Supporting Information

Heterogenized Molecular Pd(II) Catalyst on Ultrathin 2D Metal−organic Frameworks with Nanoflower-like Morphology for Isonitrile-involved Cyclization Reaction

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1. General Information

1.1 Materials and Instrumentation.

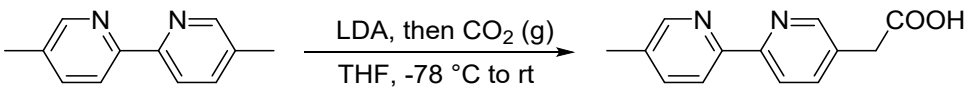
All chemicals were purchased commercially without further treatment unless stated otherwise.

PXRD patterns were collected on a Bruker D8 powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). The surface morphology of samples was characterized by a high-resolution field-emission scanning electron microscopy (FESEM, HITACHI SU8220). Transmission electron microscopy (TEM) and EDS mapping were obtained via JEOL JEM-2100F field-emission transmission electron microscope. The AFM imaging was performed on a Bruker Dimension Icon AFM. The BET surface areas and pore size measurements were obtained from N_2 adsorption/desorption isotherms at 77 K using a Micromeritics ASAP 2460 instrument. The content of Pd was determined by the inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 720ES). The Xray photoelectron spectroscopy (XPS) experiments were conducted using Thermo fisher Scientific K-Alpha+. The Pd K-edge X-ray absorption fine structure (XAFS)

measurements were performed at BL14W1 beamline in Shanghai Synchrotron Radiation Facility (SSRF), China. The hard X-ray was monochromatized with Si (311) double-crystal monochromator and the XAFS data were collected in transmission mode in the energy range from −200 below to 1000 eV above the Pd K-edge ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at a Bruker Model AM-400 (400 MHz) spectrometer 400 MHz NMR spectrometer. UV-vis spectra were collected on spectrophotometer (Shimadzu UV-3900 UV-VIS Spectrophotometer). FTIR experiments were conducted with Bruker Tensor 27 on either potassium bromide pellets or liquid films between two potassium bromide pellets.

2. Catalyst Synthesis

2.1 Synthesis of 2-(5'-methyl-[2,2'-bipyridin]-5-yl)acetic acid (Bpy)



Bpy was synthesized by a modified literature method.[1] Lithium diisopropylamide (LDA) was dissolved in THF (3 mL) and cooled to -78 °C. The resultant mixture was stirred for 2 additional hours at this temperature after the quick addition of a solution of 5,5'-dimethyl-2,2'-bipyridine (1.0 g, 5.5 mmol) in THF (12 mL). Dry CO_2 was then bubbled through at the same temperature for 1 h and the mixture was warmed to ambient temperature with CO_2 still being bubbled through. Ether (100 mL) was added to the resulting semisolid white mass, and the mixture was extracted with 1 M NaOH aqueous solution (20 mL×3). The alkaline layer was acidified to pH 1 with concentrated HCl and then extracted with ether (20 mL×3). The acidic solution was buffered to pH 5 with sodium acetate. After removal of the solvent under reduced pressure, the resulting solid was extracted into MeOH (50 mL), dried in vacuo and recrystallized from EtOH with the addition of hexanes to yield pure product as a white solid.

2.2 Synthesis of Zr-BTB

The synthesis methods were modified on the basis of previous report.[2] $ZrCl_4$ (100 mg), H_3BTB (100 mg), benzoic acid (6 g), H_2O 10 mL and DMF (30 mL) were charged in a Pyrex vial. The mixture was heated in 100 ºC oven for 24 h. After cooling down to room temperature, the product was collected by centrifugation, and washed with DMF and acetone.

2.3 Synthesis of Zr-BTB-Bpy

Zr-BTB (100 mg), Bpy (50 mg) and DMF (5 mL) were charged in a Pyrex vial. The mixture was heated in 100 ºC oven for 12 h. After cooling down to room temperature, the product was collected by centrifugation, and washed with DMF and acetone.

2.4 Synthesis of Zr-BTB-Bpy-Pd

Zr-BTB-bpy (100 mg) was dispersed into acetone (1 mL), then 20 ml acetone solution of palladium acetate was dropped. After continue stirring for 6 h at room temperature, the obtained solids were separated by centrifugation and washed with acetone.

2.5 Synthesis of Pd-UiO-67-Bpy

The UiO-67-bpy was synthesized though solvothermal route as reported.[3] Firstly, $ZrCl_4$ (121 mg, 0.52 mmol) and 2,2'-bipyridine-5,5'- dicarboxylic acid (H_2bpydc, 127 mg, 0.52 mmol) were dissolved in 20 mL of N,N-dimethylformamide (DMF). Then, the benzoic acid (1.88 g, 15.6 mmol) was added acting as a modulator to the mixture, which was further dispersed uniformly via sonication. Next, the mixture was transferred into a 20 mL Teflon-lined stainless-steel autoclave and heated to 120 °C for 24 h. The white precipitate was obtained by centrifugation and washed with DMF (3 × 10 mL), followed by soaking in acetone for 3 d and exchanging with fresh acetone every day. Finally, the UiO-67-Bpy was collected and dried under vacuum at 60 °C for one day.

$Pd(OAc)_2$ and UiO-67-Bpy (213 mg, 0.1 mmol) were dispersed in 10 mL of acetone respectively. Then the Pd(II) solution was added to MOF solution dropwise. After stirring for 6 h at 30 °C, the brown solid Pd-0.08-UiO-67-Bpy was collected via centrifugation and washed with acetone (3 × 10 mL), followed by soaking in acetone for 3 d. The solution was exchanged with fresh acetone (10 mL) every 24 h and finally

dried under vacuum at 80 °C for 12 h.

2.5 General procedure for the Synthesis of Products 3

Unless otherwise specified, N-(tert-butyl)-2,2,2-trifluoro-N-(3-phenylquinolin-2-yl) acetamide (as an example) derivatives were synthesized via the following step: 2,2,2-Trifluoro-N-(2-(phenylethynyl)phenyl)acetamide (1**a**, 28.9 mg, 0.10 mmol), tert-butyl isocyanide (2**a**, 10.4 mg, 0.125 mmol), Zr-BTB-bpy-Pd (5 mg, Pd 0.13 mol%), Li_2CO_3 (2.2 mg, 30 mmol%) were mixed in 1 mL dry DMSO. The reaction was stirred at 90 °C for 0.5 h in N_2. After the reaction finished (monitored by TLC), the mixture was quenched with H_2O, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate (30: 1) as eluent to afford the desired product 3**a**.

2.6 UV-vis and FTIR spectra

2,2,2-Trifluoro-N-(2-(phenylethynyl)phenyl)acetamide (1**a**, 28.9 mg, 0.10 mmol), different amounts of catalyst Zr-BTB-bpy-Pd (or Pd-UiO-67-Bpy) (50 mg, 100mg, 150mg) were mixed in 1 mL dry DMSO, The mixture was stirred at 90 °C for 10 min in N_2. Then the mixture was separated by centrifugation. The absorbance of the supernatant was recorded on UV-3900 spectrophotometer. After washed three times with ethyl acetate, the FT-IR experiments of the recovered catalyst were conducted.

3. Characterization of Zr-BTB, Zr-BTB-Bpy and Zr-BTB-Bpy-Pd

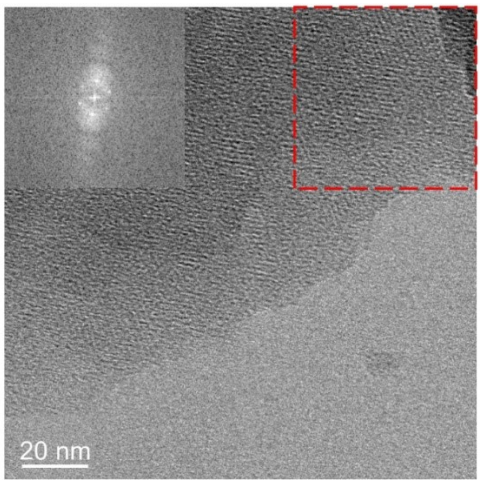


Fig. S1 HRTEM image and fast Fourier transform (FFT) patterns of Zr-BTB.

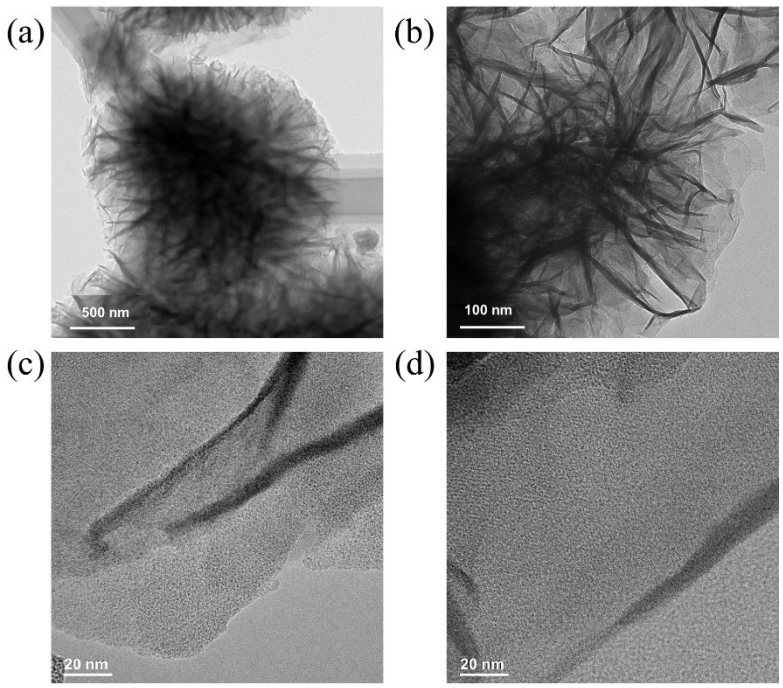


Fig. S2 TEM images of (a) Zr-BTB, (b) and (c) Zr-BTB-Bpy-Pd and (d) Zr-BTB-Bpy-Pd (used).

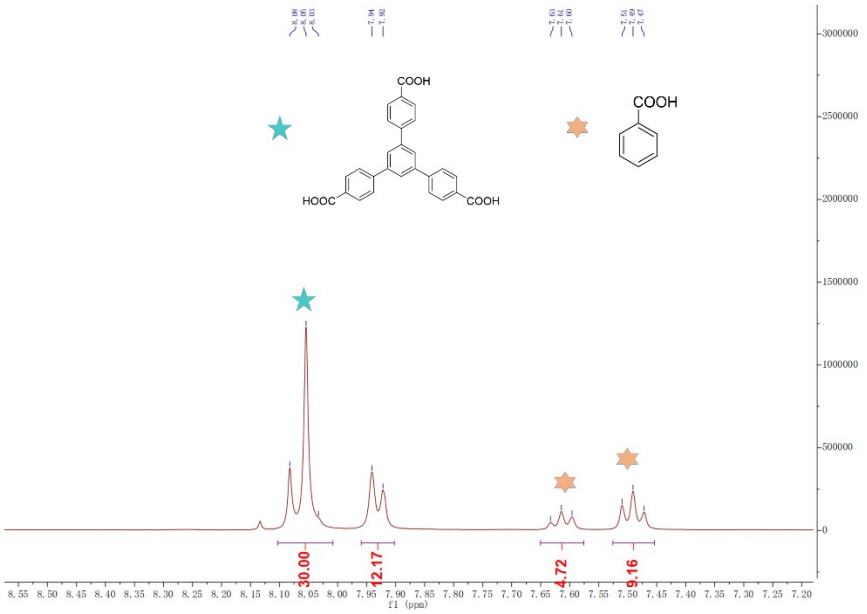


Fig. S3 ^{1}H NMR spectrum of digested Zr-BTB in DMSO-d_6.

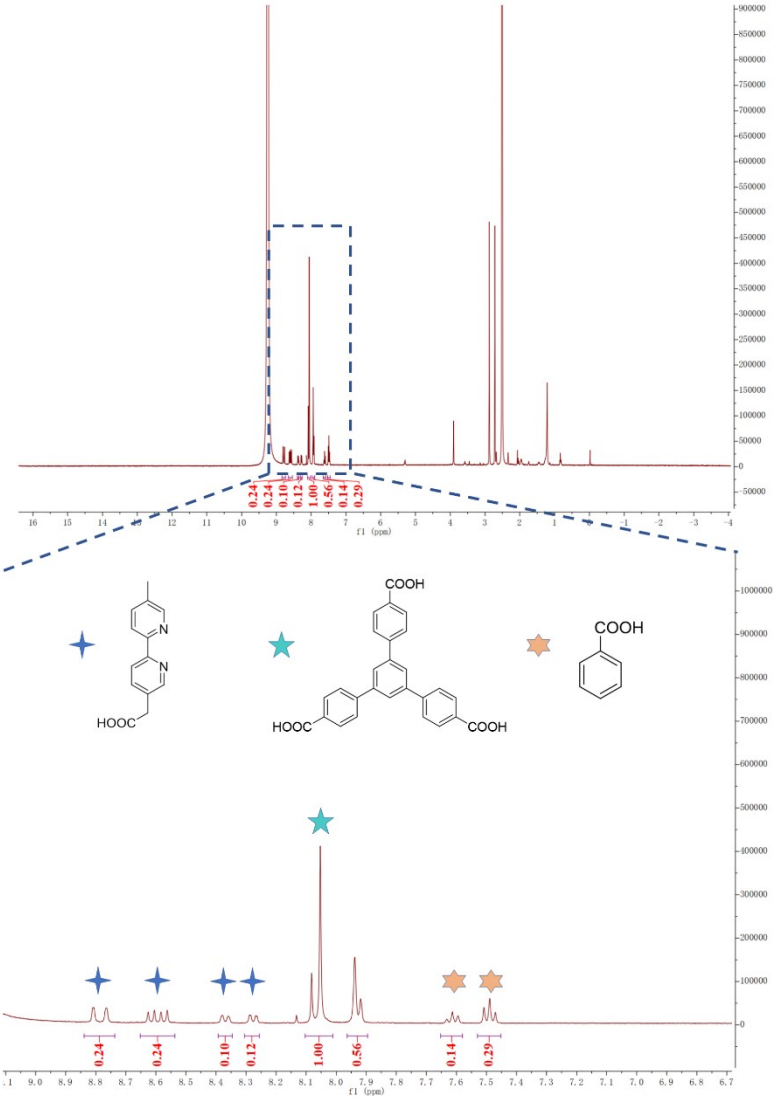


Fig. S4 ^{1}H NMR spectrum of digested Zr-BTB-Bpy in DMSO-d_6.

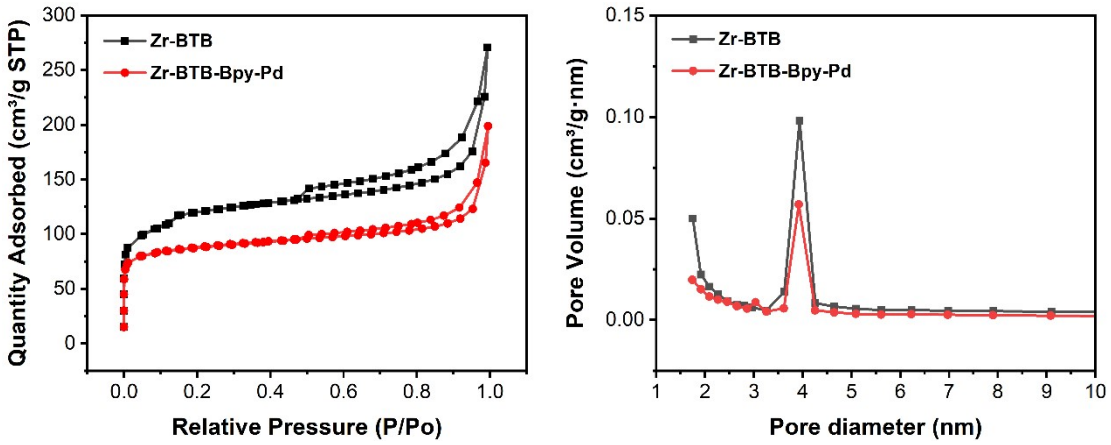


Fig. S5 N_2 adsorption and desorption isotherm profiles at 77 K and the pore size distribution of Zr-BTB and Zr-BTB-bpy-Pd.

