

# Supporting Information

## Photoredox Catalyzed Synthesis of $\beta$ -Trifluoromethyl $\beta$ -Aminoketones from *N*-Trifluoroethyl Hydroxylamine Reagent and Silyl Enol Ethers

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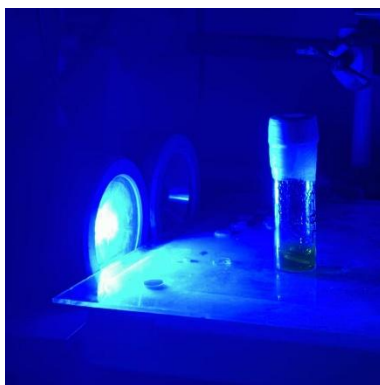
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## 1. General Information

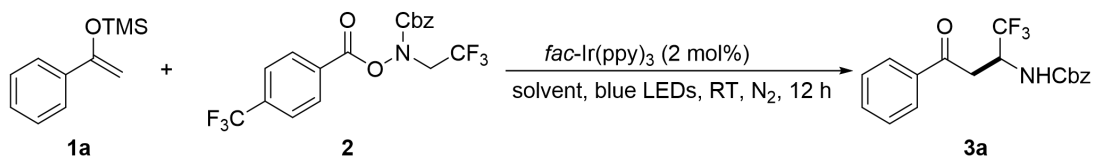
$^1\text{H}$  NMR (TMS as the internal standard),  $^{13}\text{C}$  NMR, and  $^{19}\text{F}$  NMR ( $\text{CFCl}_3$  as the external standard, with low field being positive) spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifts ( $\delta$ ) were reported in parts per million (ppm), and coupling constants ( $J$ ) were measured in Hertz (Hz). The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. For the determination of  $^{19}\text{F}$  NMR yield,  $\text{PhCF}_3$  was used as an internal standard and the relaxation delay (d1) was set to 5 s. Detection of melting point was conducted on the SGW X-4 microscopic melting point meter. HRMS-ESI data was collected by Thermo Fisher Scientific Q Exactive HF Orbitrap-FTMS. X-ray single-crystal diffraction data were collected on a XtaLAB Synergy, Dualflex, and HyPix diffractometer. LED lights were commercially sourced from Kessil (KSA 160WE-TB, 40W). Unless otherwise stated, all reactions were carried out under strictly anhydrous conditions and  $\text{N}_2$  atmosphere. The reaction vessel was placed 10 cm away from the light source, and a fan was used for cooling to maintain the reaction at room temperature. All reagents were obtained commercially and used without further purification. Substrates were either purchased from commercial sources or prepared according to literature procedures.



**Figure S1.** Reaction Setup.

## 2. Optimization of Reaction Conditions

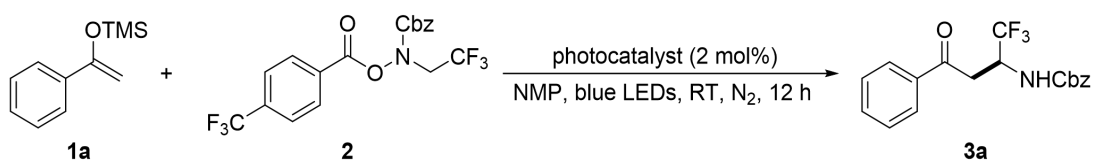
**Table S1.** Effect of solvents on this reaction<sup>a</sup>



Entry	Solvent	Yield (%) <sup>b</sup>
1	DMSO	52
2	DMF	33
3	THF	22
4	MeCN	12
5	MeOH	0
6	EtOAc	0
7	NMP	84
8	DMI	35
9	DCE	0
10	PhCF <sub>3</sub>	trace
11	DMAc	61
12	NMP/H <sub>2</sub> O = 9/1	30

<sup>a</sup>Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2** (0.10 mmol, 1.0 equiv.), *fac*-Ir(ppy)<sub>3</sub> (2 mol%), solvent (1.0 mL), blue LEDs, room temperature, N<sub>2</sub>, 12 h. <sup>b</sup>Yields were determined by <sup>19</sup>F NMR spectroscopy using PhCF<sub>3</sub> as internal standard.

**Table S2.** Effect of photocatalysts on this reaction<sup>a</sup>



Entry	Photocatalyst	Yield (%) <sup>b</sup>
1	<i>fac</i> -Ir(ppy) <sub>3</sub>	84
2	4-CzIPN	38
3	Ru(phen) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	0
4	[Ir(dtbbpy)(ppy) <sub>2</sub> ](PF <sub>6</sub> )	28
5	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (dtbbpy)(PF <sub>6</sub> )	22
6	-	0

<sup>a</sup>Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2** (0.10 mmol, 1.0 equiv.), photocatalyst (2

mol%), NMP (1.0 mL), blue LEDs, room temperature, N<sub>2</sub>, 12 h. <sup>b</sup>Yields were determined by <sup>19</sup>F NMR spectroscopy using PhCF<sub>3</sub> as internal standard.

**Table S3.** Effect of other conditions on this reaction<sup>a</sup>

Reaction scheme: **1a** (equiv.) + **2**  $\xrightarrow[\text{NMP, light source, RT, N}_2, \text{Time}]{\text{fac-Ir(ppy)}_3 \text{ (x mol\%)}}$  Product

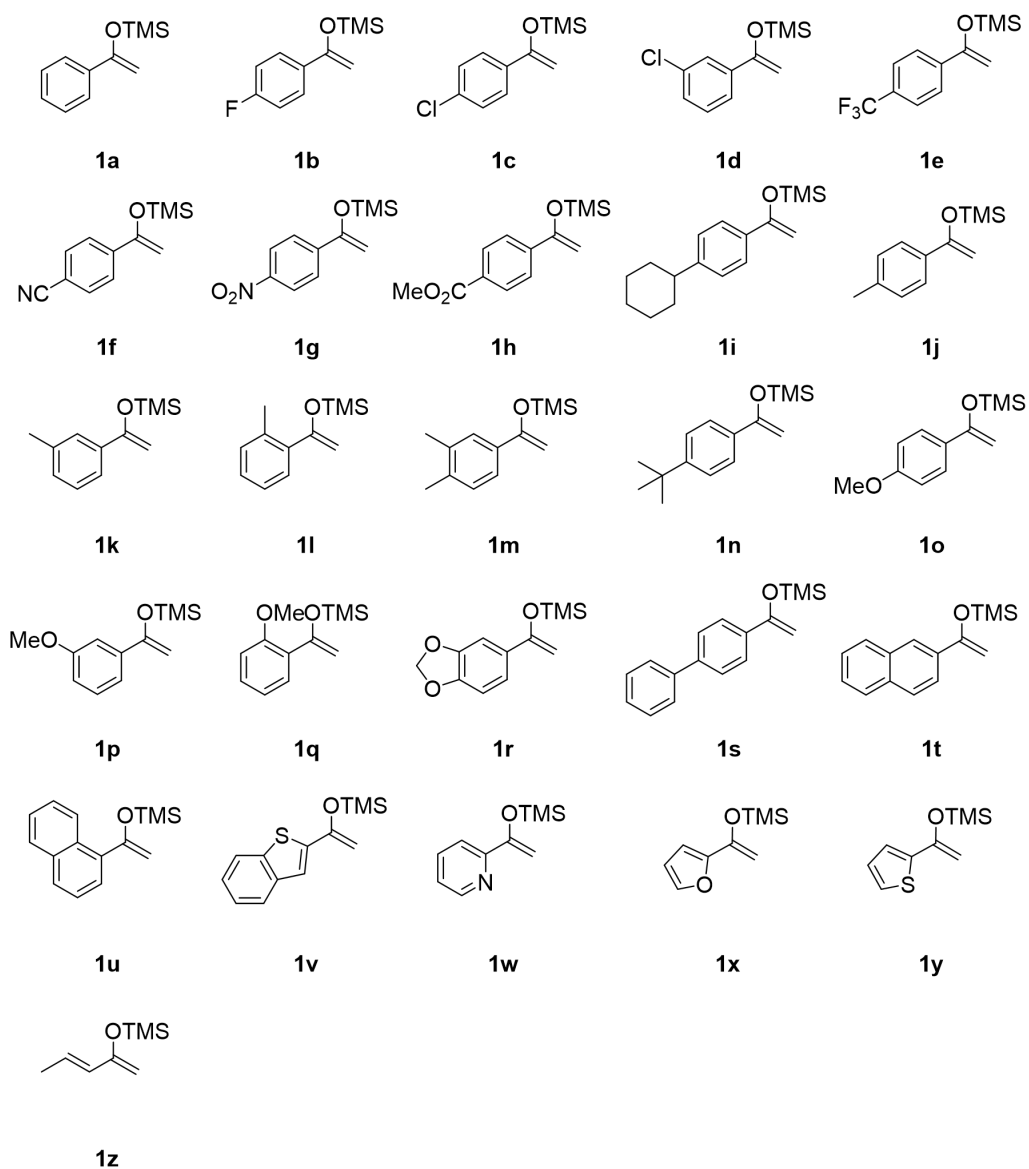
Entry	1a	Light source	<i>fac</i> -Ir(ppy) <sub>3</sub> (x mol%)	Time (h)	Yield (%) <sup>b</sup>
1	1.5	Blue LED	2	12	84
2	1.0	Blue LED	2	12	50
3	2.0	Blue LED	2	12	82
4	3.5	Blue LED	2	12	78
5	1.5	White LED	2	12	79
6	1.5	Blue LED	1	12	71
7	1.5	Blue LED	3	12	96
8	1.5	Blue LED	4	12	88
9	1.5	Blue LED	5	12	87
10	1.5	Blue LED	3	8	80
11	1.5	Blue LED	3	16	70
12	1.5	in dark	3	12	0
13 <sup>c</sup>	1.5	Blue LED	3	12	56

<sup>a</sup>Reaction conditions: **1a** (x equiv.), **2** (0.10 mmol, 1.0 equiv.), *fac*-Ir(ppy)<sub>3</sub> (x mol%), NMP (1.0 mL), light source, room temperature, N<sub>2</sub>, time. <sup>b</sup>Yields were determined by <sup>19</sup>F NMR spectroscopy using PhCF<sub>3</sub> as internal standard. <sup>c</sup>In air.

### 3. Preparation of Substrates and *N*-trifluoroethyl hydroxylamine reagent

#### 3.1 Preparation of Substrates



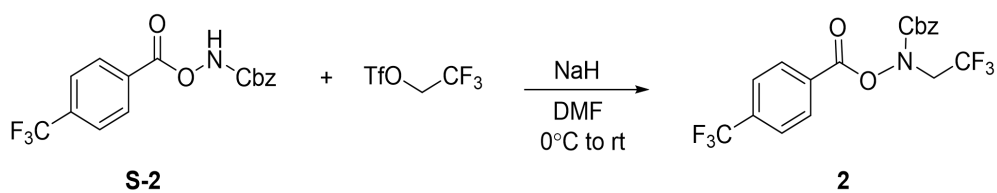


**Figure S2.** List of silyl enol ethers **1**.

Substrate **1a** (13735-81-4) was obtained commercially and used without further purification.

Substrates **1b-1z** were prepared according to the reported literatures.<sup>1</sup>

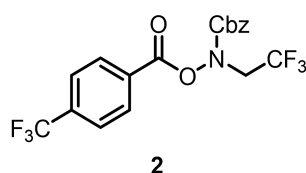
### 3.2 Preparation of *N*-fluoroalkyl hydroxylamine reagents



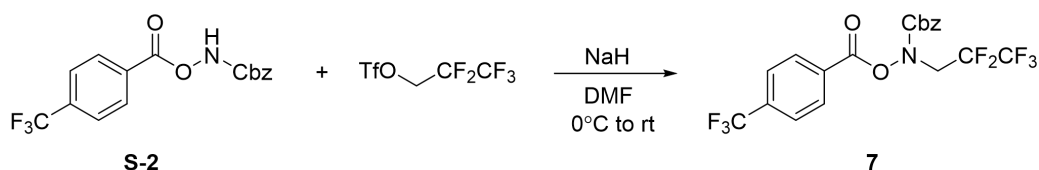
*N*-trifluoroethyl hydroxylamine reagent **2** was prepared according to the reported literature.<sup>2,3</sup>

To a solution of benzyl ((4-(trifluoromethyl)benzoyl)oxy)carbamate (**S-2**, 10 mmol, 1.0 equiv.) in dry DMF (80 mL) was added portion wise NaH (16 mmol, 1.6 equiv., 60% dispersion in mineral oil) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and 2,2,2-trifluoroethyl trifluoromethanesulfonate (15 mmol, 1.5 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. After completion of the reaction monitored by TLC, the reaction mixture was quenched by H<sub>2</sub>O, extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (PE/EtOAc = 50:1) to give the desired product **2**.

**Benzyl (2,2,2-trifluoroethyl)((4-(trifluoromethyl)benzoyl)oxy)carbamate (**2**)**



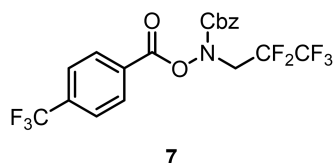
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 50:1) to afford **2** (1.81 g, 43%) as a white solid. **Mp**: 58.2-59.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.27 (m, 5H), 5.25 (s, 2H), 4.41 – 4.31 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.14, 154.57, 135.95 (q, *J* = 32.9 Hz), 134.87, 130.64, 129.91, 128.79, 128.77, 128.19, 125.98 (q, *J* = 3.8 Hz), 123.45 (q, *J* = 273.7 Hz), 123.34 (q, *J* = 280.8 Hz), 69.54, 51.50 (q, *J* = 35.3 Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.37 (s, 3F), -70.74 (t, *J* = 8.2 Hz, 3F). **MS** (ESI): *m/z* 444 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>18</sub>H<sub>13</sub>NO<sub>4</sub>F<sub>6</sub>Na [M+Na]<sup>+</sup>: 444.0646; found: 444.0651.



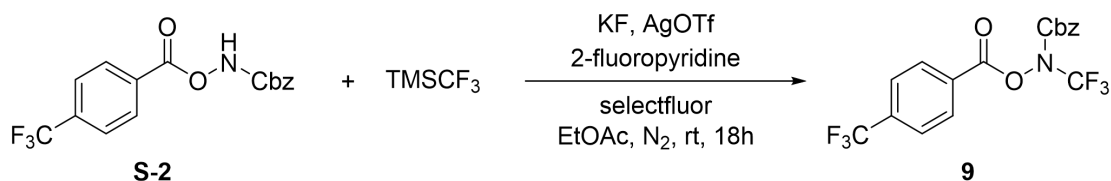
Reagent **7** was prepared according to the reported literature.<sup>2-4</sup> To a solution of benzyl ((4-(trifluoromethyl)benzoyl)oxy)carbamate (**S-2**, 10 mmol, 1.0 equiv.) in dry DMF (80 mL) was added portion wise NaH (16 mmol, 1.6 equiv., 60% dispersion in mineral oil) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and 2,2,3,3,3-pentafluoroethyl trifluoromethanesulfonate (15 mmol, 1.5 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. After completion of the reaction monitored by TLC, the reaction mixture was quenched by H<sub>2</sub>O, extracted with

CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (PE/EtOAc = 50:1) to give the desired product **7**.

**Benzyl (2,2,3,3,3-pentafluoropropyl)((4-(trifluoromethyl)benzoyl)oxy)carbamate (7)**

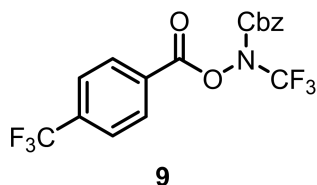


The product mixture was purified by silica gel column chromatography (PE/EtOAc = 50:1) to afford **7** (2.56 g, 54%) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.17 (m, 5H), 5.16 (s, 2H), 4.34 (d, *J* = 13.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.19, 154.64, 136.01 (q, *J* = 32.9 Hz), 134.84, 130.64, 129.87, 128.77 (d, *J* = 3.6 Hz), 128.49, 128.18, 125.99 (q, *J* = 3.7 Hz), 123.45 (q, *J* = 272.9 Hz), 118.64 (q, *J* = 286.1 Hz), 112.33 (t, *J* = 256.7 Hz), 69.62, 49.98 (t, *J* = 25.1 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.45 (s, 3F), -84.28 (s, 3F), -120.60 (s, 2F). MS (ESI): *m/z* 494 [M+Na]<sup>+</sup>; HRMS (ESI-TOF): *m/z* calculated for C<sub>19</sub>H<sub>13</sub>NO<sub>4</sub>NaF<sub>8</sub> [M+Na]<sup>+</sup>: 494.0615; found: 494.0615.



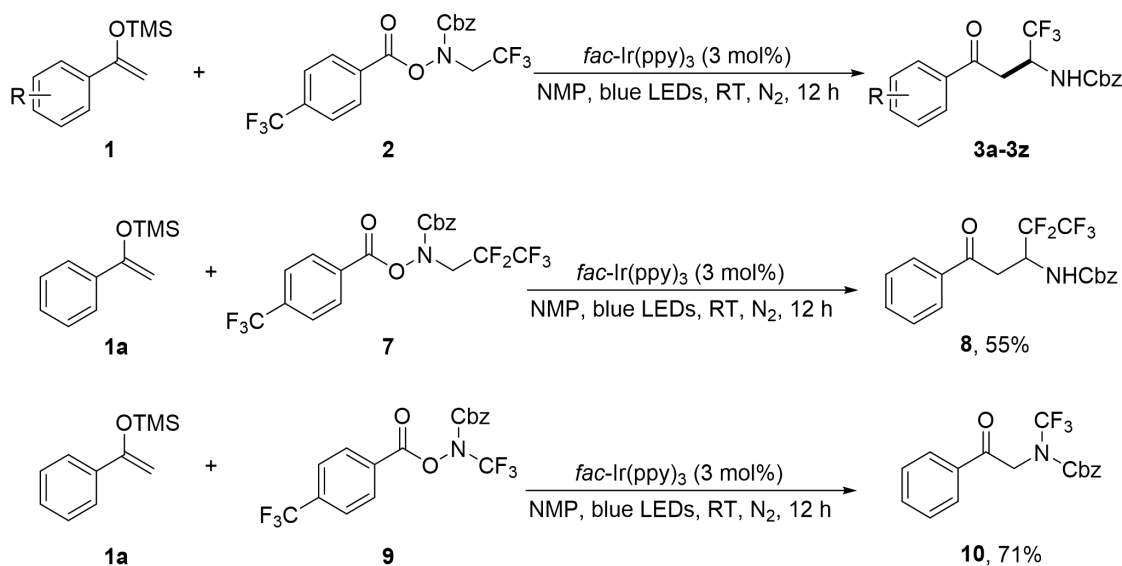
Reagent **9** was prepared according to the reported literature.<sup>3</sup> To a 500 mL vial equipped with a stirring bar, benzyl ((4-(trifluoromethyl)benzoyl)oxy)carbamate (**S-2**, 10 mmol, 1.0 equiv.), AgOTf (15 mmol, 1.5 equiv.), selectfluor (15 mmol, 1.5 equiv.), KF (20 mmol, 2.0 equiv.) were added successively in a nitrogen-filled glovebox. Then 2-fluoropyridine (15 mmol, 1.5 equiv.) and TMSCF<sub>3</sub> (20 mmol, 2.0 equiv.) in anhydrous ethyl acetate (50 mL) were added successively by syringe. The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was filtered through a plug of Celite® (eluted with ethyl acetate). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (PE/EtOAc = 100:1) to give the *N*-CF<sub>3</sub> hydroxylamine reagent **9** (1.63 g, 40%) as white solid.

**Benzyl (trifluoromethyl)((4-(trifluoromethyl)benzoyl)oxy)carbamate (9)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 100:1) to afford **9** (1.63 g, 40%) as white solid. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.20 (m, 5H), 5.25 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.87, 150.92, 136.21 (q, *J* = 33.0 Hz), 134.01, 130.88, 129.19, 129.10, 128.89, 128.30, 126.06 (q, *J* = 3.7 Hz), 123.41 (q, *J* = 272.9 Hz), 119.88 (q, *J* = 267.9 Hz), 70.34. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.04 (s, 3F), -63.45 (s, 3F). **MS** (ESI): *m/z* 408 [M+H]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>17</sub>H<sub>12</sub>NO<sub>4</sub>F<sub>6</sub> [M+H]<sup>+</sup>: 408.0671; found: 408.0673.

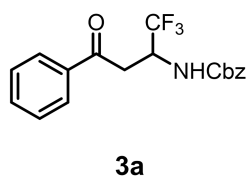
#### 4. General Procedures for Synthesis of Products



##### General Procedure:

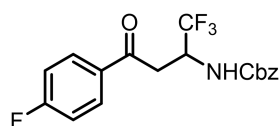
A 8 mL screw-cap vial equipped with a magnetic stir bar was charged with *N*-fluoroalkyl hydroxylamine reagent (0.2 mmol, 1.0 equiv.), *fac*-Ir(ppy)<sub>3</sub> (0.006 mmol, 3 mol%) and silyl enol ethers **1** (0.3 mmol, 1.5 equiv., if it is a solid). The vial was evacuated and backfilled with nitrogen for three times. Then, NMP (2.0 mL) was added via a syringe (If the silyl enol ethers **1** is a liquid, it is dissolved in NMP). The reaction mixture was placed at a distance of 10 cm from a 40 W blue LED and stirred at room temperature for 12 h. Then, the reaction mixture was quenched by H<sub>2</sub>O and was extracted with ethyl acetate. The combined organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **3a-3z**, **8** and **10**.

##### Benzyl (1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)carbamate (**3a**)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3a** (63.2 mg, 90%) as a white solid. **Mp**: 109.9-110.6 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (s, 5H), 5.61 (d, *J* = 9.8 Hz, 1H), 5.11 (s, 2H), 5.00 (m, 1H), 3.46 – 3.24 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 195.00, 155.68, 136.09, 135.94, 134.01, 128.96, 128.65, 128.38, 128.24, 125.20 (q, *J* = 281.9 Hz), 67.58, 49.62 (q, *J* = 31.5 Hz), 36.69. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.72 (d, *J* = 7.8 Hz, 3F). **MS** (ESI): *m/z* 374 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>18</sub>H<sub>16</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 374.0980; found: 374.0984.

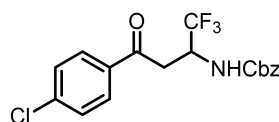
**Benzyl (1,1,1-trifluoro-4-(4-fluorophenyl)-4-oxobutan-2-yl)carbamate (3b)**



**3b**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3b** (50.7 mg, 69%) as a white solid. **Mp**: 133.6-135.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98 (m, 2H), 7.36 (s, 5H), 7.17 (t, *J* = 8.6 Hz, 2H), 5.54 (d, *J* = 9.8 Hz, 1H), 5.15 (s, 2H), 5.02 (m, 1H), 3.48 – 3.26 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.41, 167.59, 165.04, 155.62, 135.92, 132.59 (d, *J* = 3.0 Hz), 131.00 (d, *J* = 9.4 Hz), 128.70, 128.39 (d, *J* = 15.1 Hz), 125.14 (q, *J* = 282.8 Hz), 116.31, 116.09, 67.68, 49.71 (d, *J* = 31.4 Hz), 36.70. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.70 (d, *J* = 7.7 Hz, 3F), -103.46 (s, 1F). **MS** (ESI): *m/z* 392 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>F<sub>4</sub>Na [M+Na]<sup>+</sup>: 392.0886; found: 392.0888.

**Benzyl (4-(4-chlorophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3c)**

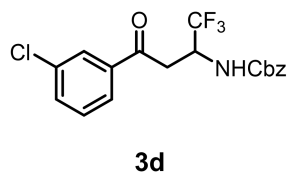


**3c**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3c** (28.7 mg, 37%) as a white solid. **Mp**: 136.2-138.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.32 (s, 5H), 5.53 (d, *J* = 9.7 Hz, 1H), 5.11 (s, 2H), 4.99 (m, 1H), 3.45 – 3.22 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.81, 155.62, 140.61,

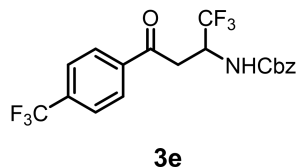
135.87, 134.40, 129.65, 129.33, 128.69, 128.46, 128.31, 125.12 (d,  $J = 282.8$  Hz), 67.67, 49.62 (d,  $J = 31.7$  Hz), 36.75.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.72 (d,  $J = 7.7$  Hz, 3F). **MS** (ESI):  $m/z$  408  $[\text{M}+\text{Na}]^+$ ; **HRMS** (ESI-TOF):  $m/z$  calculated for  $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{F}_3\text{NaCl}$   $[\text{M}+\text{Na}]^+$ : 408.0590; found: 408.0593.

**Benzyl (4-(3-chlorophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3d)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3d** (37.8 mg, 49%) as a white solid. **Mp**: 133.9-135.9 °C.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H), 7.71 (d,  $J = 7.8$  Hz, 1H), 7.48 (d,  $J = 7.7$  Hz, 1H), 7.33 (t,  $J = 7.9$  Hz, 1H), 7.23 (s, 5H), 5.46 (d,  $J = 9.7$  Hz, 1H), 5.03 (s, 2H), 4.91 (m, 1H), 3.36 – 3.14 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.74, 155.63, 137.57, 135.87, 135.37, 133.95, 130.32, 128.68, 128.45, 128.35, 128.30, 126.32, 125.09 (q,  $J = 282.8$  Hz), 67.67, 49.54 (q,  $J = 32.6$  Hz), 36.93.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.73 (d,  $J = 8.2$  Hz, 3F). **MS** (ESI):  $m/z$  408  $[\text{M}+\text{Na}]^+$ ; **HRMS** (ESI-TOF):  $m/z$  calculated for  $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{F}_3\text{NaCl}$   $[\text{M}+\text{Na}]^+$ : 408.0590; found: 408.0585.

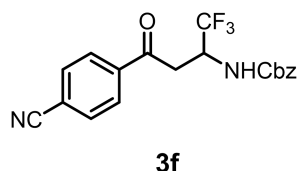
**Benzyl (1,1,1-trifluoro-4-oxo-4-(4-(trifluoromethyl)phenyl)butan-2-yl)carbamate (3e)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3e** (22.6 mg, 27%) as a white solid. **Mp**: 122.0-123.6 °C.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.0$  Hz, 2H), 7.64 (d,  $J = 8.0$  Hz, 2H), 7.23 (s, 5H), 5.53 (d,  $J = 9.7$  Hz, 1H), 5.02 (s, 2H), 4.93 (m, 1H), 3.44 – 3.19 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.13, 155.69, 138.71, 135.86, 135.22 (q,  $J = 32.9$  Hz), 128.68, 128.62, 128.46, 128.27, 126.05 (q,  $J = 3.7$  Hz), 125.09 (q,  $J = 282.0$  Hz), 123.54 (q,  $J = 272.8$  Hz), 67.69, 49.56 (q,  $J = 31.7$  Hz), 37.18.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.21 (s, 3F), -75.81 (d,  $J = 7.6$  Hz, 3F). **MS** (ESI):  $m/z$  442  $[\text{M}+\text{Na}]^+$ ; **HRMS** (ESI-TOF):  $m/z$  calculated for  $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{F}_6\text{Na}$   $[\text{M}+\text{Na}]^+$ : 442.0854; found: 442.0853.

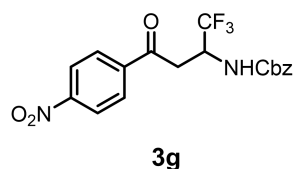
**Benzyl**

**(4-(4-cyanophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3f)**



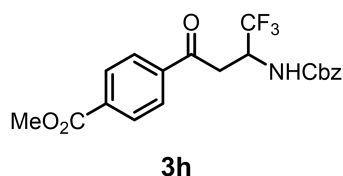
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3f** (28.6 mg, 38%) as a white solid. **Mp**: 130.9-132.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.33 (s, 5H), 5.48 (d, *J* = 9.8 Hz, 1H), 5.12 (s, 2H), 5.00 (m, 1H), 3.50 – 3.26 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.74, 155.58, 138.89, 135.77, 132.84, 128.72, 128.66, 128.53, 128.32, 124.99 (q, *J* = 282.8 Hz), 117.77, 117.25, 67.76, 49.50 (q, *J* = 31.2 Hz), 37.25. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.75 (d, *J* = 7.7 Hz, 3F). **MS** (ESI): *m/z* 399 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 399.0932; found: 399.0935.

**Benzyl (1,1,1-trifluoro-4-(4-nitrophenyl)-4-oxobutan-2-yl)carbamate (3g)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3g** (25.3 mg, 32%) as a yellow solid. **Mp**: 142.8-144.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.26 (s, 5H), 5.39 (d, *J* = 9.7 Hz, 1H), 5.05 (s, 2H), 5.00 – 4.88 (m, 1H), 3.46 – 3.23 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.57, 155.56, 150.86, 140.38, 135.80, 129.34, 128.73, 128.55, 128.32, 124.99 (q, *J* = 282.8 Hz), 124.22, 67.80, 49.59 (d, *J* = 32.2 Hz), 37.55. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.74 (d, *J* = 7.8 Hz, 3F). **MS** (ESI): *m/z* 419 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>O<sub>5</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 419.0831; found: 419.0826.

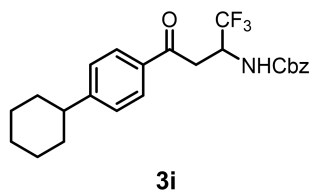
**Methyl 4-(3-(((benzyloxy)carbonyl)amino)-4,4,4-trifluorobutanoyl)benzoate (3h)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3h** (45.8 mg, 56%) as a white solid. **Mp**: 138.8-140.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ

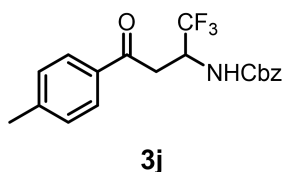
8.07 (d,  $J = 8.6$  Hz, 2H), 7.92 (d,  $J = 8.5$  Hz, 2H), 7.28 (s, 5H), 5.58 (d,  $J = 9.7$  Hz, 1H), 5.08 (s, 2H), 4.98 (m, 1H), 3.91 (s, 3H), 3.46 – 3.26 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.45, 166.12, 155.65, 139.17, 135.88, 134.62, 130.12, 128.66, 128.42, 128.28, 128.15, 125.12 (q,  $J = 282.8$  Hz), 67.63, 52.69, 49.52 (q,  $J = 31.6$  Hz), 37.18.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) -75.77 (d,  $J = 7.7$  Hz, 3F). MS (ESI):  $m/z$  432  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{20}\text{H}_{18}\text{NO}_5\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 432.1035; found: 432.1031.

**Benzyl (4-(4-cyclohexylphenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3i)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3i** (77.1 mg, 89%) as a white solid. **Mp**: 119.3-120.6 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 7.9$  Hz, 2H), 7.32 – 7.20 (m, 7H), 5.51 (d,  $J = 9.7$  Hz, 1H), 5.04 (s, 2H), 4.97 – 4.83 (m, 1H), 3.26 (m, 2H), 2.50 (d,  $J = 10.4$  Hz, 1H), 1.78 (d,  $J = 8.6$  Hz, 4H), 1.69 (d,  $J = 13.1$  Hz, 1H), 1.32 (q,  $J = 14.6, 12.9$  Hz, 4H), 1.18 (d,  $J = 11.1$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.69, 155.66, 154.87, 136.01, 134.03, 128.67, 128.51, 128.38, 128.28, 127.47, 125.24 (q,  $J = 282.8$  Hz), 67.58, 49.78 (d,  $J = 31.8$  Hz), 44.85, 36.49, 34.16, 26.80, 26.11.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.65 (d,  $J = 8.0$  Hz, 3F). MS (ESI):  $m/z$  456  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{24}\text{H}_{26}\text{NO}_5\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 456.1762; found: 456.1759.

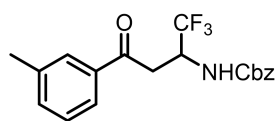
**Benzyl (1,1,1-trifluoro-4-oxo-4-(*p*-tolyl)butan-2-yl)carbamate (3j)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3j** (42.7 mg, 58%) as a white solid. **Mp**: 109.8-111.5 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.0$  Hz, 2H), 7.37 – 7.23 (m, 7H), 5.60 (d,  $J = 9.7$  Hz, 1H), 5.11 (s, 2H), 4.98 (m, 1H), 3.43 – 3.22 (m, 2H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.64, 155.67, 145.02, 135.97, 133.67, 129.64, 128.65, 128.37, 128.27, 125.23 (q,  $J = 283.8$  Hz), 67.56, 49.71 (q,  $J = 31.9$  Hz), 36.48, 21.82.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.70 (d,  $J = 7.8$  Hz, 3F). MS (ESI):  $m/z$  388  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{19}\text{H}_{18}\text{NO}_5\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 388.1136; found: 388.1140.



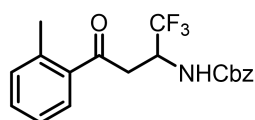
**Benzyl (1,1,1-trifluoro-4-oxo-4-(*m*-tolyl)butan-2-yl)carbamate (3k)**



**3k**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3k** (54.0 mg, 74%) as a white solid. **Mp**: 122.1-124.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 11.8 Hz, 2H), 7.43 – 7.26 (m, 7H), 5.58 (d, *J* = 9.7 Hz, 1H), 5.11 (s, 2H), 5.03 – 4.95 (m, 1H), 3.45 – 3.24 (m, 2H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 195.19, 155.66, 138.86, 136.15, 135.96, 134.80, 128.83, 128.75, 128.66, 128.39, 128.27, 125.47, 125.22 (q, *J* = 283.8 Hz), 67.58, 49.68 (q, *J* = 32.0 Hz), 36.70, 21.45. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.69 (d, *J* = 8.1 Hz, 3F). **MS** (ESI): *m/z* 388 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 388.1136; found: 388.1140.

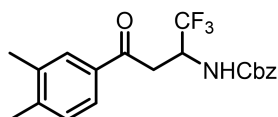
**Benzyl (1,1,1-trifluoro-4-oxo-4-(*o*-tolyl)butan-2-yl)carbamate (3l)**



**3l**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3l** (32.0 mg, 44%) as a white solid. **Mp**: 100.5-102.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.34 (s, 5H), 7.27 (t, *J* = 8.4 Hz, 2H), 5.58 (d, *J* = 9.8 Hz, 1H), 5.13 (s, 2H), 4.99 – 4.90 (m, 1H), 3.36 – 3.22 (m, 2H), 2.46 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 198.50, 155.62, 139.16, 136.50, 135.95, 132.46, 132.34, 128.68, 128.44, 128.32, 126.02, 125.17 (q, *J* = 282.8 Hz), 67.59, 49.92 (q, *J* = 31.2 Hz), 39.24, 21.50. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.73 (d, *J* = 7.9 Hz, 3F). **MS** (ESI): *m/z* 388 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 388.1137; found: 388.1136.

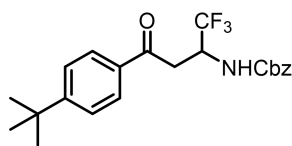
**Benzyl (4-(3,4-dimethylphenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3m)**



**3m**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3m** (66.7 mg, 88%) as a white solid. **Mp**: 110.5-112.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.32 (s, 5H), 7.21 (d, *J* = 7.8 Hz, 1H), 5.60 (d, *J* = 9.5 Hz, 1H), 5.11 (s, 2H), 5.03 – 4.92 (m, 1H), 3.43 – 3.22 (m, 2H), 2.31 (d, *J* = 3.9 Hz, 6H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.89, 155.66, 143.80, 137.41, 135.97, 134.04, 130.14, 129.34, 128.65, 128.38, 128.27, 125.99, 125.24 (q, *J* = 282.8 Hz), 67.55, 49.74 (q, *J* = 31.6 Hz), 36.43, 20.23, 19.91. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.68 (d, *J* = 7.8 Hz, 3F). **MS** (ESI): *m/z* 402 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>20</sub>H<sub>20</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 402.1293; found: 402.1295.

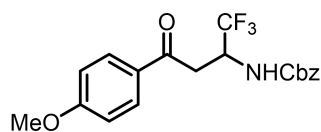
**Benzyl (4-(4-(tert-butyl)phenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3n)**



**3n**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3n** (73.6 mg, 90%) as a white solid. **Mp**: 124.6-126.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.33 (s, 5H), 5.61 (d, *J* = 9.7 Hz, 1H), 5.12 (s, 2H), 5.04 – 4.94 (m, 1H), 3.46 – 3.22 (m, 2H), 1.34 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.71, 157.94, 155.67, 135.96, 133.56, 128.66, 128.39, 128.26, 125.94, 125.22 (q, *J* = 282.8 Hz), 67.57, 49.73 (q, *J* = 32.1 Hz), 36.48, 35.33, 31.14. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.66 (d, *J* = 7.9 Hz, 3F). **MS** (ESI): *m/z* 430 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>22</sub>H<sub>24</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 430.1606; found: 430.1606.

**Benzyl**



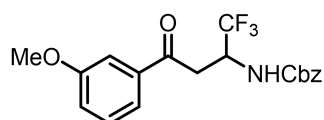
**3o**

**(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobutan-2-yl)carbamate (3o)**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3o** (61.8 mg, 81%) as a white solid. **Mp**: 133.7-135.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ

7.90 (d,  $J = 8.9$  Hz, 2H), 7.32 (s, 5H), 6.93 (d,  $J = 8.9$  Hz, 2H), 5.61 (d,  $J = 9.6$  Hz, 1H), 5.12 (s, 2H), 4.98 (m, 1H), 3.87 (s, 3H), 3.30 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.51, 164.21, 155.67, 135.99, 130.63, 129.20, 128.66, 128.33 (d,  $J = 10.8$  Hz), 125.24 (q,  $J = 282.8$  Hz), 114.12, 67.56, 55.67, 49.82 (d,  $J = 31.9$  Hz), 36.19.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.66 (d,  $J = 7.7$  Hz, 3F). MS (ESI):  $m/z$  404  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{19}\text{H}_{18}\text{NO}_4\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 404.1086; found: 404.1089.

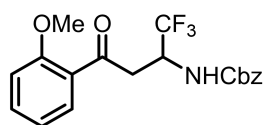
**Benzyl (1,1,1-trifluoro-4-(3-methoxyphenyl)-4-oxobutan-2-yl)carbamate (3p)**



**3p**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3p** (54.9 mg, 72%) as a white solid. **Mp**: 93.6-95.3 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.44 (m, 2H), 7.39 (d,  $J = 8.0$  Hz, 1H), 7.33 (s, 5H), 7.14 (m, 1H), 5.53 (d,  $J = 9.8$  Hz, 1H), 5.12 (s, 2H), 5.00 (m, 1H), 3.84 (s, 3H), 3.46 – 3.25 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.80, 160.08, 155.63, 137.41, 135.92, 129.96, 128.67, 128.42, 128.29, 125.18 (q,  $J = 282.8$  Hz), 120.82, 120.57, 112.40, 67.62, 55.59, 49.65 (d,  $J = 32.0$  Hz), 36.85.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.73 (d,  $J = 7.7$  Hz, 3F). MS (ESI):  $m/z$  404  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{19}\text{H}_{18}\text{NO}_4\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 404.1086; found: 404.1089.

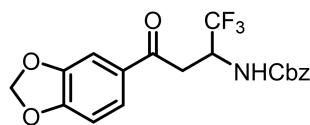
**Benzyl (1,1,1-trifluoro-4-(2-methoxyphenyl)-4-oxobutan-2-yl)carbamate (3q)**



**3q**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3q** (57.3 mg, 75%) as a white solid. **Mp**: 112.1-112.9 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.71 (m, 1H), 7.53 – 7.47 (m, 1H), 7.32 (s, 5H), 7.04 – 6.94 (m, 2H), 5.48 (d,  $J = 9.7$  Hz, 1H), 5.10 (s, 2H), 5.01 – 4.87 (m, 1H), 3.91 (s, 3H), 3.36 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.77, 158.90, 155.67, 136.04, 134.77, 130.97, 128.63, 128.34, 128.22, 126.76, 125.25 (q,  $J = 282.8$  Hz), 121.08, 111.71, 67.44, 55.63, 49.90 (q,  $J = 31.6$  Hz), 41.98.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -76.03 (d,  $J = 7.7$  Hz, 3F). MS (ESI):  $m/z$  404  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{19}\text{H}_{18}\text{NO}_4\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 404.1086; found: 404.1089.

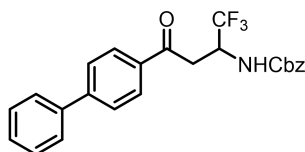
**Benzyl (4-(benzo[d][1,3]dioxol-5-yl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3r)**



**3r**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3r** (58.0 mg, 73%) as a white solid. **Mp**: 138.0-140.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.24 (s, 5H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.97 (s, 2H), 5.51 (d, *J* = 9.7 Hz, 1H), 5.04 (s, 2H), 4.88 (m, 1H), 3.31 – 3.06 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.01, 155.67, 152.58, 148.56, 135.96, 130.98, 128.65, 128.39, 128.27, 125.20 (q, *J* = 283.8 Hz) 124.76, 108.14, 107.93, 102.19, 67.57, 49.81 (q, *J* = 31.4 Hz), 36.38, 32.54. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.71 (d, *J* = 8.0 Hz, 3F). **MS** (ESI): *m/z* 418 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>19</sub>H<sub>16</sub>NO<sub>5</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 418.0878; found: 418.0869.

**Benzyl**

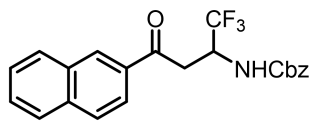


**3s**

**(4-([1,1'-biphenyl]-4-yl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3s)**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3s** (59.8 mg, 70%) as a white solid. **Mp**: 181.0-181.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.60 (m, 2H), 7.45 (m, 3H), 7.34 (s, 5H), 5.54 (d, *J* = 9.8 Hz, 1H), 5.14 (s, 2H), 5.06 – 4.96 (m, 1H), 3.52 – 3.30 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.60, 155.65, 146.74, 139.66, 135.95, 134.79, 129.16, 128.89, 128.70, 128.62, 128.44, 128.32, 127.60, 127.42, 125.21 (q, *J* = 282.8 Hz), 67.66, 49.78 (d, *J* = 32.1 Hz), 36.70. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.63 (d, *J* = 7.8 Hz, 3F). **MS** (ESI): *m/z* 450 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>24</sub>H<sub>20</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 450.1293; found: 450.1295.

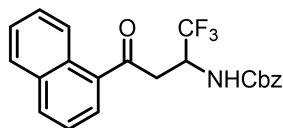
**Benzyl (1,1,1-trifluoro-4-(naphthalen-2-yl)-4-oxobutan-2-yl)carbamate (3t)**



**3t**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3t** (60.1 mg, 75%) as a white solid. **Mp**: 142.1-143.0 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.41 (d, *J* = 1.8 Hz, 1H), 8.00 – 7.83 (m, 4H), 7.59 (m, 2H), 7.31 (s, 5H), 5.62 (d, *J* = 9.7 Hz, 1H), 5.12 (s, 2H), 5.06 (m, 1H), 3.63 – 3.35 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.91, 155.69, 135.98, 135.93, 133.46, 132.48, 130.22, 129.77, 129.10, 128.93, 128.65, 128.40, 128.29, 127.96, 127.21, 125.26 (q, *J* = 282.8 Hz), 123.61, 67.62, 49.79 (q, *J* = 32.0 Hz), 36.71. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.60 (d, *J* = 7.7 Hz, 3F). **MS** (ESI): *m/z* 424 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>22</sub>H<sub>18</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 424.1136; found: 424.1140.

