

Supporting Information

Photocatalytic synthesis of polyfluoroalkylated dihydropyrazoles and tetrahydropyridazines

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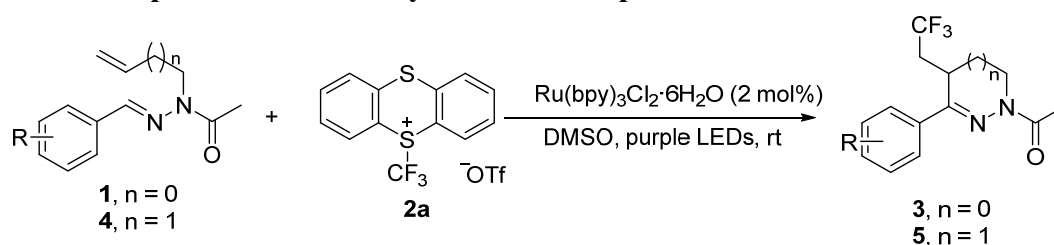
1. General Considerations

General Information: Unless otherwise noted, all chemicals were purchased from Energy Chemical or Bidepharmatech and used without further purification. All reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker-Avance 400 MHz NMR spectrometer (101 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (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

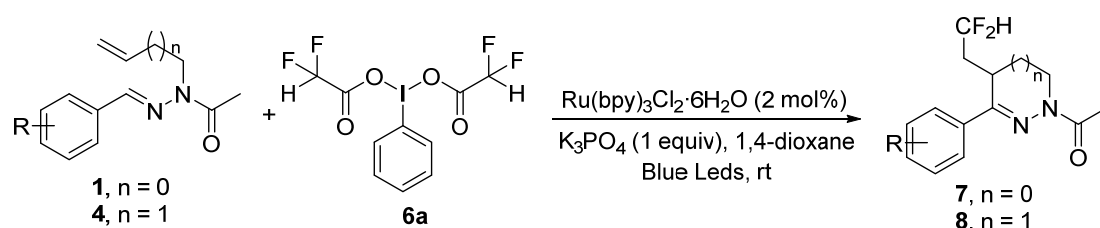
All *N*-homoallyl and *N*-allyl aldehyde hydrazones (**1a-1p**, **4a-4r**,) were prepared according to the previous report.¹ Trifluoromethyl thianthrenium triflate ($\text{TT-CF}_3^+\text{OTf}^-$, **2a**) was synthesized according to Ritter's work.² bis(difluoroacetoxy)iodo]benzene [$\text{PhI}(\text{O}_2\text{CCHF}_2)_2$] **6a** was prepared according to literature.³

2.1 General procedure for the synthesis of compounds **3** and **5**:



Under N_2 , the mixture of (*E*)-*N*-allyl-*N'*-benzylideneacetohydrazide **1** or (*E*)-*N*-homoallyl-*N'*-benzylideneacetohydrazide **4** (0.2 mmol), $\text{TT-CF}_3^+\text{OTf}^-$ **2a** (0.3 mmol, 1.5 equiv), $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (2 mol%, 3 mg) and DMSO (2 mL) were added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times) and then sealed. The mixture was stirred at room temperature under 400-410 nm purple LEDs for 16 hours. 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 give the product **3** or **5**.

2.2 General procedure for the synthesis of compounds **7** and **8**



Under N_2 , the mixture of (*E*)-*N*-allyl-*N'*-benzylideneacetohydrazide **1** or (*E*)-*N*-homoallyl-*N'*-benzylideneacetohydrazide **4** (0.2 mmol), [Bis(difluoroacetoxy)iodo]benzene **6a** (0.4 mmol, 2 equiv), $\text{Ru(bpy)}_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (2 mol%, 3 mg), K_3PO_4 (0.2 mmol) and 1,4-dioxane (2 mL) were added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times) and then sealed. The mixture was stirred at room temperature under 440-450 nm blue LEDs for 36 hours. 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 the product **7** or **8**.

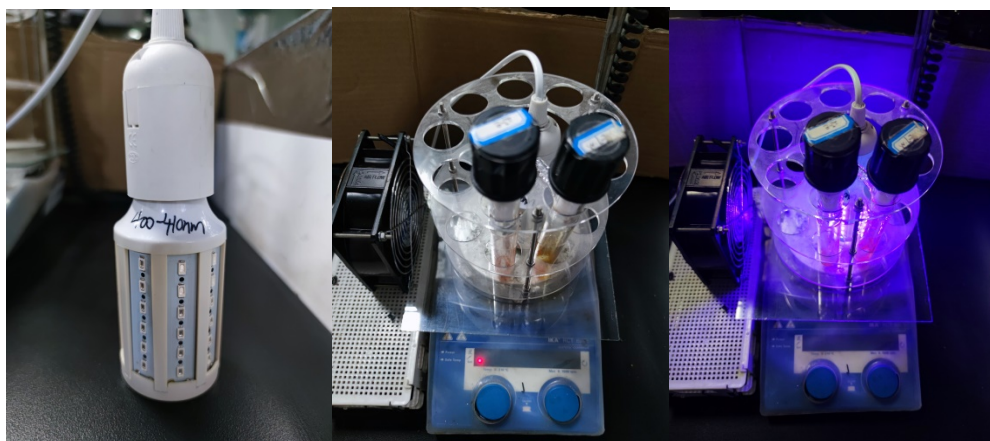


Figure S1. Photoreactor used in trifluoromethylation.

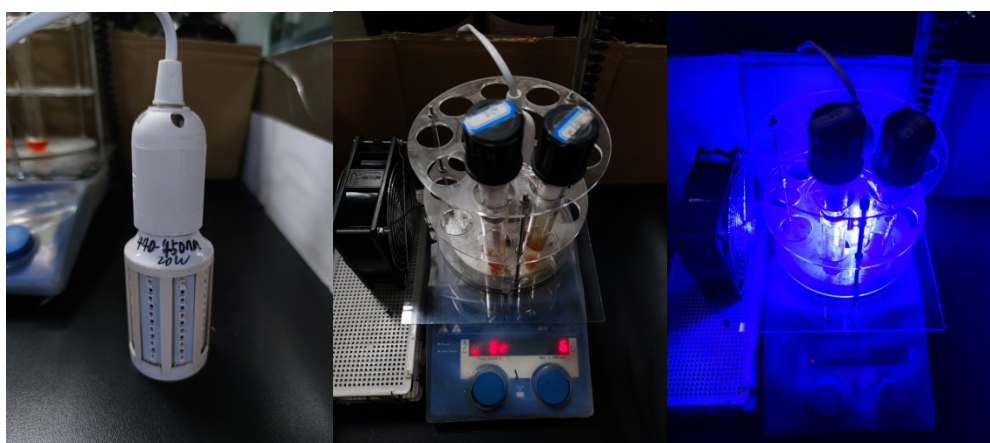


Figure S2. Photoreactor used in difluoromethylation.

The Light Source and the Material of the Irradiation Vessel:

The photochemical reaction was carried out under visible light irradiation by 20W 400-410 nm and 440-450 nm blue LED at room temperature. This blue LED was

purchased from taobao (link: https://shop152143906.taobao.com/?spm=pc_detail.29232929/evo365560b447259.shop_block.dshopinfo.2d887dd63sZzJE). The reaction vessel is a borosilicate glass tube. The distance between the tube and lamp is about 1.5 cm, and no filter is applied.

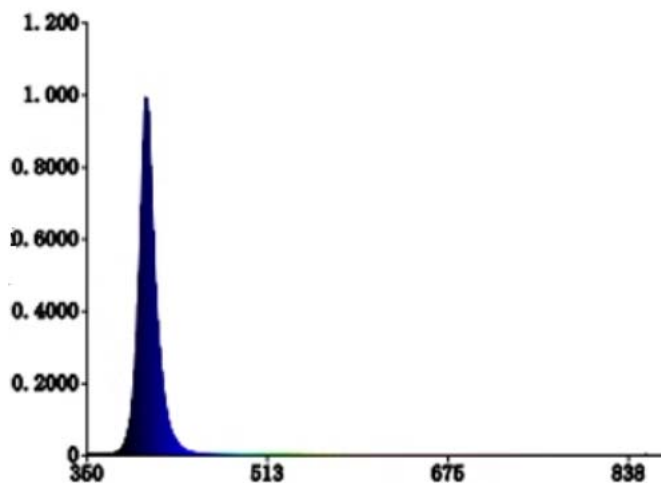


Figure S3. The spectral distribution of 20 W 400-410 nm blue LED

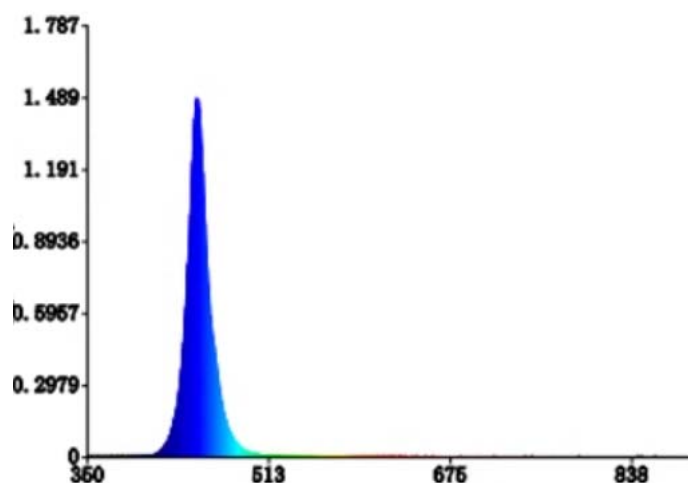
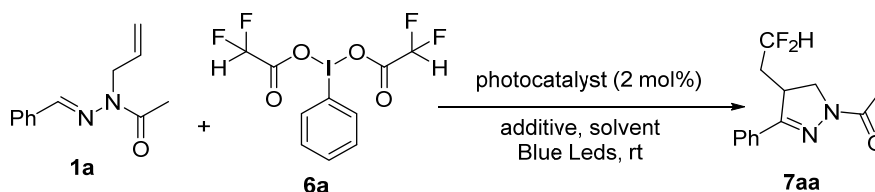


Figure S4. The spectral distribution of 20 W 440-450 nm blue LED

2.3 Screening the optimal reaction conditions for difluoromethylation/cyclization of *N*-allyl aldehyde hydrazone

Table S1. Screening the optimal reaction conditions for the difluoromethylation.^a



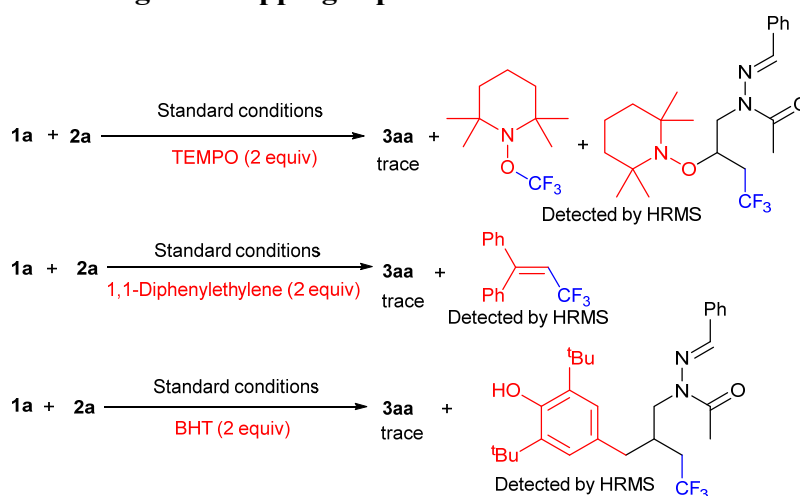
Entry	Photocatalyst (2 mol%)	Additive (1 equiv)	Solvent	Yield (%)
1	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	MeCN	31

2	EosinY	-	MeCN	27
3	5CzBN	-	MeCN	11
4	Eosin B	-	MeCN	trace
5	Rhodamine B	-	MeCN	0
6	---	-	MeCN	9
7	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	DCM	16
8	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	THF	25
9	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	Toluene	22
10	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	DMF	26
11	Ru(bpy)₃Cl₂•6H₂O	-	1,4-dioxane	41
12	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	EA	20
13	Ru(bpy) ₃ Cl ₂ •6H ₂ O	-	Acetone	0
14	Ru(bpy)₃Cl₂•6H₂O	K₃PO₄	1,4-dioxane	68
15	Ru(bpy) ₃ Cl ₂ •6H ₂ O	DABCO	1,4-dioxane	43
16	Ru(bpy) ₃ Cl ₂ •6H ₂ O	Cs ₂ CO ₃	1,4-dioxane	31
17	Ru(bpy) ₃ Cl ₂ •6H ₂ O	K ₂ CO ₃	1,4-dioxane	46

Reaction conditions: **1a** (0.2 mmol), **6a** (0.4 mmol), Ru(bpy)₃Cl₂•6H₂O (2 mol%), additive (1 equiv) and 1,4-dioxane (2 mL) under N₂ with irradiation using 20 W blue LEDs (440–450 nm) at rt for 36 h.

3 Mechanism Studies

3.1 Radical inhibiting and trapping experiments



Under standard conditions, radical inhibitor TEMPO (0.4 mmol, 62.5 mg, 2 equiv), 1,1-diphenylethylene (0.4 mmol, 72.1 mg, 2 equiv) or BHT (0.4 mmol, 88.1

mg, 2 equiv) was added, the mixture was stirred at room temperature under 400-410 nm purple LEDs for 16 hours. Then, the mixture was analyzed by HRMS.

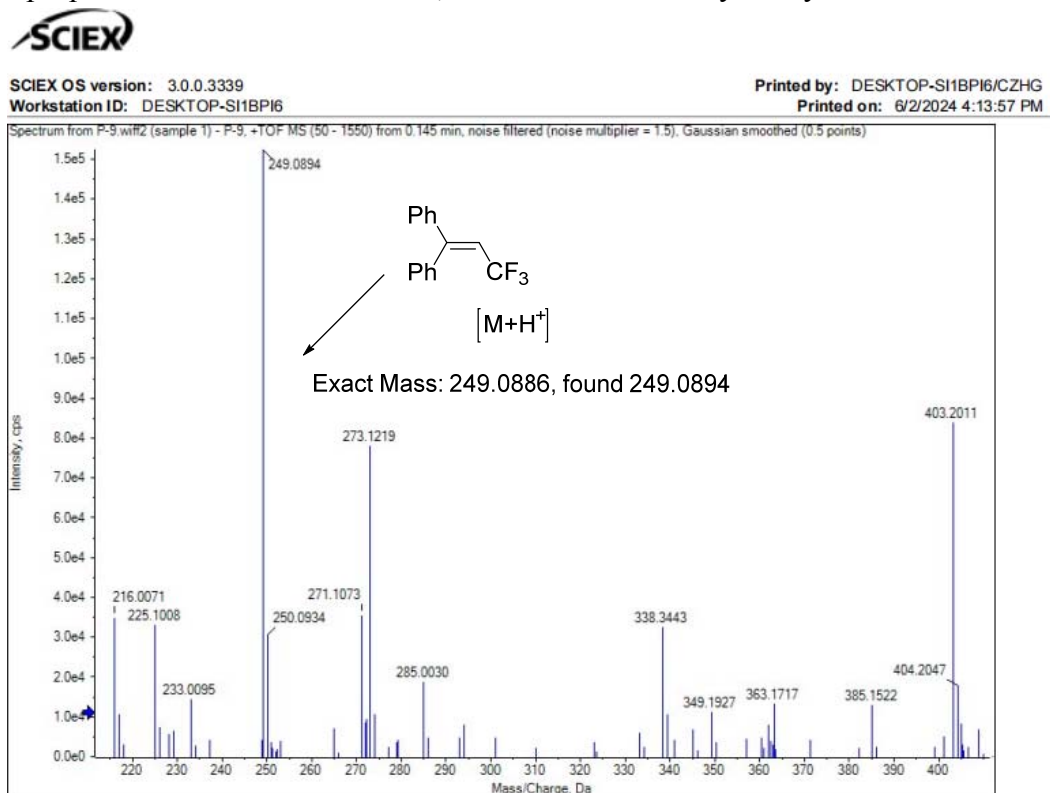
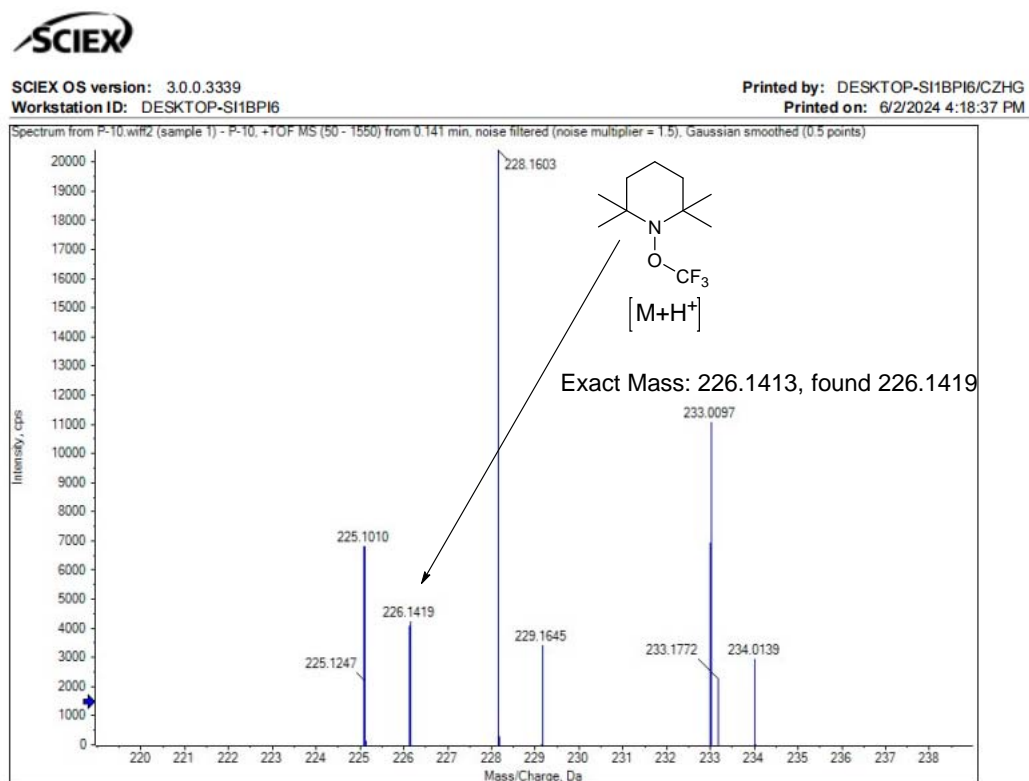
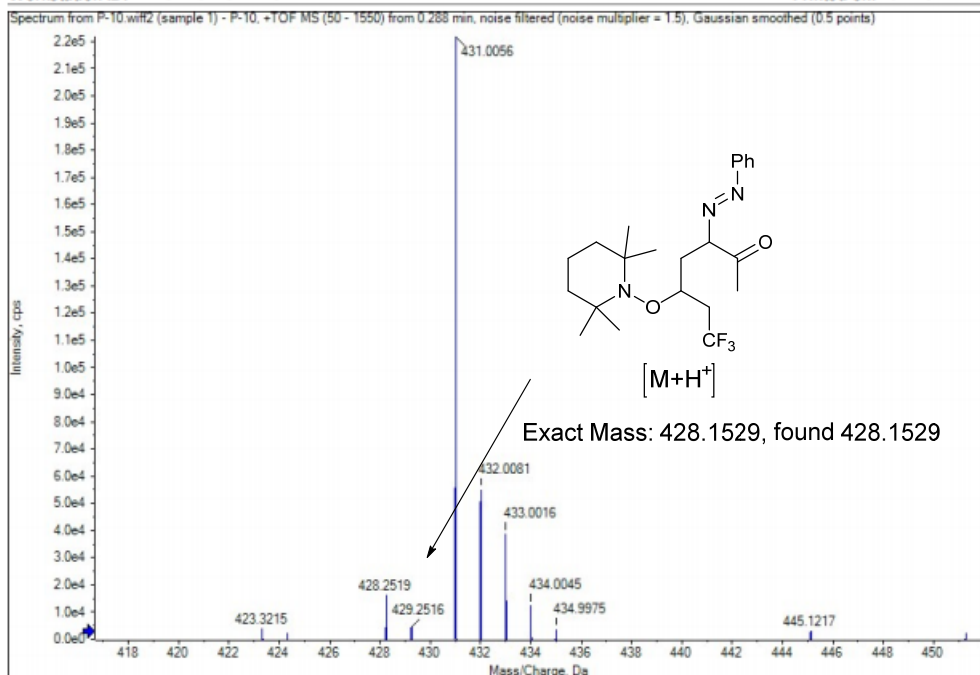


Figure S5. The HRMS spectrum for the radical-trapping experiment with 1,1-diphenylethylene.





Fig

re S6. The HRMS spectrum for the radical-trapping experiment with TEMPO

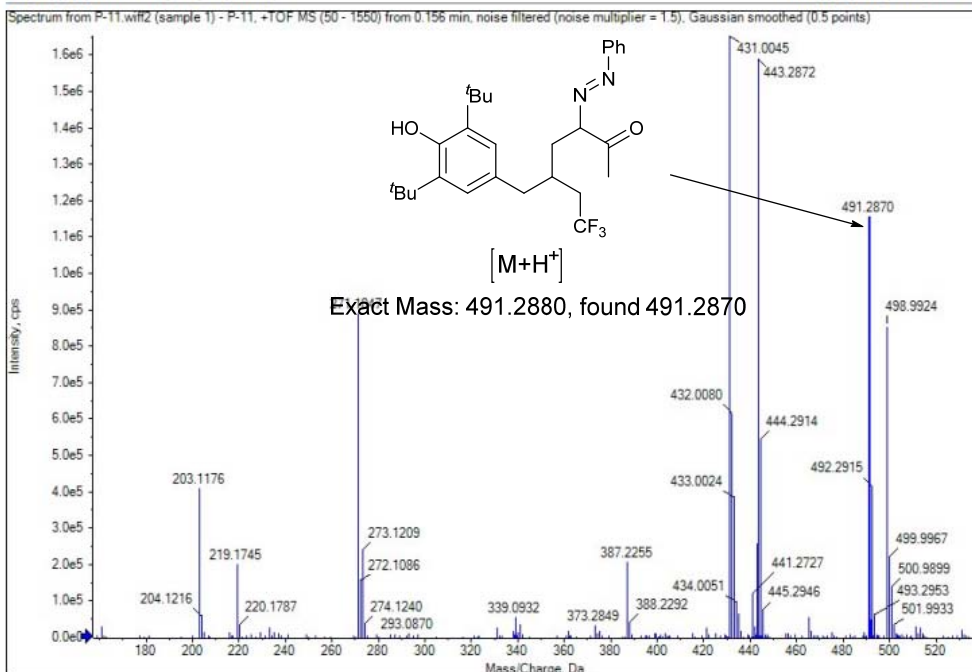


Figure S7. The HRMS spectrum for the radical-trapping experiment with BHT.

3.2 Fluorescence quenching experiments

Fluorescence quenching experiments were measured on an FS5 spectrophotometer with a 4 mL quartz cuvette ($d = 1$ cm) with a cap. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ with different concentrations of quencher in degassed DMSO in 10 mm path length quartz cuvette was collected after degassing with a stream of N_2 for 5 minutes. Linear regression of I_0/I against concentration is done in Origin 2018 (Figure S8, S9 and S10).

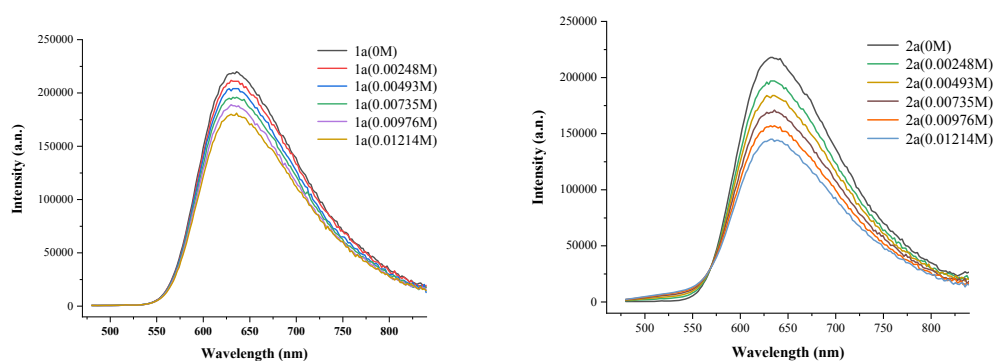


Figure S8. Fluorescence quenching of the excited $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ with different concentrations of **1a** or $\text{TT-CF}_3^+\text{OTf}^-$ **2a** in DMSO.

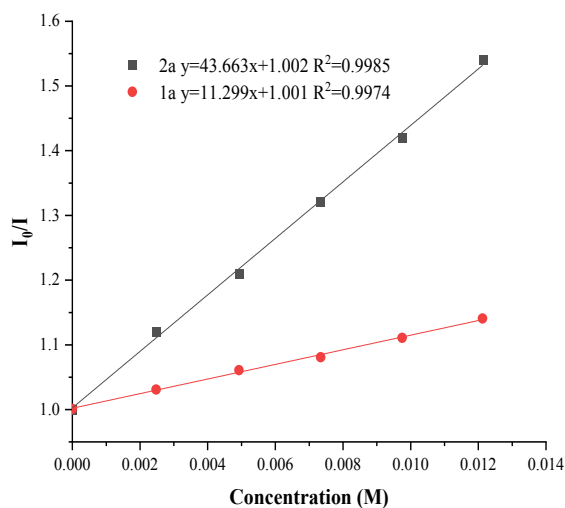


Figure S9. Stern-Volmer emission quenching studies of the excited $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ with **1a** or $\text{TT-CF}_3^+\text{OTf}^-$ **2a** in DMSO.

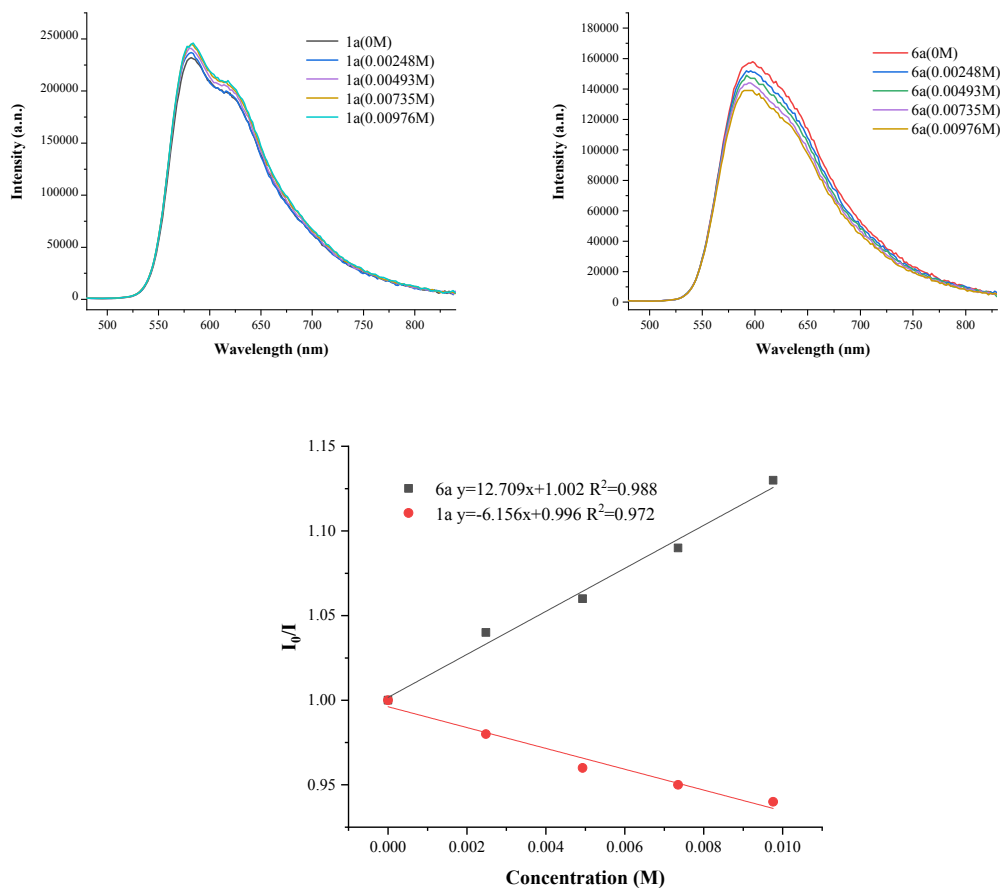


Figure S10. Fluorescence quenching and Stern-Volmer emission quenching studies of the excited $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ with **1a** or $\text{PhI}(\text{O}_2\text{CCF}_2\text{H})_2$ **6a** in 1,4-dioxane.

3.3 The mechanism for difluoromethylation/cyclization of *N*-allyl aldehyde hydrazine

The transformation was significantly suppressed by radical scavengers such as TEMPO, 1,1-diphenylethylene and BHT (Figure S11). The Stern–Volmer luminescence-quenching experiment showed that the excited $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was quenched by $\text{PhI}(\text{O}_2\text{CCHF}_2)_2$ (Figure S10). Based on the mechanistic studies, a possible mechanism is proposed in Figure S12. The single electron transfer (SET) between the excited photocatalyst $^*\text{Ru}^{2+}$ and $\text{PhI}(\text{O}_2\text{CCHF}_2)_2$ **6a** produces the difluoromethyl radical. Then, the addition of difluoromethyl radical to the double bond in **1a** forms the radical intermediate **E**, which undergoes 5-*endo*-trig cyclization to generate the *N*-centered radical intermediate **F**. Subsequently, radical **F** is oxidized by Ru^{3+} to form cation intermediate **G**, which is followed by deprotonation to afford the product **7aa**.

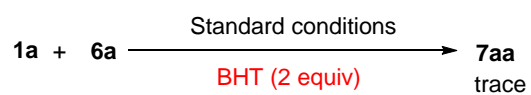
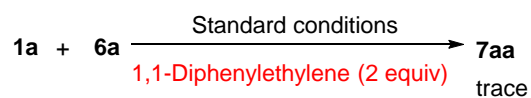
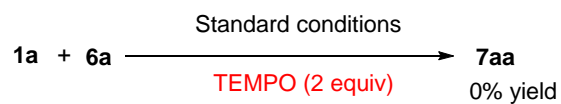


Figure S11. Mechanistic studies.

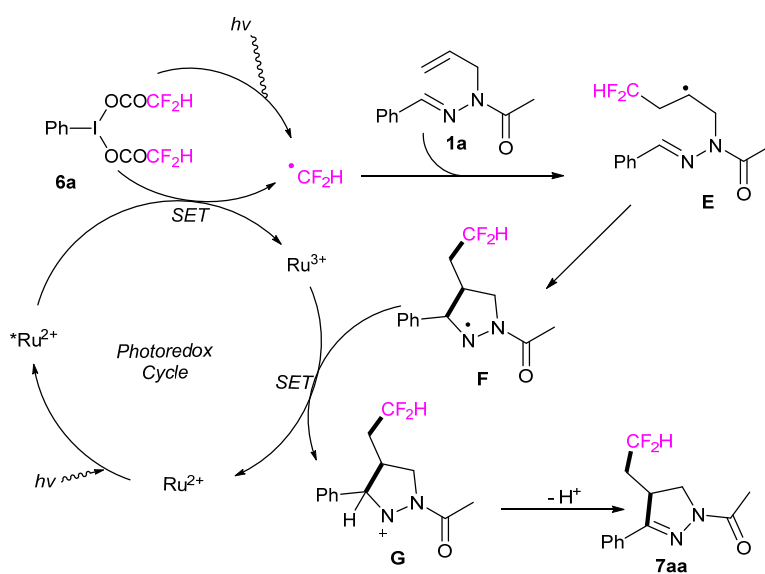
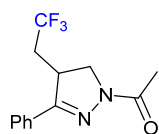
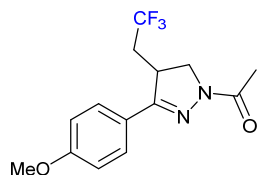


Figure S12. Proposed mechanism.

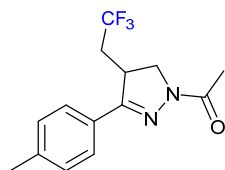
4. Characterization Data for the Products



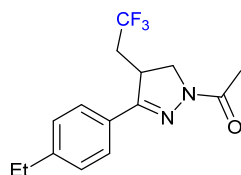
1-(3-Phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3aa, 44.9 mg, 83%), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70-7.68 (m, 2H), 7.47-7.45 (m, 3H), 4.16-4.08 (m, 2H), 3.95-3.89 (m, 1H), 2.61-2.48 (m, 1H), 2.40 (s, 3H), 2.24-2.15 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.65, 155.51, 130.61, 126.02 (q, $J_{\text{C-F}} = 278.5$ Hz), 129.51, 129.20, 126.67, 50.31, 38.49 (q, $J_{\text{C-F}} = 2.7$ Hz), 36.17 (q, $J_{\text{C-F}} = 28.6$ Hz), 21.47; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -65.32 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 271.1053, found 271.1055.



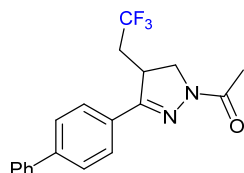
1-(3-(4-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ba, 44.4 mg, 74%), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 4.14-4.01 (m, 2H), 3.88-3.82 (m, 4H), 2.57-2.45 (m, 1H), 2.36 (s, 3H), 2.22-2.13 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.44, 161.46, 155.38, 128.28, 126.06 (q, $J_{\text{C-F}} = 278.3$ Hz), 121.94, 114.60, 55.44, 50.18, 38.53 (q, $J_{\text{C-F}} = 2.8$ Hz), 36.23 (q, $J_{\text{C-F}} = 28.3$ Hz), 21.44; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -65.36 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 301.1158, found 301.1162.



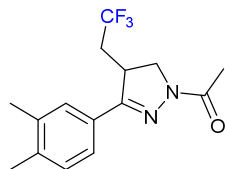
1-(3-(P-tolyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ca, 25.6 mg, 45%), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 4.15-4.05 (m, 2H), 3.92-3.85 (m, 1H), 2.59-2.49 (m, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.22-2.13 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.58, 155.67, 141.06, 129.91, 126.05 (q, $J_{\text{C-F}} = 278.4$ Hz), 126.64, 50.21, 38.51 (q, $J_{\text{C-F}} = 2.0$ Hz), 36.21 (q, $J_{\text{C-F}} = 28.7$ Hz), 21.53, 21.49; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -65.34 (t, $J = 9.8$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 285.1209, found 285.1210.



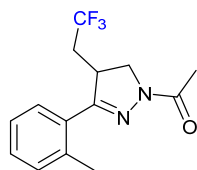
1-(3-(4-Ethylphenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3da, 35.8 mg, 60%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 4.07-3.97 (m, 2H), 3.85-3.78 (m, 1H), 2.65-2.59 (m, 2H), 2.53-2.41 (m, 1H), 2.31 (s, 3H), 2.15-2.06 (m, 1H), 1.18 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.53, 155.66, 147.30, 126.06 (q, $J_{\text{C-F}} = 278.3$ Hz), 128.72, 126.88, 126.73, 50.21, 38.49 (q, $J_{\text{C-F}} = 2.4$ Hz), 36.21 (q, $J_{\text{C-F}} = 28.7$ Hz), 28.82, 21.46, 15.34; ^{19}F NMR (752 MHz, CDCl_3) δ -65.35 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 299.1366, found 299.1363.



1-(3-([1,1'-Biphenyl]-4-yl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ea, 42.9 mg, 62%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 9.6$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.41 (t, $J = 7.2$ Hz, 1H), 4.20-4.10 (m, 2H), 3.98-3.91 (m, 1H), 2.66-2.53 (m, 1H), 2.43 (s, 3H), 2.28-2.19 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.63, 155.23, 143.31, 139.87, 129.03, 128.35, 128.09, 127.81, 126.06 (q, $J_{\text{C-F}} = 278.3$ Hz), 127.15, 127.07, 50.37, 38.48 (q, $J_{\text{C-F}} = 2.9$ Hz), 36.24 (q, $J_{\text{C-F}} = 28.6$ Hz), 21.54; ^{19}F NMR (752 MHz, CDCl_3) δ -65.26 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 347.1366, found 347.1371.

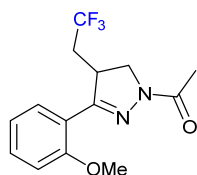


1-(3-(3,4-Dimethylphenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3fa, 38.2 mg, 64%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (s, 1H), 7.37 (dd, $J = 7.8, 1.9$ Hz, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 4.14-4.04 (m, 2H), 3.91-3.84 (m, 1H), 2.60-2.47 (m, 1H), 2.39 (s, 3H), 2.314 (s, 3H), 2.306 (s, 3H), 2.21-2.12 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.52, 155.86, 139.83, 137.66, 130.37, 126.08 (q, $J_{\text{C-F}} = 278.3$ Hz), 127.70, 126.99, 124.24, 50.14, 38.51 (q, $J_{\text{C-F}} = 2.7$ Hz), 36.25 (q, $J_{\text{C-F}} = 28.3$ Hz), 21.50, 19.92, 19.88; ^{19}F NMR (752 MHz, CDCl_3) δ -65.35 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 299.1366, found 299.1365.

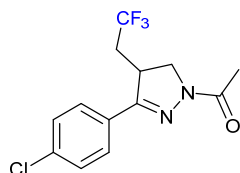


1-(3-(O-tolyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ga, 40.9 mg, 72%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.20 (m, 4H), 4.11-4.05 (m, 1H), 3.95-3.86 (m, 2H), 2.45 (s, 3H), 2.36-2.28 (m, 4H), 2.14-2.02 (m,

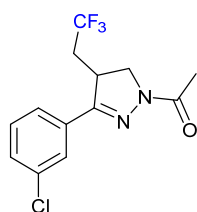
1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.55, 156.16, 138.21, 132.15, 126.02 (q, $J_{\text{C-F}} = 278.3$ Hz), 129.81, 128.45, 128.22, 126.35, 49.27, 40.61 (q, $J_{\text{C-F}} = 2.7$ Hz), 36.06 (q, $J_{\text{C-F}} = 28.7$ Hz), 22.22, 21.46; ^{19}F NMR (752 MHz, CDCl_3) δ -65.32 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 285.1209, found 285.1204.



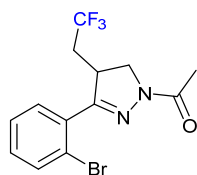
1-(3-(2-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ha), 44.4 mg, 74%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74-7.75 (m, 1H), 7.45-7.41 (m, 1H), 7.04-6.96 (m, 2H), 4.26-4.19 (m, 2H), 3.94-3.87 (m, 4H), 2.42-2.36 (m, 4H), 2.10-1.99 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.33, 157.31, 156.29, 132.05, 126.34 (q, $J_{\text{C-F}} = 278.1$ Hz), 130.06, 121.28, 118.72, 111.38, 55.20, 50.05, 41.29 (q, $J_{\text{C-F}} = 2.7$ Hz), 36.33 (q, $J_{\text{C-F}} = 28.4$ Hz), 21.45; ^{19}F NMR (752 MHz, CDCl_3) δ -65.59 (t, $J = 9.8$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 301.1158, found 301.1161.



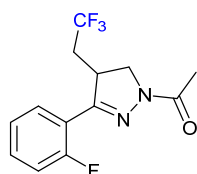
1-(3-(4-Chlorophenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ia), 48.1 mg, 79%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.7$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 4.15-4.05 (m, 2H), 3.89-3.82 (m, 1H), 2.53-2.41 (m, 1H), 2.36 (s, 3H), 2.24-2.15 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.59, 154.33, 136.56, 129.47, 128.05, 127.88, 125.92 (q, $J_{\text{C-F}} = 278.5$ Hz), 50.44, 38.37 (q, $J_{\text{C-F}} = 2.6$ Hz), 36.05 (q, $J_{\text{C-F}} = 28.6$ Hz), 21.42; ^{19}F NMR (752 MHz, CDCl_3) δ -65.29 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{ClF}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 305.0663, found 305.0661.



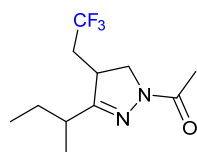
1-(3-(3-Chlorophenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ja), 42.7 mg, 70%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (s, 1H), 7.50-7.47 (m, 1H), 7.43-7.38 (m, 2H), 4.17-4.06 (m, 2H), 3.90-3.83 (m, 1H), 2.55-2.46 (m, 1H), 2.38 (s, 3H), 2.25-2.16 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.70, 154.06, 135.30, 131.39, 130.52, 130.45, 125.90 (q, $J_{\text{C-F}} = 278.4$ Hz), 126.62, 124.66, 50.46, 38.38 (q, $J_{\text{C-F}} = 2.7$ Hz), 36.03 (q, $J_{\text{C-F}} = 28.4$ Hz), 21.46; ^{19}F NMR (752 MHz, CDCl_3) δ -65.23 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{ClF}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 305.0663, found 305.0664.



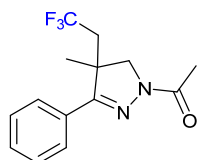
1-(3-(2-Bromophenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ka, 50.3 mg, 72%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 9.2$ Hz, 1H), 7.45-7.37 (m, 2H), 7.34-7.29 (m, 1H), 4.35-4.26 (m, 2H), 3.97-3.87 (m, 1H), 2.34-2.25 (m, 4H), 2.18-2.07 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.65, 156.32, 134.04, 131.53, 131.31, 131.18, 126.19 (q, $J_{\text{C-F}} = 278.3$ Hz), 127.89, 121.79, 49.86, 41.03 (q, $J_{\text{C-F}} = 2.5$ Hz), 35.60 (q, $J_{\text{C-F}} = 28.8$ Hz), 21.48; ^{19}F NMR (752 MHz, CDCl_3) δ -65.12 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{BrF}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 349.0158, found 349.0164.



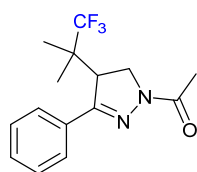
1-(3-(2-Fluorophenyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3la, 52.4 mg, 91%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.83 (m, 1H), 7.46-7.41 (m, 1H), 7.24-7.20 (m, 1H), 7.17-7.12 (m, 1H), 4.20-4.14 (m, 1H), 4.07-3.99 (m, 2H), 2.48-2.37 (m, 4H), 2.21-2.10 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.52, 160.39 (d, $J_{\text{C-F}} = 252.4$ Hz), 152.69 (d, $J_{\text{C-F}} = 2.6$ Hz), 132.38 (d, $J_{\text{C-F}} = 8.8$ Hz), 129.56 (d, $J_{\text{C-F}} = 3.2$ Hz), 125.97 (q, $J_{\text{C-F}} = 278.2$ Hz), 124.99 (d, $J_{\text{C-F}} = 3.3$ Hz), 117.83 (d, $J_{\text{C-F}} = 11.41$ Hz), 116.70 (d, $J_{\text{C-F}} = 22.3$ Hz), 50.04, 40.73 (q, $J_{\text{C-F}} = 2.8$ Hz), 36.11 (q, $J_{\text{C-F}} = 29.5$ Hz), 21.42; ^{19}F NMR (752 MHz, CDCl_3) δ -65.18 (t, $J = 10.5$ Hz, 3F), -114.29 (s, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{F}_4\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 289.0959, found 289.0964.



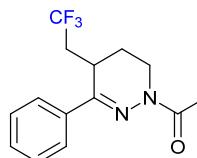
1-(3-(Sec-butyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3ma, 39.5 mg, 79%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 4.11-4.03 (m, 1H), 3.78-3.72 (m, 1H), 3.42-3.31 (m, 1H), 2.52-2.26 (m, 5H), 2.18-2.08 (m, 1H), 1.85-1.41 (m, 2H), 1.20 (d, $J = 6.7$ Hz, 1.5H), 1.15 (d, $J = 7.1$ Hz, 1.5H), 0.95 (t, $J = 7.4$ Hz, 1.5H), 0.92 (t, $J = 7.4$ Hz, 1.5H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.16, 162.54, 162.50, 125.96 (q, $J_{\text{C-F}} = 278.7$ Hz), 49.45, 49.35, 40.47 (q, $J_{\text{C-F}} = 2.1$ Hz), 40.14 (q, $J_{\text{C-F}} = 2.3$ Hz), 35.50 (q, $J_{\text{C-F}} = 28.7$ Hz), 34.63, 33.86, 27.19, 26.50, 21.33, 18.38, 16.23, 11.94, 10.89; ^{19}F NMR (752 MHz, CDCl_3) δ -65.23 (dt, $J = 18.0$ Hz, 10.5 Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 251.1366, found 251.1363.



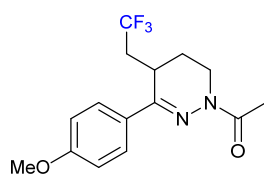
1-(4-Methyl-3-phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3na, 47.2 mg, 83%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.71-7.68 (m, 2H), 7.44-7.41 (m, 3H), 4.16 (d, $J = 12.4$ Hz, 1H), 3.91 (d, $J = 12.4$ Hz, 1H), 2.76-2.64 (m, 1H), 2.54-2.45 (m, 1H), 2.37 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.63, 158.68, 130.15, 128.90, 127.29, 125.85 (q, $J_{\text{C-F}} = 279.9$ Hz), 57.64 (q, $J_{\text{C-F}} = 2.3$ Hz), 47.76 (q, $J_{\text{C-F}} = 1.9$ Hz), 40.43 (q, $J_{\text{C-F}} = 27.6$ Hz), 24.49, 21.27; ^{19}F NMR (752 MHz, CDCl_3) δ -60.55 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 285.1209, found 285.1211.



1-(3-Phenyl-4-(1,1,1-trifluoro-2-methylpropan-2-yl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3oa, 40.0 mg, 67%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.33 (m, 5H), 4.19-4.07 (m, 2H), 2.53-2.44 (m, 1H), 2.30 (s, 3H), 1.39 (s, 3H), 1.30 (d, $J = 2.0$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.32, 154.63, 137.12, 128.68, 128.47, 128.09, 126.24 (q, $J_{\text{C-F}} = 283.0$ Hz), 44.78 (q, $J_{\text{C-F}} = 25.7$ Hz), 36.03 (q, $J_{\text{C-F}} = 4.2$ Hz), 34.60, 28.44 (q, $J_{\text{C-F}} = 1.8$ Hz), 23.25 (q, $J_{\text{C-F}} = 2.2$ Hz), 21.21; ^{19}F NMR (752 MHz, CDCl_3) δ -63.84 (d, $J = 9.8$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 299.1366, found 299.1369.

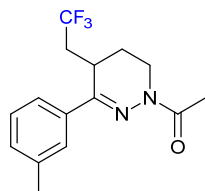


1-(3-Phenyl-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5aa, 39.8 mg, 70%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.75-7.72 (m, 2H), 7.45-7.38 (m, 3H), 4.50-4.44 (m, 1H), 3.40-3.36 (m, 1H), 3.26-3.18 (m, 1H), 2.43 (s, 1H), 2.38-2.15 (m, 3H), 1.98-1.91 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.49, 146.17, 135.23, 126.09 (q, $J_{\text{C-F}} = 279.0$ Hz), 129.63, 128.89, 125.65, 35.14 (q, $J_{\text{C-F}} = 28.0$ Hz), 34.52, 25.10 (q, $J_{\text{C-F}} = 2.3$ Hz), 21.35, 21.23; ^{19}F NMR (752 MHz, CDCl_3) δ -63.88 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 285.1209, found 285.1204.

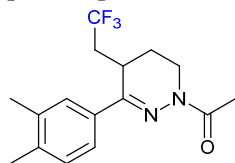


1-(3-(4-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ba, 37.5 mg, 60%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d,

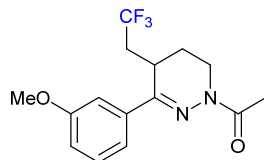
$J = 9.0$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 4.49-4.44 (m, 1H), 3.84 (s, 3H), 3.35-3.31 (m, 1H), 3.21-3.13 (m, 1H), 2.40 (s, 3H), 2.36-2.15 (m, 3H), 1.97-1.87 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.29, 160.76, 146.01, 126.4 (q, $J_{\text{C-F}} = 279.0$ Hz), 127.74, 127.08, 114.20, 55.38, 35.17 (q, $J_{\text{C-F}} = 27.7$ Hz), 34.37, 25.03 (q, $J_{\text{C-F}} = 2.6$ Hz), 21.33, 21.26; ^{19}F NMR (752 MHz, CDCl_3) δ -63.94 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 315.1315, found 315.1319.



1-(3-(M-tolyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ca, 40.7 mg, 68%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.50 (m, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 4.48-4.43 (m, 1H), 3.39-3.34 (m, 1H), 3.24-3.17 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.37-2.27 (m, 1H), 2.24-2.13 (m, 2H), 1.98-1.88 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.43, 146.44, 138.54, 135.26, 130.41, 128.76, 126.38 (q, $J_{\text{C-F}} = 278.9$ Hz), 126.37, 122.85, 35.18 (q, $J_{\text{C-F}} = 28.1$ Hz), 34.51, 25.10 (q, $J_{\text{C-F}} = 2.4$ Hz), 21.62, 21.35, 21.28; ^{19}F NMR (752 MHz, CDCl_3) δ -63.92 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 299.1366, found 299.1372.

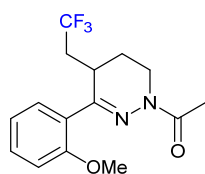


1-(3-(3,4-Dimethylphenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5da, 29.9 mg, 48%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.18 (d, $J = 7.9$ Hz, 1H), 4.48-4.44 (m, 1H), 3.37-3.34 (m, 1H), 3.24-3.16 (m, 1H), 2.42 (s, 3H), 2.37-2.33 (m, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.24-2.13 (m, 2H), 1.98-1.89 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.43, 146.62, 138.58, 137.14, 132.89, 130.12, 126.40 (q, $J_{\text{C-F}} = 278.8$ Hz), 126.90, 123.18, 35.24 (q, $J_{\text{C-F}} = 27.8$ Hz), 34.47, 25.16 (q, $J_{\text{C-F}} = 2.3$ Hz), 21.38, 21.31, 20.09, 19.69; ^{19}F NMR (752 MHz, CDCl_3) δ -63.94 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 313.1522, found 313.1518.

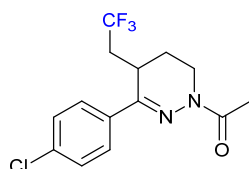


1-(3-(3-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ea, 30.2 mg, 48%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.28 (m, 3H), 6.97-6.94 (m, 1H), 4.50-4.45 (m, 1H), 3.85 (s, 1H), 3.38-3.33 (m, 1H), 3.25-3.17 (m, 1H), 2.43-2.30 (m, 4H), 2.27-2.15 (m, 2H), 1.99-1.90 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.46, 159.96, 145.96, 136.70, 129.89, 126.34 (q, $J_{\text{C-F}} = 279.2$ Hz), 118.01, 115.16, 111.23, 55.27, 35.23 (q, $J_{\text{C-F}} = 27.9$ Hz), 34.52, 25.24 (q, $J_{\text{C-F}} = 2.6$ Hz), 21.34, 21.23; ^{19}F NMR (752 MHz, CDCl_3) δ -63.92 (t, $J = 10.5$ Hz,

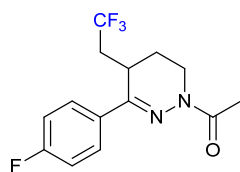
3F). HRMS (ESI) m/z calcd for $C_{15}H_{18}F_3N_2O_2$ $[M+H^+]$: 315.1315, found 315.1317.



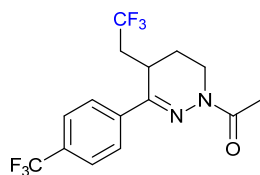
1-(3-(2-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5fa, 32.1 mg, 51%), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 2H), 7.03-6.99 (m, 1H), 6.95-6.92 (m, 1H), 4.00-3.93 (m, 1H), 3.85 (s, 3H), 3.80-3.73 (m, 1H), 3.47-3.40 (m, 1H), 2.32 (s, 3H), 2.30-2.20 (m, 2H), 1.97-1.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.40, 157.07, 149.50, 130.63, 130.44, 126.58 (q, $J_{C-F} = 278.5$ Hz), 125.93, 121.06, 110.86, 55.29, 36.74, 35.89 (q, $J_{C-F} = 28.2$ Hz), 29.43 (q, $J_{C-F} = 2.8$ Hz), 22.88, 21.22; ^{19}F NMR (752 MHz, $CDCl_3$) δ -63.75 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $C_{15}H_{18}F_3N_2O_2$ $[M+H^+]$: 315.1315, found 315.1315.



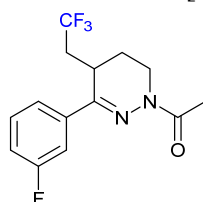
1-(3-(4-Chlorophenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ga, 42.7 mg, 67%), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, $J = 8.8$ Hz, 2H), 7.38 (d, $J = 8.7$ Hz, 2H), 4.51-4.45 (m, 1H), 3.34-3.30 (m, 1H), 3.22-3.15 (m, 1H), 2.41 (s, 3H), 2.33-2.15 (m, 3H), 1.97-1.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.37, 145.96, 135.57, 133.73, 129.08, 126.25 (q, $J_{C-F} = 278.9$ Hz), 126.89, 35.19 (q, $J_{C-F} = 28.2$ Hz), 34.45, 25.03 (q, $J_{C-F} = 2.5$ Hz), 21.31, 21.19; ^{19}F NMR (752 MHz, $CDCl_3$) δ -63.94 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $C_{14}H_{15}ClF_3N_2O$ $[M+H^+]$: 319.0820, found 319.0819.



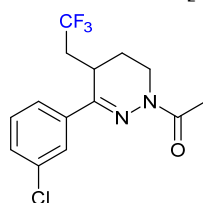
1-(3-(4-Fluorophenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ha, 37.5 mg, 62%), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.14-7.10 (m, 2H), 4.52-4.47 (m, 1H), 3.36-3.32 (m, 1H), 3.23-3.16 (m, 1H), 2.42 (s, 3H), 2.35-2.19 (m, 3H), 2.00-1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 163.56 (d, $J_{C-F} = 251.1$ Hz), 145.15, 131.38 (d, $J_{C-F} = 3.4$ Hz), 126.27 (q, $J_{C-F} = 278.8$ Hz), 127.54 (d, $J_{C-F} = 8.4$ Hz), 115.93 (d, $J_{C-F} = 21.8$ Hz), 35.19 (q, $J_{C-F} = 28.0$ Hz), 34.40, 25.14 (q, $J_{C-F} = 2.4$ Hz), 21.36, 21.25; ^{19}F NMR (752 MHz, $CDCl_3$) δ -63.96 (t, $J = 11.3$ Hz, 3F), -111.27 (s, 1F). HRMS (ESI) m/z calcd for $C_{14}H_{15}F_4N_2O$ $[M+H^+]$: 303.1115, found 303.1118.



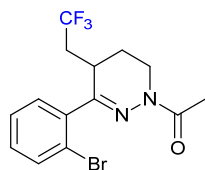
1-(4-(2,2,2-Trifluoroethyl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ia), 53.5 mg, 72%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.3$ Hz, 2H), 4.54-4.48 (m, 1H), 3.40-3.37 (m, 1H), 3.26-3.18 (m, 1H), 2.43 (s, 3H), 2.35-2.17 (m, 3H), 2.01-1.92 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.46, 144.49, 138.66, 131.16 (q, $J_{\text{C-F}} = 32.7$ Hz), 126.20 (q, $J_{\text{C-F}} = 278.8$ Hz), 125.88, 125.80 (q, $J_{\text{C-F}} = 3.8$ Hz), 123.91 (q, $J_{\text{C-F}} = 273.1$ Hz), 35.19 (q, $J_{\text{C-F}} = 28.2$ Hz), 34.55, 25.08 (q, $J_{\text{C-F}} = 2.5$ Hz), 21.31, 21.13; ^{19}F NMR (752 MHz, CDCl_3) δ -62.85 (s, 3F), -64.00 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{F}_6\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 353.1083, found 353.1076.



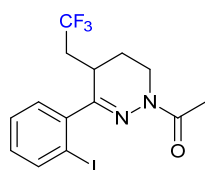
1-(3-(3-Fluorophenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ja), 36.3 mg, 60%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.36 (m, 3H), 7.12-7.07 (m, 1H), 4.52-4.46 (m, 1H), 3.35-3.30 (m, 1H), 3.24-3.16 (m, 1H), 2.42 (s, 3H), 2.36-2.16 (m, 3H), 1.98-1.88 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.43, 163.15 (d, $J_{\text{C-F}} = 243.0$ Hz), 144.70 (d, $J_{\text{C-F}} = 2.9$ Hz), 137.65 (d, $J_{\text{C-F}} = 7.5$ Hz), 130.41 (d, $J_{\text{C-F}} = 8.2$ Hz), 126.24 (q, $J_{\text{C-F}} = 278.9$ Hz), 121.08 (d, $J_{\text{C-F}} = 2.7$ Hz), 116.52 (d, $J_{\text{C-F}} = 21.6$ Hz), 112.58 (d, $J_{\text{C-F}} = 23.4$ Hz), 35.16 (q, $J_{\text{C-F}} = 28.1$ Hz), 34.52, 25.16 (q, $J_{\text{C-F}} = 2.6$ Hz), 21.32, 21.08; ^{19}F NMR (752 MHz, CDCl_3) δ -63.92 (t, $J = 10.5$ Hz, 3F), -111.95 (dt, $J = 14.3, 7.5$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{F}_4\text{N}_2\text{O}$ [$\text{M}+\text{Na}^+$]: 325.0934, found 325.0945.



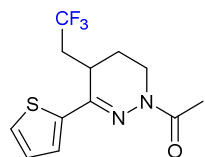
1-(3-(3-Chlorophenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ka), 54.2 mg, 85%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74-7.72 (m, 1H), 7.58-7.55 (m, 1H), 7.38-7.35 (m, 2H), 4.51-4.45 (m, 1H), 3.34-3.30 (m, 1H), 3.24-3.16 (m, 1H), 2.42 (s, 3H), 2.32-2.17 (m, 3H), 1.97-1.87 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.44, 144.64, 137.15, 135.05, 130.09, 129.53, 126.22 (q, $J_{\text{C-F}} = 278.9$ Hz), 125.87, 123.57, 35.17 (q, $J_{\text{C-F}} = 28.1$ Hz), 34.54, 25.14 (q, $J_{\text{C-F}} = 3.0$ Hz), 21.35, 21.15; ^{19}F NMR (752 MHz, CDCl_3) δ -63.91 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{ClF}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 319.0820, found 319.0822.



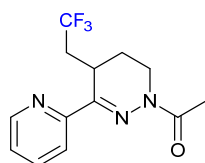
1-(3-(2-Bromophenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5la), 39.2 mg, 54%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.55 (m, 1H), 7.33-7.29 (m, 1H), 7.23-7.17 (m, 2H), 3.94-3.85 (m, 1H), 3.74-3.67 (m, 1H), 3.20-3.14 (m, 1H), 2.21-2.08 (m, 5H), 2.04-1.92 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.52, 148.55, 137.98, 133.42, 130.45, 130.37, 127.69, 126.12 (q, $J_{\text{C-F}} = 278.9$ Hz), 122.26, 36.07, 34.99 (q, $J_{\text{C-F}} = 28.5$ Hz), 29.68 (q, $J_{\text{C-F}} = 2.4$ Hz), 22.16, 21.21; ^{19}F NMR (752 MHz, CDCl_3) δ -63.64 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{BrF}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 363.0314, found 363.0309.



1-(3-(2-Iodophenyl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5ma), 41.0 mg, 50%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.90 (m, 1H), 7.43-7.39 (m, 1H), 7.22-7.20 (m, 1H), 7.12-7.07 (m, 1H), 4.08-4.01 (m, 1H), 3.73-3.66 (m, 1H), 3.18-3.12 (m, 1H), 2.30 (s, 3H), 2.23-2.03 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.57, 149.96, 141.48, 140.00, 130.39, 129.31, 128.39, 126.11 (q, $J_{\text{C-F}} = 278.8$ Hz), 97.28, 35.81, 34.71 (q, $J_{\text{C-F}} = 28.6$ Hz), 29.79 (q, $J_{\text{C-F}} = 2.2$ Hz), 22.25, 21.33; ^{19}F NMR (752 MHz, CDCl_3) δ -63.86 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{IN}_2\text{O}$ [$\text{M}+\text{H}^+$]: 411.0176, found 411.0167.

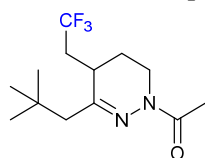


1-(3-(Thiophen-2-yl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5na), 33.6 mg, 58%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 5.0$ Hz, 1H), 7.25 (d, $J = 5.8$ Hz, 1H), 7.06-7.04 (m, 1H), 4.54-4.51 (m, 1H), 3.27-3.25 (m, 1H), 3.18-3.10 (m, 1H), 2.57-2.44 (m, 1H), 2.38 (s, 3H), 2.34-2.17 (m, 2H), 1.96-1.89 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.12, 142.64, 141.41, 126.3 (q, $J_{\text{C-F}} = 278.9$ Hz), 127.66, 127.58, 125.04, 117.47, 35.66 (q, $J_{\text{C-F}} = 28.3$ Hz), 34.34, 26.29 (q, $J_{\text{C-F}} = 1.8$ Hz), 21.07, 20.97; ^{19}F NMR (752 MHz, CDCl_3) δ -63.85 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{N}_2\text{OS}$ [$\text{M}+\text{H}^+$]: 291.0733, found 291.0734.

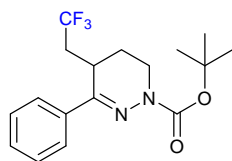


1-(3-(Pyridin-2-yl)-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1

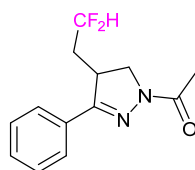
-one (50a, 49.6 mg, 87%), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.50 (d, $J = 4.4$ Hz, 1H), 7.91 (d, $J = 8.1$ Hz, 1H), 7.64 (t, $J = 7.7$ Hz, 1H), 7.19 (t, $J = 6.0$ Hz, 1H), 4.44-4.39 (m, 1H), 3.86-3.82 (m, 1H), 3.18-3.10 (m, 1H), 2.64-2.51 (m, 1H), 2.37 (s, 3H), 2.20-2.16 (m, 1H), 2.11-2.02 (m, 1H), 1.81-1.72 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.35, 153.50, 148.80, 147.37, 136.34, 126.48 (q, $J_{\text{C-F}} = 279.2$ Hz), 123.75, 120.07, 35.10, 34.62 (q, $J_{\text{C-F}} = 28.0$ Hz), 24.28 (q, $J_{\text{C-F}} = 2.8$ Hz), 21.30, 20.21; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -63.09 (t, $J = 11.3$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 286.1162, found 286.1160.



1-(3-Neopentyl-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (5pa, 22.8 mg, 41%), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.30-4.25 (m, 1H), 3.17-3.10 (m, 1H), 2.54-2.51 (m, 1H), 2.35-2.23 (m, 4H), 2.15-1.96 (m, 4H), 1.86-1.75 (m, 1H), 1.00 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.10, 149.39, 126.25 (q, $J_{\text{C-F}} = 278.7$ Hz), 47.90, 34.92 (q, $J_{\text{C-F}} = 28.4$ Hz), 34.10, 32.24, 29.97 (q, $J_{\text{C-F}} = 2.6$ Hz), 29.80, 21.30; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -64.20 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 279.1679, found 279.1682.

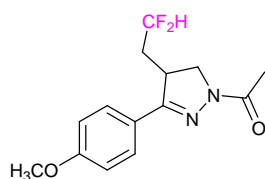


2,2-Dimethyl-1-(3-phenyl-4-(2,2,2-trifluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)propan-1-one (5qa, 47.0 mg, 72%), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 6.9$ Hz, 2H), 7.42-7.36 (m, 3H), 4.19 (d, $J = 13.5$ Hz, 1H), 3.39-3.33 (m, 2H), 2.43-2.31 (m, 1H), 2.23-2.14 (m, 2H), 2.06-1.97 (m, 1H), 1.58 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.13, 135.57, 129.21, 128.72, 126.43 (q, $J_{\text{C-F}} = 279.0$ Hz), 125.64, 81.80, 35.36 (q, $J_{\text{C-F}} = 27.8$ Hz), 28.31, 24.82 (q, $J_{\text{C-F}} = 2.0$ Hz), 21.77; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -64.16 (t, $J = 10.5$ Hz, 3F). HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 343.1628, found 343.1634.

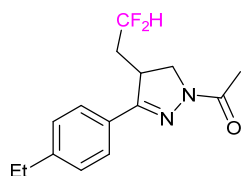


1-(4-(2,2-Difluoroethyl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7aa, 34.3 mg, 68%) colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72-7.69 (m, 2H), 7.45-7.42 (m, 3H), 6.09-5.79 (m, 1H), 4.12-4.03 (m, 2H), 3.92-3.86 (m, 1H), 2.39 (s, 3H), 2.32-2.21 (m, 1H), 2.03-1.93 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.68, 156.88, 130.47, 129.89, 129.07, 126.78, 115.47 (t, $J_{\text{C-F}} = 241.1$ Hz), 50.52, 37.98 (t, $J_{\text{C-F}} = 4.8$ Hz), 36.51 (t, $J_{\text{C-F}} = 21.0$ Hz), 21.48; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -116.66 (ddd, $J = 284.7, 55.5, 19.3, 14.5$ Hz, 1F), -117.27 (ddd, $J = 284.6, 55.8, 20.4, 16.7$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{F}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 253.1147, found

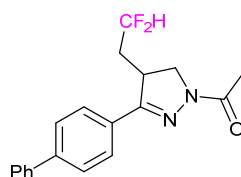
253.1149.



