Supporting Information

A concise method for cyclic *gem*-difluoroacyl scaffolds via visible-light-mediated redox-neutral cascade radical cyclizaton of alkenes

Zhen Liu, Yin Wei*[b] and Min Shi*[a,b]

[a]Key Laboratory for Advanced Materials & Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China, [b]State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, University of Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 LinglingRoad, Shanghai 200032, P. R. China. weiyin@sioc.ac.cn, mshi@mail.sioc.ac.cn

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1. General remarks

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz, respectively. HRMS spectra were recorded by EI, ESI, FI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by EI, ESI, and HRMS was measured on an Agilent Technologies 6224 TOF LC/MS instrument and a Waters Micromass GCT Permier. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC plate analysis with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure.

Reaction setup

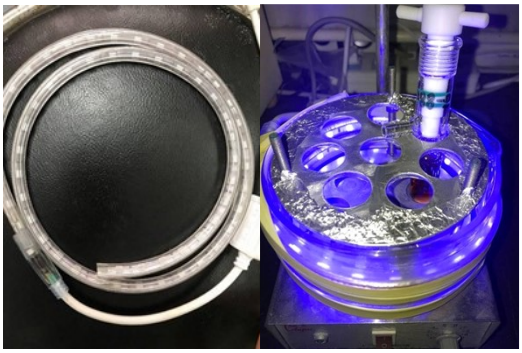
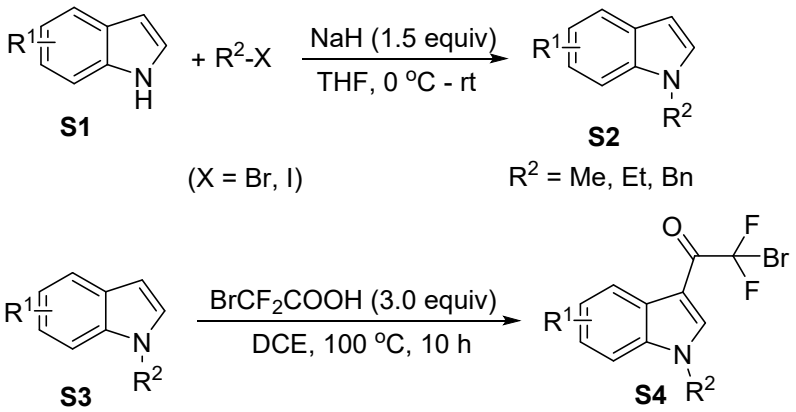


Figure S1. 8 W LEDs strip and reaction setup

As depicted in the picture, reactions were carried out in oven-dried sealed tubes. The reaction temperature was maintained at room temperature by a water bath and a fan.

2. General procedures for the synthesis of substrates 1

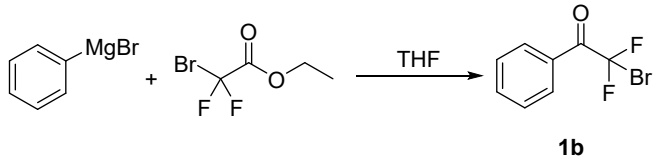
Synthesis of substrates **1a**, **1c**-**1m** and **1o.**



To a well-stirred solution of indole derivative (10 mmol, 1.0 equiv) in THF (15 mL) at 0 ℃ was added sodium hydride (60% in mineral oil, 15 mmol, 1.5 equiv). The reaction mixture was warmed to room temperature and allowed to stir for 30 min. After 30 min, the reaction flask was cooled again to 0 ℃ and alkyl halide (12 mmol, 1.2 equiv) was added dropwise. The reaction mixture was warmed to room temperature and allowed to stir until the reaction completed (monitored by TLC) and then cooled to 0 ℃ and quenched with saturated aqueous NH_4Cl solution. The product was extracted with diethyl ether (3 × 20 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated in vacuum to obtain the crude mixture which was further purified by a column chromatography (using 10% ethyl acetate/hexane) giving **S2** in up to 99% yield.[1]

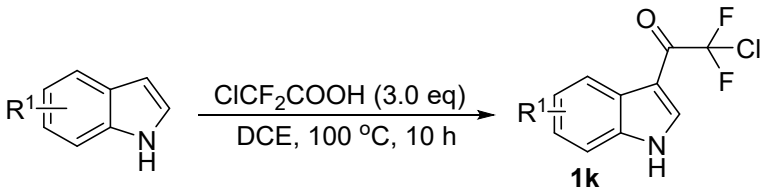
S4 were synthesized according to the previous literature.[2] **S2** (4 mmol) and bromodifluoroacetic acid (3.0 equiv) were refluxed in a 100 °C oily bath in 30 mL of DCE under an air atmosphere, and the progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the reaction mixture was cooled to room temperature. A saturated sodium bicarbonate solution (20 mL) and water (20 mL) were added, the product was extracted with ethyl acetate (30 mL), the organic layers were washed with saturated brine, and the solvent was removed on a rotary evaporator. The product was purified by a silica gel chromatography (petroleum ether/EtOAc 20/1−15/1) to afford the corresponding products **S4**.

Synthesis of substrates **1b** and **1k**.



1b

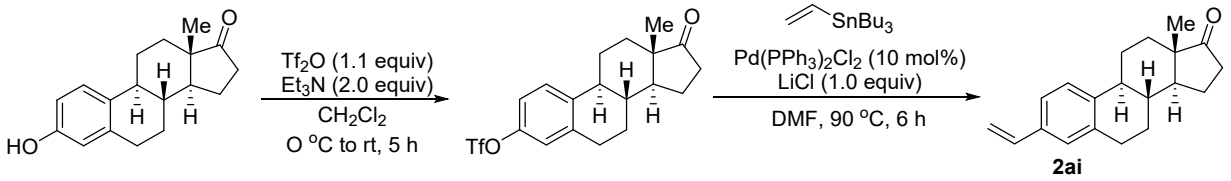
To a mixture of ethyl bromodifluoroacetate (3.2 mL, 25 mmol) and THF (30 mL) was added a newly prepared solution of arylmagnesium bromide in THF at -78 °C under an argon atmosphere. After the reaction solution was stirred at that temperature for 3 h, the mixture was quenched with 3.0 N HCl solution and then extracted with ethyl acetate. The extracted organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Flash column chromatography (silica gel, hexanes) afforded compound **1b** after concentration by a rotary evaporator (5.29 g, 90% yield).[3]



1k

Indoles (5 mmol) and chlorodifluoroacetic acid (3 equiv) were refluxed in a 100 °C oily bath in 20 mL of DCE under an air atmosphere, and the progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the reaction mixture was cooled to room temperature. Water (2 × 5 mL) was added, the organic product was extracted with ethyl acetate (20 mL), and the organic layers were washed with saturated brine, and the solvent was removed on a rotary evaporator. The product was purified by a silica gel chromatography (petroleum ether/EtOAc 20/1−15/1) to afford the corresponding product **1k**.

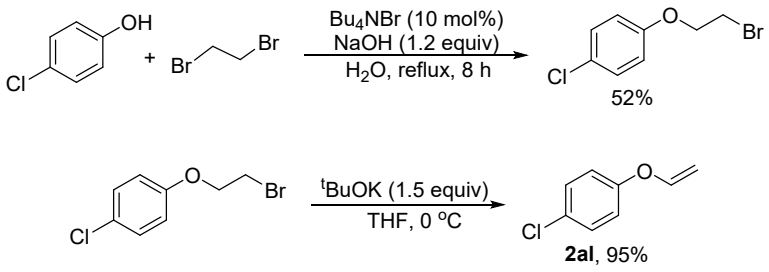
3. Procedure for the synthesis of 2ai and 2al.



2ai

An oven-dried 25 mL round bottom flask under argon was charged with estrone (0.81 g, 3.0 mmol, 1.0 equiv) and CH_2Cl_2 (10 mL, 0.3 M). The mixture was cooled to 0 °C and Et_3N (0.84 mL, 6.0 mmol, 2.0 equiv) and Tf_2O (0.55 mL, 3.3 mmol, 1.1 equiv) were added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h. The brown resulting mixture was quenched with sat. $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by a flash column chromatography (PE/EtOAc) to afford a white solid (0.97 g, 2.4 mmol, 80%) with spectroscopic data in agreement with those reported in the previous literature.

An oven-dried 25 mL round bottom flask, intermediate product (0.80 g, 2.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol, 0.1 equiv), and LiCl (84.8 mg, 2.0 mmol, 1.0 equiv) were weighed and dissolved in anhydrous DMF (10 mL). The resulting mixture was purged with argon and closed with a septum cap and equipped with a Ar balloon. To this mixture tributyl(vinyl)stannane (0.70 g, 2.2 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was then heated up to 90 °C for 6 h. After completion the reaction, the resulting reaction mixture was cooled down to room temperature and diluted with Et_2O. The mixture was washed with 1.0 M HCl, sat. $NaHCO_3$ and sat. NaCl, and then evaporated to give the crude product. The residue was purified with a column chromatography (PE/EtOAc) to afford a white solid **2ai** (0.46 g, 1.64 mmol, 82%), which had the spectroscopic data in agreement with those reported in the previous literature.[4]



2al, 95%

A 50 mL round bottom flask was charged with 4-chlorophenol (2.57 g, 20.0 mmol, 1.0 equiv), 1,2-dibromoethane (7.51 g, 40.0 mmol, 2.0 equiv), NaOH (0.96 g, 24 mmol, 1.2 equiv), Bu_4NBr (0.64 g, 2 mmol, 0.1 equiv) and H_2O (30 mL). The reaction mixture was stirred at 100 ^oC for 12 hours. After completion of the reaction, the resulting reaction mixture was cooled down to room temperature and extracted with diethyl ether (3 × 20 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated in vacuum to obtain the crude mixture, which was further purified by a column chromatography (using 10% ethyl acetate/hexane as an eluent), giving the desired intermediate in 52% yield.

An oven-dried 50 mL round bottom flask, the obtained intermediate product (2.36 g, 10 mmol, 1.0 equiv) was dissolved in anhydrous THF (25 mL). The reaction mixture was stirred at an ice bath, and ^tBuOK (1.68 g, 15 mmol, 1.5 equiv) was added in portions. After 30 minutes, the resulting reaction mixture was extracted with diethyl ether (3 × 20 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated in vacuum to obtain the crude mixture, which was further purified by a column chromatography (using 2% ethyl acetate/hexane as an eluent), giving **2al** in 95% yield [CAS: 1074-56-2].[5]

4. Optimization of reaction conditions

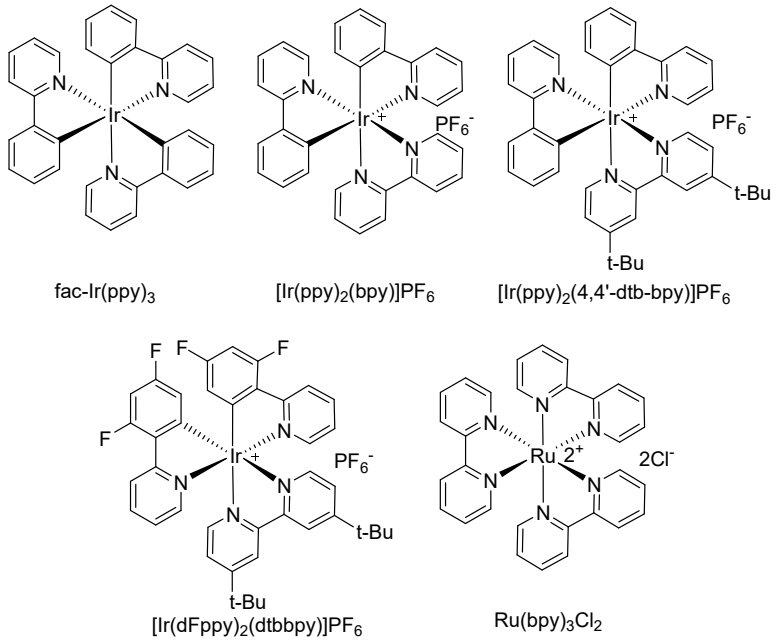
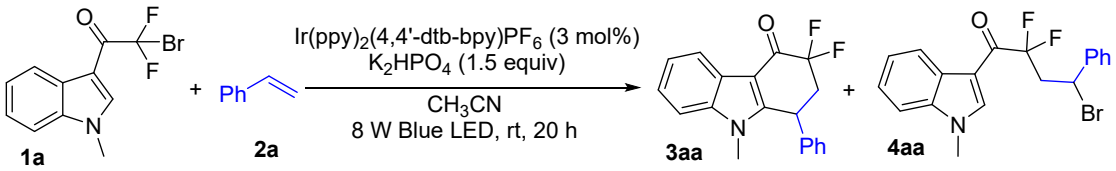


Figure S2. Structure of photocatalysts

Table S1. Optimization of the reaction conditions using **1a** and **2a** as the template substrates (equivalent ratio of reactants).



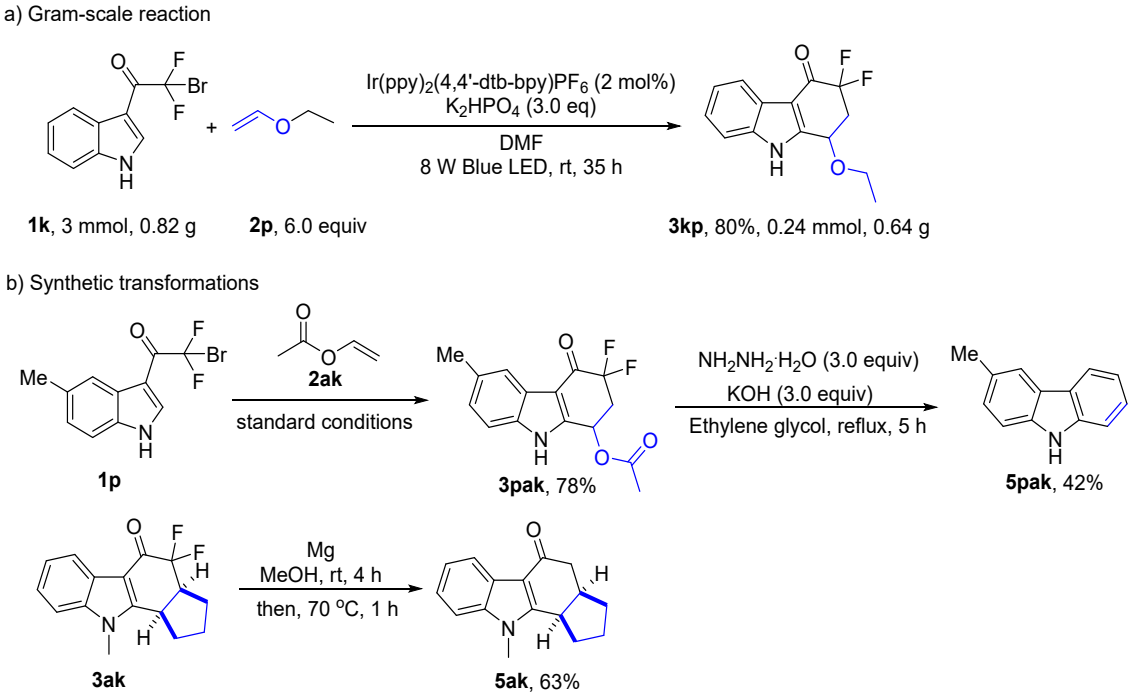
entry	**1a**	**2a**	**3aa**, yield (%)	**4aa**, yield (%)
1	1.0 equiv	3.0 equiv	35	21
2	1.0 equiv	2.0 equiv	34	18
3	1.0 equiv	1.5 equiv	25	14
4	1.5 equiv	1.0 equiv	52	6
5	2.0 equiv	1.0 equiv	51	5
6	3.0 equiv	1.0 equiv	53	9

Yields were determined by ^{1}H NMR analysis of the crude mixture using CH_2Br_2 as an internal standard.

5. General procedure for the synthesis of 3

To a 10.0 mL oven-dried tube were added substrate **1** (0.20 mmol, 1.0 equiv), $Ir(ppy)_2$(4,4'-dtb-bpy)PF_6 (0.002 mmol, 0.02 equiv), K_2HPO_4 (0.60 mmol, 3.0 equiv) and the flask was equipped with a Argon balloon for three times. Then the anhydrous degassed DMF (4.0 mL) and alkene **2** (styrene 2/3 equiv or alkene 6.0 equiv) was added to this flask via a syringe. The resulting mixture was stirred upon irradiation of 8 W blue LEDs at room temperature for 24 hours. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (petroleum ether: ethyl acetate = 20 : 1) to give the desired products **3** in 55-99% yields.

6. Scale-up experiment and synthetic transformations



Scale-up experiment:

To a 50 mL oven-dried tube were added substrate **1k** (3 mmol, 1.0 equiv), $Ir(ppy)_2(4,4'\text{-dtb-bpy})PF_6$ (0.06 mmol, 0.02 equiv), K_2HPO_4 (9.0 mmol, 3.0 equiv) and the flask was equipped with a Argon balloon for three times. Then the anhydrous degassed DMF (25 mL) and **2p** (18 mmol, 6.0 equiv) was added to this flask via a syringe. The resulting mixture was stirred upon irradiation of 8 W blue LEDs at room temperature for 35 hours. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (petroleum ether: ethyl acetate = 20 : 1) to give the desired product **3kp** in 80% yield.

Synthetic transformations:

The experimental procedures on the preparation of **3pak** was the same as those described above. To a 50 mL single-necked round flask, substrate **3aak** (1.5 mmol, 1.0 equiv) was dissolved in ethylene glycol (25 mL). Then, hydrazine hydrate (80%) (3.0 equiv) and KOH (3.0 equiv) were added to the flask under Ar atmosphere. The flask was equipped with water separator and a condenser. The mixture was refluxed for 1.5 hours and water was removed from the mixture by the separator. The reaction mixture was continuously refluxed for 2 hours. After completion, the mixture was cooled to room temperature, and ice/water was added to the reaction system upon quenching the reaction.

The pH value was then adjusted to neutral with 3.0 M HCl aqueous solution. The mixture was extracted with diethyl ether, dried over anhydrous Na_2SO_4. After evaporation of the solvents, the crude product was purified by a column chromatography with eluent (petroleum ether : ethyl acetate = 15 : 1) to afford product **5pak** in 42% yield.

Mg turnings (36.5 mg, 1.5 mmol) were added to a solution of **3ak** (82.6 mg, 0.3mmol) in MeOH (10 mL). The resulting mixture was stirred at room temperature for 1 h. After that, the reaction mixture was evaporated to dryness and re-dissolved in CH_2Cl_2 (20 mL). The solution was washed successively with sat. aq. NH_4Cl (10 mL) solution, sat. aq. NaCl (10 mL) solution, dried over $MgSO_4$ and concentrated in vacuo. Purification by a flash column chromatography afforded the title compound **5ak** as a colourless oil (45.2 mg, 63%).

7. Luminescence quenching experiments (Stern-Volmer studies) and quantum yield

Experimental procedure:

Emission intensities were recorded using a Hitachi F-2700 fluorescence spectrophotometer with a 10 nm band width. The measurements were performed using a 0.2 mM solution of photocatalyst $Ir(ppy)_2(4,4'\text{-dtb-bpy})PF_6$ in 2.0 mL of degassed DMF with varying concentration of a quencher. The samples were excited at 430 nm and emission intensity was recorded at 563 nm for $Ir(ppy)_2(4,4'\text{-dtb-bpy})PF_6$. The quenching of the excited state $Ir(III)^*$ by **1a** was carried out in DMF (Figure S3a). The results revealed that **1a** could significantly quench $Ir(ppy)_2(4,4'\text{-dtb-bpy})PF_6^*$. However, substrate **2a** could not successfully quench $Ir(ppy)_2(4,4'\text{-dtb-bpy})PF_6^*$ (Figure S3b).

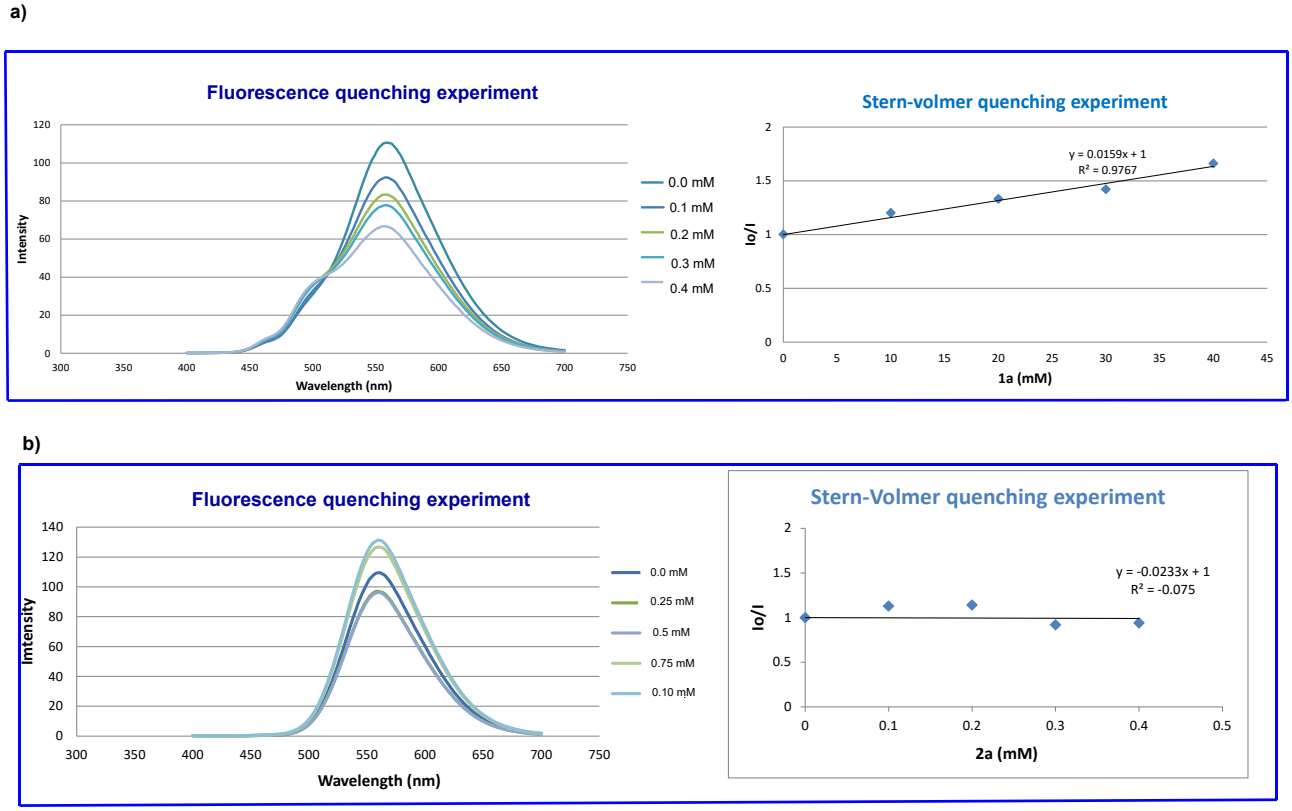


Figure S3. Stern-Volmer studies.

To further investigate the mechanism of this reaction, we employed the model reaction of **1a** and **2a** to measure the quantum yield in the formation of **3aa**.

A cuvette (sectional area 1 cm^2, height 4 cm) equipped with a magnetic stir bar was added substrate **1a** (0.15 mmol), **2a** (0.1 mmol), K_2HPO_4 (0.30 mmol, 3.0 equiv) and dry DMF (2.0 mL). After which, $Ir(ppy)_2(4,4'\text{-dtb-bpy})PF_6$ (0.002 mmol, 0.02 equiv) was added at room temperature. The heterogeneous mixture was degassed by bubbling argon for 20 min and placed at a distance (app. 5

cm) from 100 W Blue LED for 1 h, The reaction mixture was concentrated in vacuo and analyzed by ^{1}H NMR spectrum using CH_2Br_2 as an internal standard. The quantum yield is calculated to be 0.16.

$$\emptyset = \frac{n_x}{n_p} = \frac{n_x}{\frac{\Delta E \times S \times t}{N_A h v}} = \frac{n_x \times N_A \times h \times v}{\Delta E \times S \times t \times \lambda}$$

$$= \frac{0.020 \times 10^{-3}\, mol \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34}\, J.s \times 2.998 \times 10^{8}\, m.s^{-1}}{\left(4.9 \times 10^{-3}\, W.cm^{-2} \times 2\ cm^2\right) \times 3600\, s \times 415 \times 10^{-9}\, m} = 0.16$$

n_x is the amount of photochemical or photophysical events x occurred during irradiation, n_p is the number of photons absorbed by the reactant. E is the radiant power. S is the irradiated area: 2 cm^2 ; t is the irradiated time: 3600 s; N_A is the Avogadro constant: 6.022×10^{23}/mol; h is the Planck constant: 6.626×10^{-34} $J{\cdot}s$; v is the frequency of incident light; c is velocity of light 2.998×10^{8} m/s. λ is the wavelength: 415 nm; n_x was analyzed by ^{1}H NMR spectrum, ΔE was measured by ILT1400 Portable Radiometer/Photometer.

The quantum yield is lower than 1.0. However, we still cannot exclude the possible radical chain process of this reaction considering the factors of existence of inefficient initiation step or short-lived chains.[6]

8. The proposed reaction mechanism

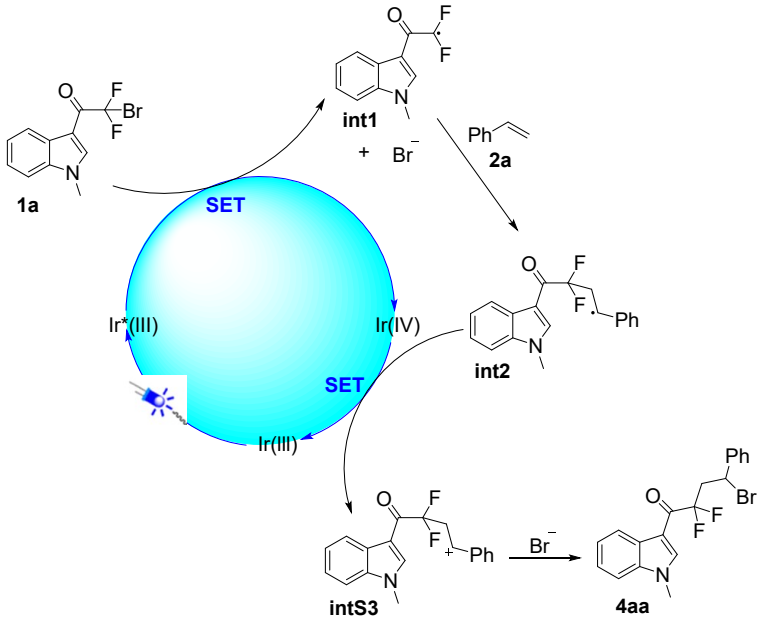


Figure S4. The proposed reaction mechanism for the formation of **4aa**.

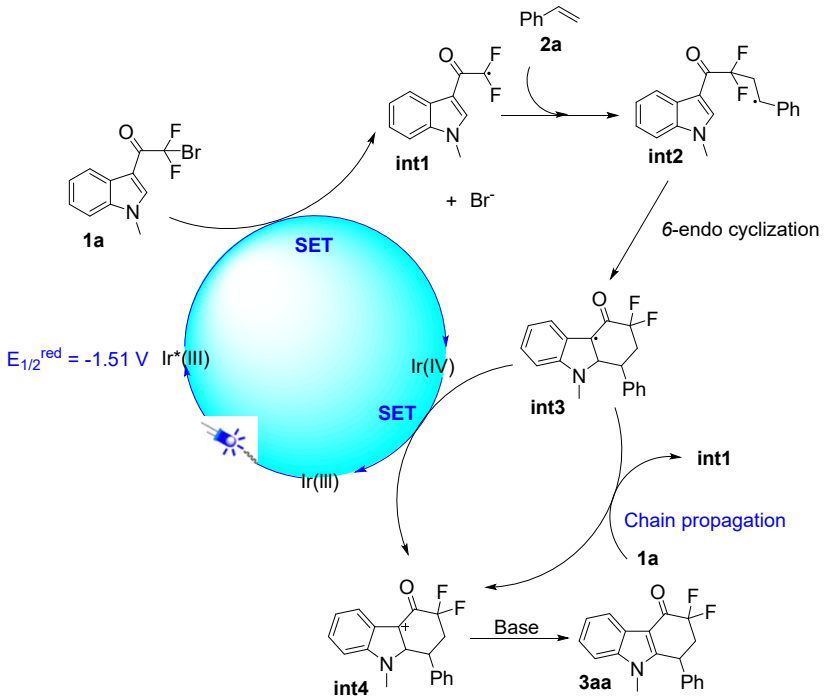
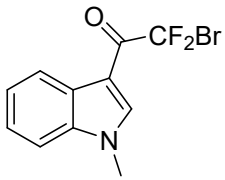


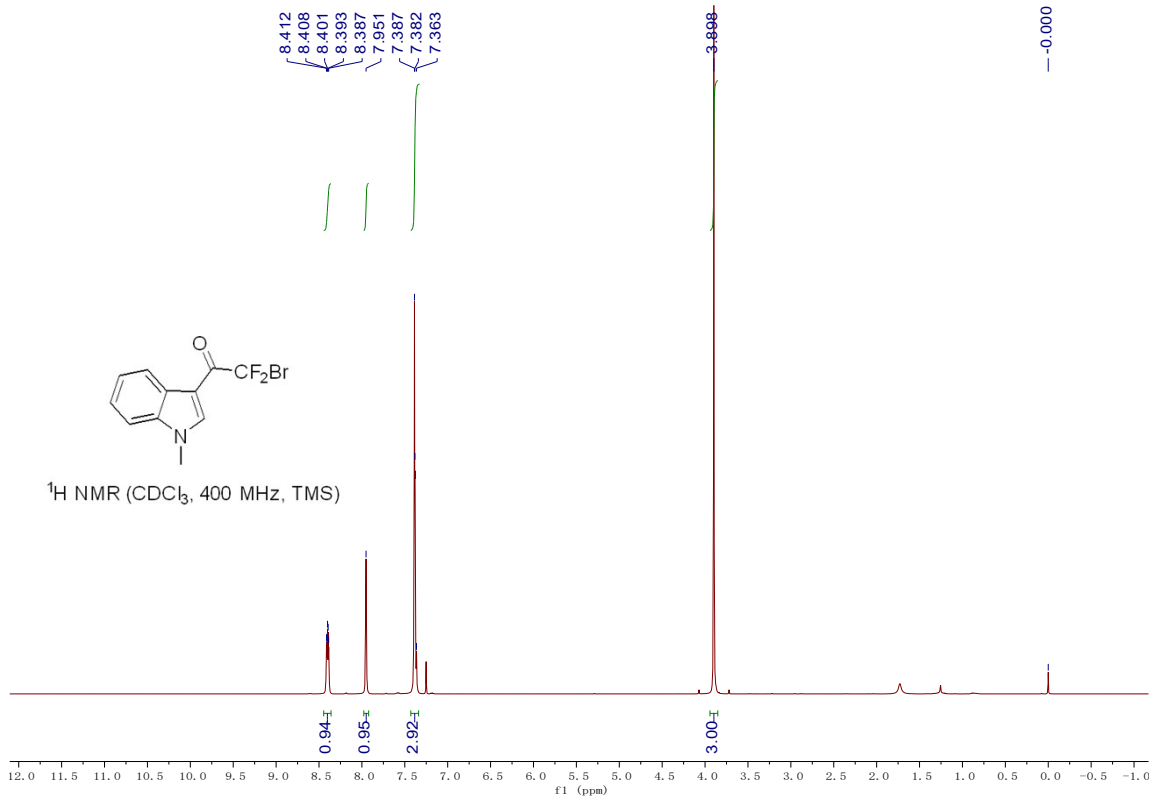
Figure S5. The proposed reaction mechanism for **3aa** if with a radical chain pathway.

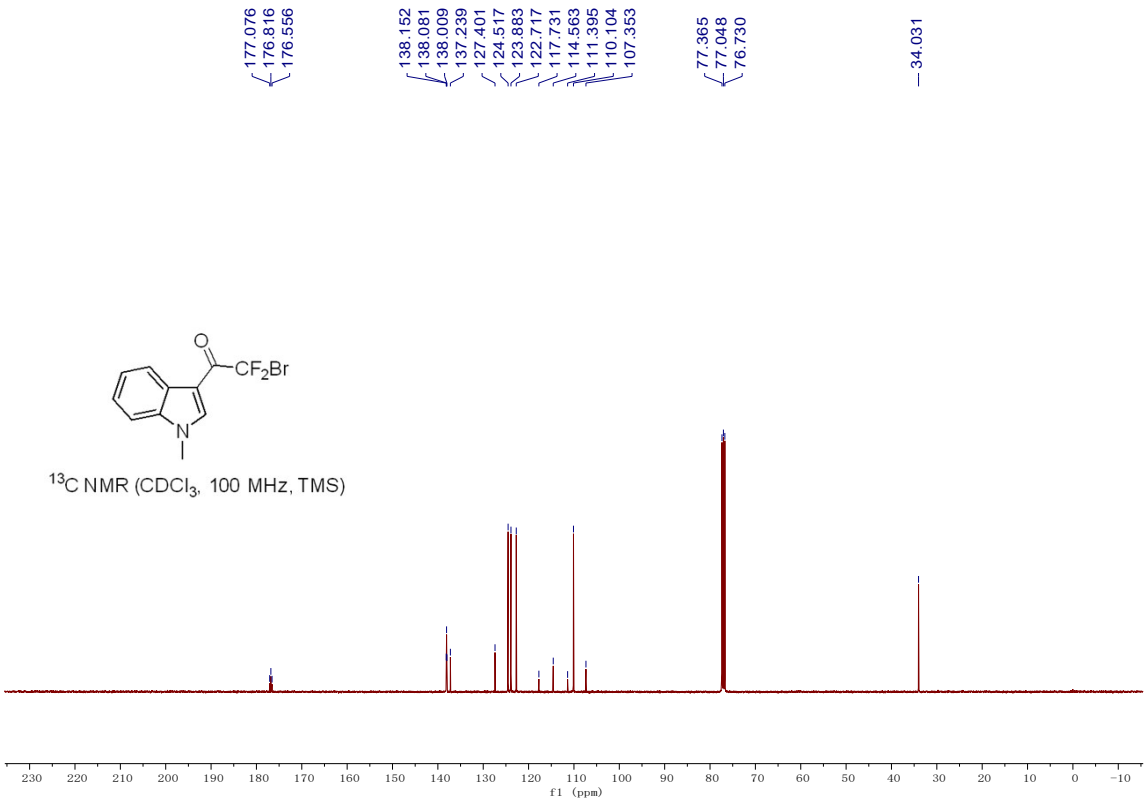
9. Spectroscopic data of substrates



2-bromo-2,2-difluoro-1-(1-methyl-1H-indol-3-yl)ethan-1-one (1a)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A brown solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.90 (s, 3H), 7.36-1.39 (m, 3H), 7.95 (s, 1H), 8.39-8.41 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 34.0, 107.4, 110.1, 114.6 (t, *J* = 316.8 Hz), 122.7, 123.9, 124.5, 127.4, 137.2, 138.1 (t, *J* = 7.1 Hz), 176.8 (t, *J* = 26.0 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.8.

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110.104
107.353
77.365
77.048
76.730
34.031
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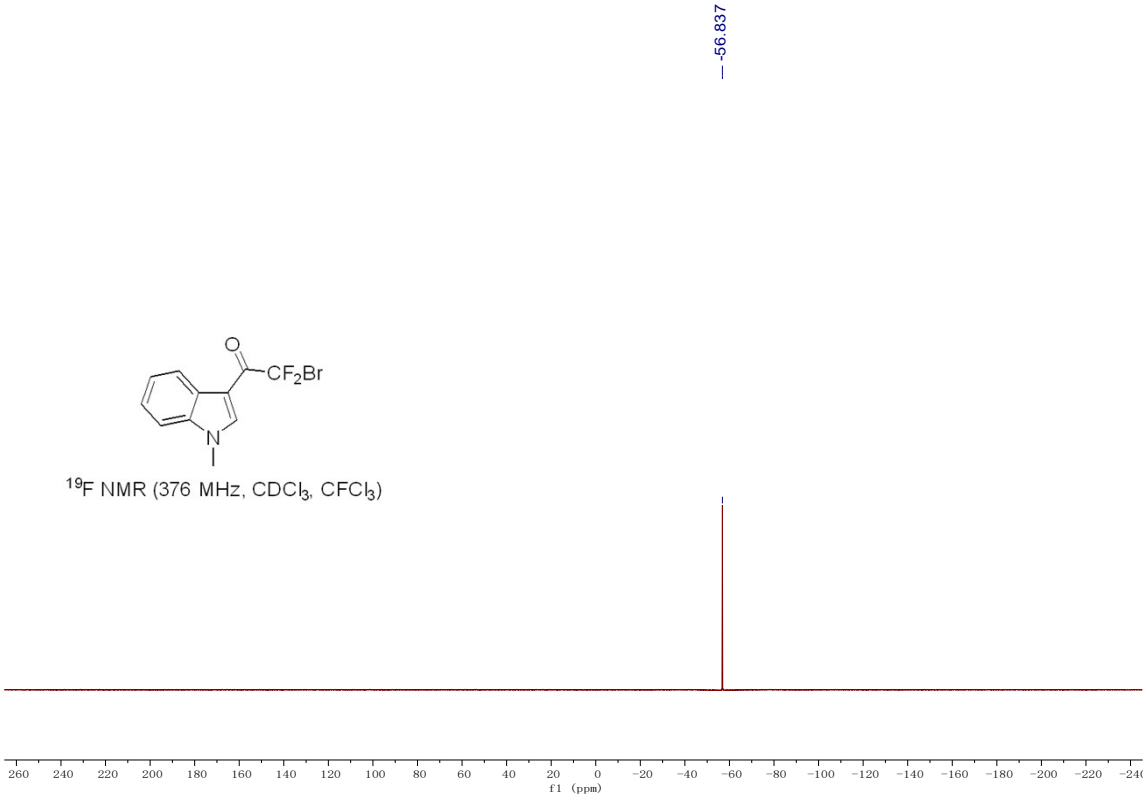
f1 (ppm)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O
CF2Br
N
19F NMR (376 MHz, CDCl3, CFCl3)
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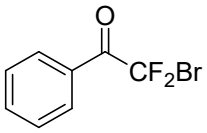
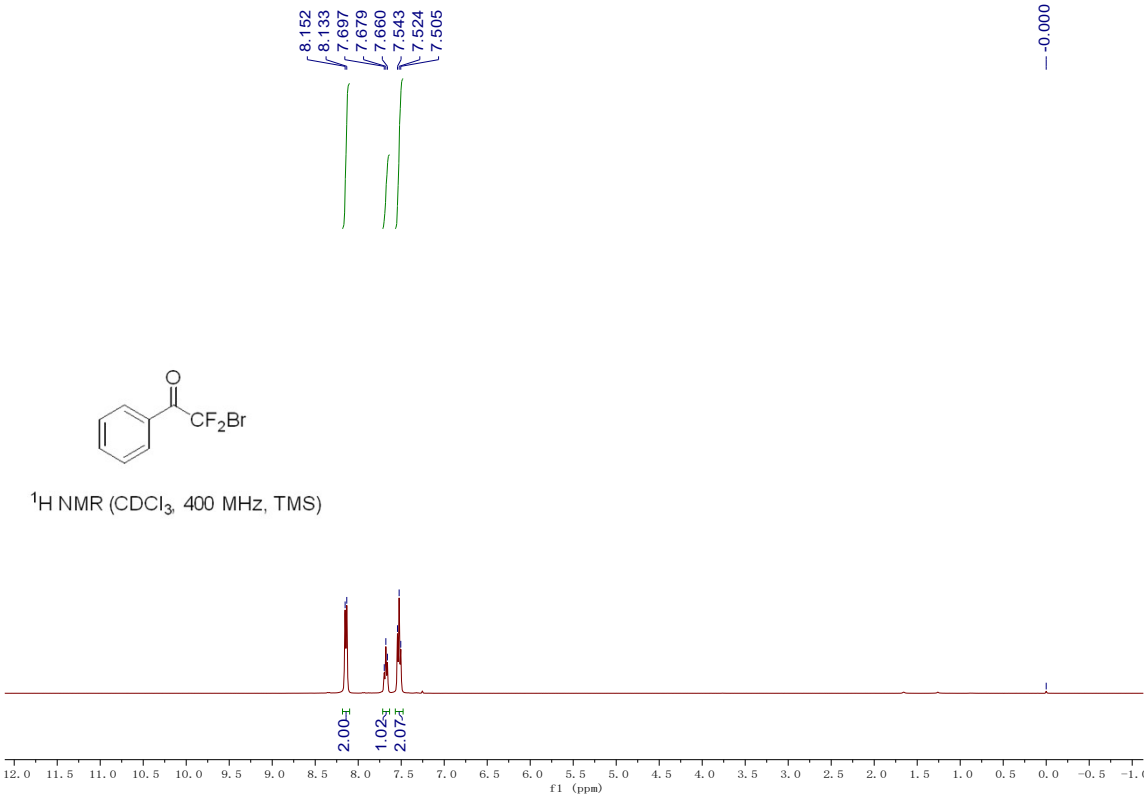
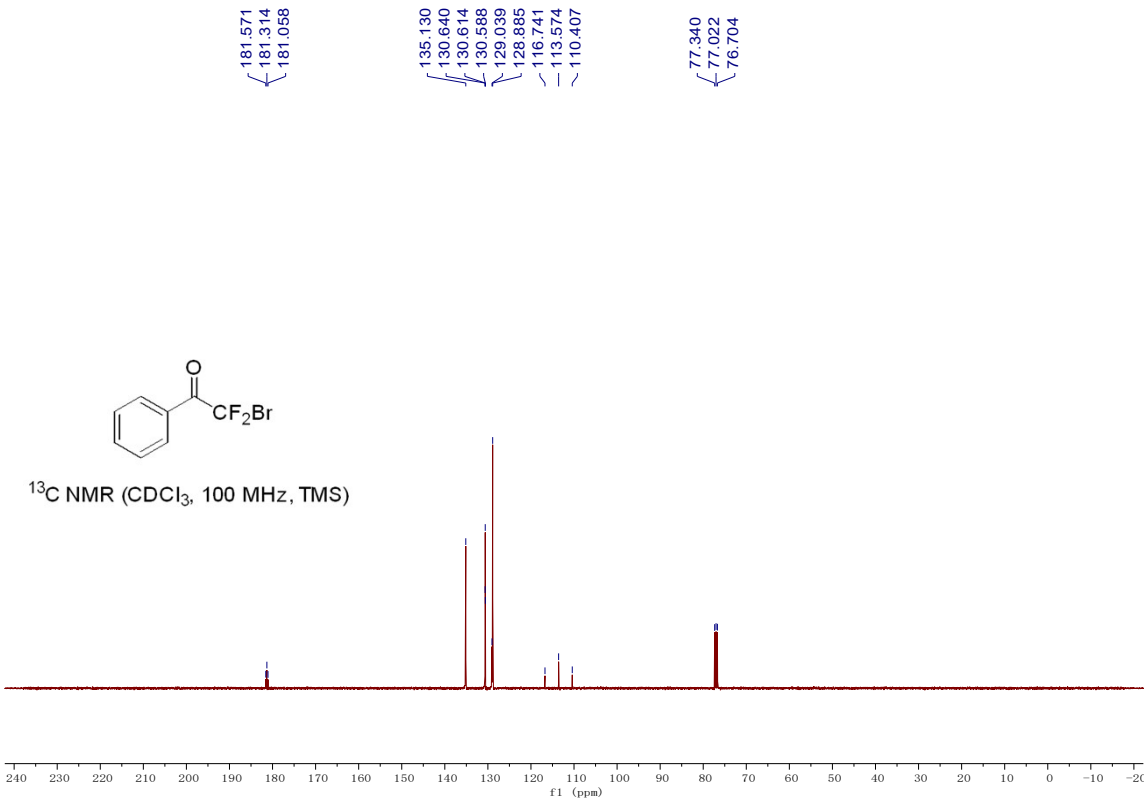
f1 (ppm)



2-bromo-2,2-difluoro-1-phenylethan-1-one (1b)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[3] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.52 (t, J = 7.6 Hz, 2H), 7.68 (t, J = 7.4Hz, 1H), 8.14 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 113.6 (t, J = 318.6 Hz), 128.9, 129.0, 130.6 (t, J = 2.6 Hz), 135.1, 181.3 (t, J = 25.8 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -57.8.

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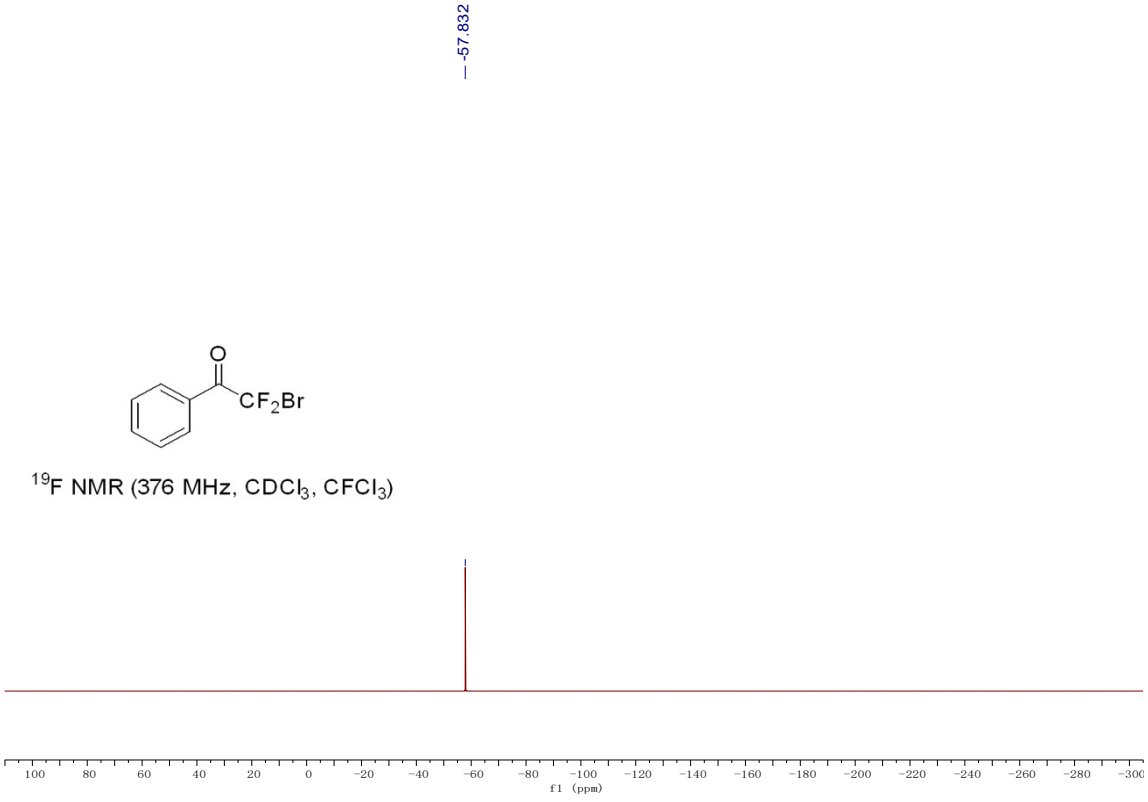
O
CF2Br
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)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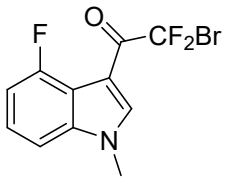
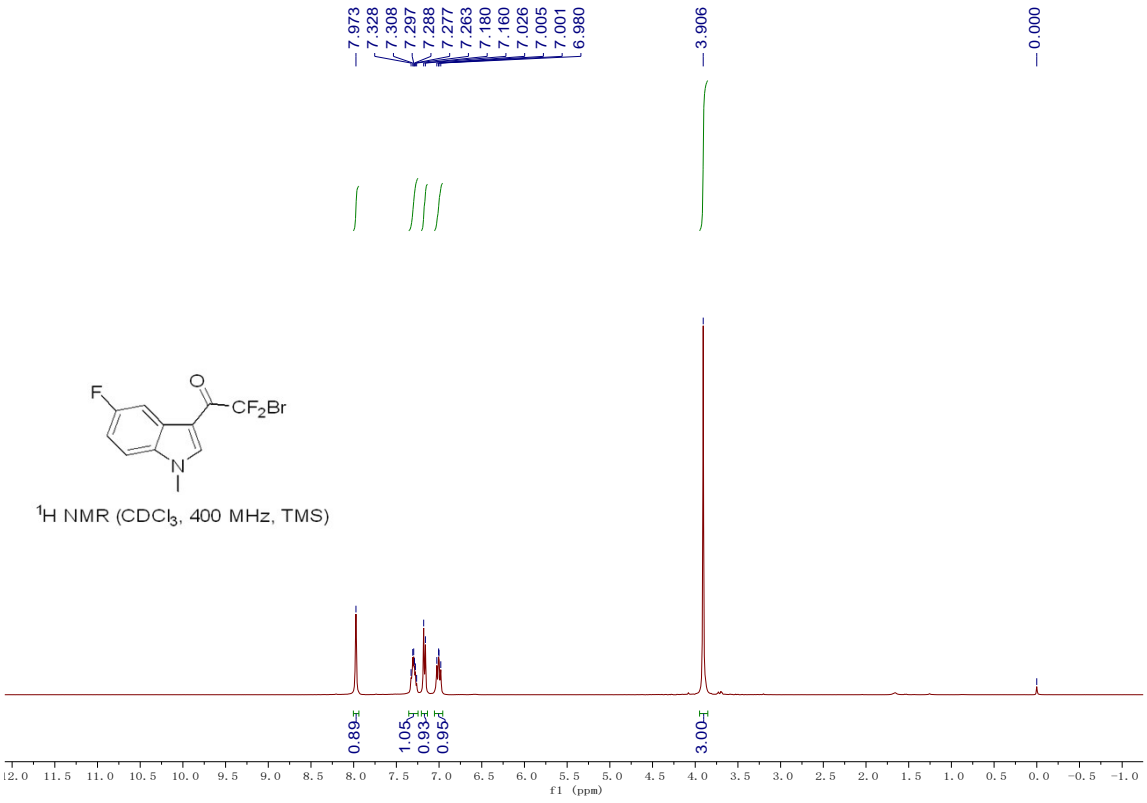
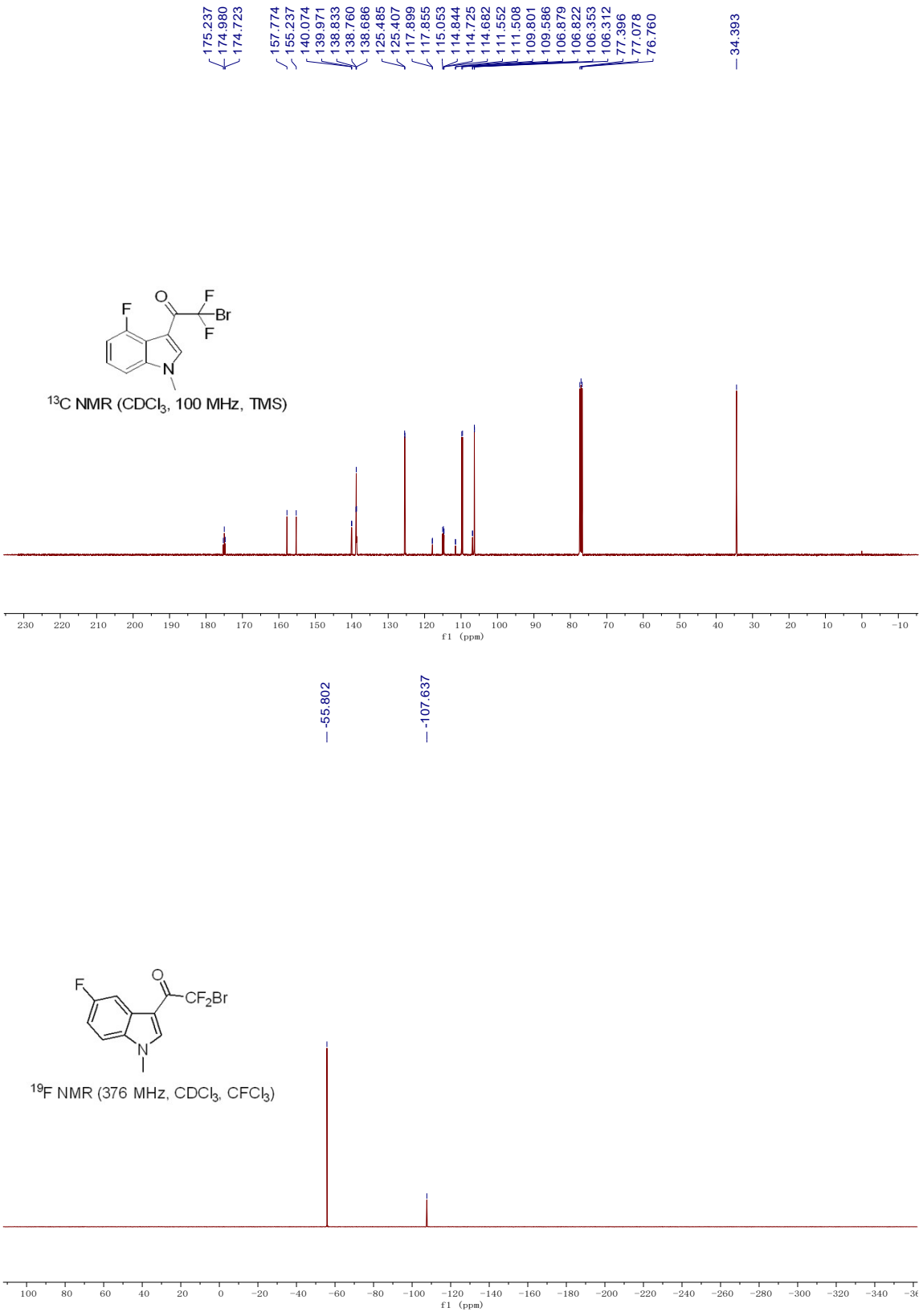
O
CF2Br
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

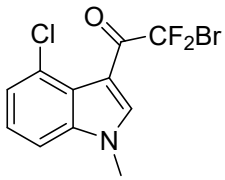


2-bromo-2,2-difluoro-1-(4-fluoro-1-methyl-1H-indol-3-yl)ethan-1-one (1c)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.91 (s, 3H), 6.98-7.03 (m, 1H), 7.17 (d, J = 8.0 Hz), 7.26-7.33 (m, 1H), 7.97 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 34.4, 106.3 (d, J = 4.1 Hz), 106.9 (d, J = 5.7 Hz), 109.7 (d, J = 21.6 Hz), 114.7 (td, J_1 = 4.3 Hz, J_2 = 317.4 Hz), 114.9 (d, J = 21.1 Hz), 125.5 (d, J = 7.9 Hz), 138.8 (t, J = 7.4 Hz), 140.0 (d, J = 10.3 Hz), 156.5 (d, J = 255.2 Hz), 175.0 (t, J = 25.9 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.6, -55.8.

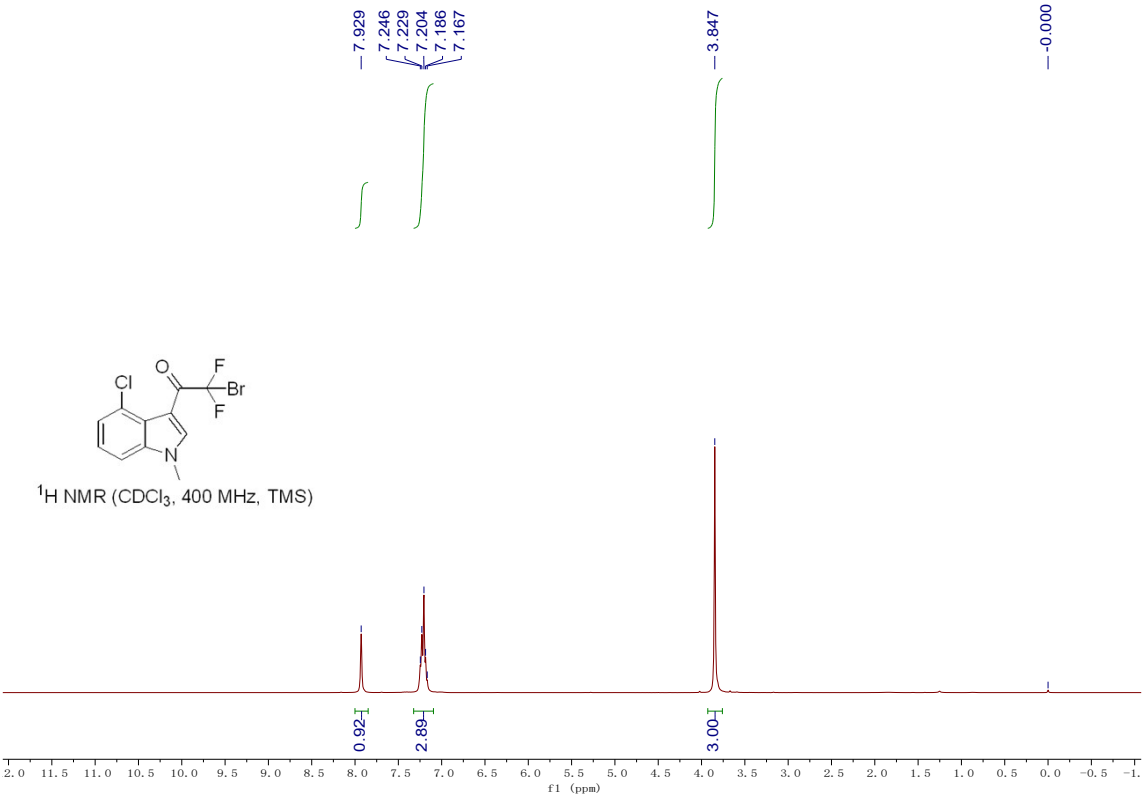


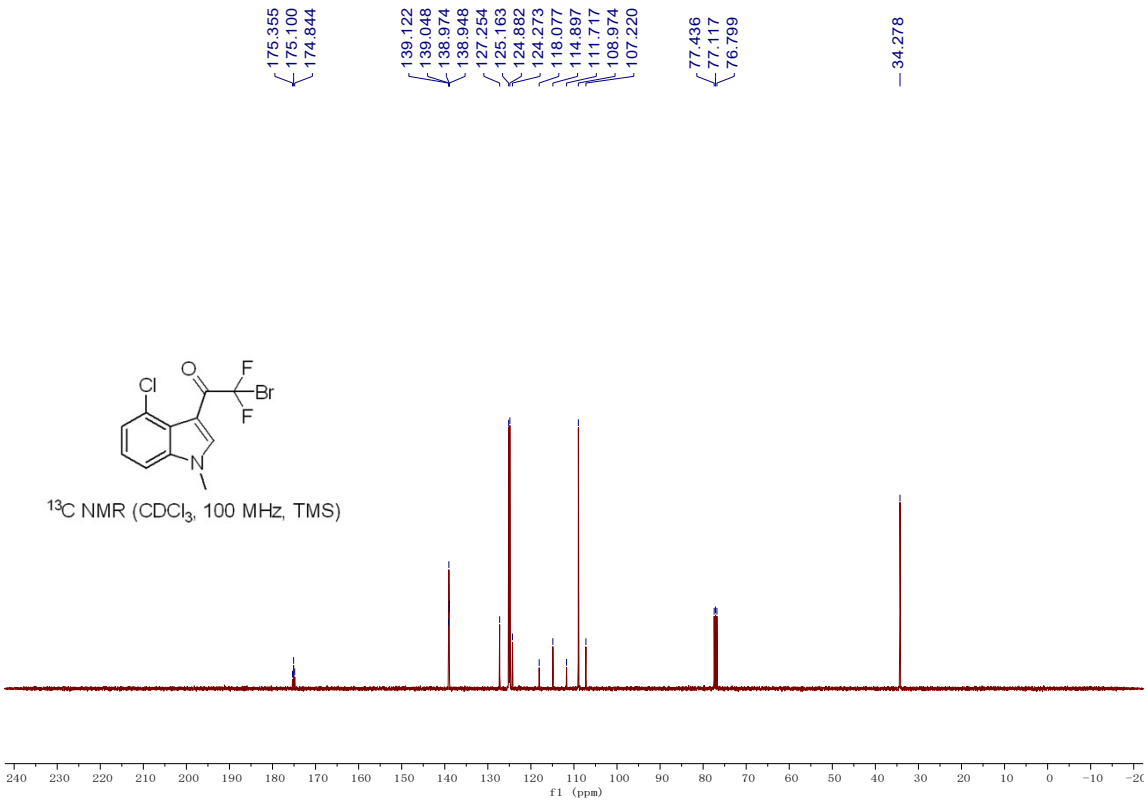

175.237
174.980
174.723
157.774
155.237
140.074
139.971
138.833
138.760
138.686
125.485
125.407
117.899
117.855
115.053
114.844
114.725
114.682
111.552
111.508
109.801
109.586
106.879
106.822
106.353
106.312
77.396
77.078
76.760
34.393
O
F
F
Br
F
N
13C NMR (CDCl3, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
-55.802
-107.637
F
O
CF2Br
N
19F NMR (376 MHz, CDCl3, CFCl3)
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340
f1 (ppm)

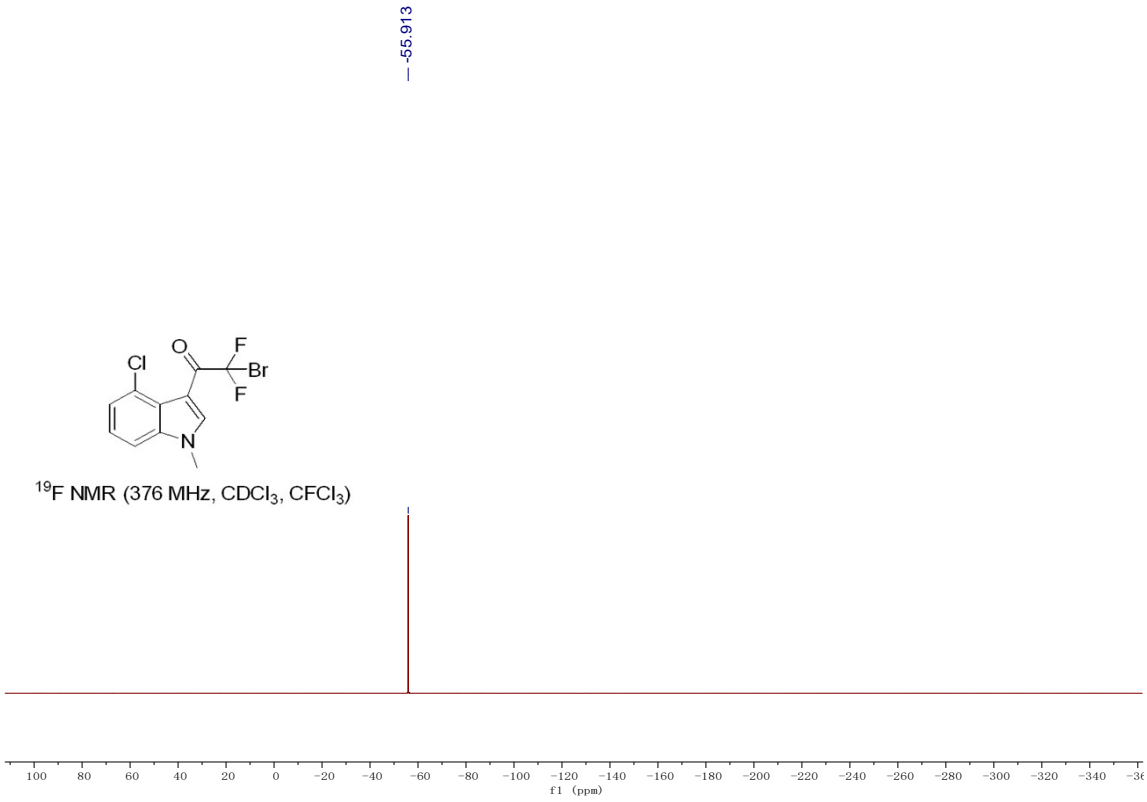


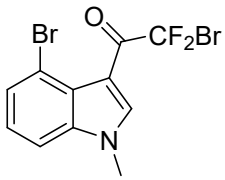
2-bromo-1-(4-chloro-1-methyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1d)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.85 (s, 3H), 7.17-7.25 (m, 3H), 7.93 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 34.3, 107.2, 109.0, 114.9 (t, J = 319.9 Hz), 124.3, 124.9, 125.2, 127.3, 138.9, 139.0 (t, J = 7.4 Hz), 175.1 (t, J = 25.7 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -55.9.



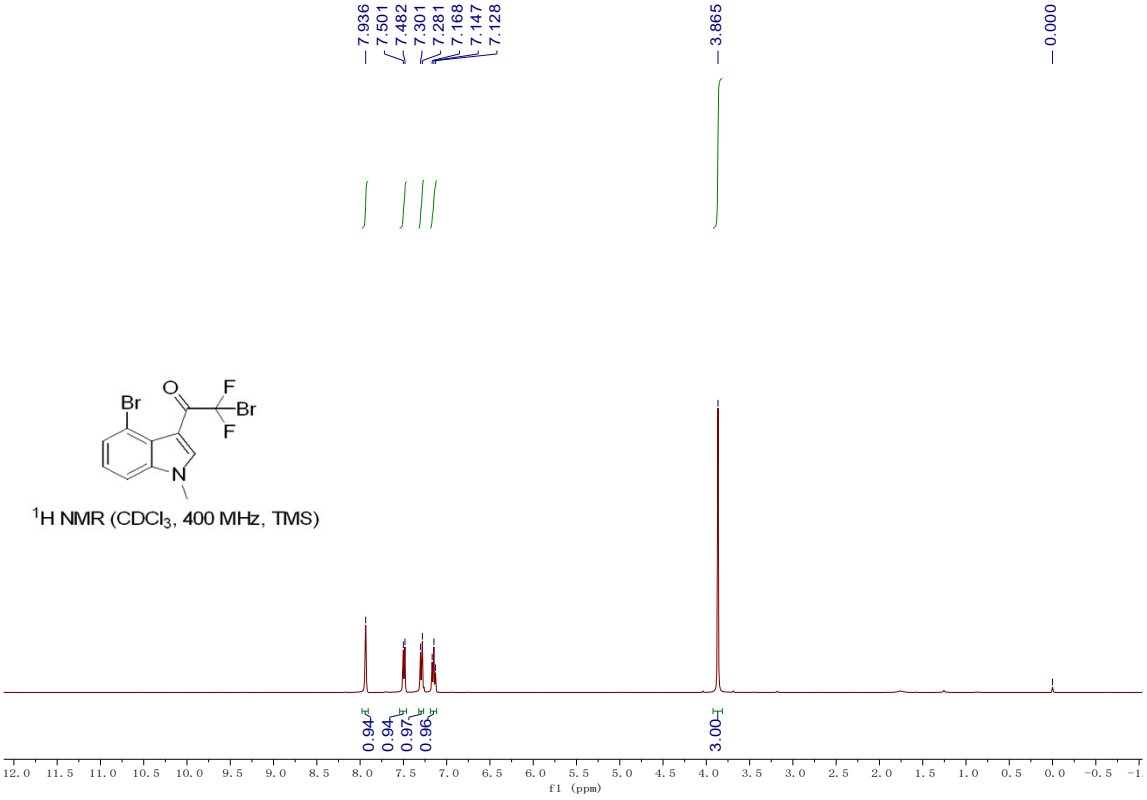

175.355
175.100
174.844
139.122
139.048
138.974
138.948
127.254
125.163
124.882
124.273
118.077
114.897
111.717
108.974
107.220
77.436
77.117
76.799
34.278
Cl
O
F
Br
F
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

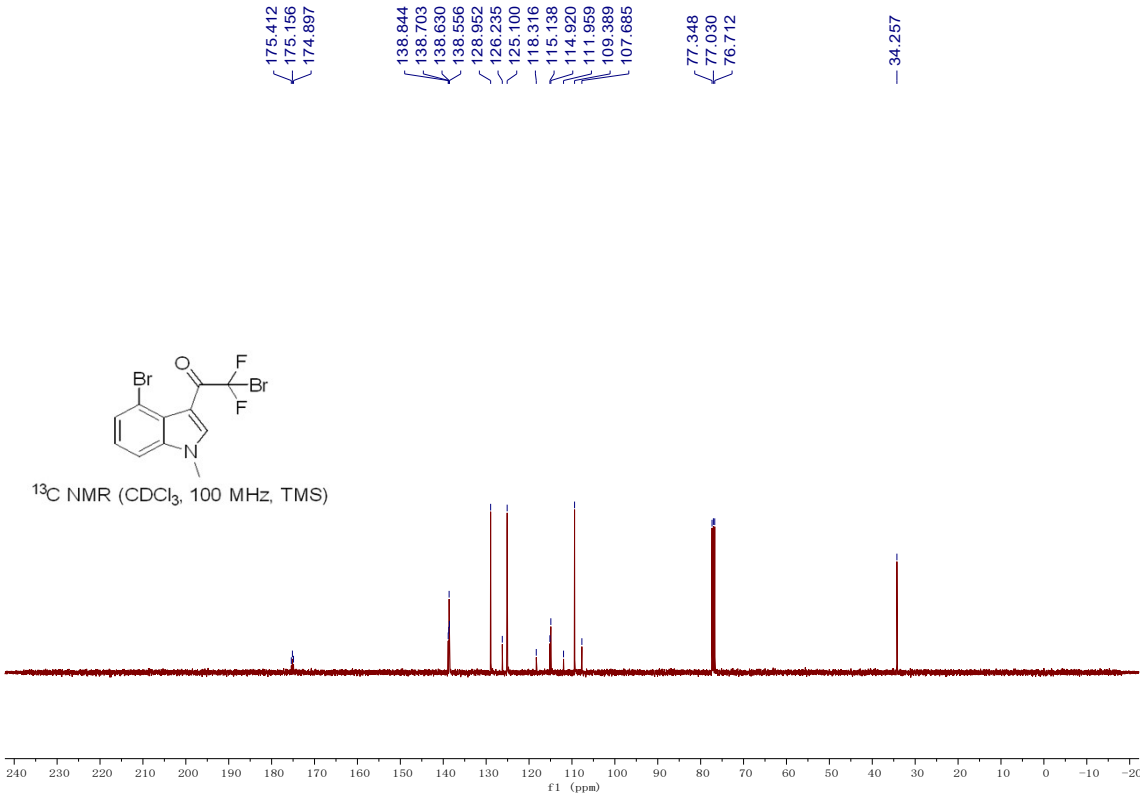

-55.913
Cl
O
F
Br
F
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

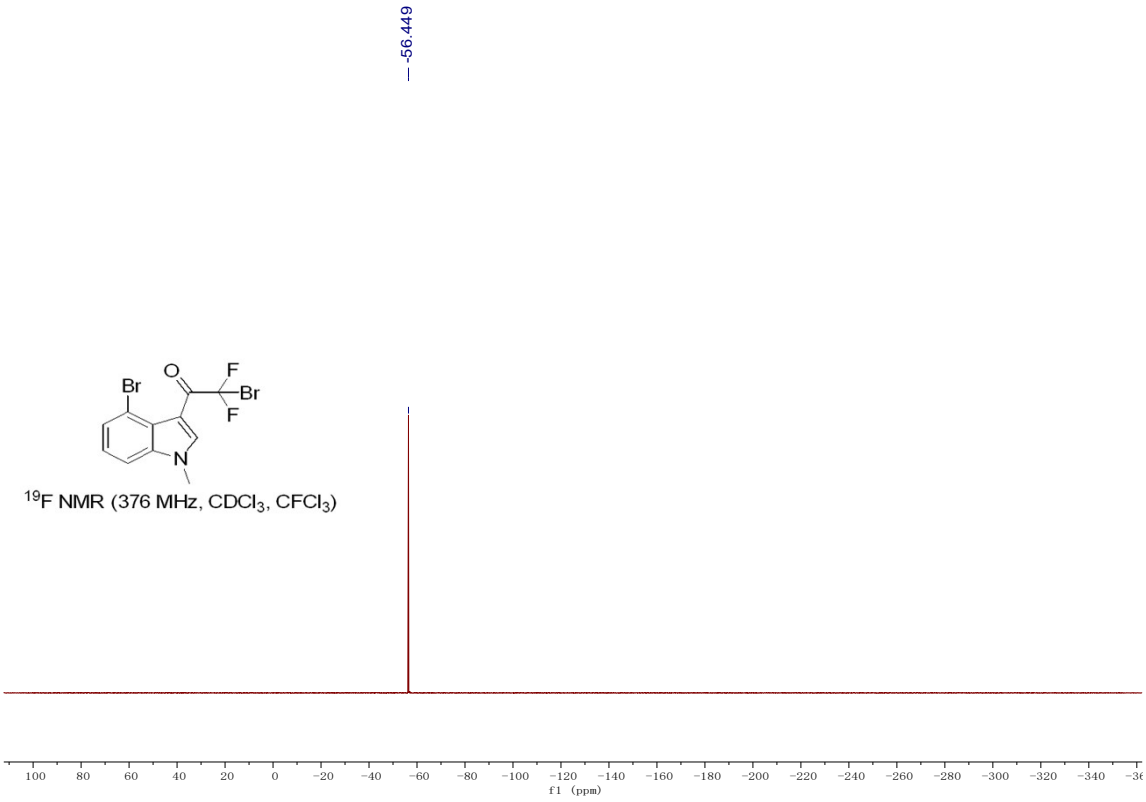


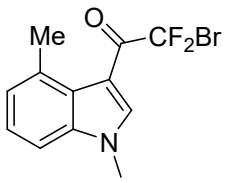
2-bromo-1-(4-bromo-1-methyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1e)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.87 (s, 3H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.94 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 34.3, 107.7, 109.4, 114.9, 115.1 (t, *J* = 317.9 Hz), 125.1, 126.2, 129.0, 138.6 (t, *J* = 7.4 Hz), 138.8, 175.2 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.4.



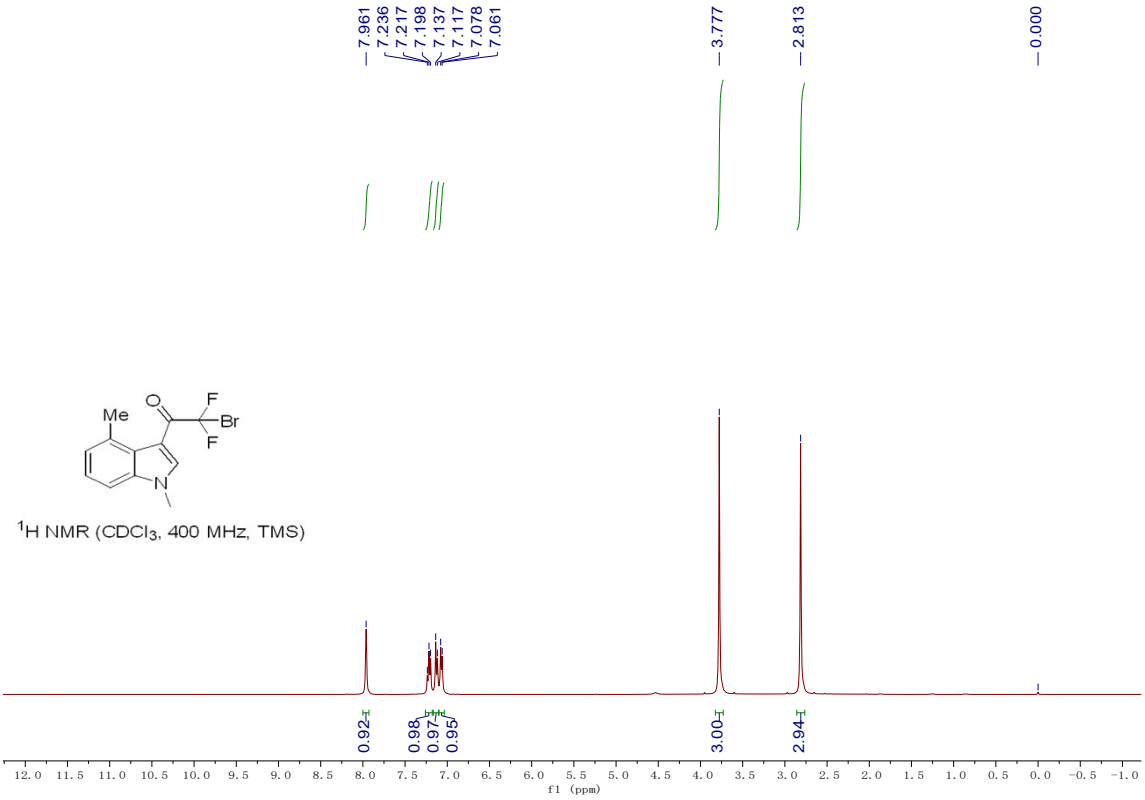

175.412
175.156
174.897
138.844
138.703
138.630
138.556
128.952
126.235
125.100
118.316
115.138
114.920
111.959
109.389
107.685
77.348
77.030
76.712
34.257
Br
O
F
Br
F
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

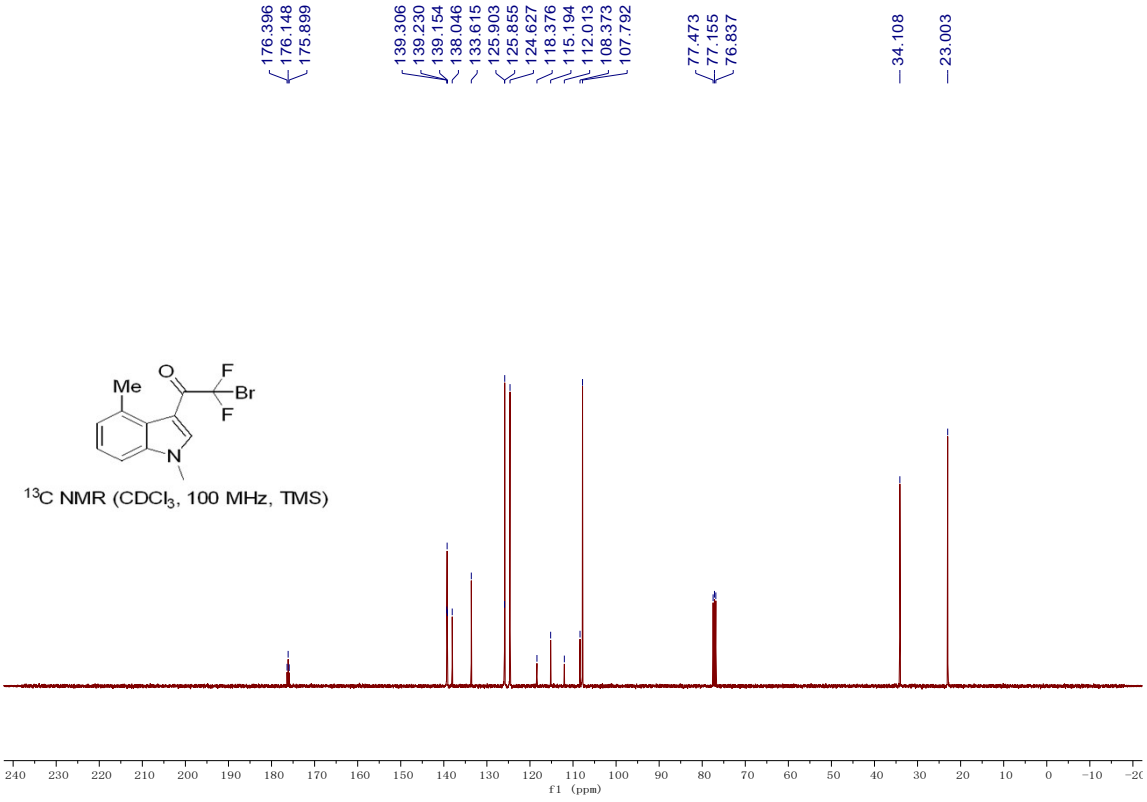

-56.449
Br
O
F
Br
F
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

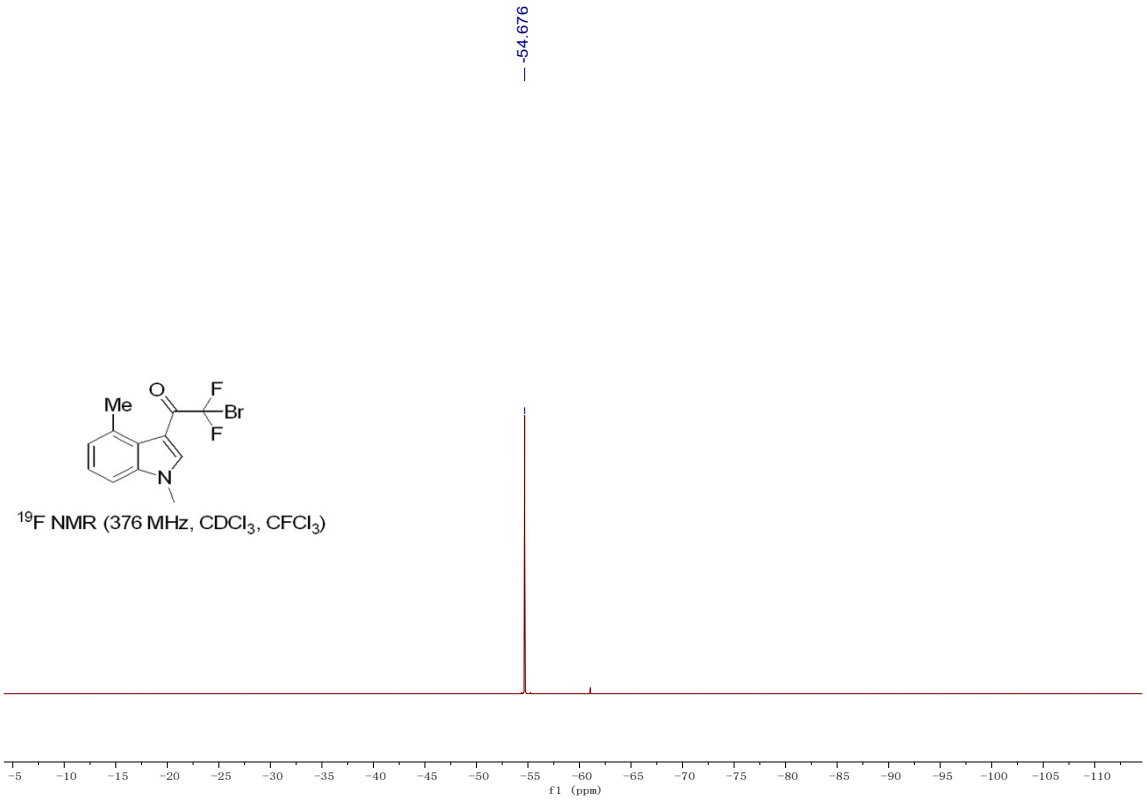


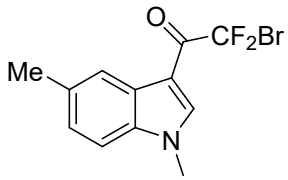
2-bromo-1-(1,4-dimethyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1f)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.81 (s, 3H), 3.78 (s, 3H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.96 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 23.0, 34.1, 107.8, 108.4, 115.2 (t, *J* = 320.1 Hz), 124.6, 125.85, 125.9, 133.6, 138.0, 139.2 (t, *J* = 7.7 Hz), 176.2 (t, *J* = 25.0 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -54.7.