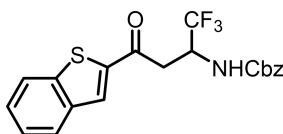
**Benzyl (1,1,1-trifluoro-4-(naphthalen-1-yl)-4-oxobutan-2-yl)carbamate (3u)**



**3u**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3u** (28.1 mg, 35%) as a yellow solid. **Mp**: 153.4-154.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.53 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.45 (m, 3H), 7.25 (s, 5H), 5.53 (d, *J* = 9.8 Hz, 1H), 5.03 (s, 2H), 5.00 – 4.92 (m, 1H), 3.38 (t, *J* = 6.9 Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 198.67, 155.63, 135.96, 134.52, 134.13, 133.91, 130.22, 128.69, 128.66, 128.56, 128.43, 128.29, 126.90, 125.73, 125.20 (q, *J* = 282.8 Hz), 124.38, 67.63, 50.19 (d, *J* = 32.4 Hz), 39.83. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.65 (d, *J* = 7.6 Hz, 3F). **MS** (ESI): *m/z* 424 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>22</sub>H<sub>18</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 424.1136; found: 424.1130.

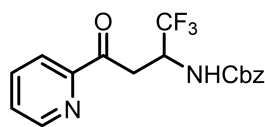
**Benzyl (4-(benzo[b]thiophen-2-yl)-1,1,1-trifluoro-4-oxobutan-2-yl)carbamate (3v)**



**3v**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3v** (32.5 mg, 40%) as a white solid. **Mp**: 137.2-138.6 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (s, 1H), 7.80 (m, 2H), 7.43 – 7.31 (m, 2H), 7.23 (s, 5H), 5.58 (d, *J* = 9.7 Hz, 1H), 5.03 (s, 2H), 4.92 (m, 1H), 3.44 – 3.19 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 189.50, 155.64, 142.96, 142.60, 138.99, 135.88, 130.15, 128.67, 128.41, 128.27, 128.13, 126.34, 125.43, 125.20 (q, *J* = 282.8 Hz), 123.14, 67.68, 49.96 (d, *J* = 31.8 Hz), 37.14, 29.83. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -75.62 (d, *J* = 7.6 Hz, 3F). **MS** (ESI): *m/z* 430 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>20</sub>H<sub>16</sub>NO<sub>3</sub>F<sub>3</sub>NaS [M+Na]<sup>+</sup>: 430.0701; found: 430.0692.

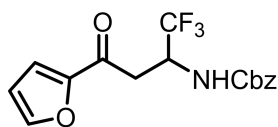
**Benzyl (1,1,1-trifluoro-4-oxo-4-(pyridin-2-yl)butan-2-yl)carbamate (3w)**



**3w**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3w** (30.3 mg, 43%) as a white solid. **Mp**: 122.1-122.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.59 (d, *J* = 4.8 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.23 (s, 5H), 5.46 (d, *J* = 9.7 Hz, 1H), 5.07 – 4.90 (m, 3H), 3.72 – 3.33 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 196.89, 155.65, 152.48, 149.20, 137.27, 136.00, 128.64, 128.35, 128.21, 127.91, 125.20 (q, *J* = 282.8 Hz), 122.27, 67.49, 49.80 (q, *J* = 32.1 Hz), 36.37. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -76.22 (d, *J* = 7.6 Hz, 3F). **MS** (ESI): *m/z* 353 [M+H]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>F<sub>3</sub> [M+H]<sup>+</sup>: 353.1113; found: 353.1110.

**Benzyl (1,1,1-trifluoro-4-(furan-2-yl)-4-oxobutan-2-yl)carbamate (3x)**

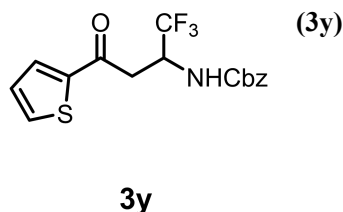


**3x**

The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3x** (46.1 mg, 68%) as a yellow solid. **Mp**: 88.2-90.0 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.58 (m, 1H), 7.38 – 7.22 (m, 6H), 6.55 (d, *J* = 9.6 Hz, 1H), 5.60 (d, *J* = 9.8 Hz, 1H), 5.11 (s, 2H), 5.01 – 4.89 (m, 1H), 3.28 (s, 1H), 3.17 (m, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 184.08, 155.59, 152.13, 147.21, 135.90, 128.66, 128.41, 128.28, 125.02 (q, *J* = 282.8 Hz), 118.27, 112.91,

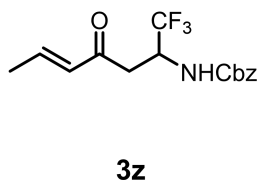
67.61, 49.63 (d,  $J = 31.9$  Hz), 36.52.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.94 (d,  $J = 7.6$  Hz, 3F). MS (ESI):  $m/z$  364  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{NO}_4\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 364.0773; found: 364.0763.

**Benzyl (1,1,1-trifluoro-4-oxo-4-(thiophen-2-yl)butan-2-yl)carbamate**



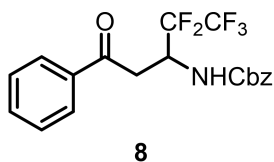
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3y** (43.5 mg, 61%) as a white solid. **Mp**: 97.2-99.2 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.57 (m, 2H), 7.23 (s, 5H), 7.09 – 7.03 (m, 1H), 5.63 (d,  $J = 9.7$  Hz, 1H), 5.02 (s, 2H), 4.88 (m, 1H), 3.32 – 3.09 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  187.92, 155.65, 143.26, 135.92, 135.11, 132.87, 128.65, 128.52, 128.38, 128.24, 125.05 (q,  $J = 282.8$  Hz), 67.59, 49.88 (q,  $J = 31.5$  Hz), 37.18.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.68 (d,  $J = 7.8$  Hz, 3F). MS (ESI):  $m/z$  380  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{NO}_3\text{F}_3\text{NaS}$   $[\text{M}+\text{Na}]^+$ : 380.0544; found: 380.0548.

**Benzyl (*E*)-(1,1,1-trifluoro-4-oxohept-5-en-2-yl)carbamate (**3z**)**



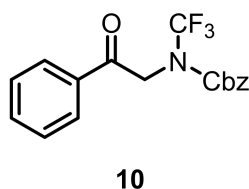
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **3z** (31.5 mg, 50%) as a white solid. **Mp**: 106.4-107.6 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (s, 5H), 6.88 – 6.77 (m, 1H), 6.06 (d,  $J = 15.9$  Hz, 1H), 5.51 (d,  $J = 9.7$  Hz, 1H), 5.05 (s, 2H), 4.80 – 4.70 (m, 1H), 2.92 – 2.76 (m, 2H), 1.84 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.92, 155.63, 145.10, 135.99, 131.41, 128.68, 128.41, 128.28, 125.09 (q,  $J = 282.8$  Hz), 67.58, 49.70 (q,  $J = 31.3$  Hz), 37.63, 18.52.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.83 (d,  $J = 8.1$  Hz, 3F). MS (ESI):  $m/z$  338  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI-TOF):  $m/z$  calculated for  $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{F}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 338.0980; found: 338.0974.

**Benzyl (1,1,1,2,2-pentafluoro-5-oxo-5-phenylpentan-3-yl)carbamate (**8**)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **8** (44.1 mg, 55%) as a white solid. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.43 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.14 (m, 5H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.05 – 4.89 (m, 3H), 3.23 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 195.05, 155.36, 136.14, 135.97, 134.02, 128.98, 128.66, 128.40, 128.25, 128.21, 120.90 – 112.43 (m), 67.62, 48.39 – 47.63 (m), 36.48. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -82.10 (s, 3F), -119.06 (d, *J* = 274.0 Hz, 1F), -125.33 (d, *J* = 273.9 Hz, 1F). **MS** (ESI): *m/z* 424 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>19</sub>H<sub>16</sub>NO<sub>3</sub>F<sub>5</sub>Na [M+Na]<sup>+</sup>: 424.0948; found: 424.0951.

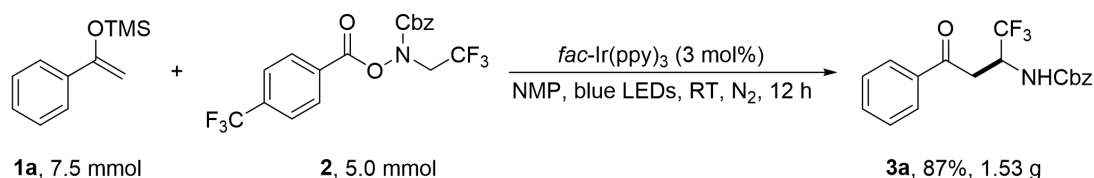
#### Benzyl (2-oxo-2-phenylethyl)(trifluoromethyl)carbamate (**10**)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford **10** (47.9 mg, 71%) as yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.25 (s, 5H), 5.18 (s, 2H), 4.89 (d, *J* = 2.0 Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.85, 152.65, 135.00, 134.29, 134.19, 129.05, 128.71, 128.56, 128.03, 127.94, 120.55 (q, *J* = 261.7 Hz), 69.05, 50.91, 50.90. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -54.83 (br s, 3F). **MS** (ESI): *m/z* 360 [M+Na]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>17</sub>H<sub>14</sub>NO<sub>3</sub>F<sub>3</sub>Na [M+Na]<sup>+</sup>: 360.0823; found: 360.0827.

## 5. Gram-Scale Reaction and Transformation of **3a**

### 5.1 Gram-Scale Reaction of **3a**

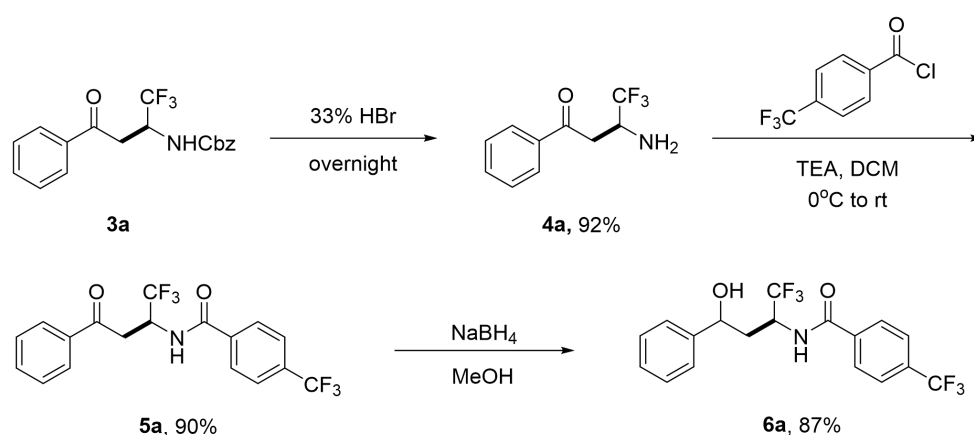


To a Schlenk flask equipped with a stir bar were added *N*-trifluoroalkyl hydroxylamine reagent **2** (2.10 g, 5.00 mmol) and *fac*-Ir(ppy)<sub>3</sub> (98.20 mg, 0.15 mmol, 3 mol %). The tube was



evacuated and backfilled with pure N<sub>2</sub> for three times. Afterwards, NMP (50 mL) and silyl enol ether **1a** (1.44 g, 7.50 mmol) were added by syringe under N<sub>2</sub> atmosphere. The tightly sealed tube was then irradiated with a 40 W blue LED (the distance between the tube and the light source was about 10 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 12 hours, the mixture was quenched by H<sub>2</sub>O and was extracted with ethyl acetate. The combined organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc = 20:1) to give the desired product **3a** (1.53 g, 87%).

## 5.2 Transformation of **3a**



A 8 mL screw-cap vial equipped with a magnetic stir bar was charged with **3a** (70.2 mg, 0.2 mmol). The vial was evacuated and backfilled with nitrogen for three times. Then, 33% HBr (1 mL) was carefully added by syringe under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for overnight. After completion of the reaction monitored by TLC, the reaction mixture was quenched by H<sub>2</sub>O, and triethylamine was added at 0°C to adjust the pH to alkaline. The mixture was then extracted with diethyl ether, The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (PE/EtOAc = 20:1) to give the desired product **4a** as a yellow solid (39.9 mg, 92%). **Mp**: 52.4-57.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 3.94 (m, 1H), 3.25 (m, 1H), 3.11 (m, 1H), 1.63 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 196.37, 136.44, 133.88, 128.92, 128.22, 126.57 (q, *J* = 280.8 Hz), 50.31 (q, *J* = 29.8 Hz), 39.41, 39.40. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -78.23 (d, *J* = 7.5 Hz, 3F). **MS** (ESI): *m/z* 218 [M+H]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>10</sub>H<sub>11</sub>NOF<sub>3</sub> [M+H]<sup>+</sup>: 218.0793; found: 218.0797.

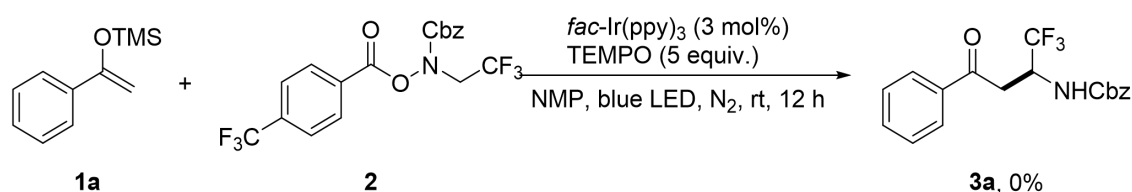
To a solution of **4a** (43.4 mg, 0.2 mmol) in DCM (2 mL) at 0 °C was added triethylamine

(101.0 mg, 1.0 mmol) followed by a slow addition of acyl chloride (41.7 mg, 0.2 mmol) under nitrogen atmosphere in a round bottomed flask. The reaction mixture was stirred at room temperature. Until completion of the reaction monitored by TLC, the reaction mixture was quenched with water, extracted with dichloromethane. Combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel (PE/EtOAc = 20:1) to give the desired product **5a** as a white solid (76.3 mg, 98%). **Mp**: 136.8-137.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.93 (m, 3H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.59 (m, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 5.47 – 5.33 (m, 1H), 3.69 (m, 1H), 3.35 (m, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 196.60, 166.04, 136.62, 136.10, 134.33, 133.74, 129.09, 128.32, 127.89, 125.87, 125.83, 125.09 (q, *J* = 283.8 Hz), 123.68 (q, *J* = 273.7 Hz), 48.81 – 48.05 (m), 35.63, 29.84. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.05 (s, 3F), -74.36 (d, *J* = 8.1 Hz, 3F). **MS** (ESI): *m/z* 390 [M+H]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>18</sub>H<sub>14</sub>NO<sub>2</sub>F<sub>6</sub> [M+H]<sup>+</sup>: 390.0929; found: 390.0933.

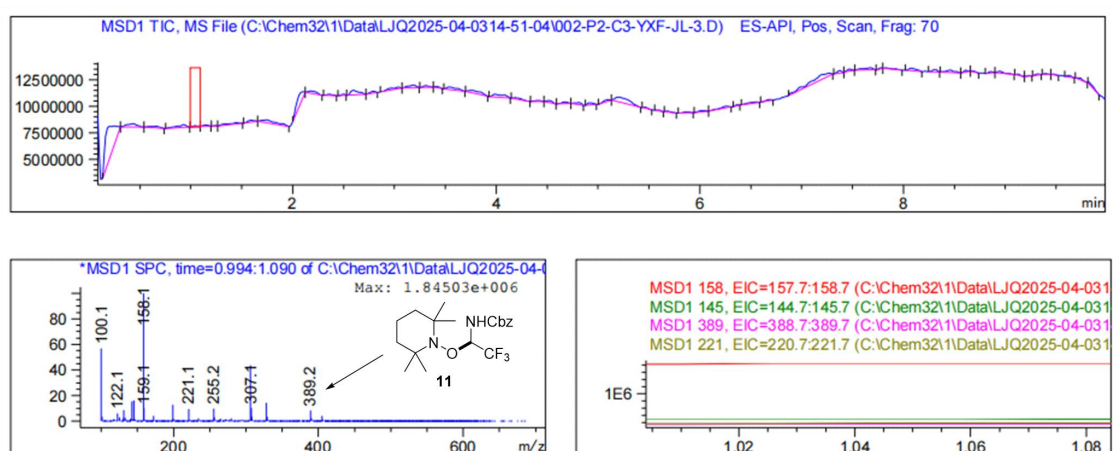
NaBH<sub>4</sub> (9.12 mg, 0.24 mmol) was added slowly to a solution of **5a** (77.8 mg, 0.2 mmol) in MeOH (2 mL) at 0 °C. The reaction mixture was stirred at room temperature. Until completion of the reaction monitored by TLC, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl solution, extracted with Et<sub>2</sub>O. Combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel (PE/EtOAc = 10:1) to give the desired product **6a** as a white solid (75.9 mg, 97%). **Mp**: 137.1-138.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 4H), 7.22 – 7.19 (m, 1H), 6.60 (d, *J* = 9.0 Hz, 1H), 4.88 (m, 1H), 4.79 (m, 1H), 2.33 (s, 1H), 2.23 – 2.07 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.64, 143.36, 136.76, 133.89 (q, *J* = 33.33 Hz), 129.04, 128.44, 127.81, 125.80, 125.76, 125.70, 125.10 (q, *J* = 282.8 Hz), 123.67 (q, *J* = 273.7 Hz), 72.03, 49.89 (q, *J* = 30.8 Hz), 36.93. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.07 (s, 3F), -76.00 (d, *J* = 7.4 Hz, 3F). **MS** (ESI): *m/z* 392 [M+H]<sup>+</sup>; **HRMS** (ESI-TOF): *m/z* calculated for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub>F<sub>6</sub> [M+H]<sup>+</sup>: 392.1085; found: 392.1085.

## 6. Mechanistic Experiment

### 6.1 Trapping Experiments



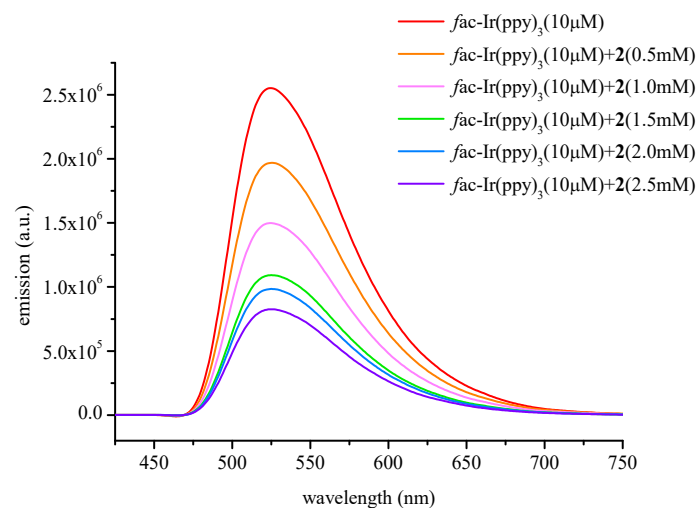
To a sealed tube equipped with a stir bar were added *N*-trifluoroalkyl hydroxylamine reagent **2** (84.2 mg, 0.2 mmol, 1.0 equiv.), *fac*-Ir(ppy)<sub>3</sub> (4.0 mg, 0.006 mmol, 3 mol %) and TEMPO (156.2 mg, 1.0 mmol, 5.0 equiv.). The tube was evacuated and backfilled with pure N<sub>2</sub> for three times. Afterwards, NMP (2.0 mL) and silyl enol ether **1a** (57.7 mg, 0.3 mmol, 1.5 equiv.) were added by syringe under N<sub>2</sub> atmosphere. The tightly sealed tube was then irradiated with a 40 W blue LEDs (the distance between the tube and the light source was about 10 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 12 hours, The <sup>19</sup>F NMR spectroscopy indicated that the formation of product **3a** was inhibited in the presence of 5.0 equiv. of TEMPO. The LC-MS showed that compound **11** *m/z* calculated for C<sub>19</sub>H<sub>28</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 389.2



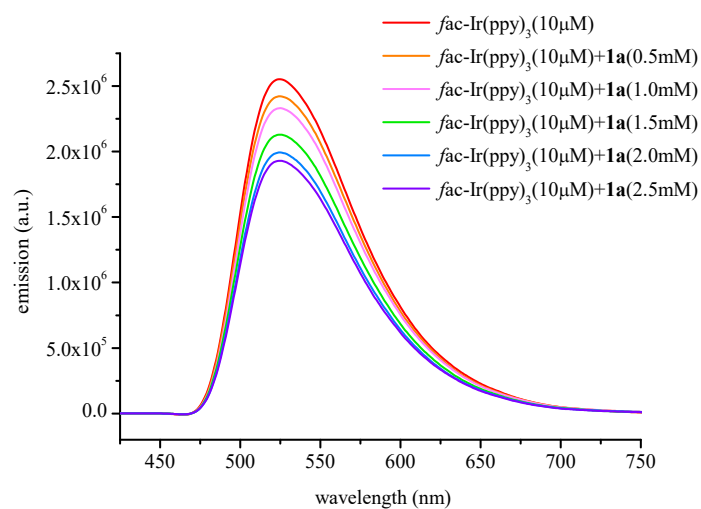
**Figure S3.** The LC-MS of Reaction Mixture.

## 6.2 Stern-Volmer Experiments

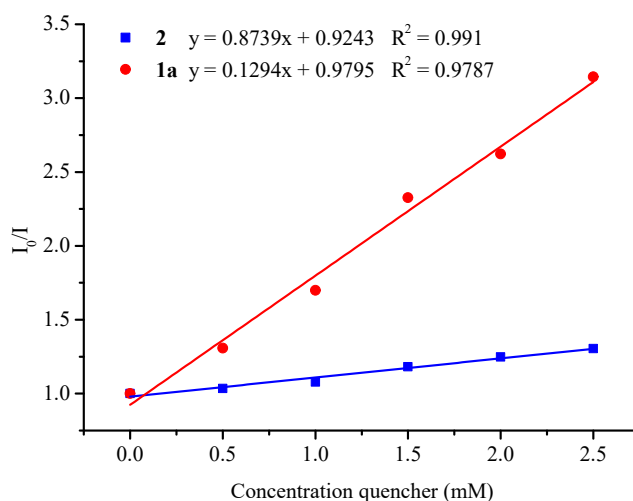
Stern-Volmer quenching experiments were carried by Edinburgh Fluorescence Spectrometer FS5, using a 10 μM solution of photocatalyst *fac*-Ir(ppy)<sub>3</sub> and variable concentrations (0.5, 1.0, 1.5, 2.0, 2.5 mM) of *N*-trifluoroalkyl hydroxylamine reagent **2**, silyl enol ether **1a** in NMP. The samples were prepared in 4 mL quartz cuvettes, equipped with PTFE stoppers. The intensity of the emission peak at 528 nm ( $\lambda_{\text{ex}}$  = 375 nm) expressed as the ratio  $I_0/I$ , where  $I_0$  is the emission intensity of photocatalyst at 528 nm in the absence of a quencher and  $I$  is the observed intensity, as a function of the quencher concentration was measured. Stern-Volmer plots for each component are given in the Supplementary Figures below.



**Figure S4** The fluorescence emission spectra of excited  $\text{fac-Ir}^{\text{III}}(\text{ppy})_3$  with different concentration of **2** in NMP (excitation wavelength: 375 nm).



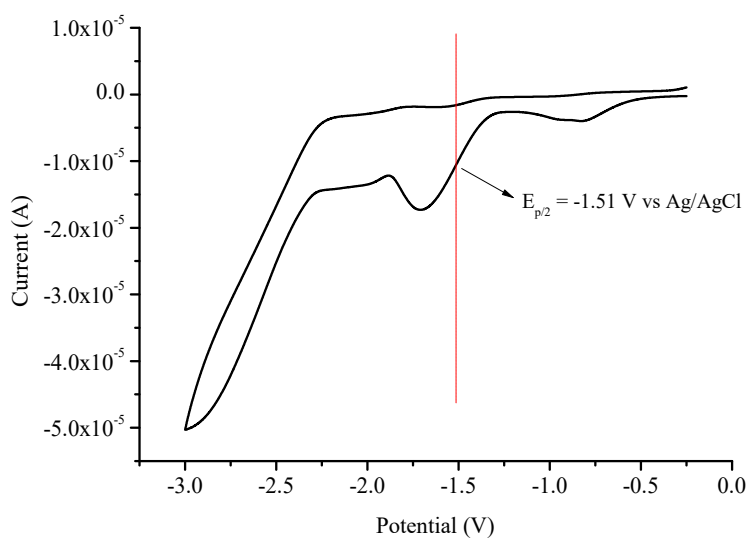
**Figure S5** The fluorescence emission spectra of excited  $\text{fac-Ir}^{\text{III}}(\text{ppy})_3$  with different concentration of **1a** in NMP (excitation wavelength: 375 nm).



**Figure S6** Stern-Volmer fluorescence quenching plot.

### 6.3 Cyclic Voltammetry Analysis

Electrochemical measurements were performed on a CHI730E electrochemical analyzer, using a standard three-electrode setup with a glassy carbon working electrode (2 mm diameter), a platinum wire counter electrode, and a non-aqueous Ag/Ag<sup>+</sup> reference electrode (degassed THF containing 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>). Samples were prepared with 0.01 mmol of substrate in 10 mL of 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in dry, degassed THF, with a scan rate of 0.05 V/s. Solutions were kept under positive pressure of nitrogen during the measurements. Data was analyzed using Origin. The obtained value for reagents **2** was referenced to Ag/Ag<sup>+</sup> and converted to SCE by subtracting 0.03 V.<sup>5</sup>

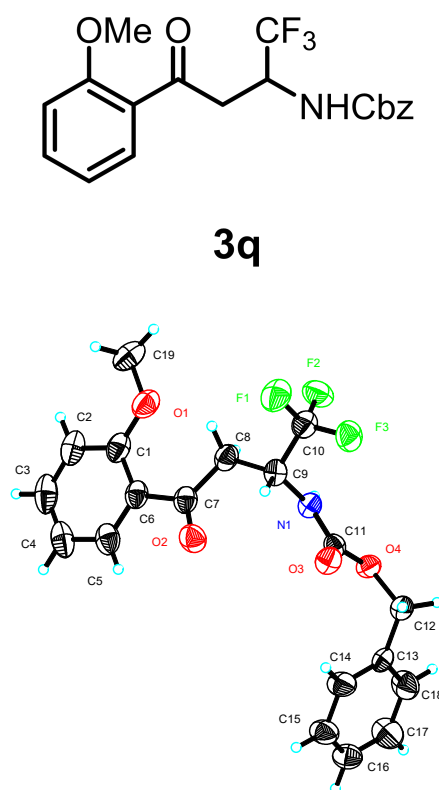


$$E_{p/2} = -1.54 \text{ V vs (SCE)}$$

**Figure S7** Cyclic voltammetry of **2** in THF from 0 V to -3.0 V.

## 7. ORTEP Drawing of the X-Ray Crystallographic Structure of Product **3q**

The crystal was obtained *via* evaporation of its hexanes/dichloromethane solvent mixture. Single-crystal diffraction data for compounds **3q** were collected on a XtaLAB Synergy, Dualflex, and HyPix diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) at 170 K, and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the nonhydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on  $F^2$ . The weighted  $R$  factor,  $wR$  and goodness-of-fit  $S$  values were obtained based on  $F^2$ . The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.



**Figure S8.** The Ellipsoids are Shown at 50% Probability Levels.

The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition number CCDC 2472368. This data can be obtained free of charge from the Cambridge Crystallographic Date Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

**Table S4. Crystal data and structure refinement for 3q**

Identification code	3q
Empirical formula	C <sub>19</sub> H <sub>18</sub> F <sub>3</sub> NO <sub>4</sub>
Formula weight	381.34
Temperature	169.99(10) K
Crystal system	monoclinic
Space group	P 2 <sub>1</sub> /n
Unit cell dimensions	a = 14.1227(12) Å    α = 90°. b = 4.9556(4) Å    β = 96.714(9)°. c = 25.231(3) Å    γ = 90°.
Volume	1753.7(3) Å <sup>3</sup>
Z	4
Density (calculated)	1.444 g/cm <sup>3</sup>
Absorption coefficient	1.050 mm <sup>-1</sup>
F(000)	792.0
Crystal size	0.15 × 0.13 × 0.1 mm <sup>3</sup>
Radiation	Cu Kα (λ = 1.54184)
Theta range for data collection	6.852 to 147.342°
Index ranges	-17 ≤ h ≤ 17, -5 ≤ k ≤ 4, -30 ≤ l ≤ 27
Reflections collected	6098
Independent reflections	3416 [R <sub>int</sub> = 0.0822, R <sub>sigma</sub> = 0.1027]
Data/restraints/parameters	3416 / 0 / 249
Goodness-of-fit on F <sup>2</sup>	1.004
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0746, wR <sub>2</sub> = 0.1786
Final R indexes [all data]	R <sub>1</sub> = 0.1106, wR <sub>2</sub> = 0.2283
Largest diff. peak/hole	0.27/-0.32 e Å <sup>-3</sup>

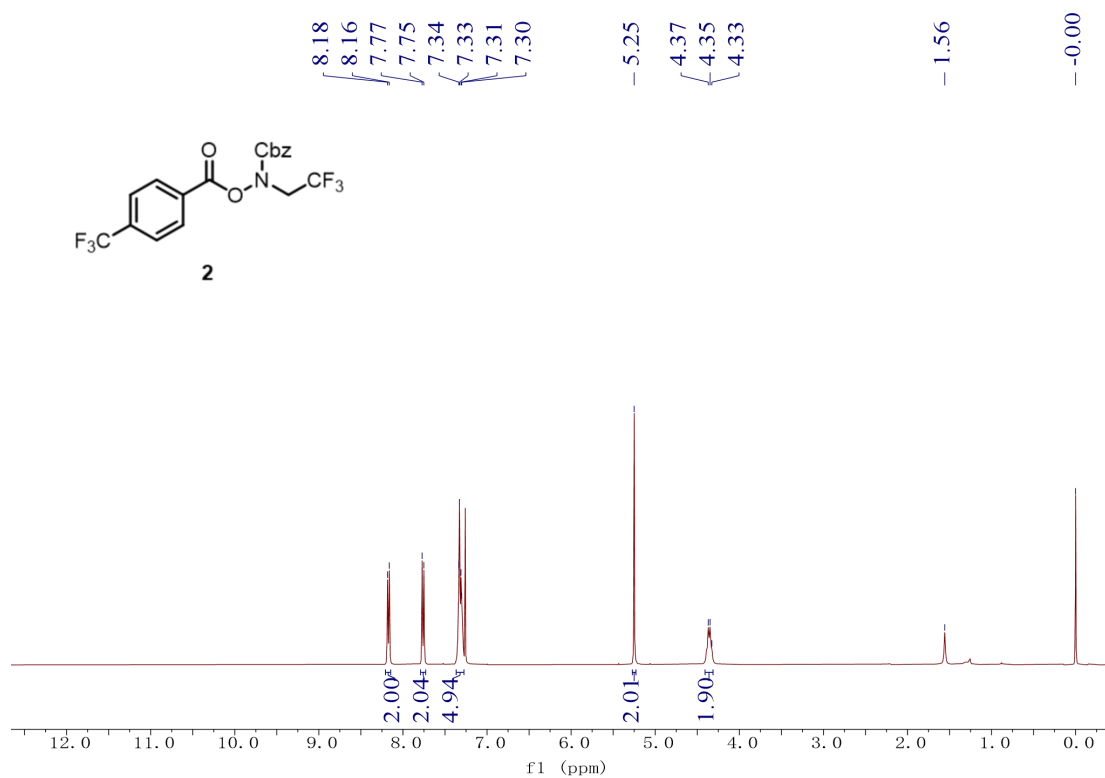
## 8. References

1. Y. Jiang, Y. Liao, Y. Zhao, F. Pan, *Org. Lett.*, 2025, **27**, 1344–1349.
2. J. Wang, S. Liu, Y. Huang, X. H. Xu, F. L. Qing, *Chem. Commun.*, 2022, **58**, 1346-1349.
3. S. Liu, Y. Huang, J. Wang, F. L. Qing, X. H. Xu, *J. Am. Chem. Soc.*, 2022, **144**, 1962-1970.
4. M. Gil-Ordóñez, A. Gallego-Gamo, P. Sarró, R. Pleixats, C. Gimbert-Suriñach, A. Vallribera, A. Granados, *J. Org. Chem.*, 2025, **90**, 2500-2509.

5. H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett*, 2016, **27**, 714-723.

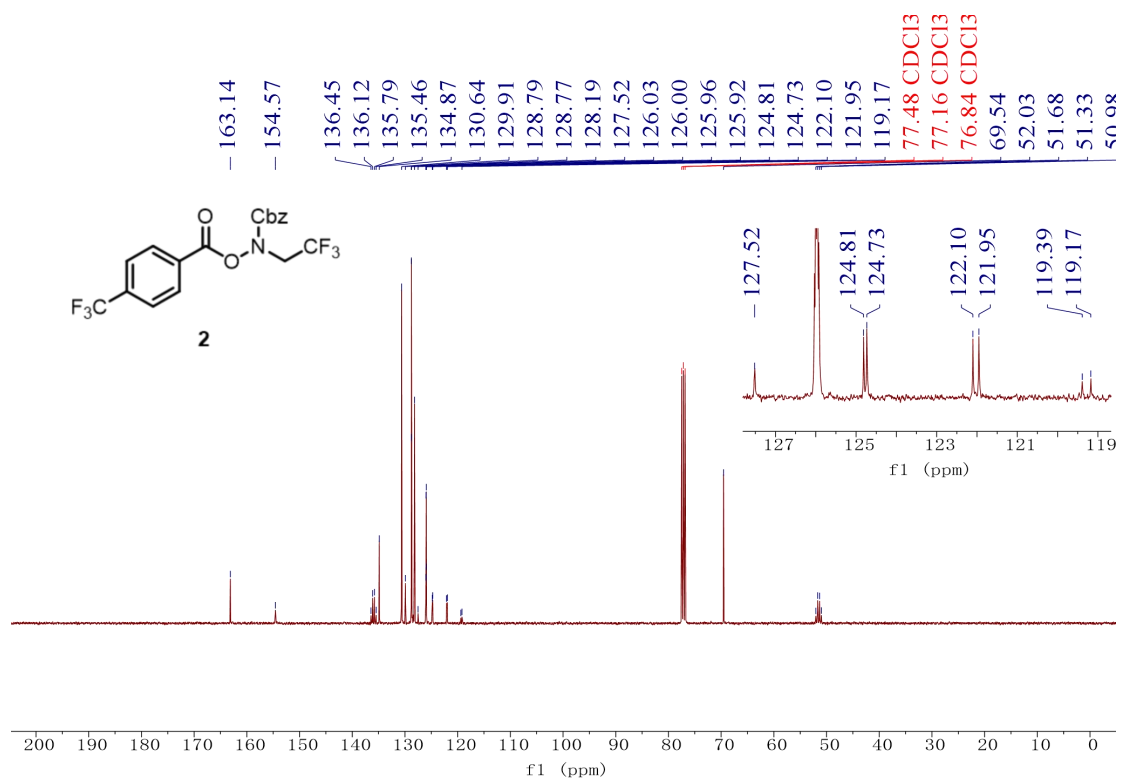
## 9. Copies of NMR Spectra for the Products

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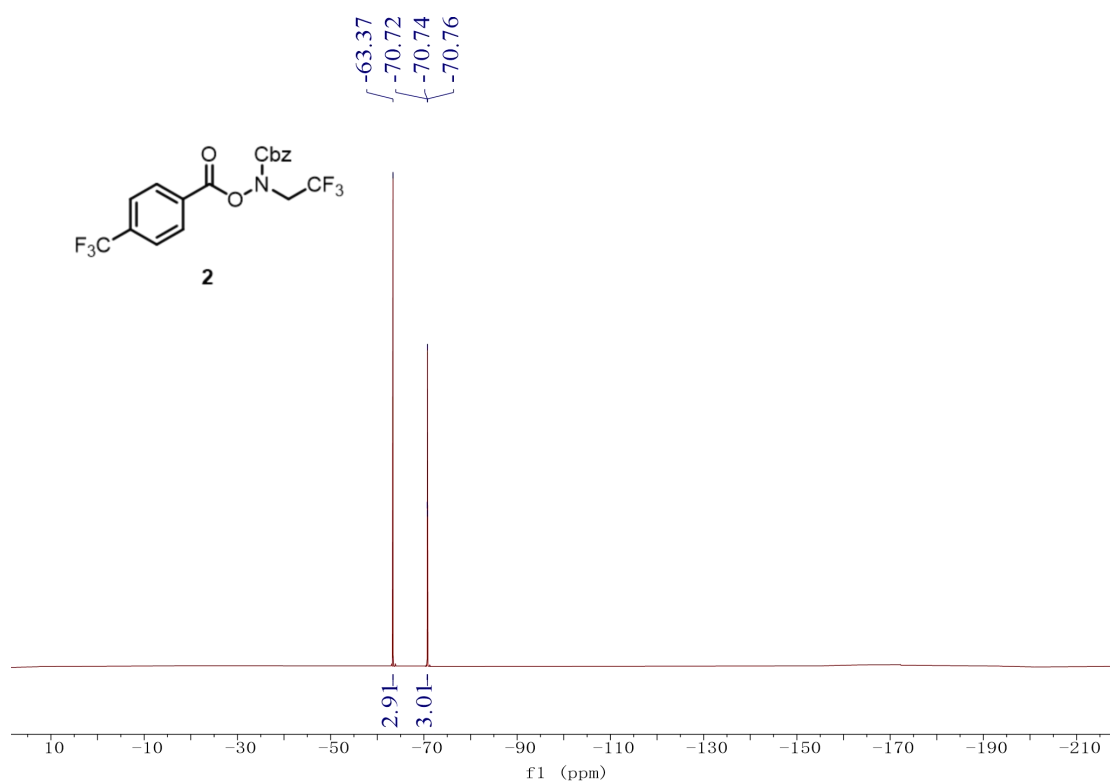


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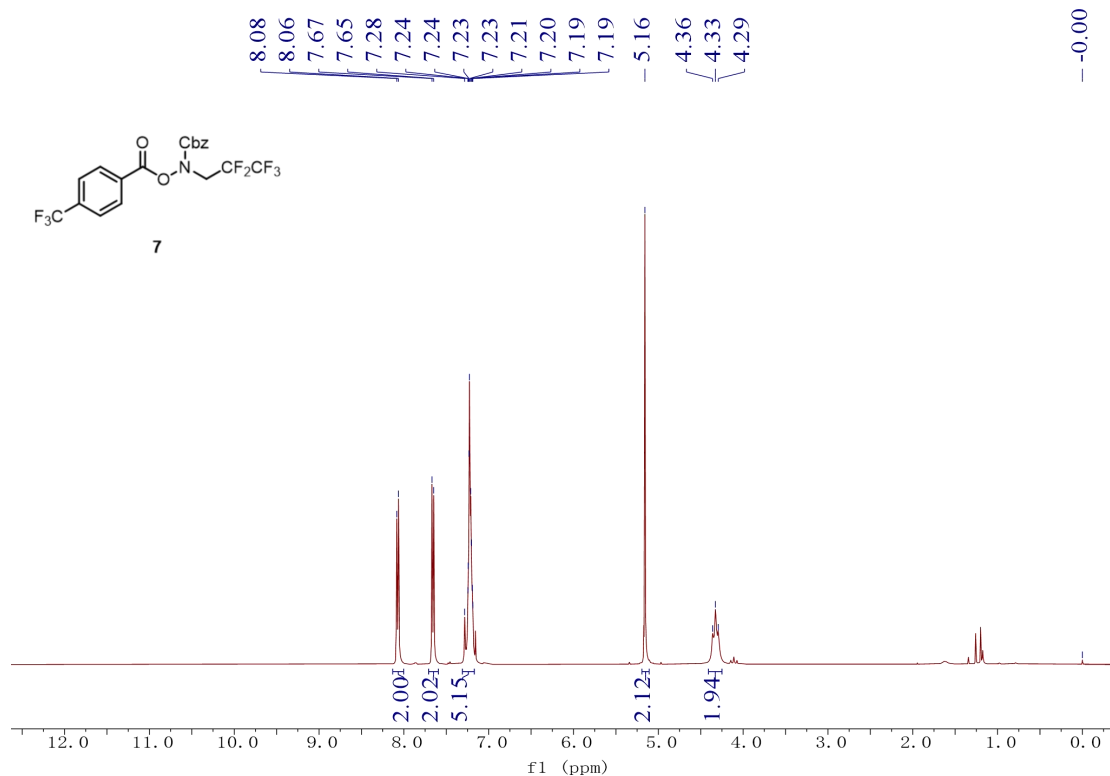




