

# Supporting Information

## Chemoselective Defluorinative Amination of (Trifluoromethyl)alkenes with Amidines: Synthesis of 6- Fluoro-1,4-dihydropyrimidines

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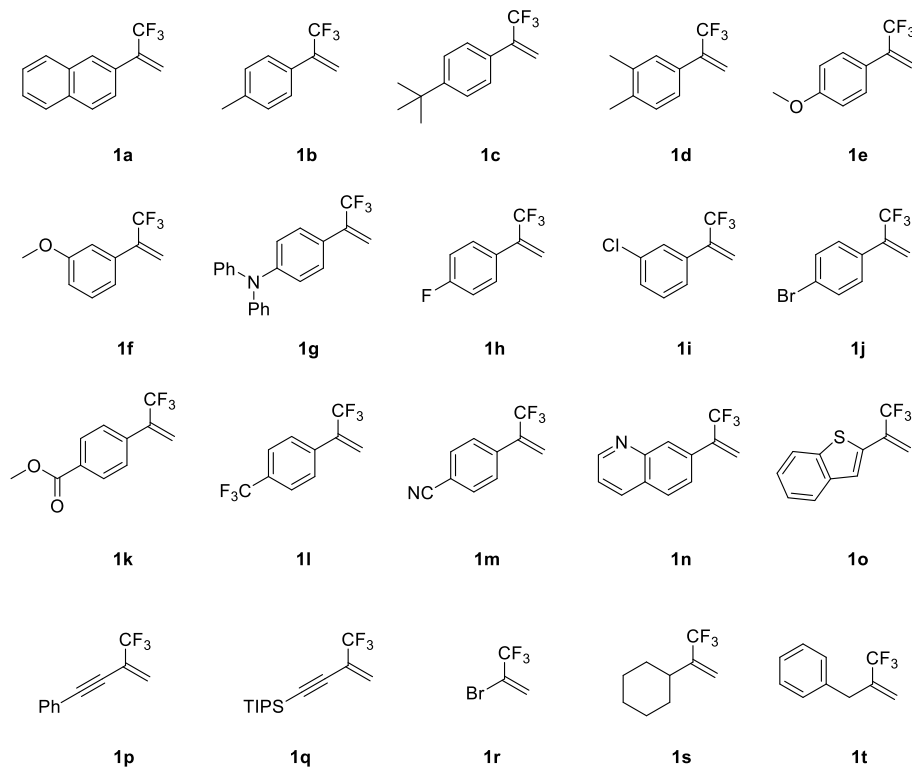
## A. General Information

Chemical shifts were reported in ppm from the solvent resonance as the internal standard ( $\text{CDCl}_3$ ,  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.16$  ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). Coupling constants were reported in Hertz (Hz).  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR data are recorded with Bruker Advance III 500 MHz. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. HRMS was carried out on a high-resolution mass spectrometer (Agilent 6210 ACPI/TOF MS). TLC was performed using commercially available 100-400 mesh silica gel plates (GF 254). Visualization was typically performed using UV light. X-ray structural analyses were conducted on a Bruker APEX-II CCD Diffractometer.

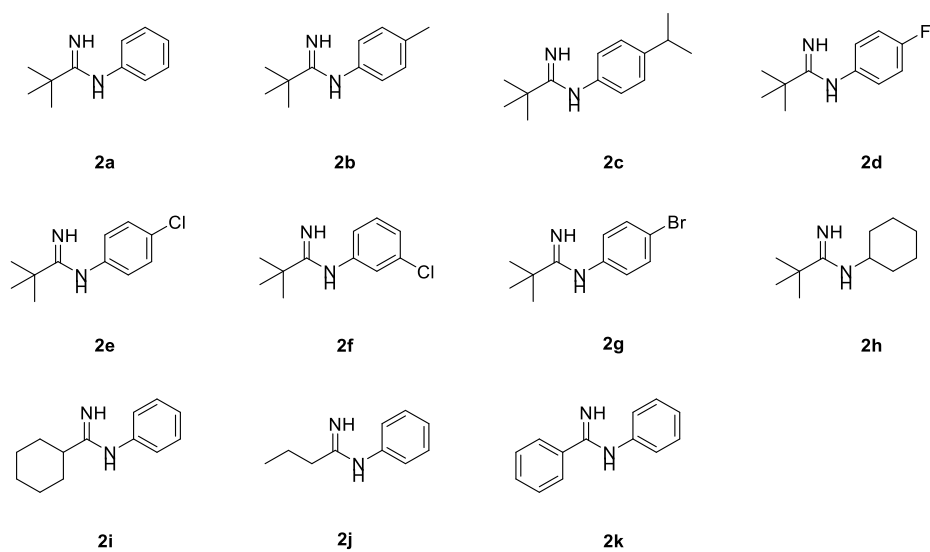
**Materials.** Commercially available reagents and solvents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200-300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures.

## B. Synthesis of (Trifluoromethyl)alkenes and *N*-arylamidine

In the scope of substrates, (trifluoromethyl)alkene **1r** was purchased directly, and (trifluoromethyl)alkenes **1a-1q**, **1s-1t** were synthesized according to the reported literatures.

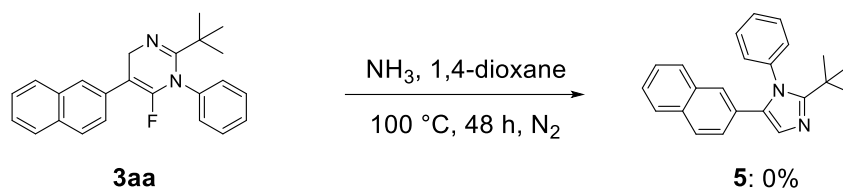


In the scope of substrates, *N*-arylamidine **2k** was purchased directly, *N*-arylamidines **2a-2j**, were synthesized according to the reported literatures.

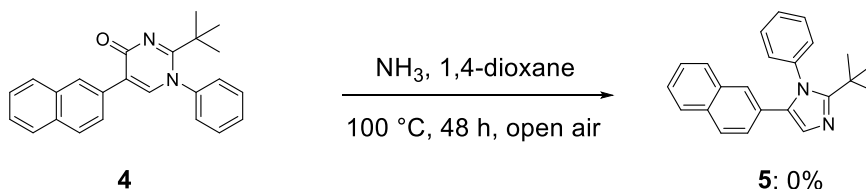


## C. Control Experiment

To a 25 mL Schlenk tube was charged with **3aa** (107.4 mg, 0.3mmol). The tube was evacuated and filled with N<sub>2</sub>, and NH<sub>3</sub> (0.4 M) solution in 1,4-dioxane (3 mL) was added. The mixture was sealed and vigorously stirred at 100 °C for 48 h. Then the mixture was cooled to room temperature, quenched with H<sub>2</sub>O (15 mL), extracted with EtOAc (15 mL × 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The yield was determined by <sup>1</sup>H NMR spectroscopy of the crude product.



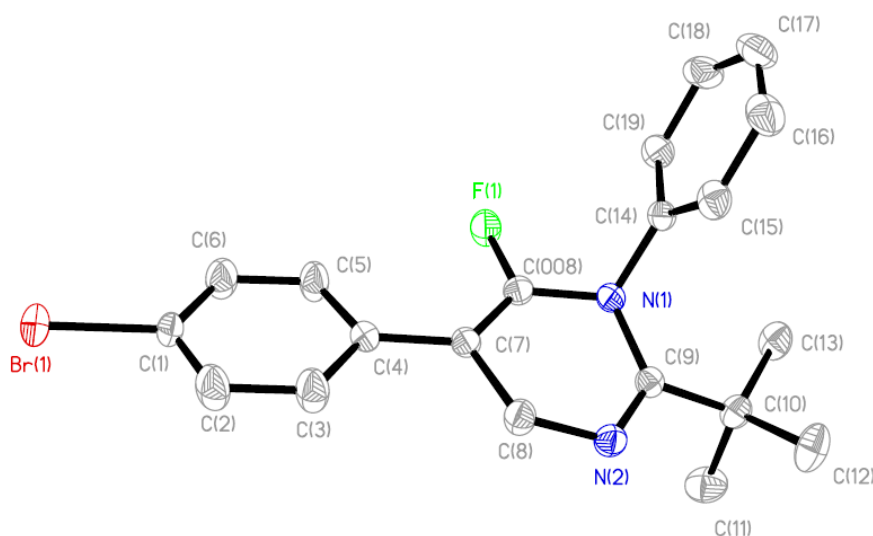
To a 25 mL over-dried Schlenk tube was charged with **4** (106.2 mg, 0.3mmol) and 1,4-dioxane (3 mL). The mixture was sealed and vigorously stirred at 100 °C for 48 h under air. Then the mixture was cooled to room temperature, quenched with H<sub>2</sub>O (15 mL), extracted with EtOAc (15 mL × 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The yield was determined by <sup>1</sup>H NMR spectroscopy of the crude product.



## D. X-ray Crystallographic Data

The preparation of crystal of **3ja**

The obtained compound **3ja** (100.4 mg, 65% yield) was dissolved in the appropriate amount of CH<sub>2</sub>Cl<sub>2</sub> in a test tube at room temperature. Then, sealed the test tube with a rubber plug. The colorless crystal of **3ja** was formed after part of solvent was volatilized. The X-ray crystallographic structures for **3ja** ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2475106.

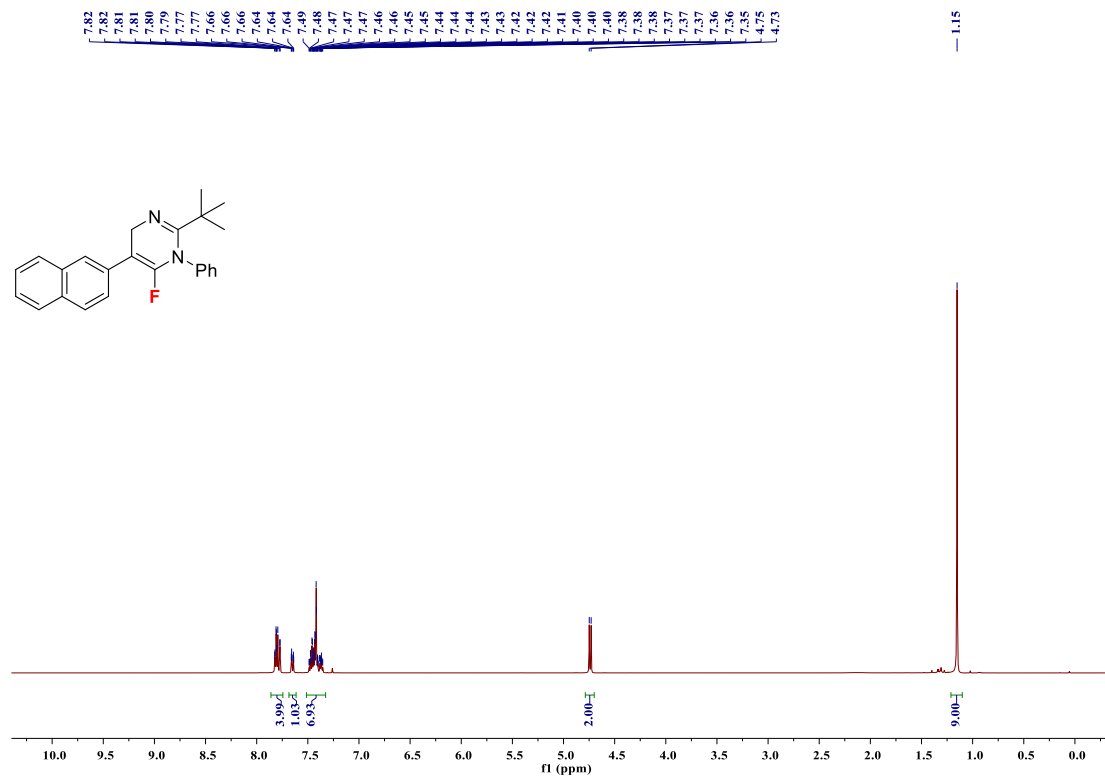


Empirical formula	C <sub>40</sub> H <sub>40</sub> Br <sub>2</sub> F <sub>2</sub> N <sub>4</sub>
Formula weight	774.58
Temperature	293(2) K
Crystal system, Space group	Triclinic, P-1
Unit cell dimensions	a = 5.8689(4) Å    alpha = 92.300(6) deg. b = 11.6621(10) Å    beta = 90.755(6) deg. c = 12.8743(10) Å    gamma = 93.448(6) deg.
Volume	878.75(12) Å <sup>3</sup>
Z	1
ρ <sub>calc</sub> /cm <sup>3</sup>	1.464
μ	3.290 mm <sup>-1</sup>
F(000)	396.0
Crystal size	0.2 × 0.1 × 0.1 mm <sup>3</sup>

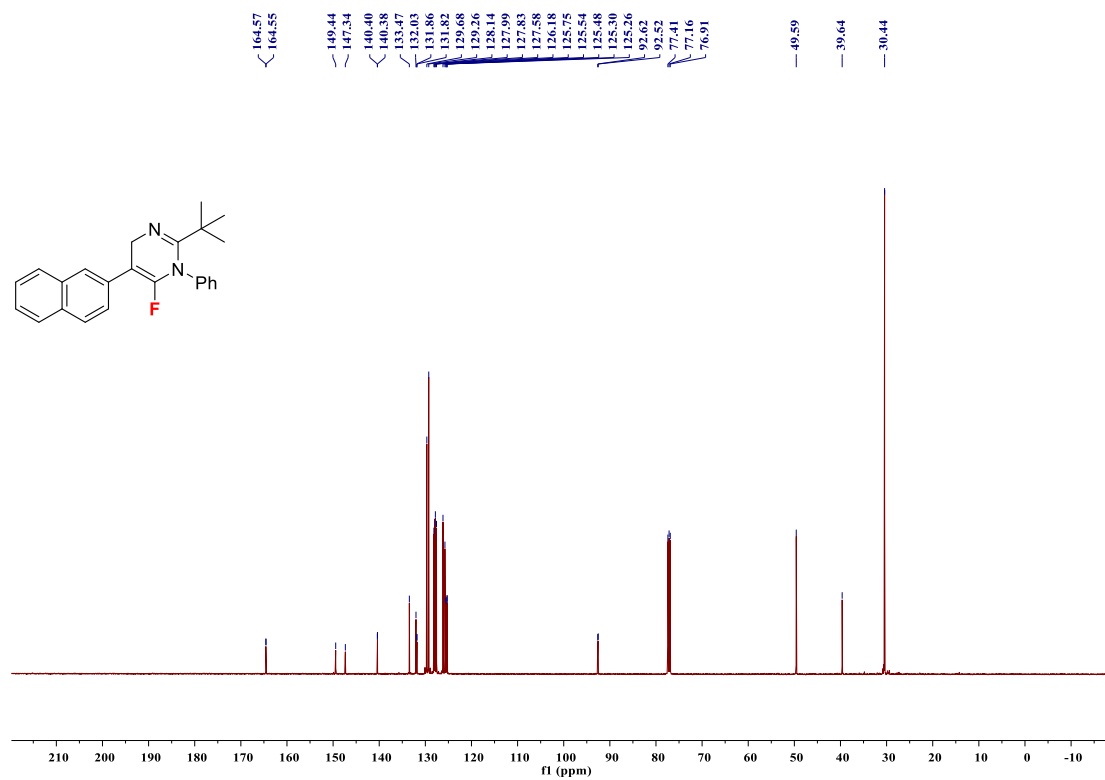
Radiation	Cu Ka ( $\lambda = 1.54184$ )
Theta range for data collection	6.872 to 142.102 deg.
Index ranges	$-4 \leq h \leq 7$ , $-14 \leq k \leq 13$ , $-15 \leq l \leq 15$
Reflections collected	5372
Independent reflections	3312 [ $R_{\text{int}} = 0.0499$ , $R_{\text{sigma}} = 0.0691$ ]
Data/restraints/parameters	3312/0/221
Goodness-of-fit on $F^2$	1.041
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0511$ , $wR_2 = 0.1377$
Final R indexes [all data]	$R_1 = 0.0588$ , $wR_2 = 0.1501$

## E. NMR Spectrum of New Compounds

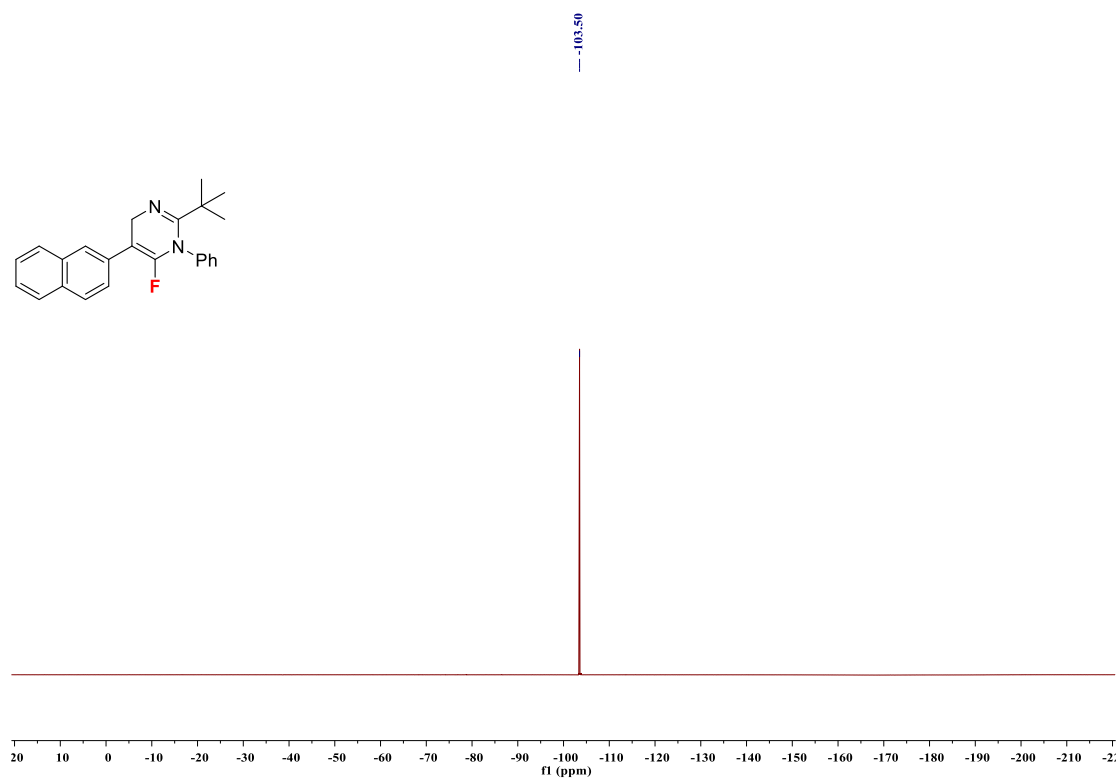
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3aa



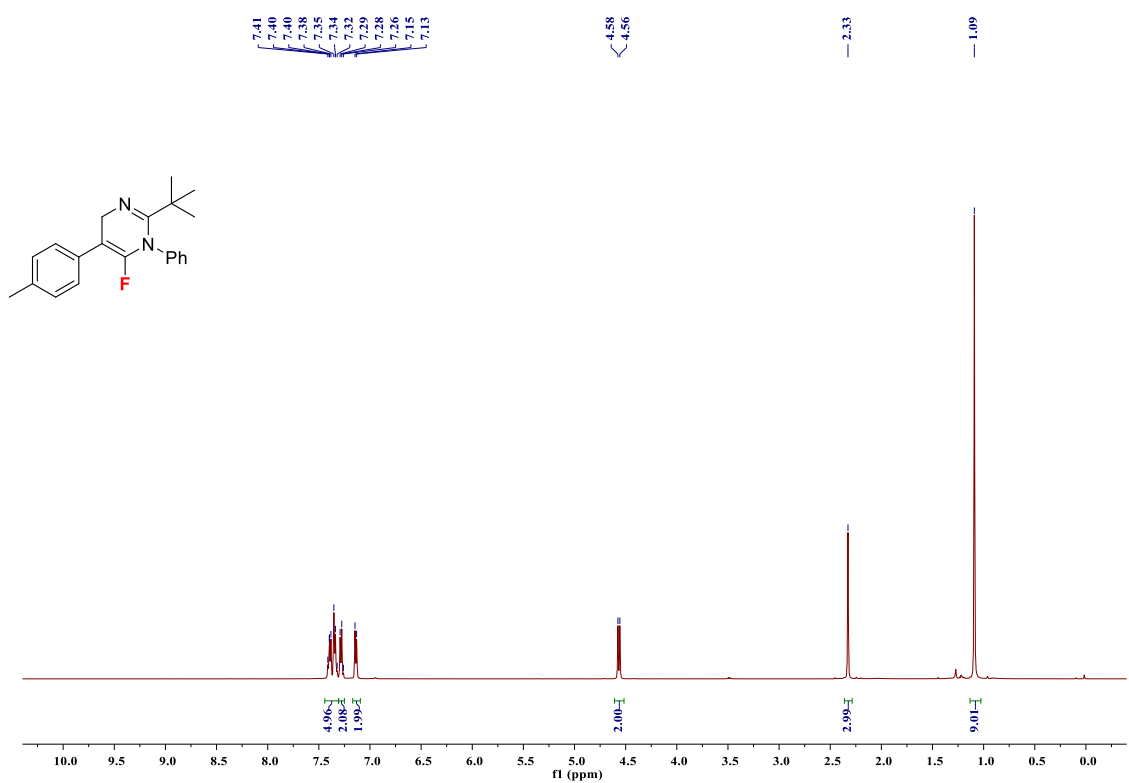
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3aa



**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) Spectrum for 3aa**

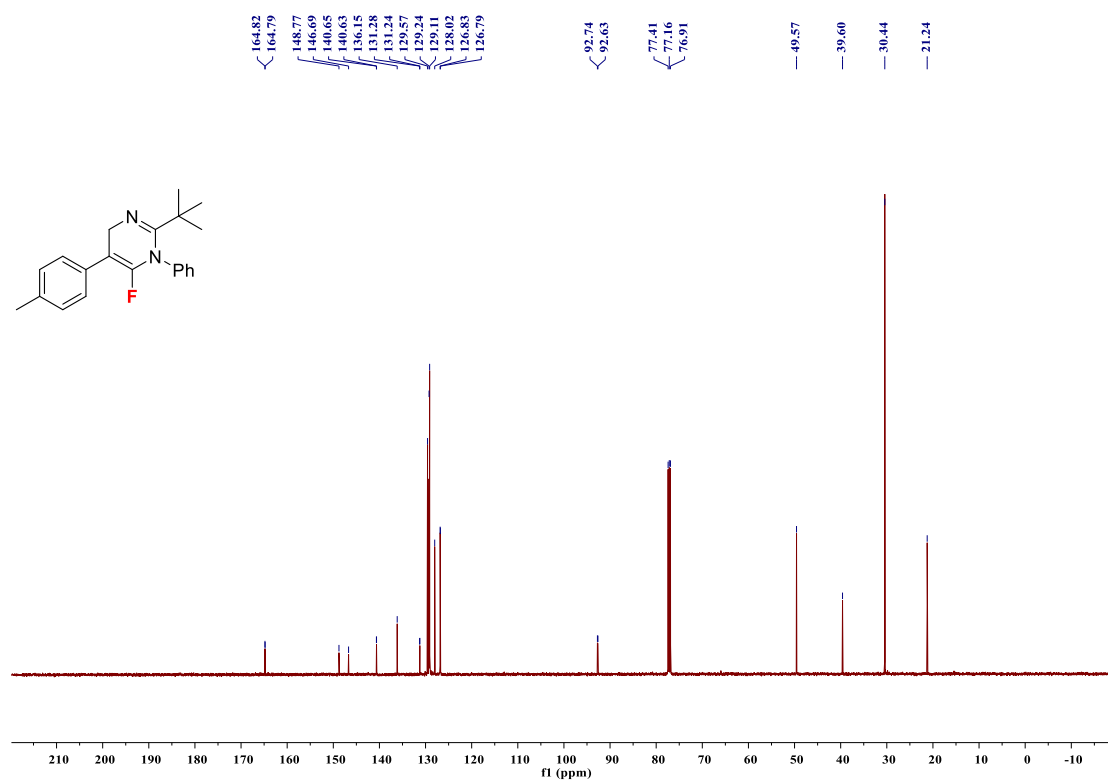


**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum for 3ba**

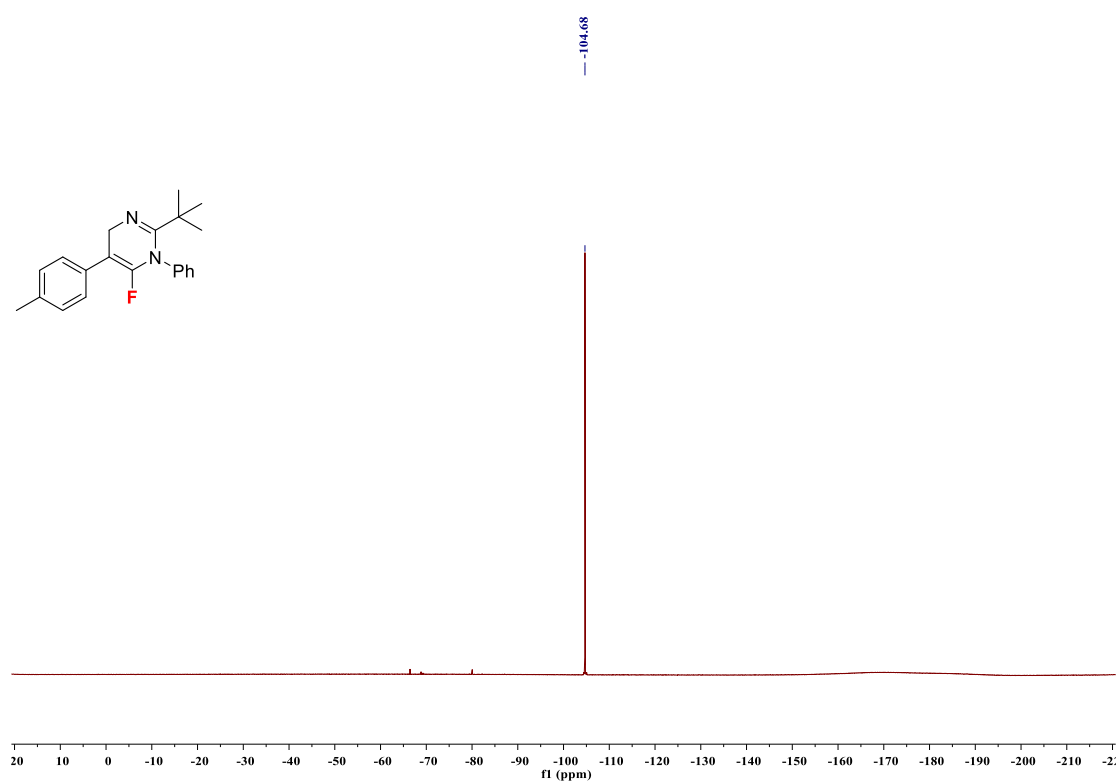




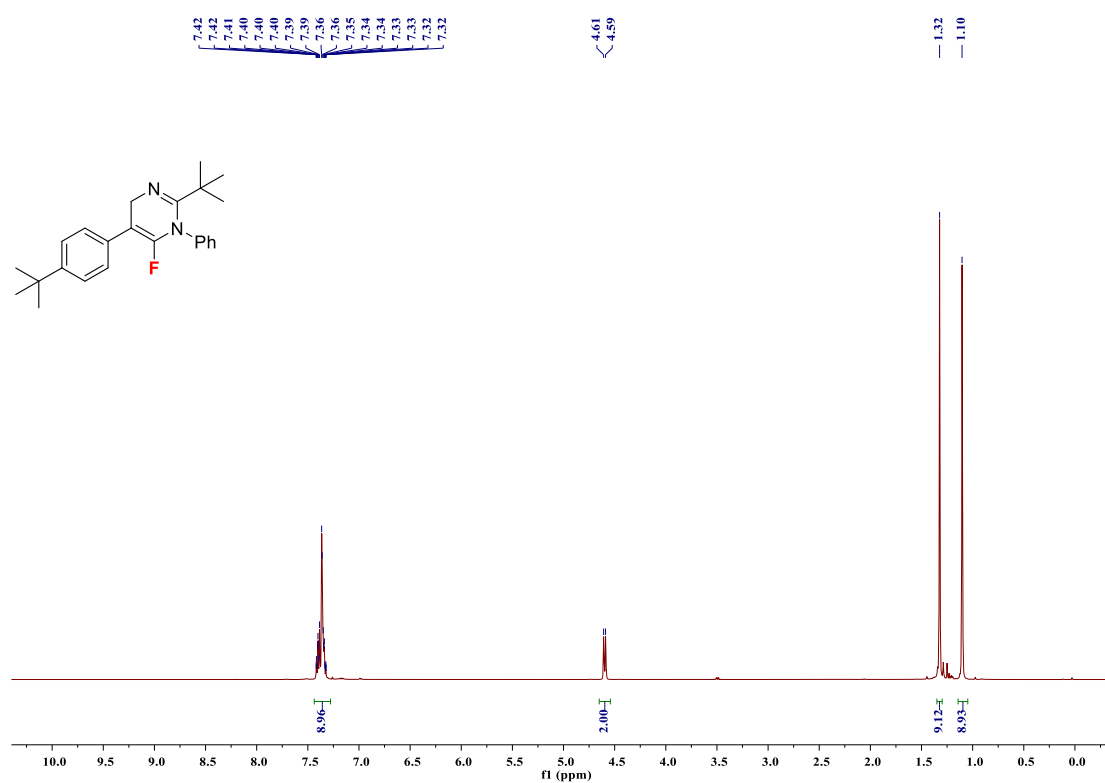
**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) Spectrum for 3ba**



