Supporting Information

An *in-situ* Generated Proton Initiated Aromatic Fluoroalkylation via Electron Donor-Acceptor Complexes Photoactivation

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1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. The NMR spectra were recorded on a Bruker Avance 400 or 600 spectrometer at 400 MHz or 600MHz in $CDCl_3$ using tetramethylsilane as the internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet of doublet. Melting points were determined using a Büchi B-540 capillary melting point apparatus. High-resolution mass spectra were obtained with a Bruker Impact II UHR-QTOF. by ESI on a TOF mass analyzer. Column chromatography was performed on silica gel (200–300 mesh).

The Material of the Irradiation Vessel

Manufacturer： Xi 'an WATTCAS experimental equipment co. LTD

Model： WP-TEC-1020HSL

Broadband source： λ = 400-405 nm

Material of the irradiation vessel：borosilicate reaction tube

Distance from the light source to the irradiation vessel：2.0 cm

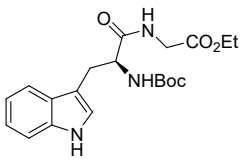
photon flux density: 5.044×10^{-8} einstein s^{-1}

Not use any filters

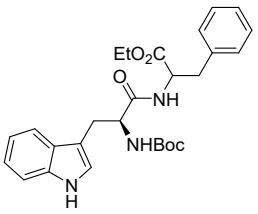
Figure S1（Photographed by author Panyi Huang）

2. Compounds Prepared According to Literature Procedures

Aryl precursors of direct C-H fluoroalkylation



1an



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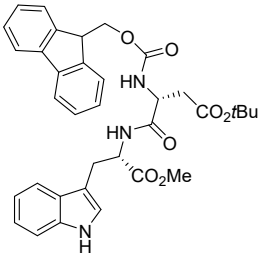

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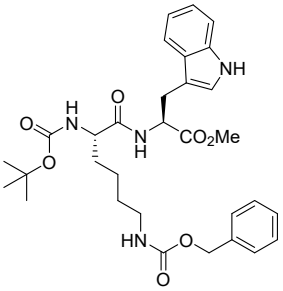
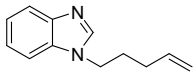


1aq

Aromatic precursors of fluoroalkylation/cyclization



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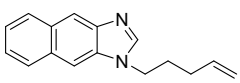

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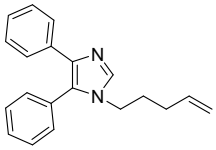

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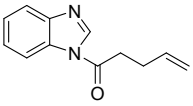

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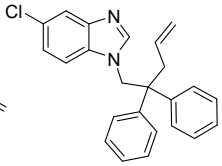

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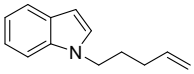

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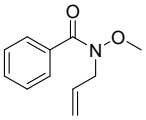

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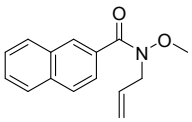

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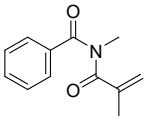

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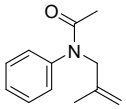

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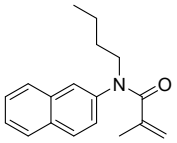

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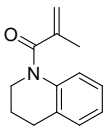

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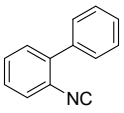

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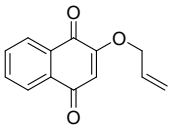

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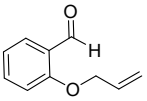
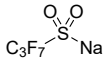
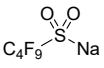


4ac

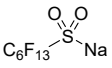
Perfluoroalkanesulfinates



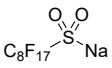
2c



2d



2e

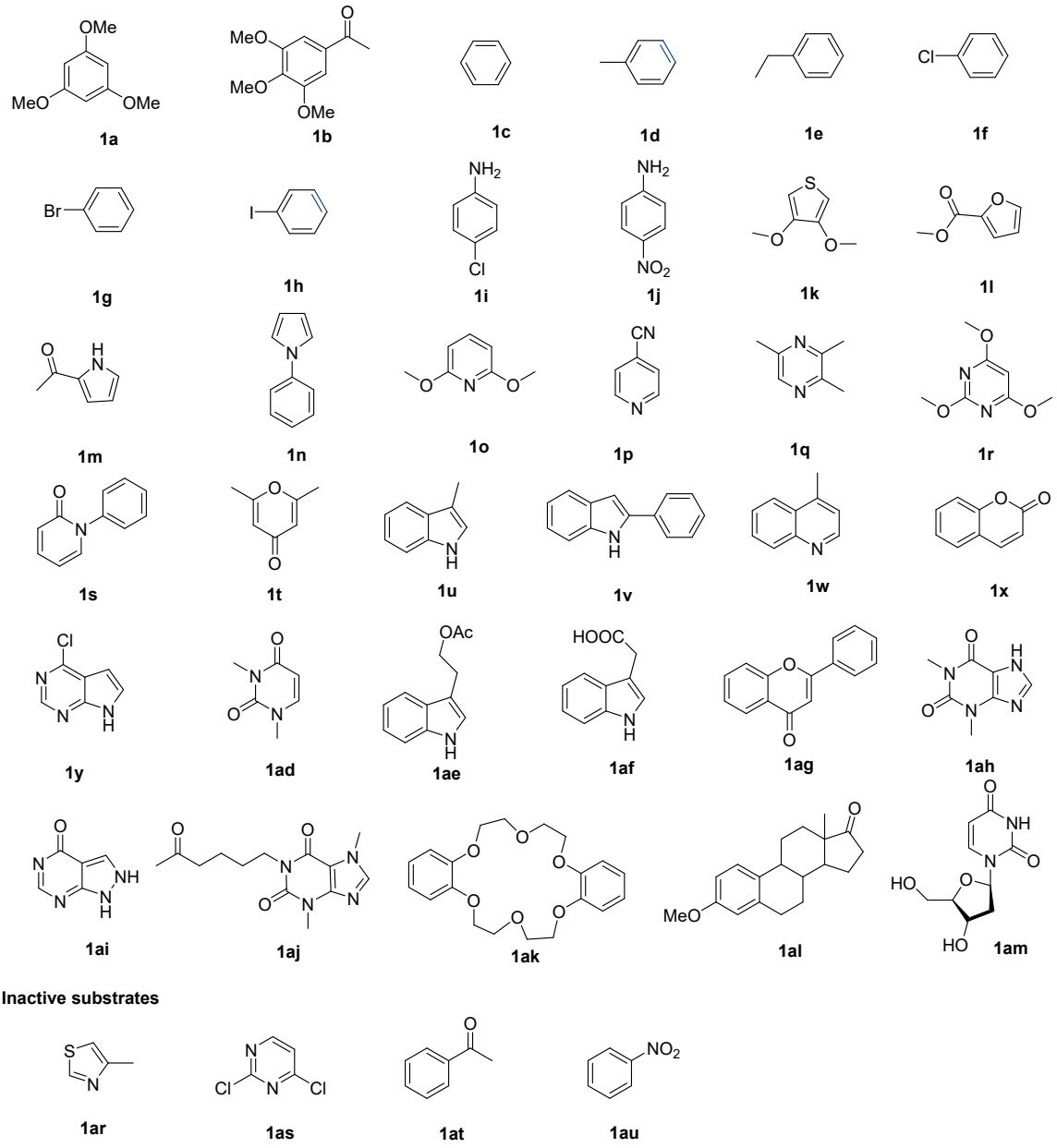


2f

The (hetero)arenes, which were used in the synthesis of products **3a**-**3z**, **3aa**-**3am** were purchased from commercial sources and used without further purification. The Trp-containing dipeptides **1an**-**1aq** were prepared according to the literature.1 **4a**-**4t** [2], **4u**-**4v** [3], **4w**, [4], **4x**-**4z** [5], **4aa** [6], **4ab**,**4ac** [7] and **2c**-**2f** [8] were prepared following the literature procedures.

3. General Procedure

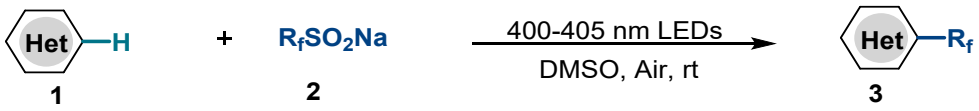
Successful substrate



Inactive substrates

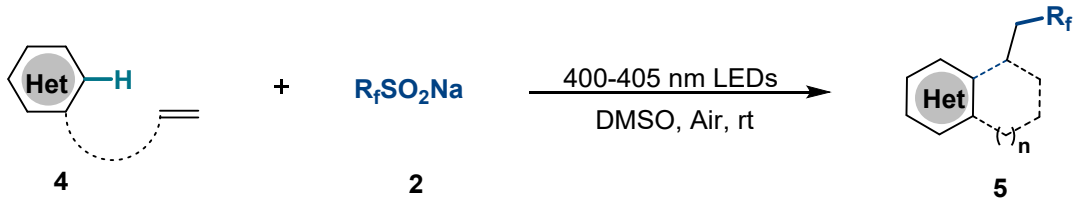
The successful implementation of this strategy has been demonstrated with a series of heteroaromatic substrates, while inactive substrates unsuitable for this approach have also been documented.

3.1 General procedure A for C-H fluoroalkylation of (hetero)arenes with fluoroalkanesulfinates



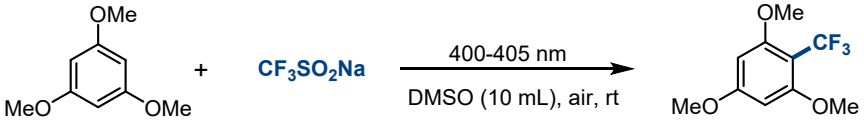
A mixture of (hetero)arenes **1** (0.3 mmol), fluoroalkanesulfinates **2** (0.45 mmol) and DMSO (2 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 6-32 h until the reaction was completed as monitored by TLC. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2 and the organic phase was then removed under vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

3.2 General procedure B for C(sp^2)-H fluoroalkylation/tandem cyclization of (hetero)arenes with fluoroalkanesulfinates



A mixture of (hetero)arenes containing unactivated alkene **4** (0.3 mmol), fluoroalkanesulfinates **2** (0.45 mmol) and DMSO (2 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 12 h. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2 and the organic phase was then removed under vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **5**.

3.3 The Gram Scale Reaction

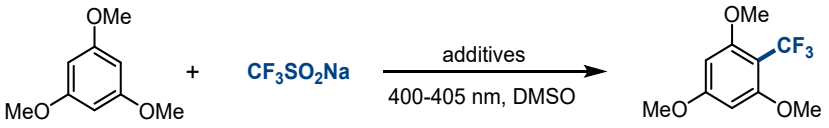


1a 6 mmol | **2a** 9 mmol | **3a** 10 h, 77%

A mixture of 1,3,5-trimethoxybenzene **1a** (6 mmol), sodium trifluoromethanesulfinate **2a** (9 mmol) and DMSO (10 mL) were added to a 50 mL reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 10 h. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2 and the organic phase was then removed under vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a** with 77% yield.

3.4 Optimizations of the Reaction Conditions

Table S1. Optimization of additive.[a]

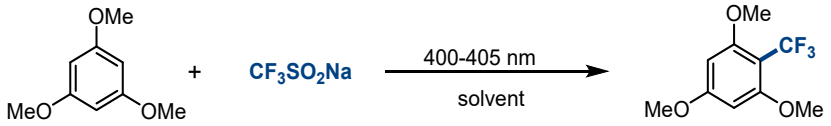


1a **2a** **3a**

Entry	additive	Yield (%)[b]
1	H_2SO_4	76
2	CF_3SO_3H	79
3	HCl	74
4	H_3PO_4	70
5	CH_3CO_2H	67
11	-	49, 78[c]

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.5 equiv.), acid (0.1 equiv), DMSO (2 mL), air, rt, 5 h irradiated under 400-405 nm. [b] Isolated yield based on **1a**.[c] 10 h, irradiation under 400-405 nm.

Table S2. Optimization of solvent.[a]

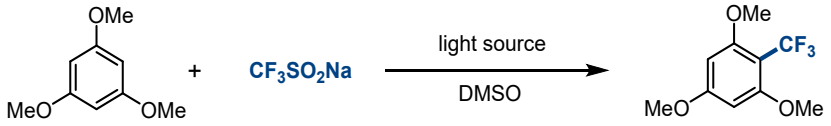


1a 2a 3a

	additive	Yield (%)[b]
1	DMSO	78
2	CH_3CN	63
3	THF	N.D.
4	CH_3CH_2OH	N.D.
5	DMF	43
6	EtOAc	68
7	DCE	65
8	DCM	32
9	H_2O	12
10	CH_3CN : H_2O = 2.5 : 1	65
11	DCE : H_2O = 2.5 : 1	68
12	DMSO : H_2O = 2.5 : 1	77

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.5 equiv.), solvent (2 mL), air, rt, 3-14 h irradiated under 400-405 nm. [b] Isolated yield based on **1a**.

Table S3. Optimization of light source.[a]



1a 2a 3a

Entry	light source	Yield (%)[b]
1	380-385 nm	59
2	400-405 nm	78
3	410-415 nm	73
4	420-425 nm	34
5	435-440 nm	N.D.
6	455-465 nm	N.D.

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.5 equiv.), DMSO (2 mL), air, rt, 10 h. [b] Isolated yield based on **1a**.

4. Mechanistic Studies

4.1 ^{19}F NMR experiments of CF_3SO_2Na irradiation for different times and CF_3SO_3H (in DMSO-*d6*) standard spectrum

In an oven-dried reaction tube equipped with a magnetic stirrer bar was charged with sodium trifluoromethanesulfinate **2a** (5 mg) and DMSO-*d6* (2.0 mL). Five tubes were then exposed to a 10 W LED lamp (400-405 nm) irradiation at room temperature in air with stirring for 0 h, 0.5 h, 2 h, 4 h, 6 h. After completion of the reaction, ^{19}F NMR analysis of the solvent (Figure S2).

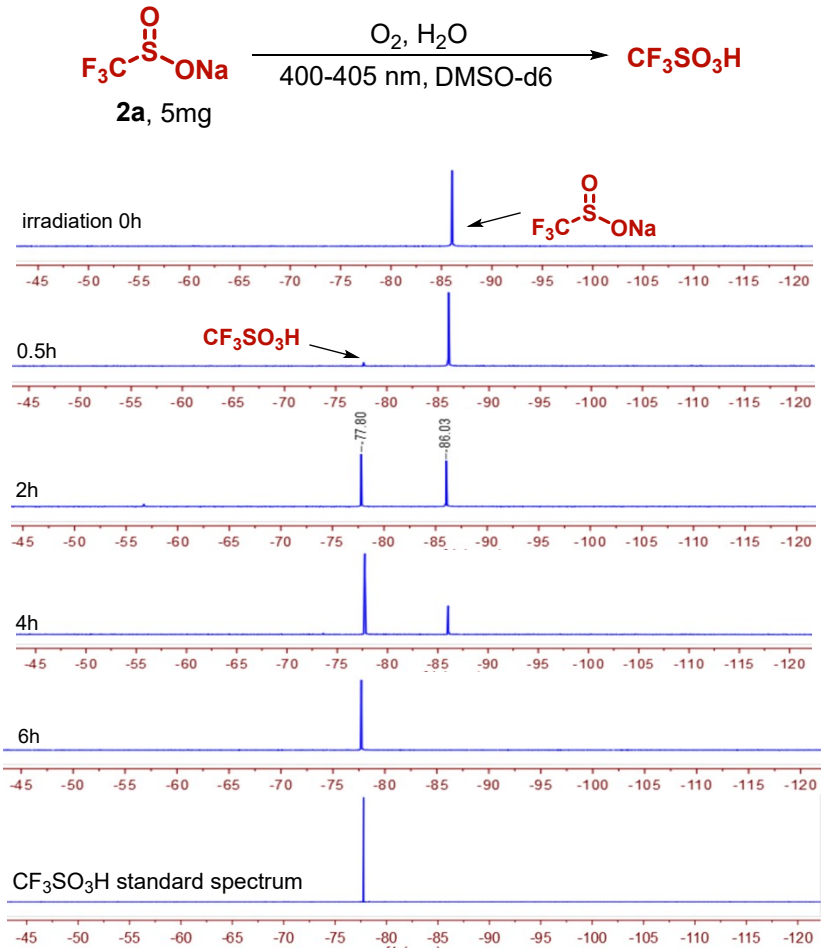


Figure S2. ^{19}F NMR spectra of CF_3SO_2Na irradiation for different times and CF_3SO_3H standard spectrum

4.2 High-resolution mass spectrometry and pH value of CF_3SO_2Na after irradiation

In an oven-dried reaction tube equipped with a magnetic stirrer bar was charged with sodium trifluoromethanesulfinate **2a** (5 mg) and CH_3CN (2.0 mL). Then the tube was exposed to a 10 W LED lamp (400-405 nm) in air, and test the pH after stirring for 0 h, 2 h, 4 h, and 6h (Figure S3). After irradiation for 6 h, the reaction was detected by HRMS shown in Figure S4, HRMS (-ESI) m/z: $[M]^-$ Calcd for $CF_3SO_3^-$ 148.9526; Found 148.9530.

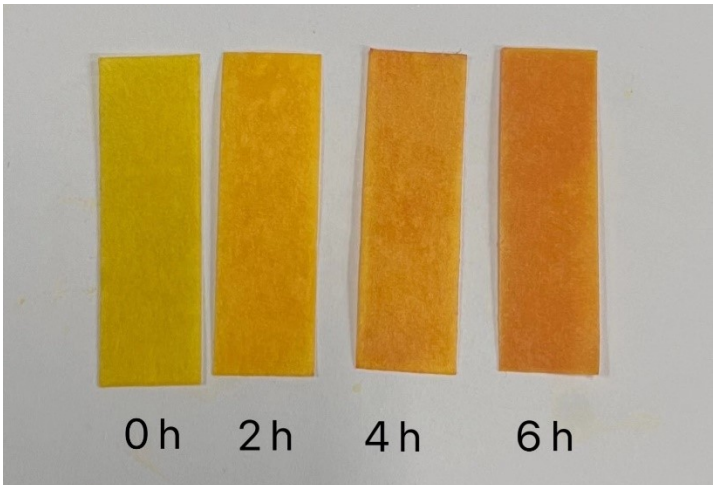


Figure S3. The pH of CF_3SO_2Na irradiation for different times.

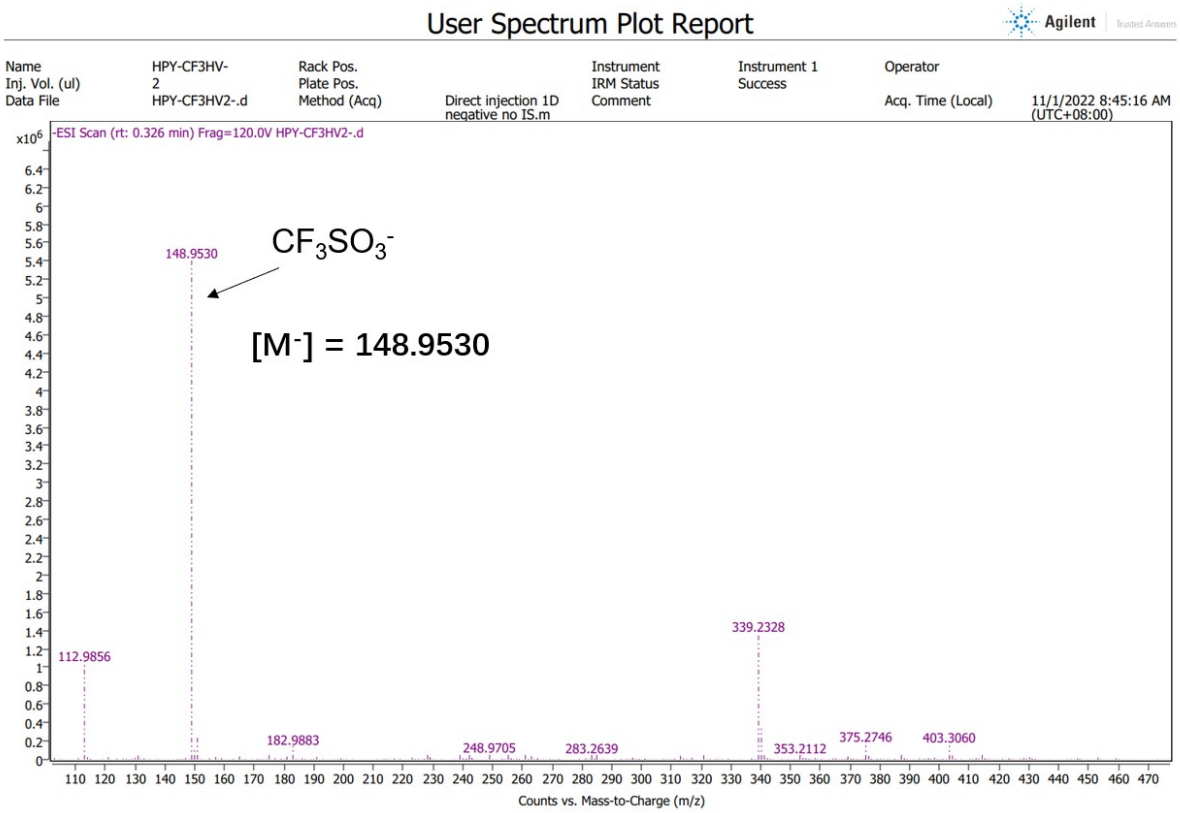
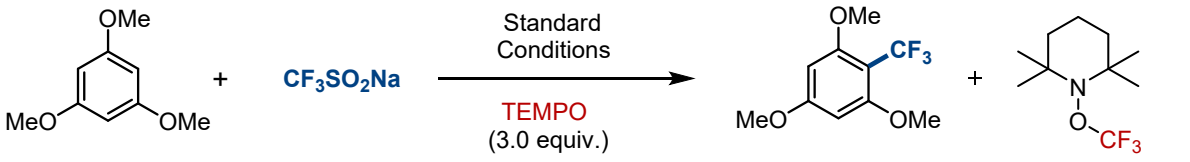


Figure S4. Mass spectra of CF_3SO_2Na irradiation for 6 h

4.3 Radical trapped experiment using TEMPO as radical scavenger



1a **2a** **3a** N.D. detected by ESI-MS

An oven-dried reaction tube equipped with a magnetic stirrer bar was charged with 1,3,5-trimethoxybenzene **(1a)** (0.3 mmol), sodium trifluoromethanesulfinate **2a** (0.45 mmol), TEMPO (0.9 mmol) and DMSO (2.0 mL). The tube was then exposed to a 10 W LED lamp (400-405 nm) irradiation

at room temperature in air with stirring for 24 h. After completion of the reaction, no **3a** was detected and the adduct **TEMPO-CF_3** was detected by ESI-MS shown in Figure S5, MS (ESI) m/z $C_{10}H_{17}F_3NO$ $[M-H]^-$: found 224.89.

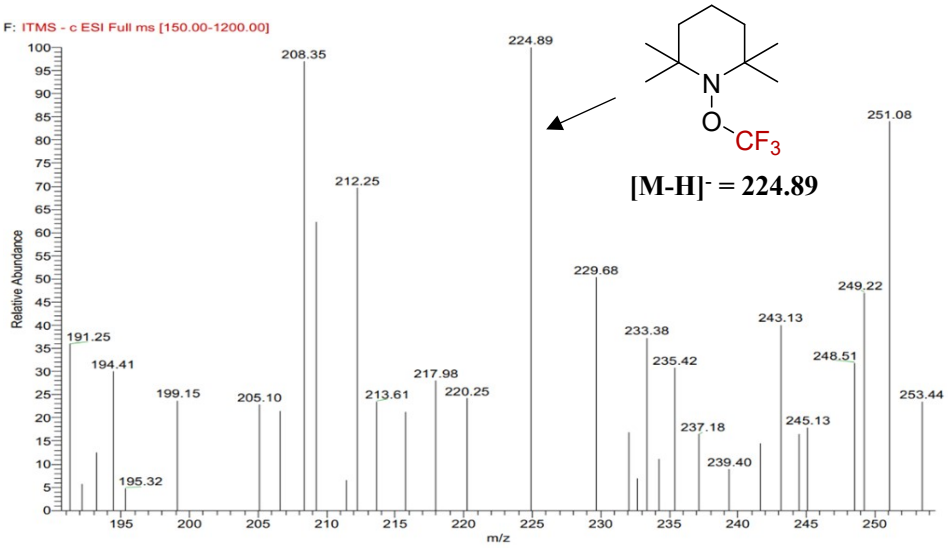
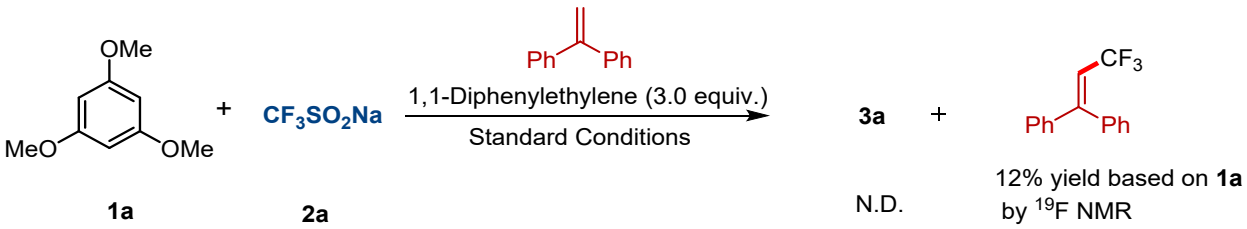


Figure S5. Mass spectra of **TEMPO-CF_3**

4.4 Radical trapped experiment using DPE as radical scavenger



In an oven-dried reaction tube equipped with a magnetic stirrer bar was charged with 1,3,5-trimethoxybenzene **(1a)** (0.3 mmol), sodium trifluoromethanesulfinate **2a** (0.45 mmol), diphenylethylene DPE (0.6 mmol) and DMSO (2.0 mL). The tube was then exposed to a 10 W LED lamp (400-405 nm) irradiation at room temperature in air with stirring for 24 h. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2 and the organic phase was then removed under vacuum. $PhOCF_3$ (internal standard, 4 mg) and $CDCl_3$ was added. Yield was calculated based on ^{19}F NMR. ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.35 (d, J_{H-F} = 8.3 Hz).

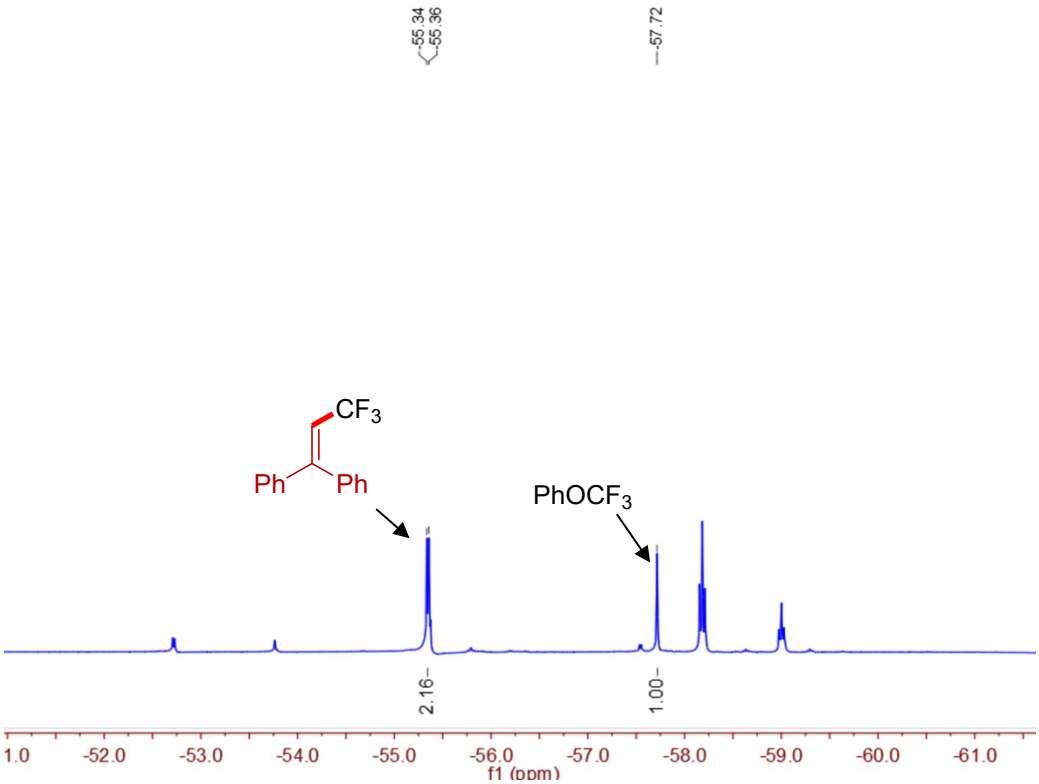
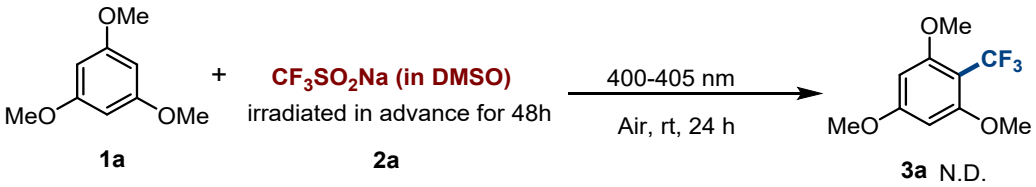


Figure S6. ^{19}F NMR spectra of the adduct **DPE-CF$_3$**.

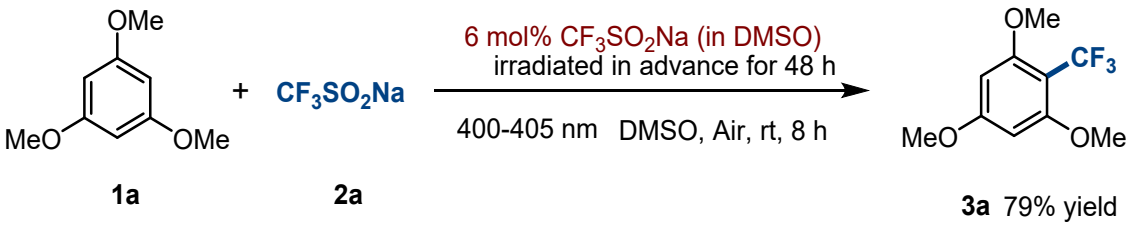
4.5 Control experiment

4.5.1 CF_3SO_2Na irradiated in advance for 48 h (2 mL)



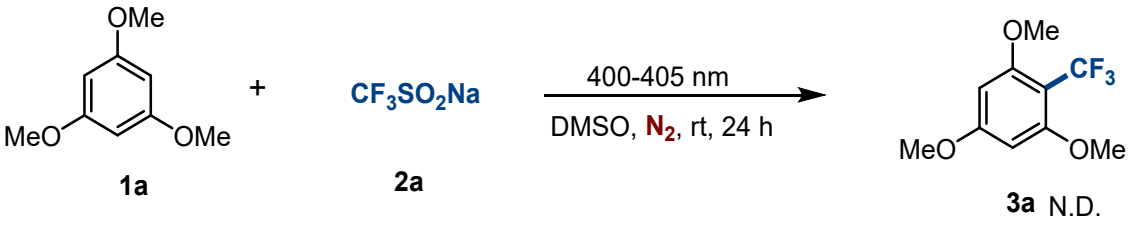
A mixture of sodium trifluoromethanesulfinate **2a** (0.3 mmol) and DMSO (2 mL) were added to a reaction tube. The reaction was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 48 h. 1,3,5-trimethoxybenzene **1a** (0.15 mmol) was then added to the reaction solution and exposed to light for 24 h. No desired products were observed.

4.5.2 CF_3SO_2Na irradiated in advance for 48 h (6 mol%)



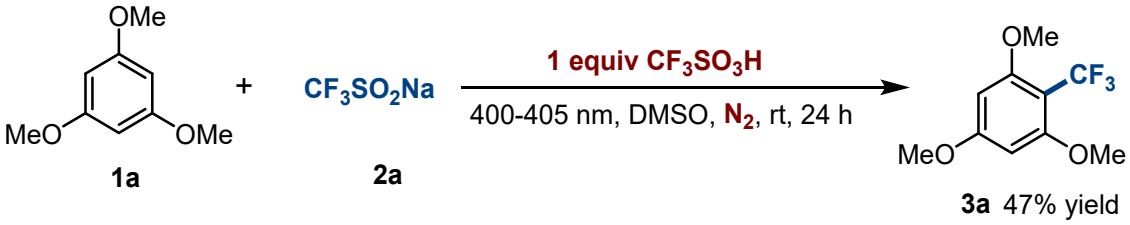
Sodium trifluoromethanesulfinate **2a** (0.3 mmol) and DMSO (2 ml) were added to a reaction tube. The reaction was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 48 h. A mixture of 1,3,5-trimethoxybenzene **1a** (0.3 mmol), sodium trifluoromethanesulfinate **2a** (0.45 mmol), 200 μL the above reaction and DMSO (2 mL) were added to another reaction tube. The reaction was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 6 h. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2 and the organic phase was then removed under vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product with 80% yield.

4.5.3 Under a nitrogen atmosphere



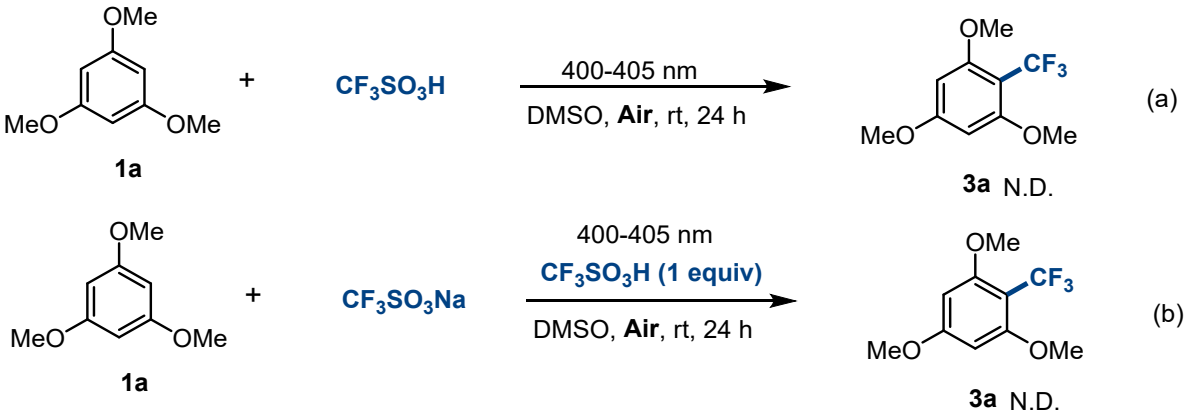
A mixture of 1,3,5-trimethoxybenzene **1a** (0.3 mmol), sodium trifluoromethanesulfinate **2a** (0.45 mmol), and DMSO (2 mL) were added to a Schlenk tube. The tube was evacuated and backfilled with N_2 for three times. The mixture was then irradiated by 400-405 nm (10 W) for 24 h. No desired products were observed.

4.5.4 Under nitrogen atmosphere with the addition of 1 equiv CF_3SO_3H.



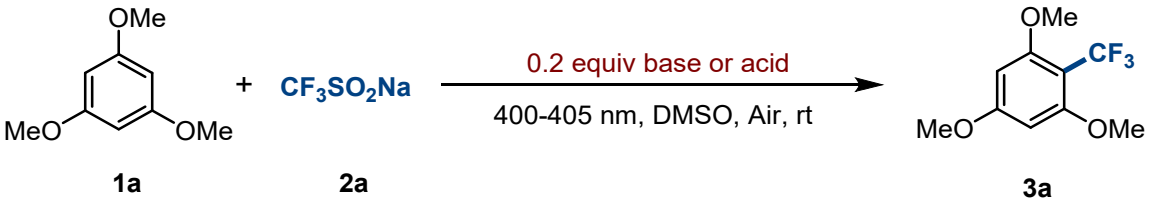
A mixture of 1,3,5-trimethoxybenzene **1a** (0.3 mmol), sodium trifluoromethanesulfinate **2a** (0.45 mmol), CF_3SO_3H (0.3 mmol) and DMSO (2 mL) were added to a Schlenk tube. The tube was evacuated and backfilled with N_2 for three times. The mixture was then irradiated by 400-405 nm (10 W) for 24 h. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2, and the organic phase was then removed under vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product with 47% yield.

4.5.5 Trifluoromethyl source studies



A mixture of 1,3,5-trimethoxybenzene **1a** (0.3 mmol), CF_3SO_3H (0.45 mmol), and DMSO (2 mL) were added to a reaction tube. The reaction was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 24 h. No desired products were observed. At the same time, the transformation was not achieved when CF_3SO_2Na was replaced with CF_3SO_3Na and 1 eq CF_3SO_3H.

4.5.6 Monitoring of reaction processes



In an oven-dried reaction tube equipped with a magnetic stirrer bar was charged with 1,3,5-trimethoxybenzene **1a** (0.3 mmol), sodium trifluoromethanesulfinate **2a** (0.45 mmol), additive (0.06 mmol) and DMSO (2 mL). Tubes were then exposed to a 10 W LED lamp (400-405 nm) irradiation at room temperature in air with stirring for 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 10 h. After radiation for the corresponding hours, the resulting mixture was extracted with CH_2Cl_2 and the organic phase was then removed under vacuum. After evaporation of the solvent, the crude reaction mixture was then purified by flash column chromatography to afford yield (**Figure S7**).

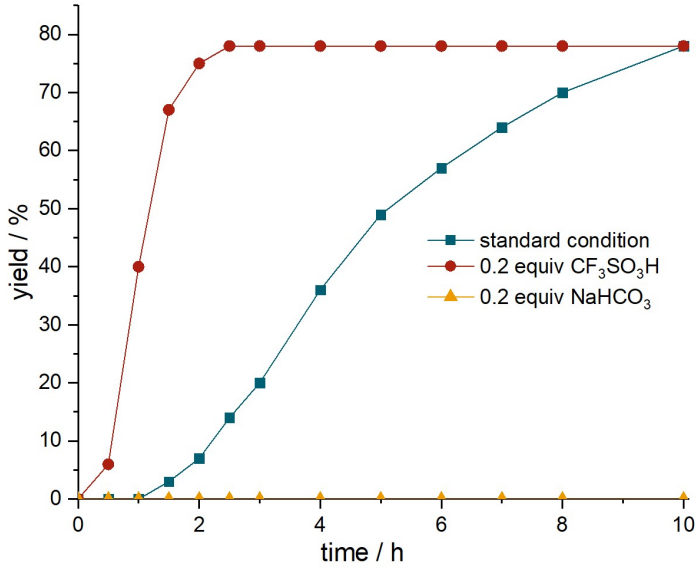
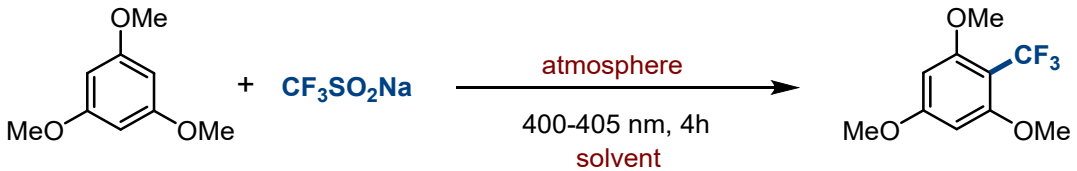


Figure S7. Monitoring of reaction processes

4.5.7 Water source investigation

Table S4. Water source investigation.[a]



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

	Solvent	Atmosphere	Yield (%)[b]
1	DMSO (Ultra-Dry)	air	45
2	DMSO (AR)	air	35
3	DMSO + 10μL H_2O	air	20
4	DMSO : H_2O = 1:1	air	15
5	DMSO (Ultra-Dry)	Dry air	8
6	DMSO (AR)	Dry air	12

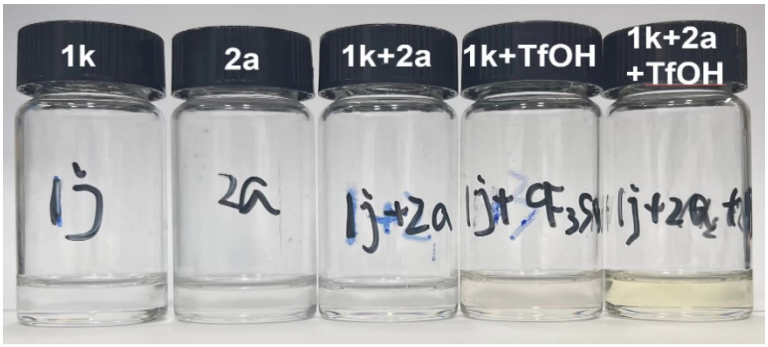
[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.5 equiv.), solvent (2 mL), rt, 4 h irradiated under 400-405 nm. [b] Isolated yield based on **1a**.

4.6 UV/Vis Studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a P6 spectrophotometer from MAPADA. Absorption spectra of individual reaction components and mixtures thereof were shown in Figure S8. When thiophene **1k** (0.1 M in DMSO) or CF_3SO_2Na **2a** (0.1 M in DMSO) only displayed absorption curves in the UV region, while the redshift of the mixed solution of **1k** and CF_3SO_3H demonstrates the possible formation of protonated aromatic hydrocarbons (green line). The

absorption band tail of the mixture of **1k**, **2a**, and CF_3SO_3H extends to the visible region (red line) compared with the mixture of **1k** and **2a** (yellow line), indicating that acid promotes the formation of an EDA complex between the aromatic hydrocarbons and the fluoroalkylsulfonate. A series of representative substrates containing O and N heteroatoms and no heteroatoms were also subjected to protonation tests, and all of them showed a slight or pronounced redshift in the absorption band tail.

A)



B)

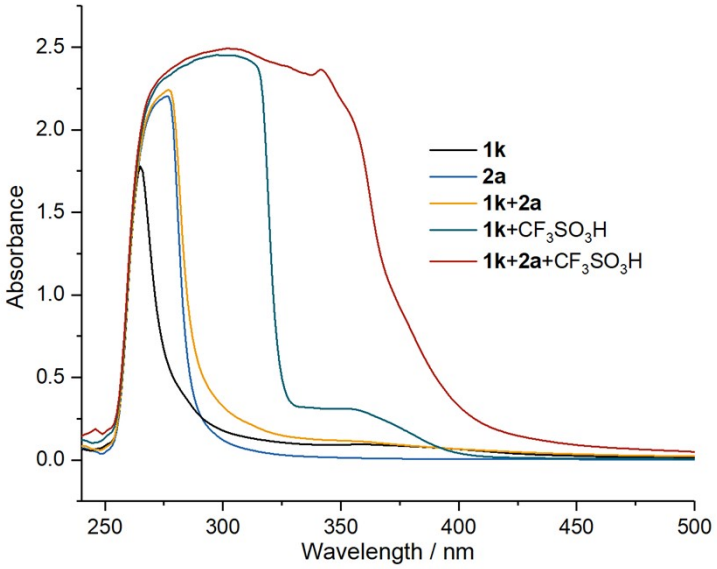


Figure S8. UV/Vis absorption spectra of individual reaction components and a combination spectra were measured in DMSO with a concentration of **A-B**: **1k** (0.1 M), **2a** (0.1 M), **1k** and **2a** (0.1 M), **1k** and CF_3SO_3H (0.1 M), **1k**, **2a**, and CF_3SO_3H (0.1 M).

Absorption spectra of individual reaction components and mixtures thereof were shown in Figure S9. Benzene **1c** (0.1 M in DMSO) or CF_3SO_2Na **2a** (0.1 M in DMSO) only displayed absorption curves in the UV region. The absorption band tail of the mixture of **1c**, **2a**, and CF_3SO_3H caused a red shift (red line) compared with the mixture of **1c** and **2a** (green line), indicating that acid promotes the formation of an EDA complex between the arenes and the fluoroalkylsulfonate.

C)

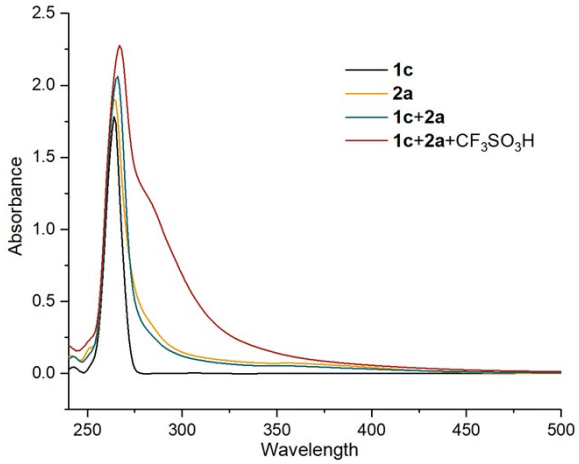


Figure S9. UV/Vis absorption spectra of individual reaction components and a combination spectra were measured in DMSO and with a concentration of **C**: **1c** (0.1 M), **2a** (0.1 M), **1c** and **2a** (0.1 M), **1c**, **2a**, and CF_3SO_3H (0.1 M).

D)

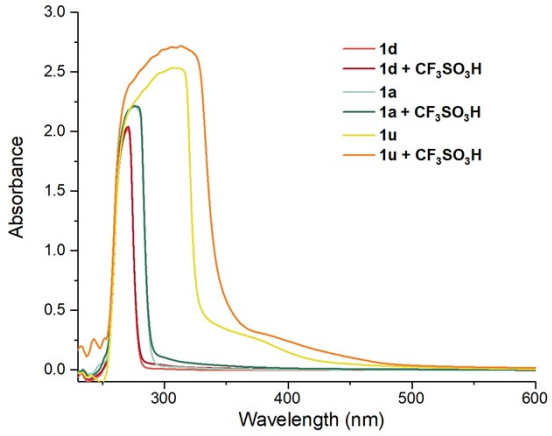


Figure S10. UV/Vis absorption spectra of individual reaction components and a combination spectra were measured in DMSO and with a concentration of **D**: **1d** (0.1 M), **1d** and CF_3SO_3H (0.1 M), **1a** (0.1 M), **1a** and CF_3SO_3H (0.1 M).

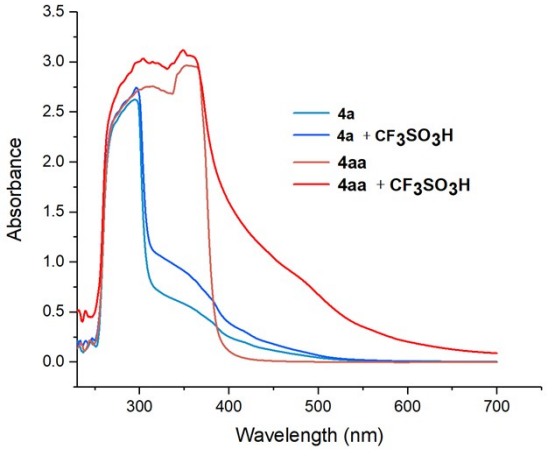


Figure S11. UV/Vis absorption spectra of individual reaction components and a combination spectra were measured in DMSO and with a concentration of **D**: **4a** (0.1 M), **4a** and CF_3SO_3H (0.1 M), **4aa** (0.1 M), and **4aa** CF_3SO_3H (0.1 M).

4.7 NMR Spectra of Titration Experiments (400 MHz, $CDCl_3$)

^1H NMR spectra of several samples (mixtures of **1d**, CF_3SO_3H and **2a**) in $CDCl_3$ were recorded at 298 K. DMSO-*d6* (δ = 2.508 ppm) was used as internal standard. The total volume of the mixture was 0.5 mL, and the amount of **1d** and CF_3SO_3H was kept constant at 0.1 mmol (0.2 M), while the amount of **2a** was varied from 0 to 0.5 mmol (0~1 M).

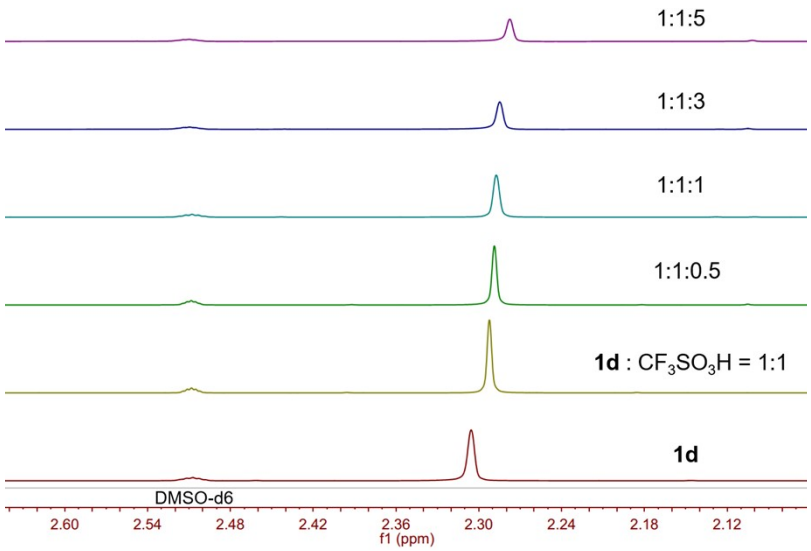


Figure S12. ^1H NMR spectra of a mixture of **1d** (1 equiv), CF_3SO_3H (1 equiv) and **2a** (0~5 equiv.) in $CDCl_3$.

4.8 Determination of Association Constant (k_{TRI})

The association constant of the EDA complex was determined by UV-Vis measurements in DMSO employing Benesi-Hildebrand method.[9] The absorbance of a constant concentration of **1k** (0.02 M) with CF_3SO_3H (0.02 M), and an increasing concentration of **2a** (0.02~0.12M) was recorded at 400 nm. The absorption spectra shown in Figures S11 recorded in a 1 cm path quartz cuvette.

To determine the k_{TRI}, the reciprocal concentration of **2a** was plotted against the reciprocal absorbance (A) of **2a** at 400 nm (Tables S4). A straight line was obtained, and by dividing the intercept through the slope: k_{TRI} = 1.98 M^{-1} for **1k** + CF_3SO_3H/**2a**.

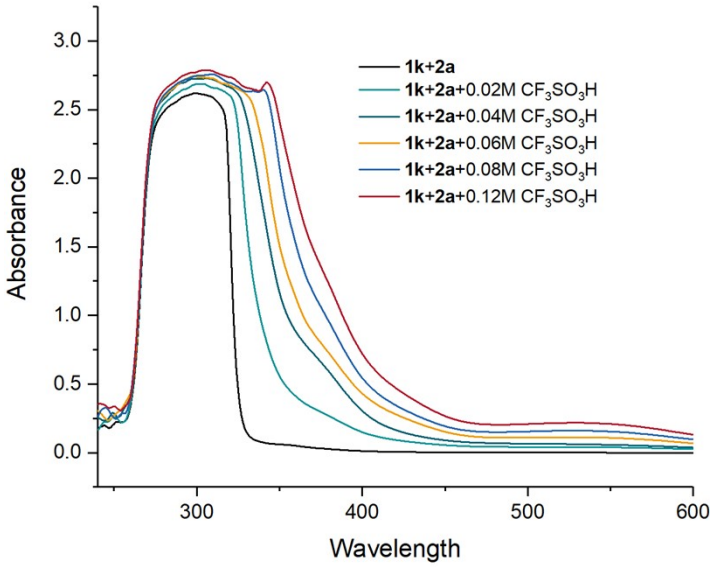


Figure S13. UV-Vis absorption spectra of **1k** (0.02 M in DMSO) and CF_3SO_3H (0.02 M in DMSO) in combination with increasing concentrations of **2a** (from 0.02 M to 0.12 M in DMSO).

Table S5. Data obtained from the UV-Vis absorption spectra of the three components in DMSO. The concentration of **1k** and CF_3SO_3H was kept at 0.02 M in DMSO.

2a (M)	**1/2a (M^{-1})**	**Abs_{EDA}**	**A_0**	**$1/(Abs_{EDA}-A_0)$**
0.02	50.0	0.137	0.012	7.299
0.04	25.0	0.292	0.012	3.420
0.06	16.6	0.420	0.012	2.383
0.08	12.5	0.533	0.012	1.876
0.12	8.3	0.710	0.012	1.410

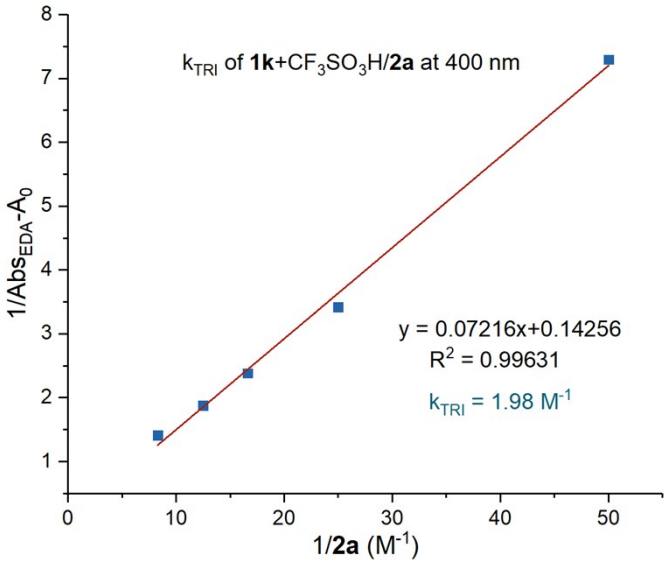


Figure S14. Benesi-Hildebrand plot for the complex generated in DMSO upon the association of **1k**, CF_3SO_3H and **2a**.

4.9 Determination of the Quantum Yield

4.9.1 Determination of the light intensity at 405 nm

According to the procedure of Yoon[10] the photon flux of the LED (λ_{max} = 405 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (5.0 mg) and sodium acetate (1.13 g) in H_2SO_4 (5.0 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (3.0 mL) was placed in a cuvette and irradiated for 90 seconds at λ_{max} = 405 nm. After irradiation, the phenanthroline solution (0.525 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the diluent solution (200μL of solution diluted with water to 3.5 mL) was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

	Non-irrad	Irrad 1	Irrad 2	Irrad 3
A_{510nm}	0.023	1.007	0.978	0.937
Average A_{510nm} of irradiation samples		0.974		

$$\textbf{mol } Fe^{2+} = (V \times \Delta A)/ (l \times \varepsilon) \quad \text{(S3)}$$

$$\textbf{mol } Fe^{2+} = (V \times \Delta A \times V_2)/ (l \times \varepsilon \times V_1) \quad \text{(S4)}$$

$$\textbf{mol } Fe^{2+} = [3.525\times10^{-3}\ L \times (0.974–0.023) \times 0.0032] / (1\ cm \times 11100\ L\ mol^{-1}cm^{-1} \times 200\times10^{-6}) = 4.832 \times 10^{-6}\ mol$$

V is the total volume (3.525×10^{-3} L) of the solution after addition of phenanthroline, V_2 is the sample being test, V_3 is the volume detected after dilution, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L $mol^{-1}cm^{-1}$)[11]. The photon flux can be calculated using eq 3.

$$\textbf{photo flux} = \text{mol } Fe^{2+}/ (\Phi \times t \times f) \quad \text{(S5)}$$

$$\textbf{photo flux} = 4.832\times10^{-6} / (1.13 \times 90 \times 0.942) = 5.044 \times 10^{-8}\ \text{einstein}\ s^{-1}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.13 for a 0.15 M solution at λ = 405 nm),[12] t is the time (90.0 s), and f is the fraction of light absorbed at λ = 405 nm (0.94246). The photon flux was calculated (average of three experiments) to be 5.044×10^{-8} einstein s^{-1}.

Determination of fraction of light absorbed at 405 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution at 405 nm was measured to be 0.942. The fraction of light absorbed (f) by this solution was calculated using eq 4, where *A* is the measured absorbance at 405 nm.

$$f = 1 – 10^{-A} \quad \text{(S6)}$$

$$f = 1 - 10^{-1.24} = 0.942$$

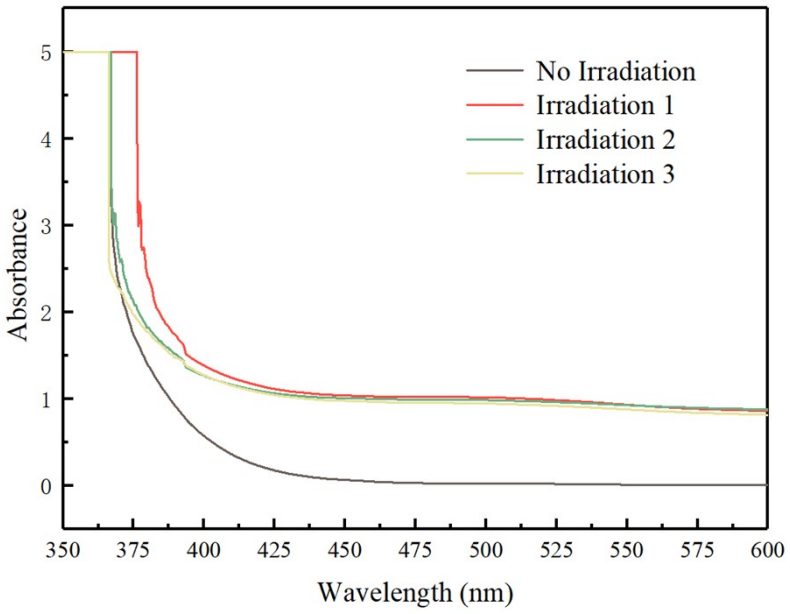


Figure S15. Absorption spectra of three irradiation experiments and non-irradiation experiment

4.9.2 Determination of the reaction quantum yield at 405 nm

A mixture of 1,3,5-trimethoxybenzene **1a** (0.3 mmol), CF_3SO_2Na **2a** (0.45 mmol) and DMSO (2 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of a 10 W LED lamp (400-405 nm) for 14400s. After irradiation, the yield of the product **3a** was determined by ^{19}F NMR based on a trifluoromethoxybenzene standard and the final yield was 31.1% (9.33×10^{-5} mol).

Quantum Yield (Φ) = moles of product formed/ (flux × f × t) (S7)

$= 9.33 \times 10^{-5}/(5.044 \times 10^{-8} \times 0.942 \times 9000)$

$= 0.14$

4.10 On/off experiments of 3a

Five parallel reactions were performed between 1,3,5-trimethoxybenzene **1a** (0.3 mmol), CF_3SO_2Na **2a** (0.45 mmol) according to the General Procedure A. The yield of **3a** was recorded at the given times. The white area indicates the light irradiation, while the grey area indicates time in the dark.

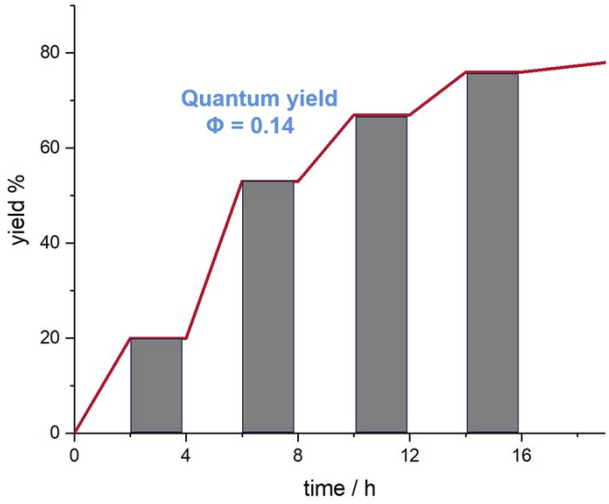


Figure S16. On/off experiments of **3a**.

5.1 Proposed mechanism of fluoroalkylation/cyclization

The reaction was initiated by the formation of CF_3SO_3H with **2a**, and H_2O under 400-405 nm light irradiation.The long chain substrate then undergo protonation to form EDA Complexes with **2a**. The charge transfer event within the complex lead to the generation of trifluoromethyl radicals with the release of sulfur dioxide under 400-405 nm irradiation. The trifluoromethyl radical was trapped by the double bond of substrate **4** to generate radical intermediate **C**. Subsequently, the radical of intermediate **C** underwent a cyclization to form cyclized intermediate **D**. After a 1,2-hydrogen shift, the intermediate **D** was transformed into the carbon radicals **E**. Finally, the oxidation and deprotonation of the carbon radicals **E** provided trifluoromethyl-substituted polycyclic benzimidazole **5** and regenerated the proton to activate another substrate.

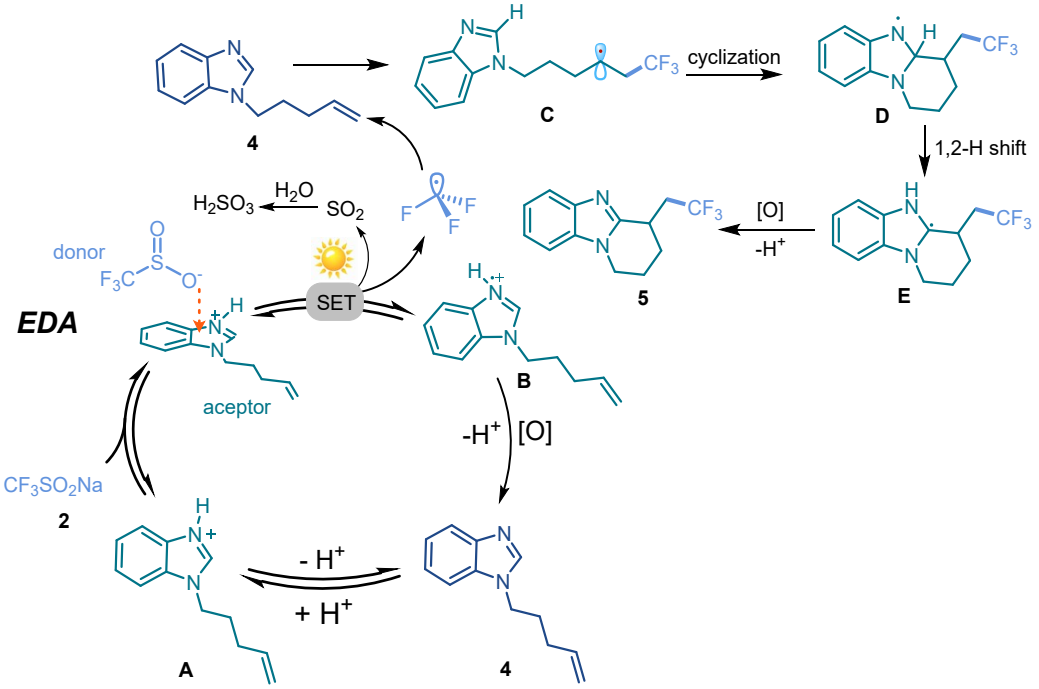
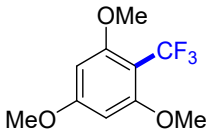


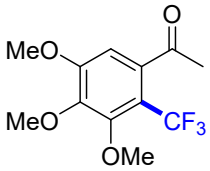
Figure S17. Proposed mechanism.

5. Characterization Data for the Products



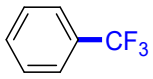
1,3,5-trimethoxy-2-(trifluoromethyl)benzene (3a)[13]

The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a white solid (55 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (s, 2H), 3.86 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.51, 160.41, 124.35 (C–F, $^{1}J_{C\text{-}F}$, J = 273.3 Hz), 100.35 (C–F, $^{2}J_{C\text{-}F}$, J = 30.1 Hz), 91.24, 56.22, 55.35. ^{19}F NMR (376 MHz, $CDCl_3$): δ -54.12.



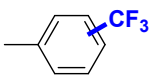
1-(3,4,5-trimethoxy-2-(trifluoromethyl)phenyl)ethan-1-one (3b) [13]

The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a white solid (58 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 3.97 (s, 3H), 3.91 (d, J = 4.4 Hz, 6H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.36, 156.27, 152.84, 143.46, 137.71 (C–F, $^{3}J_{C\text{-}F}$, J = 2.5 Hz), 123.44 (C–F, $^{1}J_{C\text{-}F}$, J = 273.3 Hz), 112.95 (C–F, $^{2}J_{C\text{-}F}$, J = 31.0 Hz), 104.49, 61.80, 60.85, 56.23, 31.34 (C–F, $^{3}J_{C\text{-}F}$, J = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.00.



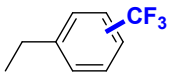
trifluorotoluene (3c)

Following the general procedure A, using benzene (0.3 mmol), CF_3SO_2Na (0.45 mmol), the reaction was run for 24 hours. Upon completion, the reaction was quenched with $CDCl_3$ (1.2 mL) and water (2 mL). The organic layer (0.5 ml) was taken and dried over anhydrous $MgSO_4$ and placed into a NMR tube. $PhOCF_3$ was added to the NMR tube and analyzed directly by ^{19}F NMR (71 % yield). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.68 (s, 3F). The fluorine signals of the product were identical to those of a commercial sample.



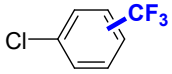
1-methyl-2-(trifluoromethyl)benzene (3d-o), 1-methyl-3-(trifluoromethyl)benzene (3d-m) and 1-methyl-4-(trifluoromethyl)benzene (3d-p).

Following the general procedure A, using toluene (0.3 mmol), CF_3SO_2Na (0.45 mmol), the reaction was run for 24 hours. Upon completion, the reaction was quenched with $CDCl_3$ (1.2 mL) and water (2 mL). The organic layer (0.5 mL) was taken and dried over anhydrous $MgSO_4$ and placed into a NMR tube. Trifluoromethoxybenzene was added to the NMR tube and analyzed directly by ^{19}F NMR (36 % yield) (**3d**-o : **3d**-m : **3d**-p = 2.3 : 1.2 : 1) and is in accordance with literature 14. The ^{19}F spectroscopic data matched reported data: **3d**-o: -61.68 ppm (lit.S14 -61.77 ppm)., **3d**-m: -62.60 ppm (lit.S14 -62.70 ppm), **3d**-p: -62.25 ppm (lit.S14 -62.37 ppm).



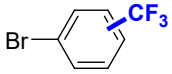
1-ethyl-2-(trifluoromethyl)benzene (3e-o), 1-ethyl-3-(trifluoromethyl)benzene (3e-m) and 1-ethyl-4-(trifluoromethyl)benzene (3e-p).

Following the general procedure A, using ethylbenzene (0.3 mmol), CF_3SO_2Na (0.45 mmol), the reaction was run for 24 hours. Upon completion, the reaction was quenched with $CDCl_3$ (1.2 mL) and water (2 mL). The organic layer (0.5 mL was taken and dried over anhydrous $MgSO_4$ and placed into a NMR tube. Trifluoromethoxybenzene was added to the NMR tube and analyzed directly by ^{19}F NMR (58 % yield) (**3e**-o : **3e**-m : **3e**-p = 1.3 : 1.2 : 1) and is in accordance with literature 15. The ^{19}F spectroscopic data matched reported data: **3e**-o: -59.96 ppm (lit.S15 -60.31 ppm), **3e**-m: -62.55 ppm (lit.S15 -62.90 ppm), **3e**-p: -62.26 ppm (lit.S15 -62.61 ppm).



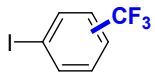
1-chloro-2-(trifluoromethyl)benzene (3f-o), 1-chloro-3-(trifluoromethyl)benzene (3f-m) and 1-chloro-4-(trifluoromethyl)benzene (3f-p).

Following the general procedure A, using chlorobenzene (0.3 mmol), CF_3SO_2Na (0.45 mmol), the reaction was run for 32 hours. Upon completion, the reaction was quenched with $CDCl_3$ (1.2 mL) and water (2 mL). The organic layer (0.5 mL) was taken and dried over anhydrous $MgSO_4$ and placed into a NMR tube. Trifluoromethoxybenzene was added to the NMR tube and analyzed directly by ^{19}F NMR (50 % yield) (**3f**-o : **3f**-m : **3f**-p = 1 : 1.2 : 1.7) and is in accordance with literature 14. The ^{19}F spectroscopic data matched reported data: **2e**-o: -62.57 ppm (lit.S14 -62.68 ppm), **2e**-m: -62.63 ppm (lit.S14 -62.74 ppm), **2e**-p: -62.88 ppm (lit.S14 -62.98 ppm).



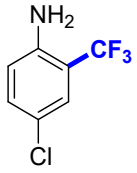
1-bromo-2-(trifluoromethyl)benzene (3g-o), 1-bromo-3-(trifluoromethyl)benzene (3g-m) and 1-bromo -4-(trifluoromethyl)benzene (3g-p).

Following the general procedure A, using bromobenzene (0.3 mmol), CF_3SO_2Na (0.45 mmol), the reaction was run for 24 hours. Upon completion, the reaction was quenched with $CDCl_3$ (1.2 mL) and water (2 mL). The organic layer (0.5 mL) was taken and dried over anhydrous $MgSO_4$ and placed into a NMR tube. Trifluoromethoxybenzene was added to the NMR tube and analyzed directly by ^{19}F NMR (31 % yield) (**3g**-o : **3g**-m : **3g**-p = 1 : 1.2 : 1.9) and is in accordance with literature 14. The ^{19}F spectroscopic data matched reported data: **2e**-o: -62.66 ppm (lit.S14 -62.78 ppm), **2e**-m: -62.71 ppm (lit.S14 -62.83 ppm), **2e**-p: -62.85 ppm (lit.S14 -62.96 ppm).



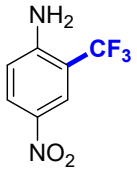
1-iodo-2-(trifluoromethyl)benzene (3h-o), 1-iodo-3-(trifluoromethyl)benzene (3h-m) and 1-iodo-4-(trifluoromethyl)benzene (3h-p).

Following the general procedure A, using iodobenzene (0.3 mmol), CF_3SO_2Na (0.45 mmol), the reaction was run for 24 hours. Upon completion, the reaction was quenched with $CDCl_3$ (1.2 mL) and water (2 mL). The organic layer (0.5 mL) was taken and dried over anhydrous $MgSO_4$ and placed into a NMR tube. Trifluoromethoxybenzene was added to the NMR tube and analyzed directly by ^{19}F NMR (65 % yield) (**3h**-o : **3h**-m : **3h**-p = 2 : 1.5 : 1) and is in accordance with literature 16. The ^{19}F spectroscopic data matched reported data: **2e**-o: -62.75 ppm (lit.S16 -62.81 ppm), **2e**-m: -62.83 ppm (lit.S16 -62.90 ppm), **2e**-p: -62.92 ppm (lit.S16 -62.99 ppm).



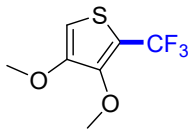
4-chloro-2-(trifluoromethyl)aniline (3i) [17]

The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a white solid (43 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.3 Hz, 1H), 7.26 (dd, J = 8.7, 2.2 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 3.84 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.08, 132.79, 126.33 (C–F, $^3J_{C\text{-}F}$, J = 5.4 Hz), 124.11 (C–F, $^1J_{C\text{-}F}$, J = 265.7 Hz), 122.32, 118.45, 114.76 (C–F, $^2J_{C\text{-}F}$, J = 30.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.24.



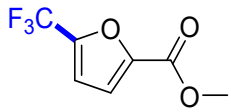
4-nitro-2-(trifluoromethyl)aniline (3j) [18]

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (32 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 2.4 Hz, 1H), 8.20 (dd, J = 9.0, 2.5 Hz, 1H), 6.80 (d, J = 9.1 Hz, 1H), 4.96 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.75, 138.02, 128.70, 124.17 (C–F, $^{3}J_{C\text{-}F}$, J =5.4 Hz), 123.62 (C–F, $^{1}J_{C\text{-}F}$, J =270.9 Hz), 116.37, 112.36 (C–F, $^{2}J_{C\text{-}F}$, J = 31.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.56.



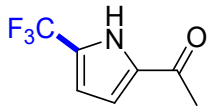
3,4-dimethoxy-2-(trifluoromethyl)thiophene (3k)[13]

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (60 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 3.96 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.51, 147.38 (C–F, $^{3}J_{C\text{-}F}$, J = 3.3 Hz), 122.21 (C–F, $^{1}J_{C\text{-}F}$, J = 268.4 Hz), 112.90 (C–F, $^{2}J_{C\text{-}F}$, J = 37.8 Hz), 98.33, 61.08, 57.50. ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.62.



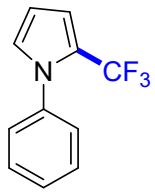
methyl 5-(trifluoromethyl)furan-2-carboxylate (3l)[19]

The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a yellow oil (25 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 2.8 Hz, 1H), 6.91 (d, J = 3.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.15, 146.30, 144.59 (C–F, $^{2}J_{C\text{-}F}$, J = 43.4 Hz), 118.31 (C–F, $^{1}J_{C\text{-}F}$, J = 261.0 Hz), 117.61, 112.85 (C–F, $^{3}J_{C\text{-}F}$, J = 2.8 Hz), 52.47. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.49.



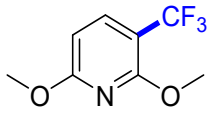
1-(5-(trifluoromethyl)-1*H*-pyrrol-2-yl)ethan-1-one (3m)[13]

The product was purified by column chromatography on silica gel (eluent: 80:1 petroleum ether: ethyl acetate) as a yellow oil (40 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 6.89 (s, 1H), 6.63 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.81, 133.49, 125.79 (C–F, $^{2}J_{C\text{-}F}$, J = 39.9 Hz), 120.38 (C–F, $^{1}J_{C\text{-}F}$, J = 266.2 Hz), 115.70, 110.91 (C–F, $^{3}J_{C\text{-}F}$, J = 2.8 Hz), 25.65. ^{19}F NMR (376 MHz, $CDCl_3$): δ -60.74.



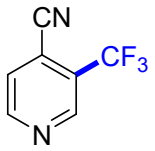
1-phenyl-2-(trifluoromethyl)-1*H*-pyrrole (3n)[13]

The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a white solid (46 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 3H), 7.47 – 7.42 (m, 2H), 6.96 – 6.92 (m, 1H), 6.83 – 6.79 (m, 1H), 6.34 (t, J = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.17, 129.01, 128.52, 127.30, 126.55, 122.28 (C–F, $^{2}J_{C\text{-}F}$, J = 38.0 Hz), 121.26 (C–F, $^{1}J_{C\text{-}F}$, J = 265.1 Hz), 112.78 (C–F, $^{3}J_{C\text{-}F}$, J = 3.4 Hz), 108.27. ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.88.



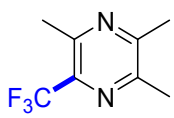
2,6-dimethoxy-3-(trifluoromethyl)pyridine (3o)[13]

The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a Colorless oil (33 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 1H), 6.33 (d, J = 8.3 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.15, 160.41, 138.69 (C–F, $^{3}J_{C\text{-}F}$, J = 4.5 Hz), 123.72 (C–F, $^{1}J_{C\text{-}F}$, J = 270.0 Hz), 104.28 (C–F, $^{2}J_{C\text{-}F}$, J = 33.4 Hz), 100.74, 53.72, 53.69. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.05.



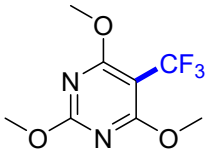
3-(trifluoromethyl)isonicotinonitrile (3p)[20]

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a Colorless oil (21 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 9.06 (d, J = 4.9 Hz, 1H), 7.76 (d, J = 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.04, 147.77 (C–F, $^{3}J_{C\text{-}F}$, J = 5.0 Hz), 126.89, 126.62 (C–F, $^{2}J_{C\text{-}F}$, J = 33.2 Hz), 121.80 (C–F, $^{1}J_{C\text{-}F}$, J = 274.2 Hz), 118.47 (C–F, $^{3}J_{C\text{-}F}$, J = 2.2 Hz), 113.21. ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.69.



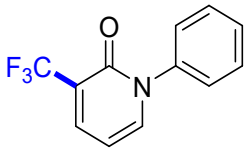
2,3,5-trimethyl-6-(trifluoromethyl)pyrazine (3q)[21]

The product was purified by column chromatography on silica gel (eluent: 80:1 petroleum ether: ethyl acetate) as a colorless oil (34 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (d, J = 1.1 Hz, 3H), 2.58 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.80, 148.73, 148.46, 138.35 (C–F, $^{2}J_{C\text{-}F}$, J = 34.1 Hz), 122.24 (C–F, $^{1}J_{C\text{-}F}$, J = 274.3 Hz), 21.90, 21.23, 20.72 (C–F, $^{3}J_{C\text{-}F}$, J =2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.17.



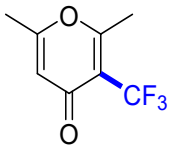
2,4,6-trimethoxy-5-(trifluoromethyl)pyrimidine (3r)[13]

The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a white solid (36 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (s, 6H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.77, 164.93, 123.43 (C–F, $^{1}J_{C\text{-}F}$, J = 271.3 Hz), 89.25 (C–F, $^{2}J_{C\text{-}F}$, J = 34.2 Hz), 55.09, 54.86. ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.99.



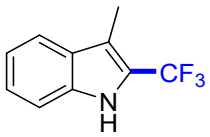
1-phenyl-3-(trifluoromethyl)pyridin-2(1*H*)-one (3s)[22]

The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (54 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 1H), 7.63 – 7.45 (m, 4H), 7.44 – 7.36 (m, 2H), 6.34 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.21, 141.96, 139.74, 139.41 (C–F, $^{3}J_{C\text{-}F}$, J = 5.0 Hz), 129.42, 129.07, 126.49, 122.62 (C–F, $^{1}J_{C\text{-}F}$, J = 270.1 Hz), 121.45 (C–F, $^{2}J_{C\text{-}F}$, J = 30.8 Hz), 104.11. ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.96.



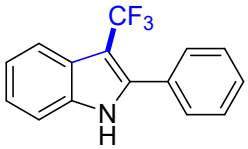
2,6-dimethyl-3-(trifluoromethyl)-4H-pyran-4-one (3t)[13]

The product was purified by column chromatography on silica gel (eluent: 2:1 petroleum ether: ethyl acetate) as a white solid (34 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H), 2.48 (q, J = 2.7 Hz, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.03, 167.18 (C–F, $^{3}J_{C\text{-}F}$, J =2.3 Hz), 165.06, 123.16 (C–F, $^{1}J_{C\text{-}F}$, J = 272.0 Hz), 116.60 (C–F, $^{2}J_{C\text{-}F}$, J = 28.9Hz), 114.75, 19.53 (C–F, $^{3}J_{C\text{-}F}$, J = 3.9 Hz), 19.50. ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.28.



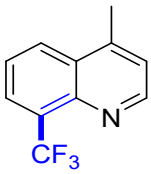
3-methyl-2-(trifluoromethyl)-1*H*-indole (3u)[13]

The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a white solid (54 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.27 – 7.21 (m, 1H), 2.49 (q, J = 3.5, 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.22, 128.09, 124.78, 122.16 (C–F, $^{1}J_{C\text{-}F}$, J = 266.8 Hz), 121.56 (C–F, $^{2}J_{C\text{-}F}$, J = 36.7 Hz), 120.41, 120.11, 114.11 (C–F, $^{3}J_{C\text{-}F}$, J = 3.0 Hz), 111.58, 8.32. ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.63.



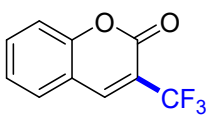
2-phenyl-3-(trifluoromethyl)-1*H*-indole (3v)[23]

The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate)as a white solid (69 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.57 – 7.50 (m, 3H), 7.46 – 7.41 (m, 1H), 7.38 – 7.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.62 (C–F, $^{3}J_{C\text{-}F}$, J = 4.1 Hz), 134.93, 131.08, 129.42, 129.06, 128.69, 125.62 (C–F, $^{3}J_{C\text{-}F}$, J = 1.7 Hz), 124.84 (C–F, $^{1}J_{C\text{-}F}$, J = 265.7 Hz), 123.50, 121.76, 120.05, 111.19, 103.52 (C–F, $^{2}J_{C\text{-}F}$, J = 35.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -52.70.



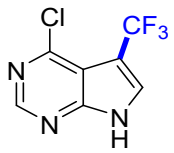
4-methyl-8-(trifluoromethyl)quinoline (3w)[24]

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (30 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 3.1 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 7.2 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 1.9 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.90, 144.61, 144.55, 128.77, 128.41, 128.07 (C–F, $^{2}J_{C\text{-}F}$, J = 29.1 Hz), 127.65 (C–F, $^{3}J_{C\text{-}F}$, J = 5.6 Hz), 124.84, 124.24 (C–F, $^{1}J_{C\text{-}F}$, J = 271.6 Hz), 122.69, 18.95. ^{19}F NMR (376 MHz, $CDCl_3$): δ -60.01.



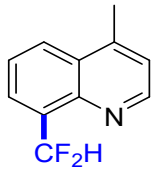
3-(trifluoromethyl)-2*H*-chromen-2-one (3x)[25]

The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (27 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.93, 154.62, 143.41 (C–F, $^{3}J_{C\text{-}F}$, J = 4.9 Hz), 134.48, 129.53, 125.32, 121.36 (C–F, $^{1}J_{C\text{-}F}$, J = 270.3 Hz), 117.66 (C–F, $^{2}J_{C\text{-}F}$, J = 33.1 Hz), 116.98, 116.78. ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.19.



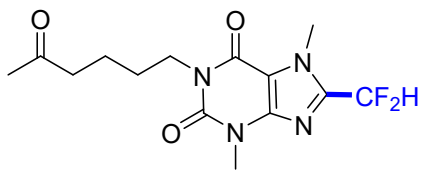
4-chloro-5-(trifluoromethyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (3y)[13]

The product was purified by column chromatography on silica gel (eluent: 6:1 petroleum ether: ethyl acetate) as a white solid (27 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.46 (s, 1H), 8.85 (s, 1H), 7.12 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.53, 152.25, 151.47, 128.39 (C–F, $^{2}J_{C\text{-}F}$, J = 40.6 Hz), 120.34 (C–F, $^{1}J_{C\text{-}F}$, J = 268.8 Hz), 117.35, 101.49 (C–F, $^{3}J_{C\text{-}F}$, J = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.64.



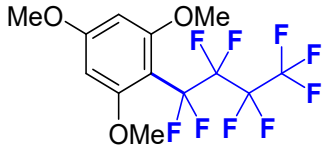
8-(difluoromethyl)-4-methylquinoline (3z)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (24 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 4.3 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 7.1 Hz, 1H), 7.87 (t, J = 55.7 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 4.2 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.25, 145.00 (C–F, $^{3}J_{C\text{-}F}$, J = 5.0 Hz), 144.80, 131.95 (C–F, $^{2}J_{C\text{-}F}$, J = 21.5 Hz), 128.09, 126.60 (C–F, $^{4}J_{C\text{-}F}$, J = 1.9 Hz), 126.19 (C–F, $^{3}J_{C\text{-}F}$, J = 6.5 Hz), 125.76, 122.44, 112.55 (C–F,$^{1}J_{C\text{-}F}$, J =236.0 Hz), 18.90. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.60. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_9F_2N$ 194.0781; Found 194.0781.



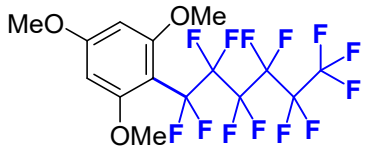
8-(difluoromethyl)-3,7-dimethyl-1-(5-oxohexyl)-3,7-dihydro-1*H*-purine-2,6-dione (3aa)[13]

The product was purified by column chromatography on silica gel (eluent: 1:1 petroleum ether: ethyl acetate) as a white solid (60 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (t, J = 52.2 Hz, 1H), 4.14 (s, 3H), 4.01 (t, J = 6.8 Hz, 2H), 3.55 (s, 3H), 2.50 (t, J = 6.8 Hz, 2H), 2.14 (s, 3H), 1.71 – 1.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.66, 155.37, 151.14, 146.92, 142.82 (C–F, $^{2}J_{C\text{-}F}$, J = 27.4 Hz), 109.73 (C–F, $^{1}J_{C\text{-}F}$, J = 236.5 Hz), 109.50, 43.09, 40.99, 32.87, 29.95, 29.70, 27.32, 20.89. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.99 (s, 1F), -115.13 (s, 1F).



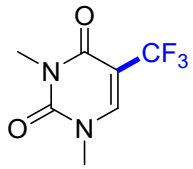
1,3,5-trimethoxy-2-(perfluorobutyl)benzene (3ab)[26]

The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a white solid (82 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 3.86 (s, 3H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.93, 161.76 (C–F, $^{3}J_{C\text{-}F}$ J =2.2 Hz), 122.86 – 105.63 (m), 98.53 (C–F, $^{2}J_{C\text{-}F}$ J =21.9 Hz), 91.72, 56.17, 55.18. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.43 – -81.77 (m, 3F), -101.88 – -103.62 (m, 2F), -121.84 – -124.57 (m, 2F), -125.19 – -126.53 (m, 2F).



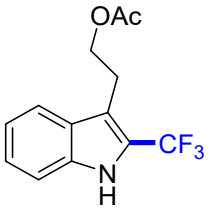
1,3,5-trimethoxy-2-(perfluorohexyl)benzene (3ac)[26]

The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a white solid (100 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (s, 2H), 3.85 (s, 3H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.02, 161.76 (C–F, $^{3}J_{C\text{-}F}$, J = 2.0 Hz), 122.04 – 104.64 (m), 98.35 (C–F, $^{2}J_{C\text{-}F}$, J = 22.0 Hz), 91.47, 55.82, 54.84 .^{119}F NMR (376 MHz, $CDCl_3$) δ -81.42 (t, J = 10.6 Hz, 3F), -101.55 – -103.72 (m, 2F), -122.19 – -122.42 (m, 2F), -122.51 (s, 2F), -123.03 (s, 2F), -125.88 – -127.98 (m, 2F).



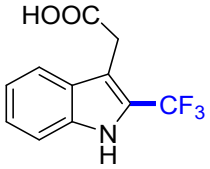
1,3-dimethyl-5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione (3ad)[13]

The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (27 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 3.50 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.69, 150.91, 143.61 (C–F, $^{2}J_{C\text{-}F}$, J = 5.8 Hz), 122.02 (C–F, $^{1}J_{C\text{-}F}$, J = 269.8 Hz), 104.04 (C–F, $^{2}J_{C\text{-}F}$, J = 33.1 Hz), 37.72, 27.99. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.82.



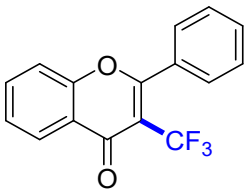
2-(2-(trifluoromethyl)-1*H*-indol-3-yl)ethyl acetate (3ae)[21]

The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a white solid (66 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 4.35 (t, J = 6.9 Hz, 2H), 3.26 (t, J = 6.7 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 135.24, 127.43, 124.95, 122.41 (C–F, $^{2}J_{C\text{-}F}$, J = 36.9 Hz), 121.90 (C–F, $^{1}J_{C\text{-}F}$, J = 267.1 Hz), 120.79, 114.04 (C–F, $^{3}J_{C\text{-}F}$, J = 2.8 Hz), 111.80, 64.08, 23.51, 20.90. ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.31.



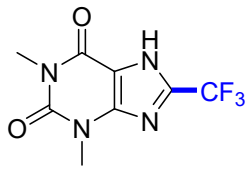
2-(2-(trifluoromethyl)-1*H*-indol-3-yl)acetic acid (3af)[21]

The product was purified by column chromatography on silica gel (eluent: 2:1 petroleum ether: ethyl acetate) as a white solid (52 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 3.98 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.48, 135.10, 127.16, 125.21, 123.04 (C–F, $^{2}J_{C\text{-}F}$, J = 26.7 Hz), 122.47 (C–F, $^{1}J_{C\text{-}F}$, J = 260.7 Hz), 121.22, 120.12, 111.84, 109.71, 29.31. ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.56.



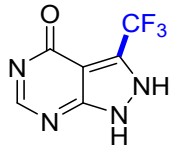
2-phenyl-3-(trifluoromethyl)-4*H*-chromen-4-one (3ag)[23]

The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (53 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.2 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.62 (t, J = 6.2 Hz, 3H), 7.58 – 7.53 (m, 2H), 7.53 – 7.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.40, 167.09 (C–F, $^{3}J_{C\text{-}F}$, J =2.5 Hz), 155.49, 134.76, 132.44, 131.41, 128.61, 128.38, 126.21, 126.16, 123.35, 122.65 (C–F, $^{1}J_{C\text{-}F}$, J =265.1 Hz), 118.01, 113.15 (C–F, $^{2}J_{C\text{-}F}$, J = 29.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -56.20.