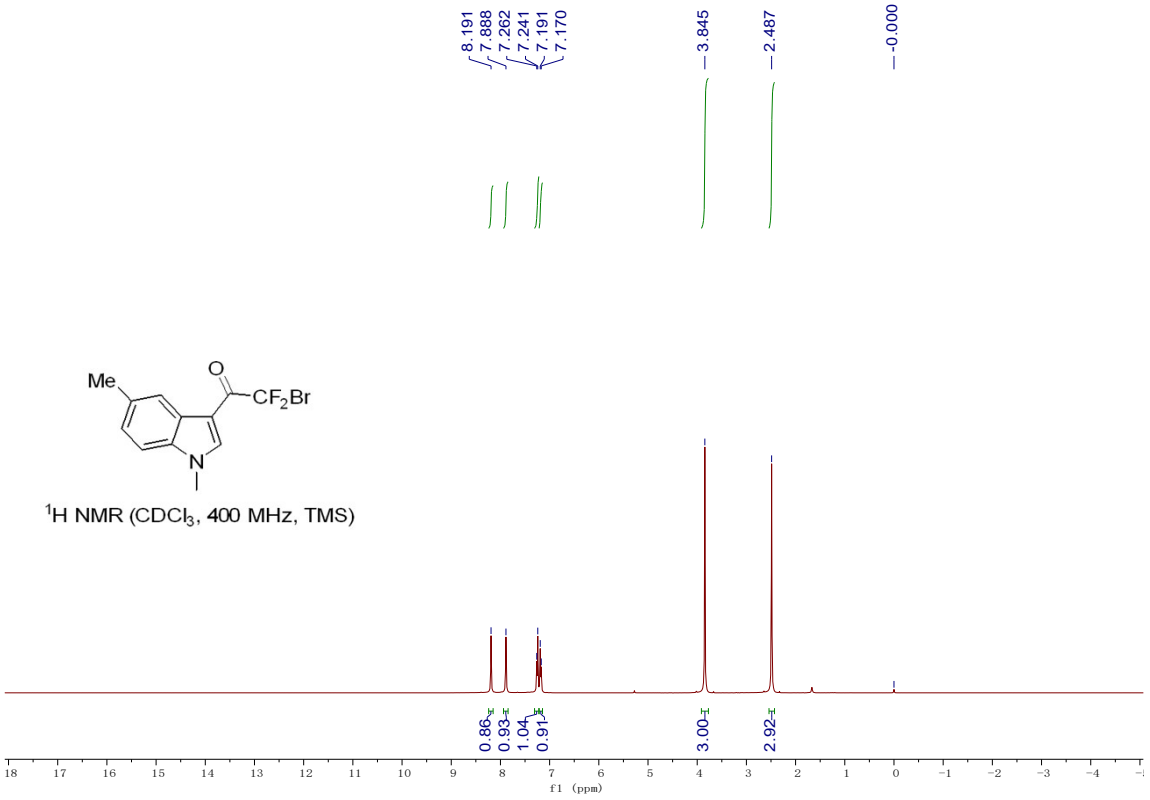

176.396
176.148
175.899
139.306
139.230
139.154
138.046
133.615
125.903
125.855
124.627
118.376
115.194
112.013
108.373
107.792
77.473
77.155
76.837
34.108
23.003
Me
O
F
Br
F
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

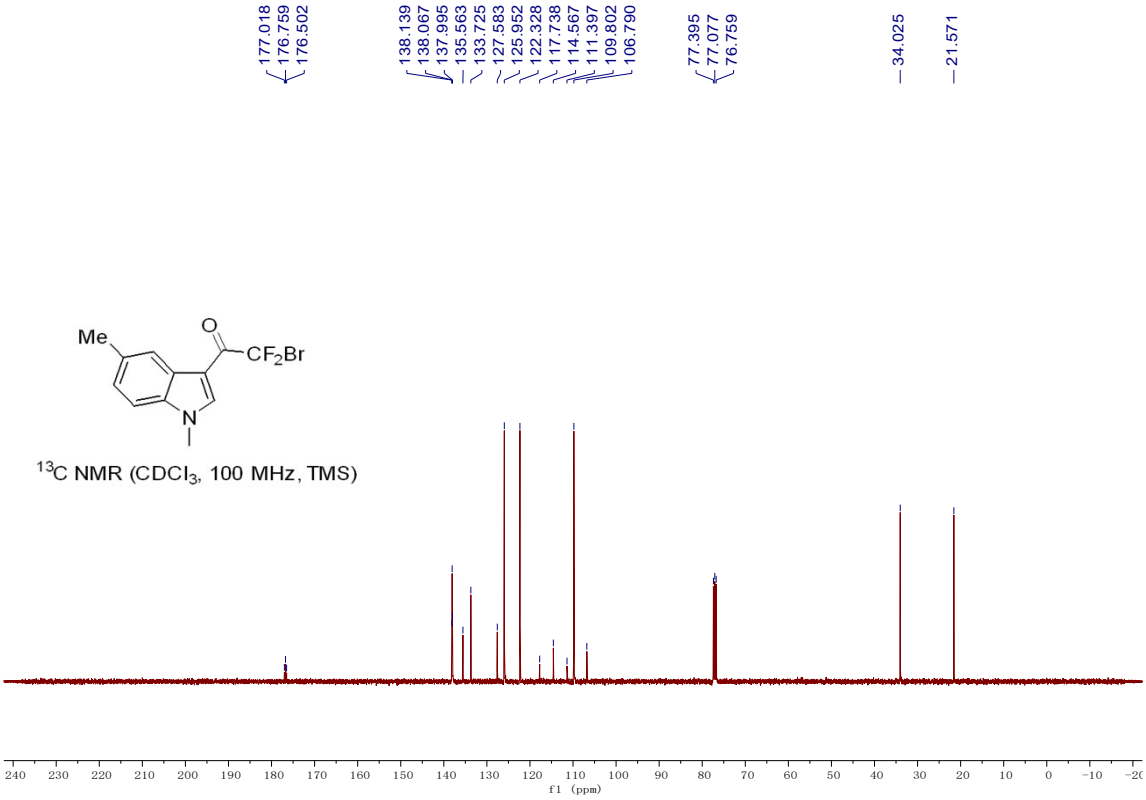

-54.676
Me
O
F
Br
F
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

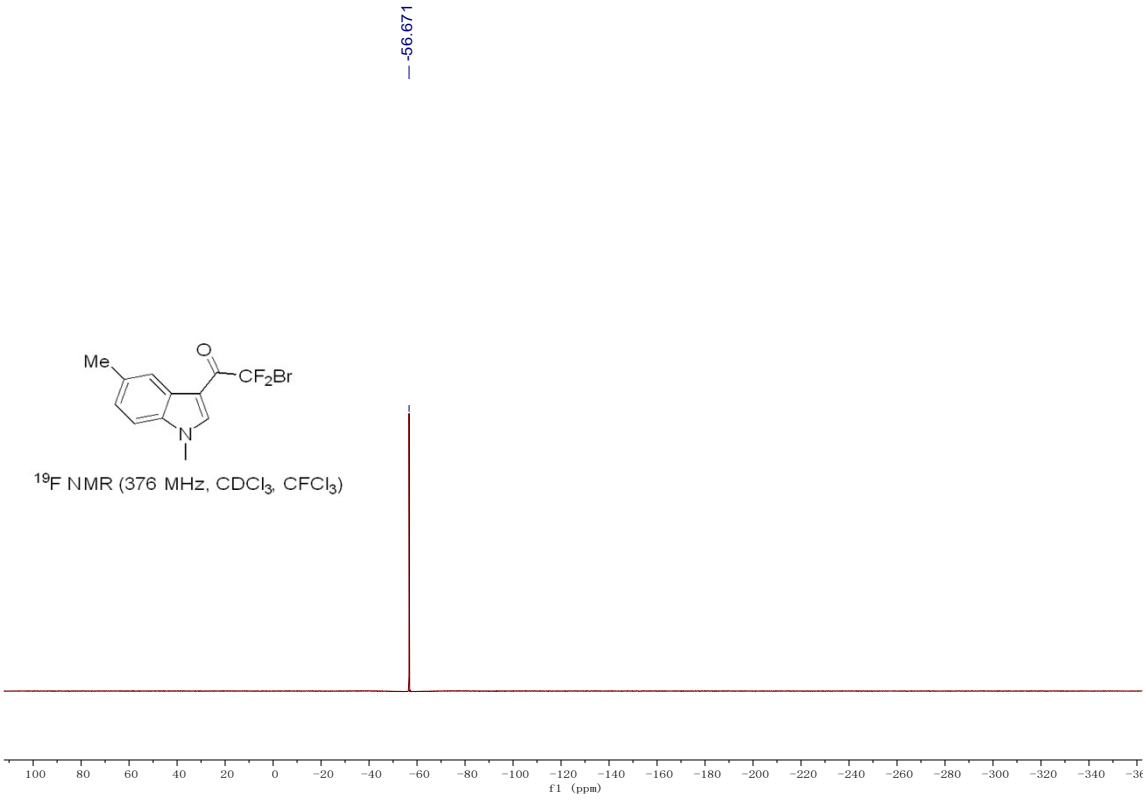


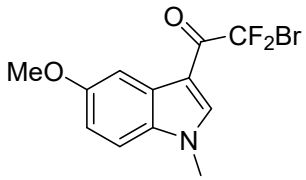
2-bromo-1-(1,5-dimethyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1g)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.49 (s, 3H), 3.85 (s, 3H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.89 (s, 1H), 8.19 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.6, 34.0, 106.8, 109.8, 114.6 (t, *J* = 318.9 Hz), 122.3, 126.0, 127.6, 133.7, 135.6, 138.1 (t, *J* = 7.3 Hz), 176.8 (t, *J* = 26.0 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -55.7.



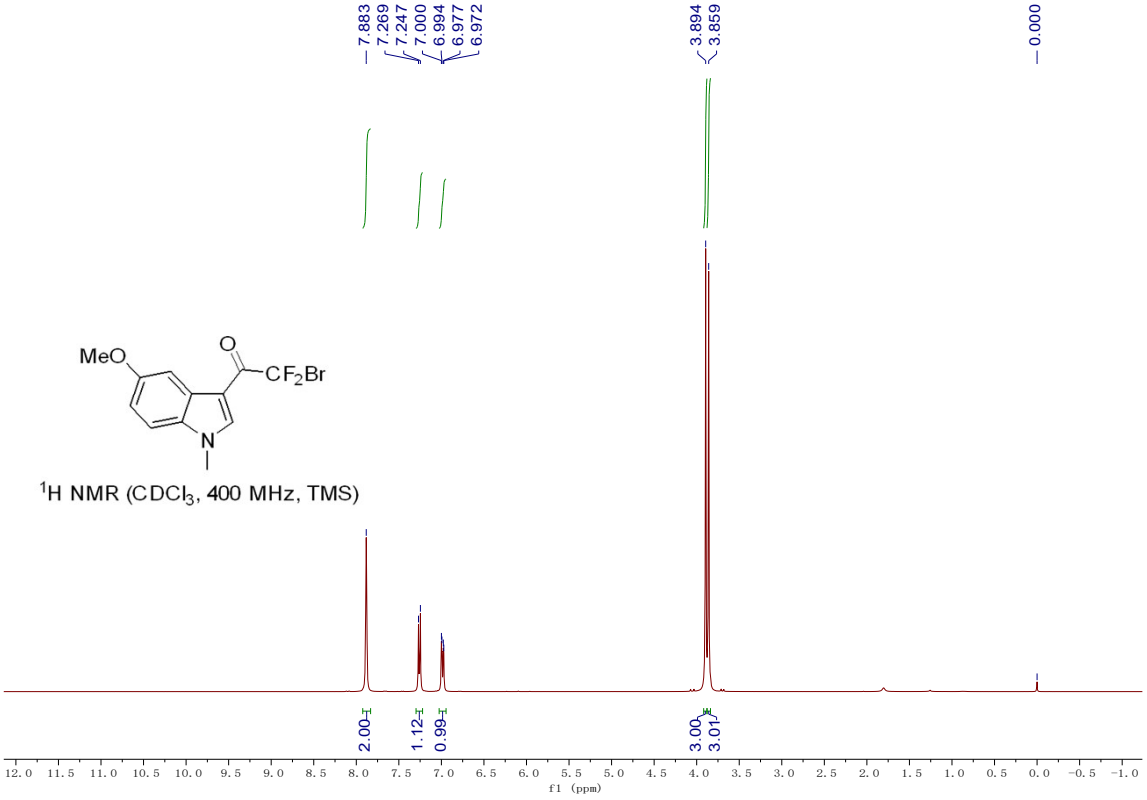

177.018
176.759
176.502
138.139
138.067
137.995
135.563
133.725
127.583
125.952
122.328
117.738
114.567
111.397
109.802
106.790
77.395
77.077
76.759
34.025
21.571
Me
O
CF2Br
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

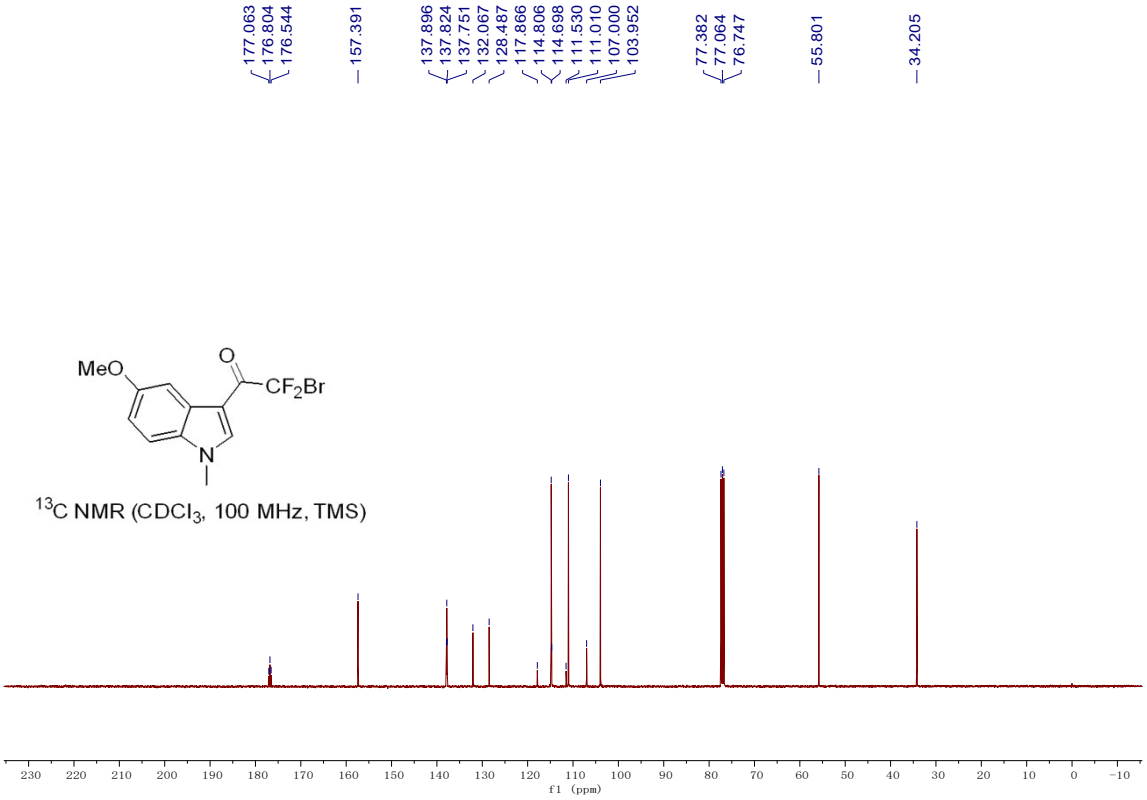

-56.671
Me
O
CF2Br
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

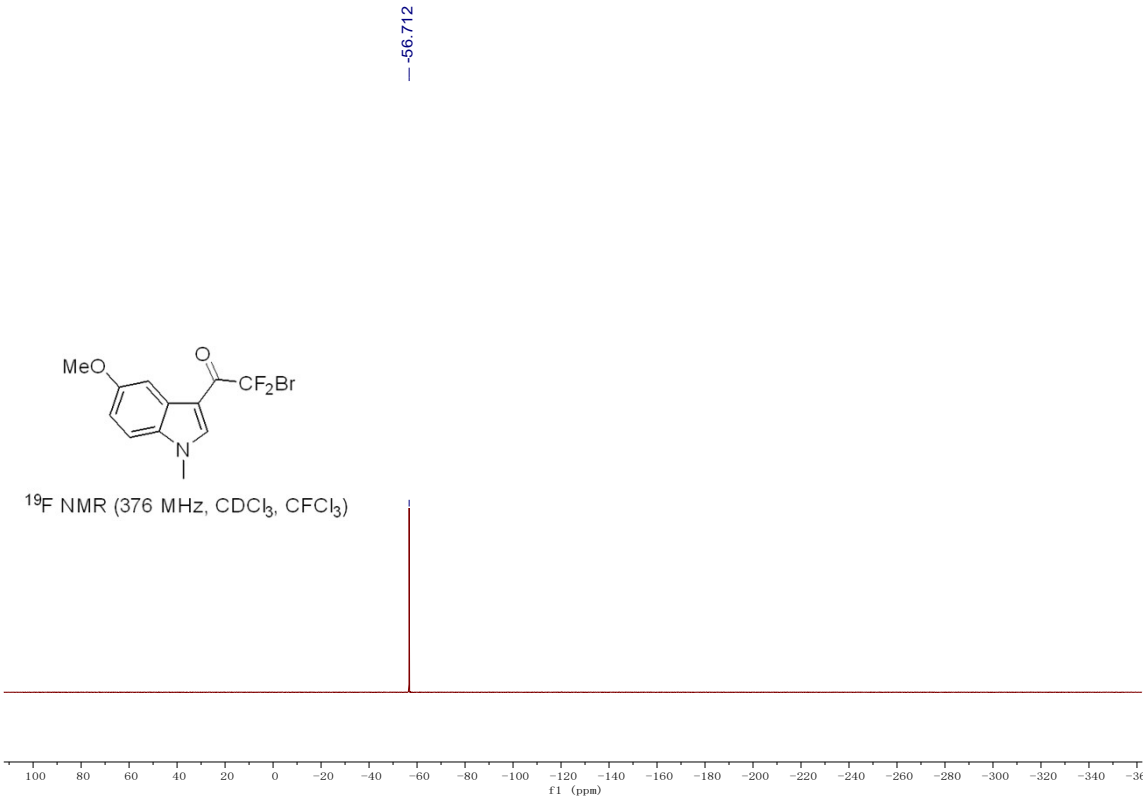


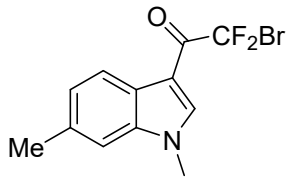
2-bromo-2,2-difluoro-1-(5-methoxy-1-methyl-1H-indol-3-yl)ethan-1-one (1h)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.86 (s, 3H), 3.89 (s, 3H), 6.99 (dd, J_1 = 2.2 Hz, J_2 = 9.0 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.88 (s, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 34.2, 55.8, 103.9, 107.0, 111.0, 114.7 (t, J = 316.8 Hz), 128.5, 132.1, 137.8 (t, J = 7.3 Hz), 157.4, 176.8 (t, J = 26.1, 26.1 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.7.



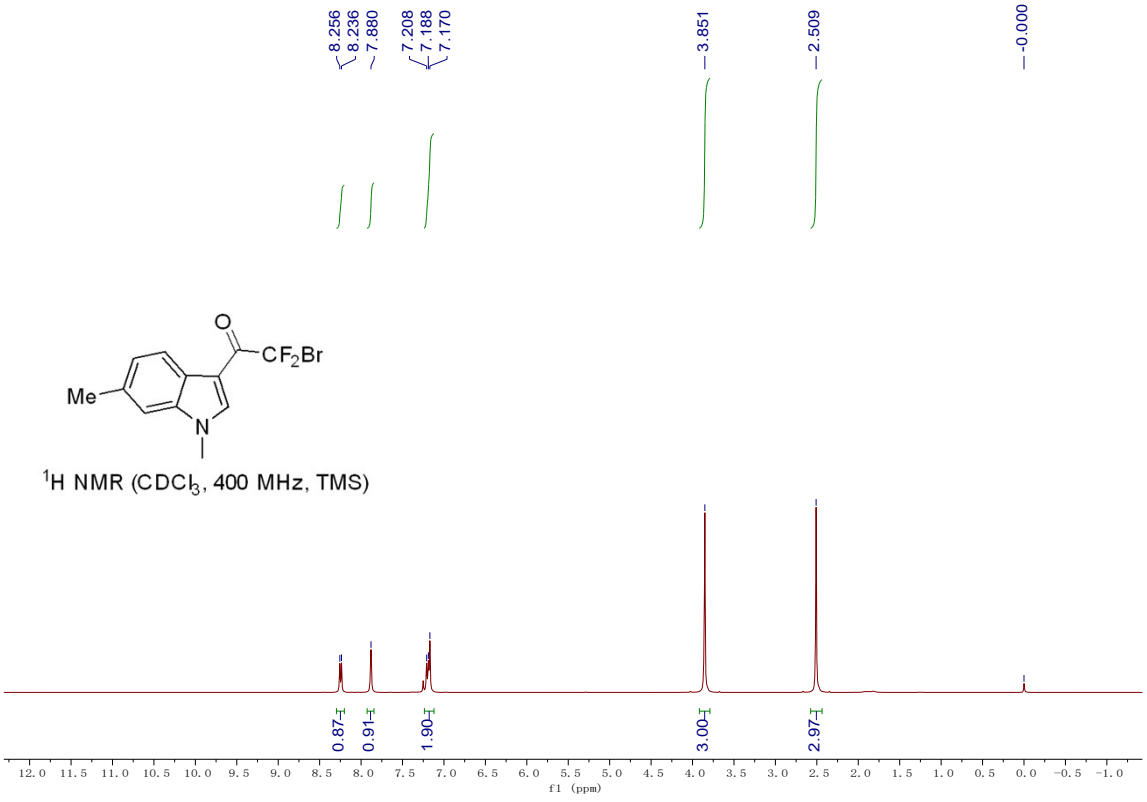

177.063
176.804
176.544
157.391
137.896
137.824
137.751
132.067
128.487
117.866
114.806
114.698
111.530
111.010
107.000
103.952
77.382
77.064
76.747
55.801
34.205
MeO
O
CF2Br
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

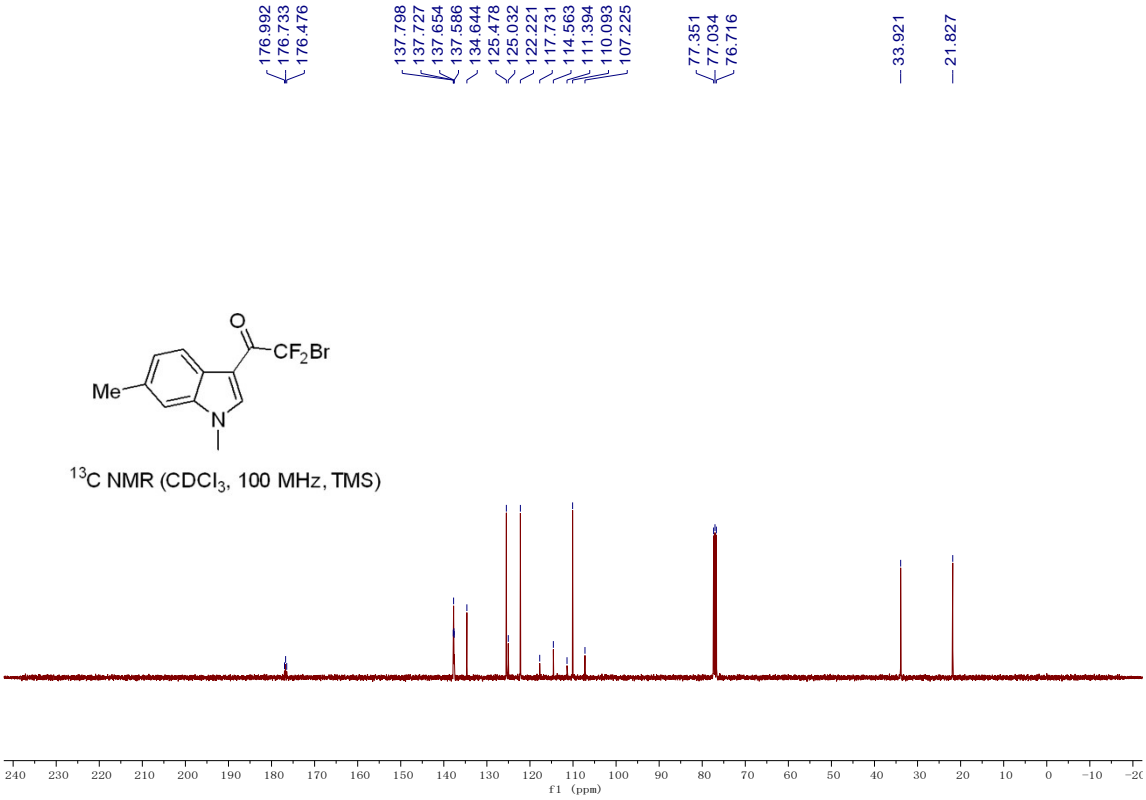

-56.712
MeO
O
CF2Br
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

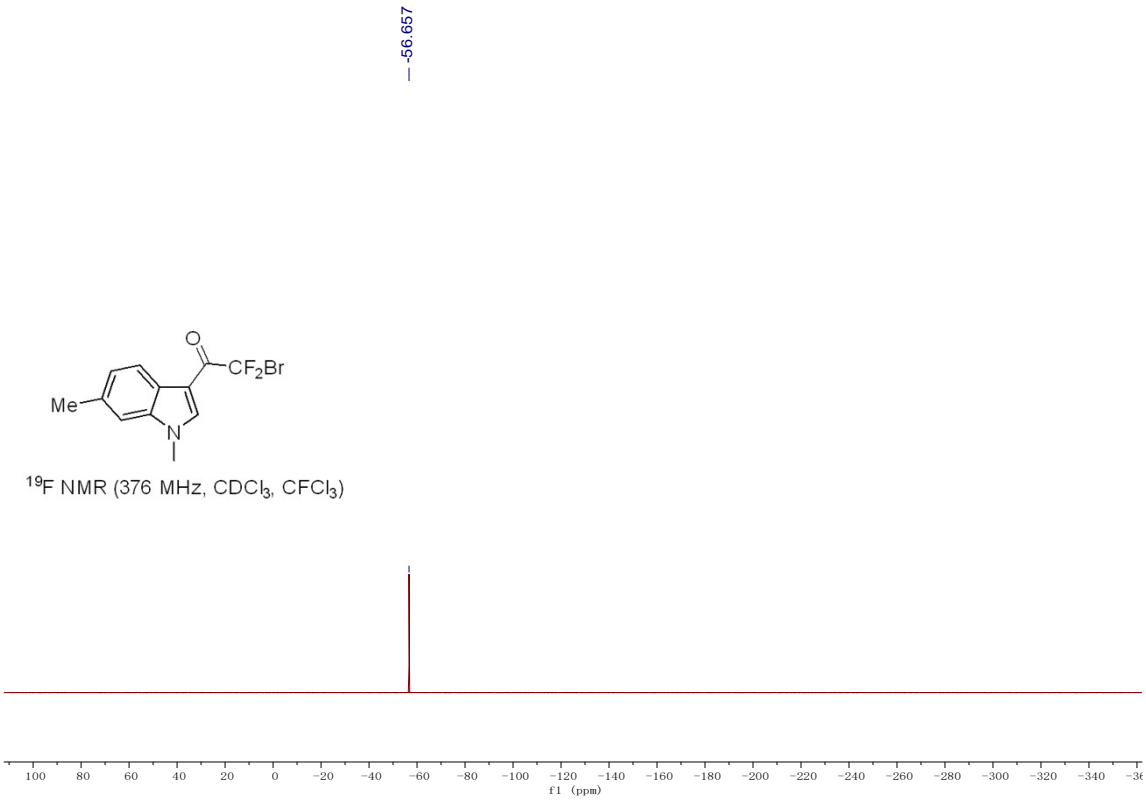


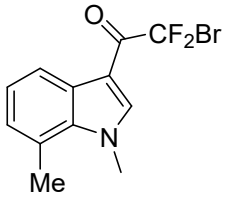
2-bromo-1-(1,6-dimethyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1i)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.51 (s, 3H), 3.85 (s, 3H), 7.17-7.21 (m, 2H), 7.88 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.8, 33.9, 107.2, 110.1, 114.6 (t, J = 318.8 Hz), 122.2, 125.0, 125.5, 134.6, 137.6, 137.7 (t, J = 7.2 Hz), 176.7 (t, J = 25.9 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.7..



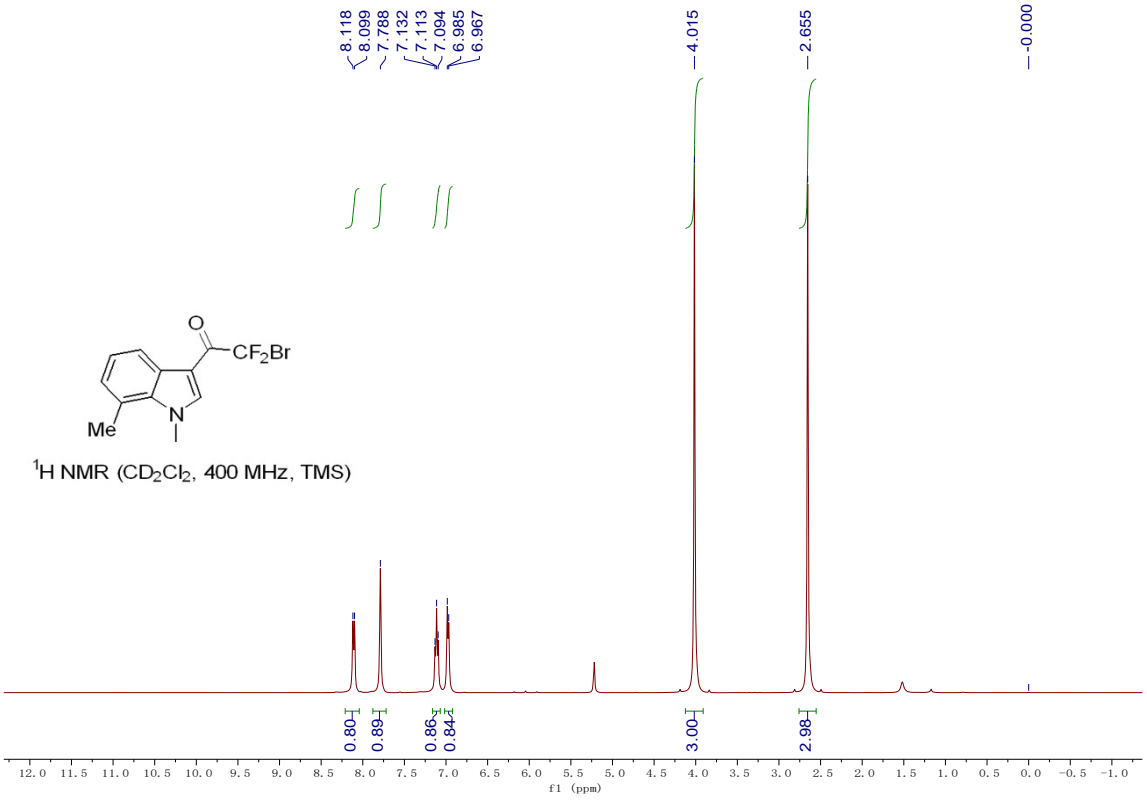

176.992
176.733
176.476
137.798
137.727
137.654
137.586
134.644
125.478
125.032
122.221
117.731
114.563
111.394
110.093
107.225
77.351
77.034
76.716
33.921
21.827
O
CF2Br
Me
N
13C NMR (CDCl3, 100 MHz, TMS)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

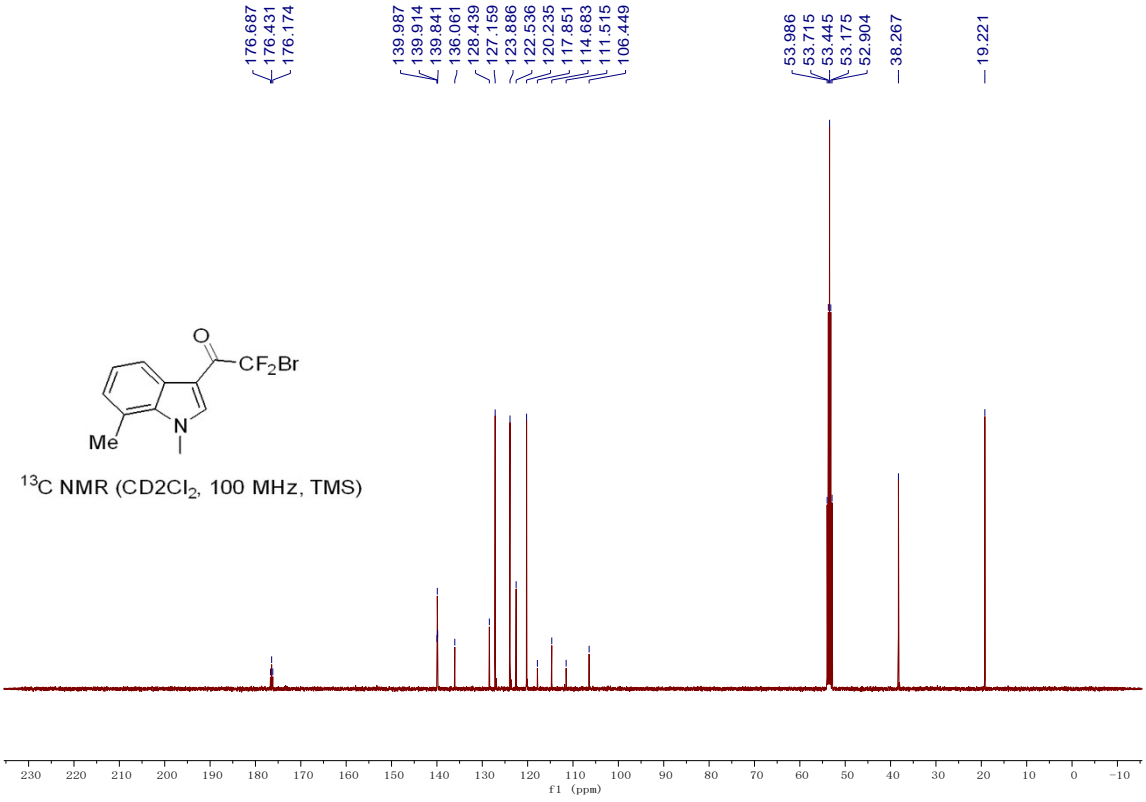

-56.657
O
CF2Br
Me
N
19F NMR (376 MHz, CDCl3, CFCl3)
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340
f1 (ppm)



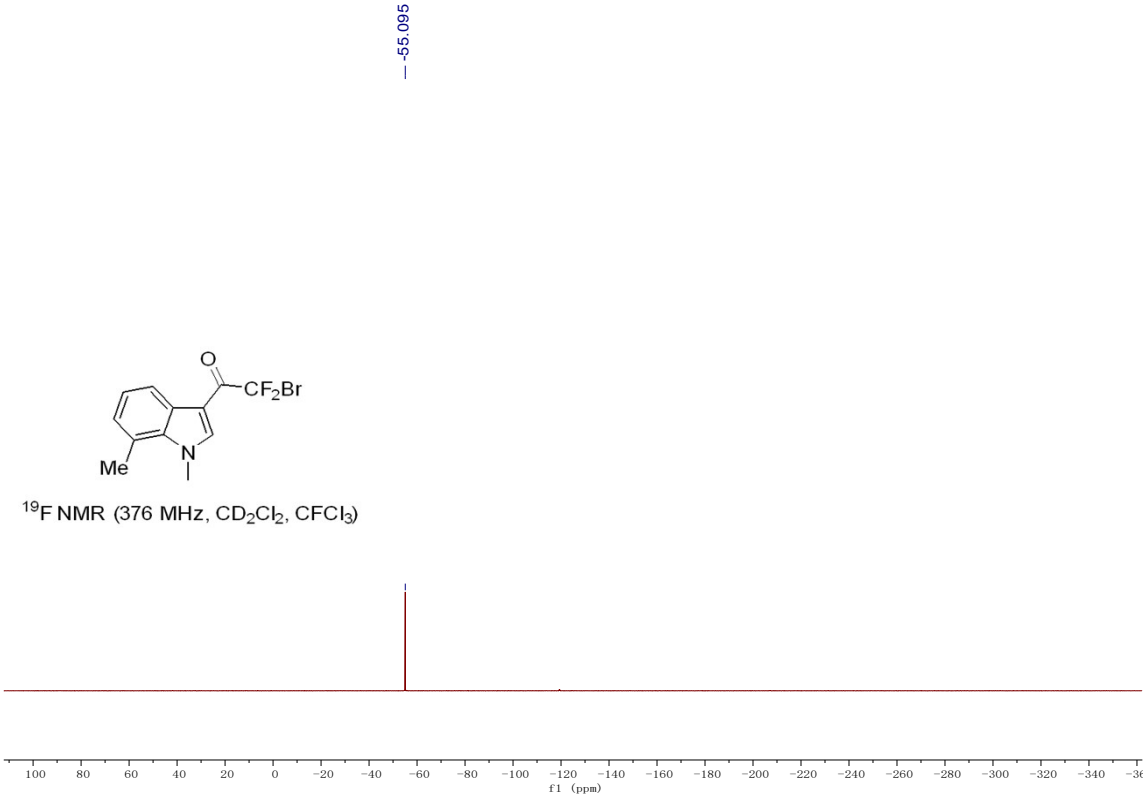
2-bromo-1-(1,7-dimethyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1j)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 2.66 (s, 3H), 4.02 (s, 3H), 6.98 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.79 (s, 1H), 8.11 (d, J = 7.8 Hz, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 19.2, 38.3, 106.4, 114.7 (t, J = 318.7 Hz), 120.2, 122.5, 123.9, 127.2, 128.4, 136.1, 139.9 (t, J = 7.3 Hz), 176.4 (t, J = 25.8 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -55.1.

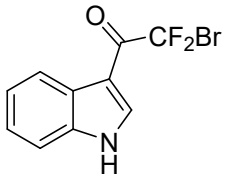




^{13}C NMR ($CD2Cl_2$, 100 MHz, TMS)

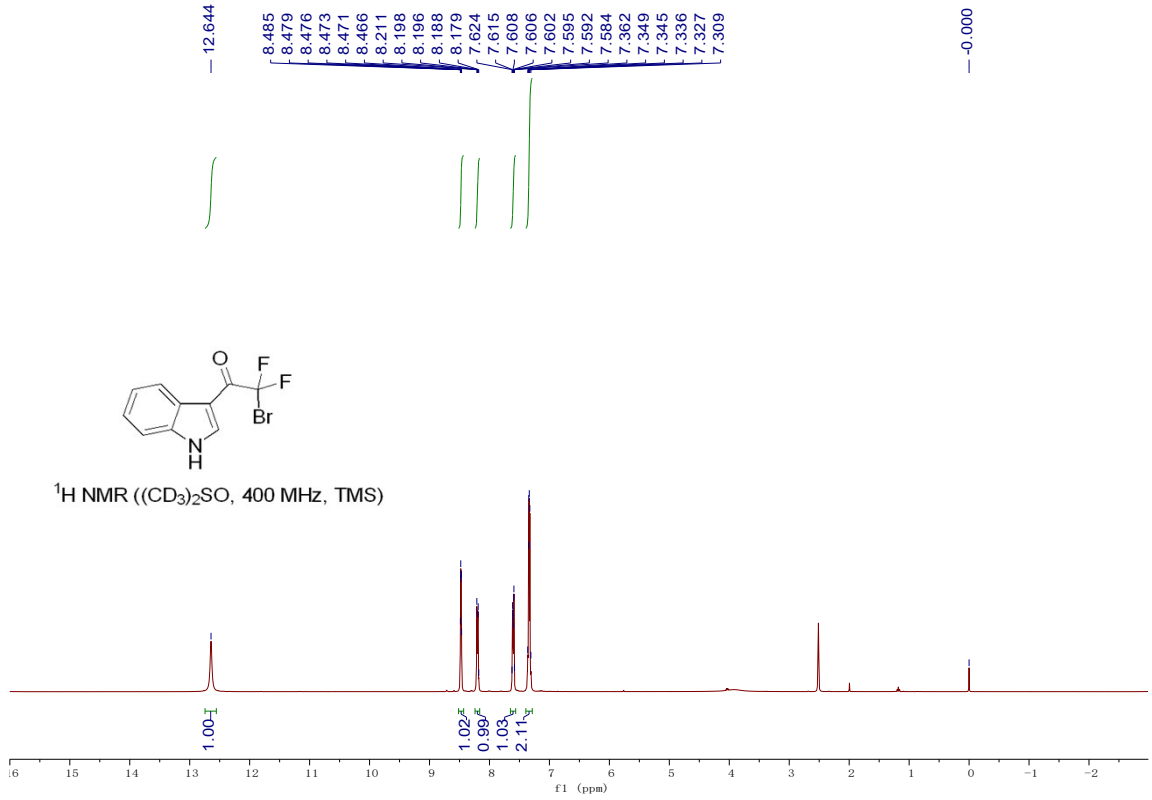


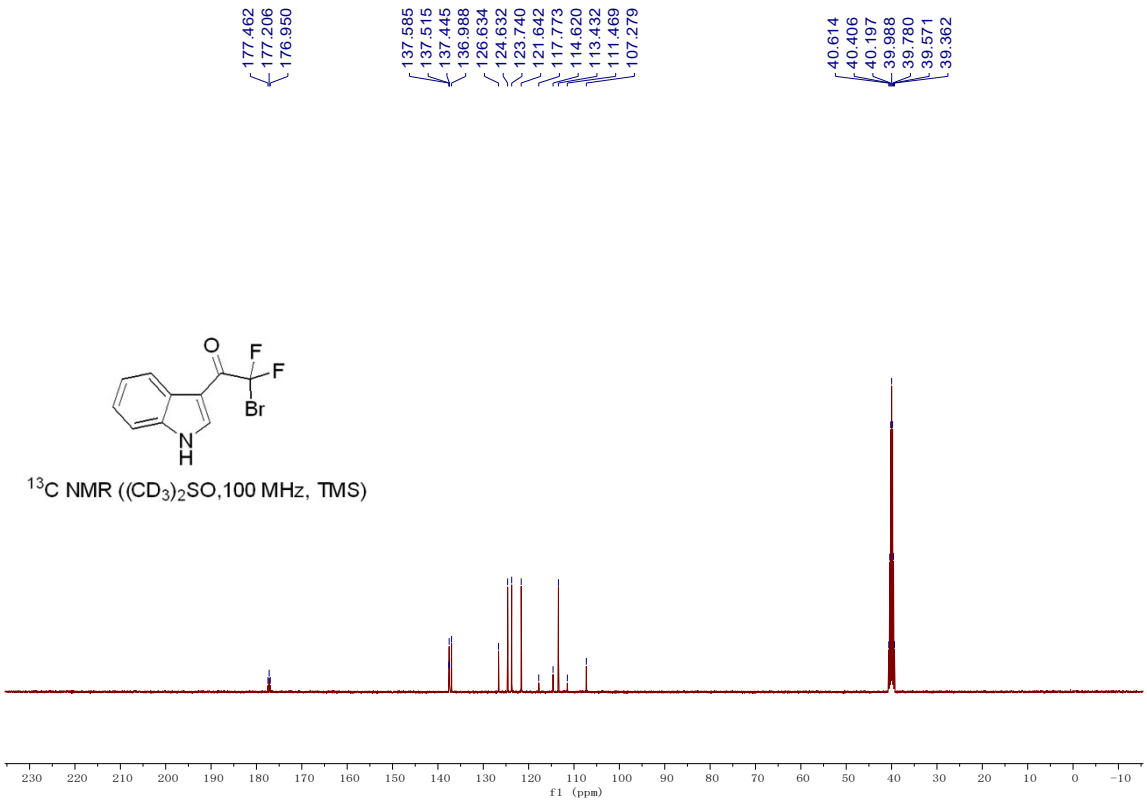
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)

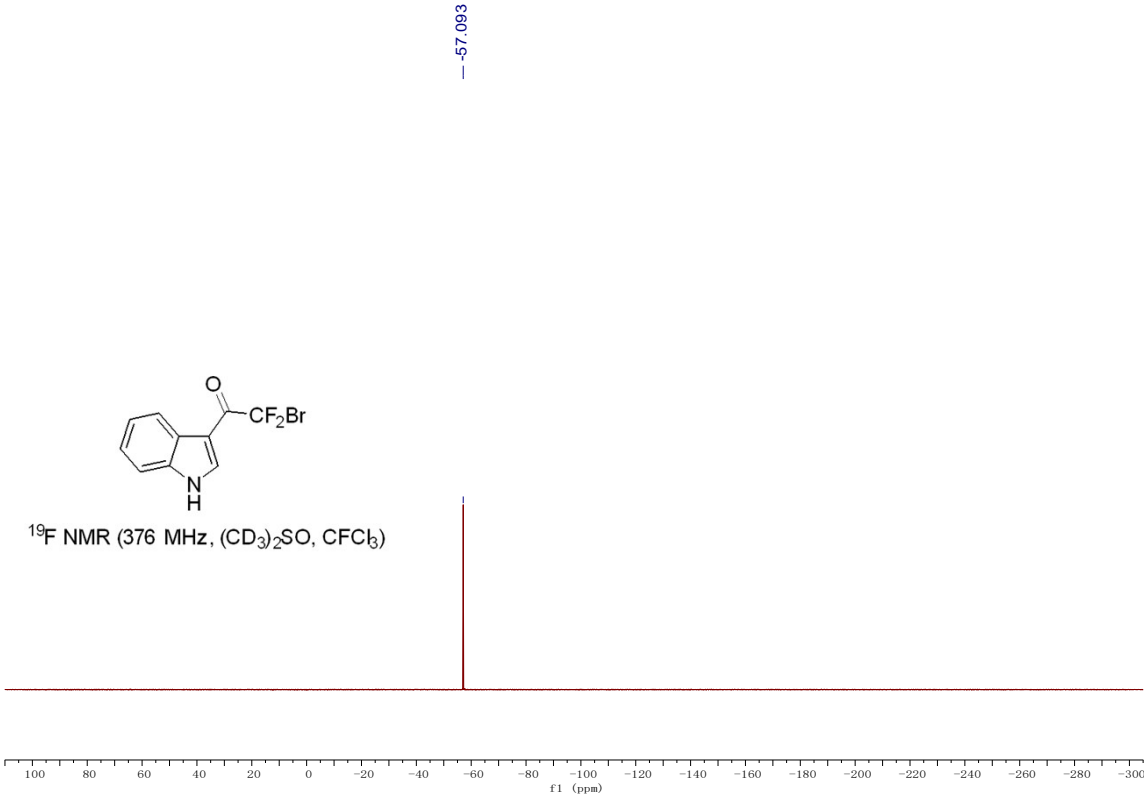


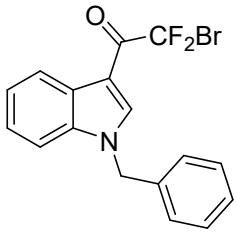
2-bromo-2,2-difluoro-1-(1H-indol-3-yl)ethan-1-one (1k)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($(CD_3)_2SO$, TMS, 400 MHz) δ 7.31-7.36 (m, 2H), 7.58-7.62 (m, 1H), 8.18-8.21 (m, 1H), 8.47-8.49 (m, 1H), 12.64 (s, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 107.3, 113.4, 114.6 (t, J = 314.9 Hz), 121.6, 123.7, 124.6, 126.6, 136.9, 137.5 (t, J = 7.0 Hz), 177.2 (t, J = 25.6 Hz). ^{19}F NMR ($(CD_3)_2SO$, $CFCl_3$, 376 MHz) δ -57.1.



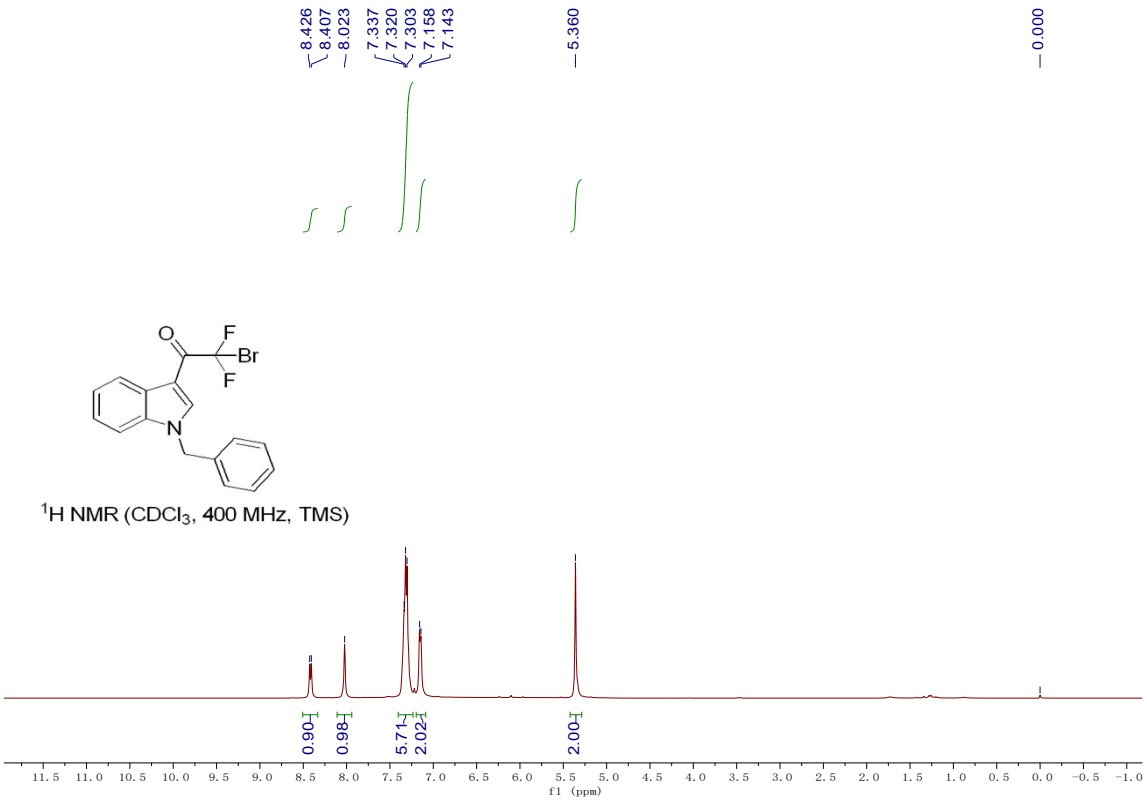

177.462
177.206
176.950
137.585
137.515
137.445
136.988
126.634
124.632
123.740
121.642
117.773
114.620
113.432
111.469
107.279
40.614
40.406
40.197
39.988
39.780
39.571
39.362
O
F
F
Br
N
H
13C NMR ((CD3)2SO,100 MHz, TMS)
f1 (ppm)

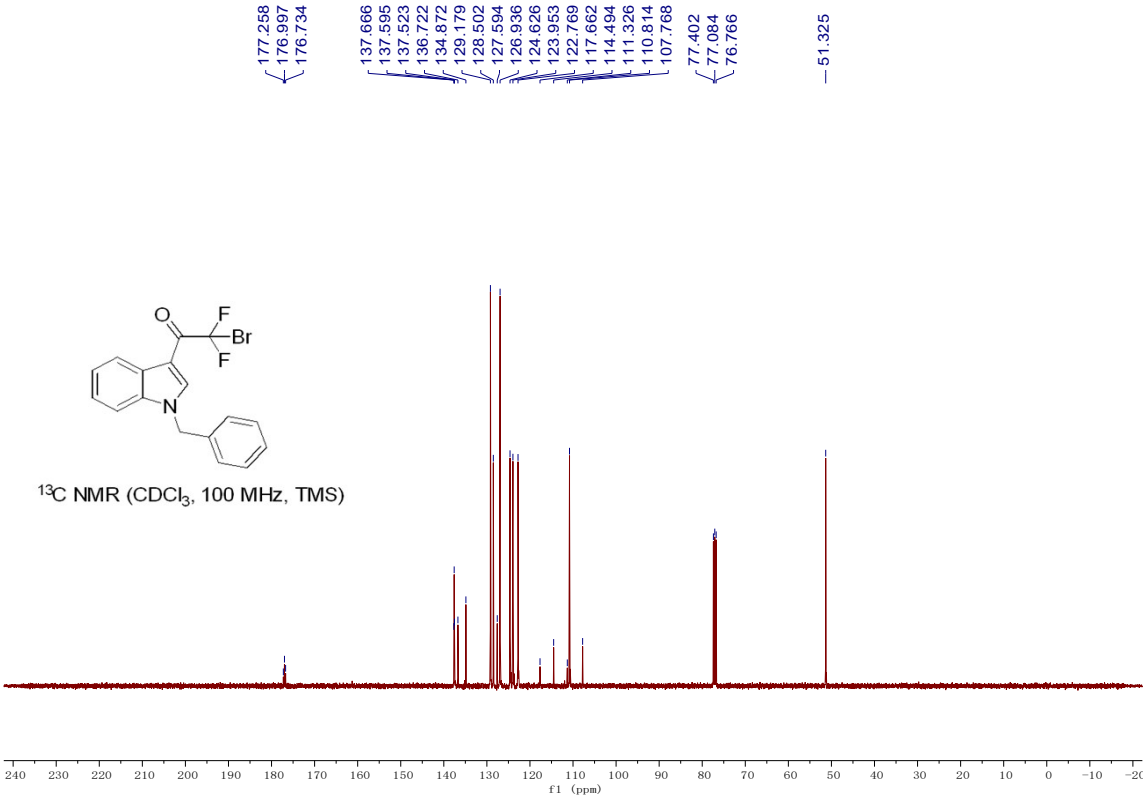

-57.093
O
CF2Br
N
H
19F NMR (376 MHz, (CD3)2SO, CFCl3)
f1 (ppm)



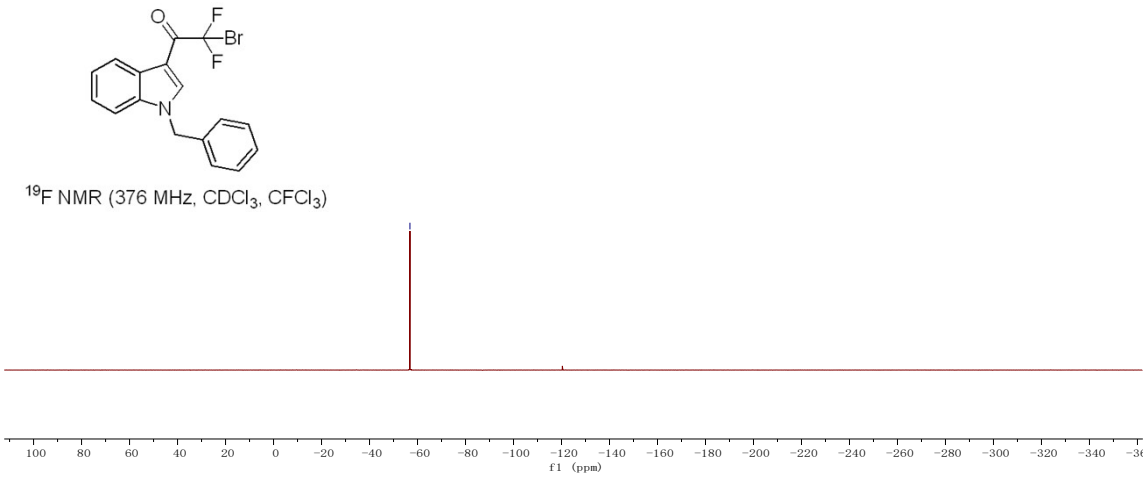
1-(1-benzyl-1H-indol-3-yl)-2-bromo-2,2-difluoroethan-1-one (1l)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.36 (s, 2H), 7.15 (d, J = 6.0 Hz, 1H), 7.30-7.34 (m, 6H), 8.02 (s, 1H), 8.42 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 51.3, 107.8, 110.8, 114.5 (t, J = 318.7 Hz), 122.8, 124.0, 124.6, 126.9, 127.6, 128.5, 129.2, 134.9, 136.7, 137.6 (t, J = 7.2 Hz), 177.0 (t, J = 26.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.8.

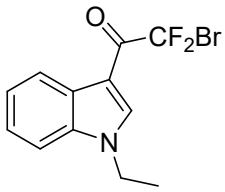




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

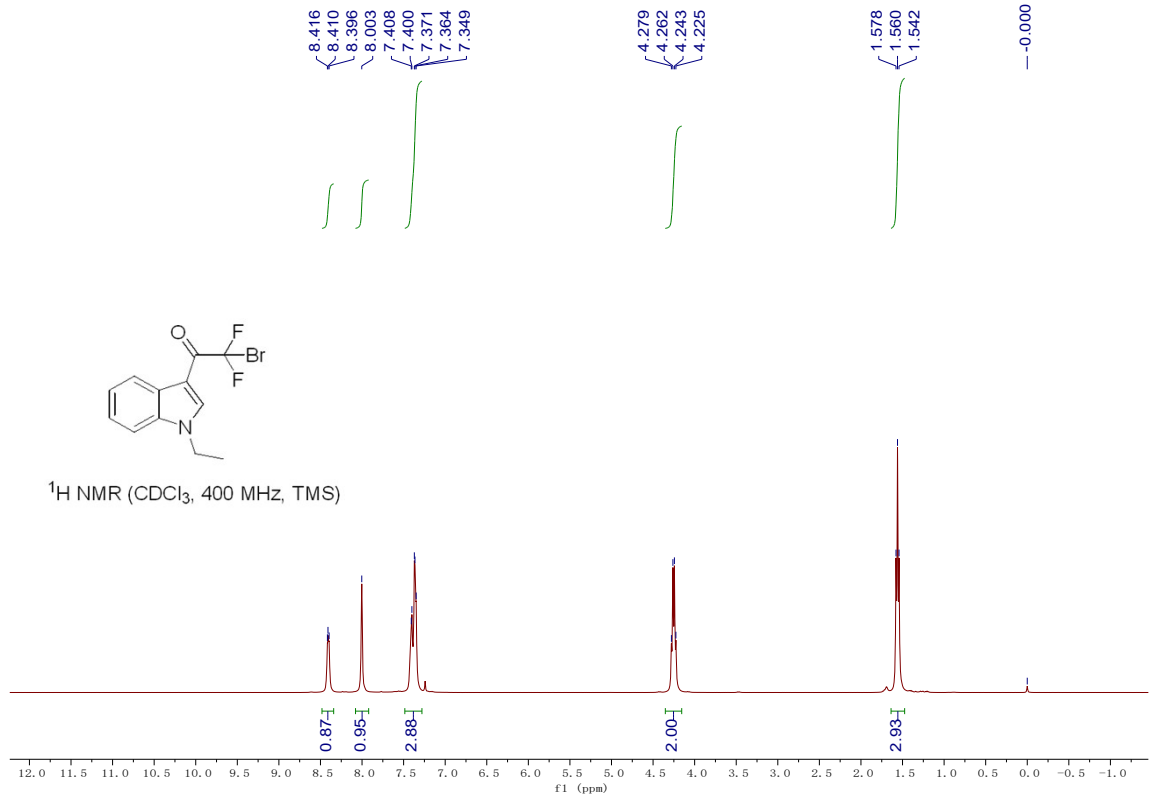


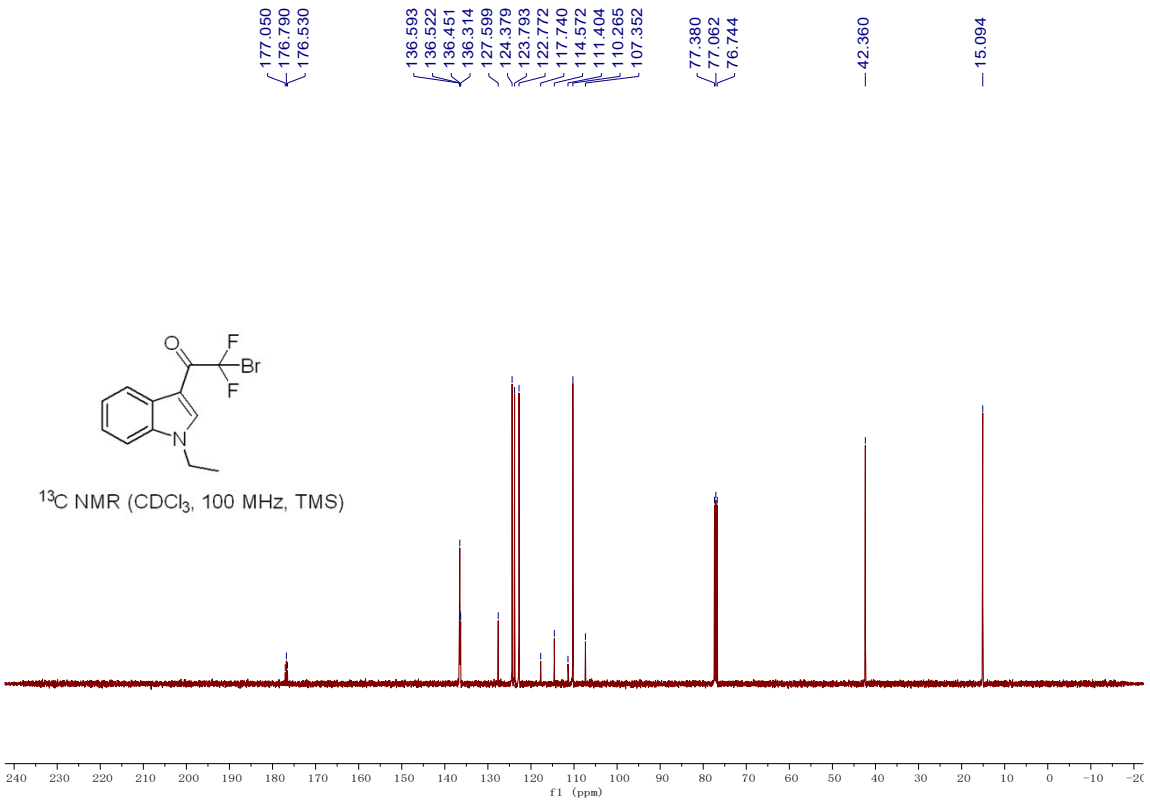
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

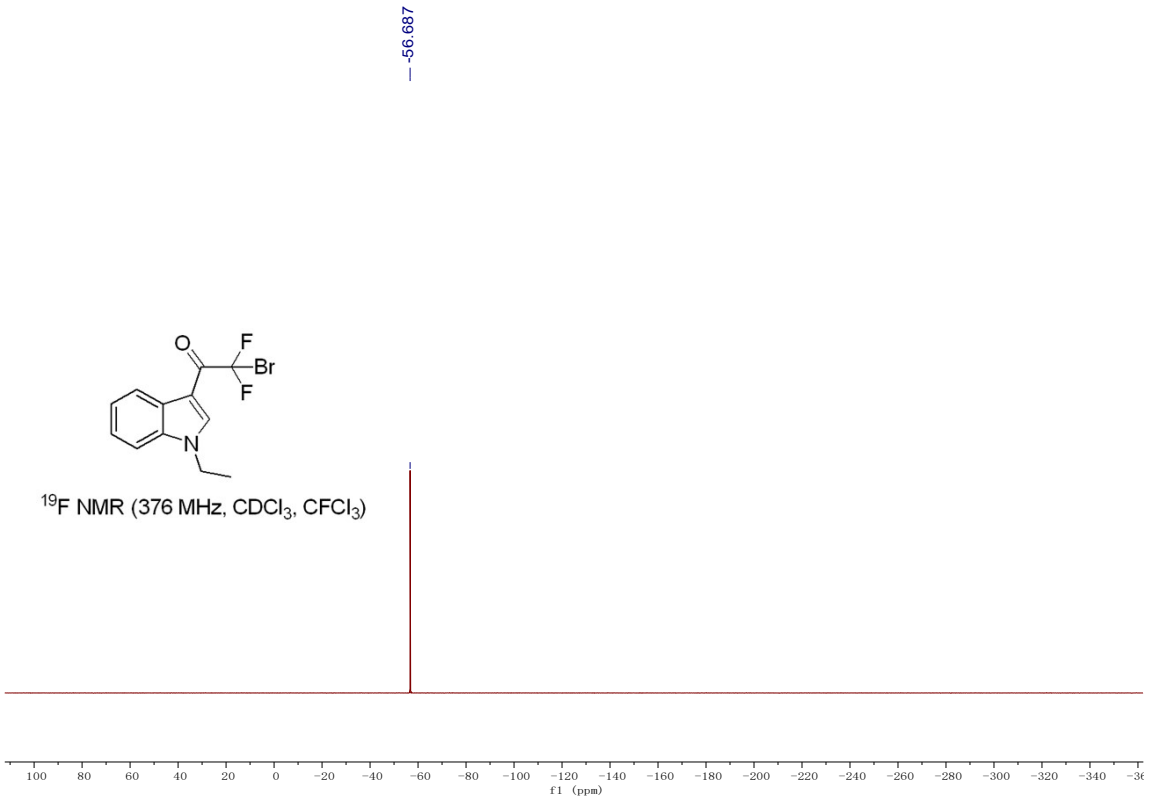


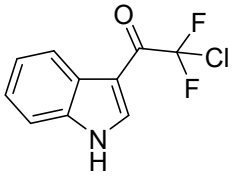
2-bromo-1-(1-ethyl-1H-indol-3-yl)-2,2-difluoroethan-1-one (1m)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.56 (t, *J* = 7.2, 7.2 Hz, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 7.35-7.41 (m, 3H), 8.00 (s, 1H), 8.40-8.42 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.1, 42.4, 107.4, 110.3, 114.6 (t, *J* = 318.7 Hz), 122.8, 123.8, 124.4, 127.6, 136.3, 136.5 (t, *J* = 7.2 Hz), 176.8 (t, *J* = 26.1 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.7.



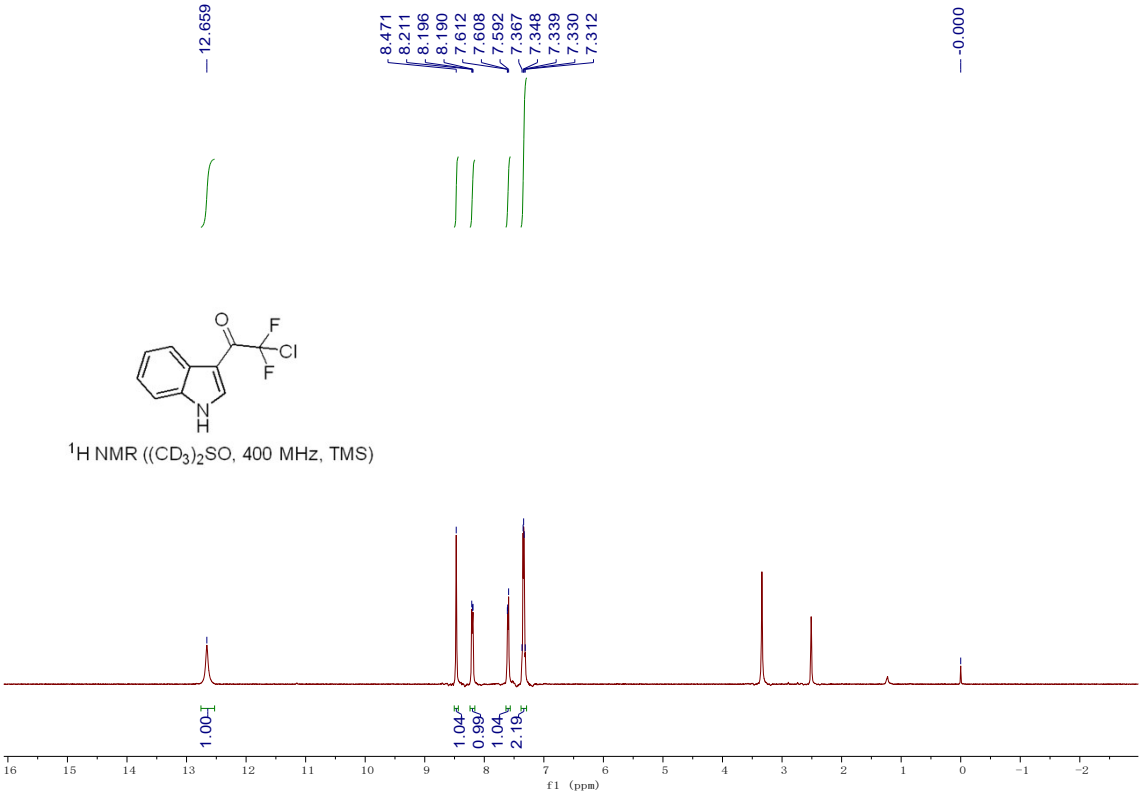

177.050
176.790
176.530
136.593
136.522
136.451
136.314
127.599
124.379
123.793
122.772
117.740
114.572
111.404
110.265
107.352
77.380
77.062
76.744
42.360
15.094
O
F
Br
F
N
13C NMR (CDCl3, 100 MHz, TMS)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

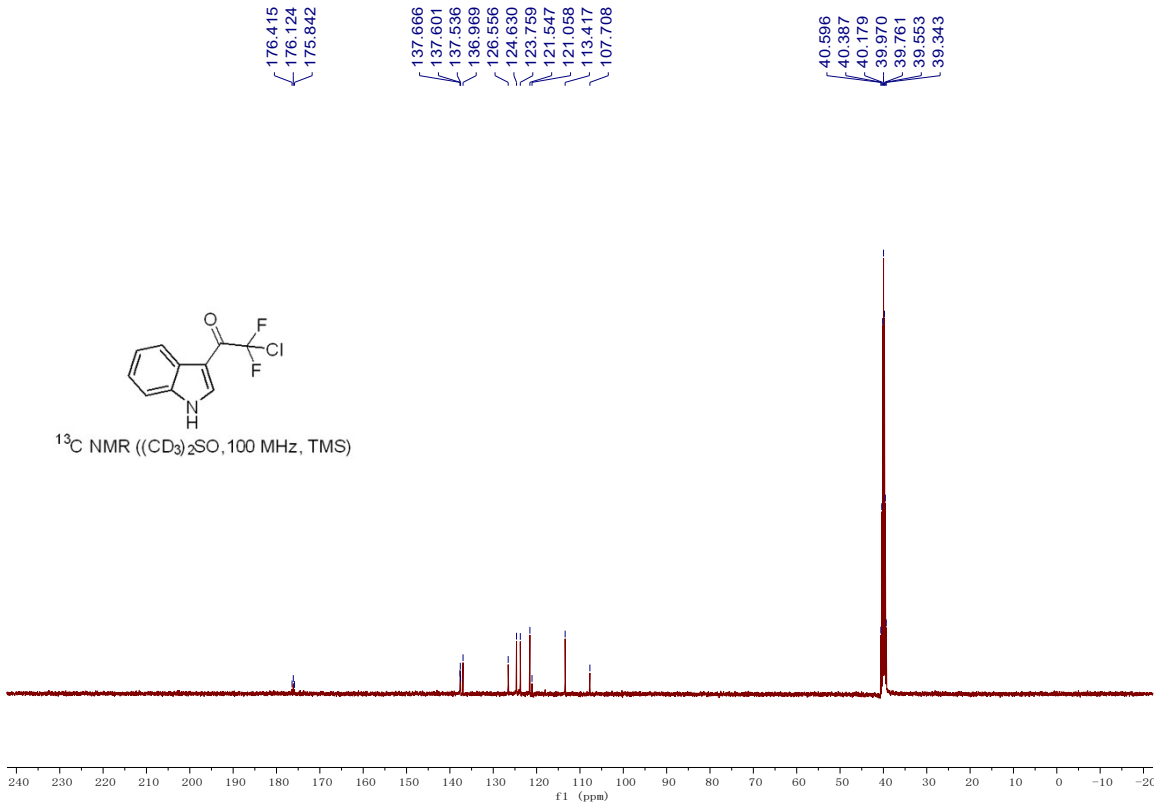

-56.687
O
F
Br
F
N
19F NMR (376 MHz, CDCl3, CFCl3)
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340
f1 (ppm)



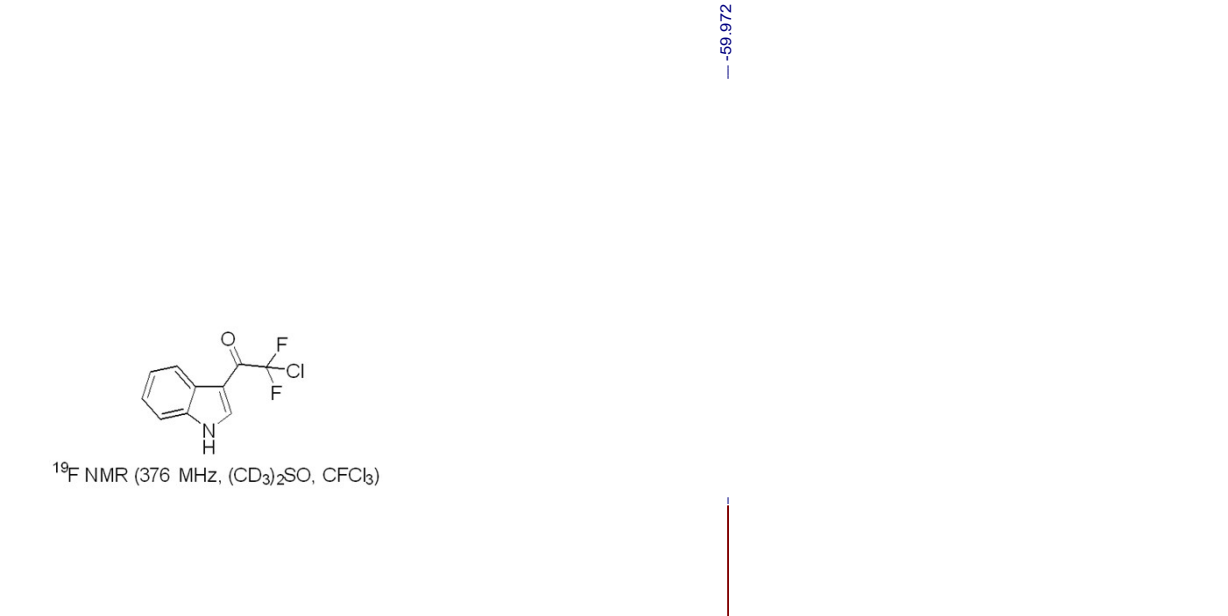
2-chloro-2,2-difluoro-1-(1H-indol-3-yl)ethan-1-one (1n)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($(CD_3)_2SO$, TMS, 400 MHz) δ 7.31-7.37 (m, 2H), 7.59-7.61 (m, 1H), 8.19-8.21 (m, 1H), 8.47 (s, 1H), 12.66 (s, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 107.3, 113.4, 121.1 (t, J = 314.9 Hz), 121.5, 123.8, 124.6, 126.6, 137.0, 137.6 (t, J = 6.5 Hz), 176.1 (t, J = 29.1 Hz). ^{19}F NMR ($(CD_3)_2SO$, $CFCl_3$, 376 MHz) δ -60.0.

