Supporting Information

Catalytic electron donor-acceptor complex triggered cascade radical trifluoromethylation/cyclization of *N*-isopentenyl aldehyde hydrazones

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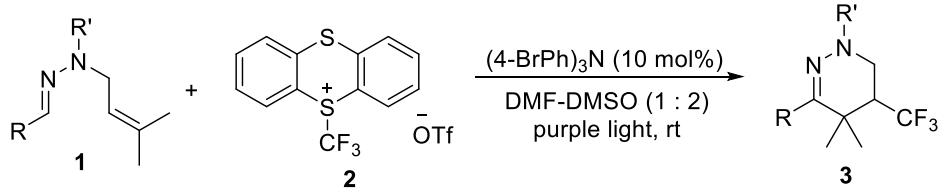
1. General Considerations

General Information: Unless otherwise noted, all chemicals were purchased and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 400M spectrometer (100 MHz for ^{13}C) and 600 MHz NMR spectrometer (150 MHz for ^{13}C). ^{19}F NMR spectra were recorded at ambient temperature on a 282 MHz spectrometer. NMR experiments are reported in δ units, parts per million (ppm). The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Emission intensities were recorded using a FS5 spectrophotometer.

2. General synthetic Procedures

All *N*-isopentenyl aldehyde hydrazones **1** were prepared according to the previous reports.[1] Trifluoromethyl thianthrenium triflate (TT-CF_3 $^{+}$OTf^{-}, **2**) was synthesized according to Ritter's work.[2]

2.1 General procedure for the synthesis of products 3



The mixture of *N*-isopentenyl aldehyde hydrazone **1** (0.2 mmol, 1 equiv.), TT-CF_3^+ OTf$^-$ **2** (0.6 mmol, 3 equiv.), (4-BrPh)$_3$N (10 mol%, 9.6 mg) and DMF : DMSO (2:1) (2 mL) were added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated for five times) and then sealed. The mixture was stirred at room temperature (25 ± 5 ℃) under 40 W 380-390 nm purple LEDs with a fan for 20 hours. Then, water (5 mL) was added, and the mixture was extracted with ethyl acetate (2×5 mL). The combined organic layers were washed with brine, and dried over Na_2SO_4. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate) to obtain product **3**. The photoreactor is shown in Figure S1.

Figure S1. Photoreactor used in this work (40 W 380-390 nm LEDs, λmax = 388 nm).

2.2 The Light Source and the Material of the Irradiation Vessel:

The photochemical reaction was carried out under visible light irradiation by a 40W 380-390 nm purple LED at room temperature. This blue LED was purchased from taobao (link: https://shop152143906.taobao.com/?spm=pc_detail.29232929/evo365560b447259.shop_block.ds

hopinfo.6cef7dd6EDPjwB). The blue LED's energy peak wavelength is 388 nm, the peak width at half-height is 12.5 nm, and irradiance@40 W is 61.54 mW/cm^2. The reaction vessel is a borosilicate glass tube. The distance between the tube and lamp is about 2 cm, and no filter is applied.

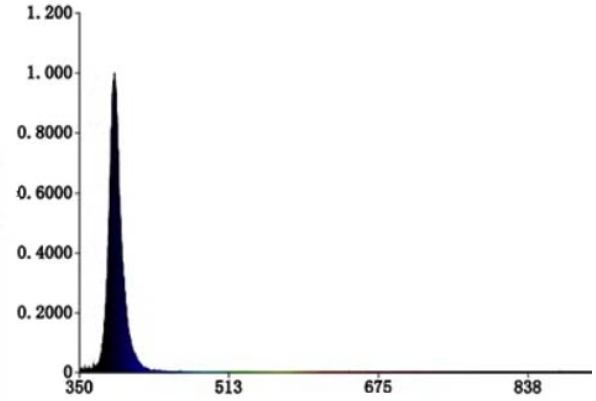
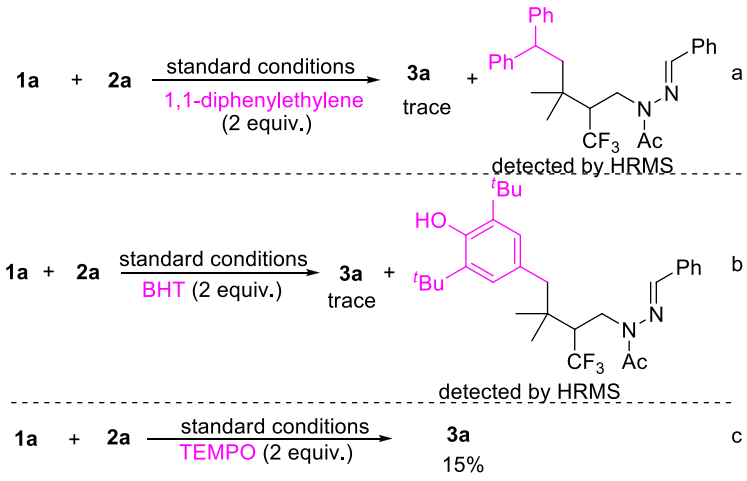


Figure S2. The spectral distribution of 40 W 380-390 nm purple LED (λmax= 388 nm)

3. Mechanism Studies

3.1 Radical inhibiting experiments



The mixture of **1** (0.2 mmol), **2** (3.0 equiv.), TBPA (10 mol%), 1,1-diphenylethylene (2 equiv.), or BHT (2 equiv.), or TEMPO (2 equiv.), DMSO:DMF (2:1, 2 mL) were added into the Schlenk tube. Then, the tube was evacuated and backfilled with nitrogen (repeated for five times) and the solution was stirred under 380-390 nm purple LEDs at room temperature for 20 h. The solution was analyzed by HRMS. The results of radical trapping were shown in Figure S3 & S4.

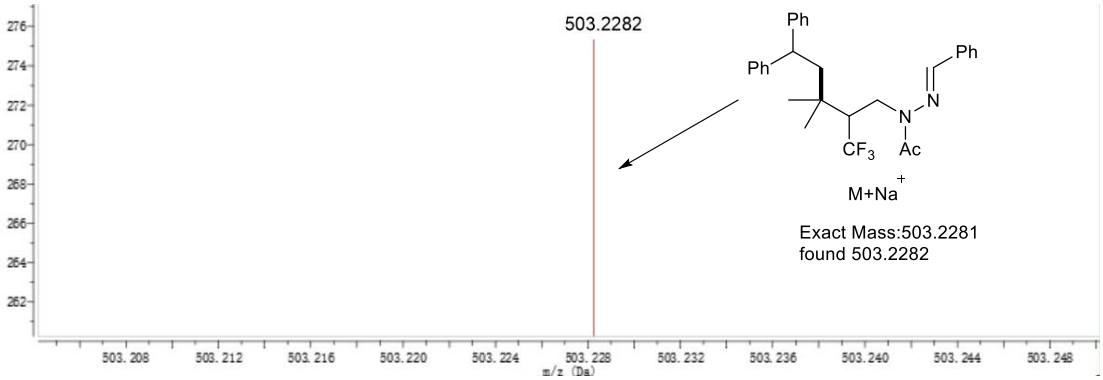


Figure S3. The HRMS spectra for the radical-trapping experiment with 1,1-diphenylethylene.

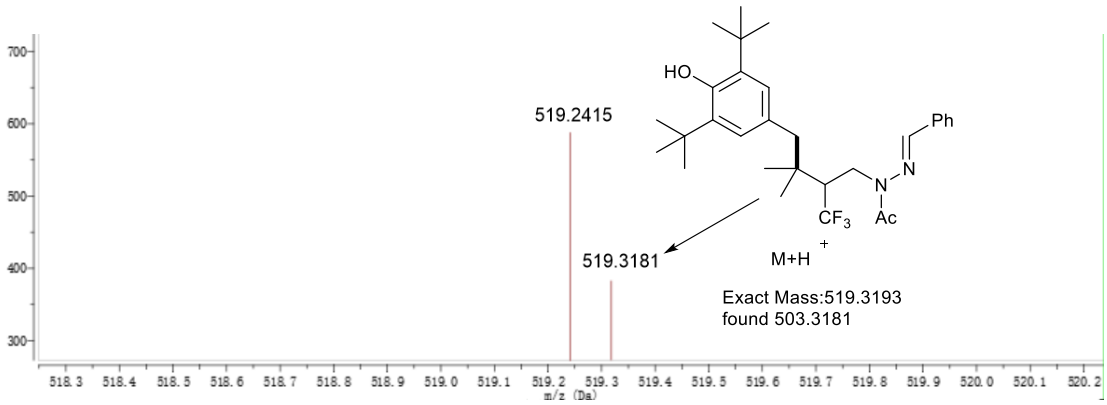


Figure S4. The HRMS spectra for the radical-trapping experiment with BHT.

3.2 UV-vis experiment

A UV-vis absorbance experiment was carried out tor confir the formation of EDA complex. As shown in Figure S5, the blue UV absorbance line came from the mixed solution of TT-$CF_3^+OTf^-$ **2** and TBPA (10 mol%) solution, red one came from TBPA solution, and black one came from TT-$CF_3^+OTf^-$. When TT-$CF_3^+OTf^-$ and TBPA ($(4\text{-BrPh})_3N$) were mixed in DMSO:DMF (2:1), the UV absorption was red-shifted and shifted to the visible region obviously, accompanied by a gradual change of the solution from colorless to yellow, strongly suggesting that TT-$CF_3^+OTf^-$-TBPA EDA complex might indeed be formed in the mixed solution.

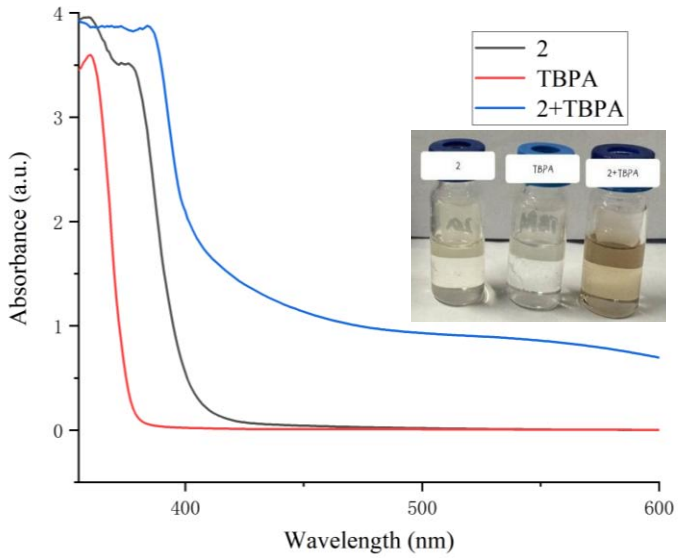
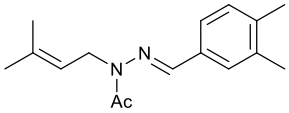
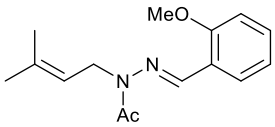


Figure S5. UV-vis absorption spectra and the color of the solutions.

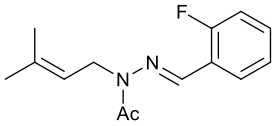
4. Characterization Data for the New Substrates



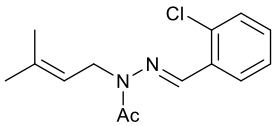
***(E)-N'*-(3,4-dimethylbenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1e**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.42 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 5.01 (t, *J* = 6.5 Hz, 1H), 4.61 (d, *J* = 6.2 Hz, 2H), 2.47 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.6, 139.5, 138.5, 137.0, 135.9, 132.6, 130.0, 128.0, 124.5, 118.3, 39.0, 25.6, 21.9, 19.8, 18.1. HRMS (ESI) m/z calcd for $C_{16}H_{23}N_2O^+$ $[M+H]^+$ 259.1805, found 259.1809.



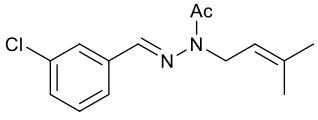
***(E)-N'*-(2-methoxybenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1f**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.32-7.29 (m, 1H), 7.23 (s, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.93-6.91 (m, 1H), 5.01 (t, *J* = 6.0 Hz, 1H), 4.60 (d, *J* = 6.3 Hz, 2H), 3.84 (s, 3H), 2.46 (s, 3H), 1.79 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.6, 159.9, 138.9, 136.3, 136.1, 129.7, 120.0, 118.1, 115.3, 111.5, 55.3, 39.1, 25.6, 21.8, 18.1. HRMS (ESI) m/z calcd for $C_{15}H_{21}N_2O_2^+$ $[M+H]^+$ 261.1598, found 261.1599.



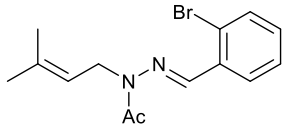
***(E)-N'*-(2-fluorobenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1g**), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92-7.90 (m, 1H), 7.88 (s, 1H), 7.35-7.31 (m, 1H), 7.18-7.15 (m, 1H), 7.09-7.06 (m, 1H), 5.00 (t, *J* = 6.8 Hz, 1H), 4.62 (d, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.7, 161.5 (d, $J_{C\text{-}F}$ = 249.2 Hz), 136.6, 132.3 (d, $J_{C\text{-}F}$ = 5.4 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.6 Hz), 126.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 124.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 122.8 (d, $J_{C\text{-}F}$ = 9.5 Hz), 117.6, 115.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 39.3, 25.6, 21.9, 17.9. HRMS (ESI) m/z calcd for $C_{14}H_{17}FN_2O^+$ $[M+H]^+$ 249.1398, found 249.1403.



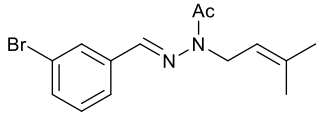
***(E)-N'*-(2-chlorobenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1i**), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.97-7.95 (m, 1H), 7.37-7.35 (m, 1H), 7.30-7.26 (m, 2H), 5.01 (d, *J* = 6.4 Hz, 1H), 4.64 (d, *J* = 6.5 Hz, 2H), 2.46 (s, 3H), 1.82 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.7, 136.6, 135.9, 134.2, 132.4, 130.3, 129.8, 127.0, 126.6, 117.8, 39.5, 25.6, 21.9, 18.2. HRMS (ESI) m/z calcd for $C_{14}H_{18}ClN_2O^+$ $[M+H]^+$ 265.1102, found 265.1105.



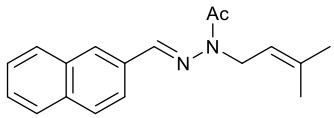
***(E)-N'*-(3-chlorobenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1j**), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.55 (s, 1H), 7.52-7.49(m, 1H), 7.33 –7.32(m, 2H), 5.00 (t, *J* = 5.9 Hz, 1H), 4.60 (d, *J* = 6.2 Hz, 2H), 2.46 (s, 3H), 1.80 (s, 3H), 1.72 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.6, 137.4, 136.8, 136.4, 134.8, 129.9, 129.4, 126.6, 125.2, 117.8, 39.2, 25.6, 21.9, 18.2. HRMS (ESI) m/z calcd for $C_{14}H_{18}ClN_2O^+$ $[M+H]^+$ 265.1102, found 265.1107.



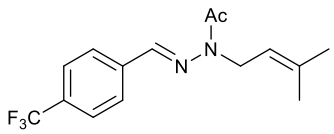
***(E)-N'*-(2-bromobenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1l**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.95-7.93 (d, *J* = 6.1 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.34-7.7.30 (m, 1H), 7.21-7.18 (m, 1H), 5.02 (t, *J* = 6.6 Hz, 1H), 4.65 (d, *J* = 6.4 Hz, 2H), 2.46 (s, 3H), 1.83 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.6, 138.3, 136.6, 133.8, 130.6, 127.6, 127.0, 124.3, 117.9, 39.6, 25.7, 21.9, 18.4. HRMS (ESI) m/z calcd for $C_{14}H_{18}BrN_2O^+$ $[M+H]^+$ 309.0597, found 309.0600.



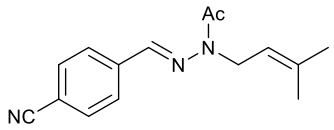
***(E)-N'*-(3-bromobenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1m**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.47 (m, 1H), 7.27 – 7.24 (m, 1H), 4.99 (t, *J* = 6.0 Hz, 1H), 4.60 (d, *J* = 6.3 Hz, 2H), 2.45 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.6, 137.2, 137.0, 136.4, 132.3, 130.2, 129.5, 125.6, 122.9, 117.8, 39.2, 25.6, 21.8, 18.2. HRMS (ESI) m/z calcd for $C_{14}H_{18}BrN_2O^+$ $[M+H]^+$ 309.0597, found 309.0595.



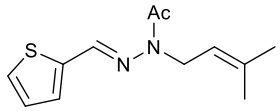
***(E)-N*-(3-methylbut-2-en-1-yl)-*N'*-(naphthalen-2-ylmethylene)acetohydrazide** (**1o**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.38 (d, *J* = 8.5 Hz, 1H), 8.18 (s, 1H), 7.78-7.75 (m, 3H), 7.47-7.45 (m, 1H), 7.43-7.39 (m, 2H), 5.00 (t, *J* = 6.7 Hz, 1H), 4.60 (d, *J* = 6.3 Hz, 2H), 2.42 (s, 3H), 1.76 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.7, 138.7, 136.2, 133.9, 130.9, 130.4, 130.1, 129.0, 126.9, 126.6, 126.1, 125.4, 123.6, 118.5, 39.2, 25.7, 22.2, 18.3. HRMS (ESI) m/z calcd for $C_{18}H_{21}N_2O^+$ $[M+H]^+$ 281.1648, found 281.1650.



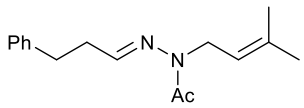
***(E)-N*-(3-methylbut-2-en-1-yl)-*N'*-(4-(trifluoromethyl)benzylidene)acetohydrazide** (**1p**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.65-7.63 (m, 2H), 5.03-5.00 (m, 1H), 4.64-4.62 (m, 2H), 2.47 (s, 3H), 1.81 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 172.7, 138.3, 137.2, 136.5, 131.2 (q, $J_{C\text{-}F}$ = 32.3 Hz), 127.0, 125.8 (q, $J_{C\text{-}F}$ = 270.5 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.9 Hz), 117.7, 39.2, 25.6, 21.8, 18.1. HRMS (ESI) m/z calcd for $C_{15}H_{18}F_3N_2O^+$ $[M+H]^+$ 299.1366, found 299.1369.



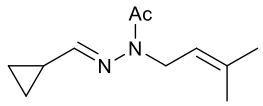
***(E)-N'*-(4-cyanobenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1q**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.60 (s, 1H), 4.99 (t, J = 6.8 Hz, 1H), 4.62 (d, J = 6.2 Hz, 2H), 2.47 (s, 3H), 1.80 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 139.2, 136.8, 136.6, 132.5, 127.2, 118.7, 117.5, 112.5, 39.4, 25.6, 21.8, 18.2. HRMS (ESI) m/z calcd for $C_{15}H_{18}F_3N_2O^+$ $[M+H]^+$ 256.1444, found 256.1440.



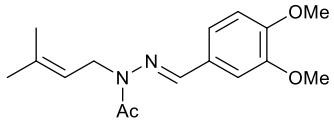
***(E)-N*-(3-methylbut-2-en-1-yl)-*N'*-(thiophen-2-ylmethylene)acetohydrazide** (**1s**), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.31-7.30 (m, 1H), 7.19 (s, 2H), 7.04-7.03 (m, 1H), 5.01 (t, J = 6.5 Hz, 1H), 4.58 (d, J = 6.1 Hz, 2H), 2.41 (m, 3H), 1.78 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 140.6, 136.3, 133.7, 128.7, 127.4, 127.2, 118.0, 39.3, 25.6, 21.6, 18.1. HRMS (ESI) m/z calcd for $C_{15}H_{18}F_3N_2O^+$ $[M+H]^+$ 256.1444, found 256.1447.



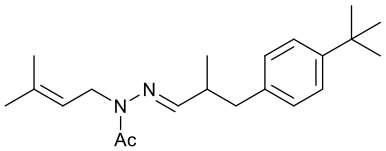
***(E)-N*-(3-methylbut-2-en-1-yl)-*N'*-(3-phenylpropylidene)acetohydrazide** (**1t**), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.18 (m, 3H), 6.97-6.96 (m, 1H), 4.87 (t, J = 6.4 Hz, 1H), 4.41 (d, J = 6.2 Hz, 2H), 2.87 (t, J = 7.7 Hz, 2H), 2.64-2.61 (m, 2H), 2.29 (s, 3H), 1.67 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 141.8, 140.9, 135.6, 128.5, 128.4, 126.1, 118.5, 38.8, 34.5, 32.9, 25.6, 21.7, 17.9. HRMS (ESI) m/z calcd for $C_{16}H_{24}N_2O^+$ $[M+H]^+$ 259.1805, found 259.1808.



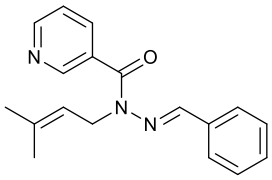
***(E)-N'*-(cyclopropylmethylene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1v**), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (d, J = 7.0 Hz, 1H), 4.96-4.86 (t, J = 7.3 Hz, 1H), 4.42 (d, J = 6.2 Hz, 2H), 2.31 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H), 0.89 (dd, J = 8.0, 2.5 Hz, 2H), 0.66 (dd, J = 4.8, 2.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 145.8, 135.5, 118.6, 38.8, 25.5, 21.7, 18.0, 14.0, 6.5. HRMS (ESI) m/z calcd for $C_{11}H_{18}N_2O^+$ $[M+H]^+$ 195.1492, found 195.1496.



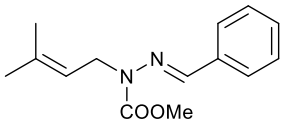
***(E)-N'*-(3,4-dimethoxybenzylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1w**), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.32 (s, 1H), 7.10-7.09 (m, 1H), 6.89-6.87 (d, J = 8.2 Hz, 1H), 5.03 (t, J = 6.3 Hz, 1H), 4.61 (d, J = 6.2 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.46 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 150.6, 149.4, 139.1, 136.0, 128.0, 121.5, 118.3, 110.8, 107.9, 56.0, 55.8, 39.1, 25.6, 21.8, 18.2. HRMS (ESI) m/z calcd for $C_{16}H_{23}N_2O_3^+$ $[M+H]^+$ 291.1703, found 291.1706.



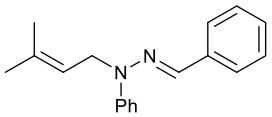
***(E)-N'*-(3-(4-(tert-butyl)phenyl)-2-methylpropylidene)-*N*-(3-methylbut-2-en-1-yl)acetohydrazide** (**1x**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 5.3 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 4.0 Hz, 1H), 4.85 (t, J = 7.9 Hz, 1H), 4.43-4.34 (m, 2H), 2.78-2.66 (m, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.31 (s, 9H), 1.13 (d, J = 6.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 148.9, 146.3, 136.5, 135.4, 128.8, 125.2, 118.6, 40.8, 38.7, 38.6, 34.4, 31.4, 25.5, 21.7, 17.9, 17.6. HRMS (ESI) m/z calcd for $C_{21}H_{33}N_2O^+$ $[M+H]^+$ 329.2587, found 329.2583.



***(E)-N'*-benzylidene-*N*-(3-methylbut-2-en-1-yl)nicotinohydrazide** (**1z**), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.68 (d, J = 4.8 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.76 (s, 1H), 7.47-7.46 (m, 2H), 7.39-7.36 (m, 1H), 7.34-7.33 (m, 3H), 5.17 (t, J = 6.6 Hz, 1H), 4.81 (d, J = 6.4 Hz, 2H), 1.86 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 150.8, 150.7, 140.7, 137.4, 137.0, 134.4, 131.4, 129.9, 128.8, 127.2, 122.5, 117.5, 40.2, 25.7, 18.3. HRMS (ESI) m/z calcd for $C_{18}H_{20}N_3O^+$ $[M+H]^+$ 293.1528 found 293.1532.

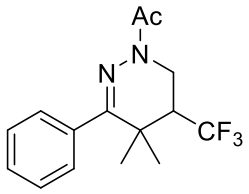


methyl (E)-2-benzylidene-1-(3-methylbut-2-en-1-yl)hydrazine-1-carboxylate (**1aa**), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.39-7.32 (m, 3H), 5.10 (t, J = 5.7 Hz, 1H), 4.57 (d, J = 5.9 Hz, 2H), 3.89 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 140.9, 136.1, 134.8, 129.6, 128.6, 127.1, 118.3, 53.8, 42.8, 25.7, 18.1. HRMS (ESI) m/z calcd for $C_{14}H_{19}N_2O_2^+$ $[M+H]^+$ 247.1441 found 247.1443.



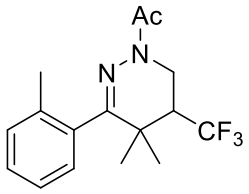
***(E)*-2-benzylidene-1-(3-methylbut-2-en-1-yl)-1-phenylhydrazine** (**1ab**), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.66 (m, 2H), 7.43 (s, 1H), 7.36-7.33 (m, 4H), 7.31-7.29 (m, 2H), 7.25-7.22 (m, 1H), 6.92-6.89 (m, 1H), 5.11 (t, J = 5.9 Hz, 1H), 4.50 (d, J = 5.8 Hz, 2H), 1.80 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 136.9, 135.6, 131.9, 129.1, 128.6, 127.7, 126.1, 120.4, 118.6, 115.1, 44.5, 25.7, 18.2. HRMS (ESI) m/z calcd for $C_{18}H_{21}N_2^+$ $[M+H]^+$ 265.1699, found 265.1703.

5. Characterization Data for the Products



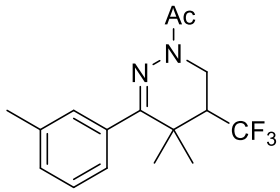
1-(4,4-Dimethyl-3-phenyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1]

(**3a**, 44 mg, 74% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 3H), 7.36-7.33 (m, 2H), 4.18-4.07 (m, 2H), 2.54-2.44 (m, 1H), 2.30 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 154.6, 137.1, 128.7, 128.4, 128.1, 126.2 (q, $J_{C\text{-}F}$ = 283.0 Hz), 45.0 (q, $J_{C\text{-}F}$ = 25.8 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.3 Hz), 34.6, 28.4, 23.2, 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9.



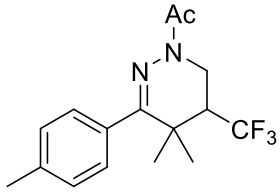
1-(4,4-Dimethyl-3-(*o*-tolyl)-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1]

(**3b**, 40 mg, 66% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.23-7.16 (m, 2H), 4.31-4.27 (m, 1H), 4.00-3.95 (m, 1H), 2.56-2.48 (m, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 1.31 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 154.3, 136.8, 135.9, 130.8, 128.8, 128.8, 126.3 (q, $J_{C\text{-}F}$ = 282.6 Hz), 125.1, 45.0 (q, $J_{C\text{-}F}$ = 25.9 Hz), 35.9 (q, $J_{C\text{-}F}$ = 4.2 Hz), 35.7, 27.517, 22.4, 21.1, 20.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8.



1-(4,4-Dimethyl-3-(*m*-tolyl)-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1]

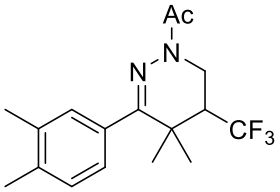
(**3c**, 38 mg, 61% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 1H), 7.23-7.20 (m, 1H), 7.14-7.12 (m, 2H), 4.19-4.14 (m, 1H), 4.11-4.06 (m, 1H), 2.51-2.45 (m, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 154.9, 137.8, 137.1, 129.3, 129.2, 127.9, 126.3 (q, $J_{C\text{-}F}$ = 283.1 Hz), 125.7, 45.1 (q, $J_{C\text{-}F}$ = 25.7 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.1 Hz), 34.6, 28.4, 23.2, 21.5, 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8.



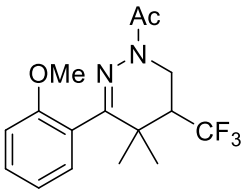
1-(4,4-Dimethyl-3-(*p*-tolyl)-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1]

(**3d**, 42 mg, 68% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 6.4 Hz 2H), 7.12 (d, J = 8.0 Hz 2H), 4.11-4.06 (m, 1H), 4.02-3.97 (m, 1H), 2.44-2.36 (m, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 1.31 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 154.7, 138.4, 134.3,

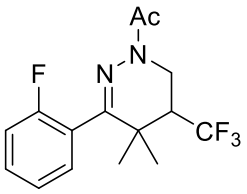
128.7, 128.6, 126.3 (q, $J_{C\text{-}F}$ = 283.1 Hz), 45.1 (q, $J_{C\text{-}F}$ = 25.6 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.0 Hz), 34.6, 28.4, 23.2, 21.2, 21.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8.



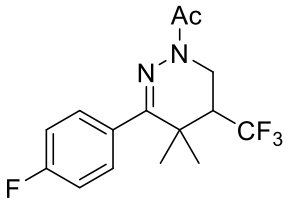
1-(3-(3,4-Dimethylphenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3e**, 40 mg, 62% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.14 (m, 1H), 7.10-7.06 (m, 2H), 4.19-4.15 (m, 1H), 4.09-4.04 (m, 1H), 2.53-2.43 (m, 1H), 2.30 (s, 9H), 1.39 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 155.0, 137.1, 136.3, 134.7, 129.9, 129.2, 126.3 (q, $J_{C\text{-}F}$ = 283.2 Hz), 126.1, 45.1 (q, $J_{C\text{-}F}$ = 25.8 Hz), 36.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 34.6, 28.4, 23.2, 21.2, 19.9, 19.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8. HRMS (ESI) m/z calcd for $C_{17}H_{22}F_3N_2O^+$ $[M+H]^+$ 327.1679, found 327.1682.



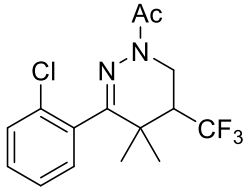
1-(3-(2-Methoxyphenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3f**, 48 mg, 62% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.29 (m, 1H), 6.95-6.91 (m, 2H), 6.87-6.85 (m, 1H), 4.18-4.14 (m, 1H), 4.11-4.06 (m, 1H), 3.84 (s, 3H), 2.52-2.46 (m, 1H), 2.30 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.2, 154.4, 138.4, 129.1, 126.2 (q, $J_{C\text{-}F}$ = 282.7 Hz), 121.0, 115.0, 113.4, 55.3, 44.8 (q, $J_{C\text{-}F}$ = 25.7 Hz), 36.0 (q, $J_{C\text{-}F}$ = 3.9 Hz), 34.6, 28.4, 23.1, 21.1.^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8. HRMS (ESI) m/z calcd for $C_{16}H_{20}F_3N_2O_2^+$ $[M+H]^+$ 329.1471, found 329.1475.



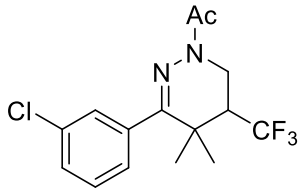
1-(3-(2-Fluorophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3g**, 38 mg, 60% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 1H), 7.23-7.18 (m, 2H), 7.15-7.10 (m, 1H), 4.30-4.26 (m, 1H), 3.98-3.93 (m, 1H), 2.26 (s, 3H), 1.33 (s, 3H), 1.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 160.1 (d, $J_{C\text{-}F}$ = 247.4 Hz), 150.6, 131.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.2 (q, $J_{C\text{-}F}$ = 282.7 Hz) , 124.6 (d, $J_{C\text{-}F}$ = 17.1 Hz), 123.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.9 (d, $J_{C\text{-}F}$ = 22.5 Hz), 44.4 (q, $J_{C\text{-}F}$ = 25.9 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.2 Hz), 35.2, 27.2, 22.3 (q, $J_{C\text{-}F}$ = 1.8 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.0, -112.3. HRMS (ESI) m/z calcd for $C_{15}H_{17}F_4N_2O^+$ $[M+H]^+$ 317.1272, found 317.1275.



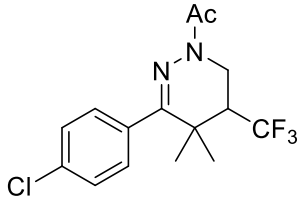
1-(3-(4-Fluorophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1] (**3h**, 42 mg, 66% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.11-7.05 (m, 2H), 4.12 (m, 2H), 2.53-2.44 (m, 1H), 2.29 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 162.7 (d, $J_{C\text{-}F}$ = 249.2 Hz), 153.6, 133.2 (d, $J_{C\text{-}F}$ = 3.4 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.3 Hz), 126.2 (q, $J_{C\text{-}F}$ = 283.1 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.6 Hz), 44.7 (q, $J_{C\text{-}F}$ = 25.8 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.3 Hz), 34.5, 28.5 (d, $J_{C\text{-}F}$ = 1.3 Hz), 23.3 (q, $J_{C\text{-}F}$ = 1.7 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9, -112.8.



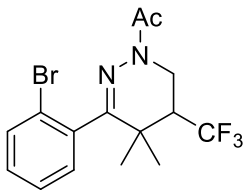
1-(3-(2-Chlorophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3i**, 44 mg, 65% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 1H), 7.37-7.33 (m, 1H), 7.31-7.28 (m, 1H), 7.28-7.24 (m, 1H), 4.44-4.41 (m, 1H), 3.80-3.78 (m, 1H), 2.62-2.52 (m, 1H), 2.26 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 152.3, 135.4, 134.0, 130.6, 130.1, 129.7, 126.3 (q, $J_{C\text{-}F}$ = 282.8 Hz), 126.2, 44.5 (q, $J_{C\text{-}F}$ = 27.2 Hz), 36.2 (q, $J_{C\text{-}F}$ = 2.1 Hz), 35.9, 29.7, 22.2 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClF_3N_2O^+$ $[M+H]^+$ 333.0976, found 333.0980.



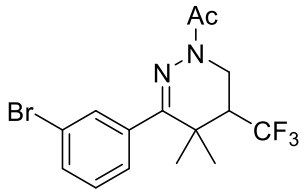
1-(3-(3-Chlorophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3j**, 40 mg, 60% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1H), 7.35-7.31 (m, 2H), 7.24-7.22 (m, 1H), 4.12 (d, J = 5.6 Hz, 2H), 2.52-2.45 (m, 1H), 2.29 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 153.0, 138.8, 134.0, 129.4, 128.8, 128.7, 126.8, 126.1 (q, $J_{C\text{-}F}$ = 283.1 Hz), 45.0 (q, $J_{C\text{-}F}$ = 25.6 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.2 Hz), 34.5, 28.5 (d, $J_{C\text{-}F}$ = 1.5 Hz), 23.3 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClF_3N_2O^+$ $[M+H]^+$ 333.0976, found 333.0983.



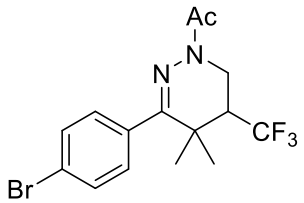
1-(3-(4-Chlorophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1] (**3k**, 46 mg, 70% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4, 2.0 Hz, 2H), 4.13-4.11 (m, 2H), 2.53-2.43 (m, 1H), 2.29 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 153.4, 135.5, 134.6, 130.0, 128.3, 126.1 (q, $J_{C\text{-}F}$ = 283.1 Hz), 45.0 (q, $J_{C\text{-}F}$ = 25.7 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.2 Hz), 34.5, 28.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 23.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 21.1. ^{19}F NMR (752 MHz, $CDCl_3$) δ -63.9.



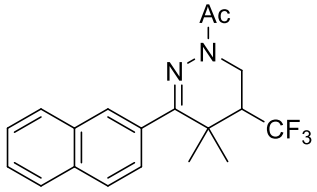
1-(3-(2-Bromophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3l**, 50 mg, 65% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.63 (m, 1H), 7.38-7.33 (m, 1H), 7.29-7.25 (m, 2H), 4.64-4.53 (m, 1H), 3.77-3.57 (m, 1H), 2.61-2.53 (m, 1H), 2.27 (s, 3H), 1.33 (s, 3H), 1.31-1.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 153.2, 137.2, 133.4, 130.3, 129.9, 126.7, 125.8 (q, $J_{C\text{-}F}$ = 282.5 Hz), 44.5 (q, $J_{C\text{-}F}$ = 27.4 Hz), 36.2 (q, $J_{C\text{-}F}$ = 5.2 Hz), 35.9, 25.4, 22.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 21.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.7. HRMS (ESI) m/z calcd for $C_{15}H_{17}BrF_3N_2O^+$ $[M+H]^+$ 377.0471, found 377.0475.



1-(3-(3-Bromophenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3m**, 46 mg, 62% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H), 7.49-7.48 (m, 1H), 7.29-7.27 (m, 2H), 4.13-4.11 (m, 2H), 2.52-2.46 (m, 1H), 2.29 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 153.0, 139.0, 131.7, 131.6, 129.6, 127.3, 126.1 (q, $J_{C\text{-}F}$ = 283.0 Hz), 122.2, 44.9 (q, $J_{C\text{-}F}$ = 25.8 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.1 Hz), 34.5, 28.5 (d, $J_{C\text{-}F}$ = 1.8 Hz), 23.3 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9. HRMS (ESI) m/z calcd for $C_{15}H_{17}BrF_3N_2O^+$ $[M+H]^+$ 377.0471, found 377.0473.

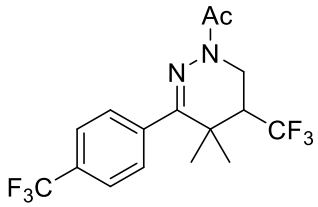


1-(3-(4-bromophenyl)-4,4-Dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[1] (**3n**, 56 mg, 74% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 6.6, 1.8 Hz, 2H), 7.15 (dd, J = 6.6 Hz, 1.8 Hz, 2H), 4.05-4.03 (m, 2H), 2.45-2.36 (m, 1H), 2.21 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 136.0, 153.4, 131.3, 130.3, 126.1 (q, $J_{C\text{-}F}$ = 283.1 Hz), 122.8, 45.0 (q, $J_{C\text{-}F}$ = 25.9 Hz), 36.1 (q, $J_{C\text{-}F}$ = 4.1 Hz), 34.5, 28.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 23.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8.

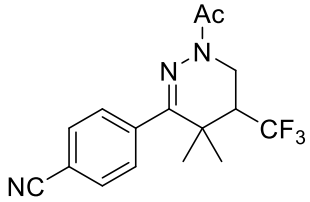


1-(4,4-Dimethyl-3-(naphthalen-2-yl)-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3o**, 48 mg, 70% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 3H), 7.49-7.43 (m, 3H), 7.40-7.36 (m, 1H), 4.21-4.10 (m, 2H), 2.56-2.48 (m, 1H), 2.34 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 154.3, 141.3, 140.3, 136.0, 129.1,

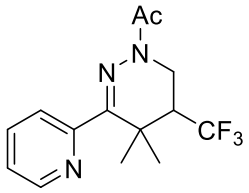
128.9, 126.6 (q, $J_{C\text{-}F}$ = 282.2 Hz), 127.7, 45.1 (q, $J_{C\text{-}F}$ = 25.8 Hz), 36.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 34.6, 28.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 23.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 21.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}F_3N_2O^+$ $[M+H]^+$ 349.1522, found 349.1525.



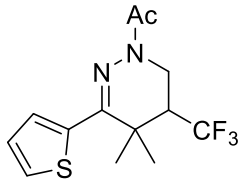
1-(4,4-Dimethyl-5-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3p**, 58 mg, 78% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 4.15-4.11 (m, 2H), 2.56-2.46 (m, 1H), 2.29 (s, 3H), 1.42 (s, 3H), 1.31 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 153.0, 140.6, 130.2 (q, $J_{C\text{-}F}$ = 30.1 Hz), 129.1, 126.01 (q, $J_{C\text{-}F}$ = 282.9 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 273.2 Hz), 44.7 (q, $J_{C\text{-}F}$ = 25.8 Hz), 36.2 (q, $J_{C\text{-}F}$ = 4.3 Hz), 34.5, 28.5 (q, $J_{C\text{-}F}$ = 1.4 Hz), 23.3 (q, $J_{C\text{-}F}$ = 1.7 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7, -63.9. HRMS (ESI) m/z calcd for $C_{16}H_{17}F_6N_2O^+$ $[M+H]^+$ 367.1240, found 367.1244.



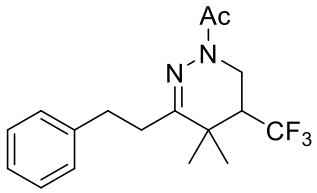
4-(1-Acetyl-4,4-dimethyl-5-(trifluoromethyl)-1,4,5,6-tetrahydropyridazin-3-yl)benzonitrile (**3q**, 46 mg, 71% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.3, 1.9 Hz, 2H), 7.50 (dd, J = 8.3, 1.9 Hz, 2H), 4.22-4.17 (m, 1H), 4.13-4.11 (m, 1H), 2.57-2.48 (m, 1H), 2.29 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 152.3, 141.6, 132.0, 129.4, 126.0 (q, $J_{C\text{-}F}$ = 283.0 Hz), 118.3, 112.4, 44.9 (q, $J_{C\text{-}F}$ = 25.9 Hz), 36.2 (q, $J_{C\text{-}F}$ = 4.1 Hz), 34.4, 28.6 (d, $J_{C\text{-}F}$ = 1.9 Hz), 23.4 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9. HRMS (ESI) m/z calcd for $C_{16}H_{17}F_3N_3O^+$ $[M+H]^+$ 324.1318, found 324.1322.



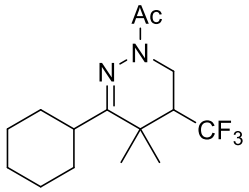
1-(4,4-Dimethyl-3-(pyridin-2-yl)-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one [错误!未定义书签。] (**3r**, 30 mg, 50% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57-8.56 (m, 1H), 7.74-7.69 (m, 1H), 7.64-7.61 (m, 1H), 7.28-7.25 (m, 1H), 4.19-4.15 (m, 1H), 4.10-4.05 (m, 1H), 2.48-2.43 (m, 1H), 2.38 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 156.1, 152.6, 147.8, 136.4, 126.3 (q, $J_{C\text{-}F}$ = 280.4 Hz), 123.1, 123.1, 45.5 (q, $J_{C\text{-}F}$ = 25.1 Hz), 35.9 (q, $J_{C\text{-}F}$ = 4.2 Hz), 34.8, 28.0, 22.5, 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.6.



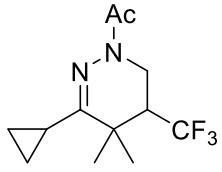
1-(4,4-Dimethyl-3-(thiophen-2-yl)-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3s**, 36 mg, 58% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.20 (m, 3H), 4.31-4.27 (m, 1H), 3.82-3.78 (m, 1H), 2.53-2.46 (m, 1H), 2.39 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 147.2, 144.4, 131.6 (q, $J_{C\text{-}F}$ = 25.8 Hz), 128.4 (q, $J_{C\text{-}F}$ = 3.9 Hz), 126.1 (q, $J_{C\text{-}F}$ = 280.1 Hz), 126.0, 45.8 (q, $J_{C\text{-}F}$ = 25.6 Hz), 35.6 (q, $J_{C\text{-}F}$ = 4.5 Hz), 35.0, 28.1, 22.9, 21.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.6. HRMS (ESI) m/z calcd for $C_{13}H_{16}F_3N_2OS^+$ $[M+H]^+$ 305.0930, found 305.0933.



1-(4,4-Dimethyl-3-phenethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3t**, 34 mg, 52% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 4.23-4.18 (m, 1H), 3.72-3.66 (m, 1H), 2.94-2.90 (m, 2H), 2.63-2.59 (m, 2H), 2.40-2.34 (m, 1H), 2.31 (s, 3H), 1.29 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 154.3, 141.7, 128.4, 128.3, 126.3 (q, $J_{C\text{-}F}$ = 282.8 Hz), 126.1, 44.8 (q, $J_{C\text{-}F}$ = 25.3 Hz), 35.5 (q, $J_{C\text{-}F}$ = 4.3 Hz), 34.6, 32.9, 32.4, 26.4 (d, $J_{C\text{-}F}$ = 2.1 Hz), 21.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.0. HRMS (ESI) m/z calcd for $C_{17}H_{22}F_3N_2O^+$ $[M+H]^+$ 327.1679, found 327.1680.

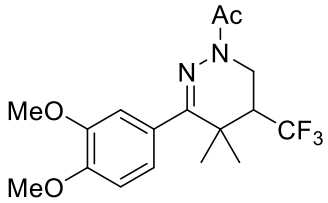


1-(3-Cyclohexyl-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one [1] (**3u**, 42 mg, 68% yield), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25-4.22 (m, 1H), 3.41-3.37 (m, 1H), 2.29-2.24 (m, 2H), 2.22 (s, 3H), 1.73-1.62 (m, 6H), 1.41-1.31 (m, 3H), 1.26 (s, 3H), 1.23-1.21 (m, 1H), 1.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 160.2, 128.1 (q, $J_{C\text{-}F}$ = 280.1 Hz), 45.4 (q, $J_{C\text{-}F}$ = 25.1 Hz), 40.0, 35.2, 35.1 (q, $J_{C\text{-}F}$ = 4.4 Hz), 33.8, 33.3, 26.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 26.3 (d, $J_{C\text{-}F}$ = 2.3 Hz), 25.9, 21.4, 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.2.

