Supporting Information

MOF-Based Pd Catalyst: A Controllable and Efficient Platform towards Cyclization Reactions of Isonitriles

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Table of Contents

1. General Information

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 17.7 s/step and a step size of 0.01995o (2θ). The content of Pd was determined by the inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 5100). The X-ray photoelectron spectroscopy (XPS) experiments were conducted using Thermo fisher Scientific with an Al Kα radiation source. SEM images and energy dispersive X-ray spectra (EDS) were collected on MERLIN Compact. Transmission electron microscopy (TEM) and EDS mapping were obtained *via* FEI Tecnai G2 F20. Thermogravimetric analyses (TGA) were performed on a TG209F1 instrument under a flow of N_2 at a heating rate of 10 °C/min. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at a Bruker Model AM-400 (400 MHz) spectrometer 400 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The concentration of Pd^{2+} in the reaction solution was detected by flame atom absorption (Z-2300). IR experiments were conducted with Bruker Tensor 27 on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using Trace 1300.

2. Material Preparation

(1) Synthesis of UiO-67-bpy. The UiO-67-bpy was synthesized though solvothermal route as reported.[1] 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.

(2) Synthesis of Pd(II)$_{0.08}$-UiO-67-bpy. $Pd(OAc)_2$ (22.5 mg, 0.105 mmol) and UiO-67-bpy (213 mg, 0.1 mmol) were dispersed in 3 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(II)$_{0.08}$-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.

(3) Synthesis of Pd(II)$_{0.09}$-UiO-67-bpy. Similar conditions were involved except $Pd(OAc)_2$ (0.2 mmol, 45 mg) was used.

(4) Synthesis of Pd(II)$_{0.15}$-UiO-67-bpy. Similar conditions were involved except $Pd(OAc)_2$ (0.3 mmol, 67.5 mg) was used.

(5) Synthesis of Pd(II)$_{0.25}$-UiO-67-bpy. Similar conditions were involved except $Pd(OAc)_2$ (0.4 mmol, 90 mg) was used.

3. Characterization of Catalysts

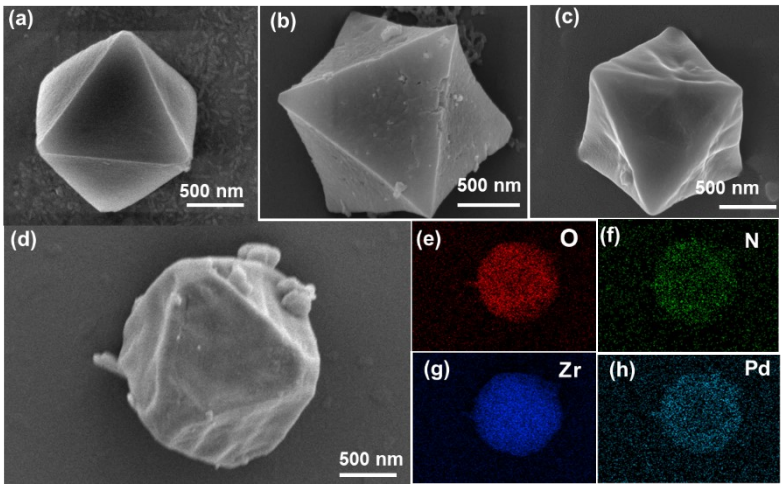


Figure S1. SEM images and EDS mapping of catalysts. (a) UiO-67-bpy, (b) $Pd(II)_{0.08}$-UiO-67-bpy, (c) $Pd(II)_{0.15}$-UiO-67-bpy, (d) $Pd(II)_{0.25}$-UiO-67-bpy, (e) $Pd(II)_{0.09}$-UiO-67-bpy and corresponding element distribution of (f) O, (g) N, (h) Zr and (i) Pd.

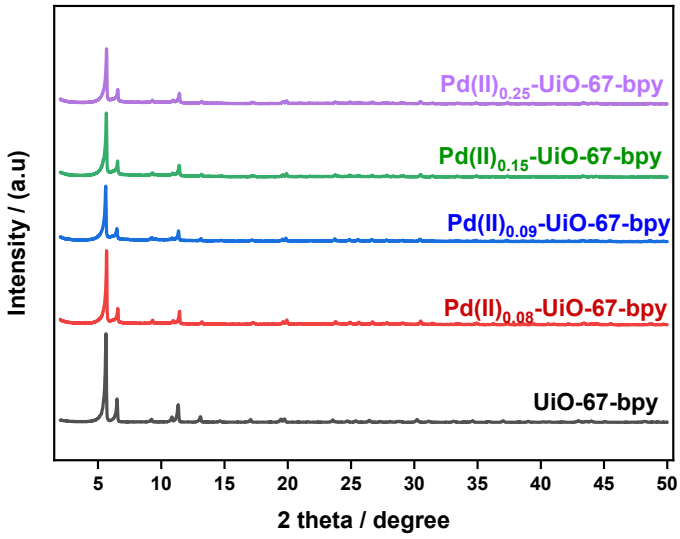


Figure S2. PXRD of UiO-67-bpy and Pd(II)x-UiO-67-bpy.

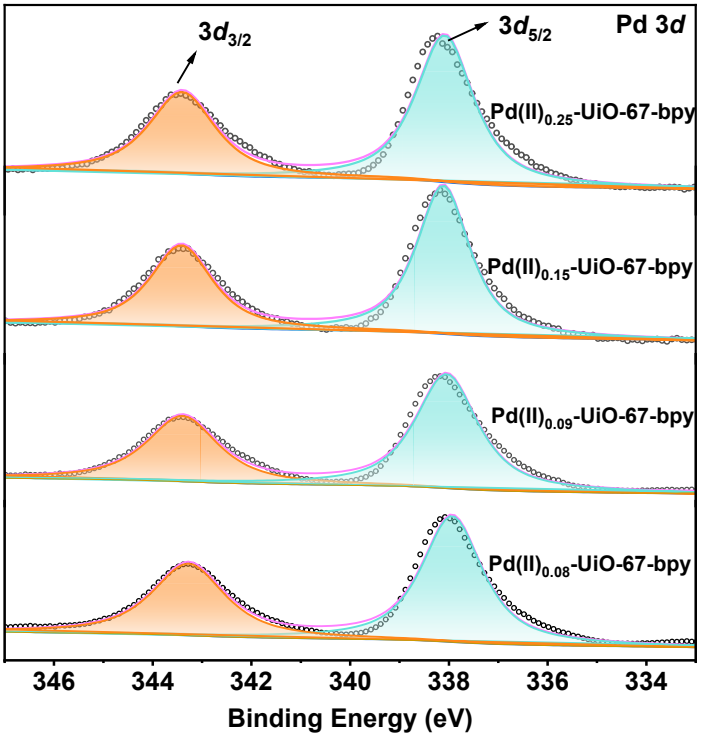


Figure S3. XPS spectra of Pd 3d for Pd(II)x-UiO-67-bpy.

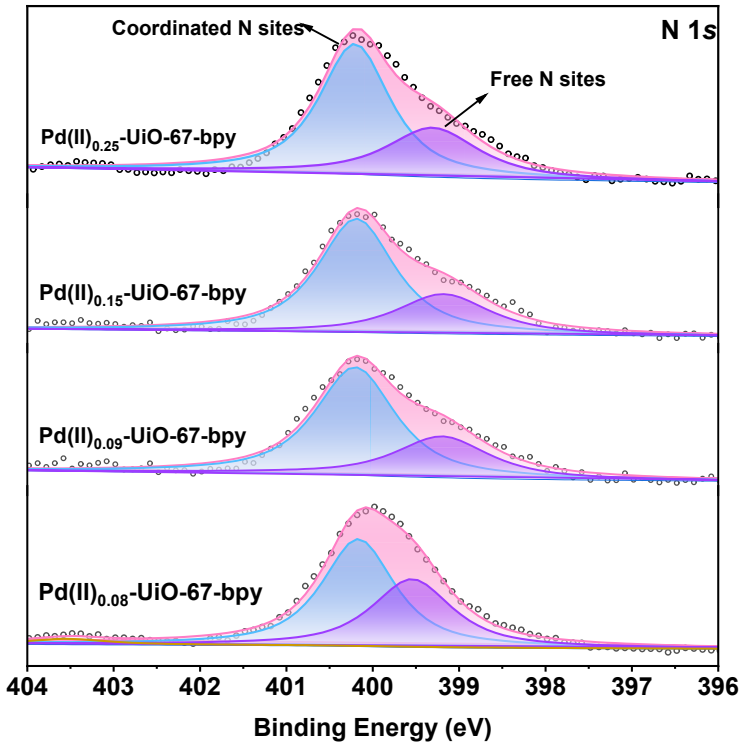


Figure S4. XPS spectra of N 1s for Pd(II)x-UiO-67-bpy.

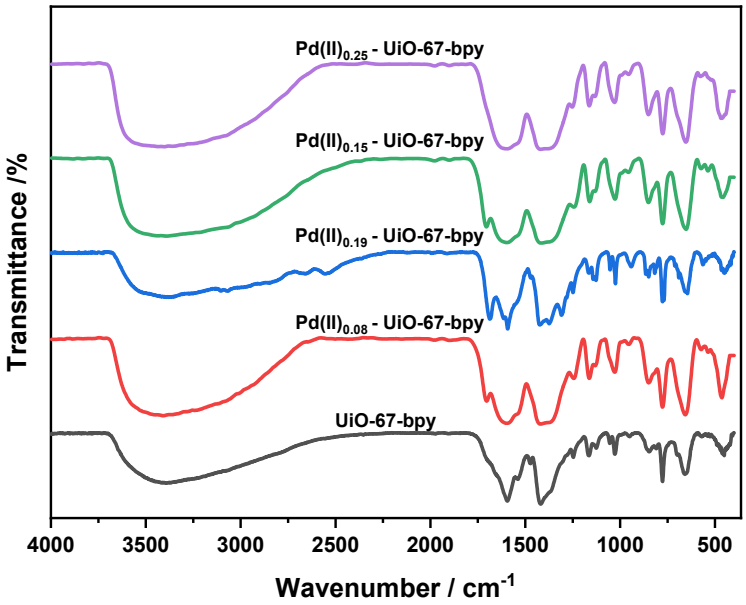


Figure S5. FI-IR images of catalysts. FI-IR images of $Pd(II)_{0.08}$-UiO-67-bpy, $Pd(II)_{0.09}$-UiO-67-bpy, $Pd(II)_{0.15}$-UiO-67-bpy and $Pd(II)_{0.25}$-UiO-67-bpy.

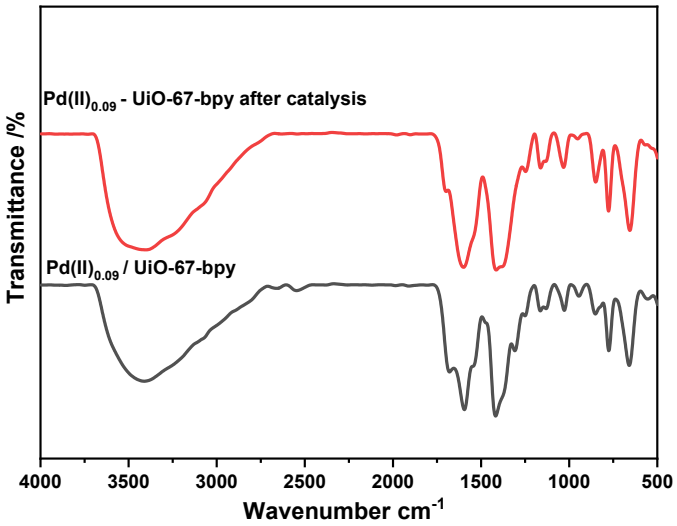


Figure S6. FI-IR images of $Pd(II)_{0.09}$-UiO-67-bpy before and after catalysis.

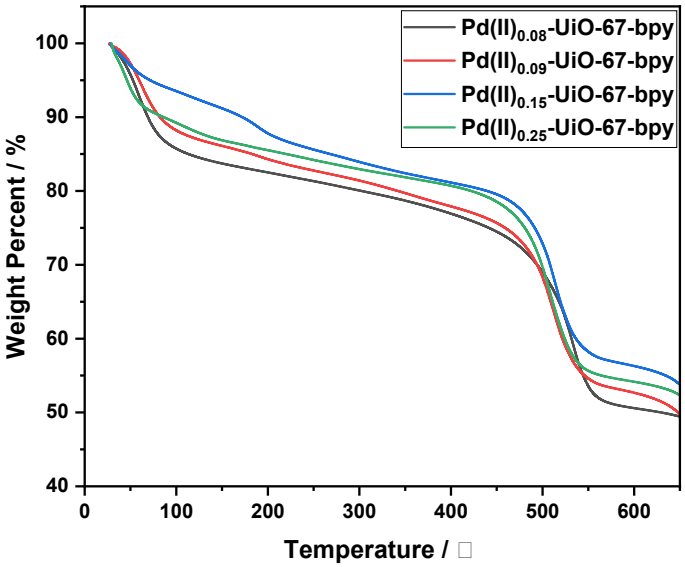


Figure S7. TGA images of catalysts. TGA images of $Pd(II)_{0.08}$-UiO-67-bpy, $(II)_{0.09}$-UiO-67-bpy, $Pd(II)_{0.15}$-UiO-67-bpy and $Pd(II)_{0.25}$-UiO-67-bpy.

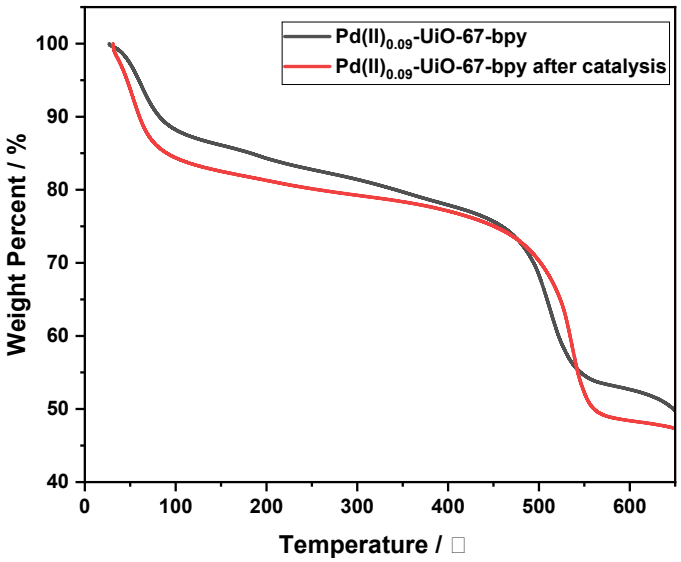


Figure S8. TGA images of $Pd(II)_{0.09}$-UiO-67-bpy before and after catalysis.

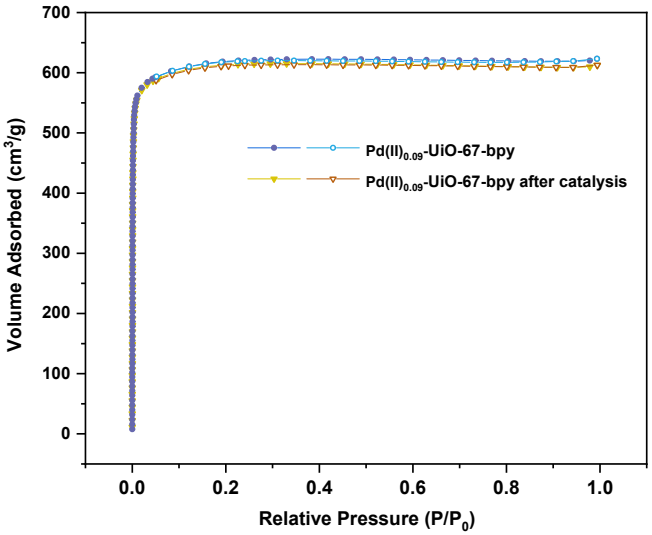


Figure S9. BET images of $Pd(II)_{0.09}$-UiO-67-bpy before and after catalysis.

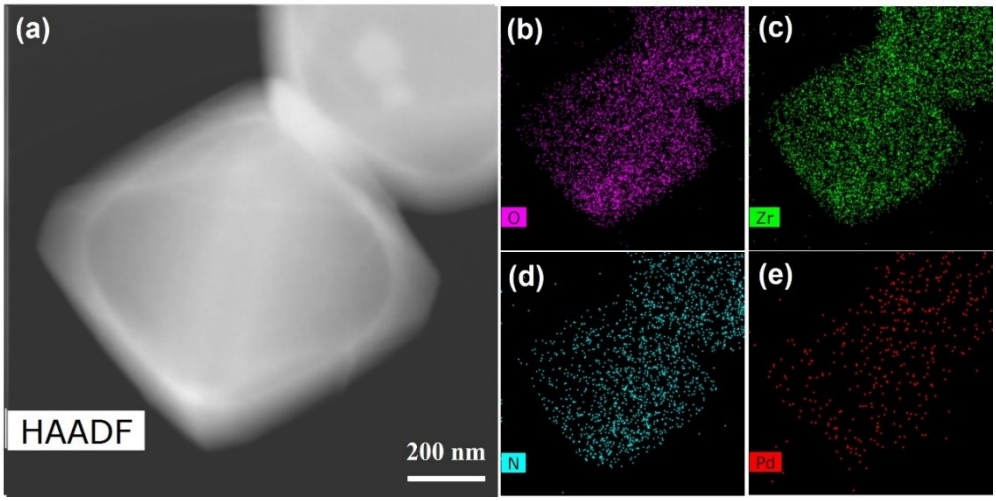


Figure S10. TEM image of (a) $Pd(II)_{0.08}$-UiO-67-bpy after catalysis and corresponding EDS mapping (b) O, (c) Zr, (d) N and (e) Pd.

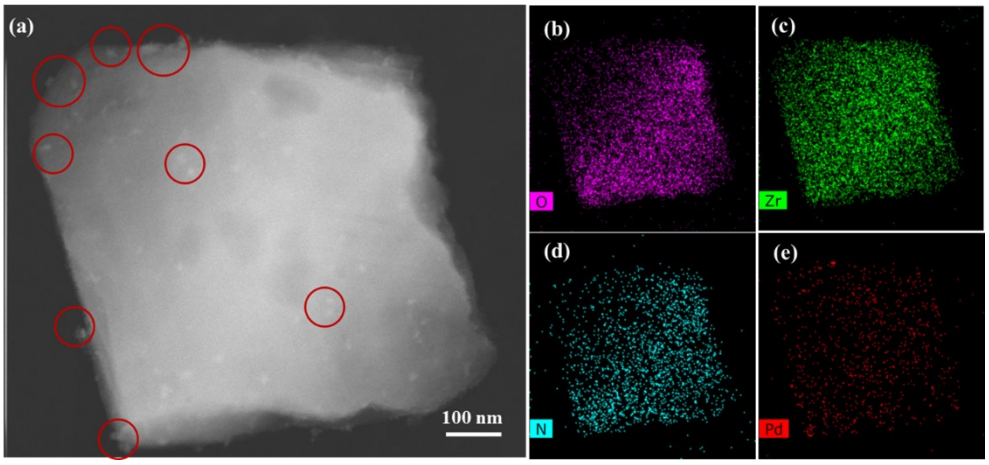


Figure S11. TEM image of (a) $Pd(II)_{0.25}$-UiO-67-bpy after catalysis and corresponding EDS mapping (b) O, (c) Zr, (d) N and (e) Pd.

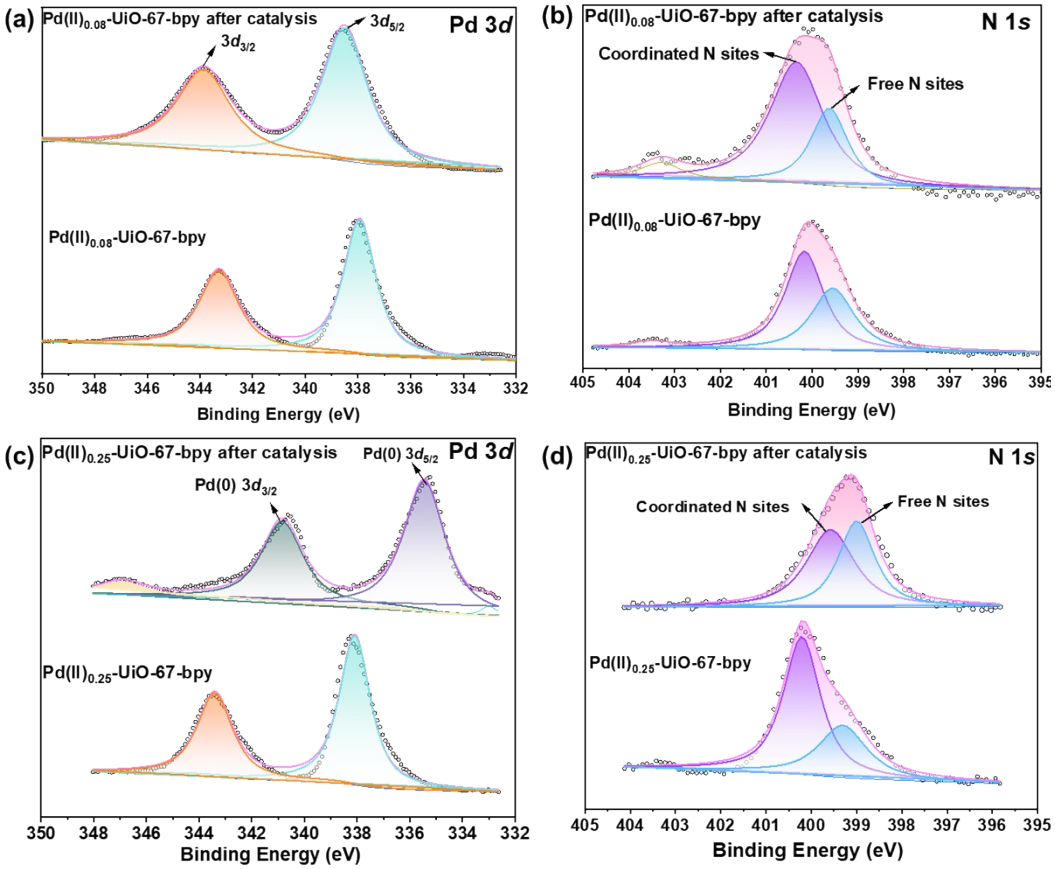


Figure S12. XPS profiles of catalysts. (a) Pd 3d level for $Pd(II)_{0.08}$-UiO-67-bpy, (b) N 1s level for $Pd(II)_{0.08}$-UiO-67-bpy, (c) Pd 3d level for $Pd(II)_{0.25}$-UiO-67-bpy, (d) N 1s level for $Pd(II)_{0.25}$-UiO-67-bpy.

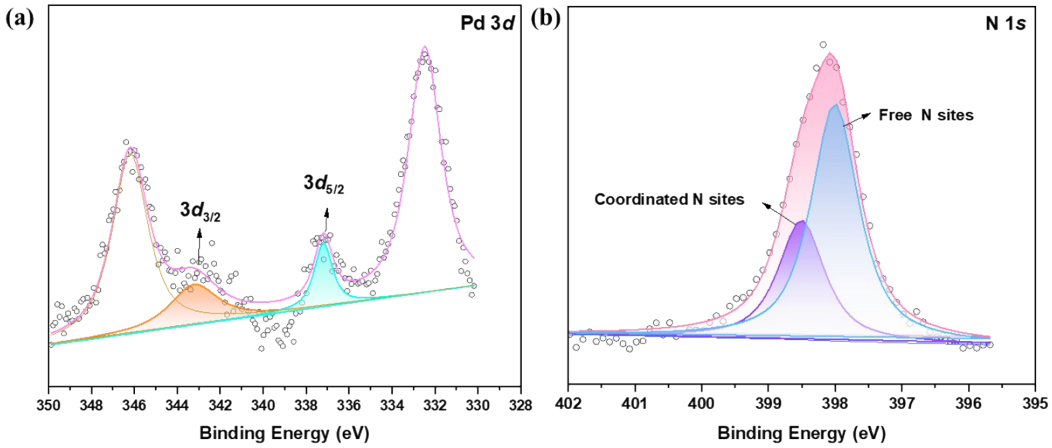


Figure S13. (a) Pd 3d level and (b) N 1s level for $Pd(II)_{0.09}$-UiO-67-bpy after catalysis *via* path b.

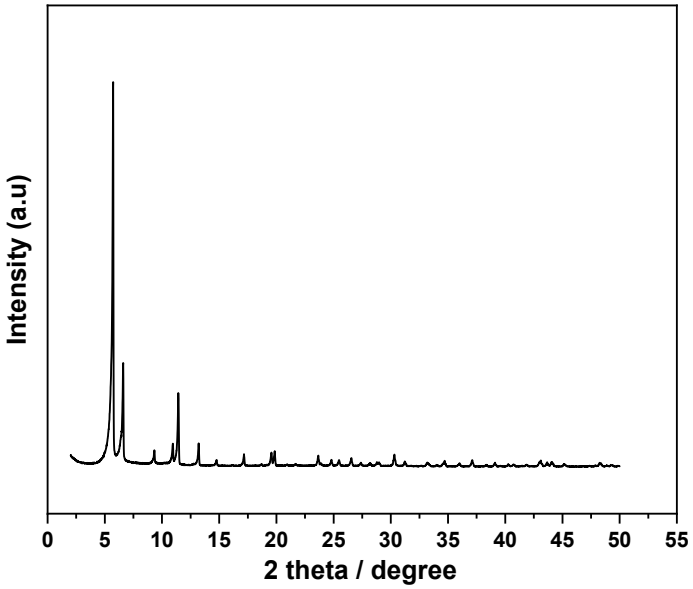


Figure S14. PXRD spectral of $Pd(II)_{0.09}$-UiO-67-bpy after catalysis *via* path b.

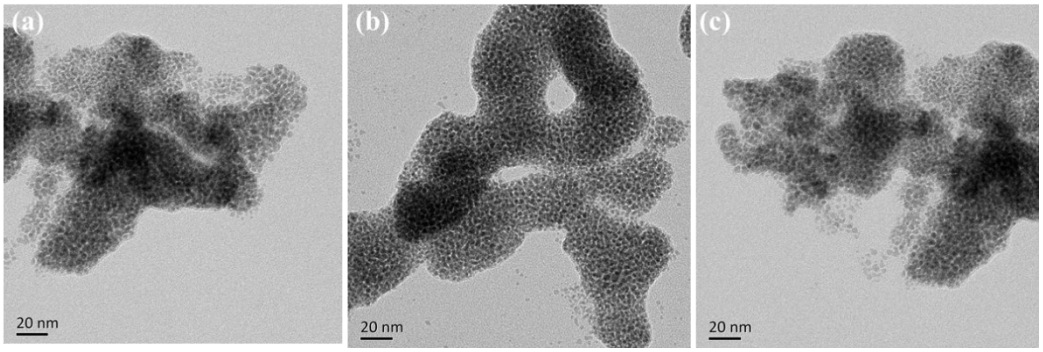


Figure S15. TEM images of homogeneous system I and II after catalysis. (a) TEM image of Pd species in homogeneous I when the reaction proceeded for 40 min, (b) 60 min, (c) TEM image of Pd species in homogeneous II when the reaction proceeded for 60 min.