Table S1 EXAFS fitting parameters at the Pd K-edge for various samples（S_0^2=0.89）

	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Pd foil	Pd-Pd	12*	2.74±0.01	0.0055	3.2±0.3	0.0039
Pd-bpy	Pd-N/O	3.6±0.3	1.98±0.01	0.0021	0.2±0.5	0.002
Zr-BTB-Bpy-Pd	Pd-N/O	3.6±0.2	2.01±0.01	0.0039	5.9±1.2	0.0095

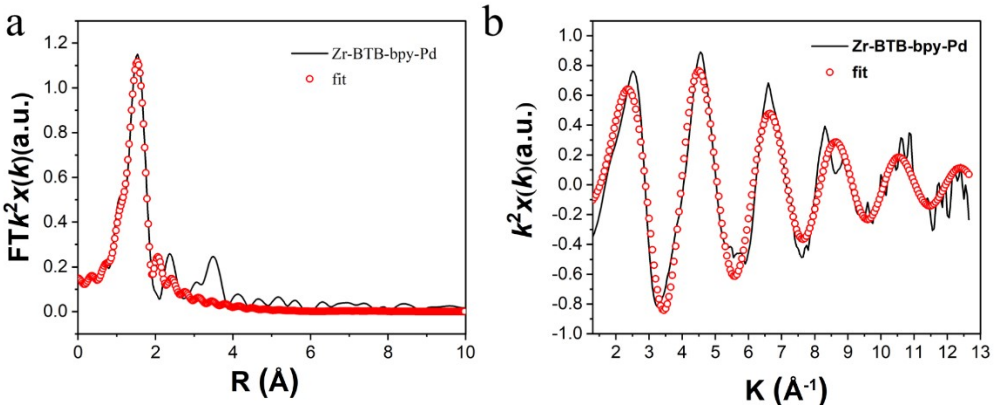


Fig. S6 (a) EXAFS spectra in R space at the Pd K-edge adsorption of Zr-BTB-bpy-Pd, (b) EXAFS spectra in K space at the Pd K-edge adsorption of Zr-BTB-bpy-Pd

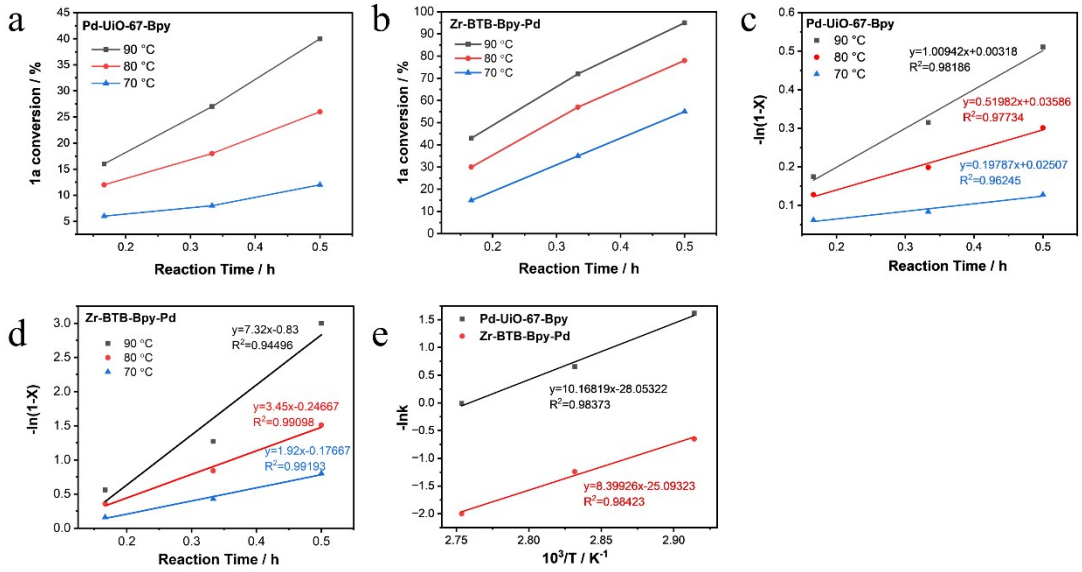


Fig. S7 Kinetic investigation of two different catalysts in the isonitrile-involved cyclization reaction. The calculated activation energies of Pd-UiO-67-Bpy and Zr-BTB-Bpy-Pd were 84.5 kJ·mol^{-1} and 69.8 kJ·mol^{-1}, respectively.

The detalied calculation process of apparent activation energy (Ea) of Pd-UiO-67-Bpy and Zr-BTB-Bpy-Pd is as follows:

We assume a first-order reaction to calculate the rate constant (k). This reaction satisfies the apparent first-order reaction rate equation: $-\ln(C/C_0) = kt$. The equation can be expressed in another way: $-\ln(1-x) = kt$, where k is the apparent rate constant of the first-order reaction, and $-\ln(1-x)$ is a function of reaction time t. A $-\ln(1-x)$ versus reaction time (t) graph was prepared first. The apparent rate constant k is obtained from the slope of the fitted straight line.

The activation energy was estimated using the Arrhenius equation: $\ln k=(-Ea)/RT+\ln A$.

A $-\ln k$ versus $10^3/T$ graph was prepared. The activation energy Ea is obtained from the slope of the fitted straight line. The calculated Ea of Pd-UiO-67-Bpy and Zr-BTB-Bpy-Pd for the cyclization reaction of **1a** and **2a** were 84.5 $kJ \cdot mol^{-1}$ and 69.8 $kJ \cdot mol^{-1}$, respectively.

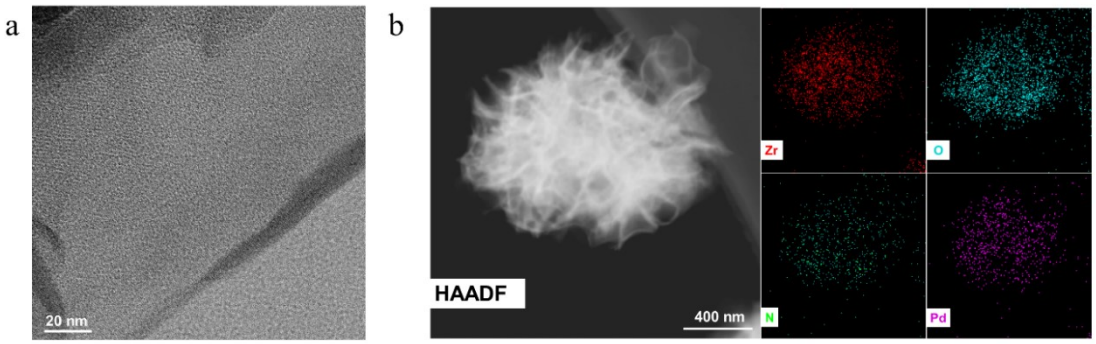


Fig. S8 (a) TEM images and (b) elements mapping images of Zr-BTB-bpy-Pd (used).

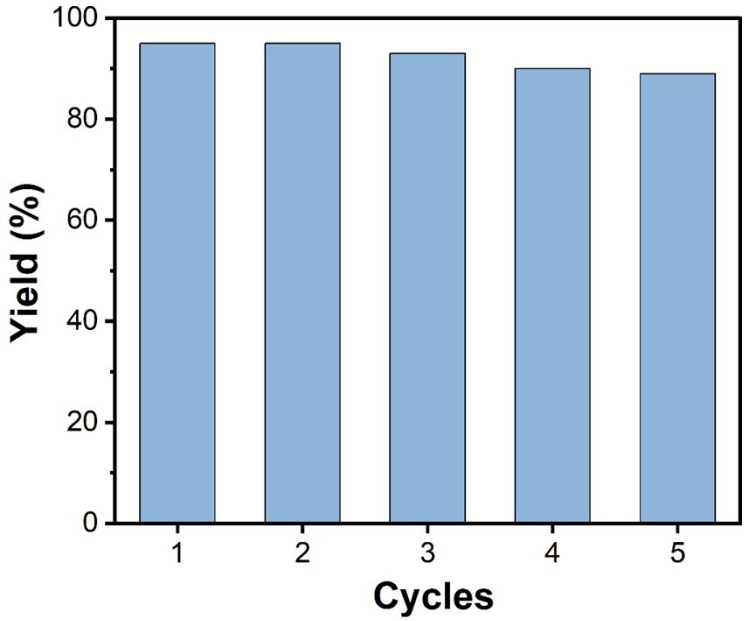


Fig. S9 Recycle test of Zr-BTB-bpy-Pd catalyzed cyclization of 2,2,2-Trifluoro-N-(2-(phenylethynyl)phenyl)acetamide with tert-butyl isocyanide.

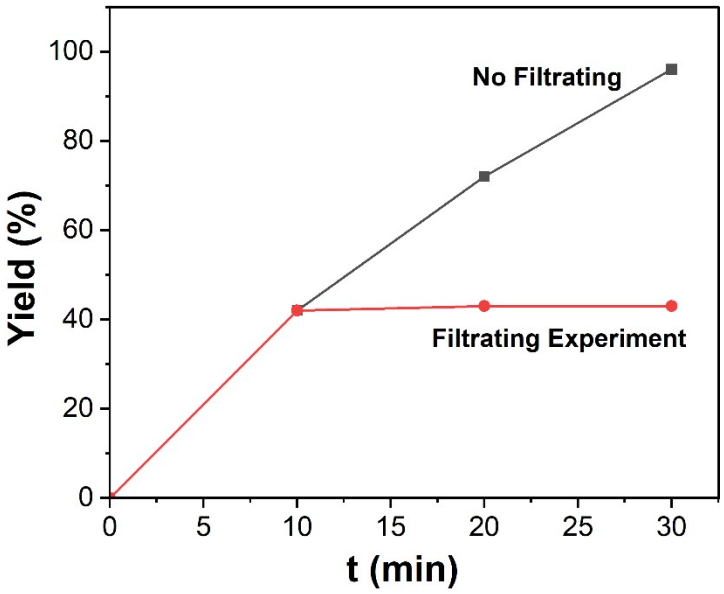
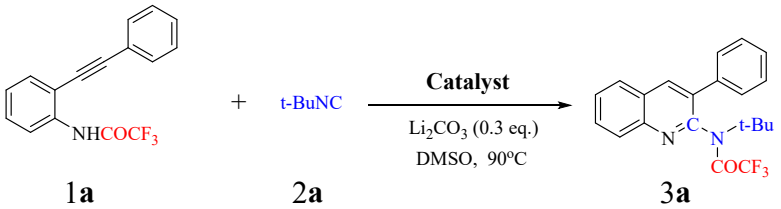


Fig. S10 Hot filtration experiment of Zr-BTB-bpy-Pd catalyzed cyclization of 2,2,2-Trifluoro-N-(2-(phenylethynyl)phenyl)acetamide with tert-butyl isocyanide.

3. Catalytic performance testing

Table S2 Optimization of Reaction Conditions



1a **2a** **3a**

Entry	Catalyst	T (min)	Yield[b] (%)	TON
1	Zr-BTB-bpy-Pd (Pd 0.05 mol%)	30	55	840
2	Zr-BTB-bpy-Pd (Pd 0.10 mol%)	30	95	950
3	Zr-BTB-bpy-Pd (Pd 0.20 mol%)	30	95.2	475
4	Zr-BTB-bpy-Pd (Pd 0.40 mol%)	30	95.1	238

[a] Reaction conditions: 1**a** (0.1 mmol), 2**a** (0.15 mmol), catalyst, Li_2CO_3 (30 mol%), dry DMSO (1 mL), at 90 °C for 30 min under N_2. [b] Isolated yield.

Table S3 Comparison of different kinds of catalysts for the cyclization reaction of 2,2,2-Trifluoro-N-(2-(phenylethynyl)phenyl)acetamide with *tert*-butyl isocyanide.

Entry	Catalyst	T (min)	Yield[b] (%)	TON
1	$Pd(OAc)_2$ (10 mol%)	10	2	0.2
2	$Pd(OAc)_2$ (10 mol%)	20	7	0.7
3	$Pd(OAc)_2$ (10 mol%)	30	11	1.1
4	$Pd(OAc)_2$ (10 mol%)	40	15	1.5
5	$Pd(OAc)_2$ (10 mol%)	50	22	2.2
6	$Pd(OAc)_2$ (10 mol%)	60	31	3.1
7	Pd-UiO-67-bpy (Pd 0.1 mol%)	10	16	160
8	Pd-UiO-67-bpy (Pd 0.1 mol%)	20	27	270
9	Pd-UiO-67-bpy (Pd 0.1 mol%)	30	40	400
10	Pd-UiO-67-bpy (Pd 0.1 mol%)	40	65	650
11	Pd-UiO-67-bpy (Pd 0.1 mol%)	50	74	740
12	Pd-UiO-67-bpy (Pd 0.1 mol%)	60	80	800
13	Zr-BTB-bpy-Pd (Pd 0.1 mol%)	10	43	430
14	Zr-BTB-bpy-Pd (Pd 0.1 mol%)	20	72	720
15	Zr-BTB-bpy-Pd (Pd 0.1 mol%)	30	95	950
16	Zr-BTB-bpy-Pd (Pd 0.1 mol%)	40	95	950
17	Zr-BTB-bpy-Pd (Pd 0.1 mol%)	50	95	950
18	Zr-BTB-bpy-Pd (Pd 0.1 mol%)	60	95	950

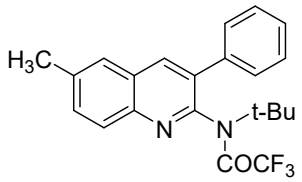
[a] Reaction conditions: 1**a** (0.1 mmol), 2**a** (0.15 mmol), catalyst, Li_2CO_3 (30 mol%), dry DMSO (1 mL), at 90 °C for 30 min under N_2. [b] Isolated yield.

4. Characterization data for all products

N-(tert-Butyl)-2,2,2-trifluoro-N-(3-phenylquinolin-2-yl)acetamide (3a)

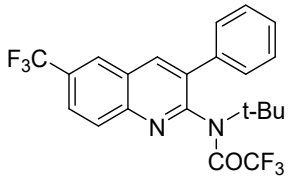
Yellow solid (95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 0.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.80 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.67 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.53-7.44 (m, 5H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.01, 157.66, 149.53, 146.02, 138.97, 137.70, 134.69, 130.20, 129.84, 129.51, 128.90, 128.42, 128.13 (d, *J* = 9.3 Hz), 127.38, 117.68, 114.80, 77.35, 77.04, 76.72, 62.81, 27.25. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.64.

N-(tert-Butyl)-2,2,2-trifluoro-N-(6-methyl-3-phenylquinolin-2-yl)acetamide (3b)



Light yellow solid (92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 0.8 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.68 (dt, *J* = 1.9, 0.9 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.54 – 7.42 (m, 5H), 2.60 (d, *J* = 1.0 Hz, 3H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.67, 148.73, 144.58, 138.26 (d, *J* = 1.7 Hz), 137.88, 134.60, 132.53, 129.83, 129.15, 128.86, 128.33, 128.24, 126.18, 117.70, 114.82, 62.74, 27.24, 21.71. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.69.

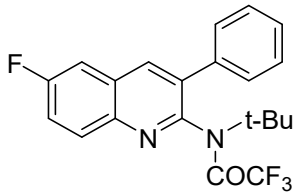
N-(tert-Butyl)-2,2,2-trifluoro-N-(3-phenyl-6-(trifluoromethyl)quinolin-2-yl)acetamide (3c)



Yellow solid (91% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 0.8 Hz, 1H), 8.26 (ddd, *J* = 10.5, 2.2, 1.3 Hz, 2H), 7.97 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.56 – 7.44 (m, 5H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.54, 151.64, 146.95, 139.62, 136.94, 136.18, 130.75, 130.17, 129.77, 129.07, 128.86, 127.20, 125.91 (d, *J* = 3.1 Hz), 125.33 (d, *J* = 4.5 Hz), 117.58, 63.12, 27.23. ^{19}F NMR (376 MHz, Chloroform-

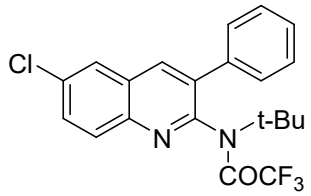
d) δ -62.58, -67.66.

N-(tert-Butyl)-2,2,2-trifluoro-N-(6-fluoro-3-phenylquinolin-2-yl)acetamide (3d)



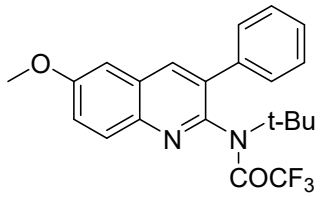
Light yellow solid (87% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 8.14 (dd, *J* = 9.1, 5.3 Hz, 1H), 7.57 – 7.42 (m, 7H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.73, 160.24, 157.97, 149.03, 143.05, 138.22 (d, *J* = 5.5 Hz), 137.32, 135.54, 132.12 (d, *J* = 9.4 Hz), 129.78, 128.95, 128.64, 120.54 (d, *J* = 25.9 Hz), 117.64, 114.75, 110.47 (d, *J* = 21.9 Hz), 62.87, 27.23. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.70, -110.86 (td, *J* = 8.4, 5.3 Hz).