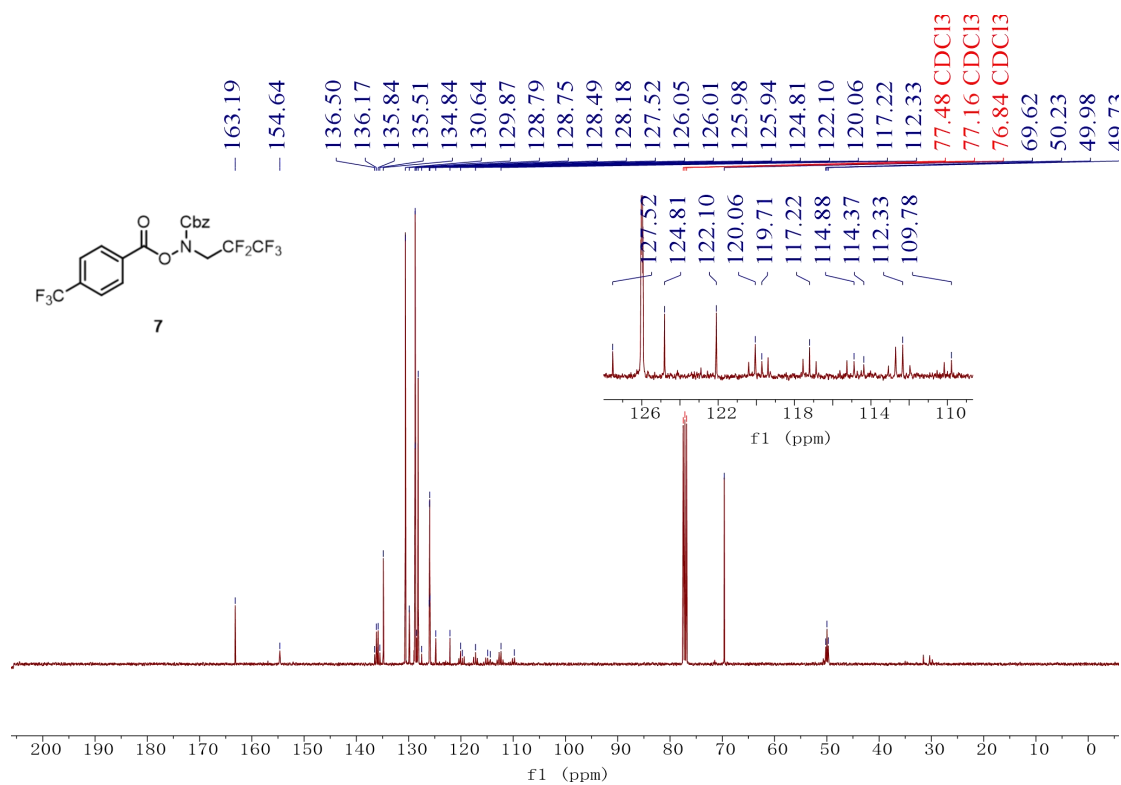
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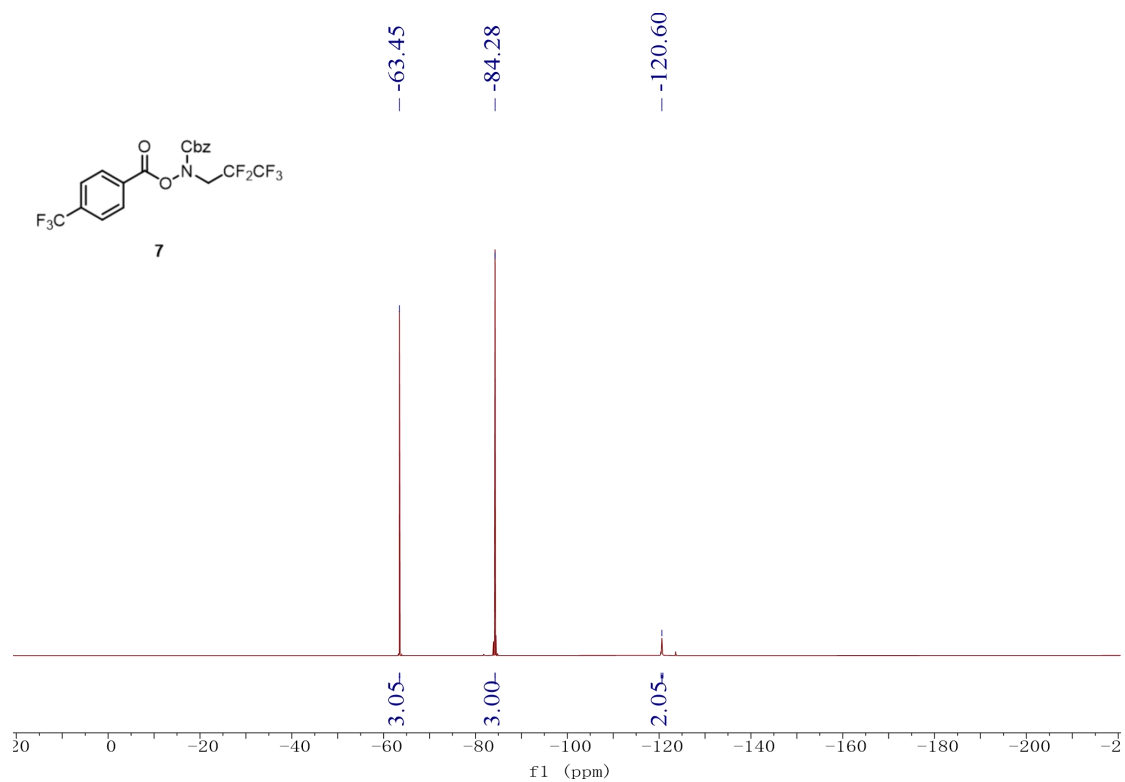
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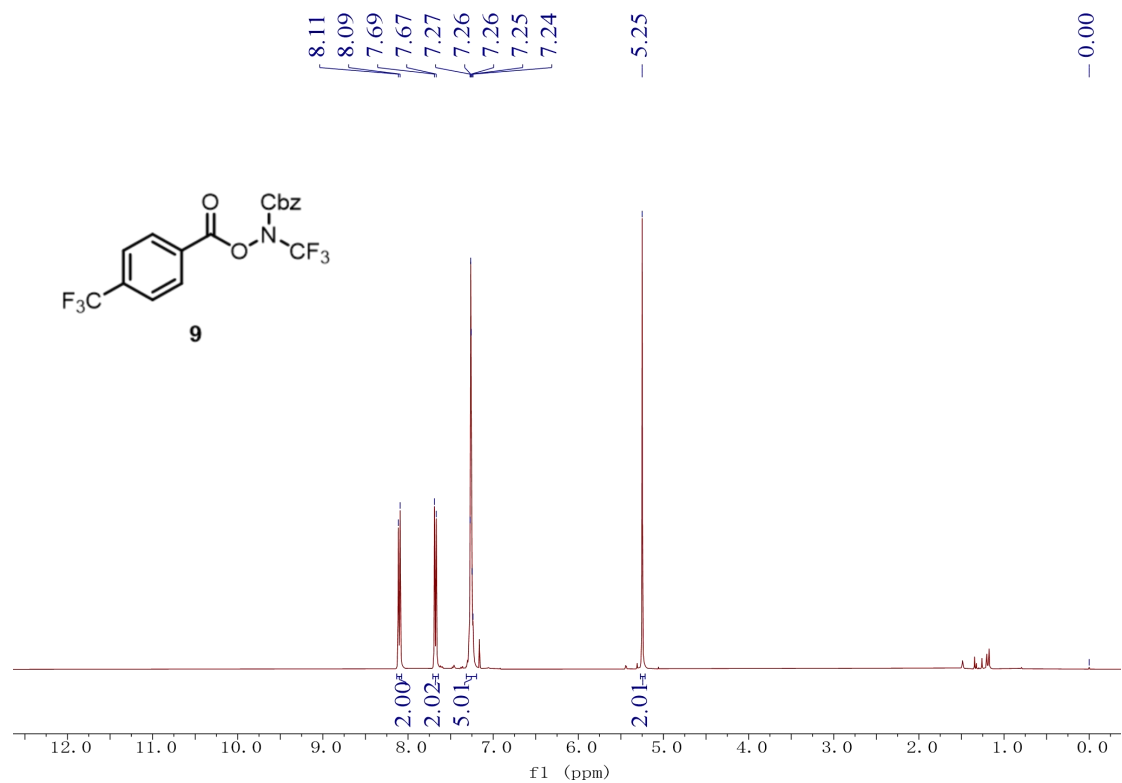
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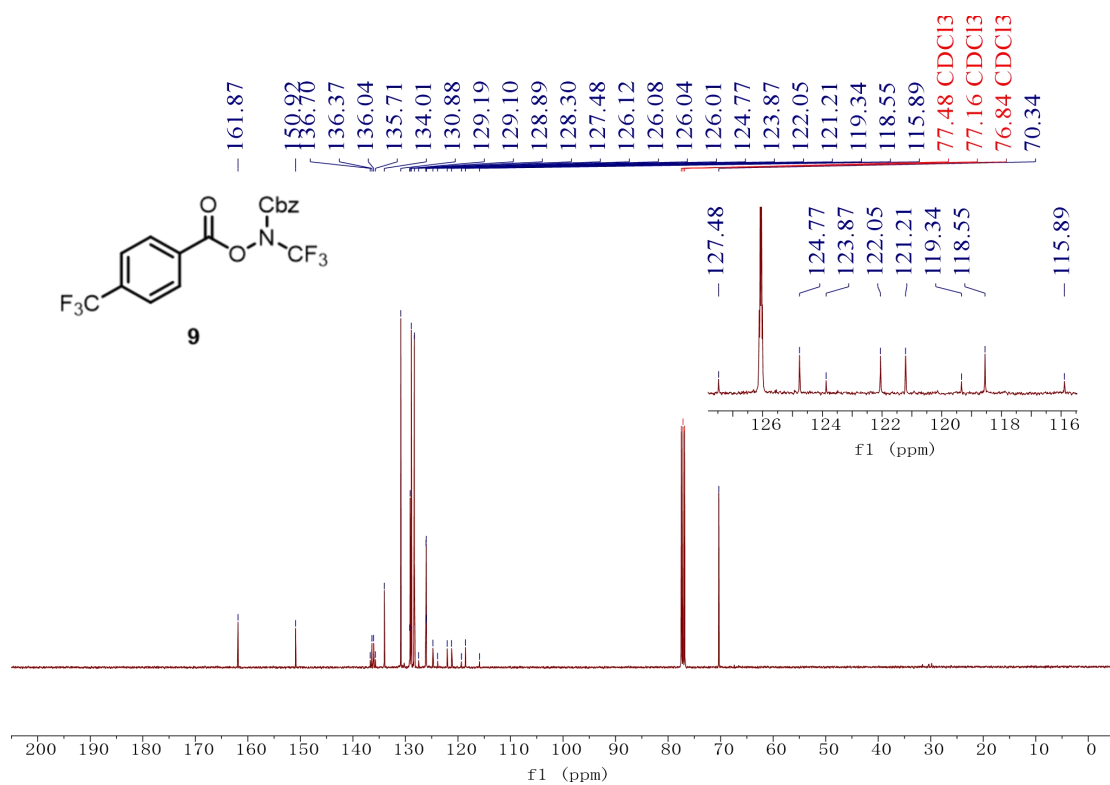
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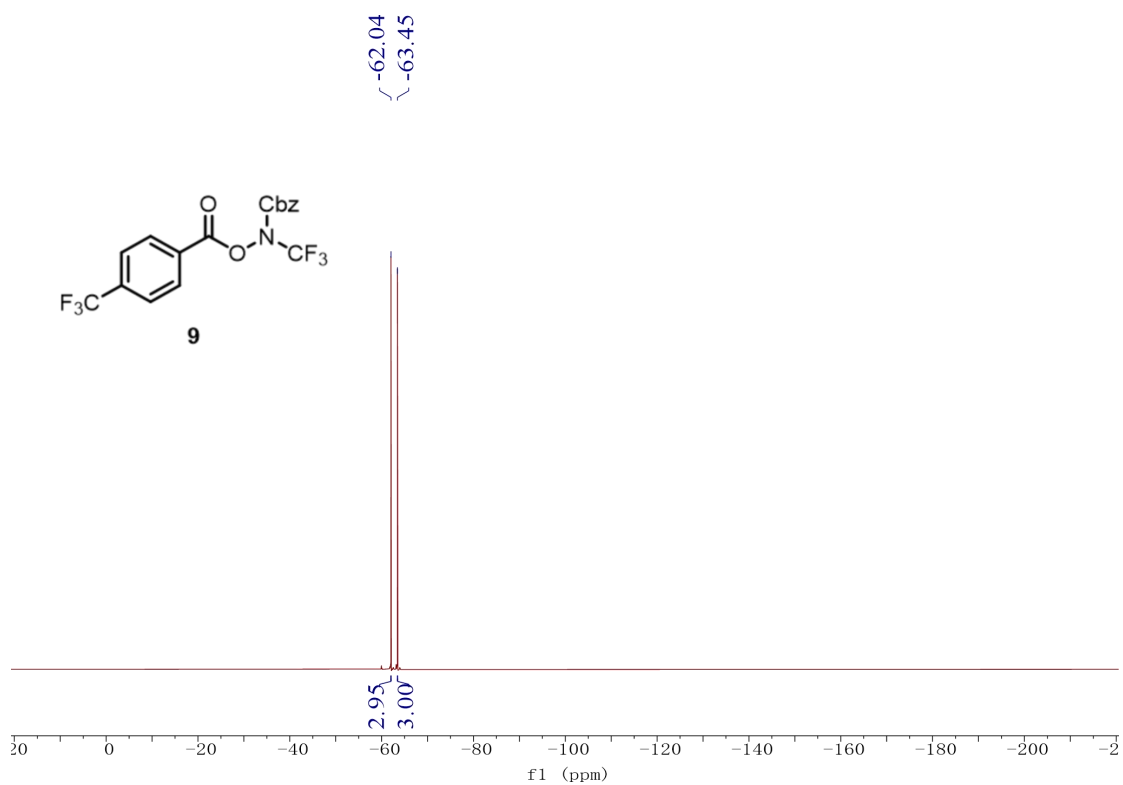
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$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



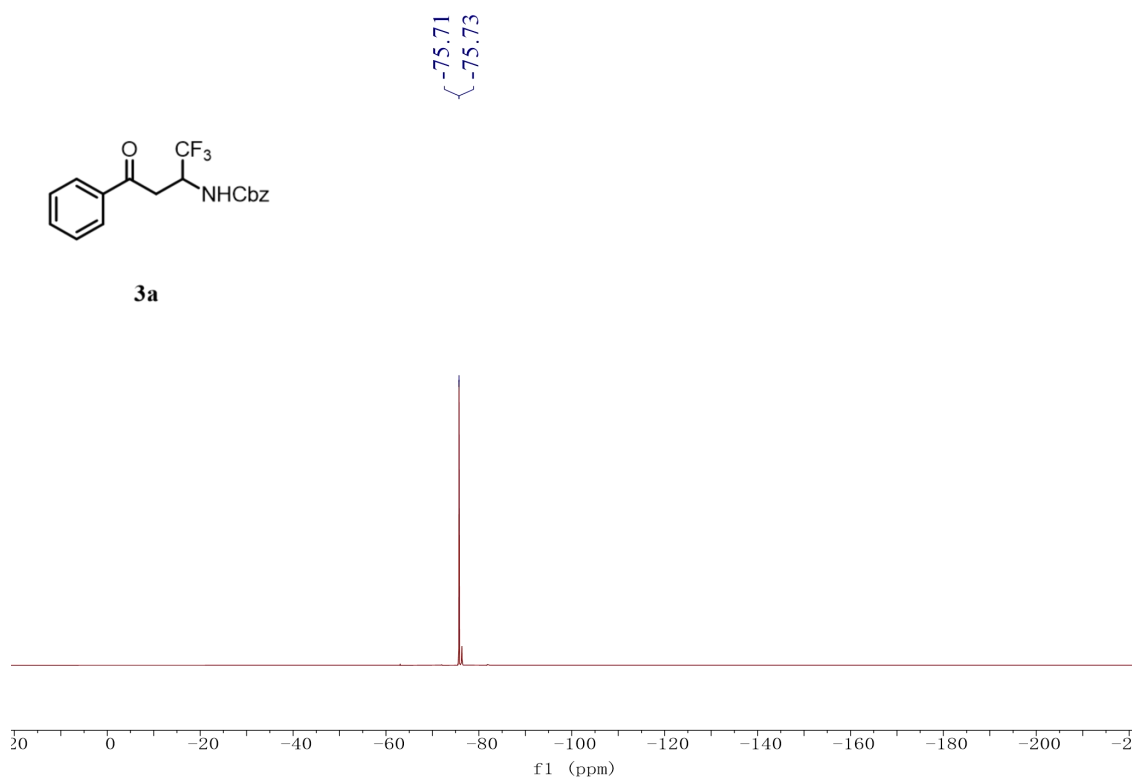
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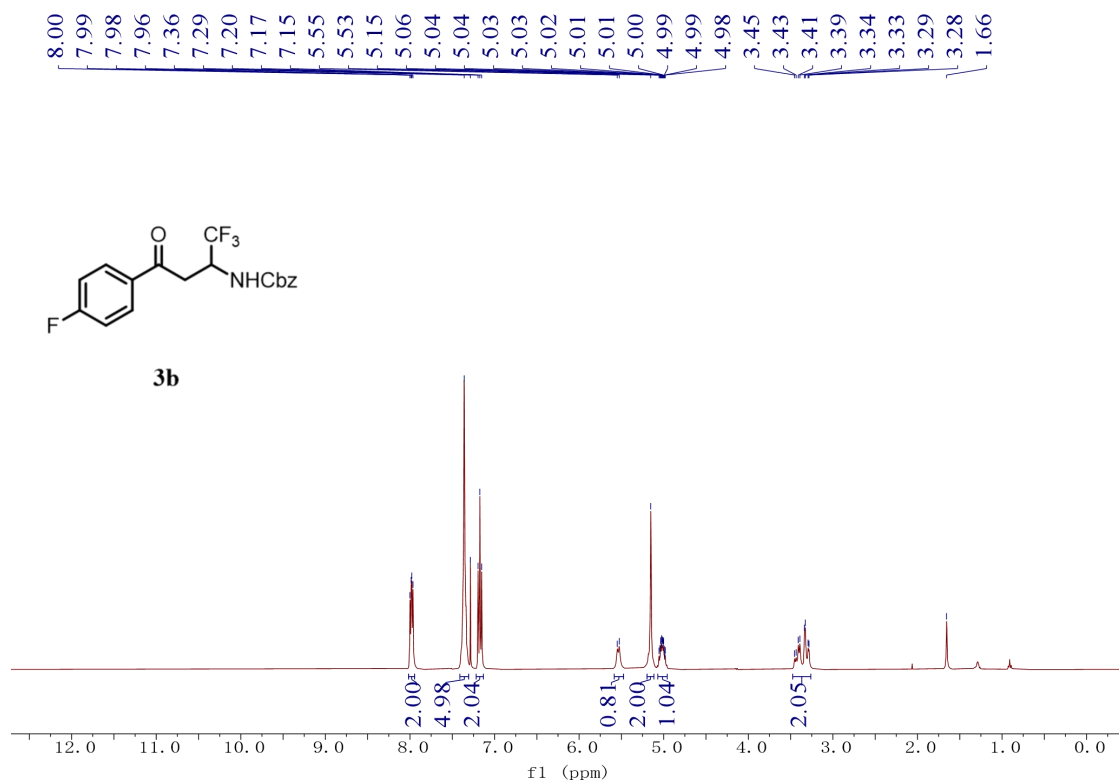
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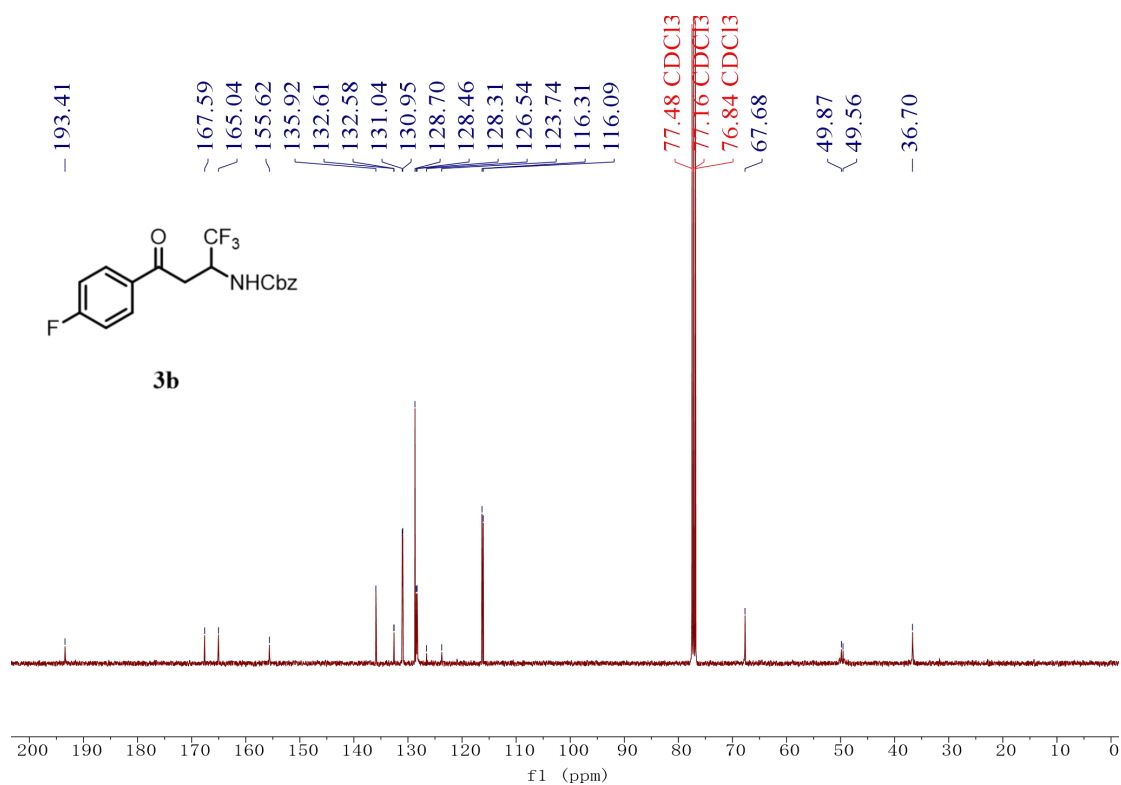
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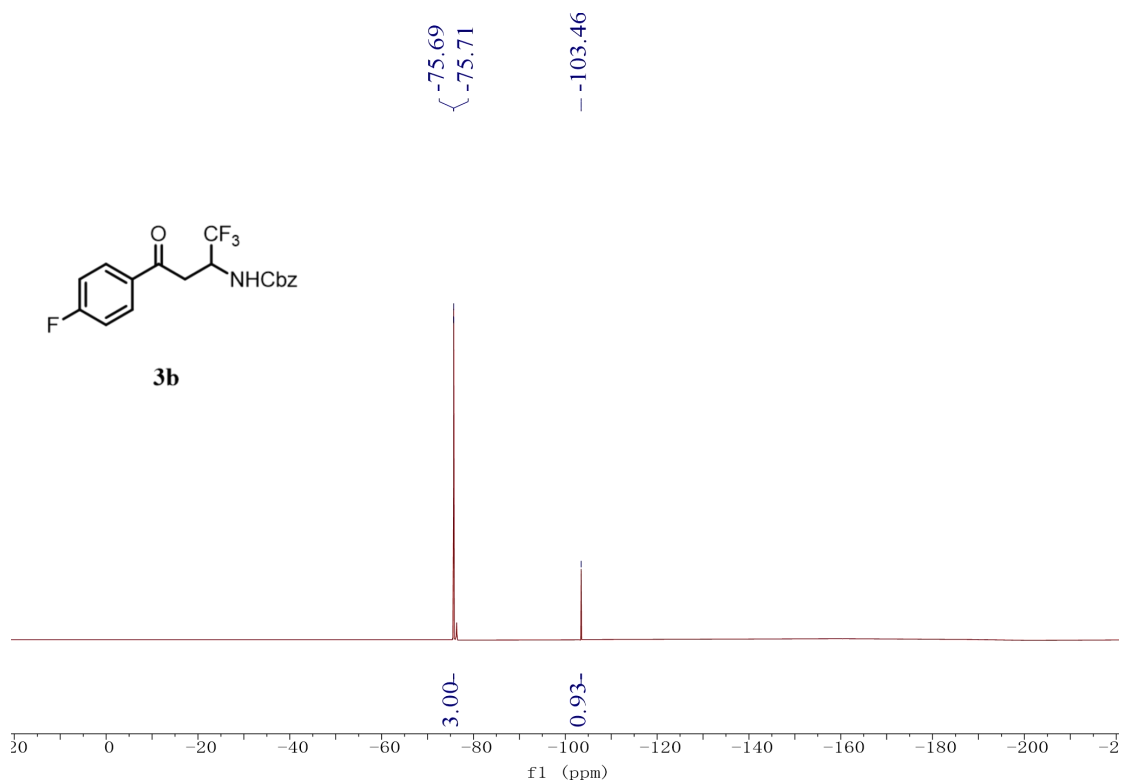
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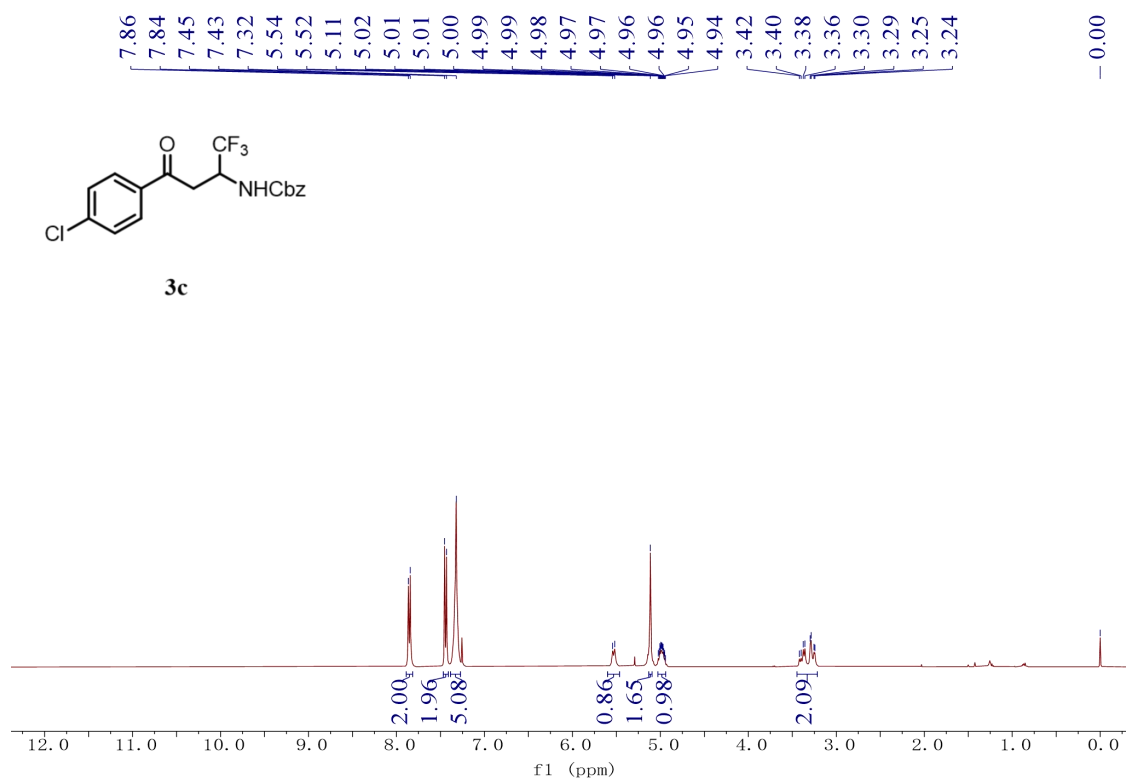
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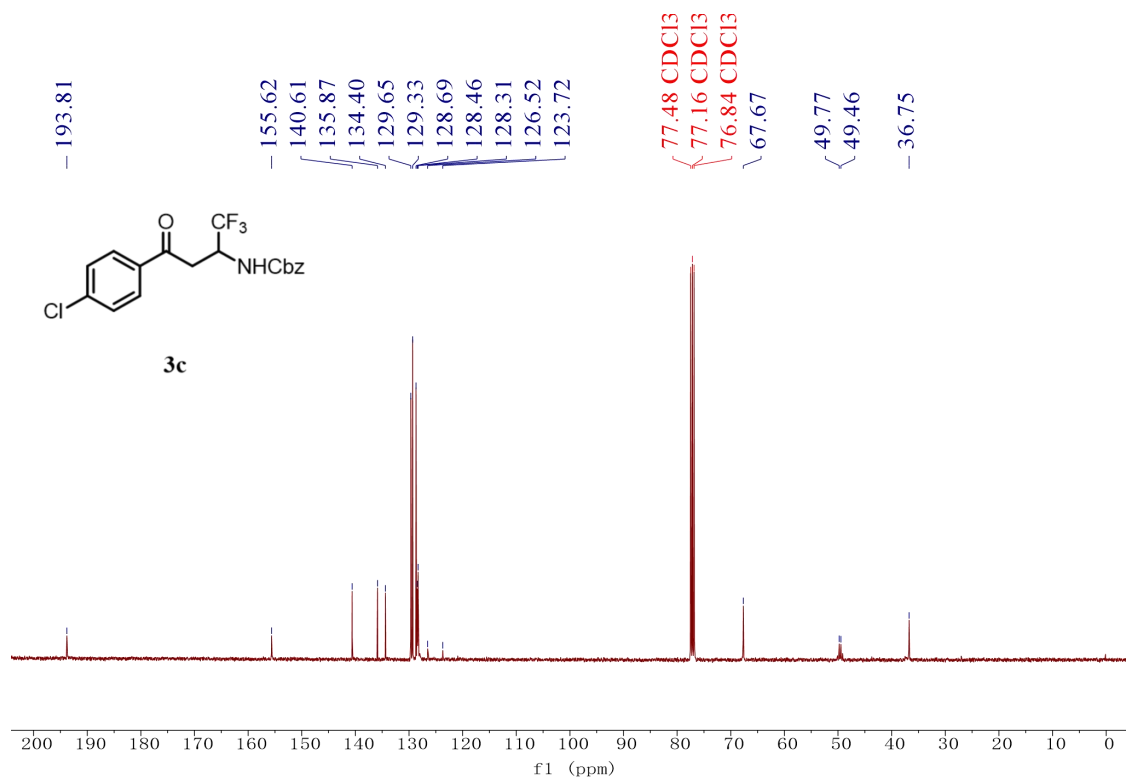
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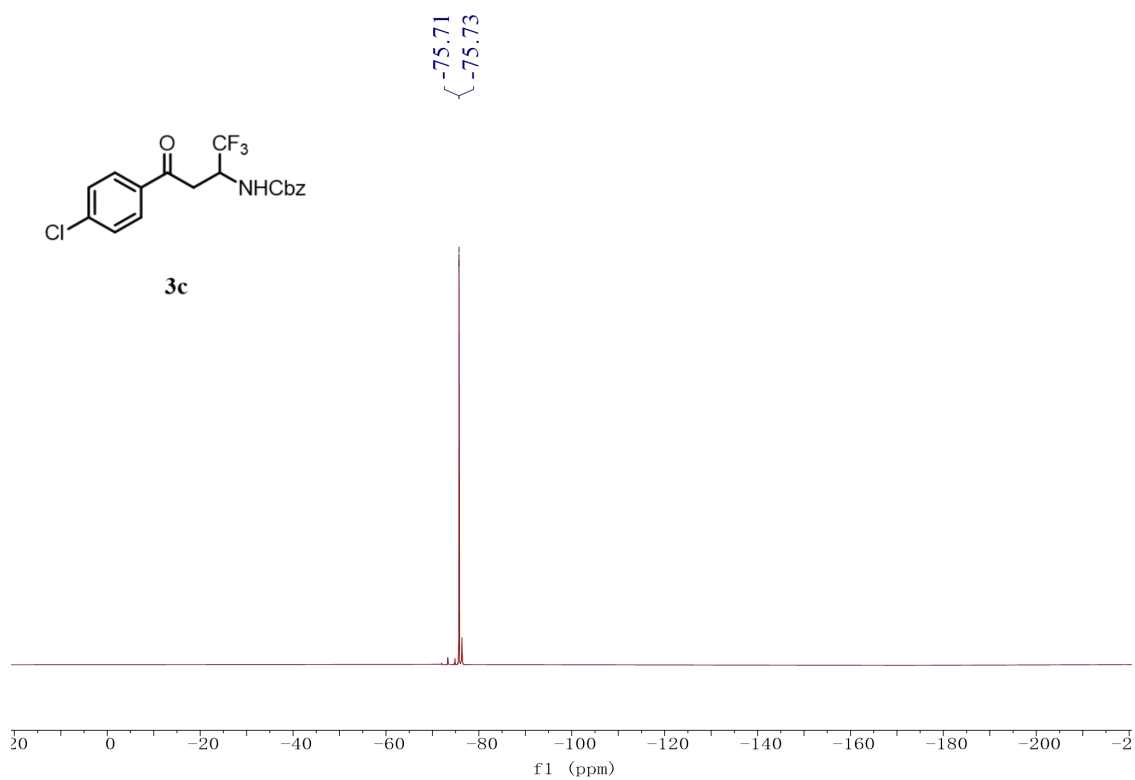


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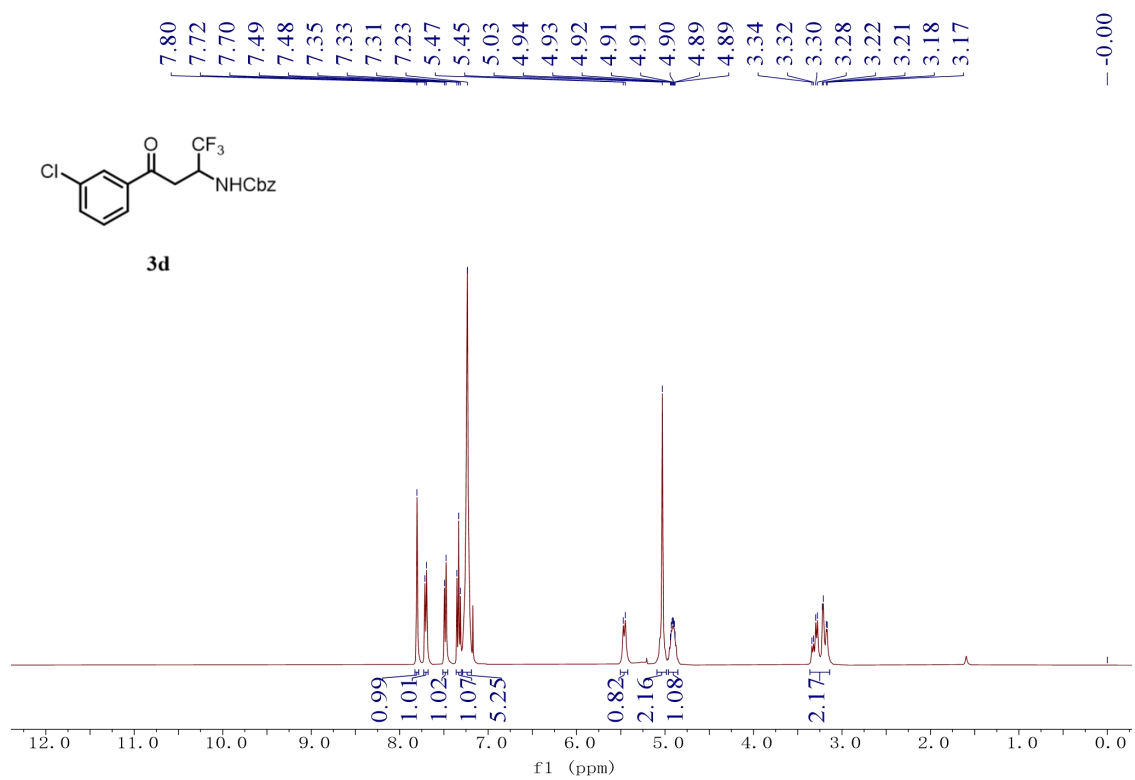




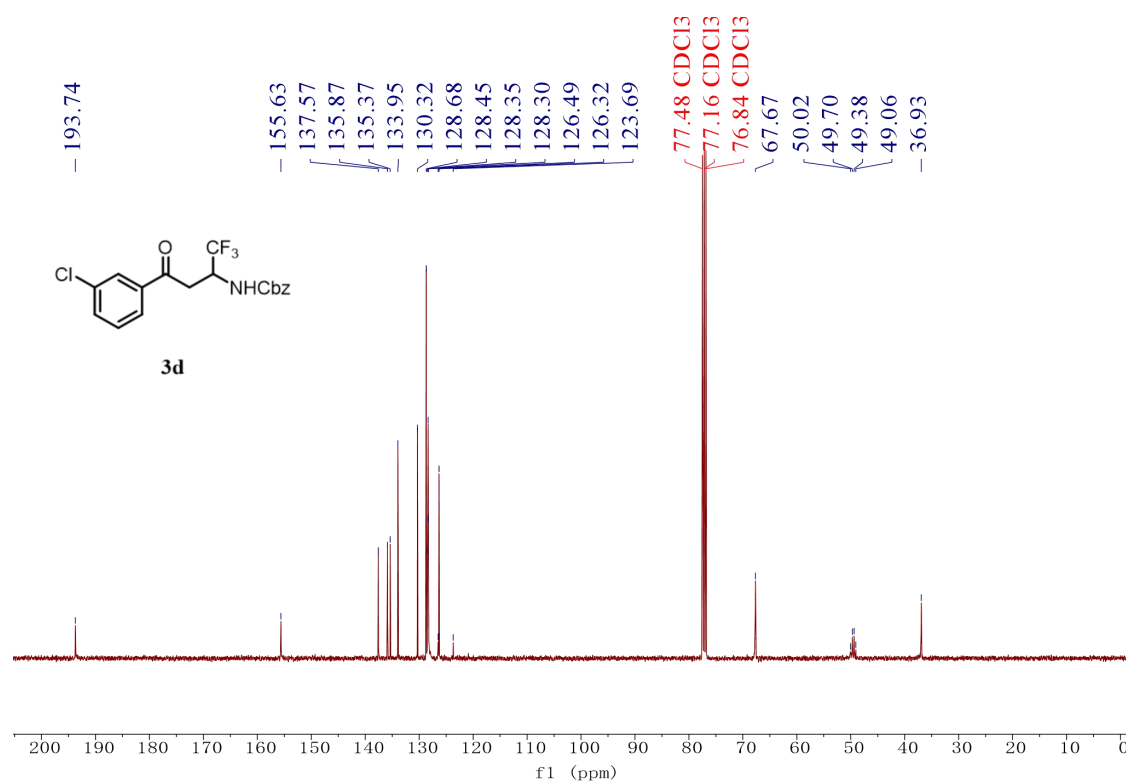
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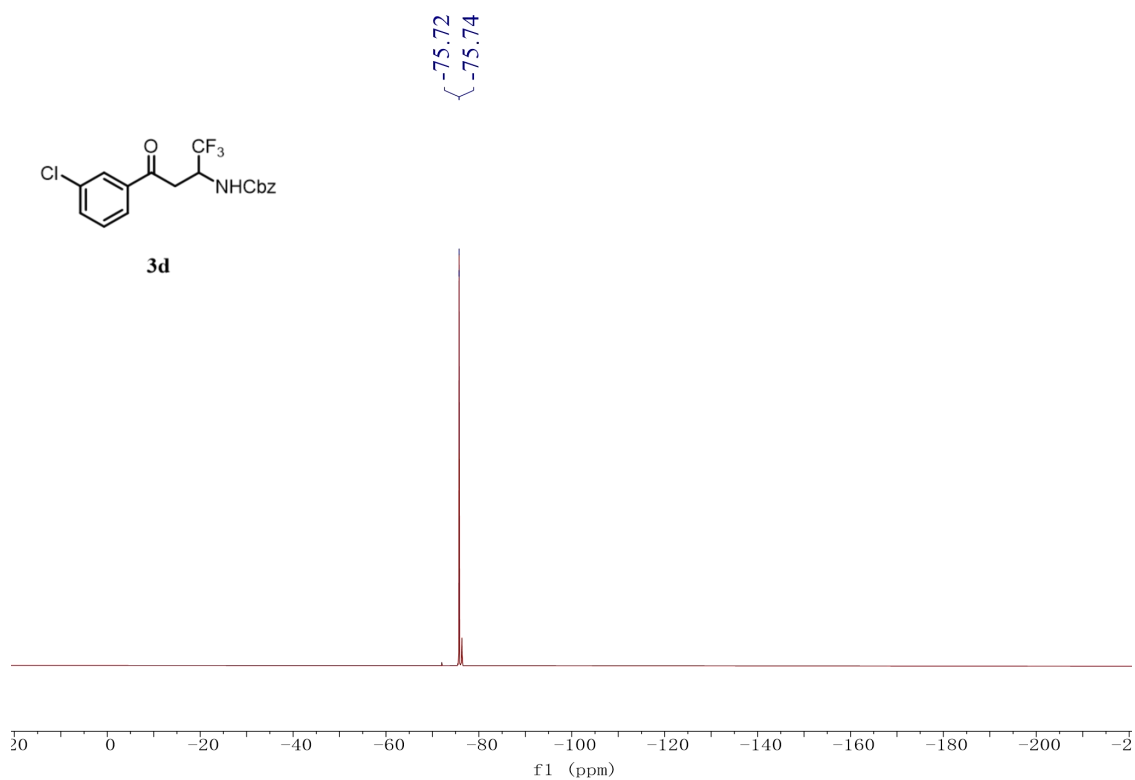
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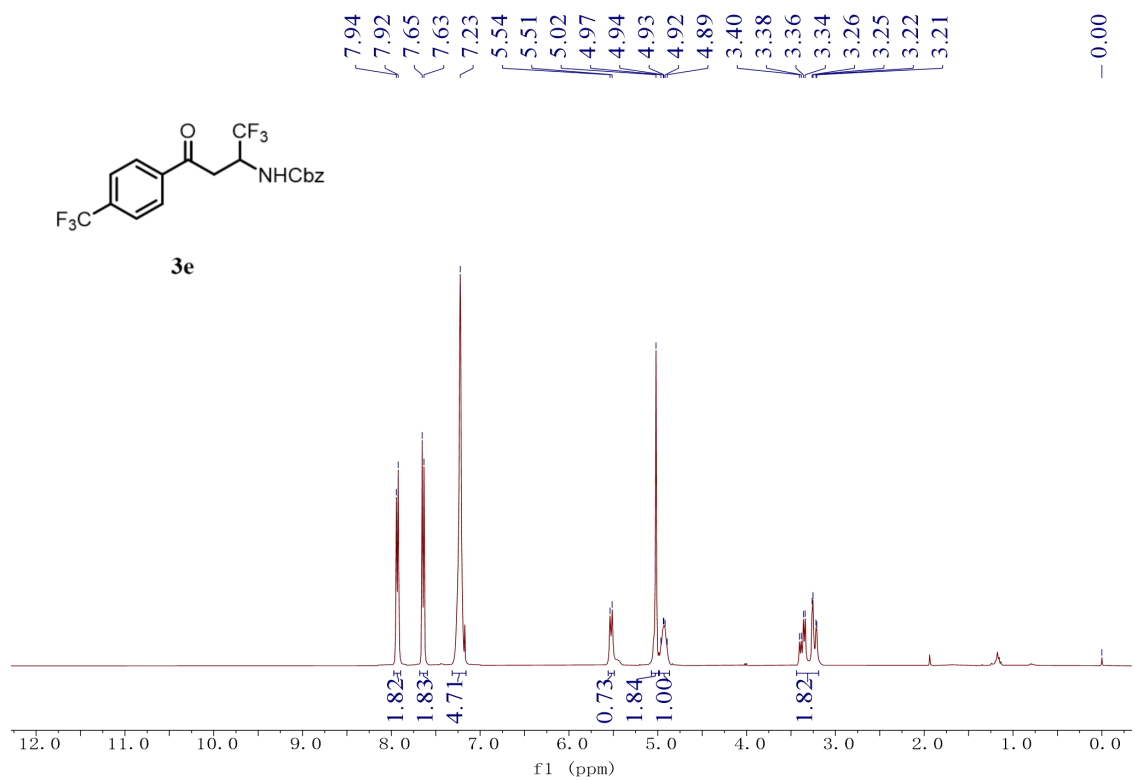
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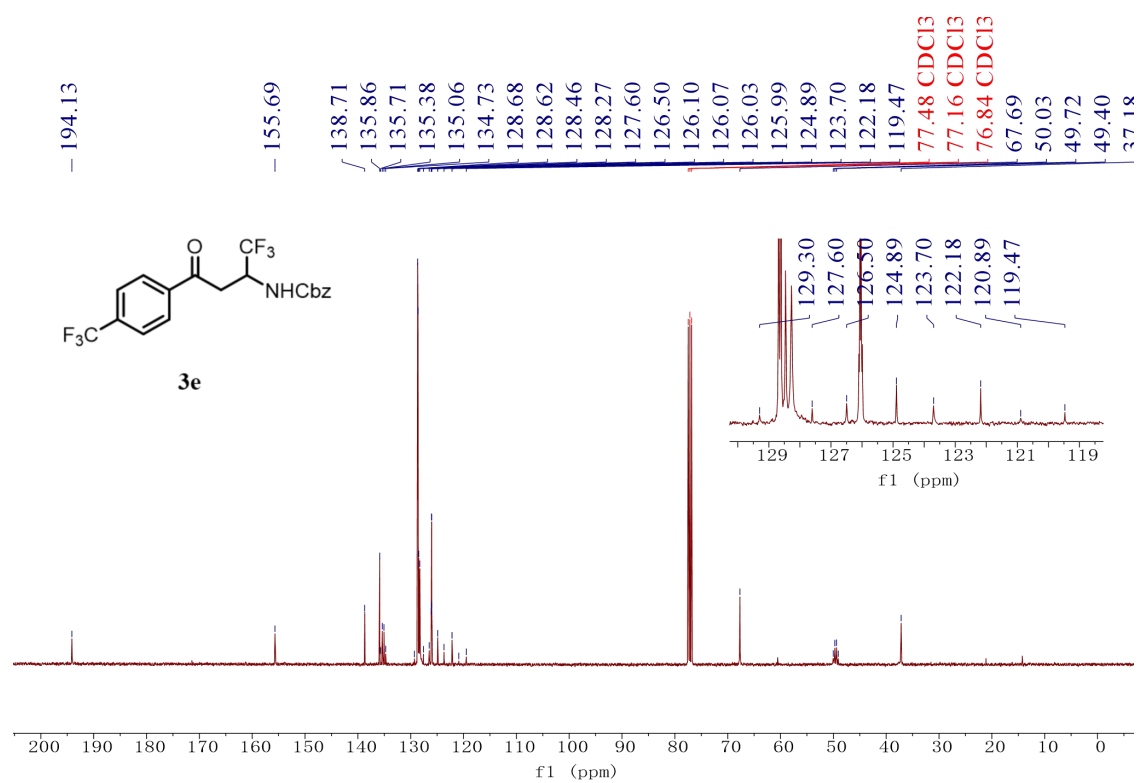
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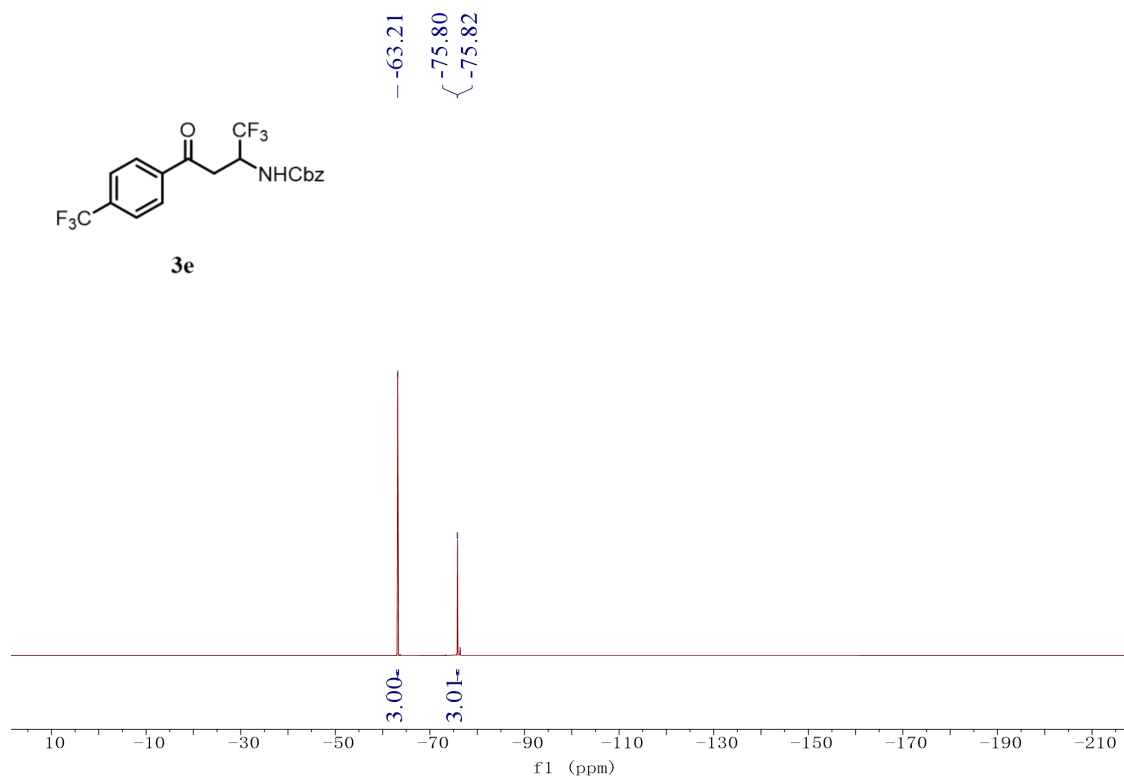
*<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)*