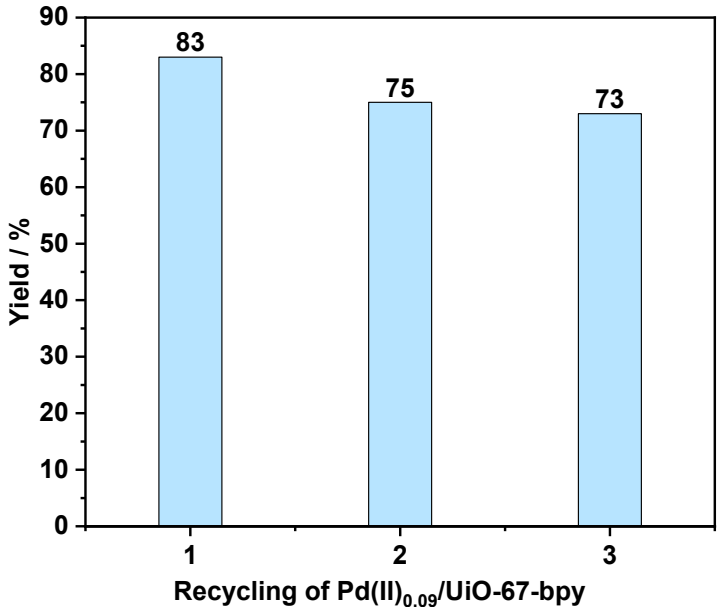
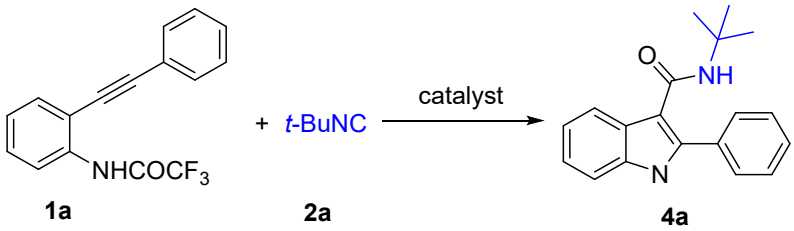


Figure S16. Reusability of $Pd(II)_{0.09}$-UiO-67-bpy

Table S1. Screening of the amout of Na_2CO_3

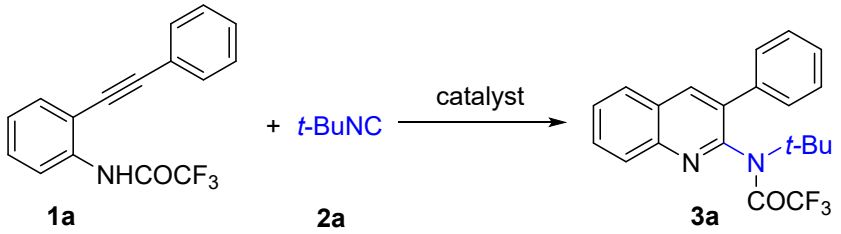


1a **2a** **4a**

Entry	Base (equiv)	Yield (%)	TON
1	Na_2CO_3 (1.0)	71	443
2	Na_2CO_3 (0.5)	68	425
3	Na_2CO_3 (0.3)	33	206
4	Na_2CO_3 (0)	n.d.	n.d.

[a]The reaction conditions were: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(II)_{0.09}$-UiO-67-bpy (Pd 0.16 mol %), dry DMSO (1 mL), air, 25 ℃ and 12 h. Yield of **4a** was determined by ^1H NMR using CH_2Br_2 as an internal standard. n.d. = not detected.

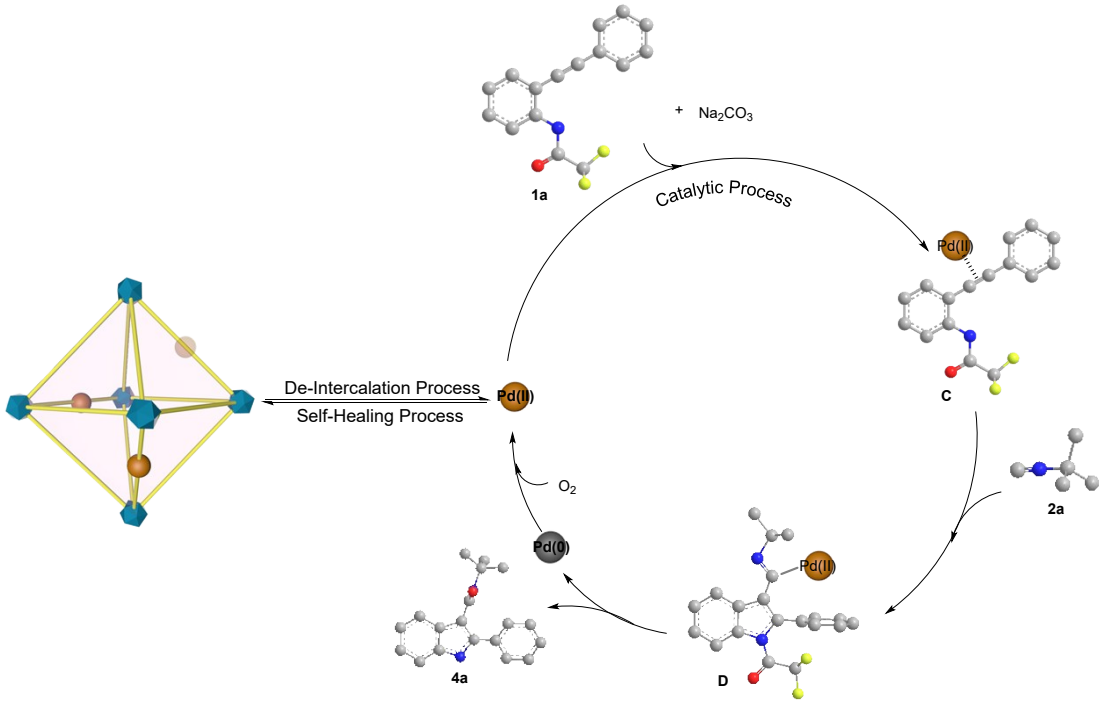
Table S2. Screening of the ratio of $Pd(OAc)_2$: bpy in Pd(II)x-UiO-bpy.



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

Entry	Catalyst	Yield (%)	TON
1	$Pd(II)_{0.08}$-UiO-67-bpy (2 mg, Pd 0.07 mol %)	50	714
2	$Pd(II)_{0.08}$-UiO-67-bpy (4 mg, Pd 0.14 mol %)	51	364
3	$Pd(II)_{0.08}$-UiO-67-bpy (8 mg, Pd 0.28 mol %)	71	254
4	$Pd(II)_{0.09}$-UiO-67-bpy (2 mg, Pd 0.08 mol %)	60	750
5	$Pd(II)_{0.09}$-UiO-67-bpy (4 mg, Pd 0.16 mol %)	83	519
6	$Pd(II)_{0.09}$-UiO-67-bpy (8 mg, Pd 0.32 mol %)	76	238
7	$Pd(II)_{0.15}$-UiO-67-bpy (2 mg, Pd 0.14 mol %)	74	529
8	$Pd(II)_{0.15}$-UiO-67-bpy (4 mg, Pd 0.28 mol %)	48	174
9	$Pd(II)_{0.15}$-UiO-67-bpy (8 mg, Pd 0.56 mol %)	50	89
10	$Pd(II)_{0.25}$-UiO-67-bpy (2 mg, Pd 0.23 mol %)	78	339
11	$Pd(II)_{0.25}$-UiO-67-bpy (4 mg, Pd 0.46 mol %)	77	167
12	$Pd(II)_{0.25}$-UiO-67-bpy (8 mg, Pd 0.92 mol %)	78	85
13	$Pd(OAc)_2$ (0.16 mol%)	n.d.	-
14	$Pd(OAc)_2$ (10 mol%)	32	3.2

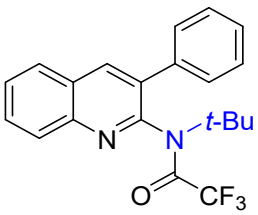
[a]The reaction conditions were: **1a** (0.1 mmol), **2a** (0.15 mmol), Li_2CO_3 (30 mol %), dry DMSO (1 mL), N_2, 100 °C and 1 h. Yield of **3a** was determined by ^{19}F NMR using CF_3Ph as an internal standard. n.d. = not detected.



Scheme S1. Possible reaction mechanism of $Pd(II)_{0.09}$-UiO-67-bpy-catalyzed cyclization of isonitriles with *N*-acyl-*o*-alkynylanilines for 1*H*-indole-3-carboxamides.

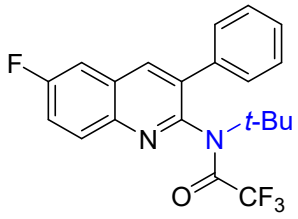
4. Characterization Data for All Products

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



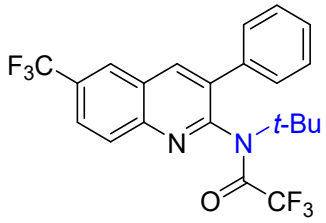
Yellow solid (31 mg, 83%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.76 (m, 1H), 7.65 (t, J = 16.1 Hz, 1H), 7.53 – 7.41 (m, 5H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.1, 157.7, 146.1, 139.1, 137.8, 134.8, 130.3, 129.6, 129.0, 128.6, 128.3, 128.2, 127.5, 117.8, 114.9, 62.9, 27.4 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.64.

N-(*tert*-Butyl)-2,2,2-trifluoro-*N*-(6-fluoro-3-phenylquinolin-2-yl)acetamide (3b)[2]



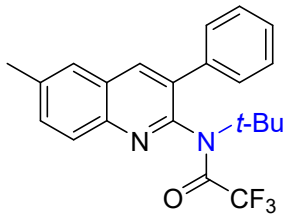
Yellow solid (30 mg, 78%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 8.14 (dd, J = 9.1, 5.3 Hz, 1H), 7.59 – 7.44 (m, 7H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.9, 160.4, 157.9 (q, J = 34.6 Hz), 149.2 (d, J = 2.8 Hz), 143.2, 138.4, 138.3, 137.5, 135.7, 132.3, 132.2, 129.9, 129.1-129.0 (m), 128.8, 120.7 (d, J = 25.9 Hz), 117.8, 114.9, 110.7, 110.5, 63.0, 27.4 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.69, -110.85 (td, J = 8.4, 5.3 Hz).

_N_-(_tert_-Butyl)-2,2,2-trifluoro-_N_-(3-phenyl-6-(trifluoromethyl)quinolin-2-yl)acetamide (3c)[2]



Yellow solid (40 mg, 91%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 8.24 (d, J = 9.5 Hz, 2H), 7.95 (dd, J = 8.8, 1.8 Hz, 1H), 7.55 – 7.43 (m, 5H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9 (q, J = 34.9 Hz), 151.8, 147.1, 139.8, 137.1, 136.3, 130.9, 129.9 (d, J = 7.0 Hz), 129.2, 129.1, 127.3, 126.0 (q, J = 2.9 Hz), 125.5(q, J = 4.4 Hz), 117.7, 63.3, 27.4 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.58, -67.65.

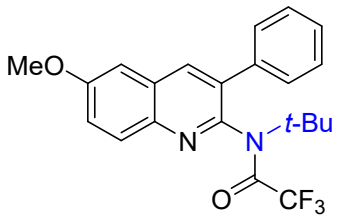
_N_-(_tert_-Butyl)-2,2,2-trifluoro-_N_-(6-methyl-3-phenylquinolin-2-yl)acetamide (3d)[2]



Yellow solid (26 mg, 67%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 8.01

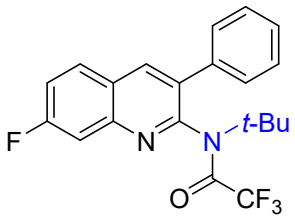
(d, J = 8.6 Hz, 1H), 7.66 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.41 (m, 5H), 2.58 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0 (d, *J* = 34.6 Hz), 148.9, 144.7, 138.4, 138.0, 134.7, 132.7, 130.0, 129.3, 129.0, 128.5, 128.4, 126.3, 117.8, 114.9, 62.9, 27.4, 21.8 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.67.

_N_-(_tert_-Butyl)-2,2,2-trifluoro-_N_-(6-methoxy-3-phenylquinolin-2-yl)acetamide (3e)[2]



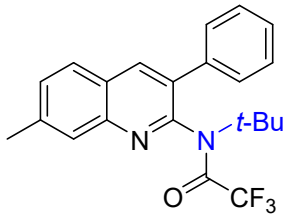
White solid (22 mg, 54%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.50 – 7.40 (m, 6H), 7.14 (d, *J* = 2.7 Hz, 1H), 3.95 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.1, 157.7 (q, *J* = 34.6 Hz), 147.3, 142.0, 137.9, 137.6, 134.9, 130.9, 129.8, 129.4, 128.9, 128.3, 123.1, 117.7, 114.8, 104.7, 62.7, 55.7, 27.2 ppm; ^{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 (3f)[2]



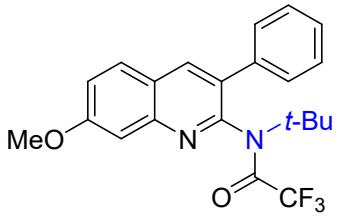
Yellow solid (35 mg, 90%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.90 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.75 (dd, *J* = 9.8, 2.5 Hz, 1H), 7.52 – 7.41 (m, 6H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.9, 162.4, 157.9 (d, *J* = 34.9 Hz), 150.7, 147.2 (d, *J* = 13.0 Hz), 139.0, 137.5, 134.2, 129.9, 129.6 (d, *J* = 10.0 Hz), 129.1, 128.6, 125.4, 118.9 (d, *J* = 25.6 Hz), 117.8, 114.9, 113.4 (d, *J* = 20.7 Hz), 63.1, 27.4 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.66, -107.96 (dd, *J* = 13.9 Hz).

***N*-(*tert*-Butyl)-2,2,2-trifluoro-*N*-(7-methyl-3-phenylquinolin-2-yl)acetamide (3g)**[2]



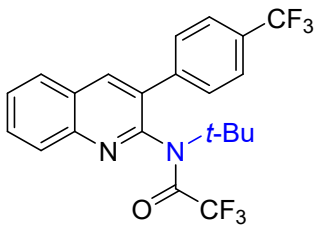
Yellow solid (24 mg, 63%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.91 (s, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.52 – 7.41 (m, 6H), 2.60 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0 (d, J = 34.7 Hz), 149.6, 146.4, 140.9, 138.8, 138.0, 133.9, 130.5, 129.9, 129.0, 128.6, 128.4, 127.2, 126.4, 117.8, 115.0, 62.9, 27.4, 22.0 ppm; ^{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 (3h)**



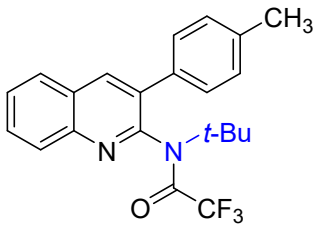
Yellow solid (25 mg, 63%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.50 – 7.39 (m, 6H), 7.29 (dd, J = 8.9, 2.5 Hz, 1H), 3.99 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 157.7, 149.8, 148.0, 138.9, 138.0, 132.4, 129.9, 129.0, 128.5, 128.3, 123.6, 121.7, 117.8, 115.0 107.3, 62.9, 55.9, 27.4 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.61. ν_{max}(KBr)/cm^{-1} 2935, 1695, 1621, 1492, 1374, 1029, 932, 758, 704, 480; HRMS-ESI (m/z): calcd for $C_{22}H_{22}F_3N_2O_2$, $[M+H]^+$: 403.1628, found 403.1622.

***N*-(*tert*-Butyl)-2,2,2-trifluoro-*N*-(3-(4-(trifluoromethyl)phenyl)quinolin-2-yl)acetamide (3i)**[2]



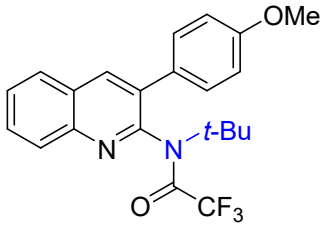
Yellow solid (35 mg, 80%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.80 (dd, J = 20.8, 7.6 Hz, 3H), 7.68 (t, J = 8.0 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.1 (d, J = 34.7 Hz), 149.2, 146.5, 141.6, 139.4, 133.3, 130.9, 130.3, 129.7, 128.6, 128.1, 127.6, 126.0 (q, J = 37 Hz), 120.9 (d, J = 41.7 Hz), 117.7, 114.9, 63.2, 27.5 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.66, -67.66.

_N_-(_tert_-Butyl)-2,2,2-trifluoro-_N_-(3-(_p_-tolyl)quinolin-2-yl)acetamide (3j)[2]



Red solid (22 mg, 55%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.79 (t, J = 7.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.35 (q, 4H), 2.45 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.1 (q, J = 34.5 Hz), 149.8, 146.0, 138.9, 138.5, 134.9, 129.8, 129.7, 129.6, 128.4, 128.1, 127.5, 117.8, 114.9, 62.9, 27.4, 21.3 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.68.

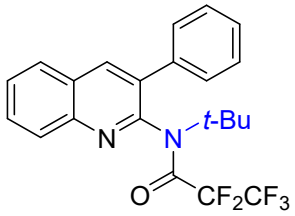
_N_-(_tert_-Butyl)-2,2,2-trifluoro-_N_-(3-(4-methoxyphenyl)quinolin-2-yl)acetamide (3k)[2]



Yellow solid (22 mg, 54%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.2 Hz 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.37 (d, J = 6.7 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.9, 158.0 (q, J = 34.6 Hz), 149.8, 145.9, 138.7,

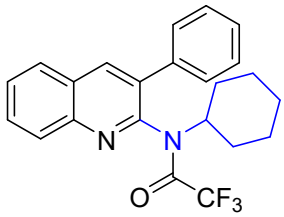
134.5, 131.2, 130.1, 130.0, 129.6, 128.4, 128.1, 127.4, 117.8, 114.5, 62.9, 55.5, 27.4 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.67.

_N_-(_tert_-Butyl)-2,2,3,3,3-pentafluoro-_N_-(3-phenylquinolin-2-yl)propanamide (3l)[2]



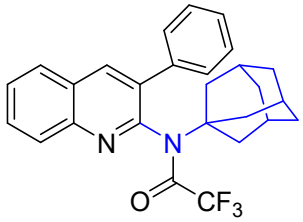
Yellow solid (25 mg, 58%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.43 (m, 5H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.1 (t, *J* = 23.6 Hz), 149.5, 146.1, 138.9, 137.9, 134.7, 130.3, 129.9, 129.7, 129.0, 128.5, 128.3, 128.2, 127.5, 119.9, 117.0, 63.3, 27.3 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.71, -111.99 (d, *J* = 10.0 Hz).

_N_-Cyclohexyl-2,2,2-trifluoro-_N_-(3-phenylquinolin-2-yl)acetamide (3m)[2]



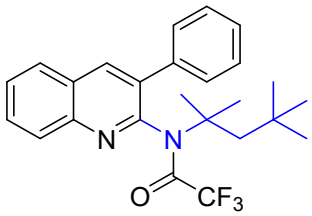
Yellow solid (14 mg, 35%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.77 (dd, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.51-7.43 (m, 5H), 3.39-3.49 (m, 1H), 1.80-1.65 (m, 3H), 1.76-1.66 (m, 2H), 1.56 (t, 2H), 1.45-1.36 (m, 2H), 1.08-0.83 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.55 (q, *J* = 35.5 Hz), 150.5, 146.1, 139.8, 137.3, 130.0, 129.5, 129.4, 129.0, 128.7, 128.1, 128. 0, 127.5, 117.8, 114.9, 63.8, 29.0, 28.2, 26.3, 26.0, 25.3 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.18.

***N*-(Adamantan-1-yl)-2,2,2-trifluoro-*N*-(3-phenylquinolin-2-yl)acetamide (3n)**[2]



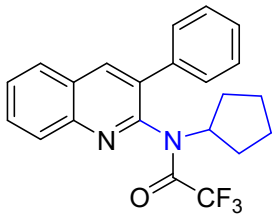
Yellow solid (25 mg, 56%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.81-7.76 (m, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.52-7.41 (m, 5H), 2.02 (d, J = 11.5 Hz, 3H), 1.88 (s, 3H), 1.61 (d, J = 11.5 Hz, 3H), 1.49-1.41 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.37 (q, J = 34.5 Hz), 149.1, 145.9, 138.9, 137.9, 135.2, 129.6, 128.9, 128.6, 128.2, 127.5, 117.7, 114.8, 64.7, 38.6, 30.1 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.65.

2,2,2-Trifluoro-*N*-(3-Phenylquinolin-2-yl)-*N*-(2,4,4-trimethylpentan-2-yl)acetamide (3o)[2]



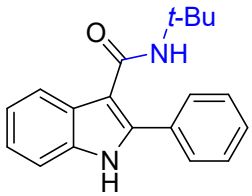
Yellow solid (28 mg, 65%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.52-7.39 (m, 5H), 2.36 (d, J = 14.6 Hz, 1H), 1.27 (s, 4H), 0.93 (s, 3H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.6 (q, J = 34.5 Hz), 149.7, 146.1, 139.1, 137.9, 135.2, 130.3, 130.1, 129.6, 129.0, 128.5, 128.2, 128.2, 127.5, 117.9, 114.9, 67.9, 49.9, 31.7, 31.5, 27.5, 27.0 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.51.

***N*-Cyclopentyl -2,2,2-trifluoro-*N*-(3-phenylquinolin-2-yl)acetamide (3p)**[2]



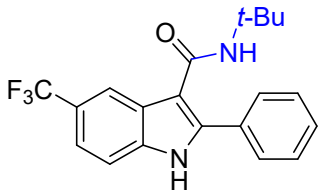
Yellow solid (14 mg, 37%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.48-7.43 (m, 5H), 3.87 (p, J = 8.3 Hz, 1H), 1.70-1.50 (m, 8H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 139.7, 130.5, 129.4, 129.1, 128.6, 128.1, 127.6, 64.1, 24.6, 24.2 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.27; ν_{max}(KBr)/cm^{-1} 2956, 1699,1584, 1487, 1410, 1371, 1186, 760, 701, 595, 482. $[M+H]^{+}$: 385.1522, found 385.1518.

N-tert-Butyl-2-phenyl-1_H_-indole-3-carboxamide (4a)[3]



White solid (19 mg, 65%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 7.73-7.69 (m, 3H), 7.52-7.48 (m, 2H), 7.43-7.40 (m, 2H), 7.19-7.13 (m, 1H), 7.12-7.06 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1, 135.4, 128.5, 128.3, 128.3, 122.1, 120.0, 119.9, 111.4, 50.4, 28.6 ppm.

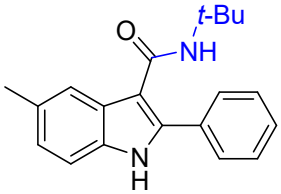
N-tert-Butyl-2-phenyl-5-trifluoromethyl-1_H_-indole-3-carboxamide (4b)[3]



White solid (18 mg, 52%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.12 (s, 1H), 8.04 (s, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.3 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.3, 139.2, 136.9,

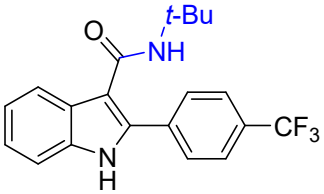
131.1, 128.9, 128.6, 126.8, 118.5, 117.3, 112.3, 111.4, 50.5, 39.5, 28.5 ppm.

N-tert-Butyl-5-methyl-2-phenyl-1_H_-indole-3-carboxamide (4c)[3]



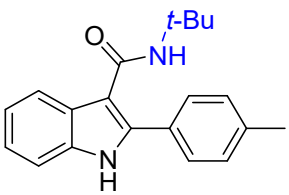
White solid (21 mg, 68%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.51 (s, 1H), 7.71-7.69 (m, 2H), 7.51-7.45 (m, 3H), 7.43-7.39 (m, 1H), 7.42 (m, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.02-6.93 (m, 2H), 2.40 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1, 136.7, 133.8, 131.9, 128.4, 128.3, 128.2, 127.7, 123.7, 119.5, 111.1, 110.5, 50.3, 21.4 ppm.

N-tert-Butyl-2-(4-trifluoromethyl)-1_H_-indole-3-carboxamide (4d)



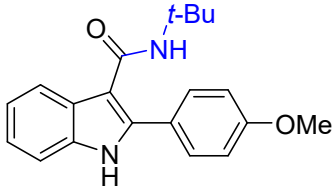
White solid (12 mg, 32%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.82 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.52 (s, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 135.9, 135.7, 134.5, 128.6, 127.1, 122.8, 120.3, 119.9, 112.8, 111.6, 50.6, 28.5 ppm; ν_{max}(KBr)/cm-1 3700, 3011, 1590, 1518, 1446, 1322, 1168, 1113, 1064, 747, 471; HRMS-ESI (m/z): calcd for $C_{20}H_{19}F_3N_2O_1$, $[M+H]^+$: 361.1517, found 361.1522.

N-tert-Butyl-2-_p_-tolyl-1_H_-indole-3-carboxamide (4e)[3]



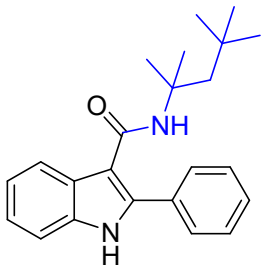
White solid (8 mg, 26%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.57 (s, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.07 (s, 1H), 7.06 (s, 1H), 2.37 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1, 137.7, 136.8, 135.3, 129.0, 128.2, 127.4, 121.9, 119.9, 119.7, 111.3, 50.3, 39.5, 28.6, 20.9 ppm.

_N_-*tert*-Butyl-2-(4-methoxylphenyl)-1*H*-indole-3-carboxamide (4f)[3]



White solid (24 mg, 74%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.53 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 7.9 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.8 Hz, 3H), 6.97 (s, 1H), 3.82 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1, 159.4, 136.9, 135.2, 129.7, 127.5, 124.1, 119.9, 119.7, 111.2, 110.0, 55.3, 50.3, 39.5, 28.6 ppm.