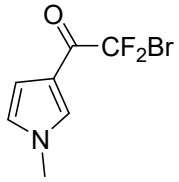




^{13}C NMR ((CD$_3$)$_2$SO,100 MHz, TMS)

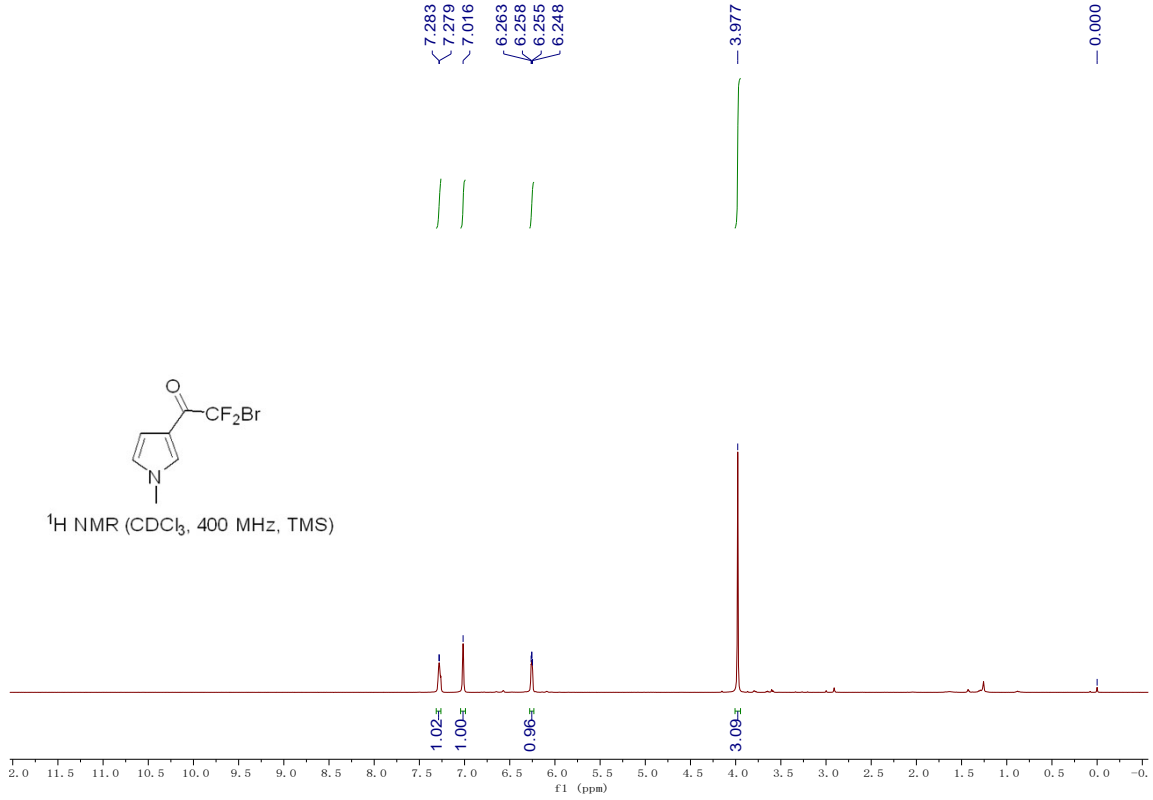


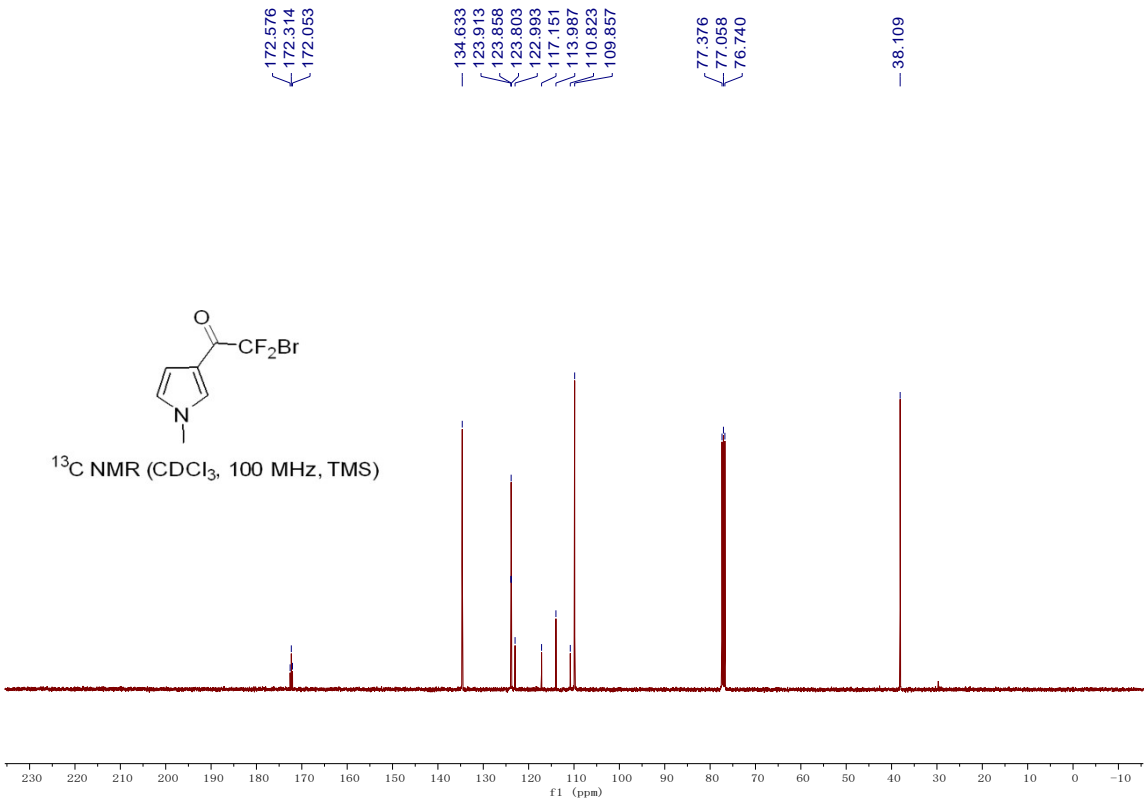
^{19}F NMR (376 MHz, (CD$_3$)$_2$SO, CFCl$_3$)

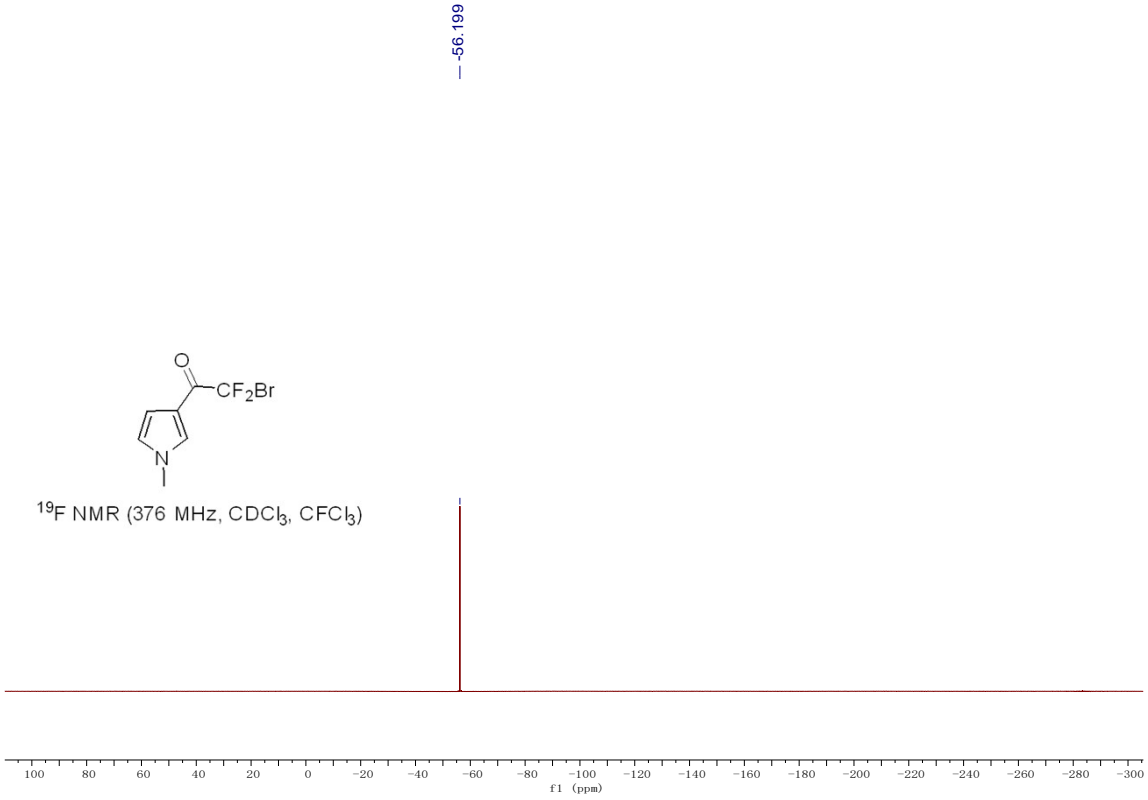


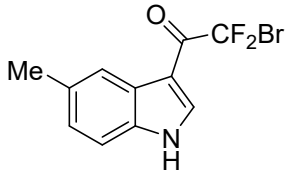
2-bromo-2,2-difluoro-1-(1-methyl-1H-pyrrol-3-yl)ethan-1-one (1o)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.98 (s, 3H), 6.25-6.26 (m, 1H), 7.02 (s, 1H), 7.27-7.28 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 38.1, 109.9, 114.0(t, J = 318.4 Hz), 123.0, 123.9 (t, J = 5.6, Hz), 134.6, 172.3 (t, J = 26.3 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -56.2.



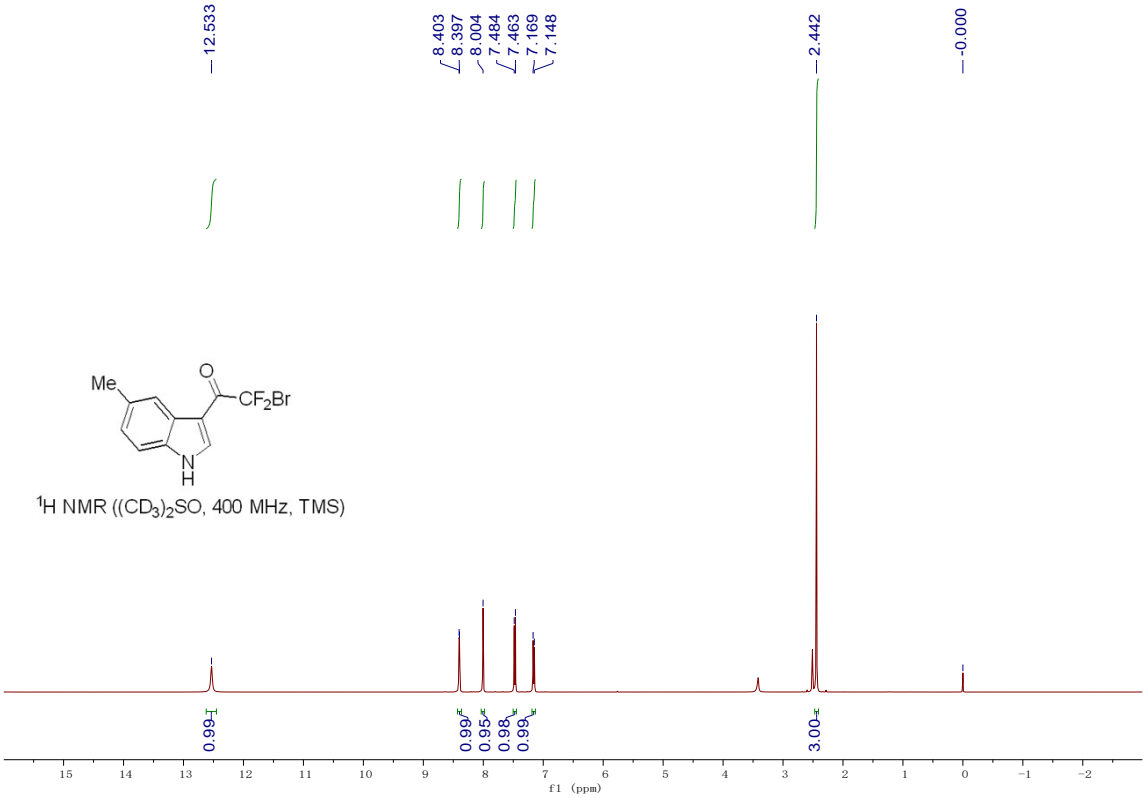

172.576
172.314
172.053
134.633
123.913
123.858
123.803
122.993
117.151
113.987
110.823
109.857
77.376
77.058
76.740
38.109
O
CF2Br
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

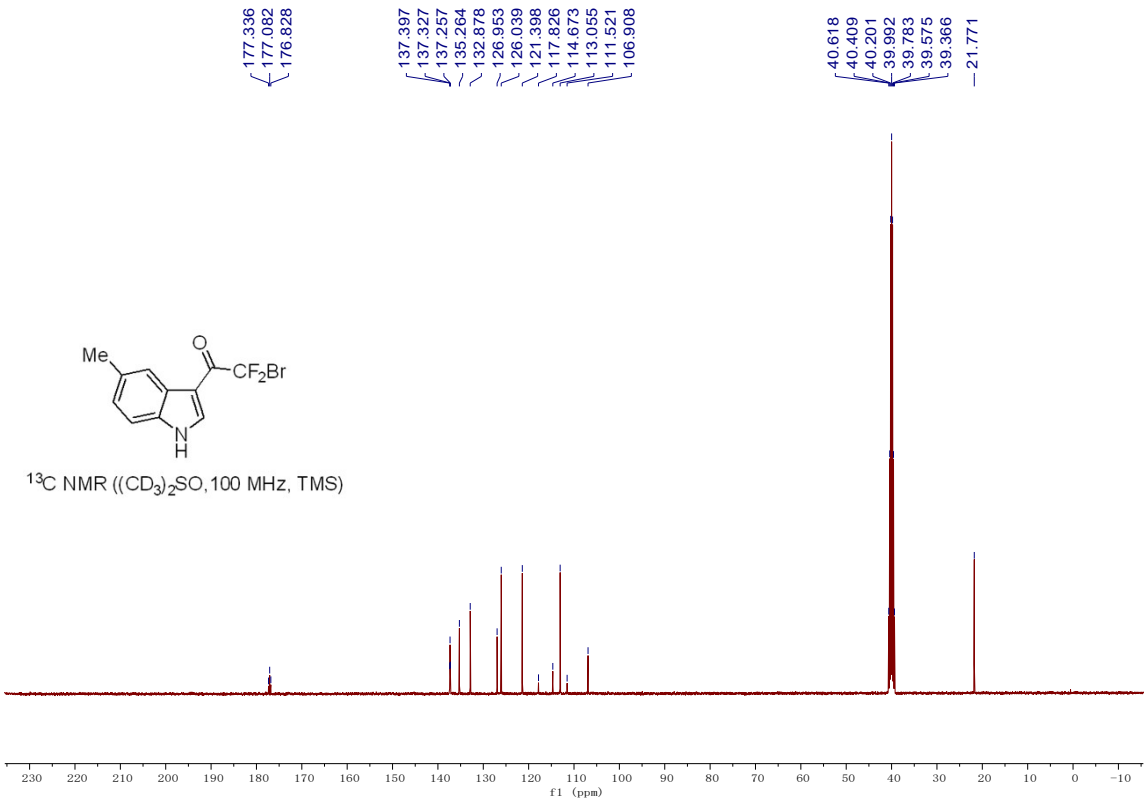

-56.199
O
CF2Br
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



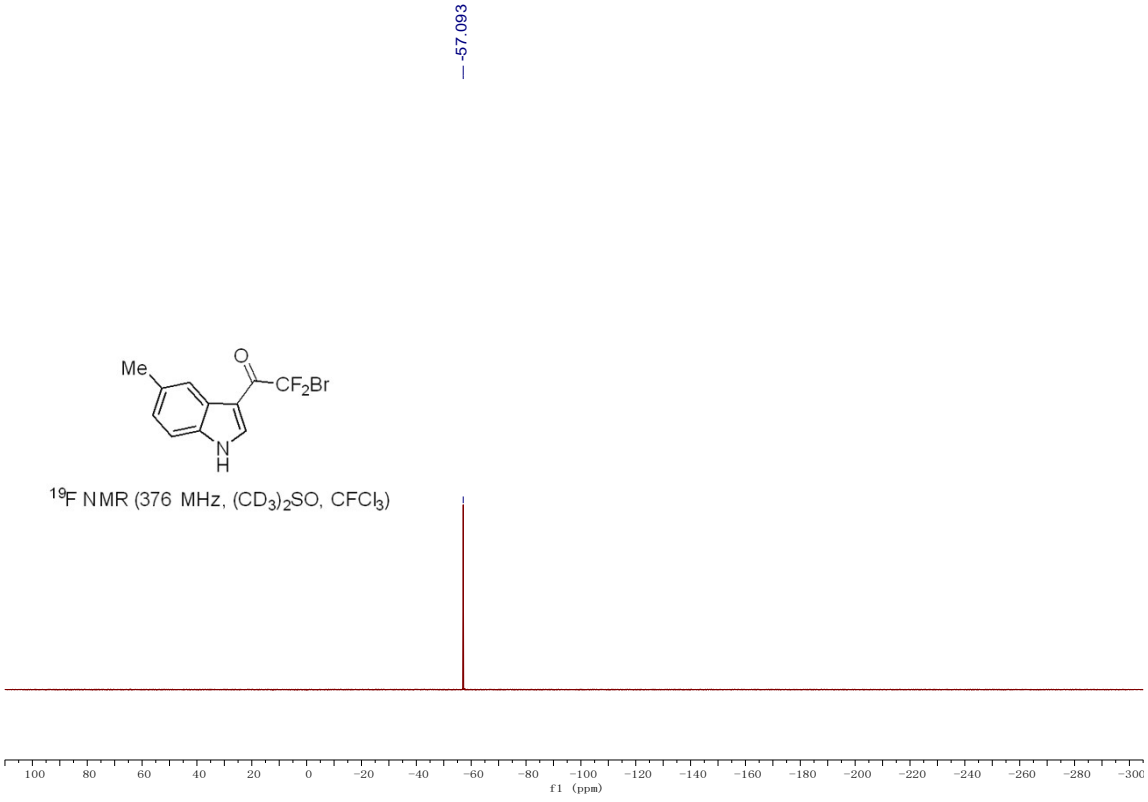
2-bromo-2,2-difluoro-1-(5-methyl-1H-indol-3-yl)ethan-1-one (1p)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[2] A colorless oil. ^{1}H NMR ($(CD_3)_2SO$, TMS, 400 MHz) δ 2.44 (s, 3H), 7.16 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 8.00 (s, 1H), 8.39-8.41 (m, 1H), 12.53 (s, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 21.8, 106.9, 113.1, 114.7 (t, J = 315.2 Hz), 121.4, 126.0, 127.0, 132.9, 135.3, 137.3 (t, J = 7.1 Hz), 177.1 (t, J = 25.6 Hz). ^{19}F NMR ($(CD_3)_2SO$, $CFCl_3$, 376 MHz) δ -57.1.



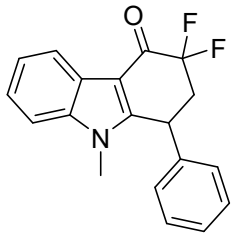


^{13}C NMR ((CD$_3$)$_2$SO,100 MHz, TMS)



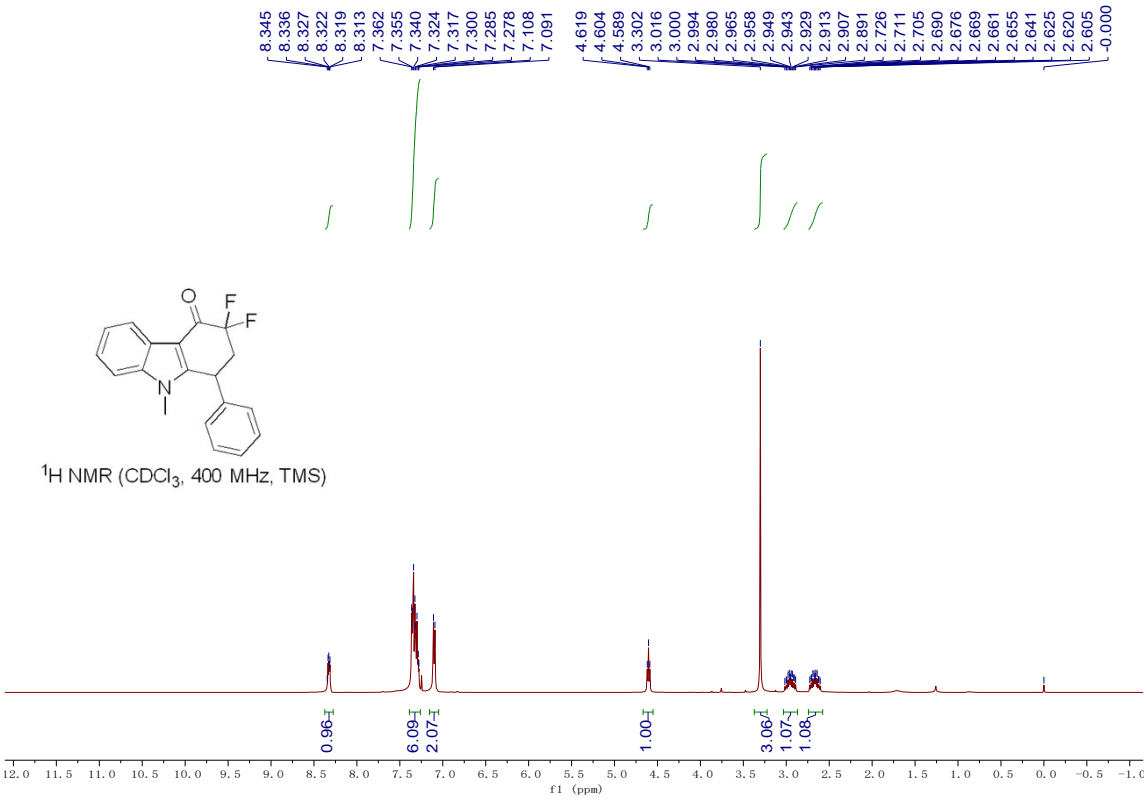
^{19}F NMR (376 MHz, (CD$_3$)$_2$SO, CFCl$_3$)

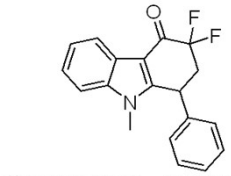
Spectroscopic data of products



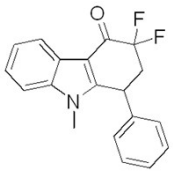
3,3-difluoro-9-methyl-1-phenyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aa)

A white solid. 48.6 mg, 78% yield. M.P.: 192-194 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.61-2.73 (m, 1H), 2.89-3.02 (m, 1H), 3.30 (s, 3H), 4.60 (t, *J* = 6.0 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 2H), 7.28-7.36 (m, 6H), 8.31-8.35 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 38.1 (dd, *J* = 5.2, 4.5 Hz), 41.4 (dd, *J* = 23.9, 22.8 Hz), 109.8, 112.1 (dd, *J* = 2.8, 2.1 Hz), 113.9 (dd, *J* = 248.9, 246.3 Hz), 122.0, 123.6, 124.5, 127.7, 128.0, 129.4, 138.7, 139.8, 151.0, 179.6 (t, *J* = 25.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.02 (ddd, *J* = 274.9, 19.7, 8.8 Hz), -105.43 (ddd, *J* = 274.8, 20.1, 8.5 Hz). IR (neat) $\tilde{\nu}$ 3318, 2973, 2880, 1454, 1379, 1328, 1088, 1046, 880 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{15}NOF_2Na$ (M+Na): 334.1019, Found: 334.1050.

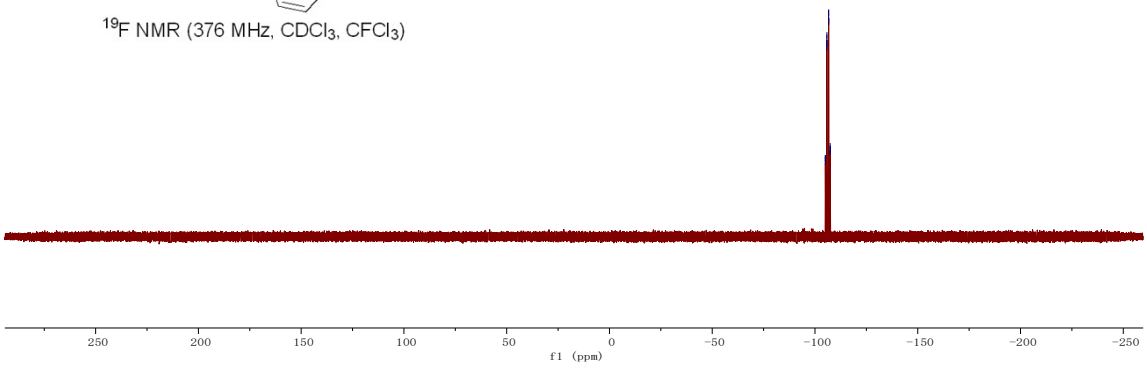


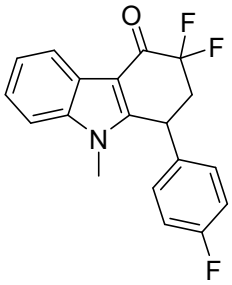


^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



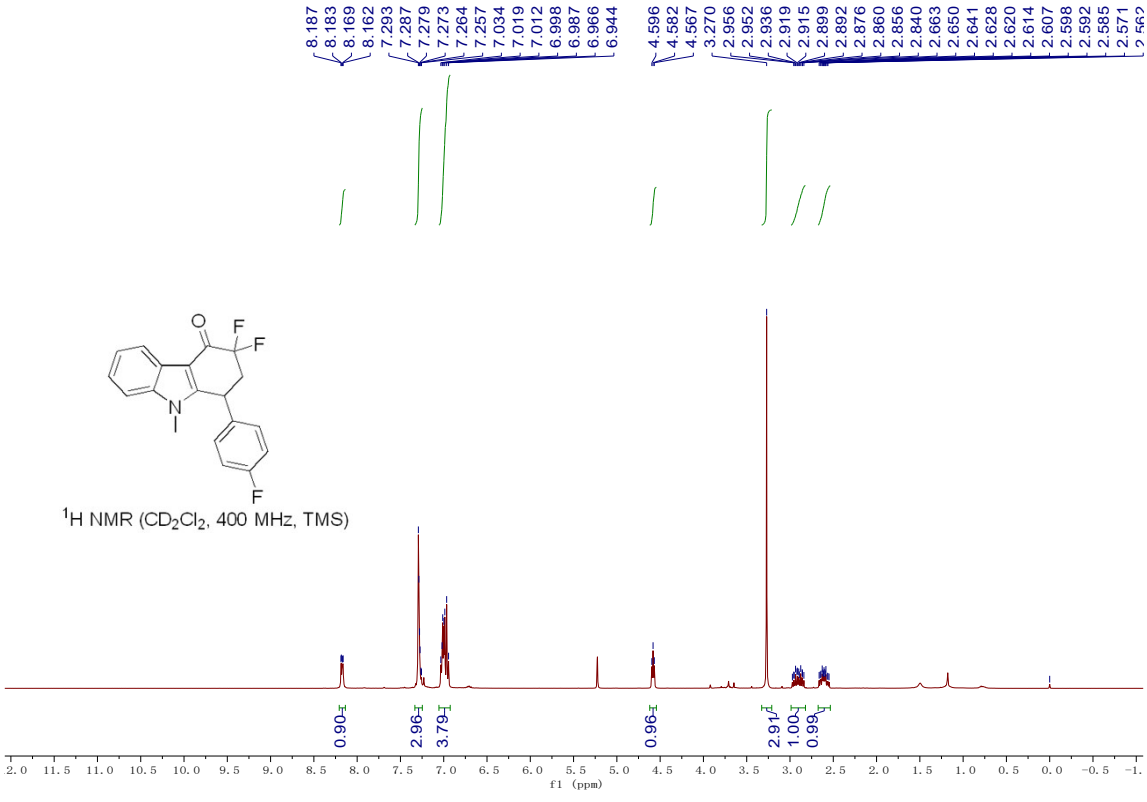
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

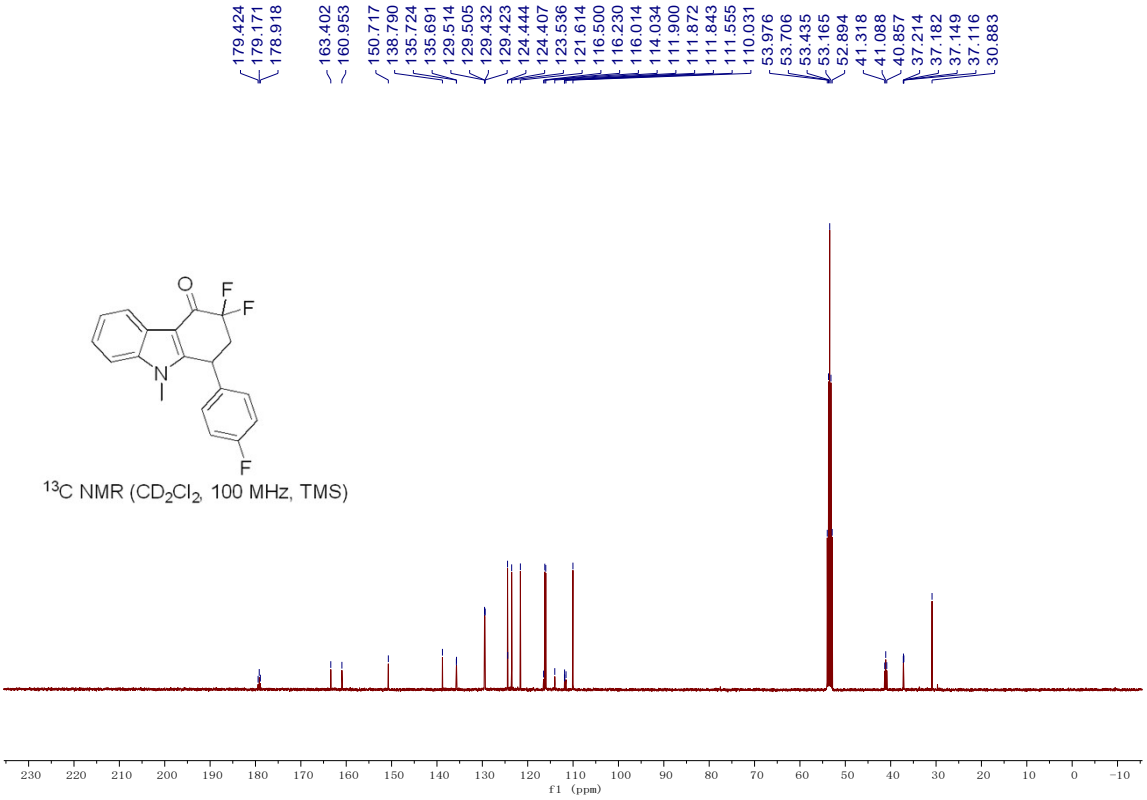


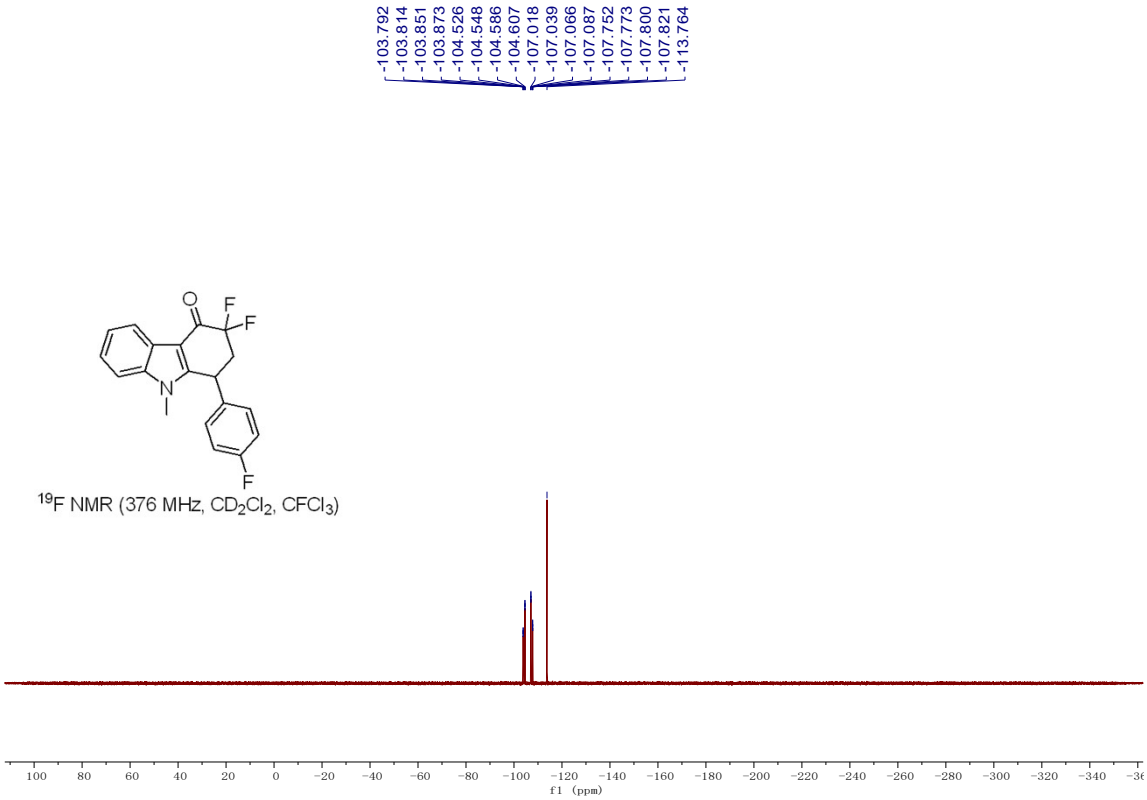


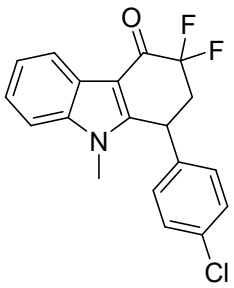
3,3-difluoro-1-(4-fluorophenyl)-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ab)

A white solid. 44.1 mg, 67% yield. M.P.: 212-214 °C. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 2.55-2.66 (m, 1H), 2.84-2.97 (m,1H), 3.27 (s, 3H), 4.58 (t, *J* = 5.6 Hz, 1H), 6.94-7.03 (m, 4H), 7.26-7.32 (m, 3H), 8.16-8.19 (m, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 30.9, 37.2 (dd, *J* = 6.6, 3.3 Hz), 41.1 (t, *J* = 23.2 Hz), 110.0, 111.9 (t, *J* = 2.9 Hz), 114.0 (dd, *J* = 246.6, 246.6 Hz), 116.1 (d, *J* = 21.8 Hz), 121.6, 123.5, 124.4, 124.44, 129.5 (dd, *J* = 8.2, 0.9 Hz), 135.7 (d, *J* = 3.3 Hz), 138.8, 150.7, 162.2 (d, *J* = 246.5 Hz), 179.2 (t, *J* = 25.5 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -113.8 (ddd, *J* = 276.0, 18.0, 7.9 Hz), -104.2 (ddd, *J* = 276.4, 22.3, 8.1 Hz). IR (neat) $\tilde{\nu}$ 3323, 2973, 2881, 1660, 1451, 1379, 1325, 1088, 1046, 880 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{15}NOF_3Na$ (M+Na): 352.0925, Found: 352.0923.



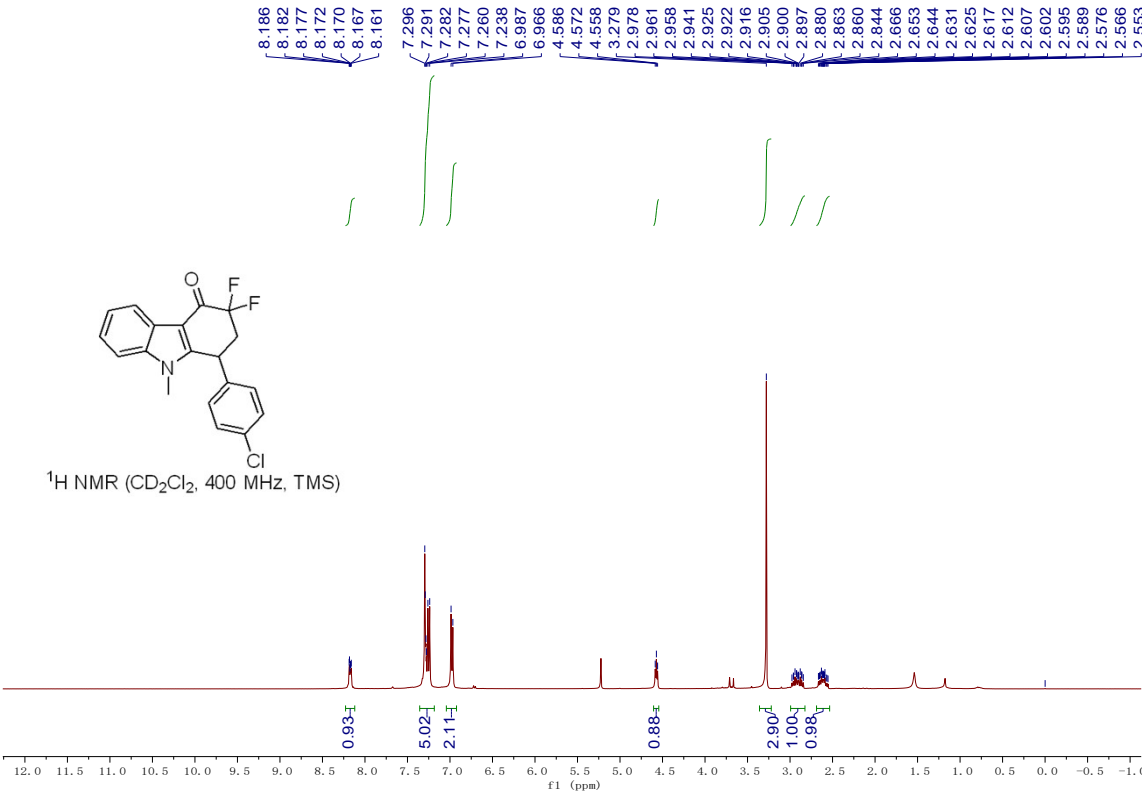

179.424
179.171
178.918
163.402
160.953
150.717
138.790
135.724
135.691
129.514
129.505
129.432
129.423
124.444
124.407
123.536
121.614
116.500
116.230
116.014
114.034
111.900
111.872
111.843
111.555
110.031
53.976
53.706
53.435
53.165
52.894
41.318
41.088
40.857
37.214
37.182
37.149
37.116
30.883
O
F
F
N
F
13C NMR (CD2Cl2, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

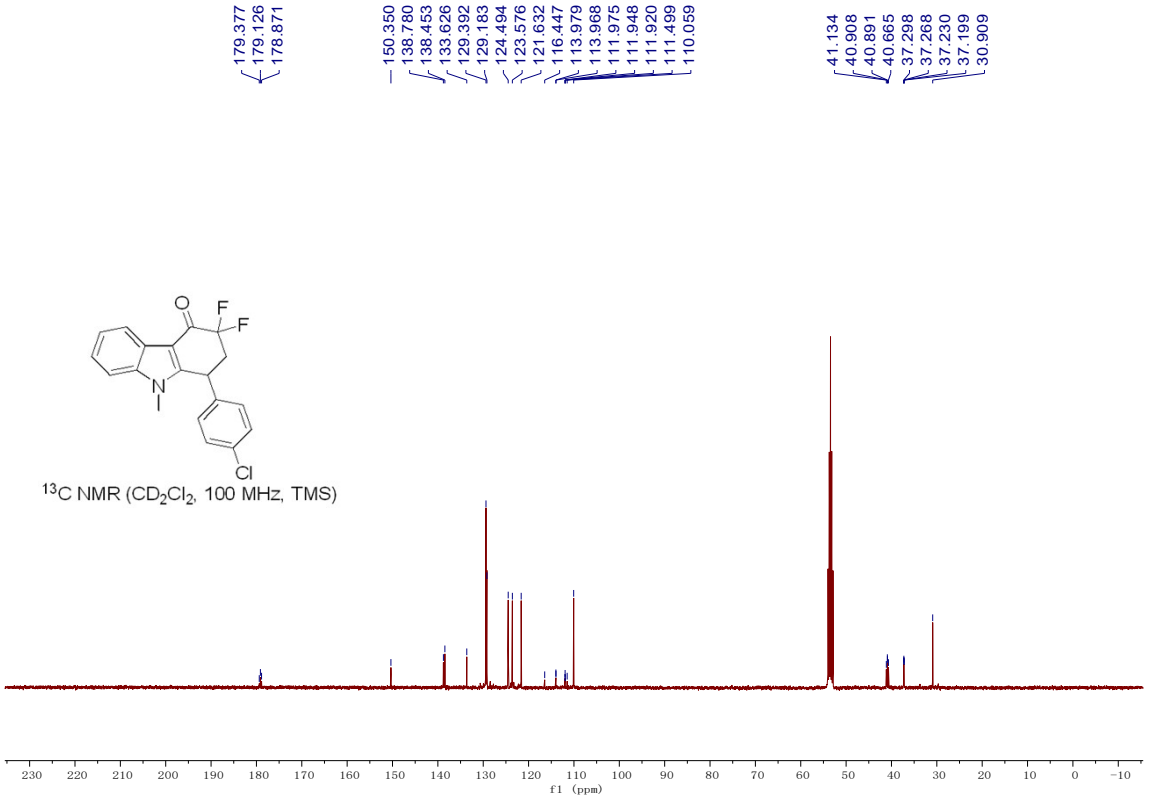

-103.792
-103.814
-103.851
-103.873
-104.526
-104.548
-104.586
-104.607
-107.018
-107.039
-107.066
-107.087
-107.752
-107.773
-107.800
-107.821
-113.764
O
F
F
N
F
19F NMR (376 MHz, CD2Cl2, CFCl3)
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340
f1 (ppm)



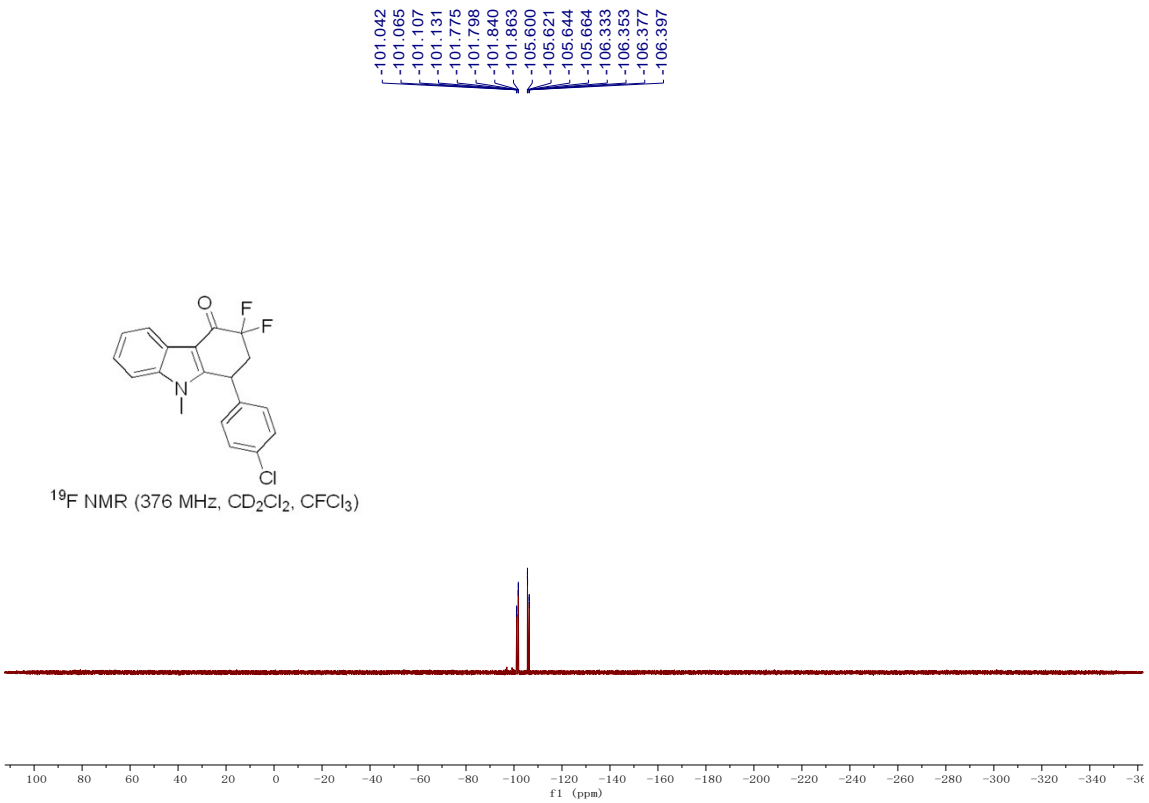
1-(4-chlorophenyl)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ac)

A white solid. 53.2 mg, 77% yield. M.P.: 216-218 °C. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 2.55-2.67 (m, 1H), 2.84-2.98 (m, 1H), 3.28 (s, 3H), 4.57 (t, *J* = 5.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.24-7.30 (m, 5H), 8.16-8.19 (m, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 30.9, 37.3 (dd, *J* = 6.8, 3.0 Hz), 40.9 (dd, *J* = 24.3, 22.6 Hz), 110.1, 111.9 (t, *J* = 2.7 Hz), 114.0 (dd, *J* = 247.9, 246.8 Hz), 121.6, 123.6, 124.5, 129.4, 133.6, 138.5, 138.8, 150.4, 179.1 (t, *J* = 25.5 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -106.0 (ddd, *J* = 275.8, 16.5, 7.8 Hz), -101.5 (ddd, *J* = 275.6, 24.5, 8.7 Hz). IR (neat) $\tilde{\nu}$ 3324, 2973, 2882, 1459, 1379, 1326, 1088, 1046, 880 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{14}NOF_2NaCl$ (M+Na): 368.0630, Found: 368.0635.

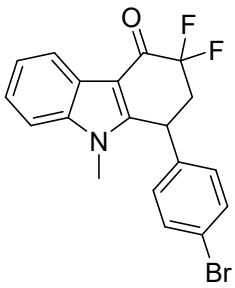




^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)

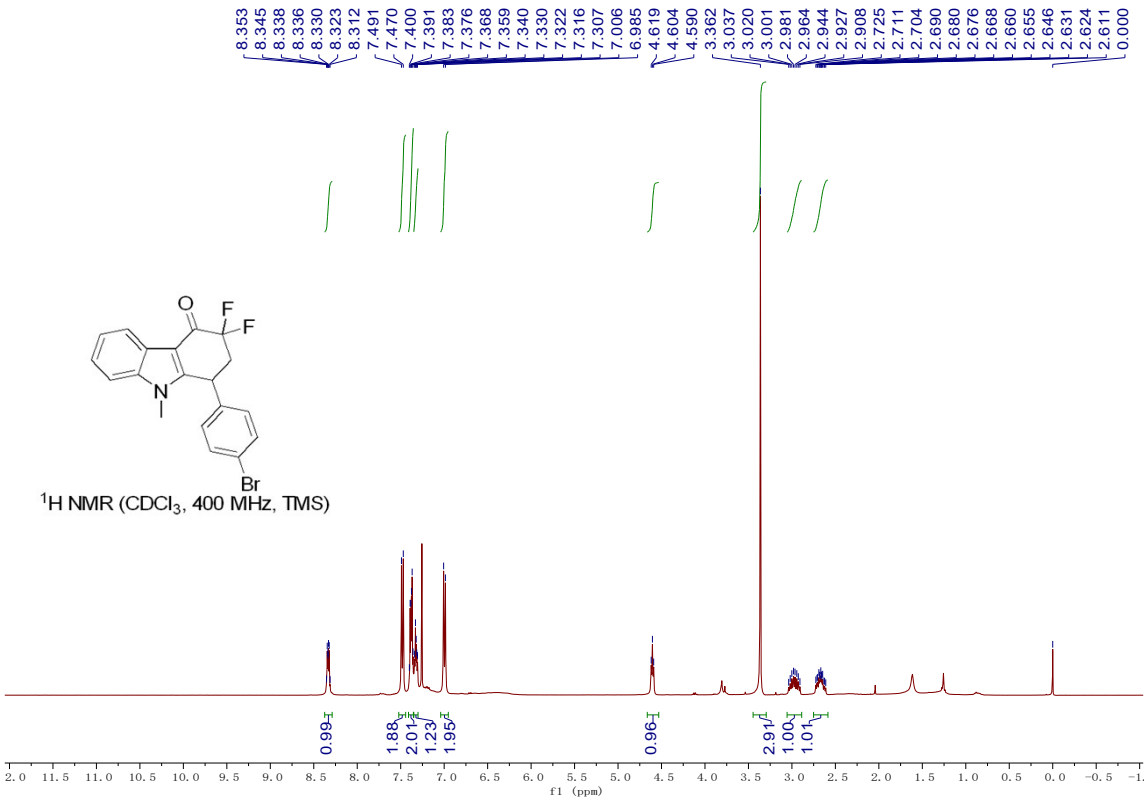


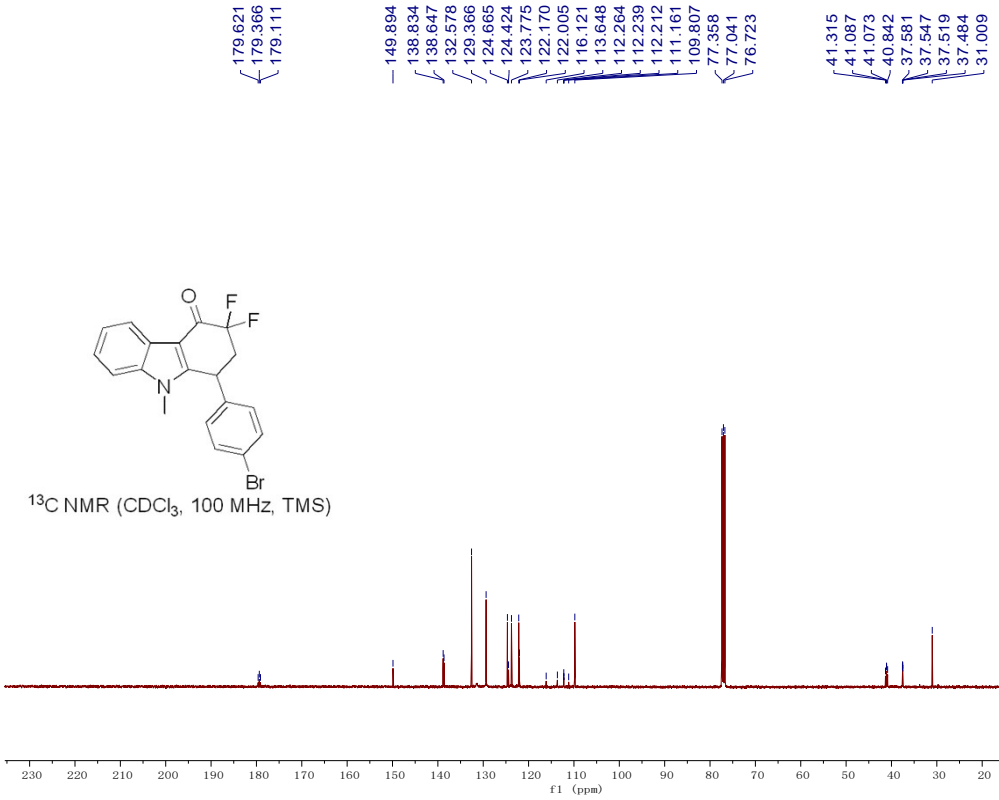
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)



1-(4-bromophenyl)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ad)

A white solid. 42.1 mg, 54% yield. M.P.: 231-233 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.61-2.73 (m, 1H), 2.91-3.04 (m,1H), 3.36 (s, 3H), 4.60 (t, *J* = 5.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.31-7.34 (m, 1H), 7.36-7.40 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 8.31-8.35 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.0, 37.5 (dd, *J* = 6.3, 3.5 Hz), 41.1 (dd, *J* = 24.5, 23.1 Hz), 109.8, 112.2 (t, *J* = 2.6 Hz), 113.6 (t, *J* = 247.3 Hz), 122.0, 122.2, 123.8, 124.4, 124.7, 129.4, 132.6, 138.6, 138.8, 149.9, 179.4 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.5 (ddd, *J* = 276.5, 17.6, 7.8 Hz), -103.8 (ddd, *J* = 276.5, 22.9, 8.3 Hz). IR (neat) $\tilde{\nu}$ 3320, 2973, 2883, 1662, 1453, 1380, 1326, 1088, 1046, 880, 760 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{14}NOF_2BrNa$ (M+Na): 412.0125, Found: 412.0101.

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179.366
179.111
149.894
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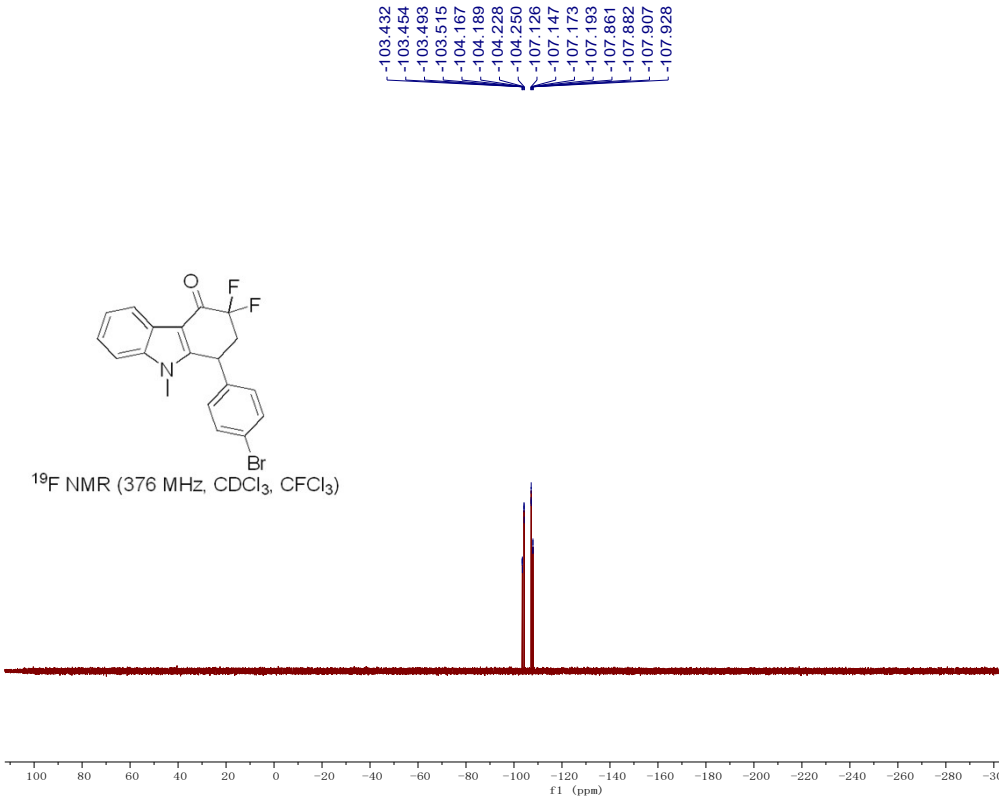
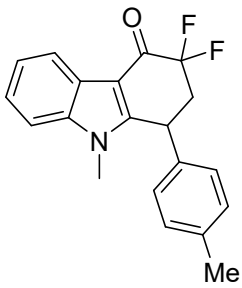
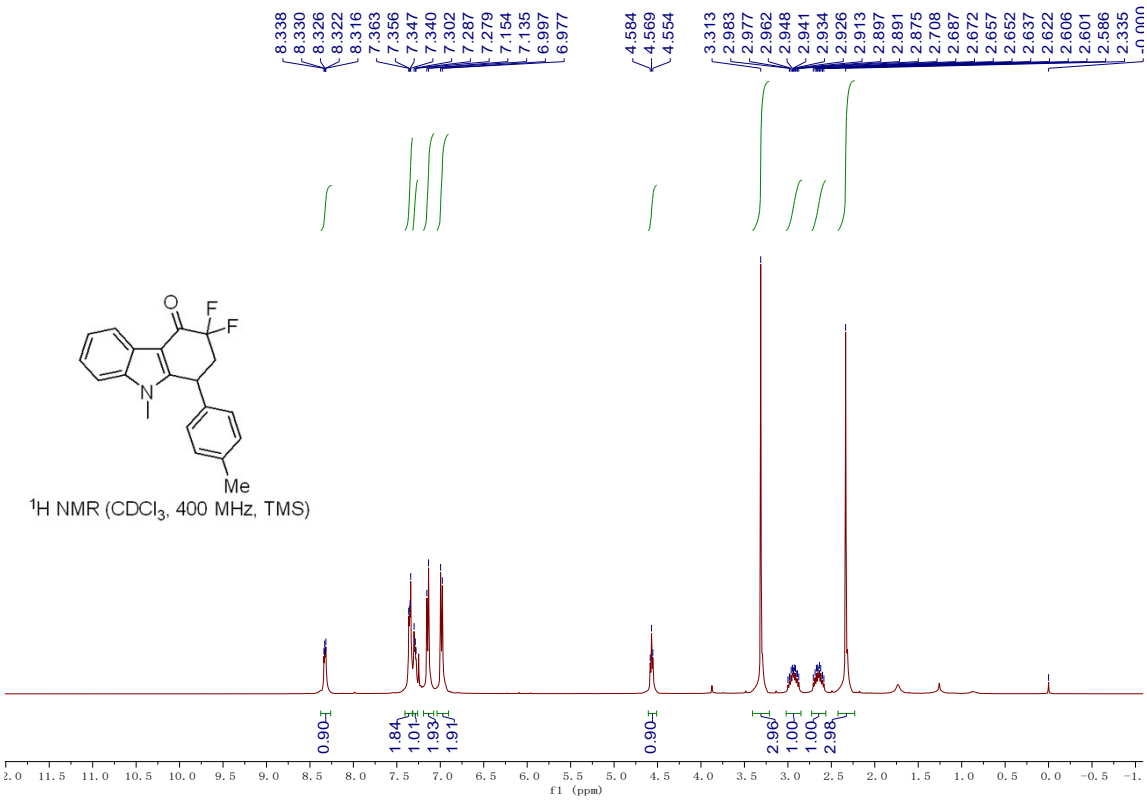
138.647
132.578
129.366
124.665
124.424
123.775
122.170
122.005
116.121
113.648
112.264
112.239
112.212
111.161
109.807
77.358
77.041
76.723
41.315
41.087
41.073
40.842
37.581
37.547
37.519
37.484
31.009
O
F
F
N
I
Br
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

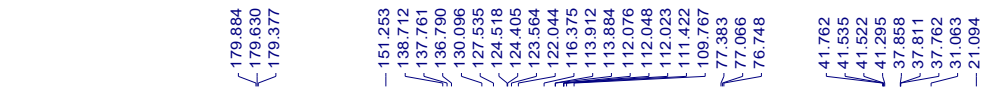

-103.432
-103.454
-103.493
-103.515
-104.167
-104.189
-104.228
-104.250
-107.126
-107.147
-107.173
-107.193
-107.861
-107.882
-107.907
-107.928
O
F
F
N
I
Br
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

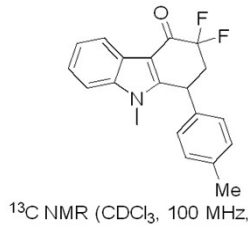


3,3-difluoro-9-methyl-1-(p-tolyl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ae)

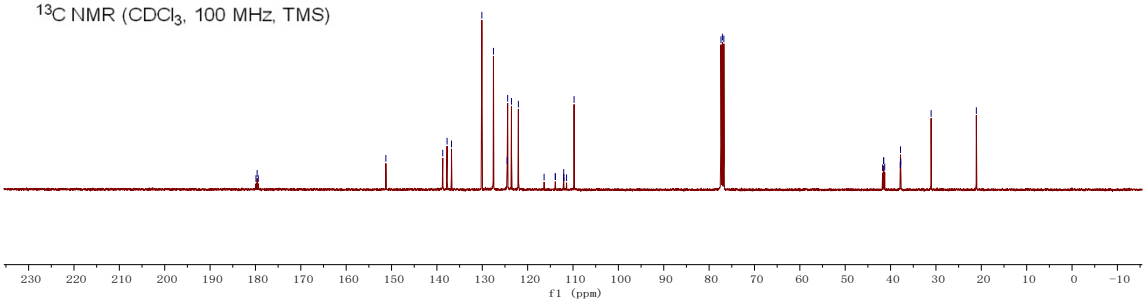
A white solid. 55.3 mg, 85% yield. M.P.: 201-203 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H), 2.59-2.71 (m, 1H), 2.88-3.00 (m,1H), 3.31 (s, 3H), 4.57 (t, *J* = 6.0 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.28-7.36 (m, 3H), 8.32-8.34 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 31.1, 37.8 (t, *J* = 4.8 Hz), 41.5 (dd, *J* = 24.0, 22.7 Hz), 109.8, 112.1 (t, *J* = 2.7 Hz), 113.9 (dd, *J* = 249.1, 246.3 Hz), 122.0, 123.6, 124.4, 124.5, 127.5, 130.1, 136.8, 137.8, 138.7, 151.3, 179.6 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.0 (ddd, *J* = 283.9, 20.1, 9.1 Hz), -105.4 (ddd, *J* = 274.5, 19.9, 8.2 Hz). IR (neat) $\tilde{\nu}$ 3328, 2973, 2925, 1664, 1526, 1458, 1378, 1086, 1046, 880, 752 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{17}NOF_2Na$ (M+Na): 348.1176, Found: 348.1203.

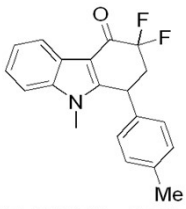




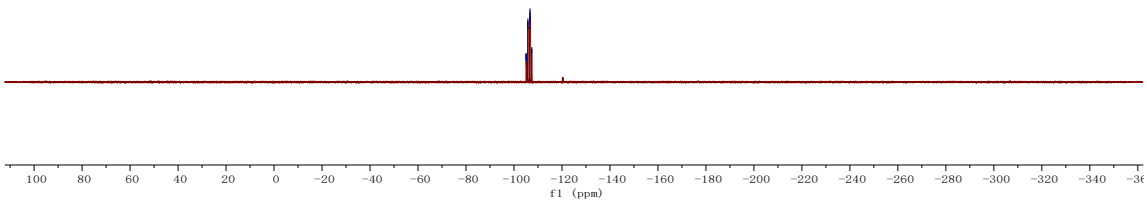


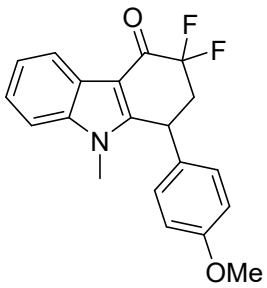
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





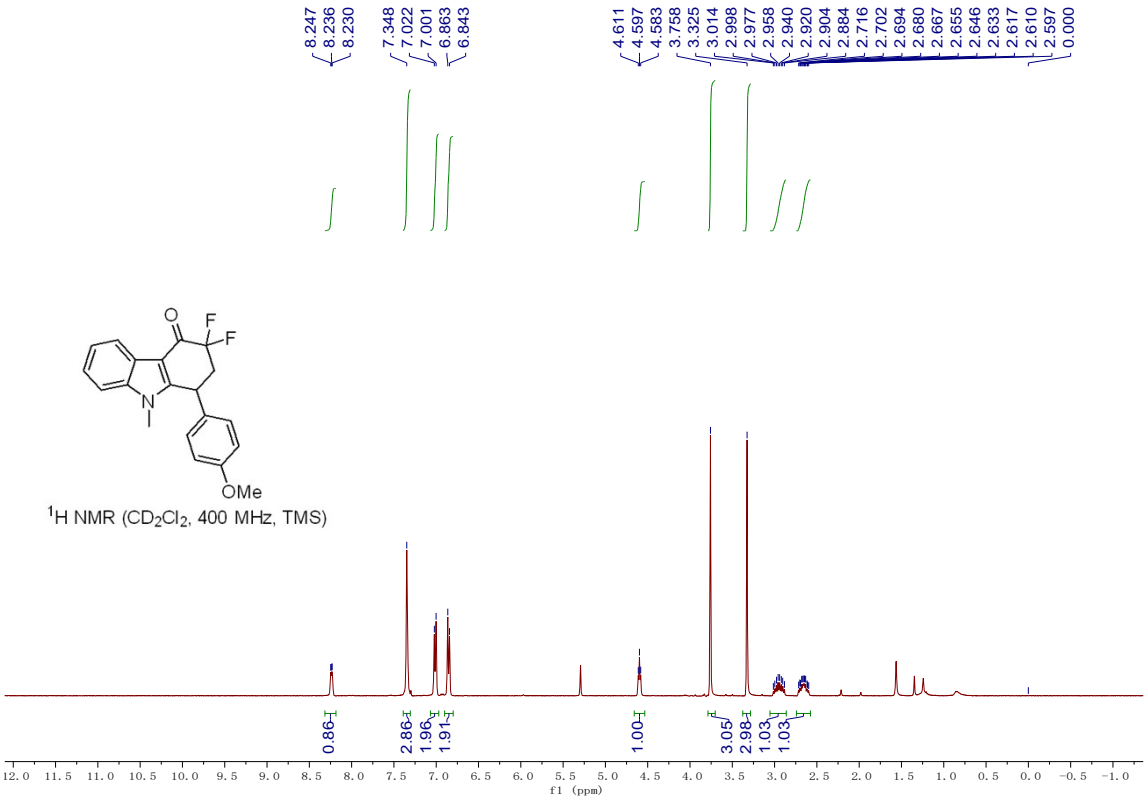
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

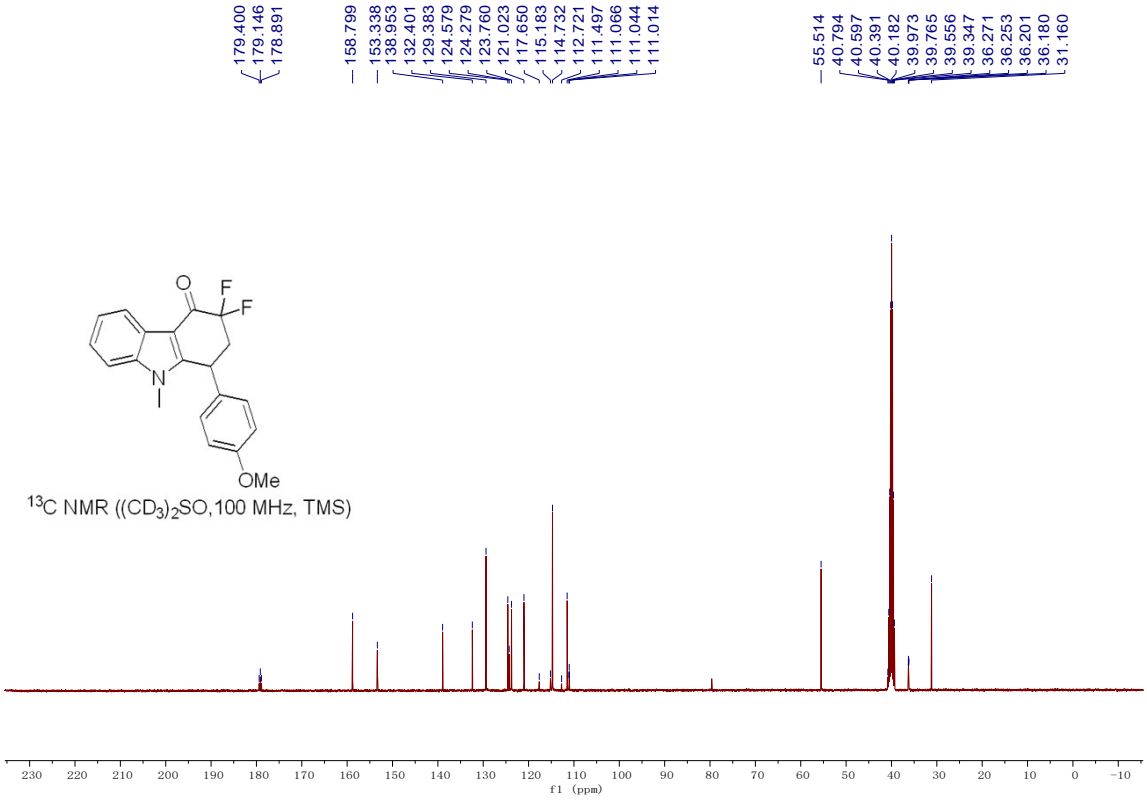




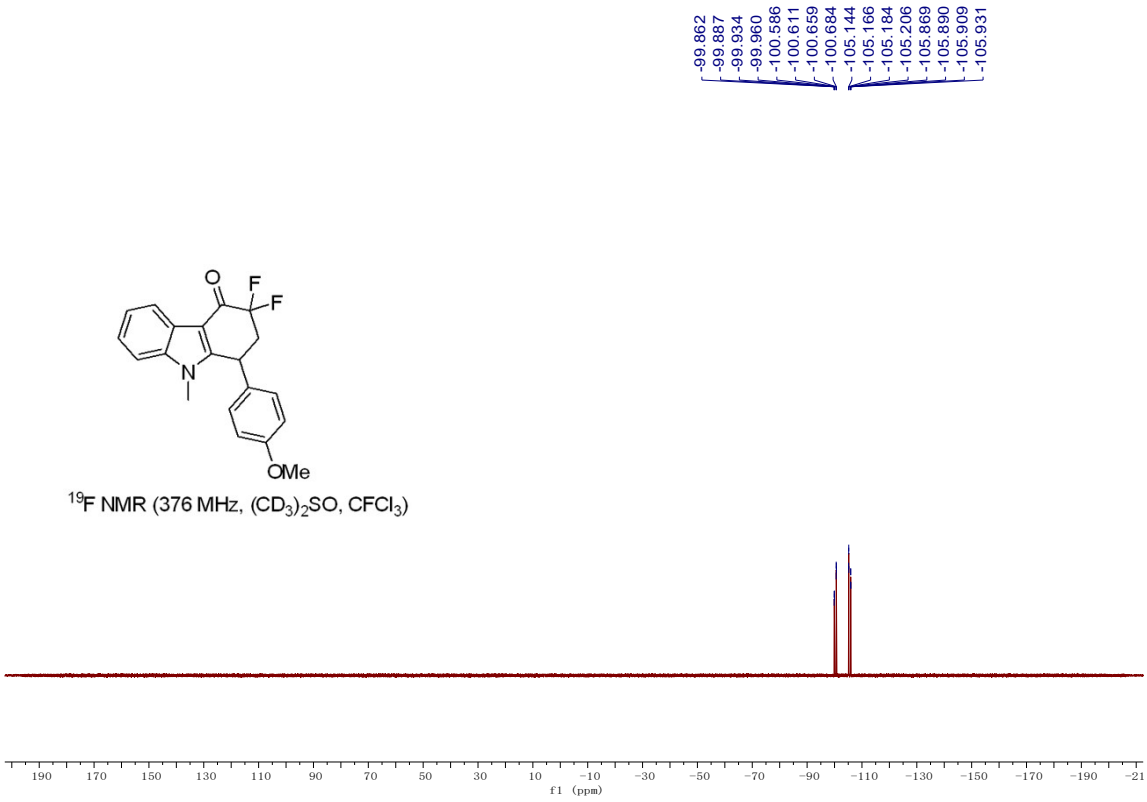
3,3-difluoro-1-(4-methoxyphenyl)-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3af)

A white solid. 54.6 mg, 80% yield. M.P.: 226-228 °C. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 2.60-2.72 (m, 1H), 2.88-3.01 (m,1H), 3.33 (s, 3H), 3.76 (s, 3H), 4.60 (t, J = 5.6 Hz, 1H), 6.85 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 7.35 (br, 3H), 8.23-8.25 (m, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 31.2, 36.2 (dd, J = 7.0, 1.8 Hz), 55.5, 110.0 (t, J = 2.6 Hz), 111.5, 114.7, 115.2 (dd, J = 246.7, 246.2 Hz), 121.0, 123.8, 124.3, 124.6, 129.4, 132.4, 139.0, 153.3, 158.8, 179.2 (t, J = 25.6 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -105.5 (ddd, J = 272.9, 15.3, 8.2 Hz), -100.3 (ddd, J = 272.8, 27.4, 9.6 Hz). IR (neat) $\tilde{\nu}$ 3225, 2962, 2870, 1450, 1366, 1325, 1020, 1002, 880 cm^{-1}. HRMS (EI) calcd. for $C_{20}H_{17}NO_2F_2$ (M^+): 341.1222, Found: 341.1226.

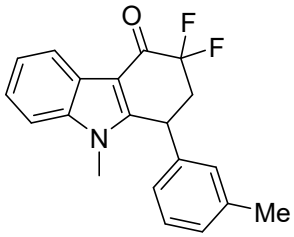




^{13}C NMR ((CD$_3$)$_2$SO,100 MHz, TMS)

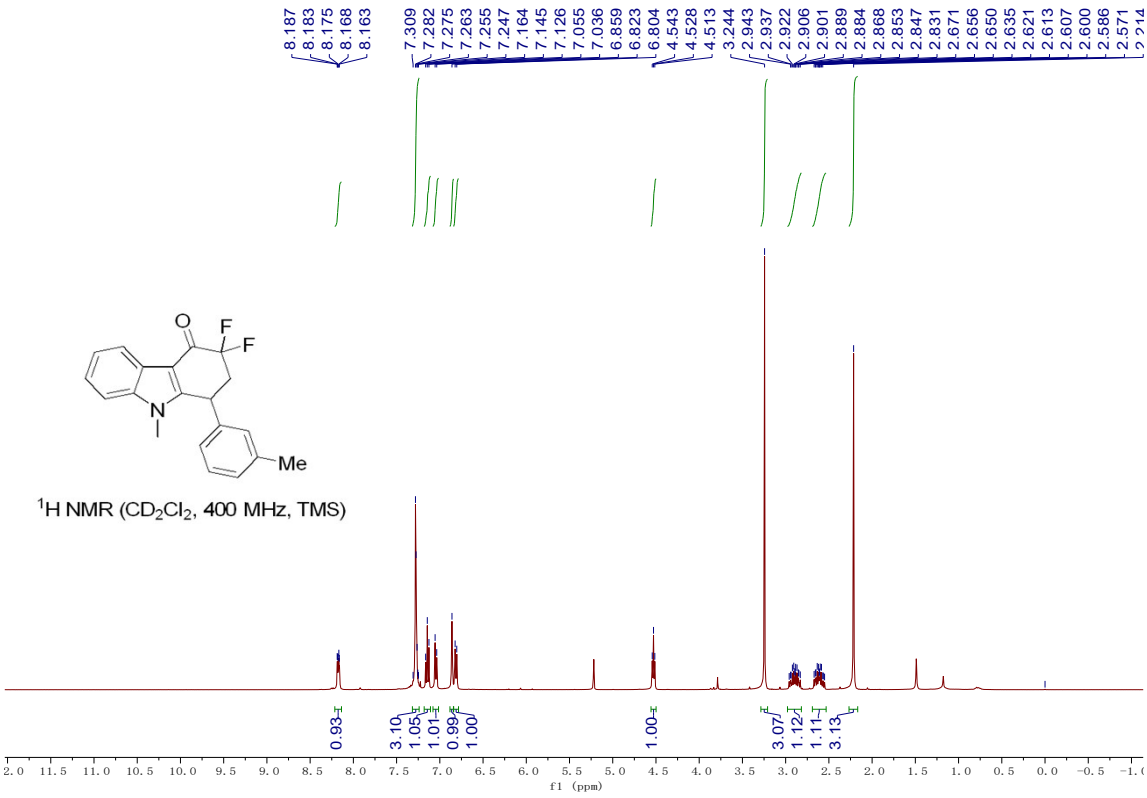


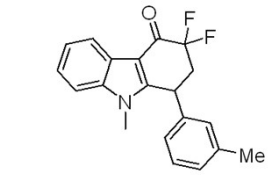
^{19}F NMR (376 MHz, (CD$_3$)$_2$SO, CFCl$_3$)



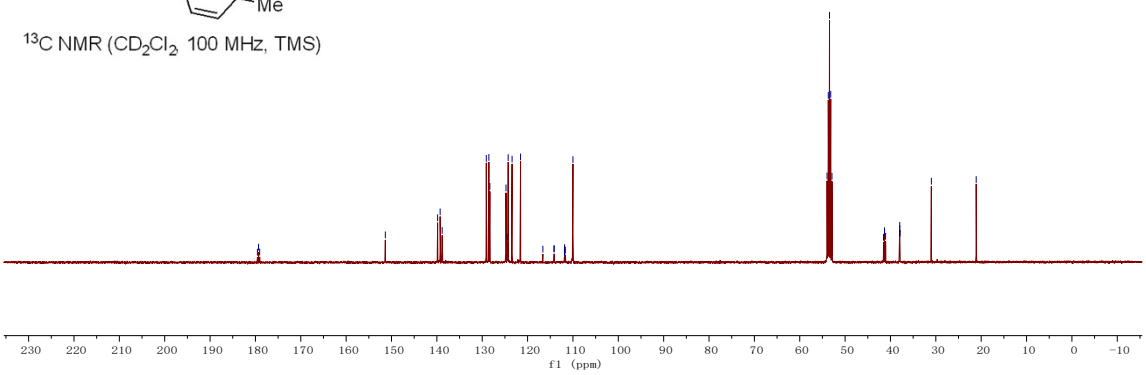
3,3-difluoro-9-methyl-1-(m-tolyl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ag)

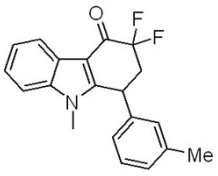
A colorless oil. 44.9 mg, 69% yield. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 2.21 (s, 3H), 2.55-2.67 (m, 1H), 2.3-2.96 (m, 1H), 3.24 (s, 3H), 4.53 (t, *J* = 6.0 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.25-7.31 (m,3H), 8.16-8.19 (m, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 21.1, 31.0, 38.0 (dd, *J* = 5.6, 4.2 Hz), 41.3 (dd, *J* = 24.3, 22.6 Hz), 110.0, 111.9 (t, *J* = 2.9, 2.9 Hz), 114.1 (dd, *J* = 248.5, 245.9 Hz), 121.6, 123.4, 124.3, 124.5, 124.8, 128.3, 128.5, 129.1, 138.8, 139.3, 139.8, 151.4, 179.31 (t, *J* = 25.5 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -107.4 (ddd, *J* = 274.9, 18.4, 6.4 Hz), -105.1 (ddd, *J* = 273.7, 20.3, 4.9 Hz). IR (neat) $\tilde{\nu}$ 2925, 1657, 1526, 1478, 1398, 1342, 1272, 1188, 1065, 1055, 864, 782, 750, 709 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{18}NOF_2$ (M+H): 326.1351, Found: 326.1355.



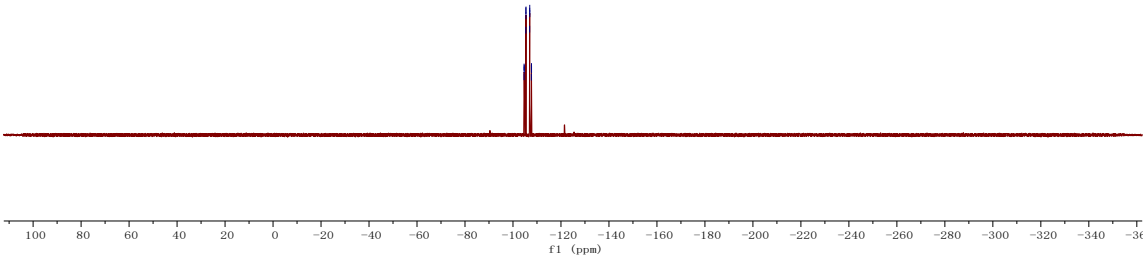


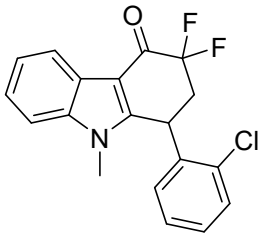
^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)





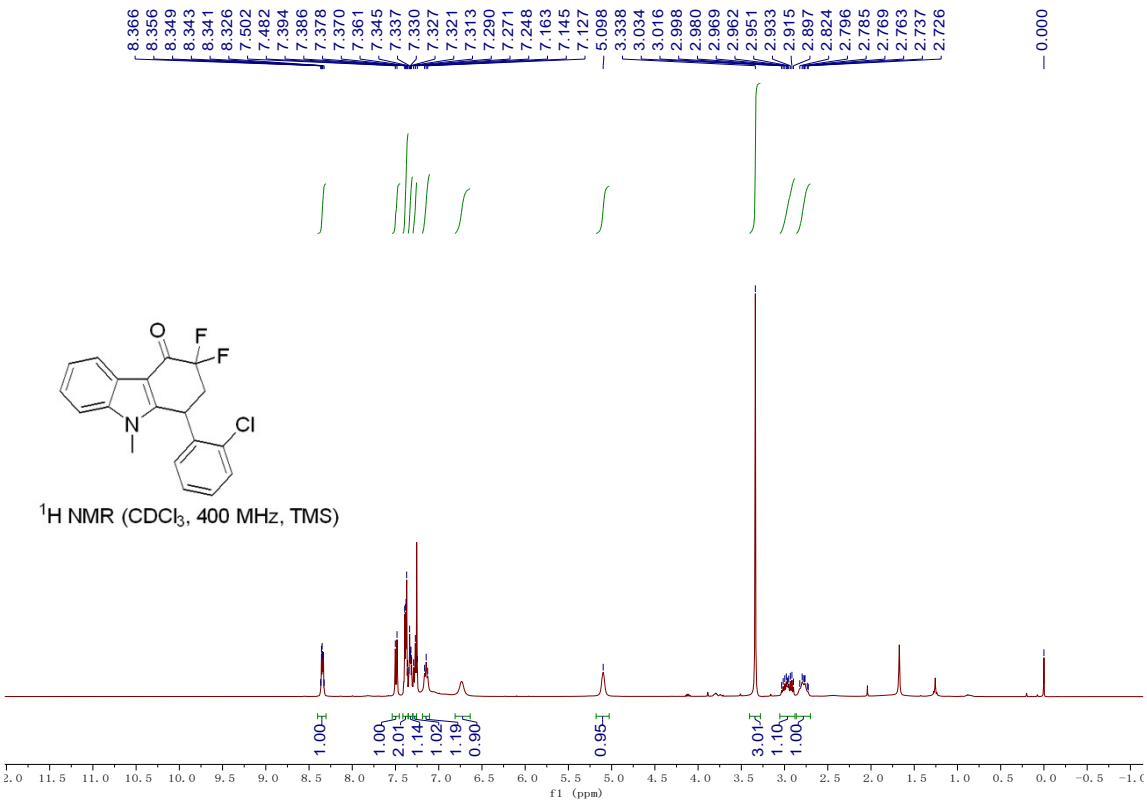
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)

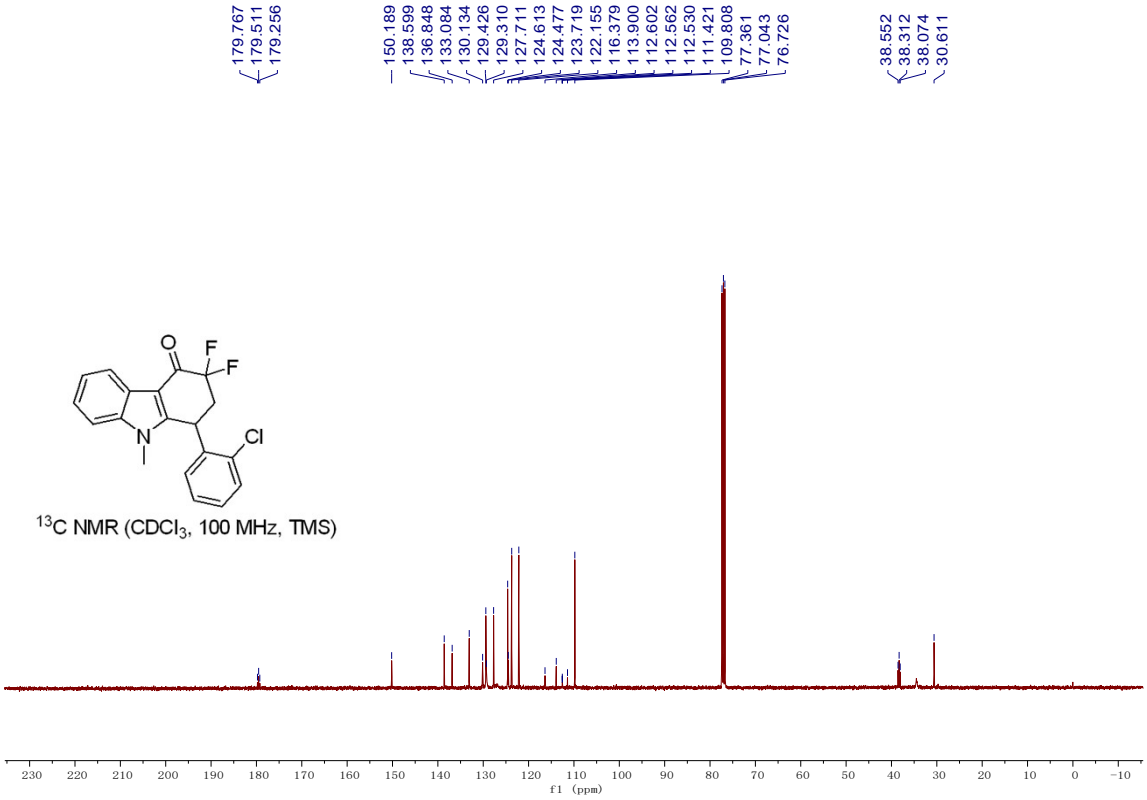




1-(2-chlorophenyl)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ah)

A white solid. 45.0 mg, 65% yield. M.P.: 147-149 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.73-2.82 (m, 1H), 2.90-3.03 (m,1H), 3.34 (s, 3H), 5.10 (s, 1H), 6.74 (br, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.31-7.35 (m, 1H), 7.36-7.40 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 8.33-8.37 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.6, 38.3 (t, *J* = 24.0 Hz), 109.8, 112.5, 112.6 (t, *J* = 3.6 Hz), 113.9 (t, *J* = 247.9 Hz), 122.2, 123.7, 124.5, 124.6, 127.7, 129.3, 129.4, 130.1, 133.1, 136.8, 138.6, 150.2, 179.5 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -102.5 (dd, *J* = 284.3, 5.6 Hz), -97.6 (ddd, *J* = 284.4, 31.4, 12.2 Hz). IR (neat) $\tilde{\nu}$ 3423, 2921, 1643, 1526, 1462, 1376, 1222, 1183, 1126, 1069, 878, 752, 739 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{15}NOF_2Cl$ (M+H): 346.0804, Found: 346.0805.