1,3-dimethyl-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (3ah)[13]

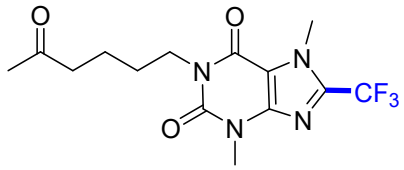
The product was purified by column chromatography on silica gel (eluent: 1:1 petroleum ether: ethyl acetate) as a white solid (52 mg, 70%). ^{1}H NMR (400 MHz, DMSO) δ 3.43 (s, 1H), 3.00 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 155.09, 151.47, 147.30, 137.77 (C–F, $^{2}J_{C\text{-}F}$, J = 41.1 Hz), 118.62 (C–F, $^{1}J_{C\text{-}F}$, J = 270.1 Hz), 109.59, 30.37, 28.41. ^{19}F NMR (376 MHz, DMSO) δ -62.74.



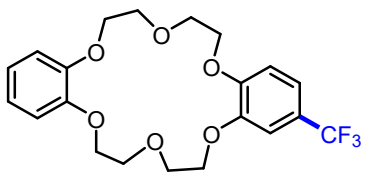
3-(trifluoromethyl)-1,2-dihydro-4*H*-pyrazolo[3,4-*d*]pyrimidin-4-one (3ai)[13]

The product was purified by column chromatography on silica gel (eluent: 2:1 petroleum ether: ethyl acetate) as a white solid (34 mg, 56%). ^{1}H NMR (400 MHz, MeOD) δ 8.08 (s, 1H). ^{13}C NMR (101 MHz, MeOD) δ 156.58, 155.06, 148.66, 137.48 (C–F,$^{2}J_{C\text{-}F}$, J =38.6 Hz), 120.52 (C–F, $^{1}J_{C\text{-}F}$, J = 268.3 Hz), 102.51.^{19}F NMR (376 MHz, MeOD) δ -63.79.

3,7-dimethyl-1-(5-oxohexyl)-8-(trifluoromethyl)-3,7-dihydro-1H-purine-2,6-dione (3aj)[13]

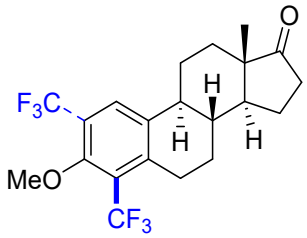


The product was purified by column chromatography on silica gel (eluent: 1:1 petroleum ether: ethyl acetate) as a white solid (66 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 3H), 4.02 (t, J = 6.8 Hz, 2H), 3.58 (s, 3H), 2.50 (t, J = 6.8 Hz, 2H), 2.14 (s, 3H), 1.68 – 1.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.45, 155.28, 151.04, 146.55, 138.90 (C–F, $^{2}J_{C\text{-}F}$, J = 40.1 Hz), 118.18 (C–F, $^{1}J_{C\text{-}F}$, J = 271.2 Hz), 109.66, 43.05, 41.09, 33.16 (C–F, $^{3}J_{C\text{-}F}$, J = 1.9 Hz), 29.93, 29.80, 27.30, 20.88. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.44.



2-(trifluoromethyl)-6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16] hexaoxacyclooctadecine (3ak)

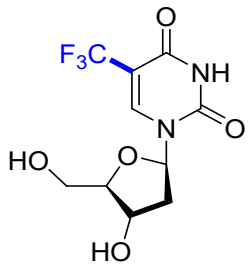
The product was purified by column chromatography on silica gel (eluent: 3:1 petroleum ether: ethyl acetate) as a white solid (59 mg, 46%), m.p. 172.2–173.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.1 Hz, 1H), 7.06 (s, 1H), 6.89 (d, J = 6.8 Hz, 5H), 4.24 – 4.02 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.15, 148.53, 148.49, 148.47, 124.28 (C–F, $^{1}J_{C\text{-}F}$, J = 273.6 Hz), 122.96 (C–F, $^{2}J_{C\text{-}F}$, J = 32.5 Hz), 121.14, 121.08, 118.51 (C–F, $^{3}J_{C\text{-}F}$, J = 3.6 Hz), 112.86, 112.80, 111.80, 109.41 (C–F, $^{3}J_{C\text{-}F}$, J = 3.2 Hz), 69.88, 69.83, 69.45, 68.69, 68.55, 68.29, 68.22. ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.52; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{23}F_3O_6Na$ 451.1345; Found 451.1346.



ratio: 2/1

(8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-4-(trifluoromethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (3al)[24]

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (48 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer: δ 7.47 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 3.87 (s, 3H), 3.17 – 3.00 (m, 2H), 2.57 – 2.51 (m, 1H), 2.42 – 2.37 (m, 1H), 2.28 – 2.23 (m, 1H), 2.19 – 2.12 (m, 1H), 2.09 – 2.02 (m, 2H), 2.01 – 1.97 (m, 1H), 1.73 – 1.65 (m, 2H), 1.56 – 1.50 (m, 4H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) for major isomer: δ 220.61, 156.86, 133.41, 131.56, 129.87, 125.39 (C–F, $^{1}J_{C\text{-}F}$, J = 257.1 Hz), 112.36, 110.49, 56.42, 50.40, 47.87, 44.47, 37.15, 35.88, 31.62, 26.42, 26.26, 21.49, 13.82. ^{19}F NMR (376 MHz, $CDCl_3$) for isomer 1: δ -53.16, for isomer 2: δ -61.73.

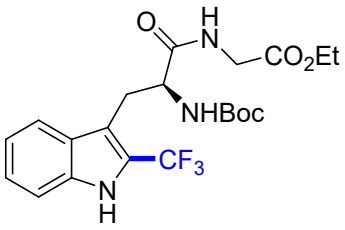


1-((2*R*,4*R*,5*R*)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione (3am)[13]

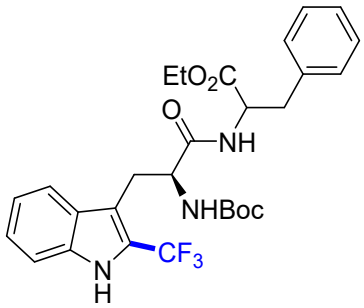
The product was purified by column chromatography on silica gel (eluent: 1:1 petroleum ether: ethyl acetate) as a white solid (42 mg, 47%). ^{1}H NMR (400 MHz, MeOD) δ 8.81 (s, 1H), 6.25 (t, J = 6.2 Hz, 1H), 4.48 – 4.35 (m, 1H), 4.03 – 3.95 (m, 1H), 3.89 – 3.72 (m, 2H), 2.43 – 2.24 (m, 2H). ^{13}C NMR (101

MHz, MeOD) δ 159.84, 149.93, 142.40 (C–F, $^{3}J_{C\text{-}F}$, J = 5.9 Hz), 122.55 (C–F, $^{1}J_{C\text{-}F}$, J = 268.9 Hz), 103.90 (C–F, $^{2}J_{C\text{-}F}$, J =32.9 Hz), 87.87, 86.13, 70.27, 60.71, 40.71. ^{19}F NMR (376 MHz, MeOD) δ -64.47.

ethyl (*S*)-(2-((tert-butoxycarbonyl)amino)-3-(2-(trifluoromethyl)-1*H*-indol-3-yl)propanoyl)glycinate (3an)[1]

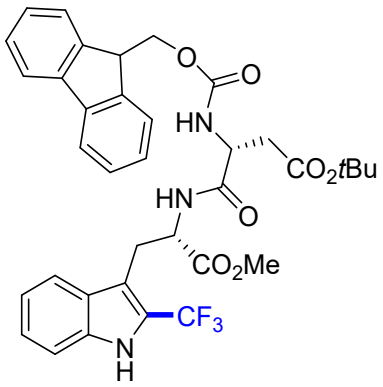


The product was purified by column chromatography on silica gel (eluent: 6:1 petroleum ether: ethyl acetate) as a white solid (96 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 43.8 Hz, 1H), 7.78 (s, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.33 (t, J = 6.2 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 6.25 (s, 1H), 5.24 (s, 1H), 4.52 (s, 1H), 4.16 (q, J = 7.1 Hz, 3H), 3.92 (dt, J = 18.3, 13.8 Hz, 2H), 3.47 – 3.31 (m, 2H), 1.37 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.28, 169.32, 155.23, 135.33, 127.17, 125.07, 122.76 (C–F, $^{2}J_{C\text{-}F}$, J = 36.6 Hz), 121.87 (C–F, $^{1}J_{C\text{-}F}$, J = 267.3 Hz), 121.00, 120.44, 112.88, 111.84, 80.11, 61.57, 54.93, 41.35, 28.14, 27.62, 14.07. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.78.



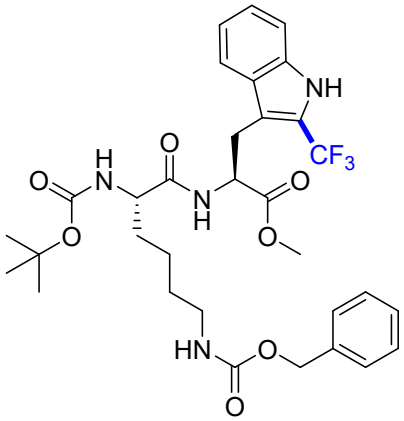
ethyl ((*S*)-2-((tert-butoxycarbonyl)amino)-3-(2-(trifluoromethyl)-1*H*-indol-3-yl)propanoyl)phenylalaninate (3ao)[1]

The product was purified by column chromatography on silica gel (eluent: 6:1 petroleum ether: ethyl acetate) as a white solid (111 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.75 (d, J = 5.9 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 12.4 Hz, 1H), 7.26 – 7.15 (m, 4H), 7.02 (s, 2H), 6.29 (s, 1H), 5.20 (s, 1H), 4.79 – 4.64 (m, 1H), 4.46 (s, 1H), 4.11 – 4.01 (m, 2H), 3.42 – 3.28 (m, 2H), 3.04 (d, J = 5.0 Hz, 2H), 1.38 (s, 9H), 1.17 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.84, 170.79, 155.18, 135.63, 135.46, 129.32, 128.44, 127.14, 127.06, 124.96, 122.78 (C–F, $^{2}J_{C\text{-}F}$, J = 36.8 Hz), 121.92 (C–F, $^{1}J_{C\text{-}F}$, J = 267.2 Hz), 120.91, 120.32, 112.59, 111.91, 80.10, 61.47, 55.21, 53.34, 38.11, 28.15, 27.56, 13.98. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.64.



tert-butyl (*R*)-3-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-(((*S*)-1-methoxy-1-oxo-3-(2-(trifluoromethyl)-1*H*-indol-3-yl)propan-2-yl)amino)-4-oxobutanoate (3ap)[1]

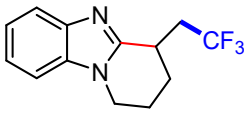
The product was purified by column chromatography on silica gel (eluent: 6:1 petroleum ether: ethyl acetate) as a white solid (140 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.79 (t, *J* = 7.8 Hz, 3H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.20 (t, *J* = 7.3 Hz, 2H), 5.83 (d, *J* = 6.4 Hz, 1H), 4.92 (q, *J* = 7.2 Hz, 1H), 4.57 (s, 1H), 4.41 (d, *J* = 6.8 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 1H), 3.64 (s, 3H), 3.47 – 3.38 (m, 2H), 2.88 (d, *J* = 16.6 Hz, 1H), 2.61 (dd, *J* = 16.7, 5.7 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.51, 171.06, 170.39, 155.87, 143.82, 143.69, 141.32, 135.33, 127.78, 127.21, 127.12, 125.10, 122.65 (C–F, $^{2}J_{C\text{-}F}$, *J* = 36.7 Hz), 121.86 (C–F, $^{1}J_{C\text{-}F}$, *J* = 267.1 Hz),121.01, 120.15, 120.04, 112.13, 111.96, 81.93, 67.24, 53.17, 52.44, 50.94, 47.09, 37.72, 27.95, 26.97.^{19}F NMR (376 MHz, $CDCl_3$): δ -57.86.



methyl (*S*)-2-((S)-6-(((benzyloxy)carbonyl)amino)-2-((tert-butoxycarbonyl)amino) hexanamido)-3-(2-(trifluoromethyl)-1*H*-indol-3-yl)propanoate (3aq)[1]

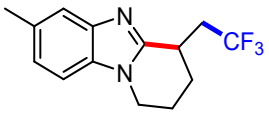
The product was purified by column chromatography on silica gel (eluent: 6:1 petroleum ether: ethyl acetate) as a white solid (128 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.32 (m, 6H), 7.20 (t, *J* = 6.9 Hz, 1H), 6.66 (d, *J* = 6.3 Hz, 1H), 5.13 (s, 2H), 4.99 (s, 2H), 4.05 (s, 1H), 3.65 (s, 3H), 3.44 (s, 1H), 3.35 (s, 1H), 3.12 (s, 2H), 1.45 (s, 15H), 1.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.86, 171.65, 156.78, 155.51, 136.51, 135.47, 128.54, 128.16, 127.23, 124.95,

122.71 (C–F, $^{2}J_{C\text{-}F}$, J = 36.6 Hz), 121.94 (C–F, $^{1}J_{C\text{-}F}$, J = 267.4 Hz), 120.88, 119.99, 112.17, 111.89, 80.19, 66.77, 54.31, 52.57, 52.47, 40.44, 31.85, 29.41, 28.26, 27.07, 21.97. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.62.



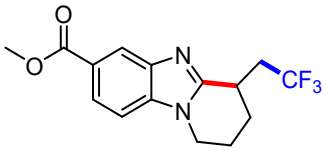
4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5a)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (66 mg, 87%), m.p. 94.2–94.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 1H), 7.39 – 7.24 (m, 3H), 4.28 – 4.18 (m, 1H), 4.05 – 3.93 (m, 1H), 3.59 – 3.48 (m, 1H), 3.47 – 3.37 (m, 1H), 2.55 – 2.45 (m, 1H), 2.43 – 2.26 (m, 2H), 2.16 – 2.05 (m, 1H), 1.81 – 1.69 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 142.5, 134.8 126.8 (C–F, $^{1}J_{C\text{-}F}$, J = 277.2 Hz), 122.5, 122.3, 119.2, 109.1, 42.4, 37.2 (C–F, $^{2}J_{C\text{-}F}$, J = 28.4 Hz), 31.5 (C–F, $^{3}J_{C\text{-}F}$, J = 1.7 Hz), 26.7, 21.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ -63.47; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3N_2$ 255.1104; Found 255.1091.



7-methyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5b)

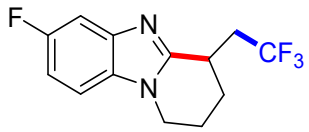
The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (56 mg, 70%), m.p. 143.1–144.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 4.24 – 4.21 (m, 1H), 3.98 (td, J = 11.4, 4.8 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.45 – 3.38 (m, 1H), 2.50 (s, 3H), 2.49 – 2.46 (m, 1H), 2.41 – 2.34 (m, 1H), 2.33 – 2.28 (m, 1H), 2.15 – 2.07 (m, 1H), 1.75 (m, 1H).^{13}C NMR (151MHz, $CDCl_3$) δ 152.0, 142.6, 132.9, 132.2, 126.8 (C–F, $^{1}J_{C\text{-}F}$, J = 277.8 Hz), 123.8, 119.0, 118.6, 108.6, 42.4, 37.2 (C–F, $^{2}J_{C\text{-}F}$, J = 28.4 Hz), 31.4 (C–F, $^{3}J_{C\text{-}F}$, J = 2.7 Hz), 26.7, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -63.35; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3N_2$ 269.1260; Found 269.1250.



methyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine-7-carboxylate (5c)

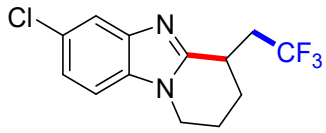
The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (72 mg, 77%), m.p. 171.6–172.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H),

8.01 (dd, J = 8.4, 1.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 4.31 – 4.26 (m, 1H), 4.02 (td, J = 11.4, 4.8 Hz, 1H), 3.96 (s, 3H), 3.55 – 3.47 (m, 1H), 3.47 – 3.41 (m, 1H), 2.53 – 2.48 (m, 1H), 2.45 – 2.37 (m, 1H), 2.36 – 2.32 (m, 1H), 2.17 – 2.09 (m, 1H), 1.82 – 1.73 (m, 1H).^{13}C NMR (151MHz, $CDCl_3$) δ 167.6, 154.0, 142.0, 138.0, 126.8 (C–F, $^1J_{C\text{-}F}$, J = 277.4 Hz), 124.7, 124.1, 121.5, 108.8, 52.1, 42.7, 37.1 (C–F, $^2J_{C\text{-}F}$, J = 28.4 Hz), 31.6 (C–F, $^3J_{C\text{-}F}$, J =2.7 Hz), 26.5, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -63.44; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}F_3N_2O_2$ 313.1158; Found 313.1153.



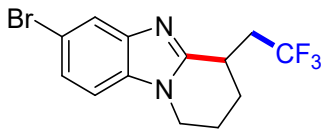
7-fluoro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5d)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (68 mg, 83%), m.p. 120.5–121.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, J = 9.4, 2.4 Hz, 1H), 7.20 (dd, J = 8.4, 4.8 Hz, 1H), 7.00 (td, J = 8.4, 2.4 Hz, 1H), 4.23 – 4.18 (m, 1H), 3.97 (td, J = 11.4, 4.8 Hz, 1H), 3.51 – 3.43 (m, 1H), 3.43 – 3.36 (m, 1H), 2.50 – 2.44 (m, 1H), 2.40 – 2.33 (m, 1H), 2.33 – 2.28 (m, 1H), 2.14 – 2.05 (m, 1H), 1.78 – 1.70 (m, 1H). ^{13}C NMR (151MHz, $CDCl_3$) δ 159.55 (C–F, $^1J_{C\text{-}F}$, J = 237.2 Hz), 153.66, 142.78 (C–F, $^3J_{C\text{-}F}$, J = 12.7 Hz), 131.34, 127.65 (C–F, $^1J_{C\text{-}F}$, J = 277.3 Hz), 110.52 (C–F, $^2J_{C\text{-}F}$, J = 26.5 Hz), 109.34 (C–F, $^2J_{C\text{-}F}$, J = 12.4 Hz), 105.00 (C–F, $^2J_{C\text{-}F}$, J = 24.3 Hz), 42.48, 37.06 (C–F, $^2J_{C\text{-}F}$, J = 28.4 Hz), 31.47 (C–F, $^4J_{C\text{-}F}$, J = 2.8 Hz), 26.47, 21.54. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.50, -120.61; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}F_4N_2$ 273.1009; Found 273.0998.



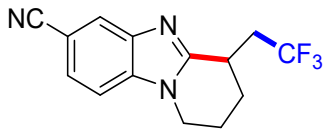
7-chloro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5e)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (71 mg, 82%), m.p. 125.7–126.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1H), 7.24 – 7.17 (m, 2H), 4.23 – 4.18 (m, 1H), 3.96 (td, J = 11.6, 5.0 Hz, 1H), 3.54 – 3.34 (m, 2H), 2.54 – 2.43 (m, 1H), 2.44 – 2.26 (m, 2H), 2.15 – 2.04 (m, 1H), 1.79 – 1.69 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.51, 143.24, 133.44, 127.99, 126.72 (C–F, $^1J_{C\text{-}F}$, J = 277.3 Hz), 122.71, 118.96, 109.83, 42.51, 37.04 (C–F, $^2J_{C\text{-}F}$, J = 28.4 Hz), 31.47 (C–F, $^3J_{C\text{-}F}$, J = 2.8 Hz), 26.48 (C–F, $^4J_{C\text{-}F}$, J = 1.4 Hz), 21.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.46.; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}ClF_3N_2$ 289.0714; Found 289.0712.



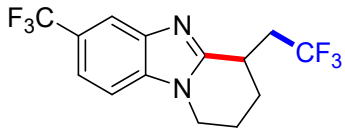
7-bromo-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5f)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (81 mg, 81%), m.p. 114.5–115.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 1H), 7.42 – 7.25 (m, 1H), 7.23 – 7.08 (m, 1H), 4.19 (s, 1H), 3.98 (td, J = 17.9, 8.8 Hz, 1H), 3.54 – 3.37 (m, 2H), 2.51 – 2.45 (m, 1H), 2.44 – 2.31 (m, 1H), 2.31 – 2.26 (m, 1H), 2.19 – 2.00 (m, 1H), 1.84 – 1.64 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.36, 143.73, 133.76, 126.72 (C–F, $^{1}J_{C\text{-}F}$, J = 277.8 Hz), 125.40, 122.04, 115.50, 110.30, 42.53, 37.05 (C–F, $^{2}J_{C\text{-}F}$, J = 28.3 Hz), 31.46 (C–F, $^{3}J_{C\text{-}F}$, J = 2.9 Hz), 26.47, 21.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.45; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}BrF_3N_2$ 333.0209; Found 333.0199.



4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine-7-carbonitrile (5g)

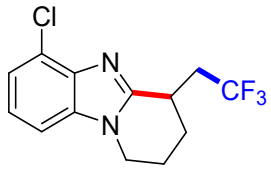
The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (63 mg, 76%), m.p. 159.1–160.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.50 (dd, J = 8.3, 1.5 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 4.32 – 4.28 (m, 1H), 4.04 (td, J = 11.6, 5.0 Hz, 1H), 3.53 – 3.39 (m, 2H), 2.58 – 2.48 (m, 1H), 2.47 – 2.32 (m, 2H), 2.18 – 2.10 (m, 1H), 1.82 – 1.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_{3)}$ δ 155.08, 142.09, 137.58, 126.61 (C–F, $^{1}J_{C\text{-}F}$, J = 277.0 Hz), 125.86, 124.12, 119.88, 110.20, 105.66, 42.79, 36.98 (C–F, $^{2}J_{C\text{-}F}$, J = 28.6 Hz), 31.63 (C–F, $^{3}J_{C\text{-}F}$, J = 2.9 Hz), 26.39, 21.49. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.15.; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}F_3N_3$ 280.1056; Found 280.1052.



4-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-1,2,3,4 tetrahydrobenzo[4,5]imidazo [1,2-*a*]pyridine (5h)

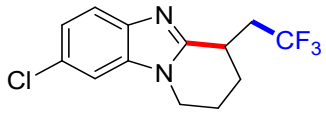
The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (69 mg, 71%), m.p. 117.3–118.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.57 – 7.51 (m, 1H), 7.41 (d, J = 8.4 Hz, 1H), 4.32 – 4.29 (m, 1H), 4.04 (td, J = 11.5, 4.9 Hz, 1H), 3.52 – 3.45 (m, 2H), 2.53 – 2.51 (m, 1H), 2.48 – 2.32 (m, 2H), 2.21 – 2.10 (m, 1H), 1.83 – 1.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.32, 141.87, 136.76, 126.68 (C–F, $^{1}J_{C\text{-}F}$, J = 276.67 Hz), 124.91 (C–F, $^{2}J_{C\text{-}F}$, J = 31.71 Hz), 124.82 (C–F, $^{1}J_{C\text{-}F}$, J = 271.30 Hz), 119.32 (C–F, $^{3}J_{C\text{-}F}$, J = 3.7 Hz), 116.83 (C–F, $^{3}J_{C\text{-}F}$, J = 4.3 Hz), 109.49, 42.68, 37.03 (C–F, $^{2}J_{C\text{-}F}$, J = 28.3 Hz), 31.58 (C–F, $^{3}J_{C\text{-}F}$, J = 2.8 Hz), 26.49,

21.54.^{19}F NMR (565 MHz, $CDCl_3$) δ -60.64, -63.47; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}F_6N_2$ 323.0977; Found 323.0974.



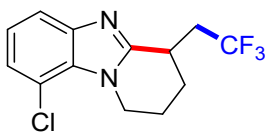
6-chloro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5i)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (63 mg, 73%), m.p. 82.2–83.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dq, J = 7.7, 1.4 Hz, 1H), 7.27 – 7.16 (m, 2H), 4.27 – 4.21 (m, 1H), 4.01 (td, J = 11.0, 4.4 Hz, 1H), 3.66 – 3.53 (m, 1H), 3.51 – 3.44 (m, 1H), 2.52 – 2.46 (m, 1H), 2.44 – 2.28 (m, 2H), 2.15 – 2.08 (m, 1H), 1.78 (q, J = 12.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.95, 139.68, 135.82, 126.73 (C–F, $^1J_{C\text{-}F}$, J = 277.3 Hz), 124.07, 122.89, 122.53, 107.84, 42.82, 37.14 (C–F, $^2J_{C\text{-}F}$, J = 28.2 Hz), 31.51 (C–F, $^3J_{C\text{-}F}$, J = 3.3 Hz), 29.70, 26.34. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.16; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}ClF_3N_2$ 289.0714; Found 289.0704.



8-chloro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5j)

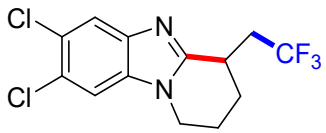
The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (71 mg, 82%), m.p. 112.1–113.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 8.6, 1H), 7.27 (t, J = 1.8 Hz, 1H), 7.22 (dt, J = 8.6, 1.9 Hz, 1H), 4.18 – 4.14 (m, 1H), 3.92 (td, J = 11.5, 5.0 Hz, 1H), 3.52 – 3.35 (m, 2H), 2.48 – 2.45 (m, 1H), 2.40 – 2.27 (m, 2H), 2.10 – 2.07 (m, 1H), 1.78 – 1.69 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.13, 141.04, 135.43, 128.07, 126.72 (C–F, $^1J_{C\text{-}F}$, J = 277.2 Hz), 123.04, 119.95, 109.30, 42.49, 37.03 (C–F, $^2J_{C\text{-}F}$, J = 28.4 Hz), 31.50 (C–F, $^3J_{C\text{-}F}$, J = 2.9 Hz), 26.56, 21.56. ^{19}F NMR (565 MHz, $CDCl_3$): δ -63.43; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}ClF_3N_2$ 289.0714; Found 289.0705.



9-chloro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5k)

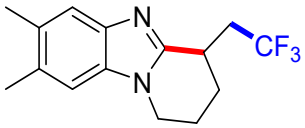
The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (57 mg, 66%), m.p. 128.0–129.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.22 – 7.13 (m, 2H), 4.93 – 4.89 (m, 1H), 4.35 (td, J = 11.9, 5.0 Hz, 1H), 3.54 – 3.38 (m,

2H), 2.48 – 2.42 (m, 1H), 2.40 – 2.34 (m, 1H), 2.31 – 2.28 (m, 1H), 2.15 – 2.03 (m, 1H), 1.74 – 1.72 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.31, 144.41, 131.16, 126.74 (C–F, $^{1}J_{C\text{-}F}$, J = 277.4 Hz), 123.72, 122.95, 118.01, 116.27, 45.54, 37.28 (C–F, $^{2}J_{C\text{-}F}$, J = 28.3 Hz), 31.88 (C–F, $^{3}J_{C\text{-}F}$, J = 2.9 Hz), 26.01, 22.07. ^{19}F NMR (565 MHz, $CDCl_3$): δ -63.43; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}ClF_3N_2$ 289.0714; Found 289.0713.



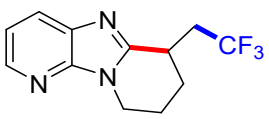
7,8-dichloro-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5l)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (78 mg, 81%), m.p. 143.9–144.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 1.2 Hz, 1H), 7.39 (d, J = 1.2 Hz, 1H), 4.21 – 4.16 (m, 1H), 3.95 (td, J = 11.6, 5.0 Hz, 1H), 3.47 – 3.37 (m, 2H), 2.56 – 2.44 (m, 1H), 2.43 – 2.03 (m, 3H), 1.84 – 1.69 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.34, 141.75, 134.07, 126.6 (C–F, $^{1}J_{C\text{-}F}$, J = 277.7 Hz), 126.44, 126.34, 120.38, 110.55, 42.66, 36.96 (C–F, $^{2}J_{C\text{-}F}$, J = 28.5 Hz), 31.56 (C–F, $^{3}J_{C\text{-}F}$, J = 2.7 Hz), 26.38, 21.50.^{19}F NMR (376 MHz, $CDCl_3$): δ -63.46; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}Cl_2F_3N_2$ 323.0324; Found 323.0322.



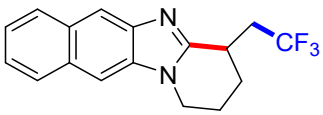
7,8-dimethyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5m)

The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (72 mg, 85%), m.p. 181.4–182.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.07 (s, 1H), 4.21 – 4.11 (m, 1H), 3.90 (td, J = 11.6, 5.1 Hz, 1H), 3.52 – 3.45 (m, 1H), 3.43 – 3.33 (m, 1H), 2.49 – 2.42 (m, 2H), 2.40 – 2.38 (m, 6H), 2.36 – 2.23 (m, 1H), 2.09 – 2.03 (m, 1H), 1.74 – 1.68 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.29, 140.96, 133.34, 131.40, 131.22, 126.88 (C–F, $^{1}J_{C\text{-}F}$, J = 277.4 Hz), 119.18, 109.38, 42.31, 37.15 (C–F, $^{2}J_{C\text{-}F}$, J = 28.1 Hz), 31.39 (C–F, $^{3}J_{C\text{-}F}$, J = 2.7 Hz), 26.72, 21.69, 20.53, 20.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.41; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_3N_3$ 283.1417; Found 283.1413.



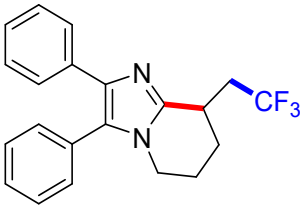
6-(2,2,2-trifluoroethyl)-6,7,8,9-tetrahydroimidazo[1,2-*a*:5,4-*b*']dipyridine (5n)

The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (57 mg, 74%), m.p. 129.4–130.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 – 8.34 (m, 1H), 7.98 – 7.96 (m, 1H), 7.26 – 7.21 (m, 1H), 4.50 – 4.47 (m, 1H), 4.04 (td, J = 12.0, 4.9 Hz, 1H), 3.53 – 3.39 (m, 2H), 2.54 – 2.47 (m, 1H), 2.43 – 2.29 (m, 2H), 2.10 – 2.07 (m, 1H), 1.78 – 1.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.63, 147.75, 143.48, 134.71, 126.71 (C–F, $^{1}J_{C\text{-}F}$, J = 277.5 Hz), 126.57, 118.53, 41.47, 36.90 (C–F, $^{2}J_{C\text{-}F}$, J = 28.5 Hz), 31.71 (C–F, $^{3}J_{C\text{-}F}$, J = 2.9 Hz), 26.63, 21.47. ^{19}F NMR (565 MHz, $CDCl_3$): δ -63.49; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}F_3N_3$ 256.1056; Found 256.1042.



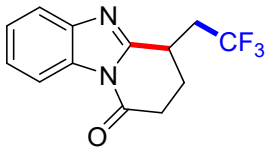
4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyridine (5o)

The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a white solid (53 mg, 60%), m.p. 176.6–177.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.10 – 7.90 (m, 2H), 7.77 – 7.62 (m, 1H), 7.53 – 7.39 (m, 2H), 4.33 (s, 1H), 4.03 (t, J = 13.7 Hz, 1H), 3.59 (t, J = 13.5 Hz, 1H), 3.49 (s, 1H), 2.56 – 2.50 (m, 1H), 2.49 – 2.41 (m, 1H), 2.41 – 2.34 (m, 1H), 2.26 – 2.05 (m, 2H), 1.95 – 1.65 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.47, 142.25, 135.64, 130.55, 130.26, 128.56, 127.44, 126.78 (C–F, $^{1}J_{C\text{-}F}$, J = 277.8 Hz), 124.40, 123.61, 115.93, 104.88, 42.36, 36.96 (C–F, $^{2}J_{C\text{-}F}$, J = 28.7 Hz), 31.86 (C–F, $^{3}J_{C\text{-}F}$, J = 2.4 Hz), 26.54, 21.67. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.39; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}F_3N_2$ 305.1260; Found 305.1270.



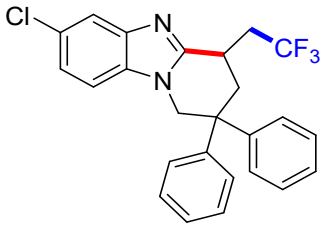
2,3-diphenyl-8-(2,2,2-trifluoroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (5p)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (94 mg, 88%), m.p. 169.5–171.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.40 (m, 5H), 7.38 – 7.34 (m, 2H), 7.26 – 7.19 (m, 2H), 7.19 – 7.13 (m, 1H), 3.83 – 3.64 (m, 2H), 3.57 – 3.50 (m, 1H), 3.44 – 3.30 (m, 1H), 2.44 – 2.31 (m, 2H), 2.15 – 2.10 (m, 1H), 1.97 – 1.93 (m, 1H), 1.78 – 1.64 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.13, 136.98, 134.61, 130.83, 130.65, 129.78 (C–F, $^{1}J_{C\text{-}F}$, J = 277.7 Hz),128.96, 128.46, 127.96, 126.84, 126.33, 125.65, 43.86, 37.60 (C–F, $^{2}J_{C\text{-}F}$, J = 27.6 Hz), 31.64 (C–F, $^{3}J_{C\text{-}F}$, J = 2.8 Hz), 26.75, 22.03. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.26; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}F_3N_2$ 357.1573; Found 357.1552.



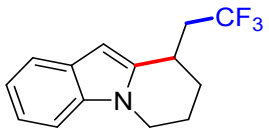
4-(2,2,2-trifluoroethyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridin-1(2*H*)-one (5q)

The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (56 mg, 69%), m.p. 103.0–103.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 6.5 Hz, 1H), 7.83 – 7.63 (m, 1H), 7.49 – 7.35 (m, 2H), 3.51 (dt, J = 43.1, 12.9 Hz, 2H), 3.13 – 2.80 (m, 2H), 2.65 – 2.39 (m, 2H), 2.09 – 2.00(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.03, 154.41, 142.15, 131.61, 126.52 (C–F, $^{1}J_{C\text{-}F}$, J = 275.1 Hz), 125.55, 125.49, 119.57, 115.47, 35.76 (C–F, $^{2}J_{C\text{-}F}$, J = 28.9 Hz), 33.10, 31.23 (C–F, $^{3}J_{C\text{-}F}$, J = 3.0 Hz), 26.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.50; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}F_3N_2O$ 269.0896; Found 269.0895.



7-chloro-2,2-diphenyl-4-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5] imidazo[1,2-*a*]pyridine (5r)

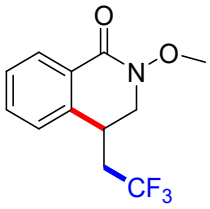
The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (100 mg, 76%), m.p. 156.9–158.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.41 – 7.24 (m, 9H), 7.01 (d, J = 6.8 Hz, 2H), 4.97 (d, J = 12.9 Hz, 1H), 4.11 (d, J = 13.0 Hz, 1H), 3.53 – 3.39 (m, 1H), 3.19 – 3.10 (m, 1H), 2.97 (s, 1H), 2.68 (t, J = 12.4 Hz, 1H), 2.49 (d, J = 17.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.90, 145.49, 142.22, 132.71, 129.09, 128.93, 127.48, 127.25, 126.67, 126.57 (C–F, $^{1}J_{C\text{-}F}$, J = 276.3 Hz), 126.52, 123.13, 119.25, 109.78, 51.75, 45.83, 37.57, 36.82 (C–F, $^{2}J_{C\text{-}F}$, J = 28.7 Hz), 28.76 (C–F, $^{3}J_{C\text{-}F}$, J = 3.0 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -63.06; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}ClF_3N_2$ 441.1340; Found 441.1334.



9-(2,2,2-trifluoroethyl)-6,7,8,9-tetrahydropyrido[1,2-a]indole (5s)[27]

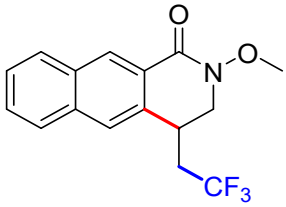
The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a white solid (48 mg, 64%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0, 1H), 7.14 (t, J = 8.0 Hz, 1H), 6.32 (s, 1H), 4.27 – 4.22 (m, 1H), 3.96 – 3.89 (m, 1H), 3.44 – 3.37 (m, 1H), 2.95 – 2.81 (m, 1H), 2.47 – 2.23 (m, 3H), 2.12 – 2.02 (m, 1H), 1.65 (q, J = 8.0 Hz, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 138.45, 136.41, 127.81, 126.73 (C-F, $^1J_{C-F}$, J = 275.8 Hz), 121.05, 120.01, 108.88, 99.99, 97.48, 42.13, 39.04 (C-F, $^2J_{C-F}$, J = 27.4 Hz), 29.93, 27.18, 22.01. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.32.



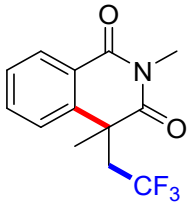
2-methoxy-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one (5t)[3]

The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (60 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.91 (s, 3H), 3.85 – 3.79 (m, 1H), 3.51 – 3.43 (m, 1H), 2.78 – 2.63 (m, 1H), 2.47 – 2.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13, 139.04, 132.95, 128.86, 128.25, 127.91, 126.86, 126.10 (C-F, $^1J_{C-F}$, J = 275.8 Hz), 61.90, 51.25, 37.32 (C-F, $^2J_{C-F}$, J = 28.0 Hz), 33.78 (C-F, $^3J_{C-F}$, J == 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.70.



2-methoxy-4-(2,2,2-trifluoroethyl)-3,4-dihydrobenzo[g]isoquinolin-1(2H)-one (5u)

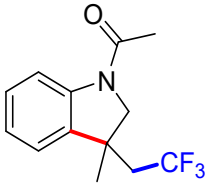
The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (60 mg, 65%), m.p. 97.5-98.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.97 – 7.91 (m, 2H), 7.71 – 7.61 (m, 2H), 4.18 – 4.03 (m, 3H), 3.97 (s, 3H), 2.94 – 2.79 (m, 1H), 2.40 – 2.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.84, 136.54, 135.74, 129.39, 128.84, 128.63, 128.19, 127.85, 126.18 (C-F, $^1J_{C-F}$, J = 234.4 Hz), 125.74, 124.06, 123.14, 62.05, 50.44, 34.94 (C-F, $^2J_{C-F}$, J = 27.8 Hz), 30.06 (C-F, $^3J_{C-F}$, J = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.80; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}F_3NO_2$ 310.1055; Found 310.1051.



2, 4-dimethyl-4-(2, 2, 2-trifluoroethyl)isoquinoline-1, 3(2*H*,4*H*)-dione (5v)[28]

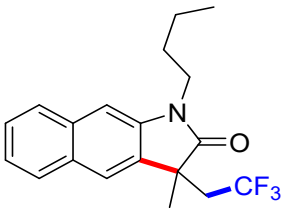
The product was purified by column chromatography on silaaica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a Colorless oil (58 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.9 Hz, 1H), 7.68 (td,

J = 7.8, 1.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 3.43 (d, J = 7.6 Hz, 3H), 3.41 – 3.30 (m, 1H), 2.89 – 2.76 (m, 1H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.65, 163.86, 140.51, 133.81, 129.29, 128.06, 125.64, 124.96 (C-F, $^1J_{C\text{-}F}$, J=277.0Hz), 124.21, 44.45 (C-F, $^2J_{C\text{-}F}$, J=27.4Hz), 43.56 (C-F, $^3J_{C\text{-}F}$, J=2.0Hz), 31.18, 27.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.47.



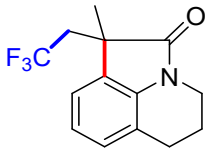
1-(3-methyl-3-(2,2,2-trifluoroethyl)indolin-1-yl)ethan-1-one (5w)[29]

The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (52 mg, 68%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.15 –7.08 (m, 2H), 4.13 (d, J = 12.0 Hz, 1H), 3.85 (d, J = 12.0 Hz ,1H), 2.58 – 2.47 (m, 2H), 2.27 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.63, 141.30, 137.53, 128.75, 126.24 (C-F, $^1J_{C\text{-}F}$, J = 284.4 Hz), 124.07, 121.93, 117.31, 61.01, 43.20 (C-F, $^2J_{C\text{-}F}$, J = 26.7 Hz), 41.06, 26.08, 24.23. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.43.



1-butyl-3-methyl-3-(2,2,2-trifluoroethyl)-1H-benzo[f]indol-2(3H)-one (5x)

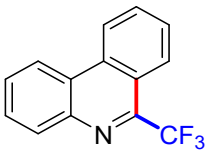
The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a White solid (79 mg, 80%), m.p. 101.7–102.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.50 – 7.41 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 4.31 – 3.98 (m, 2H), 3.51 (dd, J = 15.0, 10.7 Hz, 1H), 2.79 (dd, J = 15.0, 10.0 Hz, 1H), 1.80 – 1.71 (m, 5H), 1.52 (dp, J = 14.7, 7.2 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.06, 135.08, 134.96, 133.72, 126.79, 126.57, 126.49, 125.50 (C-F, $^1J_{C\text{-}F}$, J=277.5Hz), 123.39, 122.66, 119.28, 108.81, 45.34 (C-F, $^2J_{C\text{-}F}$, J=26.6Hz), 43.66 (C-F, $^3J_{C\text{-}F}$, J=2.1Hz), 42.51, 33.31, 28.37, 20.29, 13.88. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.47; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}F_3NO$ 336.1575; Found 336.1576.



1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (5y)[21]

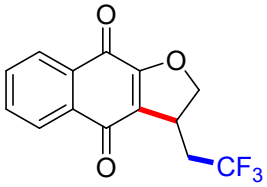
The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (67 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 4.0, 1H), 3.75 (t, J = 8.0 Hz, 2H), 2.84 – 2.63 (m, 4H), 2.07 – 2.01 (m, 2H),

1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.35, 138.69, 129.70, 127.28, 125.42 (C-F, $^{1}J_{C\text{-}F}$, J = 276.3 Hz), 122.08, 121.48, 120.51, 45.66, 40.48 (C-F, $^{2}J_{C\text{-}F}$, J = 28.1 Hz), 39.06, 24.62, 24.56, 21.14. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.82.



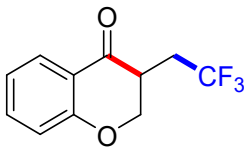
6-(trifluoromethyl)phenanthridine (5z)[30]

The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a white solid (67mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 8.0 Hz, 1H), 8.65 – 8.63 (m, 1H), 8.42 (d, J = 8.0, 2H), 8.34 – 8.31 (m, 1H), 7.96 (t, J = 8.0 Hz, 1H), 7.86 – 7.78 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.51 (C-F, $^{2}J_{C\text{-}F}$, J = 32.9 Hz), 141.73, 133.95, 131.37, 131.32, 129.34, 129.21, 128.06, 125.92 (C-F, $^{3}J_{C\text{-}F}$, J = 3.3 Hz), 125.10, 122.53, 122.07, 121.94 (C-F, $^{1}J_{C\text{-}F}$, J = 275.4 Hz), 121.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.46.



3-(2,2,2-trifluoroethyl)-2,3-dihydronaphtho[2,3-b]furan-4,9-dione (5aa)

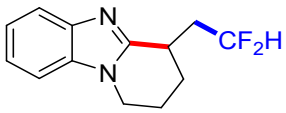
The product was purified by column chromatography on silica gel (eluent: 35:1 petroleum ether: ethyl acetate) as a White solid (51mg, 61%), m.p. 129.8–130.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, J = 6.7 Hz, 2H), 7.85 – 7.69 (m, 2H), 4.96 (t, J = 10.1 Hz, 1H), 4.64 (t, J = 8.8 Hz, 1H), 4.06 – 3.91 (m, 1H), 3.28 – 3.12 (m, 1H), 2.41 – 2.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.94, 177.54, 160.82, 134.54, 133.32, 132.97, 131.38, 126.50, 126.15, 126.1 (C-F, $^{1}J_{C\text{-}F}$, J = 275.5Hz), 123.31, 77.90, 36.25, 35.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.96; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}F_3O_3$ 283.0582; Found 283.0584.



3-(2,2,2-trifluoroethyl)chroman-4-one (5ab)[31]

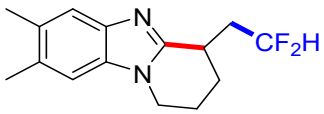
The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a Colorless oil (48 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.9, 1.5 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 4.74 (dd, J = 11.4, 5.1 Hz, 1H), 4.27 (t, J = 11.7 Hz, 1H), 3.20 – 3.03 (m, 2H), 2.16 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.72, 161.56, 136.40, 127.59, 126.62 (C-F, $^{1}J_{C\text{-}F}$, J=279.9Hz), 121.80, 120.07, 117,89, 69.77 (C-F, $^{3}J_{C\text{-}F}$, J=1.7Hz), 40.52 (C-F, $^{3}J_{C\text{-}F}$, J=2.0Hz), 29.61 (C-F, $^{2}J_{C\text{-}F}$, J=30.0Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -

64.02.



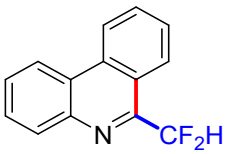
4-(2,2-difluoroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (5ac)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (60mg, 85%), m.p. 88.7–89.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 1H), 7.35 – 7.28 (m, 3H), 6.58 – 6.23 (m, 1H), 4.27 – 4.19 (m, 1H), 4.06 – 3.96 (m, 1H), 3.39 – 3.31 (m, 1H), 2.89 – 2.72 (m, 1H), 2.34 – 2.12 (m, 4H), 1.85 – 1.72 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.24, 142.50, 134.60, 122.38, 122.22, 119.16, 116.80 (C–F, $^{1}J_{C\text{-}F}$, J = 237.5 Hz), 109.00, 42.43, 38.05 (C–F, $^{2}J_{C\text{-}F}$, J = 21.4 Hz), 31.31 (C–F, $^{3}J_{C\text{-}F}$, J = 6.4, 4.9 Hz), 27.52, 21.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.09, -113.85, -117.32, -118.12. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_2N_2$ 237.1203; Found 237.1206.



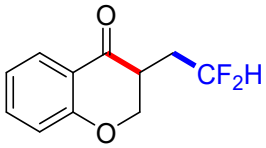
4-(2,2-difluoroethyl)-7,8-dimethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (5ad)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (65mg, 83%), m.p. 167.3–168.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.10 (s, 1H), 6.40 (t, J = 56.6 Hz, 1H), 4.17 (s, 1H), 3.97 (s, 1H), 3.33 (s, 1H), 2.89 – 2.67 (m, 1H), 2.48 – 2.04 (m, 10H), 1.88 – 1.72 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.31, 140.94, 133.11, 131.26, 131.12, 119.20, 116.88 (C–F, $^{1}J_{C\text{-}F}$, J = 237.5 Hz), 109.31, 42.37, 38.07 (C–F, $^{2}J_{C\text{-}F}$, J = 21.3 Hz), 31.25 (C–F, $^{1}J_{C\text{-}F}$, J = 4.9 Hz), 27.53, 21.76, 20.51, 20.34. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.01, -113.76, -117.30, -118.06. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_2N_2$ 265.1516; Found 265.1519.



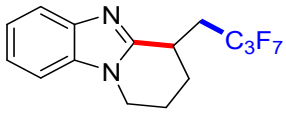
6-(difluoromethyl)phenanthridine (5ae)[32]

The product was purified by column chromatography on silica gel (eluent: petroleum ether) as a white solid (58 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.3 Hz, 1H), 8.66 – 8.57 (m, 2H), 8.24 (d, J = 8.8 Hz, 1H), 7.93 (t, J = 7.6 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.06 (t, J = 54.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.35 (C-F, $^{2}J_{C\text{-}F}$, J = 26.5 Hz), 142.39, 133.80, 131.24, 130.57, 129.10, 128.65, 127.80, 126.46 (C-F, $^{3}J_{C\text{-}F}$, J = 4.3 Hz), 124.97, 122.41, 122.16, 118.35 (C-F, $^{1}J_{C\text{-}F}$, J = 243.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.47, -110.42.



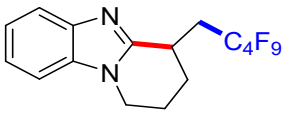
3-(2,2,2-trifluoroethyl)chroman-4-one (5af)[33]

The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a Colorless oil (47 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.74 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.27 (t, *J* = 11.7 Hz, 1H), 3.20 – 3.03 (m, 2H), 2.16 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.72, 161.56, 136.40, 127.59, 126.62 (C-F, $^{1}J_{C\text{-}F}$, *J*=279.9Hz), 121.80, 120.07, 117,89, 69.77 (C-F, $^{3}J_{C\text{-}F}$, *J*=1.7Hz), 40.52 (C-F, $^{3}J_{C\text{-}F}$, *J*=2.0Hz), 29.61 (C-F, $^{2}J_{C\text{-}F}$, *J*=30.0Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.02.



4-(4,4,4,4,4,4,4-heptafluoro-4λ^{8}-but-2-yn-1-yl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5ag)

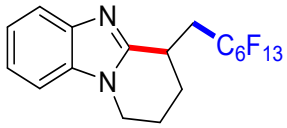
The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (82 mg, 78%), m.p. 87.3–88.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 1H), 7.35 – 7.24 (m, 3H), 4.25 – 4.22 (m, 1H), 3.98 (td, *J* = 11.5, 5.0 Hz, 1H), 3.57 – 3.53 (m, 1H), 3.53 – 3.46 (m, 1H), 2.55 – 2.52 m, 1H), 2.38 – 2.30 (m, 1H), 2.33 – 2.25 (m, 1H), 2.19 – 2.06 (m, 1H), 1.80 – 1.78 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.28, 142.38, 134.83, 122.50, 122.36, 120.10 - 107.15 (m), 119.16, 109.05, 42.38, 33.69 (C–F, $^{2}J_{C\text{-}F}$, *J* = 20.6 Hz), 30.57 (C–F, $^{3}J_{C\text{-}F}$, *J* = 4.3 Hz), 27.37 (C–F, $^{3}J_{C\text{-}F}$, *J* = 3.8 Hz), 21.68. ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.32 (t, *J* = 9.8 Hz, 3F), -110.34 – -116.63 (m, 2F), -127.37 – -127.60 (m, 2F). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}F_7N_2$ 355.1040; Found 355.1028.



4-(5,5,5,5,5,5,5,5,5-nonafluoro-5λ^{12}-penta-2,4-diyn-1-yl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5ah)

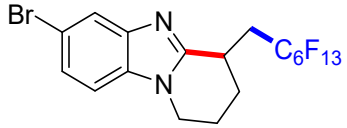
The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (91 mg, 75%), m.p. 109.8–110.8 ℃. 1H NMR (400 MHz, CDCl3) δ 7.80 – 7.71 (m, 1H), 7.38 – 7.22 (m, 3H), 4.29 – 4.16 (m, 1H), 3.98 (td, *J* = 11.5, 5.0 Hz, 1H), 3.66 – 3.45 (m, 2H), 2.59 – 2.48 (m, 1H), 2.42 – 2.22 (m, 2H), 2.21 – 2.01 (m, 1H), 1.78 (dd, *J* = 23.5, 11.0 Hz, 1H).^{13}C NMR

(101 MHz, $CDCl_3$) δ 152.29, 142.43, 134.85, 122.47, 122.34, 121.63 – 108.62 (m), 119.17, 109.06, 42.37, 33.84 (C–F, $^2J_{C\text{-}F}$, J = 20.7 Hz), 30.60 (C–F, $^3J_{C\text{-}F}$, J = 4.5 Hz), 27.38 (C–F, $^3J_{C\text{-}F}$, J = 3.8 Hz), 21.69. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.05 (t, J = 9.4 Hz, 3F), -109.77 – -119.84 (m,2F), -124.13 – -124.28 (m, 2F), -125.76 – -126.02 (m, 2F). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}F_9N_2$ 405.1008; Found 405.0978.



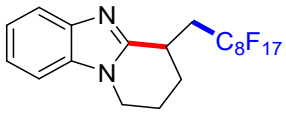
4-(7,7,7,7,7,7,7,7,7,7,7,7,7-tridecafluoro-7λ^{16}-hepta-2,4,6-triyn-1-yl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5ai)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (110 mg, 73%), m.p. 115.4–116.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 1H), 7.35 – 7.25 (m, 2H), 4.25 – 4.21 (m, 1H), 3.98 (td, J = 11.6, 5.0 Hz, 1H), 3.67 – 3.44 (m, 2H), 2.56 – 2.52 (m, 1H), 2.34 – 2.28 (m, 1H), 2.17 – 2.06 (m, 1H), 1.83 – 1.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.31, 142.42, 134.84, 122.47, 122.34, 121.75 – 110.49 (m), 119.17, 109.06, 42.37, 33.92 (C–F, $^2J_{C\text{-}F}$, J = 20.6 Hz), 30.62 (C–F, $^3J_{C\text{-}F}$, J = 4.5 Hz), 27.37 (C–F, $^3J_{C\text{-}F}$, J = 3.8 Hz), 21.69. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.85 (t, J = 10.0 Hz, 3F), -109.58 – -115.63 (m, 2F), -121.80 (s, 2F), -122.90 (s, 2F), -123.23 – -123.39 (m, 2F), -126.11 – -126.34 (m, 2F); HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}F_{13}N_2$ 505.0944; Found 505.0924.



7-bromo-4-(7,7,7,7,7,7,7,7,7,7,7,7,7-tridecafluoro-7λ^{16}-hepta-2,4,6-triyn-1-yl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5aj)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (121 mg, 70%), m.p. 170.3–171.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 1.8 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.17 (d, J = 8.5 Hz, 1H), 4.25 – 4.19 (m, 1H), 3.98 (td, J = 11.6, 5.0 Hz, 1H), 3.57 – 3.51 (m, 1H), 3.50 – 3.40 (m, 1H), 2.56 – 2.53 (m, 1H), 2.43 – 2.25 (m, 1H), 2.21 – 2.07 (m, 2H), 1.81 – 1.78 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.44, 143.70, 133.81, 125.34, 122.07, 121.73 – 107.87 (m), 115.43, 110.25, 42.51, 33.85 (C–F, $^2J_{C\text{-}F}$, J = 20.7 Hz), 30.60 (C–F, $^3J_{C\text{-}F}$, J = 4.4 Hz), 27.18 (C–F, $^3J_{C\text{-}F}$, J = 3.7 Hz), 21.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.81 (t, J = 10.0 Hz, 3F), -109.61 – -115.50 (m, 2F), -121.77 (s, 2F), -122.86 (s, 2F), -123.21 – -123.43 (m, 2F), -126.04 – -126.29 (m, 2F); HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}BrF_{13}N_2$ 583.0049; Found 583.0028.



4-(9,9,9,9,9,9,9,9,9,9,9,9,9,9,9,9,9-heptadecafluoro-9λ^{20}-nona-2,4,6,8-tetrayn-1-yl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5ak)

The product was purified by column chromatography on silica gel (eluent: 25:1 petroleum ether: ethyl acetate) as a white solid (123 mg, 68%), m.p. 125.4–126.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 1H), 7.36 – 7.25 (m, 3H), 4.29 – 4.25 (m, 1H), 4.01 (td, *J* = 11.5, 5.0 Hz, 1H), 3.66 – 3.51 (m, 1H), 2.58 – 2.54 (m, 1H), 2.44 – 2.25 (m, 1H), 2.22 – 2.07 (m, 1H), 1.83 – 1.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.30, 142.40, 134.84, 122.47, 122.33, 121.45 – 107.52 (m), 119.16, 109.05, 42.36, 33.94 (C–F, $^{2}J_{C\text{-}F}$, *J* = 20.5 Hz), 30.62 (C–F, $^{3}J_{C\text{-}F}$, *J* = 4.4 Hz), 27.36 (C–F, $^{3}J_{C\text{-}F}$, *J* = 3.8 Hz), 21.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.79 (t, *J* = 9.9 Hz, 3F), -109.53 – -115.57 (m, 2F), -121.56 (s, 2F), -121.95 (s, 4F), -122.76 (s, 2F), -123.24 (s, 2F), -126.17 (s, 2F); HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}F_{17}N_2$ 605.0880; Found 605.0853.

6. References

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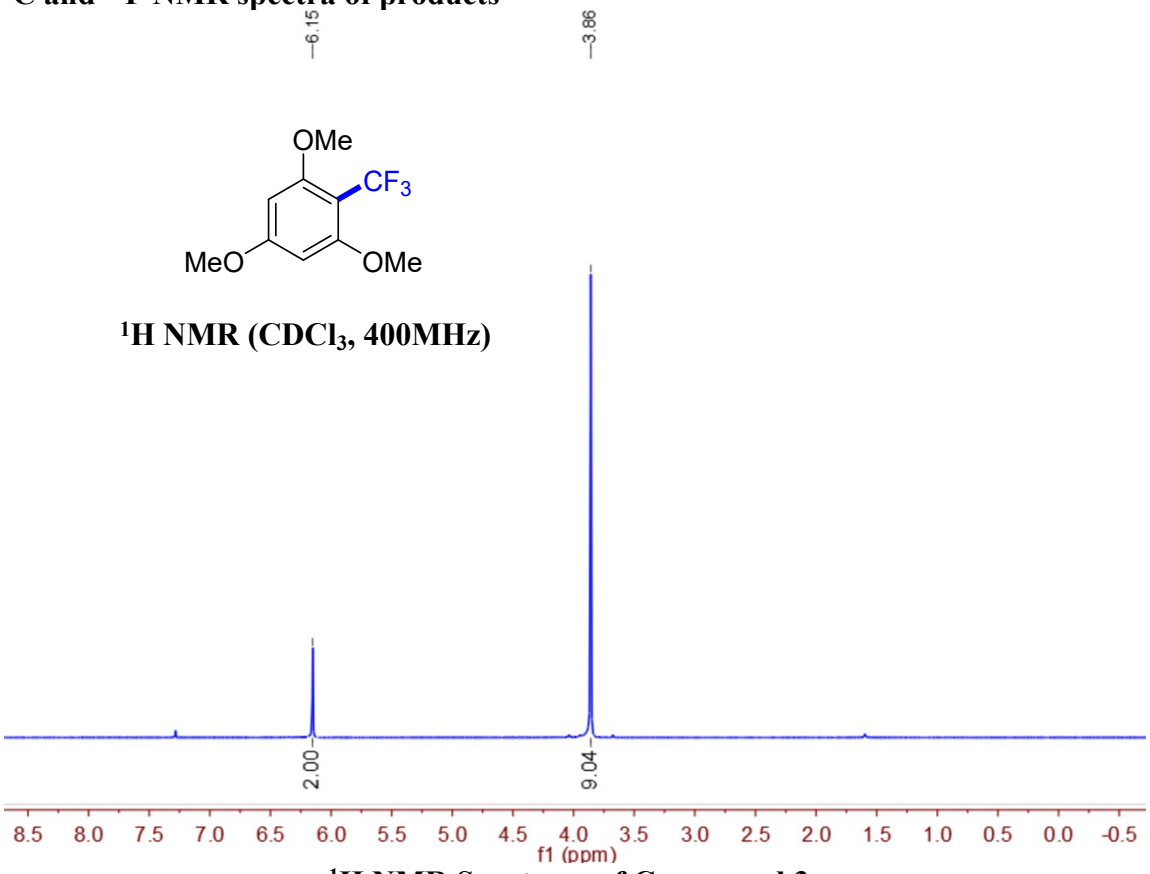
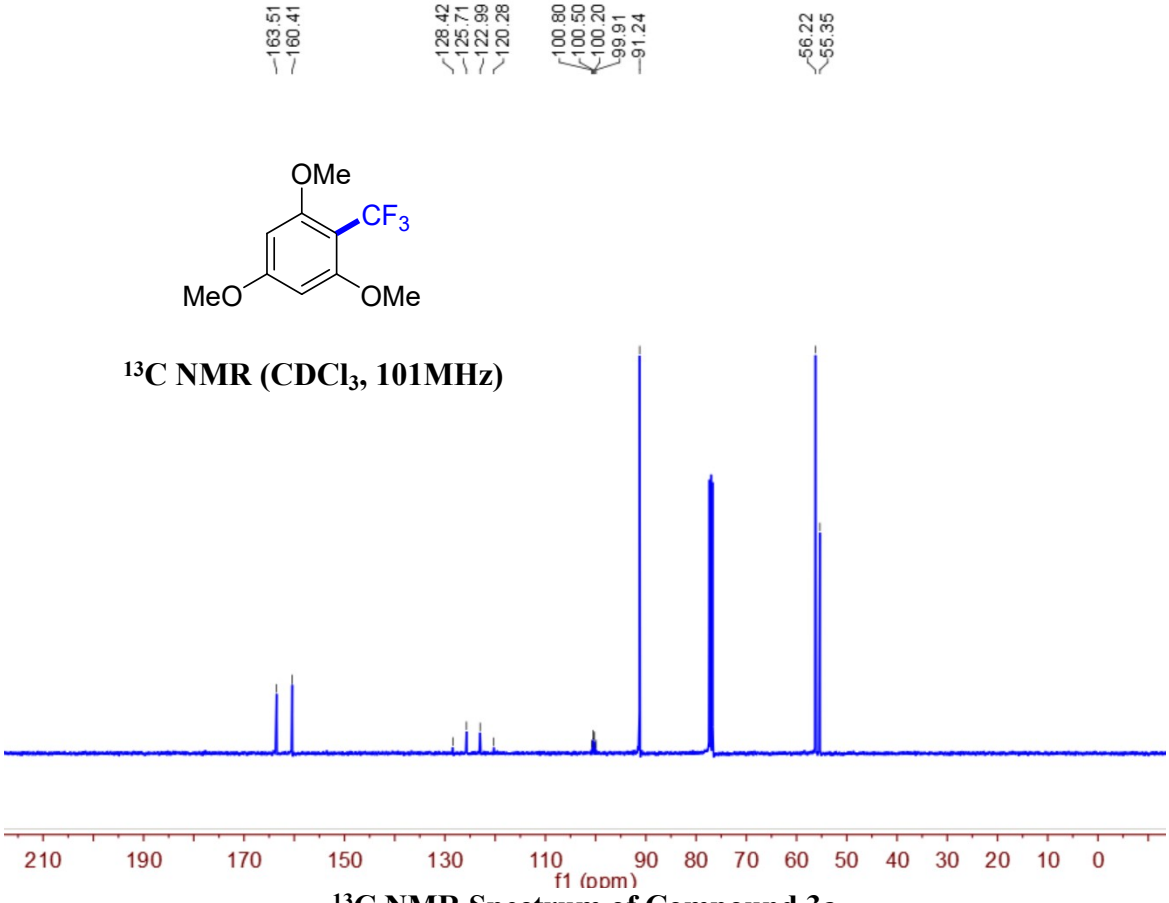
7. ^{1}H, ^{13}C and ^{19}F NMR spectra of products



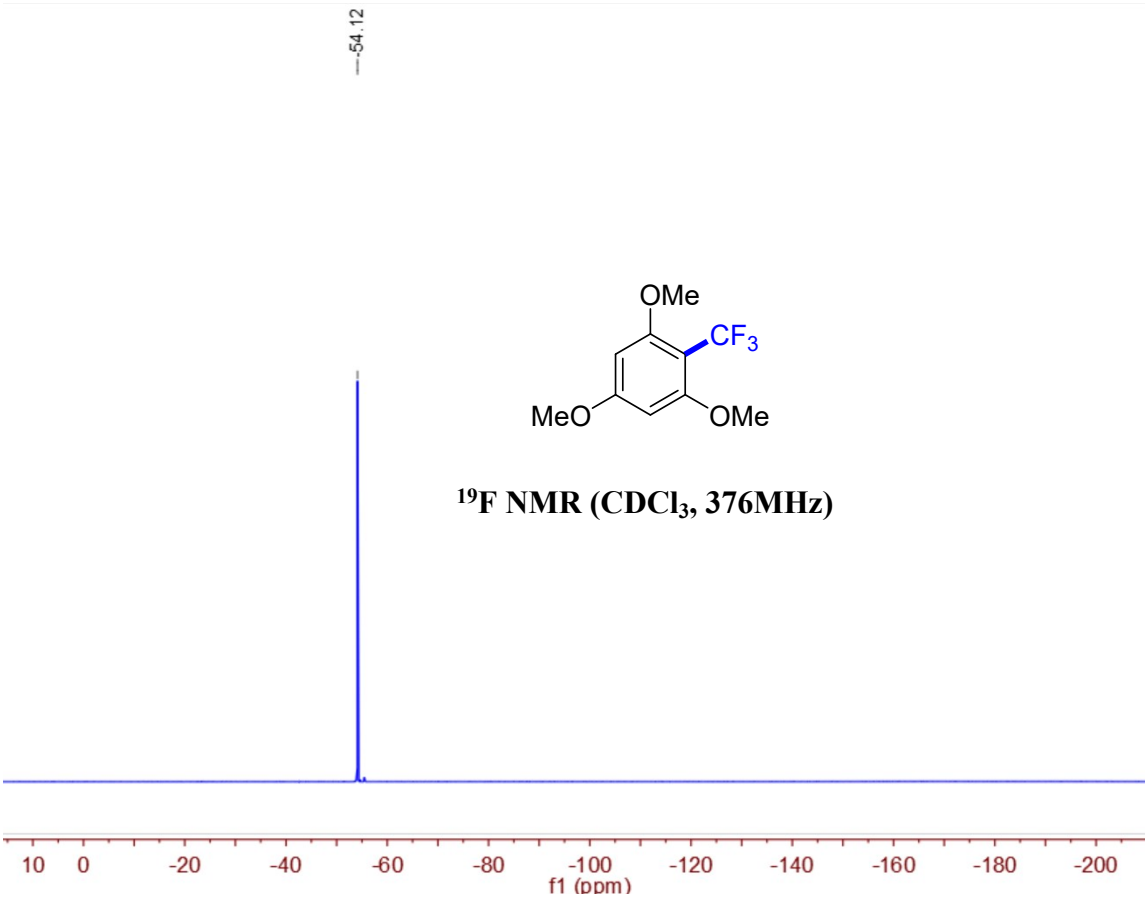
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3a



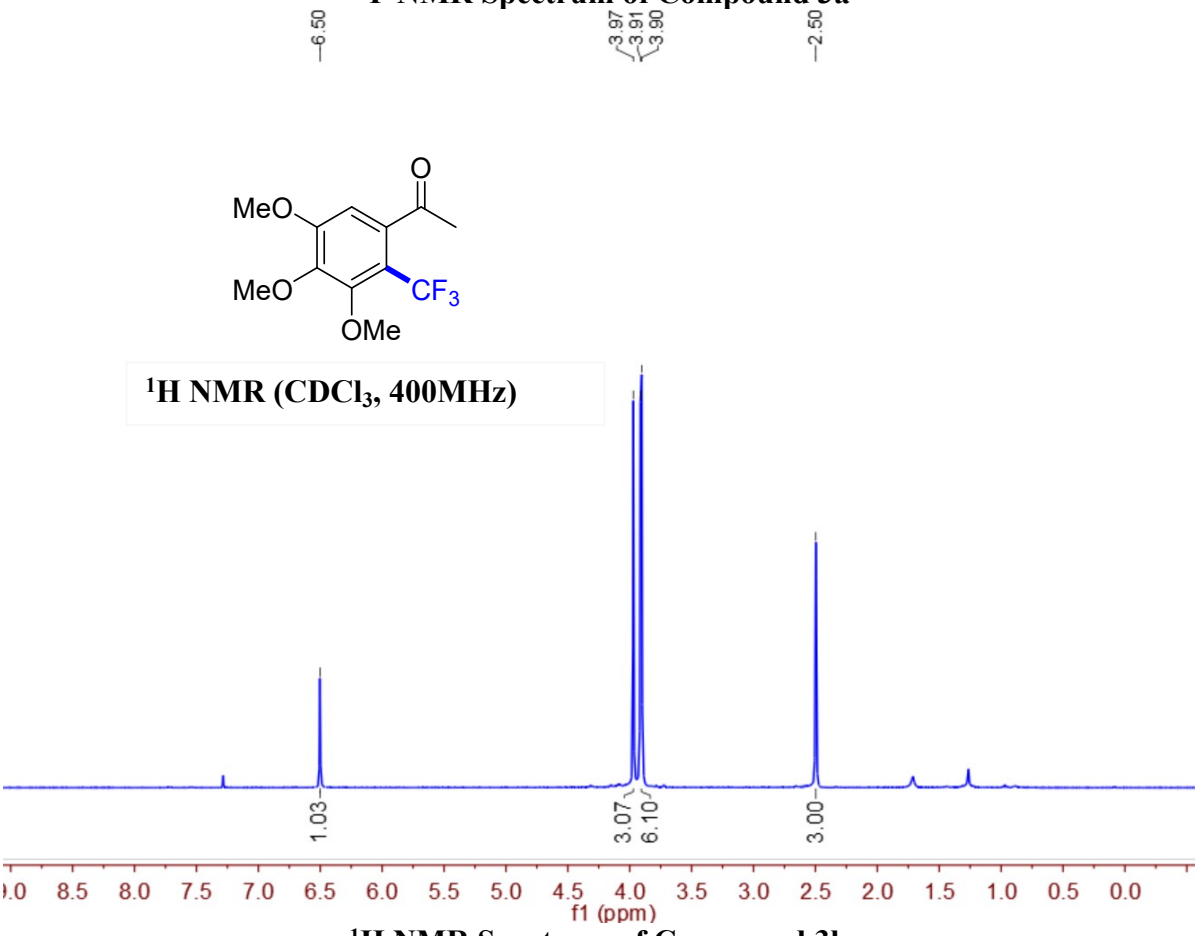
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3a



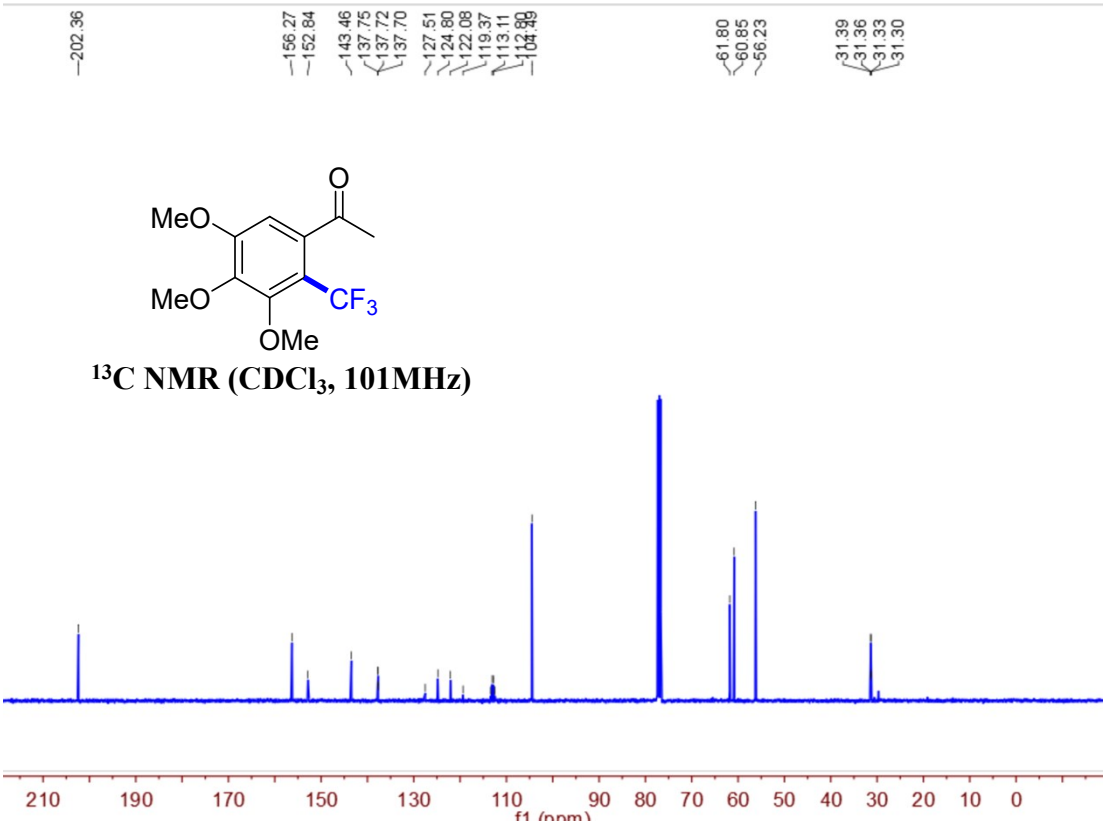
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3a



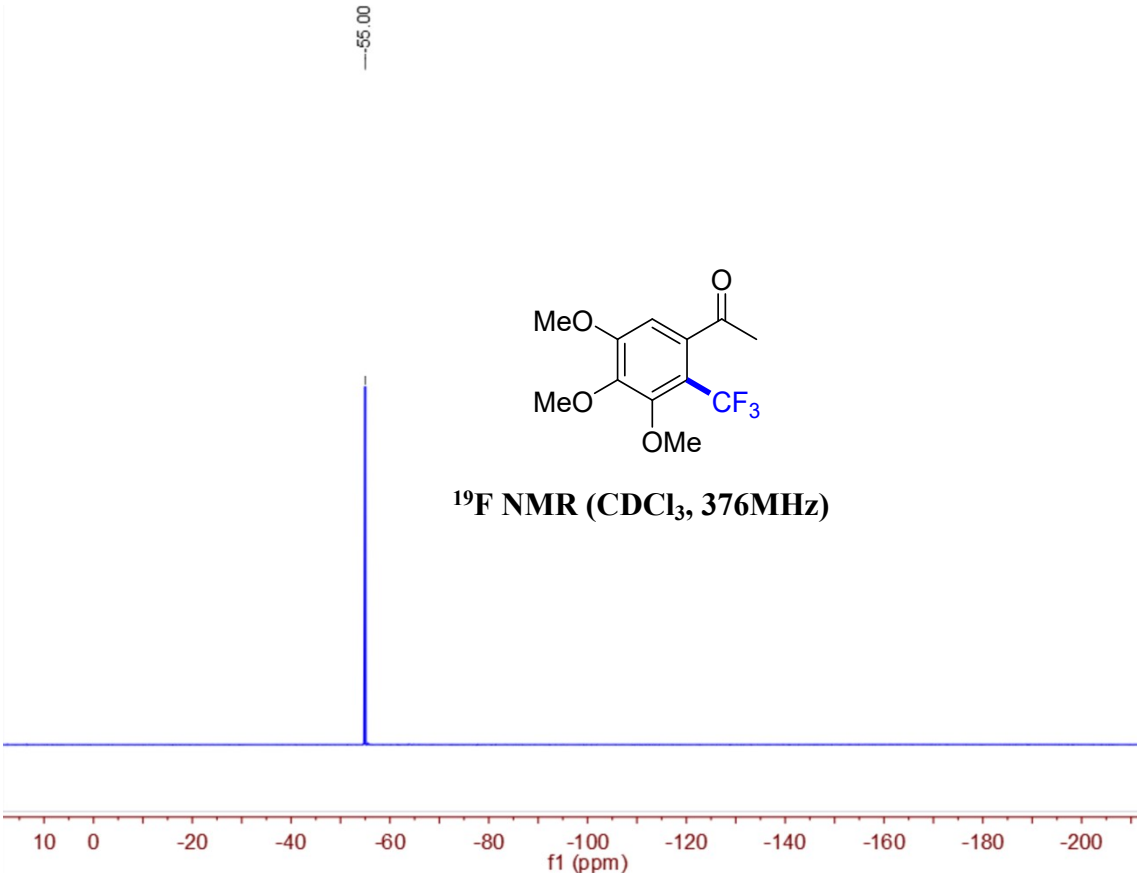
^{1}H NMR (CDCl$_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3b



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

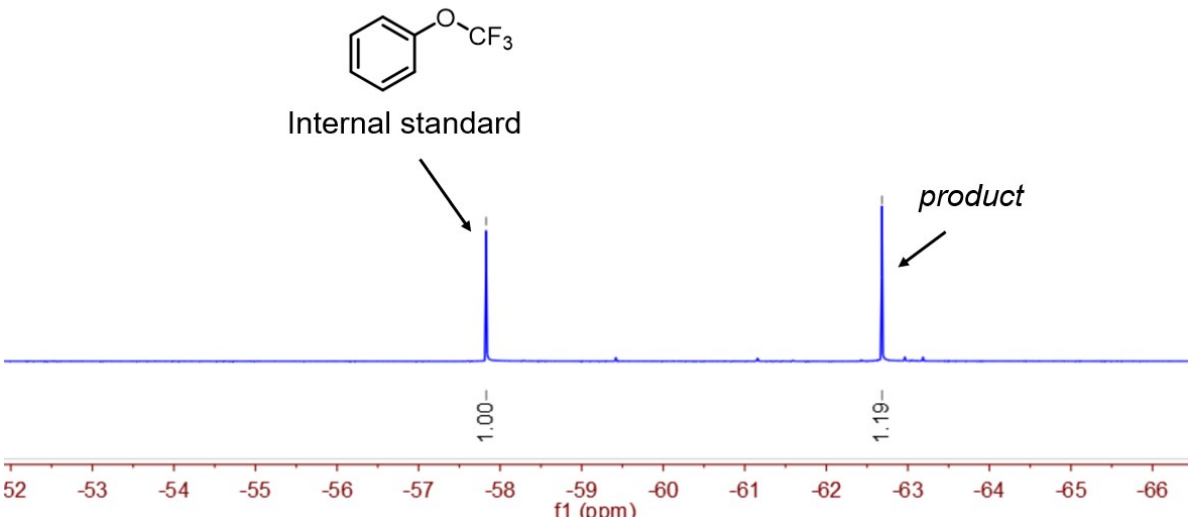
^{13}C NMR Spectrum of Compound 3b



^{19}F NMR ($CDCl_3$, 376MHz)

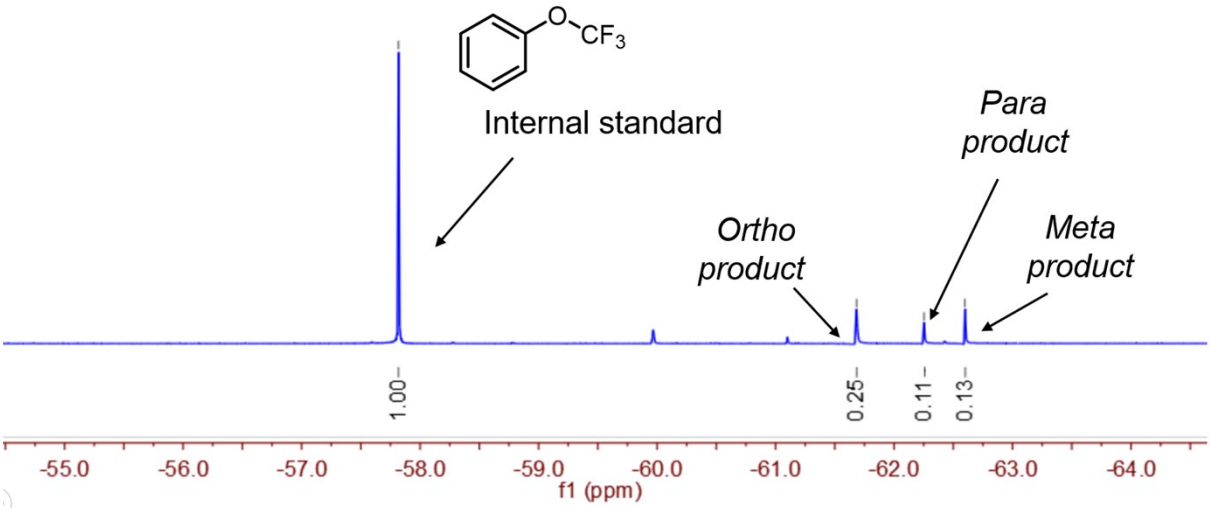
^{19}F NMR Spectrum of Compound 3b

^{19}F NMR ($CDCl_3$, 376MHz)



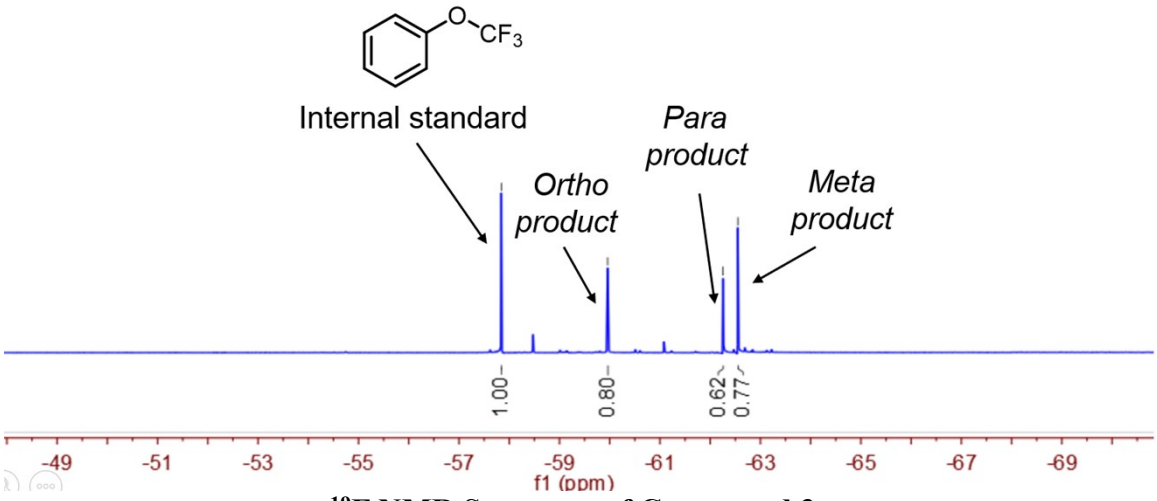
^{19}F NMR Spectrum of Compound 3c

^{19}F NMR ($CDCl_3$, 376MHz)



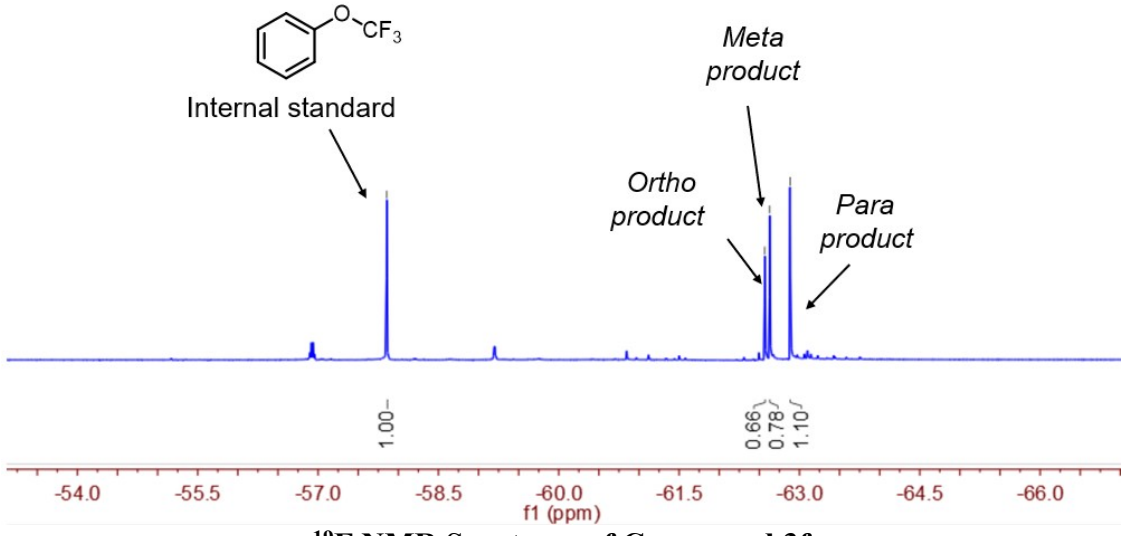
^{19}F NMR Spectrum of Compound 3d

^{19}F NMR ($CDCl_3$, 376MHz)

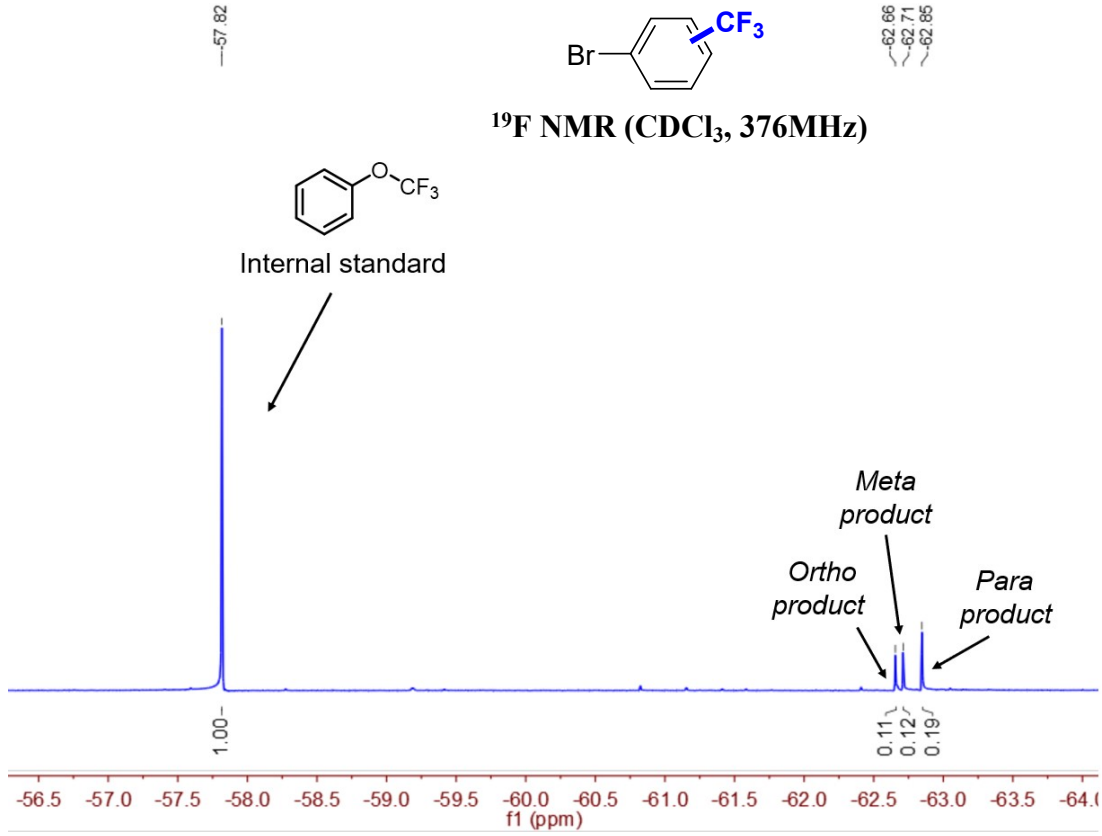


^{19}F NMR Spectrum of Compound 3e

^{19}F NMR ($CDCl_3$, 376MHz)