N-(tert-Butyl)-N-(6-chloro-3-phenylquinolin-2-yl)-2,2,2-trifluoroacetamide (3e)



Light yellow solid (84% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 2.2 Hz, 1H), 7.73 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.56 – 7.42 (m, 5H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.75 (d, *J* = 34.6 Hz), 149.84, 144.34, 137.93, 137.23, 135.71, 134.04, 131.15 (d, *J* = 10.4 Hz), 129.78, 128.99, 128.73 (d, *J* = 8.4 Hz), 126.04, 62.95, 27.23. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.68 (d, *J* = 1.9 Hz).

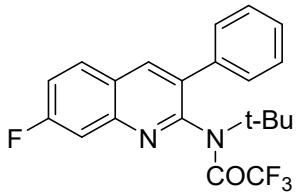
N-(tert-Butyl)-2,2,2-trifluoro-N-(6-methoxy-3-phenylquinolin-2-yl)acetamide (3f)



White solid (81% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 7.52 – 7.43 (m, 6H), 7.17 (d, *J* = 2.8 Hz, 1H), 3.98 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.05, 157.87 (d, *J* = 34.5 Hz), 147.25, 141.99, 137.88, 137.62, 134.85, 130.90, 129.80, 129.38, 128.85, 128.34, 123.09, 104.72, 62.71,

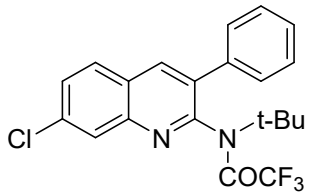
55.67, 29.72, 27.24. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.67.

N-(tert-Butyl)-2,2,2-trifluoro-N-(7-fluoro-3-phenylquinolin-2-yl)acetamide (3g)



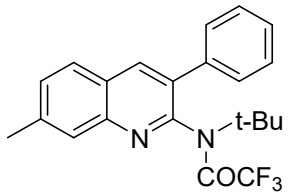
Light yellow solid (99% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 0.8 Hz, 1H), 7.92 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.77 (dd, *J* = 9.8, 2.6 Hz, 1H), 7.56 – 7.42 (m, 6H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.75, 162.25, 157.75 (d, *J* = 34.8 Hz), 150.60, 147.03 (d, *J* = 13.0 Hz), 138.85, 137.41, 134.07, 131.43, 129.78, 129.47 (d, *J* = 10.0 Hz), 128.95, 128.51, 125.22, 118.73 (d, *J* = 25.5 Hz), 117.63, 114.75, 113.24 (d, *J* = 20.7 Hz), 62.93, 27.23. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.67, -107.94 (dd, *J* = 9.7, 2.6 Hz).

N-(tert-Butyl)-N-(7-chloro-3-phenylquinolin-2-yl)-2,2,2-trifluoroacetamide (3h)



Light yellow solid (98% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.62 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.53 – 7.42 (m, 5H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.75 (d, *J* = 34.8 Hz), 150.57, 146.34, 138.76, 137.29, 136.25, 134.96, 129.76, 129.21, 128.97, 128.60 (d, *J* = 3.3 Hz), 128.49, 126.53, 117.61, 114.73, 62.97, 27.22. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.65.

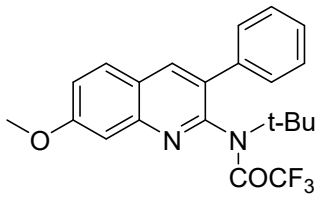
N-(tert-Butyl)-2,2,2-trifluoro-N-(7-methyl-3-phenylquinolin-2-yl)acetamide (3i)



Light orange solid (98% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.94 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.44 (m, 6H), 2.62 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.84 (d, *J* = 34.7 Hz), 149.46, 146.29,

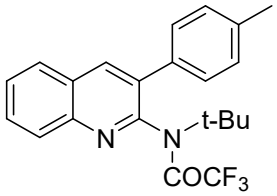
140.79, 138.65, 137.87, 133.77 (d, *J* = 1.4 Hz), 130.37, 129.82, 128.85, 128.45, 128.27, 127.02, 126.24, 117.70, 114.82, 62.74, 27.24, 21.89. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.65.

N-(tert-Butyl)-2,2,2-trifluoro-N-(7-methoxy-3-phenylquinolin-2-yl)acetamide (3j)



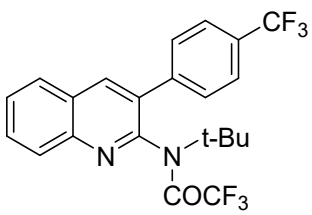
Yellow solid (93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.51 – 7.42 (m, 7H), 7.34 – 7.28 (m, 1H), 4.01 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.45, 157.75 (d, *J* = 34.8 Hz), 149.65, 147.91, 138.70, 137.89, 132.29, 129.79, 128.86, 128.39, 128.18, 123.49 (d, *J* = 6.2 Hz), 121.53, 117.72, 114.84, 107.89, 107.16, 62.77, 55.73, 27.26. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.61.

N-(tert-Butyl)-2,2,2-trifluoro-N-(3-(p-tolyl)quinolin-2-yl)acetamide (3k)



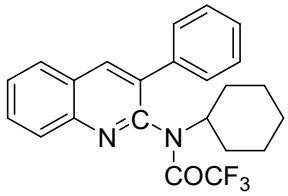
Red solid (99% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.17 – 8.10 (m, 1H), 7.91 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.78 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.66 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.37 – 7.31 (m, 4H), 2.45 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.84 (d, *J* = 34.5 Hz), 148.73, 144.58, 138.26 (d, *J* = 1.7 Hz), 137.88, 134.60, 132.53, 129.83, 129.15, 128.86, 128.28 (d, *J* = 9.5 Hz), 126.18, 117.70, 114.82, 62.74, 27.24, 21.71. ^{19}F NMR (376 MHz,) δ -67.68 (h, *J* = 10.9, 9.3 Hz).

N-(tert-Butyl)-2,2,2-trifluoro-N-(3-(4-(trifluoromethyl)phenyl)quinolin-2-yl)acetamide (3l)



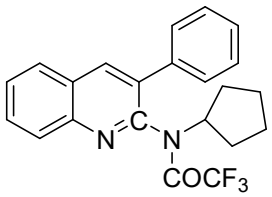
Light yellow solid (99% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 0.8 Hz, 1H), 8.19 – 8.14 (m, 1H), 7.97 – 7.92 (m, 1H), 7.85 – 7.77 (m, 3H), 7.71 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.64 – 7.58 (m, 2H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.95 (d, *J* = 34.7 Hz), 149.03, 146.33, 141.44, 139.26, 133.18, 130.78 (d, *J* = 6.0 Hz), 130.20, 129.59, 128.42, 127.94, 127.47, 125.86 (q, *J* = 3.6 Hz), 125.21 (d, *J* = 10.3 Hz), 123.15, 122.55, 121.01, 120.60, 117.61, 114.73, 111.16, 63.02, 29.71, 27.32. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.66, -67.66.

N-Cyclohexyl-2,2,2-trifluoro-N-(3-phenylquinolin-2-yl)acetamide (3m)



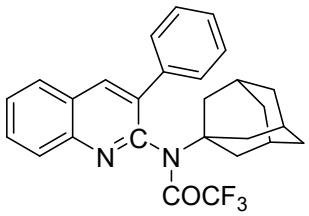
Light yellow solid (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.21 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.52 – 7.41 (m, 5H), 3.52 – 3.31 (m, 1H), 1.76 – 1.60 (m, 2H), 1.56 (t, *J* = 11.2 Hz, 2H), 1.47 – 1.32 (m, 2H), 1.12 – 0.75 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.60 (d, *J* = 35.6 Hz), 150.32, 145.93, 139.65, 137.20, 132.48, 130.32, 129.30 (d, *J* = 9.5 Hz), 128.87, 128.53, 127.90 (d, *J* = 5.3 Hz), 127.40, 117.68, 114.81, 63.70, 28.88, 28.07, 26.04 (d, *J* = 24.1 Hz), 25.16. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.18.

N-Cyclopentyl -2,2,2-trifluoro-N-(3-phenylquinolin-2-yl)acetamide (3n)



Yellow solid (67% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.80 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.66 (td, *J* = 7.5, 6.8, 1.2 Hz, 1H), 7.55 – 7.41 (m, 5H), 3.89 (p, *J* = 8.1 Hz, 1H), 1.71 – 1.30 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.37, 146.06, 139.61, 136.93, 130.34, 129.25, 128.94, 128.49, 127.99 (d, *J* = 13.7 Hz), 127.42, 63.99, 28.40 (d, *J* = 13.4 Hz), 24.24 (d, *J* = 39.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.27.

N-(Adamantan-1-yl)-2,2,2-trifluoro-N-(3-phenylquinolin-2-yl)acetamide (3o)



Yellow solid (88% yield); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.19 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.81-7.76 (m, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.52-7.41 (m, 5H), 2.02 (d, J = 11.5 Hz, 3H), 1.88 (s, 3H), 1.61 (d, J = 11.5 Hz, 3H), 1.49-1.41 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.25 (d, *J* = 34.5 Hz), 148.98, 145.85, 138.78, 137.76, 135.02 (d, *J* = 1.6 Hz), 130.13 (d, *J* = 15.7 Hz), 129.49, 128.81, 128.46, 128.09 (d, *J* = 6.0 Hz), 127.37, 117.54, 114.66, 64.54, 38.43, 35.94, 29.99. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.65.

5. Supplementary references

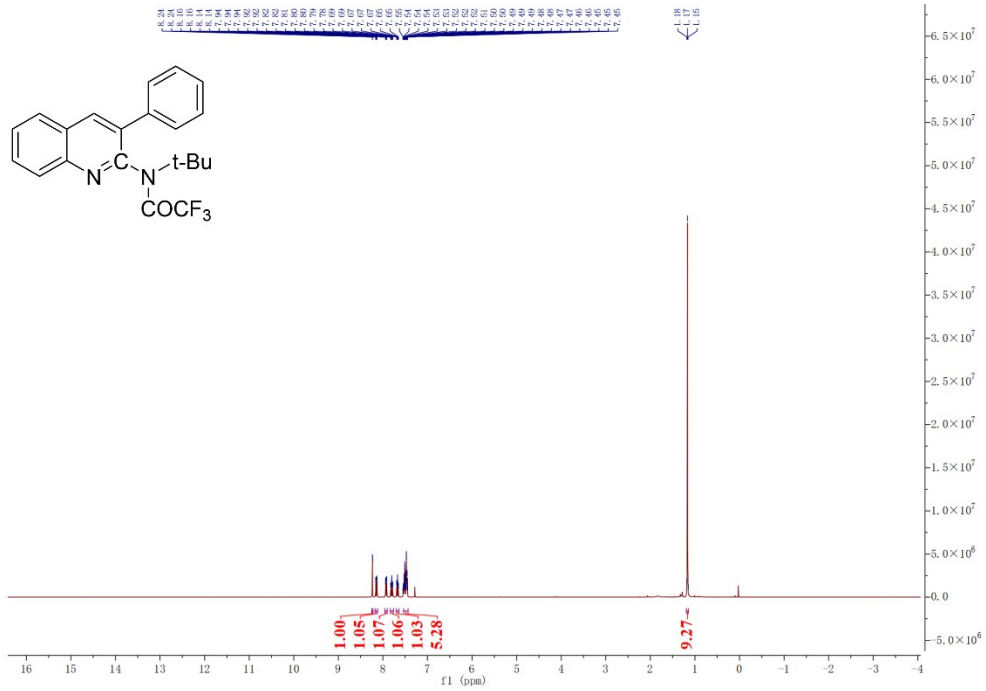
1 G. Lan, Z. Li, S. S. Veroneau, Y.-Y. Zhu, Z. Xu, C. Wang and W. Lin, *J. Am. Chem. Soc*., 2018, **140**, 12369-12373.

2 Y. Wang, L. Feng, J. Pang, J. Li, N. Huang, G. S. Day, L. Cheng, H. F. Drake, Y. Wang, C. Lollar, J. Qin, Z. Gu, T. Lu, S. Yuan and H. C. Zhou, *Adv. Sci. (Weinh)*, 2019, **6**, 1802059.

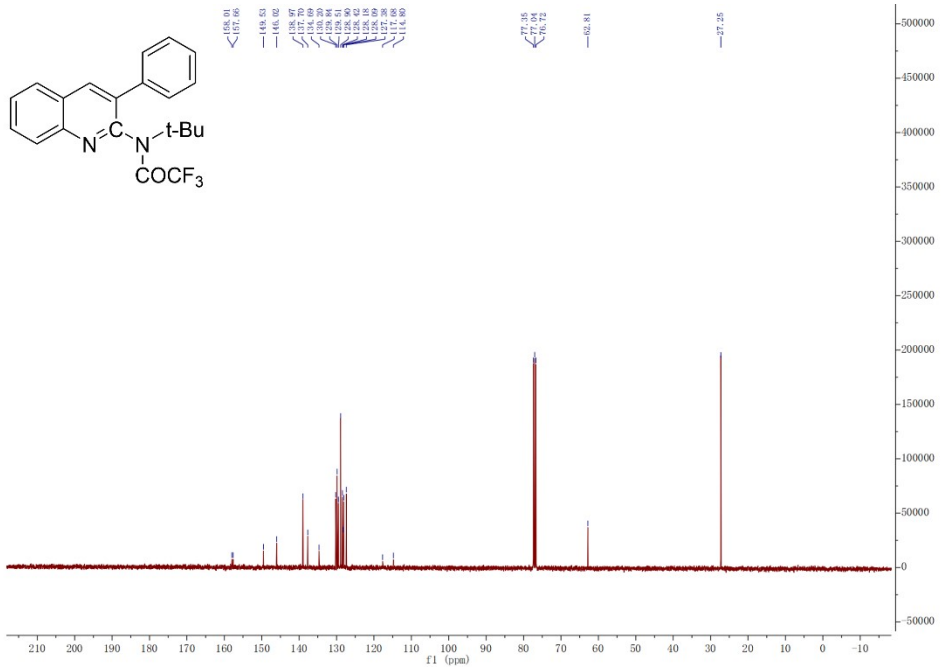
3 Y. Xia, J. Li, M. Li, Y. Ren, H. Jiang and W. Wu, *Green Chem*., 2022, **24**, 9203-9210.

Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

^{1}H NMR of **3a**



^{13}C NMR of **3b**



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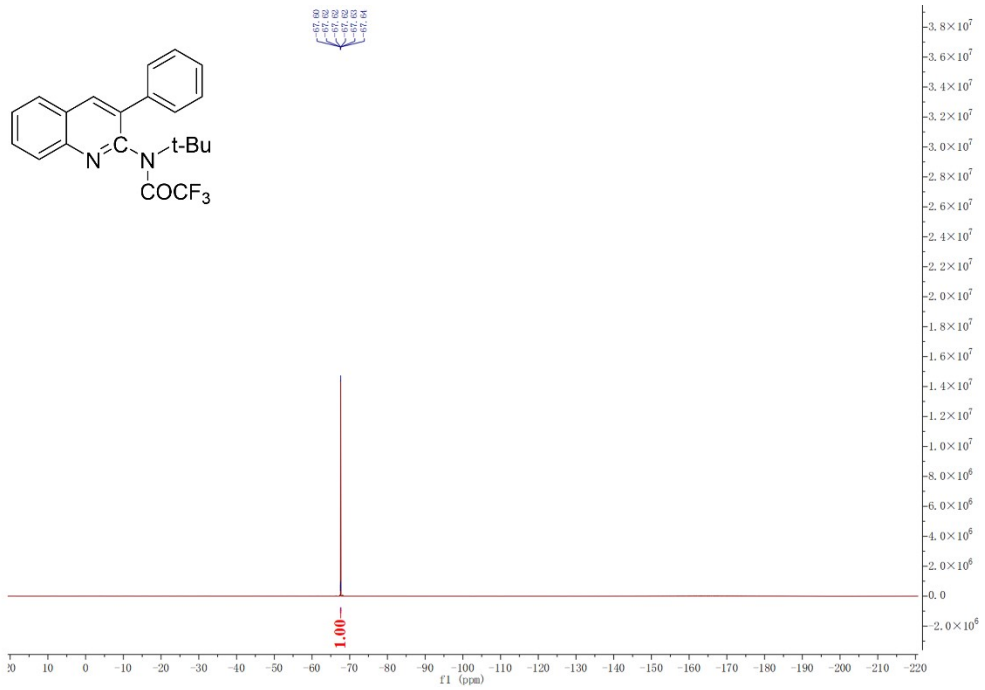

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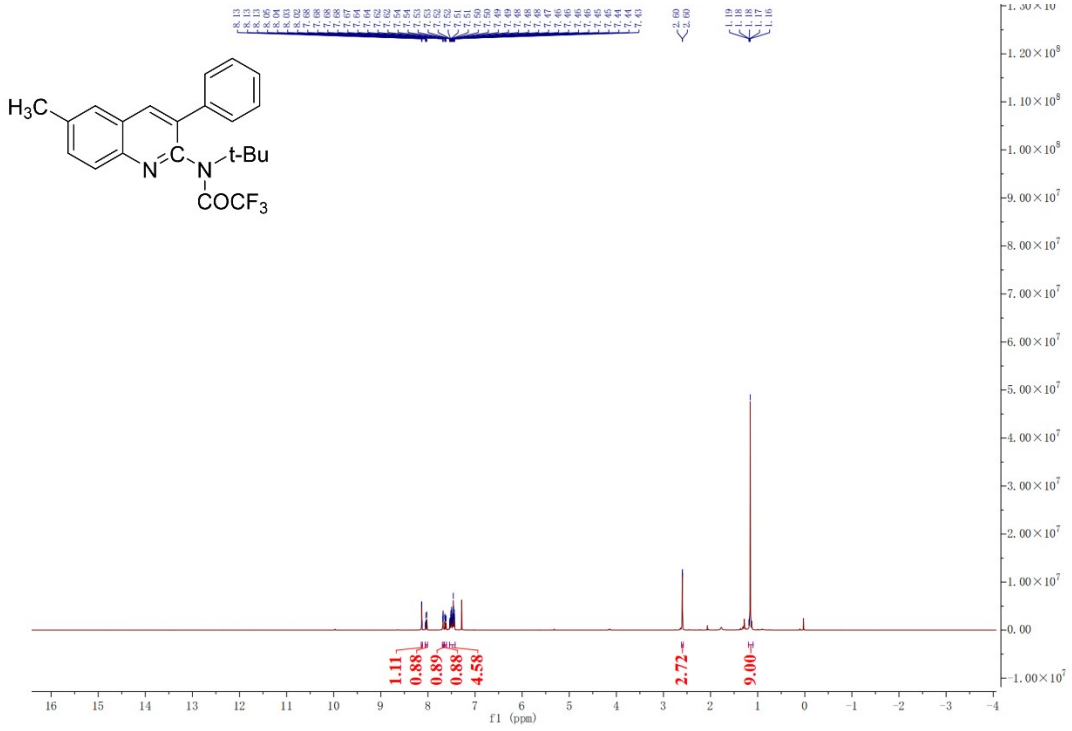

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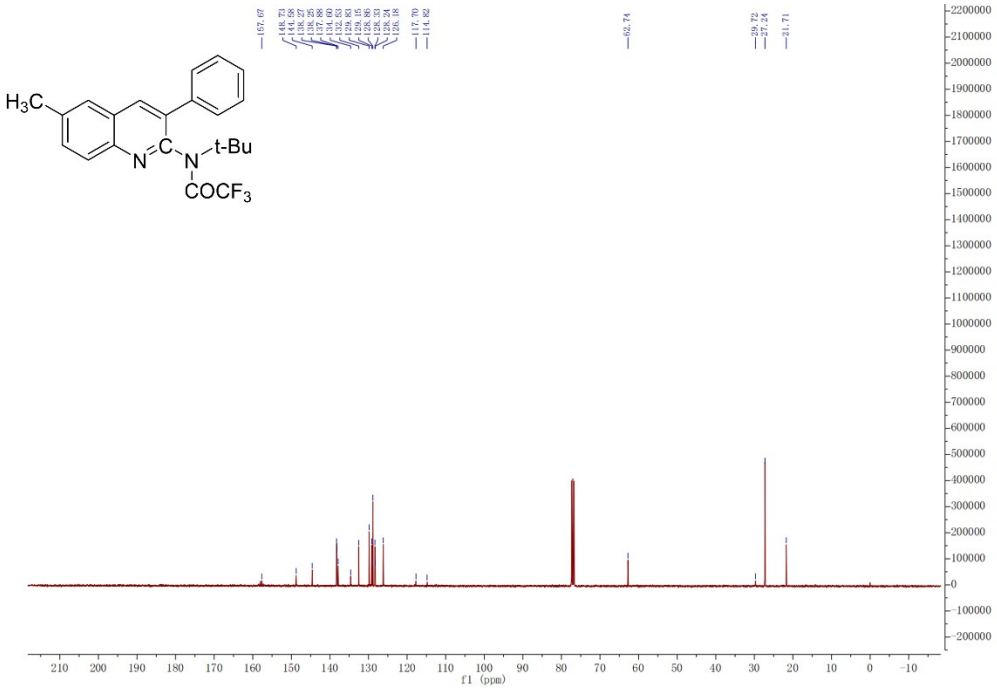

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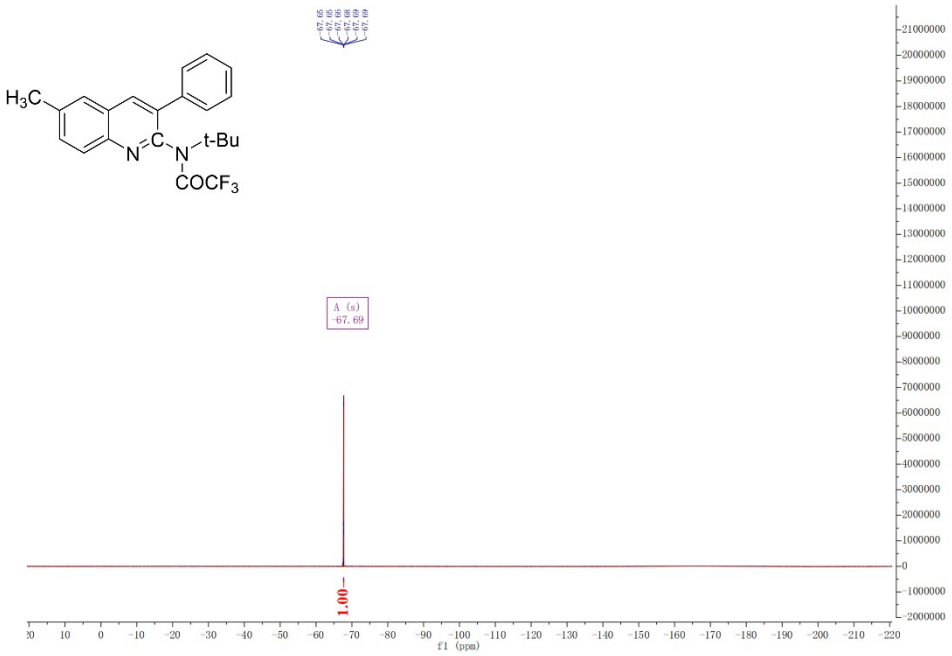
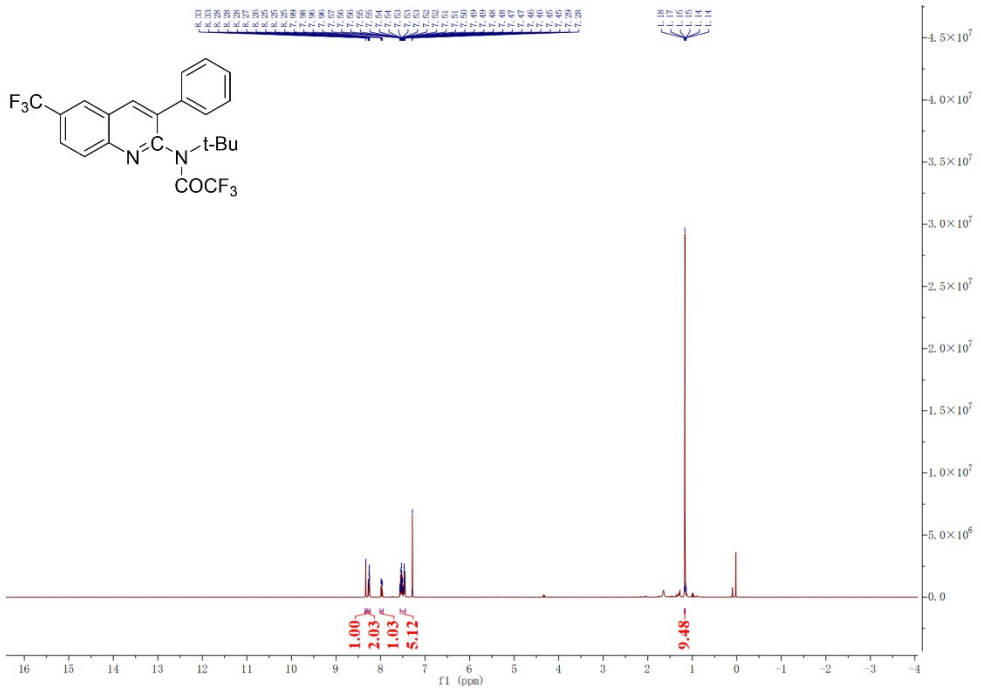
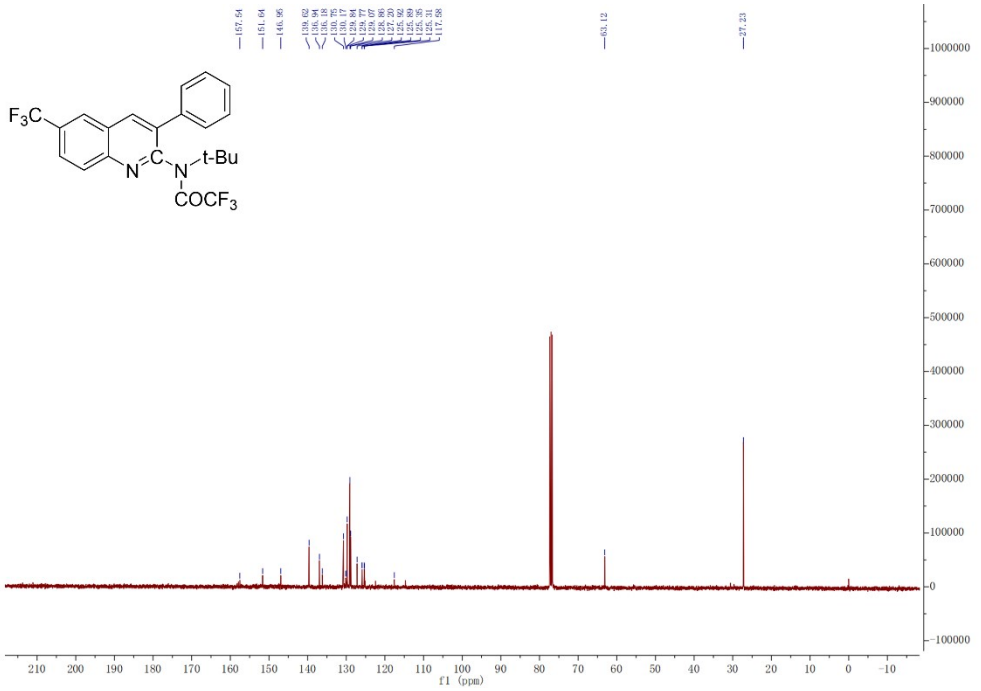


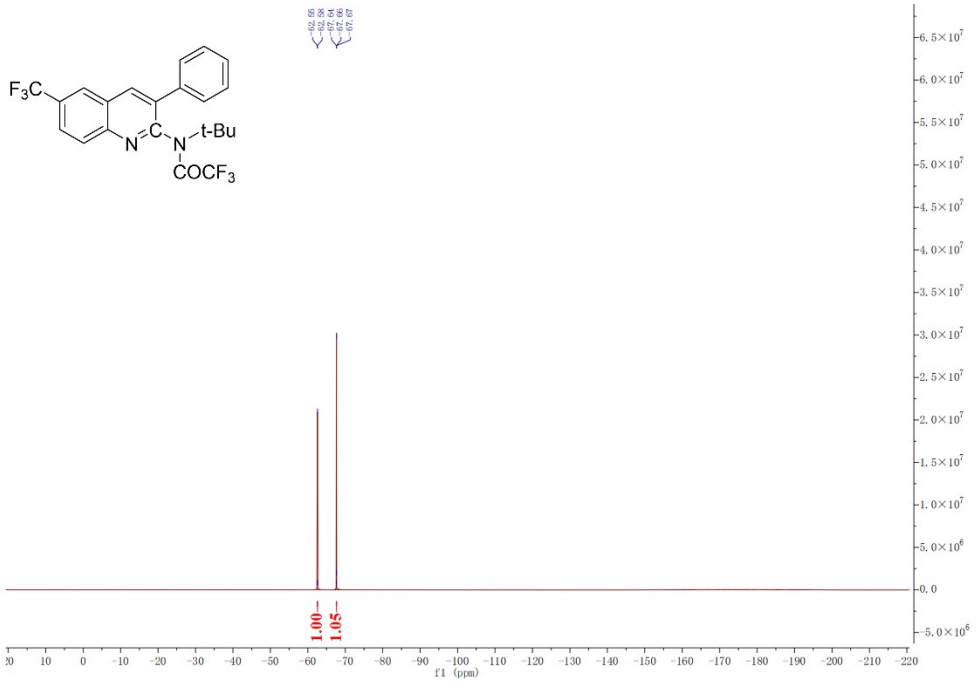
^{1}H NMR of **3c**



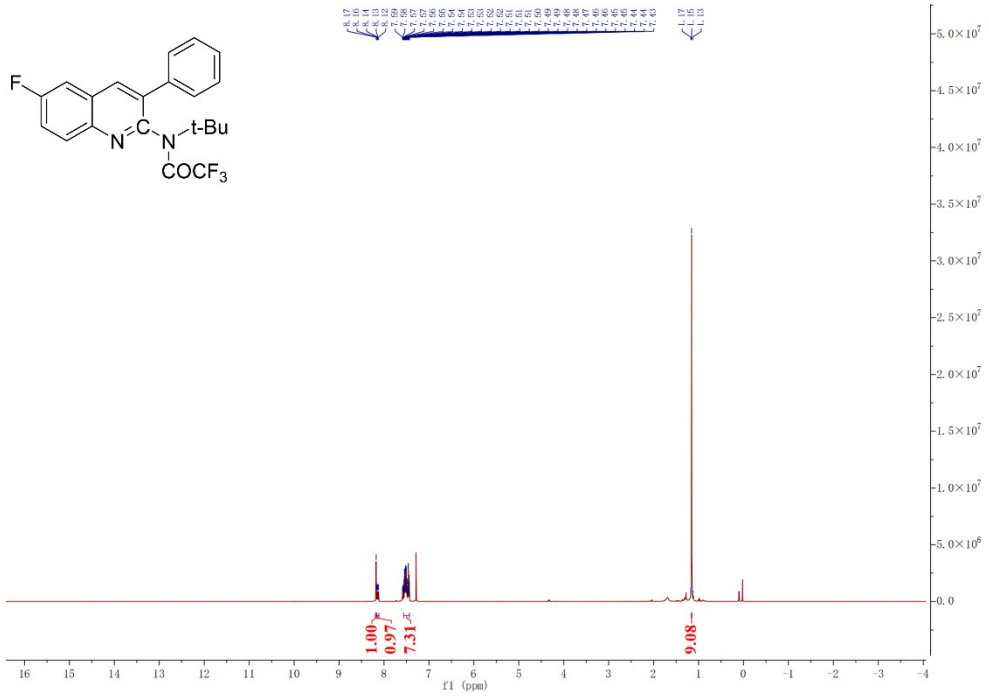
^{13}C NMR of **3c**



^{19}F NMR of **3c**



^{1}H NMR of **3d**



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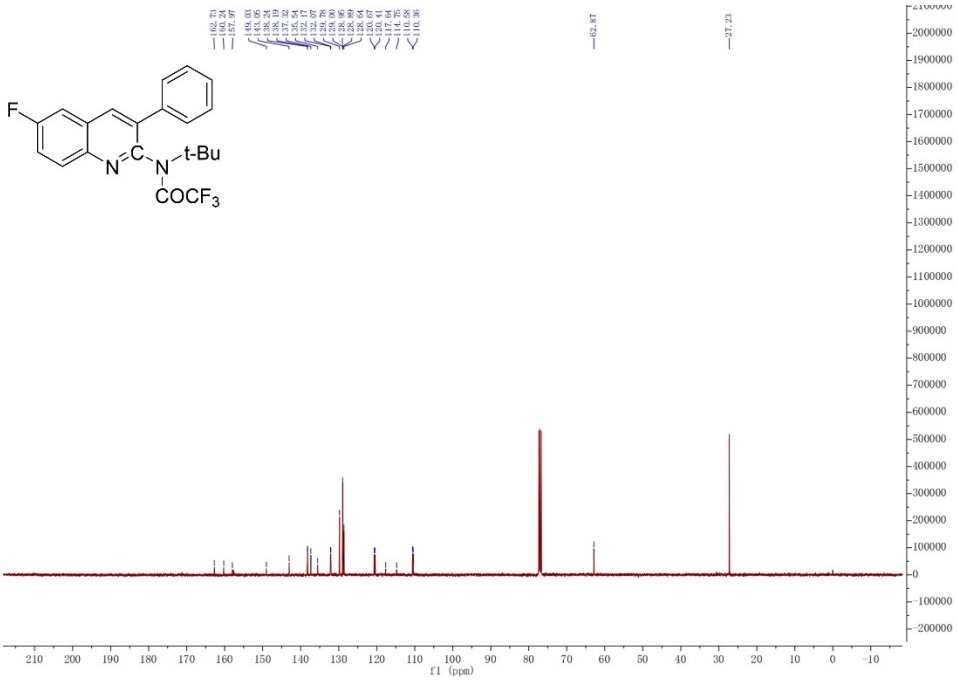