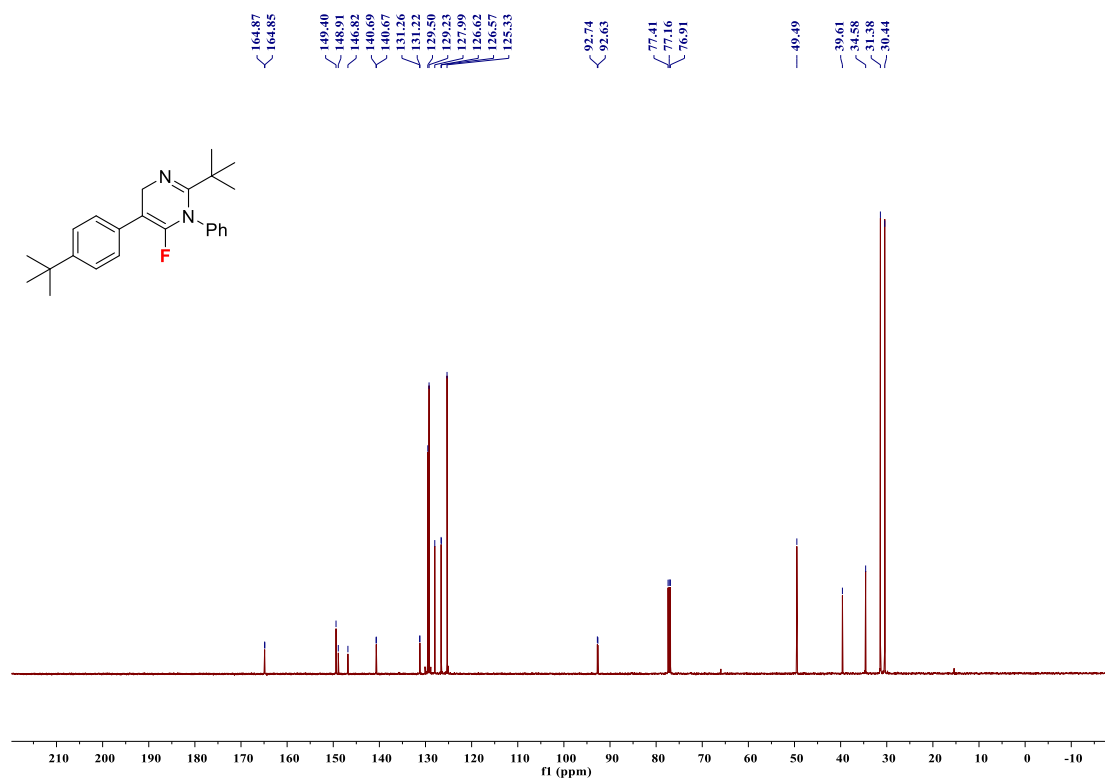
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) Spectrum for 3ba**



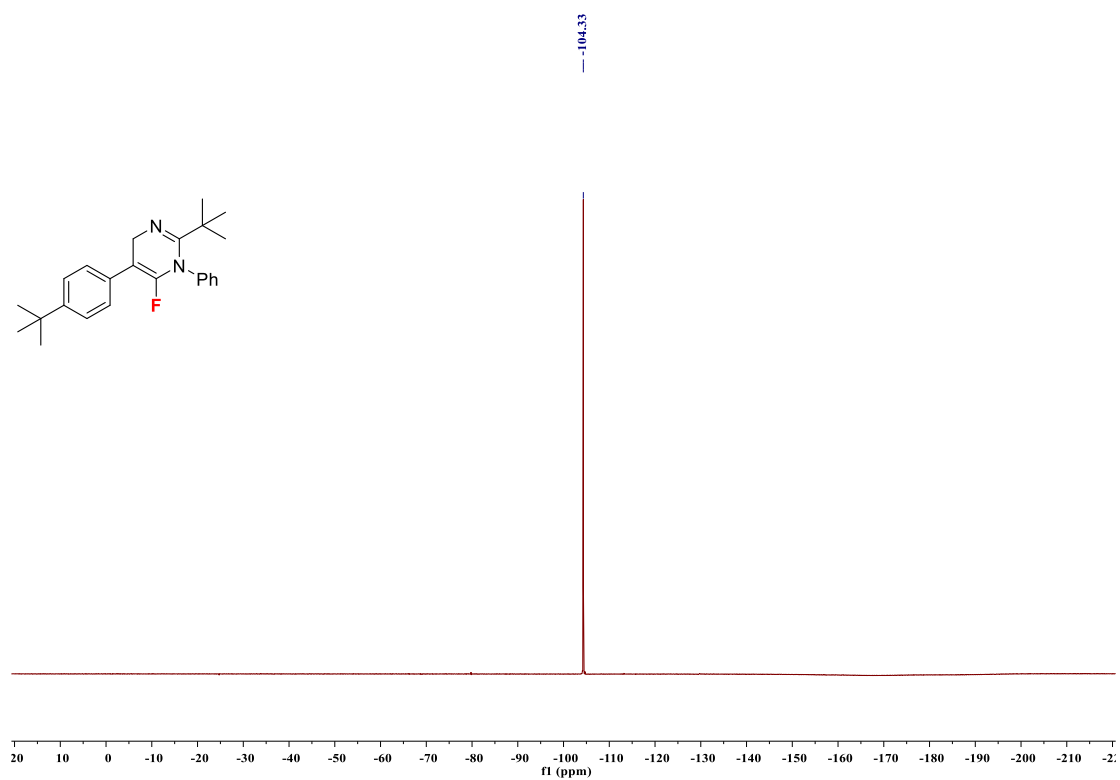
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ca**



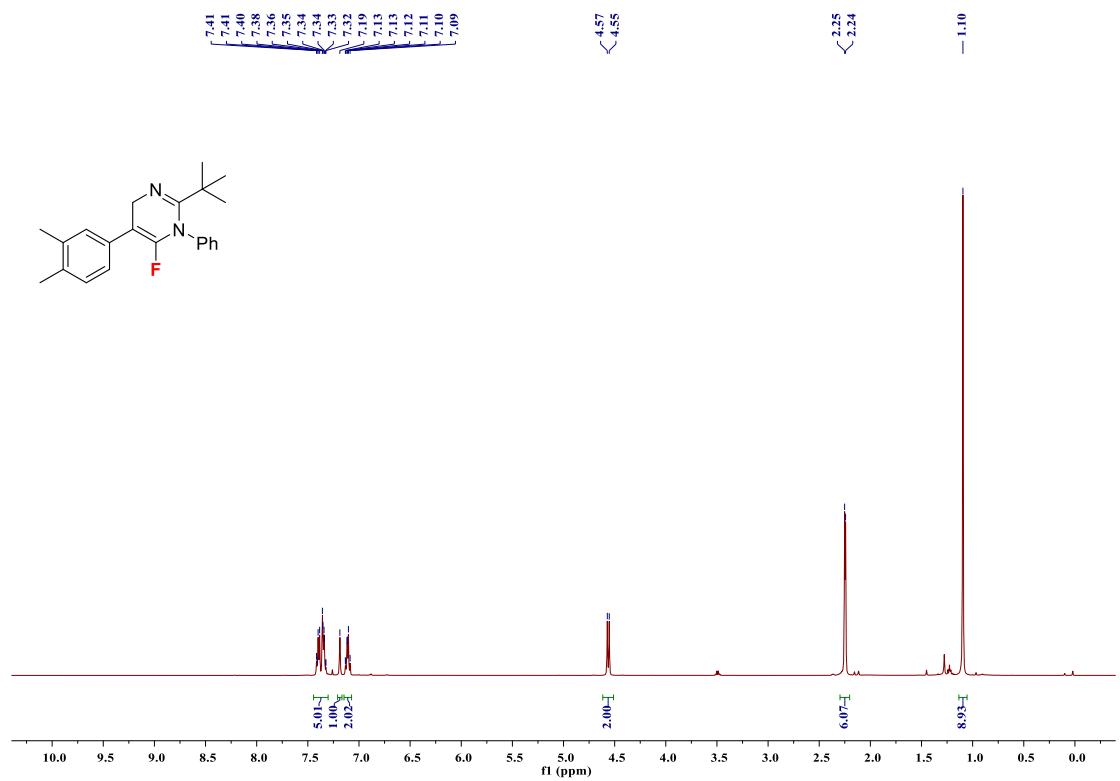
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ca**



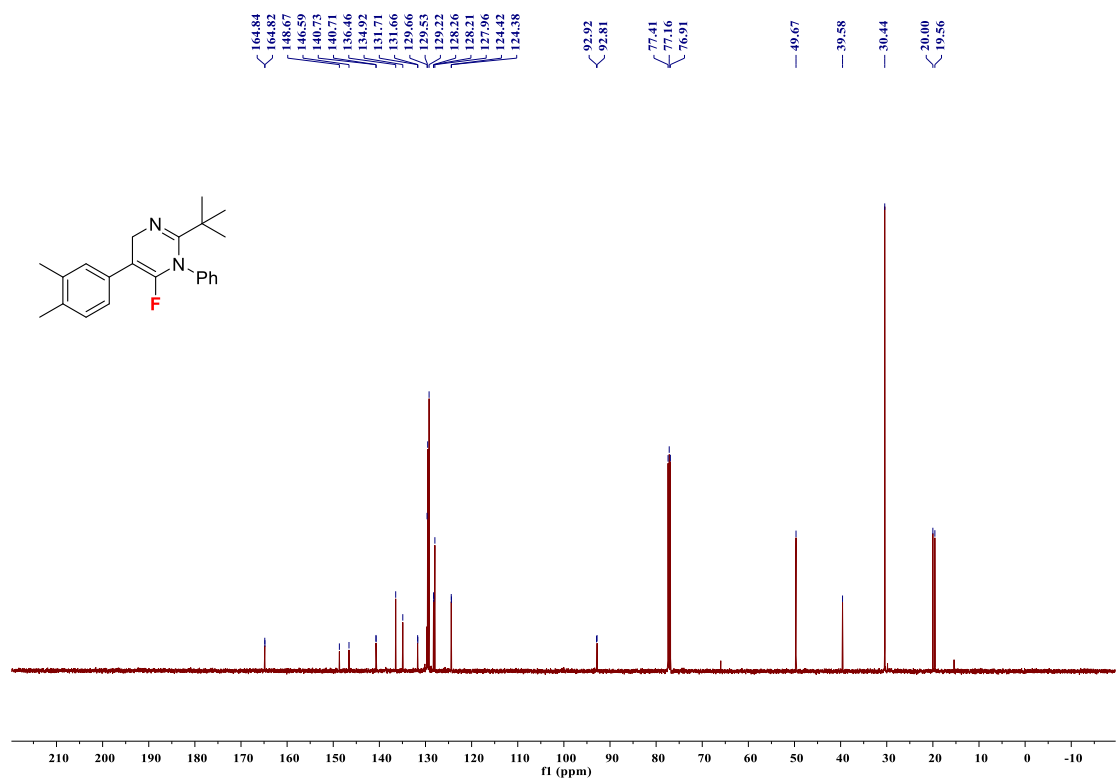
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ca**



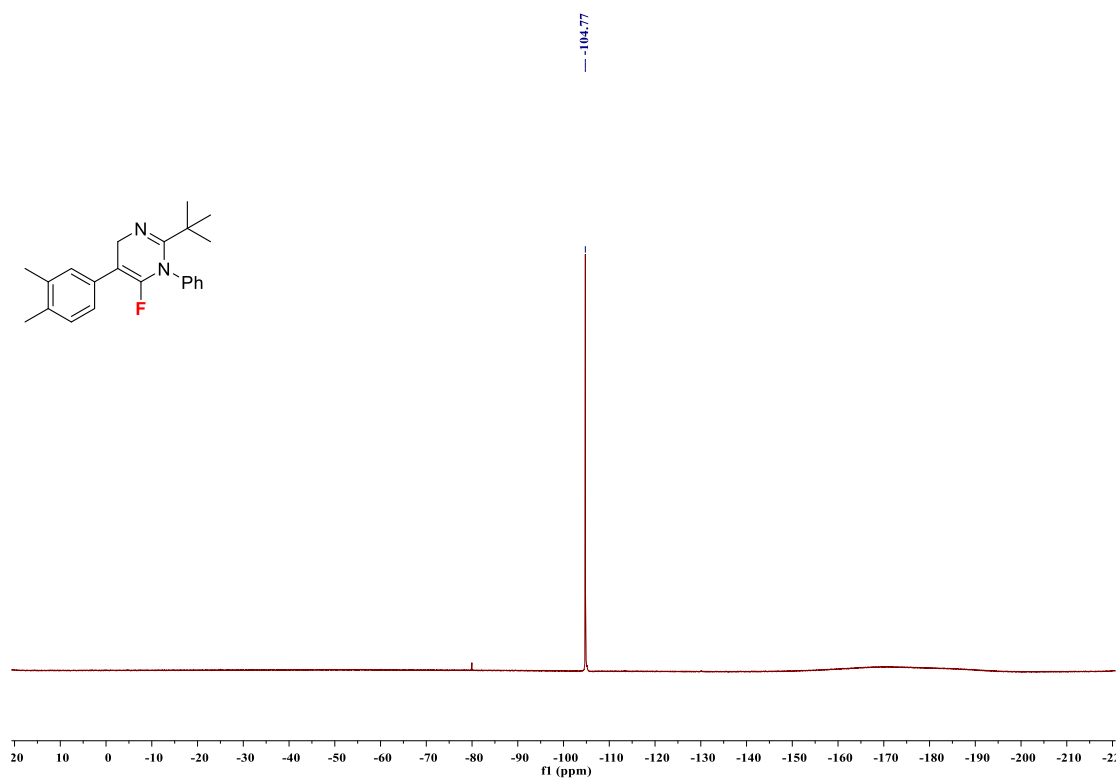
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3da**



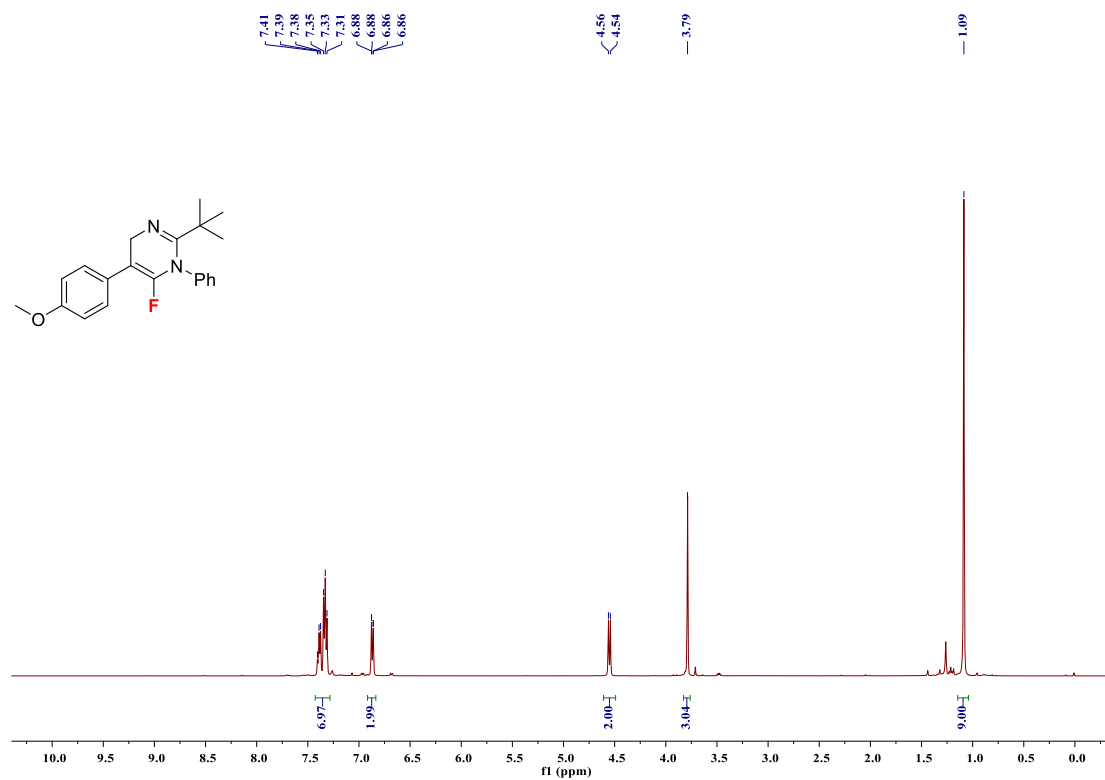
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3da**



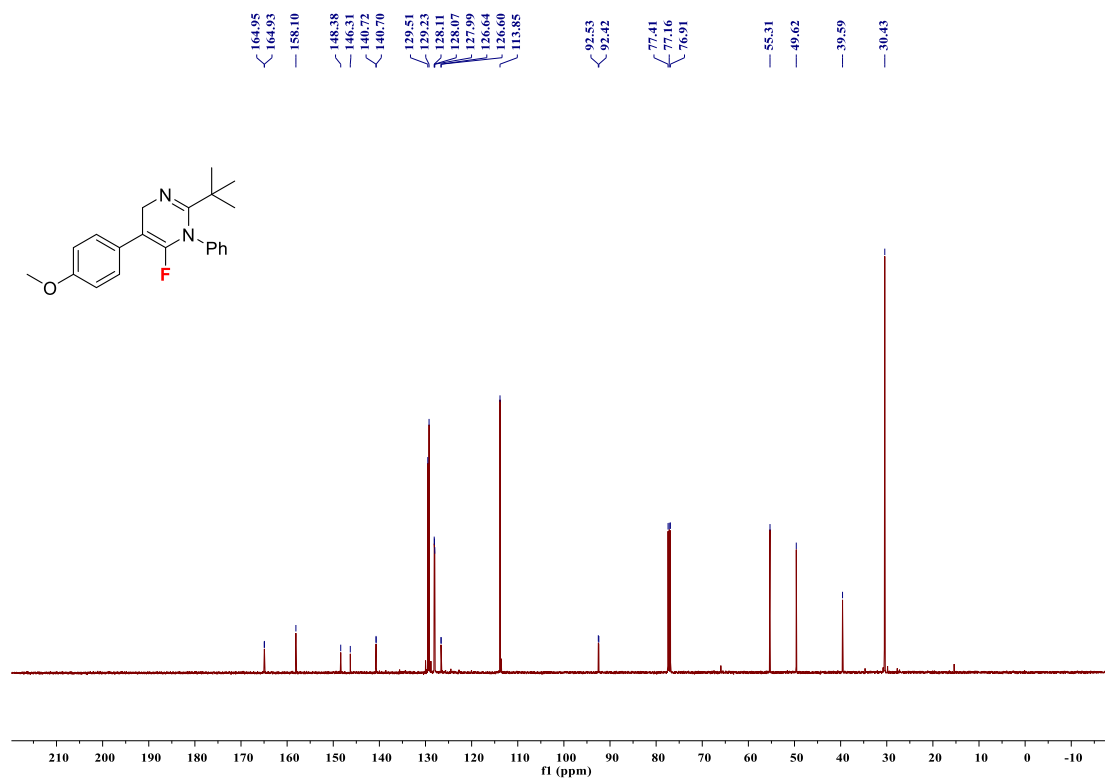
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3da**



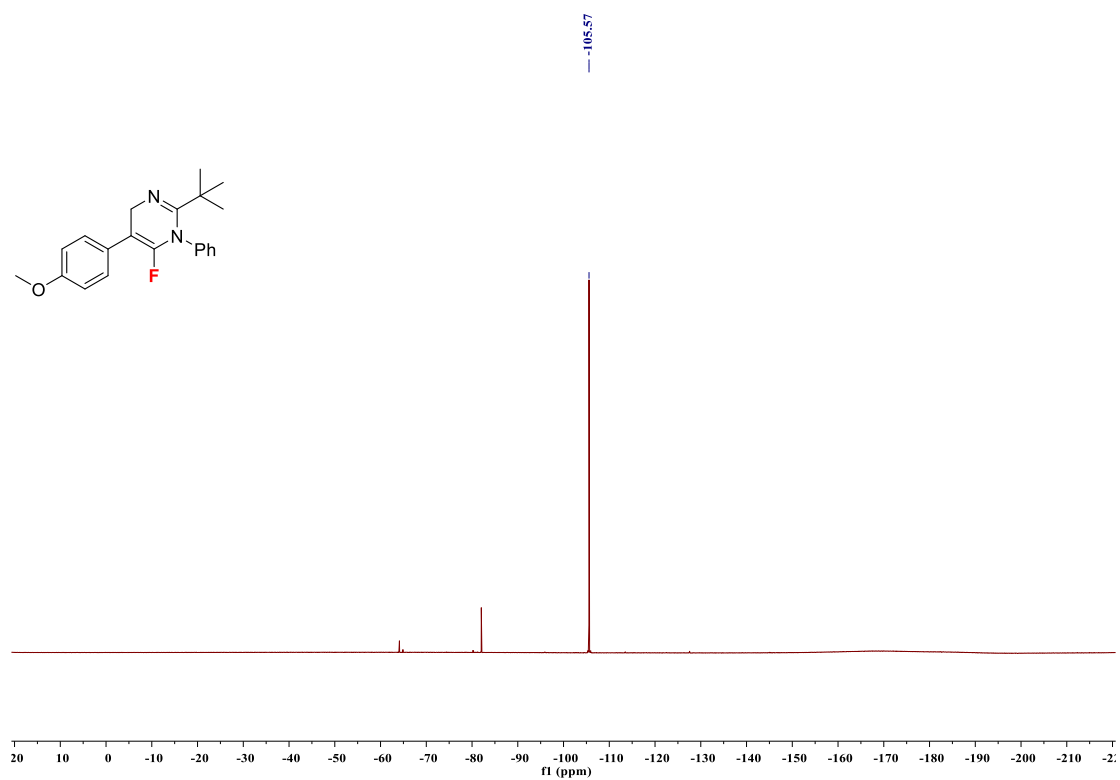
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ea**



