

## *Supporting Information*

### **Visible-light photoredox-catalyzed radical aryldifluoromethylation of *N*-acrylamides with *S*-(difluoromethyl)sulfonium salt**

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## 1. General Experimental Information

Reagents and solvents were commercially available and were used without any further purification unless otherwise indicated.  $^1\text{H}$  NMR spectra were recorded on either a Bruker Ascend 400 MHz (400 MHz) spectrometer, a Bruker Ascend 500 MHz (500 MHz) spectrometer or a Bruker Ascend 600 MHz (600 MHz) spectrometer at ambient temperature unless otherwise indicated. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in  $\text{CDCl}_3$ , integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment.  $^{13}\text{C}$  NMR spectra were recorded on either a Bruker Ascend 500 MHz (126 MHz) spectrometer or a Bruker Ascend 600 MHz (151 MHz) spectrometer at ambient temperature and were proton decoupled. Chemical shifts are reported in ppm from tetramethylsilane on the scale with the solvent resonance employed as the internal standard.  $^{19}\text{F}$  NMR spectra were recorded on a Bruker Ascend 400 MHz (377 MHz) spectrometer or a Bruker Ascend 500 MHz (471 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm from  $\text{CFCl}_3$  as the internal standard. ESI-MS analysis were performed in positive ionization mode on an Agilent 1260-Infinity LC/MSD resolution mass spectrometer. All high-resolution mass spectra were obtained on a Thermo Scientific Q-Exactive (HR/AM) Orbitrap mass spectrometer. Reactions were monitored by TLC (detection with UV light). Flash chromatography: silica gel (300-400 mesh). Visible light irradiation was performed by Blue LED lamps ( $\lambda = 450 \text{ nm}$ ;  $3 \text{ W} \times 4$ ) for preparative scale. Regent **2** was synthesized based on reported procedure and analytical data are in agreement with those reported in the literature.<sup>1</sup>

## 2. Reaction Apparatus

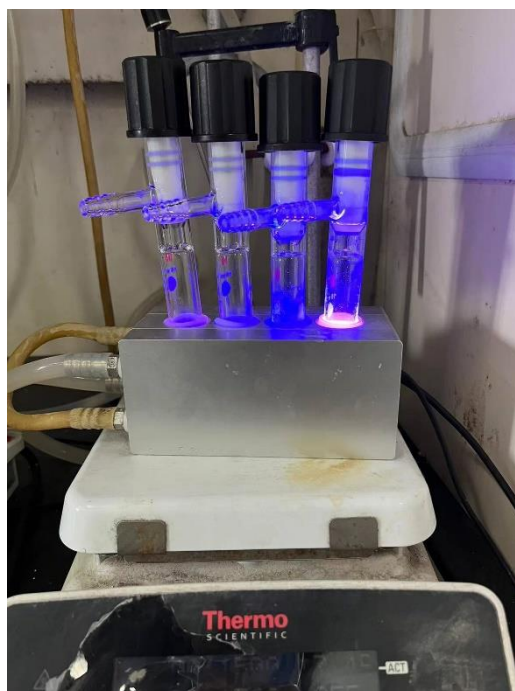


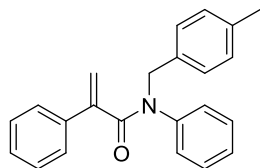
Figure S1. reaction apparatus

## 3. Characterization Data for *N*-arylacrylamide **1**

All known *N*-arylacrylamide **1** (**1aa**, **1ac-1ah**, **1ba-1bv**, **1ca**) were prepared according to a

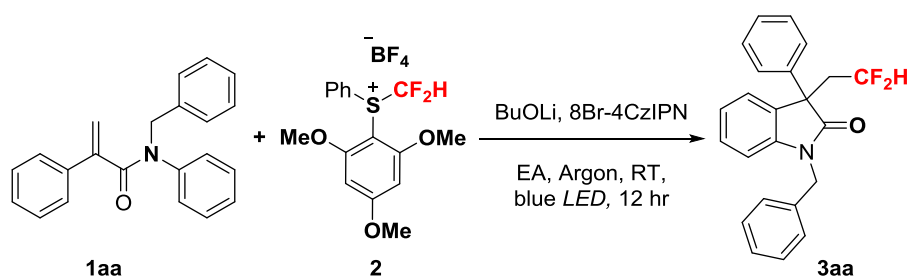
reported method, and analytical data are in agreement with those reported in the literature.<sup>2,3</sup>

#### **N-(4-methylbenzyl)-N,2-diphenylacrylamide (1ab)** (New compound)



**1ab** was purified by silica gel chromatography (PE/EA = 10/1) as a white solid in 51% yield, Mp: 83.2-83.9 °C. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.09 (m, 7H), 7.06 (dd, *J* = 16.9, 7.1 Hz, 5H), 6.72 (s, 2H), 5.43 (s, 1H), 5.35 (s, 1H), 4.97 (s, 2H), 2.31 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 170.4, 145.8, 142.1, 137.1, 134.4, 129.1, 128.8, 128.2, 128.3, 127.90, 127.1, 126.1, 117.7, 52.7, 21.2 (one carbon peak was missing due to overlapping). HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>18</sub>F<sub>2</sub>NO<sub>3</sub><sup>+</sup> 328.1657, found 328.1690.

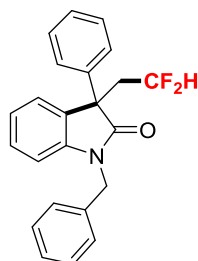
#### **4. General procedure for synthesis of Products 3**



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added *N*-arylacrylamide **1aa** (0.1 mmol, 31.3 mg, 1.0 equiv.), *S*-(difluoromethyl)sulfonium salt **2** (0.2 mmol, 83.0 mg, 2.0 equiv.), <sup>t</sup>BuOLi (0.2 mmol, 16.0 mg, 2.0 equiv.) and 8Br-4CzIPN (0.003 mmol, 4.3 mg, 3 mol%). The flask was flushed with argon, followed by the addition of ethyl acetate (2.5 ml). The tube was placed at a distance of ~2 mm away from blue LED lamps ( $\lambda = 450$  nm, 3 W  $\times$  4), then the reaction mixture was stirred under irradiation of blue LEDs overnight at room temperature. The mixture was evaporated in vacuo after reaction accomplished. The product was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate).

#### **5. Characterization Data for Difluoromethylated lindolin-2-one**

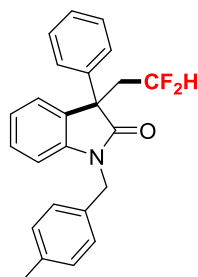
##### **1-benzyl-3-(2,2-difluoroethyl)-3-phenylindolin-2-one (3aa)** (New compound)



Following the general procedure for the preparation of products **3**, **3aa** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a white solid (29.0 mg, 80%). Mp: 85.8-87.2 °C. <sup>1</sup>H NMR

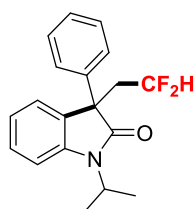
(400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.22 (m, 12H), 7.11 (td,  $J = 7.5, 1.1$  Hz, 1H), 6.81 (d,  $J = 7.9$  Hz, 1H), 5.57 (tdd,  $J = 56.1, 6.6, 3.2$  Hz, 1H), 4.99 – 4.79 (m, 2H), 3.16 (tdd,  $J = 14.2, 12.5, 6.6$  Hz, 1H), 2.80 (dddd,  $J = 23.6, 14.4, 13.0, 3.2$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  177.3, 143.0, 139.3, 135.6, 129.9, 129.0, 128.9, 128.8, 127.9, 127.7, 127.3, 126.6, 125.2, 122.9, 115.3 (t,  $J = 240.3$  Hz), 110.0, 52.5 (dd,  $J = 7.3, 3.3$  Hz), 44.2, 41.2 (t,  $J = 22.4$  Hz).  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -113.9 (m). HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{F}_2\text{NO}^+$  364.1468, found 364.1502.

### 3-(2,2-difluoroethyl)-1-(4-methylbenzyl)-3-phenylindolin-2-one (3ab) (New compound)



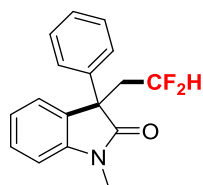
Following the general procedure for the preparation of products **3**, **3ab** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a white solid (31.1 mg, 81%). Mp: 133.3-134.8 °C.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.32 (d,  $J = 4.1$  Hz, 4H), 7.27 (q,  $J = 4.9$  Hz, 2H), 7.24 (d,  $J = 9.1$  Hz, 1H), 7.14 (d,  $J = 7.9$  Hz, 2H), 7.10 (t,  $J = 8.2$  Hz, 3H), 6.82 (d,  $J = 7.9$  Hz, 1H), 5.56 (tdd,  $J = 56.1, 6.4, 3.0$  Hz, 1H), 4.87 (q,  $J = 15.6$  Hz, 2H), 3.15 (ddt,  $J = 20.5, 13.9, 6.6$  Hz, 1H), 2.88 – 2.69 (m, 1H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  177.3, 143.1, 139.4, 137.4, 132.6, 129.9, 129.5, 129.0, 128.9, 127.9, 127.4, 126.6, 125.2, 122.9, 115.4 (t,  $J = 240.3$  Hz), 110.0, 52.5 (dd,  $J = 7.3, 3.4$  Hz), 44.0, 41.2 (t,  $J = 22.4$  Hz), 21.1.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -113.8 (m). HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{22}\text{F}_2\text{NO}^+$  378.1625, found 378.1659.

### 3-(2,2-difluoroethyl)-1-isopropyl-3-phenylindolin-2-one (3ac) (New compound)



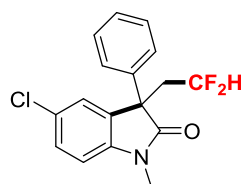
Following the general procedure for the preparation of products **3**, **3ac** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a white solid (22.2 mg, 70%). Mp: 57.4-59.0 °C.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.34 (t,  $J = 7.8$  Hz, 1H), 7.32 – 7.28 (m, 2H), 7.26 (dd,  $J = 11.2, 7.5$  Hz, 4H), 7.11 (t,  $J = 7.0$  Hz, 2H), 5.48 (tdd,  $J = 56.2, 6.8, 3.0$  Hz, 1H), 4.61 (p,  $J = 7.0$  Hz, 1H), 3.10 (tdd,  $J = 14.1, 11.8, 6.8$  Hz, 1H), 2.72 (dddd,  $J = 27.1, 14.3, 9.9, 3.1$  Hz, 1H), 1.47 (dd,  $J = 7.0, 1.7$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  176.9, 142.6, 139.6, 130.6, 128.9, 128.8, 127.7, 126.4, 125.3, 122.3, 115.4 (t,  $J = 240.3$  Hz), 110.5, 52.1 (dd,  $J = 7.8, 2.8$  Hz), 44.2, 41.1 (t,  $J = 22.3$  Hz), 19.3, 19.1.  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -114.4 (m). HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{20}\text{F}_2\text{NONa}^+$  316.1468, found 316.1503.

### 3-(2,2-difluoroethyl)-1-methyl-3-phenylindolin-2-one (3ad) (Known)<sup>4</sup>



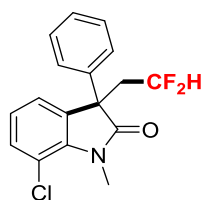
Following the general procedure for the preparation of products **3**, **3ad** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (21.5 mg, 73%). Mp: 123.8-124.4 °C. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.39 (td, *J* = 7.8, 1.1 Hz, 1H), 7.31 (qd, *J* = 8.4, 7.9, 3.1 Hz, 5H), 7.28 – 7.25 (m, 1H), 7.16 (td, *J* = 7.6, 0.9 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.52 (tdd, *J* = 56.1, 6.5, 3.3 Hz, 1H), 3.22 (s, 3H), 3.06 (tdd, *J* = 14.4, 12.0, 6.6 Hz, 1H), 2.76 (dddd, *J* = 26.6, 14.5, 9.7, 3.3 Hz, 1H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.2 (m).

**5-chloro-3-(2,2-difluoroethyl)-1-methyl-3-phenylindolin-2-one (3ae)** (New compound)



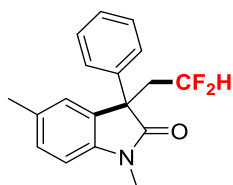
Following the general procedure for the preparation of products **3**, **3ae** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (26.7 mg, 83%). Mp: 95.8-97.8 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.36 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 4H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.57 (tdd, *J* = 55.9, 6.3, 3.4 Hz, 1H), 3.22 (s, 3H), 3.05 (tdd, *J* = 14.5, 12.6, 6.4 Hz, 1H), 2.75 (dddd, *J* = 25.8, 14.6, 11.3, 3.4 Hz, 1H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 176.8, 142.4, 138.3, 131.7, 129.1, 129.0, 128.3, 128.1, 126.4, 125.7, 115.1 (t, *J* = 240.5 Hz), 109.8, 52.7 (dd, *J* = 7.3, 3.4 Hz), 41.2 (t, *J* = 22.4 Hz), 26.8. <sup>19</sup>F NMR (471 MHz, Chloroform-*d*) δ -114.1 (m). HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>ClF<sub>2</sub>NO<sup>+</sup> 322.0766, found 322.0800.

**7-chloro-3-(2,2-difluoroethyl)-1-methyl-3-phenylindolin-2-one (3af)** (New compound)



Following the general procedure for the preparation of products **3**, **3af** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a white solid (10.2 mg, 39%). Mp: 153.5-154.1 °C. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 3H), 7.29 – 7.25 (m, 3H), 7.16 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.08 – 7.04 (m, 1H), 5.54 (tdd, *J* = 56.0, 6.3, 3.5 Hz, 1H), 3.60 (s, 3H), 3.10 (tdd, *J* = 14.6, 12.2, 6.3 Hz, 1H), 2.73 (dddd, *J* = 24.9, 14.4, 10.8, 3.5 Hz, 1H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 177.5, 139.9, 138.7, 132.8, 131.4, 129.0, 128.1, 126.4, 123.8, 123.6, 116.3, 115.1 (t, *J* = 240.5 Hz), 52.2 (dd, *J* = 7.1, 3.5 Hz), 41.3 (t, *J* = 22.5 Hz), 30.1. <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.3 (m). HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>ClF<sub>2</sub>NO<sup>+</sup> 322.0766, found 322.0799.

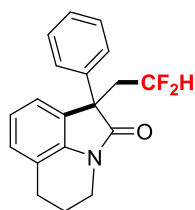
**3-(2,2-difluoroethyl)-1,5-dimethyl-3-phenylindolin-2-one (3ag)** (New compound)



Following the general procedure for the preparation of products **3**, **3ag** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a yellow oil (23.6 mg, 78%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 4.1 Hz, 4H), 7.26 (dd, *J* = 9.9, 2.8 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.10 (s, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.52 (tdd, *J* = 56.1, 6.6, 3.3 Hz, 1H), 3.20 (s, 3H), 3.05 (tdd, *J* = 14.3, 12.1, 6.6 Hz, 1H), 2.73 (dddd, *J* = 25.8, 14.2, 10.4, 3.3 Hz, 1H), 2.38 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 177.2, 141.5, 139.3, 132.5, 130.0, 129.5, 128.8, 127.8, 126.6, 125.9, 115.4 (t, *J* = 240.2 Hz), 108.6, 52.6 (dd, *J* = 7.8, 2.9 Hz), 41.2 (t, *J* = 22.4 Hz), 26.7, 21.3. <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.0 (m). HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>18</sub>F<sub>2</sub>NO<sup>+</sup> 302.1312, found 302.1347.

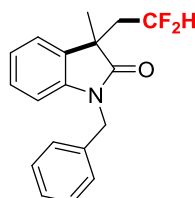
### 1-(2,2-difluoroethyl)-1-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (**3ah**)

(New compound)



Following the general procedure for the preparation of products **3**, **3ah** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (15.1 mg, 60%). Mp: 94.3-96.7 °C. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.54 (tdd, *J* = 56.1, 6.6, 3.0 Hz, 1H), 3.74 (dt, *J* = 12.1, 5.8 Hz, 1H), 3.67 (dt, *J* = 12.6, 5.7 Hz, 1H), 3.00 (ddt, *J* = 20.7, 14.0, 6.7 Hz, 1H), 2.82 (t, *J* = 6.0 Hz, 2H), 2.75 (dddd, *J* = 27.1, 13.8, 9.5, 3.0 Hz, 1H), 2.01 (p, *J* = 5.9 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 176.0, 139.6, 138.9, 128.8, 128.3, 127.8, 127.8, 126.7, 123.2, 122.3, 121.0, 115.5 (t, *J* = 240.2 Hz), 53.7 (dd, *J* = 8.0, 2.7 Hz), 41.5 (t, *J* = 22.3 Hz), 39.2, 24.7, 21.1. <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -113.9 (m). HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>18</sub>F<sub>2</sub>NO<sup>+</sup> 314.1312, found 314.1345.

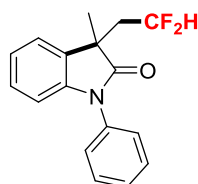
### 1-benzyl-3-(2,2-difluoroethyl)-3-methylindolin-2-one (**3ba**) (Known)<sup>5</sup>



Following the general procedure for the preparation of products **3**, **3ba** was purified by silica gel chromatography (PE/EtOAc = 5/1) as a colorless oil (14.8 mg, 49%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 5H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 5.62 (tdd, *J* = 56.0, 6.4, 3.4 Hz, 1H), 4.97 (d, *J* = 15.6 Hz,

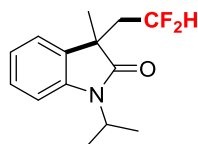
1H), 4.87 (d,  $J = 15.7$  Hz, 1H), 2.59 (qd,  $J = 14.2, 6.5$  Hz, 1H), 2.40 – 2.28 (m, 1H), 1.47 (s, 3H).  
 $^{19}\text{F}$  NMR (377 MHz, Chloroform- $d$ )  $\delta$  -114.1 (m).

**3-(2,2-difluoroethyl)-3-methyl-1-phenylindolin-2-one (3bb)** (Known)<sup>4</sup>



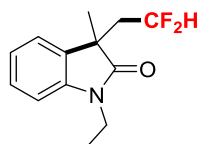
Following the general procedure for the preparation of products **3**, **3bb** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (25.8 mg, 90%).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.53 (t,  $J = 7.8$  Hz, 2H), 7.44 – 7.37 (m, 3H), 7.31 – 7.28 (m, 1H), 7.26 – 7.20 (m, 1H), 7.13 (td,  $J = 8.3, 7.5, 0.8$  Hz, 1H), 6.84 (d,  $J = 7.9$  Hz, 1H), 5.63 (tdd,  $J = 56.1, 6.8, 3.2$  Hz, 1H), 2.64 (dtd,  $J = 14.5, 13.5, 6.8$  Hz, 1H), 2.38 (dddd,  $J = 20.9, 16.5, 14.6, 3.2$  Hz, 1H), 1.54 (s, 3H).  $^{19}\text{F}$  NMR (377 MHz, Chloroform- $d$ )  $\delta$  -114.7 (m).

**3-(2,2-difluoroethyl)-1-isopropyl-3-methylindolin-2-one (3bc)** (Known)<sup>5</sup>



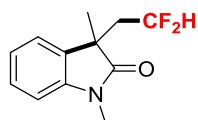
Following the general procedure for the preparation of products **3**, **3bc** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a colorless oil (14.4 mg, 57%).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) 7.31 – 7.19 (m, 1H), 7.10 – 7.01 (m, 2H), 5.51 (tdd,  $J = 56.2, 6.6, 3.3$  Hz, 1H), 4.63 (hept,  $J = 7.3$  Hz, 1H), 2.51 (qd,  $J = 13.9, 6.6$  Hz, 1H), 2.26 (dddd,  $J = 20.1, 17.7, 14.6, 3.3$  Hz, 1H), 1.47 (dd,  $J = 7.0, 4.5$  Hz, 6H), 1.39 (s, 3H).  $^{19}\text{F}$  NMR (377 MHz, Chloroform- $d$ )  $\delta$  -114.5 (m).

**3-(2,2-difluoroethyl)-1-ethyl-3-methylindolin-2-one (3bd)** (Known)<sup>5</sup>



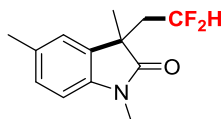
Following the general procedure for the preparation of products **3**, **3bd** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a colorless oil (14.7 mg, 62%).  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.30 (td,  $J = 7.7, 1.2$  Hz, 1H), 7.23 (d,  $J = 6.9$  Hz, 1H), 7.08 (td,  $J = 7.6, 0.8$  Hz, 1H), 6.89 (d,  $J = 7.8$  Hz, 1H), 5.55 (tdd,  $J = 56.1, 6.5, 3.4$  Hz, 1H), 3.85 (dq,  $J = 14.5, 7.2$  Hz, 1H), 3.70 (dq,  $J = 14.4, 7.2$  Hz, 1H), 2.52 (qd,  $J = 14.1, 6.5$  Hz, 1H), 2.28 (dddd,  $J = 19.0, 17.8, 14.6, 3.4$  Hz, 1H), 1.40 (s, 3H), 1.25 (t,  $J = 7.2$  Hz, 3H).  $^{19}\text{F}$  NMR (377 MHz, Chloroform- $d$ )  $\delta$  -114.3 (ddd,  $J = 56.1, 18.3, 13.9$  Hz).

**3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3be)** (Known)<sup>4</sup>



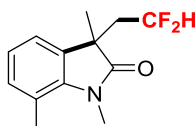
Following the general procedure for the preparation of products **3**, **3be** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a colorless oil (18.4 mg, 82%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.59 (tdd, *J* = 56.1, 6.3, 3.5 Hz, 1H), 3.23 (s, 3H), 2.50 (qd, *J* = 14.3, 6.3 Hz, 1H), 2.39 – 2.18 (m, 1H), 1.42 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.2 (m).

**3-(2,2-difluoroethyl)-1,3,5-trimethylindolin-2-one (3bf)** (Known)<sup>6</sup>



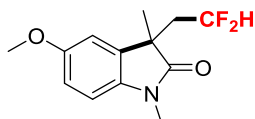
Following the general procedure for the preparation of products **3**, **3bf** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a yellow oil (21.5 mg, 90%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.60 (tdd, *J* = 56.2, 6.4, 3.5 Hz, 1H), 3.21 (s, 3H), 2.48 (qd, *J* = 14.4, 6.4 Hz, 1H), 2.36 (s, 3H), 2.26 (dtd, *J* = 21.3, 14.8, 3.5 Hz, 1H), 1.40 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.2 (m).

**3-(2,2-difluoroethyl)-1,3,7-trimethylindolin-2-one (3bg)** (Known)<sup>5</sup>



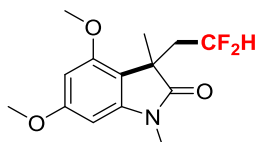
Following the general procedure for the preparation of products **3**, **3bg** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a yellow oil (7.6 mg, 32%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.09 – 7.00 (m, 2H), 7.00 – 6.91 (m, 1H), 5.57 (tdd, *J* = 56.2, 6.4, 3.4 Hz, 1H), 3.51 (s, 3H), 2.59 (s, 3H), 2.49 (qd, *J* = 14.4, 6.5 Hz, 1H), 2.24 (dtd, *J* = 22.2, 14.5, 3.4 Hz, 1H), 1.39 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.3 (m).

**3-(2,2-difluoroethyl)-5-methoxy-1,3-dimethylindolin-2-one (3bh)** (Known)<sup>4</sup>



Following the general procedure for the preparation of products **3**, **3bh** was purified by silica gel chromatography (PE/EtOAc = 5/1) as a colorless oil (18.2 mg, 71%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 6.85 – 6.81 (m, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.62 (tdd, *J* = 56.1, 6.3, 3.5 Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 2.49 (tdd, *J* = 14.7, 13.6, 6.3 Hz, 1H), 2.26 (dtd, *J* = 21.7, 14.7, 3.5 Hz, 1H), 1.40 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.2 (m).

**3-(2,2-difluoroethyl)-4,6-dimethoxy-1,3-dimethylindolin-2-one (3bi)** (New compound)

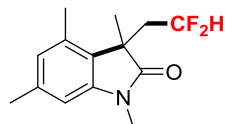


Following the general procedure for the preparation of products **3**, **3bi** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a colorless oil (20.6 mg, 72%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 6.17 (d, *J* = 1.9 Hz, 1H), 6.11 (d, *J* = 1.9 Hz, 1H), 5.46 (d, *J* = 3.3 Hz, 1H), 3.84 (s, 6H), 3.18 (s, 3H), 2.63 – 2.26 (m, 2H), 1.41 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ



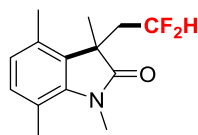
180.2, 161.8, 156.6, 144.9, 115.8 (t,  $J = 239.3$  Hz), 109.2, 92.3, 88.5, 55.5 (d,  $J = 30.1$  Hz), 44.4 (dd,  $J = 8.2, 3.0$  Hz), 39.7 (t,  $J = 21.5$  Hz), 26.6, 22.8.  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -115.2 (m). HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{18}\text{F}_2\text{NO}_3^+$  286.1210, found 286.1244.

**3-(2,2-difluoroethyl)-1,3,4,6-tetramethylindolin-2-one (3bj)** (Known)<sup>5</sup>



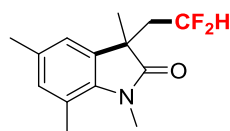
Following the general procedure for the preparation of products **3**, **3bj** was purified by silica gel chromatography (PE/EtOAc = 20/1) as a yellow oil (21.0 mg, 83%).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  6.67 (s, 1H), 6.55 (s, 1H), 5.42 (tdd,  $J = 56.1, 6.5, 3.3$  Hz, 1H), 3.20 (s, 3H), 2.70 – 2.56 (m, 1H), 2.45 (dddd,  $J = 24.7, 14.9, 11.9, 3.3$  Hz, 1H), 2.34 (s, 6H), 1.45 (s, 3H).  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -114.9 (m).

**3-(2,2-difluoroethyl)-1,3,4,7-tetramethylindolin-2-one (3bk)** (Known)<sup>7</sup>



Following the general procedure for the preparation of products **3**, **3bk** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (10.9 mg, 43%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.93 (d,  $J = 7.9$  Hz, 1H), 6.73 (d,  $J = 7.9$  Hz, 1H), 5.42 (tdd,  $J = 56.1, 6.5, 3.3$  Hz, 1H), 3.50 (s, 3H), 2.65 (ddt,  $J = 21.9, 14.2, 7.4$  Hz, 1H), 2.55 (s, 3H), 2.54 – 2.40 (m, 1H), 2.35 (s, 3H), 1.45 (s, 3H).  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -115.1 (m).

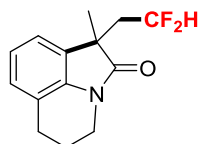
**3-(2,2-difluoroethyl)-1,3,5,7-tetramethylindolin-2-one (3bl)** (New compound)



Following the general procedure for the preparation of products **3**, **3bl** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a yellow oil (5.8 mg, 23%).  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  6.85 (s, 1H), 6.83 (s, 1H), 5.58 (tdd,  $J = 56.3, 6.5, 3.3$  Hz, 1H), 3.48 (s, 3H), 2.54 (s, 3H), 2.48 (qd,  $J = 14.5, 6.6$  Hz, 1H), 2.29 (s, 3H), 2.26 – 2.13 (m, 1H), 1.37 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  179.9, 138.3, 132.8, 132.6, 132.2, 121.4, 119.9, 115.3 (t,  $J = 239.7$  Hz), 44.0 (dd,  $J = 7.0, 3.6$  Hz), 41.7 (t,  $J = 21.8$  Hz), 29.7, 24.8, 20.8, 18.9.  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -114.3 (m). HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{18}\text{F}_2\text{NO}^+$  254.1312, found 254.1346.

**1-(2,2-difluoroethyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3bm)**

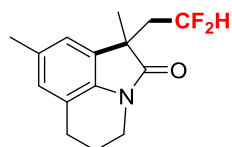
(Known)<sup>8</sup>



Following the general procedure for the preparation of products **3**, **3bm** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a colorless oil (20.8 mg, 83%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.09 – 7.03 (m, 2H), 7.00 – 6.95 (m, 1H), 5.62 (tdd, *J* = 56.2, 6.4, 3.5 Hz, 1H), 3.81 – 3.65 (m, 2H), 2.80 (td, *J* = 6.0, 1.7 Hz, 2H), 2.48 (tdd, *J* = 14.7, 13.4, 6.4 Hz, 1H), 2.34 – 2.22 (m, 1H), 2.01 (tt, *J* = 6.1, 5.1 Hz, 2H), 1.42 (s, 3H). <sup>19</sup>F NMR (471 MHz, Chloroform-*d*) δ -114.2 (m).

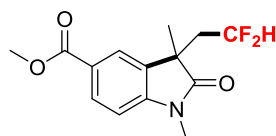
**1-(2,2-difluoroethyl)-1,8-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3bn)**

(New compound)



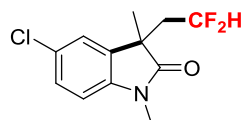
Following the general procedure for the preparation of products **3**, **3bn** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a colorless oil (17.9 mg, 68%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 6.87 (s, 2H), 5.63 (tdd, *J* = 56.2, 6.4, 3.5 Hz, 1H), 3.76 – 3.59 (m, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.56 – 2.40 (m, 1H), 2.33 (s, 3H), 2.26 (dddd, *J* = 23.7, 14.6, 13.0, 3.5 Hz, 1H), 1.99 (p, *J* = 6.0 Hz, 2H), 1.40 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 177.9, 136.3, 131.8, 130.6, 127.7, 121.4, 120.3, 115.4 (t, *J* = 239.7 Hz), 46.0 (dd, *J* = 6.6, 3.9 Hz), 41.2 (t, *J* = 21.8 Hz), 39.0, 24.6, 24.1, 21.4, 21.3. <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.2 (ddt, *J* = 51.5, 22.1, 13.9 Hz). HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>18</sub>F<sub>2</sub>NO<sup>+</sup> 266.1312, found 266.1346.