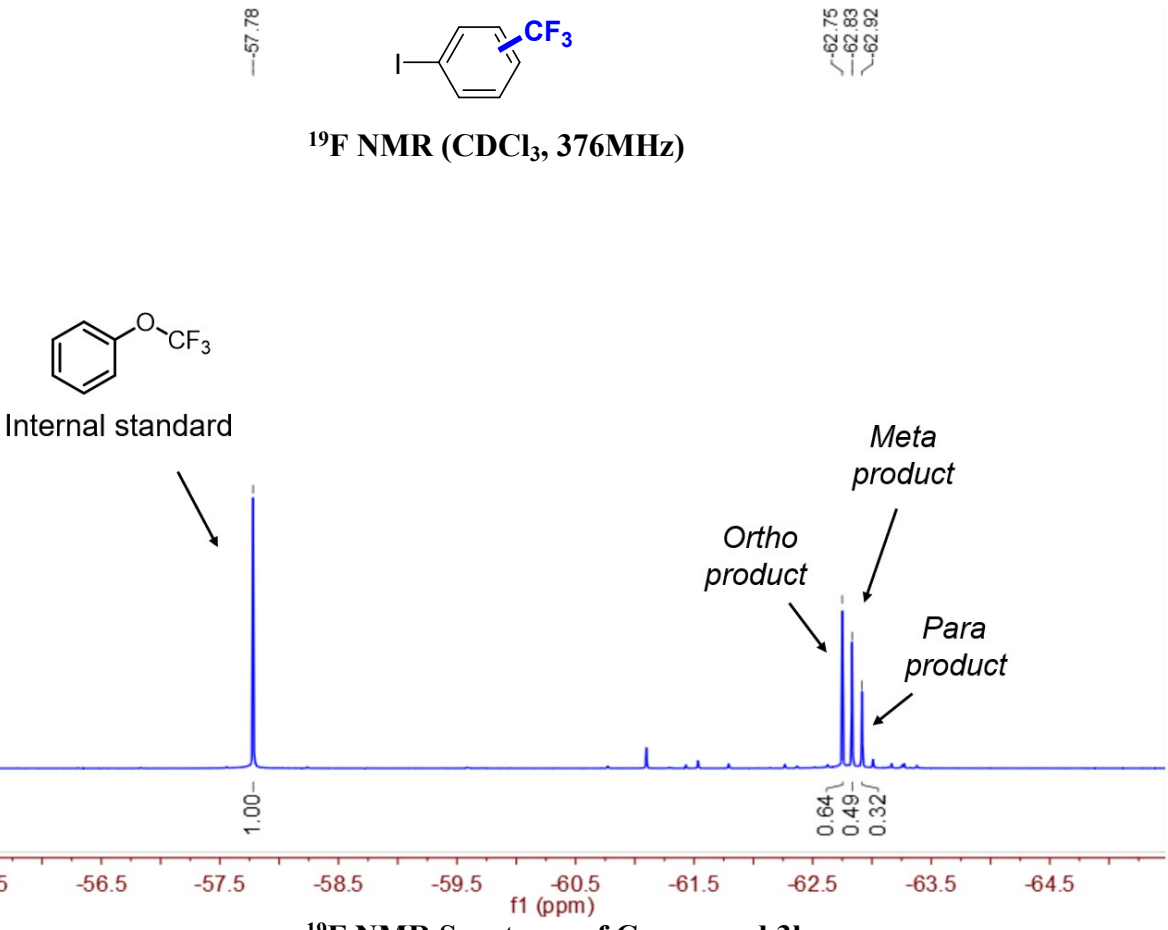


^{19}F NMR Spectrum of Compound 3f



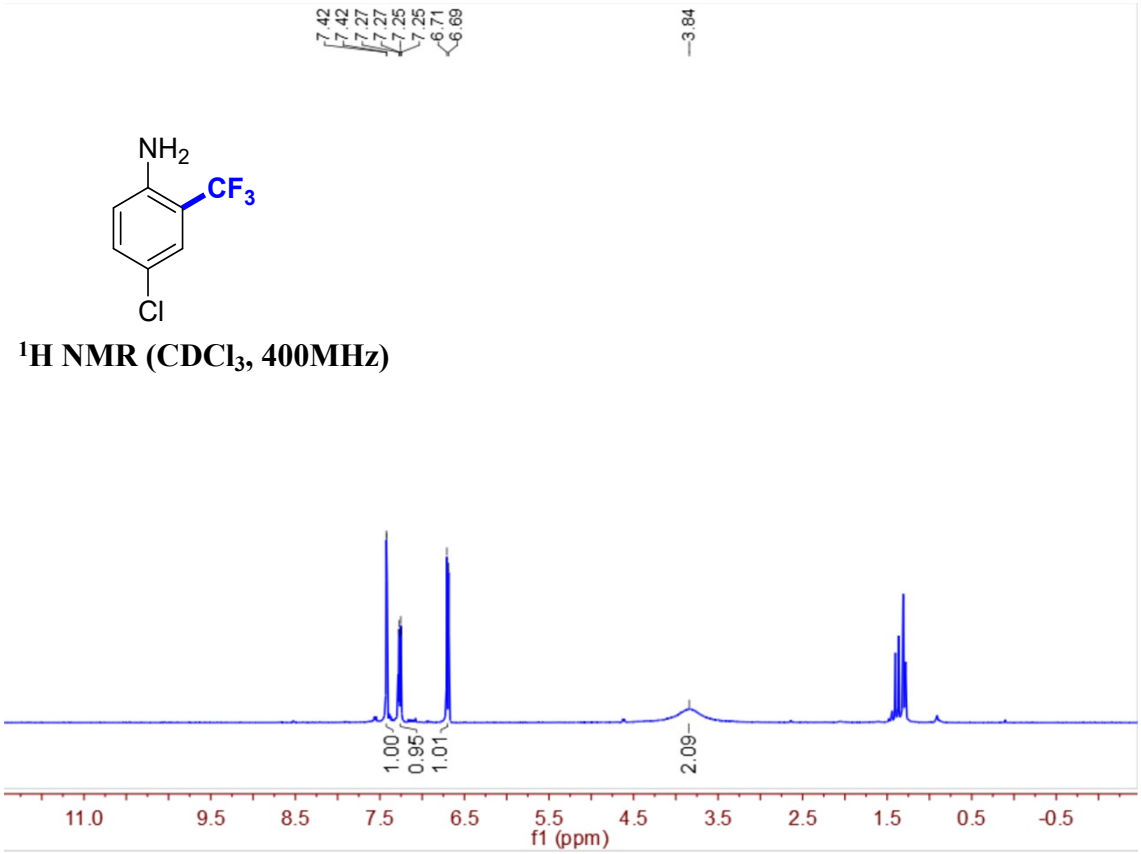
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3g



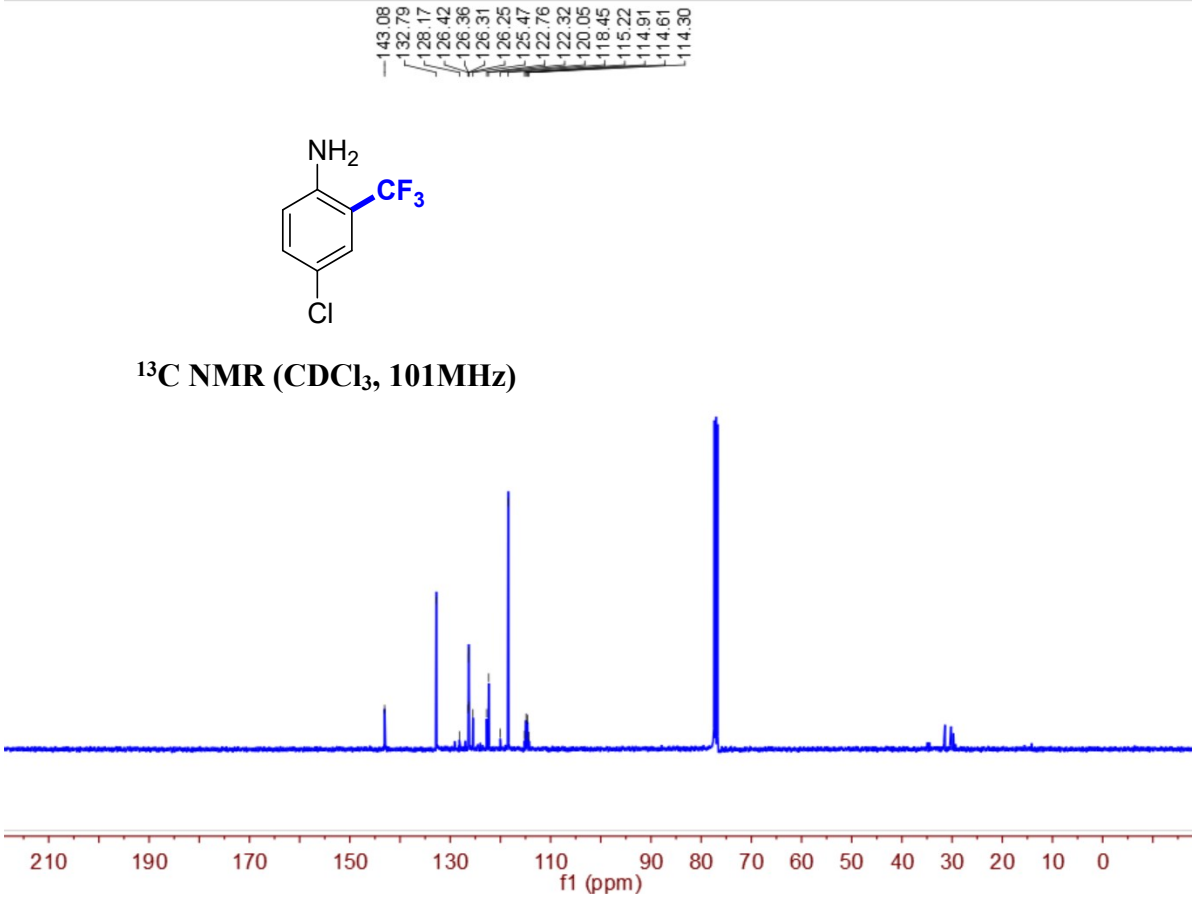
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3h



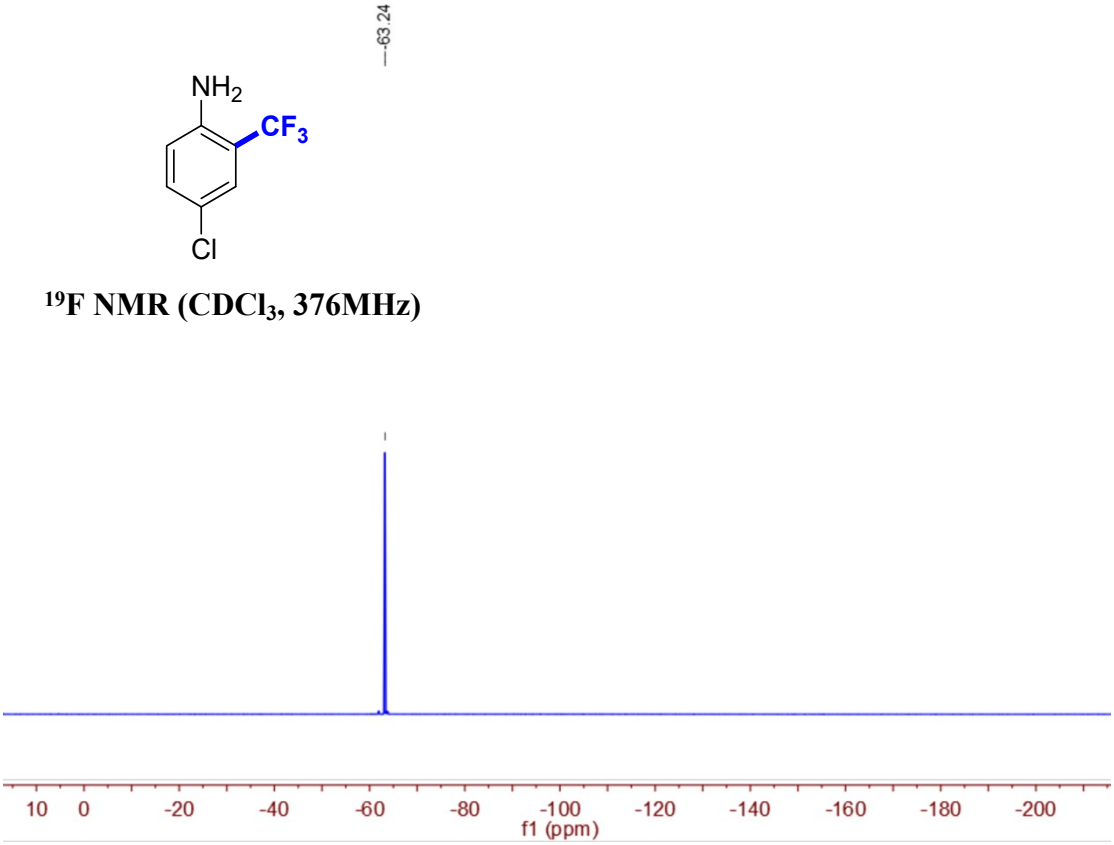
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3i



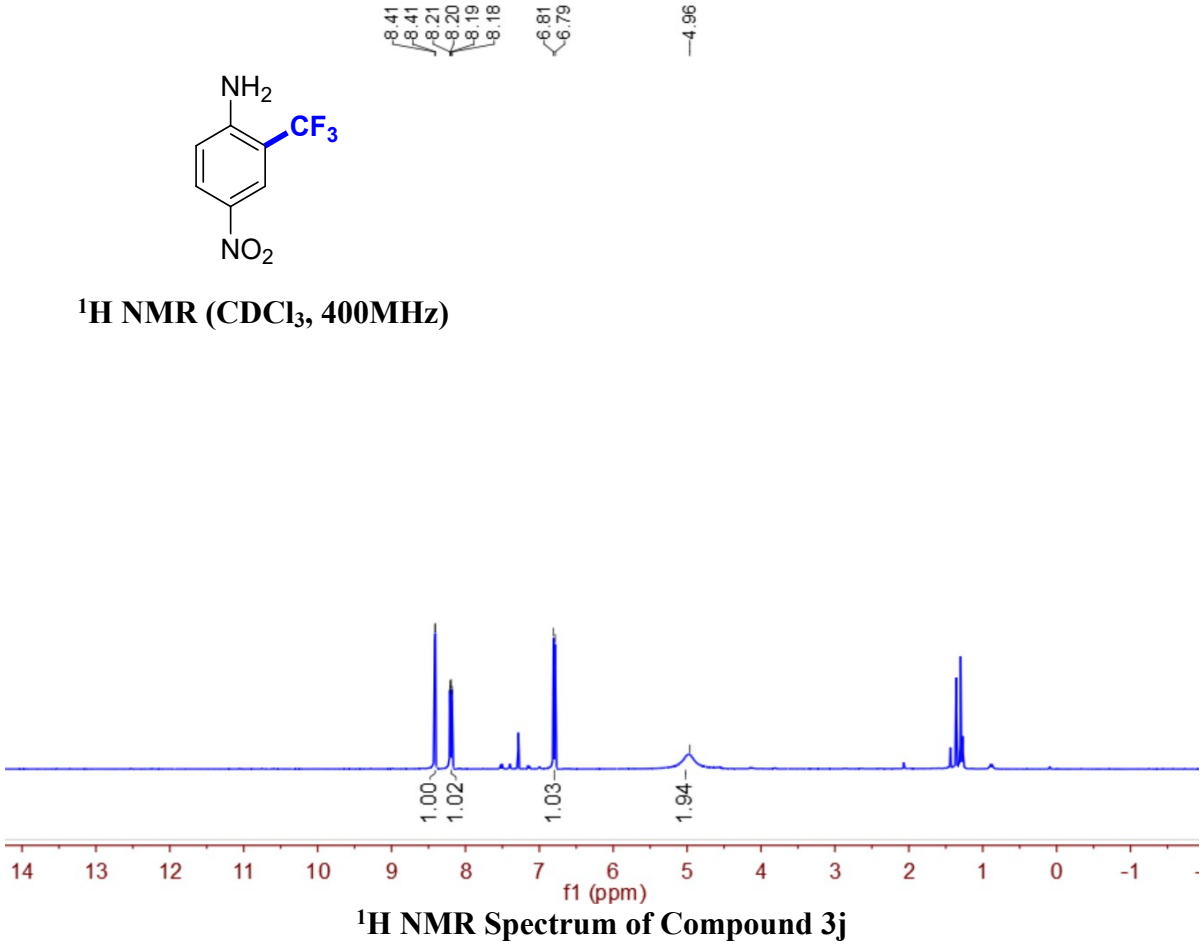
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3i



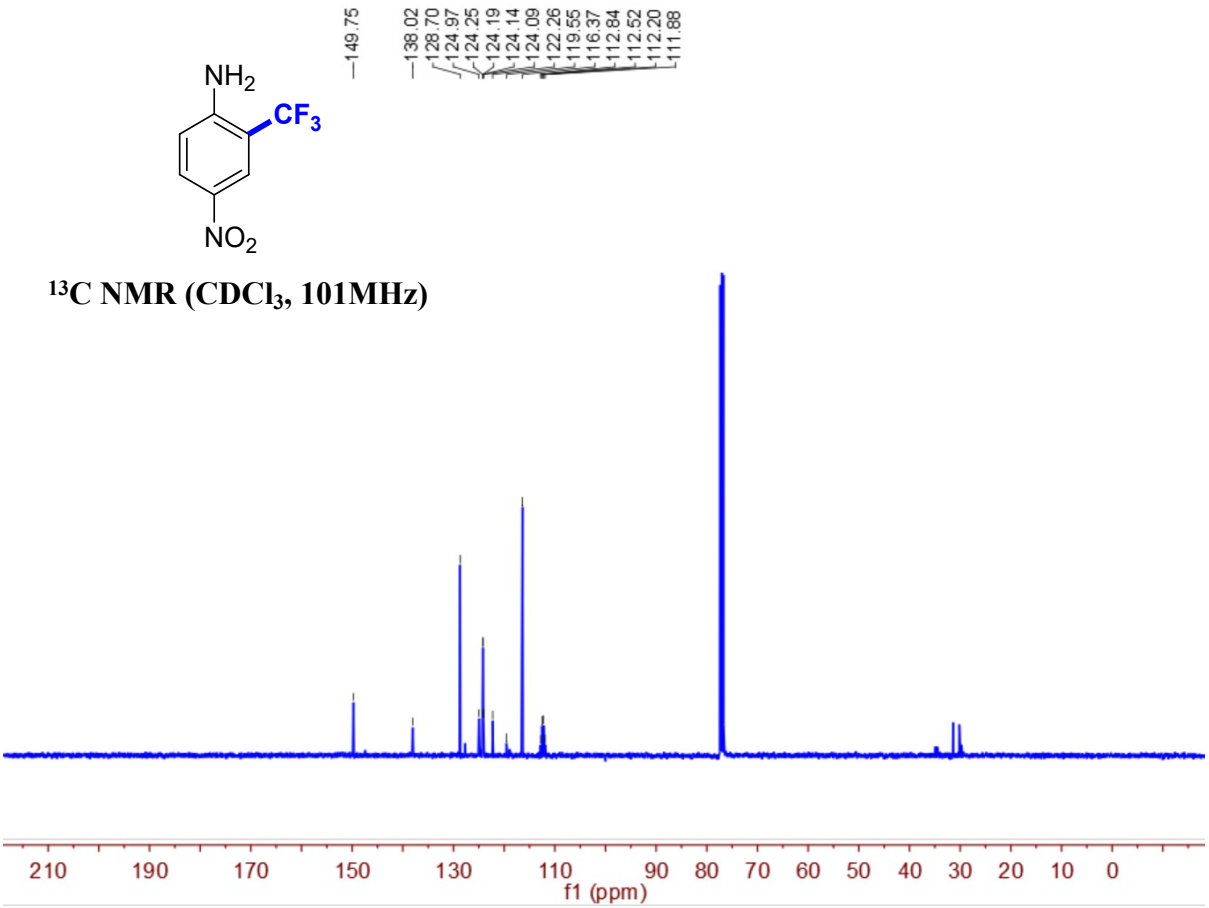
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3i



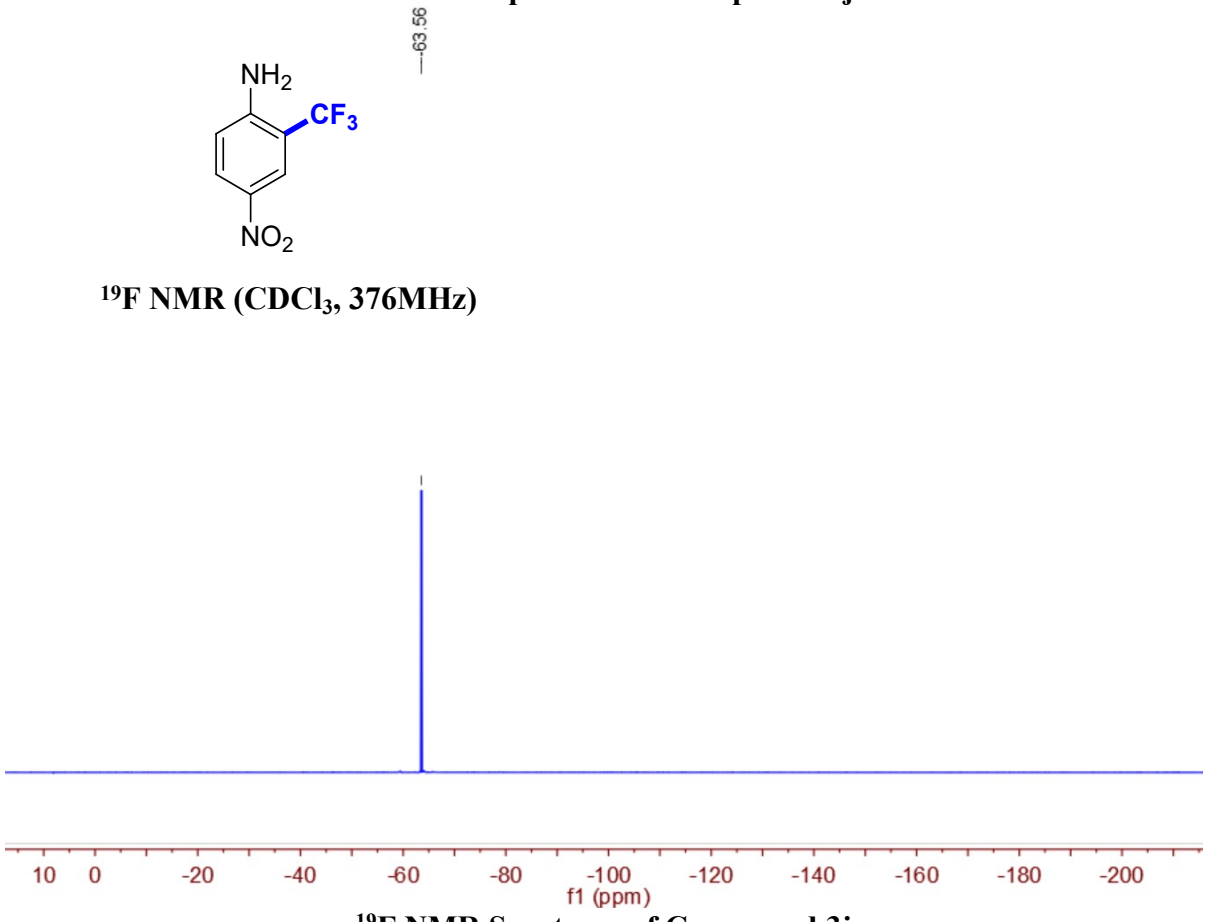
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3j



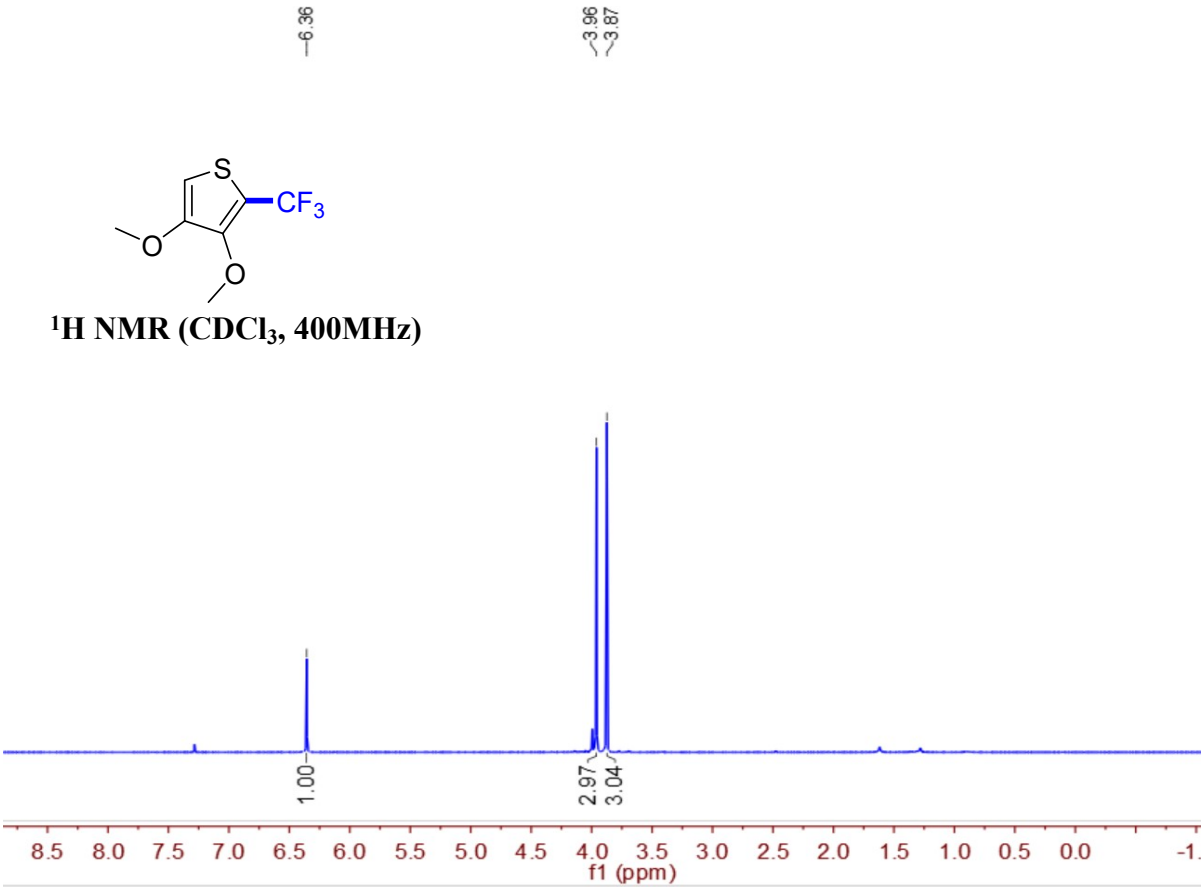
^{13}C NMR (CDCl$_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3j



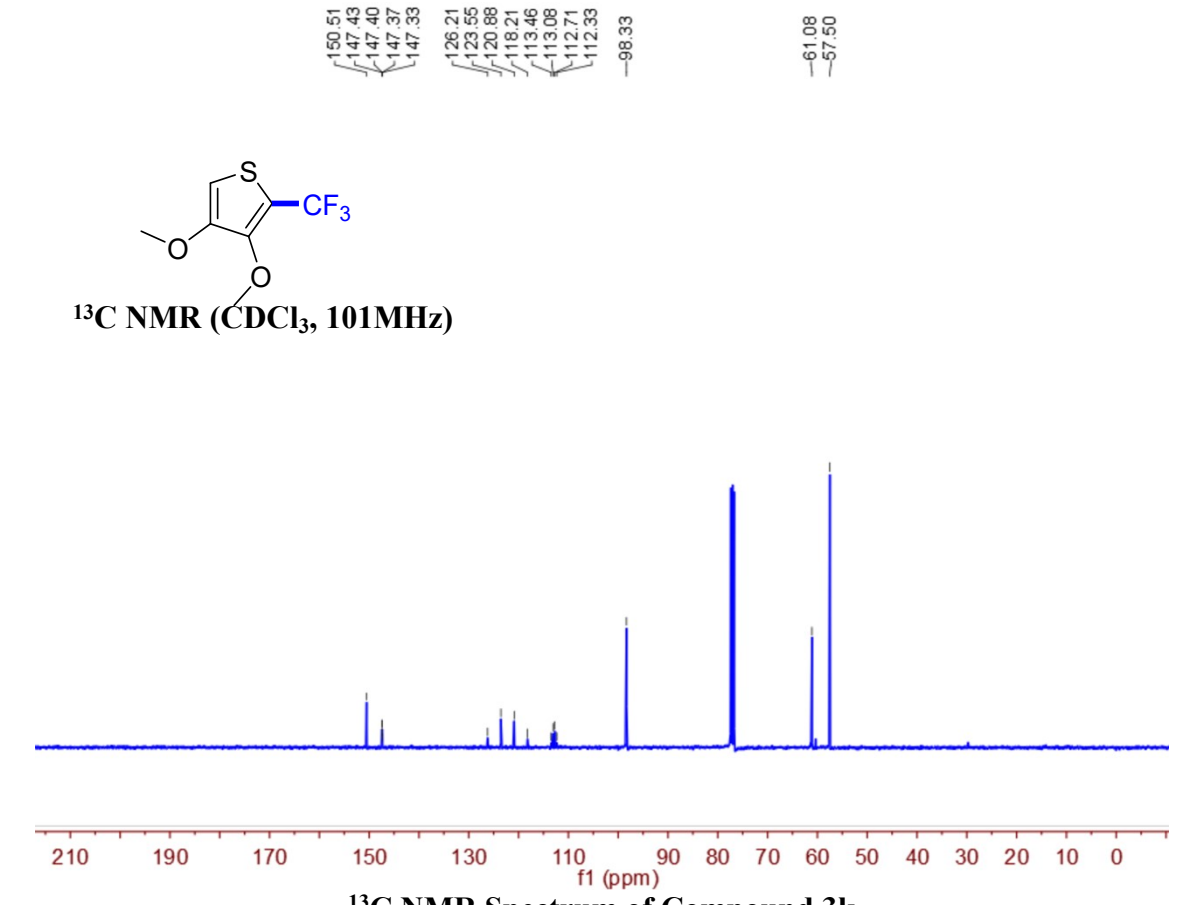
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3j



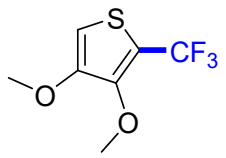
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3k



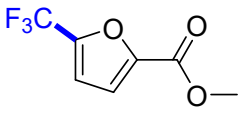
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3k



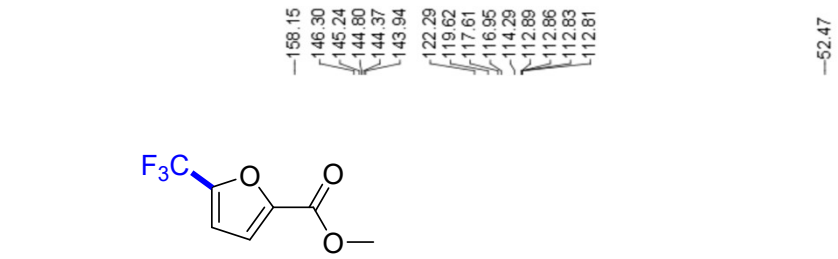
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3k



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

^{1}H NMR Spectrum of Compound 3l



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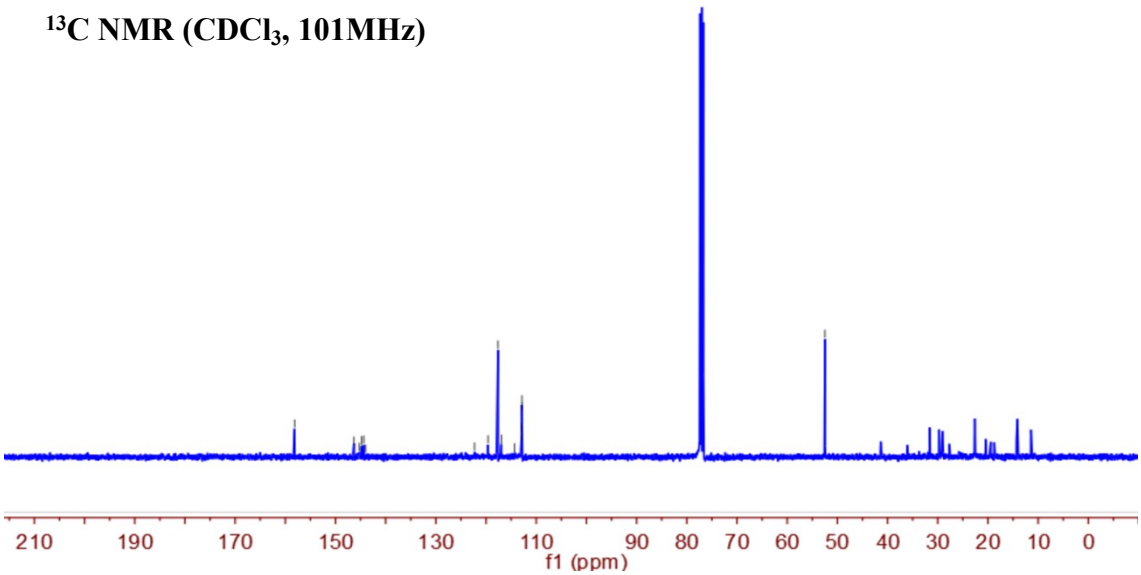
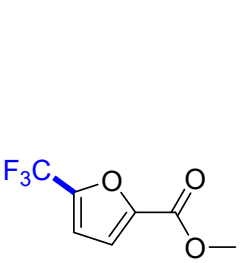


^{13}C NMR Spectrum of Compound 3l



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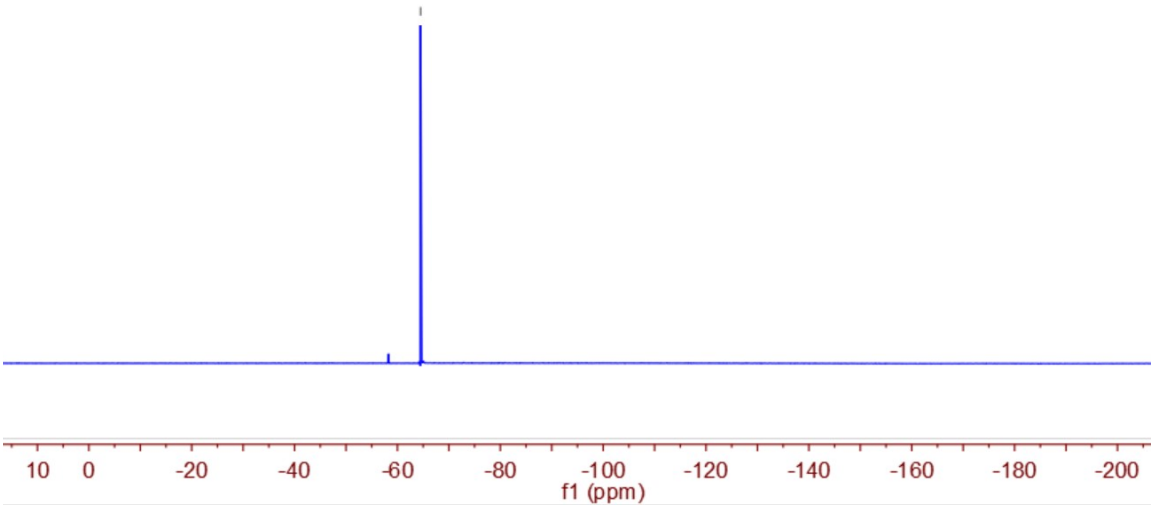
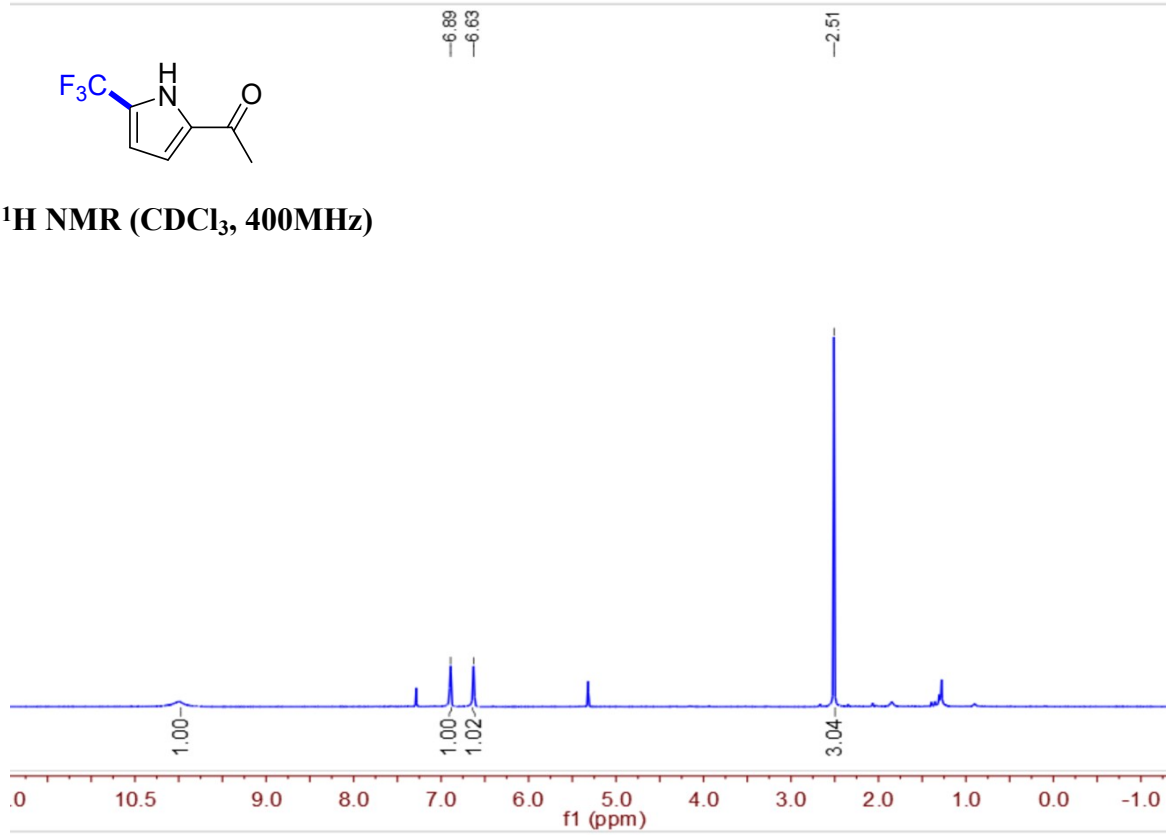
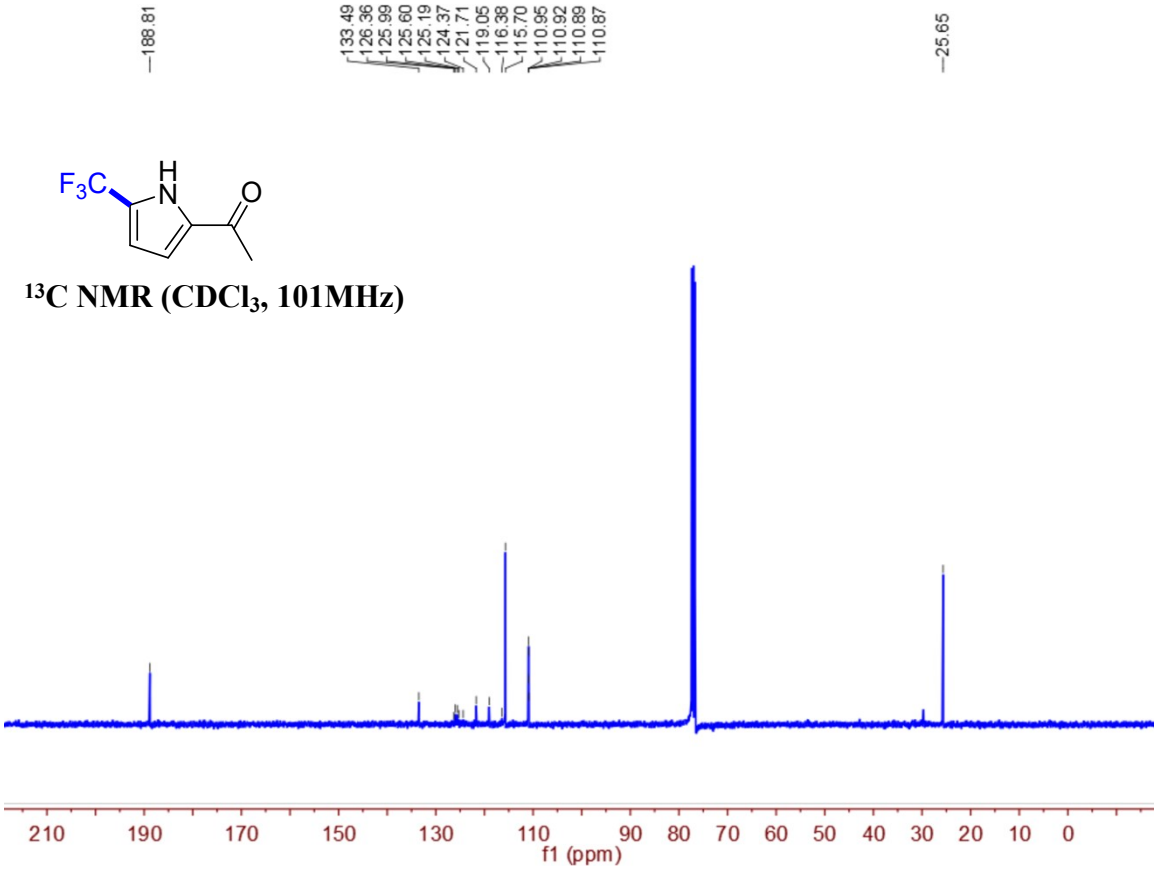


^{19}F NMR Spectrum of Compound 3l



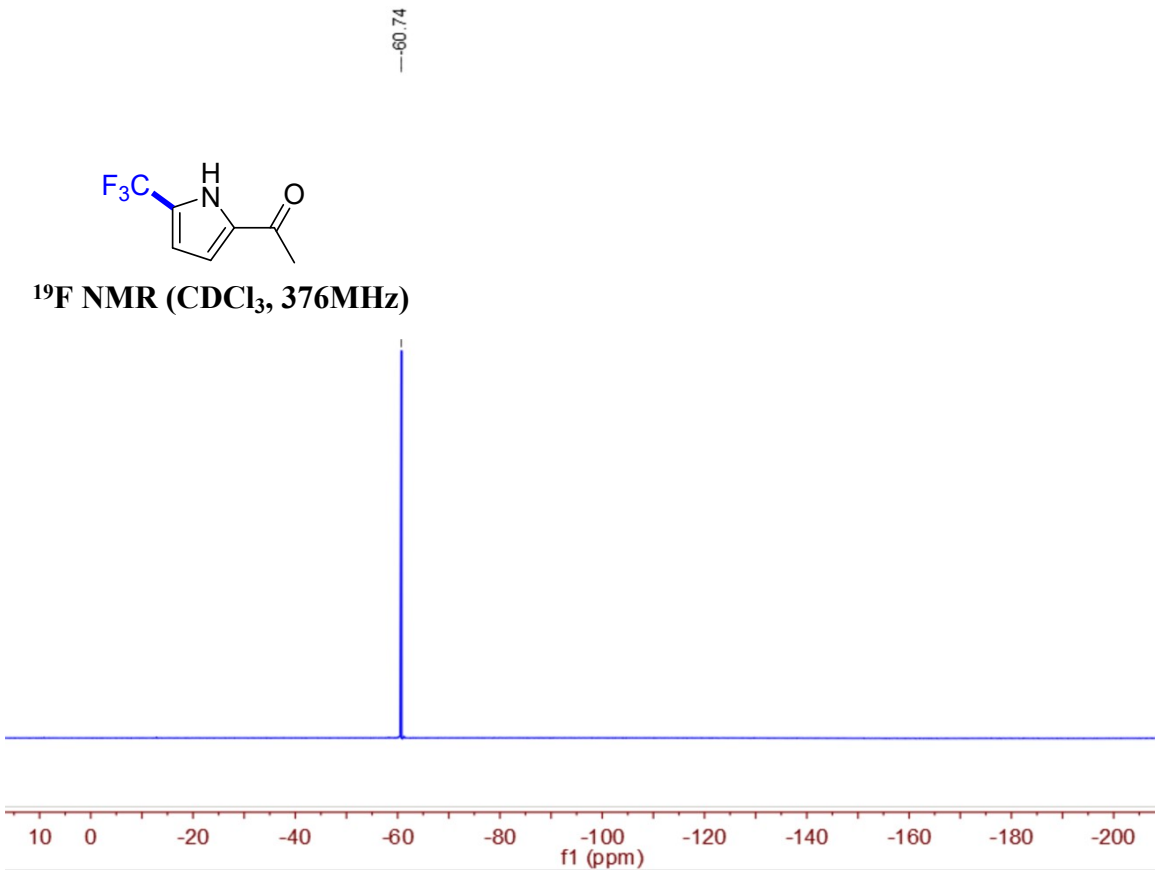
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3m



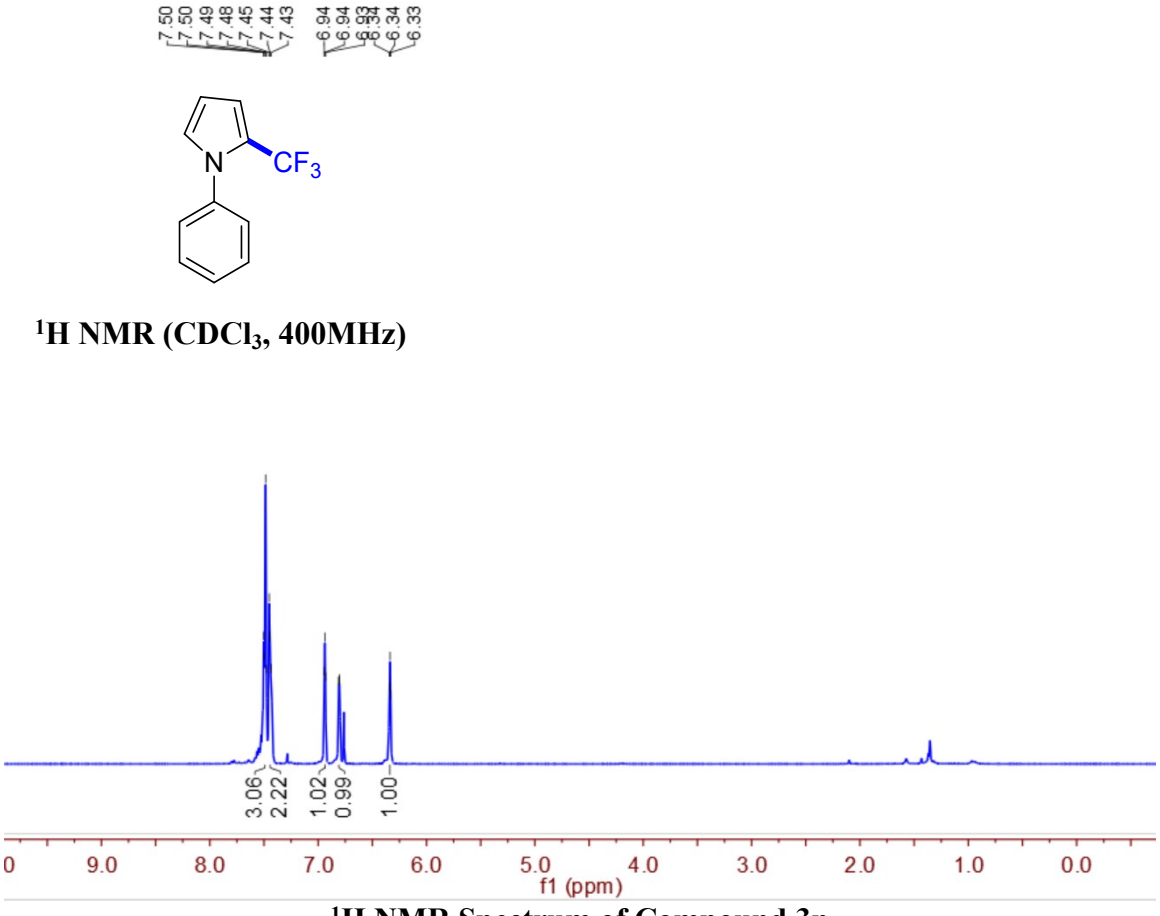
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3m



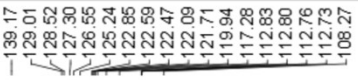
^{19}F NMR ($CDCl_3$, 376MHz)

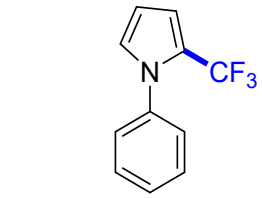
^{19}F NMR Spectrum of Compound 3m



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

^{1}H NMR Spectrum of Compound 3n





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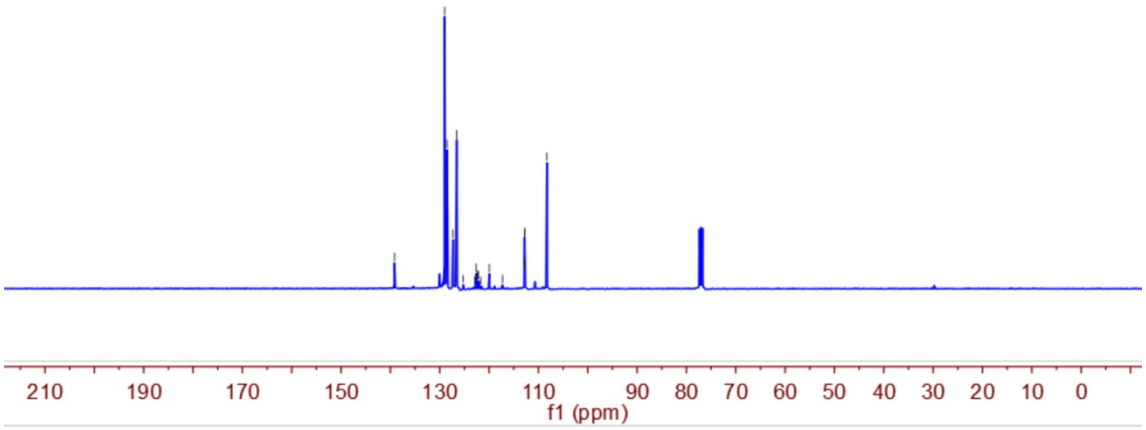
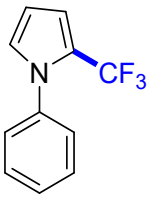
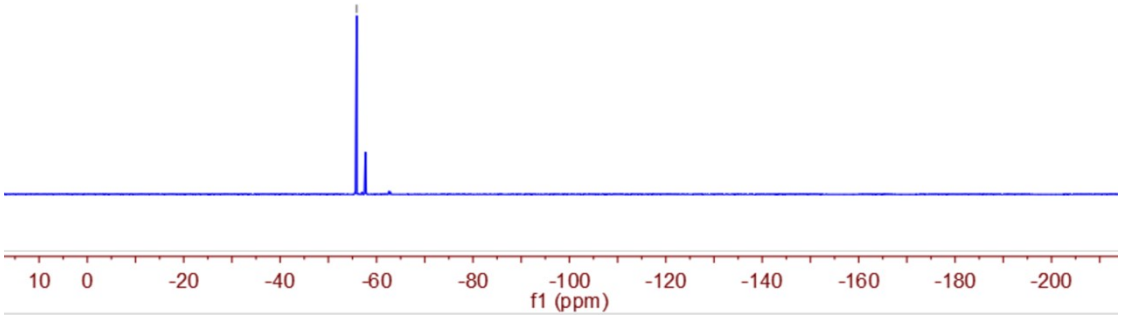


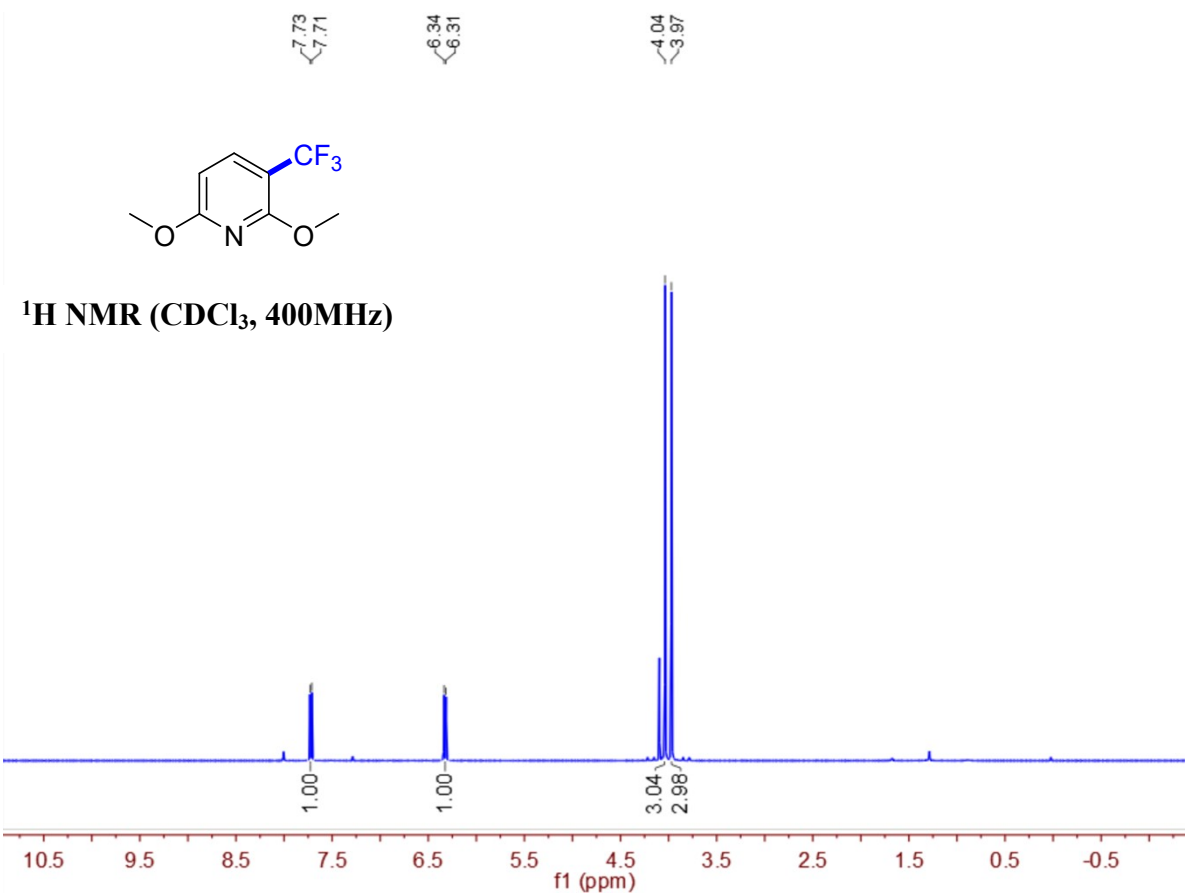
^{13}C NMR Spectrum of Compound 3n



^{19}F NMR ($CDCl_3$, 376MHz)

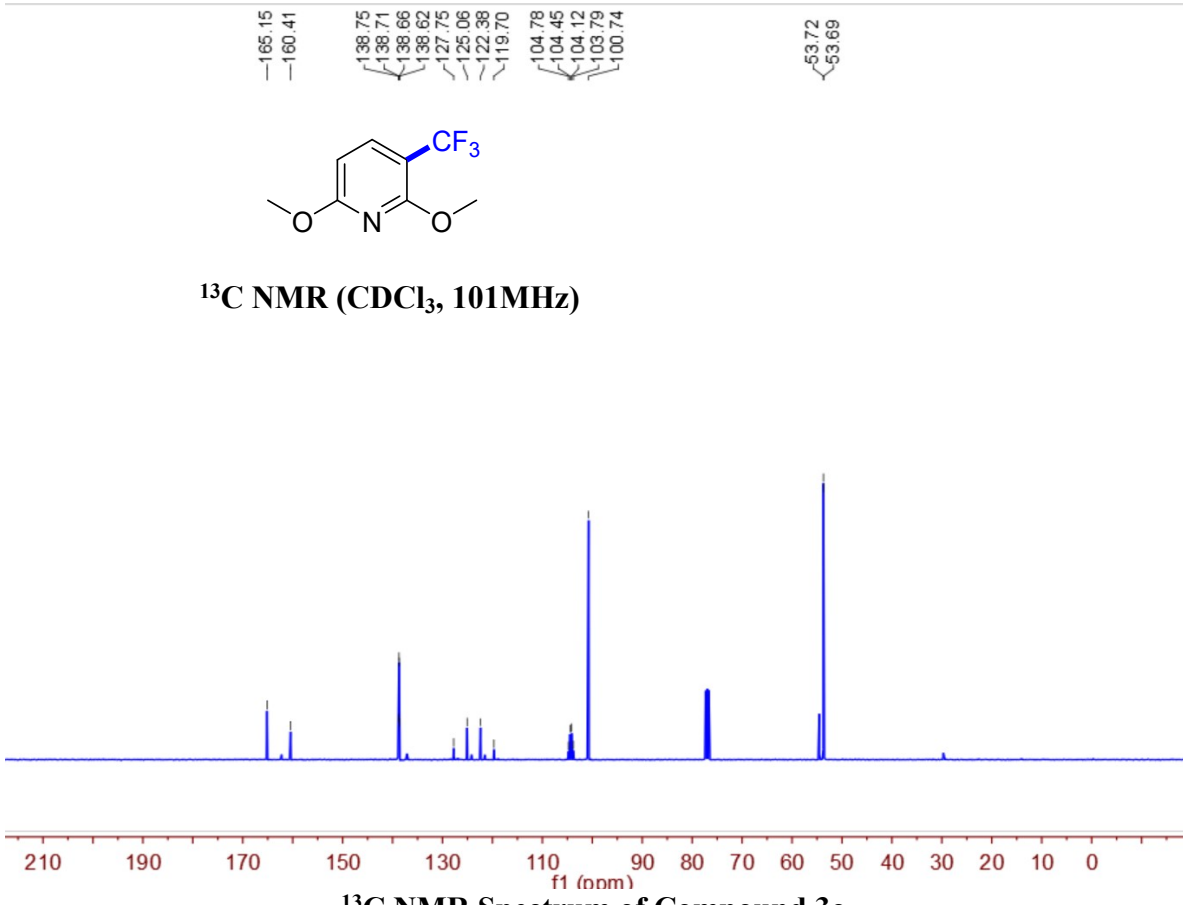


^{19}F NMR Spectrum of Compound 3n



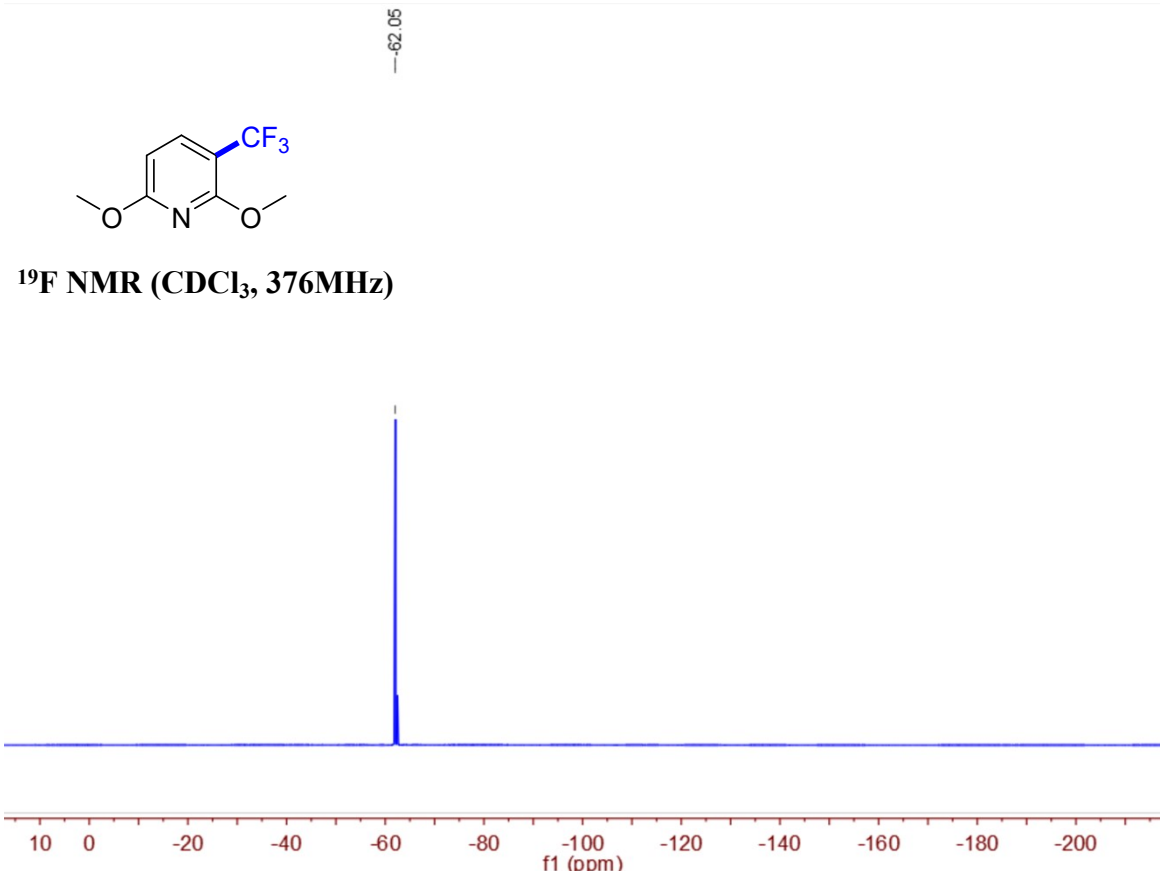
^{1}H NMR (CDCl$_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3o



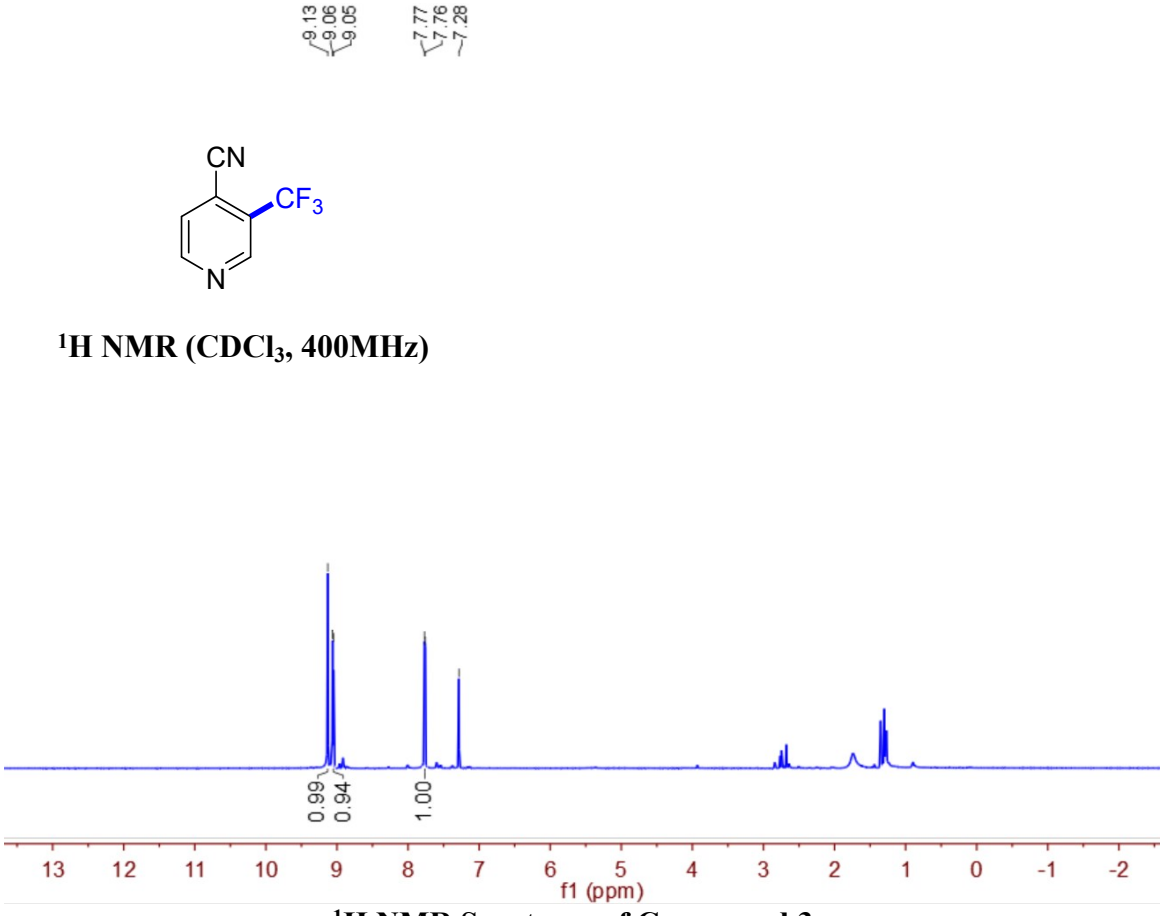
^{13}C NMR (CDCl$_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3o



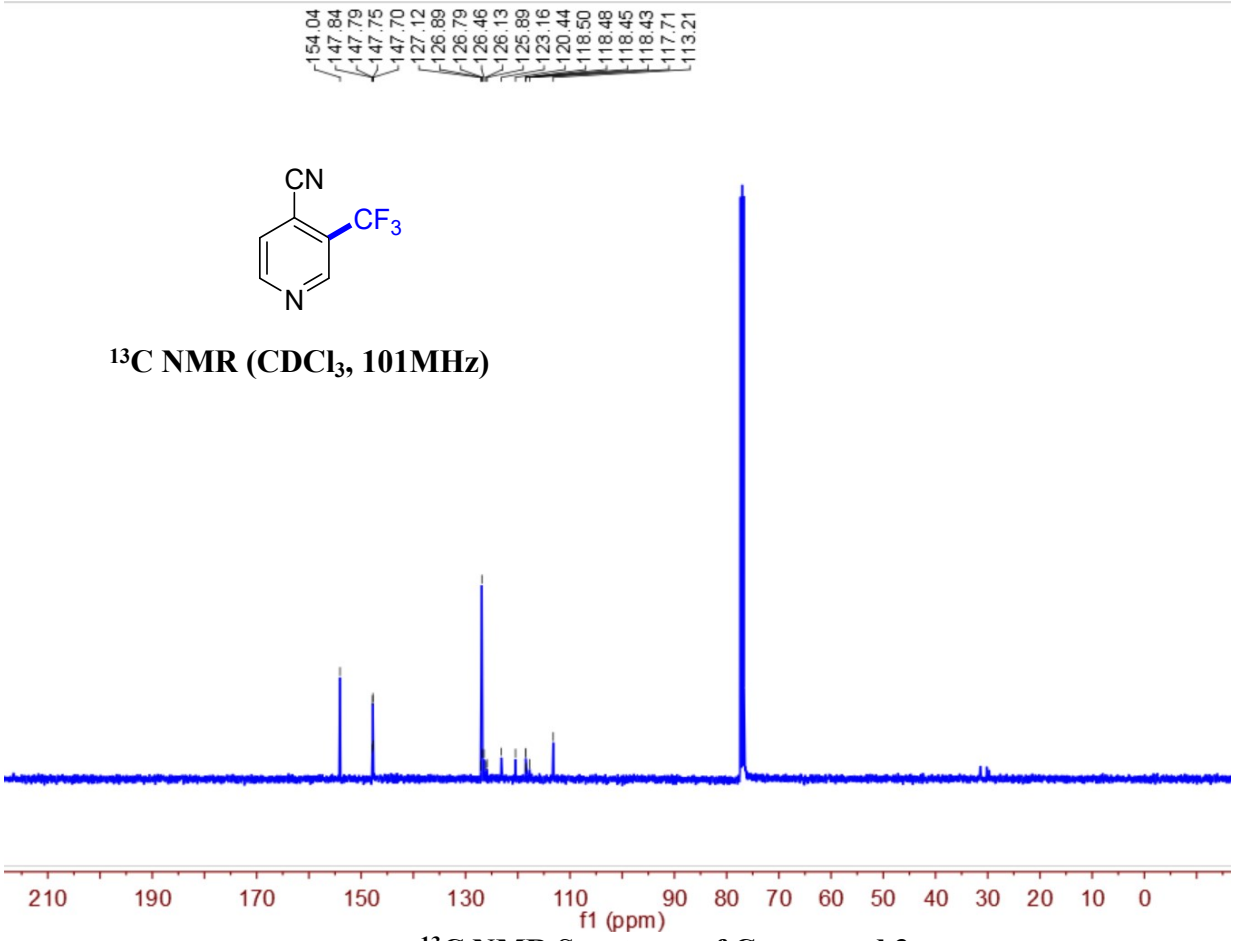
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3o



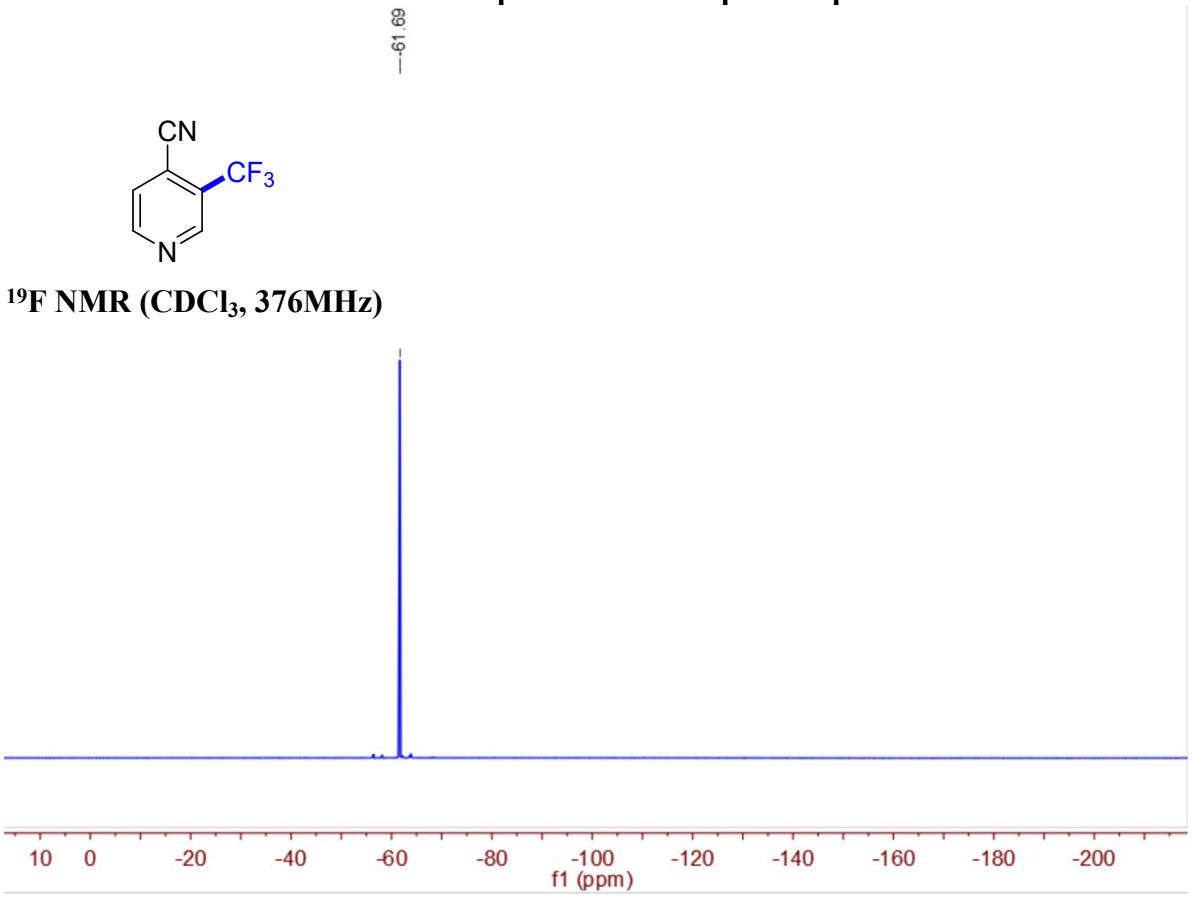
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3p



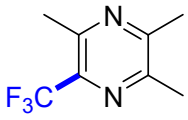
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3p



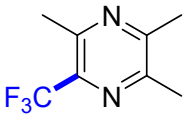
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3p



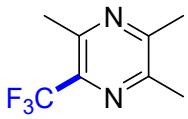
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3q

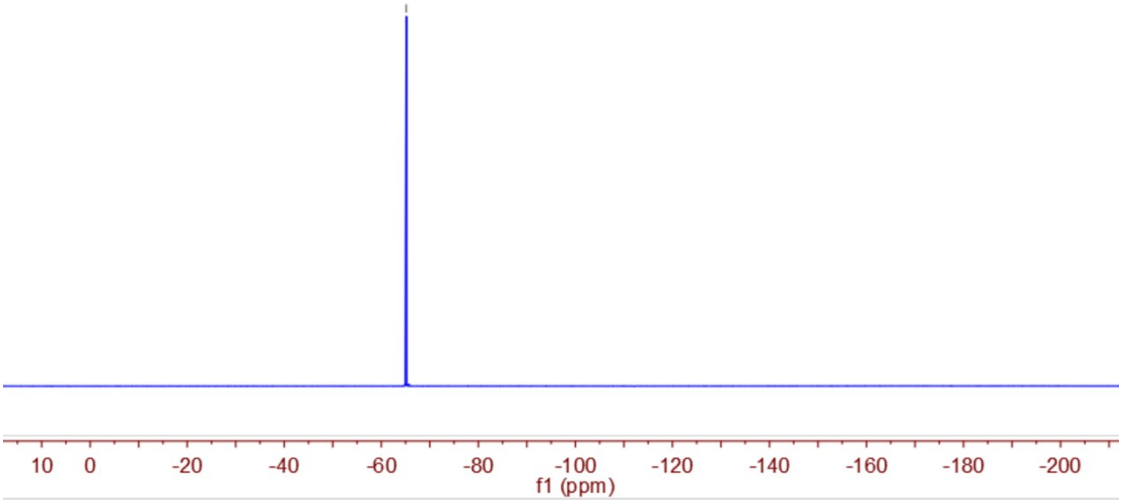


^{13}C NMR ($CDCl_3$, 101MHz)

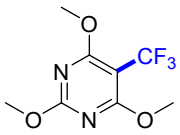
^{13}C NMR Spectrum of Compound 3q



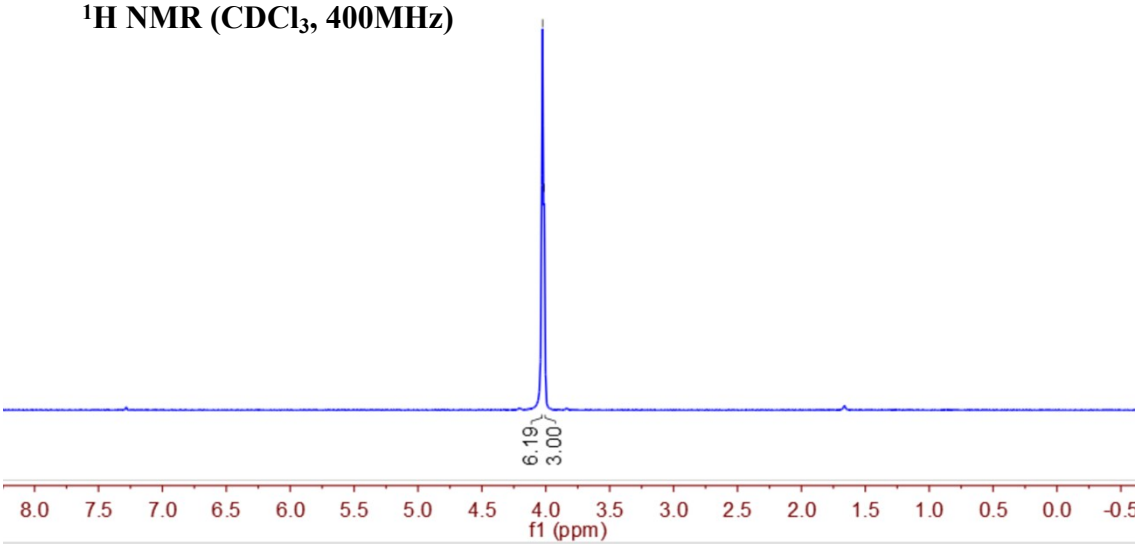
^{19}F NMR ($CDCl_3$, 376MHz)



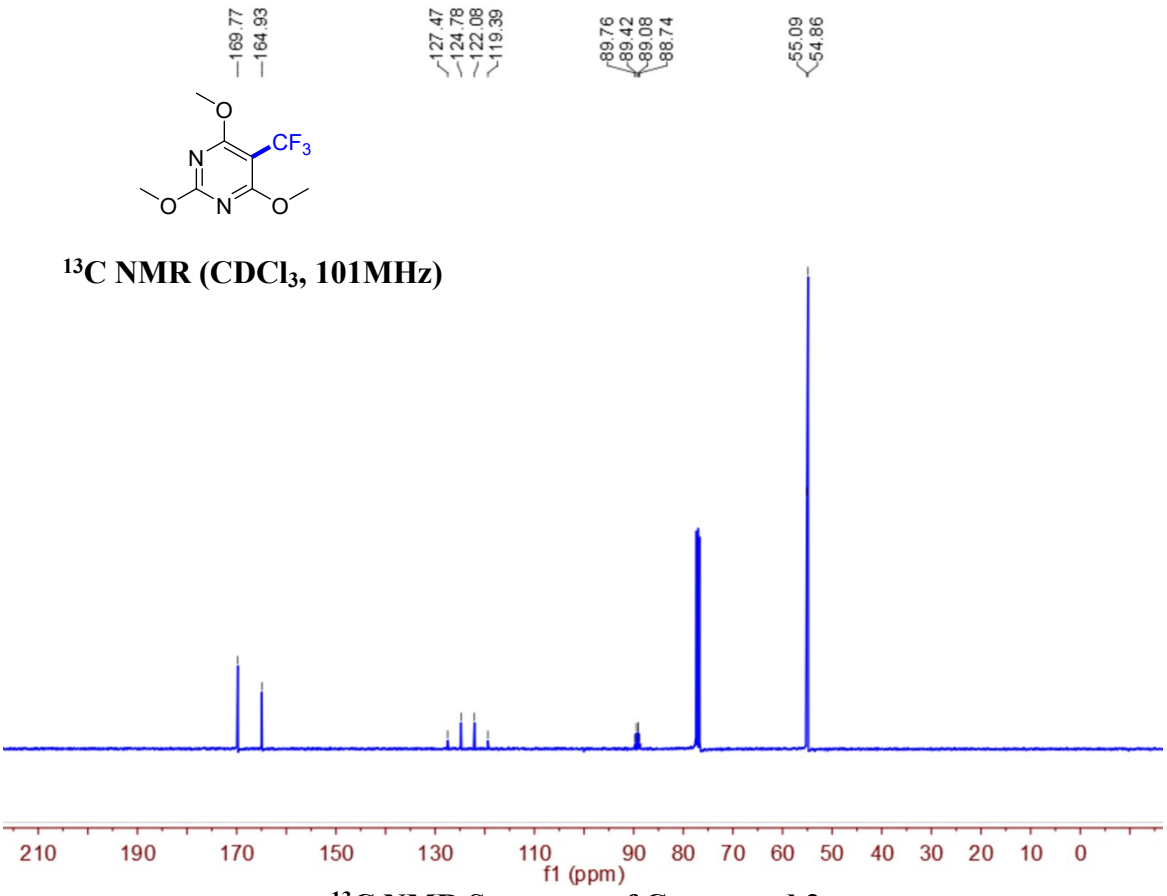
^{19}F NMR Spectrum of Compound 3q



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

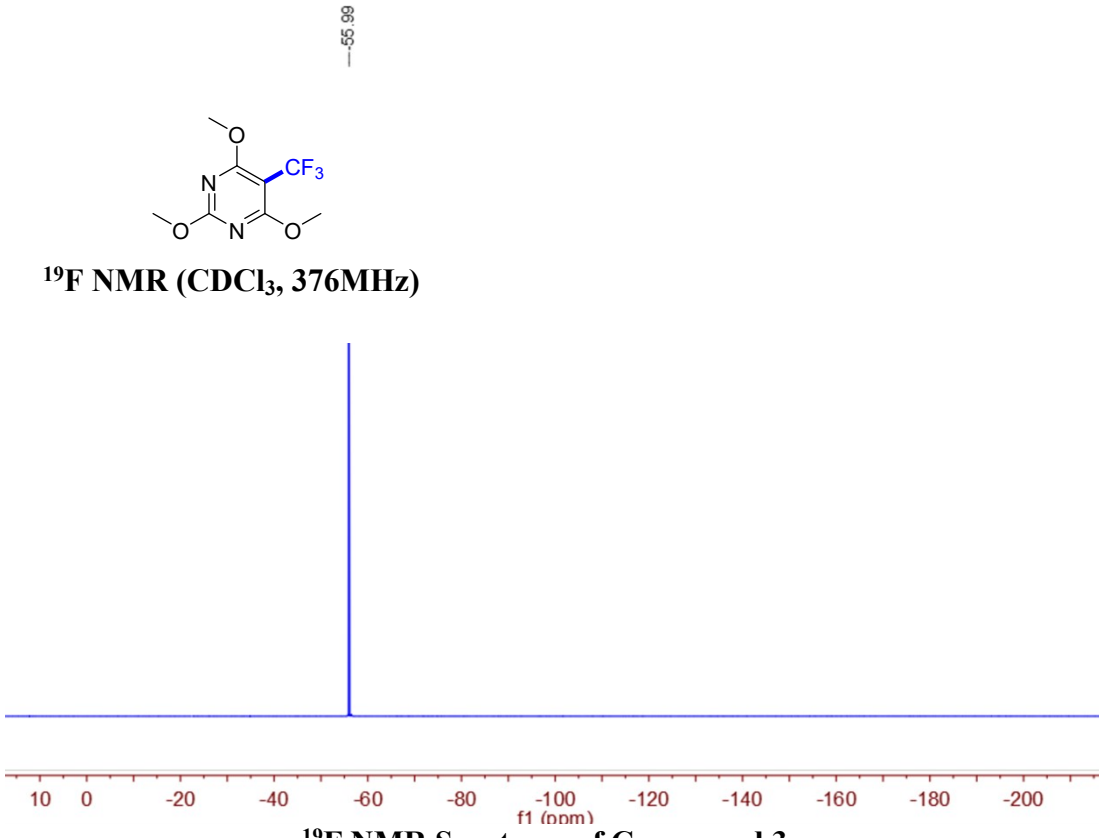


^{1}H NMR Spectrum of Compound 3r



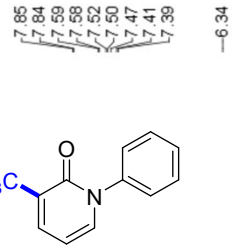
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3r

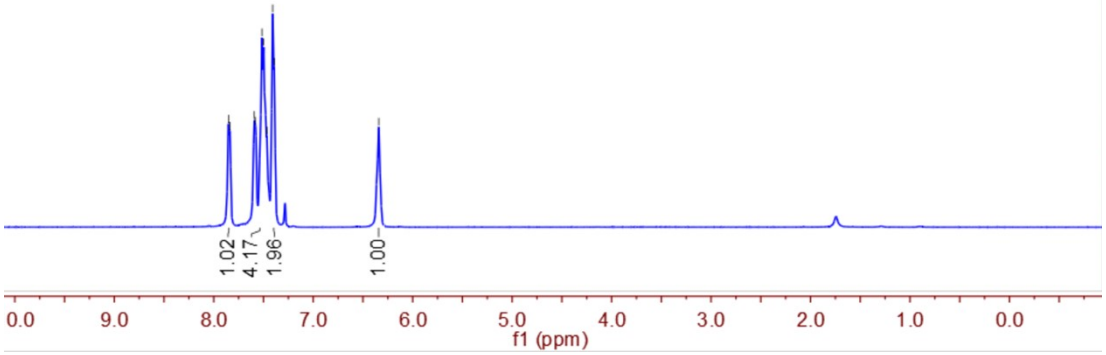


^{19}F NMR ($CDCl_3$, 376MHz)

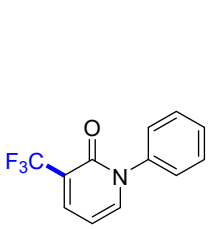
^{19}F NMR Spectrum of Compound 3r



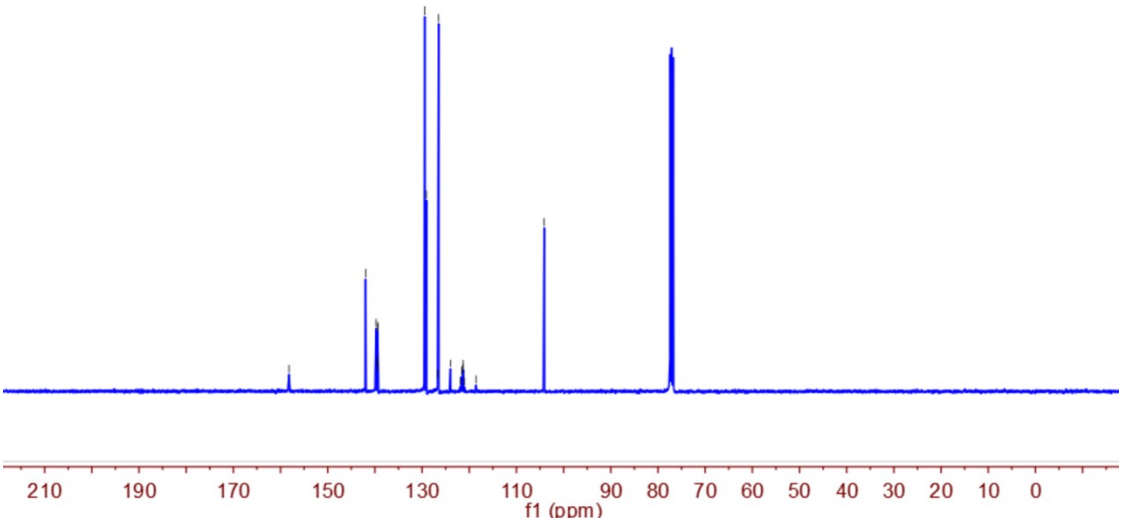
^{1}H NMR ($CDCl_3$, 400MHz)