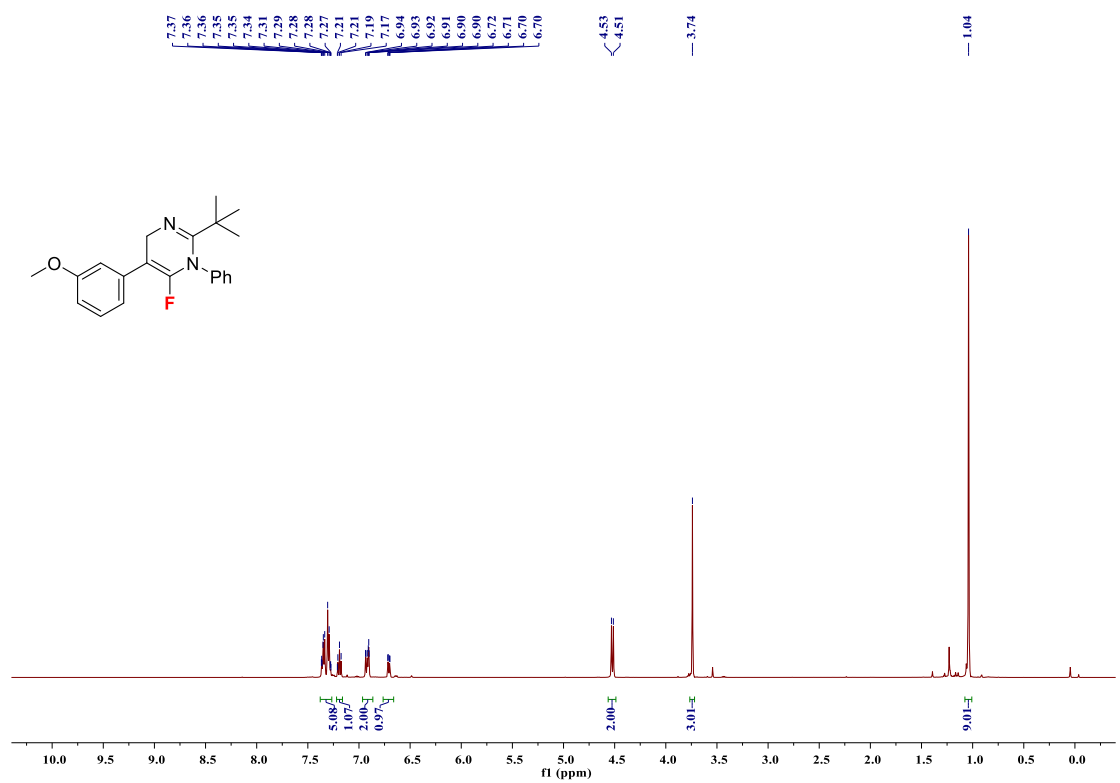
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ea**



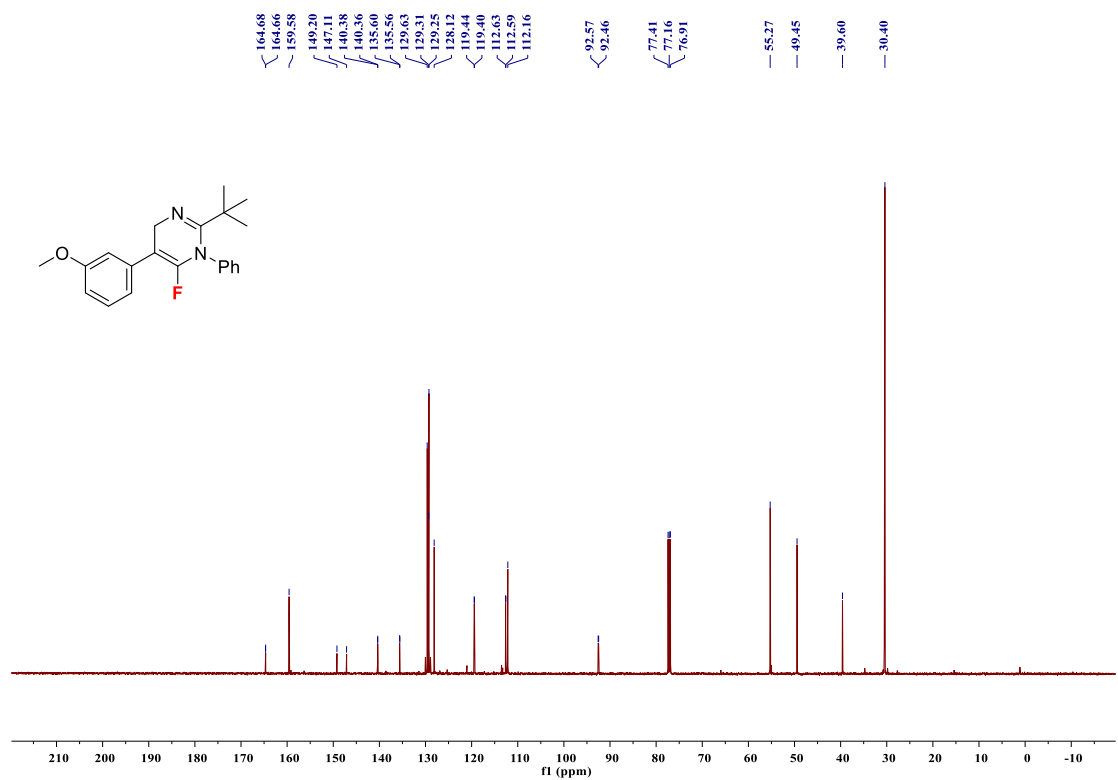
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ea**



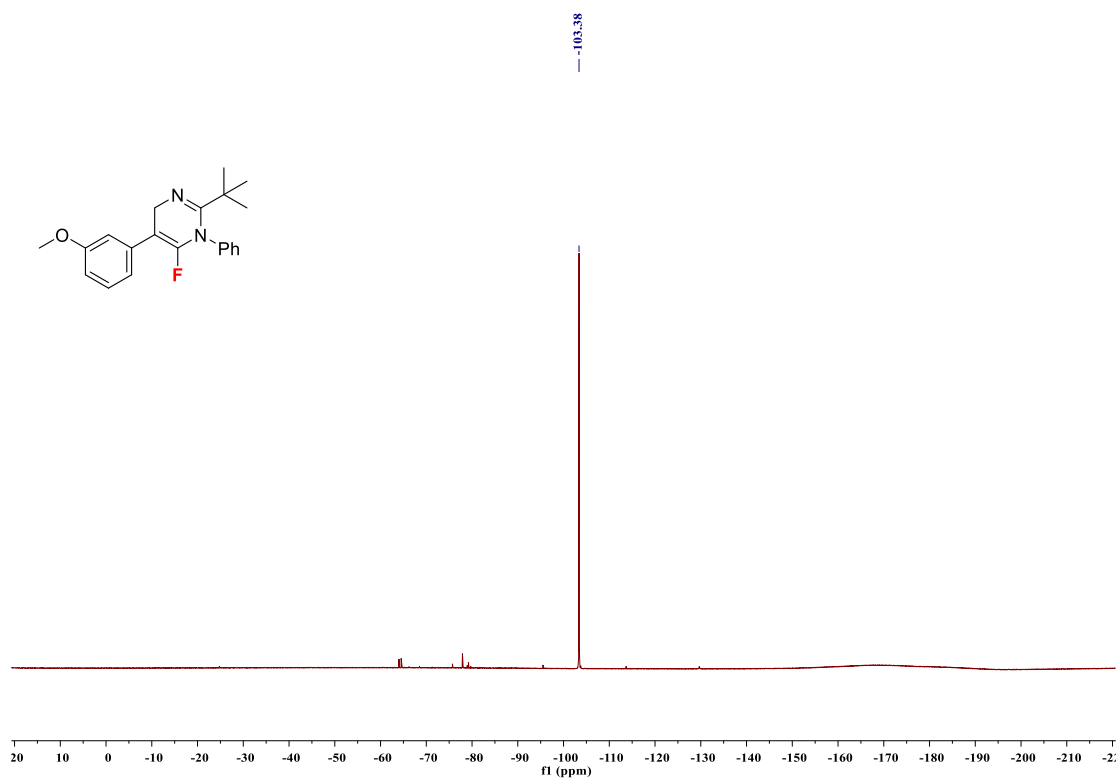
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3fa



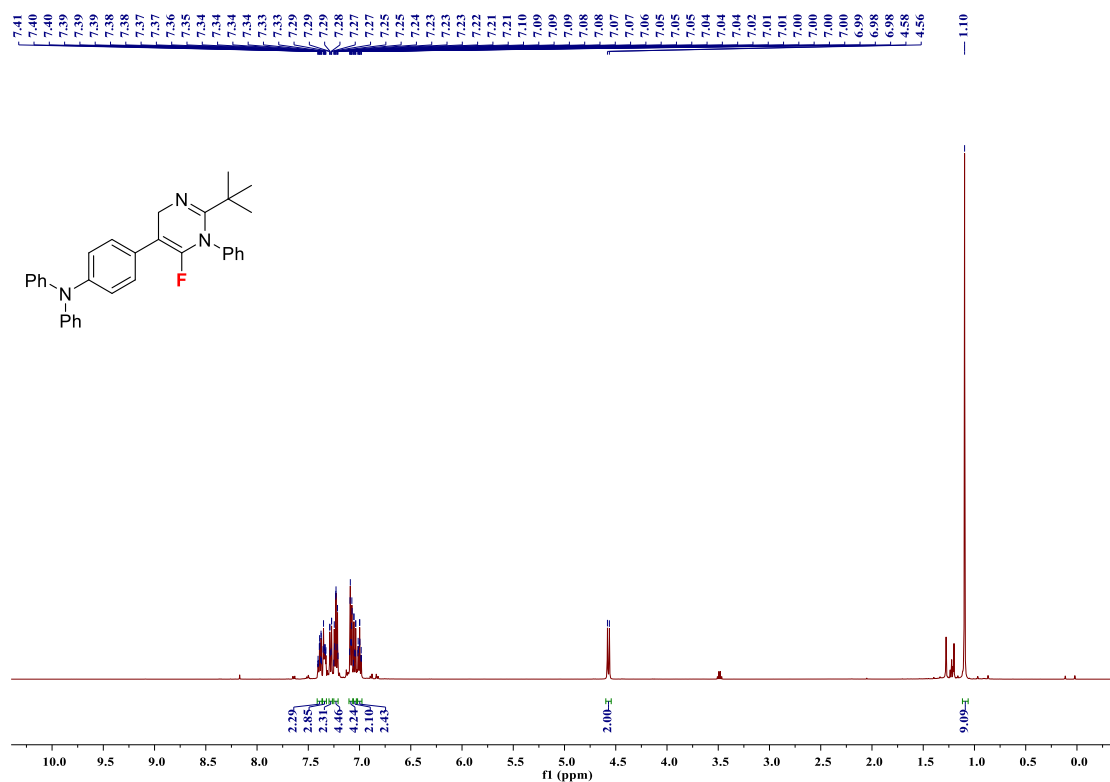
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3fa



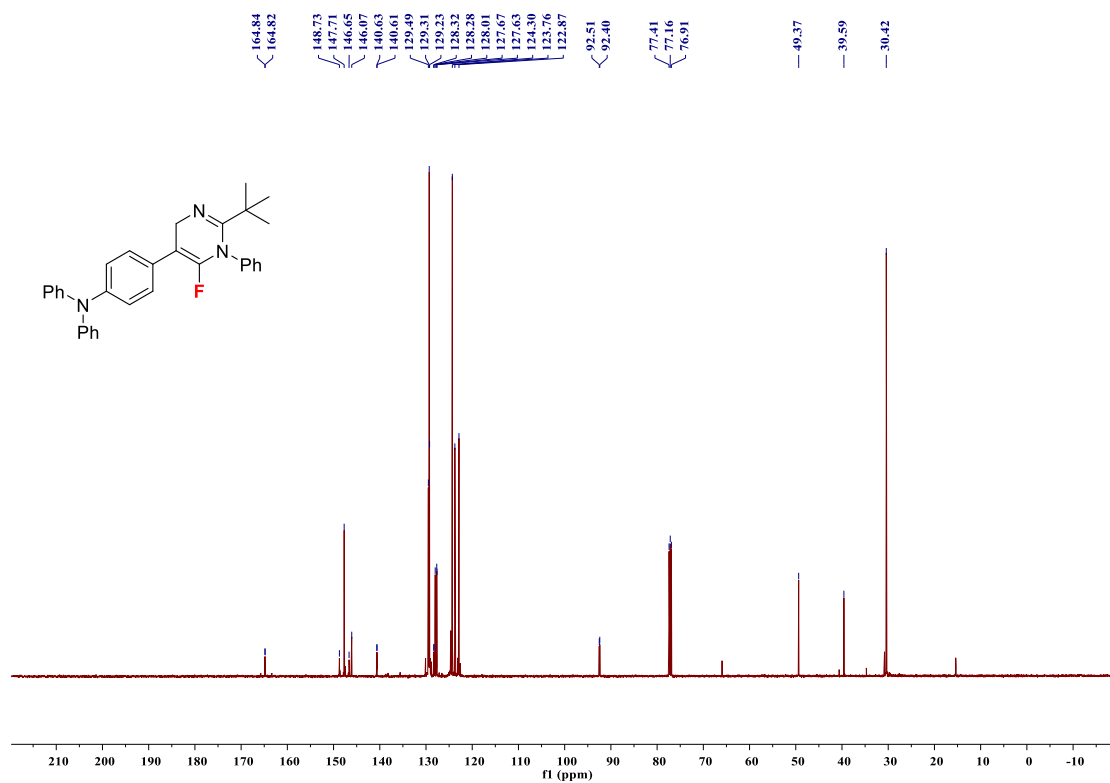
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3fa



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ga

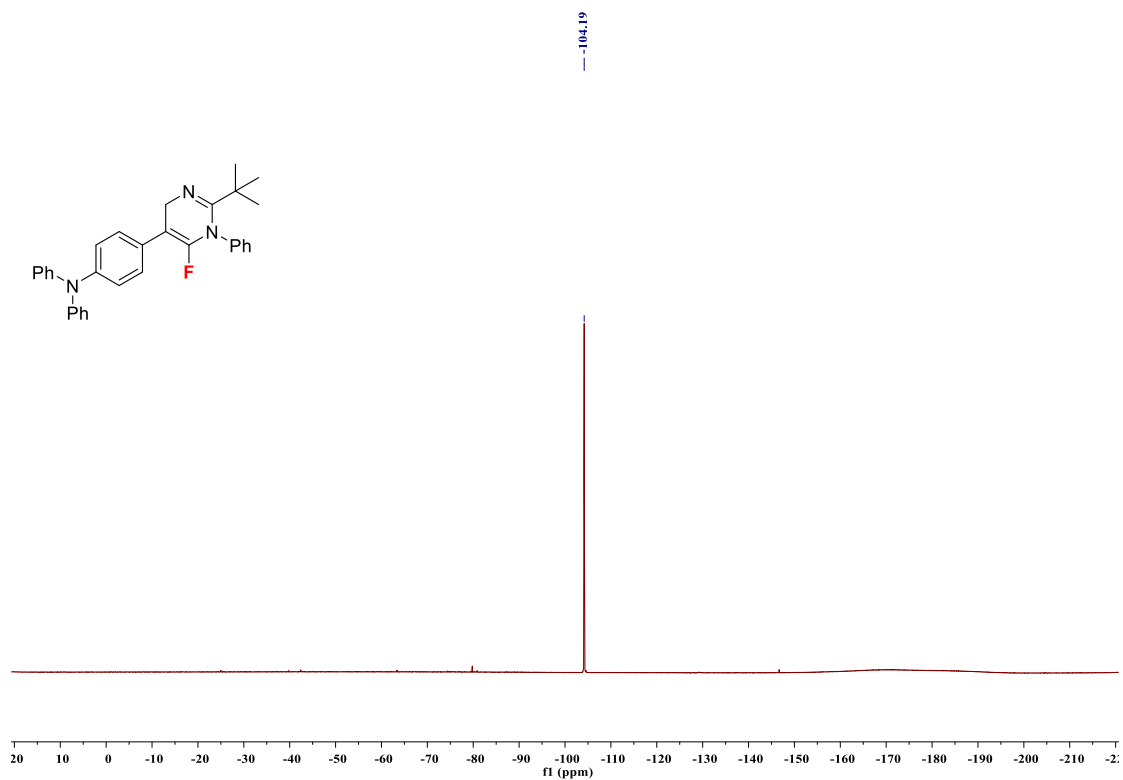


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ga**

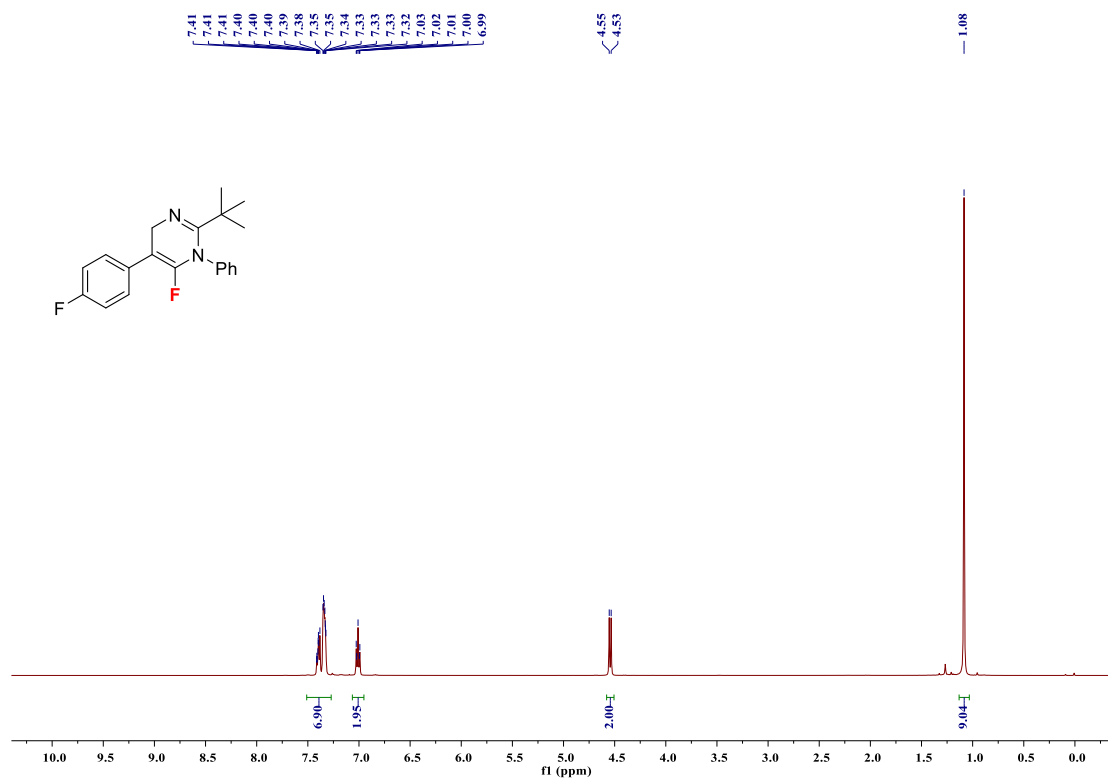


**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ga**

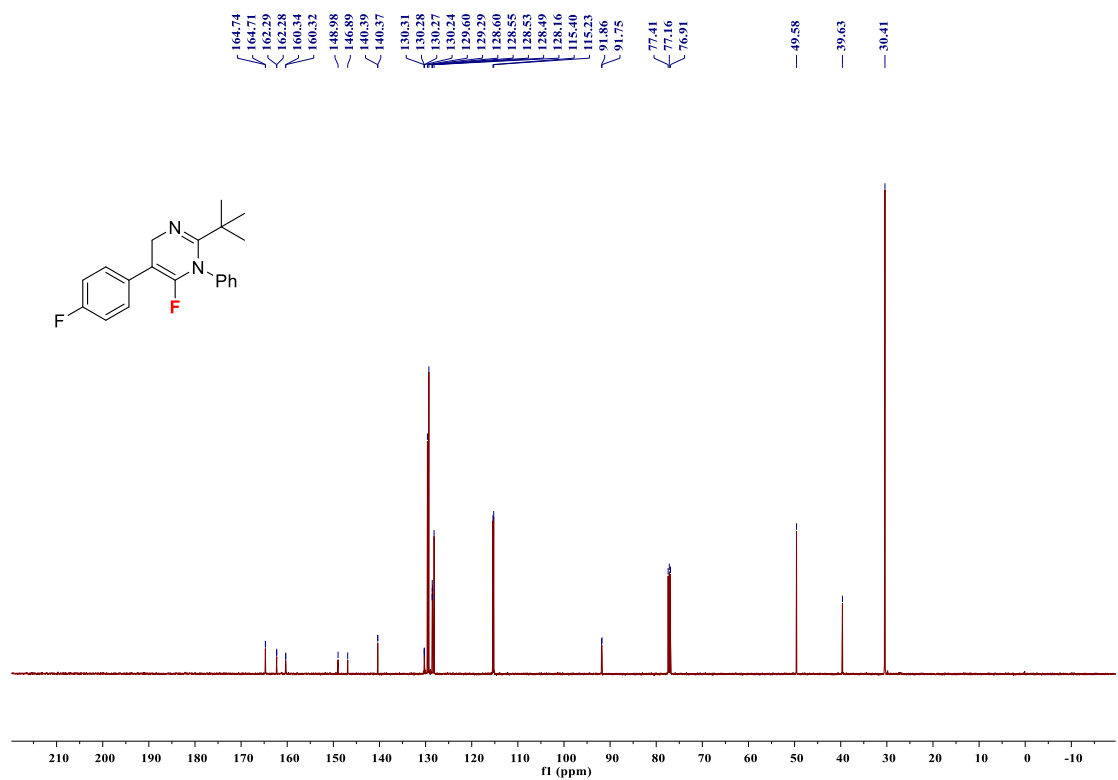




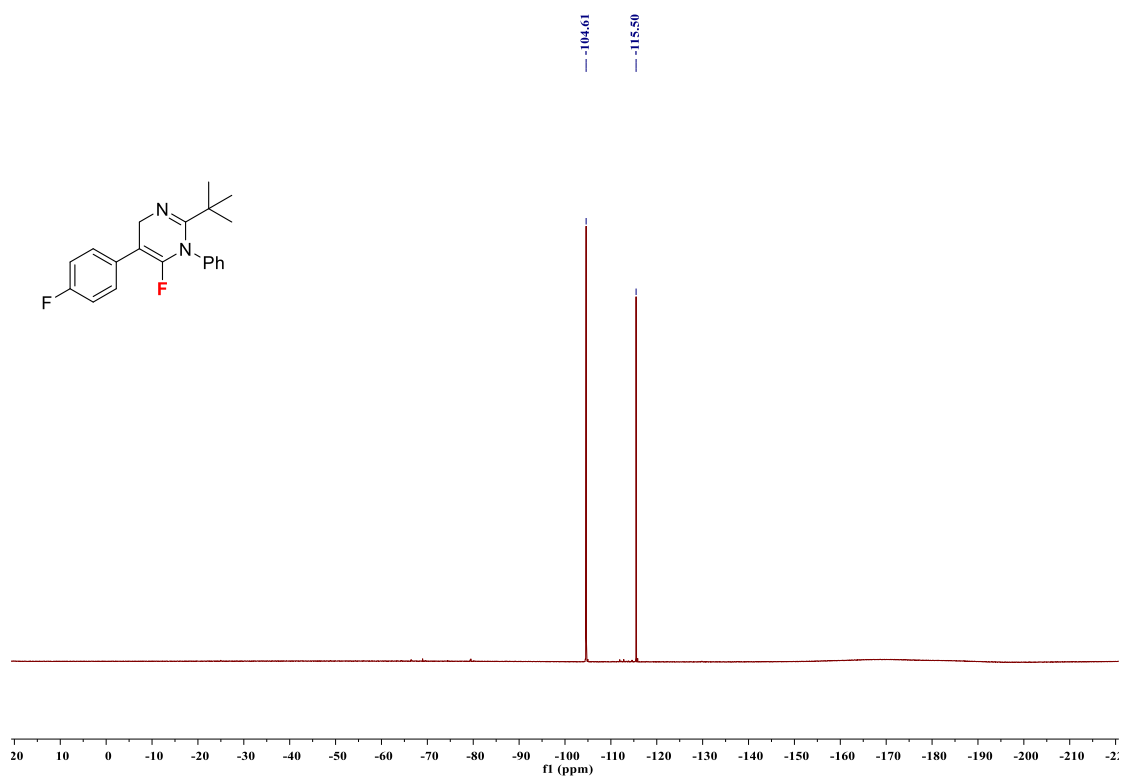
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ha



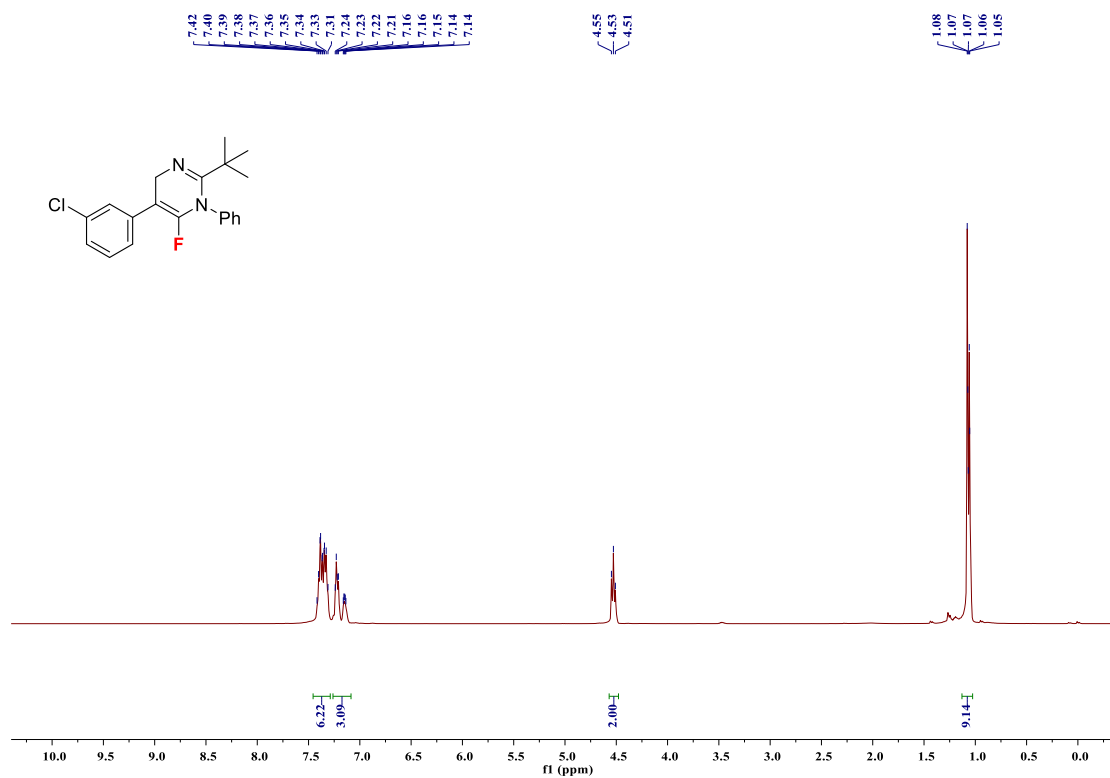
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ha