**methyl 3-(2,2-difluoroethyl)-1,3-dimethyl-2-oxindoline-5-carboxylate (3bo)** (Known)<sup>4</sup>



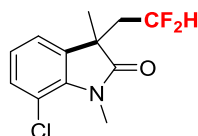
Following the general procedure for the preparation of products **3**, **3bo** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (24.1 mg, 85%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 5.57 (tdd, *J* = 56.0, 6.3, 3.4 Hz, 1H), 3.92 (s, 3H), 3.27 (s, 3H), 2.55 (qd, *J* = 14.2, 6.4 Hz, 1H), 2.34 (dddd, *J* = 20.0, 16.0, 14.7, 3.5 Hz, 1H), 1.44 (s, 3H). <sup>19</sup>F NMR (471 MHz, Chloroform-*d*) δ -114.6 (m).

**5-chloro-3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3bp)** (Known)<sup>6</sup>



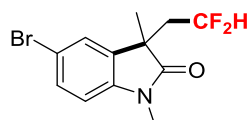
Following the general procedure for the preparation of products **3**, **3bp** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (22.0 mg, 85%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.21 (d, *J* = 2.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.62 (tdd, *J* = 55.9, 6.1, 3.5 Hz, 1H), 3.22 (s, 3H), 2.51 (qd, *J* = 14.4, 6.2 Hz, 1H), 2.33 – 2.19 (m, 1H), 1.41 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.3 (ddd, *J* = 55.9, 17.9, 14.3 Hz).

**7-chloro-3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3bq)** (Known)<sup>5</sup>



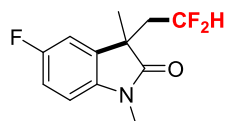
Following the general procedure for the preparation of products **3**, **3bq** was purified by silica gel chromatography (PE/EtOAc = 20/1) as a colorless oil (6.3 mg, 22%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 5.60 (tdd, *J* = 55.9, 6.2, 3.6 Hz, 1H), 3.60 (s, 3H), 2.51 (qd, *J* = 14.4, 6.2 Hz, 1H), 2.36 – 2.14 (m, 1H), 1.40 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.3 (m).

**5-bromo-3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3br)** (Known)<sup>4</sup>



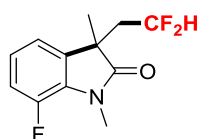
Following the general procedure for the preparation of products **3**, **3br** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (24.3 mg, 80%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.62 (tdd, *J* = 56.0, 6.2, 3.5 Hz, 1H), 3.21 (s, 3H), 2.50 (qd, *J* = 14.4, 6.2 Hz, 1H), 2.27 (tdd, *J* = 18.1, 14.7, 3.6 Hz, 1H), 1.41 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.3 (ddd, *J* = 55.9, 17.9, 14.3 Hz).

**3-(2,2-difluoroethyl)-5-fluoro-1,3-dimethylindolin-2-one (3bs)** (Known)<sup>5</sup>



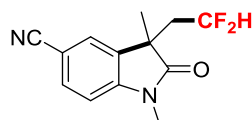
Following the general procedure for the preparation of products **3**, **3bs** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (21.0 mg, 86%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.05 – 6.96 (m, 2H), 6.80 (dd, *J* = 8.3, 4.1 Hz, 1H), 5.62 (tdd, *J* = 55.9, 6.1, 3.6 Hz, 1H), 3.22 (s, 3H), 2.50 (qd, *J* = 14.6, 6.0 Hz, 1H), 2.37 – 2.13 (m, 1H), 1.41 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.2 (m, 2F), -120.1 (td, *J* = 8.8, 4.4 Hz, 1F).

**3-(2,2-difluoroethyl)-7-fluoro-1,3-dimethylindolin-2-one (3bt)** (Known)<sup>5</sup>



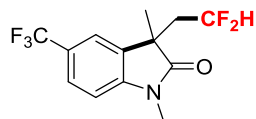
Following the general procedure for the preparation of products **3**, **3bt** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a colorless oil (5.3 mg, 22%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 6.90 (m, 3H), 5.60 (tdd, *J* = 56.0, 6.2, 3.6 Hz, 1H), 3.44 (s, 3H), 2.51 (qd, *J* = 14.4, 6.2 Hz, 1H), 2.27 (tdd, *J* = 18.1, 14.7, 3.6 Hz, 1H), 1.41 (s, 3H). <sup>19</sup>F NMR (377 MHz, Chloroform-*d*) δ -114.4 (ddd, *J* = 56.0, 17.9, 14.3 Hz, 2F), -135.9 (m, 1F).

**3-(2,2-difluoroethyl)-1,3-dimethyl-2-oxindoline-5-carbonitrile (3bu)** (Known)<sup>5</sup>



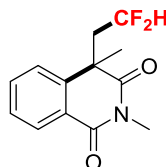
Following the general procedure for the preparation of products **3**, **3bu** was purified by silica gel chromatography (PE/EtOAc = 15/1) as a white solid (21.0 mg, 84%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.65 (d,  $J$  = 8.1 Hz, 1H), 7.50 (s, 1H), 6.95 (d,  $J$  = 8.1 Hz, 1H), 5.62 (tt,  $J$  = 55.7, 4.7 Hz, 1H), 3.27 (s, 3H), 2.54 (qd,  $J$  = 14.7, 5.9 Hz, 1H), 2.34 (dddd,  $J$  = 22.7, 15.1, 13.0, 3.6 Hz, 1H), 1.44 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -114.4 (m).

### 3-(2,2-difluoroethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (**3bv**) (Known)<sup>5</sup>



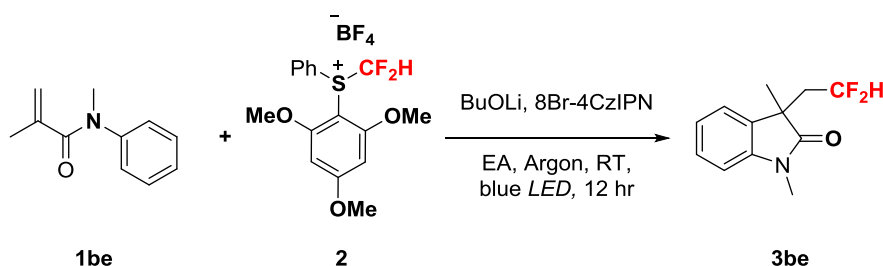
Following the general procedure for the preparation of products **3**, **3bv** was purified by silica gel chromatography (PE/EtOAc = 10/1) as a white solid (22.3 mg, 76%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.60 (d,  $J$  = 8.2 Hz, 1H), 7.46 (s, 1H), 6.95 (d,  $J$  = 8.2 Hz, 1H), 5.61 (tdd,  $J$  = 55.9, 5.6, 3.9 Hz, 1H), 3.27 (s, 3H), 2.54 (qd,  $J$  = 14.5, 6.1 Hz, 1H), 2.41 – 2.24 (m, 1H), 1.45 (s, 3H).  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -61.4 (s, 1F), -114.4 (m, 2F).

### 4-(2,2-difluoroethyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (**3ca**) (Known)<sup>9</sup>



Following the general procedure for the preparation of products **3**, **3ca** was purified by silica gel chromatography (PE/EtOAc = 20/1) as a colorless oil (20.3 mg, 80%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.29 (d,  $J$  = 7.9 Hz, 1H), 7.68 (t,  $J$  = 7.6 Hz, 1H), 7.56 – 7.41 (m, 2H), 5.38 (tdd,  $J$  = 56.5, 5.8, 2.6 Hz, 1H), 3.40 (s, 3H), 3.09 – 2.90 (m, 1H), 2.59 – 2.33 (m, 1H), 1.67 (s, 3H).  $^{19}\text{F}$  NMR (377 MHz, Chloroform-*d*)  $\delta$  -115.7 (m).

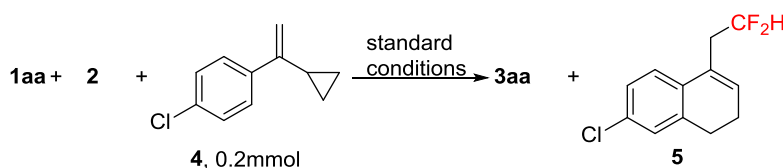
## 6. 1.0 mmol Scale Procedure for Radical Difluoromethylation of **1be**



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added *N*-arylacrylamide **1be** (1.0 mmol, 175 mg, 1.0 equiv. ), S-(difluoromethyl)sulfonium salt **2** (2.0 mmol, 828 mg, 2.0 equiv. ),  $t\text{BuOLi}$  (2.0 mmol, 160 mg, 2.0 equiv. ) and 8Br-4CzIPN (0.03 mmol, 43 mg, 3 mol%). The flask was flushed with argon, followed by the addition of ethyl acetate (10 ml). The tube was placed at a distance of ~2 mm away from blue LED lamps ( $\lambda$  = 450 nm, 3 W  $\times$  4), then the reaction mixture was stirred under irradiation of blue LEDs overnight at room temperature. The mixture was evaporated in vacuo after reaction accomplished. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 10/1) to afford the desired product 3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (**3be**) as a colorless oil (135 mg, 60%).

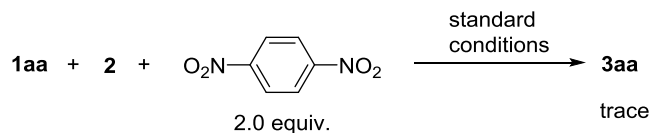
## 7. Mechanistic Experiments.

### Radical-clock experiment



**7-chloro-4-(2,2-difluoroethyl)-1,2-dihydronaphthalene (5).**<sup>10</sup> To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 1-chloro-4-(1-cyclopropylvinyl)benzene **4** (0.2 mmol, 35.7 mg, 2.0 equiv.), **1a** (0.1 mmol, 31.3 mg, 1.0 equiv.), **2** (0.2 mmol, 83.0 mg, 2.0 equiv.), 8Br-4CzIPN (0.003 mmol, 4.3 mg, 3 mol%), <sup>t</sup>BuOLi (0.2 mmol, 4.8 mg, 2.0 equiv.). The flask was flushed with argon, followed by the addition of ethyl acetate (2.5 mL). The tube was placed at a distance of ~2 mm away from blue LED lamps ( $\lambda = 450$  nm, 3 W  $\times$  4), and the reaction mixture was stirred under irradiation of blue LEDs overnight at room temperature. The reaction mixture was evaporated in vacuo after reaction accomplished. The residue was purified by flash column chromatography on silica gel with PE to afford **5** as a colorless oil in 14% yield, and with PE/EtOAc = 10/1 to afford **3aa** in 41% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.18 (dd,  $J = 8.3, 1.8$  Hz, 1H), 7.15 – 7.10 (m, 2H), 7.02 – 6.97 (m, 1H), 6.04 (t,  $J = 4.4$  Hz, 1H), 5.90 (tt,  $J = 56.7, 4.7$  Hz, 1H), 2.96 (td,  $J = 16.5, 4.5$  Hz, 2H), 2.74 (t,  $J = 8.1$  Hz, 2H), 2.29 (dt,  $J = 12.3, 6.5$  Hz, 2H). <sup>19</sup>F NMR (471 MHz, Chloroform-*d*)  $\delta$  -113.9 (dt,  $J = 56.7, 16.5$  Hz).

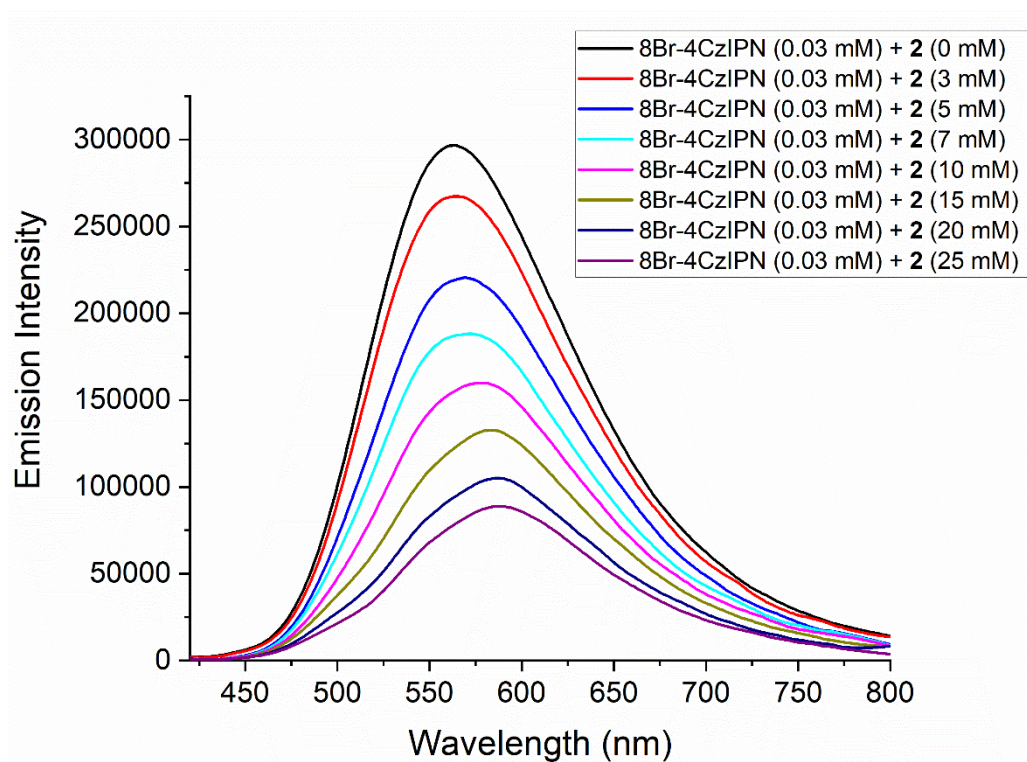
### Radical inhibition experiment



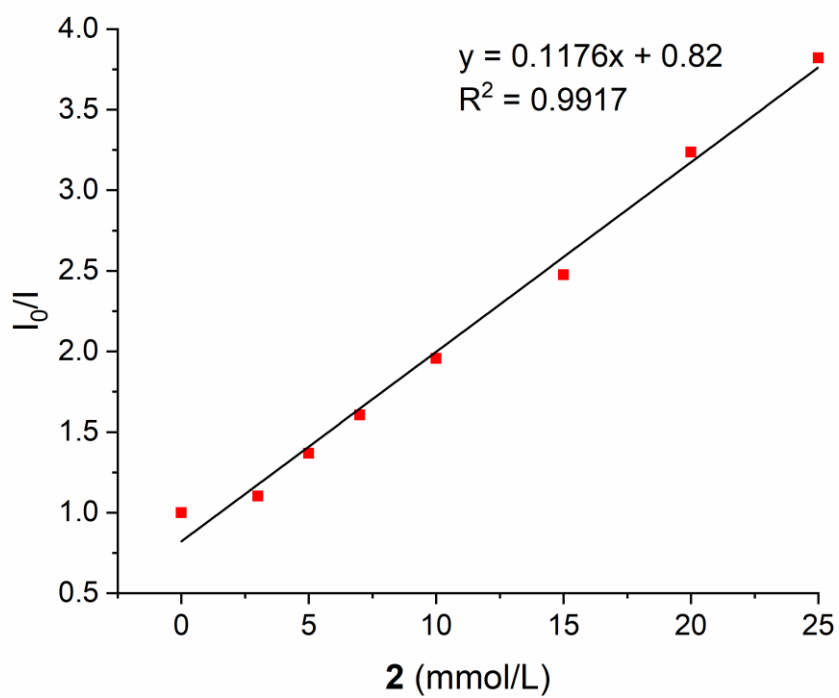
To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 1,4-dinitrobenzene (0.2 mmol, 33.6 mg, 2.0 equiv.), **1aa** (0.1 mmol, 31.3 mg, 1.0 equiv.), **2** (0.2 mmol, 83.0 mg, 2.0 equiv.), 8Br-4CzIPN (0.003 mmol, 4.3 mg, 3 mol%), <sup>t</sup>BuOLi (0.2 mmol, 16.0 mg, 2.0 equiv.). The flask was flushed with argon, followed by the addition of ethyl acetate (2.5 mL). The tube was placed at a distance of ~2 mm away from blue LED lamps ( $\lambda = 450$  nm, 3 W  $\times$  4), and the reaction mixture was stirred under irradiation of blue LEDs overnight at room temperature. The reaction mixture was evaporated in vacuo after reaction accomplished. The residue was monitored by <sup>19</sup>F NMR using PhF (0.1 mmol) as the internal standard, and no **3aa** was detected.

## 8. Fluorescence Quenching Experiment

Fluorescence spectra were collected on Edinburgh Instruments FS5 Spectrofluorometer. All 8Br-4CzIPN solutions were excited at 342 nm and emission intensity at 563 nm was observed. The measurements were carried out mixing a  $3 \times 10^{-5}$  M solution of 8Br-4CzIPN in MeCN (3 ml) with the appropriate amount of quencher in a quartz cuvette.  $I_0$  and  $I$  represent the intensities of the emission in the absence and presence of the quencher at 563 nm. Increasing amounts of reagent **2** were added to a solution of 8Br-4CzIPN, and an emission spectrum of the solution was recorded after each addition.



**Figure S2.** Emission spectra of 8Br-4CzIPN showing the quenching effect of increasing concentrations of **2**.



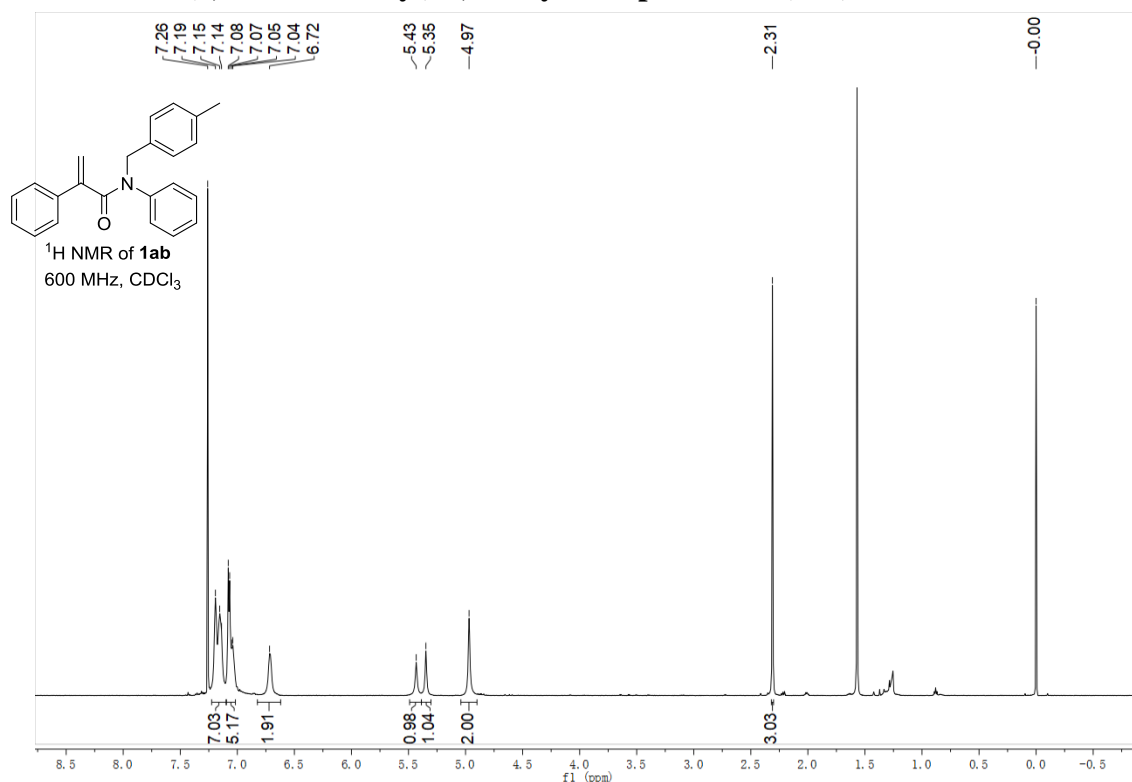
**Figure S3.** The Liner relationship over the increasing concentration of **2**.

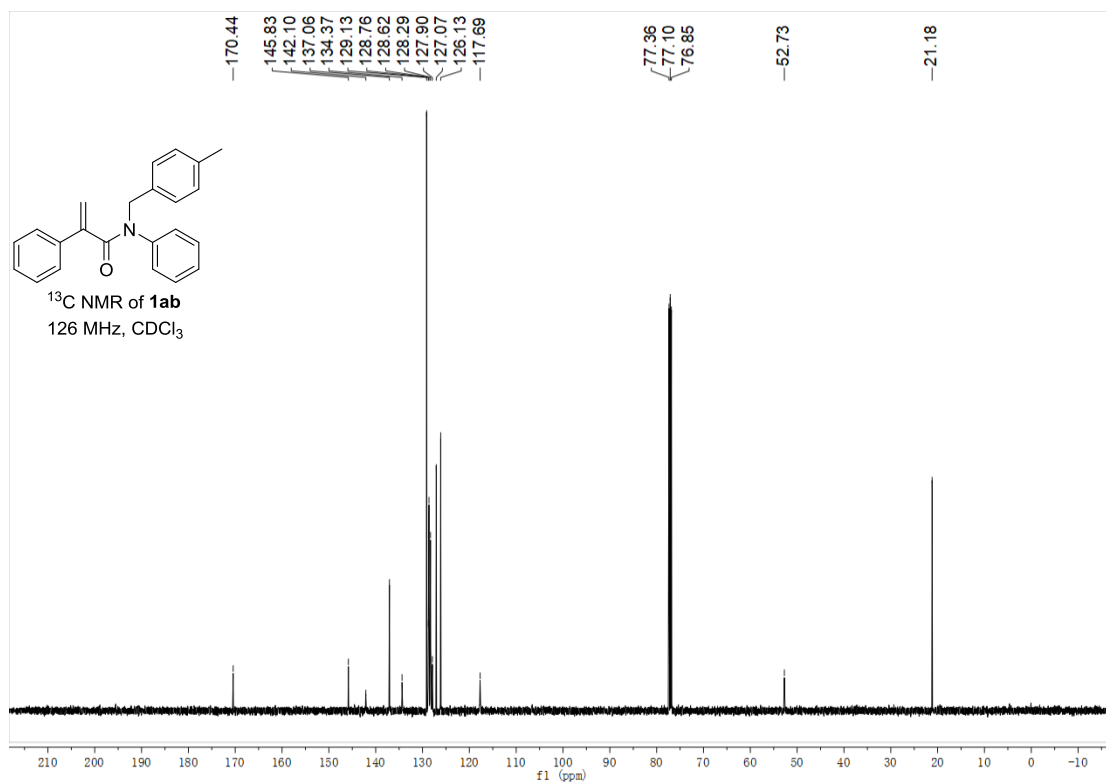
## 9. References

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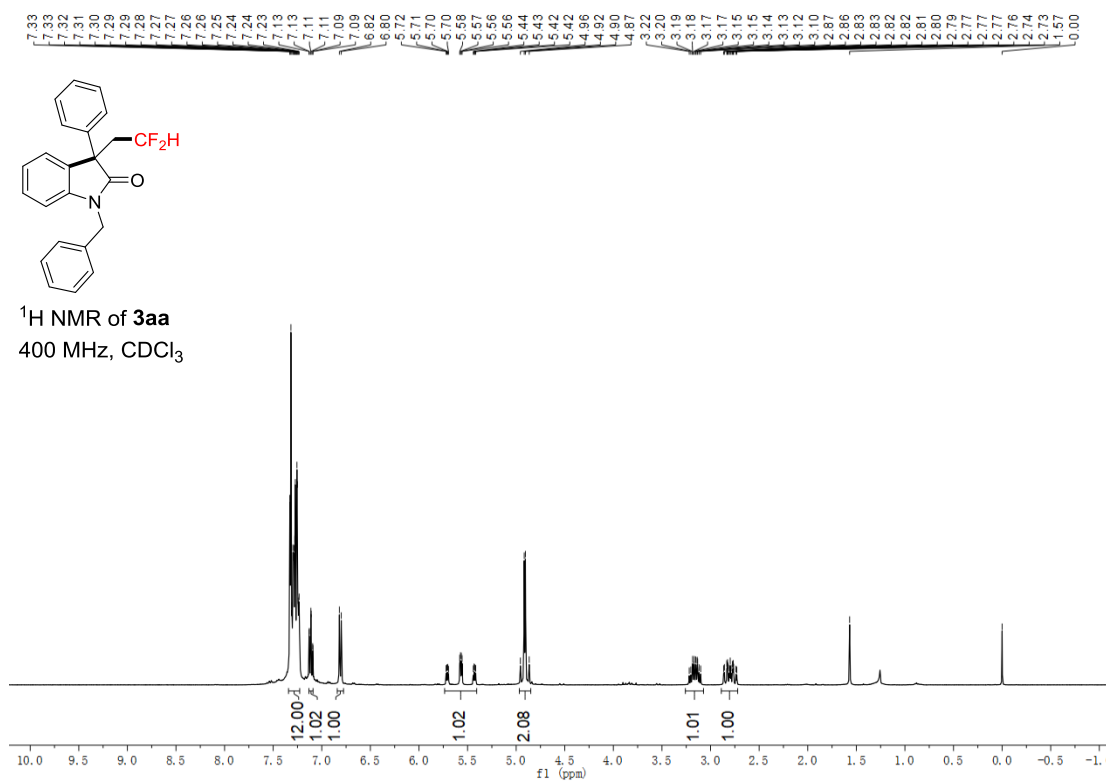
## 10. NMR Spectra for New Compounds

### 7-chloro-4-(2,2-difluoroethyl)-1,2-dihydronaphthalene (1ab)

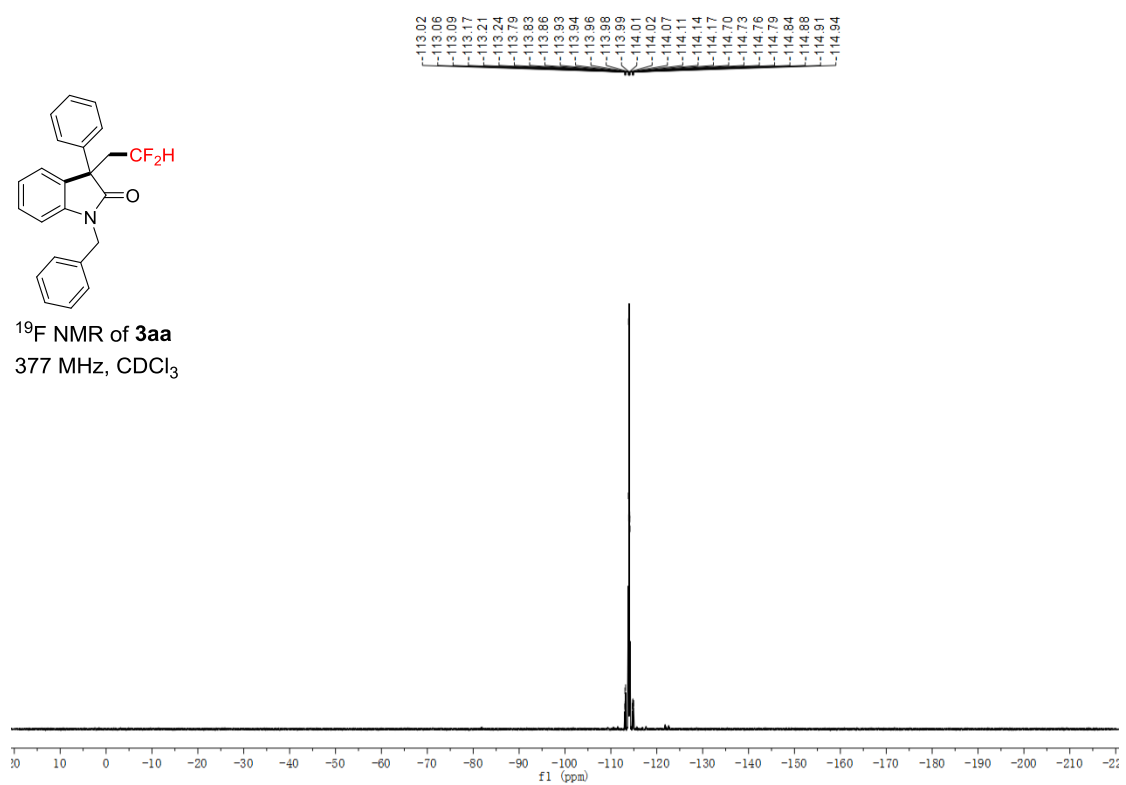
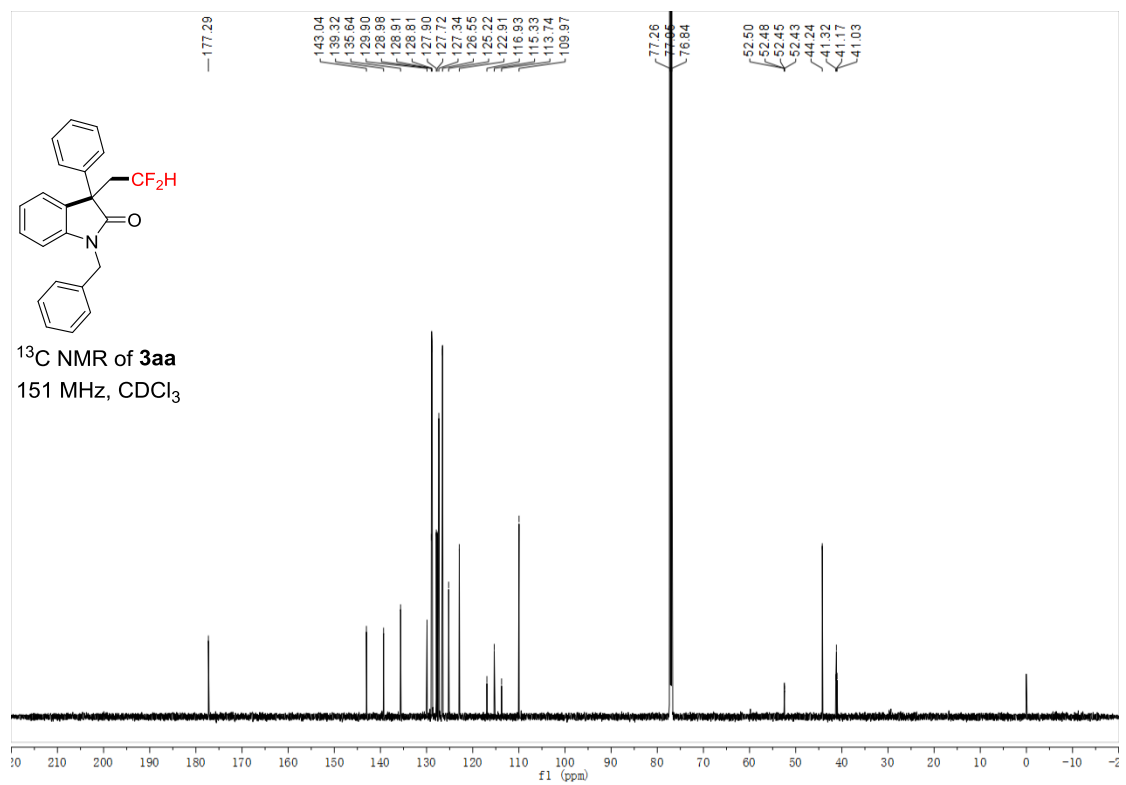