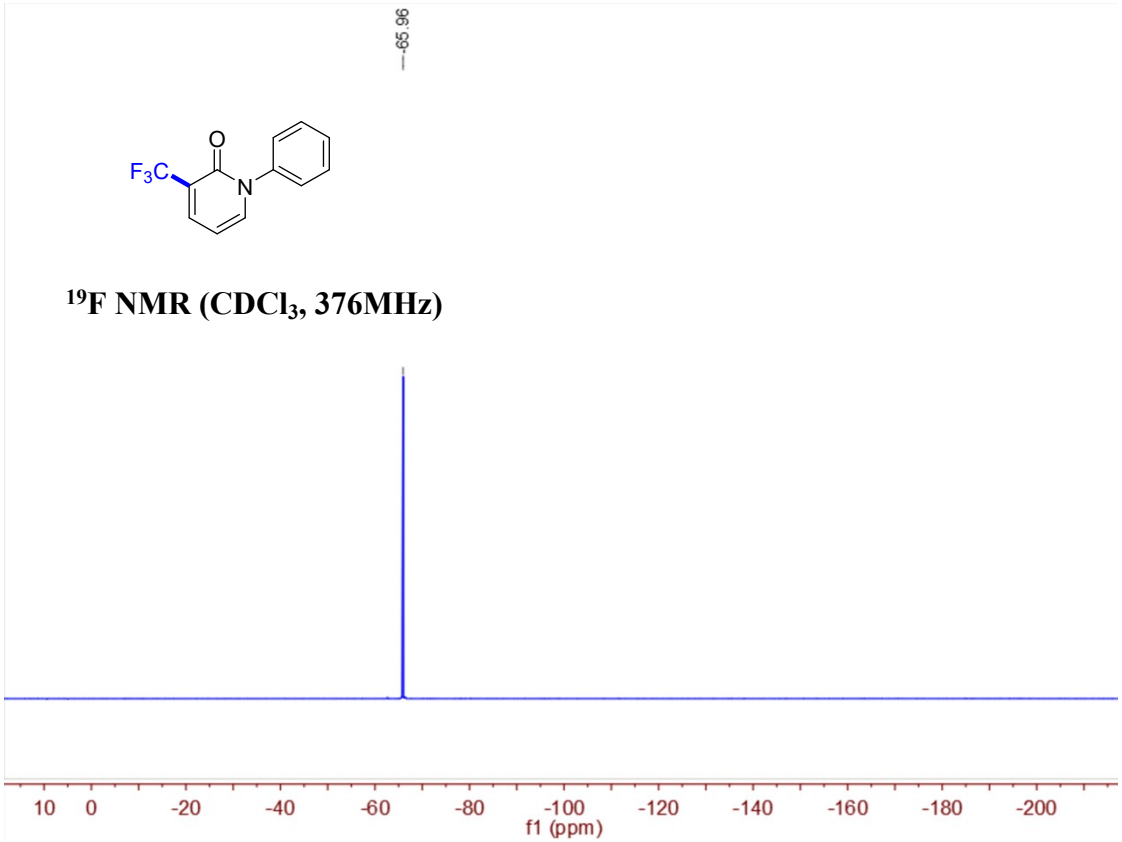
^{1}H NMR Spectrum of Compound 3s



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

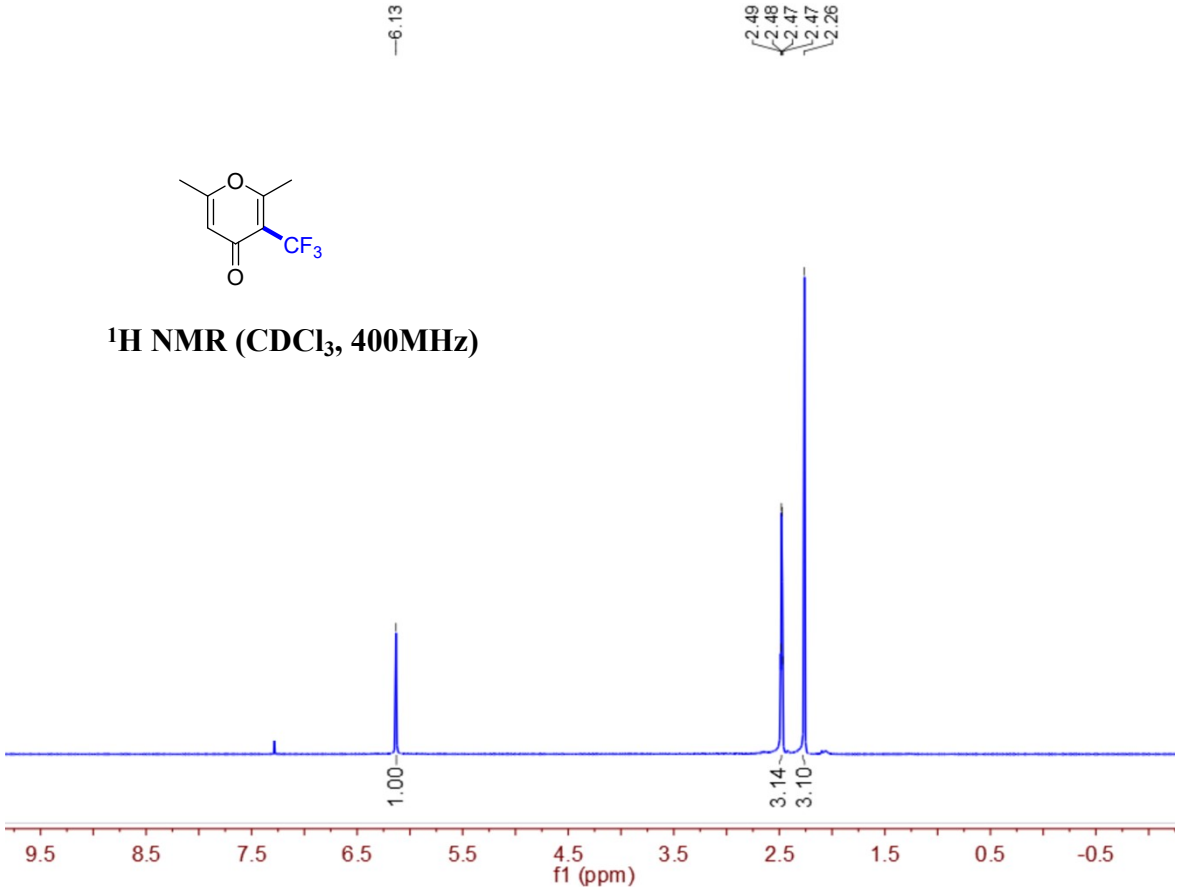


^{13}C NMR Spectrum of Compound 3s



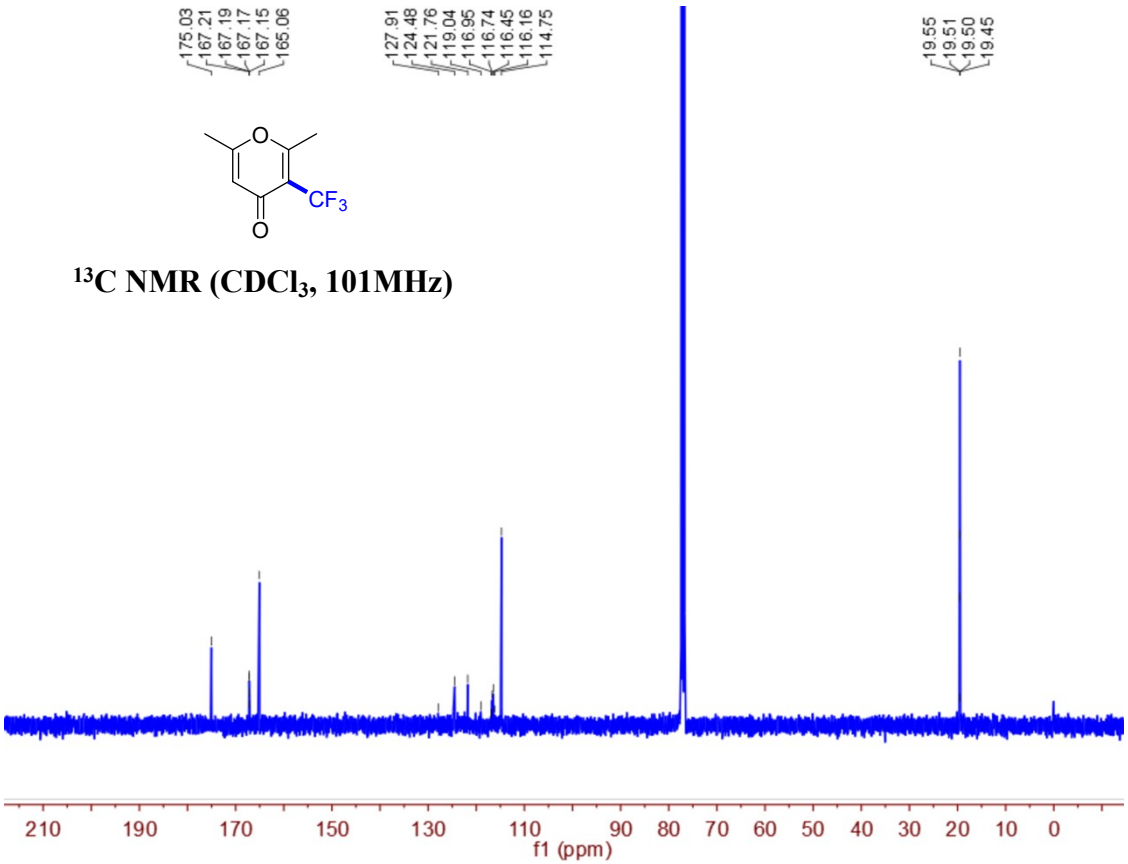
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3s



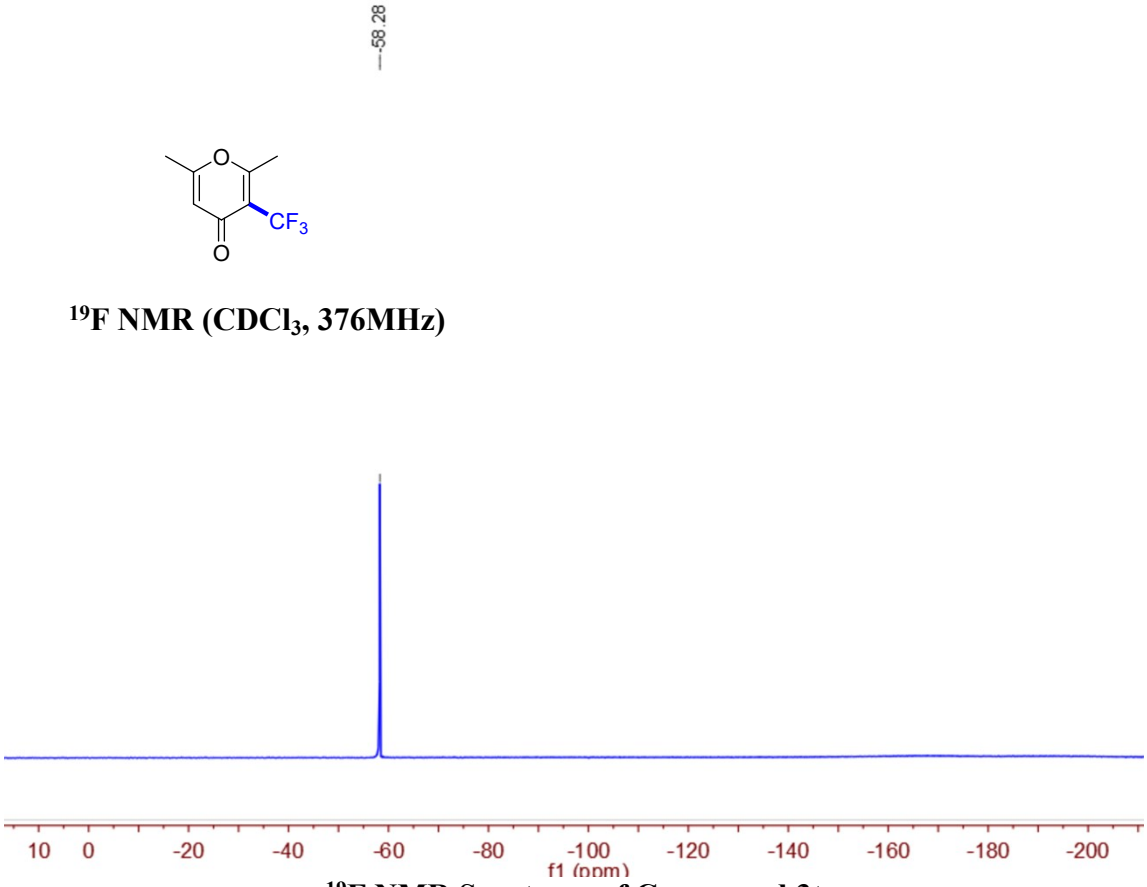
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3t



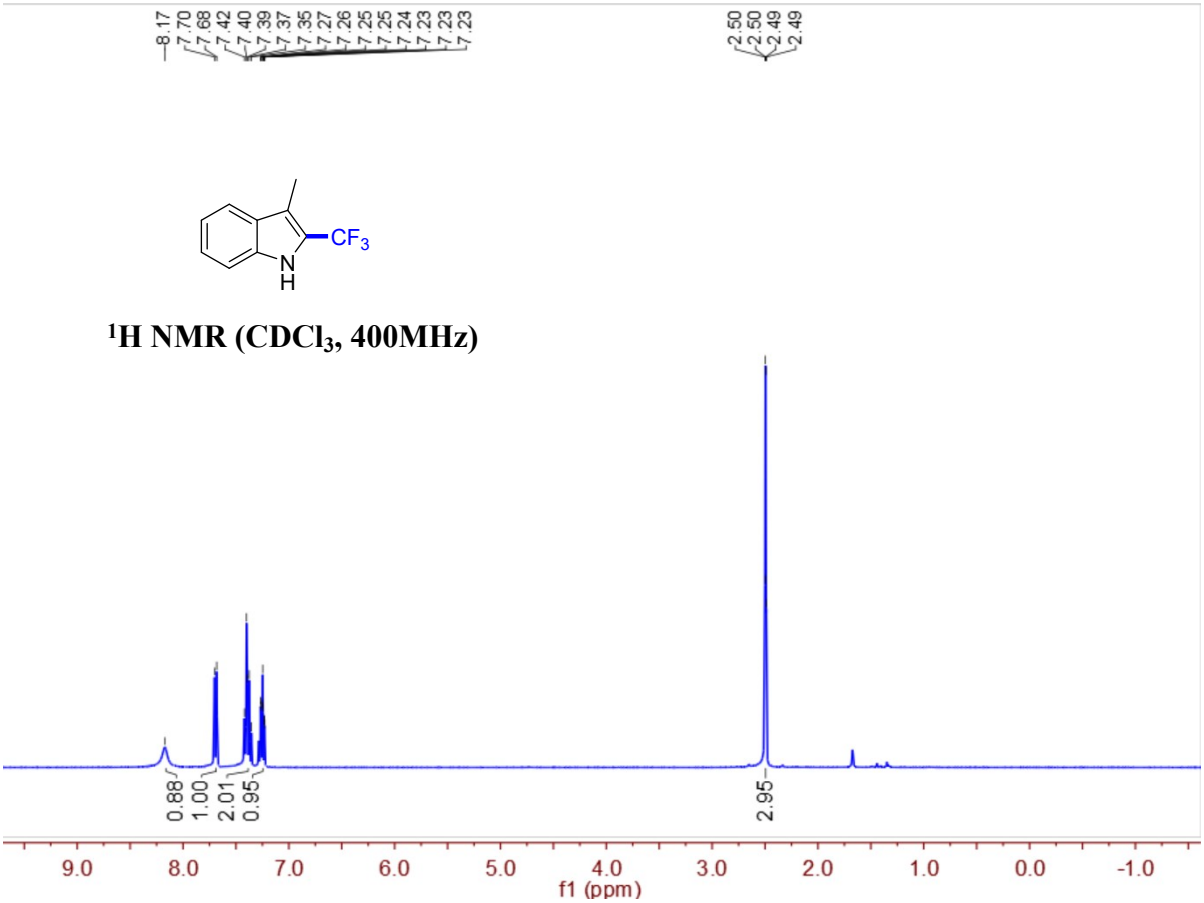
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3t



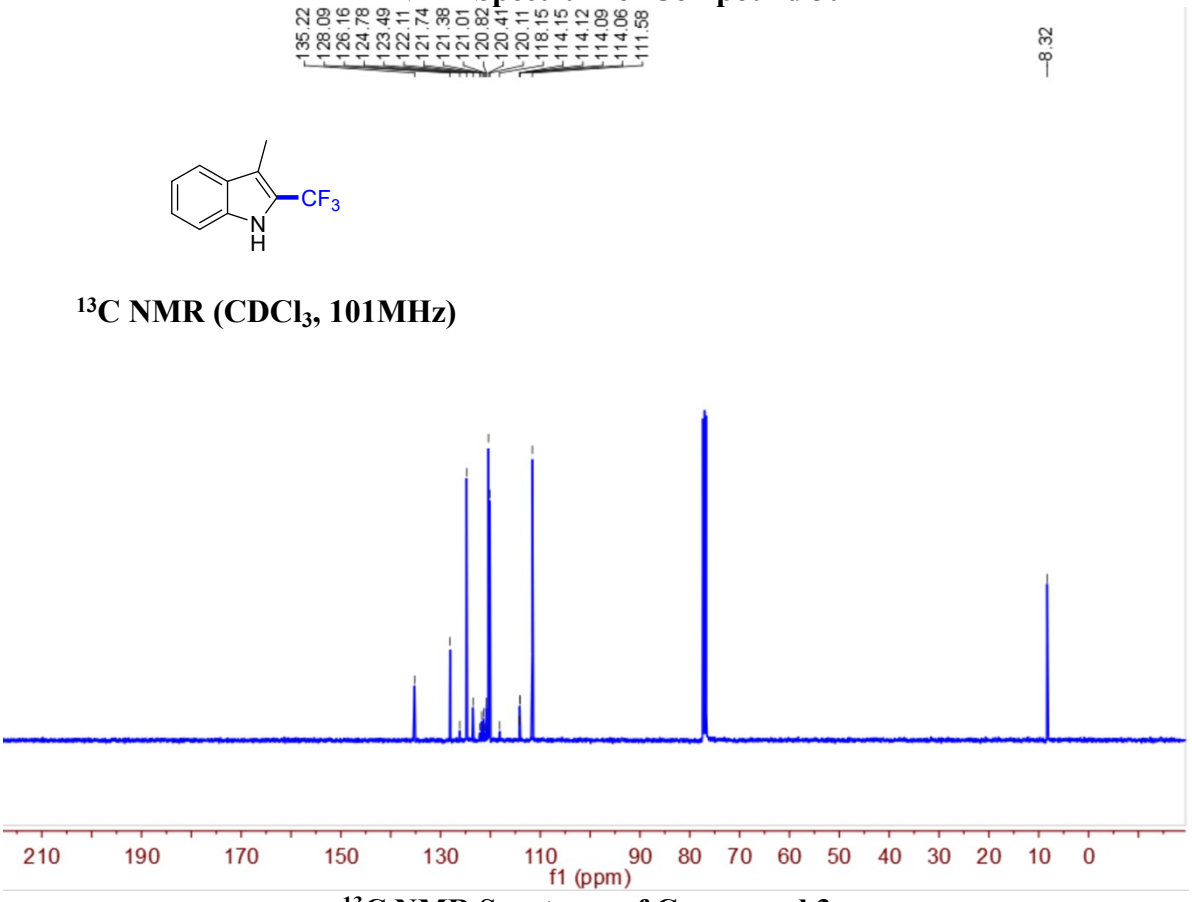
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3t



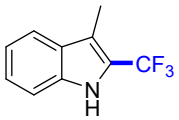
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3u



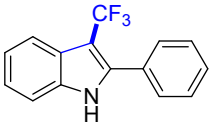
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3u

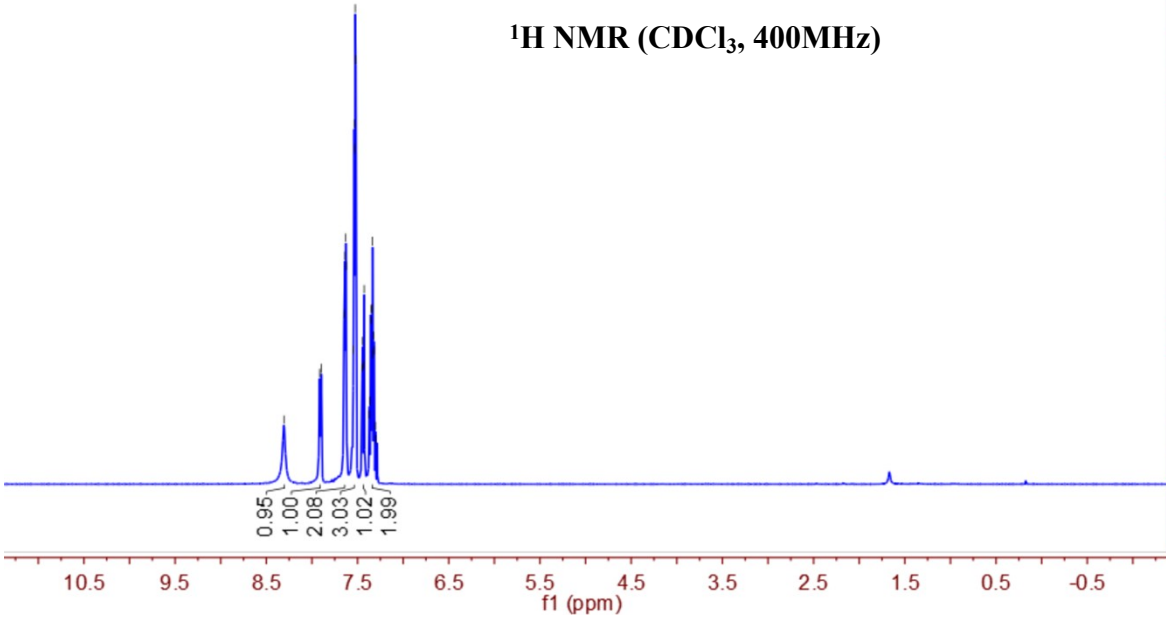


^{19}F NMR ($CDCl_3$, 376MHz)

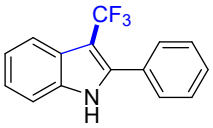
^{19}F NMR Spectrum of Compound 3u



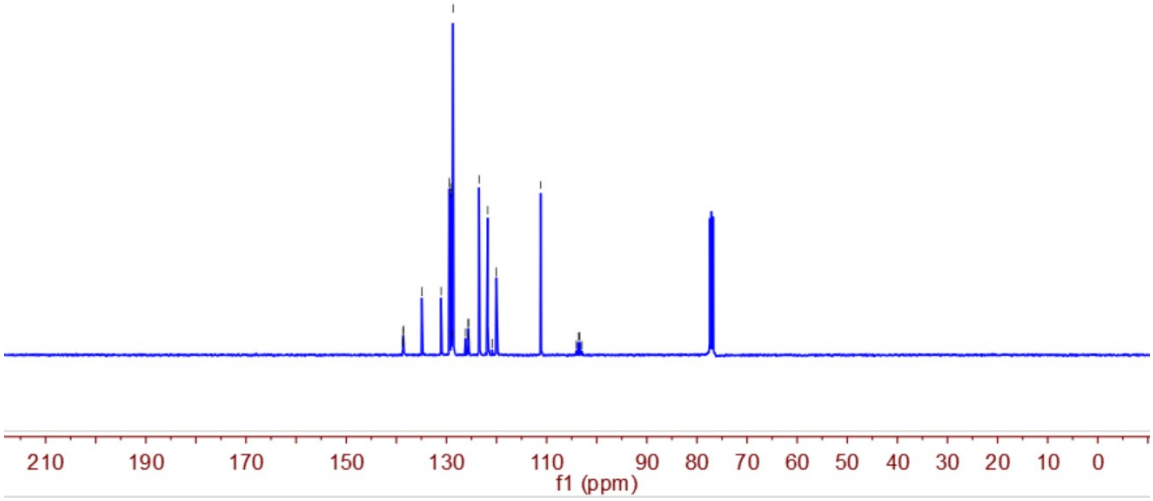
^{1}H NMR ($CDCl_3$, 400MHz)



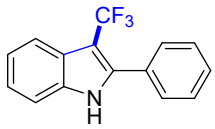
^{1}H NMR Spectrum of Compound 3v



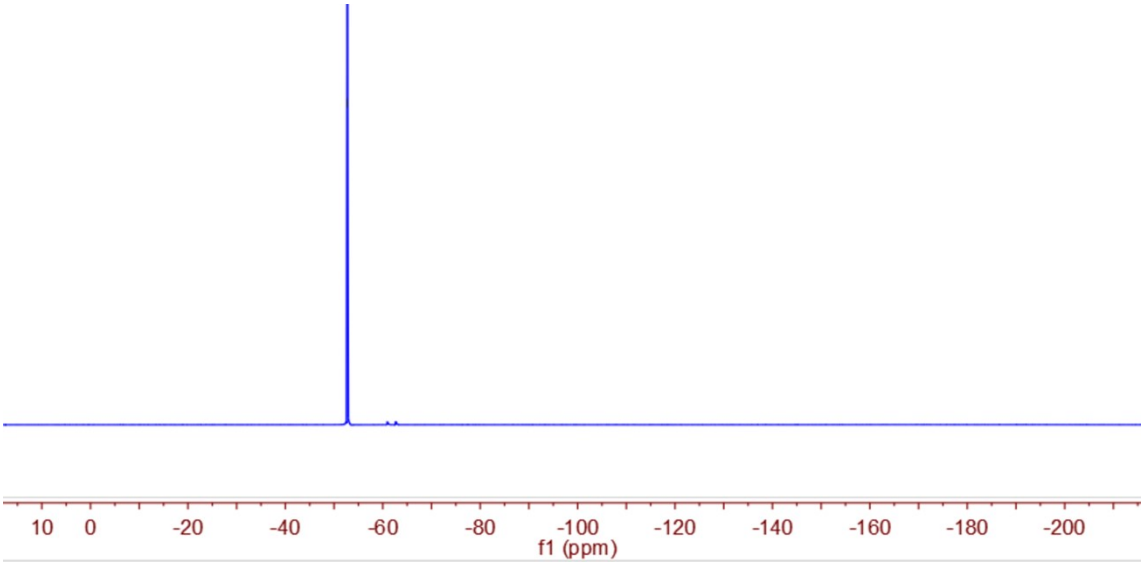
^{13}C NMR ($CDCl_3$, 101MHz)



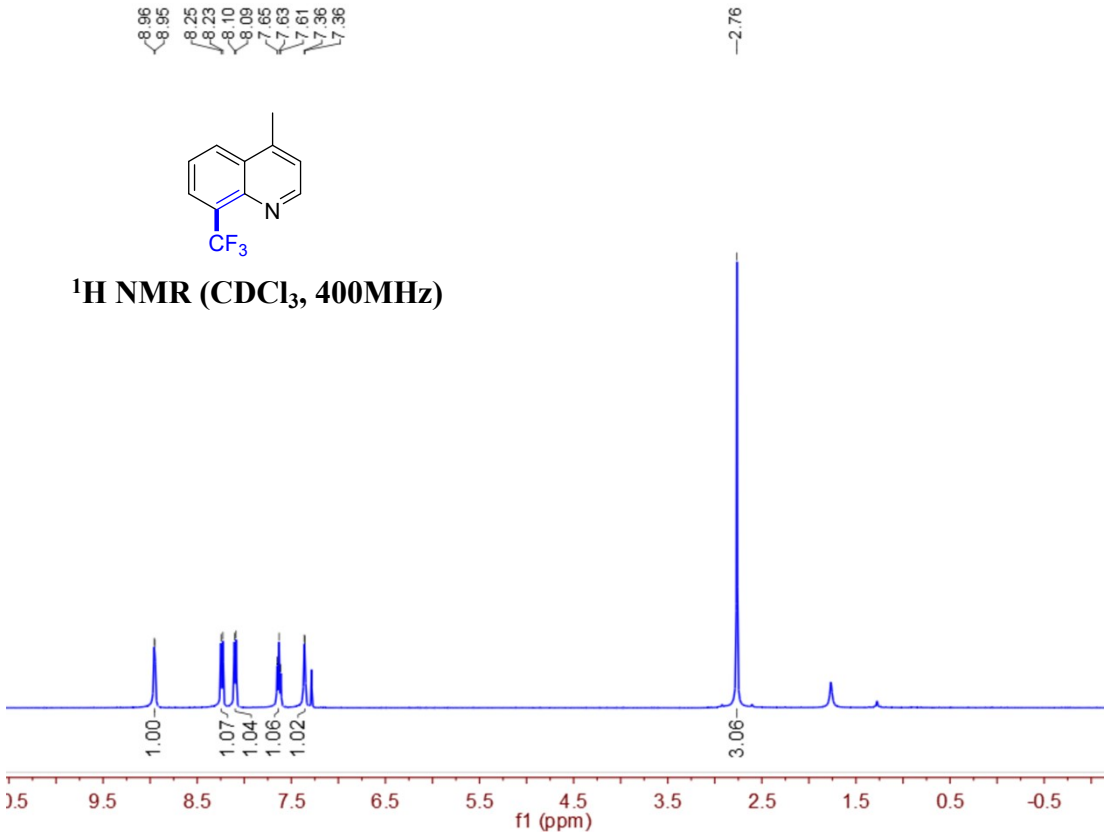
^{13}C NMR Spectrum of Compound 3v



^{19}F NMR ($CDCl_3$, 376MHz)

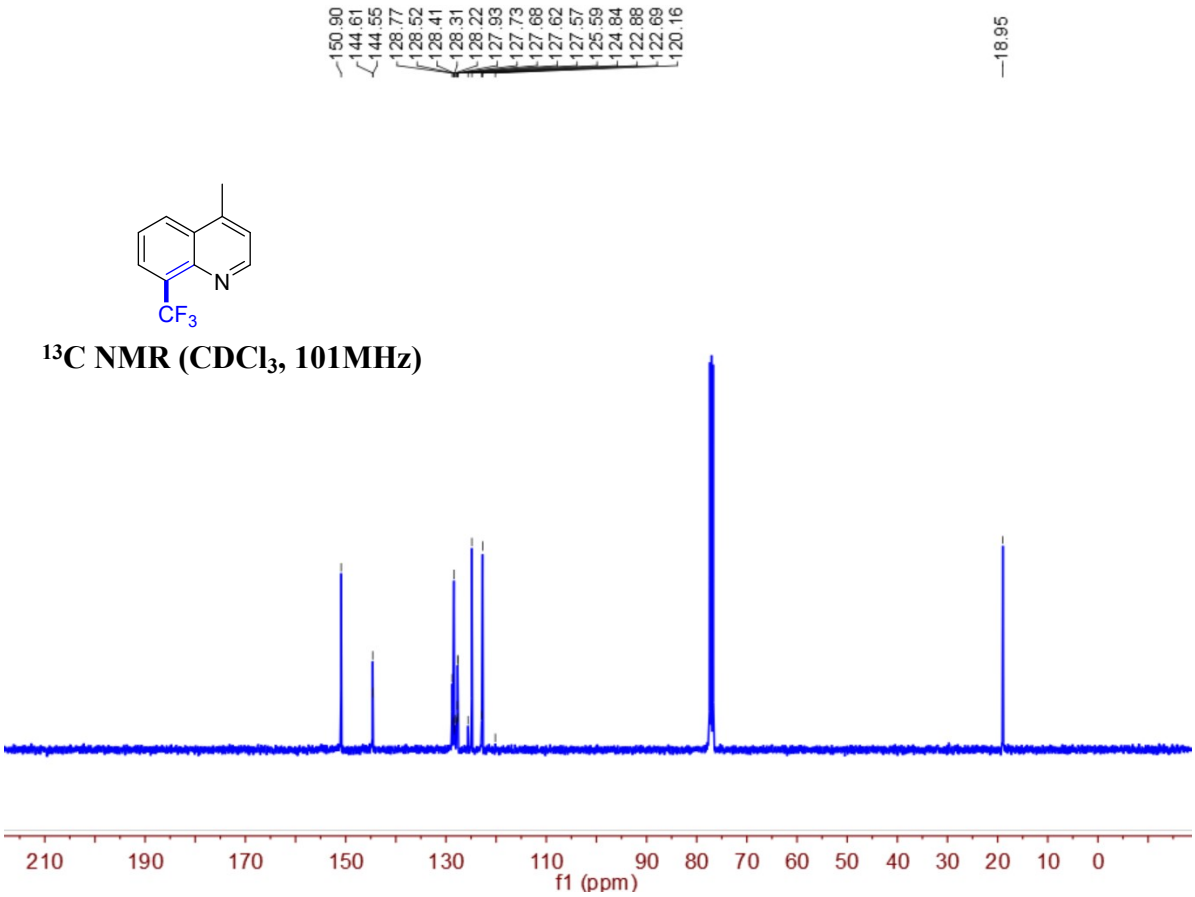


^{19}F NMR Spectrum of Compound 3v



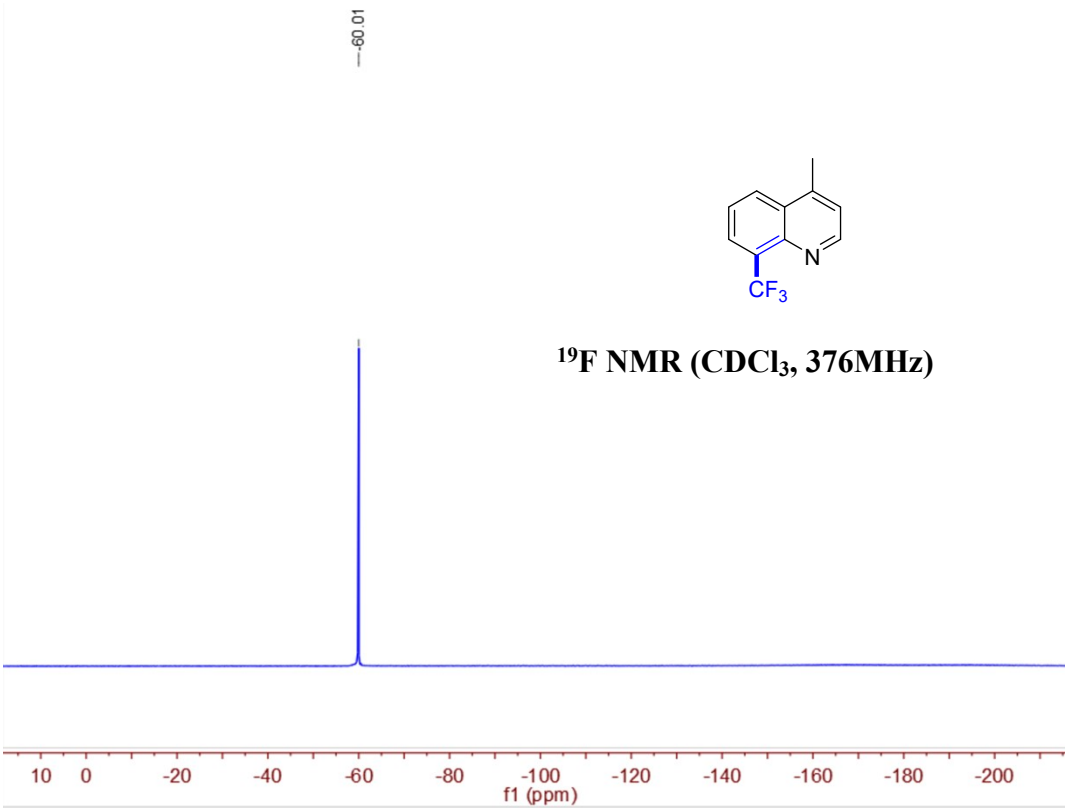
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3w



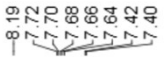
^{13}C NMR ($CDCl_3$, 101MHz)

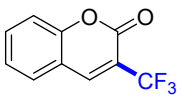
^{13}C NMR Spectrum of Compound 3w



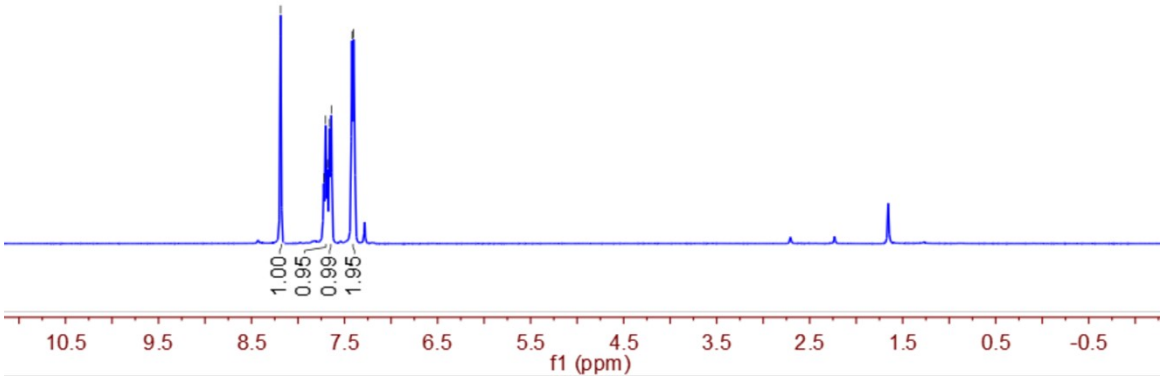
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3w

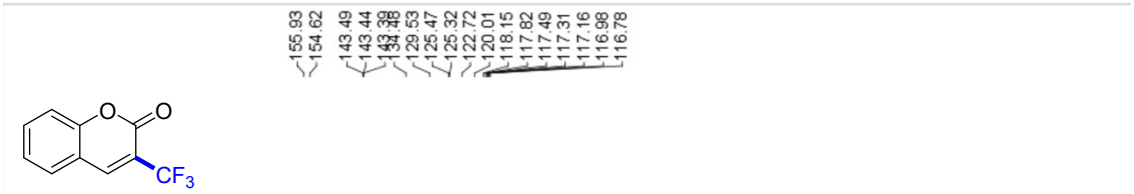




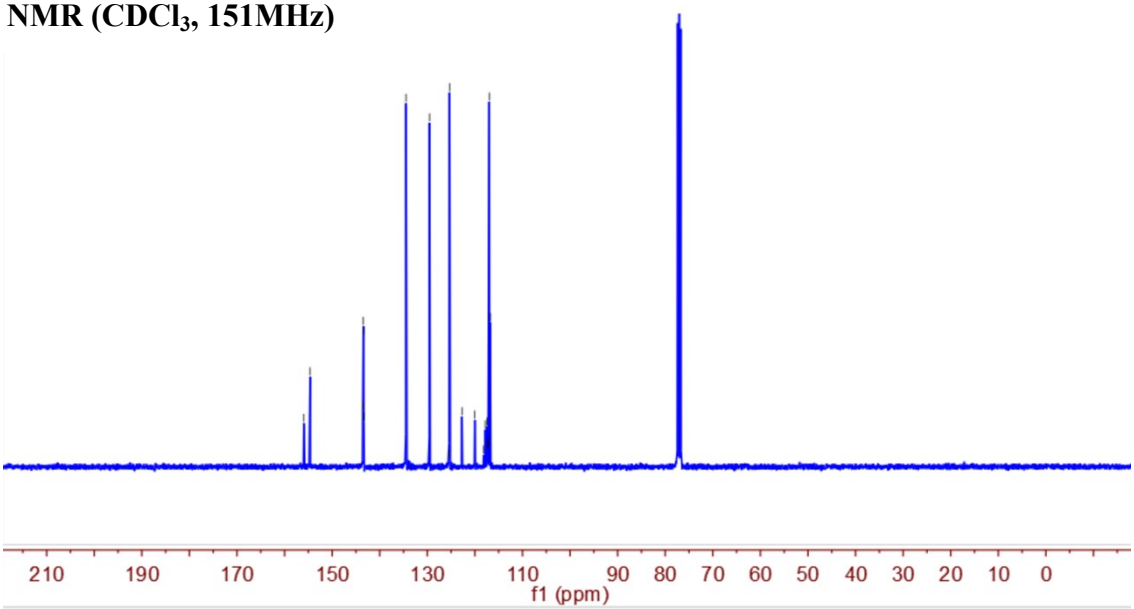
^{1}H NMR (CDCl$_3$, 400MHz)



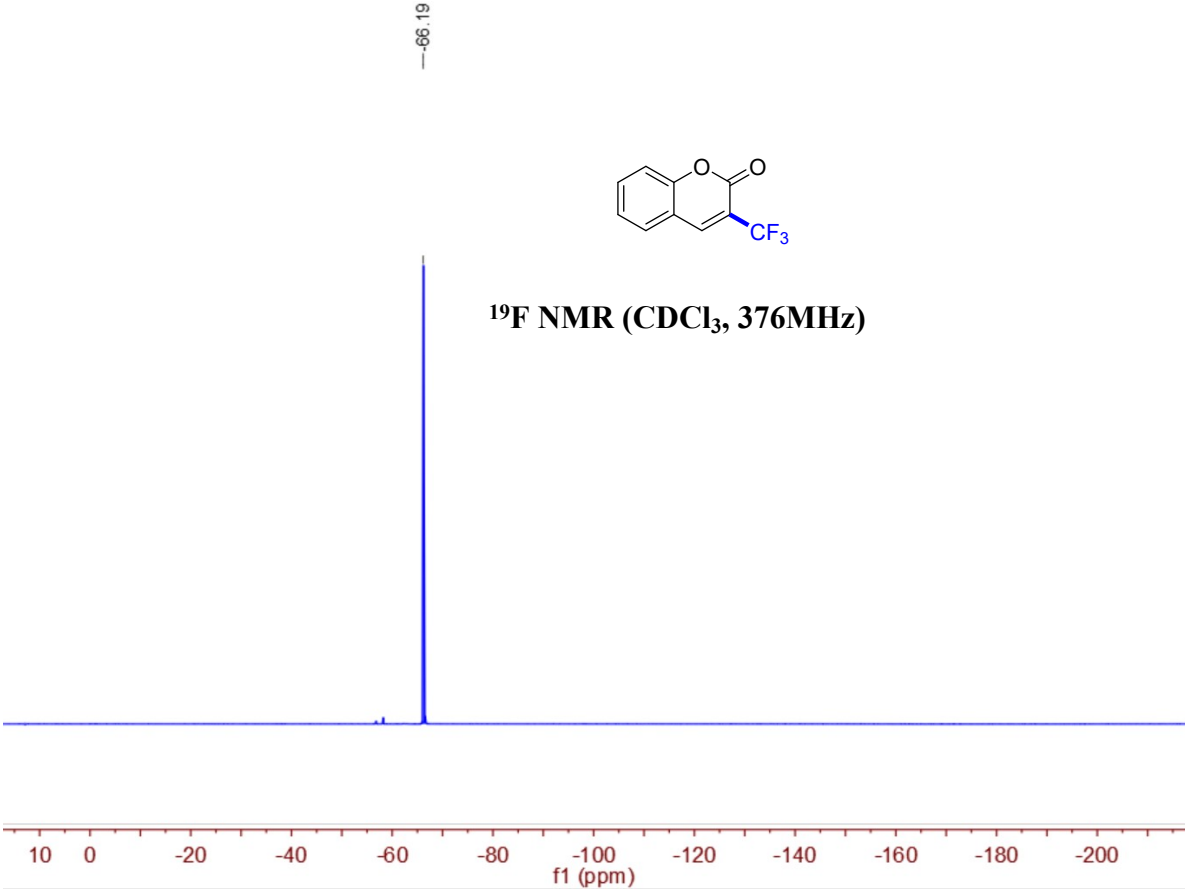
^{1}H NMR Spectrum of Compound 3x



^{13}C NMR ($CDCl_3$, 151MHz)

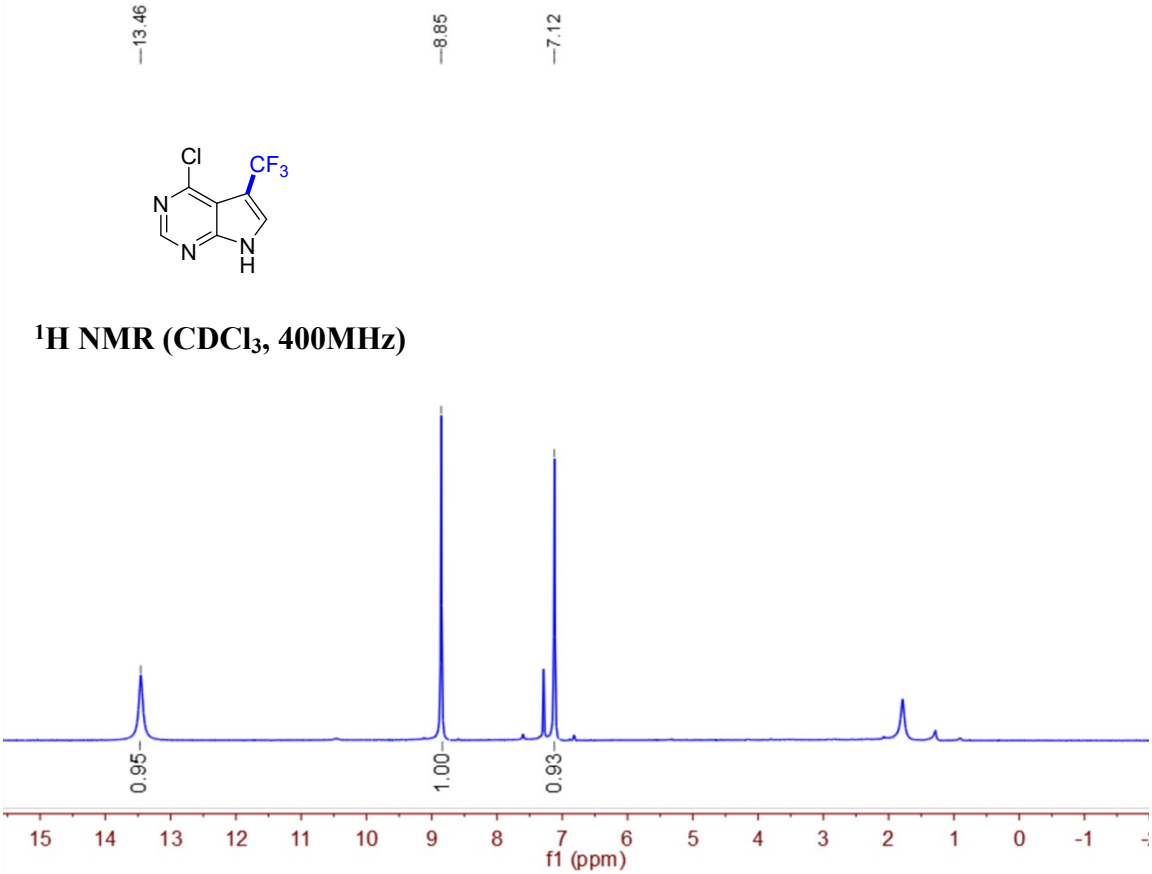


^{13}C NMR Spectrum of Compound 3x



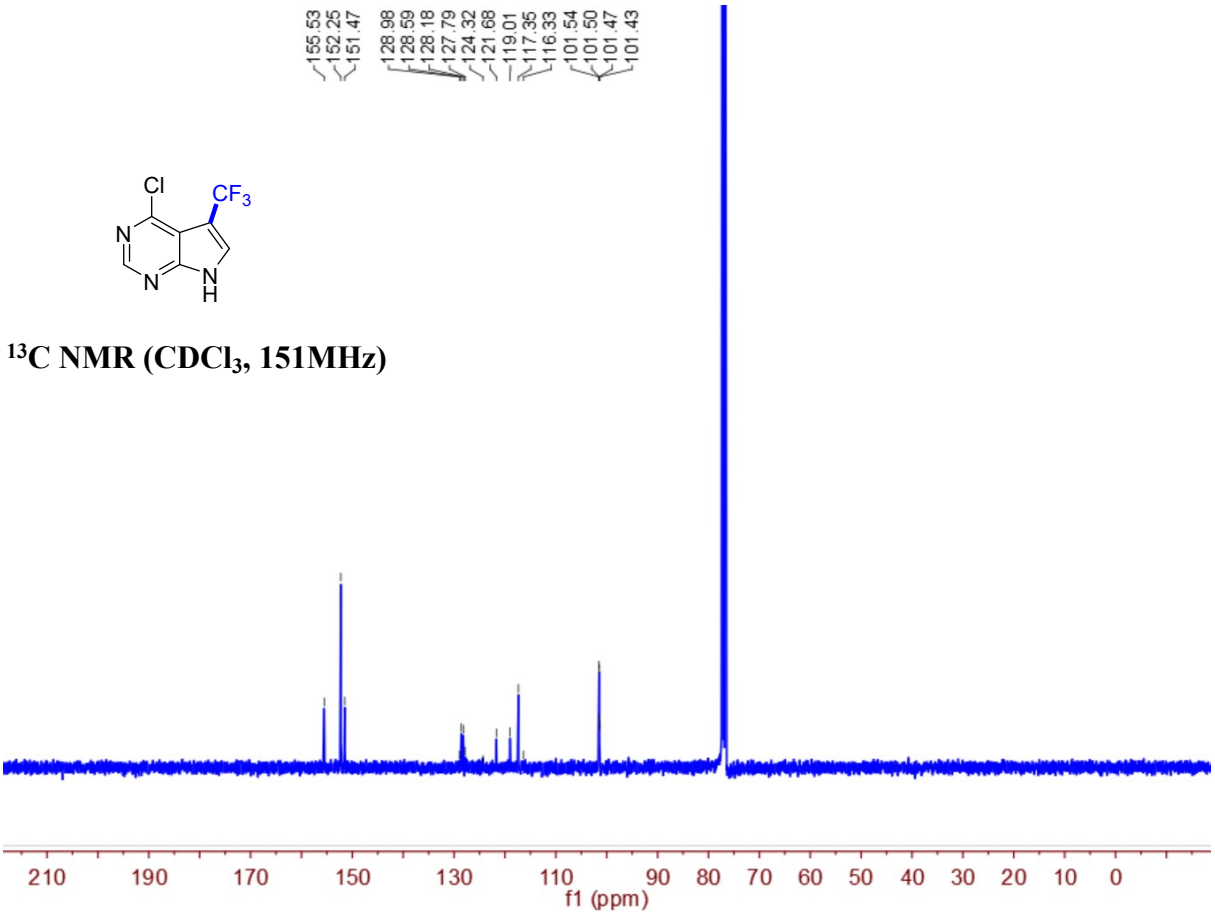
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3x



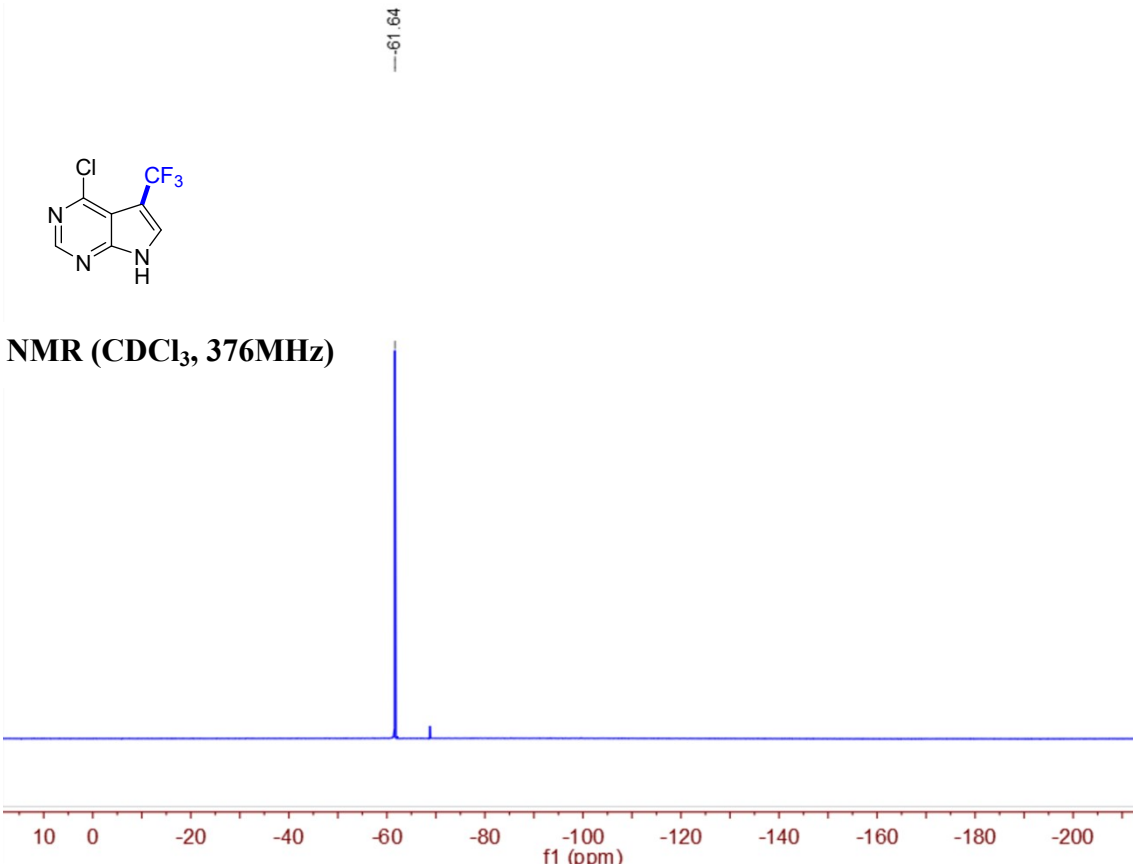
^{1}H NMR (CDCl$_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3y



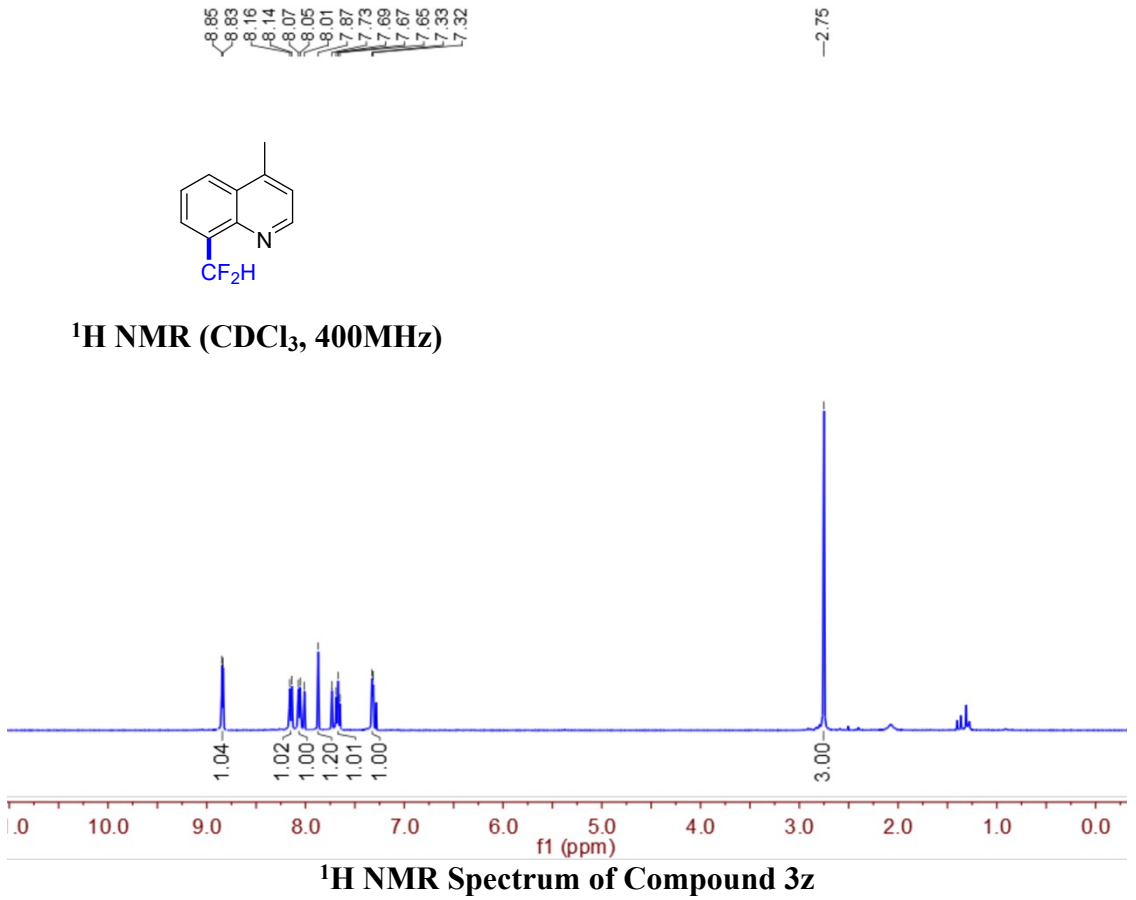
^{13}C NMR (CDCl$_3$, 151MHz)

^{13}C NMR Spectrum of Compound 3y



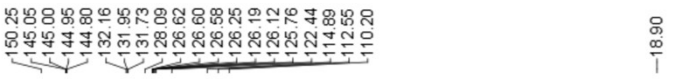
^{19}F NMR ($CDCl_3$, 376MHz)

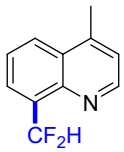
^{19}F NMR Spectrum of Compound 3y



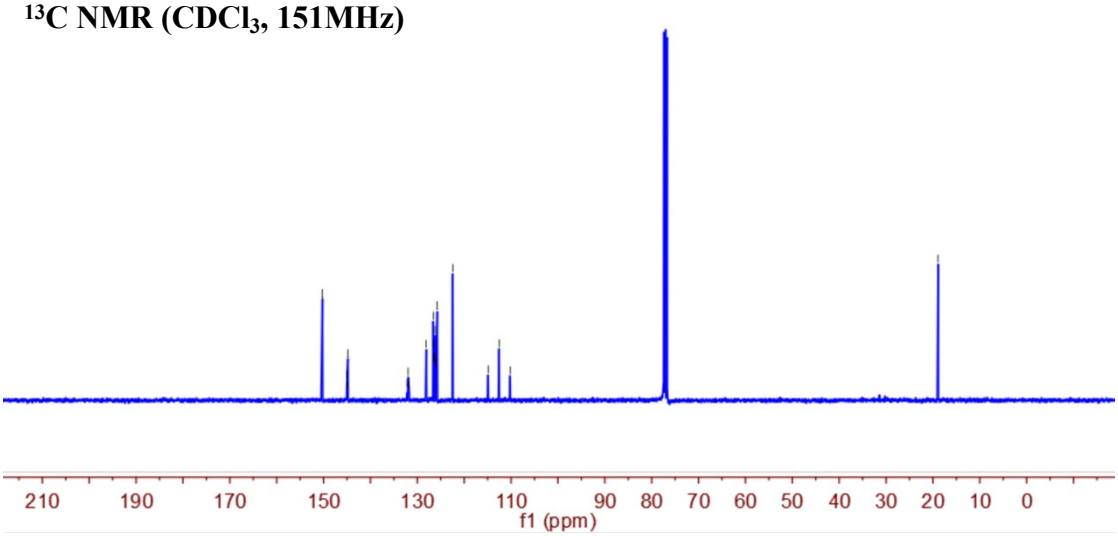
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3z

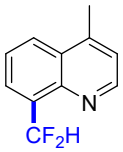




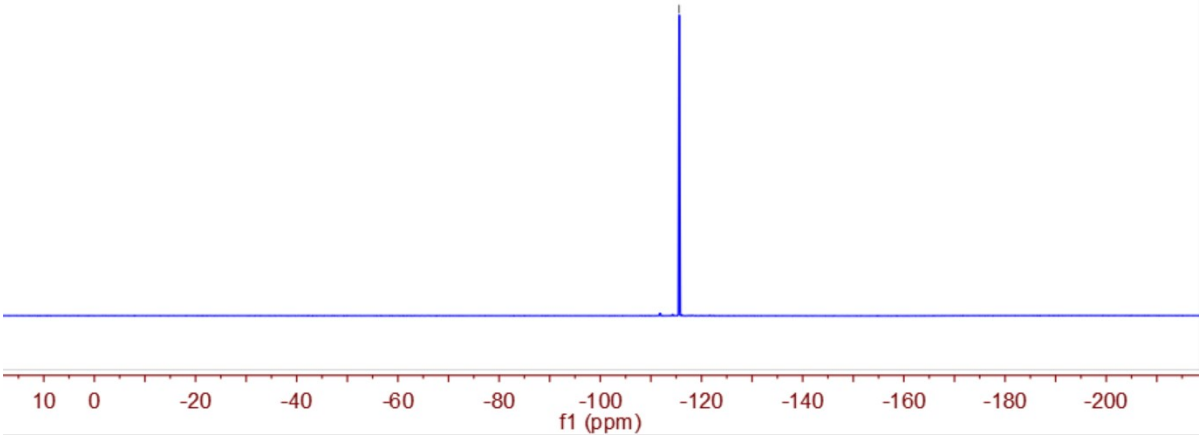
^{13}C NMR ($CDCl_3$, 151MHz)



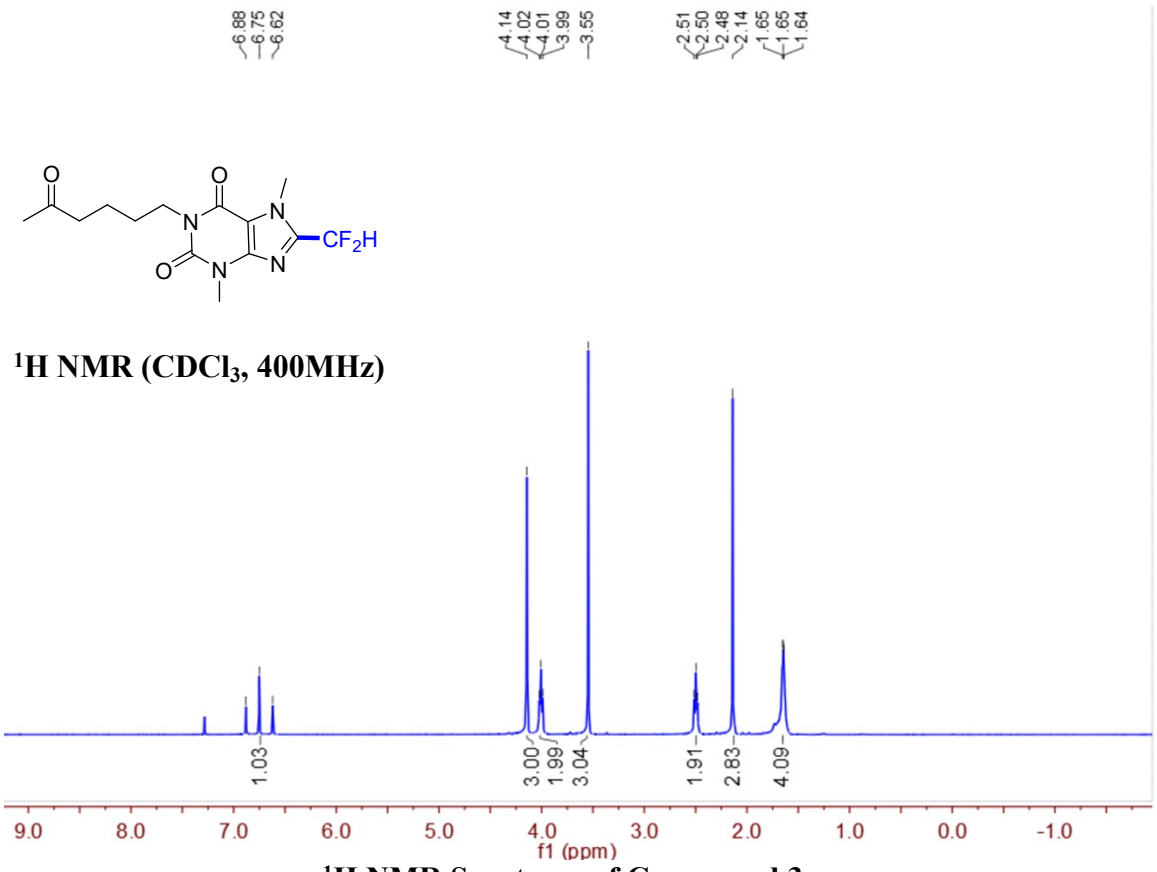
^{13}C NMR Spectrum of Compound 3z



^{19}F NMR ($CDCl_3$, 376MHz)

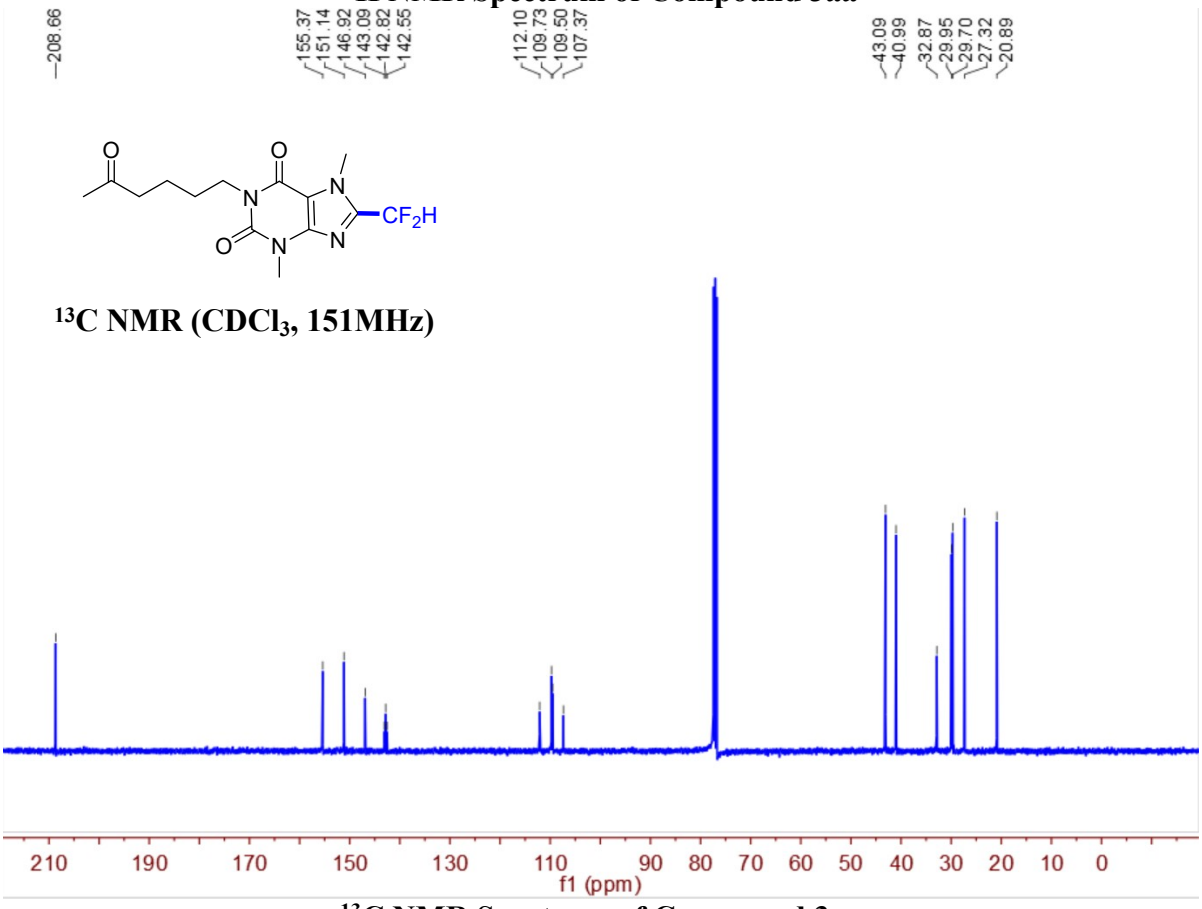


^{19}F NMR Spectrum of Compound 3z



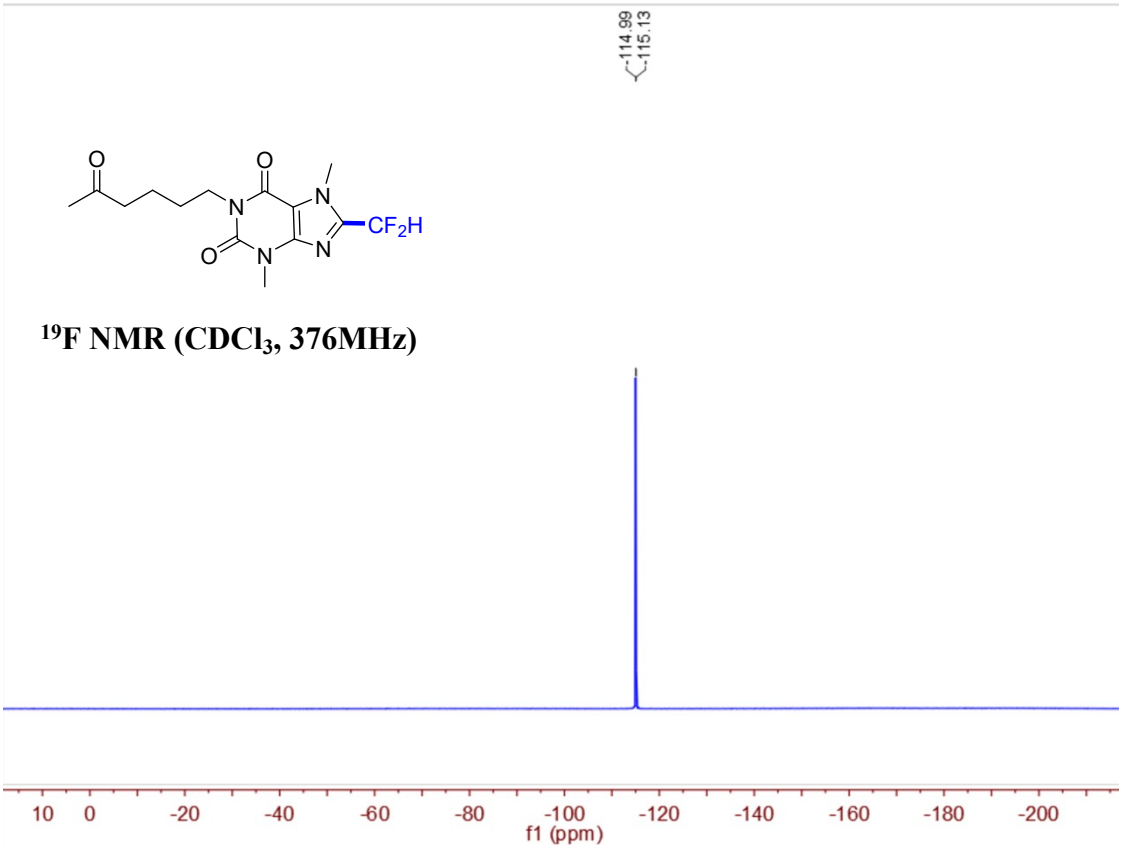
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3aa



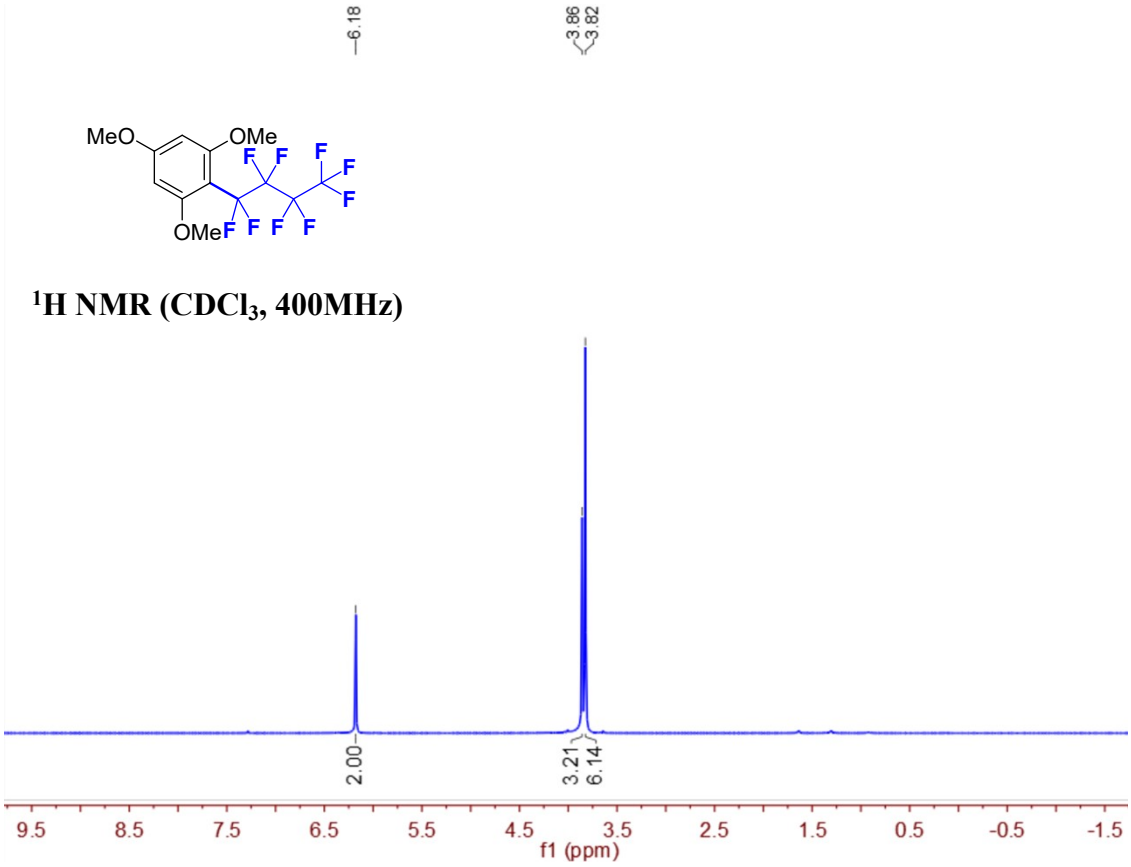
^{13}C NMR ($CDCl_3$, 151MHz)

^{13}C NMR Spectrum of Compound 3aa



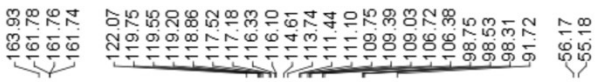
^{19}F NMR ($CDCl_3$, 376MHz)

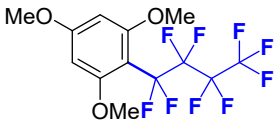
^{19}F NMR Spectrum of Compound 3aa



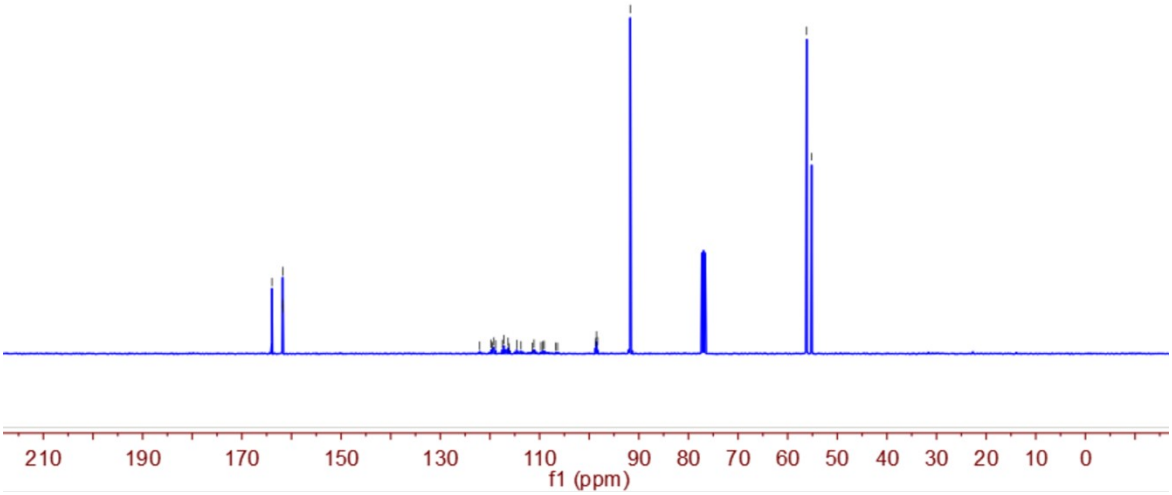
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ab

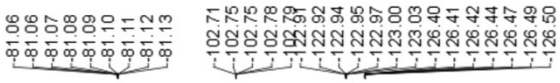


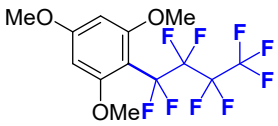


^{13}C NMR ($CDCl_3$, 151MHz)

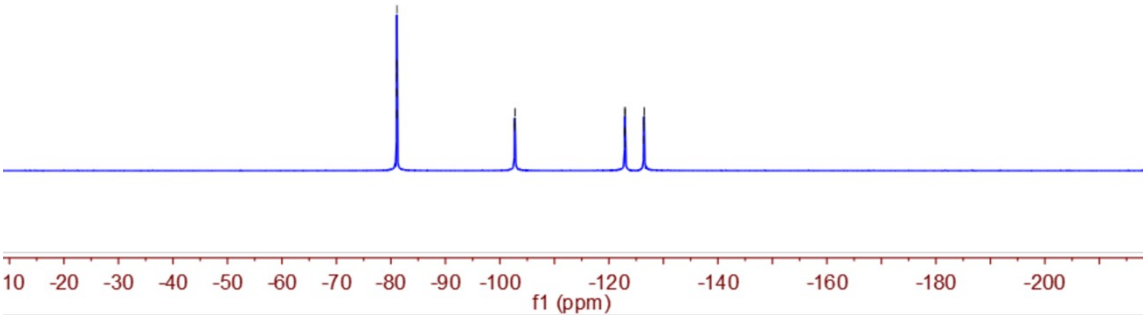


^{13}C NMR Spectrum of Compound 3ab

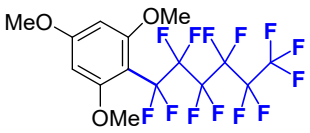




^{19}F NMR ($CDCl_3$, 376MHz)

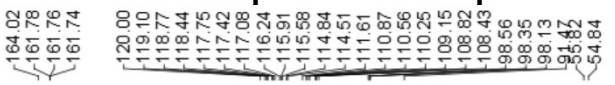


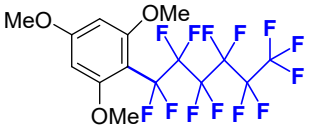
^{19}F NMR Spectrum of Compound 3ab



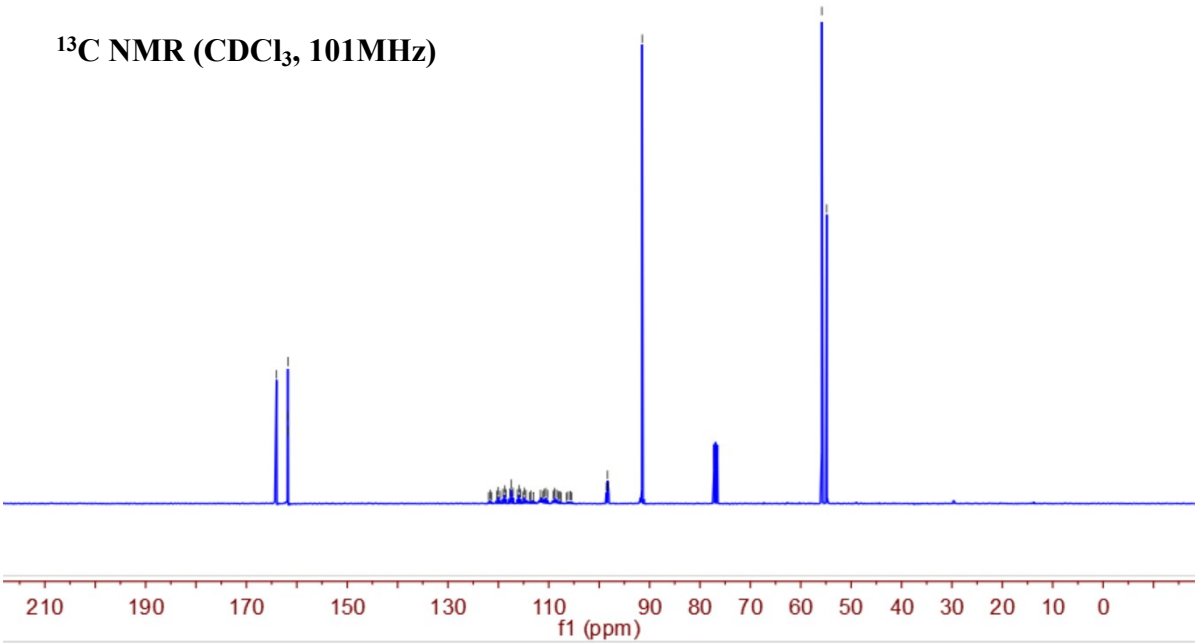
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ac

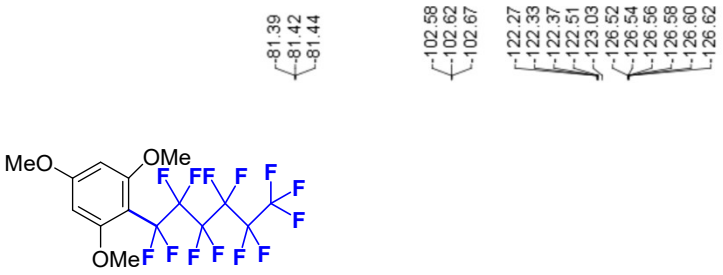




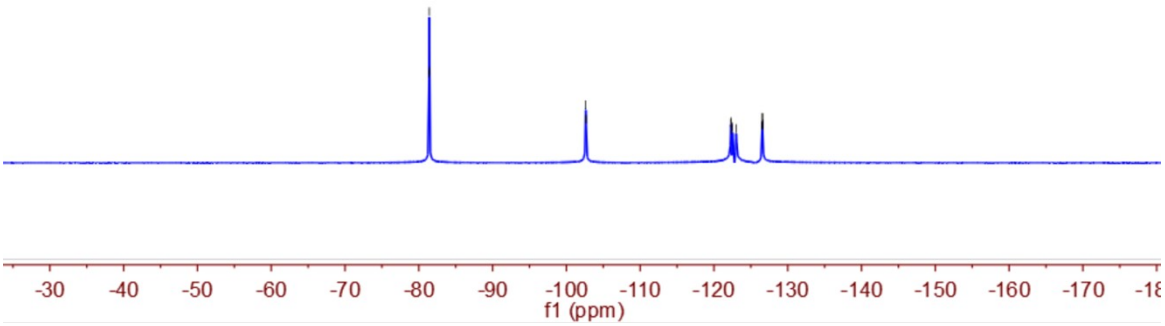
^{13}C NMR ($CDCl_3$, 101MHz)



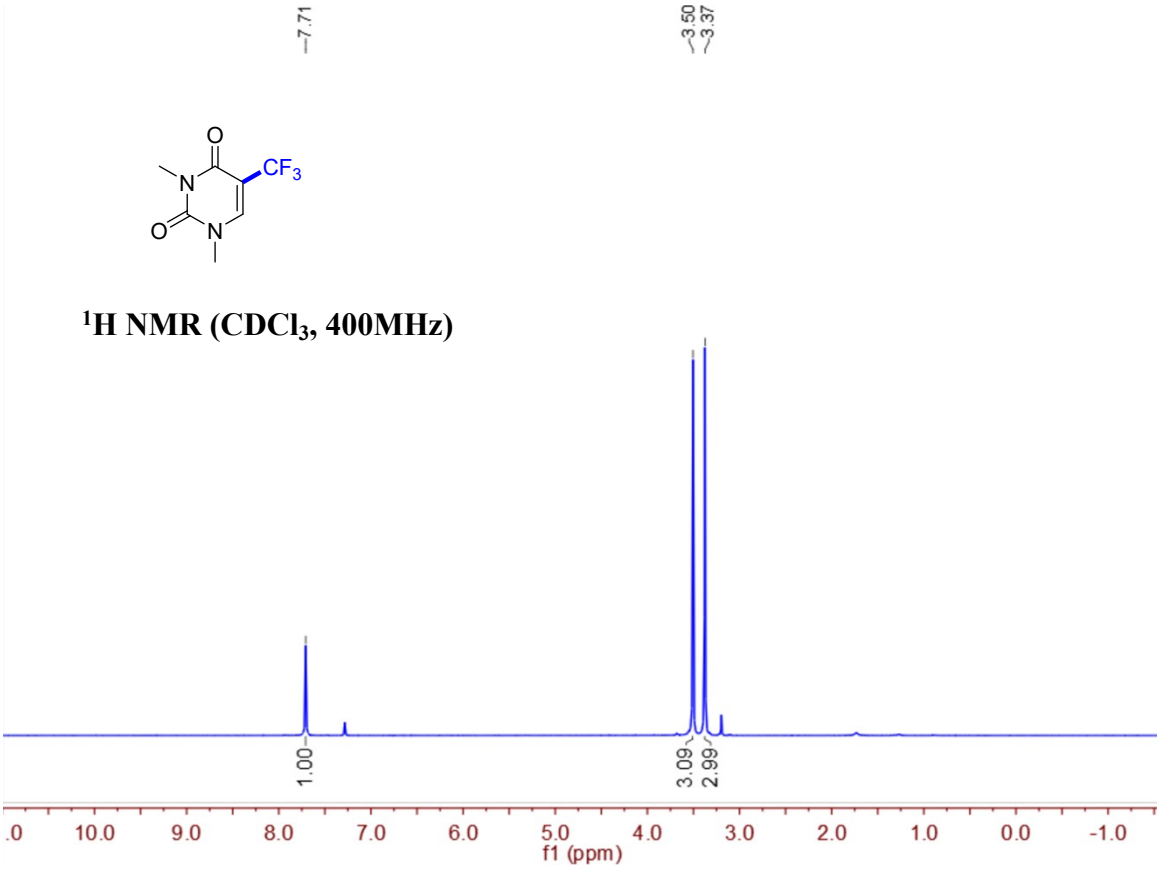
^{13}C NMR Spectrum of Compound 3ac



^{19}F NMR ($CDCl_3$, 376MHz)

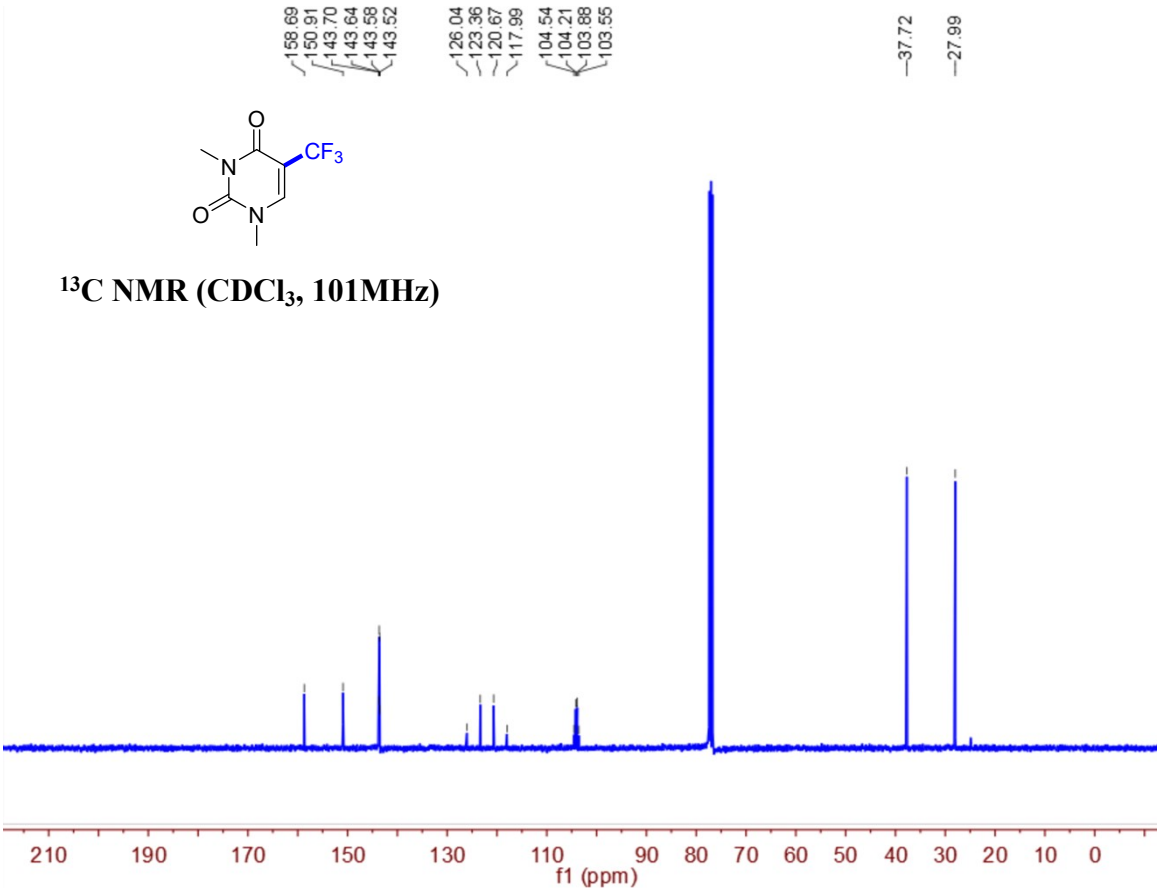


^{19}F NMR Spectrum of Compound 3ac



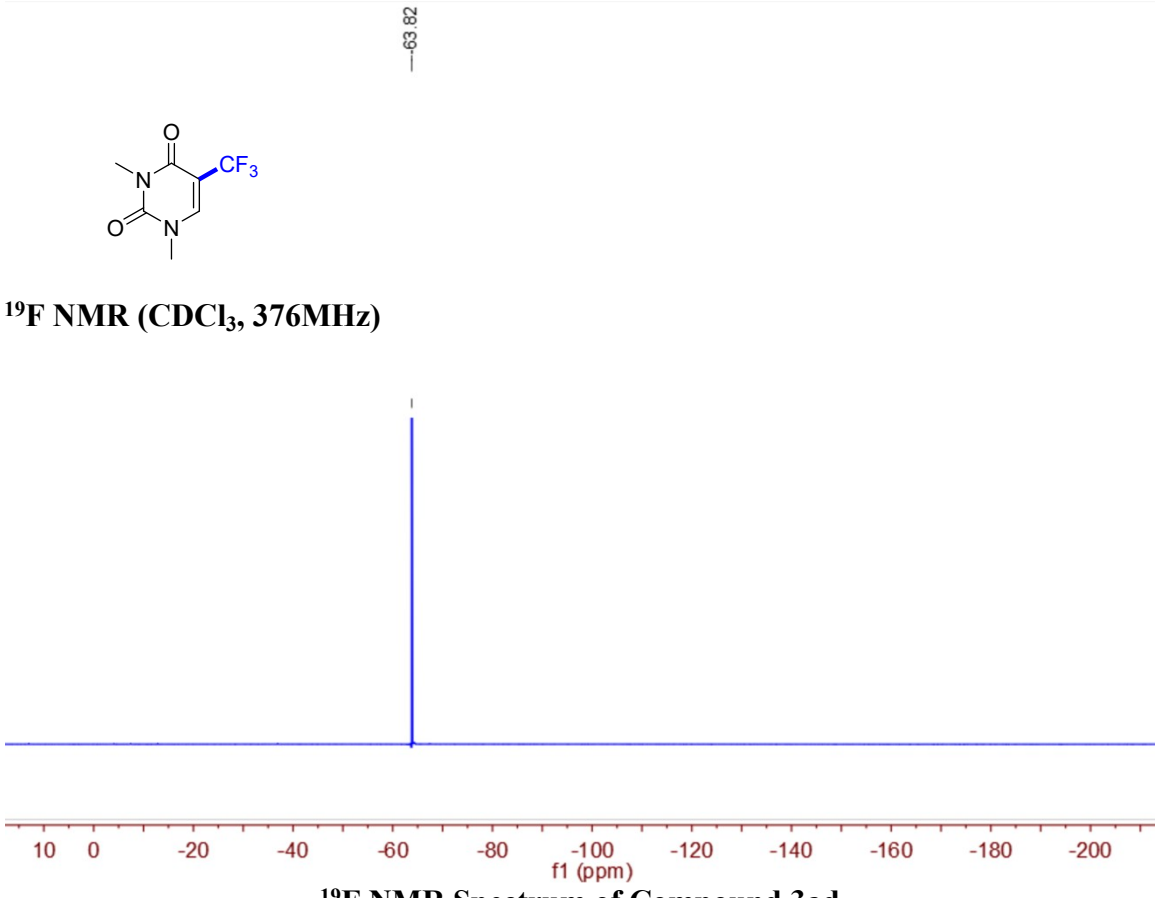
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ad