_N_-(2,4,4-Trimethylpentan-2-yl)-2-phenyl-1*H*-indole-3-carboxamide (4g)



White solid (26 mg, 75%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.44 (d, J = 7.4 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.15 (t, J = 7.0 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.78 (s, 1H), 1.75 (s, 2H), 1.33 (s, 6H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.8, 135.4, 131.9, 128.7, 128.4, 122.0, 120.0, 111.3, 111.0, 54.2, 50.9, 39.5, 31.2, 28.9 ppm; ν_{max}(KBr)/cm^{-1} 3698, 2956, 1723, 1629, 1514, 1450, 1222, 1002, 743, 695, 640, 487, HRMS-ESI (m/z): calcd for $C_{23}H_{29}N_2O_1$, $[M+H]^+$: 349.2269, found 349.2274.

5. Reference

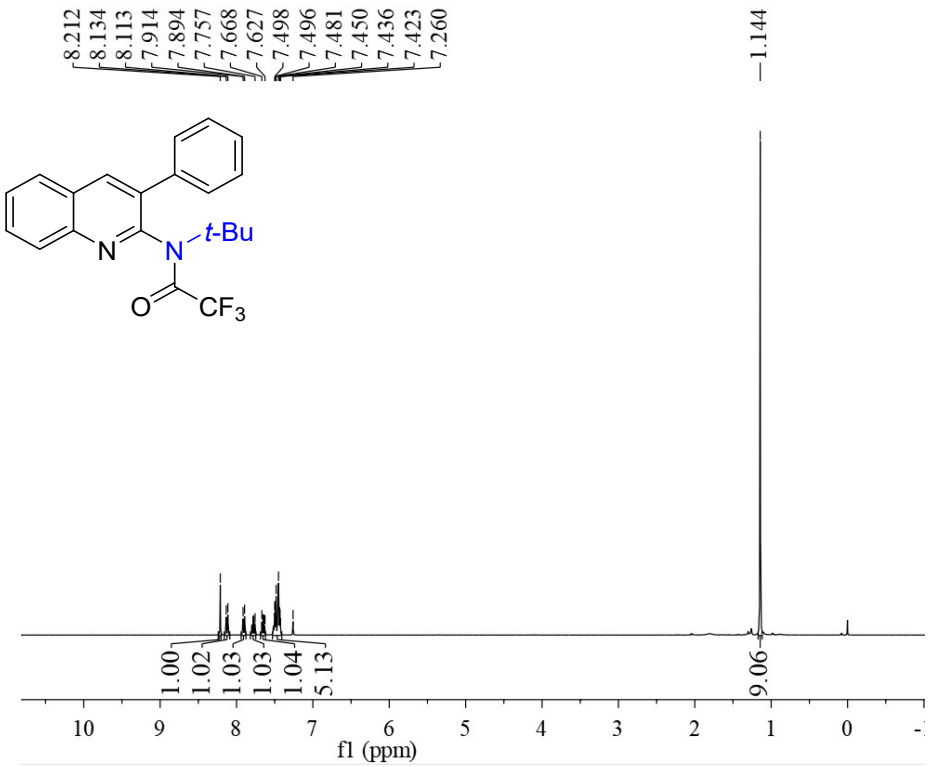
1. X. Li, R. Van Zeeland, R. V. Maligal-Ganesh, Y. Pei, G. Power, L. Stanley and W. Huang, *ACS Catal.*, 2016, **6**, 6324.

2. M. Li, J. Zheng, W. Hu, C. Li, J. Li, S. Fang, H. Jiang and W. Wu, *Org. Lett.*, 2018, **20**, 7245.

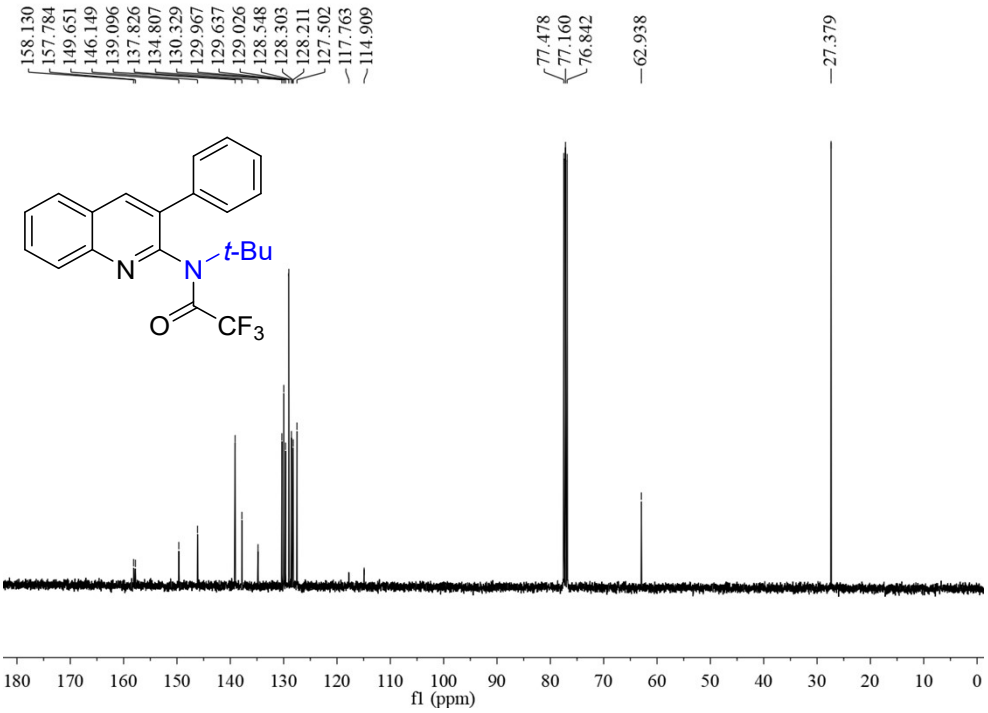
3. Z. Hu, D. Liang, J. Zhao, J. Huang and Q. Zhu, *Chem. Commun.,* 2012*,* **48***,* 7371.

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

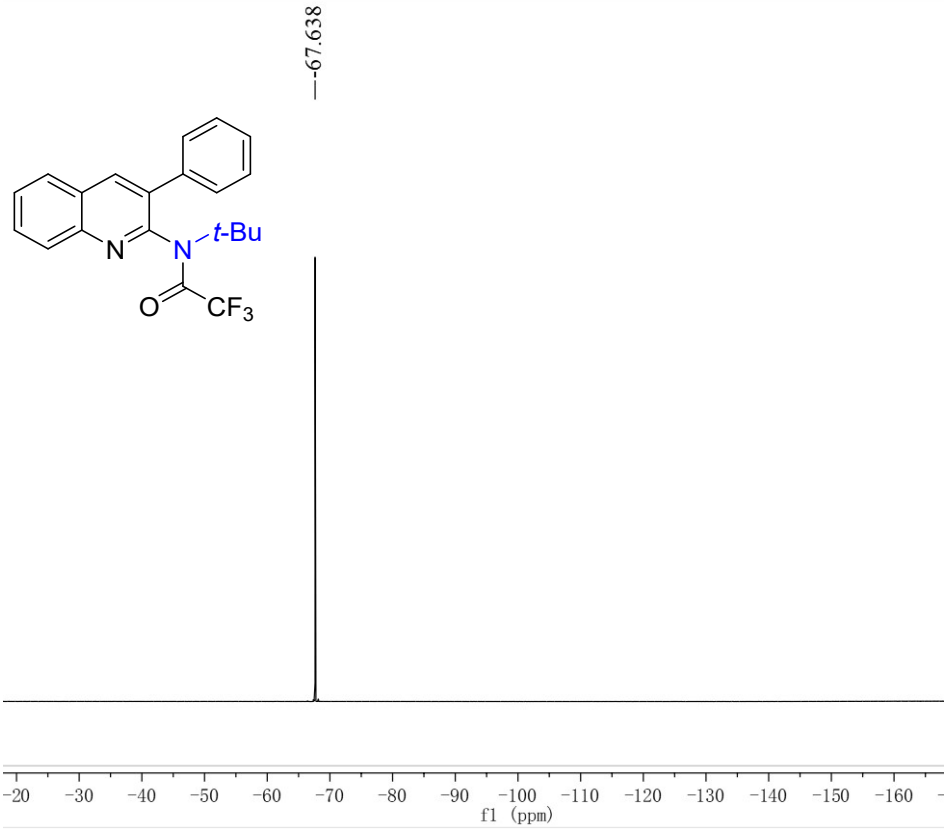
^{1}H NMR of **3a**



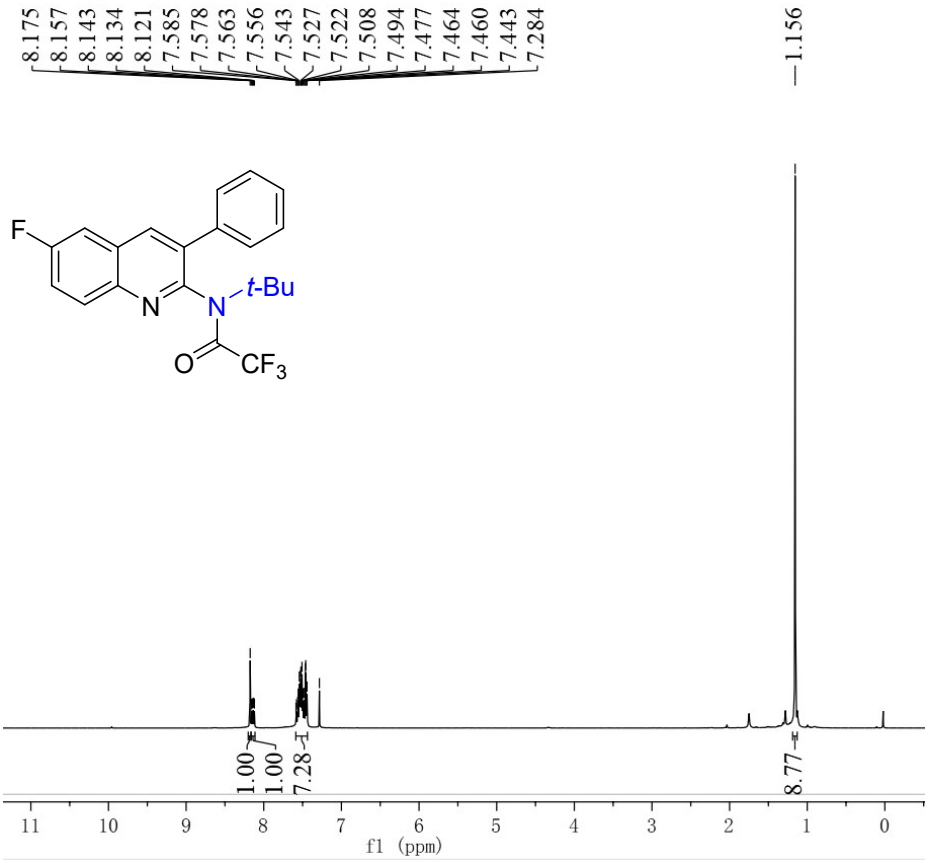
^{13}C NMR of **3a**



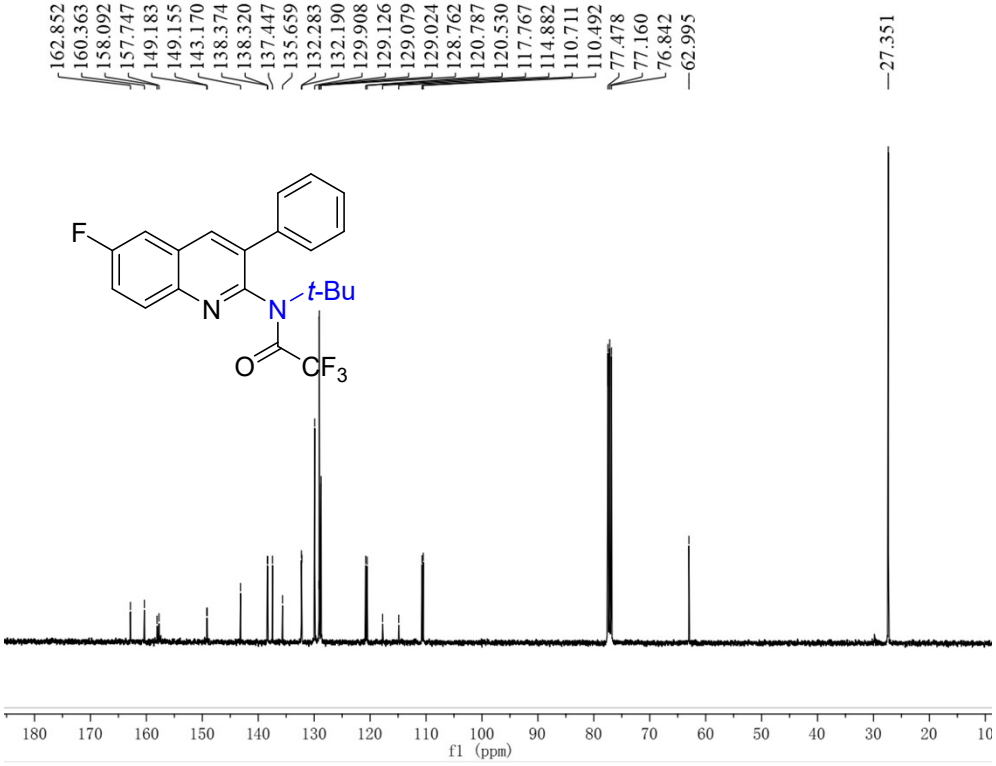
^{19}F NMR of **3a**


-67.638
N
N
t-Bu
O
CF3
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

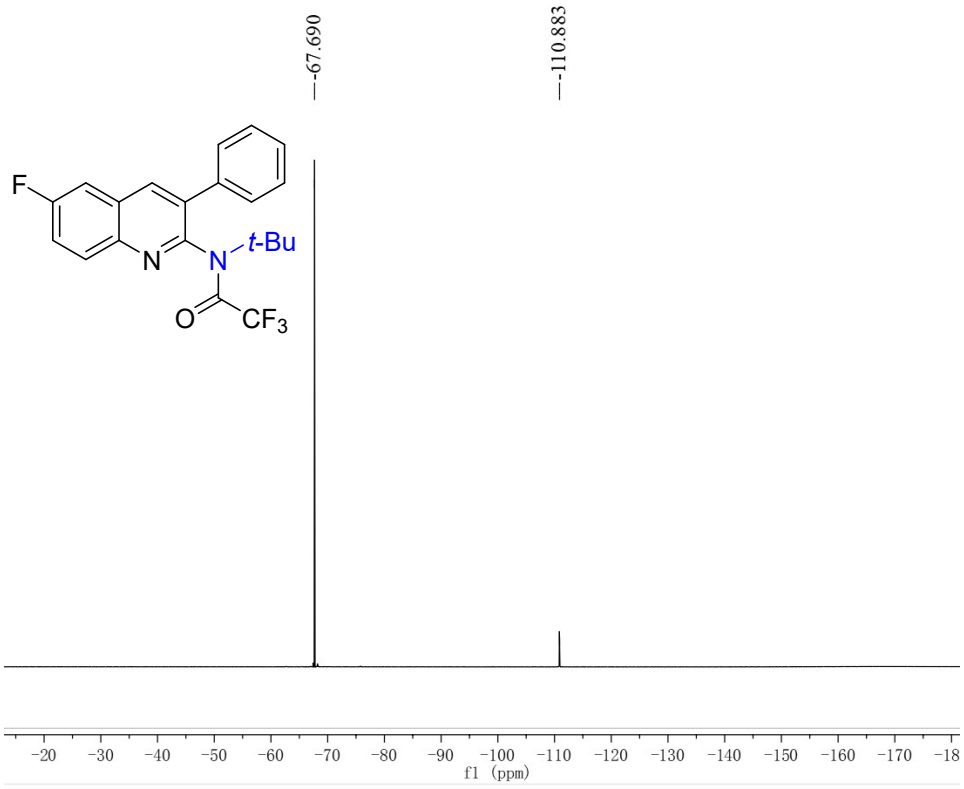
^{1}H NMR of **3b**



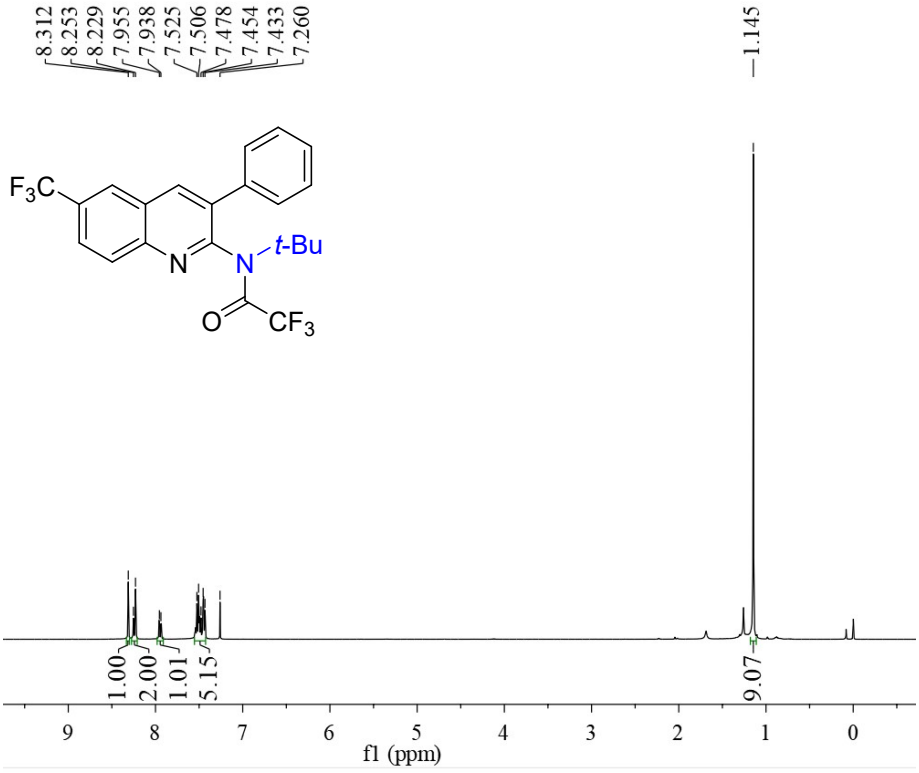
^{13}C NMR of **3b**



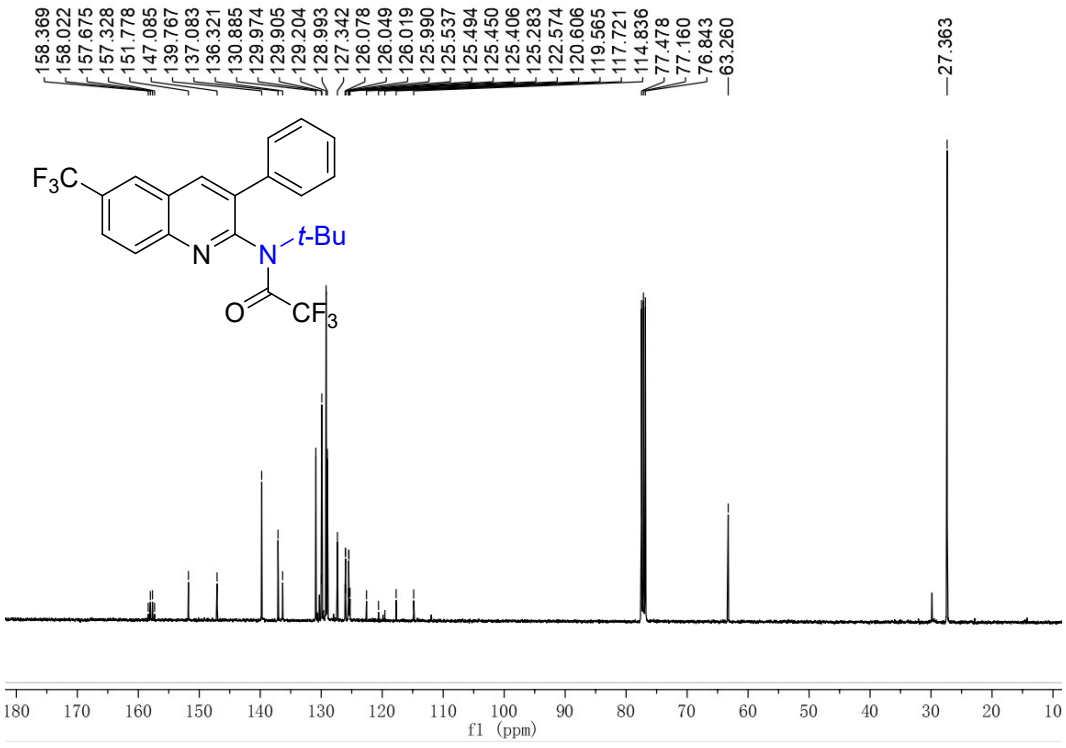
^{19}F NMR of **3b**


-67.690
-110.883
F
N
N
t-Bu
O
CF3
−20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −18
f1 (ppm)

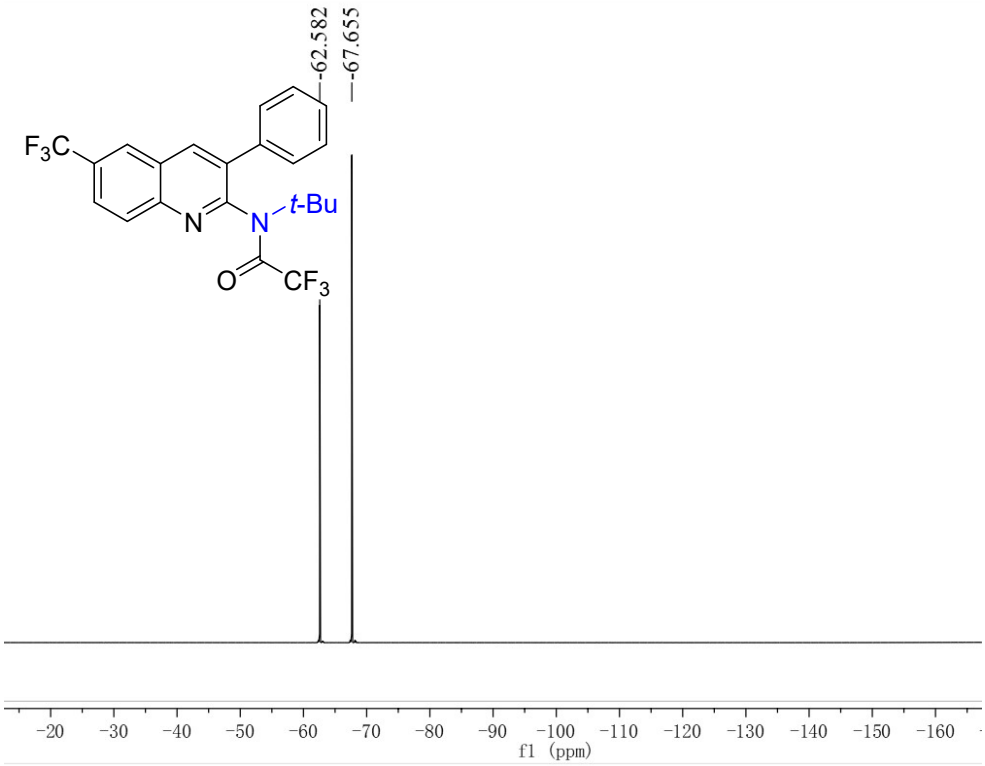
^{1}H NMR of **3c**



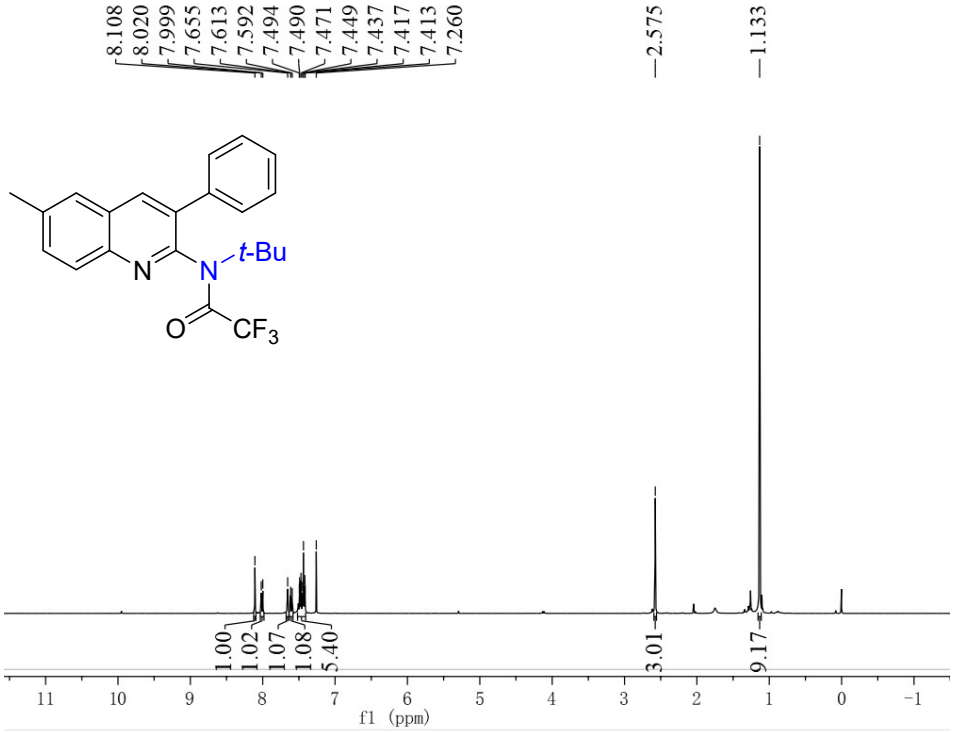
^{13}C NMR of **3c**



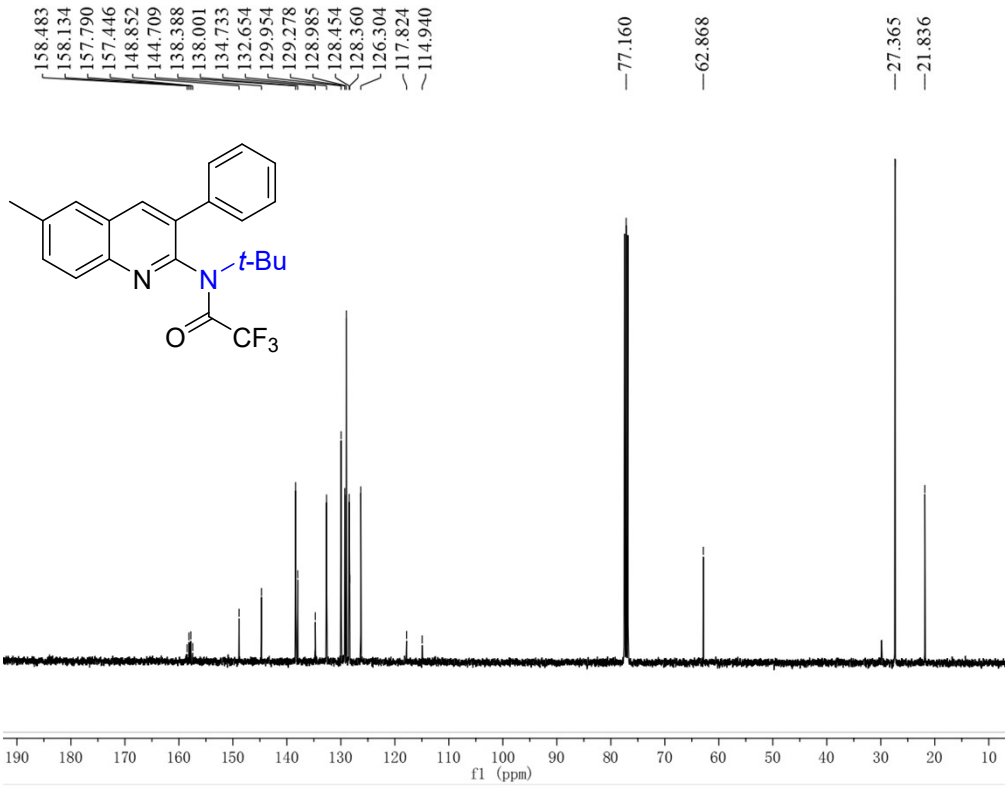
^{19}F NMR of **3c**


-62.582
-67.655
F3C
N
N
t-Bu
O
CF3
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