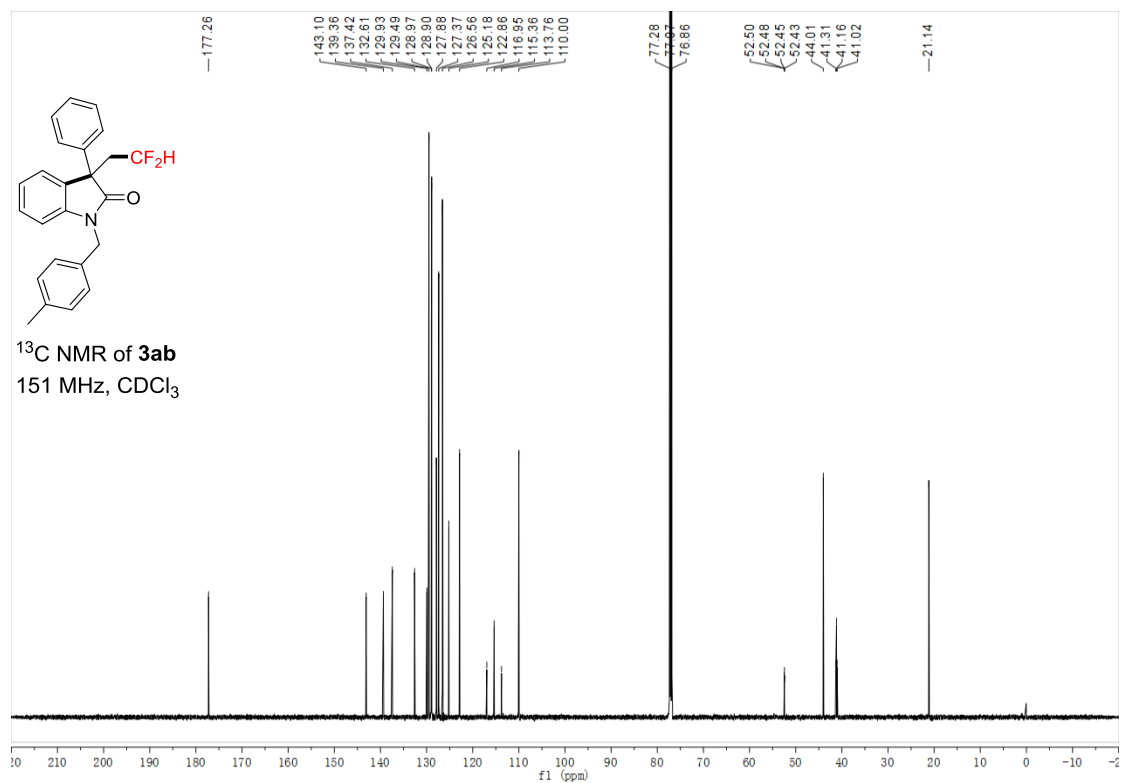
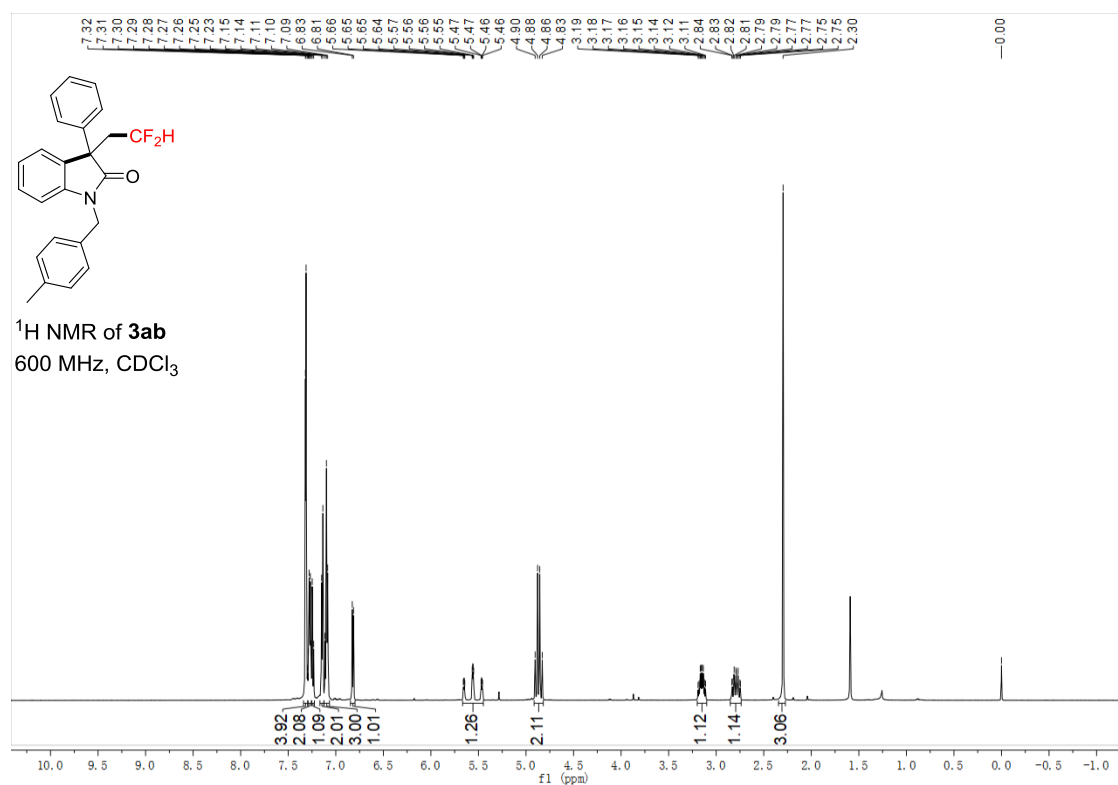
**1-benzyl-3-(2,2-difluoroethyl)-3-phenylindolin-2-one (3aa)**

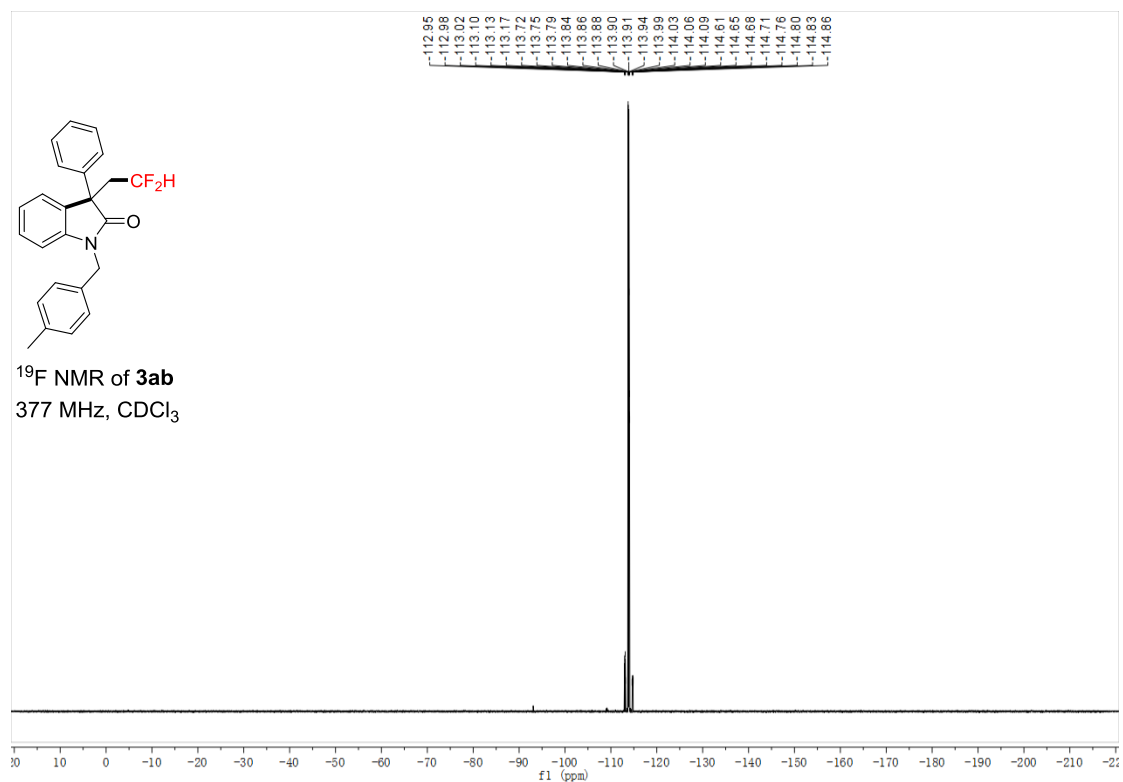




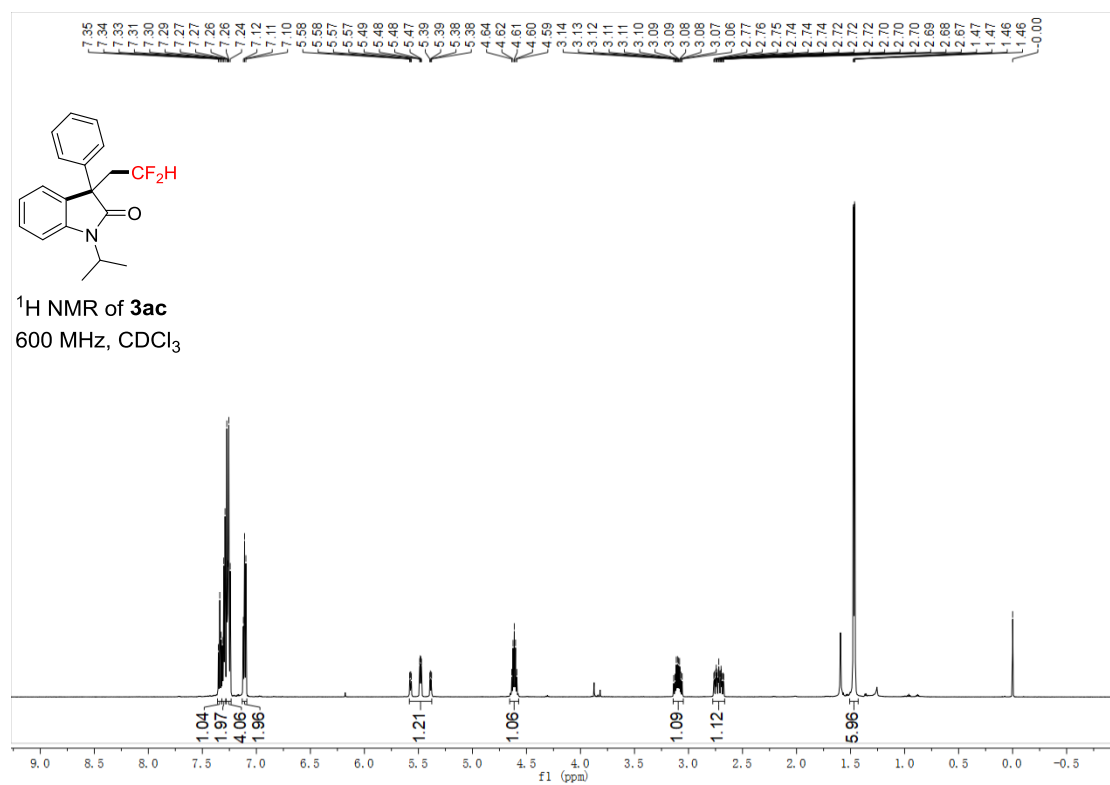


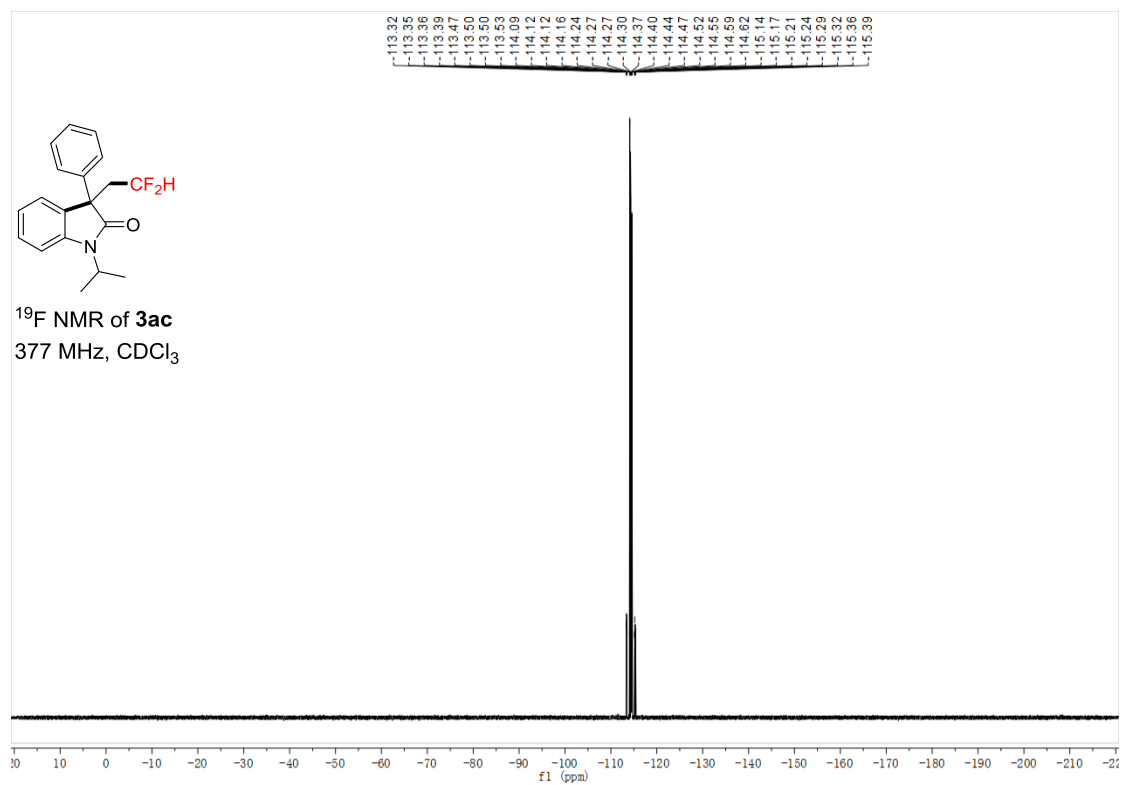
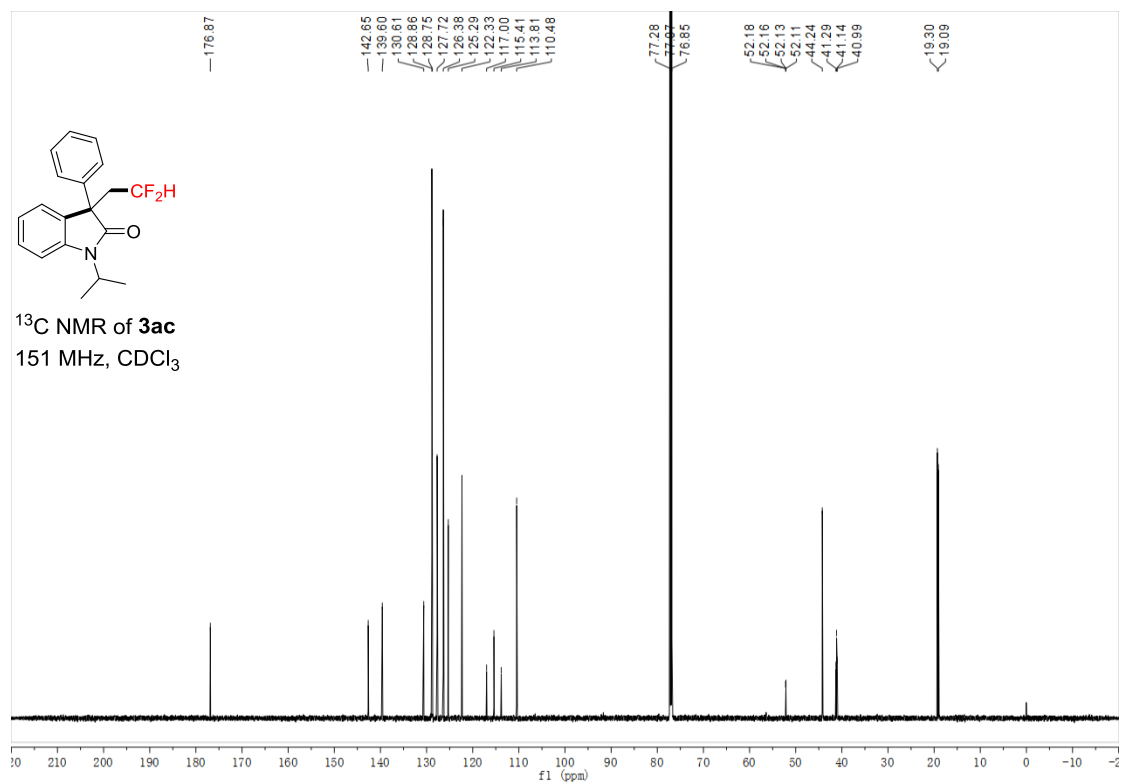
### 3-(2,2-difluoroethyl)-1-(4-methylbenzyl)-3-phenylindolin-2-one (3ab)



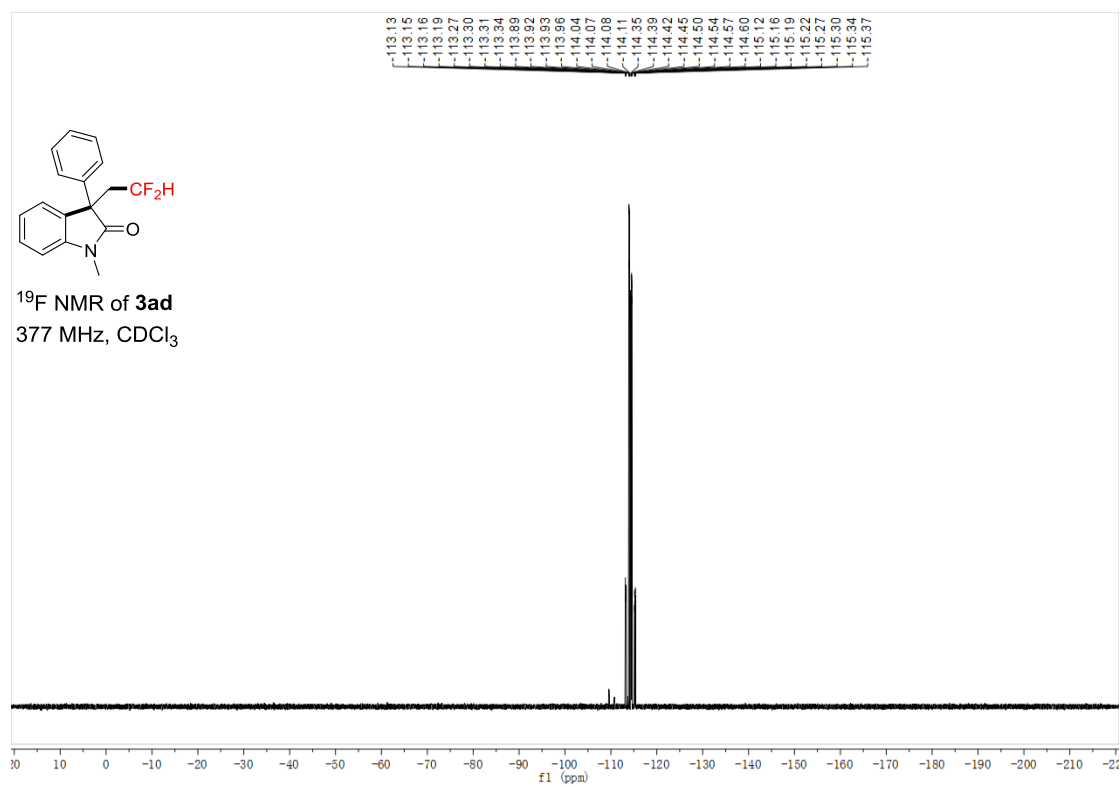
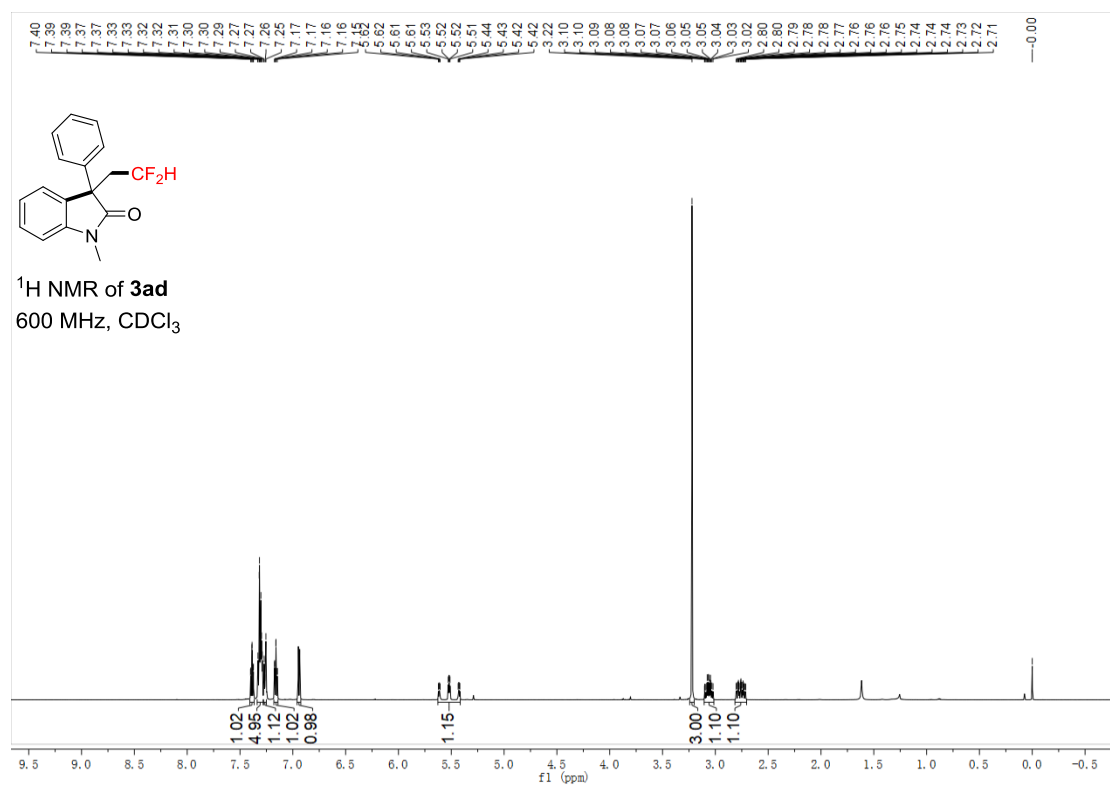


**3-(2,2-difluoroethyl)-1-isopropyl-3-phenylindolin-2-one (3ac)**

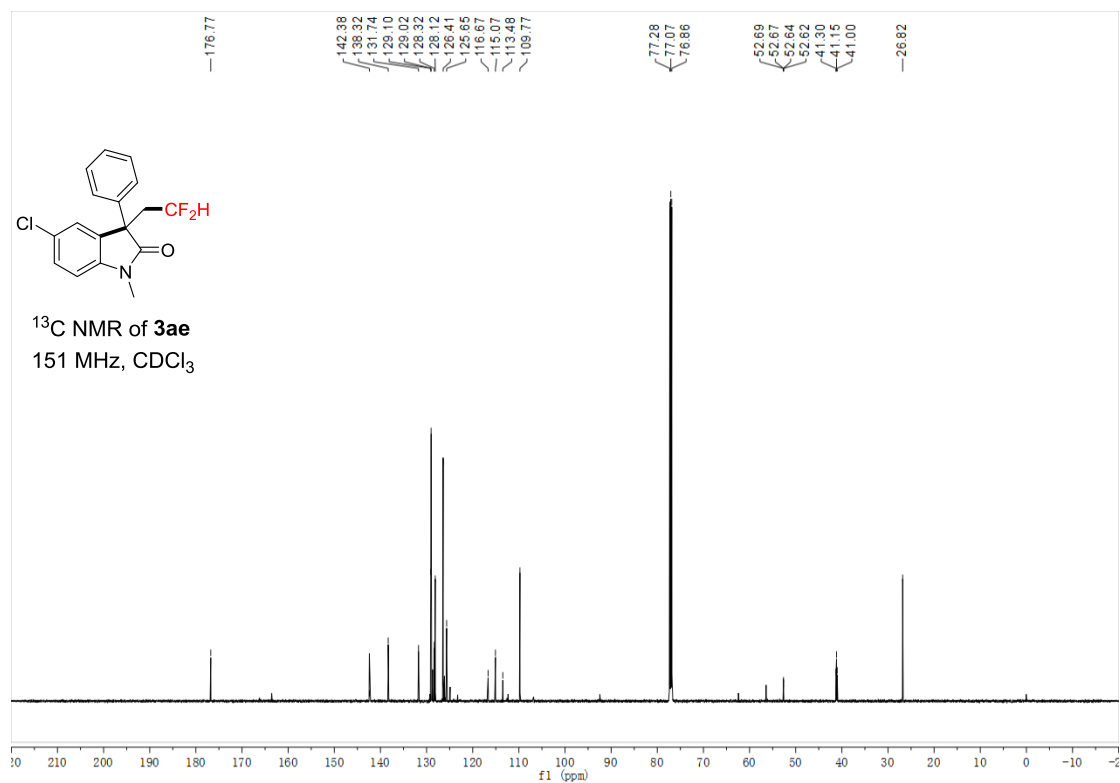
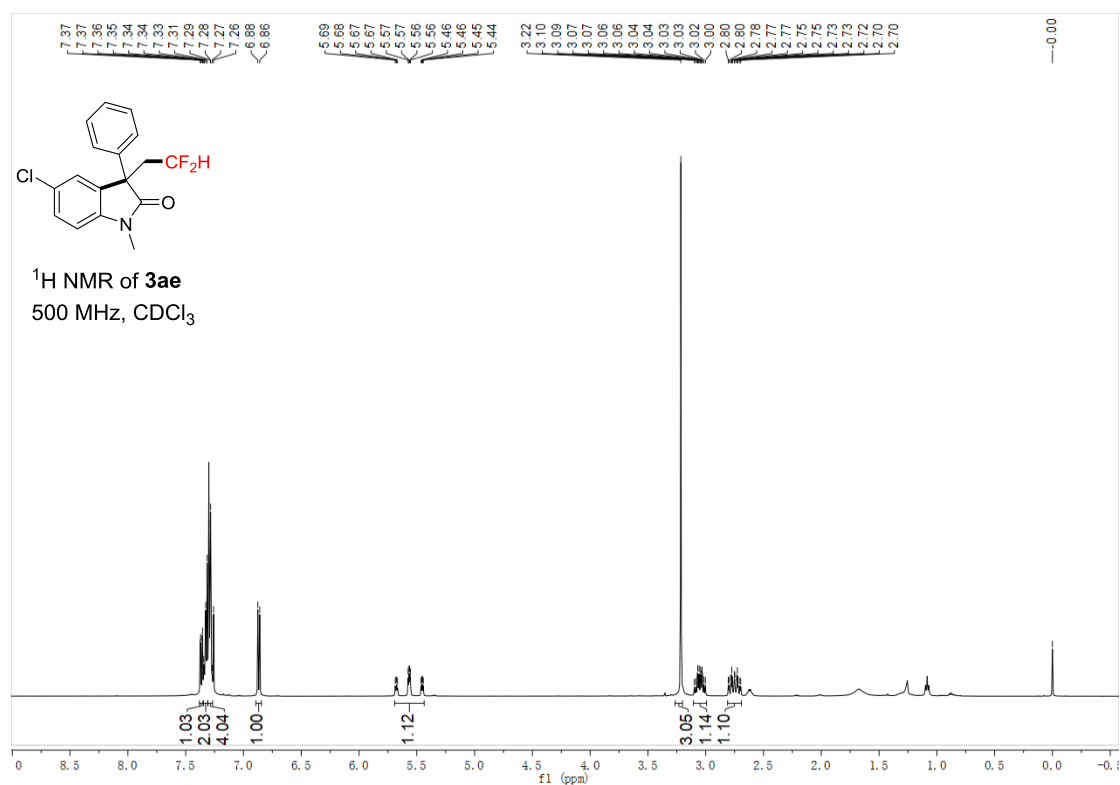


