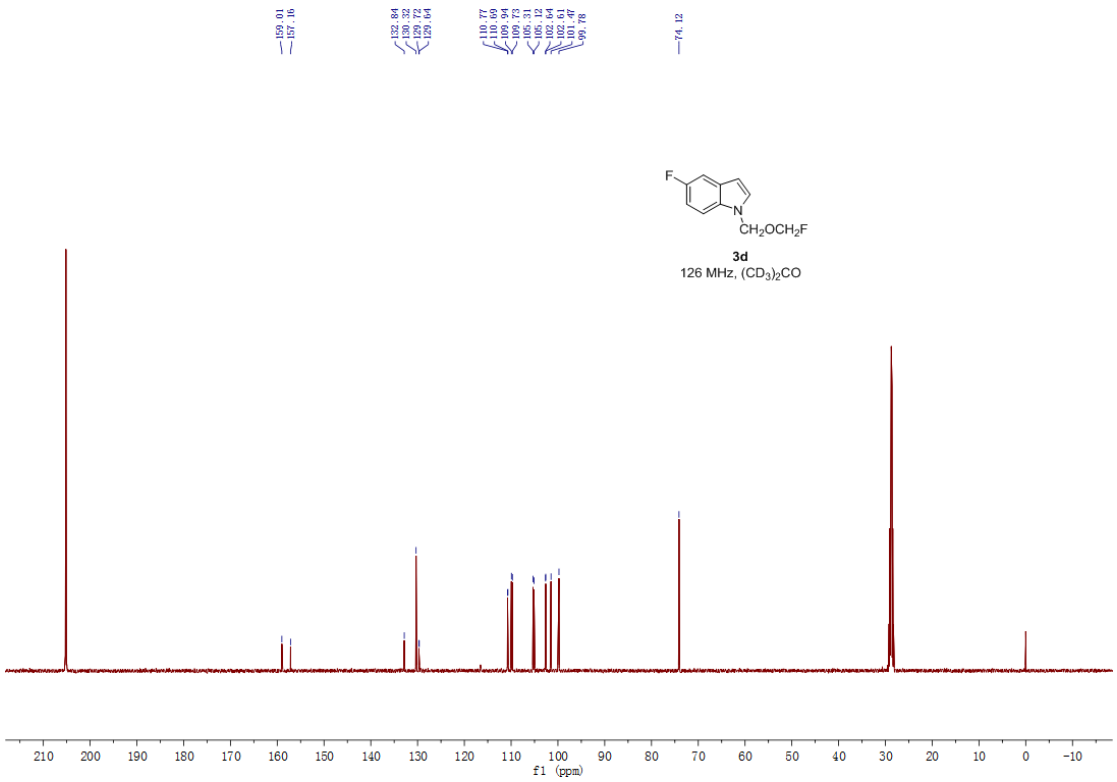
f1 (ppm)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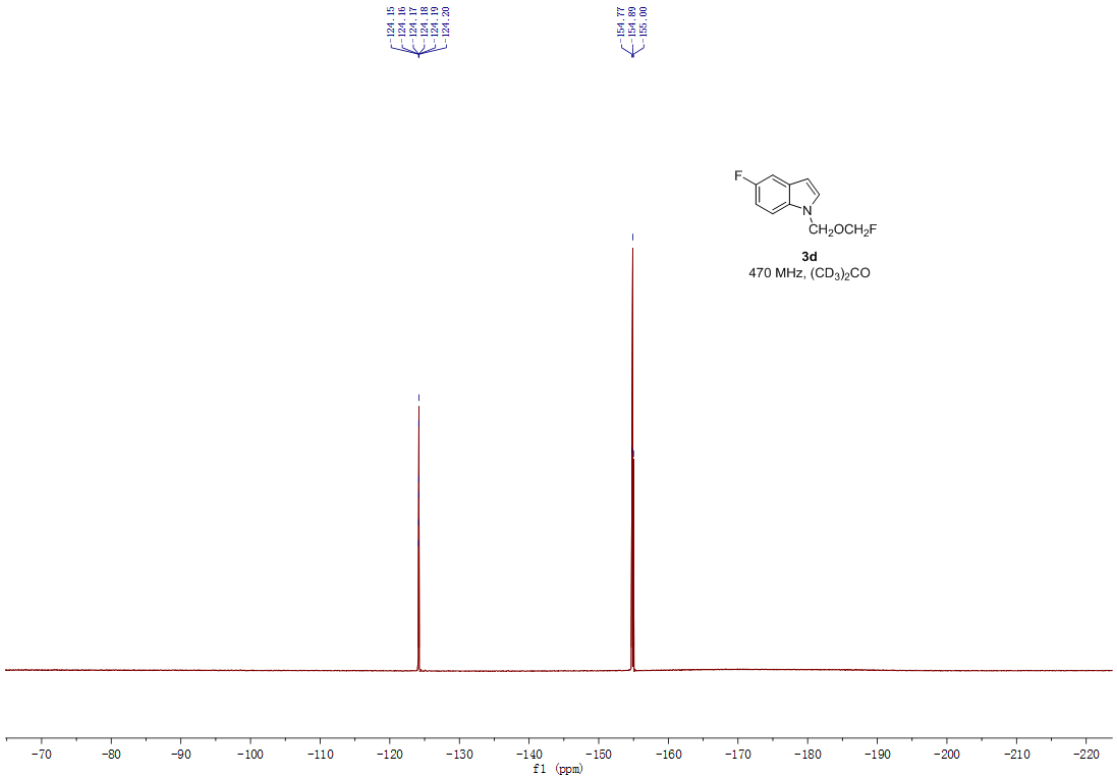
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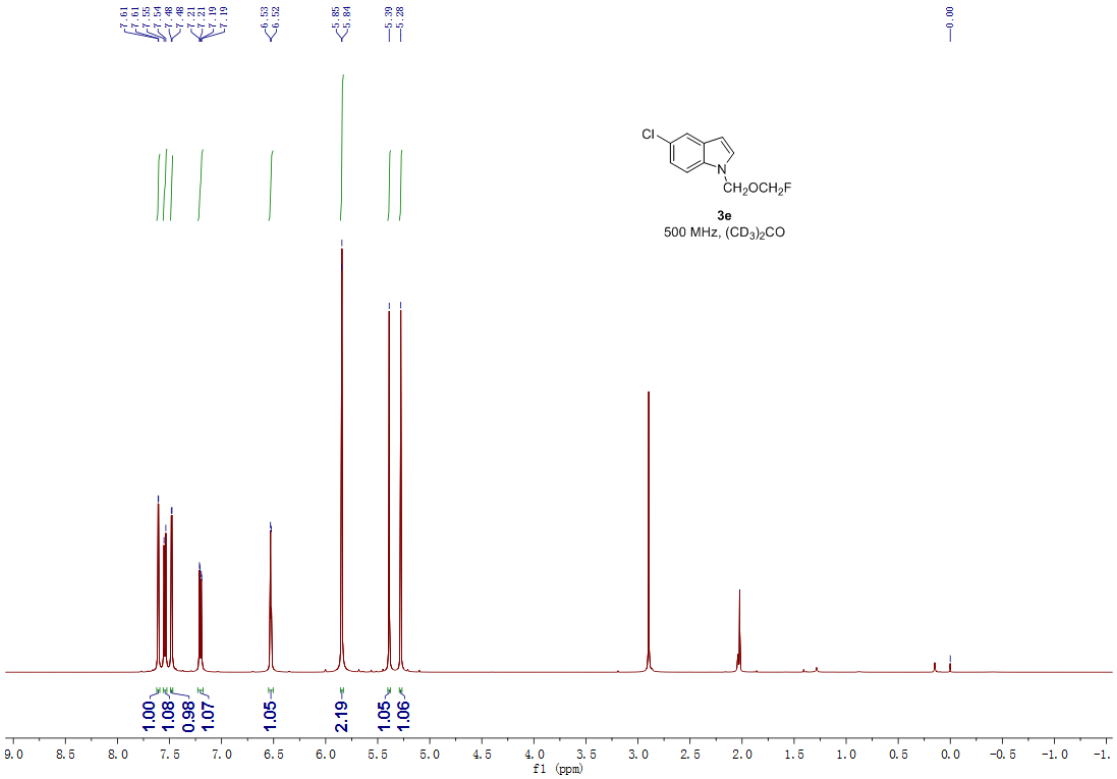
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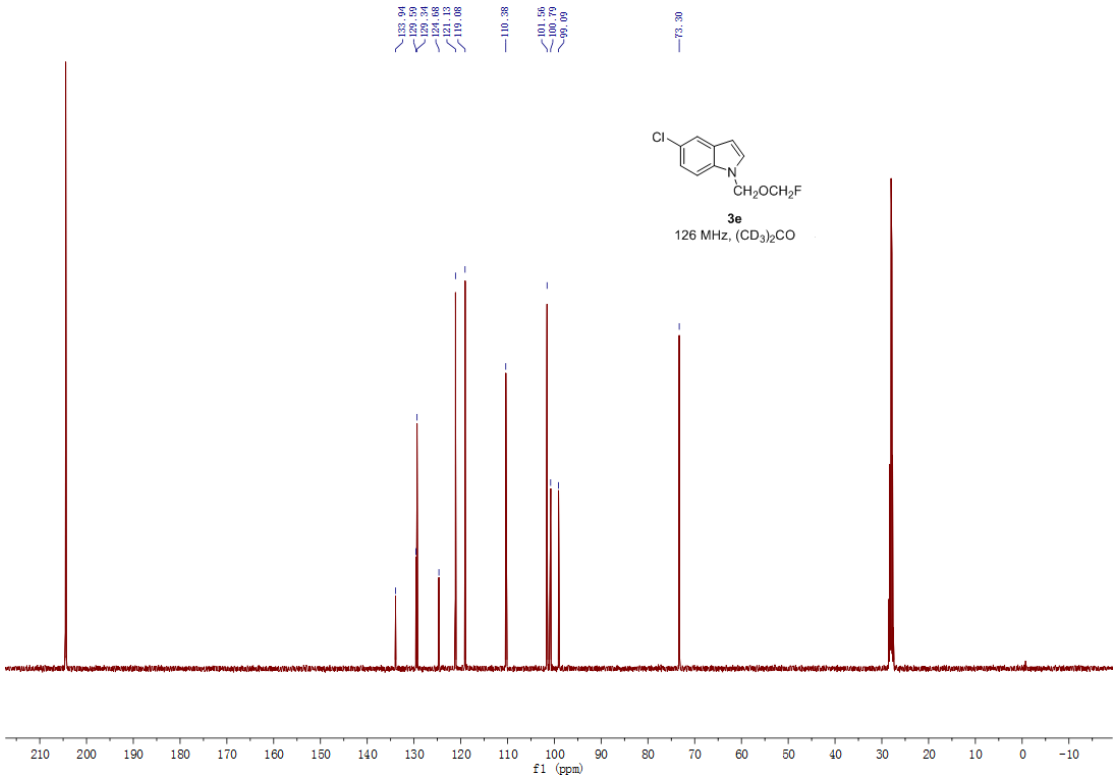
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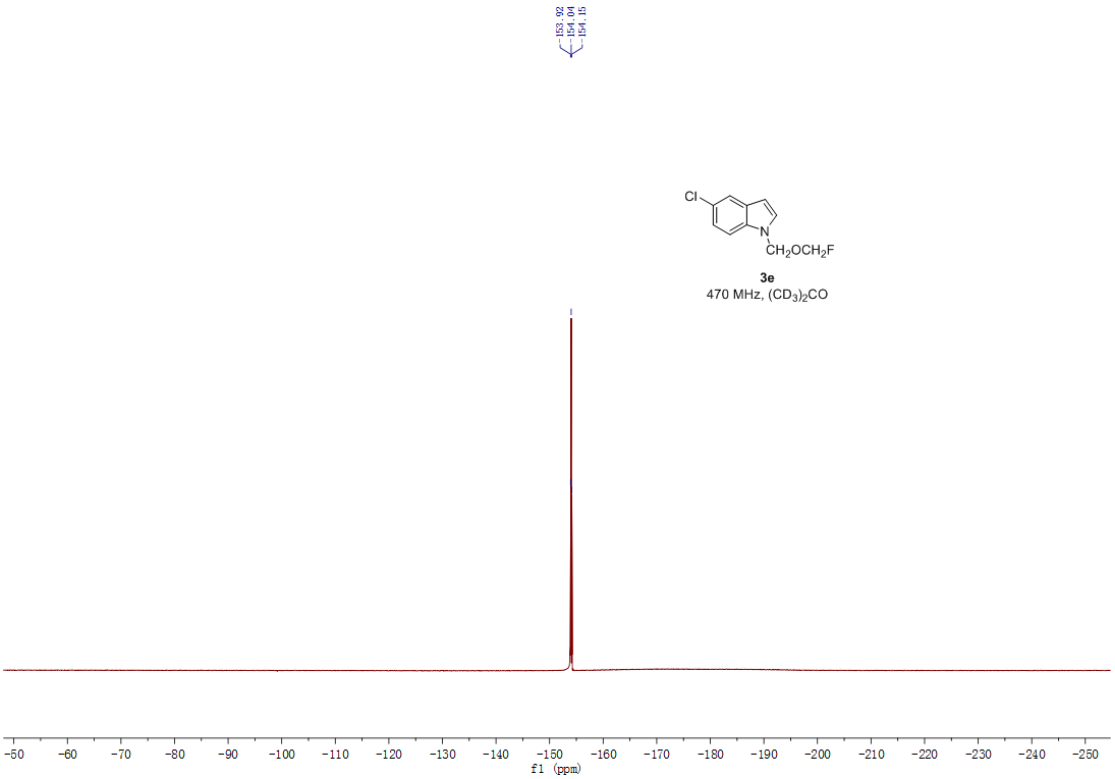
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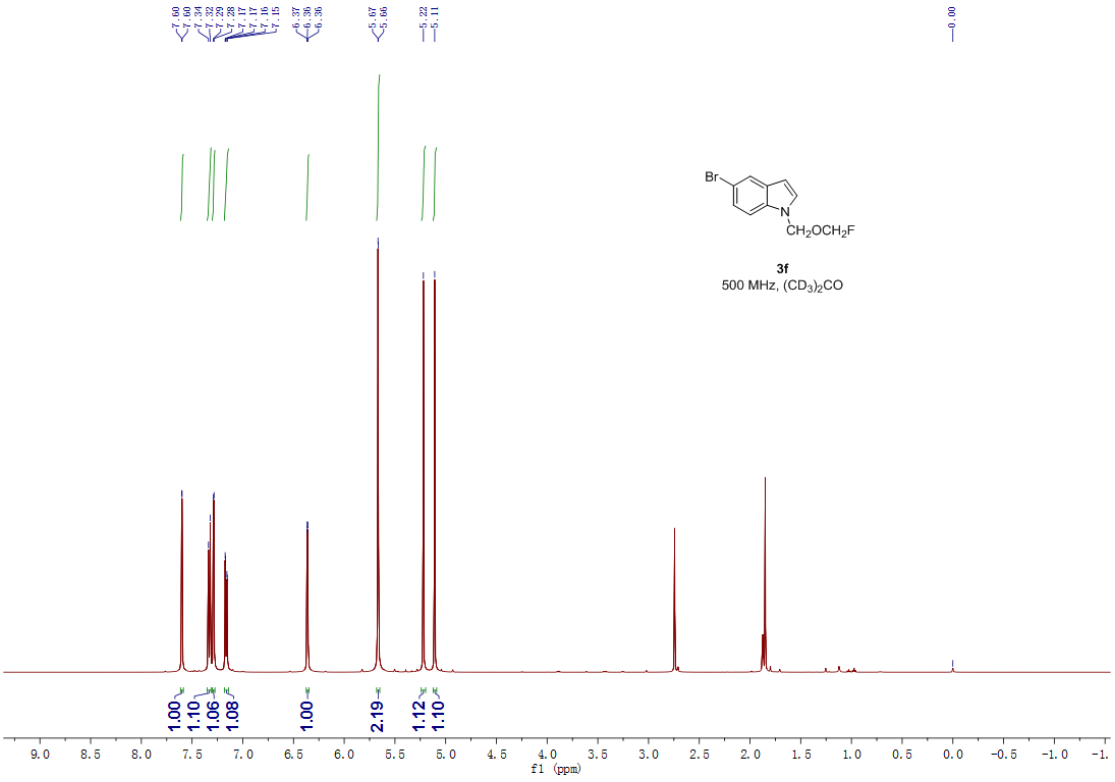
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3f
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2.19
1.12
1.10
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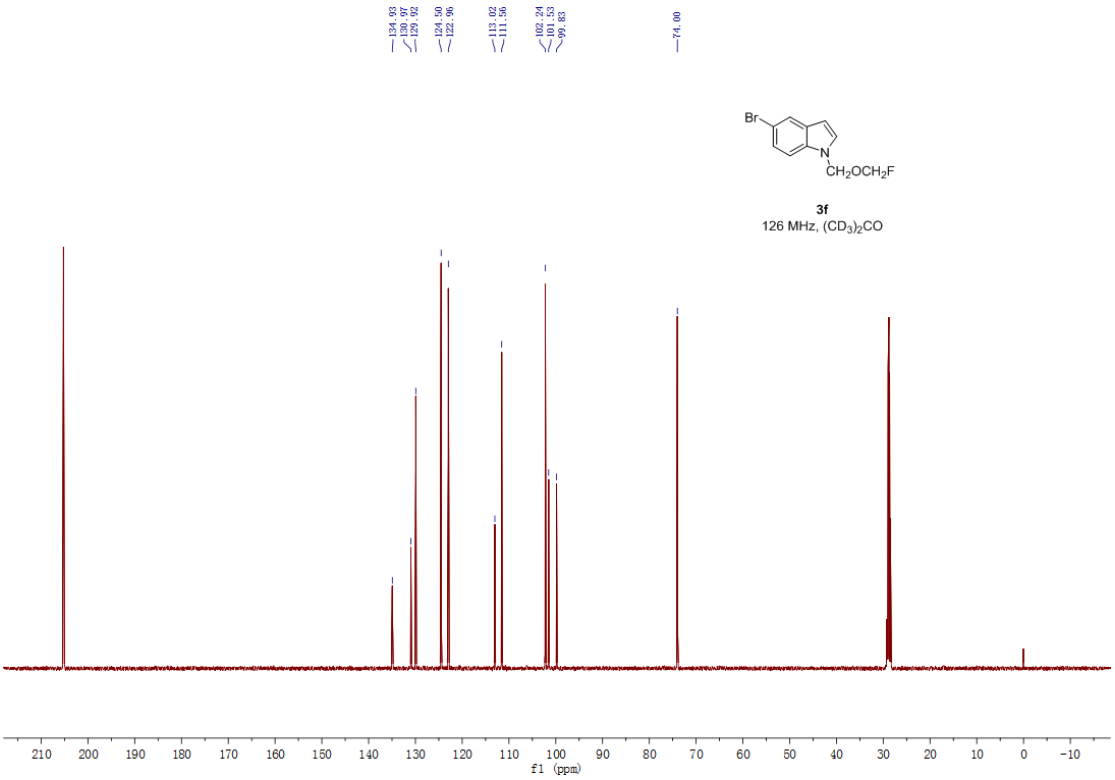
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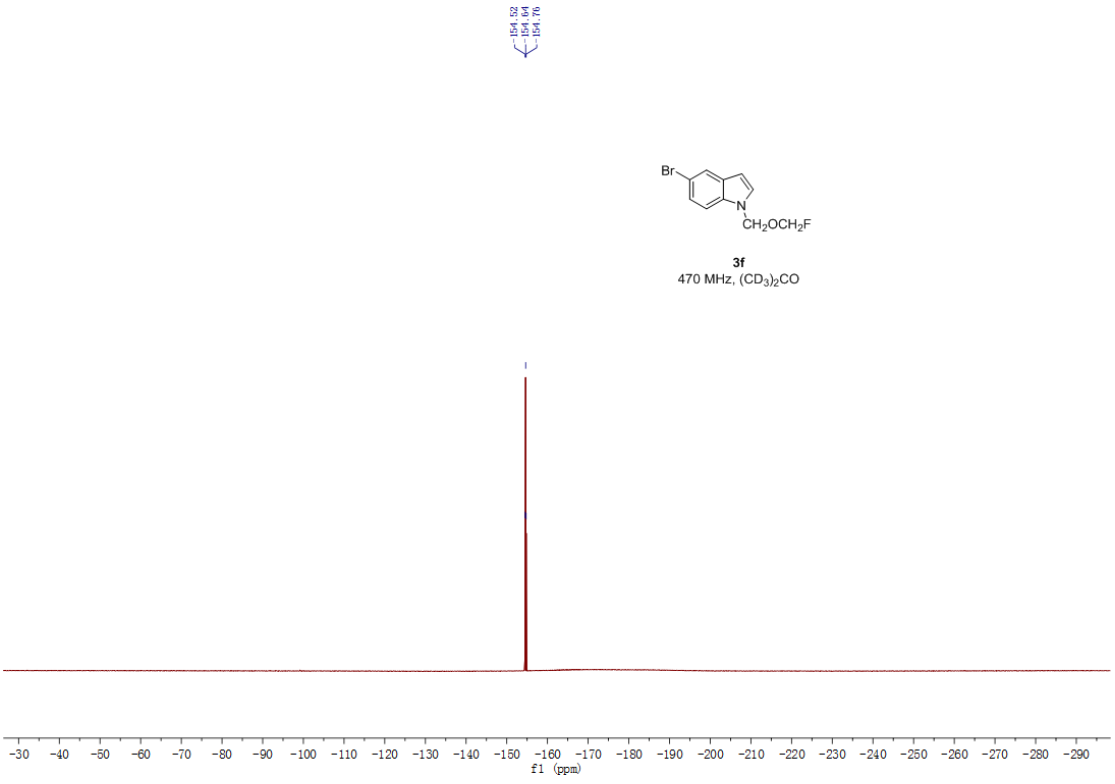
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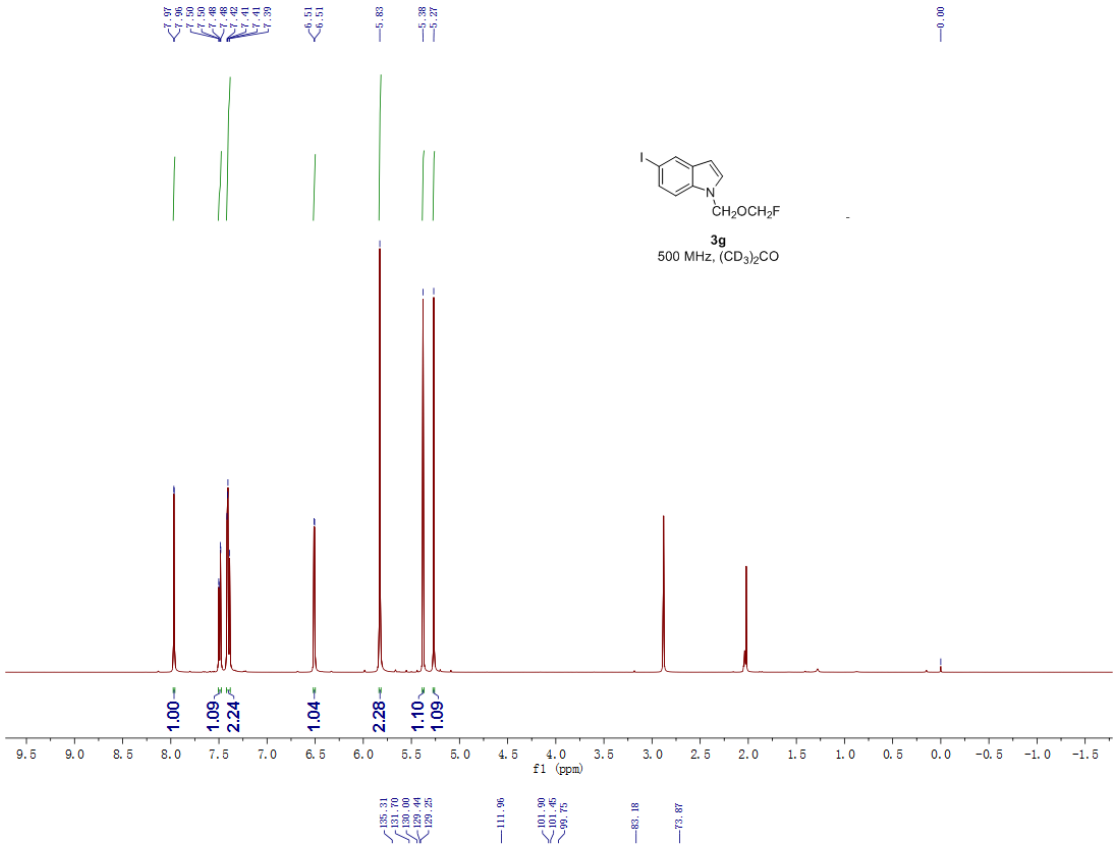
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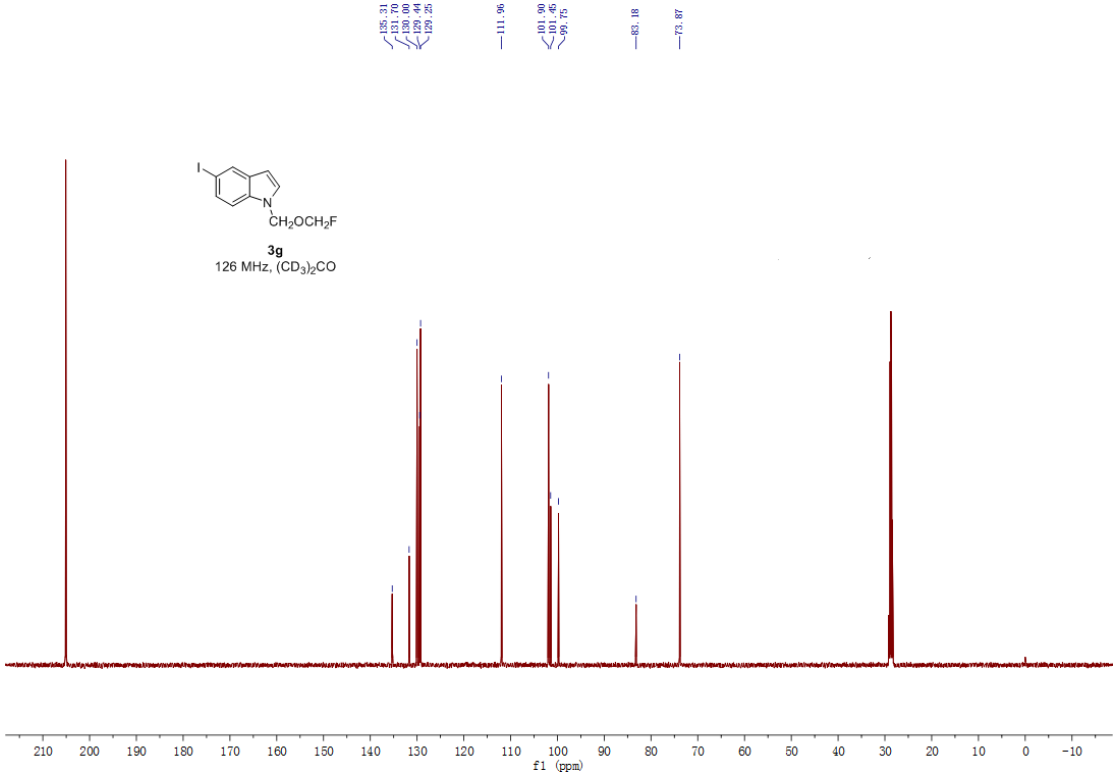
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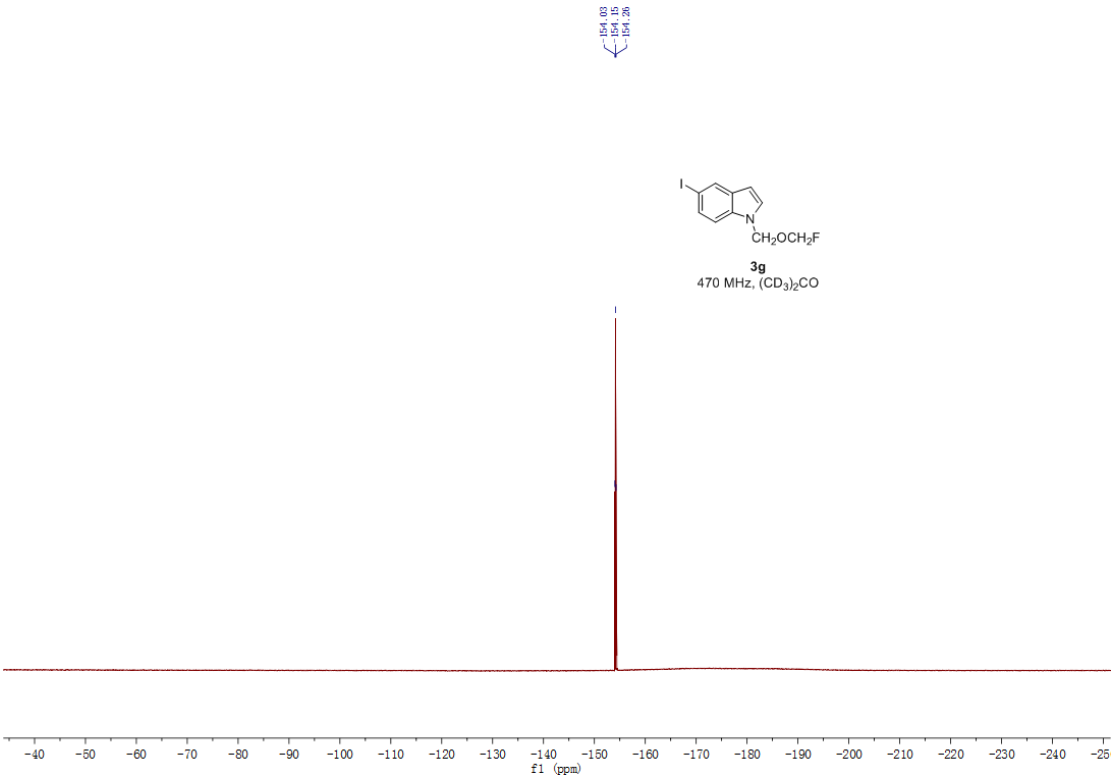