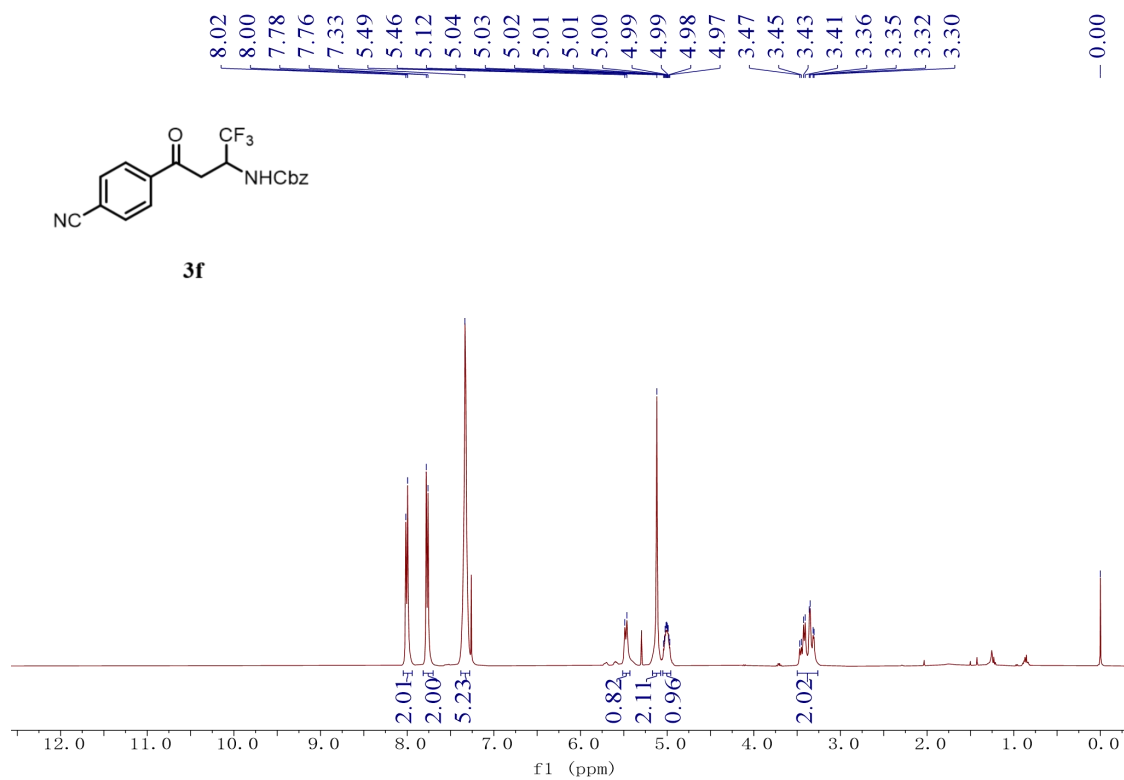
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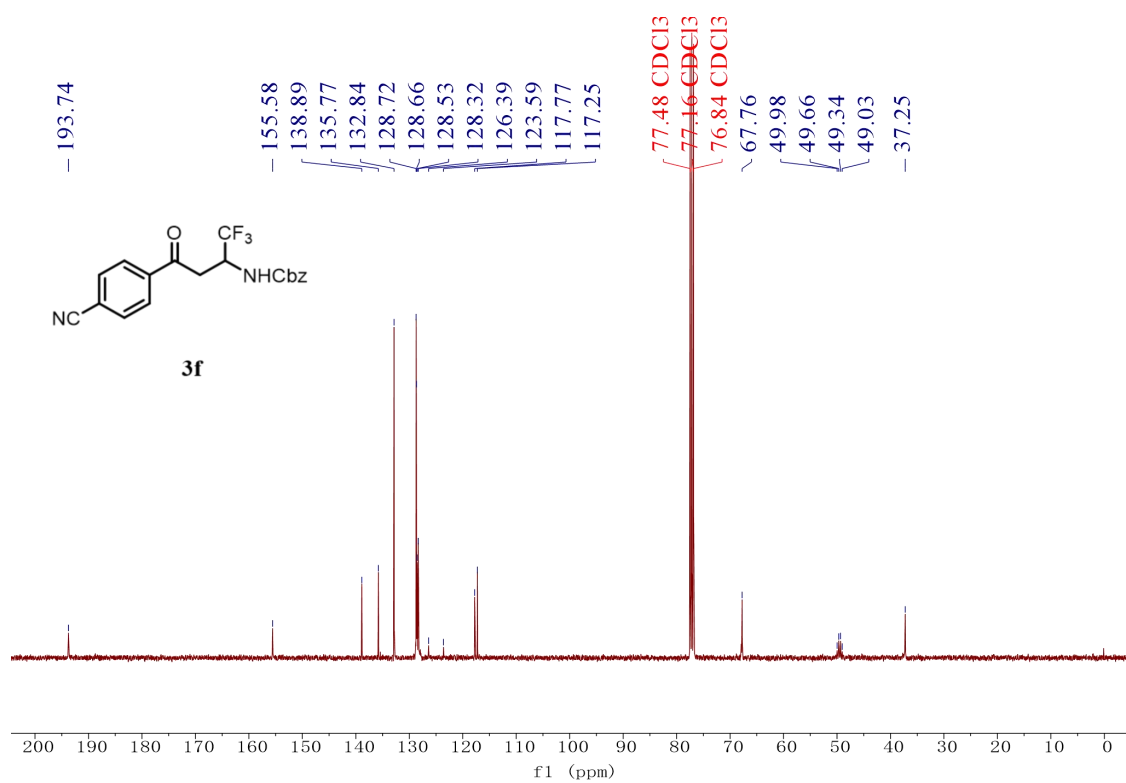
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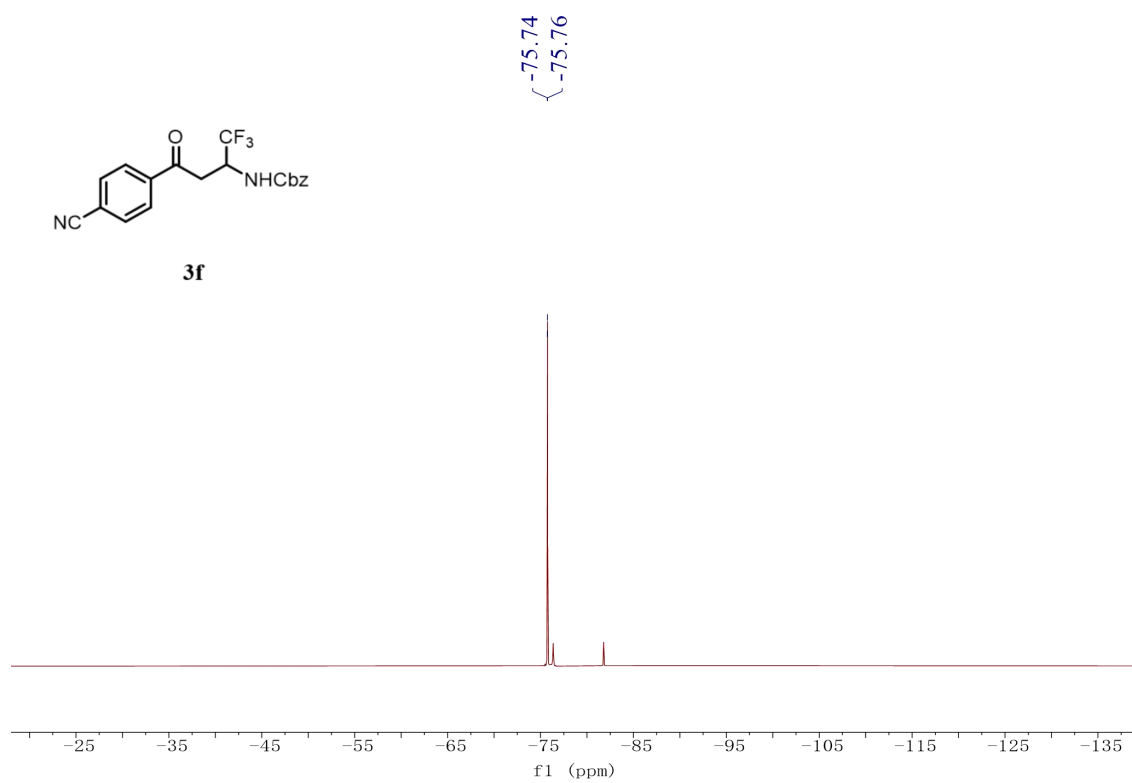
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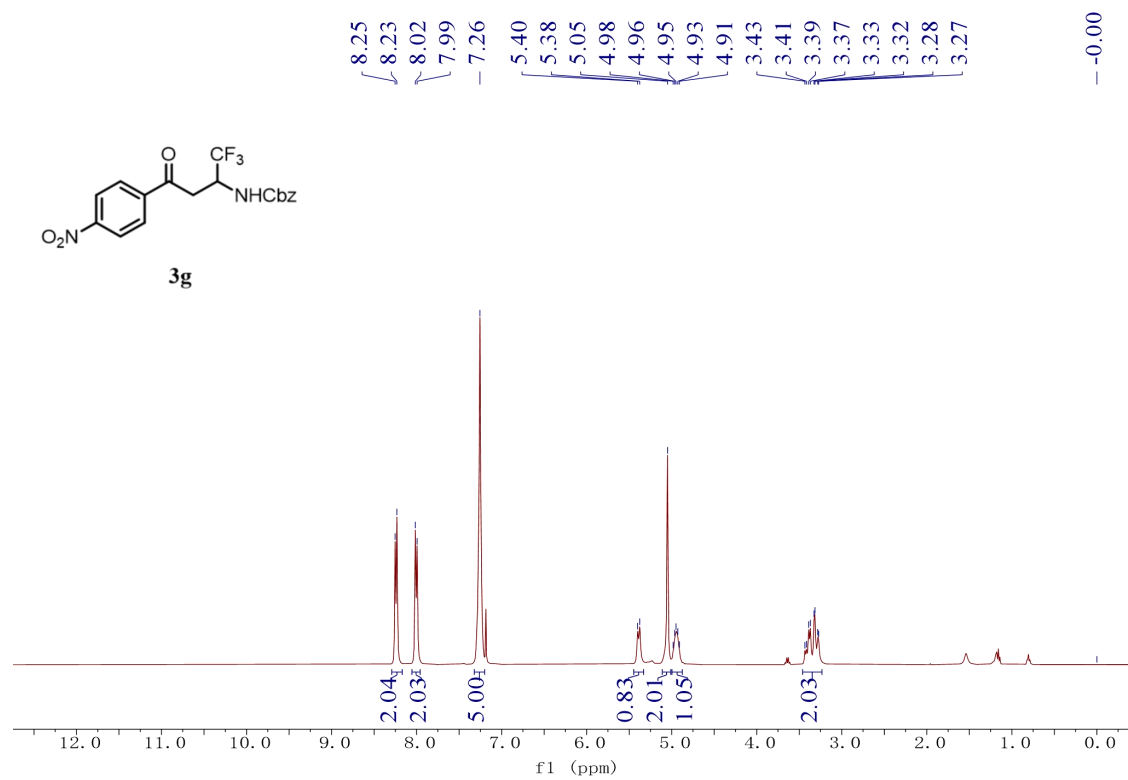
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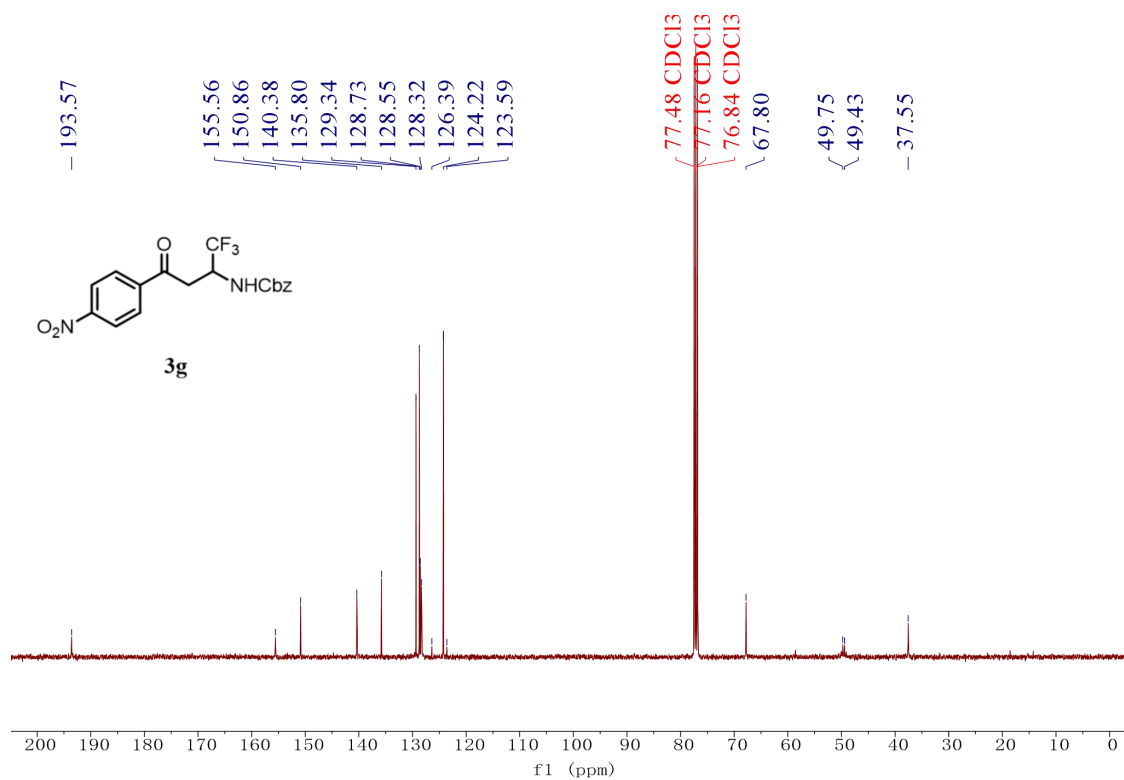
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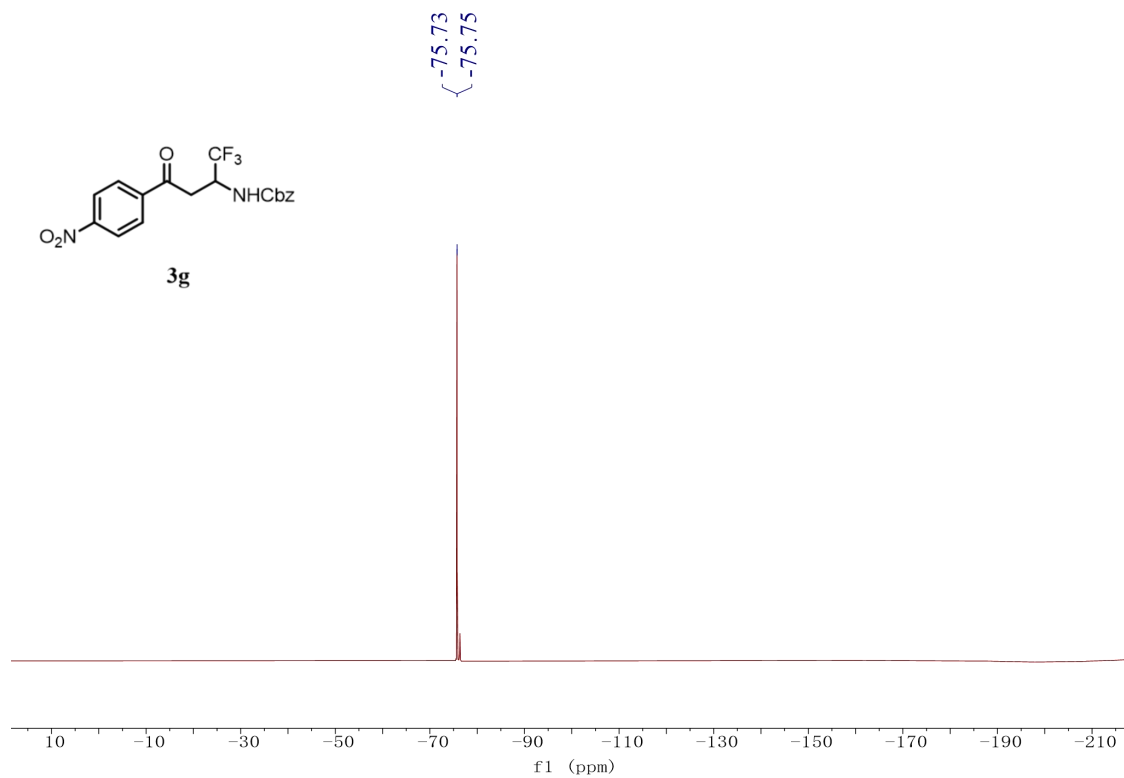
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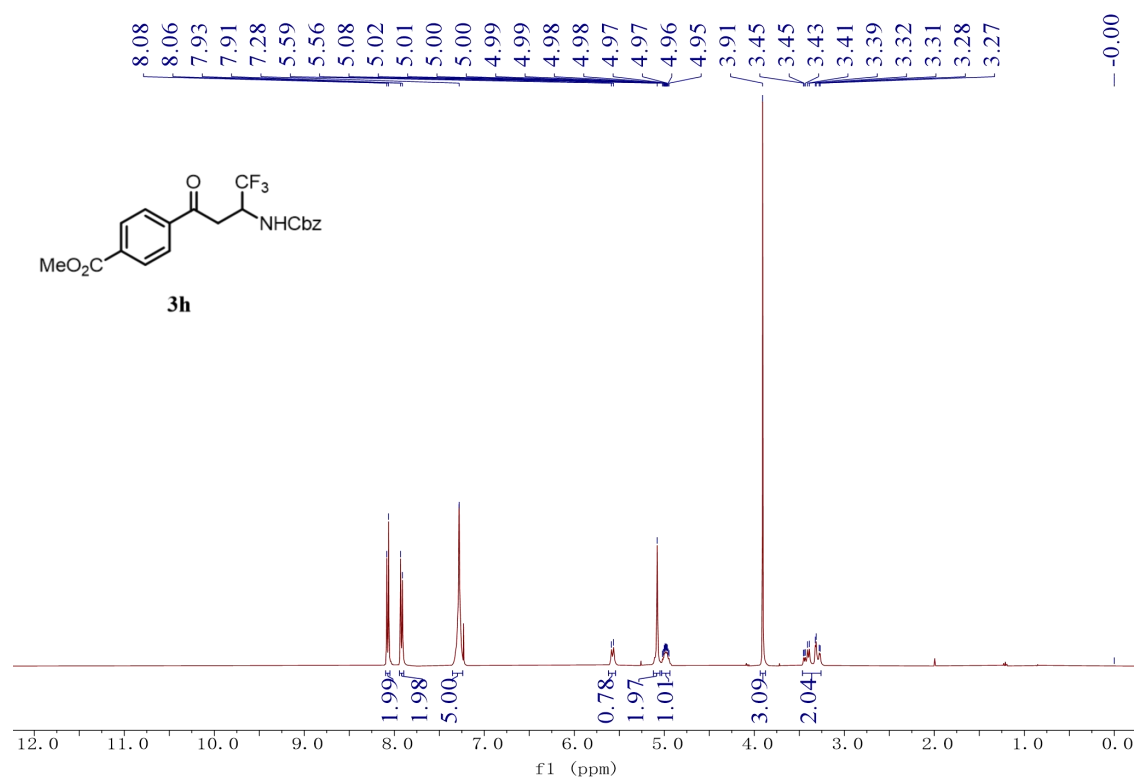


**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**

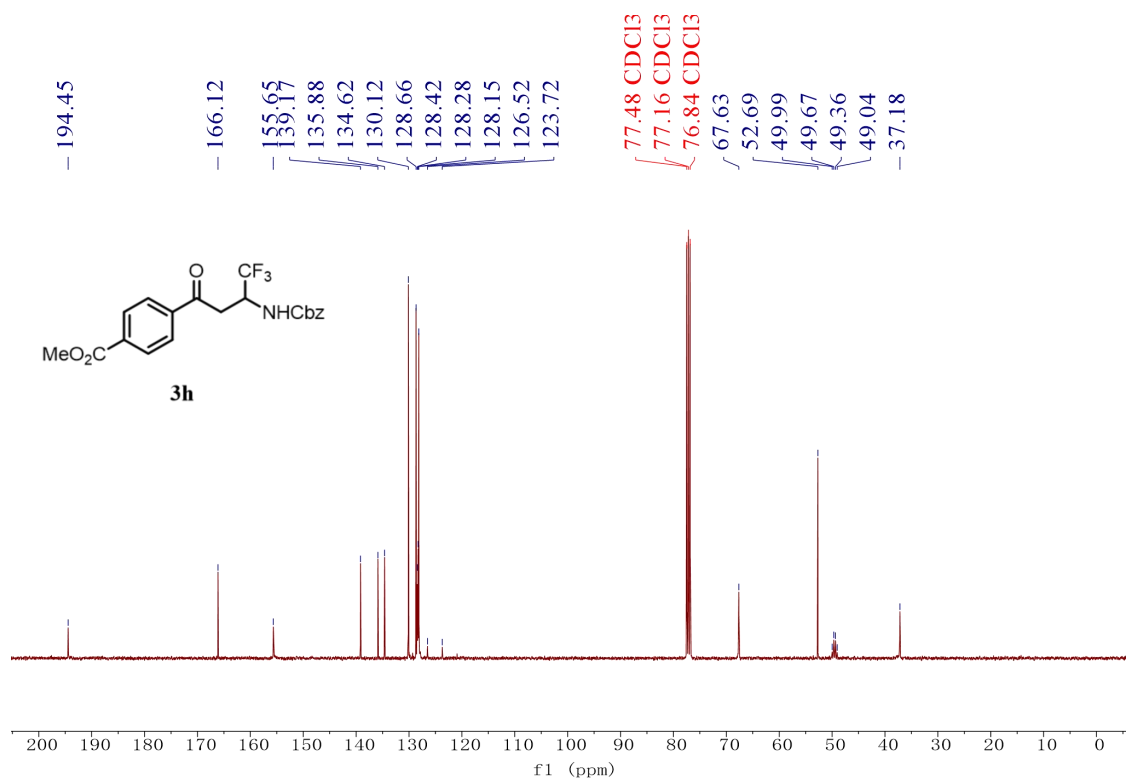




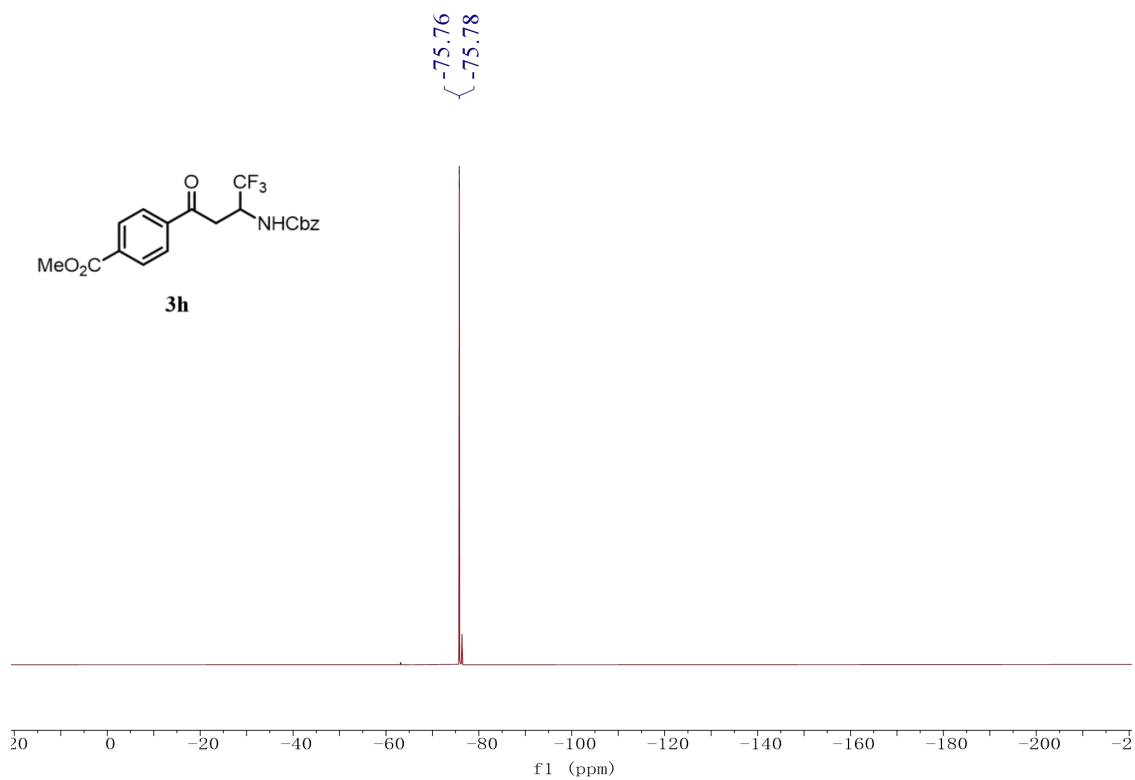
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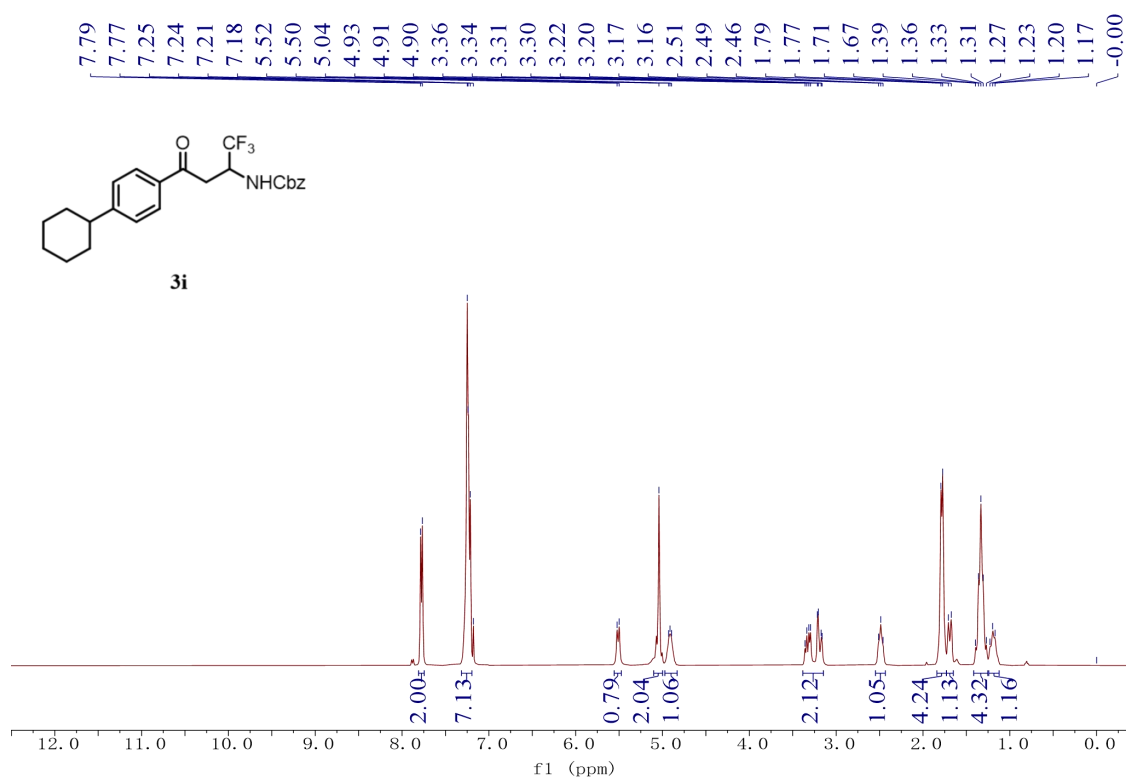
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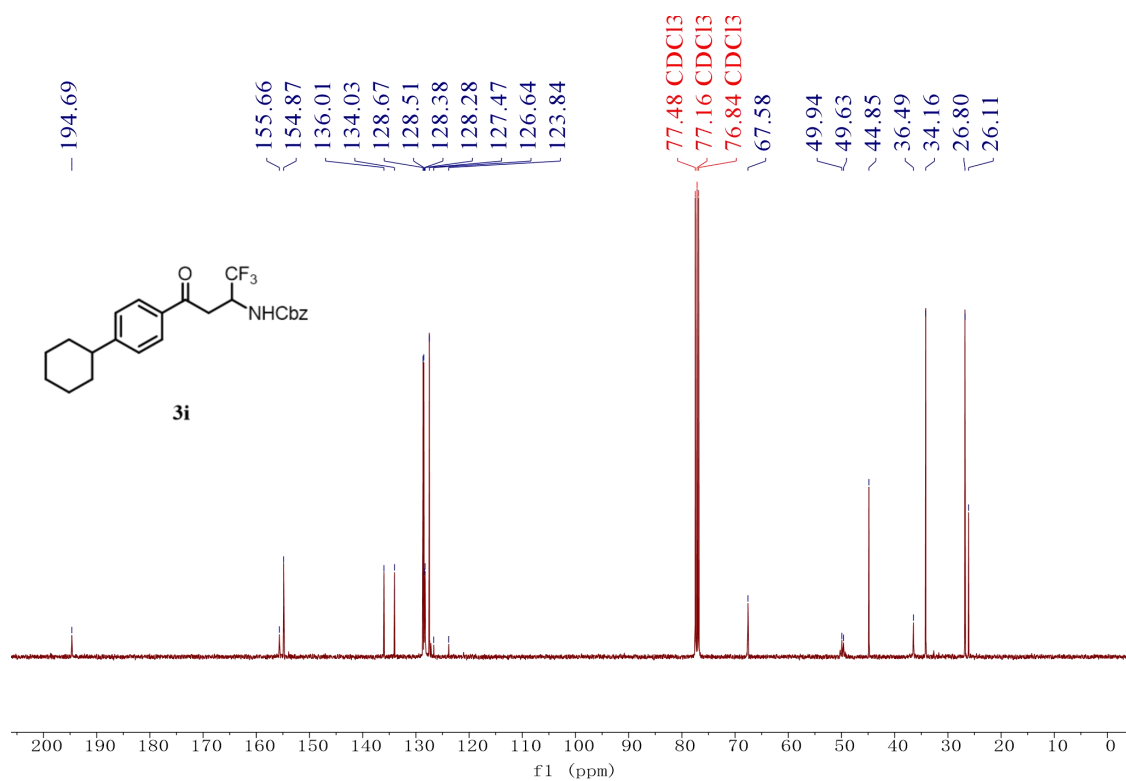
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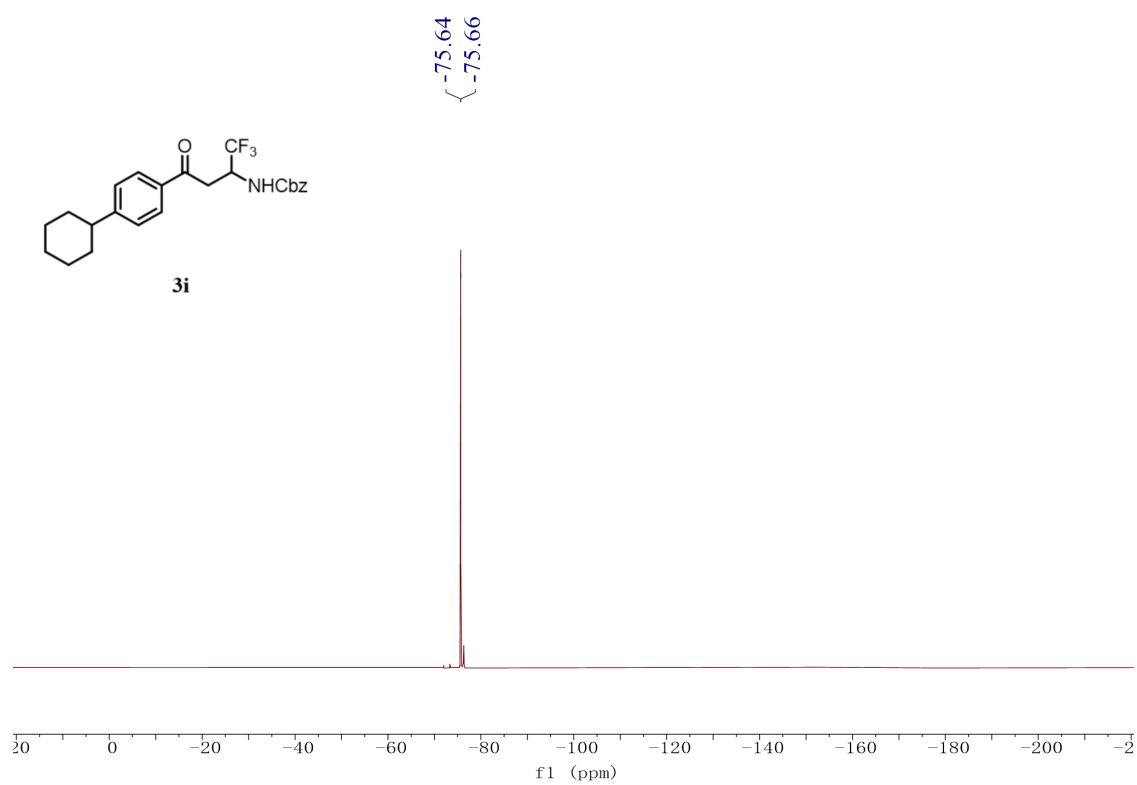
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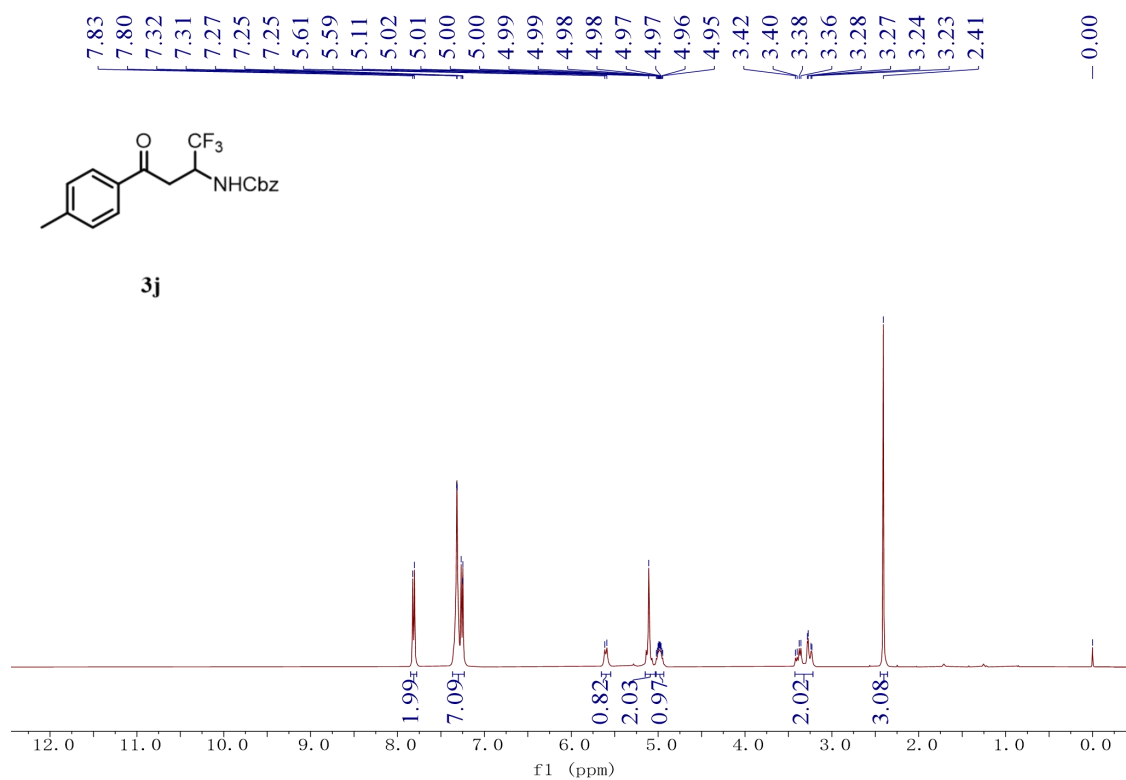
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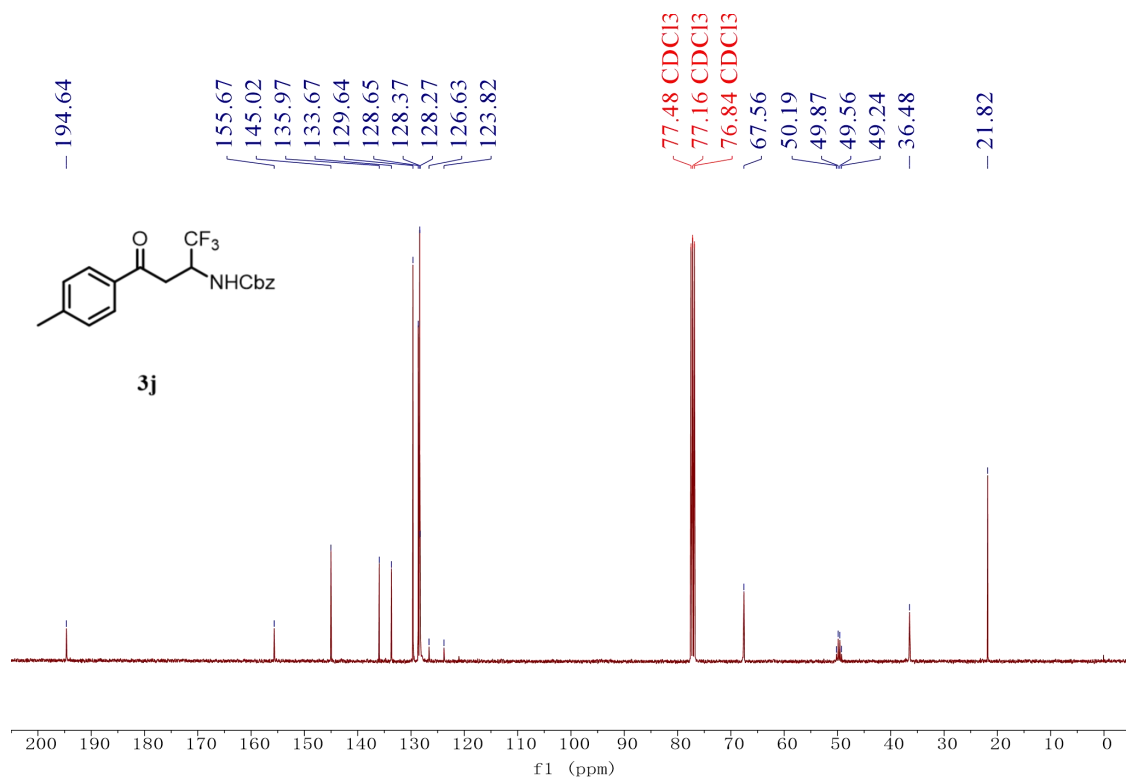
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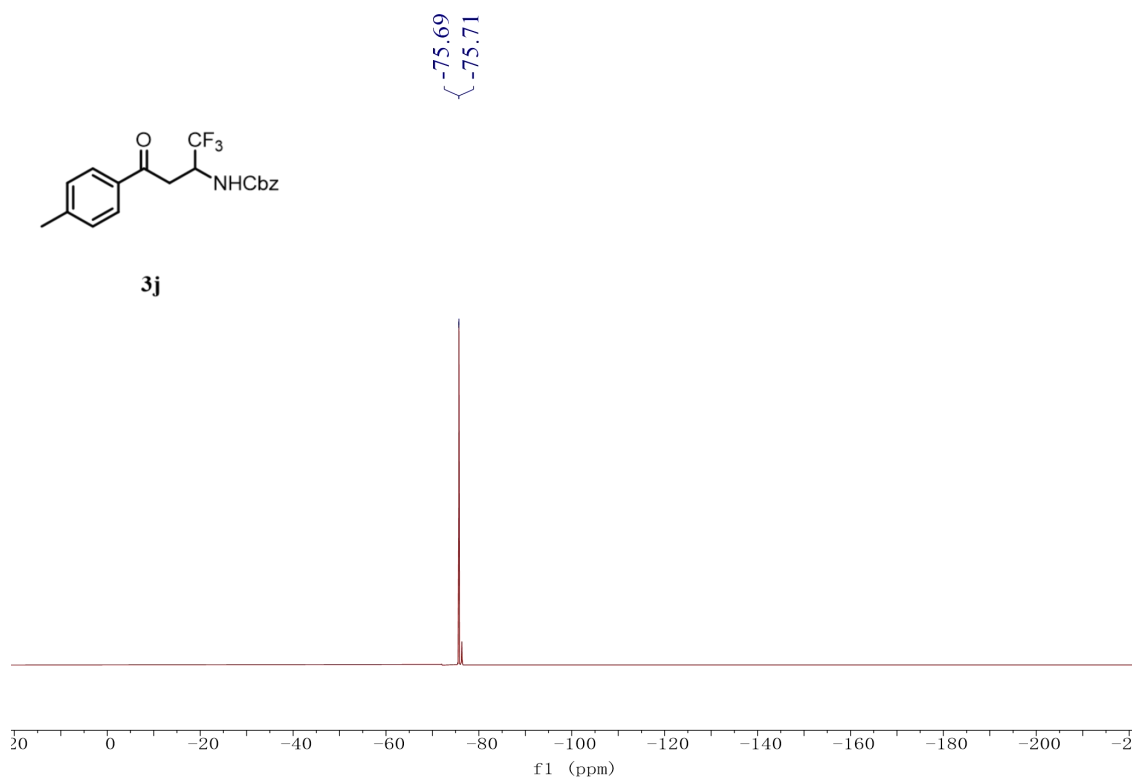
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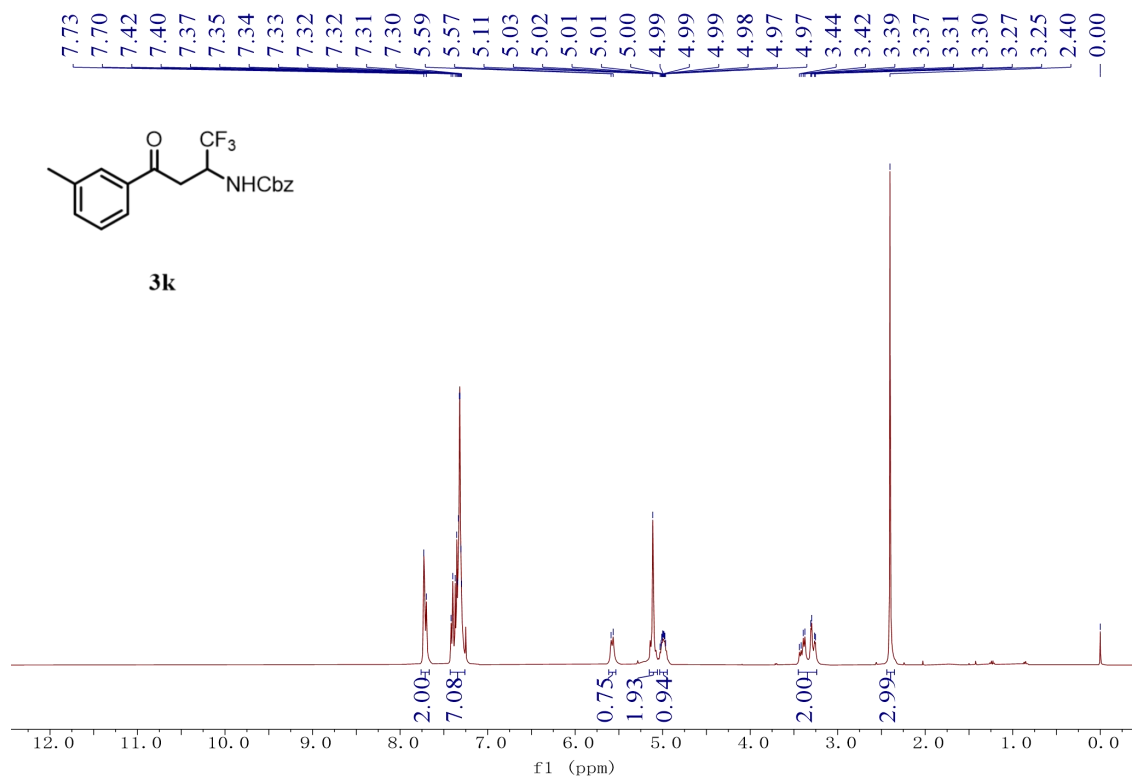
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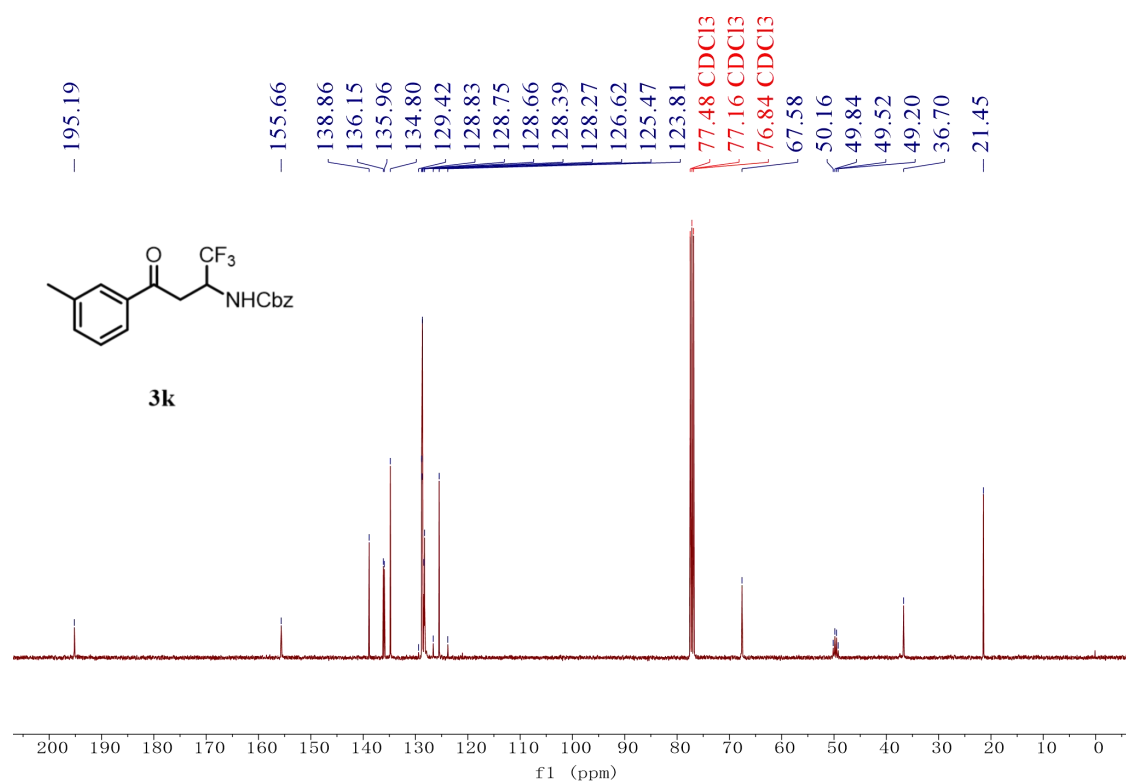
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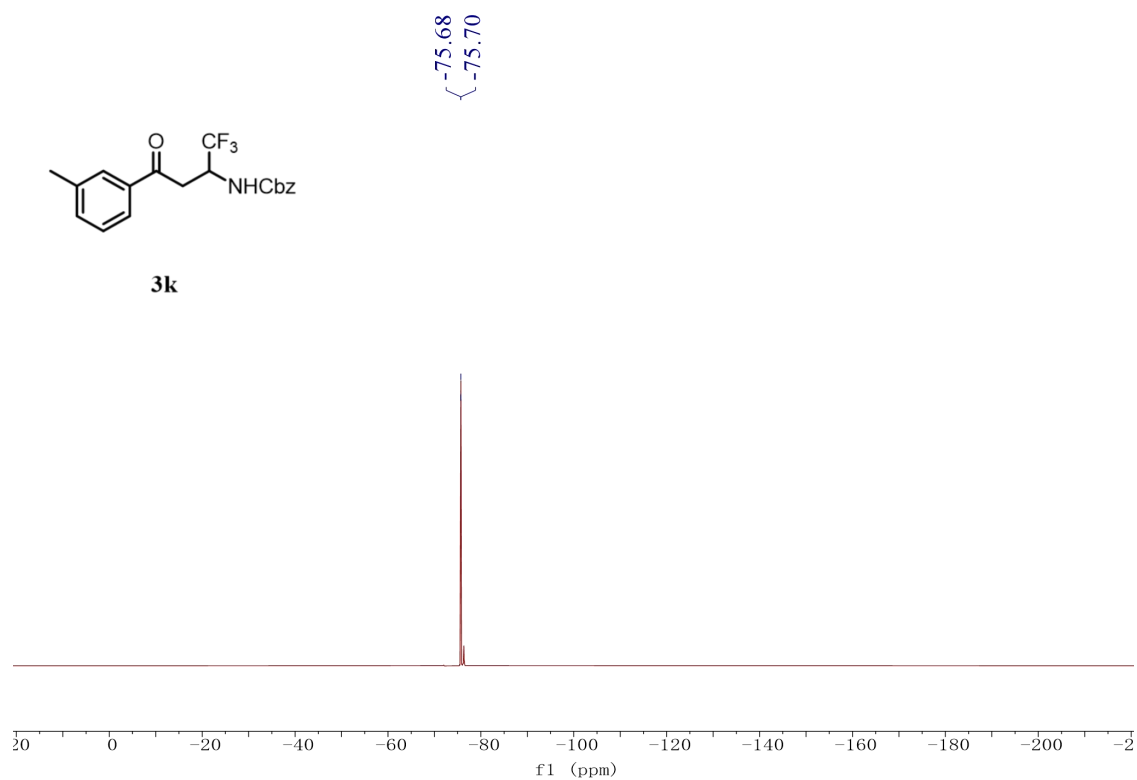
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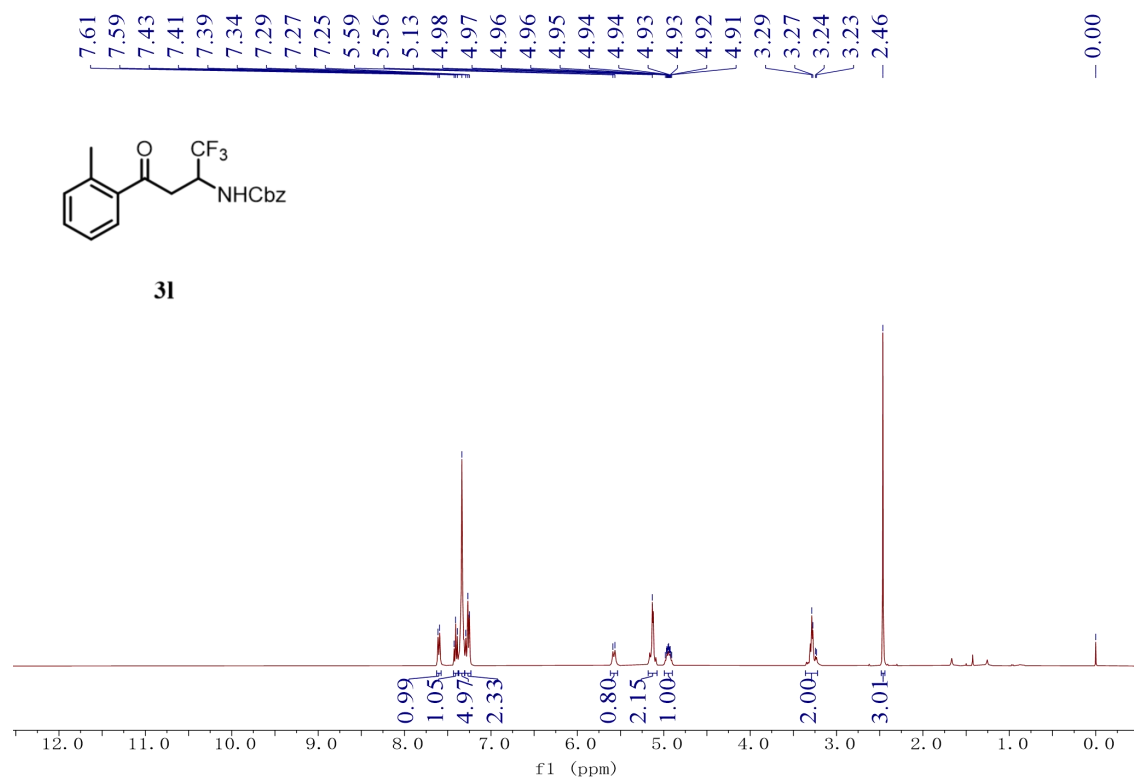
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$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