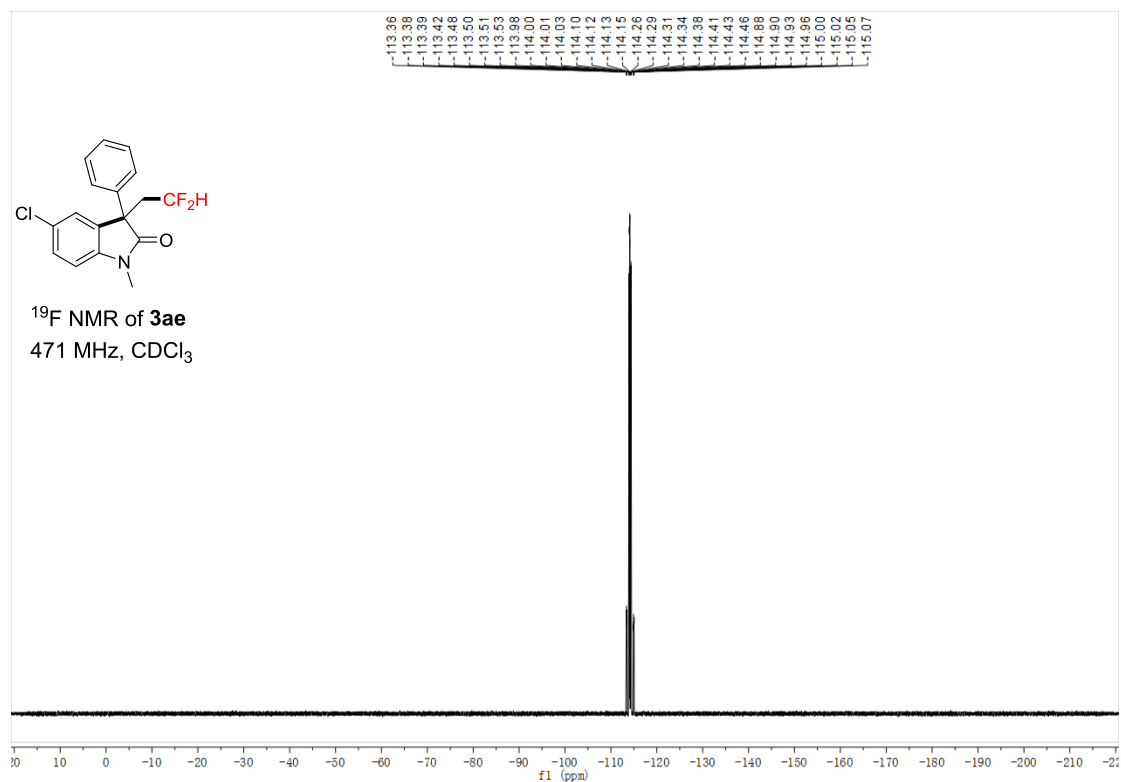


### 3-(2,2-difluoroethyl)-1-methyl-3-phenylindolin-2-one (3ad)

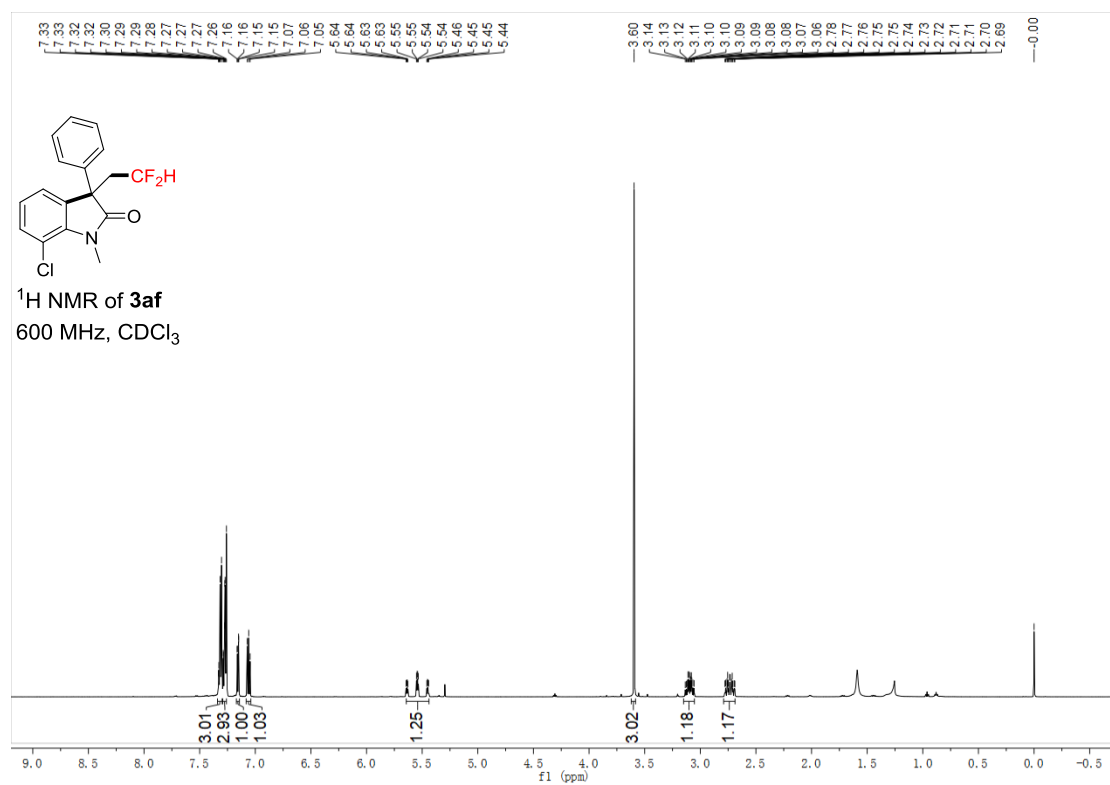


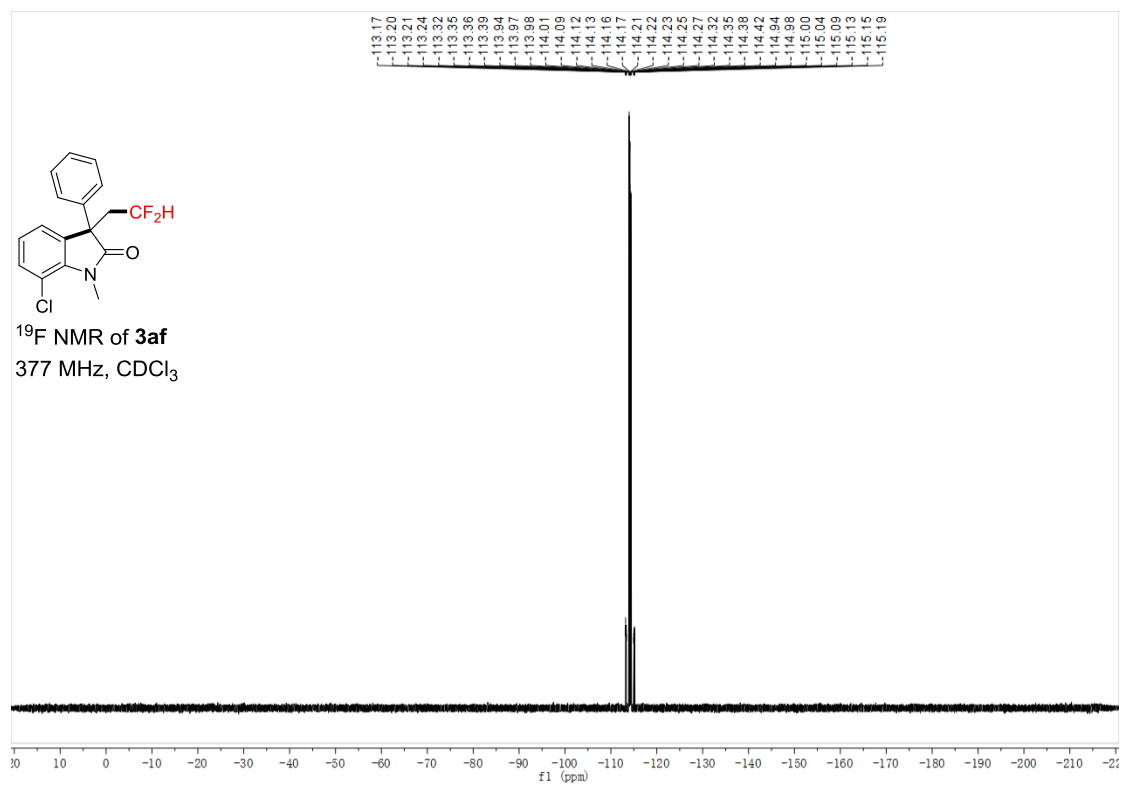
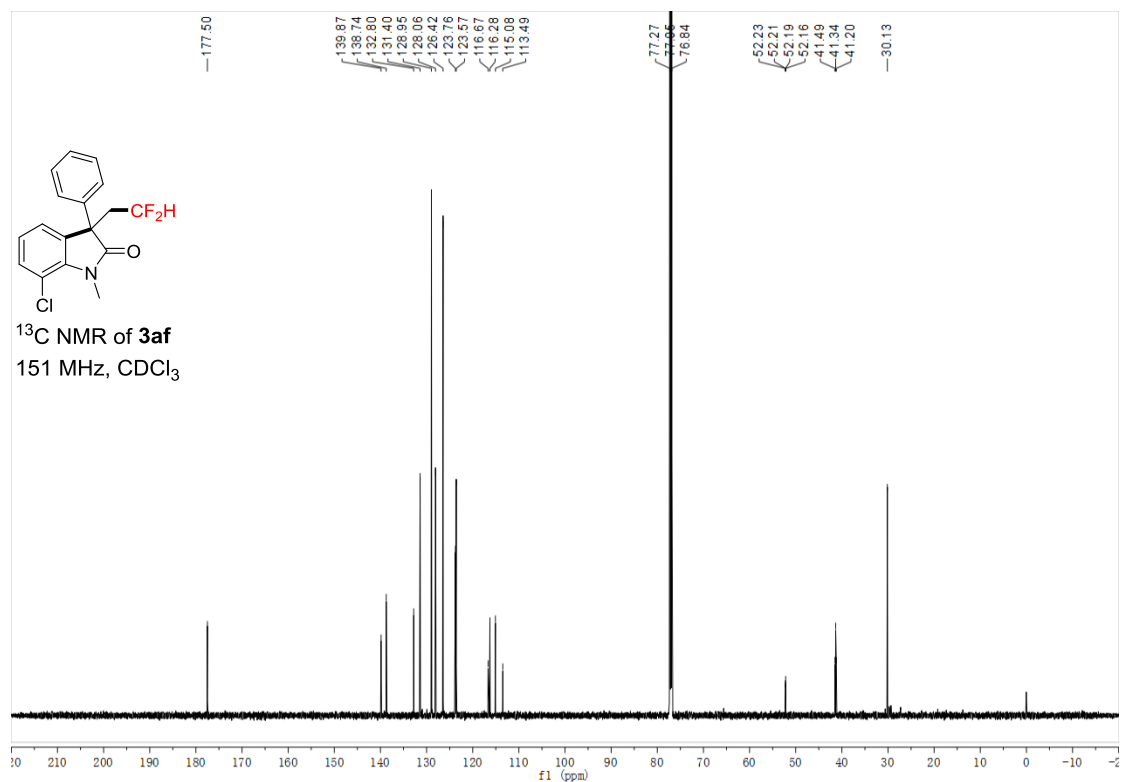
**5-chloro-3-(2,2-difluoroethyl)-1-methyl-3-phenylindolin-2-one (3ae)**





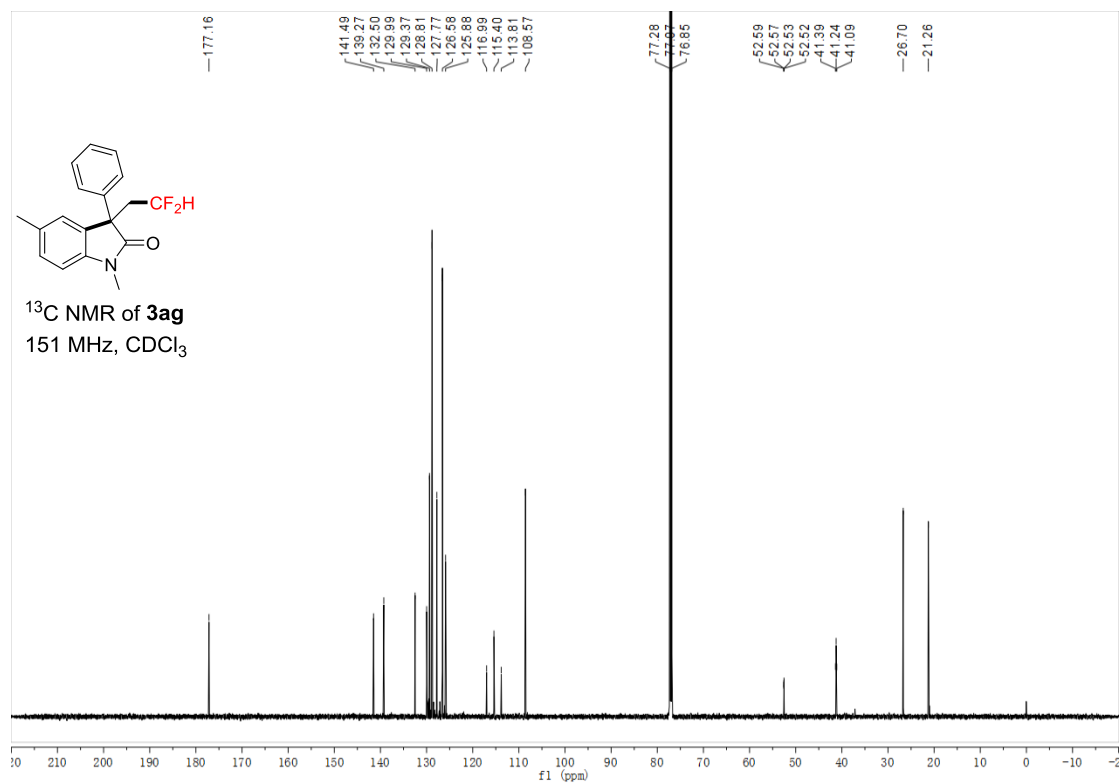
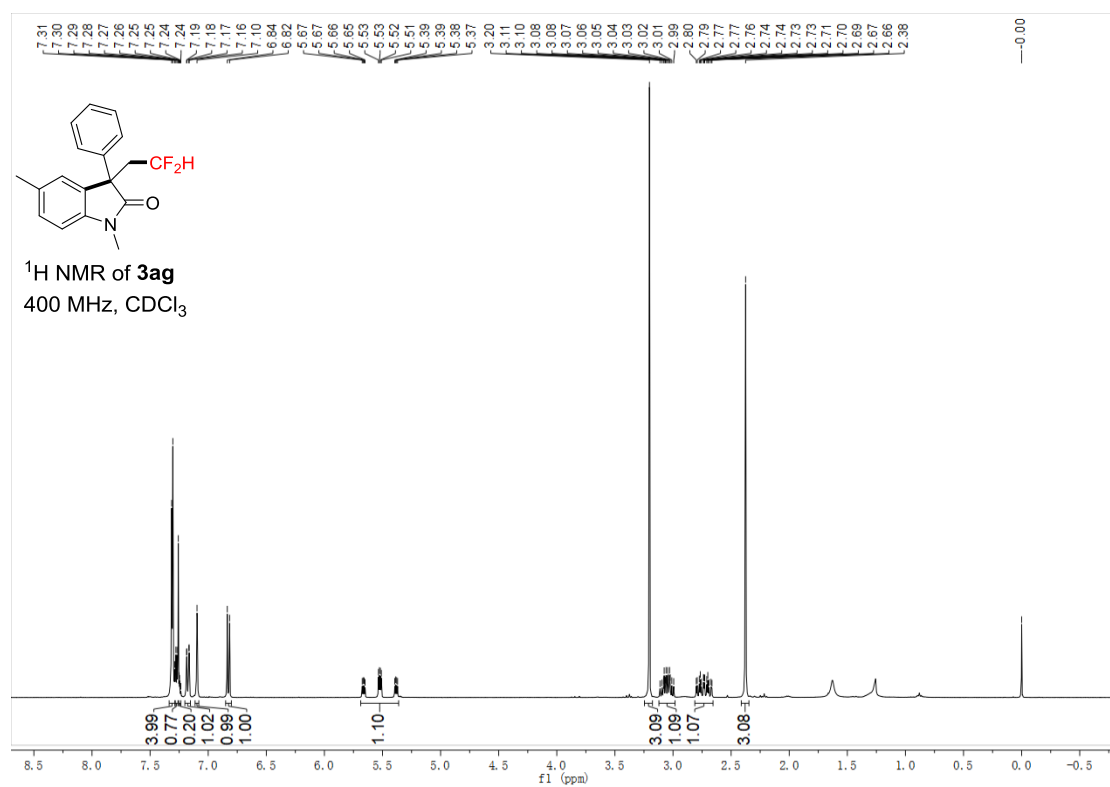
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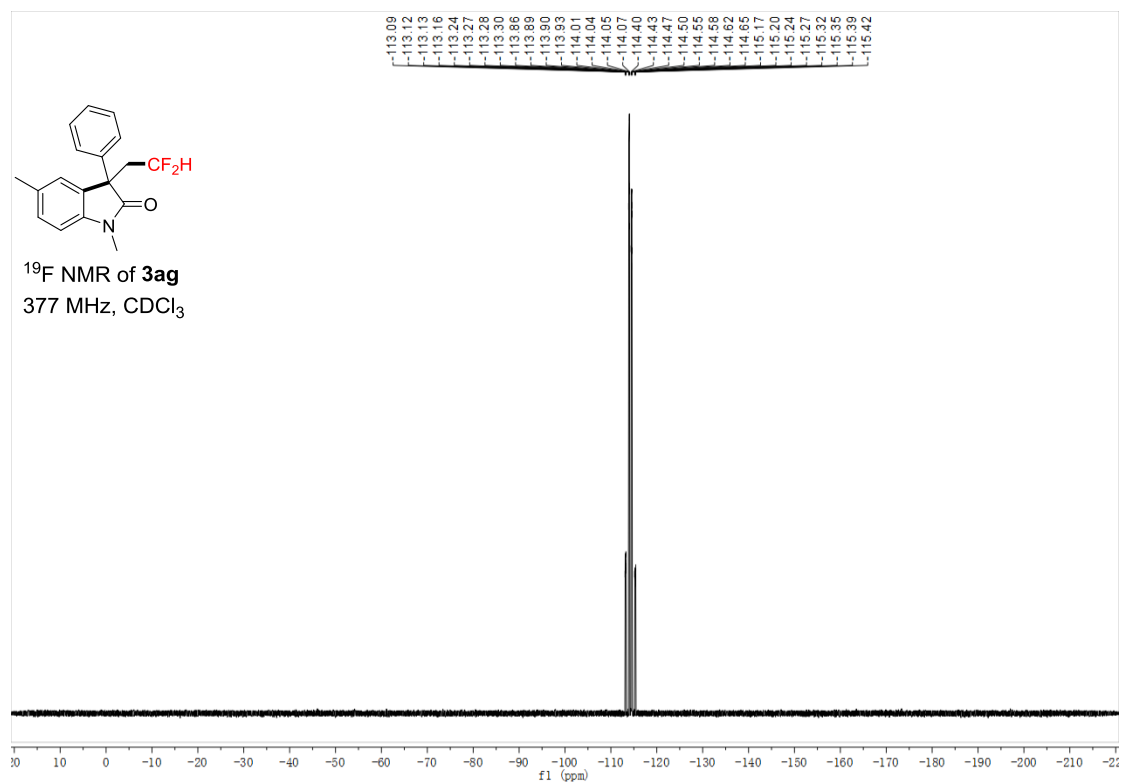




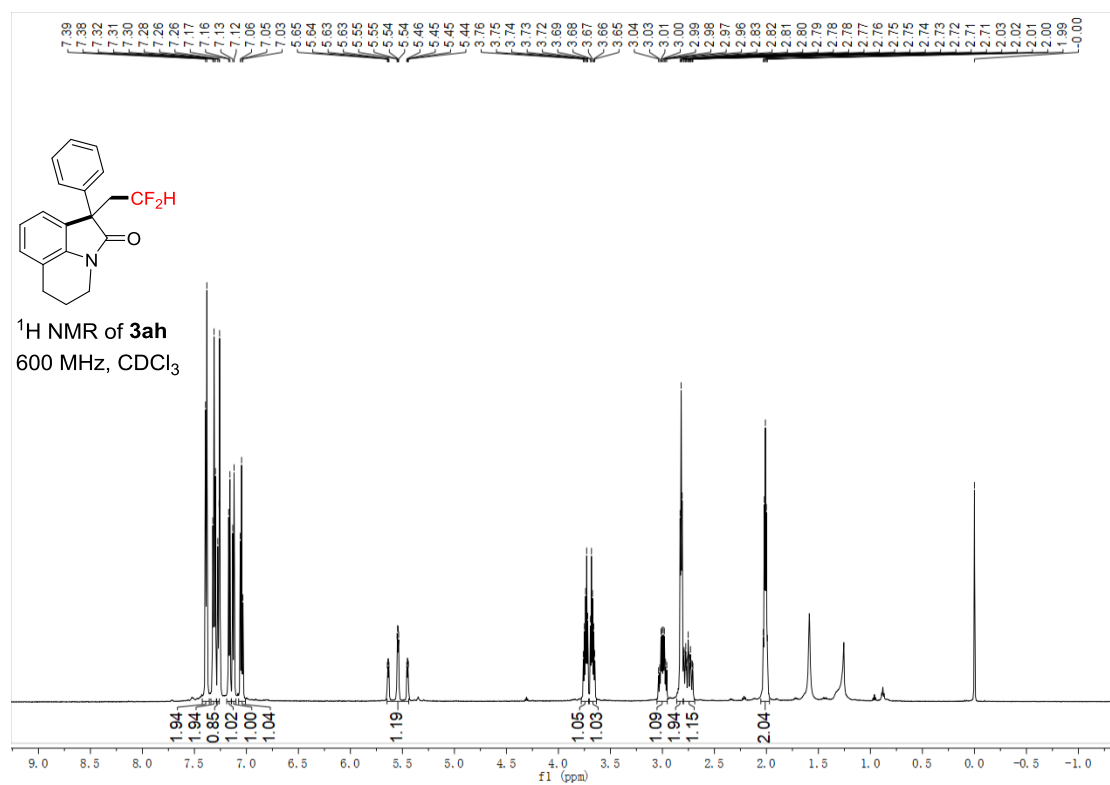


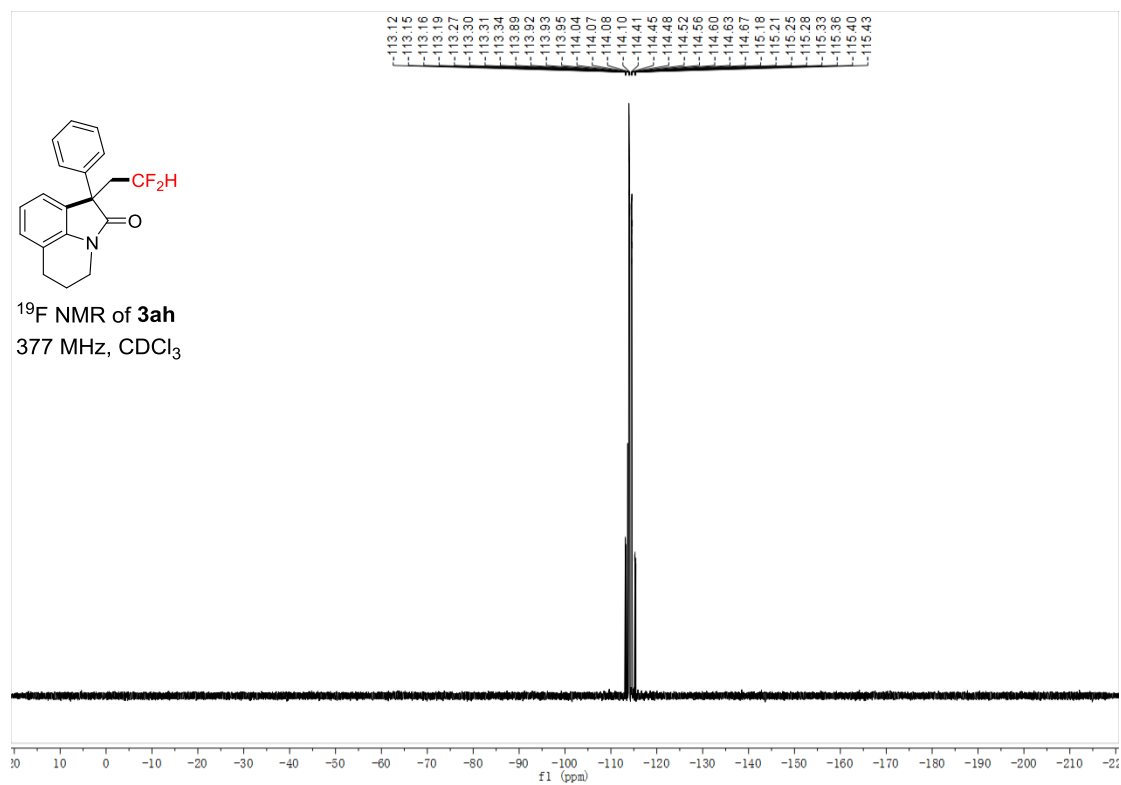
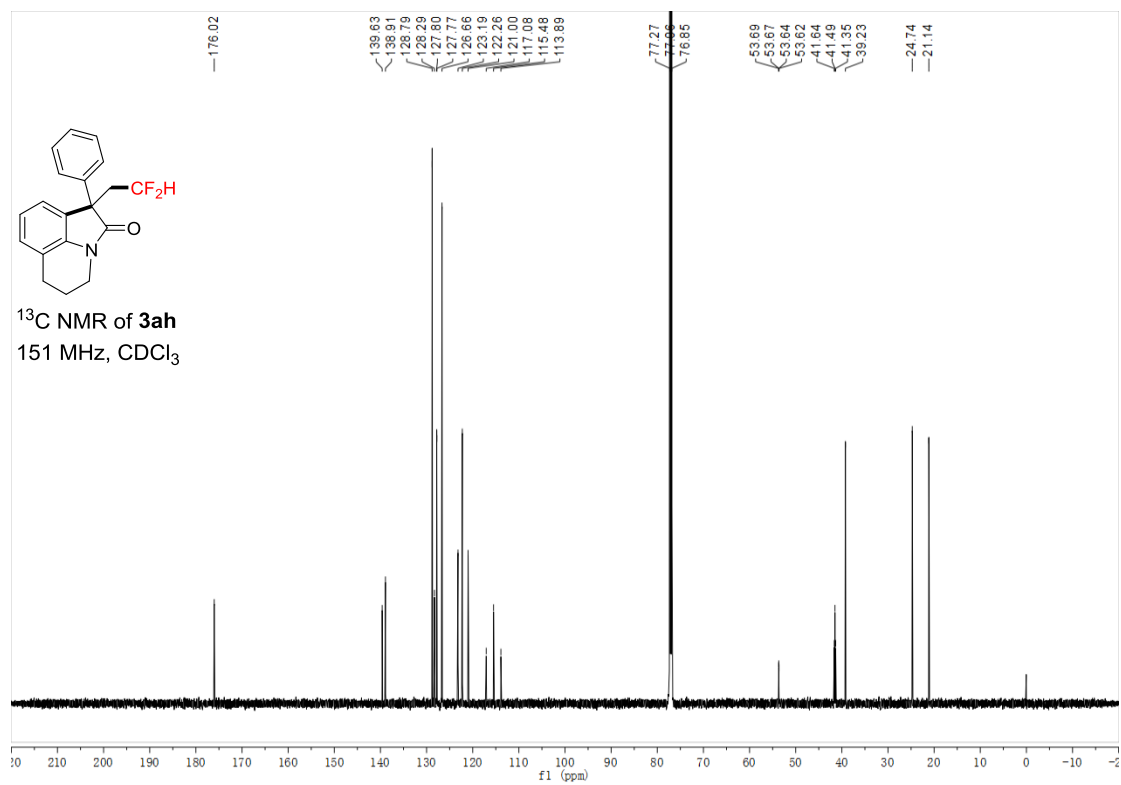
### 3-(2,2-difluoroethyl)-1,5-dimethyl-3-phenylindolin-2-one (3ag)