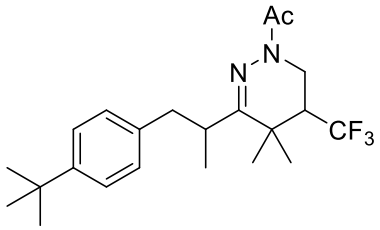


1-(3-Cyclopropyl-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3v**, 26 mg, 48% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.28-4.23 (m, 1H), 3.59-3.53 (m, 1H), 2.40-2.30 (m, 1H), 2.23 (s, 3H), 1.64-1.60 (m, 1H), 1.44 (s, 3H), 1.38 (s, 3H),

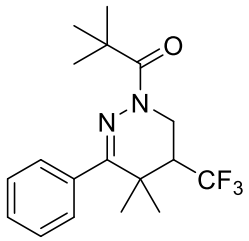
0.85-0.75 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 157.0, 128.2 (q, $J_{C\text{-}F}$ = 280.2 Hz), 45.1 (q, $J_{C\text{-}F}$ = 25.1 Hz), 35.4, 35.2 (q, $J_{C\text{-}F}$ = 4.4 Hz), 27.1, 22.1, 20.9, 11.9, 8.1, 7.81. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.1. HRMS (ESI) m/z calcd for $C_{12}H_{18}F_3N_2O^+$ $[M+H]^+$ 263.1366, found 263.1370.



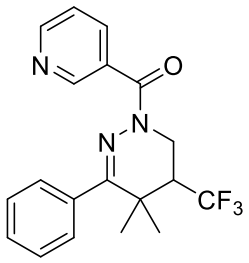
1-(3-(3,4-Dimethoxyphenyl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one (**3w**, 36 mg, 50% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87-6.84 (m, 1H), 6.81-6.78 (m, 2H), 4.10-3.98 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 2.46-2.36 (m, 1H), 2.24 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 154.3, 149.3, 148.4, 129.8, 129.1, 126.3 (q, $J_{C\text{-}F}$ = 280.2 Hz), 121.3, 112.2, 110.5, 56.0, 55.9, 45.0 (q, $J_{C\text{-}F}$ = 25.2 Hz), 36.0 (q, $J_{C\text{-}F}$ = 4.4 Hz), 34.7, 28.5, 23.3, 21.2.^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8. HRMS (ESI) m/z calcd for $C_{17}H_{22}F_3N_2O_3^+$ $[M+H]^+$ 359.1577, found 359.1579.



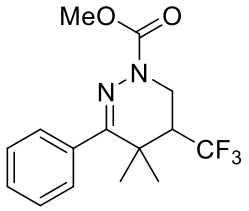
1-(2-(1-(4-(*tert*-Butyl)phenyl)propan-2-yl)-4,4-dimethyl-5-(trifluoromethyl)-5,6-dihydropyri midin-1(4*H*)-yl)ethan-1-one (**3x**, 44 mg, 55% yield), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2H), 7.06-7.02 (m, 2H), 4.43-4.40 (m, 0.52H), 4.10-4.07 (m, 0.52H), 3.70-3.66 (m, 0.53H), 3.25-3.20 (m, 0.49H), 2.93-2.86 (m, 1H), 2.81-2.74 (m, 1H), 2.68-2.62 (m, 1H), 2.38 (s, 3H), 2.33-2.29 (m, 0.54H), 2.23-2.20 (m, 0.44H), 1.31-1.26 (m, 12H), 1.19-1.16 (m, 3H), 0.81 (s, 1.50H), 0.77 (s, 1.51H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.7, 159.6, 159.2, 149.2, 137.6, 137.5, 129.0, 128.9, 126.3 (q, $J_{C\text{-}F}$ = 282.5 Hz), 125.1, 125.1, 45.5 (q, $J_{C\text{-}F}$ = 25.1 Hz), 44.8 (q, $J_{C\text{-}F}$ = 25.1 Hz), 43.1, 42.5, 37.6, 37.5, 35.6, 35.3 (q, $J_{C\text{-}F}$ = 3.6 Hz), 35.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 34.9, 34.4, 31.4, 31.2, 25.9, 25.7, 21.8, 21.6, 21.2, 21.1, 19.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.2. HRMS (ESI) m/z calcd for $C_{22}H_{32}F_3N_2O^+$ $[M+H]^+$ 397.2461, found 397.2463.



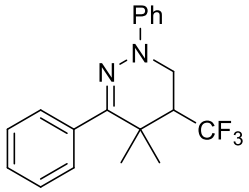
1-(4,4-Dimethyl-3-phenyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)-2,2-dimethylpr opan-1-one[1] (**3y**, 42 mg, 62% yield), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.37 (m, 3H), 7.35-7.32 (m, 2H), 4.18-4.13 (m, 1H), 4.07-4.02 (m, 1H), 2.53-2.43 (m, 1H), 1.39 (s, 3H), 1.29 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.4, 152.4, 137.4, 128.5, 128.2, 128.0, 126.3 (q, $J_{C\text{-}F}$ = 280.2 Hz), 45.2 (q, $J_{C\text{-}F}$ = 25.2 Hz), 40.2, 37.0 (q, $J_{C\text{-}F}$ = 4.4 Hz), 34.3, 28.7, 27.7, 23.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9.



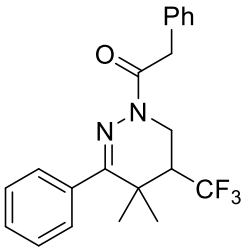
(4,4-Dimethyl-3-phenyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)(pyridin-3-yl)methanone (**3z**, 36 mg, 50% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96-8.95 (m, 1H), 8.58-8.57 (m, 1H), 8.04-8.02 (m, 1H), 7.36-7.25 (m, 6H), 4.42-4.37 (m, 1H), 4.26-4.21 (m, 1H), 2.67-2.62 (m, 1H), 1.47 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 156.2, 151.0, 151.0, 137.7, 136.5, 130.0, 128.6, 128.4, 128.2, 126.2 (q, $J_{C\text{-}F}$ = 280.7 Hz), 122.6, 45.6 (q, $J_{C\text{-}F}$ = 25.5 Hz), 37.2 (q, $J_{C\text{-}F}$ = 4.2 Hz), 34.8, 28.9, 23.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3N_3O^+$ $[M+H]^+$ 362.1475, found 332.1478.



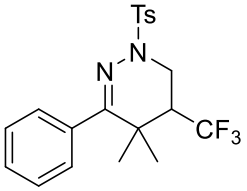
Methyl 4,4-dimethyl-3-phenyl-5-(trifluoromethyl)-5,6-dihydropyridazine-1(4*H*)-carboxylate (**3aa**, 38 mg, 60% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.34 (m, 3H), 7.33-7.29 (m, 2H), 4.20-4.13 (m, 1H), 4.04-3.99 (m, 1H), 3.85 (s, 3H), 2.59-2.49 (m, 1H), 1.36 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 154.7, 136.7, 129.0, 128.4, 128.1, 126.2 (q, $J_{C\text{-}F}$ = 283.0 Hz), 54.0, 45.3 (q, $J_{C\text{-}F}$ = 25.8 Hz), 38.6 (q, $J_{C\text{-}F}$ = 4.3 Hz), 34.7, 28.2, 23.1 (d, $J_{C\text{-}F}$ = 4.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9. HRMS (ESI) m/z calcd for $C_{15}H_{18}F_3N_2O_2^+$ $[M+H]^+$ 315.1315, found 315.1320.



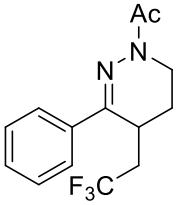
4,4-Dimethyl-1,3-diphenyl-5-(trifluoromethyl)-1,4,5,6-tetrahydropyridazine (**3ab**, 36 mg, 53% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.38-7.28 (m, 8H), 4.39-4.33 (m, 1H), 4.24-4.19 (m, 1H), 2.65-2.56 (m, 1H), 1.45 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 155.0, 136.4, 134.0, 130.7, 130.147, 128.5, 128.0, 127.4, 126.2 (q, $J_{C\text{-}F}$ = 283.2 Hz), 45.5 (q, $J_{C\text{-}F}$ = 25.6 Hz), 37.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 34.7, 29.0 (d, $J_{C\text{-}F}$ = 1.6 Hz), 23.4 (d, $J_{C\text{-}F}$ = 2.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}F_3N_2^+$ $[M+H]^+$ 333.1573, found 333.1577.



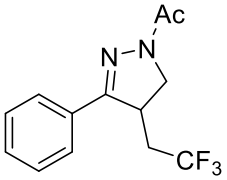
1-(4,4-Dimethyl-3-phenyl-5-(trifluoromethyl)-5,6-dihydropyridazin-1(4*H*)-yl)-2-phenylethan-1-one[1] (**3ac**, 44 mg, 60% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.38 (m, 3H), 7.29-7.20 (m, 7H), 4.14-4.06 (m, 2H), 4.02-4.01 (m, 2H), 2.51-2.43 (m, 1H), 1.36 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 154.9, 137.0, 135.5, 129.6, 128.7, 128.5, 128.3, 128.1, 126.6, 126.2 (q, $J_{C\text{-}F}$ = 280.4 Hz), 44.9 (q, $J_{C\text{-}F}$ = 25.4 Hz), 41.0, 40.0, 36.4 (d, $J_{C\text{-}F}$ = 4.2 Hz), 34.7, 28.4, 23.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8.



4,4-Dimethyl-3-phenyl-1-tosyl-5-(trifluoromethyl)-1,4,5,6-tetrahydropyridazine[1] (**3ad**, 44 mg, 53% yield), white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.36-7.31 (m, 5H), 7.12-7.10 (m, 2H), 4.06-4.02 (m, 1H), 3.25-3.20 (m, 1H), 2.72-2.63 (m, 1H), 2.46 (s, 3H), 1.27 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.4, 136.2, 132.2, 129.4, 129.1, 128.6, 128.4, 127.8, 126.3 (q, $J_{C\text{-}F}$ = 280.1 Hz), 46.2 (q, $J_{C\text{-}F}$ = 25.4 Hz), 40.6 (q, $J_{C\text{-}F}$ = 3.4 Hz), 35.3, 27.3, 22.8, 21.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.1.



1-(3-Phenyl-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4*H*)-yl)ethan-1-one[3] (**5aa**, 40 mg, 70% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 7.45-7.40 (m, 3H), 4.50-4.44 (m, 1H), 3.40-3.36 (m, 1H), 3.26-3.19 (m, 1H), 2.43 (s, 3H), 2.32-2.29 (m, 1H), 2.27-2.15 (m, 2H), 2.00-1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 146.2, 135.2, 129.6, 128.9, 126.3 (q, $J_{C\text{-}F}$ = 275.3 Hz), 125.6, 35.4 (q, $J_{C\text{-}F}$ = 27.9 Hz), 34.5, 25.1 (q, $J_{C\text{-}F}$ = 2.3 Hz), 21.3, 21.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.9.



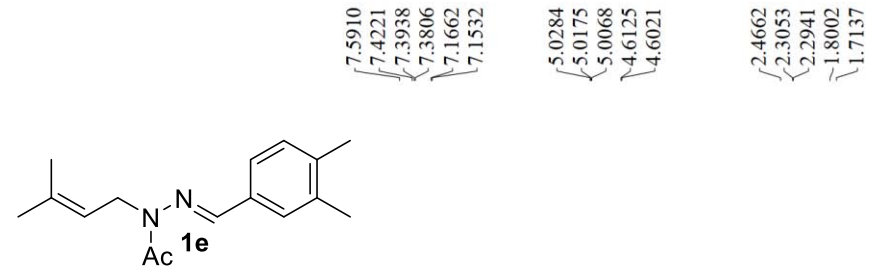
1-(3-Phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1*H*-pyrazol-1-yl)ethan-1-one[3] (**5ab**, 38 mg, 69% yield), colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.47-7.45 (m, 3H), 4.17-4.08 (m, 2H), 3.96-3.86 (m, 1H), 2.58-2.49 (m, 1H), 2.40 (s, 3H), 2.27-2.16 (m, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 169.6, 155.5, 130.3, 129.5, 129.2, 126.5, 126.0 (q, J_{C-F} = 278.3 Hz), 50.3 (d, J_{C-F} = 1.6 Hz), 38.5 (d, J_{C-F} = 2.6 Hz), 36.4 (q, J_{C-F} = 28.4 Hz), 21.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.3.

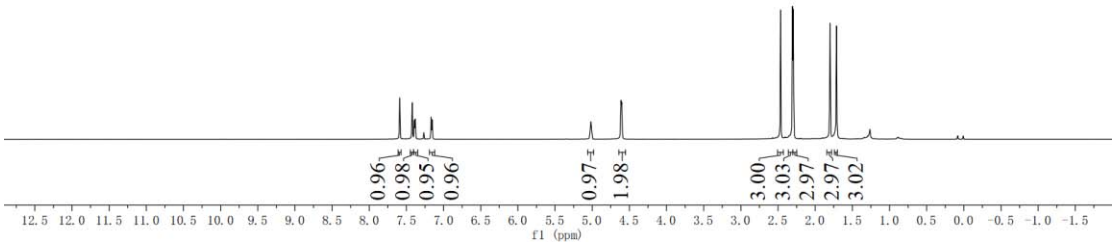
6. References

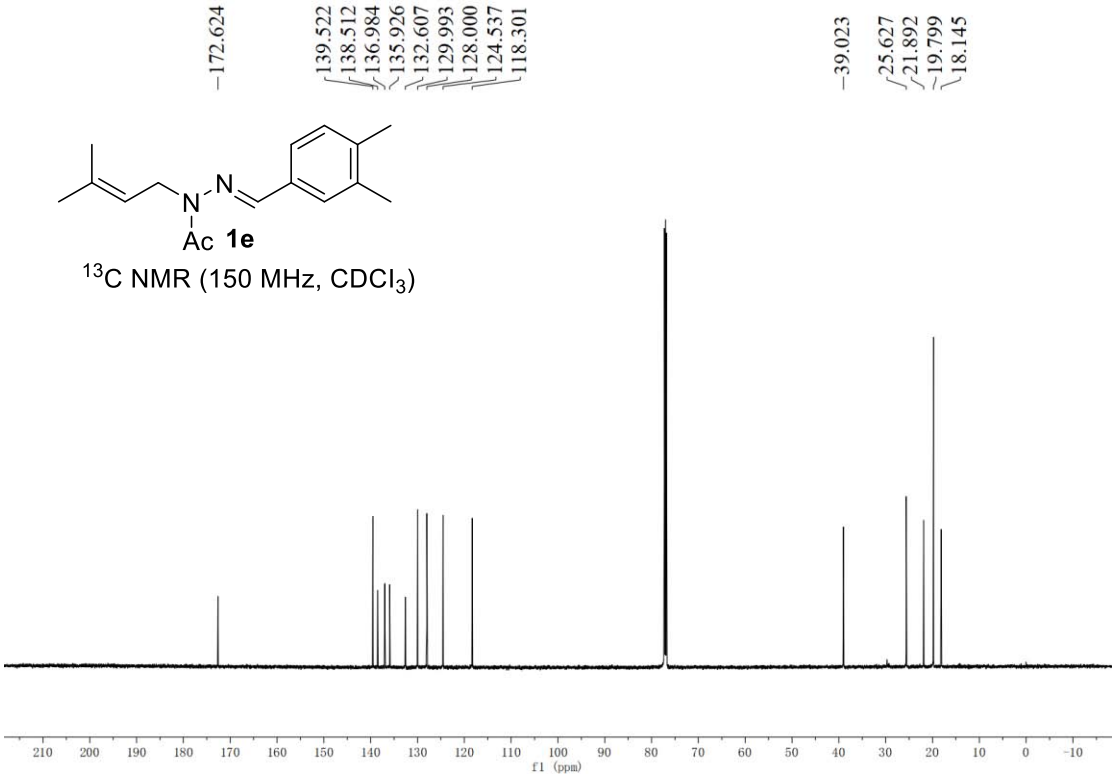
1. Y. Ren, Y. Zhou, K.-H. Wang, J. Wang, D. Huang and Y. Hu, *Org. Lett*., 2025, **27**, 7033.
2. H. Jia, A. P. Häring, F. Berger, L. Zhang and T. Ritter, *J. Am. Chem. Soc*., 2021, **143**, 7623.
3. L. Liu, C. Xiang, C. Pan and J.-T. Yu, *Chem. Commun*., 2024, **60**, 10764.

7. Copies of ^{1}H NMR and ^{13}C NMR Spectra

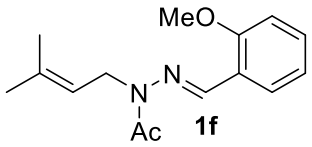


^{1}H NMR (600 MHz, $CDCl_3$)



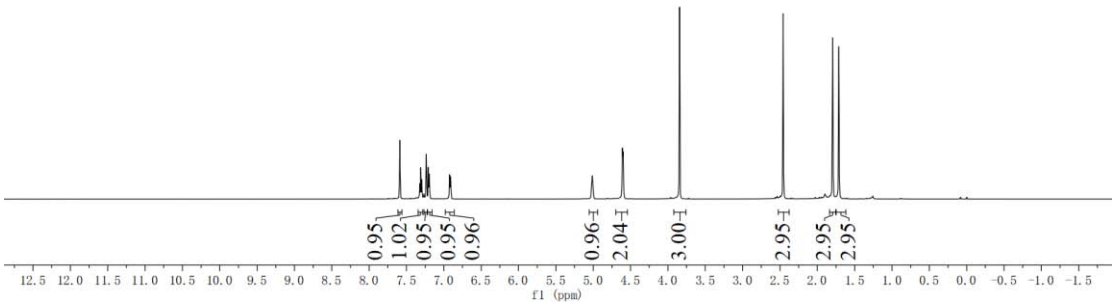


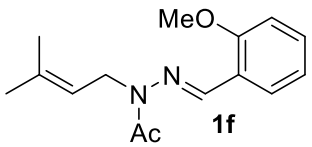
^{13}C NMR (150 MHz, $CDCl_3$)



1f

^{1}H NMR (600 MHz, $CDCl_3$)





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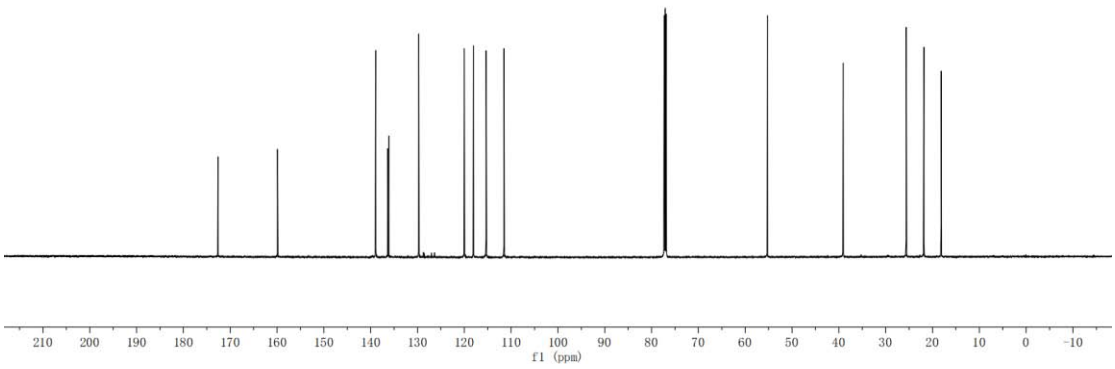
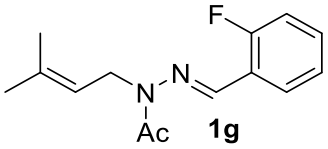
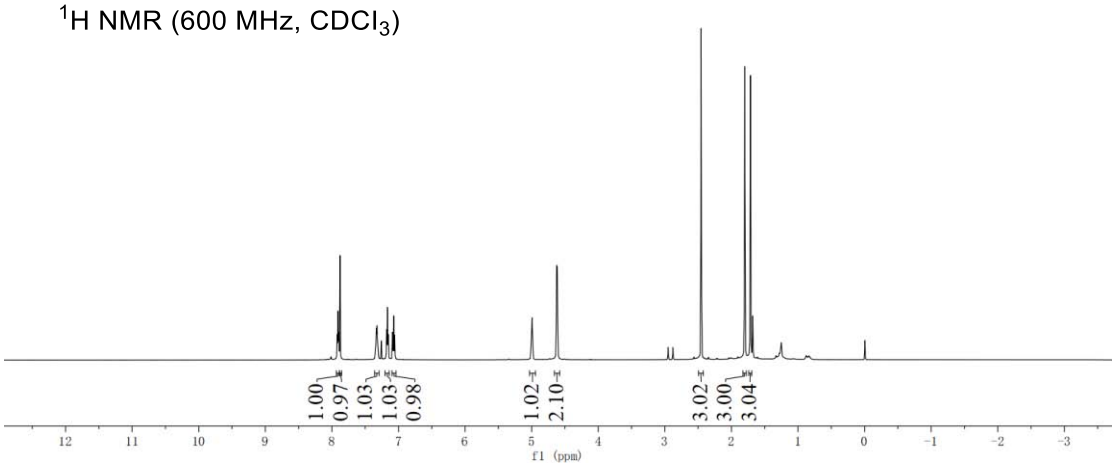
^{13}C NMR (150 MHz, $CDCl_3$)

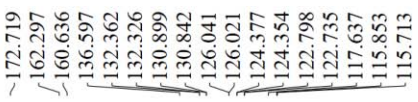


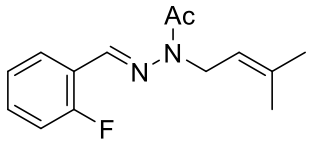


1g

^{1}H NMR (600 MHz, $CDCl_3$)

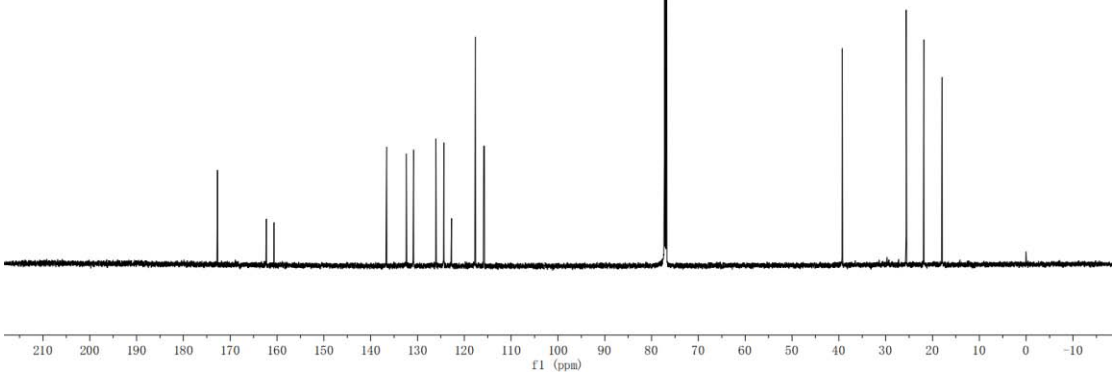


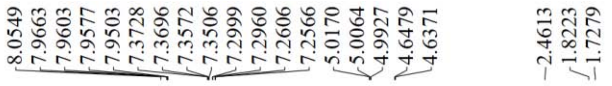


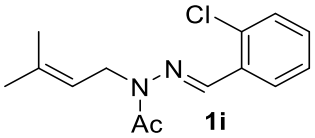


1g

^{13}C NMR (150 MHz, $CDCl_3$)

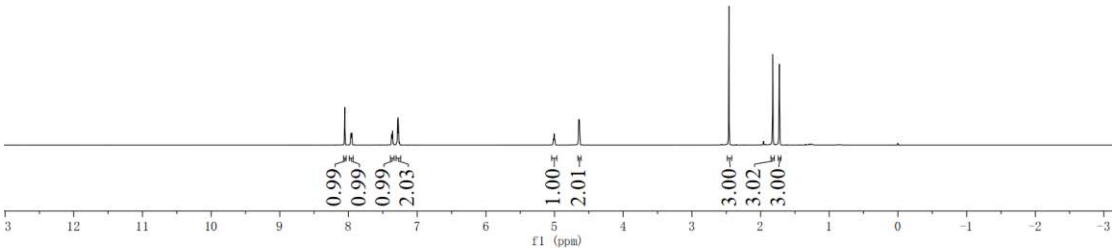


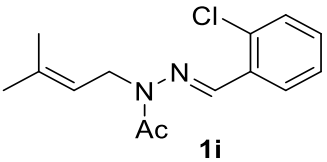




1i

^{1}H NMR (600 MHz, $CDCl_3$)





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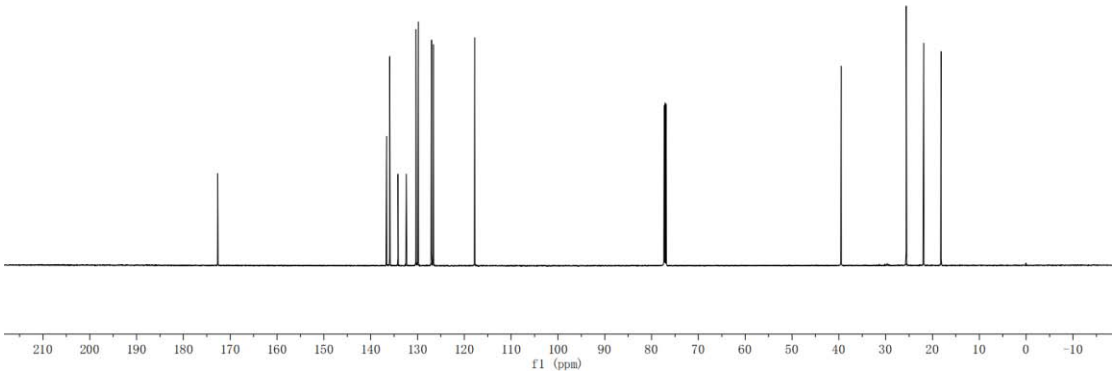
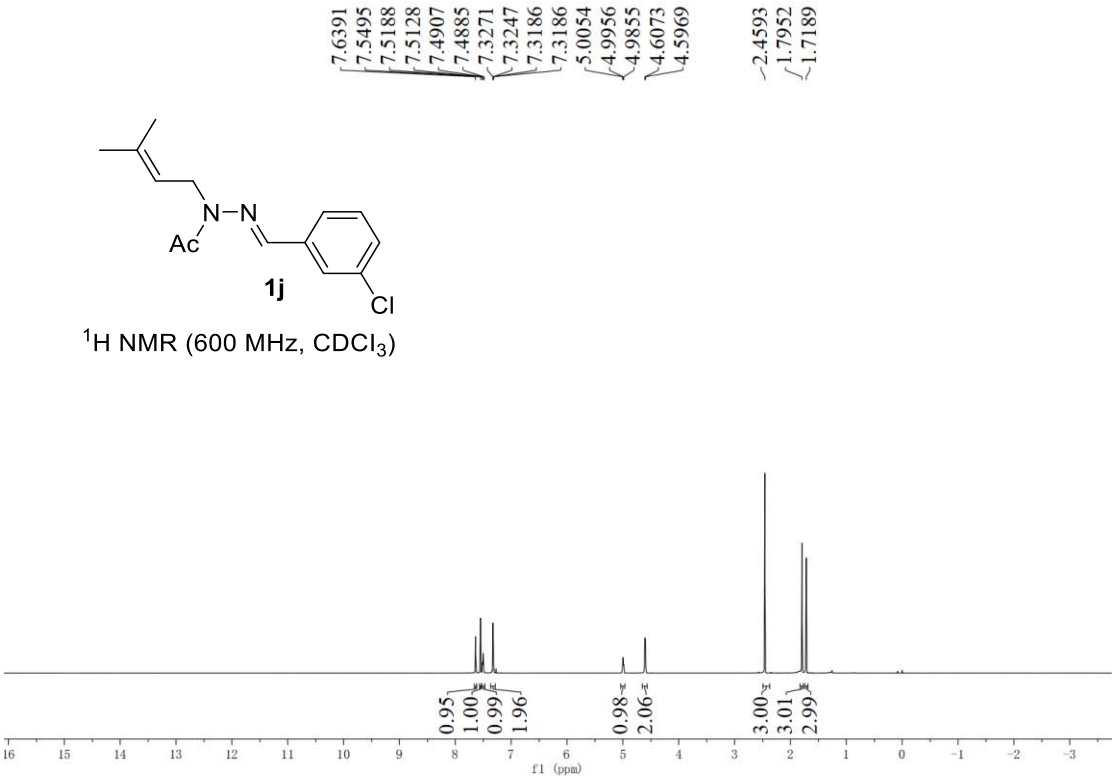
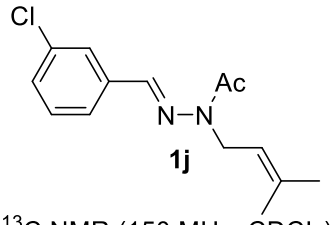
^{13}C NMR (150 MHz, $CDCl_3$)



1j

^{1}H NMR (600 MHz, $CDCl_3$)





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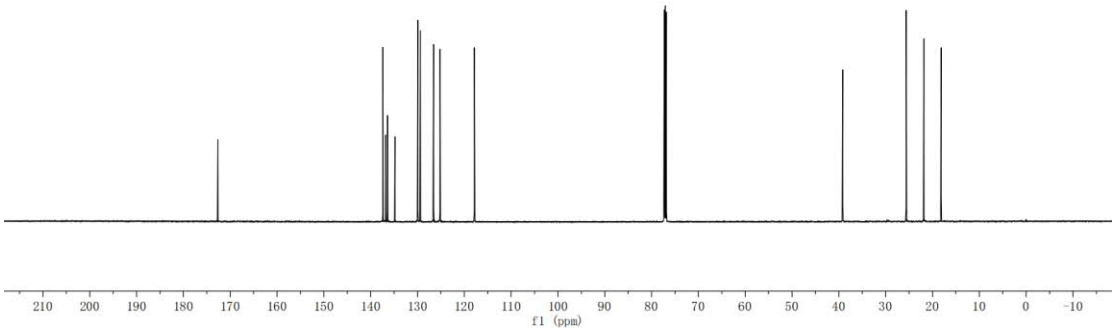
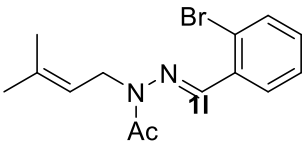
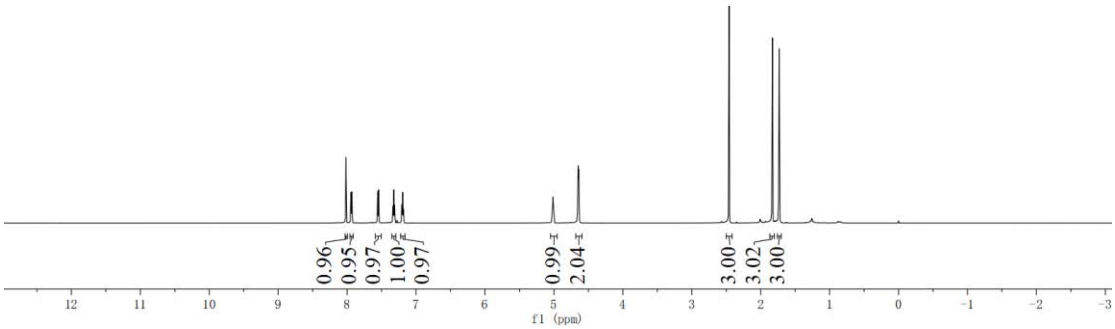
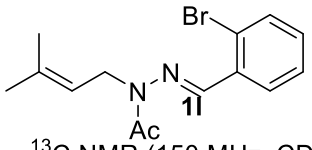


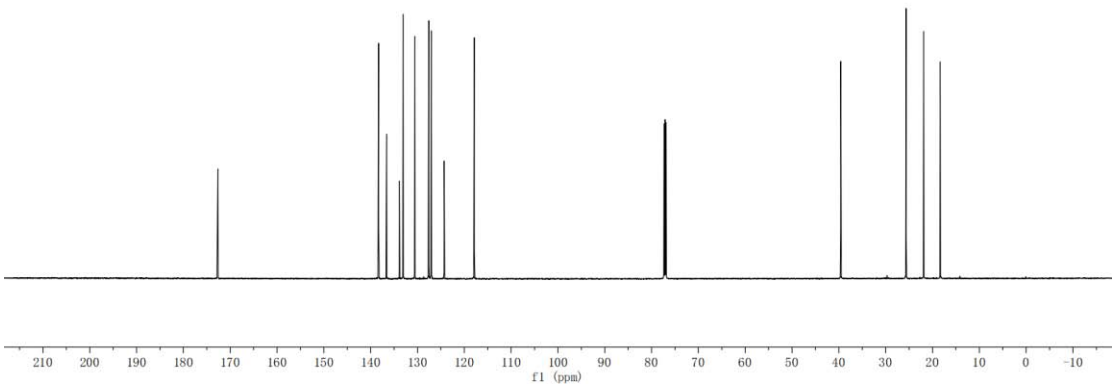


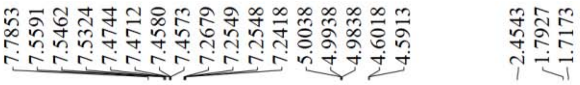
^{1}H NMR (600 MHz, $CDCl_3$)

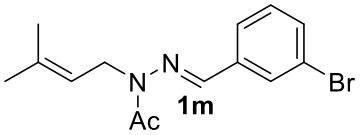




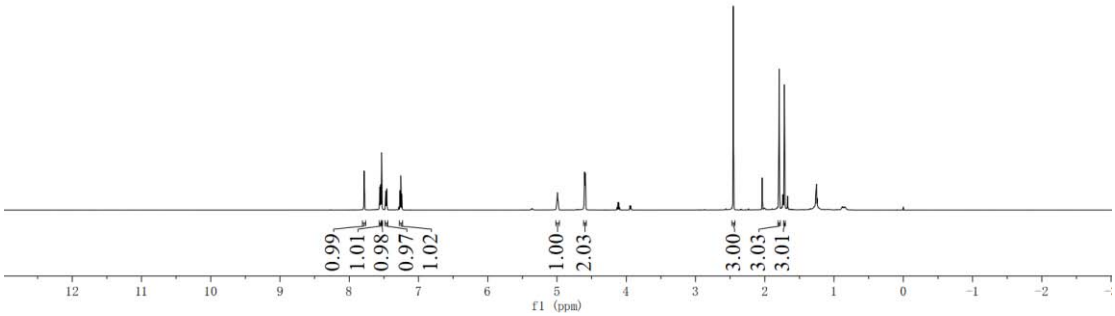
^{13}C NMR (150 MHz, $CDCl_3$)

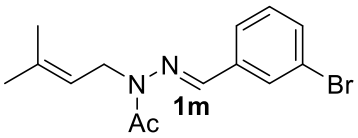




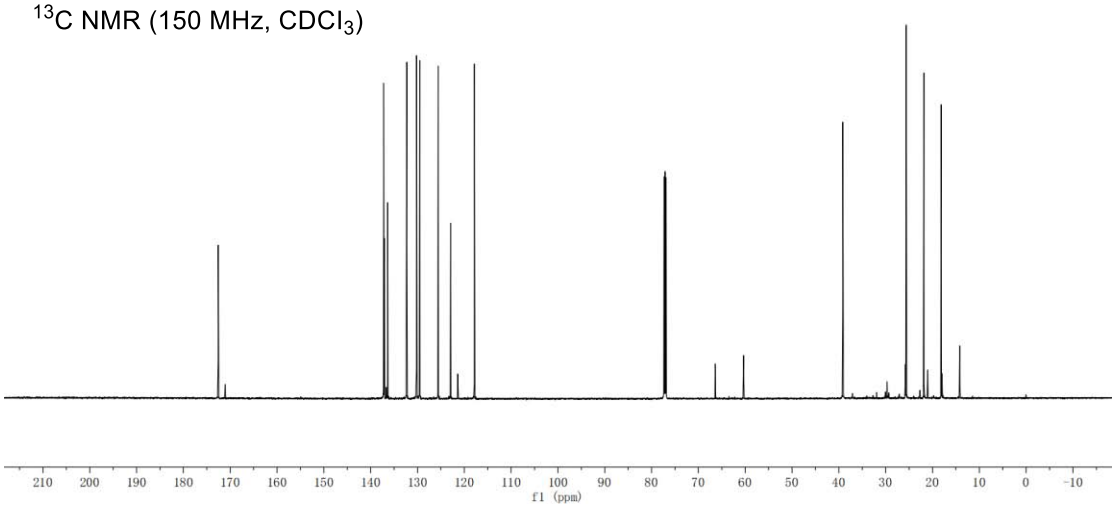


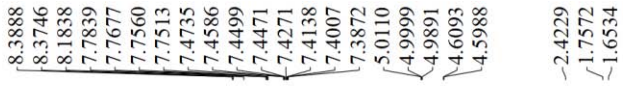
^{1}H NMR (600 MHz, $CDCl_3$)

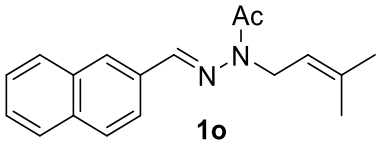




^{13}C NMR (150 MHz, $CDCl_3$)

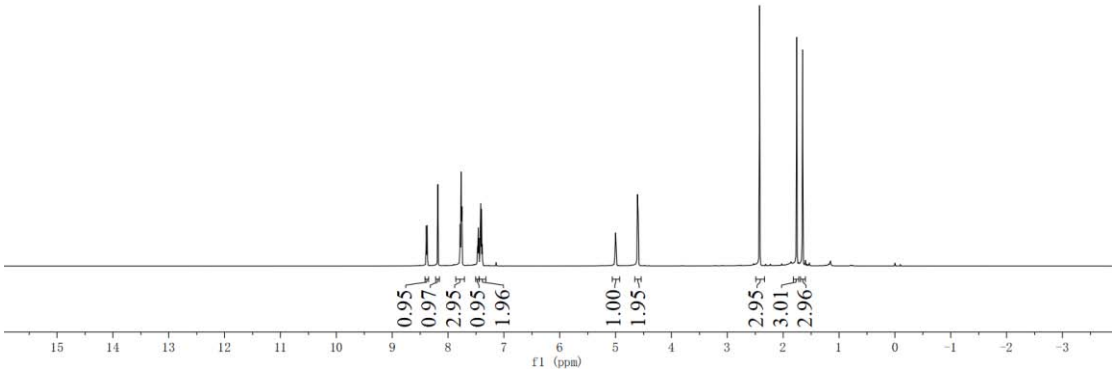


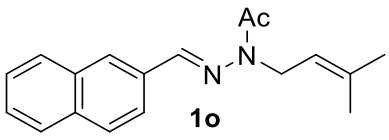




1o

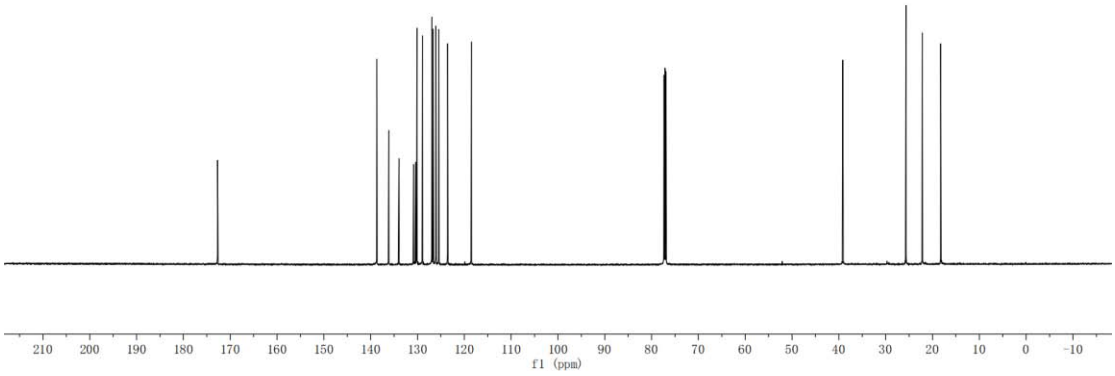
^{1}H NMR (600 MHz, $CDCl_3$)



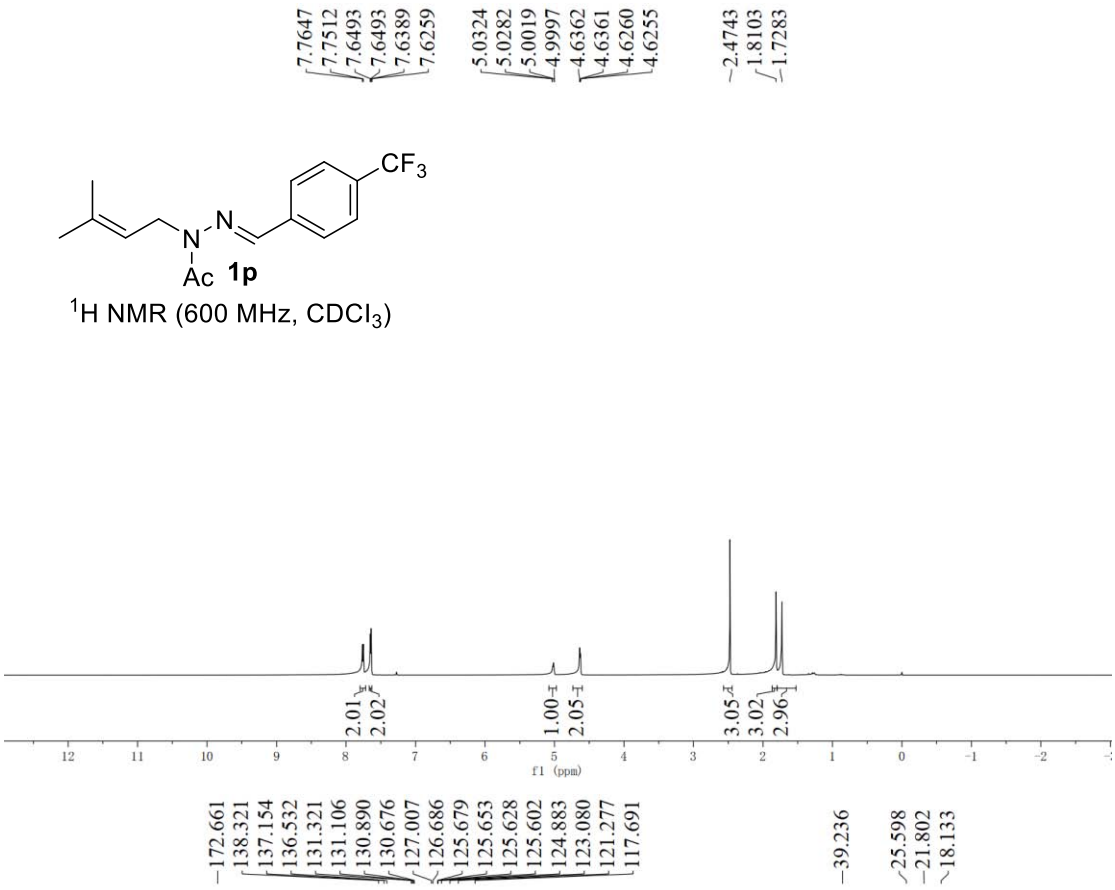


1o

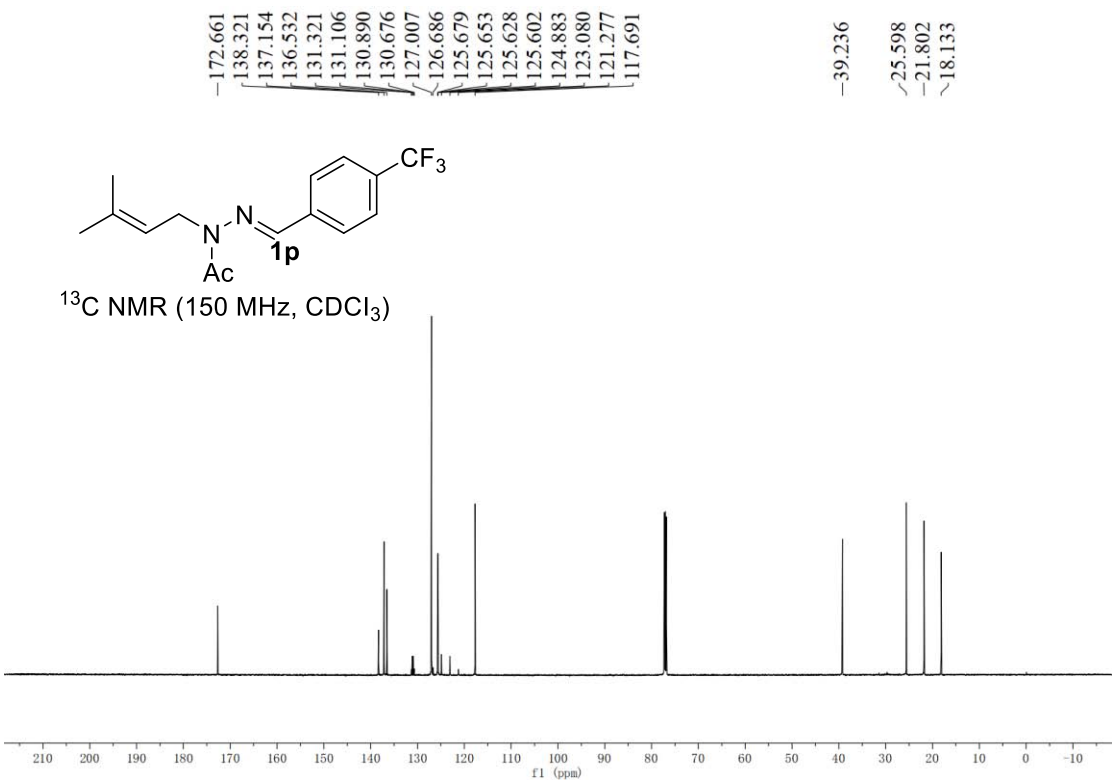
^{13}C NMR (150 MHz, $CDCl_3$)