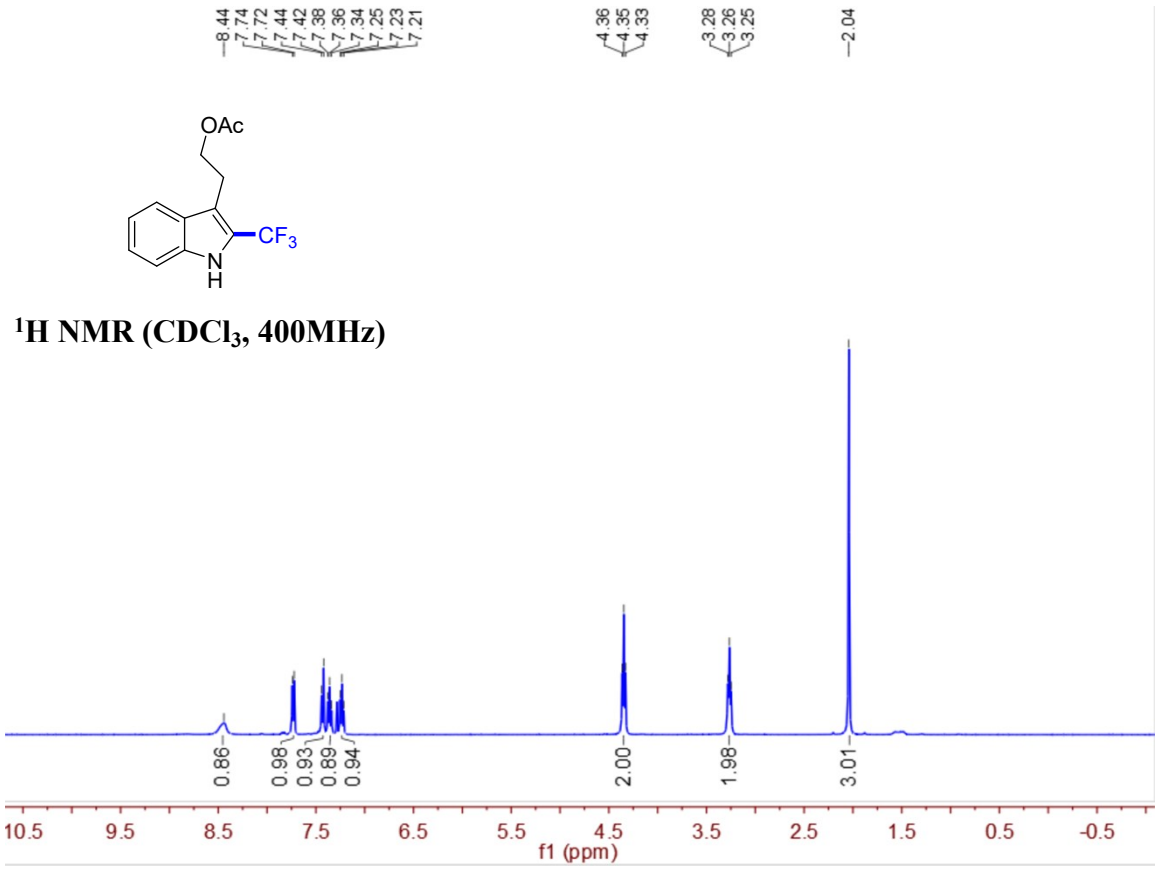
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3ad



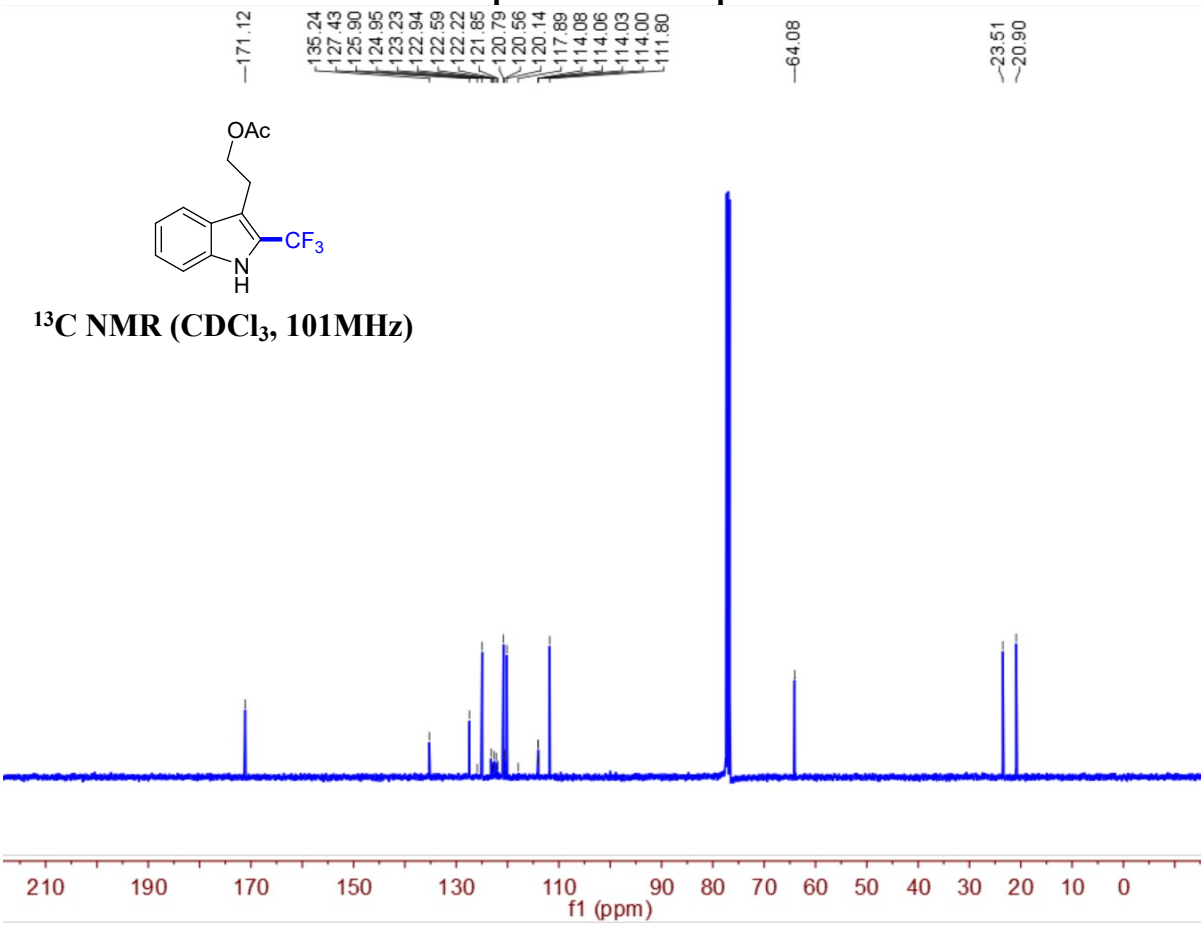
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3ad



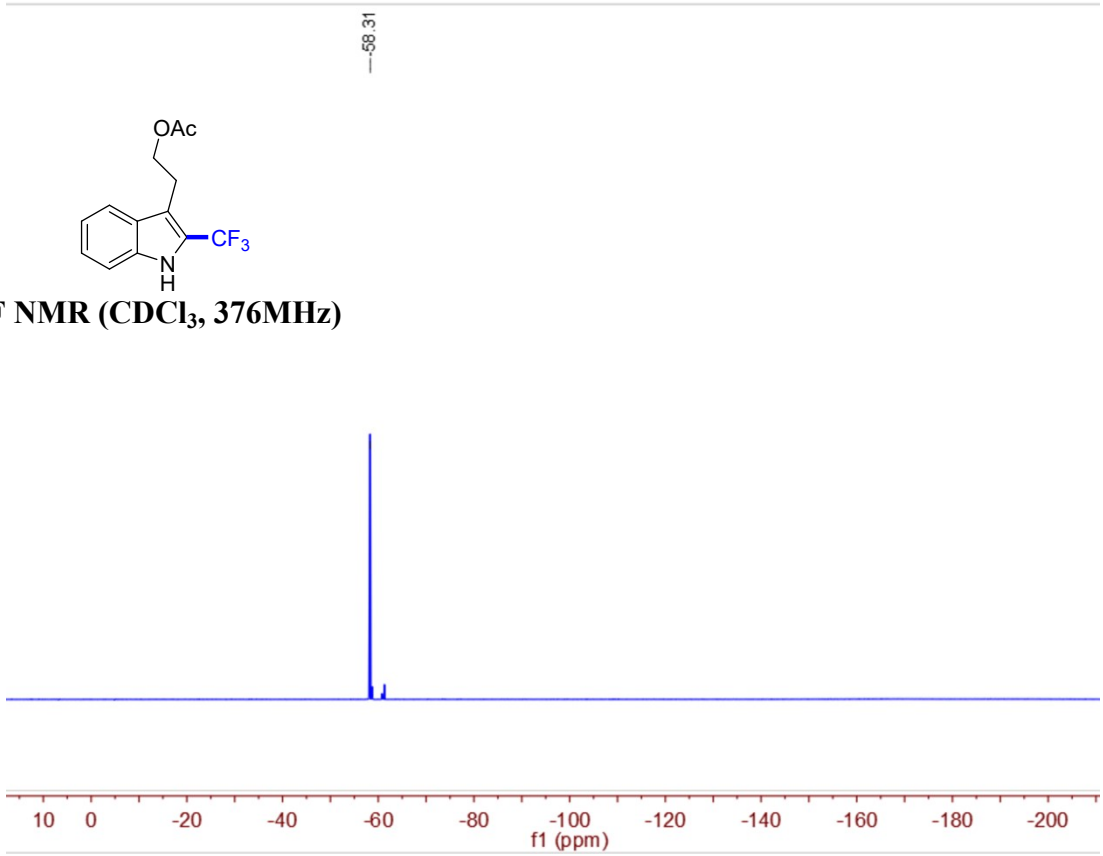
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ae



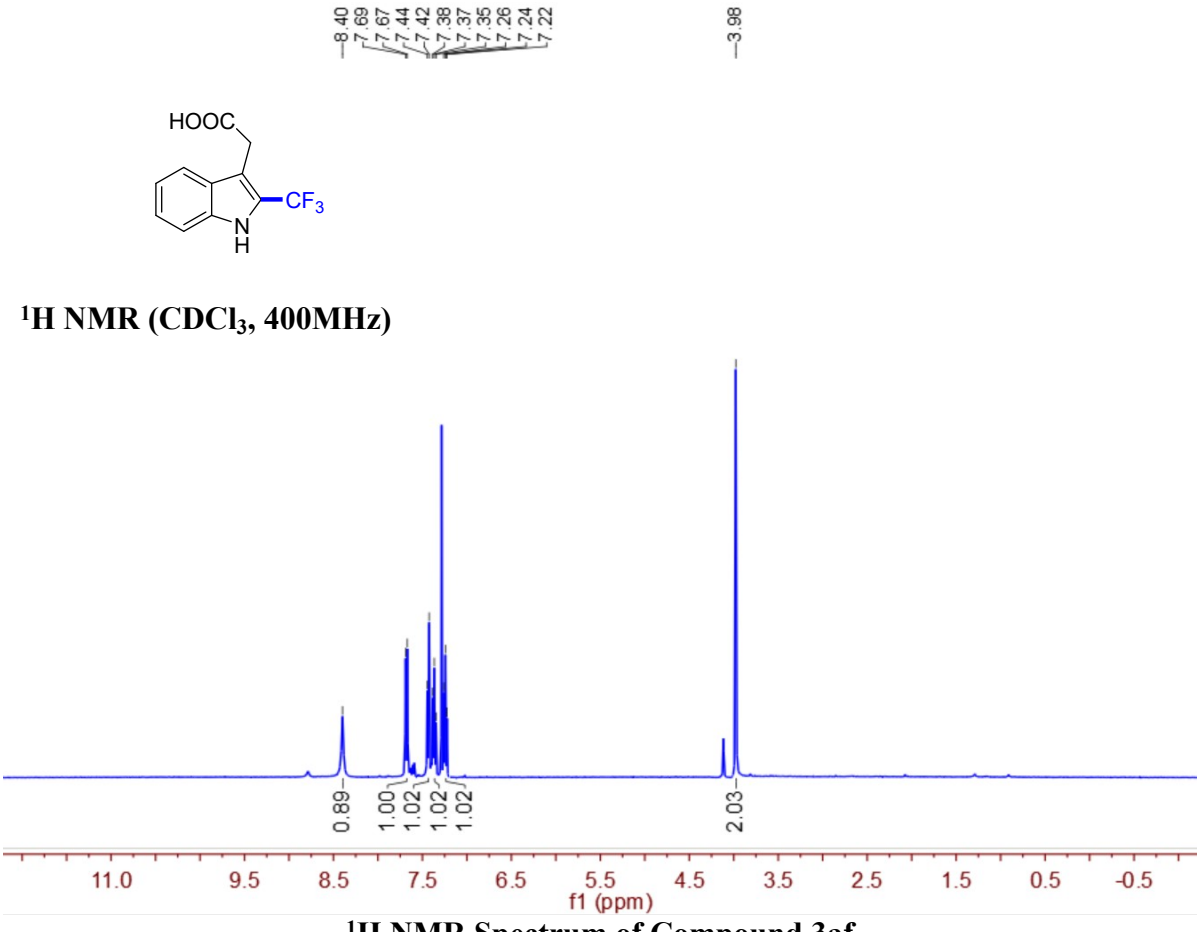
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3ae



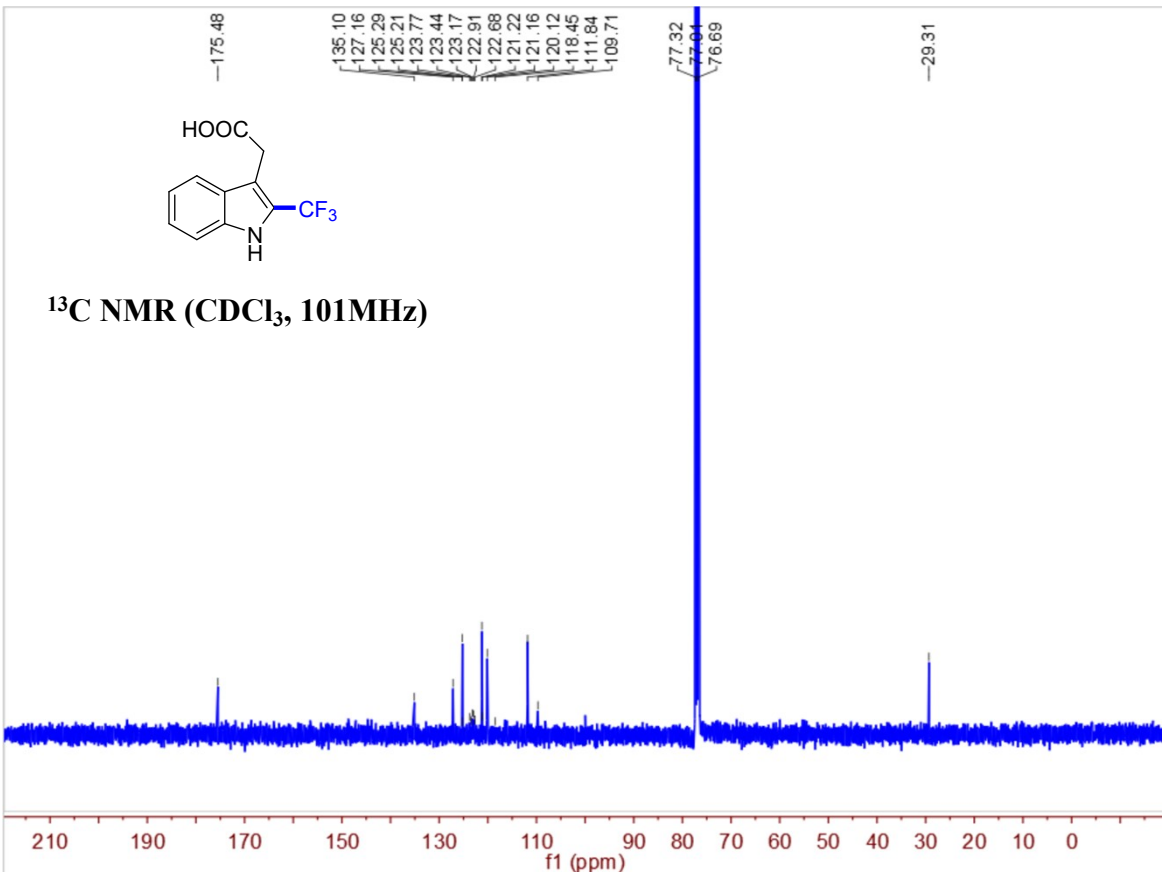
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3ae



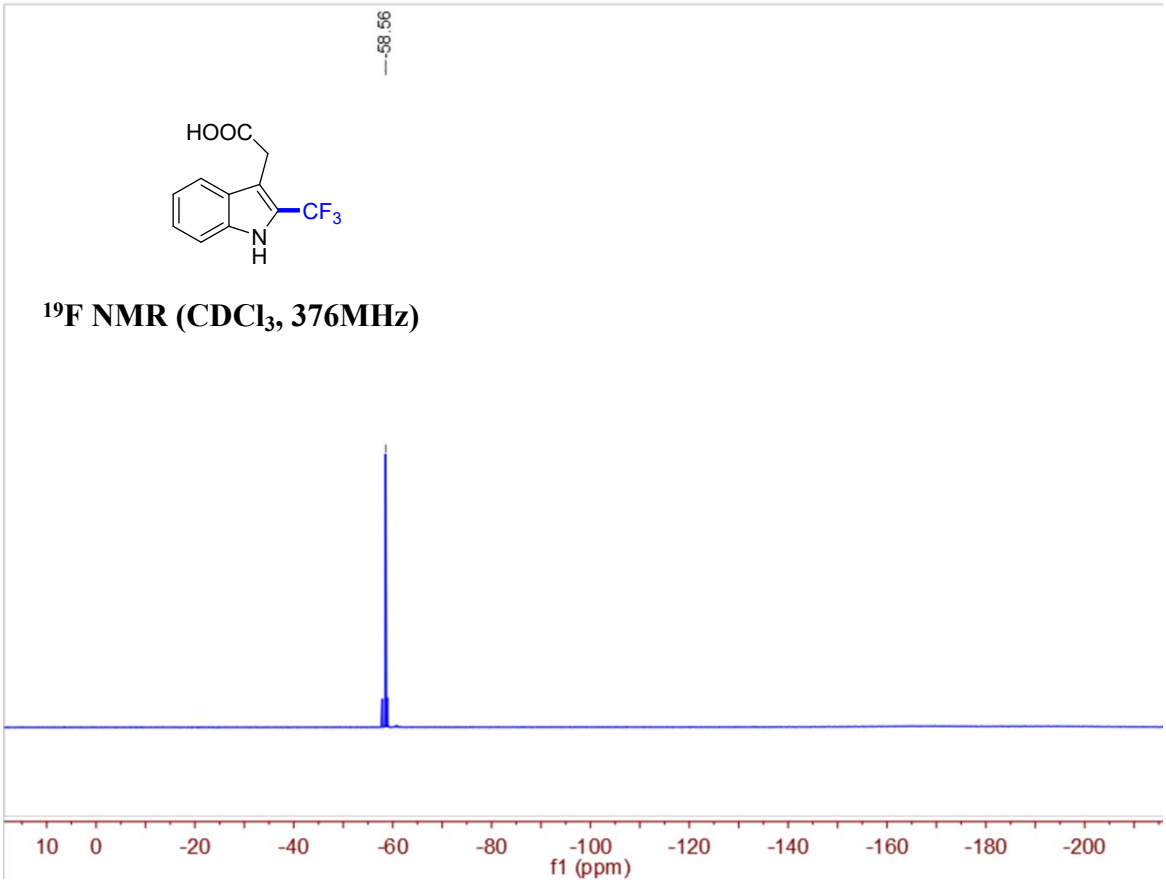
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3af



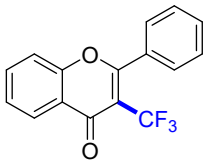
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3af

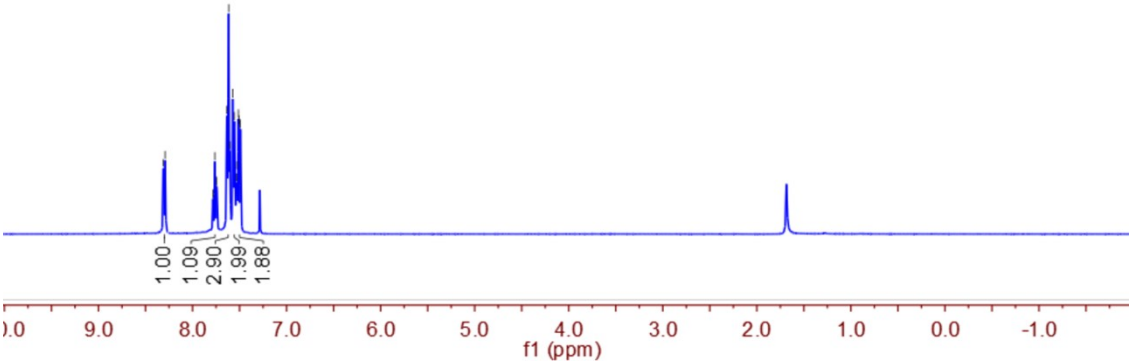


^{19}F NMR ($CDCl_3$, 376MHz)

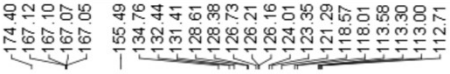
^{19}F NMR Spectrum of Compound 3af

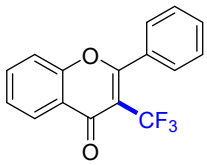


^{1}H NMR ($CDCl_3$, 400MHz)

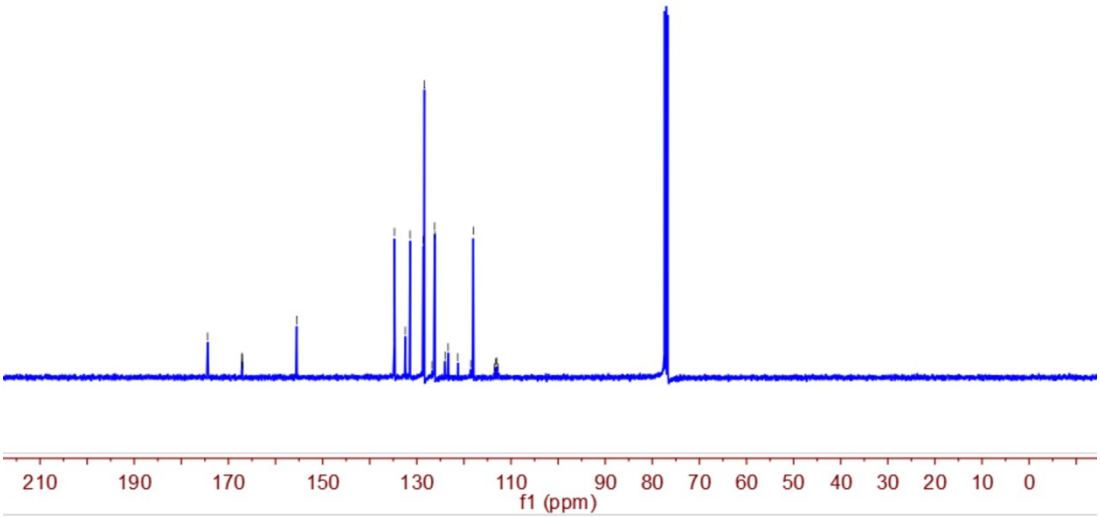


^{1}H NMR Spectrum of Compound 3ag

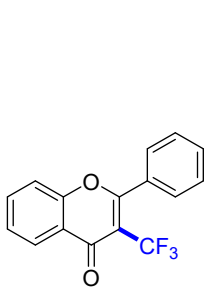




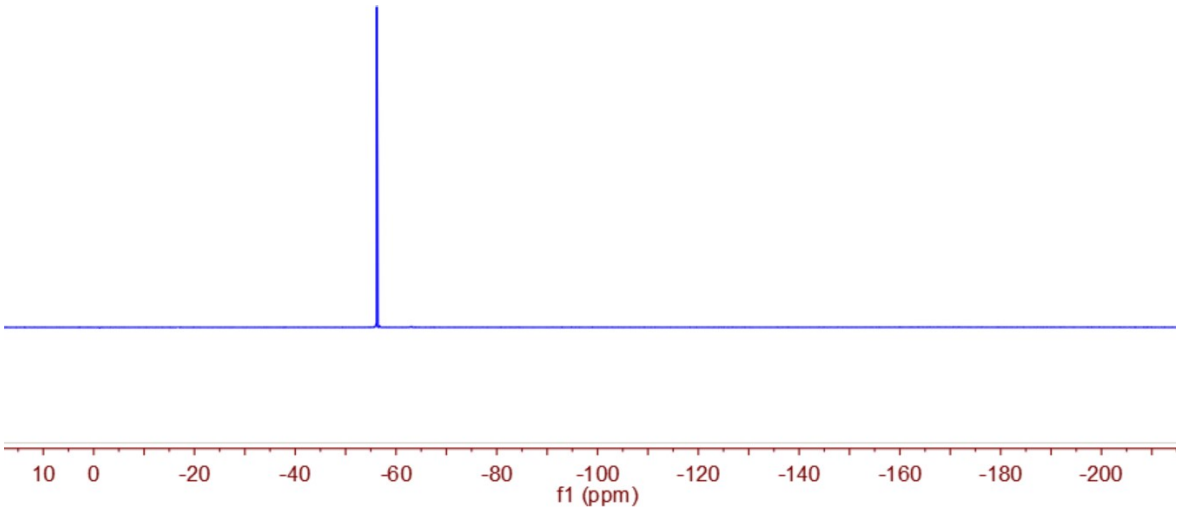
^{13}C NMR ($CDCl_3$, 101MHz)



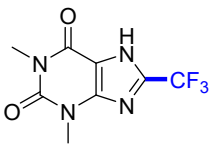
^{13}C NMR Spectrum of Compound 3ag



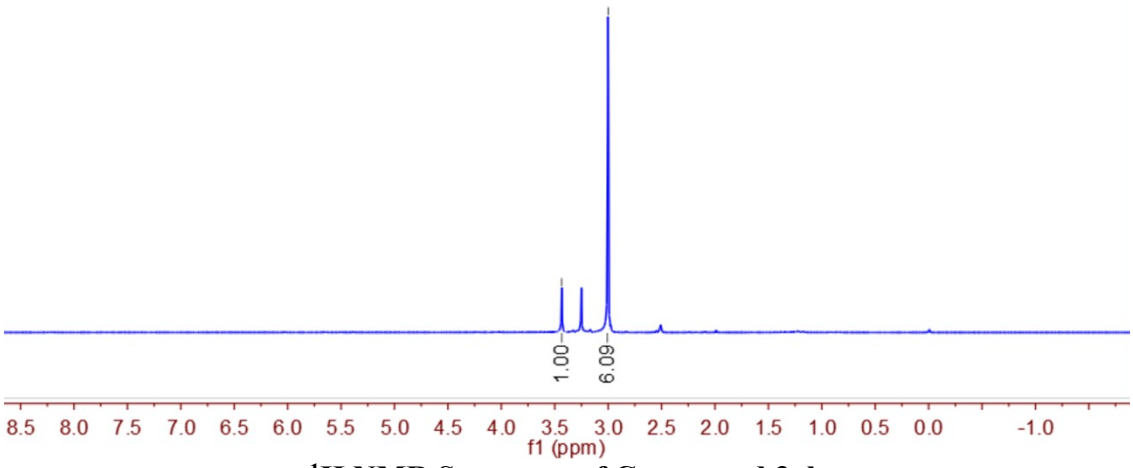
^{19}F NMR ($CDCl_3$, 376MHz)



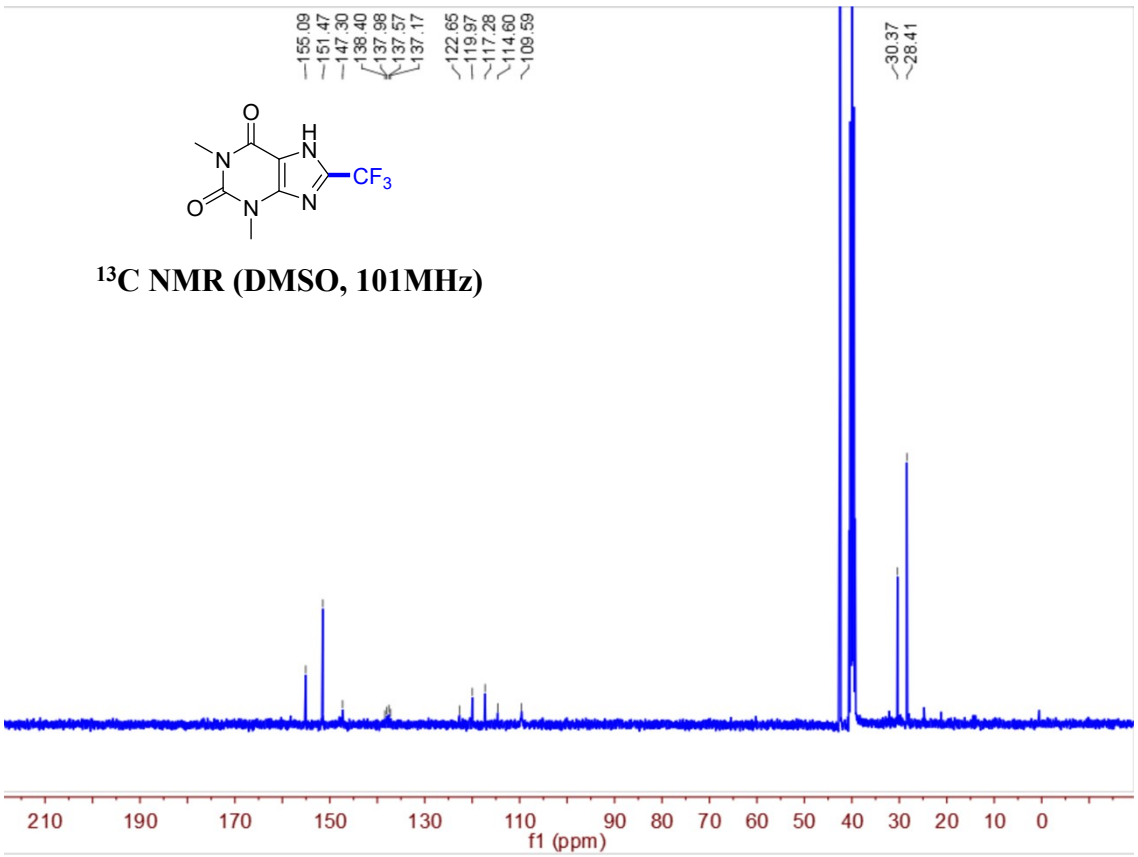
^{19}F NMR Spectrum of Compound 3ag



^{1}H NMR (DMSO, 400MHz)

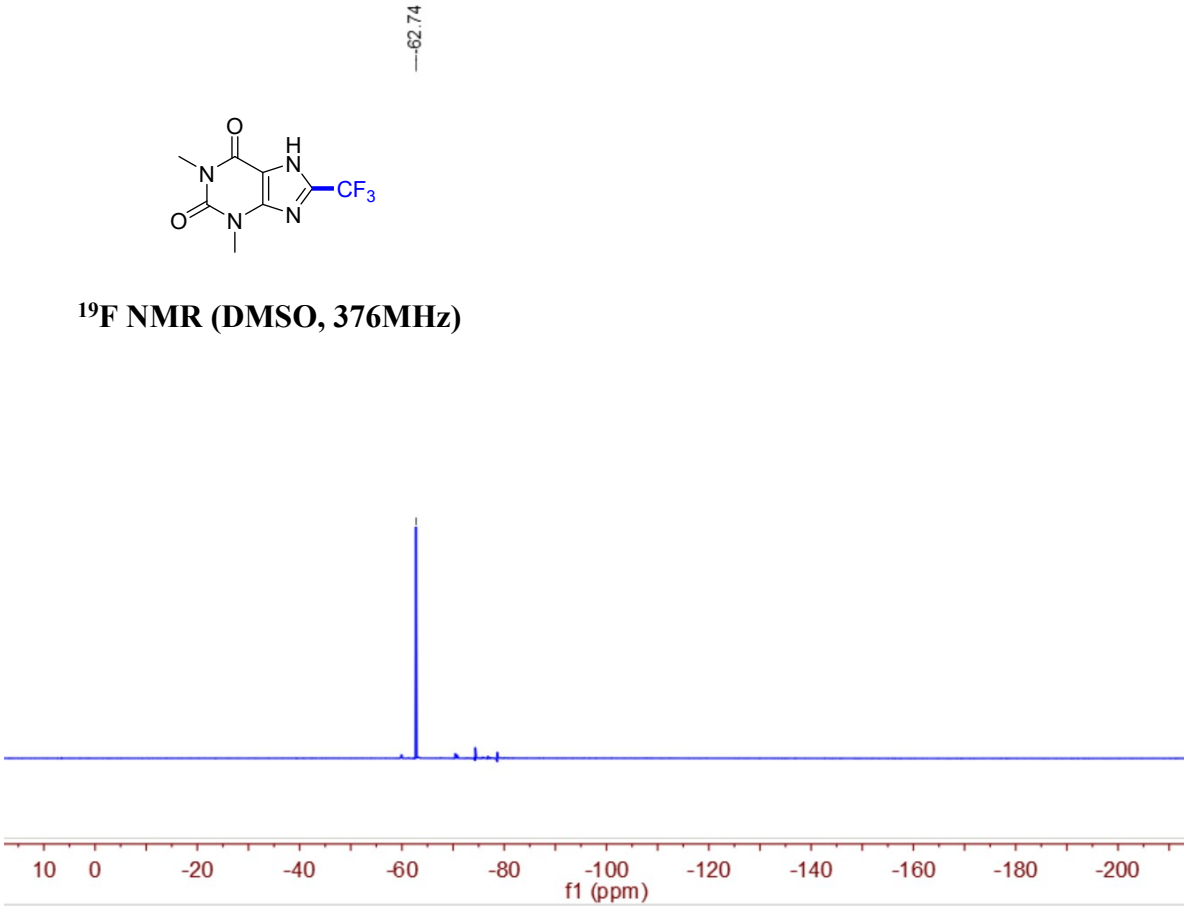


^{1}H NMR Spectrum of Compound 3ah



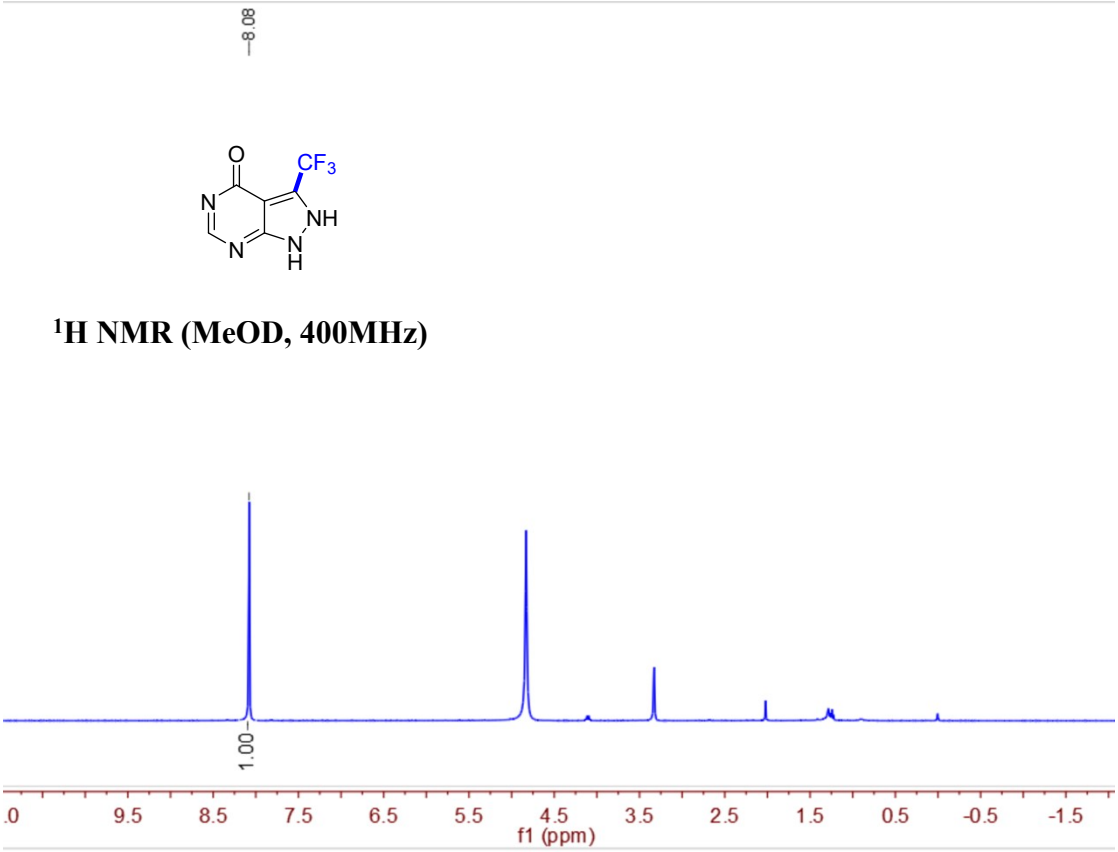
^{13}C NMR (DMSO, 101MHz)

^{13}C NMR Spectrum of Compound 3ah



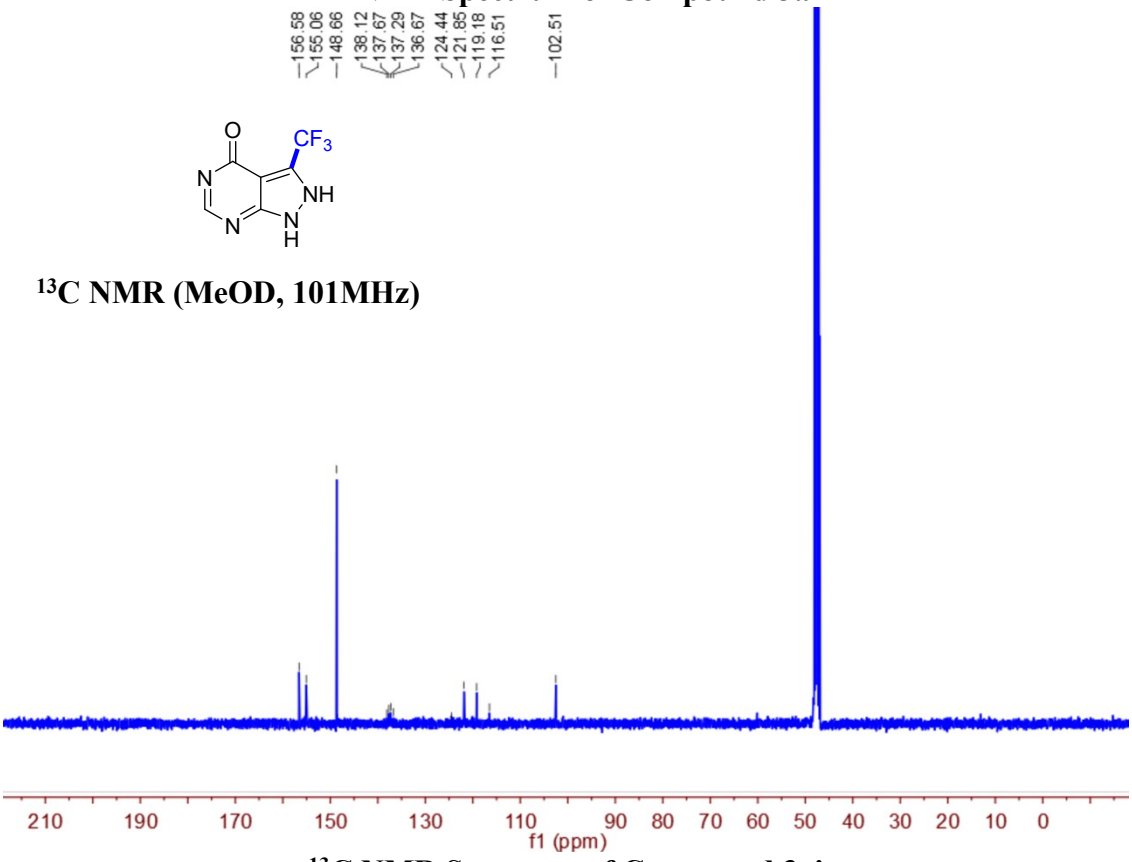
^{19}F NMR (DMSO, 376MHz)

^{19}F NMR Spectrum of Compound 3ah



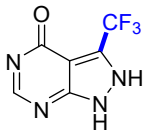
^{1}H NMR (MeOD, 400MHz)

^{1}H NMR Spectrum of Compound 3ai

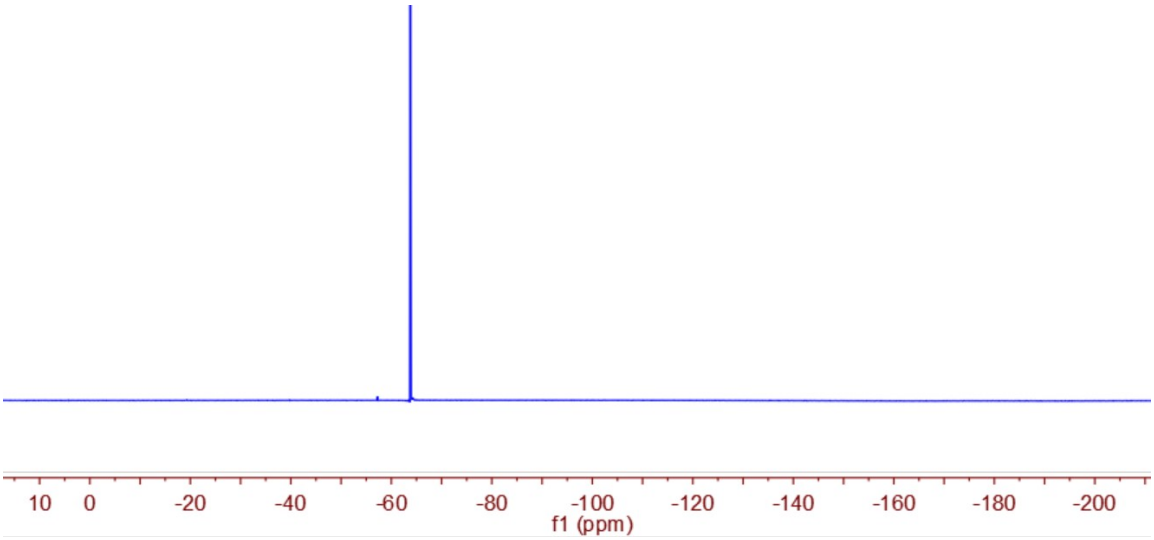


^{13}C NMR (MeOD, 101MHz)

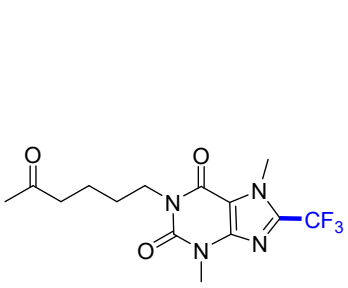
^{13}C NMR Spectrum of Compound 3ai



^{19}F NMR (MeOD, 376MHz)

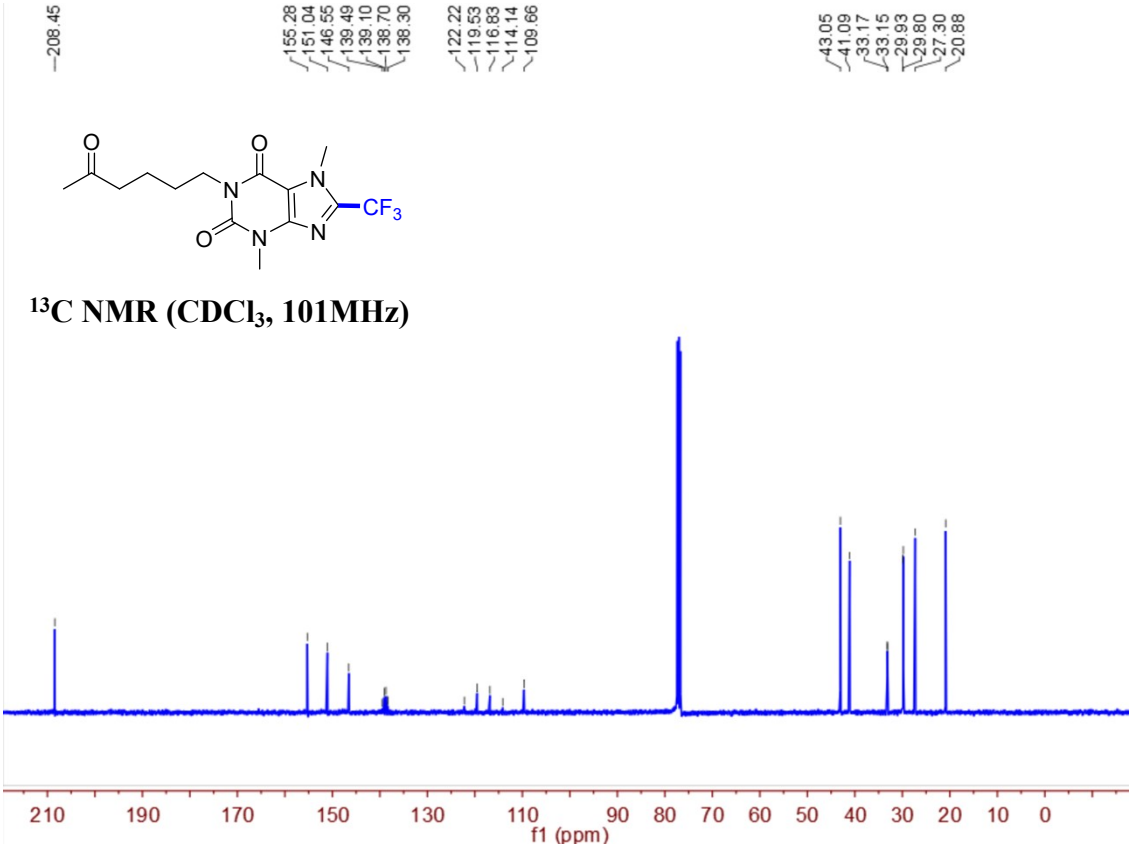


^{19}F NMR Spectrum of Compound 3ai



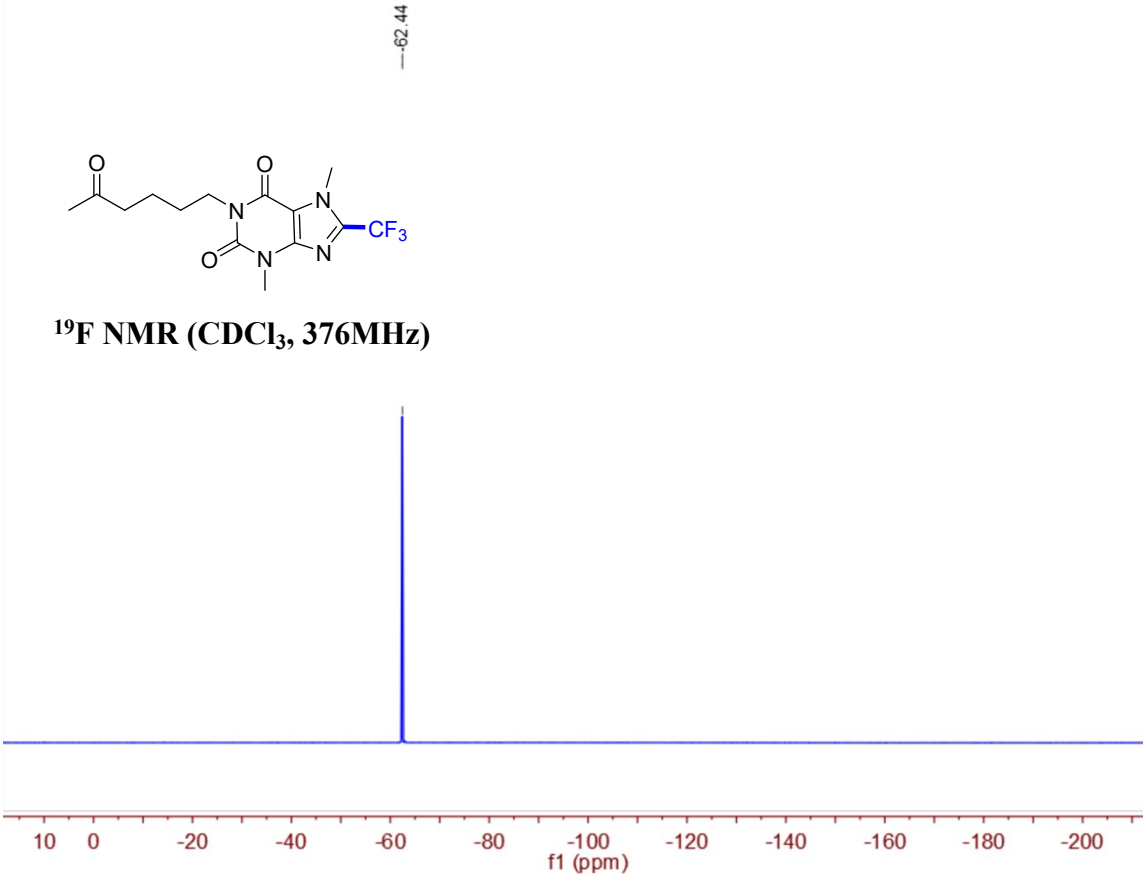
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3aj



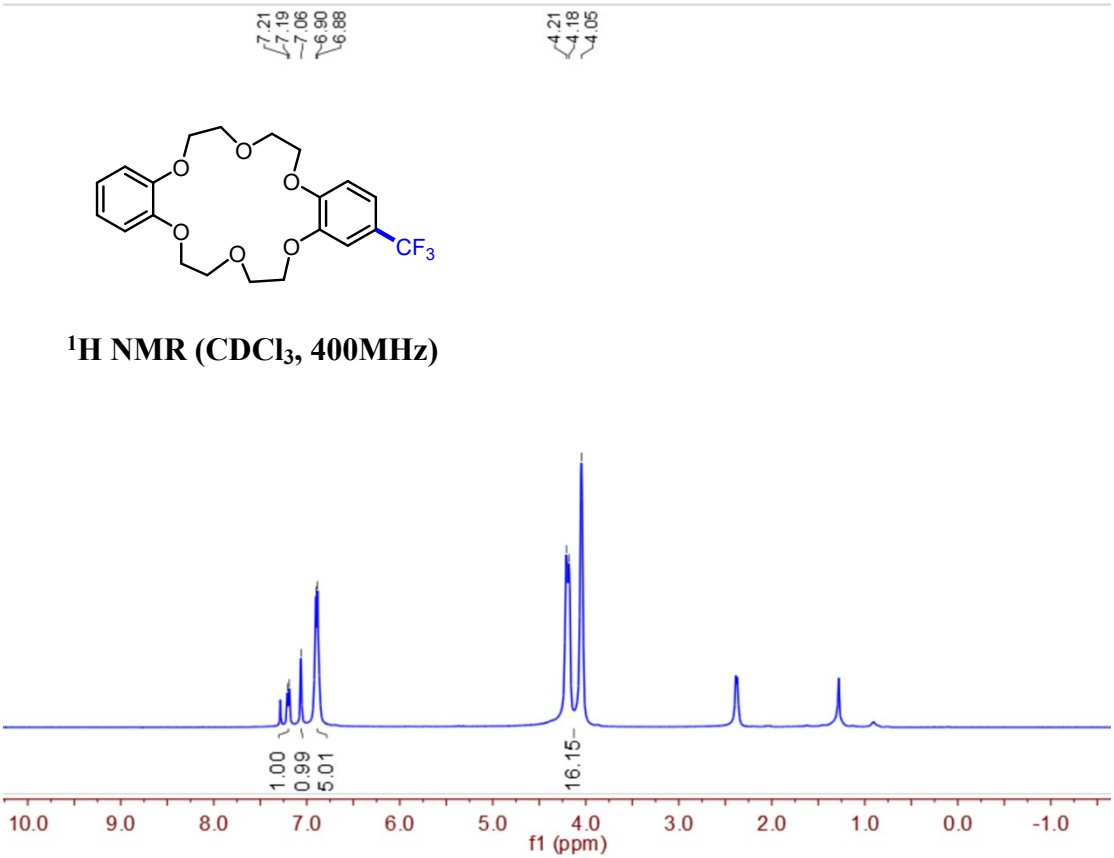
^{13}C NMR (CDCl$_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3aj



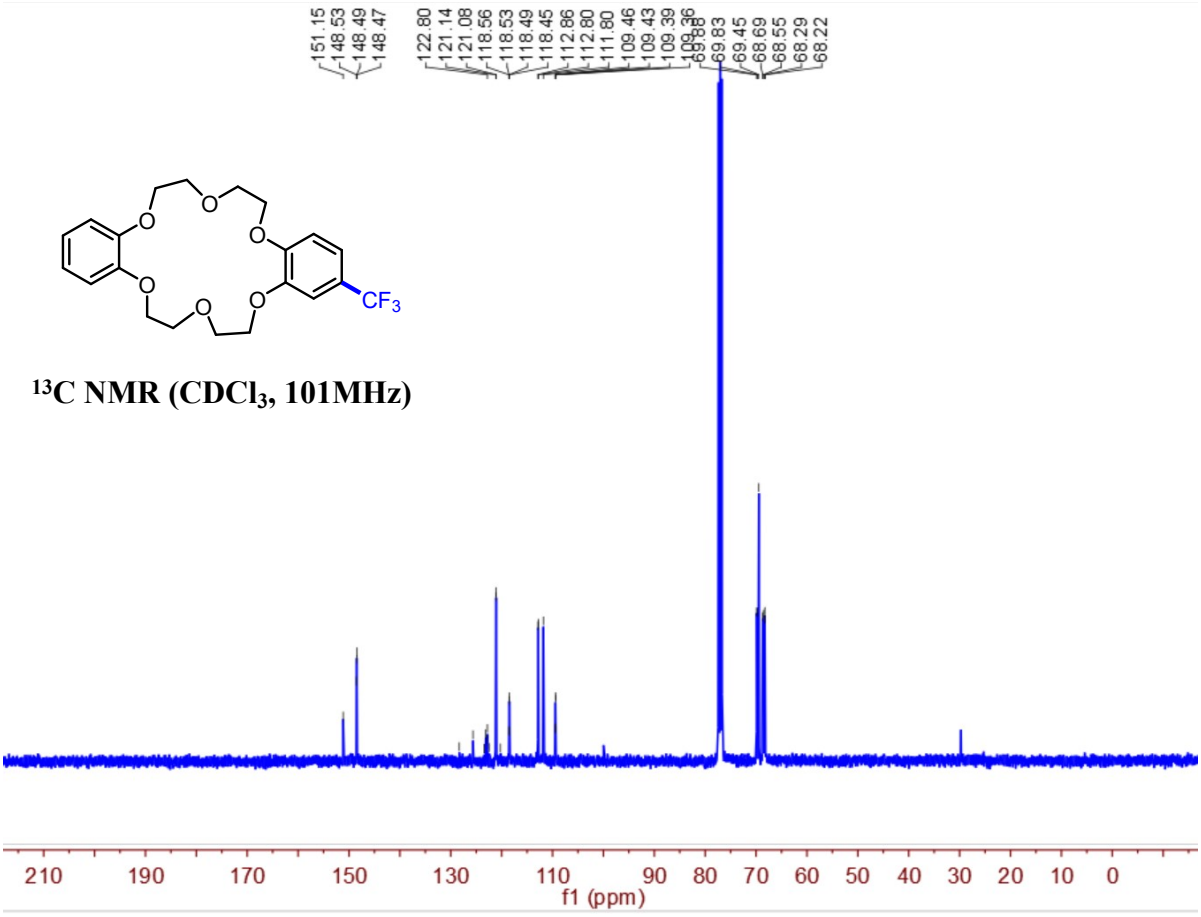
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3aj



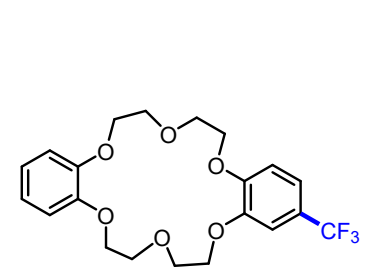
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ak

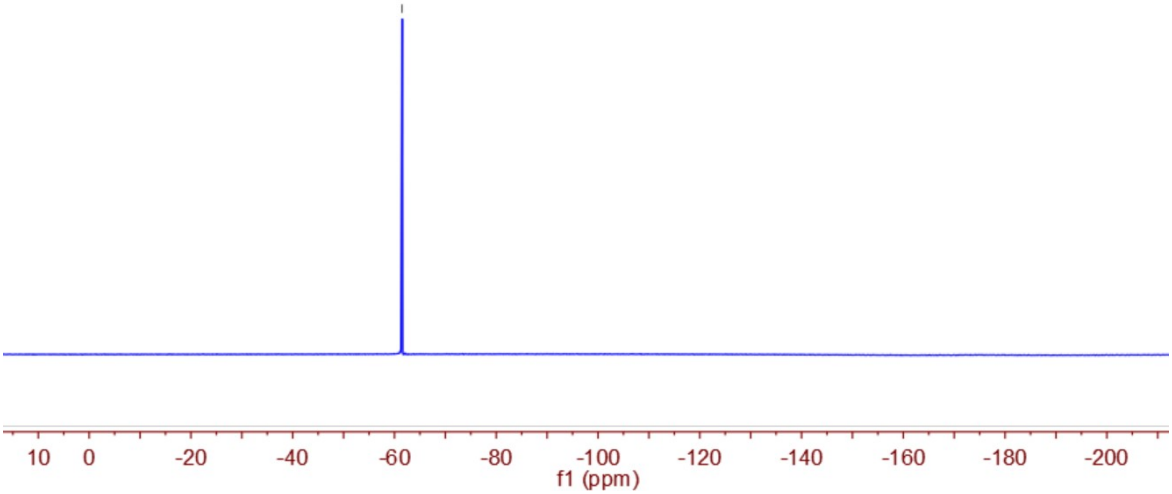


^{13}C NMR ($CDCl_3$, 101MHz)

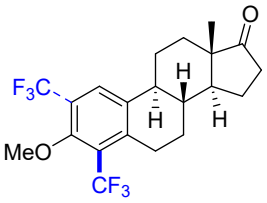
^{13}C NMR Spectrum of Compound 3ak



^{19}F NMR ($CDCl_3$, 376MHz)



^{19}F NMR Spectrum of Compound 3ak



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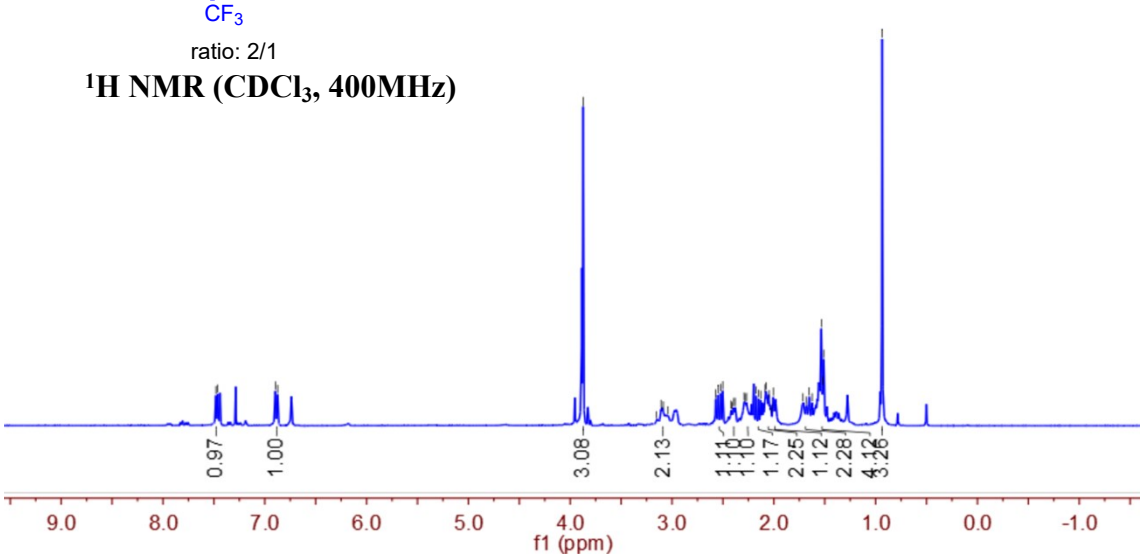
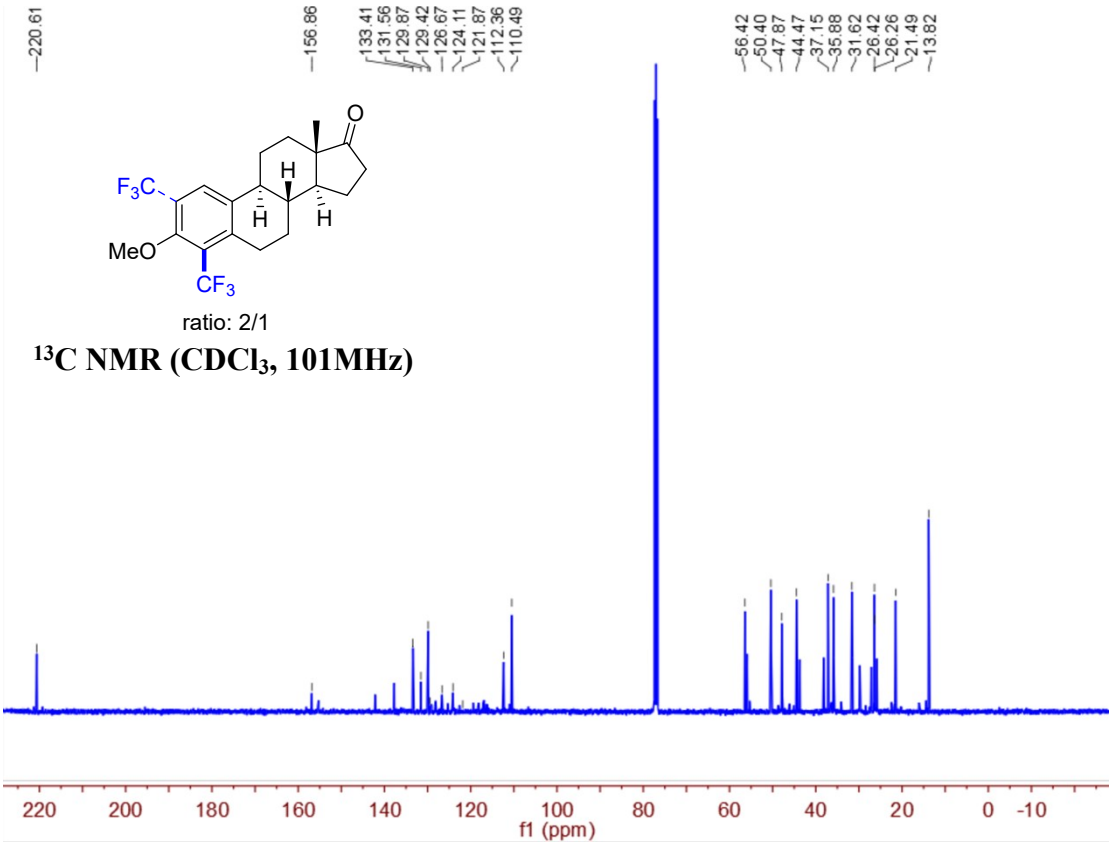
^{1}H NMR ($CDCl_3$, 400MHz)

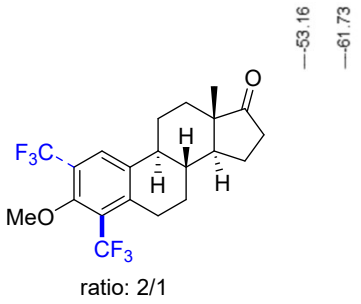


^{1}H NMR Spectrum of Compound 3al

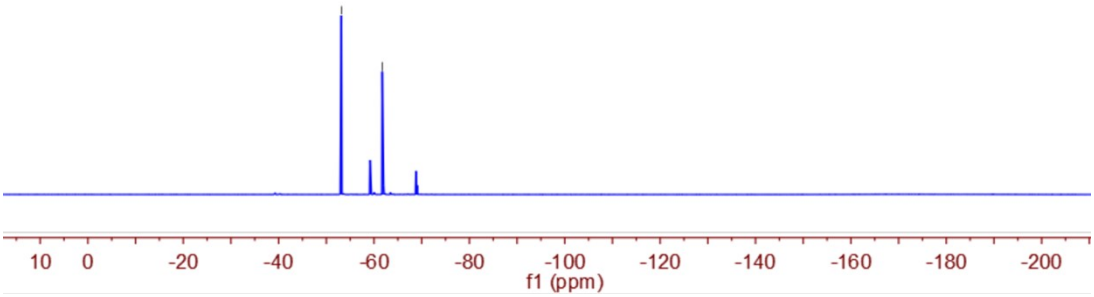


^{13}C NMR ($CDCl_3$, 101MHz)

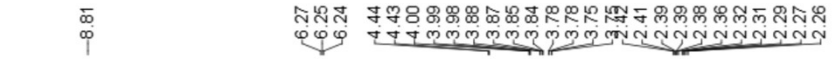
^{13}C NMR Spectrum of Compound 3al

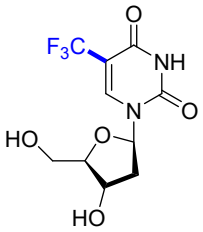


^{19}F NMR ($CDCl_3$, 376MHz)

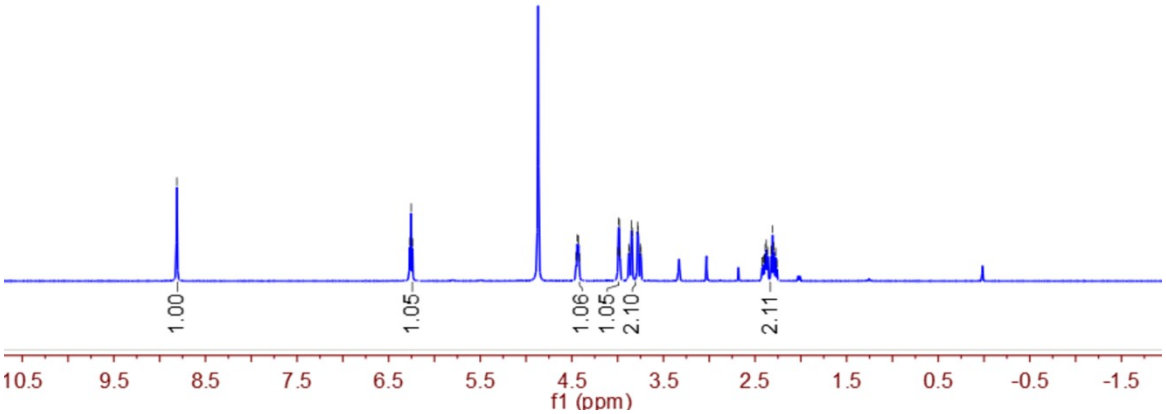


^{19}F NMR Spectrum of Compound 3al

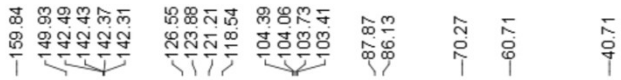


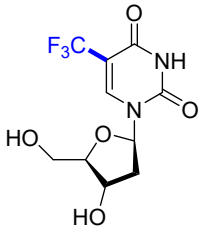


^{1}H NMR (MeOD, 400MHz)



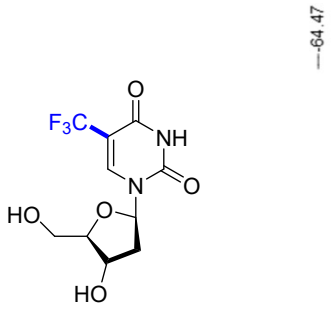
^{1}H NMR Spectrum of Compound 3am



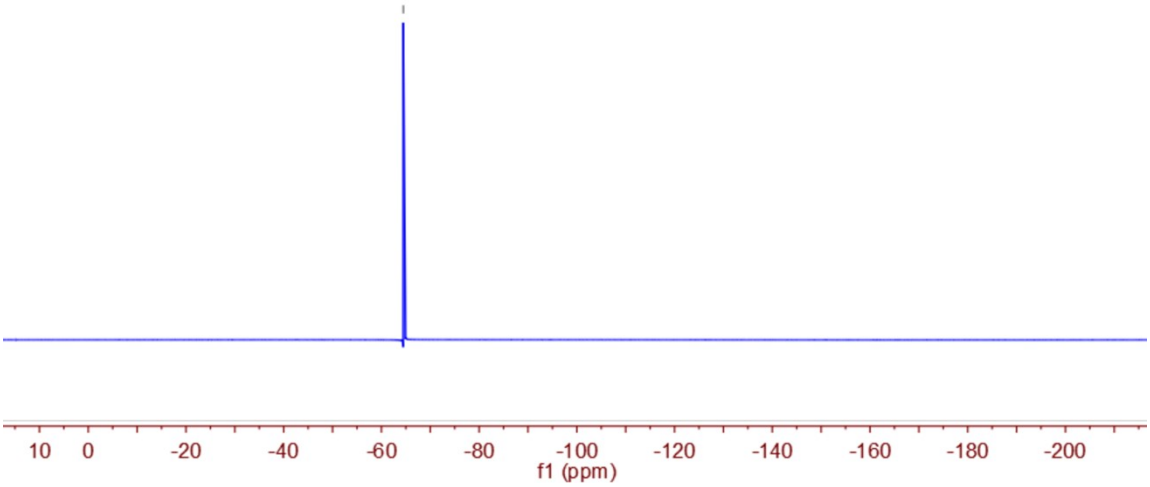


^{13}C NMR (MeOD, 101MHz)

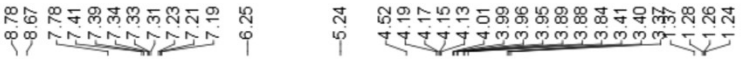
^{13}C NMR Spectrum of Compound 3am

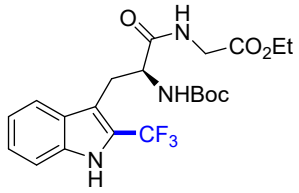


^{19}F NMR (MeOD, 376MHz)

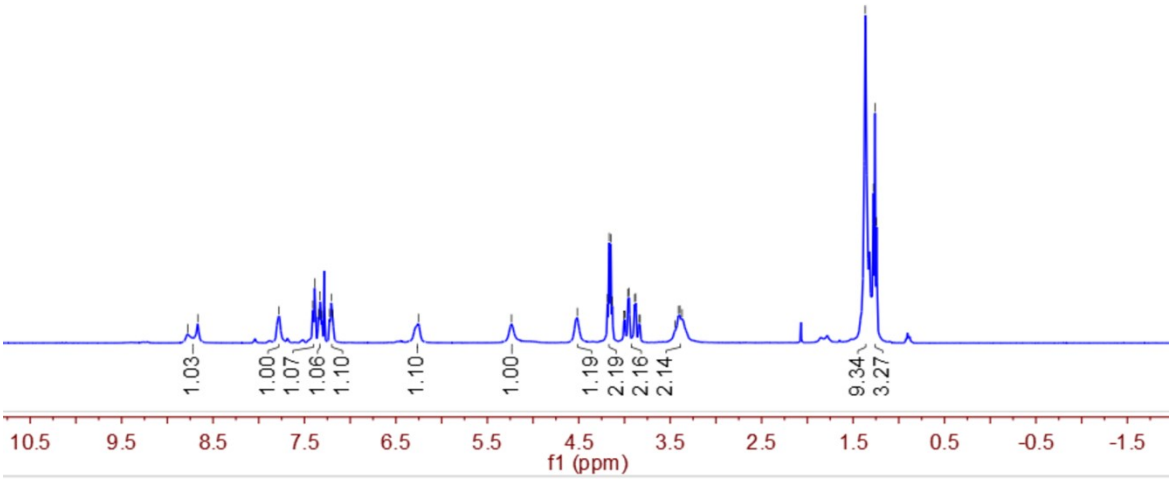


^{19}F NMR Spectrum of Compound 3am

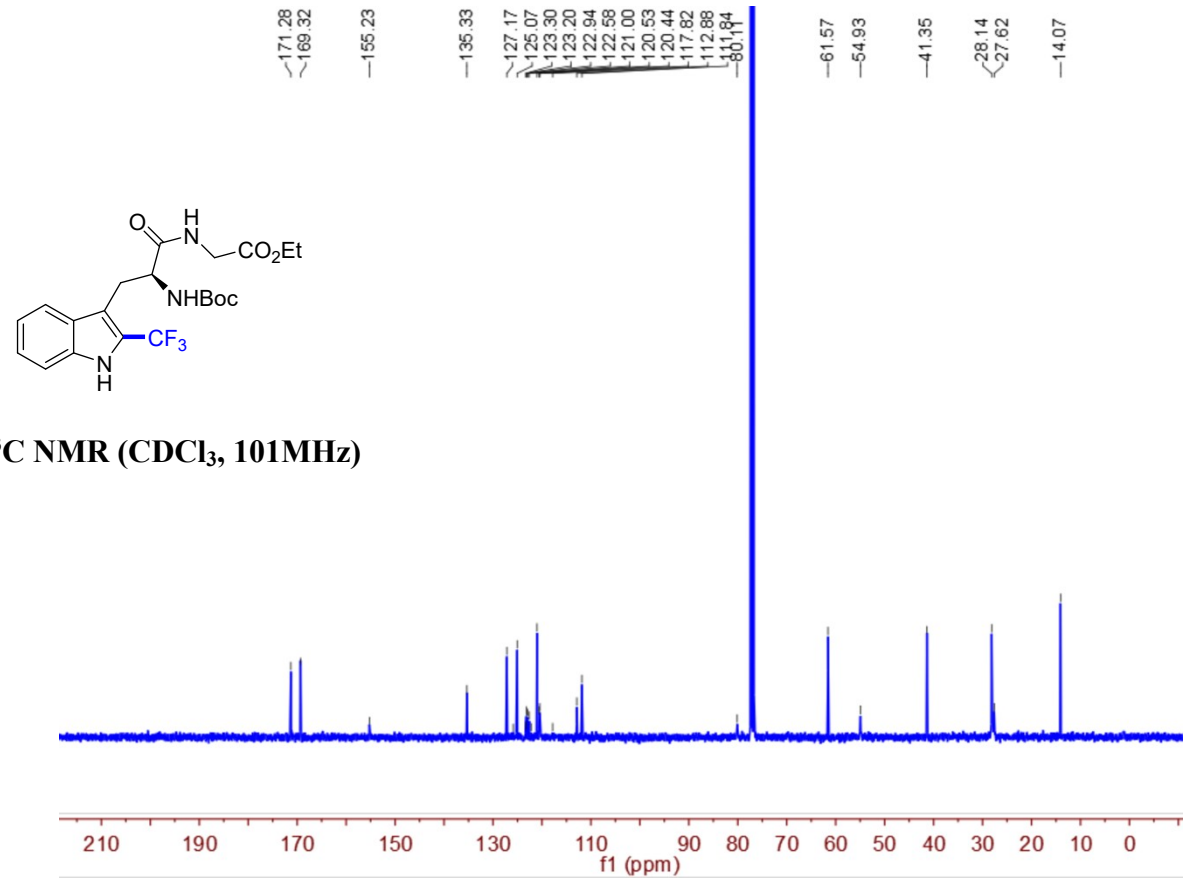




^{1}H NMR ($CDCl_3$, 400MHz)

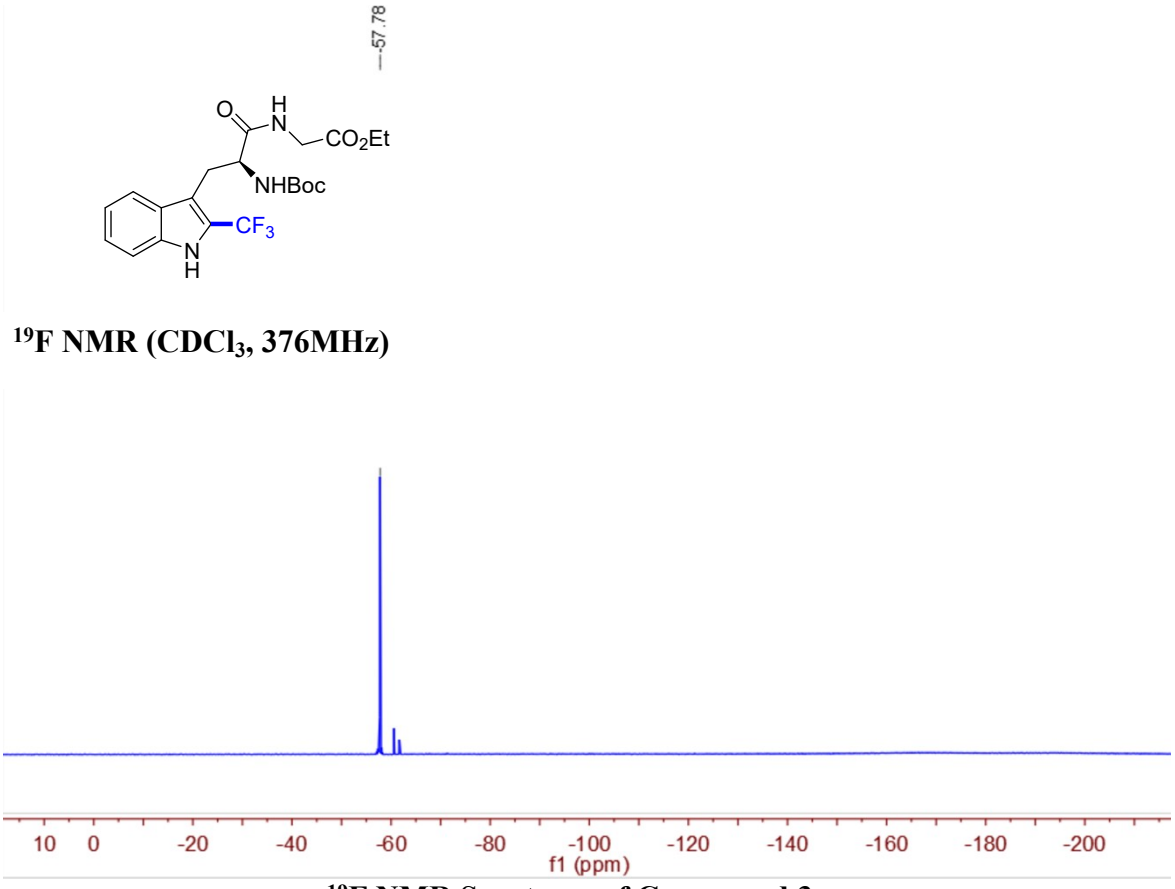


^{1}H NMR Spectrum of Compound 3an



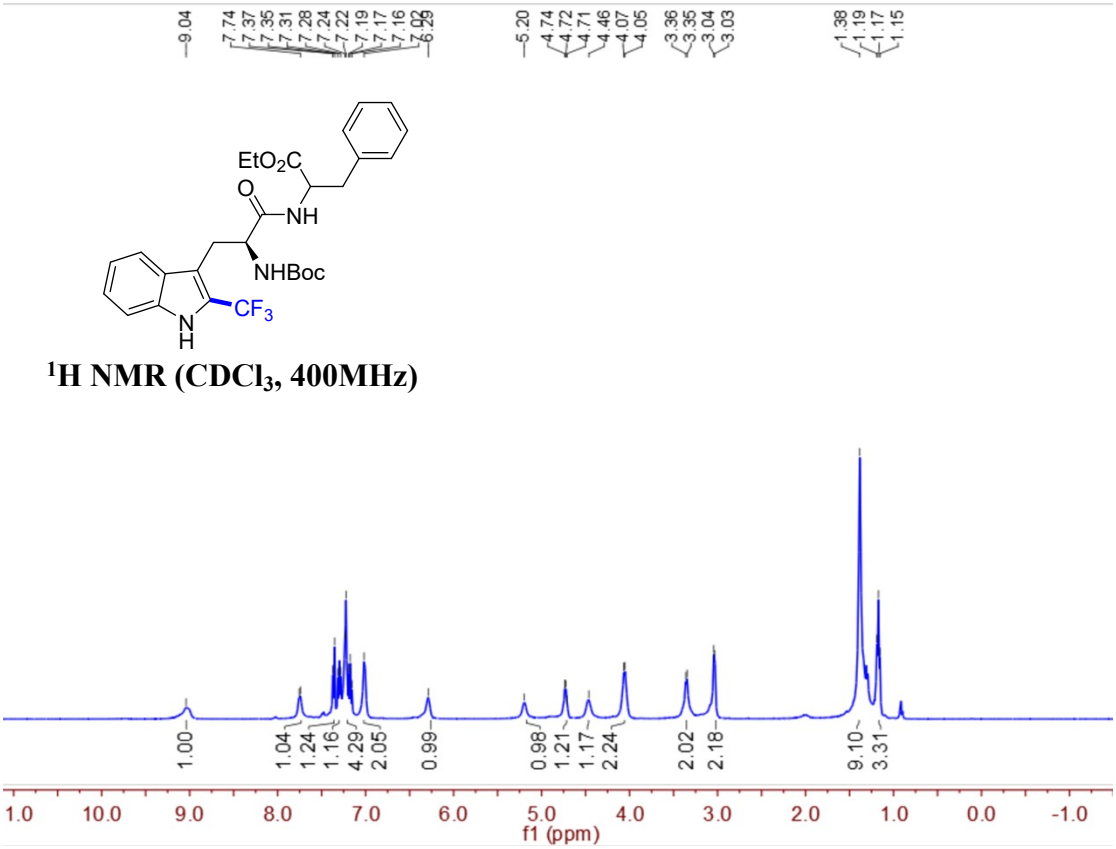
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3an



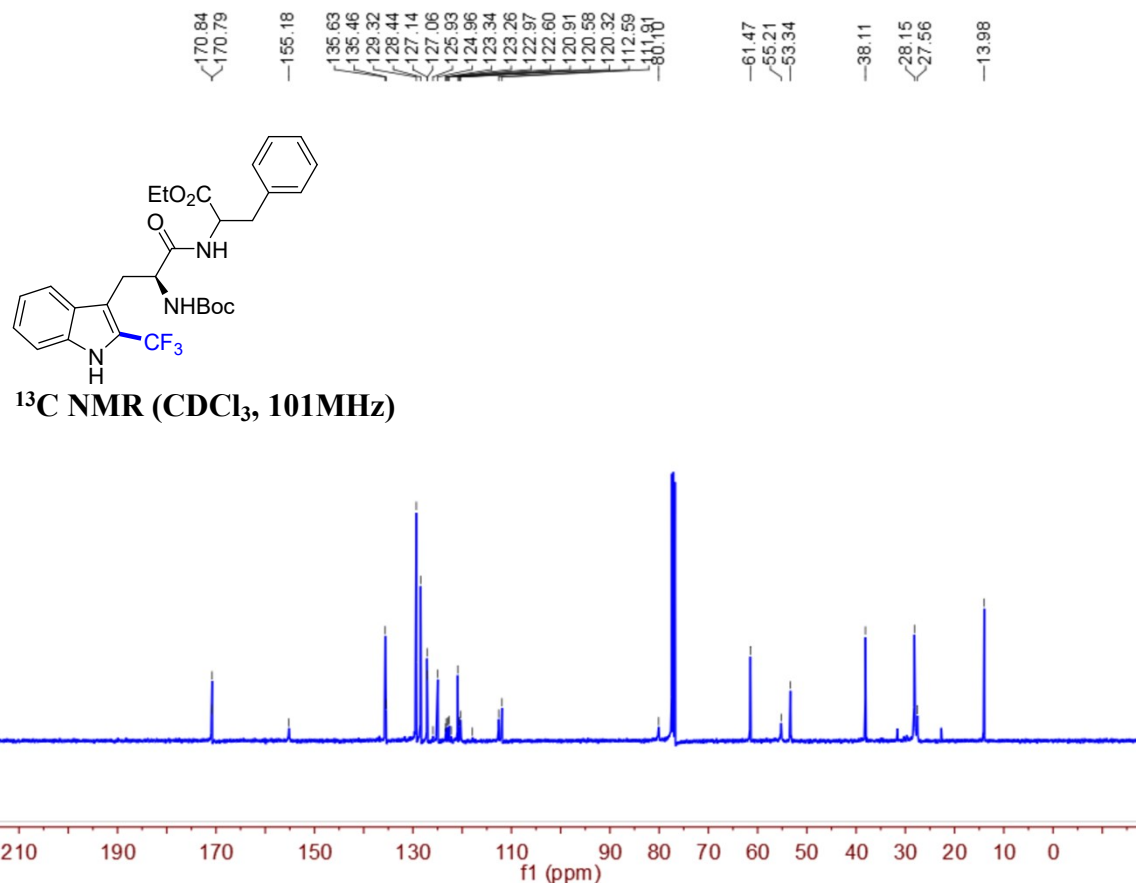
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3an