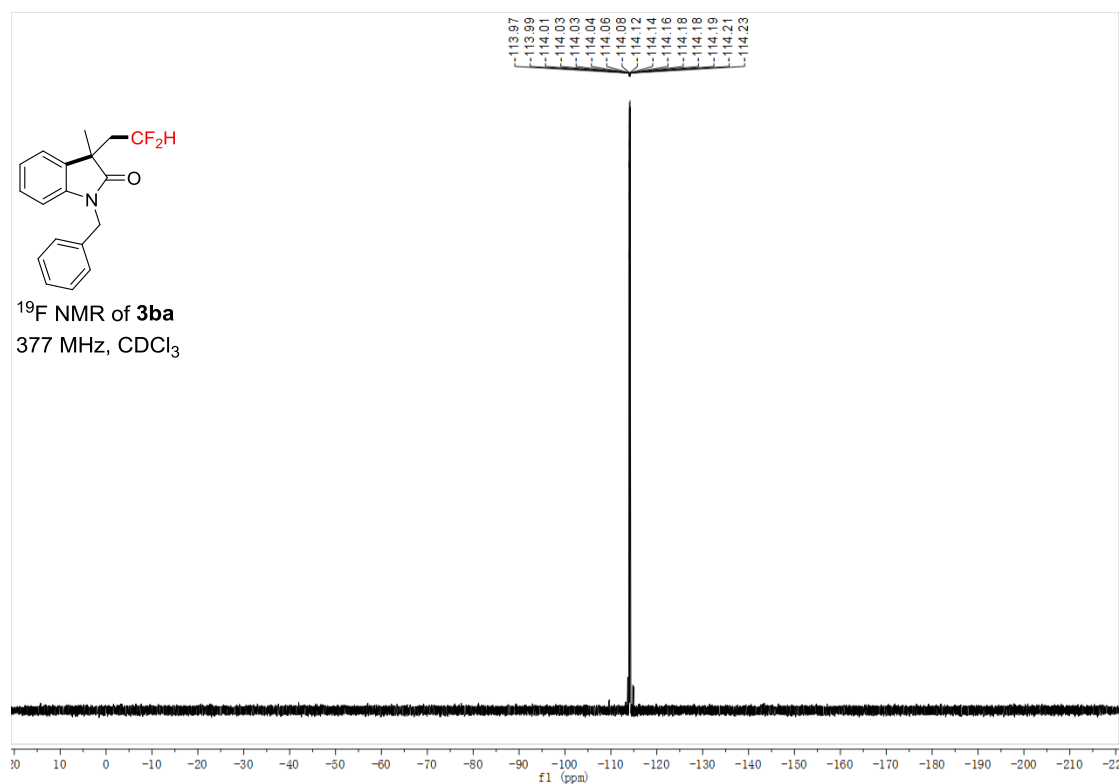
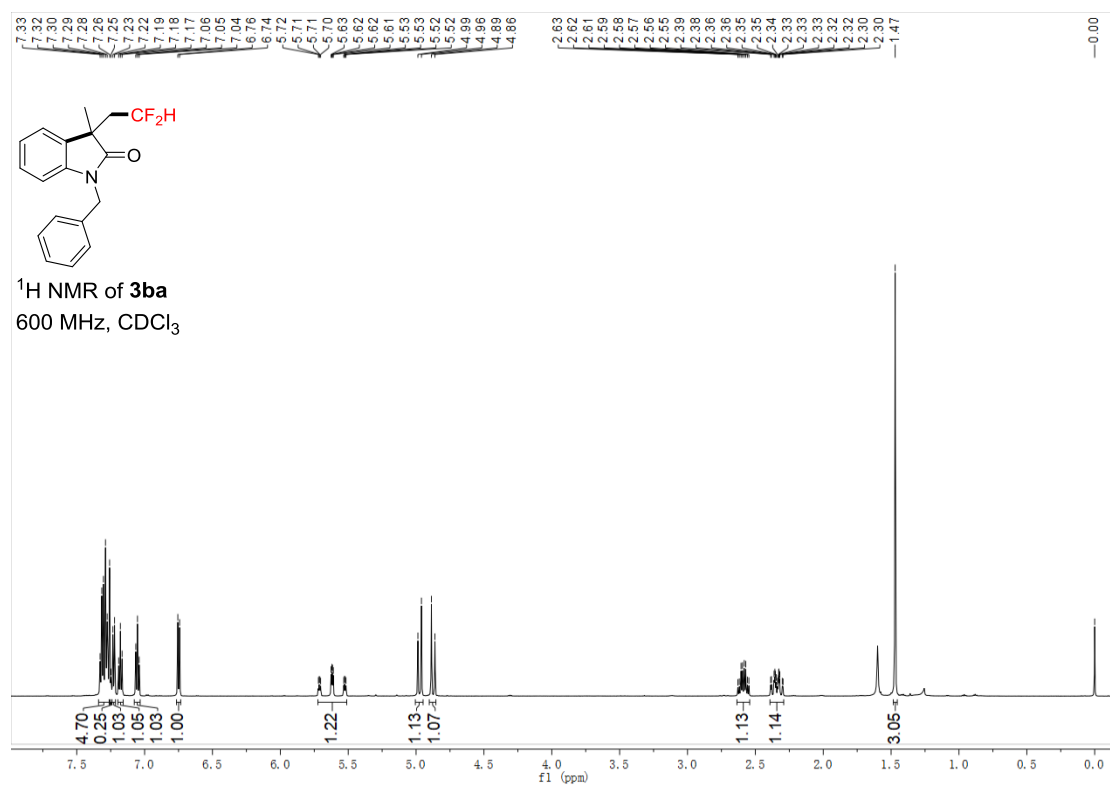


**1-(2,2-difluoroethyl)-1-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3ah)**

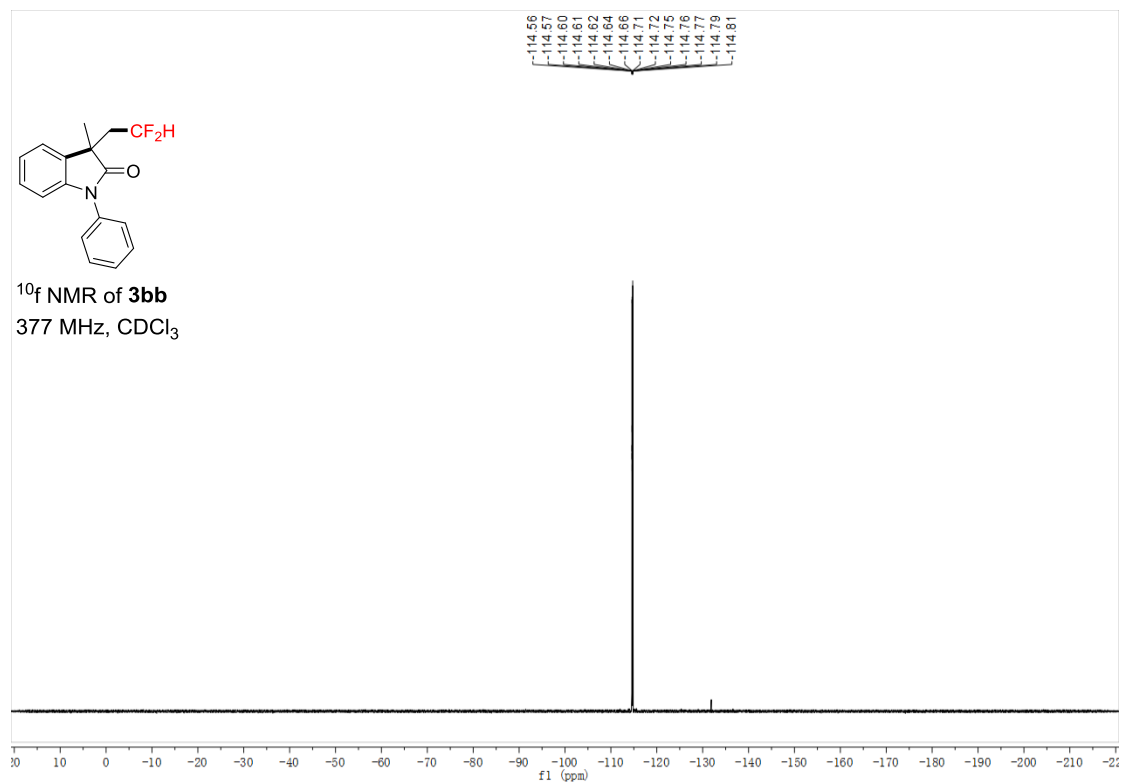
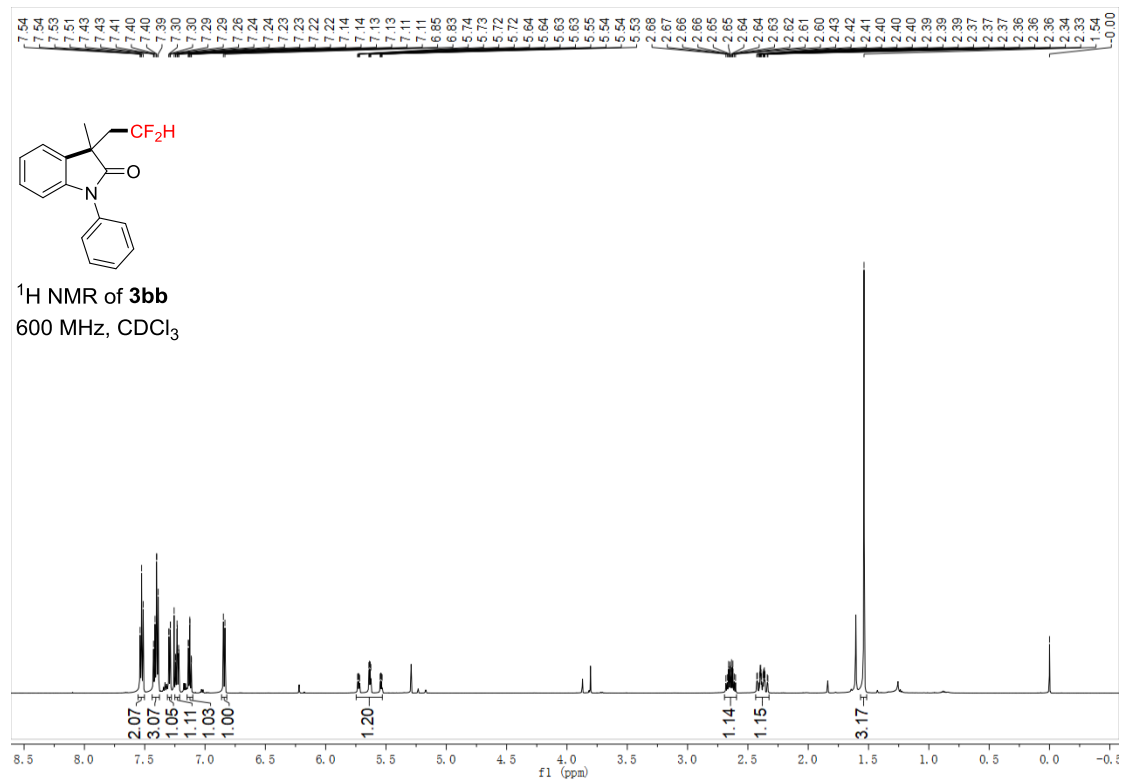




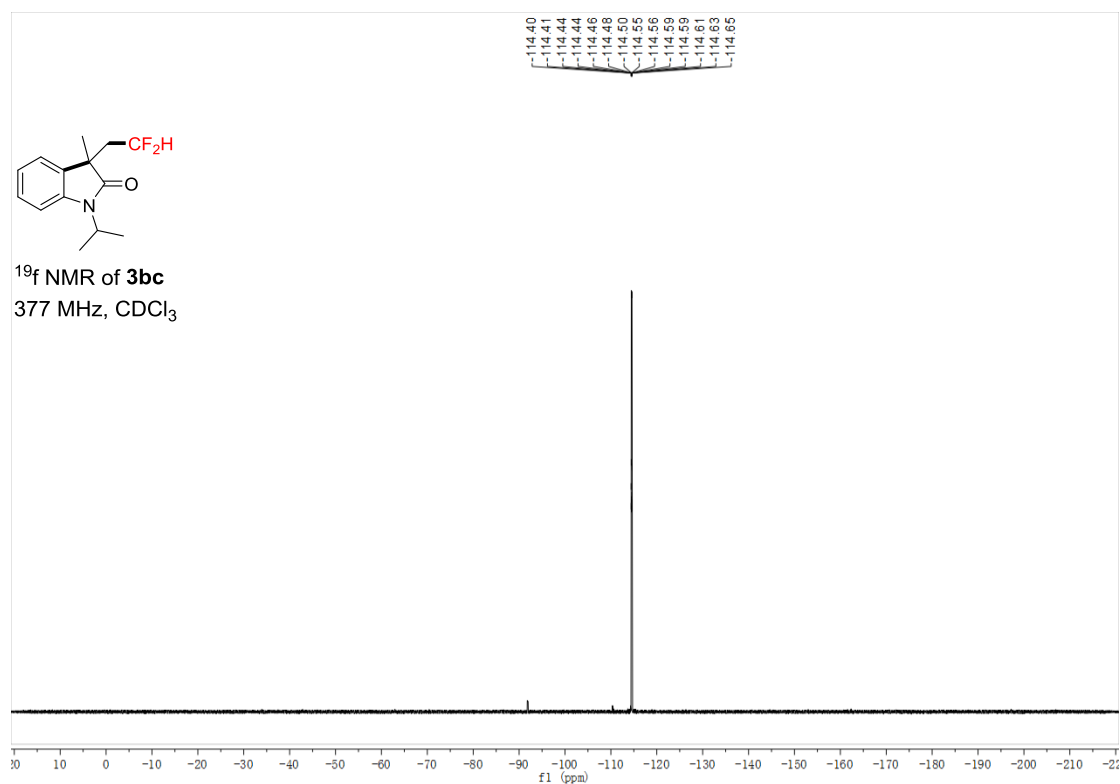
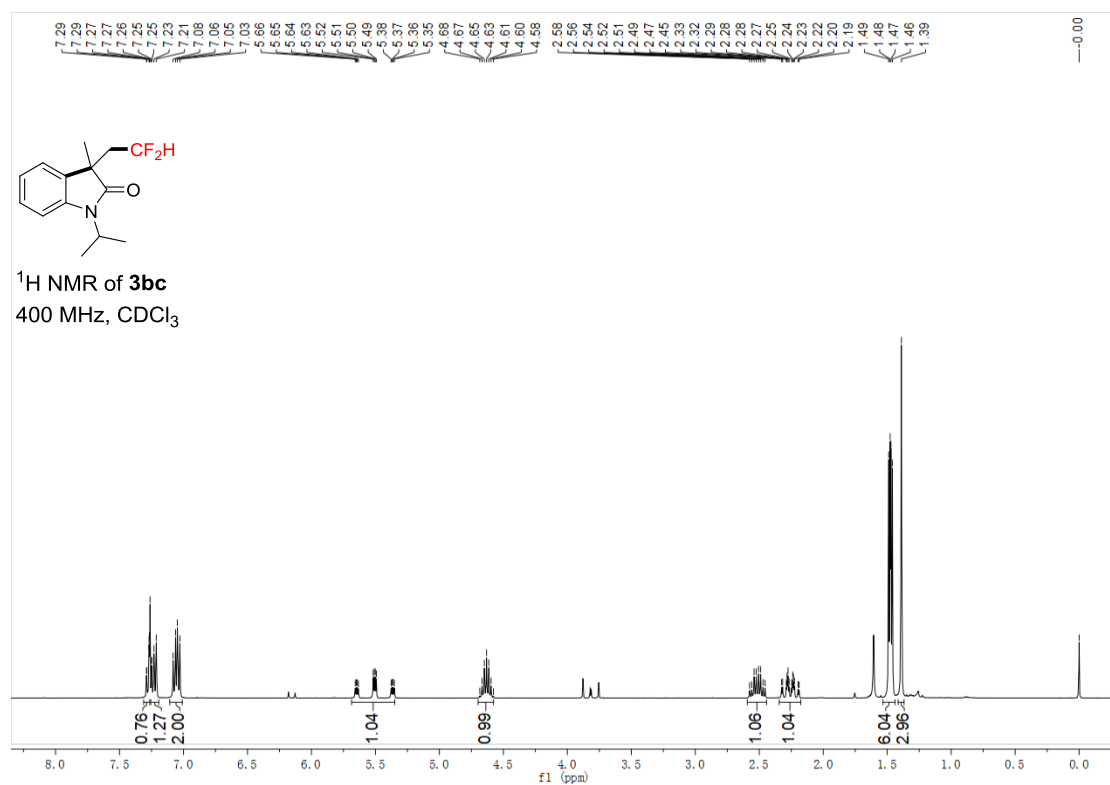
### 1-benzyl-3-(2,2-difluoroethyl)-3-methylindolin-2-one (3ba)



### 3-(2,2-difluoroethyl)-3-methyl-1-phenylindolin-2-one (3bb)

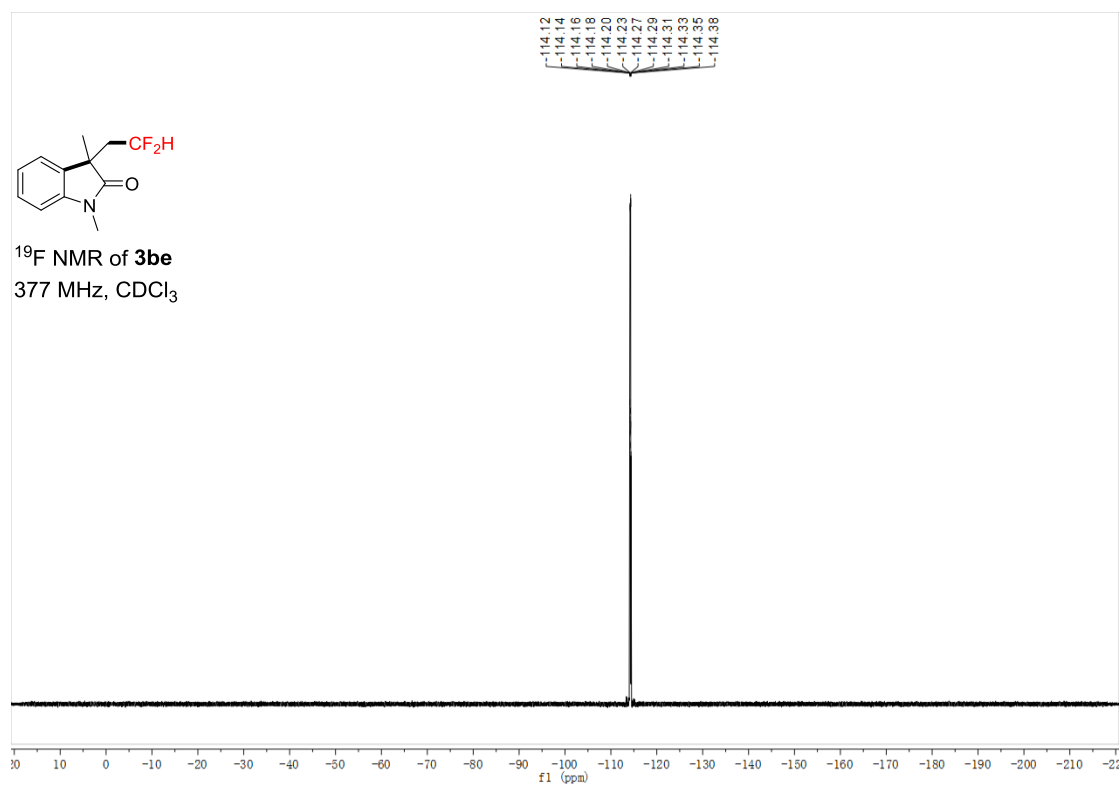
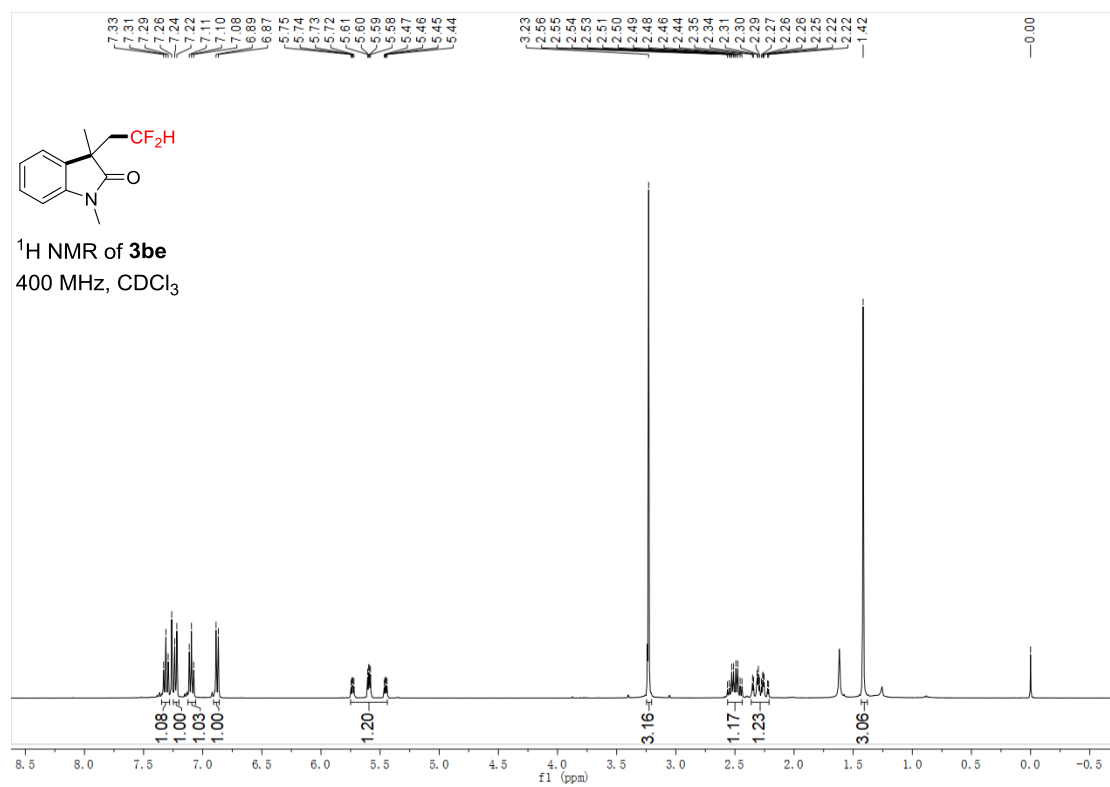


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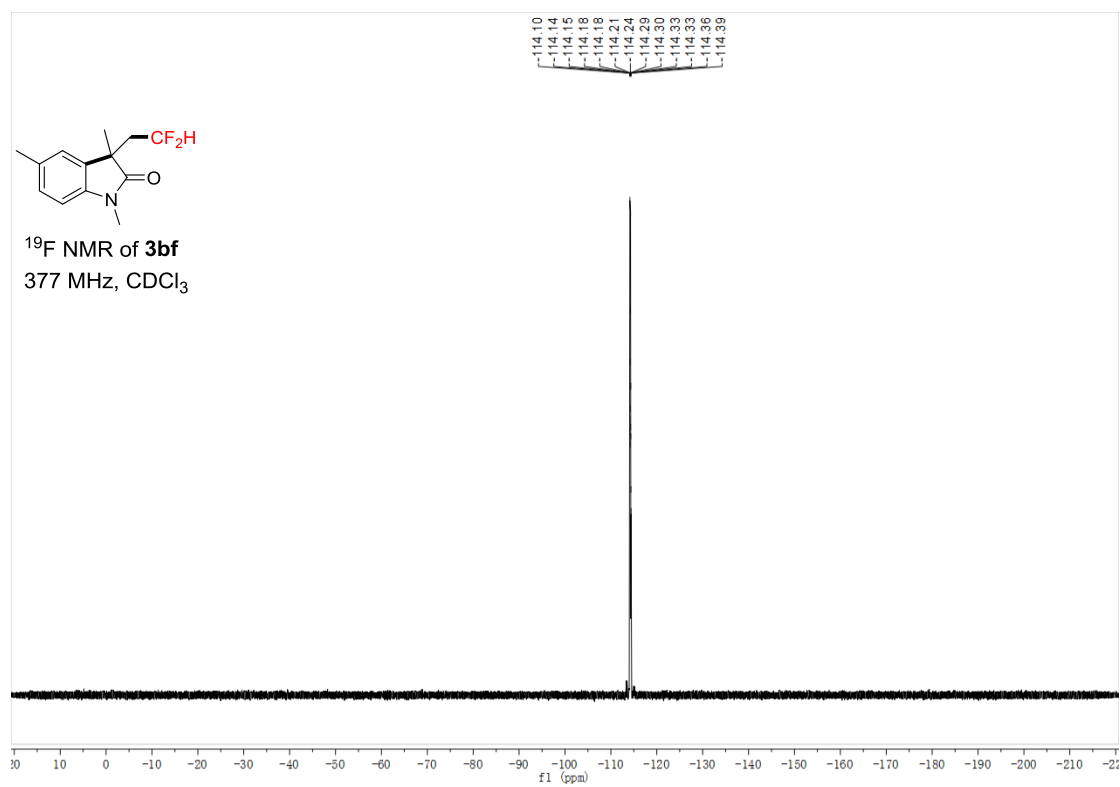
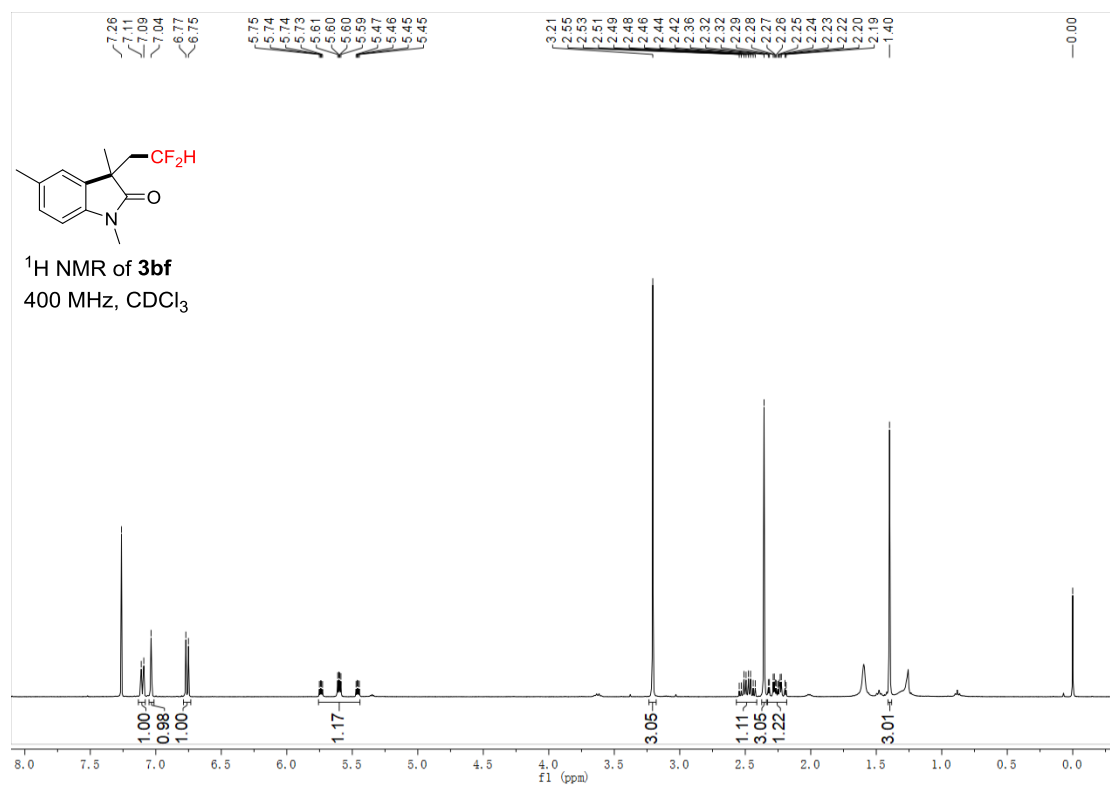


### 3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3be)

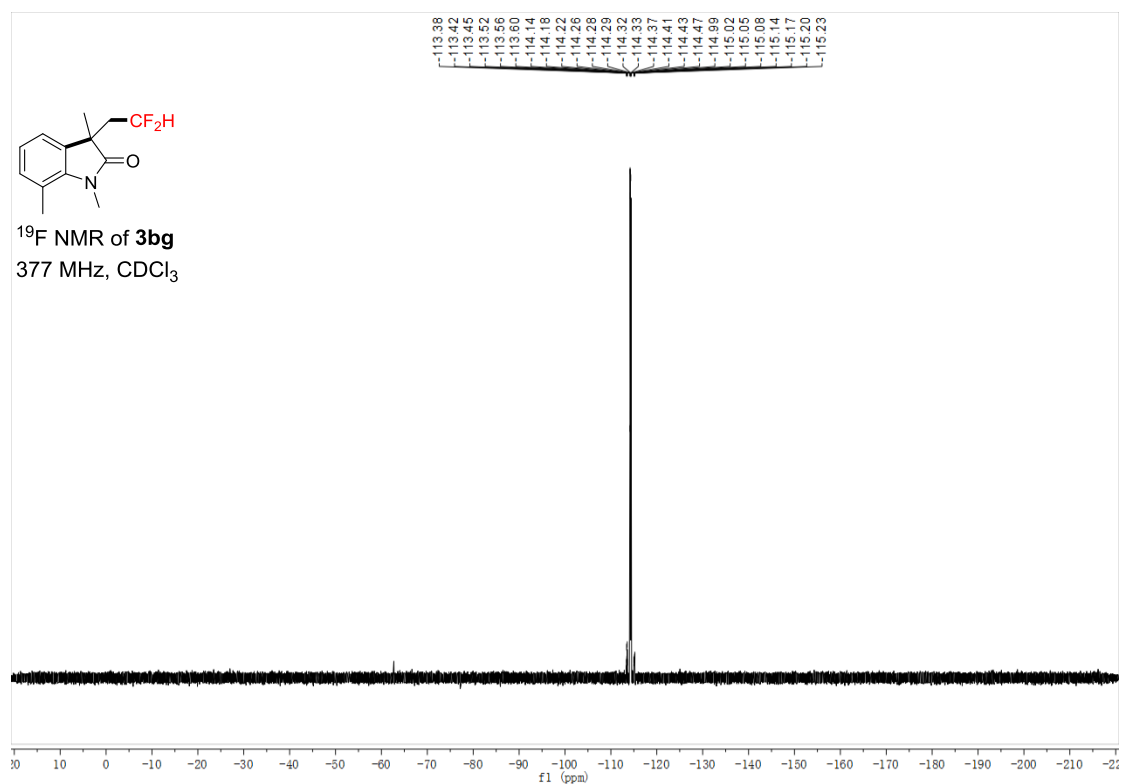
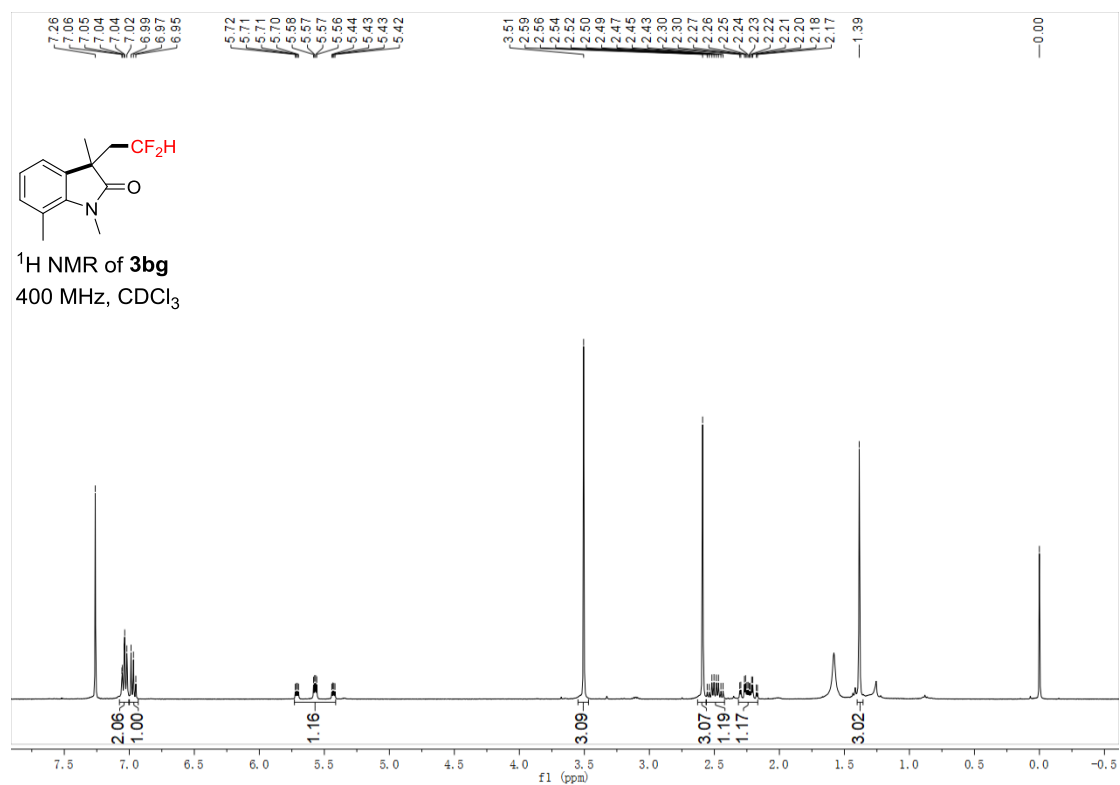