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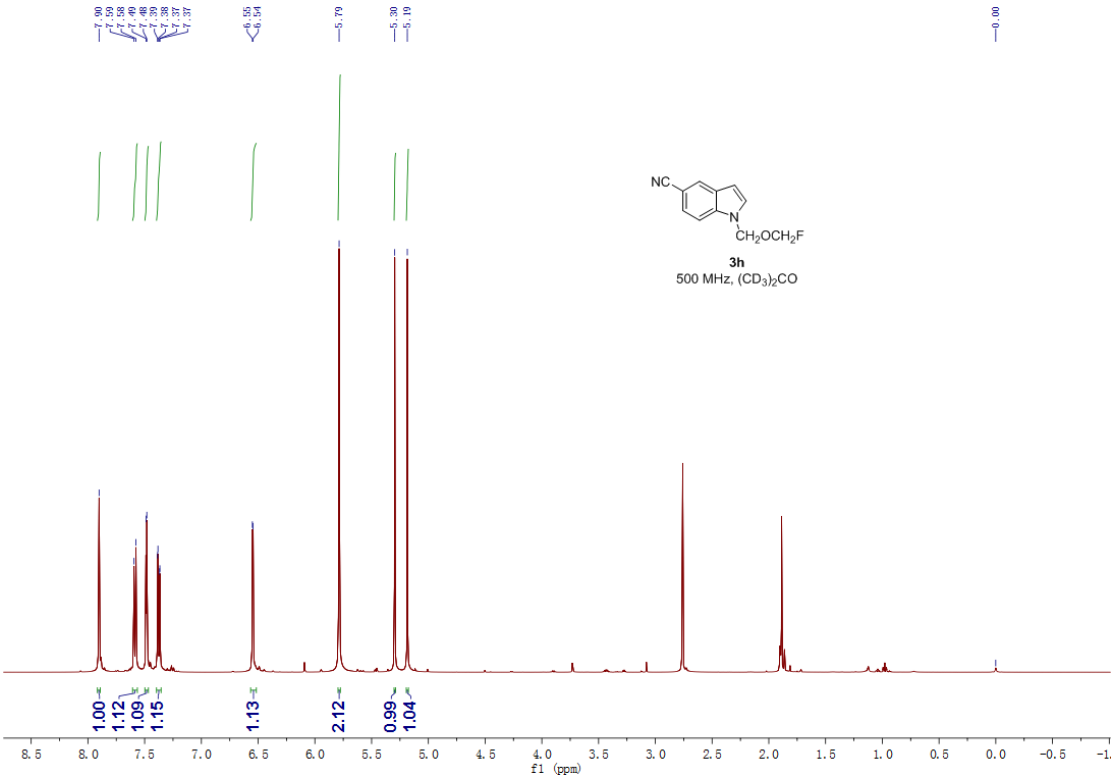
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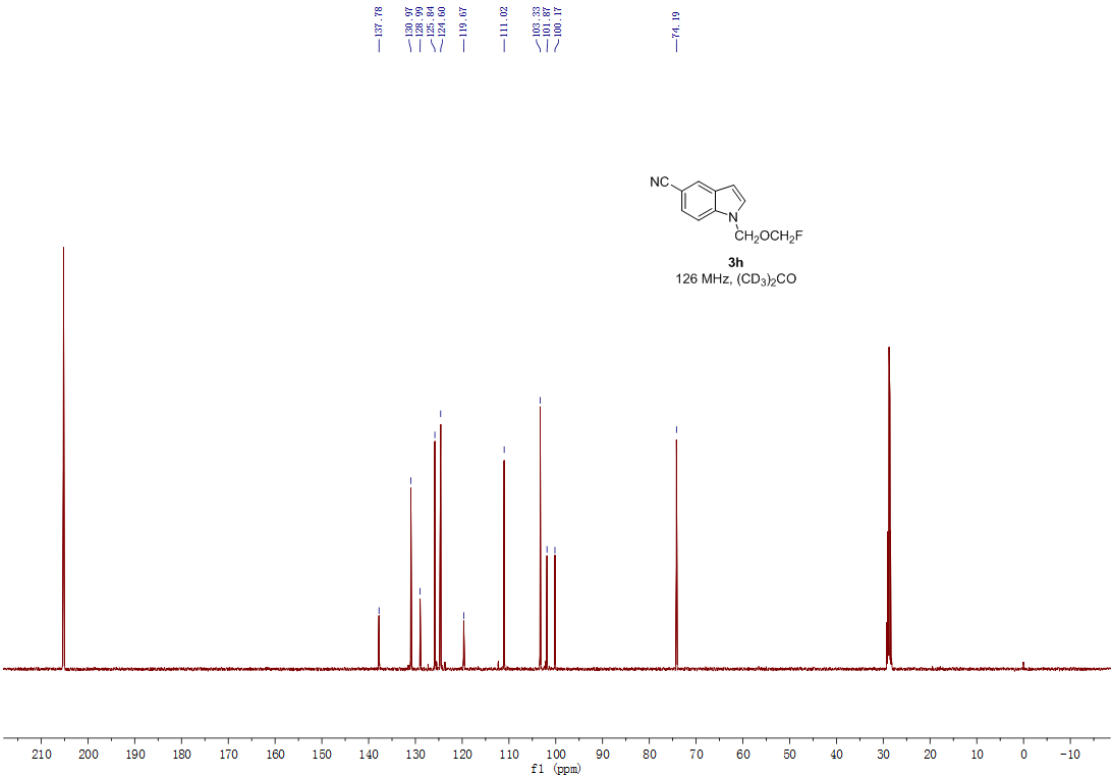
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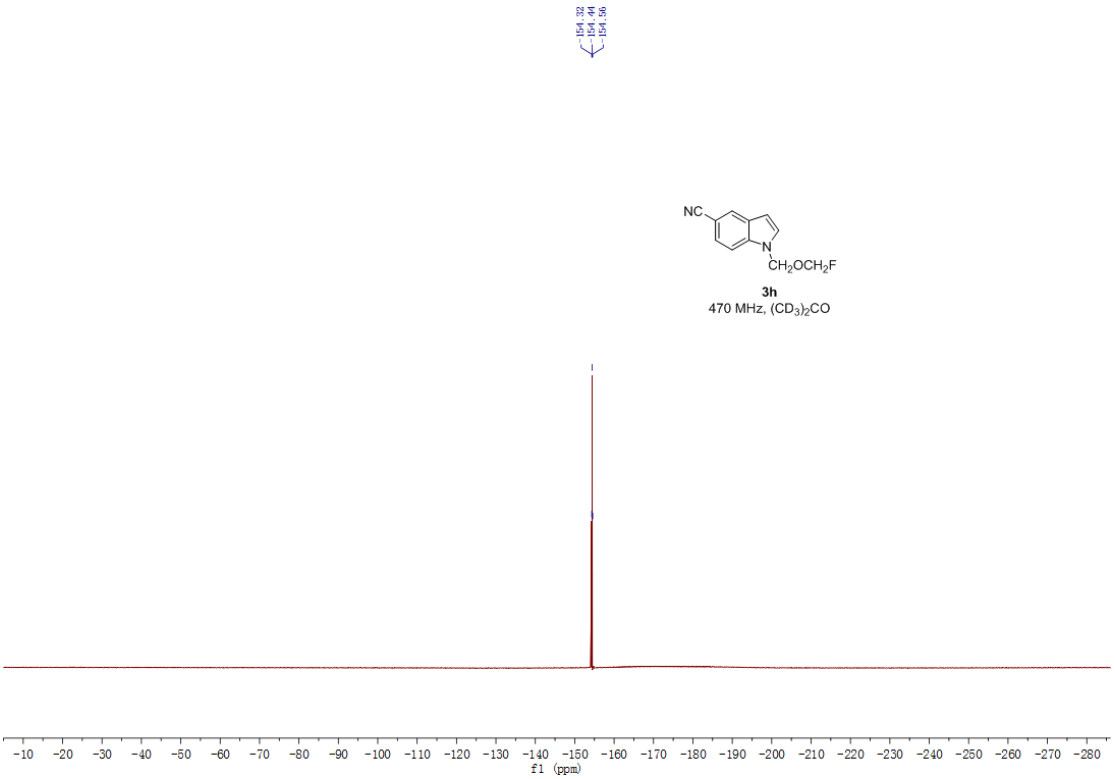
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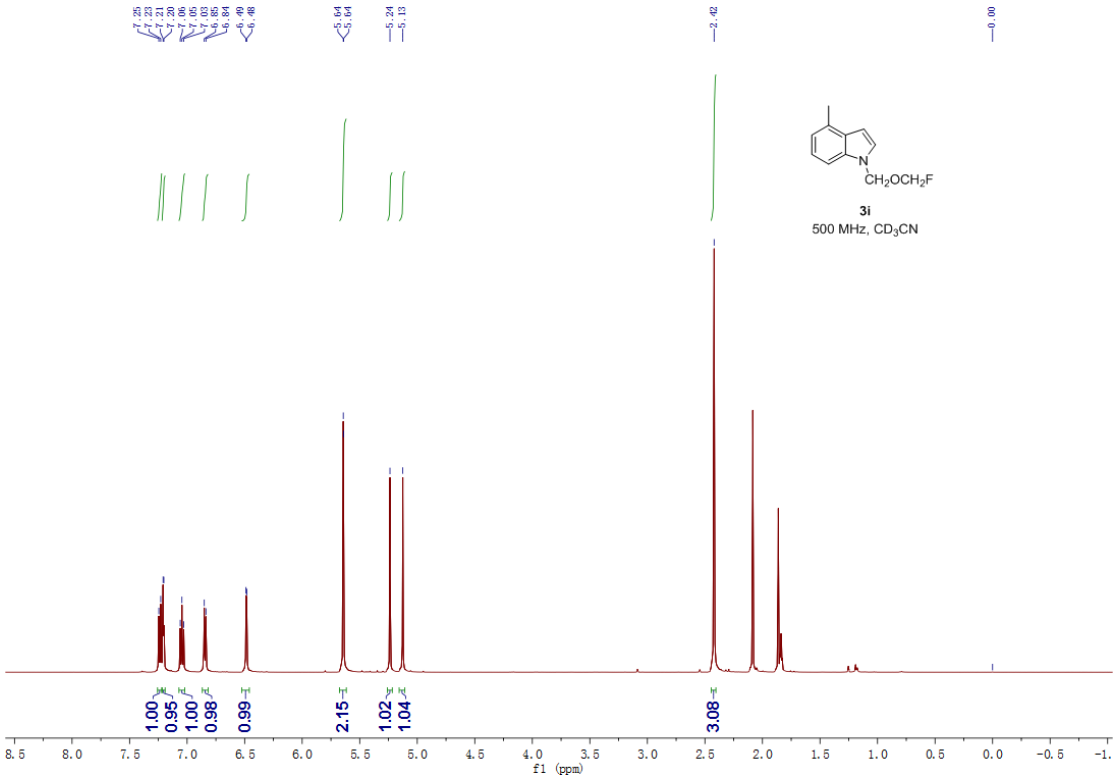
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CH2OCH2F
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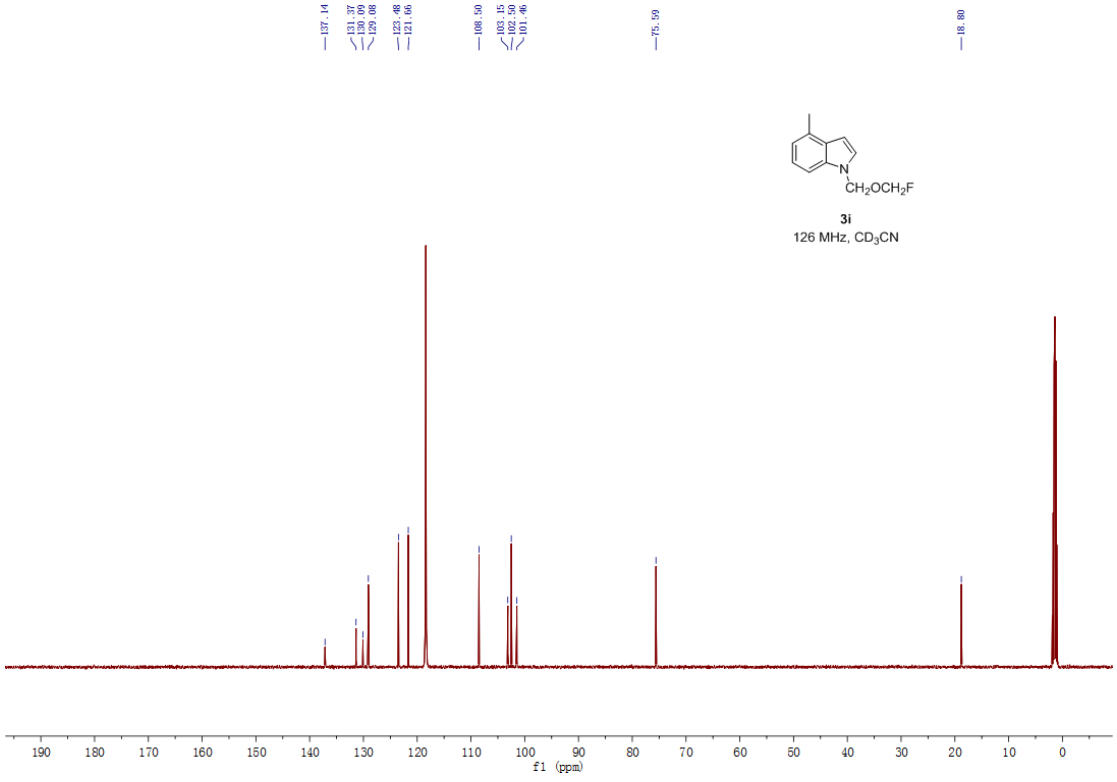
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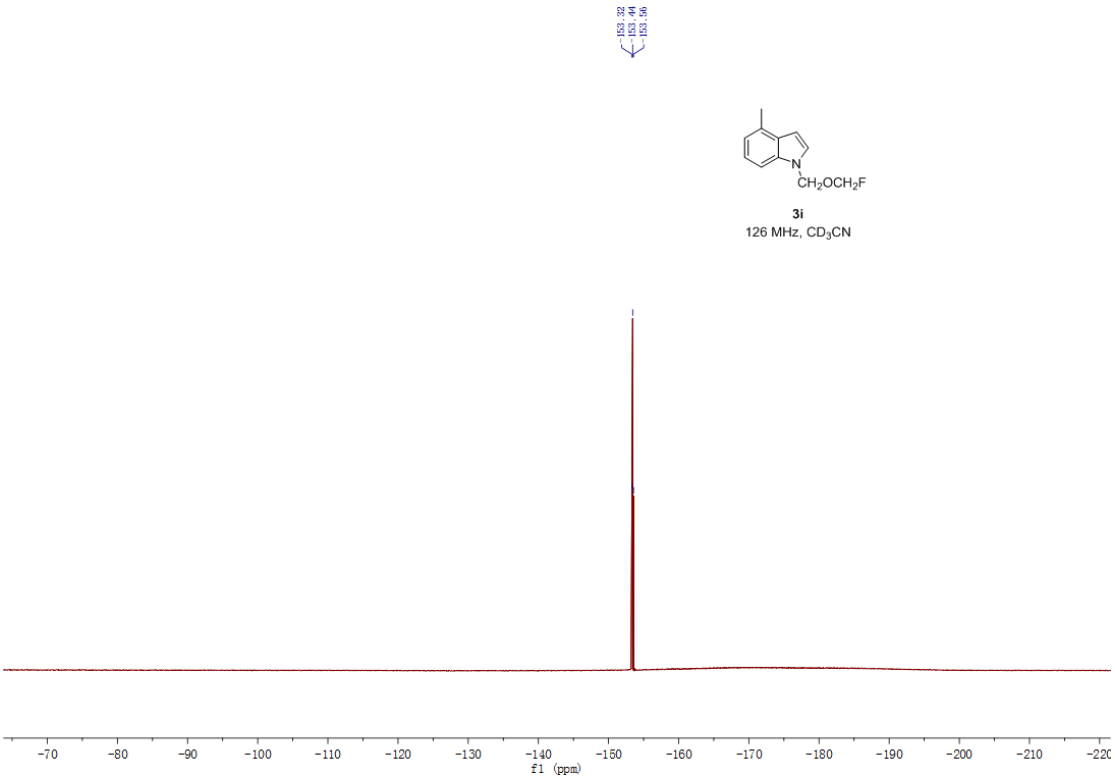
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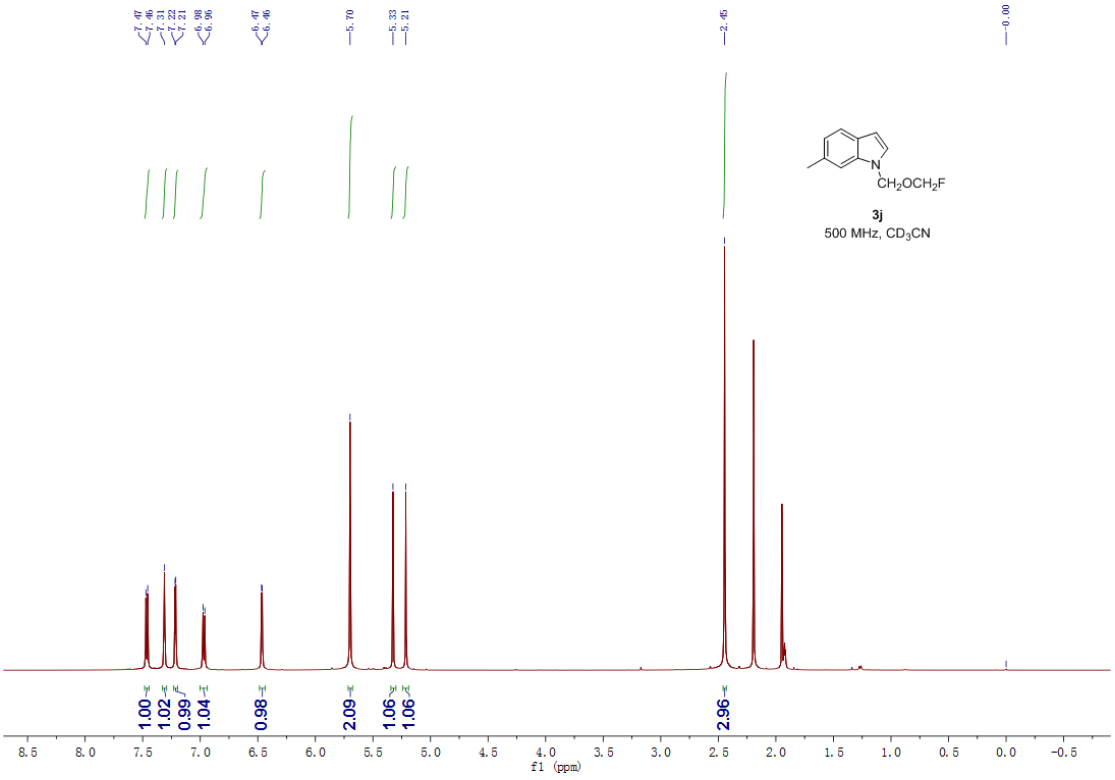
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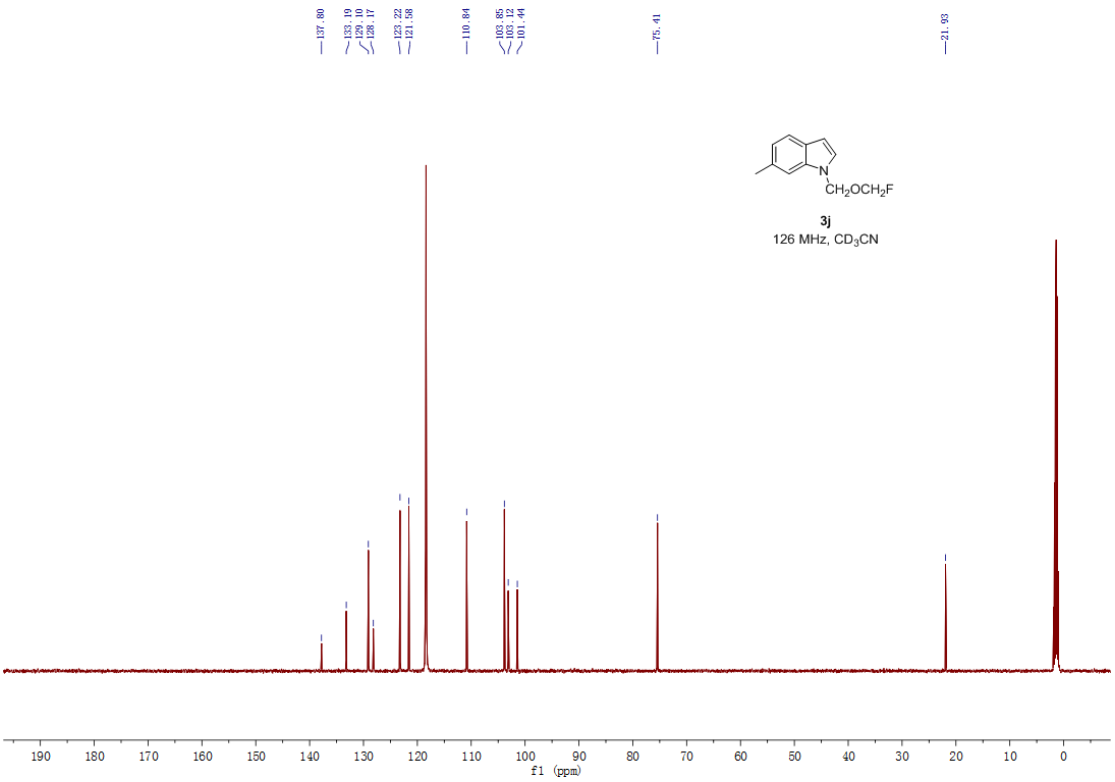
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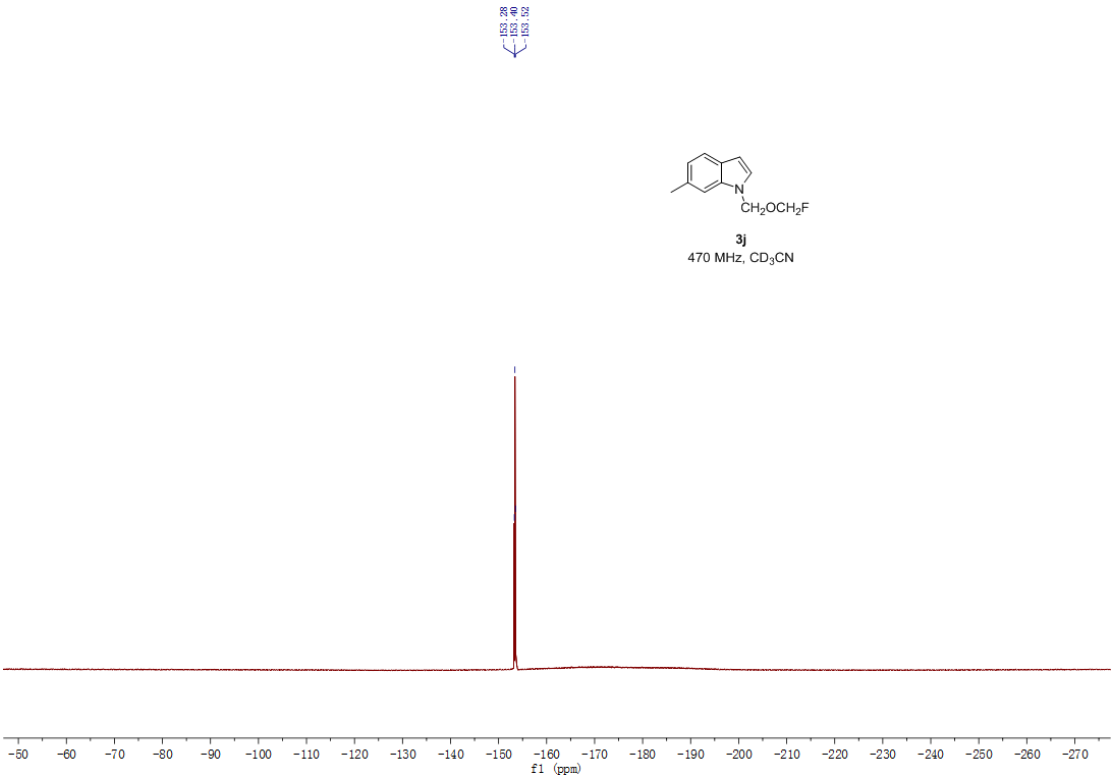
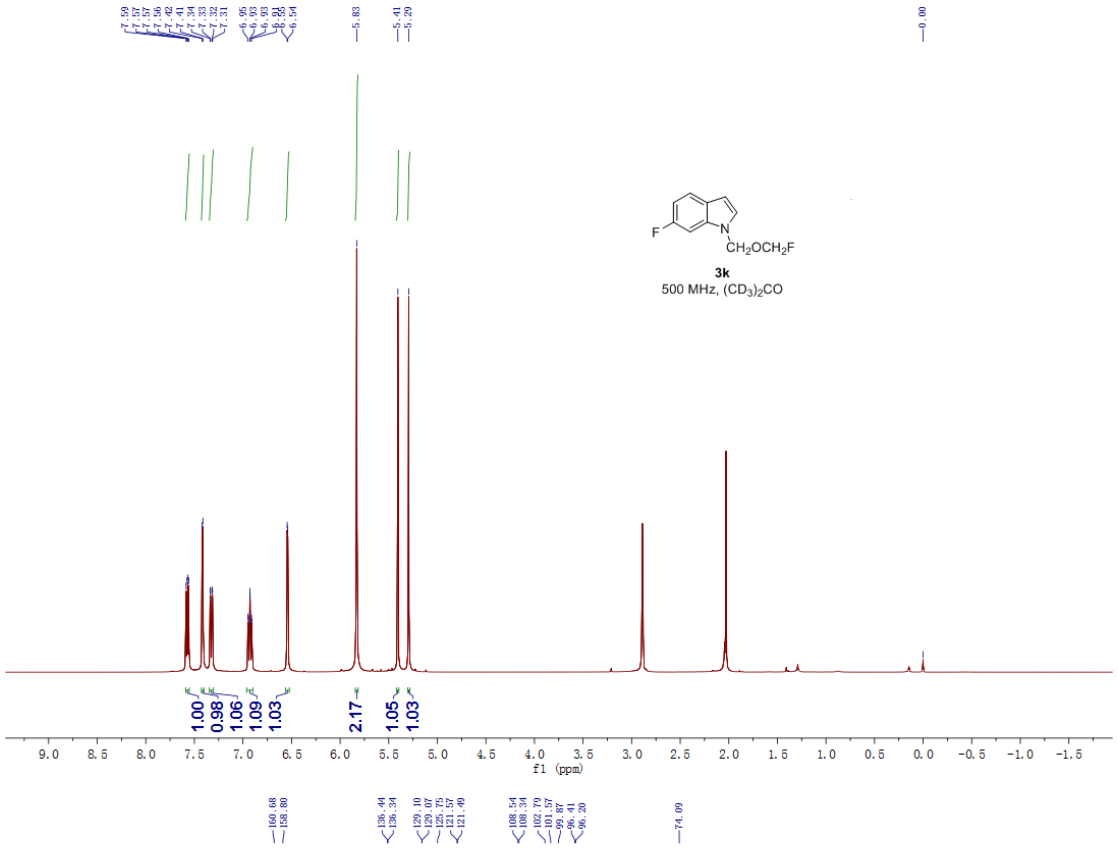
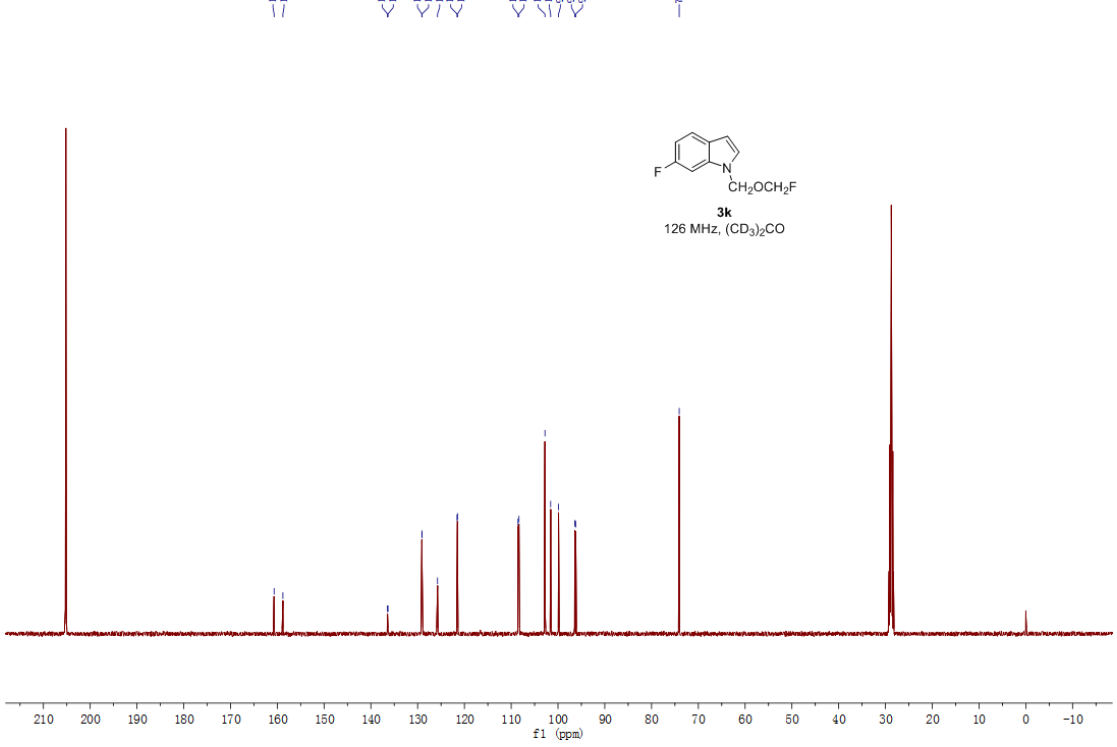
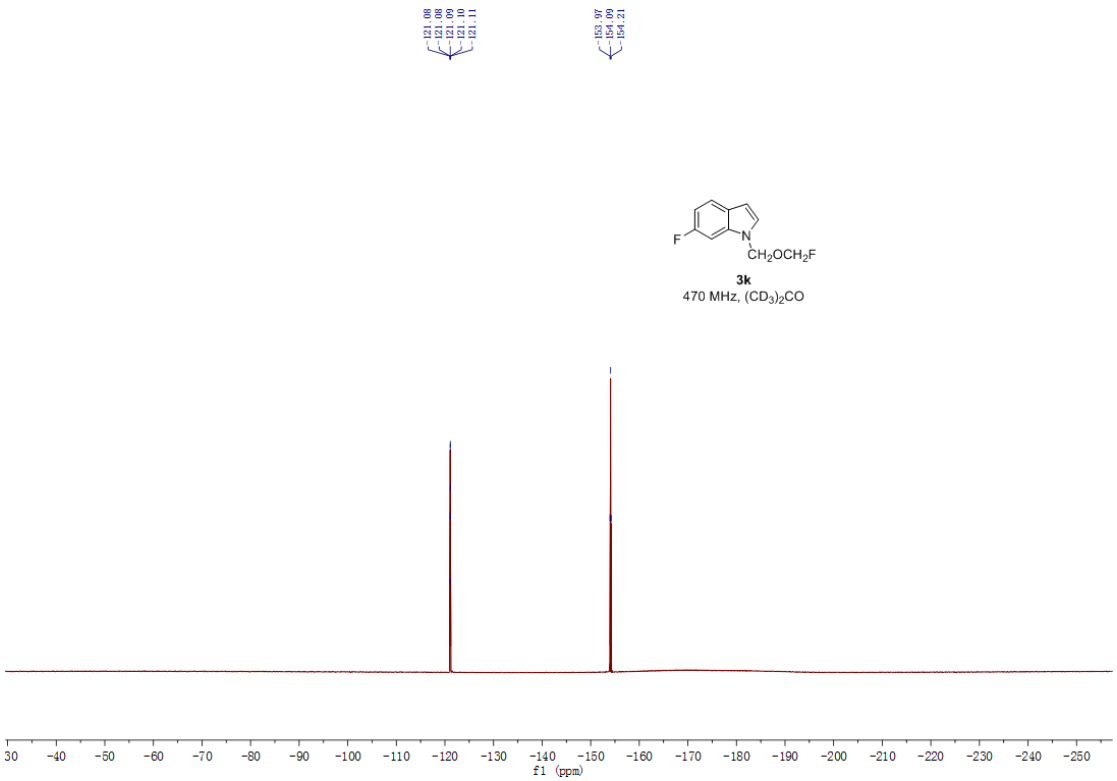
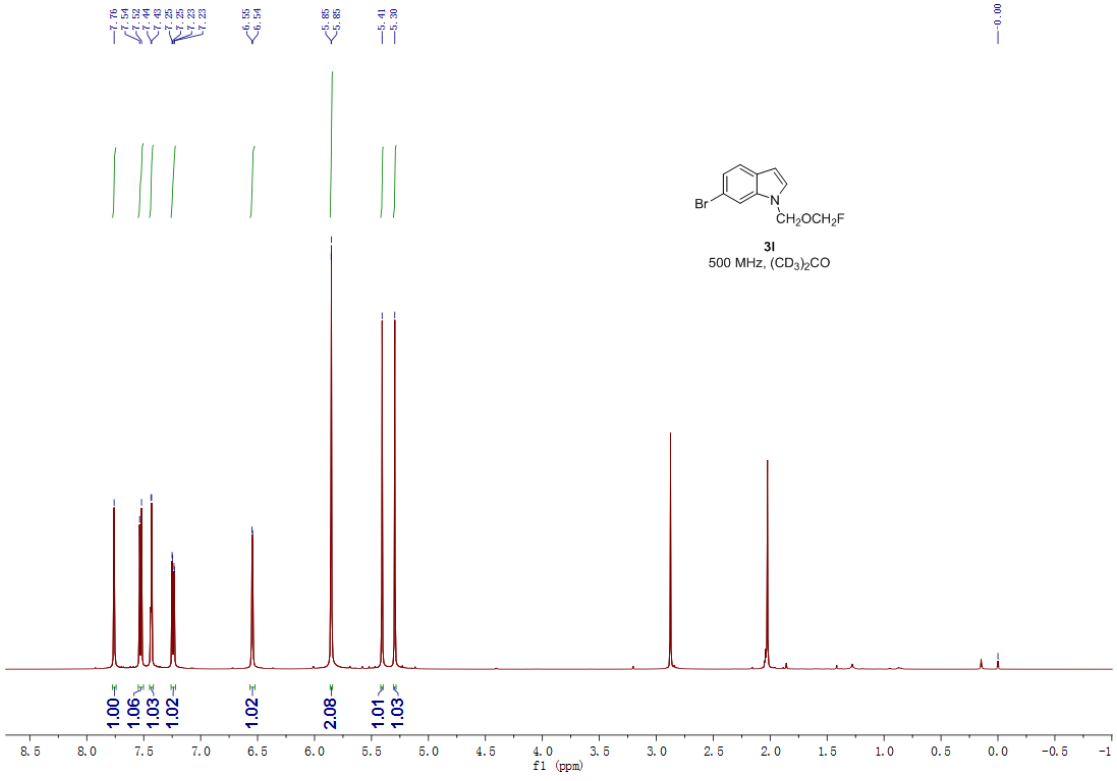
f1 (ppm)