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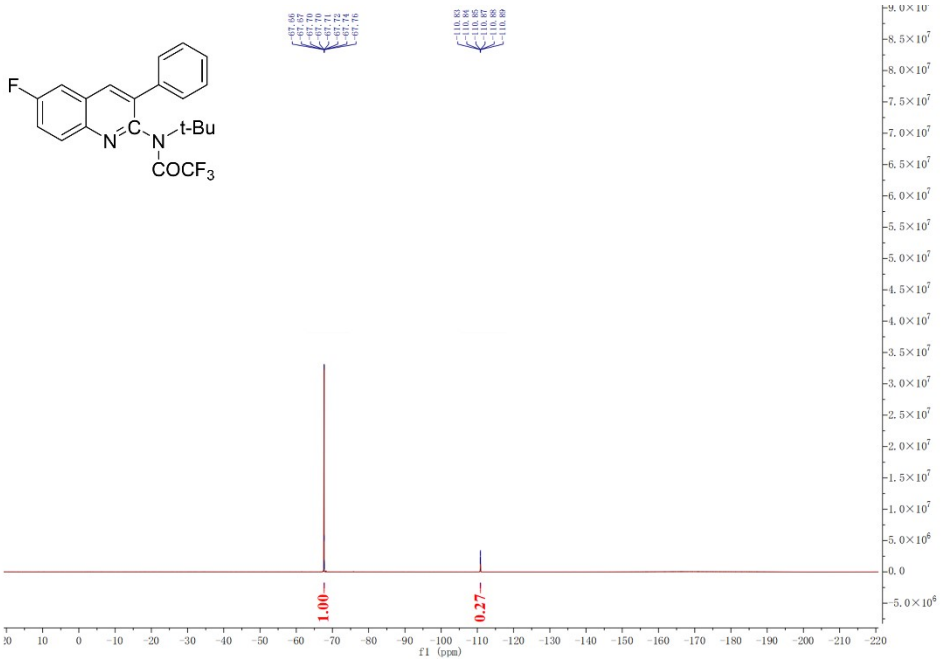

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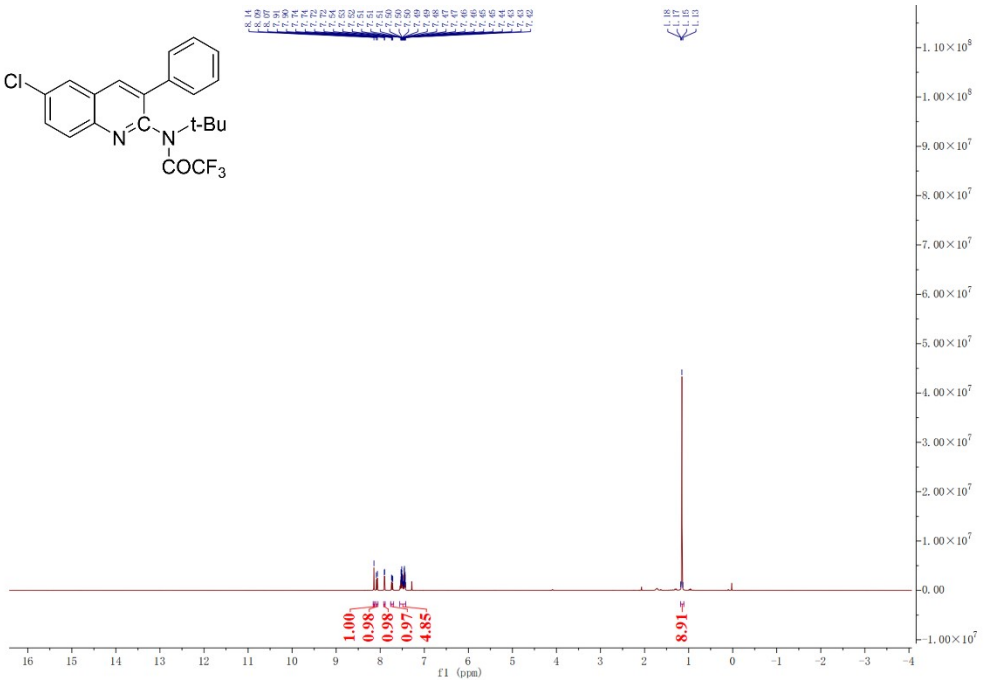

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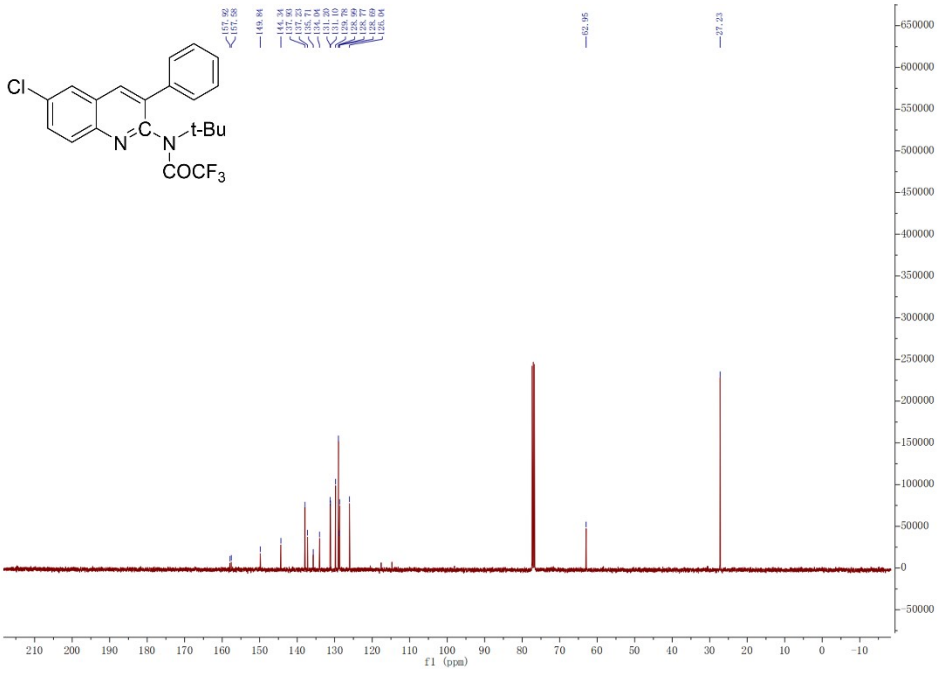

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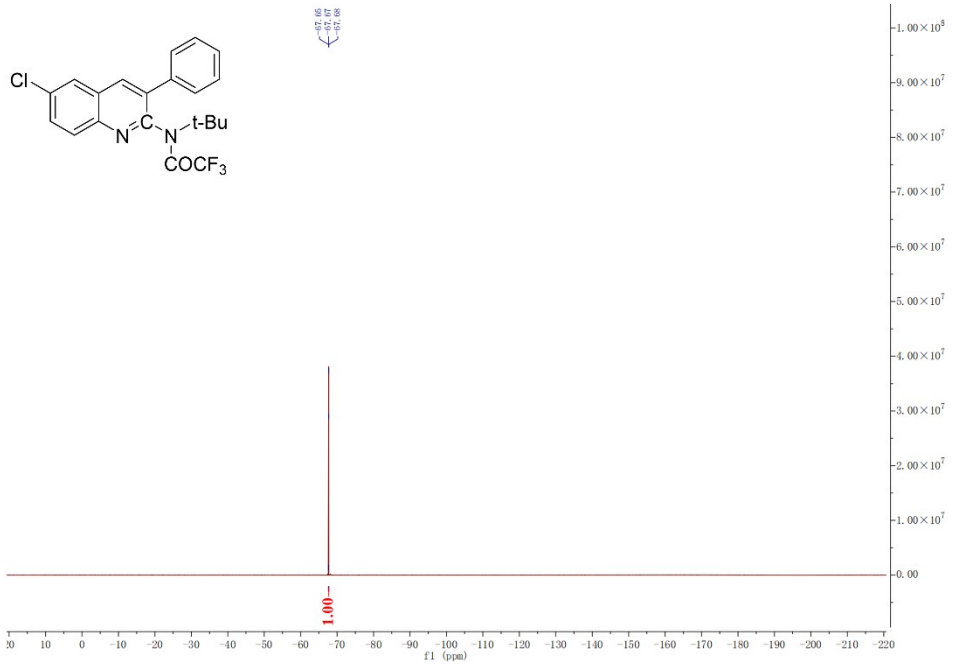
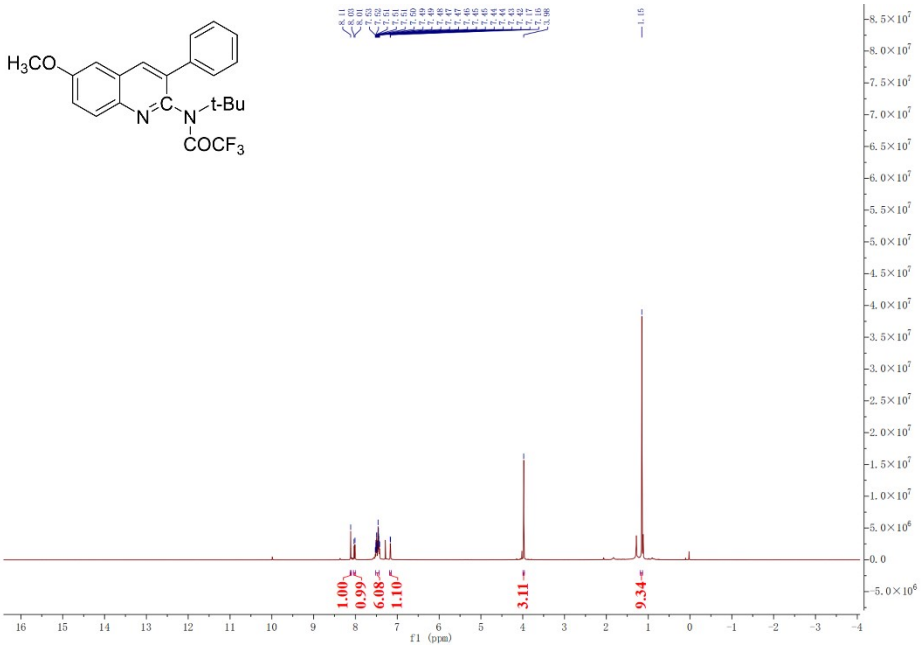


^{1}H NMR of **3f**



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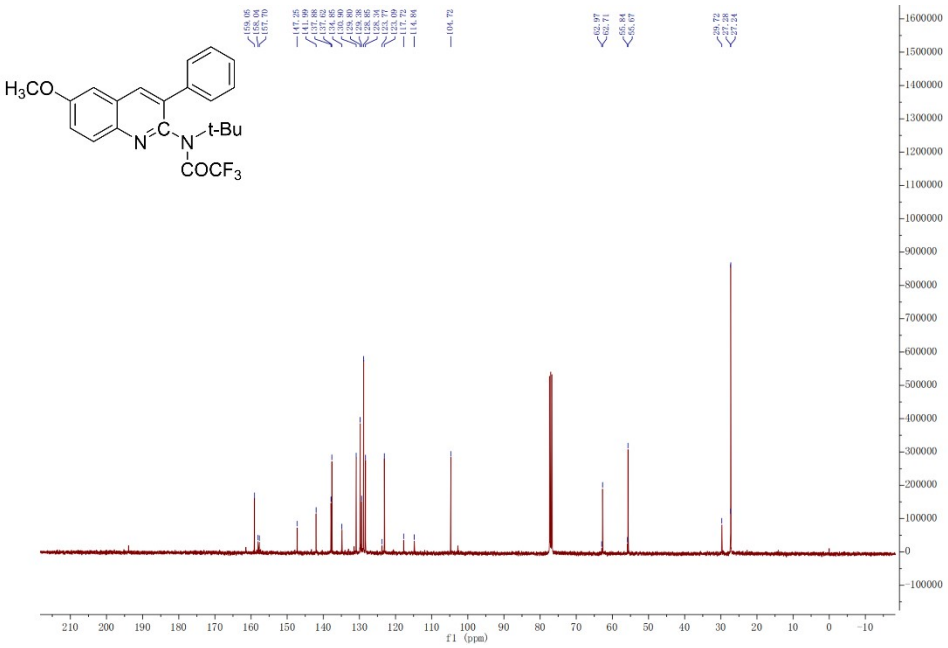
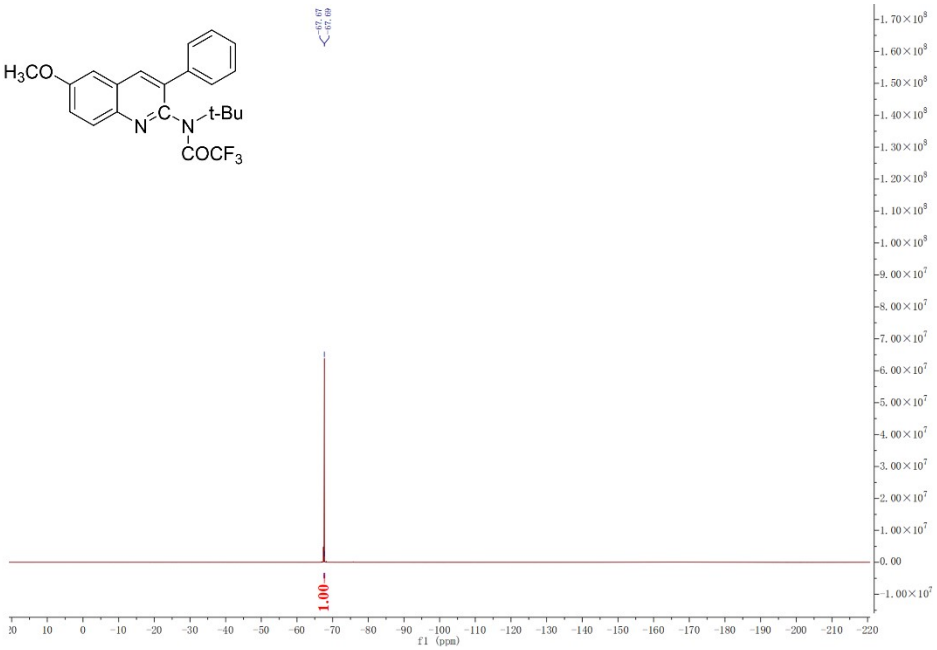
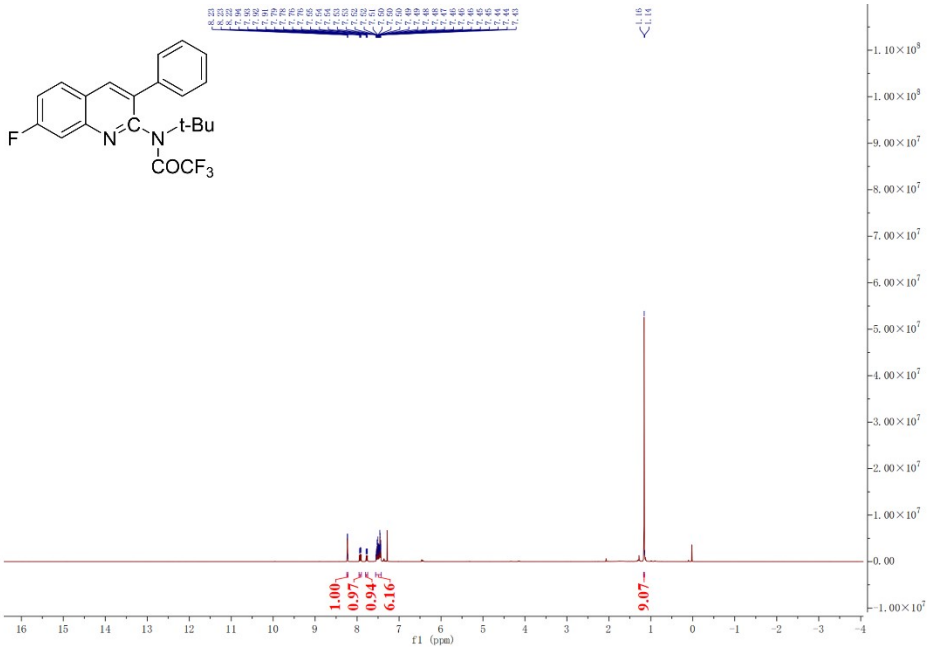