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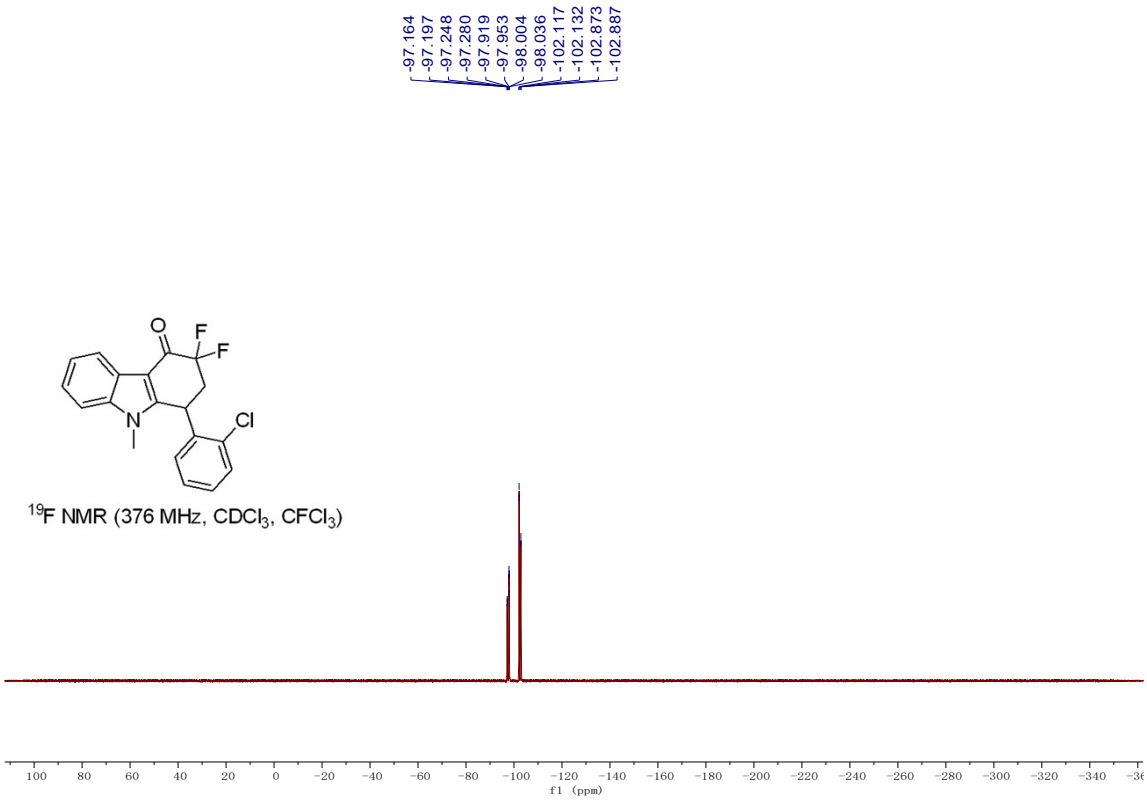
124.477
123.719
122.155
116.379
113.900
112.602
112.562
112.530
111.421
109.808
77.361
77.043
76.726
38.552
38.312
38.074
30.611
O
F
F
N
Cl
13C NMR (CDCl3, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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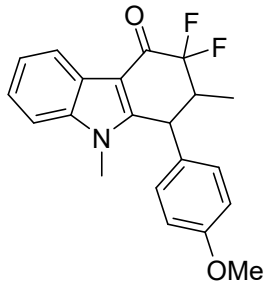
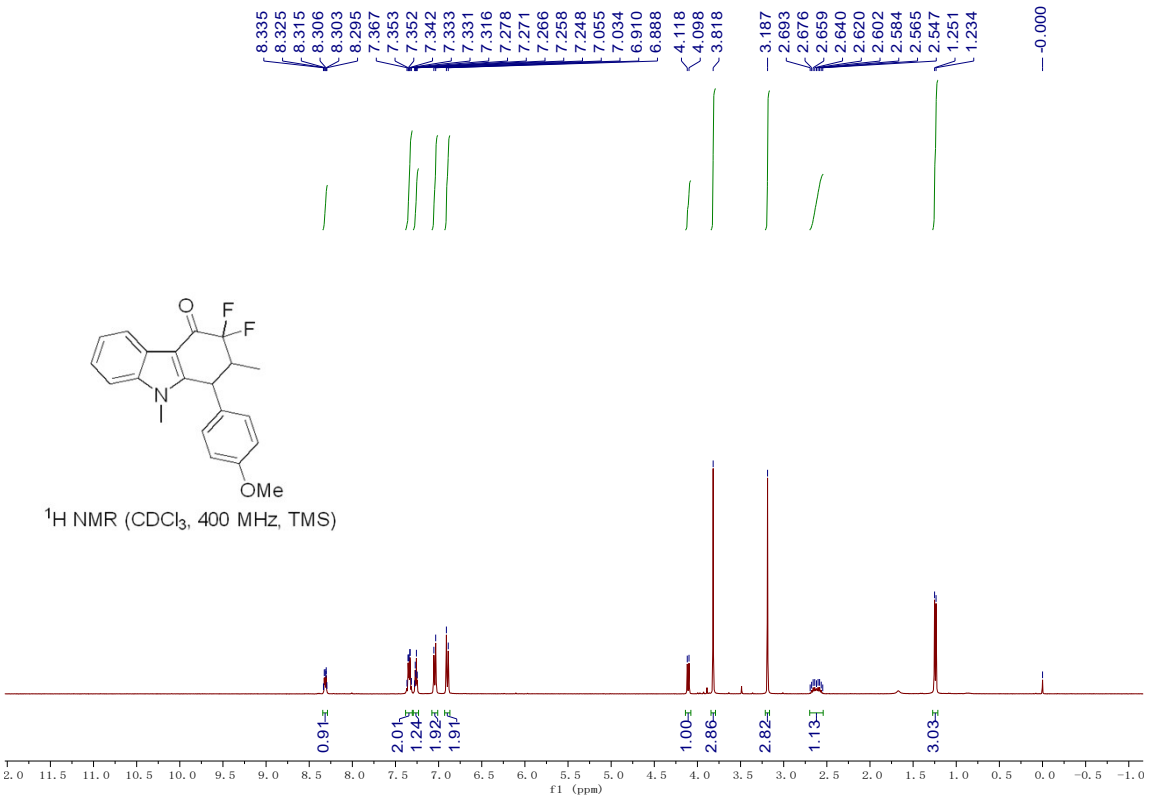
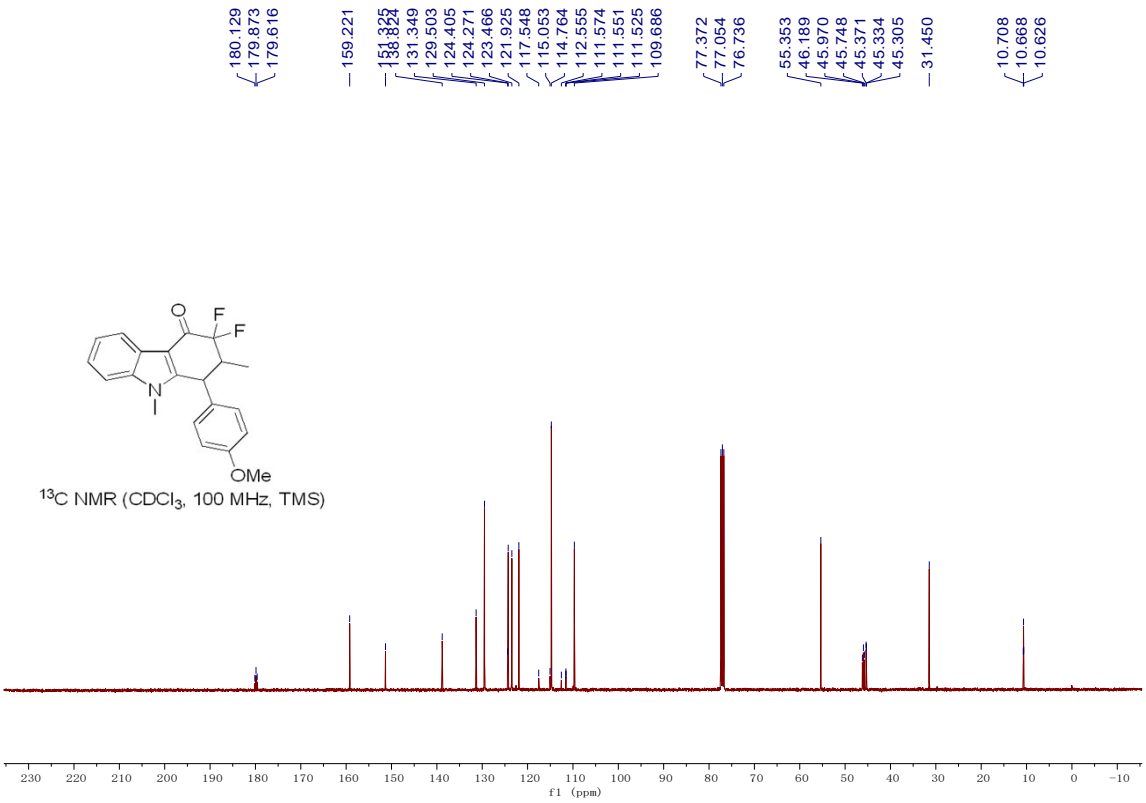
-97.248
-97.280
-97.919
-97.953
-98.004
-98.036
-102.117
-102.132
-102.873
-102.887
O
F
F
N
Cl
19F NMR (376 MHz, CDCl3, CFCl3)
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340
f1 (ppm)



3,3-difluoro-1-(4-methoxyphenyl)-2,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ai)

A colorless oil. 54.0 mg, 76% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (d, J = 6.8 Hz, 3H), 2.55-2.69 (m, 1H), 3.19 (s,3H), 3.82 (s, 3H), 4.11 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 7.25-7.28 (m, 1H), 7.32-7.37 (m, 2H), 8.30-8.34 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 10.7 (t, J = 4.2, 4.2 Hz), 31.5, 45.3 (t, J = 3.7 Hz), 46.0 (t, J = 21.9 Hz), 55.4, 109.7, 111.6 (t, J = 2.4 Hz), 114.8, 115.1 (t, J = 249.5 Hz), 121.9, 123.5, 124.3, 124.4, 129.5, 131.3, 138.8, 151.3, 159.2, 179.87 (t, J = 25.8 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -117.4 (dd, J = 269.4, 23.2 Hz), -116.3 (d, J = 269.1 Hz). IR (neat) $\tilde{\nu}$ 2936, 2844, 1660, 1612, 1513, 1473, 1463, 1390, 1344, 1269, 1249, 1184, 1080, 1030, 993, 873, 836, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{19}NO_2F_2Na$ (M+Na): 378.1276, Found: 378.1280.

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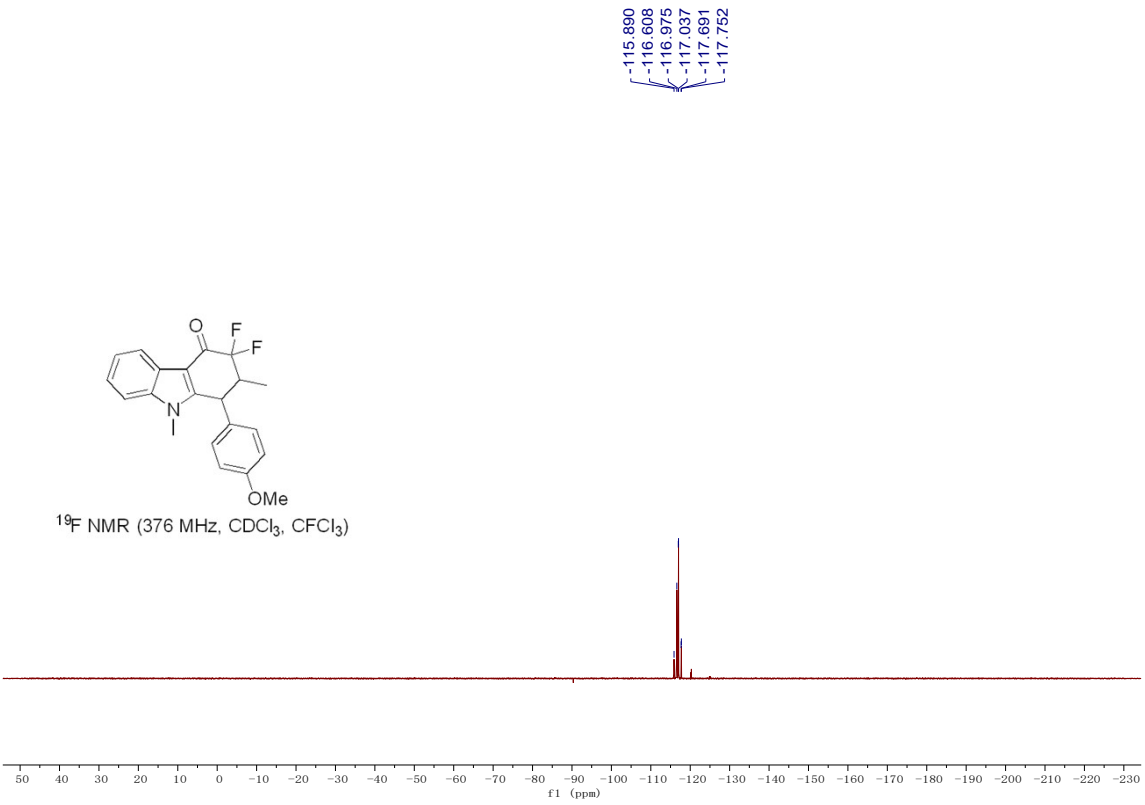
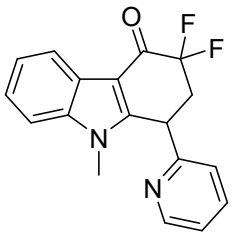
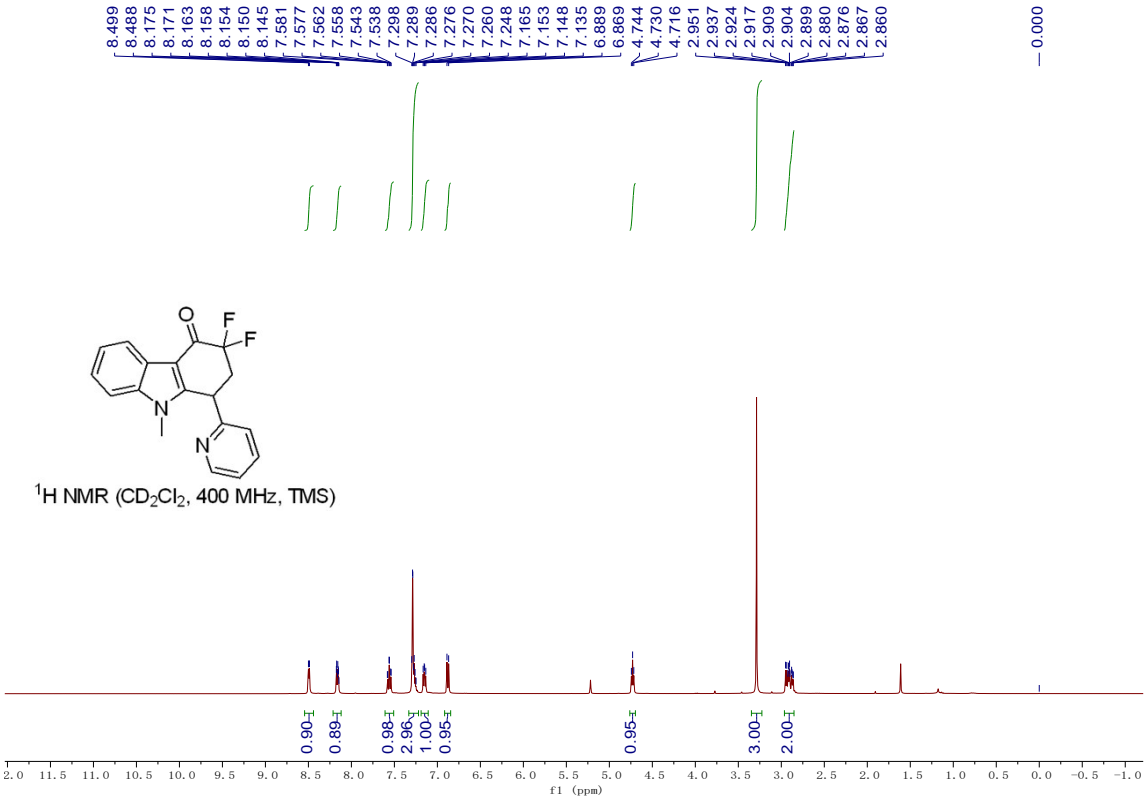
179.873
179.616
159.221
131.349
129.503
124.405
124.271
123.466
121.925
117.548
115.053
114.764
112.555
111.574
111.551
111.525
109.686
77.372
77.054
76.736
55.353
46.189
45.970
45.748
45.371
45.334
45.305
31.450
10.708
10.668
10.626
F
F
O
N
OMe
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

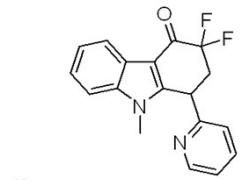

-115.890
-116.608
-116.975
-117.037
-117.691
-117.752
F
F
O
N
OMe
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



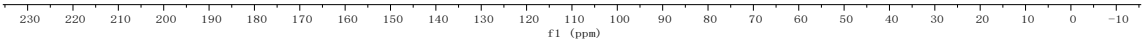
3,3-difluoro-9-methyl-1-(pyridin-2-yl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aj)

A colorless oil. 46.2 mg, 74% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.86-2.98 (m, 2H), 3.29 (s, 3H), 4.73 (t, *J* = 5.6 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 7.14-7.17 (m, 1H), 7.25-7.30 (m, 3H),7.56 (td, *J* = 7.6, 1.6 Hz), 8.15-8.18 (m, 1H), 8.49 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.8, 39.4 (dd, *J* = 24.5, 23.1 Hz), 40.1 (dd, *J* = 6.8, 2.9 Hz), 110.1, 111.7 (t, *J* = 2.8 Hz), 114.3 (t, *J* = 248.6 Hz), 121.6, 122.1 (d, *J* = 2.0 Hz), 122.7, 123.5, 124.4, 124.5, 137.2, 138.7, 150.1, 150.4, 159.0, 179.14 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -108.1 (ddd, *J* = 275.2, 10.5, 10.5 Hz), -103.4 (ddd, *J* = 277.9, 16.9, 16.9 Hz). IR (neat) $\tilde{\nu}$ 2927, 1646, 1589, 1483, 1464, 1270, 1180, 1066, 1055, 1046, 908, 864, 778, 751, 737 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{15}N_2OF_2$ (M+H): 313.1147, Found: 313.1143.

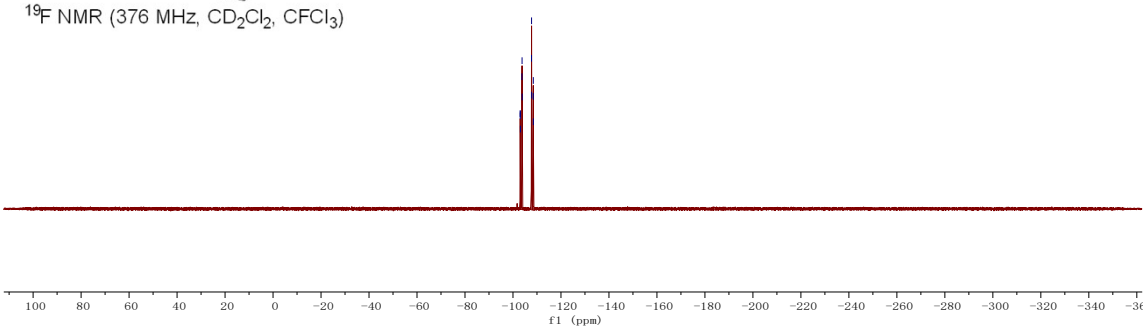


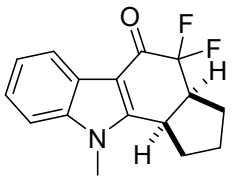


^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)



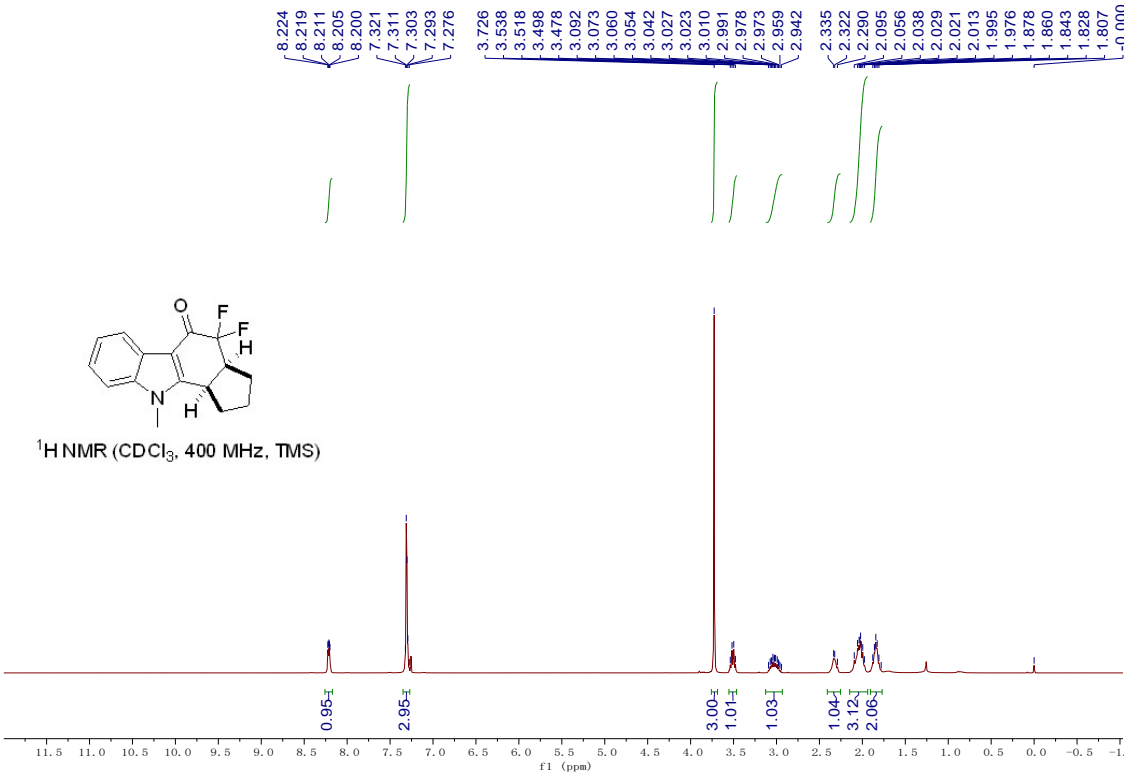
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)

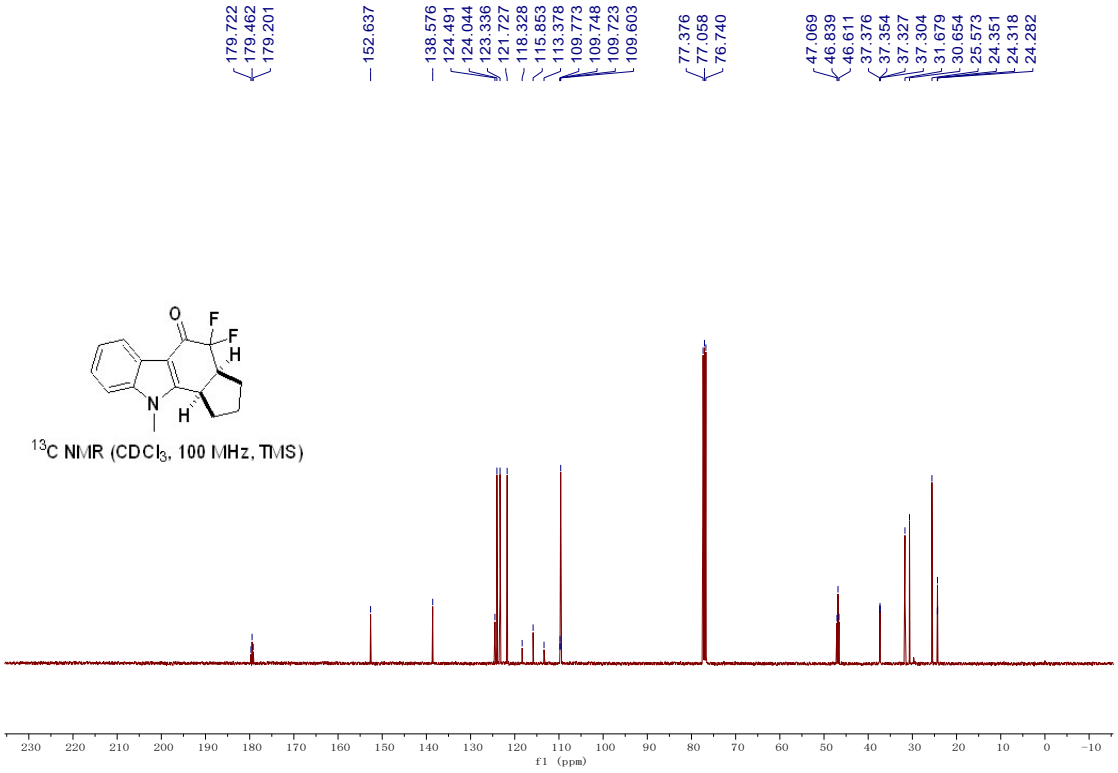




4,4-difluoro-10-methyl-2,3,3a,4,10,10b-hexahydrocyclopenta[a]carbazol-5(1H)-one (3ak)

A white solid. 54.5 mg, 99% yield. M.P.: 190-192 °C. A white solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.78-1.88 (m, 2H), 1.98-2.10 (m, 3H), 2.29-2.34 (m, 1H), 2.94-3.09 (m, 1H), 3.48-3.54 (m, 1H), 3.73 (s, 3H), 7.28-7.32 (m, 3H), 8.20-8.22 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 24.3 (t, J = 3.5 Hz), 25.6, 30.7, 31.7, 37.3 (dd, J = 4.9, 2.2 Hz), 46.8 (t, J = 23.1 Hz), 109.6, 109.8 (t, J = 2.5 Hz), 115.9 (t, J = 249.0 Hz), 121.7, 123.3, 124.0, 124.5, 138.6, 152.6, 179.5 (t, J = 26.2 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -109.1 (dd, J = 273.3, 20.6 Hz), -107.9 (dd, J = 273.3, 11.8 Hz). IR (neat) $\tilde{\nu}$ 2951, 2923, 2853, 1667, 1526, 1482, 1465, 1401, 1060, 862, 753 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{16}NOF_2$ (M+H): 276.1195, Found: 276.1198.

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123.336
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118.328
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113.378
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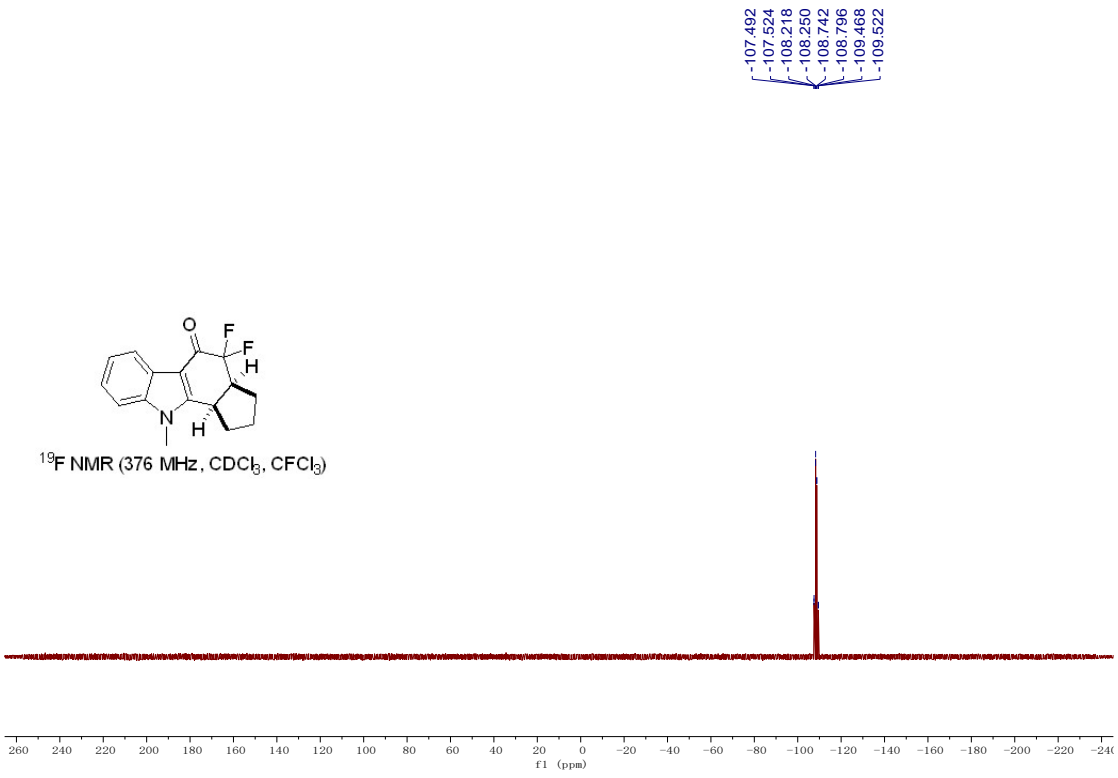
109.748
109.723
109.603
77.376
77.058
76.740
47.069
46.839
46.611
37.376
37.354
37.327
37.304
31.679
30.654
25.573
24.351
24.318
24.282
O
F
F
H
N
H
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)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-108.218
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-108.742
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-109.522
O
F
F
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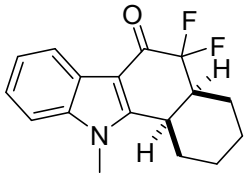
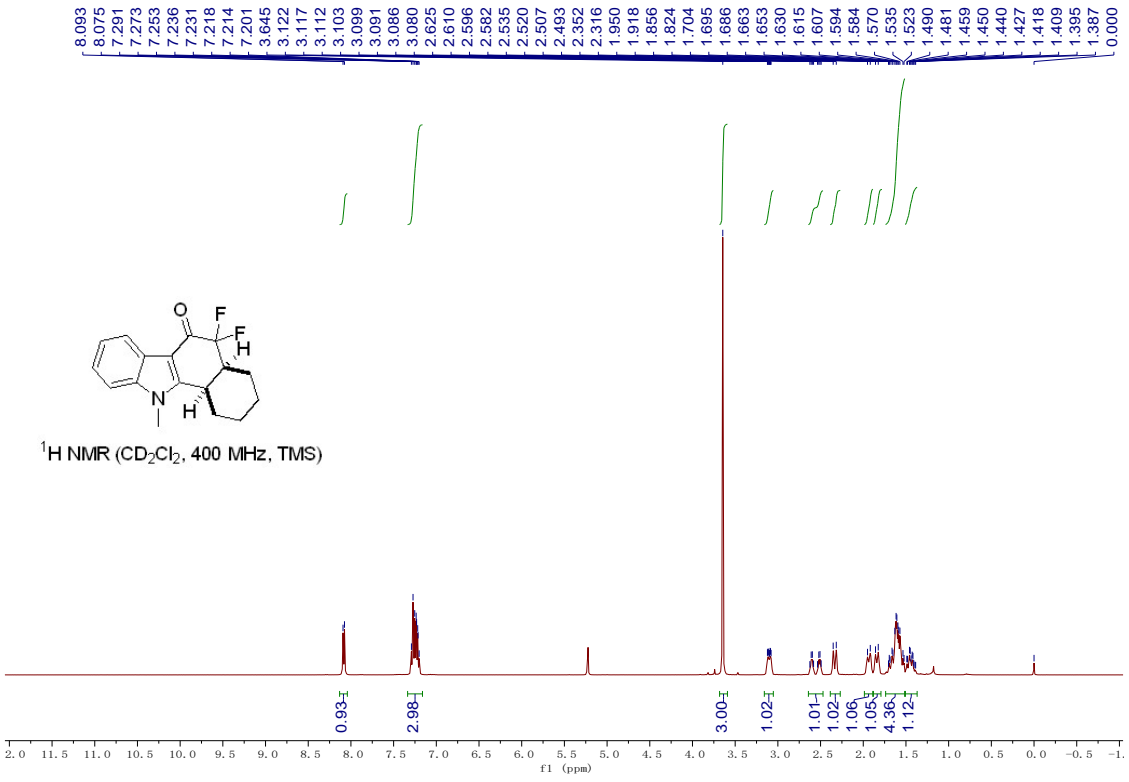
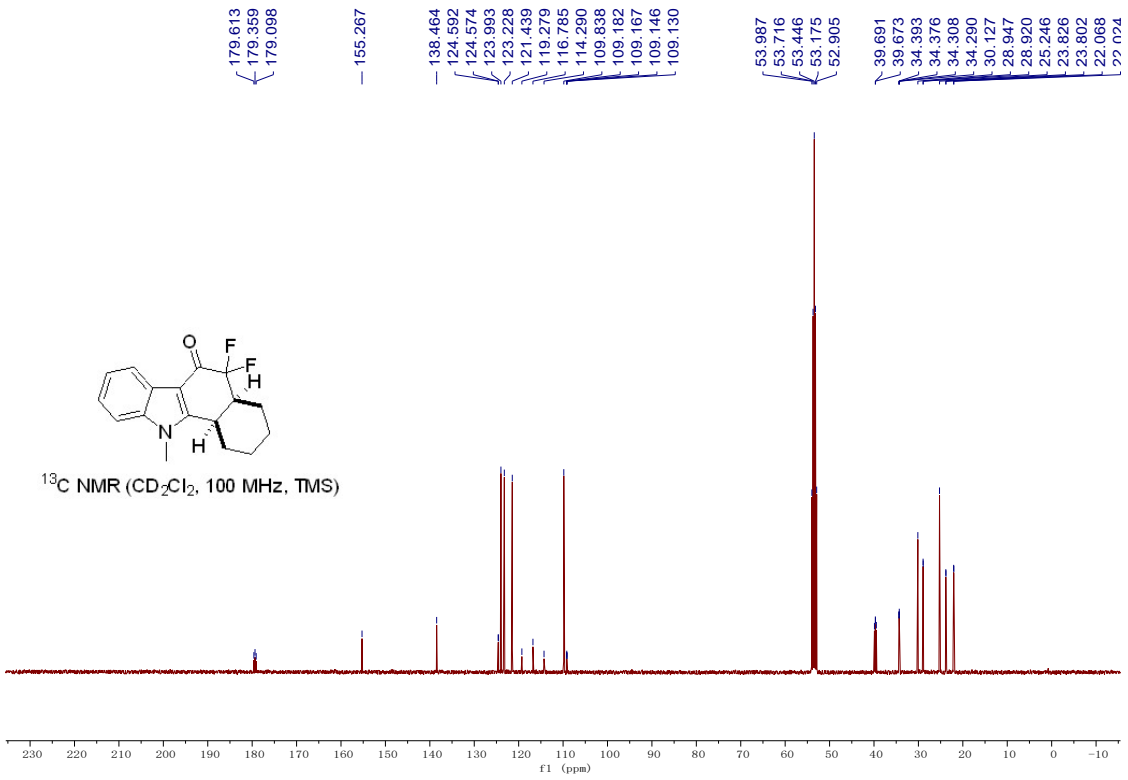
N
H
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



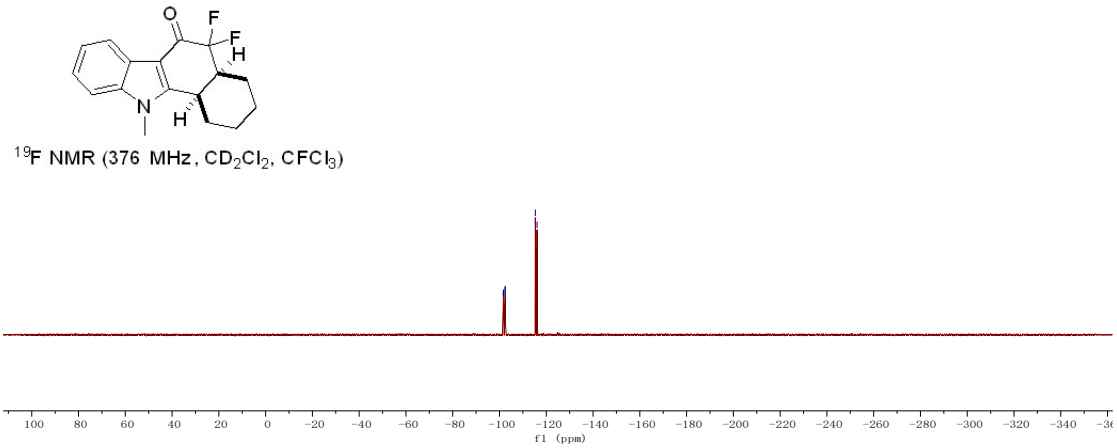
5,5-difluoro-11-methyl-1,2,3,4,4a,5,11,11b-octahydro-6H-benzo[a]carbazol-6-one (3al)

A white solid. 47.4 mg, 82% yield. M.P.: 231-233 °C. A white solid. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 1.39-1.49 (m, 1H), 1.52-1.70 (m, 4H), 1.84 (d, *J* = 12.8 Hz, 1H), 1.93 (d, *J* = 12.8 Hz, 1H), 2.33 (d, *J* = 14.4 Hz, 1H), 2.49-2.63 (m, 1H), 3.08-3.12 (m, 1H), 3.65 (s, 3H), 7.20-7.29 (m, 3H), 8.08 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 22.1 (d, *J* = 4.4 Hz), 23.8 (d, *J* = 2.4 Hz), 25.2, 28.9 (d, *J* = 2.7 Hz), 30.1, 34.3 (dd, *J* = 8.5, 1.8 Hz), 39.7 (dd, *J* = 22.5, 20.7 Hz), 109.2 (dd, *J* = 3.7, 1.5 Hz), 109.8, 116.8 (t, *J* = 251.0 Hz), 121.4, 123.2, 124.0, 124.6 (d, *J* = 1.8 Hz), 138.5, 155.3, 179.4 (t, *J* = 26.2 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -115.7 (d, *J* = 277.0 Hz), -102.0 (dd, *J* = 278.7, 36.0 Hz). IR (neat) $\tilde{\nu}$ 2938, 2855, 1660, 1527, 1406, 1153, 1052, 1013, 870, 761 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{18}NOF_2$ (M+H): 290.1351, Found: 290.1356.

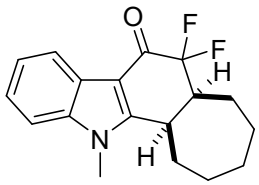




^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)

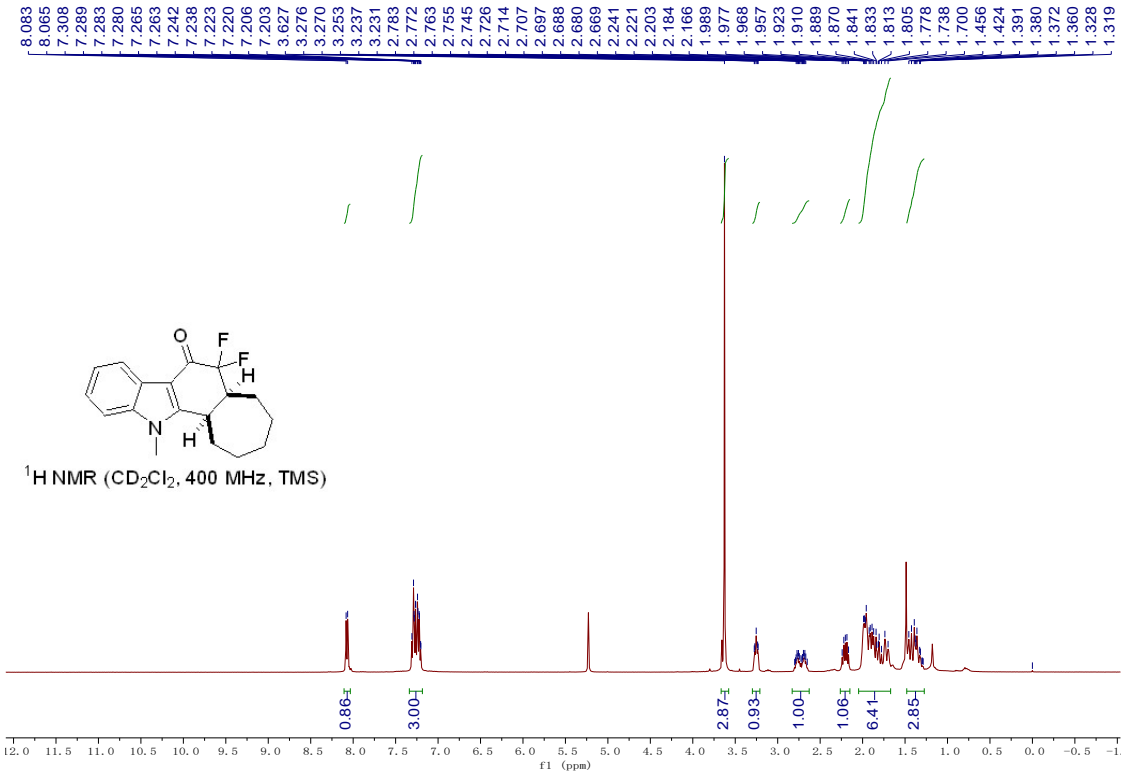


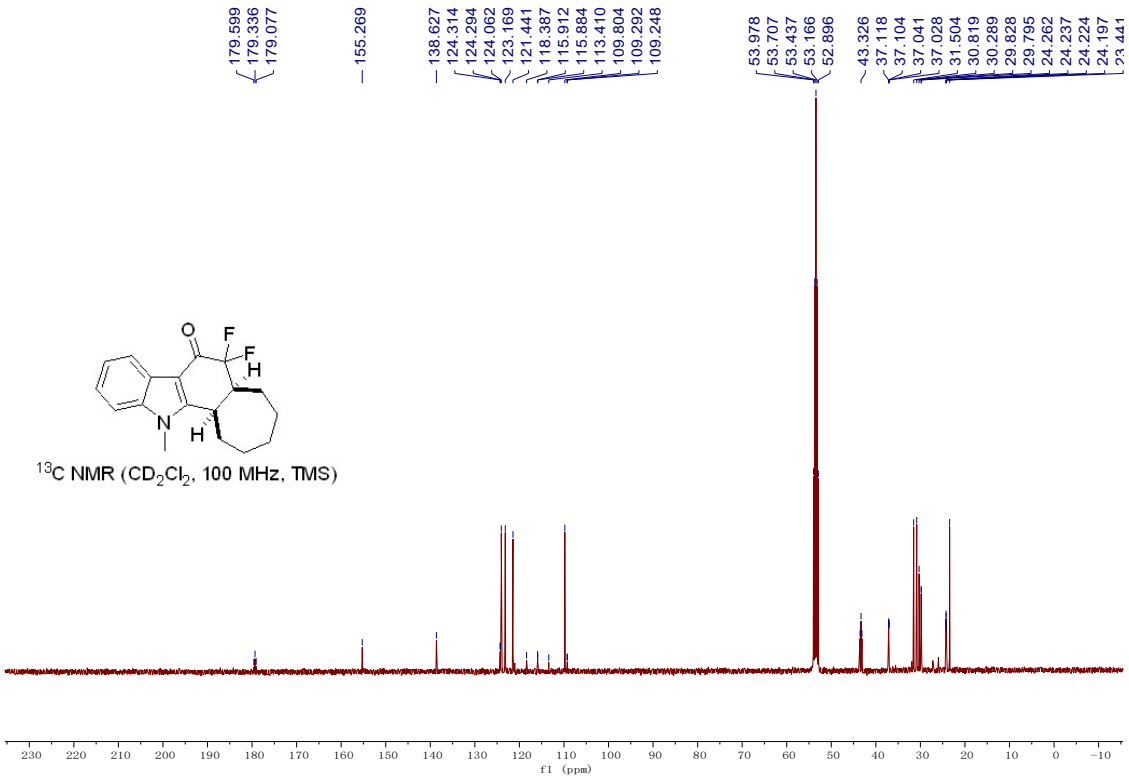
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)



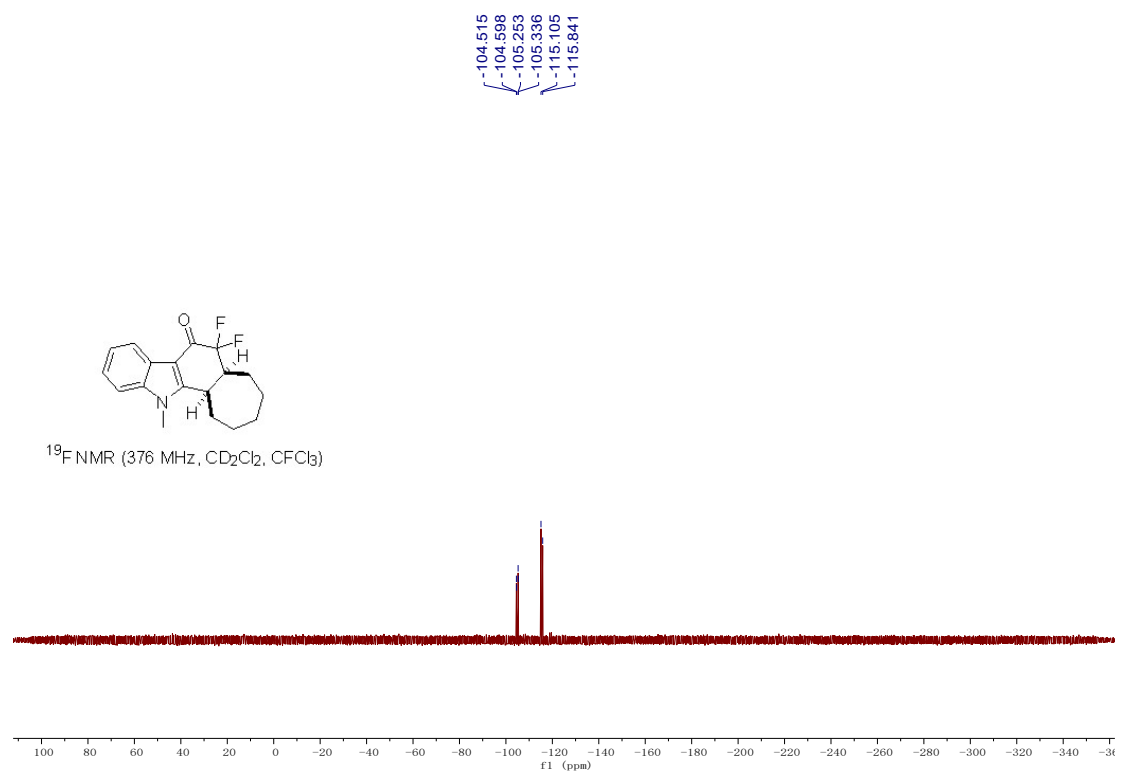
6,6-difluoro-12-methyl-2,3,4,5,5a,6,12,12b-octahydrocyclohepta[a]carbazol-7(1H)-one (3am)

A white solid. 42.5 mg, 70% yield. M.P.: 242-244 °C. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 1.29-1.46 (m, 3H), 1.70-1.99 (m, 6H), 2.17-2.24 (m, 1H), 2.65-2.80 (m, 1H), 2.65-2.80 (m, 1H), 3.23-3.28 (m,1H), 3.63 (s, 3H), 7.20-7.31 (m, 3H), 8.07 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 23.4, 24.2 (dd, *J* = 4.0, 2.7 Hz), 29.8 (d, *J* = 3.3 Hz), 30.3, 30.8, 31.5, 37.1 (dd, *J* = 7.7, 1.4 Hz), 43.3 (t, *J* = 21.3 Hz), 109.3 (d, *J* = 4.5 Hz), 115.9 (dd, *J* = 250.3, 247.5 Hz), 121.4, 123.2, 124.1, 124.3 (d, *J* = 2.0 Hz), 138.6, 155.3, 179.3 (t, *J* = 26.3 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -115.5 (d, *J* = 276.9 Hz), -104.9 (dd, *J* = 277.7, 31.3 Hz). IR (neat) $\tilde{\nu}$ 2923, 2851, 1668, 1476, 1464, 1183, 1064, 1031, 960, 867, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{20}NOF_2$ (M+H): 304.1508, Found: 304.1513.

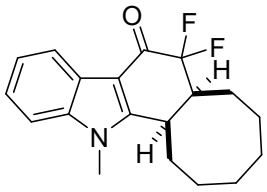




^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)

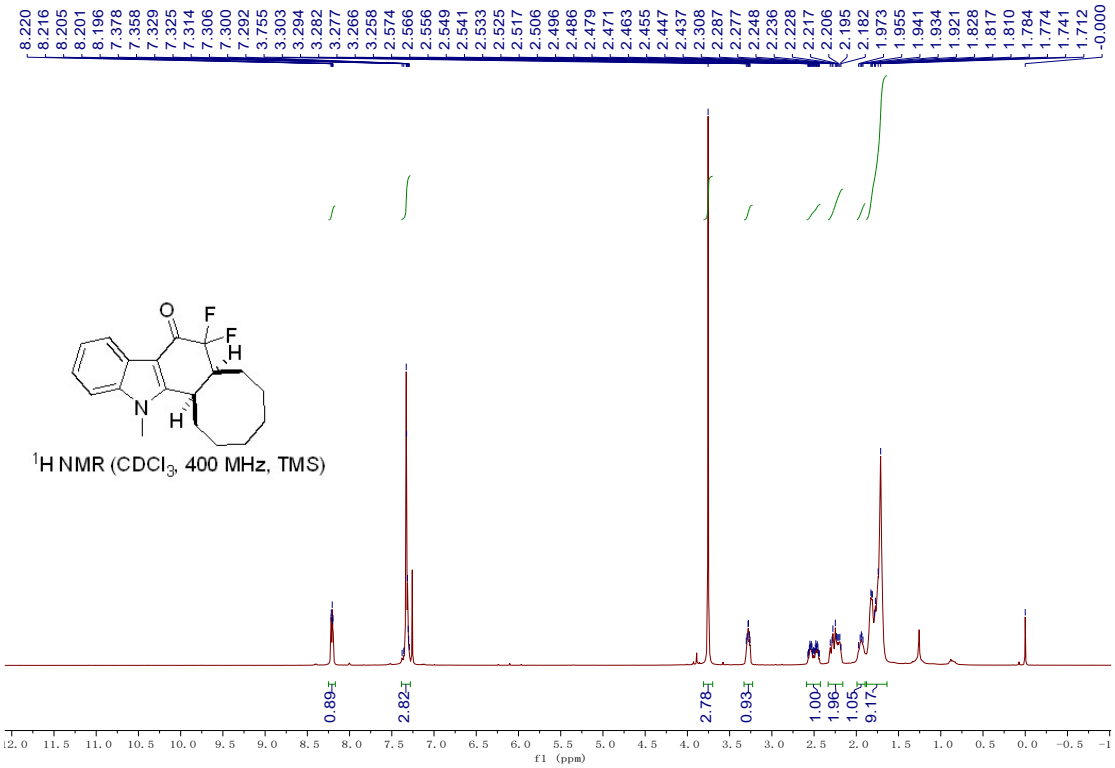


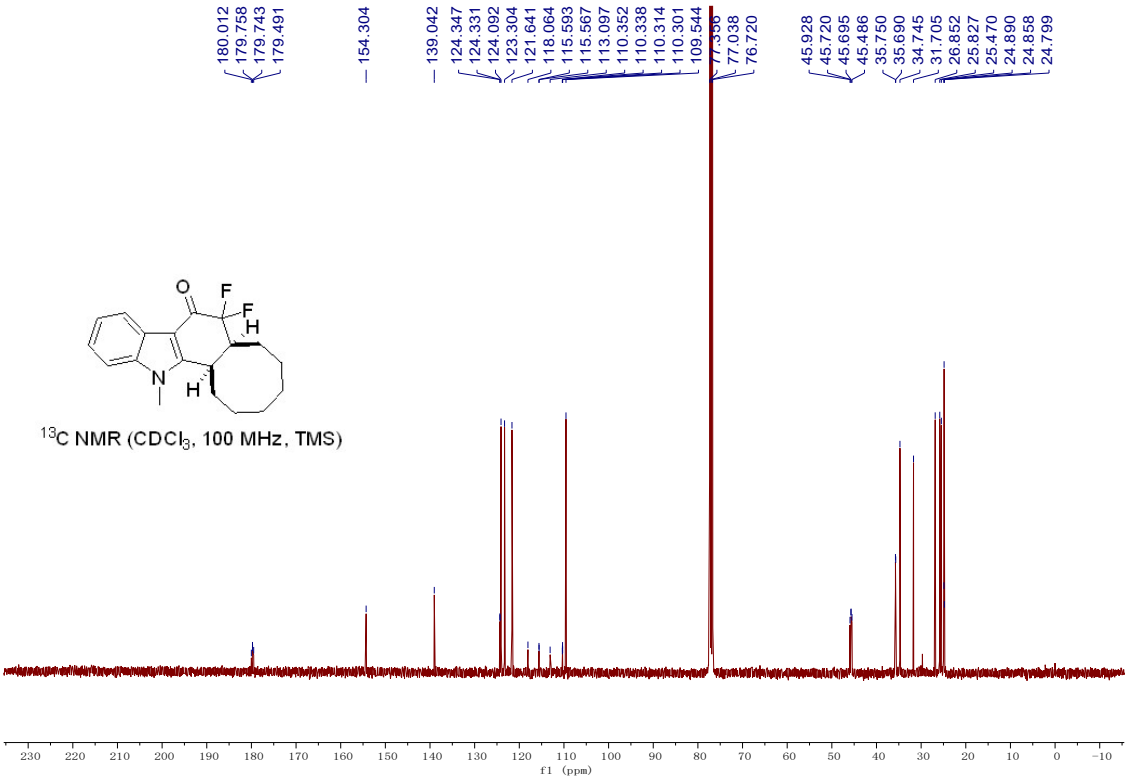
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)



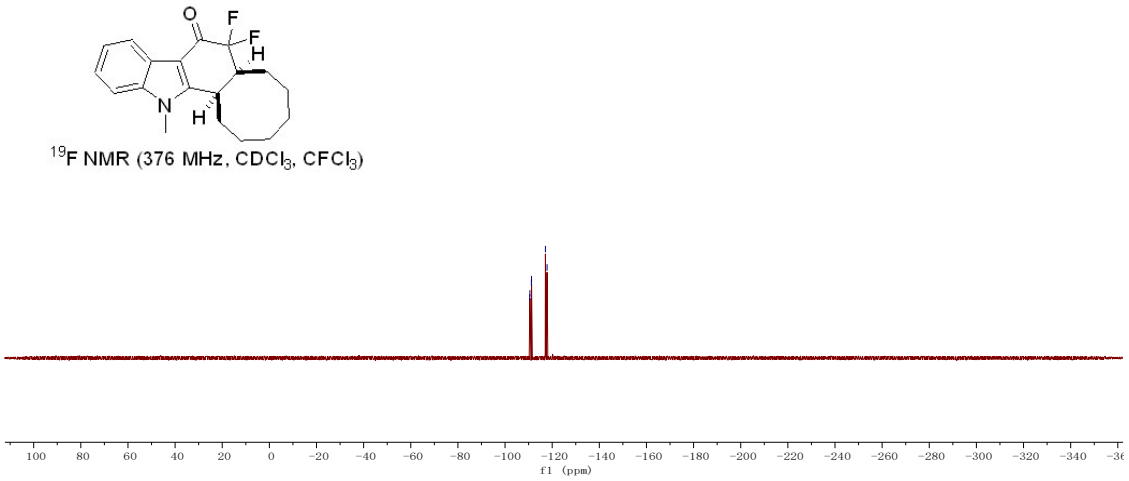
7,7-difluoro-13-methyl-1,2,3,4,5,6,6a,7,13,13b-decahydro-8H-cycloocta[a]carbazol-8-one (3an)

A white solid. 60.3 mg, 95% yield. M.P.: 236-238 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.71-1.83 (m, 9H), 1.92-1.97 (m, 1H), 2.18-2.31 (m, 2H), 2.44.2.57 (m, 1H), 3.26-3.30 (m,1H), 3.76 (s, 3H), 7.29-7.38 (m, 3H), 8.21-8.22 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 24.9 (t, J = 4.5 Hz), 25.5, 25.8, 26.9, 31.7, 34.7, 35.7 (d, J = 6.0 Hz), 45.7 (dd, J = 23.5, 20.9 Hz), 109.5, 110.3 (dd, J = 3.7, 1.3 Hz), 115.6 (dd, J = 249.7, 247.1 Hz), 121.6, 123.3, 124.1, 124.3 (d, J = 1.6 Hz), 139.0, 154.3, 179.7 (dd, J = 26.9, 25.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -117.5 (d, J = 264.9 Hz), -110.9 (dd, J = 264.9, 26.5 Hz). IR (neat) $\tilde{\nu}$ 2973, 2924, 2868, 1667, 1466, 1087, 1047, 880, 746 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{22}NOF_2$ (M+H): 318.1664, Found: 318.1669.

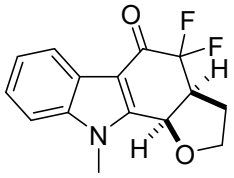




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

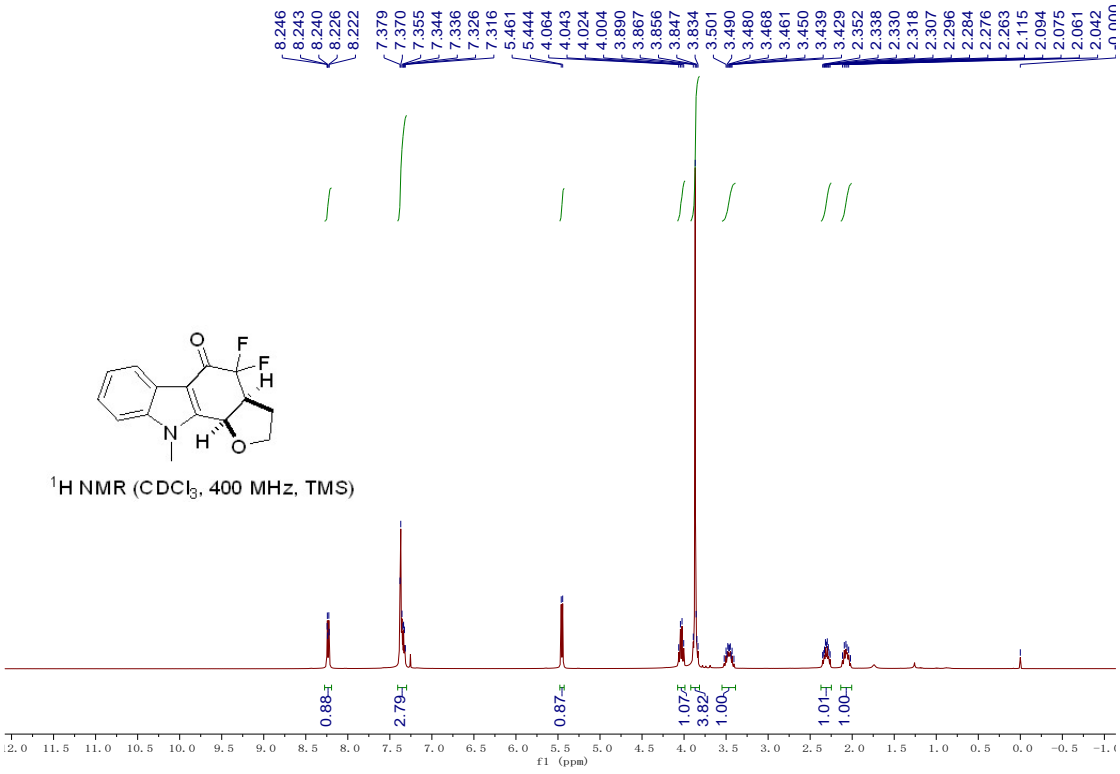


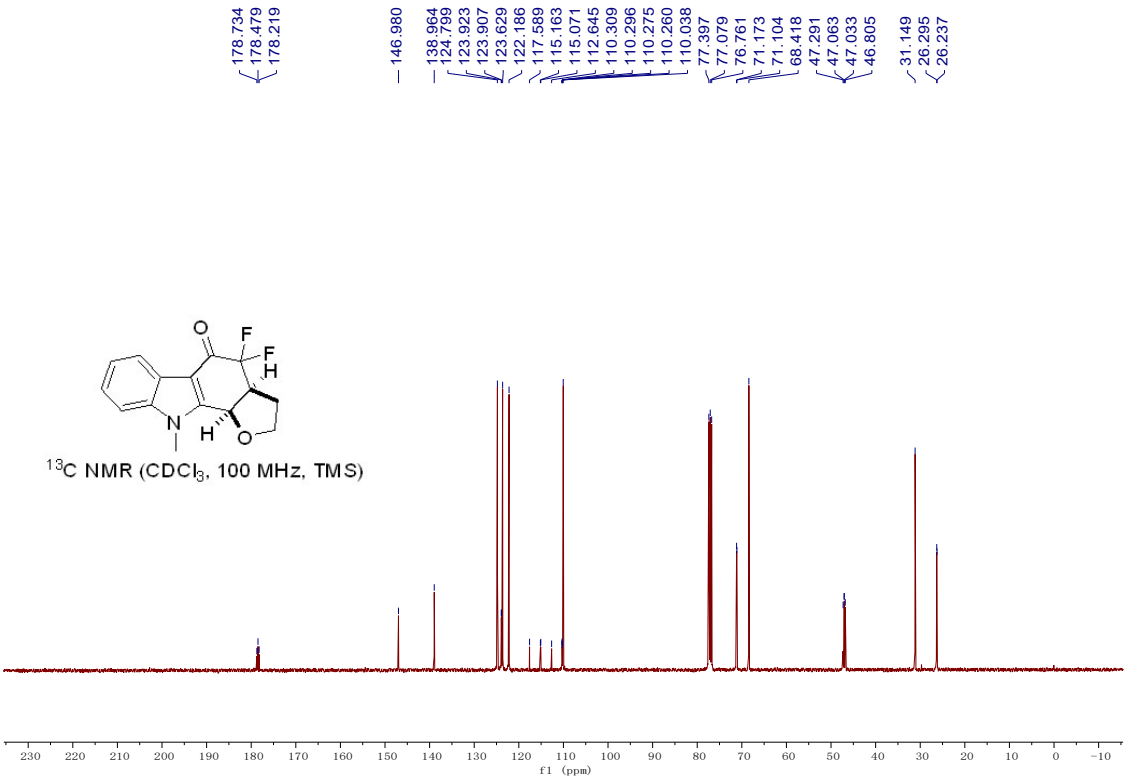
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



4,4-difluoro-10-methyl-2,3,3a,4,10,10b-hexahydro-5H-furo[2,3-a]carbazol-5-one (3ao)

A white solid. 54.3 mg, 98% yield. M.P.: 116-118 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.02-2.12 (m, 1H), 2.26-2.35 (m, 1H), 3.41-3.52 (m, 1H), 3.83-3.89 (m,1H), 3.87 (s, 3H), 4.03 (q, J = 8.0 Hz, 1H), 5.45 (d, J = 7.2 Hz, 1H), 7.32-7.38 (m, 3H), 8.22-8.25 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.3 (d, J = 5.8 Hz), 31.1, 47.1 (dd, J = 25.9, 23.0 Hz), 68.4, 71.1 (d, J = 7.0 Hz), 110.0, 110.3 (dd, J = 3.5, 1.4 Hz), 115.1 (dd, J = 253.4, 244.1 Hz), 122.2, 123.6, 123.9, 123.9 (d, J = 1.6 Hz), 124.8, 139.0, 147.0, 178.5 (t, J = 25.9 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -112.5 (dd, J = 277.8, 7.7 Hz), -95.3 (dd, J = 277.7, 12.3 Hz). IR (neat) $\tilde{\nu}$ 2950, 2894, 1677, 1667, 1480, 1452, 1401, 1212, 1064, 1028, 903, 782, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{14}NO_2F_2$ (M+H): 278.0987, Found: 278.0979.

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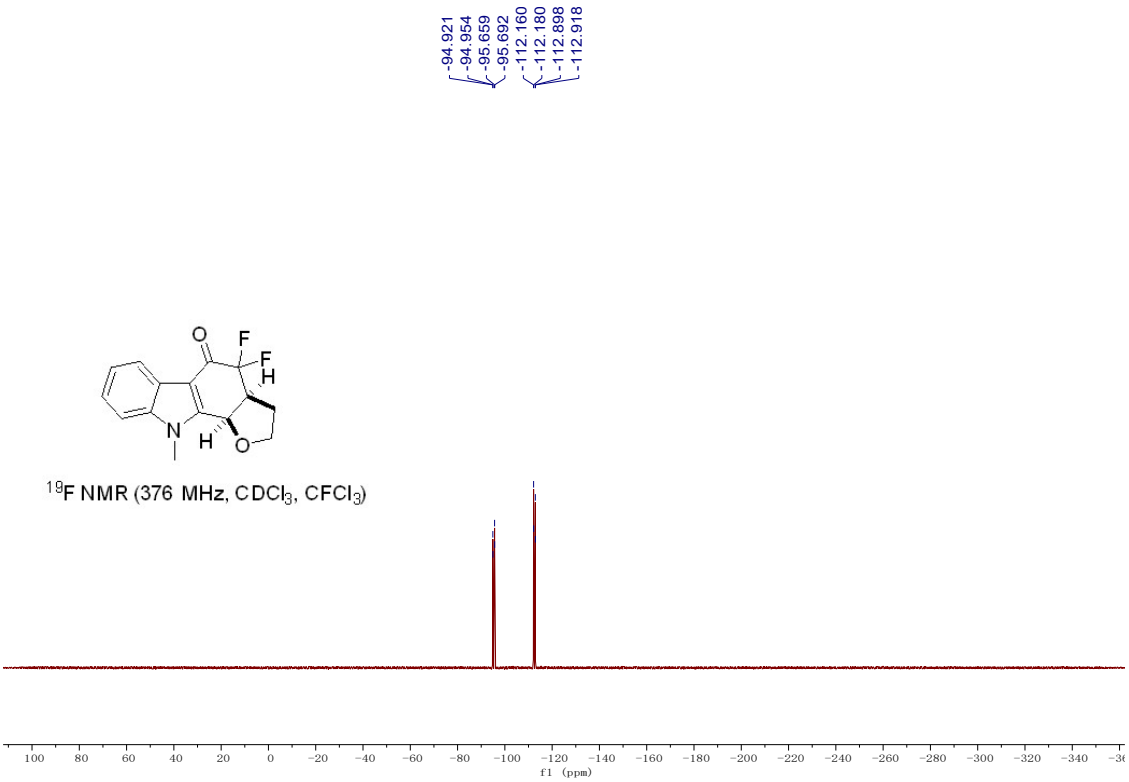
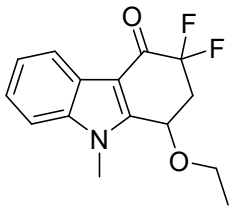
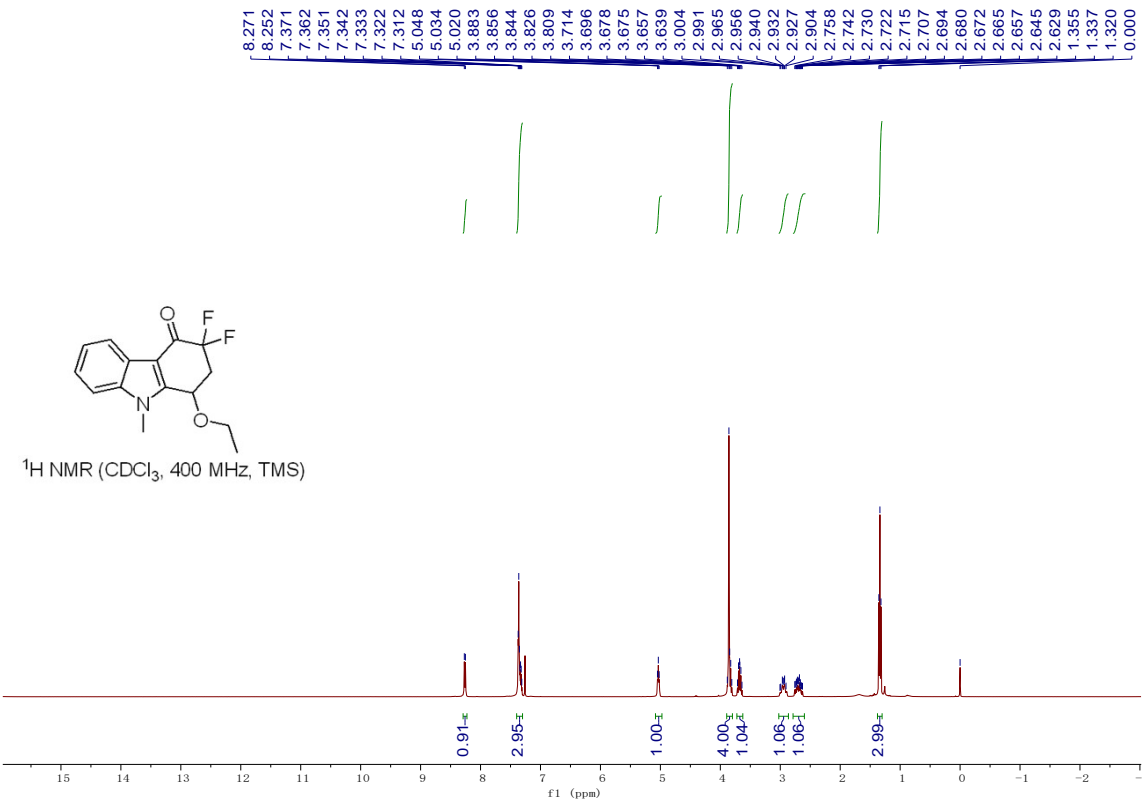
123.629
122.186
117.589
115.163
115.071
112.645
110.309
110.296
110.275
110.260
110.038
77.397
77.079
76.761
71.173
71.104
68.418
47.291
47.063
47.033
46.805
31.149
26.295
26.237
O
F
F
H
N
H
O
13C NMR (CDCl3, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

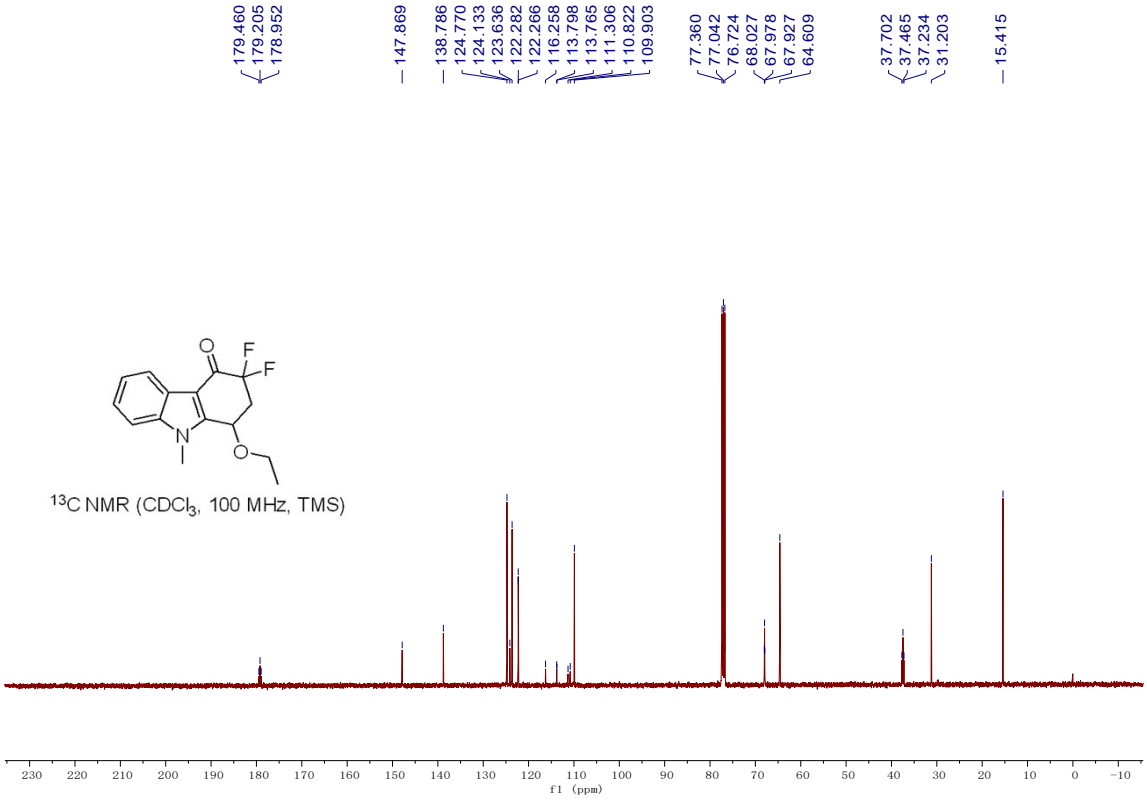

-94.921
-94.954
-95.659
-95.692
-112.160
-112.180
-112.898
-112.918
O
F
F
H
N
H
O
19F NMR (376 MHz, CDCl3, CFCl3)
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340
f1 (ppm)



1-ethoxy-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ap)

A white solid. 52.5 mg, 94% yield. M.P.: 106-108 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.34 (t, *J* = 7.2 Hz, 3H), 2.63-2.76 (m, 1H), 2.89-3.00 (m, 1H), 3.64-3.71 (m, 1H), 3.81-3.88 (m, 1H), 3.86 (s, 3H), 5.03 (t, *J* = 5.6 Hz, 1H), 7.31-7.37 (m, 3H), 8.26 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 31.2, 37.5 (t, *J* = 23.6 Hz), 64.6, 68.0 (t, *J* = 5.0, 5.0 Hz), 109.9, 110.8, 111.3, 113.8 (dd, *J* = 249.3, 246.0 Hz), 122.26, 122.3, 123.6, 124.1, 124.8, 138.8, 147.9, 179.2 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.4 (ddd, *J* = 277.9, 22.0, 9.5 Hz), -104.1 (ddd, *J* = 277.9, 17.2, 8.3 Hz). IR (neat) $\tilde{\nu}$ 2976, 2929, 2873, 1674, 1482, 1399, 1339, 1294, 1184, 1095, 1054, 867, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{16}NOF_2$ (M+H): 280.1144, Found: 280.1143.