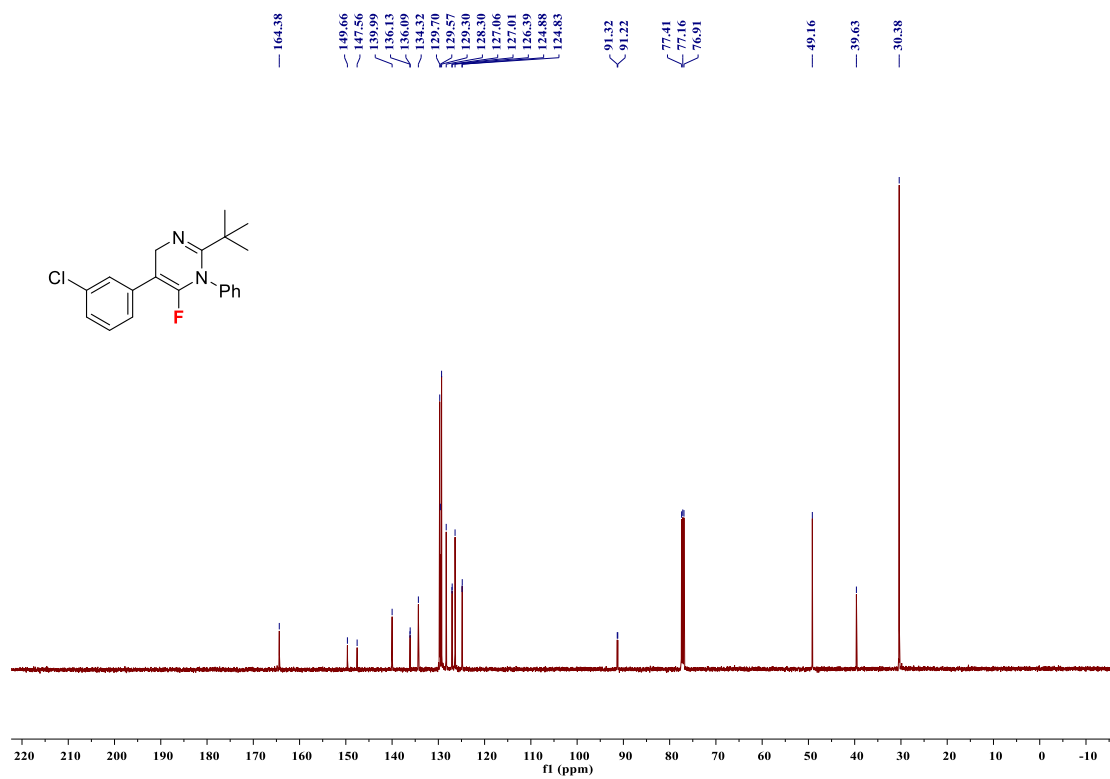
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3a



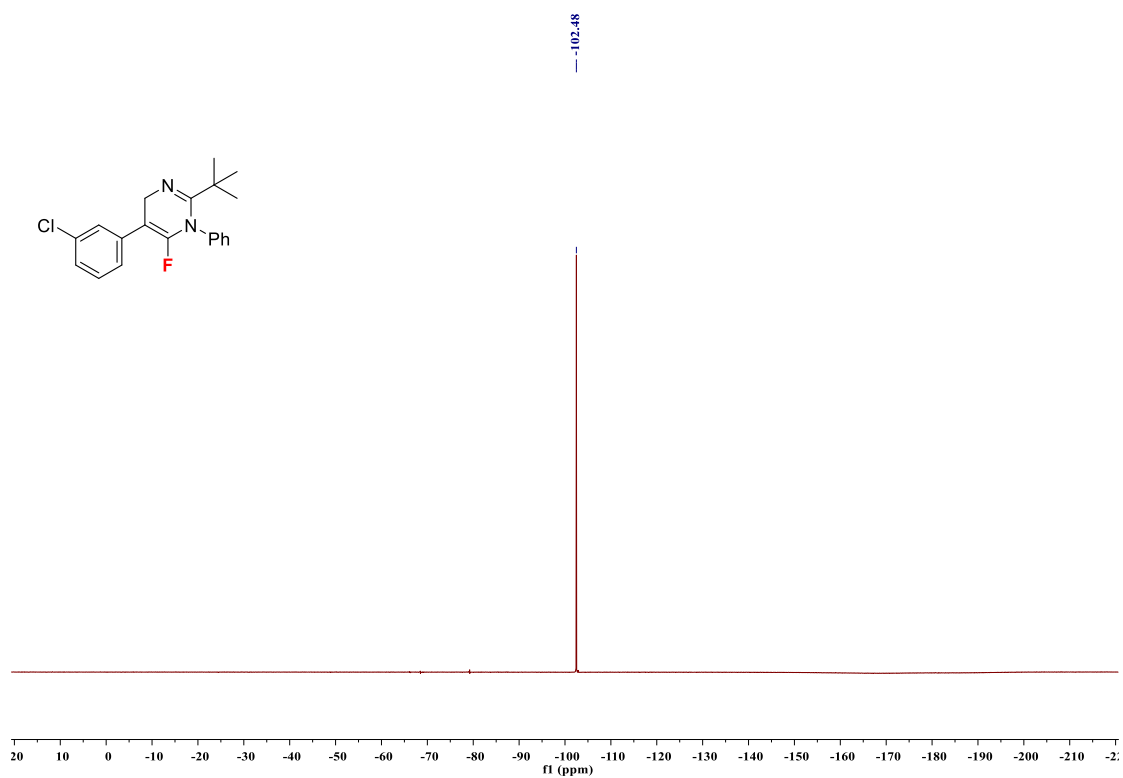
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3a



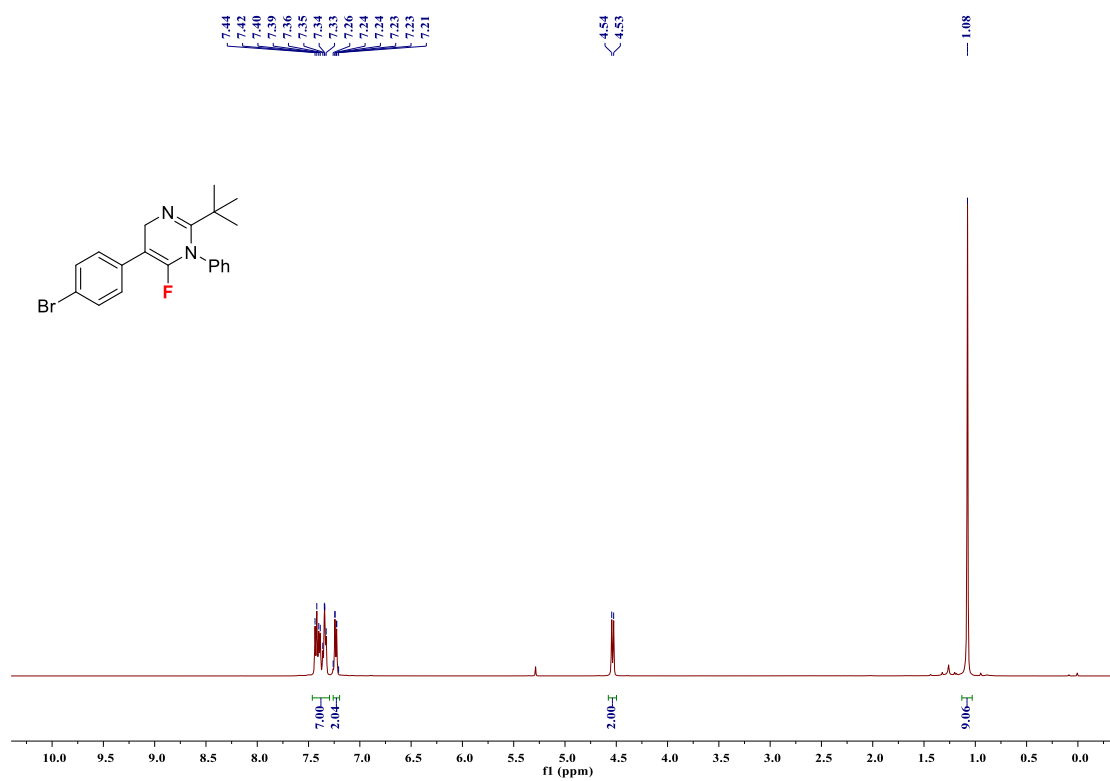
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ia



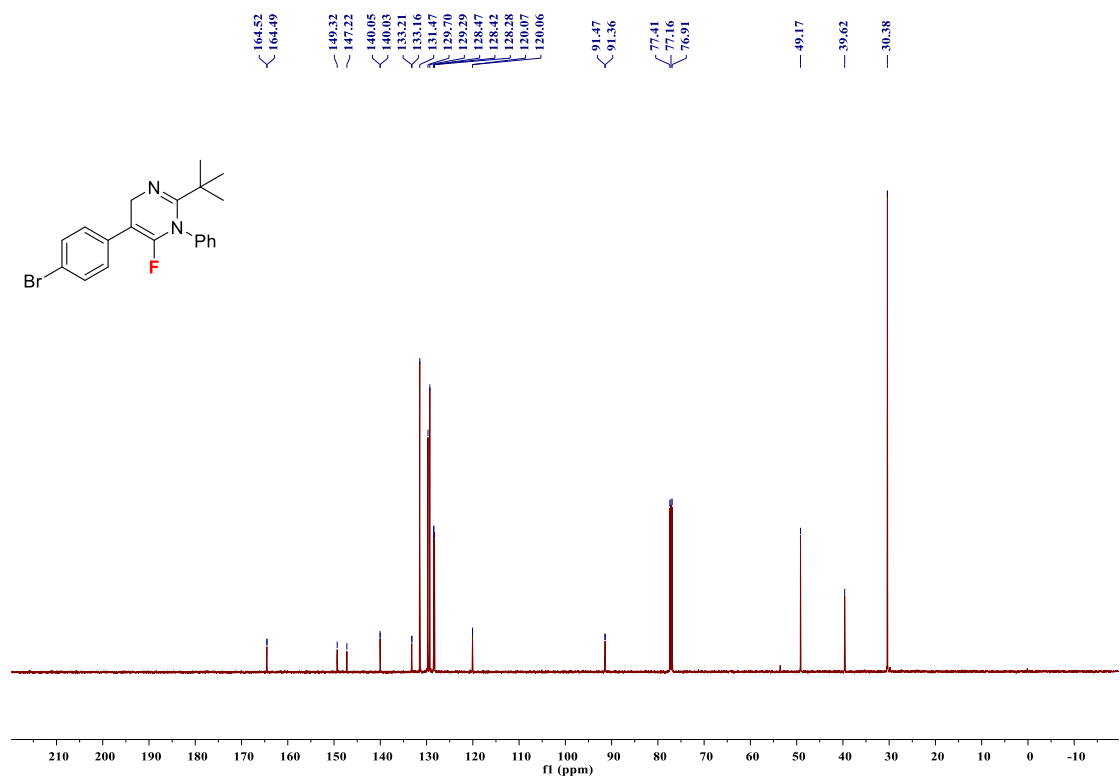
### <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ia



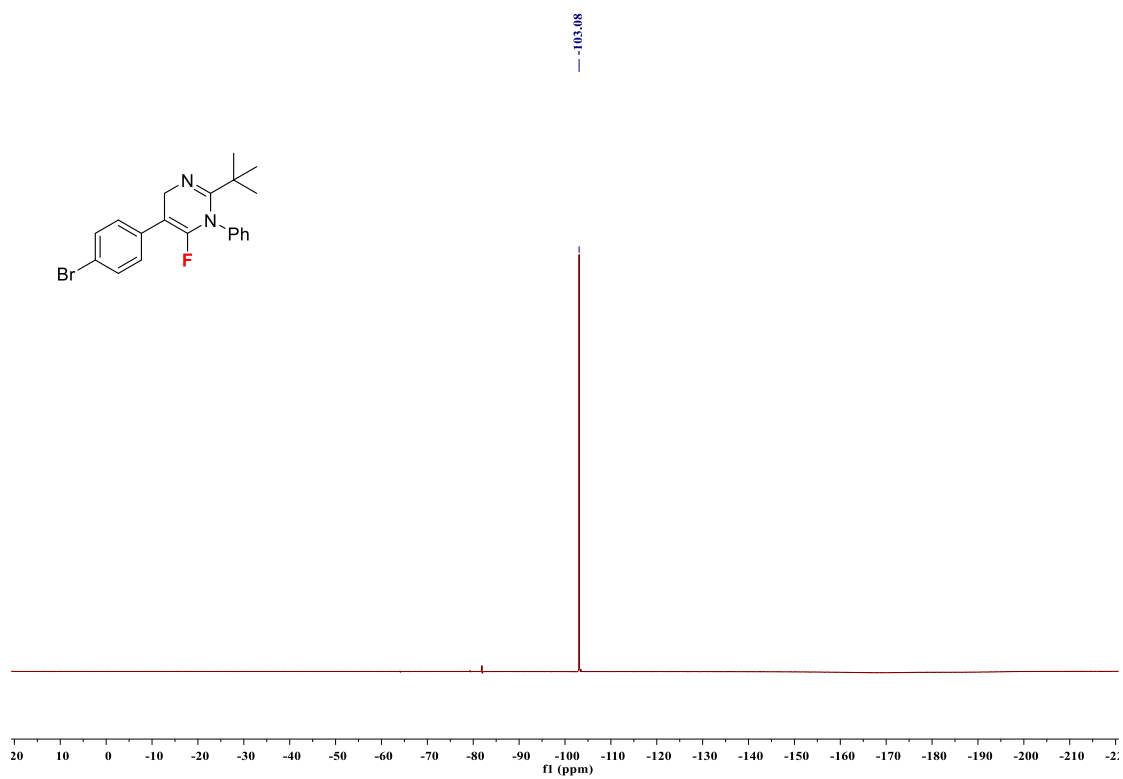
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum for 3ja



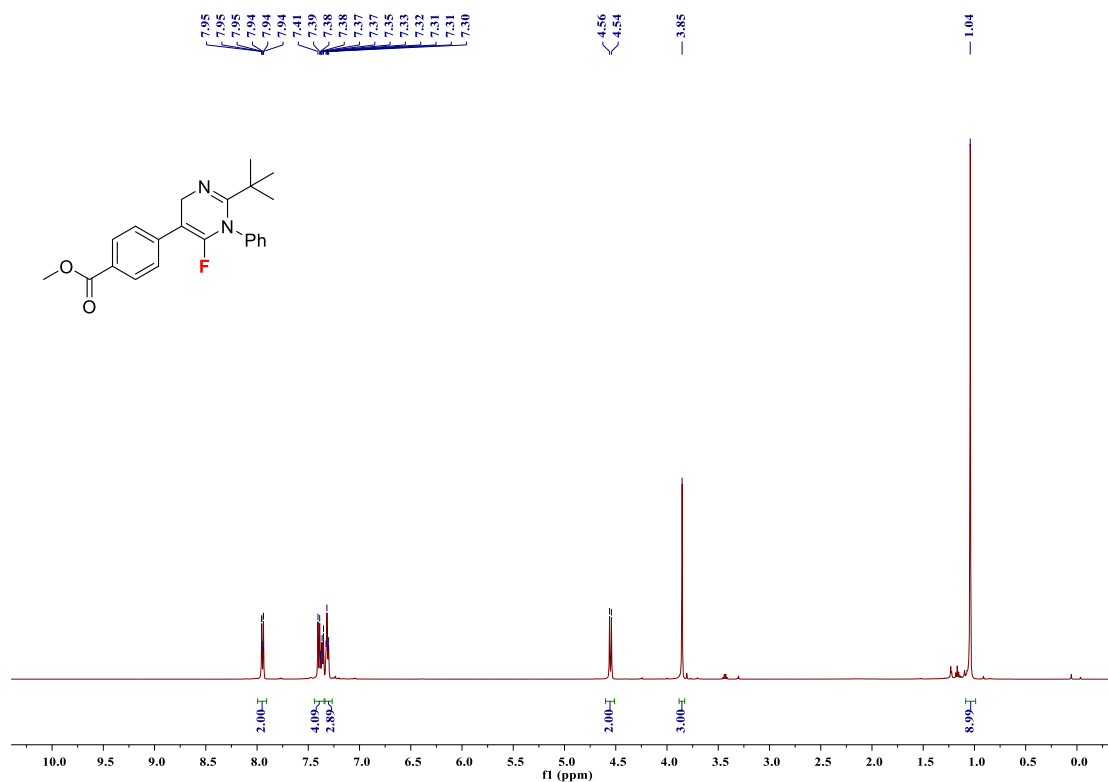
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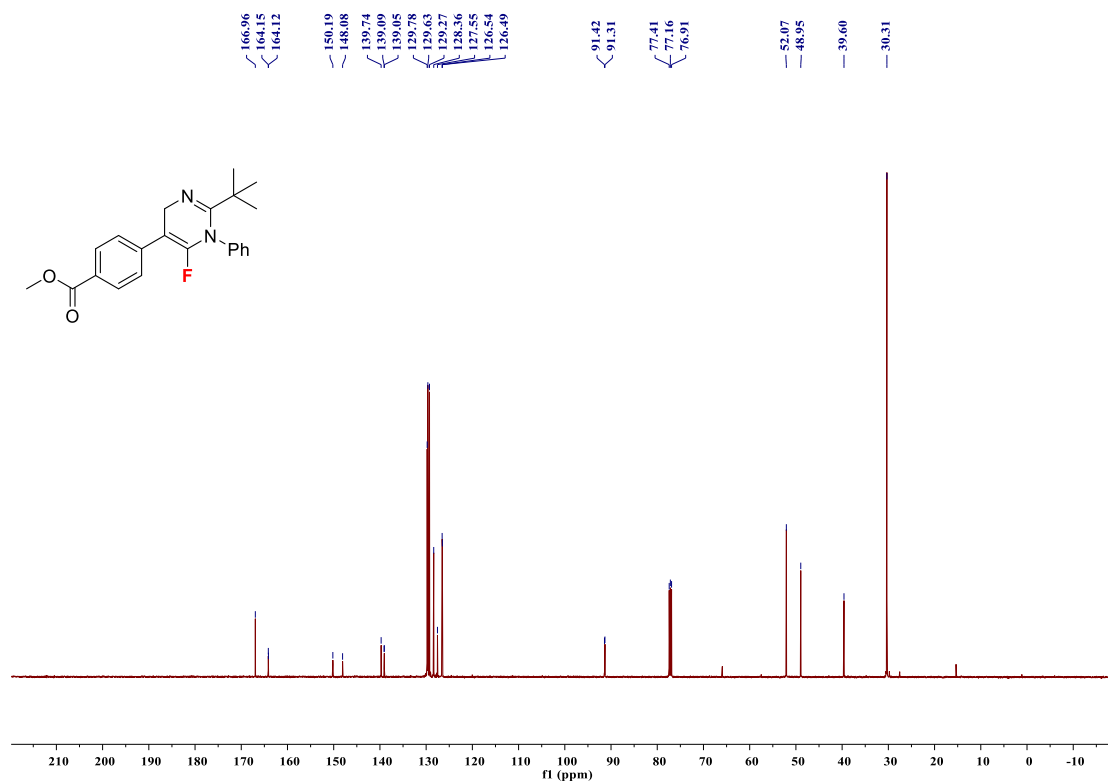
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ja**



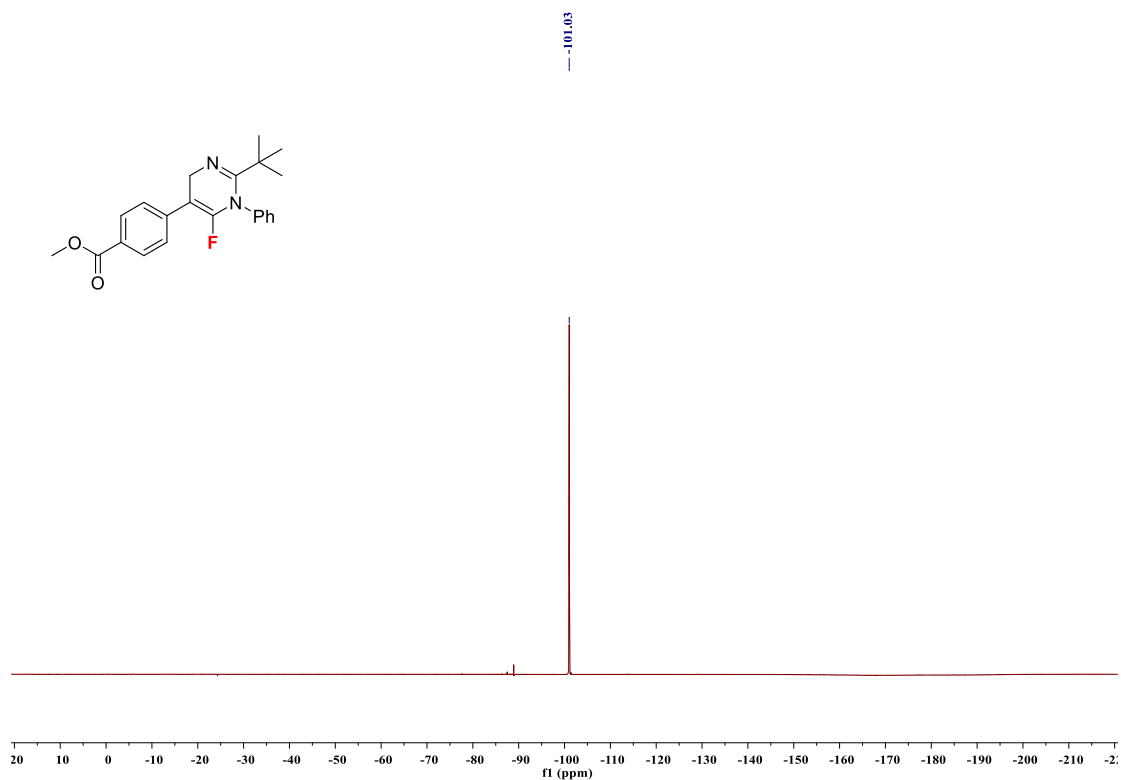
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ka**



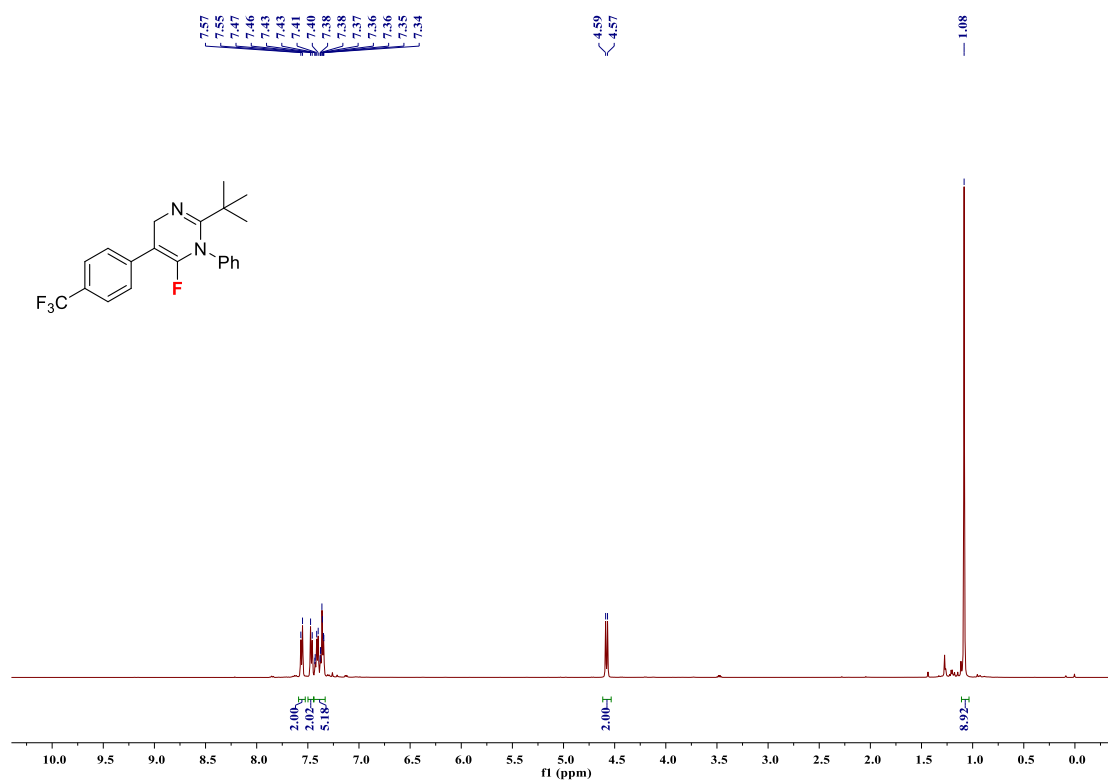
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ka**



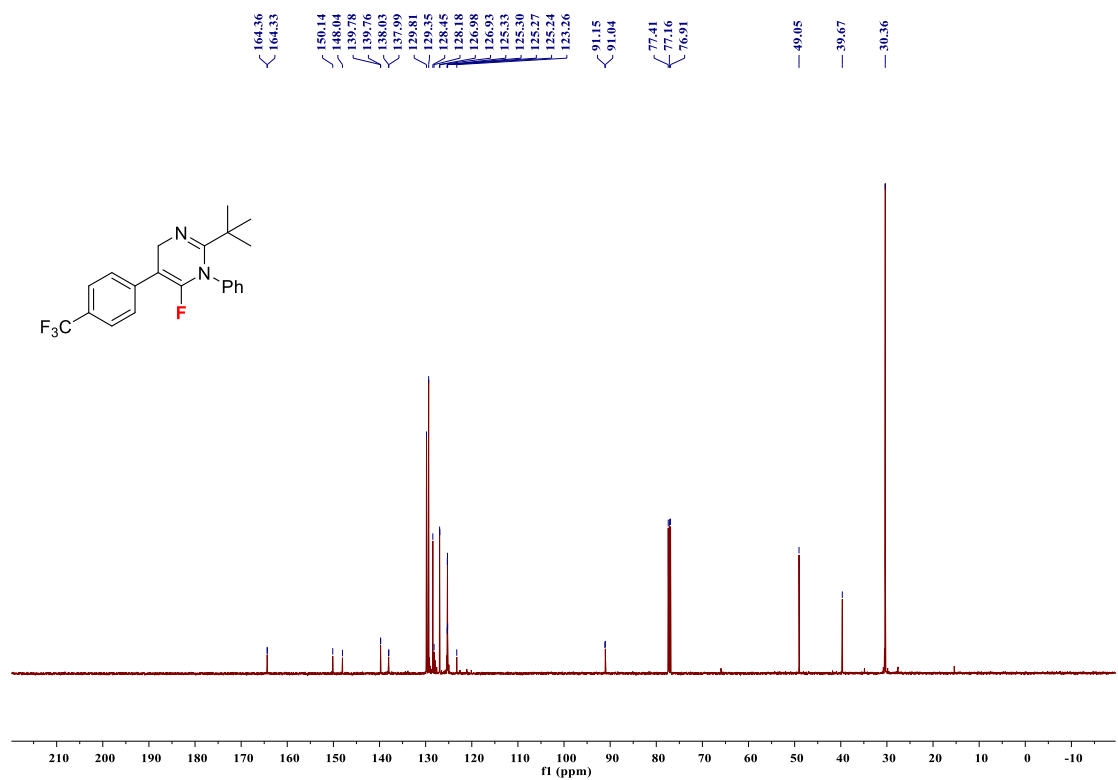
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ka**