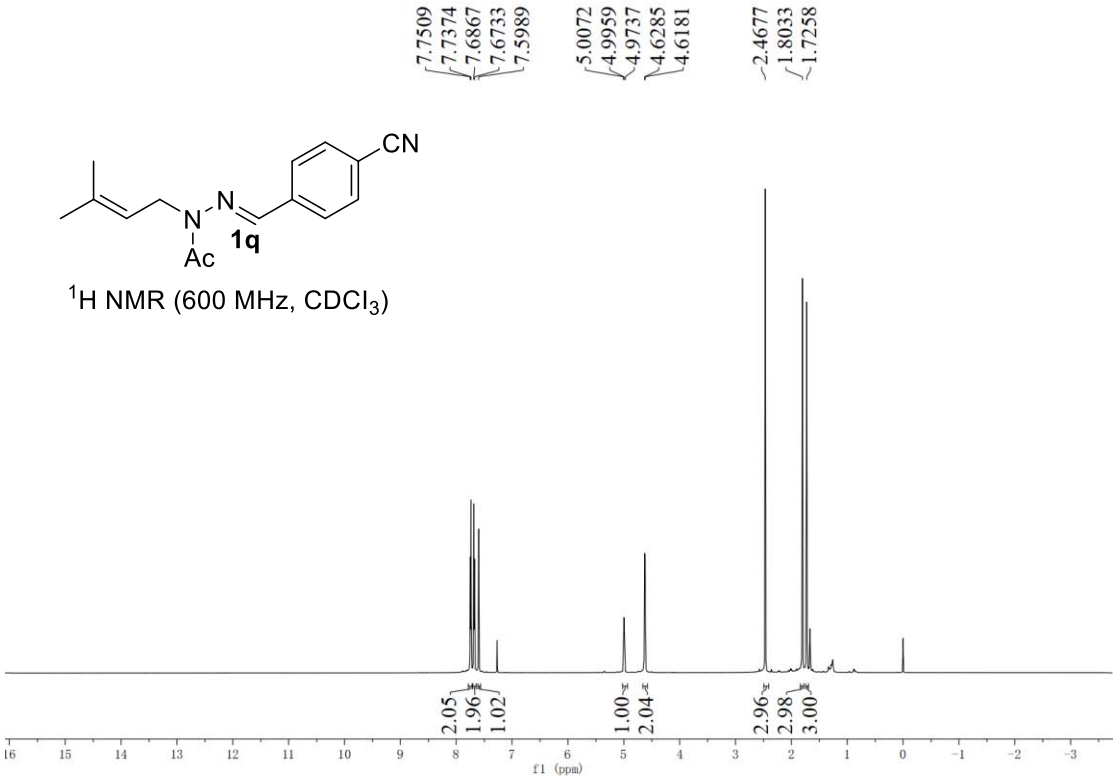


^{1}H NMR (600 MHz, $CDCl_3$)

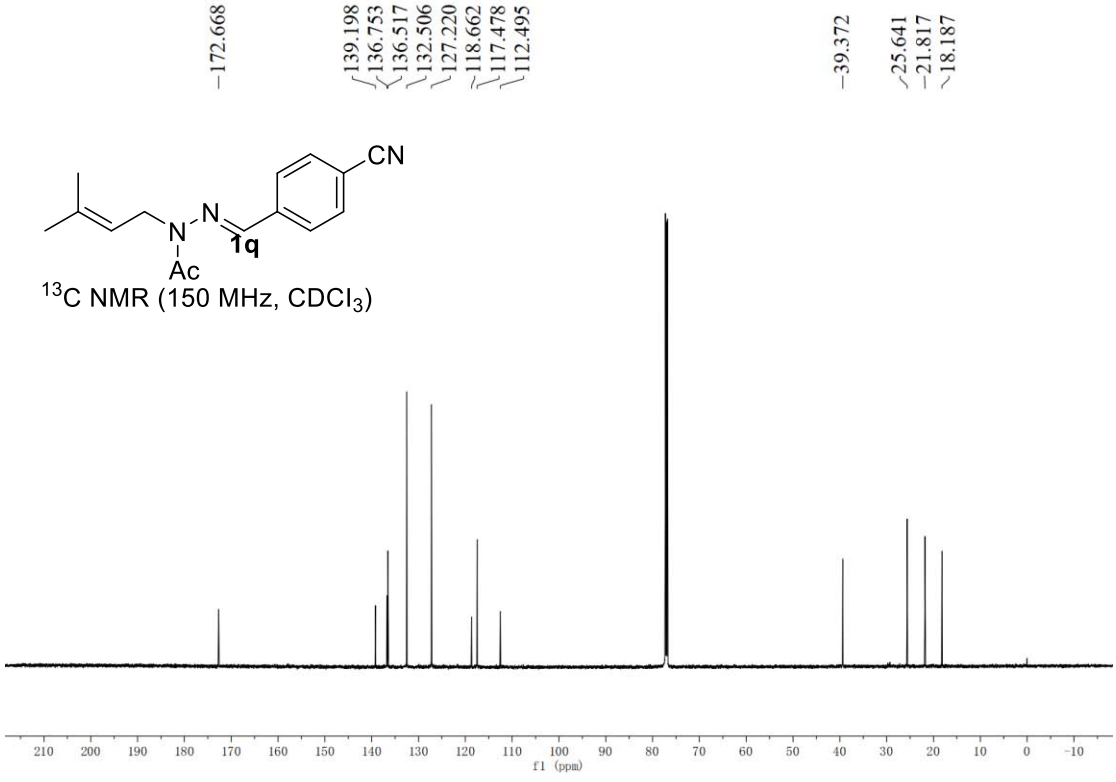


^{13}C NMR (150 MHz, $CDCl_3$)

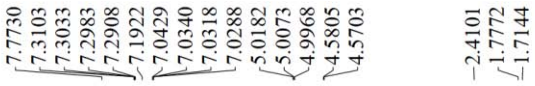


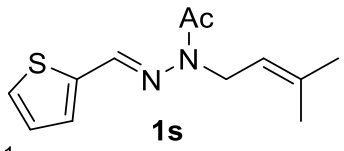


^{1}H NMR (600 MHz, $CDCl_3$)



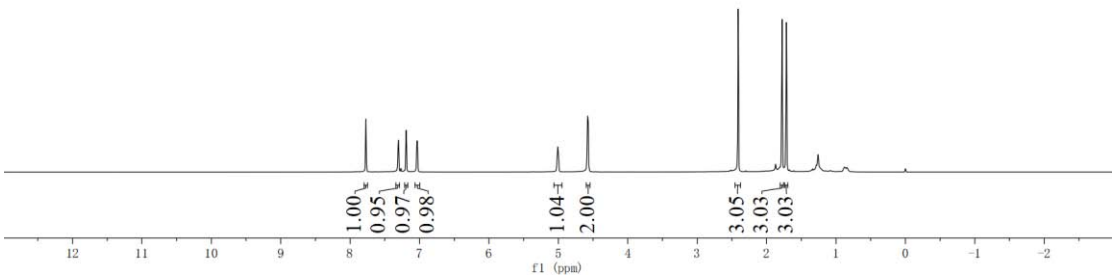
^{13}C NMR (150 MHz, $CDCl_3$)

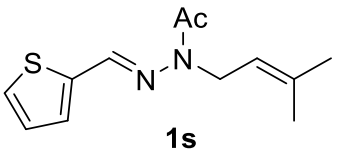




1s

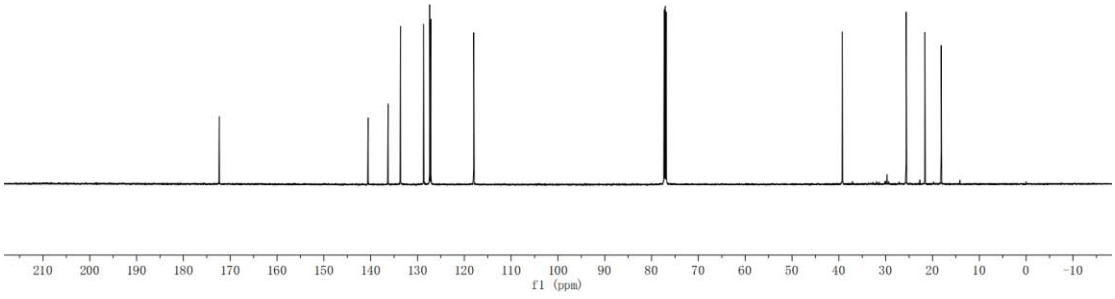
^{1}H NMR (600 MHz, $CDCl_3$)

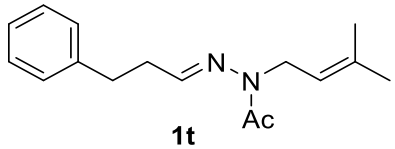




1s

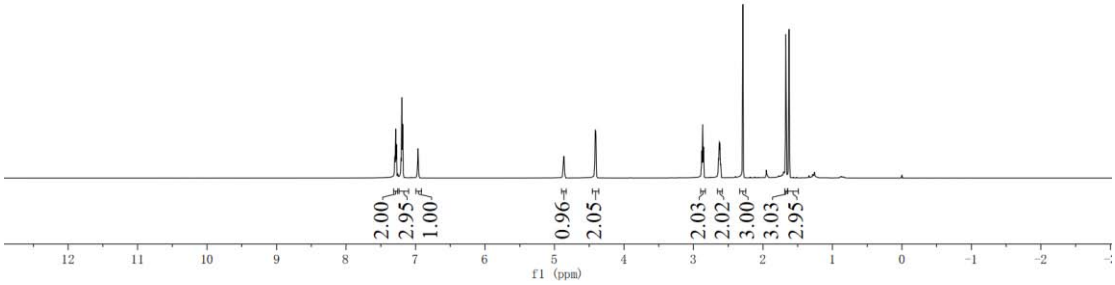
^{13}C NMR (150 MHz, $CDCl_3$)

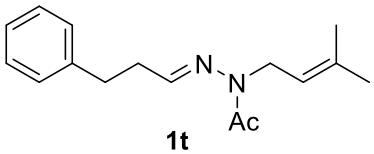




1t

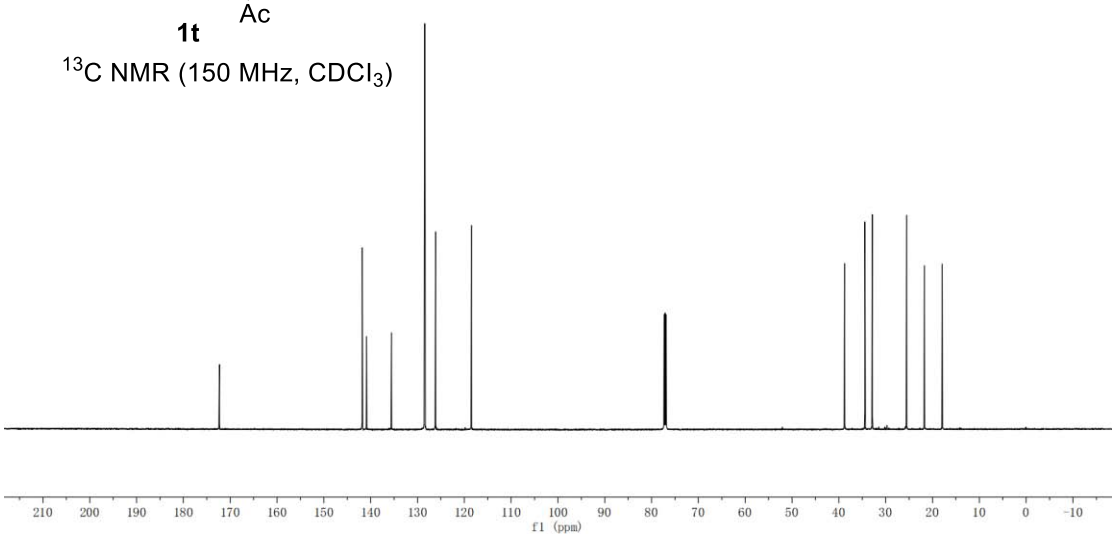
^{1}H NMR (600 MHz, $CDCl_3$)





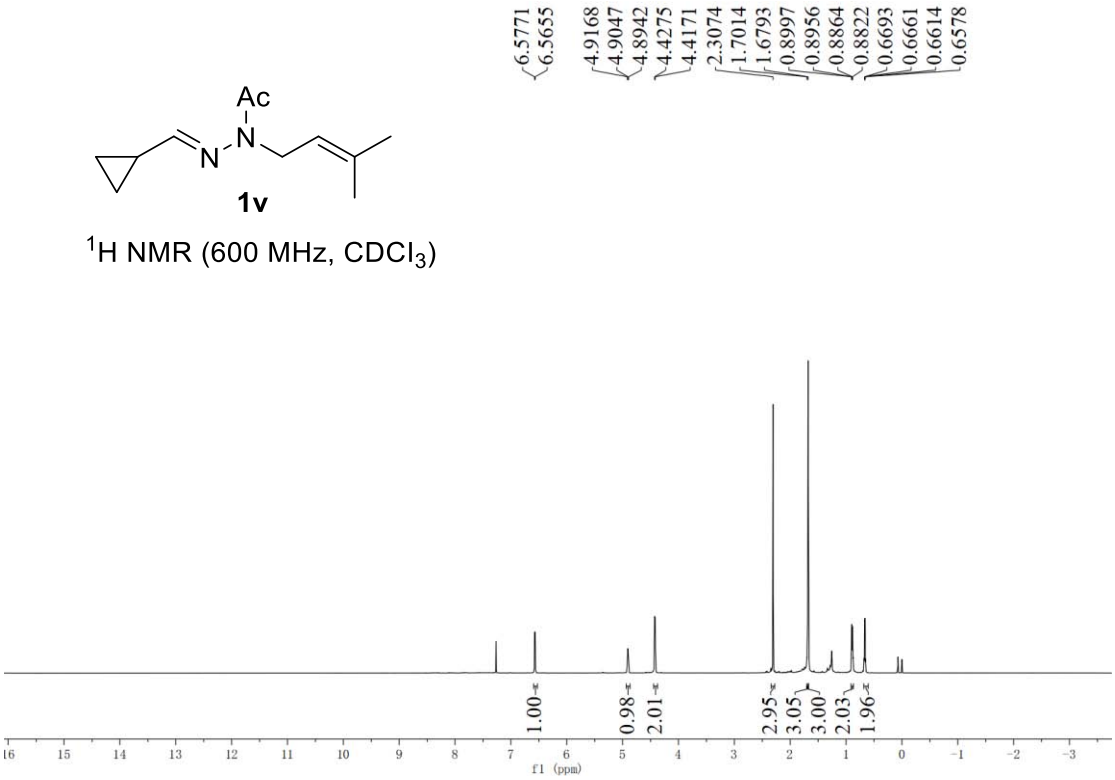
1t

^{13}C NMR (150 MHz, $CDCl_3$)



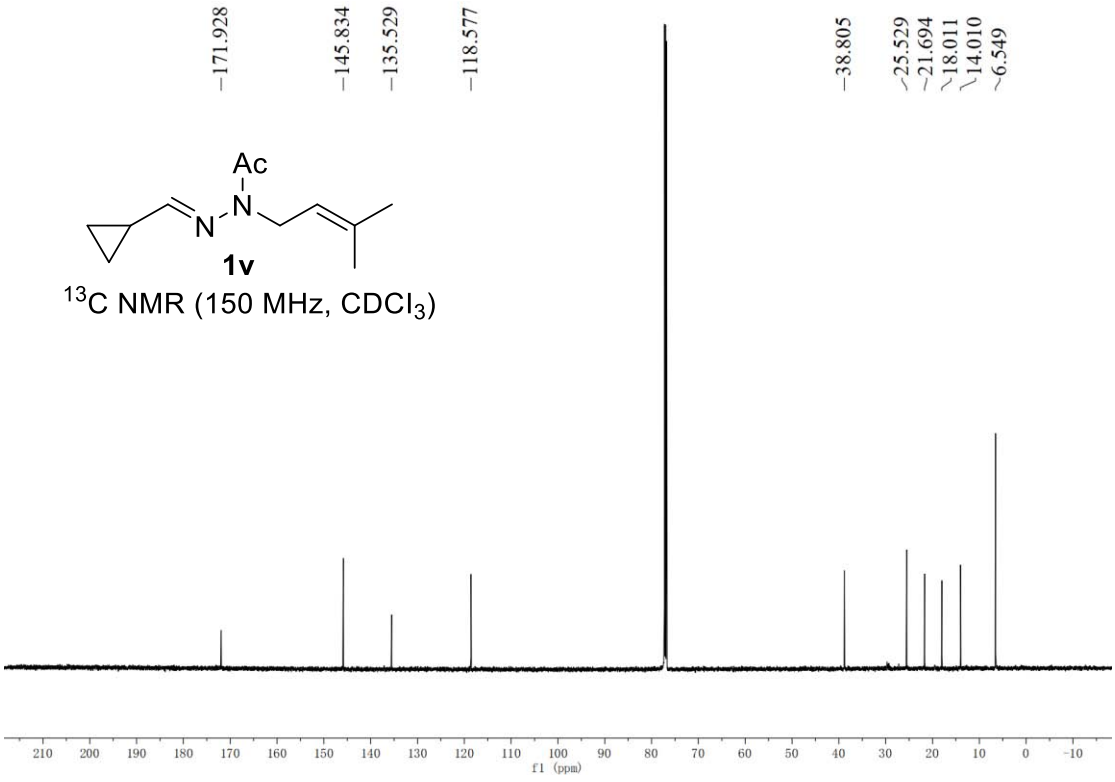
1v

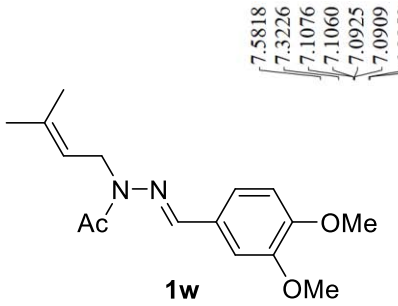
^{1}H NMR (600 MHz, $CDCl_3$)



1v

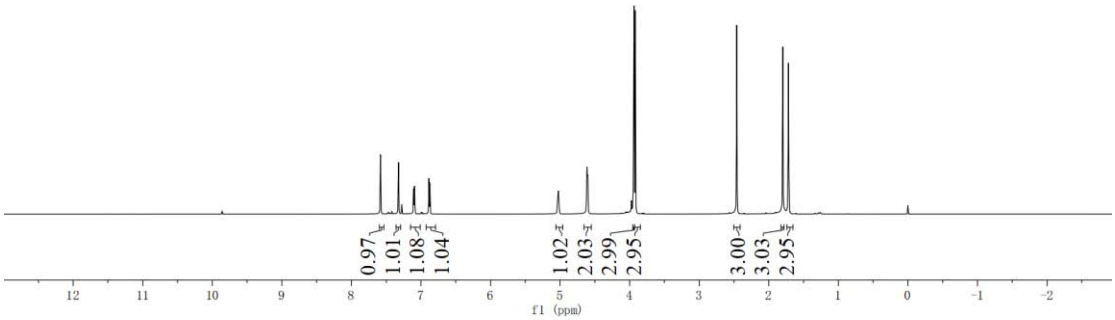
^{13}C NMR (150 MHz, $CDCl_3$)





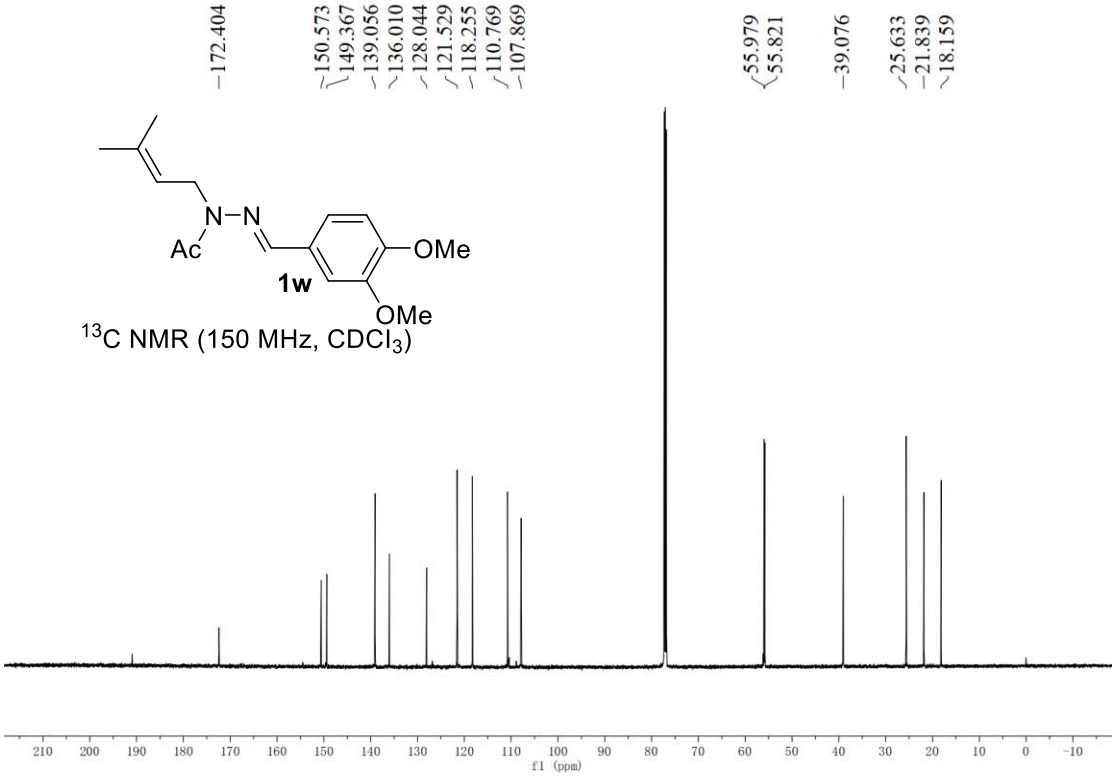
1w

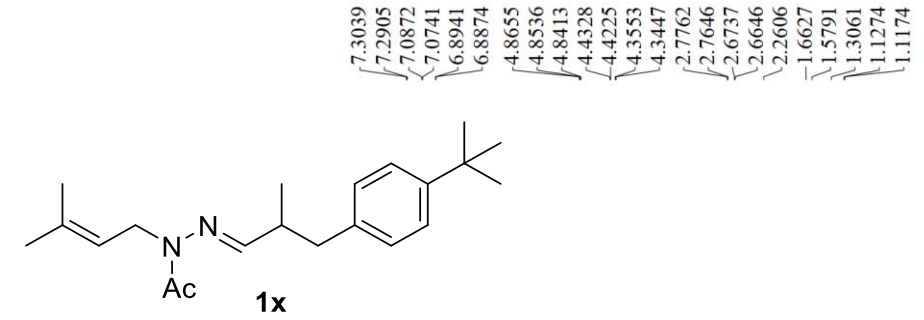
^{1}H NMR (600 MHz, $CDCl_3$)



1w

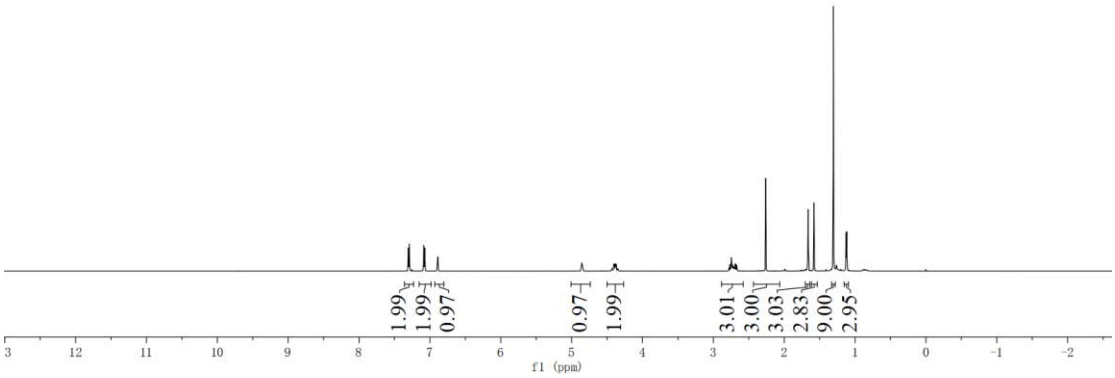
^{13}C NMR (150 MHz, $CDCl_3$)

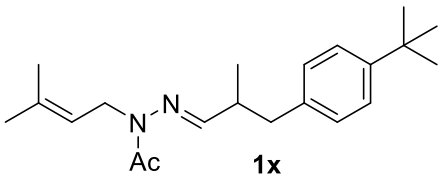




1x

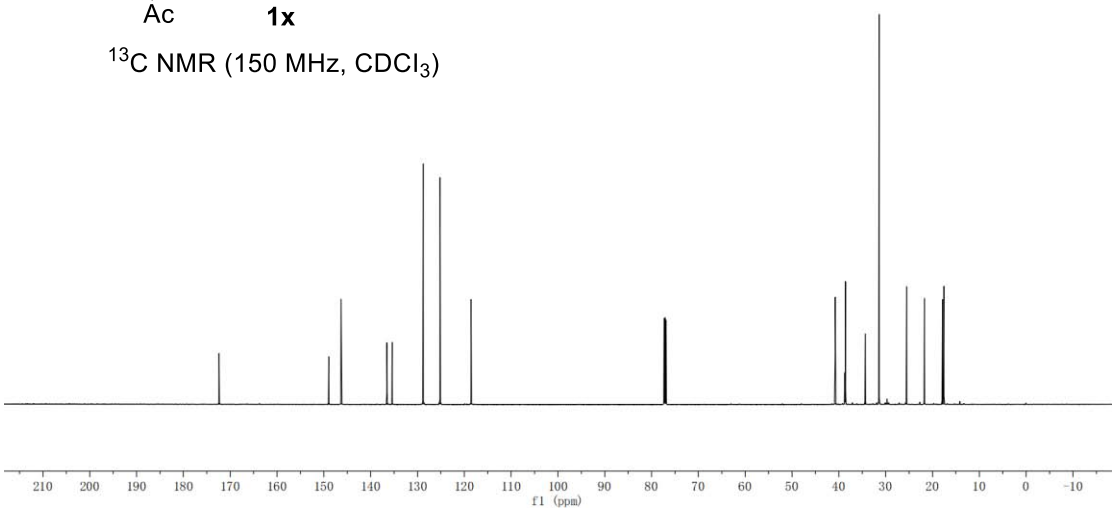
^{1}H NMR (600 MHz, $CDCl_3$)

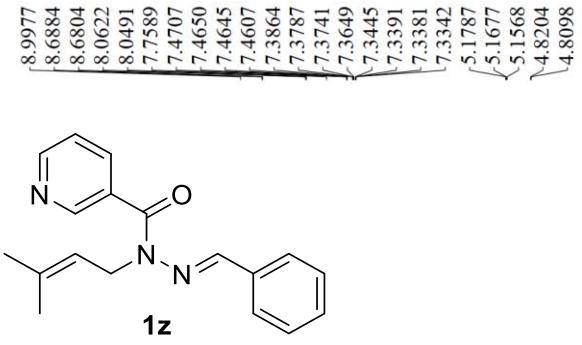




1x

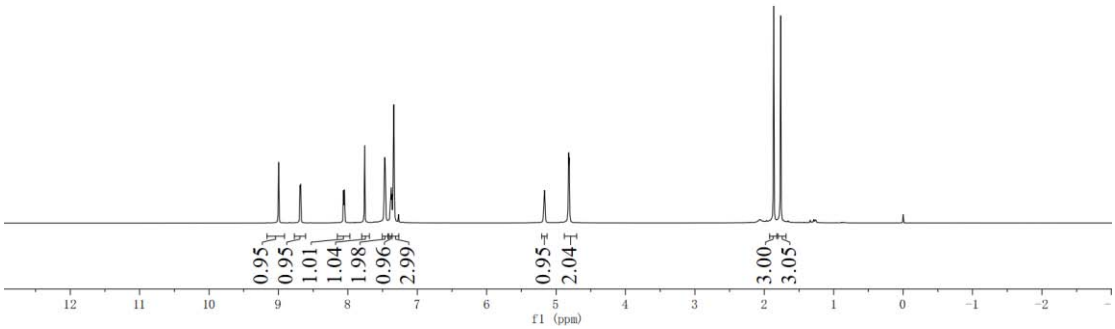
^{13}C NMR (150 MHz, $CDCl_3$)

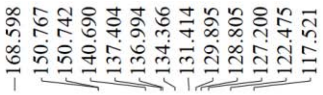


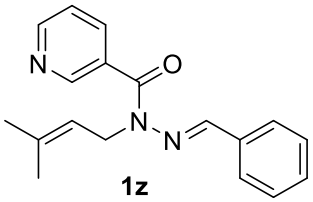


1z

^{1}H NMR (600 MHz, $CDCl_3$)

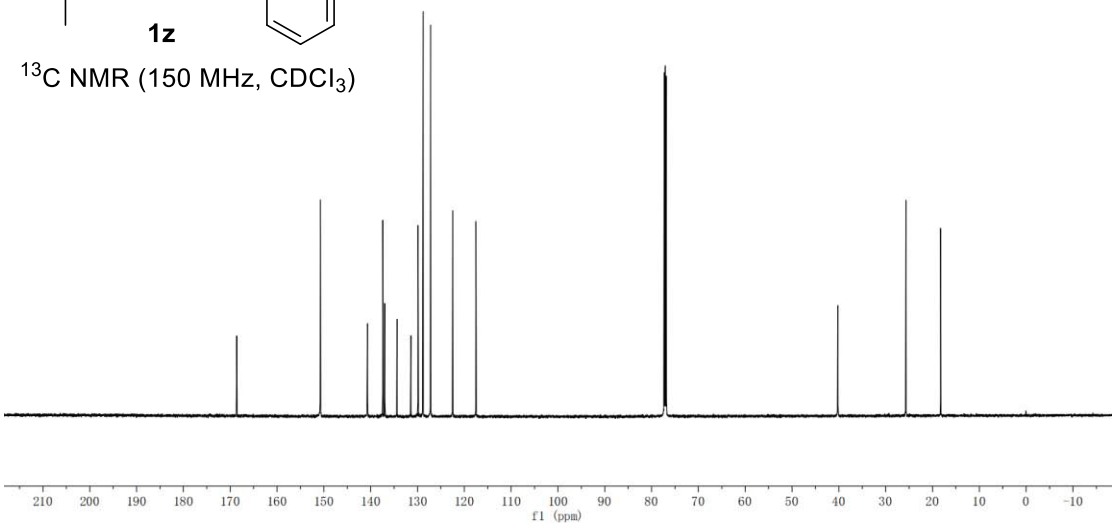


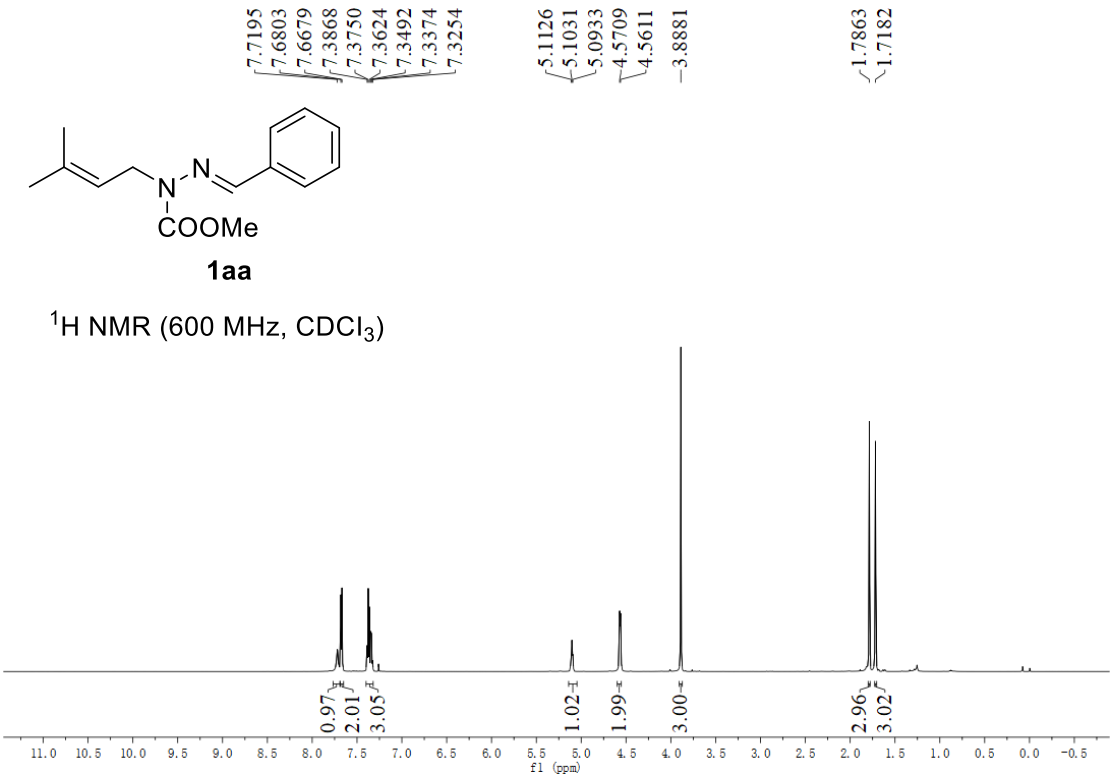




1z

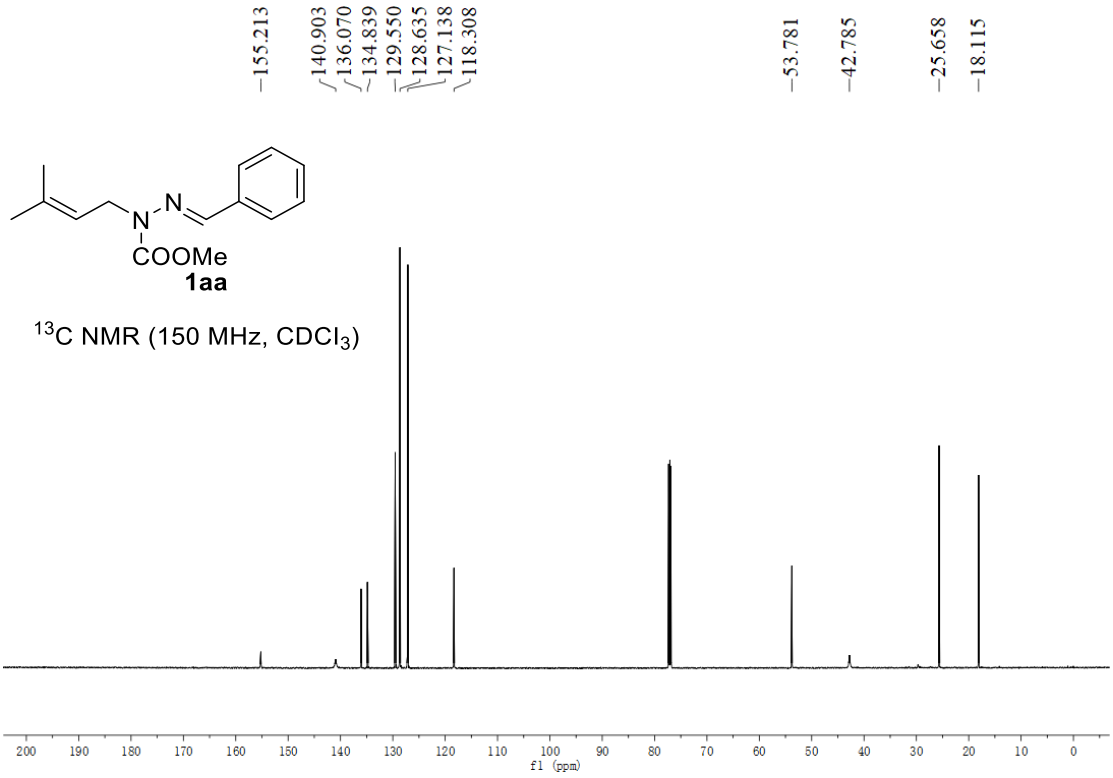
^{13}C NMR (150 MHz, $CDCl_3$)





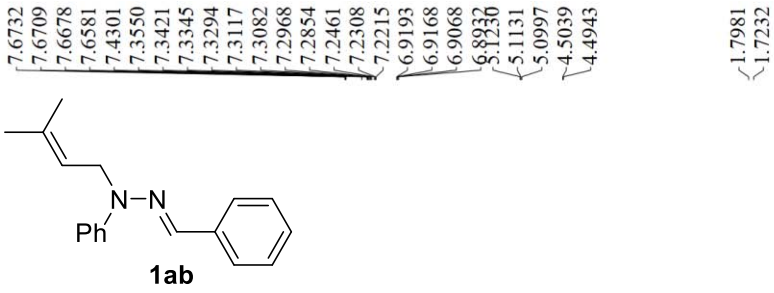
1aa

^{1}H NMR (600 MHz, $CDCl_3$)



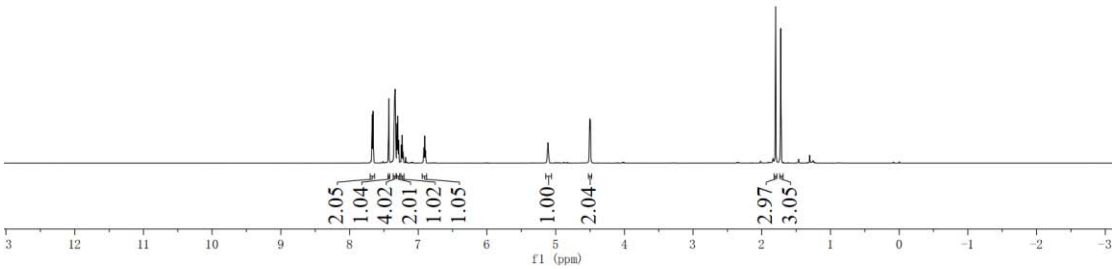
1aa

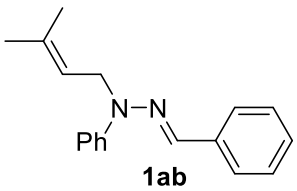
^{13}C NMR (150 MHz, $CDCl_3$)



1ab

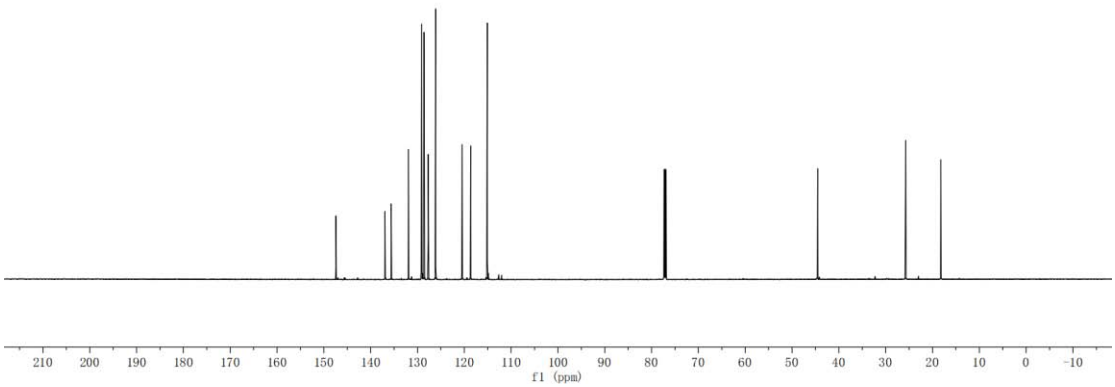
^{1}H NMR (600 MHz, $CDCl_3$)

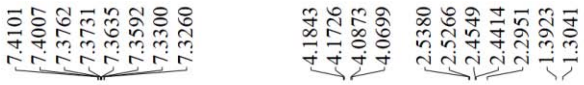


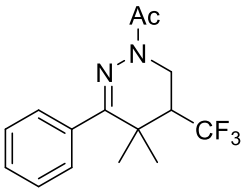


1ab

^{13}C NMR (150 MHz, $CDCl_3$)

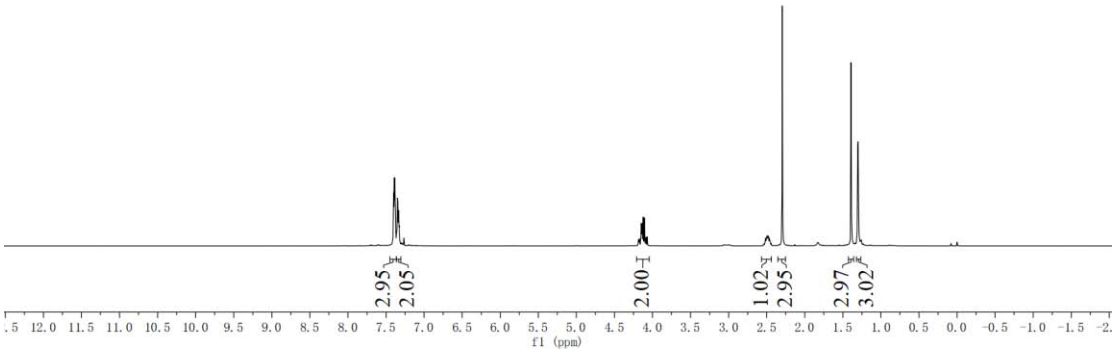


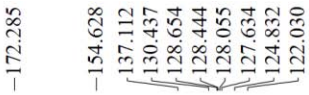


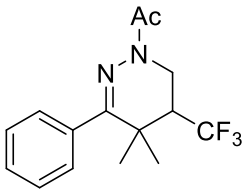


3a

^{1}H NMR (400 MHz, $CDCl_3$)