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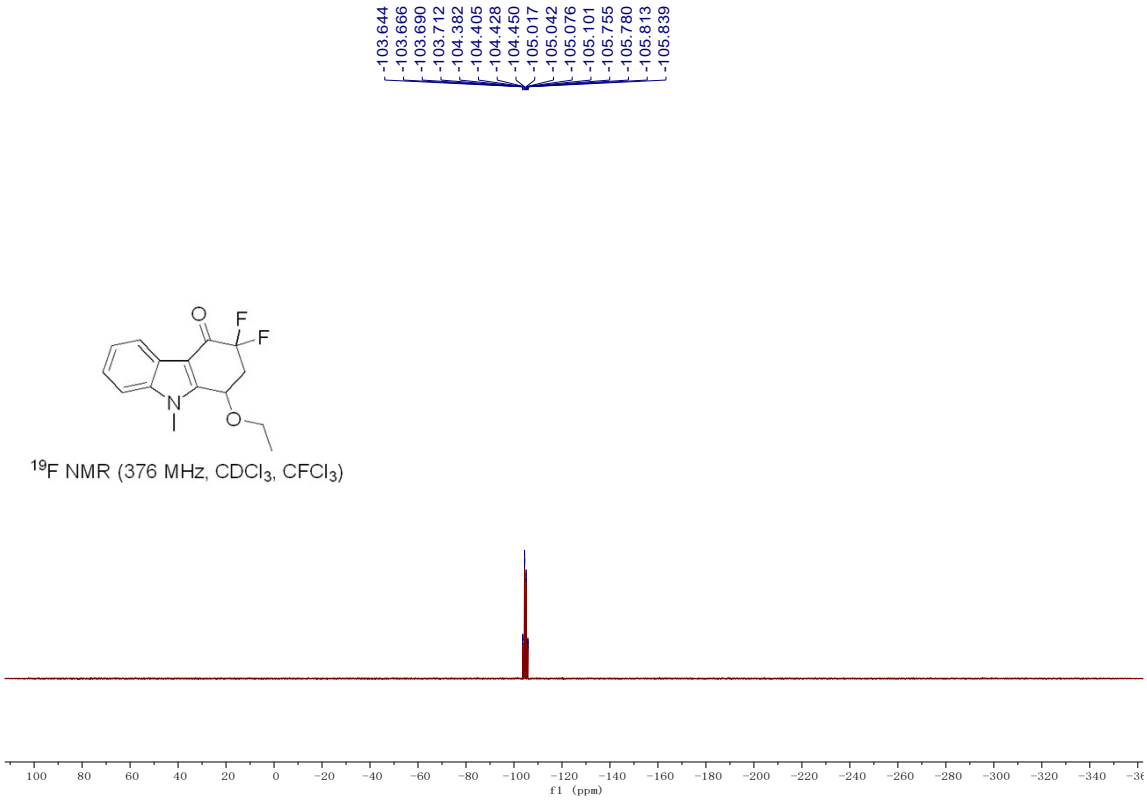
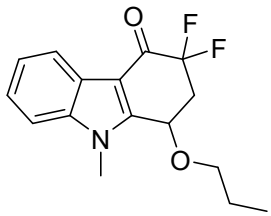
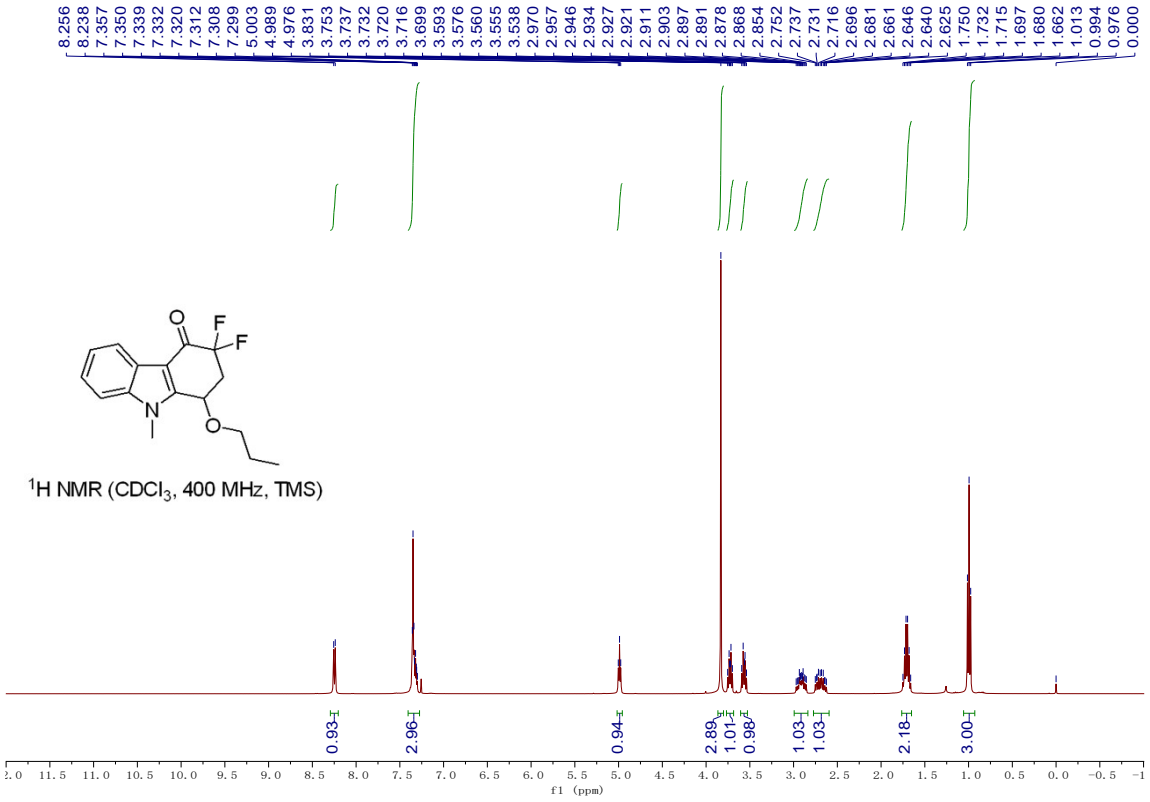
179.205
178.952
147.869
138.786
124.770
124.133
123.636
122.282
122.266
116.258
113.798
113.765
111.306
110.822
109.903
77.360
77.042
76.724
68.027
67.978
67.927
64.609
37.702
37.465
37.234
31.203
15.415
F
F
O
N
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

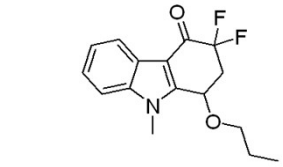

-103.644
-103.666
-103.690
-103.712
-104.382
-104.405
-104.428
-104.450
-105.017
-105.042
-105.076
-105.101
-105.755
-105.780
-105.813
-105.839
F
F
O
N
O
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



3,3-difluoro-9-methyl-1-propoxy-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aq)

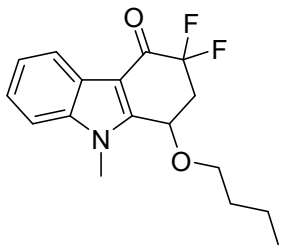
A white solid. 57.5 mg, 98% yield. M.P.: 112-114 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.66-1.75 (m, 2H), 2.63-2.75 (m, 1H), 2.85-2.97 (m, 1H), 3.54-3.59 (m, 1H), 3.70-3.75 (m, 1H), 3.83 (s, 1H), 4.99 (t, *J* = 5.6 Hz, 1H), 7.30-7.36 (m,3H), 8.25 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 10.7, 23.2, 31.2, 37.3 (dd, *J* = 23.6, 22.3 Hz), 68.0 (t, *J* = 5.5 Hz), 70.9, 109.9, 110.8 (t, *J* = 2.7 Hz), 113.8 (dd, *J* = 251.7, 246.6 Hz), 122.2, 123.6, 124.1, 124.8, 138.8, 148.0, 179.2 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.4 (ddd, *J* = 277.9, 22.0, 9.4 Hz), -104.3 (ddd, *J* = 277.9, 17.3, 8.3 Hz). IR (neat) $\tilde{\nu}$ 2977, 2923, 2868, 1654, 1482, 1405, 1327, 1187, 1116, 1098, 1060, 868, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{18}NOF_2$ (M+H): 294.1300, Found: 294.1308.





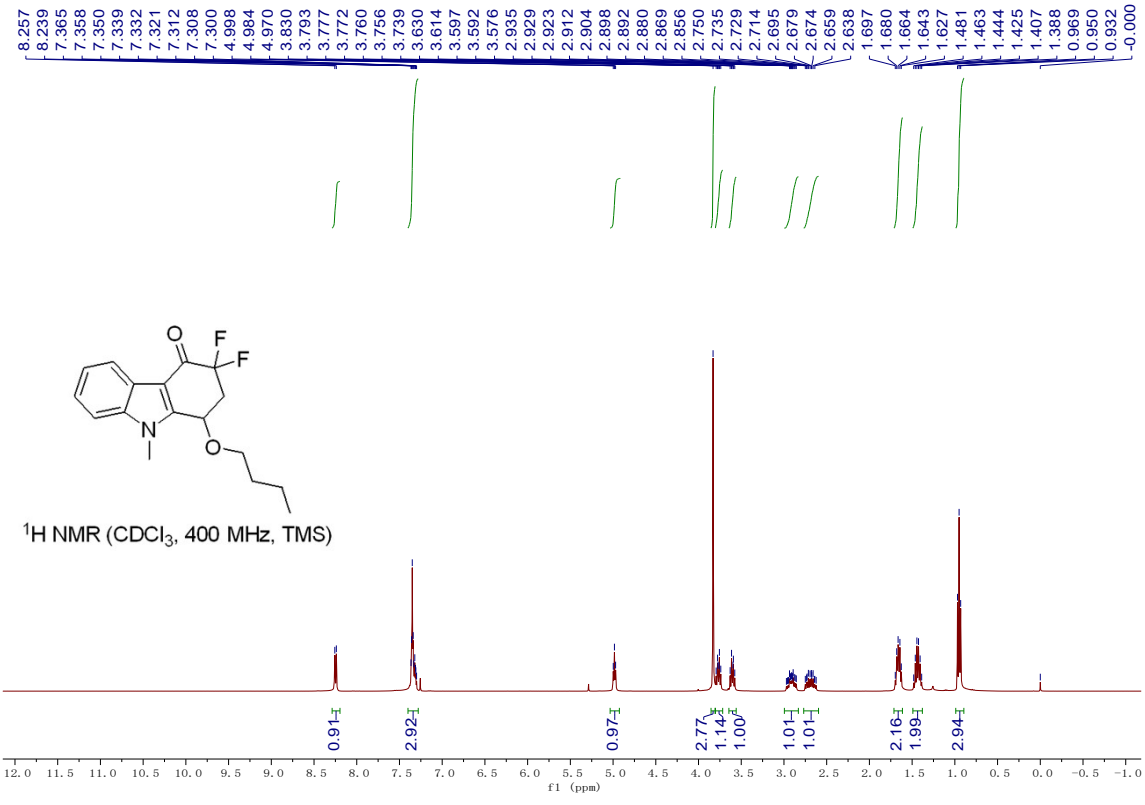
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

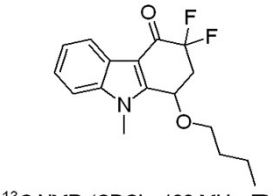
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



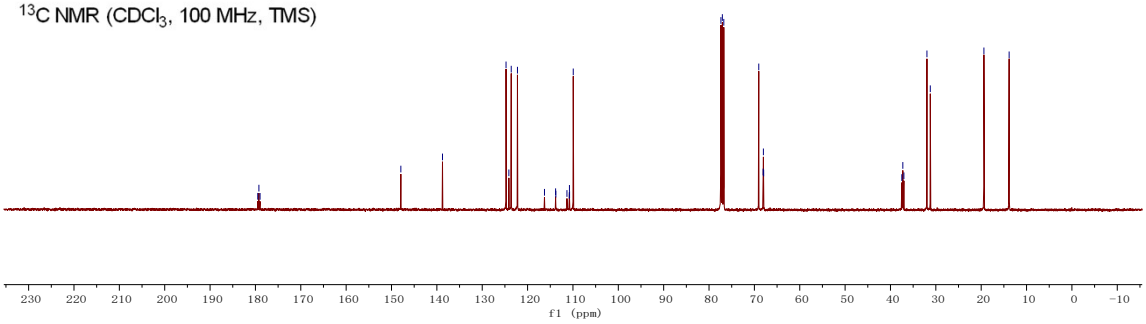
2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl4-(2-benzoylcyclopropyl)benzoate (3ar)

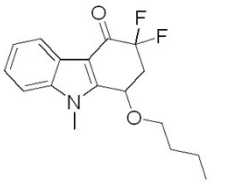
A white solid. 59.0 mg, 96% yield. M.P.: 98-100 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.95 (t, *J* = 7.4 Hz, 1H), 1.39-1.48 (m, 2H), 1.63-1.70 (m, 2H), 2.62-2.75 (m, 1H), 2.86-2.97 (m, 1H), 3.58-3.63 (m, 1H), 3.74-3.79 (m, 1H), 3.83 (s, 3H), 4.98 (t, *J* = 5.6 Hz, 1H), 7.30-7.37 (m, 3H), 8.25 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.8, 19.4, 31.2, 32.0, 37.3 (dd, *J* = 5.5, 5.5 Hz), 68.0 (t, *J* = 5.5, 5.5 Hz), 69.0, 109.9, 179.2 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.4 (ddd, *J* = 277.9, 22.0, 9.5 Hz), -104.1 (ddd, *J* = 277.9, 17.2, 8.3 Hz). IR (neat) $\tilde{\nu}$ 2971, 2928, 2873, 1672, 1482, 1457, 1329, 1185, 1090, 1047, 880, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{20}NO_2F_2$ (M+H): 308.1457, Found: 308.1458.



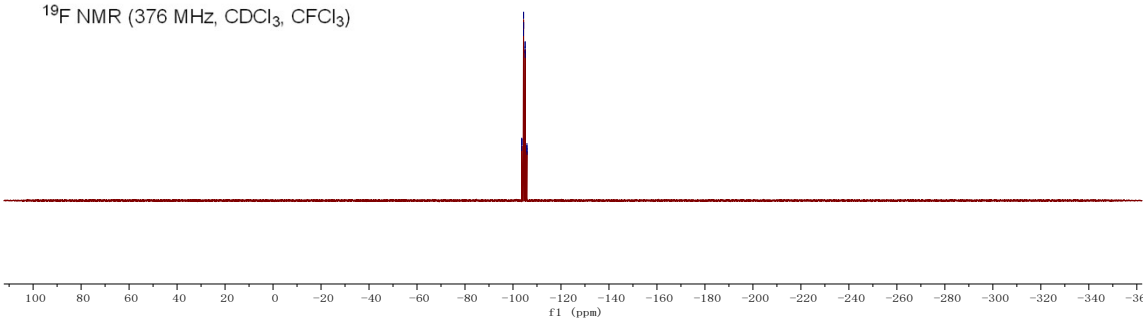


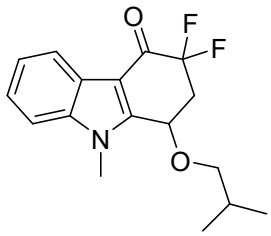
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





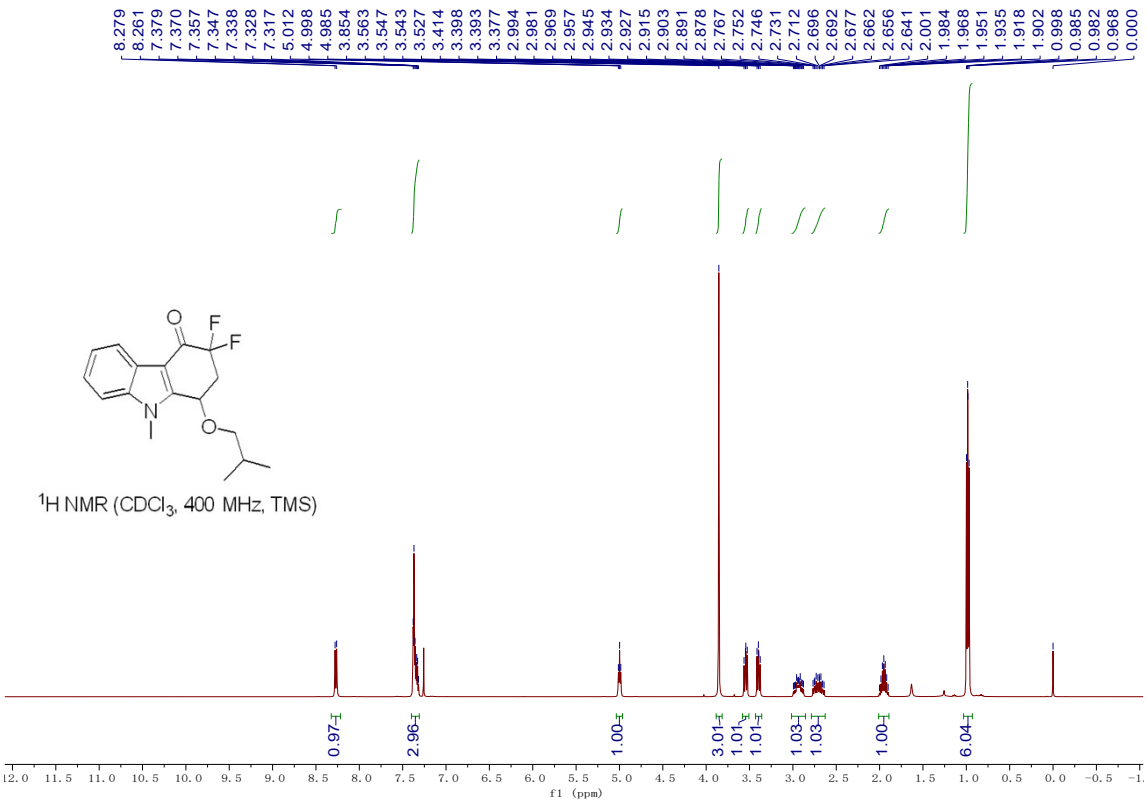
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

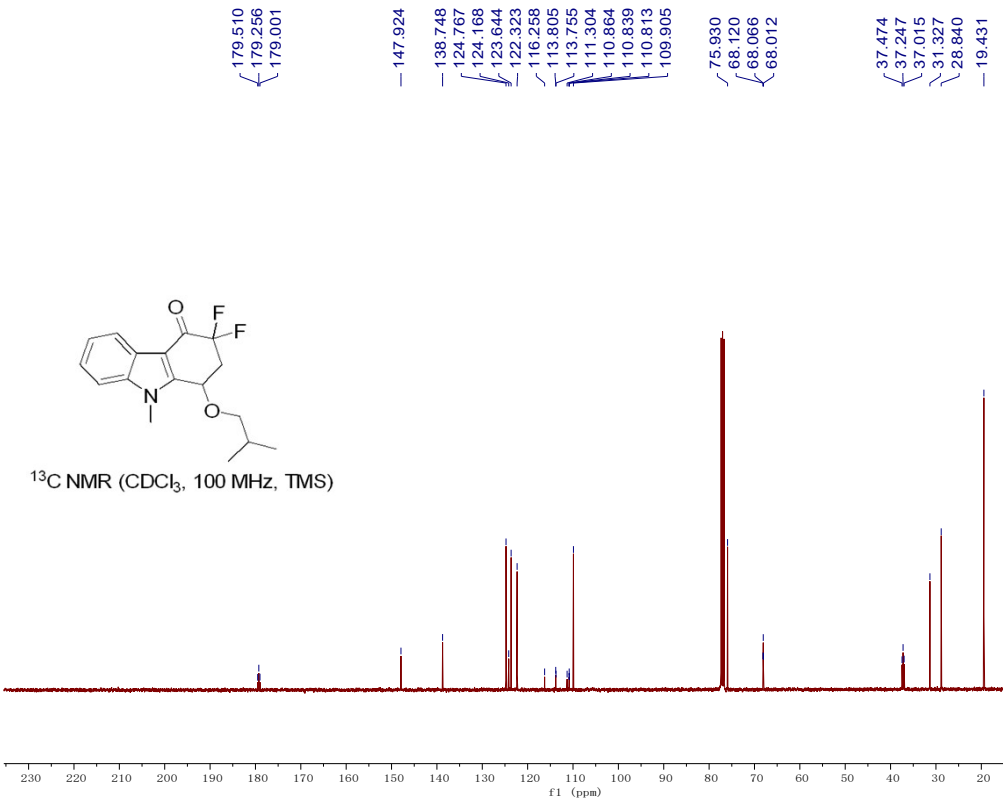




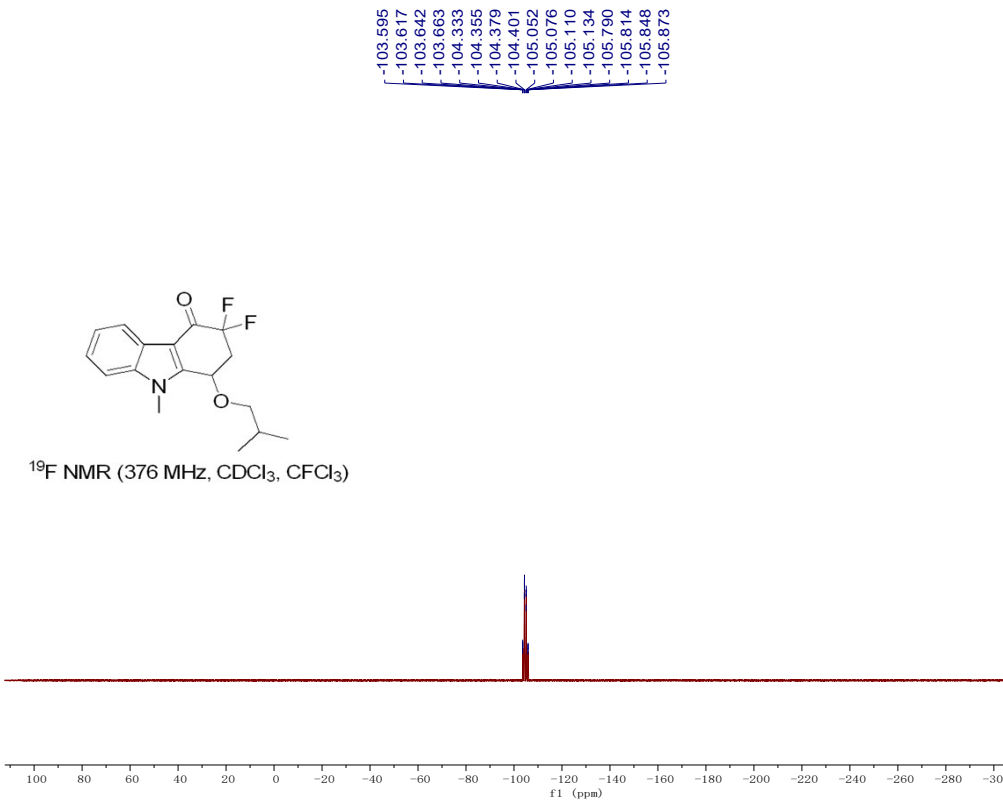
3,3-difluoro-1-isobutoxy-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3as)

A white solid. 60.2 mg, 98% yield. M.P.: 101-103 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.97 (d, *J* = 5.6 Hz, 3H), 0.99 (d, *J* = 5.2 Hz, 3H), 1.90-2.00 (m, 1H), 2.64-2.77 (m, 1H), 2.88-2.99 (m, 1H), 3.40 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.54 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.85 (s, 3H), 5.00 (t, *J* = 5.6 Hz, 1H), 7.32-7.38 (m, 3H), 8.27 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.4, 28.8, 31.3, 37.2 (dd, *J* = 23.2, 22.7 Hz), 68.1 (t, *J* = 5.4 Hz), 109.9, 110.8 (t, *J* = 2.6 Hz), 113.8 (dd, *J* = 251.7, 246.7 Hz), 122.3, 123.6, 124.2, 124.8, 138.7, 147.9, 179.0, 179.3 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.5 (ddd, *J* = 277.8, 21.8, 9.1 Hz), -104.0 (ddd, *J* = 277.8, 17.4, 8.1 Hz). IR (neat) $\tilde{\nu}$ 2964, 2924, 2855, 1655, 1483, 1404, 1326, 1186, 1117, 1098, 1062, 1050, 867, 748, 736 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{20}NO_2F_2$ (M+H): 308.1457, Found: 308.1463.

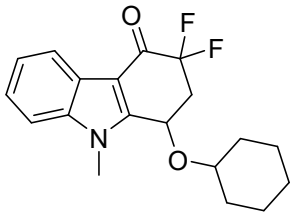




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

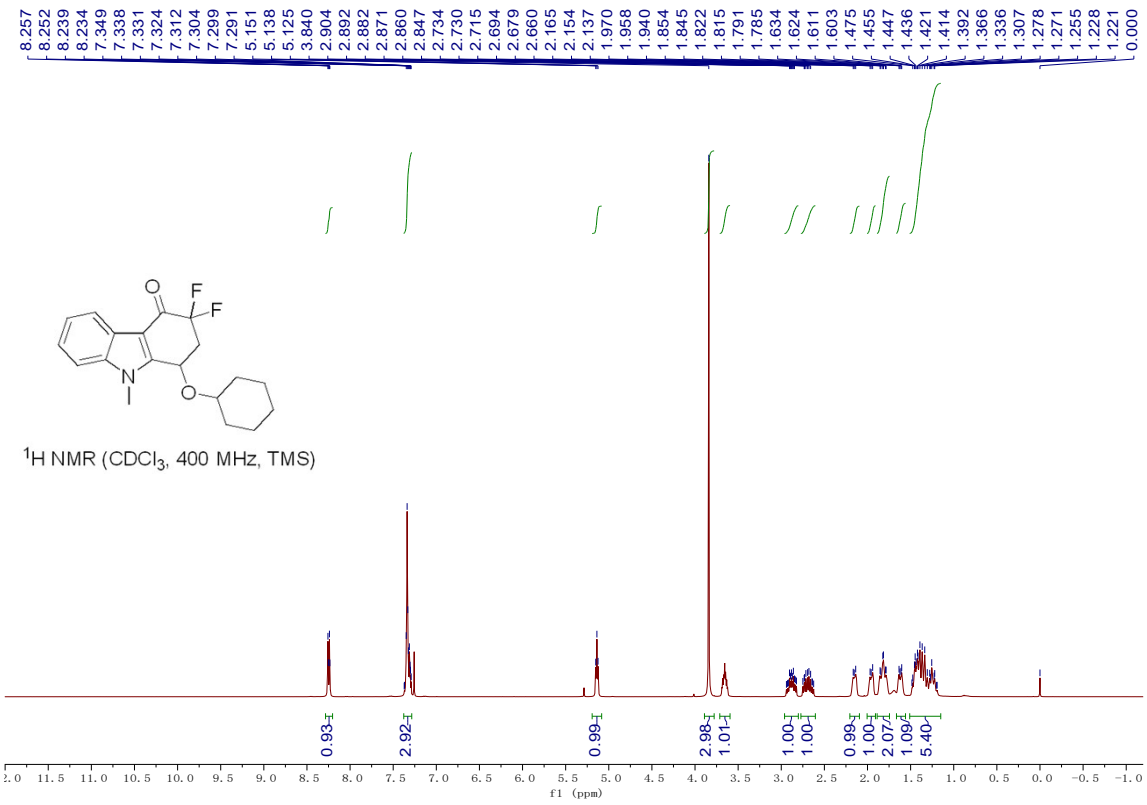


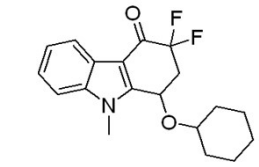
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



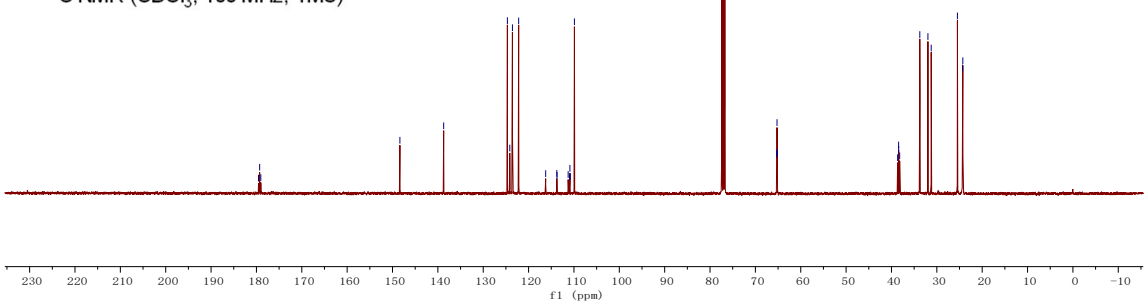
1-(cyclohexyloxy)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3at)

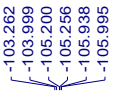
A brown oil. 65.3 mg, 98% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.19-1.49 (m, 5H), 1.60-1.63 (m, 1H), 1.79-1.85 (m, 2H), 1.94-1.97 (m, 1H), 2.14-2.17 (m, 1H), 2.62-2.75 (m, 1H), 2.82-2.94 (m,1H), 3.62-3.69 (m, 1H), 3.84 (s, 3H), 5.14 (t, J = 5.2 Hz, 1H), 7.29 – 7.37 (m, 3H), 8.23-8.26 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 24.3 (d, J = 6.4 Hz), 25.5, 31.2, 32.0, 33.8, 38.4 (dd, J = 23.2, 22.9 Hz), 65.2 (t, J = 5.5, 5.5 Hz), 109.9, 110.9 (t, J = 2.6, 2.6 Hz), 113.8 (dd, J = 252.0, 246.3 Hz), 122.2, 123.6, 124.1, 124.7, 138.7, 148.4, 179.3 (t, J = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -102.6 (dd, J = 277.5, 21.1 Hz), -103.6 (d, J = 277.1 Hz). IR (neat) $\tilde{\nu}$ 2932, 2857, 1670, 1481, 1451, 1331, 1294, 1183, 1128, 1090, 1052, 867, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{22}NO_2F_2$ (M+H): 334.1613, Found: 334.1616.

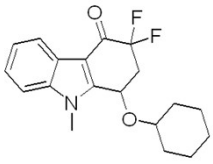




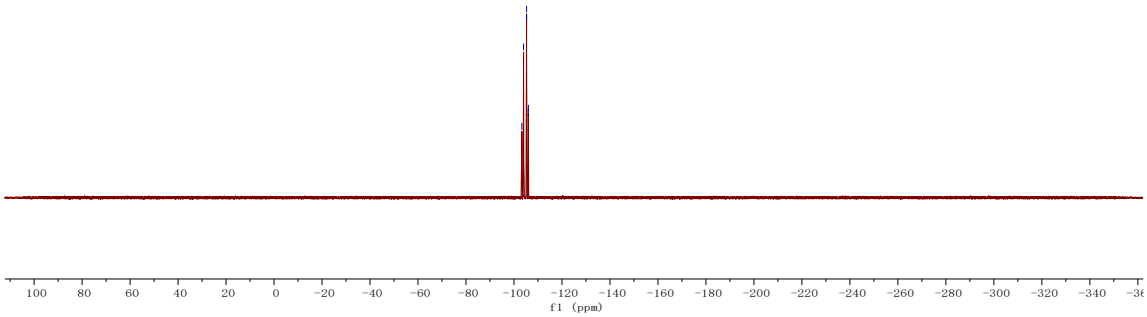
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

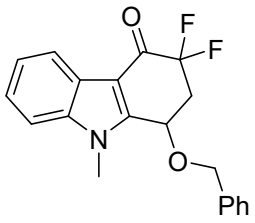






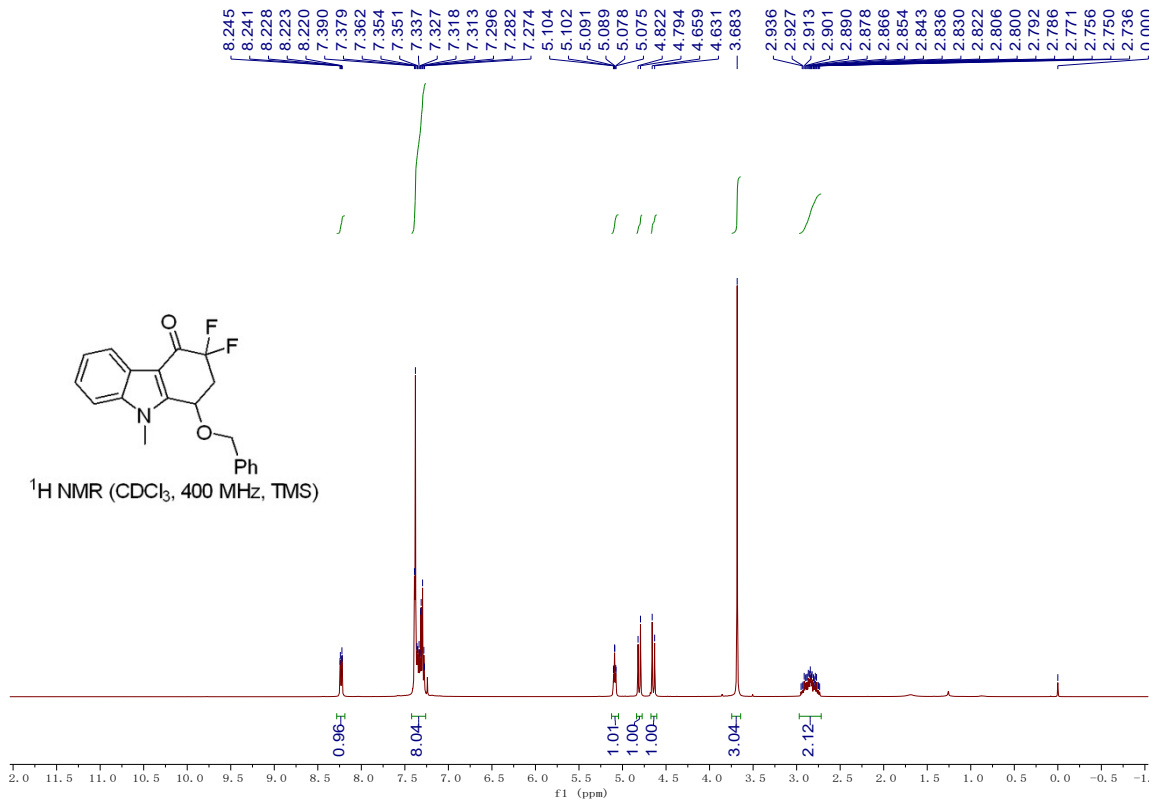
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

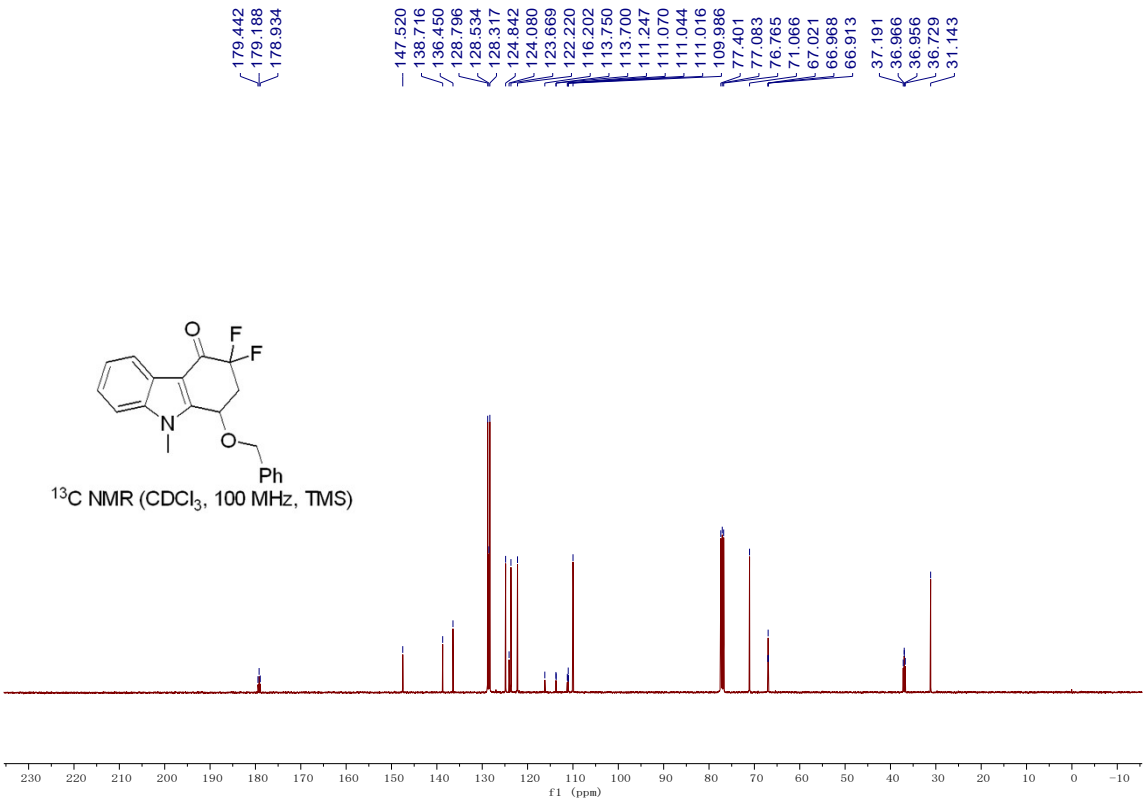




1-(benzyloxy)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3au)

A white solid. 66.9 mg, 98% yield. M.P.: 120-122 °C. 47.5 mg, 98% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.74-2.95 (m, 2H), 3.68 (s, 3H), 4.65 (d, J = 11.2 Hz, 1H), 4.81 (d, J = 11.2 Hz, 1H), 5.09 (td, J = 5.2, 0.8 Hz, 1H), 7.27-7.39 (m, 8H), 8.22-8.25 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 37.0 (dd, J = 23.5, 22.5 Hz), 67.0 (t, J = 5.5, 5.5 Hz), 71.1, 110.0, 111.0 (t, J = 2.7, 2.7 Hz), 113.7 (dd, J = 251.8, 246.8 Hz), 122.2, 123.7, 124.1, 124.8, 128.3, 128.5, 128.8, 136.5, 138.7, 147.5, 179.19 (t, J = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.6 (ddd, J = 278.6, 19.9, 9.0 Hz), -102.9 (ddd, J = 278.5, 18.5, 8.2 Hz). IR (neat) $\tilde{\nu}$ 2926, 2884, 1678, 1669, 1482, 1455, 1408, 1297, 1186, 1090, 1061, 1009, 866, 750, 734 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{18}NO_2F_2$ (M+H): 342.1300, Found: 342.1293.

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116.202
113.750
113.700
111.247
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111.016
109.986
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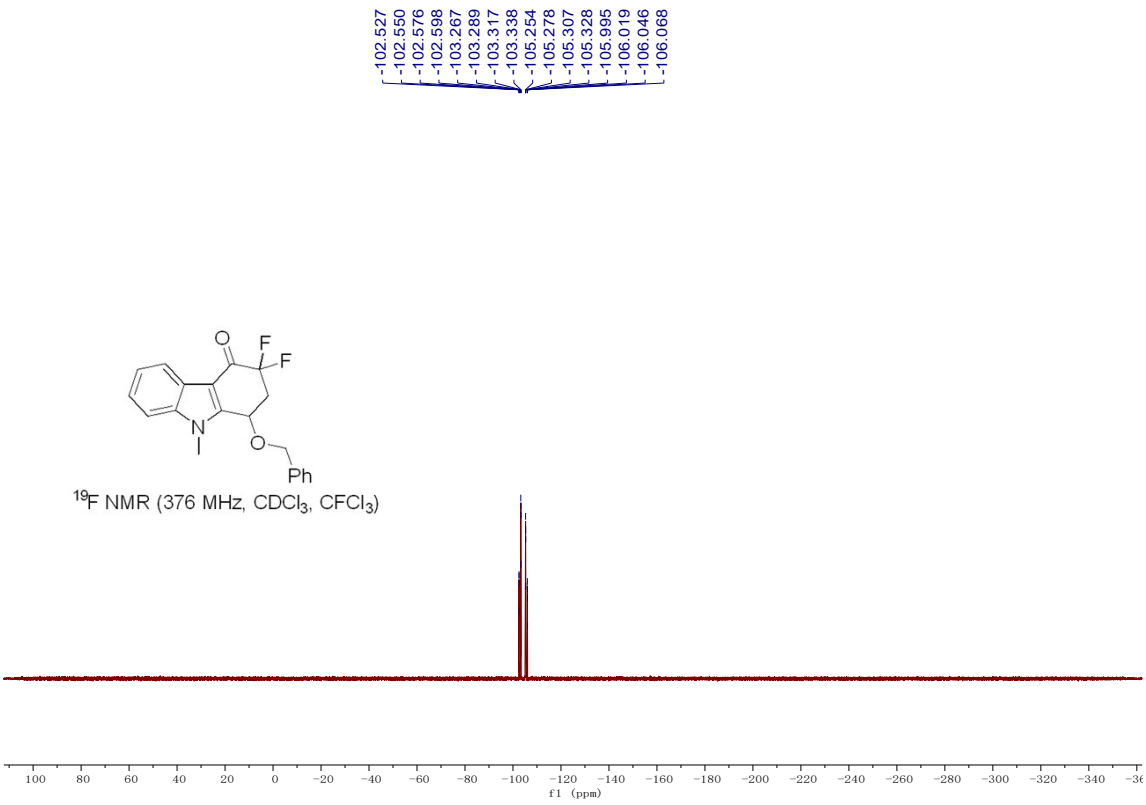
77.083
76.765
71.066
67.021
66.968
66.913
37.191
36.966
36.956
36.729
31.143
F
F
O
N
O
Ph
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)


-102.527
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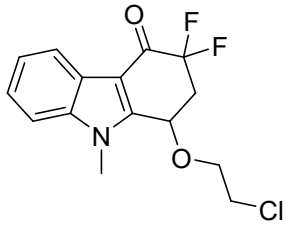
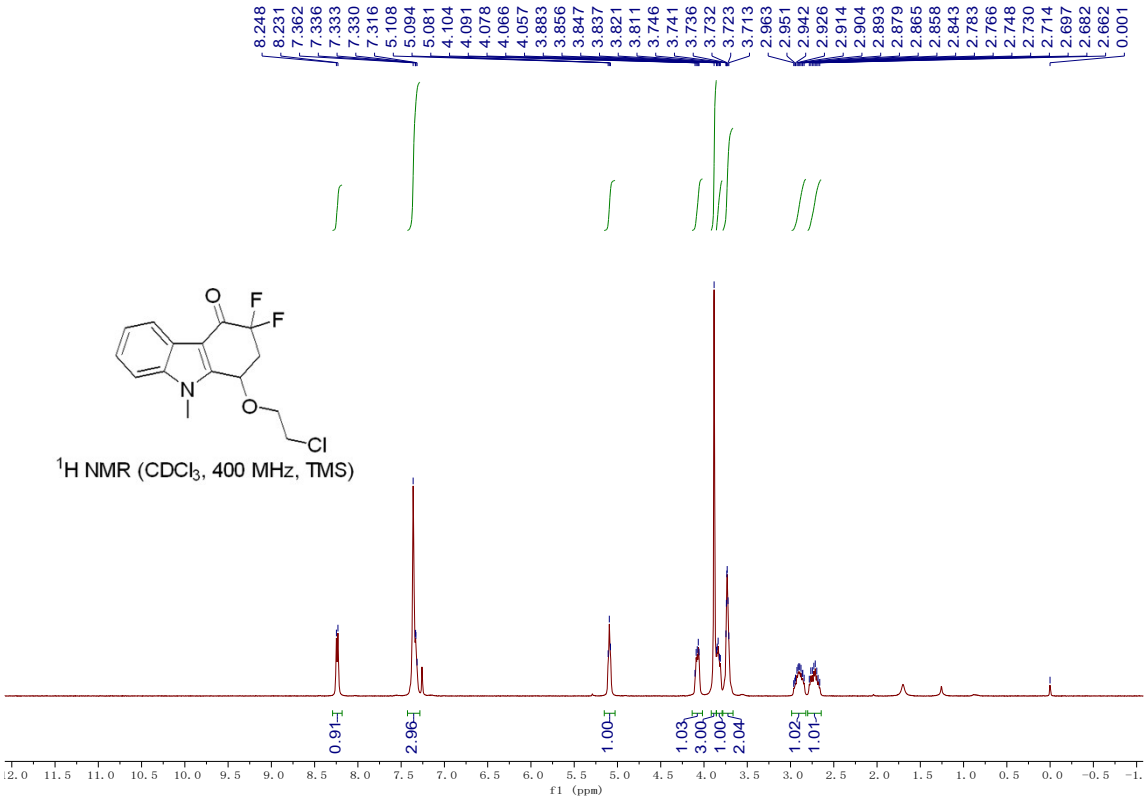
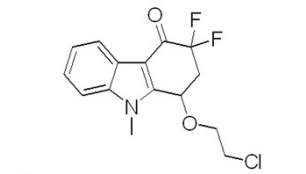
-102.576
-102.598
-103.267
-103.289
-103.317
-103.338
-105.254
-105.278
-105.307
-105.328
-105.995
-106.019
-106.046
-106.068
F
F
O
N
O
Ph
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



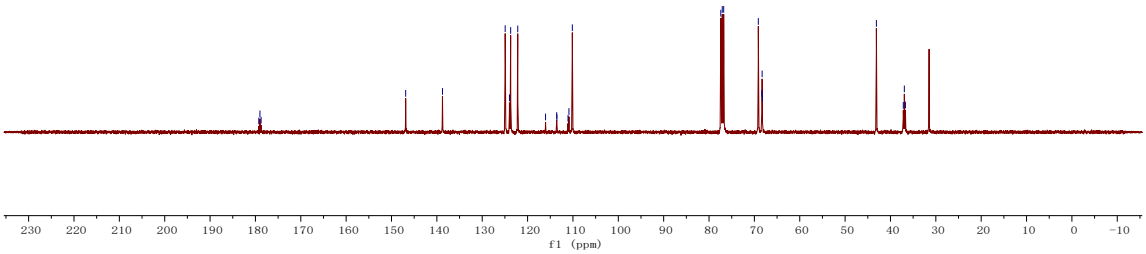
1-(2-chloroethoxy)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3av)

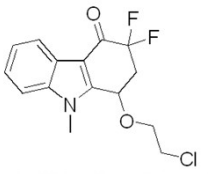
A white solid. 59.6 mg, 95% yield. M.P.: 122-124 °C. 50.2 mg, 97% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.66-2.78 (m, 1H), 2.84-2.96 (m, 1H), 3.71-3.75 (m, 2H), 3.81-3.86 (m, 1H), 3.88 (s, 3H), 4.06-4.10 (m, 1H), 5.09 (t, *J* = 5.6 Hz, 1H), 7.32-7.36 (m, 3H), 8.24 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.5, 36.9 (t, *J* = 23.4, 23.4 Hz), 43.1, 68.3 (t, *J* = 5.4 Hz), 69.1, 110.1, 110.9 (t, *J* = 2.5 Hz), 113.6 (dd, *J* = 251.6, 246.8 Hz), 122.2, 123.7, 124.0, 124.9, 138.8, 146.9, 179.0 (t, *J* = 25.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.8 (ddd, *J* = 278.9, 20.9, 8.6 Hz), -103.3 (ddd, *J* = 278.8, 19.1, 7.6 Hz). IR (neat) $\tilde{\nu}$ 2942, 2876 1663, 1478, 1462, 1395, 1323, 1888, 1128, 1106, 1084, 1054, 1010, 948, 885, 863, 751, 735, 656 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{15}NO_2F_2Cl$ (M+H): 314.0754, Found: 314.0759.



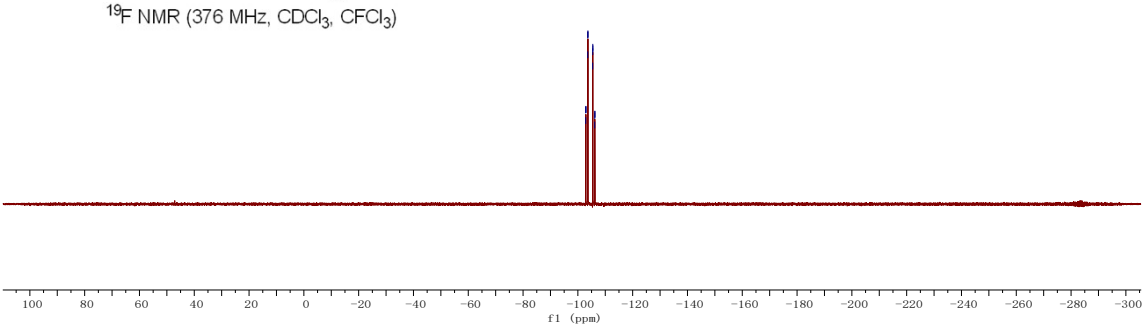


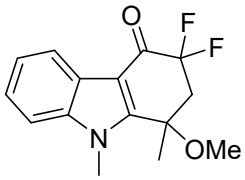
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





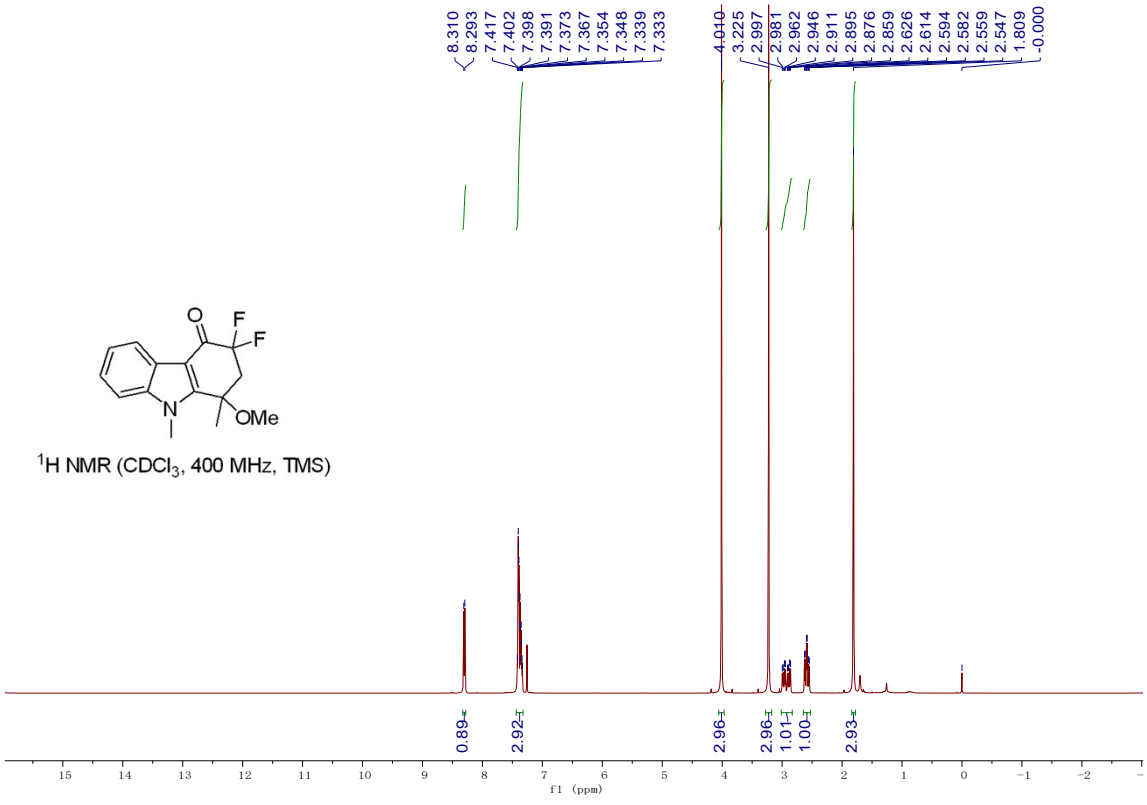
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

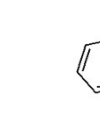




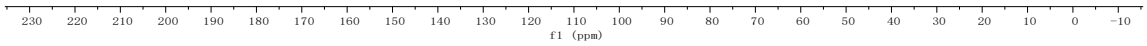
3,3-difluoro-1-methoxy-1,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aw)

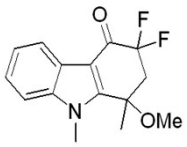
A white solid. 54.7 mg, 98% yield. M.P.: 119-121 °C. 58.2 mg, 96% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.81 (s, 3H), 2.59 (td, *J* = 12.8, 4.8 Hz, 1H), 2.86-3.00 (m, 1H), 3.22 (s, 3H), 4.01 (s, 3H), 7.33 – 7.42 (m, 3H), 8.30 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.3, 31.3, 42.2 (dd, *J* = 23.8, 21.5 Hz), 51.1, 74.0 (dd, *J* = 11.6, 1.6 Hz), 109.9, 111.4 (dd, *J* = 4.1, 1.5 Hz), 114.0 (dd, *J* = 251.0, 245.8 Hz), 122.3, 123.8, 124.4 (d, *J* = 2.0 Hz), 124.9, 139.0, 150.8, 179.2 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.9 (d, *J* = 279.4 Hz), -97.5 (ddd, *J* = 279.2, 34.5, 12.5 Hz). IR (neat) $\tilde{\nu}$ 2973, 2930, 2882, 1451, 1379, 1088, 1046, 880 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{15}NO_2F_2Na$ (M+Na): 302.0969, Found: 302.0962.



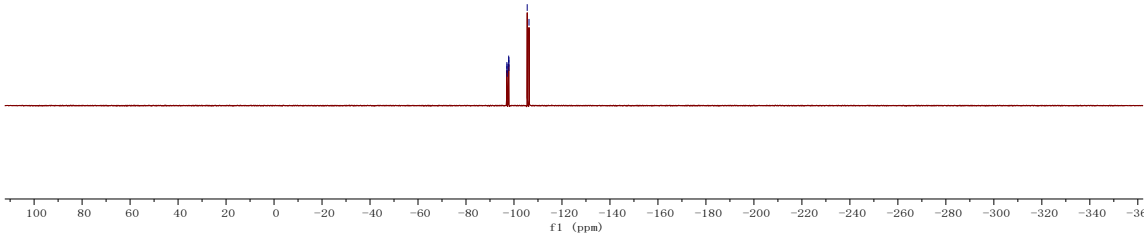


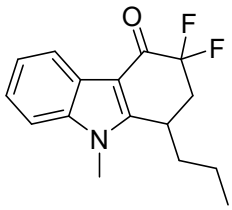
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





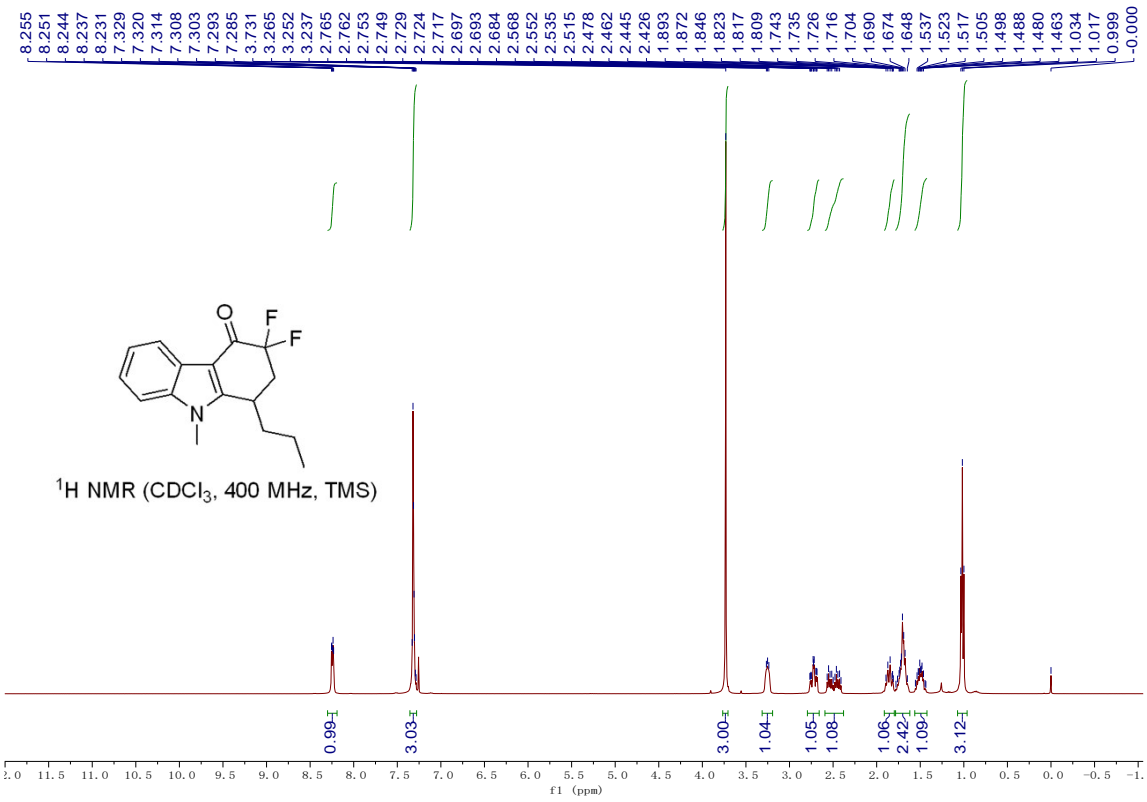
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

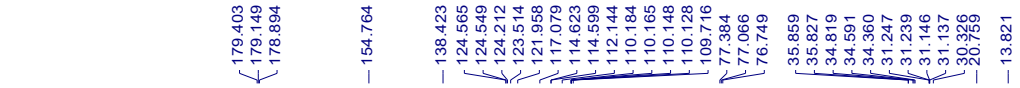


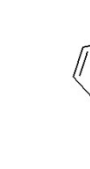


3,3-difluoro-9-methyl-1-propyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ax)

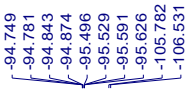
A white solid. 54.4 mg, 98% yield. M.P.: 90-92 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.02 (t, *J* = 7.0 Hz, 3H), 1.44-1.56 (m, 1H), 1.65-1.78 (m, 2H), 1.81-1.89 (m, 1H), 2.41-2.57 (m, 1H), 2.68-2.77 (m, 1H), 3.26 (t, *J* = 5.6 Hz, 1H), 3.73 (s, 3H), 7.29-7.33 (m, 3H), 8.23-8.26 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.8, 20.8, 30.3, 31.2 (dd, *J* = 10.1, 0.8 Hz), 34.6 (t, *J* = 23.1, 23.1 Hz), 35.8 (d, *J* = 3.2 Hz), 109.7, 110.2 (dd, *J* = 3.7, 2.0 Hz), 114.6 (dd, *J* = 249.4, 247.0 Hz), 122.0, 123.5, 124.2, 124.5, 124.6 (d, *J* = 1.6 Hz), 138.4, 154.8, 179.2 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.2 (d, *J* = 282.0 Hz), -95.2 (ddd, *J* = 283.0, 35.8, 12.4 Hz). IR (neat) $\tilde{\nu}$ 2972, 2920, 2879, 1660, 1456, 1406, 1088, 1046, 880, 754 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NOF_2Na$ (M+Na): 300.1176, Found: 300.1184.

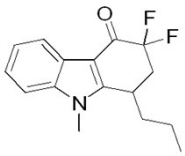




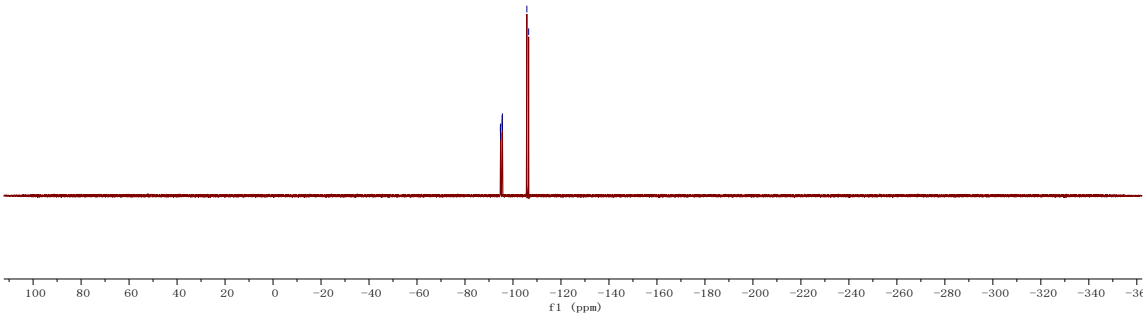


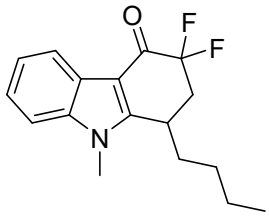
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





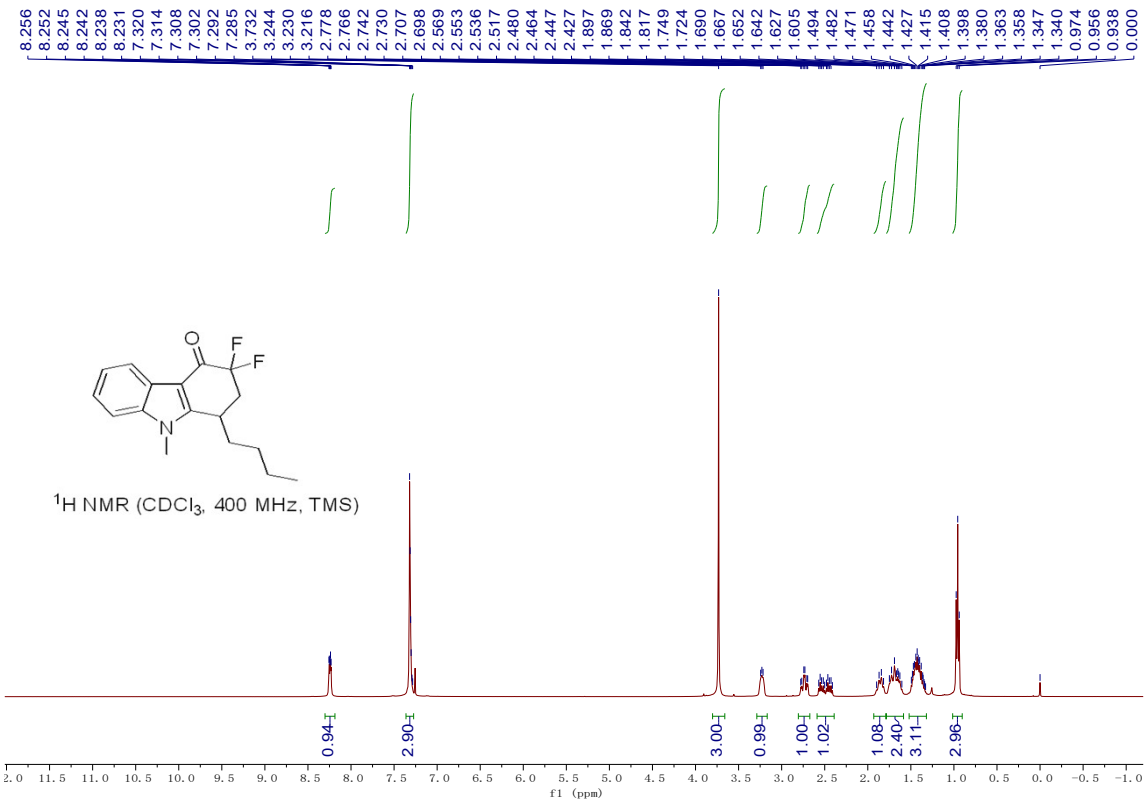
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

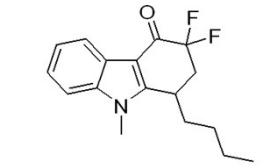




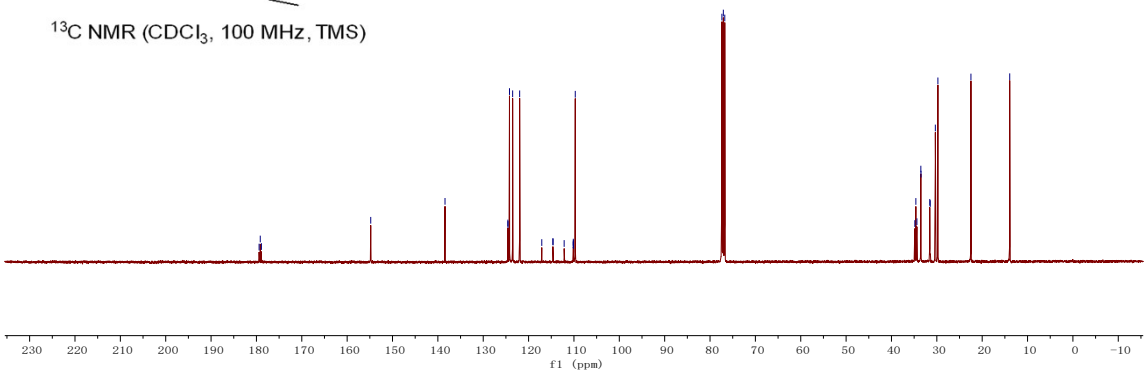
1-butyl-3,3-difluoro-9-methyl-3,9-dihydro-4H-carbazol-4-one (3ay)

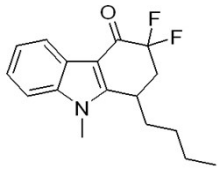
A white solid. 57.1 mg, 98% yield. M.P.: 121-123 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.33-1.49 (m, 3H), 1.61-1.75 (m, 2H), 1.82-1.90 (m, 1H), 2.41-2.57 (m, 1H), 2.70-2.78 (m, 1H), 3.23 (t, *J* = 5.6 Hz, 1H), 3.73 (s, 3H), 7.29-7.32 (m, 3H), 8.23-8.26 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.9, 22.5, 29.8, 30.3, 31.5 (d, *J* = 10.2 Hz), 33.5 (d, *J* = 3.2 Hz), 34.6 (t, *J* = 23.1 Hz), 109.7, 110.1 (dd, *J* = 3.7, 1.9 Hz), 114.6 (dd, *J* = 249.4, 247.1 Hz), 122.0, 123.5, 124.2, 124.6 (d, *J* = 1.6 Hz), 138.4, 154.8, 179.2 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.0 (d, *J* = 281.1 Hz), -95.1 (ddd, *J* = 280.1, 18.0, 13.5 Hz). IR (neat) $\tilde{\nu}$ 2973, 2933, 2880, 1455, 1380, 1088, 1046, 880 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{19}NOF_2Na$ (M+Na): 314.1332, Found: 314.1355.



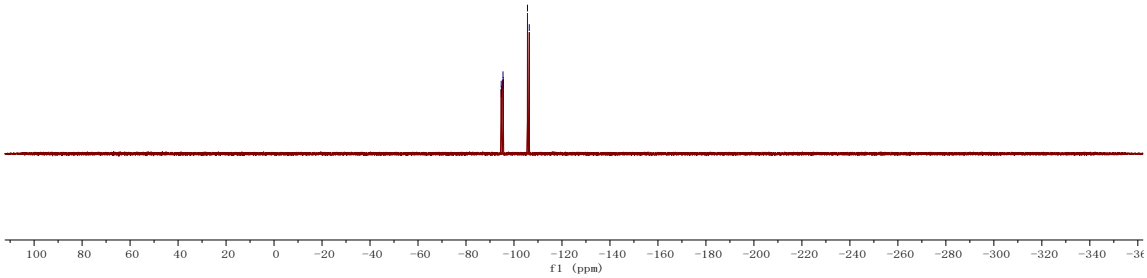


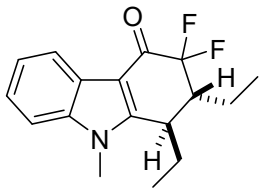
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





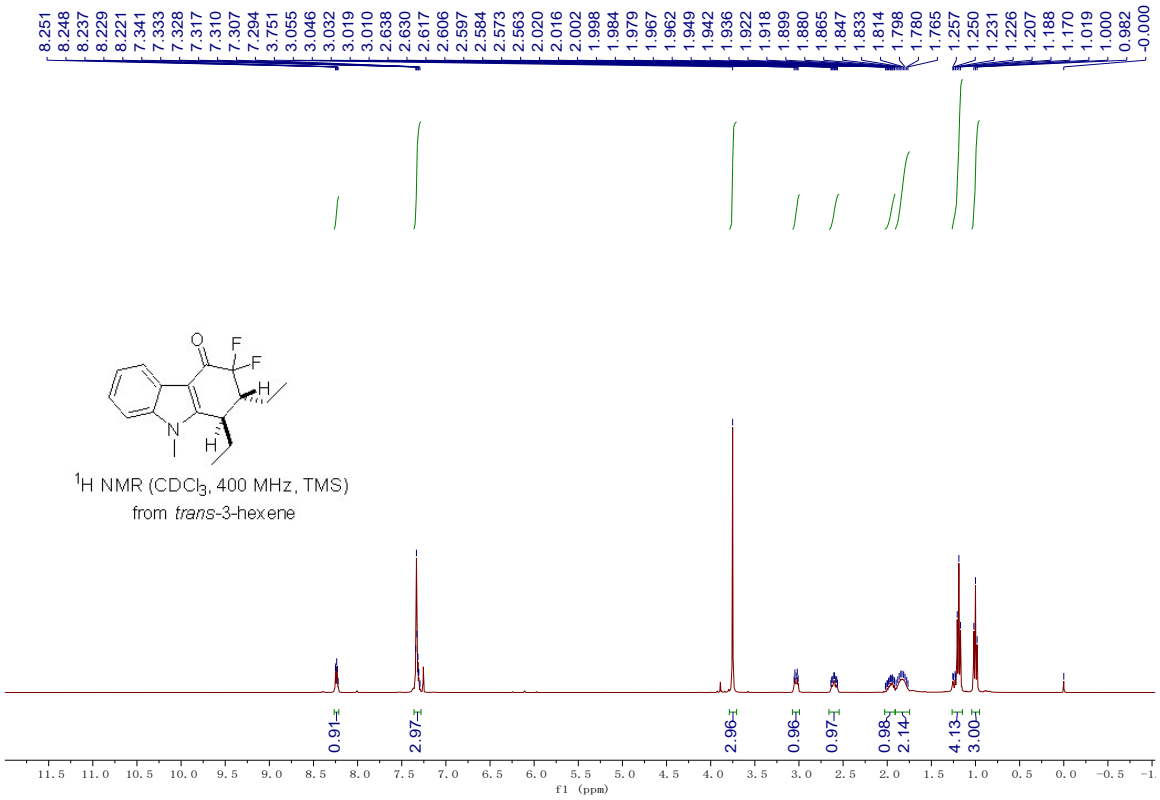
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

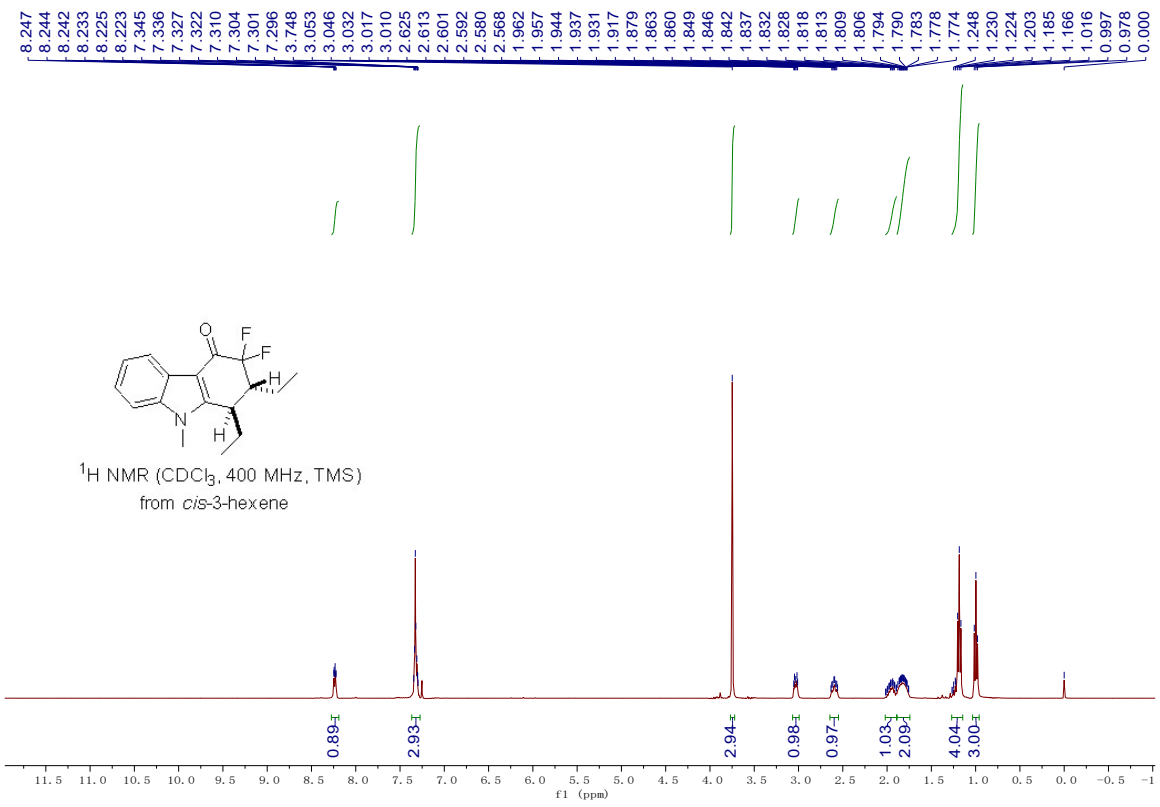




1,2-diethyl-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3az)

A white solid. 56.5 mg, 97% yield (from *trans*-3-hexene). 56.9 mg, 96% (from *cis*-3-hexene). M.P.: 111-113 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.00 (t, *J* = 7.4 Hz, 3H), 1.19 (t, *J* = 7.4 Hz, 3H), 1.23-1.26 (m, 1H), 1.77-1.90 (m, 2H), 1.92-2.02 (m, 1H), 2.56-2.64 (m, 2H), 3.03 (dt, *J* = 10.8, 3.6 Hz, 1H).), 3.75 (s, 3H), 7.29-7.34 (m, 3H), 8.22-8.25 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 12.4, 12.5, 21.8 (dd, *J* = 7.8, 3.9 Hz), 27.1 (d, *J* = 5.2 Hz), 30.3, 38.4 (dd, *J* = 7.1, 1.6 Hz), 45.6 (dd, *J* = 20.2, 19.5 Hz), 109.6 (dd, *J* = 4.0, 1.2 Hz), 109.7, 116.6 (dd, *J* = 254.8, 246.4 Hz), 122.0, 123.5, 124.1, 124.5 (d, *J* = 2.0 Hz), 138.6, 153.6 (d, *J* = 1.3 Hz), 178.8 (dd, *J* = 26.5, 25.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -116.9 (d, *J* = 279.3 Hz), -91.7 (dd, *J* = 279.4, 13.2 Hz). IR (neat) $\tilde{\nu}$ 2973, 2925, 2882, 1658, 1456, 1380, 1088, 1046, 880 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{19}NOF_2Na$ (M+Na): 314.1332, Found: 314.1350.

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7.336
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7.322
7.310
7.304
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7.296
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3.046
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1.016
0.997
0.978
0.000
O
F
F
H
N
H
1H NMR (CDCl3, 400 MHz, TMS)
from cis-3-hexene
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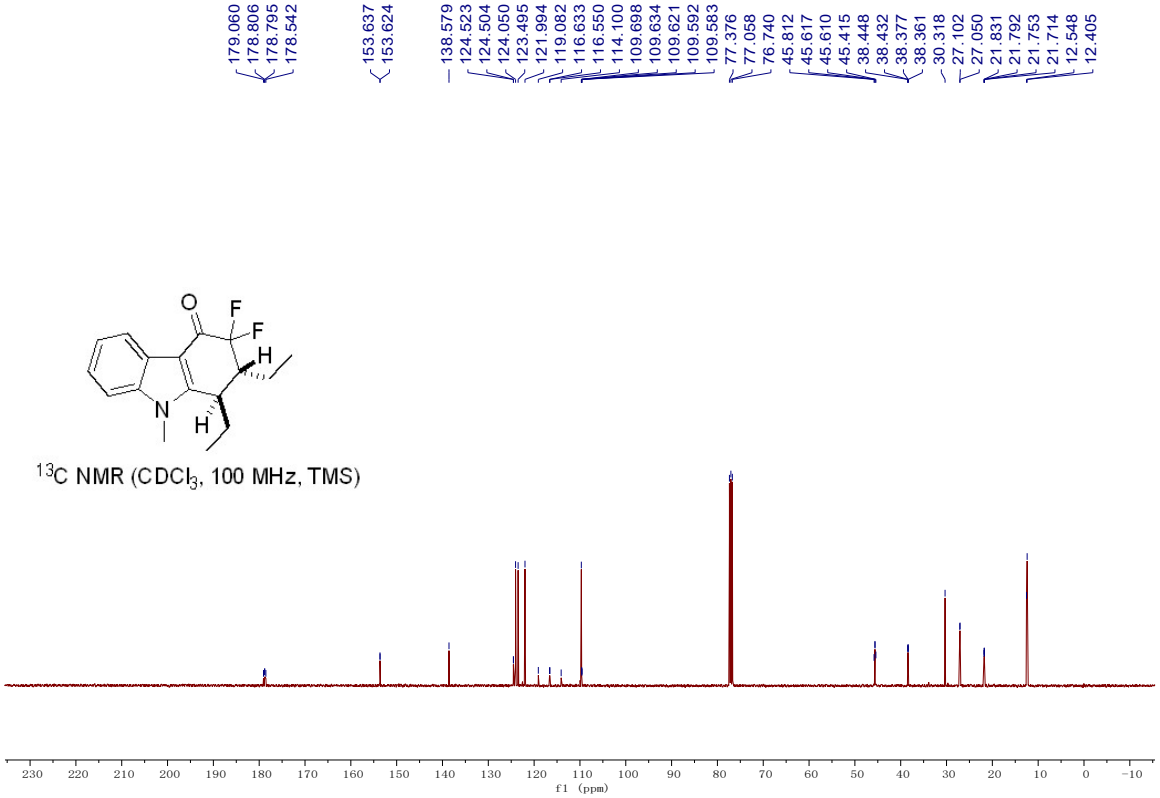
2.93
2.94
0.98
0.97
1.03
2.09
4.04
3.00
f1 (ppm)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116.550
114.100
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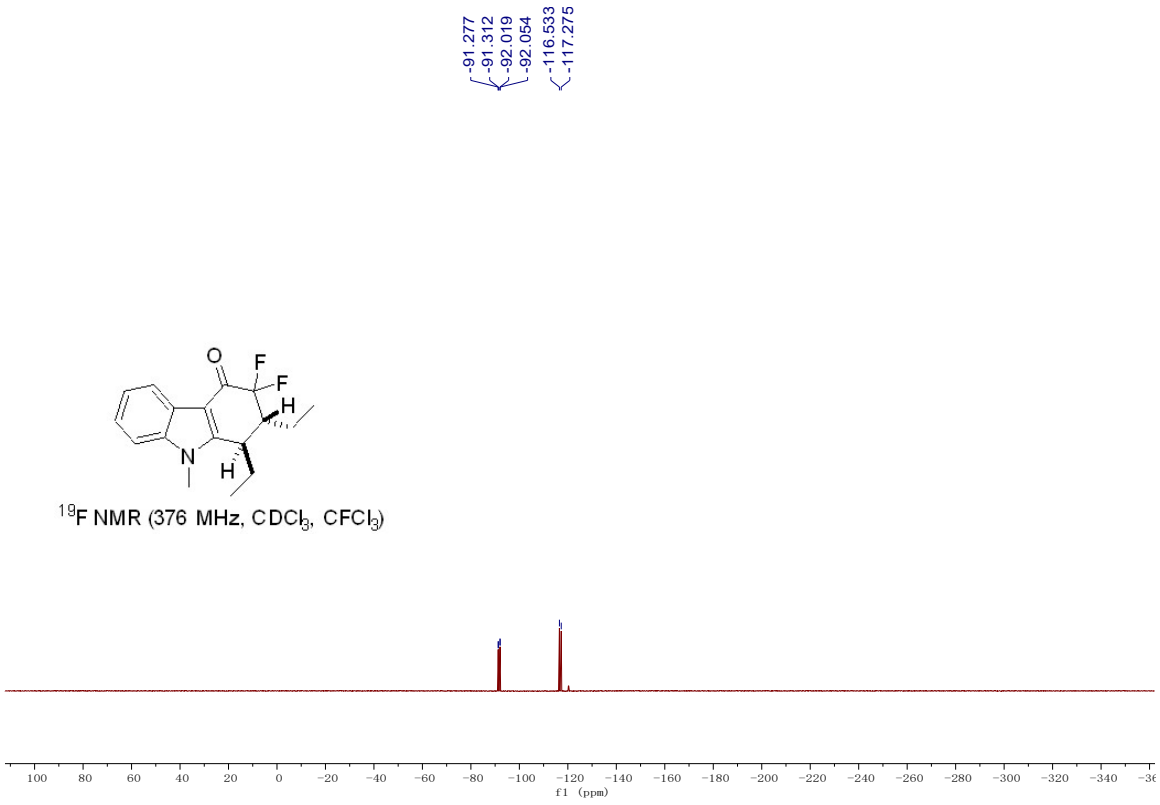
109.634
109.621
109.592
109.583
77.376
77.058
76.740
45.812
45.617
45.610
45.415
38.448
38.432
38.377
38.361
30.318
27.102
27.050
21.831
21.792
21.753
21.714
12.548
12.405
O
F
F
H
N
H
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)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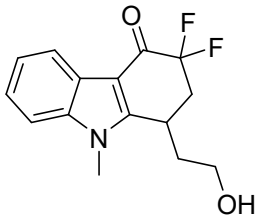
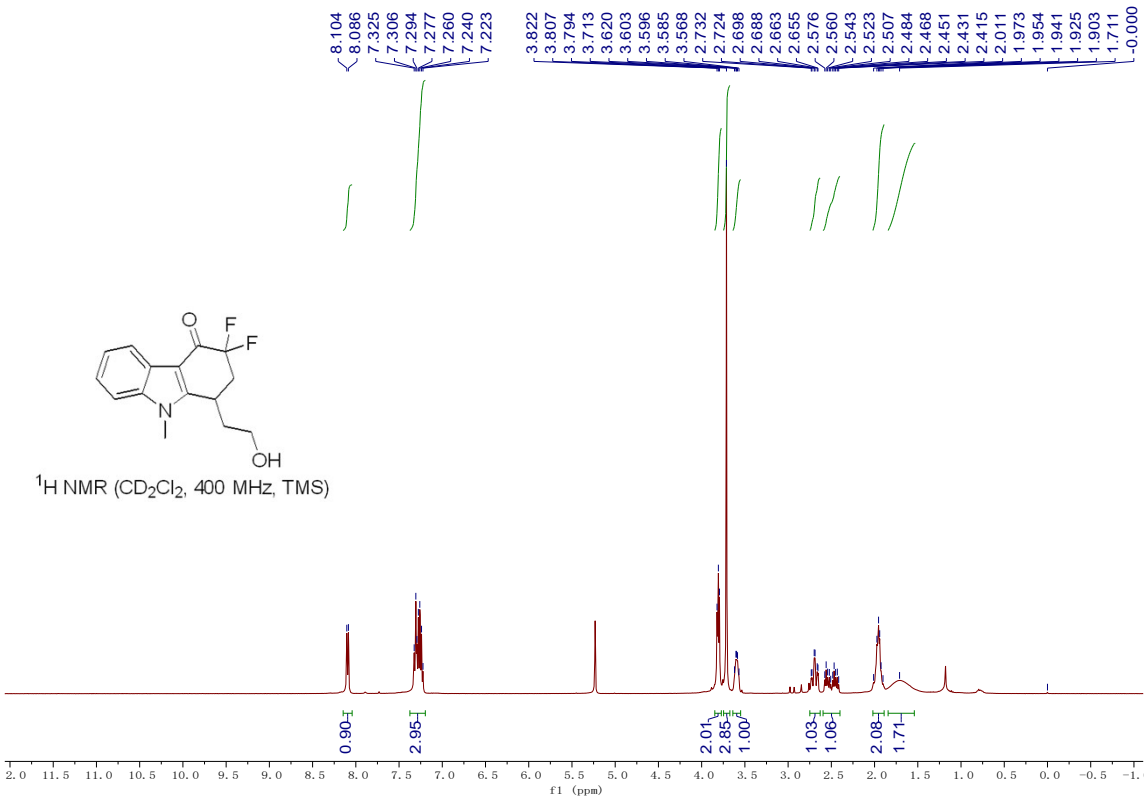
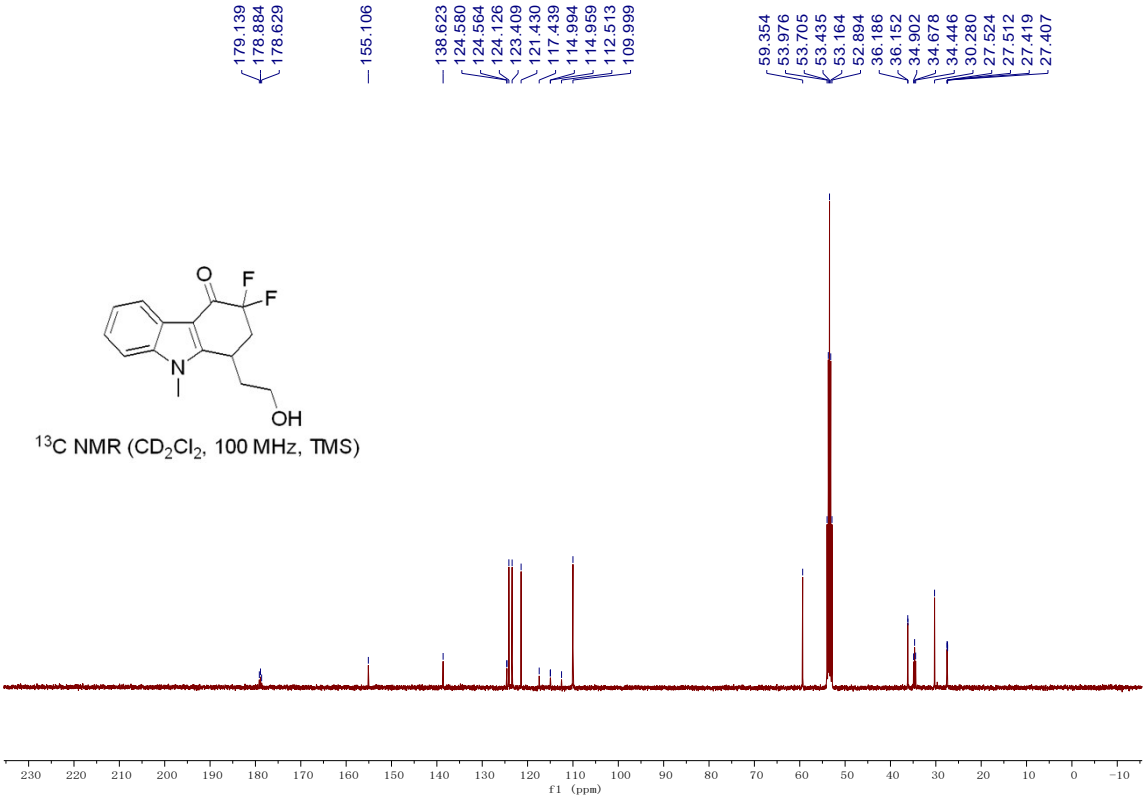
-92.054
-116.533
-117.275
O
F
F
H
N
H
19F NMR (376 MHz, CDCl3, CFCl3)
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -340
f1 (ppm)



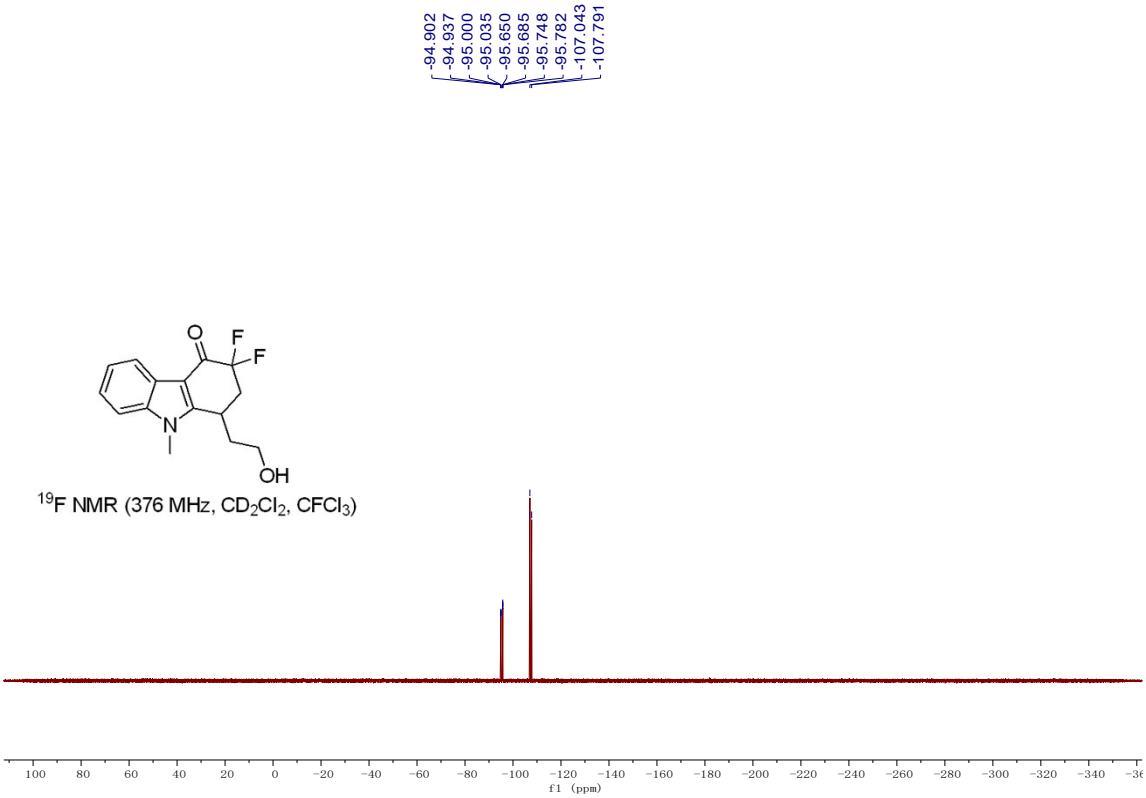
3,3-difluoro-1-(2-hydroxyethyl)-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aad)

A white solid. 54.7 mg, 98% yield. M.P.: 142-144 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.71 (br, 1H), 1.90-2.01 (m, 2H), 2.42-2.58 (m, 1H), 2.66-2.73 (m, 1H), 3.57-3.62 (m, 1H), 3.71 (s, 3H), 3.81 (t, J = 5.6 Hz, 2H), 7.22-7.33 (m, 3H), 8.09 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.4 (dd, J = 10.5, 1.2 Hz), 30.3, 34.7 (t, J = 23.0 Hz), 36.2 (d, J = 3.4 Hz), 59.4, 110.0, 110.1 (t, J = 1.8 Hz), 115.0 (dd, J = 248.0, 244.5 Hz), 121.4, 123.4, 124.1, 124.6 (d, J = 1.6 Hz), 138.6, 155.1, 179.0 (d, J = 25.7 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.4 (d, J = 281.8 Hz), -95.3 (ddd, J = 281.2, 36.6, 12.8 Hz). IR (neat) $\tilde{\nu}$ 2922, 2855, 1668, 1640, 1481, 1464, 1405, 1348, 1324, 1258, 1128, 1097, 1056, 868, 783, 752, 686 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{16}NO_2F_2$ (M+H): 280.1144, Found: 280.1150.