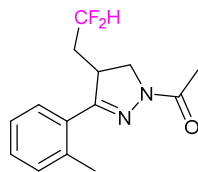
1-(4-(2,2-Difluoroethyl)-3-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ba, 44.1 mg, 78%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.7$ Hz, 2H), 6.95 (d, $J = 8.7$ Hz, 2H), 6.07-5.79 (m, 1H), 4.05 (d, $J = 7.4$ Hz, 2H), 3.88-3.78 (m, 4H), 2.37 (s, 3H), 2.32-2.19 (m, 1H), 2.04-1.89 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.49, 161.36, 156.73, 128.39, 122.37, 115.51 (t, $J_{\text{C-F}} = 240.9$ Hz), 114.48, 55.45, 50.40, 38.05 (t, $J_{\text{C-F}} = 4.9$ Hz), 36.63 (t, $J_{\text{C-F}} = 21.1$ Hz), 21.46; ^{19}F NMR (752 MHz, CDCl_3) δ -116.57 (dddd, $J = 284.5, 55.6, 19.2, 13.9$ Hz, 1F), -117.32 (dddd, $J = 284.5, 55.8, 20.4, 16.8$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 283.1253, found 283.1249.



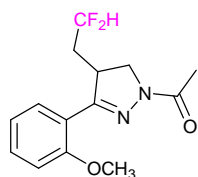
1-(4-(2,2-Difluoroethyl)-3-(4-ethylphenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7da, 22.4 mg, 40%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 7.0$ Hz, 2H), 6.06-5.78 (m, 1H), 4.09-4.02 (m, 2H), 3.87-3.82 (m, 1H), 2.67 (q, $J = 7.6$ Hz, 2H), 2.37 (s, 3H), 2.29-2.20 (m, 1H), 2.02-1.91 (m, 1H), 1.24 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.78, 157.32, 147.22, 128.60, 127.21, 126.87, 115.51 (t, $J_{\text{C-F}} = 241.2$ Hz), 50.44, 38.08 (t, $J_{\text{C-F}} = 4.9$ Hz), 36.59 (t, $J_{\text{C-F}} = 21.1$ Hz), 28.83, 21.40, 15.35; ^{19}F NMR (752 MHz, CDCl_3) δ -116.64 (ddt, $J = 284.5, 55.6, 17.8$ Hz, 1F), -117.25 (ddt, $J = 284.5, 55.8, 18.6$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{F}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 281.1460, found 281.1461.



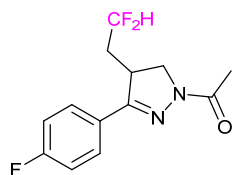
1-(3-([1,1'-Biphenyl]-4-yl)-4-(2,2-difluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ea, 40.7 mg, 62%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.7$ Hz, 2H), 7.69 (d, $J = 1.6$ Hz, 2H), 7.62 (d, $J = 1.6$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.7$ Hz, 1H), 6.12-5.82 (m, 1H), 4.15-4.09 (m, 2H), 3.95-3.88 (m, 1H), 2.43-2.26 (m, 4H), 2.10-1.94 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.64, 156.56, 143.16, 139.96, 128.99, 128.78, 128.02, 127.68, 127.25, 127.06, 115.50 (t, $J_{\text{C-F}} = 241.2$ Hz), 50.59, 38.00 (t, $J_{\text{C-F}} = 4.8$ Hz), 36.60 (t, $J_{\text{C-F}} = 21.2$ Hz), 21.50; ^{19}F NMR (752 MHz, CDCl_3) δ -116.58 (dddd, $J = 284.5, 55.6, 19.3, 14.2$ Hz, 1F), -117.22 (dddd, $J = 284.5, 55.8, 20.4, 16.6$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 329.1460, found 329.1465.



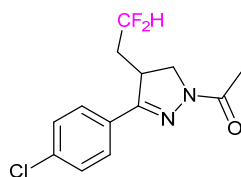
1-(4-(2,2-Difluoroethyl)-3-(o-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ga, 36.8 mg, 69%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.20 (m, 4H), 5.95-5.65 (m, 1H), 4.11-4.05 (m, 1H), 3.90-3.85 (m, 2H), 2.46 (s, 3H), 2.29 (s, 3H), 2.16-2.05 (m, 1H), 1.94-1.80 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.61, 157.62, 138.11, 132.02, 129.69, 128.90, 128.45, 126.24, 115.46 (t, $J_{\text{C-F}} = 241.1$ Hz), 49.51, 40.22 (t, $J_{\text{C-F}} = 4.6$ Hz), 36.40 (t, $J_{\text{C-F}} = 20.9$ Hz), 22.24, 21.50; ^{19}F NMR (752 MHz, CDCl_3) δ -116.82 (dt, $J = 17.7, 9.5$ Hz, 1F), -116.88 (dt, $J = 17.7, 9.5$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 267.1303, found 267.1301.



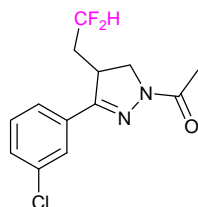
1-(4-(2,2-Difluoroethyl)-3-(2-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ha, 16.9 mg, 30%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 5.99-5.71 (m, 1H), 4.24-4.12 (m, 2H), 3.87-3.79 (m, 4H), 2.37 (s, 3H), 2.20-2.07 (m, 1H), 1.91-1.77 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.54, 157.93, 157.48, 131.92, 130.08, 121.21, 119.17, 115.89 (t, $J_{\text{C-F}} = 241.1$ Hz), 111.39, 55.32, 50.20, 40.92 (t, $J_{\text{C-F}} = 4.8$ Hz), 36.67 (t, $J_{\text{C-F}} = 20.9$ Hz), 21.40; ^{19}F NMR (752 MHz, CDCl_3) δ -116.41 (ddt, $J = 284.3, 56.4, 18.0$ Hz, 1F), -116.88 (ddt, $J = 283.5, 55.6, 17.3$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 283.1253, found 283.1256.



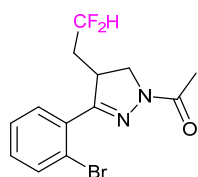
1-(4-(2,2-difluoroethyl)-3-(4-fluorophenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ia, 41.6 mg, 77%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.72-7.69 (m, 2H), 7.16-7.12 (m, 2H), 6.10-5.80 (m, 1H), 4.13-4.07 (m, 2H), 3.89-3.83 (m, 1H), 2.38-2.21 (m, 4H), 2.04-1.94 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.64, 163.92 (d, $J_{\text{C-F}} = 252.7$ Hz), 155.88, 128.80 (d, $J_{\text{C-F}} = 8.5$ Hz), 126.14 (d, $J_{\text{C-F}} = 3.5$ Hz), 116.3 (d, $J_{\text{C-F}} = 22.1$ Hz), 115.37 (d, $J_{\text{C-F}} = 241.2$ Hz), 50.62, 37.99 (t, $J_{\text{C-F}} = 4.8$ Hz), 36.43 (t, $J_{\text{C-F}} = 21.0$ Hz), 21.44; ^{19}F NMR (752 MHz, CDCl_3) δ -109.08 (ddd, $J = 13.5, 8.1, 5.2$ Hz, 1F), -116.67 (dddd, $J = 284.8, 55.6, 19.9, 13.7$ Hz, 1F), -117.41 (dddd, $J = 285.0, 55.8, 21.3, 16.3$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 271.1053, found 271.1052.



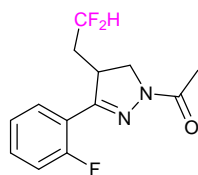
1-(3-(4-Chlorophenyl)-4-(2,2-difluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ja, 37.8 mg, 66%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 6.08-5.80 (m, 1H), 4.12-4.07 (m, 2H), 3.88-3.82 (m, 1H), 2.38 (s, 3H), 2.29-2.17 (m, 1H), 2.01-1.90 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.66, 155.73, 136.42, 129.35, 128.41, 128.01, 115.34 (t, $J_{\text{C-F}} = 241.1$ Hz), 50.68, 37.84 (t, $J_{\text{C-F}} = 4.6$ Hz), 36.40 (t, $J_{\text{C-F}} = 21.0$ Hz), 21.46; ^{19}F NMR (752 MHz, CDCl_3) δ -116.67 (dddd, $J = 284.8, 55.4, 19.7, 13.8$ Hz, 1F), -117.38 (dddd, $J = 285.0, 55.7, 21.0, 16.0$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 287.0757, found 287.0760.



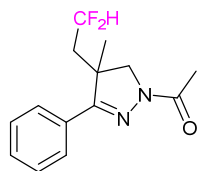
1-(3-(3-Chlorophenyl)-4-(2,2-difluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ka, 36.7 mg, 64%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.52 (d, $J = 7.0$ Hz, 1H), 7.42-7.36 (m, 2H), 6.10-5.81 (m, 1H), 4.13-4.06 (m, 2H), 3.88-3.81 (m, 1H), 2.39-2.18 (m, 4H), 2.07-1.94 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.83, 155.54, 135.18, 131.75, 130.41, 130.33, 126.70, 124.83, 115.32 (t, $J_{\text{C-F}} = 241.2$ Hz), 50.71, 37.88 (t, $J_{\text{C-F}} = 4.7$ Hz), 36.36 (t, $J_{\text{C-F}} = 21.1$ Hz), 21.45; ^{19}F NMR (752 MHz, CDCl_3) δ -116.69 (dddd, $J = 284.9, 55.6, 19.8, 14.5$ Hz, 1F), -117.28 (dddd, $J = 285.1, 55.7, 20.7, 16.3$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 287.0757, found 287.0759.



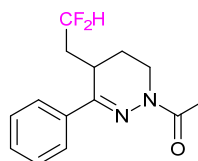
1-(3-(2-Bromophenyl)-4-(2,2-difluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7la, 39.6 mg, 60%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.9$ Hz, 1H), 7.45-7.37 (m, 2H), 7.31 (t, $J = 7.9$ Hz, 1H), 5.97-5.69 (m, 1H), 4.32-4.21 (m, 2H), 3.91-3.87 (m, 1H), 2.35 (s, 3H), 2.09-1.99 (m, 1H), 1.94-1.82 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.71, 157.63, 133.98, 131.63, 131.34, 131.26, 127.80, 121.88, 115.42 (t, $J_{\text{C-F}} = 241.5$ Hz), 50.12, 40.78 (t, $J_{\text{C-F}} = 4.5$ Hz), 35.94 (t, $J_{\text{C-F}} = 21.2$ Hz), 21.49; ^{19}F NMR (752 MHz, CDCl_3) δ -115.84 (dddd, $J = 284.7, 55.7, 18.4, 15.1$ Hz, 1F), -116.91 (ddt, $J = 284.7, 55.8, 17.9$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{BrF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 331.0252, found 331.0245.



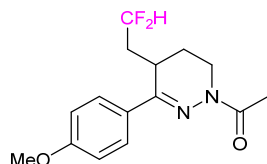
1-(4-(2,2-Difluoroethyl)-3-(2-fluorophenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7ma, 38.4 mg, 71%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.80 (m, 1H), 7.49-7.38 (m, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.17-7.11 (m, 1H), 6.06-5.76 (m, 1H), 4.20-4.13 (m, 1H), 4.00-3.92 (m, 2H), 2.38-2.13 (m, 4H), 2.01-1.88 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.62, 160.50 (d, $J_{\text{C-F}} = 252.7$ Hz), 154.06 (d, $J_{\text{C-F}} = 2.7$ Hz), 132.22 (d, $J_{\text{C-F}} = 8.8$ Hz), 129.60 (d, $J_{\text{C-F}} = 3.3$ Hz), 124.91 (d, $J_{\text{C-F}} = 3.3$ Hz), 118.20 (d, $J_{\text{C-F}} = 11.4$ Hz), 115.69 (t, $J_{\text{C-F}} = 241.5$ Hz), 116.65 (d, $J_{\text{C-F}} = 22.1$ Hz), 50.30, 40.51 (q, $J_{\text{C-F}} = 4.9$ Hz), 36.47 (t, $J_{\text{C-F}} = 21.1$ Hz), 21.42; ^{19}F NMR (752 MHz, CDCl_3) δ -114.09 (s, 1F), -115.66 (ddt, $J = 284.9, 55.7, 16.8$ Hz, 1F), -116.96 (ddt, $J = 285.7, 55.8, 17.7$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 271.1053, found 271.1056.



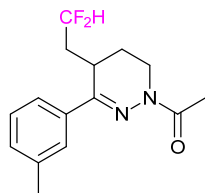
1-(4-(2,2-Difluoroethyl)-4-methyl-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (7oa, 35.7 mg, 67%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74-7.71 (m, 2H), 7.44-7.41 (m, 3H), 5.99-5.69 (m, 1H), 4.14 (d, $J = 12.2$ Hz, 1H), 3.85 (d, $J = 12.2$ Hz, 1H), 2.41-2.24 (m, 5H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.65, 158.98, 130.42, 130.13, 128.90, 127.25, 115.50 (t, $J_{\text{C-F}} = 241.4$ Hz), 57.67, 47.90 (t, $J_{\text{C-F}} = 4.6$ Hz), 41.64 (t, $J_{\text{C-F}} = 21.0$ Hz), 25.29, 21.27; ^{19}F NMR (752 MHz, CDCl_3) δ -112.28 (dddd, $J = 290.7, 55.2, 18.3, 13.8$ Hz, 1F), -113.65 (dddd, $J = 290.6, 55.6, 20.2, 13.8$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 267.1303, found 267.1301.



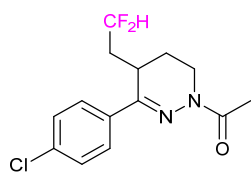
1-(4-(2,2-Difluoroethyl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8aa, 33.6 mg, 63%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.73 (m, 2H), 7.45-7.38 (m, 3H), 6.09-5.79 (m, 1H), 4.48-4.42 (m, 1H), 3.35-3.22 (m, 2H), 2.43 (s, 3H), 2.17-2.08 (m, 2H), 2.00-1.92 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.55, 147.48, 135.69, 129.50, 128.79, 125.76, 115.79 (t, $J_{\text{C-F}} = 241.1$ Hz), 35.87 (t, $J_{\text{C-F}} = 20.9$ Hz), 34.76, 24.87 (t, $J_{\text{C-F}} = 4.6$ Hz), 21.84, 21.38; ^{19}F NMR (752 MHz, CDCl_3) δ -75.65 (d, $J = 262.6$ Hz, 2F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 267.1303, found 267.1299.



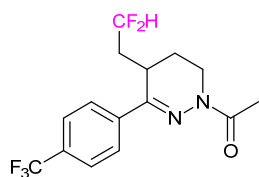
1-(4-(2,2-Difluoroethyl)-3-(4-methoxyphenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ba, 29.0 mg, 49%) colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.4$ Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 2H), 6.08-5.78 (m, 1H), 4.47-4.42 (m, 1H), 3.85 (s, 3H), 3.30-3.18 (m, 2H), 2.41 (s, 3H), 2.14-1.90 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.38, 160.70, 147.34, 129.66, 128.24, 127.18, 115.83 (t, $J_{\text{C-F}} = 241.1$ Hz), 114.12, 55.39, 35.94 (t, $J_{\text{C-F}} = 21.0$ Hz), 34.64, 24.80 (t, $J_{\text{C-F}} = 4.7$ Hz), 21.89, 21.35; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -115.43 (ddt, $J = 283.1, 56.2, 18.6$ Hz, 1F), -116.89 (ddt, $J = 290.6, 55.9, 16.6$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M}+\text{H}^+]$: 297.1409, found 297.1412.



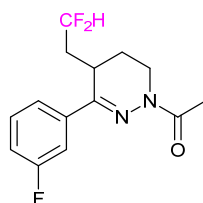
1-(4-(2,2-Difluoroethyl)-3-(m-tolyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ca, 39.2 mg, 61%) colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54-5.51 (m, 2H), 7.31 (t, $J = 7.7$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 6.07-5.78 (m, 1H), 4.46-4.41 (m, 1H), 3.33-3.22 (m, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 2.15-1.91 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.50, 147.76, 138.43, 135.74, 130.28, 128.66, 126.46, 122.96, 115.83 (t, $J_{\text{C-F}} = 241.2$ Hz), 35.95 (t, $J_{\text{C-F}} = 20.9$ Hz), 34.77, 25.02 (t, $J_{\text{C-F}} = 4.6$ Hz), 21.92, 21.62, 21.37; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -115.28 (ddt, $J = 283.1, 56.0, 18.5$ Hz, 1F), -116.91 (ddt, $J = 283.1, 55.9, 16.8$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 281.1460, found 281.1458.



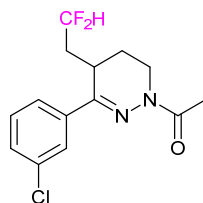
1-(3-(4-chlorophenyl)-4-(2,2-difluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ga, 28.3 mg, 47%) colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.6$ Hz, 2H), 7.37 (d, $J = 8.6$ Hz, 2H), 6.09-5.79 (m, 1H), 4.48-4.43 (m, 1H), 3.29-3.12 (m, 2H), 2.41 (s, 3H), 2.16-1.90 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.45, 146.27, 135.43, 134.15, 128.97, 127.01, 115.65 (t, $J_{\text{C-F}} = 241.3$ Hz), 35.82 (t, $J_{\text{C-F}} = 21.1$ Hz), 34.67, 24.73 (t, $J_{\text{C-F}} = 4.1$ Hz), 21.75, 21.35; $^{19}\text{F NMR}$ (752 MHz, CDCl_3) δ -115.66 (dddd, $J = 283.4, 56.0, 20.1, 18.6$ Hz, 1F), -116.88 (ddt, $J = 283.3, 55.8, 16.6$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 301.0914, found 301.0919.



1-(4-(2,2-Difluoroethyl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ia, 33.4 mg, 50%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.2$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 6.11-5.81 (m, 1H), 4.50-4.43 (m, 1H), 3.35-3.21 (m, 2H), 2.43 (s, 3H), 2.19-1.91 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.55, 145.86, 139.07, 131.03 (q, $J_{\text{C-F}} = 32.5$ Hz), 125.99, 125.71 (q, $J_{\text{C-F}} = 3.8$ Hz), 123.96 (q, $J_{\text{C-F}} = 273.0$ Hz), 115.58 (t, $J_{\text{C-F}} = 241.3$ Hz), 35.77 (t, $J_{\text{C-F}} = 20.9$ Hz), 34.77, 24.77 (t, $J_{\text{C-F}} = 4.3$ Hz), 21.68, 21.33; ^{19}F NMR (752 MHz, CDCl_3) δ -62.79 (s, 3F), -115.79 (dddd, $J = 283.9, 56.0, 20.1, 17.7$ Hz, 1F), -116.91 (dddd, $J = 283.7, 55.7, 17.4, 15.2$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{F}_5\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 335.1177, found 335.1168.

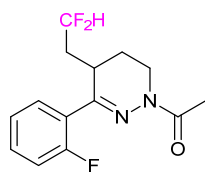


1-(4-(2,2-difluoroethyl)-3-(3-fluorophenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ja, 32.4 mg, 57%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.46 (m, 2H), 7.41-7.35 (m, 1H), 7.11-7.06 (m, 1H), 6.11-5.81 (m, 1H), 4.49-4.44 (m, 1H), 3.30-3.19 (m, 2H), 2.42 (s, 3H), 2.17-1.92 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.53, 163.12 (d, $J_{\text{C-F}} = 246.7$ Hz), 146.03 (d, $J_{\text{C-F}} = 2.8$ Hz), 138.07 (d, $J_{\text{C-F}} = 7.5$ Hz), 130.29 (d, $J_{\text{C-F}} = 8.3$ Hz), 121.24 (d, $J_{\text{C-F}} = 2.8$ Hz), 116.38 (d, $J_{\text{C-F}} = 21.6$ Hz), 115.66 (t, $J_{\text{C-F}} = 241.2$ Hz), 112.63 (d, $J_{\text{C-F}} = 23.3$ Hz), 35.78 (t, $J_{\text{C-F}} = 21.0$ Hz), 34.74, 24.87 (t, $J_{\text{C-F}} = 4.5$ Hz), 21.65, 21.37; ^{19}F NMR (752 MHz, CDCl_3) δ -112.14 (d, $J = 9.2$ Hz, 1F), -115.52 (ddt, $J = 283.5, 56.0, 19.3$ Hz, 1F), -116.90 (ddt, $J = 283.7, 55.8, 16.5$ Hz, 1F). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 285.1209, found 285.1212.

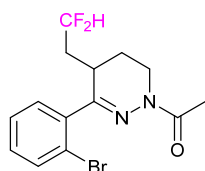


1-(3-(3-Chlorophenyl)-4-(2,2-difluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ka, 36.7 mg, 61%) colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (s, 1H), 7.60-7.57 (m, 1H), 7.37-7.32 (m, 2H), 6.10-5.80 (m, 1H), 4.48-4.42 (m, 1H), 3.29-3.19 (m, 2H), 2.42 (s, 3H), 2.17-1.91 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.51, 145.95, 137.57, 134.92, 129.99, 129.40, 125.91, 123.74, 115.65 (t, $J_{\text{C-F}} = 241.4$ Hz), 35.77 (t, $J_{\text{C-F}} = 20.8$ Hz), 34.75, 24.85 (t, $J_{\text{C-F}} = 4.5$ Hz), 21.69, 21.39; ^{19}F NMR (752 MHz, CDCl_3) δ -115.51 (dddd, $J = 283.6, 56.0, 20.1, 17.3$ Hz, 1F), -116.89 (ddt, $J = 283.7, 55.7, 16.1$ Hz, 1F). HRMS (ESI) m/z calcd for

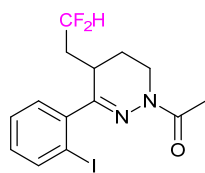
C₁₄H₁₆ClF₂N₂O [M+H⁺]: 301.0914, found 301.0909.



1-(4-(2,2-Difluoroethyl)-3-(2-fluorophenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8la, 39.2 mg, 69%) colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (t, *J* = 7.6 Hz, 1H), 7.41-7.35 (m, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13-7.08 (m, 1H), 6.00-5.70 (m, 1H), 4.04-3.98 (m, 1H), 3.74-3.67 (m, 1H), 3.27-3.21 (m, 1H), 2.35 (s, 3H), 2.15-1.80 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 172.48, 160.42 (d, *J*_{C-F} = 248.0 Hz), 146.66 (d, *J*_{C-F} = 2.5 Hz), 130.92 (d, *J*_{C-F} = 8.5 Hz), 130.08 (d, *J*_{C-F} = 3.5 Hz), 124.80 (d, *J*_{C-F} = 12.2 Hz), 124.61 (d, *J*_{C-F} = 3.3 Hz), 115.98 (t, *J*_{C-F} = 241.2 Hz), 116.35 (d, *J*_{C-F} = 22.8 Hz), 36.38 (t, *J*_{C-F} = 21.1 Hz), 36.07, 28.91 (q, *J*_{C-F} = 5.3 Hz), 22.78, 21.20; ¹⁹F NMR (752 MHz, CDCl₃) δ -113.74 (ddt, *J* = 284.3, 56.4, 17.3 Hz, 1F), 115.12 (d, *J* = 10.5 Hz, 1F), -116.29 (dddd, *J* = 284.3, 56.4, 19.5, 15.8 Hz, 1F). HRMS (ESI) *m/z* calcd for C₁₄H₁₆F₃N₂O [M+H⁺]: 285.1209, found 285.1207.



1-(3-(2-bromophenyl)-4-(2,2-difluoroethyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8ma, 24.2 mg, 35%) colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 2H), 5.86-5.55 (m, 1H), 3.93-3.87 (m, 1H), 3.74-3.67 (m, 1H), 3.12-3.06 (m, 1H), 2.25-2.07 (m, 4H), 1.92-1.71 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.62, 149.96, 138.38, 133.37, 130.46, 130.24, 127.62, 122.22, 115.75 (t, *J*_{C-F} = 241.3 Hz), 36.24, 35.59 (t, *J*_{C-F} = 21.2 Hz), 29.64 (t, *J*_{C-F} = 5.1 Hz), 22.64, 21.24; ¹⁹F NMR (752 MHz, CDCl₃) δ -114.15 (ddt, *J* = 283.6, 56.0, 17.4 Hz, 1F), -116.46 (ddt, *J* = 283.9, 55.9, 17.7 Hz, 1F). HRMS (ESI) *m/z* calcd for C₁₄H₁₆BrF₂N₂O [M+H⁺]: 345.0409, found 345.0415.



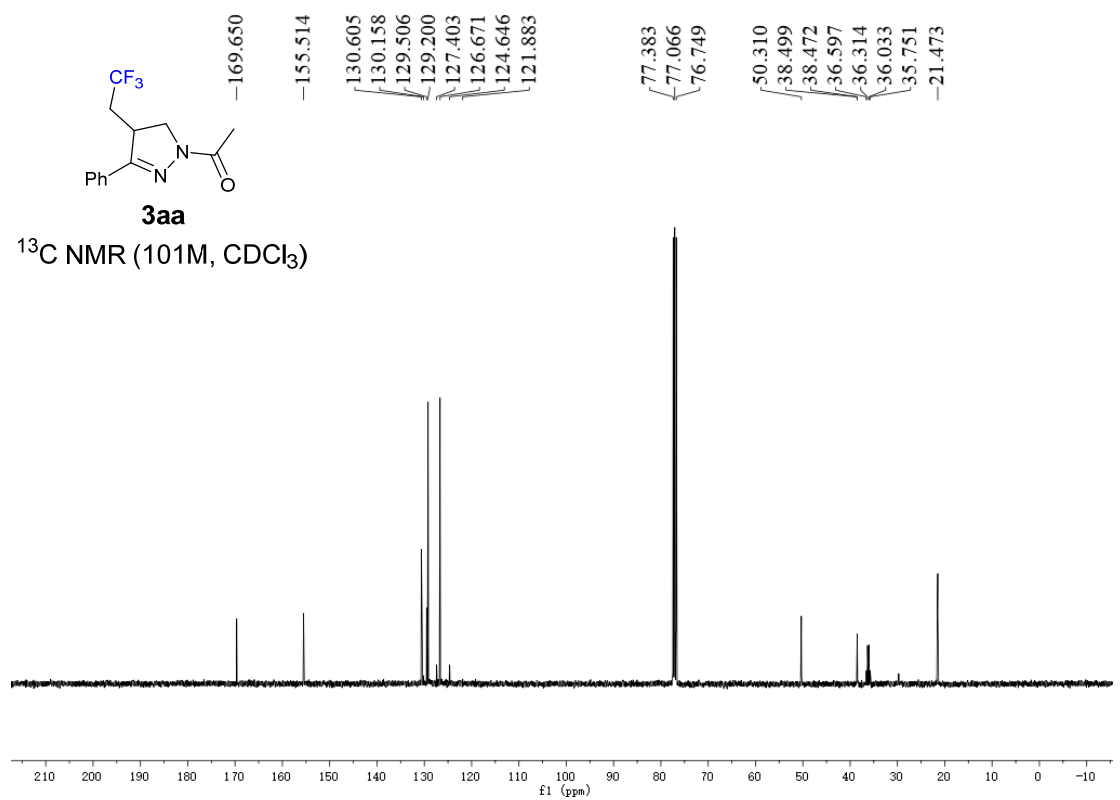
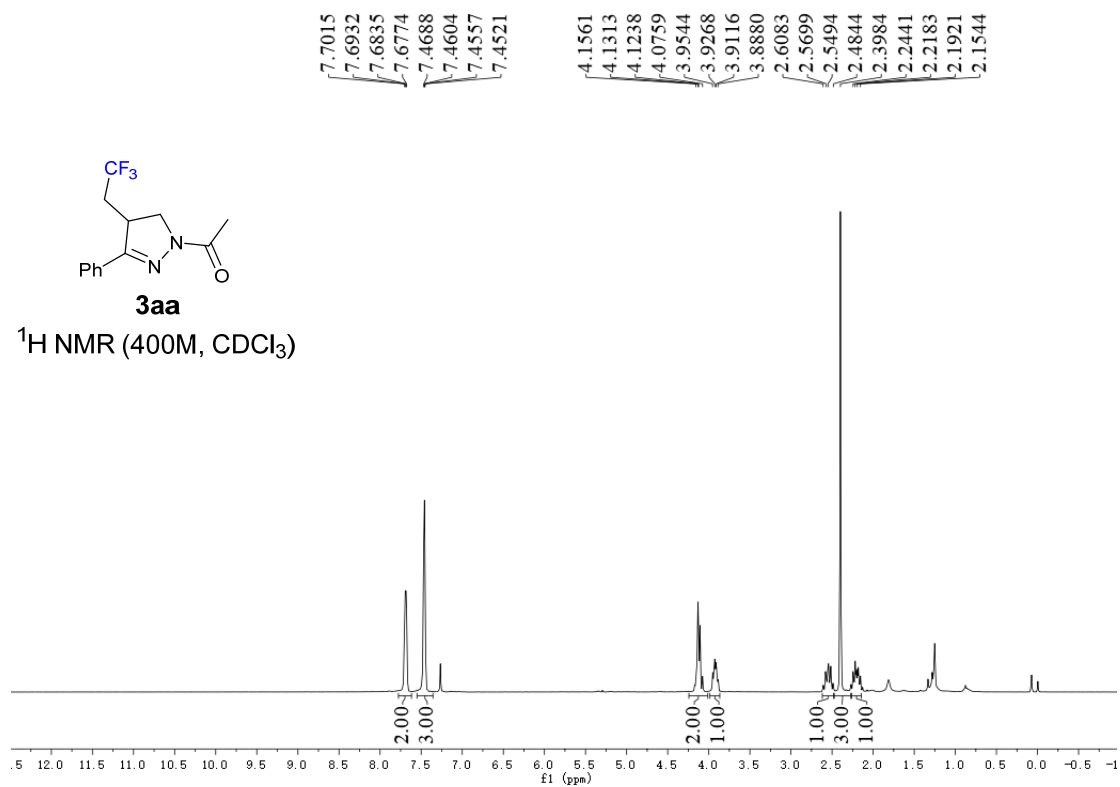
1-(4-(2,2-Difluoroethyl)-3-(2-iodophenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (8na, 37.4 mg, 48%) colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 5.92-5.61 (m, 1H), 4.07-4.02 (m, 1H), 3.73-3.66 (m, 1H), 3.09-3.06 (m, 1H), 2.31 (s, 3H), 2.23-2.15 (m, 1H), 2.04-1.81 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.67, 151.31, 141.91, 139.97, 130.25, 129.37, 128.31, 115.70 (t, *J*_{C-F} = 241.3 Hz), 97.22, 35.97, 35.38 (t, *J*_{C-F} = 21.3 Hz), 29.73 (t, *J*_{C-F} = 5.1 Hz), 22.77, 21.36; ¹⁹F NMR (752 MHz, CDCl₃) δ -114.25 (ddt, *J* = 283.6, 56.1, 17.4 Hz, 1F), -116.68 (ddt, *J* = 283.7,

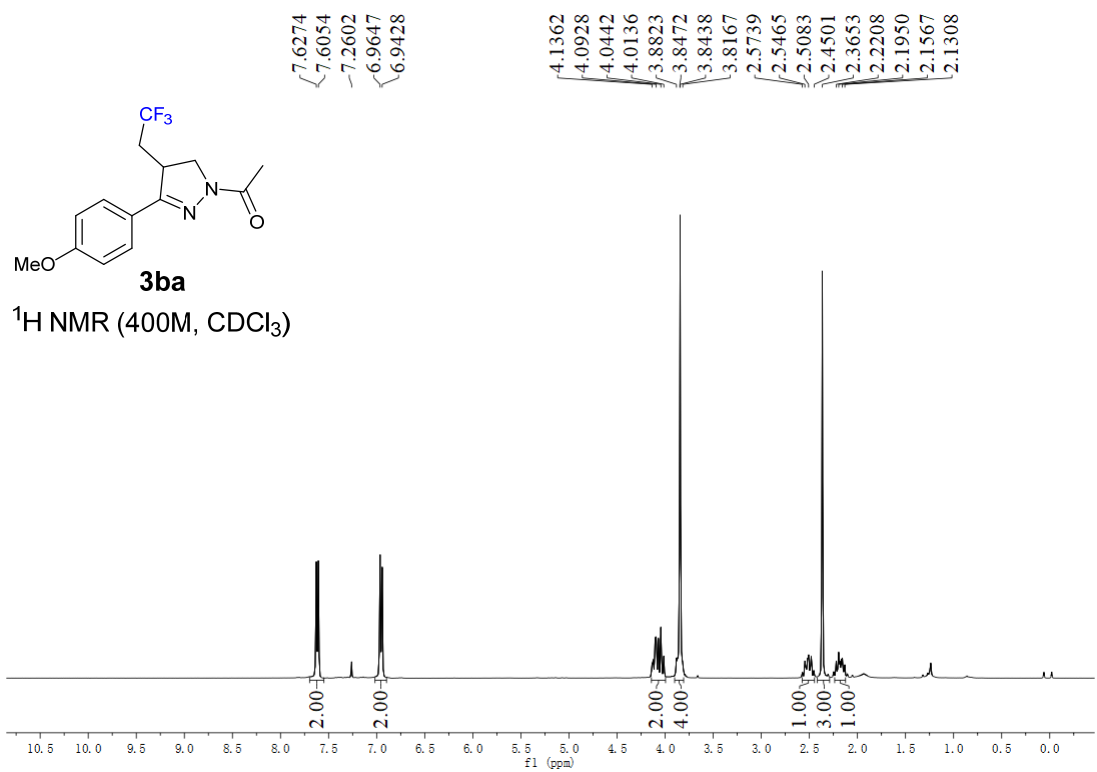
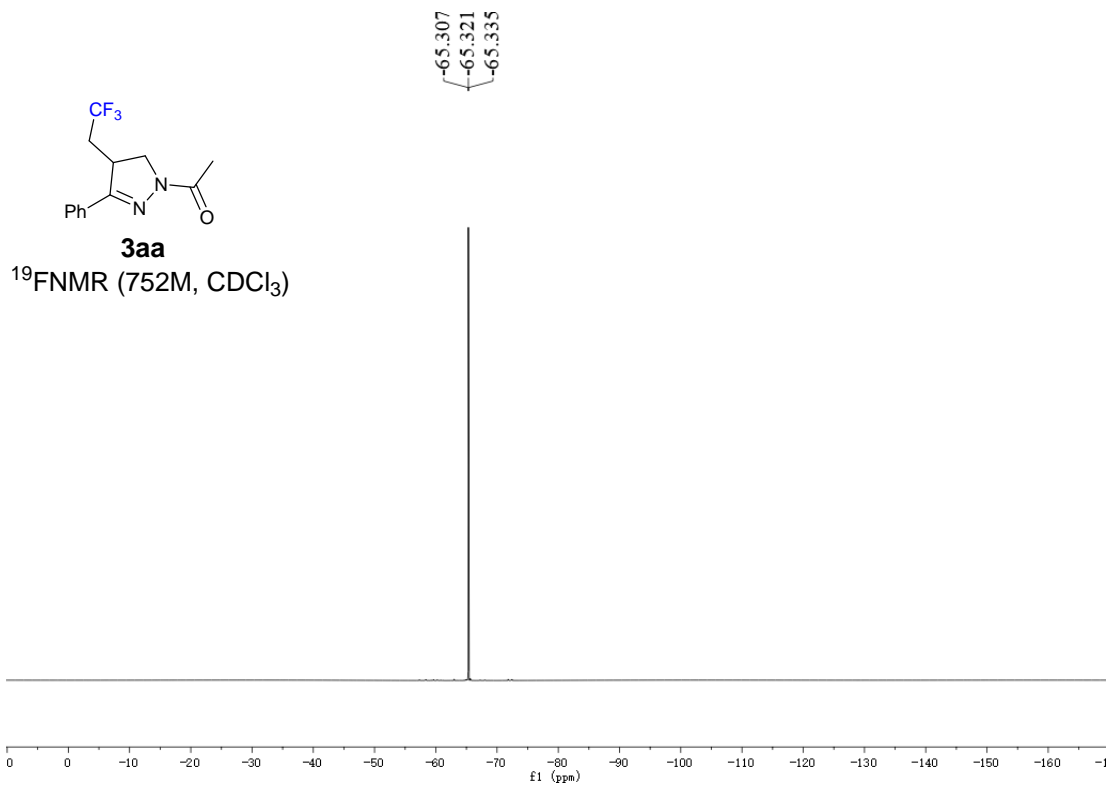
56.2, 17.3 Hz, 1F). HRMS (ESI) m/z calcd for C₁₄H₁₆IF₂N₂O [M+H⁺]: 393.0270, found 393.0261.

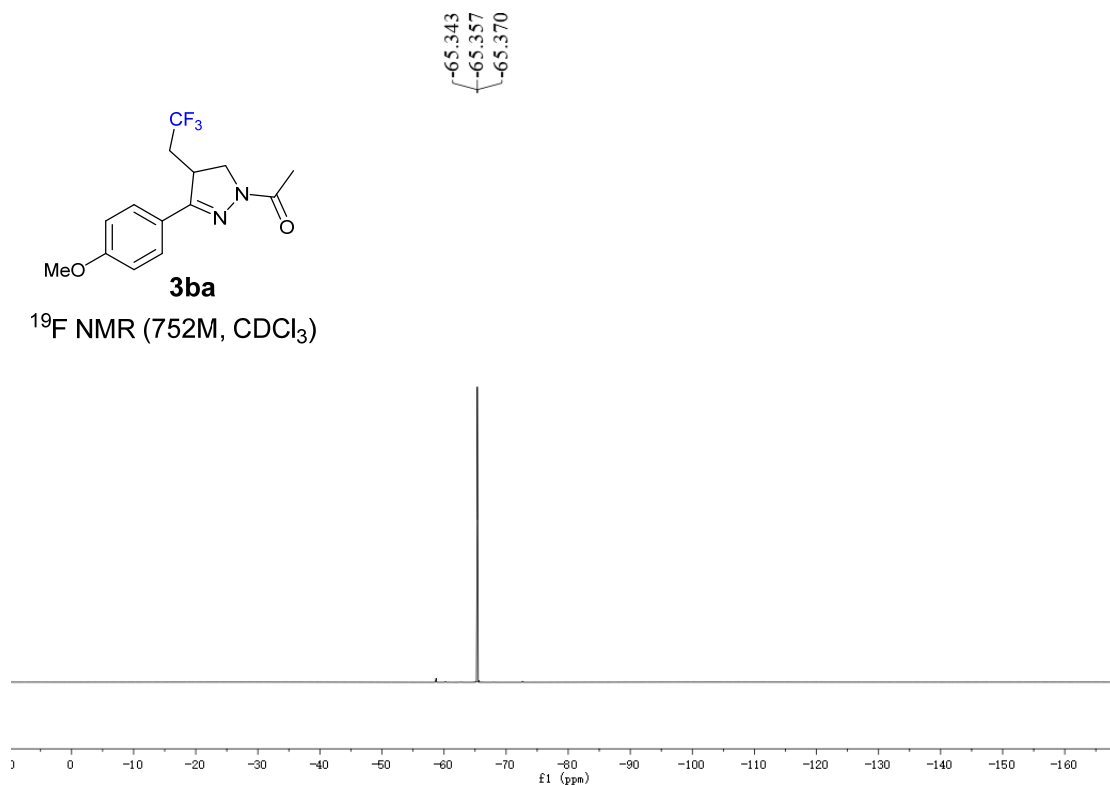
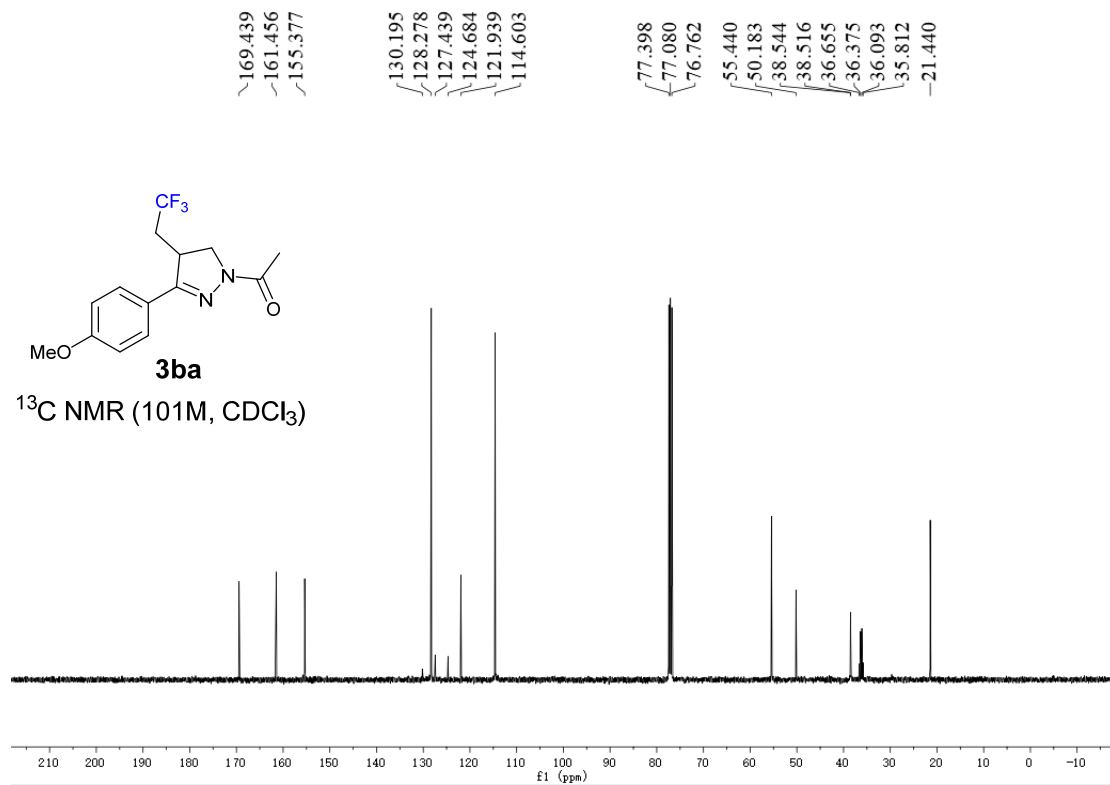
5. References

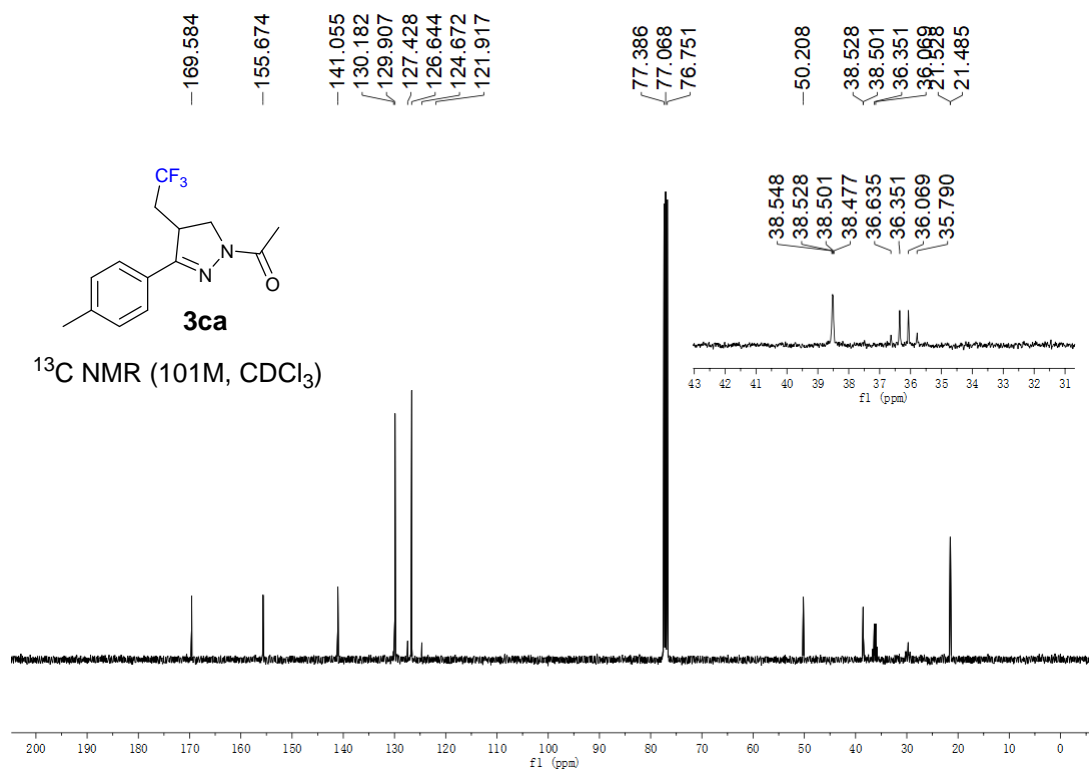
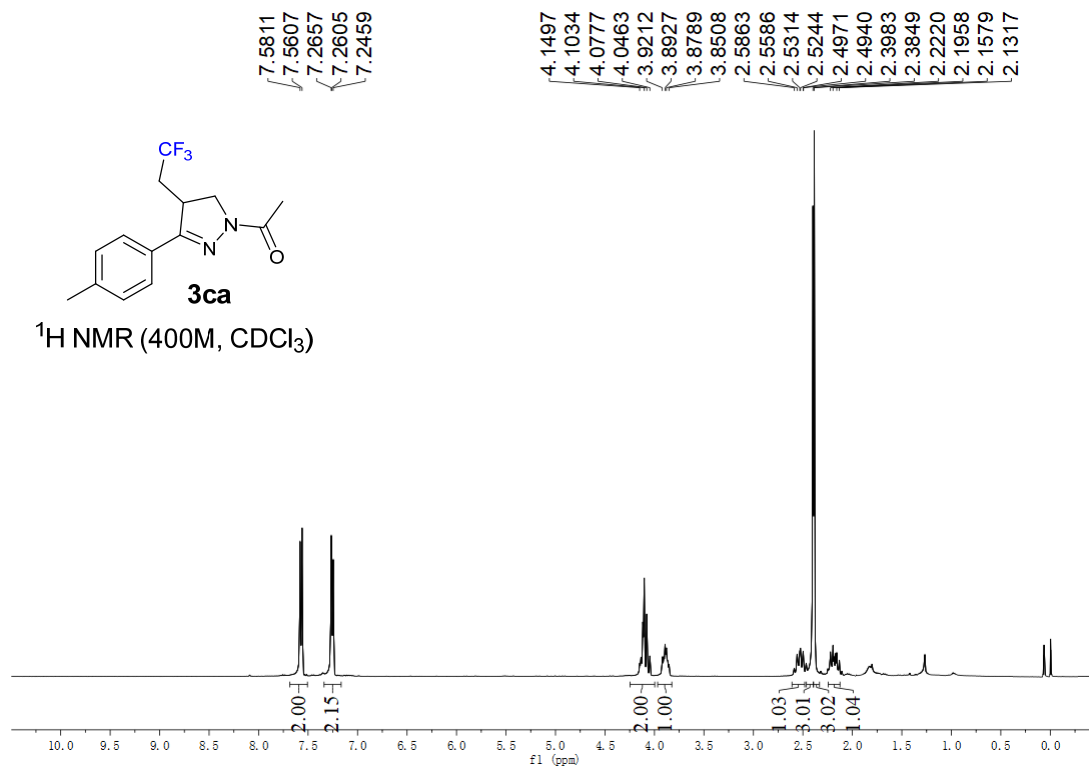
1. Y. Wu, X. Wu, L. Liu, J.-T. Yu and C. Pan, *Org. Lett.*, 2024, **26**, 122.
2. H. Jia, A. P. Häring, F. Berger, L. Zhang and T. Ritter, *J. Am. Chem. Soc.*, 2021, **143**, 7623.
3. R. Sakamoto, H. Kashiwagi and K. Maruoka, *Org. Lett.*, 2017, **19**, 5126.

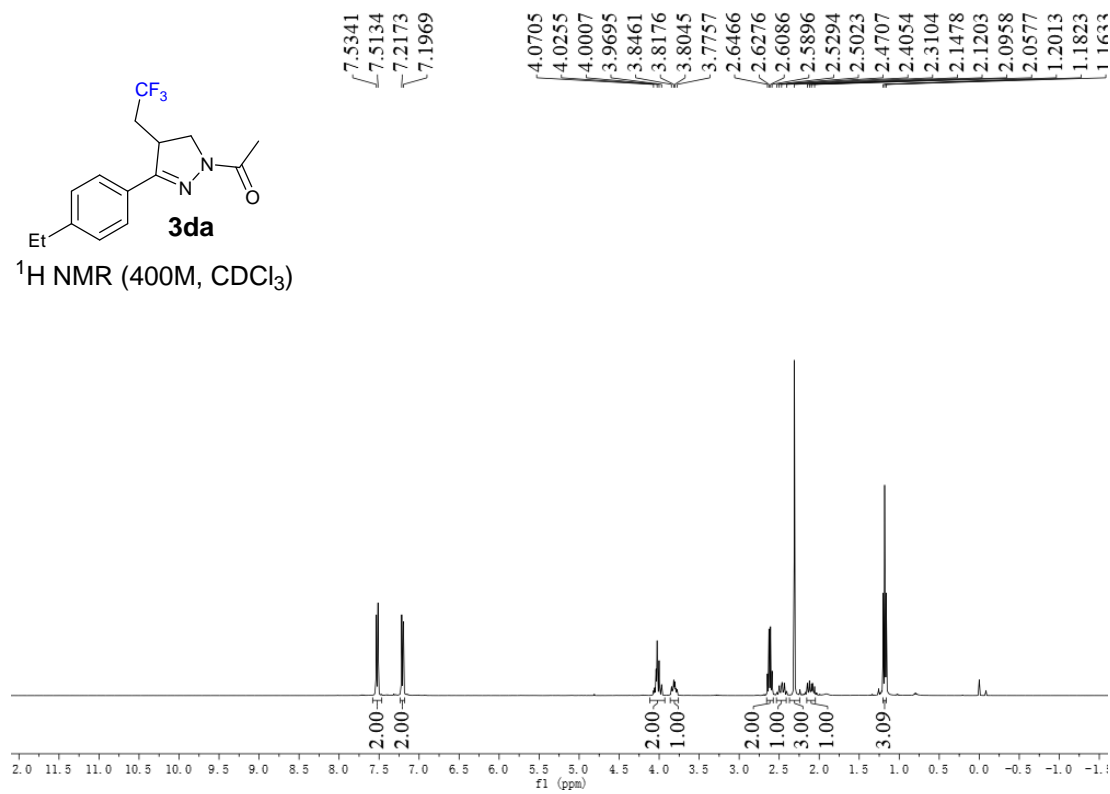
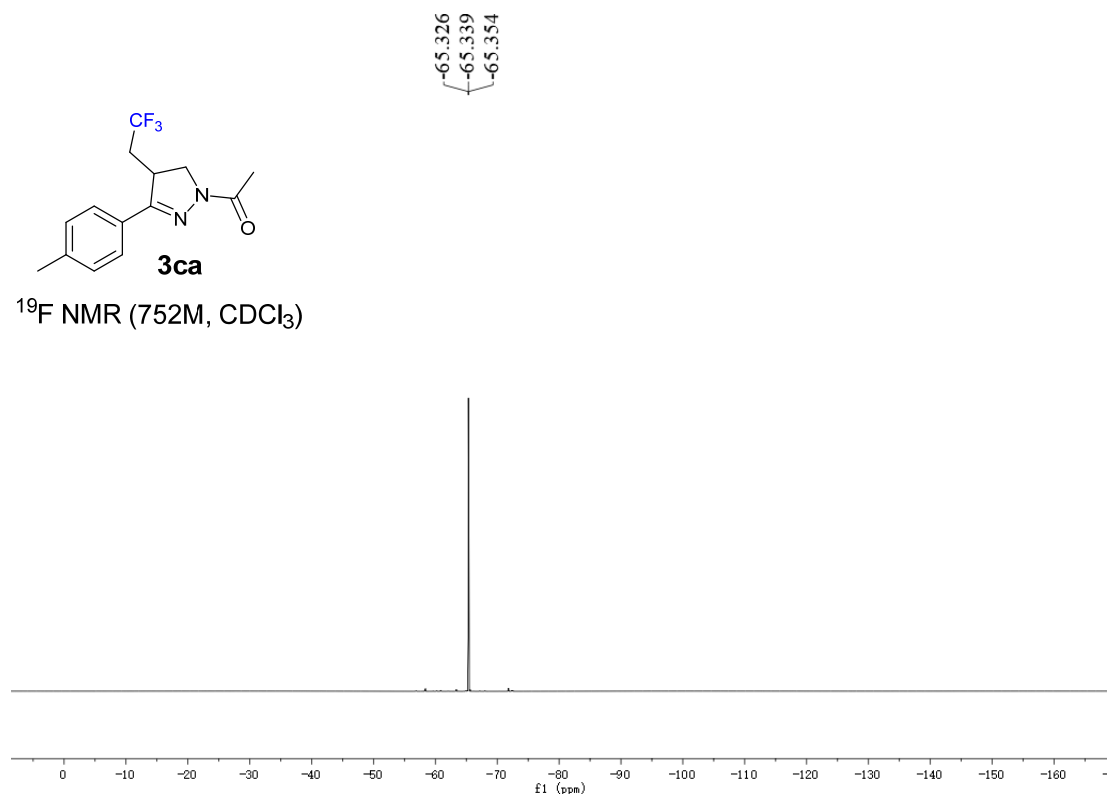
6. Copies of the ^1H NMR, ^{13}C NMR and ^{19}F NMR Spectra

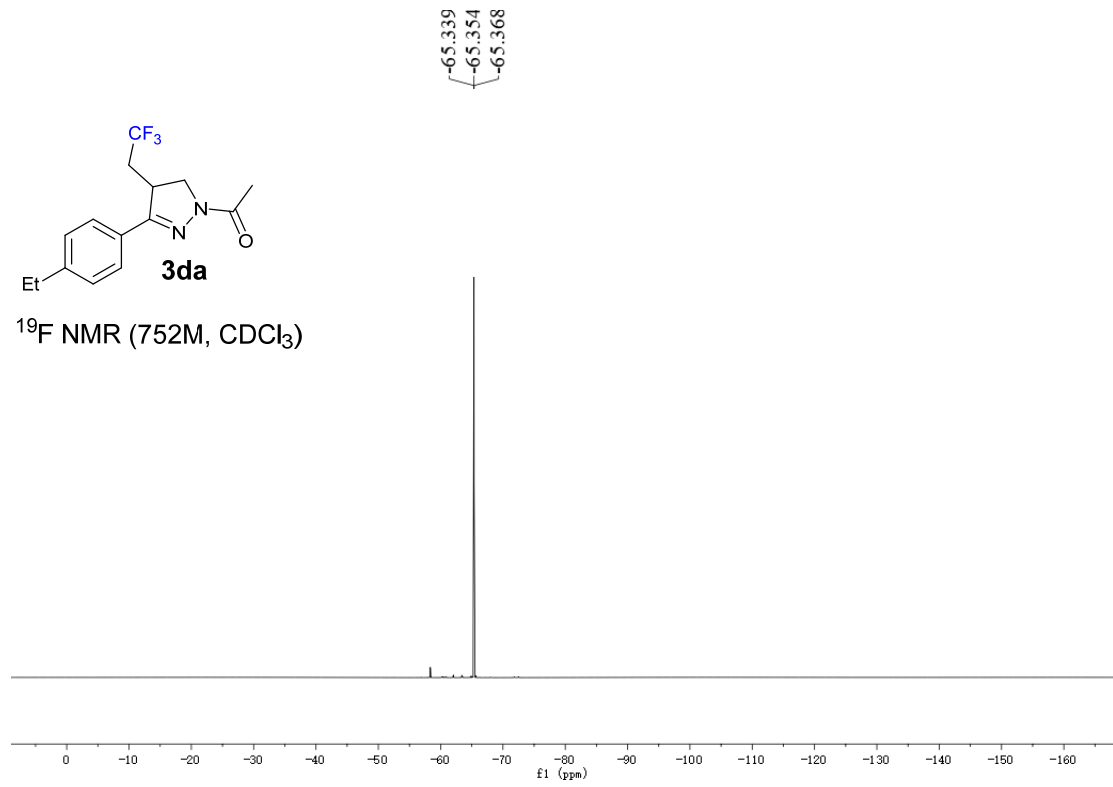
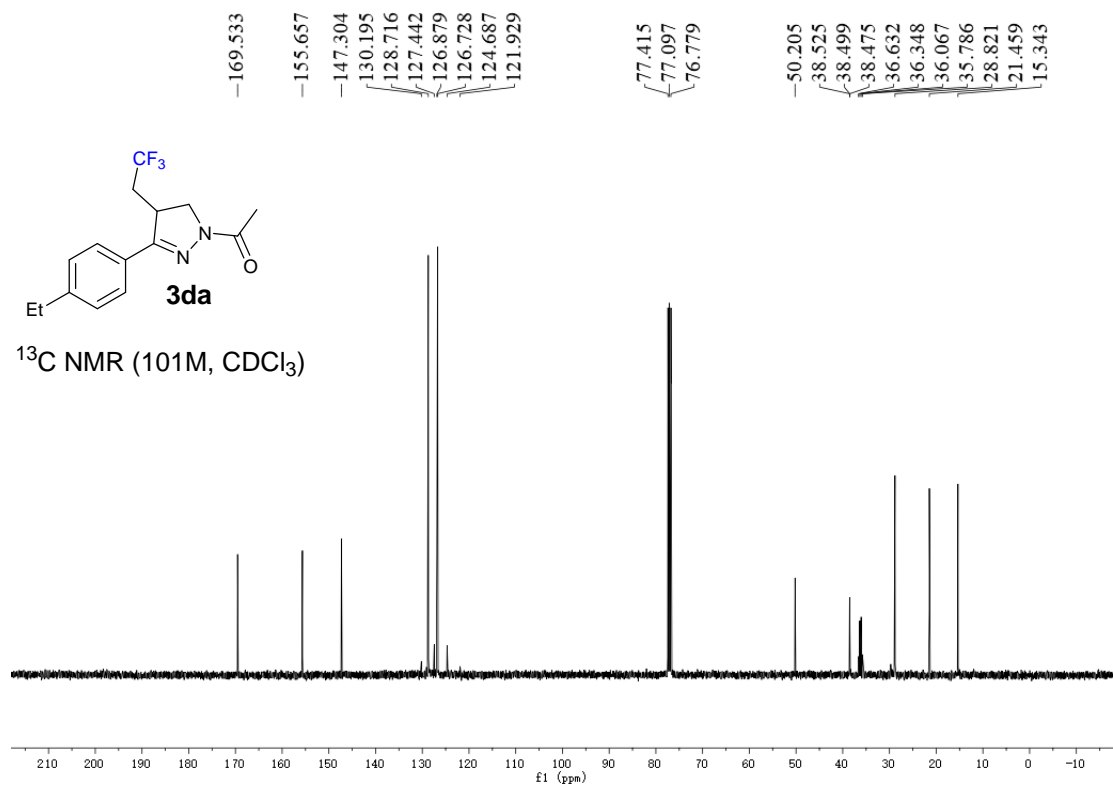


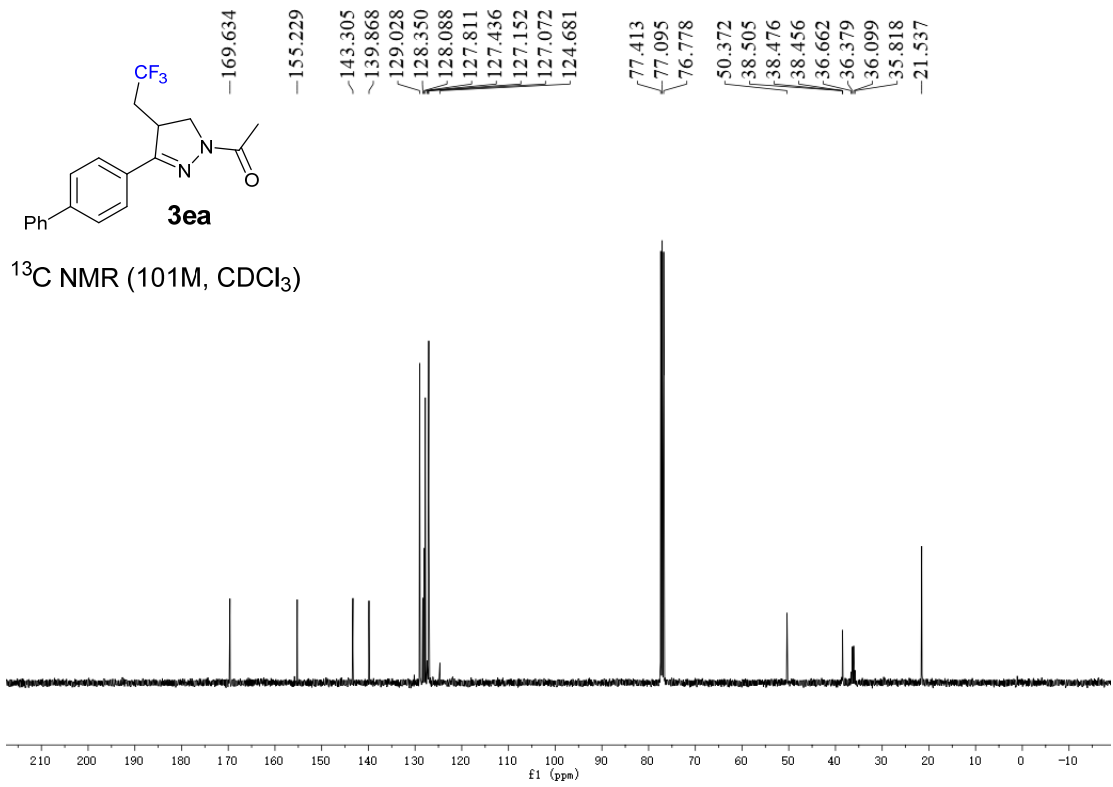
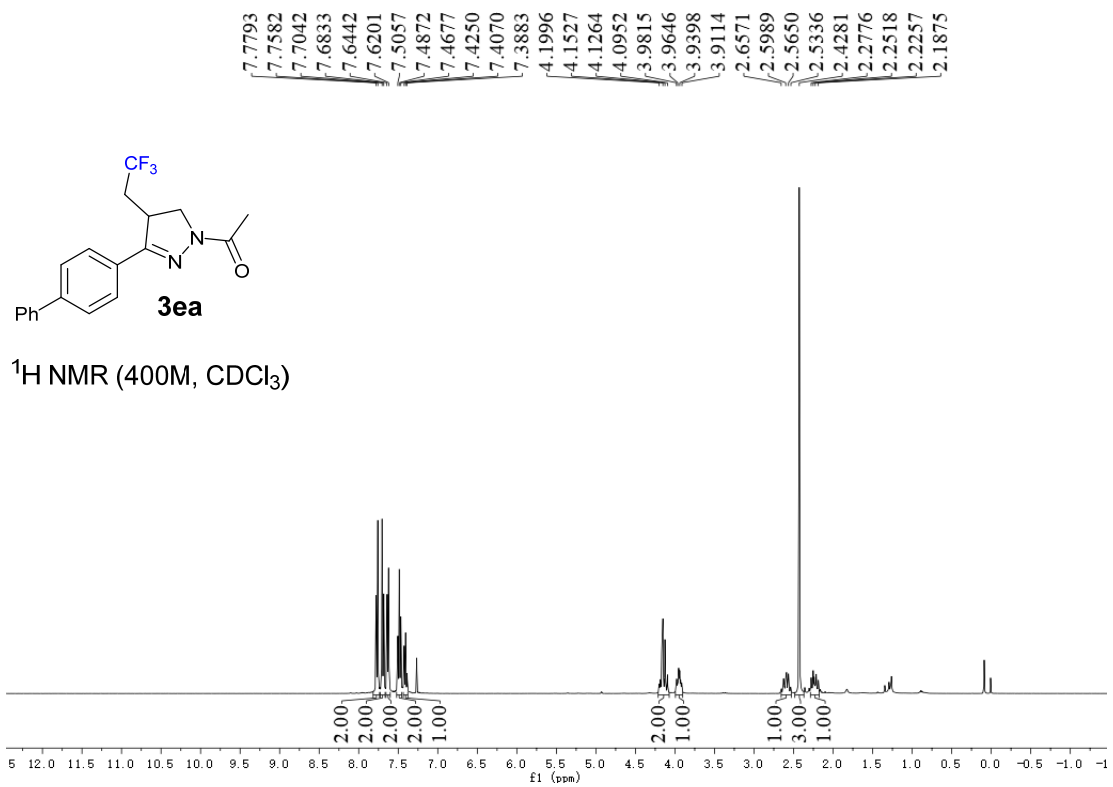