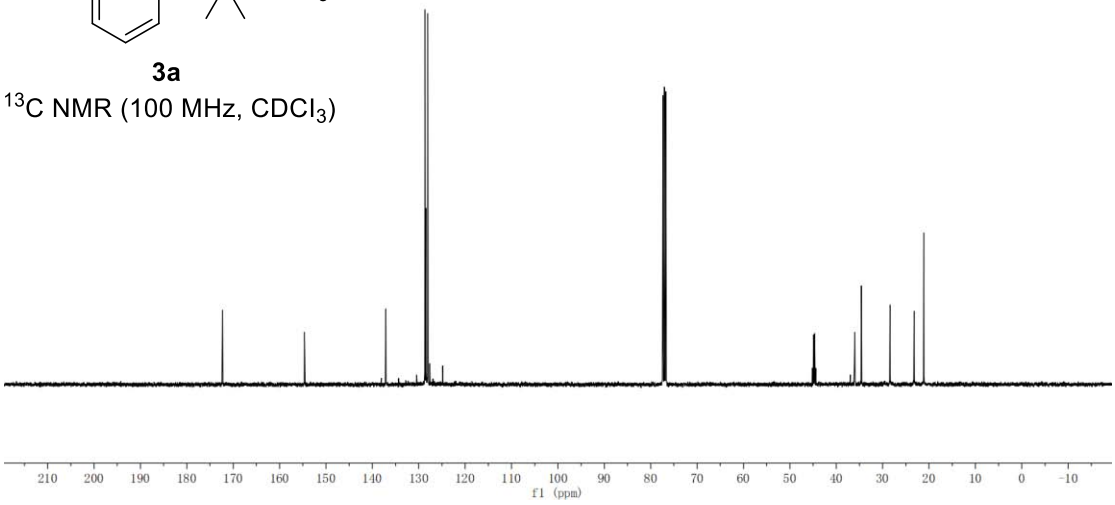






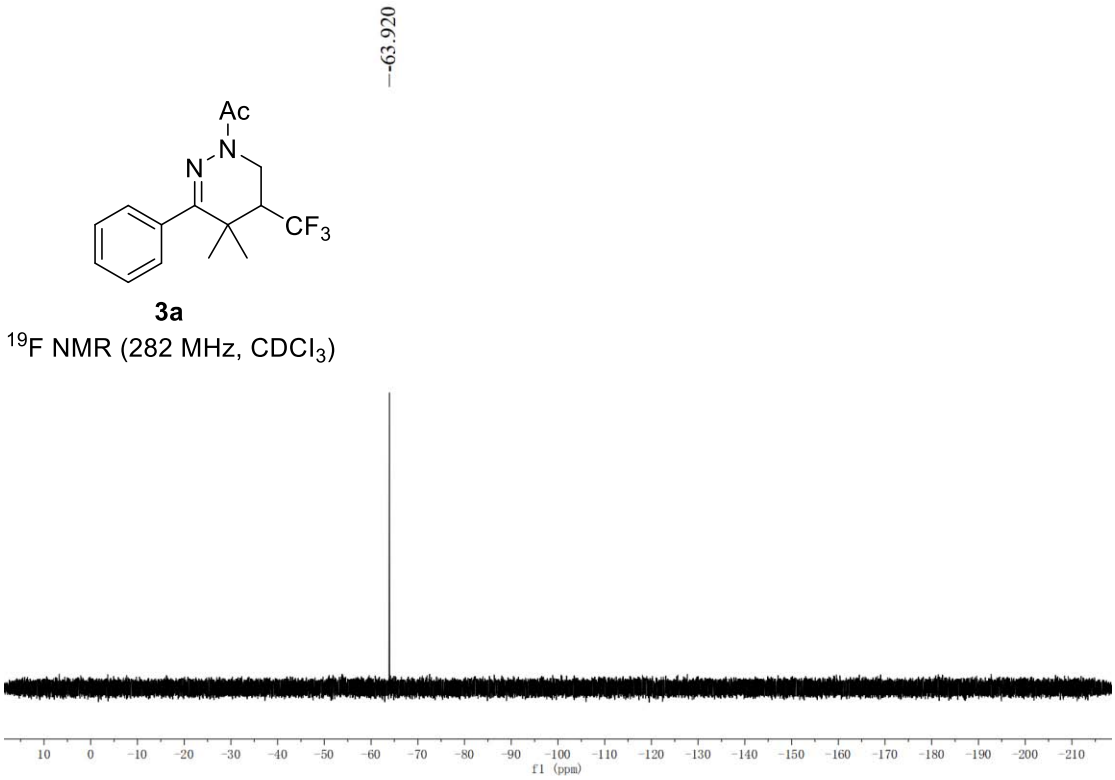
3a

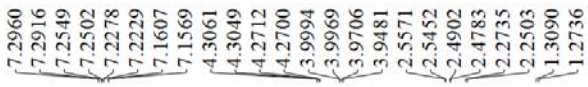
^{13}C NMR (100 MHz, $CDCl_3$)

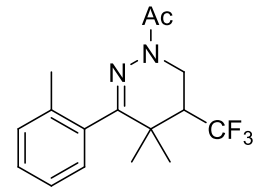


3a

^{19}F NMR (282 MHz, $CDCl_3$)

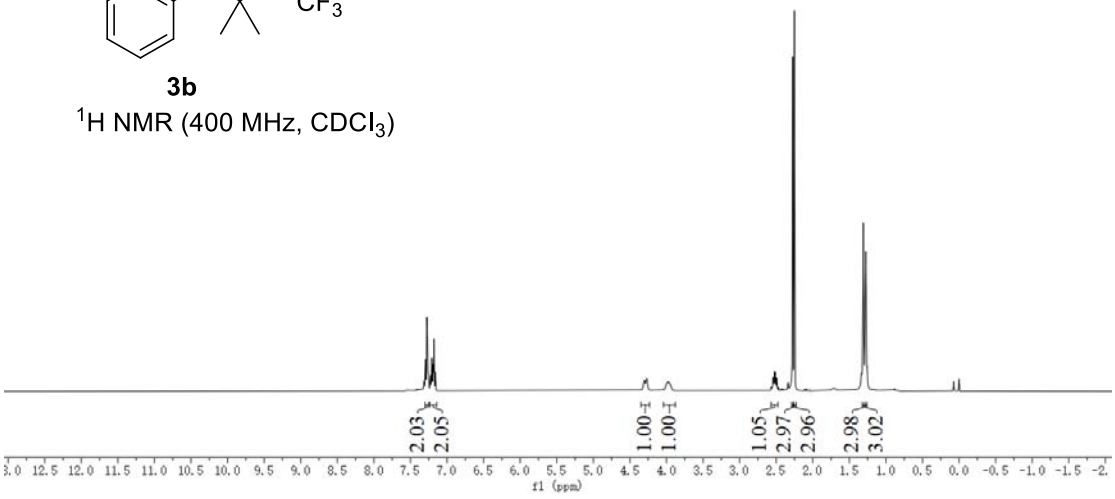


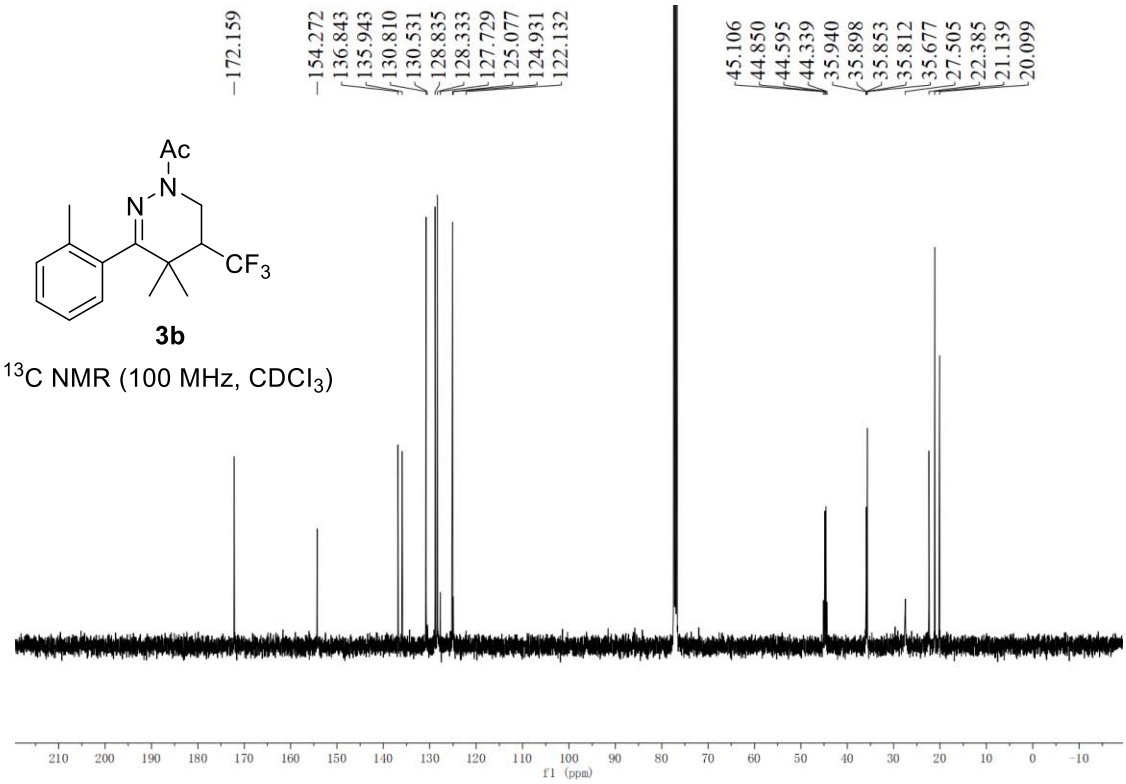




3b

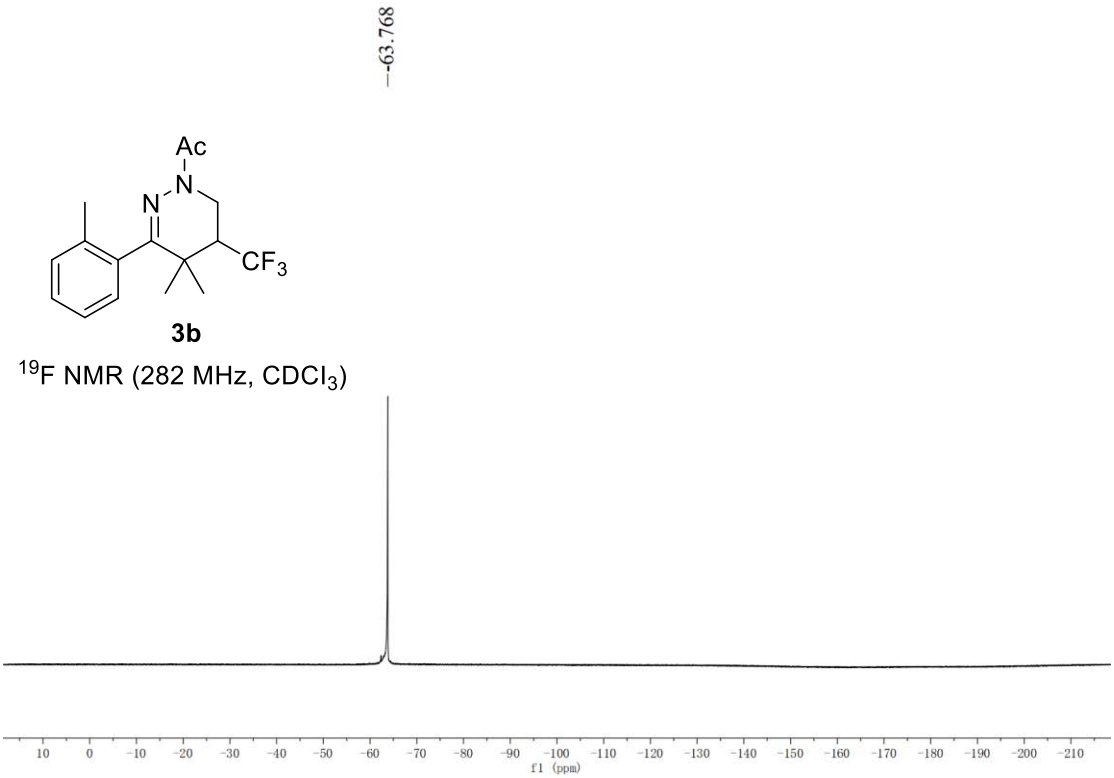
^{1}H NMR (400 MHz, $CDCl_3$)





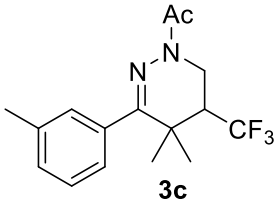
3b

^{13}C NMR (100 MHz, $CDCl_3$)



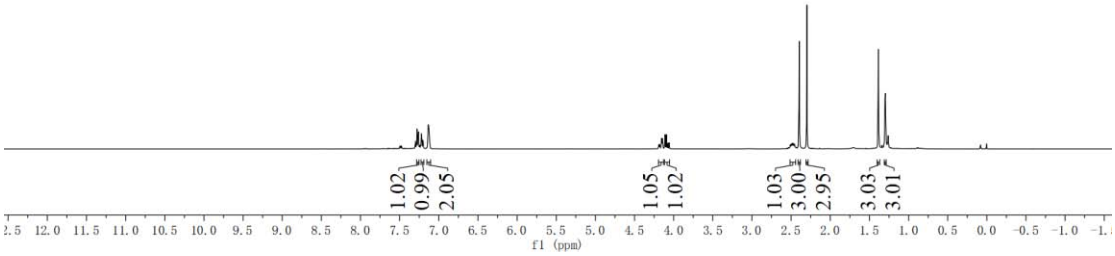
3b

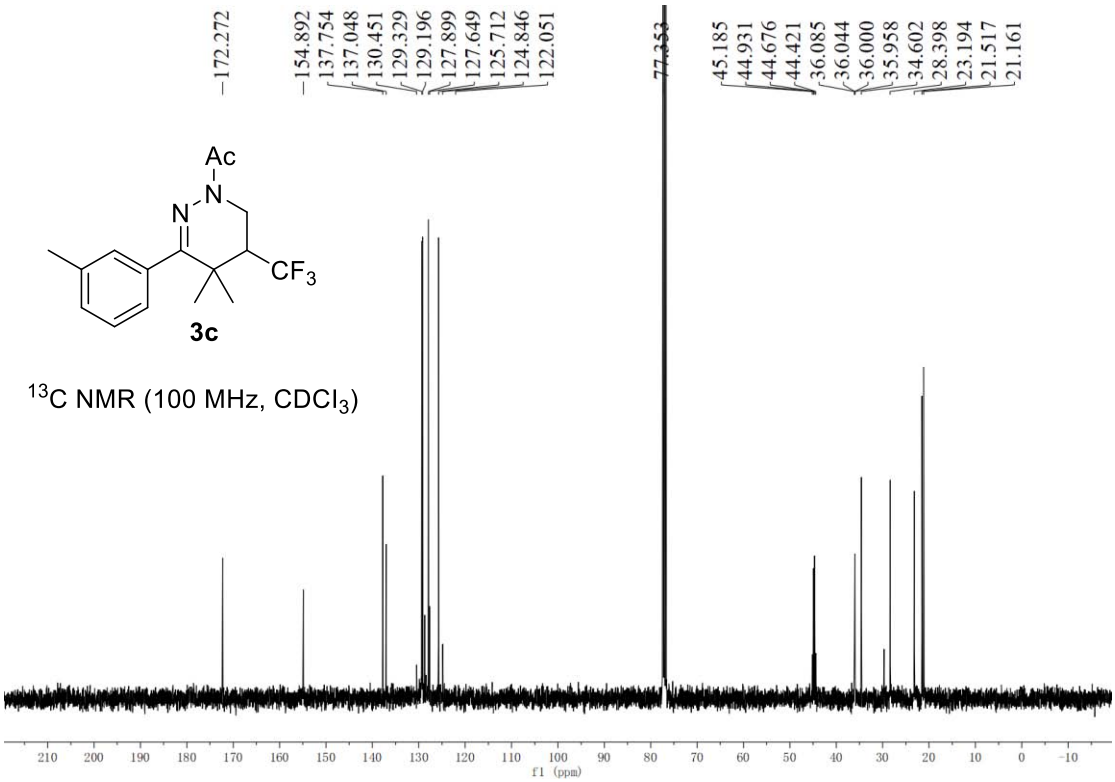
^{19}F NMR (282 MHz, $CDCl_3$)



3c

^{1}H NMR (400 MHz, $CDCl_3$)



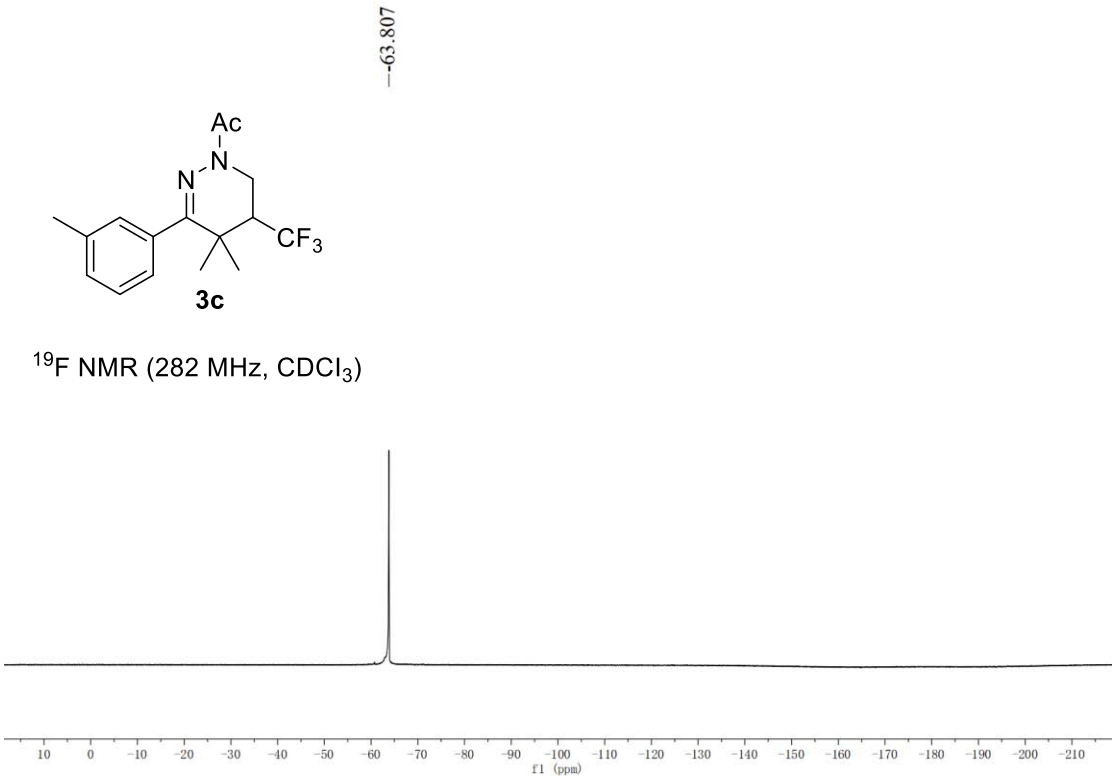


3c

^{13}C NMR (100 MHz, $CDCl_3$)

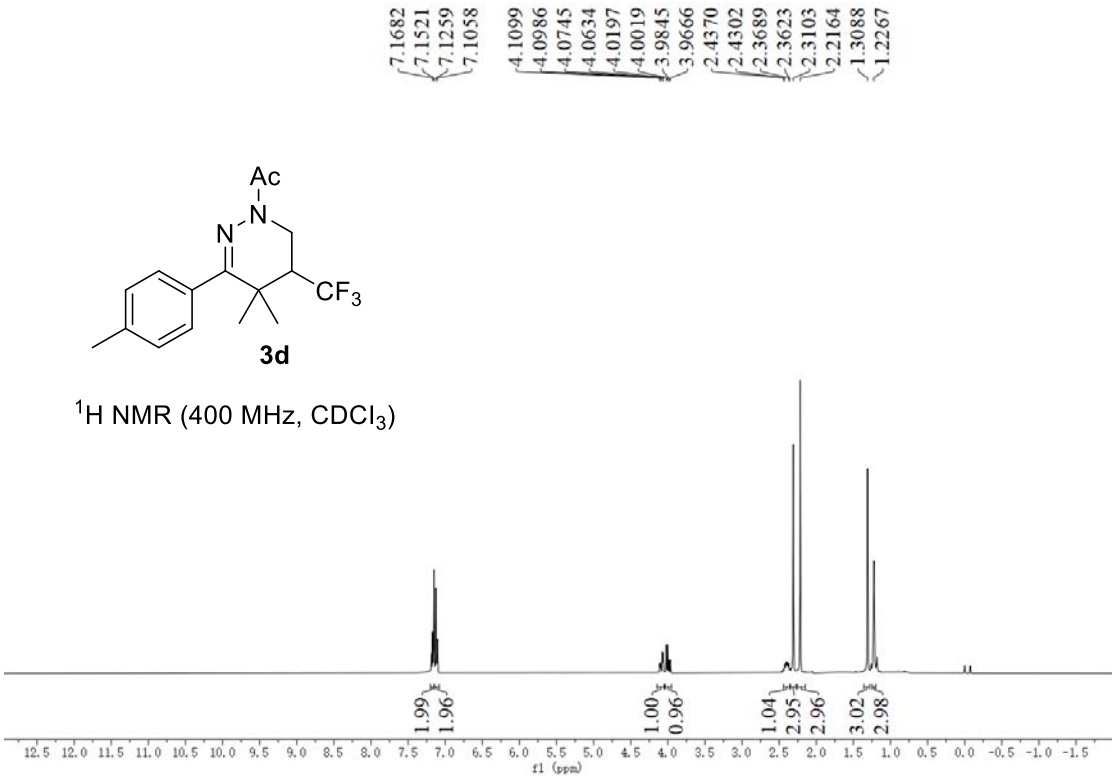
3c

^{19}F NMR (282 MHz, $CDCl_3$)



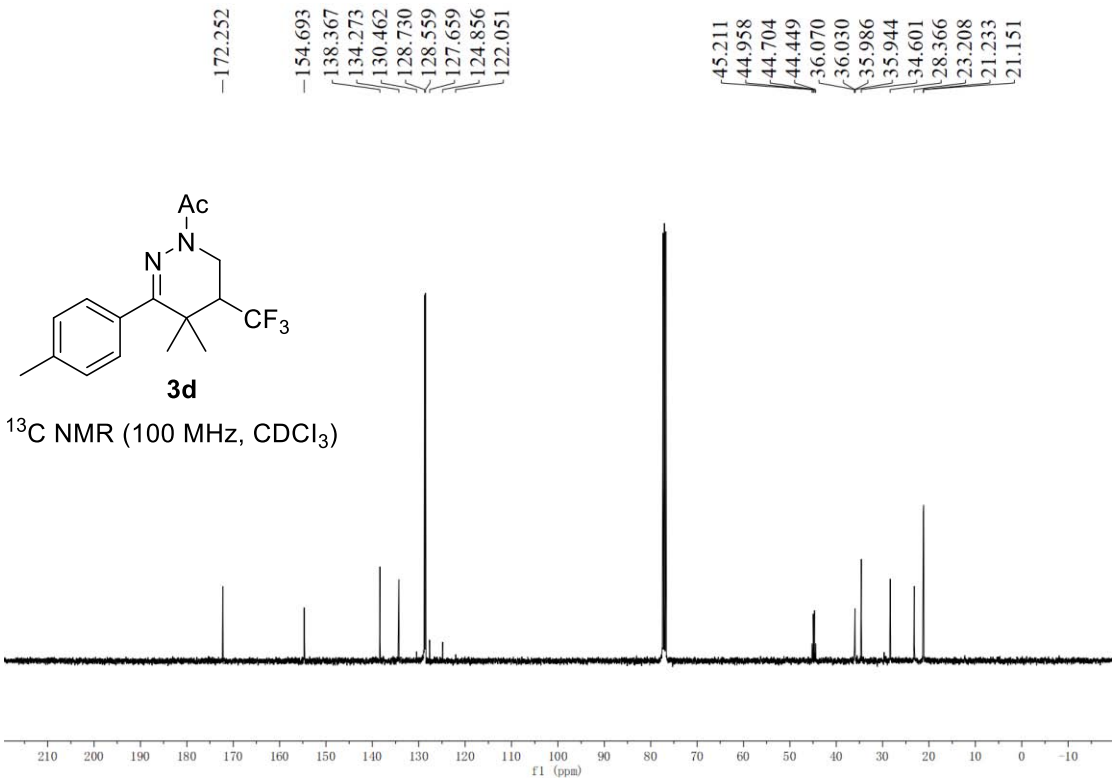
3d

^{1}H NMR (400 MHz, $CDCl_3$)



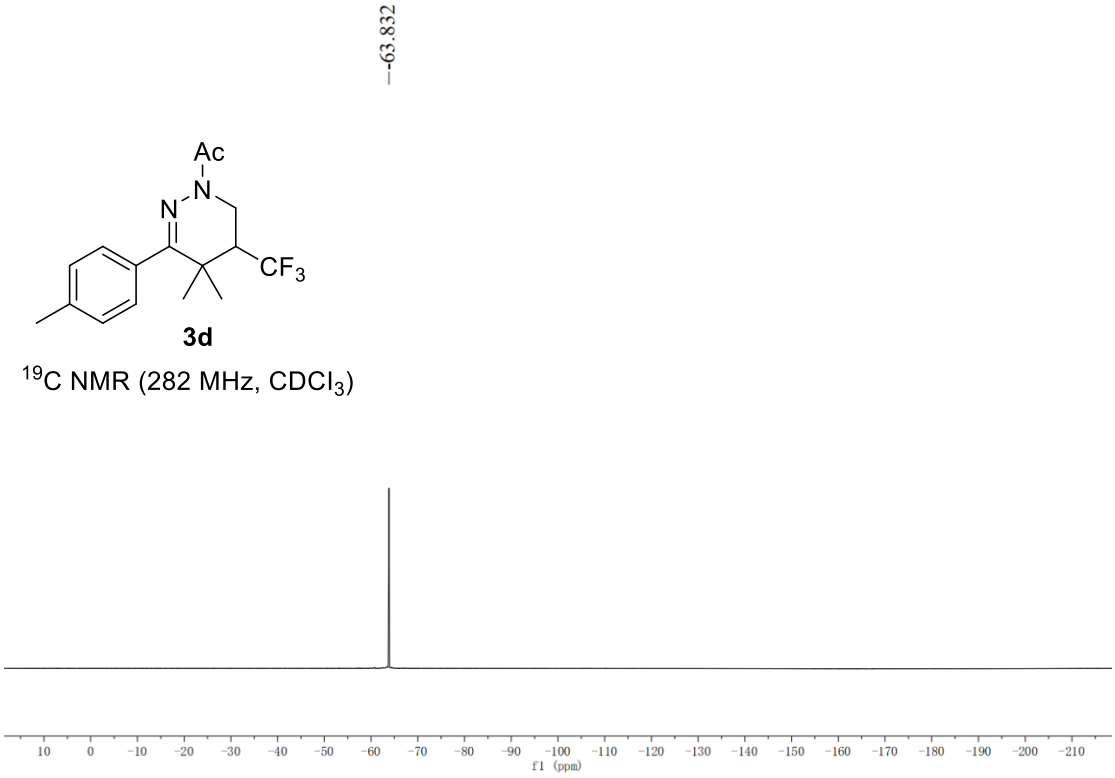
3d

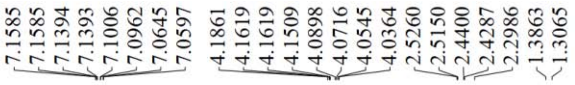
^{13}C NMR (100 MHz, $CDCl_3$)

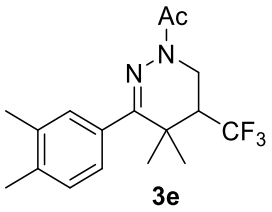


3d

^{19}C NMR (282 MHz, $CDCl_3$)

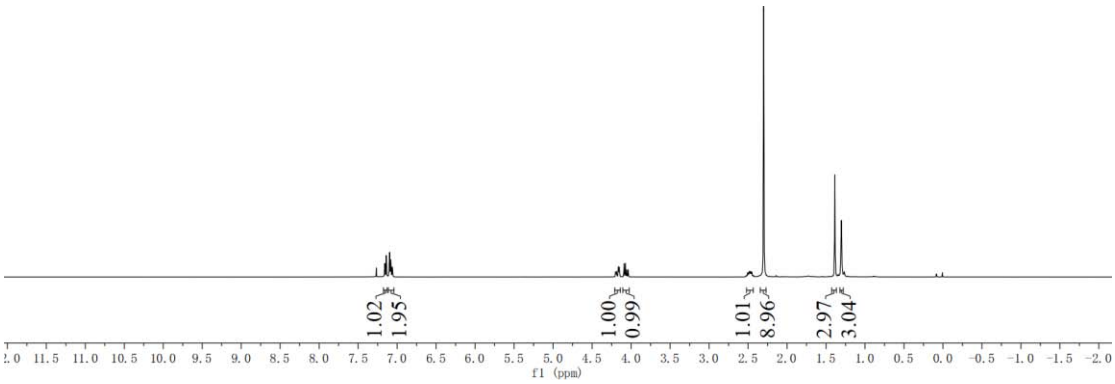


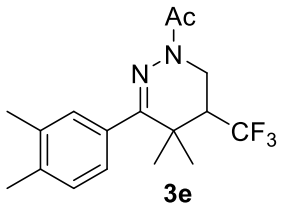




3e

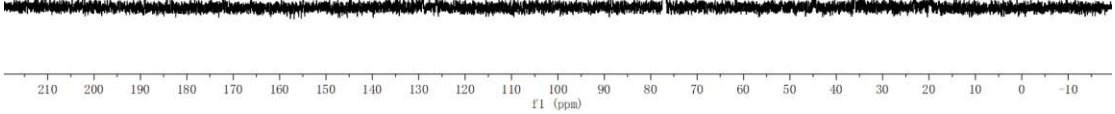
^{1}H NMR (400 MHz, $CDCl_3$)





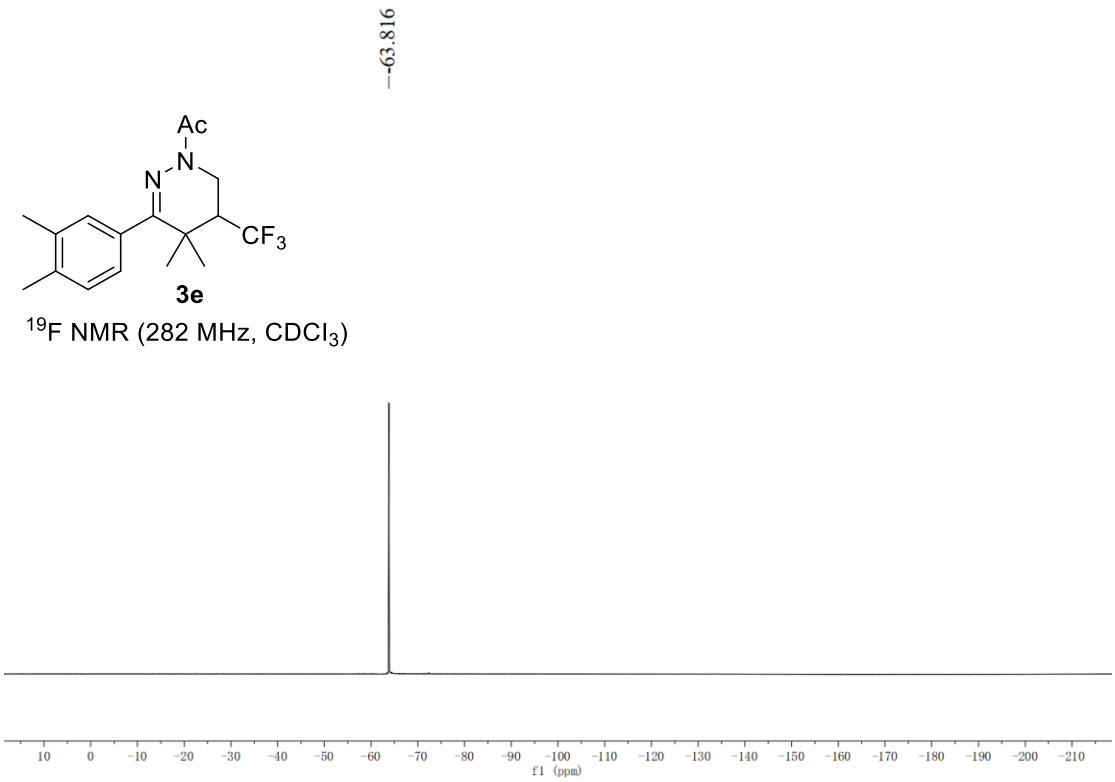
3e

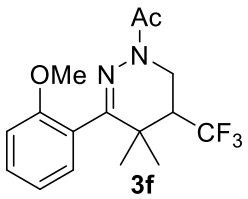
^{13}C NMR (100 MHz, $CDCl_3$)



3e

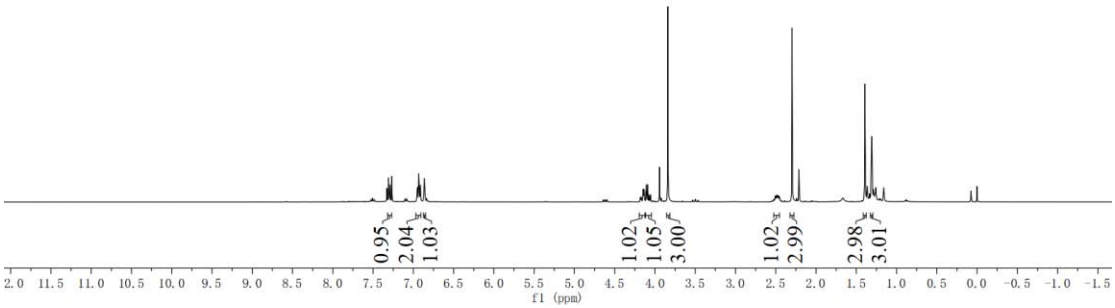
^{19}F NMR (282 MHz, $CDCl_3$)

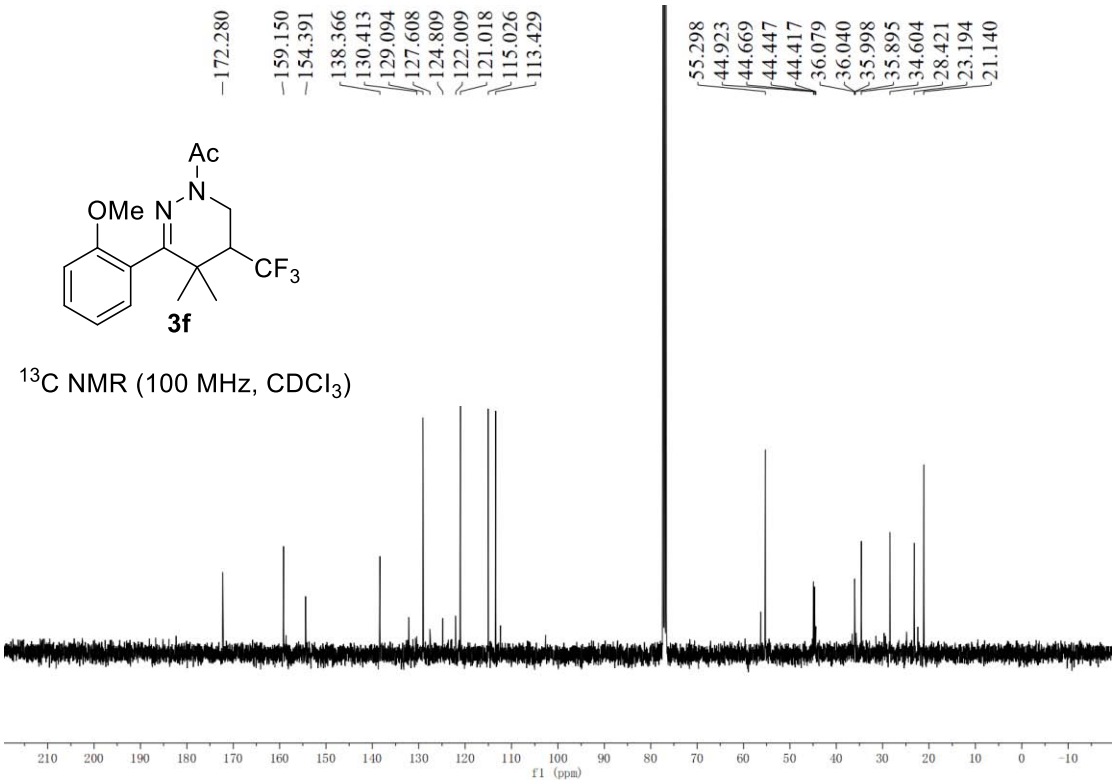




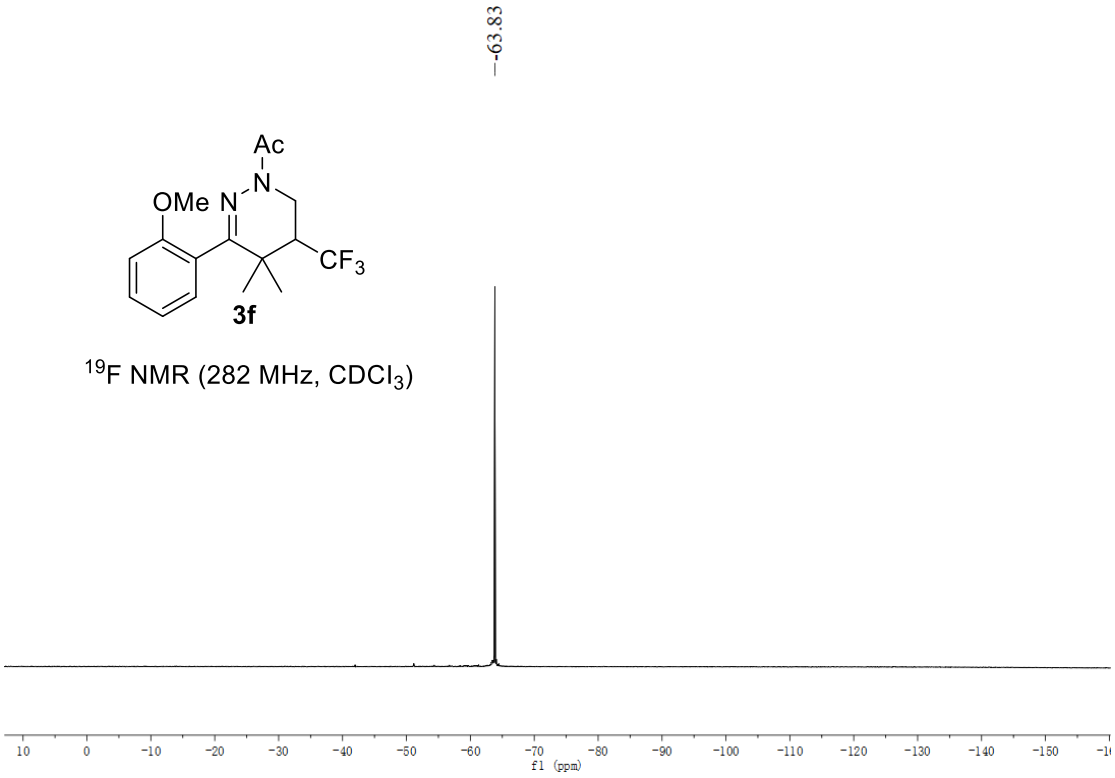
3f

^{1}H NMR (400 MHz, $CDCl_3$)

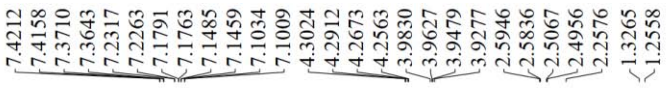


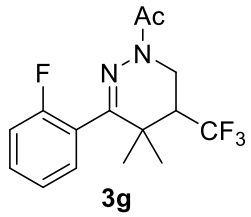


^{13}C NMR (100 MHz, $CDCl_3$)



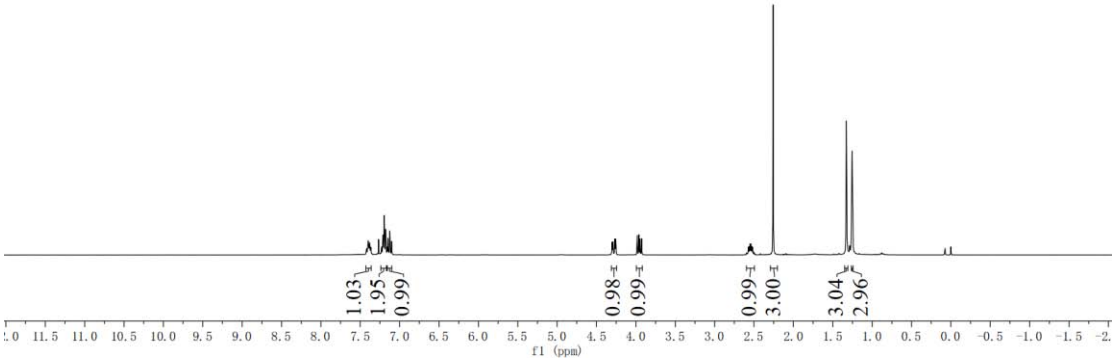
^{19}F NMR (282 MHz, $CDCl_3$)

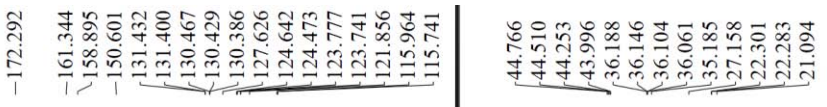


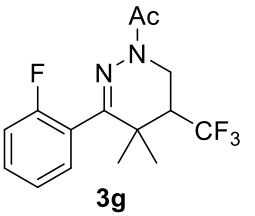


3g

^{1}H NMR (400 MHz, $CDCl_3$)

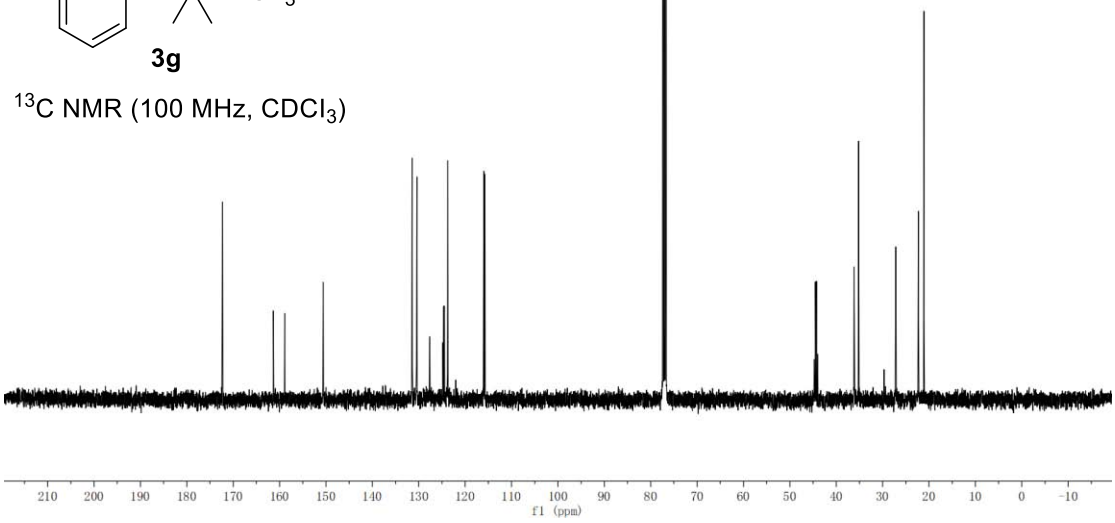






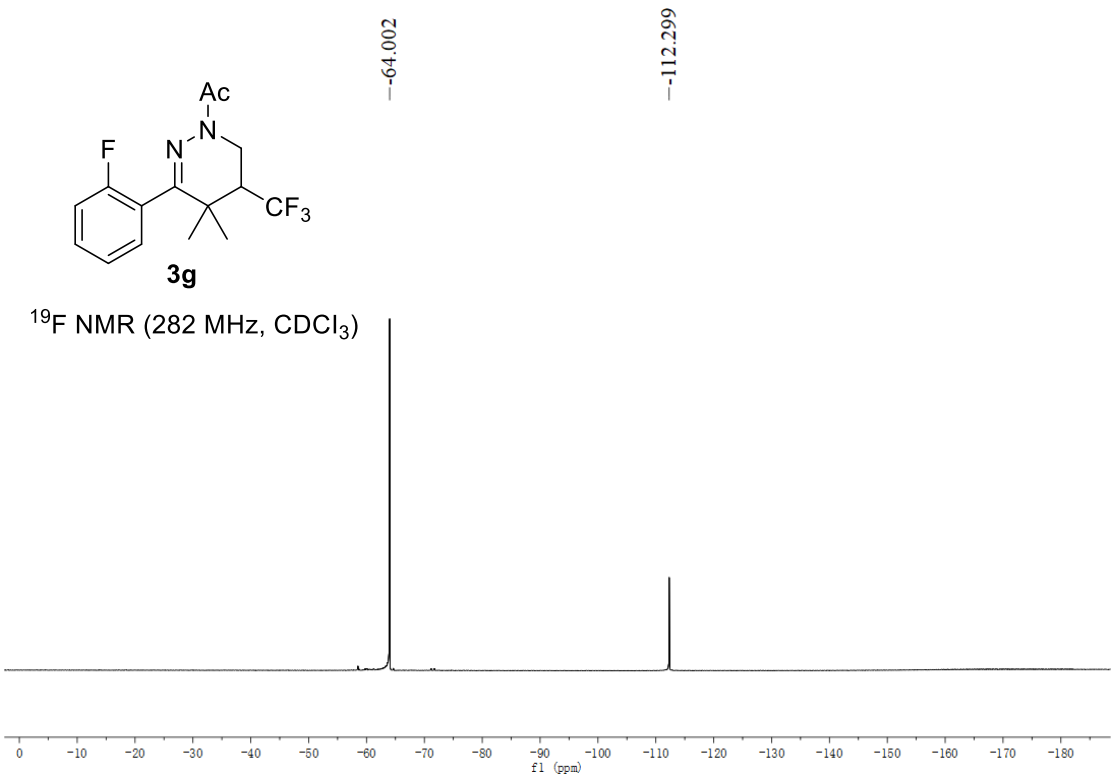
3g

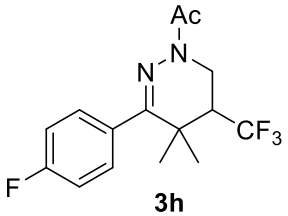
^{13}C NMR (100 MHz, $CDCl_3$)