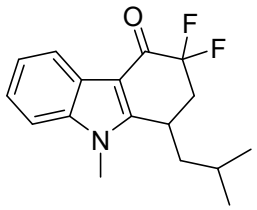




^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)

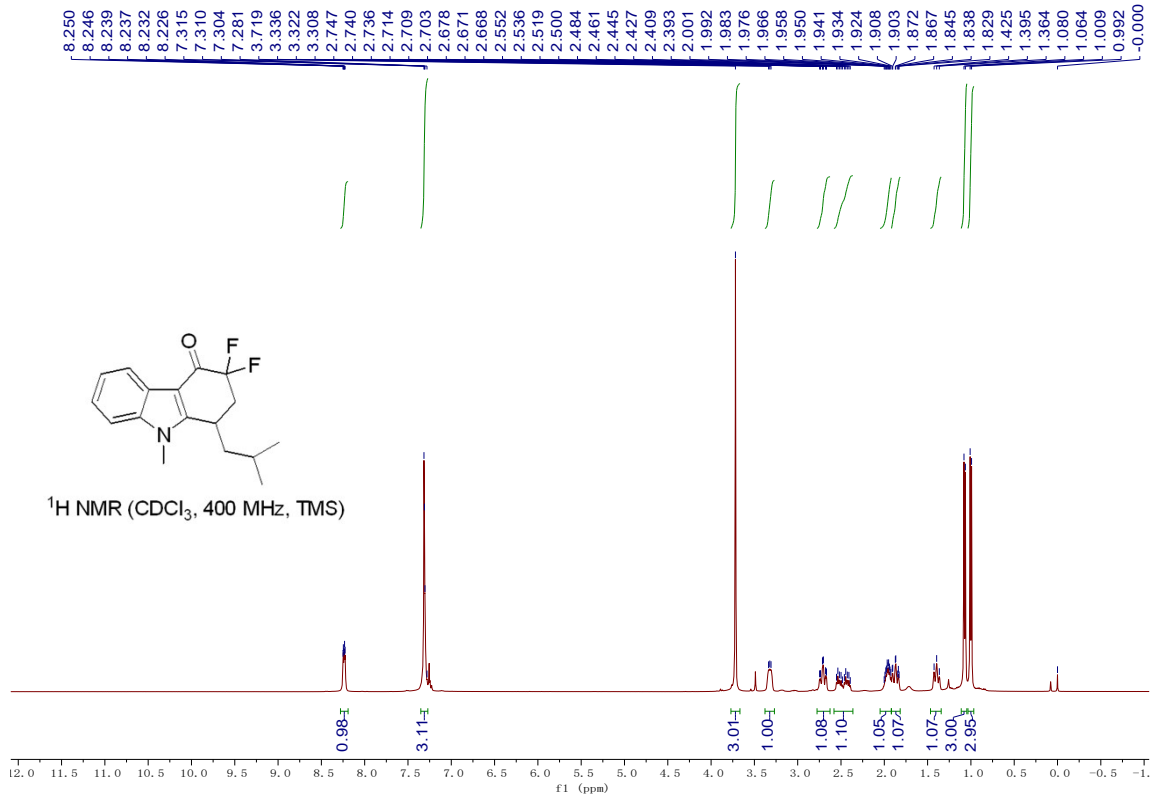


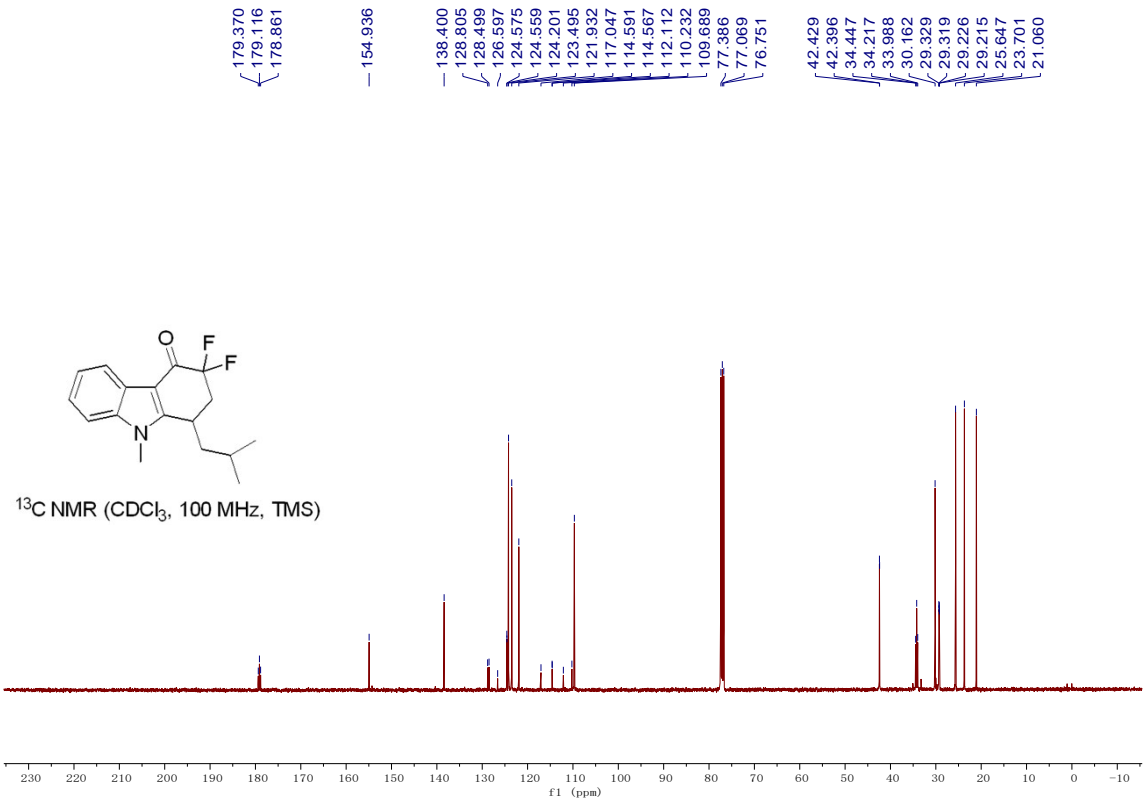
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)

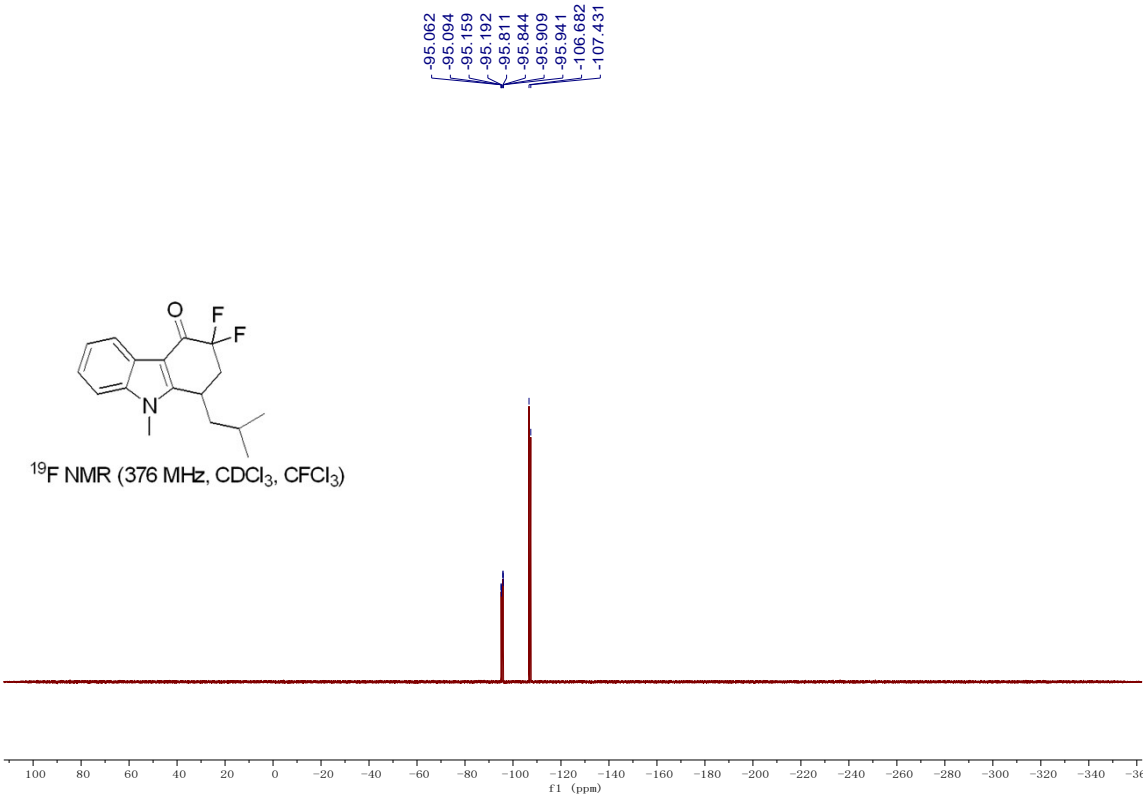


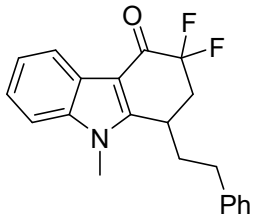
3,3-difluoro-1-isobutyl-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aaa)

A white solid. 56.5 mg, 97% yield. M.P.: 166-168 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.00 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3H), 1.40 (t, *J* = 12.2 Hz, 1H), 1.83-1.91 (m, 1H), 1.92-2.00 (m, 1H), .2.39-2.55 (m, 1H), 2.67-2.75 (m, 1H), 3.31-3.34 (m, 1H), 3.72 (s, 3H), 7.28-7.32 (m, 3H), 8.23-8.25 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 23.7, 25.6, 29.3 (dd, *J* = 10.3, 1.0 Hz), 30.2 (t, *J* = 23.1 Hz), 42.4 (d, *J* = 3.3 Hz), 109.7, 110.2 (t, *J* = 1.8 Hz), 114.6 (dd, *J* = 248.0, 245.6 Hz), 121.9, 123.5, 124.2, 124.6 (d, *J* = 1.5 Hz), 126.6, 128.5, 128.8, 138.4, 154.9, 179.1 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.1 (d, *J* = 282.0 Hz), -95.5 (ddd, *J* = 282.0, 36.7, 12.3 Hz). IR (neat) $\tilde{\nu}$ 2961, 2873, 1661, 1482, 1403, 1260, 1196, 1153, 1126, 1051, 986, 870, 753 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{20}NOF_2$ (M+H): 292.1508, Found: 292.1503.



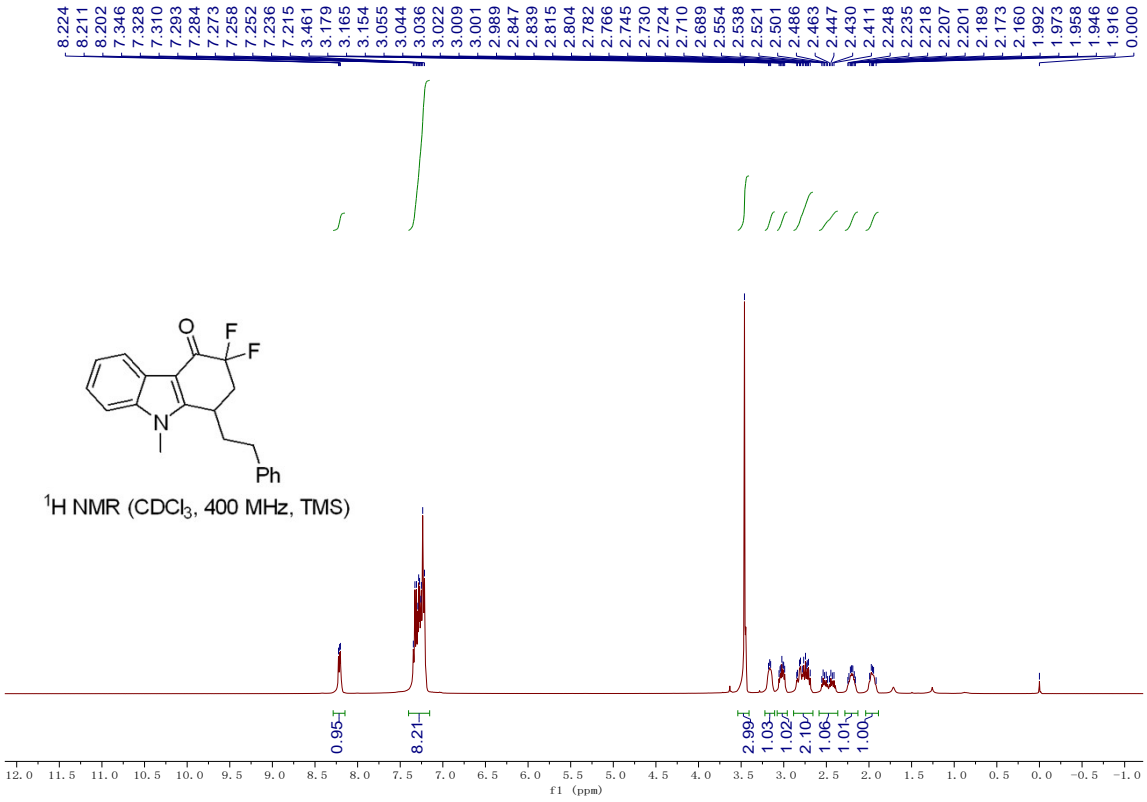

179.370
179.116
178.861
154.936
138.400
128.805
128.499
126.597
124.575
124.559
124.201
123.495
121.932
117.047
114.591
114.567
112.112
110.232
109.689
77.386
77.069
76.751
42.429
42.396
34.447
34.217
33.988
30.162
29.329
29.319
29.226
29.215
25.647
23.701
21.060
O
F
F
N
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

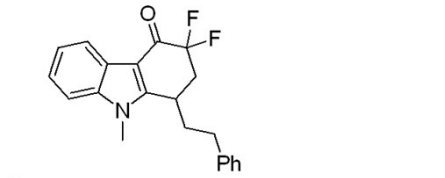

-95.062
-95.094
-95.159
-95.192
-95.811
-95.844
-95.909
-95.941
-106.682
-107.431
O
F
F
N
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



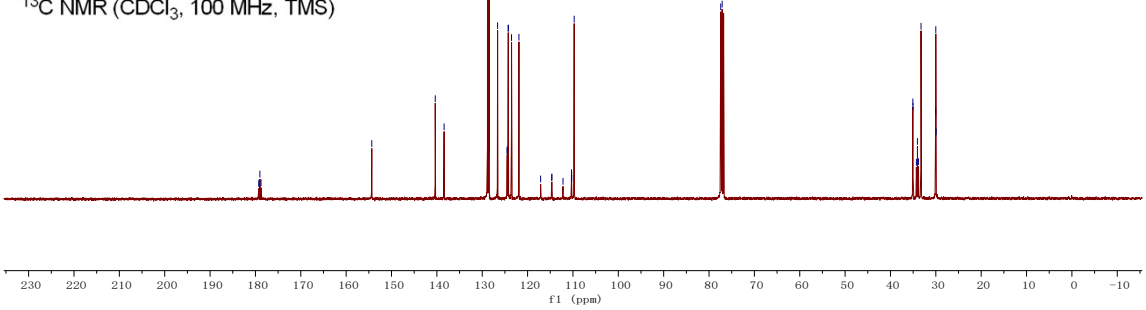
3,3-difluoro-9-methyl-1-phenethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aab)

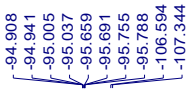
A white solid. 66.5 mg, 98% yield. M.P.: 92-94 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.92-1.99 (m, 1H), 2.16-2.25 (m, 1H), 2.41-2.55 (m, 1H), 2.69-2.85 (m, 2H), 2.99-3.06 (m, 1H), 3.17 (t, *J* = 5.6 Hz, 1H), 3.46 (s, 3H), 7.22-7.35 (m, 8H), 8.20-8.22 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.0 (dd, *J* = 5.9, 3.1 Hz), 33.3, 34.1 (t, *J* = 23.1 Hz), 35.1 (d, *J* = 3.4 Hz), 109.7, 110.3 (dd, *J* = 3.7, 1.8 Hz), 114.7 (dd, *J* = 250.0, 246.7 Hz), 121.9, 123.5, 124.3, 124.5 (d, *J* = 1.5 Hz), 126.6, 128.5, 128.8, 138.4, 140.4, 154.3, 179.0 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.0 (d, *J* = 282.2 Hz), -95.4 (ddd, *J* = 282.4, 36.5, 12.4 Hz). IR (neat) $\tilde{\nu}$ 2954, 2922, 1667, 1478, 1453, 1404, 1348, 1192, 1128, 1053, 866, 761, 751, 699 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}NOF_2$ (M+H): 340.1508, Found: 340.1502.

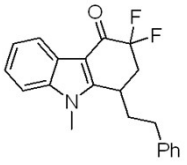




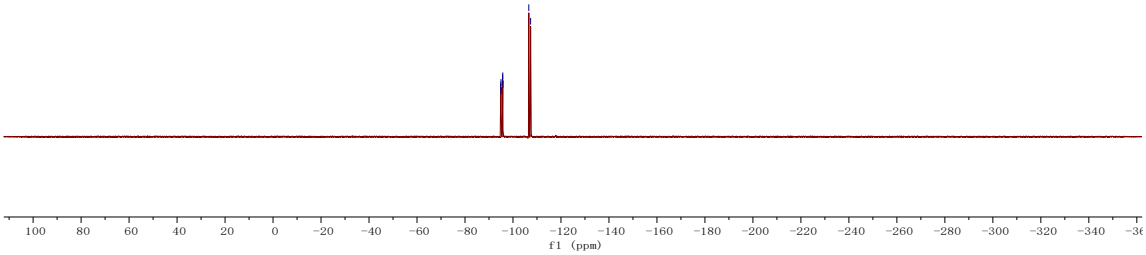
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

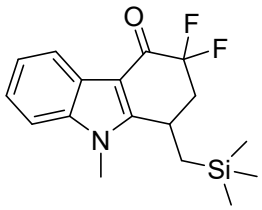






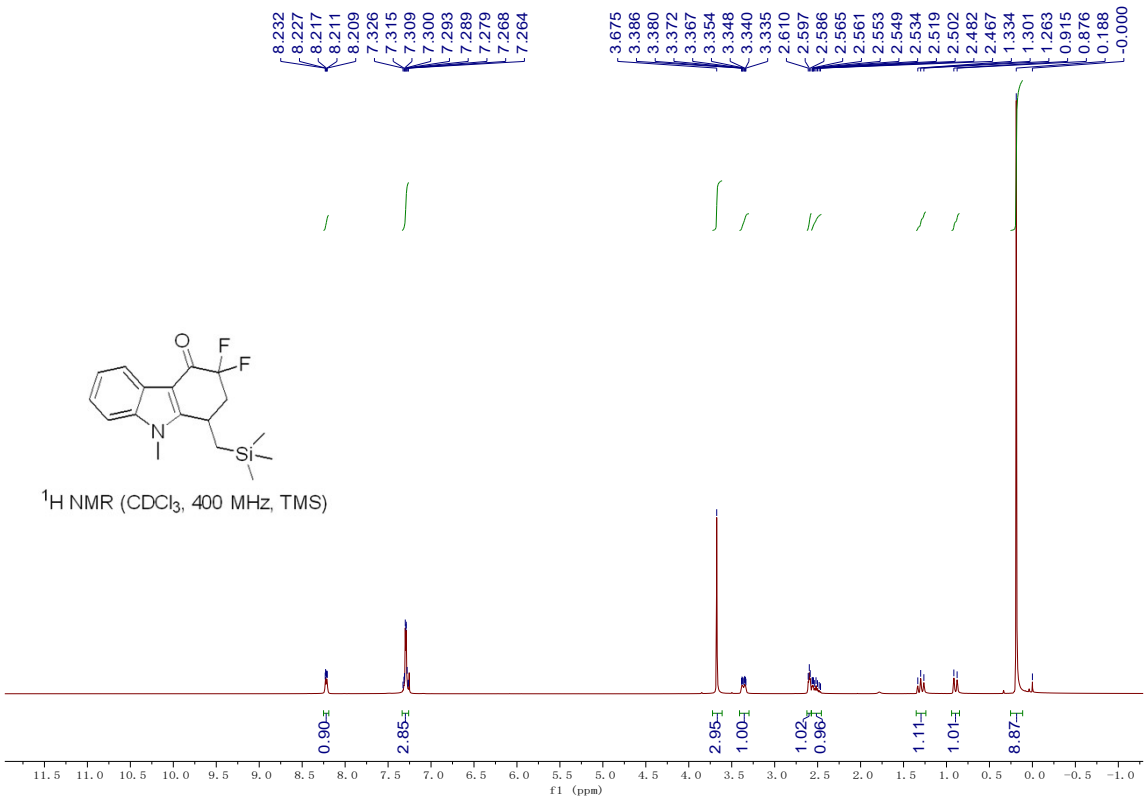
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

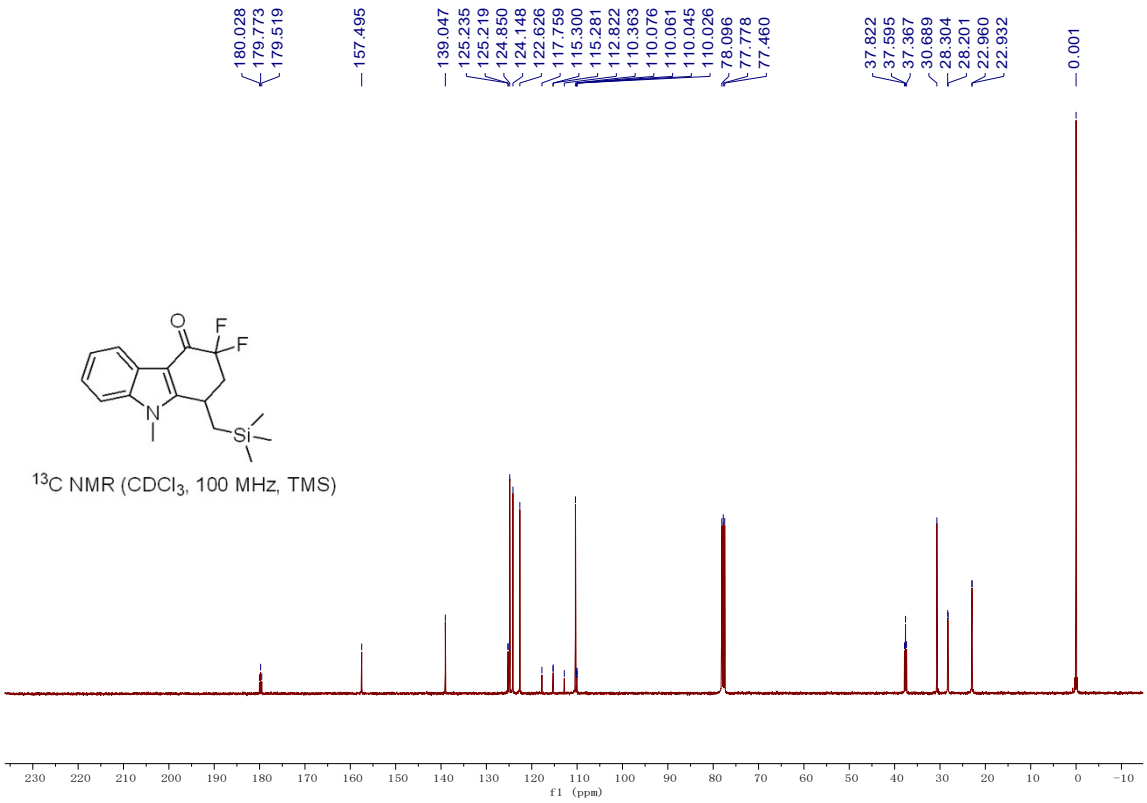


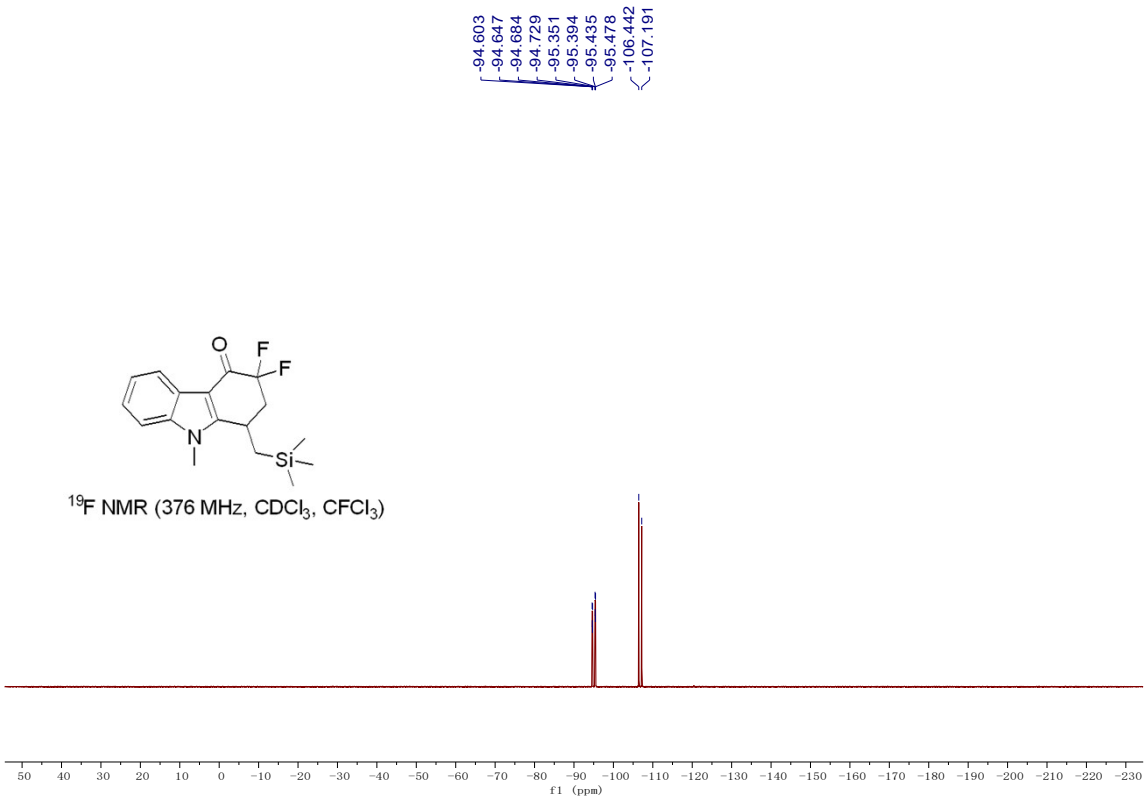


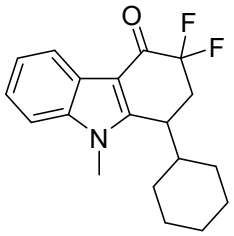
3,3-difluoro-9-methyl-1-((trimethylsilyl)methyl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aae)

A white solid. 63.0 mg, 98% yield. M.P.: 142-144 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.19 (s, 9H), 0.90 (d, J = 15.2 Hz, 1H), 1.30 (t, J = 14.2 Hz, 1H), 2.47-2.57 (m, 1H), 2.60 (t, J = 4.6 Hz, 1H), 3.34-3.39 (m, 1H), 3.68 (s, 3H), 7.26-7.33 (m, 3H), 8.21-8.23 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.0, 23.0 (d, J = 2.8 Hz), 28.3 (d, J = 10.4 Hz), 30.7, 37.6 (t, J = 22.9 Hz), 110.1 (dd, J = 3.4, 1.7 Hz), 110.4, 115.3 (dd, J = 249.4, 247.5 Hz), 122.6, 124.1, 124.9, 125.6 (d, J = 1.6 Hz), 139.0, 157.5, 179.8 (t, J = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.8 (d, J = 281.9 Hz), -95.0 (ddd, J = 281.9, 31.2, 16.4 Hz). IR (neat) $\tilde{\nu}$ 2984, 2864, 1658, 1481, 1424, 1347, 1191, 1163, 1067, 1052, 866, 836, 758, 692 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{22}NOF_2Si$ (M+H): 322.1433, Found: 322.1438.



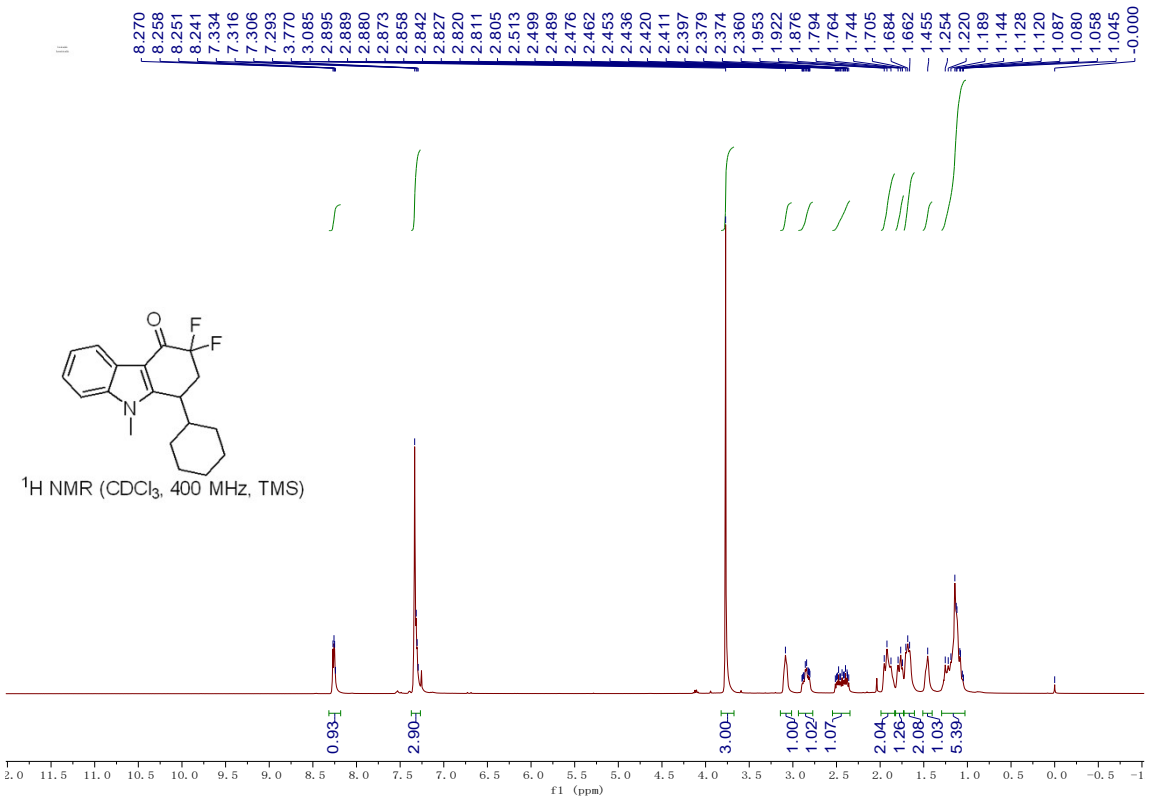

180.028
179.773
179.519
157.495
139.047
125.235
125.219
124.850
124.148
122.626
117.759
115.300
115.281
112.822
110.363
110.076
110.061
110.045
110.026
78.096
77.778
77.460
37.822
37.595
37.367
30.689
28.304
28.201
22.960
22.932
0.001
O
F
F
N
Si
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

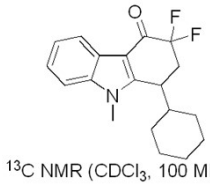

-94.603
-94.647
-94.684
-94.729
-95.351
-95.394
-95.435
-95.478
-106.442
-107.191
O
F
F
N
Si
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



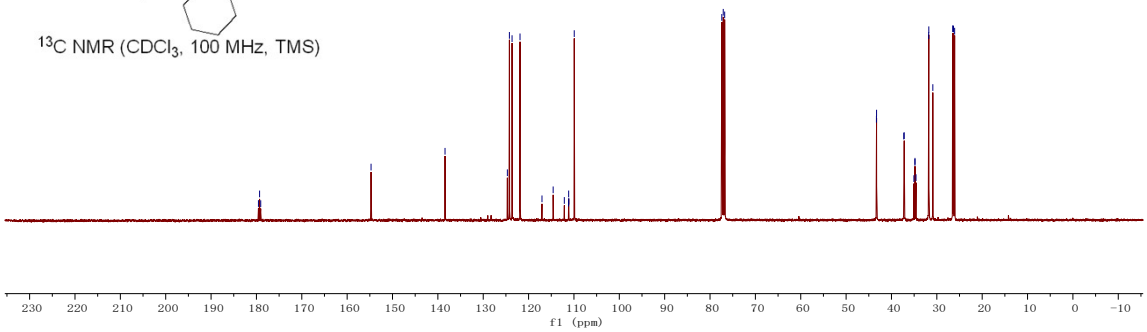
1-cyclohexyl-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aac)

A white solid. 50.8 mg, 80% yield. M.P.: 118-120 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.05-1.25 (m, 5H), 1.46 (br, 1H), 1.66-1.71 (m, 2H), 1.74-1.79 (m, 1H), 1.88-1.95 (m, 2H), 2.36-2.51 (m, 1H), 2.81-2.90 (m, 1H), 3.09 (t, J = 5.6 Hz, 1H), 7.29-7.33 (m, 3H), 8.24-8.27 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.1, 26.3, 26.5, 30.9, 31.8 (d, J = 2.9 Hz), 34.8 (dd, J = 23.7, 22.7 Hz), 37.2 (d, J = 9.4 Hz), 43.3 (d, J = 3.0 Hz), 109.9, 111.2 (t, J = 2.9 Hz), 114.6 (t, J = 246.2 Hz), 121.9, 123.6, 124.2, 124.7, 138.4, 154.7, 179.3 (t, J = 25.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -102.5 (dd, J = 284.3, 5.6 Hz), -97.6 (ddd, J = 284.4, 31.4, 12.2 Hz). IR (Acetone) $\tilde{\nu}$ 2932, 2855, 1659, 1479, 1401, 1274, 1126, 1052, 1031, 865, 755 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}NOF_2$ (M+H): 318.1664, Found: 318.1663.

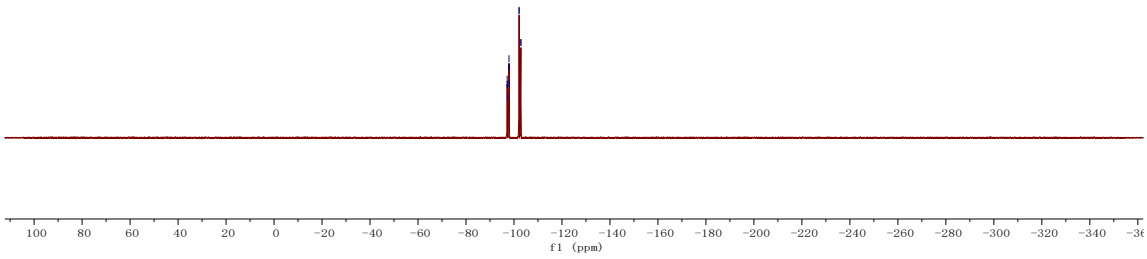


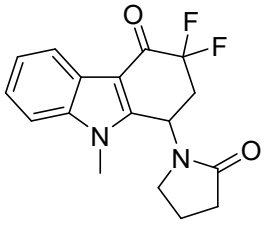


^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



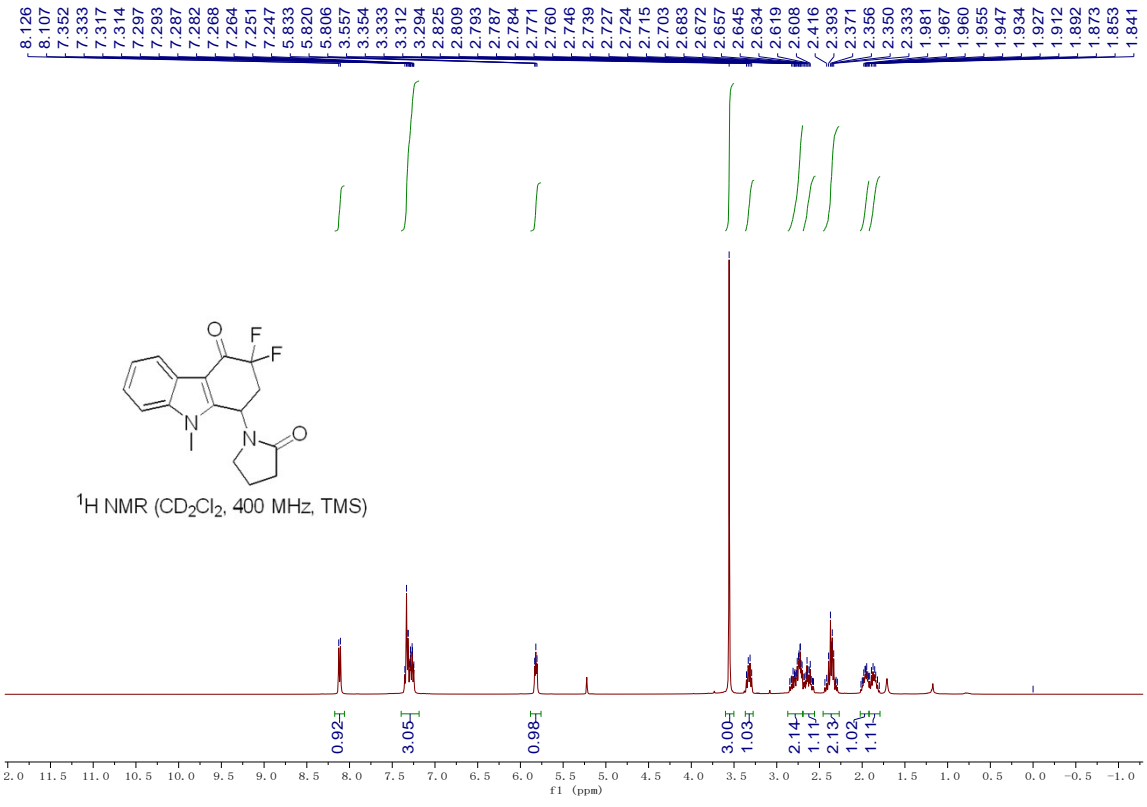
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

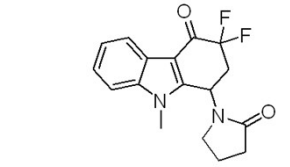




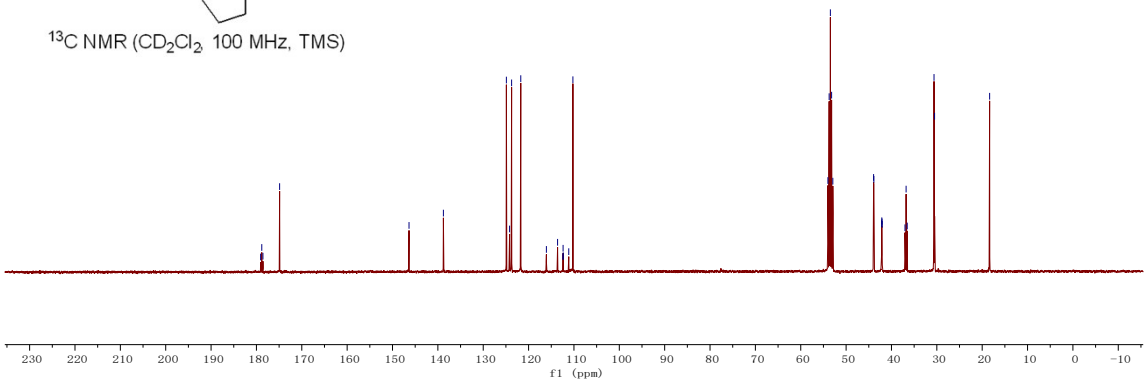
3,3-difluoro-9-methyl-1-(2-oxopyrrolidin-1-yl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aaf)

A white solid. 62.4 mg, 98% yield. M.P.: 197-199 °C. ^{1}H NMR (CD_2Cl_2, TMS, 400 MHz) δ 1.80-1.91 (m, 1H), 1.93-2.01 (m, 1H), 2.57-2.68 (m, 1H), 2.70-2.85 (m, 2H), 3.29-3.35 (m, 1H), 3.56 (s, 3H), 5.82 (t, *J* = 5.4 Hz, 2H), 7.25-7.35 (m, 3H), 8.12 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (CD_2Cl_2, TMS, 100 MHz) δ 18.4, 30.5, 30.6, 36.8 (t, *J* = 24.8 Hz), 42.1 (dd, *J* = 8.0, 3.7 Hz), 43.9 (d, *J* = 6.0 Hz), 110.2, 112.4 (t, *J* = 2.8 Hz), 113.6 (dd, *J* = 246.6, 246.4 Hz), 121.7, 123.7, 124.2, 124.9, 138.8, 146.4, 174.9, 178.8 (t, *J* = 25.6 Hz). ^{19}F NMR (CD_2Cl_2, $CFCl_3$, 376 MHz) δ -108.8 (d, *J* = 278.1 Hz), -100.4 (ddd, *J* = 279.4, 25.5, 10.0 Hz). IR (neat) $\tilde{\nu}$ 2972, 2920, 2879, 1660, 1456, 1406, 1088, 1046, 880, 754 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{16}N_2O_2F_2Na$ (M+Na): 341.1072, Found: 341.1065.

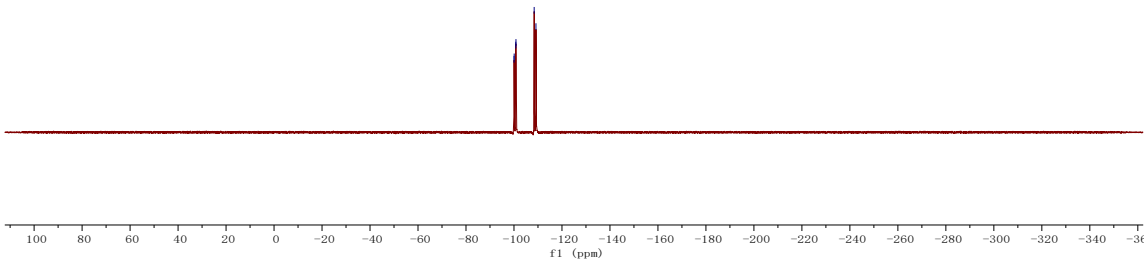


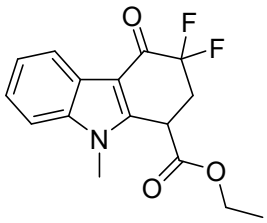


^{13}C NMR (CD_2Cl_2, 100 MHz, TMS)



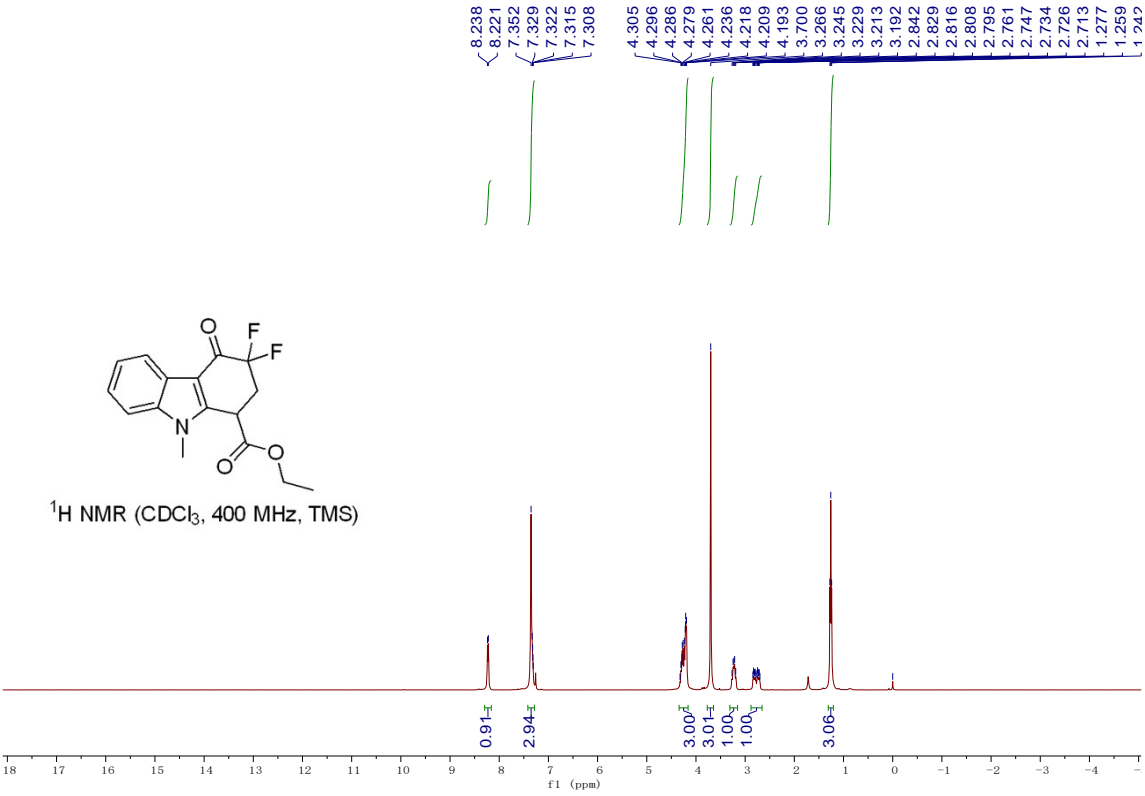
^{19}F NMR (376 MHz, CD_2Cl_2, $CFCl_3$)

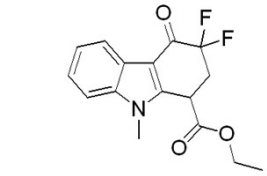




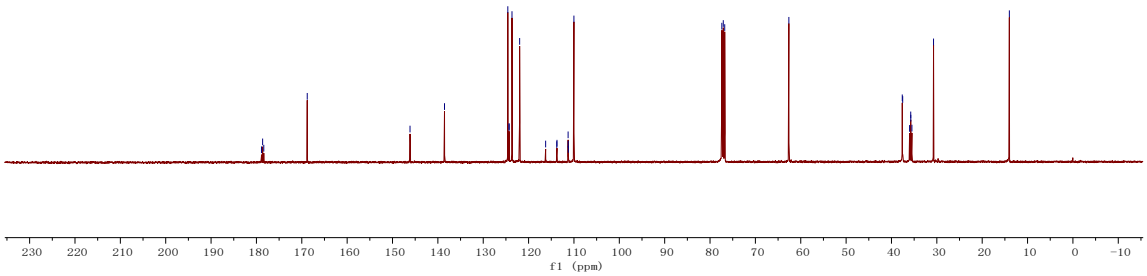
ethyl 3,3-difluoro-9-methyl-4-oxo-2,3,4,9-tetrahydro-1H-carbazole-1-carboxylate (3aag)

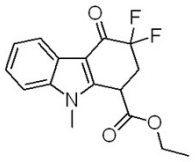
A white solid. 38.1 mg, 62% yield. M.P.: 168-170 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.26 (t, *J* = 7.0 Hz, 3H), 2.70-2.84 (m, 1H), 3.19-3.27 (m, 1H), 3.70 (s, 1H), 4.19-4.32 (m, 3H), 7.31-7.35 (m, 3H), 8.23 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 14.0, 30.7, 35.8 (dd, *J* = 26.3, 25.1 Hz), 37.6 (d, *J* = 9.4 Hz), 62.6, 110.0, 111.3 (t, *J* = 2.5 Hz), 113.7 (dd, *J* = 250.1, 245.3 Hz), 122.0, 123.7, 124.3 (d, *J* = 1.4 Hz), 124.6, 138.5, 146.1, 168.8, 178.6 (t, *J* = 25.7 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -112.7 (d, *J* = 274.8 Hz), -102.8 (ddd, *J* = 277.2, 32.9, 9.4 Hz). IR (neat) $\tilde{\nu}$ 2993, 2924, 1719, 1672, 1483, 1457, 1321, 1227, 1183, 1069, 1058, 1020, 863, 751, 740 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{15}NO_3F_2Na$ (M+Na): 330.0918, Found: 330.0920.



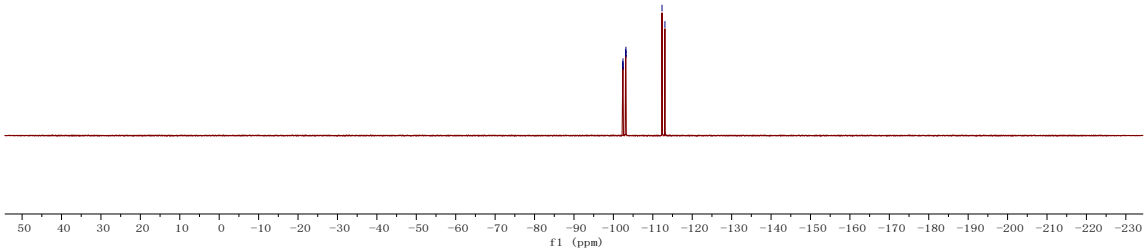


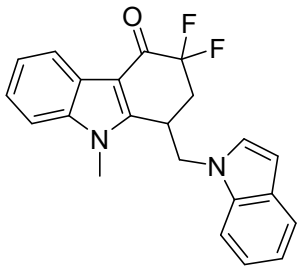
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





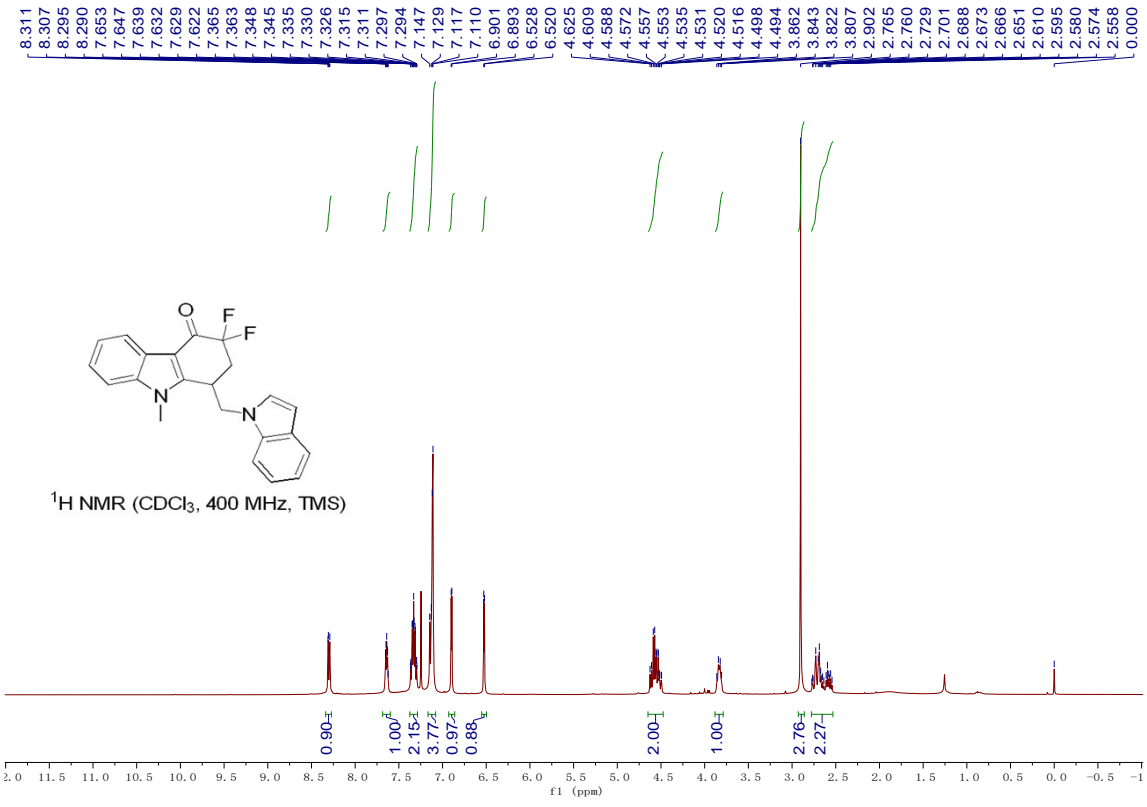
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

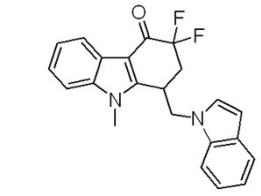




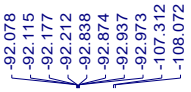
1-((1H-indol-1-yl)methyl)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aah)

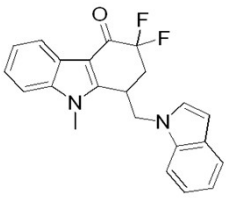
A white solid. 47.4 mg, 65% yield. M.P.: 180-182 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.54-2.77 (m, 2H), 2.90 (s, 3H), 3.81-3.86 (m, 1H), 4.49-4.63 (m, 2H), 6.52 (d, *J* = 3.2 Hz, 1H), 6.90 (d, *J* = 3.2 Hz, 1H), 7.11-7.15 (m, 4H), 7.29-7.37 (m, 2H), 7.62-7.65 (m, 1H), 8.29-8.31 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 29.5, 32.7 (dd, *J* = 10.4, 1.8 Hz), 36.1 (t, *J* = 24.1 Hz), 51.0 (d, *J* = 4.9 Hz), 102.8, 108.6, 110.1, 110.6 (dd, *J* = 3.4, 1.4 Hz), 114.3 (dd, *J* = 252.0, 244.5 Hz), 120.1, 121.5, 122.1, 122.4, 124.0, 124.5 (d, *J* = 1.5 Hz), 124.7, 128.0, 128.8, 135.7, 138.4, 150.8 (d, *J* = 1.6 Hz), 178.6 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -107.7 (d, *J* = 286.1 Hz), -92.5 (ddd, *J* = 286.2, 37.3, 13.6 Hz). IR (neat) $\tilde{\nu}$ 3095, 2864, 1665, 1480, 1463, 1404, 1362, 1311, 1282, 1183, 1056, 879, 751, 728 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{18}N_2OF_2Na$ (M+Na): 387.1279, Found: 387.1285.



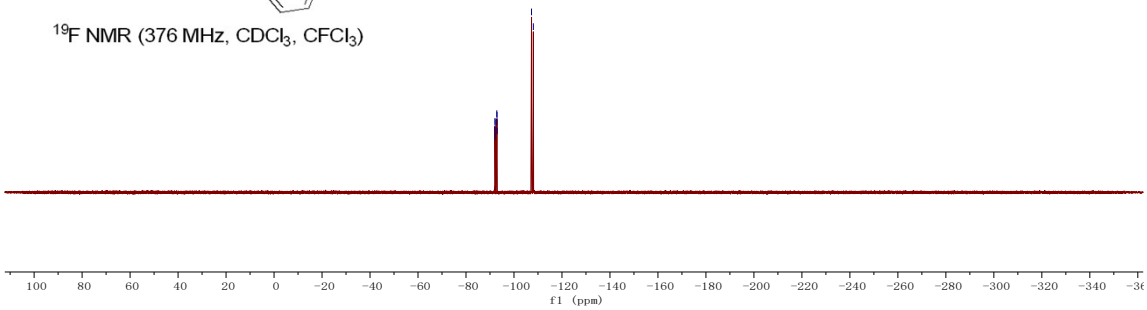


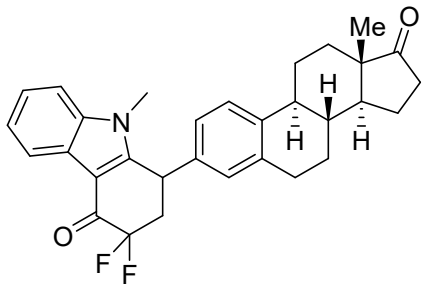
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





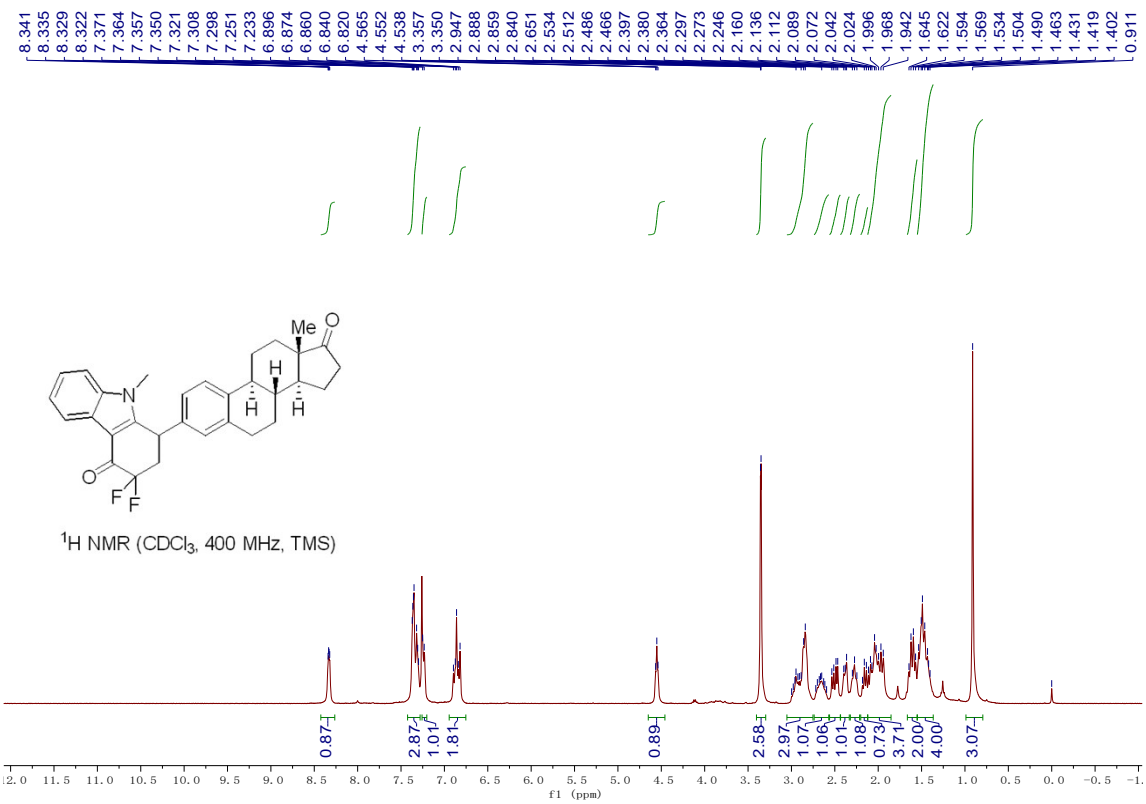
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



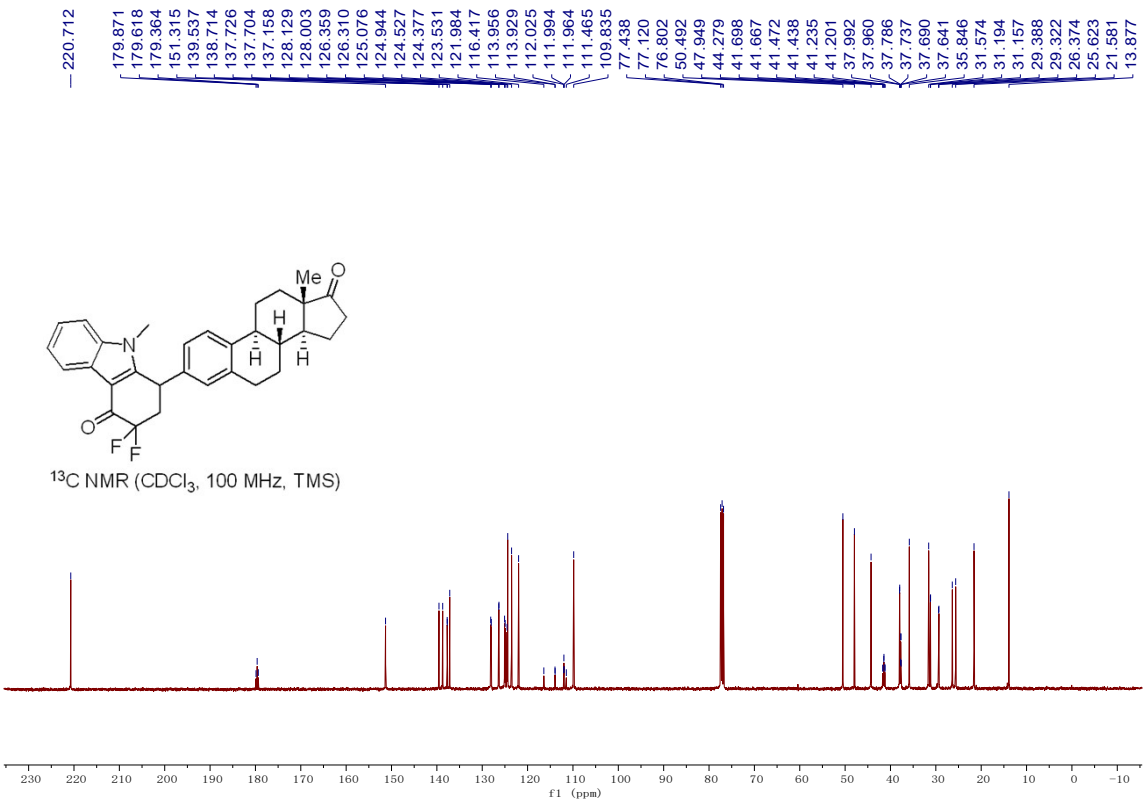


3,3-difluoro-9-methyl-1-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aai)

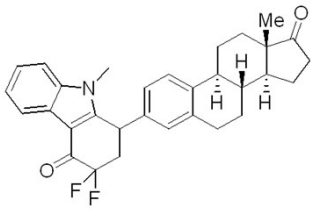
A white solid. 73.1 mg, 75% yield. M.P.: 118-120 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.91 (s, 3H), 1.40-1.53 (m, 4H), 1.57-1.65 (m, 2H), 1.94-2.11 (m, 4H), 2.14-2.18 (m, 1H), 2.25-2.30 (m, 1H), 2.36-2.40 (m, 1H), 2.47-2.53 (m, 1H), 2.66-2.72 (m, 1H), 2.84-3.00 (m, 3H), 3.35 (d, *J* = 2.8 Hz, 3H), 4.55 (t, *J* = 5.6 Hz, 1H), 6.82-6.90 (m, 2H), 7.23-7.25 (m, 1H), 7.30-7.37 (m, 3H), 8.32-8.34 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.9, 21.6, 25.6, 26.4, 29.4 (d, *J* = 6.7 Hz), 31.2 (d, *J* = 3.8 Hz), 31.6, 35.8, 37.7 (q, *J* = 4.9 Hz), 38.0 (d, *J* = 3.2 Hz), 41.5 (td, *J* = 23.8, 3.3 Hz), 44.3, 47.9, 50.5, 109.8, 111.5, 112.0 (t, *J* = 3.1 Hz), 113.9 (dd, *J* = 248.8, 246.1 Hz), 122.0, 123.5, 124.4, 124.5, 124.9, 125.1, 126.3 (d, *J* = 4.9 Hz), 128.0, 128.1, 137.2, 137.7 (d, *J* = 2.2 Hz), 138.7, 139.5, 151.3, 179.6 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.9 (ddd, *J* = 275.5, 19.5, 8.5 Hz), -105.1 (dddd, *J* = 274.8, 78.7, 20.3, 7.9 Hz). IR (neat) $\tilde{\nu}$ 2930, 2860, 1734, 1667, 1475, 1455, 1401, 1342, 1275, 1185, 1071, 910, 865, 727 cm^{-1}. HRMS (ESI) calcd. for $C_{31}H_{31}NO_2F_2Na$ (M+Na): 510.2221, Found: 510.2230.



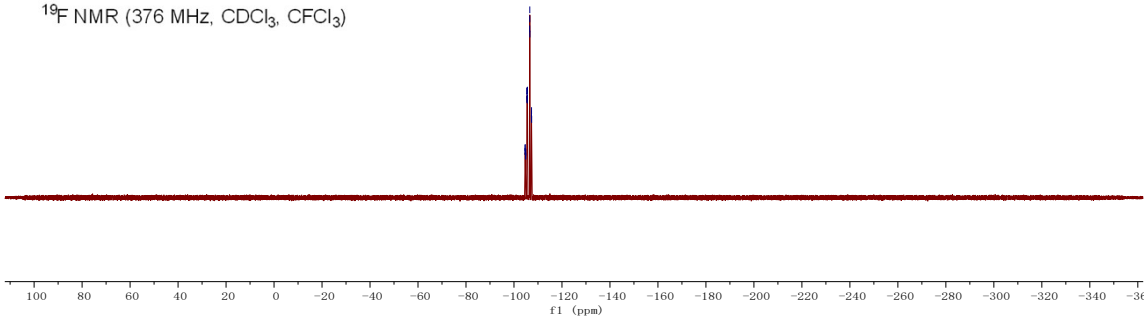
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

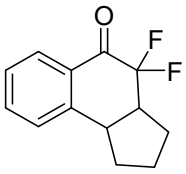


^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



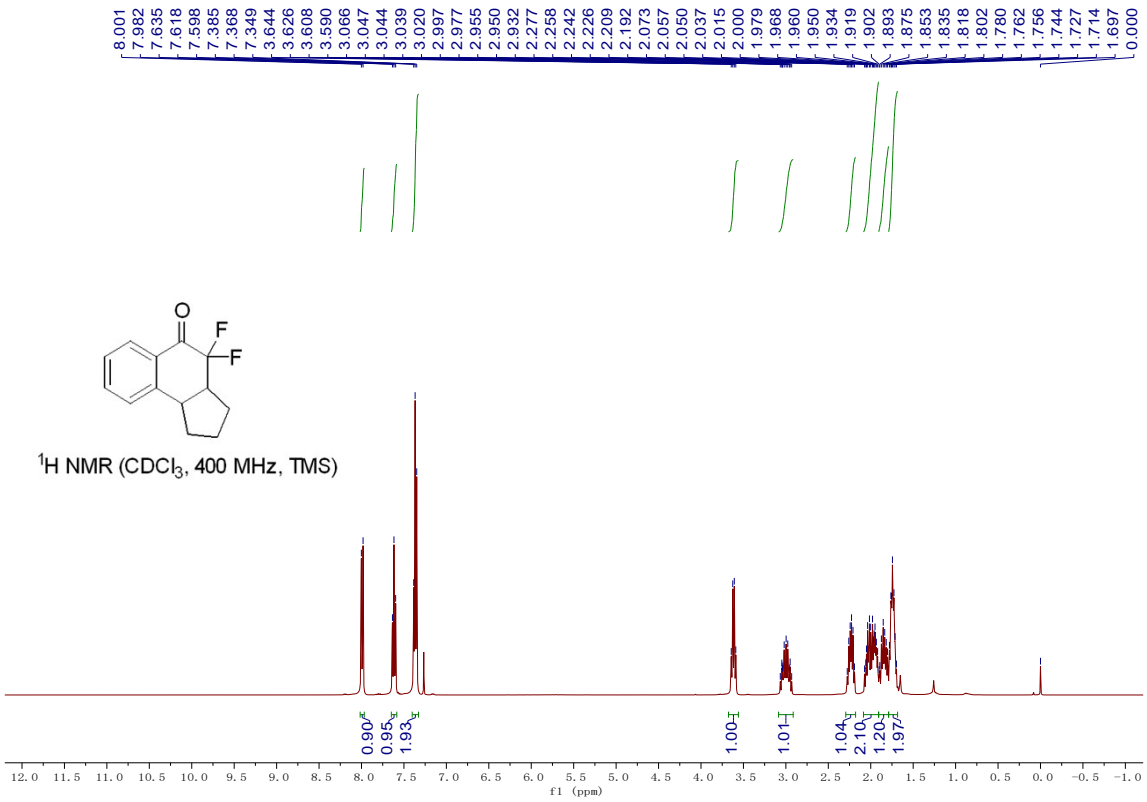
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

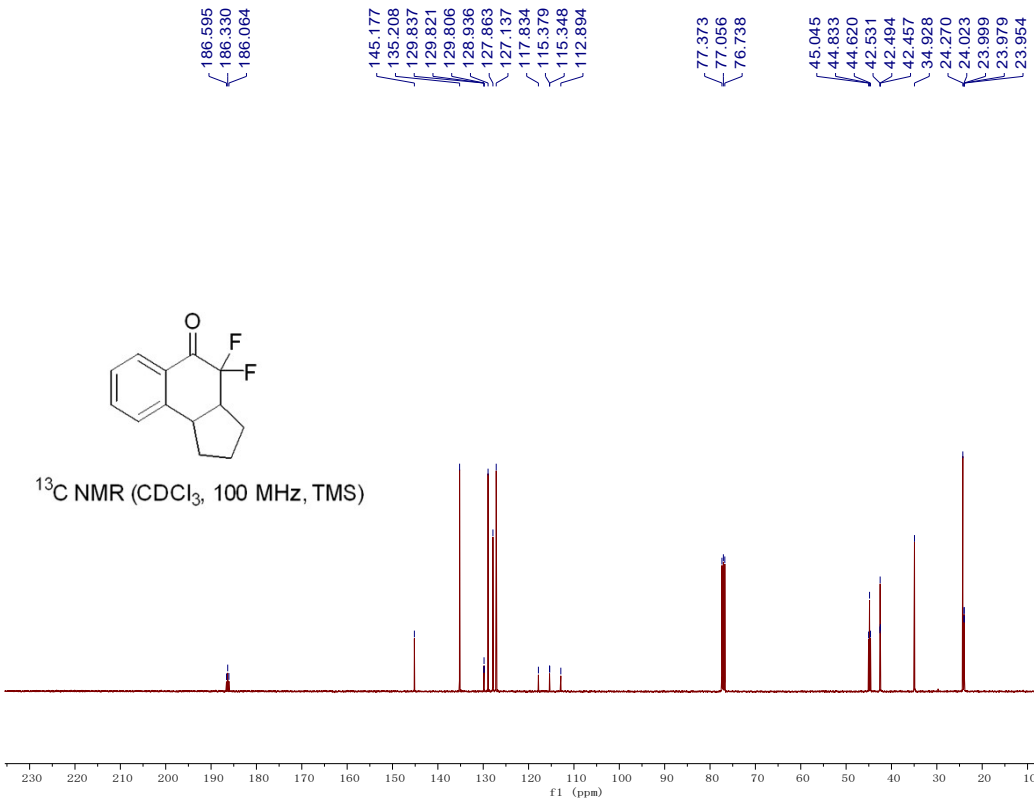




4,4-difluoro-1,2,3,3a,4,9b-hexahydro-5H-cyclopenta[a]naphthalen-5-one (3bk)

A colorless oil. 36.5 mg, 82% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.70-1.78 (m, 2H), 1.80-1.90 (m, 1H), 1.92-2.07 (m, 2H), 2.19-2.28 (m, 1H), 2.93-3.07 (m, 1H), 3.62 (q, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 24.0 (dd, *J* = 4.5, 2.5 Hz), 24.3, 34.9 (d, *J* = 1.5 Hz), 42.5 (t, *J* = 3.8 Hz), 44.8 (t, *J* = 21.3 Hz), 115.4 (dd, *J* = 250.1, 246.9 Hz), 127.1, 127.9, 128.9, 129.8 (t, *J* = 1.6 Hz), 135.2, 145.2, 186.3 (t, *J* = 26.7 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -113.8 (dd, J = 265.8, 18.8 Hz), -106.5 (dd, J = 265.9, 11.0 Hz). IR (neat) $\tilde{\nu}$ 2962, 2877, 1713, 1602, 1479, 1455, 1259, 1193, 1159, 1094, 1045, 954, 938, 751, 739 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{12}OF_2$ (M^+): 222.0851, Found: 222.0856.