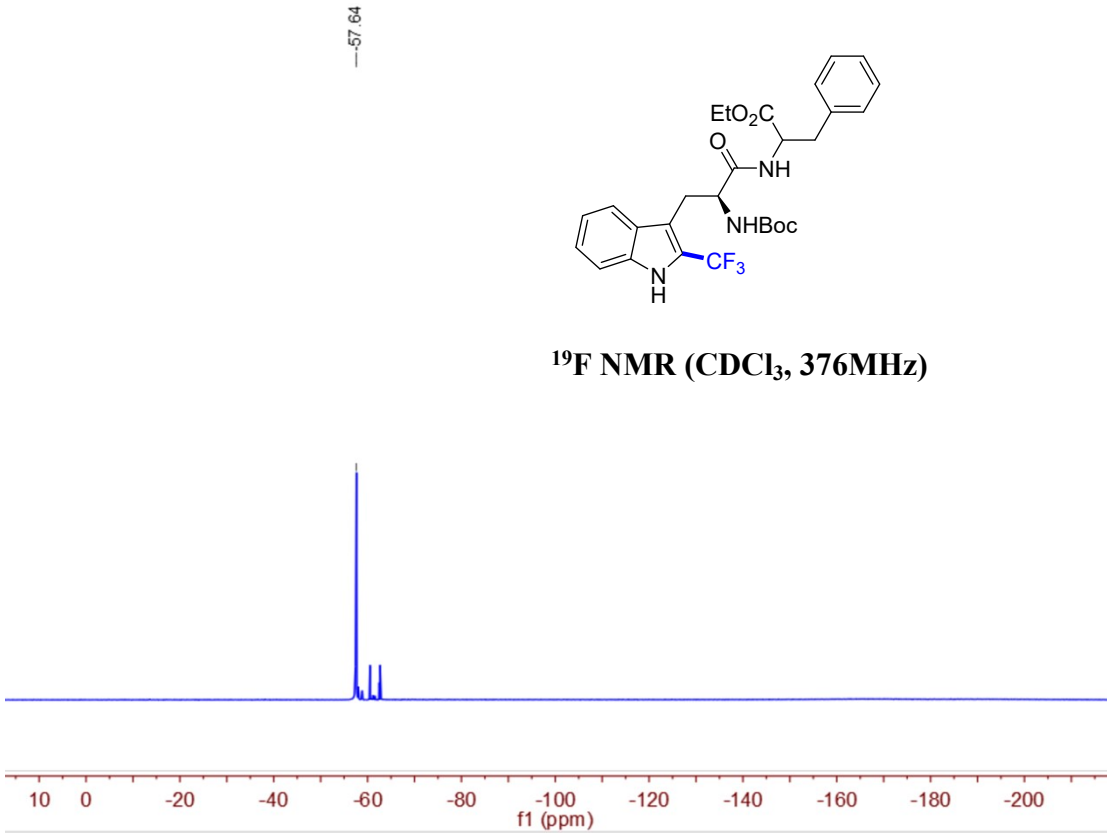
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ao



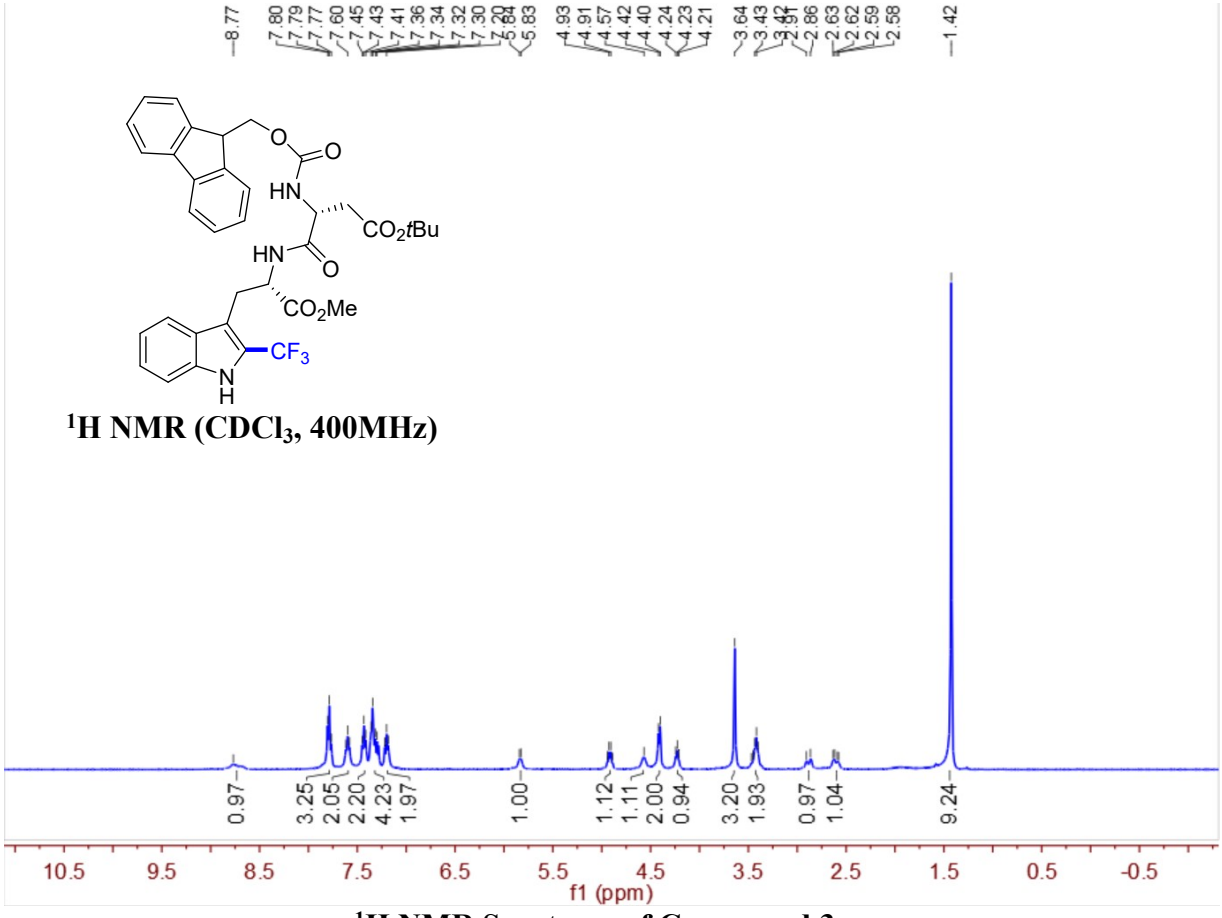
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3ao



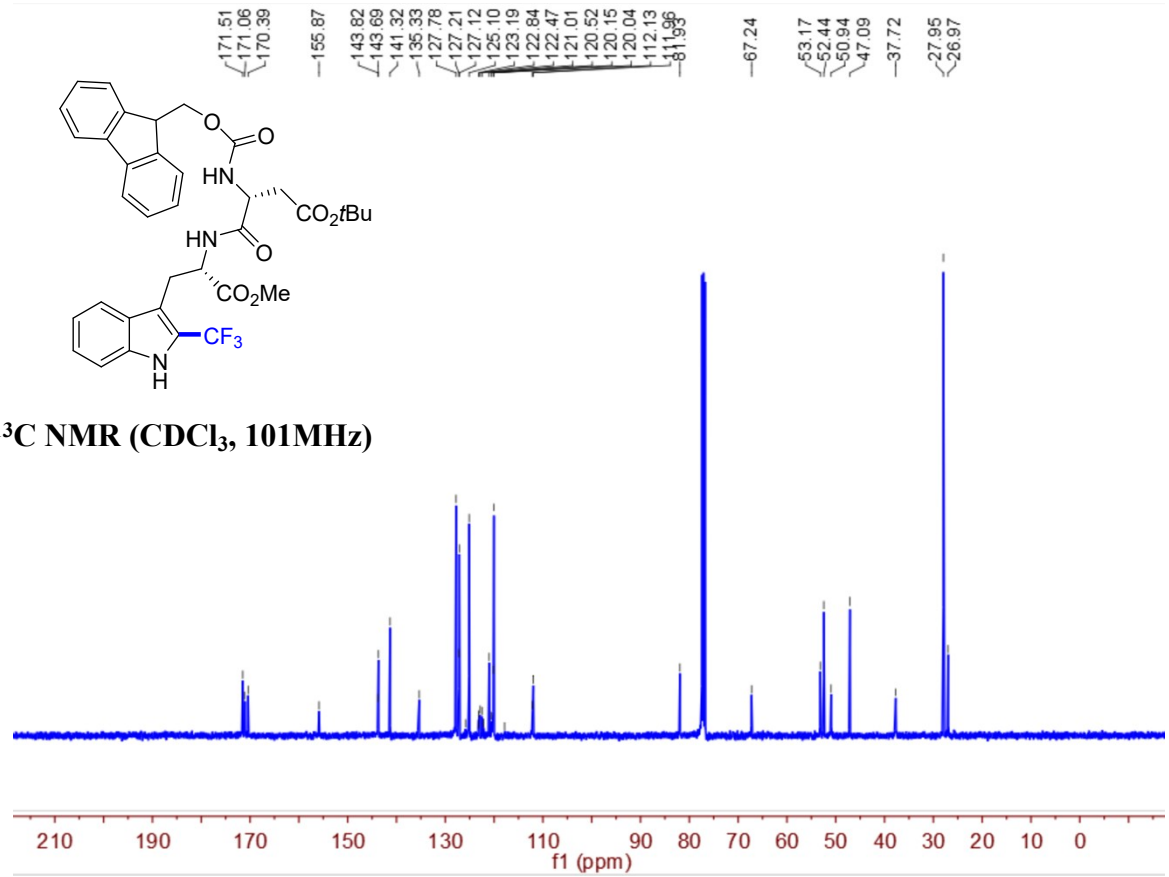
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3ao



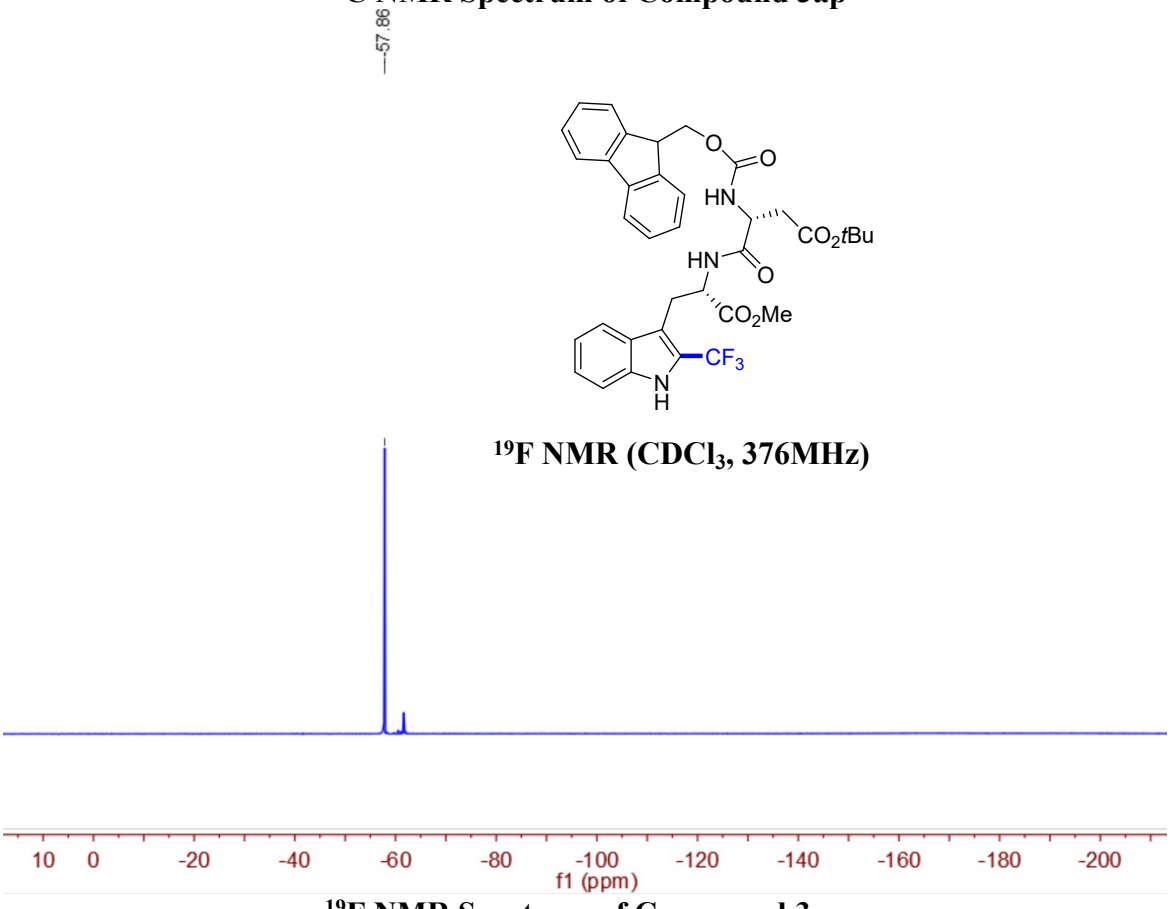
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3ap



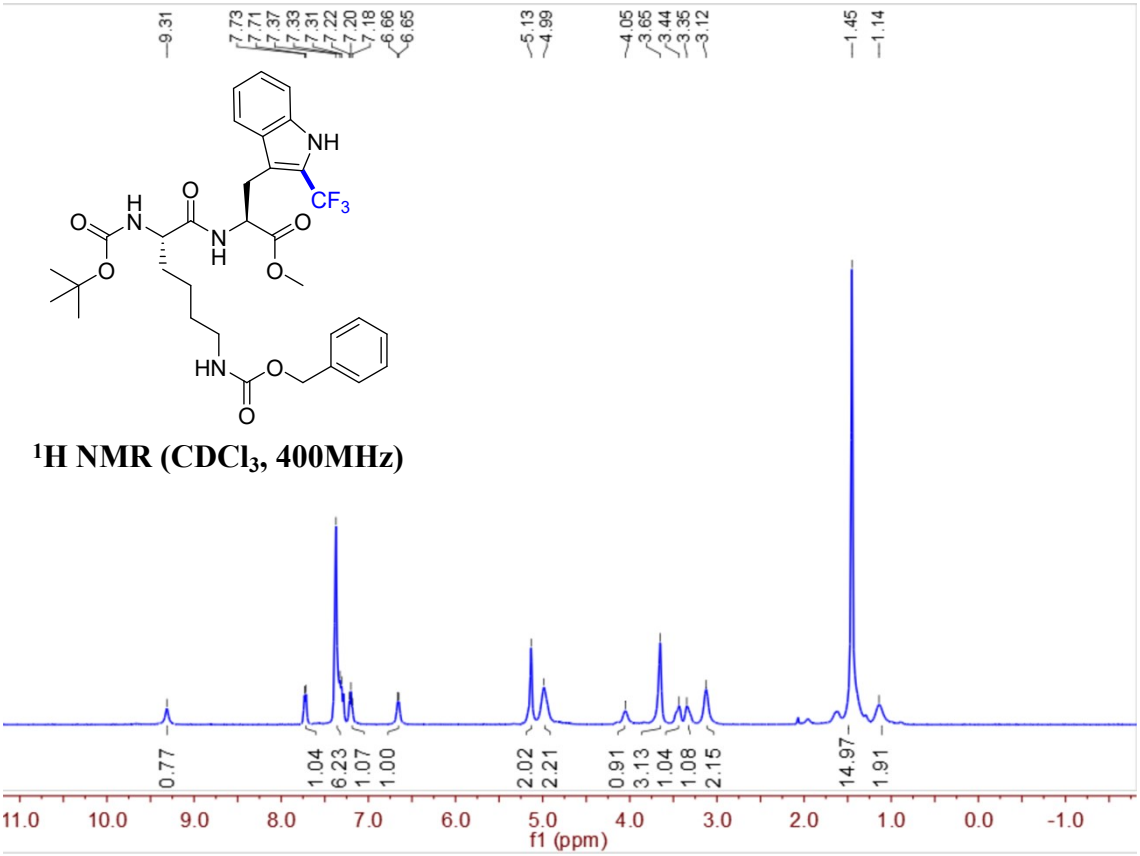
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 3ap



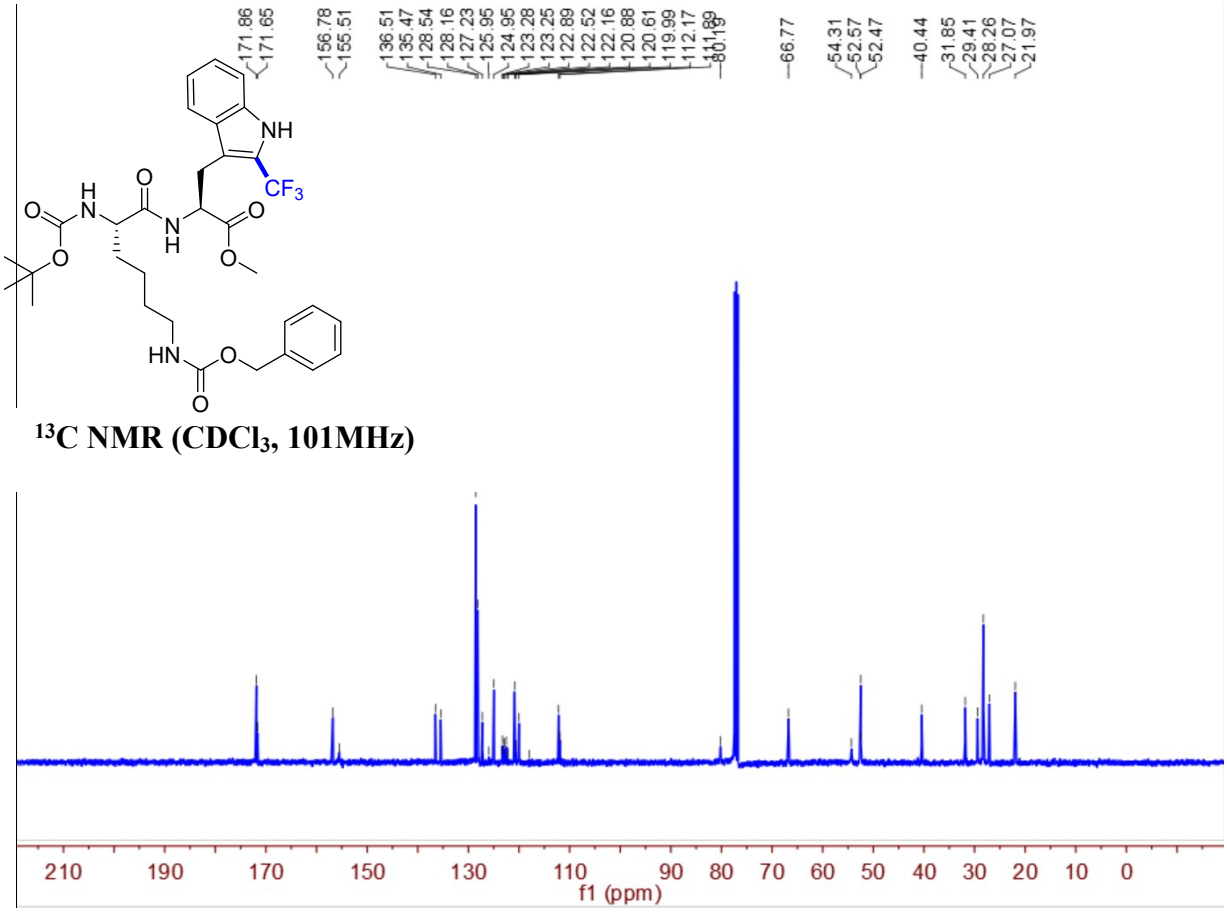
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 3ap



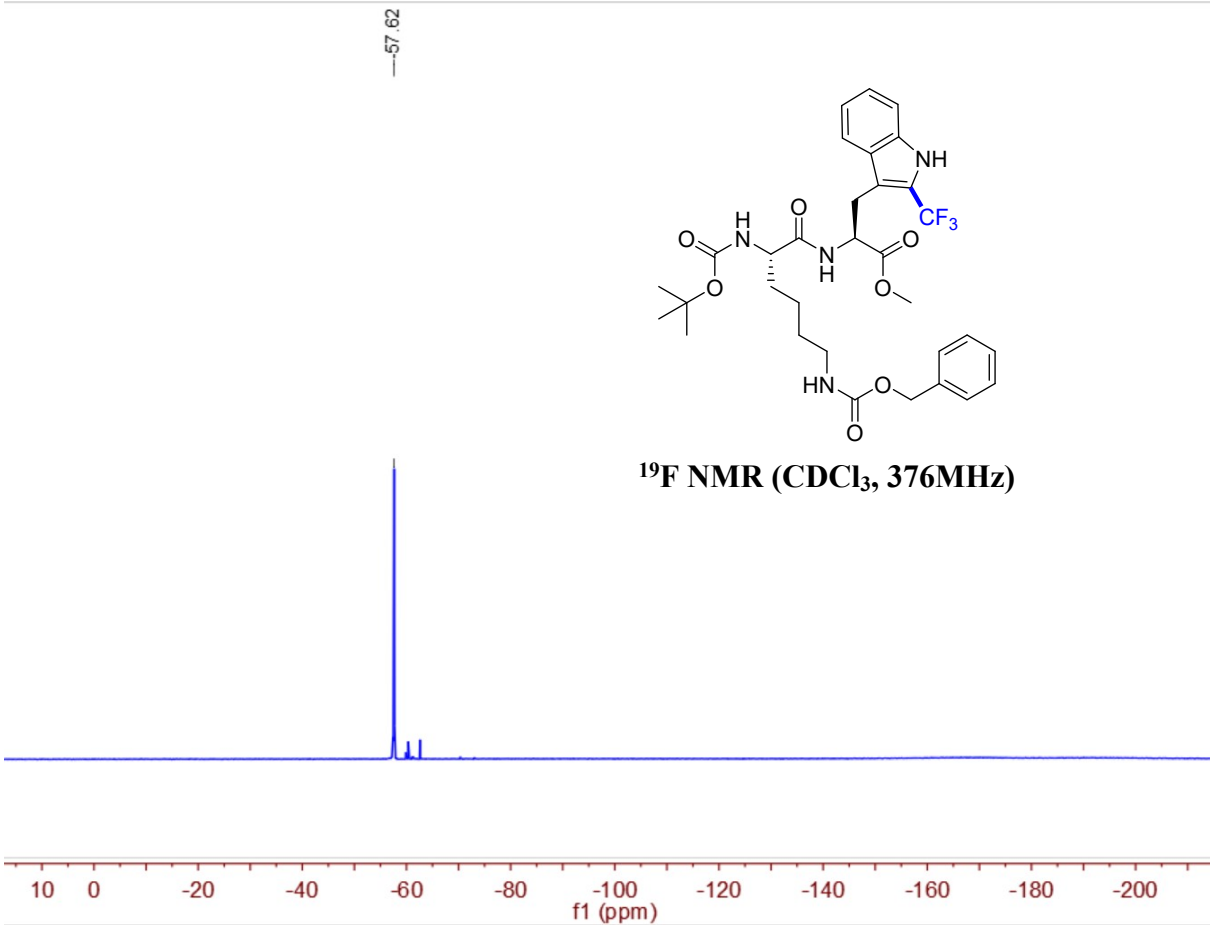
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 3aq

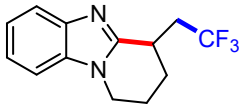


^{13}C NMR ($CDCl_3$, 101MHz)

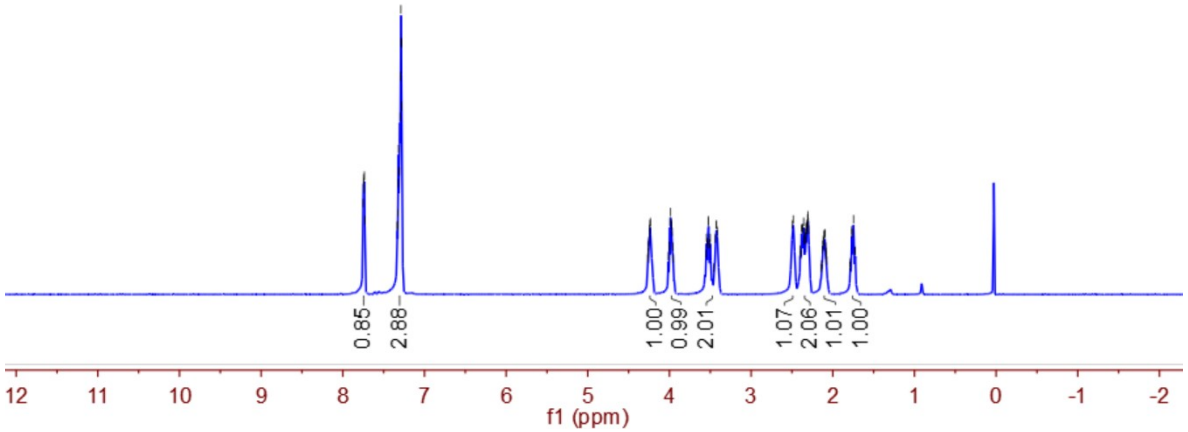
^{13}C NMR Spectrum of Compound 3aq



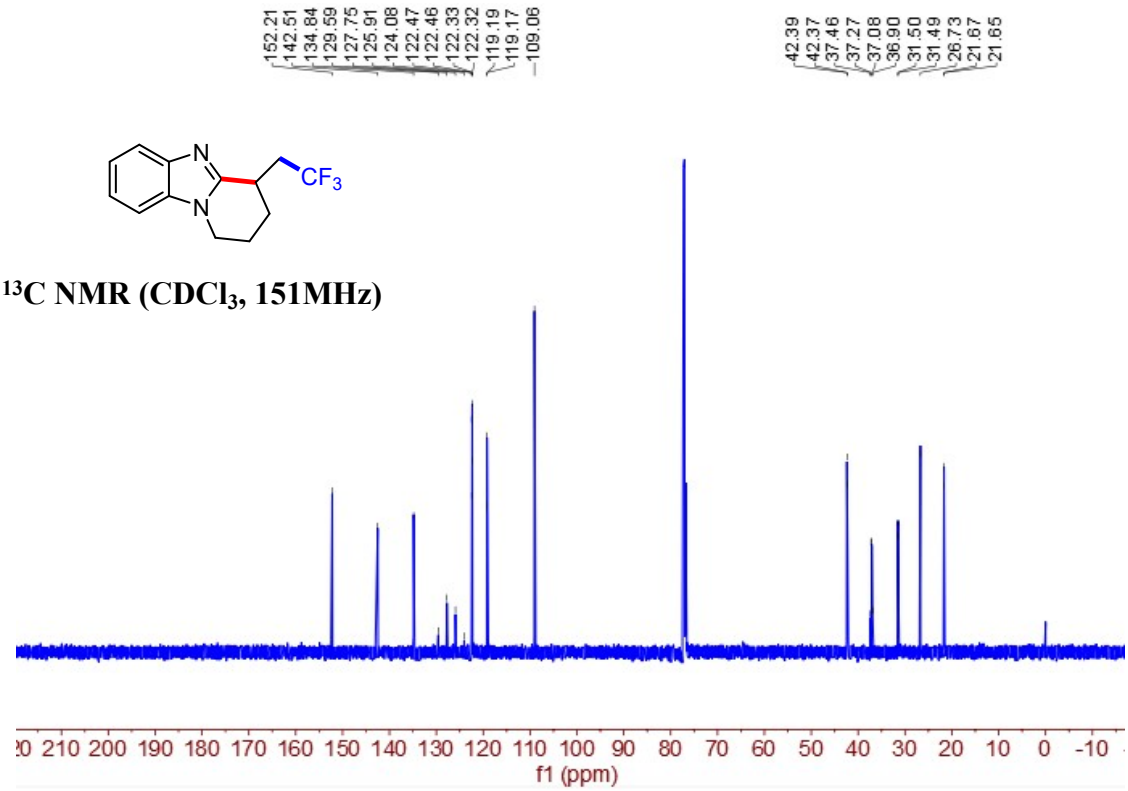
^{19}F NMR Spectrum of Compound 3aq



^{1}H NMR (CDCl$_3$, 600MHz)

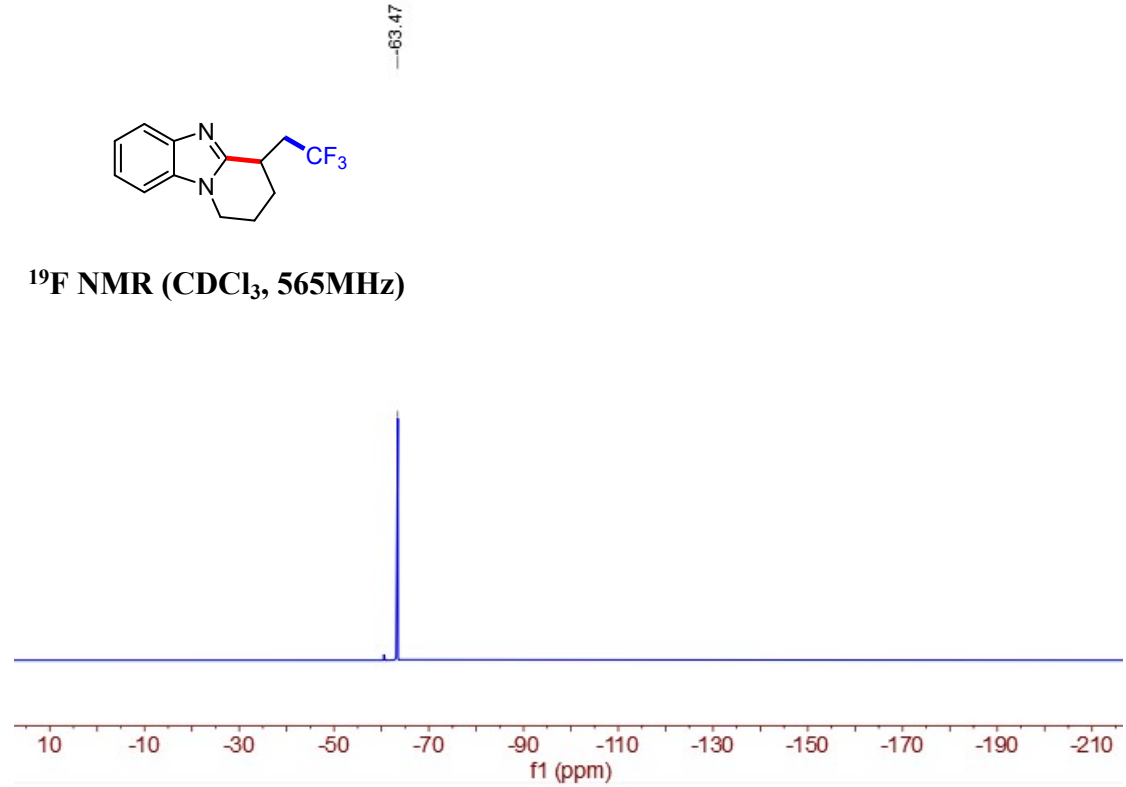


^{1}H NMR Spectrum of Compound 5a



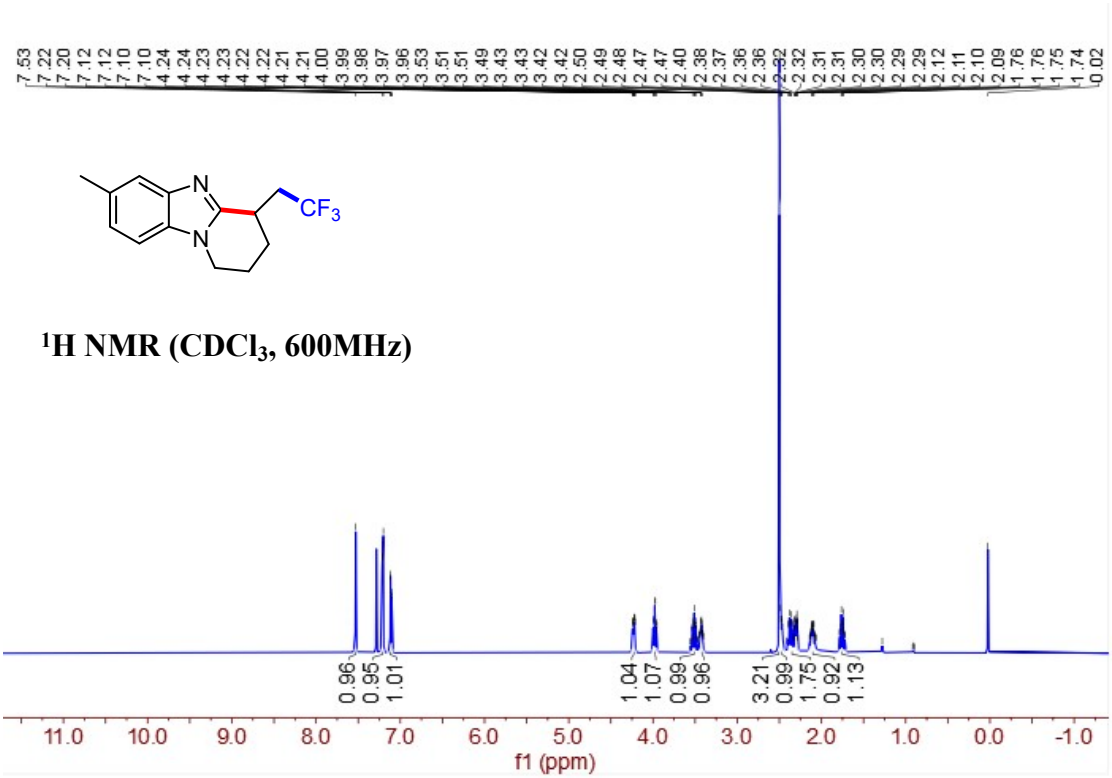
^{13}C NMR ($CDCl_3$, 151MHz)

^{13}C NMR Spectrum of Compound 5a



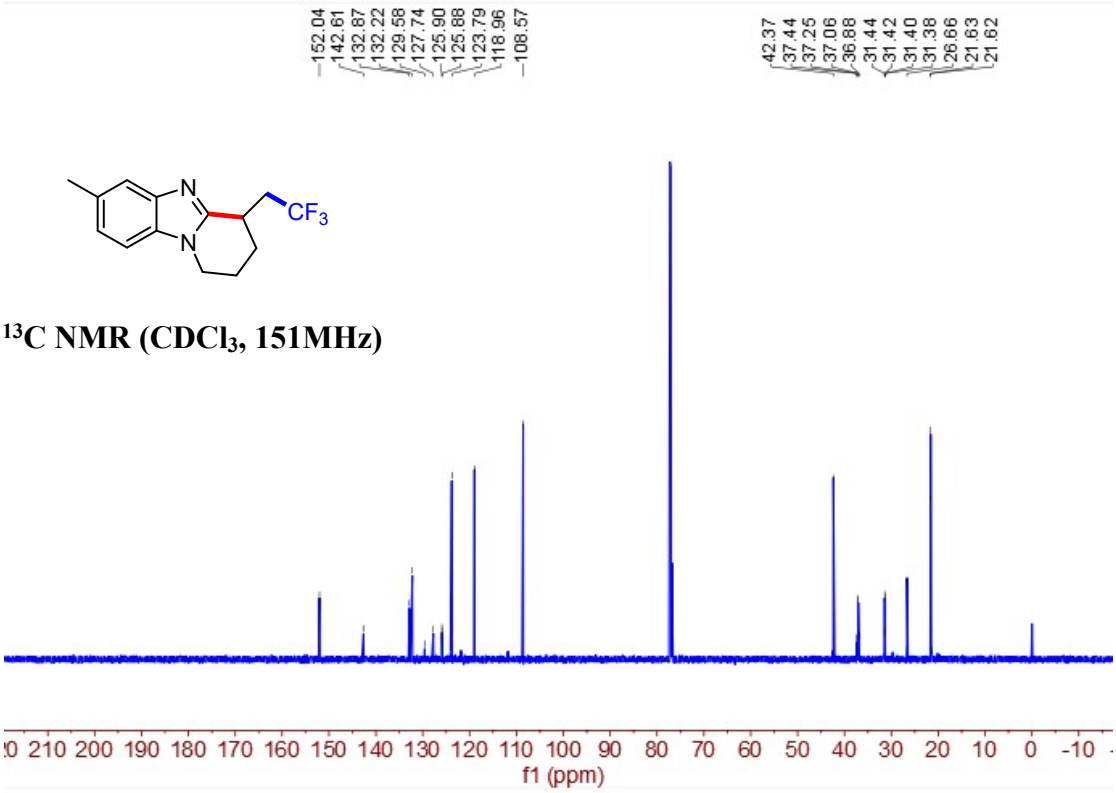
^{19}F NMR ($CDCl_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5a



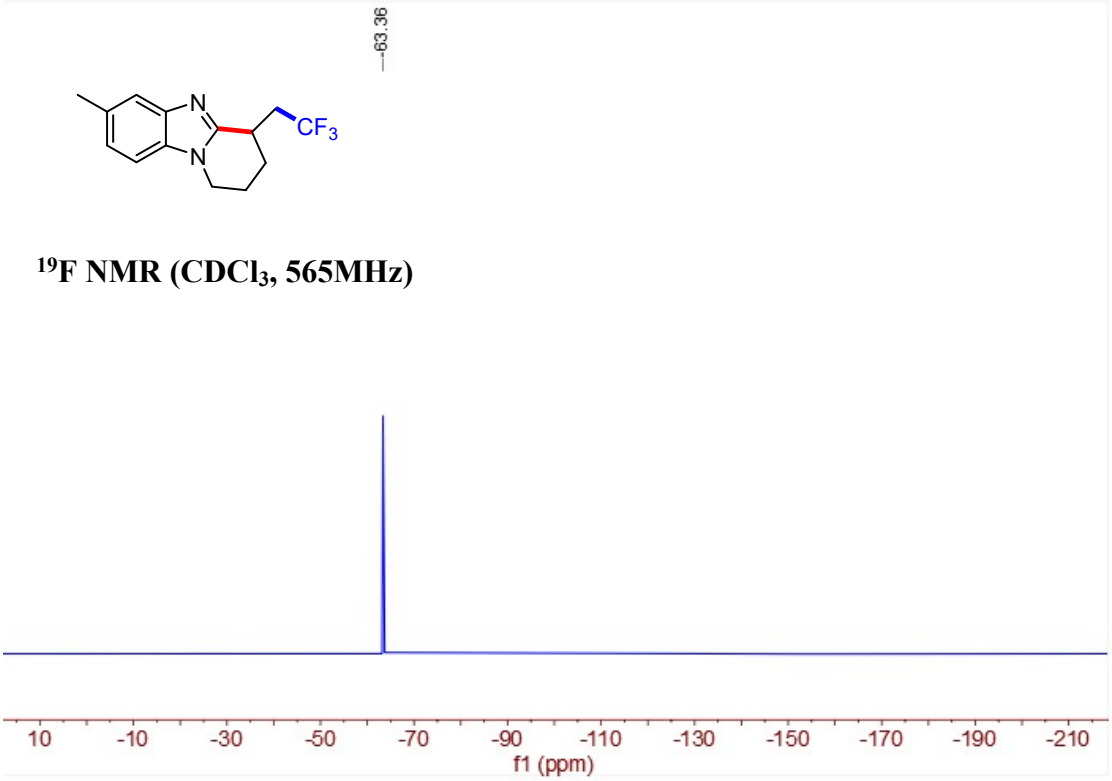
^{1}H NMR (CDCl$_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5b



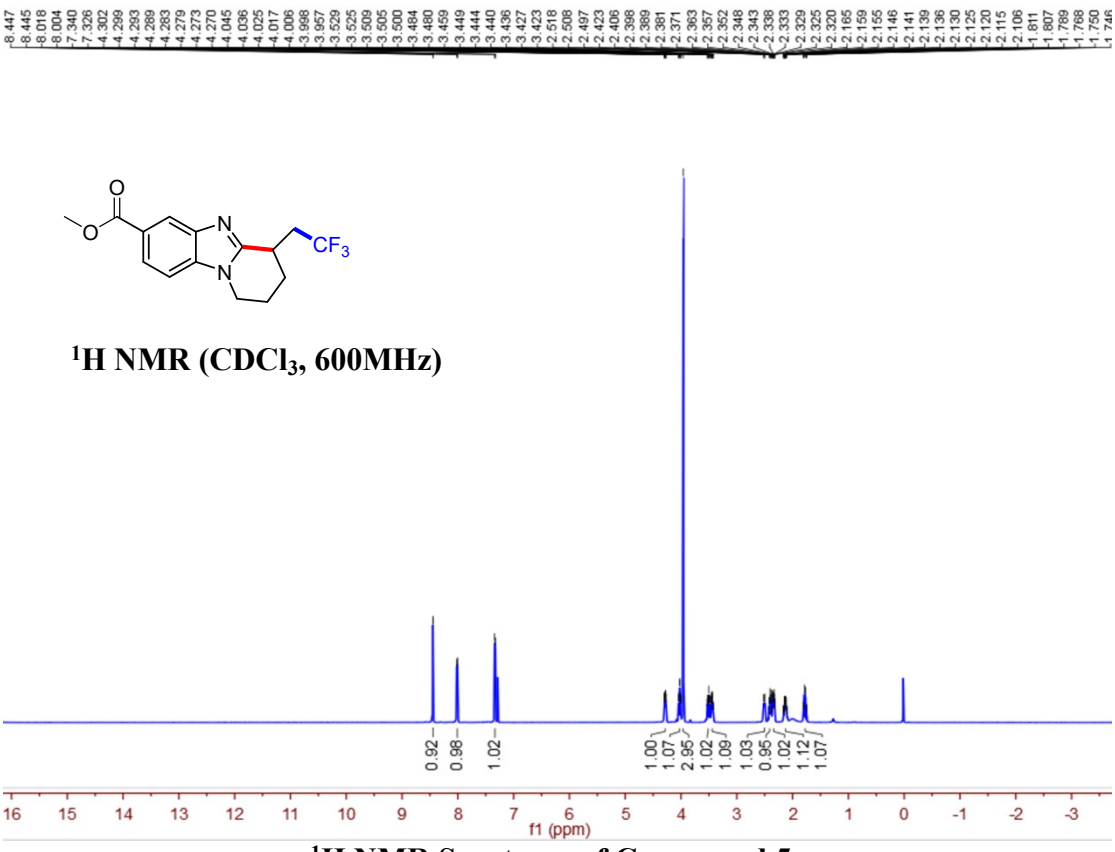
^{13}C NMR (CDCl$_3$, 151MHz)

^{13}C NMR Spectrum of Compound 5b



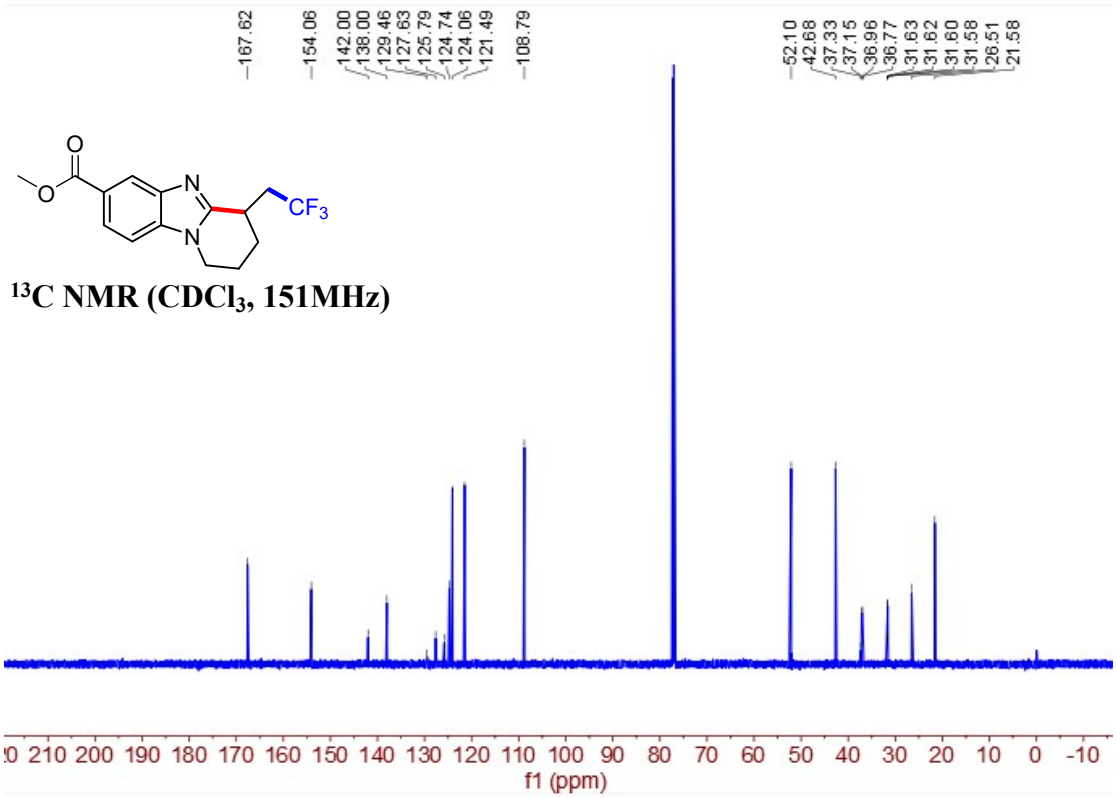
^{19}F NMR (CDCl$_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5b



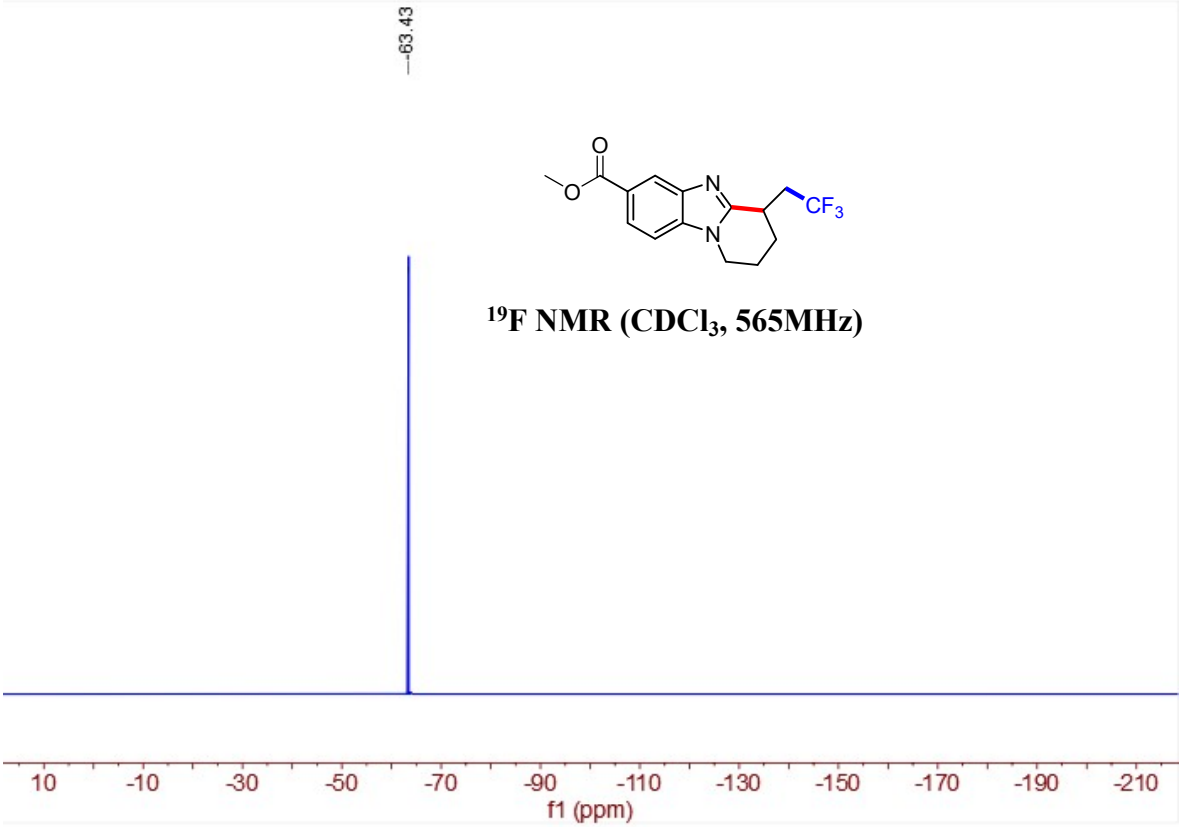
^{1}H NMR (CDCl$_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5c



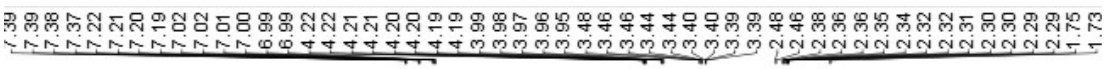
^{13}C NMR ($CDCl_3$, 151MHz)

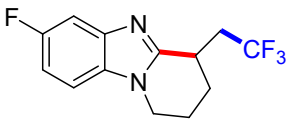
^{13}C NMR Spectrum of Compound 5c



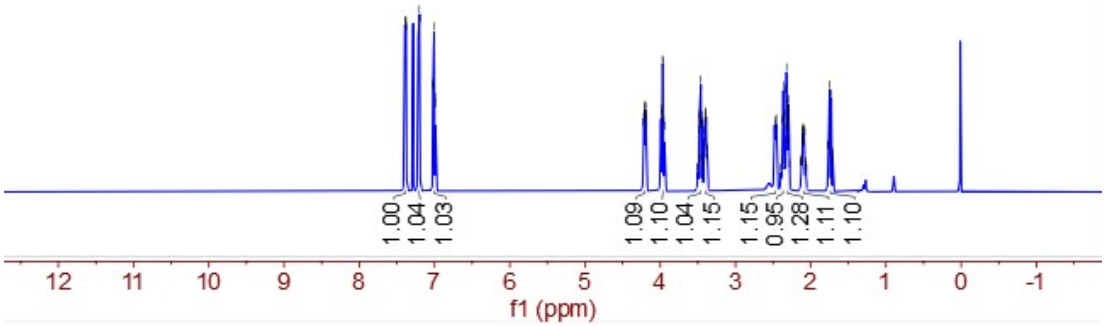
^{19}F NMR ($CDCl_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5c

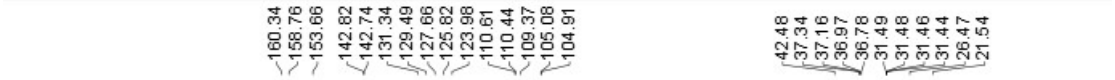


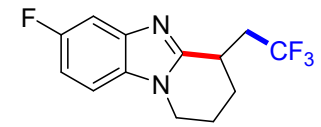


^{1}H NMR ($CDCl_3$, 600MHz)

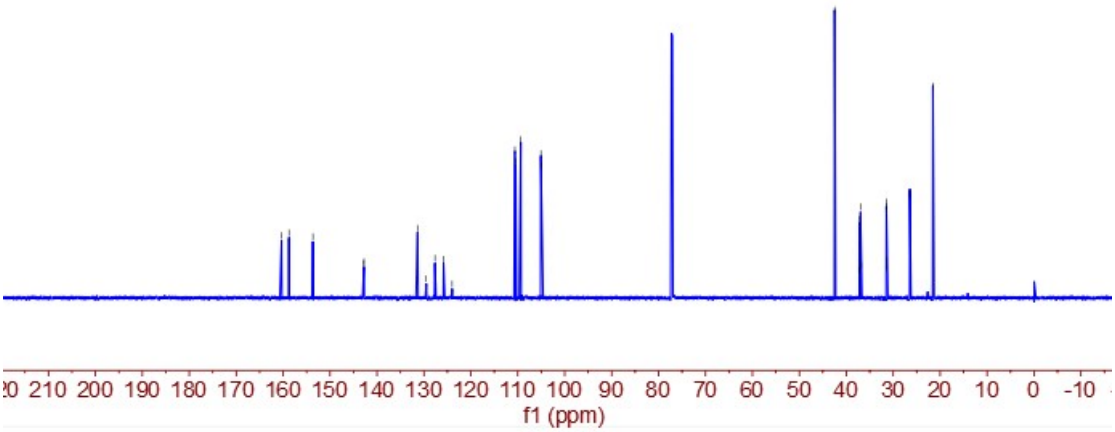


^{1}H NMR Spectrum of Compound 5d

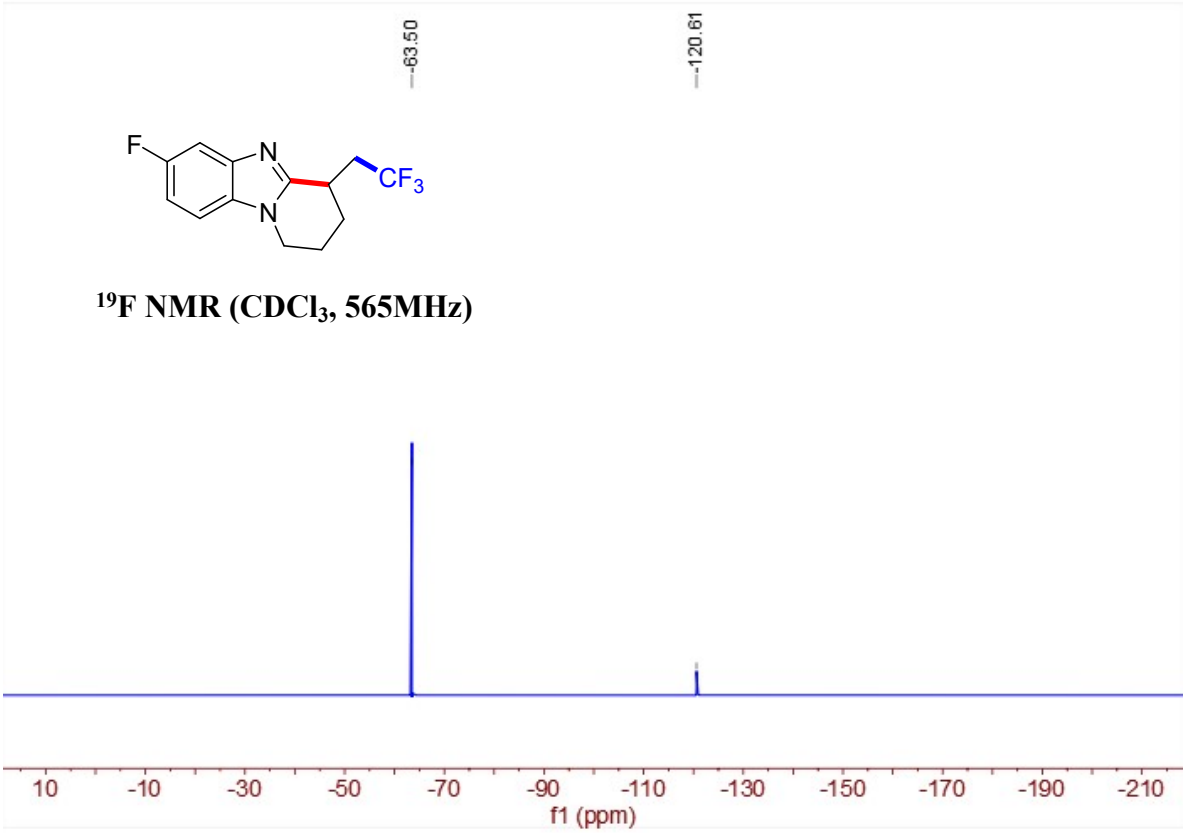




^{13}C NMR ($CDCl_3$, 151MHz)

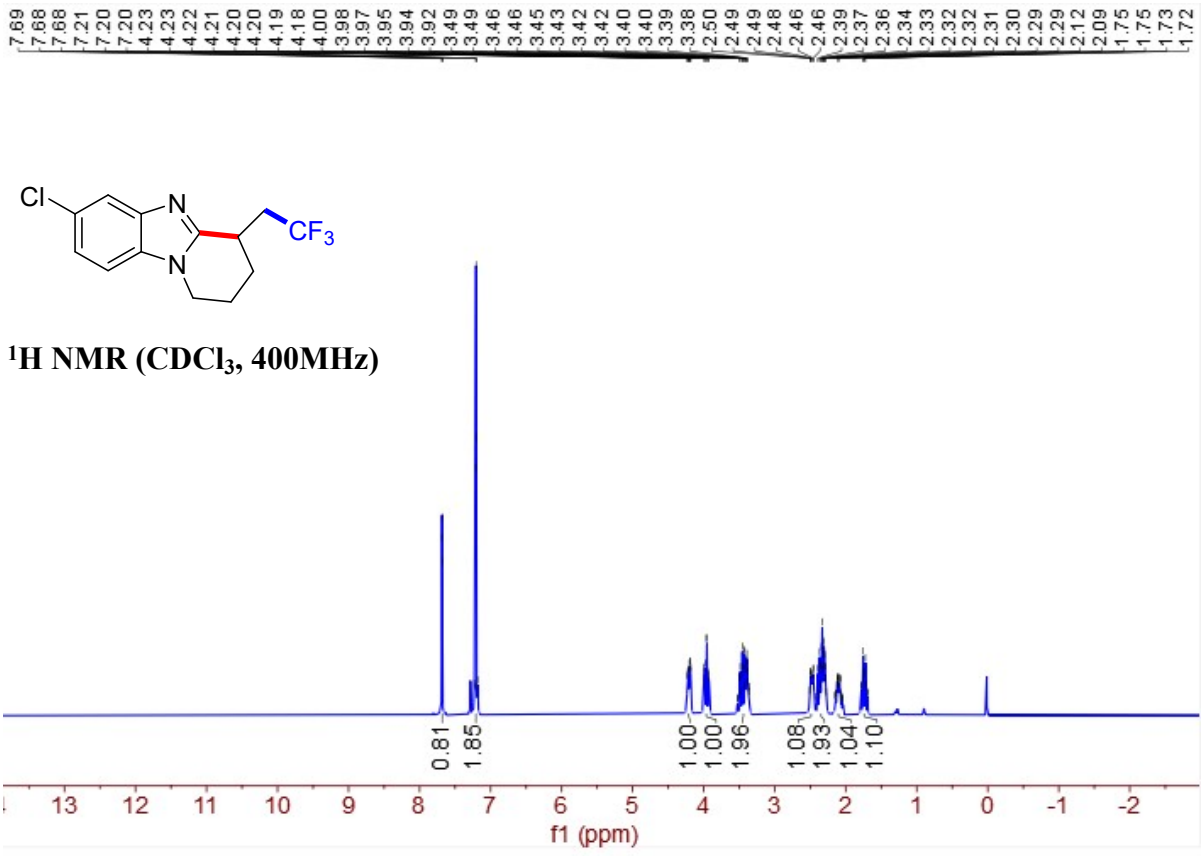


^{13}C NMR Spectrum of Compound 5d



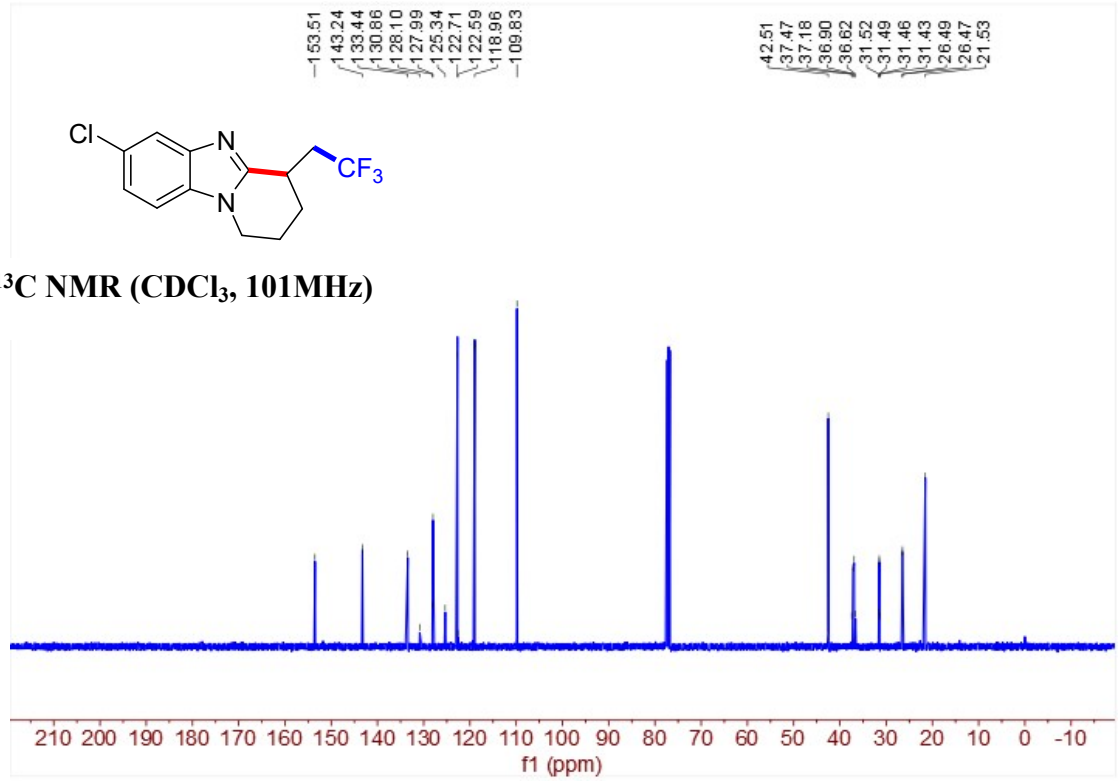
^{19}F NMR ($CDCl_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5d



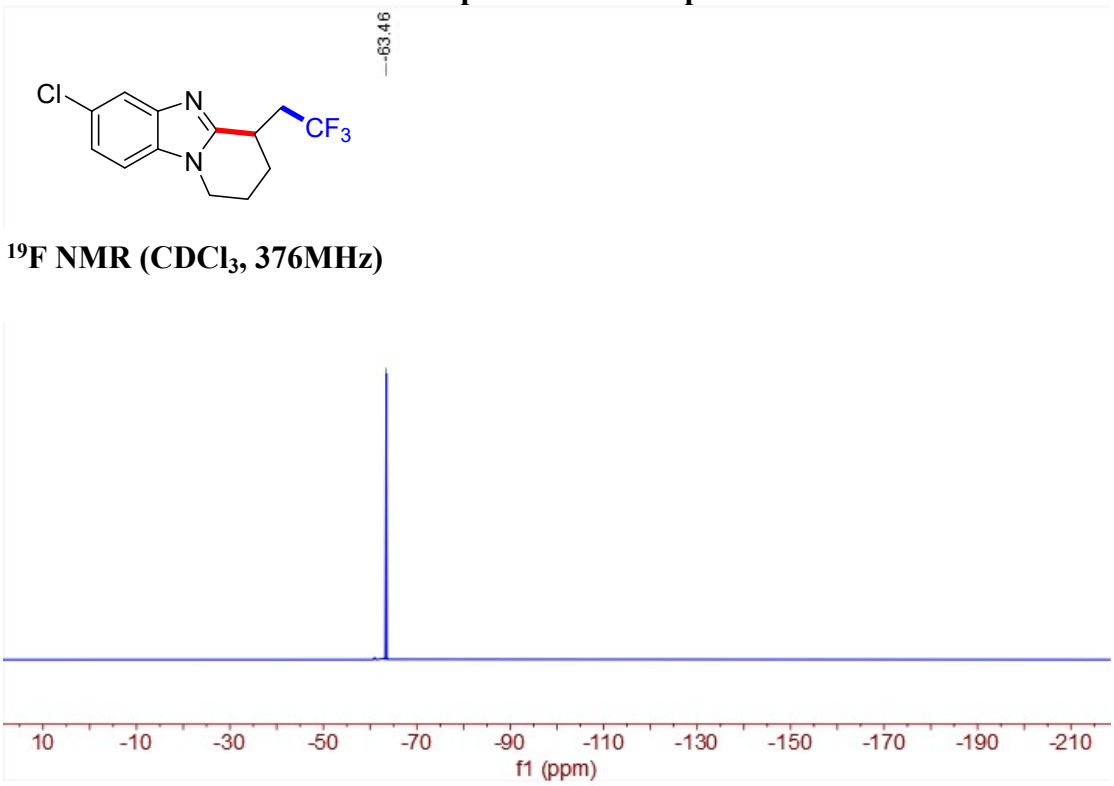
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5e



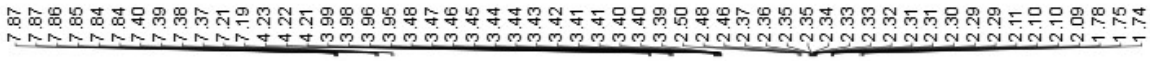
^{13}C NMR ($CDCl_3$, 101MHz)

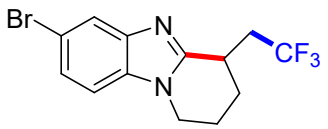
^{13}C NMR Spectrum of Compound 5e



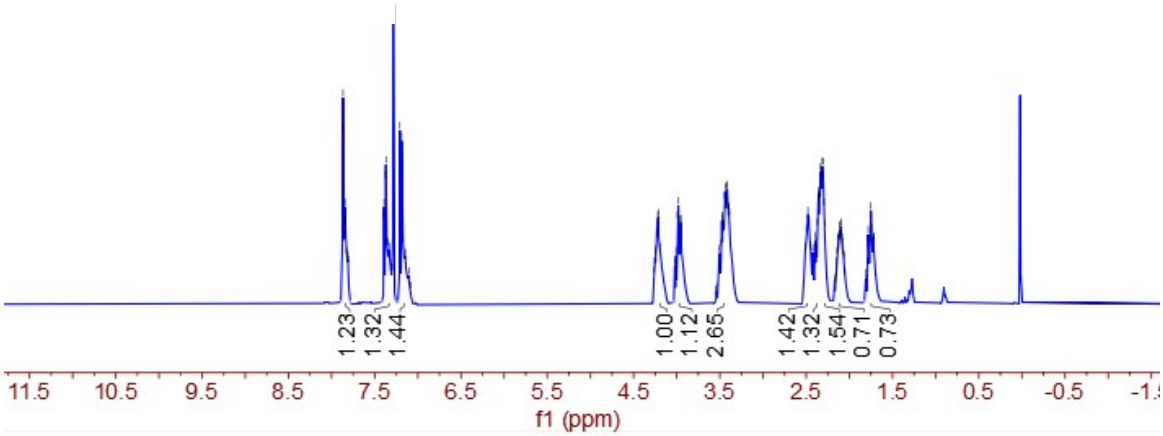
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5e





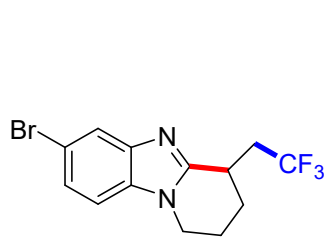
^{1}H NMR ($CDCl_3$, 400MHz)



^{1}H NMR Spectrum of Compound 5f

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

^{13}C NMR Spectrum of Compound 5f

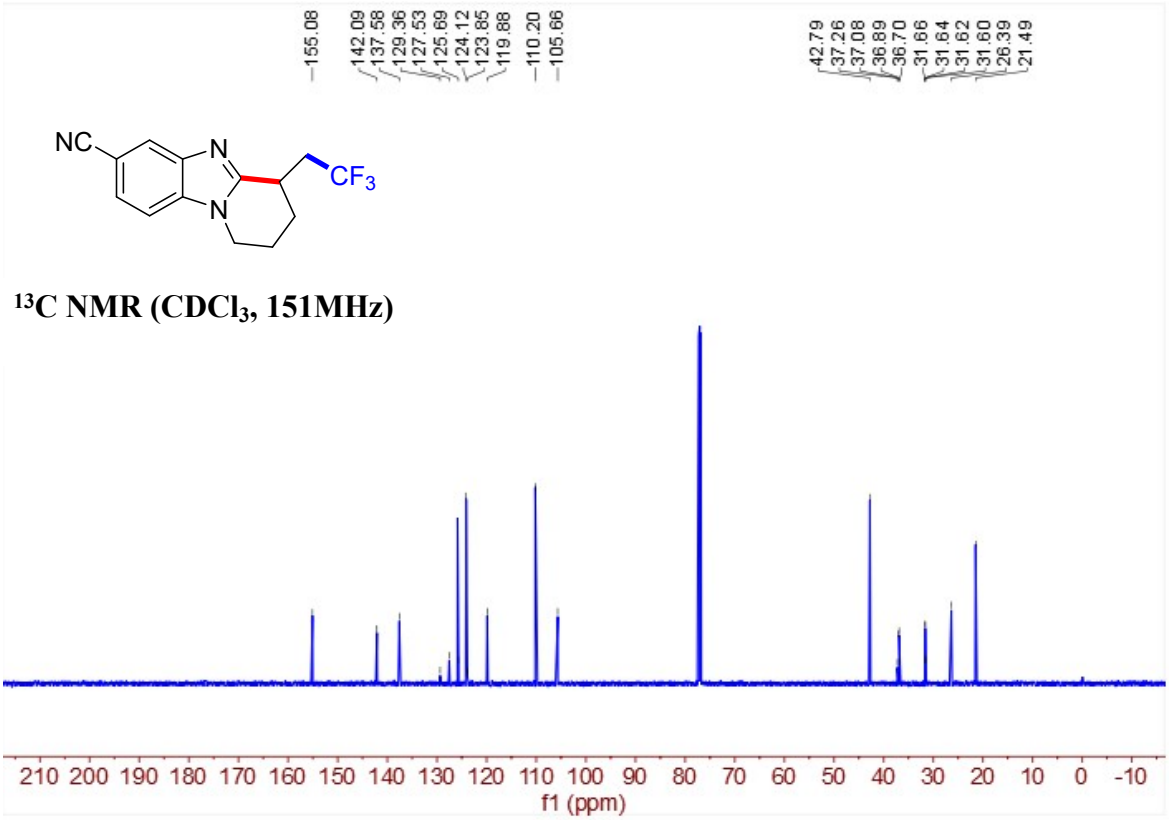


^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5f

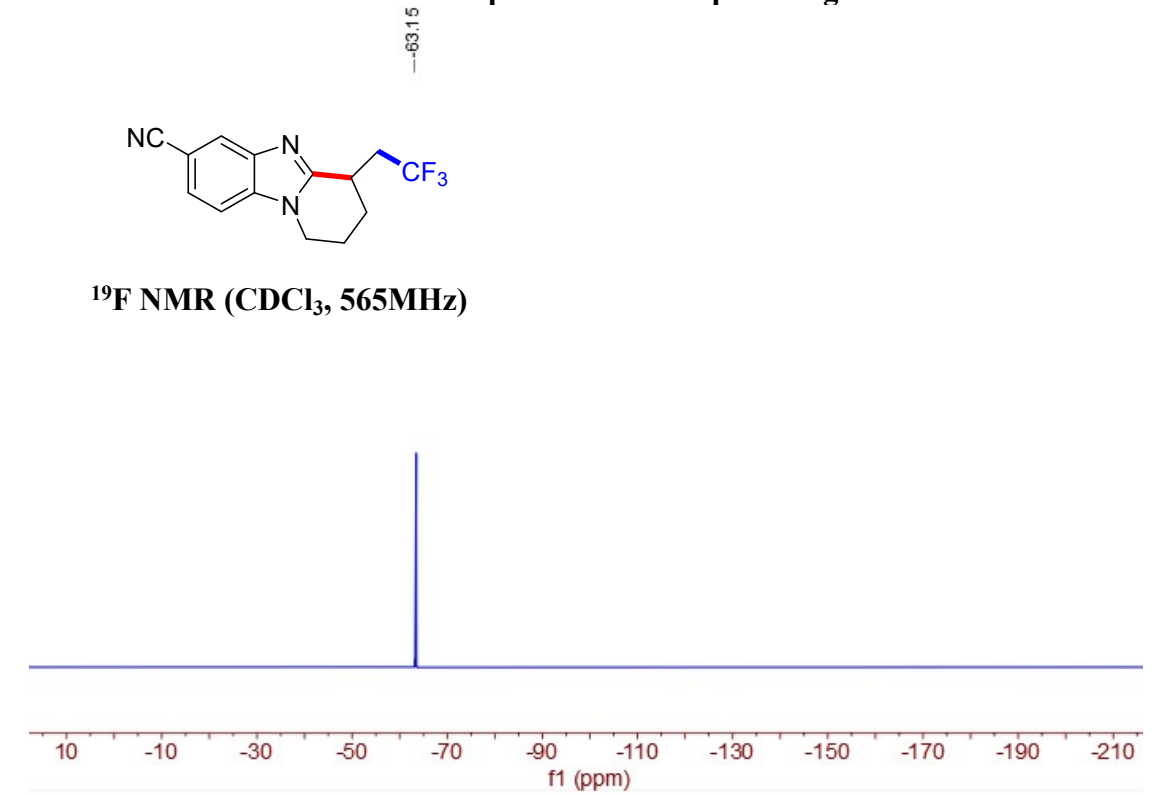
^{1}H NMR ($CDCl_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5g



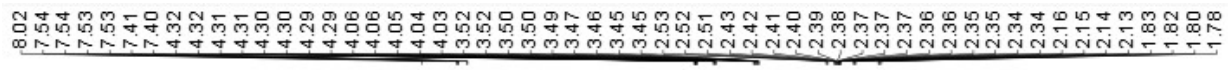
^{13}C NMR ($CDCl_3$, 151MHz)

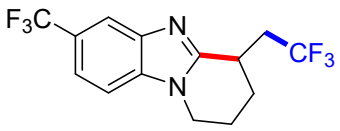
^{13}C NMR Spectrum of Compound 5g



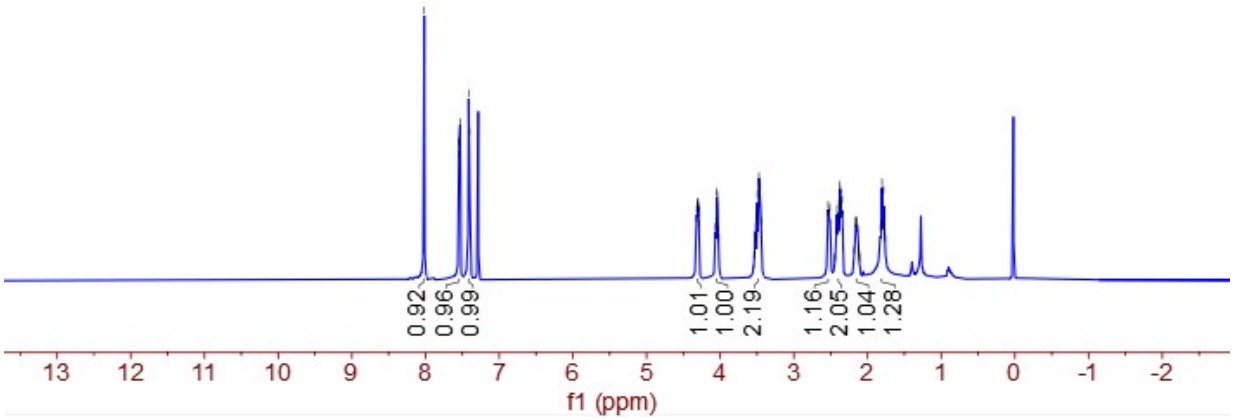
^{19}F NMR ($CDCl_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5g

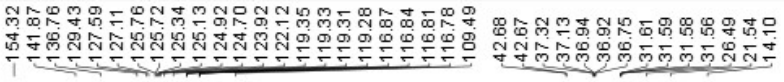


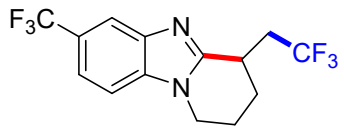


^{1}H NMR ($CDCl_3$, 600MHz)

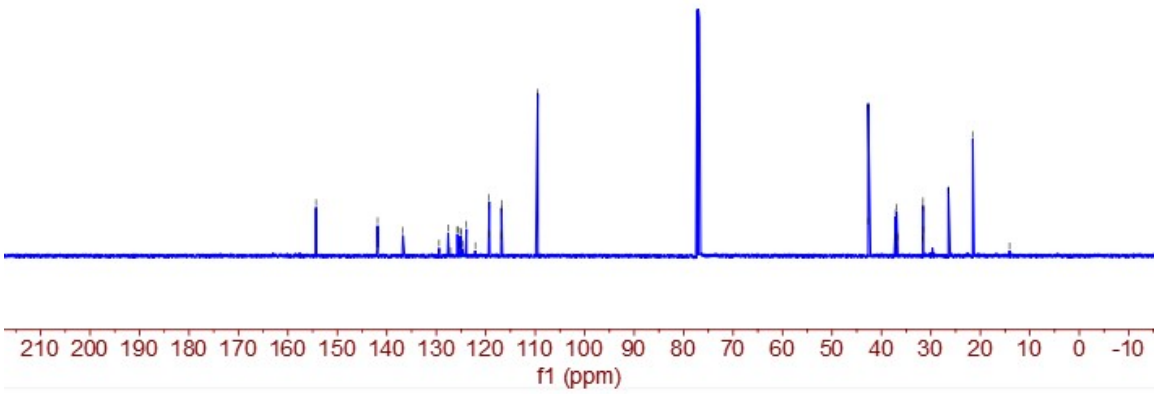


^{1}H NMR Spectrum of Compound 5h

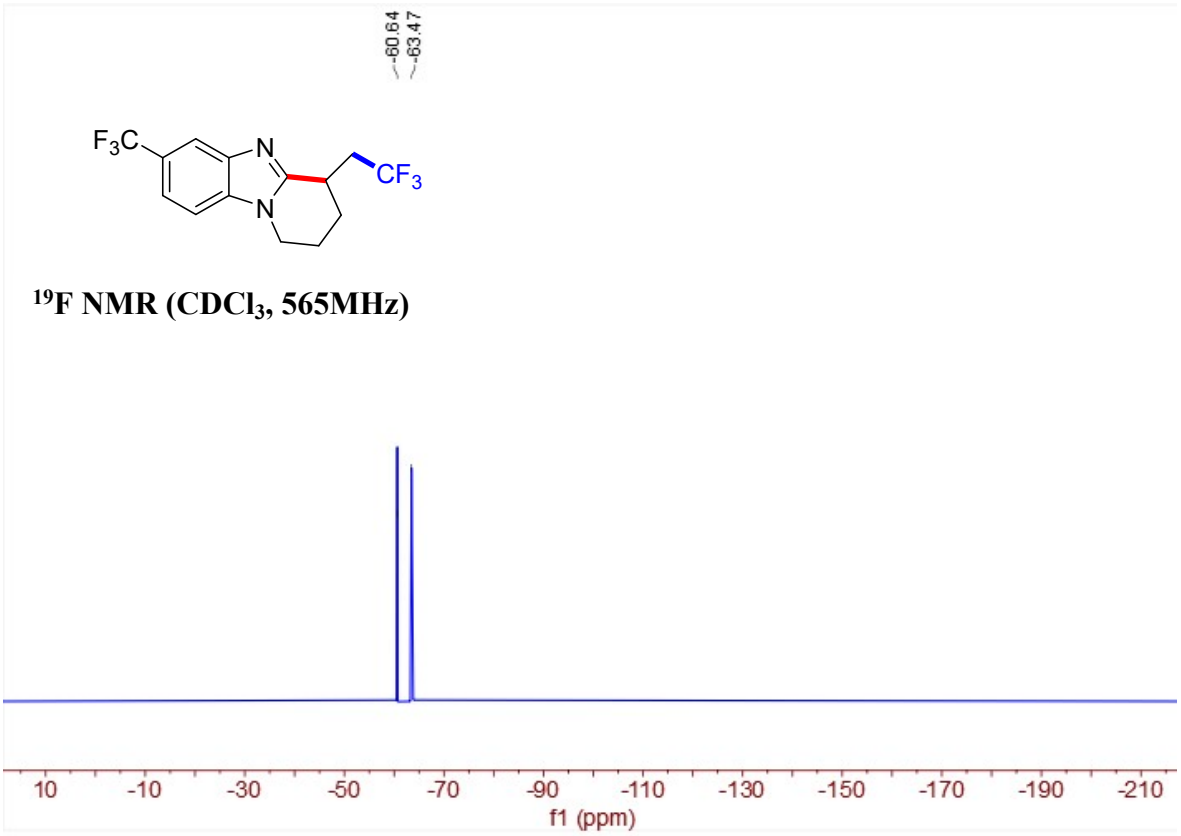




^{13}C NMR ($CDCl_3$, 151MHz)

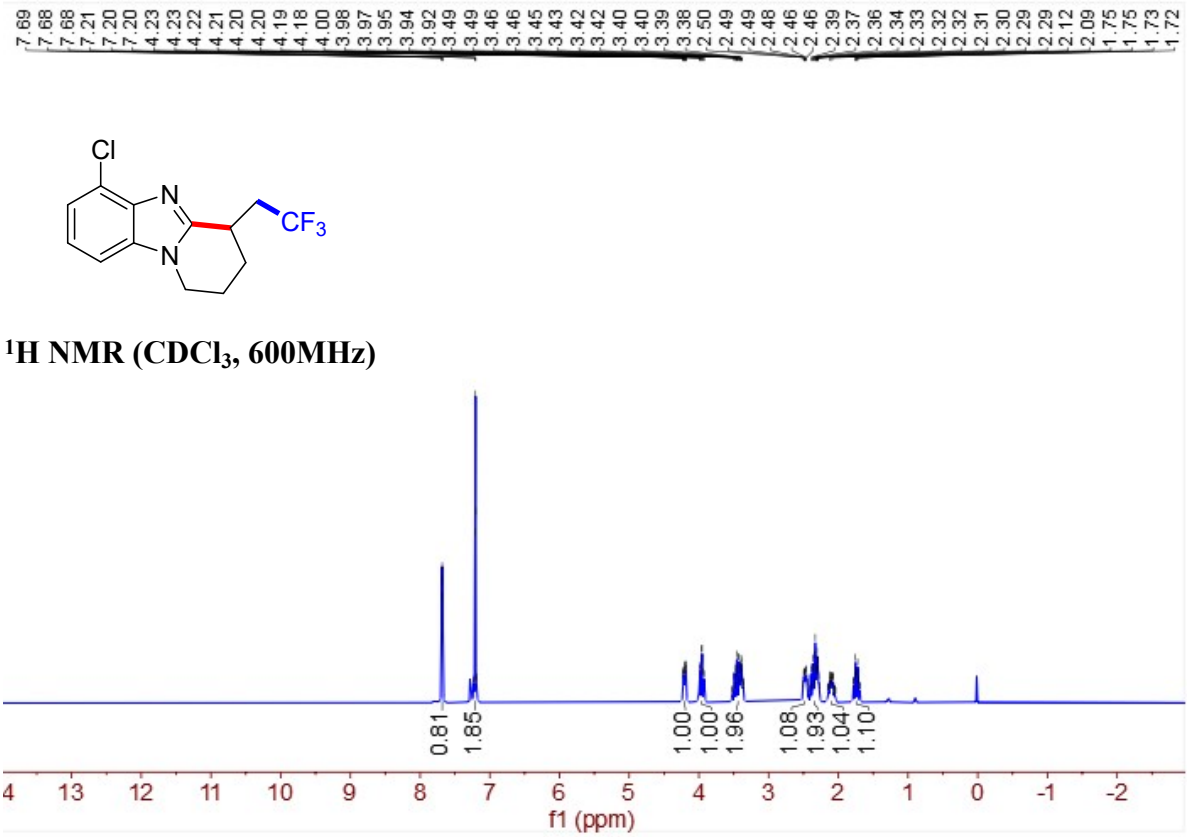


^{13}C NMR Spectrum of Compound 5h



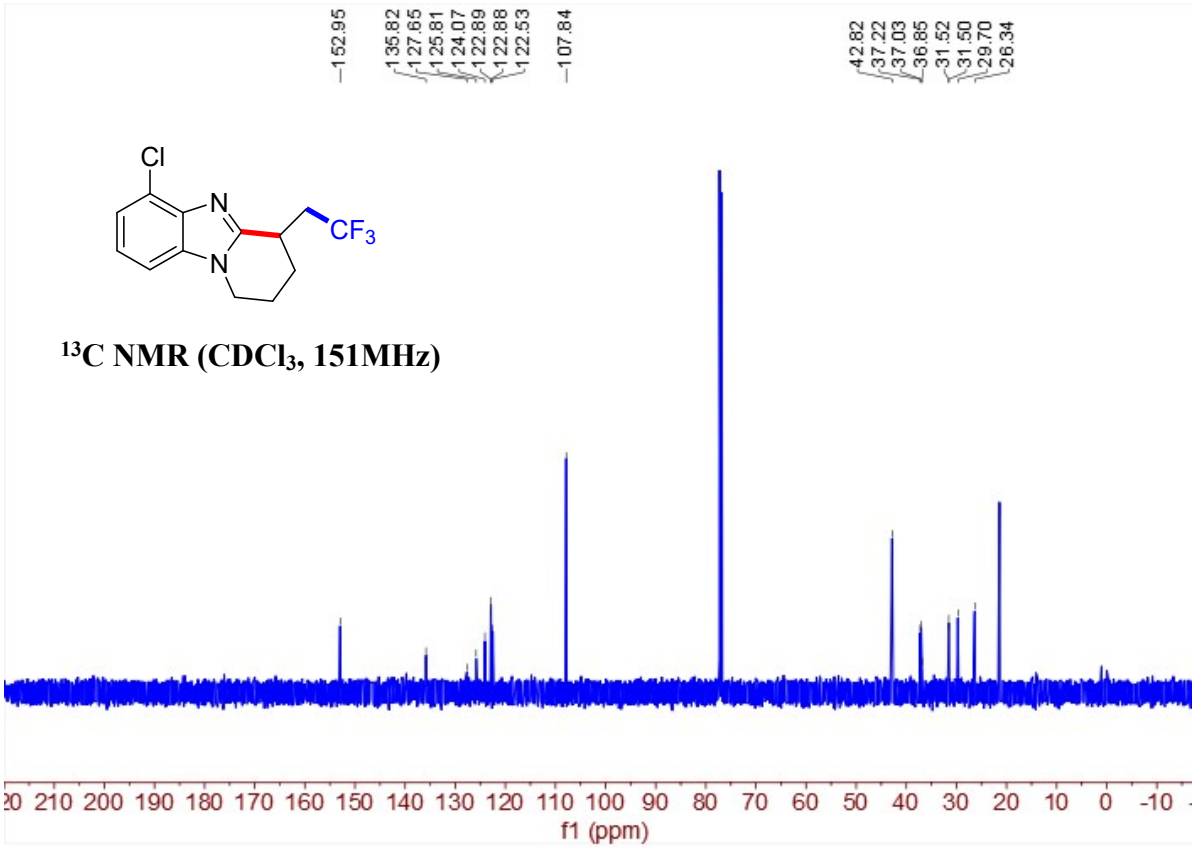
^{19}F NMR (CDCl$_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5h



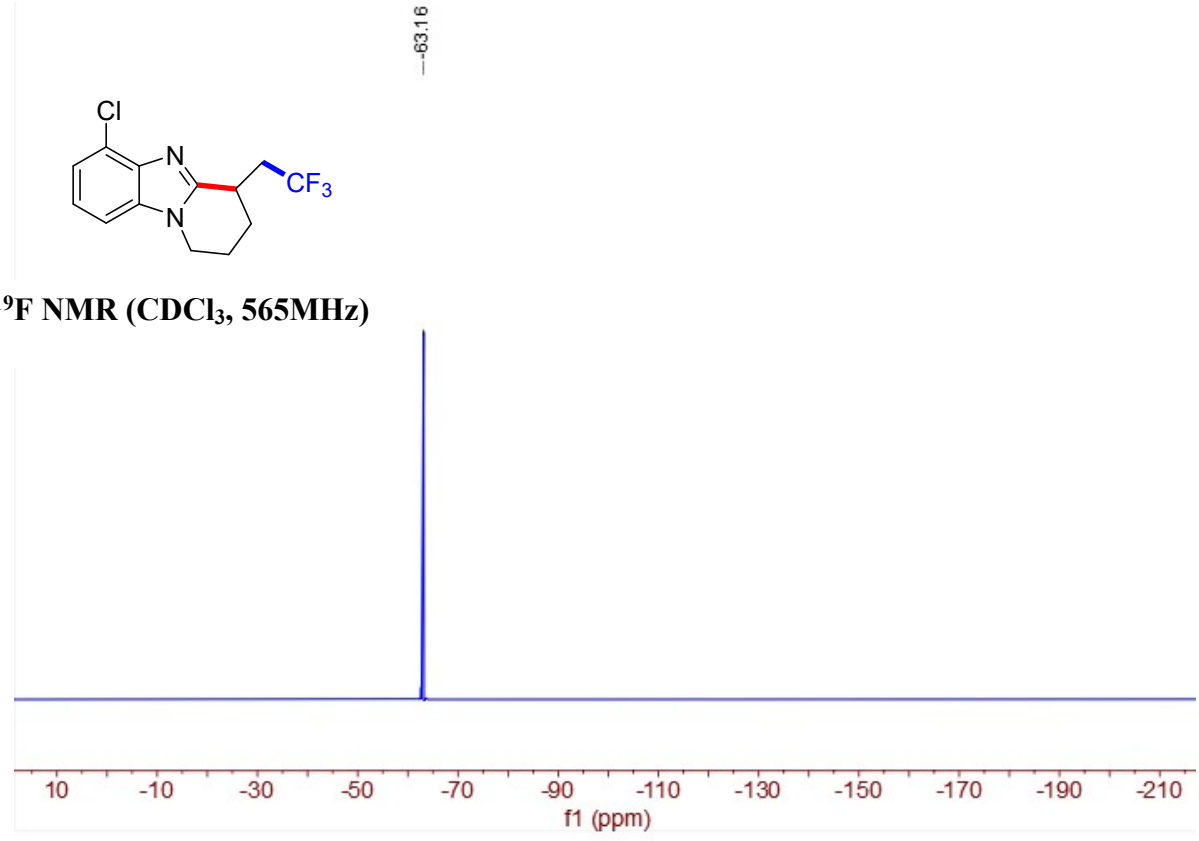
^{1}H NMR (CDCl$_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5i