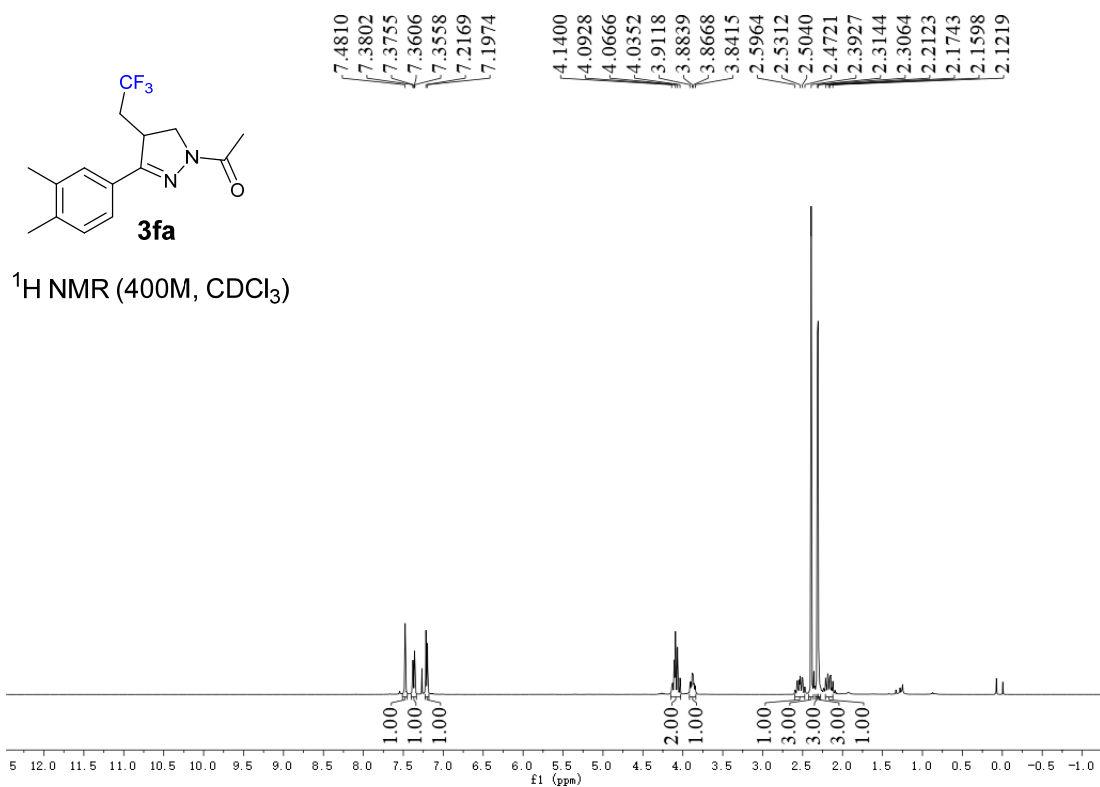
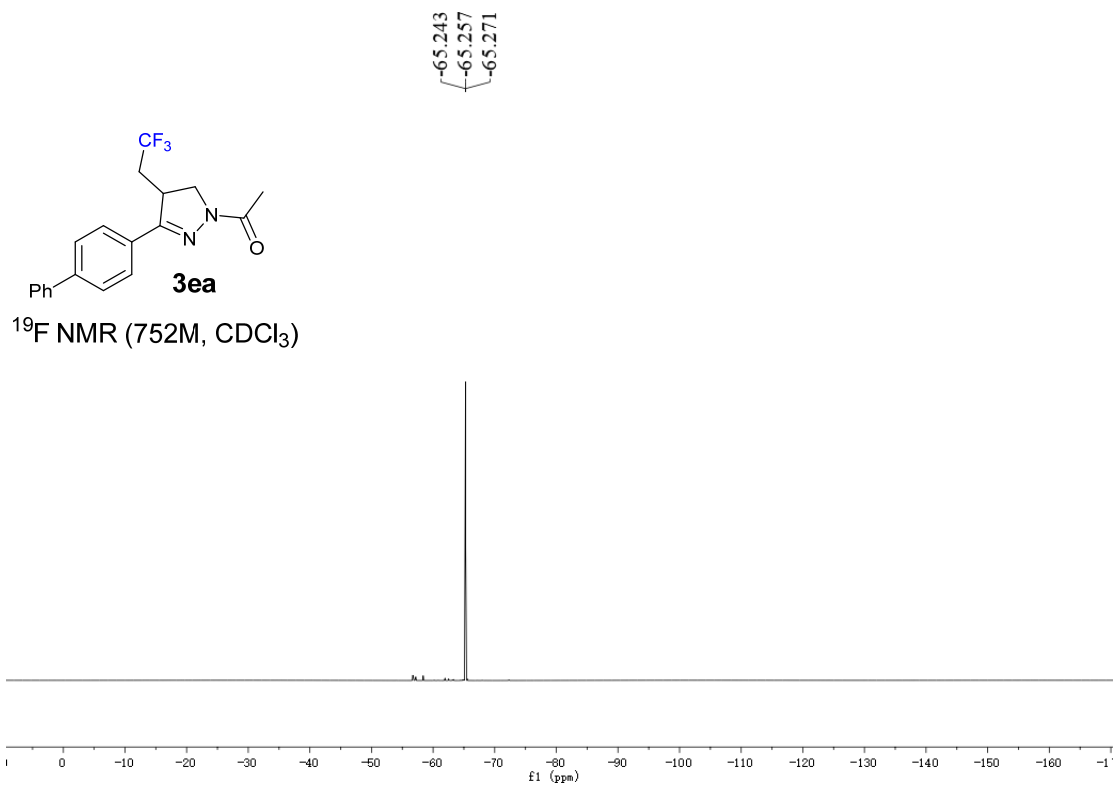


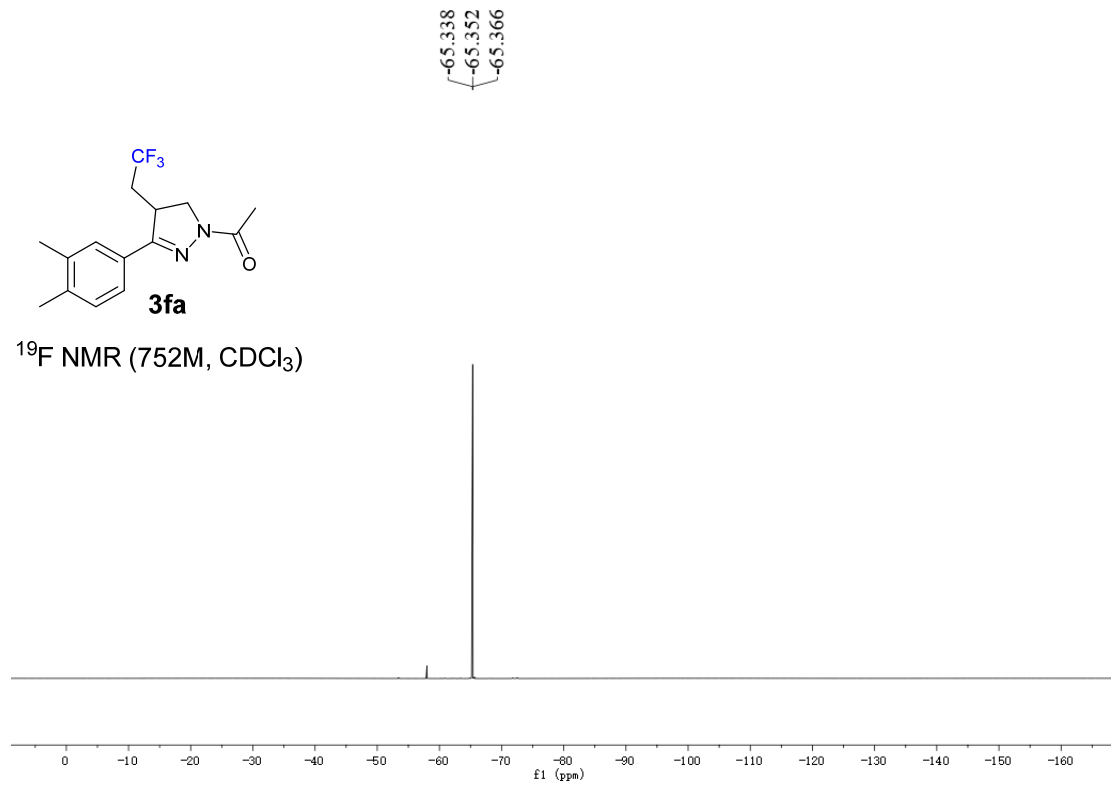
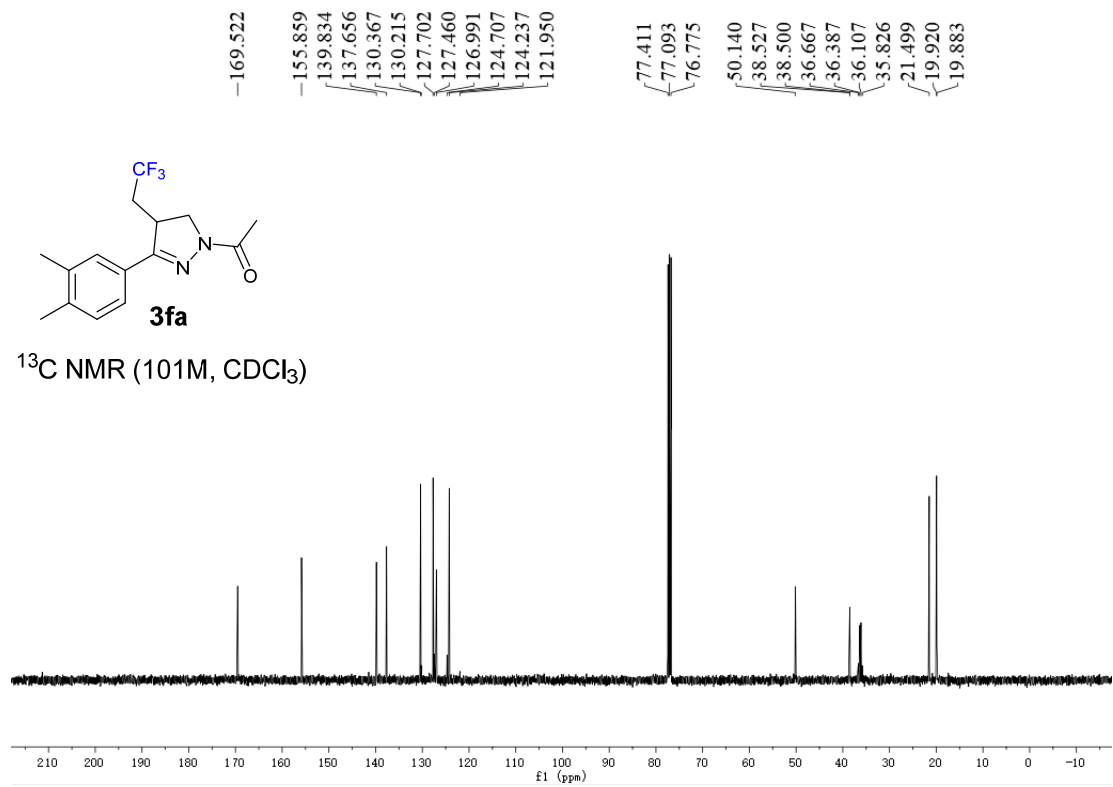


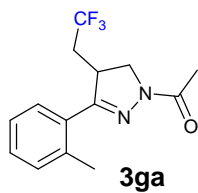




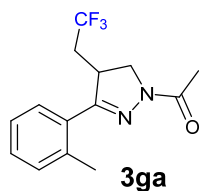
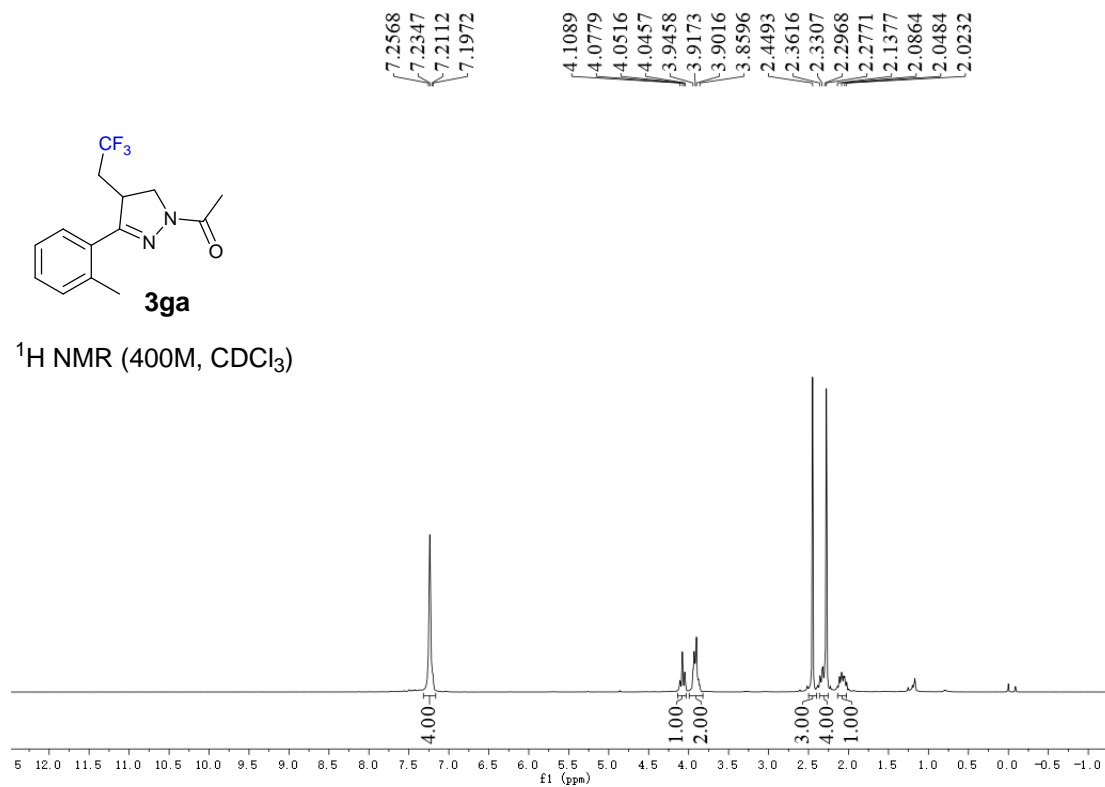




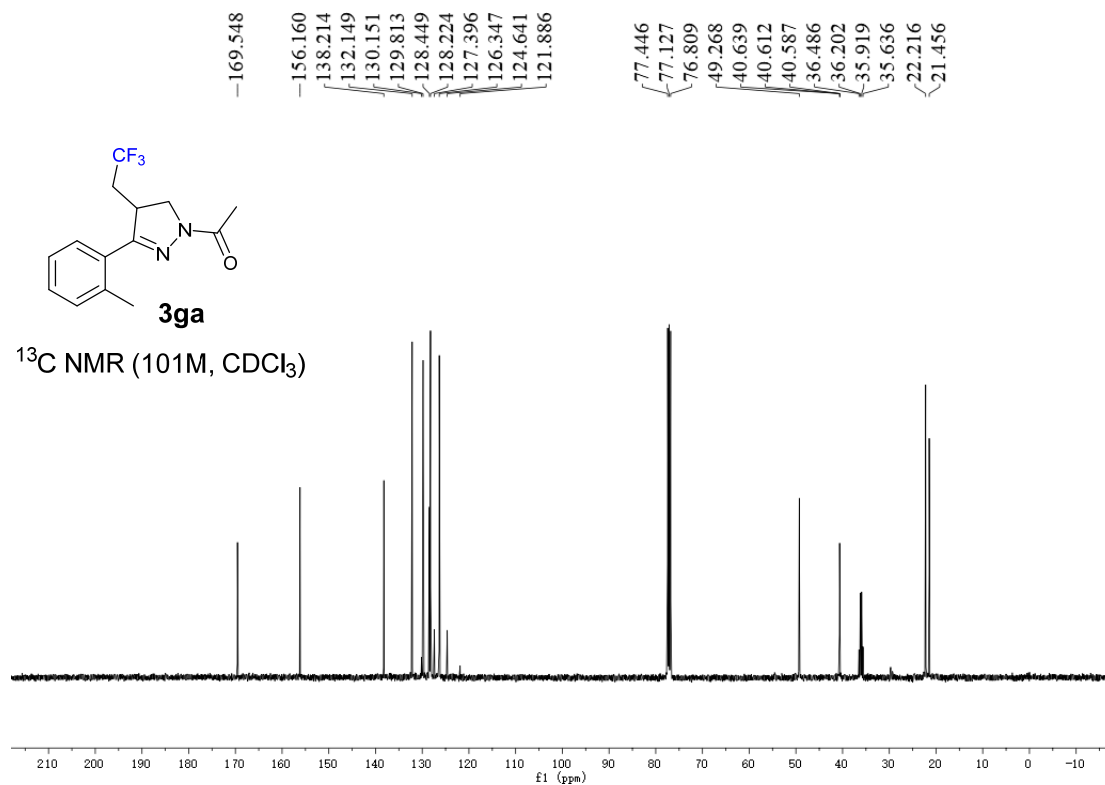


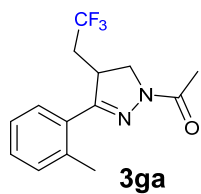


$^1\text{H NMR}$ (400M, CDCl_3)

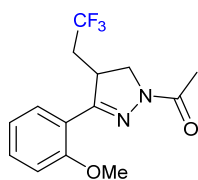
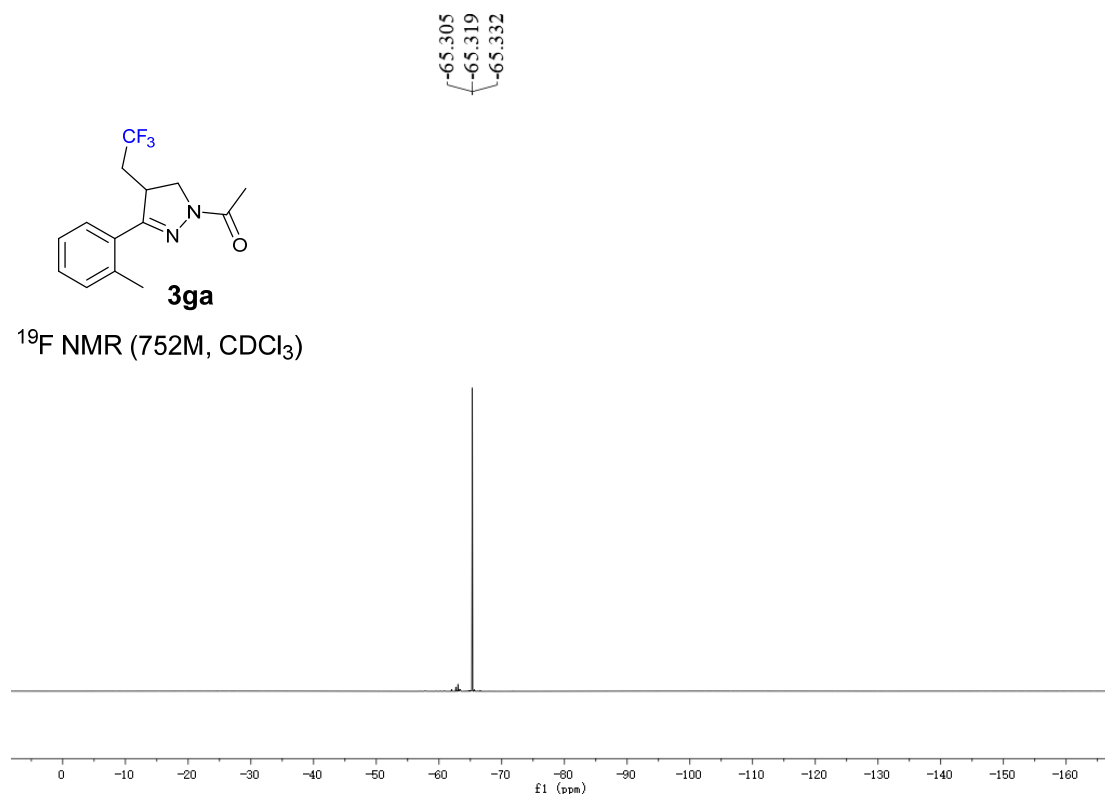


$^{13}\text{C NMR}$ (101M, CDCl_3)

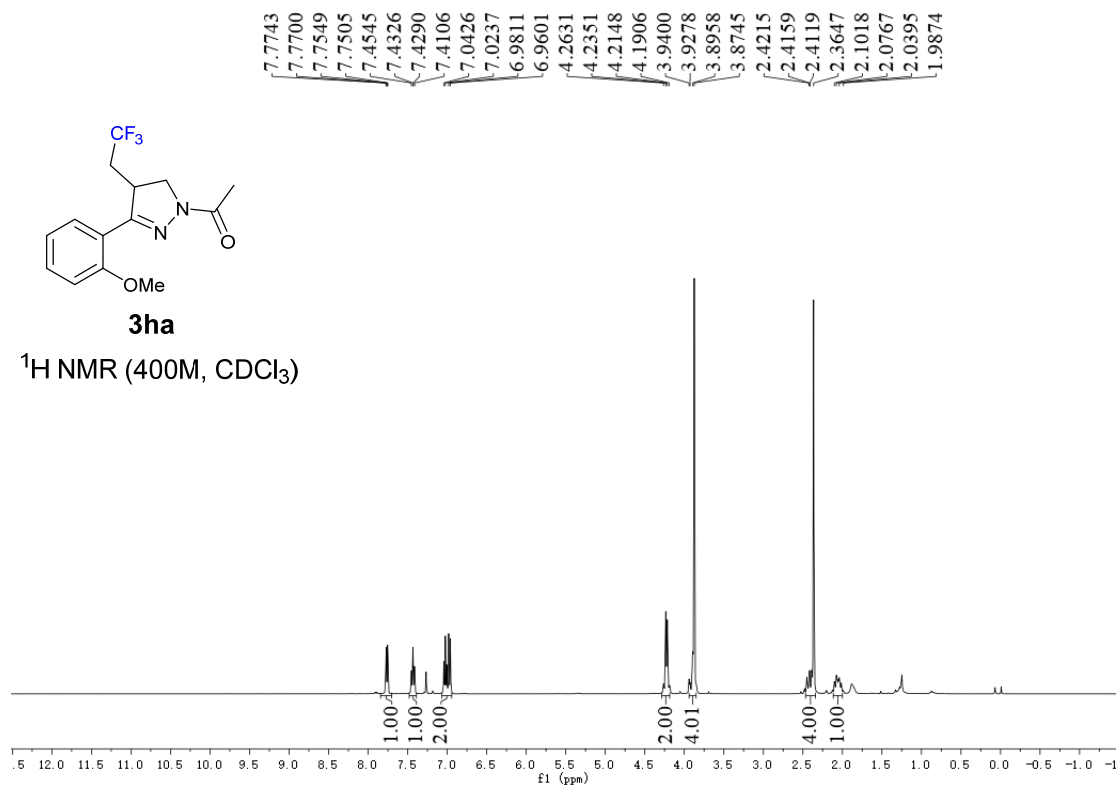


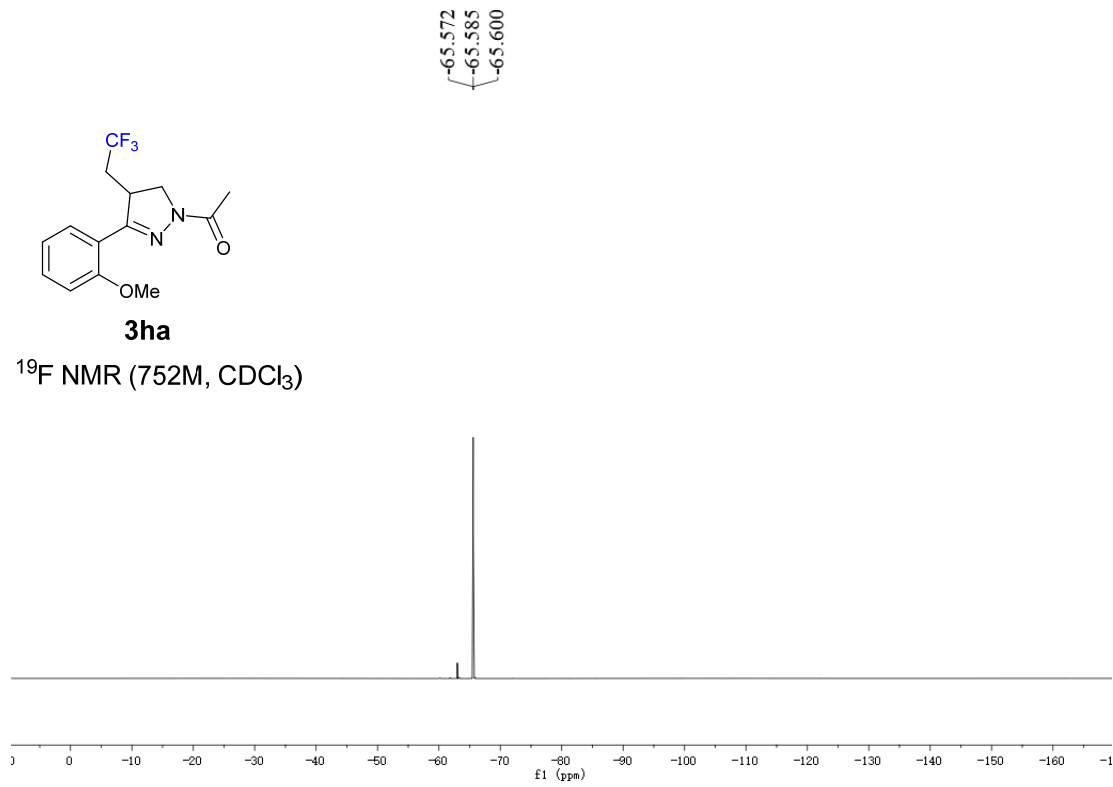
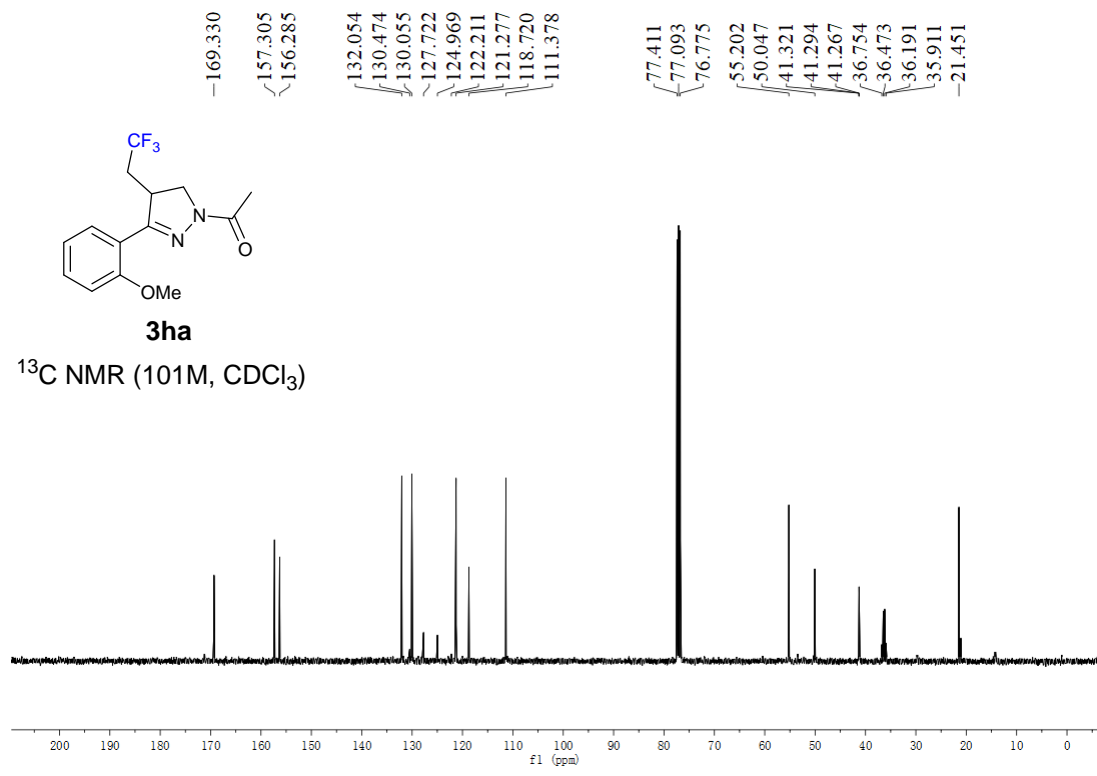


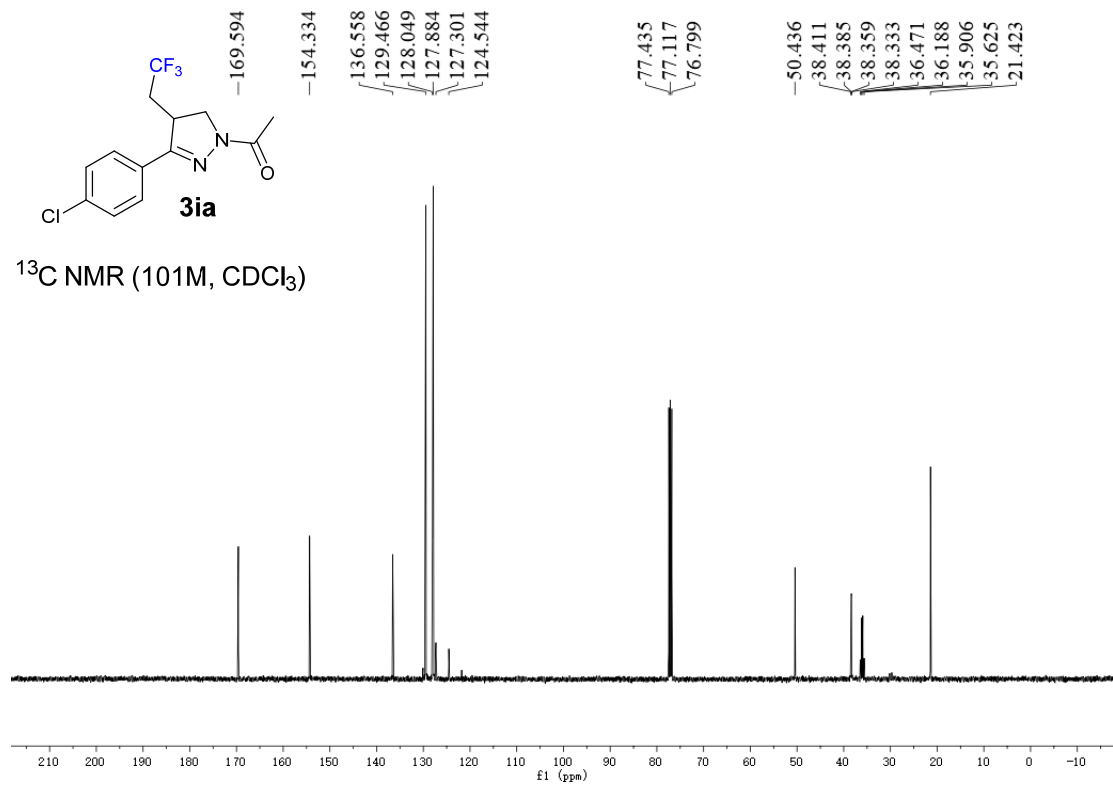
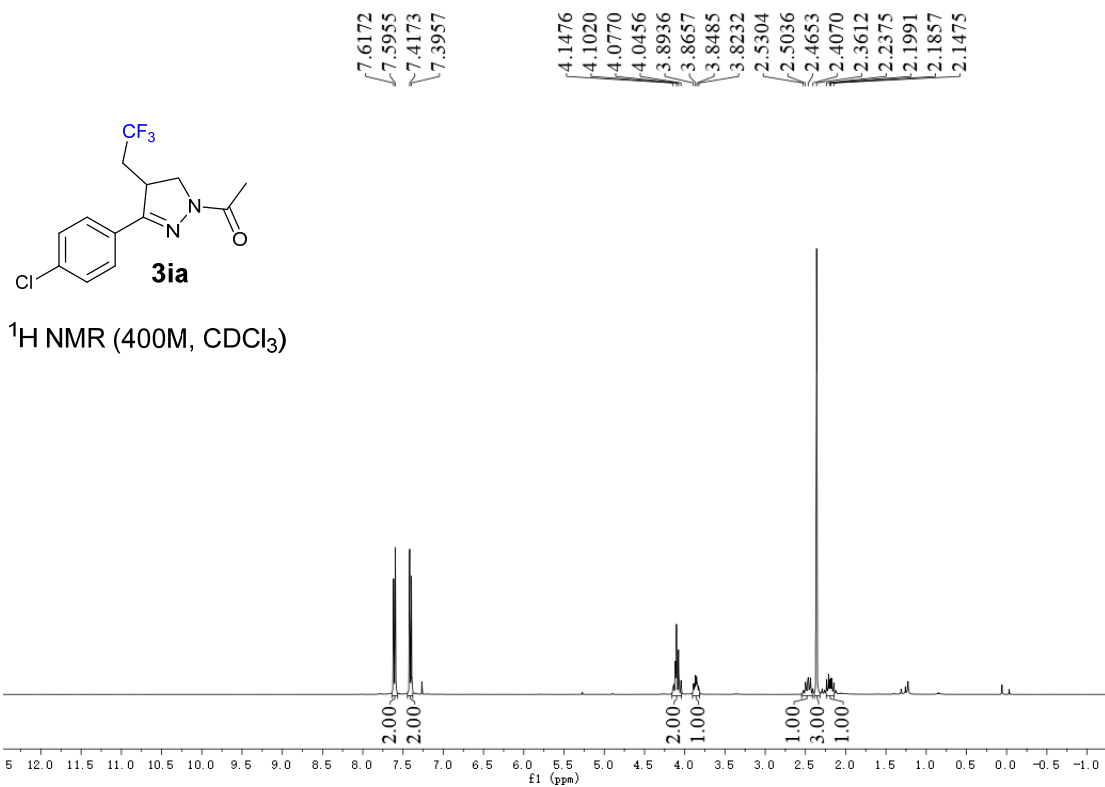
^{19}F NMR (752M, CDCl_3)

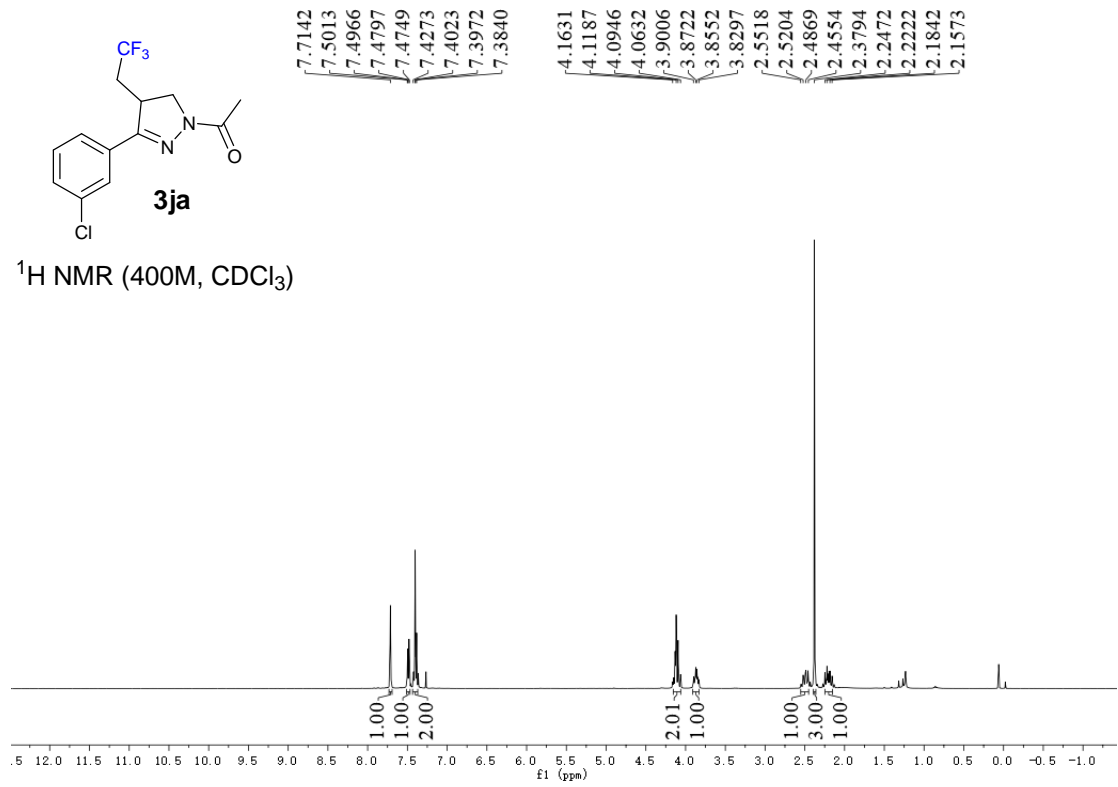
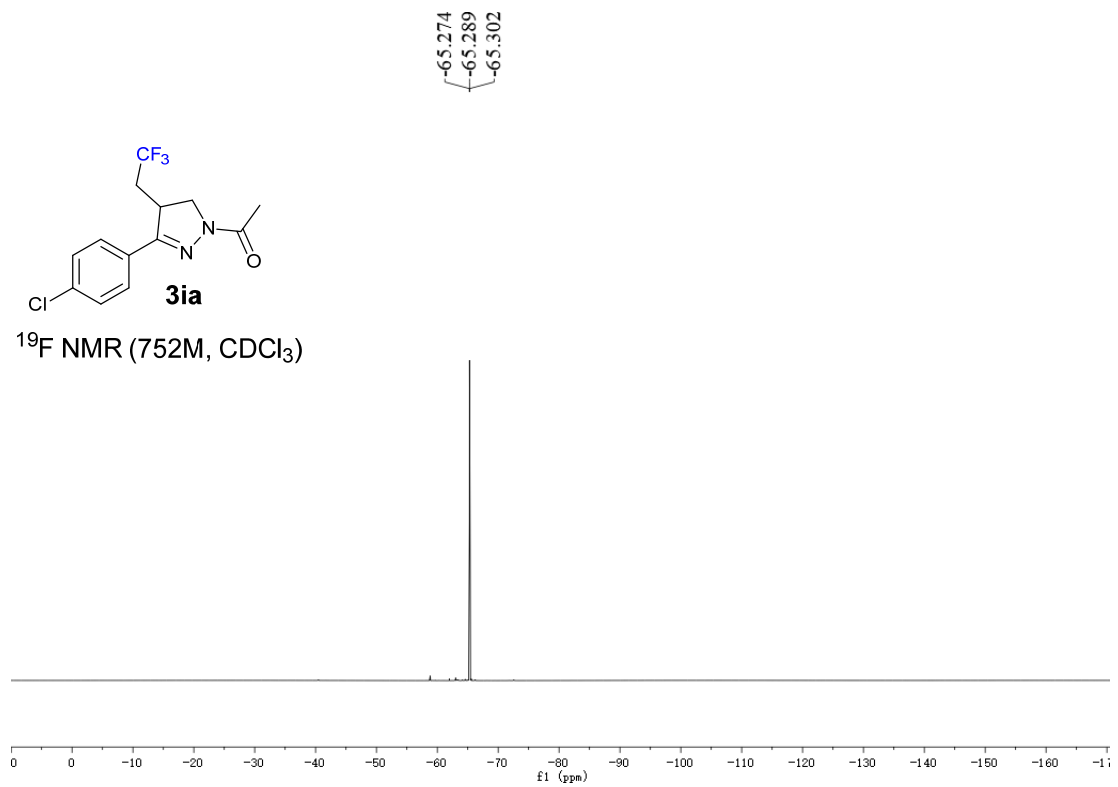


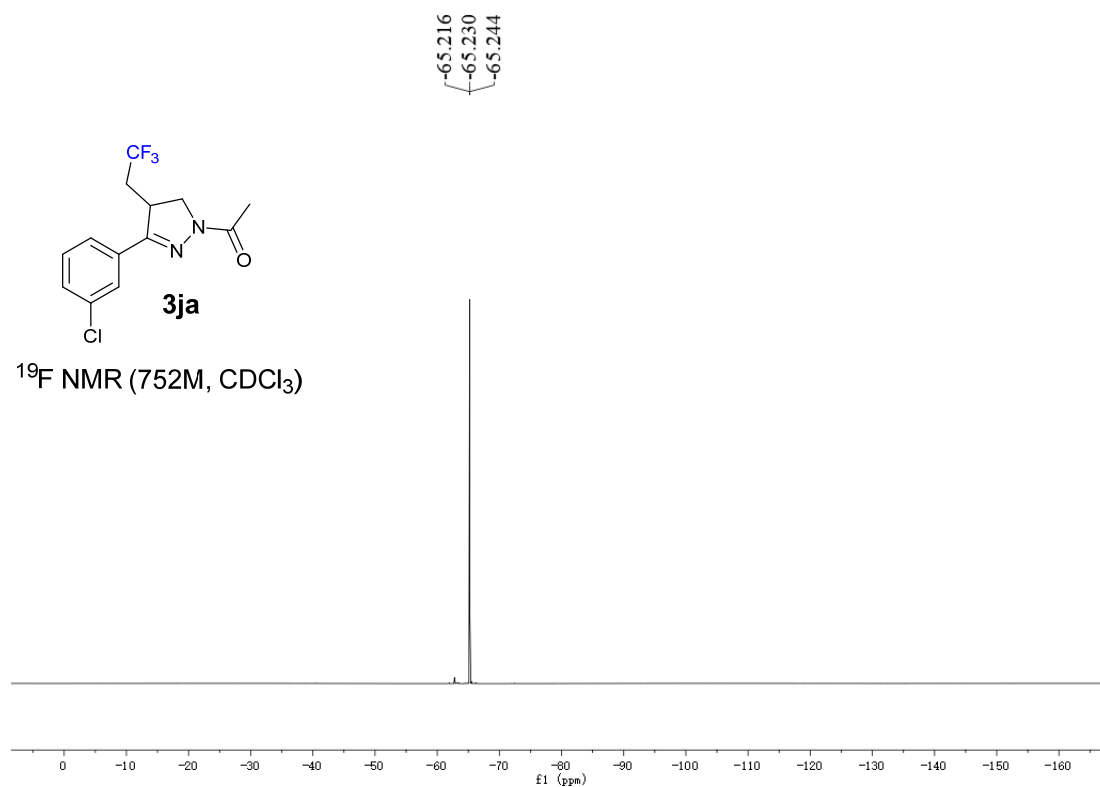
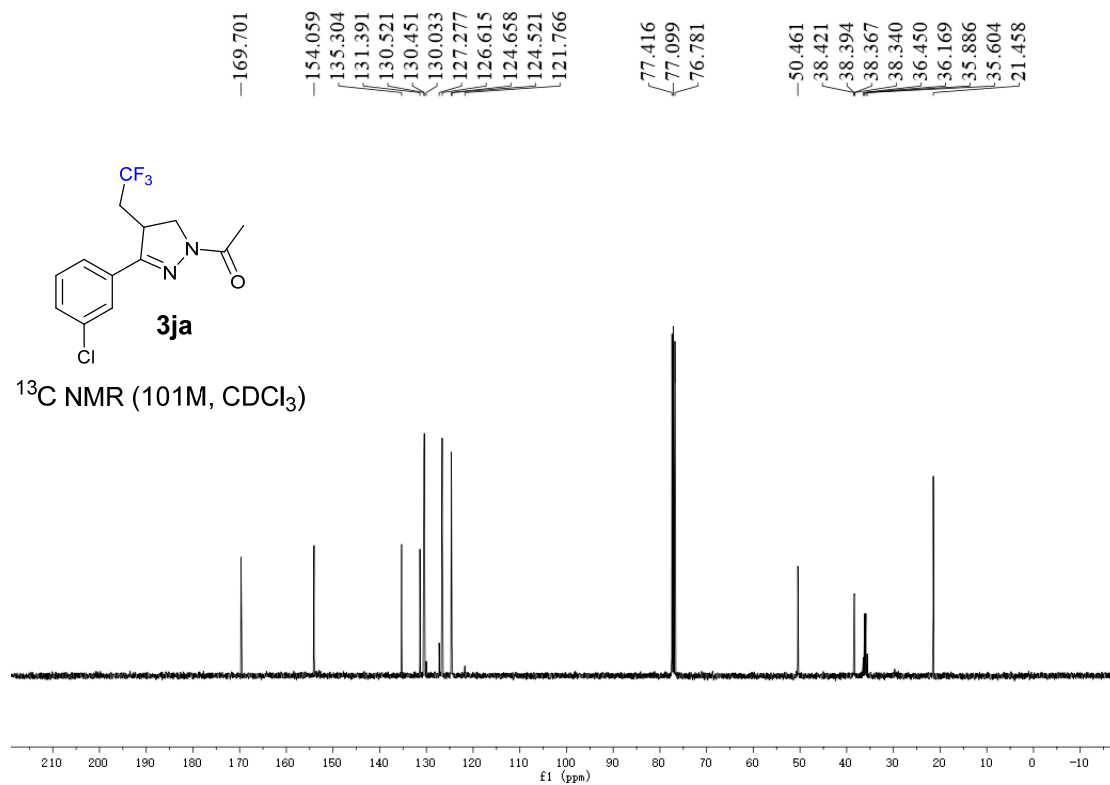
^1H NMR (400M, CDCl_3)

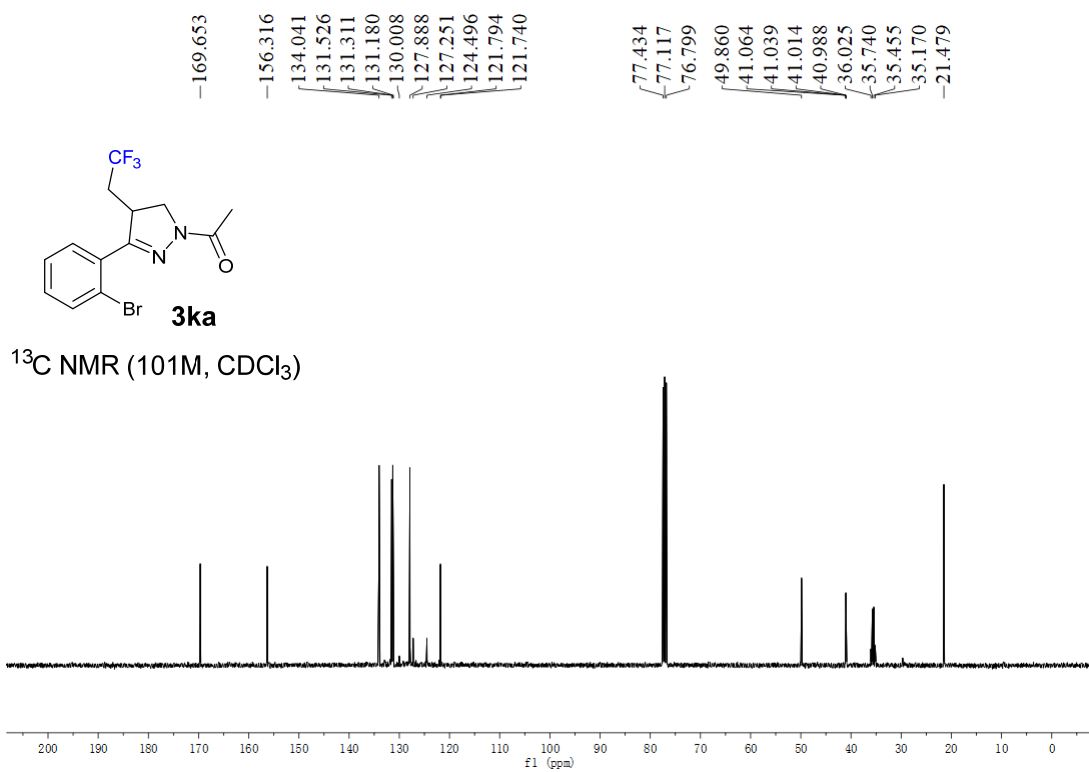
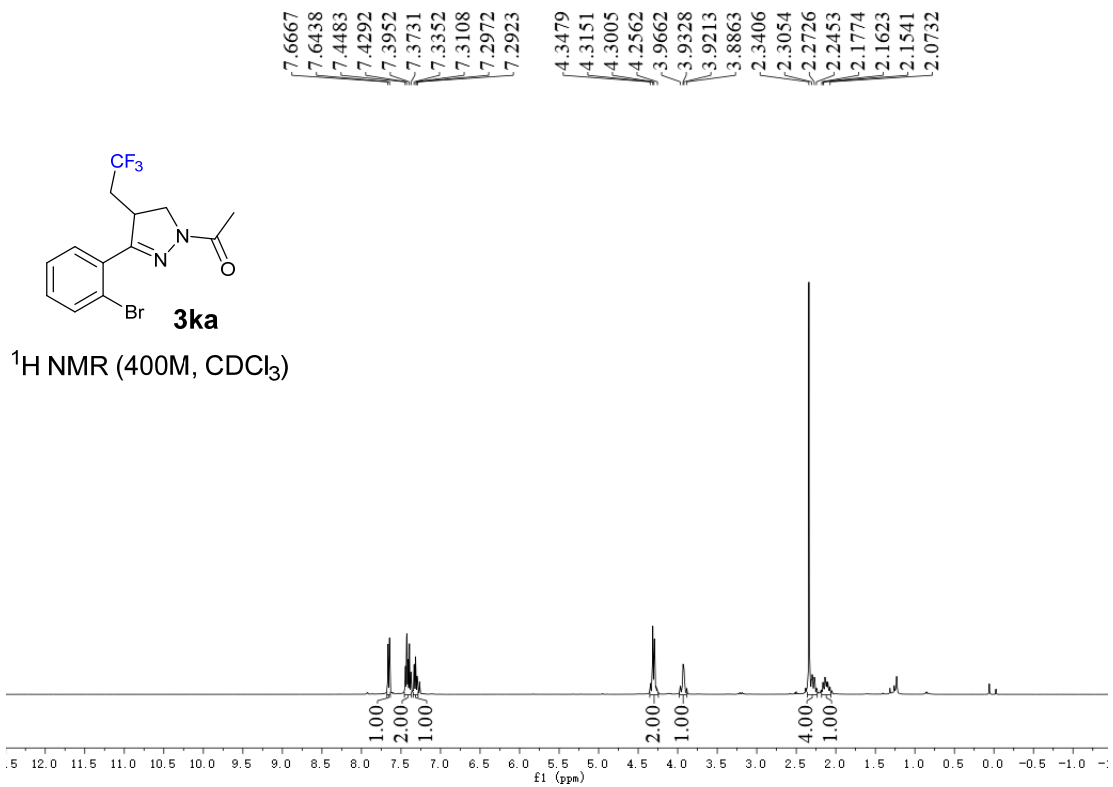


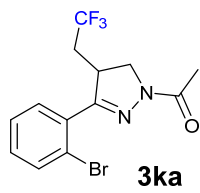




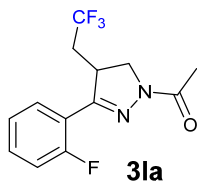
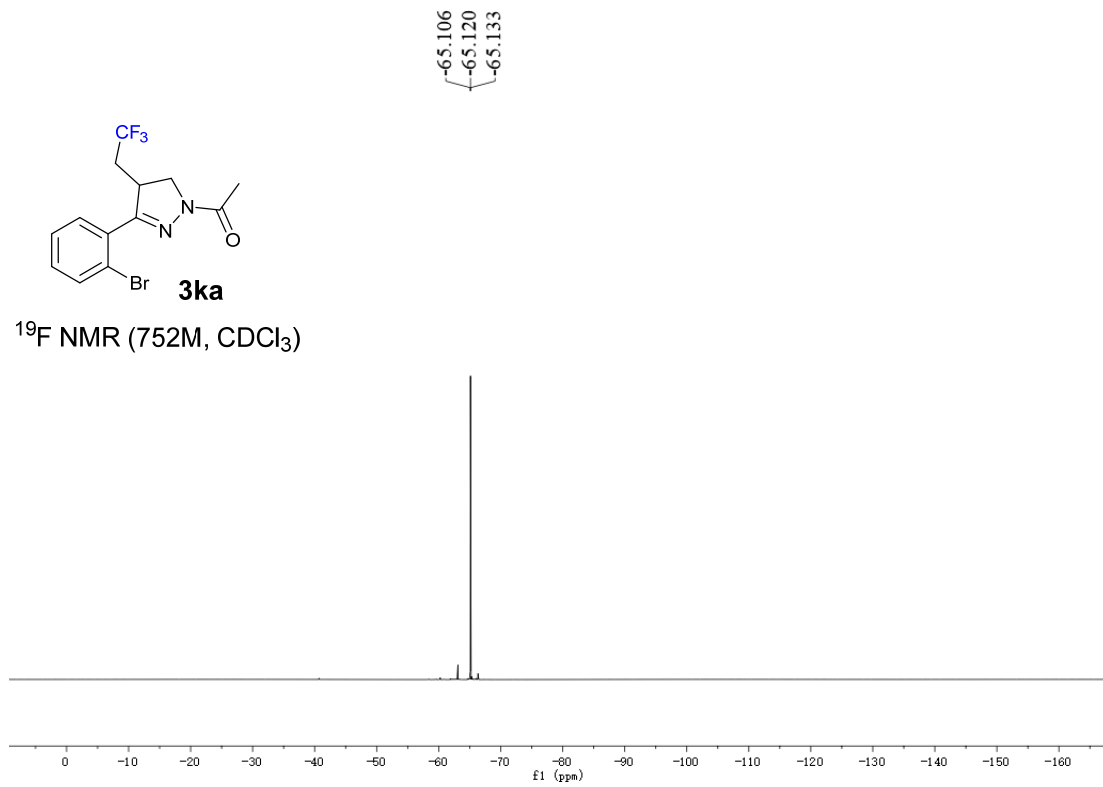




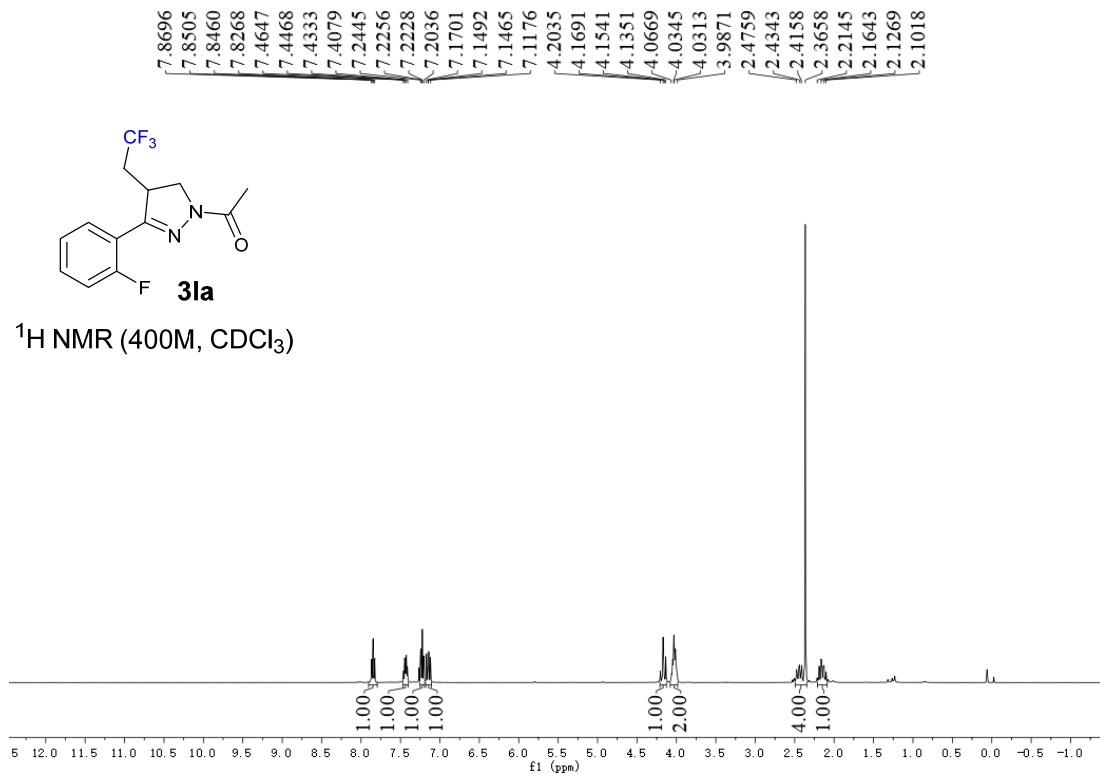




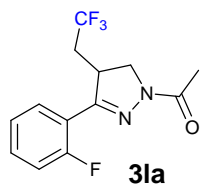
^{19}F NMR (752M, CDCl_3)



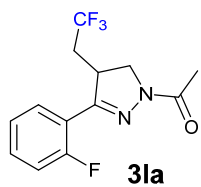
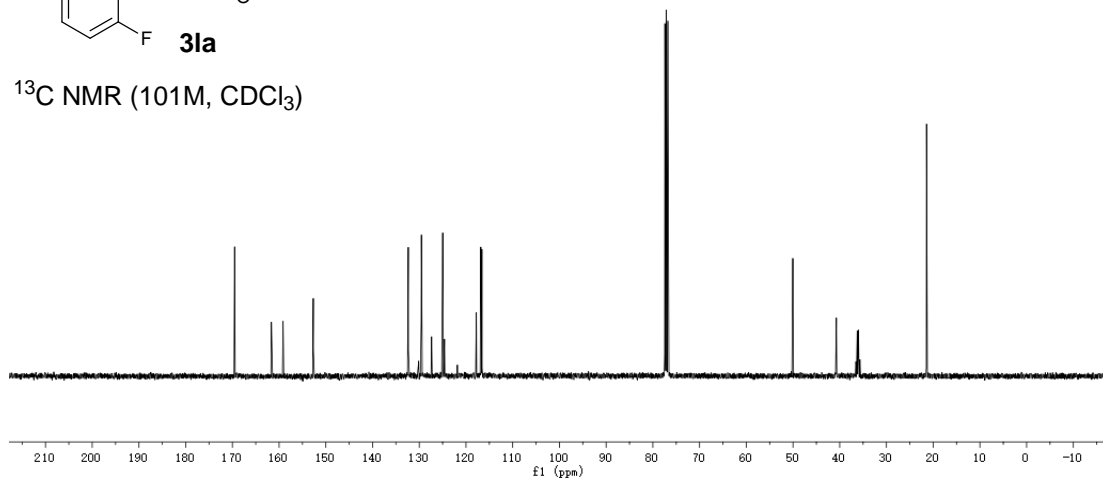
^1H NMR (400M, CDCl_3)



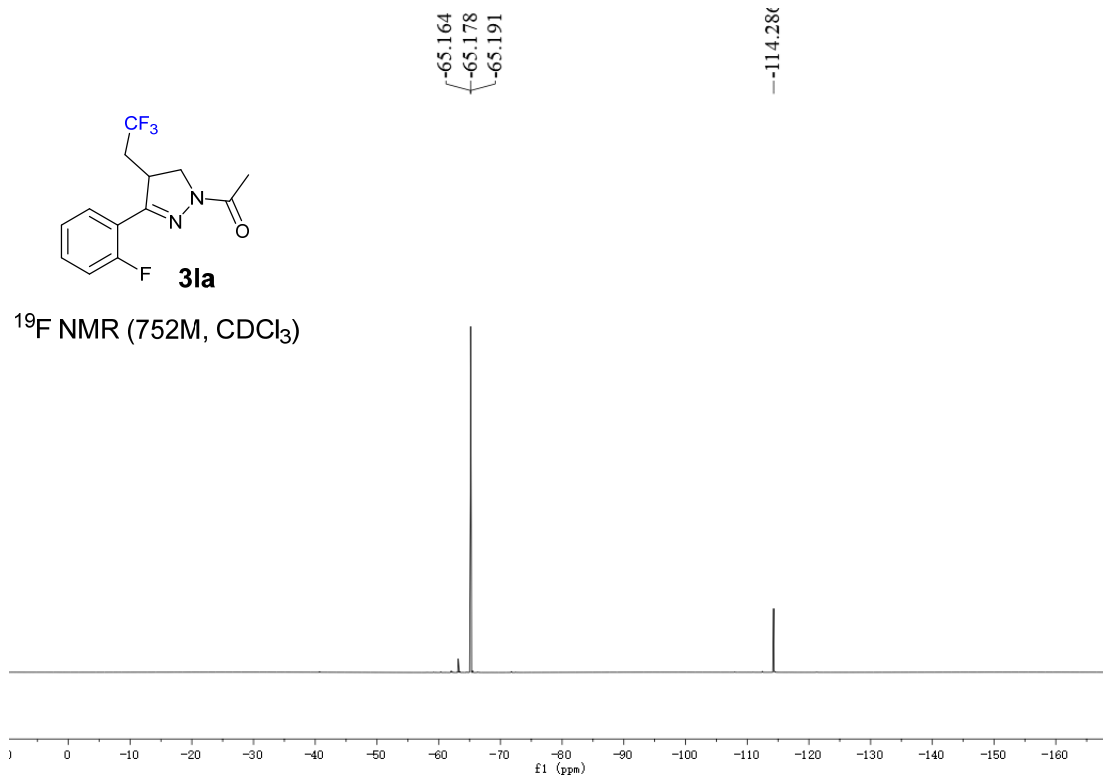
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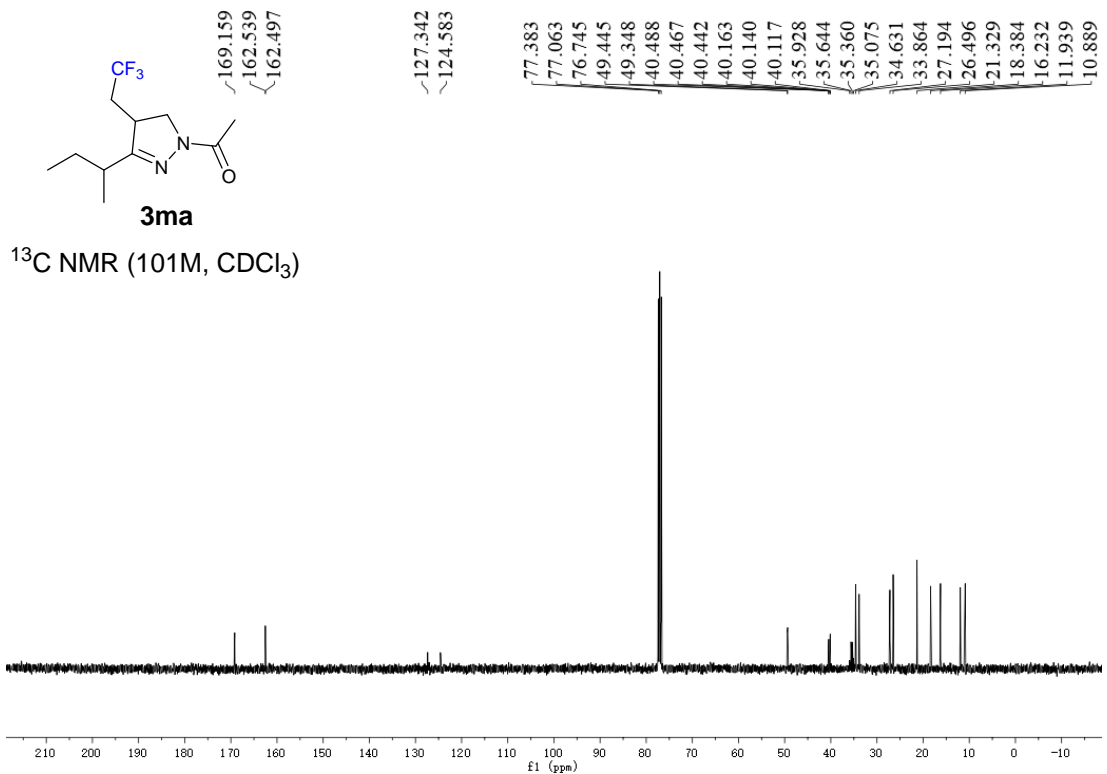
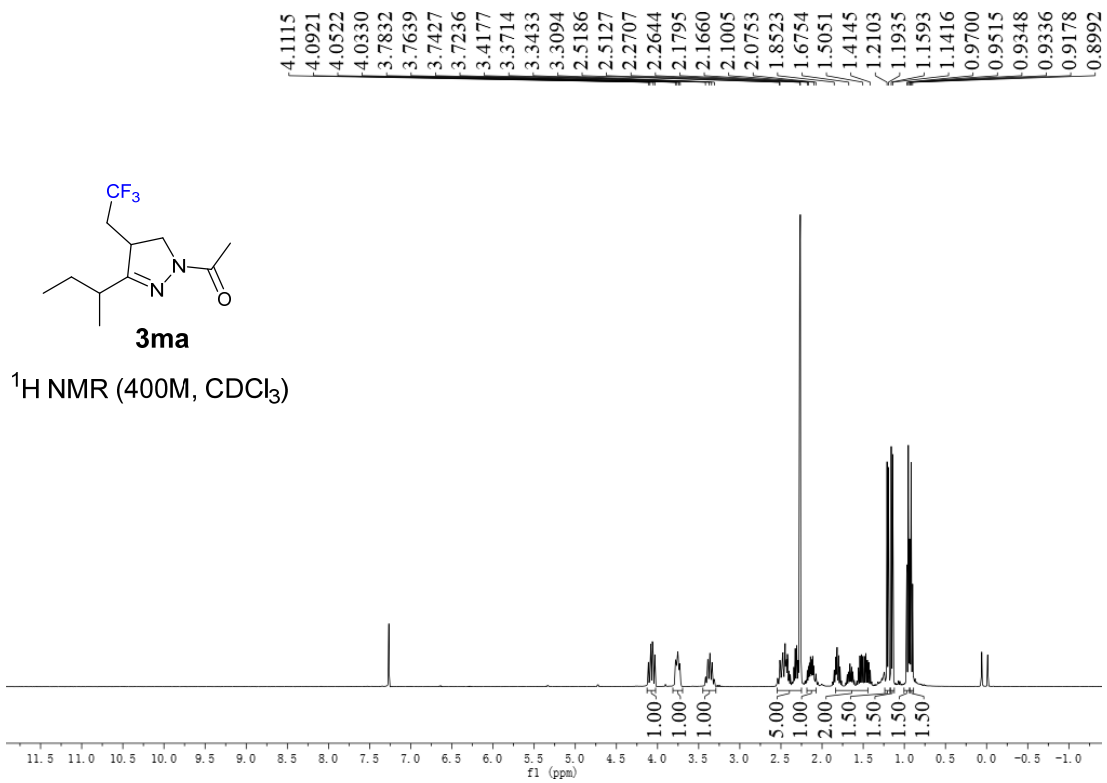