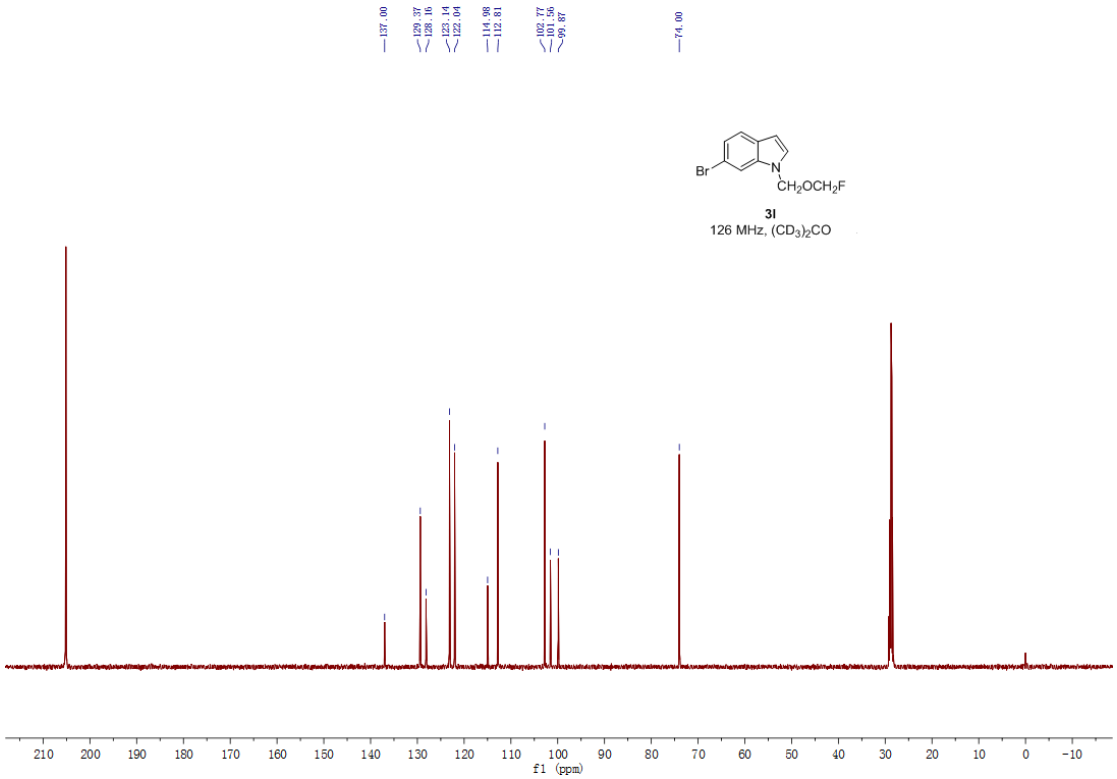

153.28
153.40
153.52
CH2OCH2F
3j
470 MHz, CD3CN
f1 (ppm)

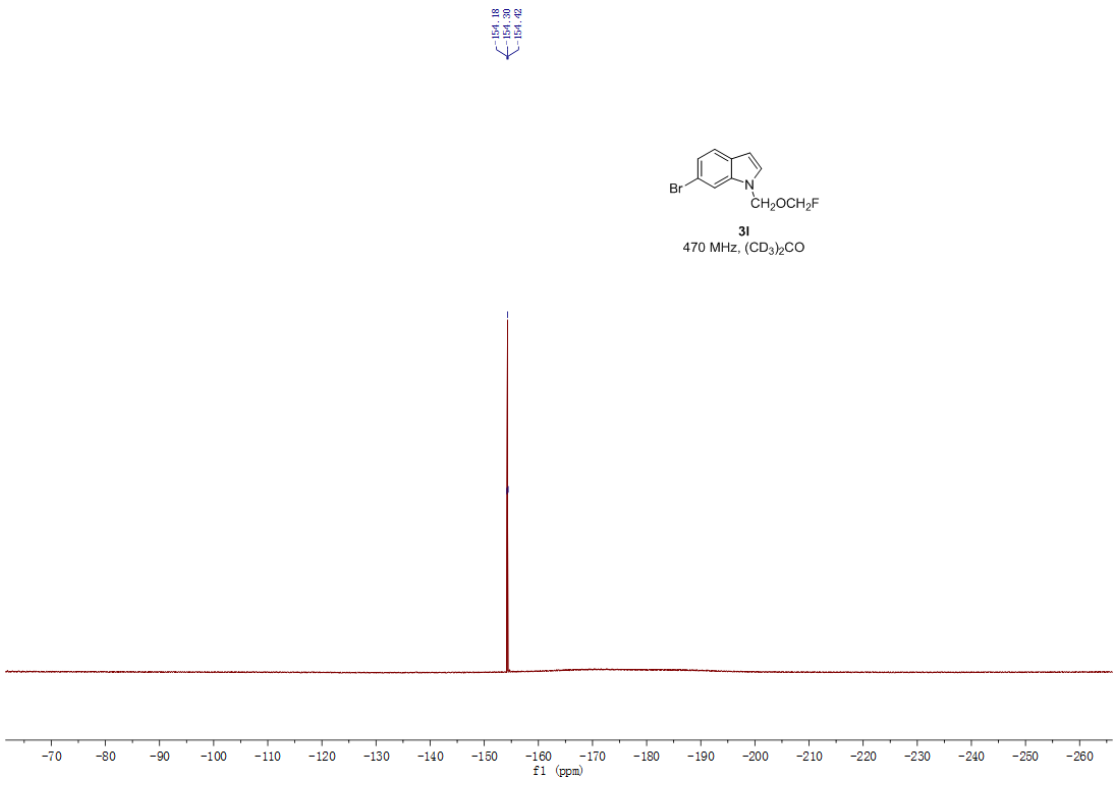

7.59
7.57
7.57
7.56
7.42
7.41
7.34
7.33
7.32
7.31
6.95
6.93
6.93
6.91
6.54
5.83
5.41
5.29
0.00
F
N
CH2OCH2F
3k
500 MHz, (CD3)2CO
1.00
0.98
1.06
1.09
1.03
2.17
1.05
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

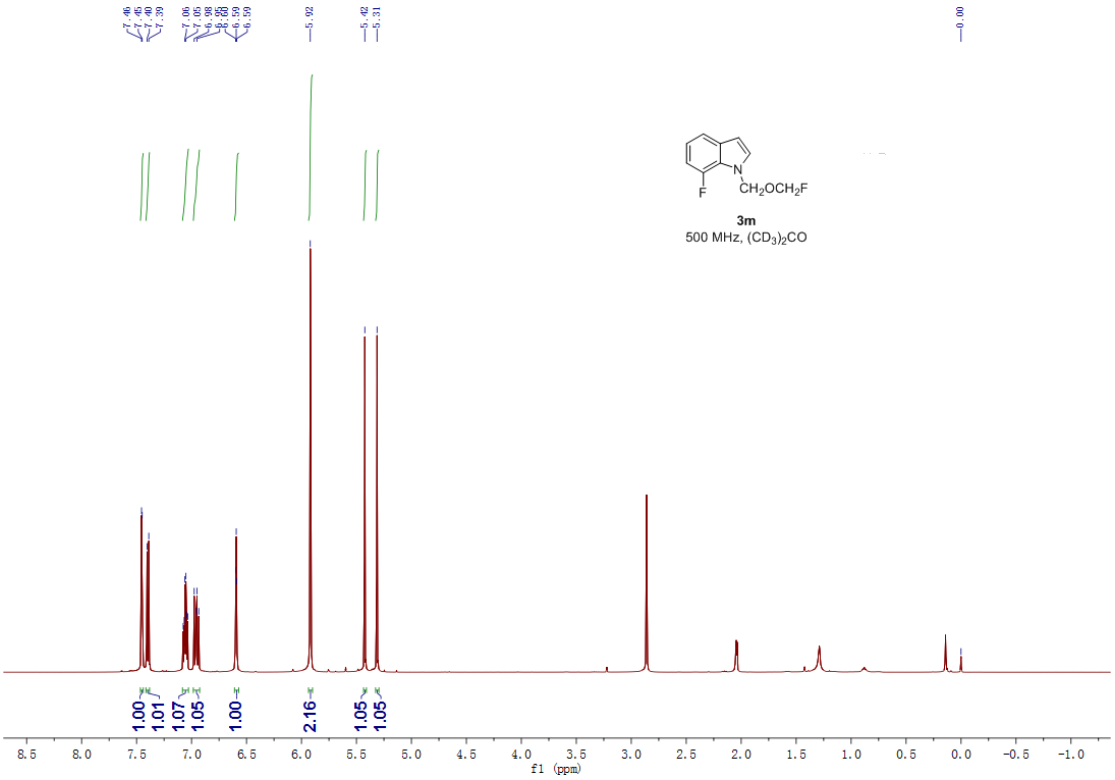

160.68
158.80
136.44
136.34
129.10
129.07
125.75
121.57
121.49
108.54
108.34
102.79
101.57
98.87
98.41
96.20
74.09
F
N
CH2OCH2F
3k
126 MHz, (CD3)2CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

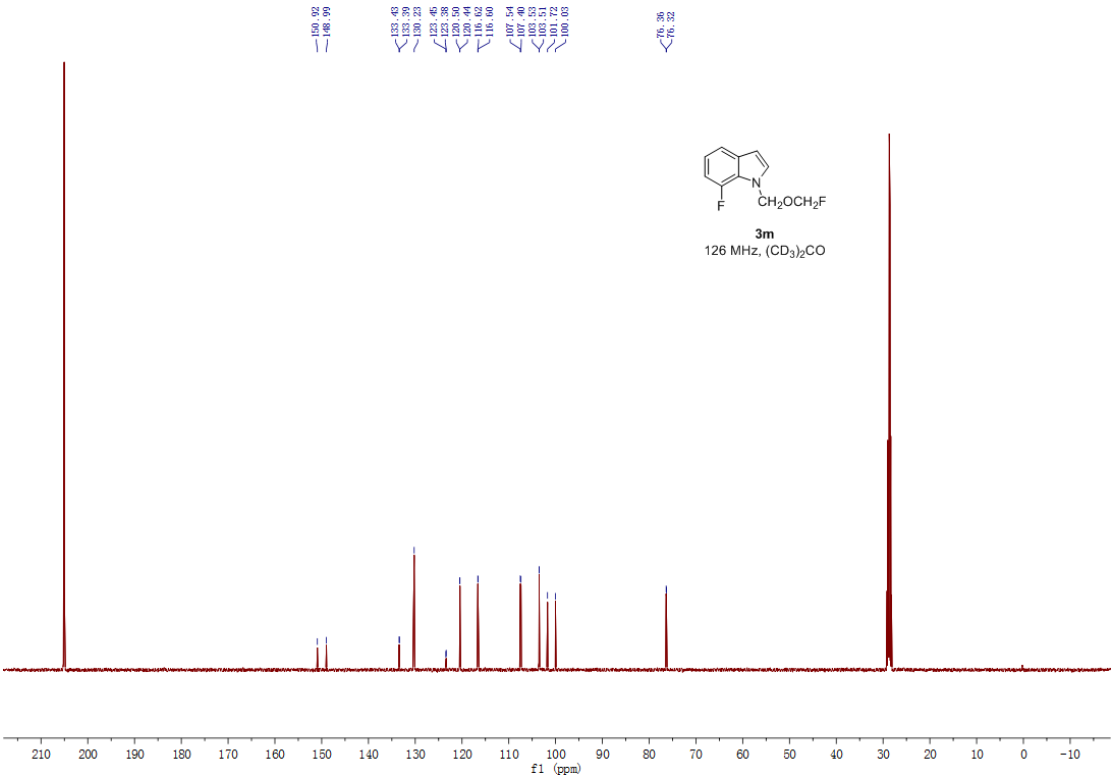

121.08
121.08
121.09
121.10
121.11
153.97
154.09
154.21
F
N
CH2OCH2F
3k
470 MHz, (CD3)2CO
f1 (ppm)

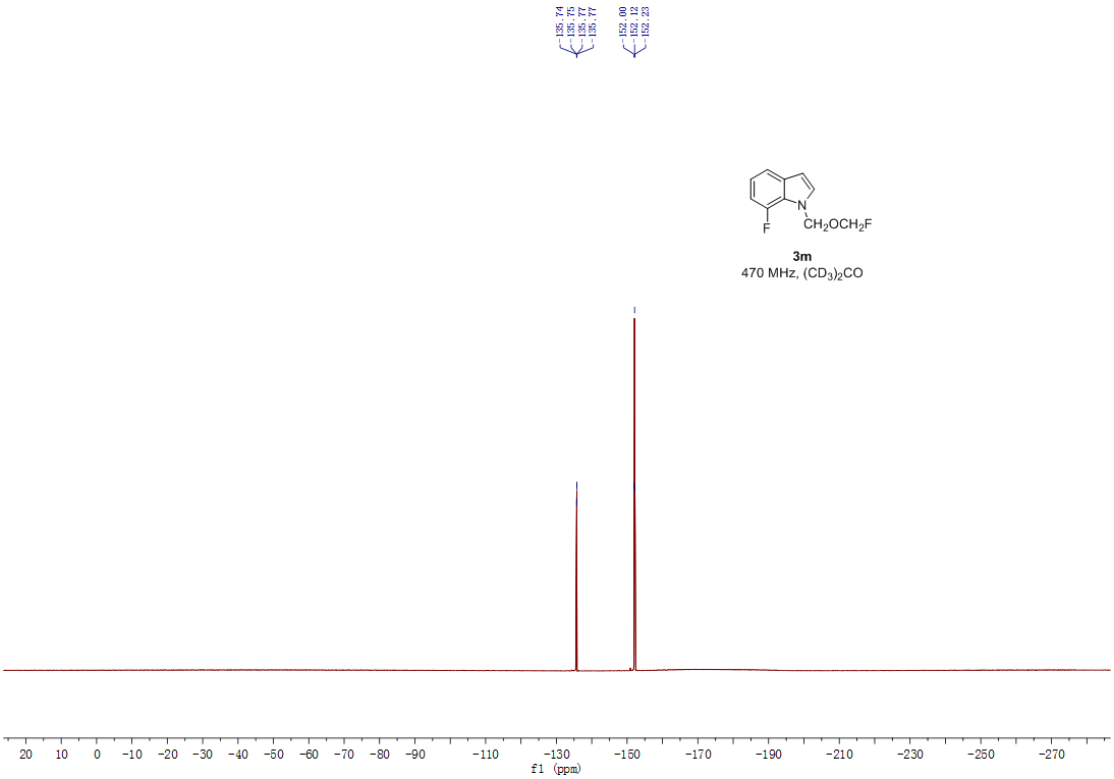

7.76
7.54
7.53
7.44
7.43
7.25
7.24
7.23
7.23
6.55
6.54
5.85
5.85
5.41
5.39
-0.00
Br
N
CH2OCH2F
3l
500 MHz, (CD3)2CO
1.00
1.06
1.03
1.02
1.02
2.08
1.01
1.03
f1 (ppm)