^{19}F NMR of **3f**



^{1}H NMR of **3g**



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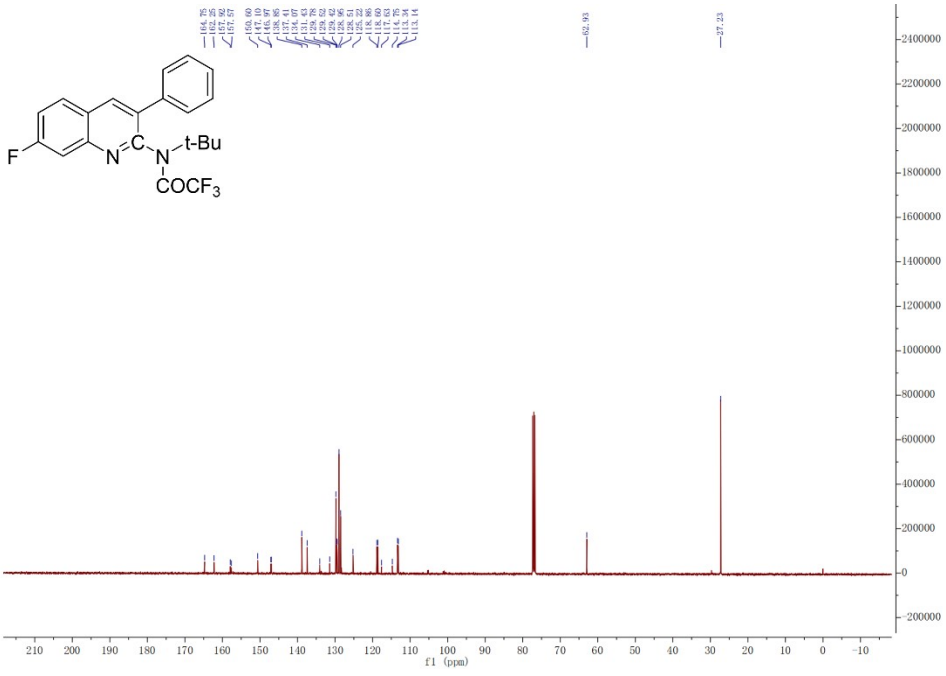
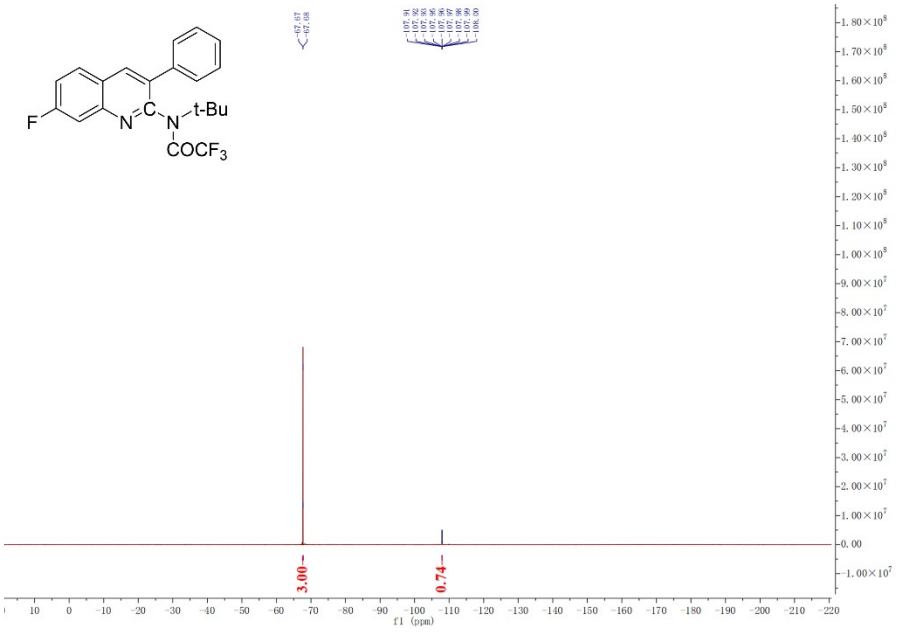
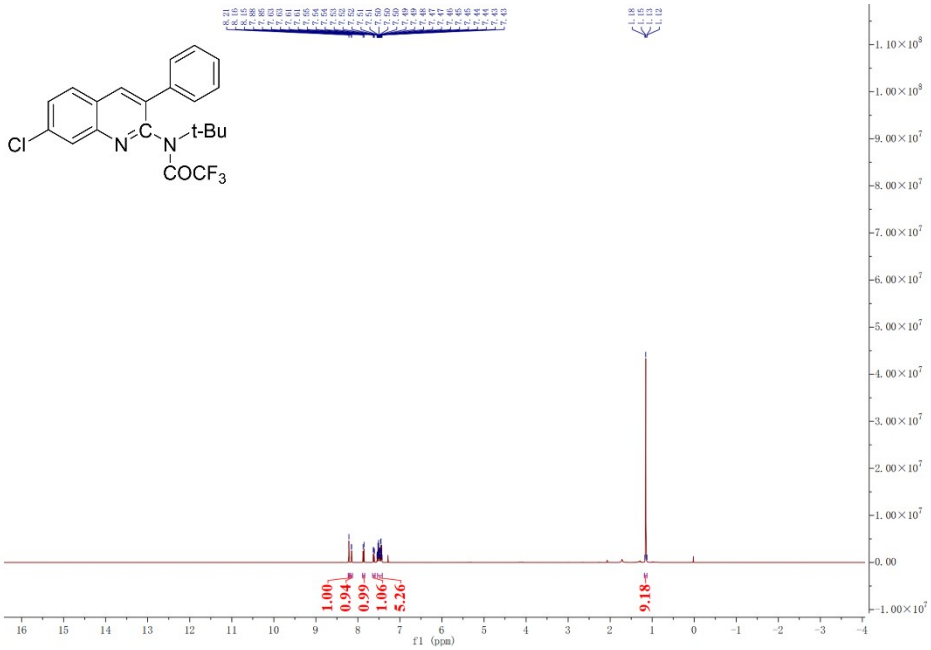


^{19}F NMR of **3g**



^{1}H NMR of **3h**



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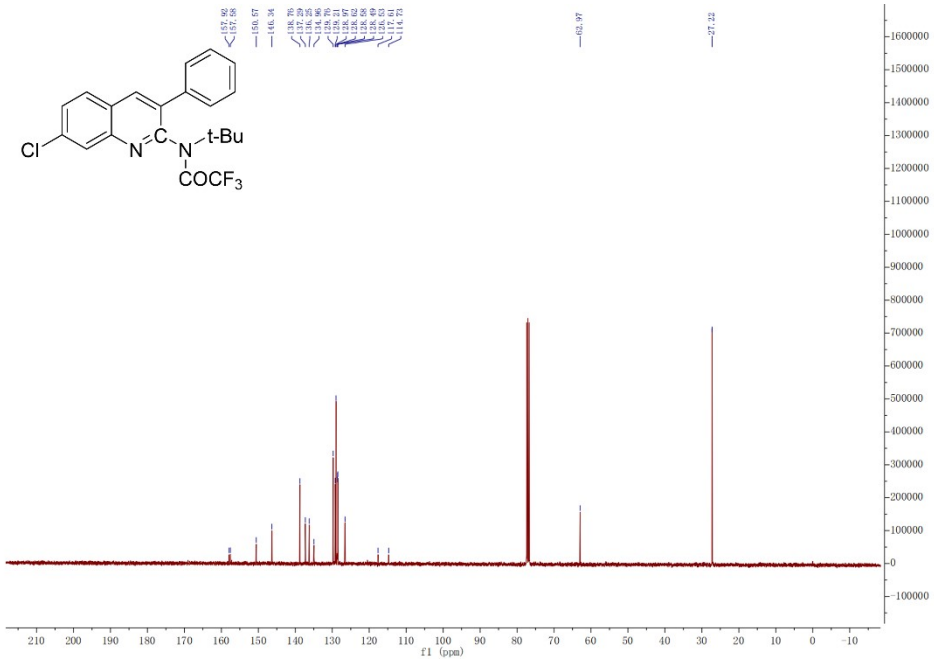

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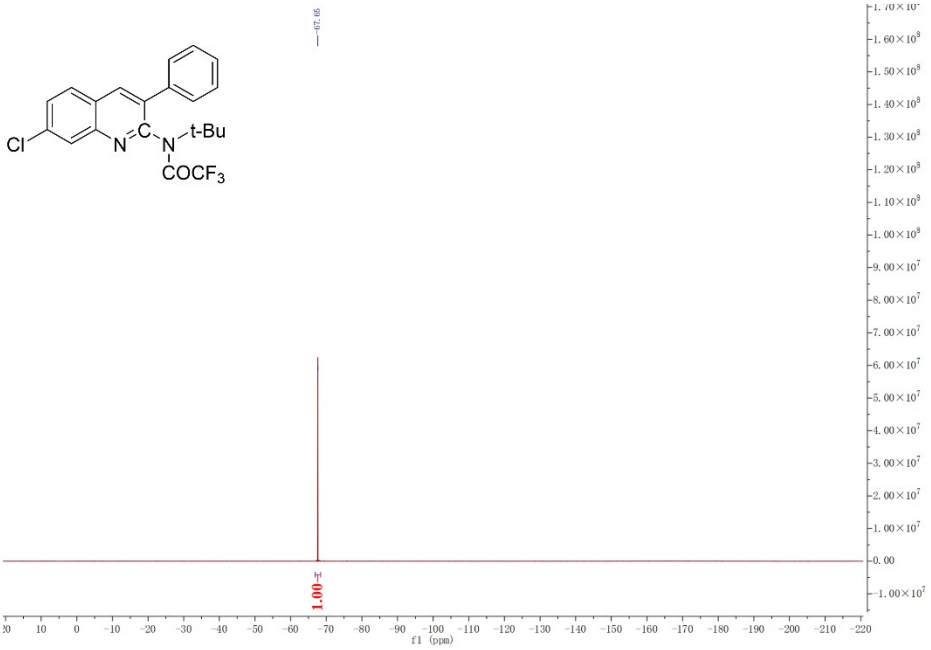
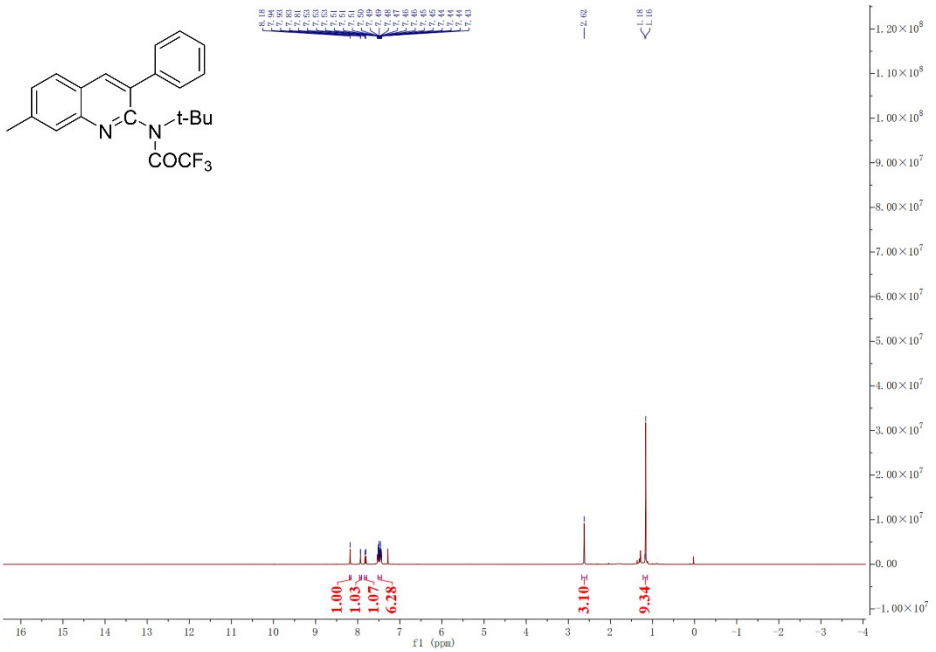
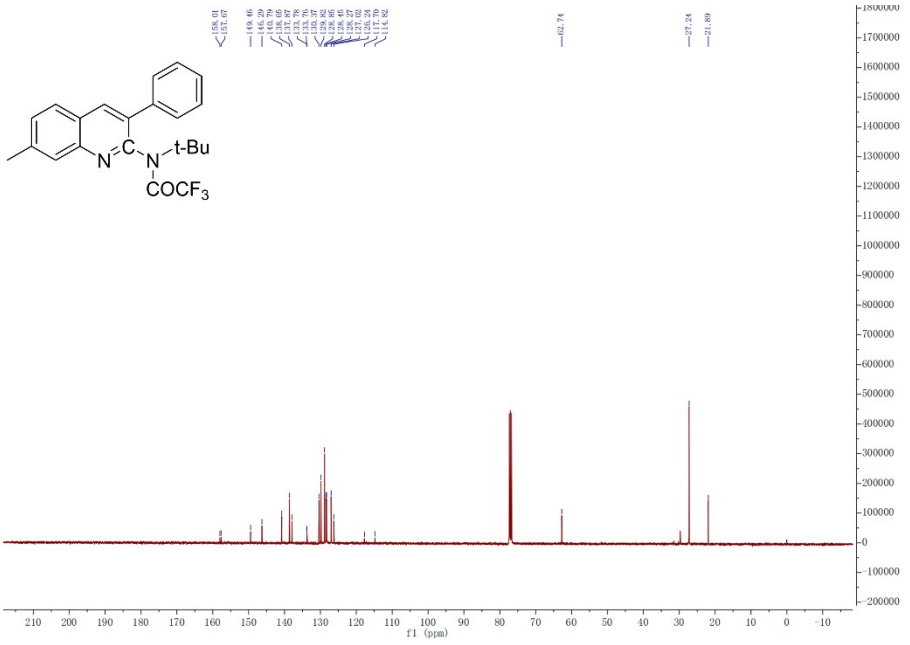