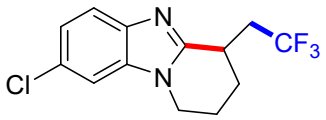
^{13}C NMR ($CDCl_3$, 151MHz)

^{13}C NMR Spectrum of Compound 5i

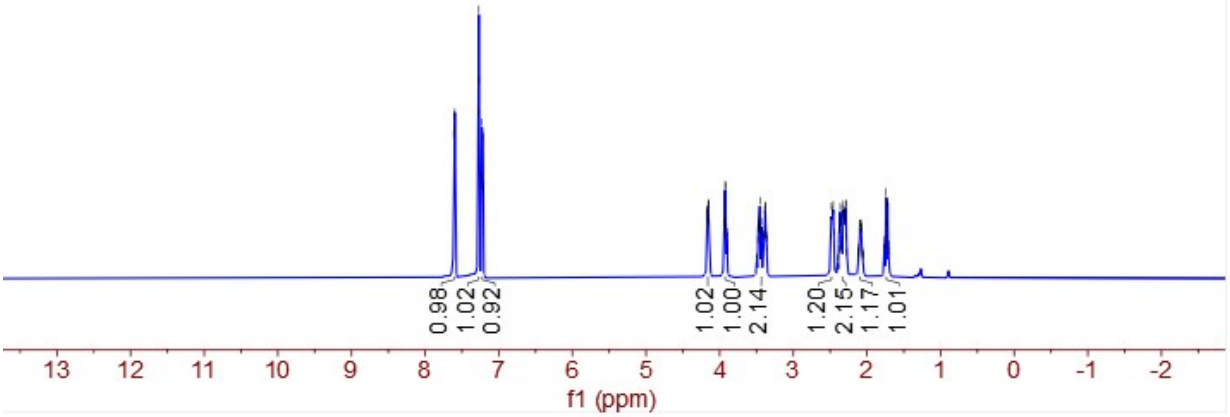


^{19}F NMR ($CDCl_3$, 565MHz)

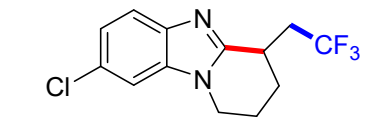
^{19}F NMR Spectrum of Compound 5i



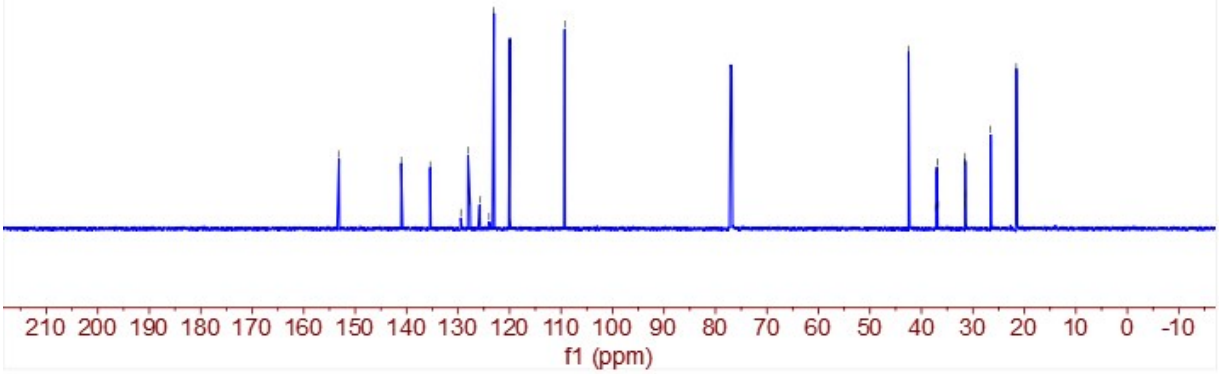
^{1}H NMR ($CDCl_3$, 600MHz)



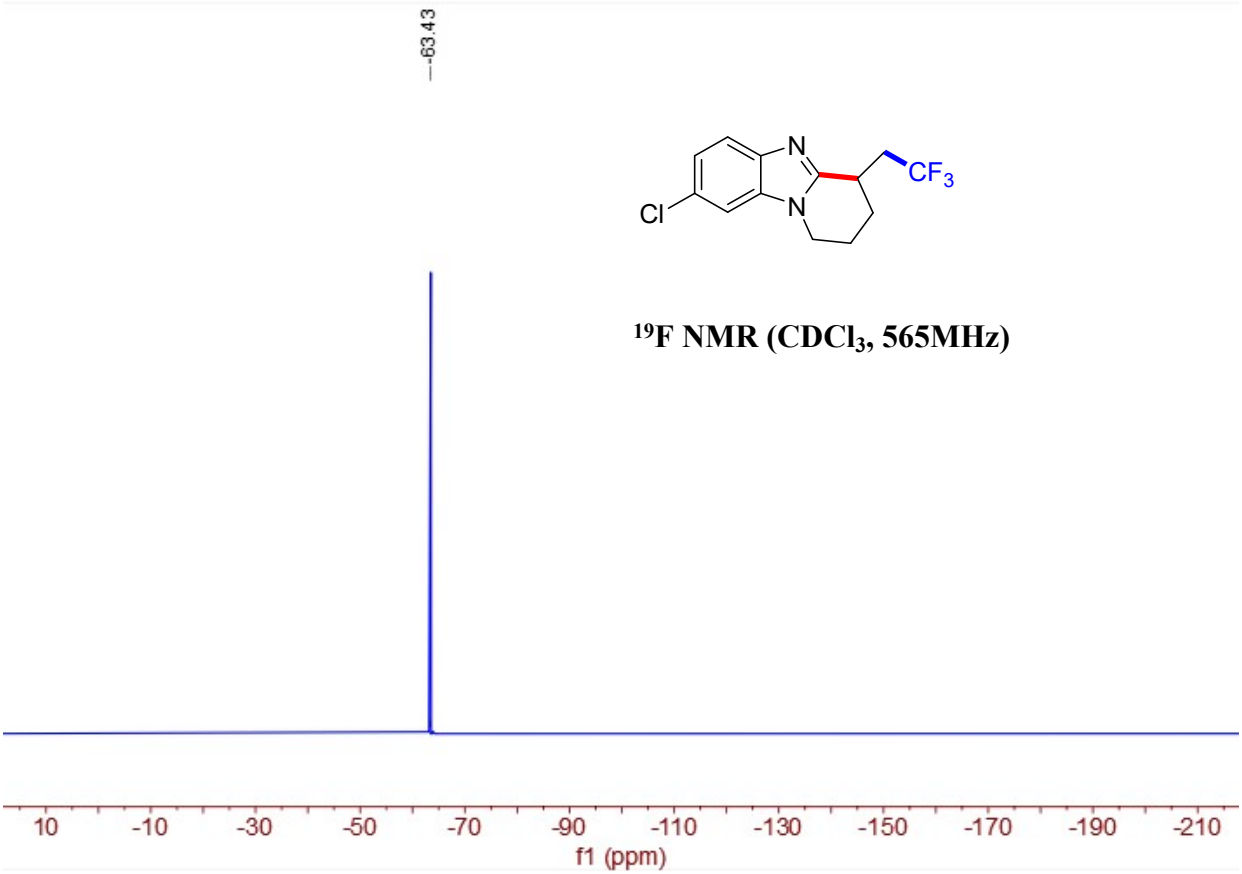
^{1}H NMR Spectrum of Compound 5j



^{13}C NMR ($CDCl_3$, 151MHz)

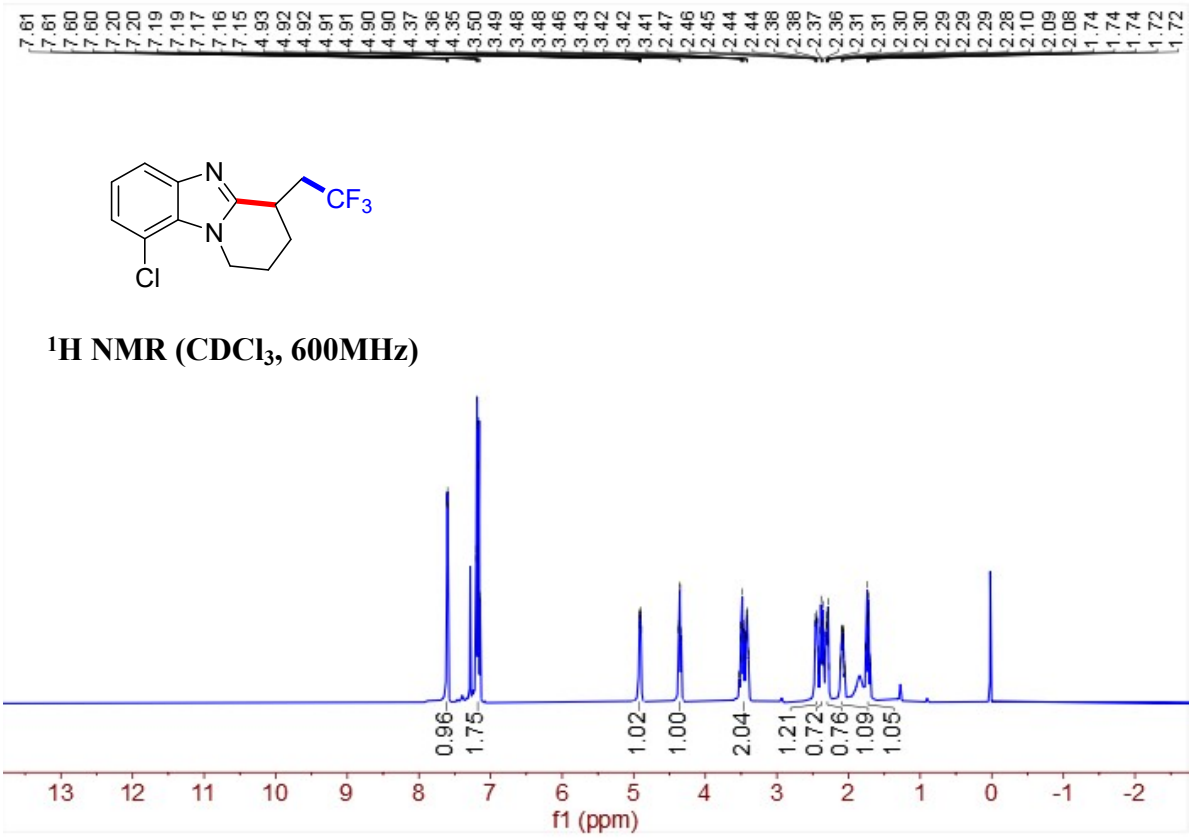


^{13}C NMR Spectrum of Compound 5j



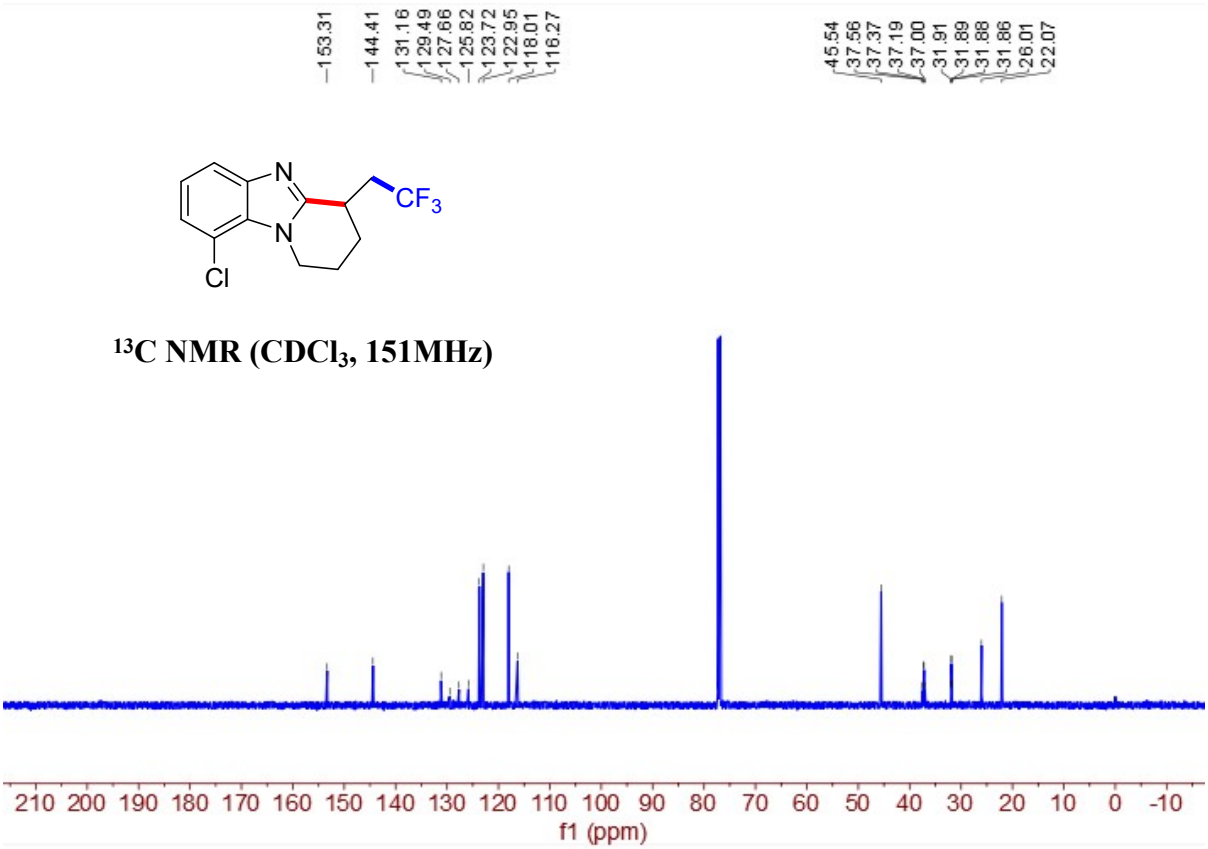
^{19}F NMR ($CDCl_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5j



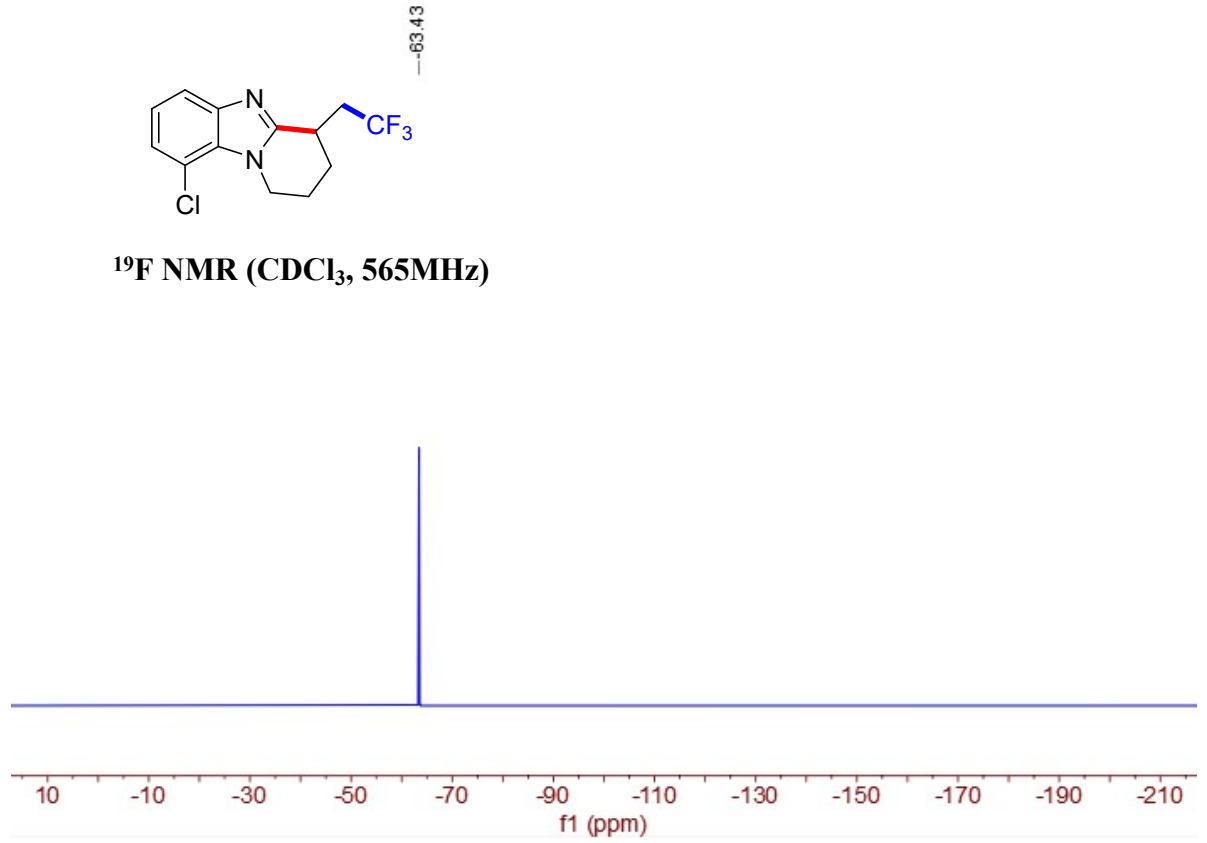
^{1}H NMR ($CDCl_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5k



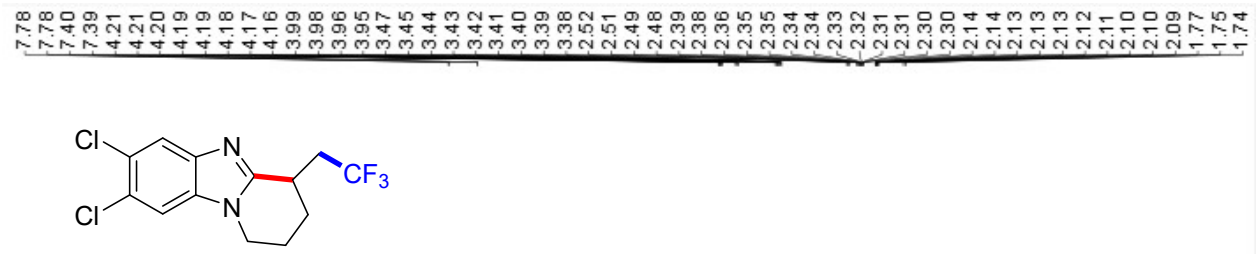
^{13}C NMR ($CDCl_3$, 151MHz)

^{13}C NMR Spectrum of Compound 5k

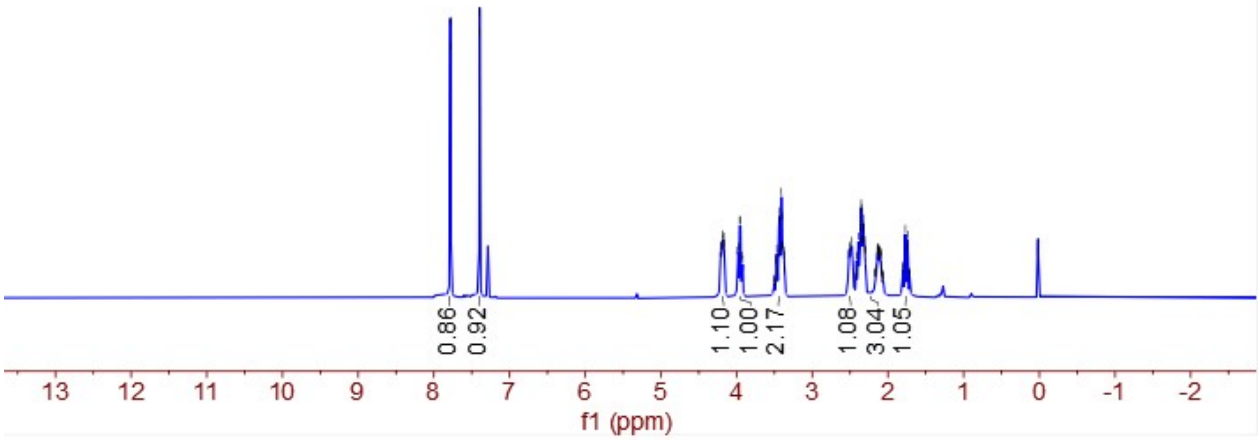


^{19}F NMR ($CDCl_3$, 565MHz)

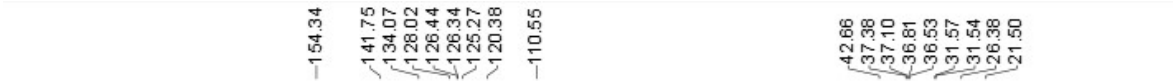
^{19}F NMR Spectrum of Compound 5k

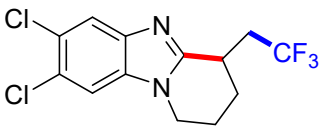


^{1}H NMR ($CDCl_3$, 400MHz)

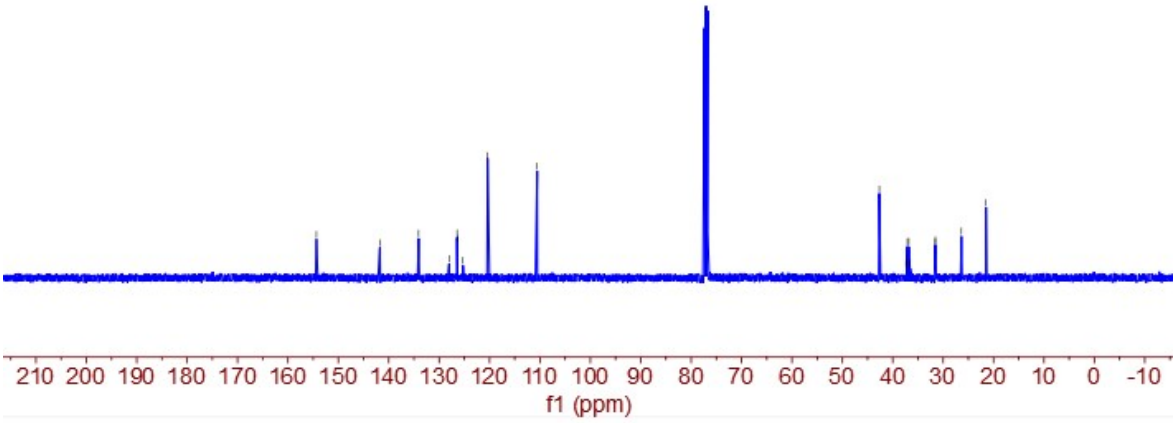


^{1}H NMR Spectrum of Compound 5l

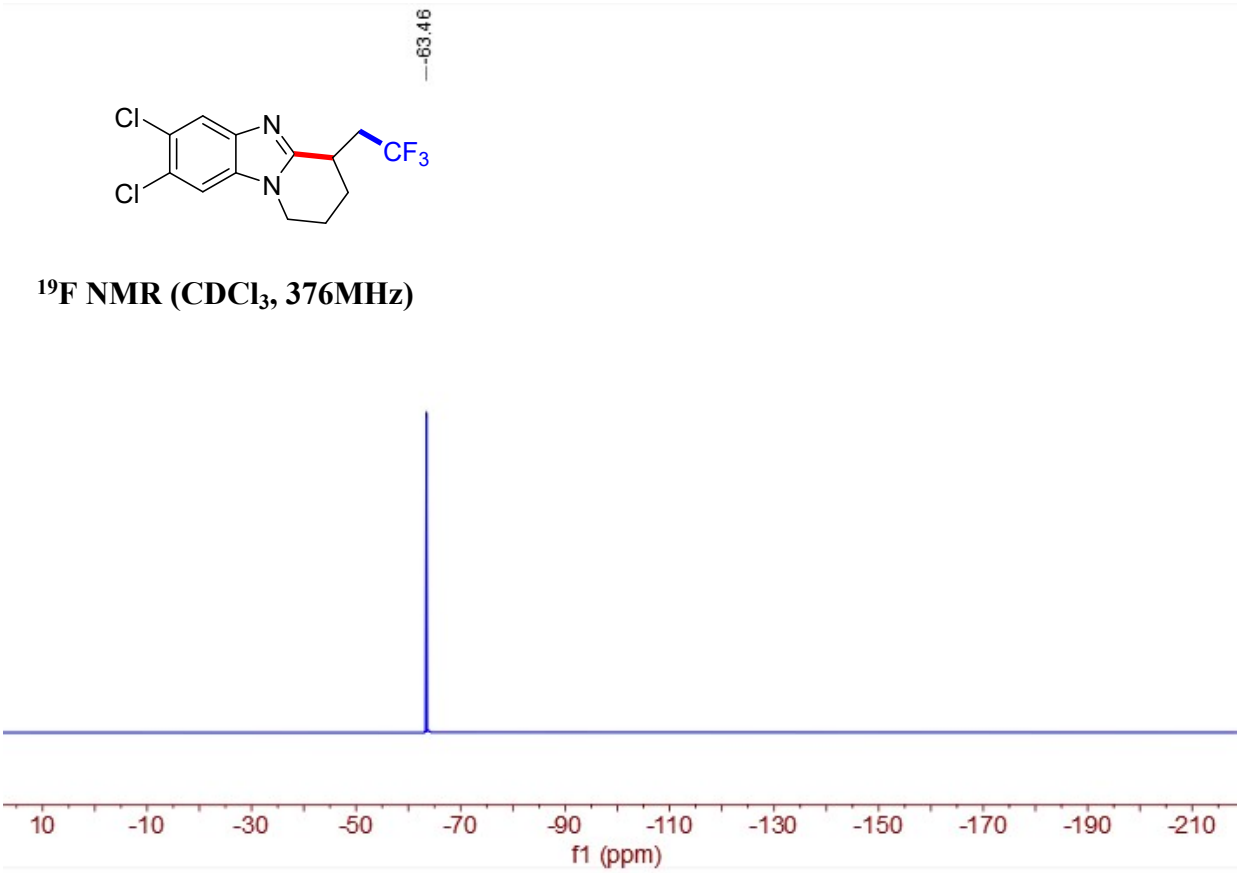




^{13}C NMR ($CDCl_3$, 101MHz)

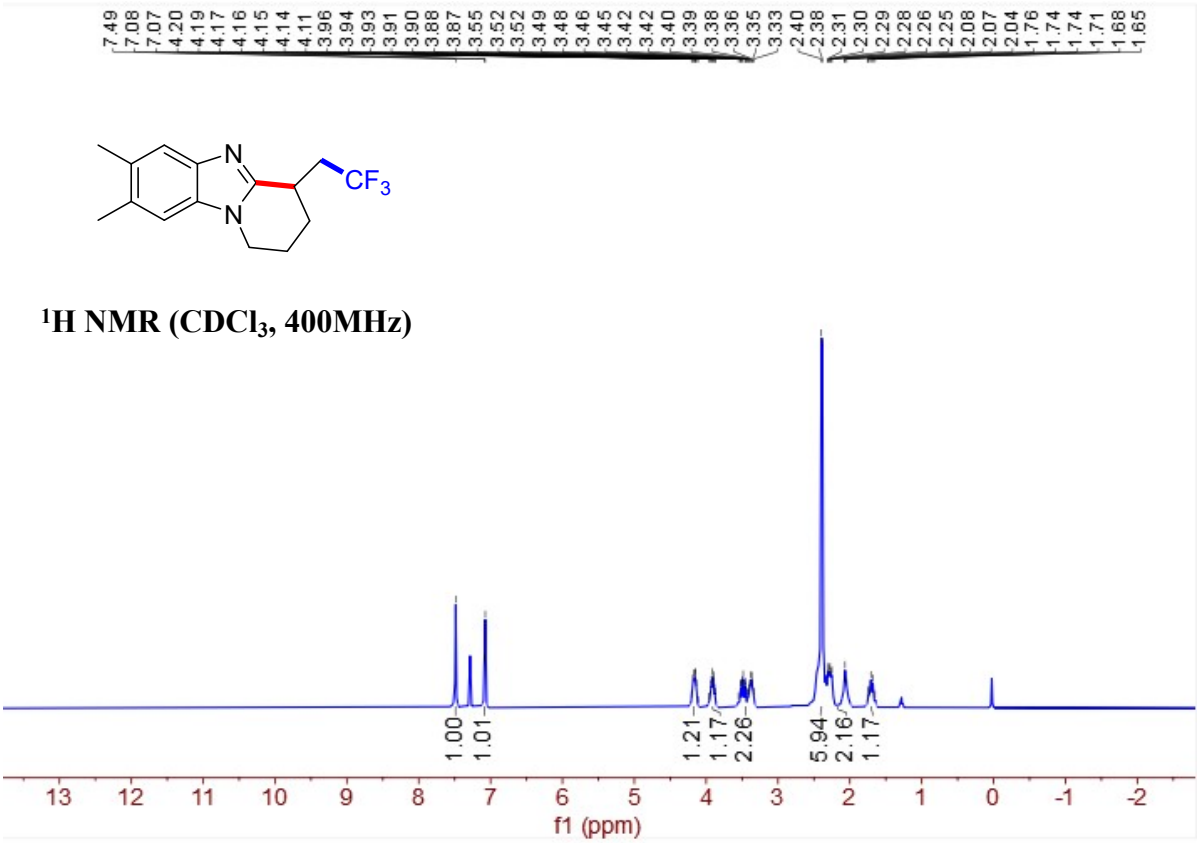


^{13}C NMR Spectrum of Compound 5l



^{19}F NMR ($CDCl_3$, 376MHz)

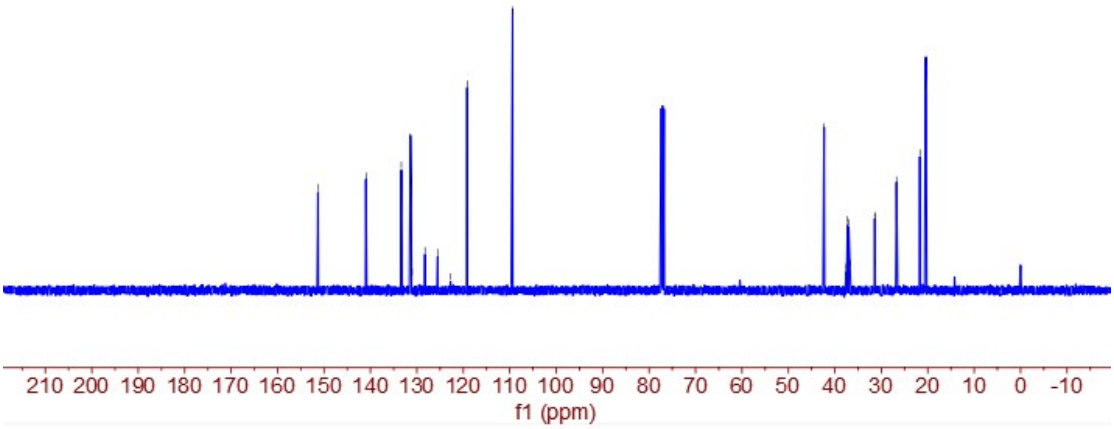
^{19}F NMR Spectrum of Compound 5l



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

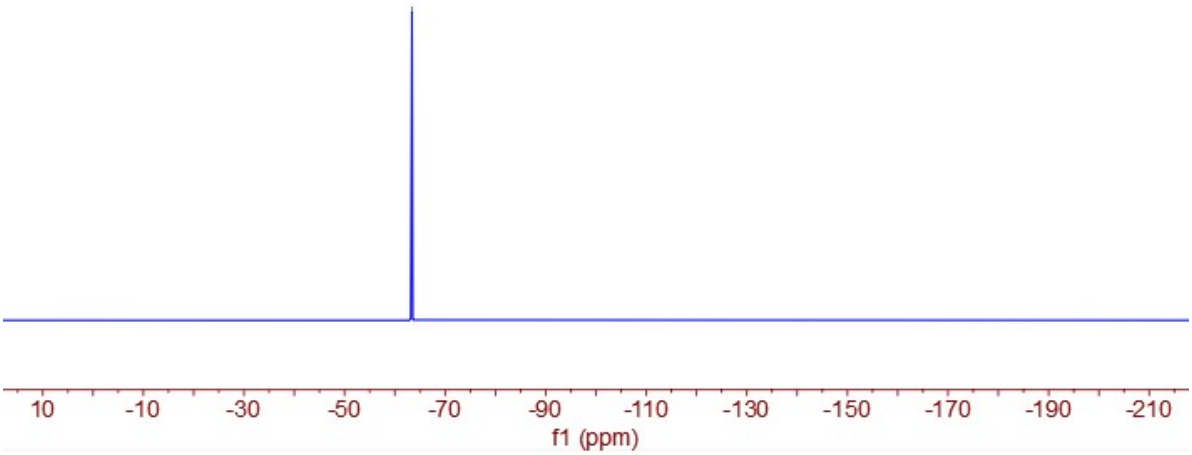
^{1}H NMR Spectrum of Compound 5m

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

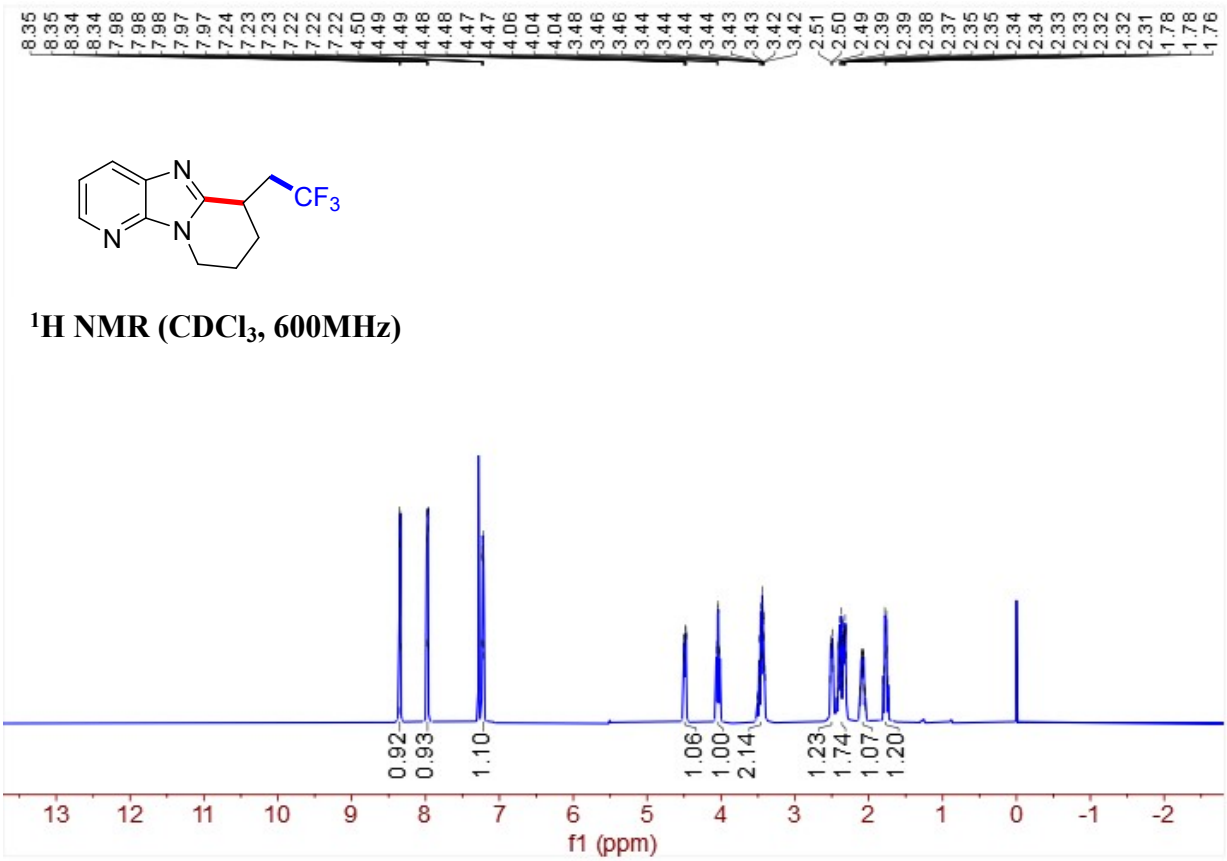


^{13}C NMR Spectrum of Compound 5m

^{19}F NMR ($CDCl_3$, 376MHz)

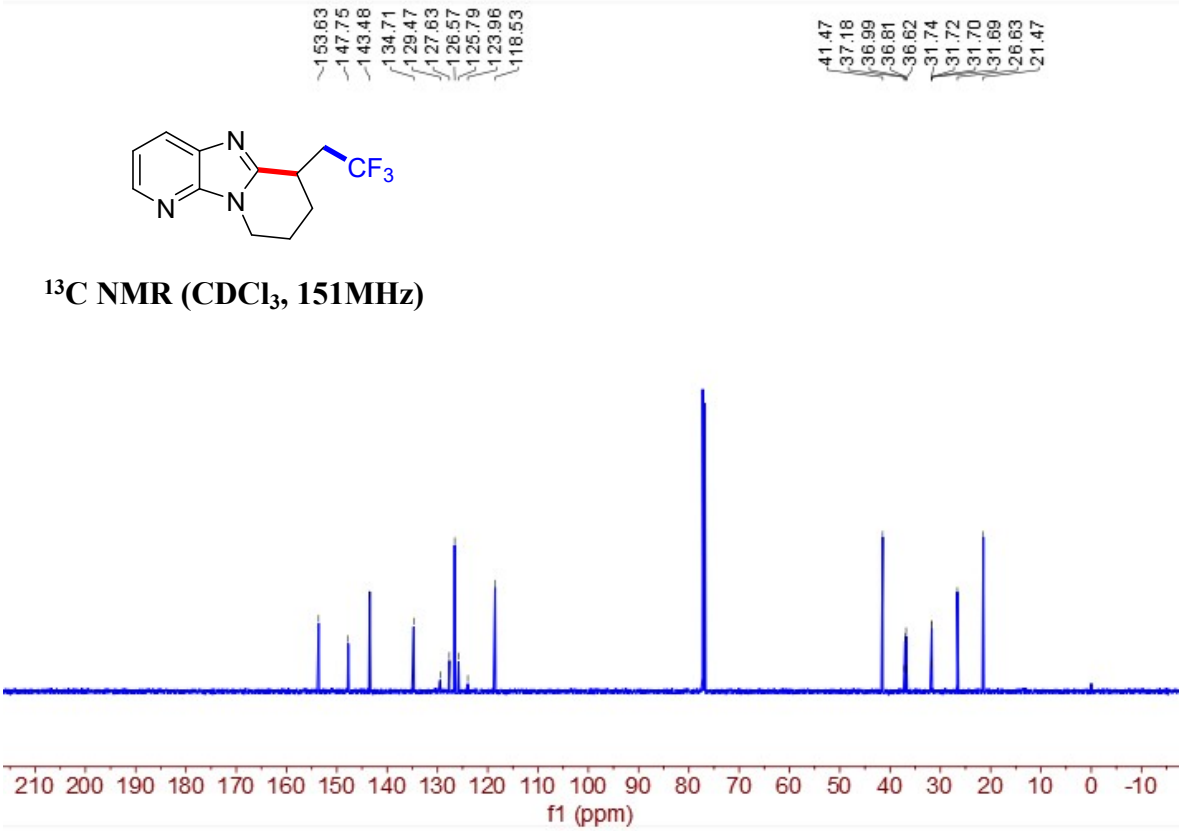


^{19}F NMR Spectrum of Compound 5m



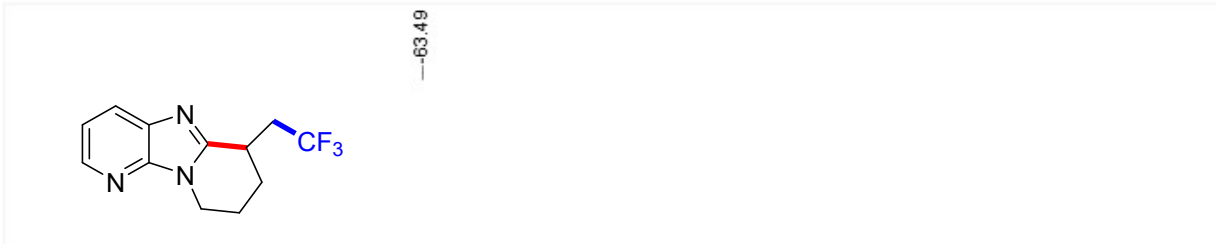
^{1}H NMR ($CDCl_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5n

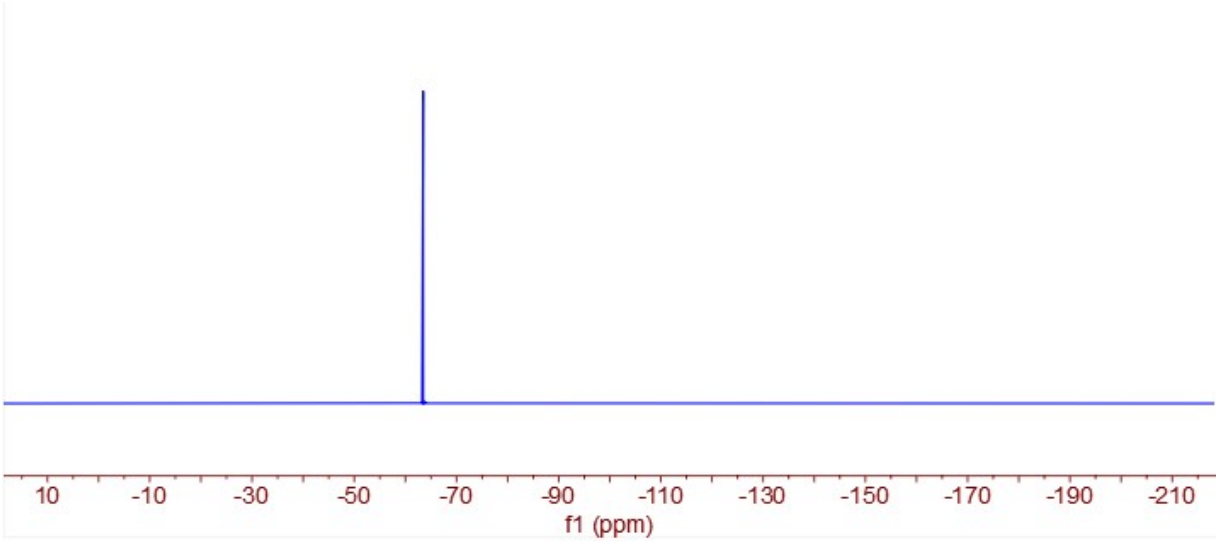


^{13}C NMR ($CDCl_3$, 151MHz)

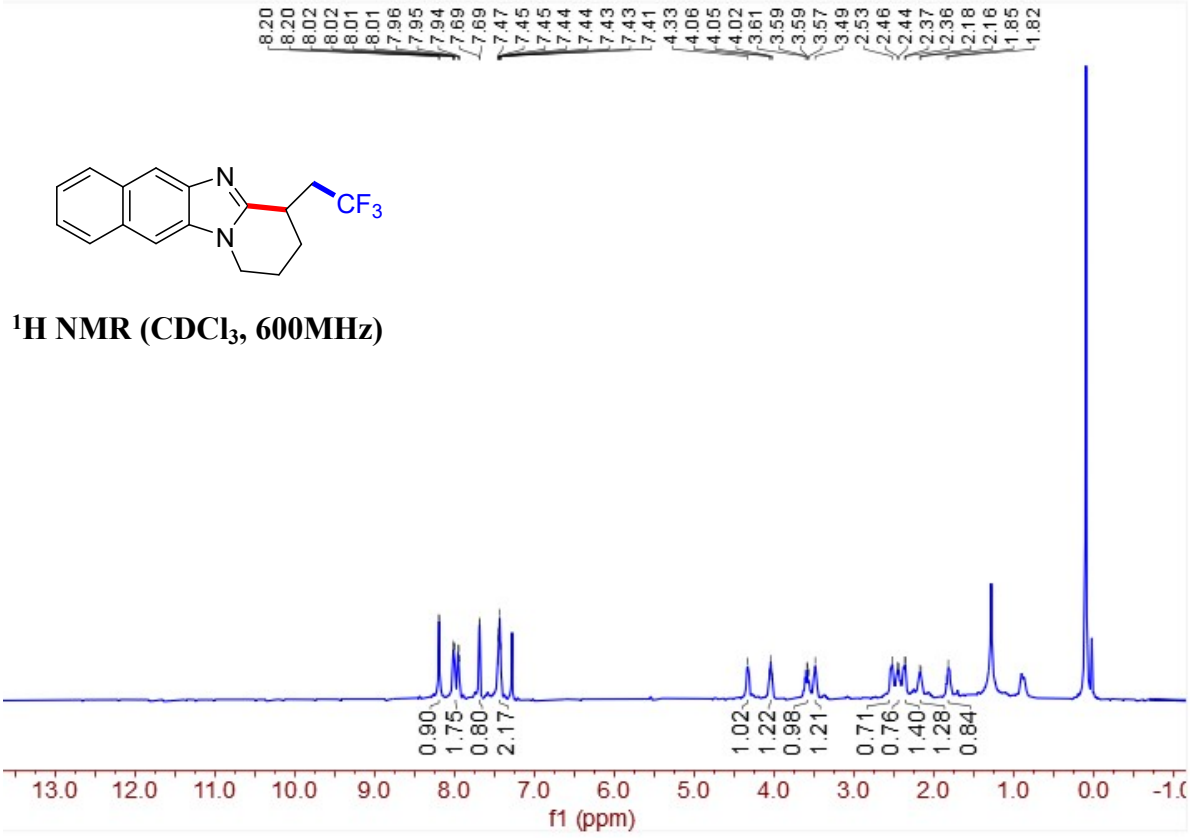
^{13}C NMR Spectrum of Compound 5n



^{19}F NMR ($CDCl_3$, 565MHz)

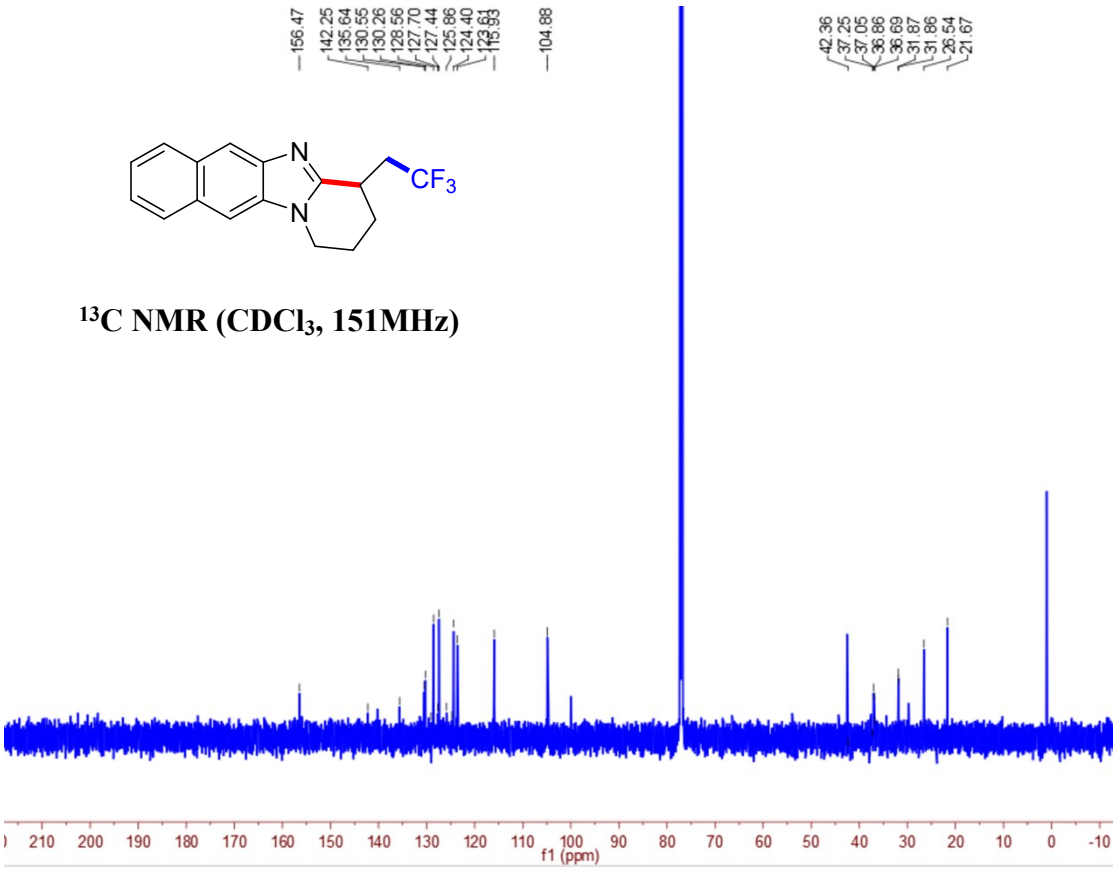


^{19}F NMR Spectrum of Compound 5n



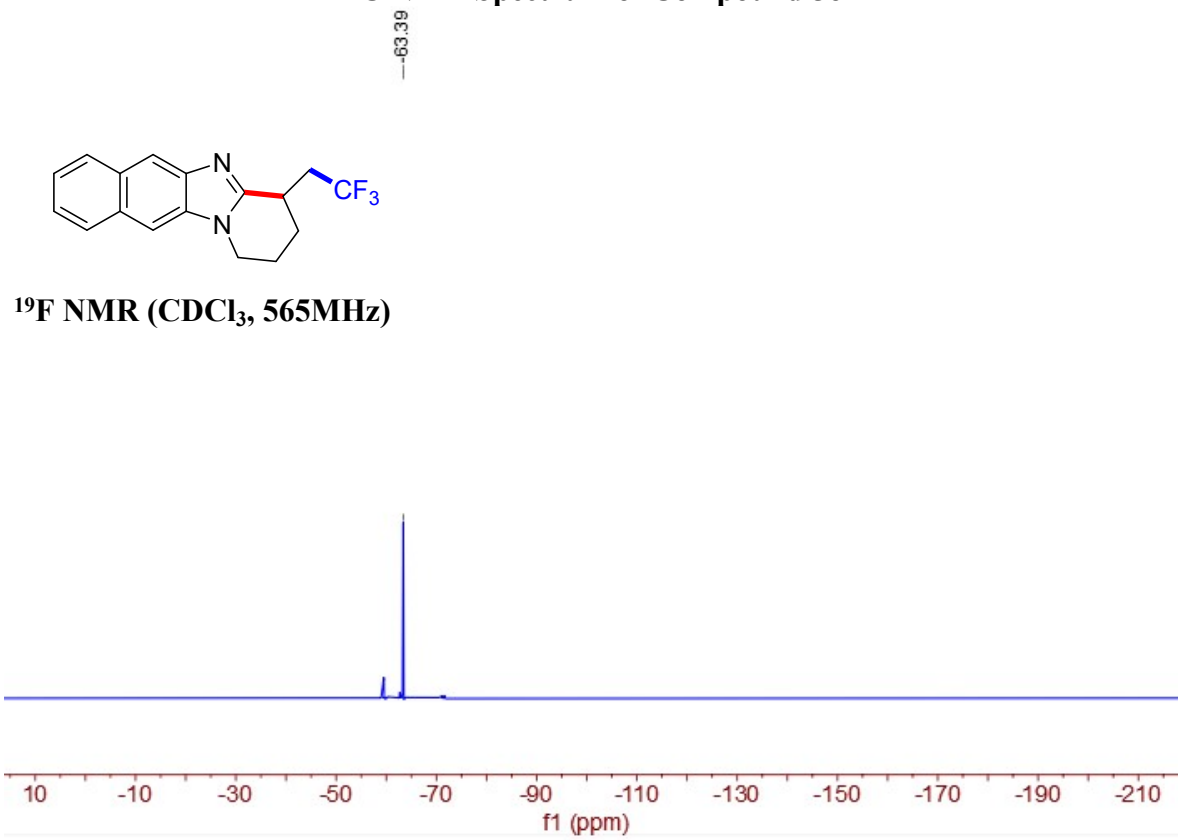
^{1}H NMR ($CDCl_3$, 600MHz)

^{1}H NMR Spectrum of Compound 5o



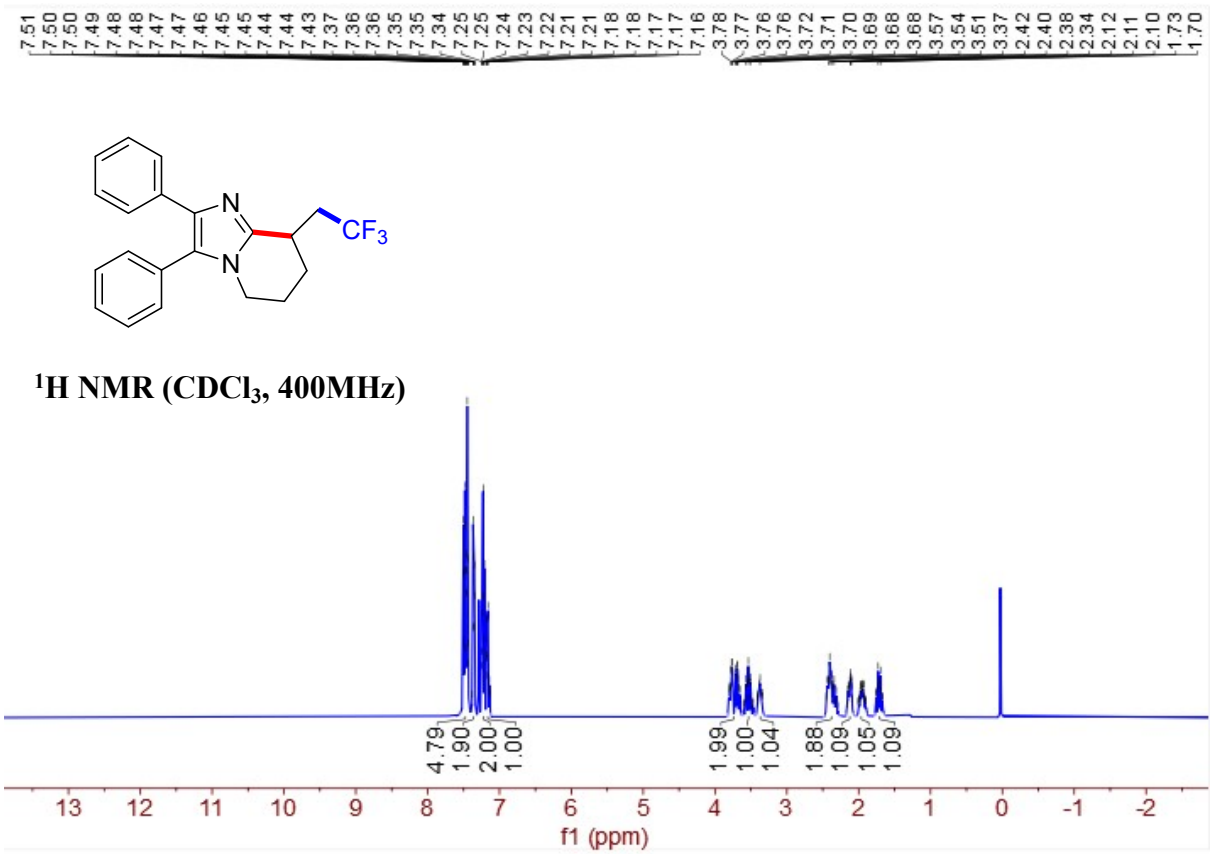
^{13}C NMR ($CDCl_3$, 151MHz)

^{13}C NMR Spectrum of Compound 5o



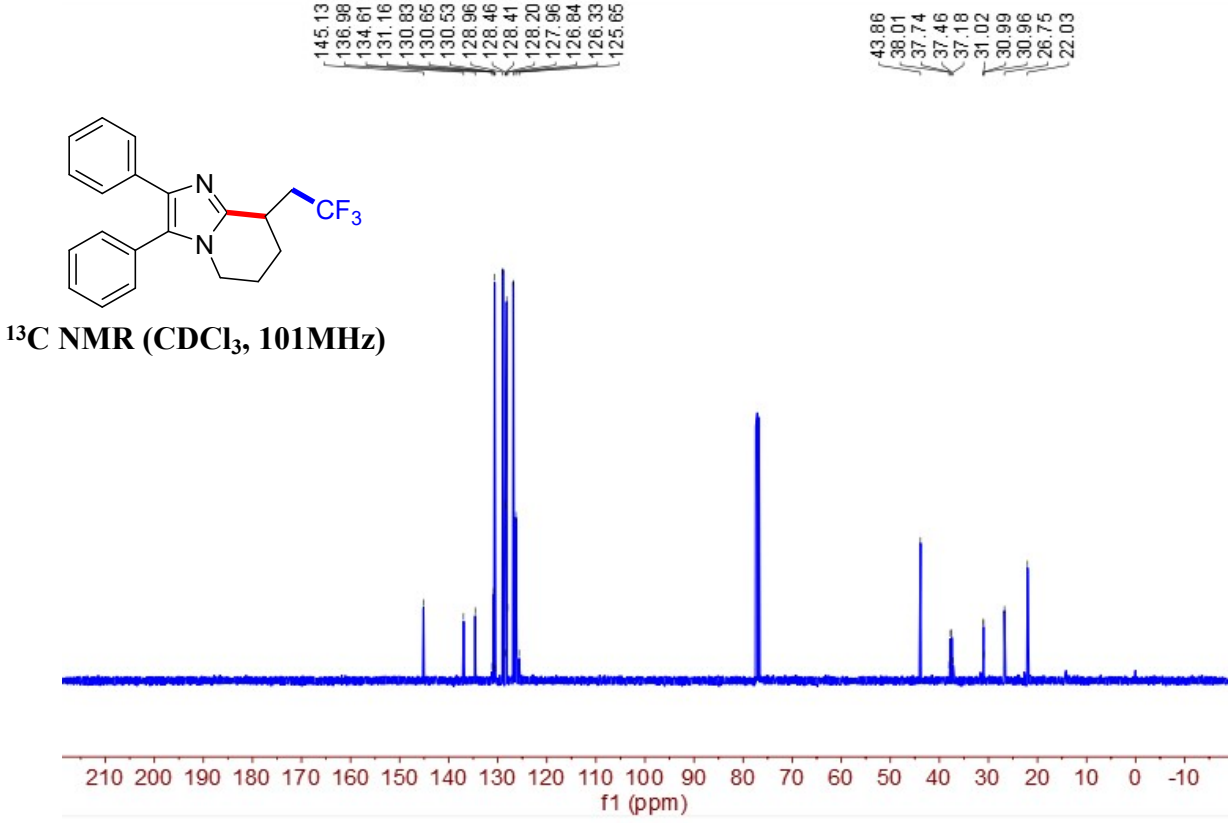
^{19}F NMR ($CDCl_3$, 565MHz)

^{19}F NMR Spectrum of Compound 5o



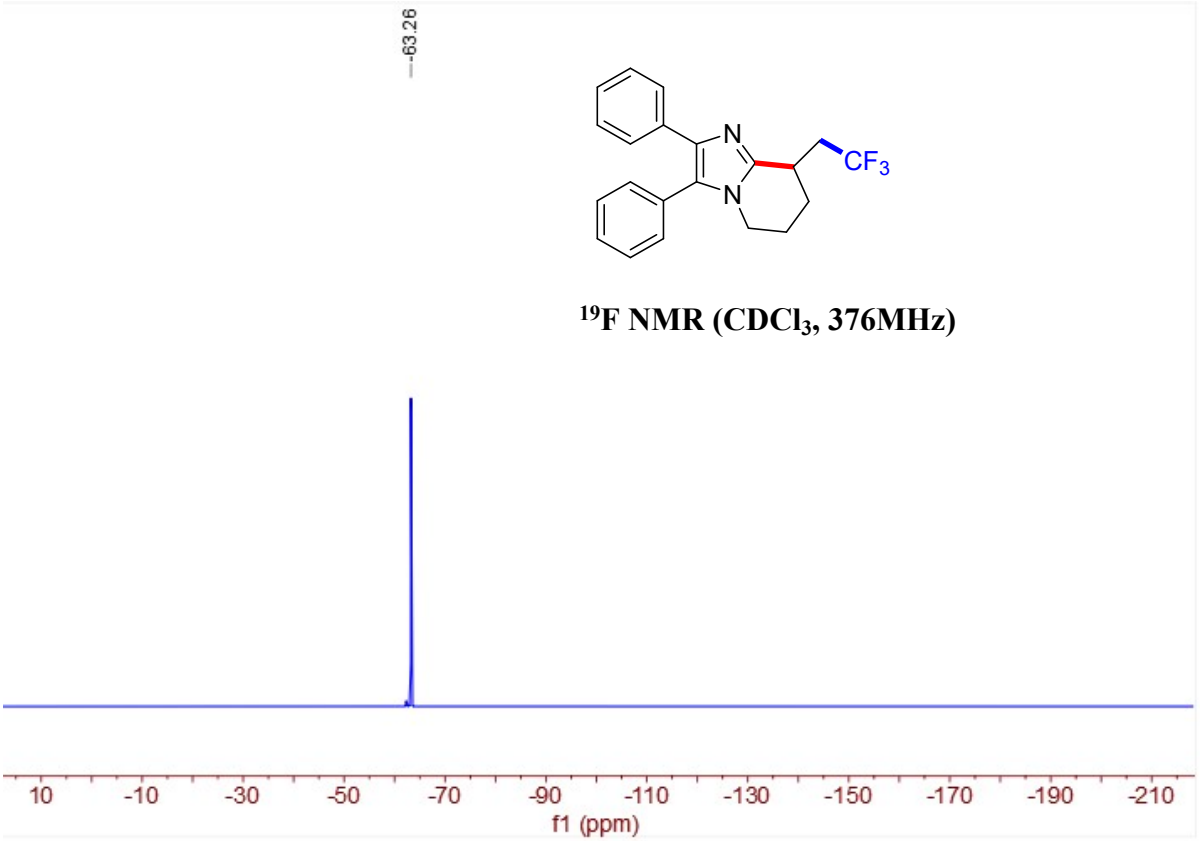
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5p



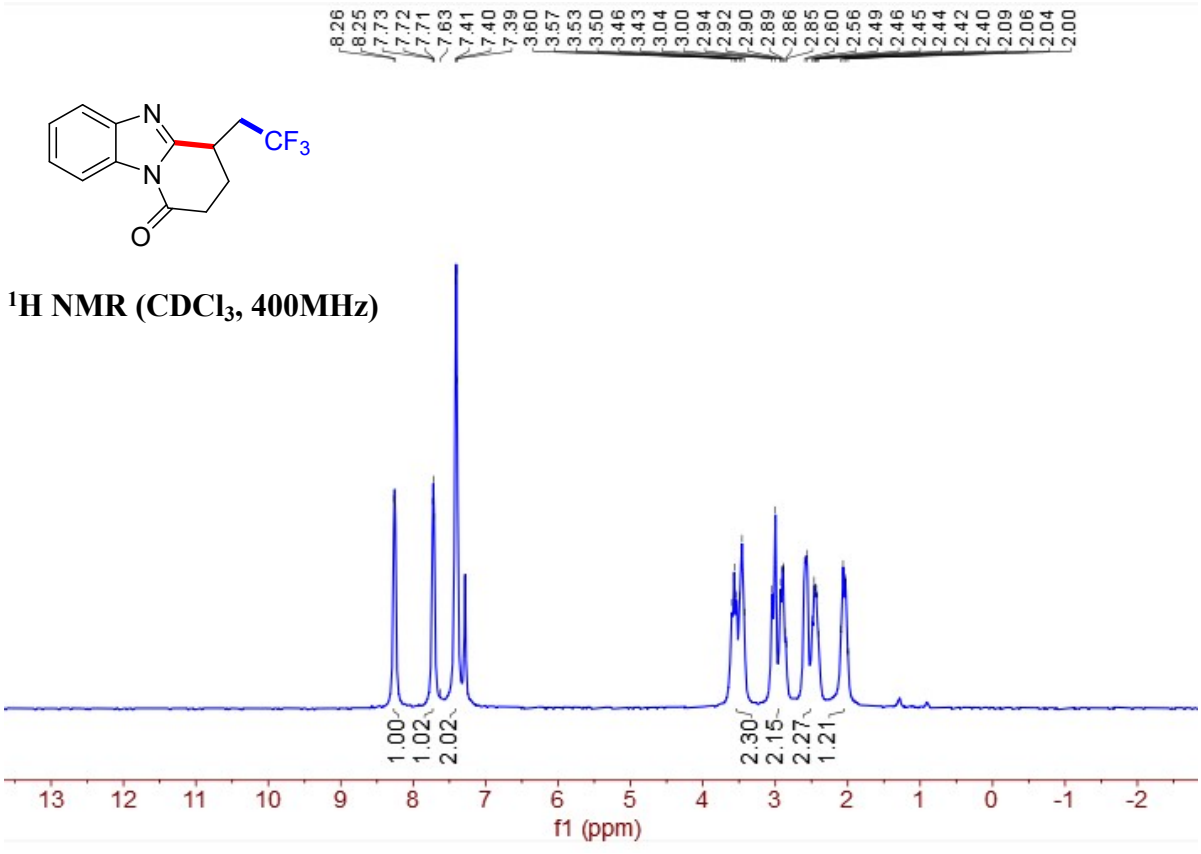
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 5p



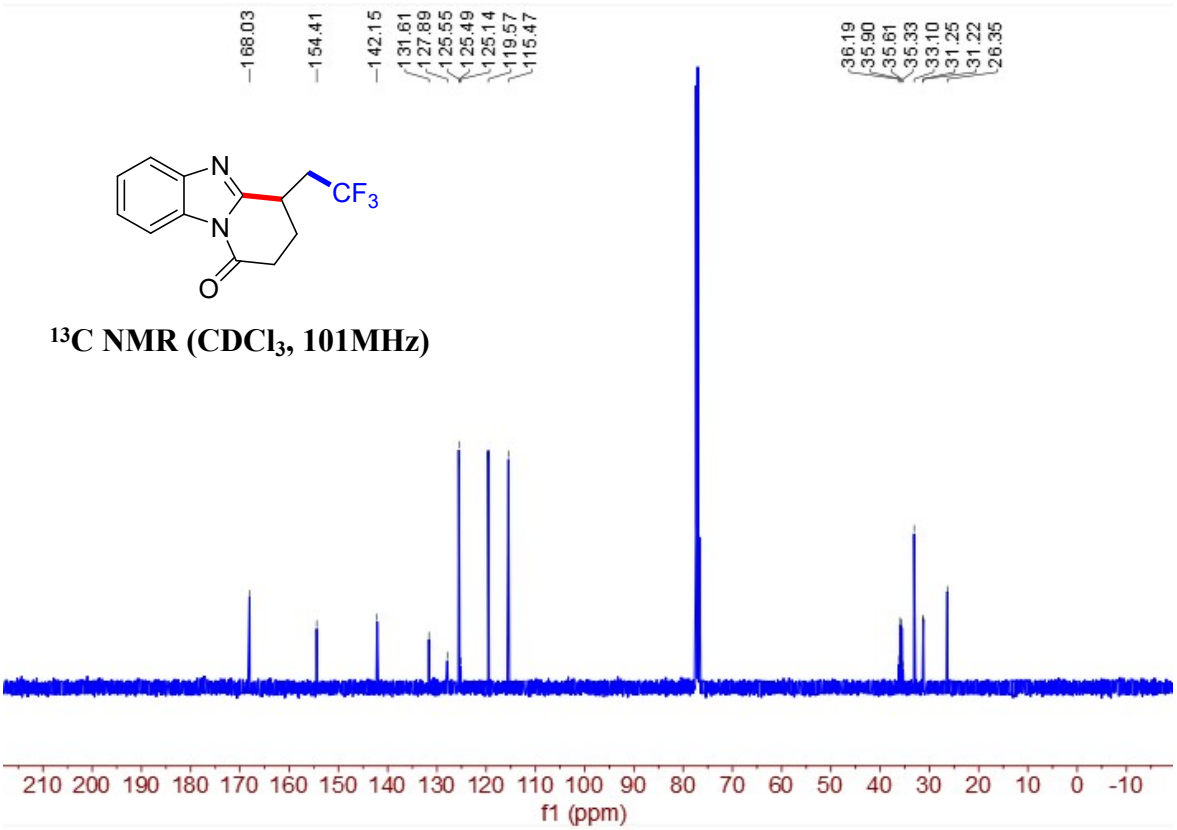
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5p



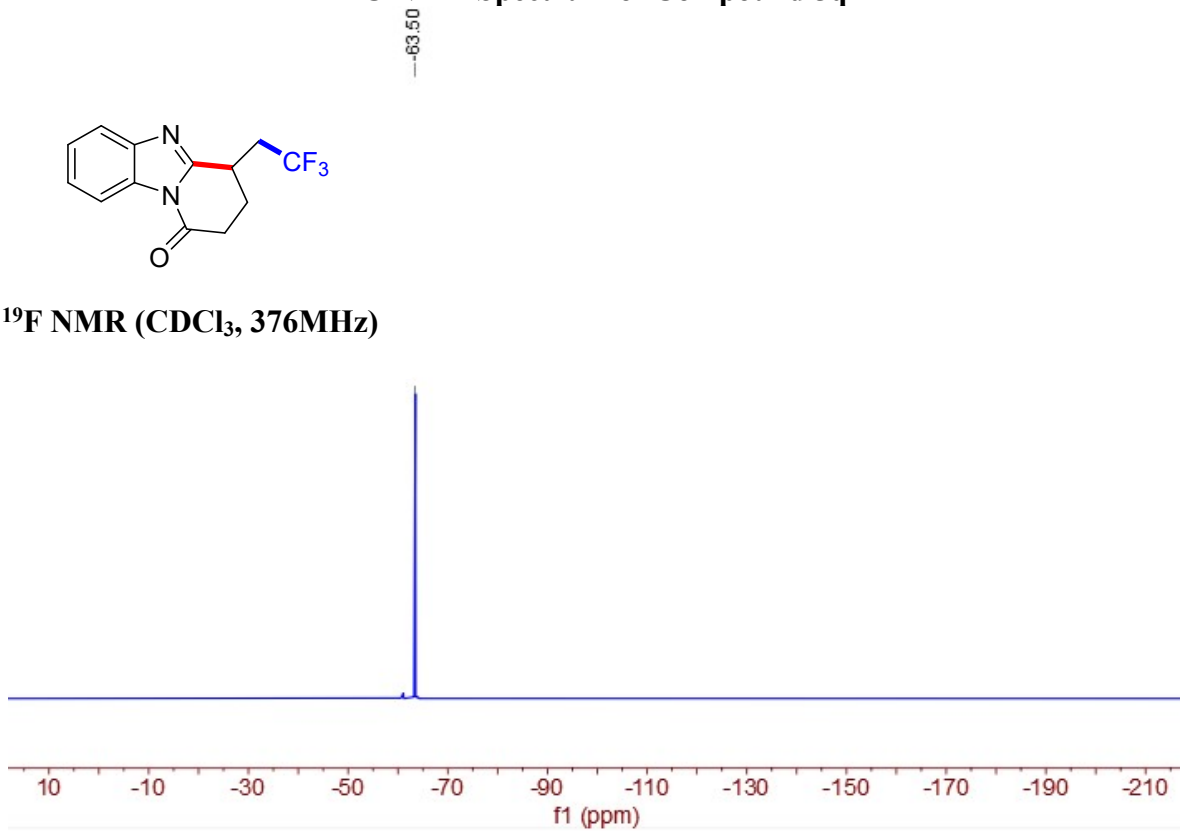
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5q



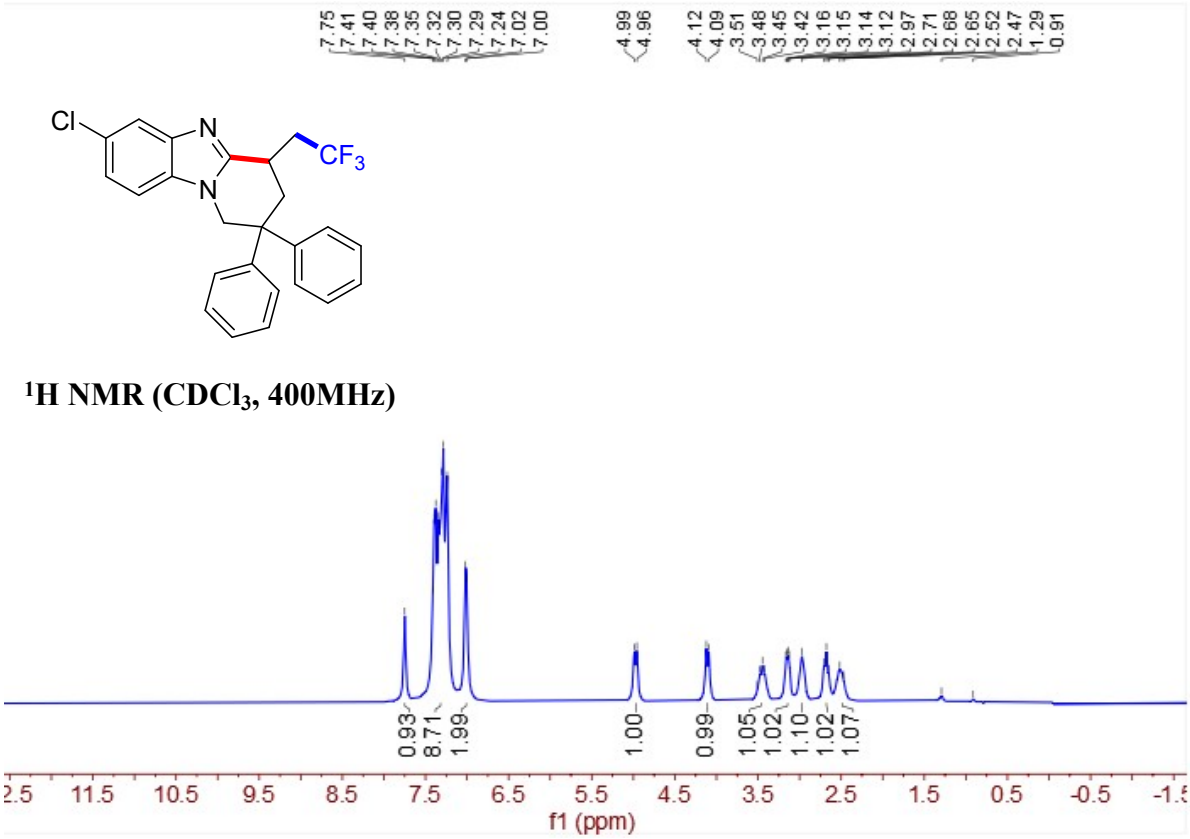
^{13}C NMR (CDCl$_3$, 101MHz)

^{13}C NMR Spectrum of Compound 5q



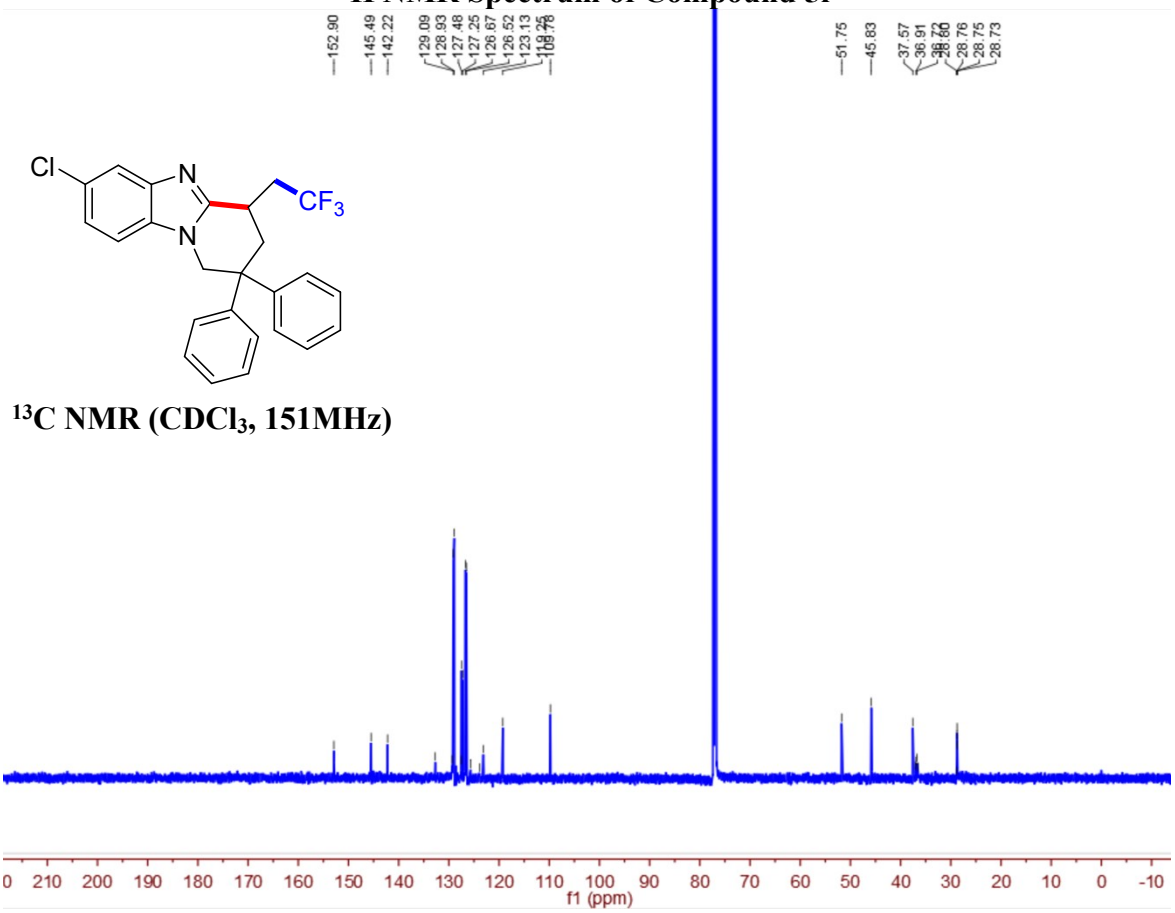
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5q



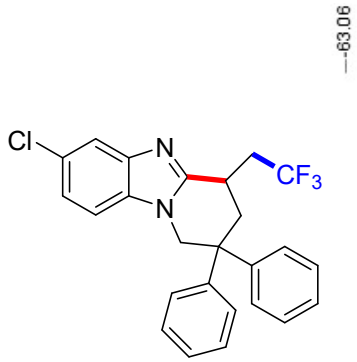
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5r

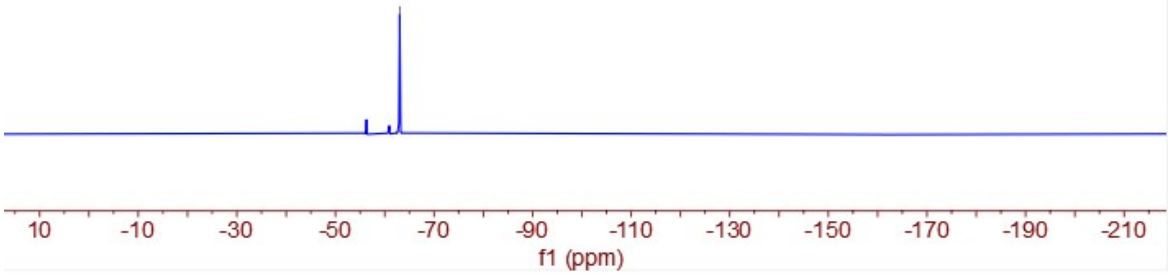


^{13}C NMR ($CDCl_3$, 151MHz)

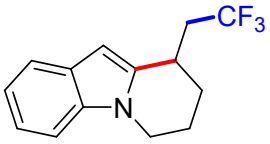
^{13}C NMR Spectrum of Compound 5r



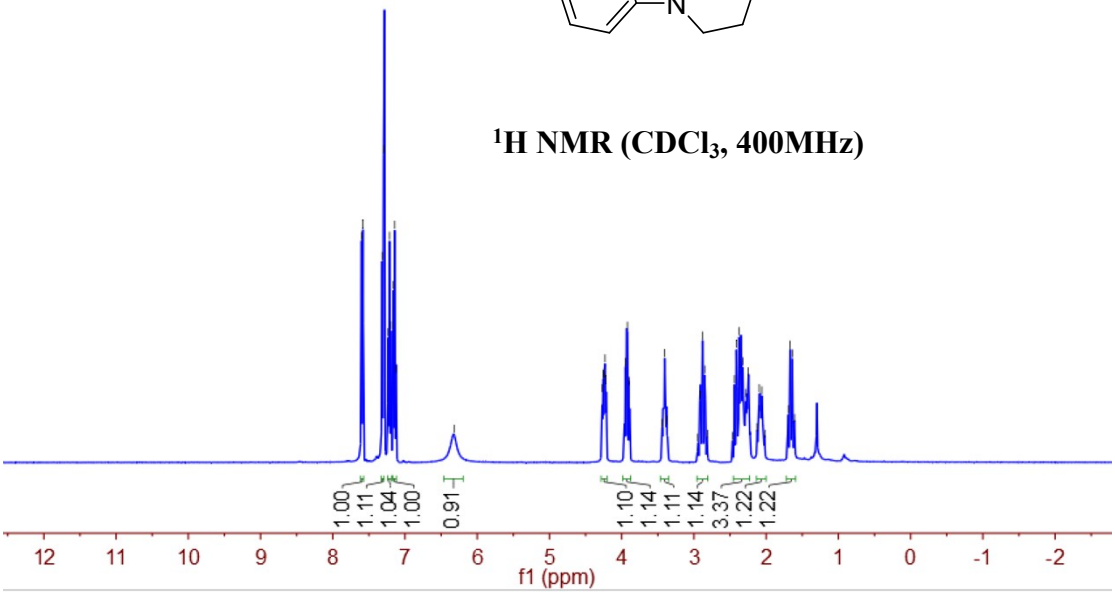
^{19}F NMR ($CDCl_3$, 376MHz)



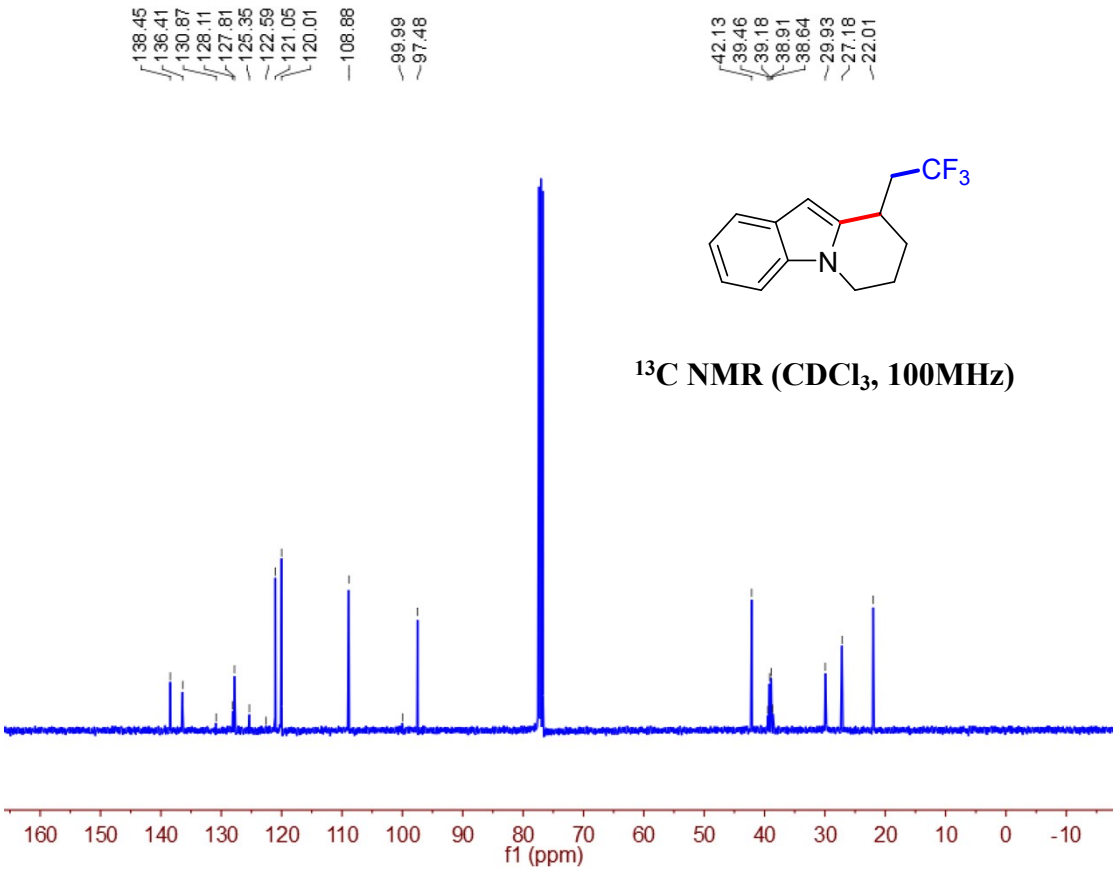
^{19}F NMR Spectrum of Compound 5r



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

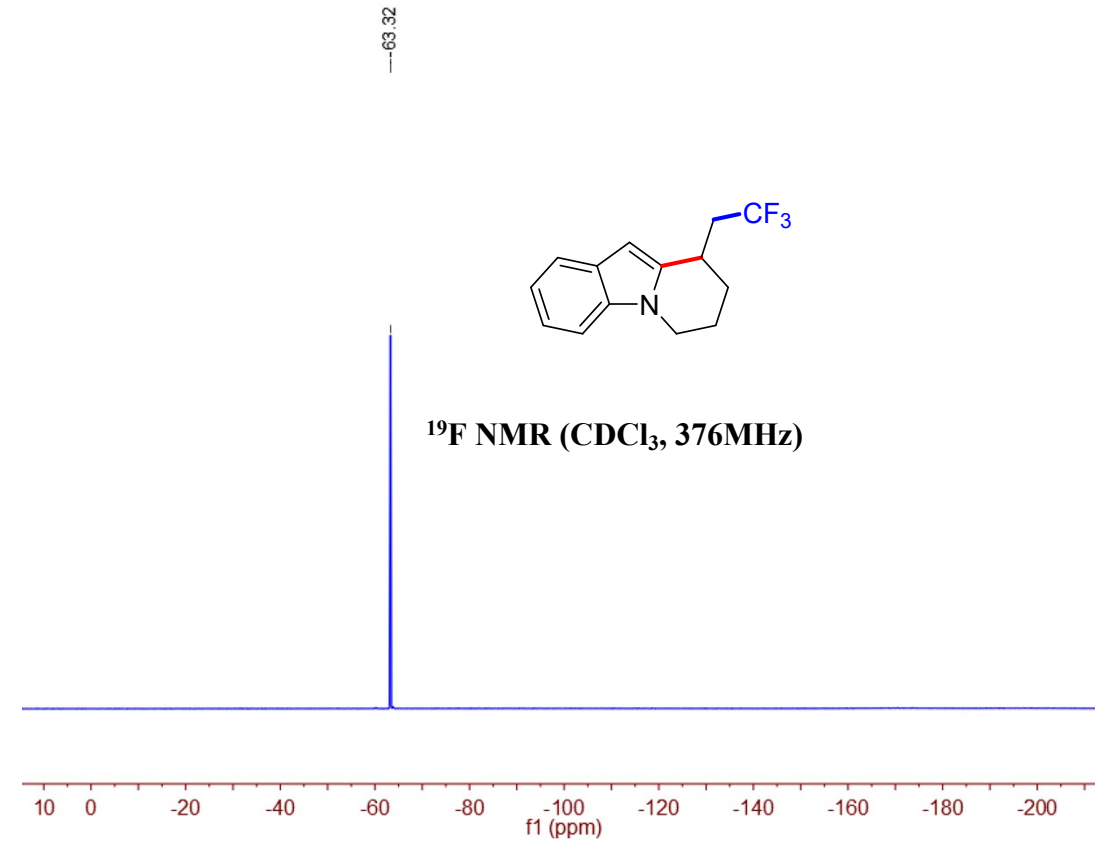


^{1}H NMR Spectrum of Compound 5s



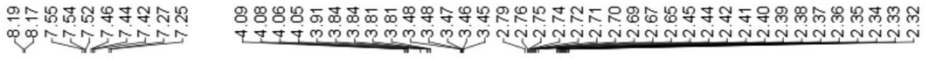
^{13}C NMR (CDCl$_3$, 100MHz)