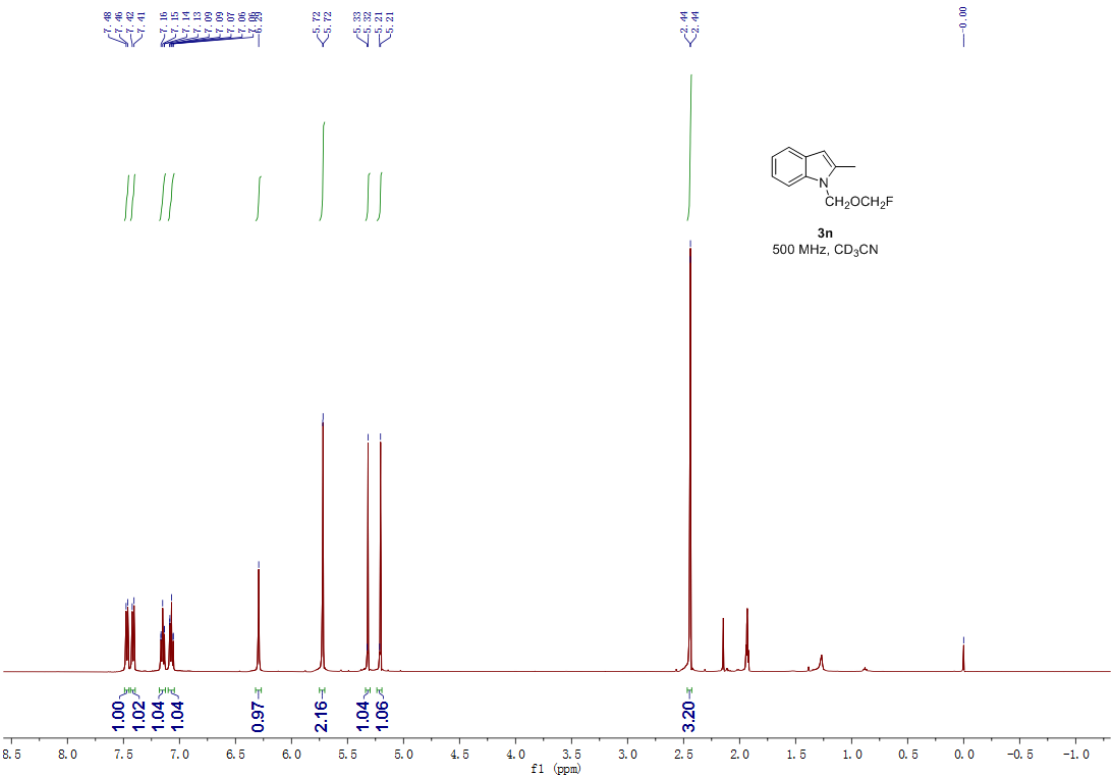

137.00
129.37
128.16
123.14
122.04
114.98
112.81
102.77
101.56
99.87
74.00
Br
N
CH2OCH2F
3l
126 MHz, (CD3)2CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

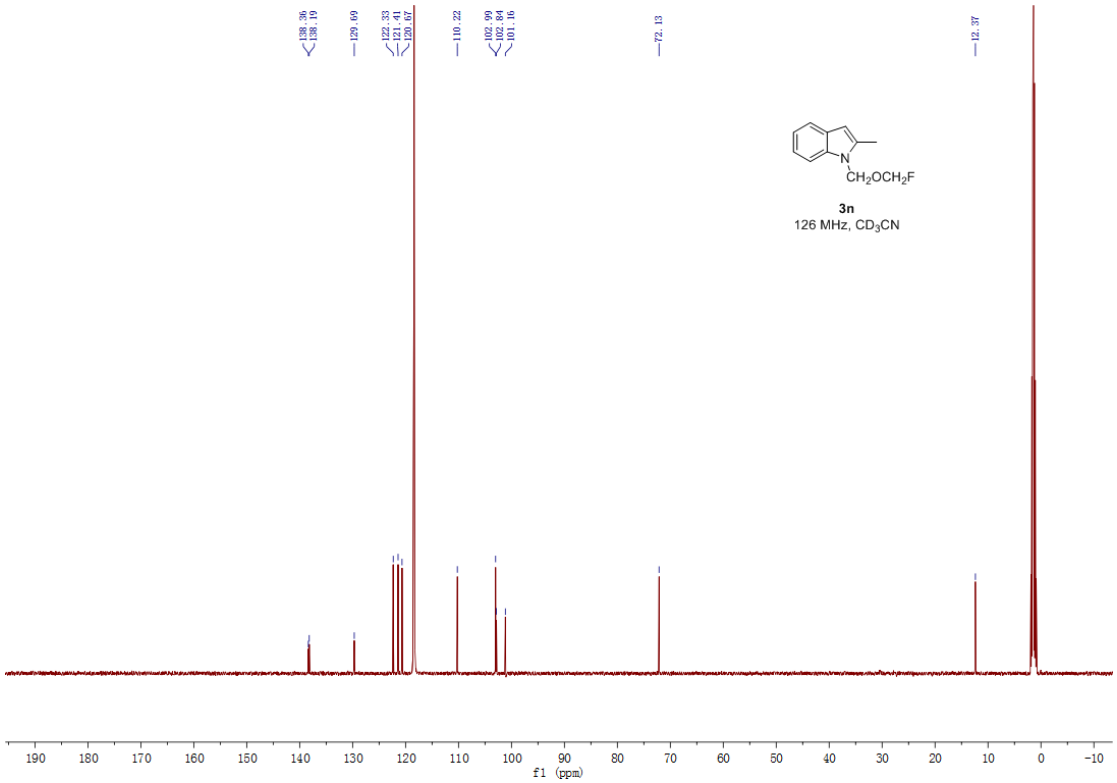

154.18
154.30
154.42
Br
N
CH2OCH2F
3l
470 MHz, (CD3)2CO
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260
f1 (ppm)

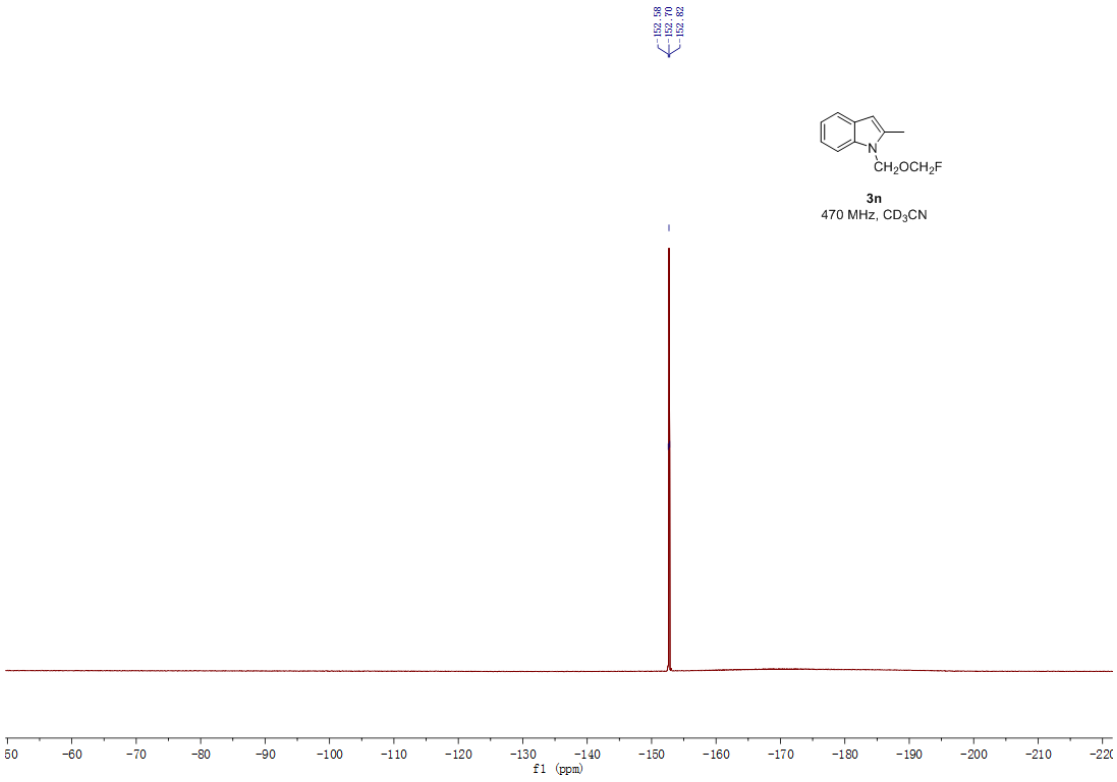

7.46
7.45
7.40
7.39
7.06
7.05
6.98
6.60
6.59
6.59
5.92
5.42
5.31
0.00
N
F
CH2OCH2F
3m
500 MHz, (CD3)2CO
1.00
1.01
1.07
1.05
1.00
2.16
1.05
1.05
f1 (ppm)

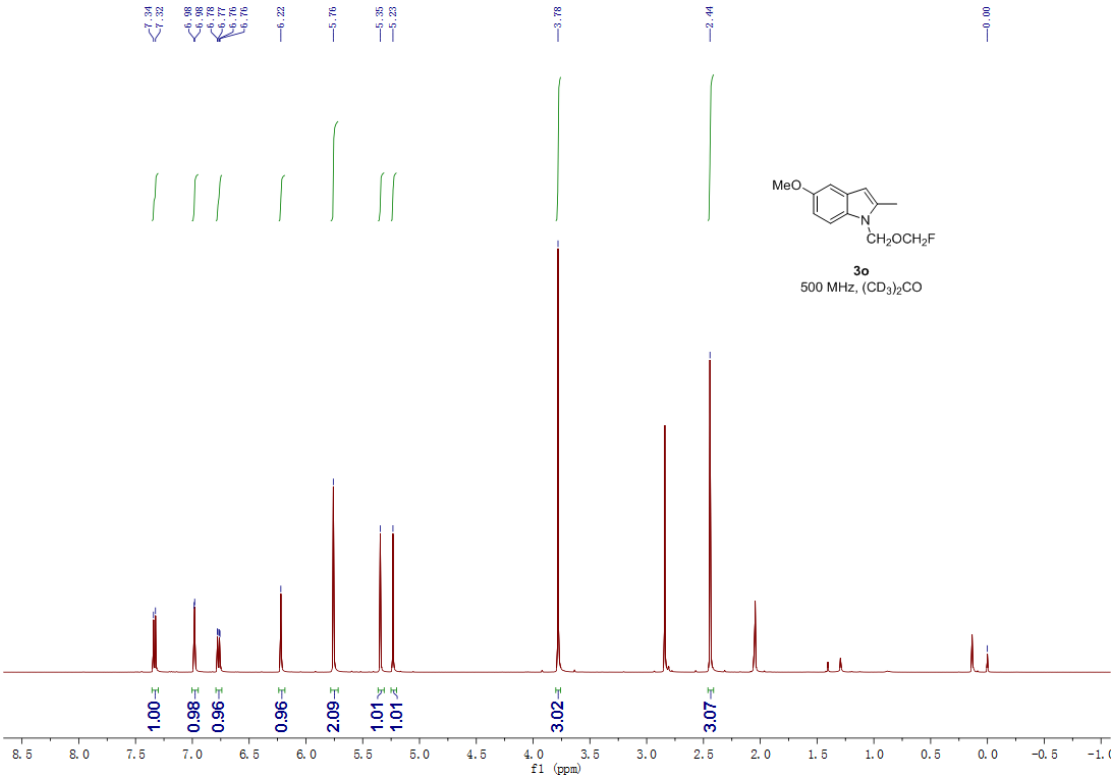

150.92
148.99
133.43
133.39
130.23
123.45
123.38
120.50
120.44
116.62
116.60
107.54
107.40
103.53
103.51
101.72
100.03
76.36
76.32
N
F
CH2OCH2F
3m
126 MHz, (CD3)2CO
f1 (ppm)

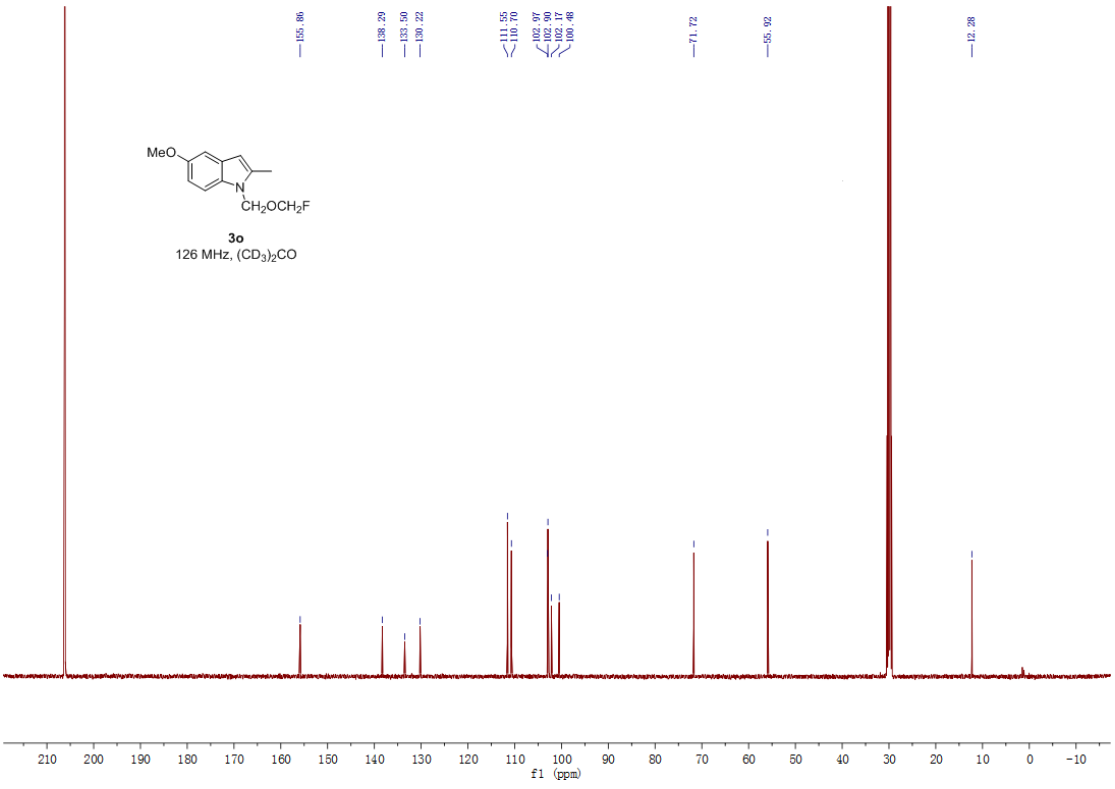

135.74
135.75
135.77
135.77
152.00
152.12
152.23
F
N
CH2OCH2F
3m
470 MHz, (CD3)2CO
f1 (ppm)

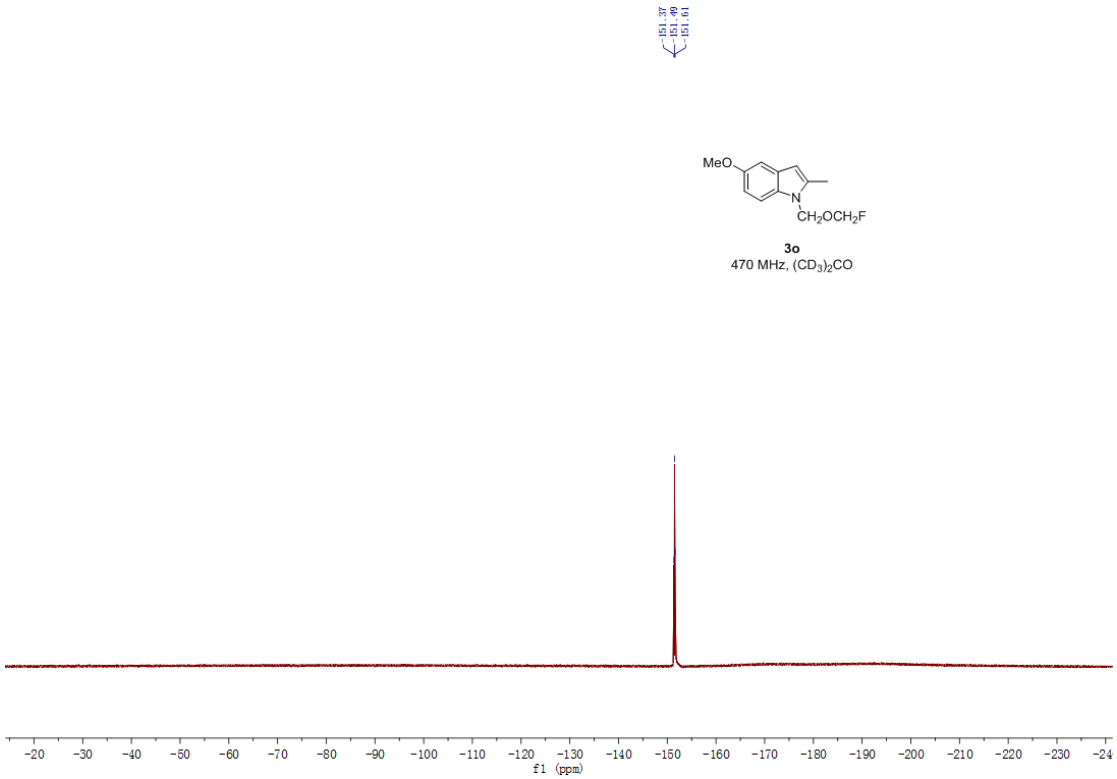

7.48
7.46
7.42
7.41
7.16
7.15
7.14
7.13
7.09
7.09
7.07
7.06
6.99
6.98
5.72
5.72
5.33
5.21
5.21
2.44
2.44
0.00
N
CH2OCH2F
3n
500 MHz, CD3CN
1.00
1.02
1.04
1.04
0.97
2.16
1.04
1.06
3.20
f1 (ppm)

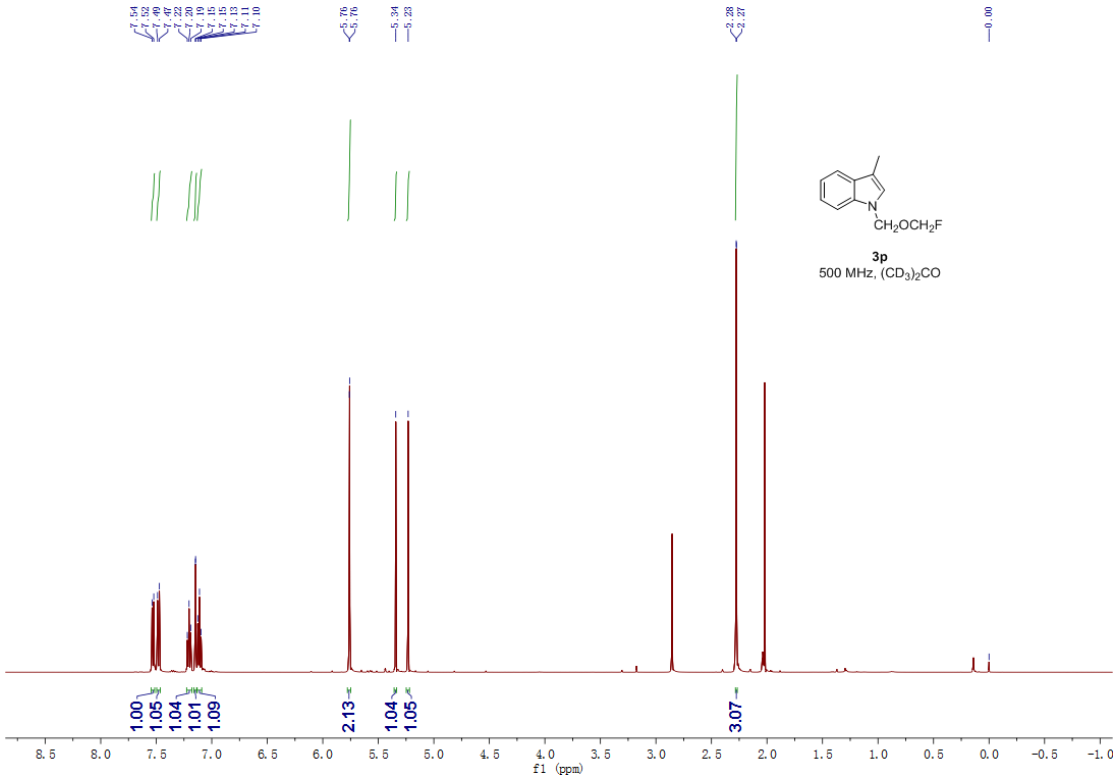

138.36
138.19
129.69
122.33
121.41
120.67
110.22
102.99
102.84
101.16
72.13
12.37
CH2OCH2F
3n
126 MHz, CD3CN
f1 (ppm)

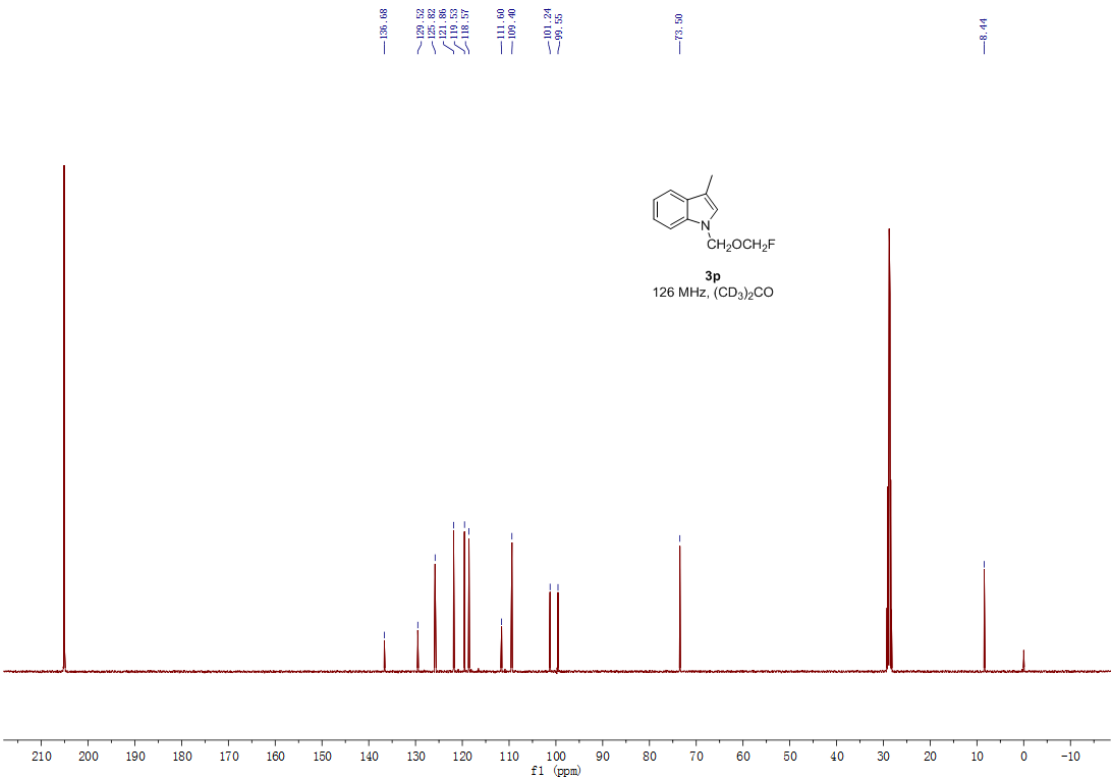

152.58
152.70
152.82
CH2OCH2F
3n
470 MHz, CD3CN
f1 (ppm)

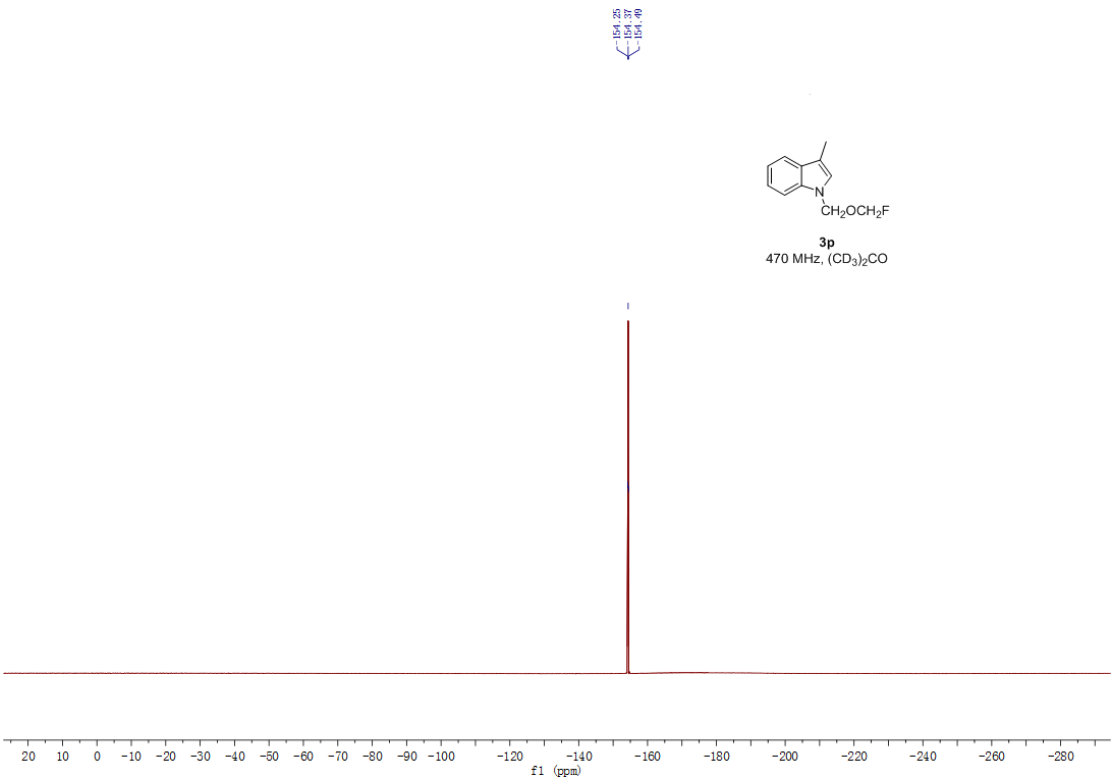

7.34
7.32
6.98
6.98
6.78
6.77
6.76
6.76
6.22
5.76
5.35
5.23
3.78
2.44
0.00
MeO
N
CH2OCH2F
3o
500 MHz, (CD3)2CO
1.00
0.98
0.96
0.96
2.09
1.01
1.01
3.02
3.07
f1 (ppm)