^{1}H NMR of **3i**

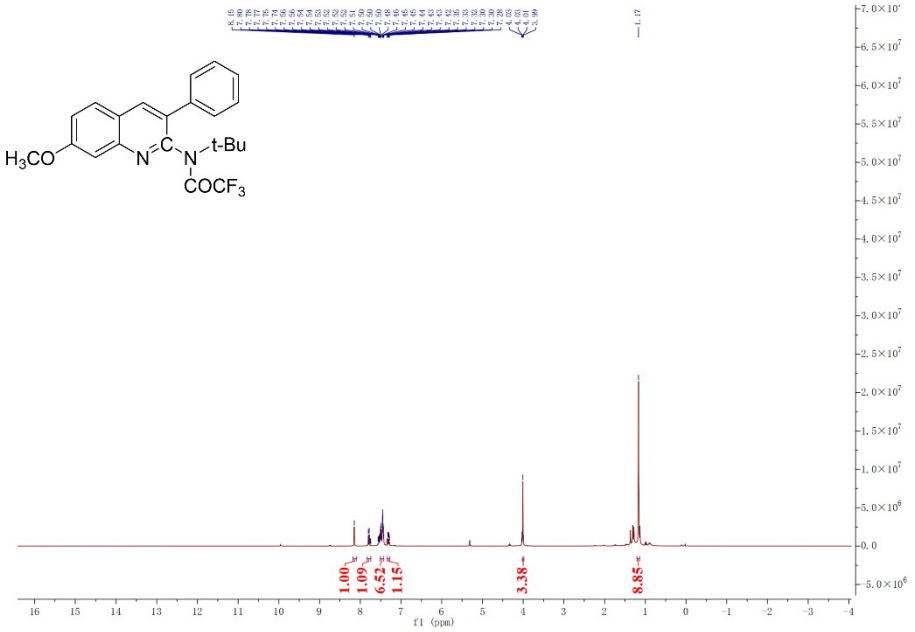


^{13}C NMR of **3i**

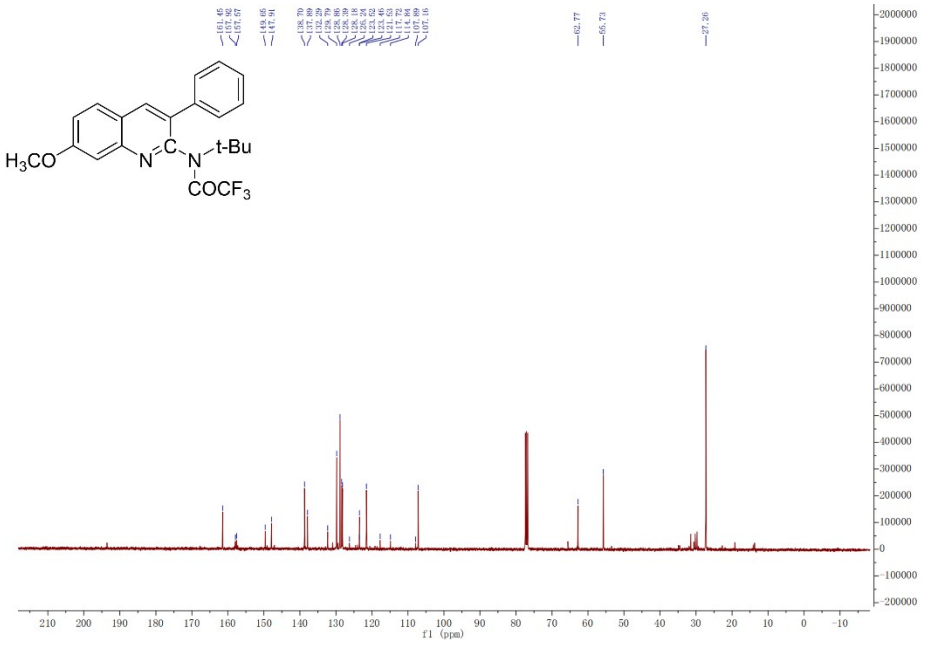


^{19}F NMR of **3i**

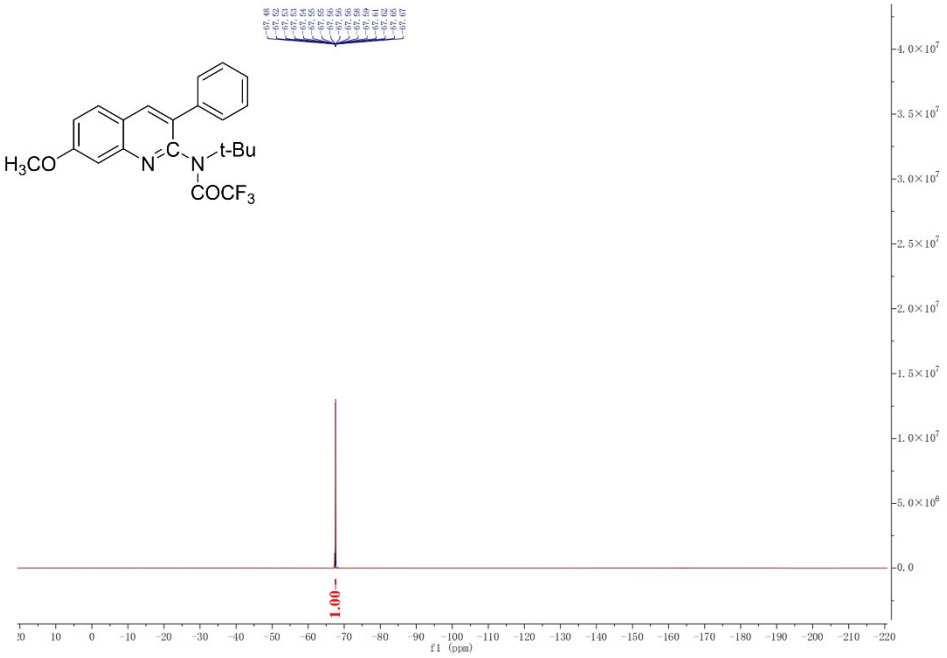
^{1}H NMR of **3j**



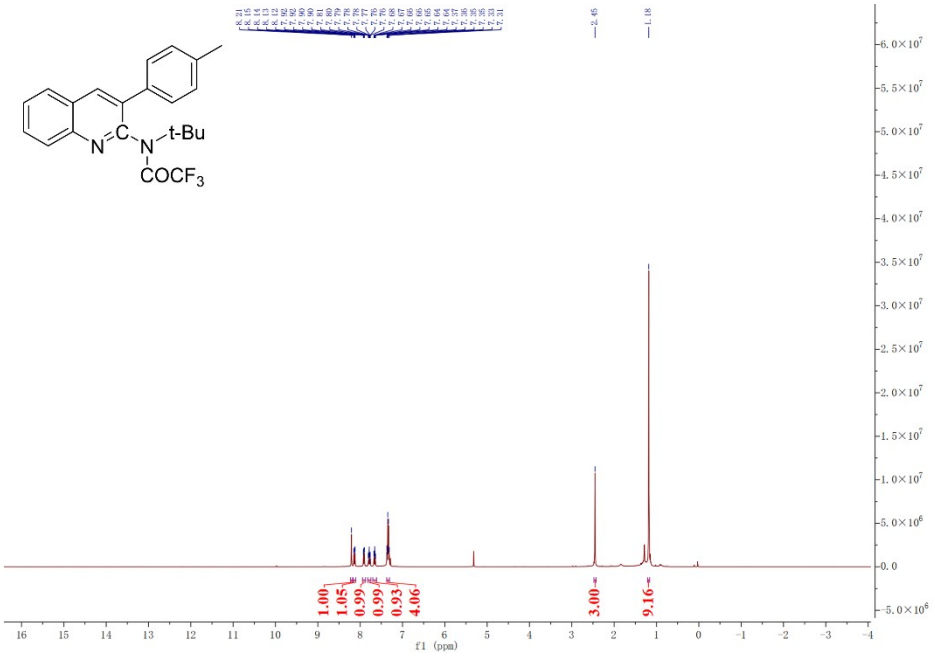
^{13}C NMR of **3j**



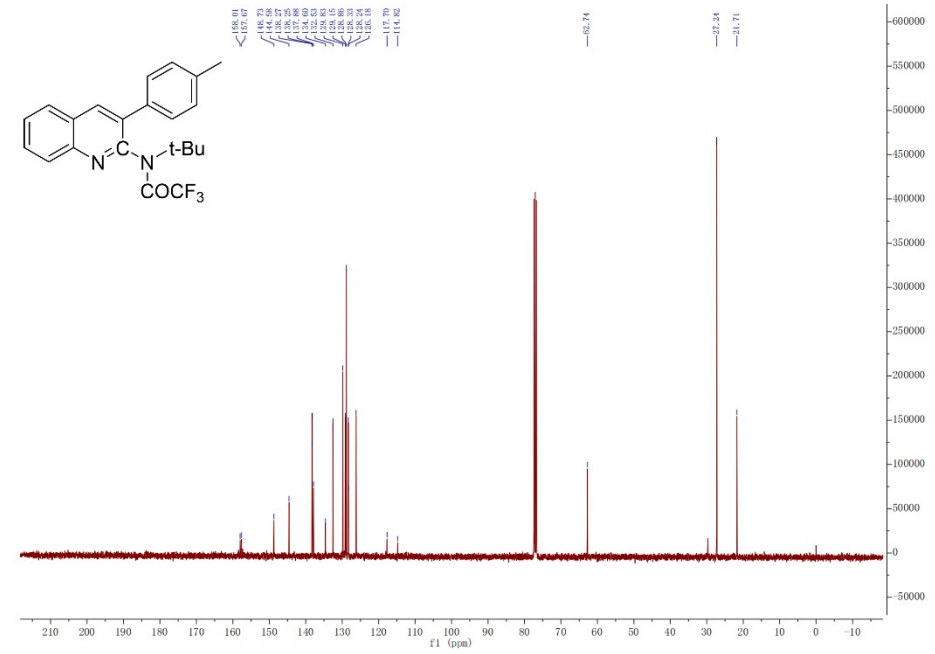
^{19}F NMR of **3j**



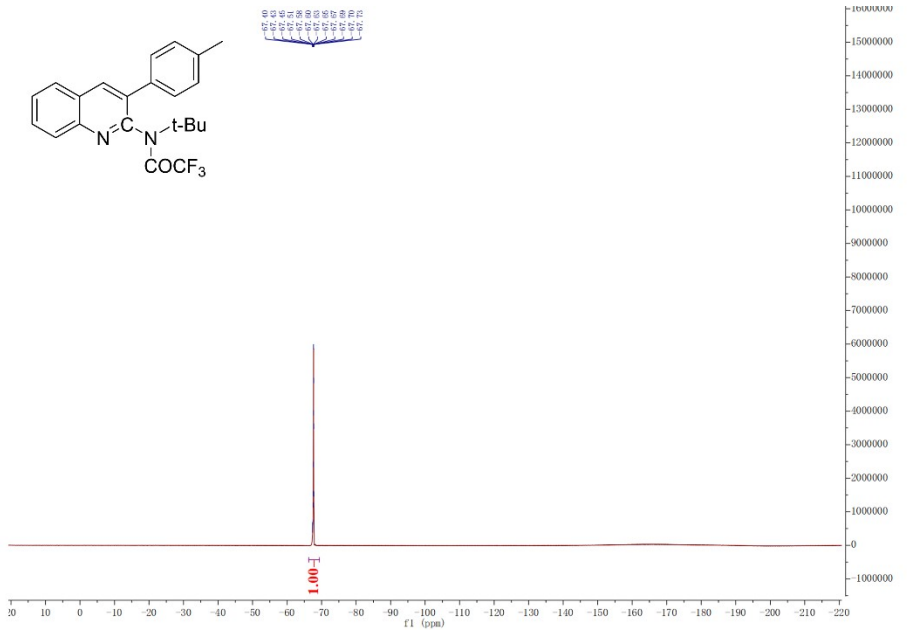
^{1}H NMR of **3k**



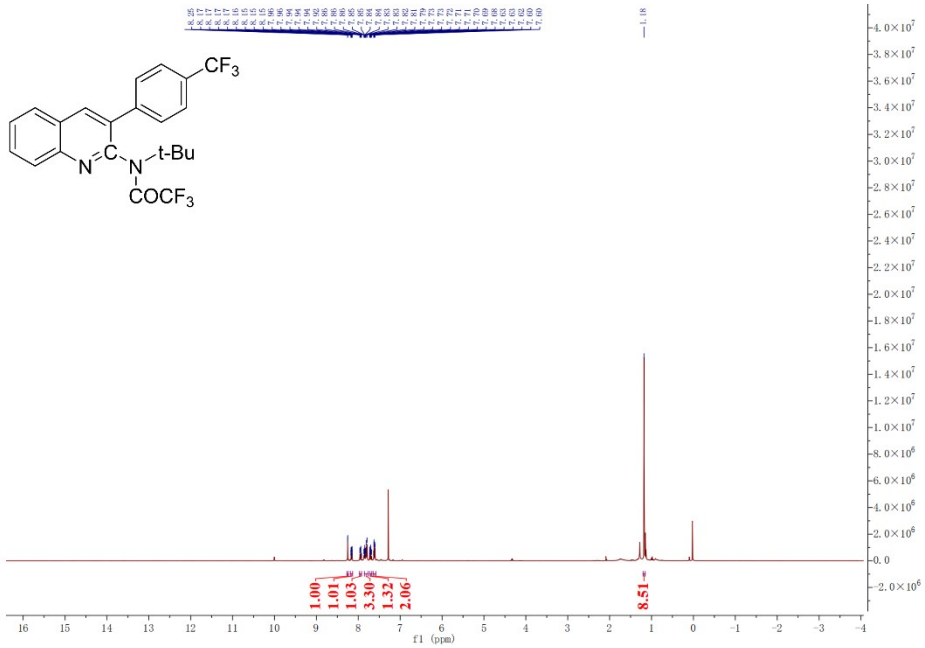
^{13}C NMR of **3k**



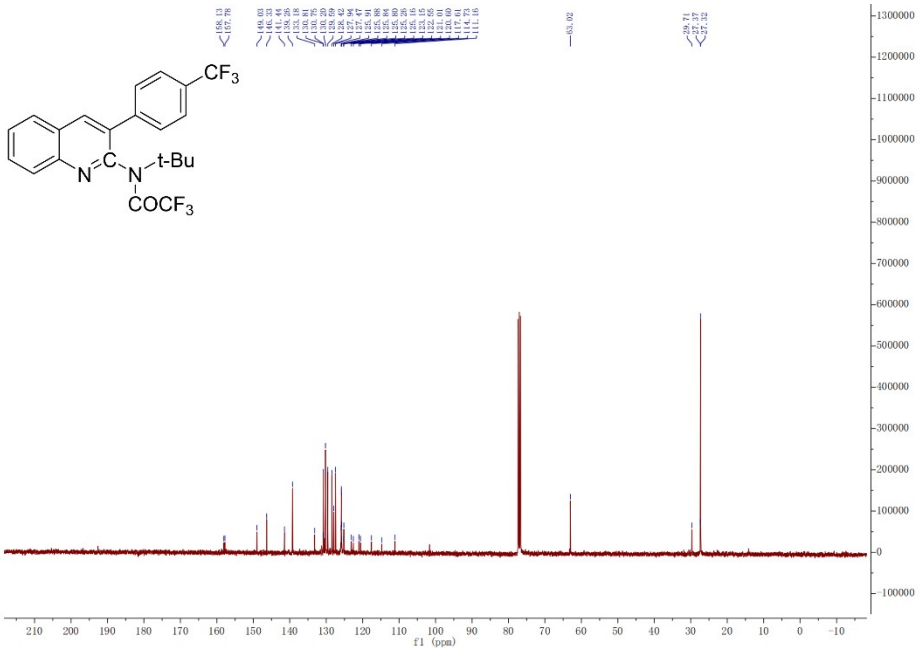
^{19}F NMR of **3k**



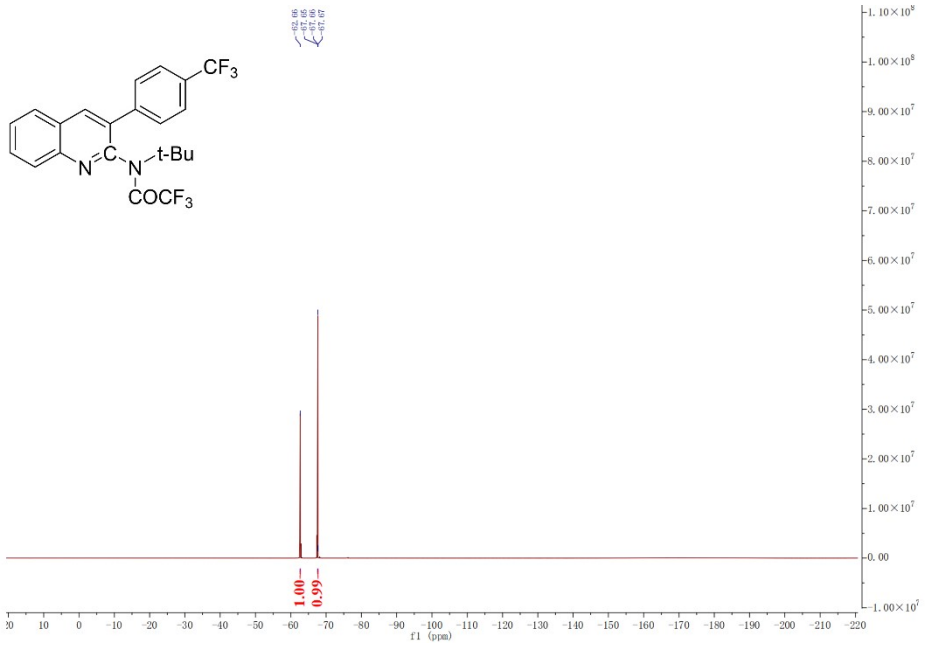
^{1}H NMR of **3l**