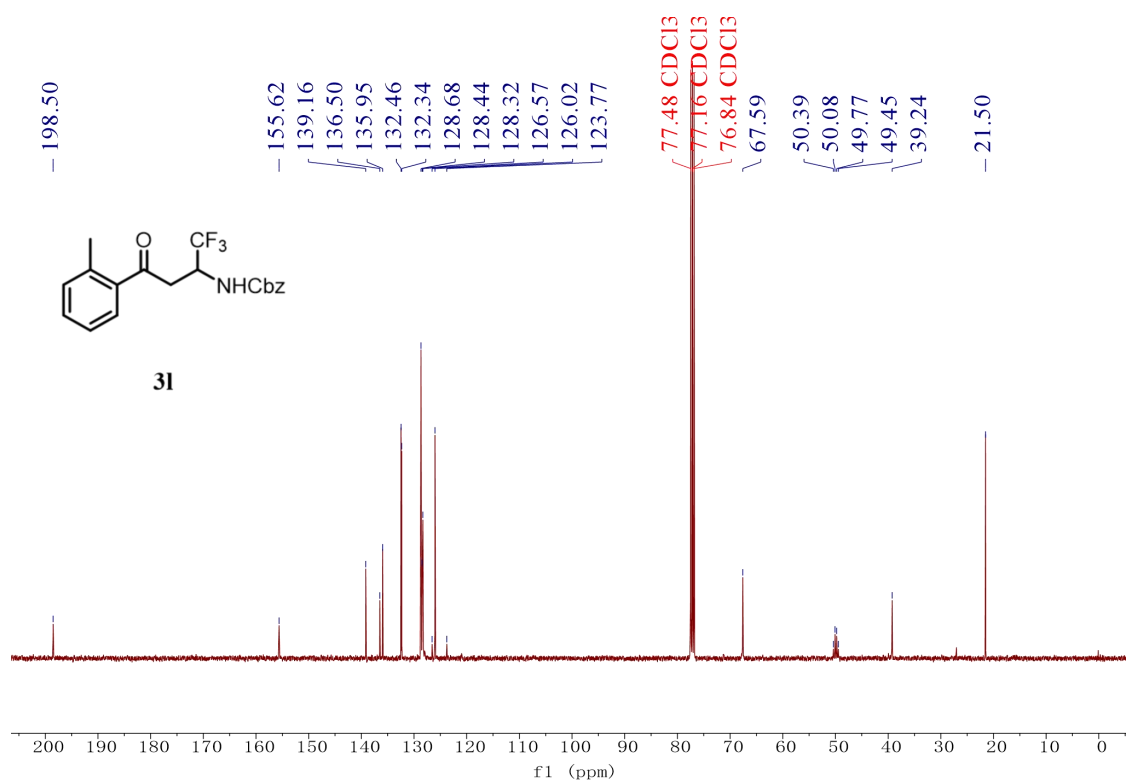


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

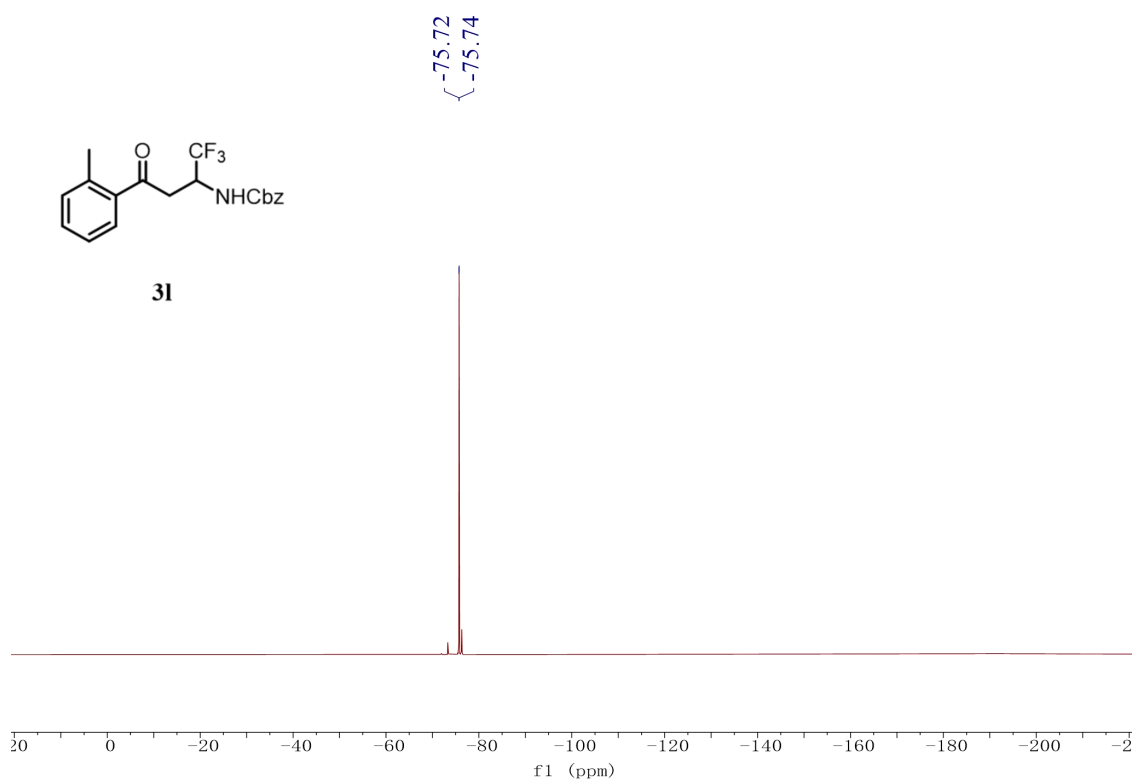




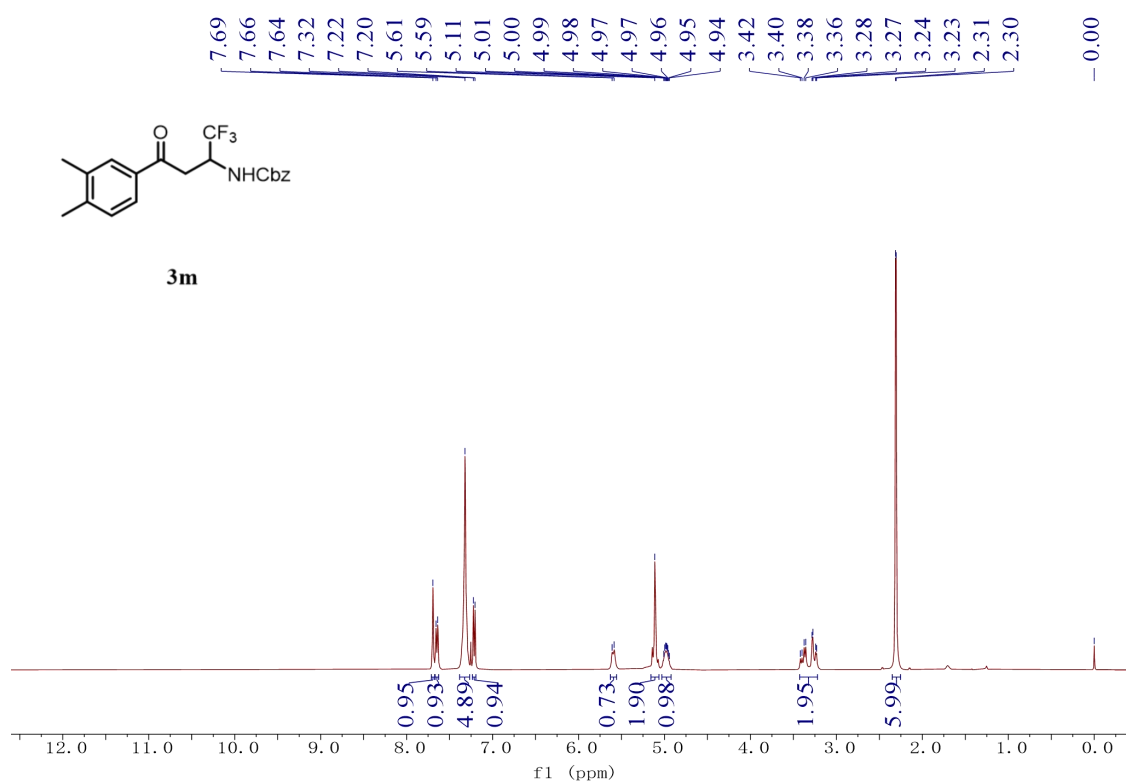
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



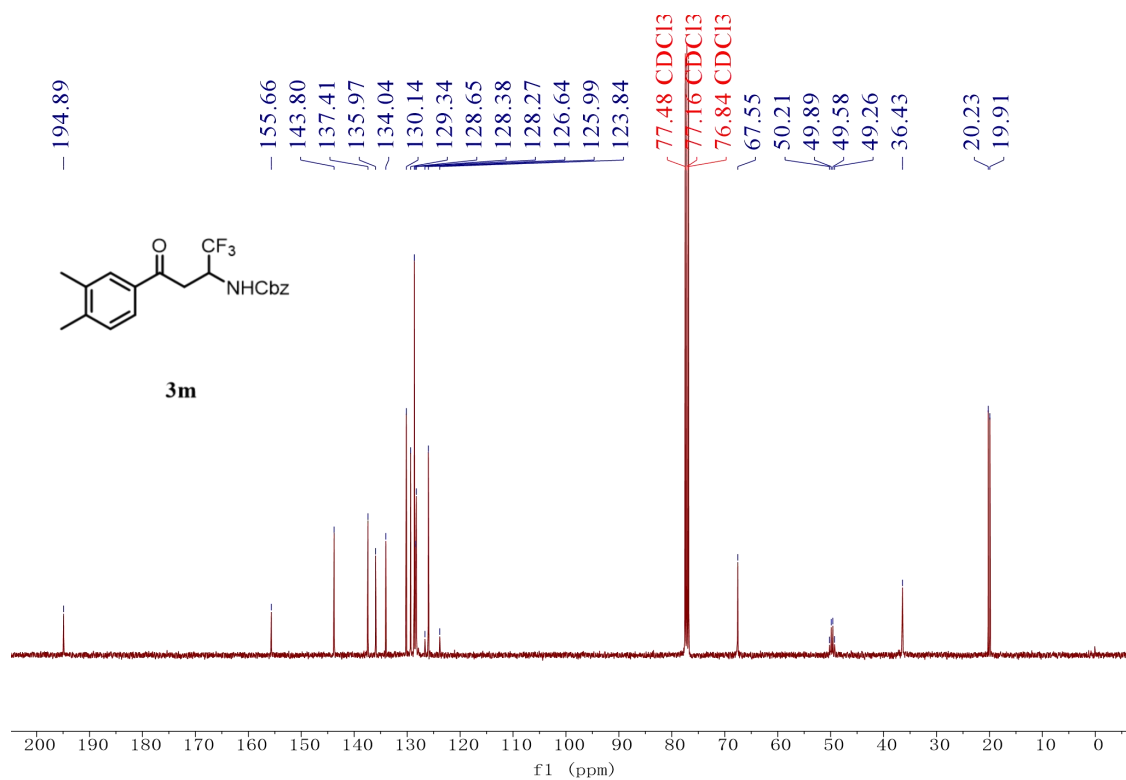
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



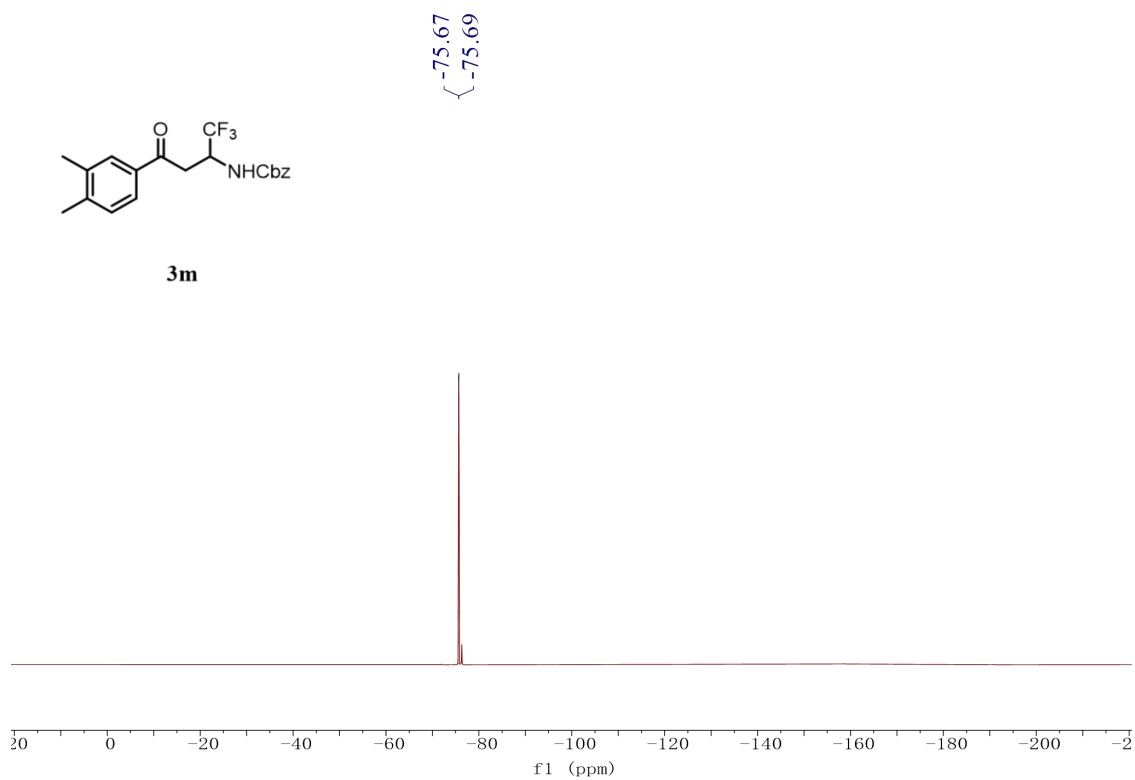
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



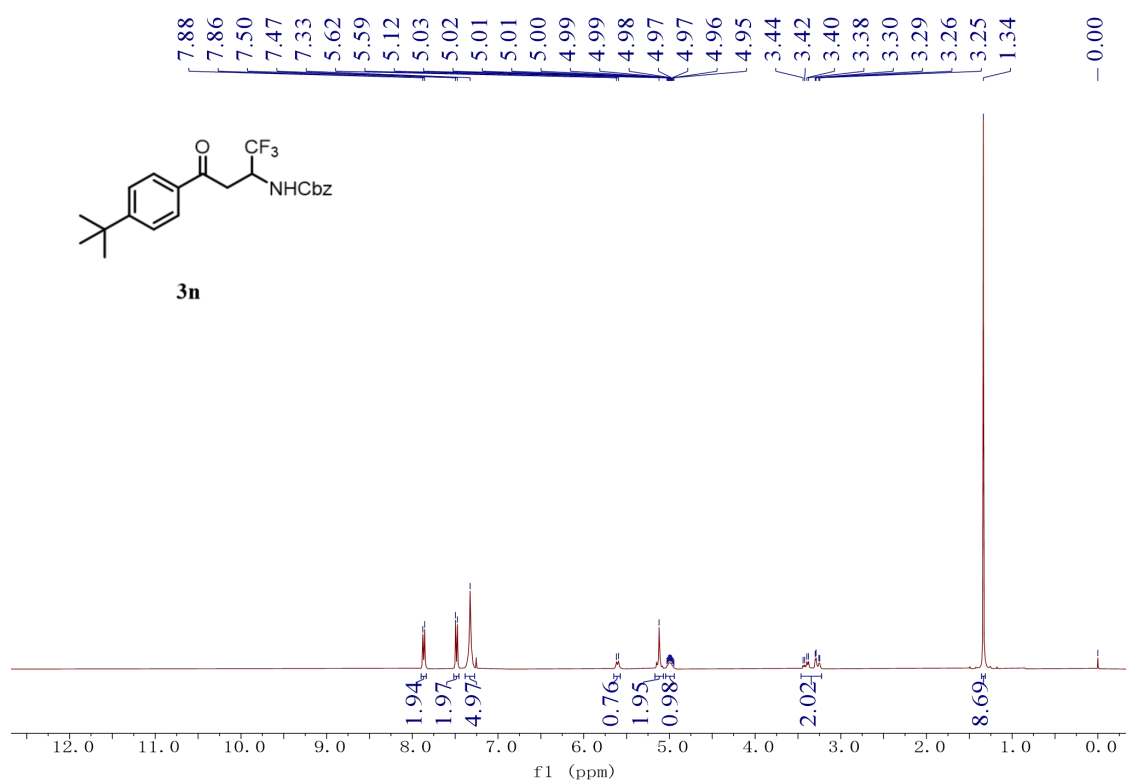
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



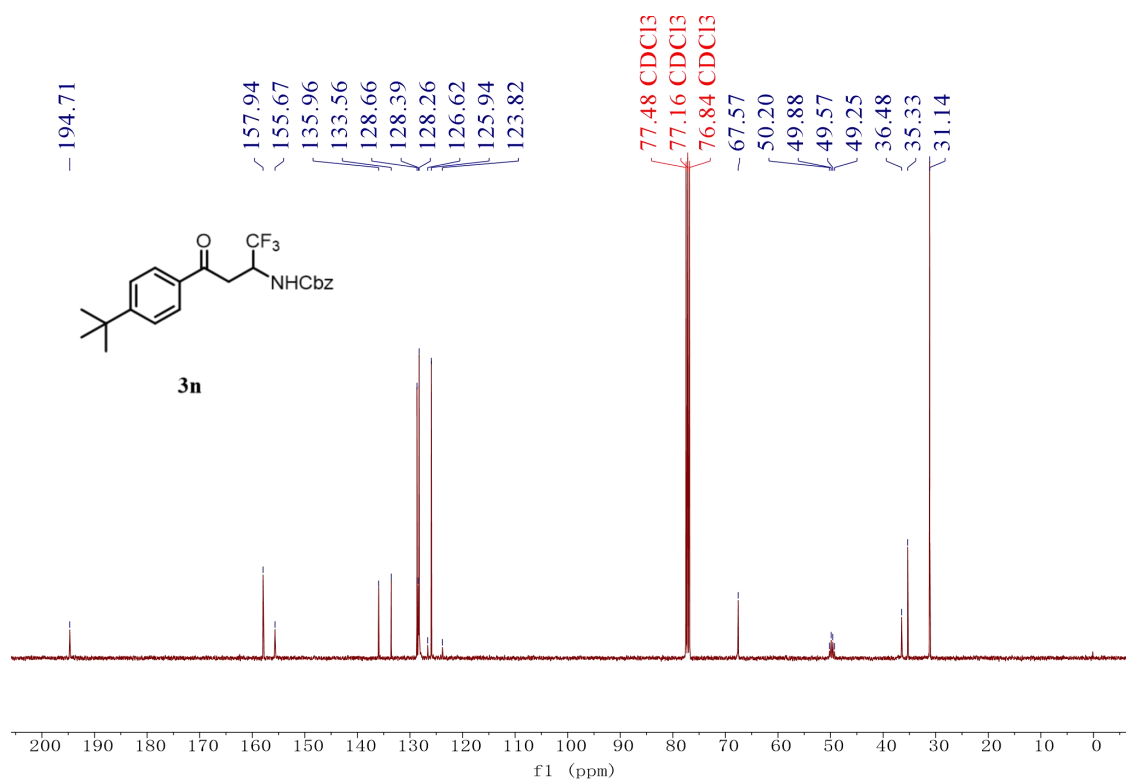
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



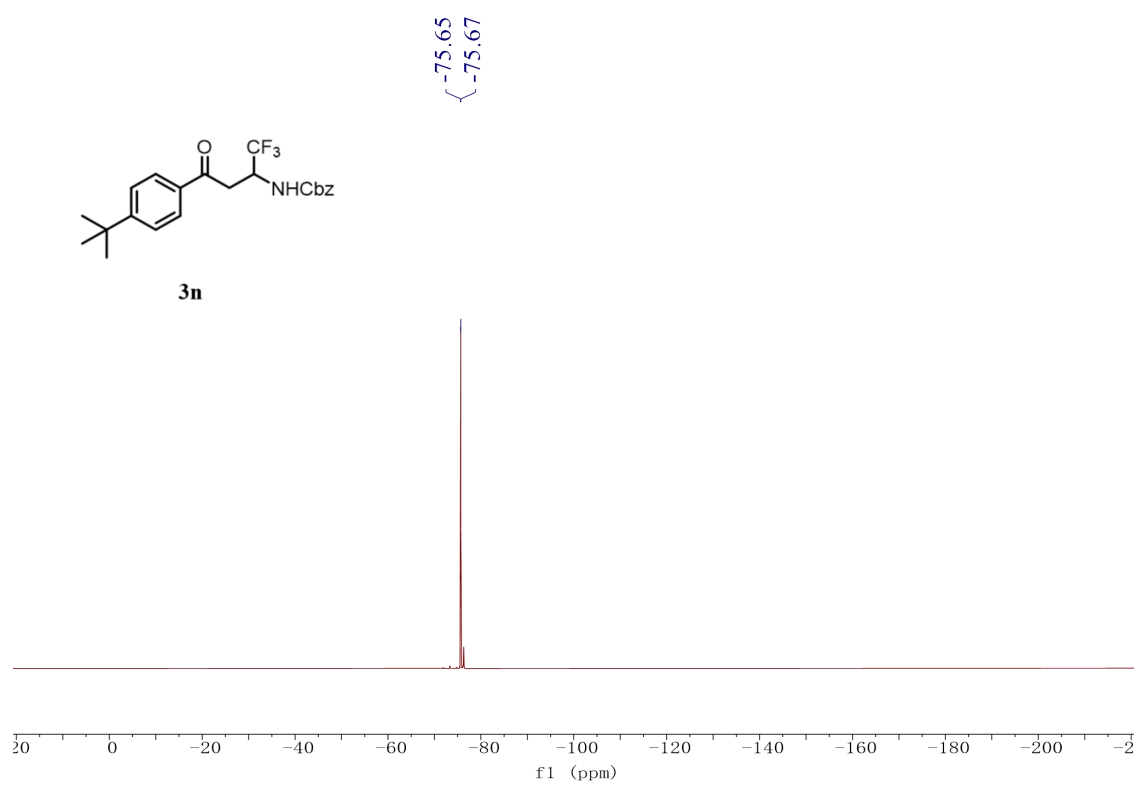
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



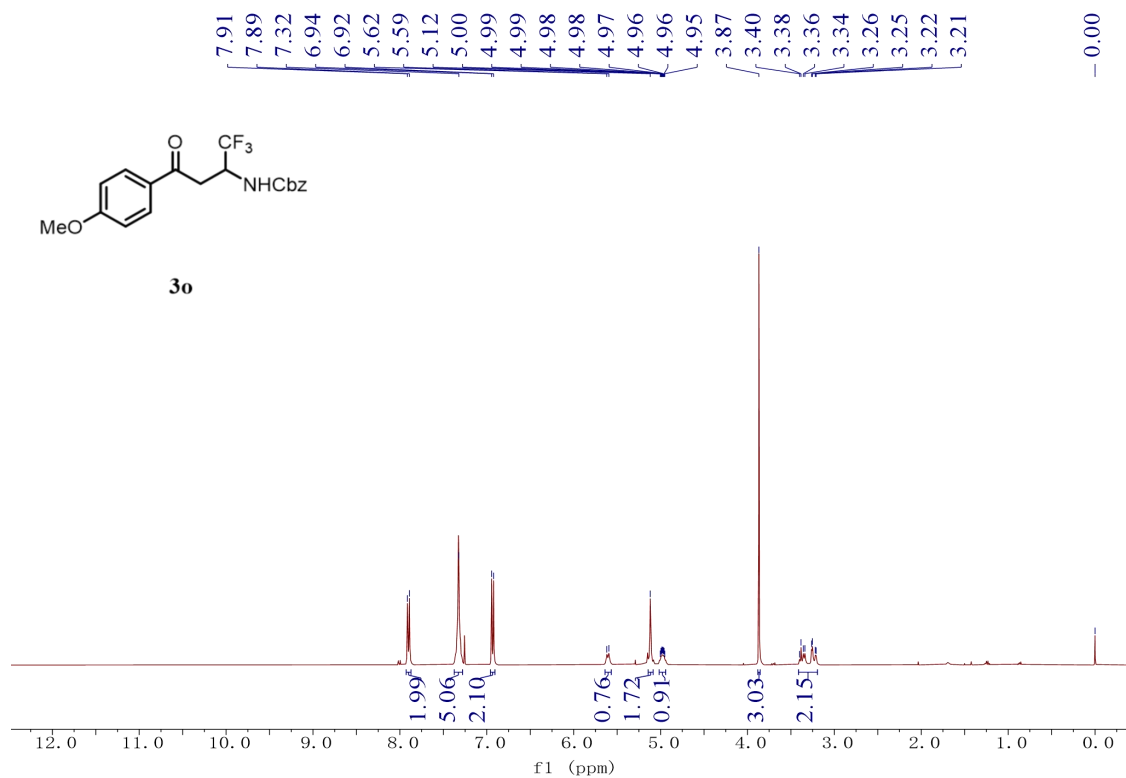
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



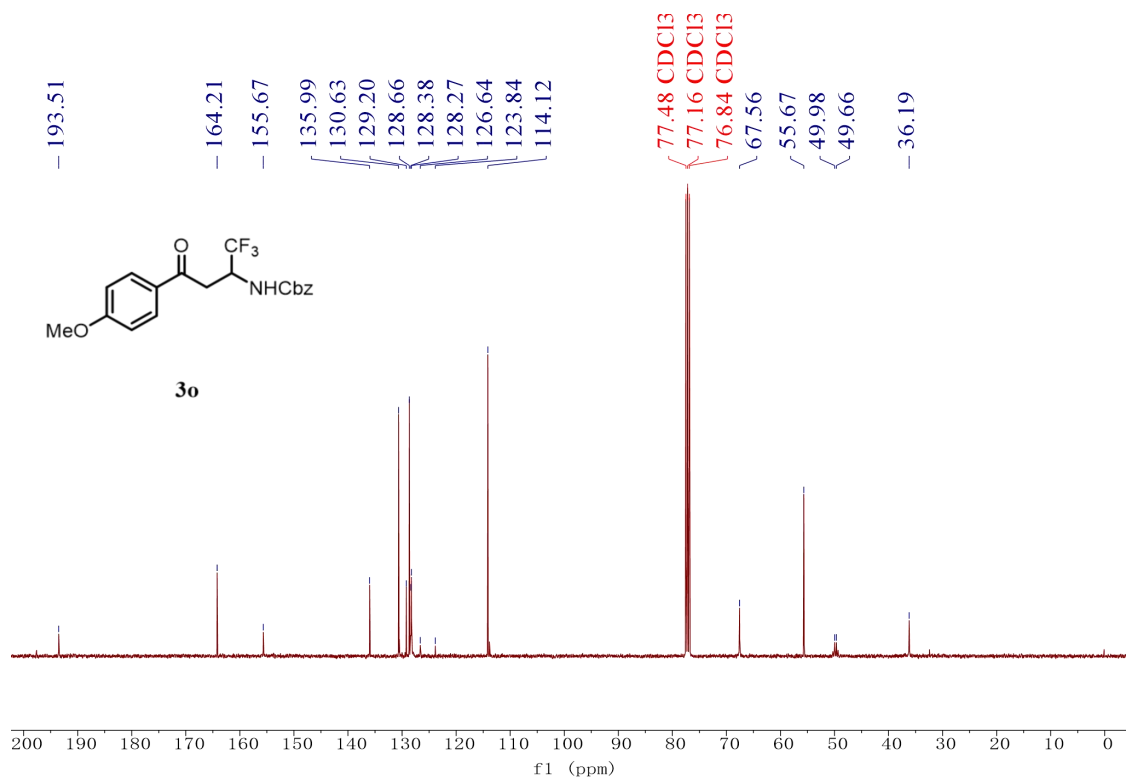
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



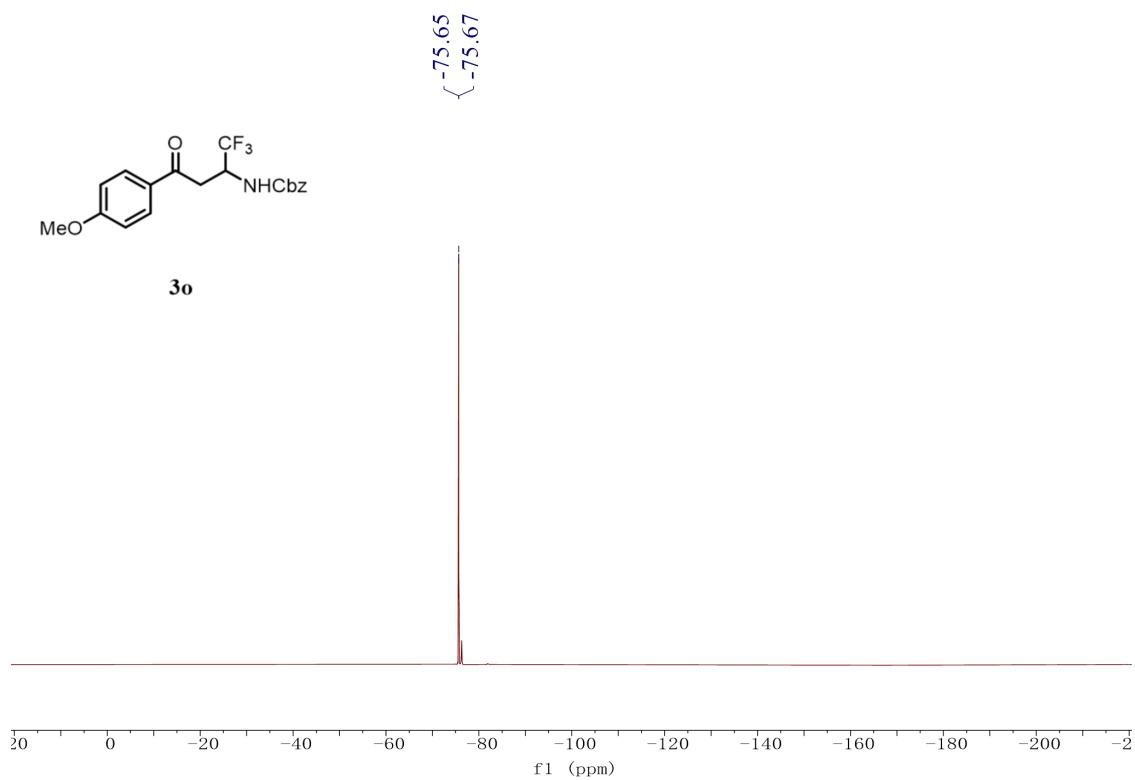
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