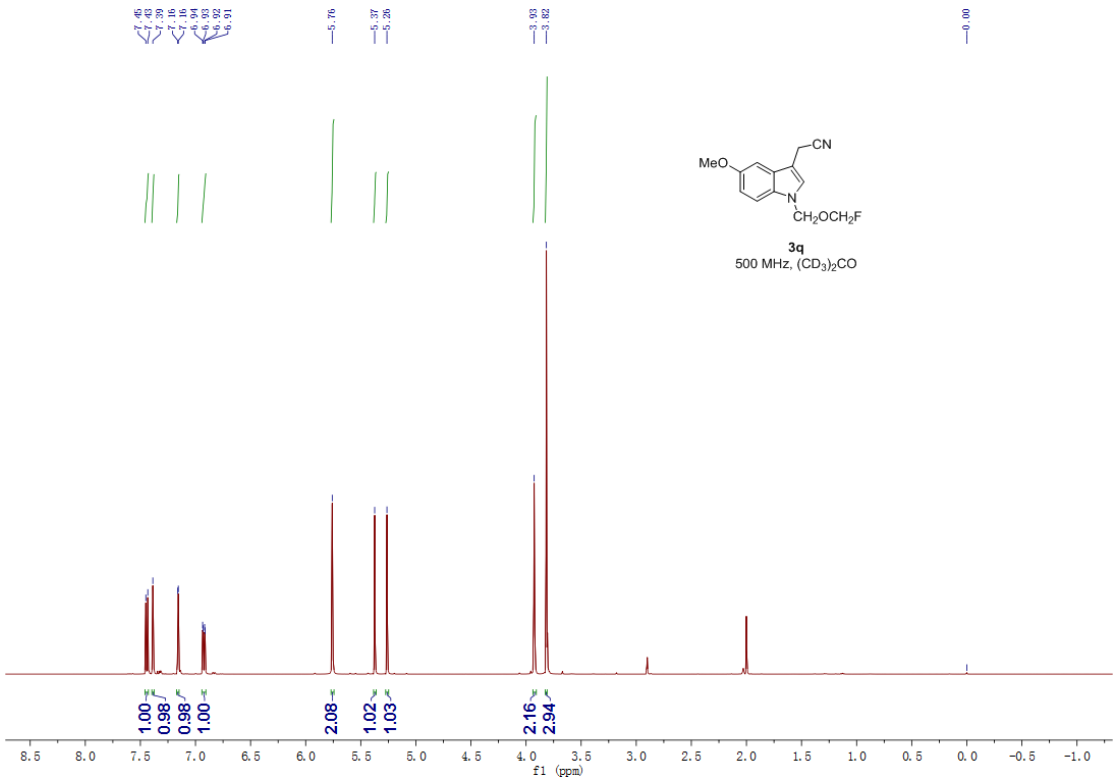

155.86
138.29
133.50
130.22
111.55
110.70
102.97
102.90
102.17
100.48
71.72
55.92
12.28
MeO
N
CH2OCH2F
3o
126 MHz, (CD3)2CO
f1 (ppm)

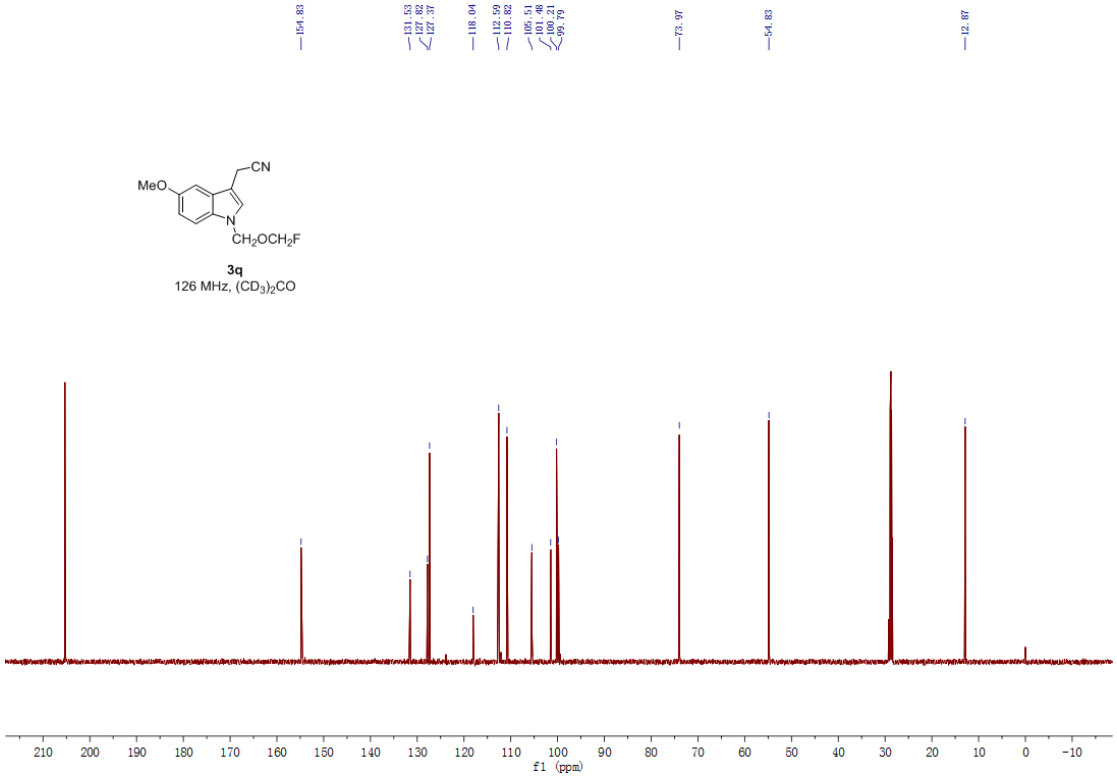

151.37
151.49
151.61
MeO
N
CH2OCH2F
3o
470 MHz, (CD3)2CO
f1 (ppm)

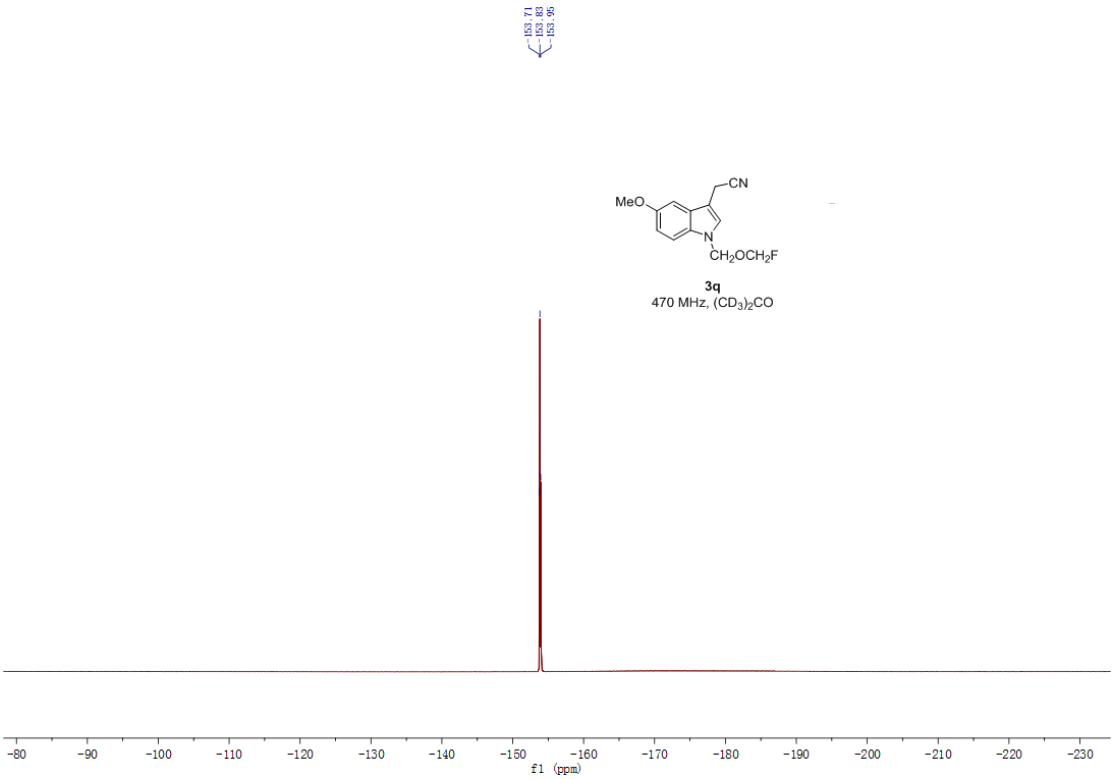

7.54
7.52
7.49
7.47
7.22
7.20
7.19
7.15
7.15
7.13
7.11
7.10
5.76
5.76
5.34
5.23
2.28
2.27
0.00
N
CH2OCH2F
3p
500 MHz, (CD3)2CO
1.00
1.05
1.04
1.01
1.09
2.13
1.04
1.05
3.07
f1 (ppm)

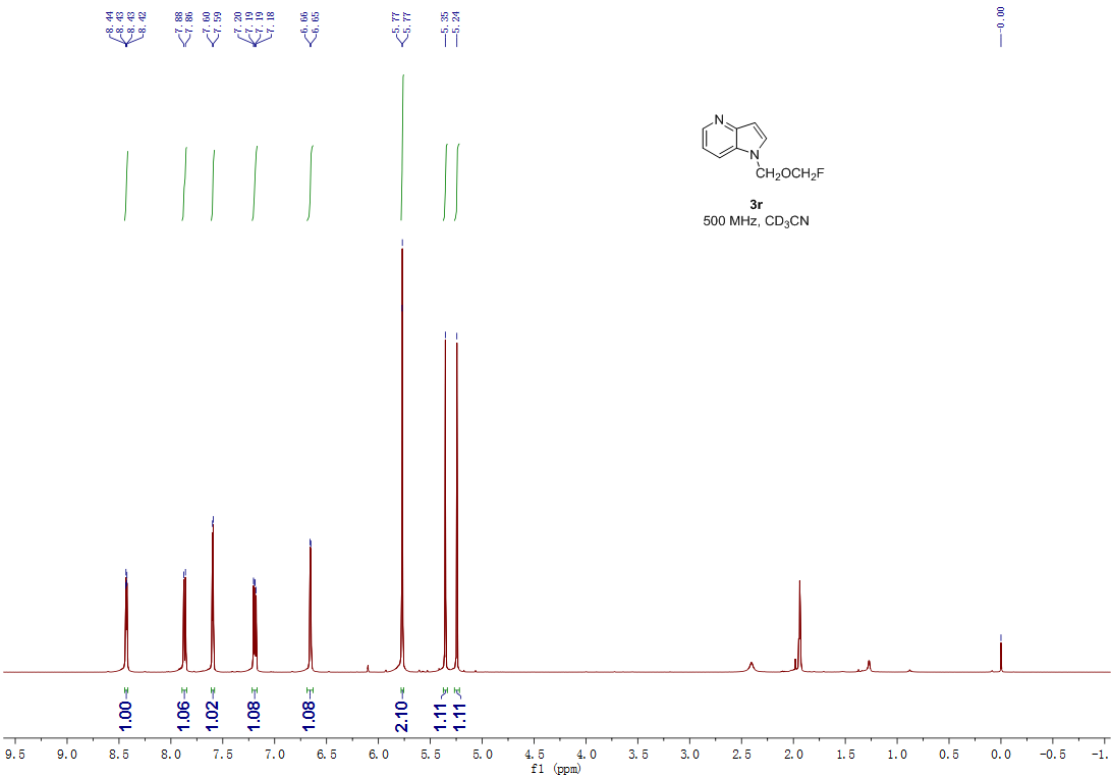

136.68
129.52
125.82
121.86
119.53
118.57
111.60
109.40
101.24
99.55
73.50
8.44
CH2OCH2F
3p
126 MHz, (CD3)2CO
f1 (ppm)

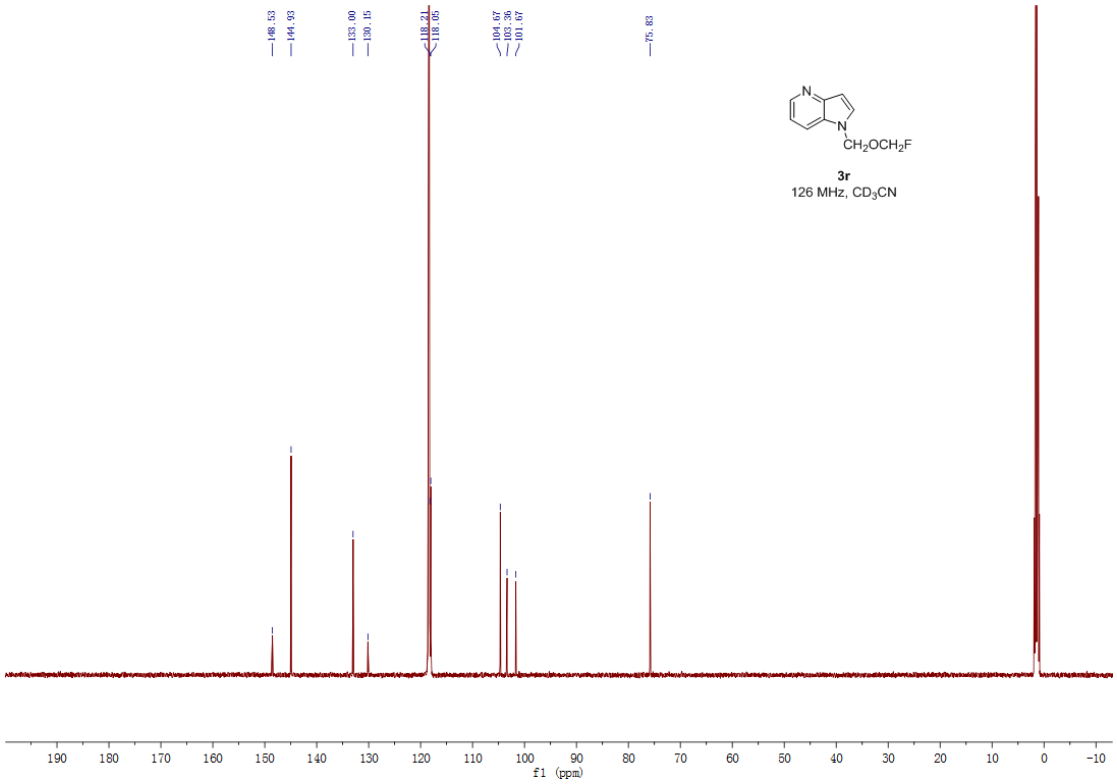

154.25
154.37
154.49
CH2OCH2F
3p
470 MHz, (CD3)2CO
f1 (ppm)

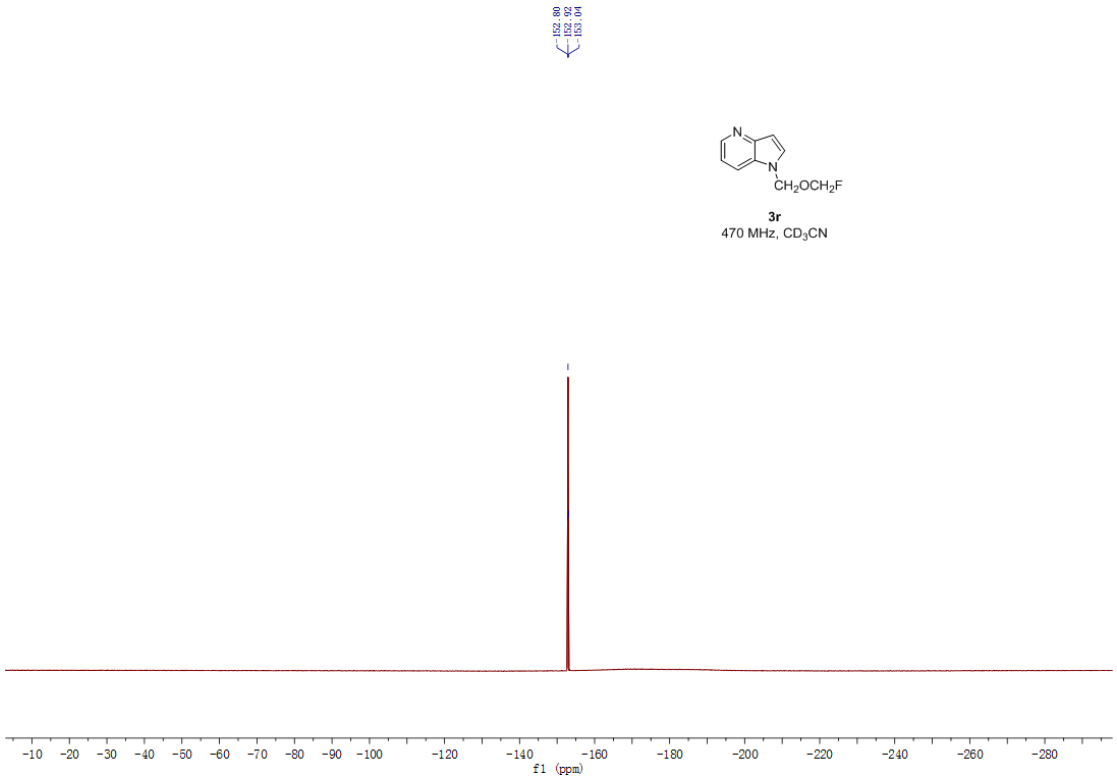

7.45
7.43
7.39
7.16
7.16
6.94
6.93
6.92
6.91
5.76
5.37
5.26
3.93
3.82
0.00
MeO
CN
N
CH2OCH2F
3q
500 MHz, (CD3)2CO
1.00
0.98
0.98
1.00
2.08
1.02
1.03
2.16
2.94
f1 (ppm)

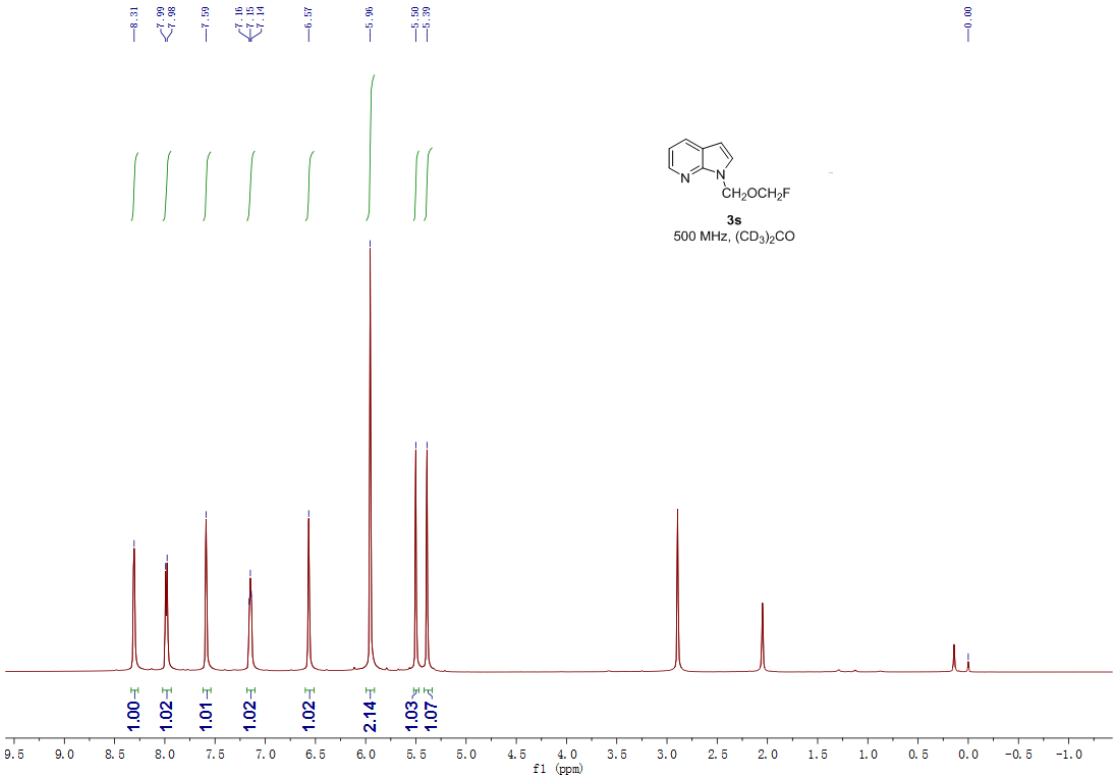

154.83
131.53
127.82
127.37
118.04
112.59
110.82
105.51
101.48
100.21
99.79
73.97
54.83
12.87
MeO
CN
N
CH2OCH2F
3q
126 MHz, (CD3)2CO
f1 (ppm)

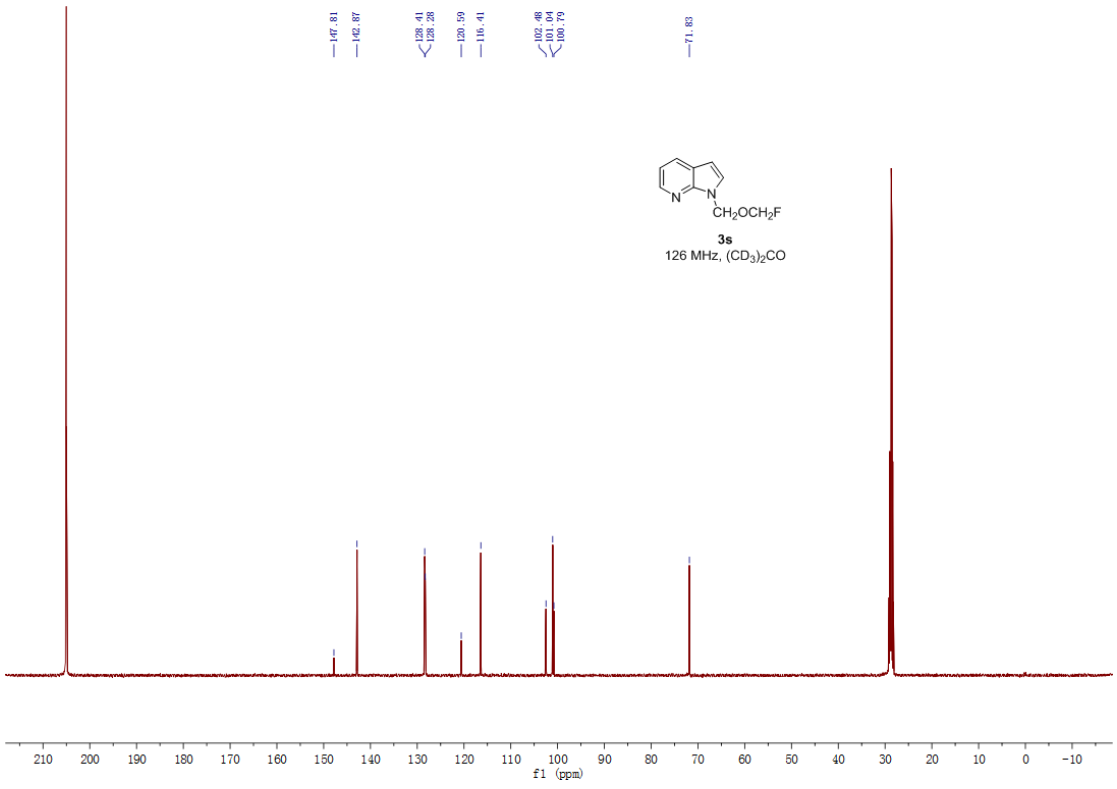

153.71
153.83
153.95
CN
MeO
N
CH2OCH2F
3q
470 MHz, (CD3)2CO
-80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

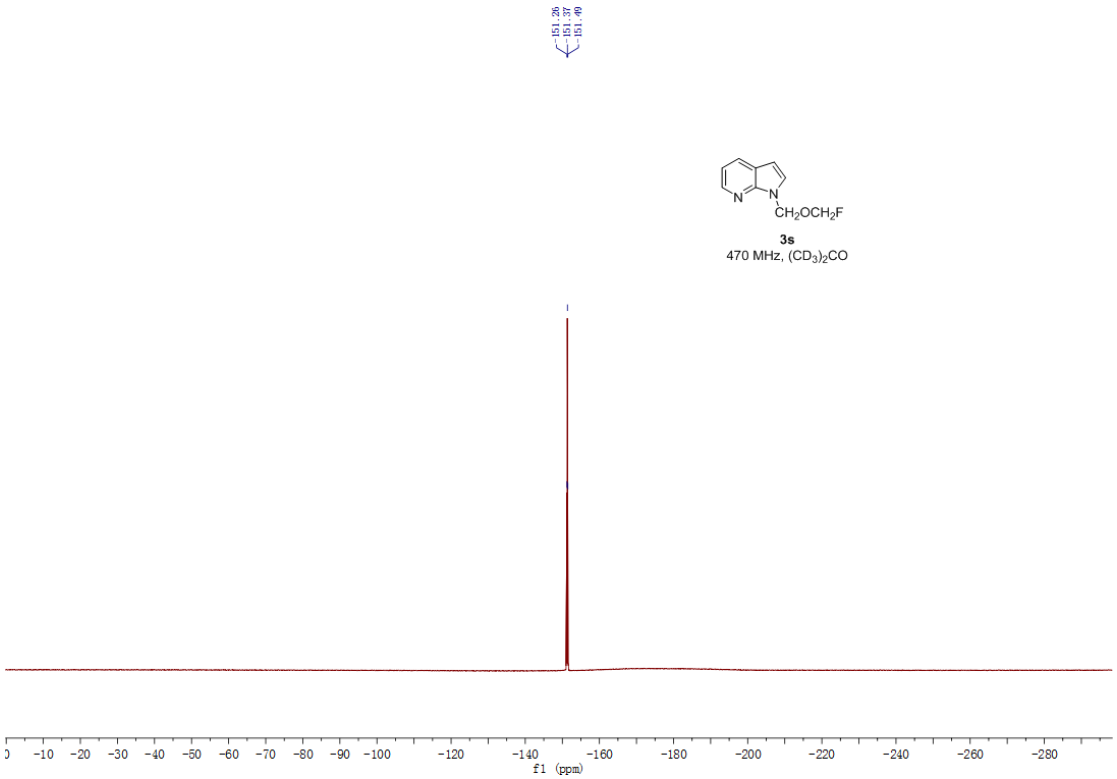

8.44
8.43
8.43
8.42
7.88
7.86
7.60
7.59
7.20
7.19
7.19
7.18
6.66
6.65
5.77
5.77
5.35
5.34
0.00
N
N
CH2OCH2F
3r
500 MHz, CD3CN
1.00
1.06
1.02
1.08
1.08
2.10
1.11
1.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