3g

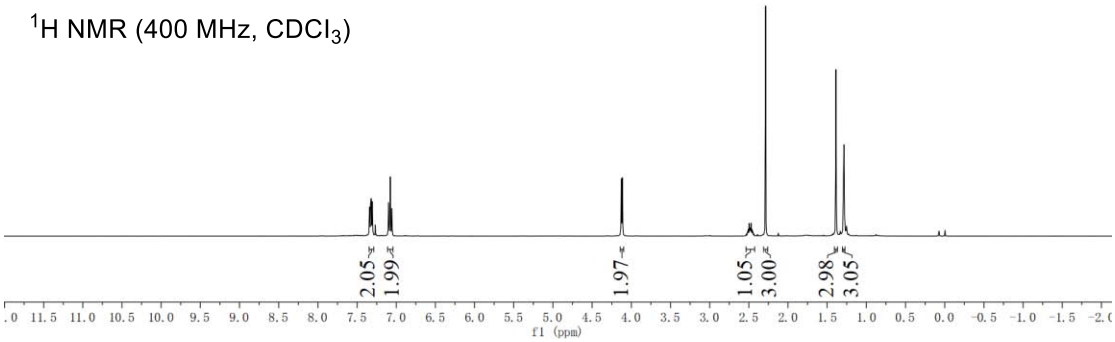
^{19}F NMR (282 MHz, $CDCl_3$)

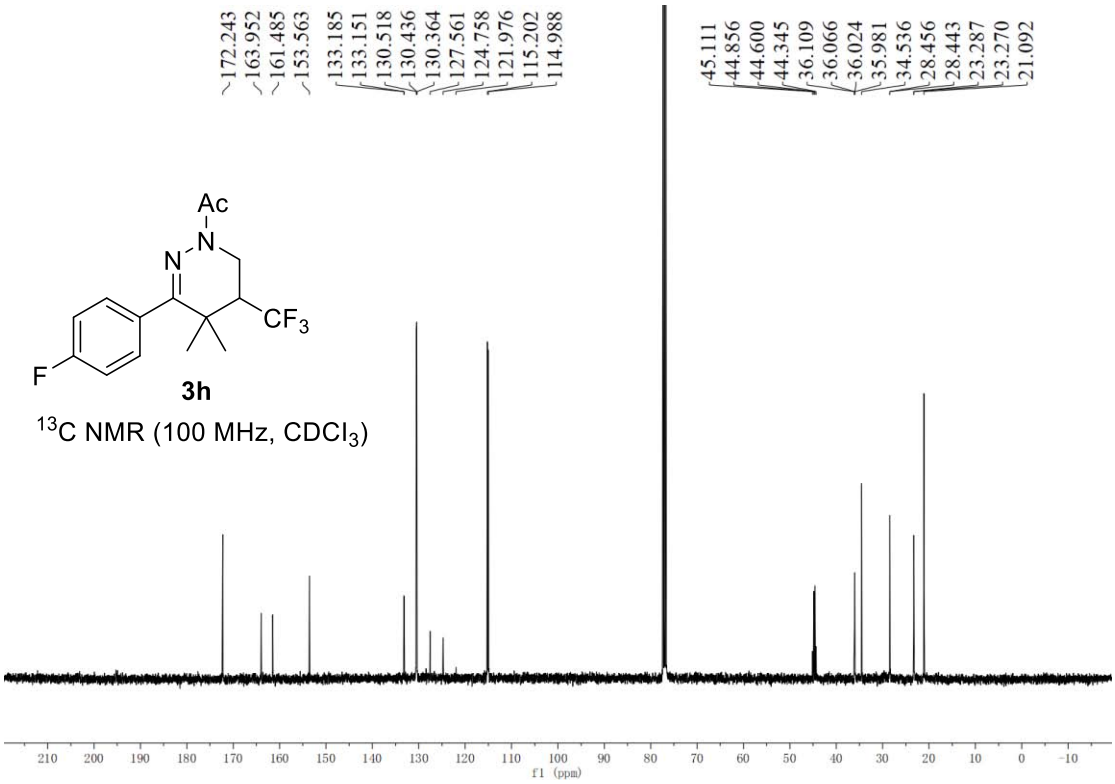




3h

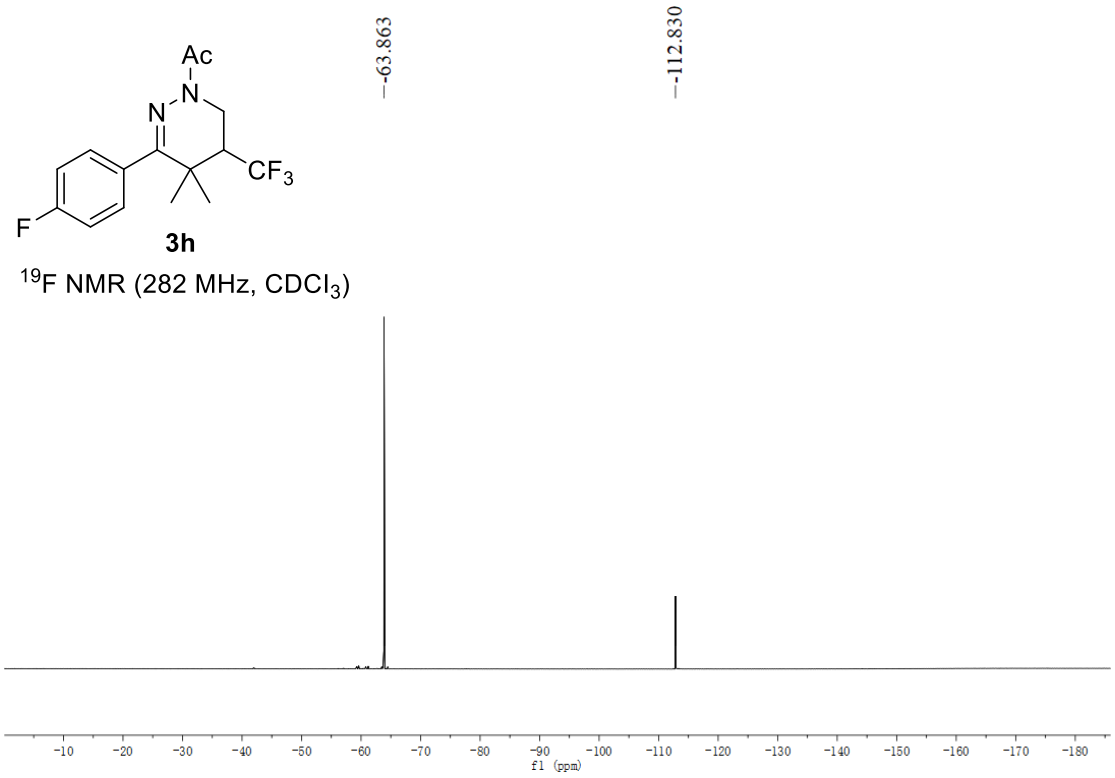
^{1}H NMR (400 MHz, $CDCl_3$)





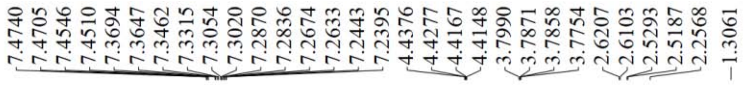
3h

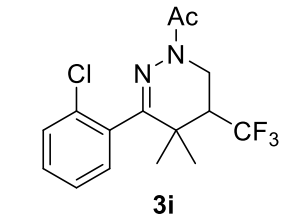
^{13}C NMR (100 MHz, $CDCl_3$)



3h

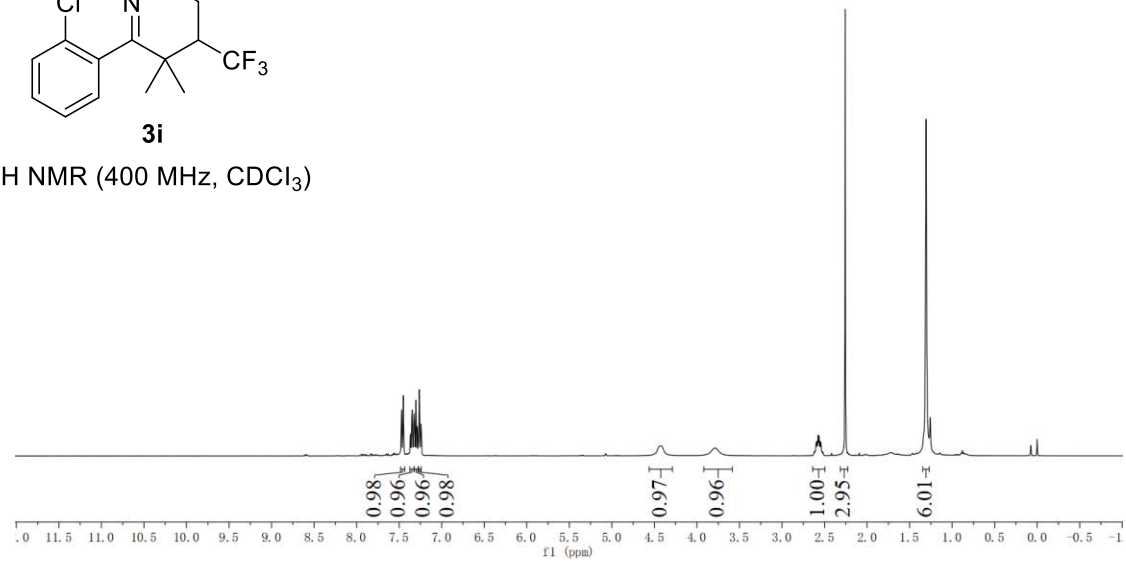
^{19}F NMR (282 MHz, $CDCl_3$)

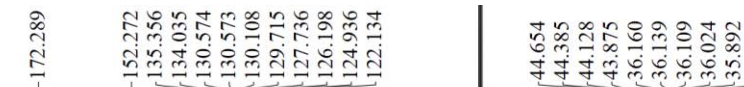


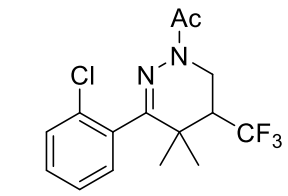


3i

^{1}H NMR (400 MHz, $CDCl_3$)

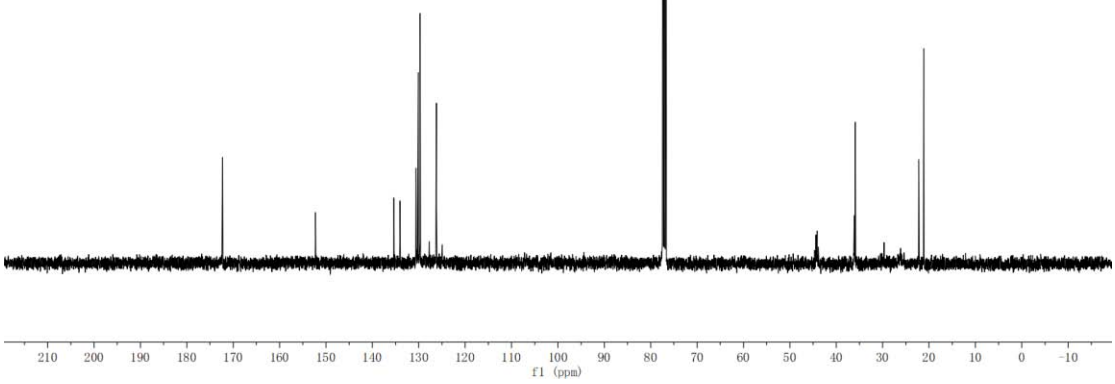






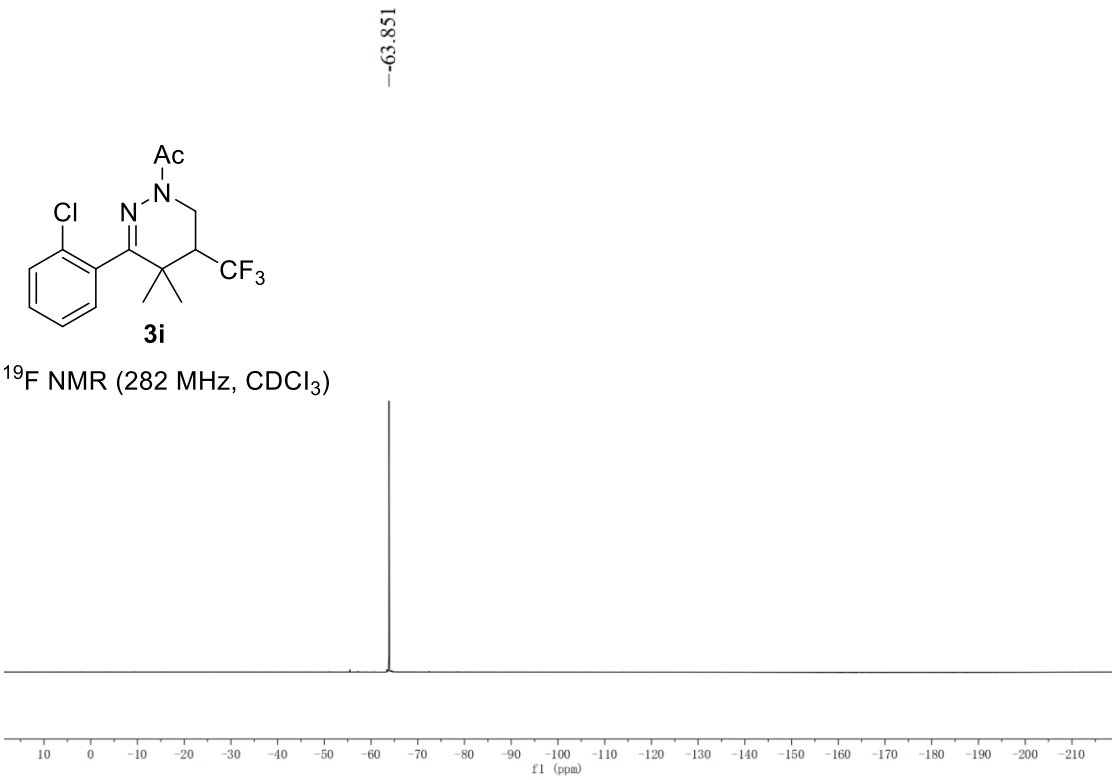
3i

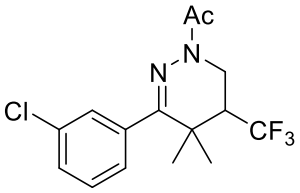
^{13}C NMR (100 MHz, $CDCl_3$)



3i

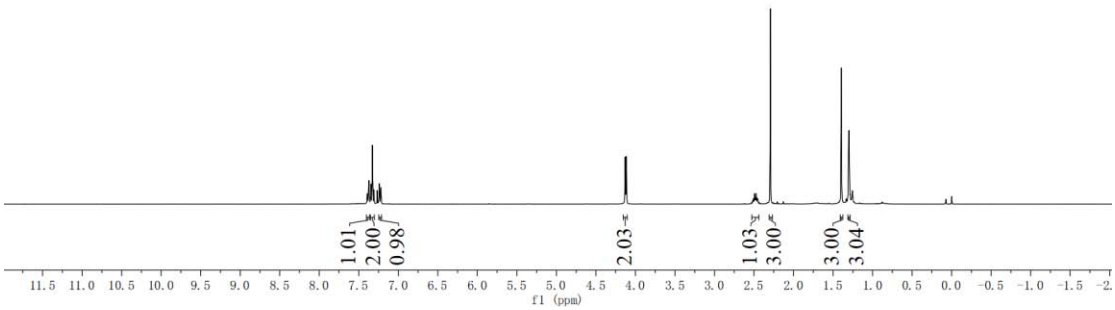
^{19}F NMR (282 MHz, $CDCl_3$)

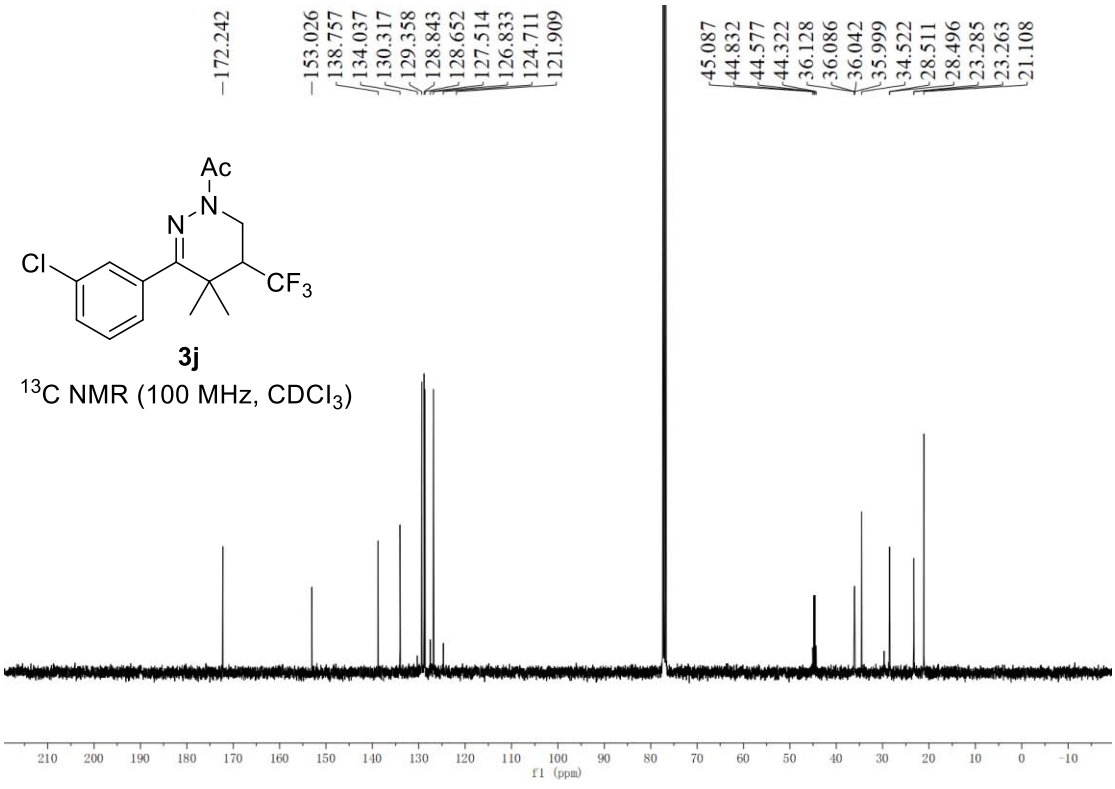




3j

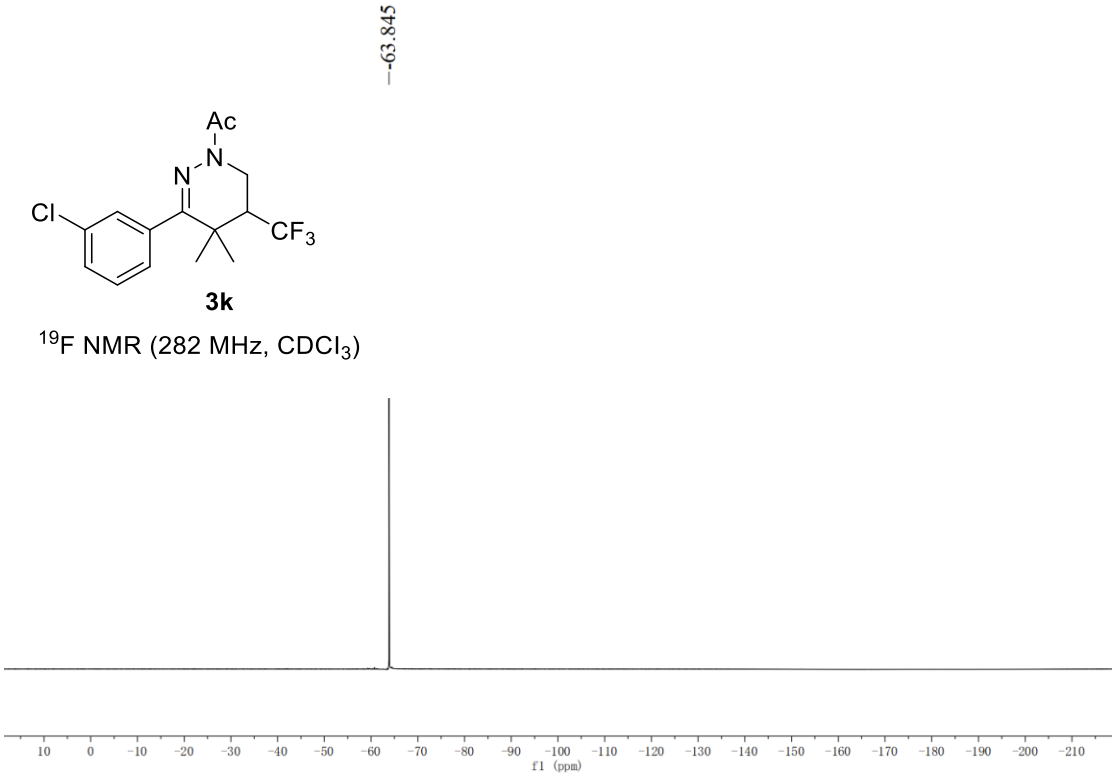
^{1}H NMR (400 MHz, $CDCl_3$)





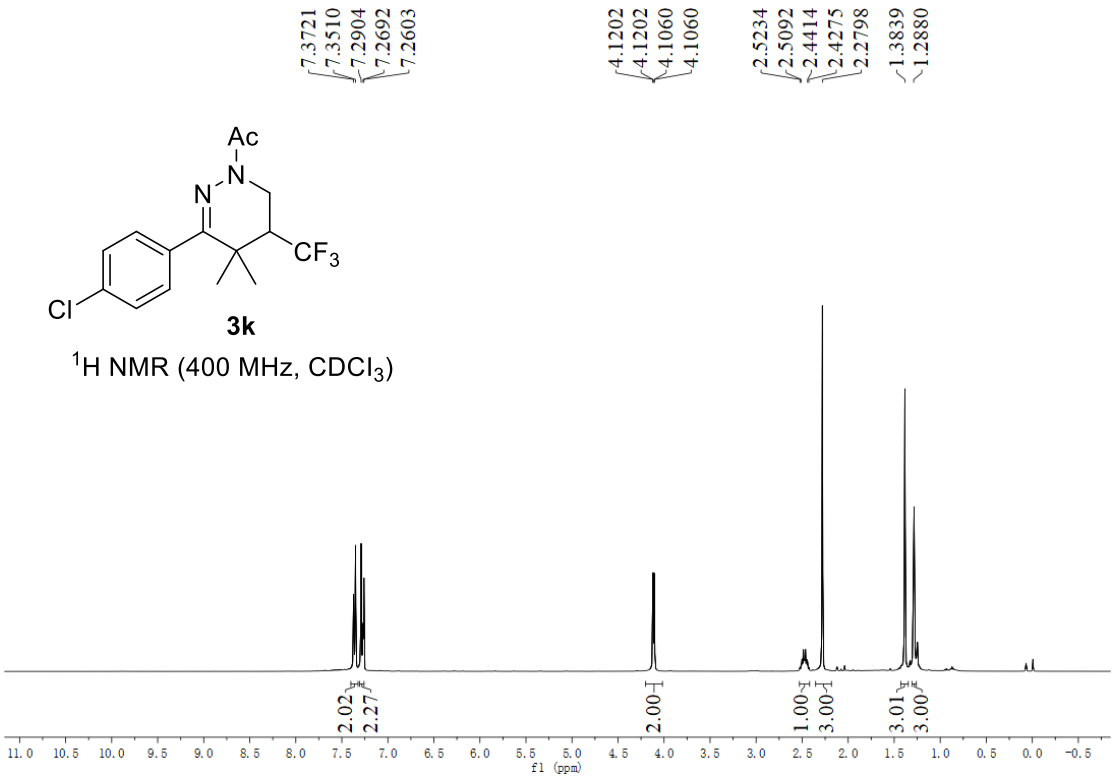
3j

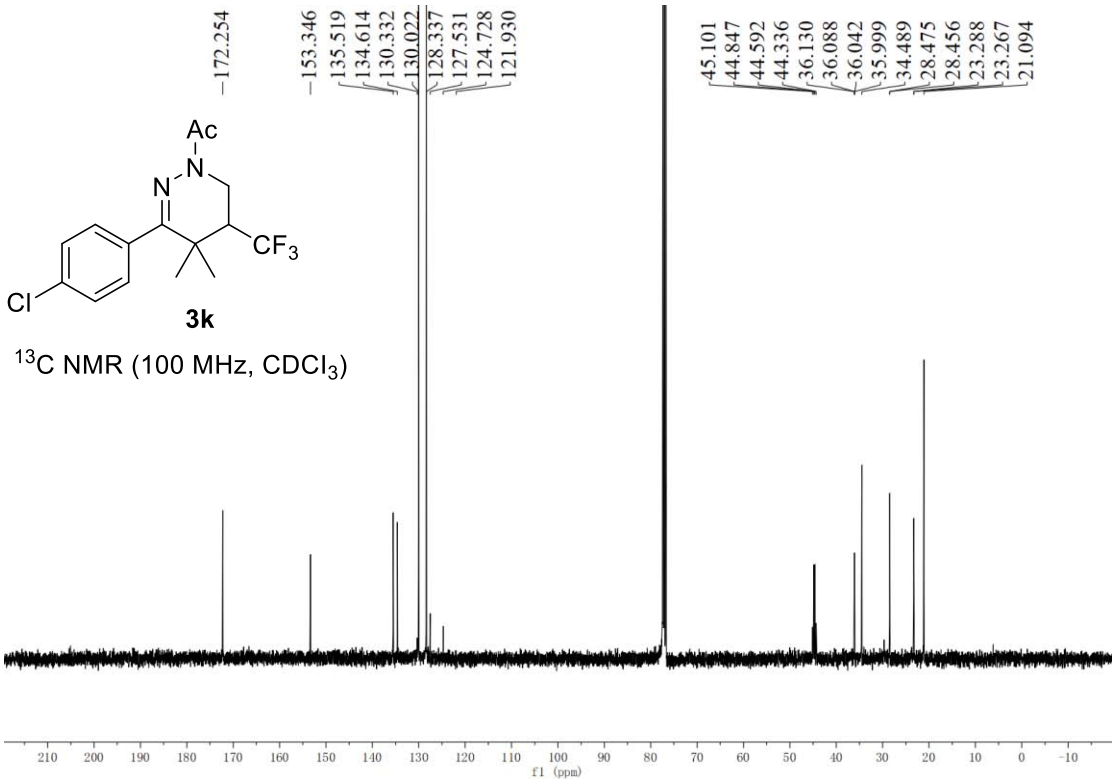
^{13}C NMR (100 MHz, $CDCl_3$)



3k

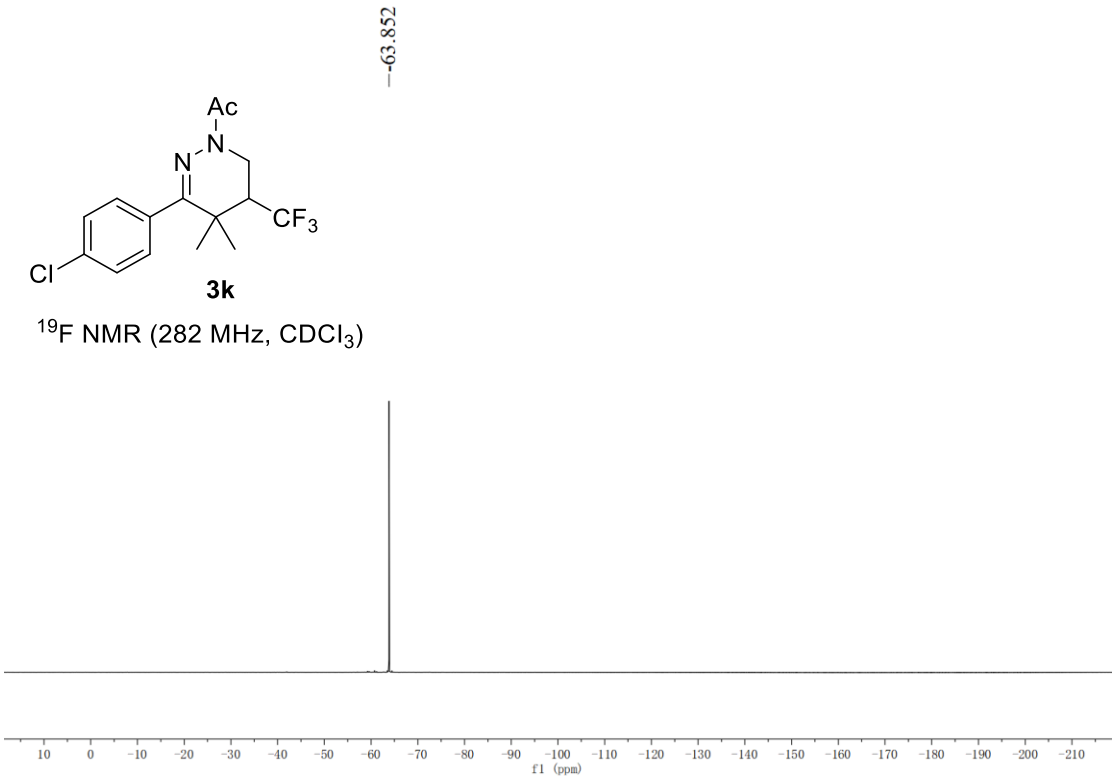
^{19}F NMR (282 MHz, $CDCl_3$)

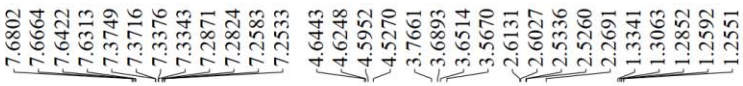

7.3721
7.3510
7.2904
7.2692
7.2603
4.1202
4.1202
4.1060
4.1060
2.5234
2.5092
2.4414
2.4275
2.2798
1.3839
1.2880
Ac
N
N
CF3
Cl
3k
1H NMR (400 MHz, CDCl3)
2.02
2.27
2.00
1.00
3.00
3.01
3.00
f1 (ppm)

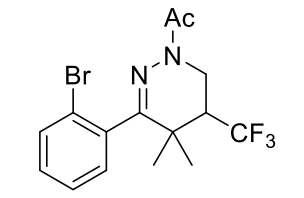

172.254
153.346
135.519
134.614
130.332
130.022
128.337
127.531
124.728
121.930
45.101
44.847
44.592
44.336
36.130
36.088
36.042
35.999
34.489
28.475
28.456
23.288
23.267
21.094
Ac
N
N
CF3
Cl
3k
13C NMR (100 MHz, CDCl3)
f1 (ppm)

3k

^{19}F NMR (282 MHz, $CDCl_3$)

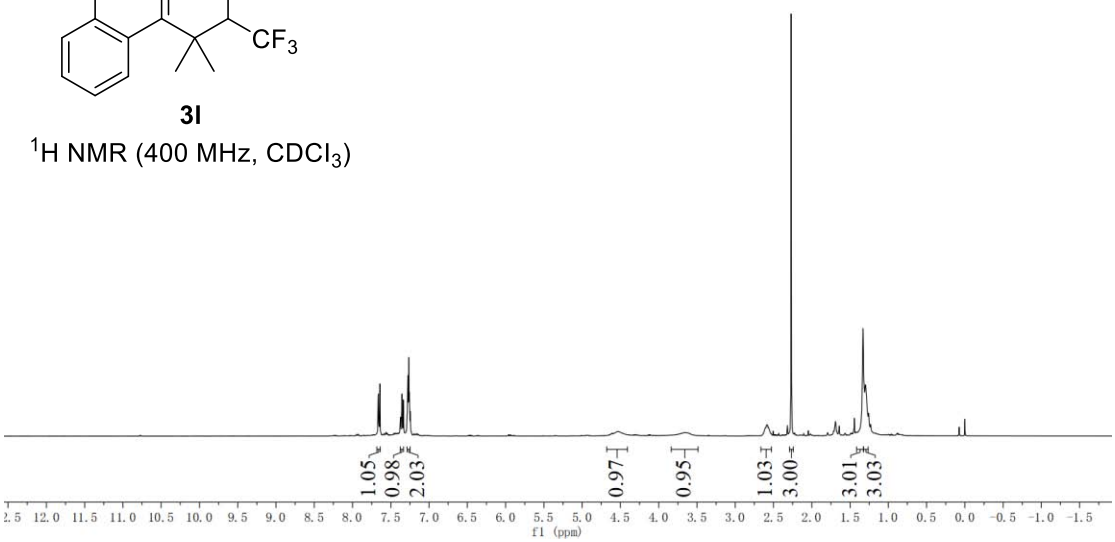


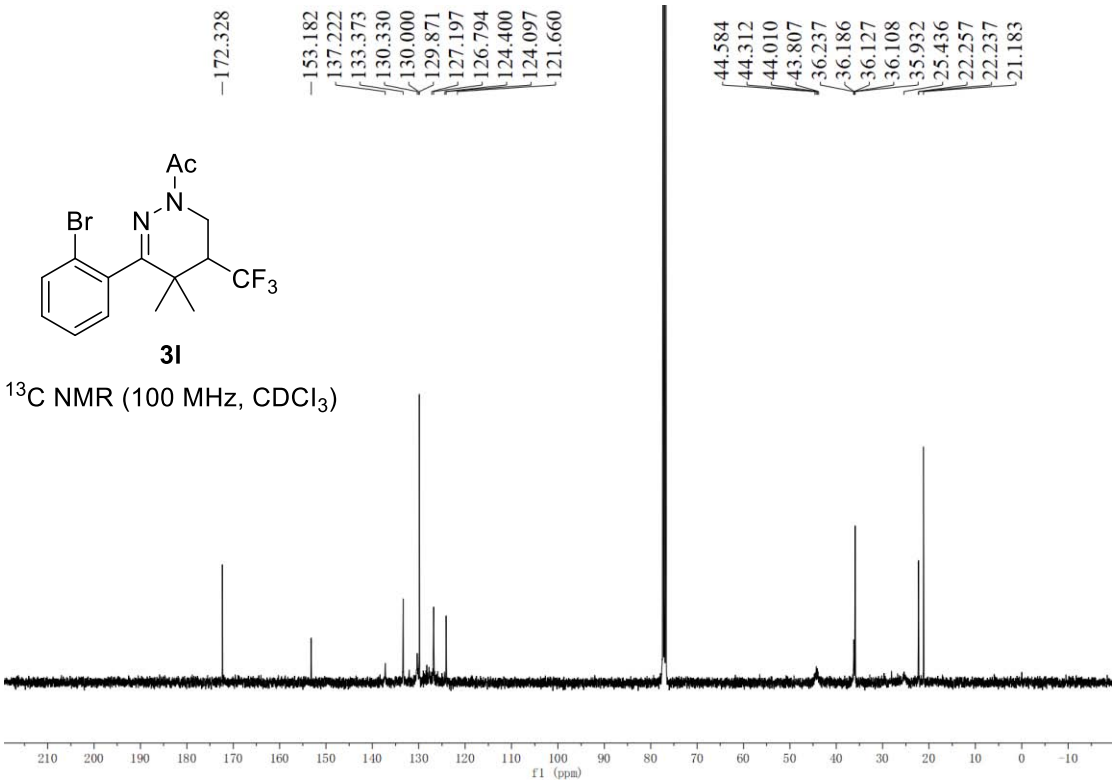




3l

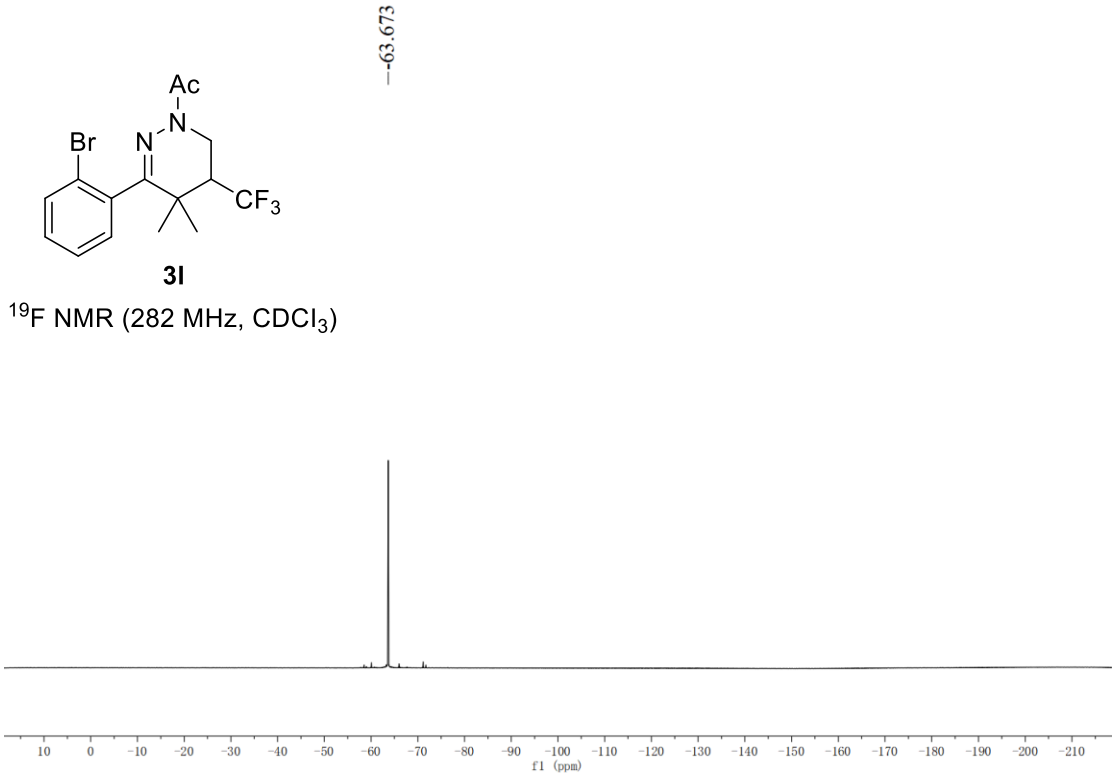
^{1}H NMR (400 MHz, $CDCl_3$)





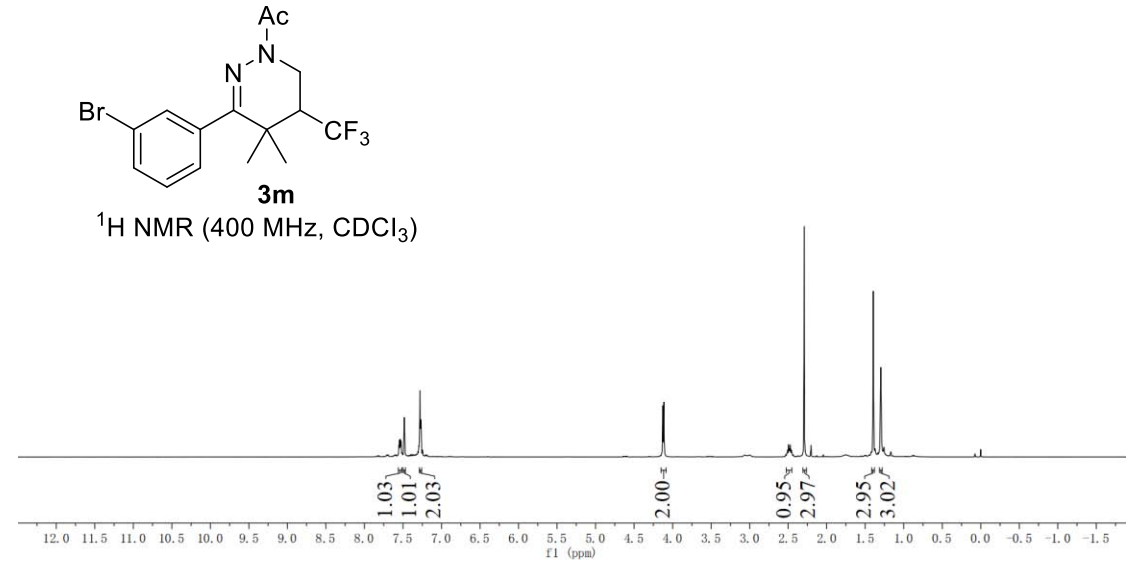
3l

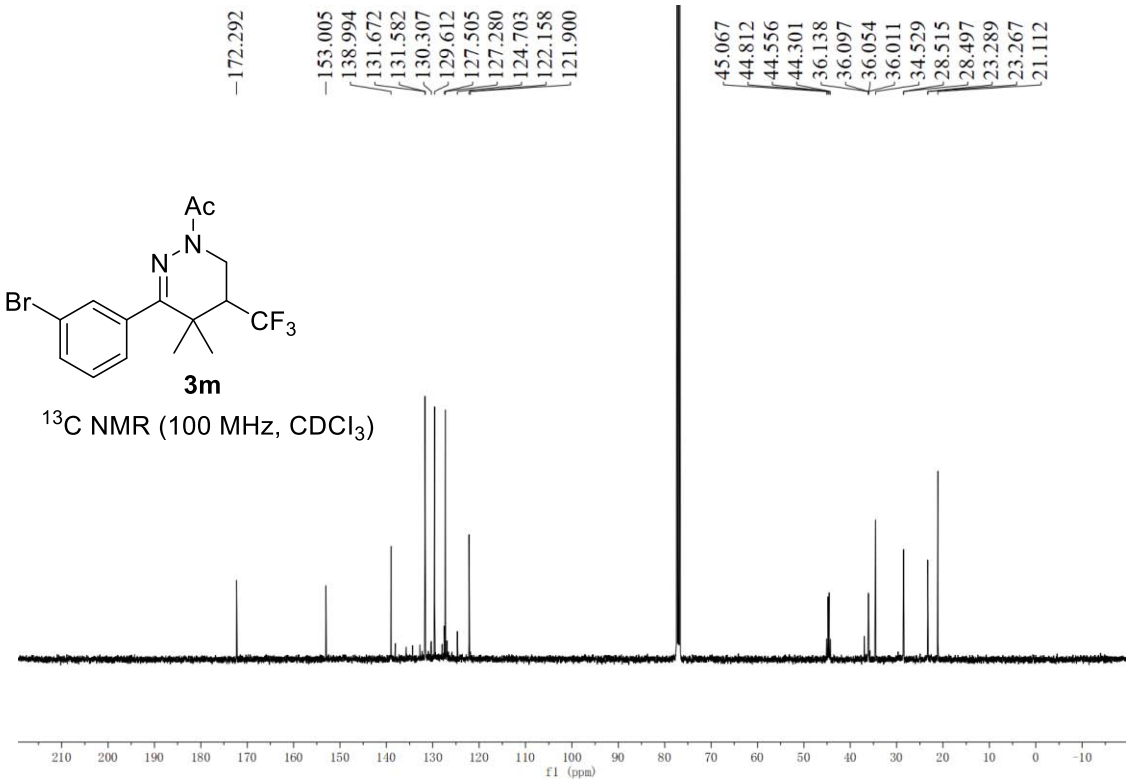
^{13}C NMR (100 MHz, $CDCl_3$)



3l

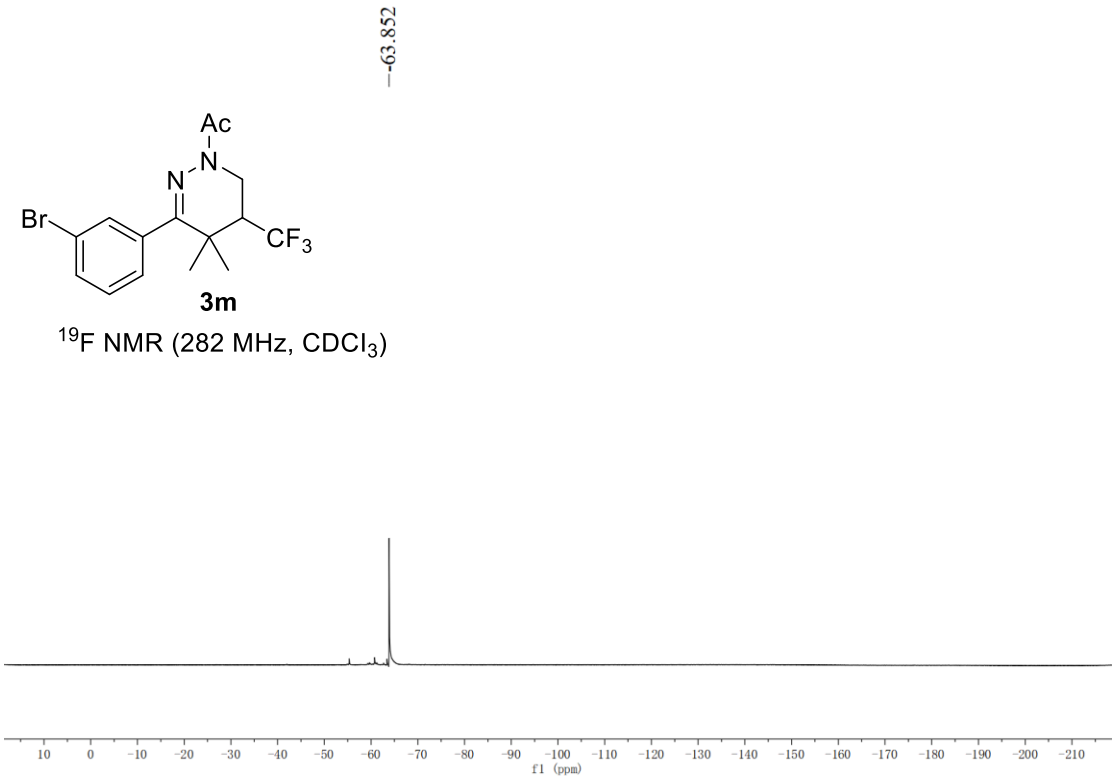
^{19}F NMR (282 MHz, $CDCl_3$)