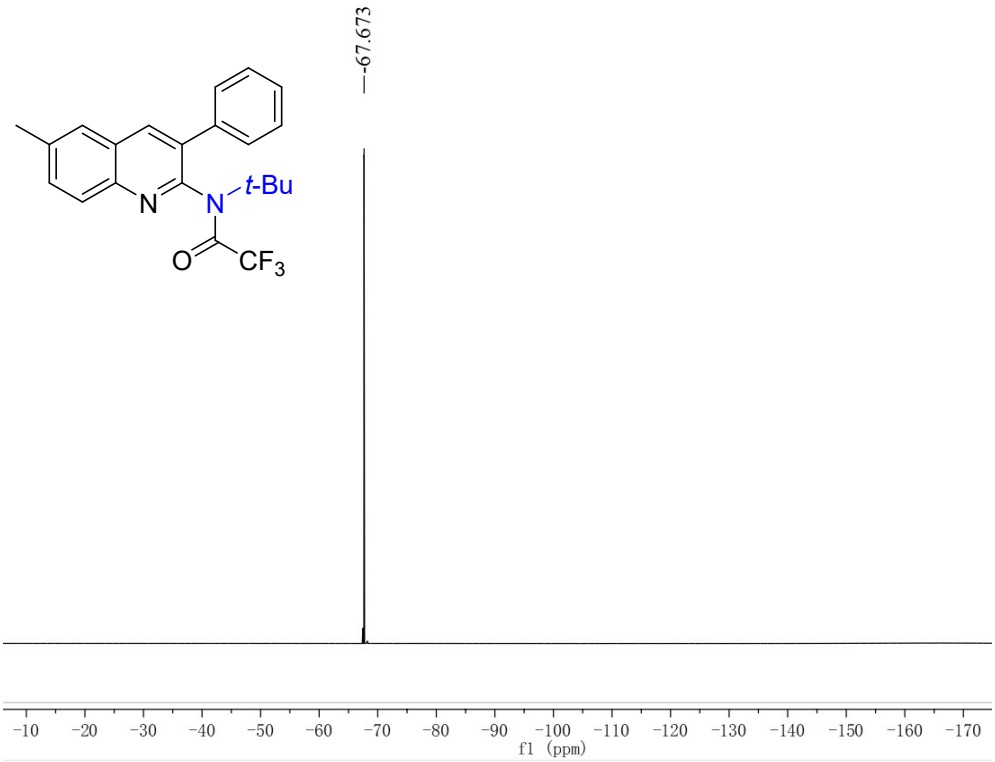
^{1}H NMR of **3d**



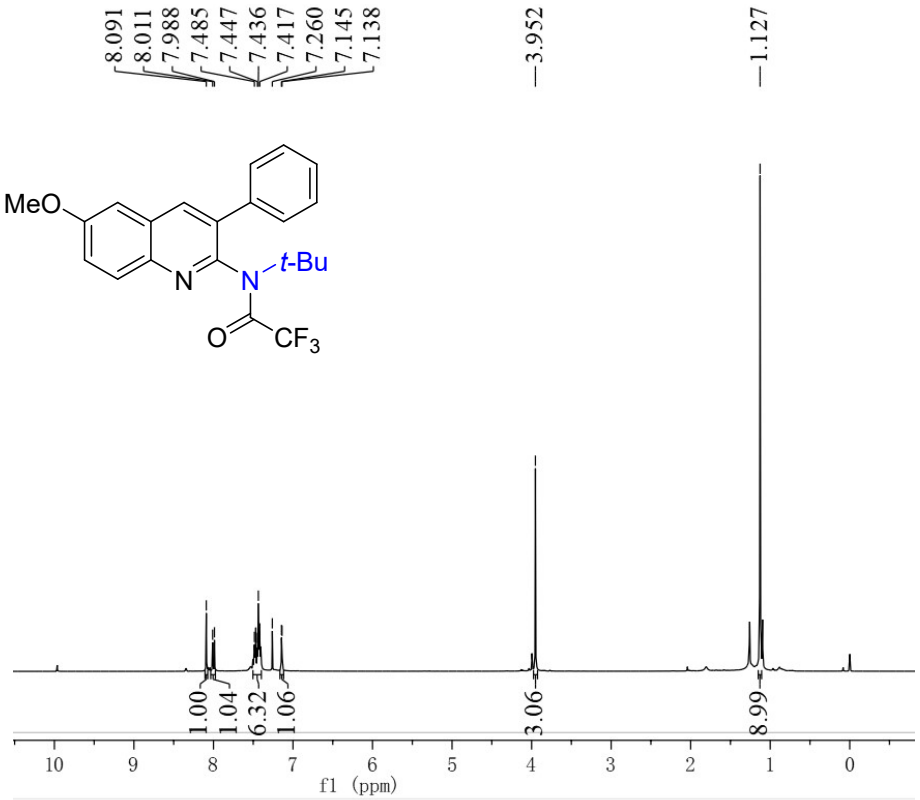
^{13}C NMR of **3d**



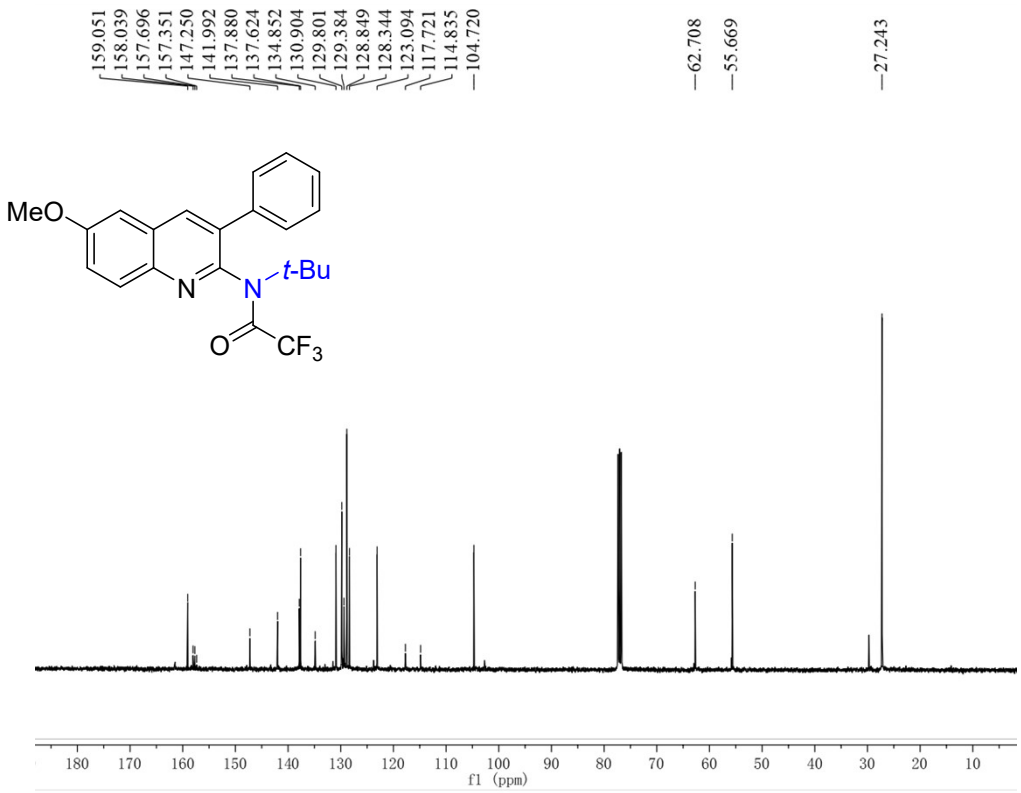
^{19}F NMR of **3d**


-67.673
N
N
t-Bu
O
CF3
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

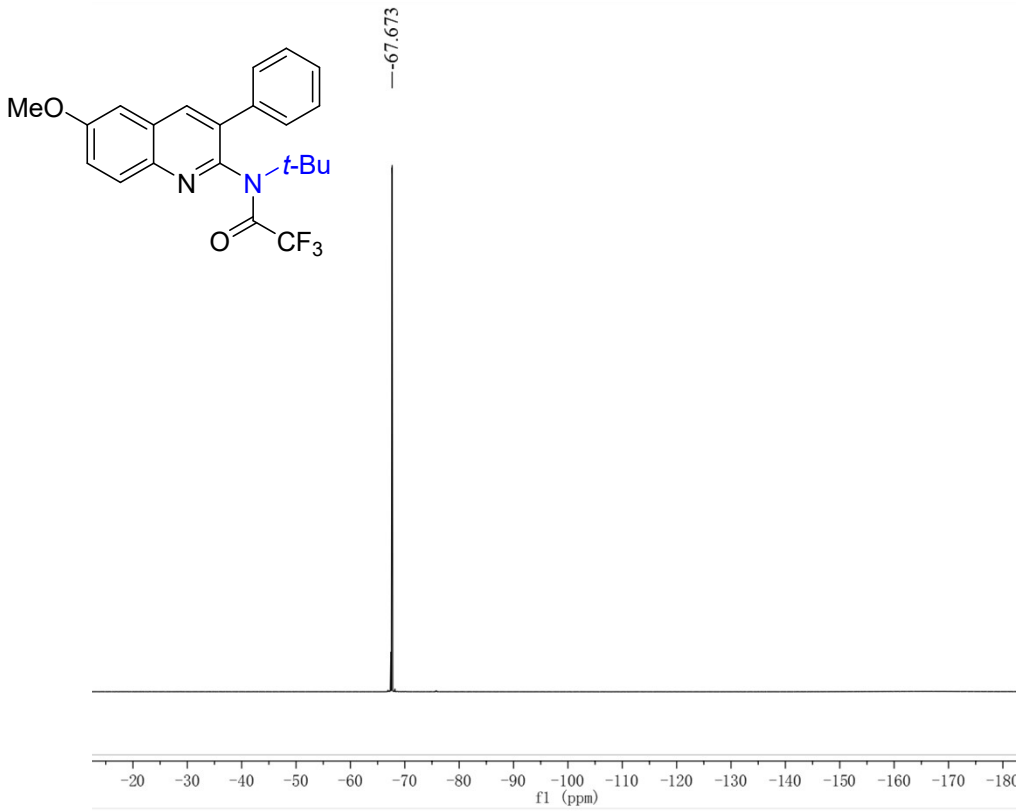
^{1}H NMR of **3e**



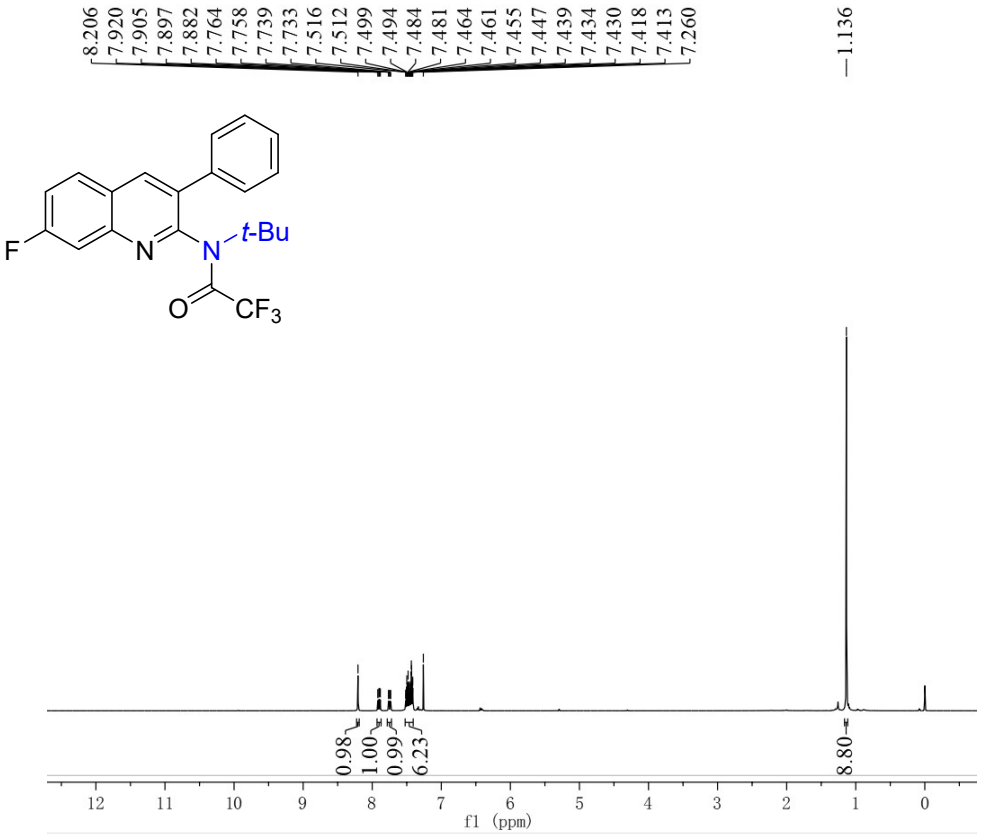
^{13}C NMR of **3e**



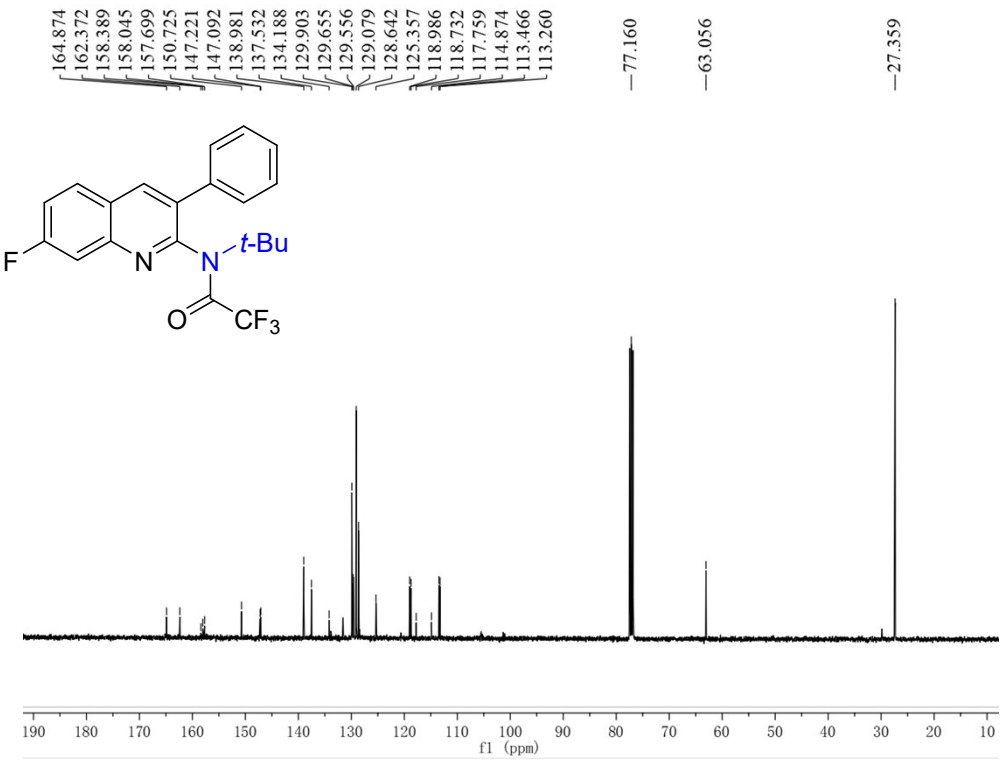
^{19}F NMR of **3e**


MeO
N
N
t-Bu
O
CF3
-67.673
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

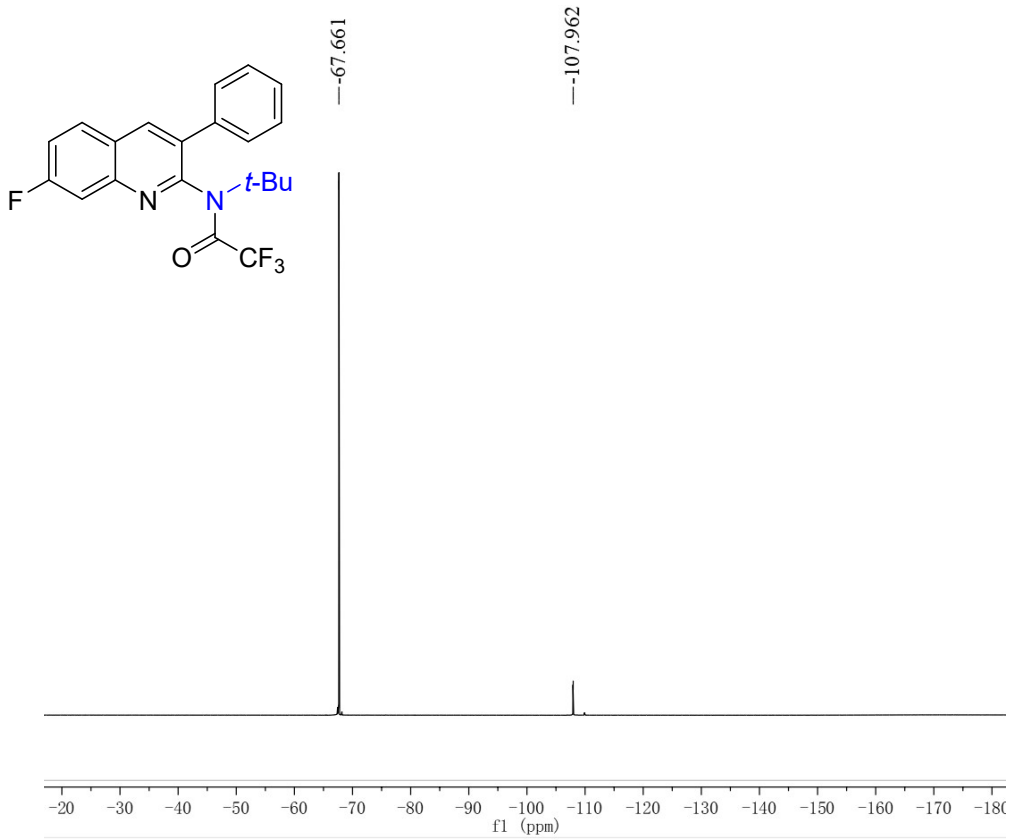
^{1}H NMR of **3f**



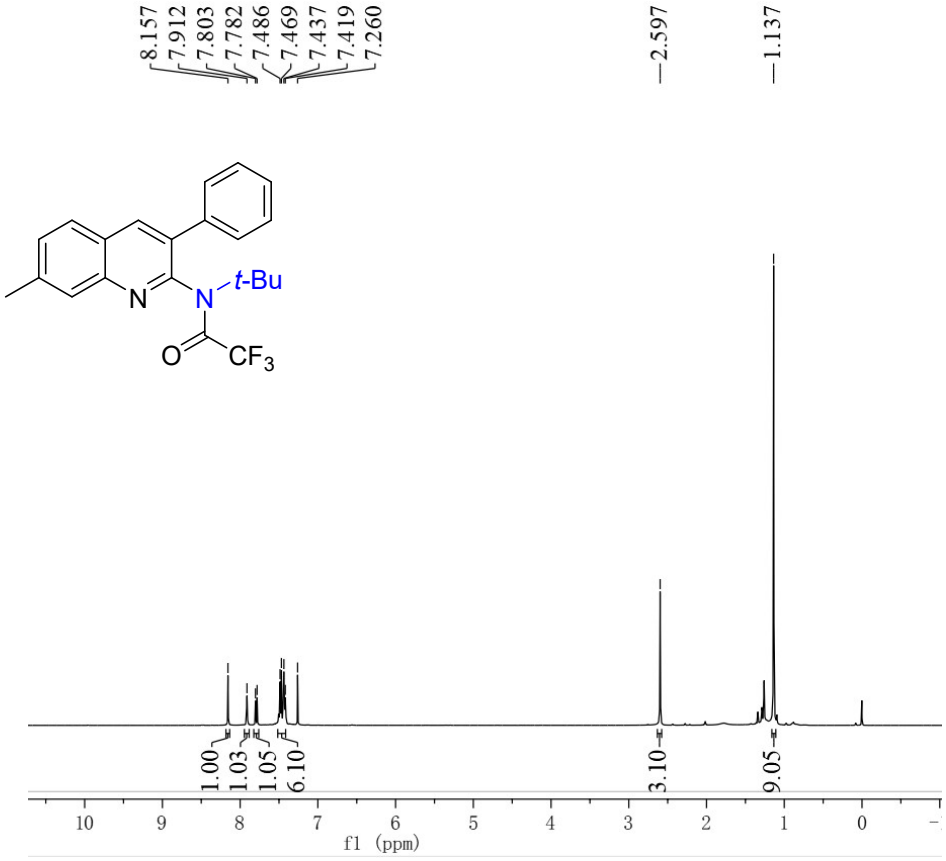
^{13}C NMR of **3f**



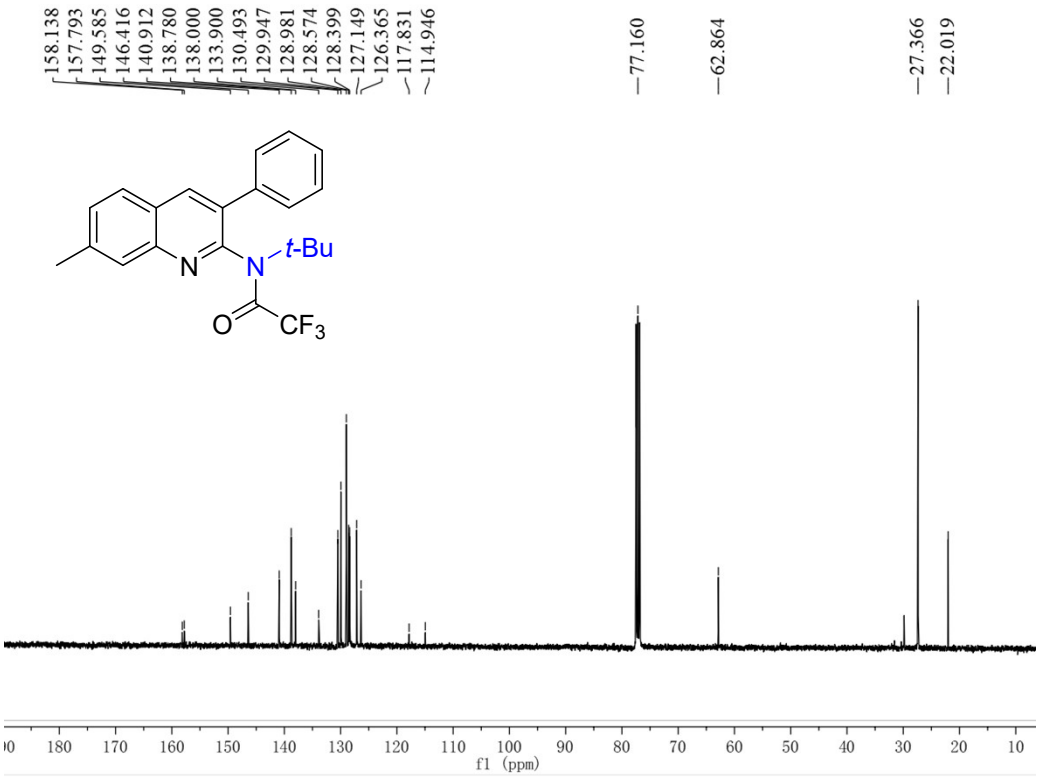
^{19}F NMR of **3f**


-67.661
-107.962
F
N
N
t-Bu
O
CF3
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