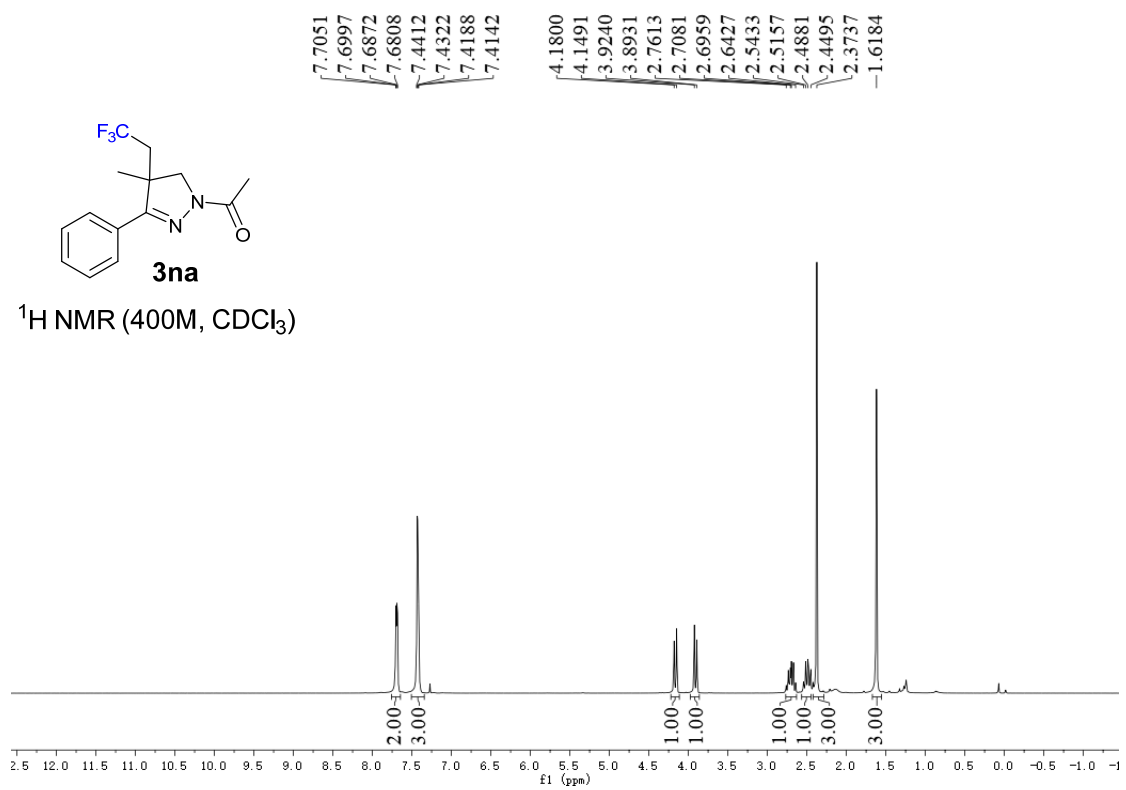
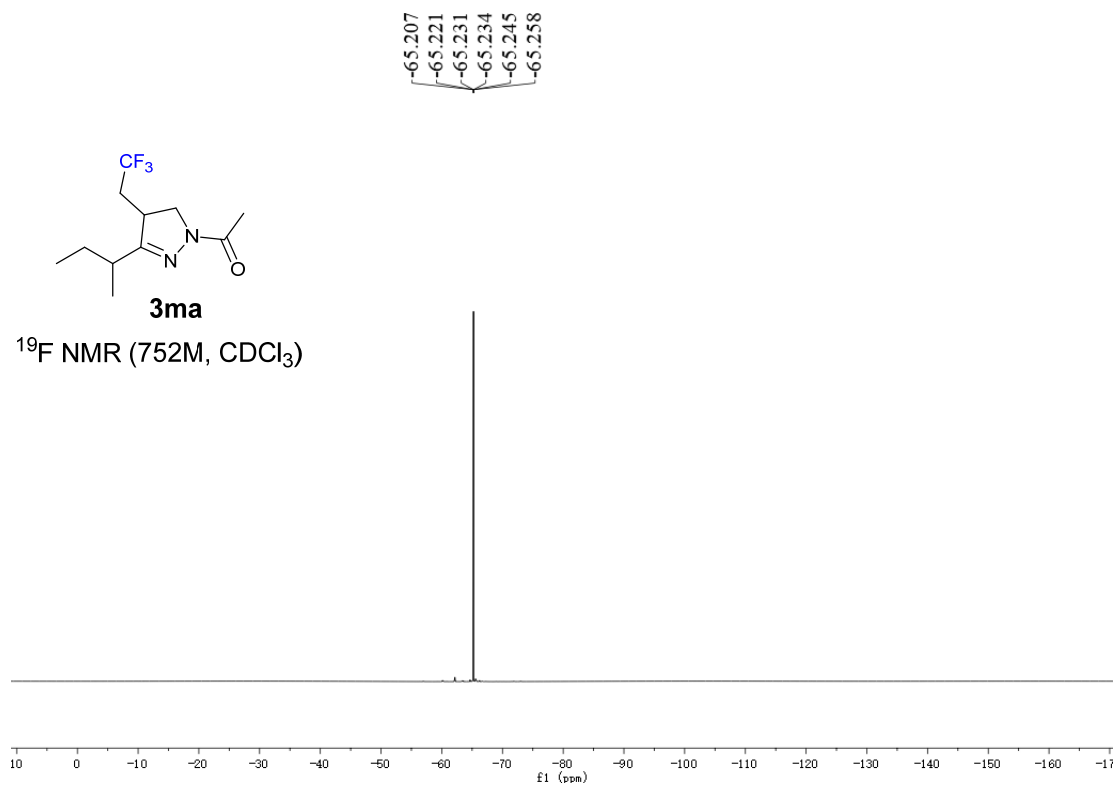
^{13}C NMR (101M, CDCl_3)

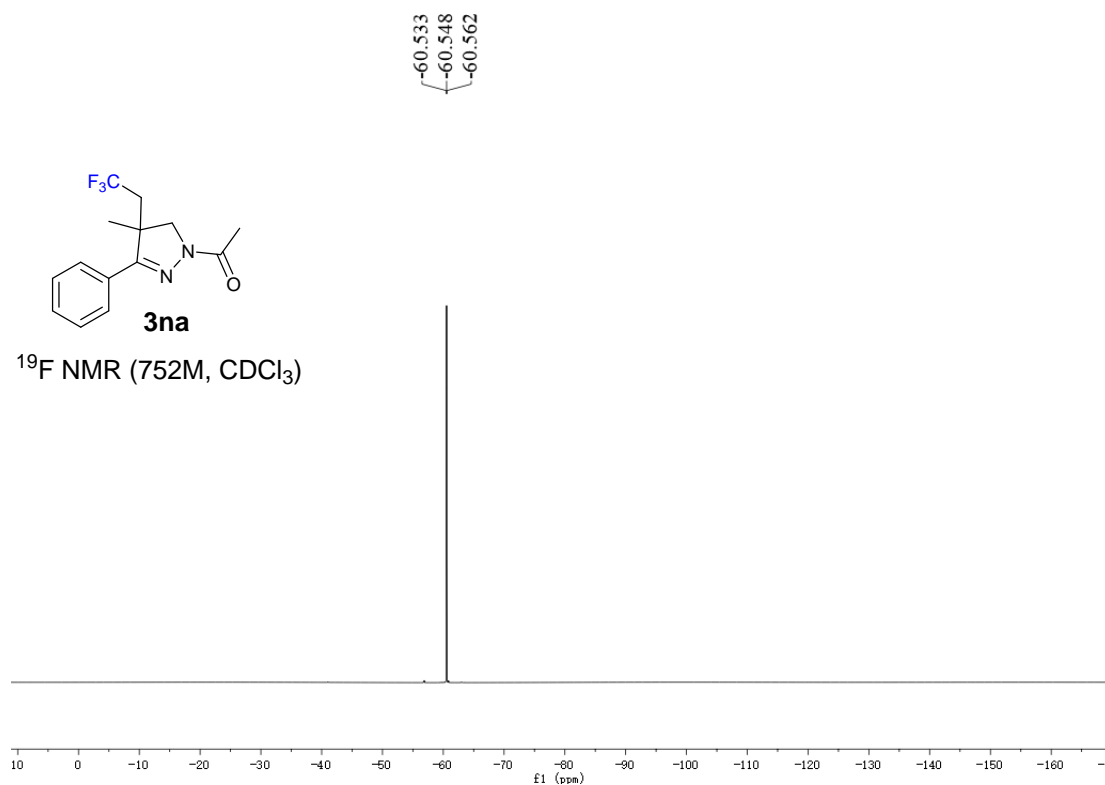
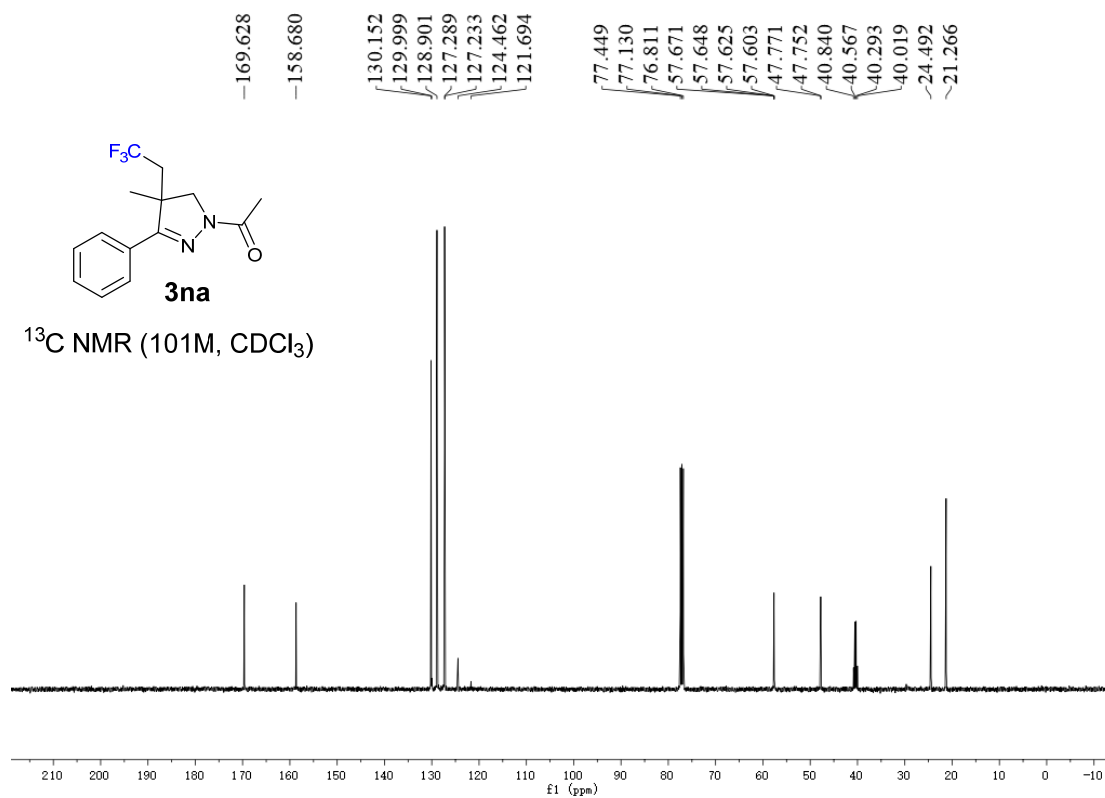


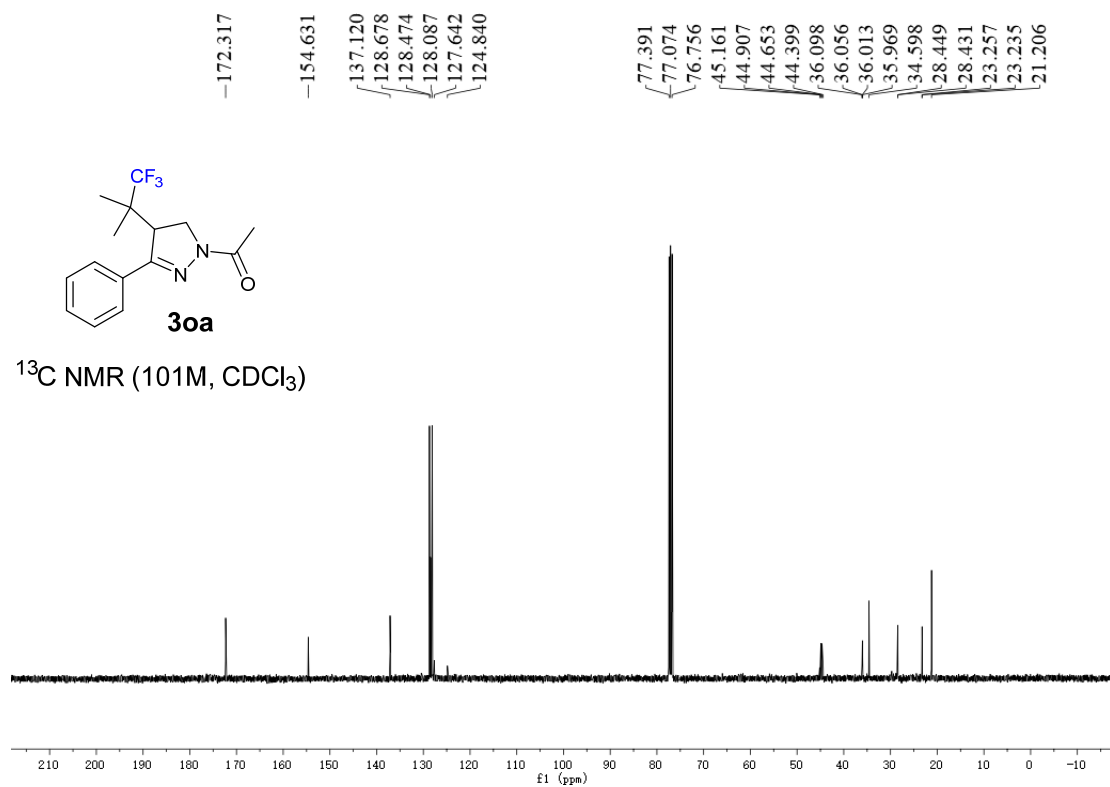
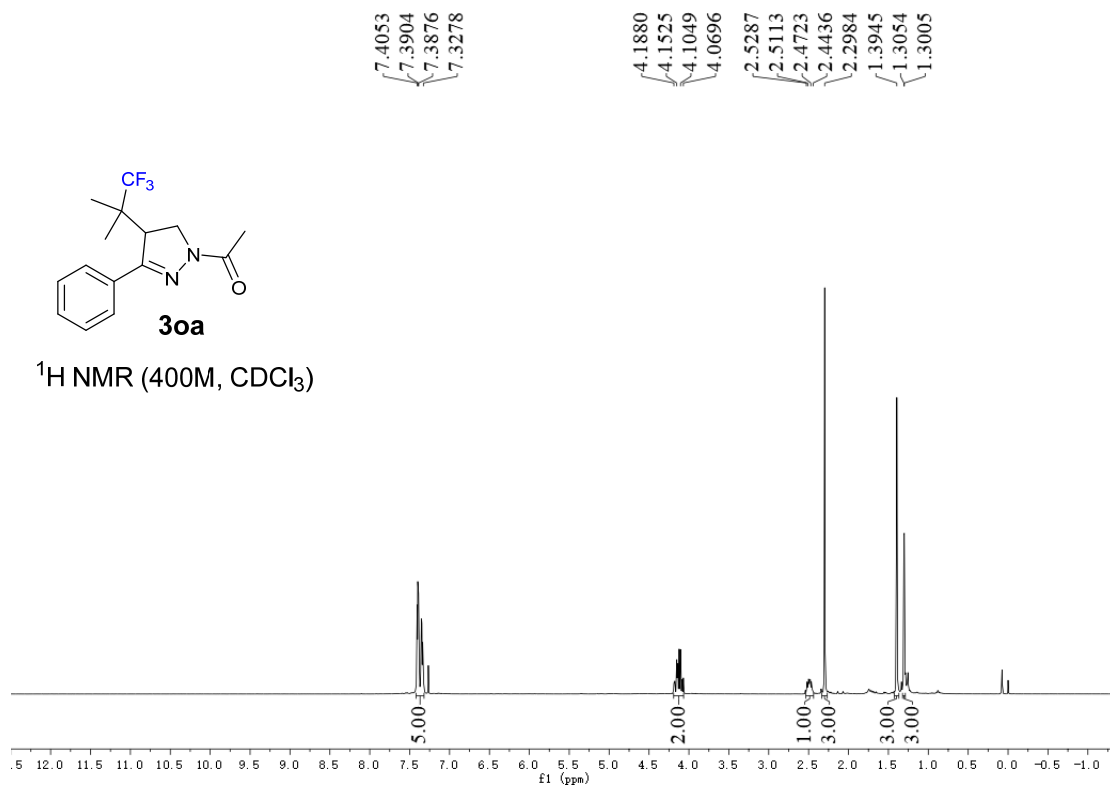
^{19}F NMR (752M, CDCl_3)

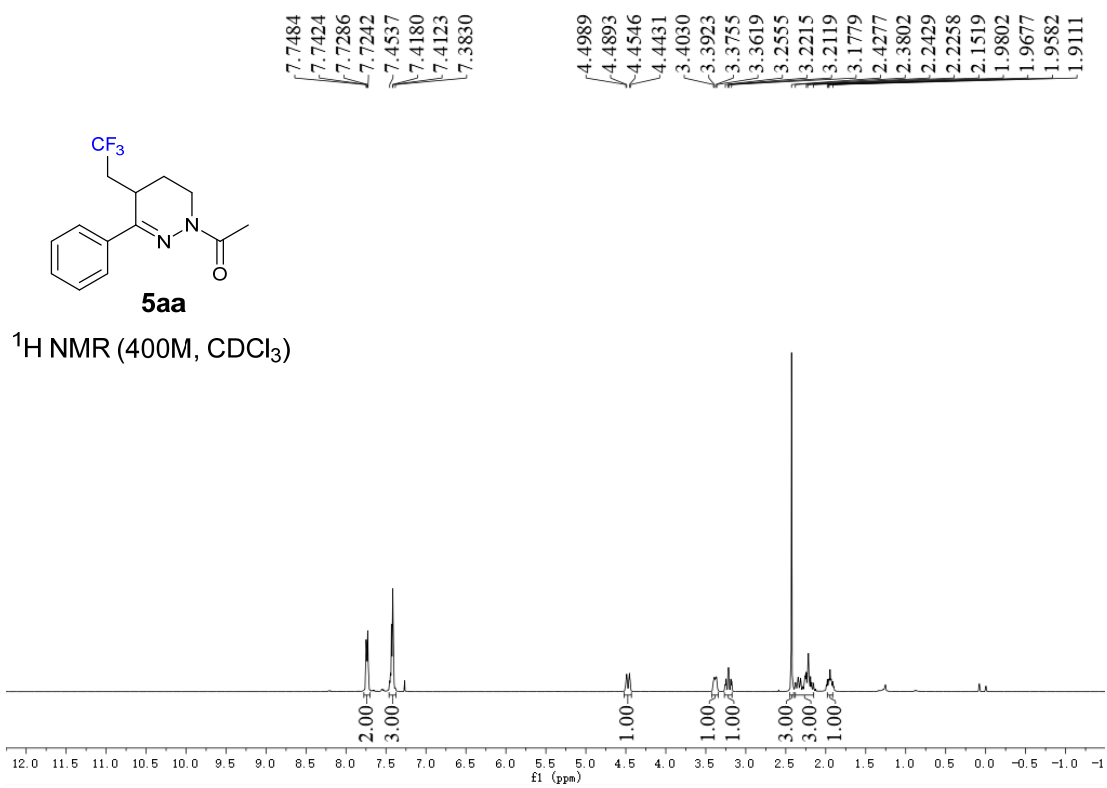
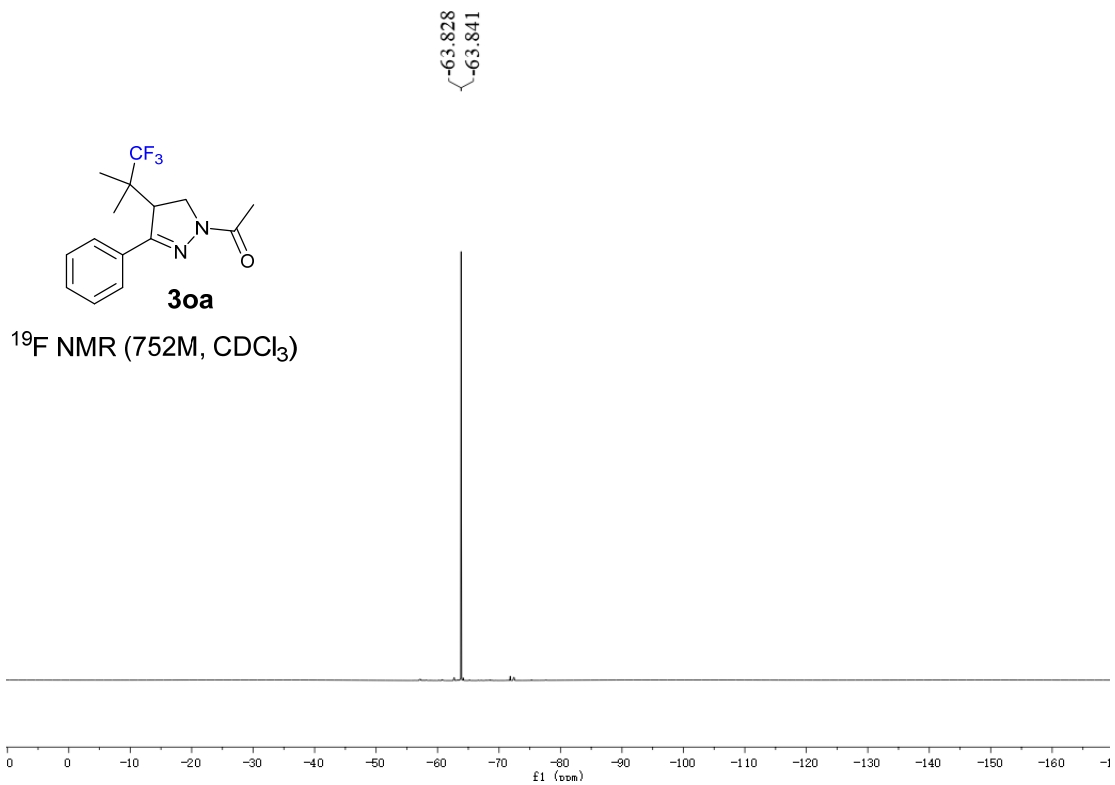


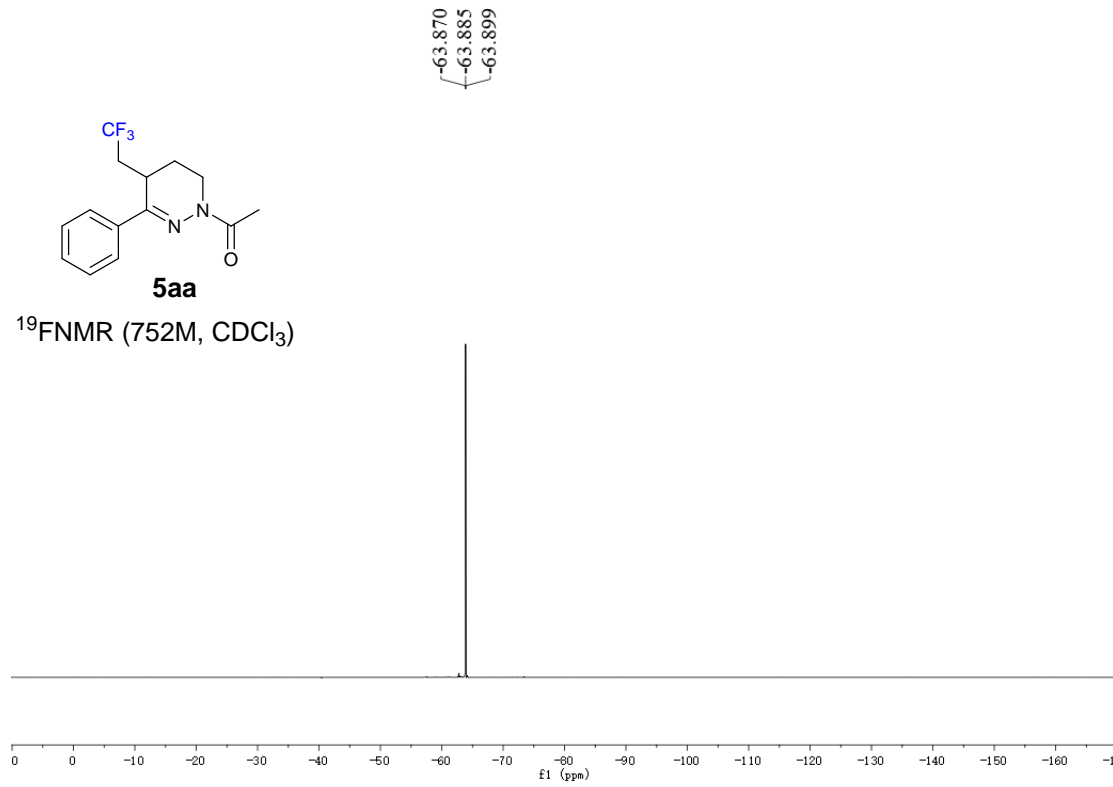
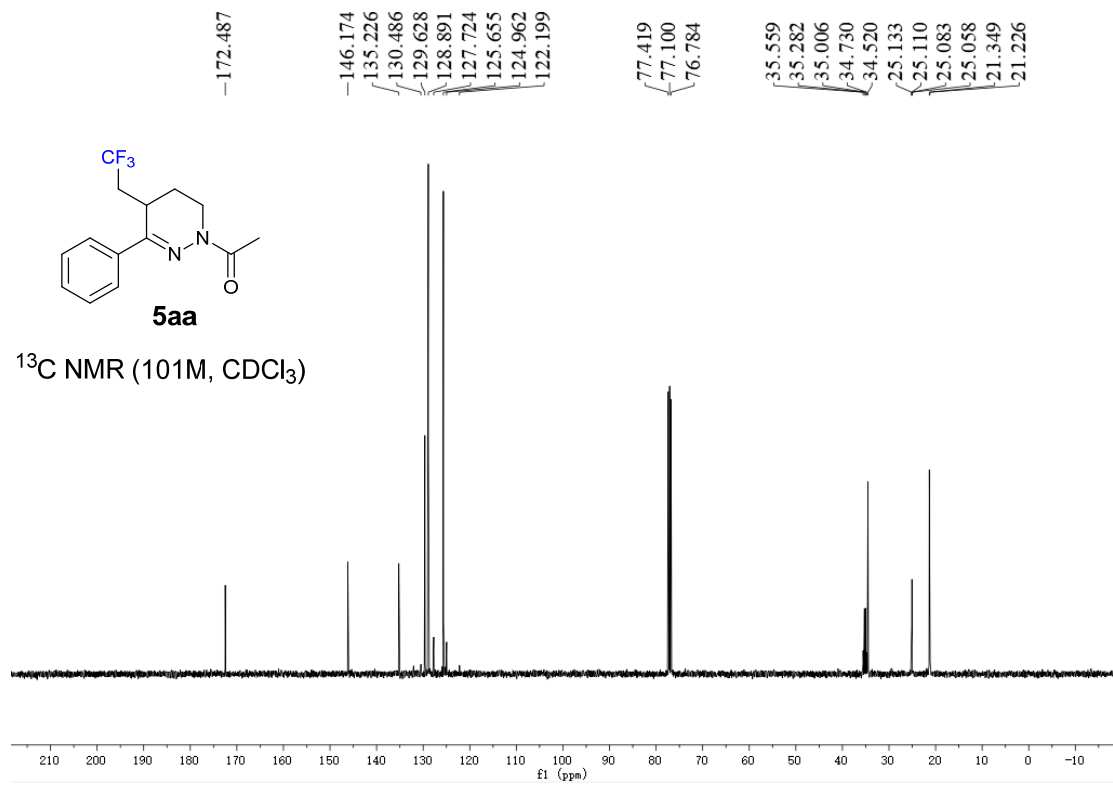


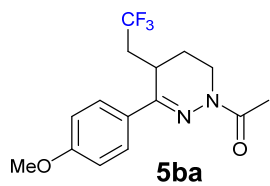




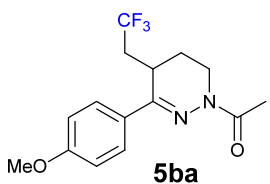
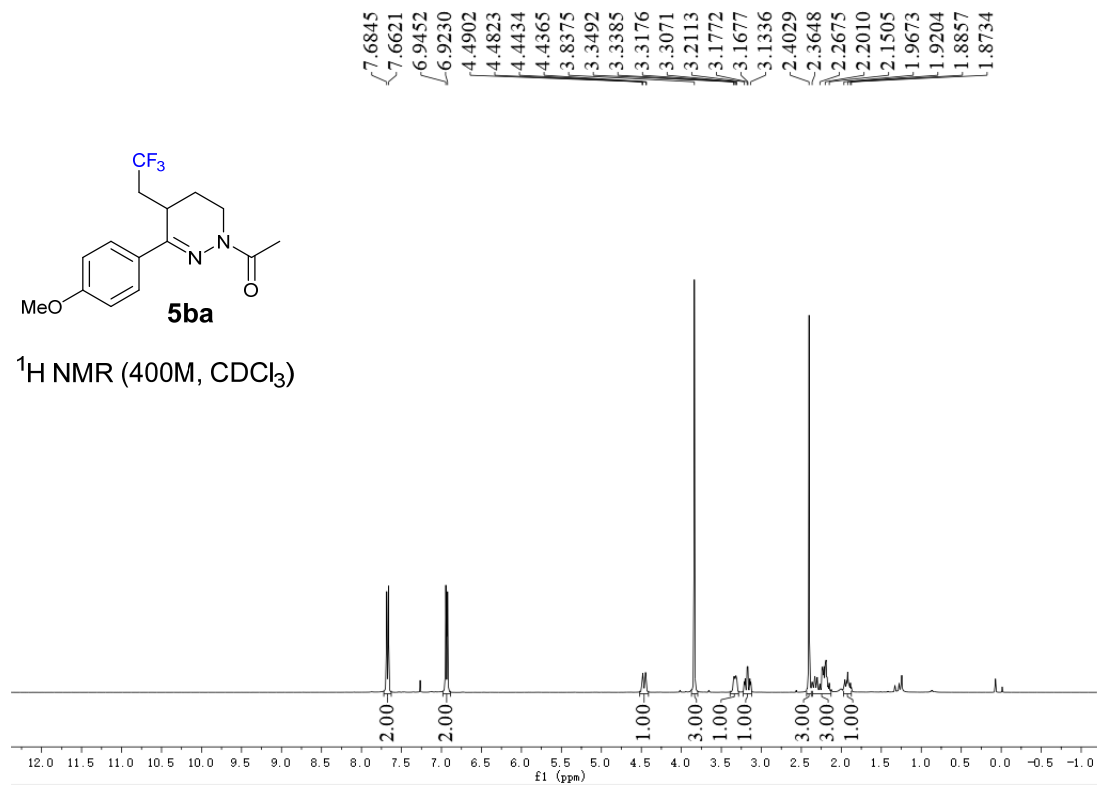




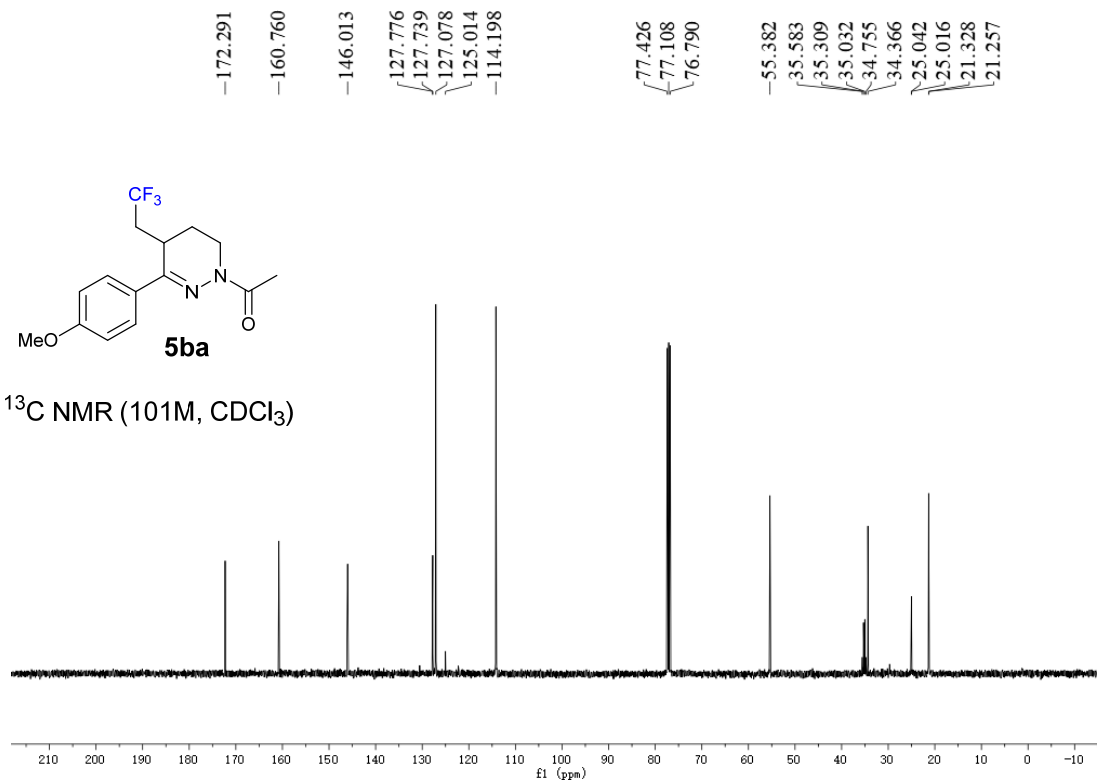


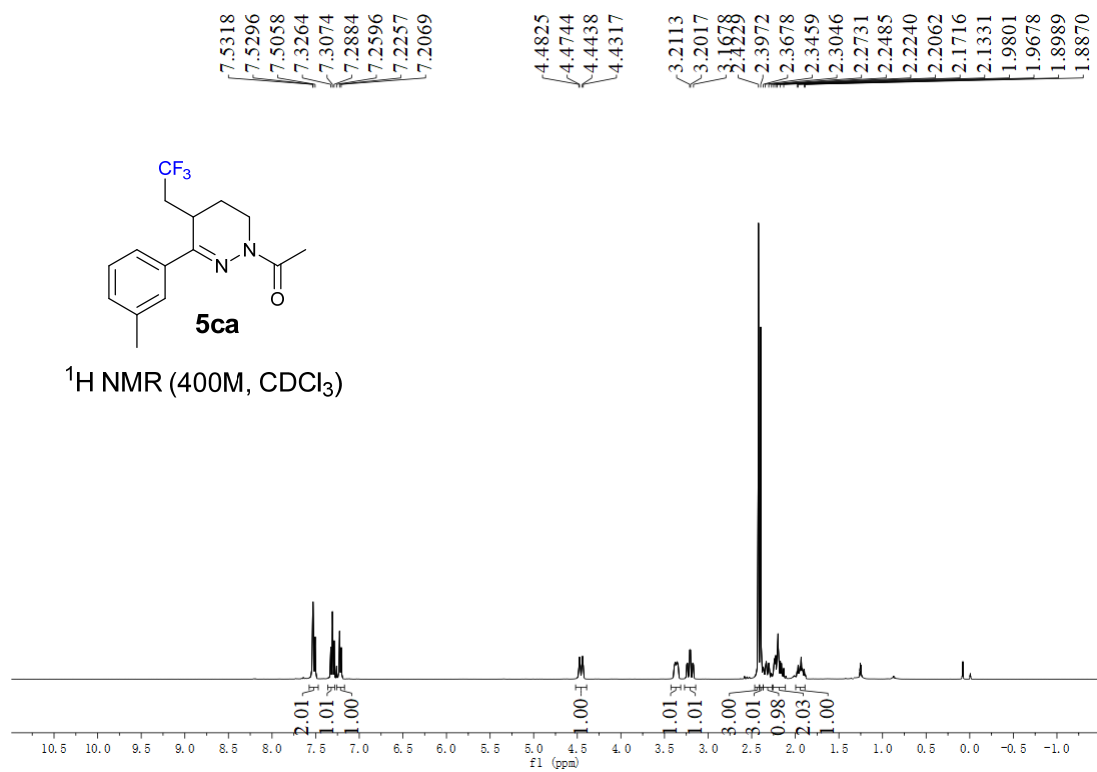
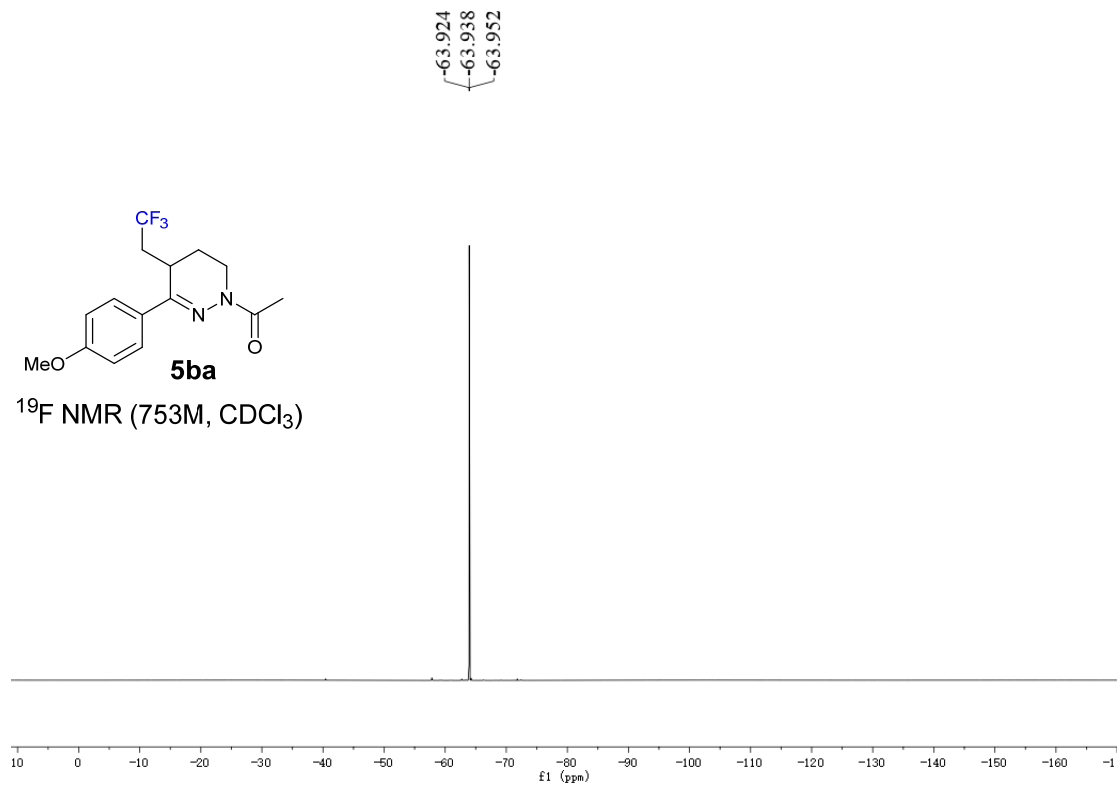


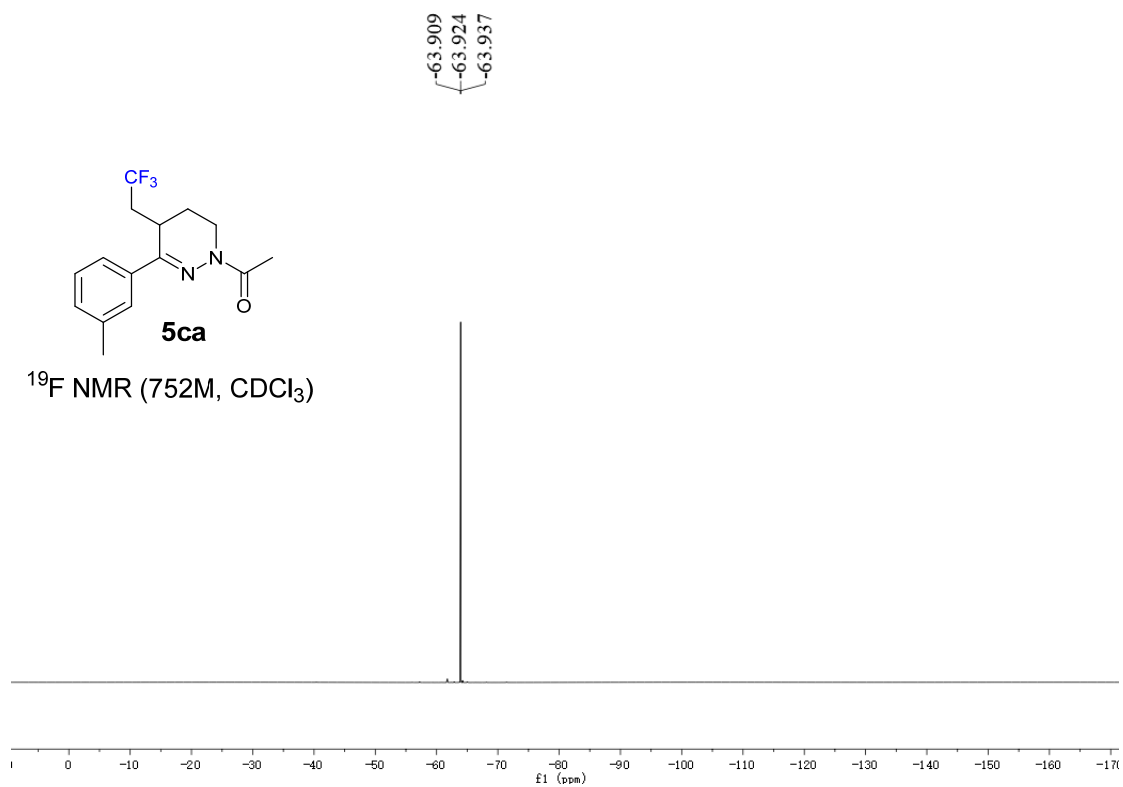
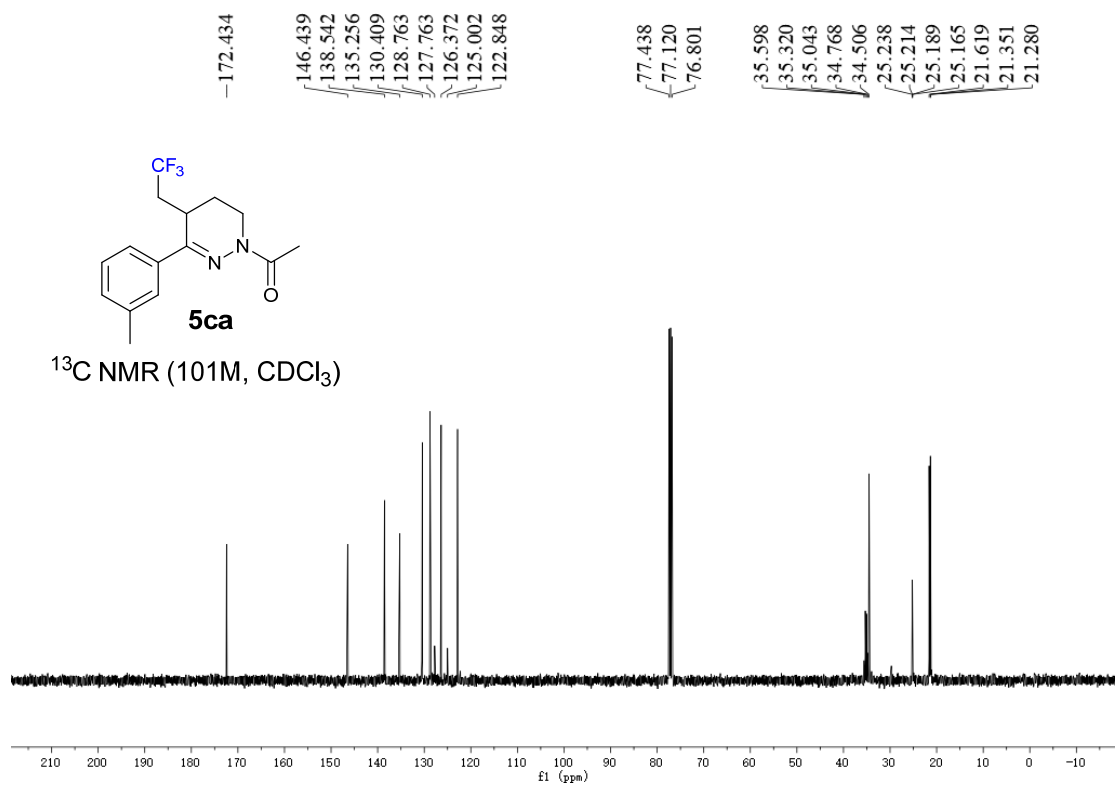
$^1\text{H NMR}$ (400M, CDCl_3)

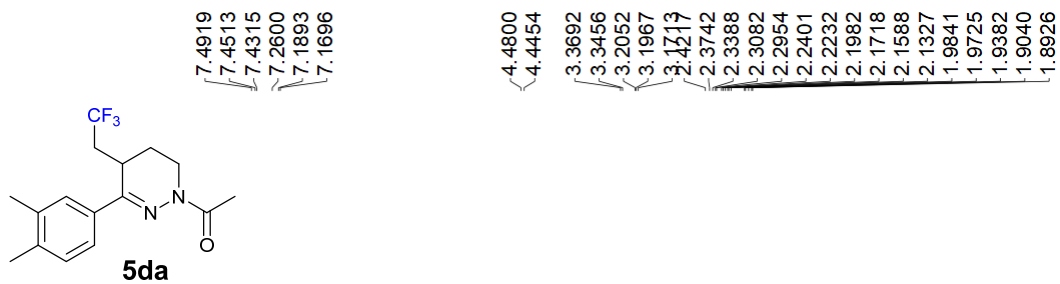


$^{13}\text{C NMR}$ (101M, CDCl_3)

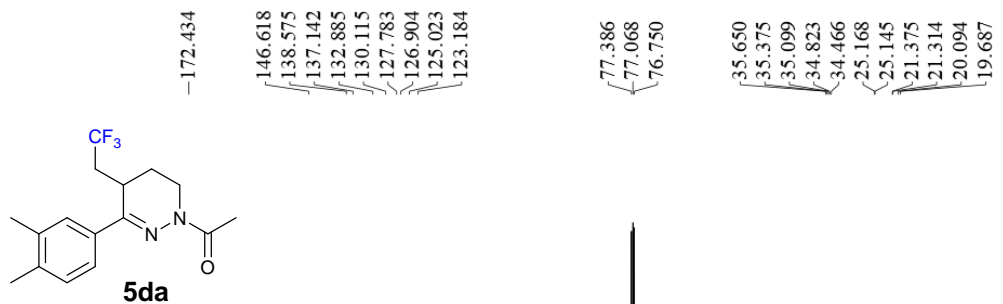
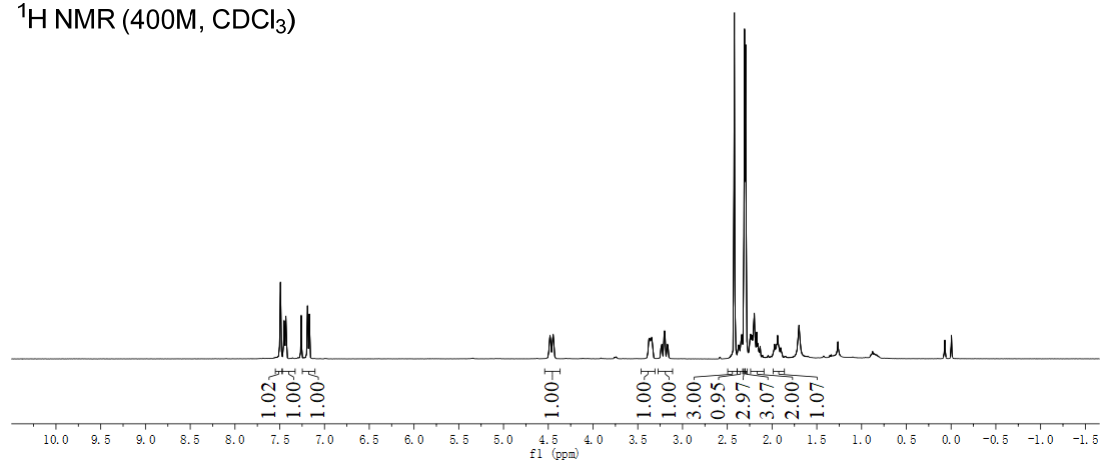




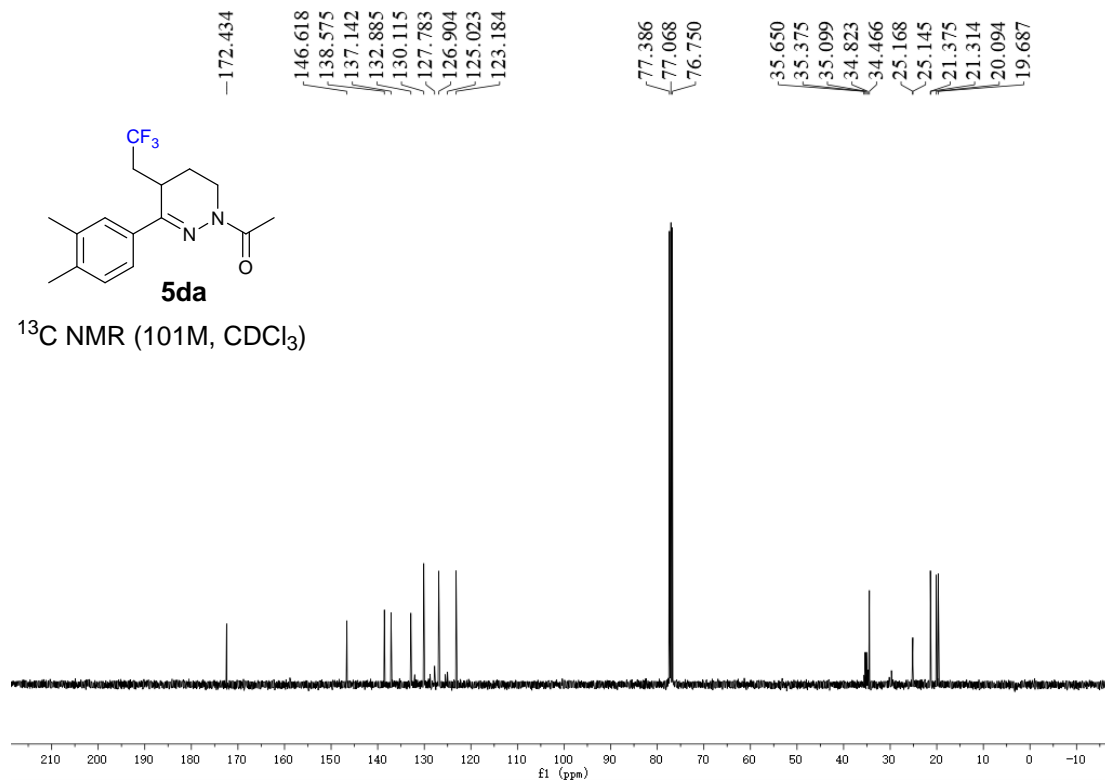


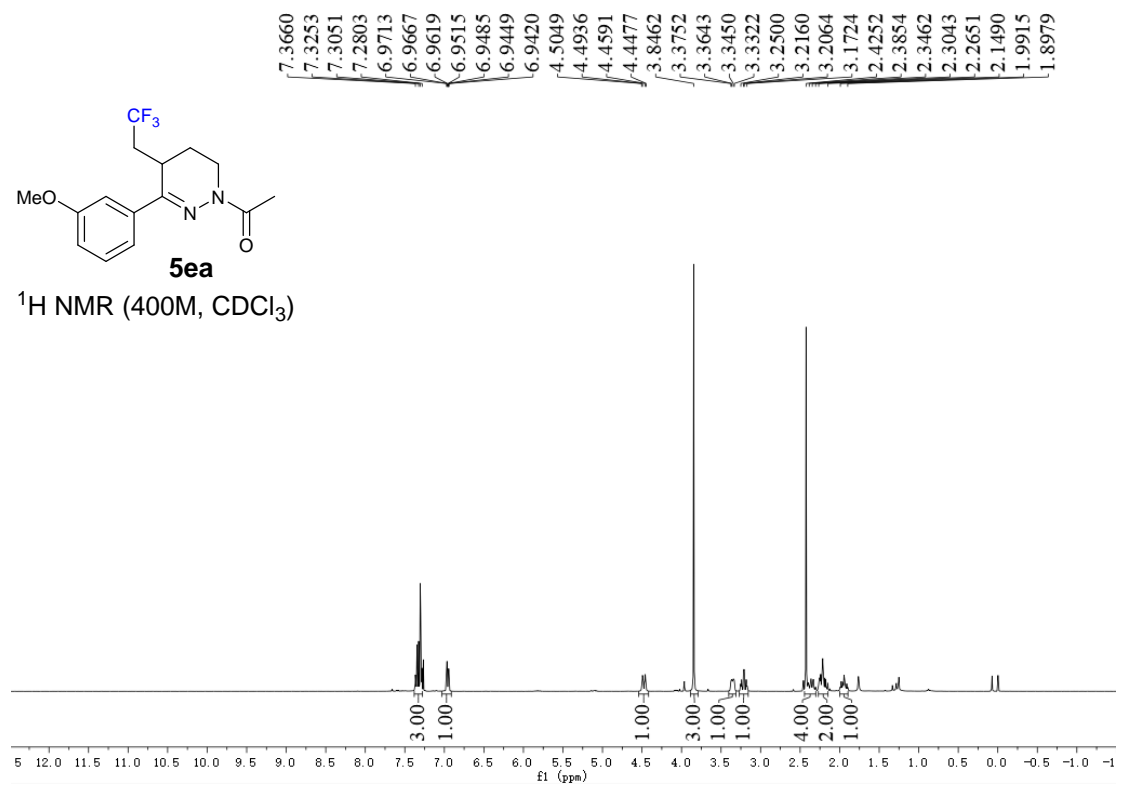
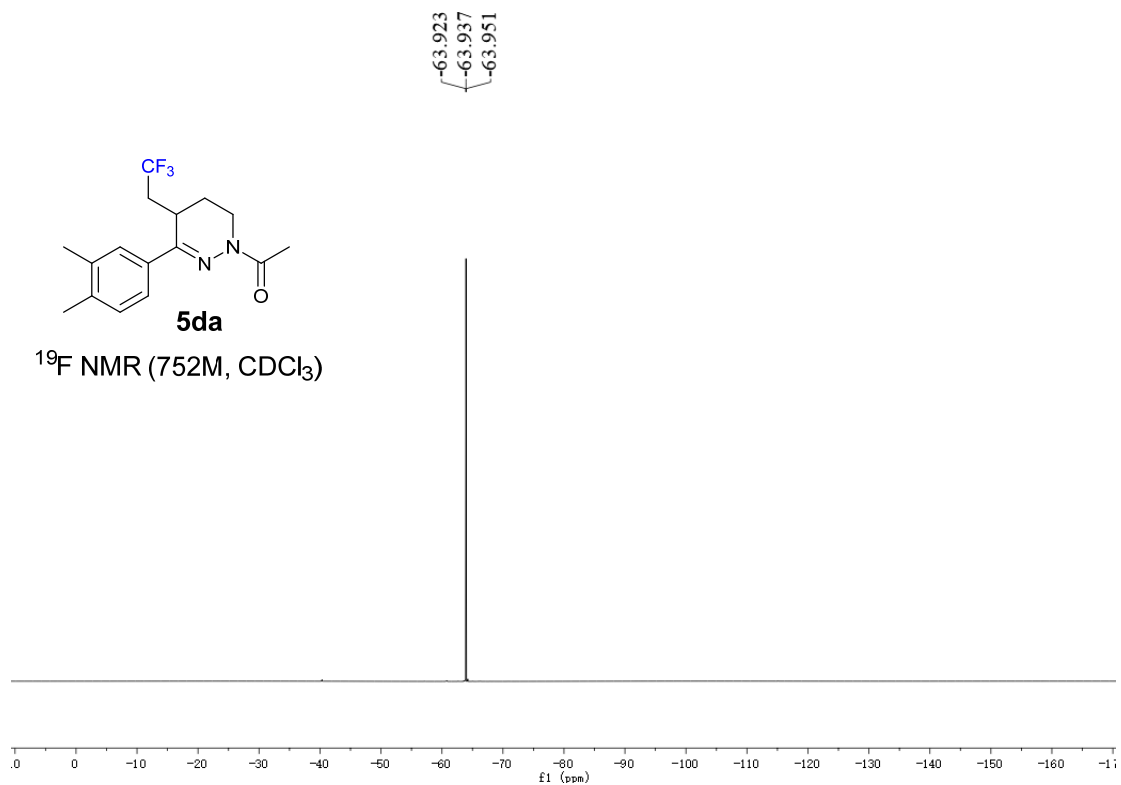


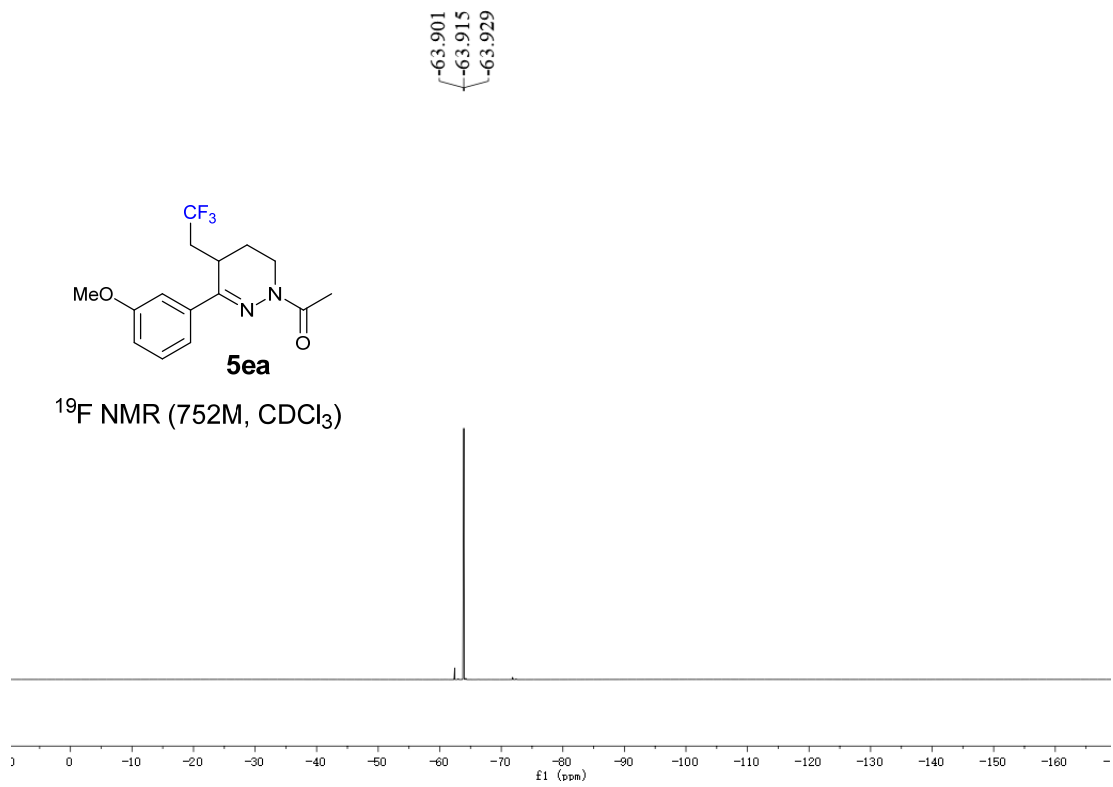
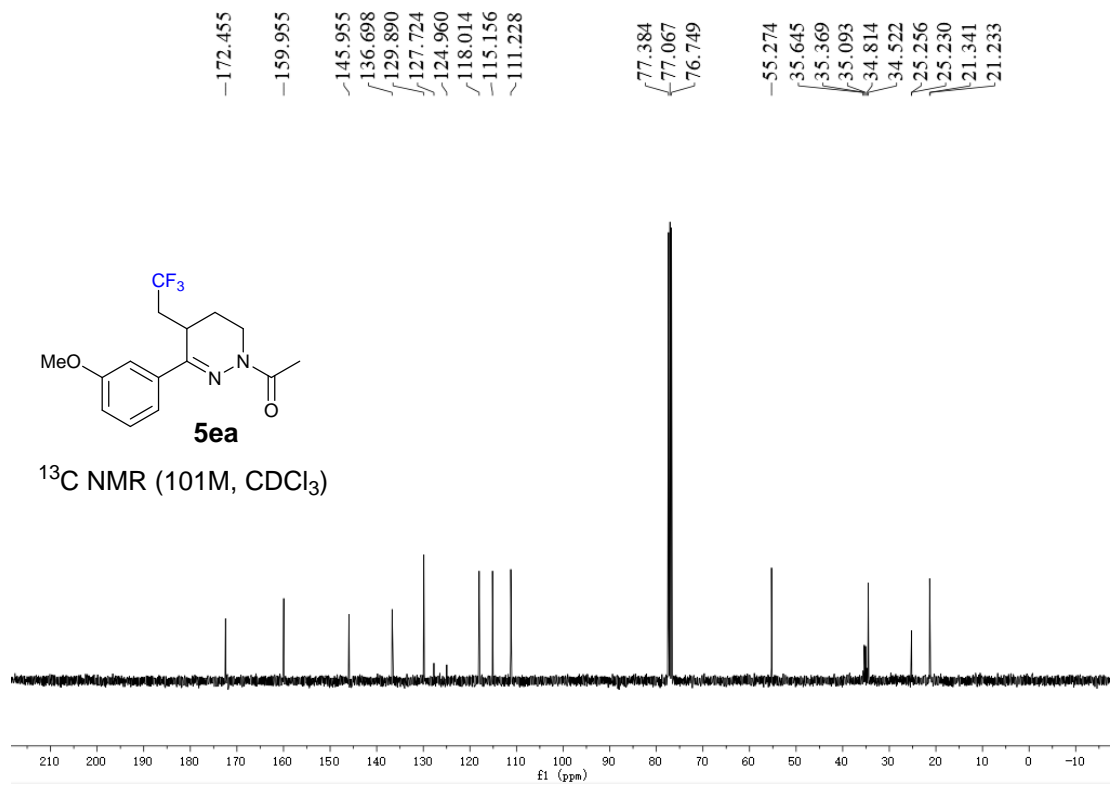
¹H NMR (400M, CDCl₃)

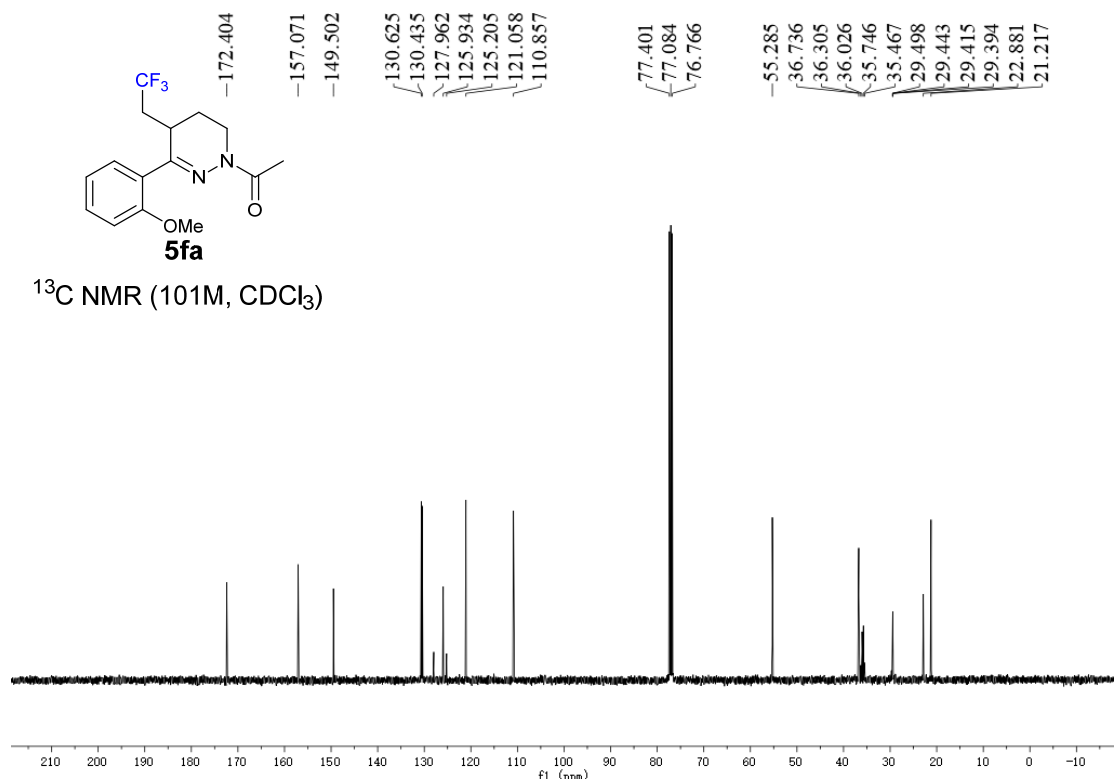
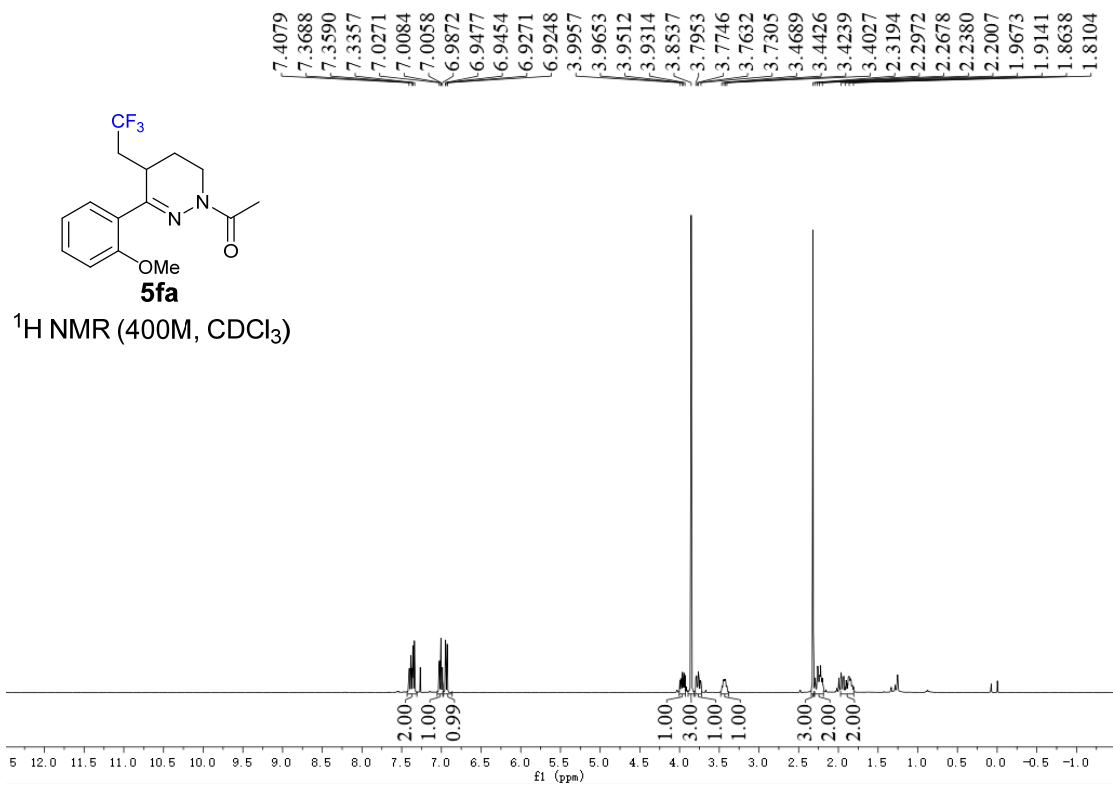