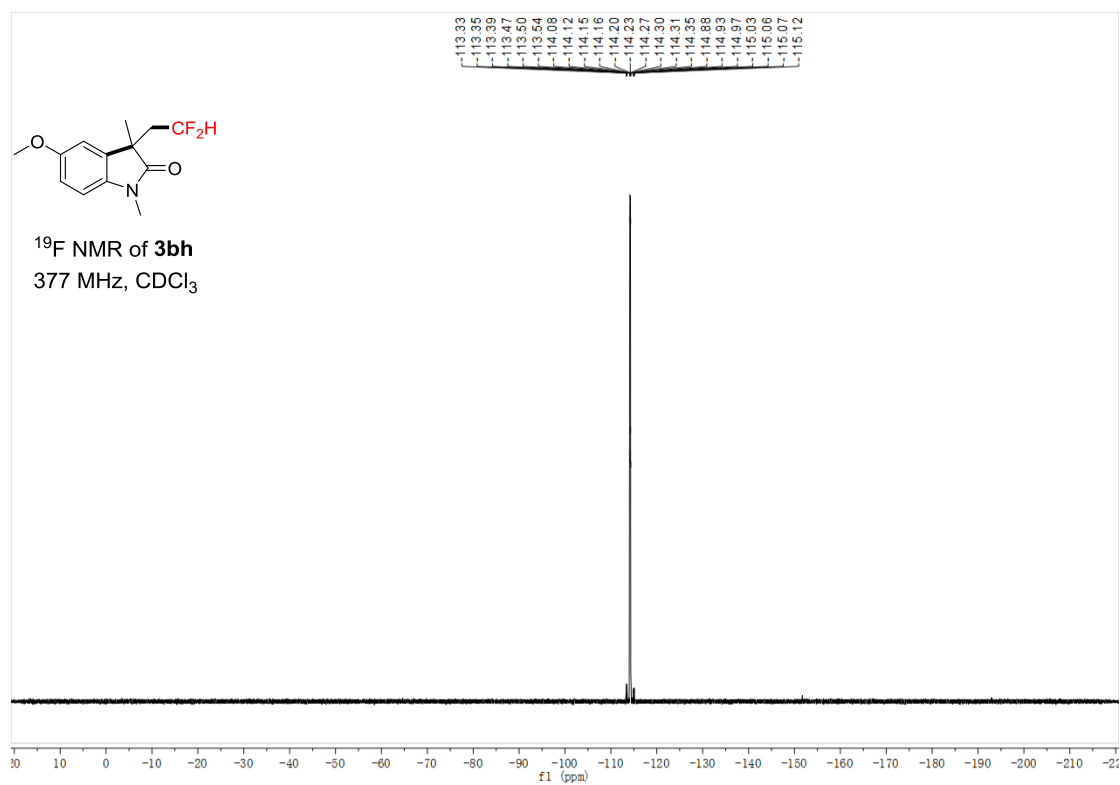
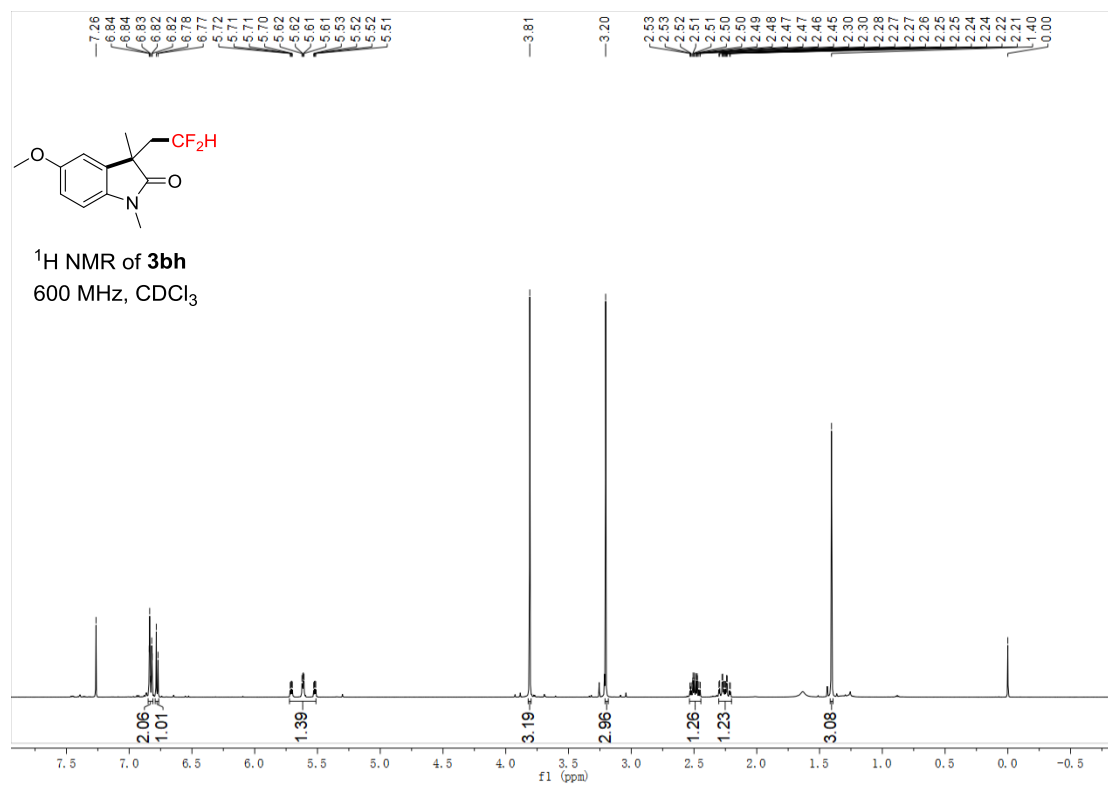
### 3-(2,2-difluoroethyl)-1,3,5-trimethylindolin-2-one (3bf)



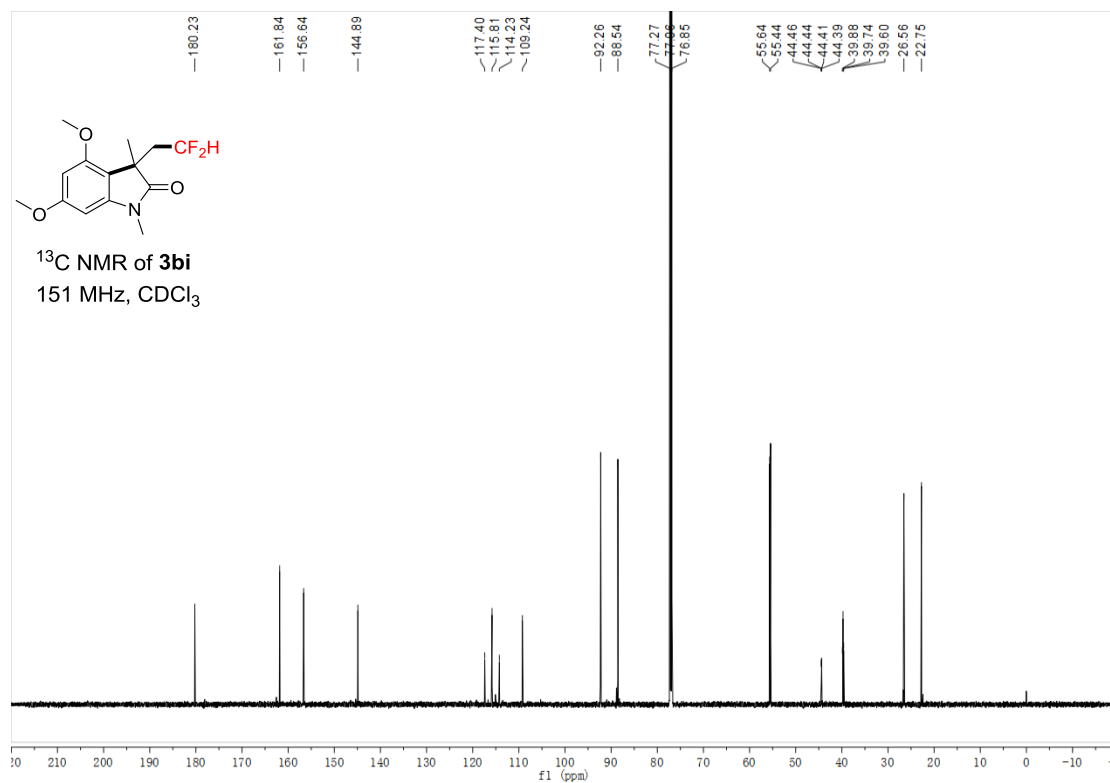
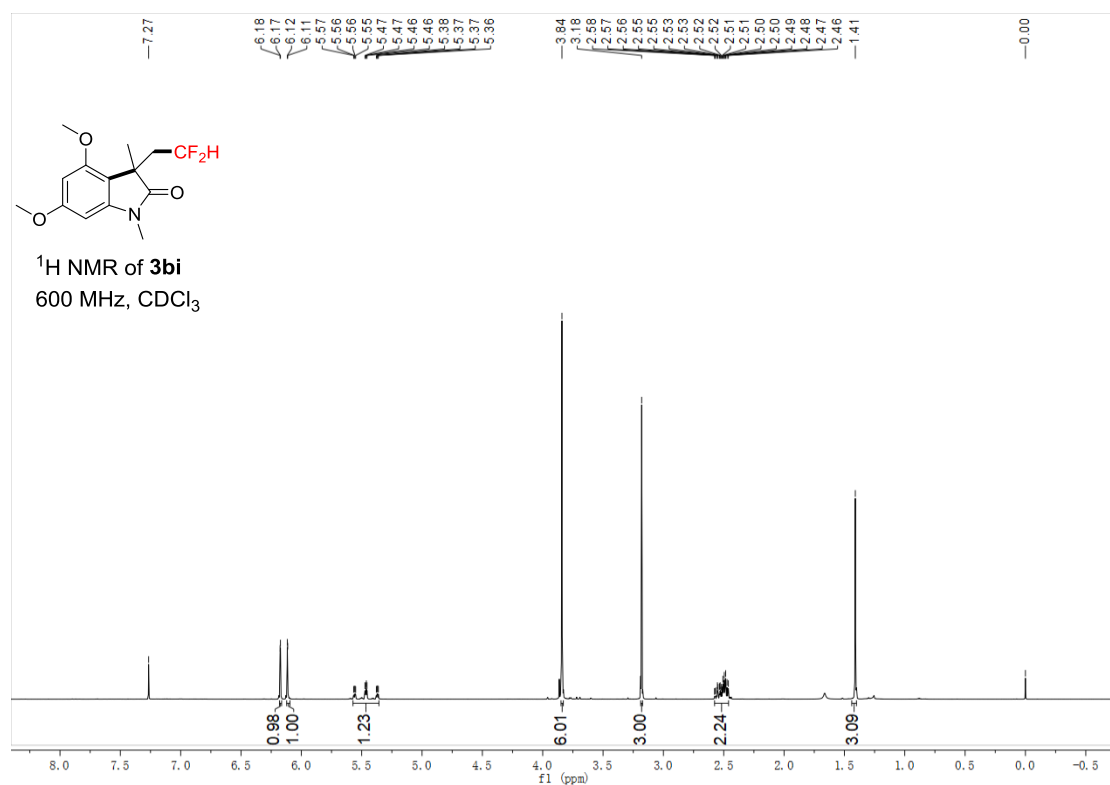
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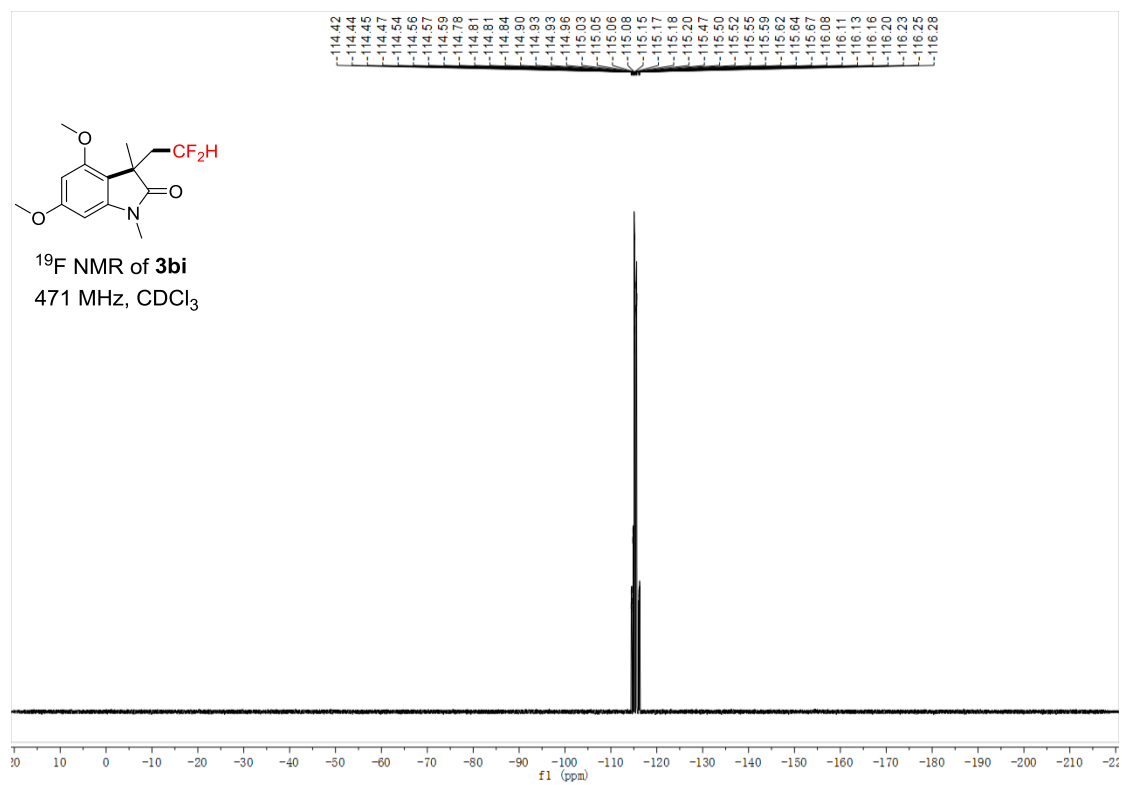


### 3-(2,2-difluoroethyl)-5-methoxy-1,3-dimethylindolin-2-one (3bh)

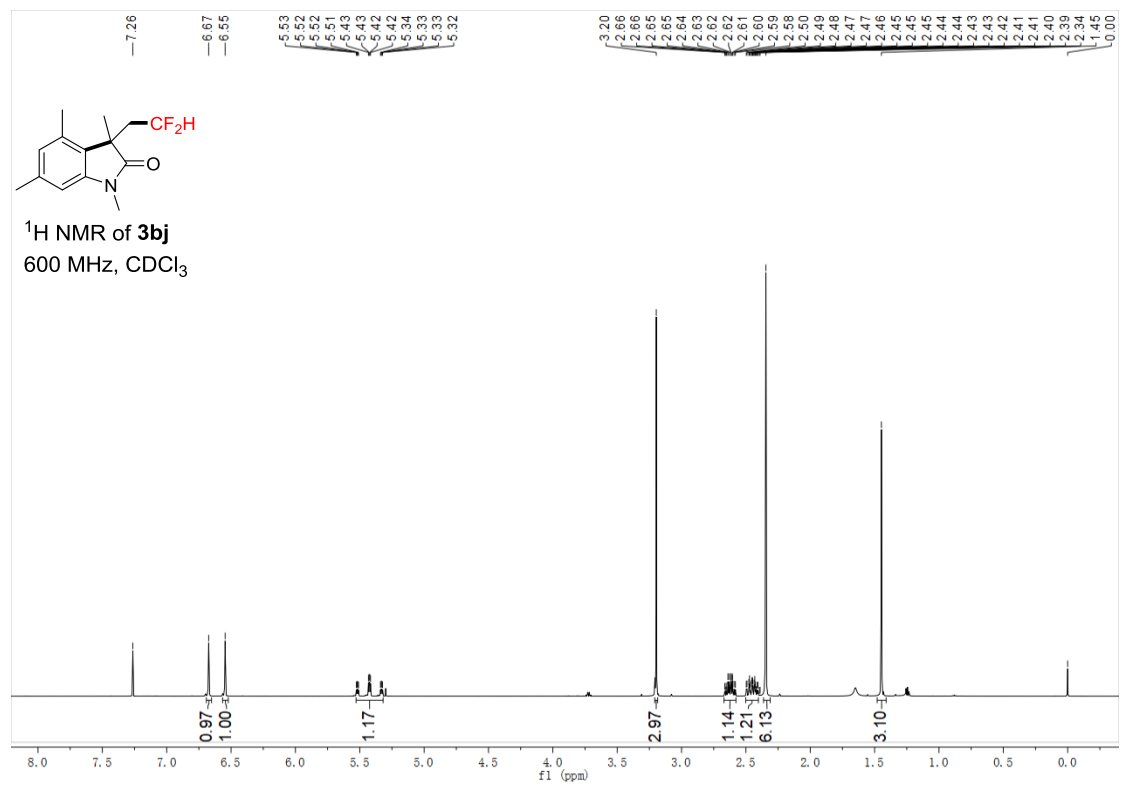


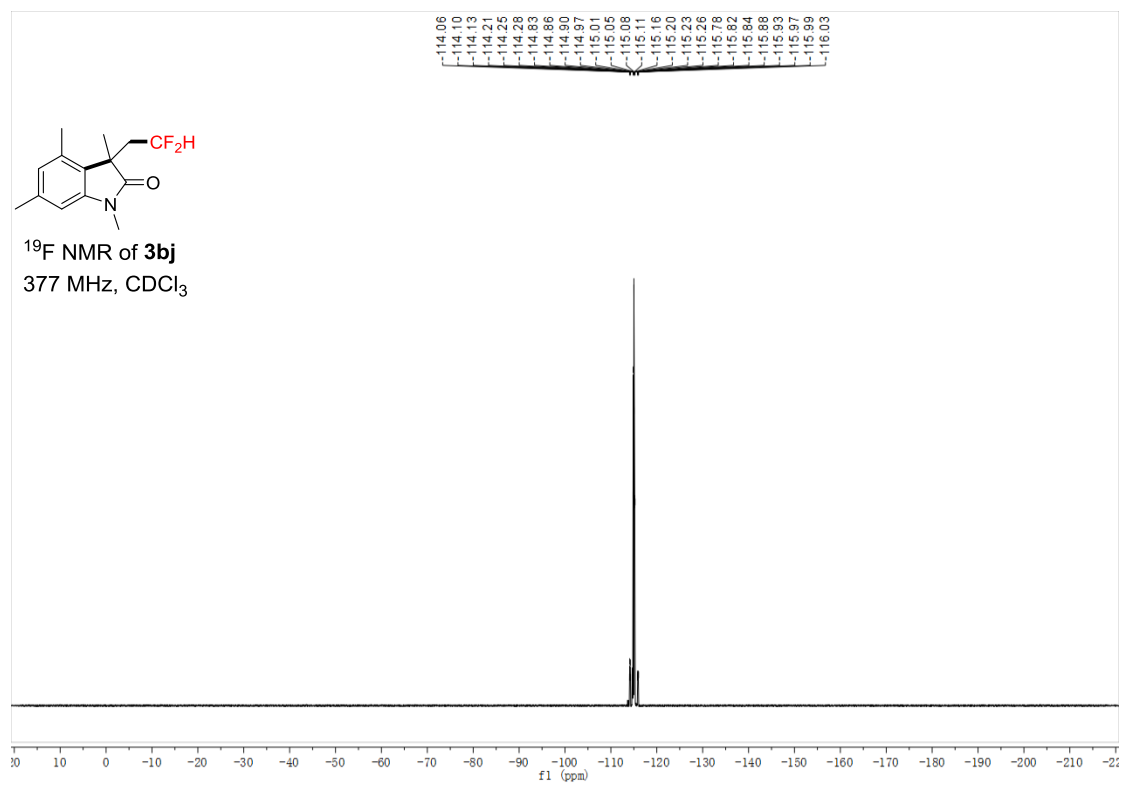
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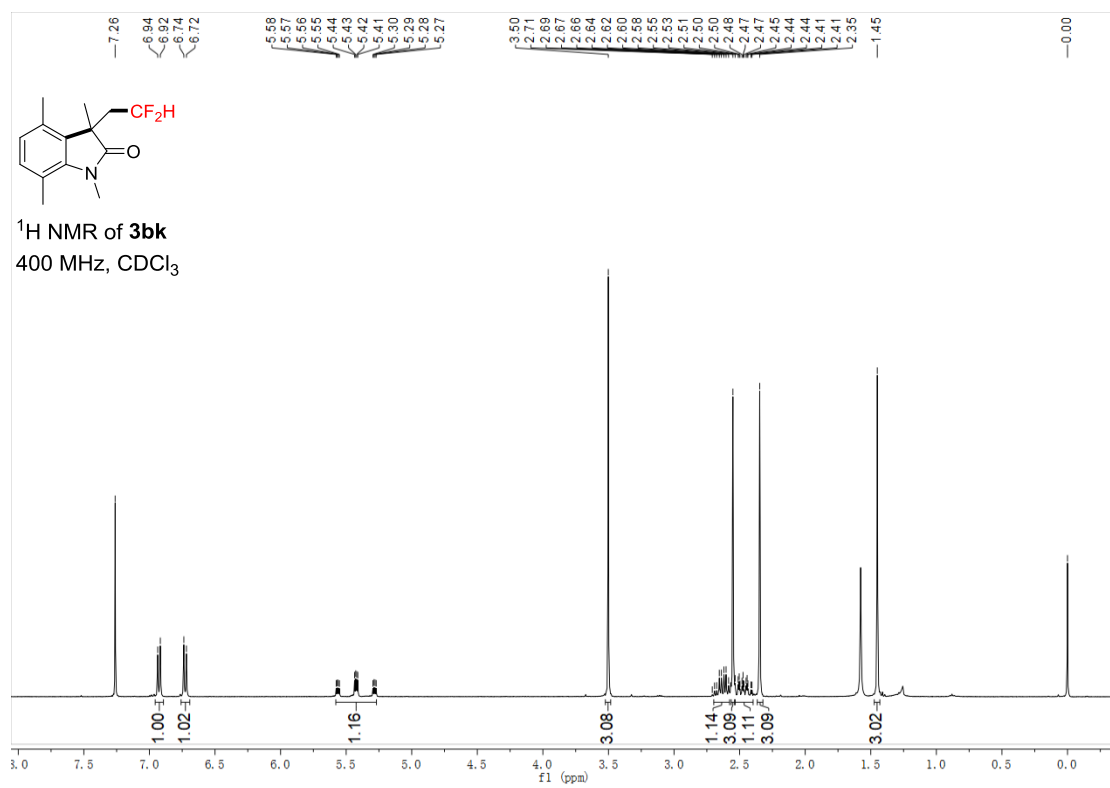


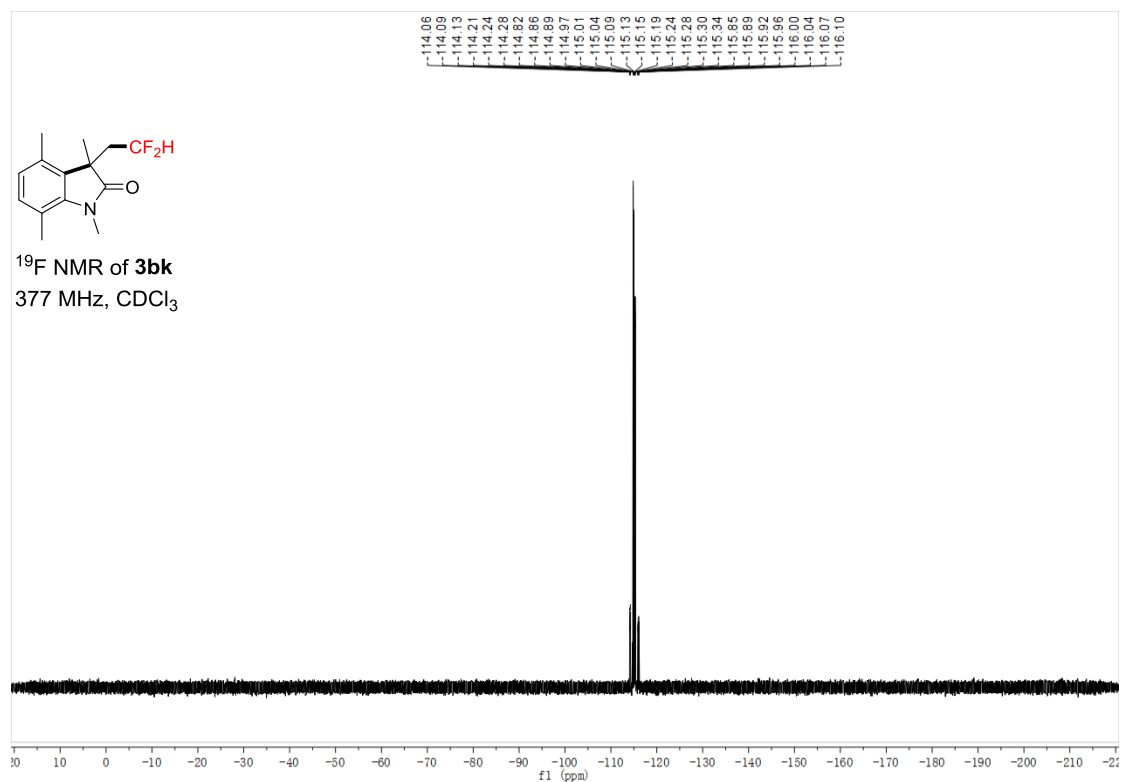
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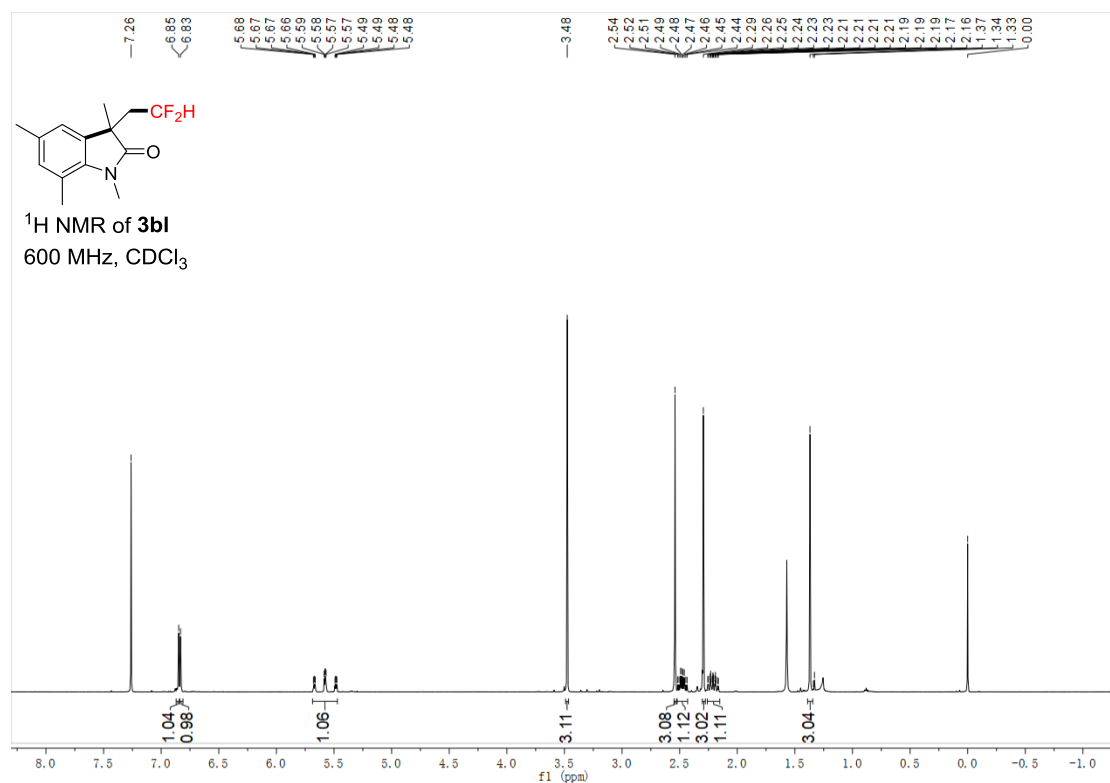