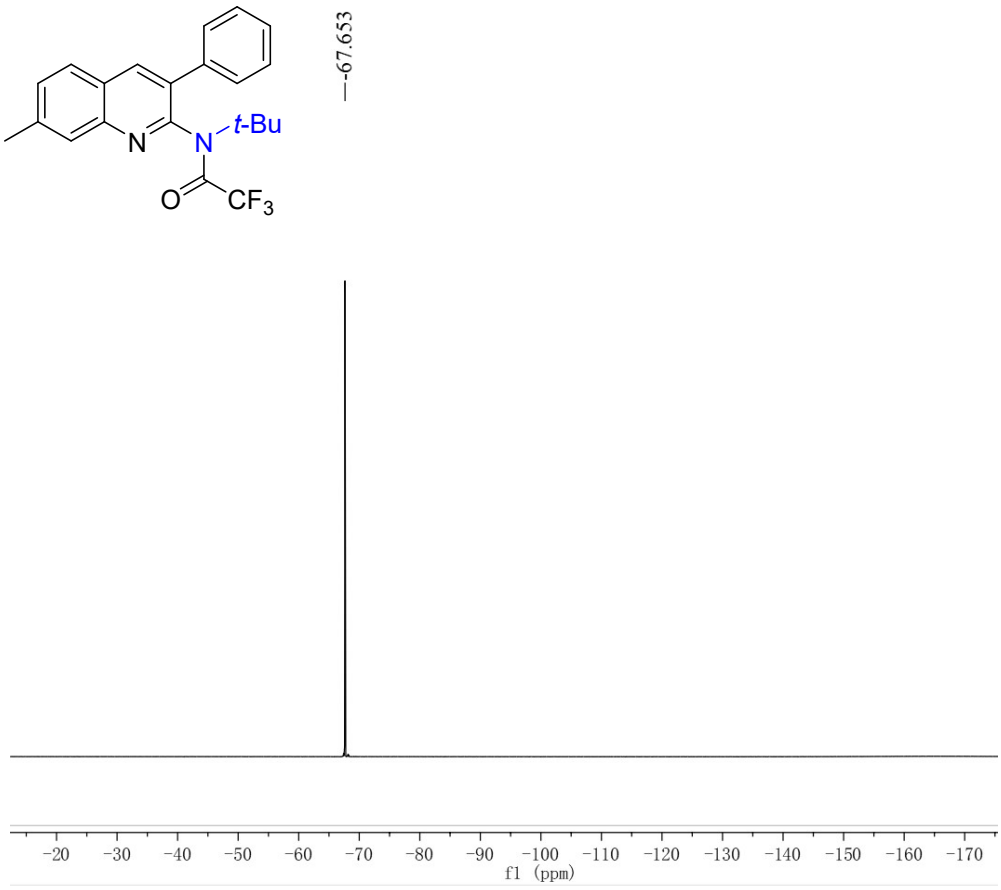
^{1}H NMR of **3g**



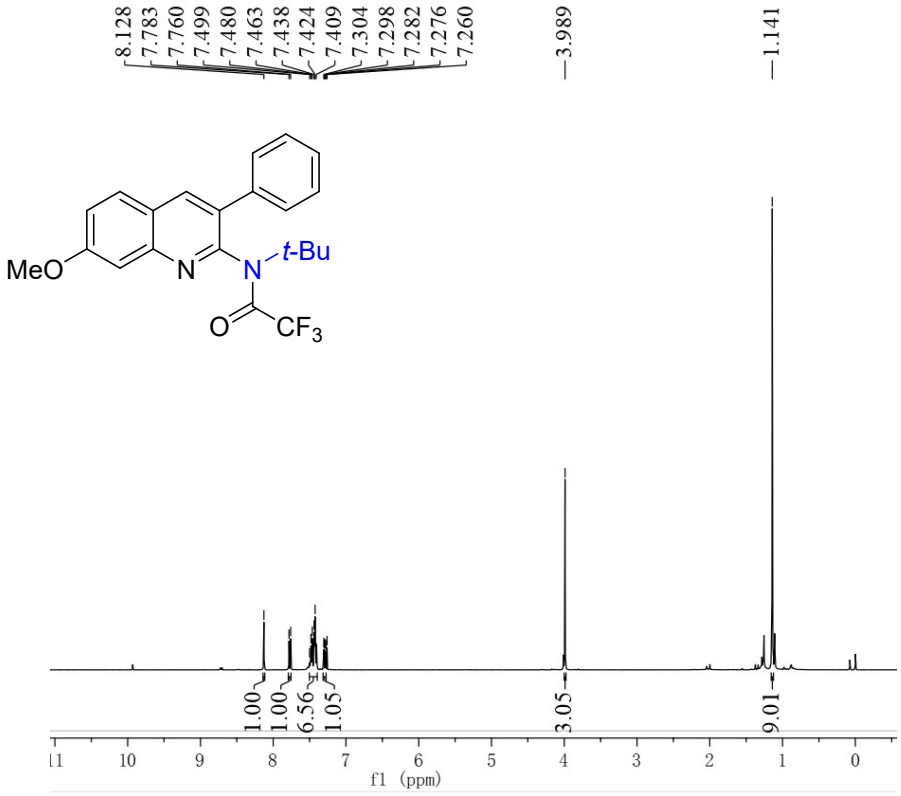
^{13}C NMR of **3g**



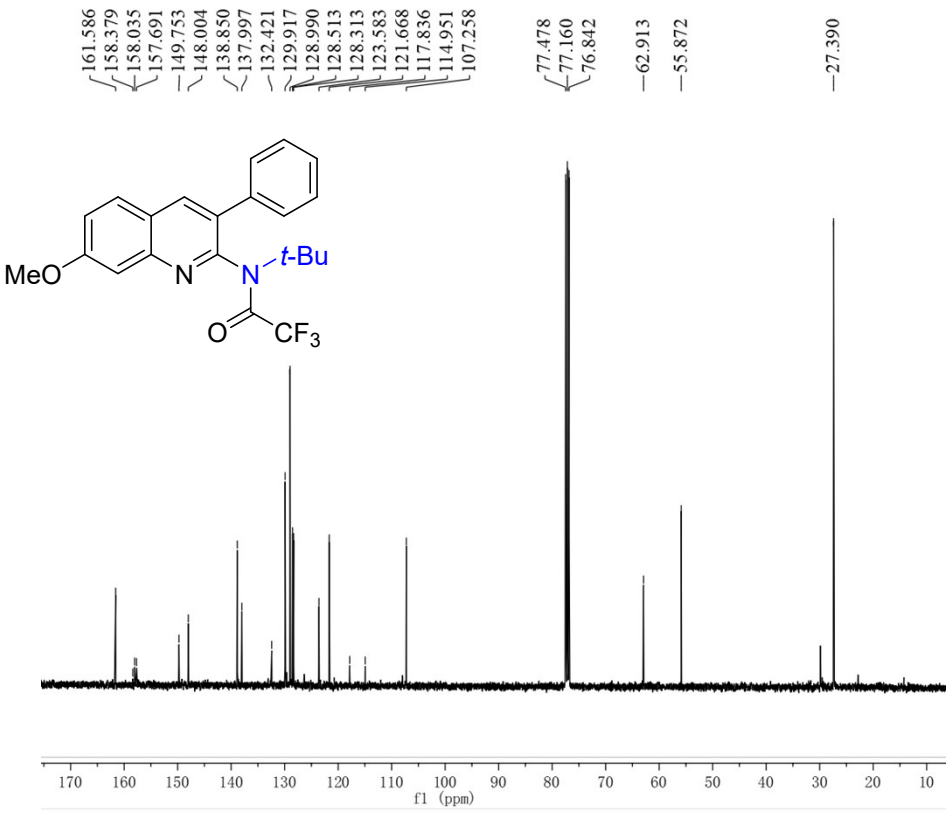
^{19}F NMR of **3g**


-67.653
N
N
t-Bu
O
CF3
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

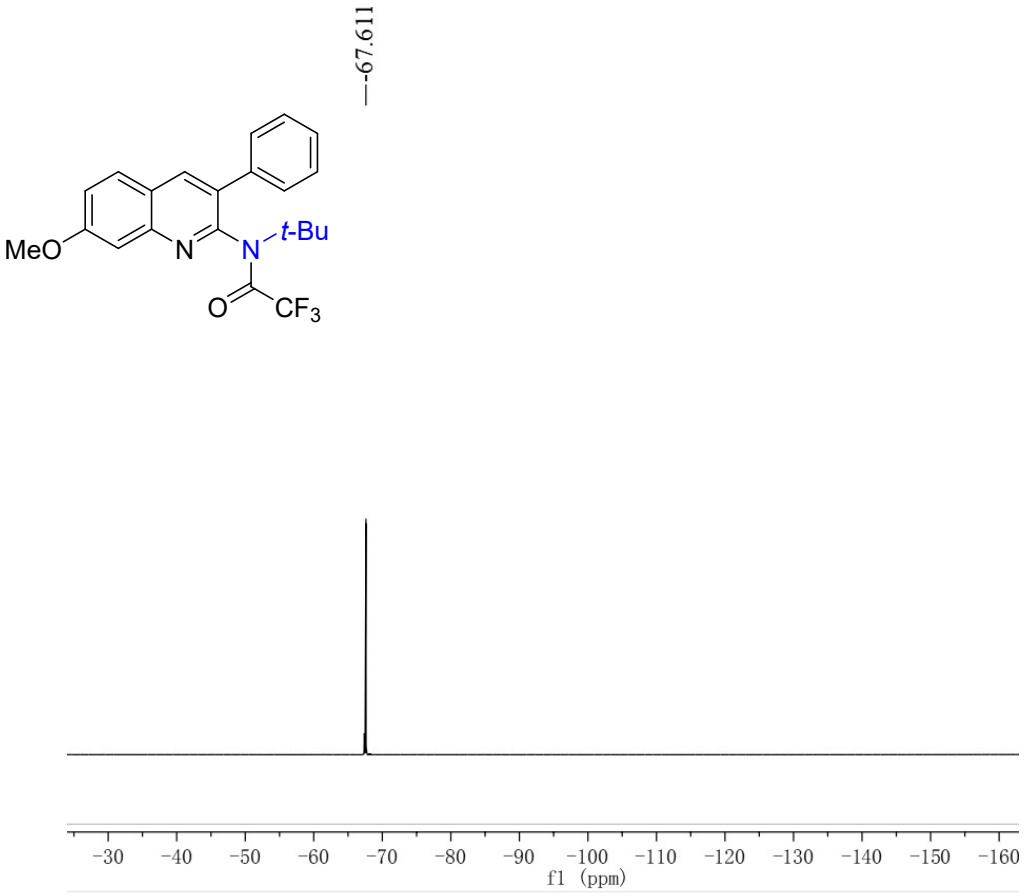
^{1}H NMR of **3h**



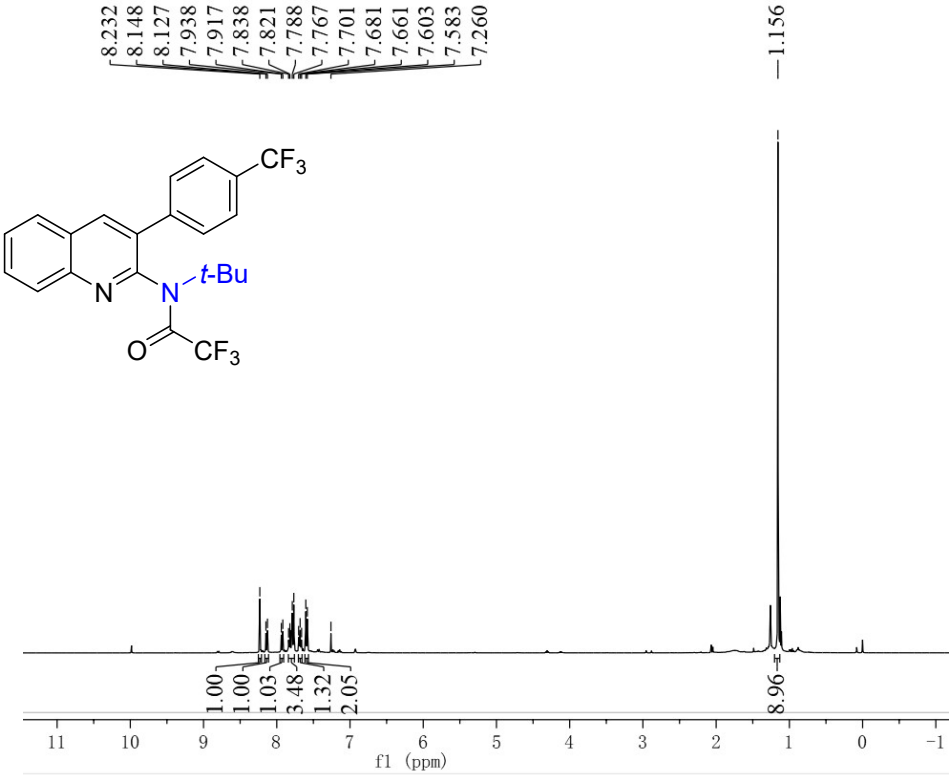
^{13}C NMR of **3h**



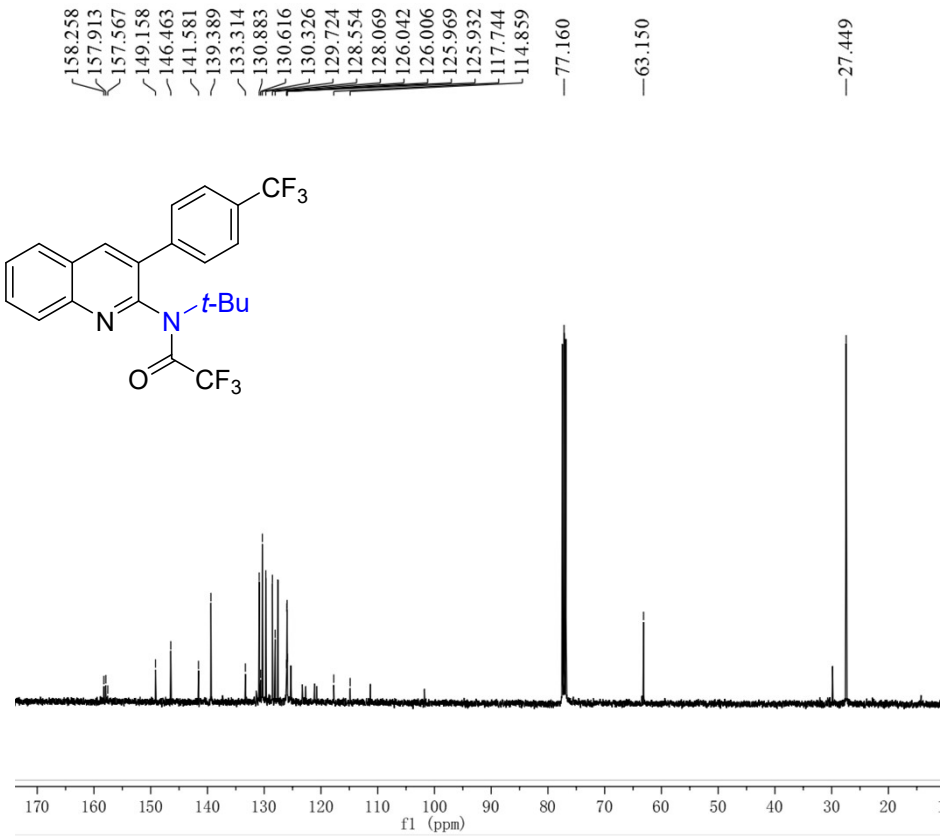
^{19}F NMR of **3h**


-67.611
MeO
N
N
t-Bu
O
CF3
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)

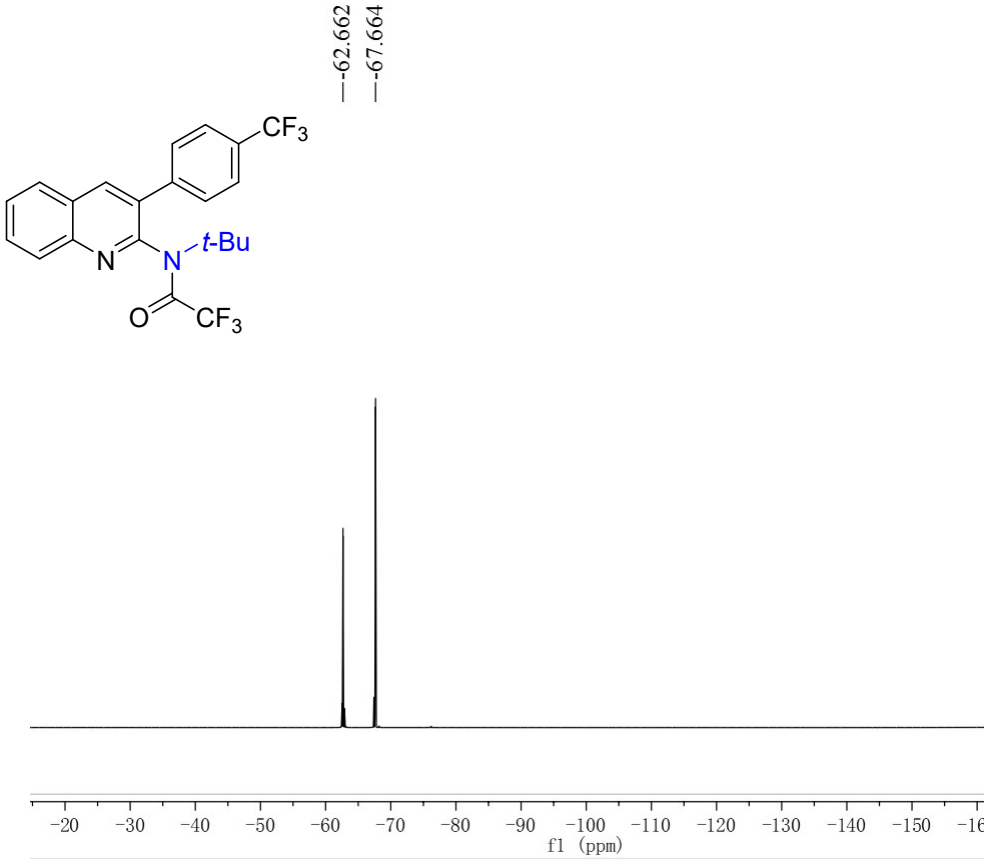
^{1}H NMR of **3i**



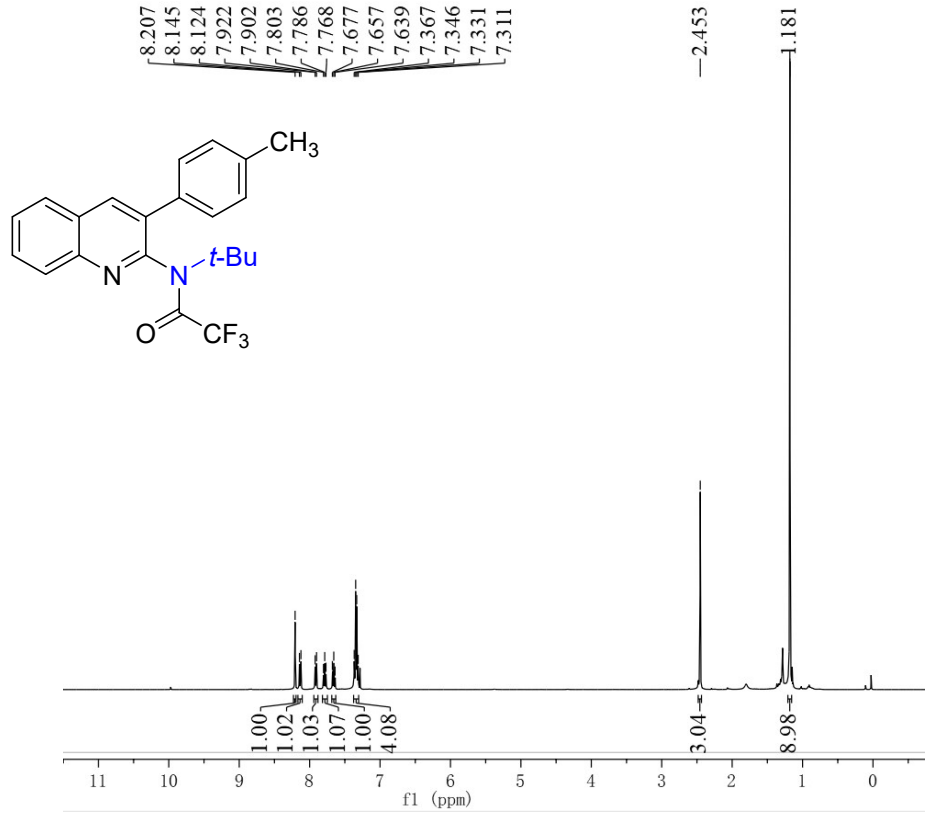
^{13}C NMR of **3i**



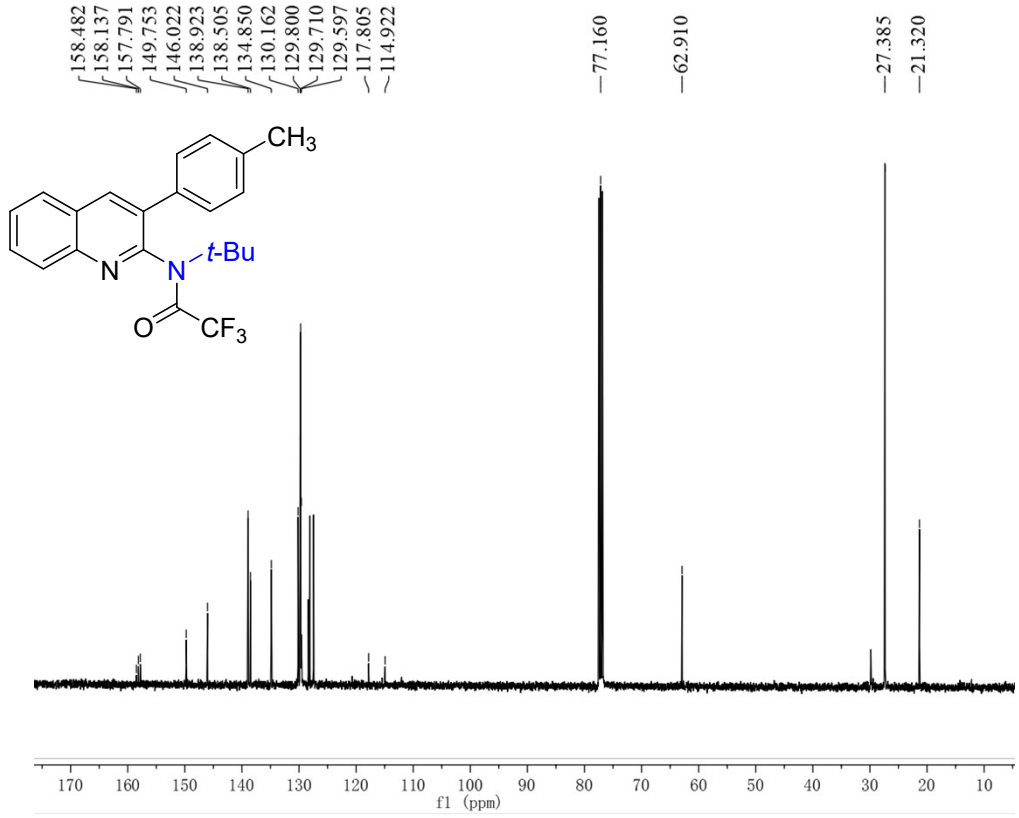
^{19}F NMR of **3i**


−62.662
−67.664
CF3
t-Bu
N
N
O
CF3
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)

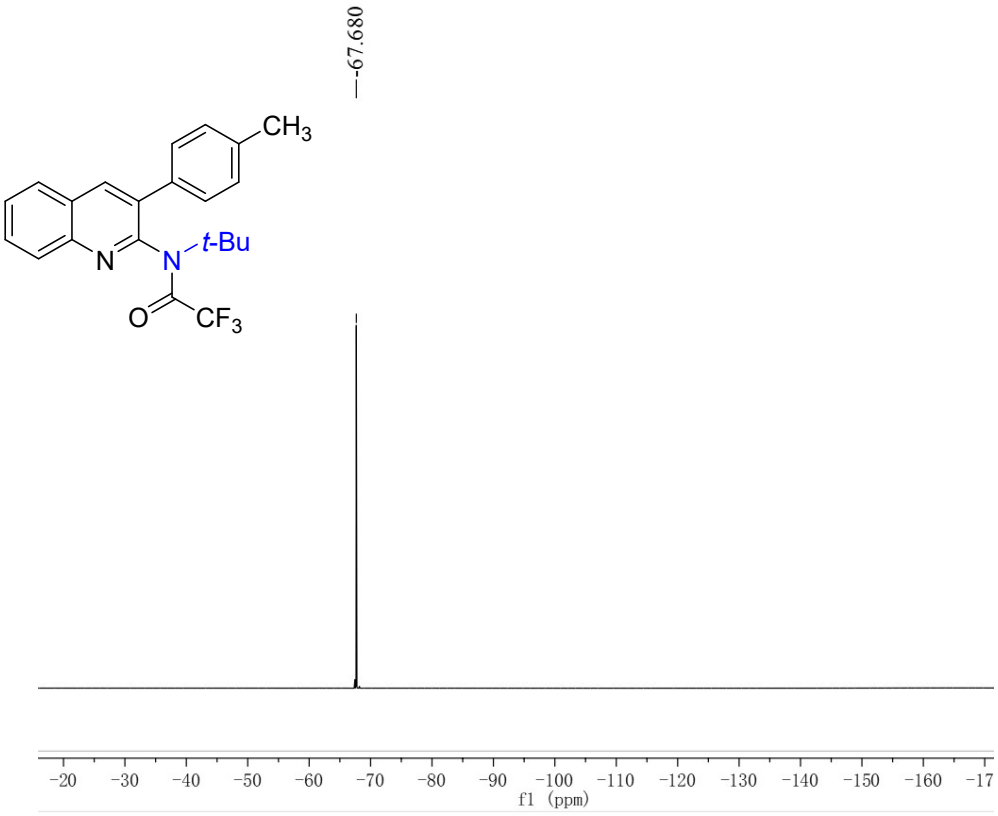
^{1}H NMR of **3j**



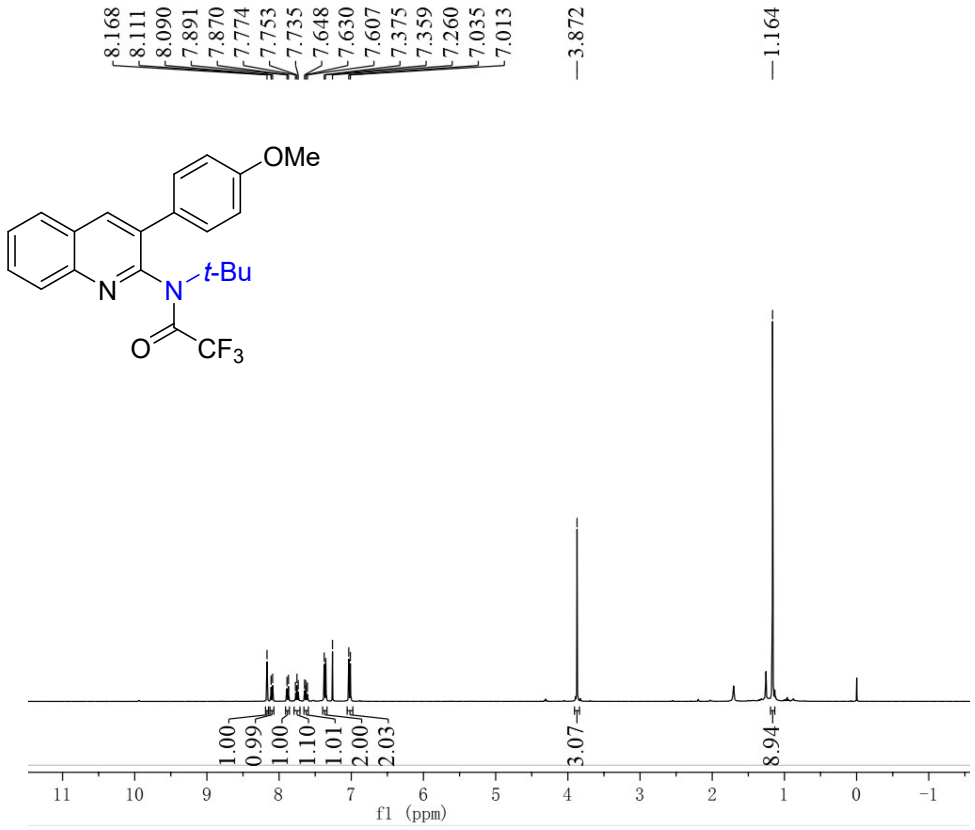
^{13}C NMR of **3j**



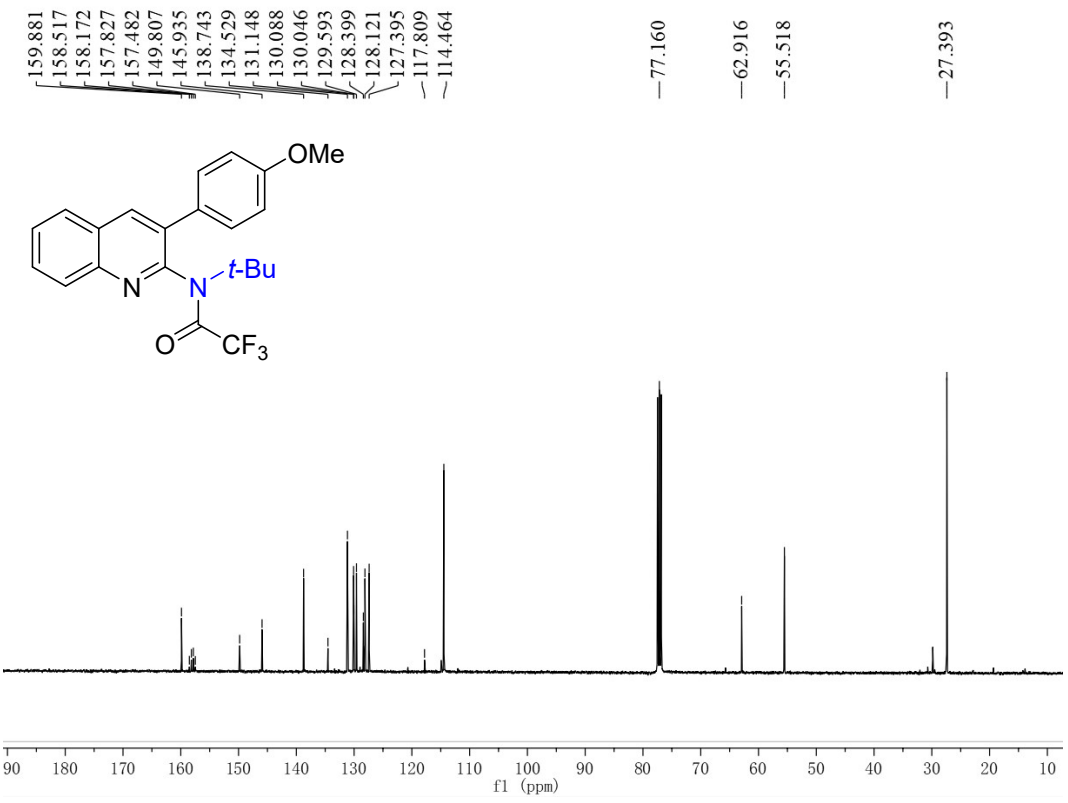
^{19}F NMR of **3j**


-67.680
CH3
N
N
t-Bu
O
CF3
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-17
f1 (ppm)