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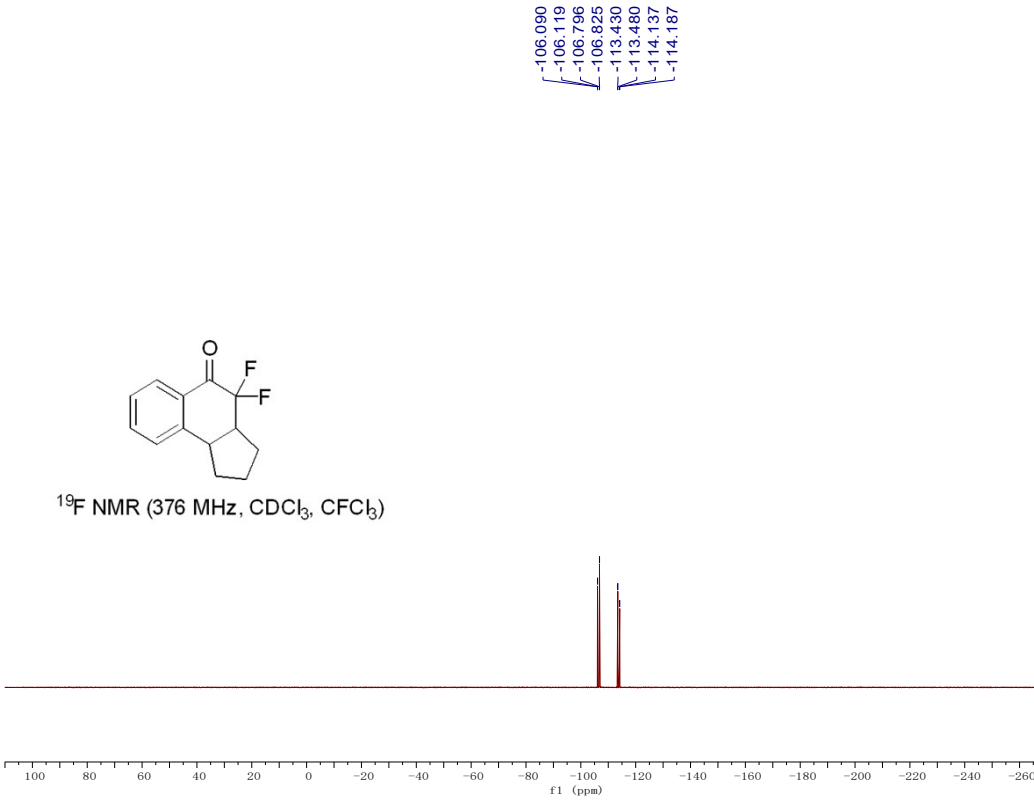
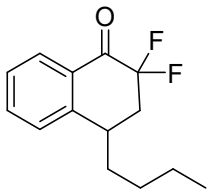
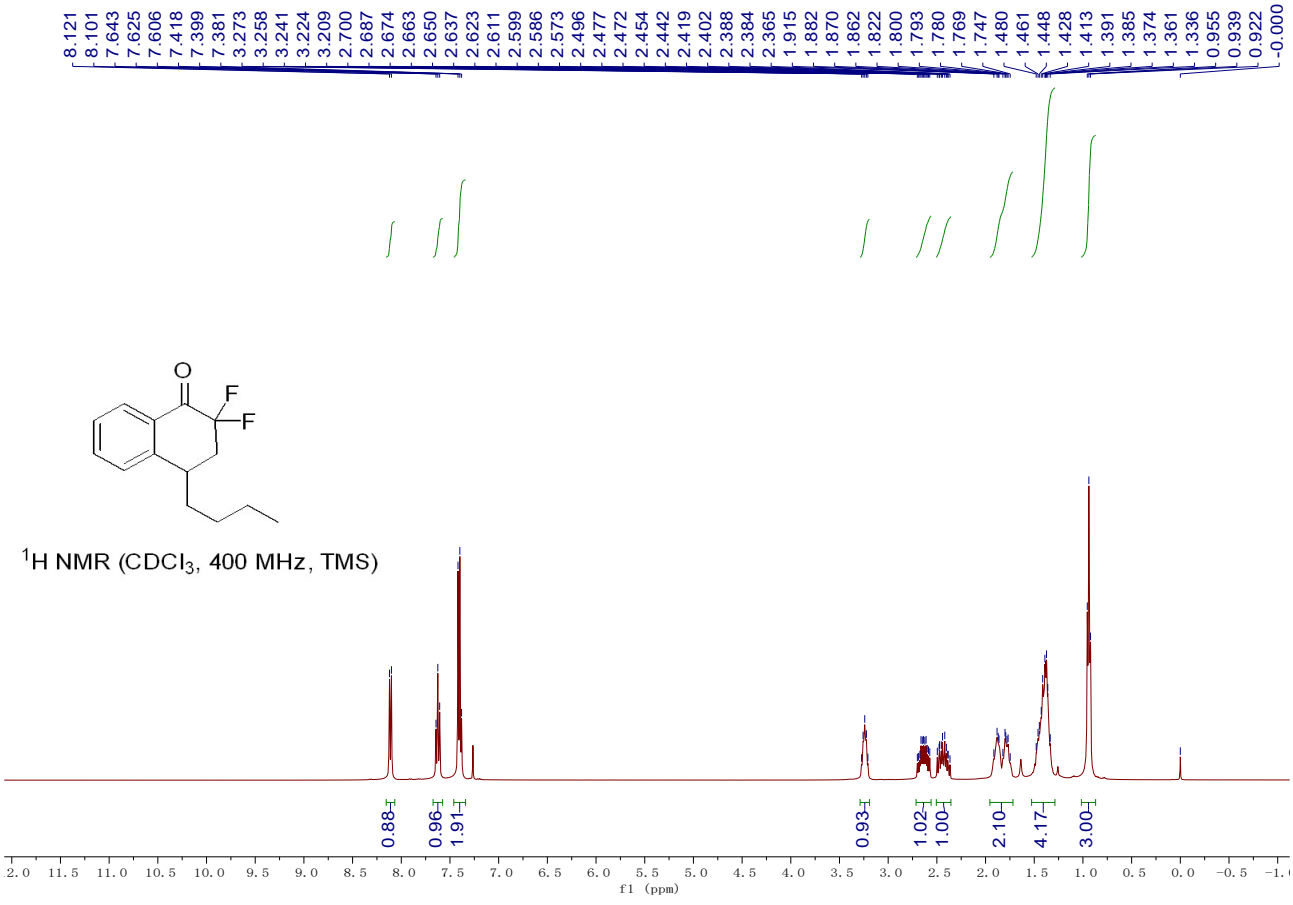
186.330
186.064
145.177
135.208
129.837
129.821
129.806
128.936
127.863
127.137
117.834
115.379
115.348
112.894
77.373
77.056
76.738
45.045
44.833
44.620
42.531
42.494
42.457
34.928
24.270
24.023
23.999
23.979
23.954
O
F
F
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

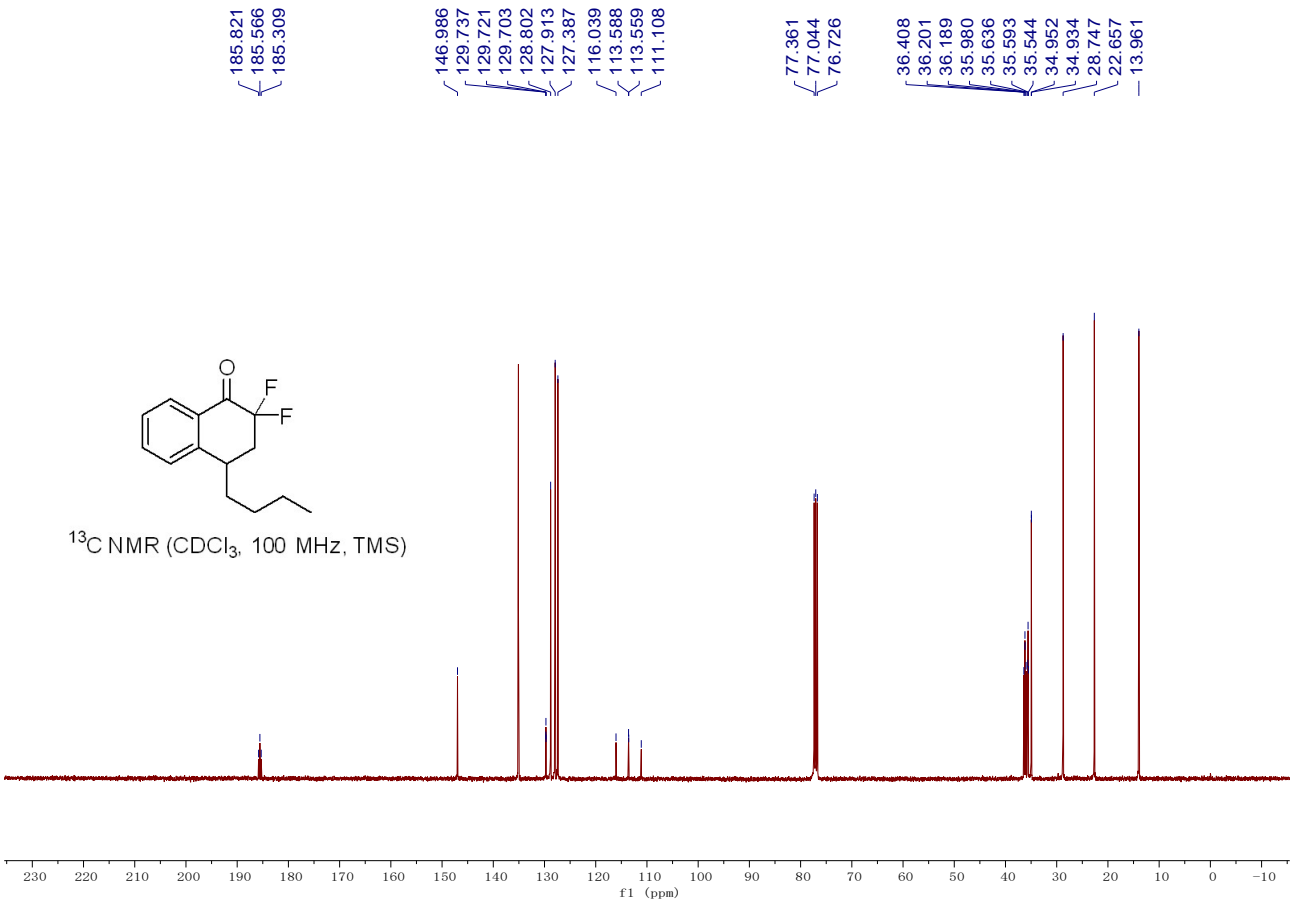

-106.090
-106.119
-106.796
-106.825
-113.430
-113.480
-114.137
-114.187
O
F
F
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



4-butyl-2,2-difluoro-3,4-dihydronaphthalen-1(2H)-one (3by)

A colorless oil. 40.5 mg, 85% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.94 (t, *J* = 6.4 Hz, 3H), 1.34-1.48 (m, 4H), 1.75-1.92 (m, 2H), 2.37-2.50 (m, 1H), 2.57-2.70 (m, 1H), 3.21-3.27 (m, 1H), 7.38-7.42 (m, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 14.0, 22.7, 28.7, 34.9 (d, *J* = 1.8 Hz), 35.6 (dd, *J* = 4.9, 4.3 Hz), 36.2 (dd, *J* = 22.1, 20.9 Hz), 113.6 (dd, *J* = 248.0, 245.1 Hz), 127.4, 127.9, 128.8, 129.7 (t, *J* = 1.7 Hz), 135.1, 147.0, 185.6 (t, *J* = 25.7, 25.7 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.6 (ddd, *J* = 276.6, 20.9, 10.4 Hz), -105.2 (ddd, *J* = 276.6, 20.7, 9.3 Hz). IR (neat) $\tilde{\nu}$ 2958, 2932, 2863, 1709, 1600, 1456, 1228, 1202, 1156, 1129, 1094, 1056, 935, 753, 697 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{16}OF_2$ (M^+): 238.1164, Found: 238.1171.

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127.387
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113.559
111.108
77.361
77.044
76.726
36.408
36.201
36.189
35.980
35.636
35.593
35.544
34.952
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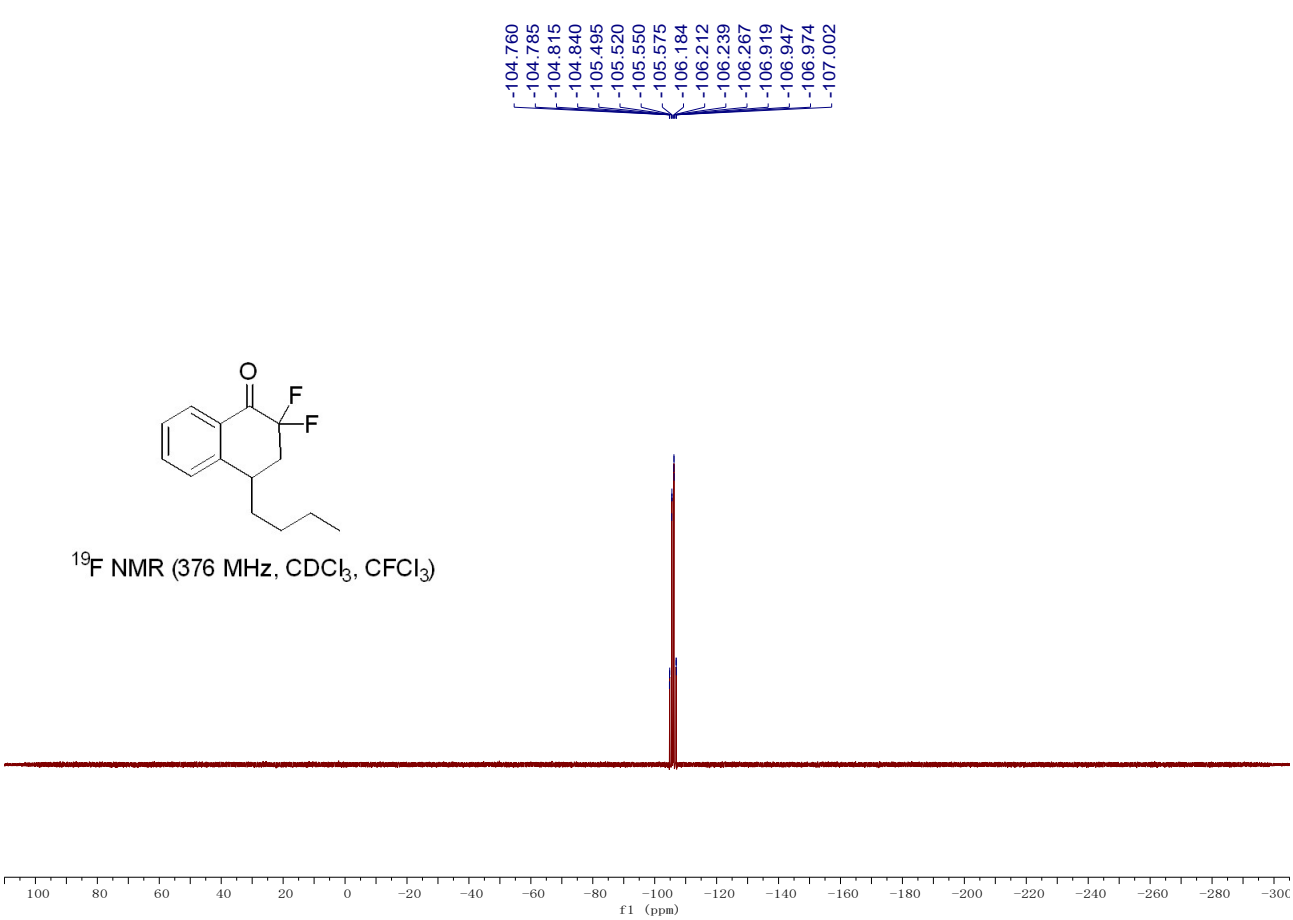
28.747
22.657
13.961
O
F
F
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)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-104.815
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-105.550
-105.575
-106.184
-106.212
-106.239
-106.267
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-106.974
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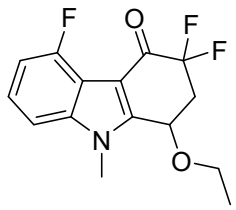
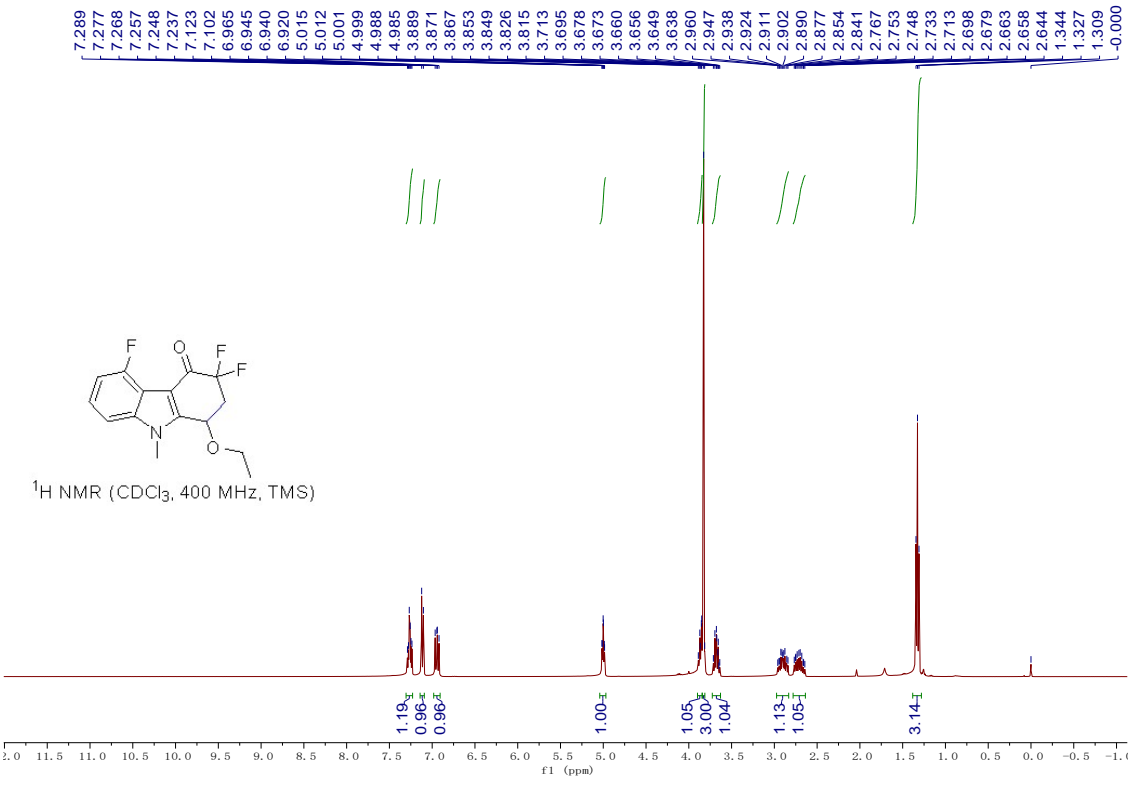
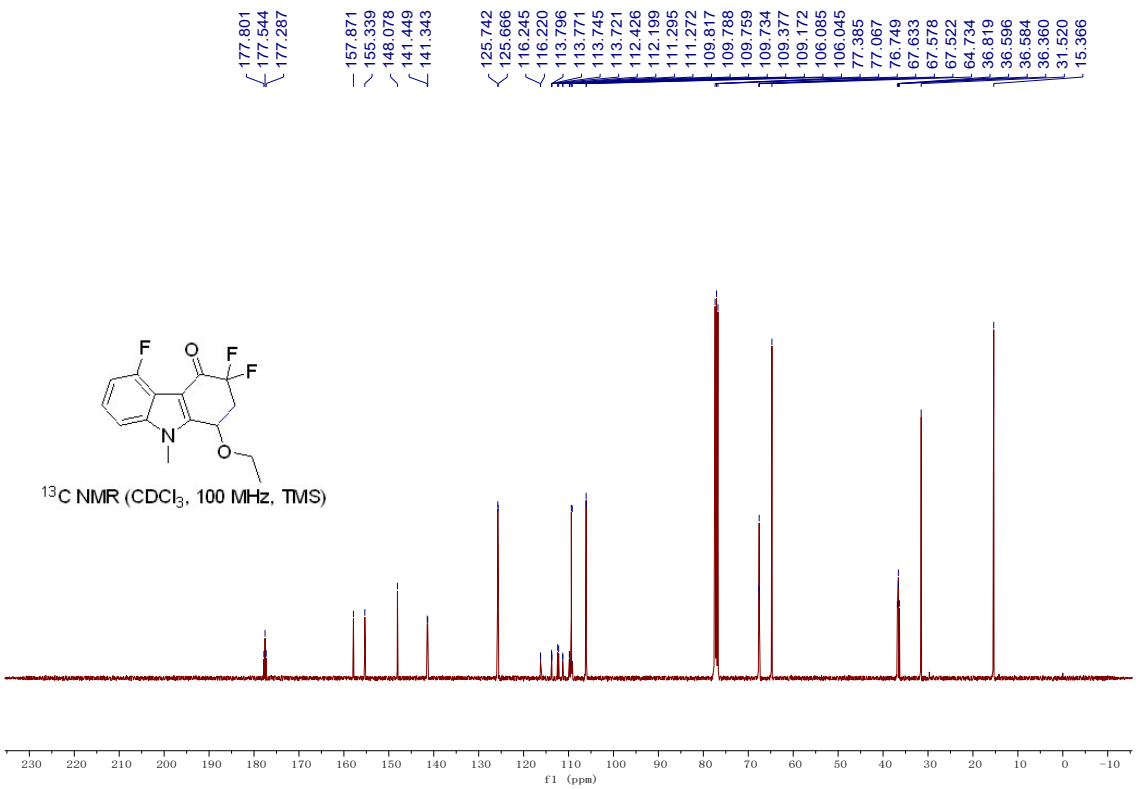
O
F
F
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



1-ethoxy-3,3,5-trifluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3cp)

A white solid. 57.7 mg, 97% yield. M.P.: 130-132 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.33 (t, *J* = 7.0 Hz, 3H), 2.64-2.77 (m, 1H), 2.84-2.94 (m, 1H), 3.64-3.71 (m, 1H), 3.83 (s, 3H), 3.85-3.89 (m, 1H), 5.00 (td, *J* = 5.6, 1.2 Hz, 1H), 6.94 (dd, *J* = 10.0, 8.0 Hz, 1H) 7.11 (d, *J* = 8.2 Hz, 1H), 7.24-7.29 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 31.5, 36.6 (dd, *J* = 23.5, 22.3 Hz), 64.7, 67.6 (t, *J* = 5.5 Hz), 106.1 (d, *J* = 4.1 Hz), 109.3 (d, *J* = 20.6 Hz), 109.8 (dd, *J* = 5.8, 2.9 Hz), 112.3 (d, *J* = 22.8 Hz), 113.7 (ddd, *J* = 250.0, 244.9, 2.5 Hz), 125.7 (d, *J* = 7.6 Hz), 141.4 (d, *J* = 10.6 Hz), 148.1, 155.6 (d, *J* = 254.8 Hz), 177.5 (t, *J* = 25.8 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -108.7, -105.30 (ddd, *J* = 275.6, 21.5, 8.5 Hz), -103.20 (ddd, *J* = 275.7, 18.9, 7.6 Hz). IR (neat) $\tilde{\nu}$ 2999, 2951, 2909, 2881, 1690, 1578, 1488, 1438, 1392, 1297, 1248, 1179, 1088, 1065, 1054, 1039, 909, 859, 787, 759 726 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{14}NO_2F_3Na$ (M+Na): 320.0869, Found: 320.0871.

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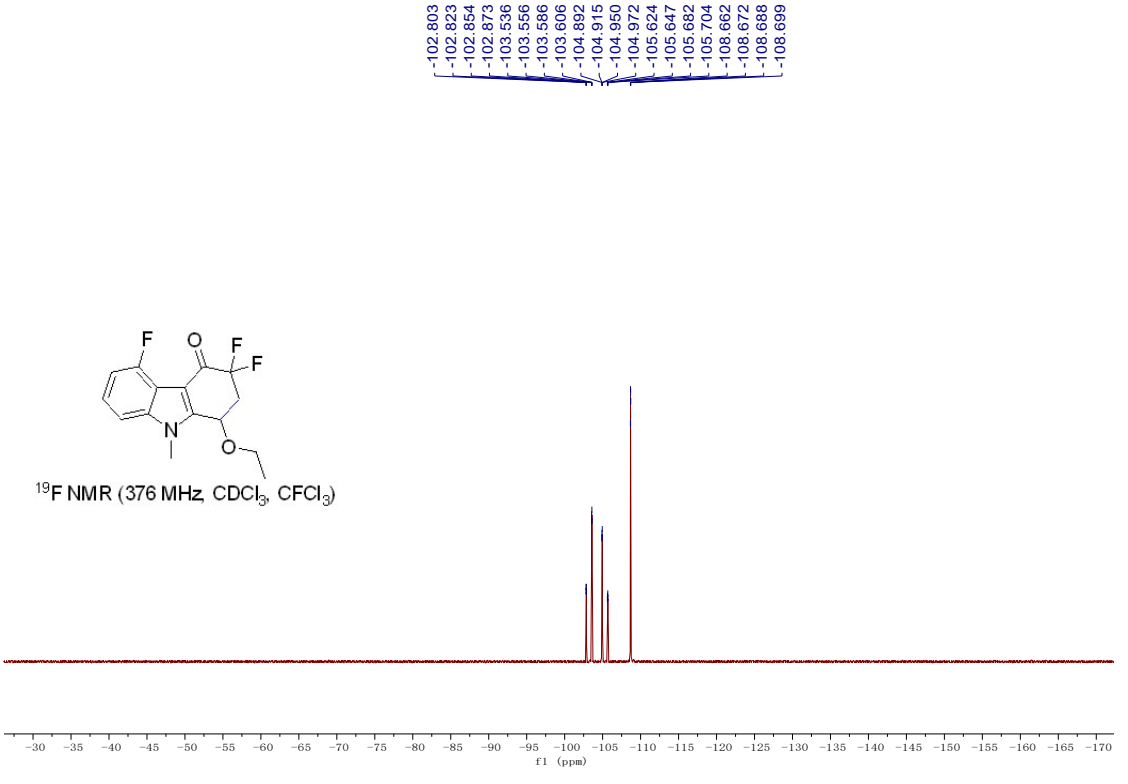
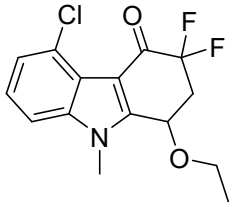
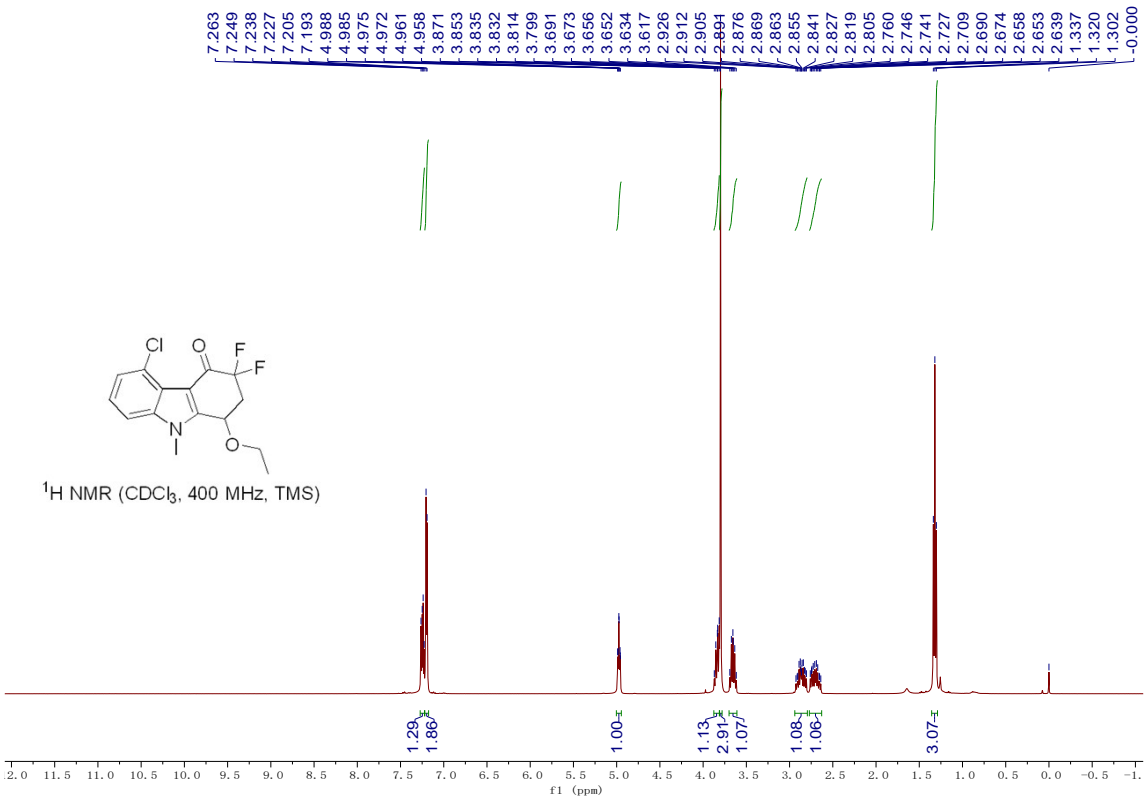
77.067
76.749
67.633
67.578
67.522
64.734
36.819
36.596
36.584
36.360
31.520
15.366
F
O
F
F
N
O
13C NMR (CDCl3, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

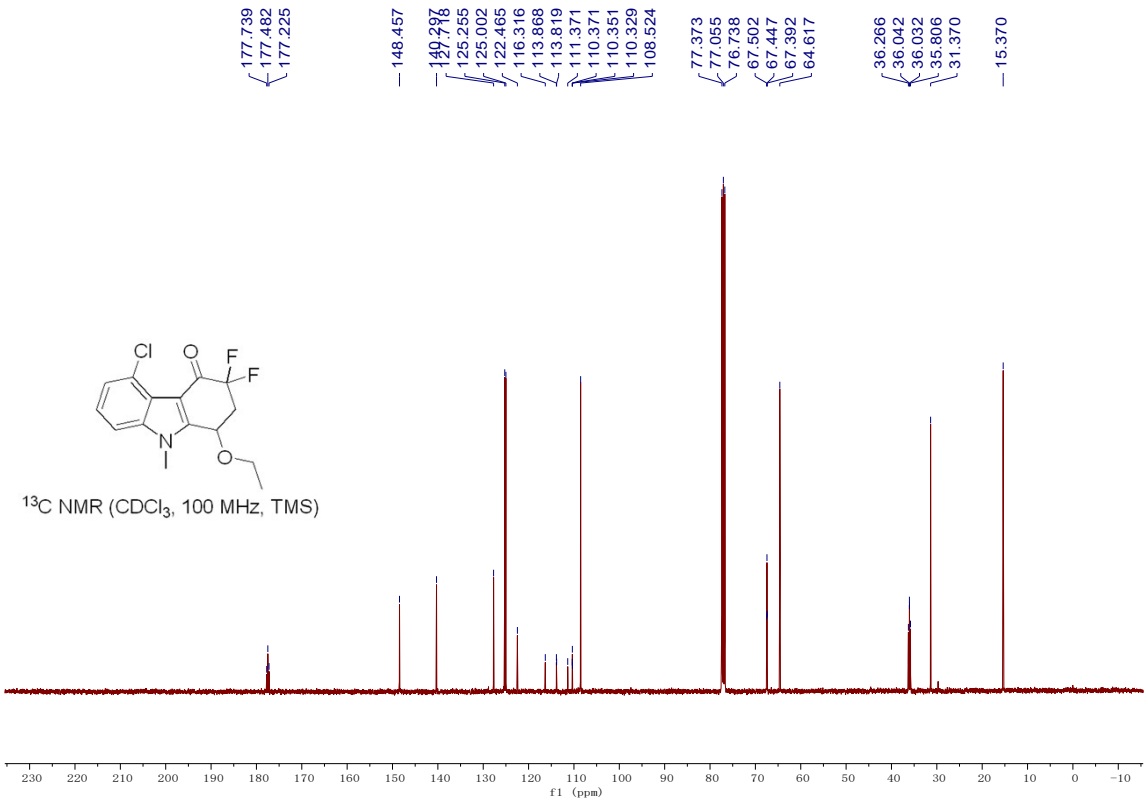

-102.803
-102.823
-102.854
-102.873
-103.536
-103.556
-103.586
-103.606
-104.892
-104.915
-104.950
-104.972
-105.624
-105.647
-105.682
-105.704
-108.662
-108.672
-108.688
-108.699
F
O
F
F
N
O
19F NMR (376 MHz, CDCl3, CFCl3)
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)



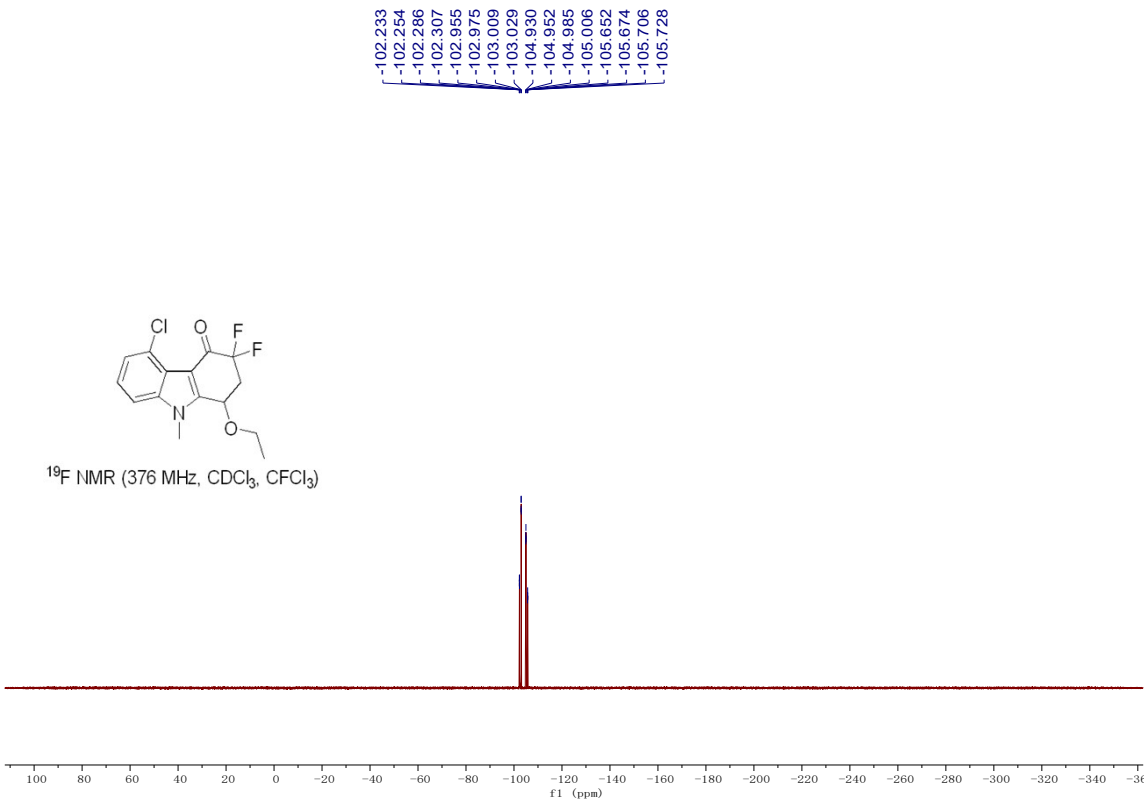
5-chloro-1-ethoxy-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3dp)

A white solid. 62.1 mg, 99% yield. M.P.: 170-172 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.32 (t, *J* = 7.0 Hz, 3H), 2.64-2.76 (m, 1H), 2.81-2.93 (m, 1H), 3.62-3.69 (m, 1H), 3.80 (s, 3H), 3.81-3.87 (m, 1H), 4.98 (td, *J* = 5.4, 1.2 Hz, 1H), 7.20 (d, *J* = 4.8 Hz, 2H), 7.23-7.26 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 31.4, 36.0 (dd, *J* =23.4, 22.4 Hz), 64.6, 67.5 (t, *J* = 5.6 Hz), 108.5, 110.4 (t, *J* = 2.1 Hz), 113.8 (dd, *J* = 251.2, 246.3 Hz), 122.5, 125.0, 125.3, 127.7, 140.3, 148.5, 177.5 (t, *J* = 25.8 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.3 (ddd, *J* = 271.7, 20.5, 8.2 Hz), -102.6 (ddd, *J* = 271.7, 20.2, 7.8 Hz). IR (neat) $\tilde{\nu}$ 2983, 2959, 2925, 2896, 2868, 1691, 1561, 1475, 1427, 1475, 1428, 1336, 1293, 1191, 1178, 1120, 1093, 1076, 1041, 853, 785, 764, 753 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{14}NO_2F_2ClNa$ (M+Na): 336.0573, Found: 336.0580.

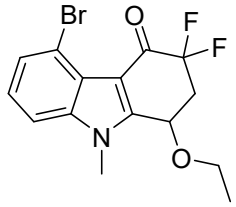




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

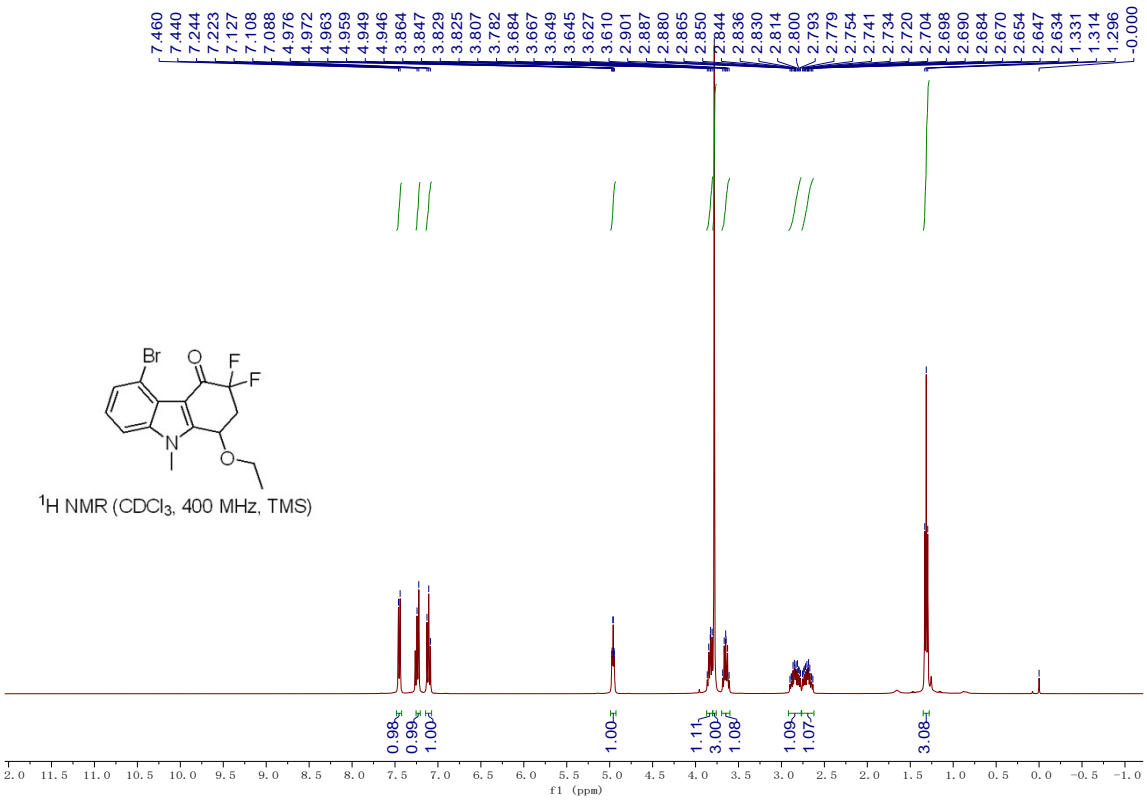


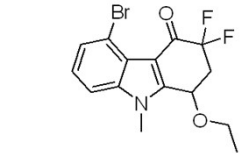
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



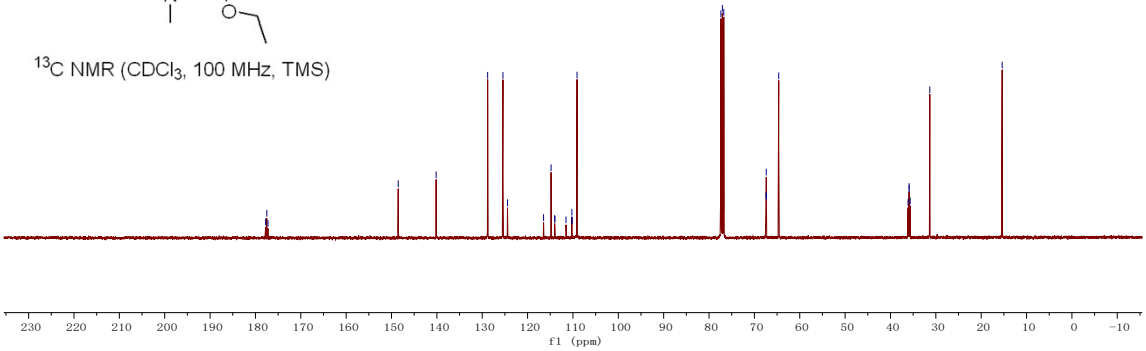
5-bromo-1-ethoxy-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ep)

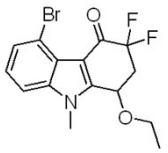
A white solid. 70.2 mg, 98% yield. M.P.: 167-169 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.31 (t, *J* = 7.0 Hz, 3H), 2.63-2.75 (m, 1H), 2.78-2.90 (m, 1H), 3.61-3.68 (m, 1H), 3.78 (s, 3H), 3.81-3.86 (m, 1H), 4.96 (td, *J* = 5.2, 1.6 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 31.3, 35.9 (dd, *J* = 23.3, 22.4 Hz), 64.6, 67.4 (t, *J* = 5.5 Hz), 109.1, 110.2 (t, *J* = 2.0 Hz), 114.0 (dd, *J* =249.6, 244.9 Hz), 116.5, 124.4, 125.4, 128.8, 140.2, 148.5, 177.5 (t, *J* = 25.9 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.4 (ddd, *J* = 271.0, 20.3, 7.9 Hz), -102.6 (ddd, *J* = 270.9, 20.3, 7.8 Hz). IR (neat) $\tilde{\nu}$ 2988, 2955, 2923, 2852, 1690, 1558, 1473, 1417, 1337, 1294, 1273, 1189, 1174, 1094, 1070, 1041, 914, 856, 783, 764, 751 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{14}NO_2F_2BrNa$ (M+Na): 380.0068, Found: 380.0074.



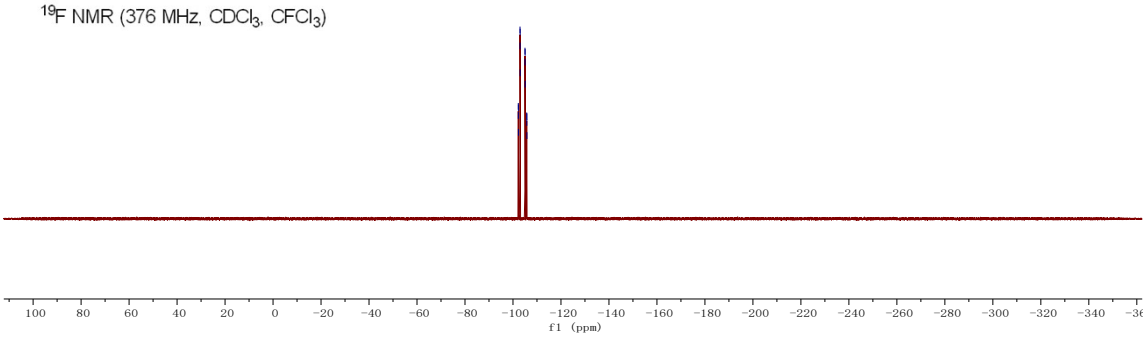


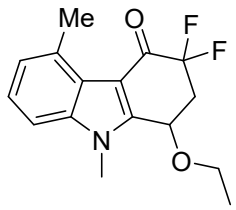
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





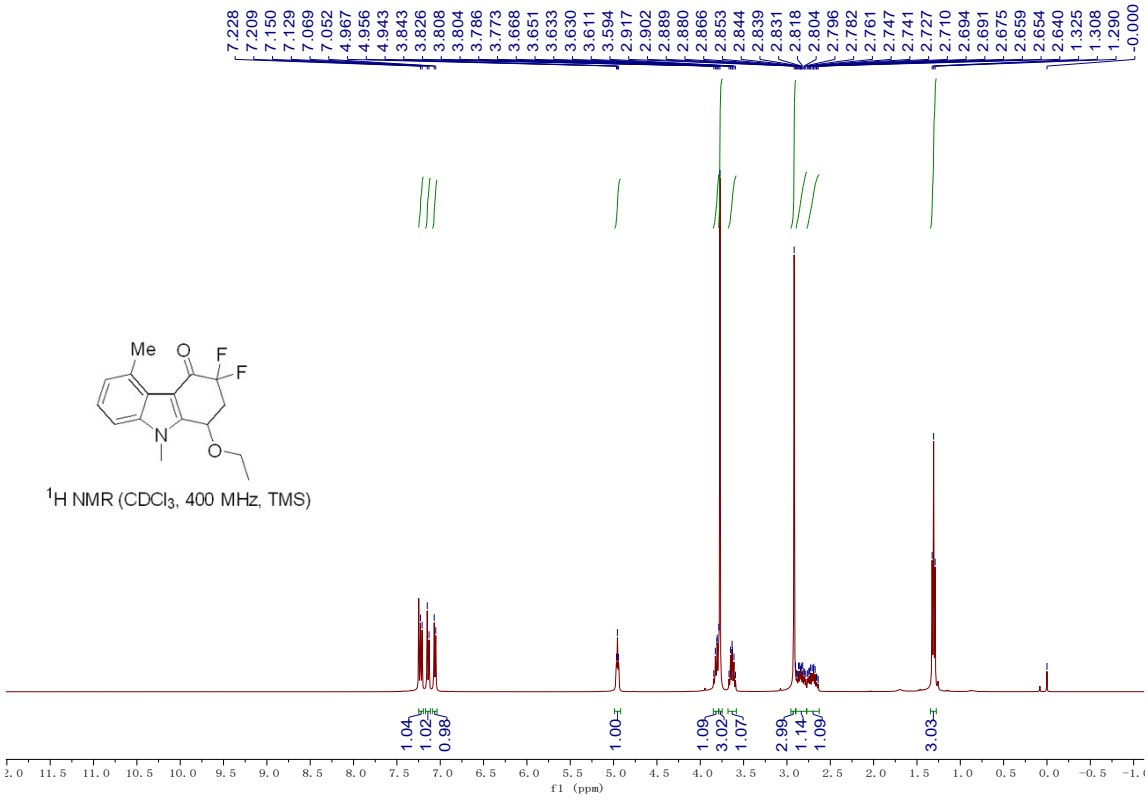
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

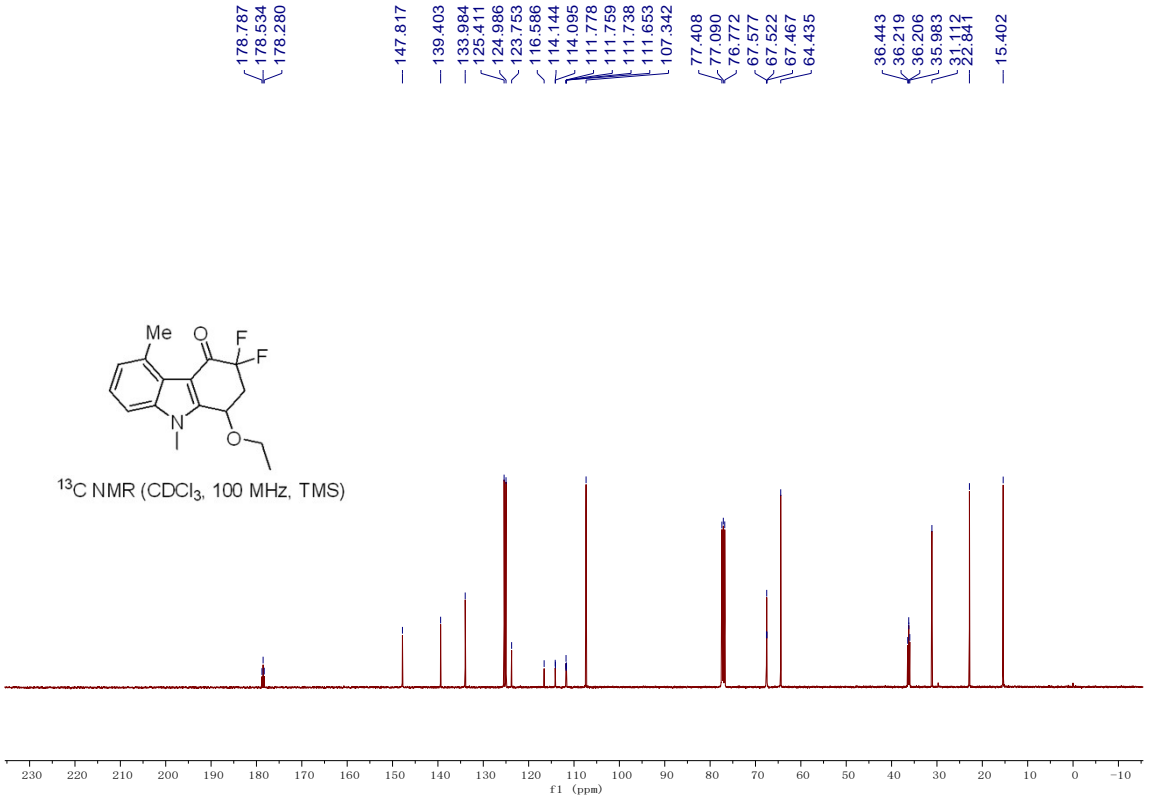




1-ethoxy-3,3-difluoro-5,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3fp)

A white solid. 55.7 mg, 95% yield. M.P.: 125-127 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.31 (t, *J* = 7.0 Hz, 3H), 2.64-2.76 (m, 1H), 2.78-2.90 (m, 1H), 2.92 (s, 3H), 3.59-3.67 (m, 1H), 3.77 (s, 3H), 3.79-3.84 (m, 1H), 4.96 (t, *J* = 5.4 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 22.8, 31.1, 36.2 (dd, *J* = 23.7, 22.4 Hz), 64.4, 67.5 (t, *J* = 5.6 Hz), 111.7, 111.8 (t, *J* = 2.0 Hz), 114.1 (dd, *J* = 249.1, 244.2 Hz), 123.8, 125.0, 125.4, 134.0, 139.4, 147.8, 178.5 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -104.7 (ddd, *J* = 272.8, 20.5, 8.5 Hz), -102.2 (ddd, *J* = 272.8, 19.7, 7.9 Hz). IR (neat) $\tilde{\nu}$ 2975, 2927, 2898, 2876, 1692, 1577, 1524, 1481, 1451, 1428, 1338, 1302, 1283, 1180, 1092, 1062, 1039, 914, 855, 835, 760 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NO_2F_2Na$ (M+Na): 316.1120, Found: 316.1120.

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178.534
178.280
147.817
139.403
133.984
125.411
124.986
123.753
116.586
114.144
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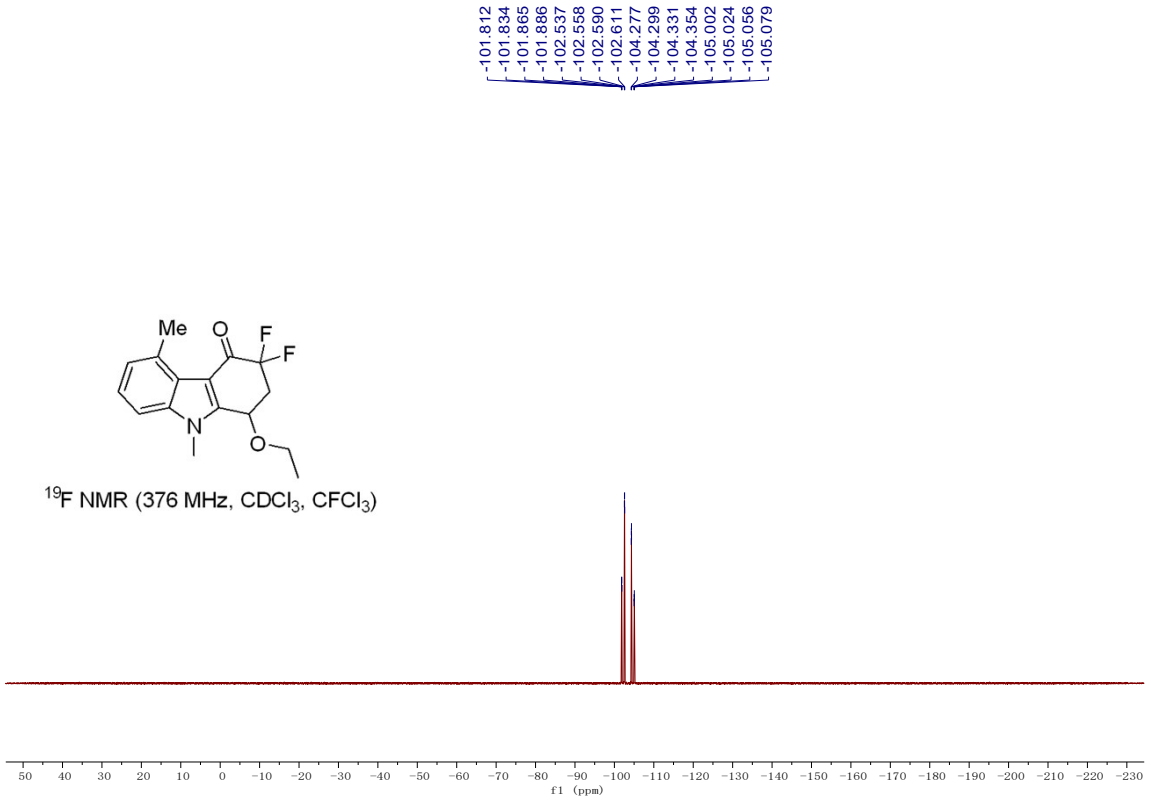
111.778
111.759
111.738
111.653
107.342
77.408
77.090
76.772
67.577
67.522
67.467
64.435
36.443
36.219
36.206
35.983
31.112
22.841
15.402
Me
O
F
F
N
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)


-101.812
-101.834
-101.865
-101.886
-102.537
-102.558
-102.590
-102.611
-104.277
-104.299
-104.331
-104.354
-105.002
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Me
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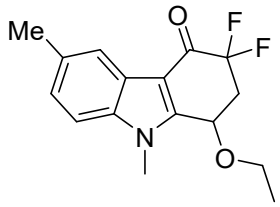
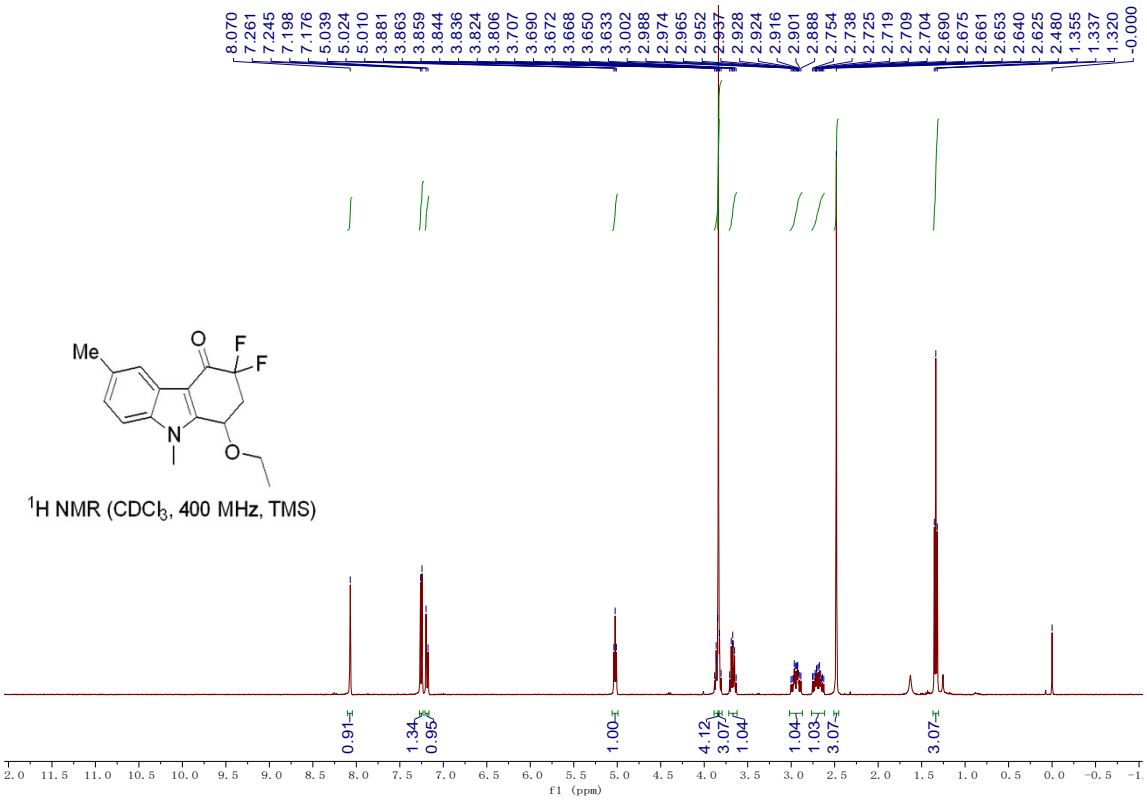
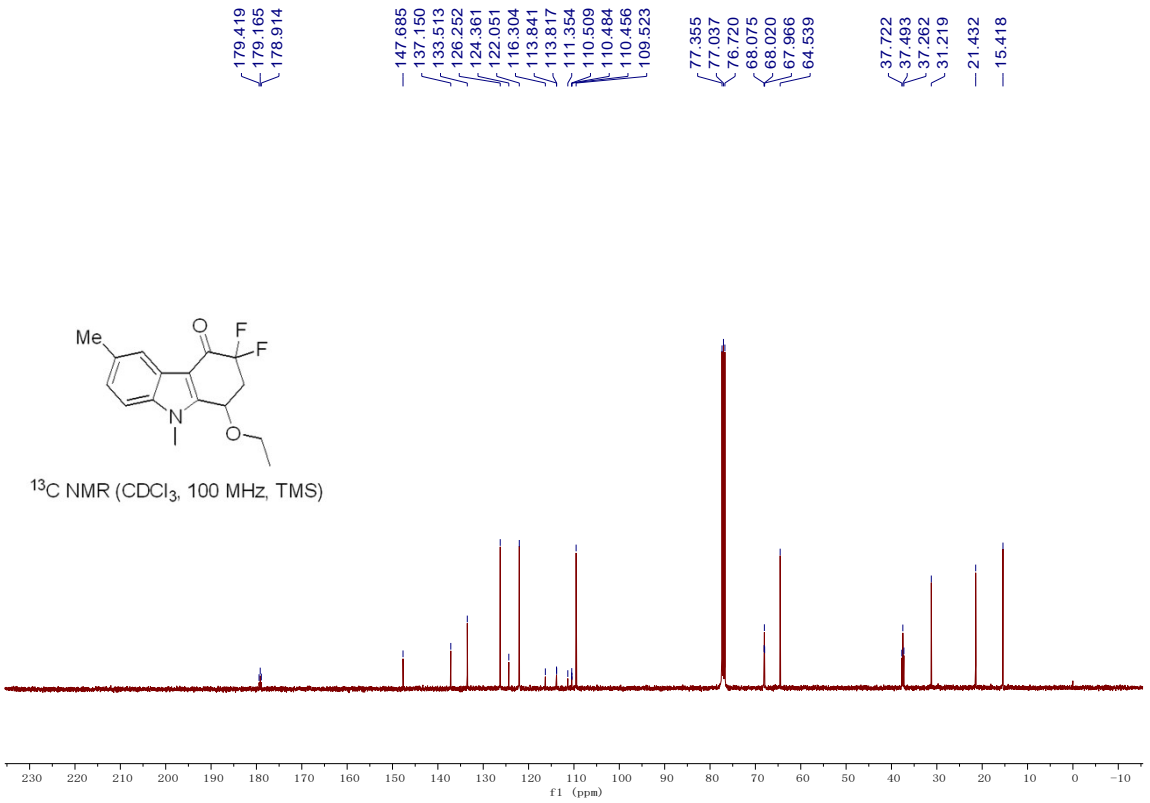
F
F
N
O
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)



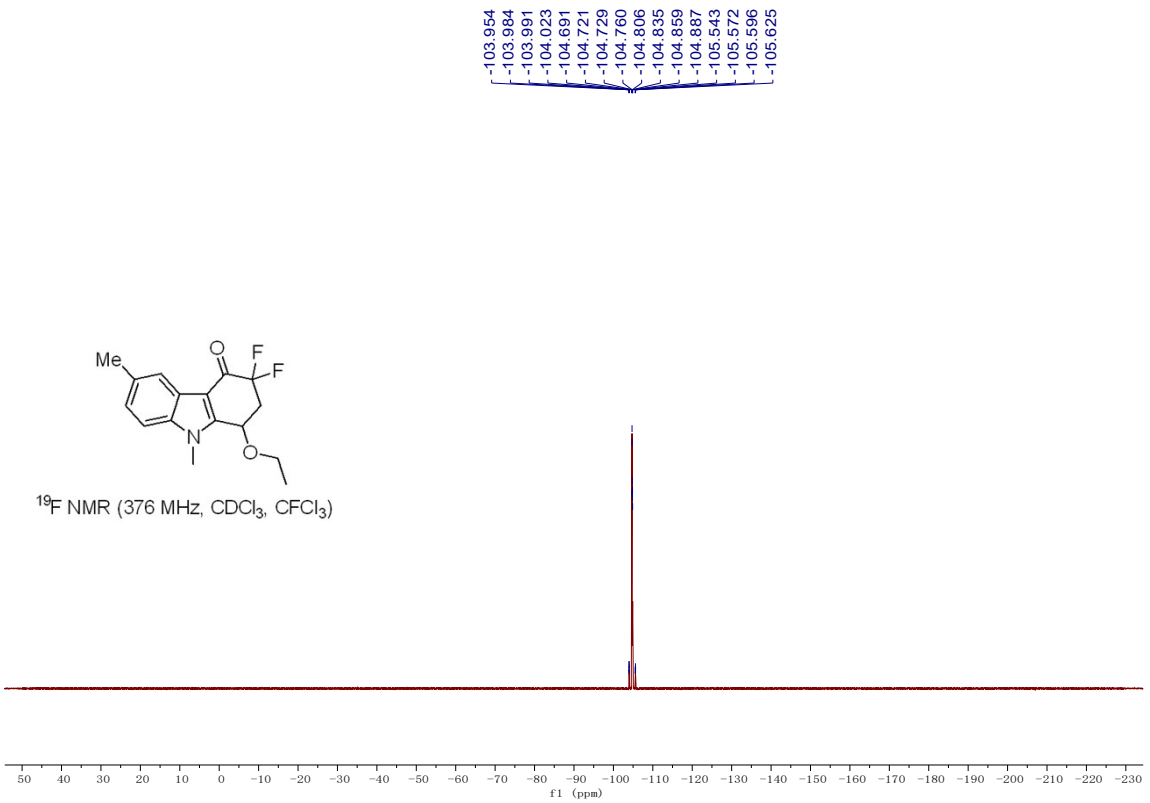
1-ethoxy-3,3-difluoro-6,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3gp)

A white solid. 48.1 mg, 82% yield. M.P.: 102-104 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.34 (t, *J* = 7.0 Hz, 3H), 2.48 (s, 3H), 2.63-2.75 (m, 1H), 2.89-3.00 (m, 1H), 3.63-3.71 (m, 1H), 3.81-3.88 (m, 1H), 3.84 (s, 3H), 5.02 (t, *J* = 5.6 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 6.4 Hz, 1H), 8.07 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 21.4, 31.2, 37.5 (t, *J* = 23.1 Hz), 64.5, 68.0 (t, *J* = 5.5 Hz), 109.5, 110.5 (t, *J* = 2.7 Hz), 113.8 (dd, *J* = 250.3, 247.8 Hz), 122.1, 124.4, 126.3, 133.5, 137.2, 147.7, 179.2 (t, *J* = 25.4 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.2 (ddd, *J* = 277.1, 19.9, 10.9 Hz), -104.3 (ddd, *J* = 277.1, 13.9, 11.3 Hz). IR (neat) $\tilde{\nu}$ 2976, 2927, 2878, 1661, 1538, 1494, 1458, 1418, 1295, 1189, 1089, 1050, 919, 903, 794 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NO_2F_2Na$ (M+Na): 316.1120, Found: 316.1120.

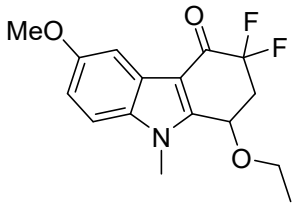




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

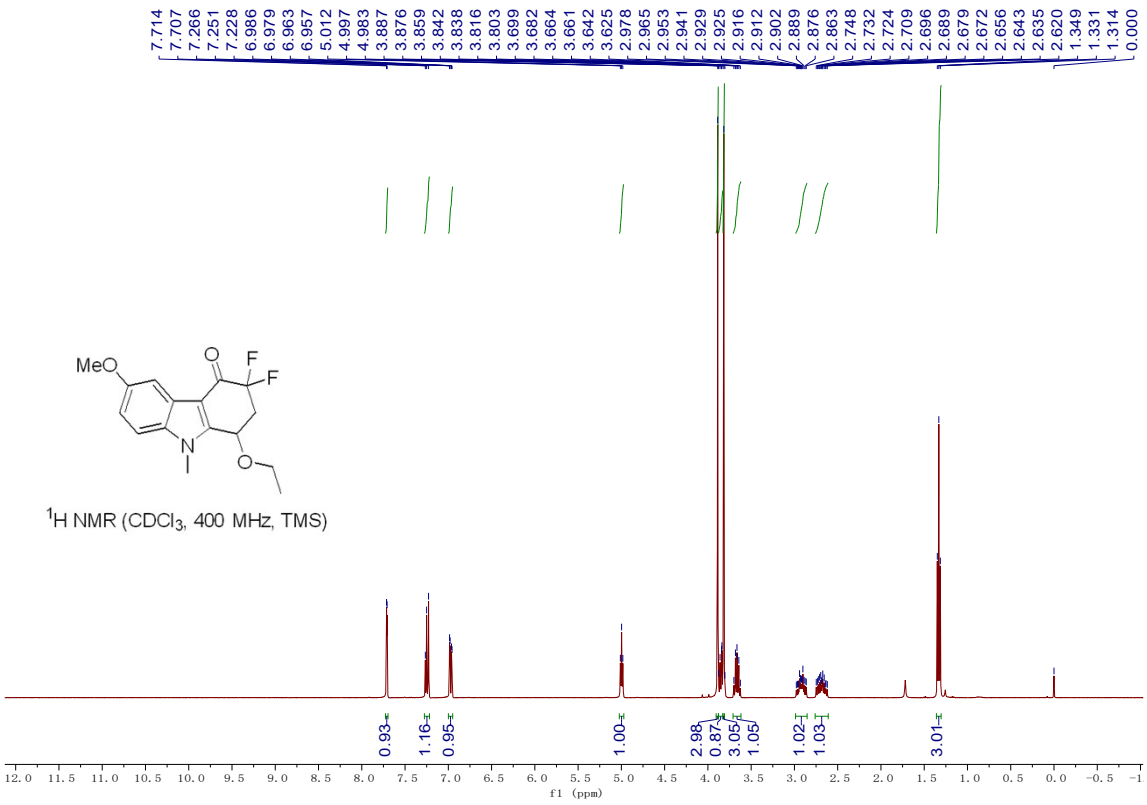


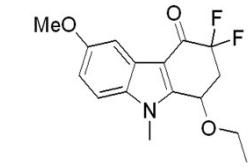
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



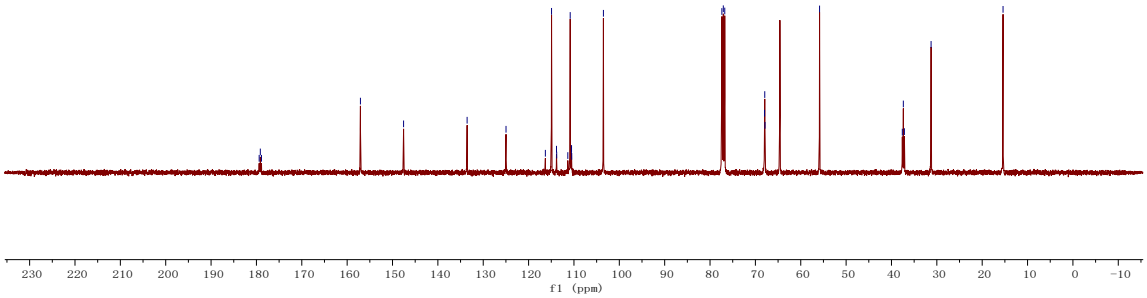
1-ethoxy-3,3-difluoro-6-methoxy-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3hp)

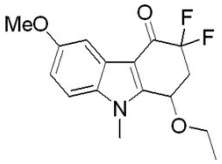
A white solid. 58.2 mg, 94% yield. M.P.: 124-126 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.33 (t, *J* = 7.0 Hz, 3H), 2.62-2.75 (m, 1H), 2.86-2.98 (m, 1H), 3.63-3.70 (m, 1H), 3.80-3.88 (m, 1H), 3.82 (s, 3H), 3.89 (s, 3H), 5.00 (t, *J* = 5.8 Hz, 1H), 6.97 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.25 (t, *J* =5.6 Hz, 1H), 7.71 (d, *J* = 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 31.3, 37.4 (t, *J* = 23.1 Hz), 55.9, 64.6, 67.9 (t, *J* = 5.3 Hz), 103.5, 110.5 (t, *J* = 2.7 Hz), 110.8, 113.8 (dd, *J* = 249.8, 245.5 Hz), 114.9, 116.3, 125.0, 133.6, 147.6, 157.1, 179.1 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.3 (ddd, *J* = 277.9, 21.1, 10.0 Hz), -104.4 (ddd, *J* = 277.5, 15.8, 9.4 Hz). IR (neat) $\tilde{\nu}$ 2983, 2943, 2907, 2842, 1664, 1618, 1488, 1463, 1439, 1341, 1259, 1231, 1200, 1079, 1047, 860, 813, 752 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NO_3F_2Na$ (M+Na): 332.1069, Found: 332.1063.



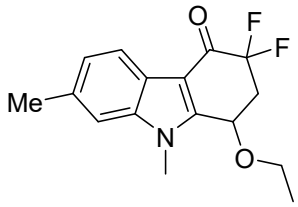


^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



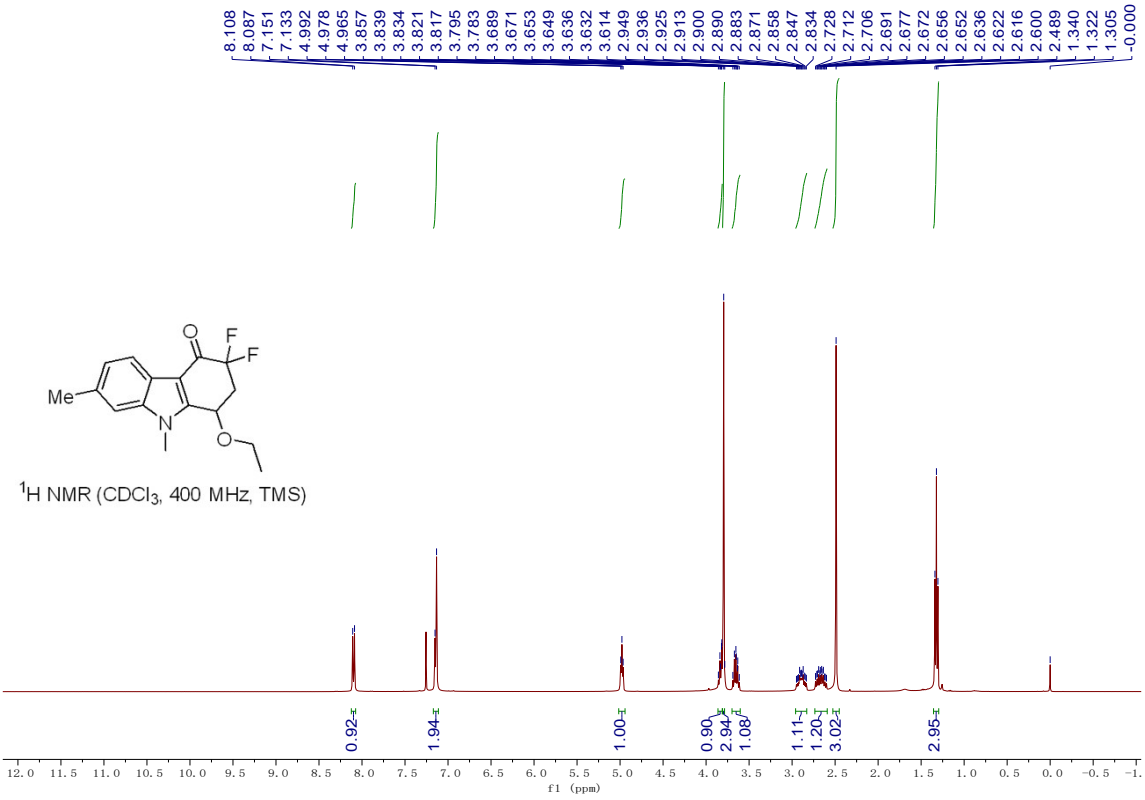


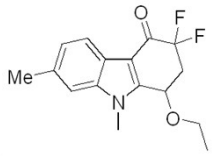
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



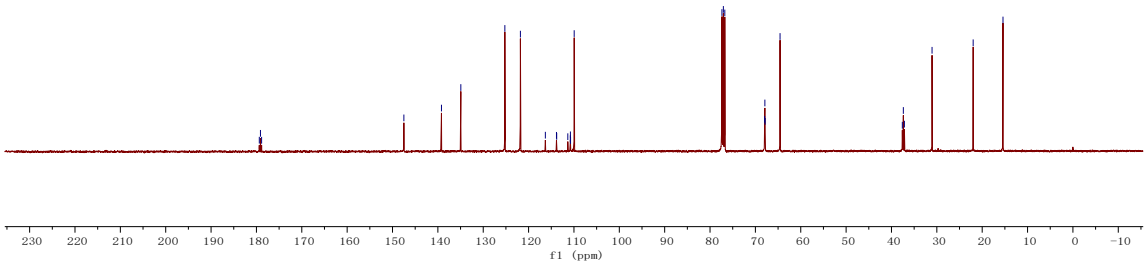
1-ethoxy-3,3-difluoro-7,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3ip)

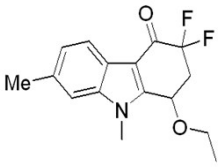
A white solid. 56.3 mg, 96% yield. M.P.: 136-138 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.32 (t, *J* = 7.0 Hz, 3H), 2.49 (s, 3H), 2.60-2.73 (m, 1H), 2.83-2.95 (m, 1H), 2.83-2.95 (m, 1H), 3.61-3.69 (m, 1H), 3.78-3.86 (m, 1H), 3.80 (s, 3H), 4.98 (t, *J* = 5.6 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 22.0, 31.1, 37.4 (t, *J* = 23.1 Hz), 109.9, 110.8 (d, *J* = 2.9 Hz), 113.8 (dd, *J* = 251.4, 246.6 Hz), 121.8, 125.2, 134.9, 139.2, 147.5, 179.1 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.5 (ddd, *J* = 277.7, 17.4, 9.7 Hz), -102.5 (ddd, *J* = 277.6, 19.8, 10.0 Hz). IR (neat) $\tilde{\nu}$ 2987, 2943, 2912, 2881, 1669, 1541, 1481, 1312, 1279, 1188, 1113, 1087, 1047, 905, 830, 813 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NO_2F_2Na$ (M+Na): 316.1120, Found: 316.1120.



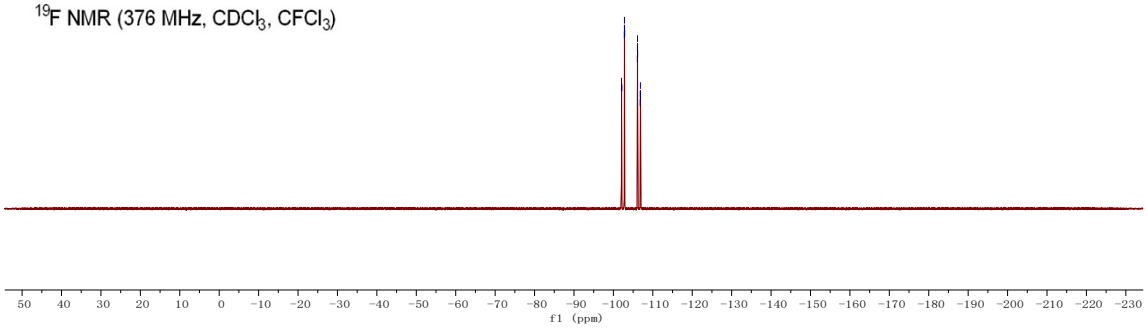


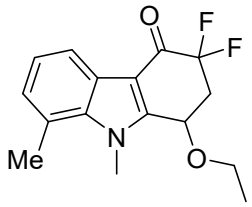
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





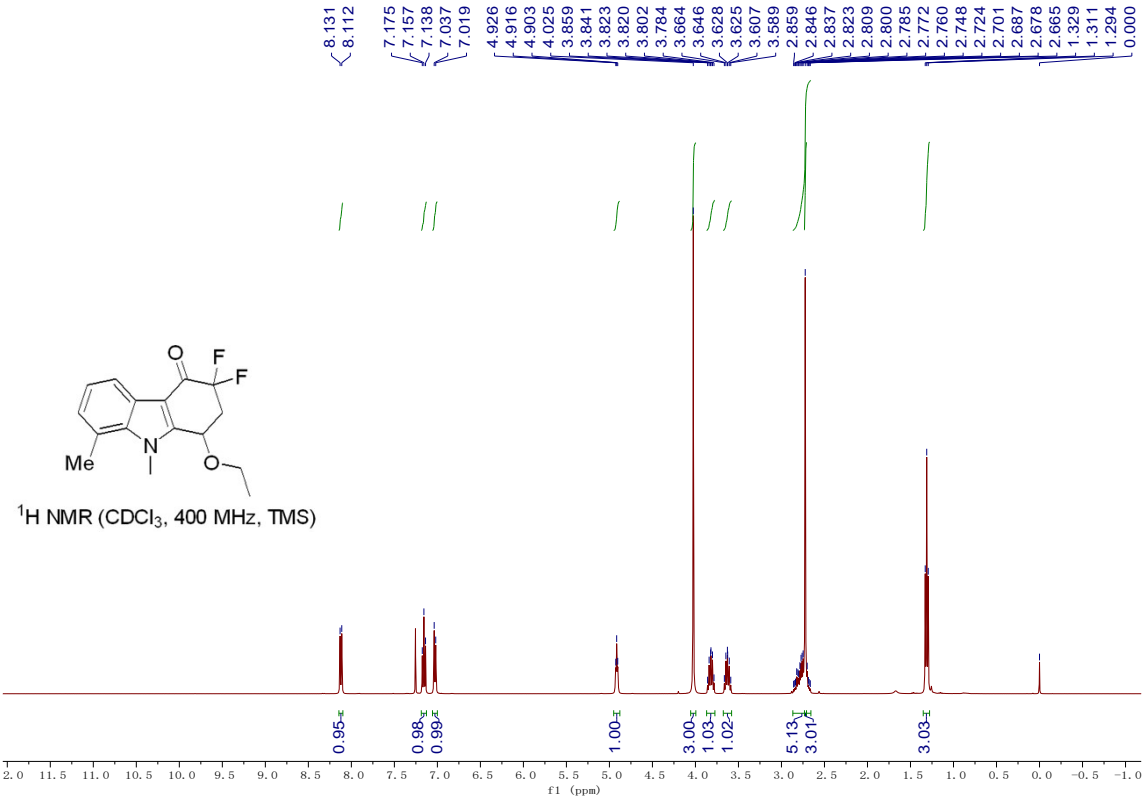
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

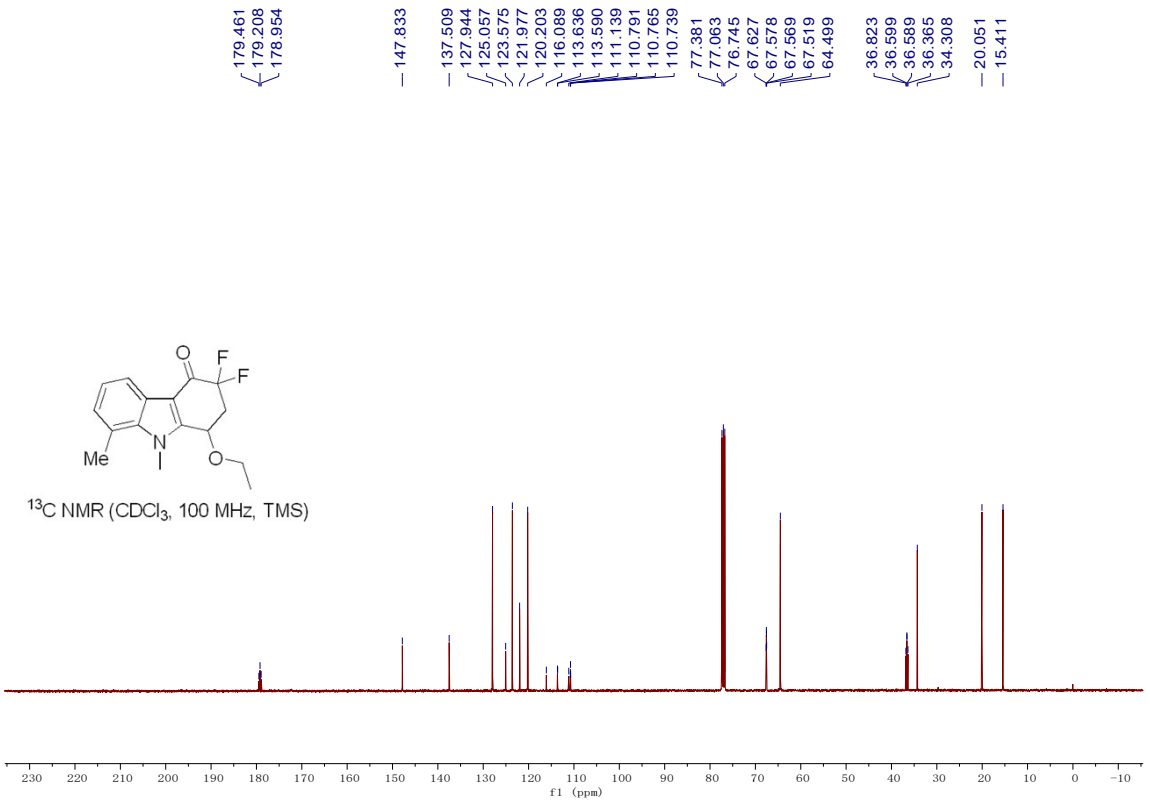


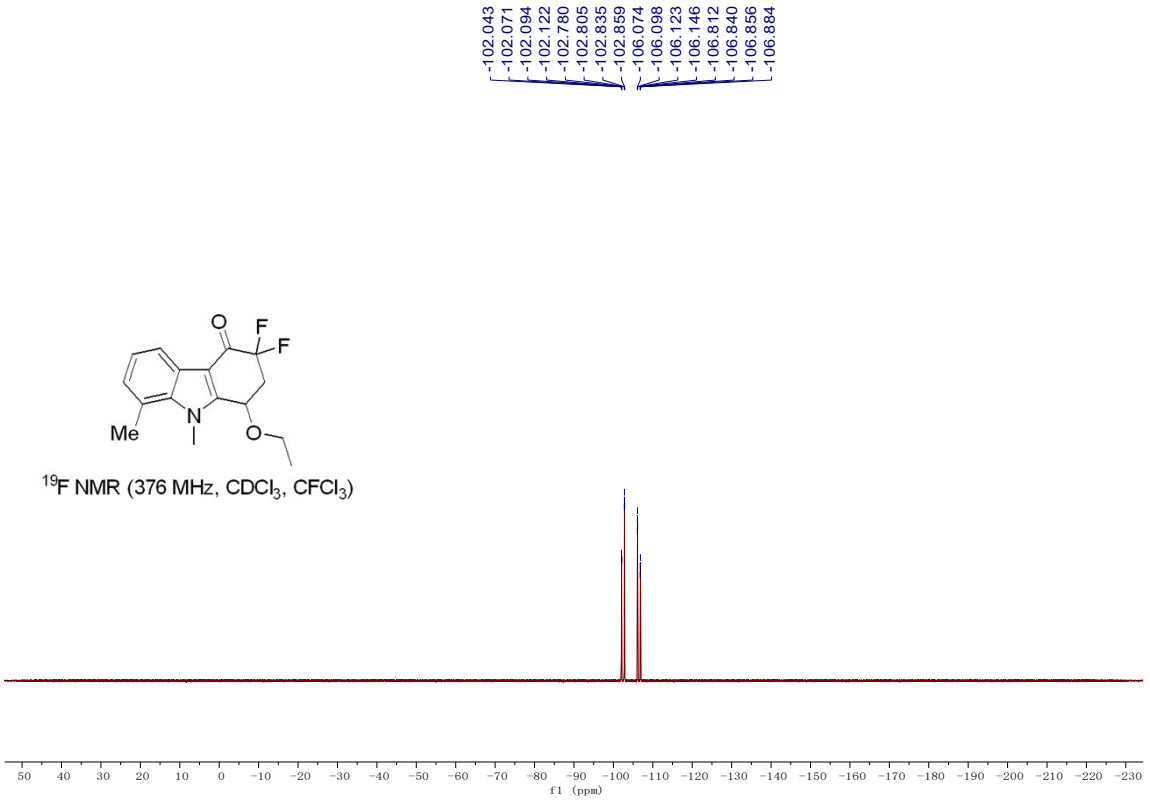


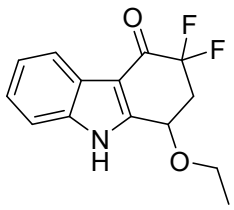
1-ethoxy-3,3-difluoro-8,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3jp)

A white solid. 55.7 mg, 95% yield. M.P.: 157-159 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.31 (t, *J* = 7.0 Hz, 3H), 2.67-2.86 (m, 1H), 2.72 (s, 3H), 3.59-3.66 (m, 1H), 3.78-3.86 (m, 1H), 4.03 (s, 3H), 4.91 (t, *J* = 5.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.4, 20.1, 34.3, 36.6 (dd, *J* = 23.4, 22.4 Hz), 64.5, 67.6 (dd, *J* = 5.8, 4.9 Hz), 110.8 (t, *J* = 2.6 Hz), 113.6 (dd, *J* = 251.4, 246.7 Hz), 120.2, 122.0, 123.6, 125.1, 127.9, 137.5, 147.8, 179.2 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.5 (ddd, *J* = 277.7, 17.4, 9.7 Hz), -102.5 (ddd, *J* = 277.6, 19.8, 10.0 Hz). IR (neat) $\tilde{\nu}$ 2973, 2930, 2909, 2863, 1652, 1543, 1483, 1411, 1395, 1326, 1193, 1096, 1063, 1010, 940, 845, 831, 795, 745 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NO_2F_2Na$ (M+Na): 316.1120, Found: 316.1121.