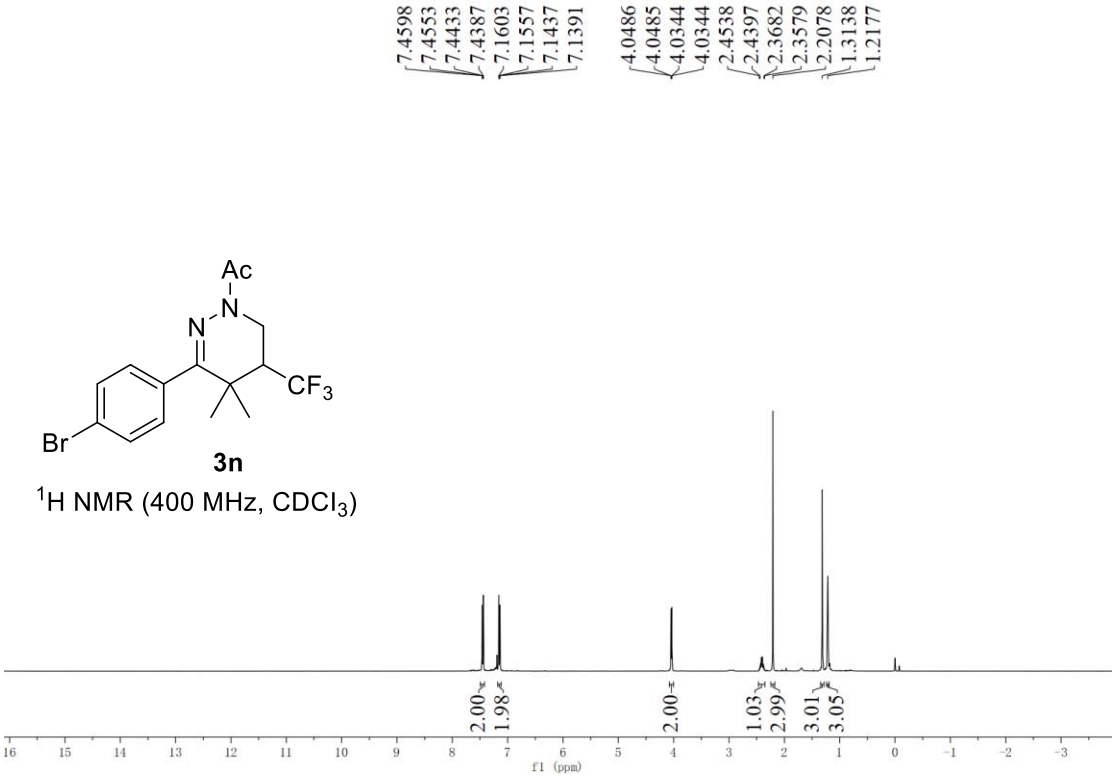

7.5633
7.5571
7.5282
7.5233
7.4877
7.4850
7.4822
7.4784
7.2922
7.2809
7.2683
7.2645
4.1277
4.1277
4.1134
4.1134
2.5163
2.5078
2.4627
2.4570
2.2925
1.3954
1.2952
Ac
N
N
Br
CF3
3m
1H NMR (400 MHz, CDCl3)
1.03
1.01
2.03
2.00
0.95
2.97
2.95
3.02
f1 (ppm)


172.292
153.005
138.994
131.672
131.582
130.307
129.612
127.505
127.280
124.703
122.158
121.900
45.067
44.812
44.556
44.301
36.138
36.097
36.054
36.011
34.529
28.515
28.497
23.289
23.267
21.112
Ac
N
N
Br
CF3
3m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

3m

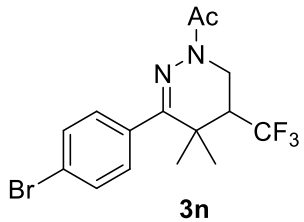
^{19}F NMR (282 MHz, $CDCl_3$)





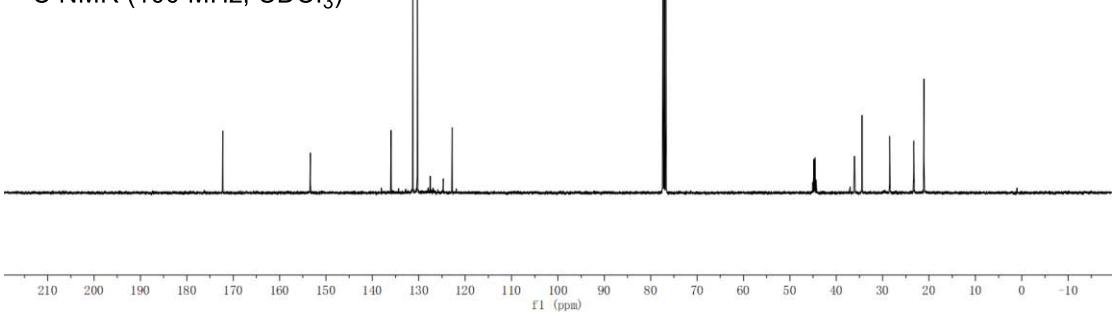
3n

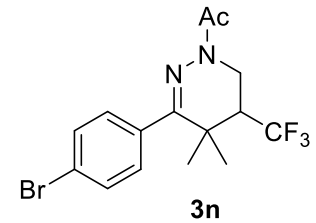
^{1}H NMR (400 MHz, $CDCl_3$)



3n

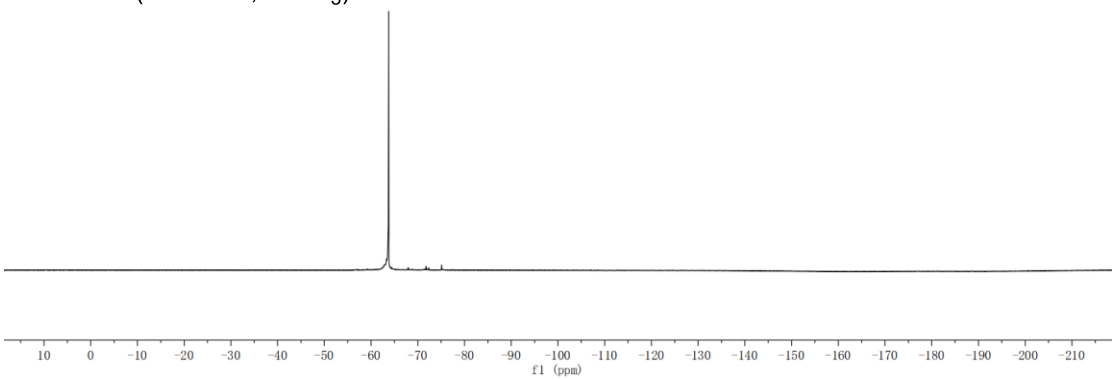
^{13}C NMR (100 MHz, $CDCl_3$)

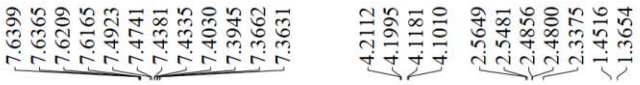


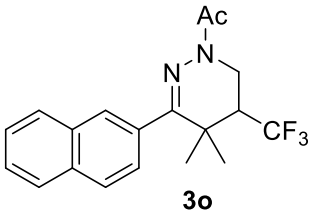


3n

^{19}F NMR (282 MHz, $CDCl_3$)

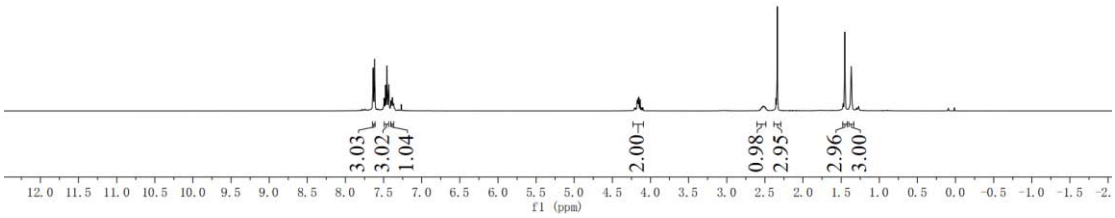


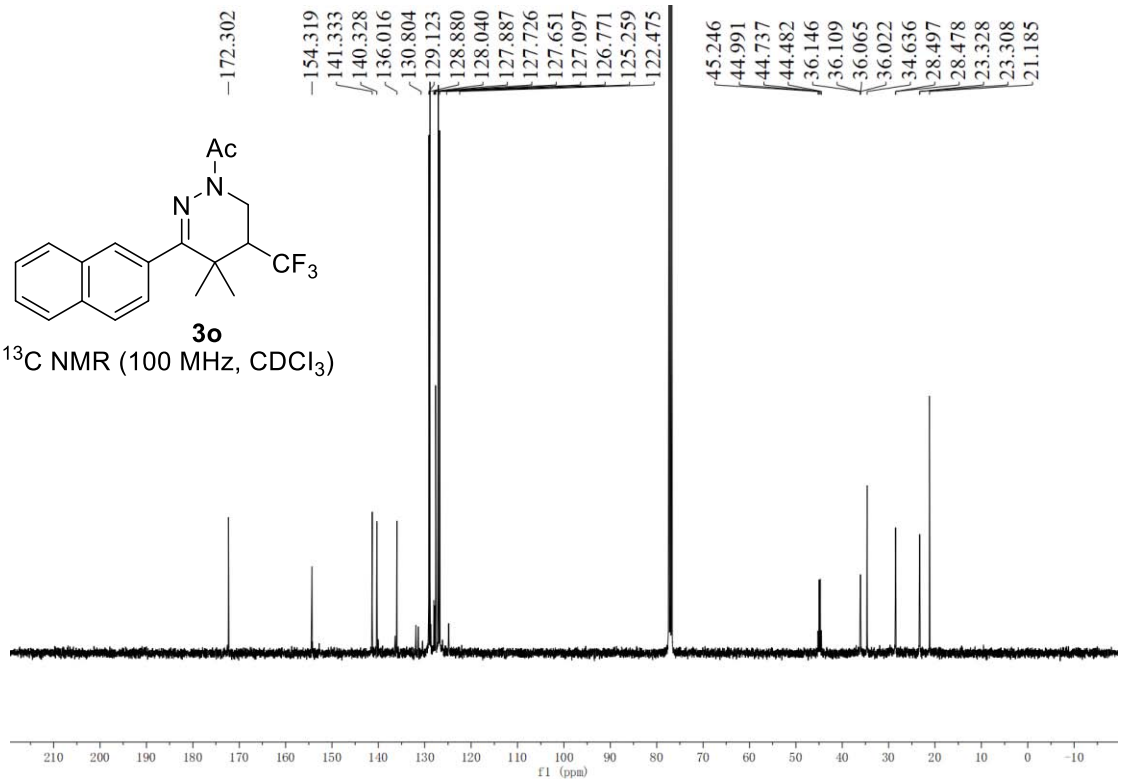




3o

^{1}H NMR (400 MHz, $CDCl_3$)



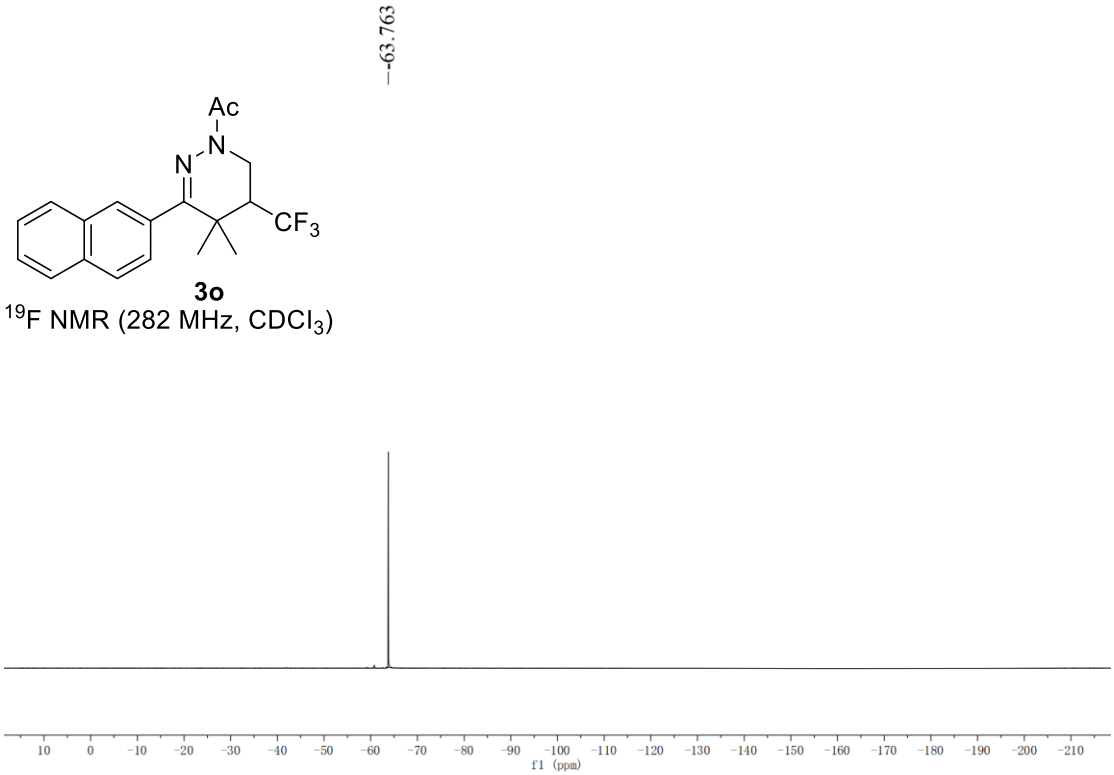


3o

^{13}C NMR (100 MHz, $CDCl_3$)

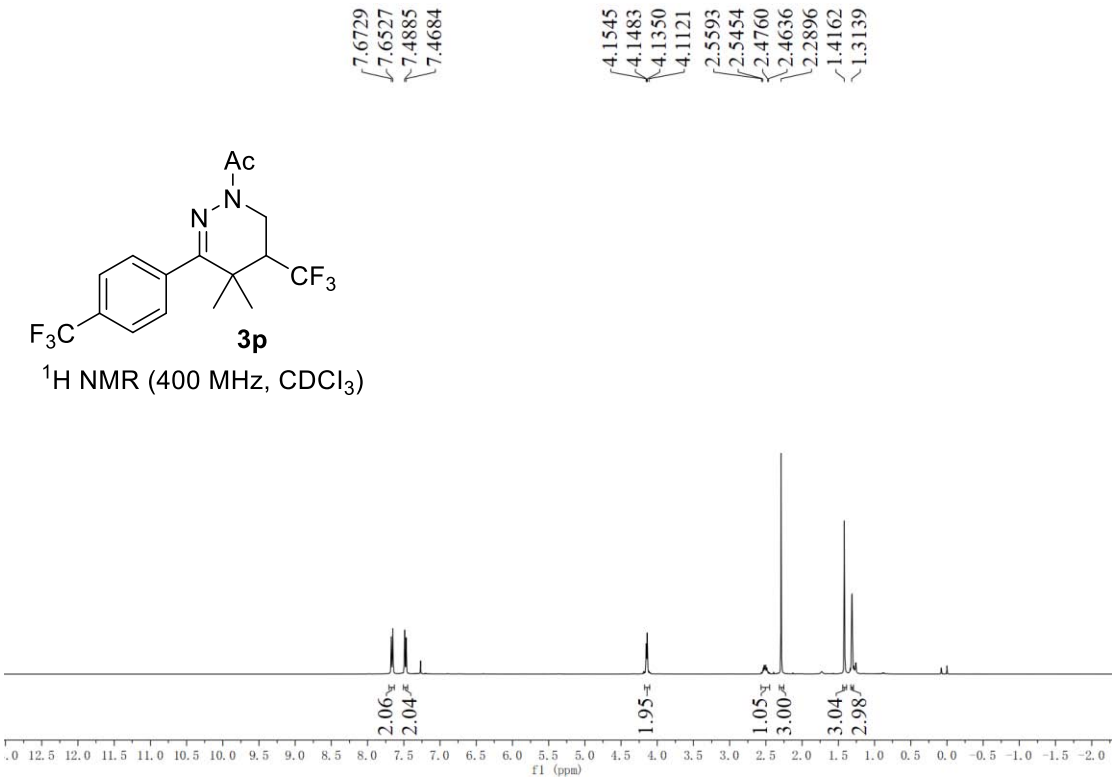
3o

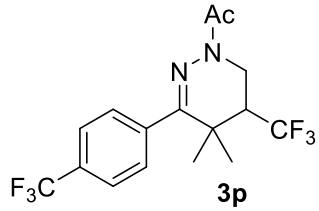
^{19}F NMR (282 MHz, $CDCl_3$)



3p

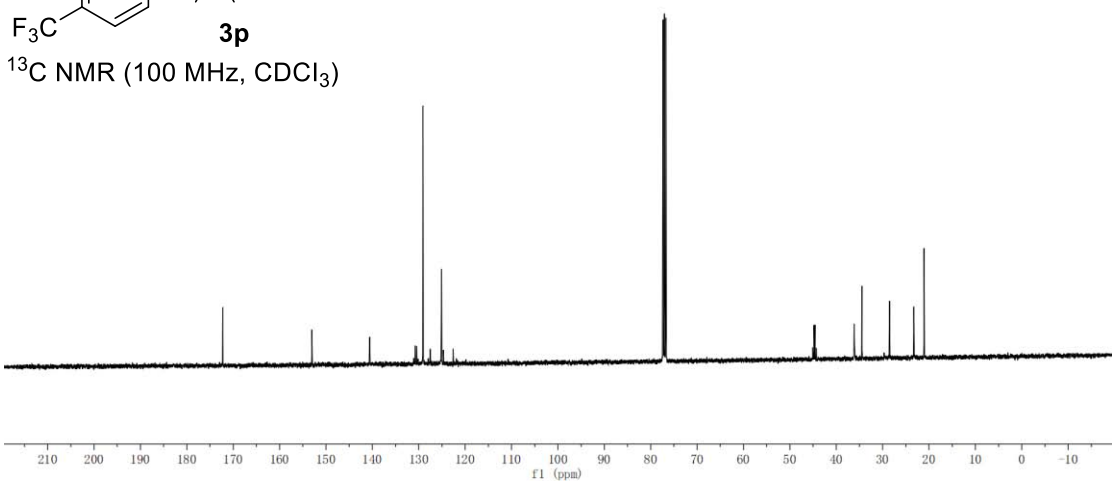
^{1}H NMR (400 MHz, $CDCl_3$)

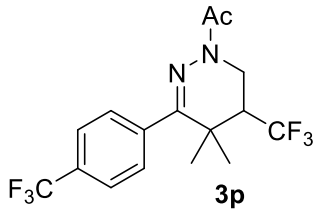




3p

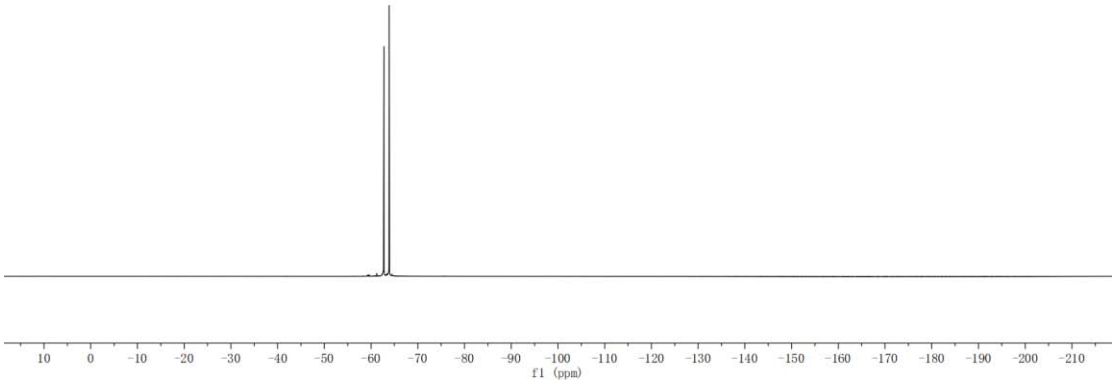
^{13}C NMR (100 MHz, $CDCl_3$)

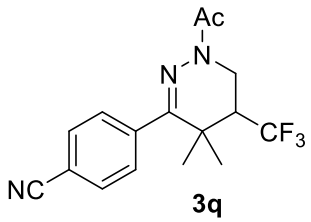




3p

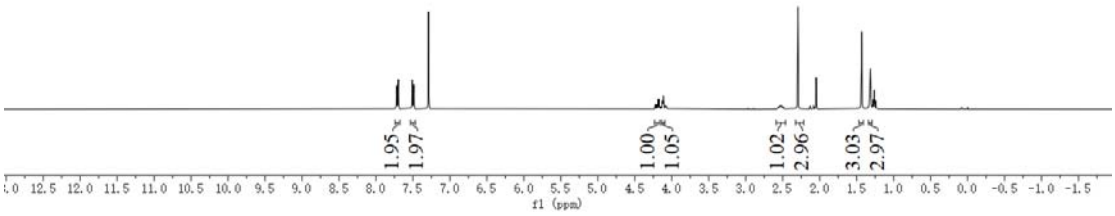
^{19}F NMR (282 MHz, $CDCl_3$)

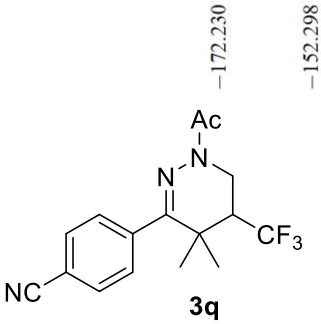




3q

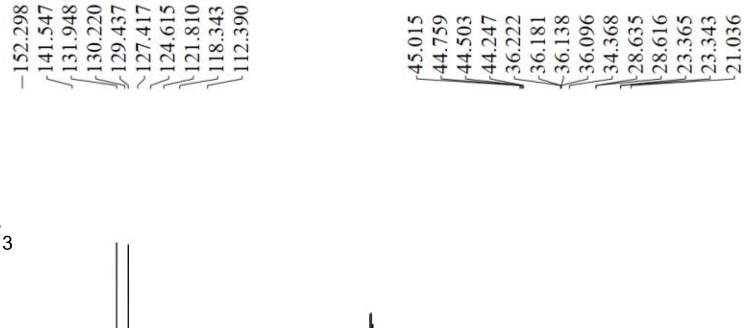
^{1}H NMR (400 MHz, $CDCl_3$)

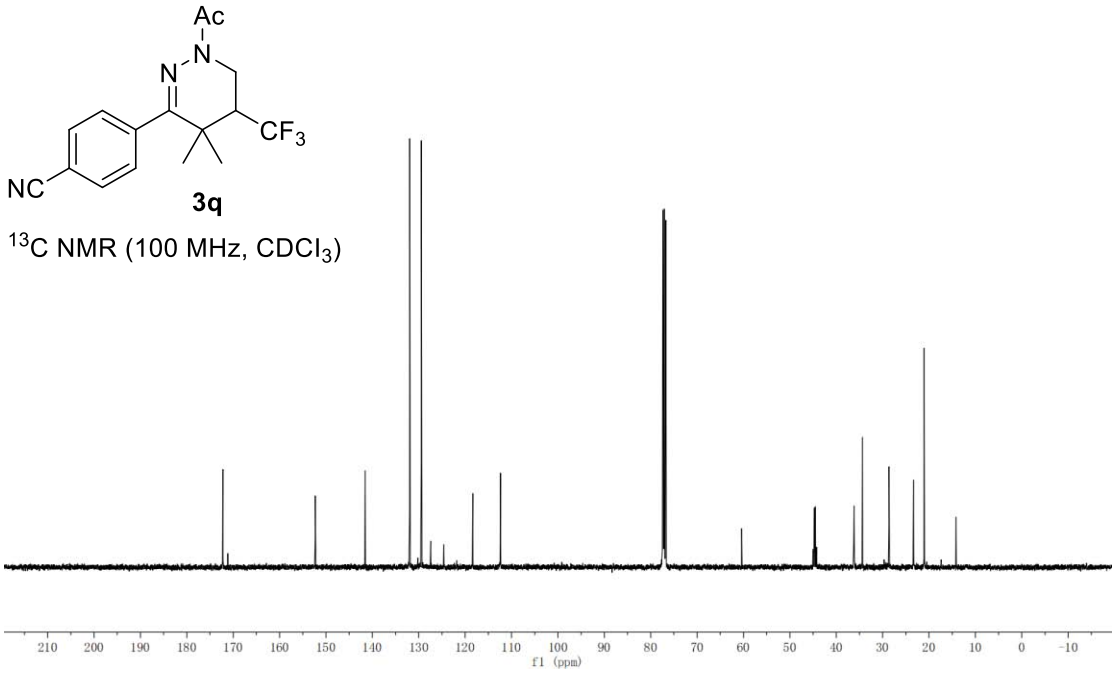




3q

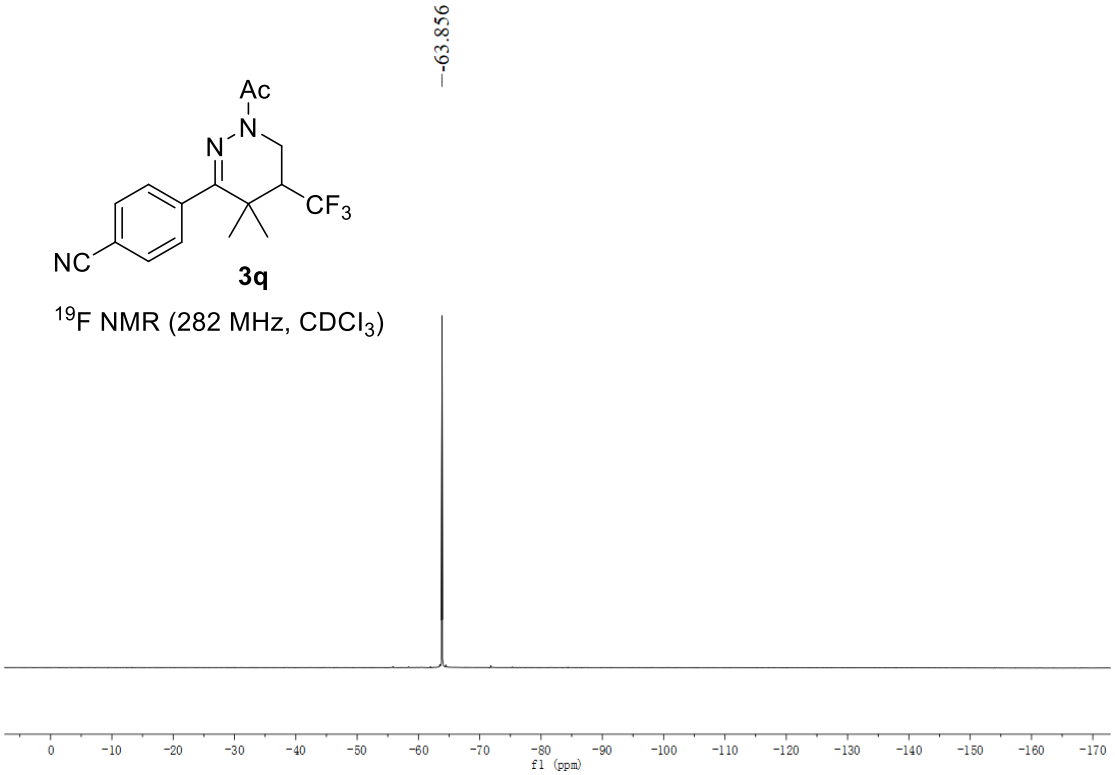
^{13}C NMR (100 MHz, $CDCl_3$)

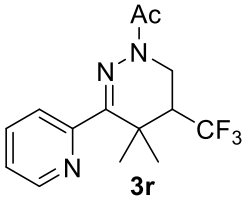




3q

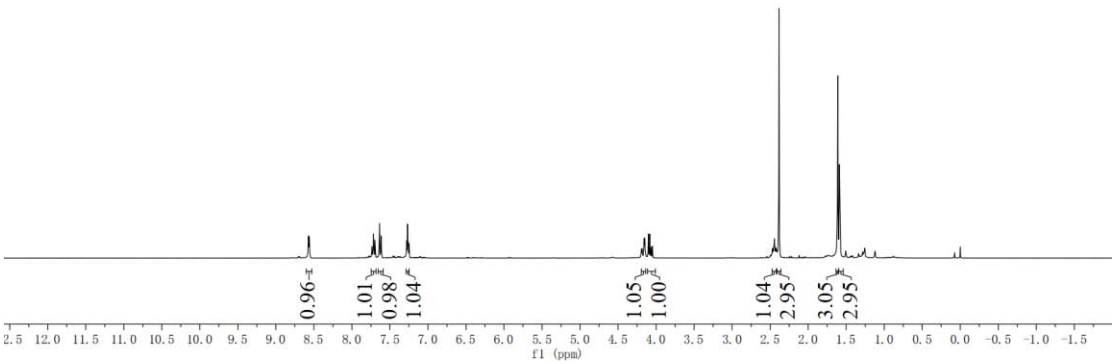
^{19}F NMR (282 MHz, $CDCl_3$)





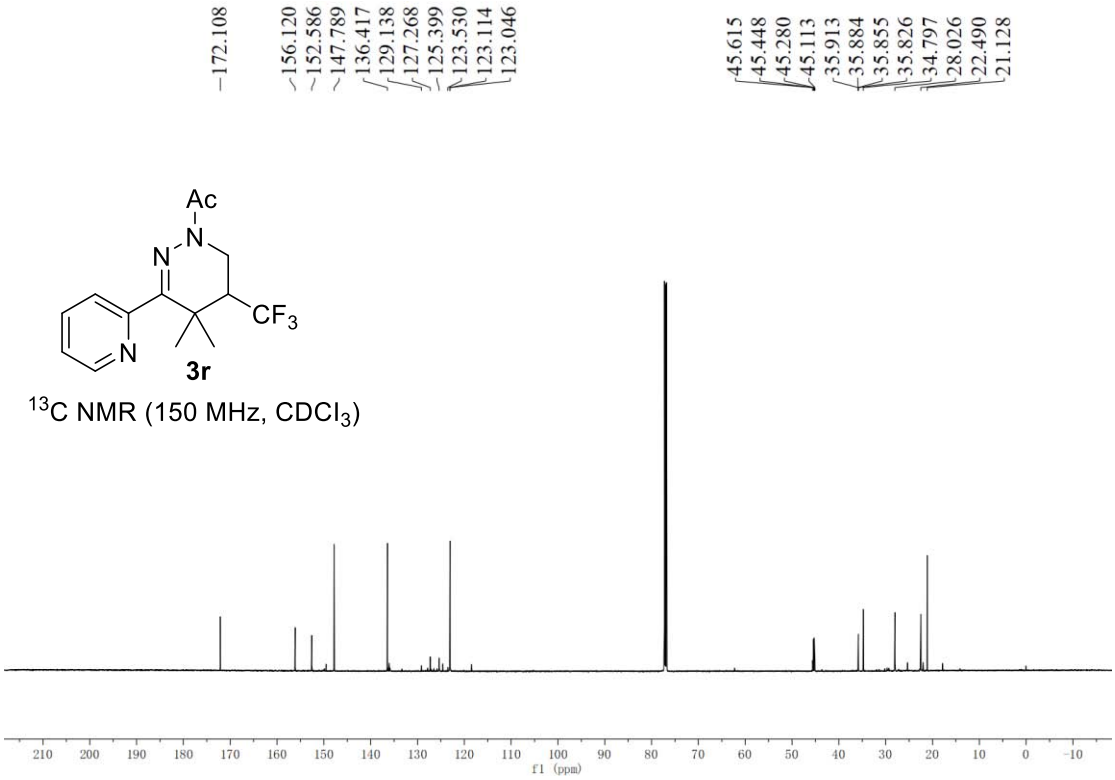
3r

^{1}H NMR (400 MHz, $CDCl_3$)



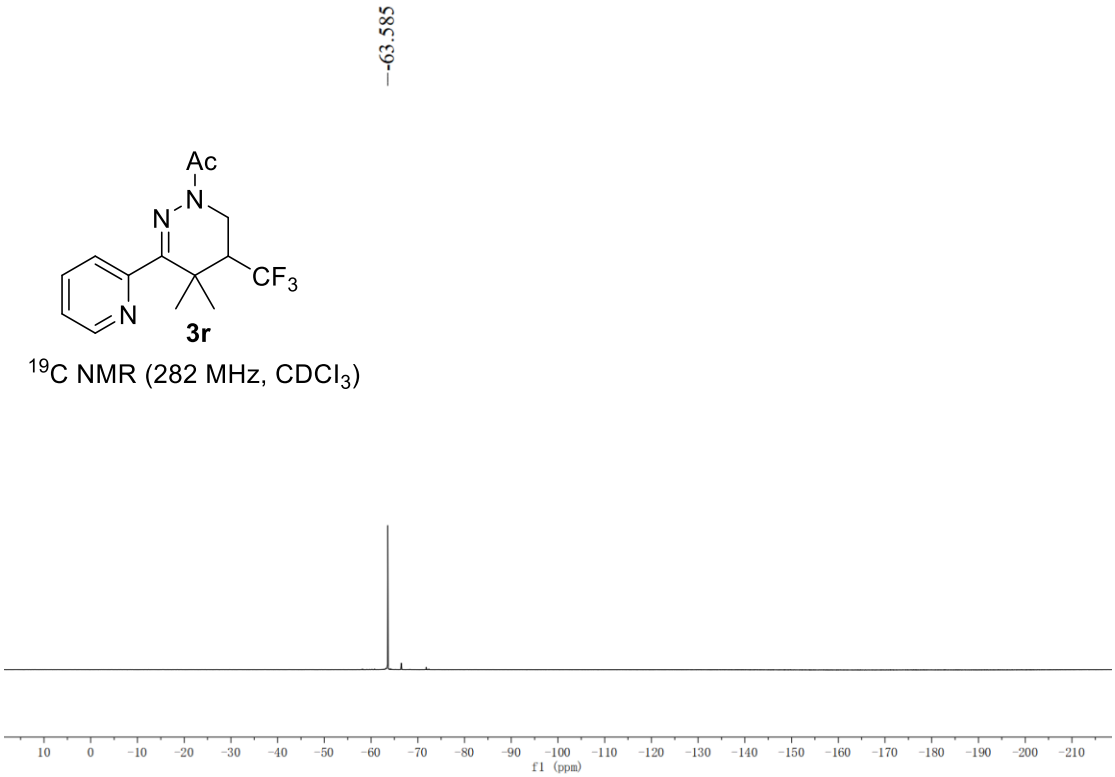
3r

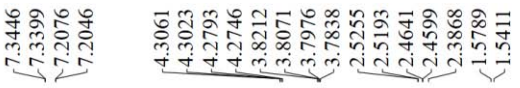
^{13}C NMR (150 MHz, $CDCl_3$)

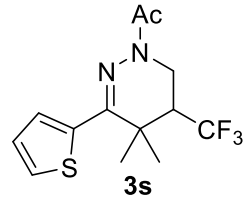


3r

^{19}C NMR (282 MHz, $CDCl_3$)

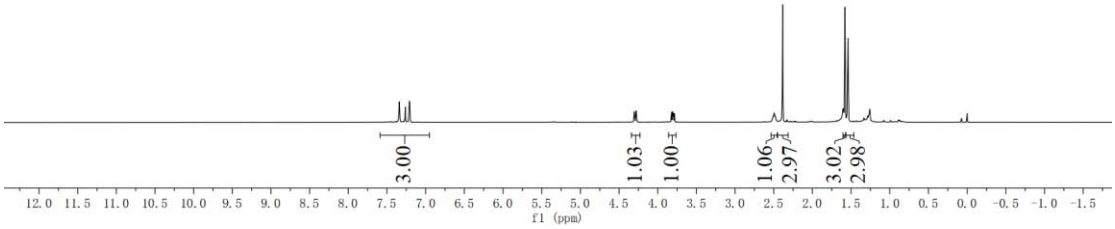


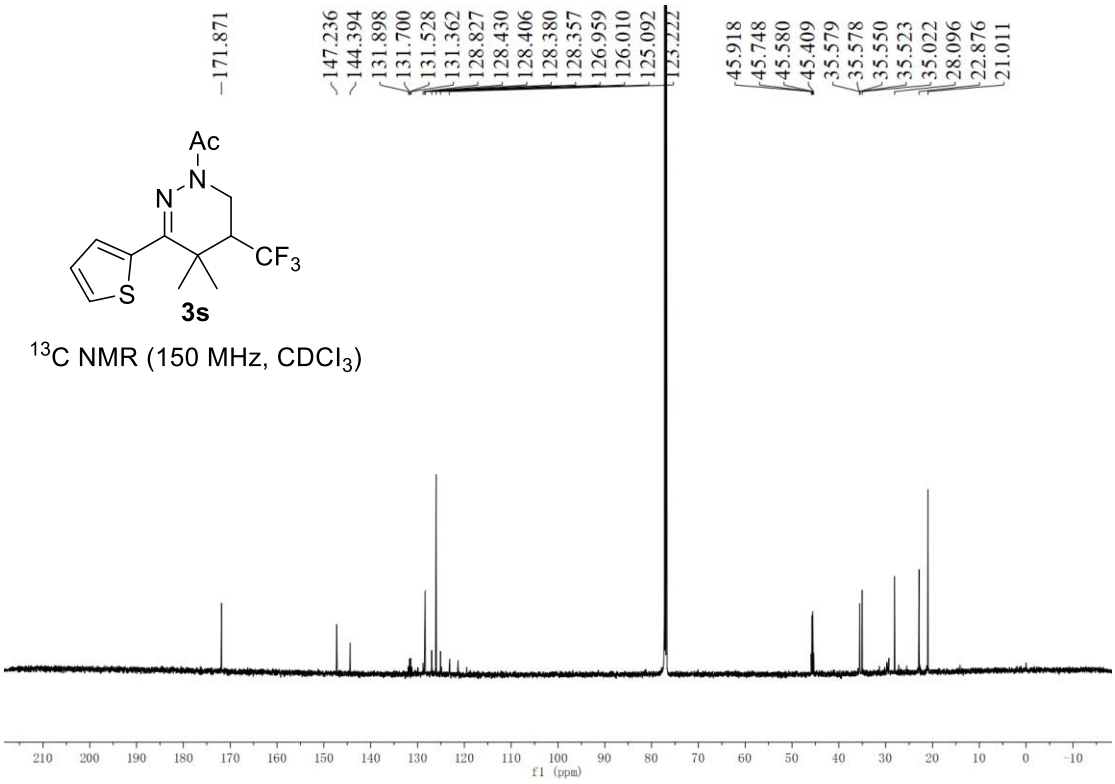




3s

^{1}H NMR (600 MHz, $CDCl_3$)



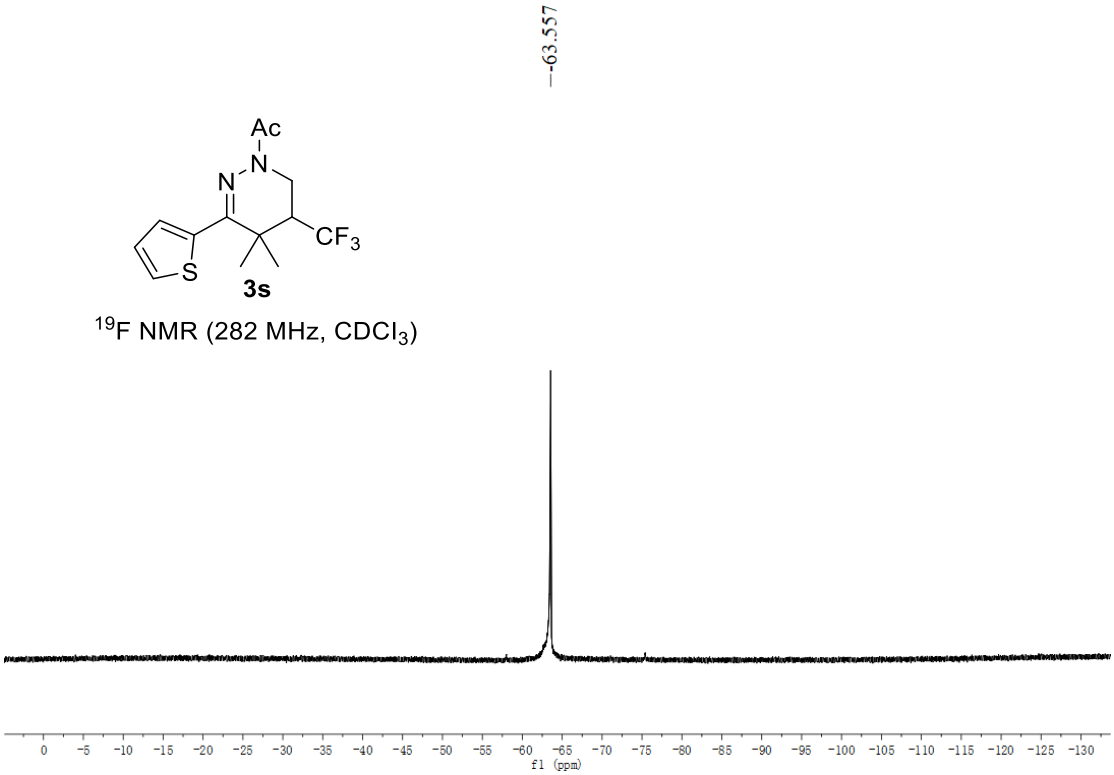


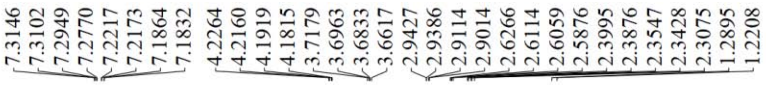
3s

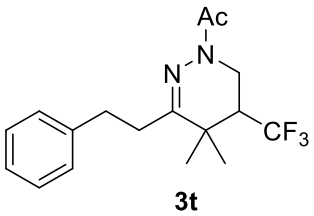
^{13}C NMR (150 MHz, $CDCl_3$)

3s

^{19}F NMR (282 MHz, $CDCl_3$)