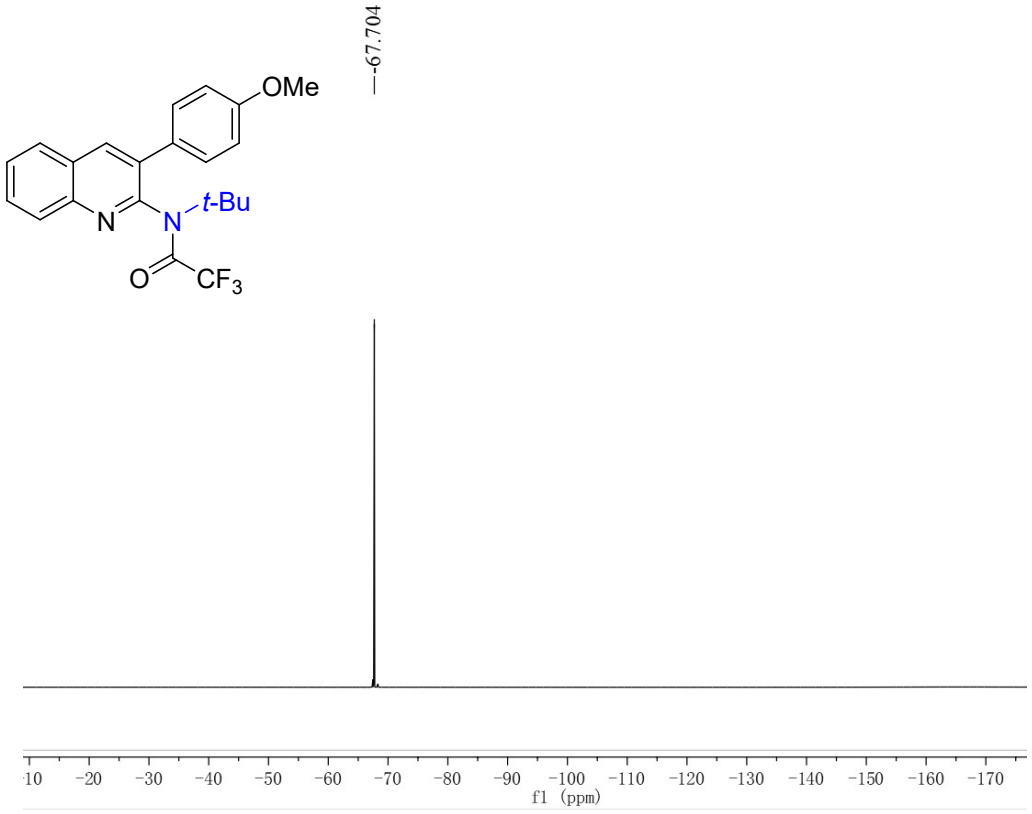
^{1}H NMR of **3k**



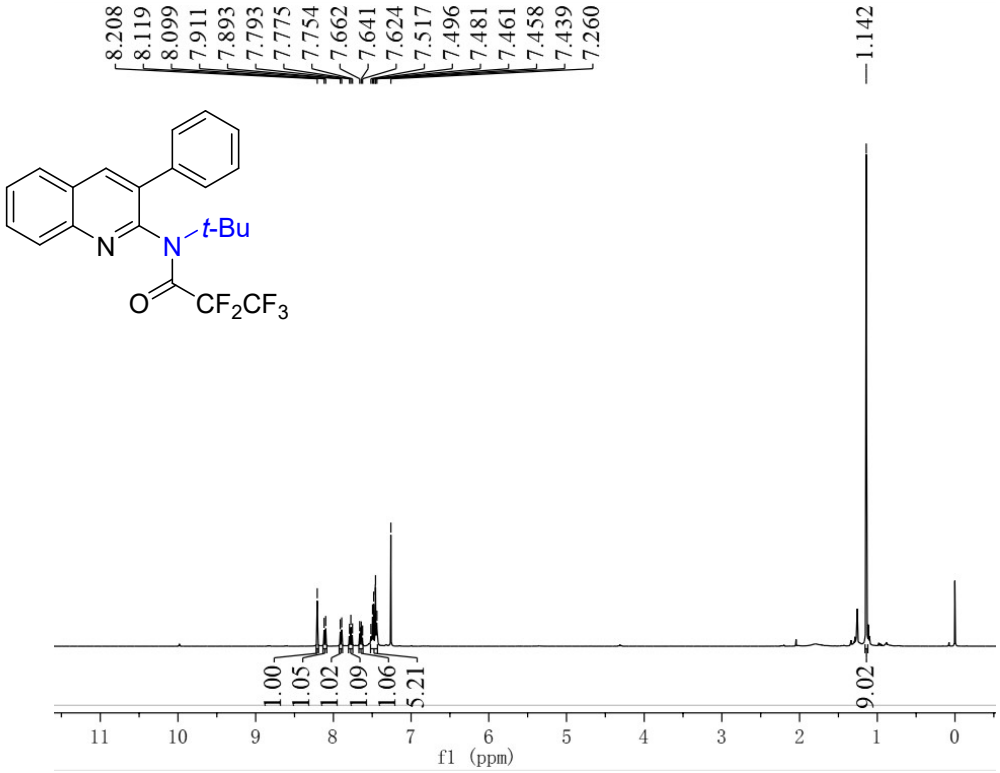
^{13}C NMR of **3k**



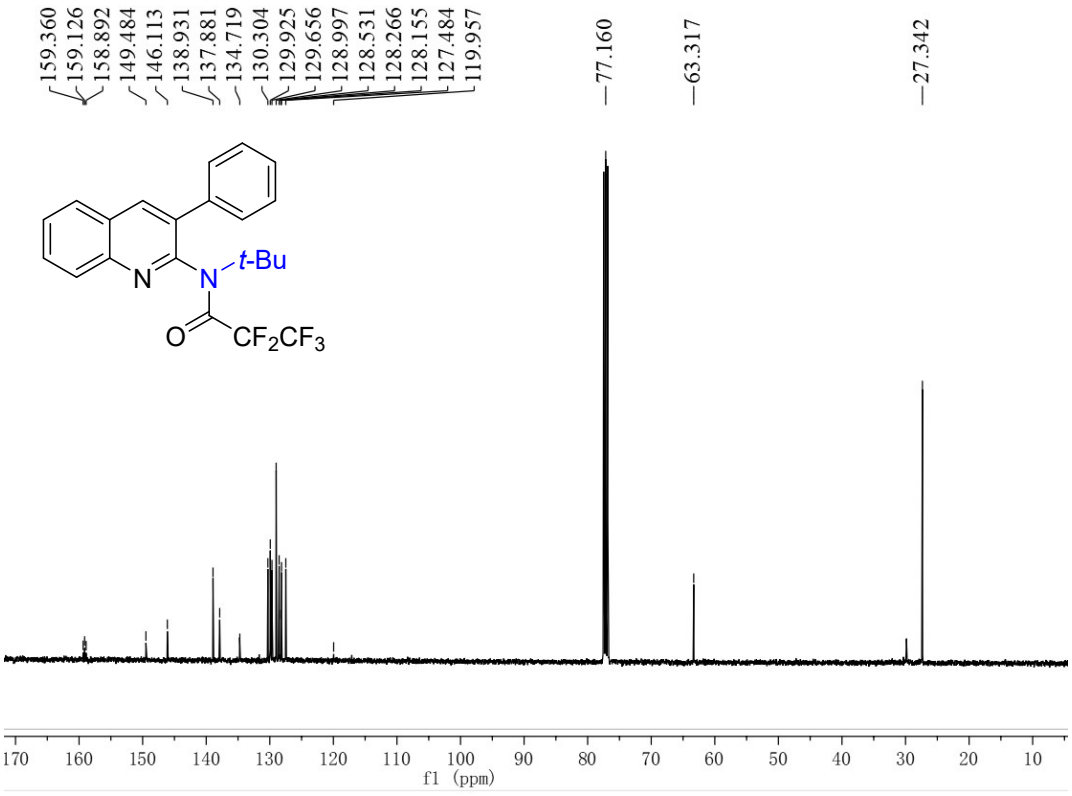
^{19}F NMR of **3k**


-67.704
OMe
N
t-Bu
O
CF3
10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

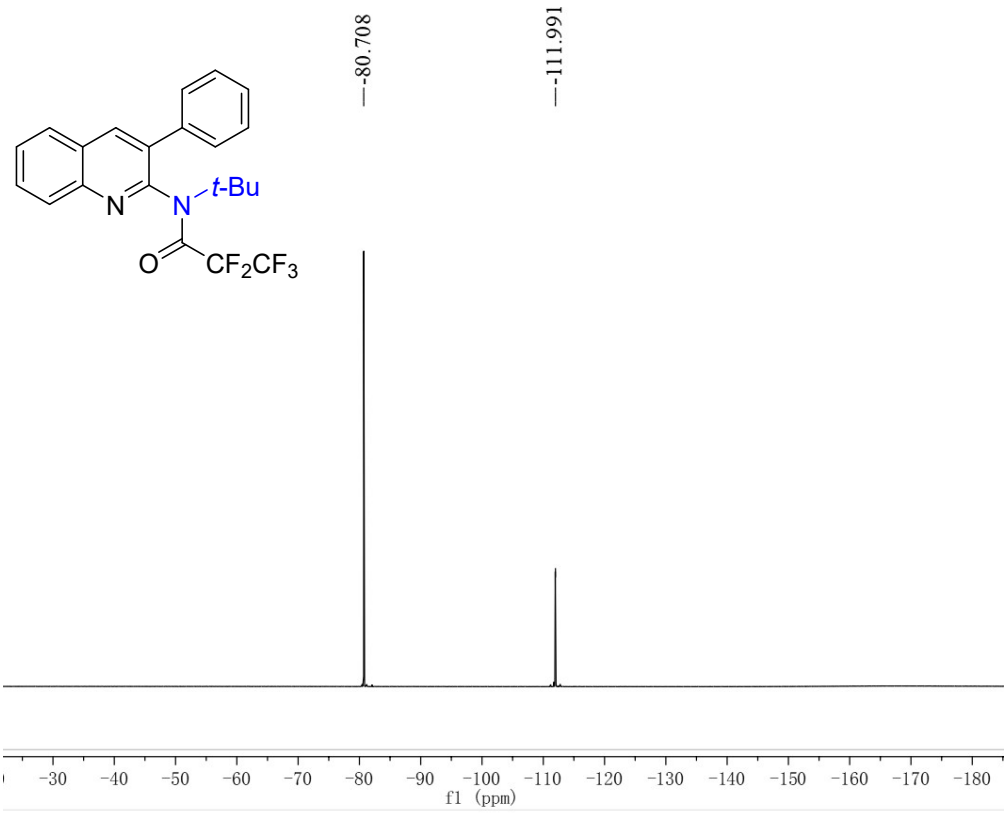
^{1}H NMR of **3l**



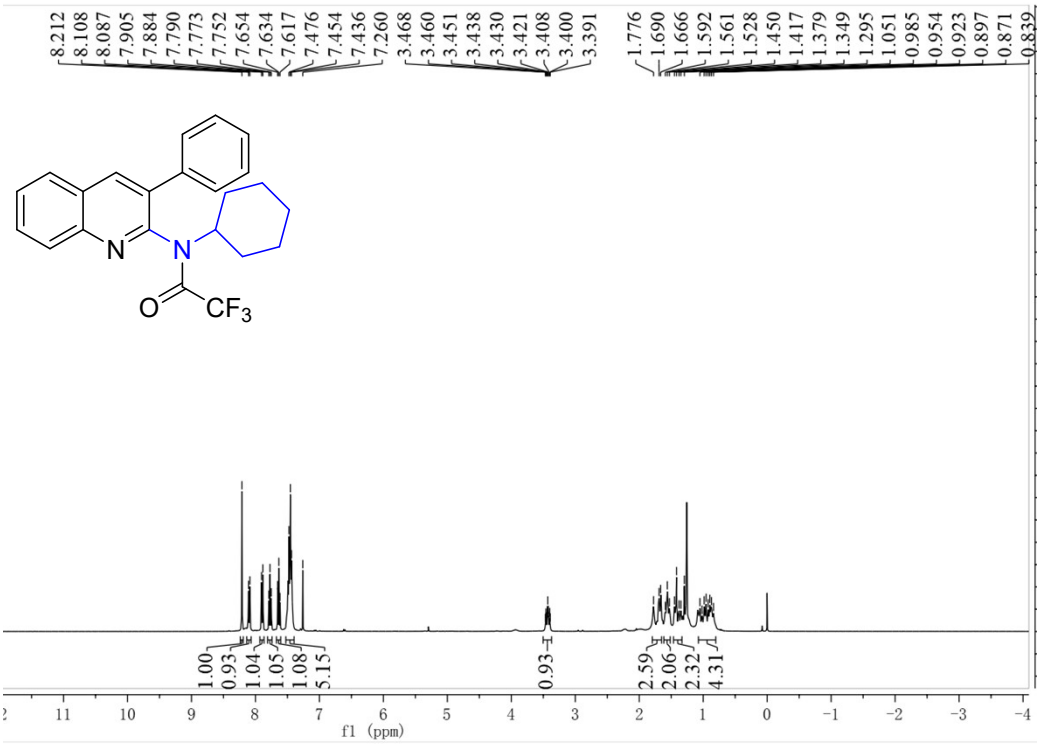
^{13}C NMR of **3l**



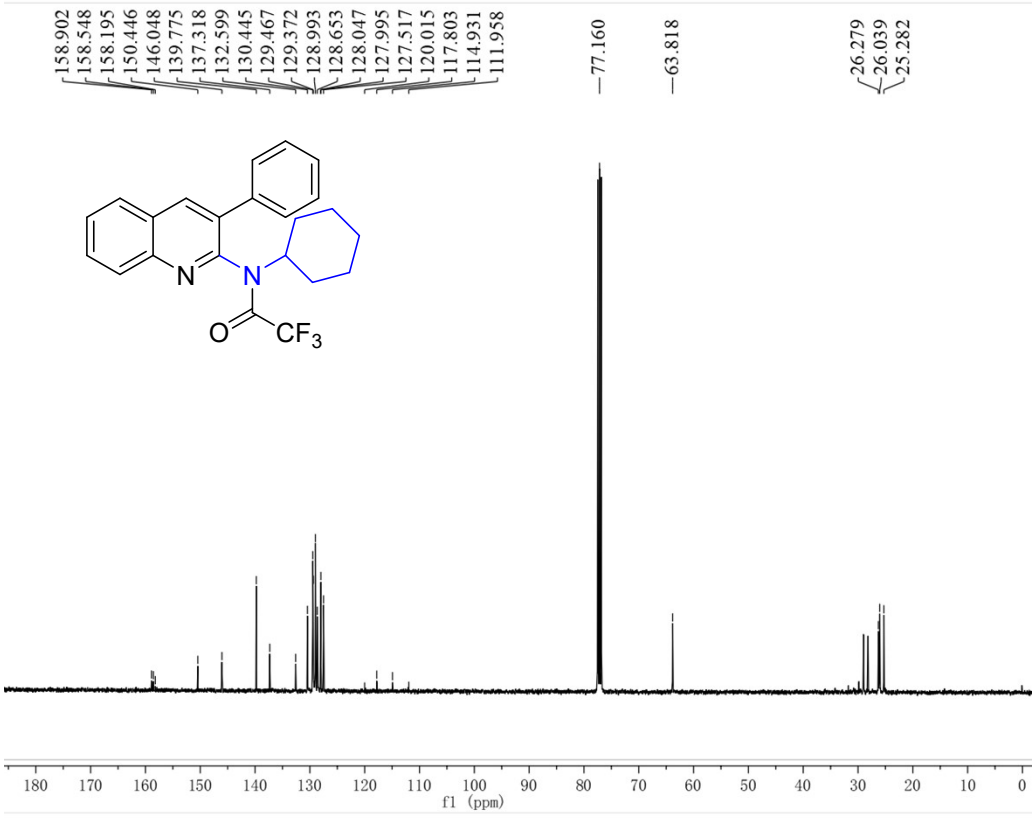
^{19}F NMR of **3l**


-80.708
-111.991
t-Bu
N
N
O
CF2CF3
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

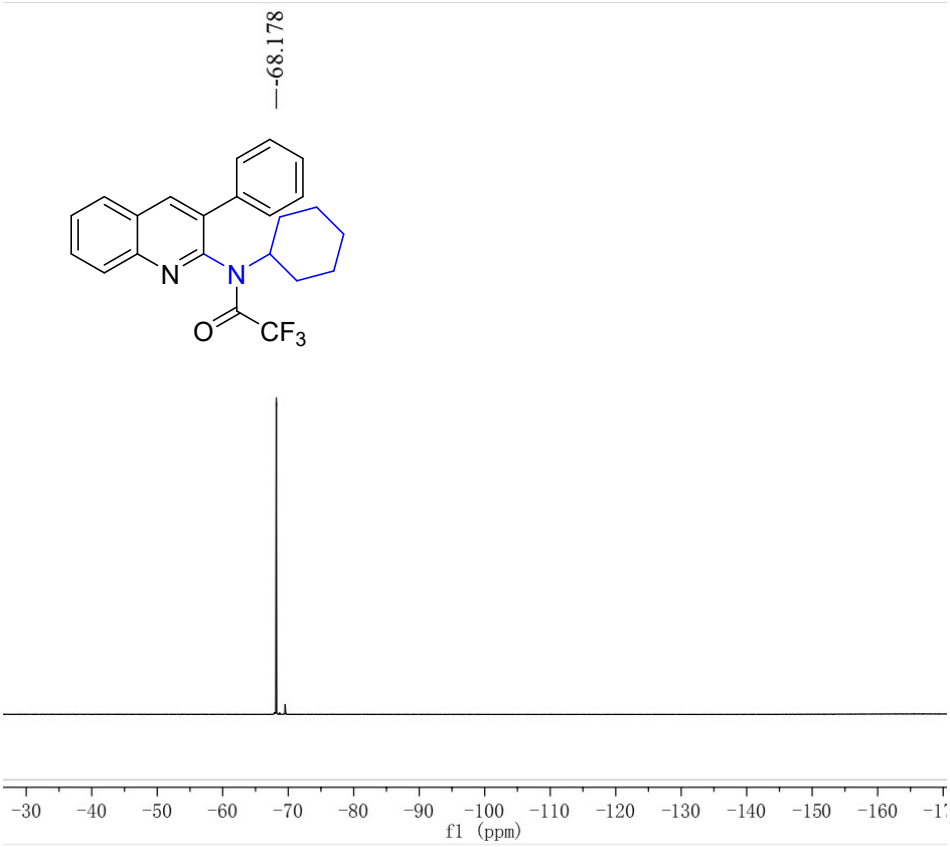
^{1}H NMR of **3m**



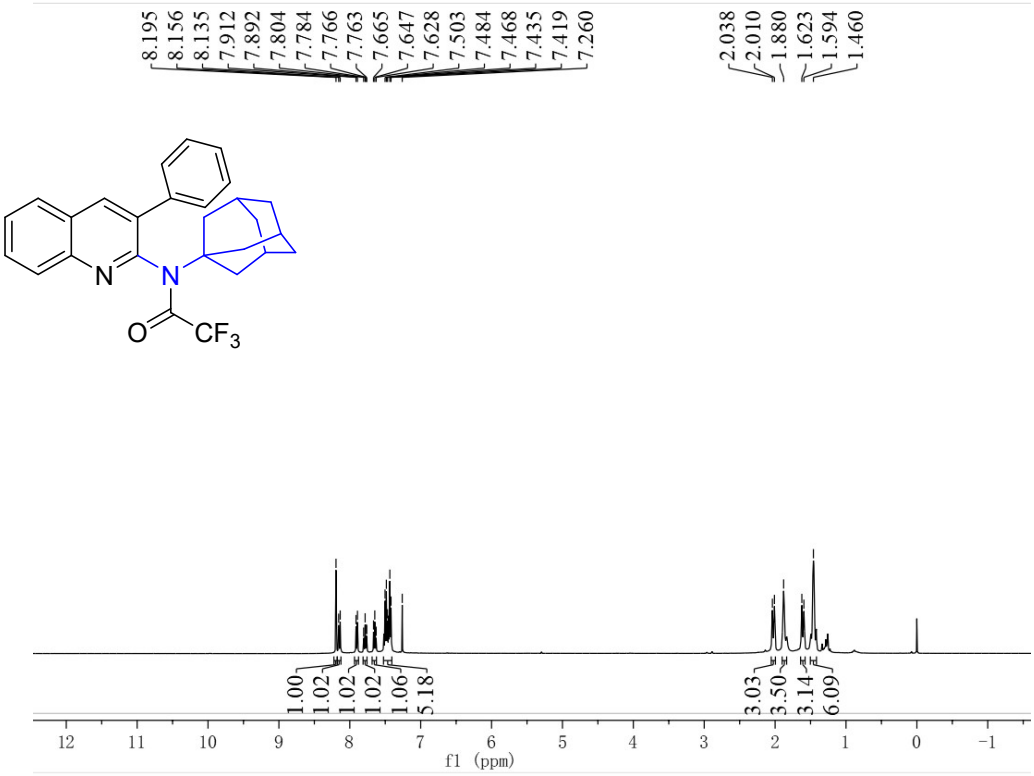
^{13}C NMR of **3m**



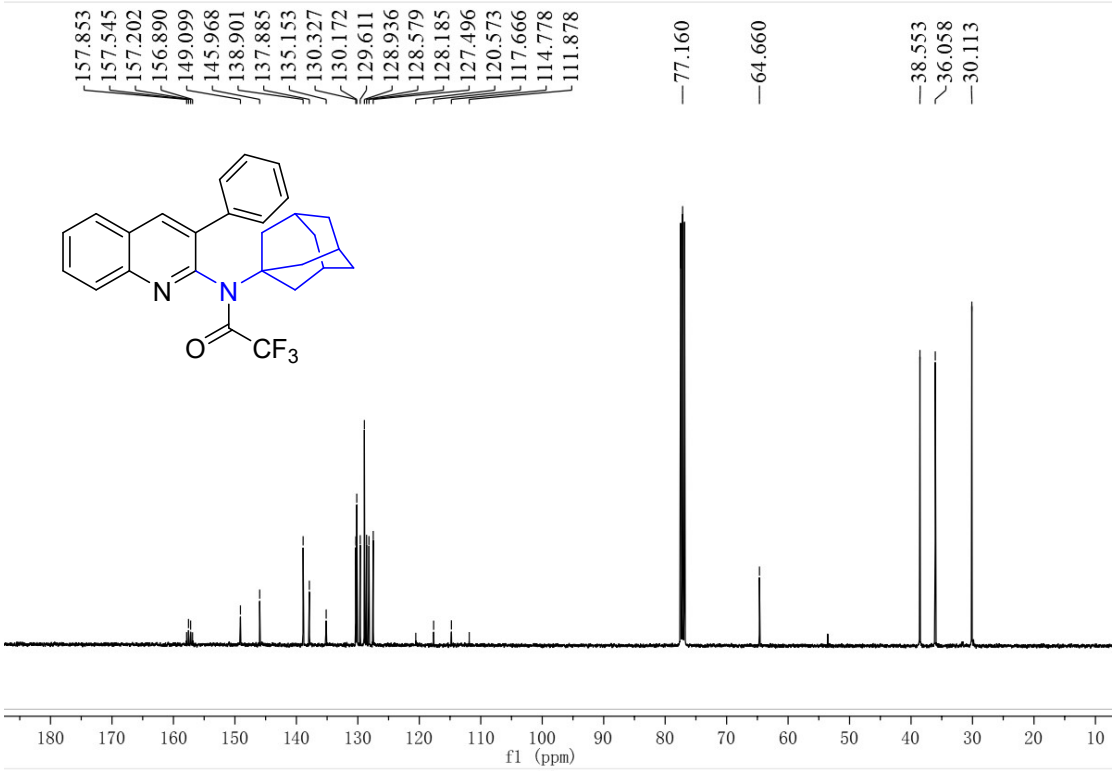
^{19}F NMR of **3m**


-68.178
N
N
O
CF3
−30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160
f1 (ppm)