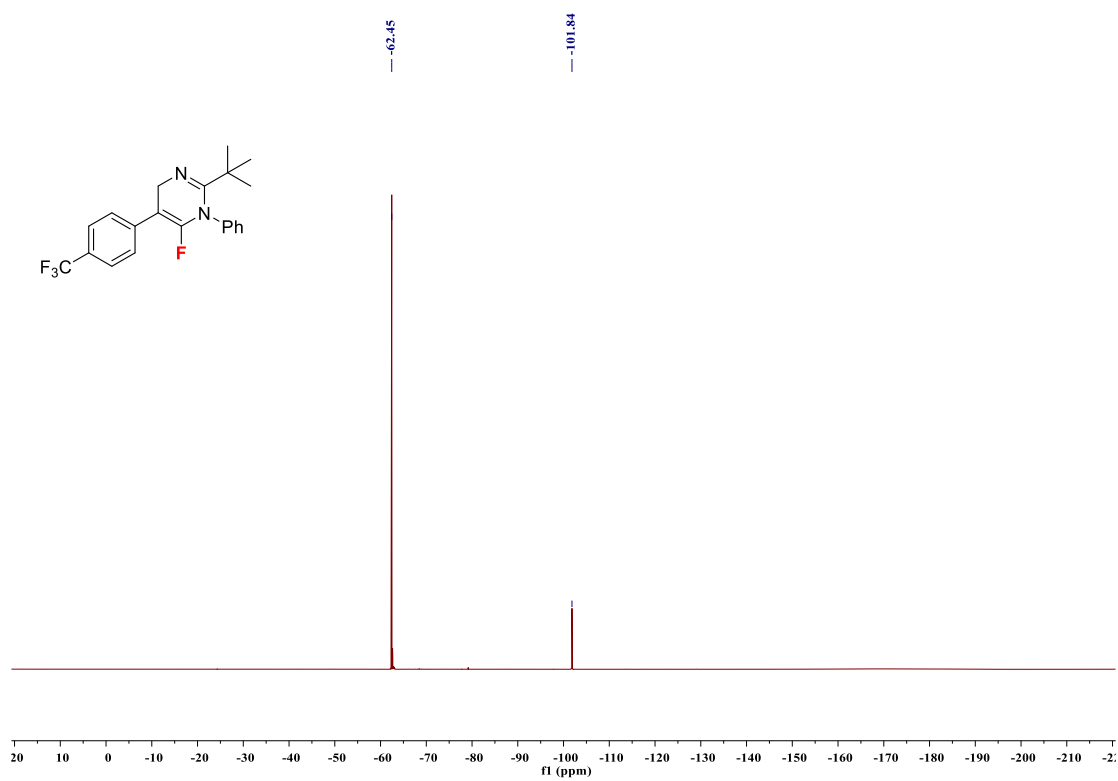
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3la**



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3la**

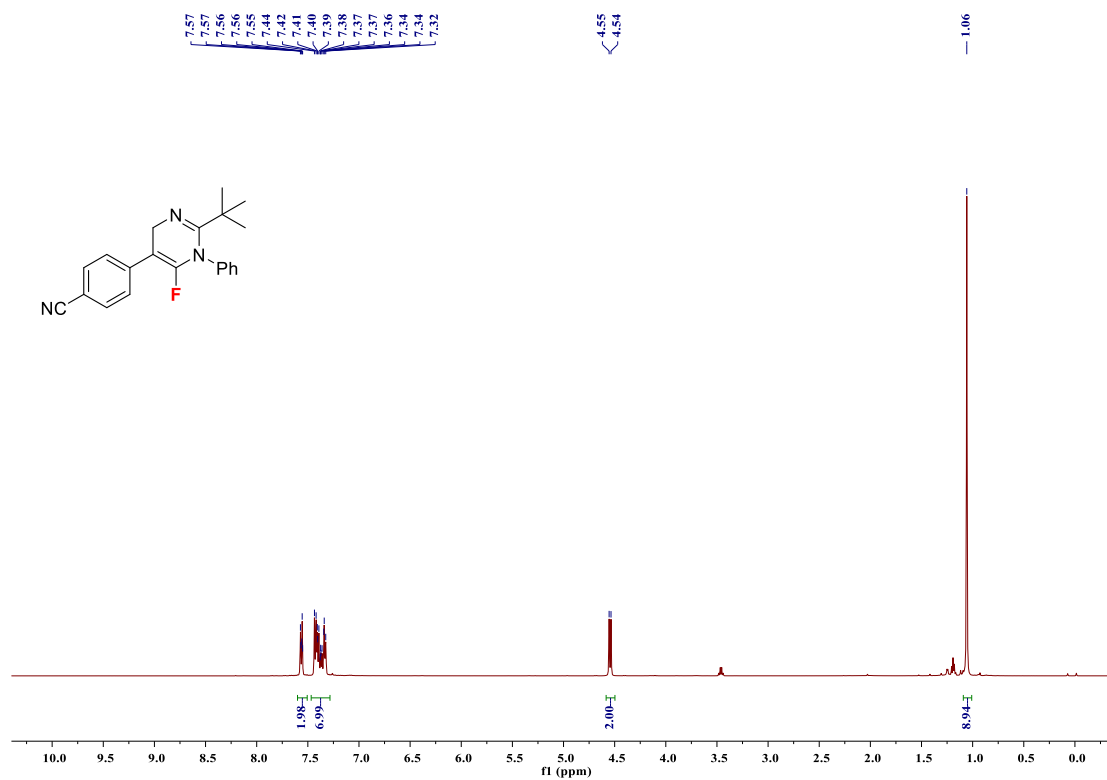


**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3la**

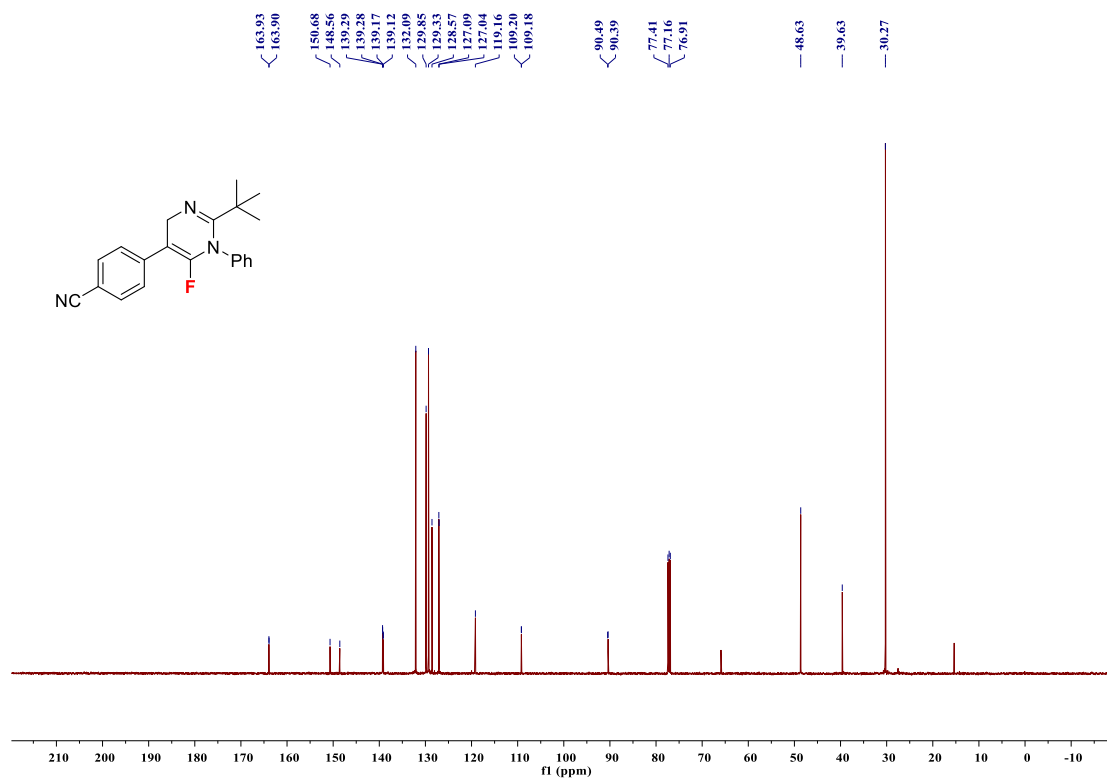


**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ma**

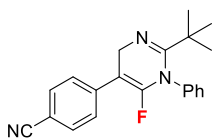




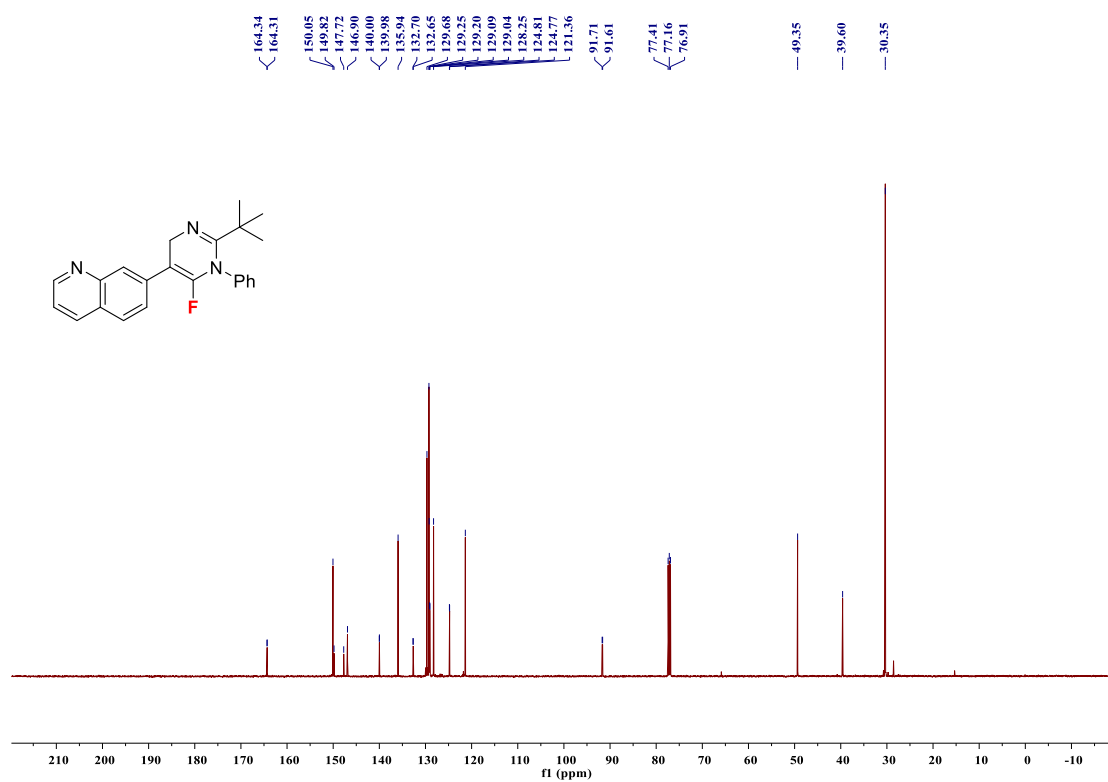
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ma



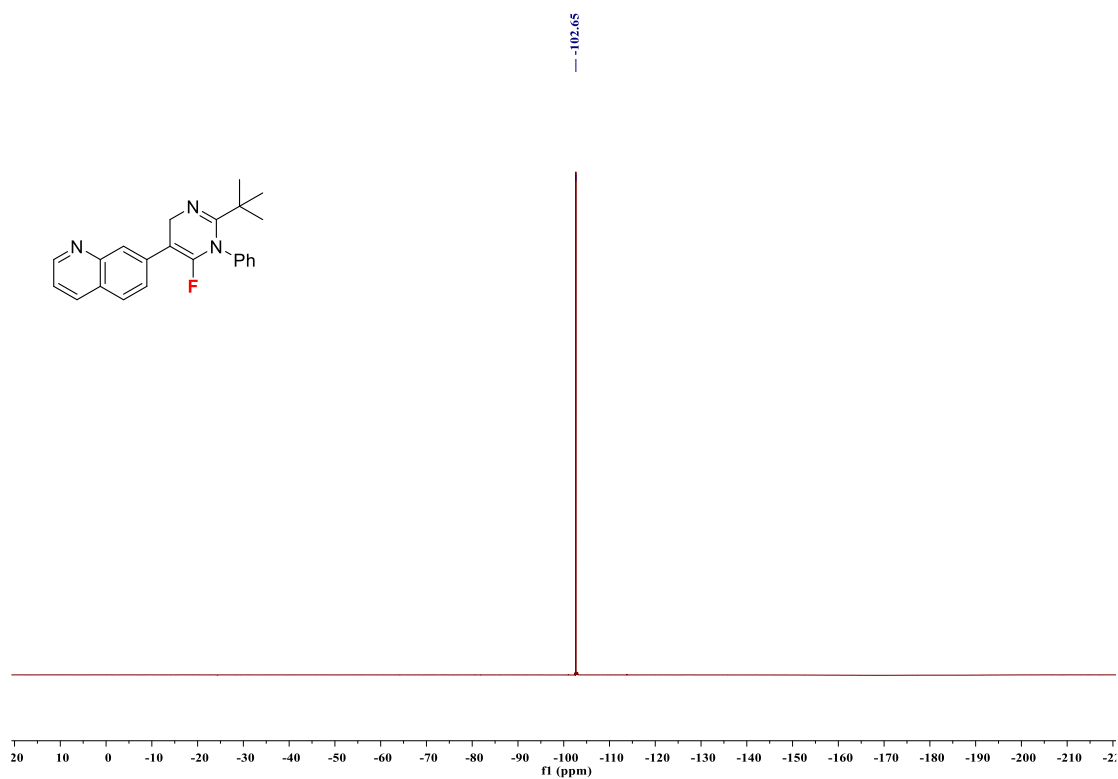
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ma

CC(C)(C)N1C=CC(=C2C=CC(=CC=C2N)C=C1F)C3=CC=CC=C3

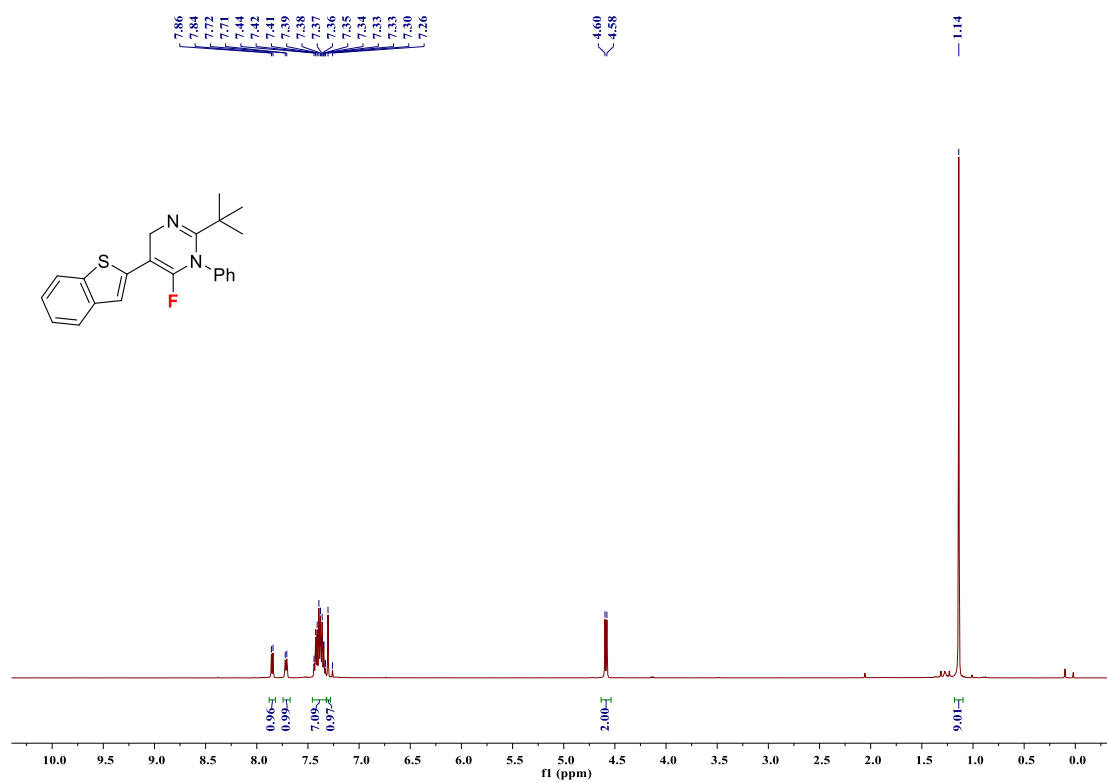
S26



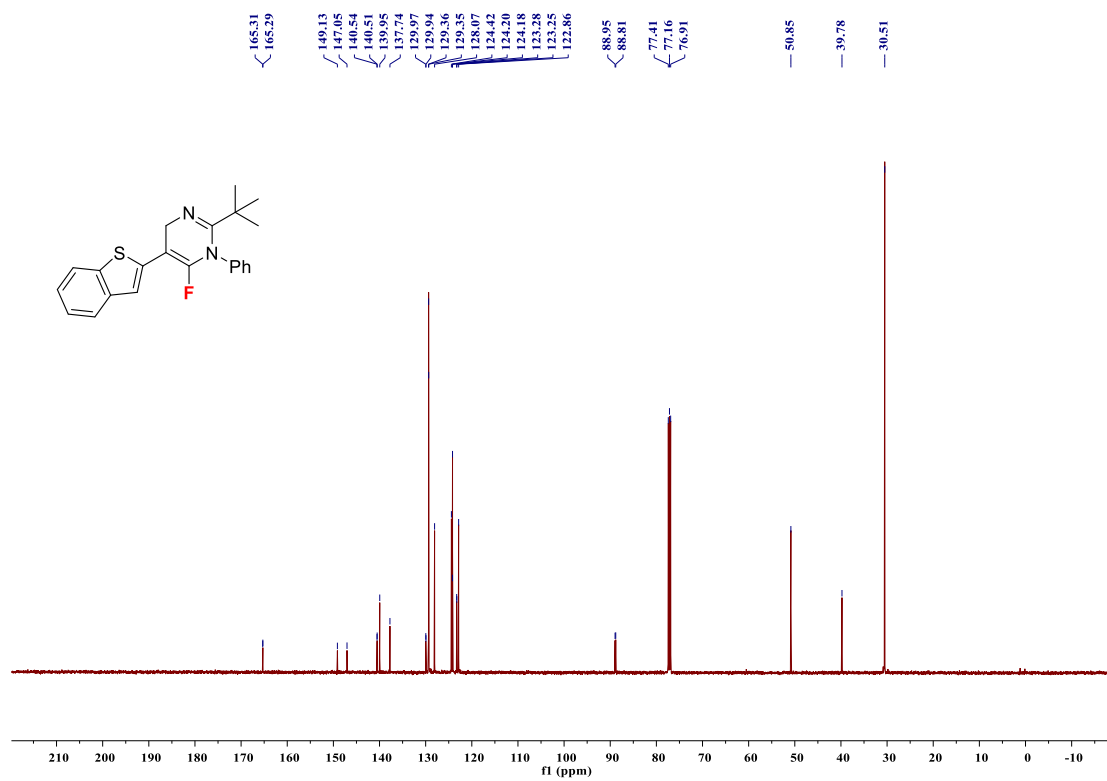
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3na**



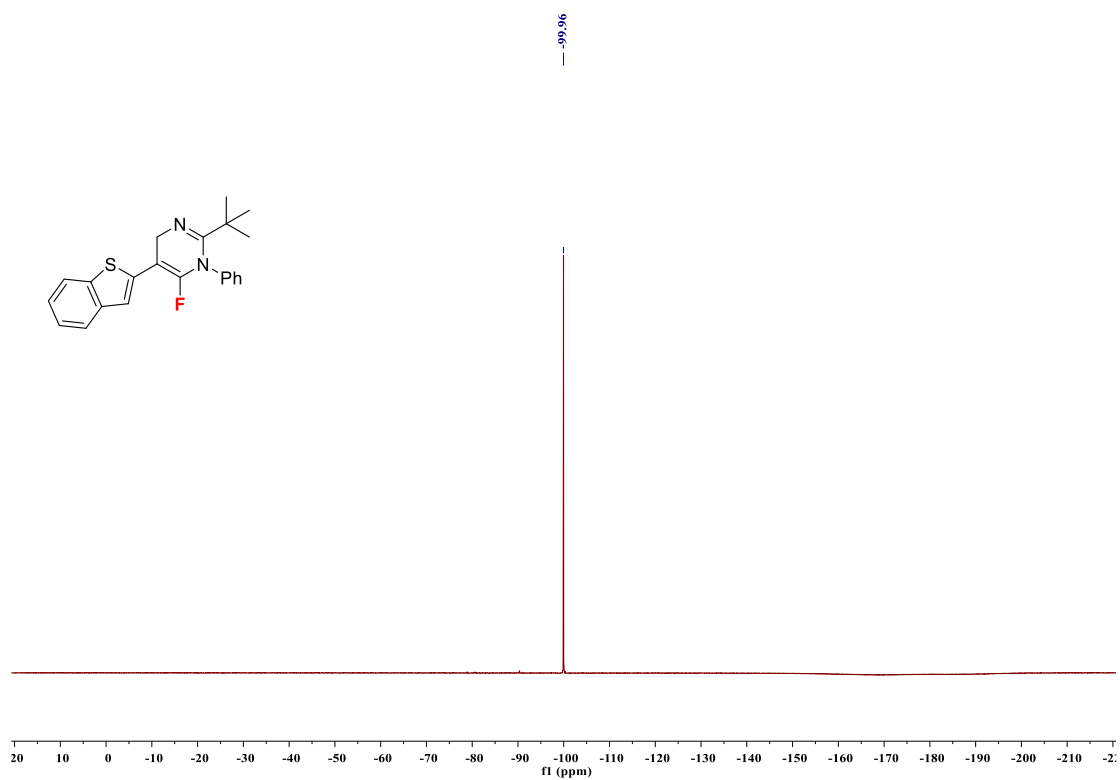
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3na**



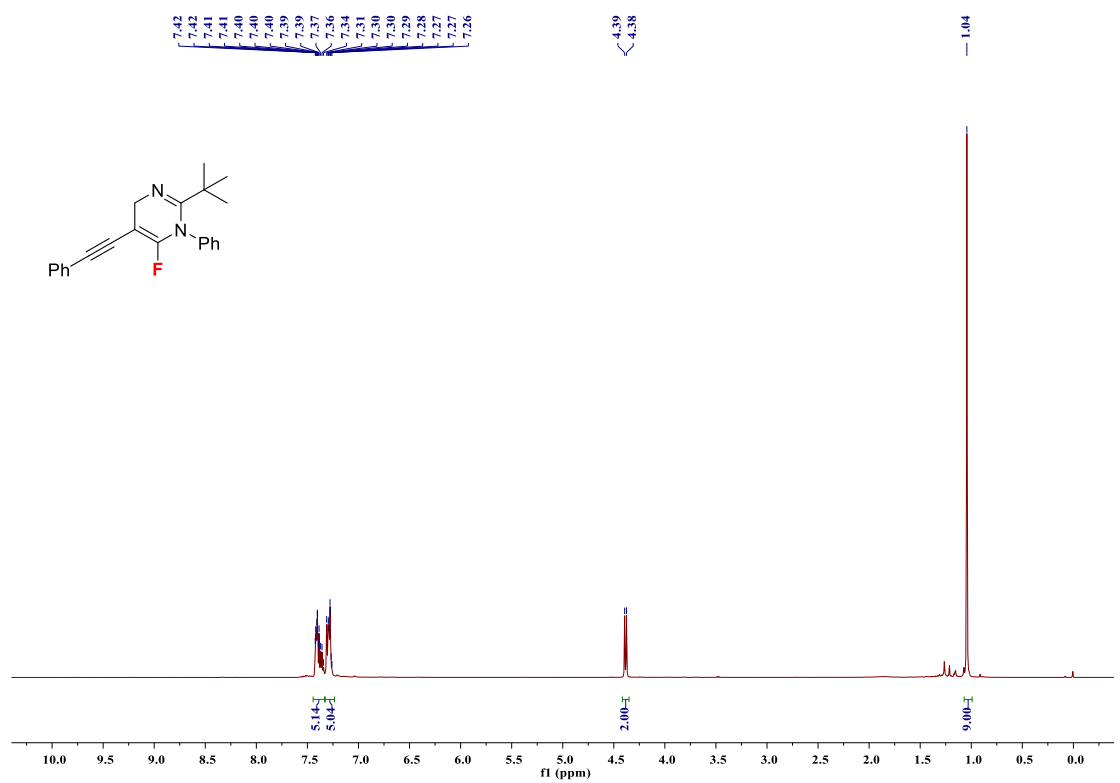
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 30a**