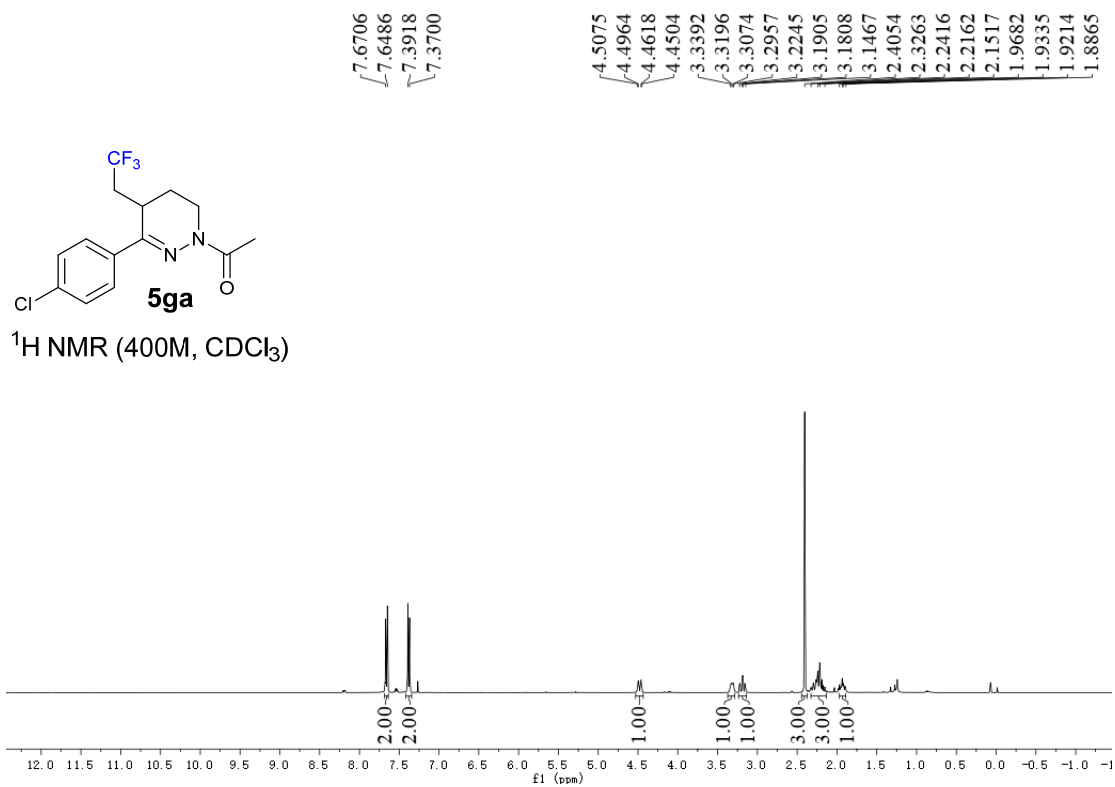
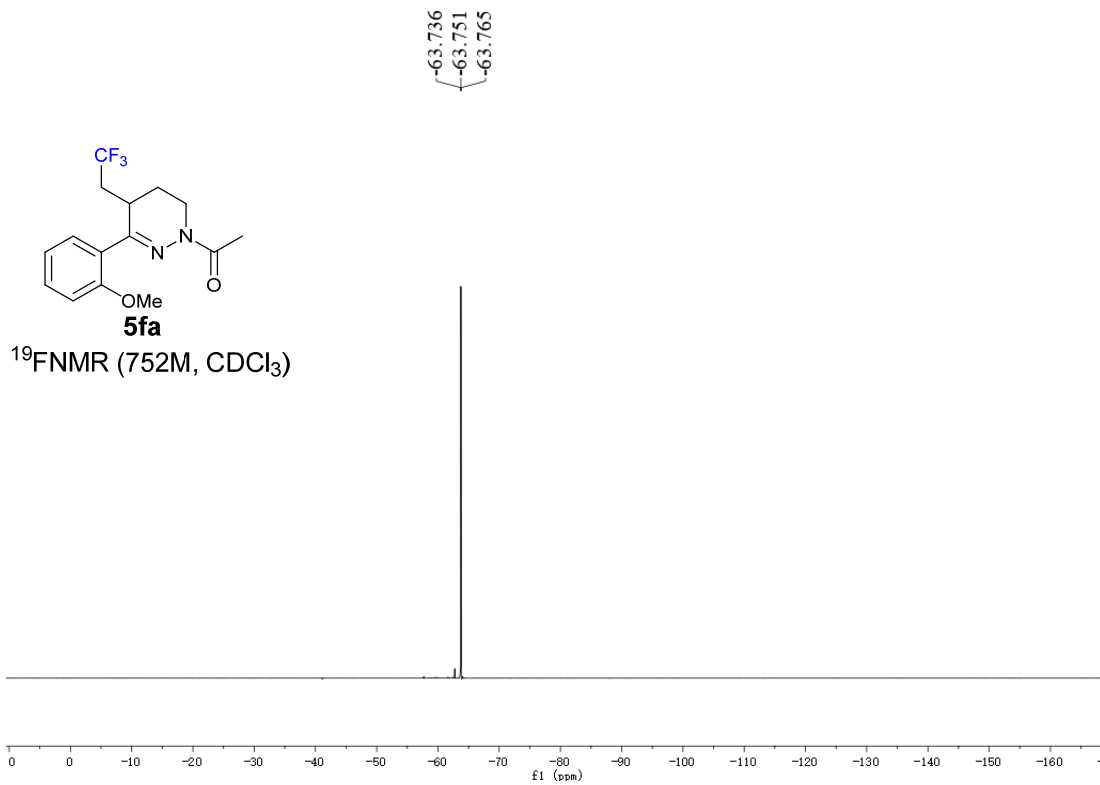
¹³C NMR (101M, CDCl₃)

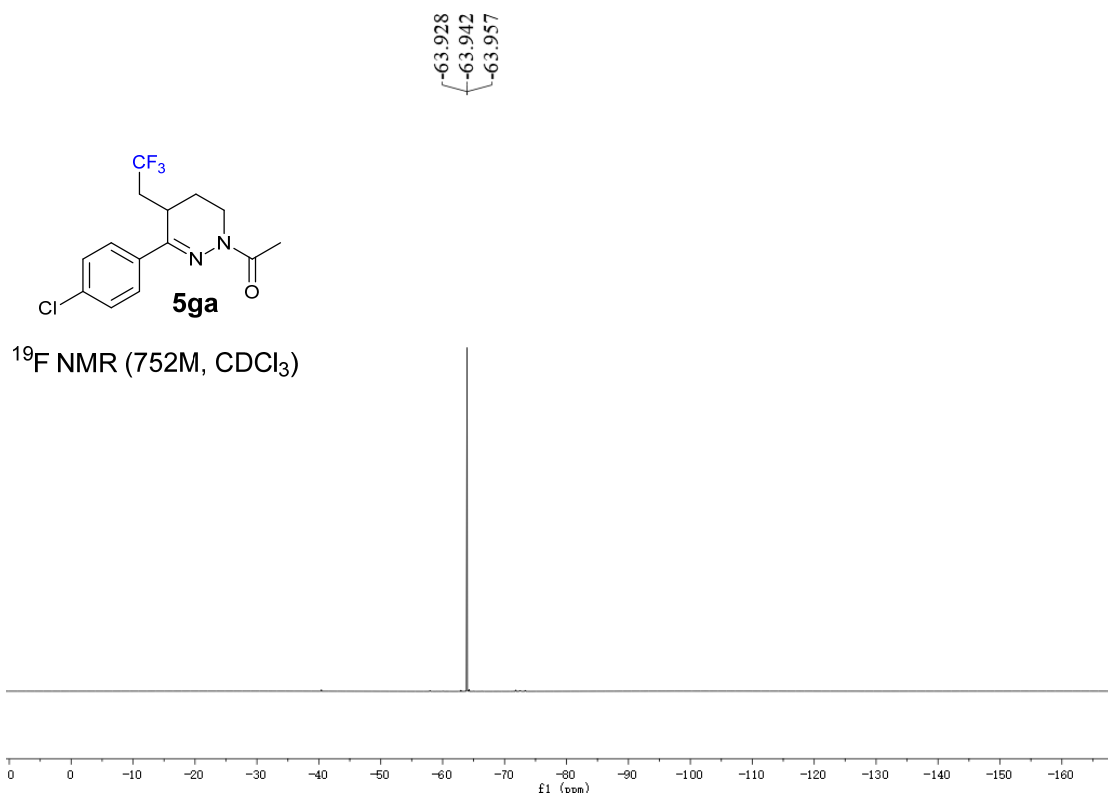
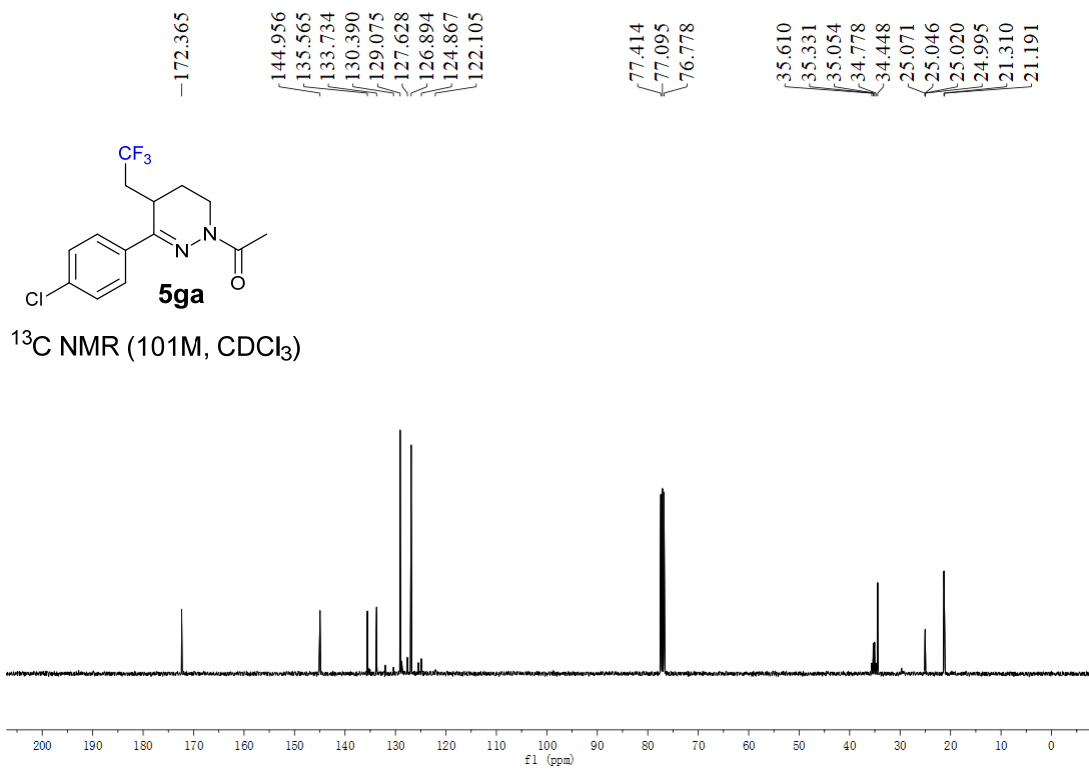


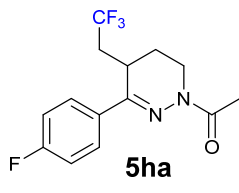




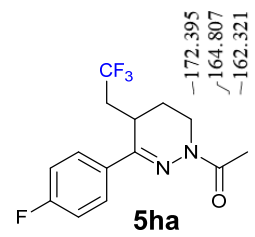
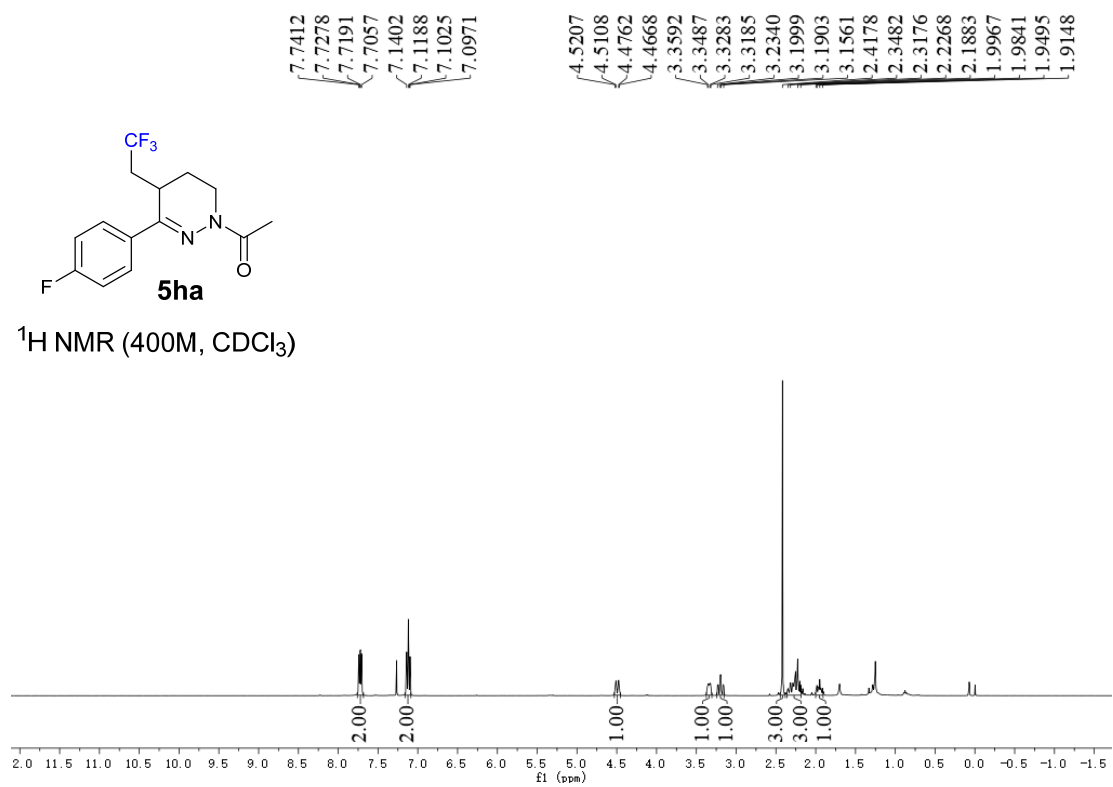




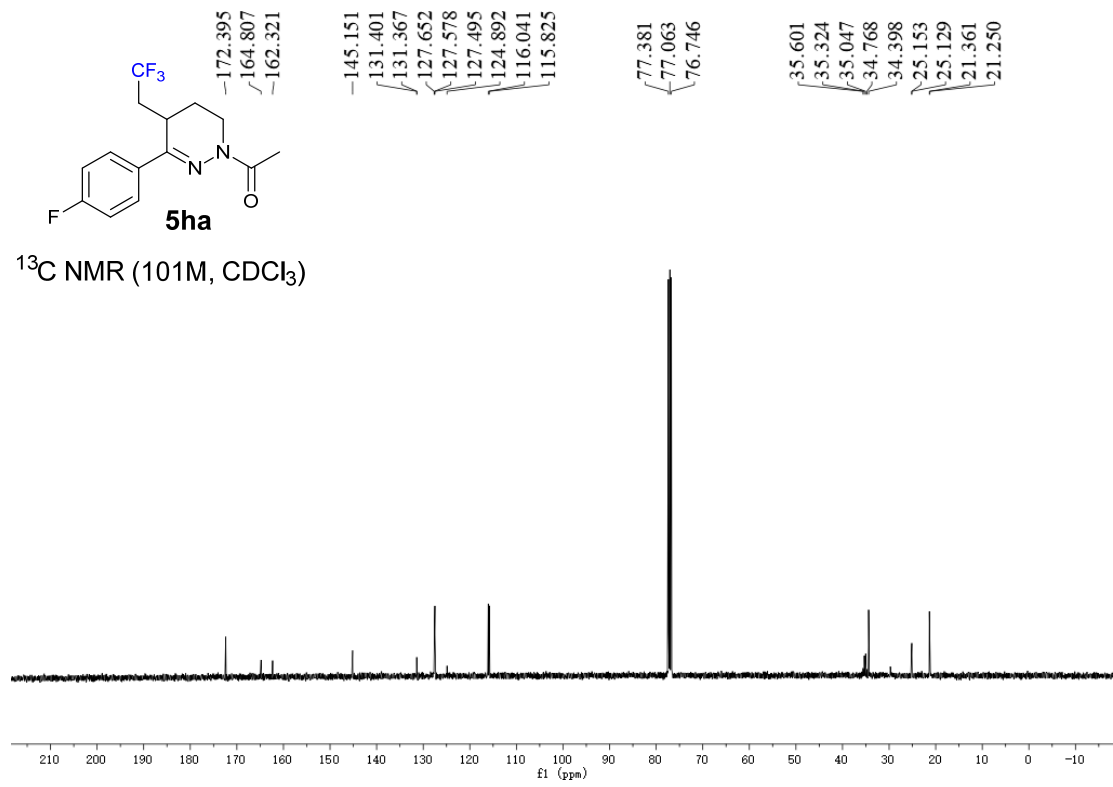


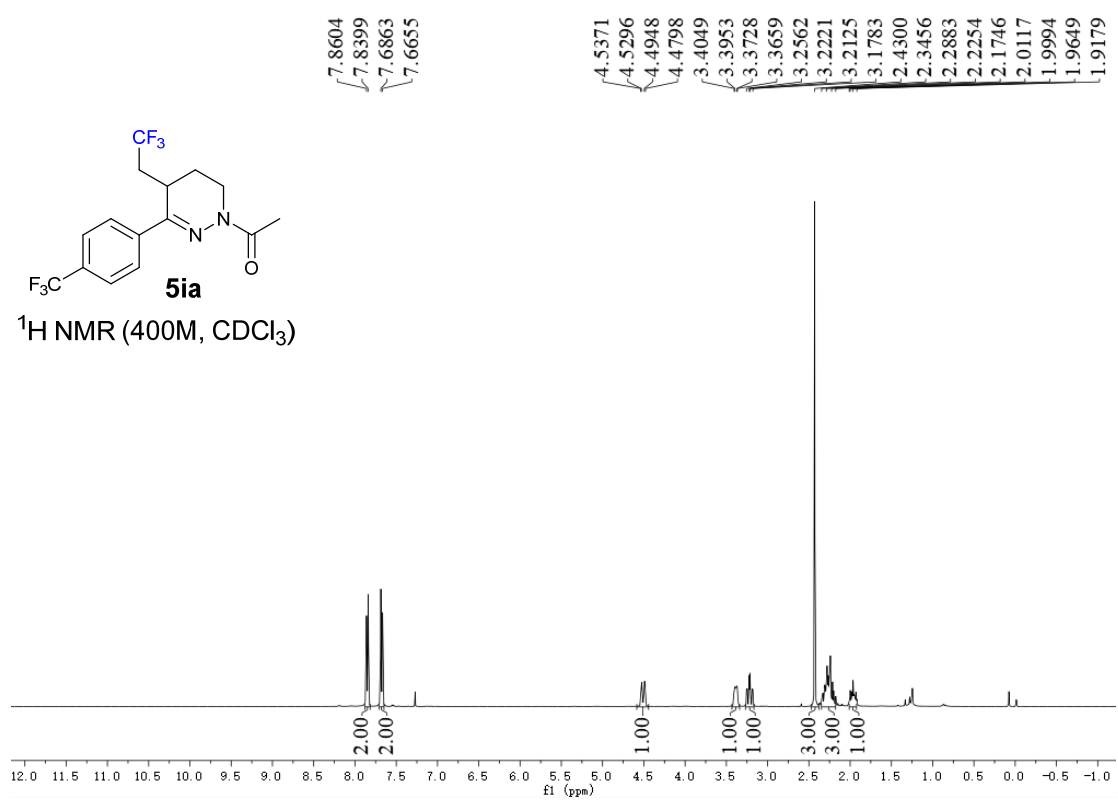
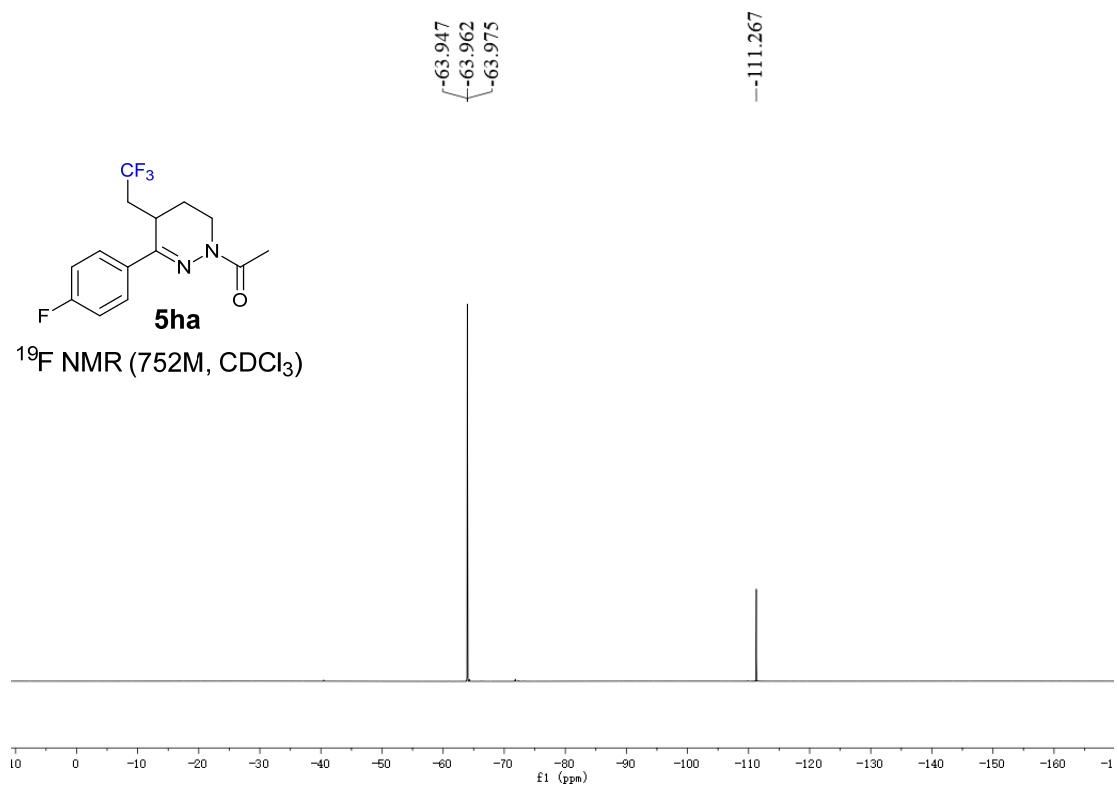


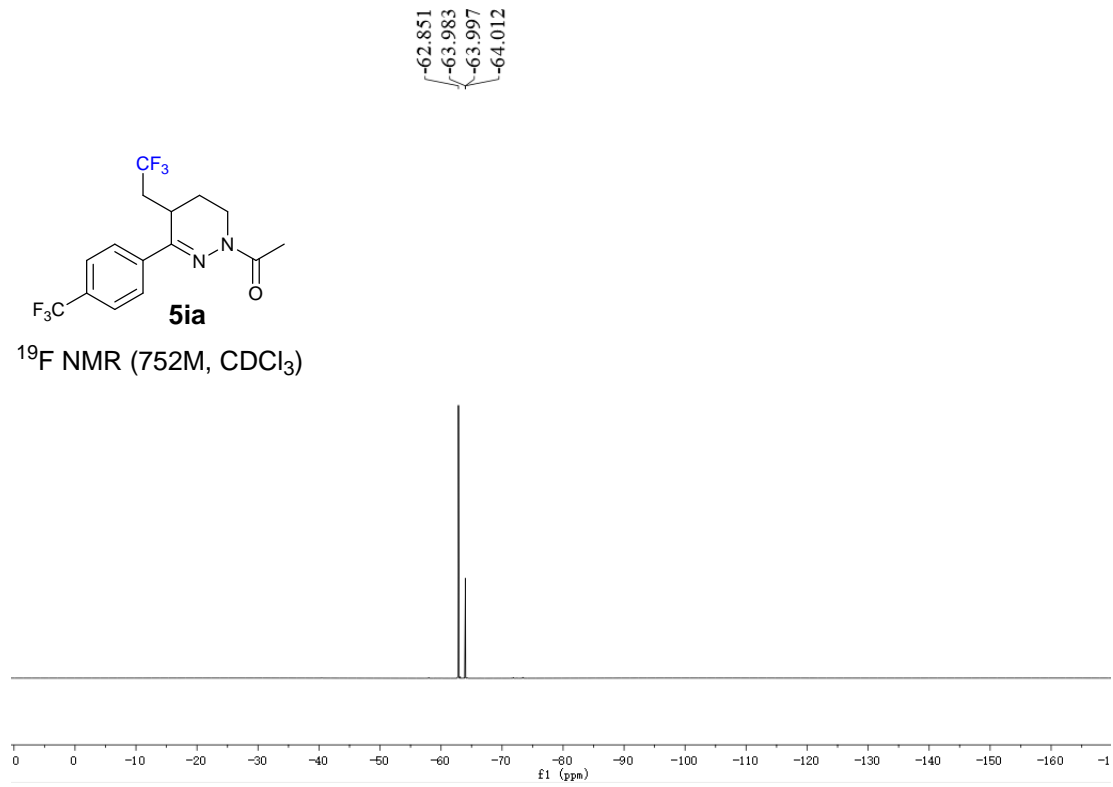
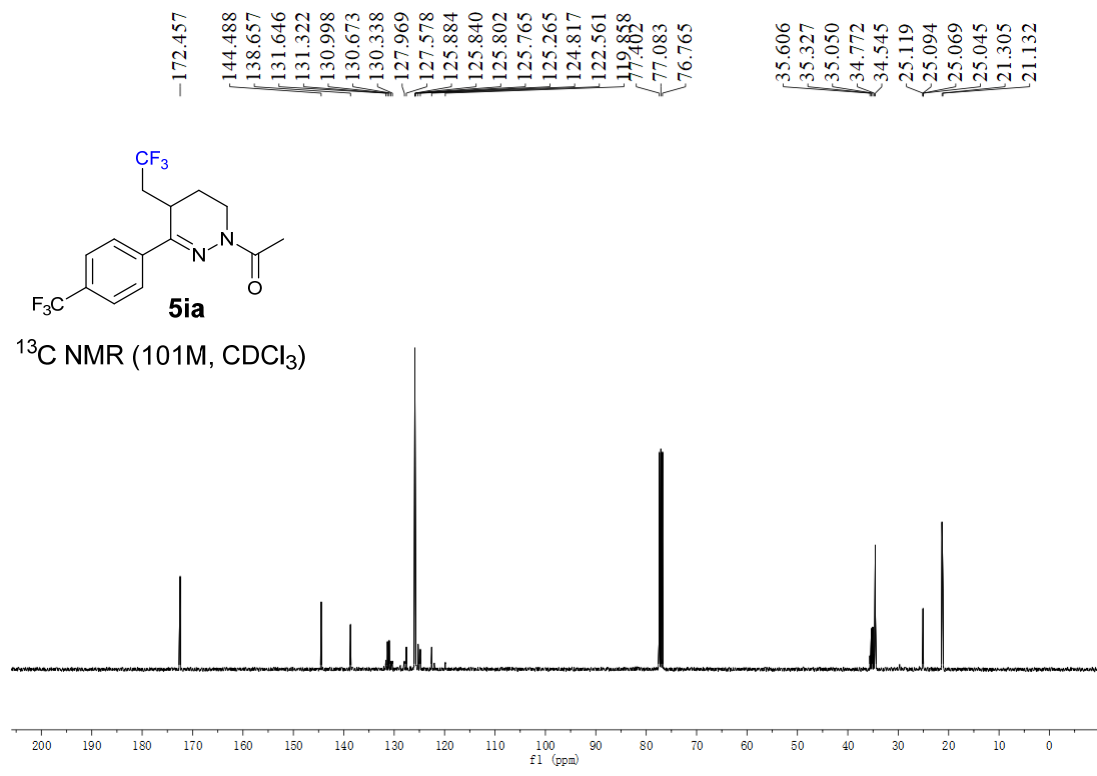
¹H NMR (400M, CDCl₃)

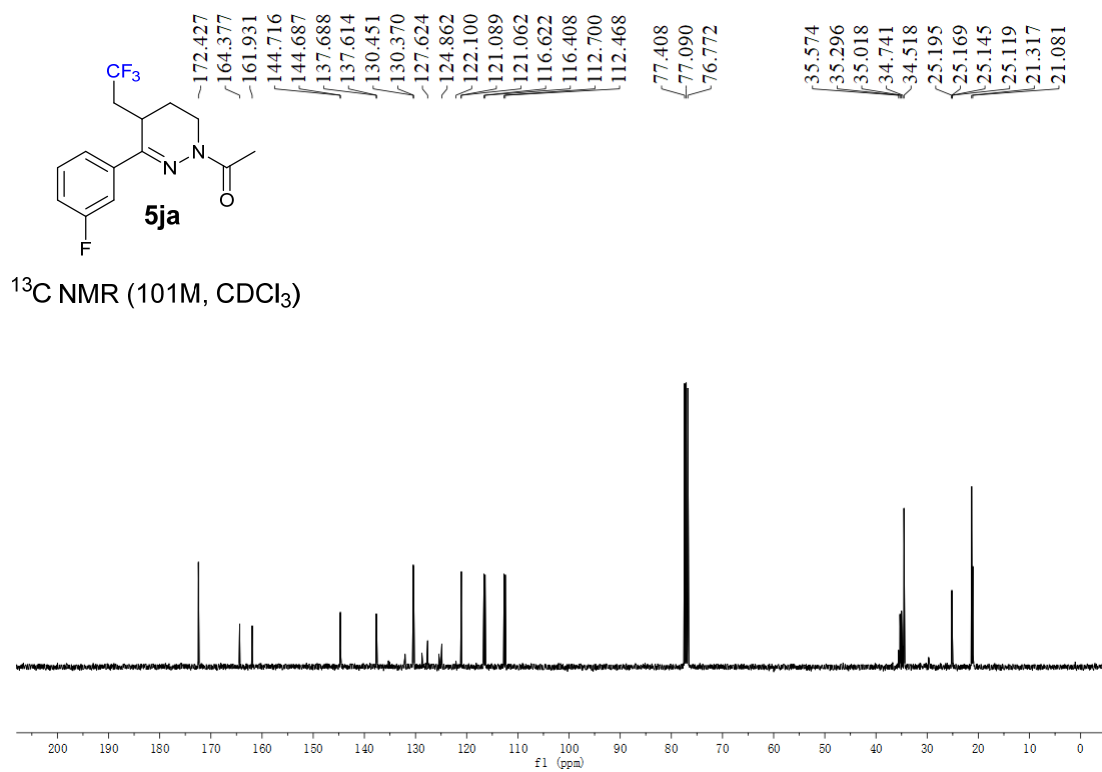
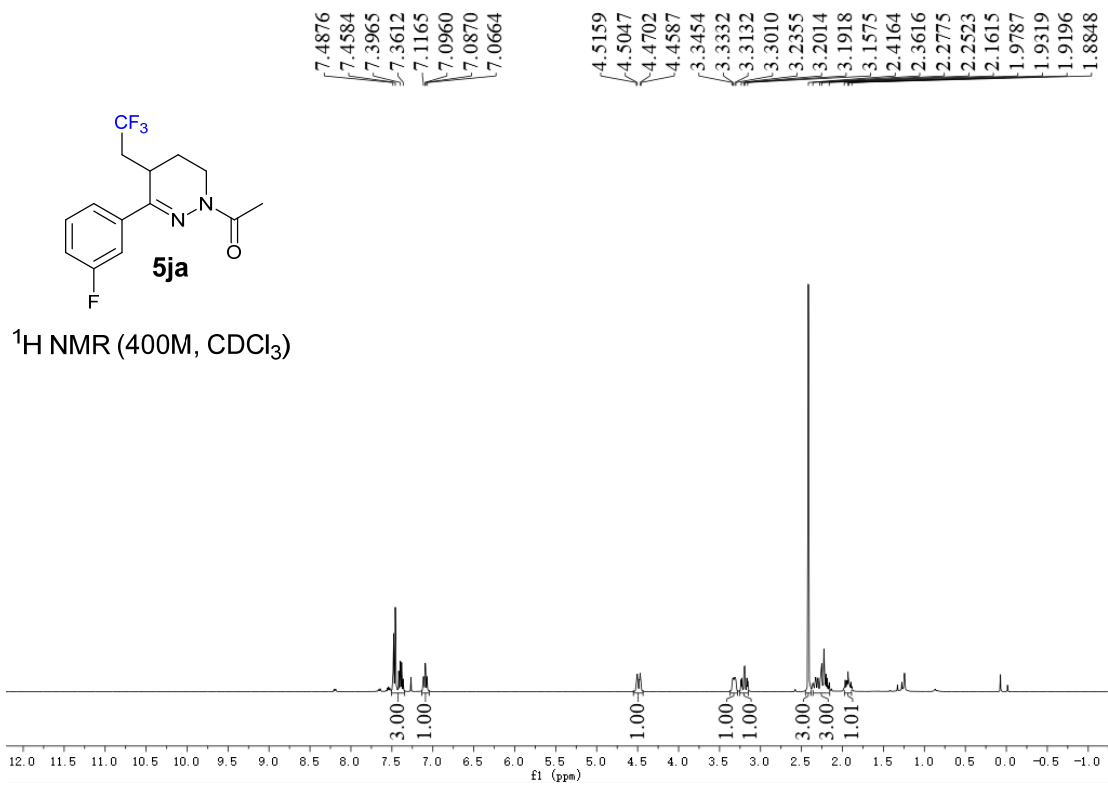


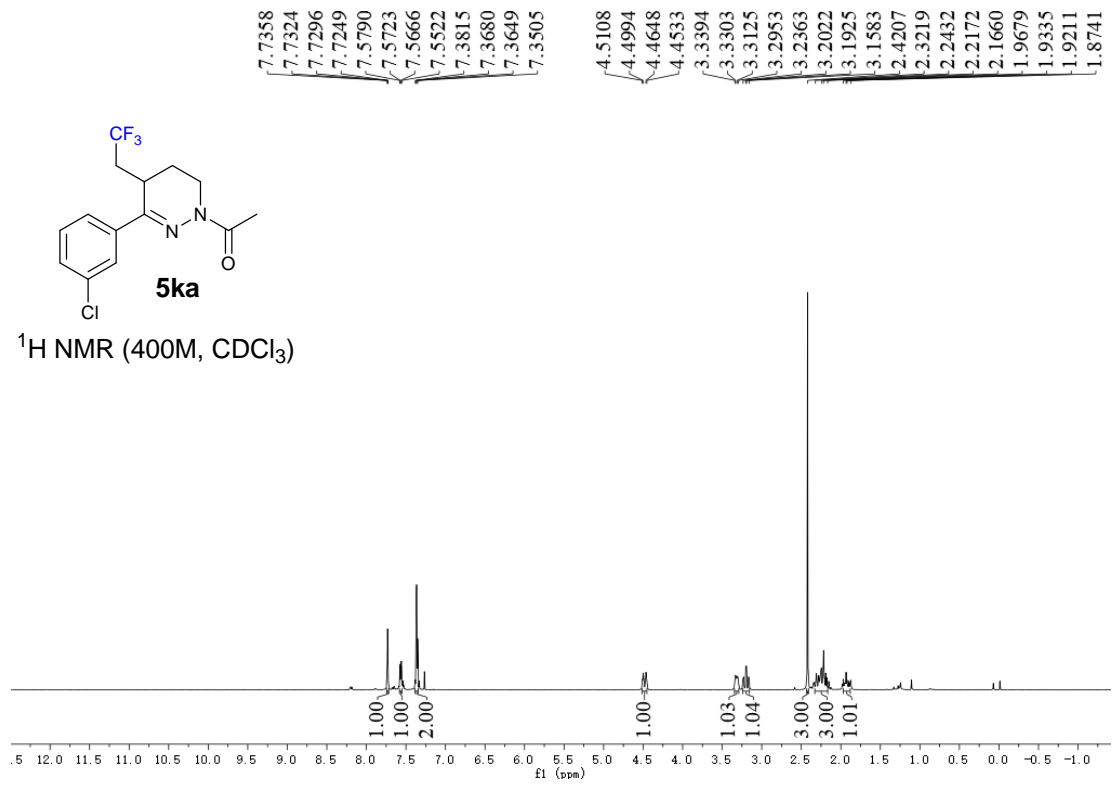
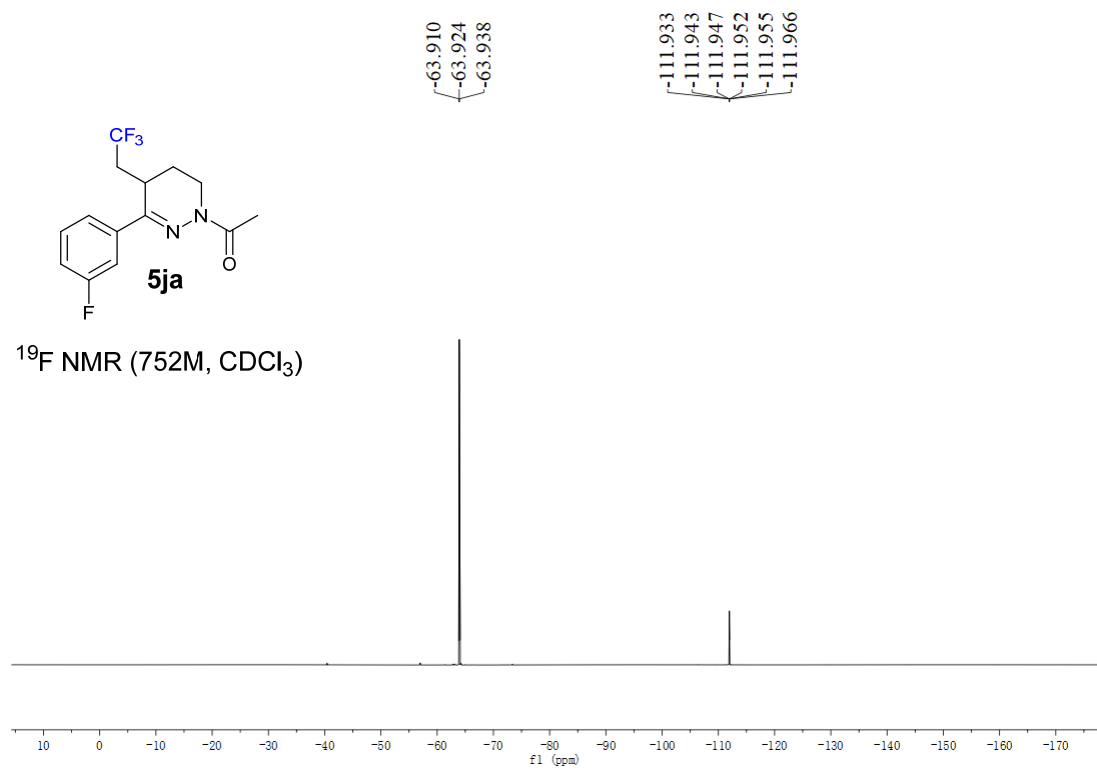
¹³C NMR (101M, CDCl₃)

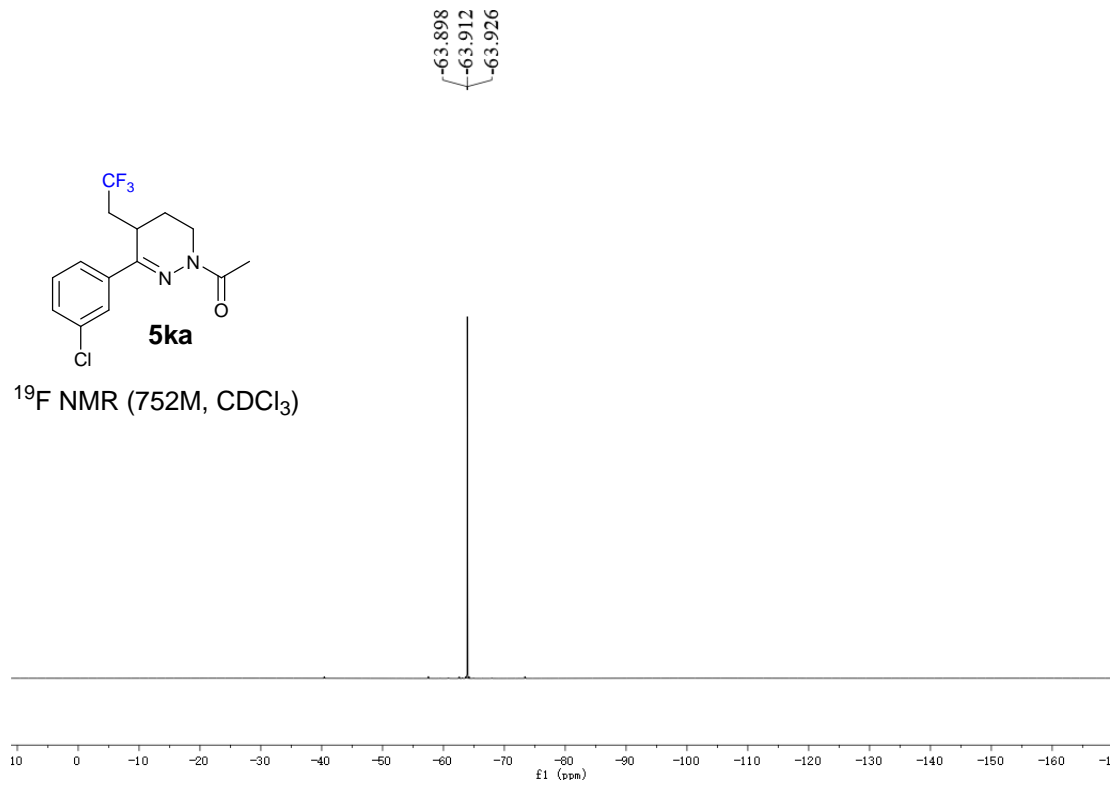
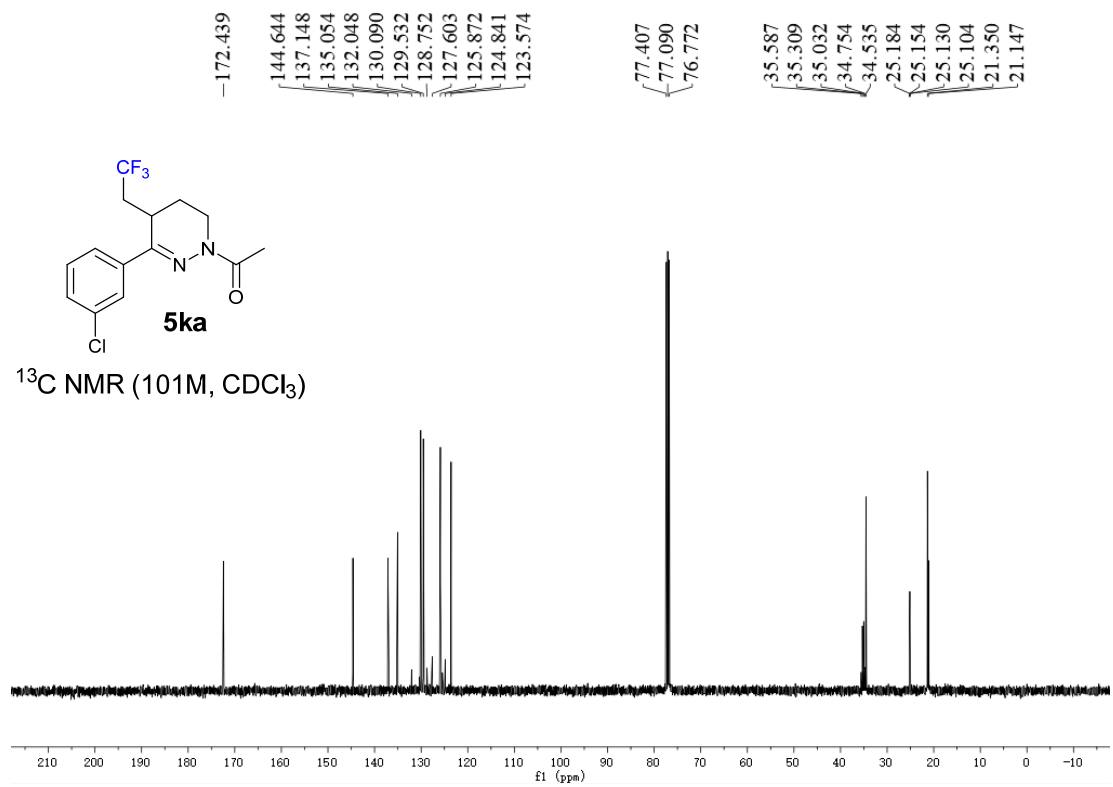


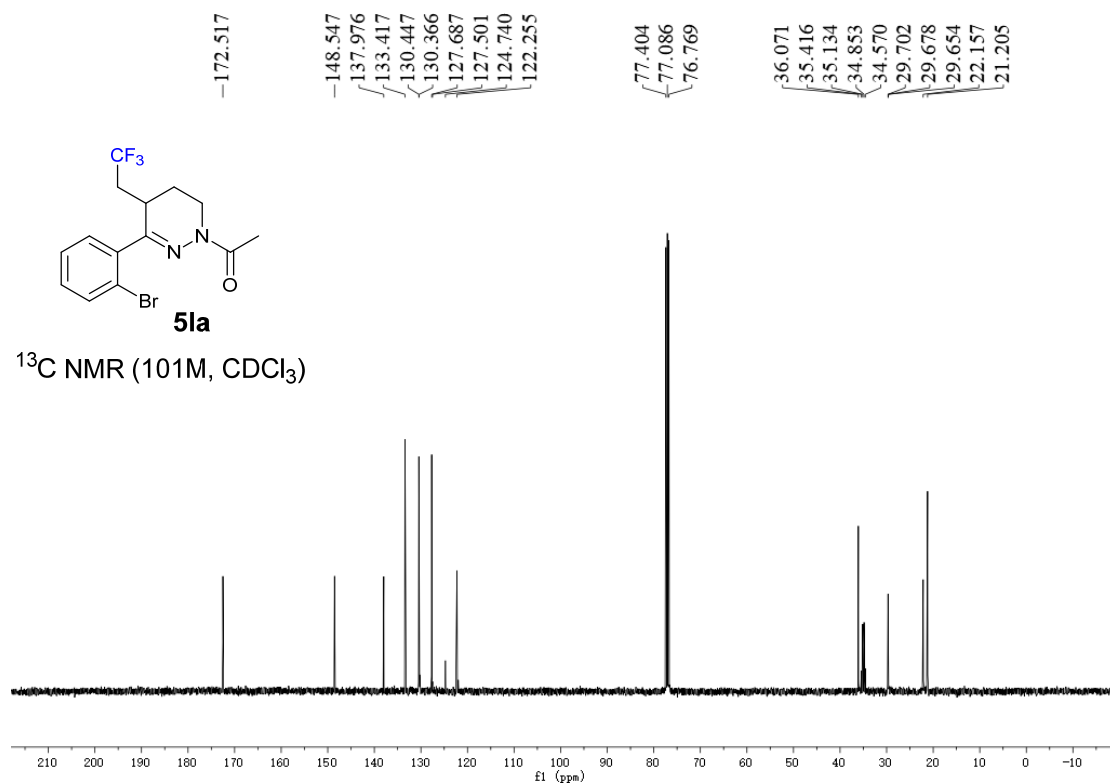
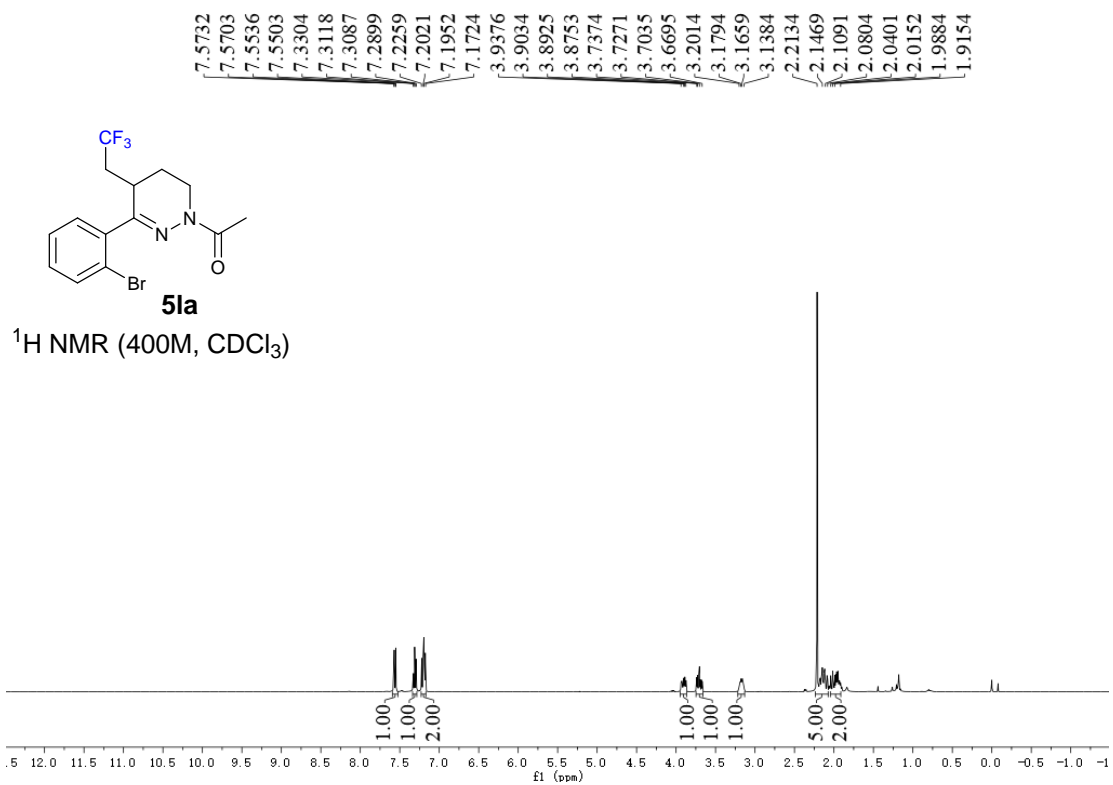


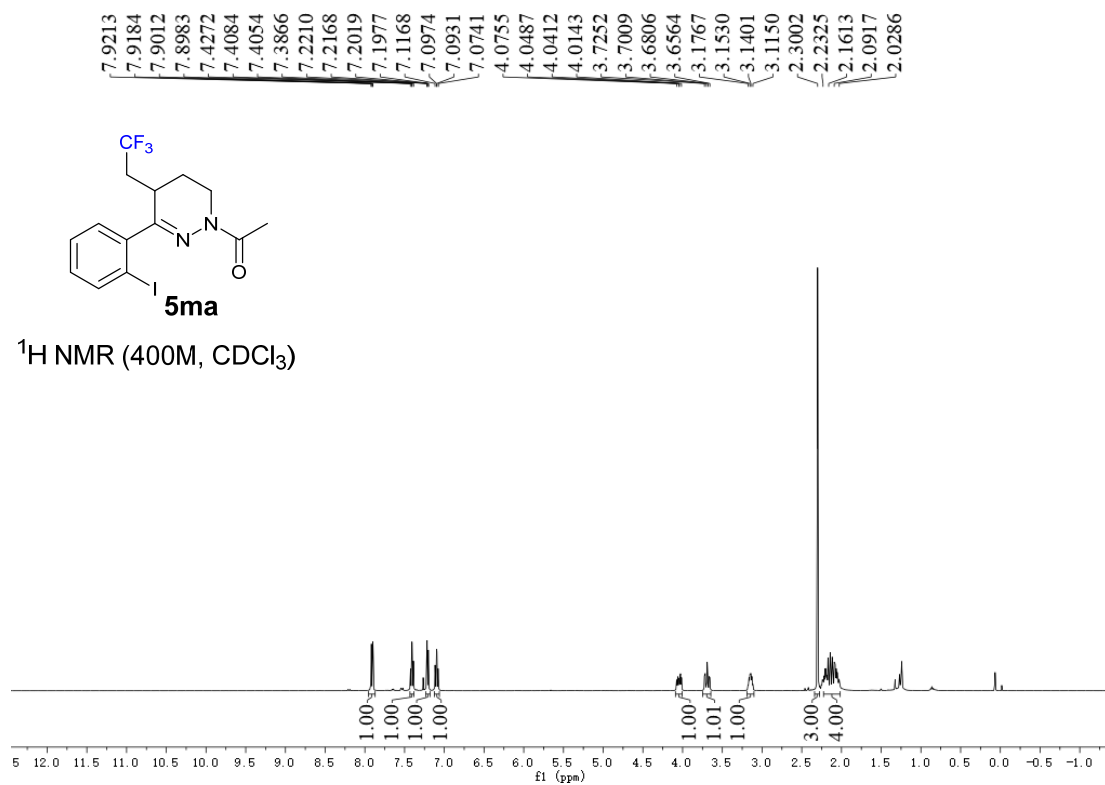
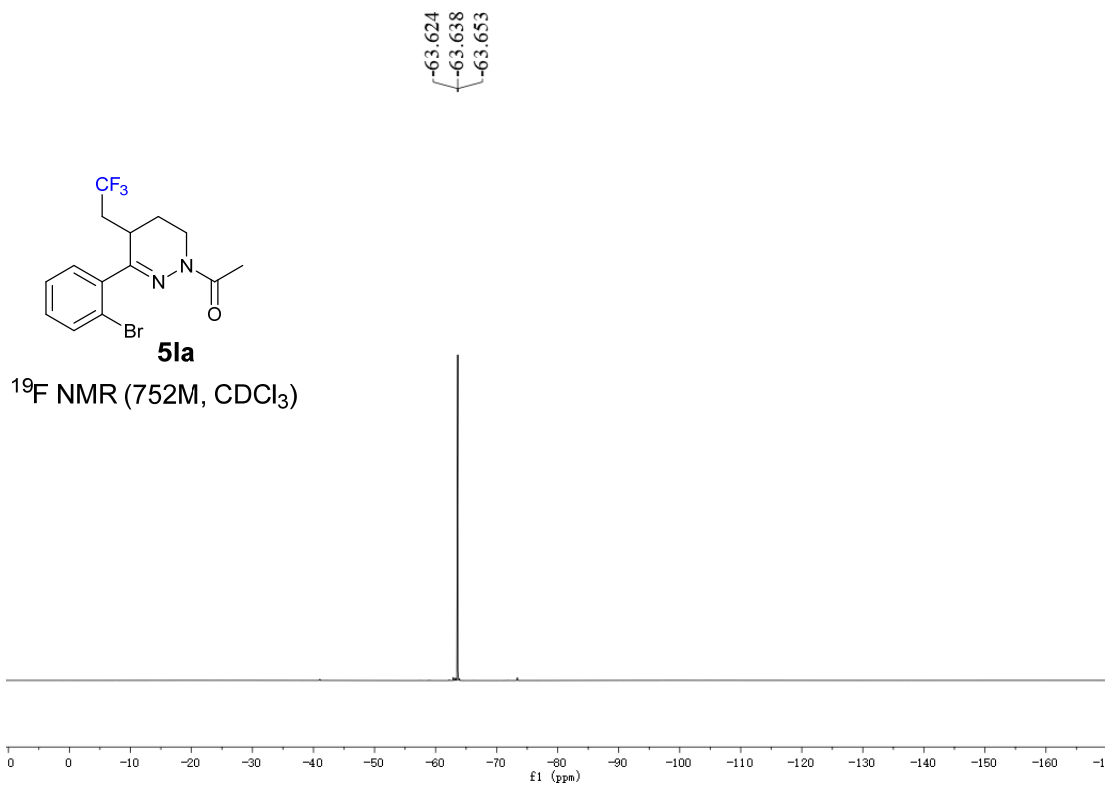


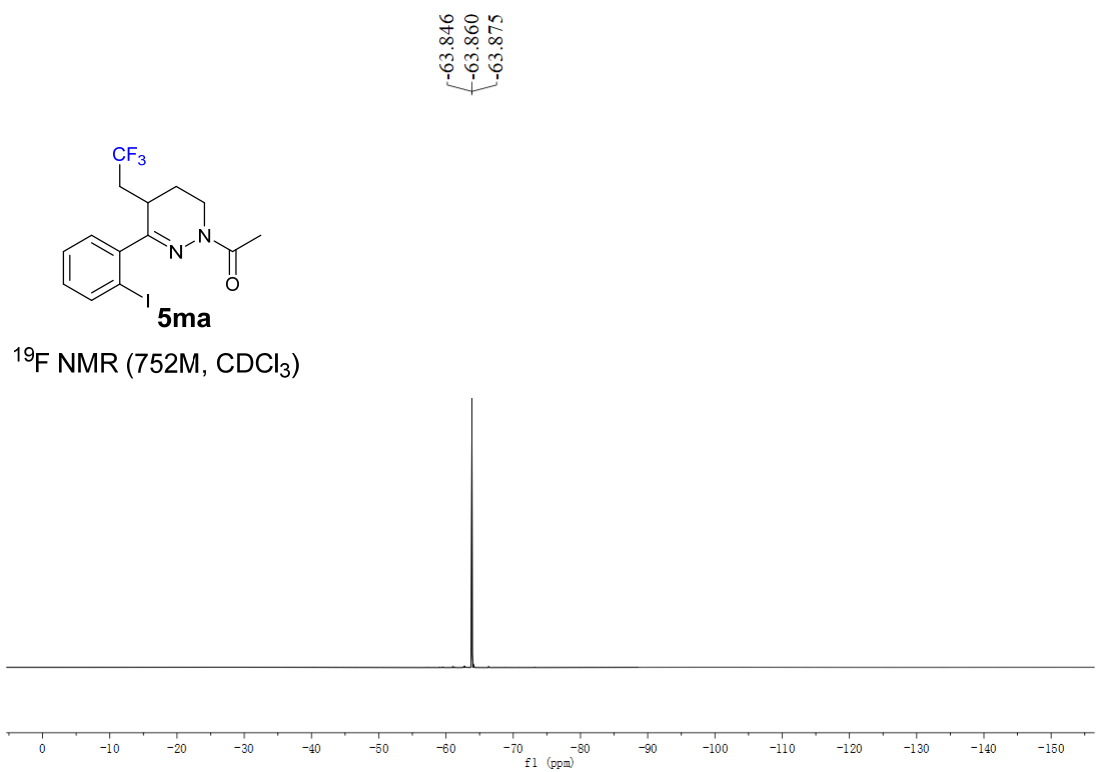
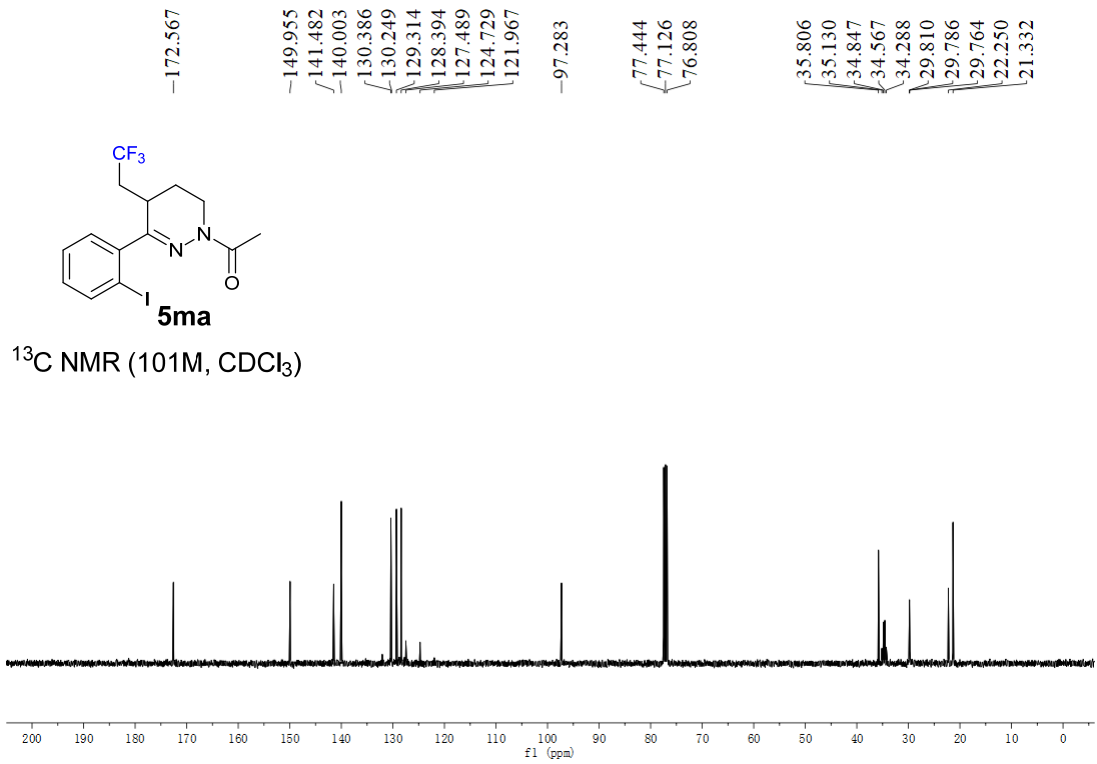


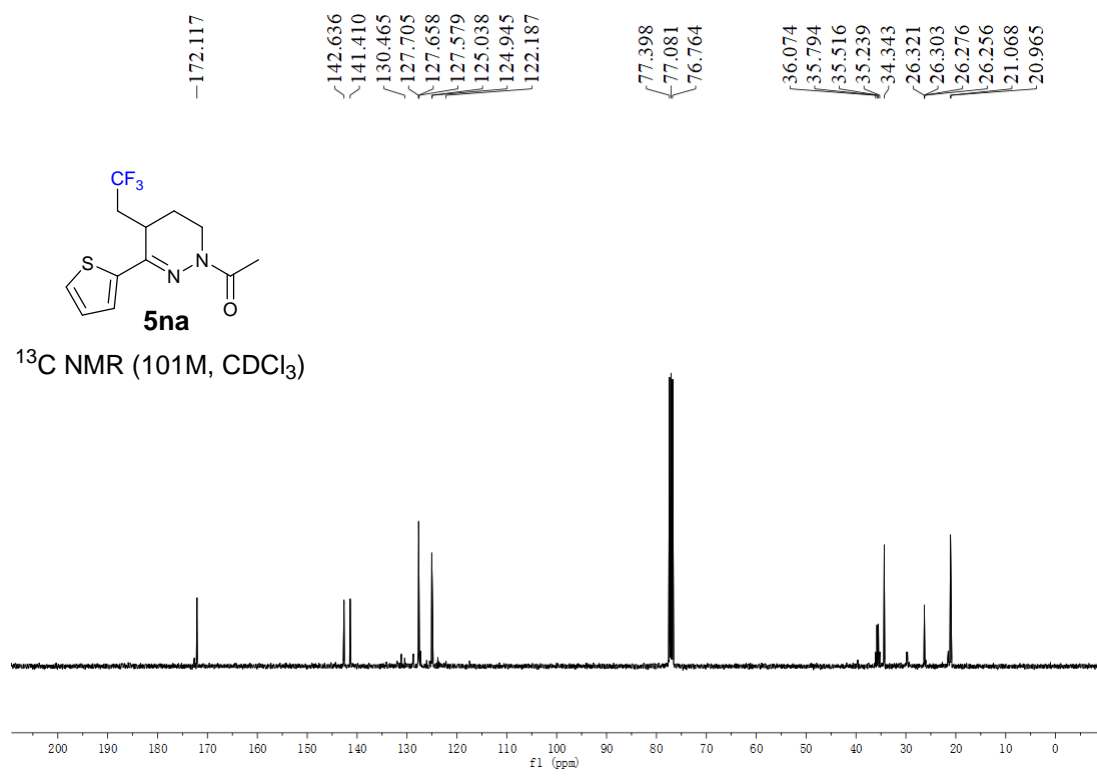
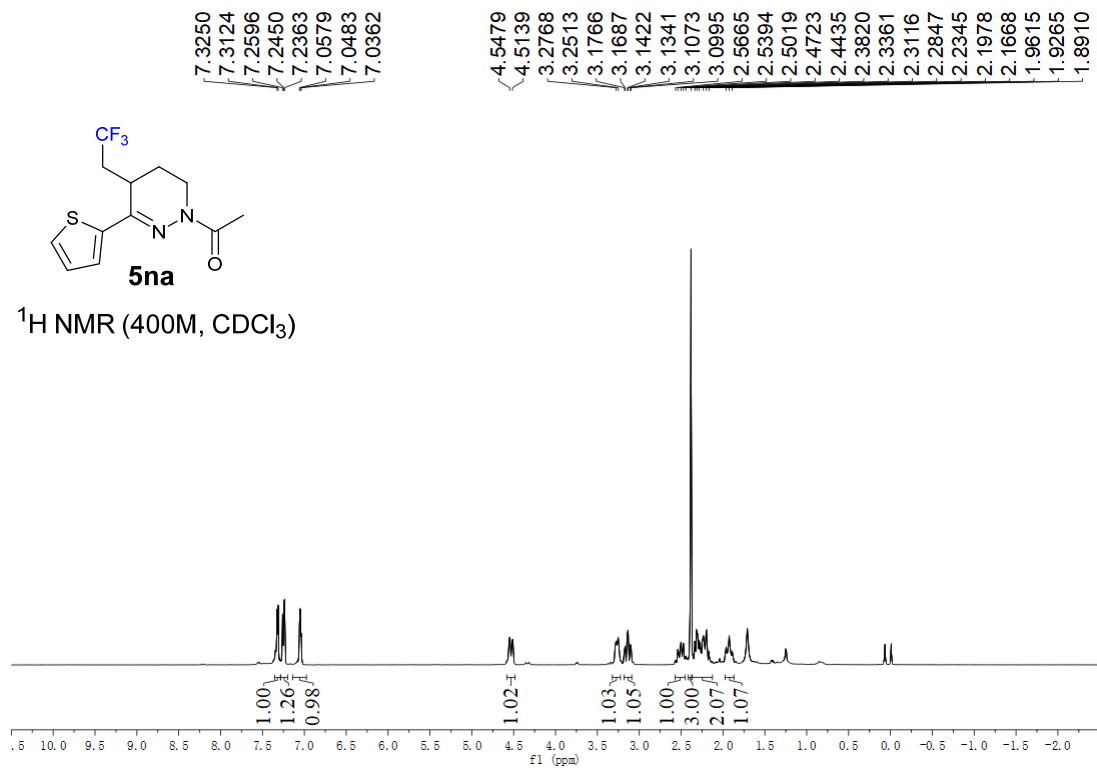