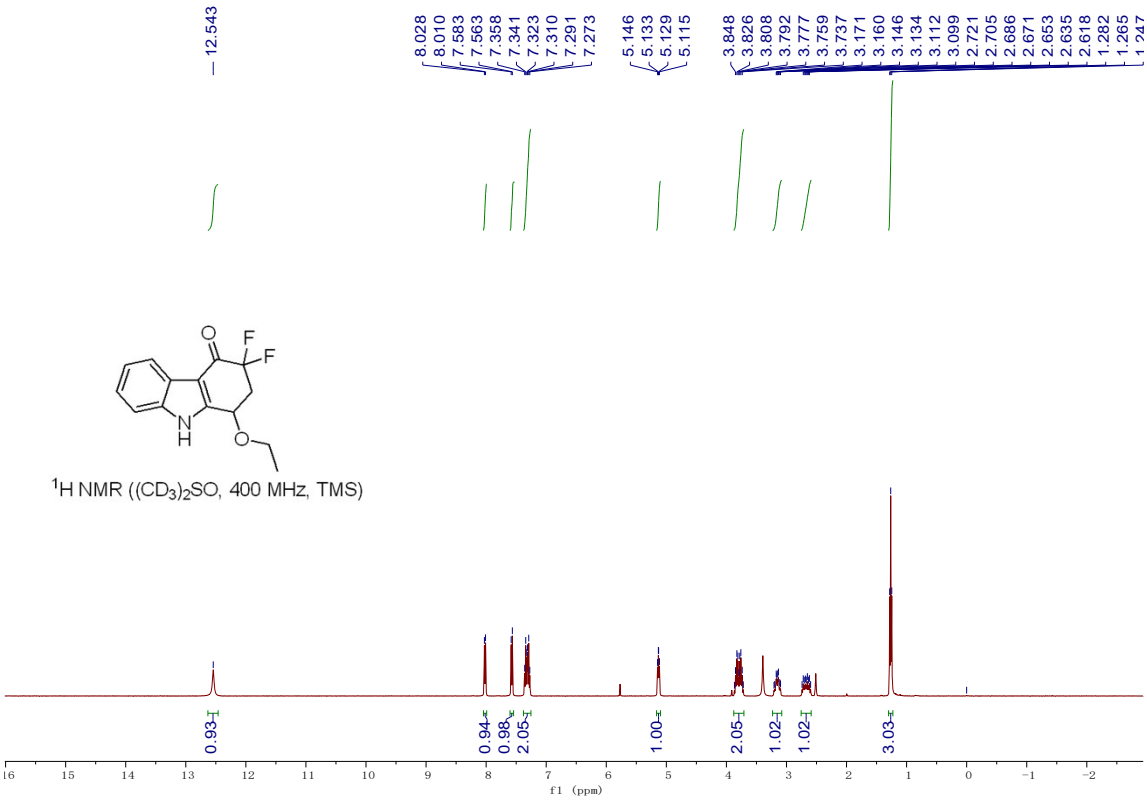

179.461
179.208
178.954
147.833
137.509
127.944
125.057
123.575
121.977
120.203
116.089
113.636
113.590
111.139
110.791
110.765
110.739
77.381
77.063
76.745
67.627
67.578
67.569
67.519
64.499
36.823
36.599
36.589
36.365
34.308
20.051
15.411
O
F
F
Me
N
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

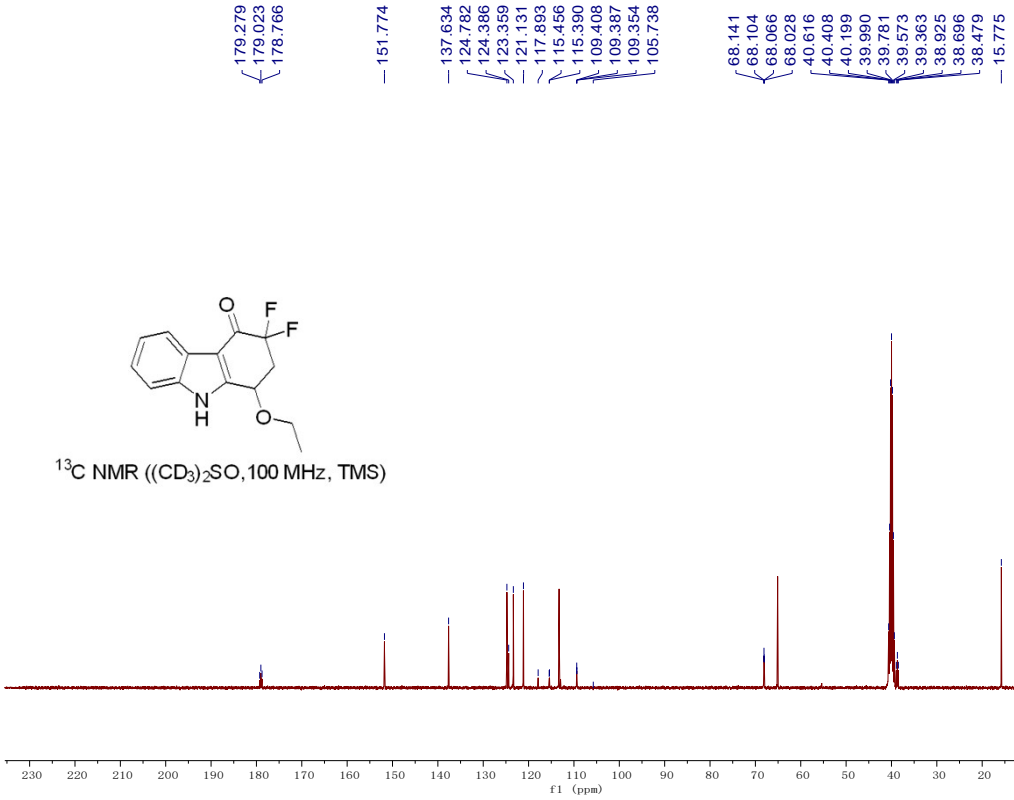

-102.043
-102.071
-102.094
-102.122
-102.780
-102.805
-102.835
-102.859
-106.074
-106.098
-106.123
-106.146
-106.812
-106.840
-106.856
-106.884
O
F
F
Me
N
O
19F NMR (376 MHz, CDCl3, CFCl3)
f1 (ppm)

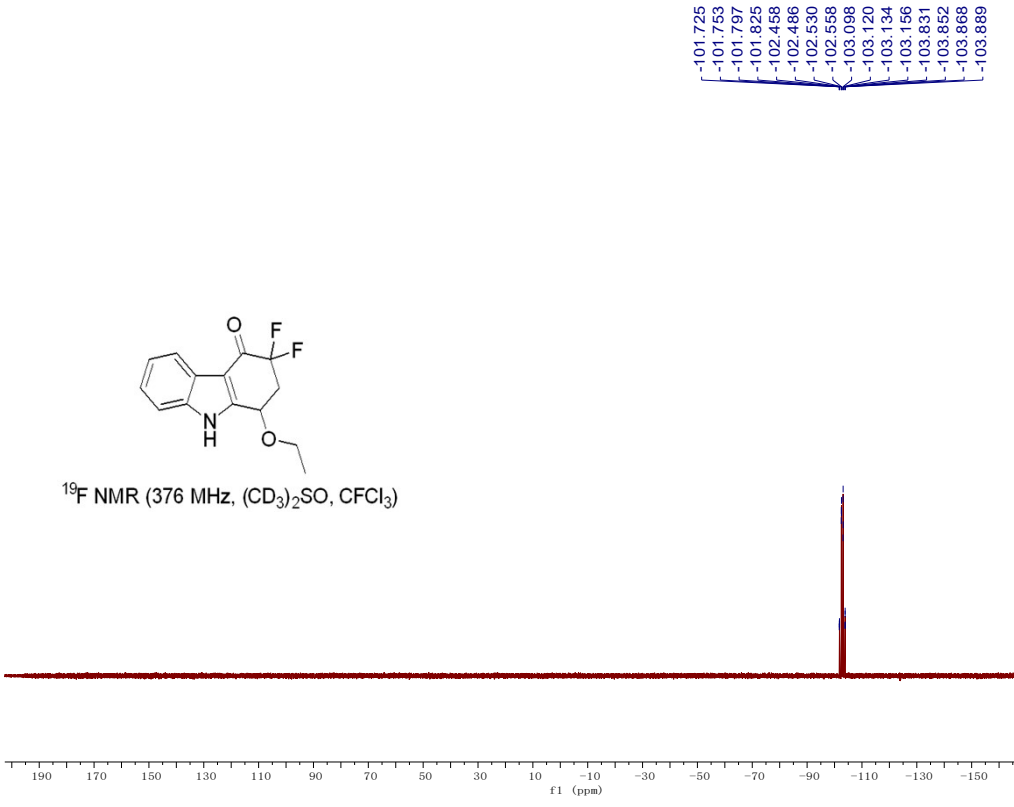


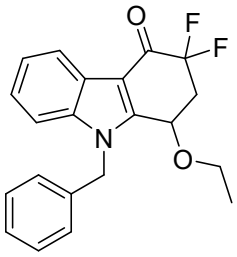
1-ethoxy-3,3-difluoro-1,2,3,9-tetrahydro-4H-carbazol-4-one (3kp)

A white solid. 45.1 mg, 85% yield. M.P.: 191-193 °C. ^{1}H NMR ($(CD_3)_2SO$, TMS, 400 MHz) δ 1.26 (t, *J* = 7.0 Hz, 3H), 2.60-2.74 (m, 1H), 3.10-3.21 (m, 1H), 3.72-3.87 (m, 2H), 5.13 (dd, *J* = 6.8, 5.2 Hz, 1H), 7.27-7.36 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 12.5 (s, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 15.8, 38.7 (t, *J* = 22.4 Hz), 65.1, 68.1 (dd, *J* = 7.6, 3.8 Hz), 109.4 (dd, *J* = 3.3, 2.1 Hz), 109.4, 113.0, 115.4 (dd, *J* = 250.3, 243.7 Hz), 121.1, 123.4, 124.4, 124.8, 137.6, 151.8, 179.0 (t, *J* = 25.8 Hz). ^{19}F NMR ($(CD_3)_2SO$, $CFCl_3$, 376 MHz) δ -103.5 (ddd, *J* = 276.0, 13.8, 8.1 Hz), -102.1 (ddd, *J* = 275.8, 27.2, 10.4 Hz). IR (neat) $\tilde{\nu}$ 3185, 2979, 2920, 2883, 2847, 1649, 1587, 1470, 1456, 1379, 1353, 1284, 1180, 1121, 1091, 1045, 915, 880, 784, 758 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{13}NO_2F_2$ (M^+): 265.0909, Found: 265.0912.



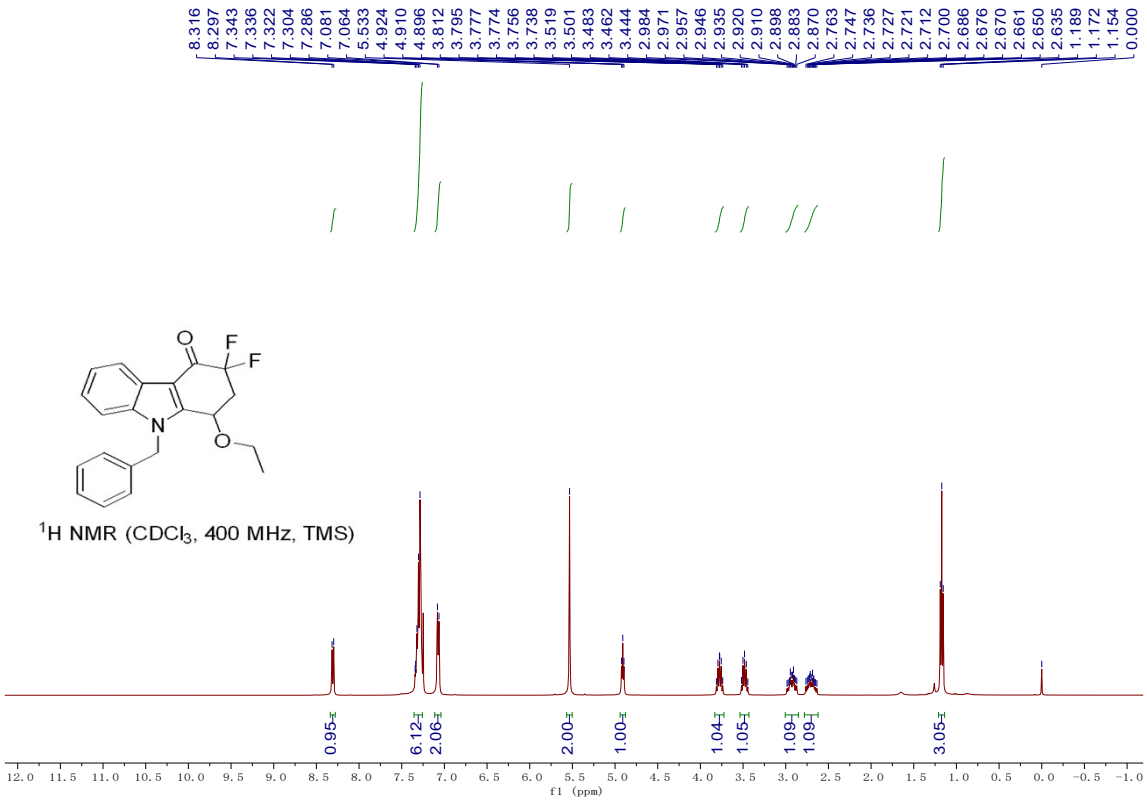

179.279
179.023
178.766
151.774
137.634
124.782
124.386
123.359
121.131
117.893
115.456
115.390
109.408
109.387
109.354
105.738
68.141
68.104
68.066
68.028
40.616
40.408
40.199
39.990
39.781
39.573
39.363
38.925
38.696
38.479
15.775
O
F
F
N
H
O
^{13}C NMR ((CD$_3$)$_2$SO,100 MHz, TMS)
f1 (ppm)

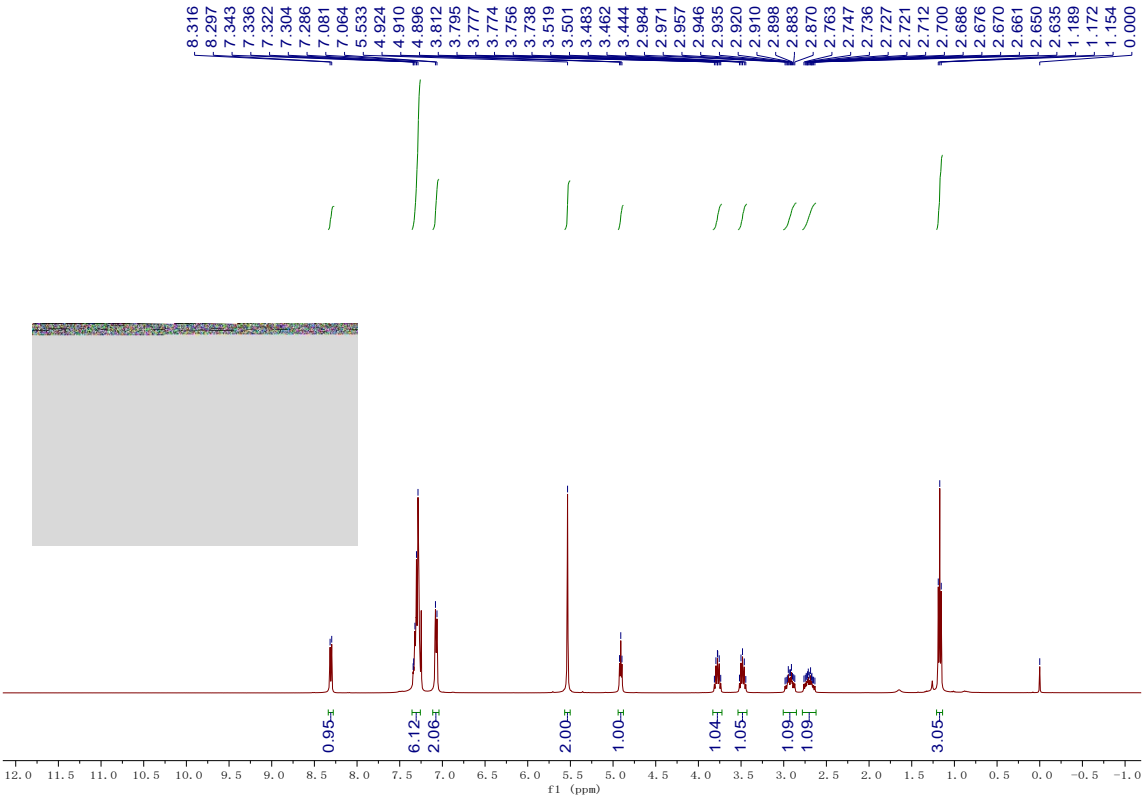

-101.725
-101.753
-101.797
-101.825
-102.458
-102.486
-102.530
-102.558
-103.098
-103.120
-103.134
-103.156
-103.831
-103.852
-103.868
-103.889
O
F
F
N
H
O
^{19}F NMR (376 MHz, (CD$_3$)$_2$SO, CFCl$_3$)
f1 (ppm)

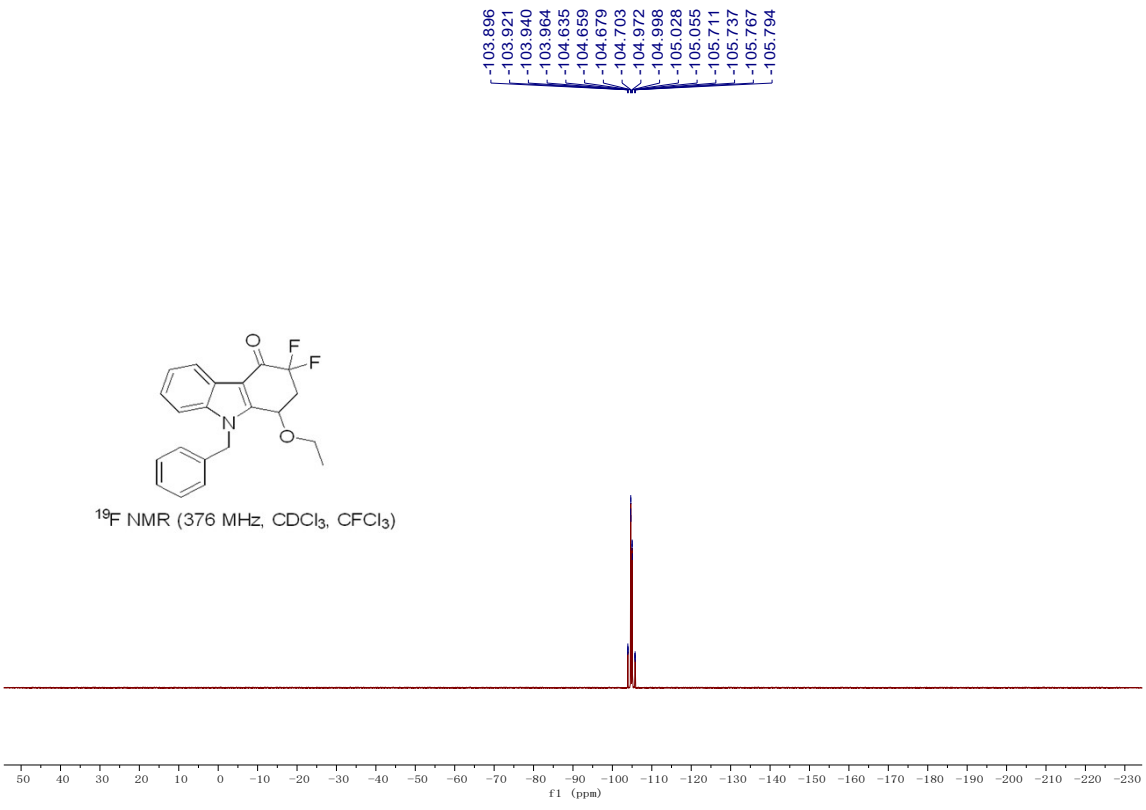


9-benzyl-1-ethoxy-3,3-difluoro-1,2,3,9-tetrahydro-4H-carbazol-4-one (3lp)

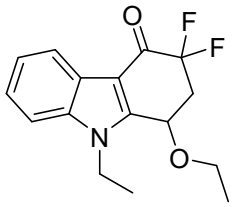
A white solid. 54.6 mg, 93% yield. M.P.: 101-103 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.17 (t, *J* = 7.0 Hz, 3H), 2.64-2.76 (m, 1H), 2.87-2.98 (m, 1H), 3.44-3.52 (m, 1H), 3.74-3.81 (m, 1H), 4.91 (t, *J* = 5.6 Hz, 1H), 5.53 (s, 2H), 7.07 (d, *J* = 6.8 Hz, 2H), 7.29-7.34 (m, 6H), 8.31 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.2, 37.5 (t, *J* = 23.0 Hz), 48.2, 64.8, 68.1 (t, *J* = 5.4 Hz), 110.7, 111.2 (t, *J* = 2.6 Hz), 113.7 (dd, *J* = 249.5, 246.0 Hz), 122.4, 123.8, 124.3, 125.0, 126.2, 127.9, 129.0, 135.7, 138.6, 147.9, 179.5 (t, *J* = 25.6 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.4 (ddd, *J* = 278.2, 21.4, 10.0 Hz), -104.3 (ddd, *J* = 278.1, 16.5, 9.2 Hz). IR (neat) $\tilde{\nu}$ 2981, 2930, 2902, 2869, 1685, 1529, 1472, 1449, 1438, 1287, 1178, 1092, 1052, 863, 755, 738 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{19}NO_2F_2Na$ (M+Na): 378.1276, Found: 378.1288.





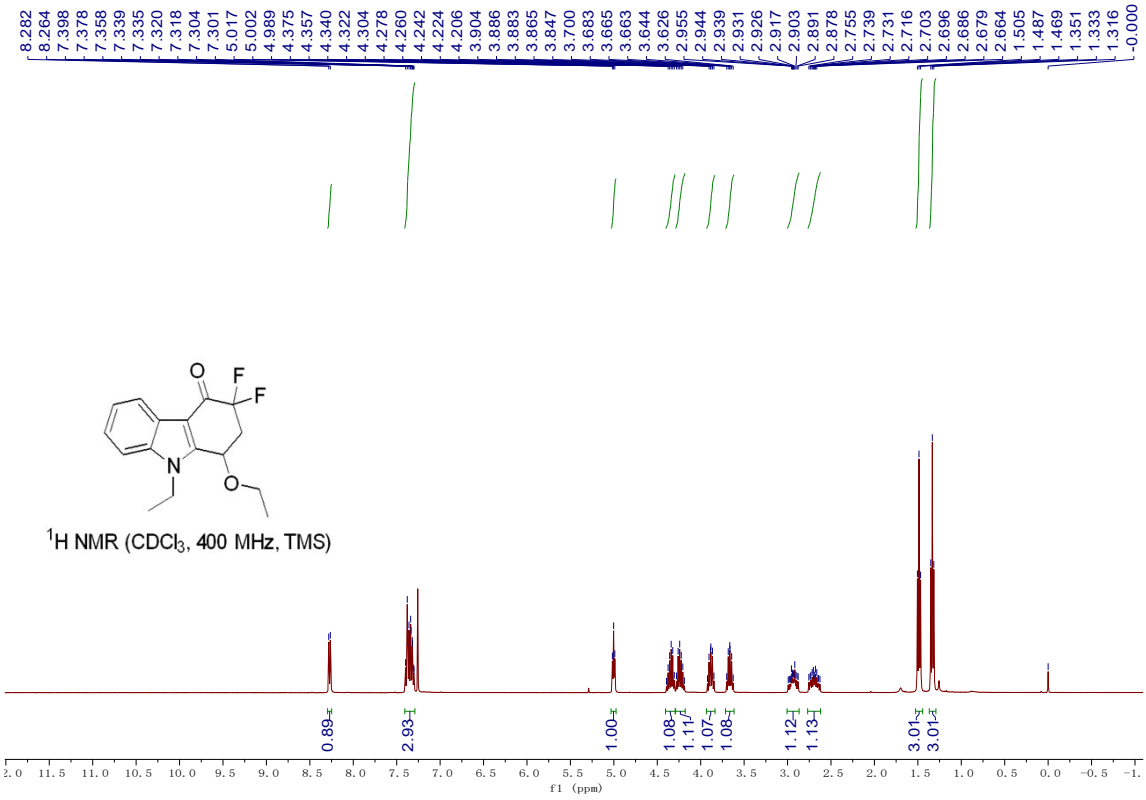


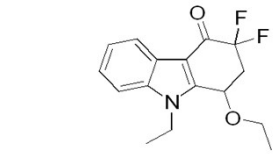
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



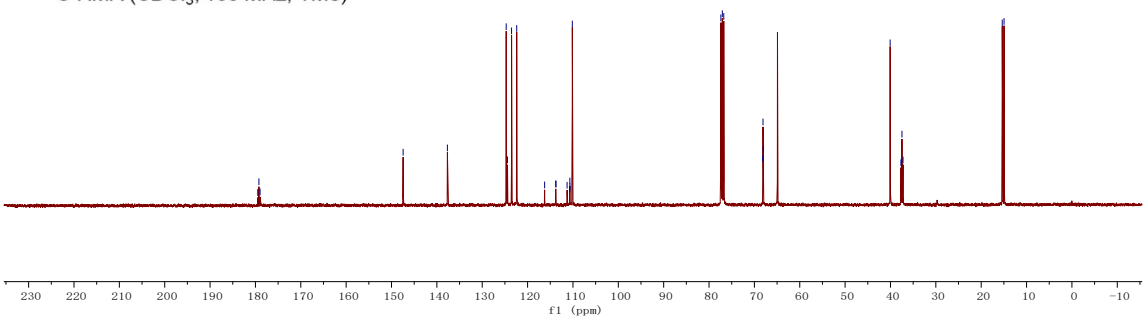
1-ethoxy-9-ethyl-3,3-difluoro-1,2,3,9-tetrahydro-4H-carbazol-4-one (3mp)

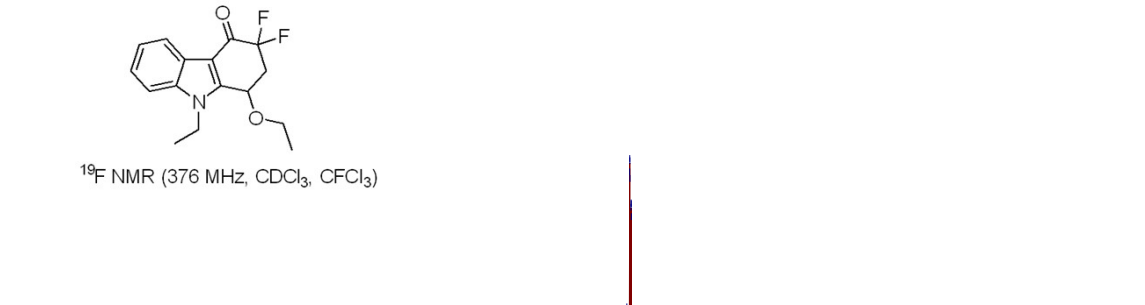
A colorless oil. 68.2 mg, 96% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.33 (t, *J* = 7.0 Hz, 3H), 1.49 (t, *J* = 7.2 Hz, 3H), 2.63-2.76 (m, 1H), 2.88-2.99 (m, 1H), 3.63-3.70 (m, 1H), 3.85-3.92 (m, 1H), 4.19-4.28 (m, 1H), 4.30-4.39 (m, 1H), 5.00 (t, *J* = 5.6 Hz, 1H), 7.30-7.40 (m, 3H), 8.27 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.0, 15.4, 37.5 (t, *J* = 23.0 Hz), 40.1, 64.9, 68.1 (t, *J* = 5.4 Hz), 110.1, 110.7 (t, *J* = 2.4 Hz), 113.8 (dd, *J* = 251.1, 247.0 Hz), 122.4, 123.5, 124.4, 124.7, 137.7, 147.4, 179.2 (t, *J* = 25.5 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -105.4 (ddd, *J* = 278.2, 21.4, 10.0 Hz), -104.3 (ddd, *J* = 278.1, 16.5, 9.2 Hz). IR (neat) $\tilde{\nu}$ 2977, 2940, 2876, 1668, 1536, 1477, 1450, 1404, 1294, 1183, 1095, 1054, 879, 86, 756, 733 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{17}NO_2F_2Na$ (M+Na): 316.1120, Found: 316.1117.



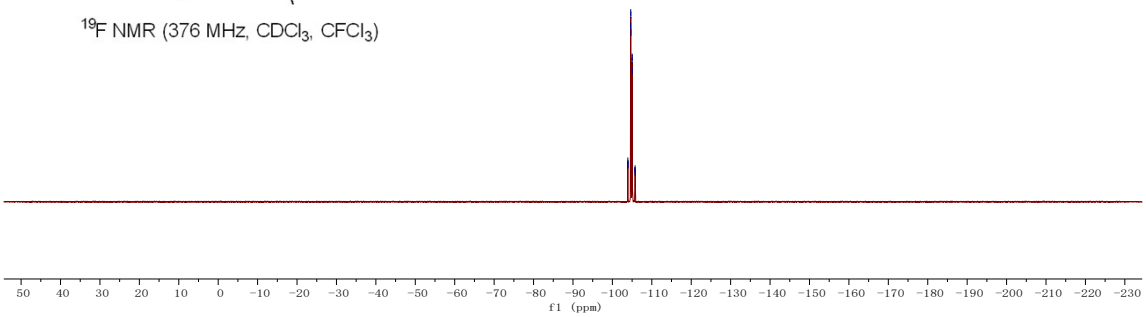


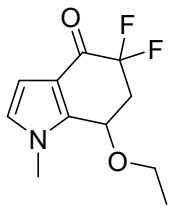
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)





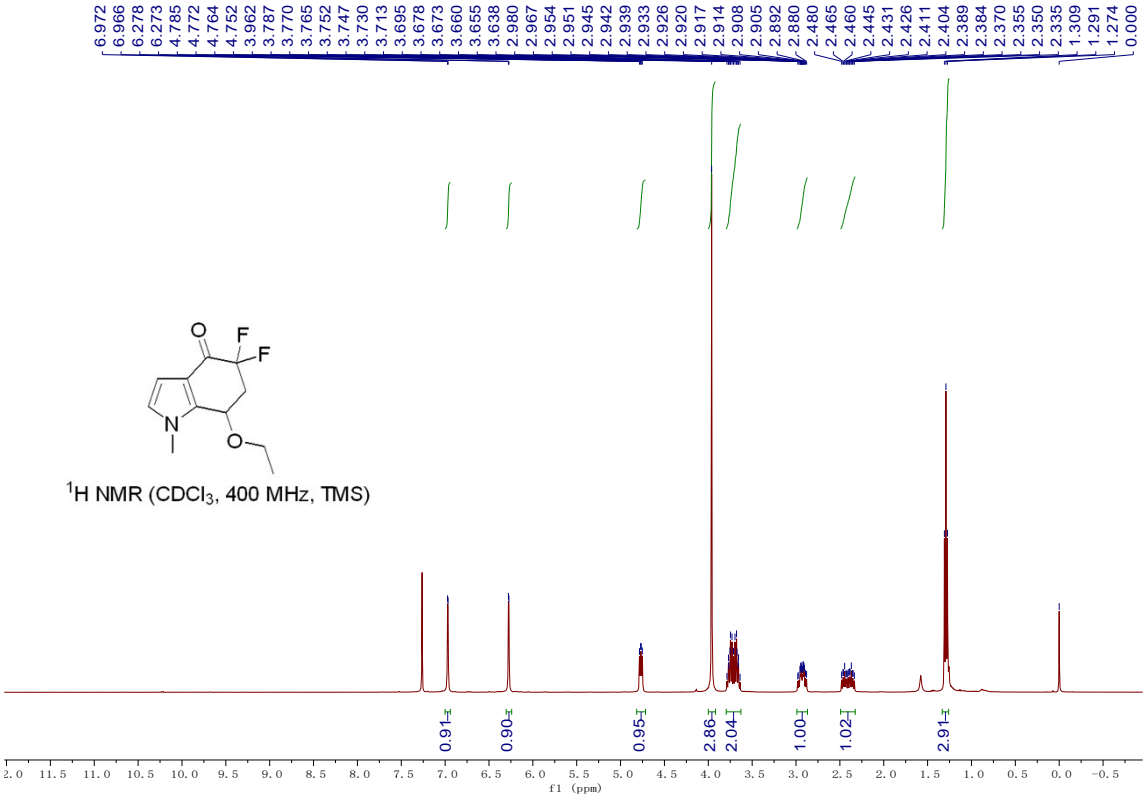
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)

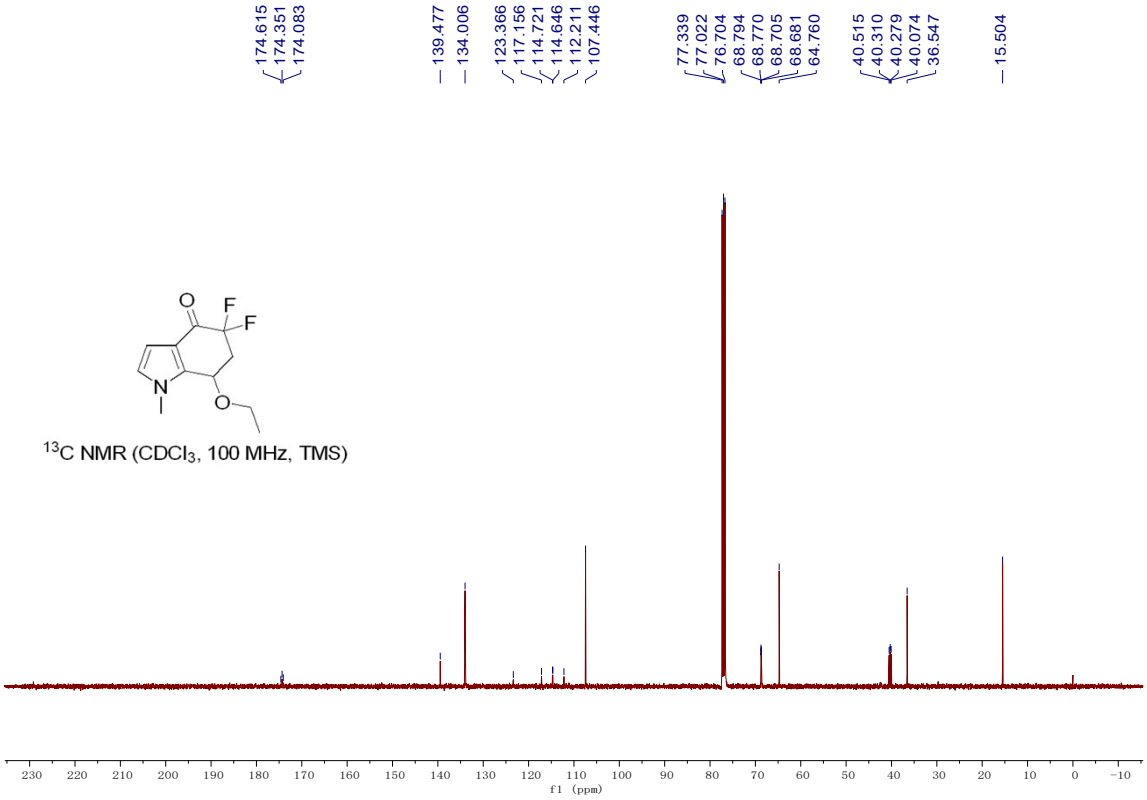




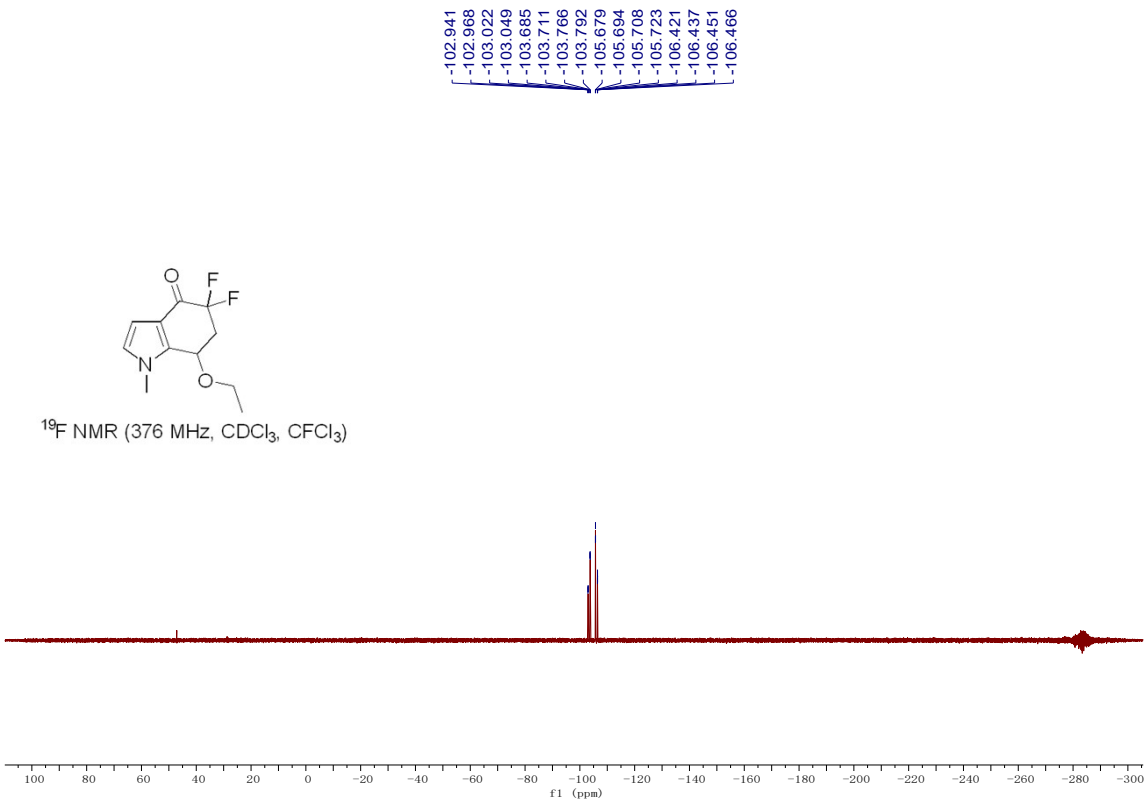
7-ethoxy-5,5-difluoro-1-methyl-1,5,6,7-tetrahydro-4H-indol-4-one (3op)

A colorless oil. 32.1 mg, 70% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.29 (t, J = 7.0 Hz, 3H), 2.34-2.48 (m, 1H), 2.88-2.98 (m, 1H), 3.64-3.79 (m, 2H), 3.96 (s, 3H), 4.77 (dd, J = 8.4, 5.2 Hz, 1H), 6.28 (d, J = 2.0 Hz, 1H), 6.97 (d, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.5, 36.5, 40.3 (dd, J = 23.8, 20.6 Hz), 64.8, 68.7 (dd, J = 8.9, 2.4 Hz), 107.4, 114.7 (dd, J = 252.6, 245.1 Hz), 123.4, 134.0, 139.5, 174.4 (t, J = 26.8 Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -106.1 (ddd, J = 279.5, 11.1, 5.8 Hz), -103.4 (ddd, J = 279.7, 30.5, 10.2 Hz). IR (neat) $\tilde{\nu}$ 2946, 2923, 2854, 1660, 1456, 1400 1078, 1055, 880, 754 cm^{-1}. HRMS (ESI) calcd. for $C_{11}H_{14}NOF_2Na$ (M+Na): 252.0812, Found: 252.0816.

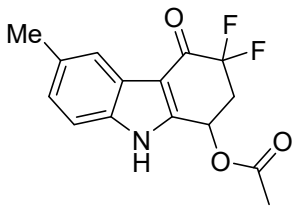




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

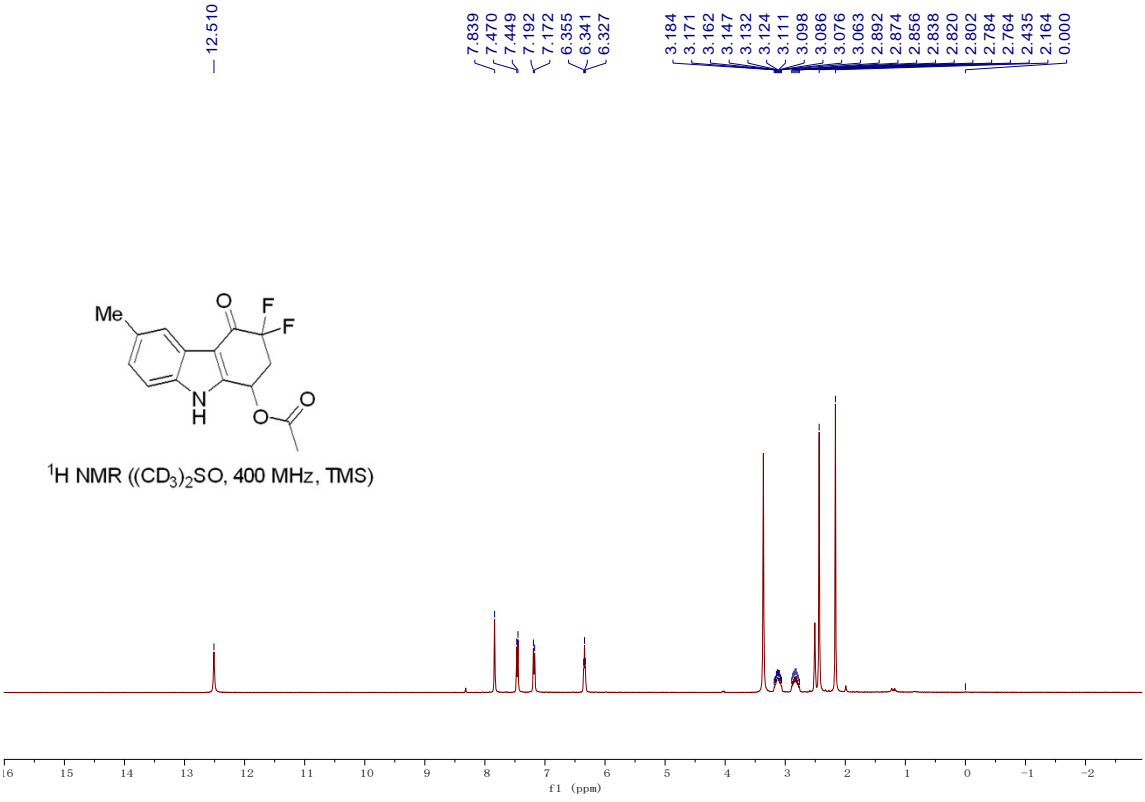


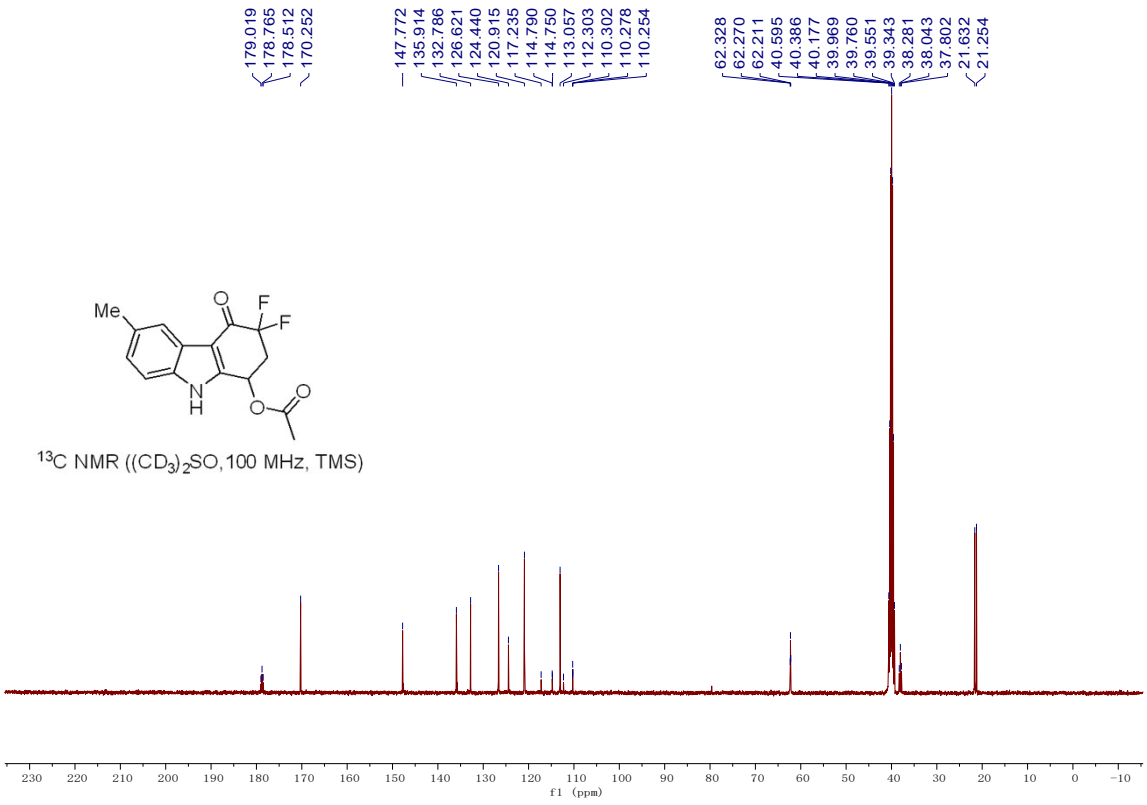
^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$)



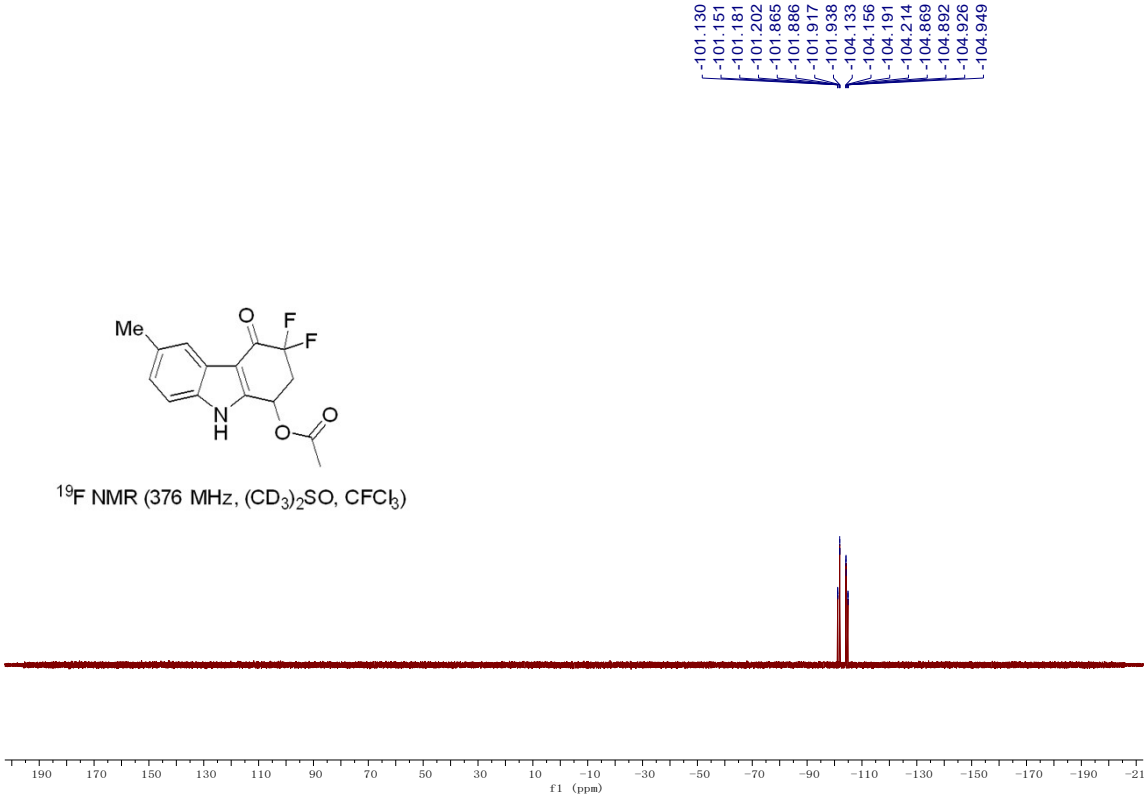
3,3-difluoro-6-methyl-4-oxo-2,3,4,9-tetrahydro-1H-carbazol-1-yl acetate (3pak)

A white solid. 45.8 mg, 78% yield. M.P.: 199-201 °C. ^{1}H NMR ($(CD_3)_2SO$, TMS, 400 MHz) δ 2.16 (s, 3H), 2.44 (s, 3H), 2.76-2.89 (m, 1H), 3.06-3.18 (m, 1H), 6.34 (t, *J* = 5.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 12.51 (s, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 21.3, 21.6, 38.0 (t, *J* = 24.1 Hz), 62.3 (t, *J* = 5.9 Hz), 110.3 (t, *J* = 2.4 Hz), 114.8 (dd, *J* = 248.5, 244.5 Hz), 120.9, 124.4, 126.6, 132.8, 135.9, 147.8, 170.3, 178.8 (t, *J* = 25.5 Hz). ^{19}F NMR ($(CD_3)_2SO$, $CFCl_3$, 376 MHz) δ -104.5 (ddd, *J* = 276.7, 21.4, 8.6 Hz), -101.53 (ddd, *J* = 276.9, 19.6, 8.0 Hz). IR (neat) $\tilde{\nu}$ 3200, 2980, 2922, 2853, 1648, 1456, 1375, 1353, 1321, 1283, 1179, 1120, 1091, 1045, 915, 880, 784, 758, 741 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{13}NO_2F_2$ (M^+): 265.0909, Found: 265.0911.

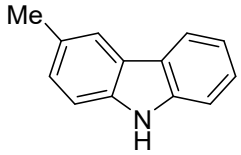




^{13}C NMR ((CD$_3$)$_2$SO,100 MHz, TMS)

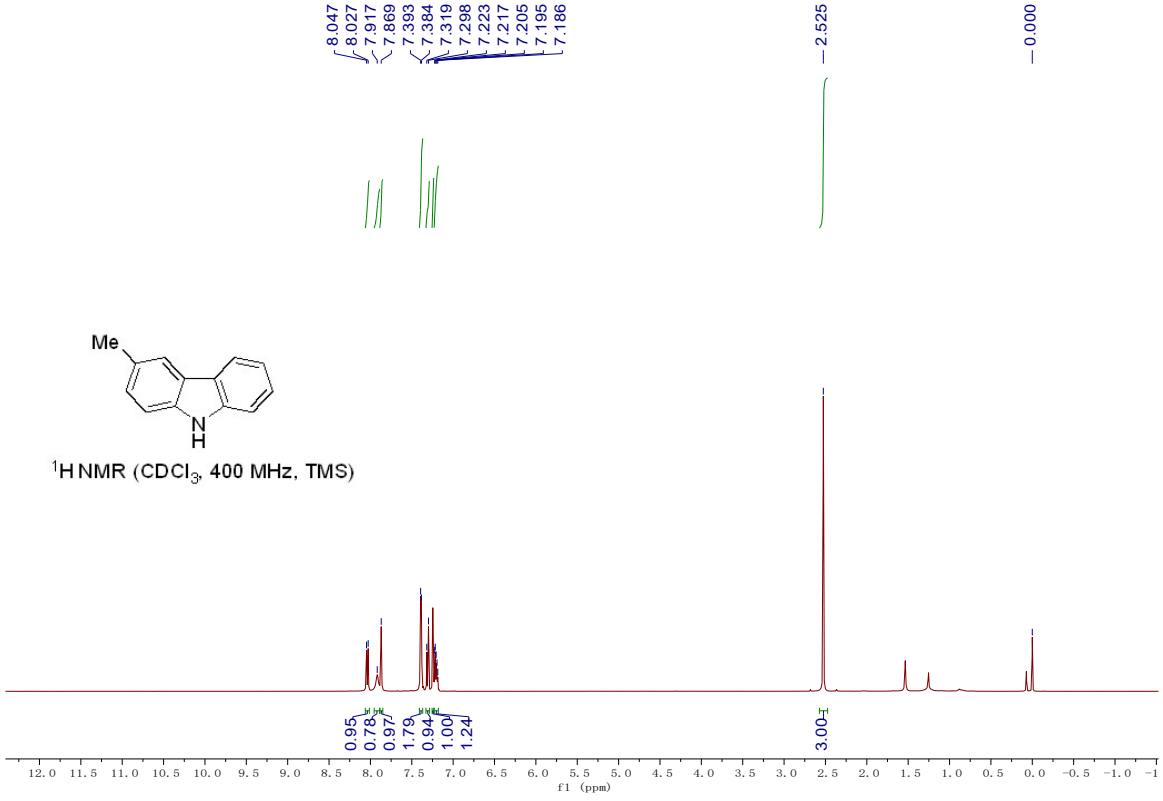


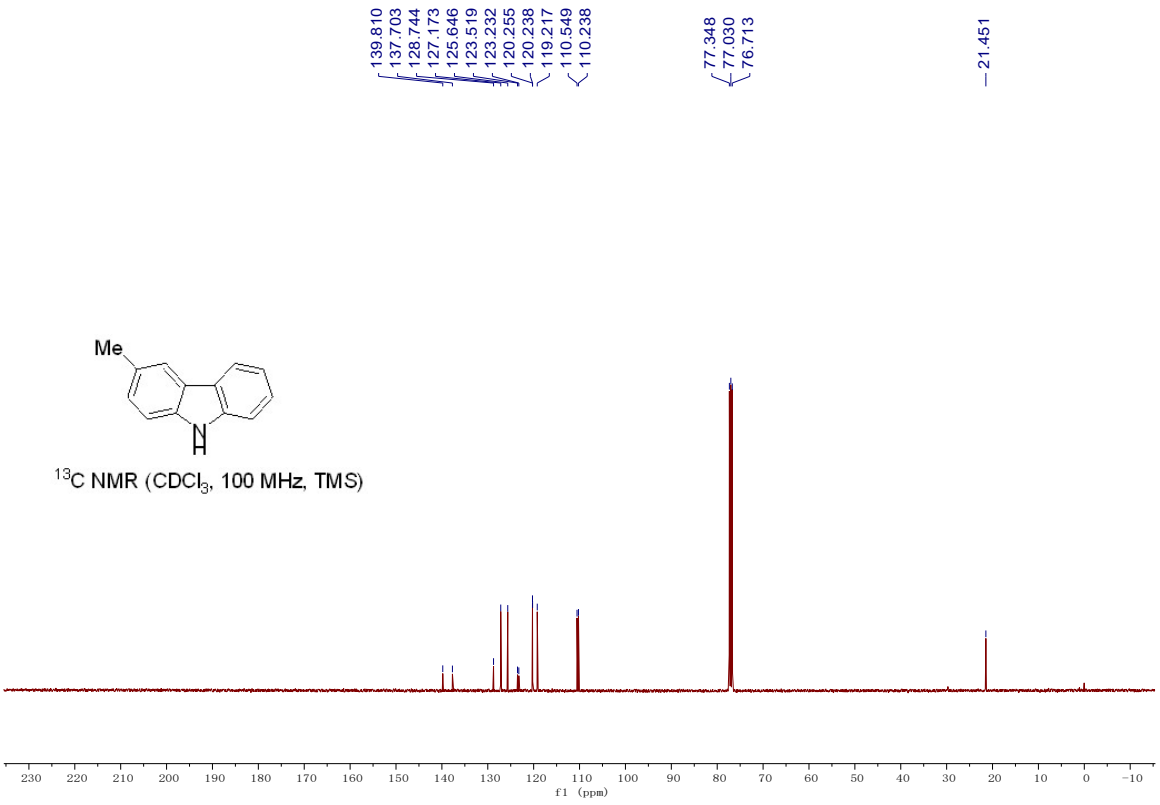
^{19}F NMR (376 MHz, (CD$_3$)$_2$SO, CFCl$_3$)

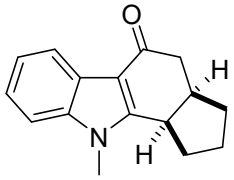


3-methyl-9H-carbazole (5pak)

This is a known compound and its spectroscopic data are consistent with those in the previous literature.[7] A colorless oil. 114.2 mg, 42% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.53 (s, 3H), 7.19-7.22 (m, 1H), 7.25 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.87 (s, 1H), 7.92 (br, 1H), 8.03 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.5, 110.2, 110.5, 119.2, 120.2, 120.3, 123.2, 123.5, 125.6, 127.2, 128.7, 137.7, 139.8.

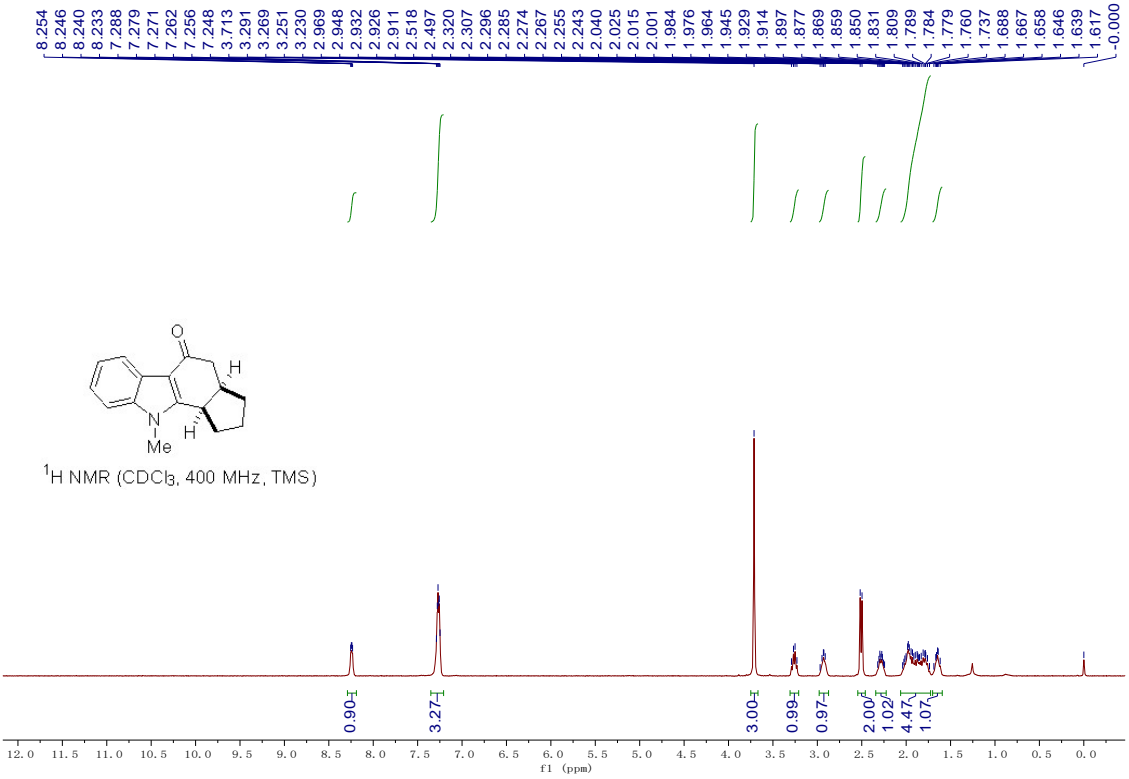


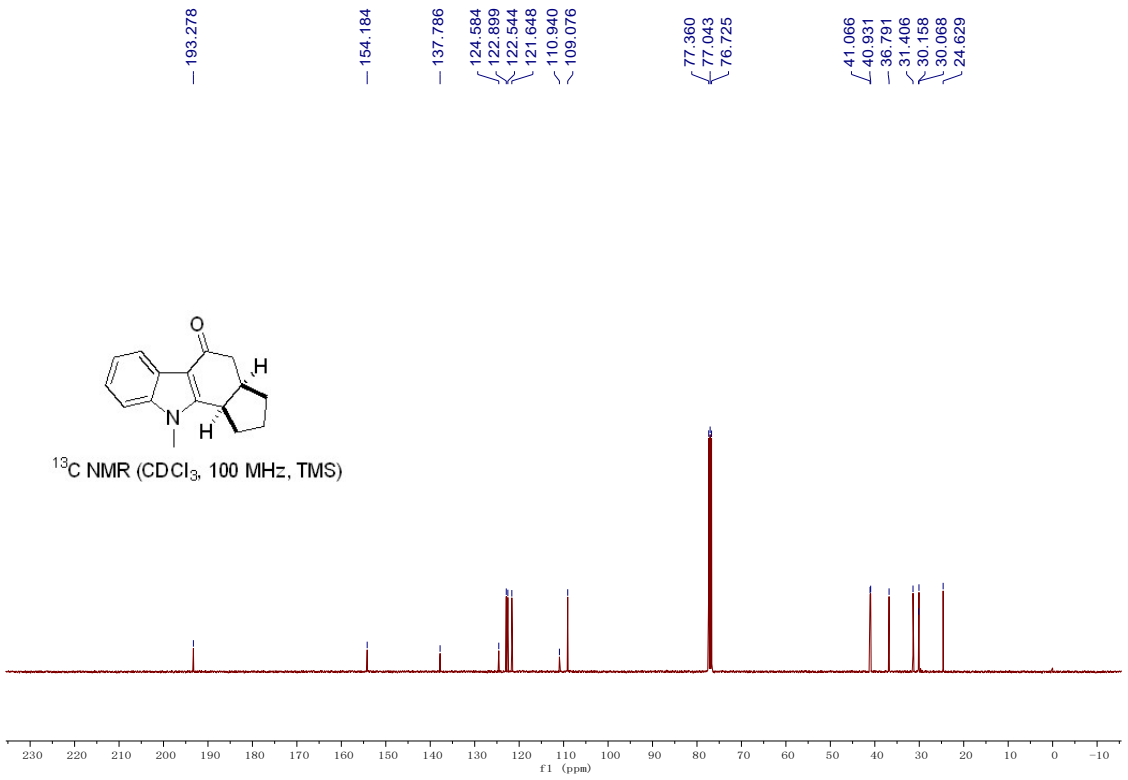

139.810
137.703
128.744
127.173
125.646
123.519
123.232
120.255
120.238
119.217
110.549
110.238
77.348
77.030
76.713
21.451
Me
N
H
13C NMR (CDCl3, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

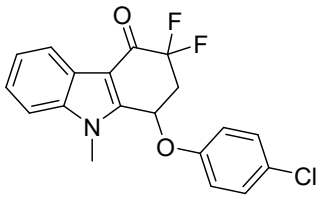


10-methyl-2,3,3a,4,10,10b-hexahydrocyclopenta[*a*]carbazol-5(1*H*)-one (5ak)

A white solid. 226.2 mg, 63% yield. M.P.: 190-192 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.62-1.69 (m, 1H), 1.74-2.04 (m, 4H), 2.24-2.32 (m, 1H), 2.50 (d, J = 8.4 Hz, 2H) 2.91-2.97 (m, 1H), 3.23-3.29 (m, 1H), 3.71 (s, 3H), 7.25-7.29 (m, 3H), 8.23-8.25 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 24.6, 30.1, 30.2, 31.4, 36.8, 40.9, 41.1, 109.1, 110.9, 121.6, 122.5, 122.9, 124.6, 137.8, 154.2, 193.3. IR (neat) $\tilde{\nu}$ 2951, 2923, 2853, 1670, 1542, 1450, 1423, 1401, 1060, 862, 770 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{18}NO$ (M+H): 240.1383, Found: 240.1383.

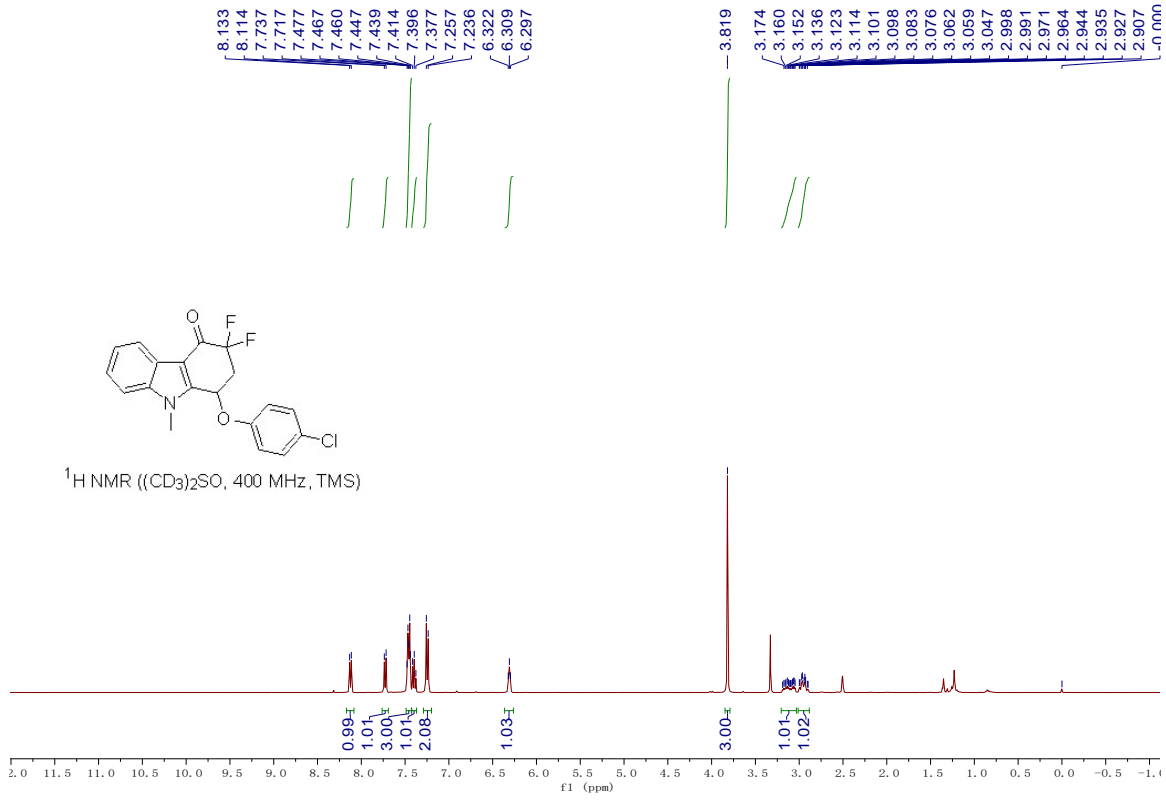


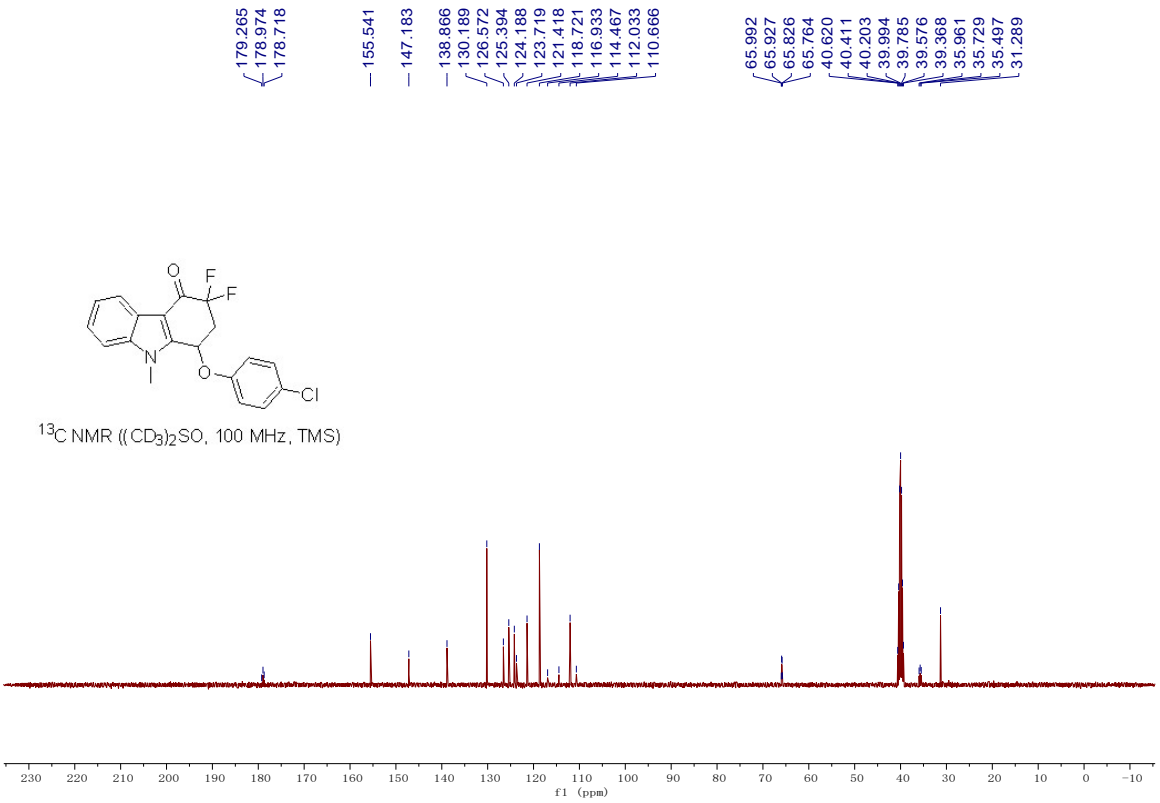

193.278
154.184
137.786
124.584
122.899
122.544
121.648
110.940
109.076
77.360
77.043
76.725
41.066
40.931
36.791
31.406
30.158
30.068
24.629
O
H
N
H
13C NMR (CDCl3, 100 MHz, TMS)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



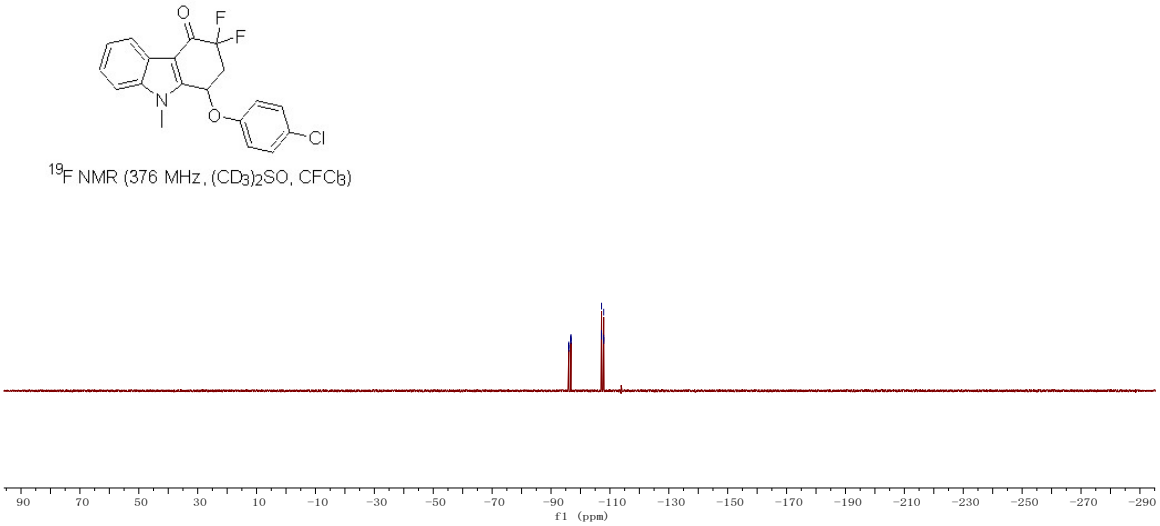
1-(4-chlorophenoxy)-3,3-difluoro-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (3aal)

A white solid. 0.94 g, 86% yield (3 mmol scale). M.P.: 212-215 °C. ^{1}H NMR ($(CD_3)_2SO$, TMS, 400 MHz) δ 2.90-3.00 (m, 1H), 3.05-3.19 (m, 1H), 3.82 (s, 3H), 6.31 (t, J = 4.8 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.44-7.48 (m, 3H), 7.72 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($(CD_3)_2SO$, TMS, 100 MHz) δ 31.3, 35.7 (t, J = 23.2 Hz), 65.9 (dd, J = 10.1, 6.5 Hz), 110.7 (t, J = 2.3 Hz), 112.0, 114.5 (t, J = 275.3 Hz), 118.7, 121.4, 123.7, 124.2, 125.4, 126.6, 130.2, 138.9, 147.2, 155.5, 179.0 (t, J = 29.1 Hz). ^{19}F NMR ($(CD_3)_2SO$, $CFCl_3$, 376 MHz) δ -107.52 (dt, J = 278.3, 8.4 Hz), -96.39 (ddd, J = 277.1, 30.3, 10.7 Hz). IR (neat) $\tilde{\nu}$ 2955, 2923, 2853, 1668, 1581, 1481, 1398, 1361, 1335, 1234, 1212, 1083, 1055, 882, 867 779, 751 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{14}NO_2F_2ClNa$ (M+Na): 384.0573, Found: 384.0572.



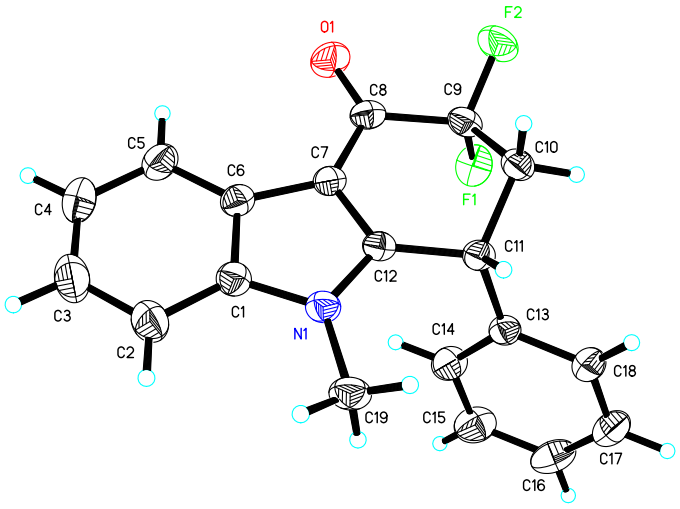


^{13}C NMR ($(CD_3)_2SO$, 100 MHz, TMS)

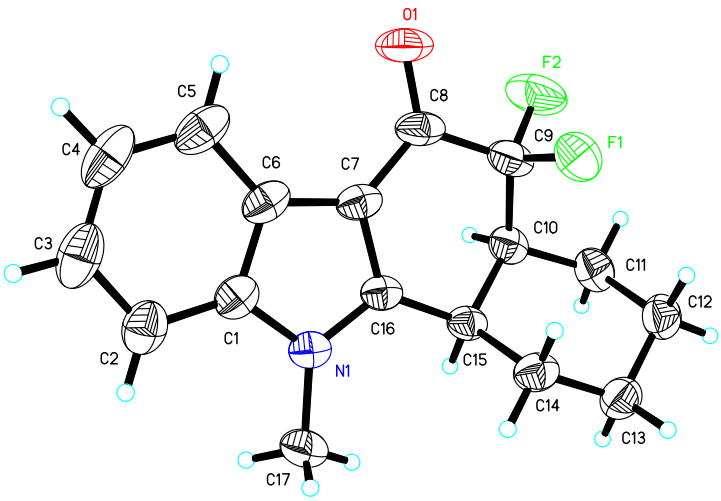


^{19}F NMR (376 MHz, $(CD_3)_2SO$, $CFCl_3$)

10. X-Ray structures



The crystal data of **3aa** have been deposited in CCDC with number 2116700. Empirical Formula: $C_{19}H_{15}F_2NO$; Formula Weight: 311.32; Crystal Color, Habit: colorless; Crystal Dimensions: 0.130 x 0.110 x 0.090 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 5.5106(2) Å, alpha = 70.0900(10) deg. b = 7.7117(3) Å, beta = 86.9720(10) deg. c = 9.6692(3) Å, gamma = 85.4380(10) deg.; V = 384.97(2) $Å^3$; Space group: P 1; Z = 1; D_{calc} = 1.343 g/cm^3; F_{000} = 162; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0310, 0.0783.



The crystal data of **3al** have been deposited in CCDC with number 2123014. Empirical Formula: $C_{17}H_{17}F_2NO$; Formula Weight: 289.32; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.150 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.9237(4) Å, alpha = 90 deg. b = 10.5309(4) Å, beta = 114.4820(10) deg. c = 12.4165(3) Å, gamma = 90 deg.; V = 1418.93(8) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1418.93(8) g/cm^3; F_{000} = 608; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0427, 0.1043.

11. References

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