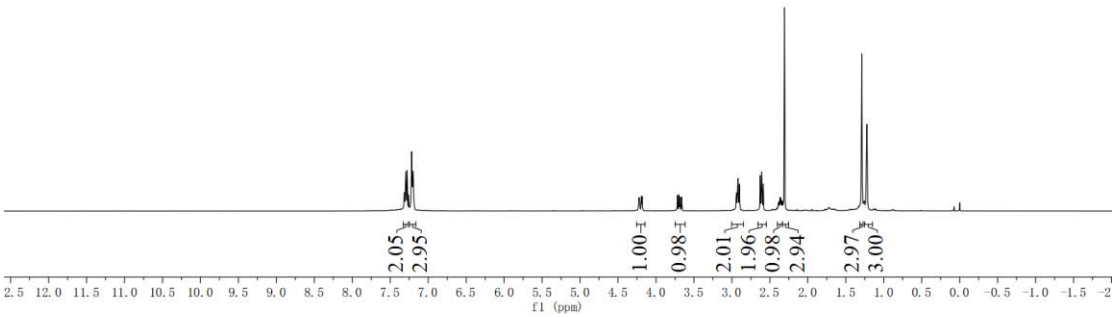


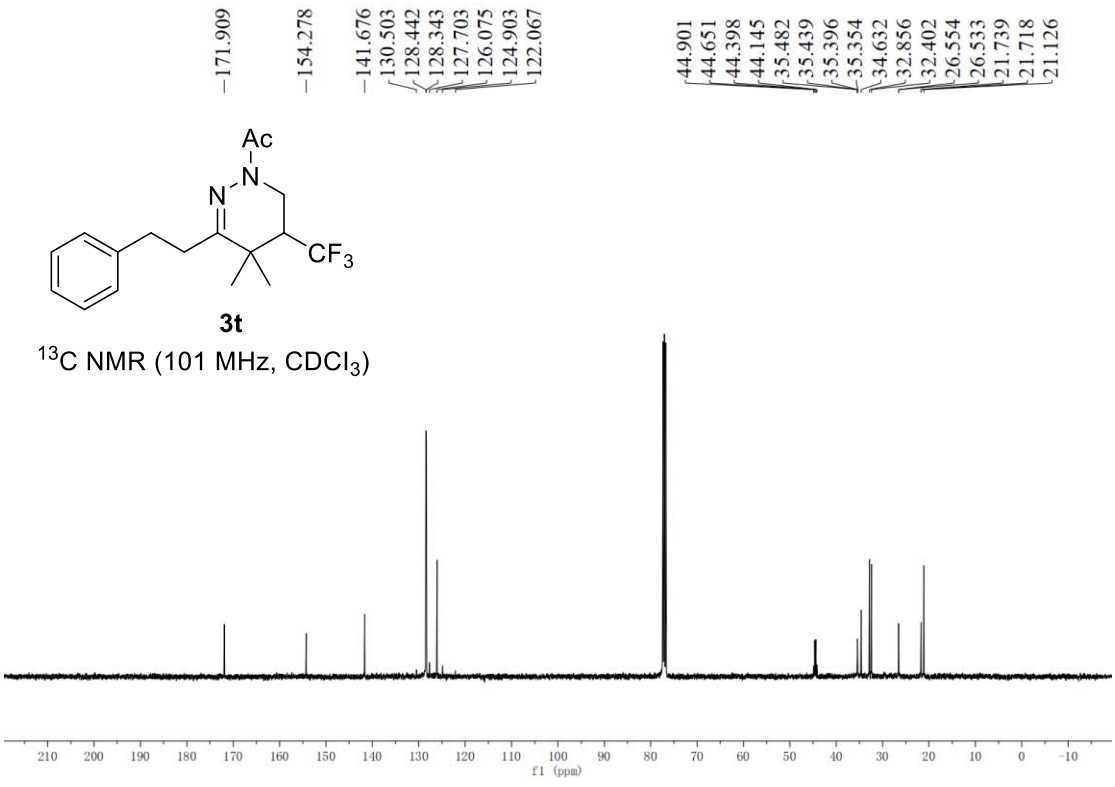




3t

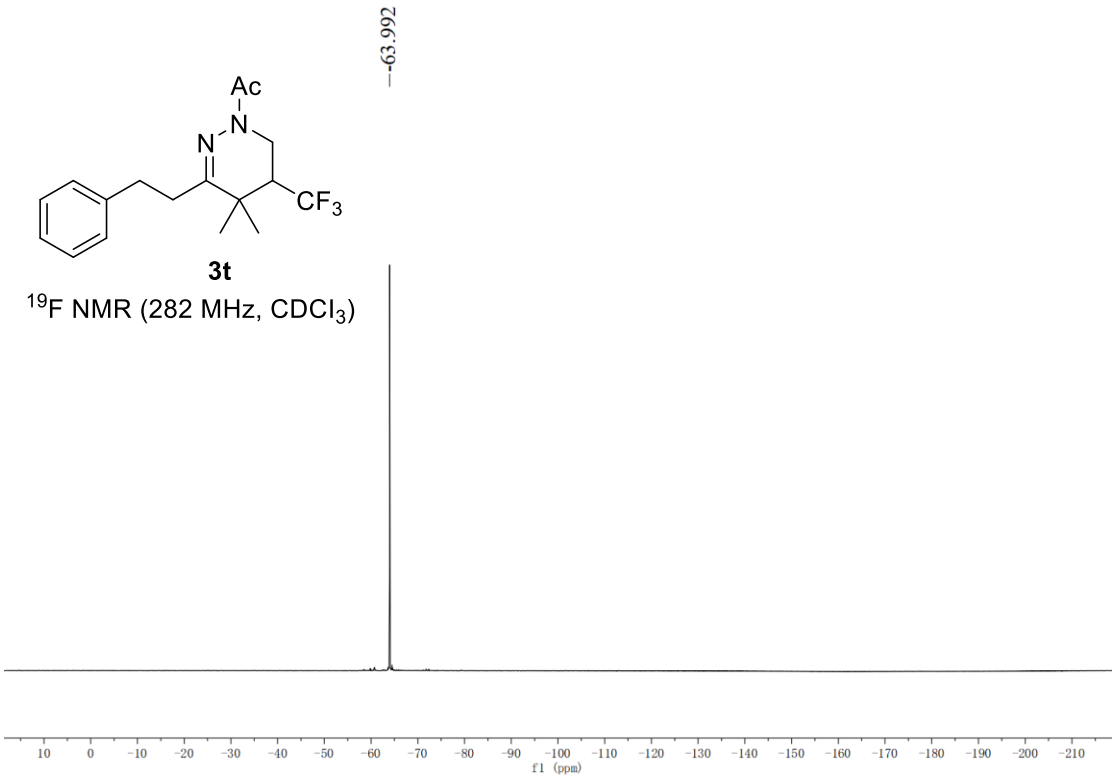
^{1}H NMR (400 MHz, $CDCl_3$)





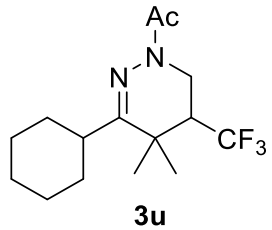
3t

^{13}C NMR (101 MHz, $CDCl_3$)



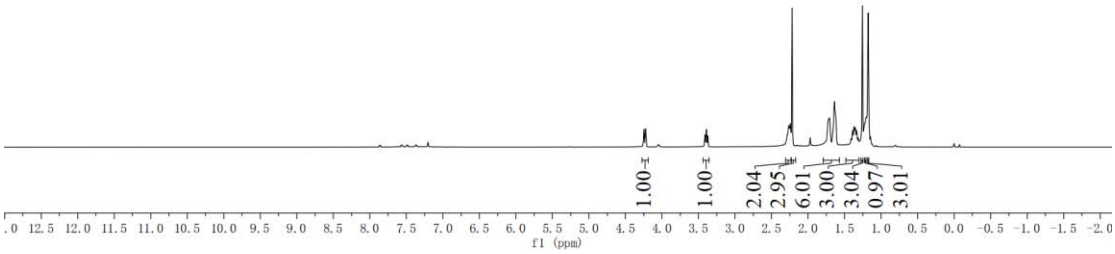
3t

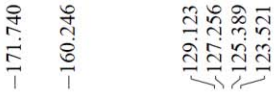
^{19}F NMR (282 MHz, $CDCl_3$)

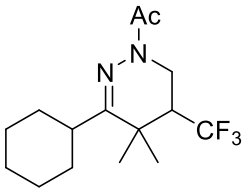


3u

^{1}H NMR (600 MHz, $CDCl_3$)

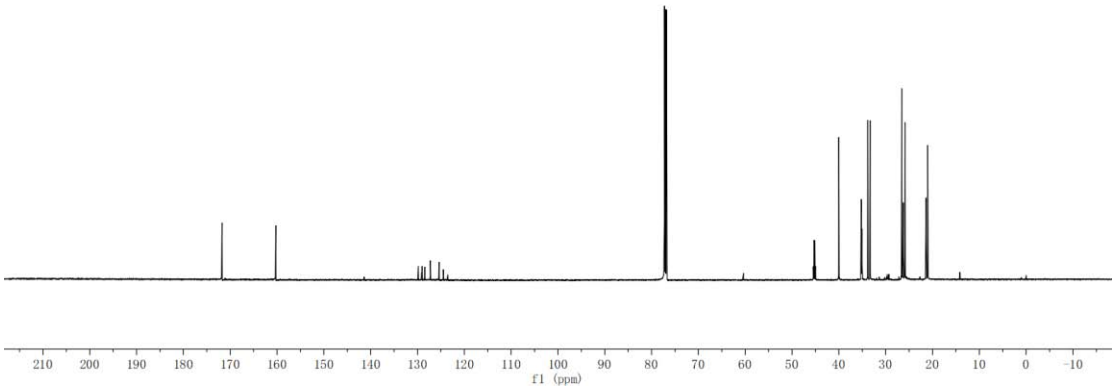






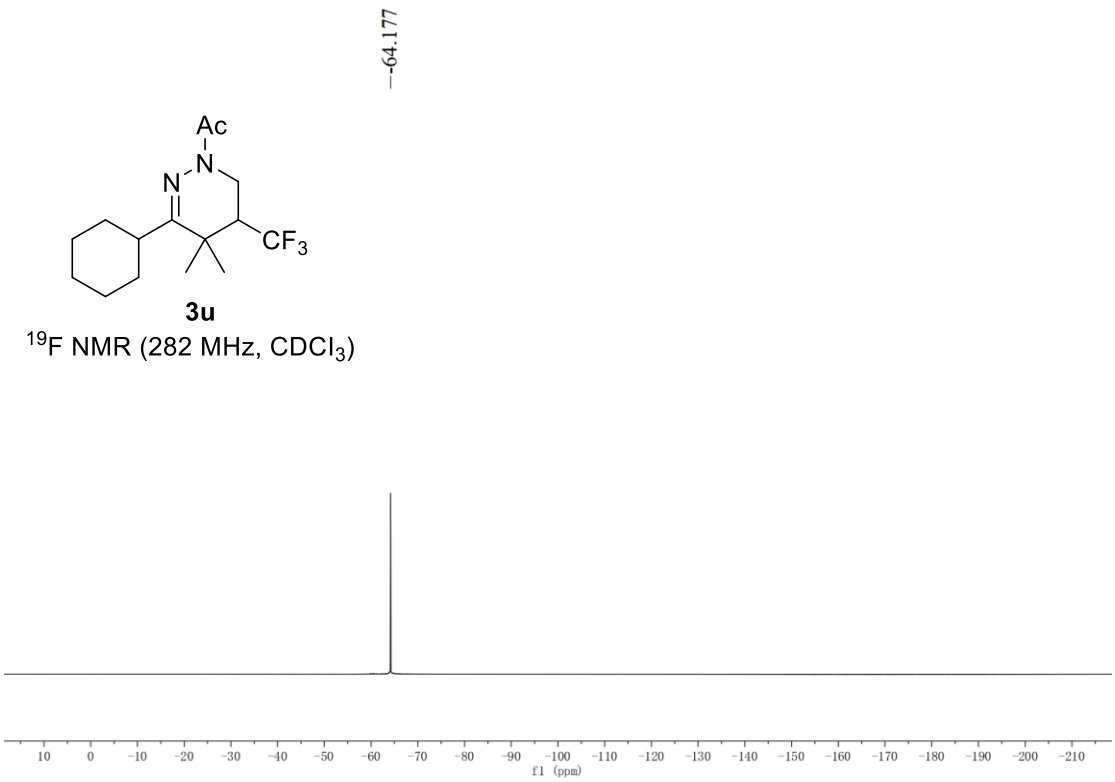
3u

^{13}C NMR (100 MHz, $CDCl_3$)



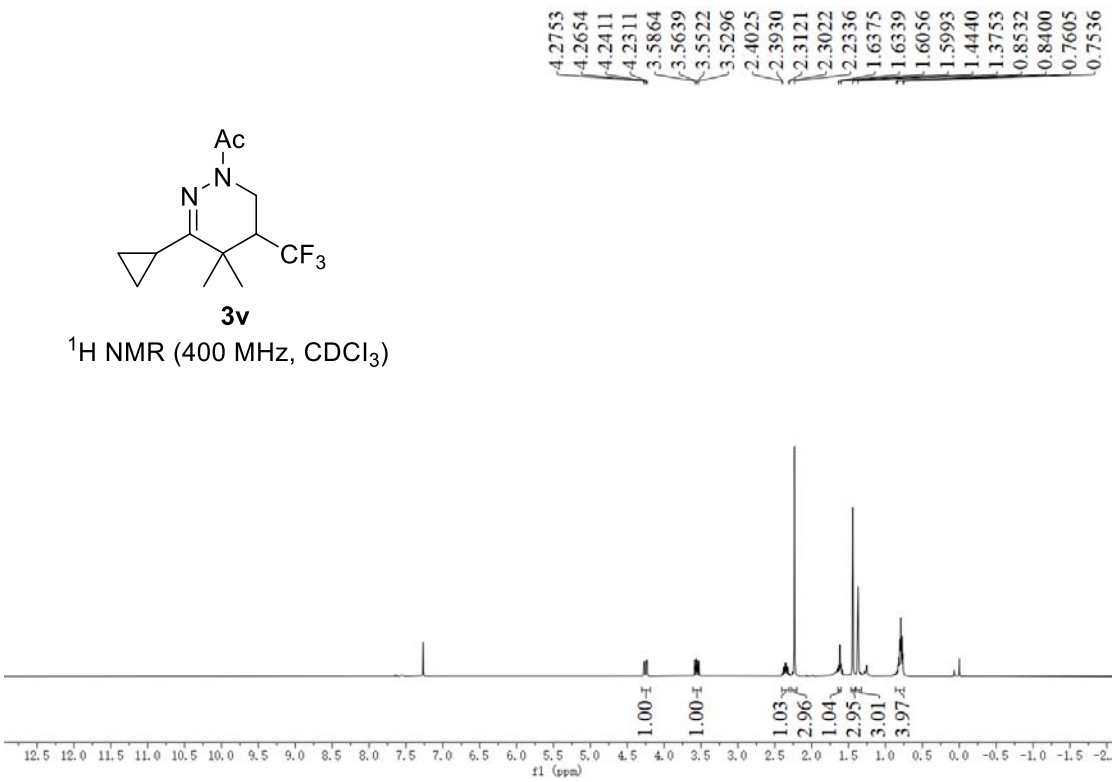
3u

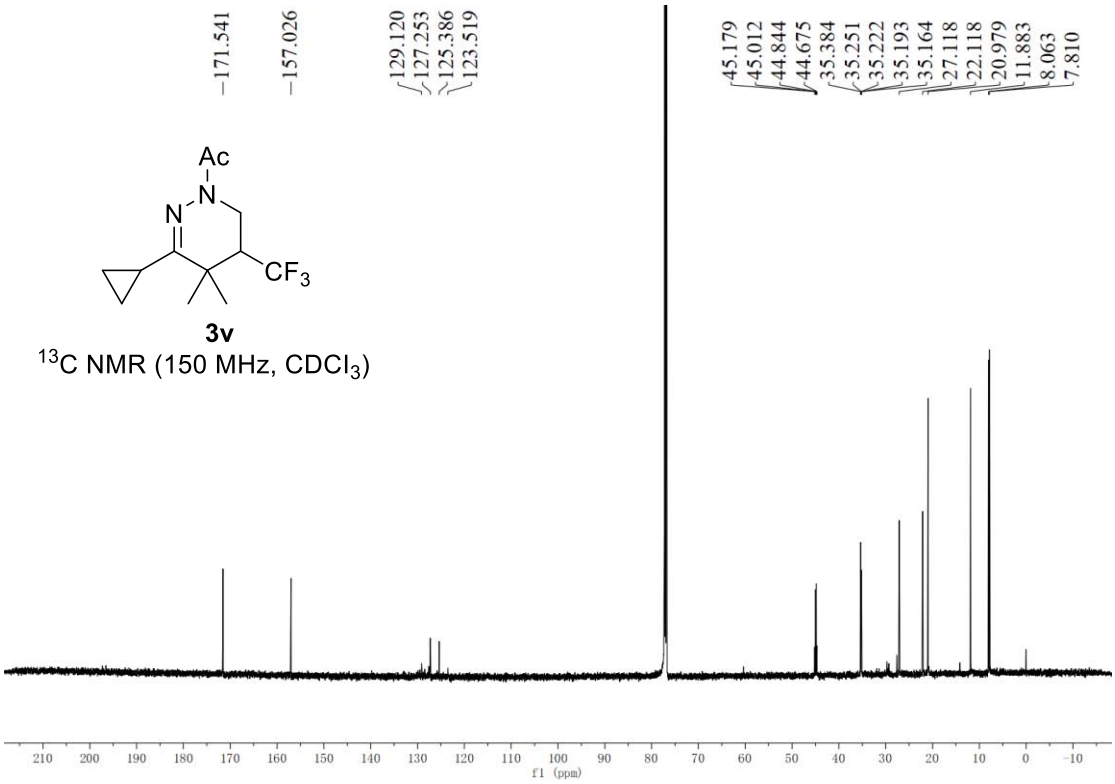
^{19}F NMR (282 MHz, $CDCl_3$)



3v

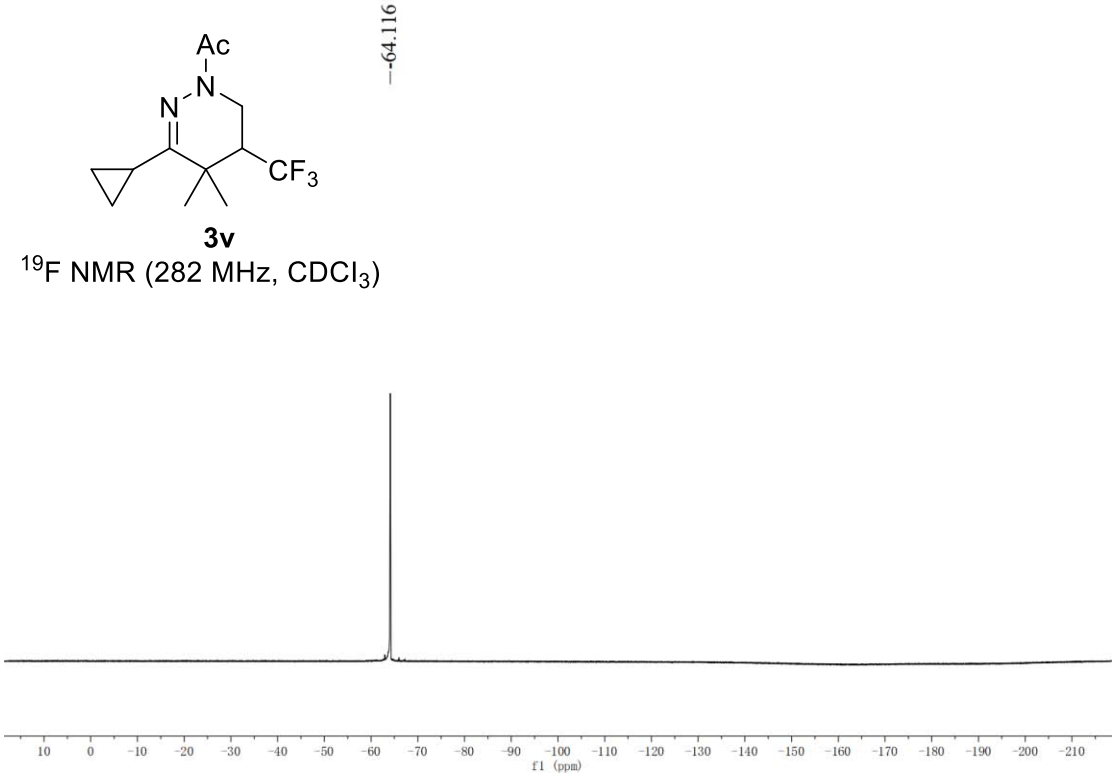
^{1}H NMR (400 MHz, $CDCl_3$)





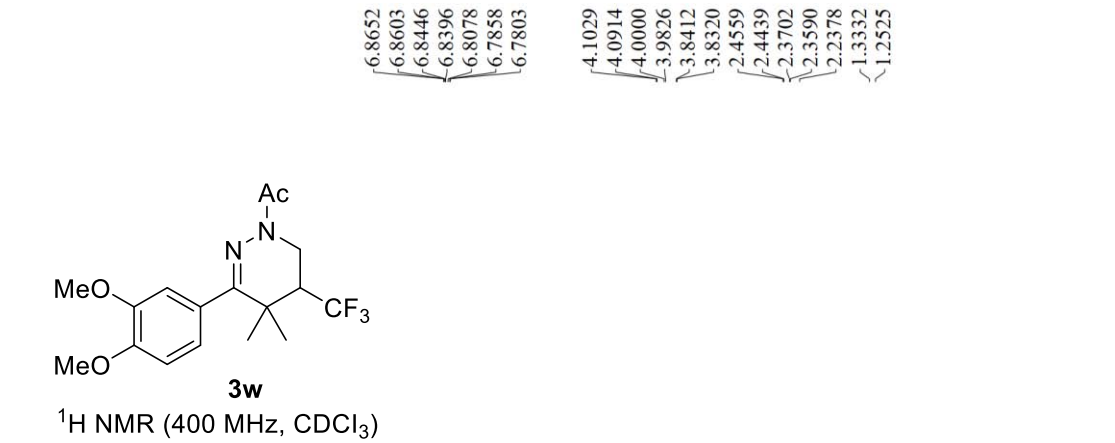
3v

^{13}C NMR (150 MHz, $CDCl_3$)



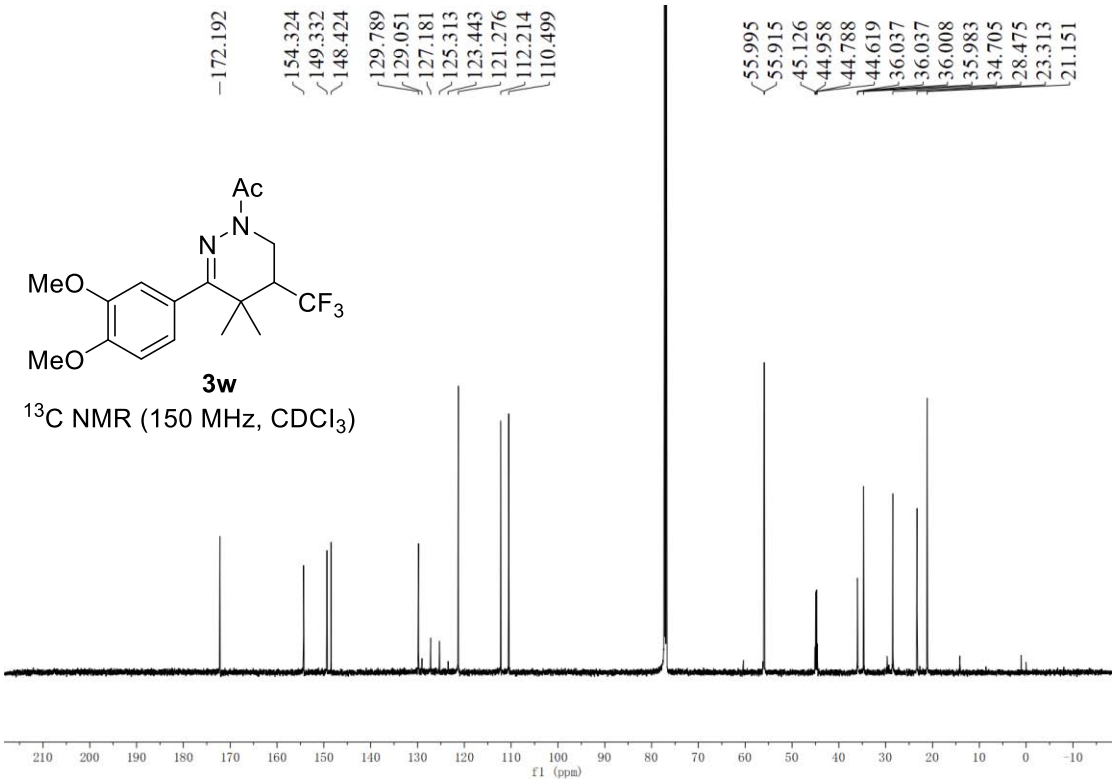
3v

^{19}F NMR (282 MHz, $CDCl_3$)



3w

^{1}H NMR (400 MHz, $CDCl_3$)

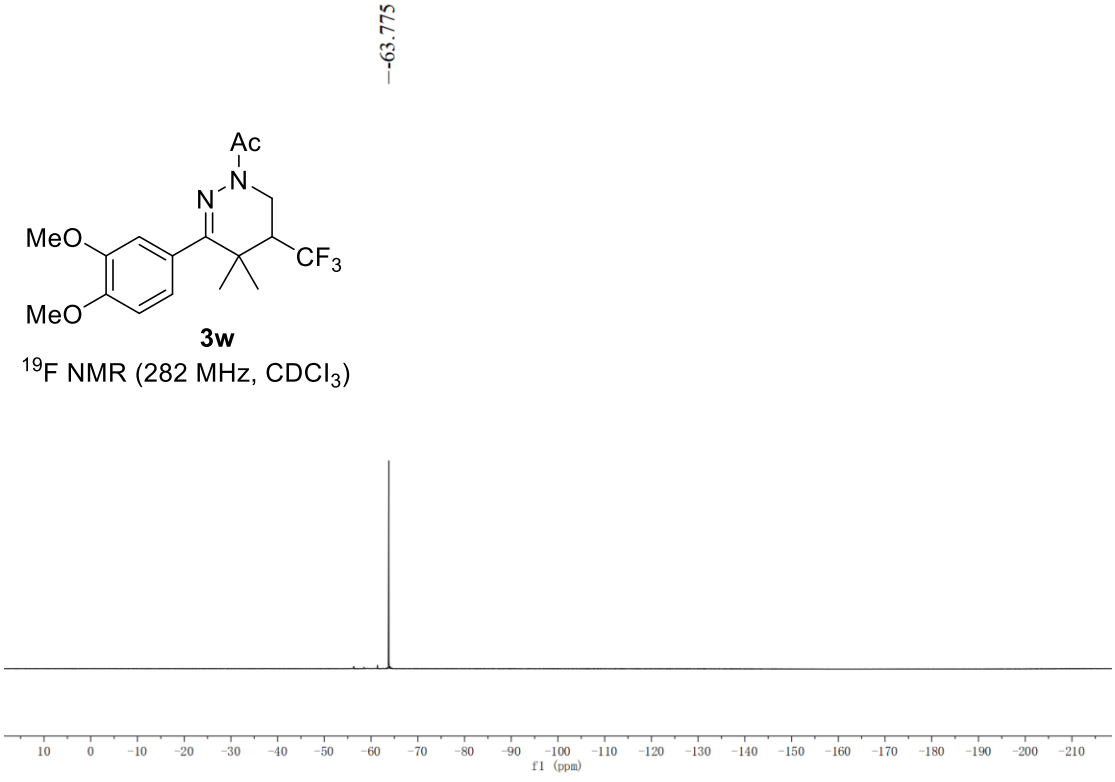


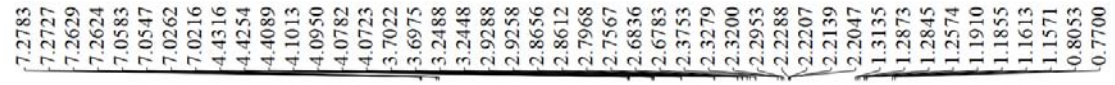
3w

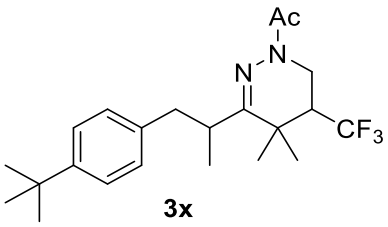
^{13}C NMR (150 MHz, $CDCl_3$)

3w

^{19}F NMR (282 MHz, $CDCl_3$)

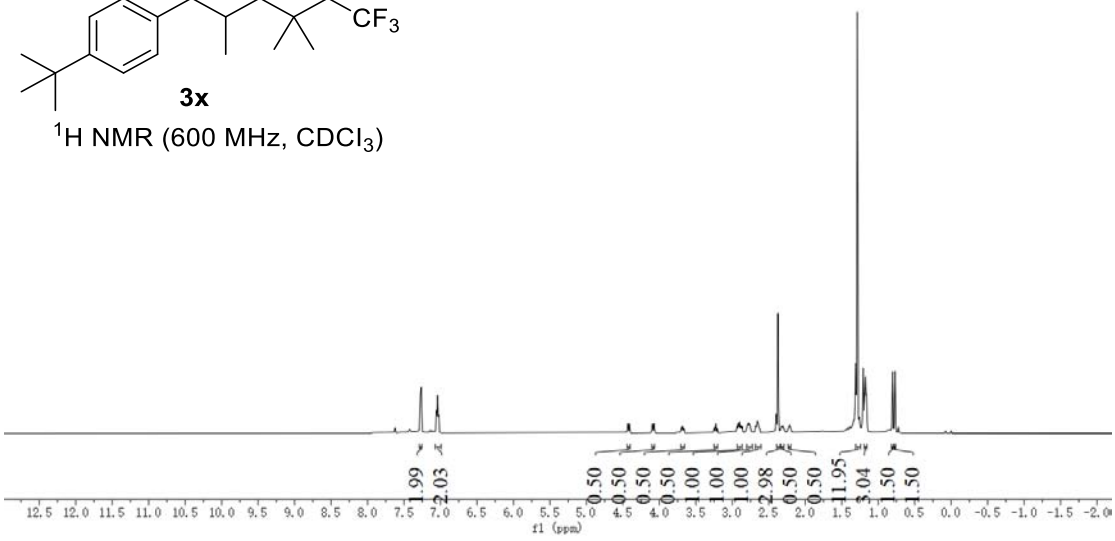


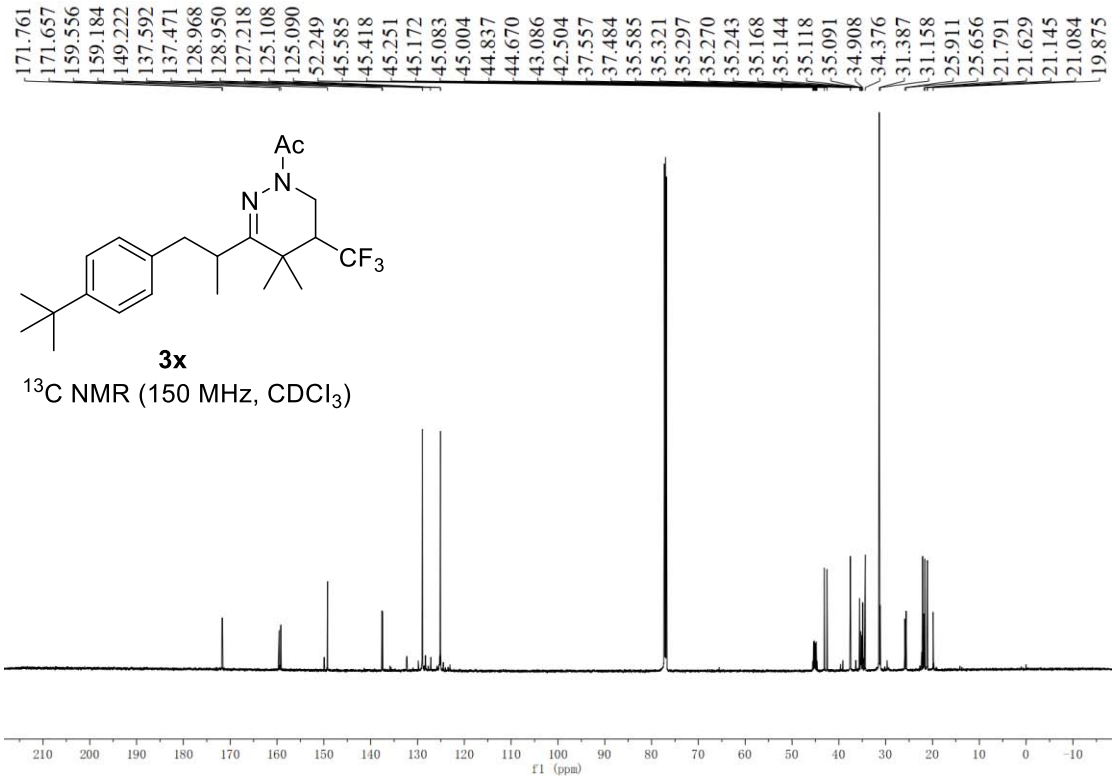




3x

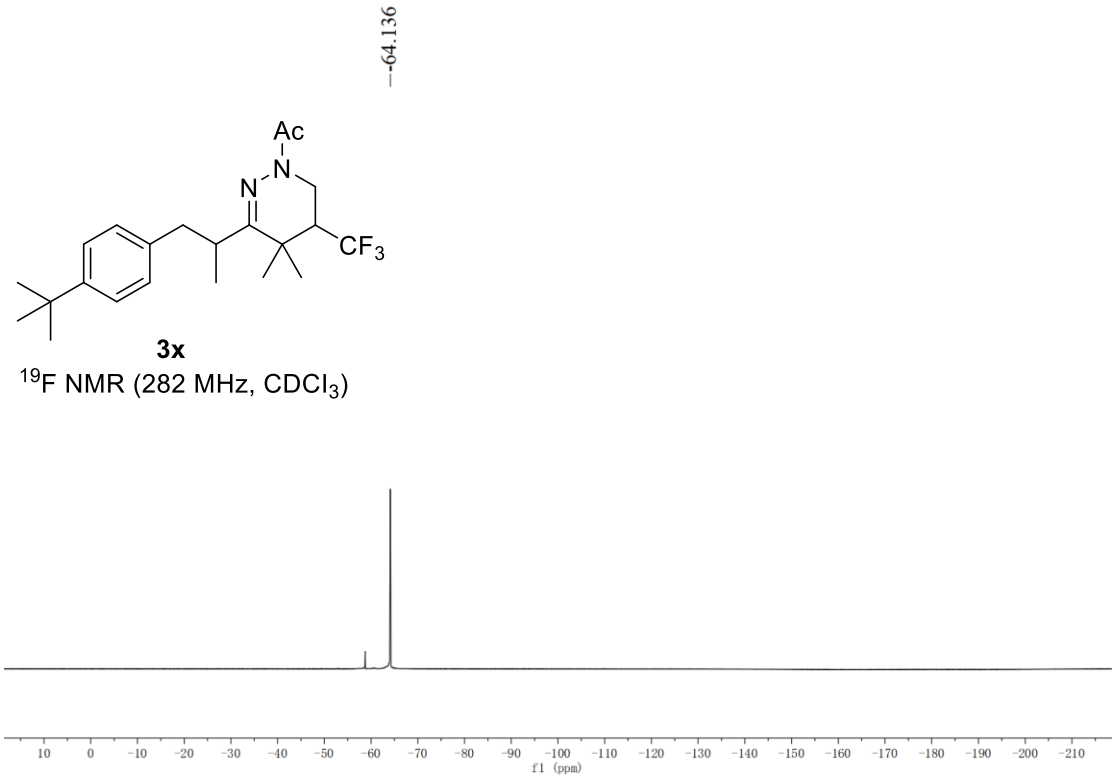
^{1}H NMR (600 MHz, $CDCl_3$)





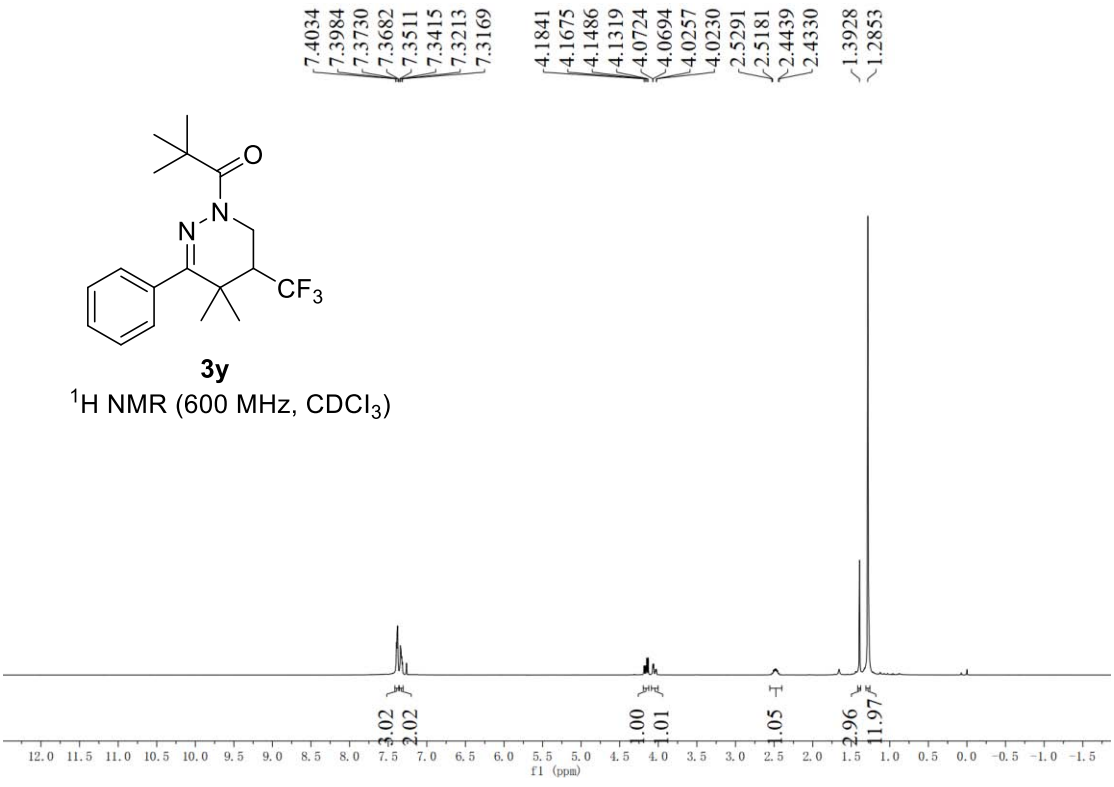
3x

^{13}C NMR (150 MHz, $CDCl_3$)



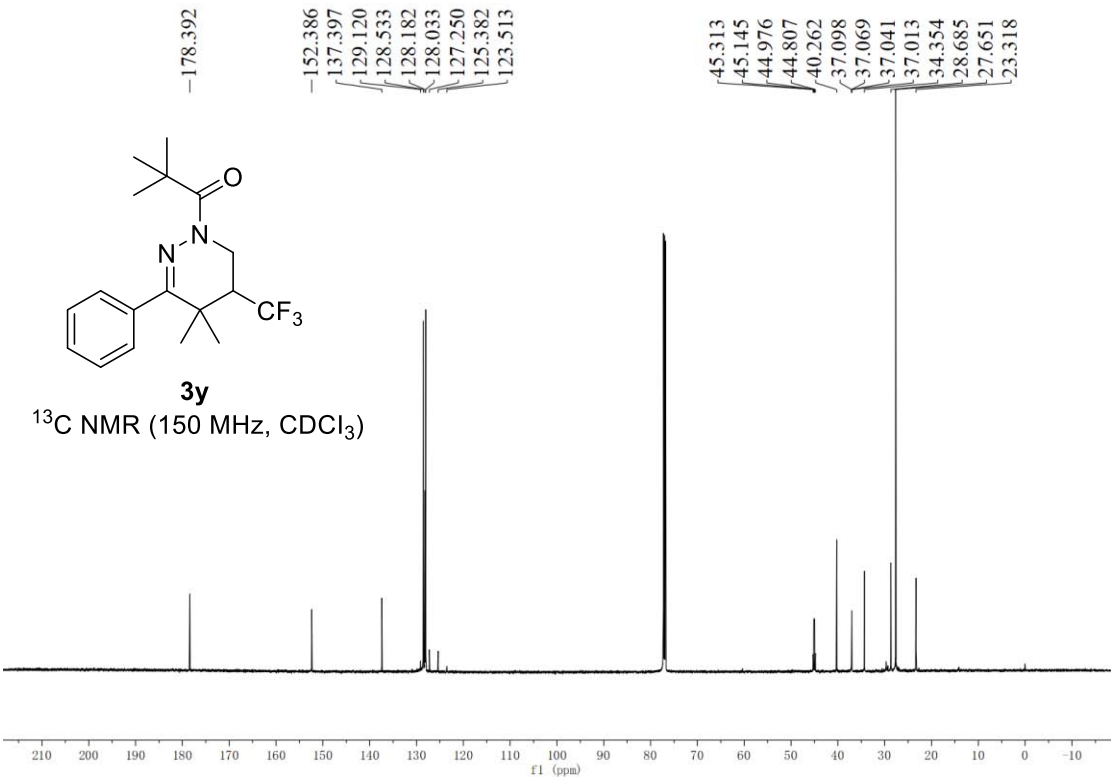
3x

^{19}F NMR (282 MHz, $CDCl_3$)



3y

^{1}H NMR (600 MHz, $CDCl_3$)

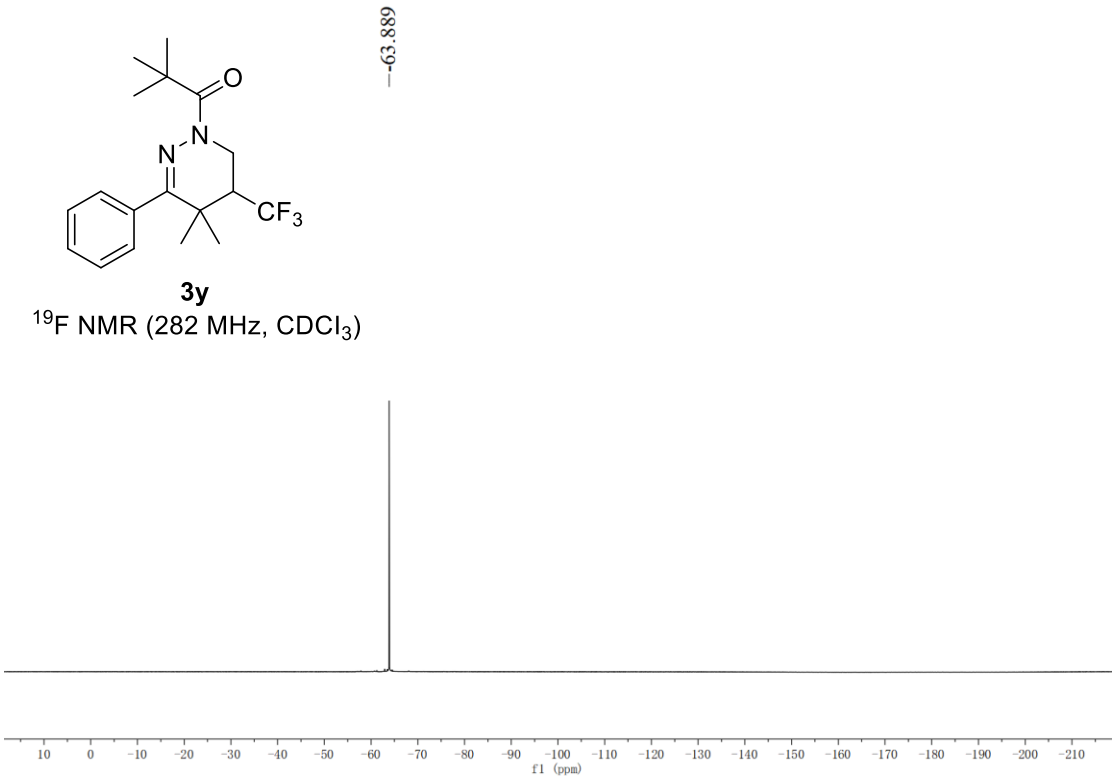


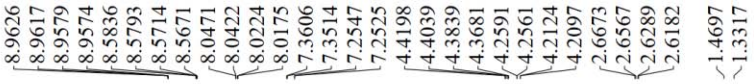
3y

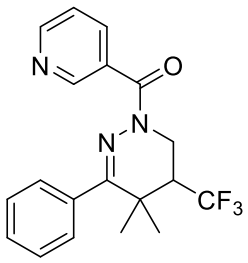
^{13}C NMR (150 MHz, $CDCl_3$)

3y

^{19}F NMR (282 MHz, $CDCl_3$)

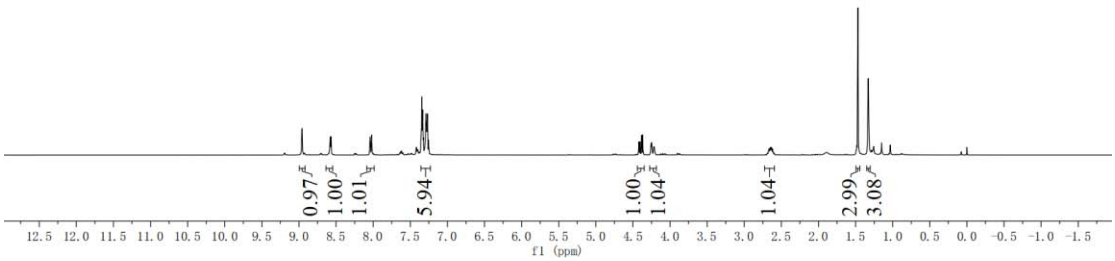


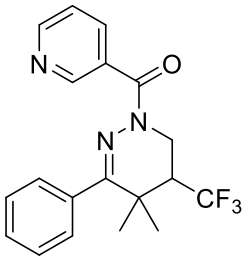




3z

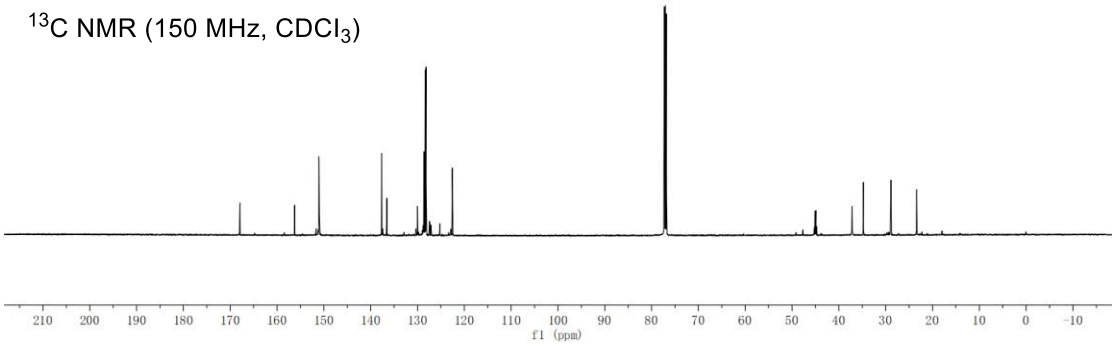
^{1}H NMR (600 MHz, $CDCl_3$)