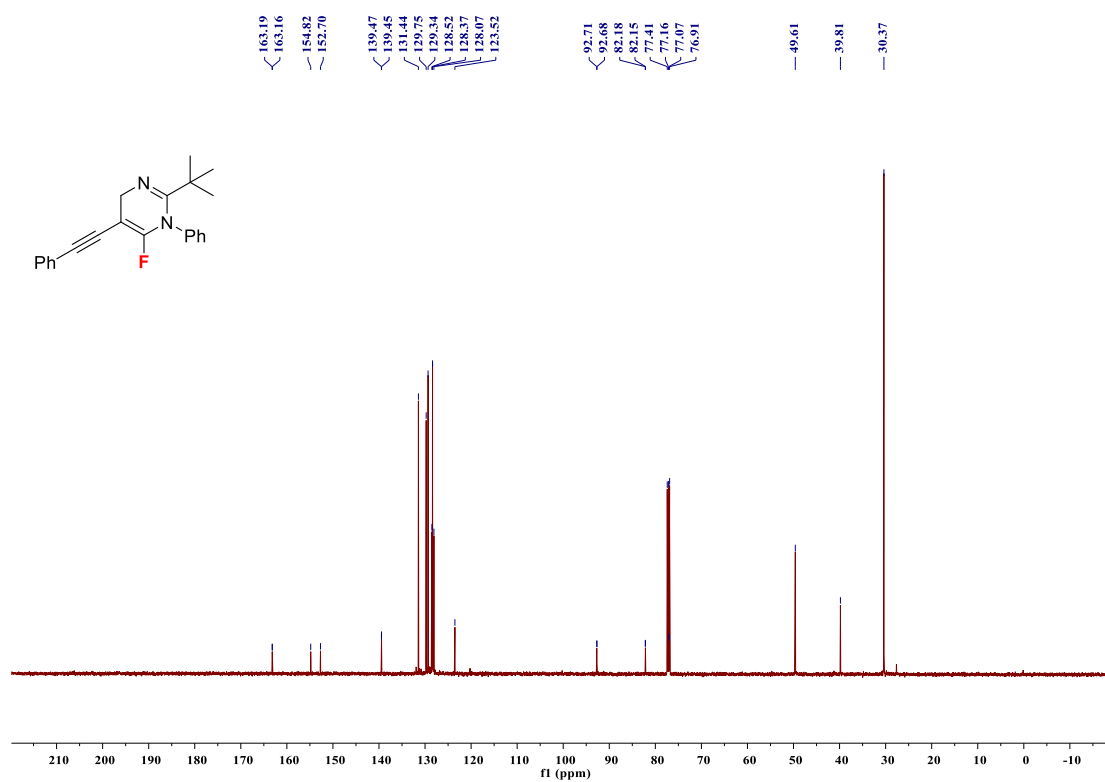
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 30a**



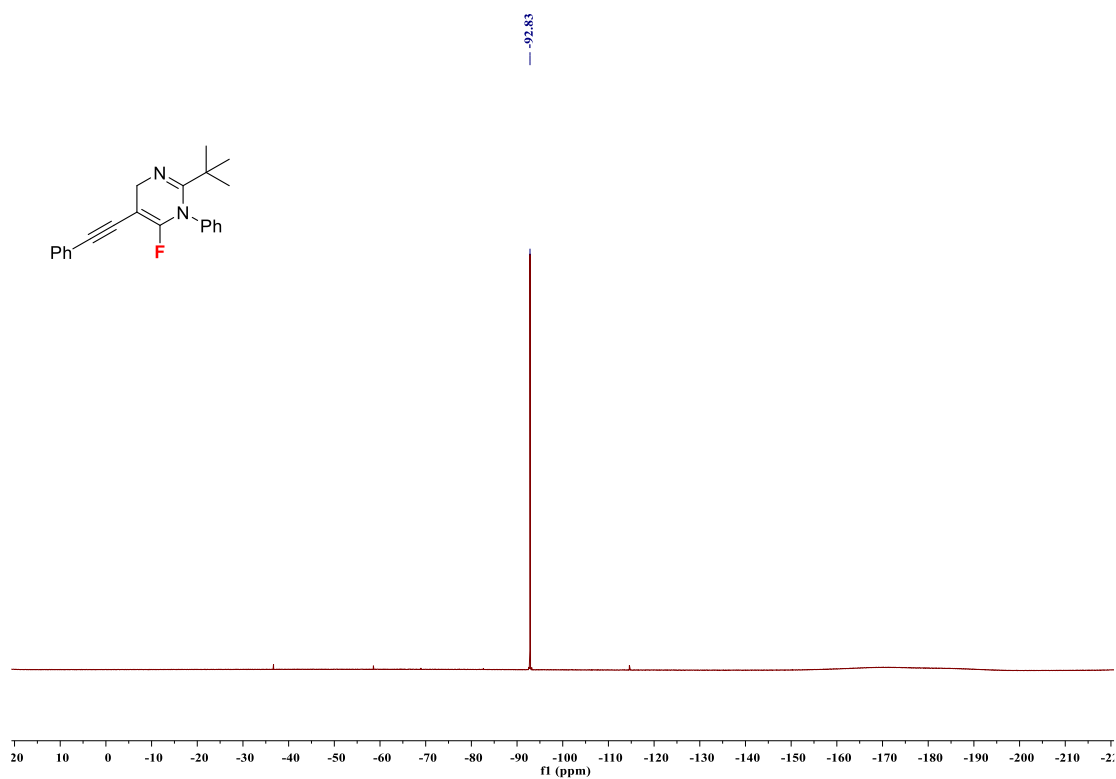
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3pa**



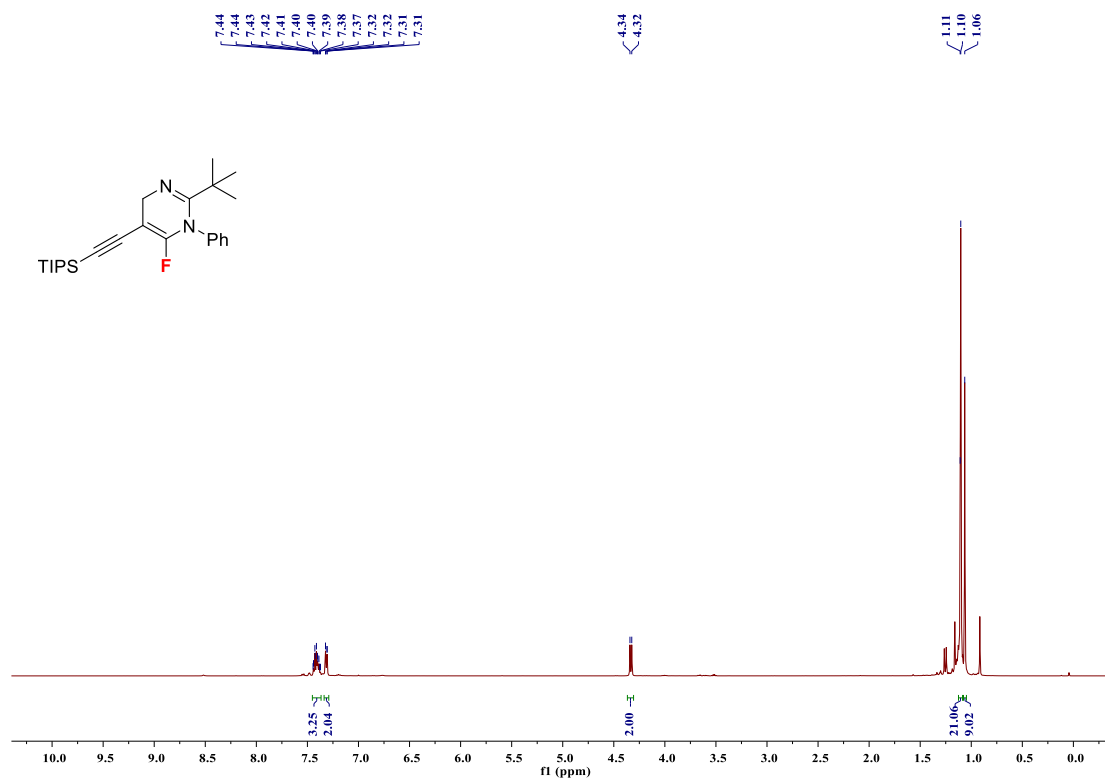
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3pa**



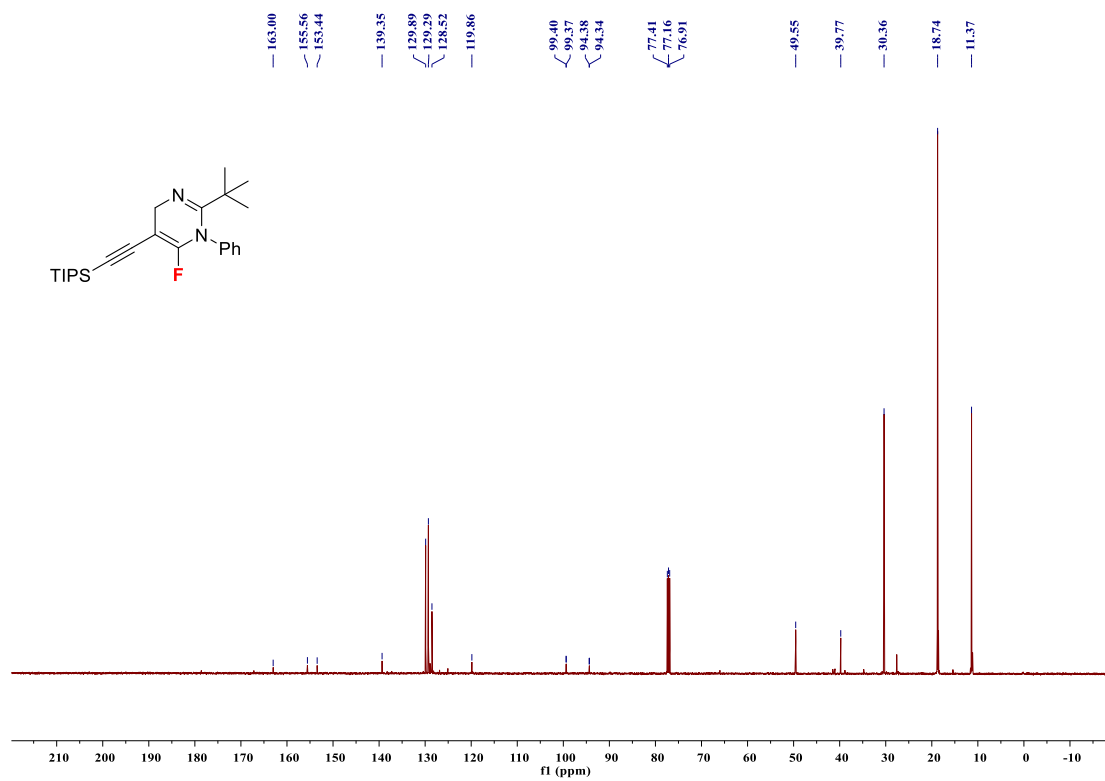
### <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3pa



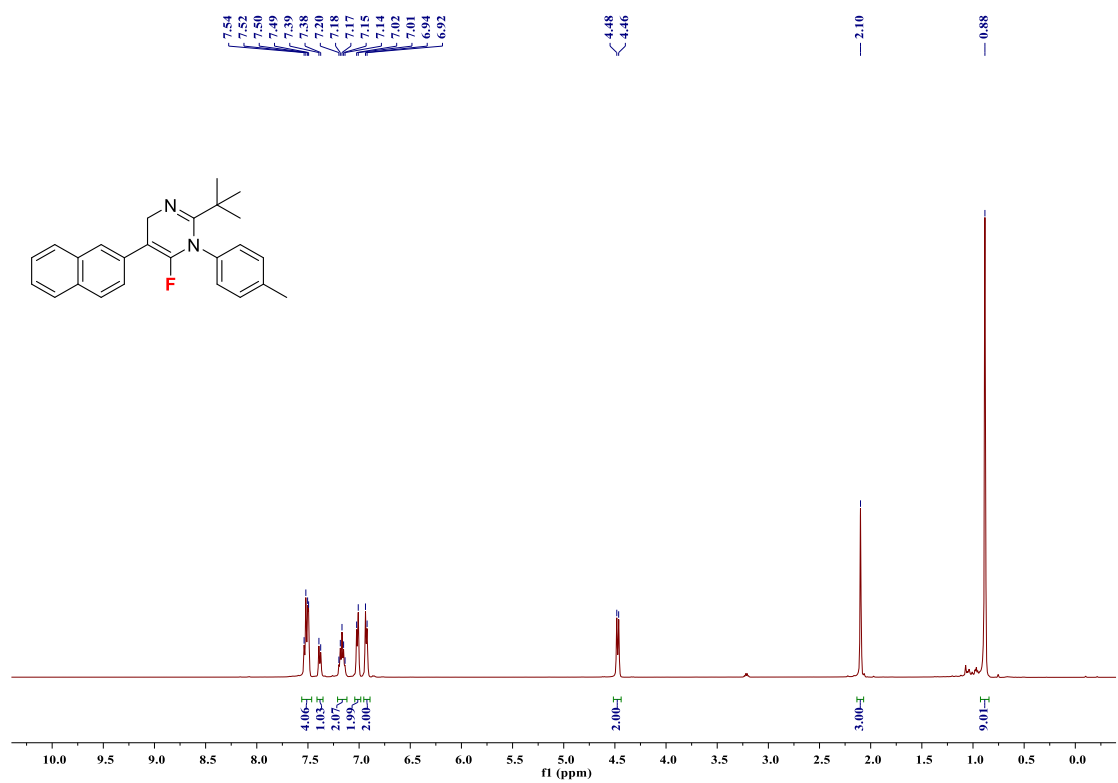
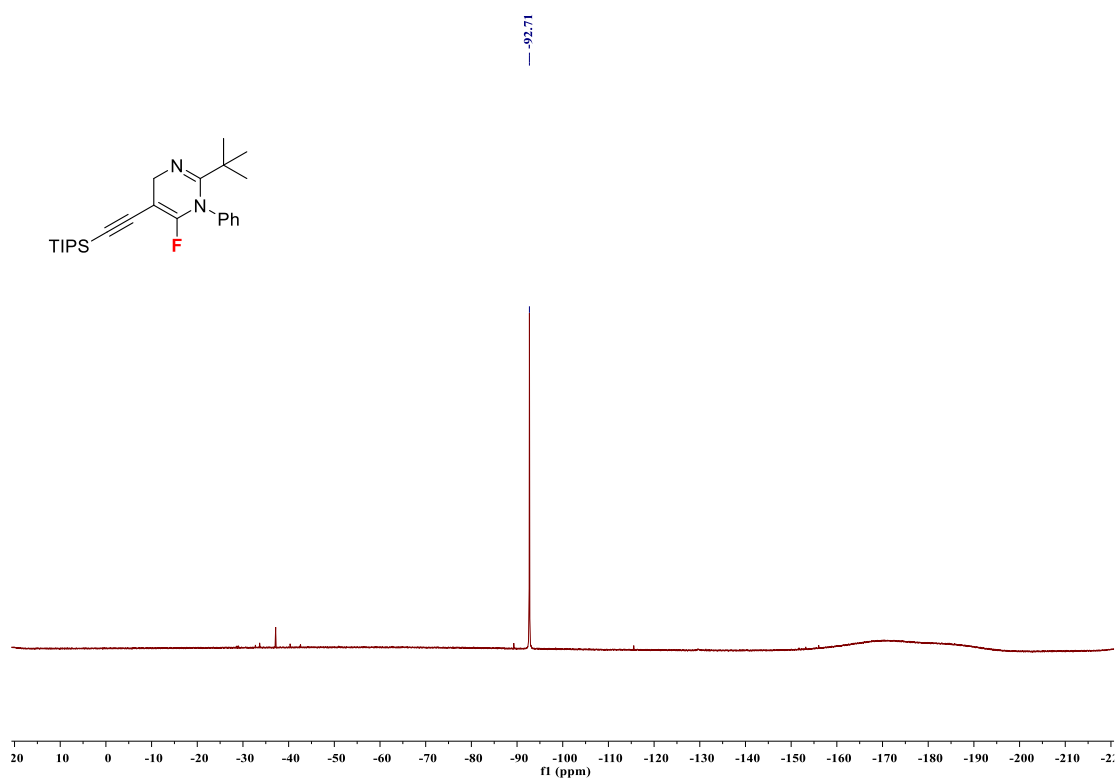
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3qa



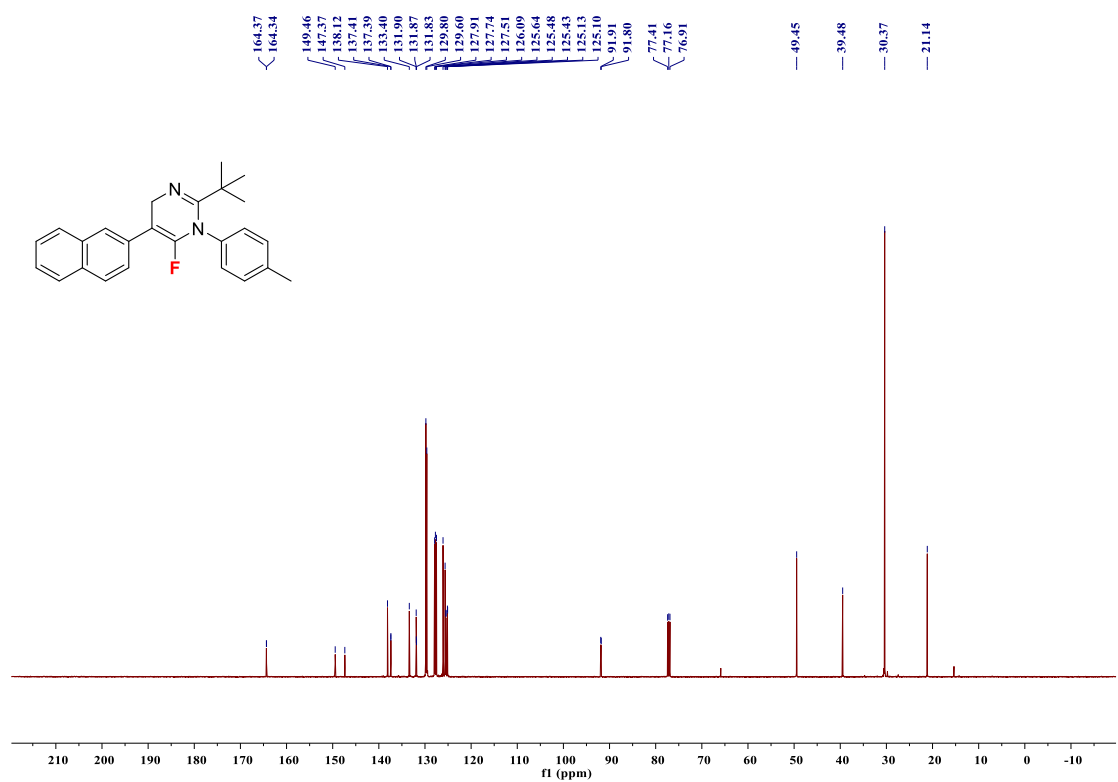
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) Spectrum for 3qa



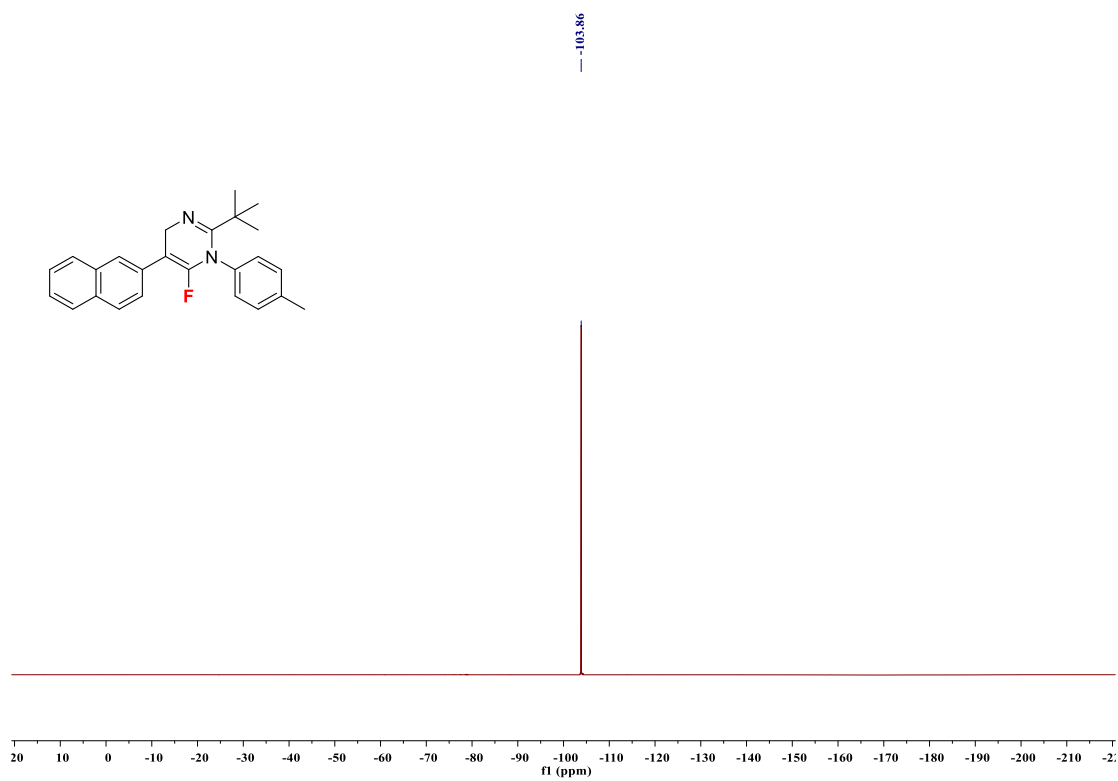
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) Spectrum for 3qa



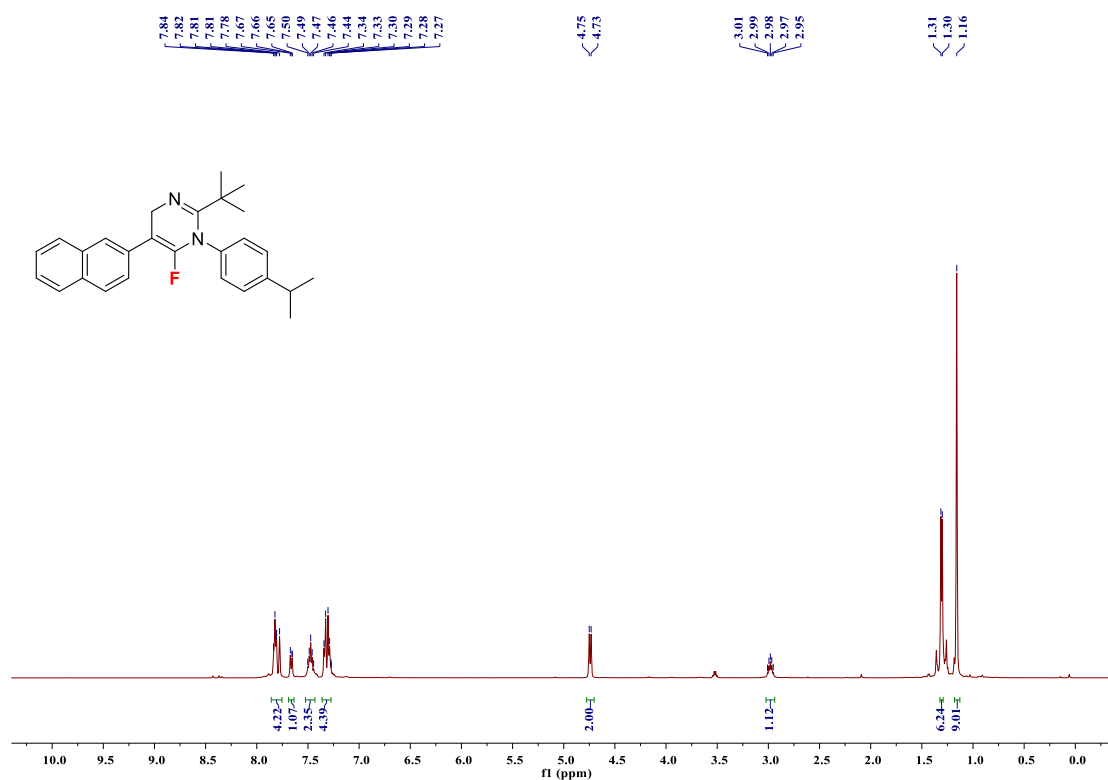




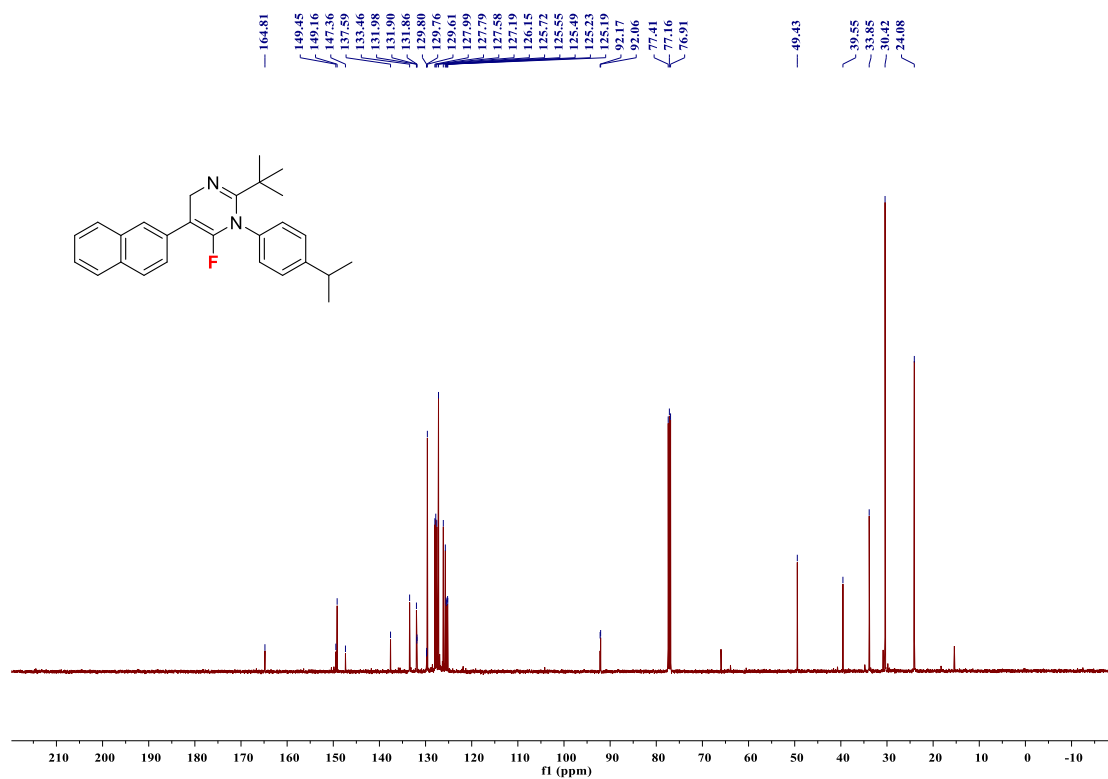
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ab**