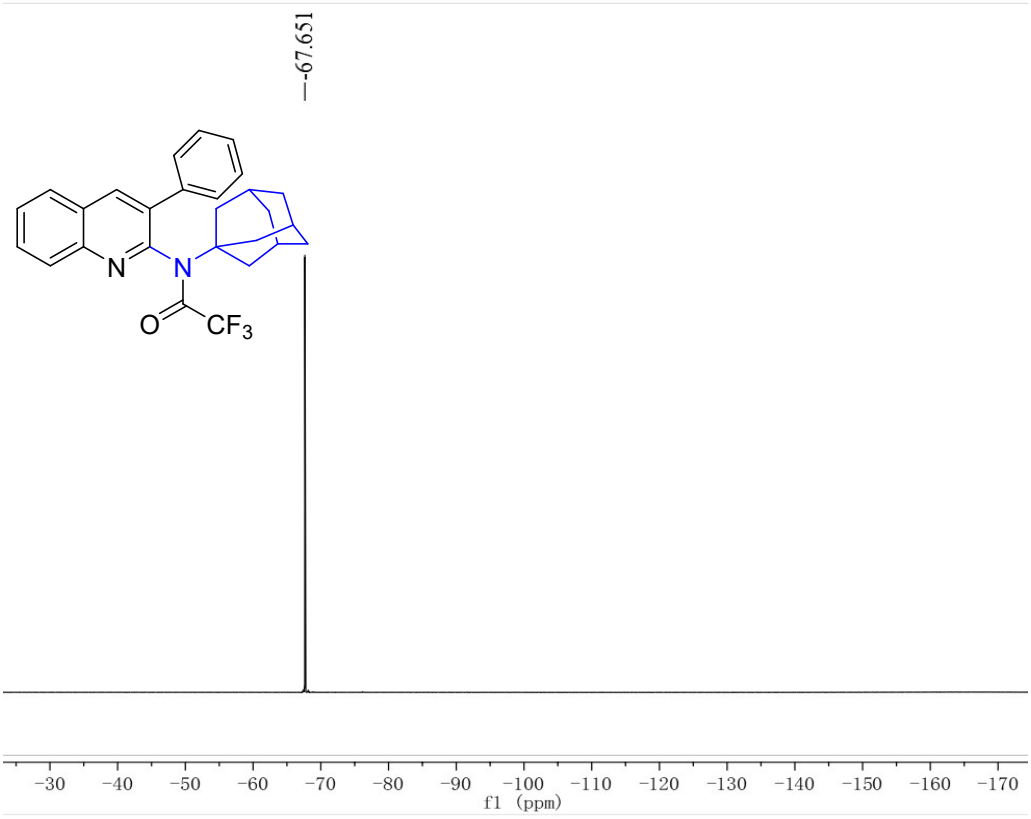
^{1}H NMR of **3n**



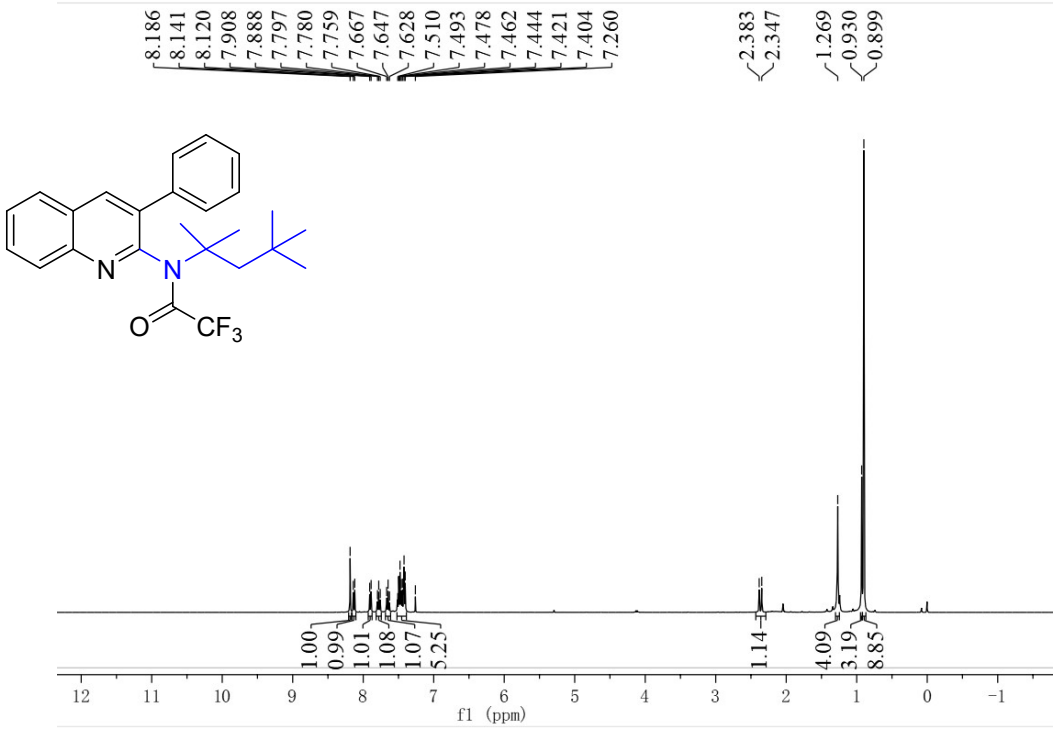
^{13}C NMR of **3n**



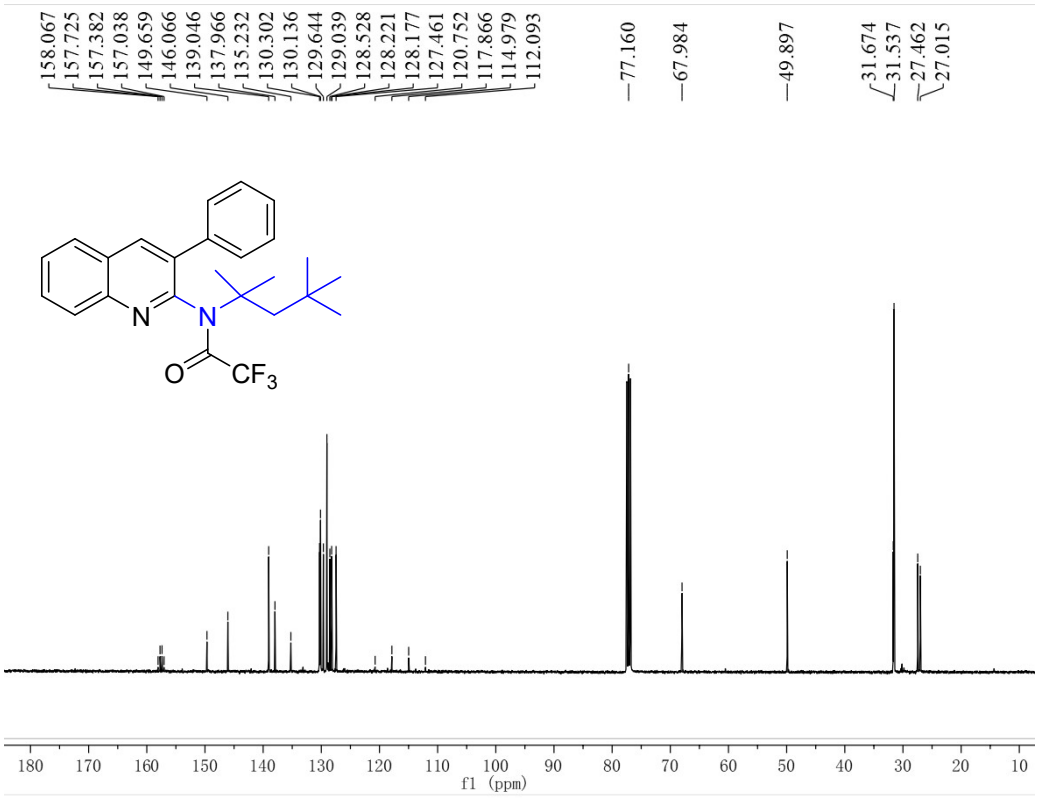
^{19}F NMR of **3n**


-67.651
N
N
O
CF3
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
f1 (ppm)