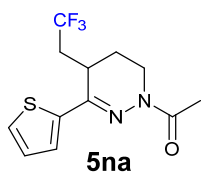




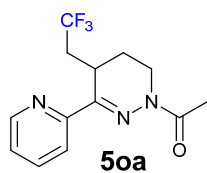




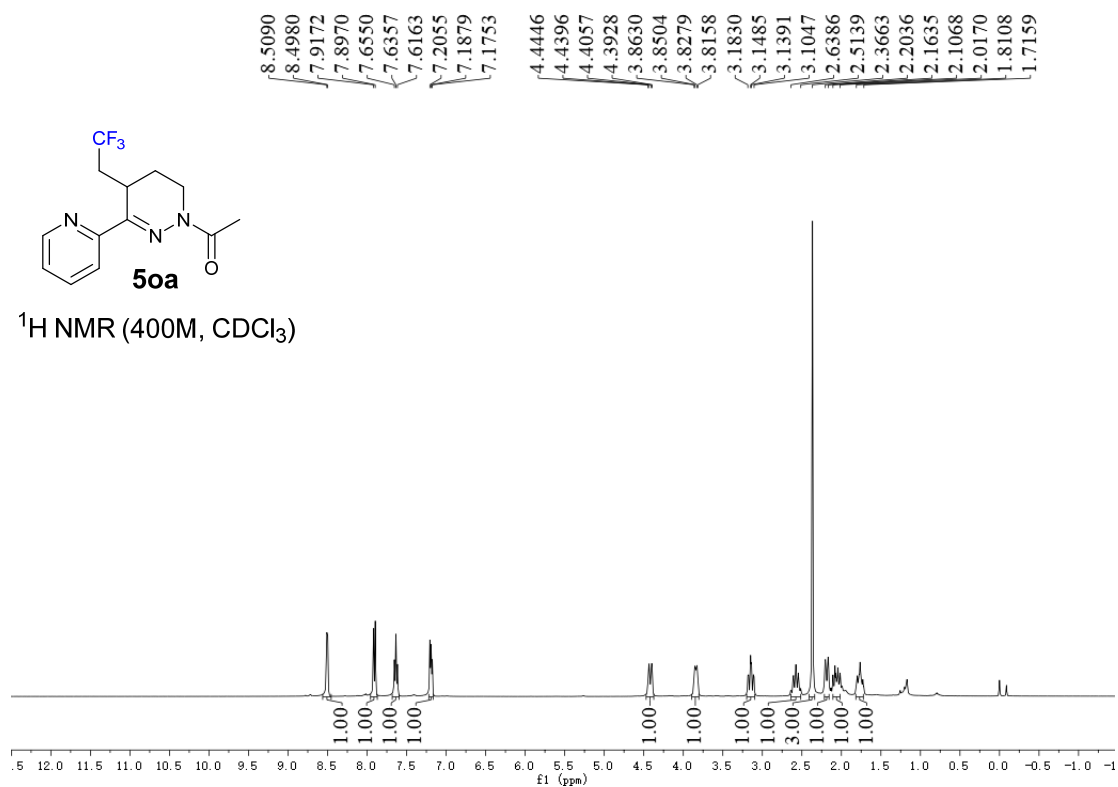


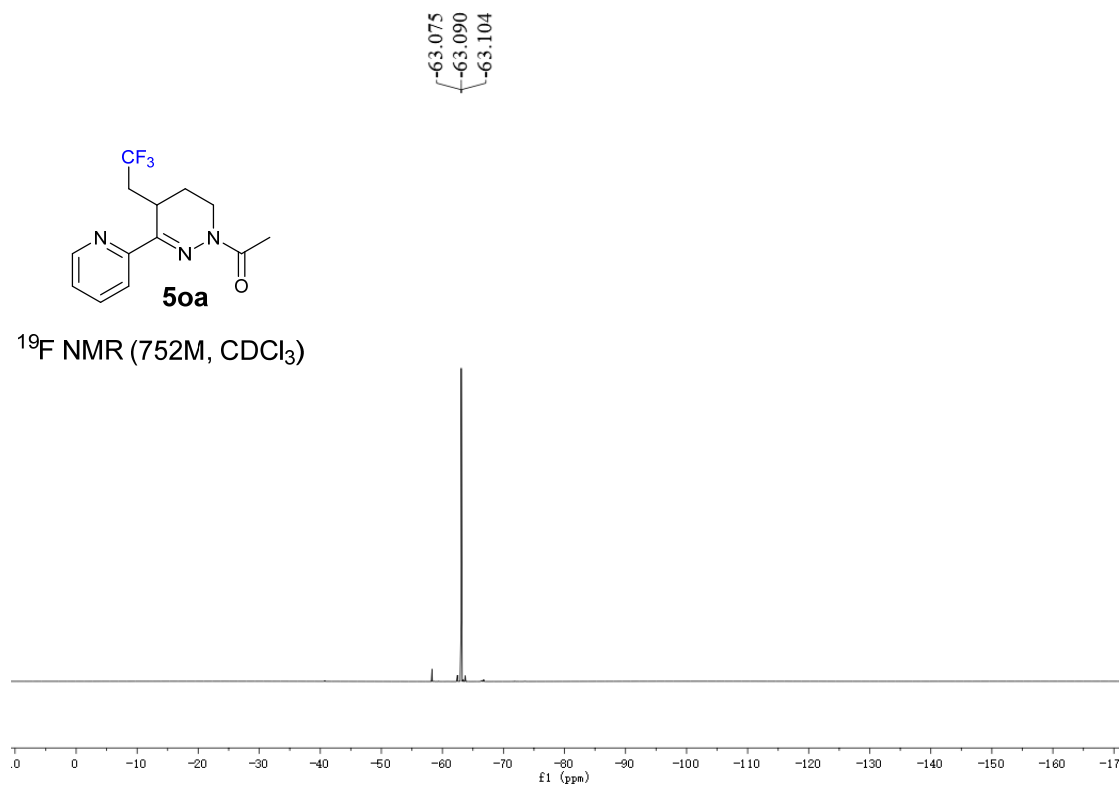
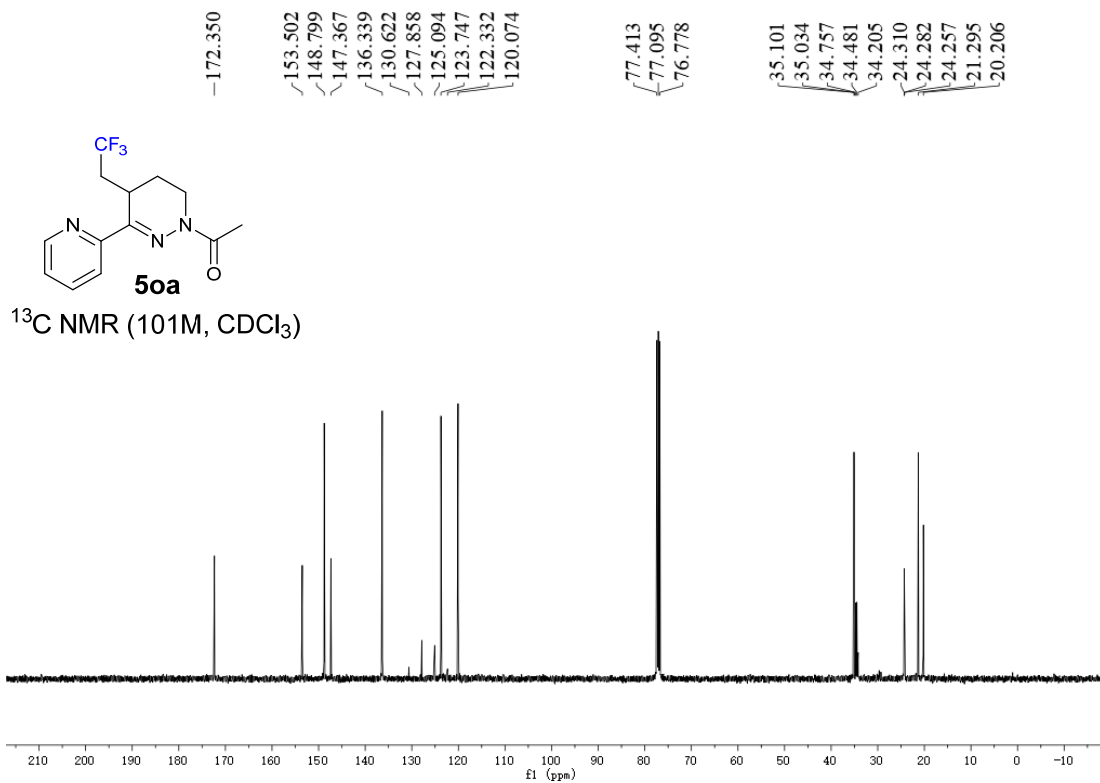


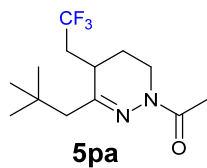
^{19}F NMR (752M, CDCl_3)



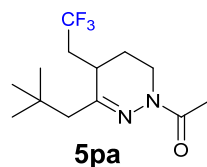
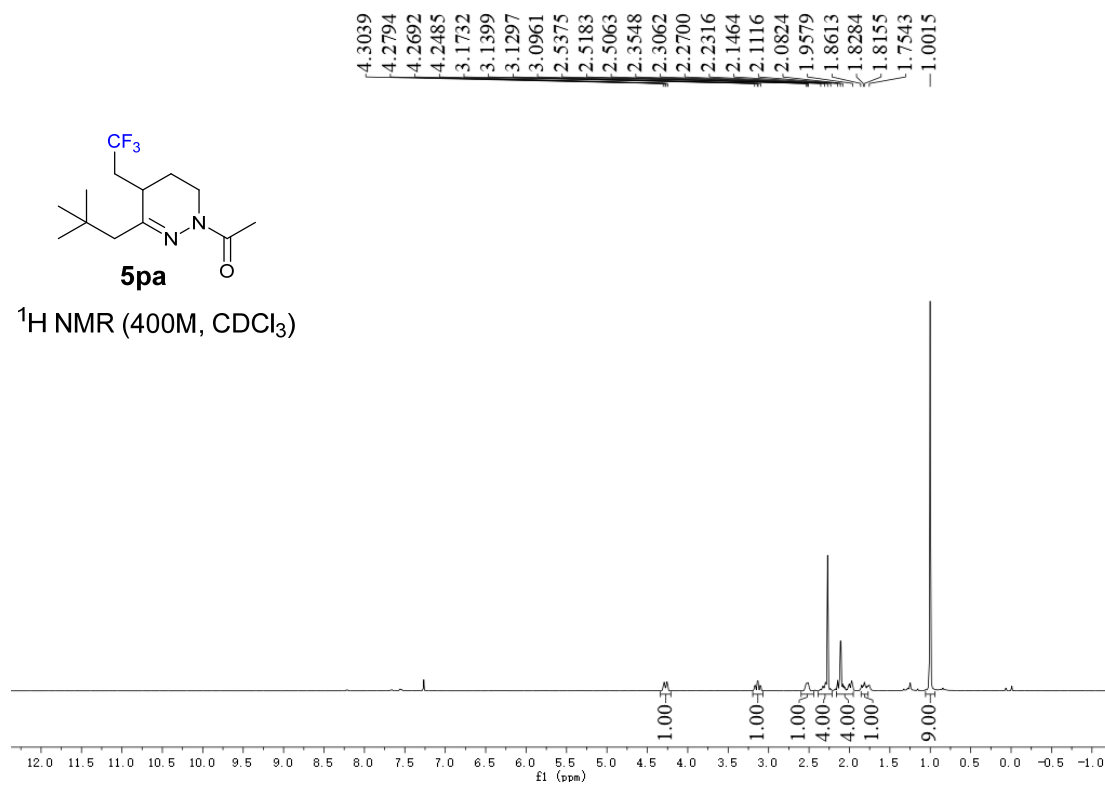
^1H NMR (400M, CDCl_3)



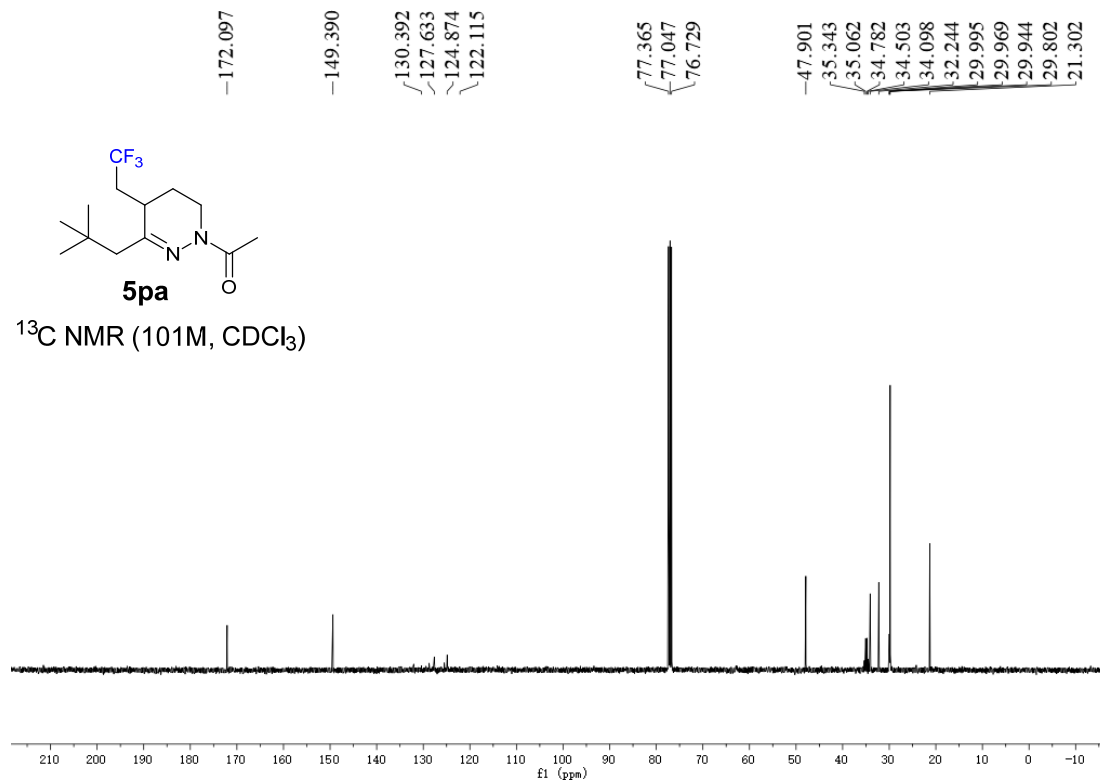


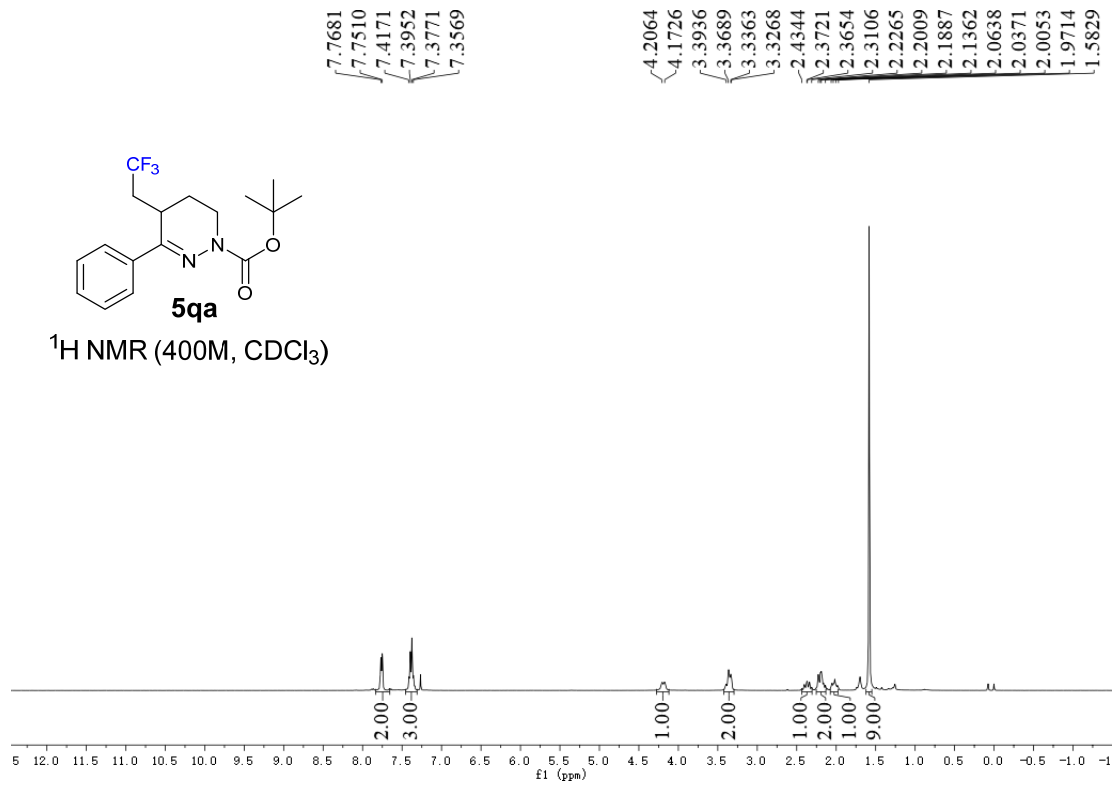
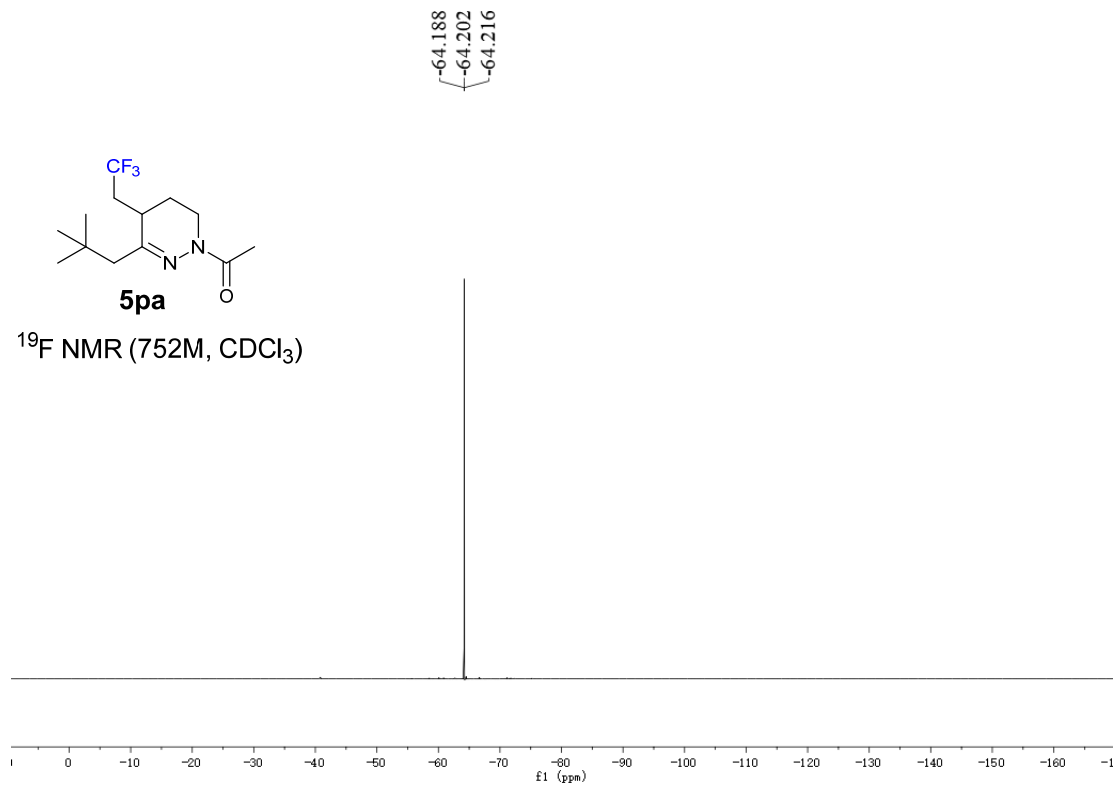


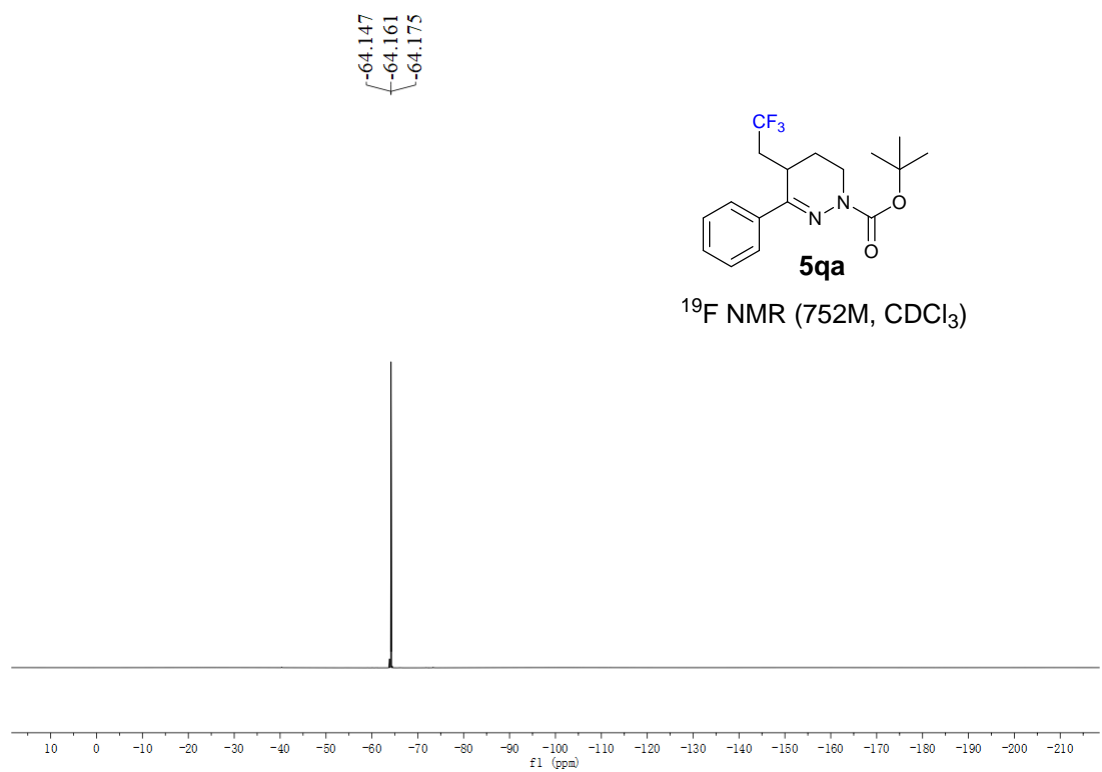
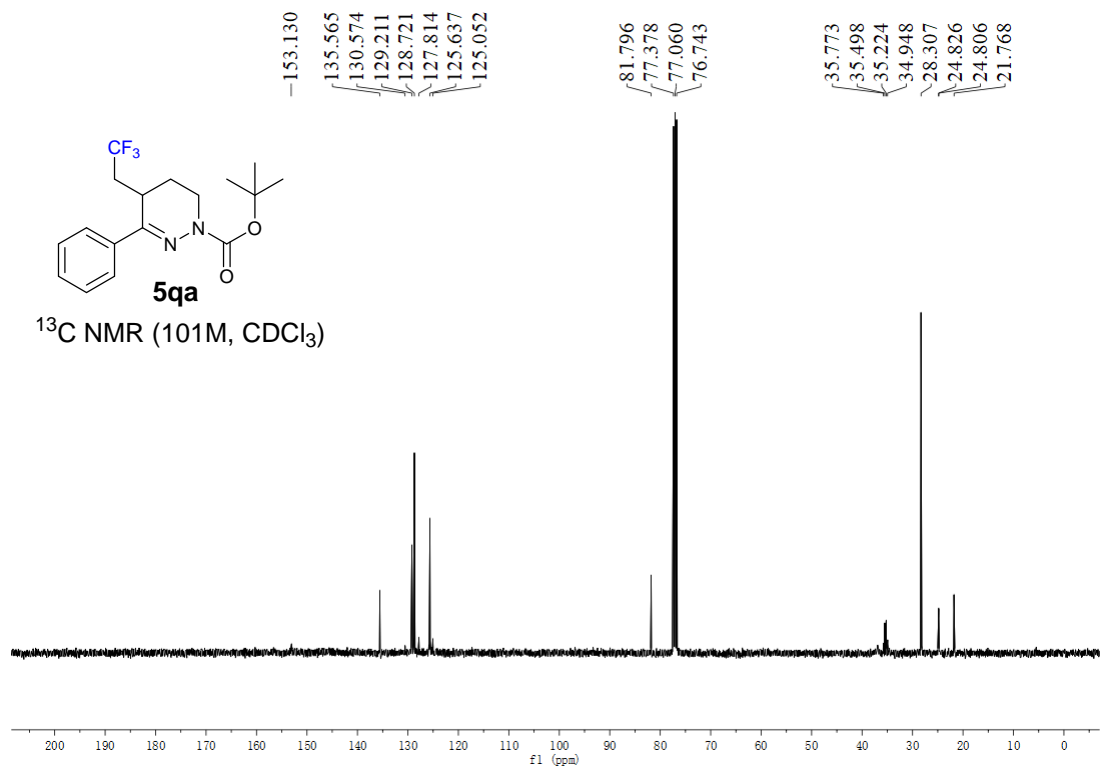
$^1\text{H NMR}$ (400M, CDCl_3)

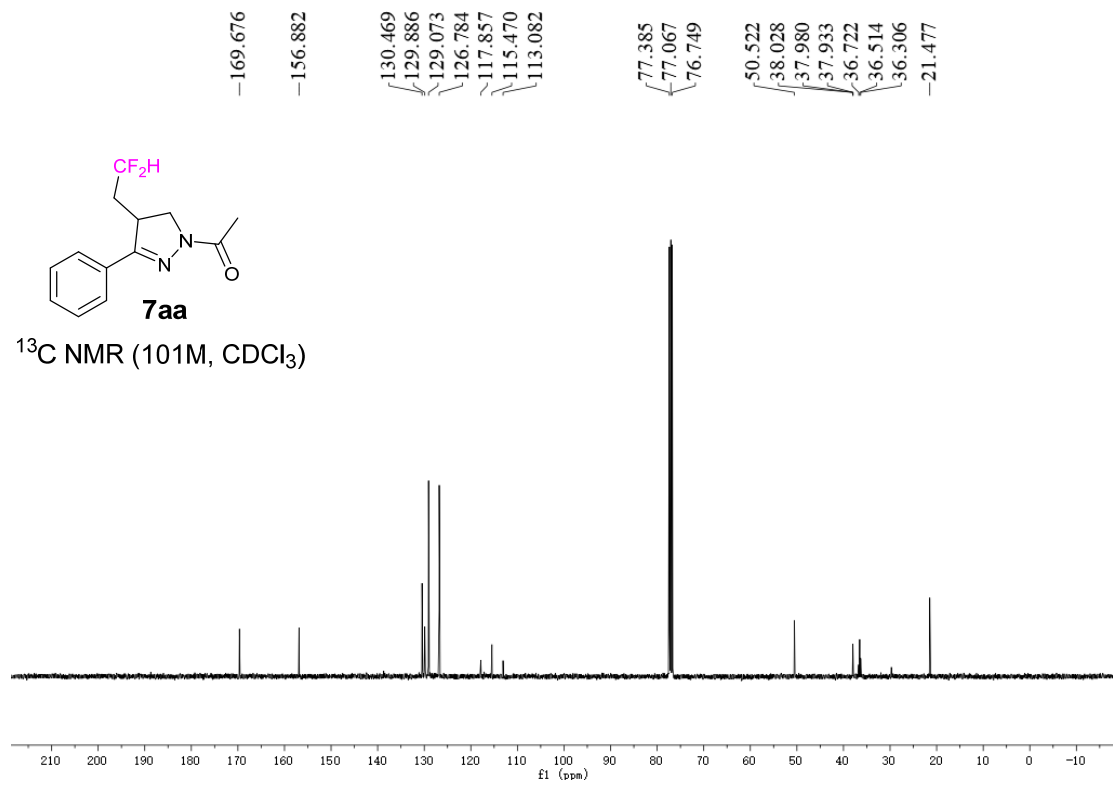
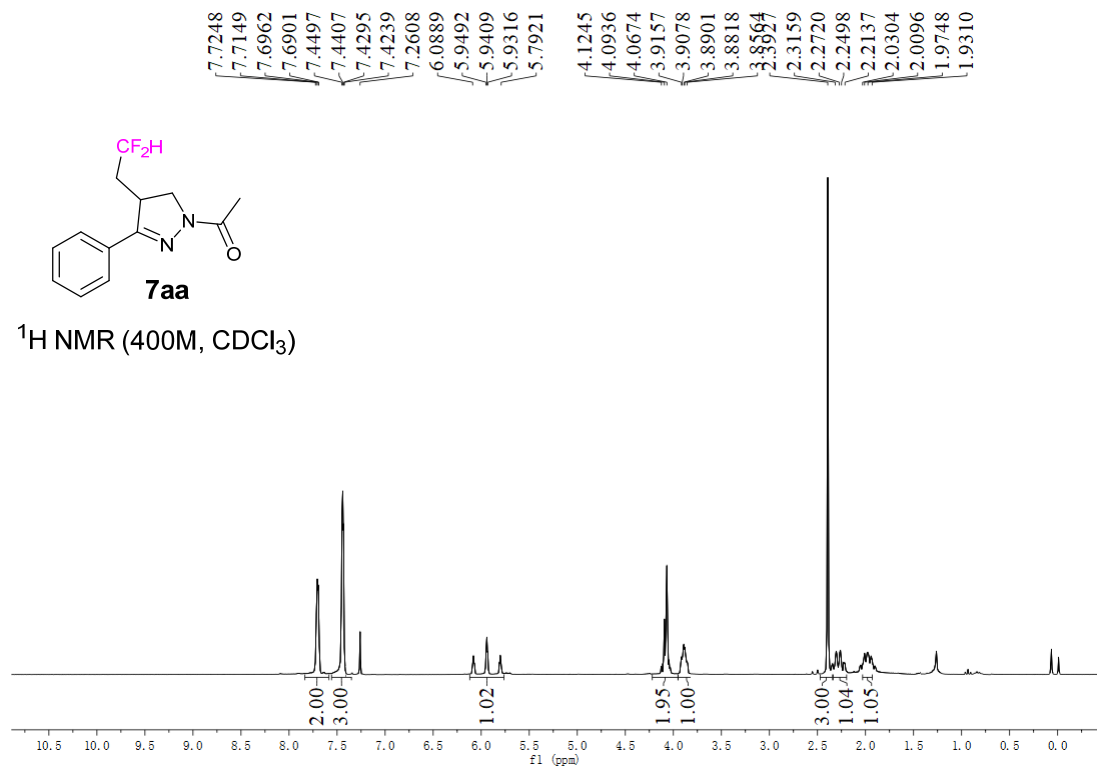


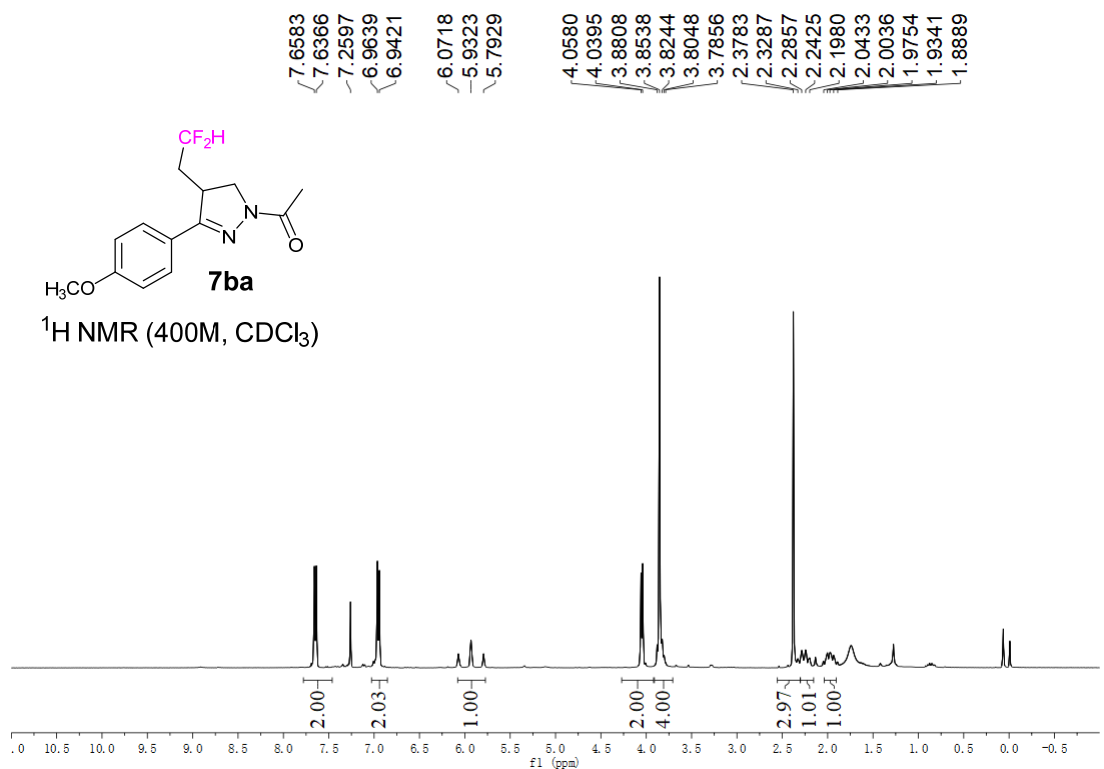
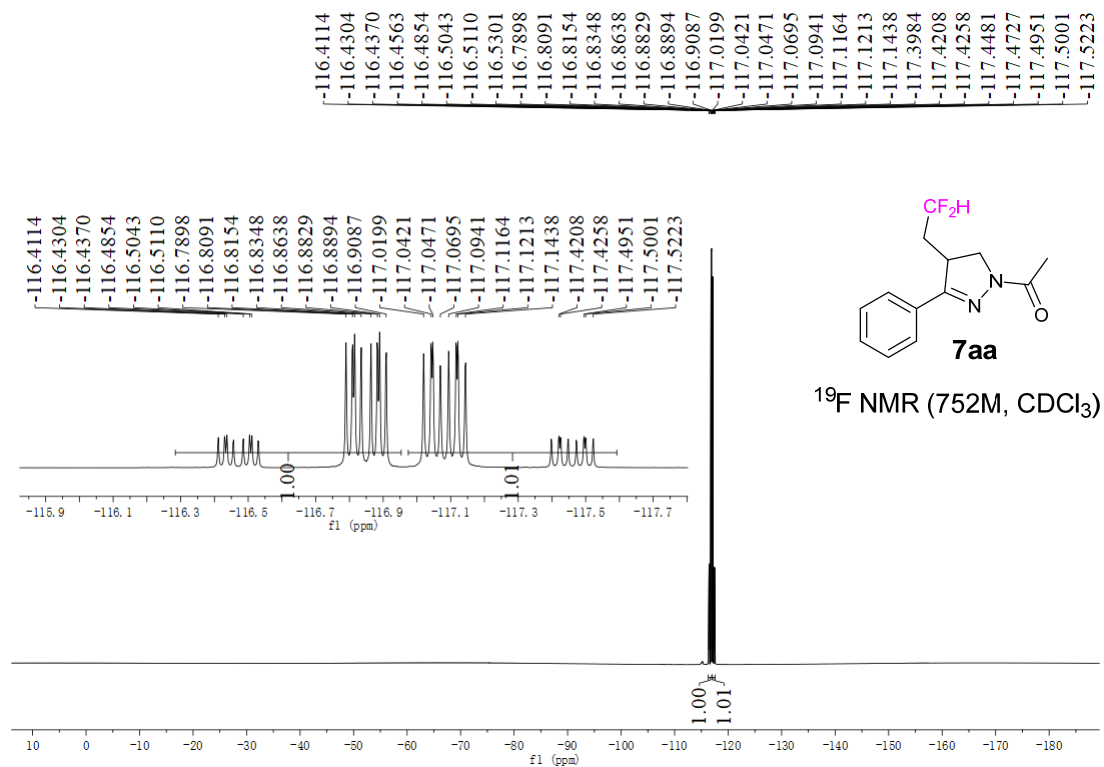
$^{13}\text{C NMR}$ (101M, CDCl_3)

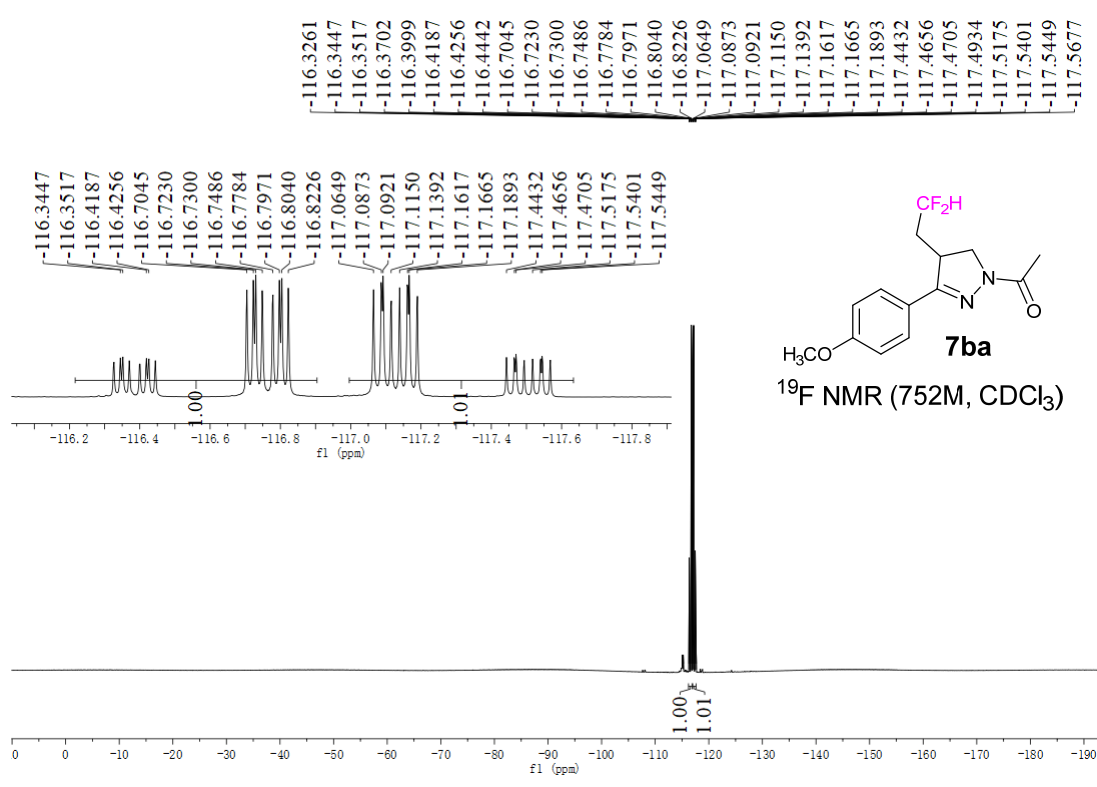
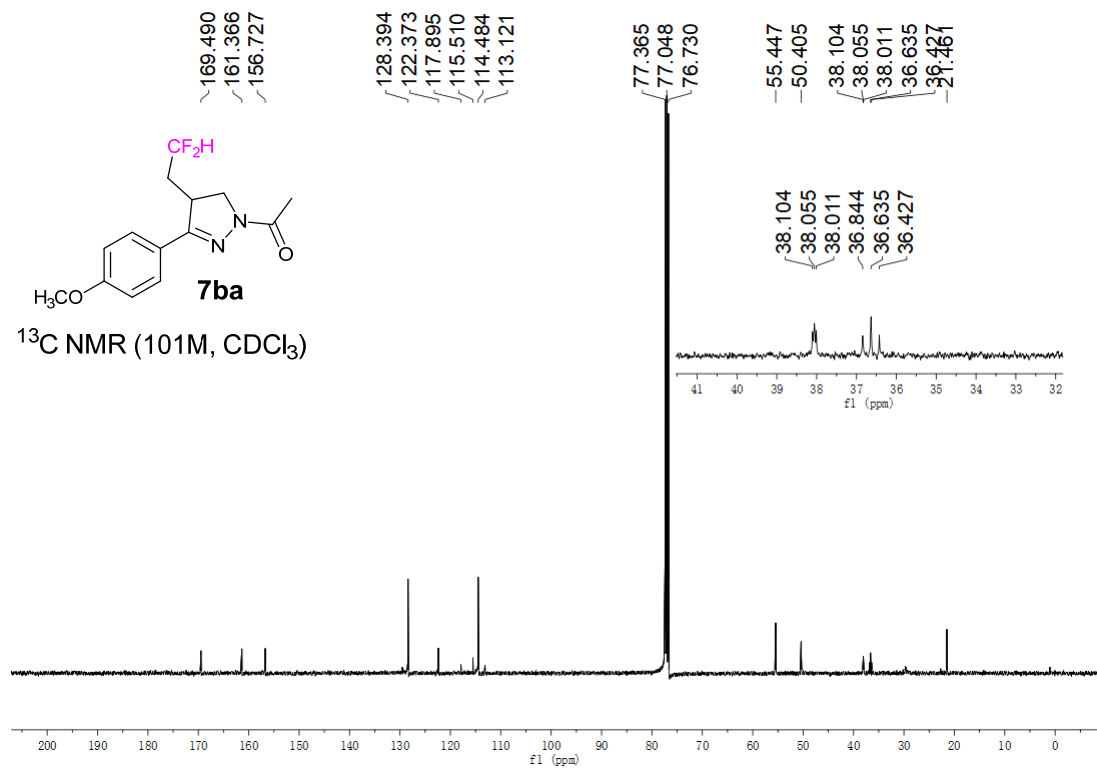


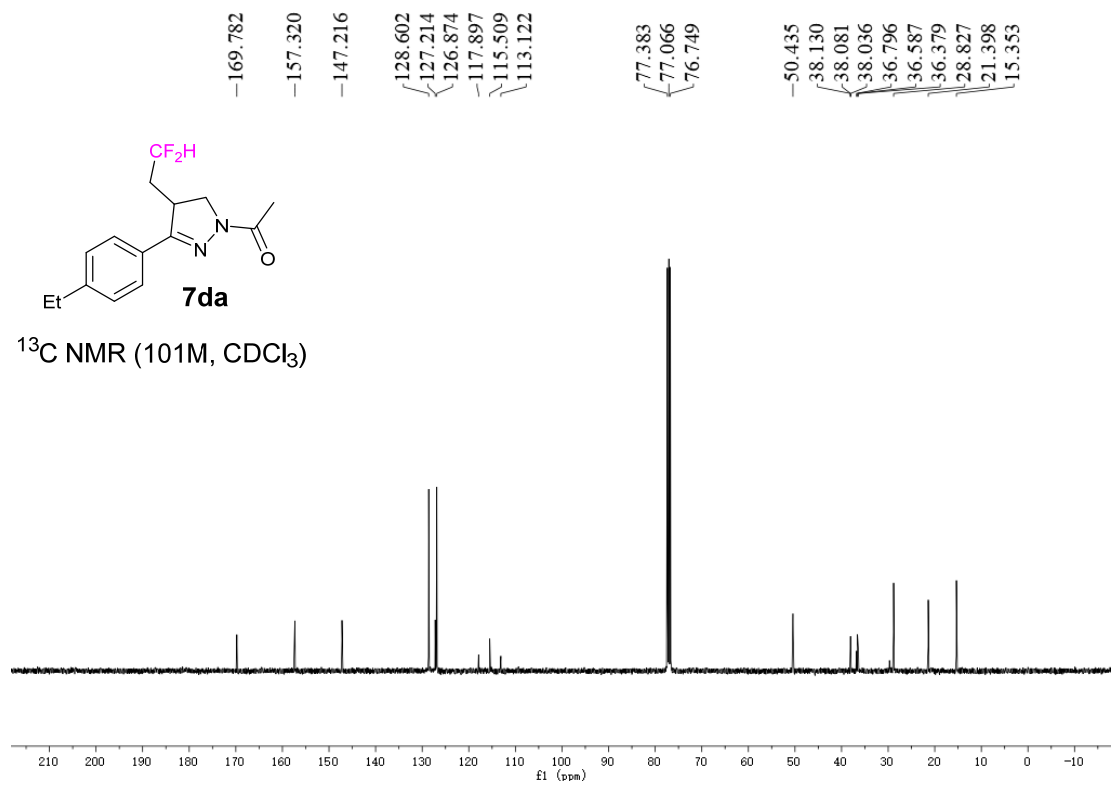
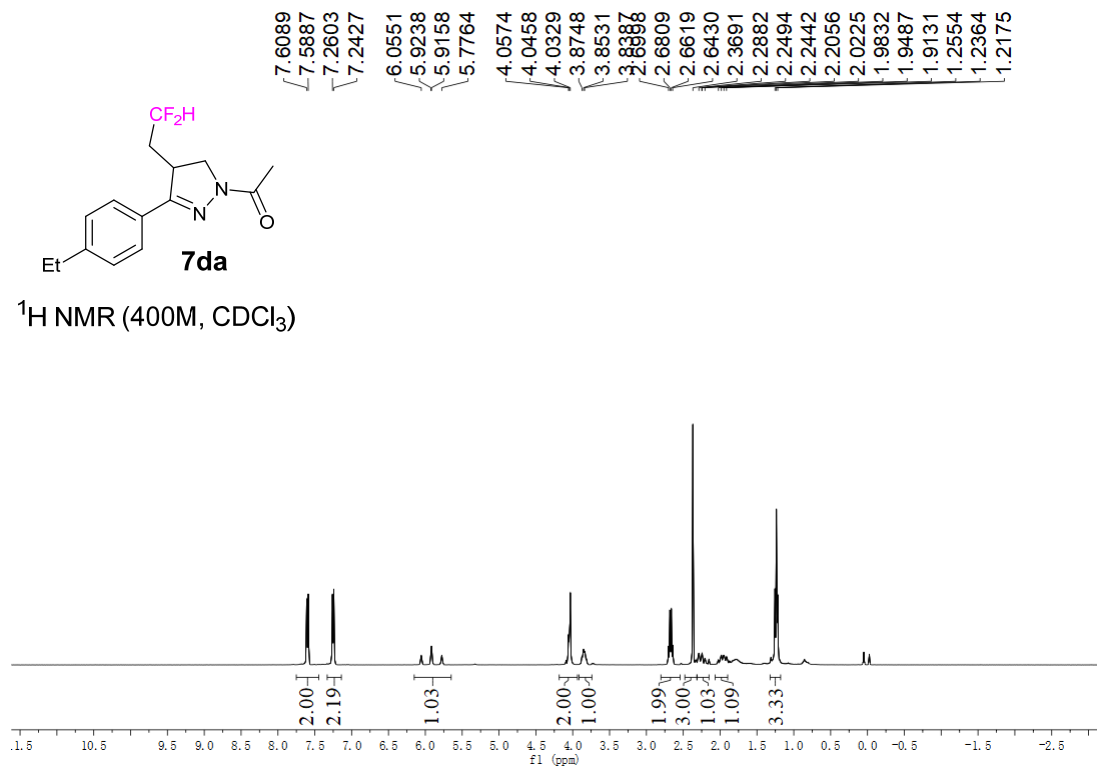


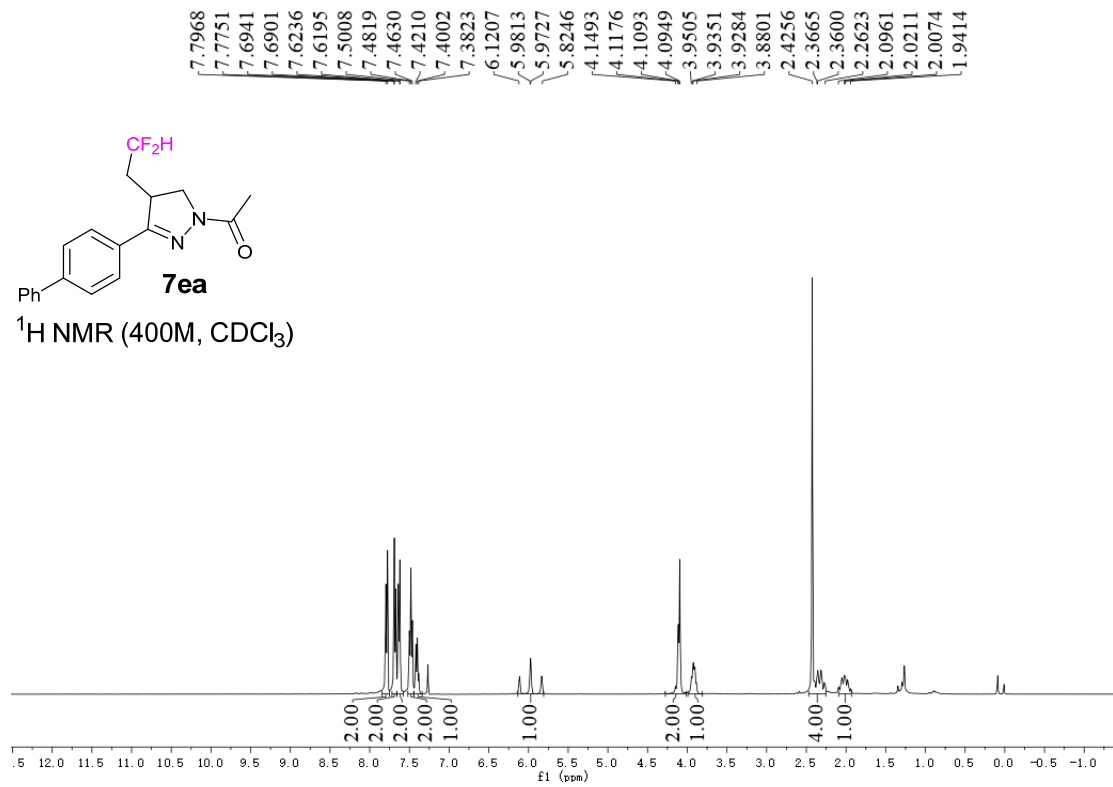
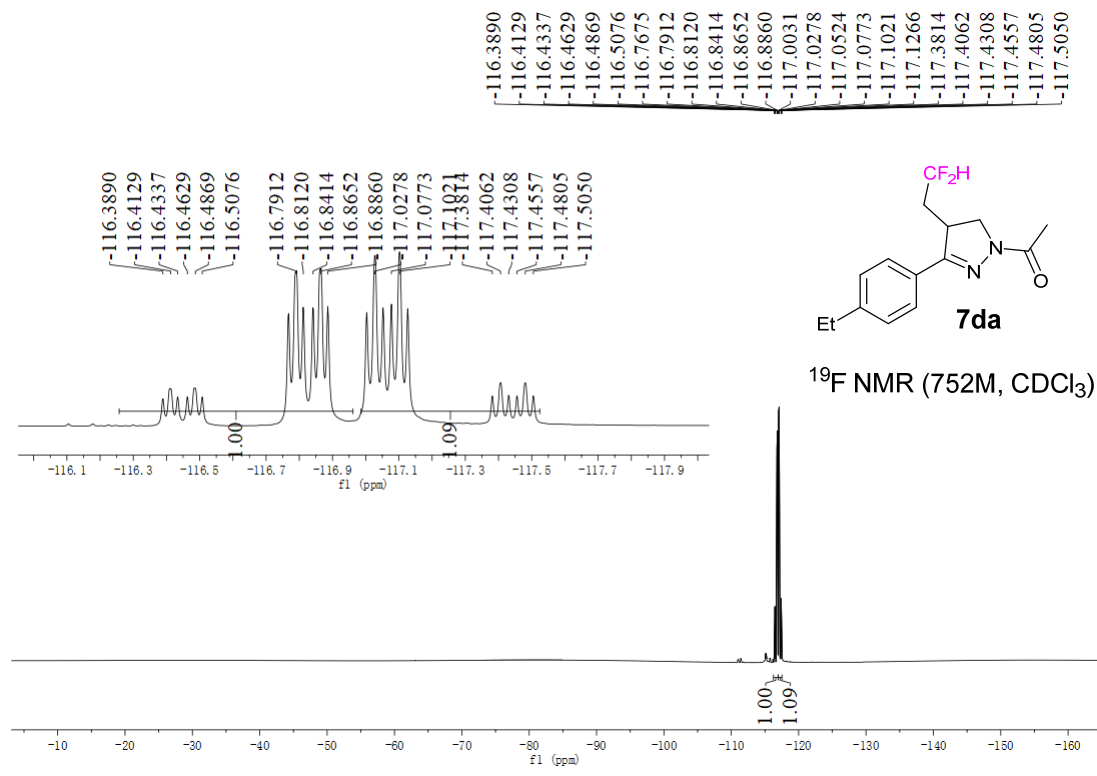


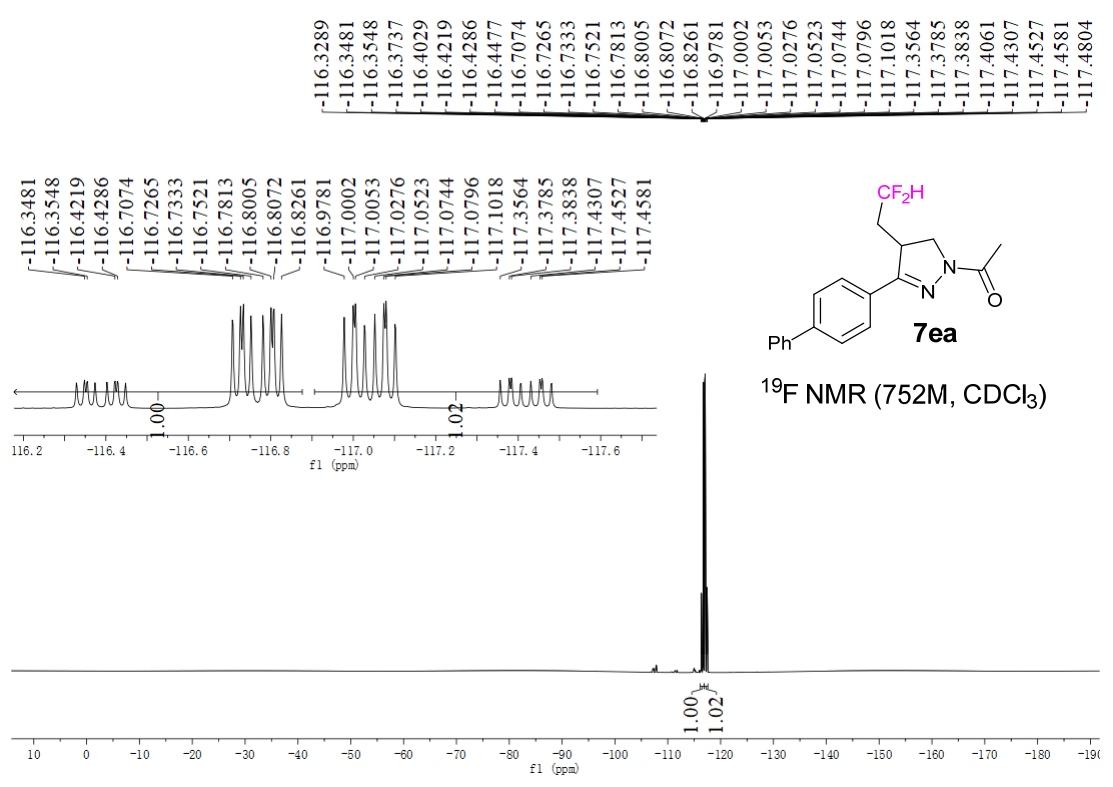
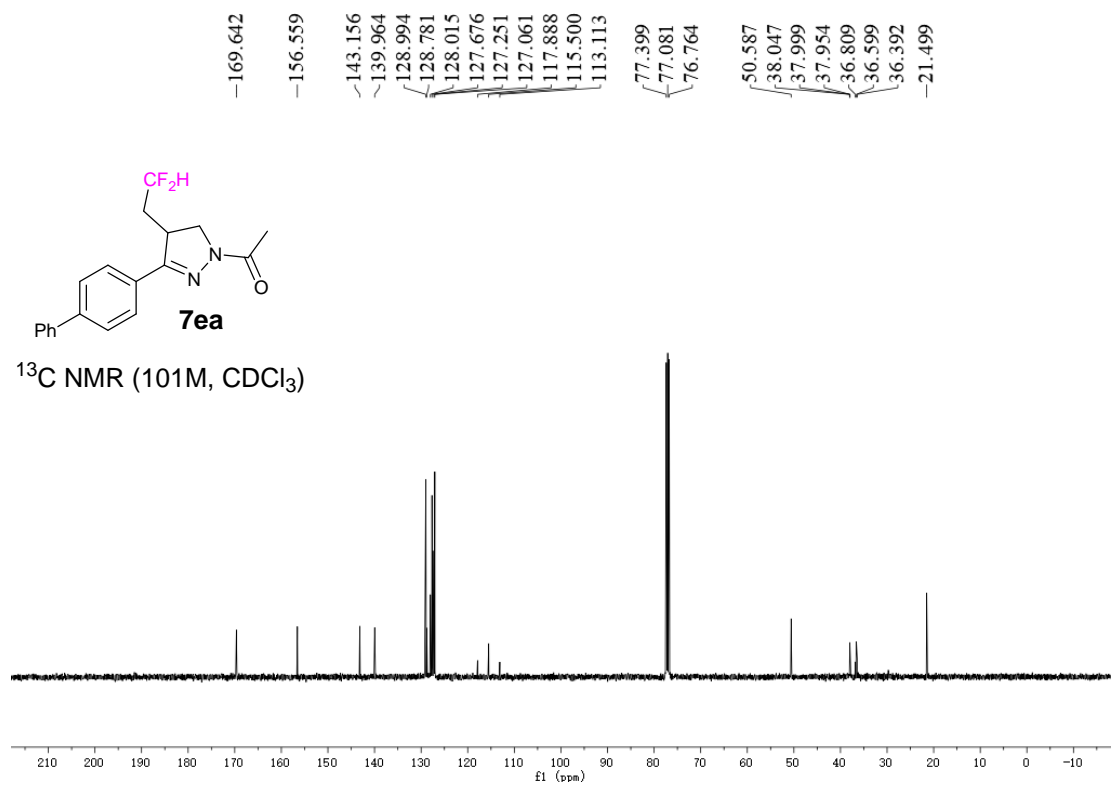


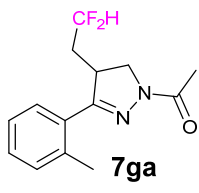




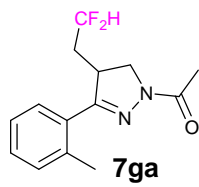
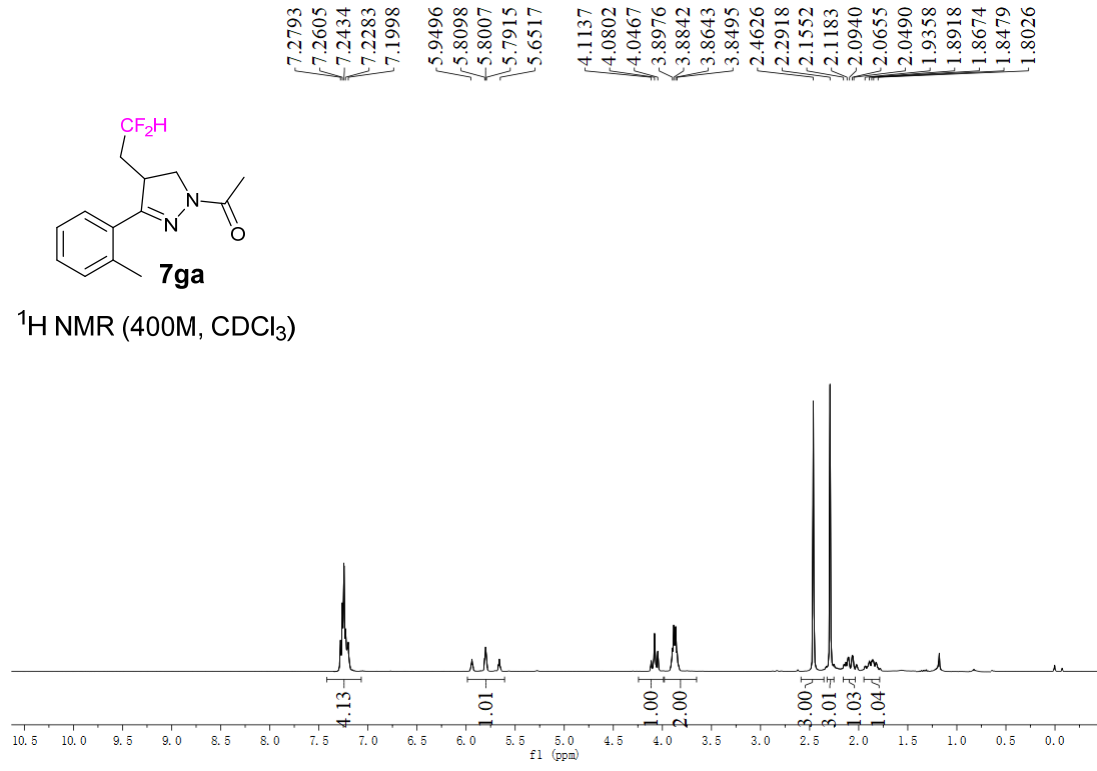