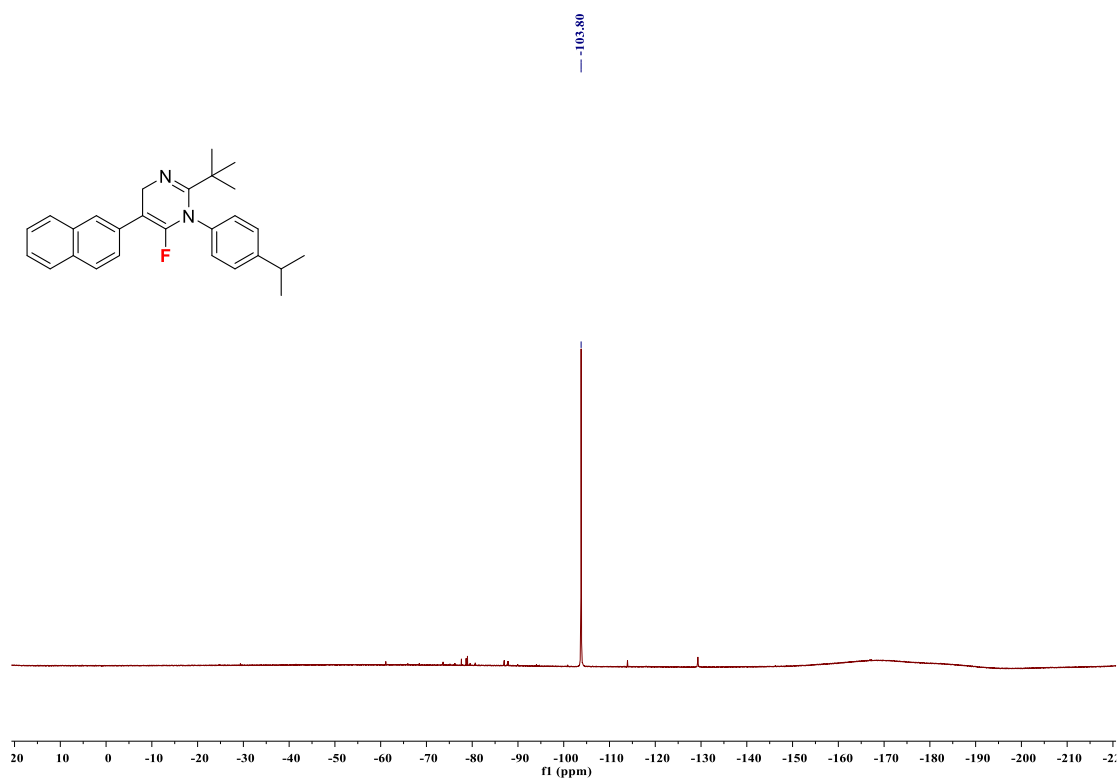
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ac**



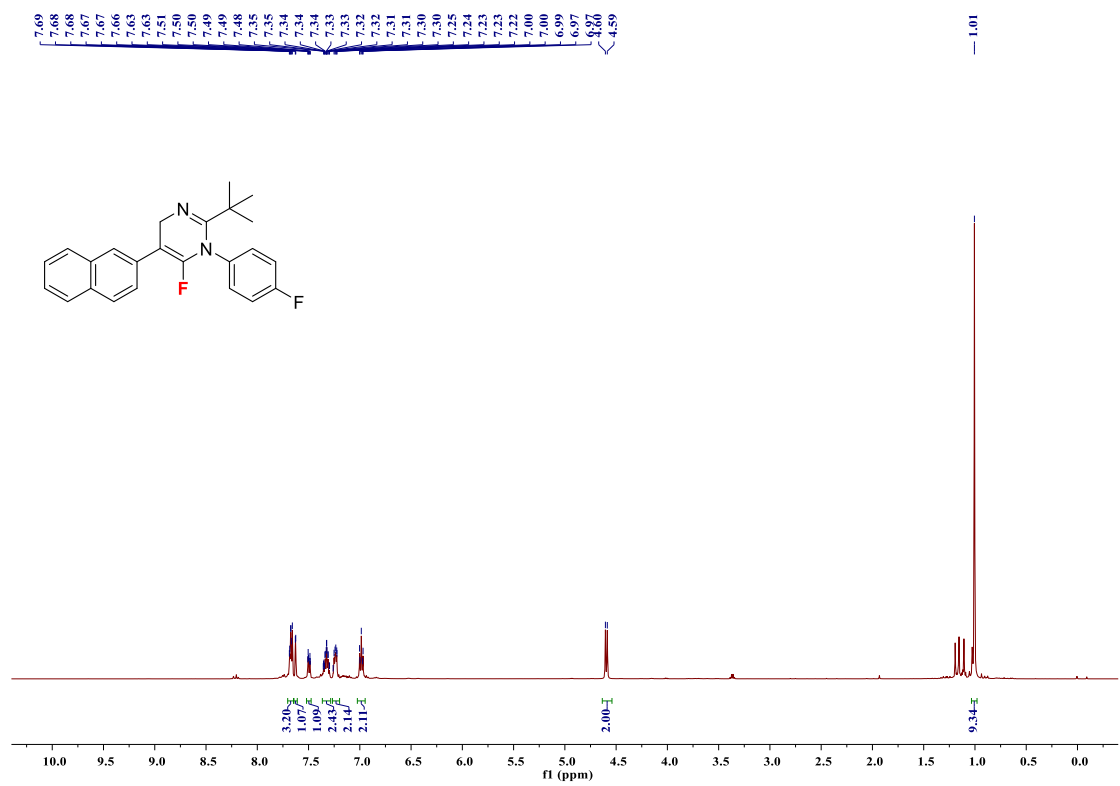
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ac**



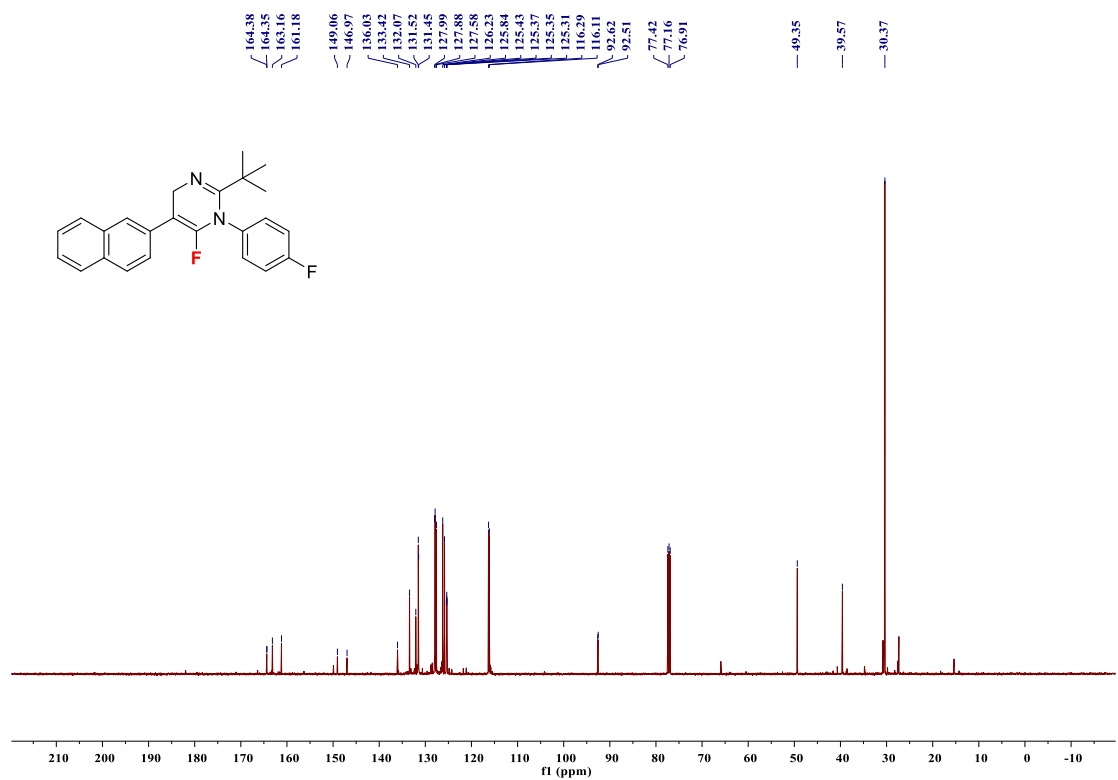
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ac**



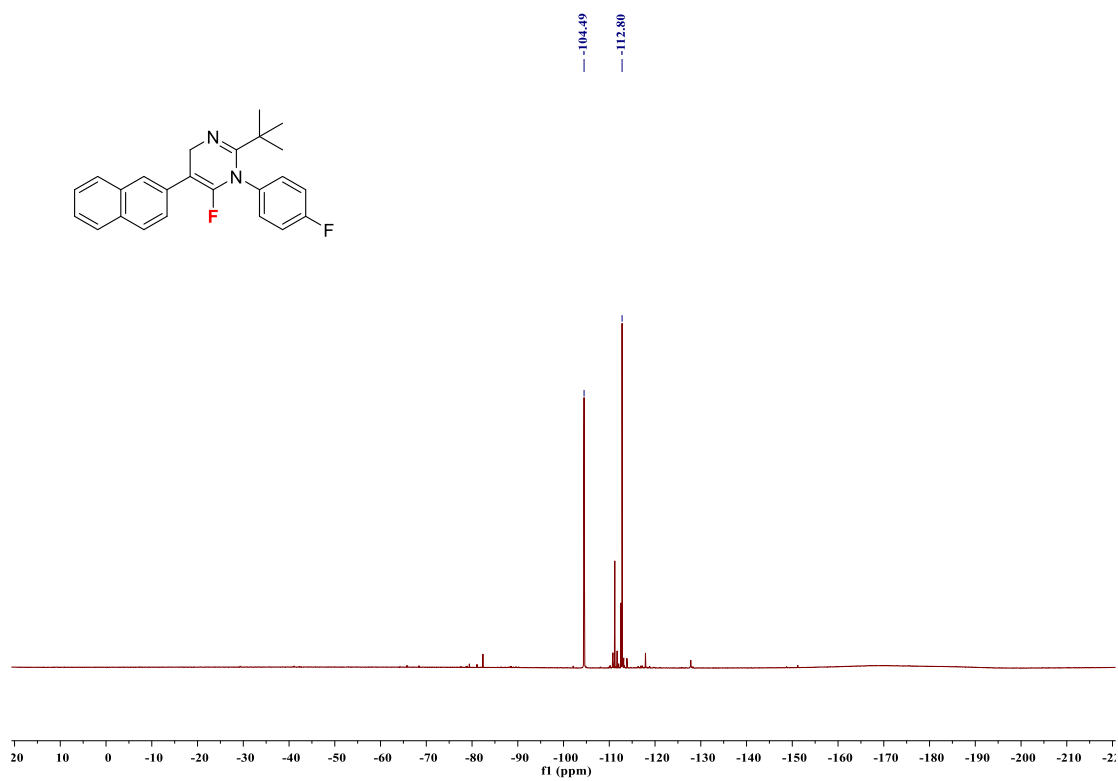
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ad



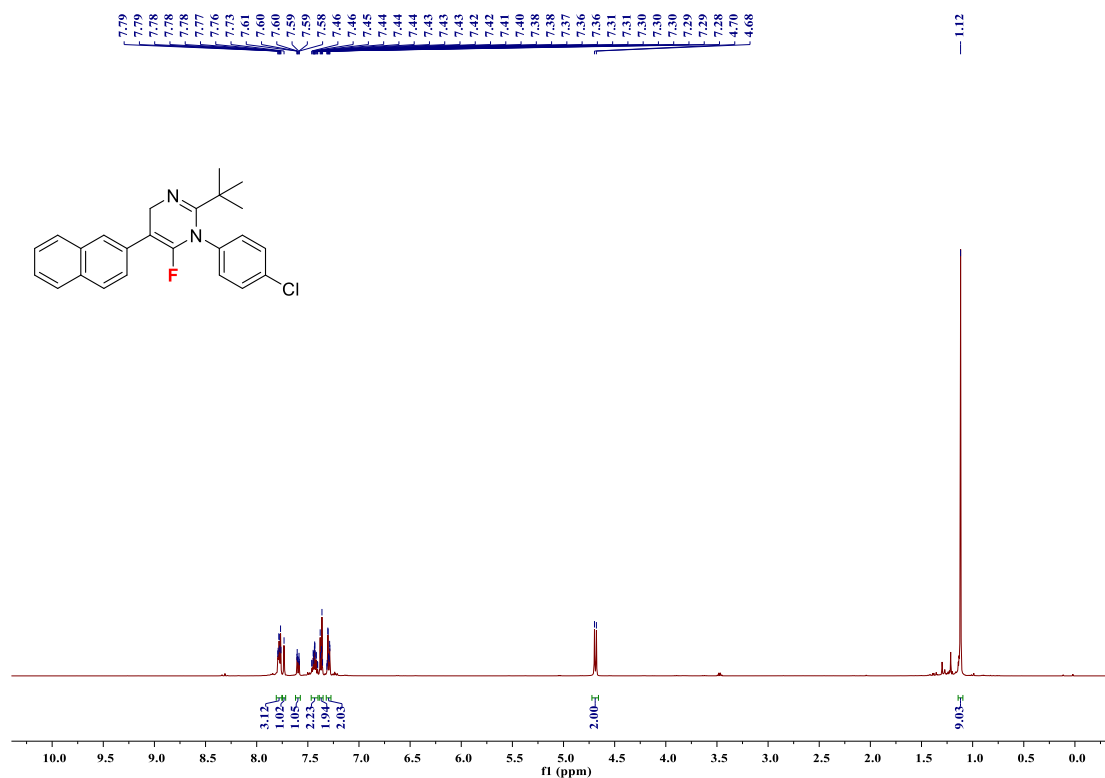
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ad



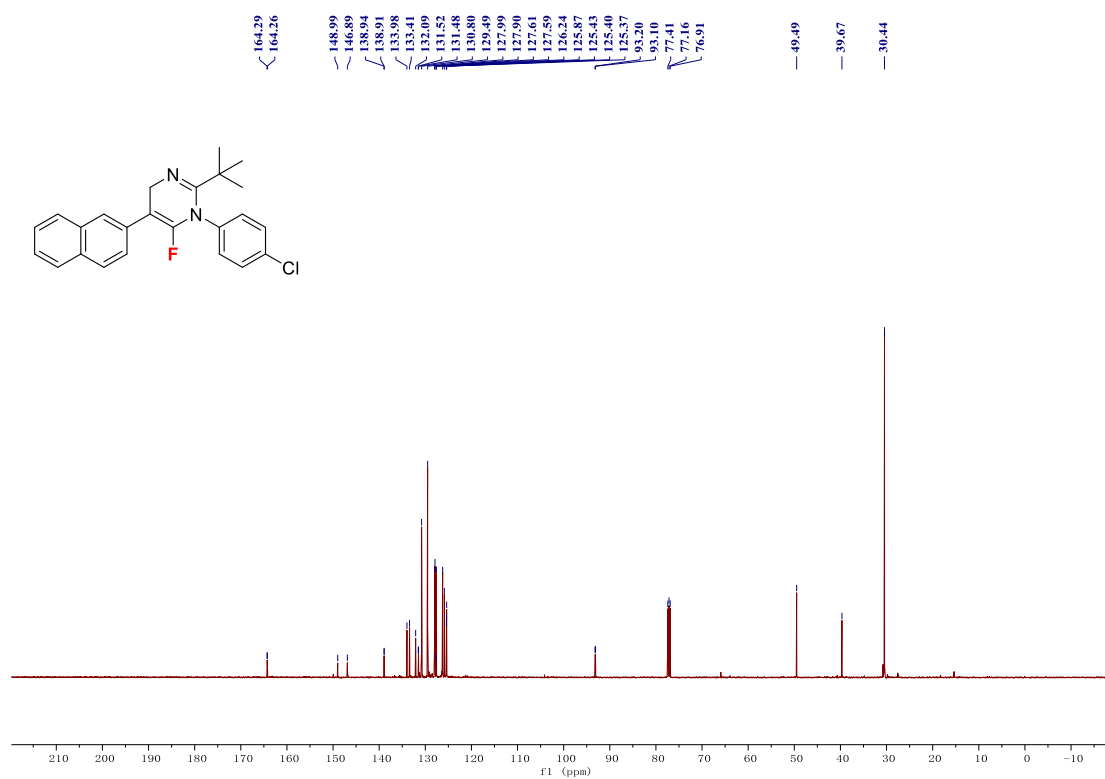
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ad



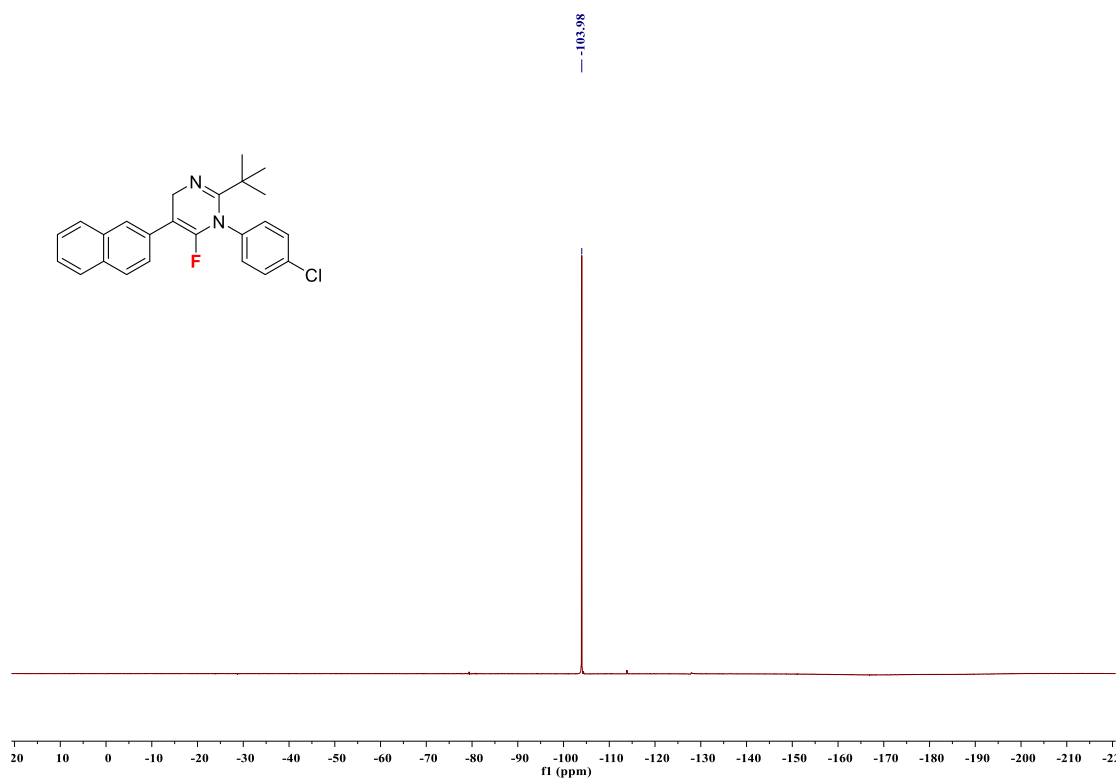
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ae



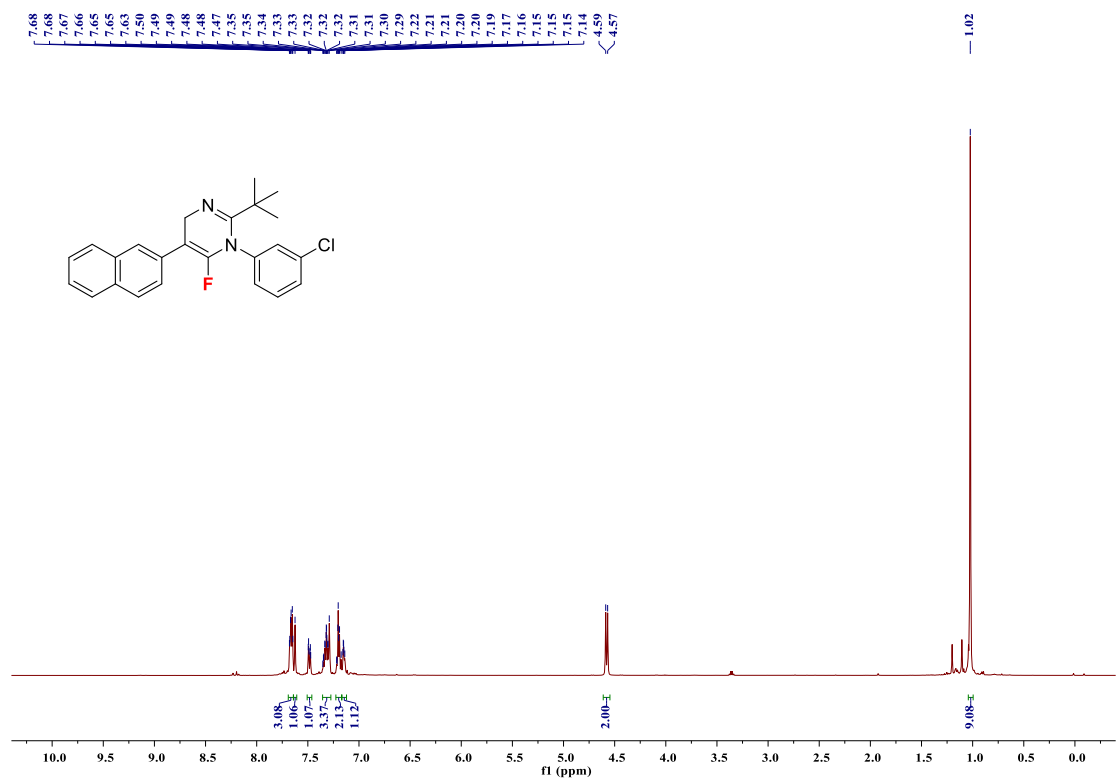
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ae



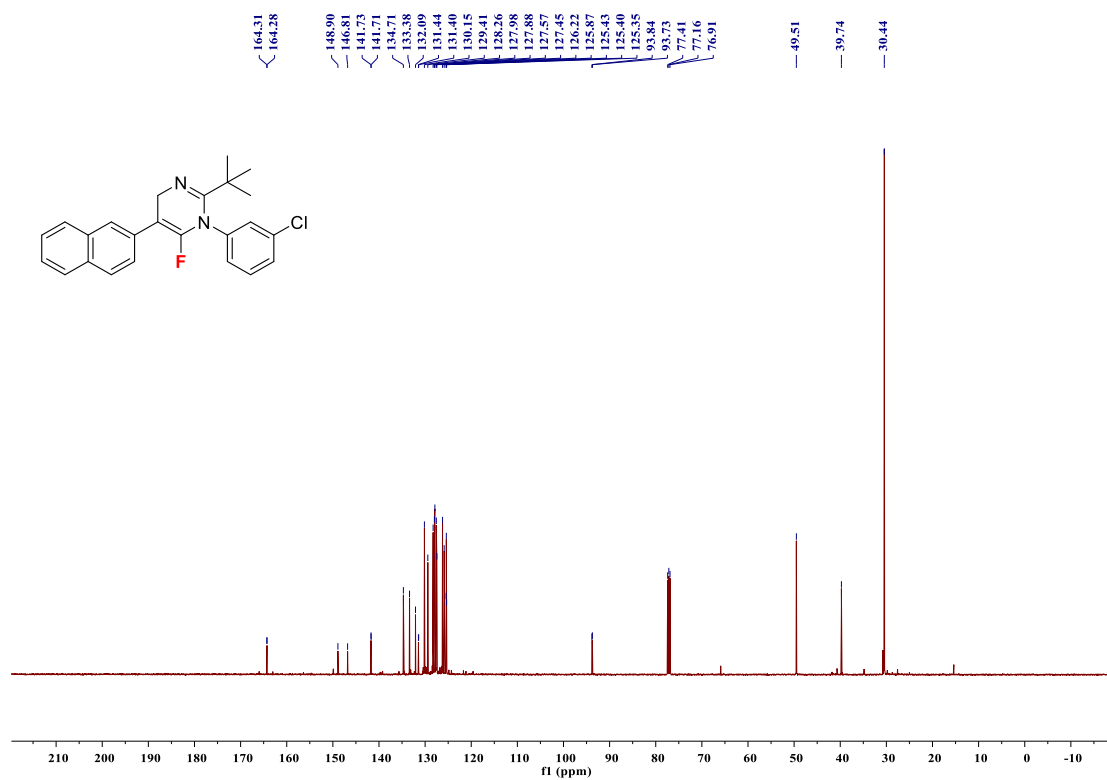
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ae