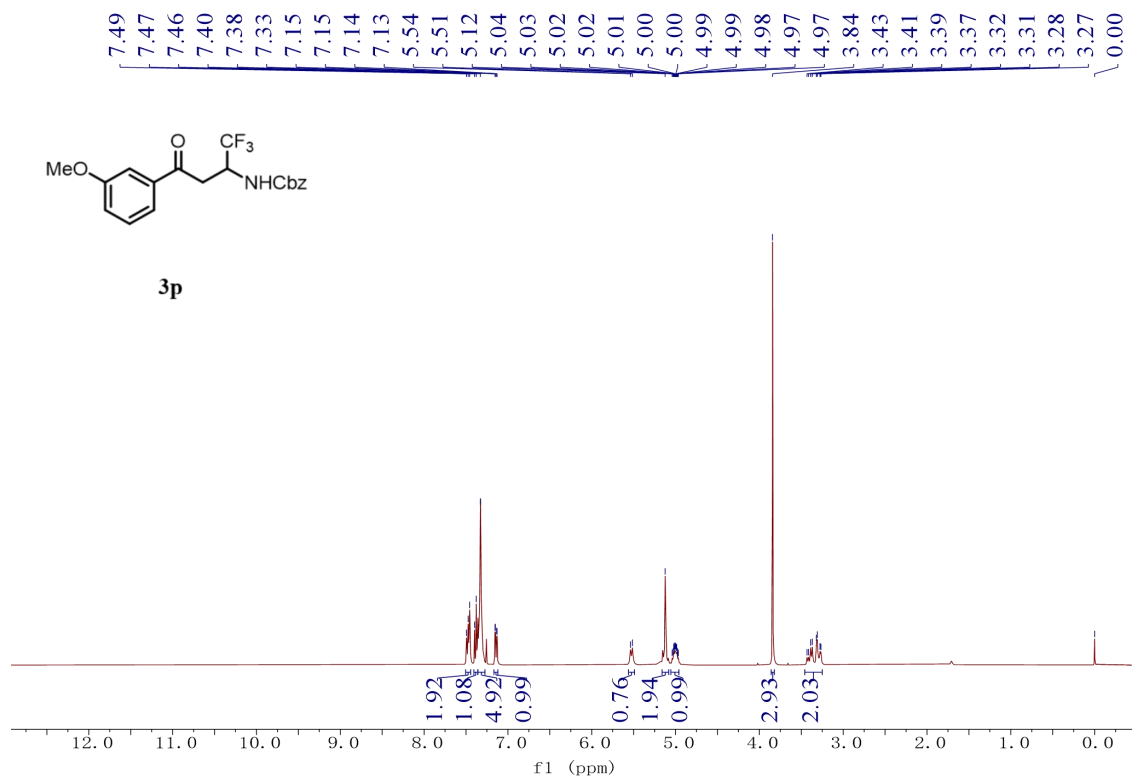
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



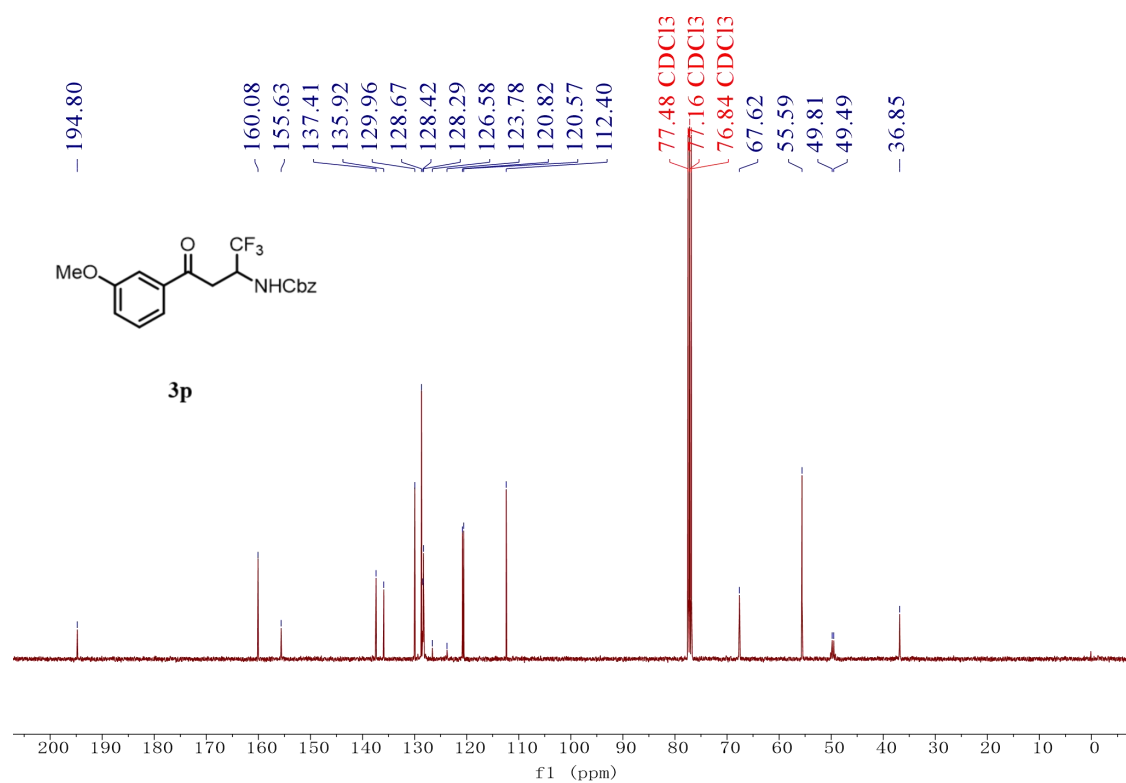
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

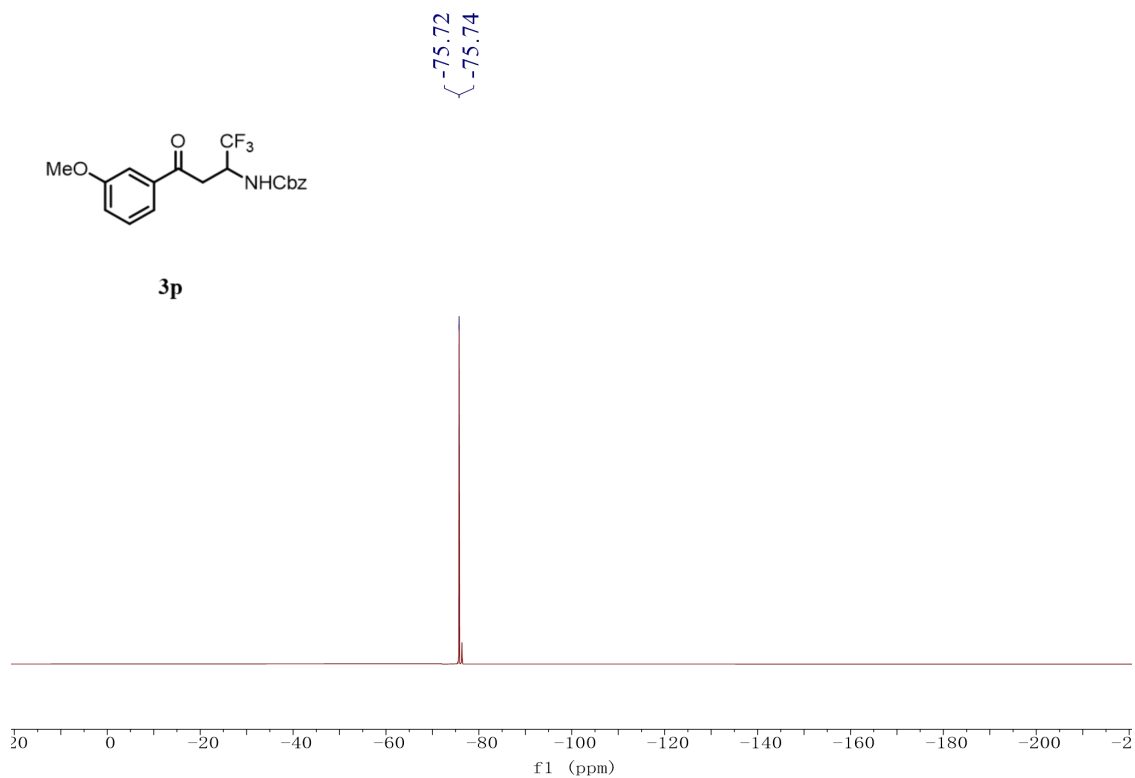


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

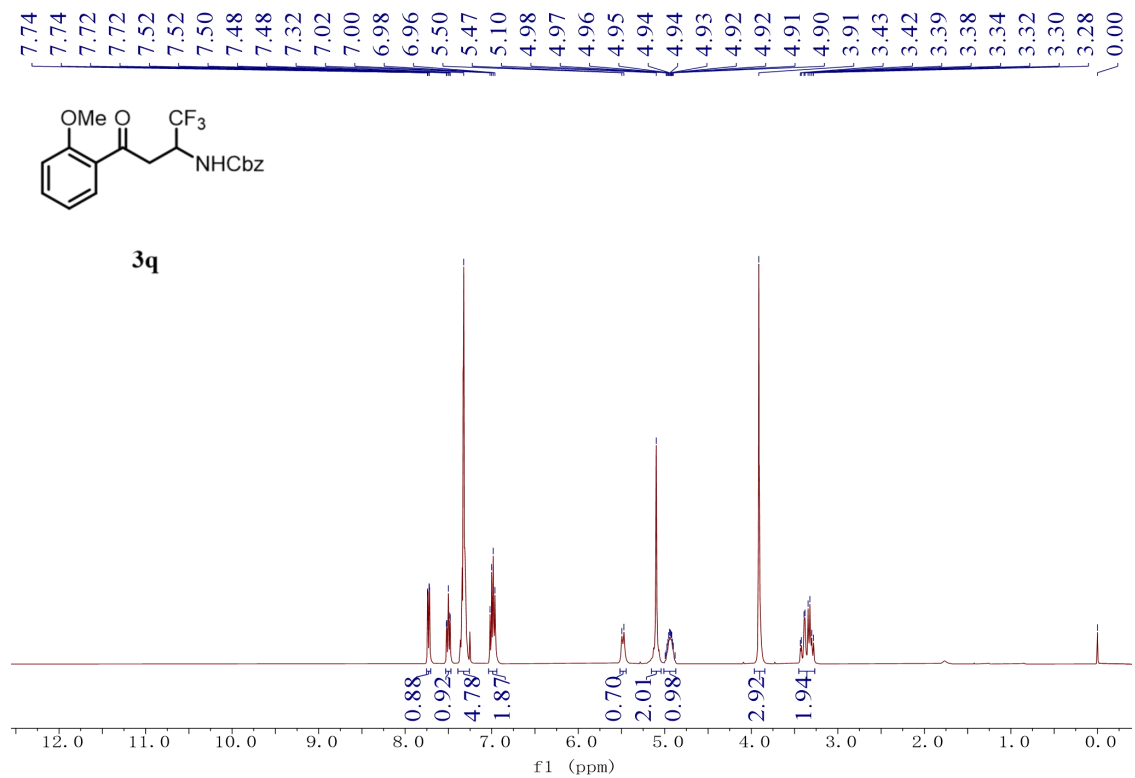


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

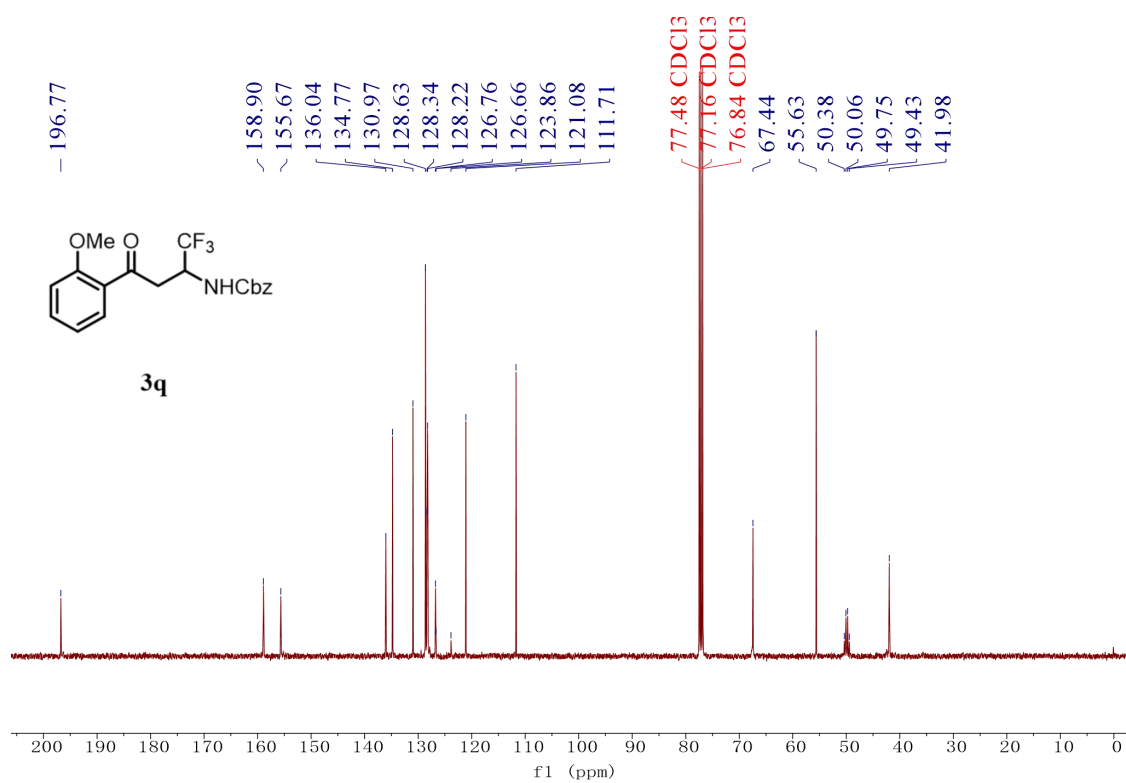




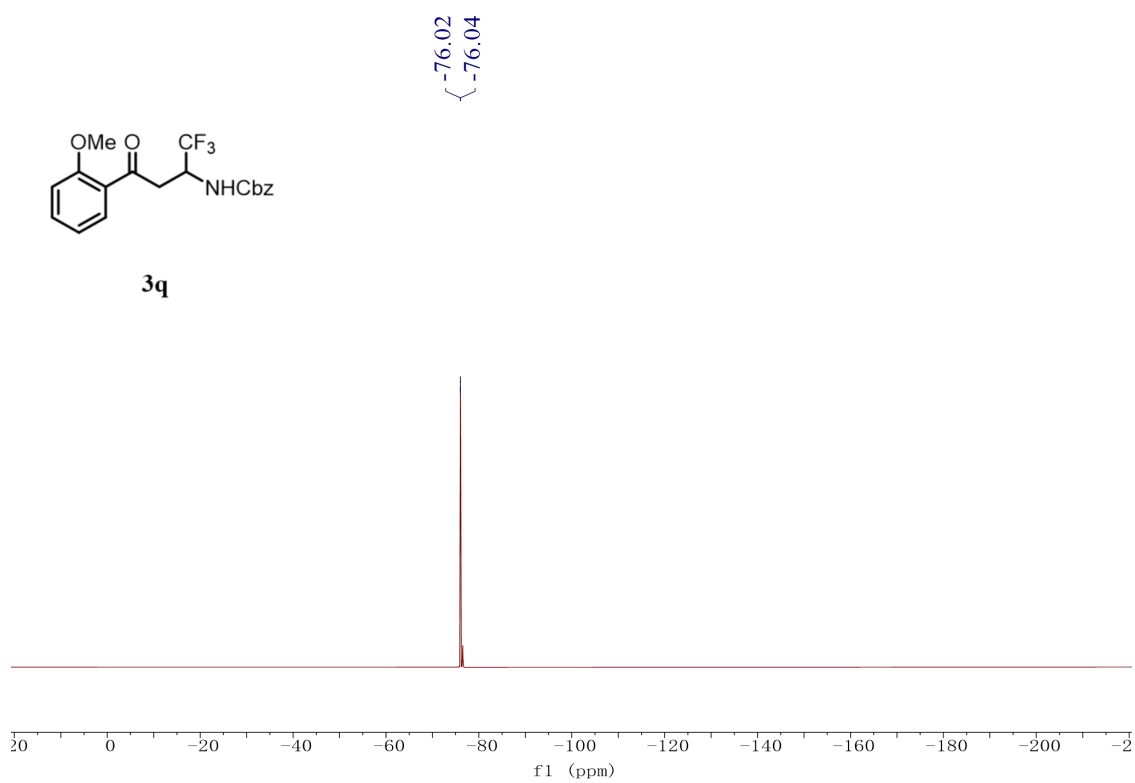
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



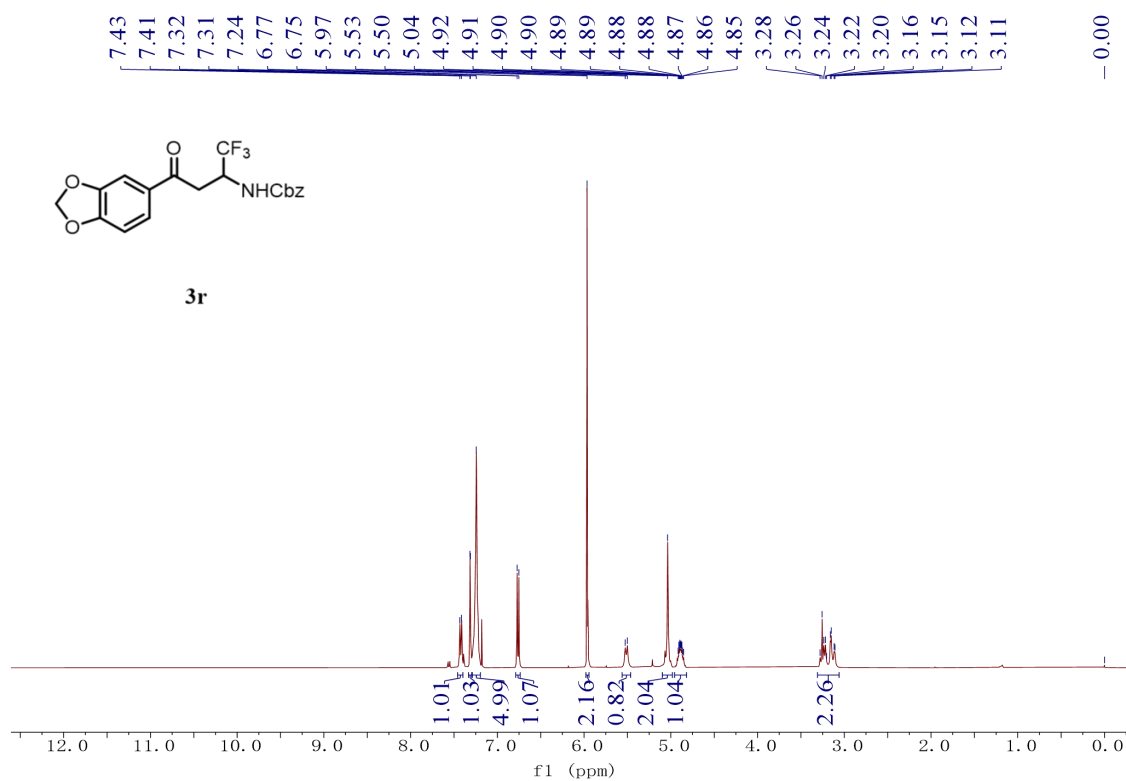
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



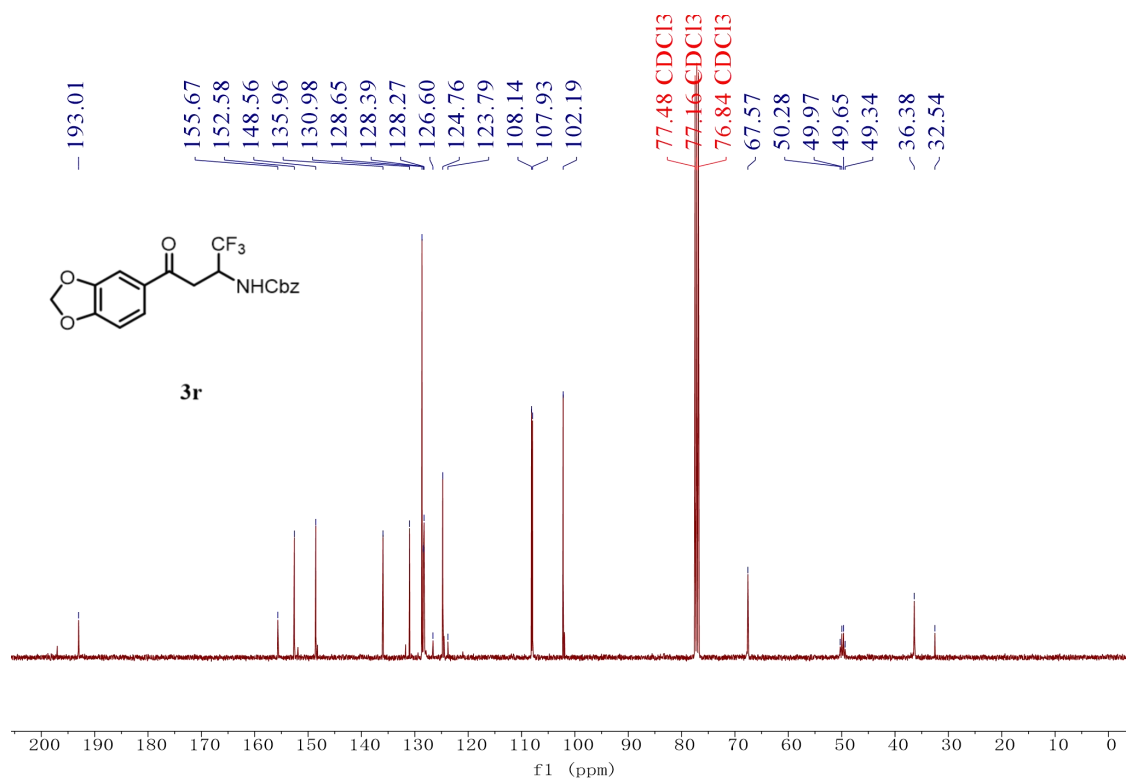
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



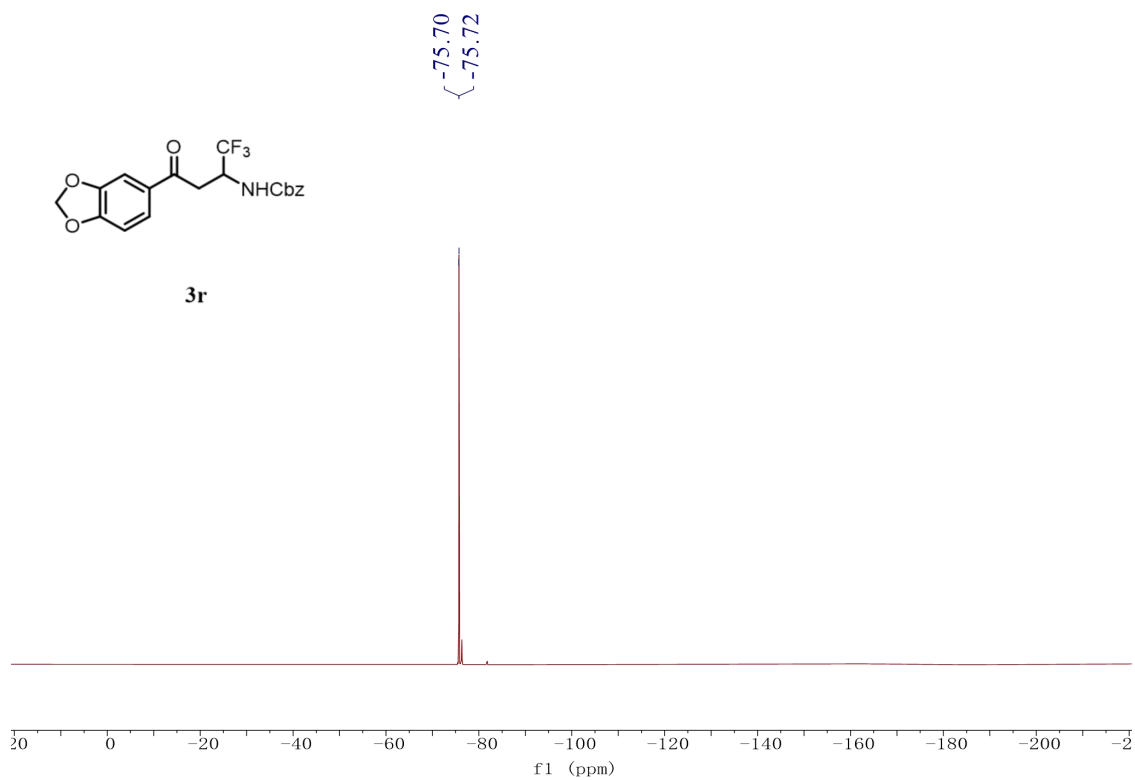
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



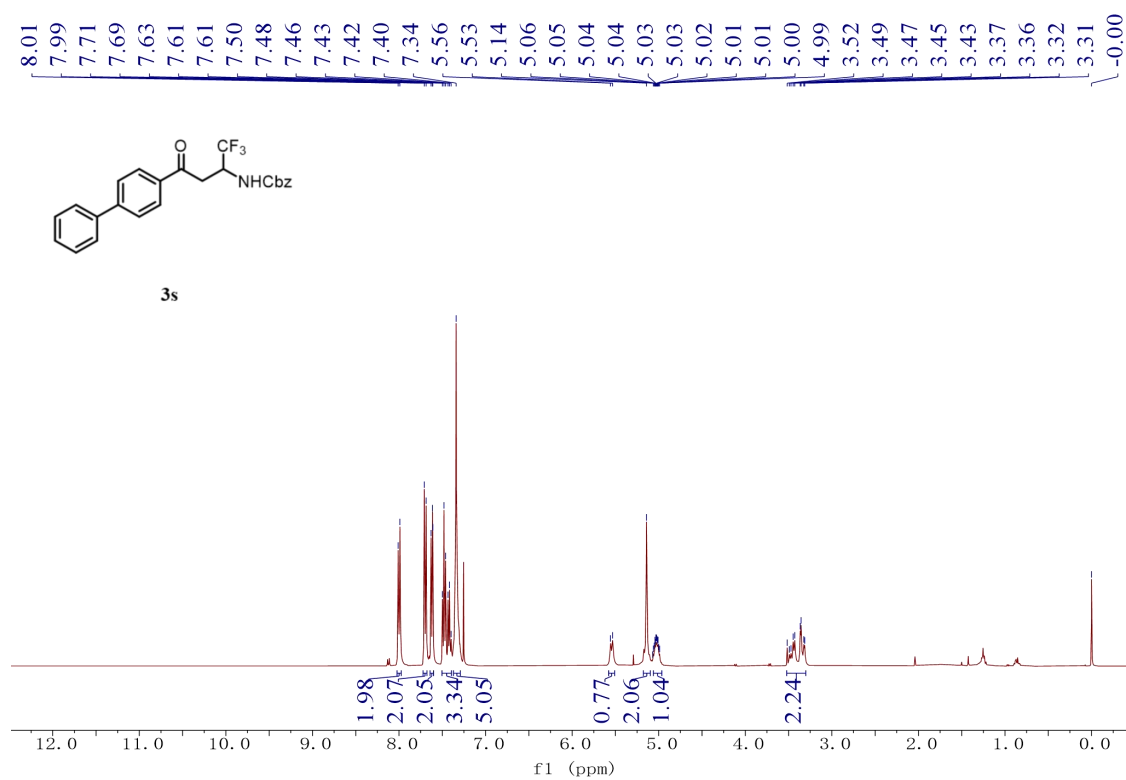
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



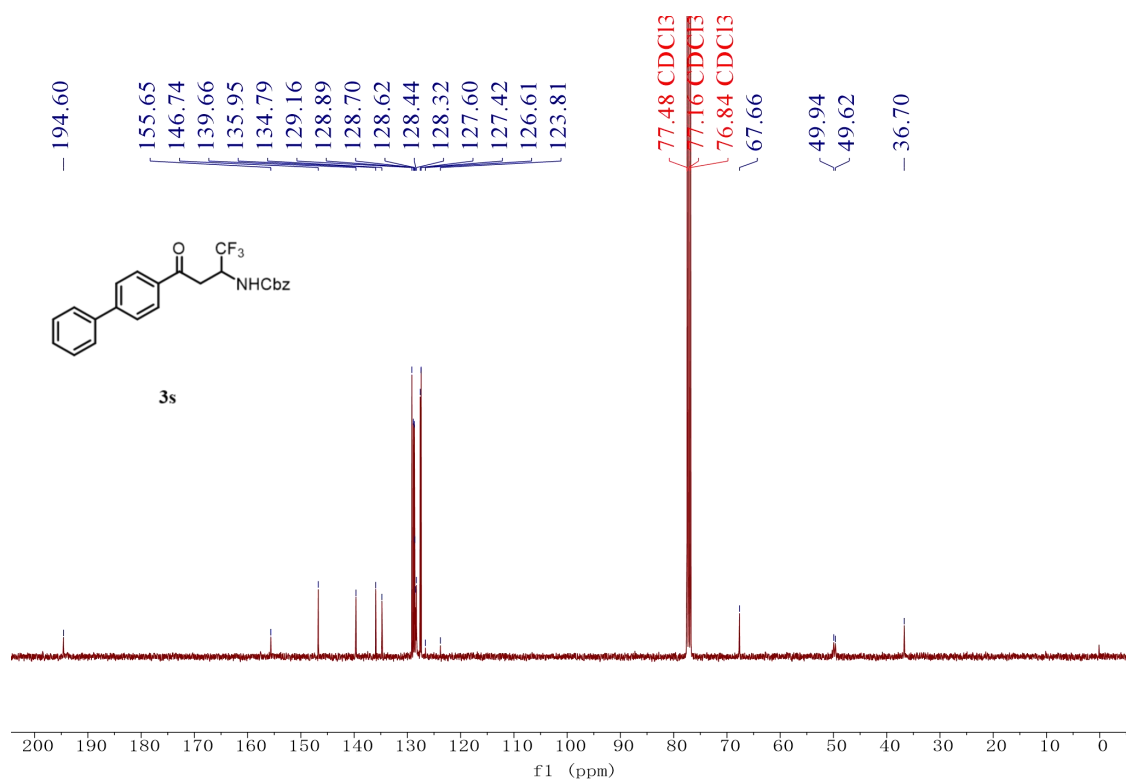
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



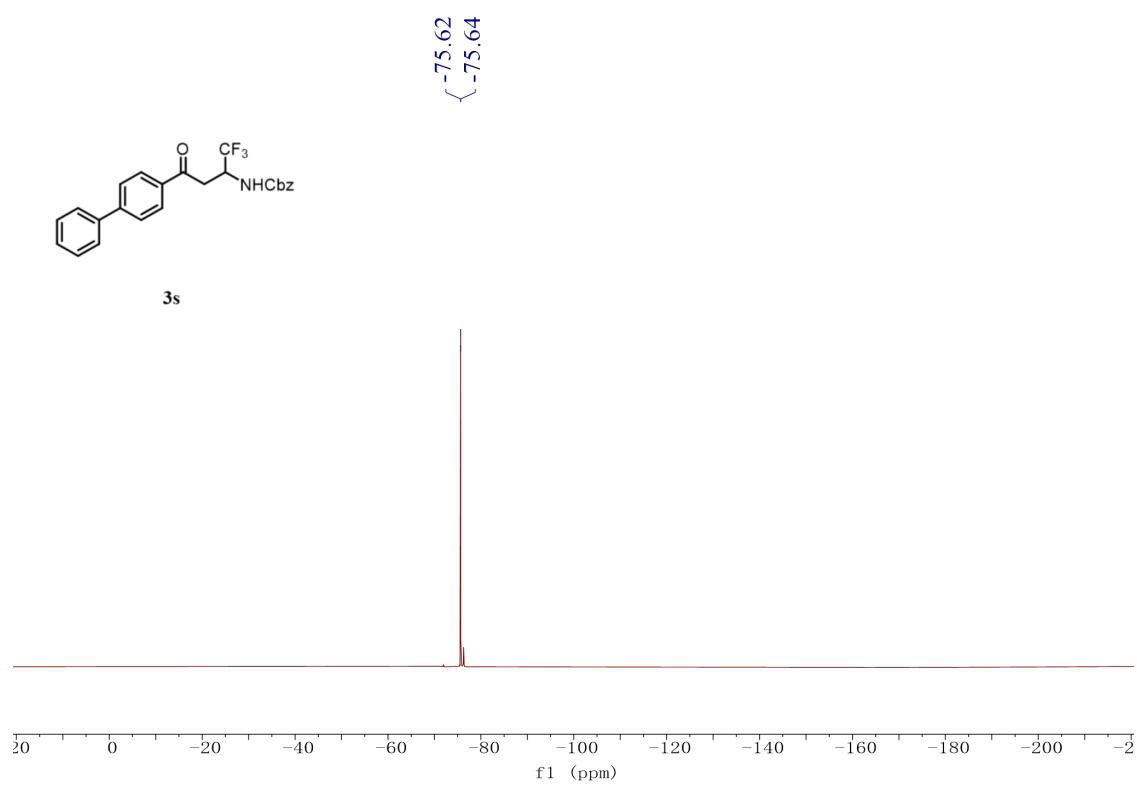
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



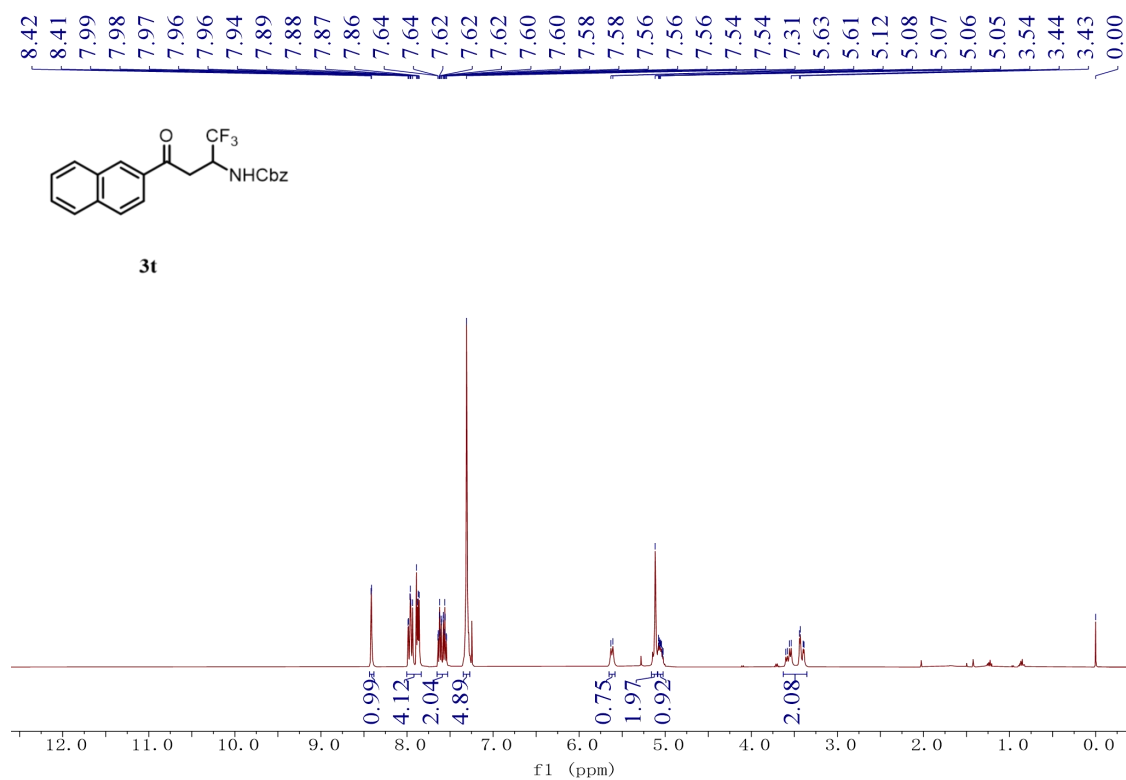
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



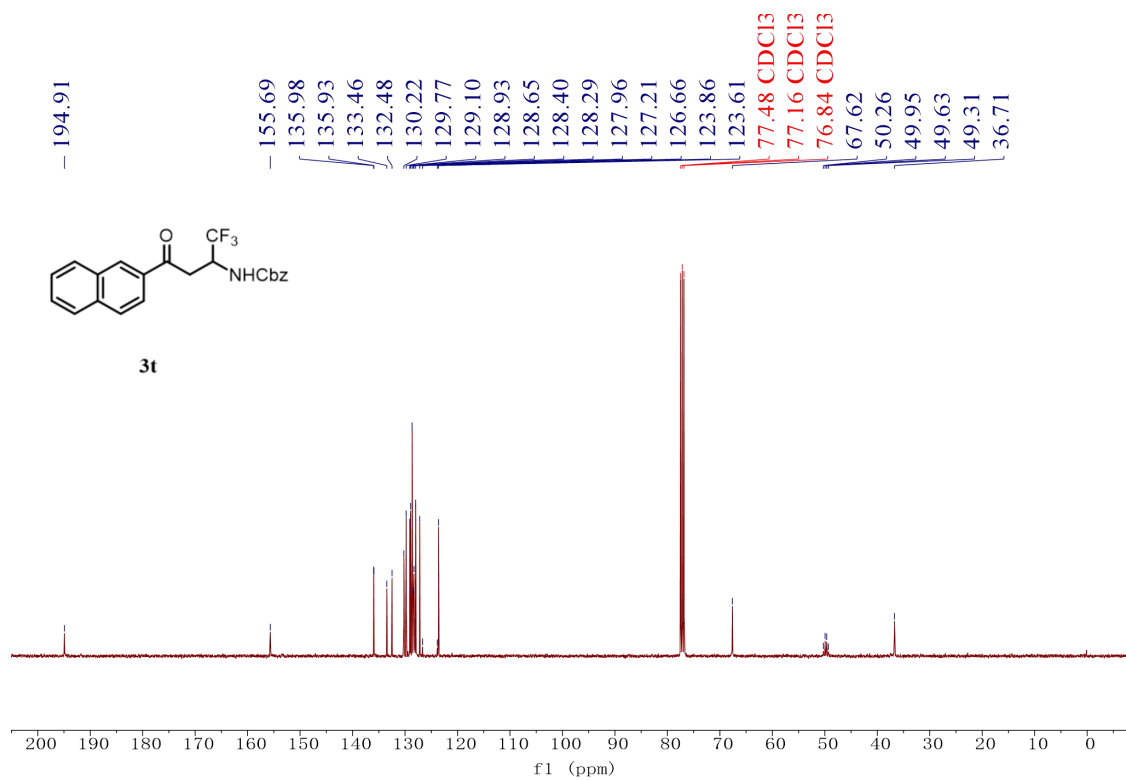
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



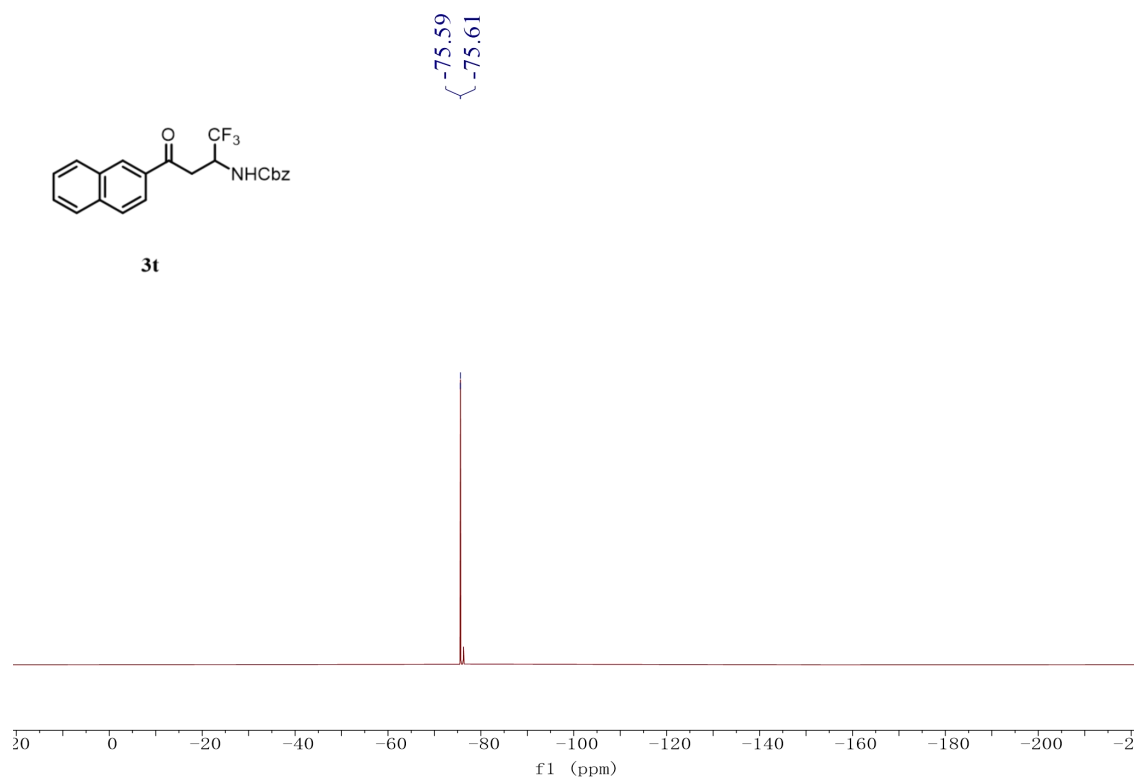
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