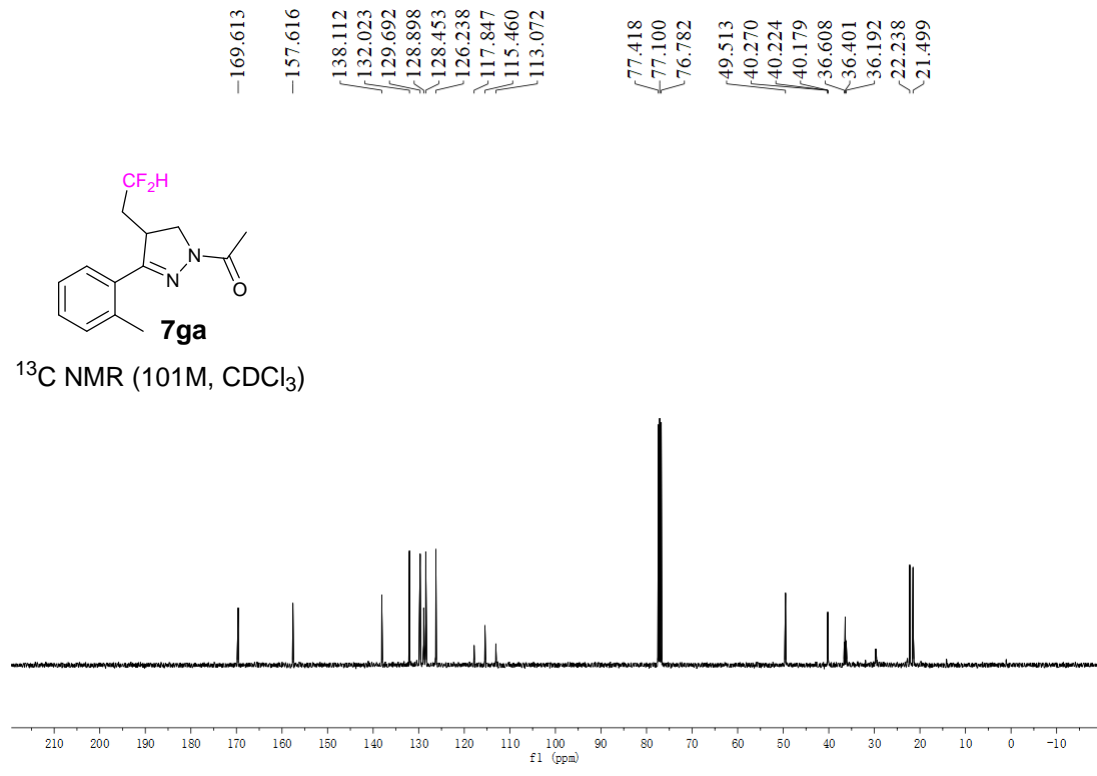


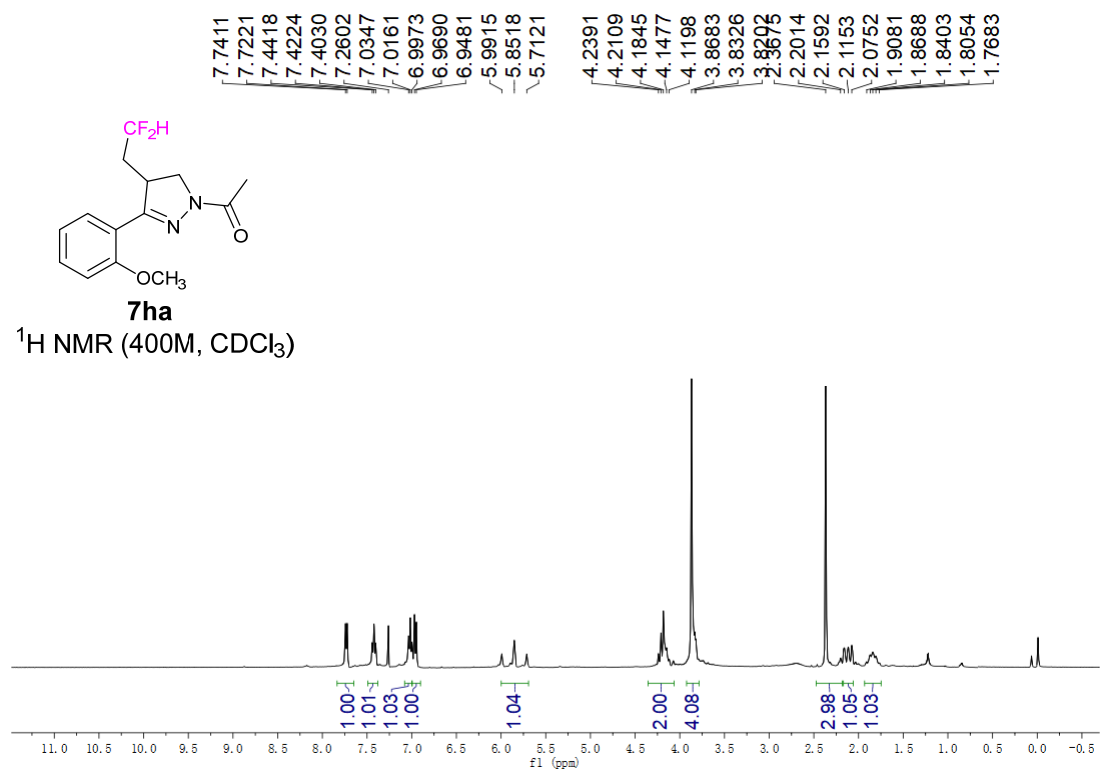
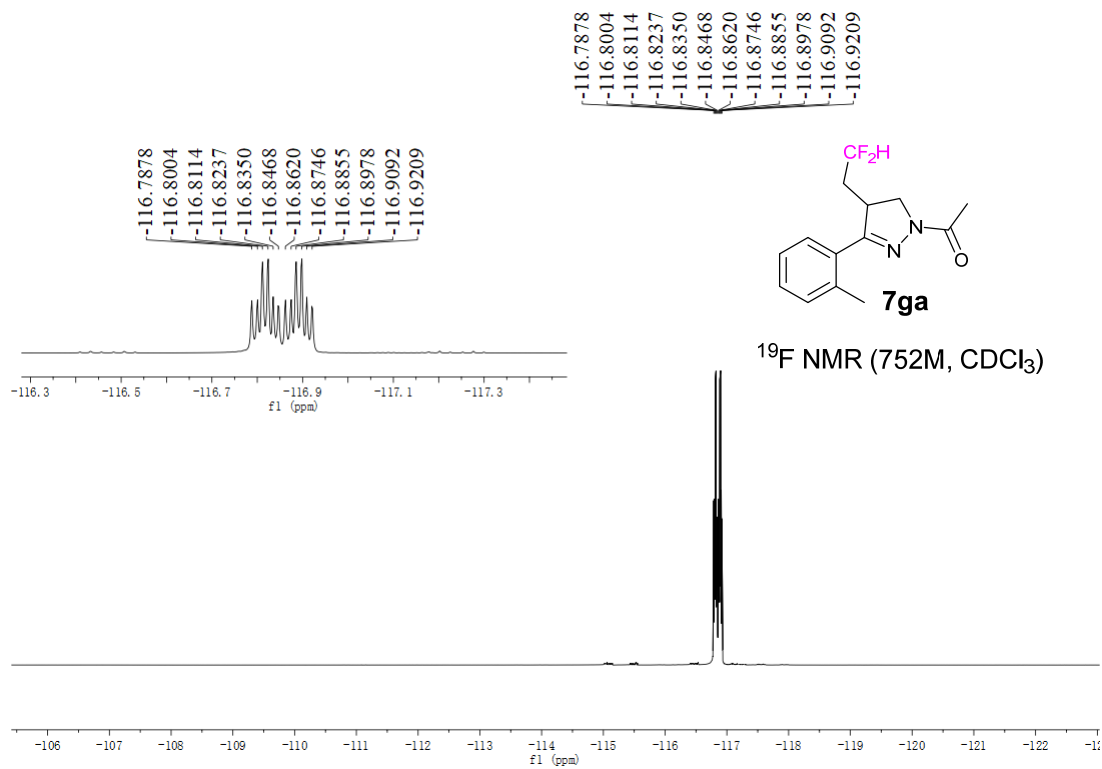


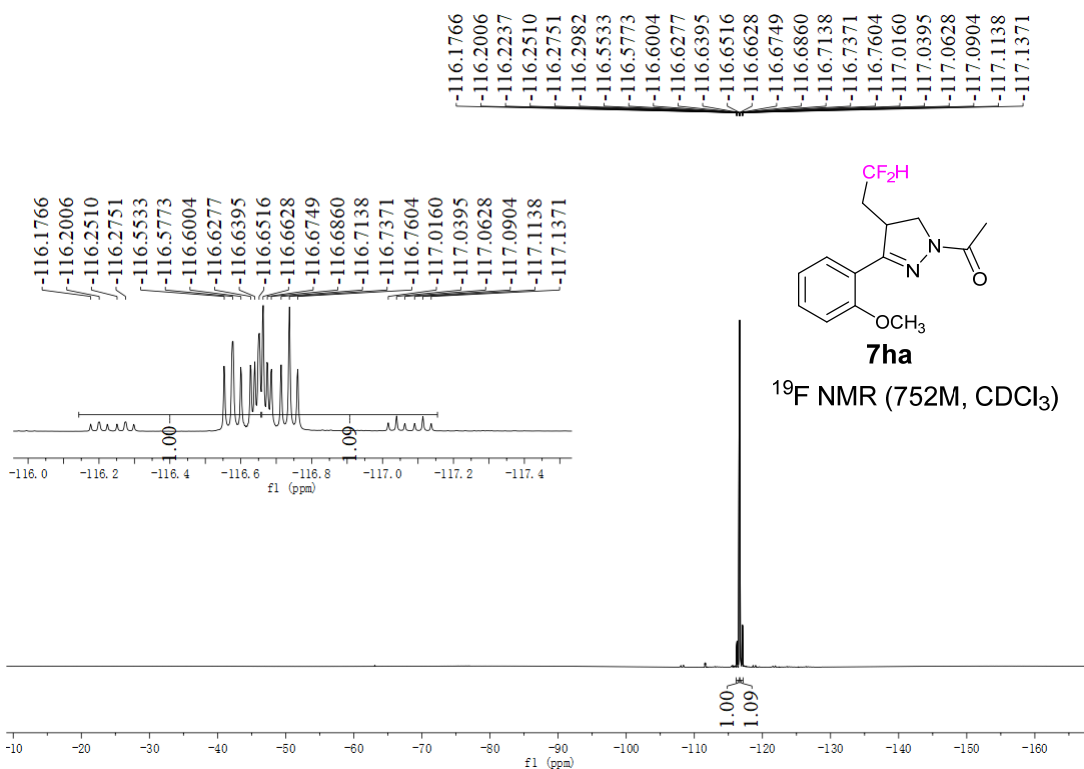
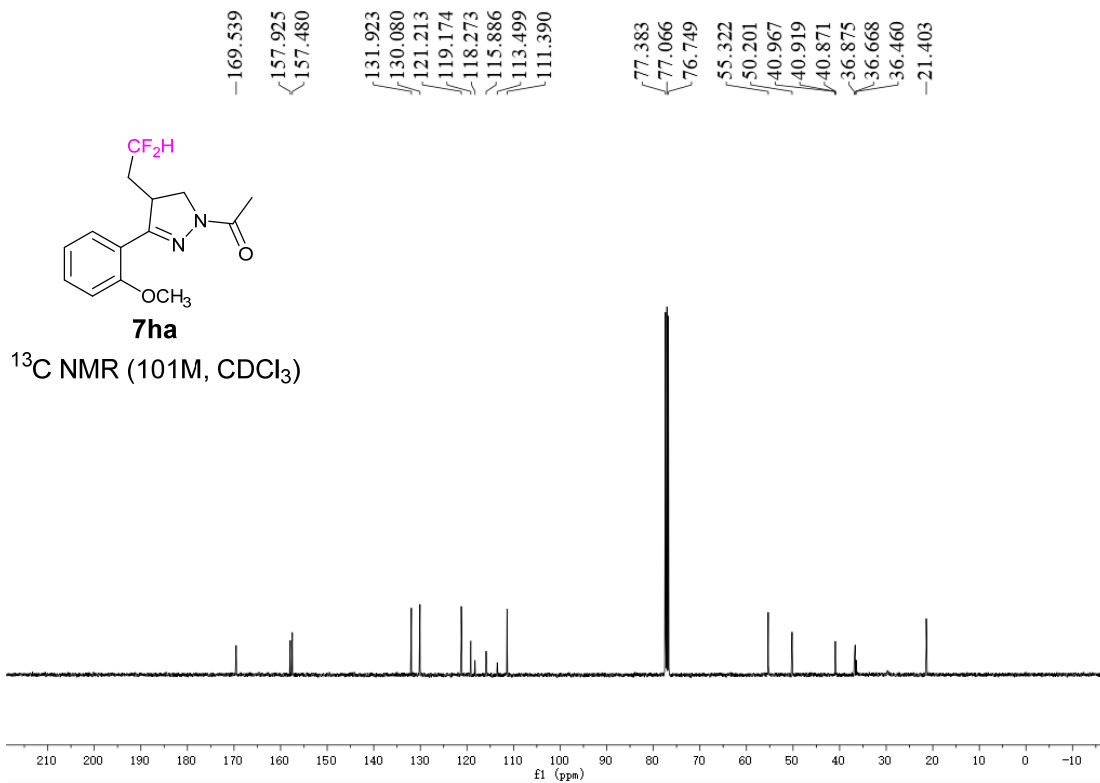
$^1\text{H NMR}$ (400M, CDCl_3)

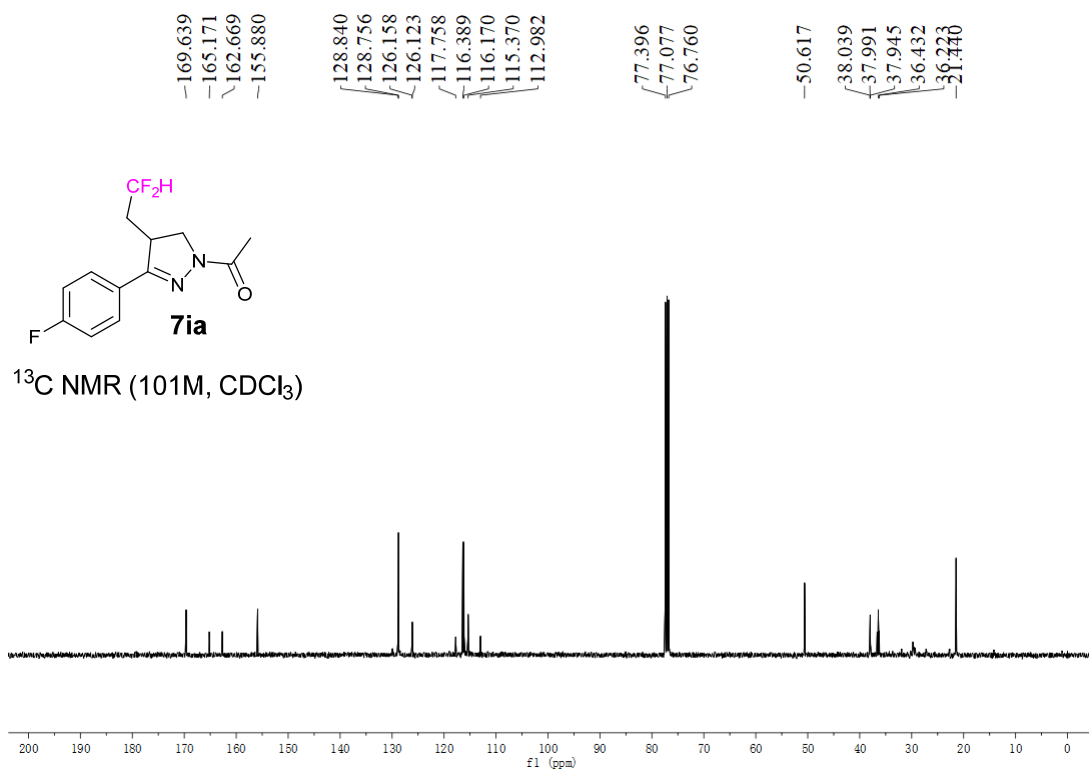
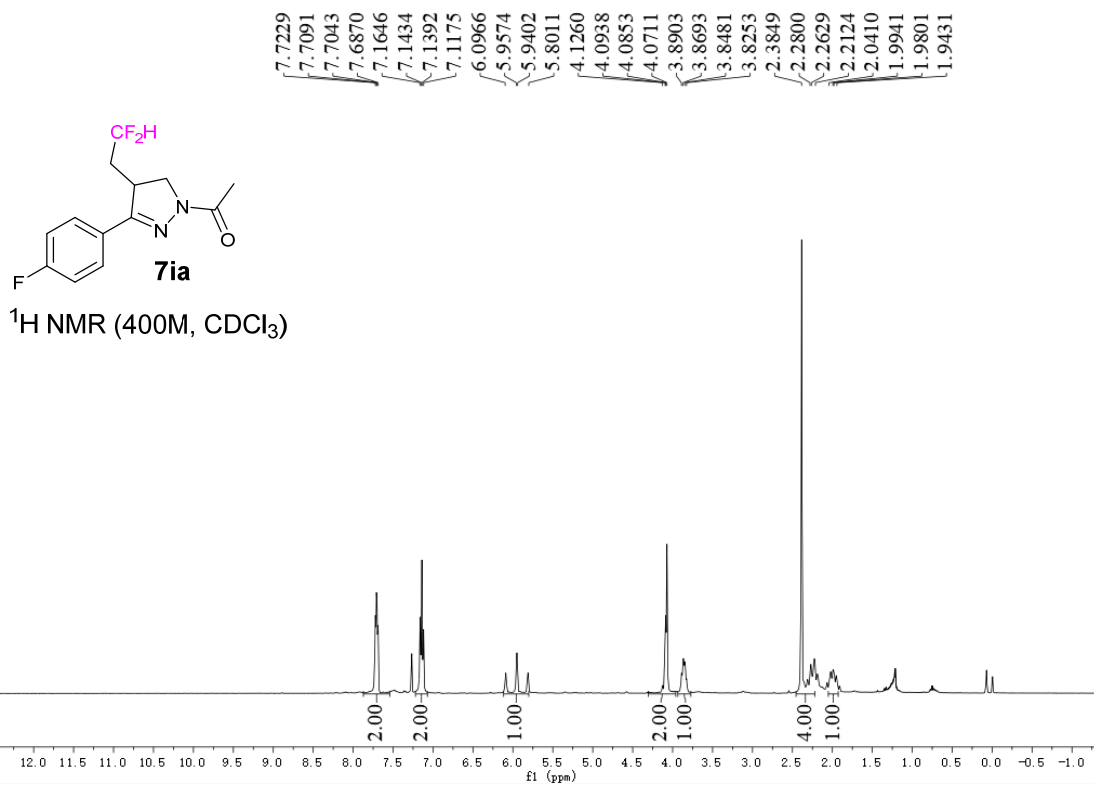


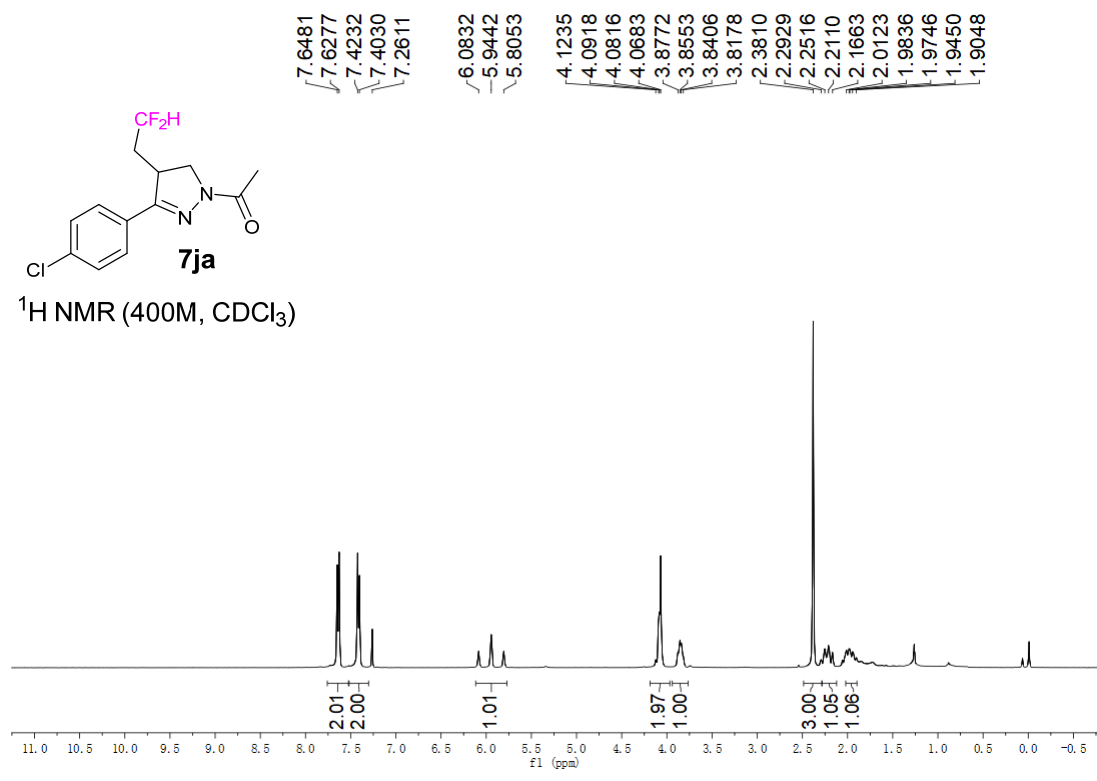
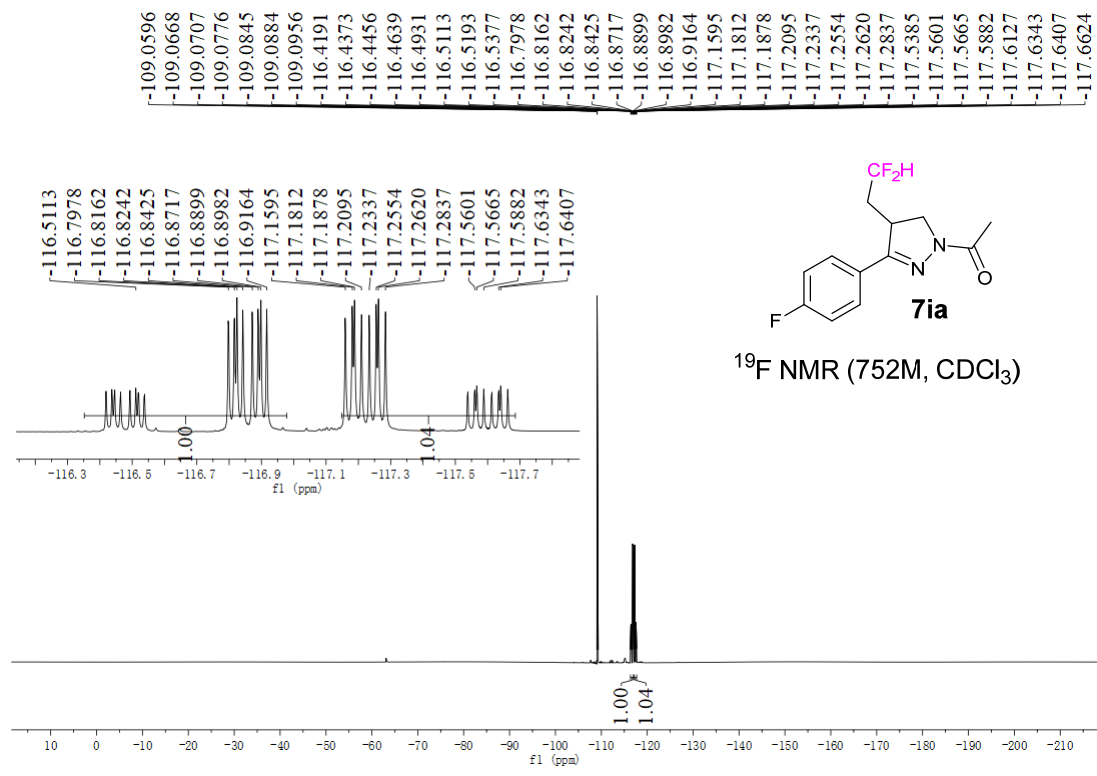
$^{13}\text{C NMR}$ (101M, CDCl_3)

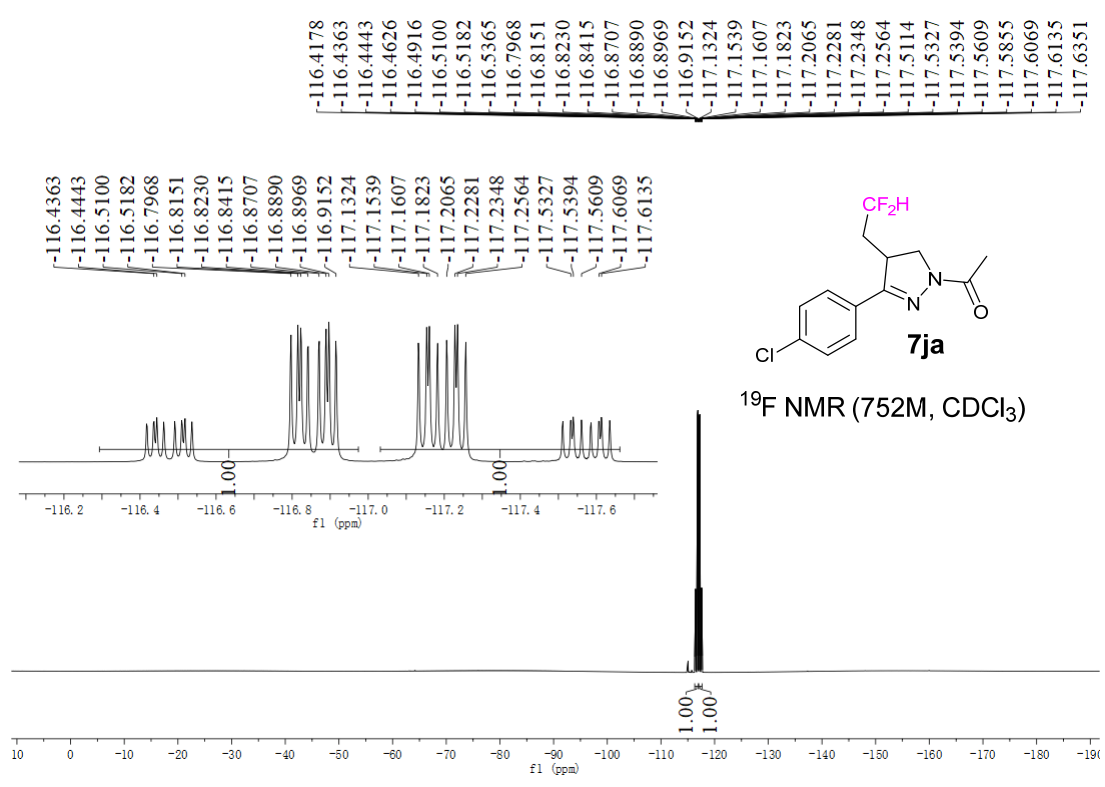
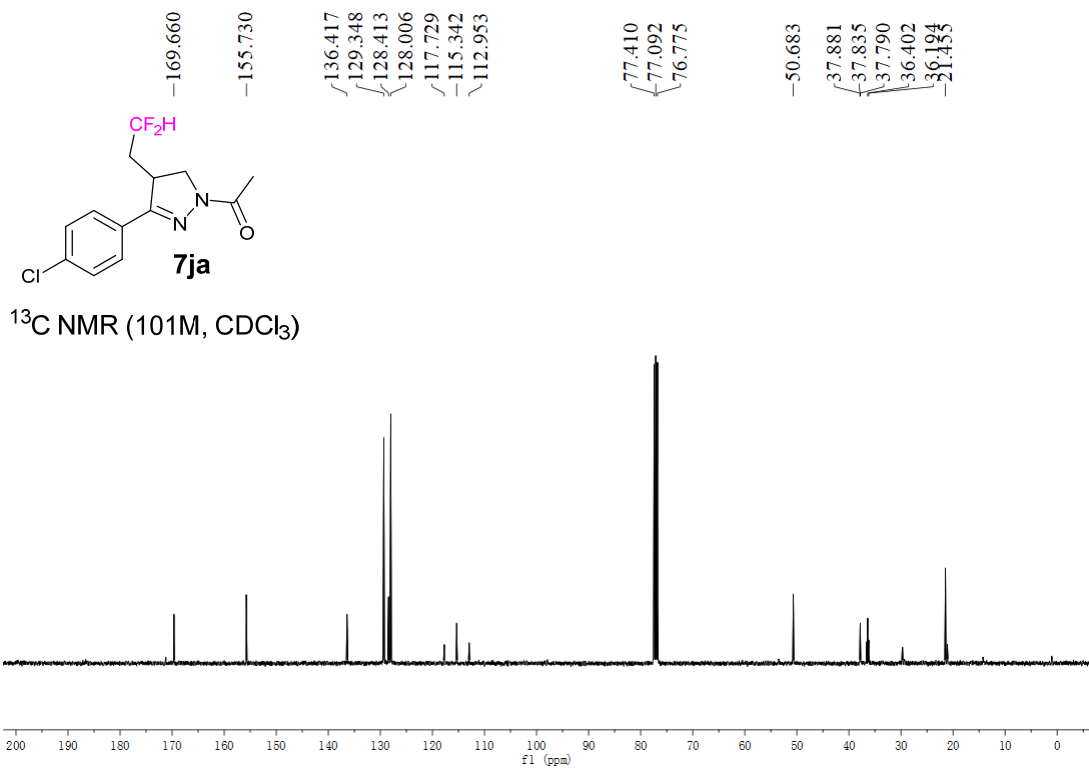


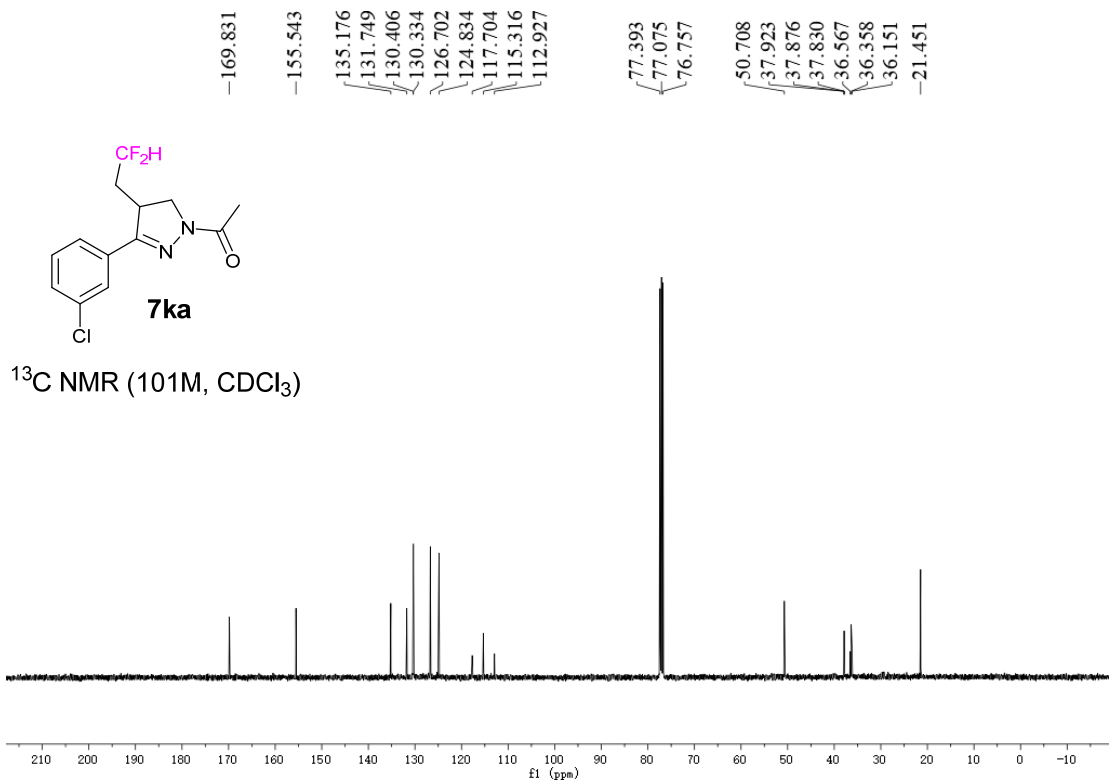
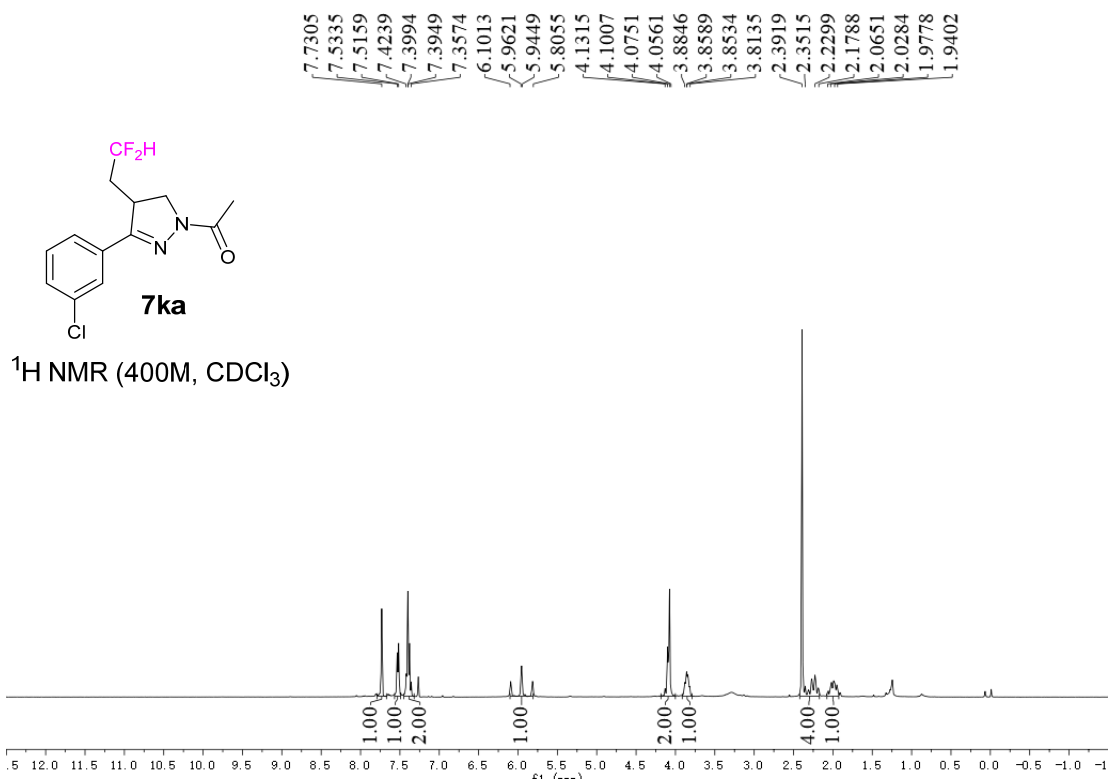


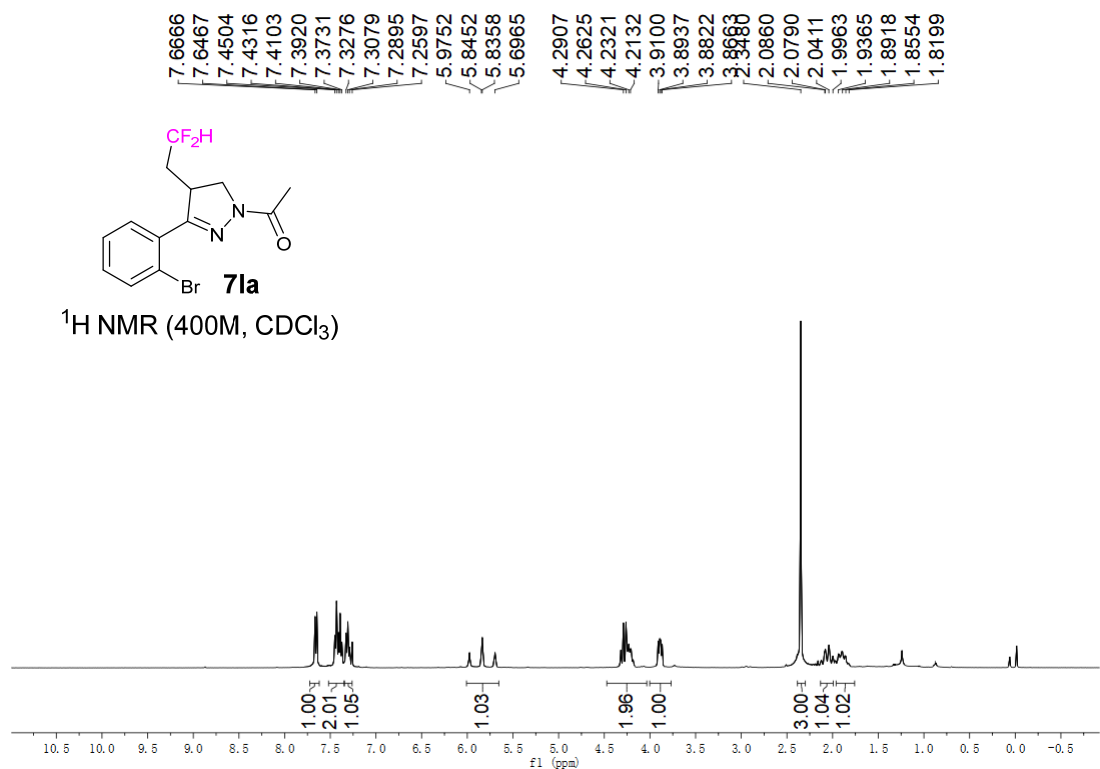
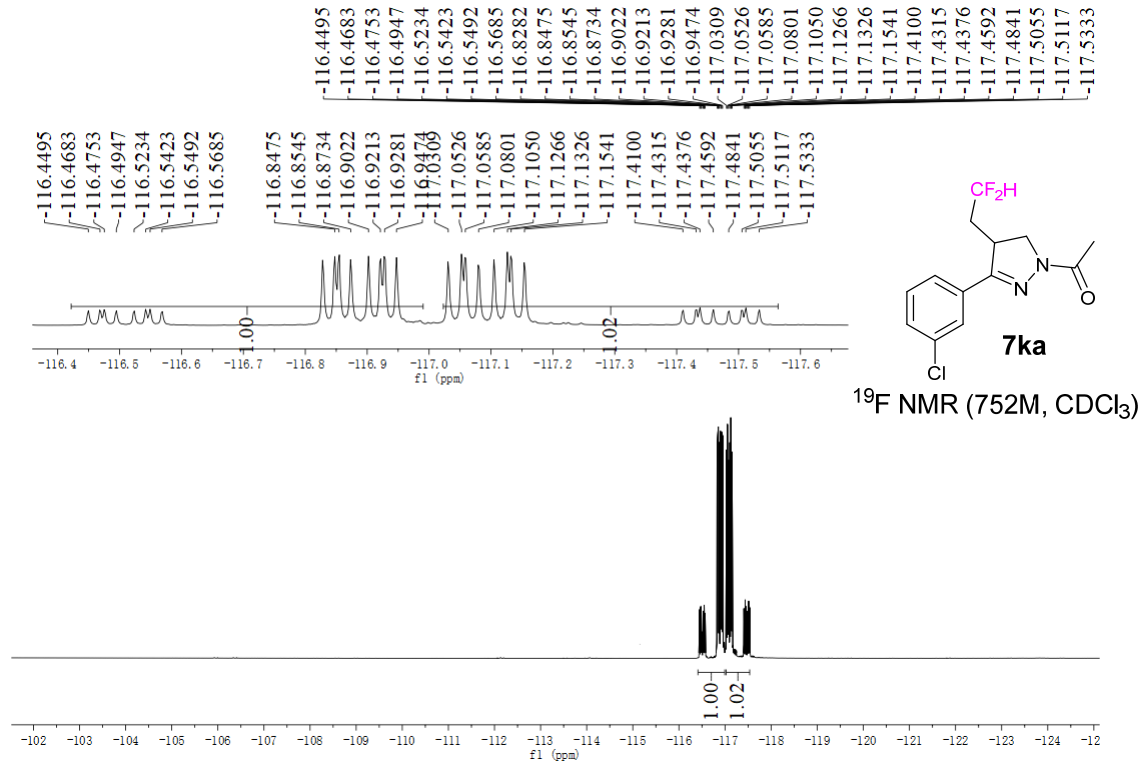


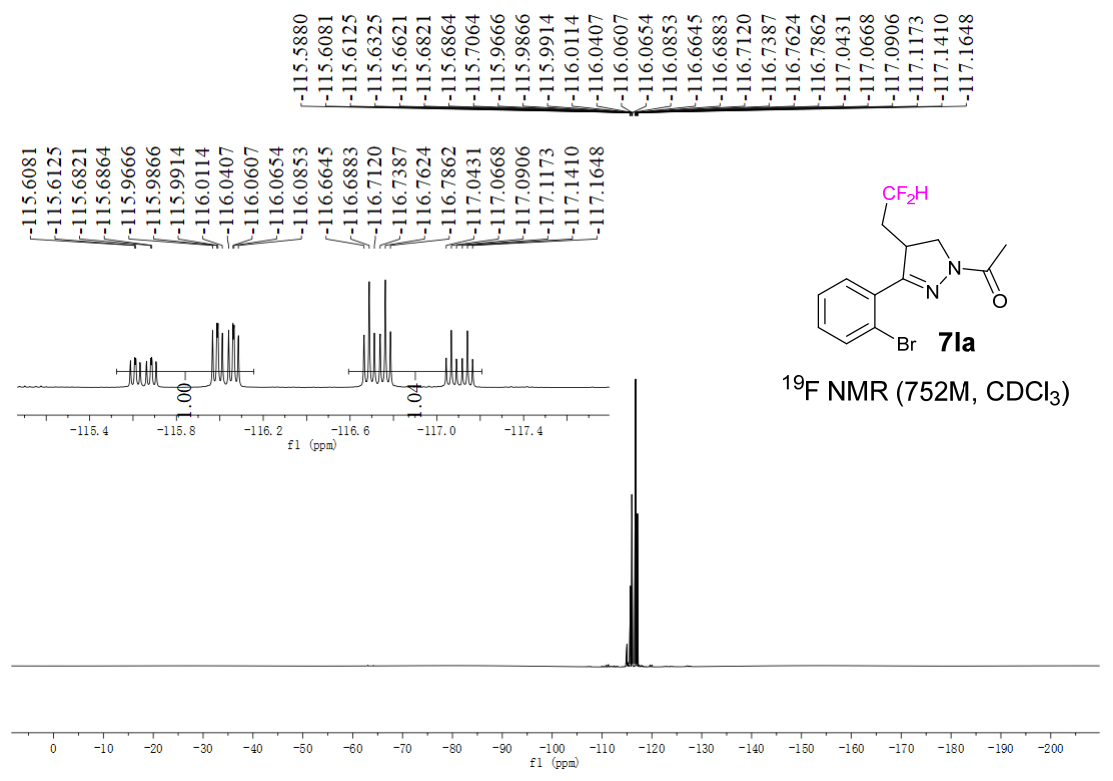
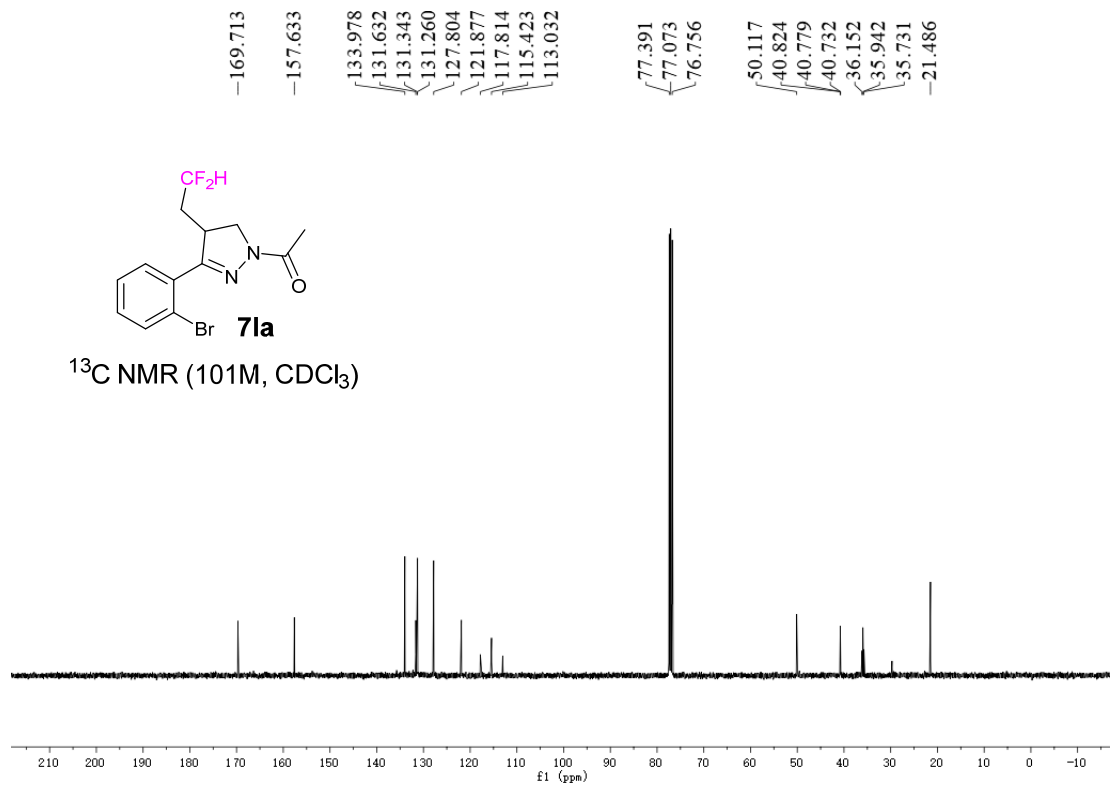


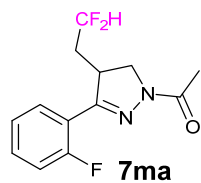




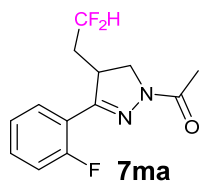
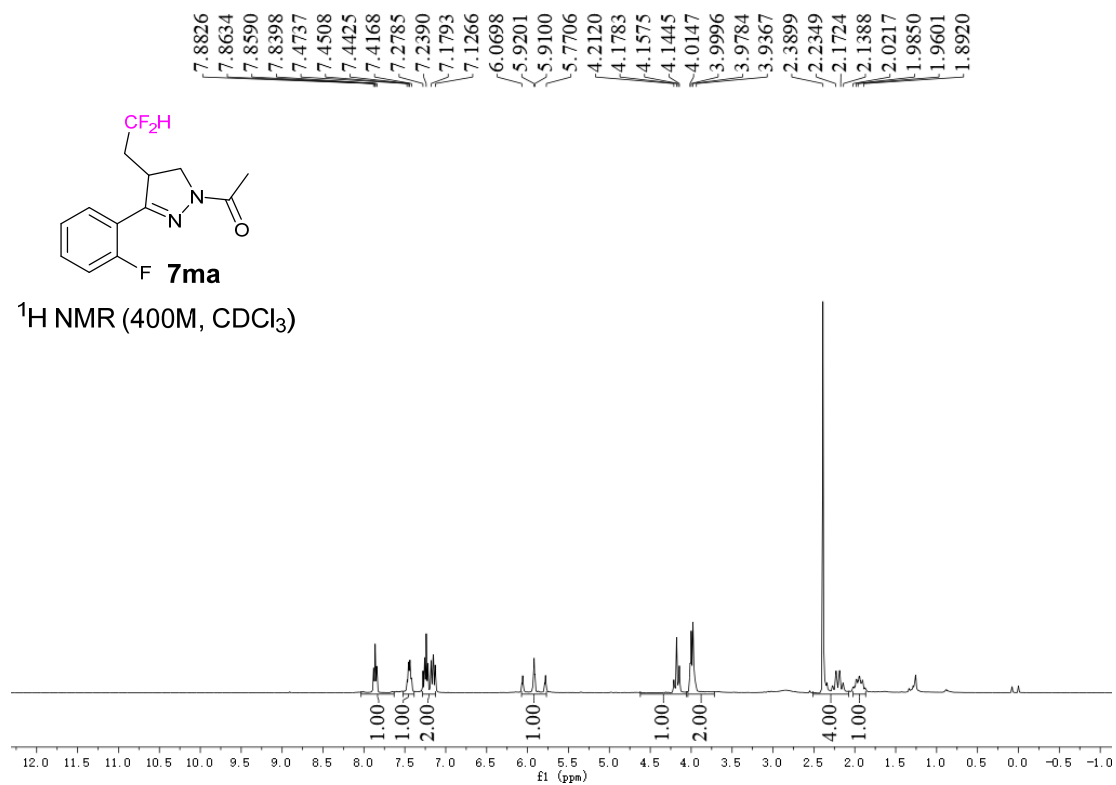




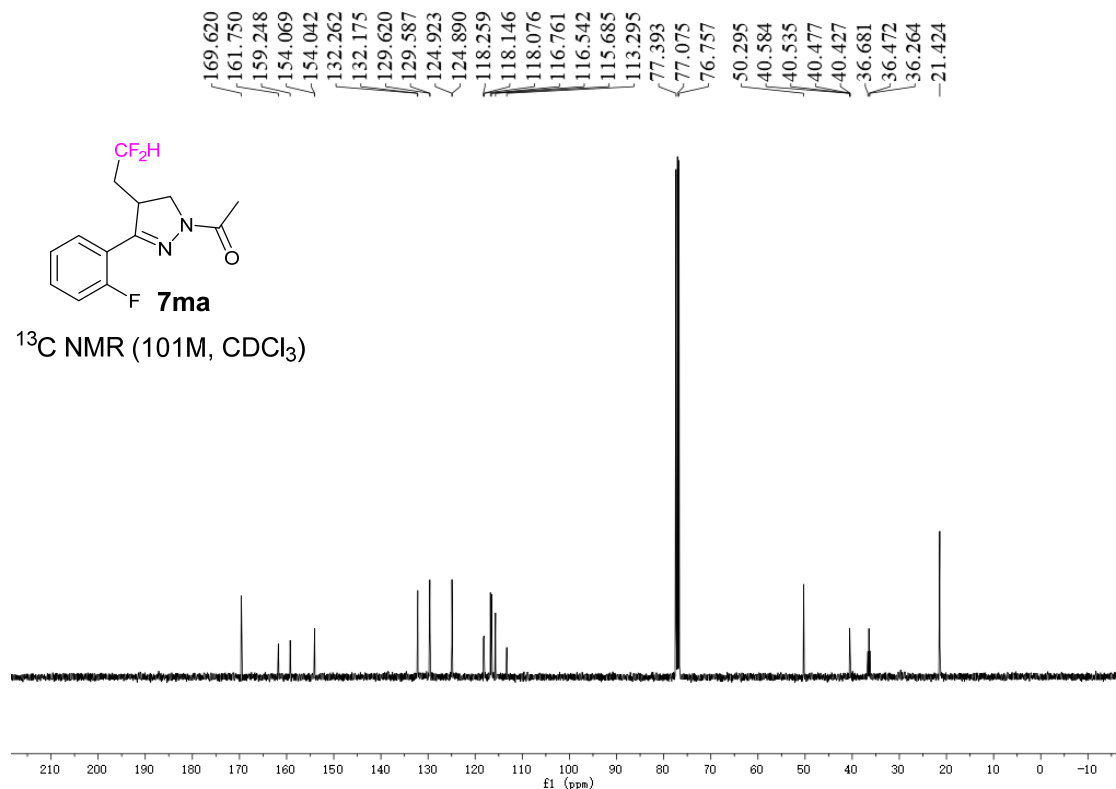


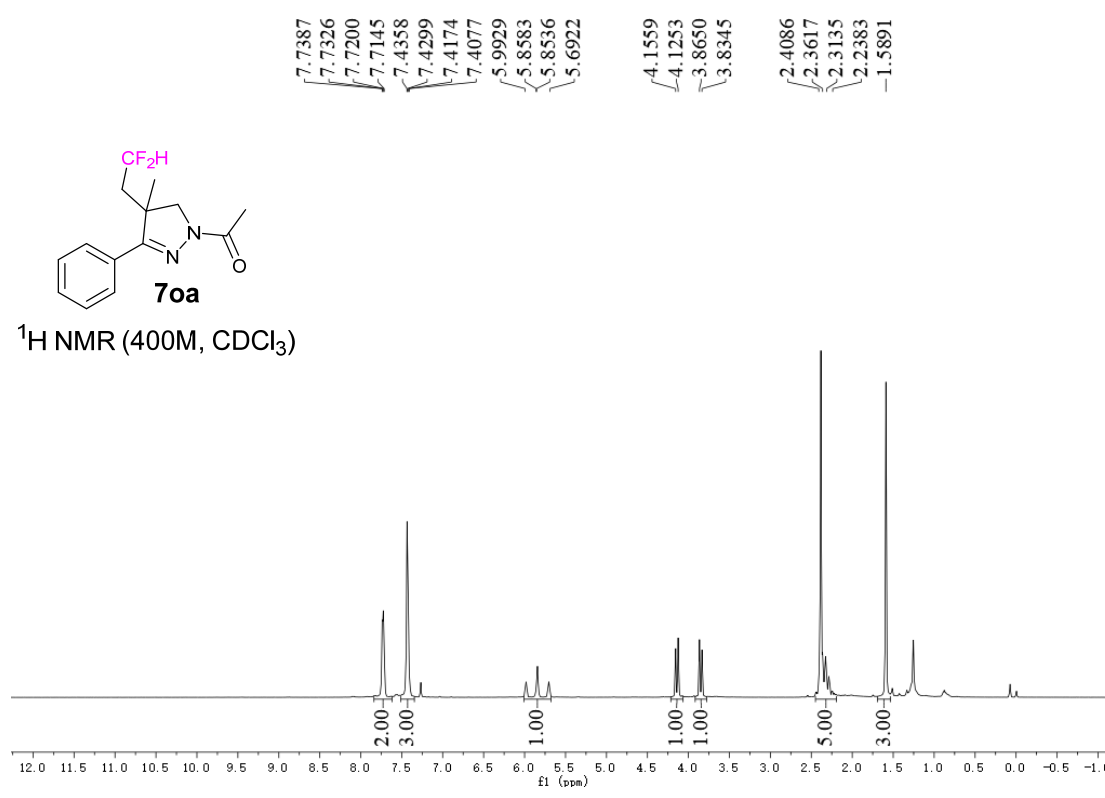
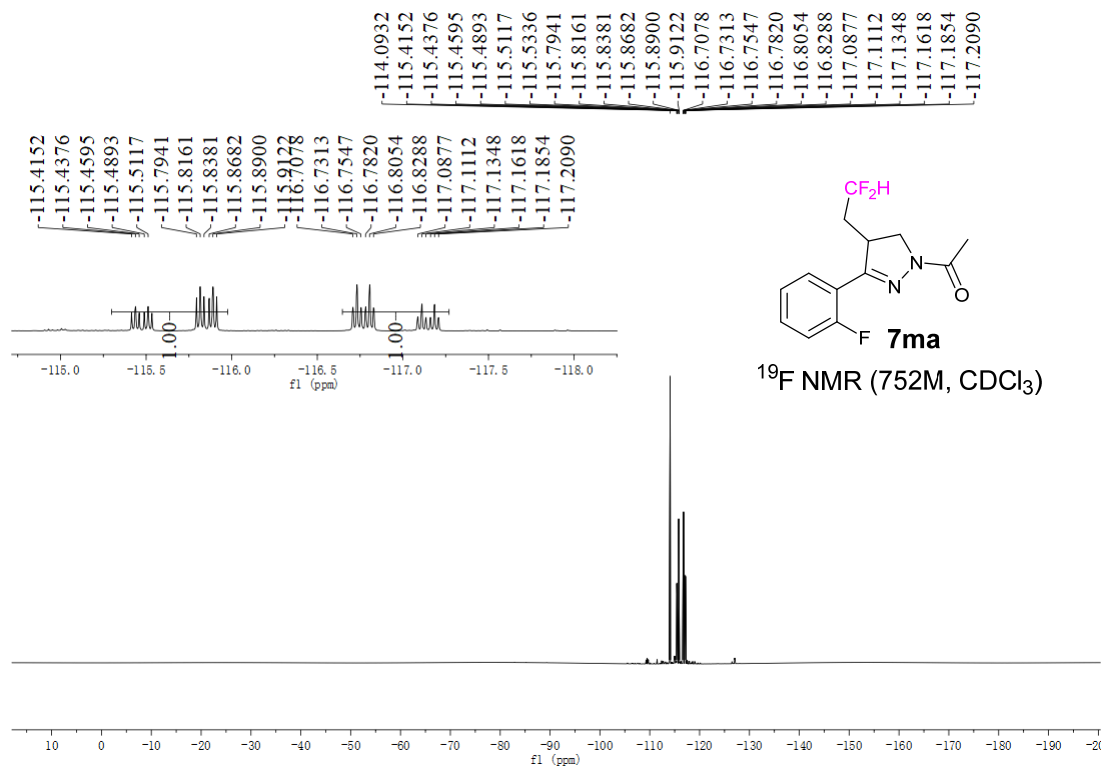


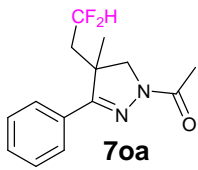
¹H NMR (400M, CDCl₃)



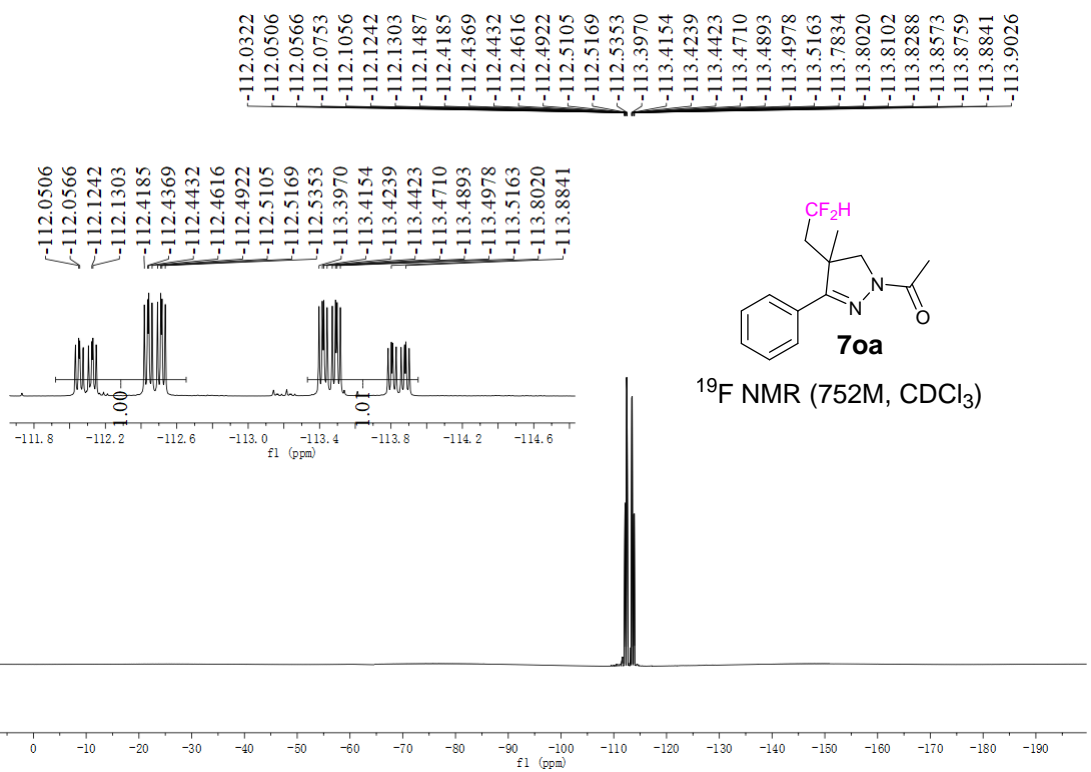
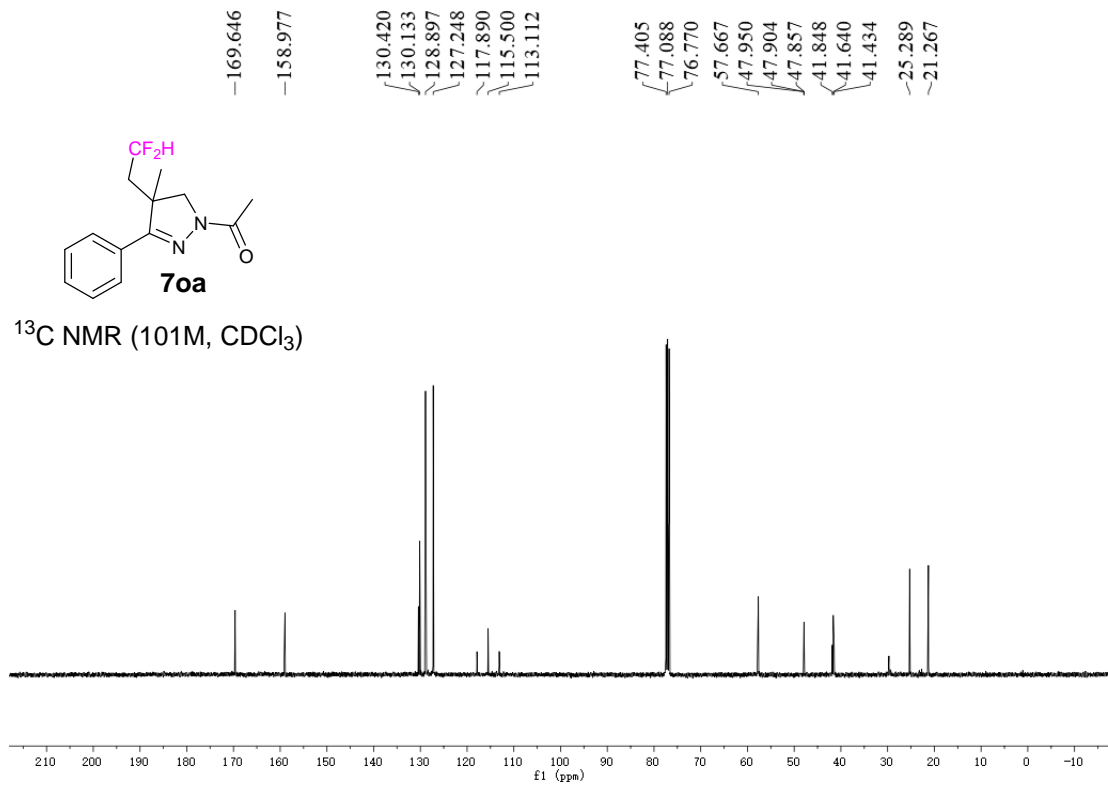
¹³C NMR (101M, CDCl₃)

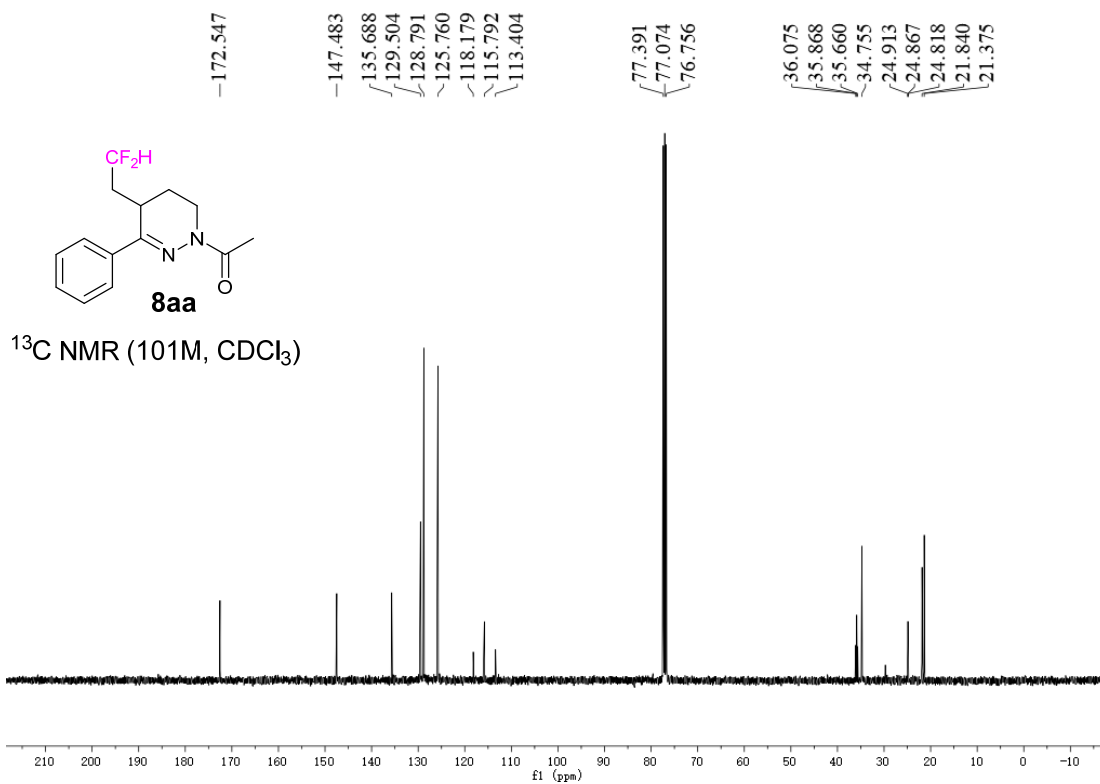
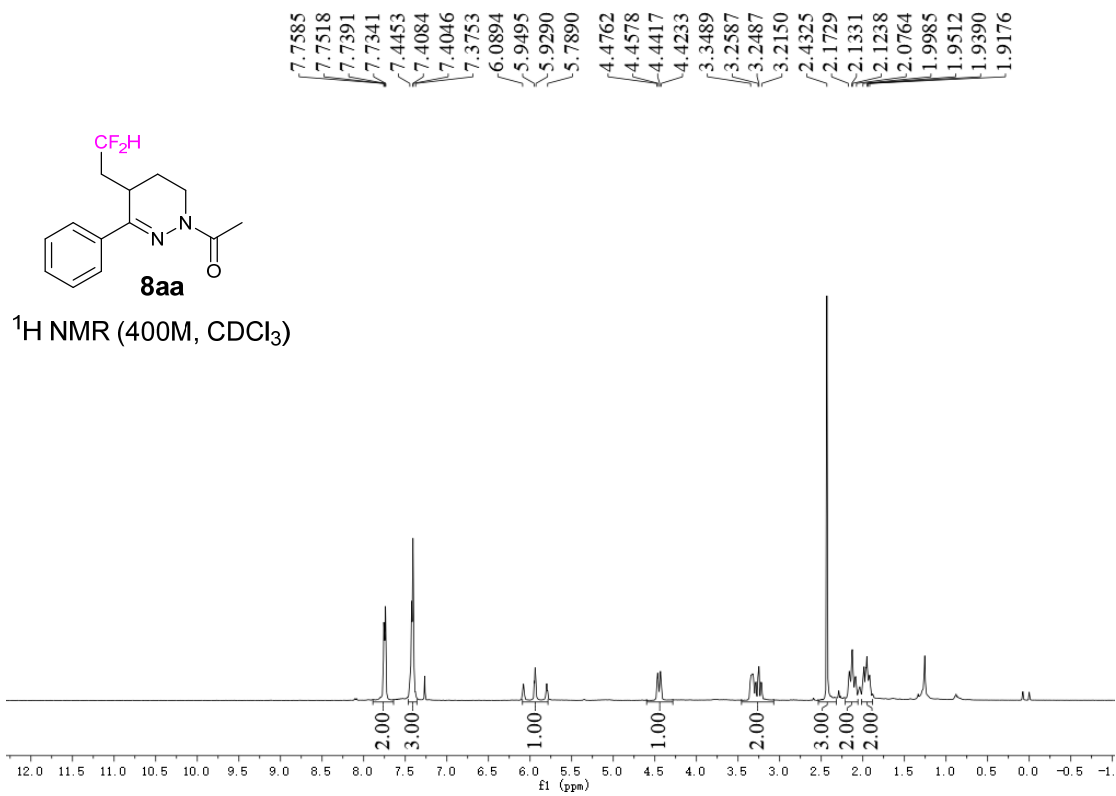