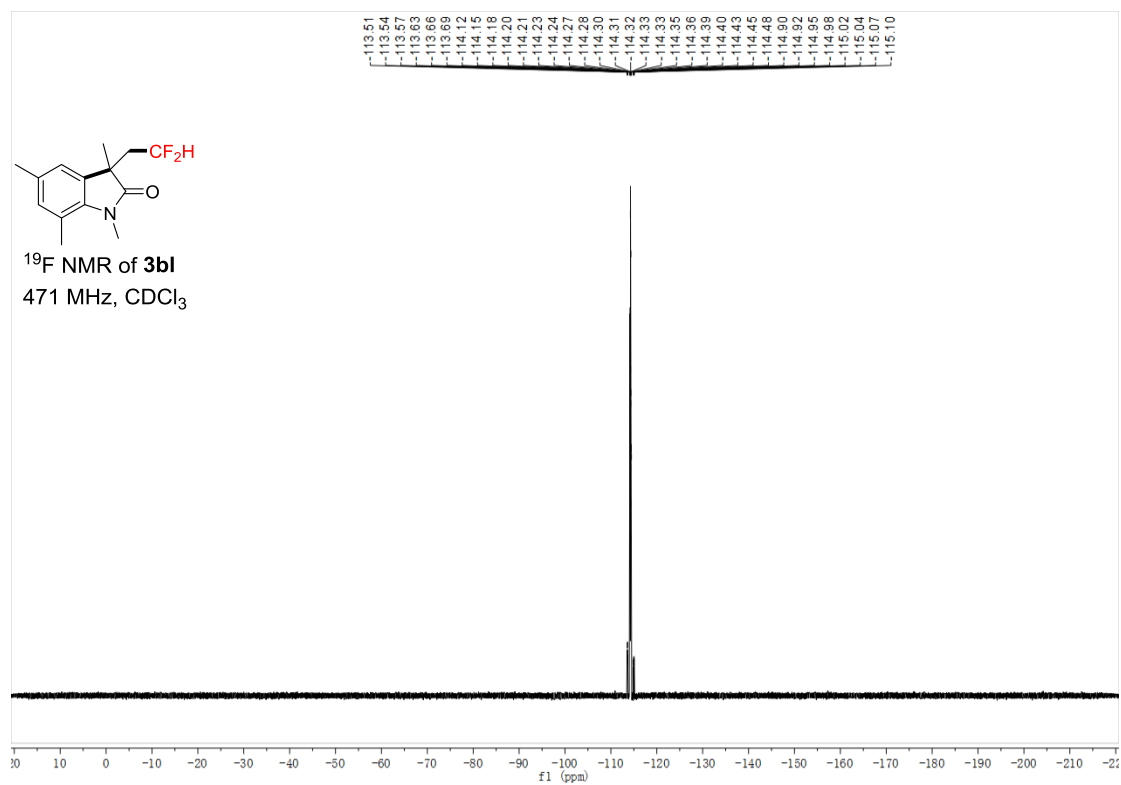
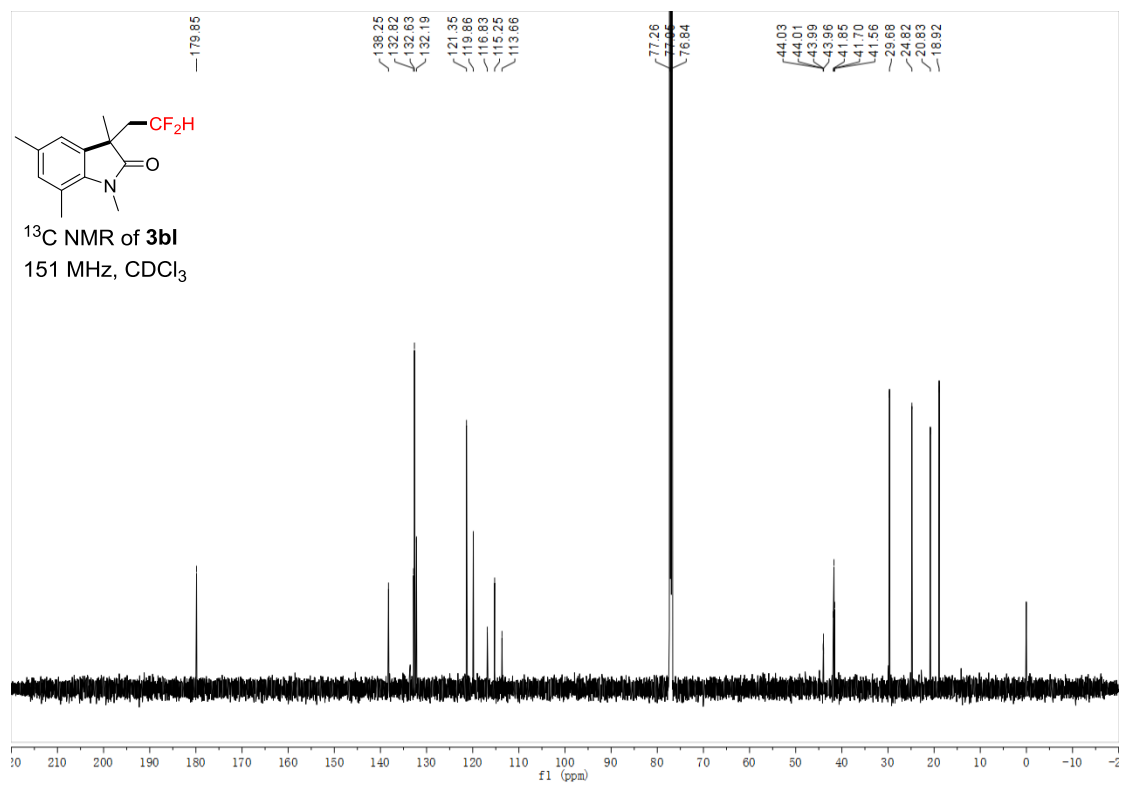
**3-(2,2-difluoroethyl)-1,3,4,7-tetramethylindolin-2-one (3bk)**





**3-(2,2-difluoroethyl)-1,3,5,7-tetramethylindolin-2-one (3bl)**

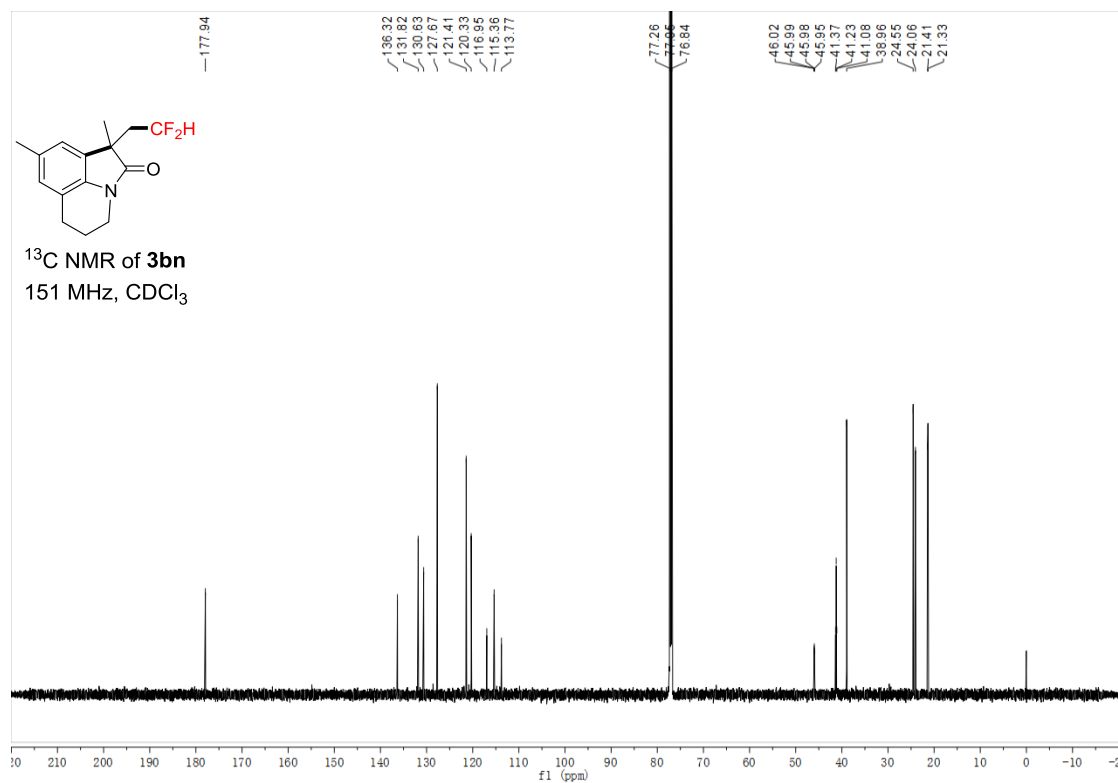
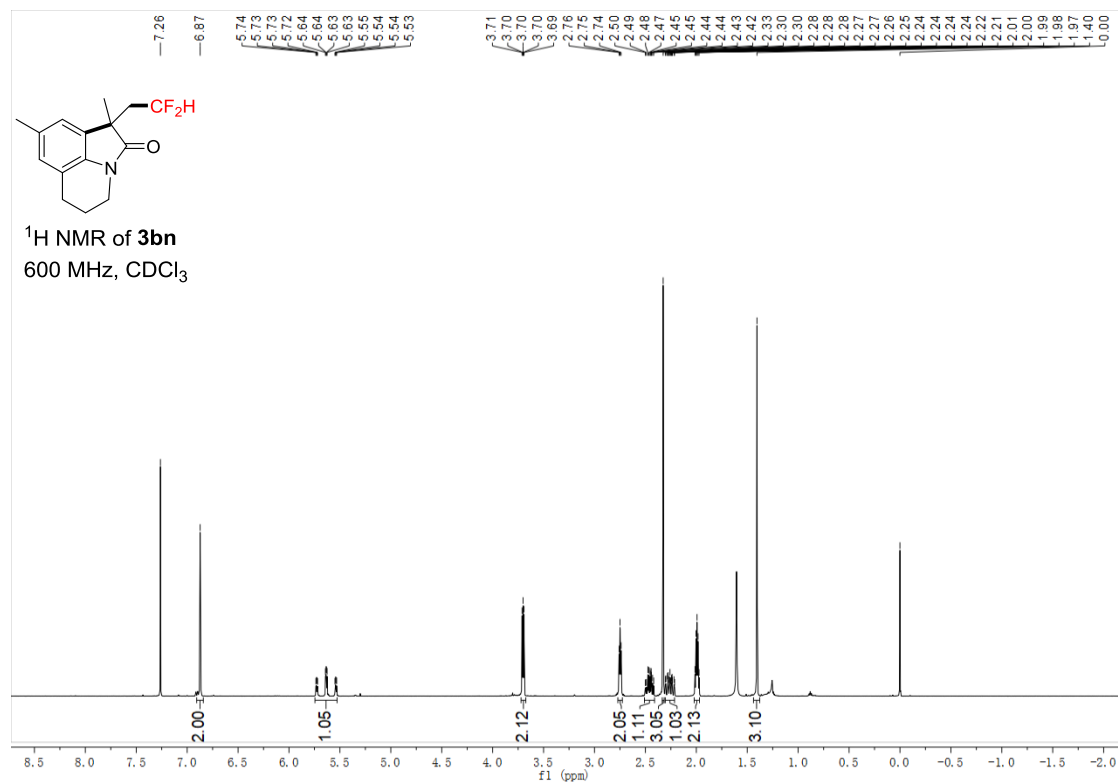


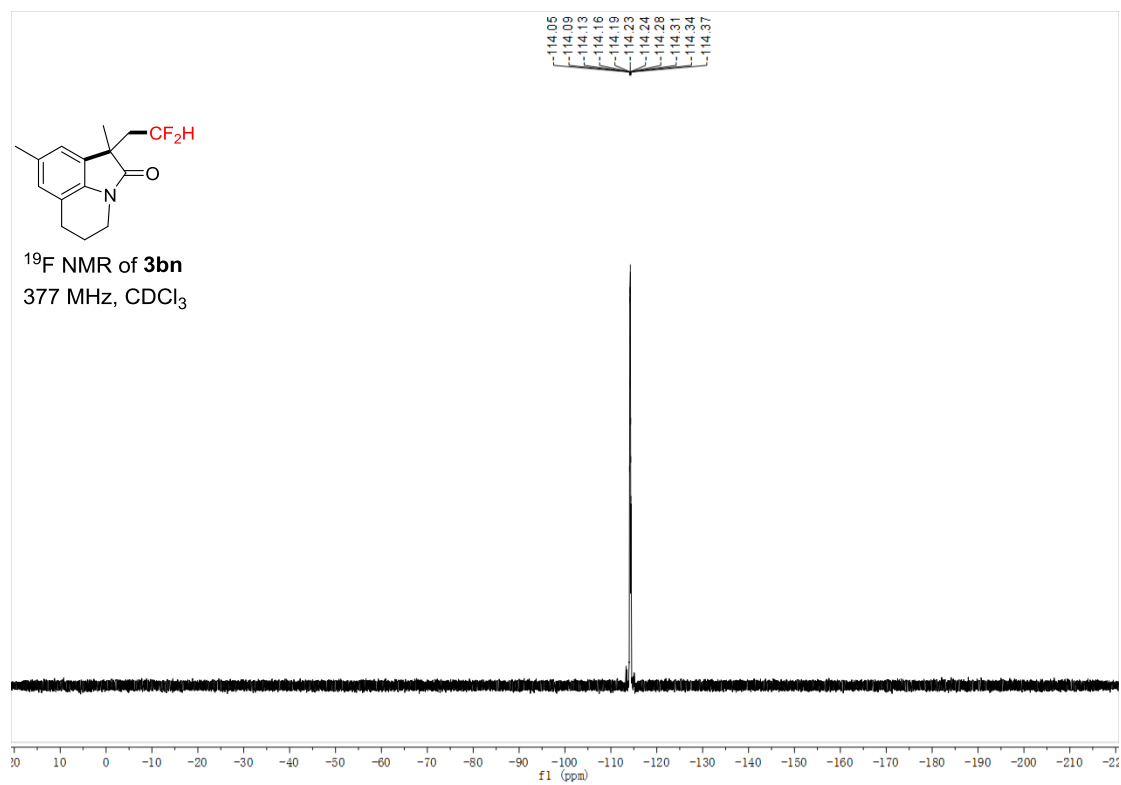




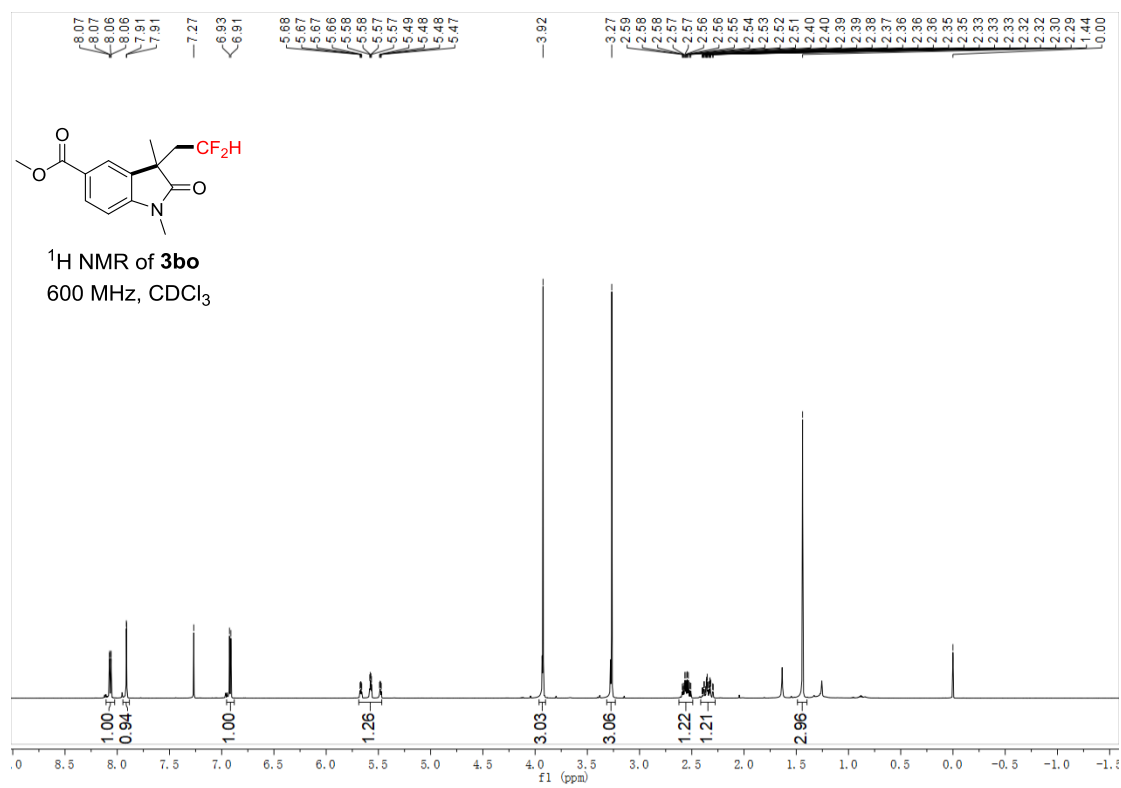


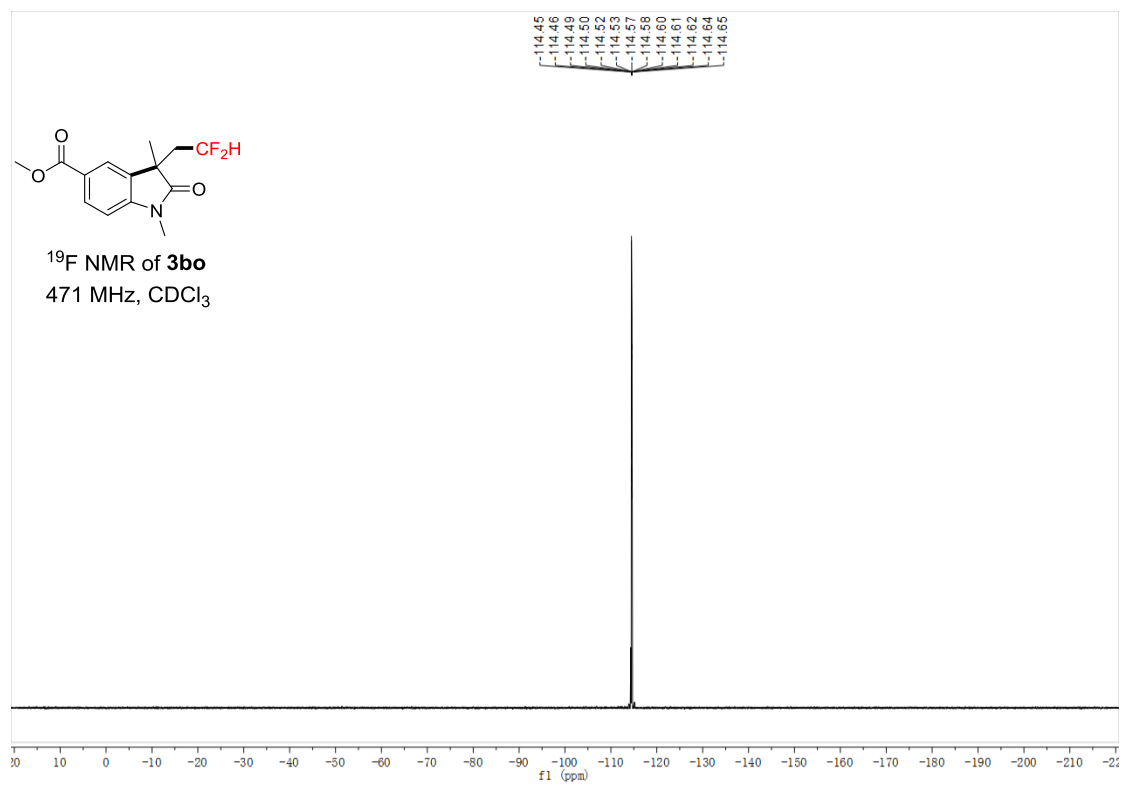
**1-(2,2-difluoroethyl)-1,8-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3bn)**



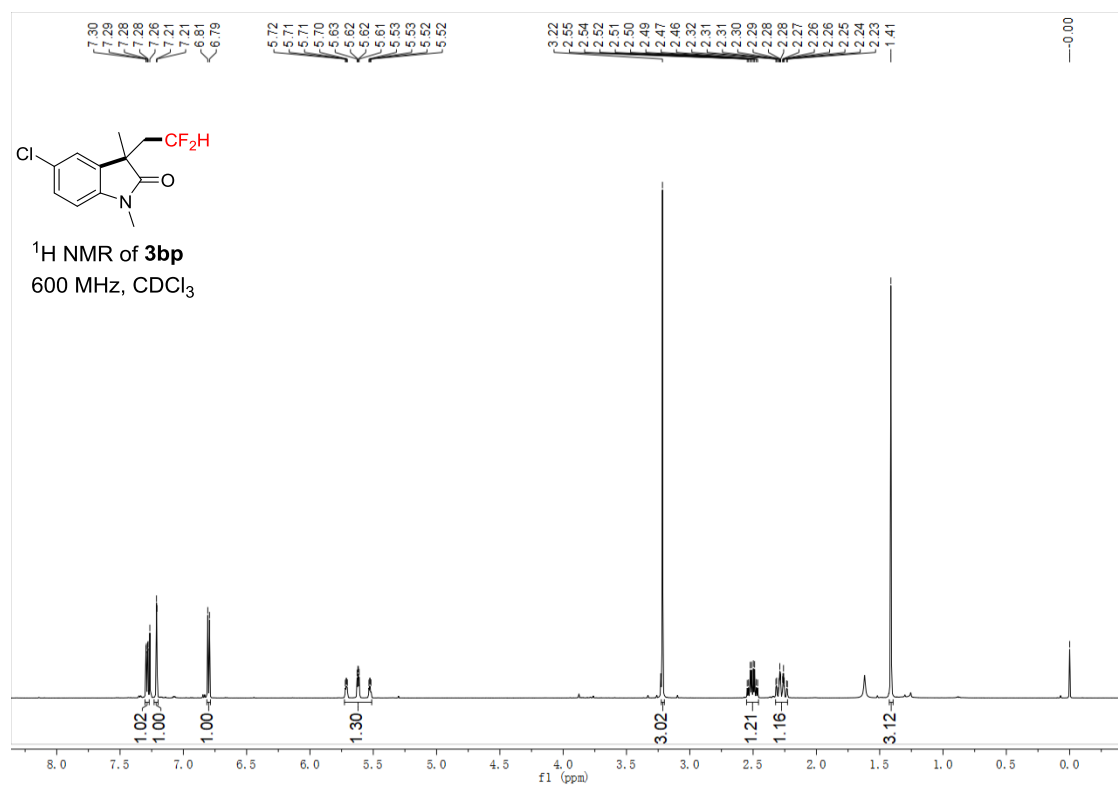


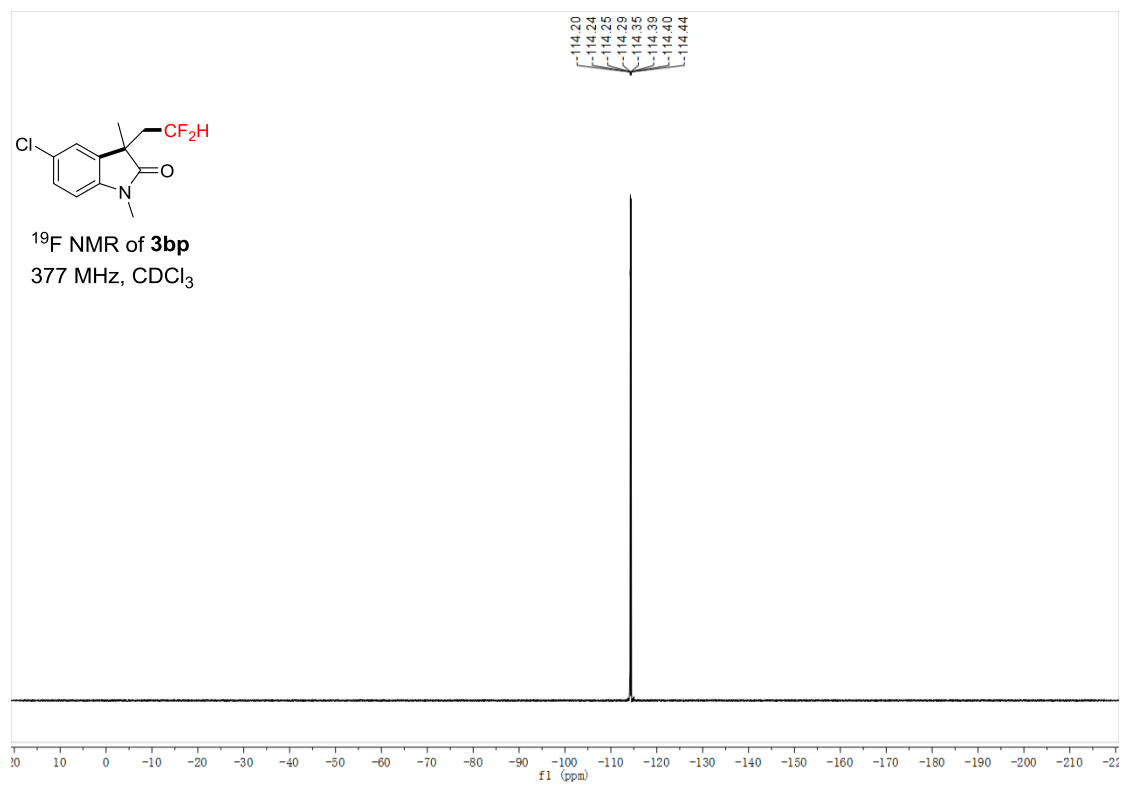
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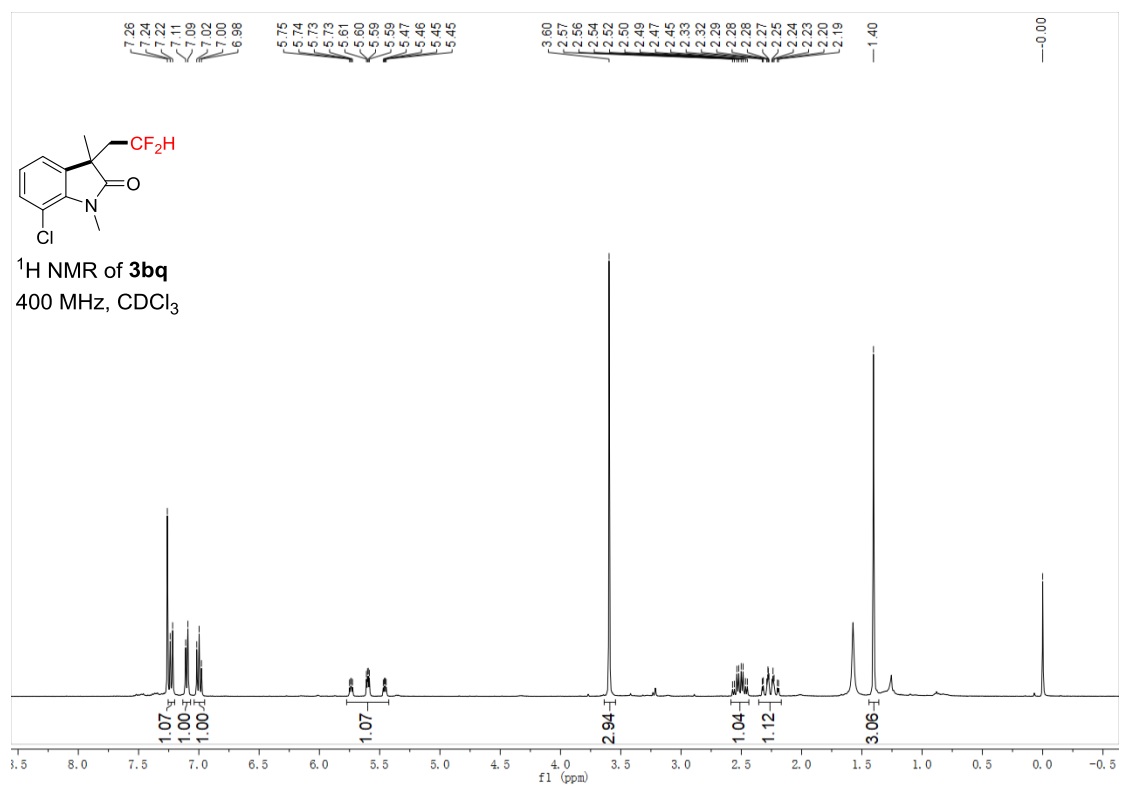


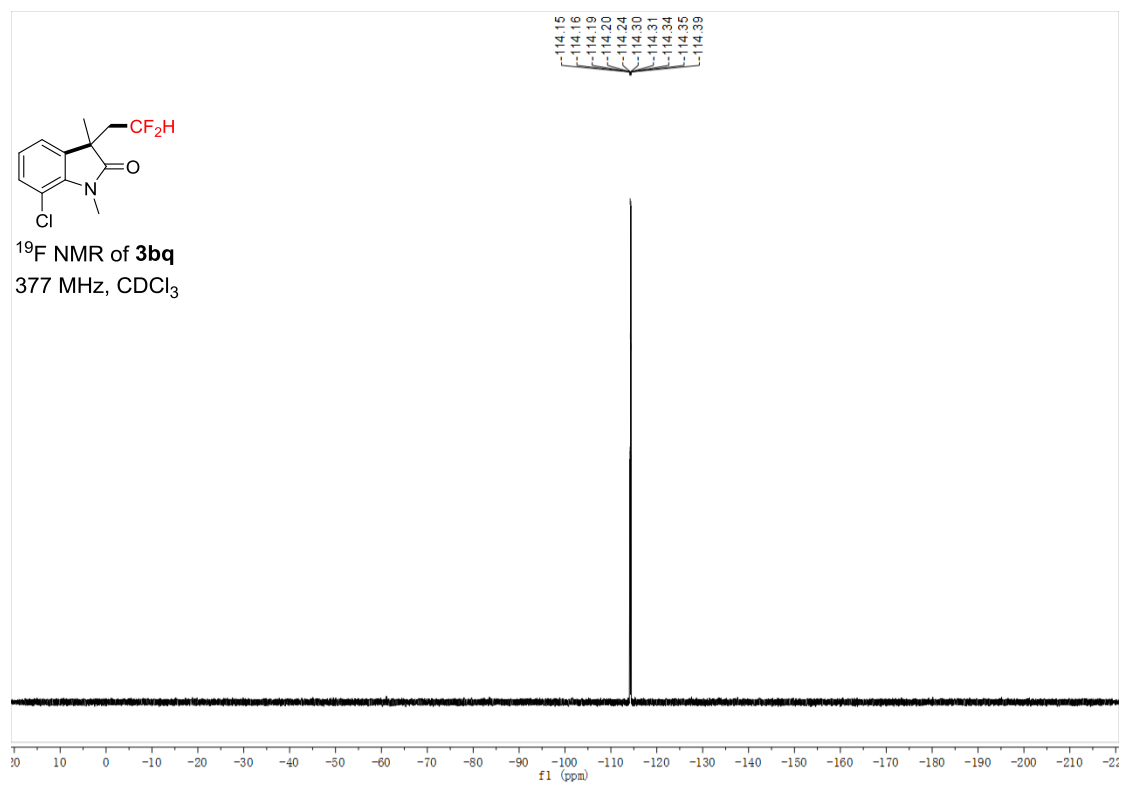
**5-chloro-3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3bp)**