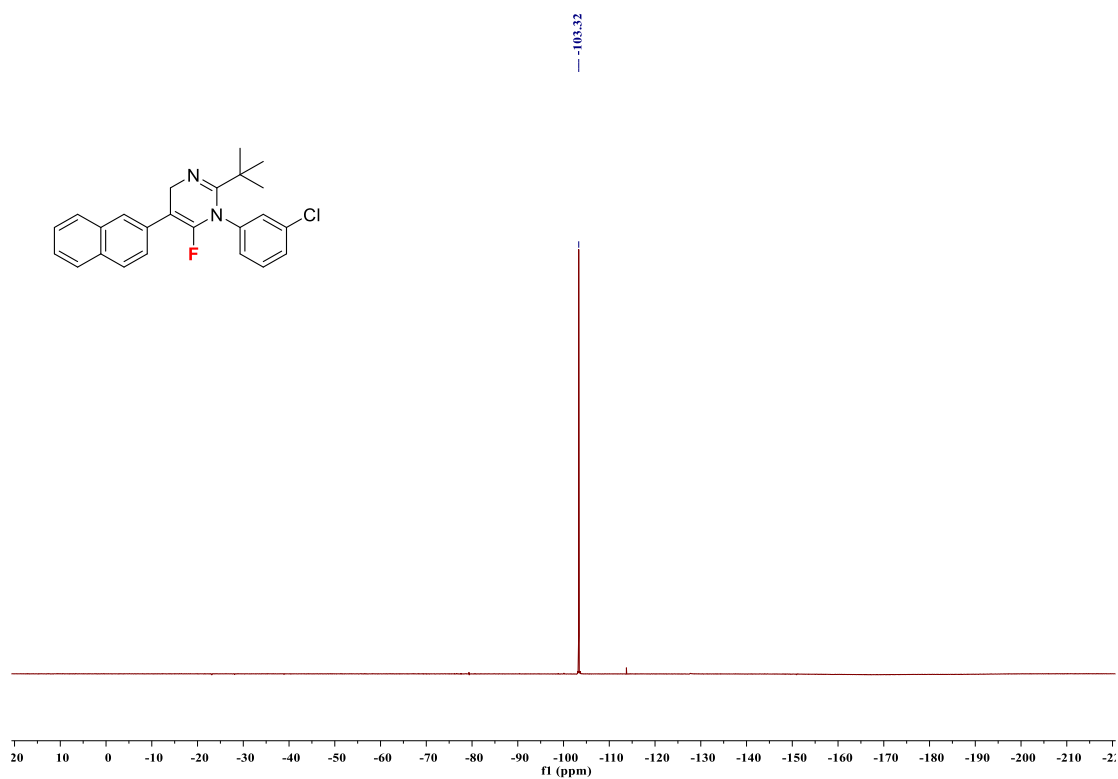
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3af



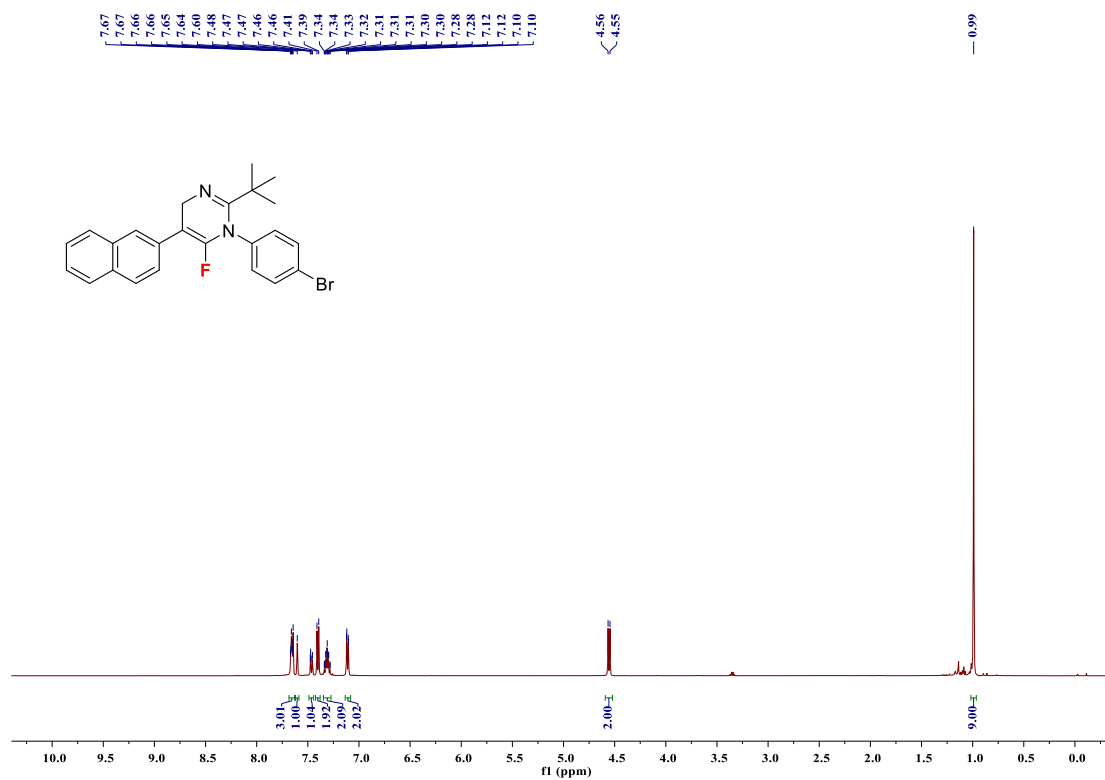
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3af



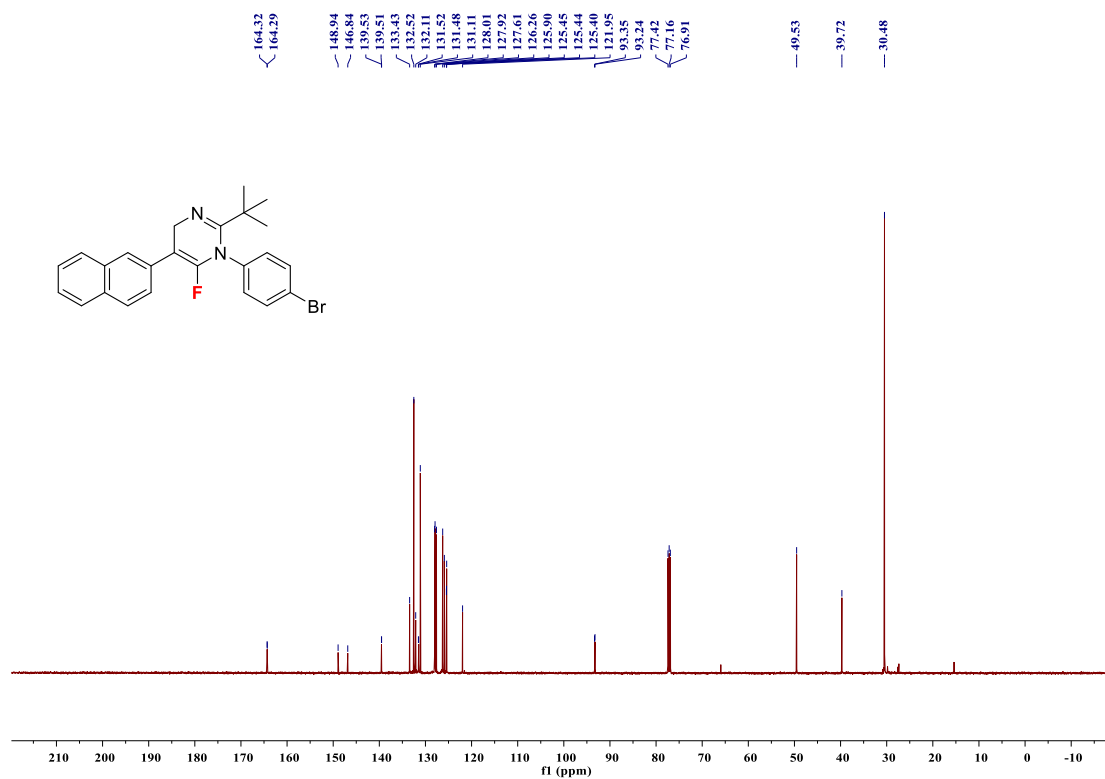
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3af**



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ag**

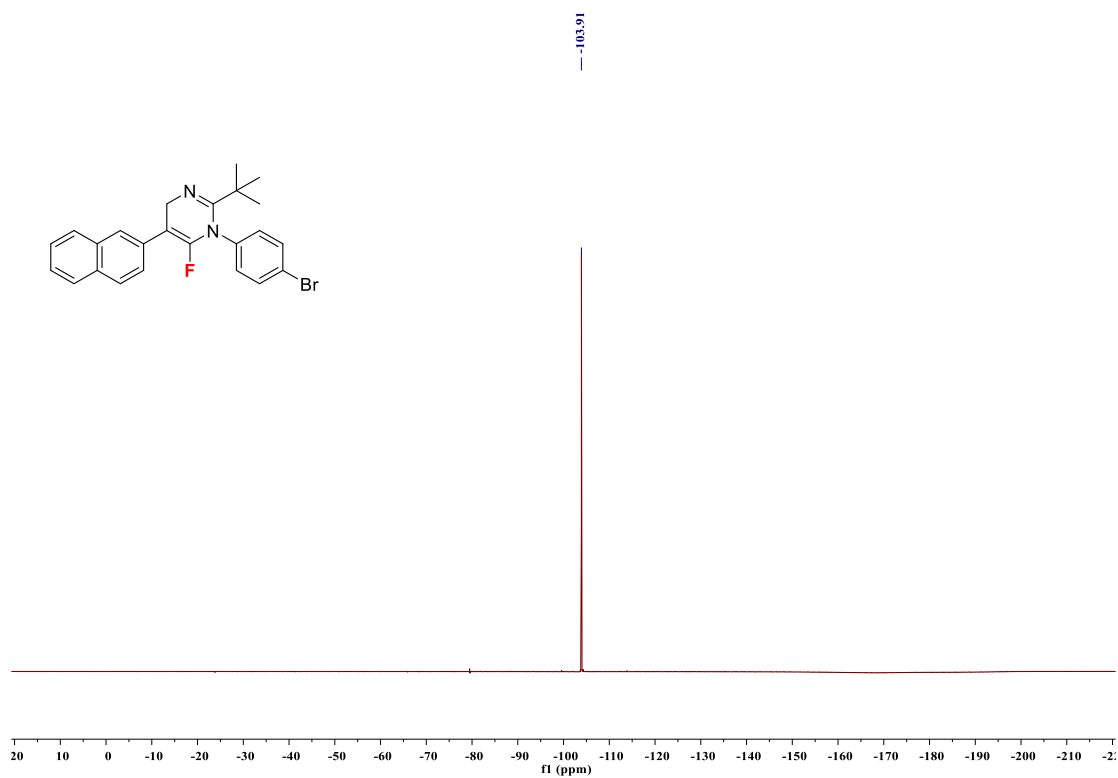


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ag**

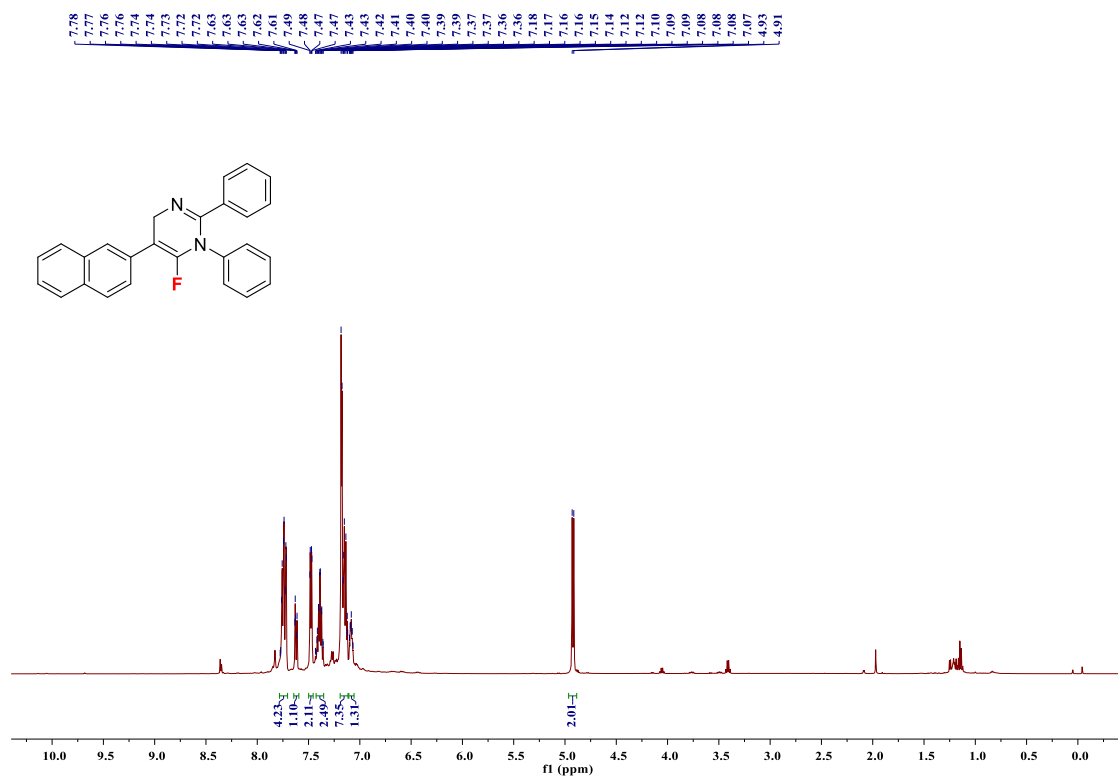


**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ag**

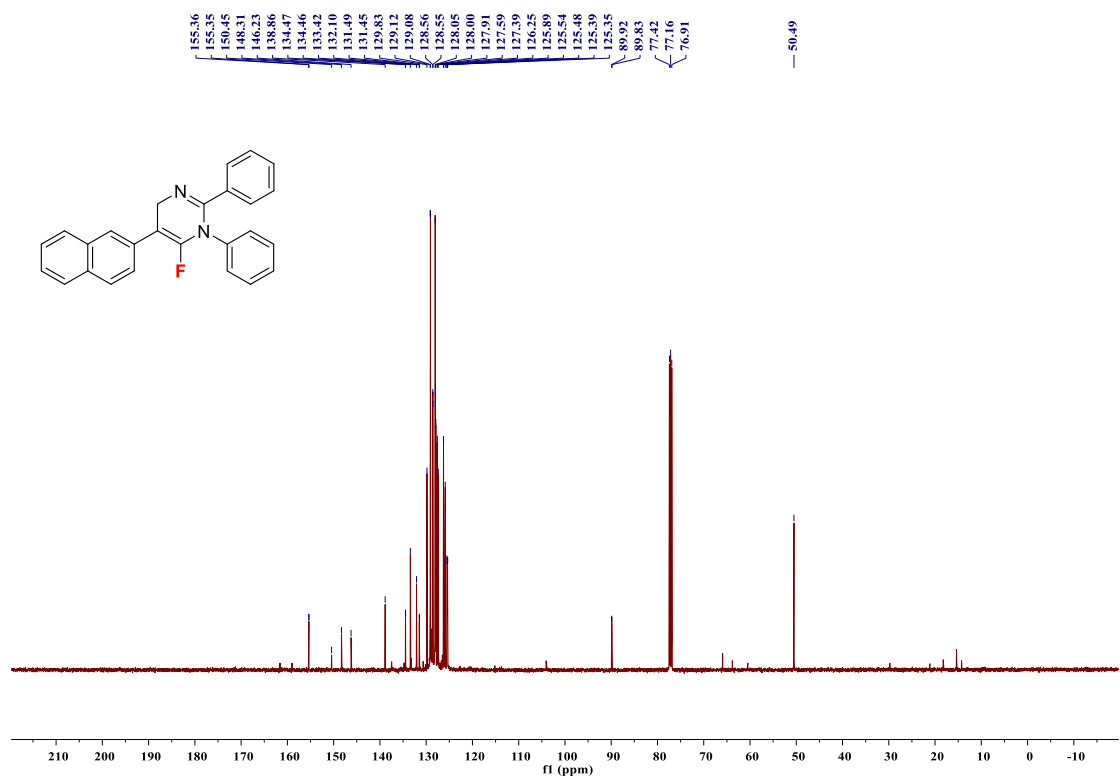




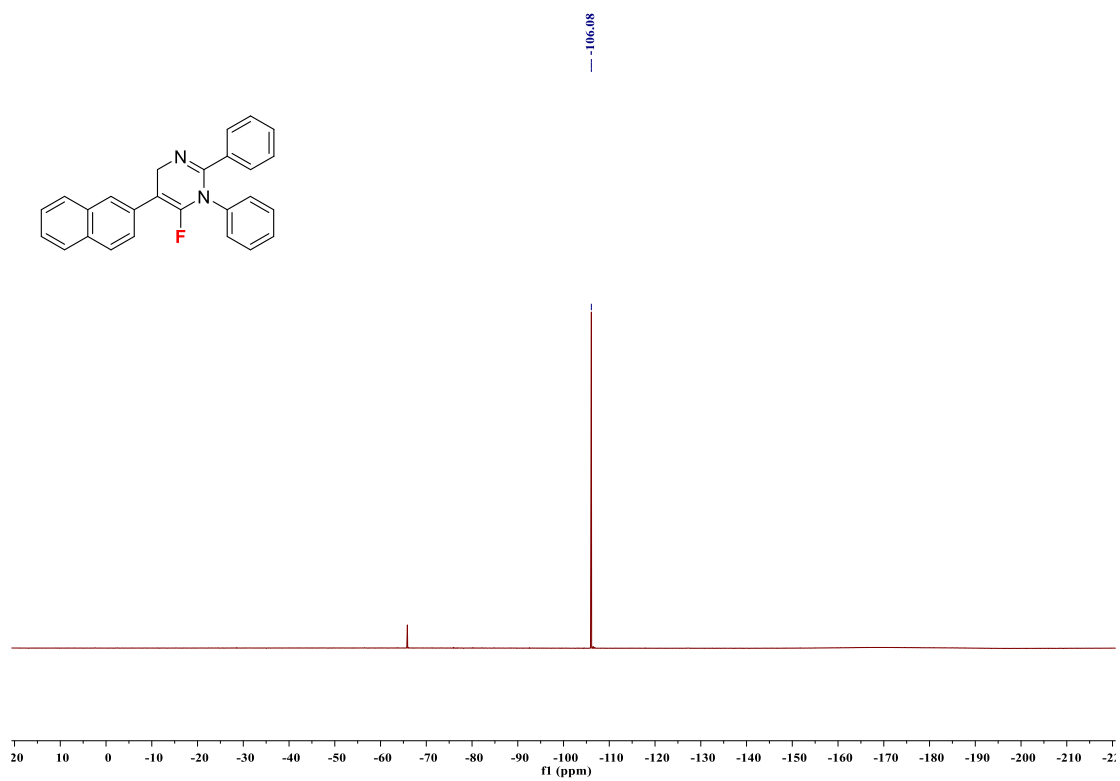
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 3ak



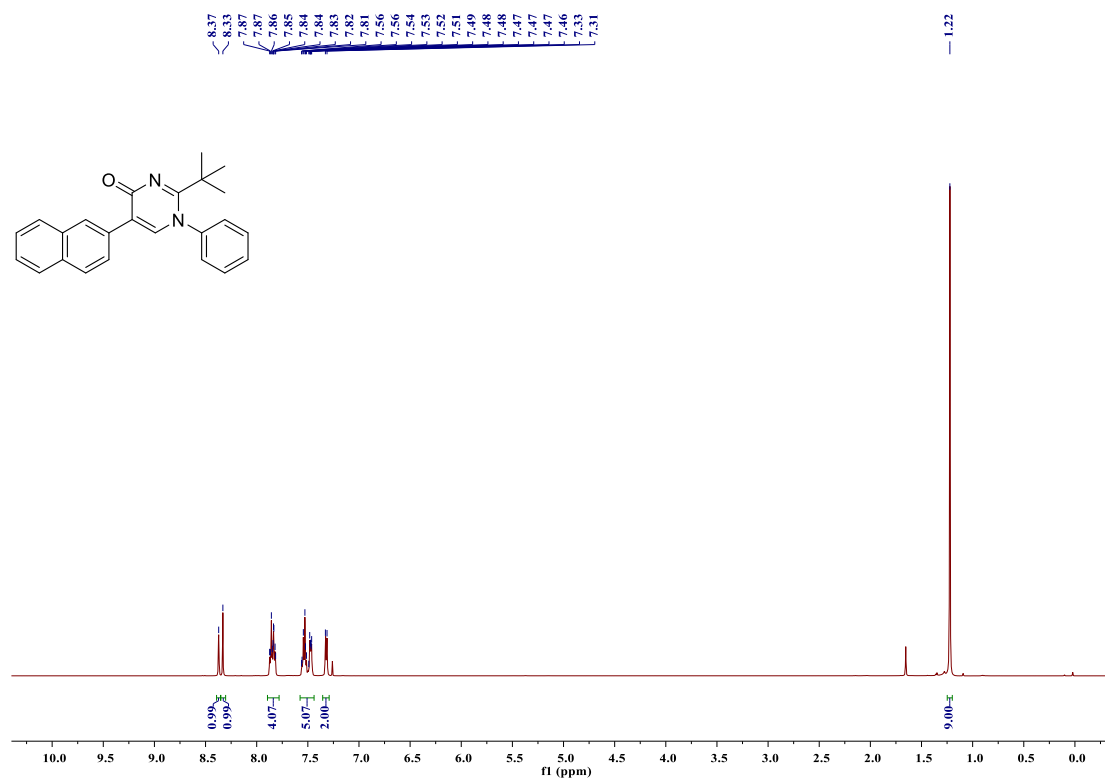
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 3ak



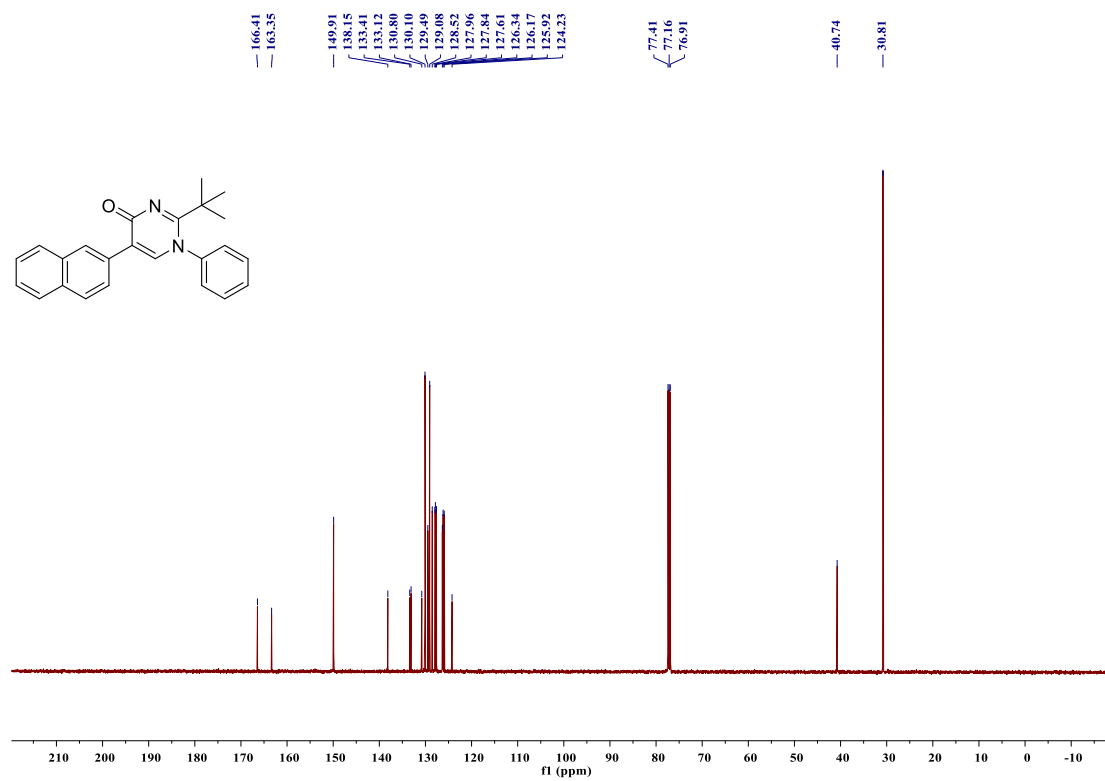
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) Spectrum for 3ak



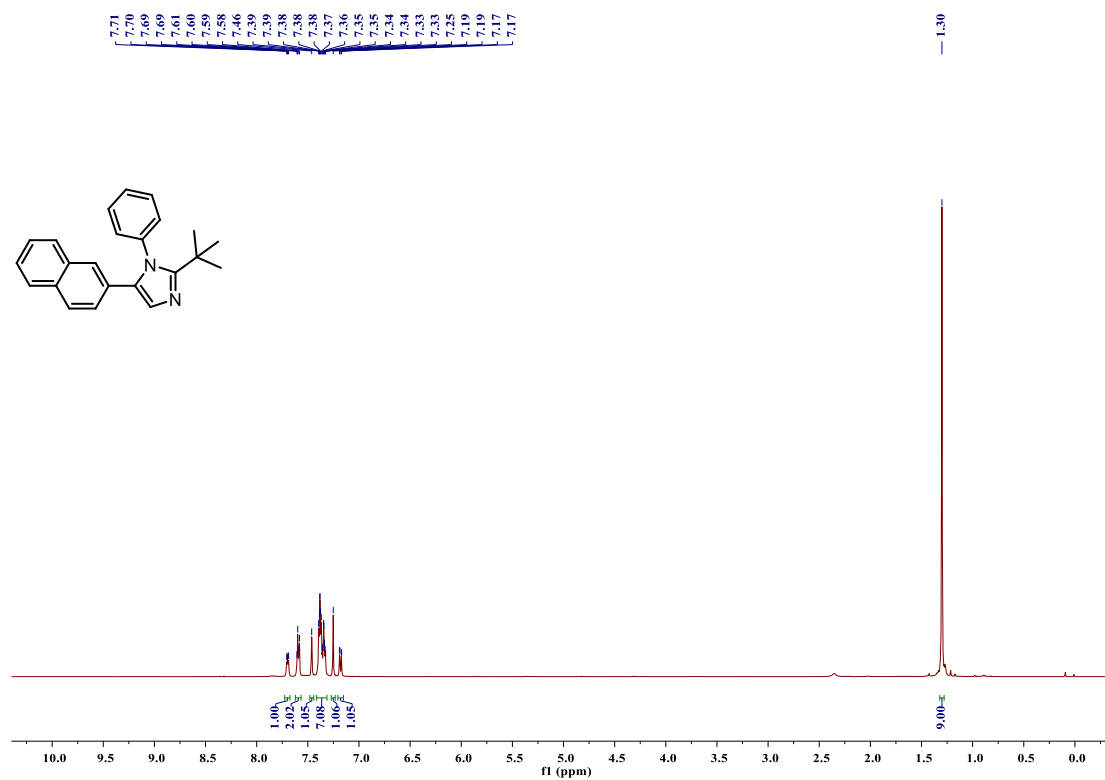
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 4



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 4**



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum for 5**



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum for 5