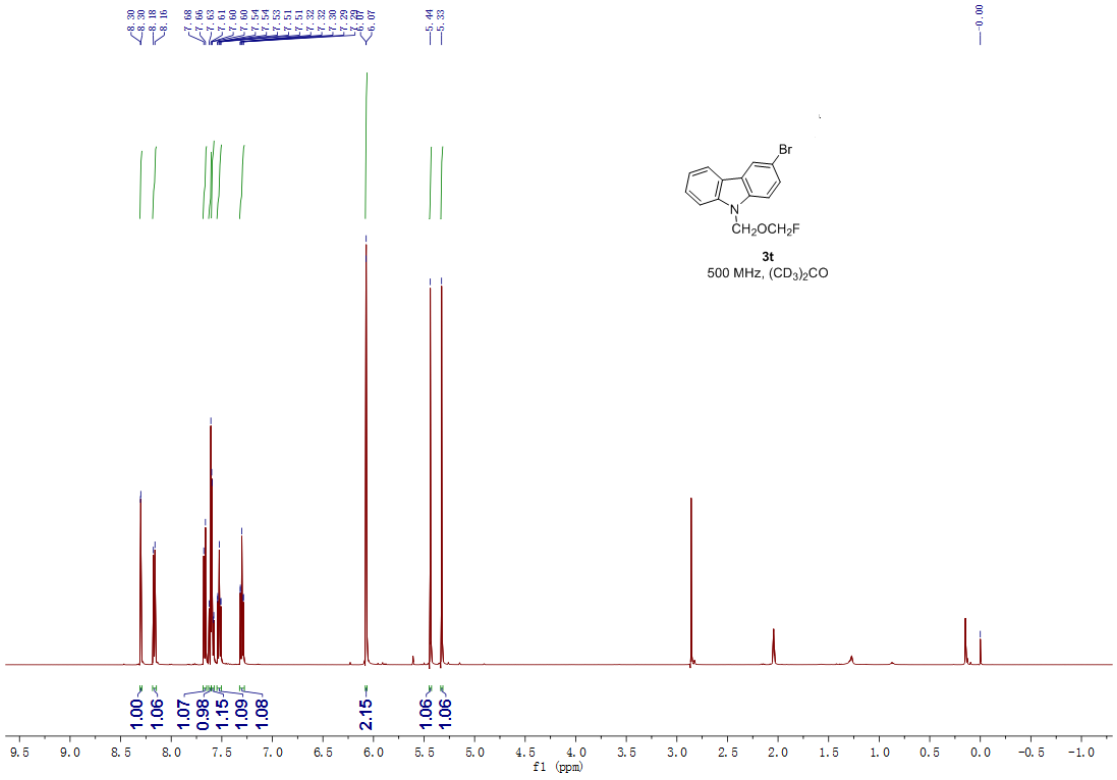

148.53
144.93
133.00
130.15
118.21
118.05
104.67
103.36
101.67
75.83
N
N
CH2OCH2F
3r
126 MHz, CD3CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

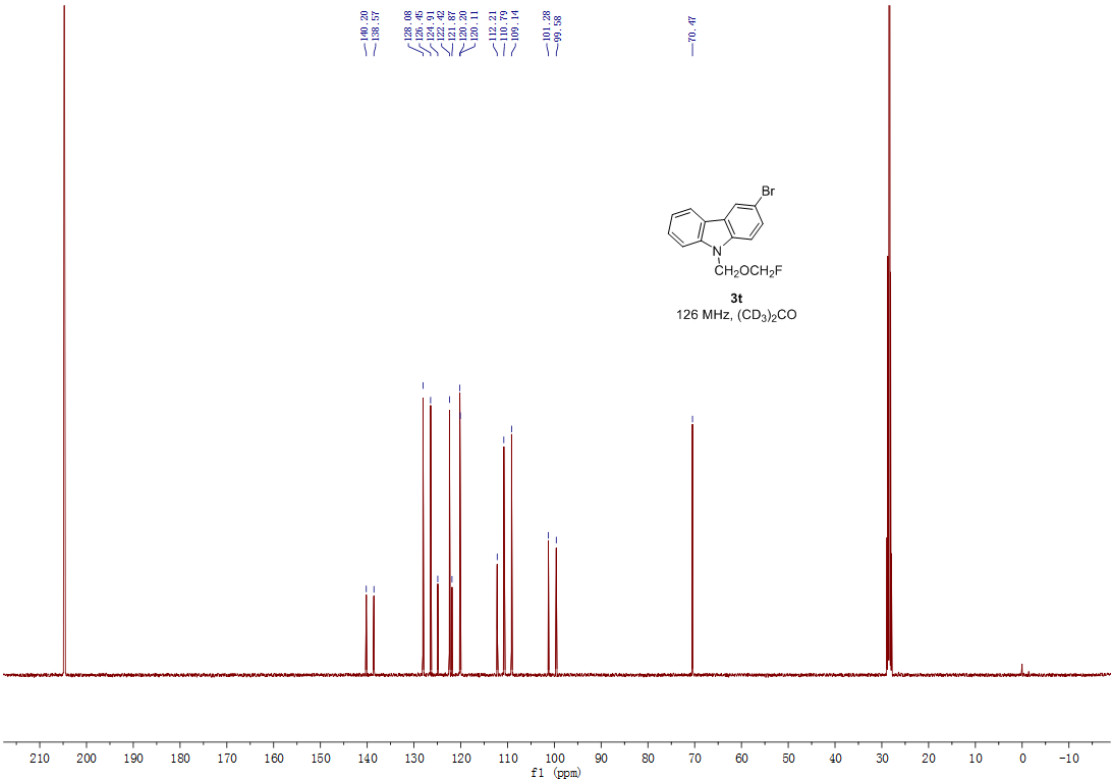

152.80
152.92
153.04
N
N
CH2OCH2F
3r
470 MHz, CD3CN
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

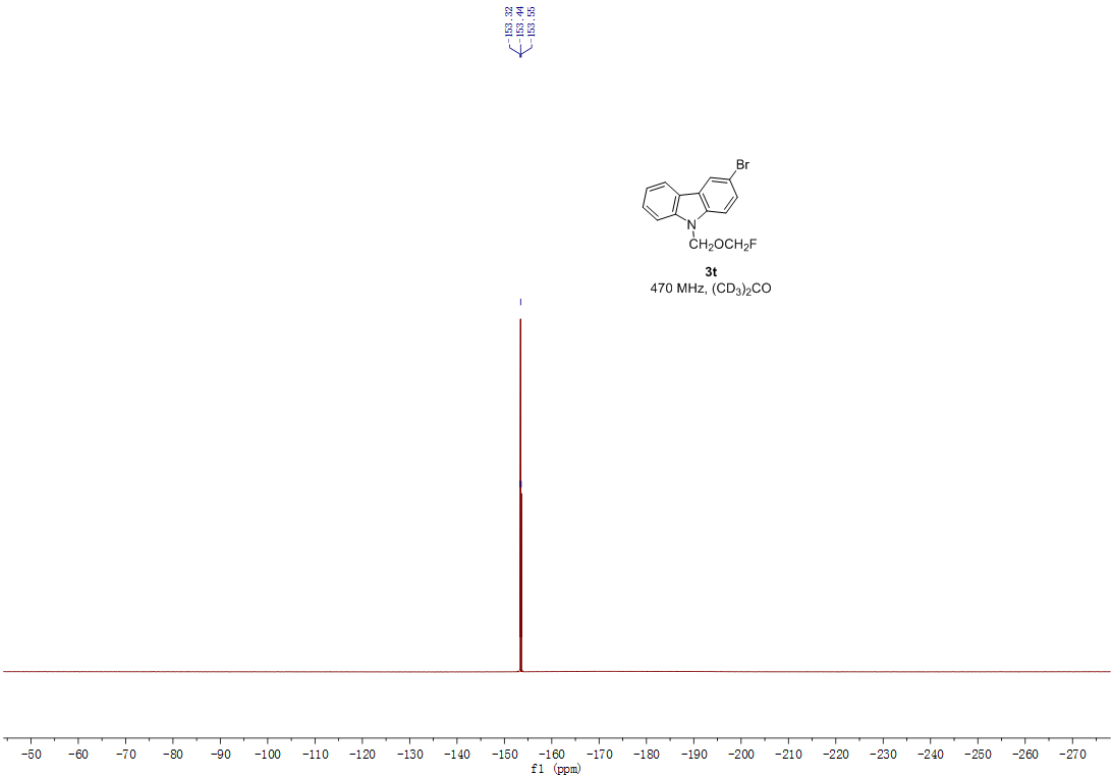

8.31
7.99
7.98
7.59
7.16
7.15
7.14
6.57
5.96
5.50
5.39
0.00
1.00
1.02
1.01
1.02
1.02
2.14
1.03
1.07
f1 (ppm)
CH2OCH2F
3s
500 MHz, (CD3)2CO

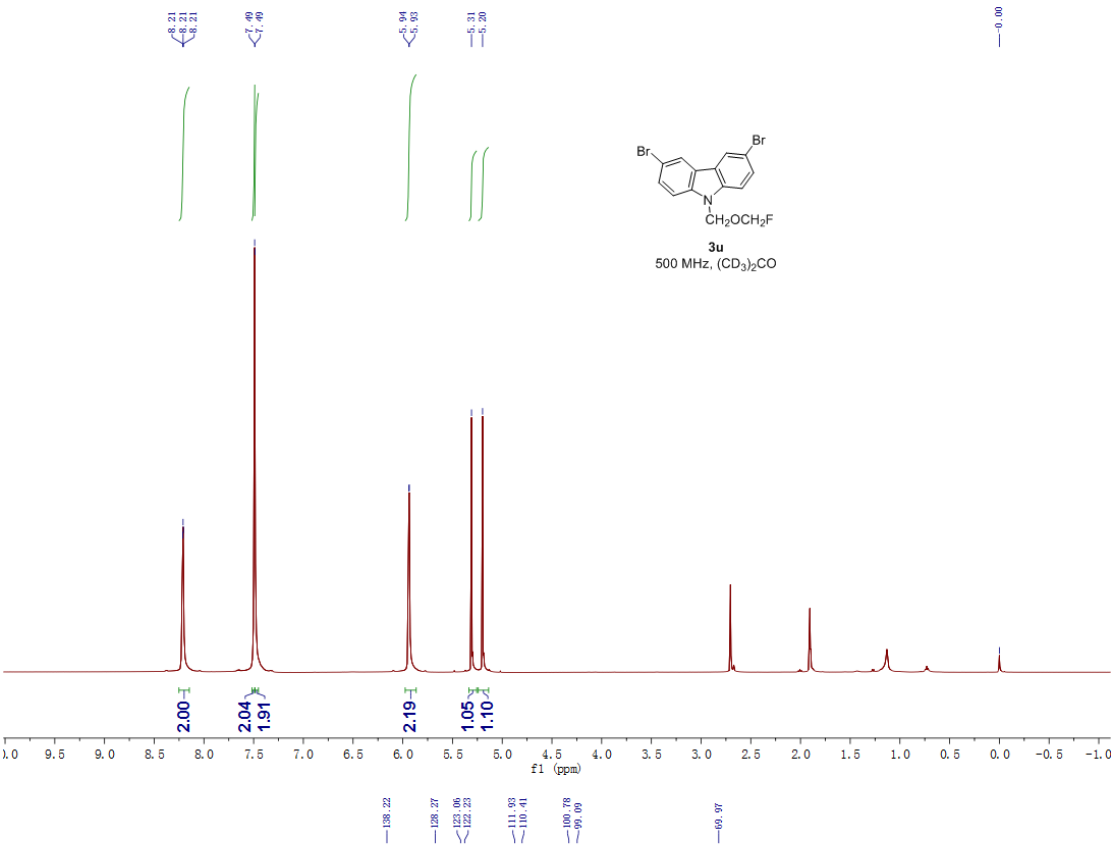

147.81
142.87
128.41
128.28
120.59
116.41
102.48
101.04
100.79
71.83
f1 (ppm)
CH2OCH2F
3s
126 MHz, (CD3)2CO

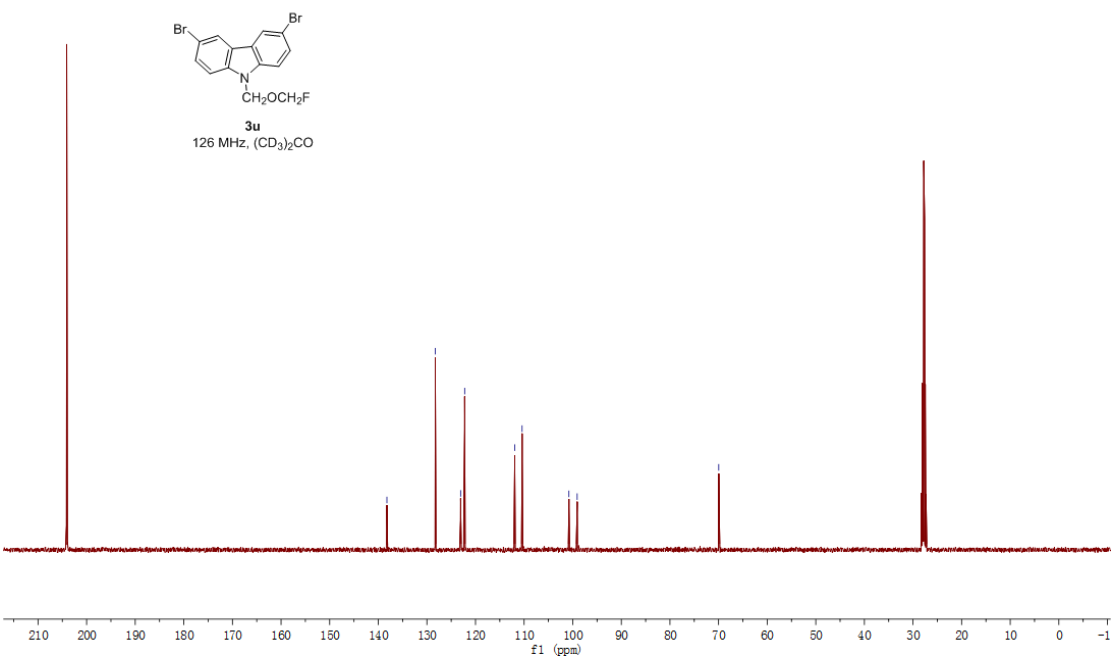

151.26
151.37
151.49
CH2OCH2F
3s
470 MHz, (CD3)2CO
f1 (ppm)

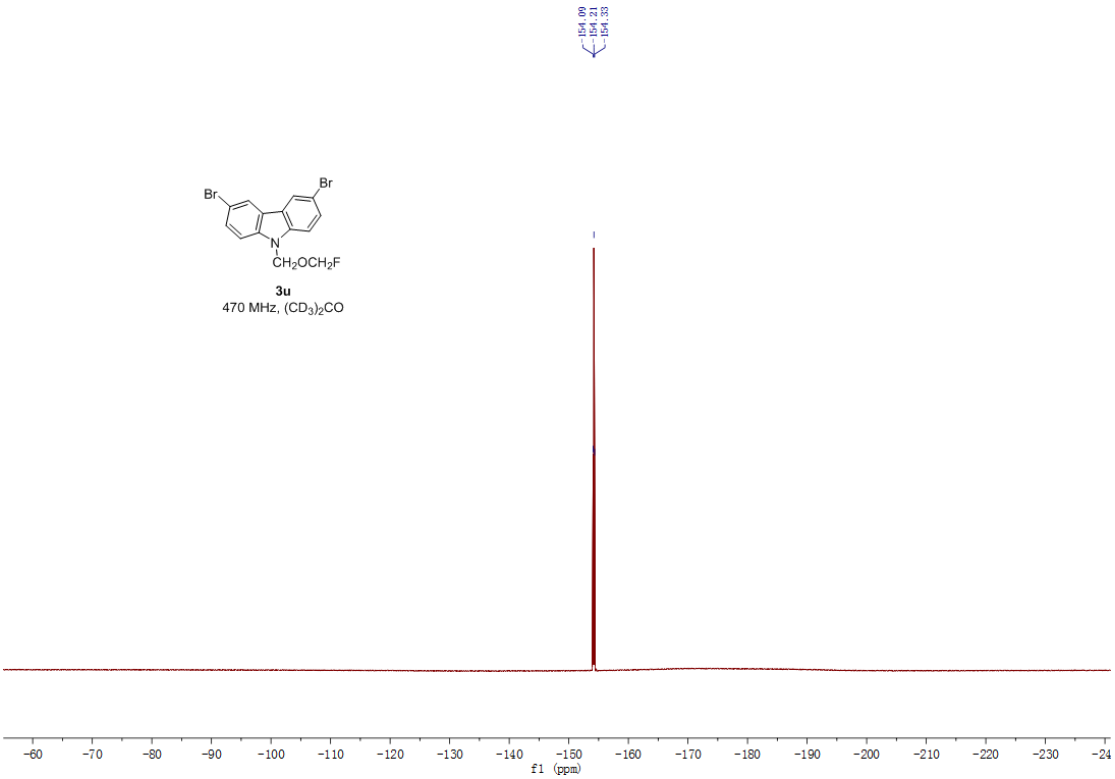

8.30
8.30
8.18
8.16
7.68
7.66
7.63
7.61
7.61
7.60
7.60
7.54
7.54
7.53
7.51
7.51
7.32
7.32
7.30
7.29
6.07
5.44
5.33
0.00
Br
CH2OCH2F
3t
500 MHz, (CD3)2CO
1.00
1.06
1.07
0.98
1.15
1.09
1.08
2.15
1.06
1.06
f1 (ppm)

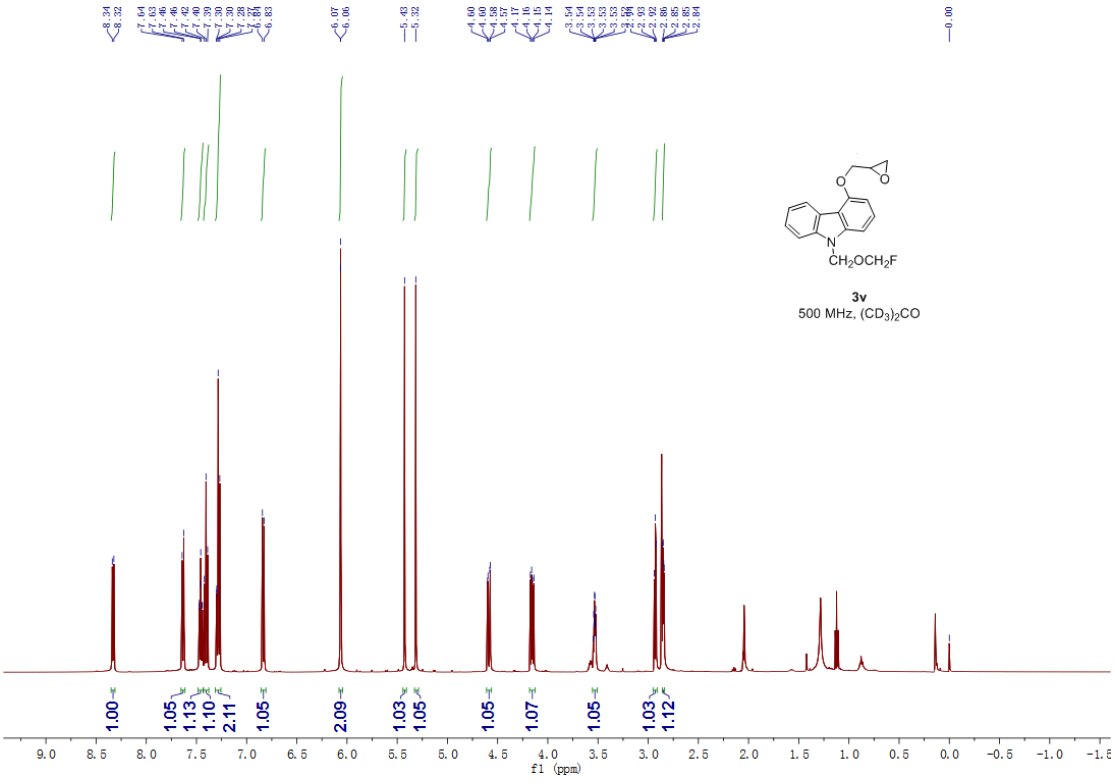

140.20
138.57
128.08
126.45
124.01
122.42
121.87
120.20
120.11
112.21
110.79
109.14
101.28
99.38
70.47
Br
N
CH2OCH2F
3t
126 MHz, (CD3)2CO
f1 (ppm)

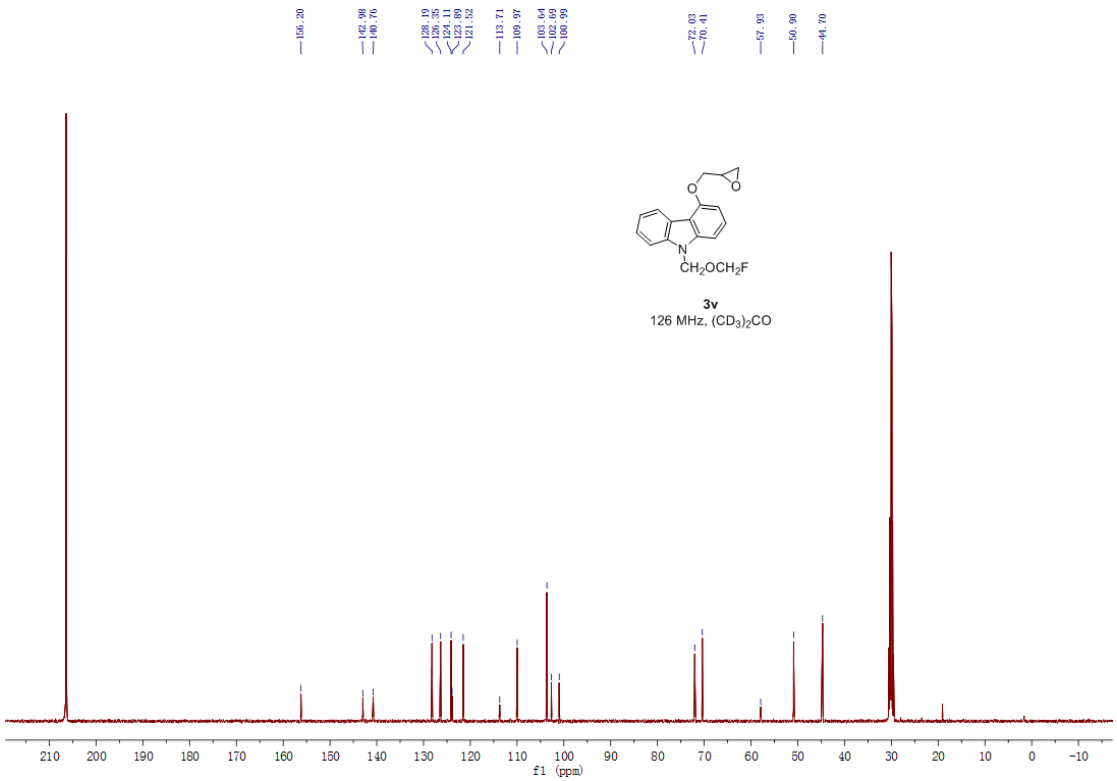

153.32
153.44
153.55
Br
N
CH2OCH2F
3t
470 MHz, (CD3)2CO
f1 (ppm)

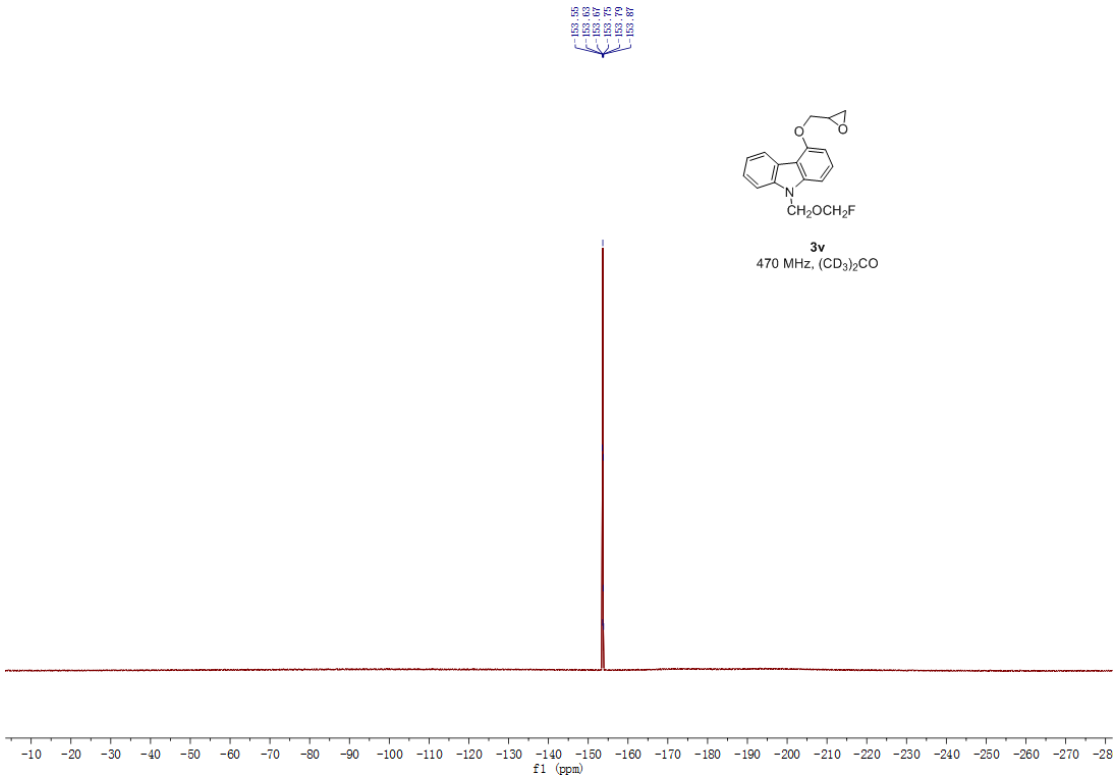

8.21
8.21
8.21
7.49
7.49
5.94
5.93
5.31
5.20
0.00
Br
Br
N
CH2OCH2F
3u
500 MHz, (CD3)2CO
2.00
2.04
1.91
2.19
1.05
1.10
f1 (ppm)

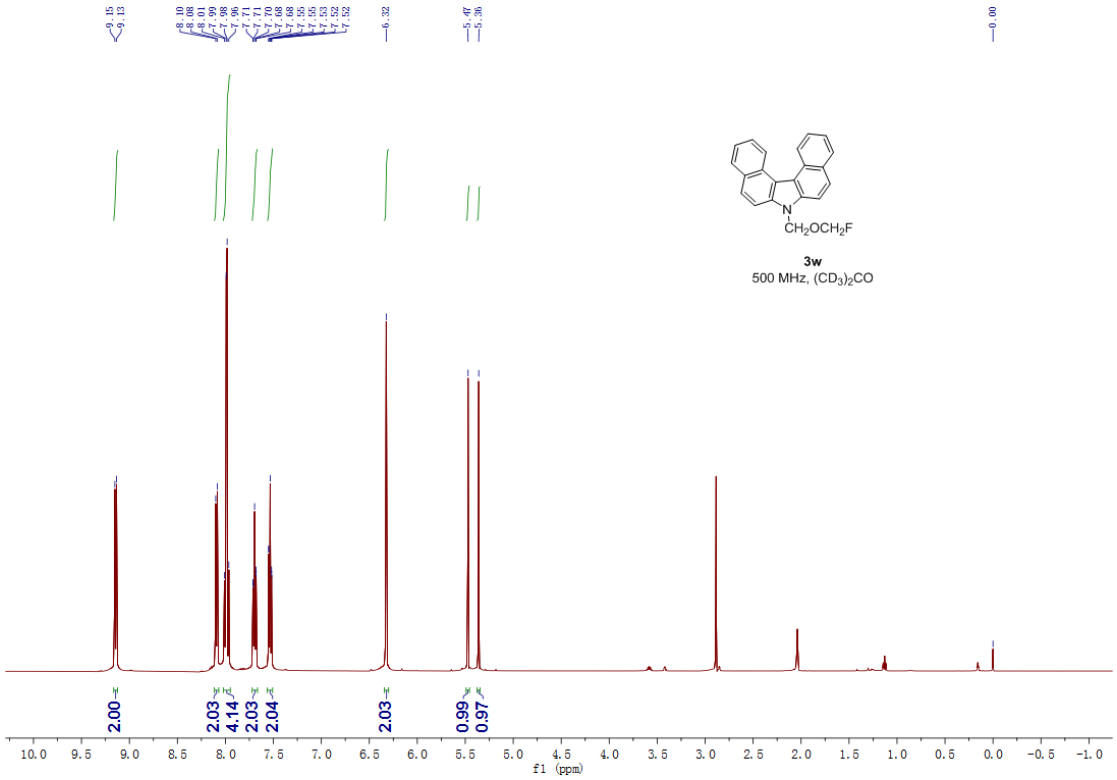

138.22
128.27
123.06
122.23
111.93
110.41
100.78
99.09
69.97
Br
Br
N
CH2OCH2F
3u
126 MHz, (CD3)2CO
f1 (ppm)