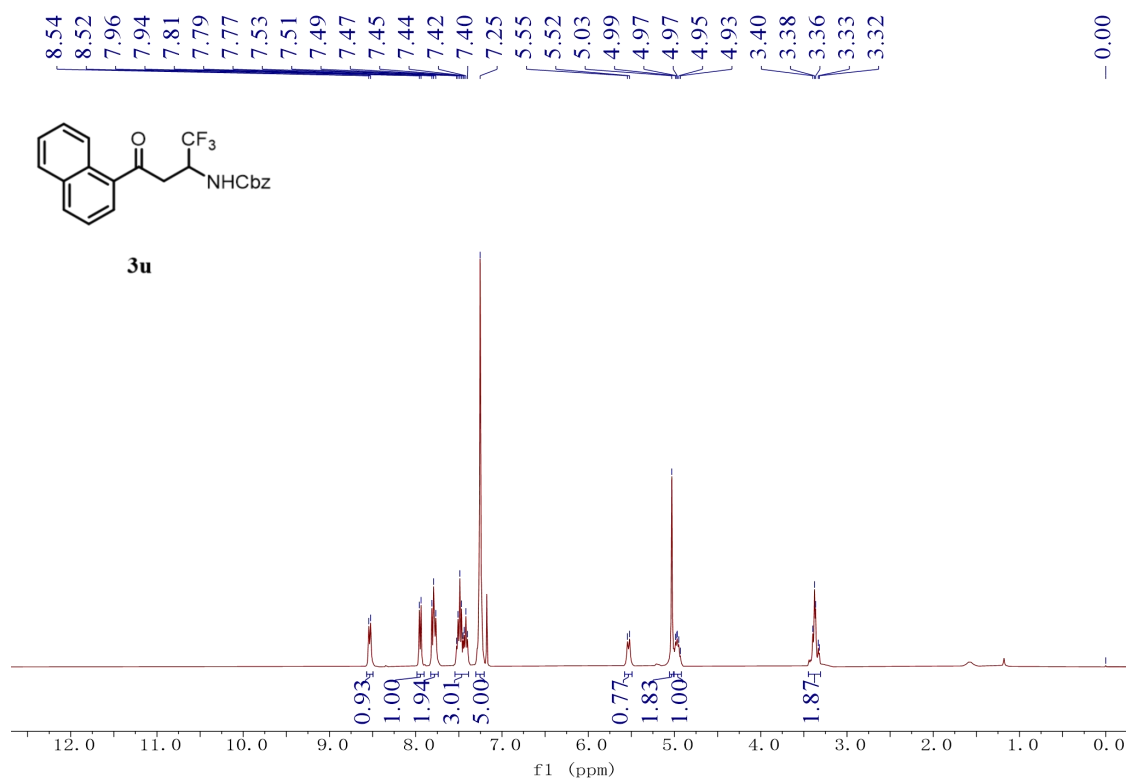


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

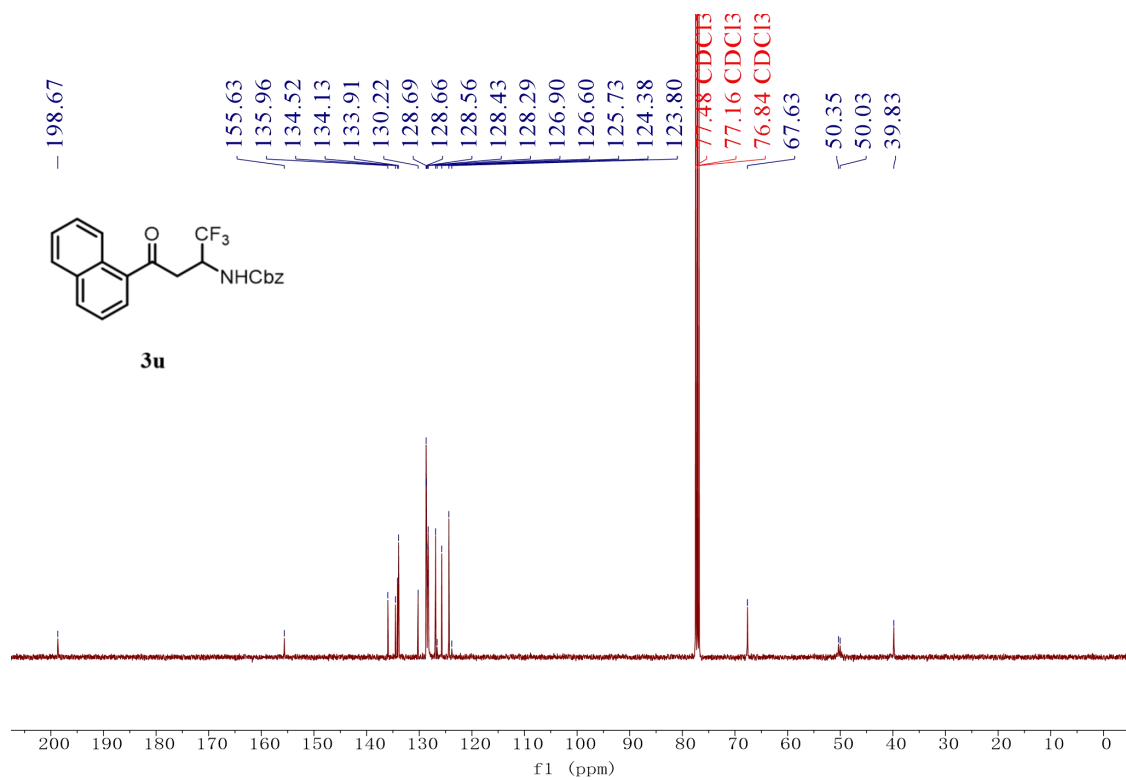


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

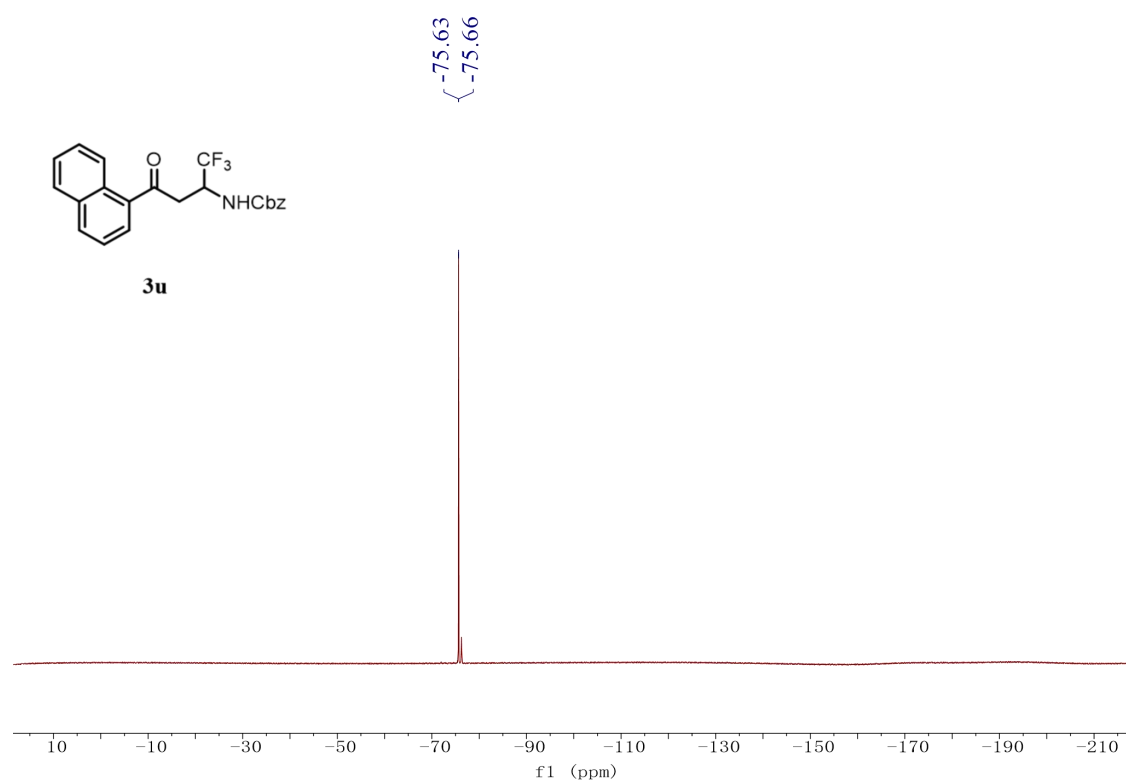




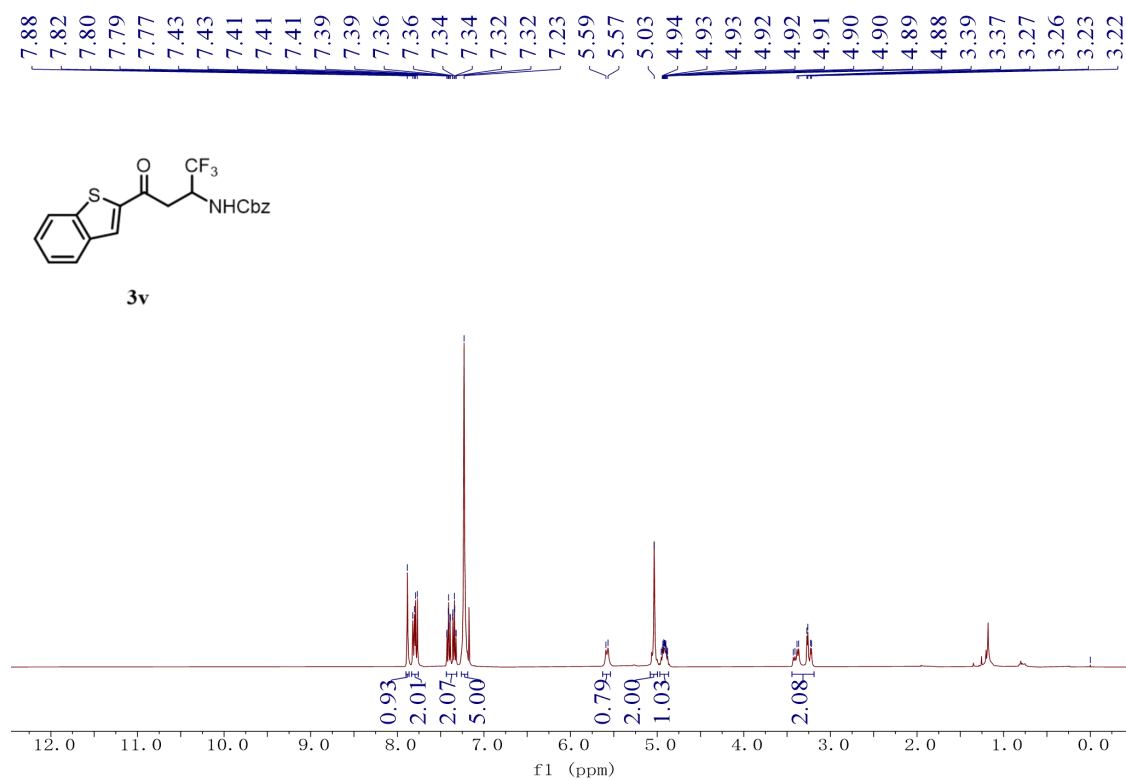
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



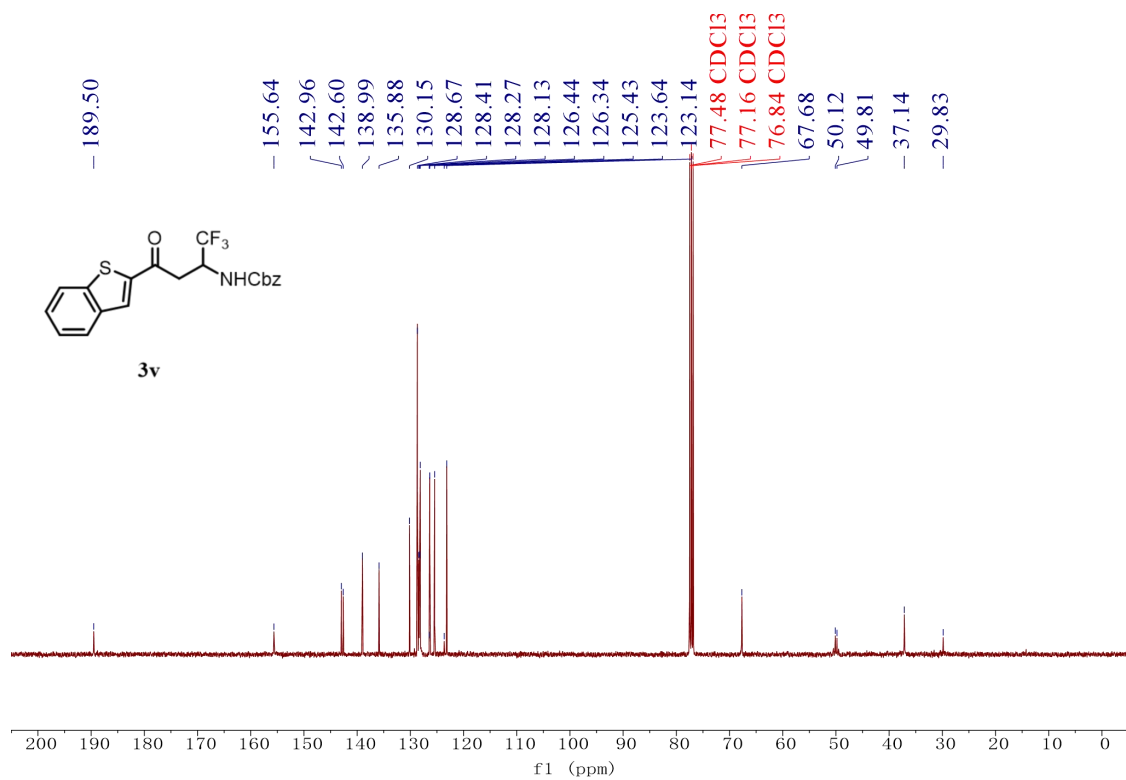
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



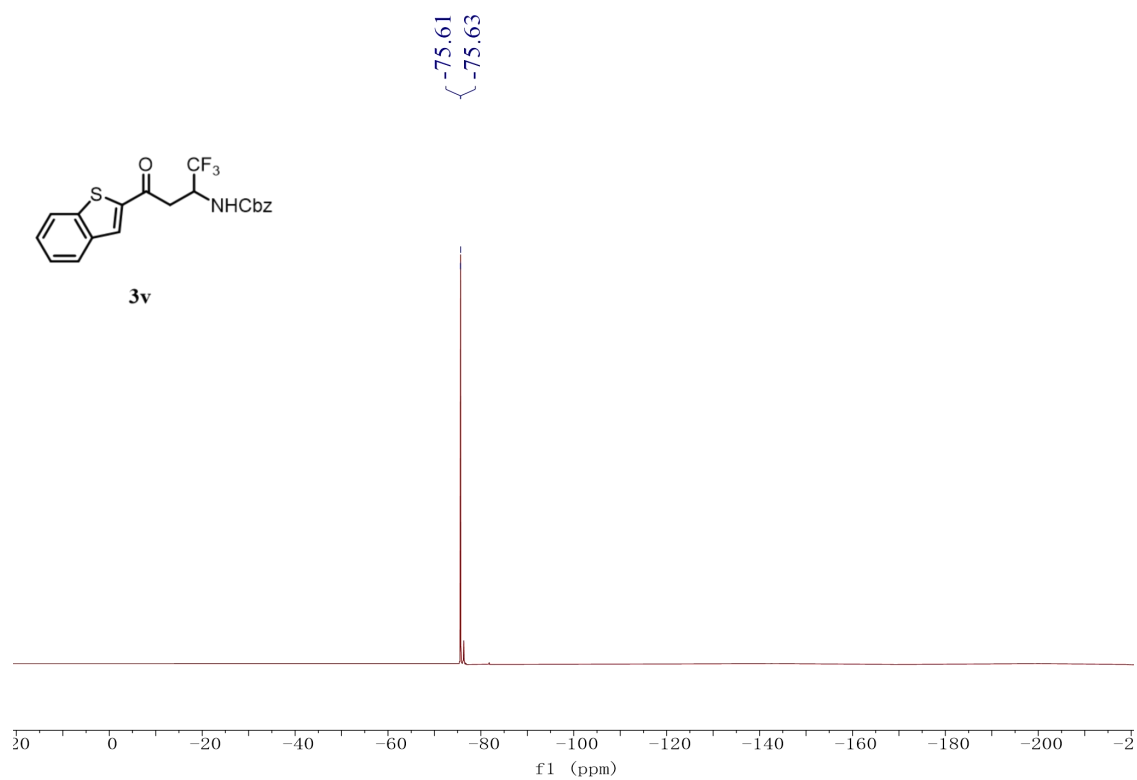
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



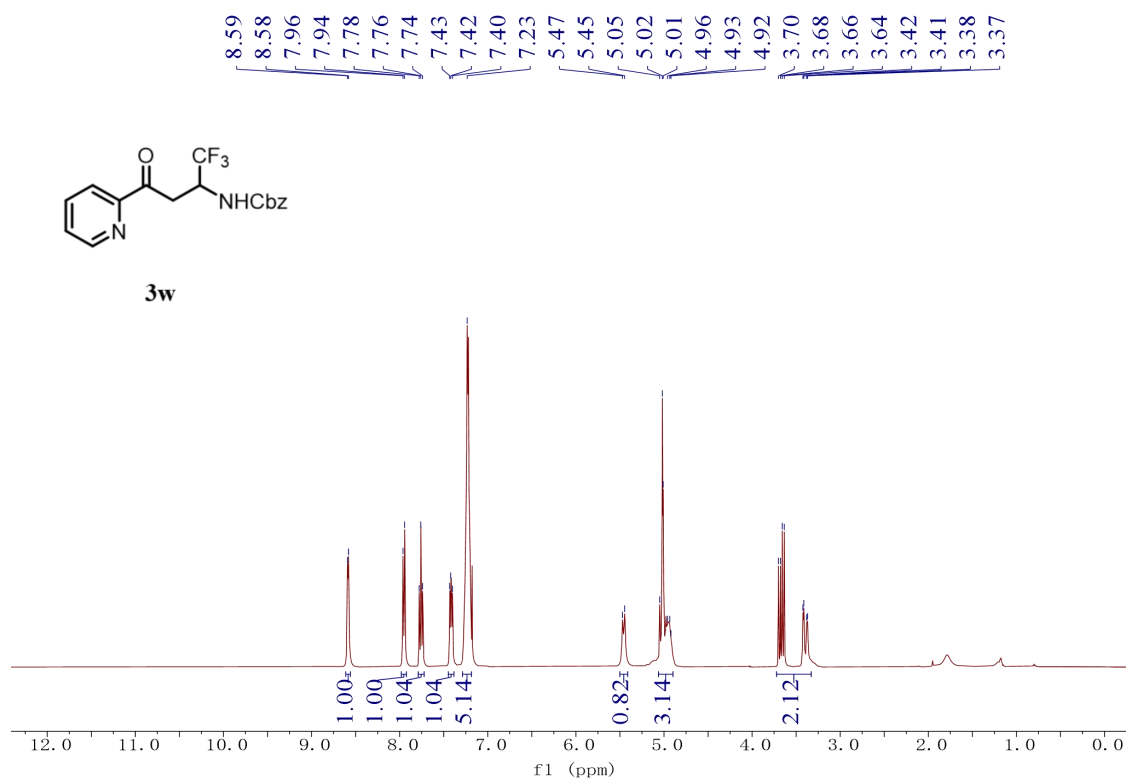
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



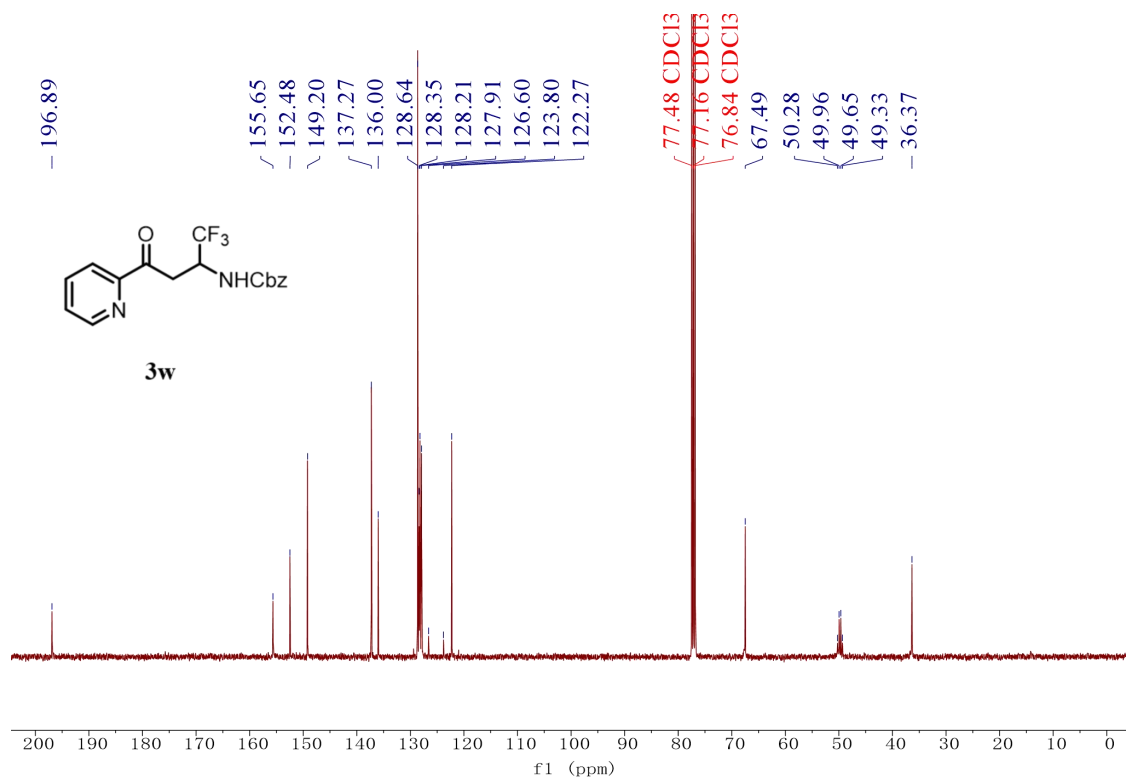
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



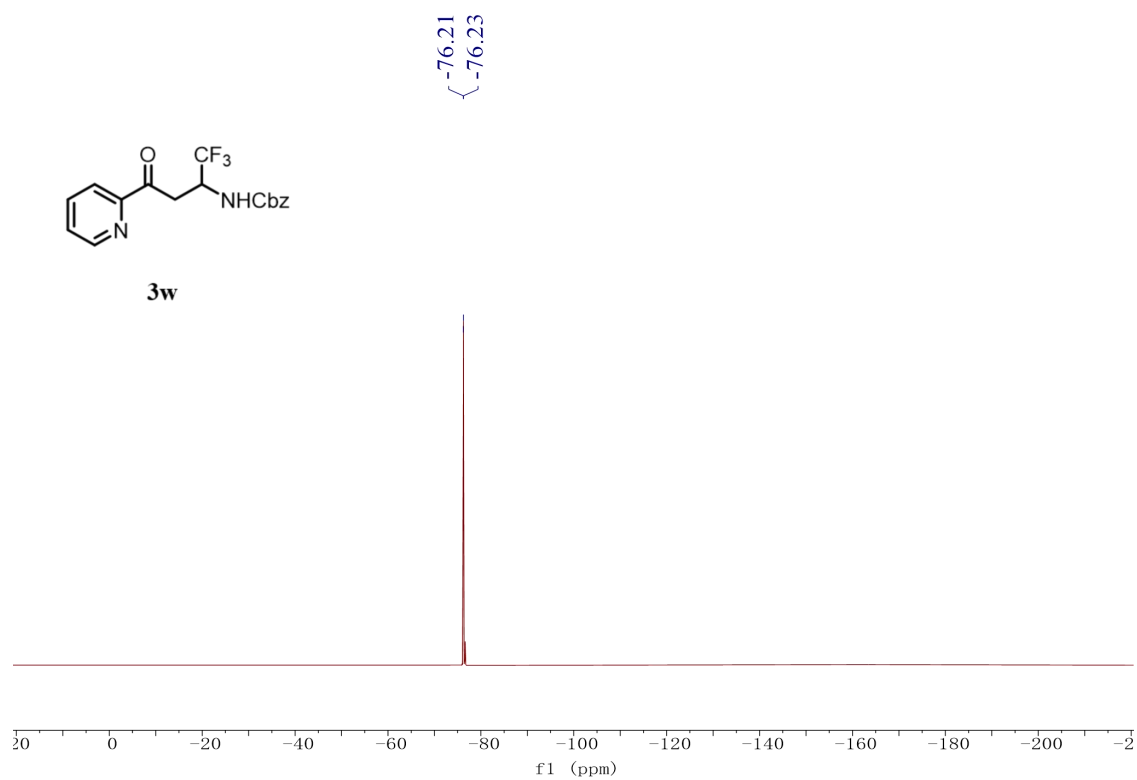
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



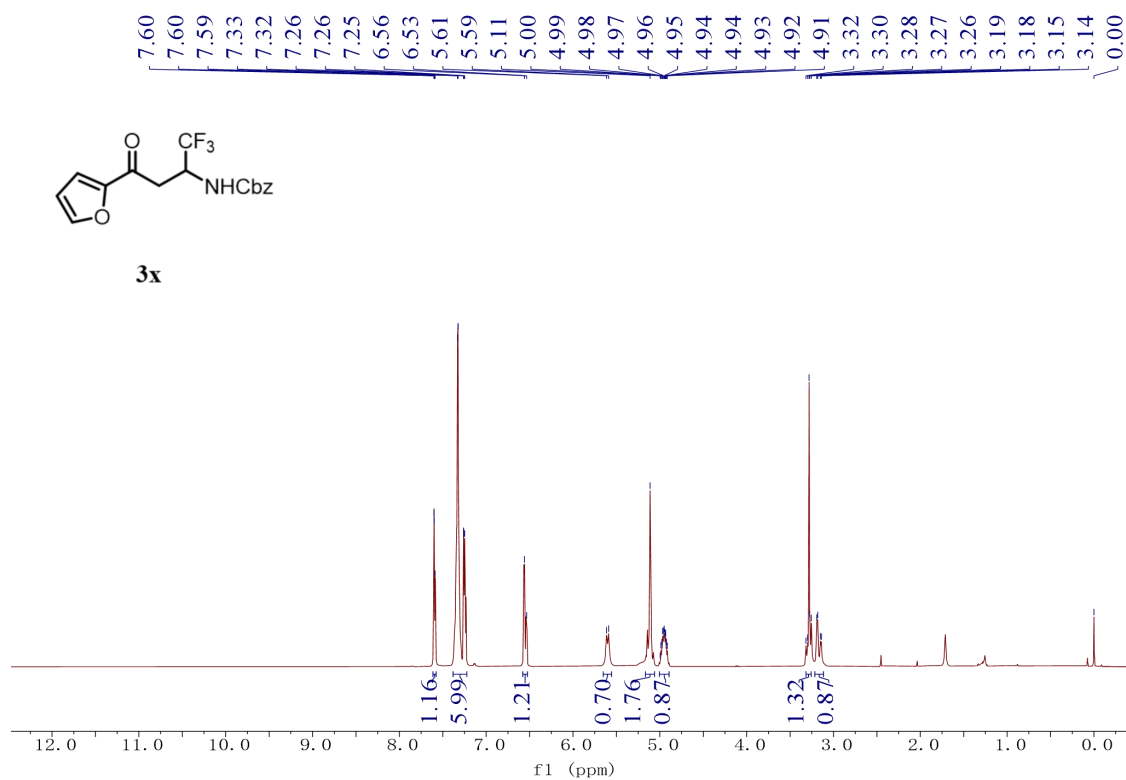
<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)



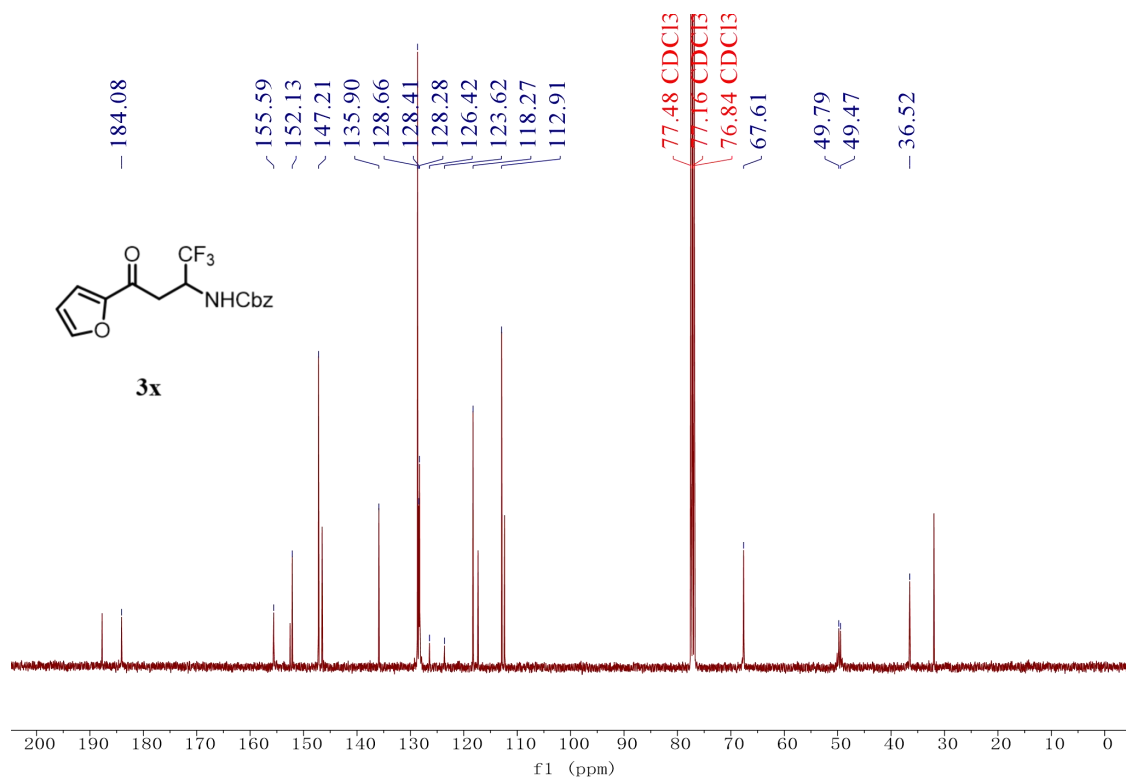
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



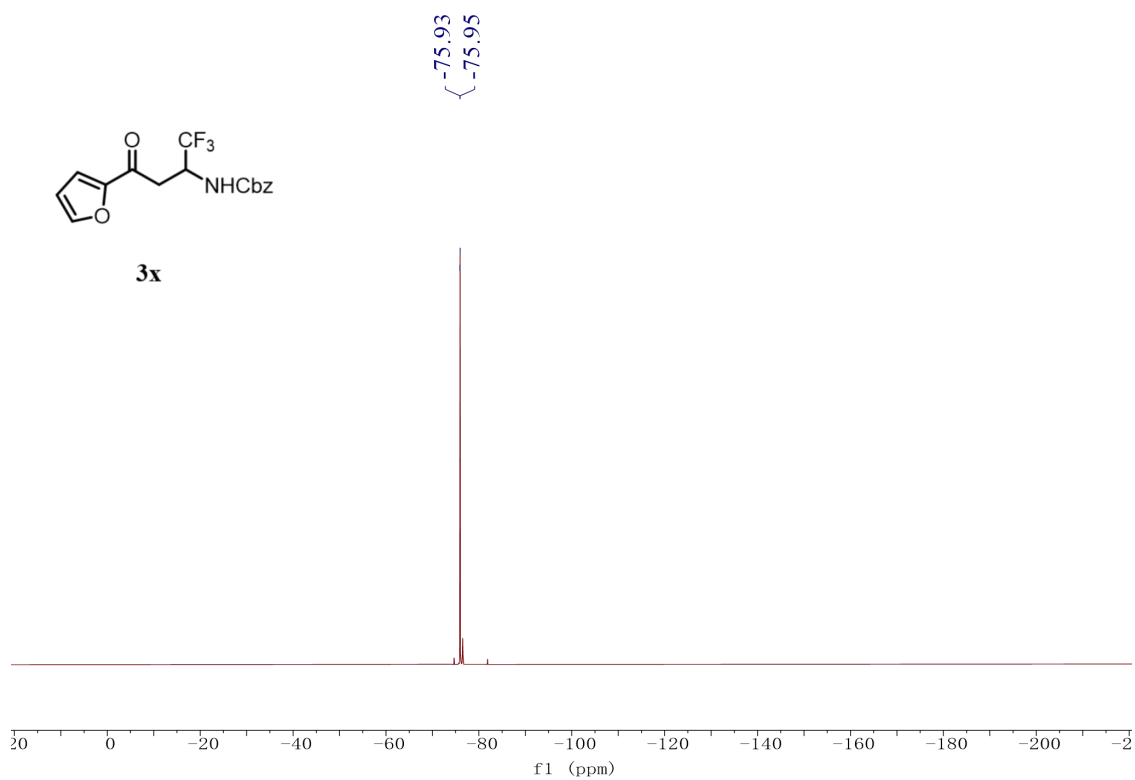
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



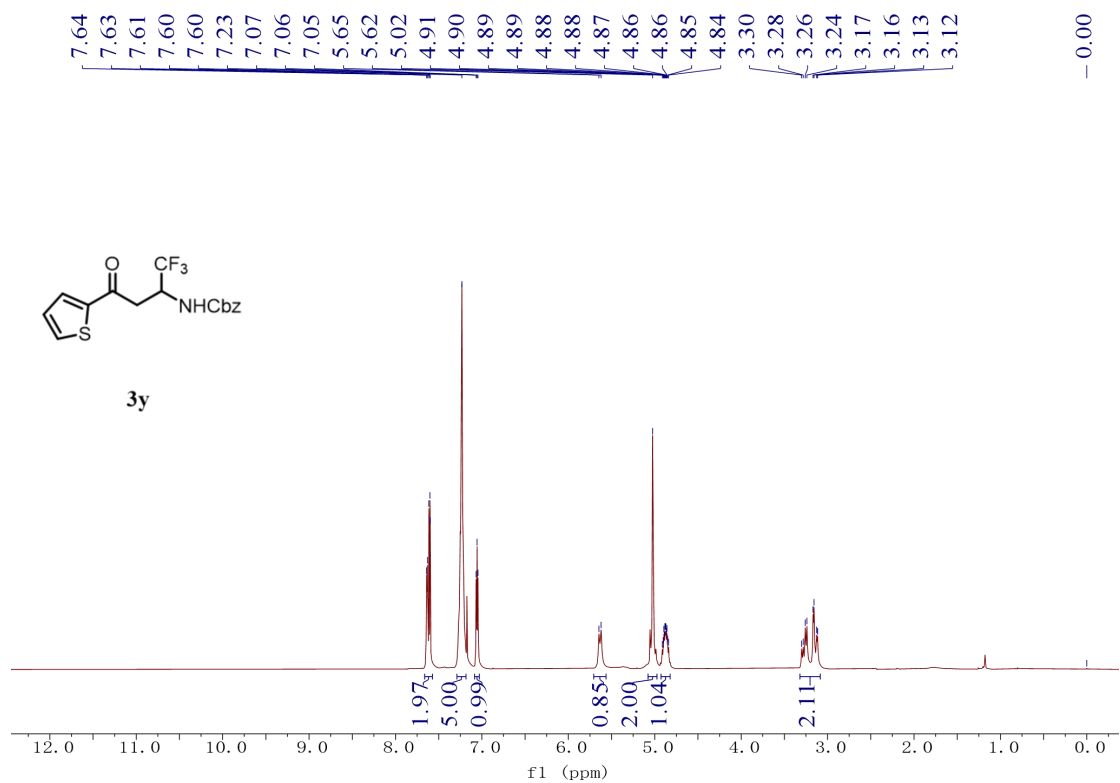
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

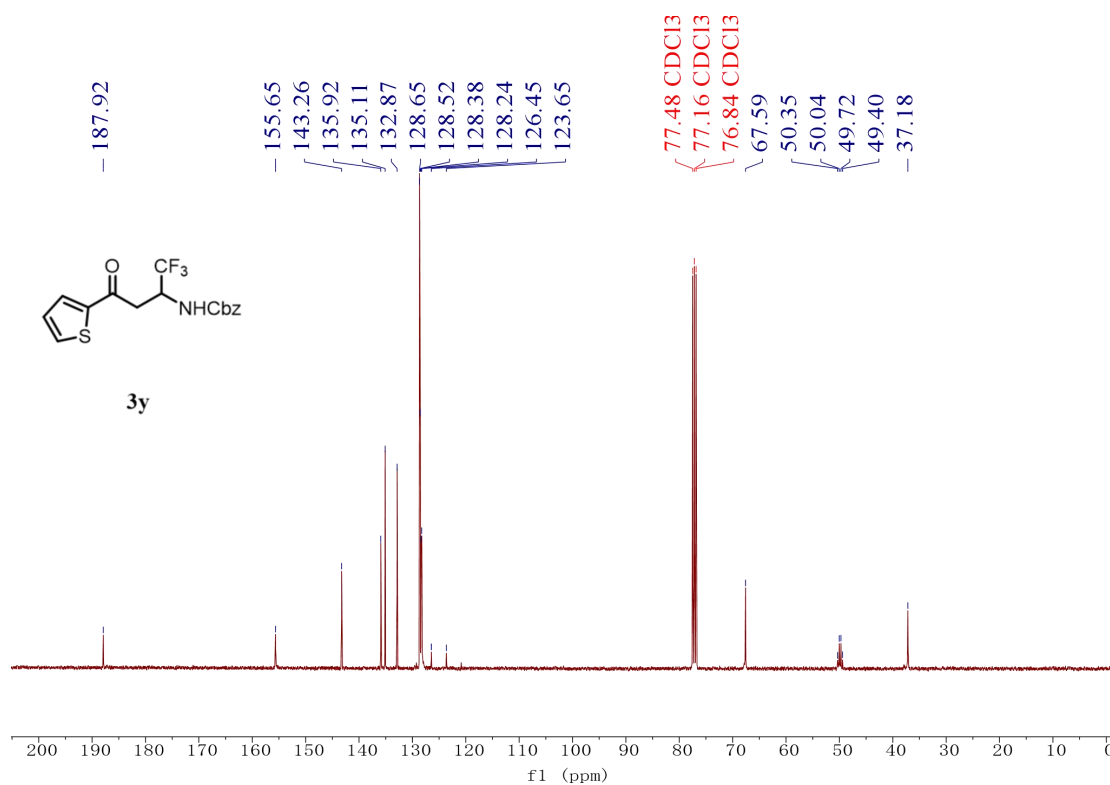


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

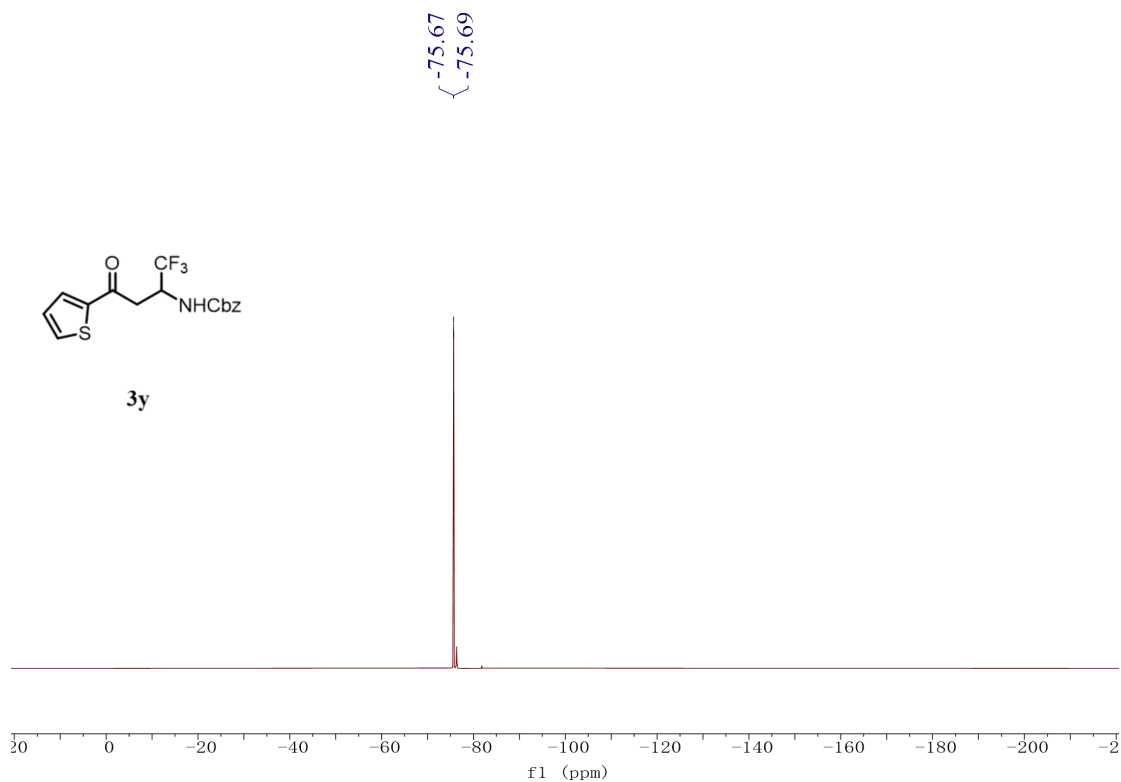




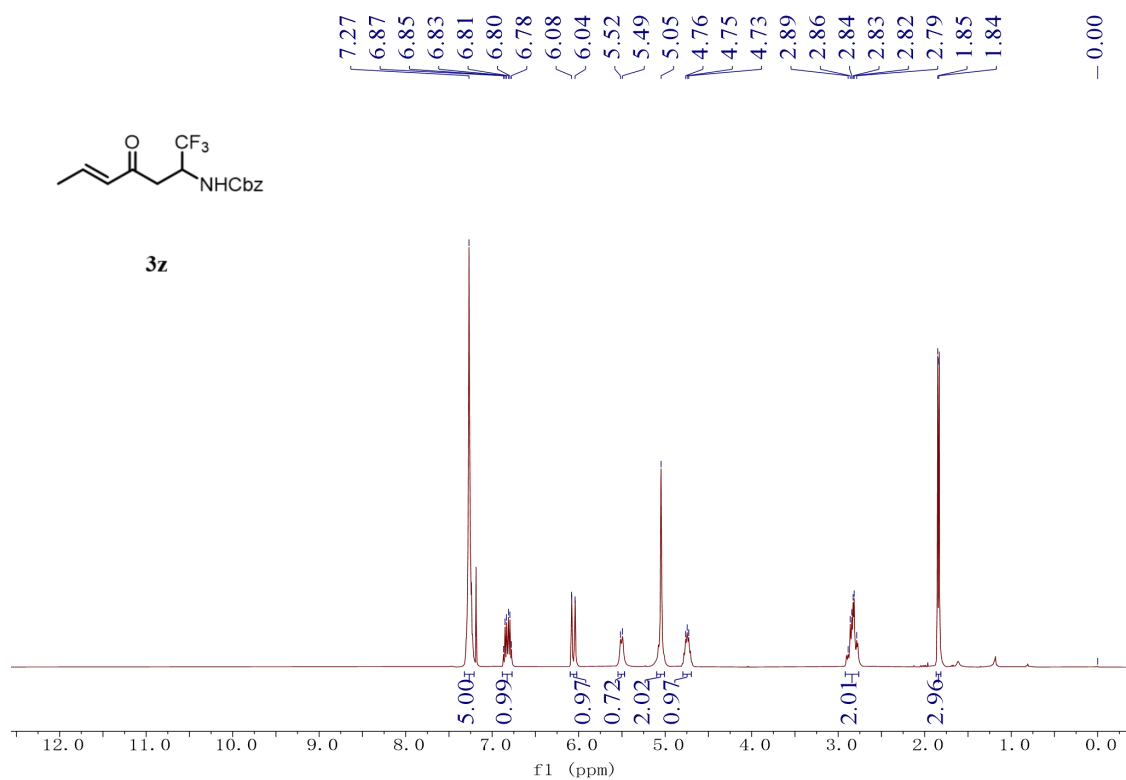
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