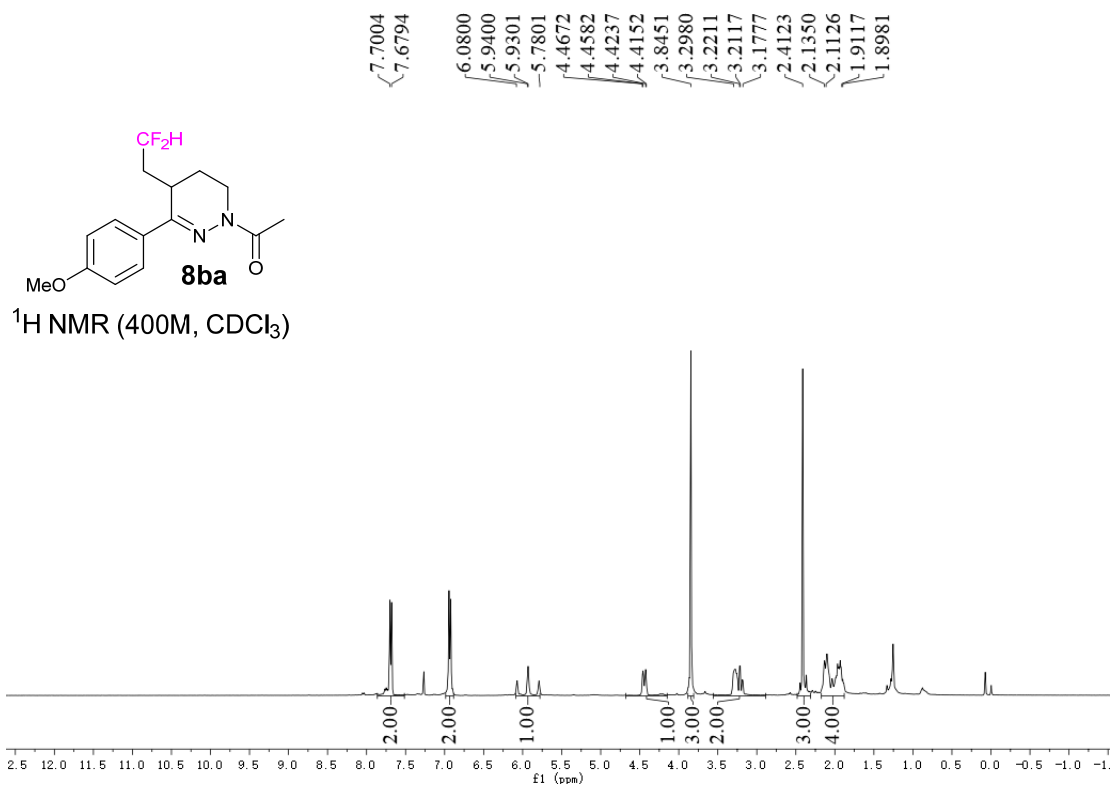
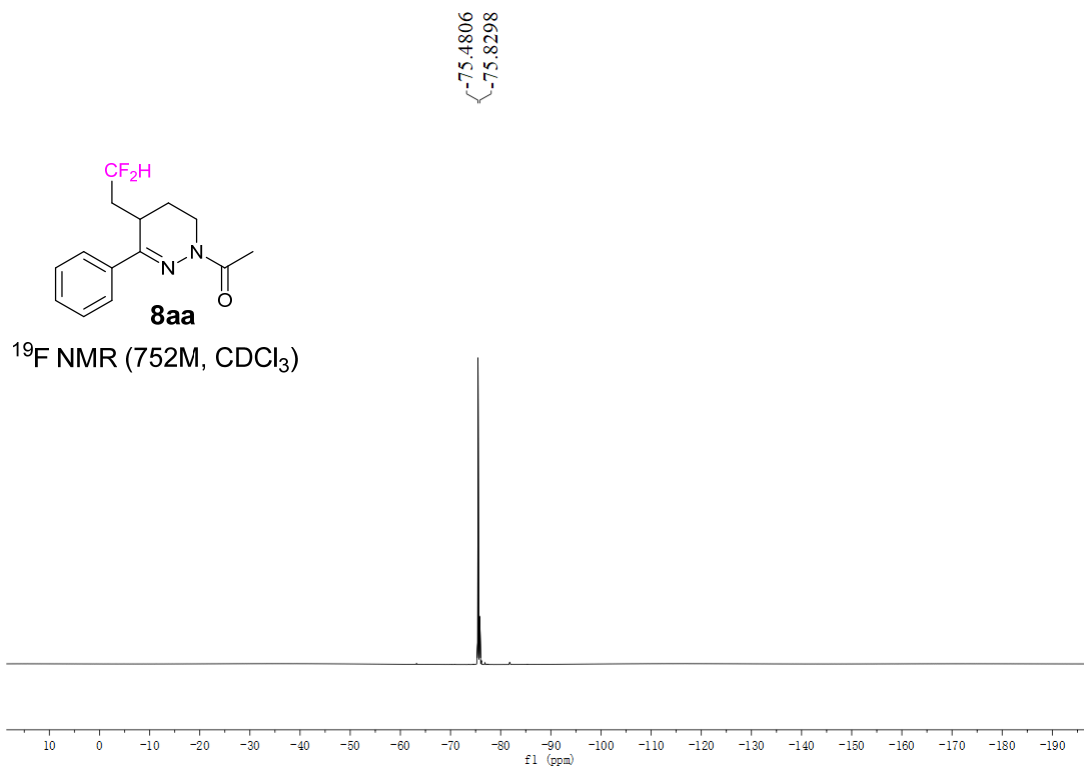


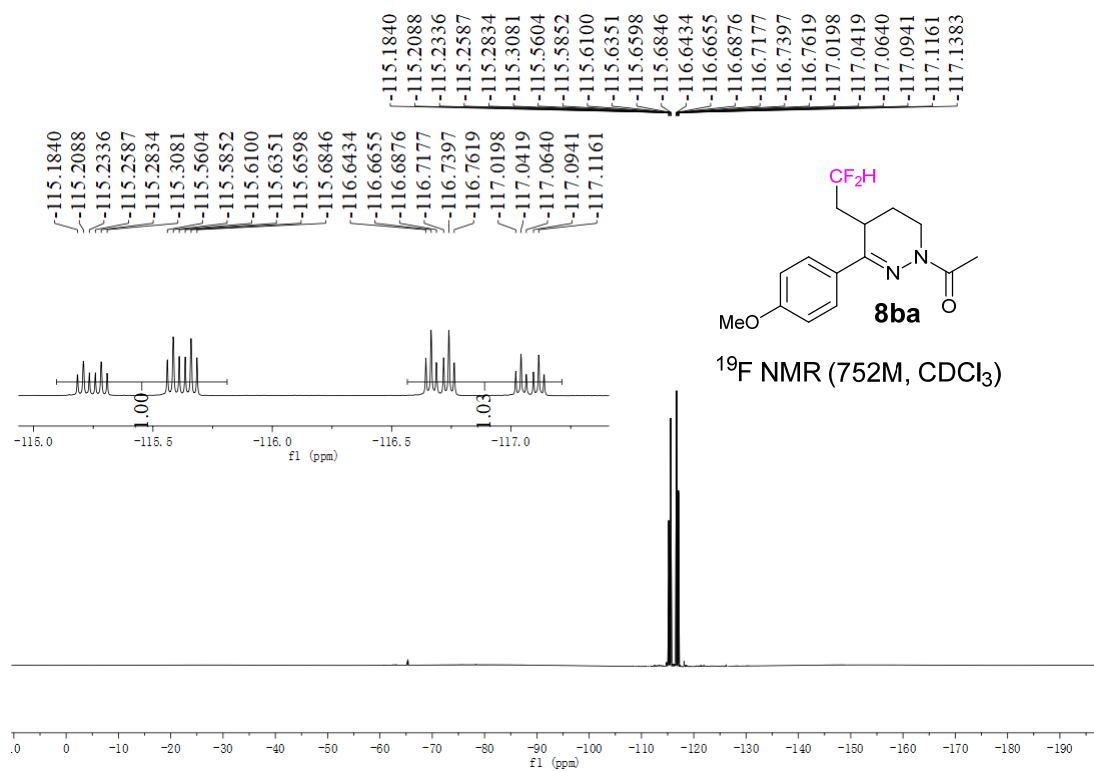
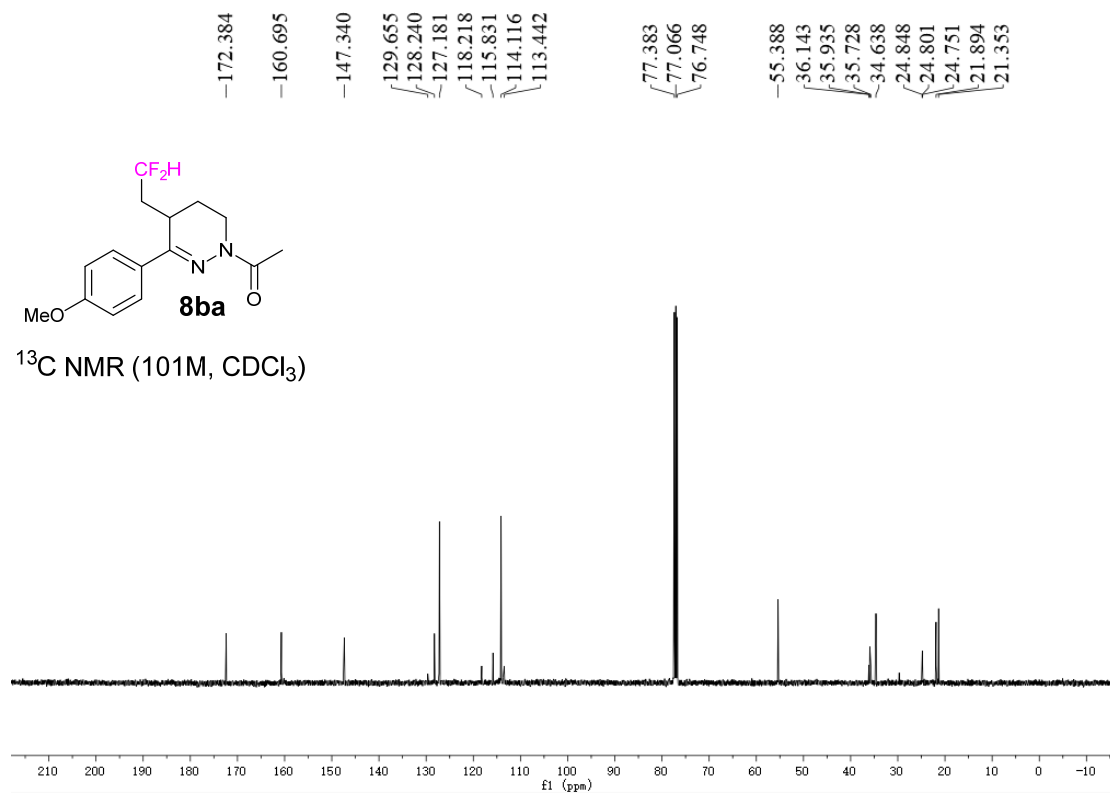


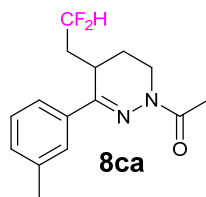
¹³C NMR (101M, CDCl₃)



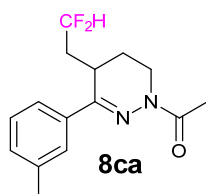
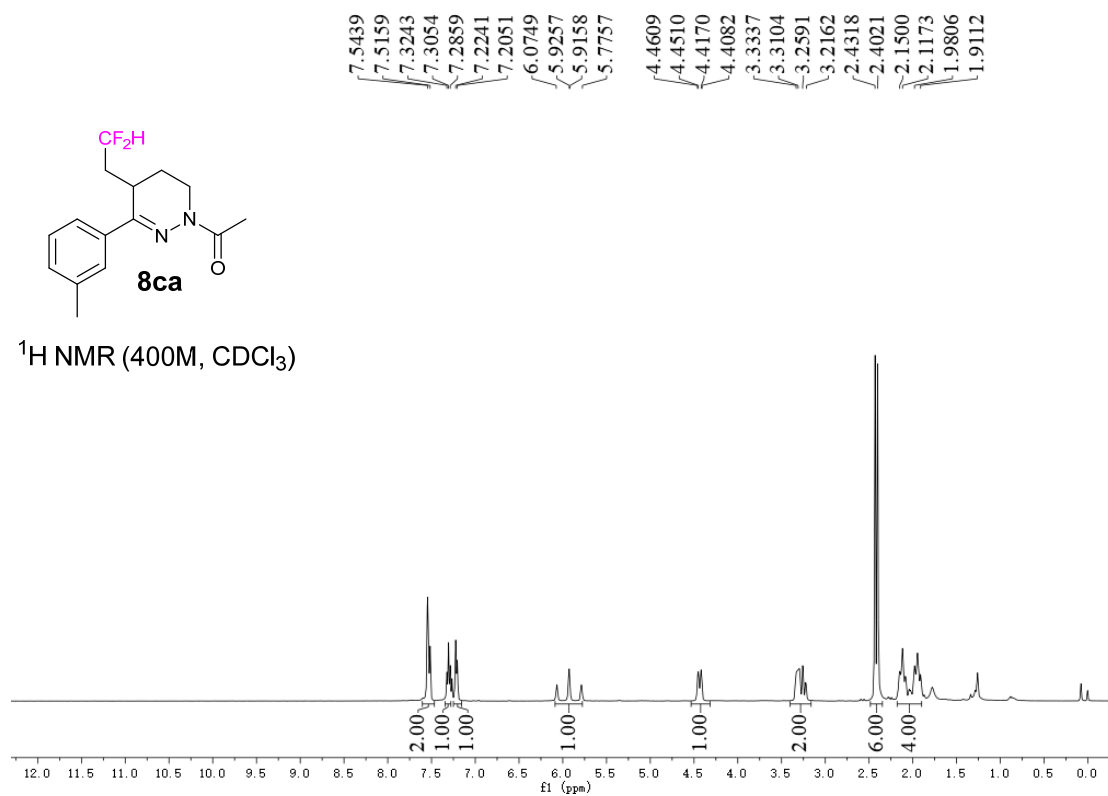




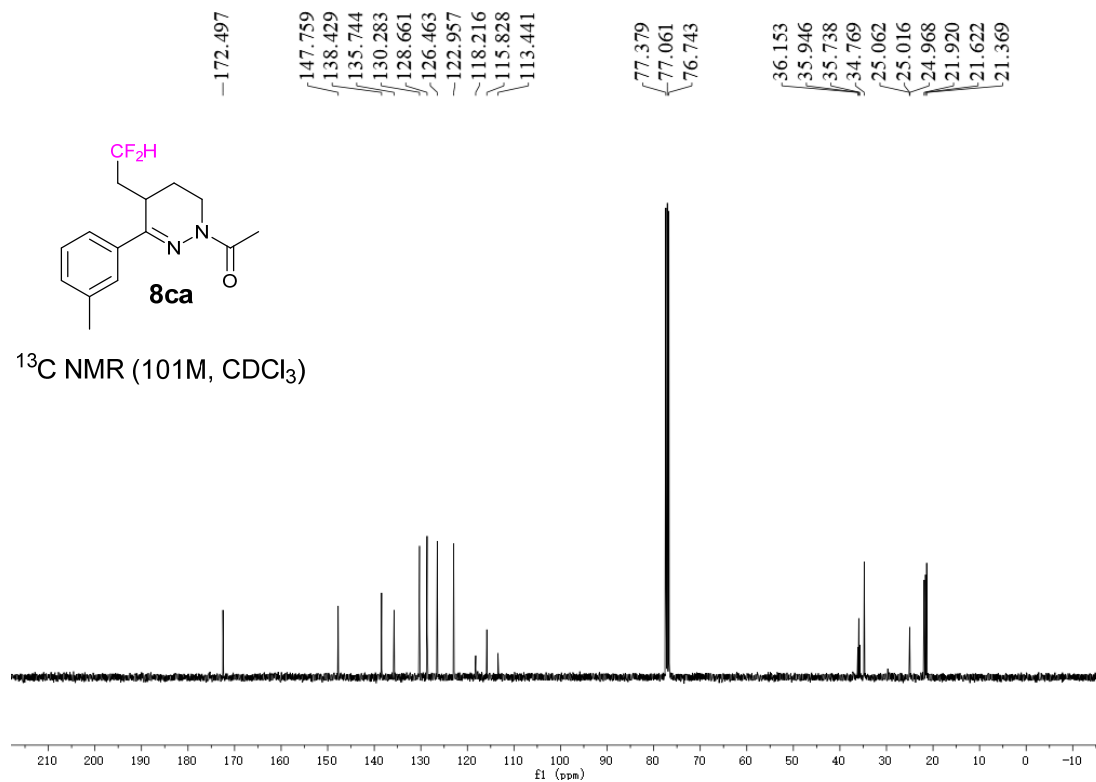


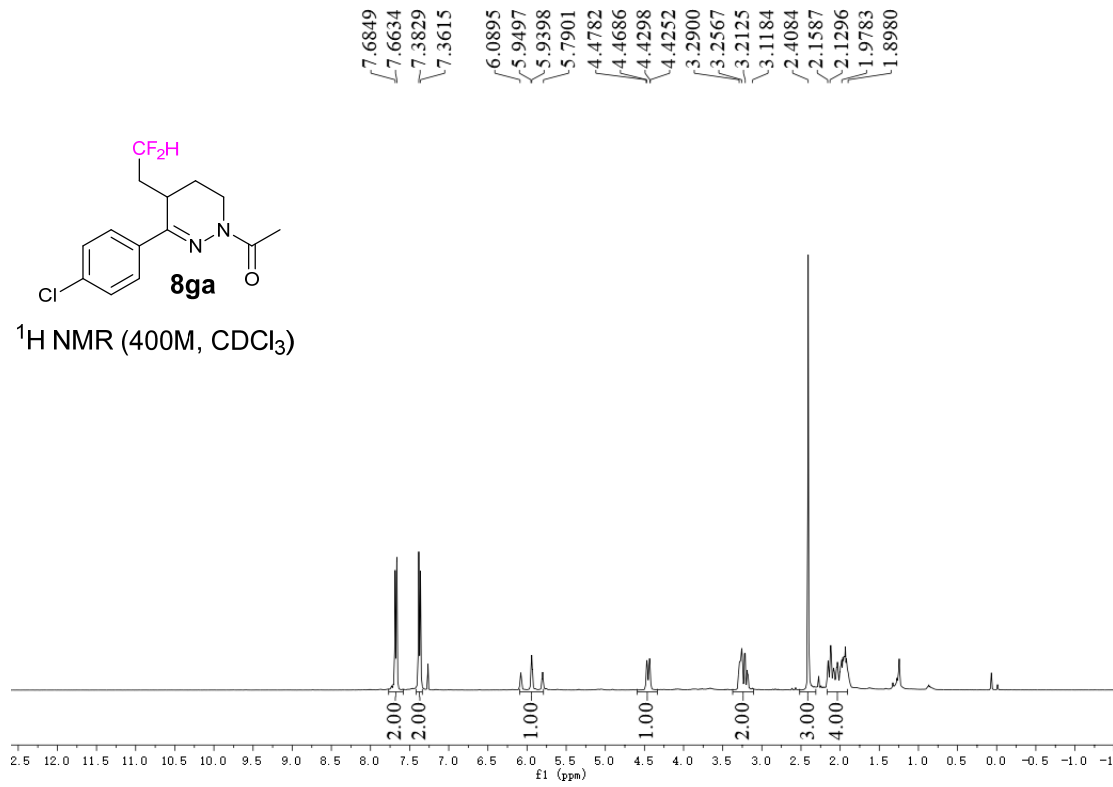
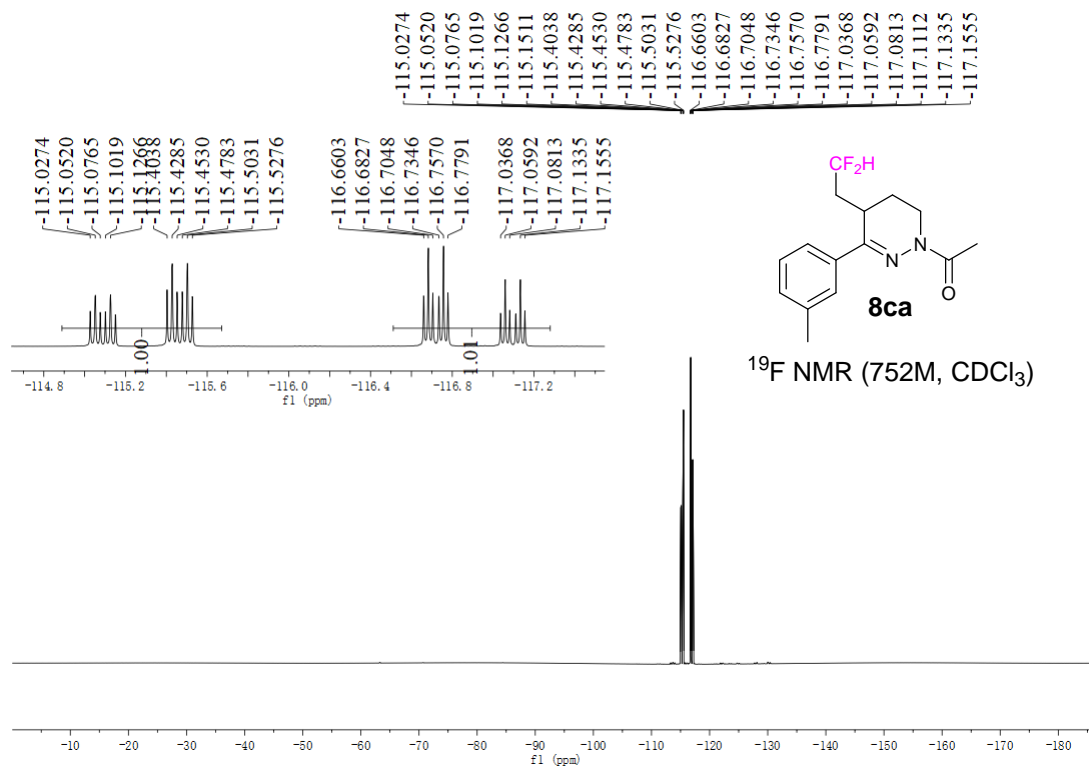


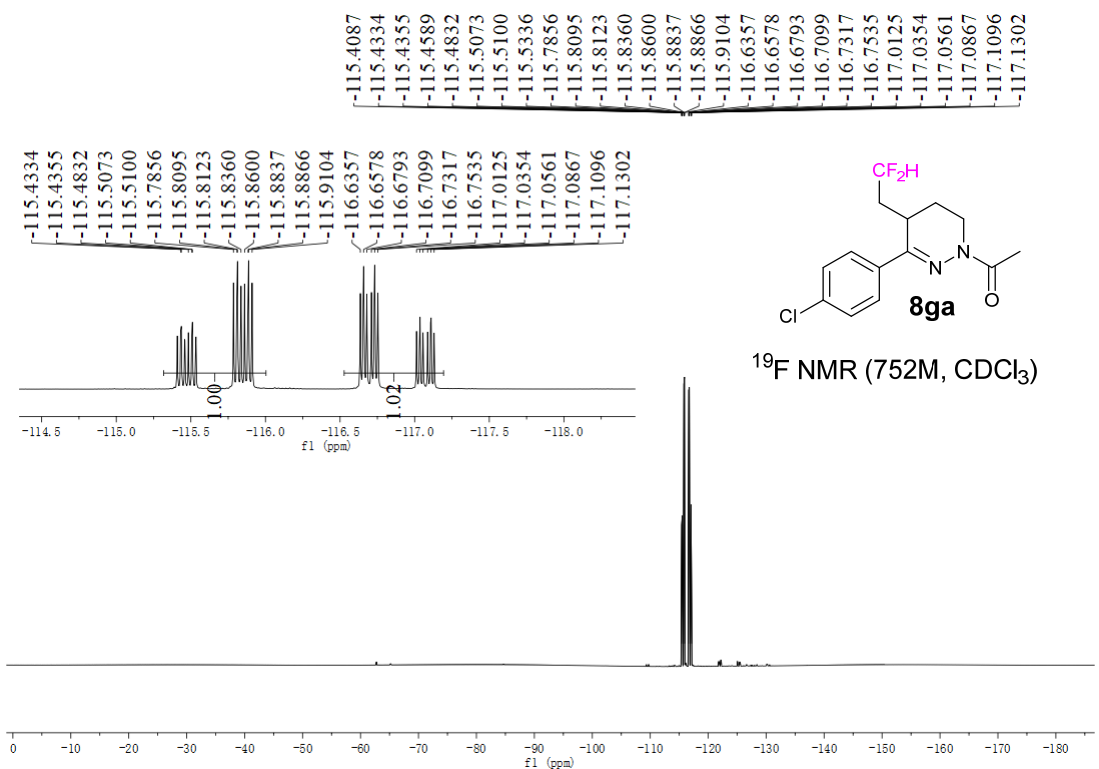
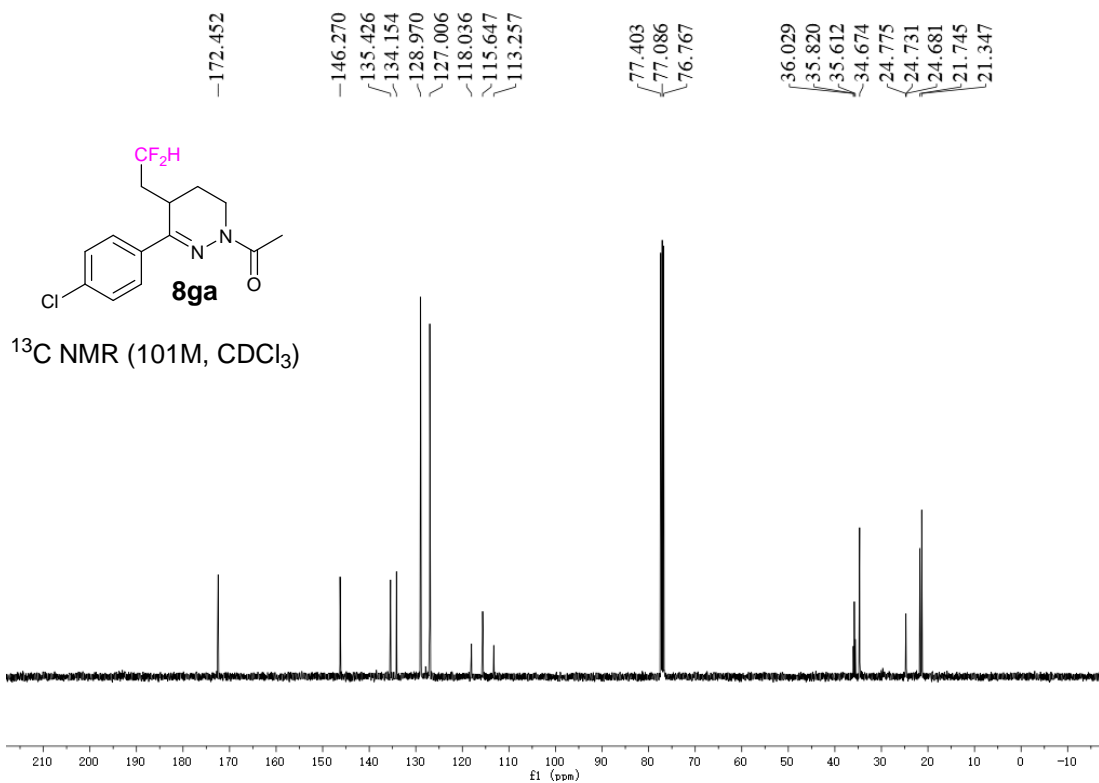
^1H NMR (400M, CDCl_3)

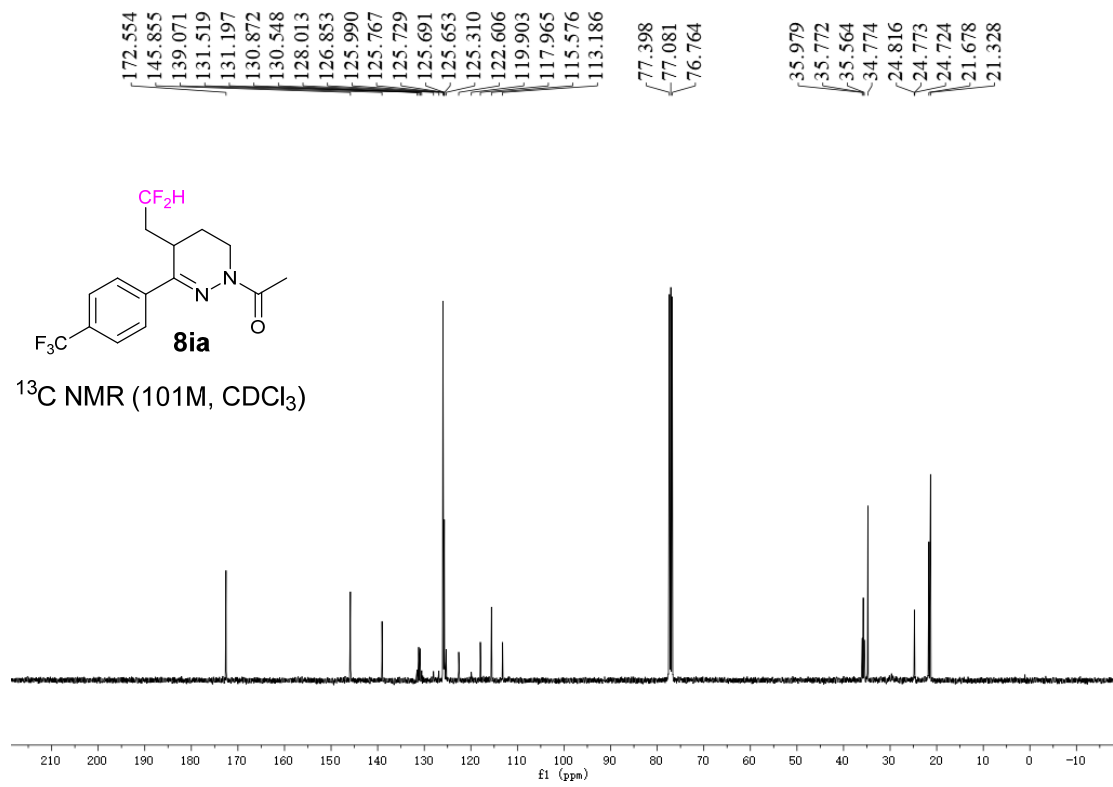
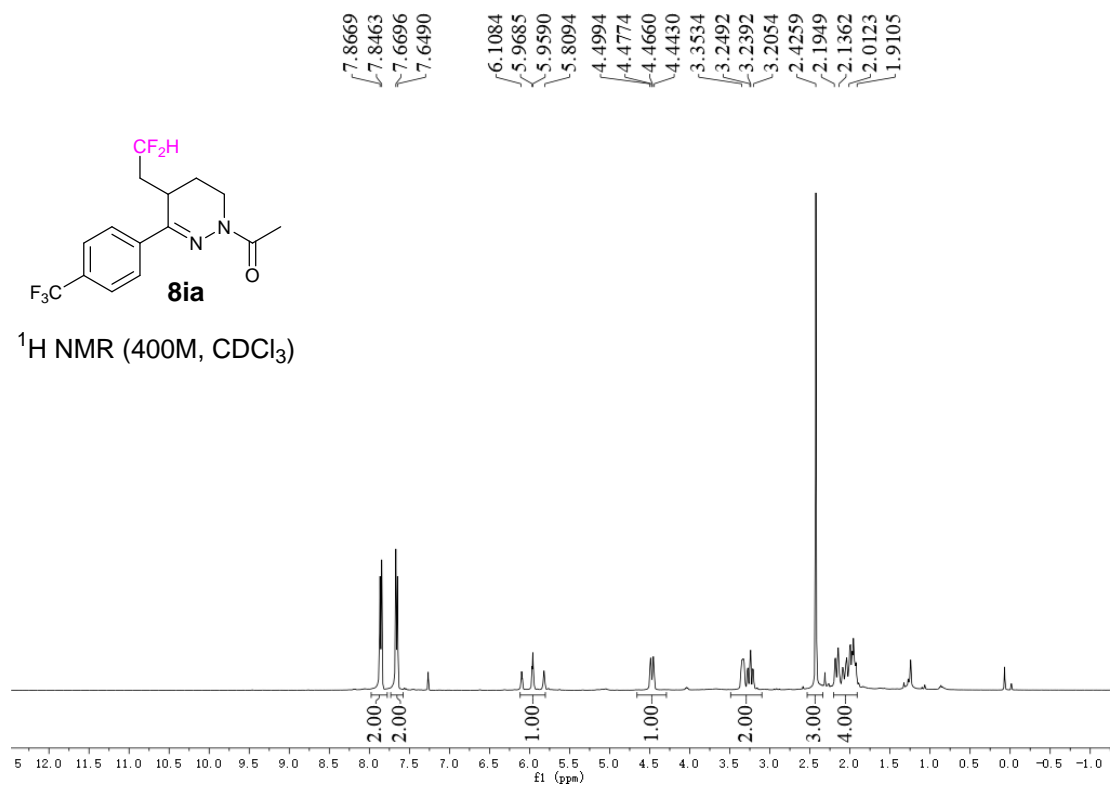


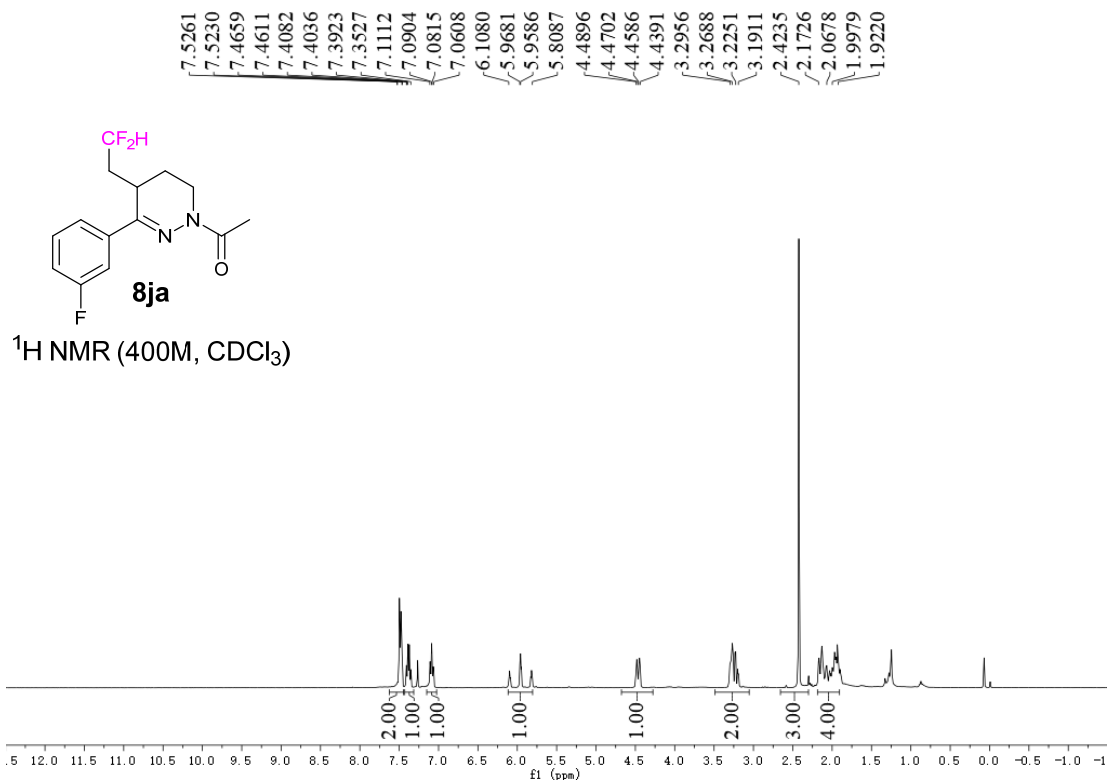
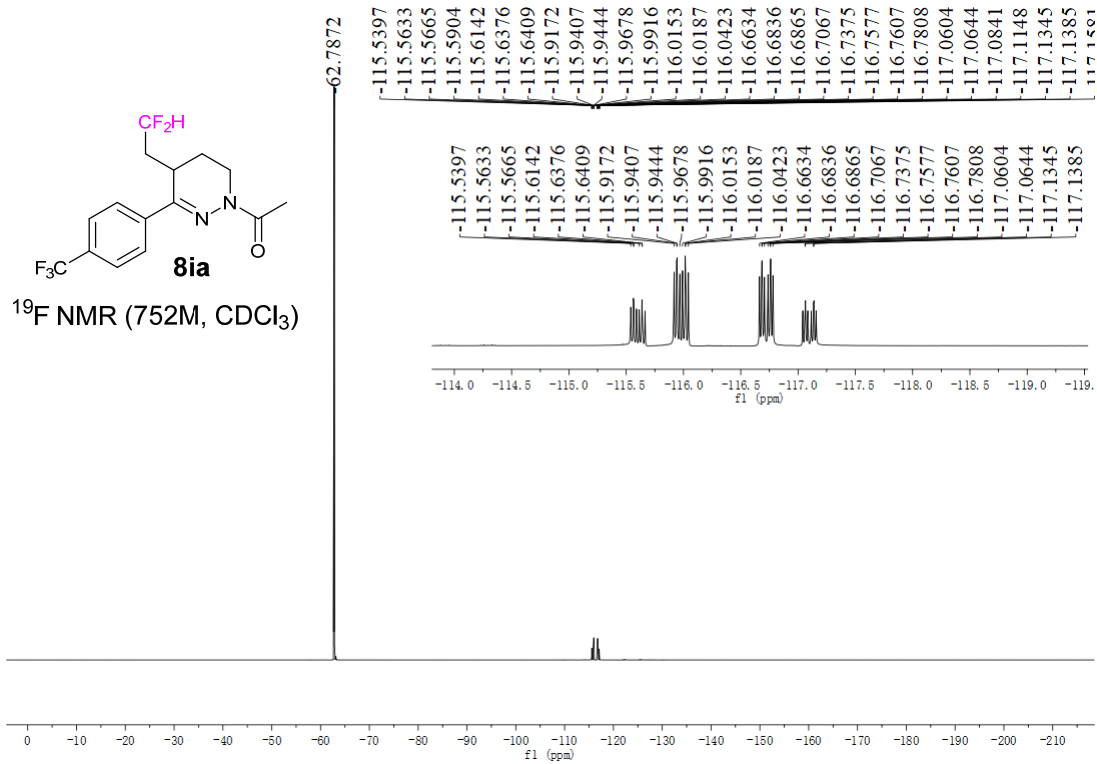
^{13}C NMR (101M, CDCl_3)

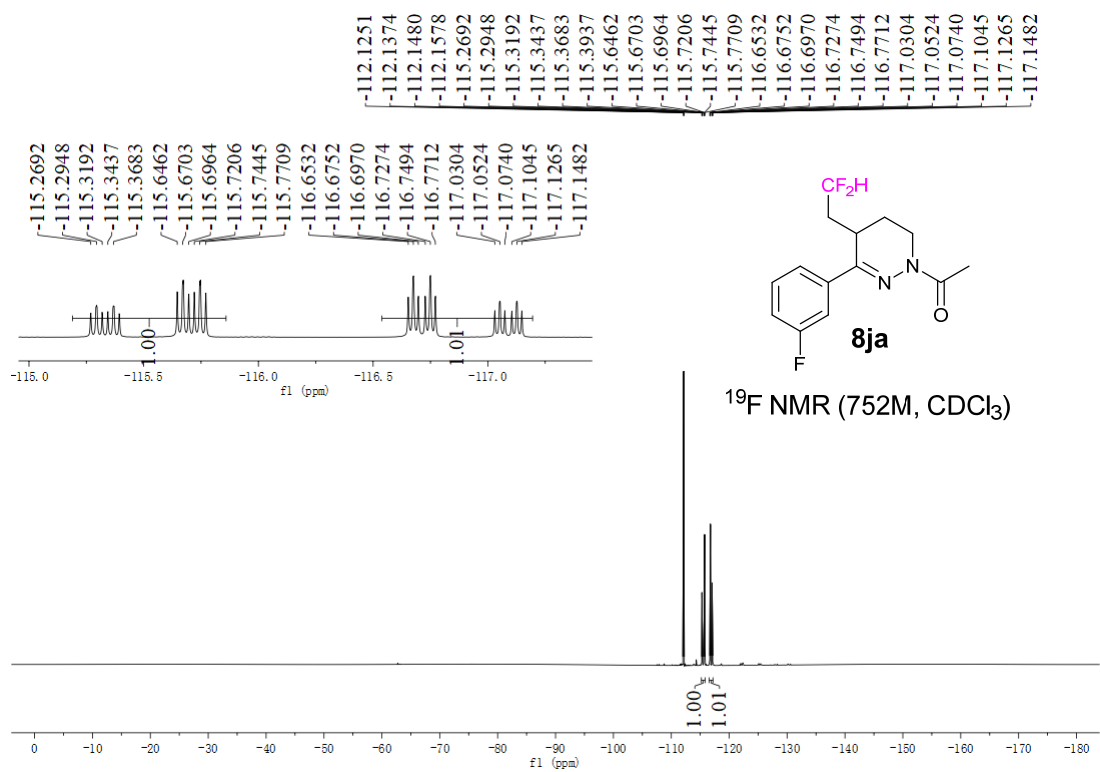
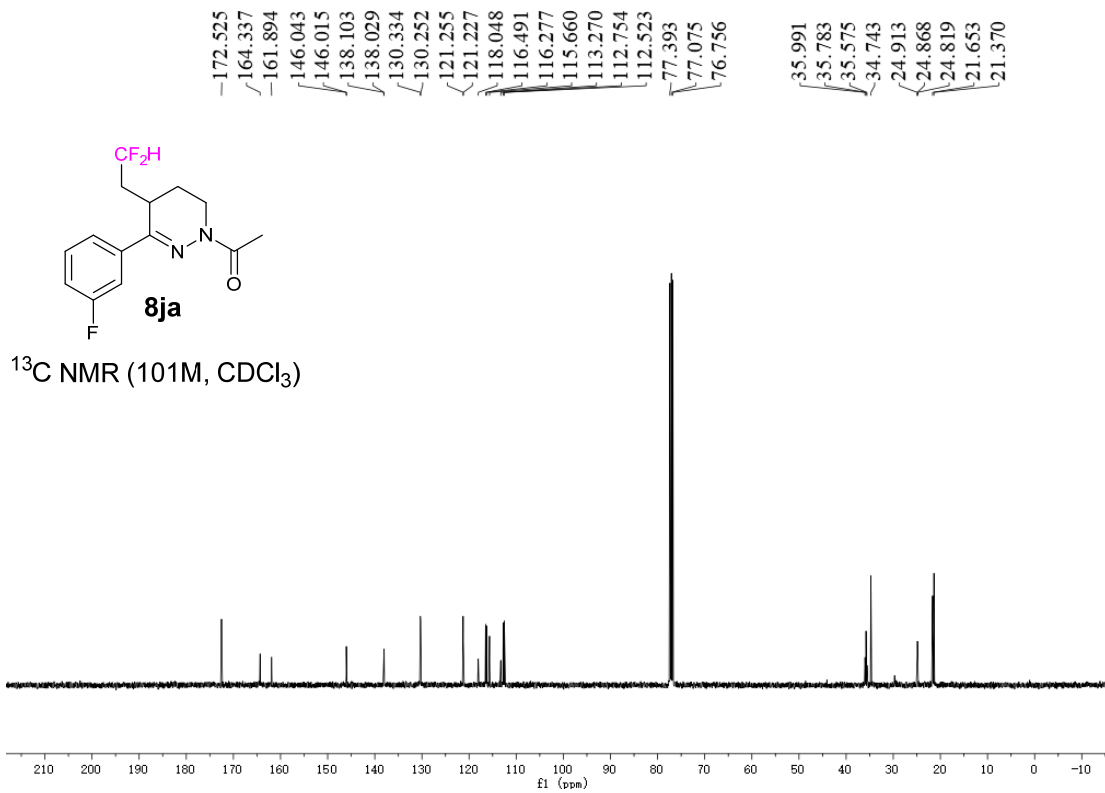


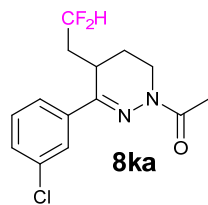




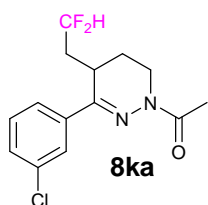
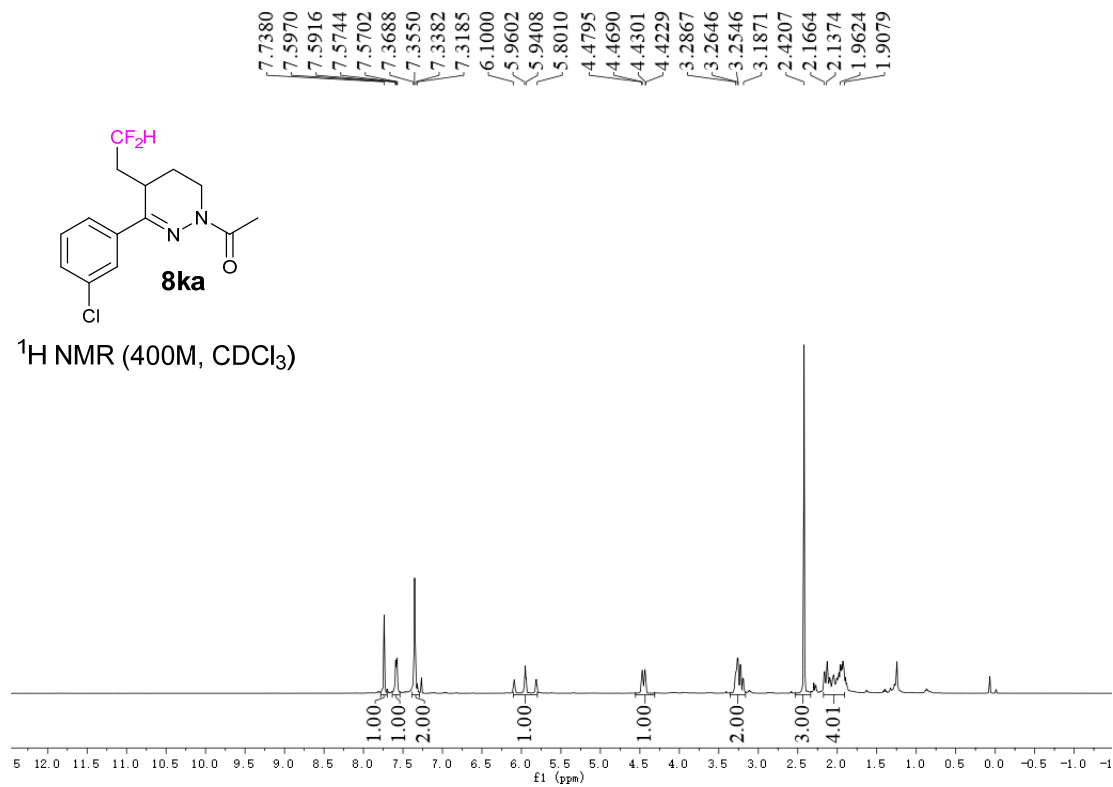




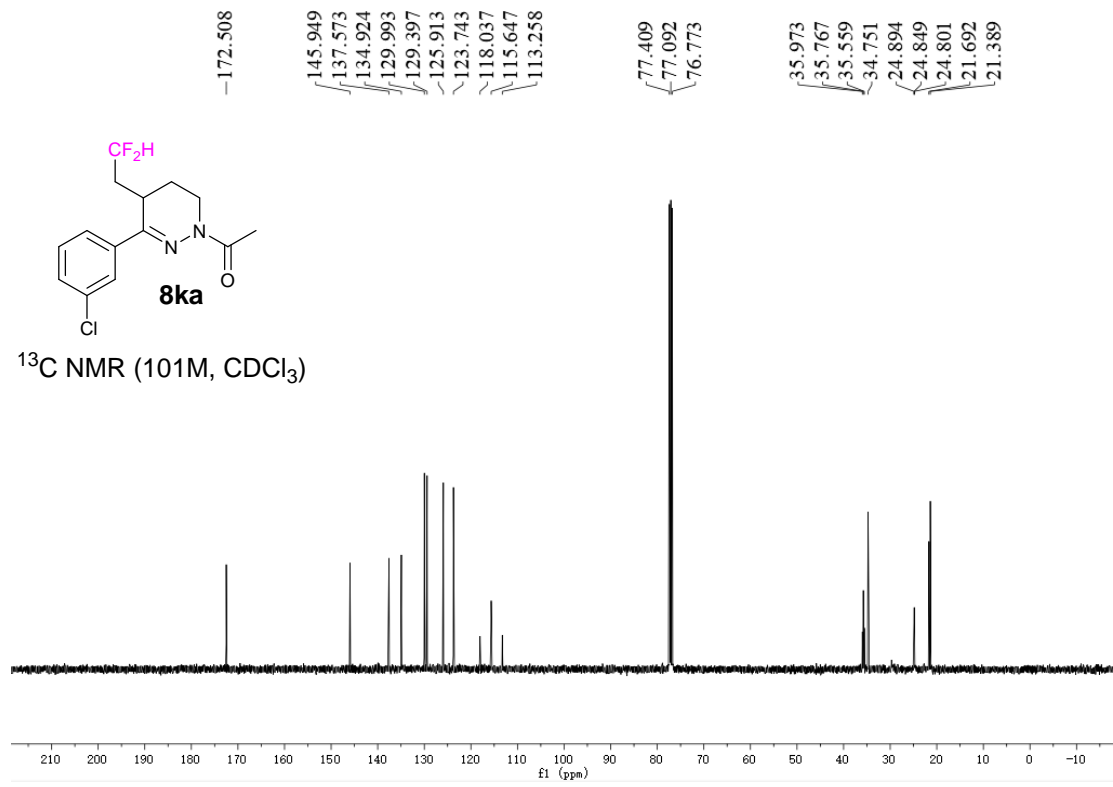


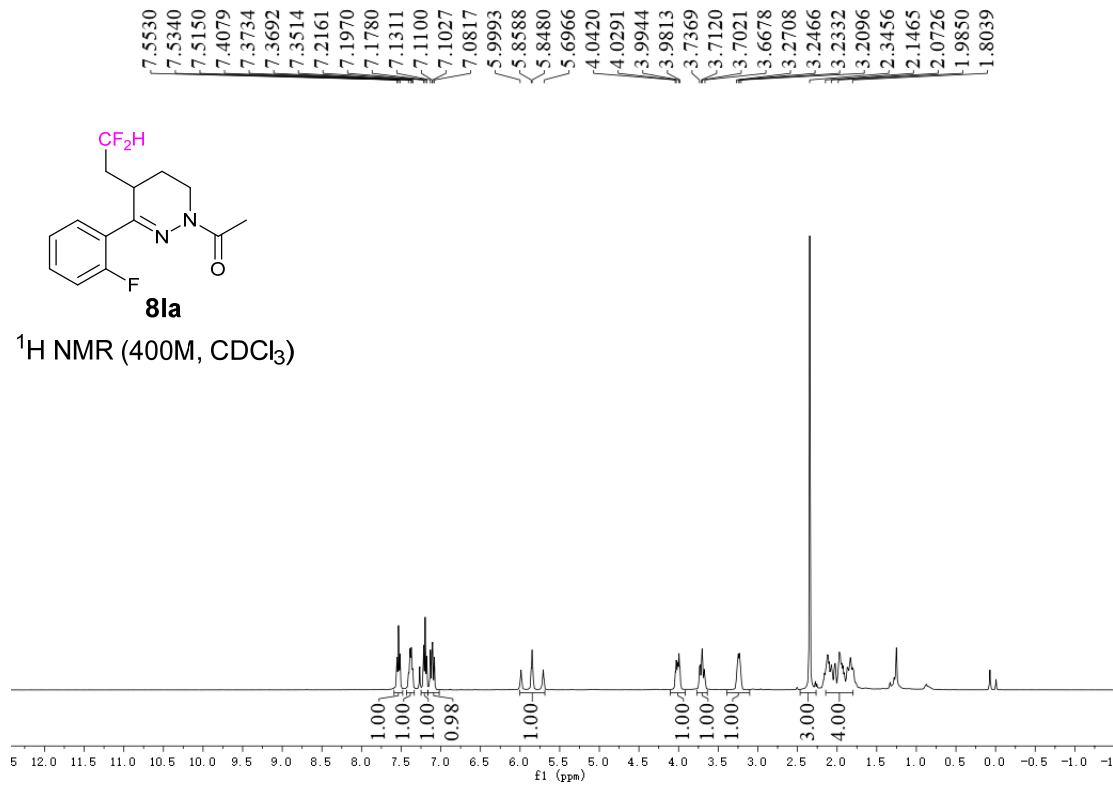
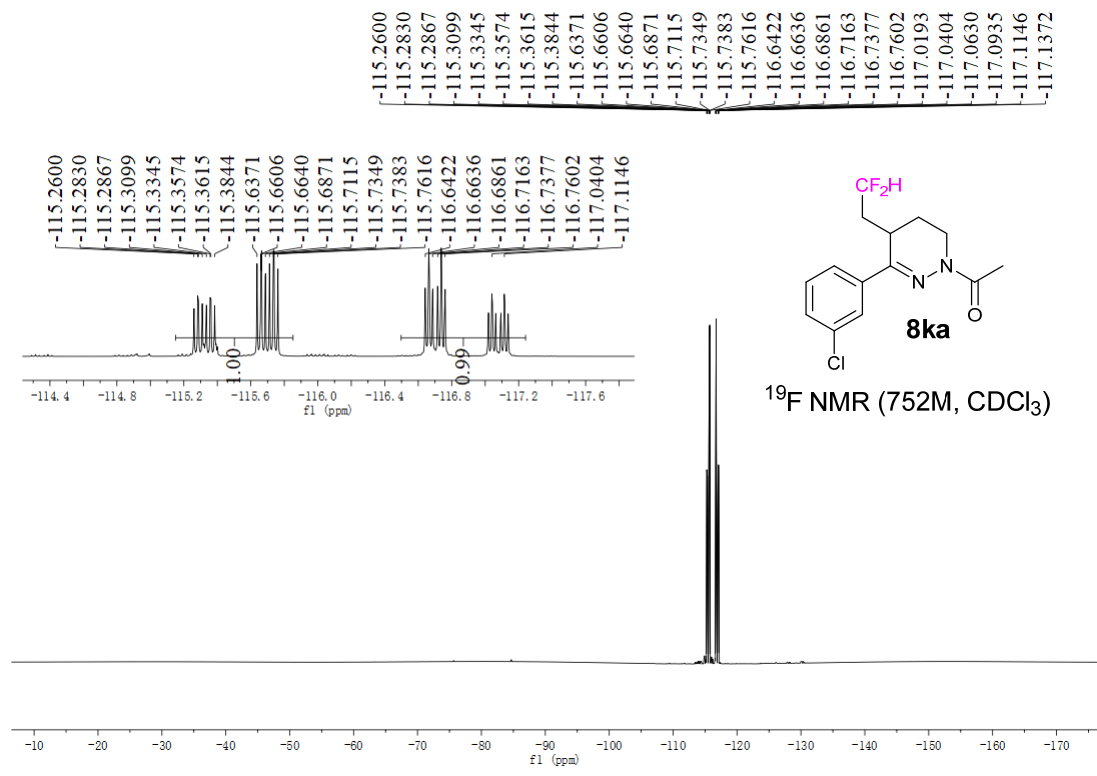


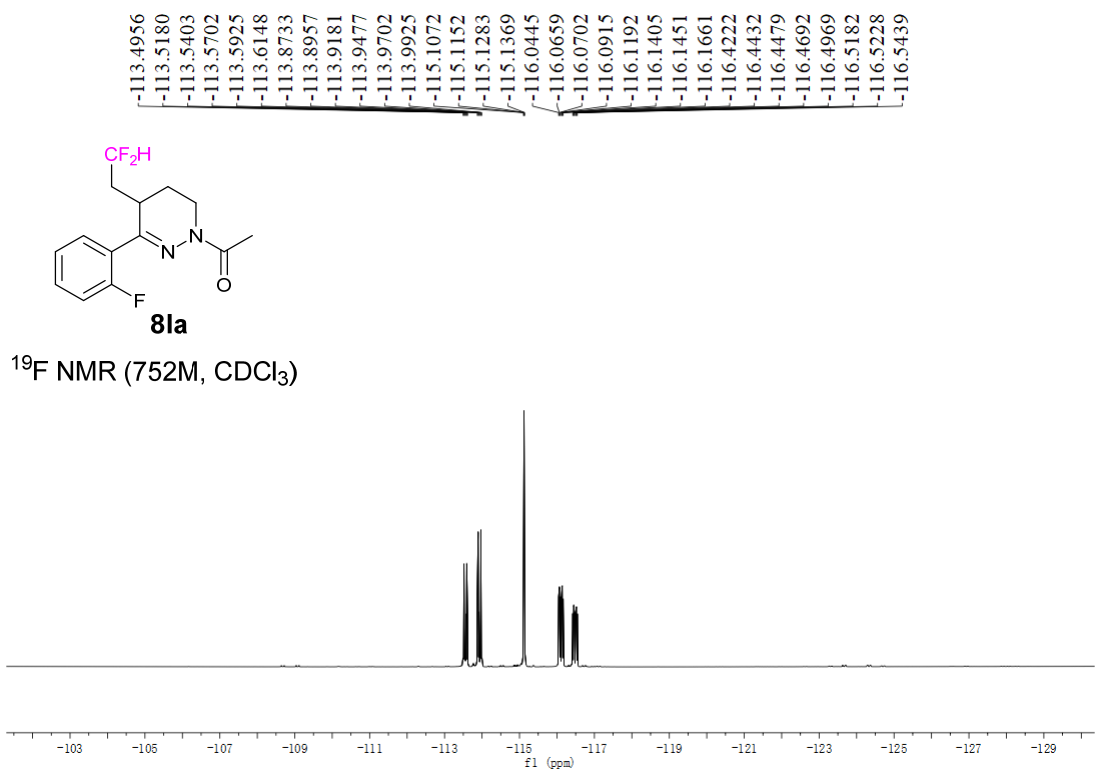
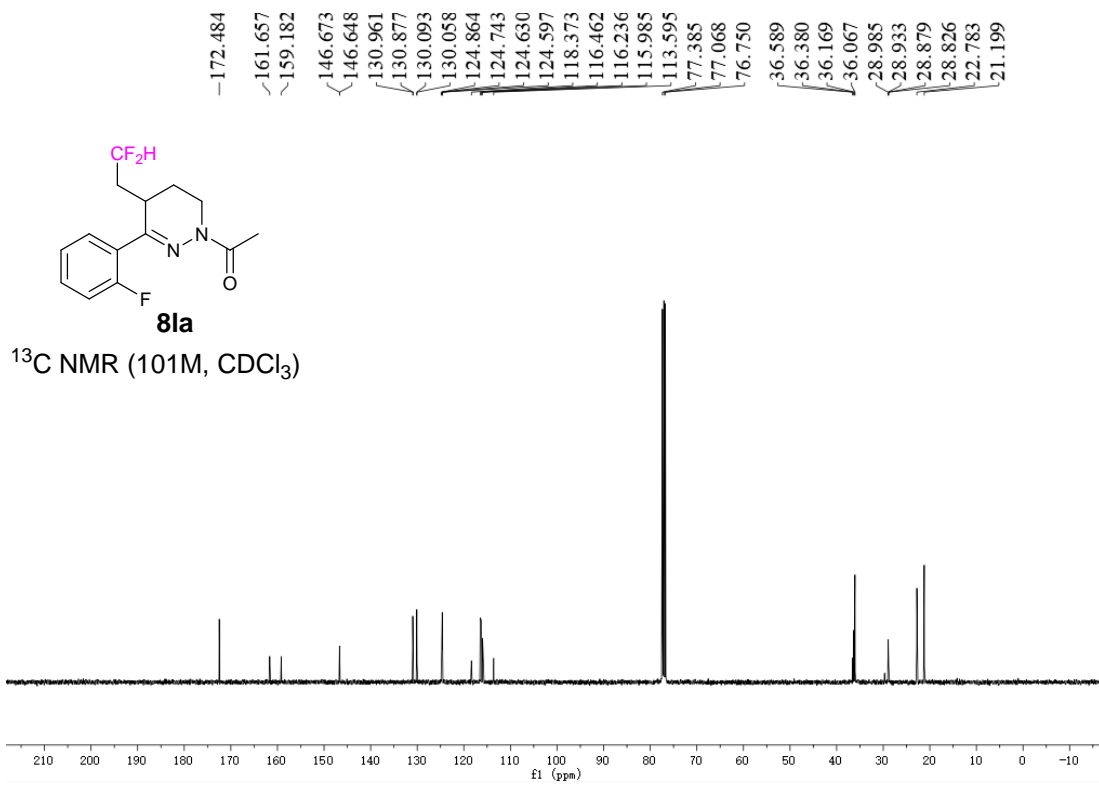
¹H NMR (400M, CDCl₃)

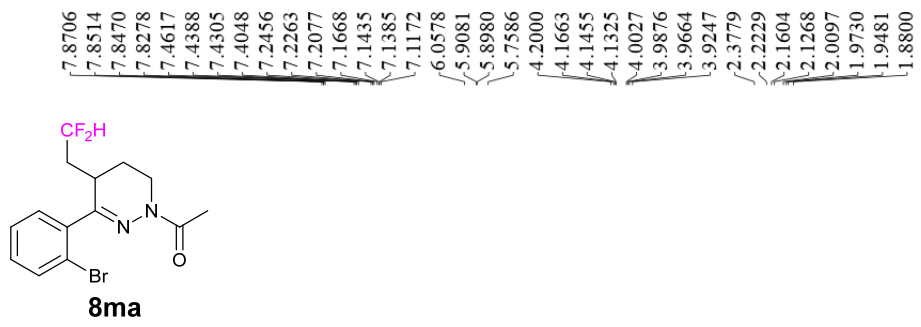


¹³C NMR (101M, CDCl₃)

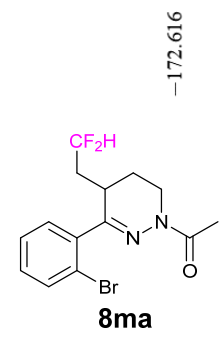
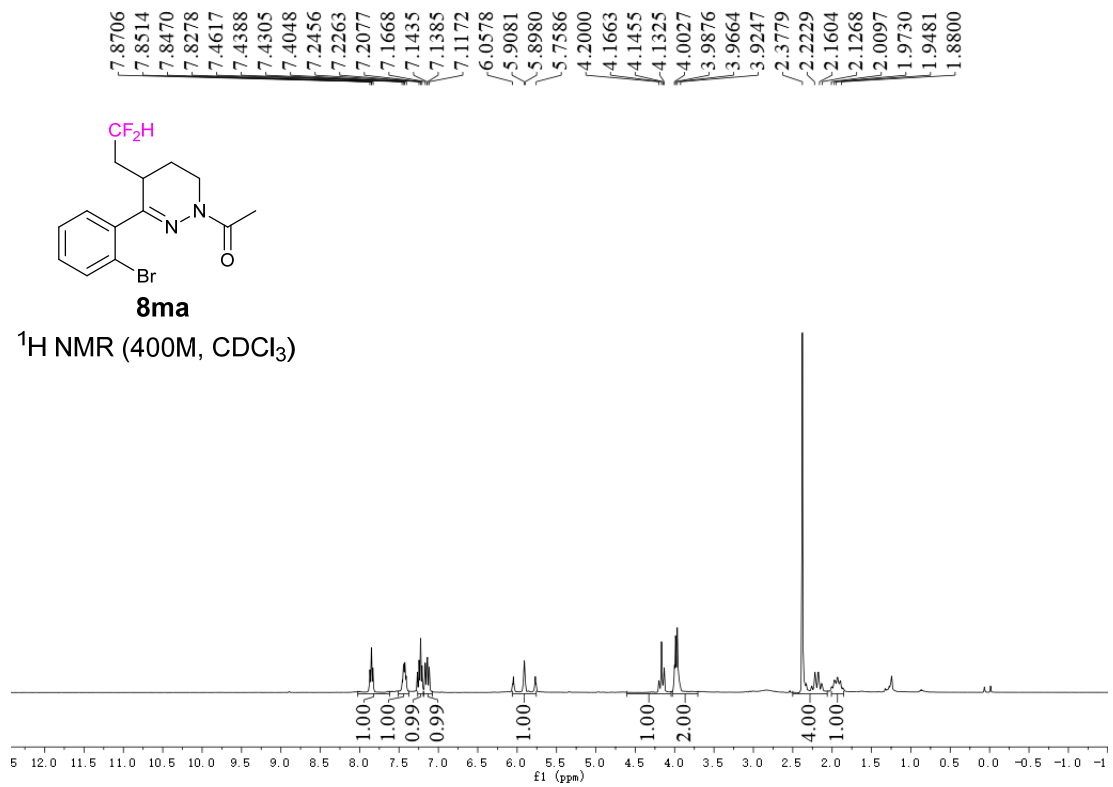








¹H NMR (400M, CDCl₃)



¹³C NMR (101M, CDCl₃)