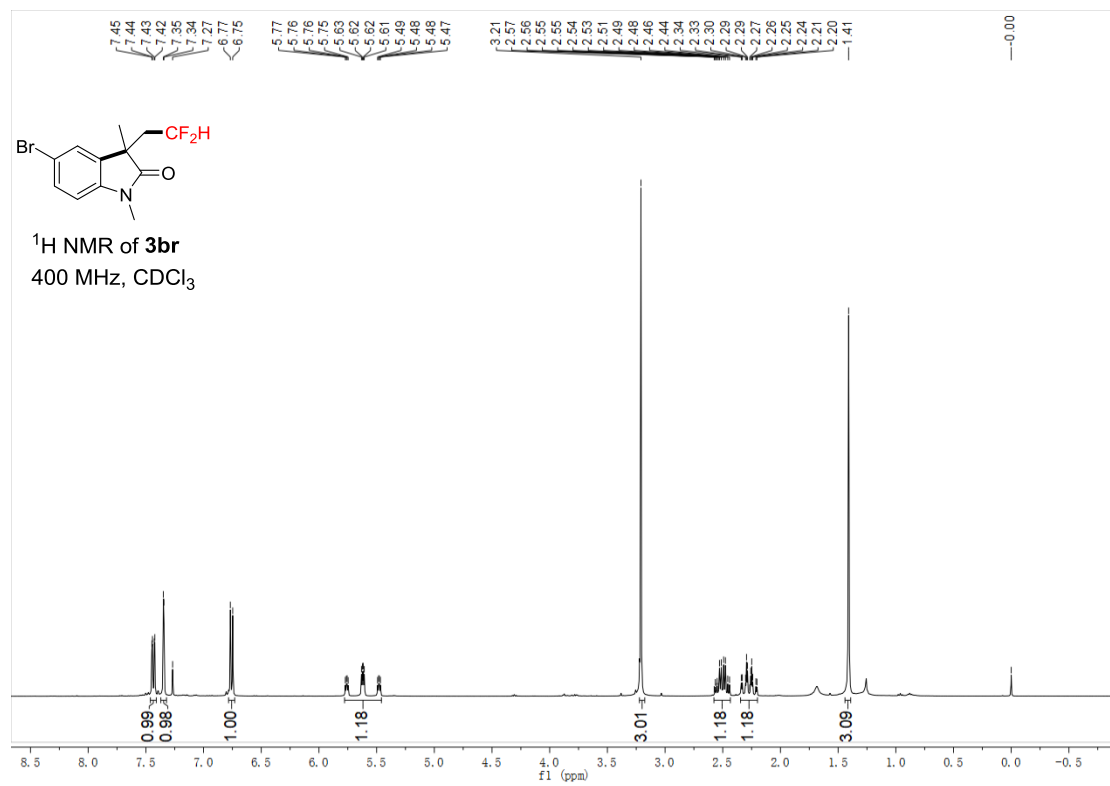


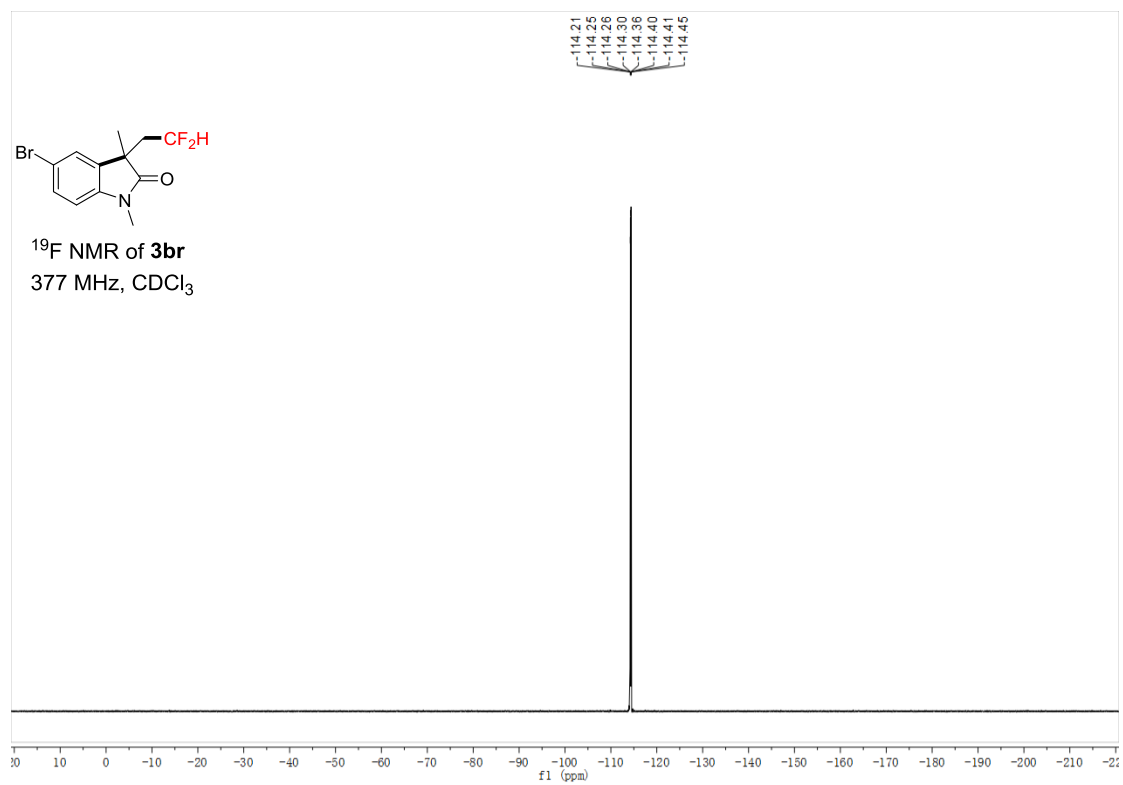
**7-chloro-3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3bq)**



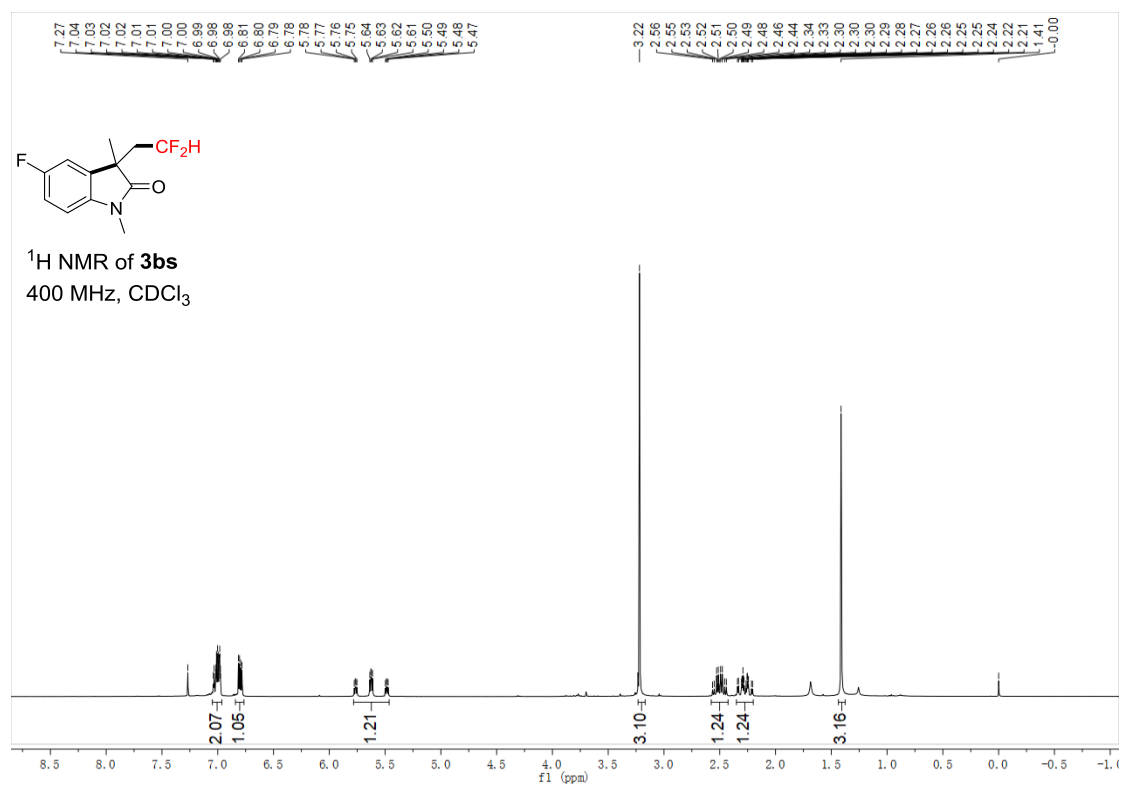


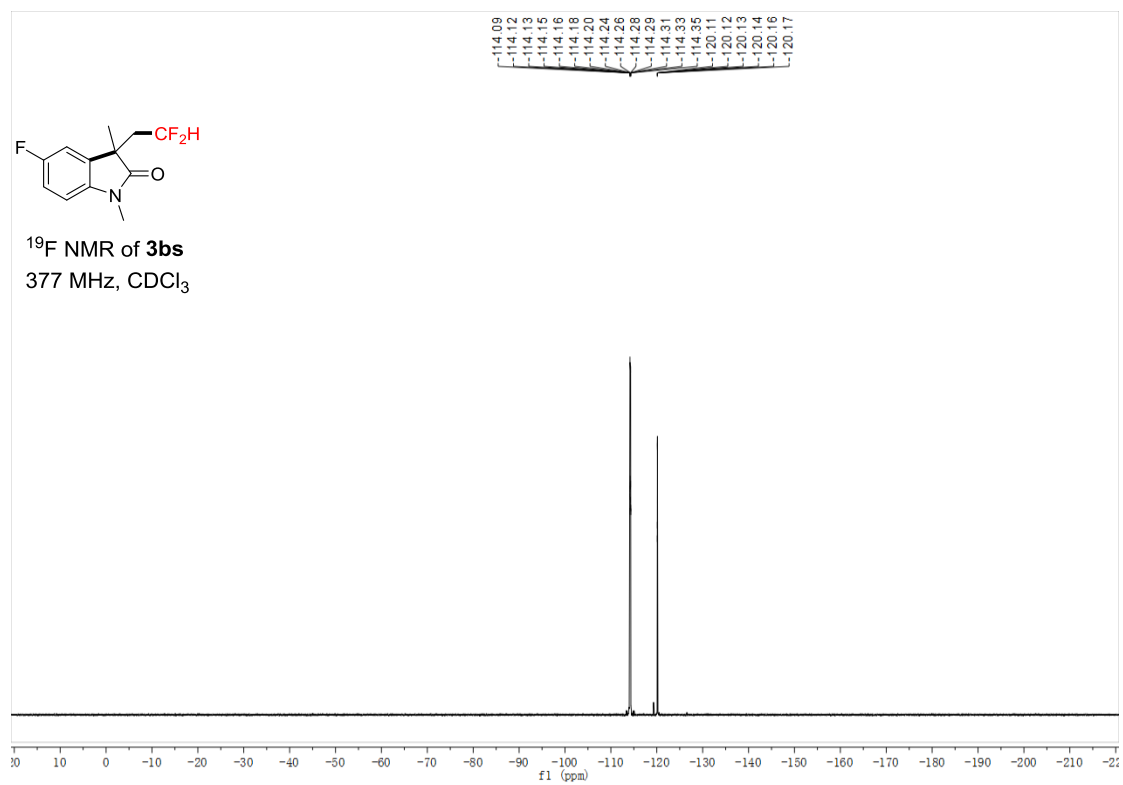
**5-bromo-3-(2,2-difluoroethyl)-1,3-dimethylindolin-2-one (3br)**



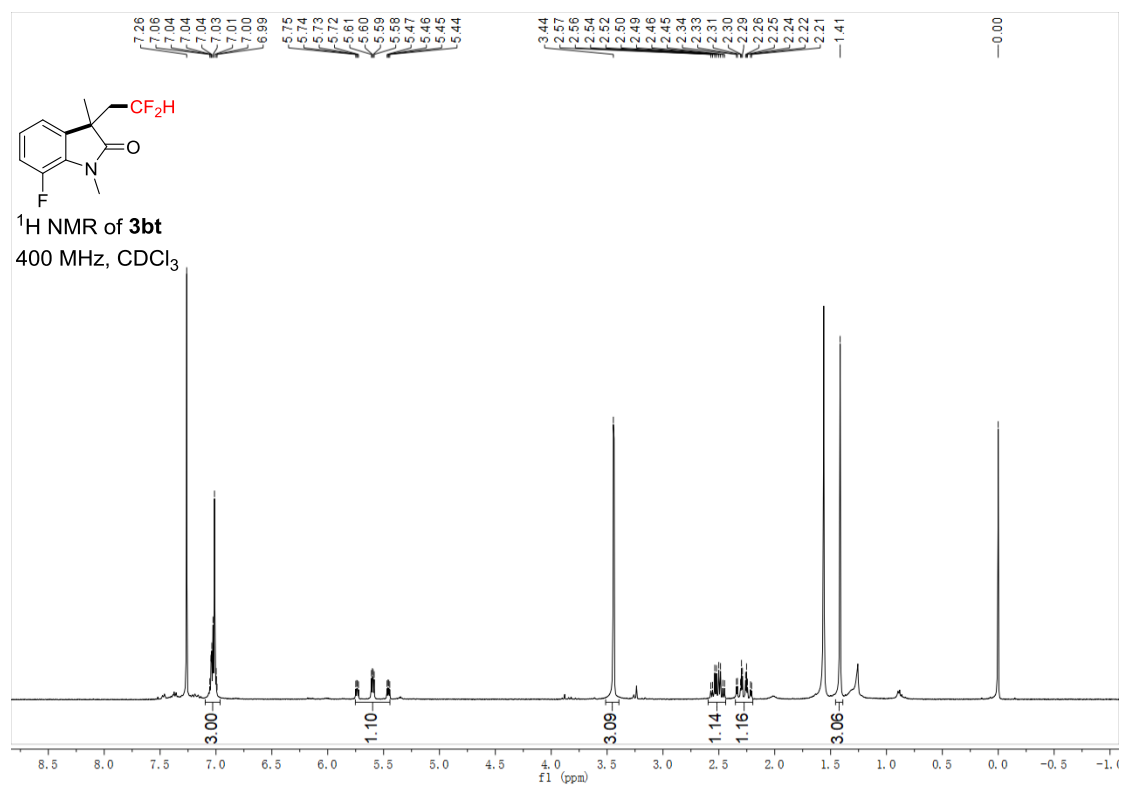


**3-(2,2-difluoroethyl)-5-fluoro-1,3-dimethylindolin-2-one (3bs)**

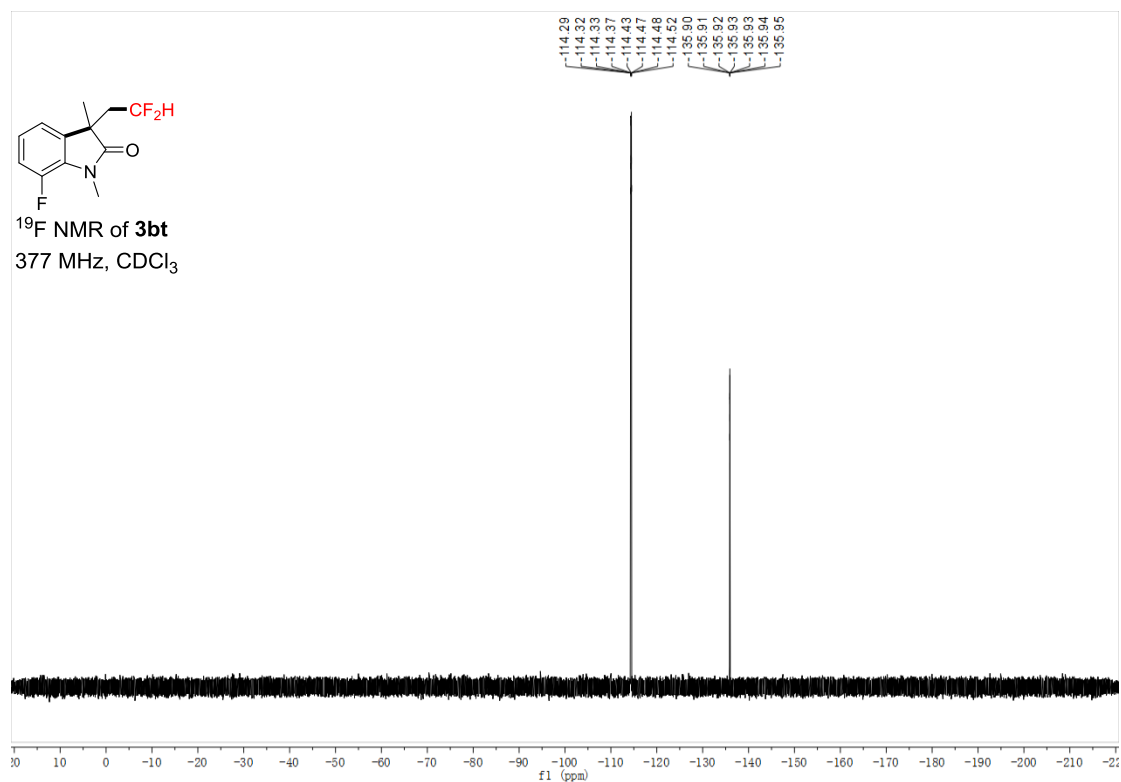




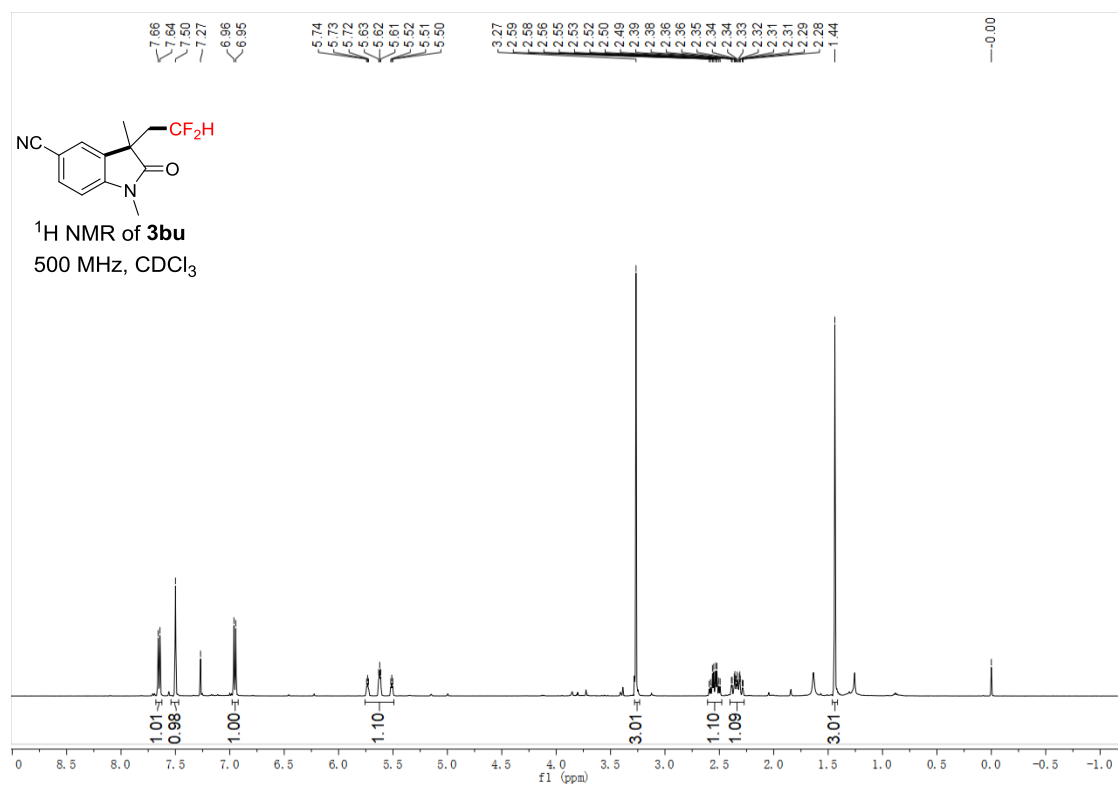
**3-(2,2-difluoroethyl)-7-fluoro-1,3-dimethylindolin-2-one (3bt)**

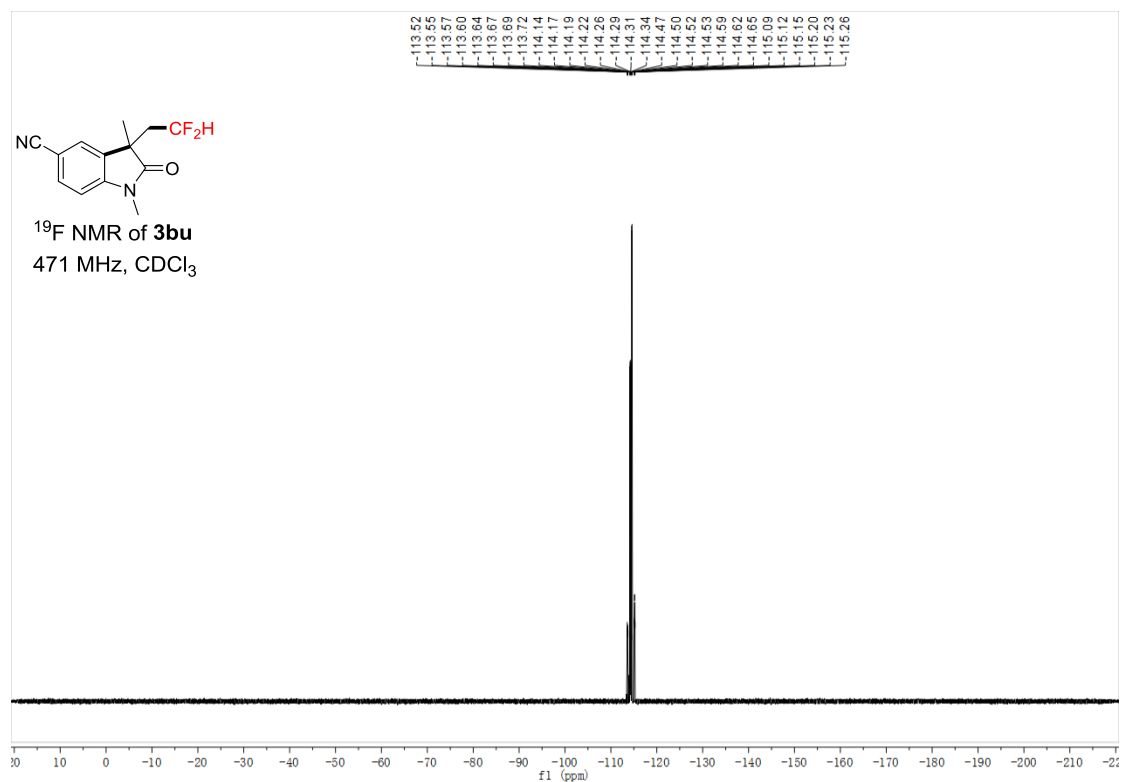




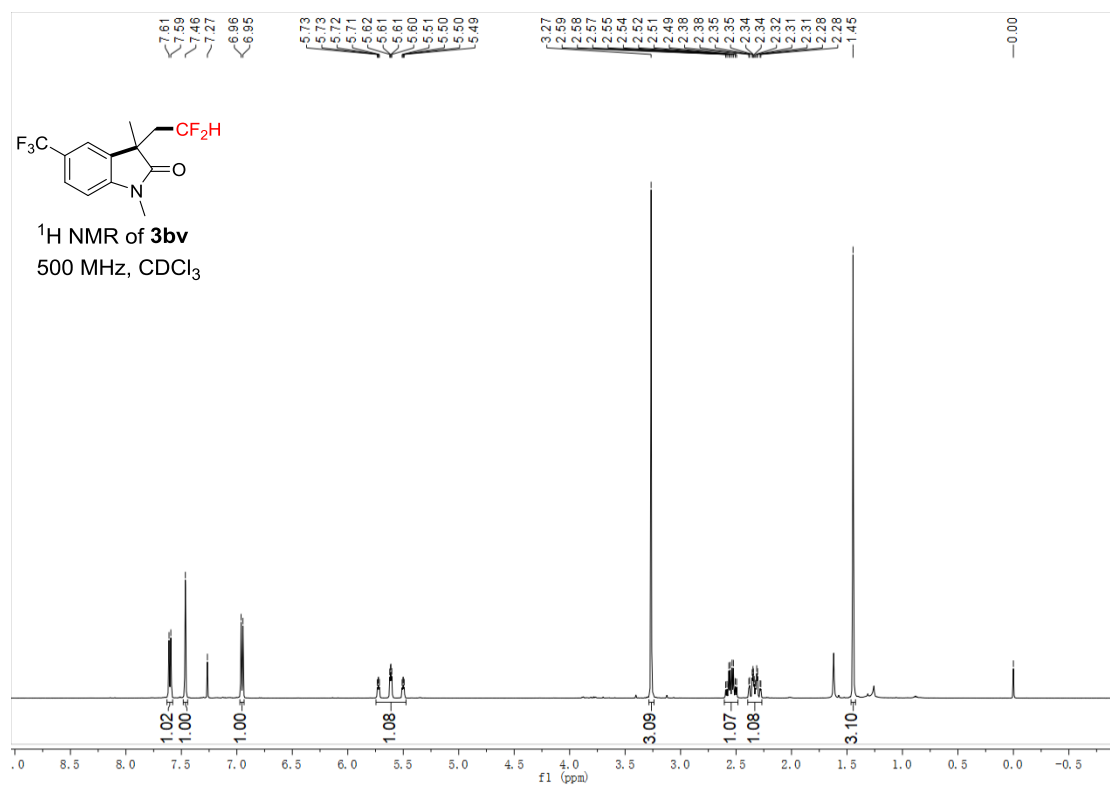


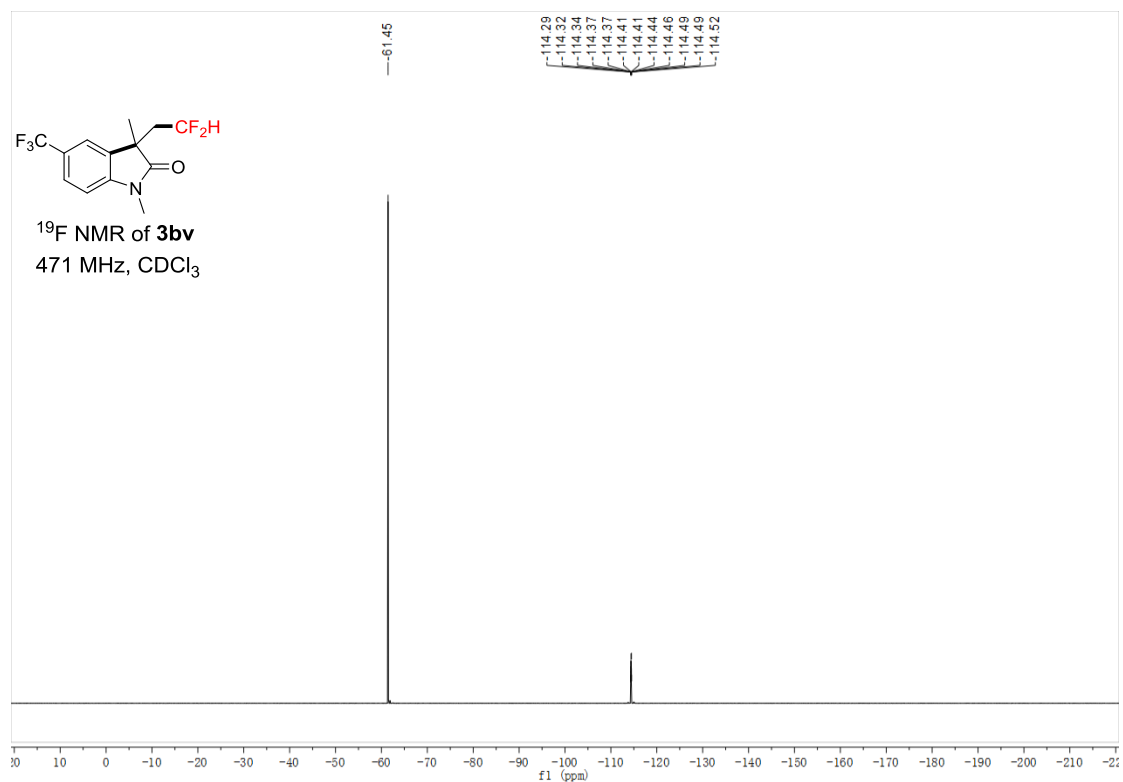
**3-(2,2-difluoroethyl)-1,3-dimethyl-2-oxindoline-5-carbonitrile (3bu)**





**3-(2,2-difluoroethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3bv)**





**4-(2,2-difluoroethyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (**3ca**)**