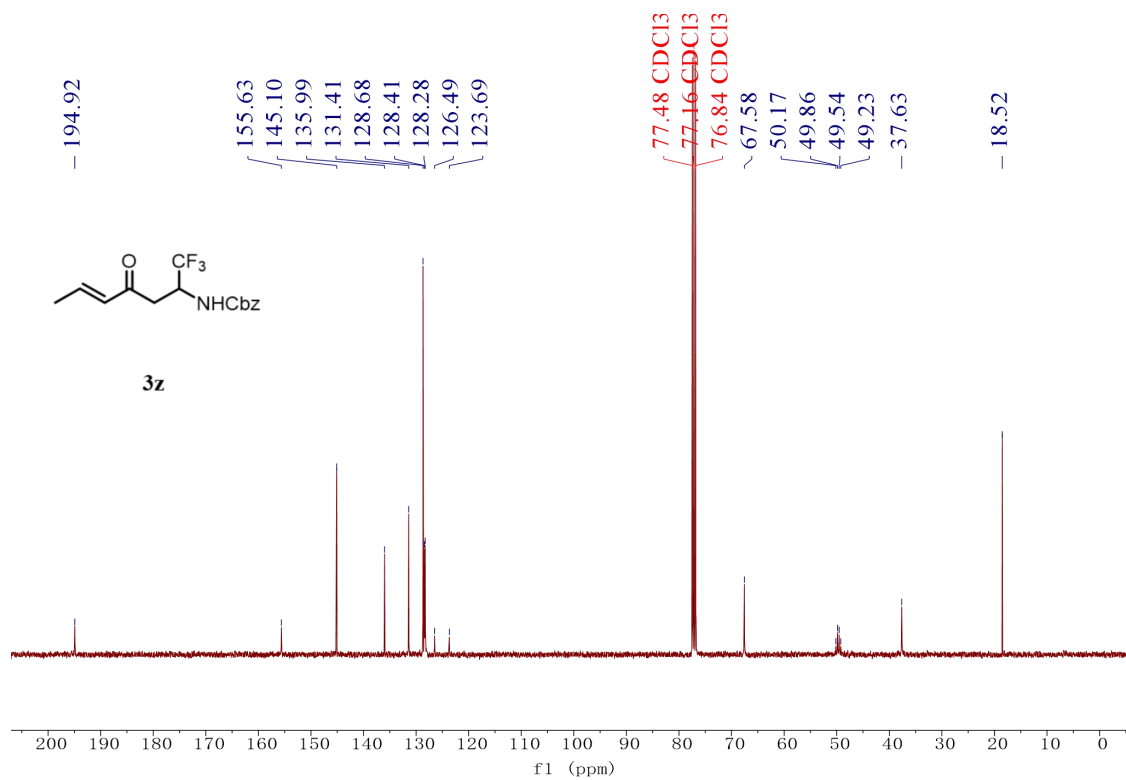
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



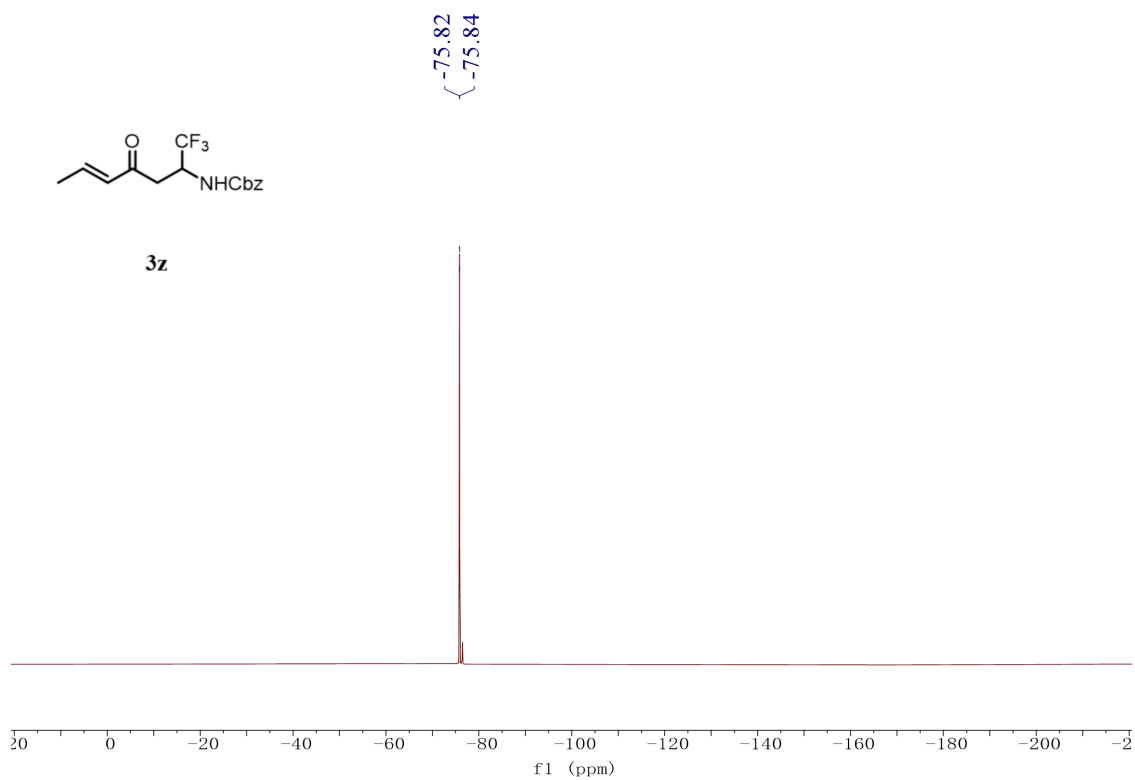
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



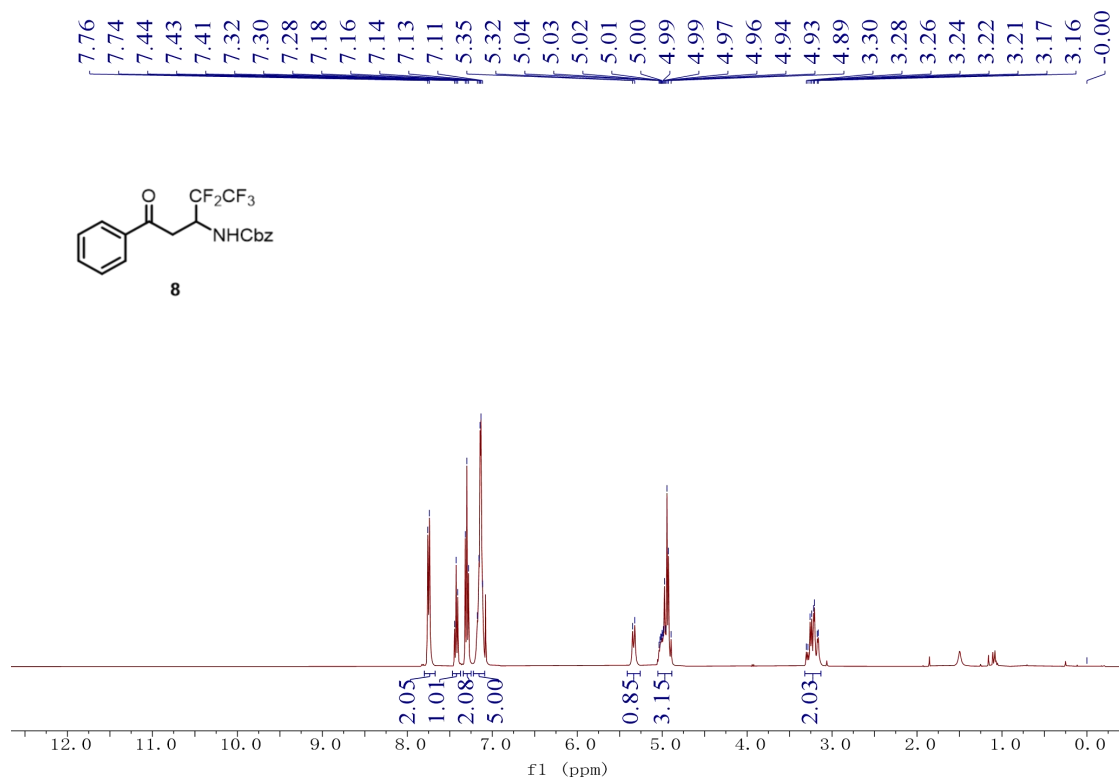
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



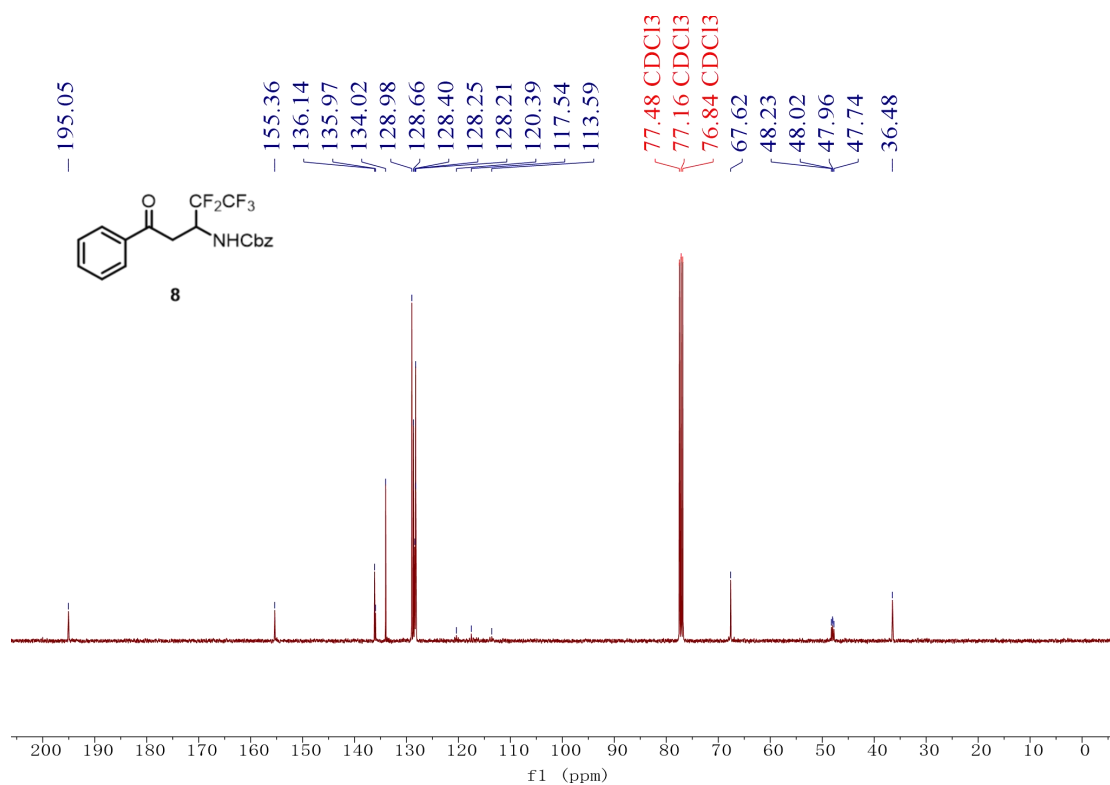
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



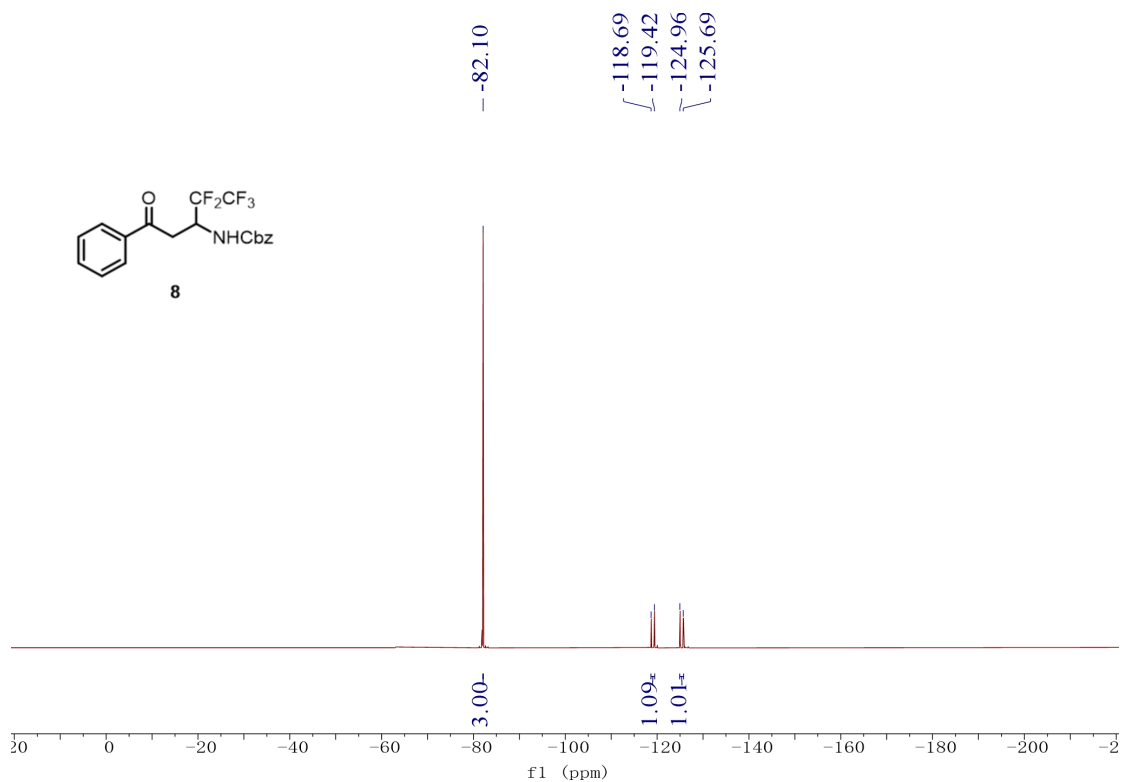
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



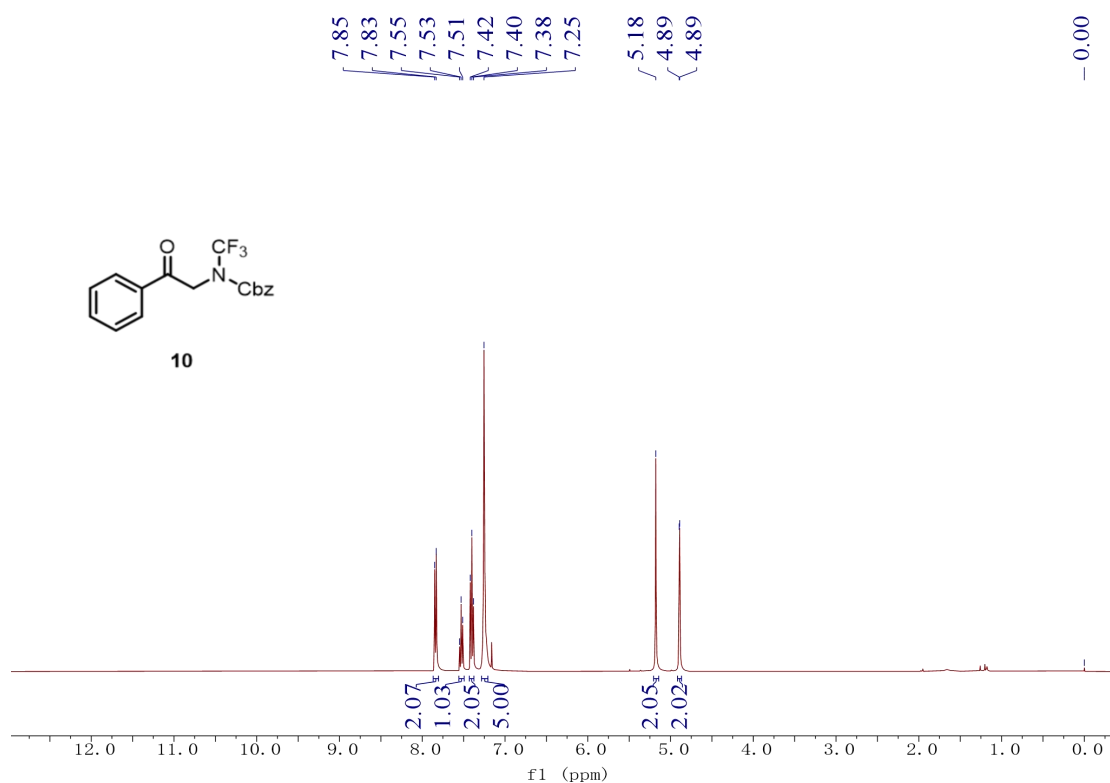
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



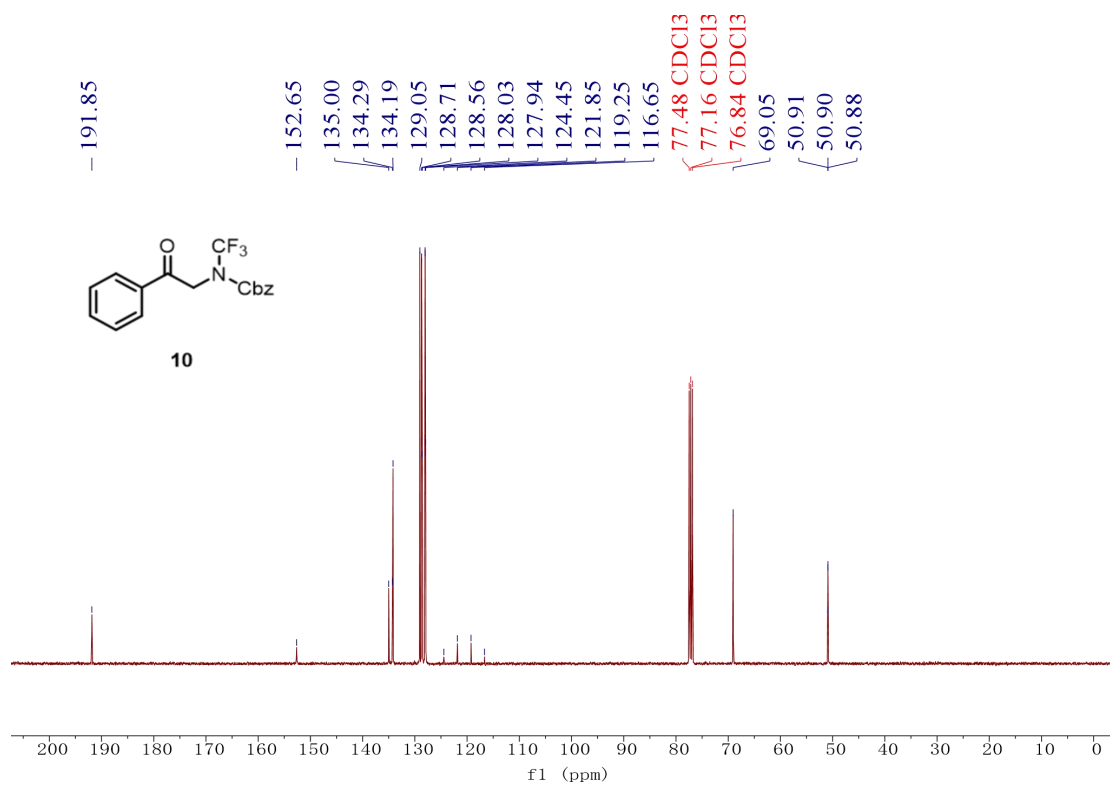
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



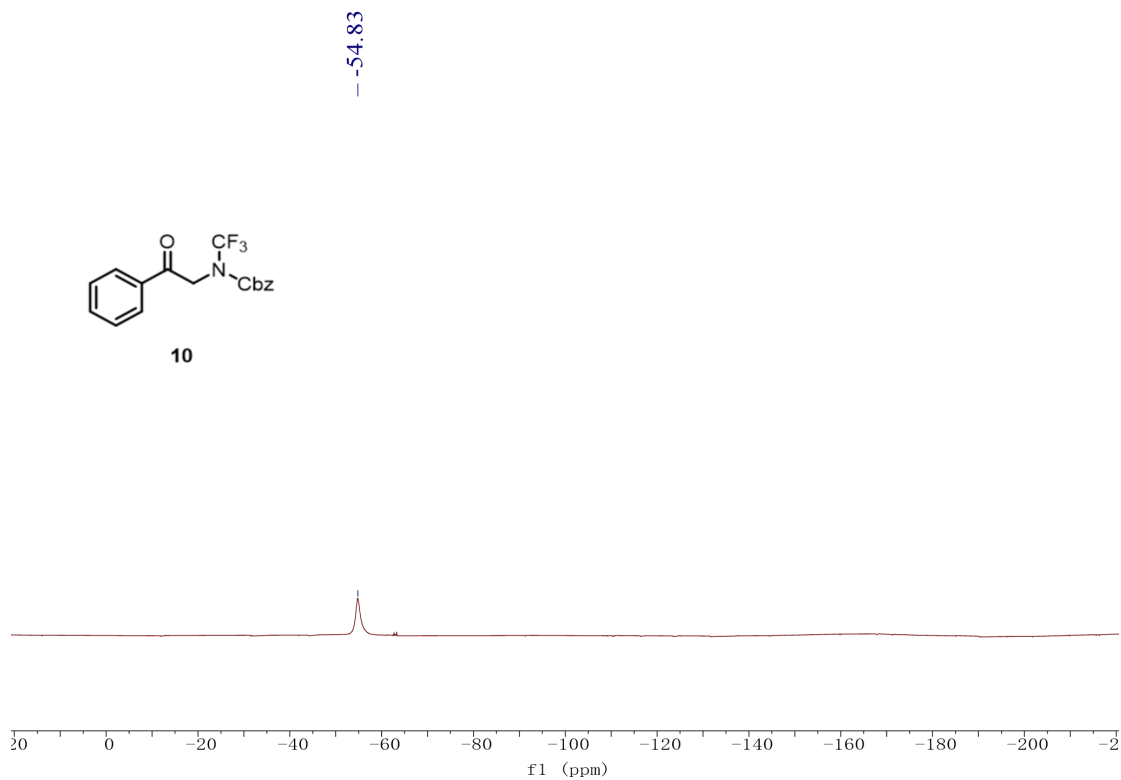
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



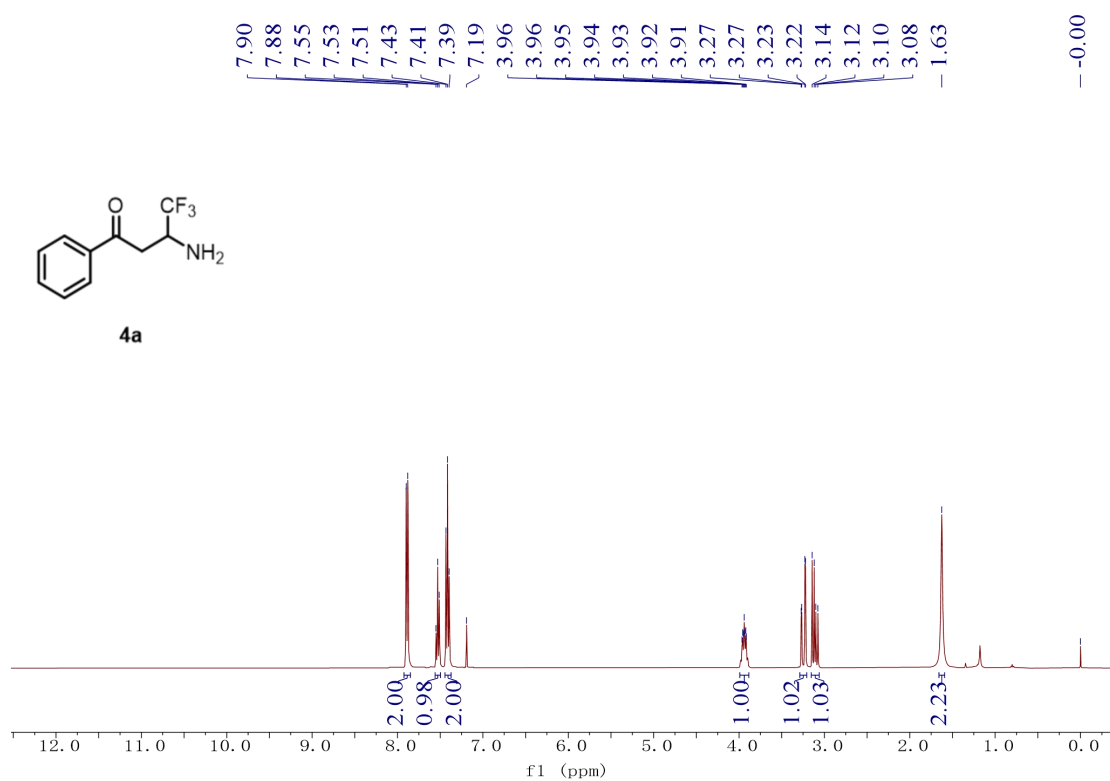
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



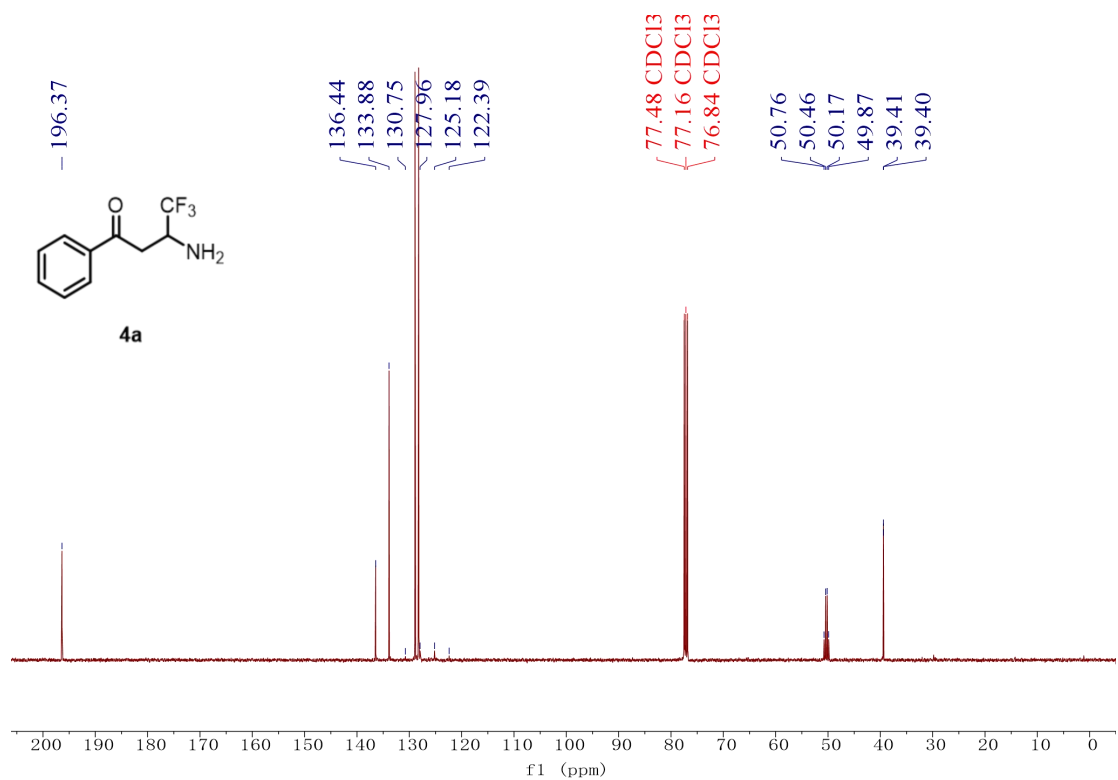
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



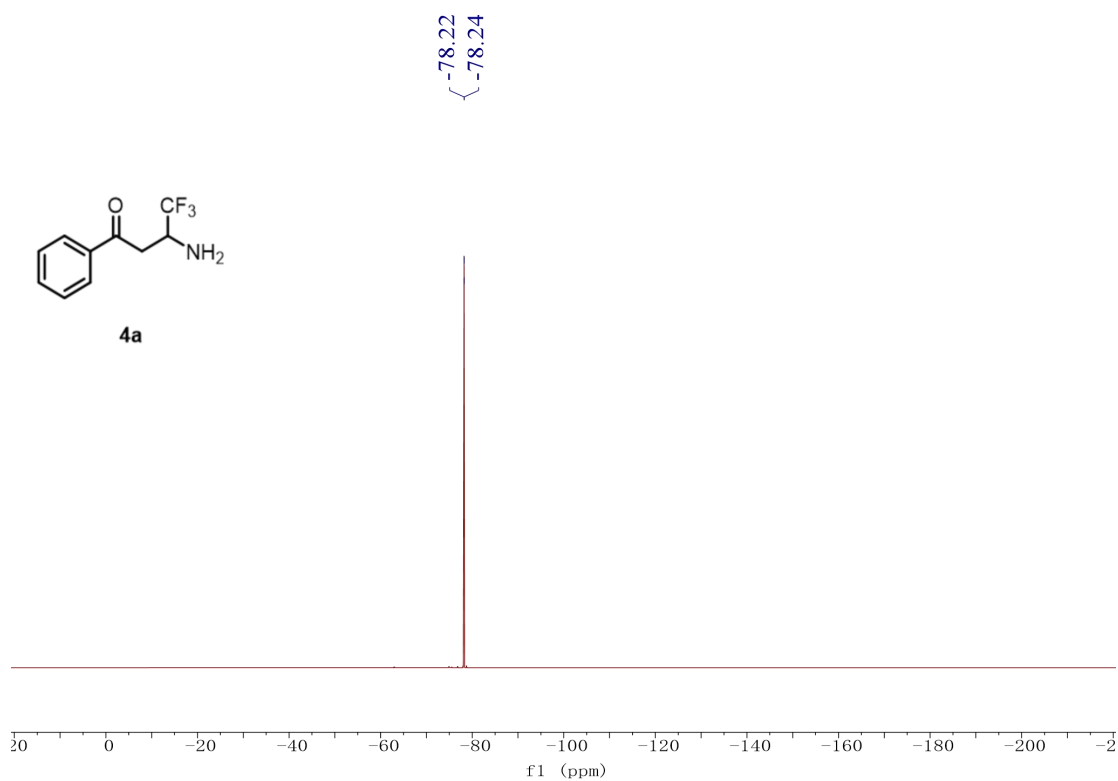
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



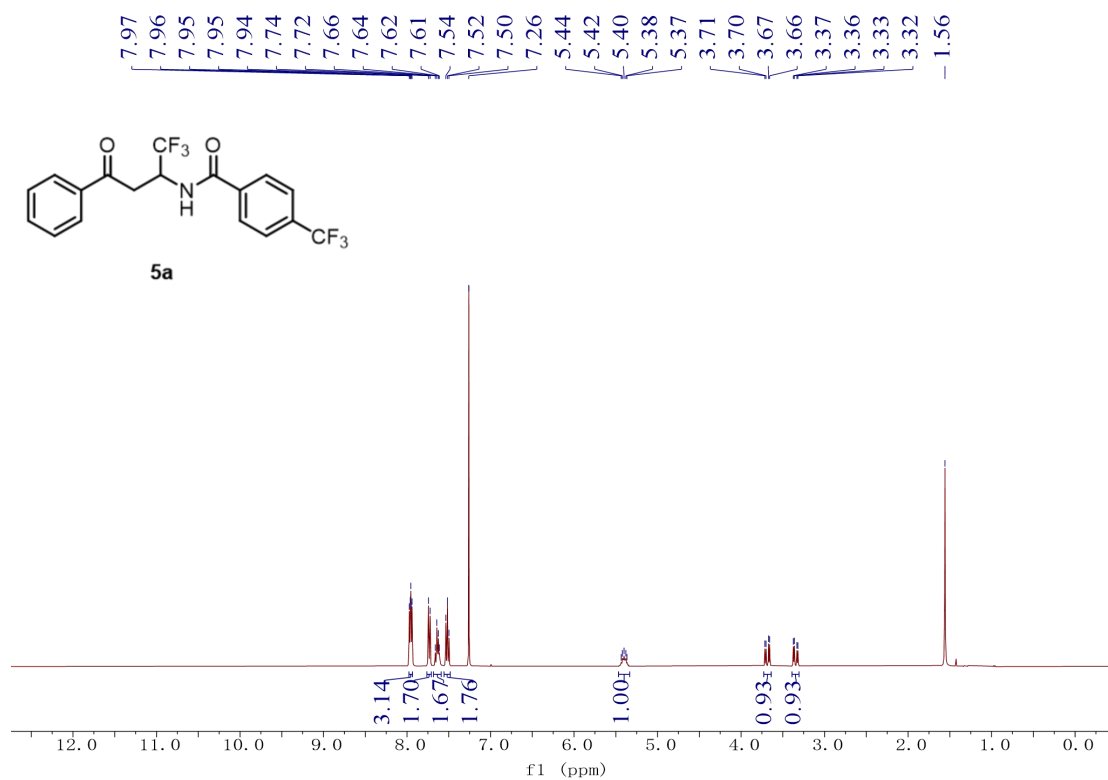
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



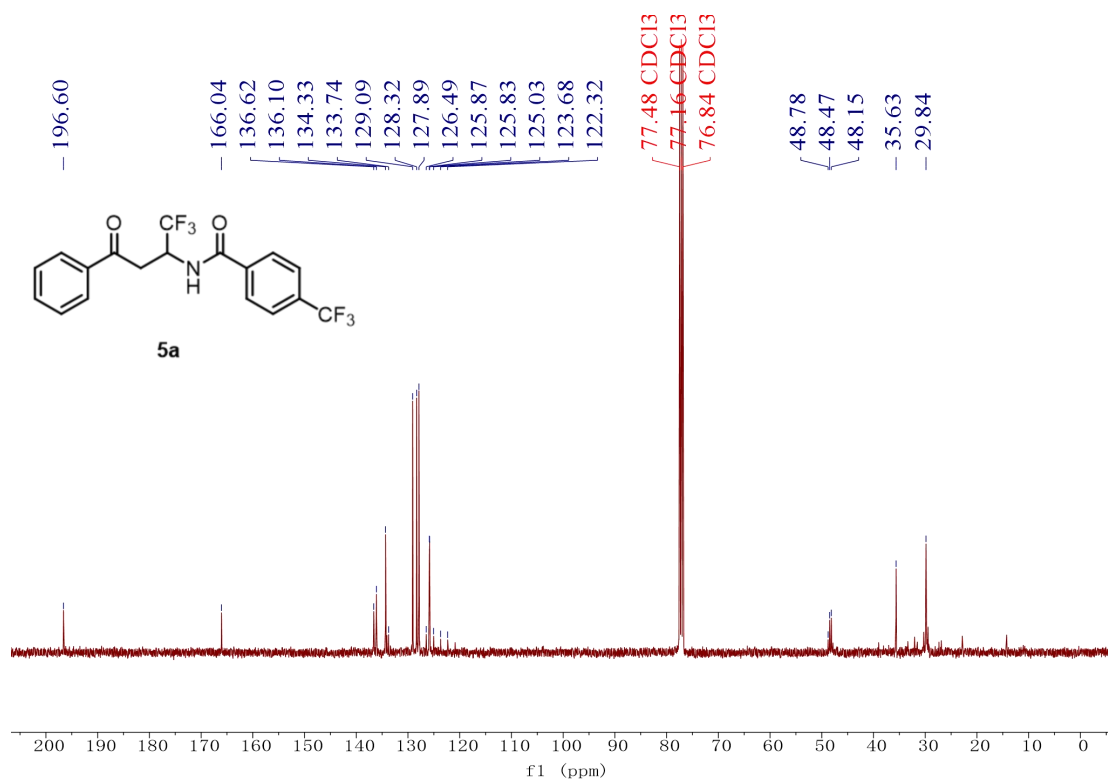
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

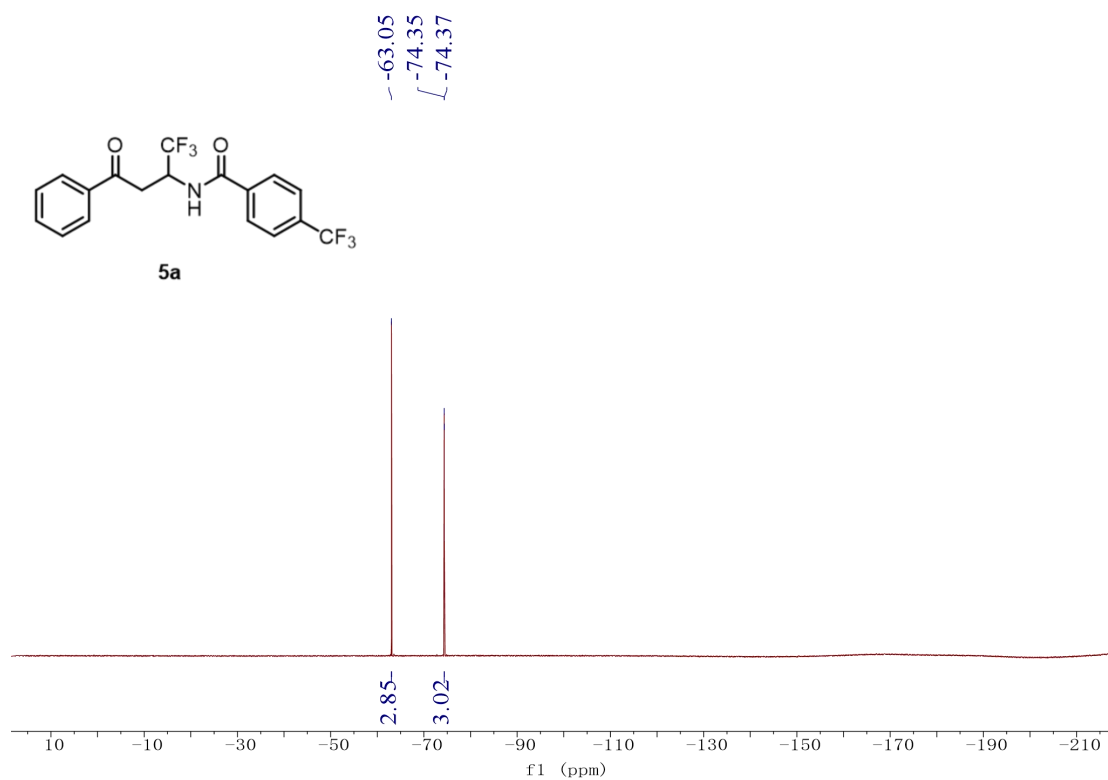


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

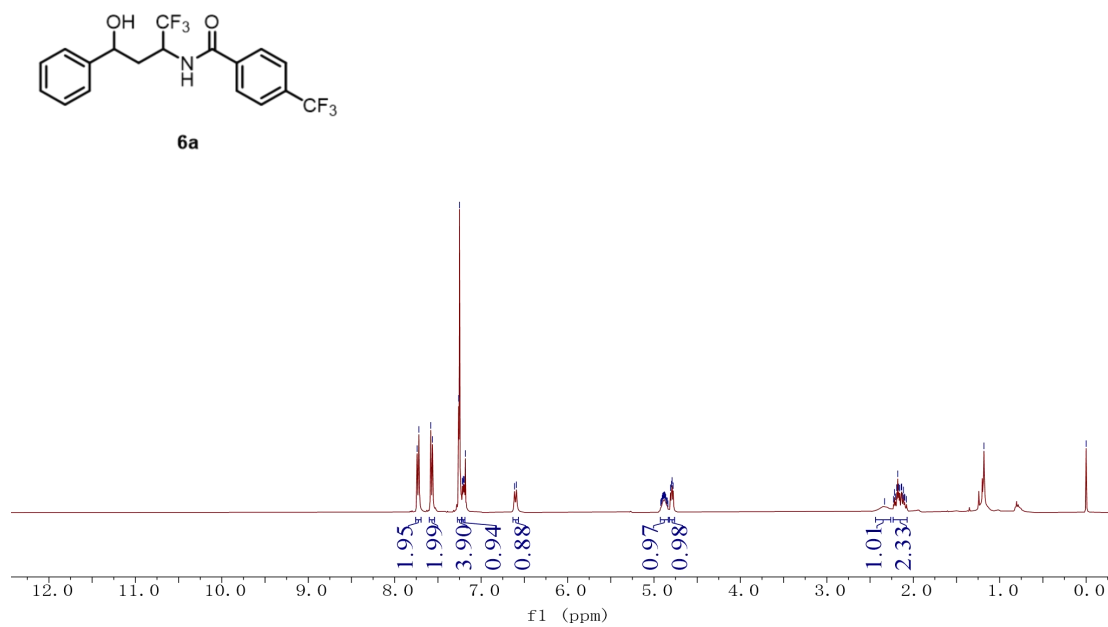


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

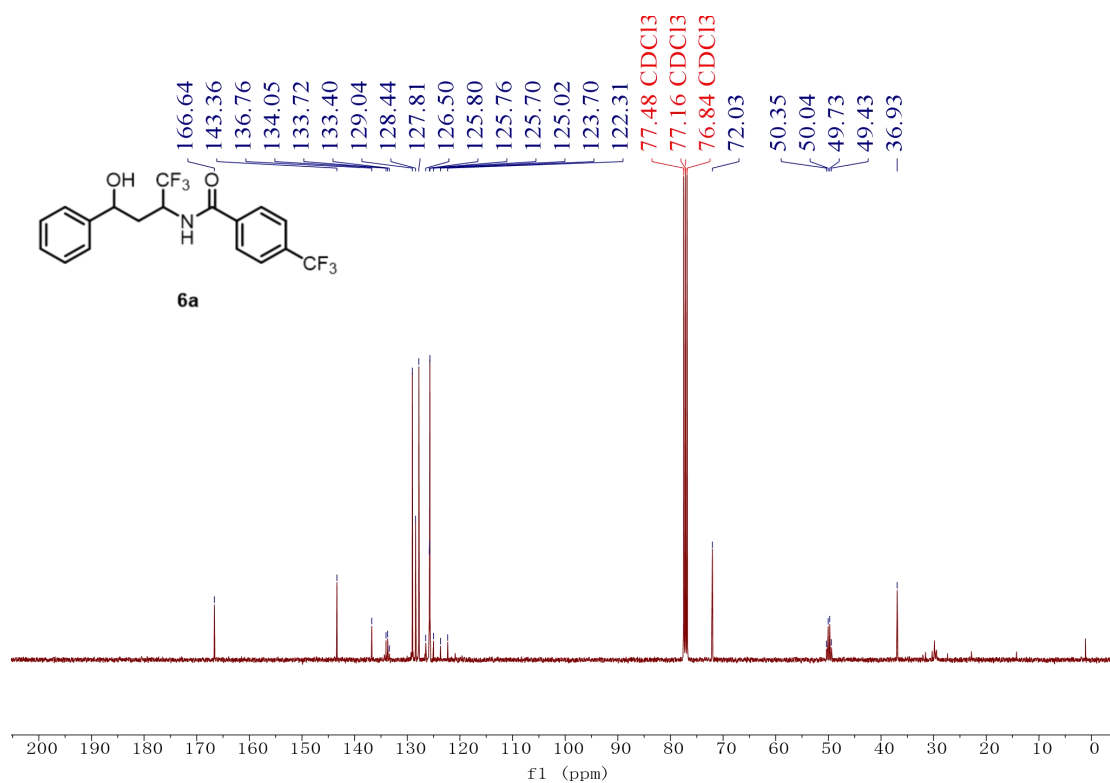




$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