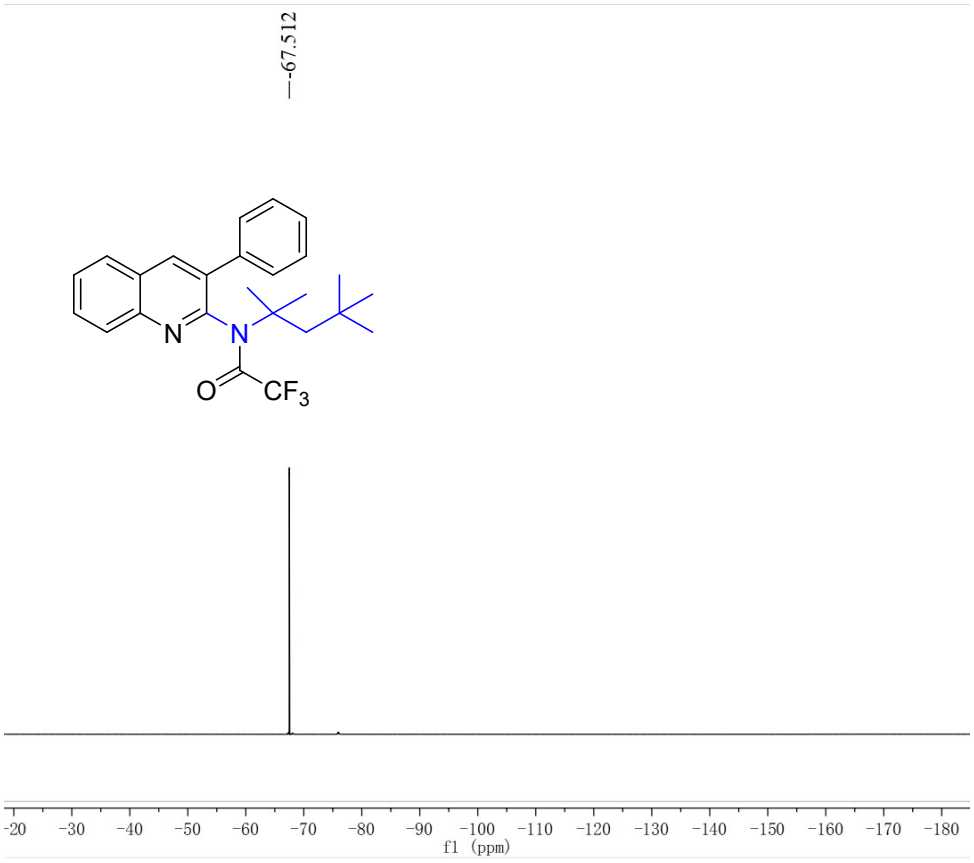
^{1}H NMR of **3o**



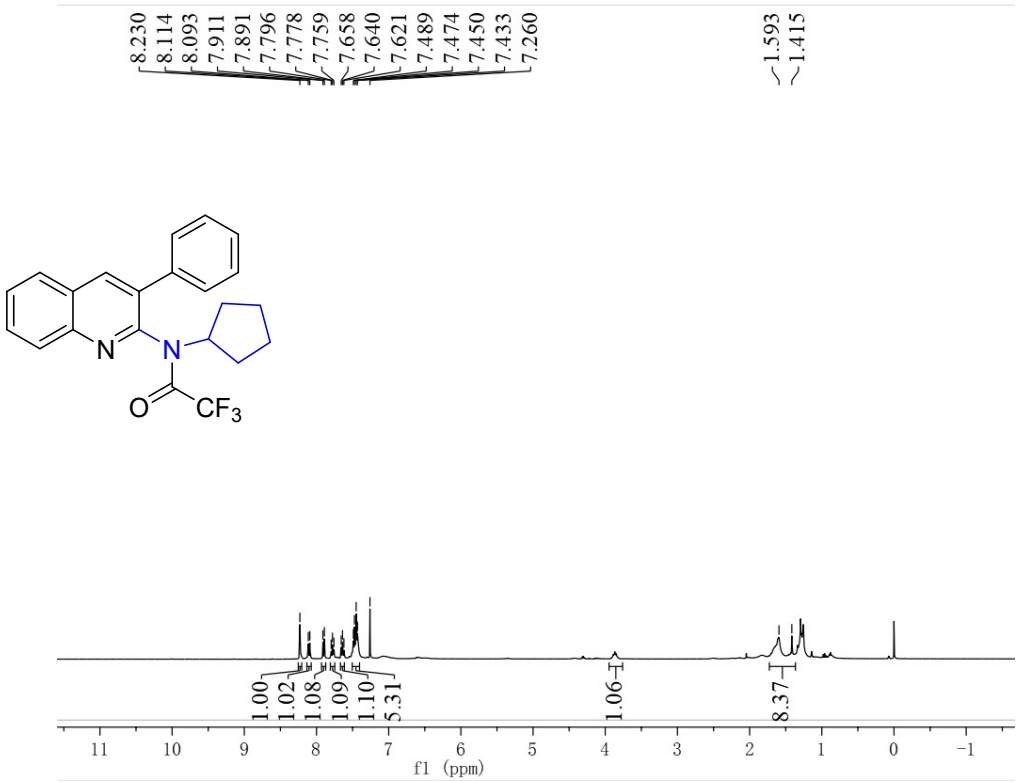
^{13}C NMR of **3o**



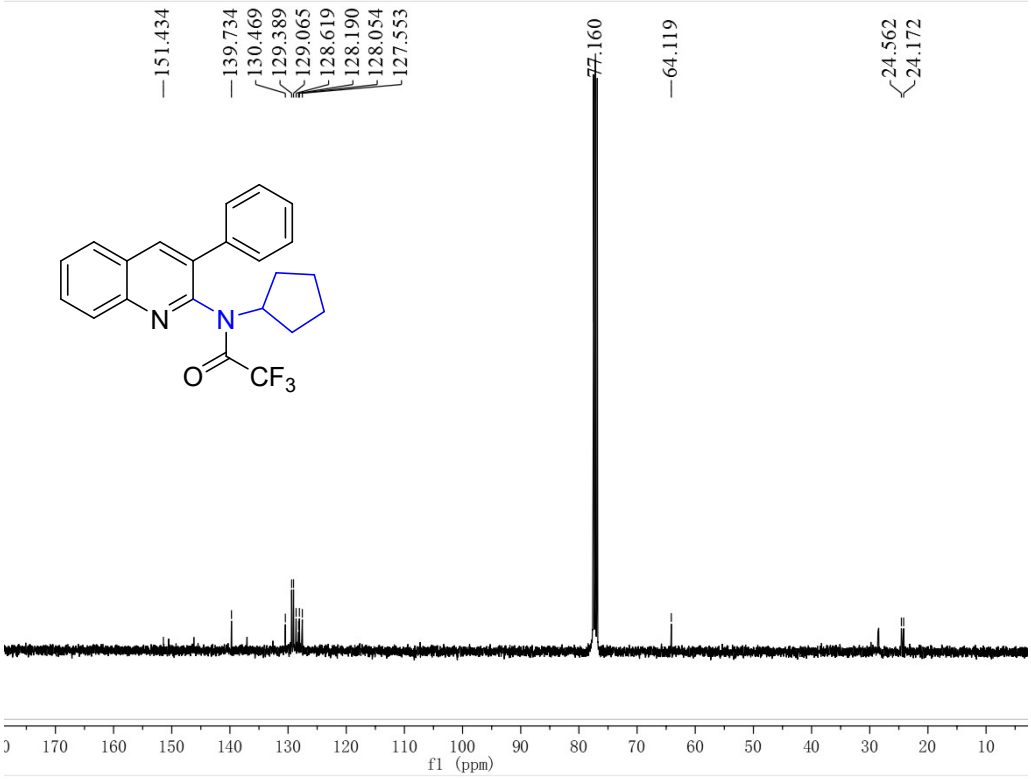
^{19}F NMR of **3o**


-67.512
N
N
O
CF3
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

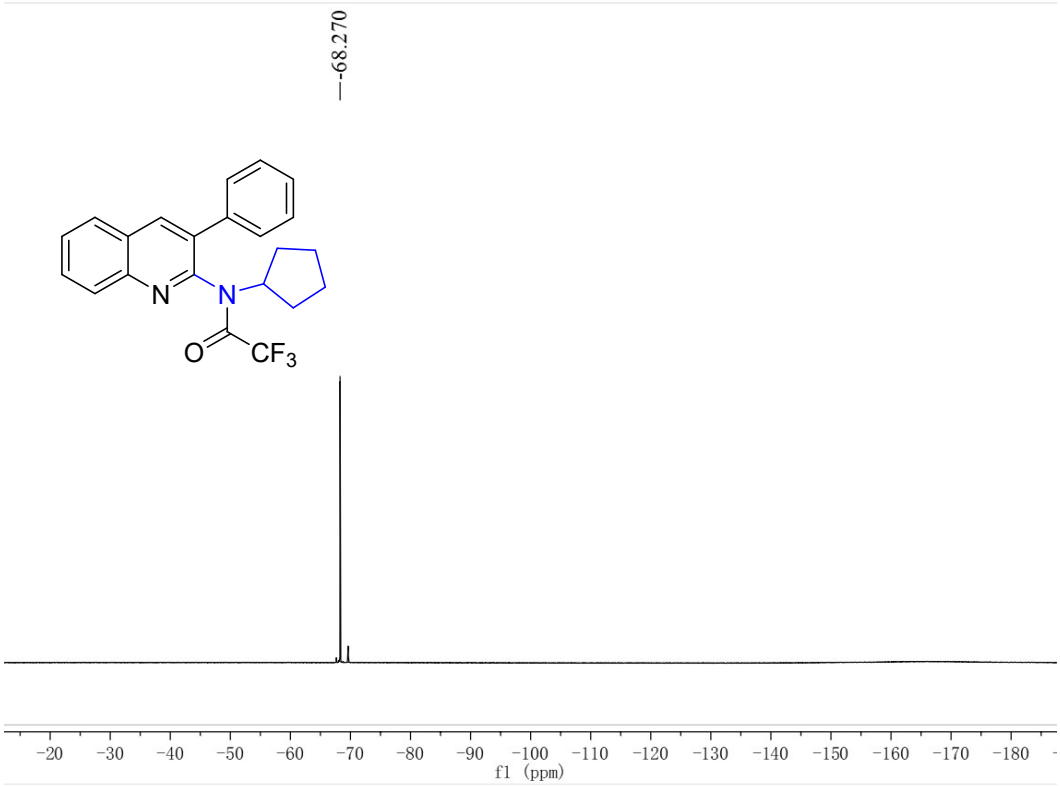
^{1}H NMR of **3p**



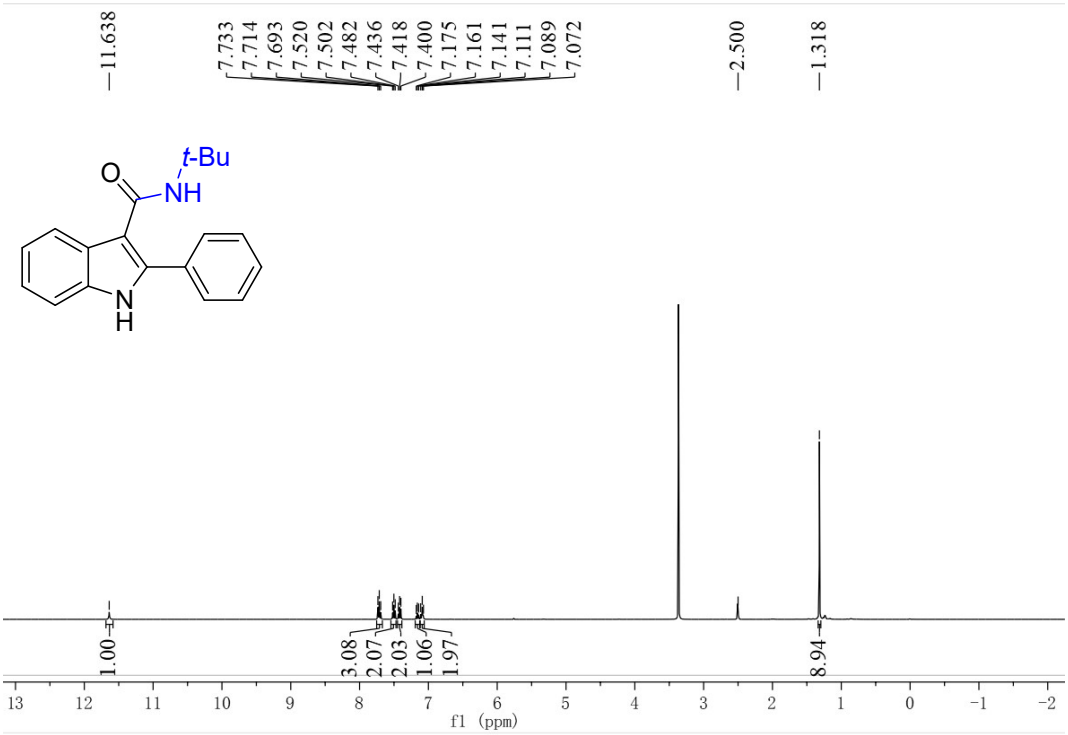
^{13}C NMR of **3p**



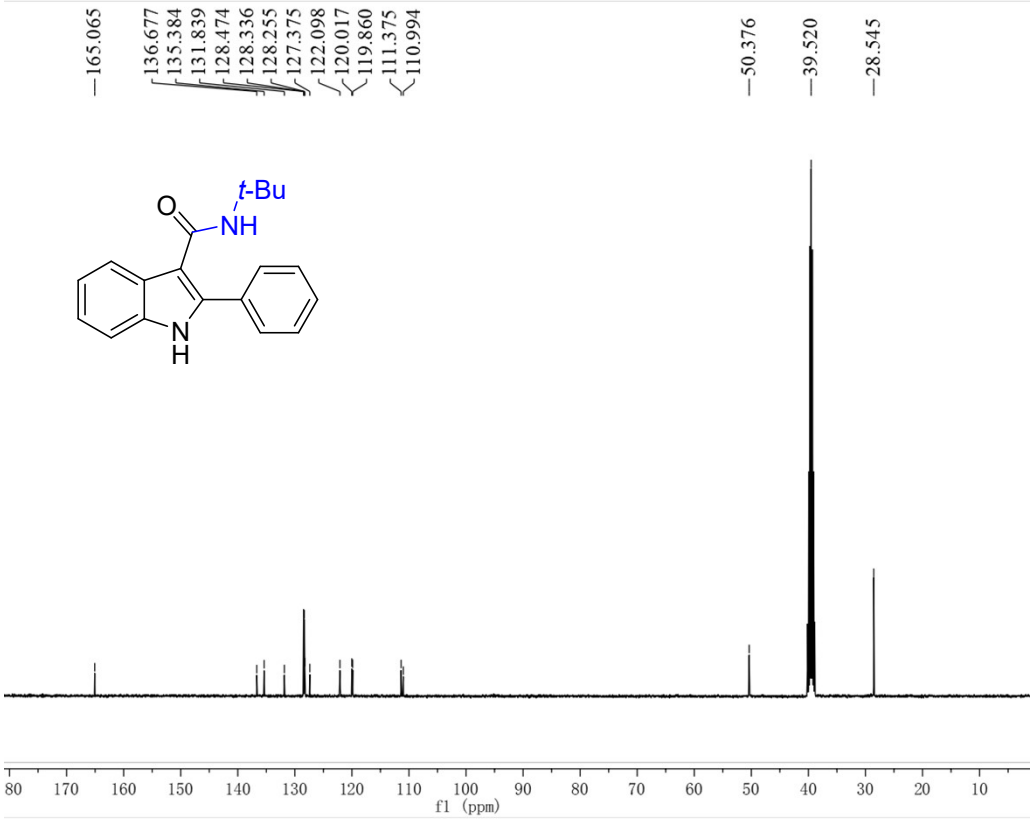
^{19}F NMR of **3p**


-68.270
N
N
O
CF3
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

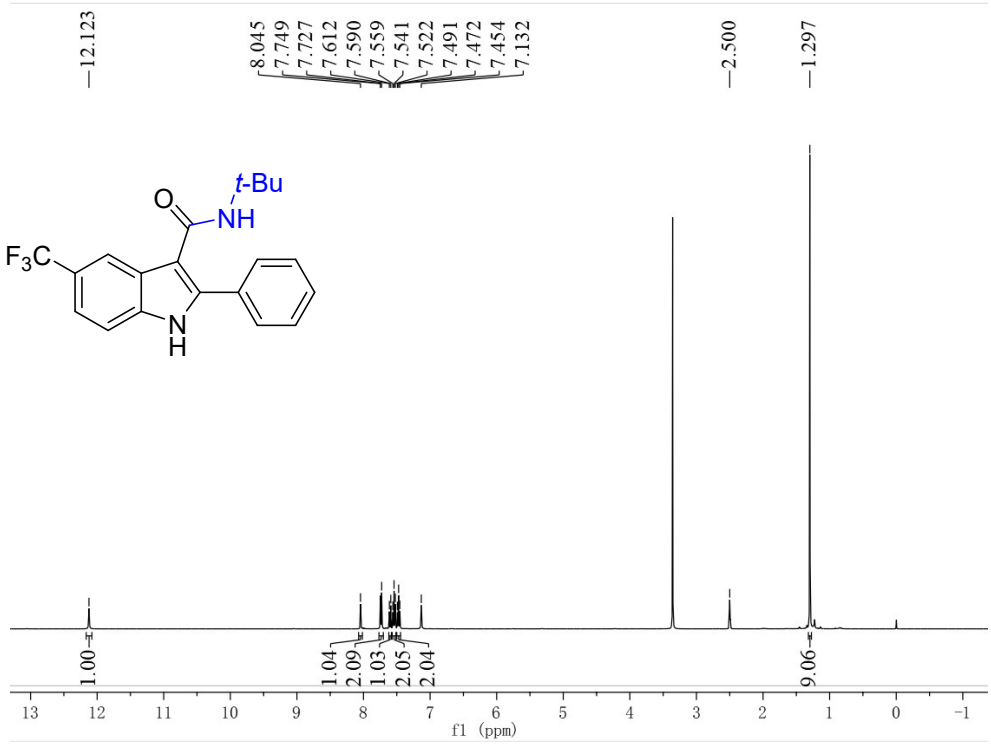
^{1}H NMR of **4a**



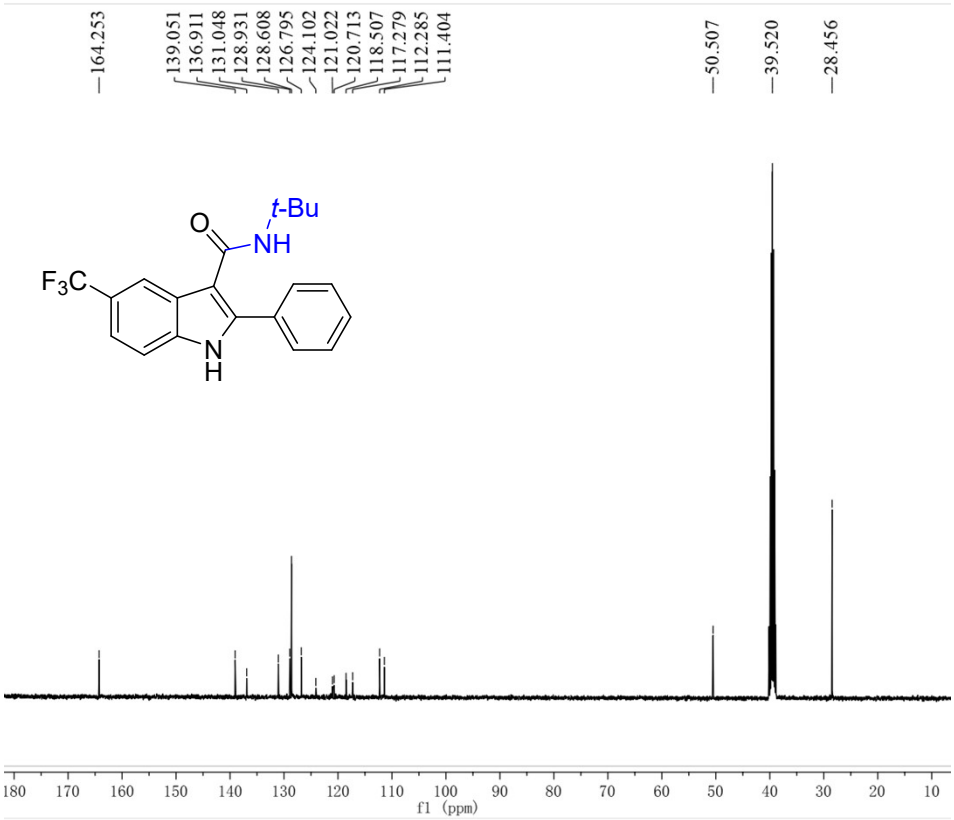
^{13}C NMR of **4a**



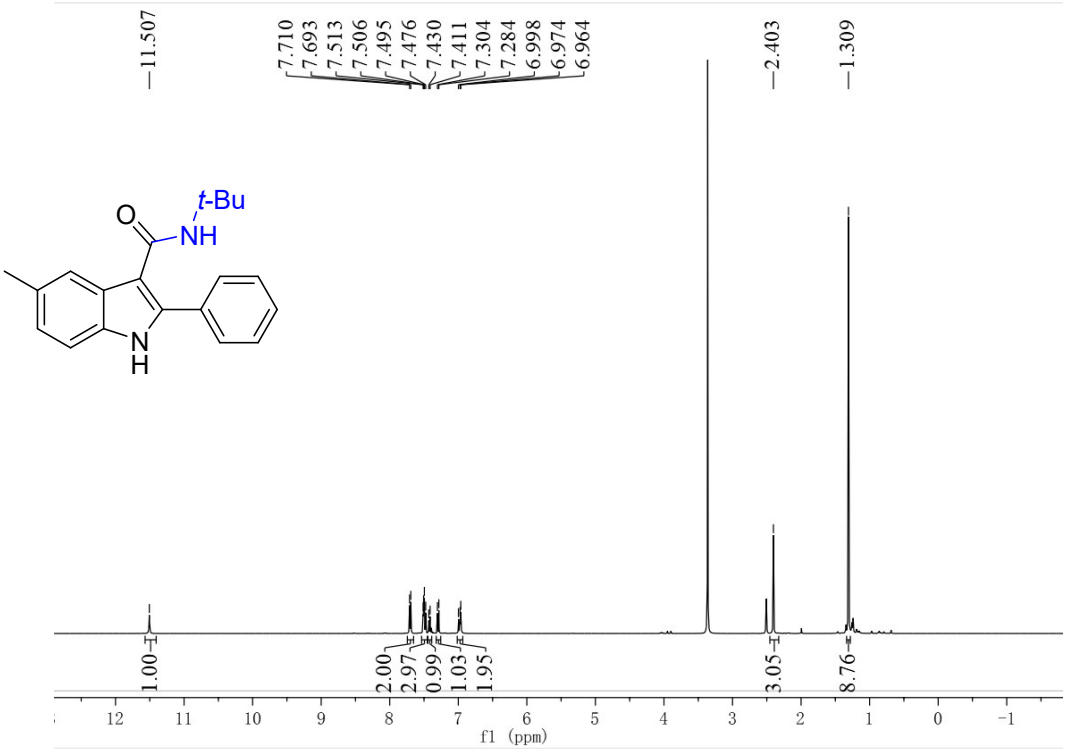
^{1}H NMR of **4b**



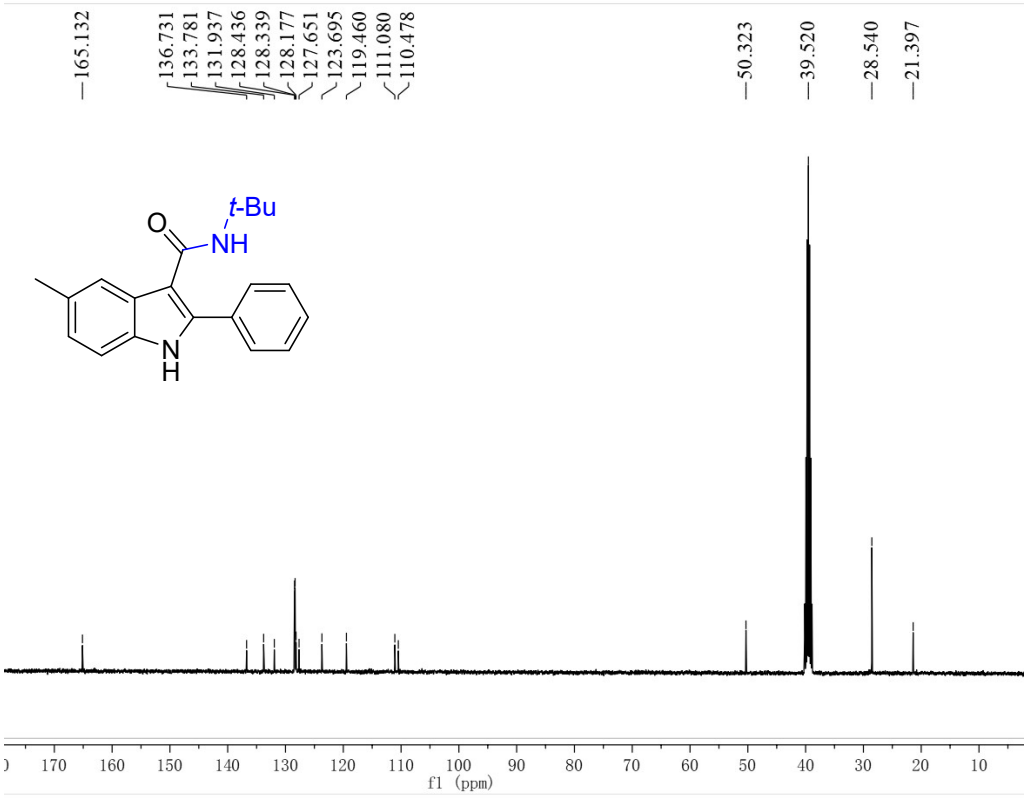
^{13}C NMR of **4b**



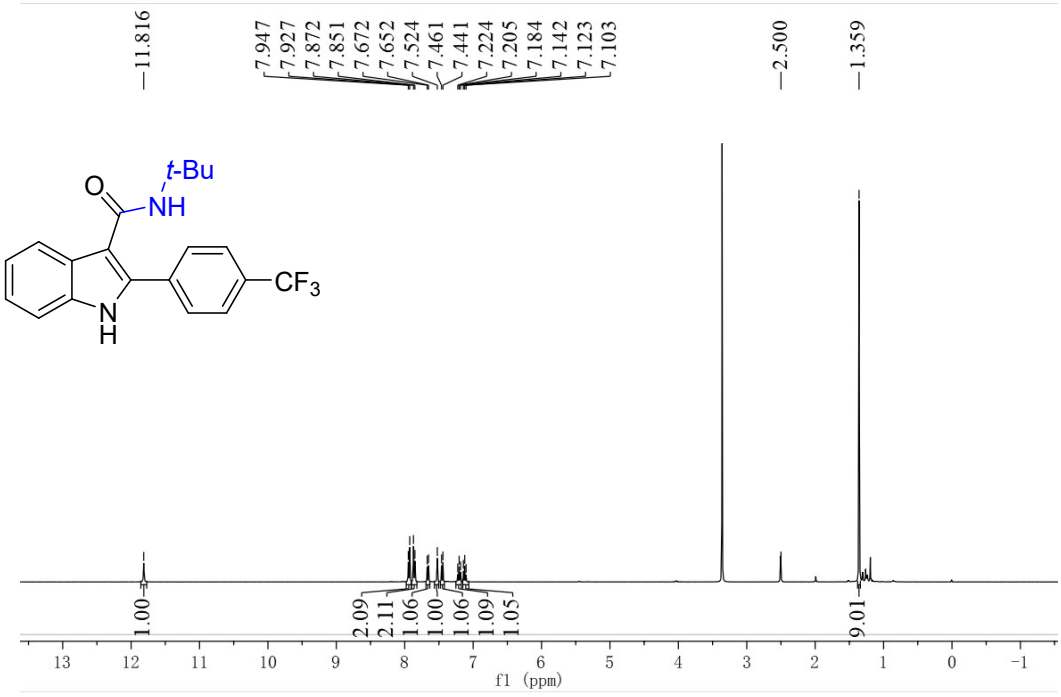
^{1}H NMR of **4c**



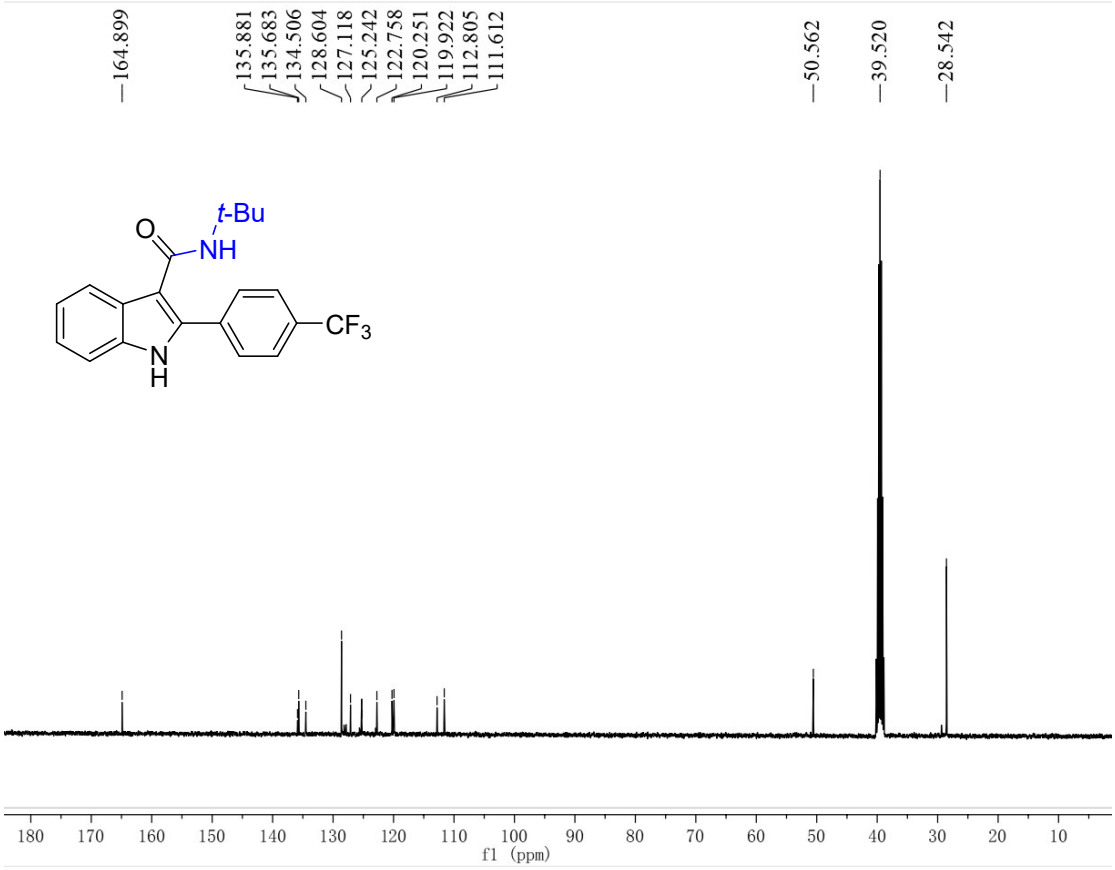
^{13}C NMR of **4c**



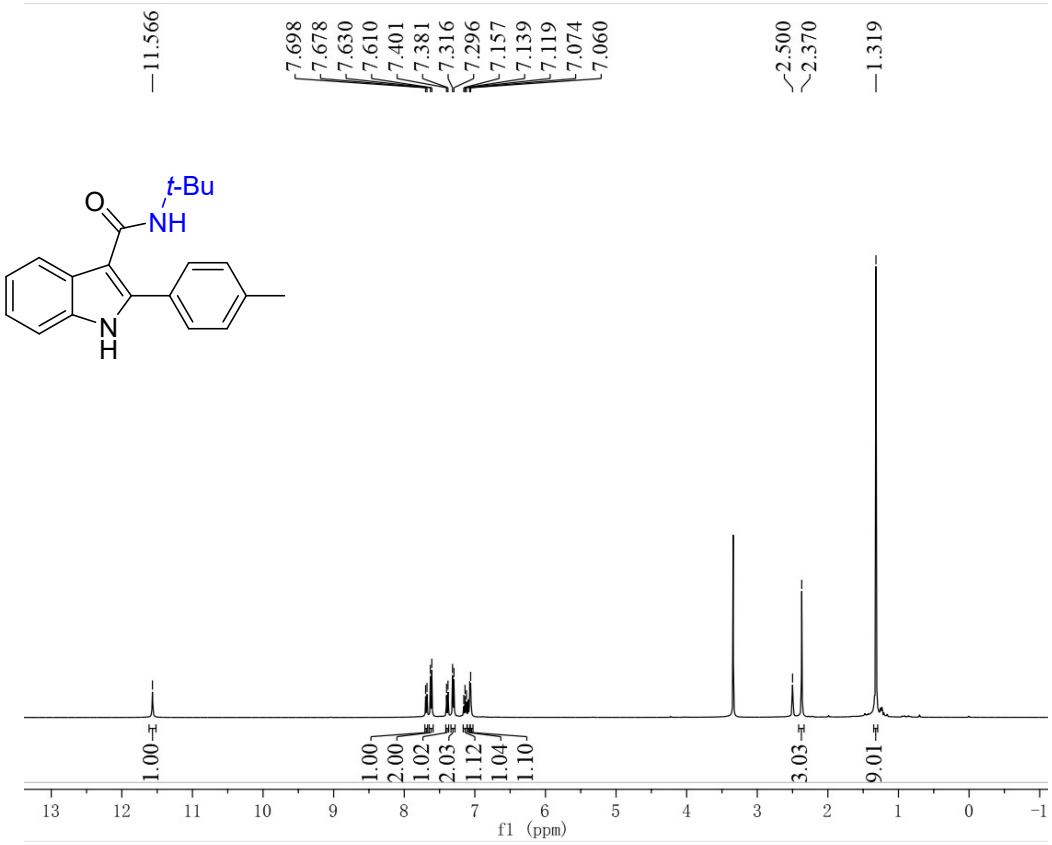
^{1}H NMR of **4d**



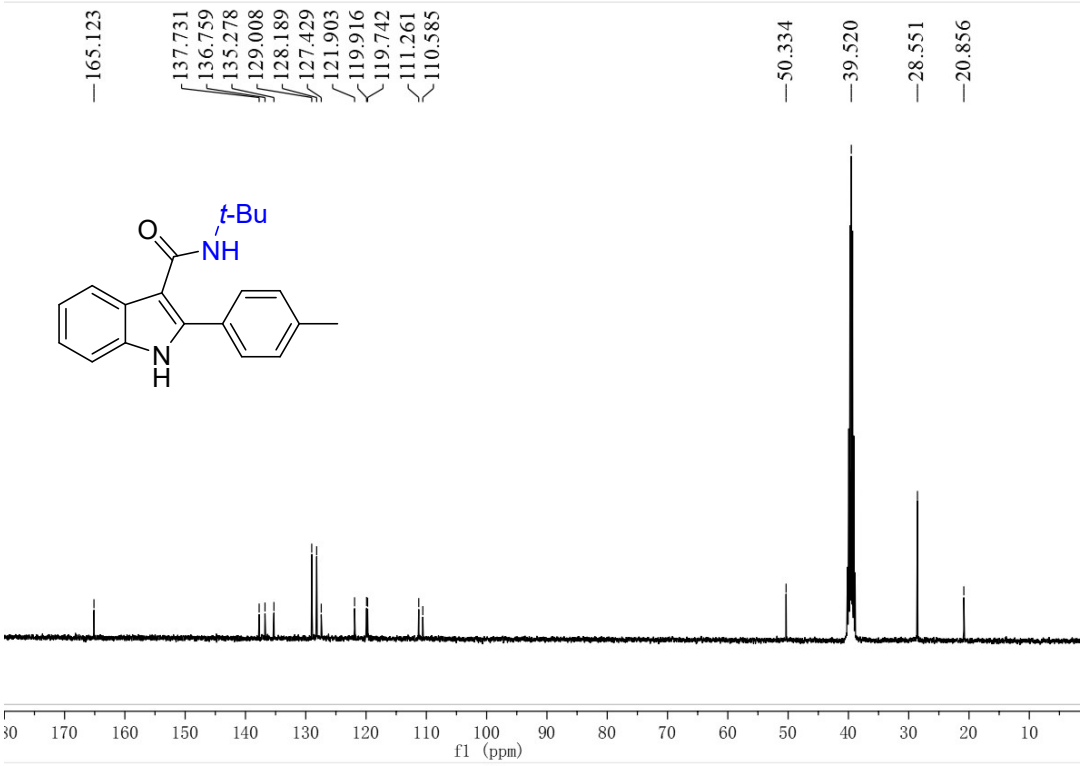
^{13}C NMR of **4d**



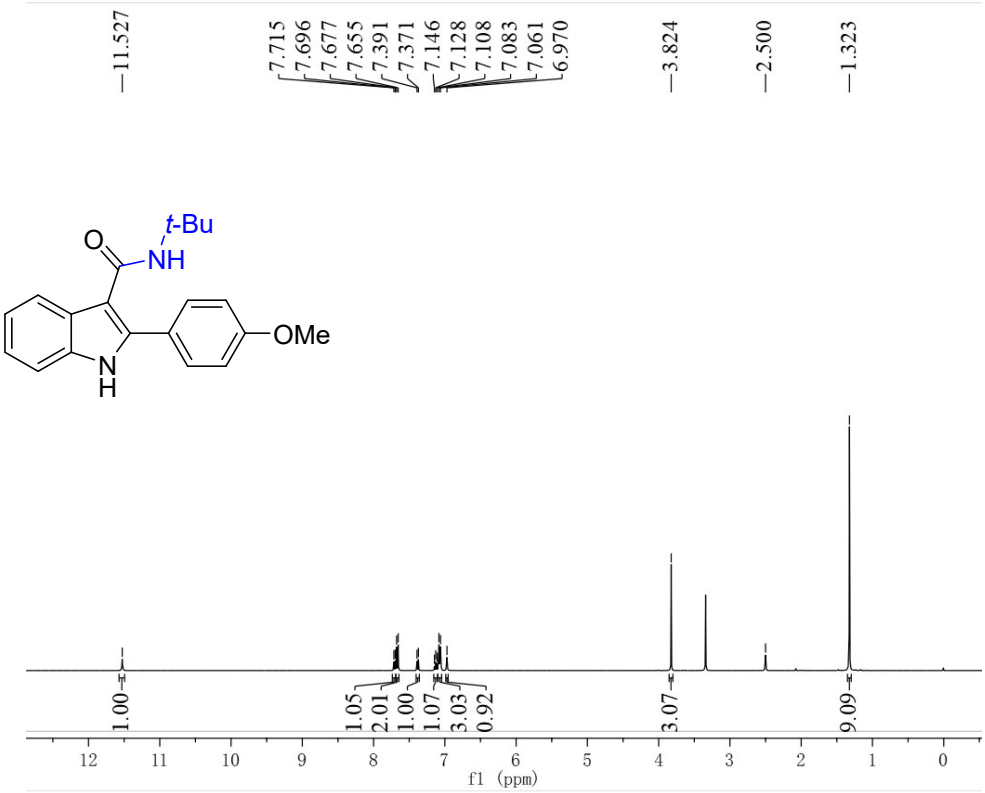
^{1}H NMR of **4e**



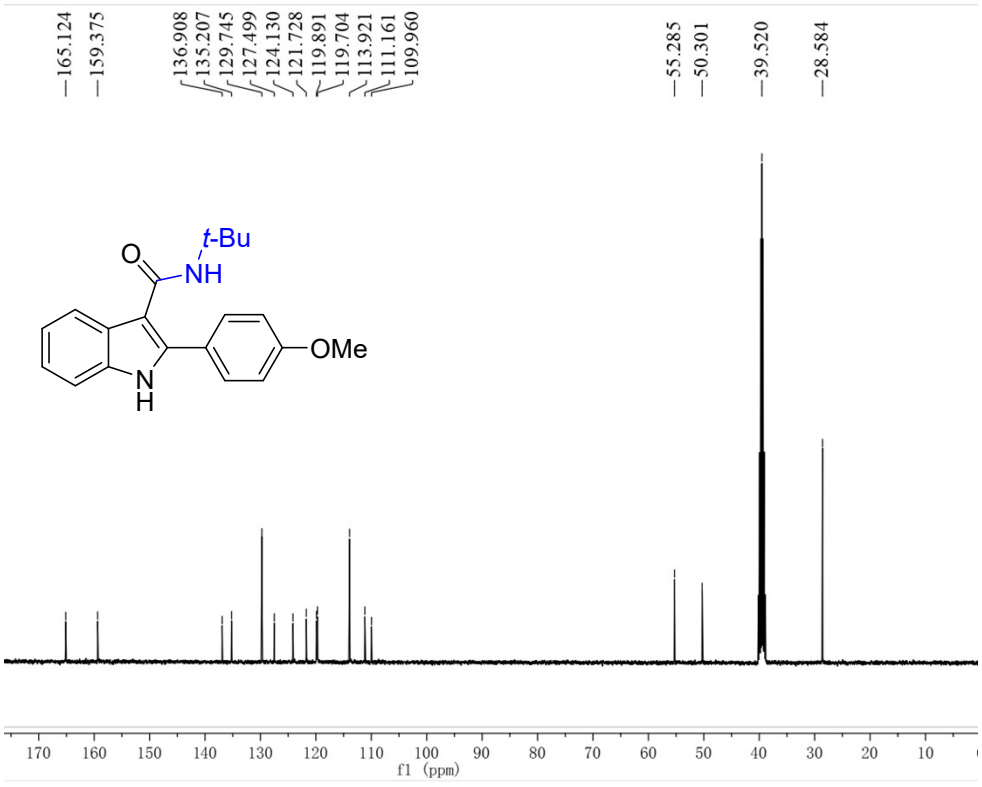
^{13}C NMR of **4e**



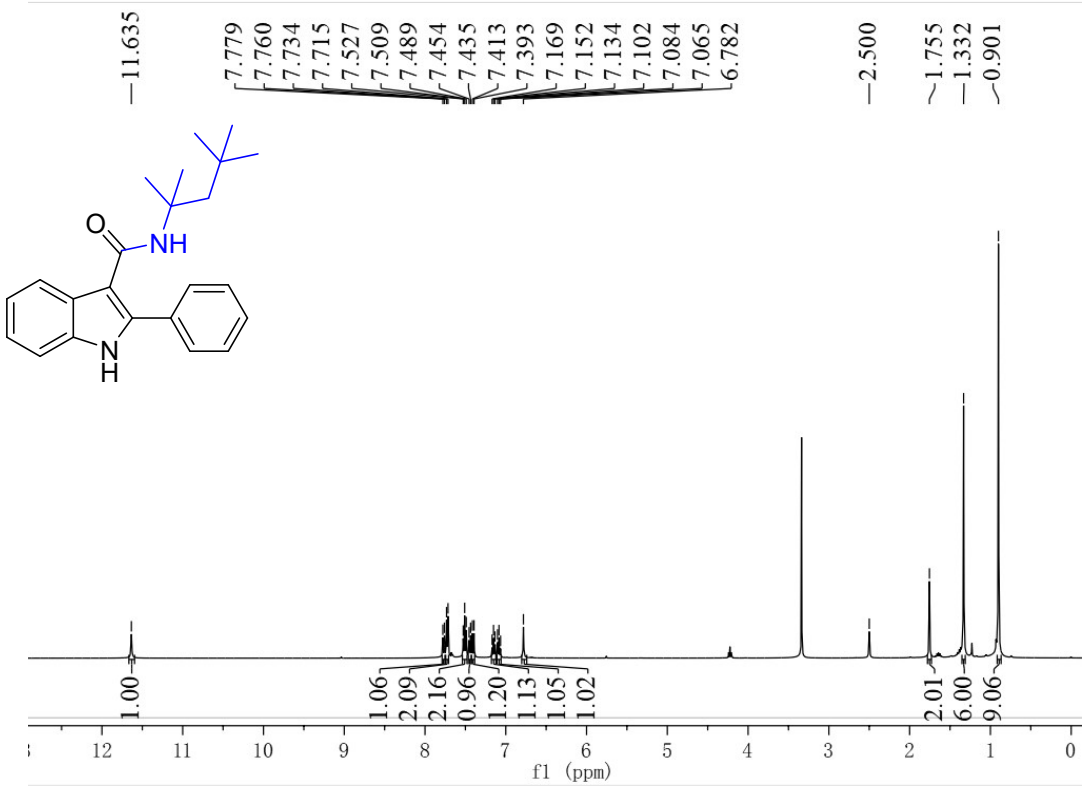
^{1}H NMR of **4f**



^{13}C NMR of **4f**



^{1}H NMR of **4g**



^{13}C NMR of **4g**