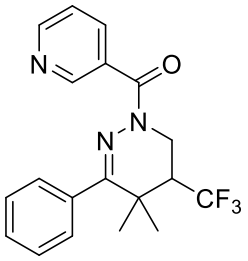




3z

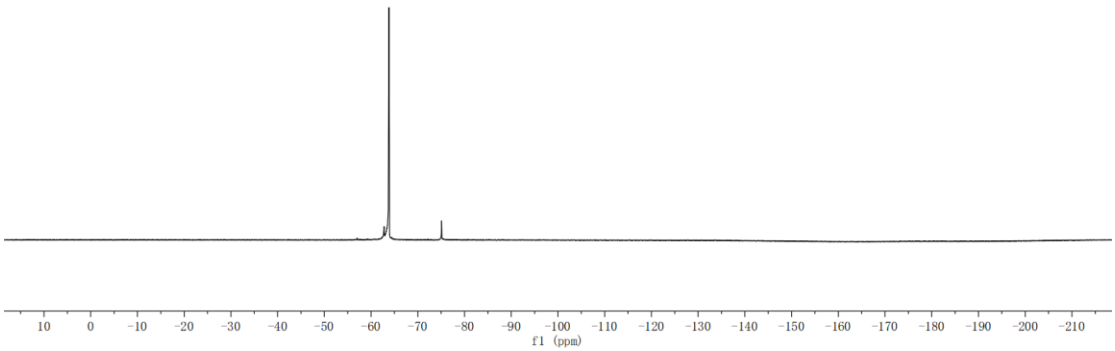
^{13}C NMR (150 MHz, $CDCl_3$)

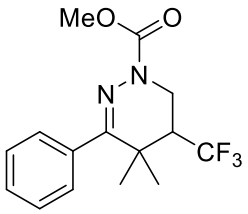




3z

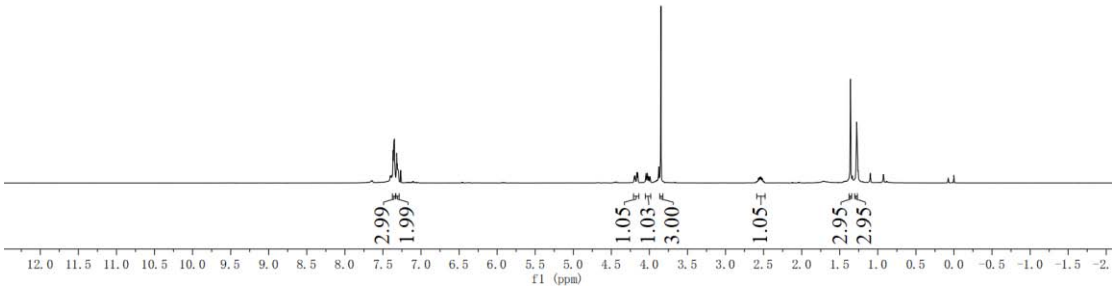
^{19}F NMR (282 MHz, $CDCl_3$)





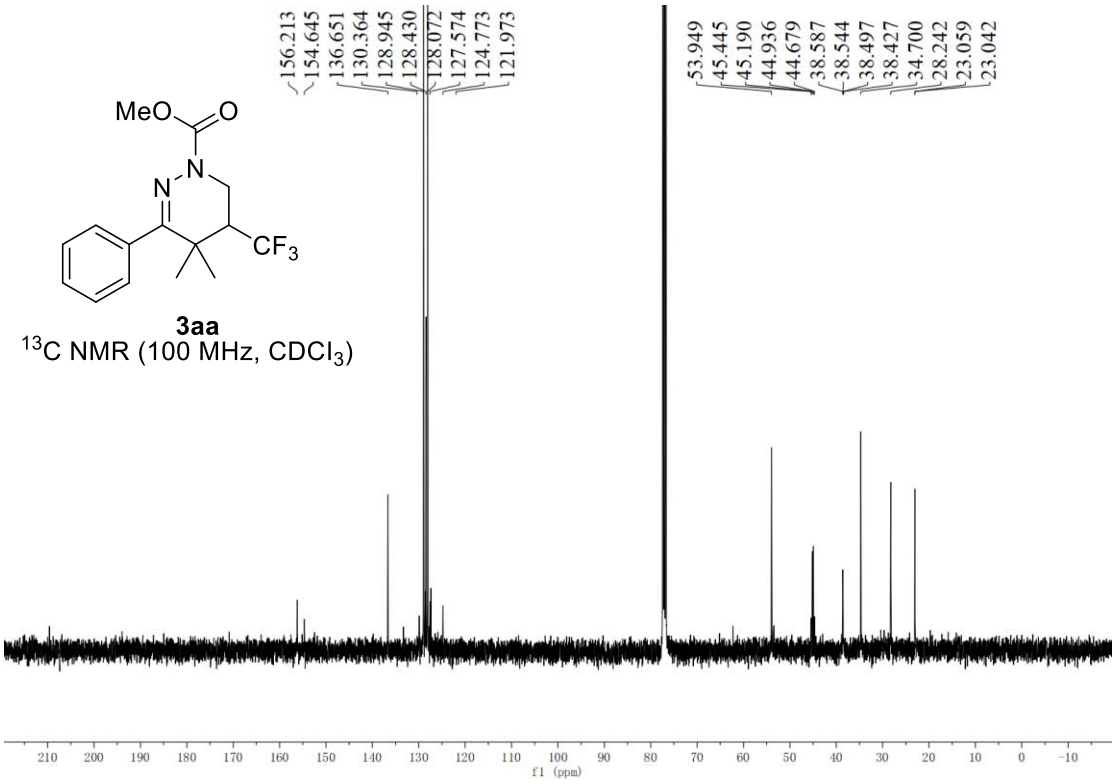
3aa

^{1}H NMR (400 MHz, $CDCl_3$)



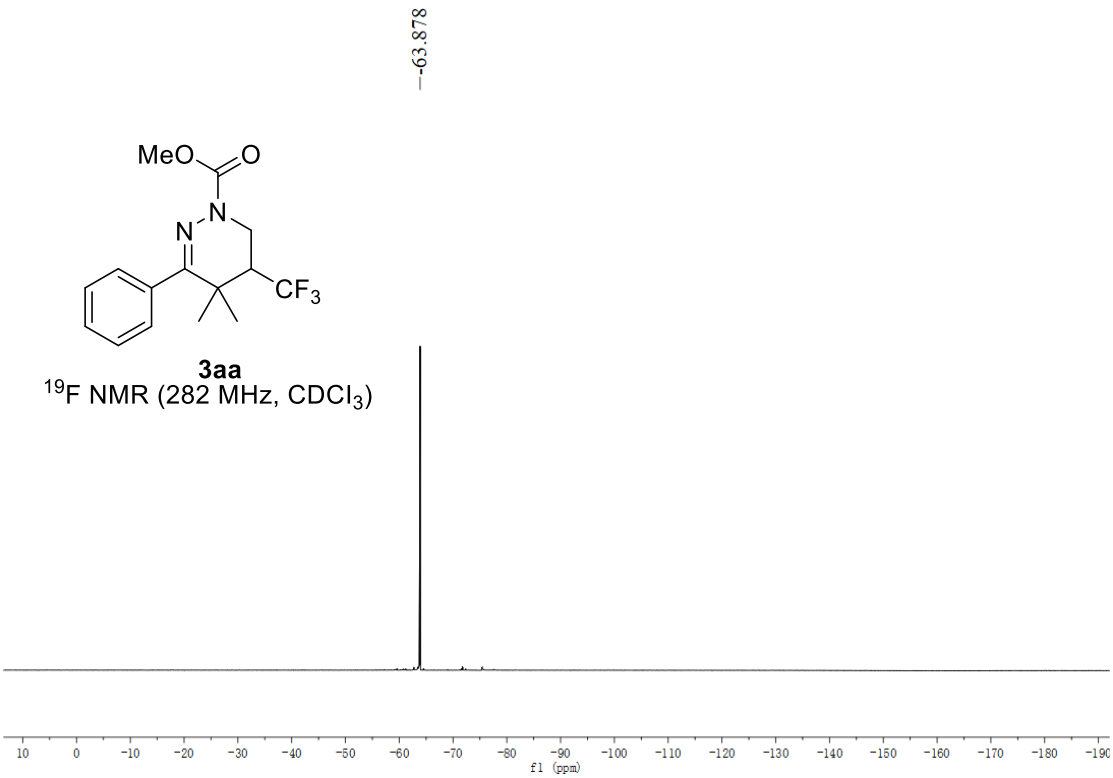
3aa

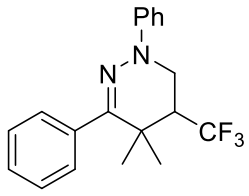
^{13}C NMR (100 MHz, $CDCl_3$)



3aa

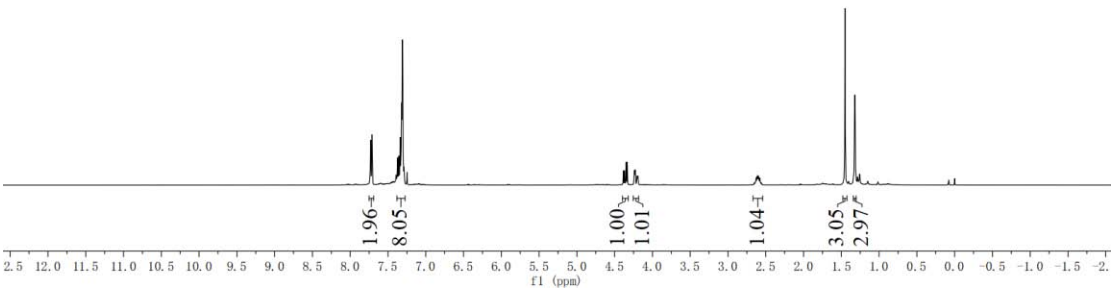
^{19}F NMR (282 MHz, $CDCl_3$)

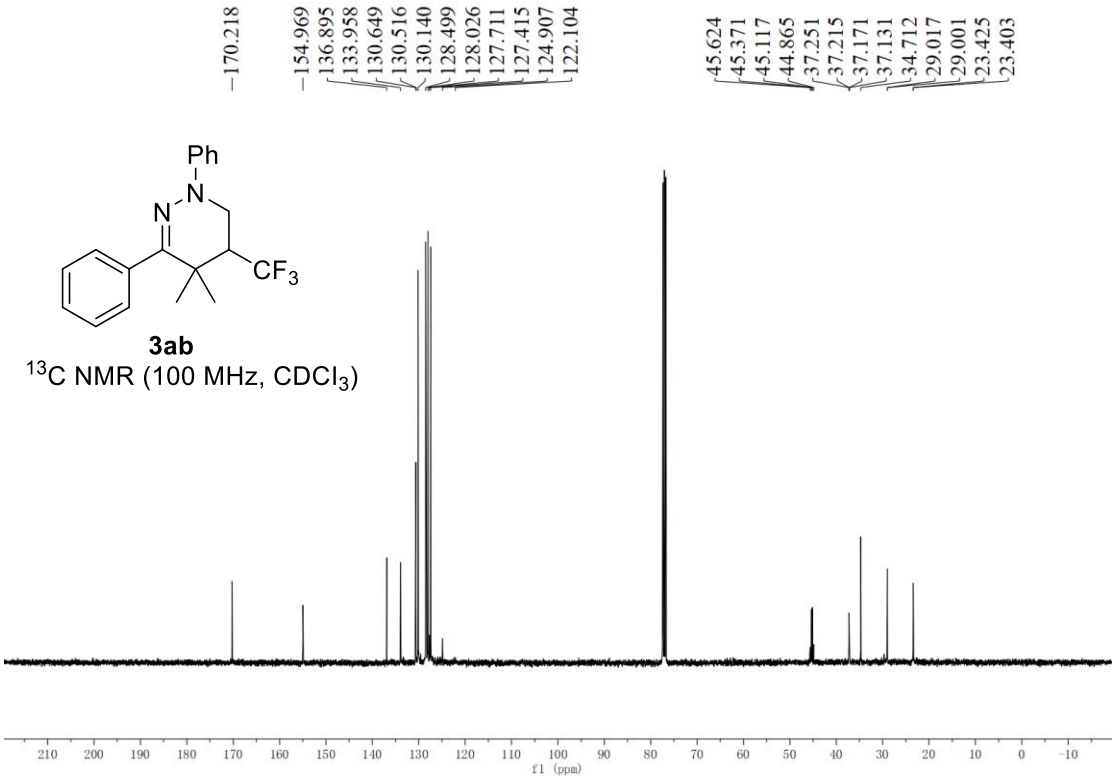




3ab

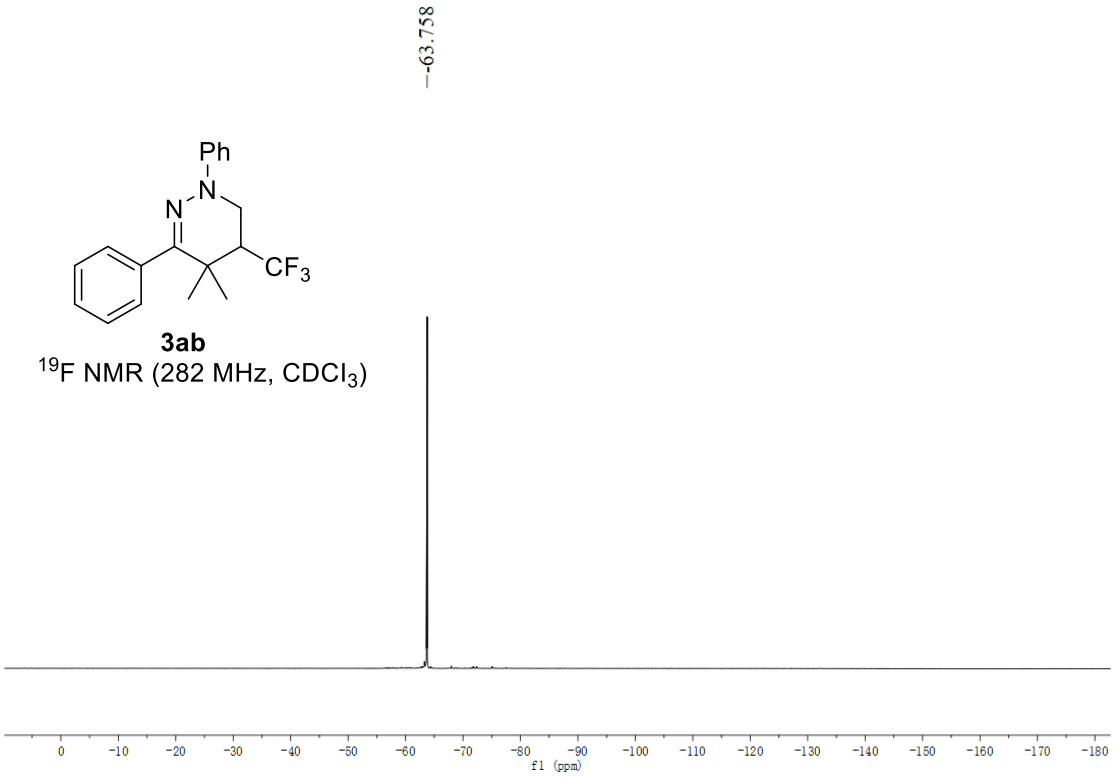
^{1}H NMR (400 MHz, $CDCl_3$)





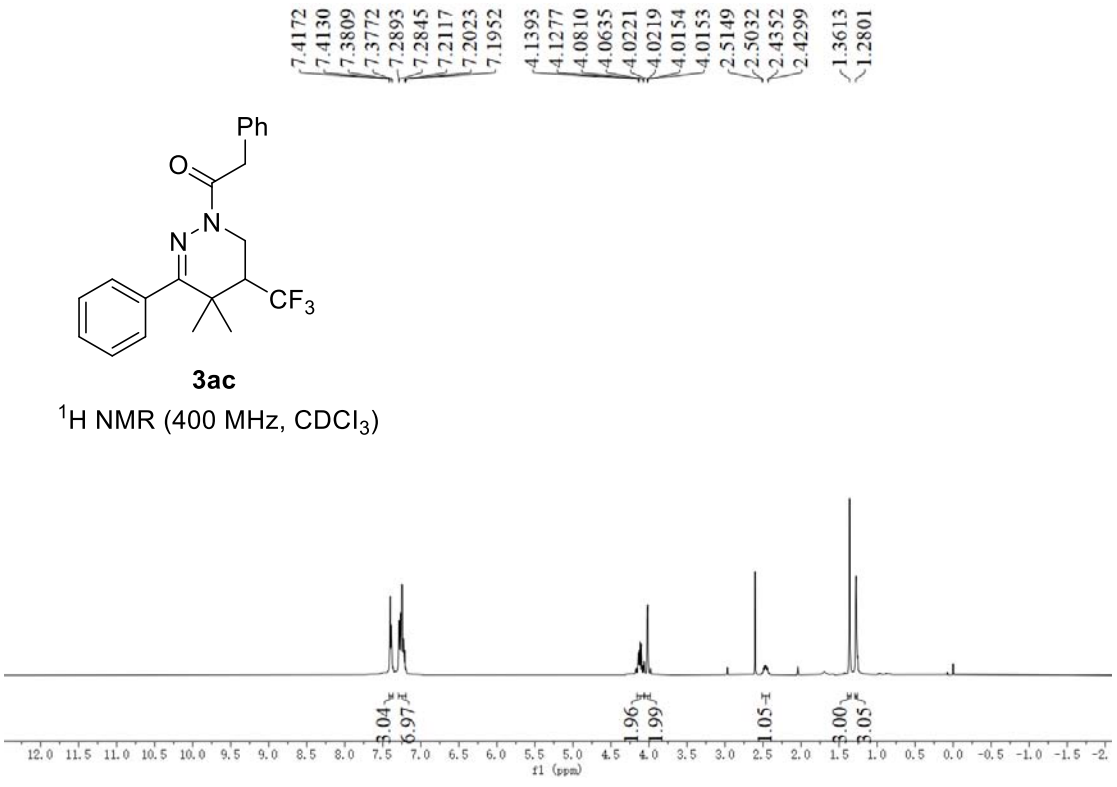
3ab

^{13}C NMR (100 MHz, $CDCl_3$)



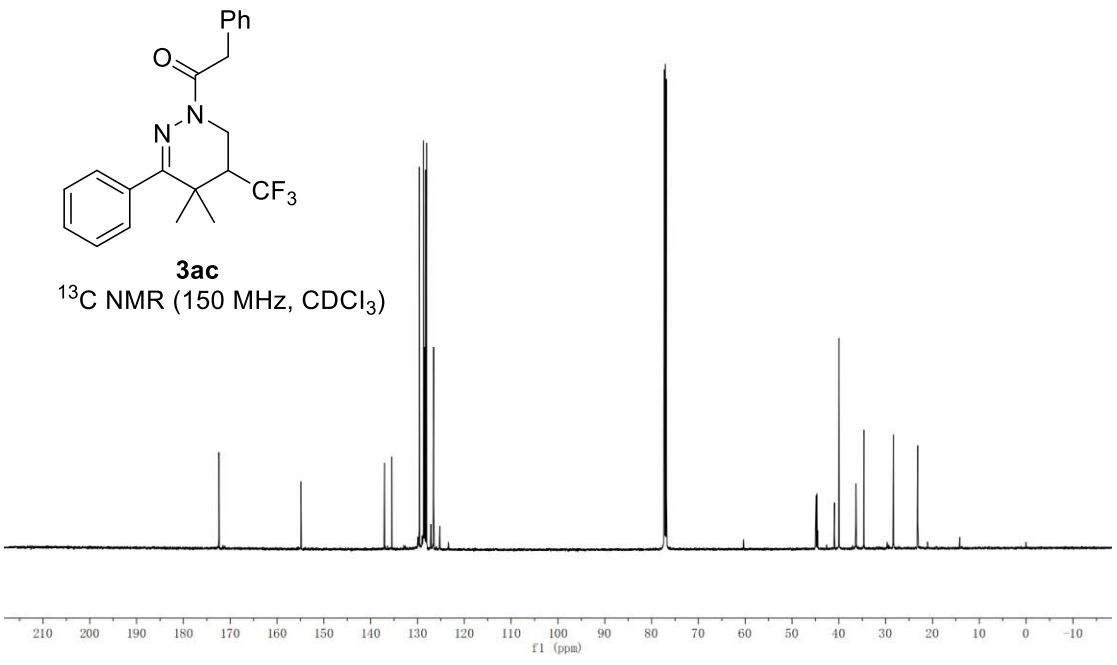
3ab

^{19}F NMR (282 MHz, $CDCl_3$)



3ac

^{1}H NMR (400 MHz, $CDCl_3$)

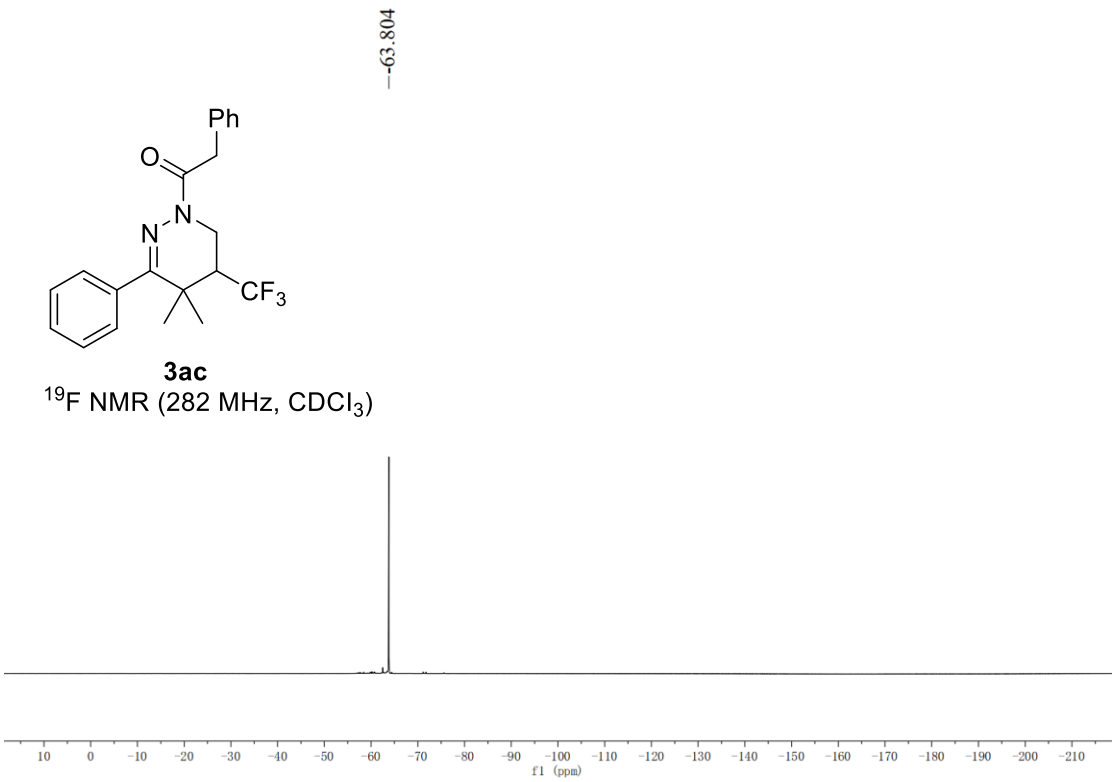


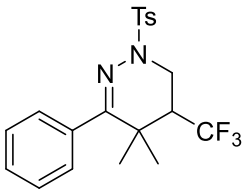
3ac

^{13}C NMR (150 MHz, $CDCl_3$)

3ac

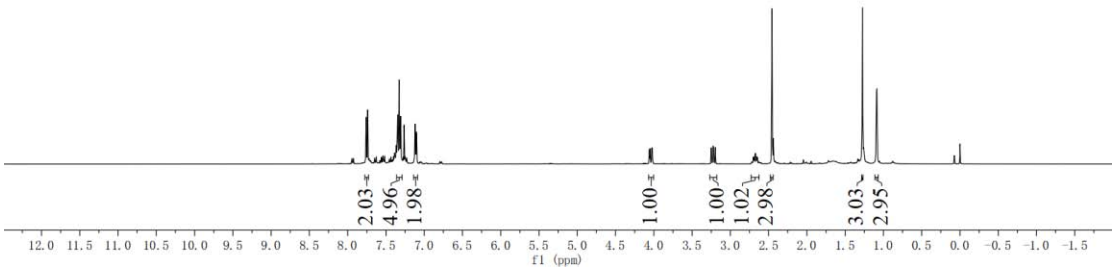
^{19}F NMR (282 MHz, $CDCl_3$)

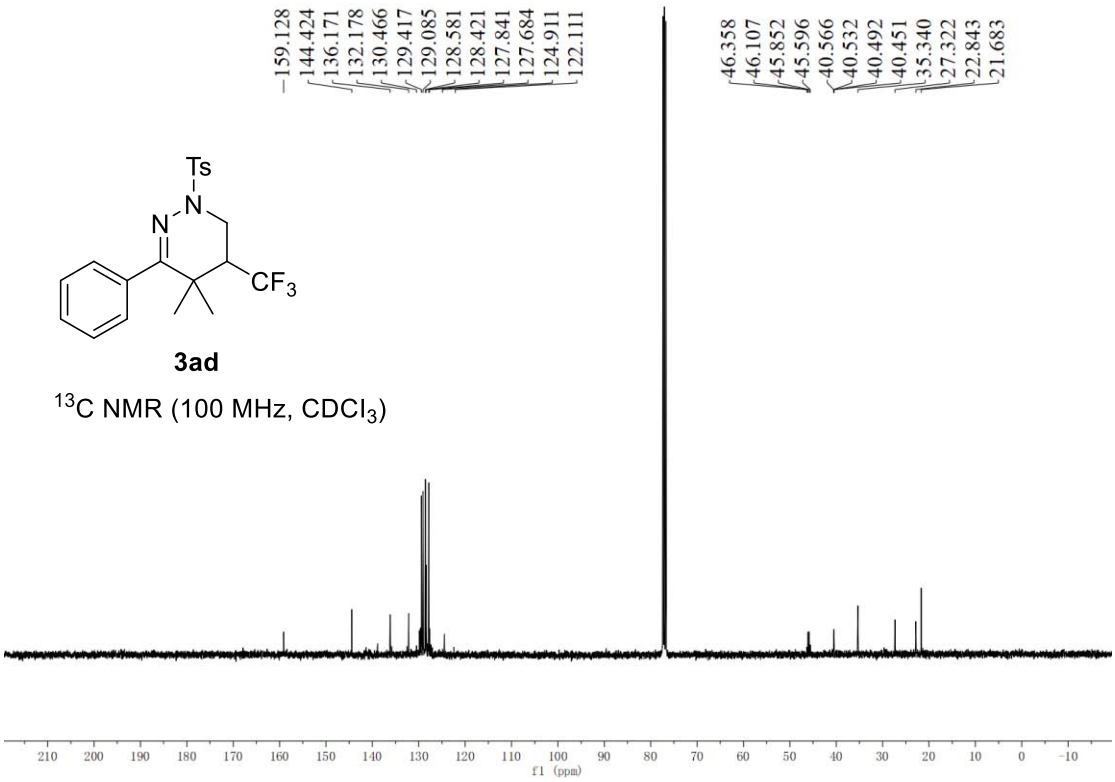




3ad

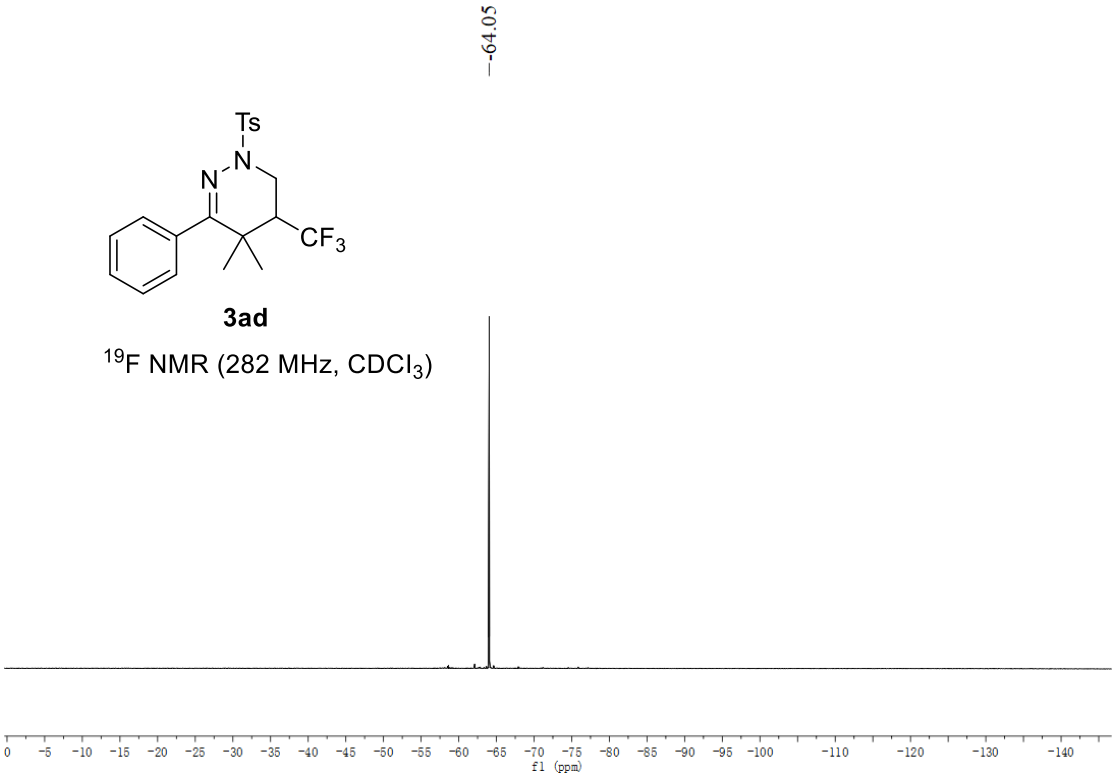
^{1}H NMR (400 MHz, $CDCl_3$)





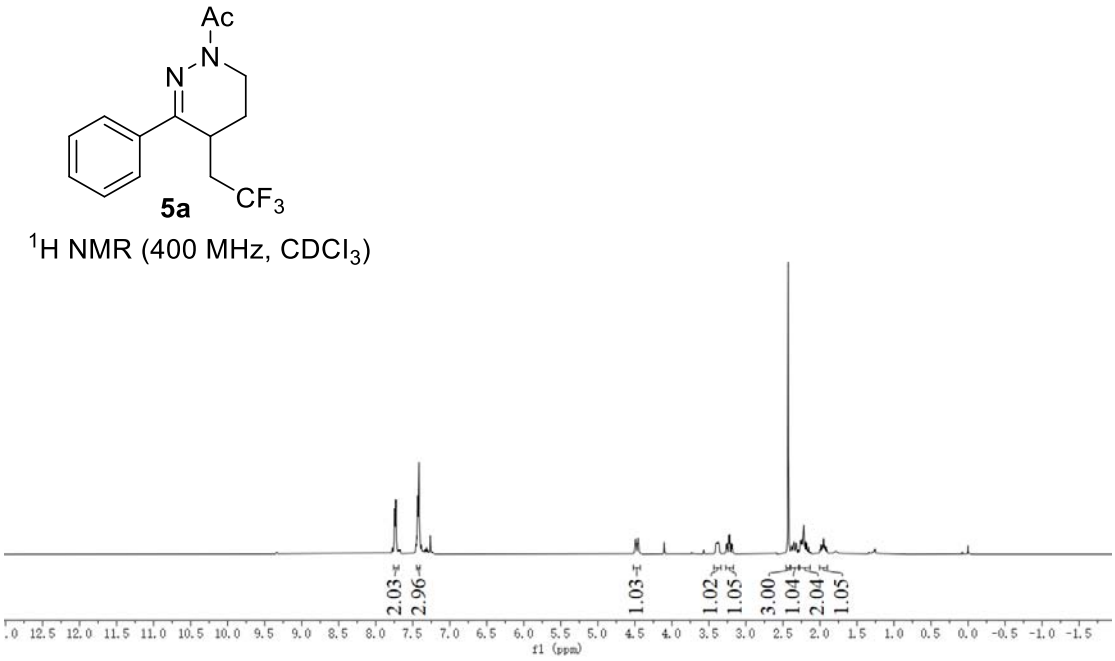
3ad

^{13}C NMR (100 MHz, $CDCl_3$)



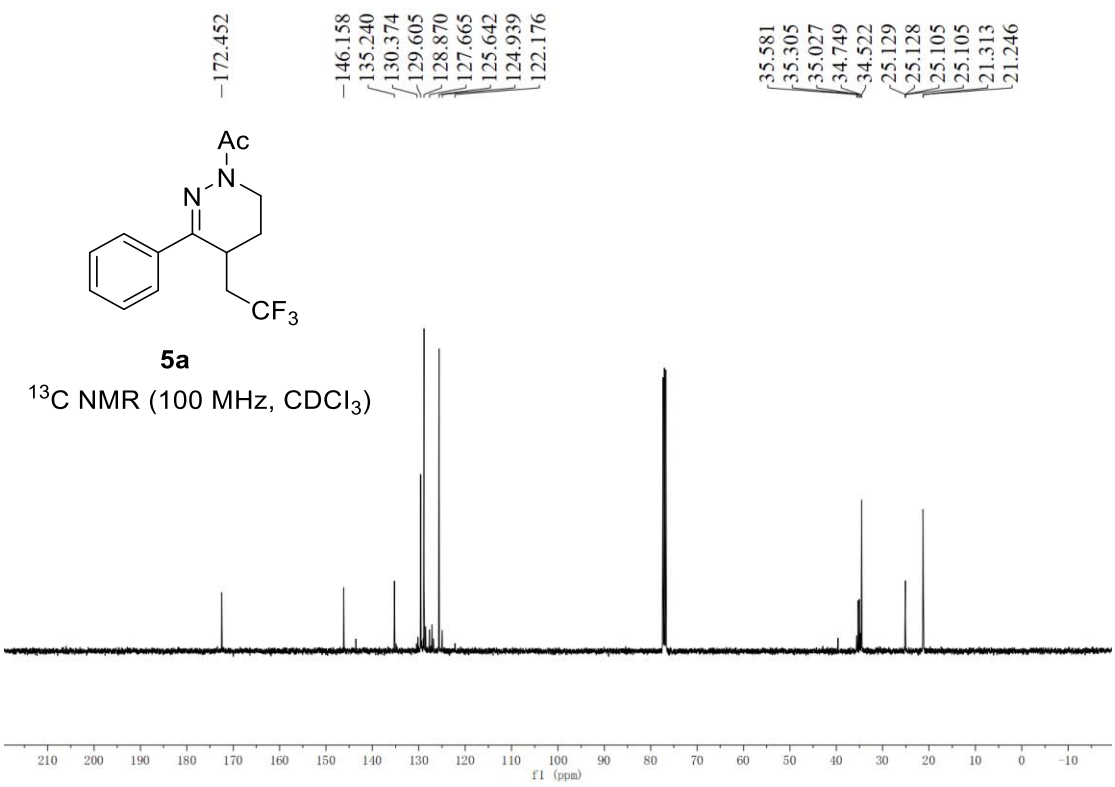
3ad

^{19}F NMR (282 MHz, $CDCl_3$)



5a

^{1}H NMR (400 MHz, $CDCl_3$)

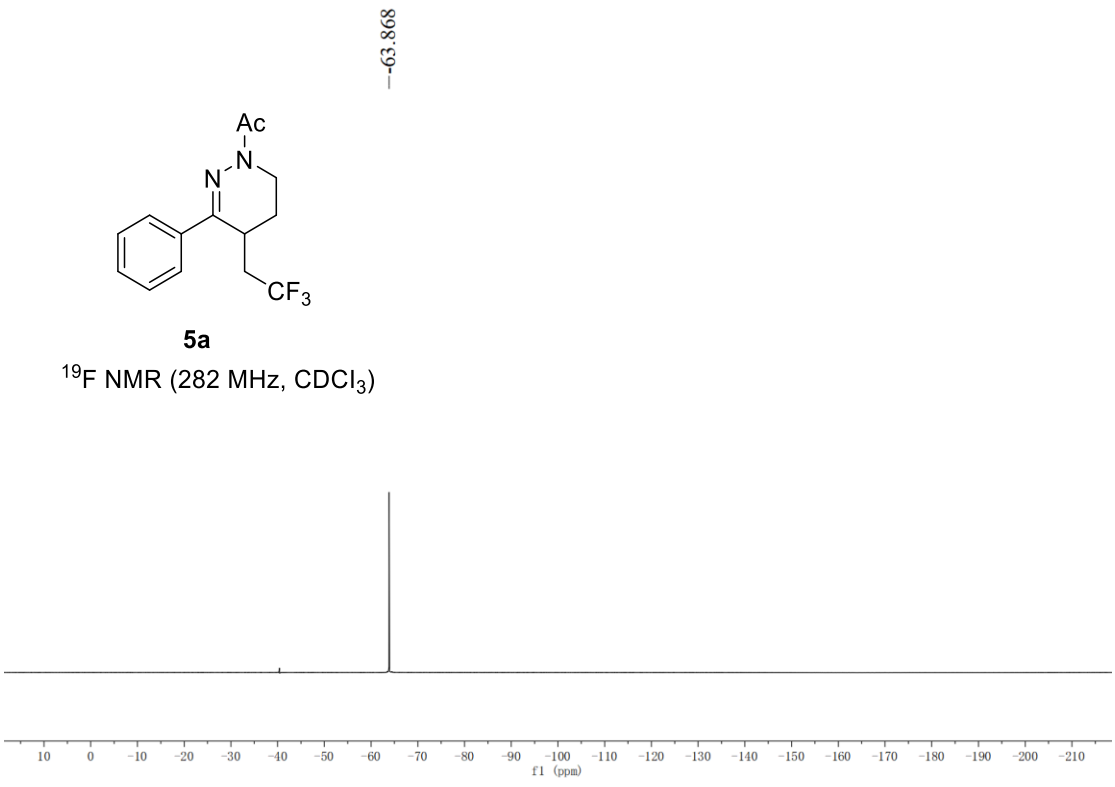


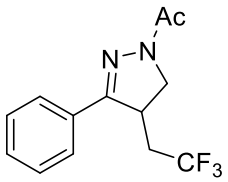
5a

^{13}C NMR (100 MHz, $CDCl_3$)

5a

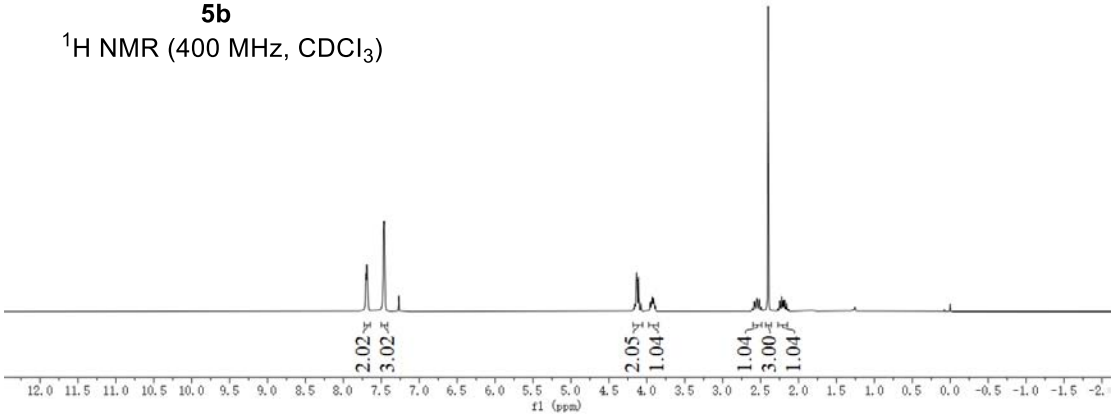
^{19}F NMR (282 MHz, $CDCl_3$)

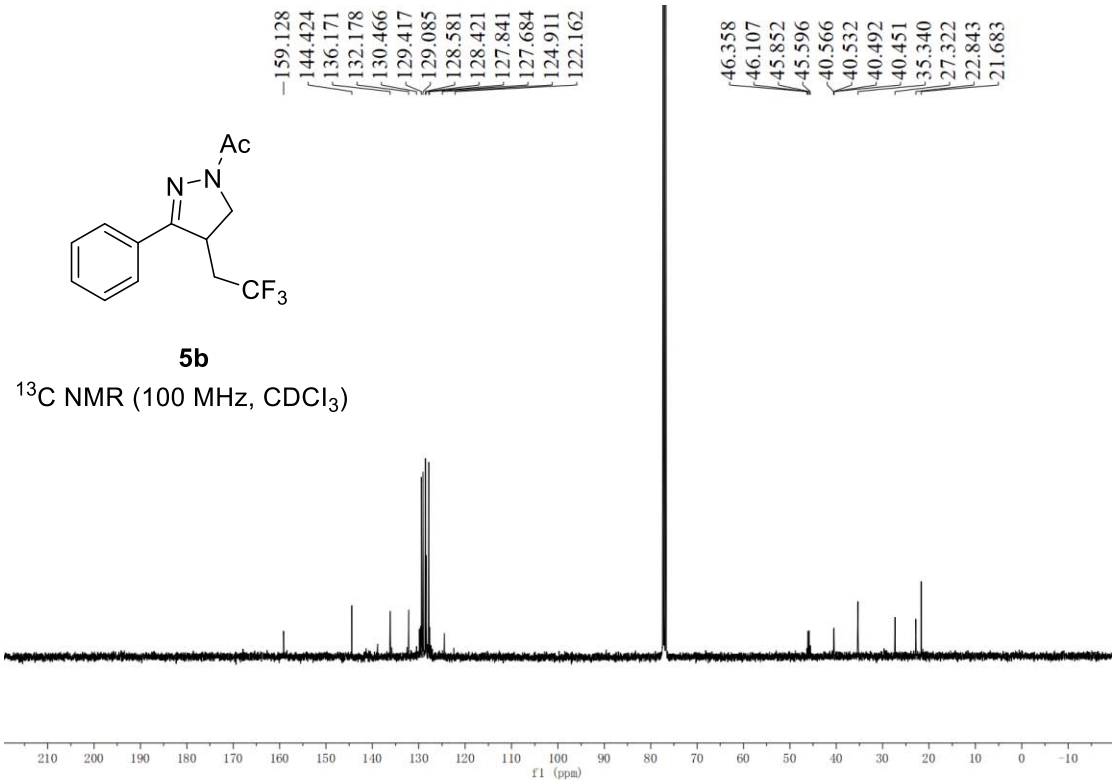




5b

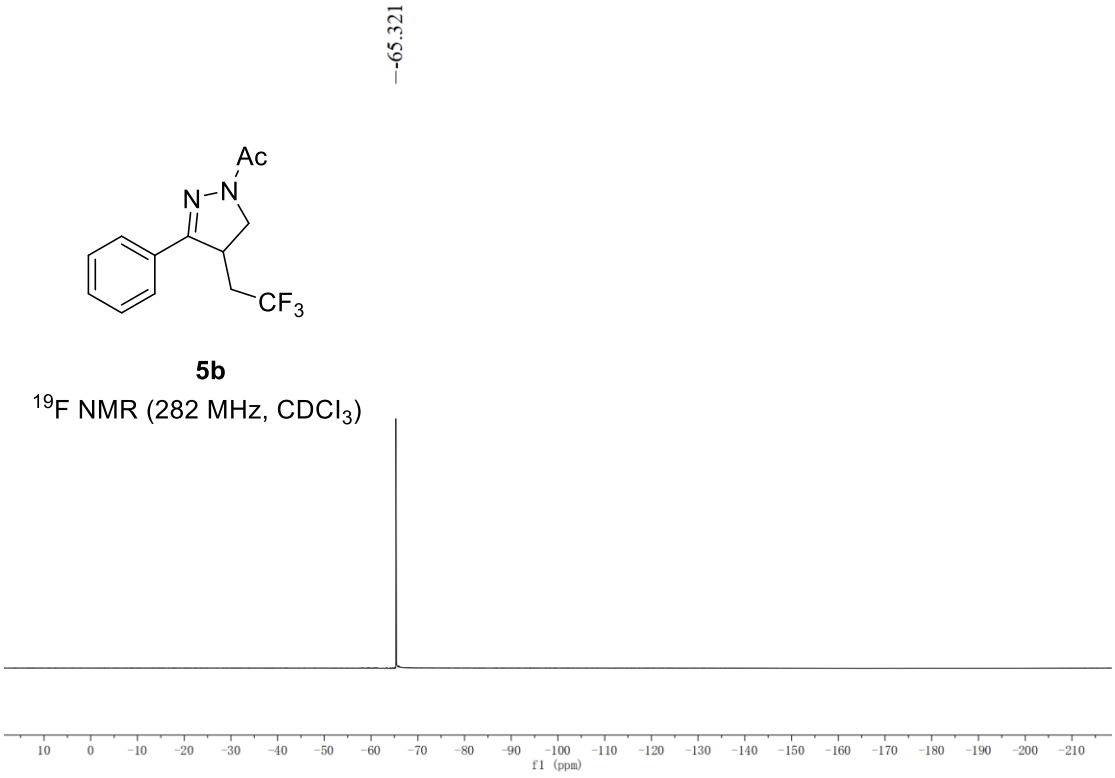
^{1}H NMR (400 MHz, $CDCl_3$)





5b

^{13}C NMR (100 MHz, $CDCl_3$)



5b

^{19}F NMR (282 MHz, $CDCl_3$)