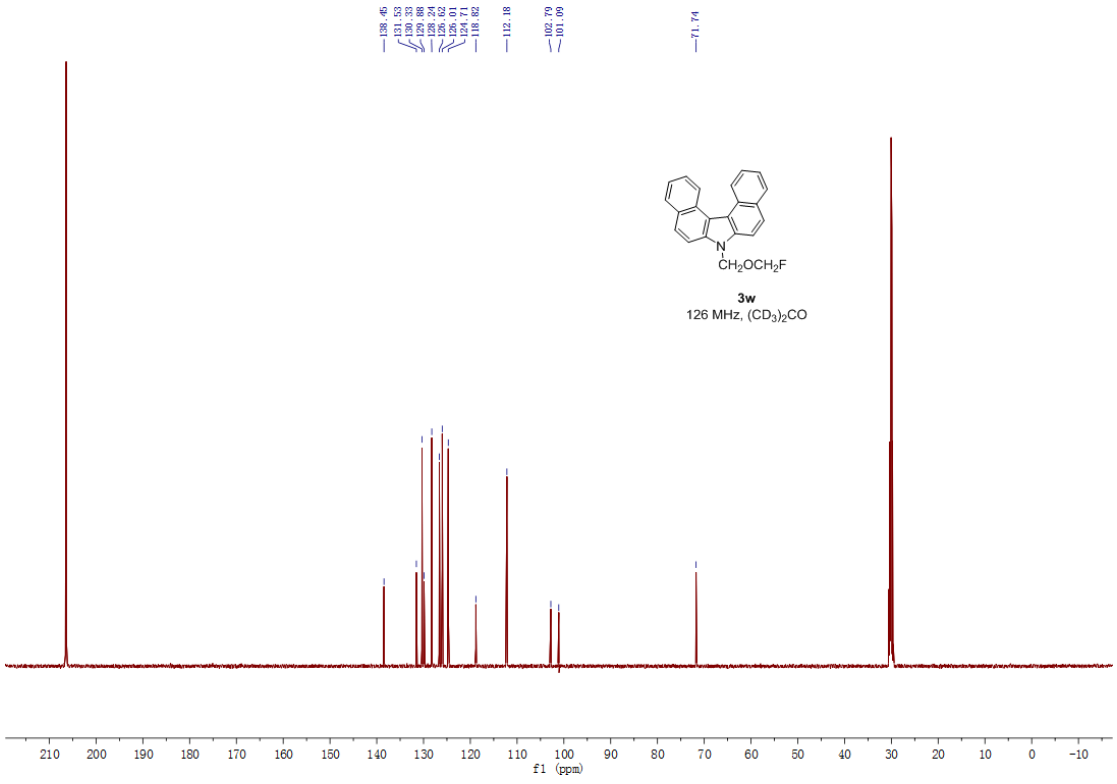

Br
Br
N
CH2OCH2F
3u
470 MHz, (CD3)2CO
f1 (ppm)

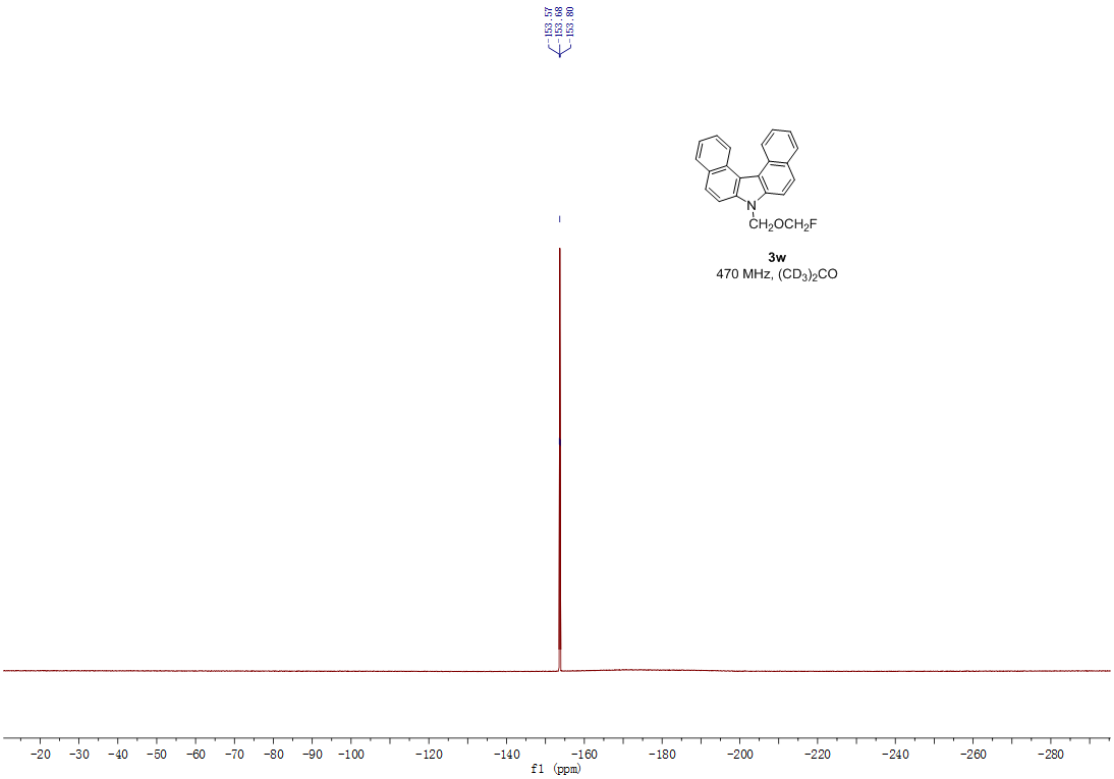

O
O
N
CH2OCH2F
3v
500 MHz, (CD3)2CO
f1 (ppm)

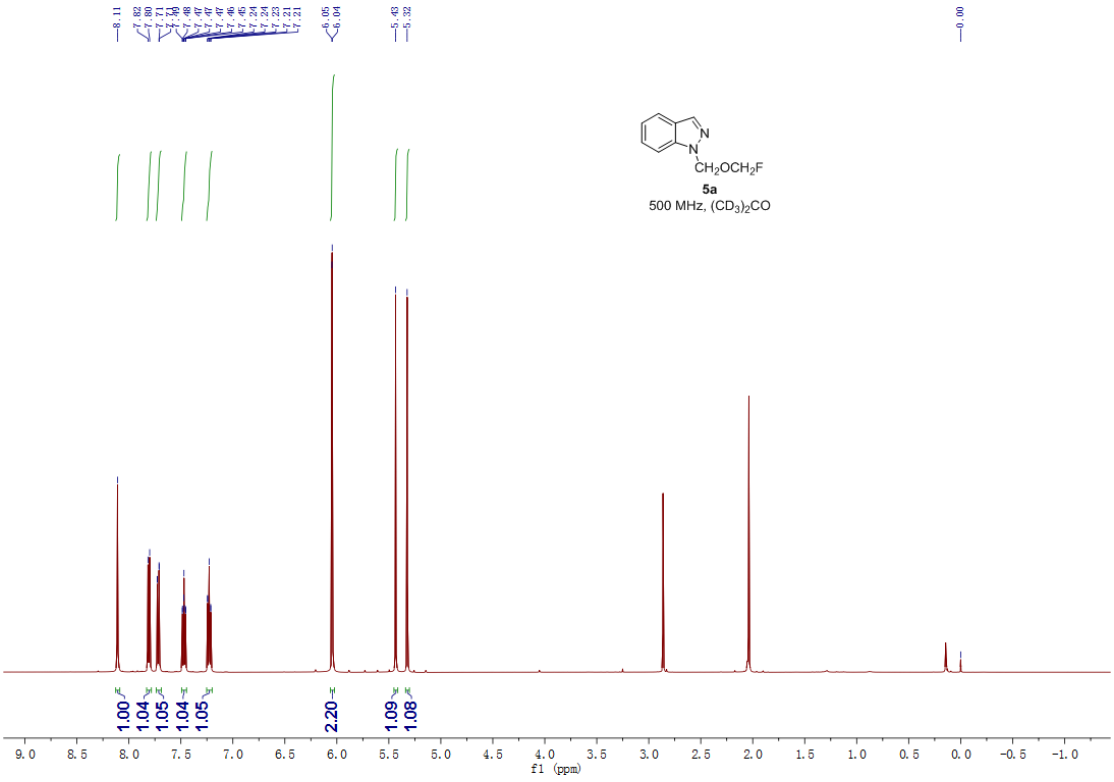

156.20
142.98
140.76
128.19
126.35
124.11
123.89
121.52
113.71
109.97
103.64
102.69
100.99
72.03
70.41
57.93
50.90
44.70
O
O
N
CH2OCH2F
3v
126 MHz, (CD3)2CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

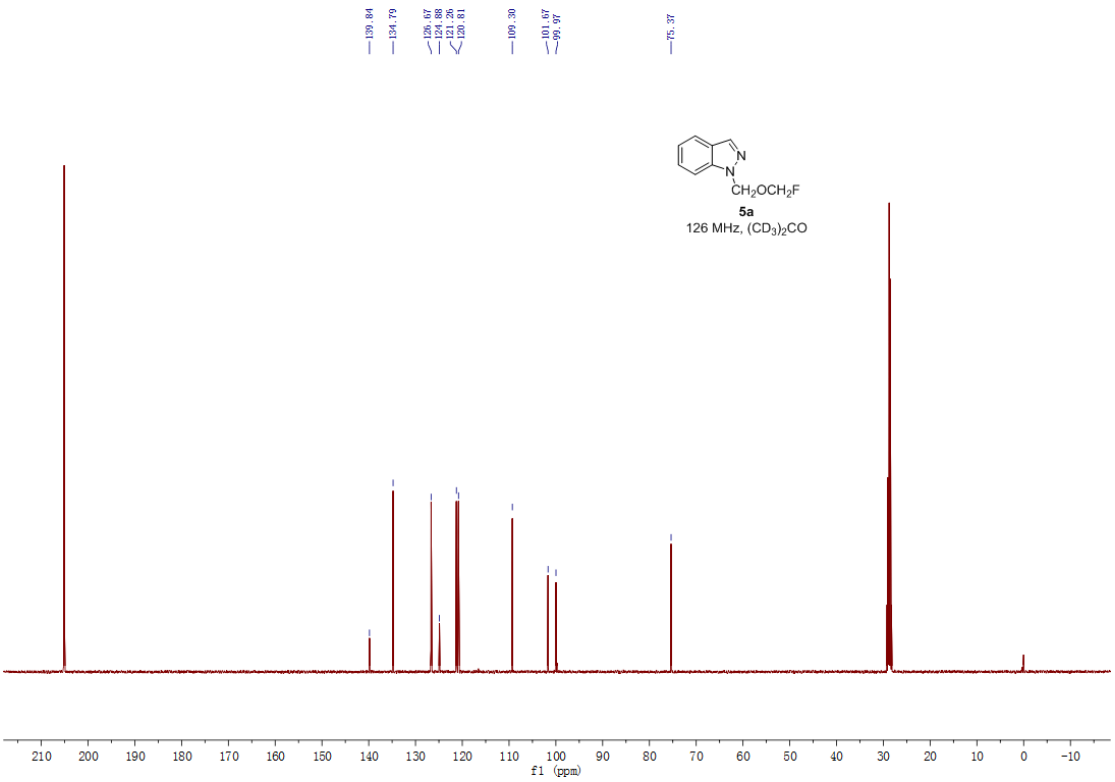

153.55
153.63
153.67
153.75
153.79
153.87
O
O
N
CH2OCH2F
3v
470 MHz, (CD3)2CO
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -28
f1 (ppm)

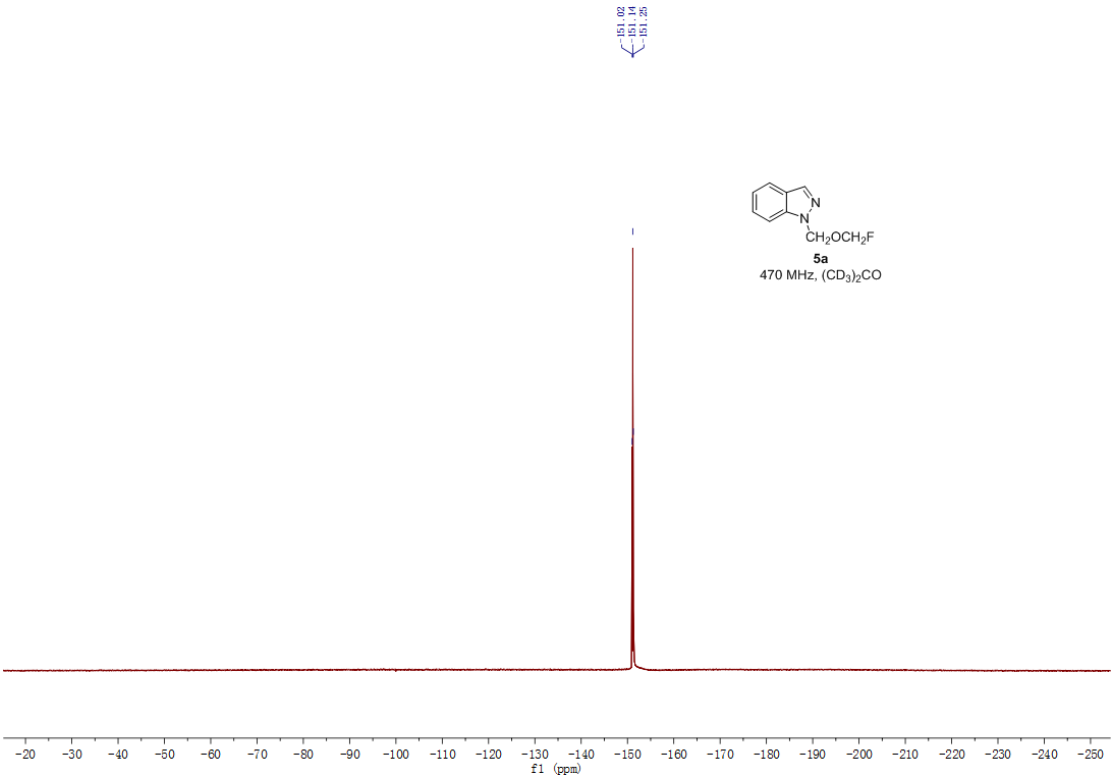

9.15
9.13
8.10
8.08
8.01
7.99
7.98
7.96
7.71
7.71
7.70
7.68
7.68
7.55
7.55
7.53
7.52
7.52
6.32
5.47
5.36
0.00
N
CH2OCH2F
3w
500 MHz, (CD3)2CO
2.00
2.03
4.14
2.03
2.04
2.03
0.99
0.97
f1 (ppm)

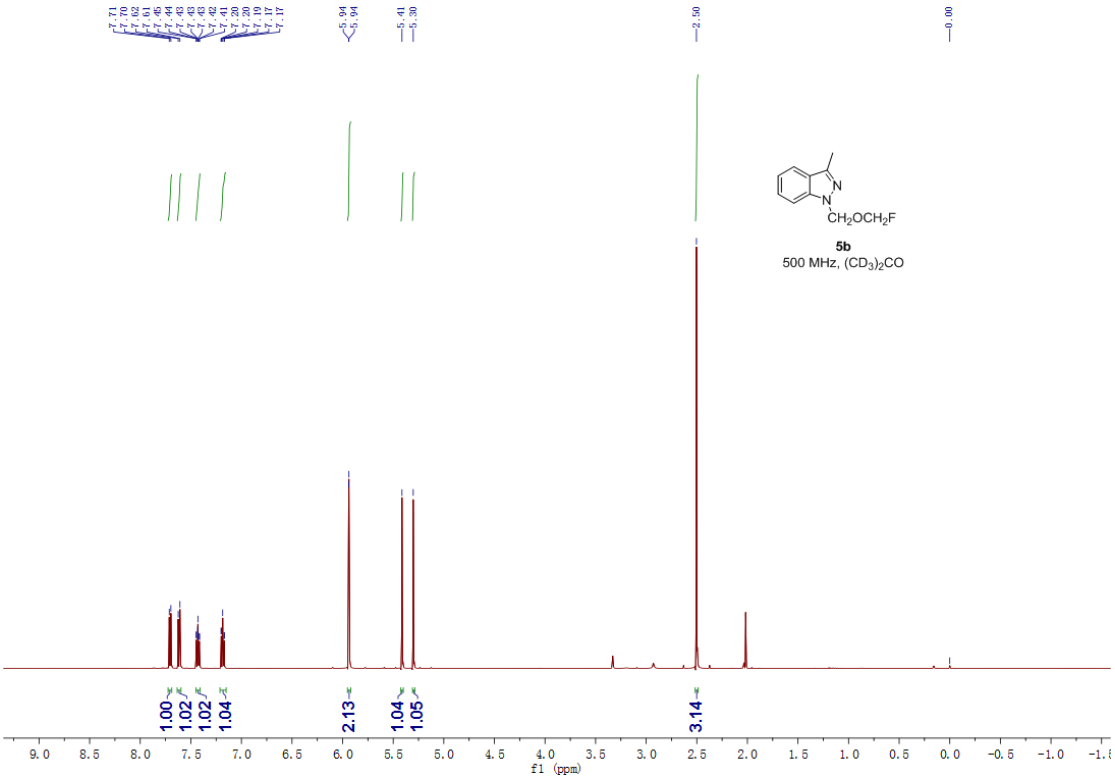

138.45
131.53
130.33
129.88
128.24
126.62
126.01
124.71
118.82
112.18
102.79
101.09
71.74
N
CH2OCH2F
3w
126 MHz, (CD3)2CO
f1 (ppm)

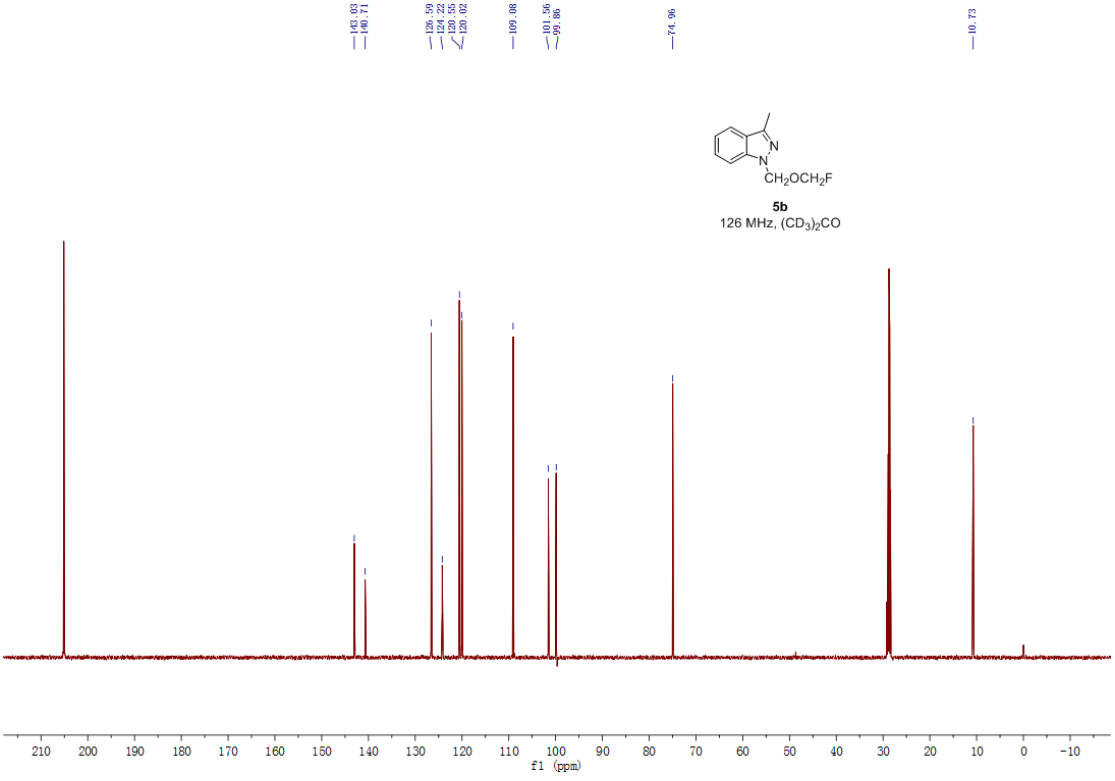

153.57
155.68
155.80
CH2OCH2F
3w
470 MHz, (CD3)2CO
f1 (ppm)

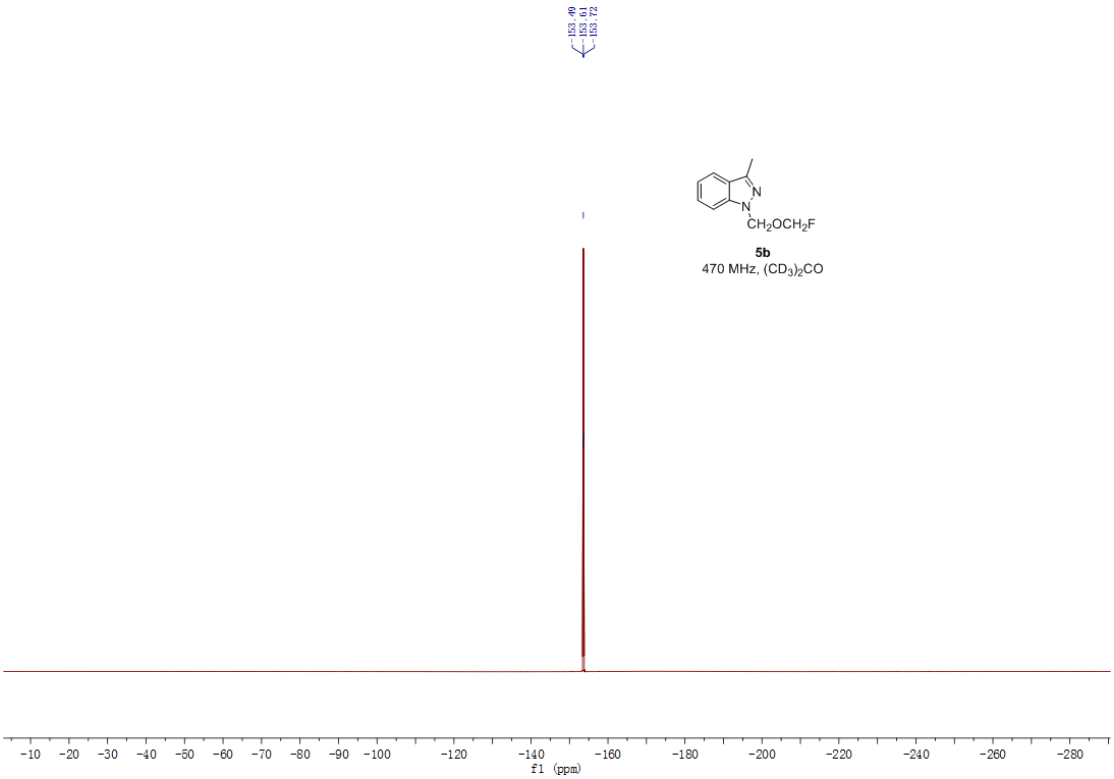

8.11
7.82
7.80
7.71
7.70
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.24
7.24
7.23
7.21
6.05
6.04
5.43
5.32
0.00
CH2OCH2F
5a
500 MHz, (CD3)2CO
1.00
1.04
1.05
1.04
1.05
2.20
1.09
1.08
f1 (ppm)

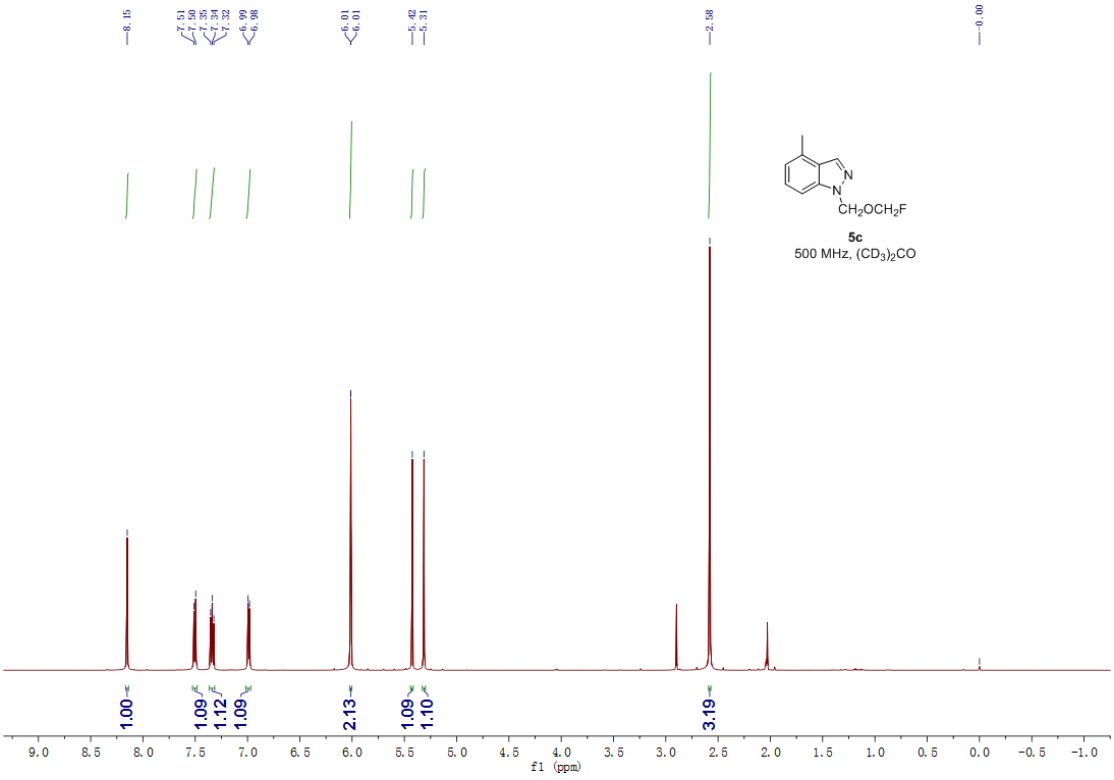

139.84
134.79
126.67
124.88
121.26
120.81
109.30
101.67
99.97
75.37
CH2OCH2F
5a
126 MHz, (CD3)2CO
f1 (ppm)