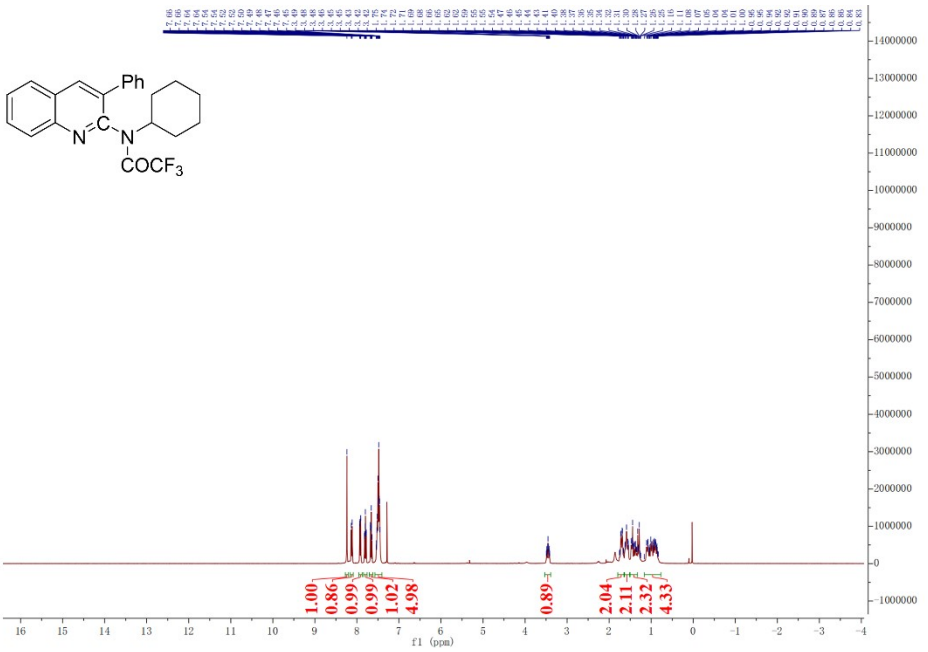
^{13}C NMR of **3l**



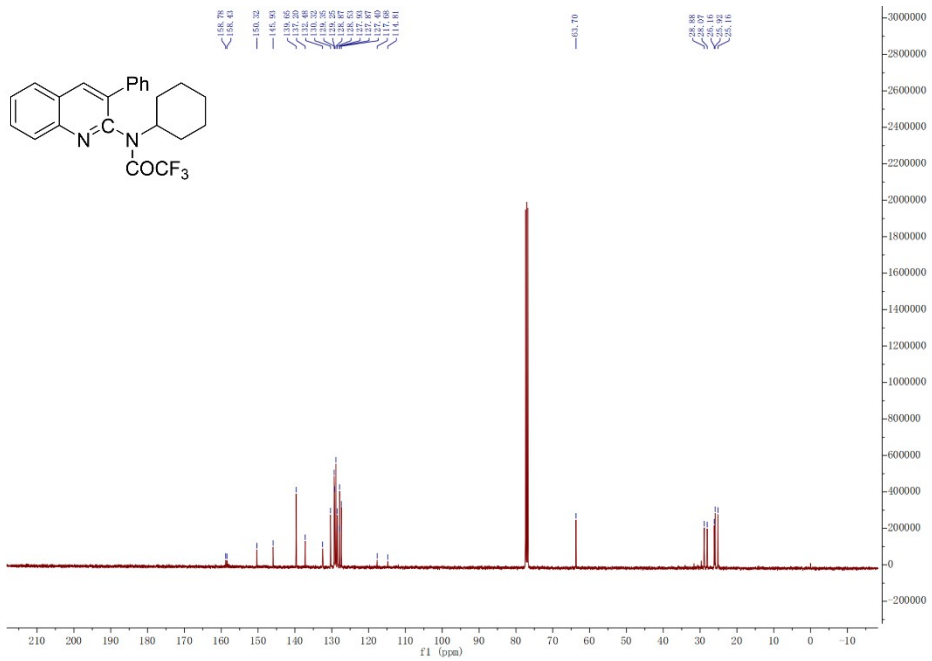
^{19}F NMR of **3l**



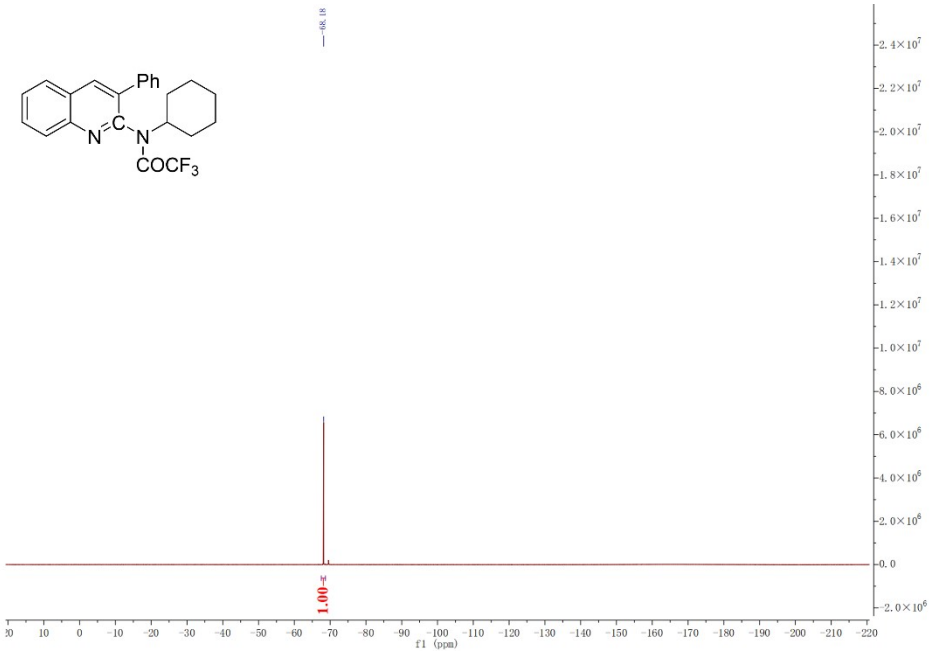
^{1}H NMR of **3m**



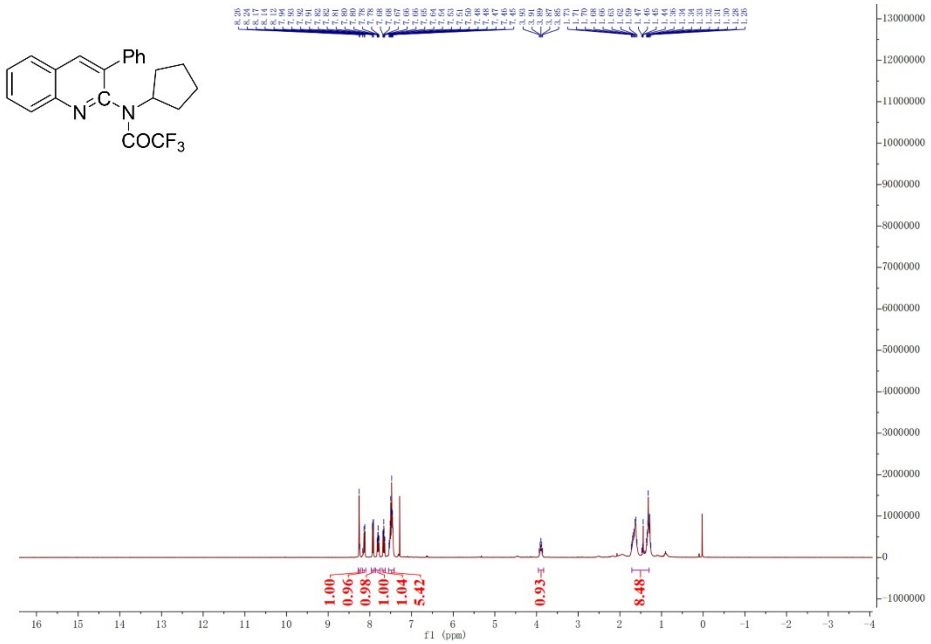
^{13}C NMR of **3m**



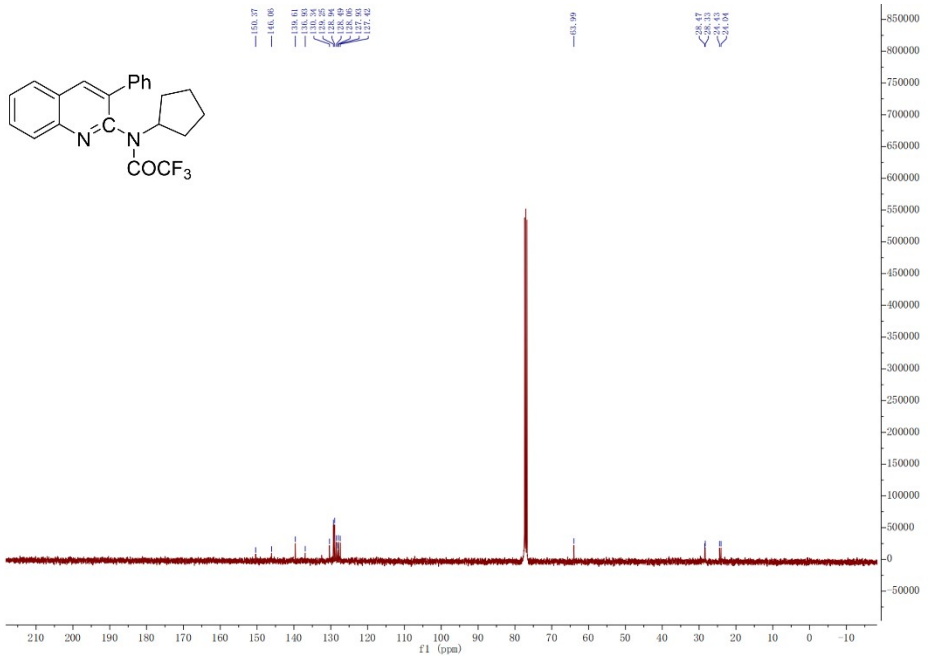
^{13}F NMR of **3m**



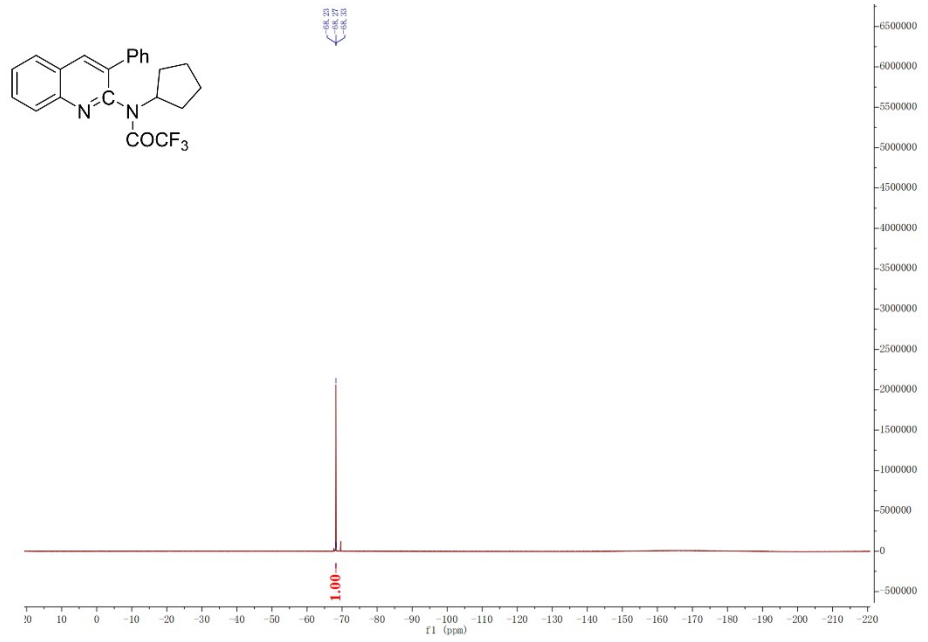
^{1}H NMR of **3n**



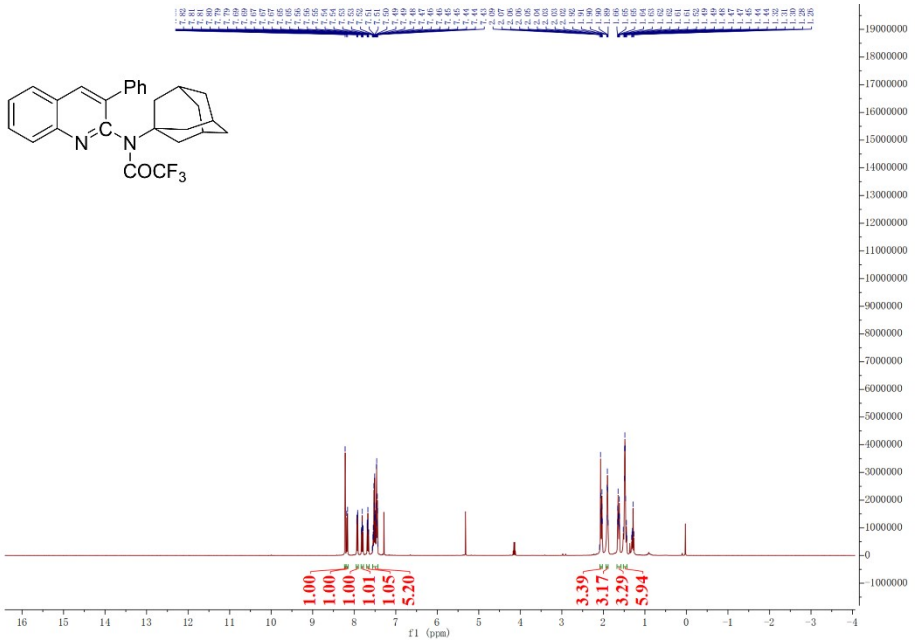
^{13}C NMR of **3n**



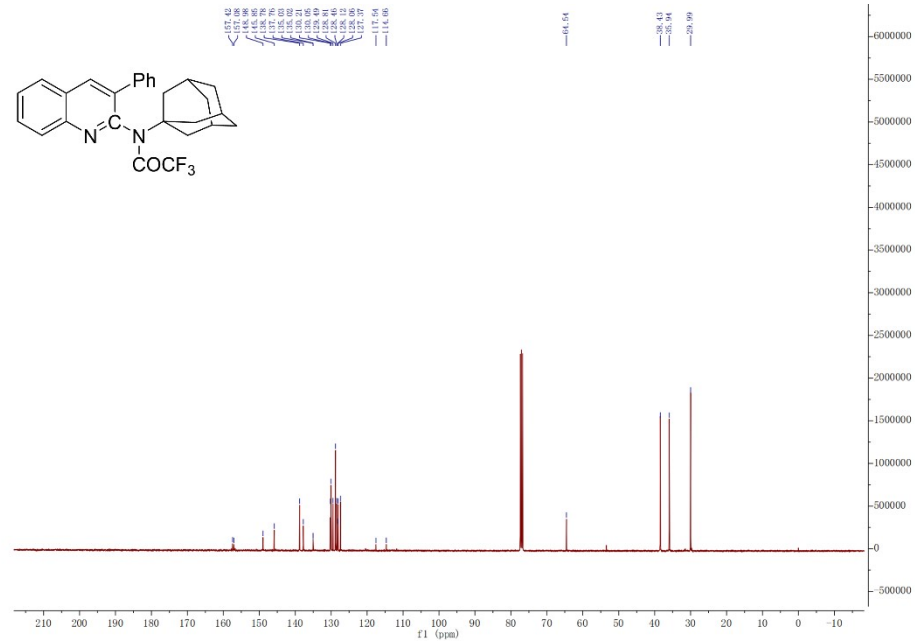
^{19}F NMR of **3n**



^{1}H NMR of **3o**



^{13}C NMR of **3o**



^{19}F NMR of **3o**