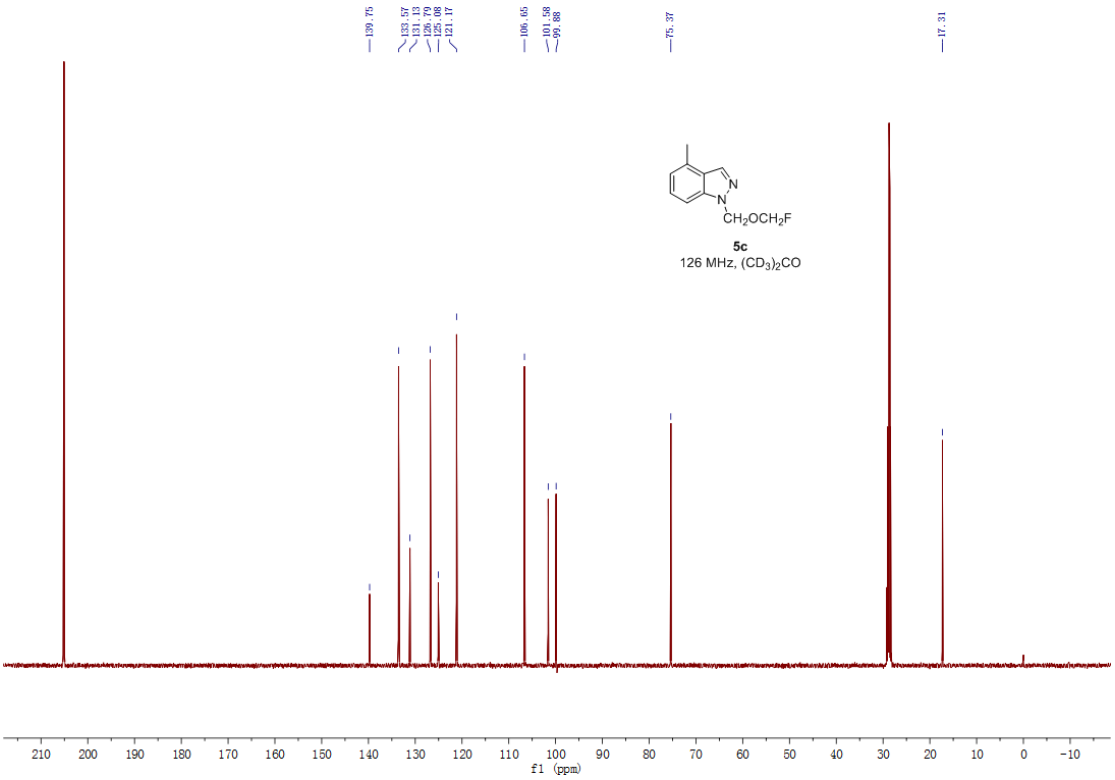

151.02
151.14
151.25
CH2OCH2F
5a
470 MHz, (CD3)2CO
f1 (ppm)

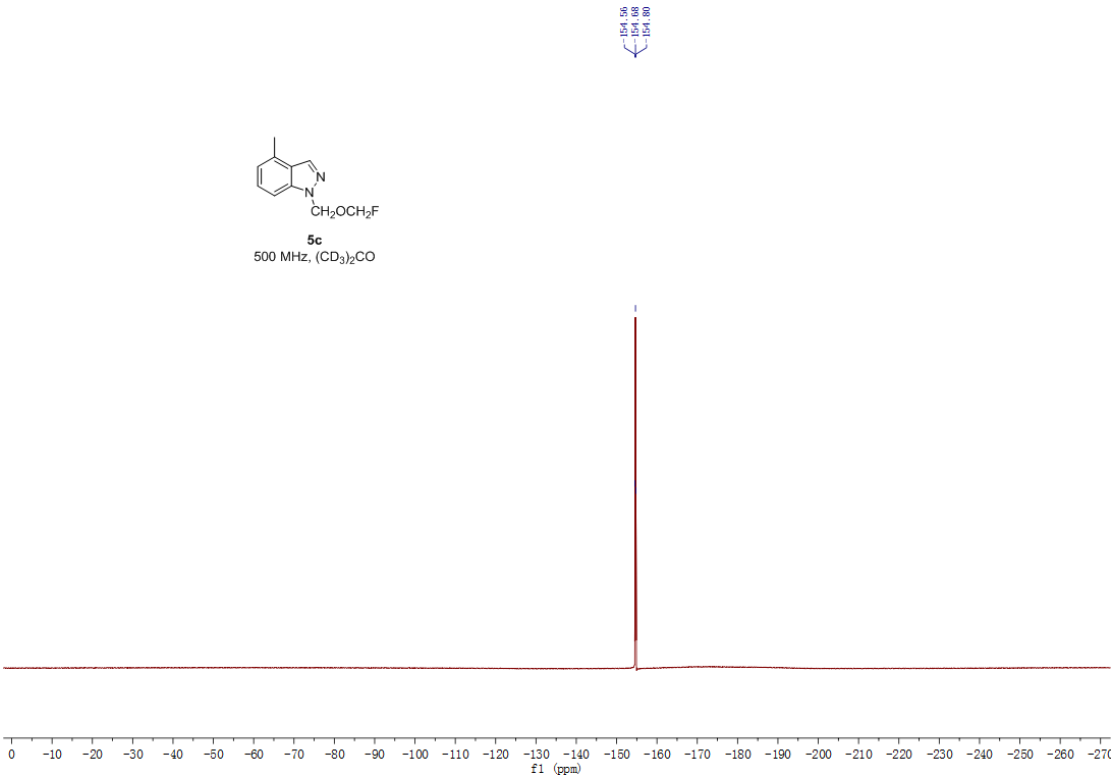

7.71
7.70
7.62
7.61
7.45
7.44
7.43
7.43
7.43
7.42
7.41
7.20
7.19
7.17
7.17
5.94
5.94
5.41
5.30
2.50
0.00
N
N
CH2OCH2F
5b
500 MHz, (CD3)2CO
1.00
1.02
1.02
1.04
2.13
1.04
1.05
3.14
f1 (ppm)

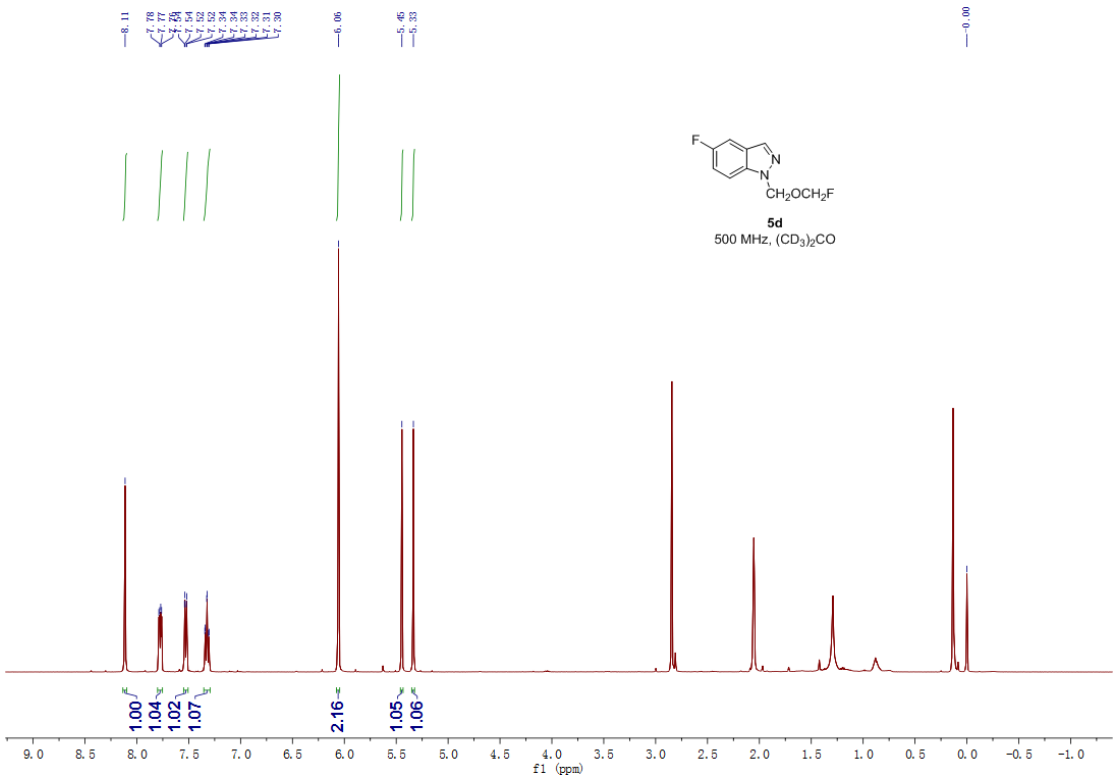

143.03
140.71
126.59
124.22
120.55
120.02
109.08
101.56
99.86
74.96
10.73
N
N
CH2OCH2F
5b
126 MHz, (CD3)2CO
f1 (ppm)

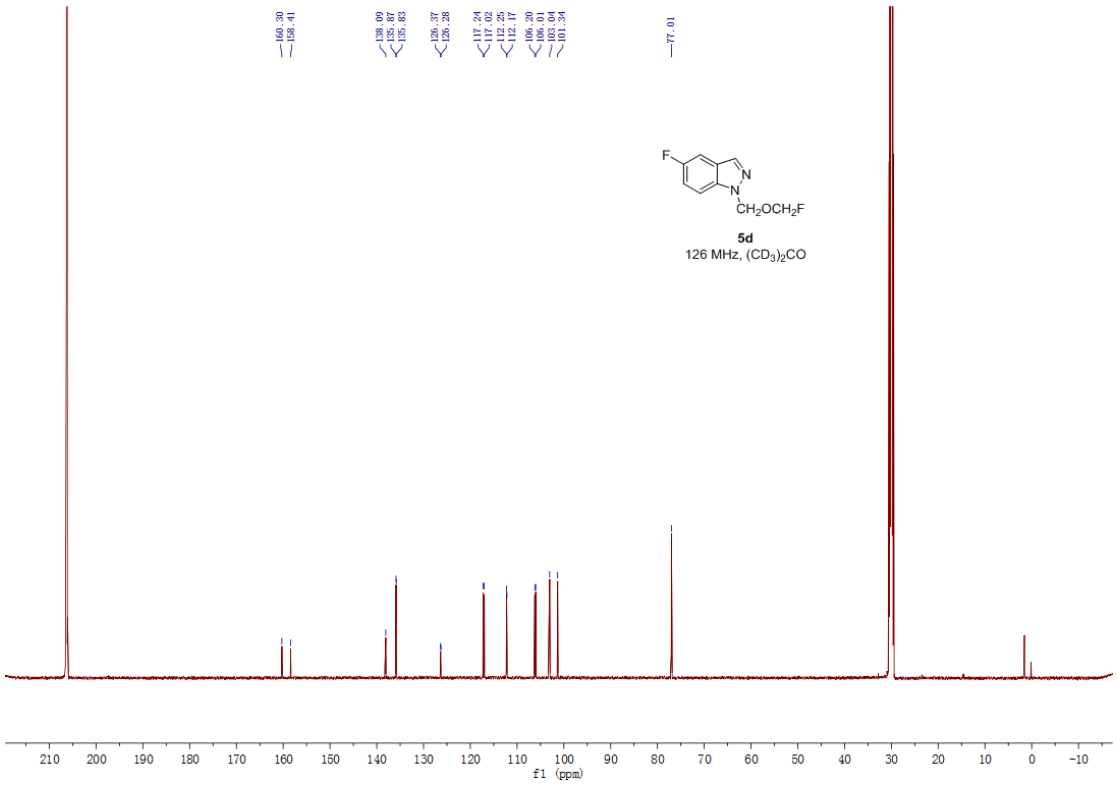

-153.49
-153.61
-153.72
CH2OCH2F
5b
470 MHz, (CD3)2CO
f1 (ppm)

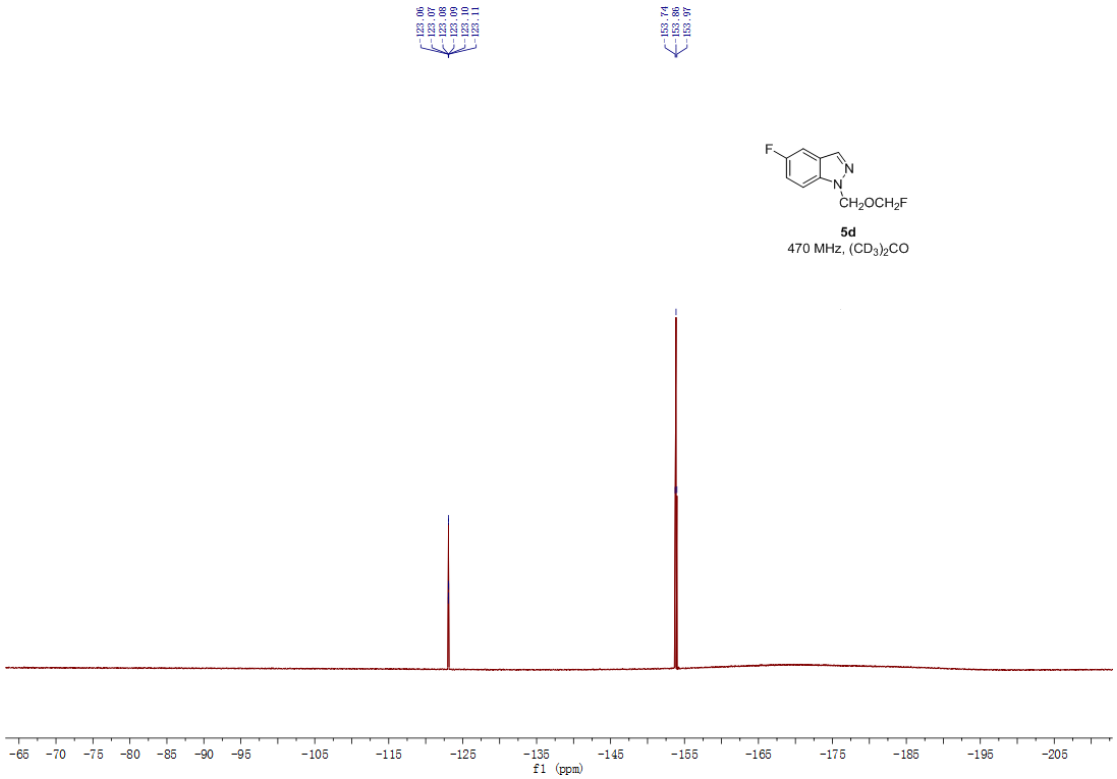

8.15
7.51
7.50
7.35
7.34
7.32
6.99
6.98
6.01
6.01
5.42
5.31
2.58
0.00
CH2OCH2F
5c
500 MHz, (CD3)2CO
1.00
1.09
1.12
1.09
2.13
1.09
1.10
3.19
f1 (ppm)

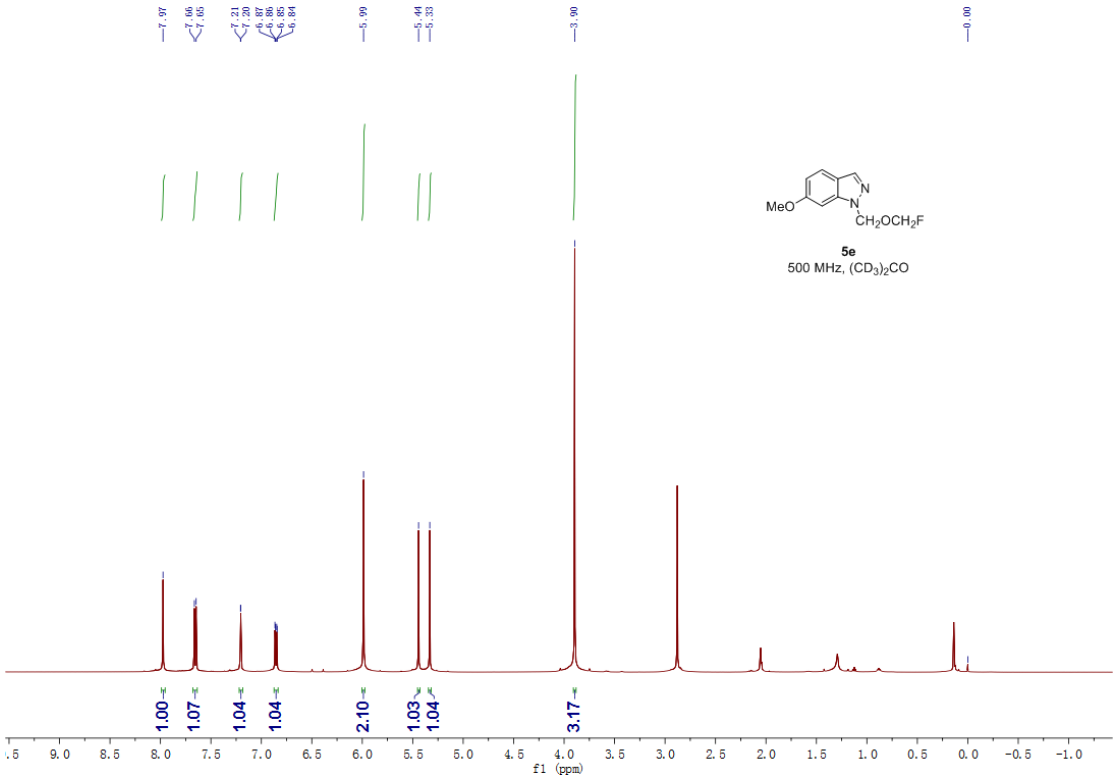

139.75
133.57
111.13
126.79
125.08
121.17
106.65
101.58
99.88
75.37
17.31
N
N
CH2OCH2F
5c
126 MHz, (CD3)2CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

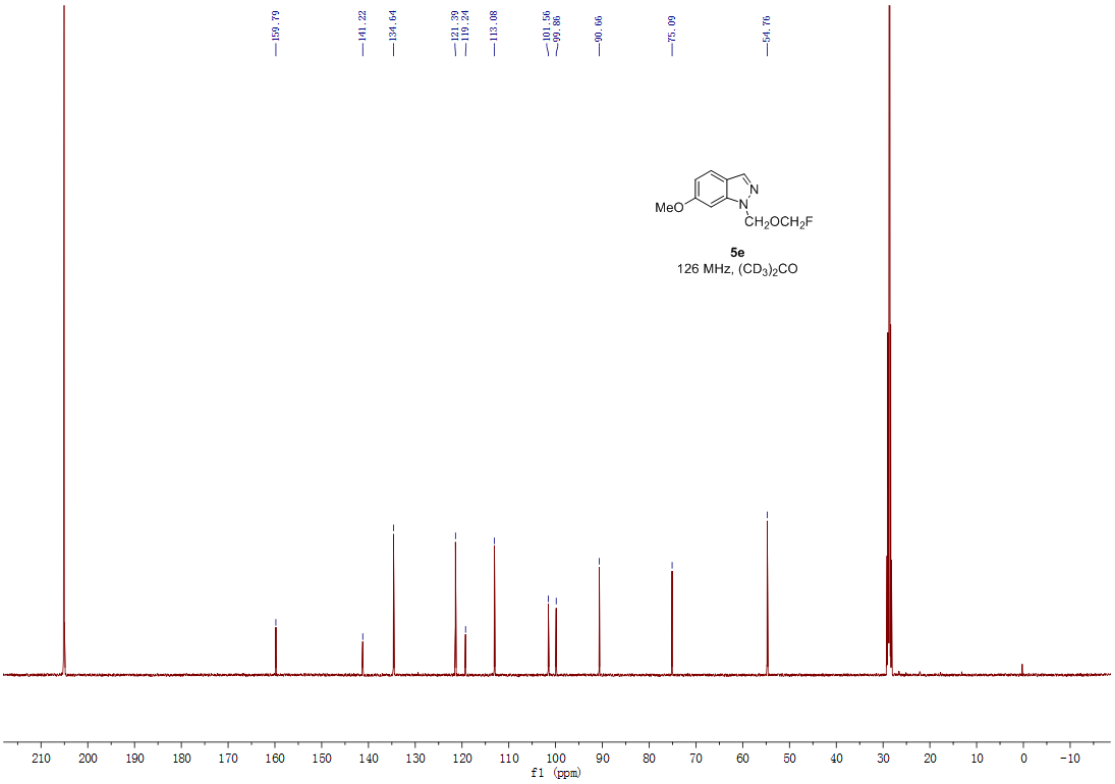

154.56
154.68
154.80
N
N
CH2OCH2F
5c
500 MHz, (CD3)2CO
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)

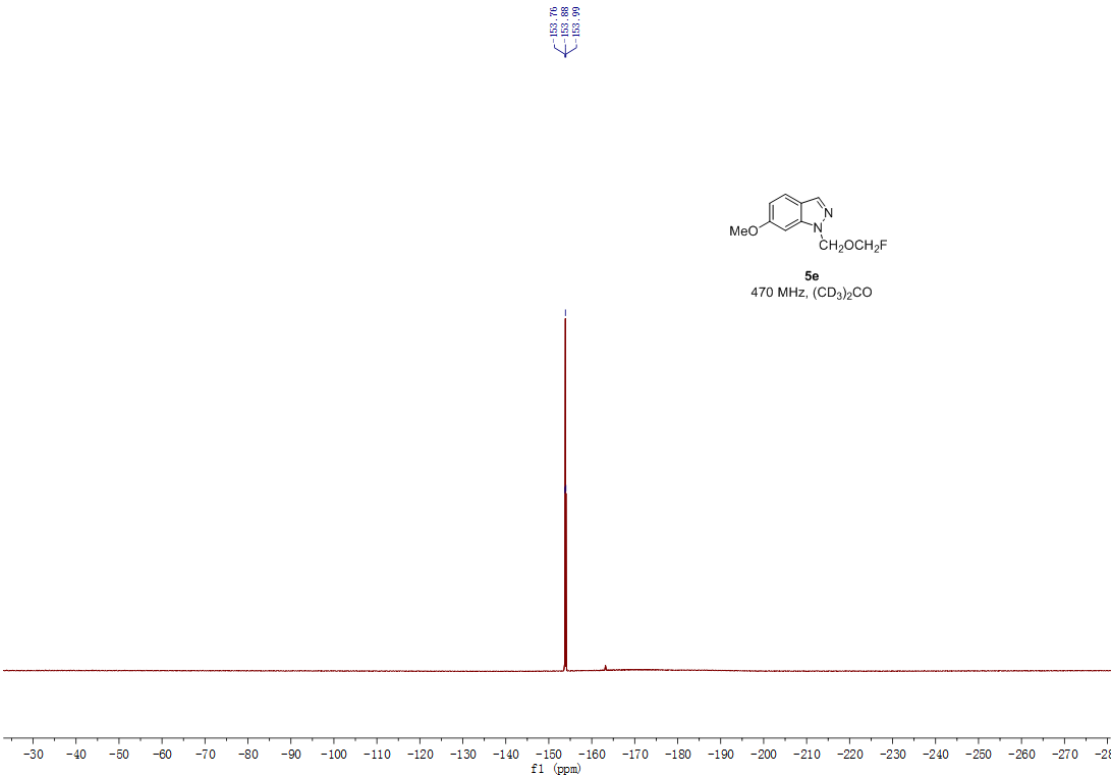

8.11
7.78
7.77
7.76
7.75
7.54
7.52
7.52
7.34
7.34
7.33
7.32
7.31
7.30
6.06
5.45
5.33
0.00
F
N
N
CH2OCH2F
5d
500 MHz, (CD3)2CO
1.00
1.04
1.02
1.07
2.16
1.05
1.06
f1 (ppm)


160.30
158.41
138.09
135.87
135.83
125.37
125.28
117.24
117.02
112.25
112.17
106.20
106.01
103.04
101.34
77.01
F
N
N
CH2OCH2F
5d
126 MHz, (CD3)2CO
f1 (ppm)


123.06
123.07
123.08
123.09
123.10
123.11
153.74
153.86
153.97
F
N
N
CH2OCH2F
5d
470 MHz, (CD3)2CO
-65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175 -185 -195 -205
f1 (ppm)

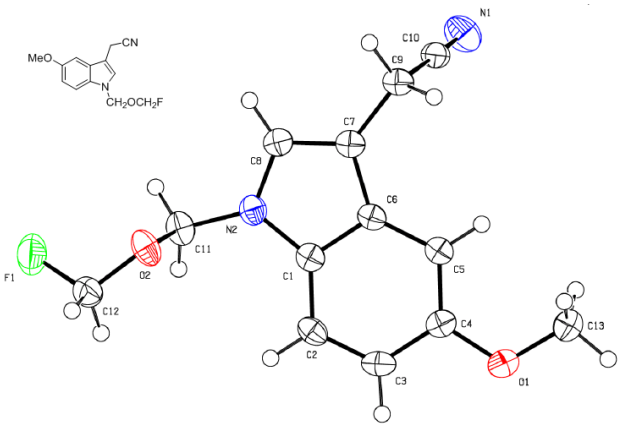

7.97
7.66
7.65
7.21
7.20
6.87
6.86
6.85
6.84
5.99
5.44
5.33
3.90
0.00
MeO
N
N
CH2OCH2F
5e
500 MHz, (CD3)2CO
1.00
1.07
1.04
1.04
2.10
1.03
1.04
3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


159.79
141.22
134.64
121.39
119.24
113.08
101.56
99.86
90.66
75.09
54.76
MeO
N
N
CH2OCH2F
5e
126 MHz, (CD3)2CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


153.76
153.88
153.99
MeO
N
N
CH2OCH2F
5e
470 MHz, (CD3)2CO
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)

3. X-Ray Crystallographic Data of 3q

The white crystals of **3q** were obtained by using the solvent vapor diffusion method in ether solution. Crystallographic data of complexes was collected at 296 K on a Bruker APEX-II CCD system equipped with graphite-monochromated Mo-Kα radiation (λ = 0.071073 nm) using ω-φ scan technique. Diffraction data were integrated by the SAINT program, which was also used for intensity corrections for Lorentz and polarization effects. Semi-empirical absorption correction was applied using SADABS. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package.



Thermal ellipsoids for **3q** are shown at 50% probability level.

Formula	C13H13FN2O2
Formula weight	248.25
Crystal system	Orthorhombic
space group	*P*21
a (Å)	4.2319(3)
b (Å)	14.2453(9)
c (Å)	19.5737(12)
α (º)	90.00
β (º)	90.00
γ (º)	90.00
Volume(Å^3)	1179.99(13)
Z	4
T (K)	173(2)
D_{calcd} (g/m^3)	1.397

$F(000)$	520
Reflections collected	2065
Unique reflections	1900
Goof	1.055
$R_1[I> 2\sigma(I)]$	0.0342
$wR_2[I>2\sigma(I)]$	0.0886[a]
CCDC NO.	1889210

[a] $w = 1/[\sigma^2(F_0)^2+(0.0512P)^2 +0.1488P]$, where $P = (F_0^2 + 2F_c^2)/3$;