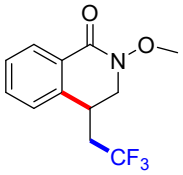
^{13}C NMR Spectrum of Compound 5s



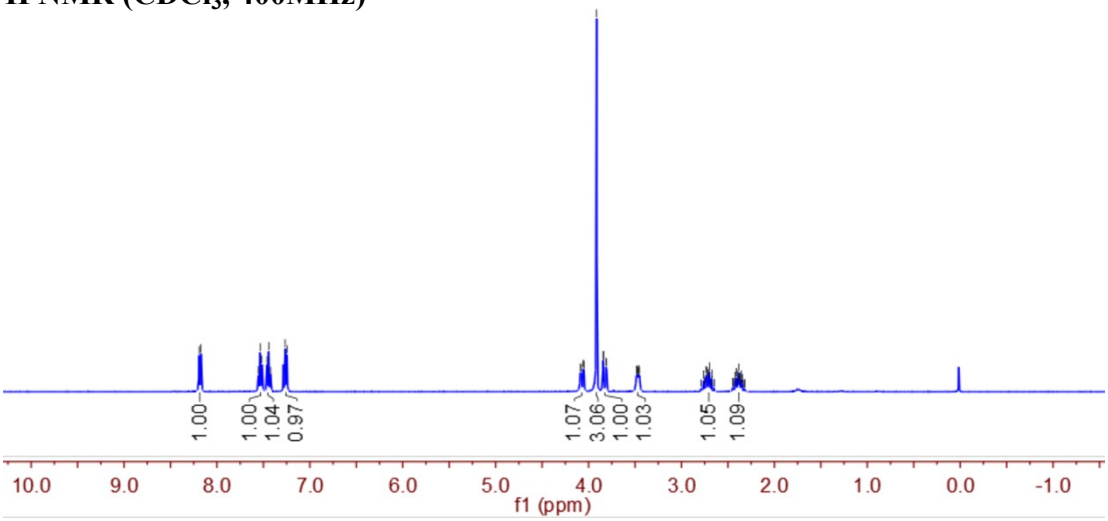
^{19}F NMR (CDCl$_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5s

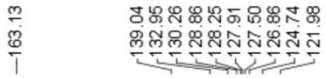


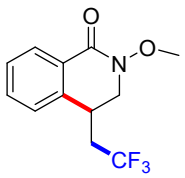


^{1}H NMR ($CDCl_3$, 400MHz)

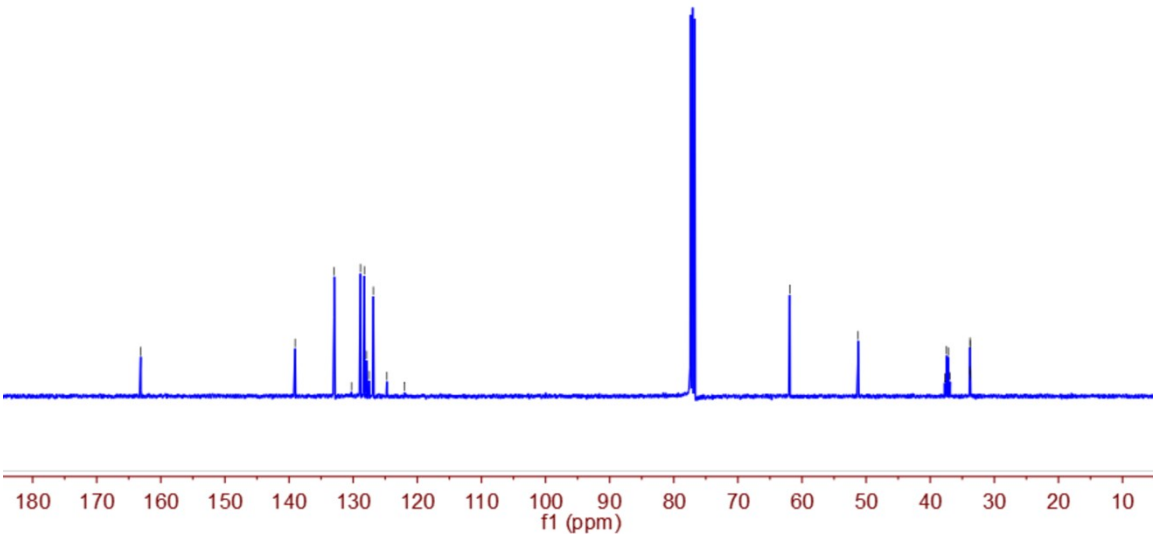


^{1}H NMR Spectrum of Compound 5t

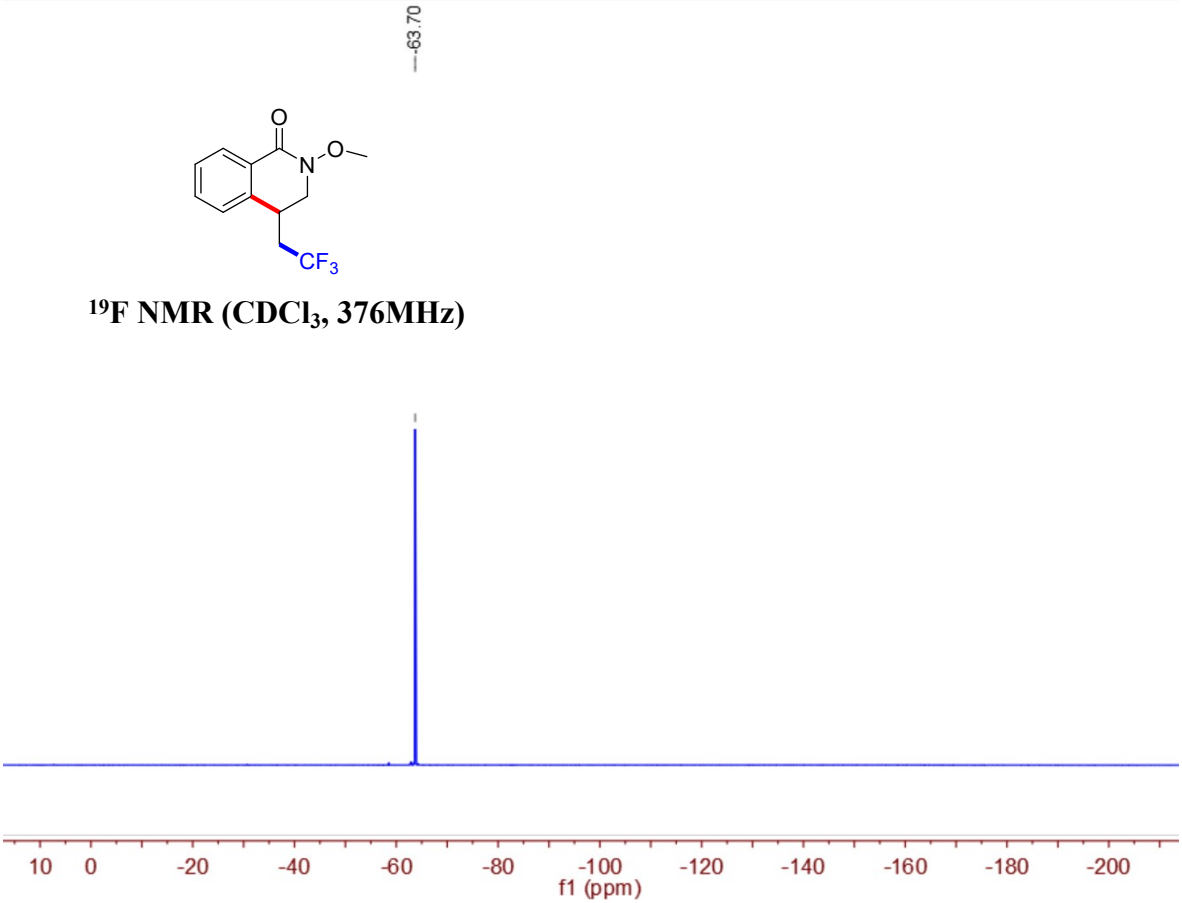




^{13}C NMR ($CDCl_3$, 101MHz)

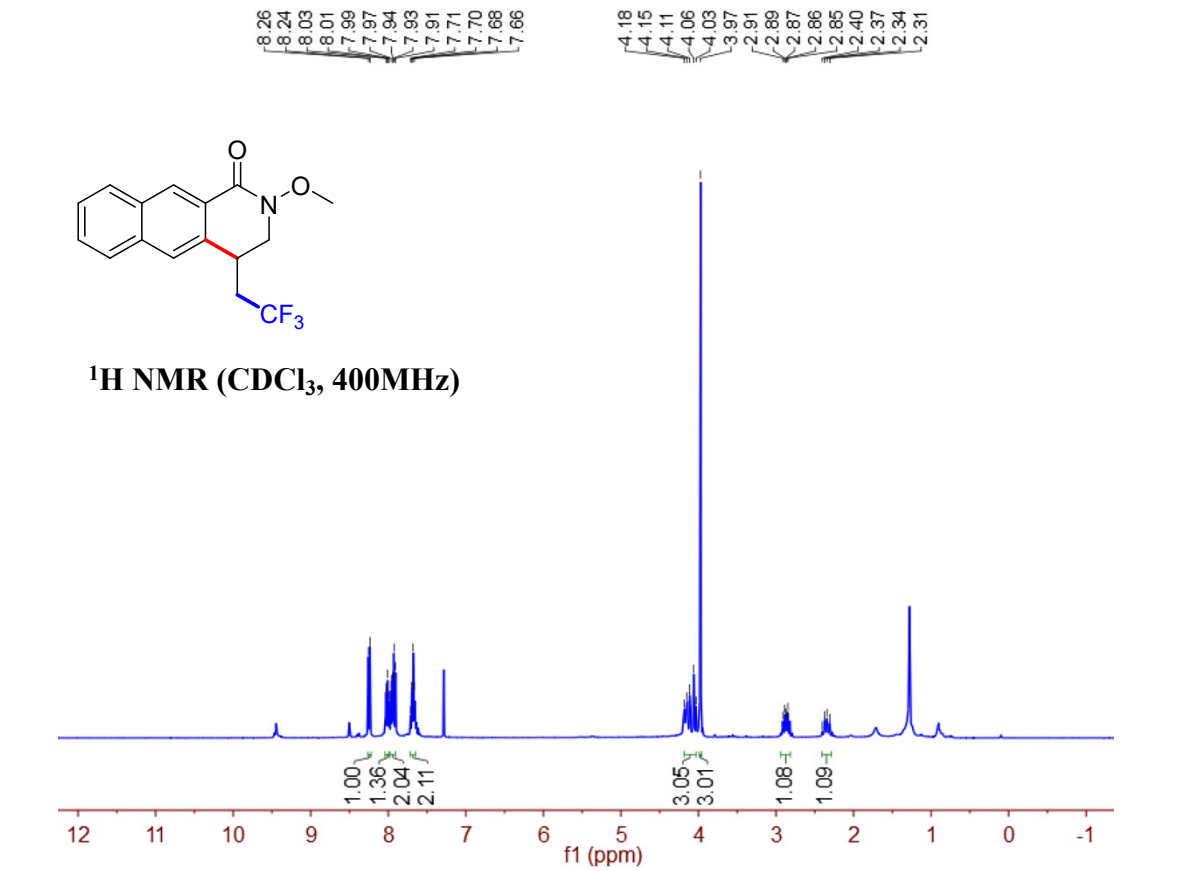


^{13}C NMR Spectrum of Compound 5t



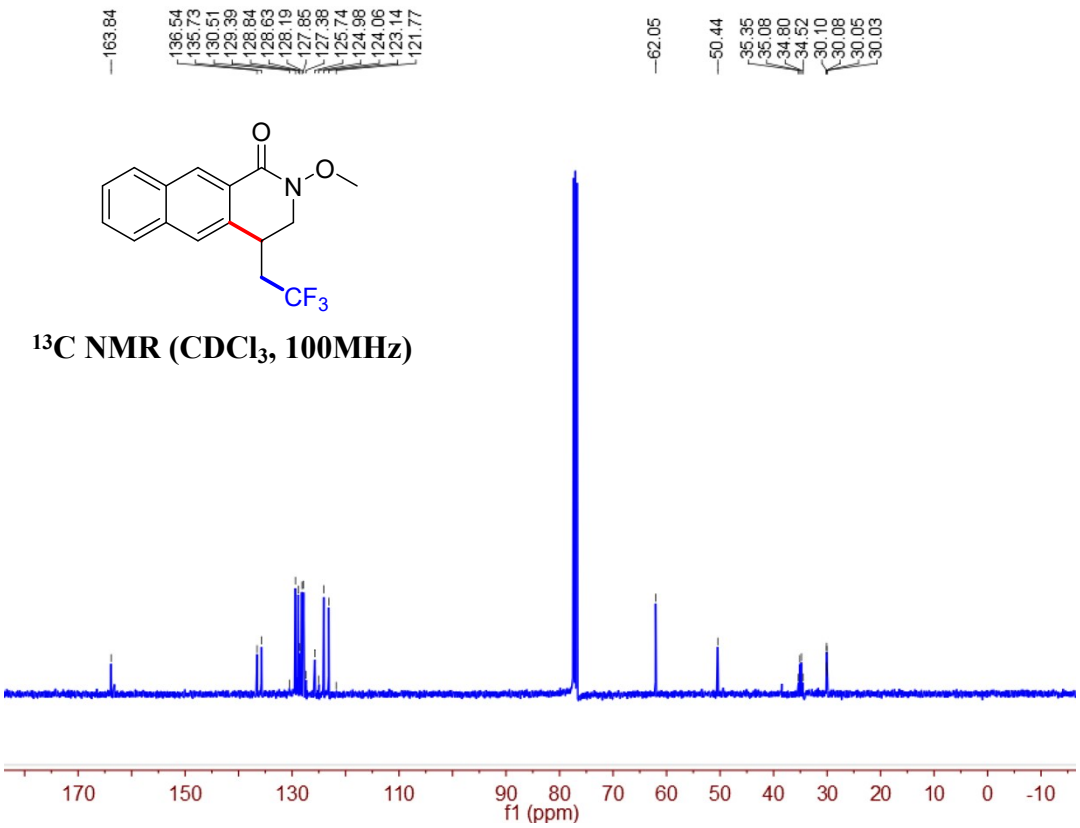
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5t



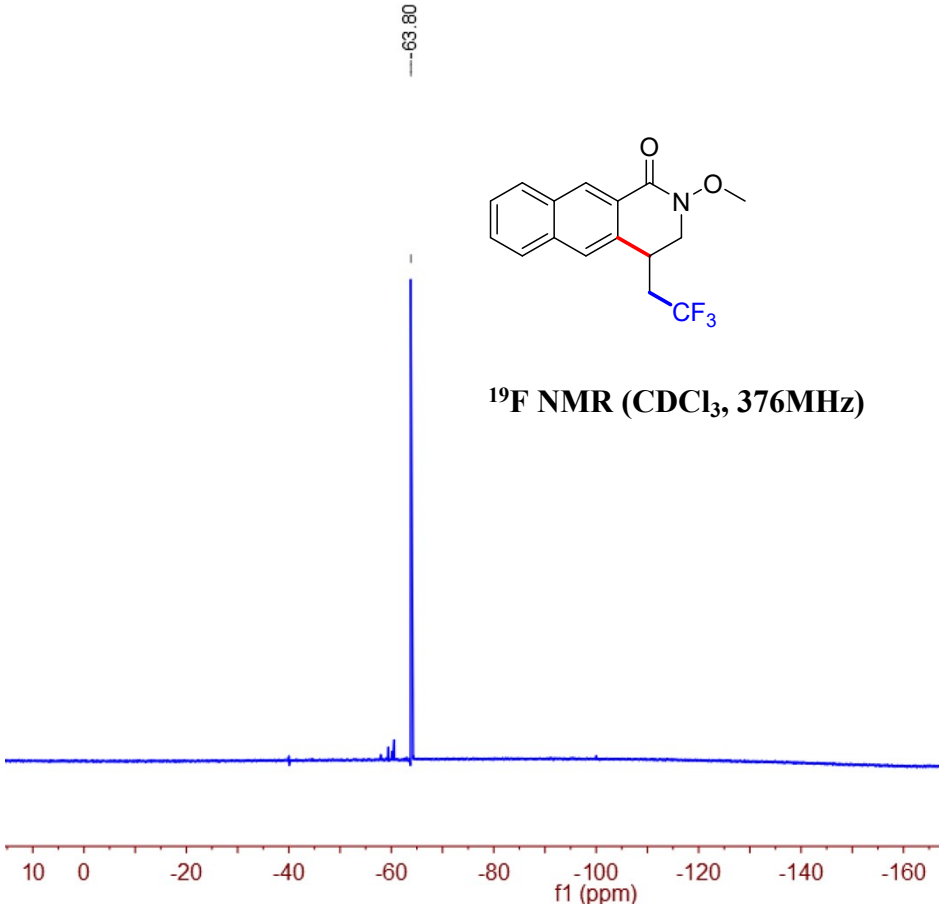
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5u



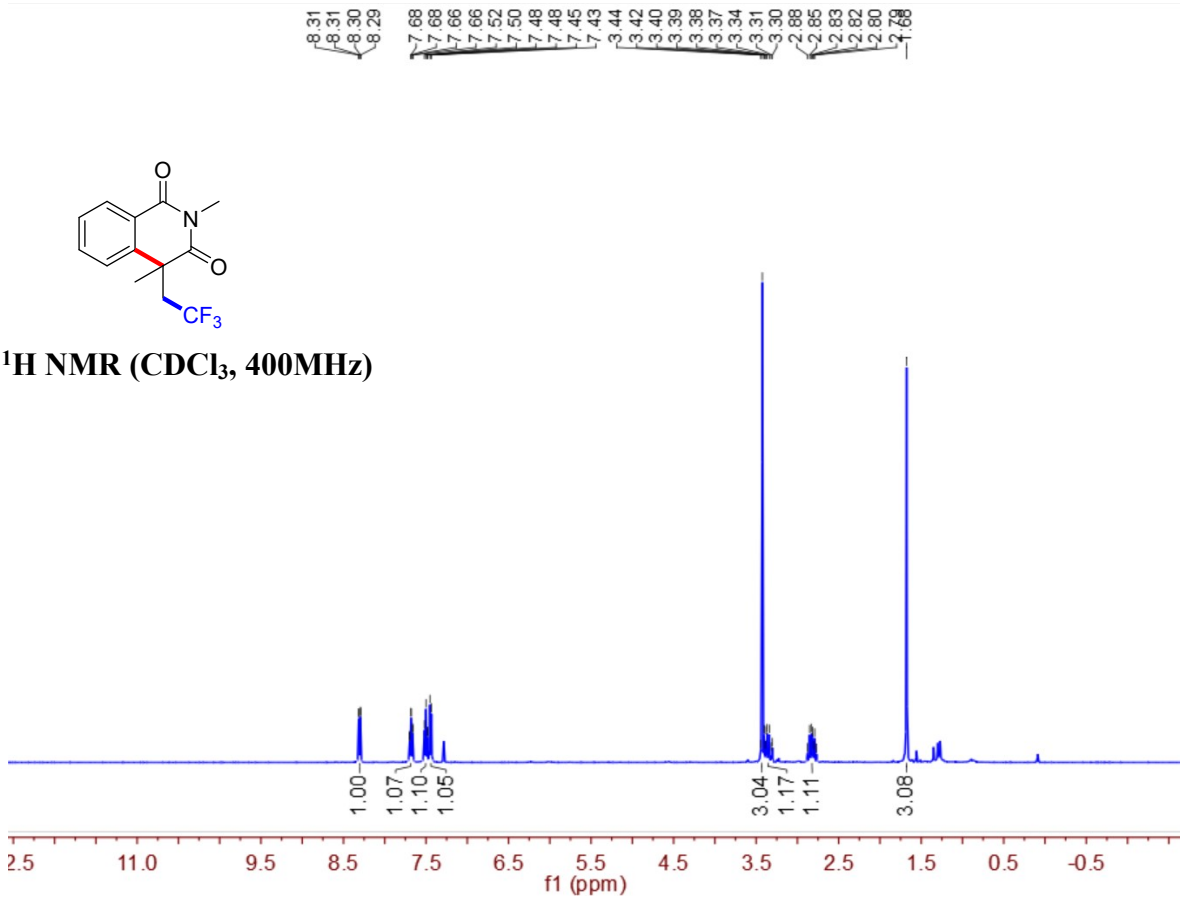
^{13}C NMR ($CDCl_3$, 100MHz)

^{13}C NMR Spectrum of Compound 5u



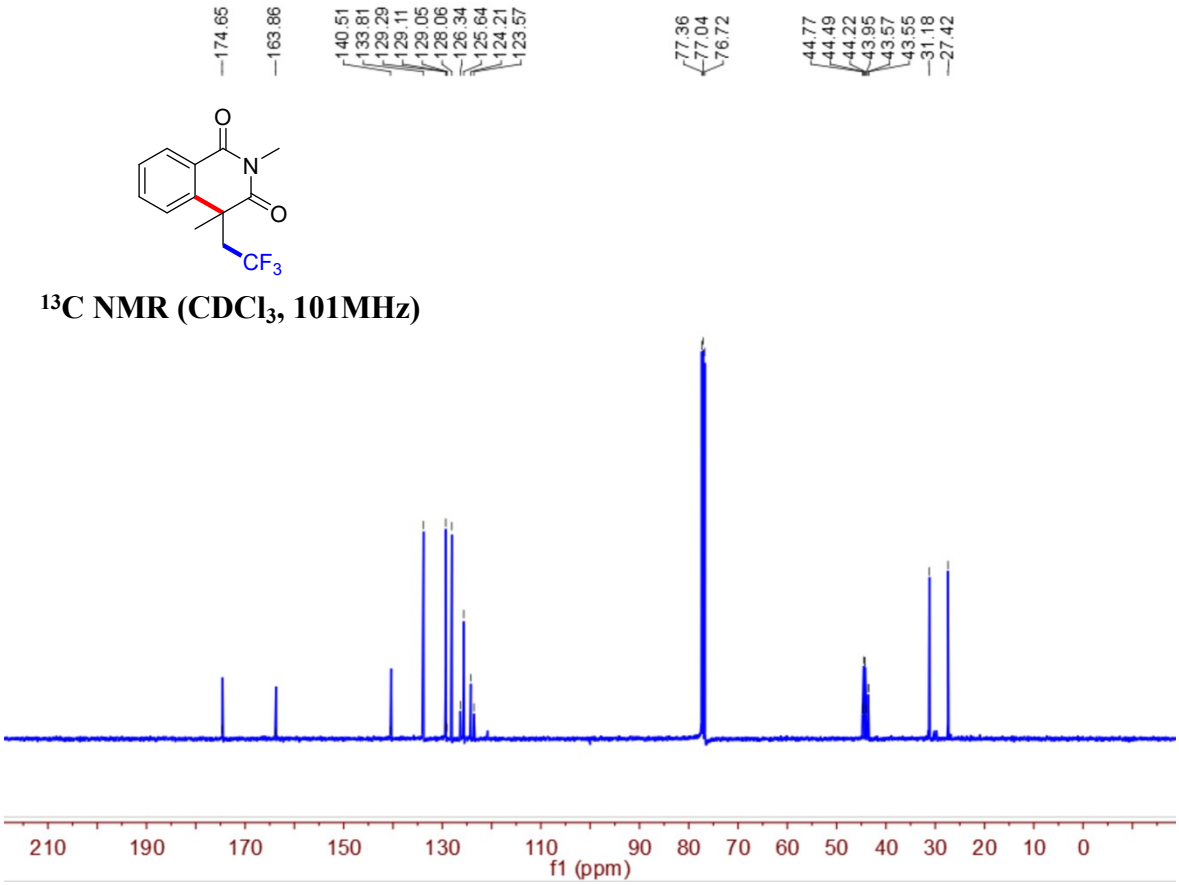
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5u



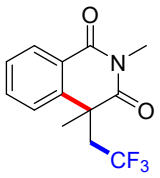
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5v



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

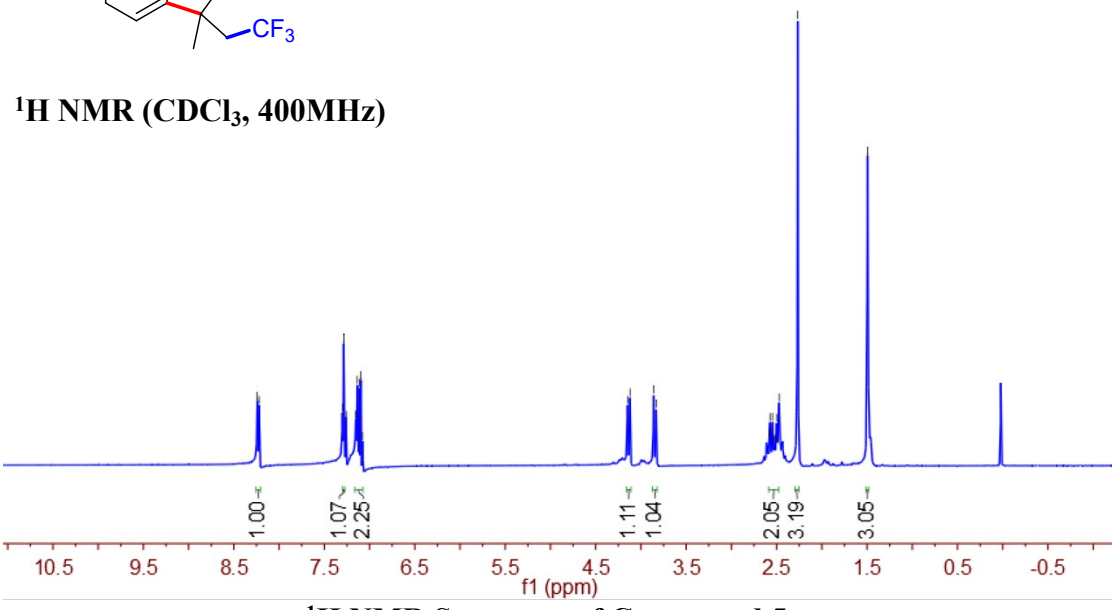
^{13}C NMR Spectrum of Compound 5v



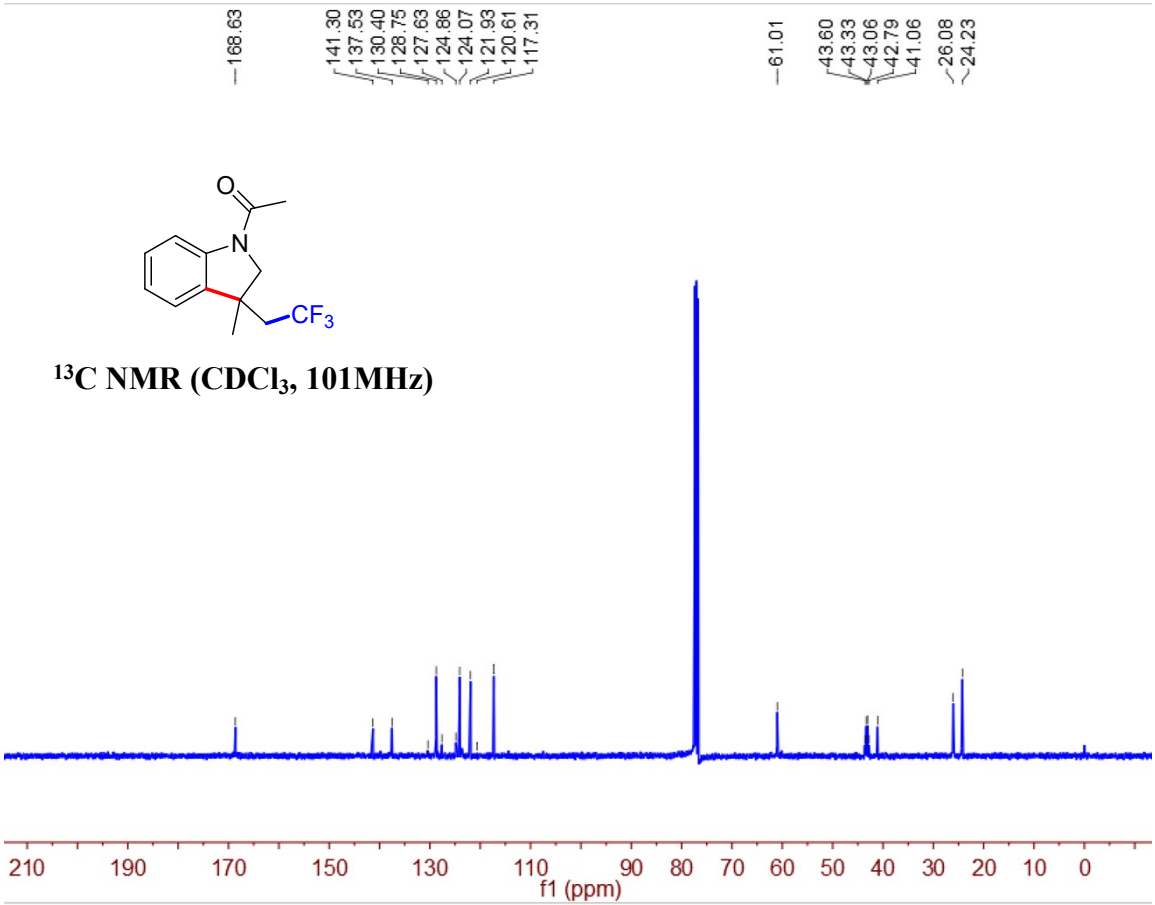
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5v

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

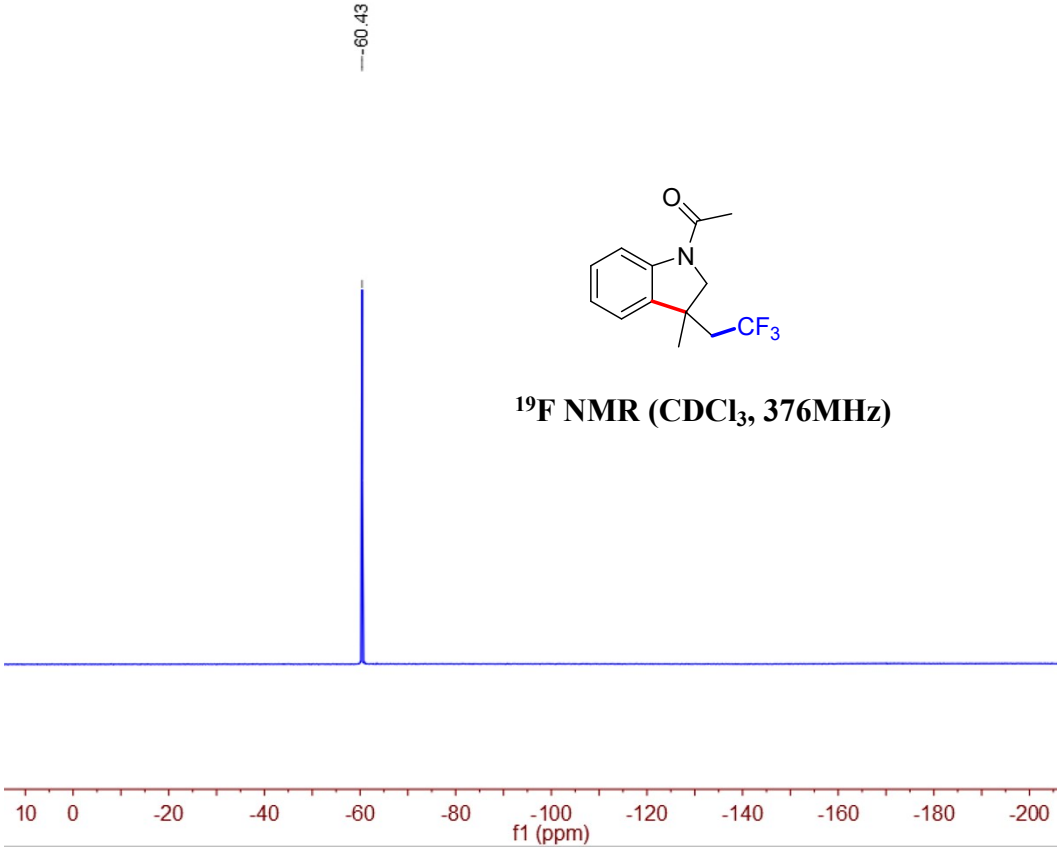


^{1}H NMR Spectrum of Compound 5w



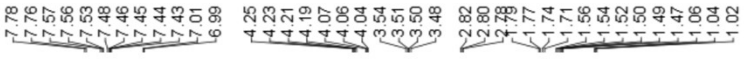
^{13}C NMR ($CDCl_3$, 101MHz)

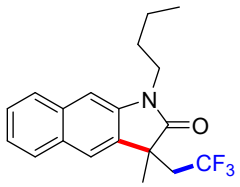
^{13}C NMR Spectrum of Compound 5w



^{19}F NMR ($CDCl_3$, 376MHz)

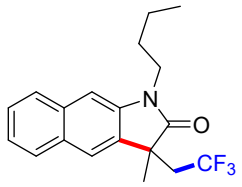
^{19}F NMR Spectrum of Compound 5w



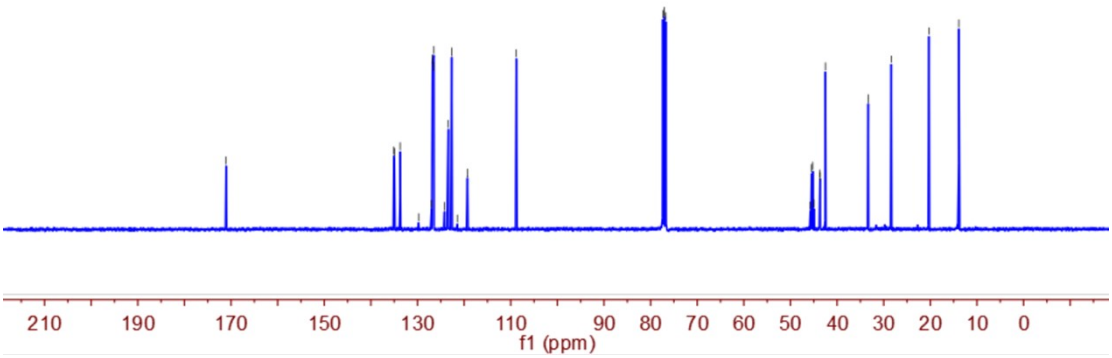


^{1}H NMR ($CDCl_3$, 400MHz)

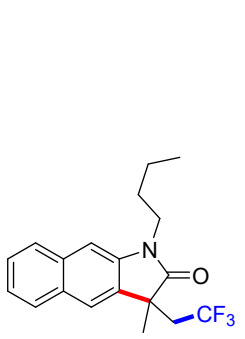
^{1}H NMR Spectrum of Compound 5x



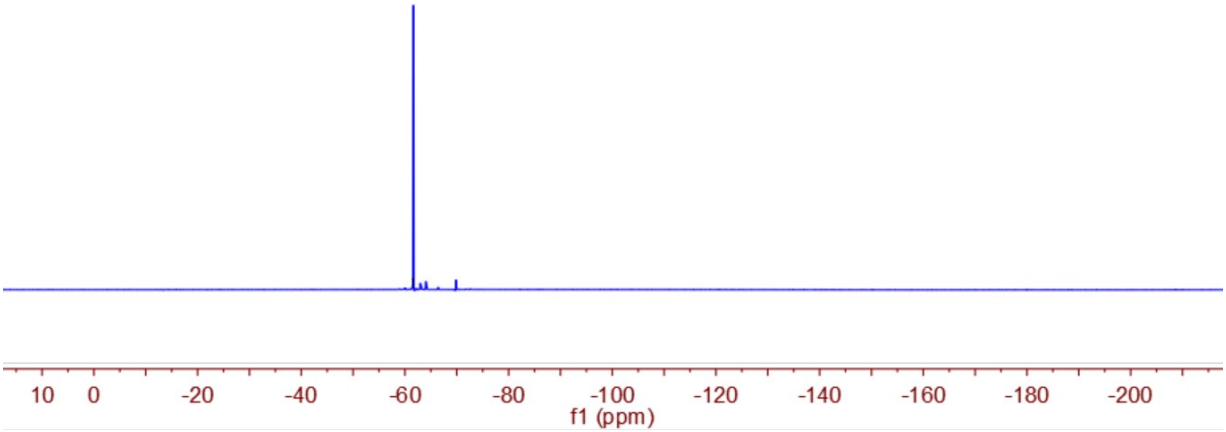
^{13}C NMR ($CDCl_3$, 101MHz)



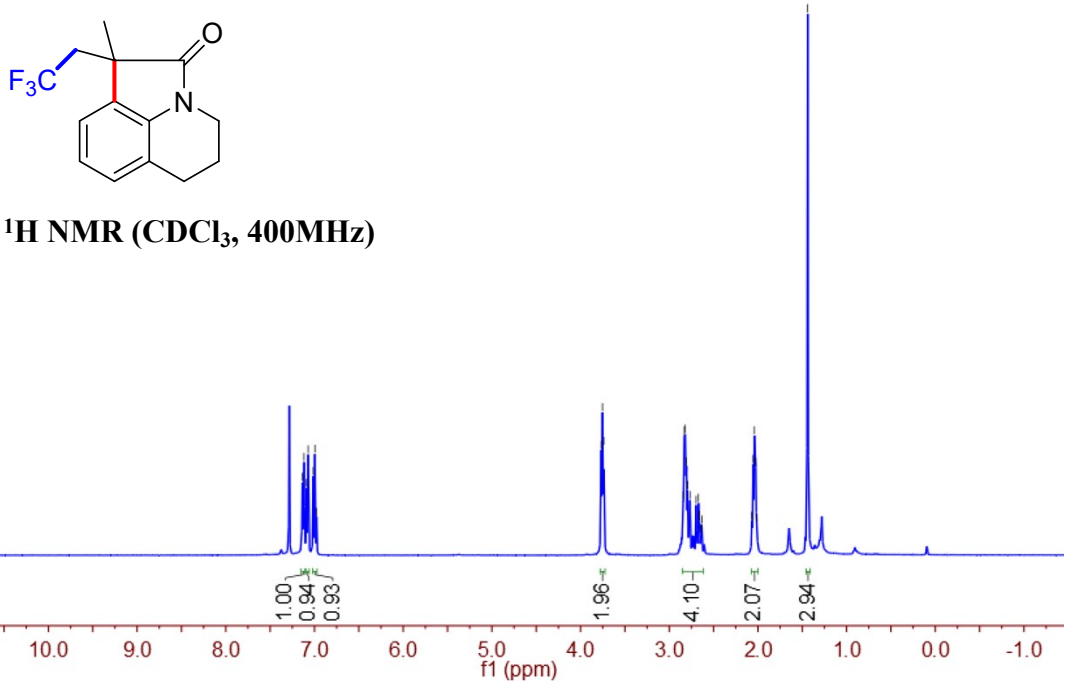
^{13}C NMR Spectrum of Compound 5x



^{19}F NMR ($CDCl_3$, 376MHz)

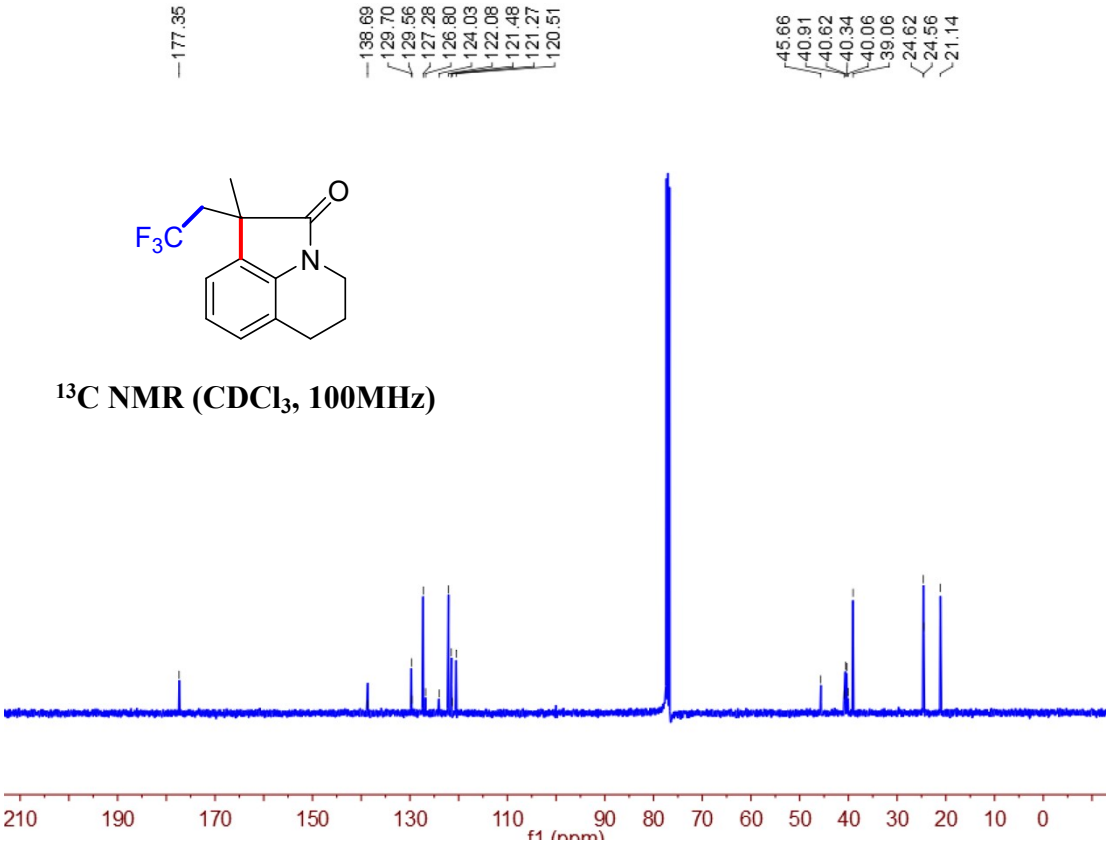


^{19}F NMR Spectrum of Compound 5x



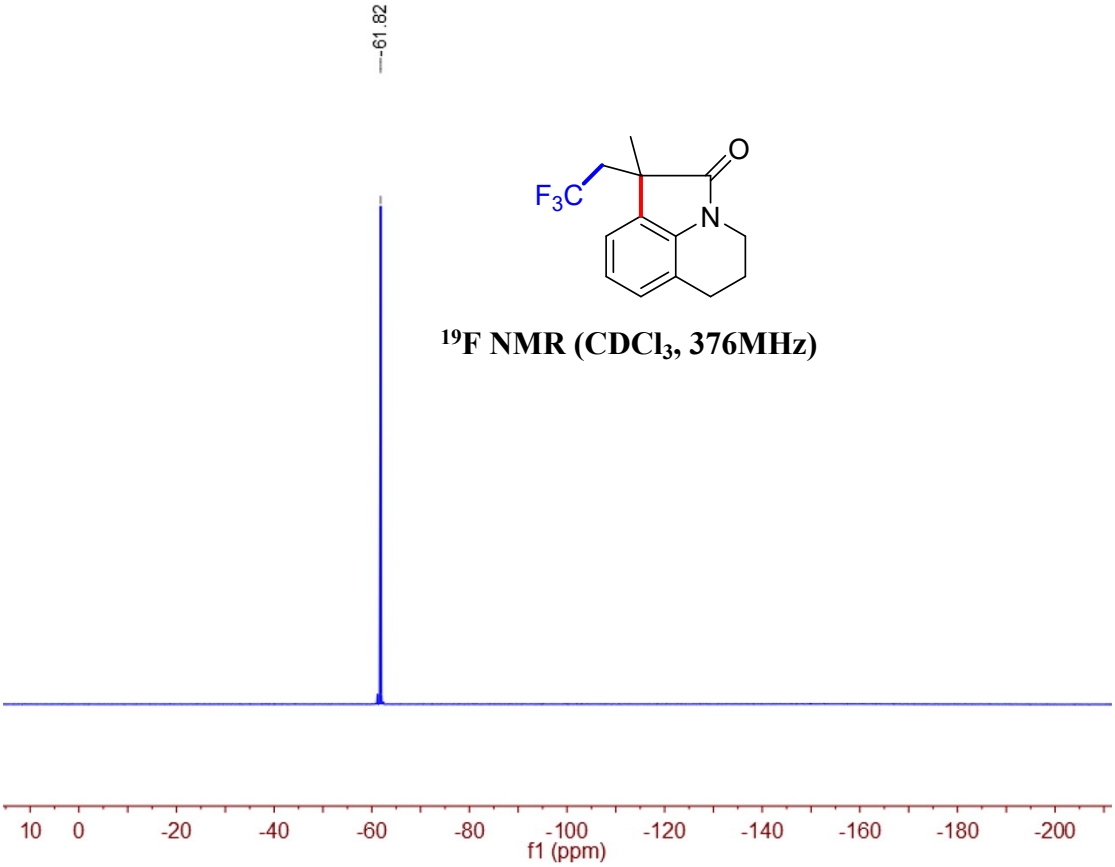
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5y



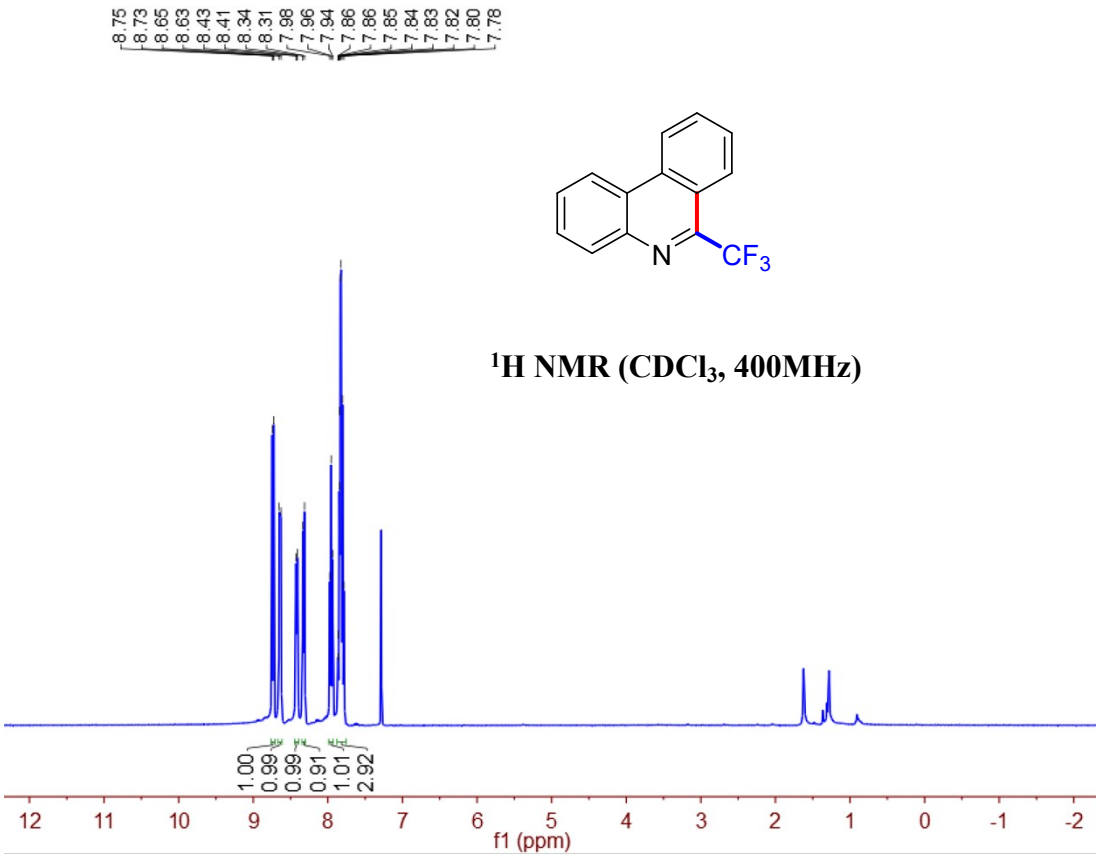
^{13}C NMR ($CDCl_3$, 100MHz)

^{13}C NMR Spectrum of Compound 5y



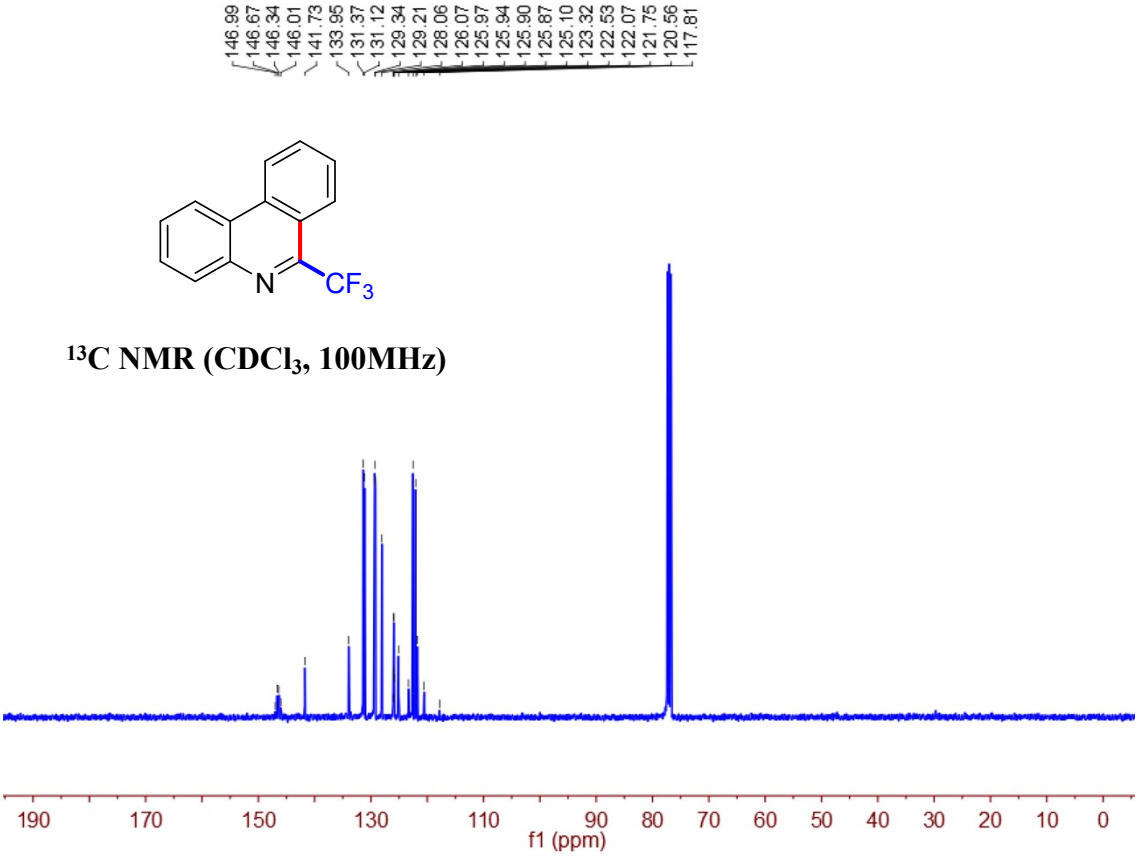
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5y



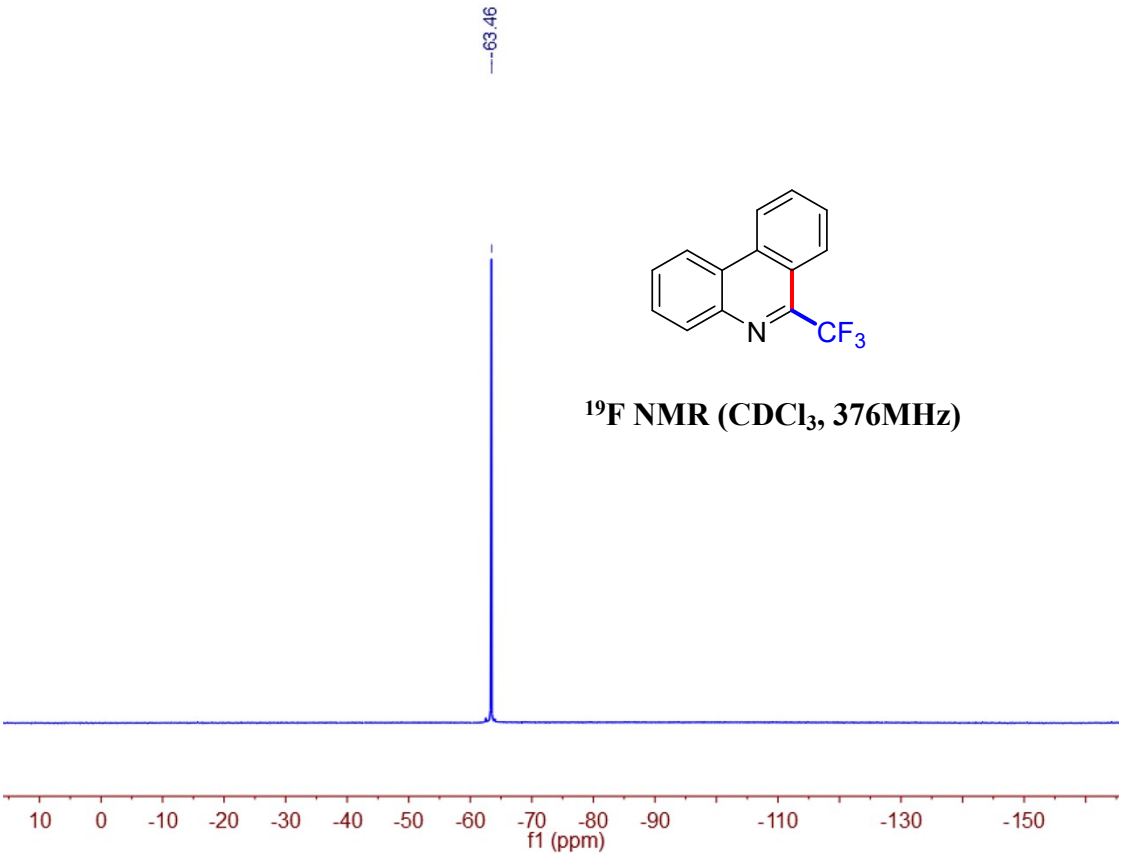
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5z



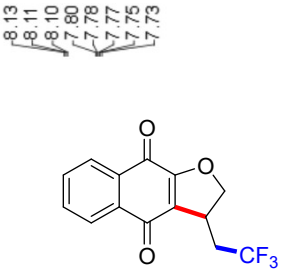
^{13}C NMR ($CDCl_3$, 100MHz)

^{13}C NMR Spectrum of Compound 5z

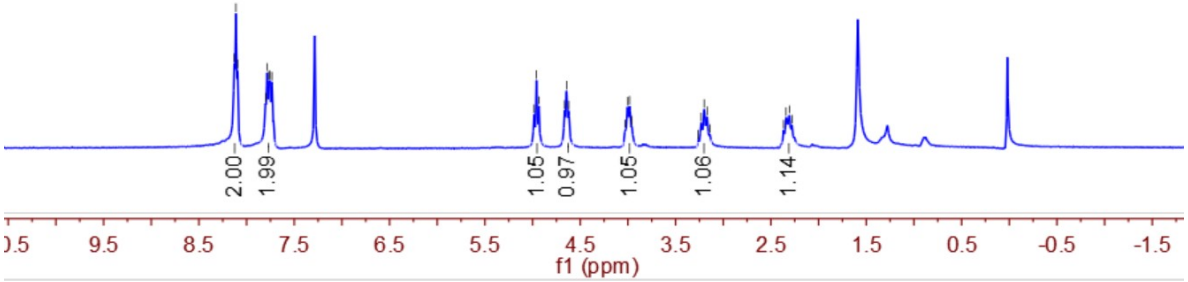


^{19}F NMR ($CDCl_3$, 376MHz)

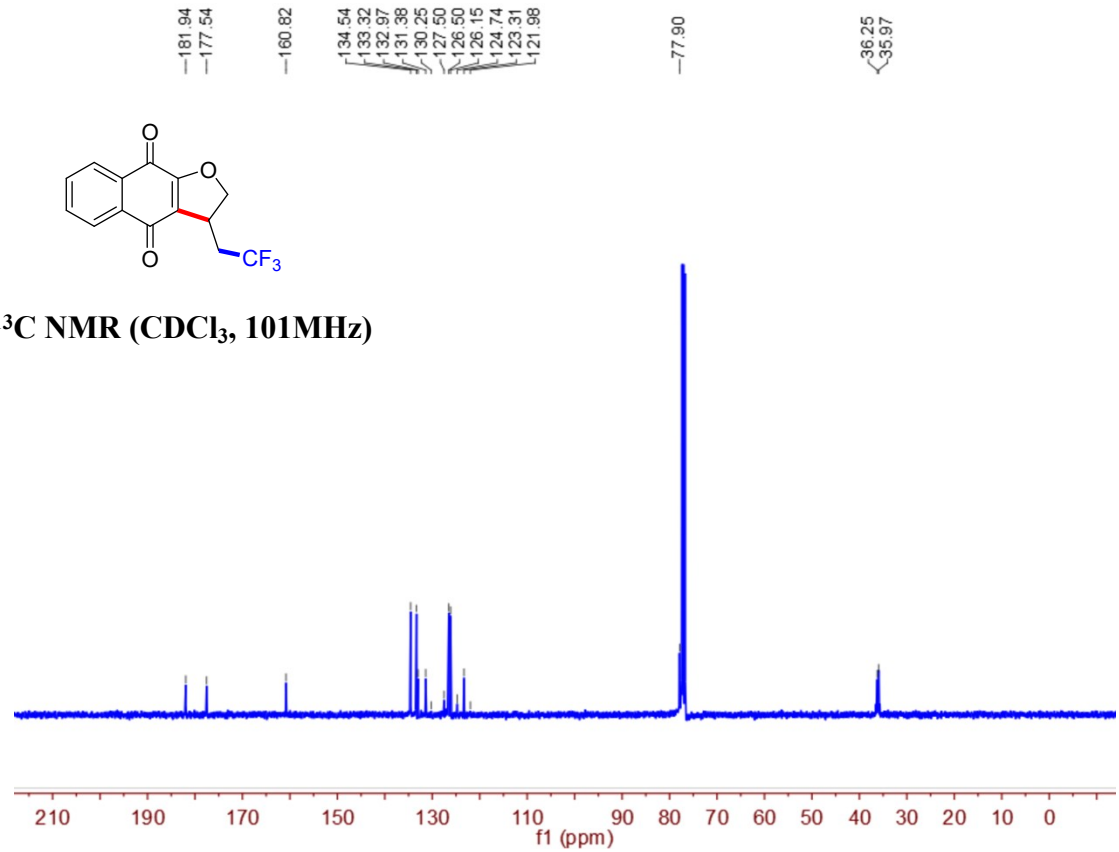
^{19}F NMR Spectrum of Compound 5z



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

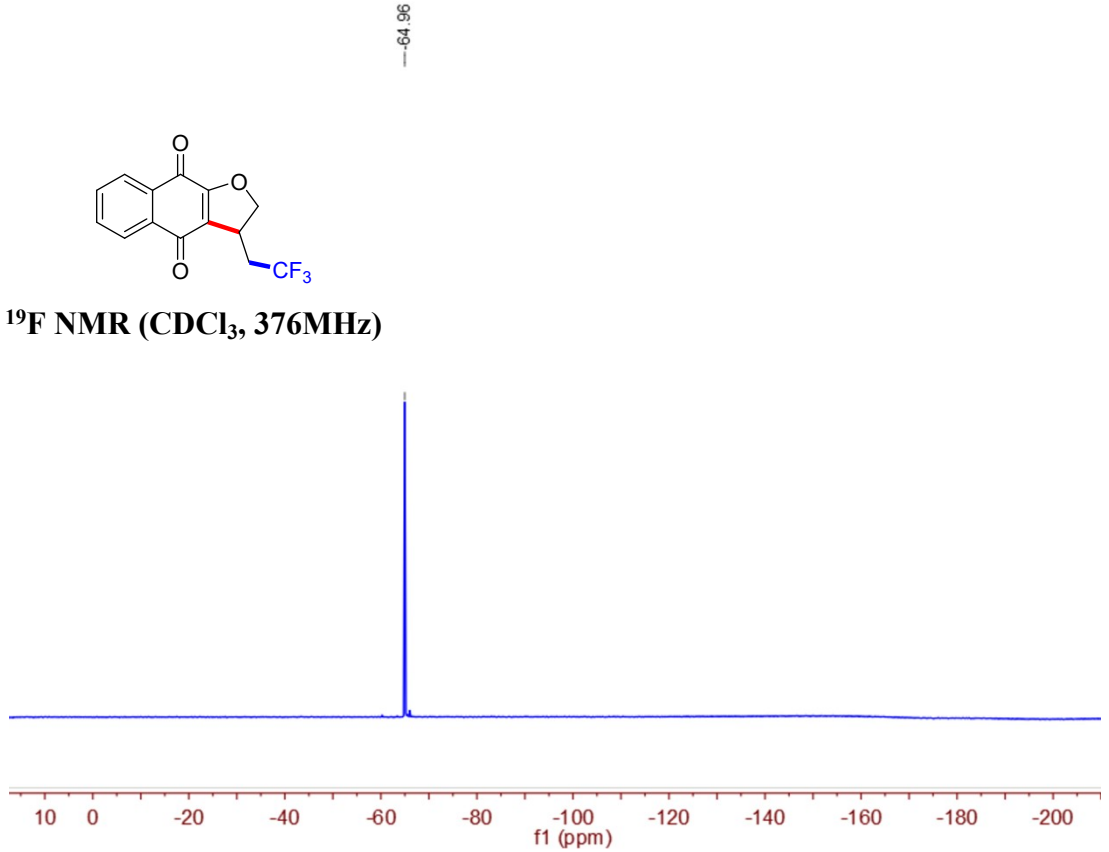


^{1}H NMR Spectrum of Compound 5aa



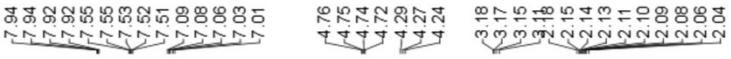
^{13}C NMR ($CDCl_3$, 101MHz)

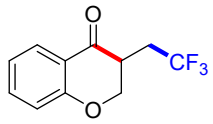
^{13}C NMR Spectrum of Compound 5aa



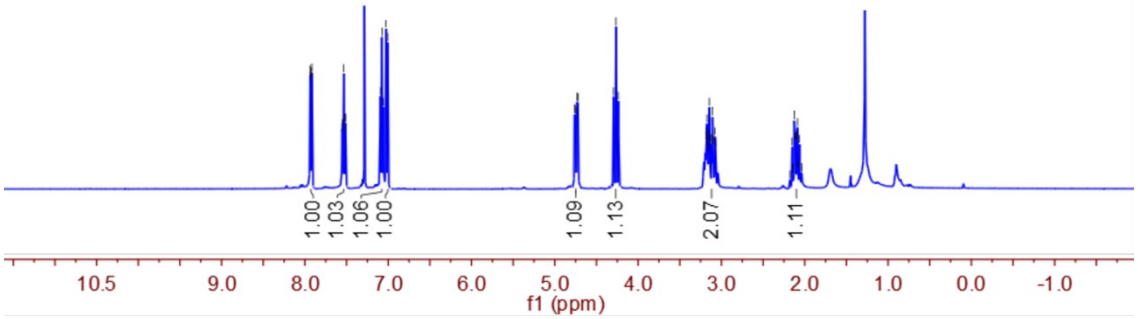
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5aa

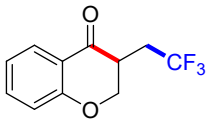




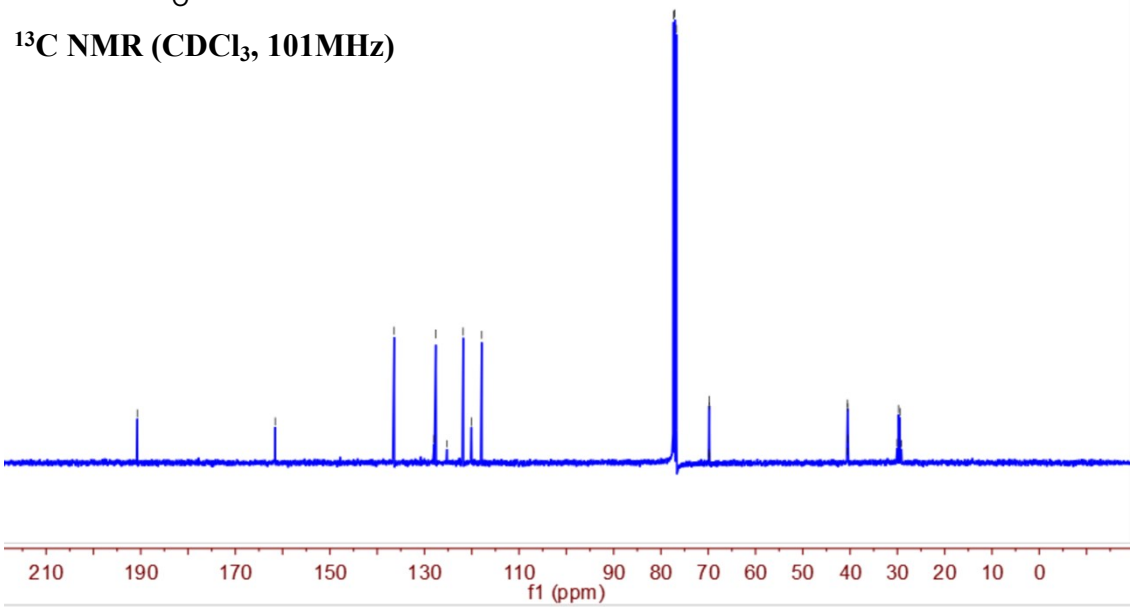
^{1}H NMR ($CDCl_3$, 400MHz)



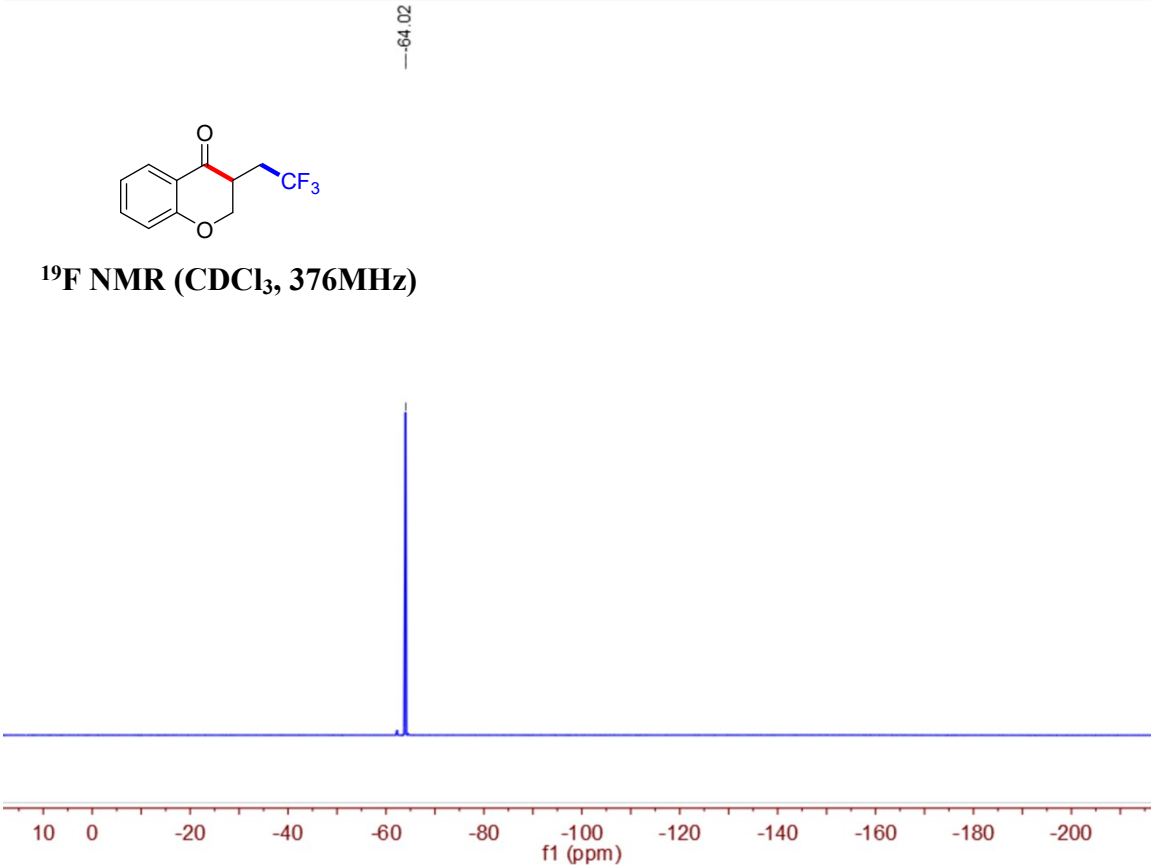
^{1}H NMR Spectrum of Compound 5ab



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

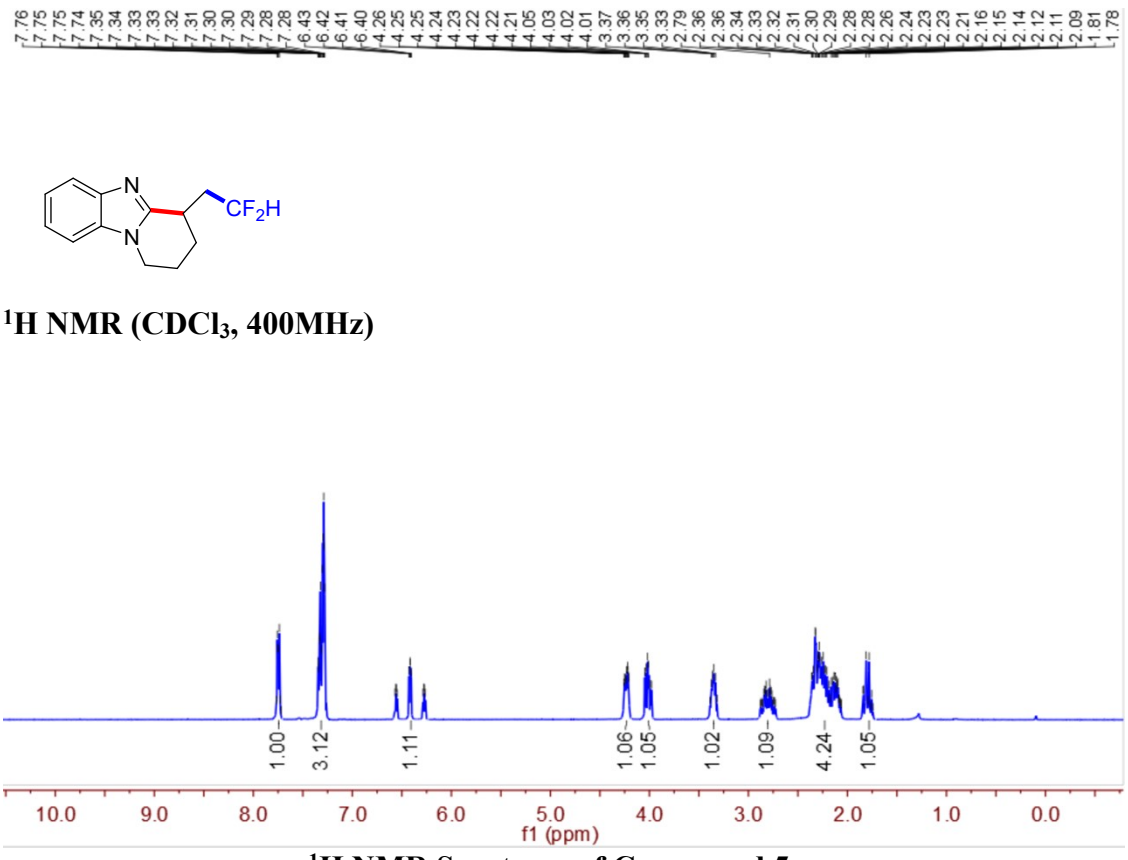


^{13}C NMR Spectrum of Compound 5ab



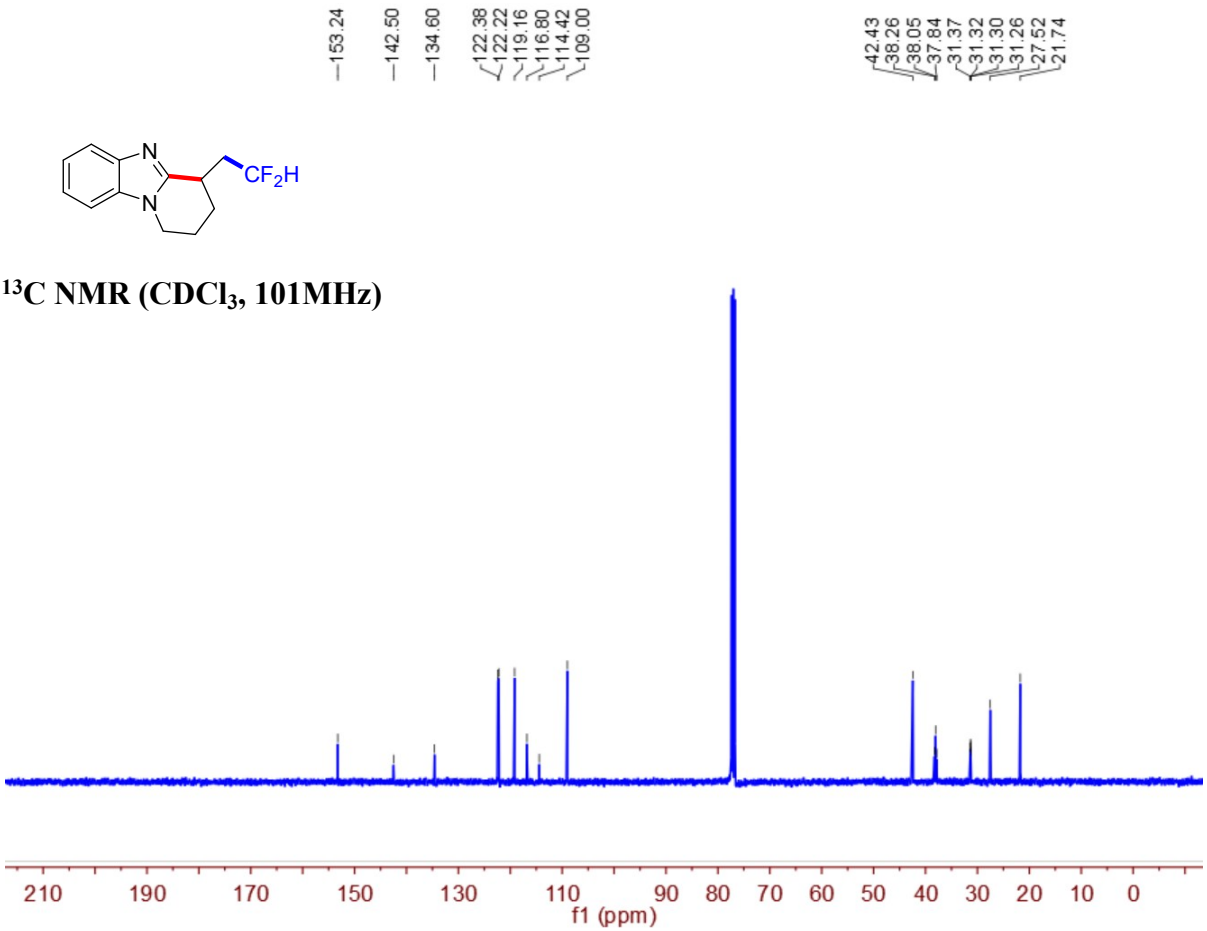
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5ab



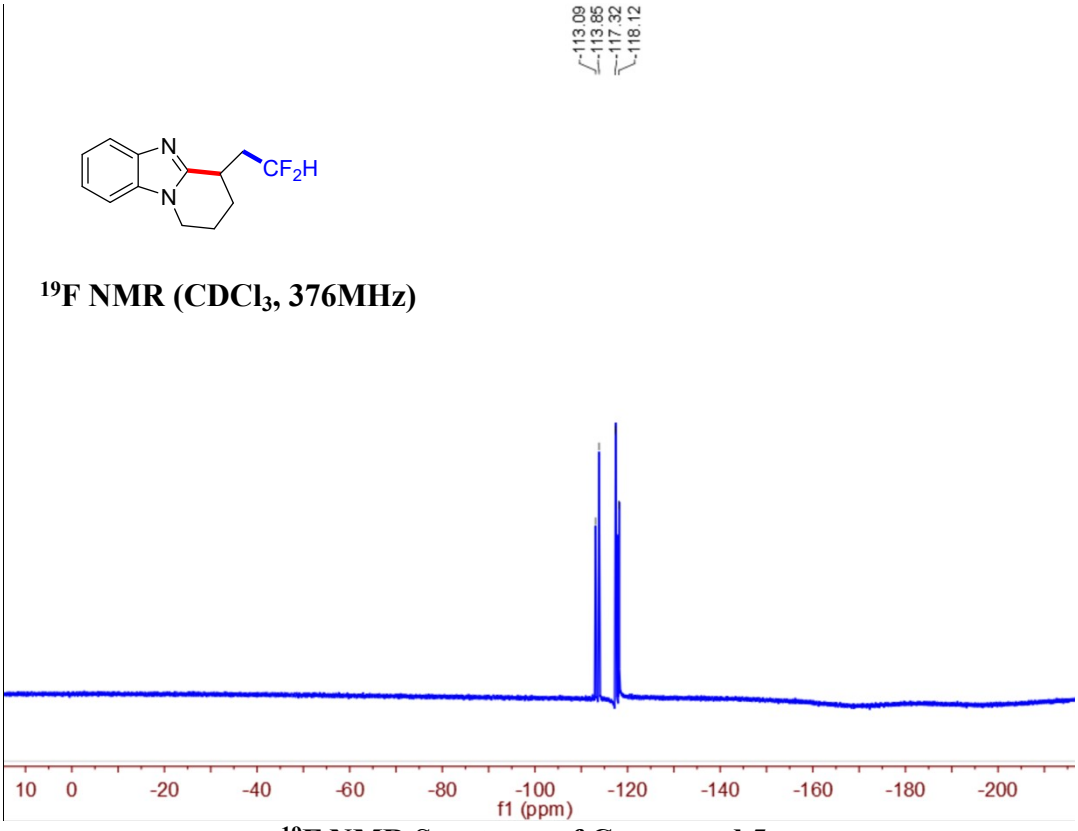
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5ac



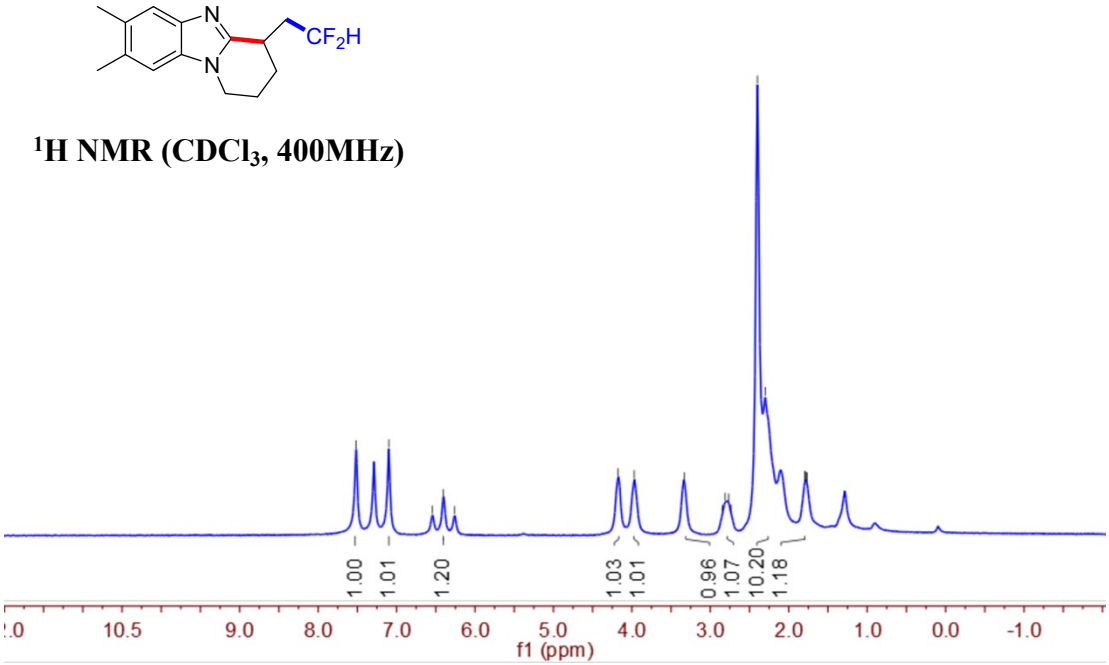
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 5ac



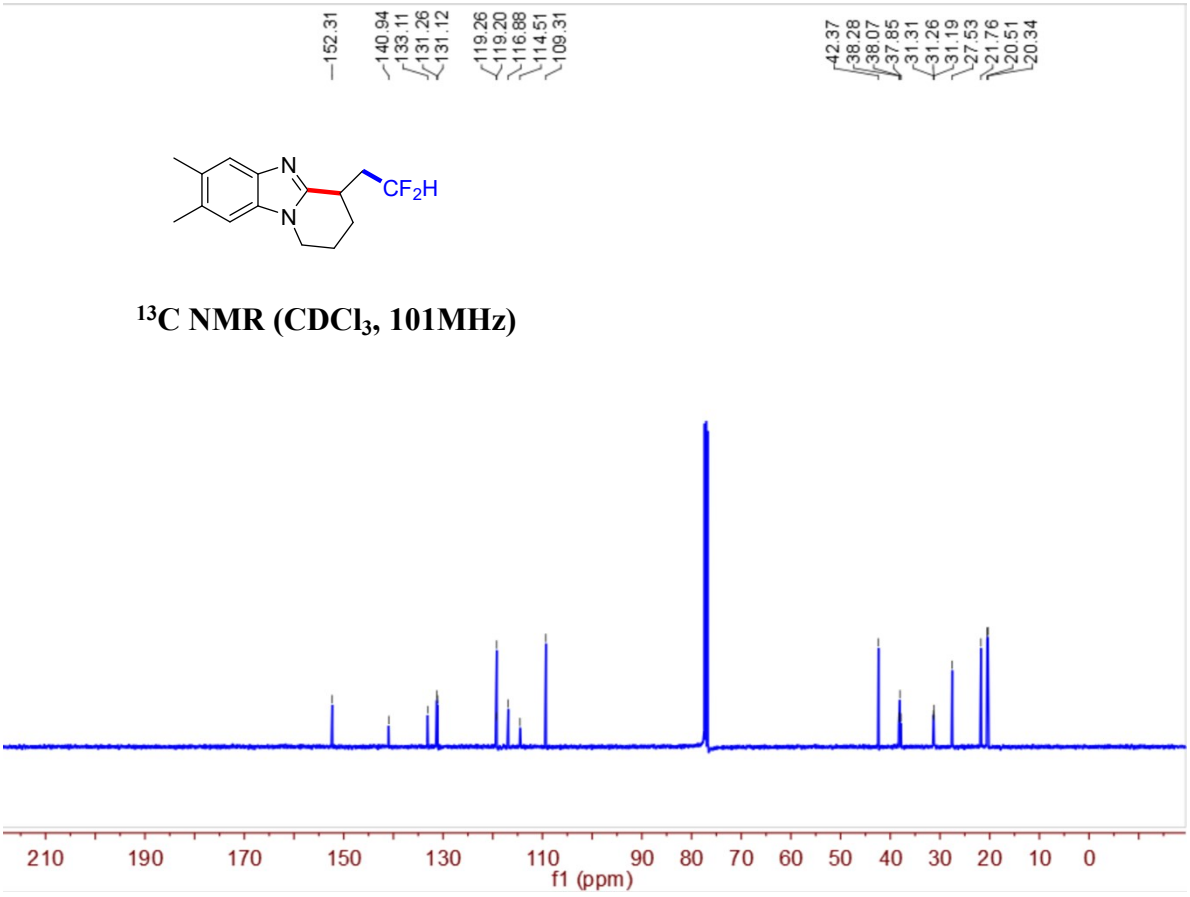
^{19}F NMR ($CDCl_3$, 376MHz)

^{19}F NMR Spectrum of Compound 5ac



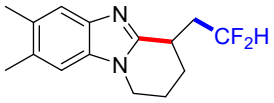
^{1}H NMR ($CDCl_3$, 400MHz)

^{1}H NMR Spectrum of Compound 5ad

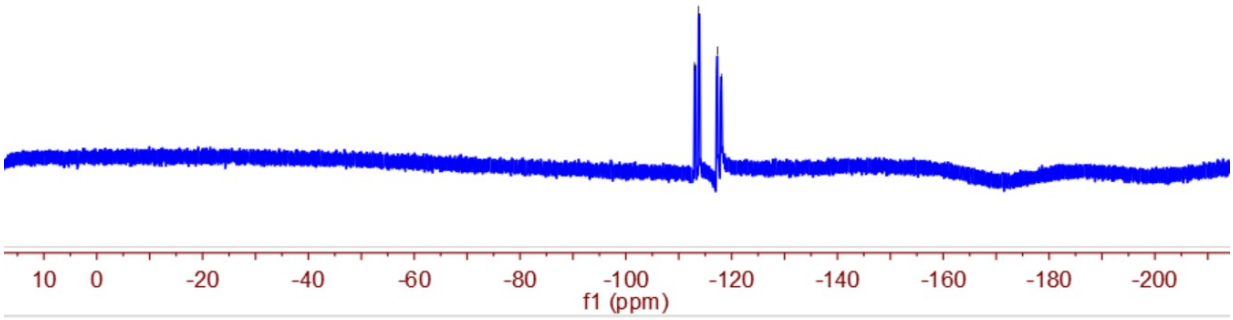


^{13}C NMR ($CDCl_3$, 101MHz)

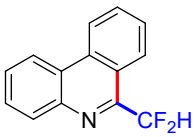
^{13}C NMR Spectrum of Compound 5ad



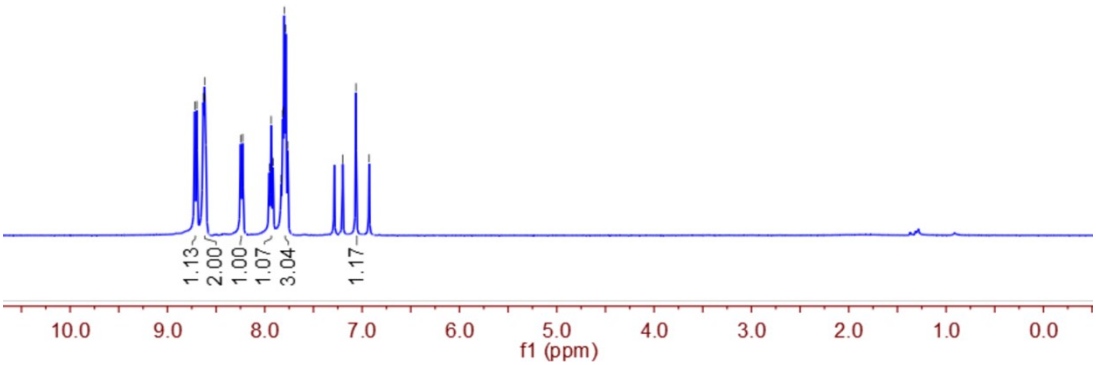
^{19}F NMR ($CDCl_3$, 376MHz)



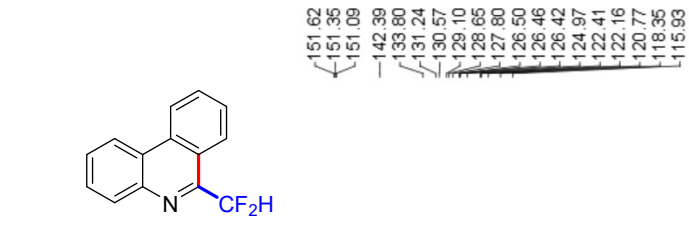
^{19}F NMR Spectrum of Compound 5ad



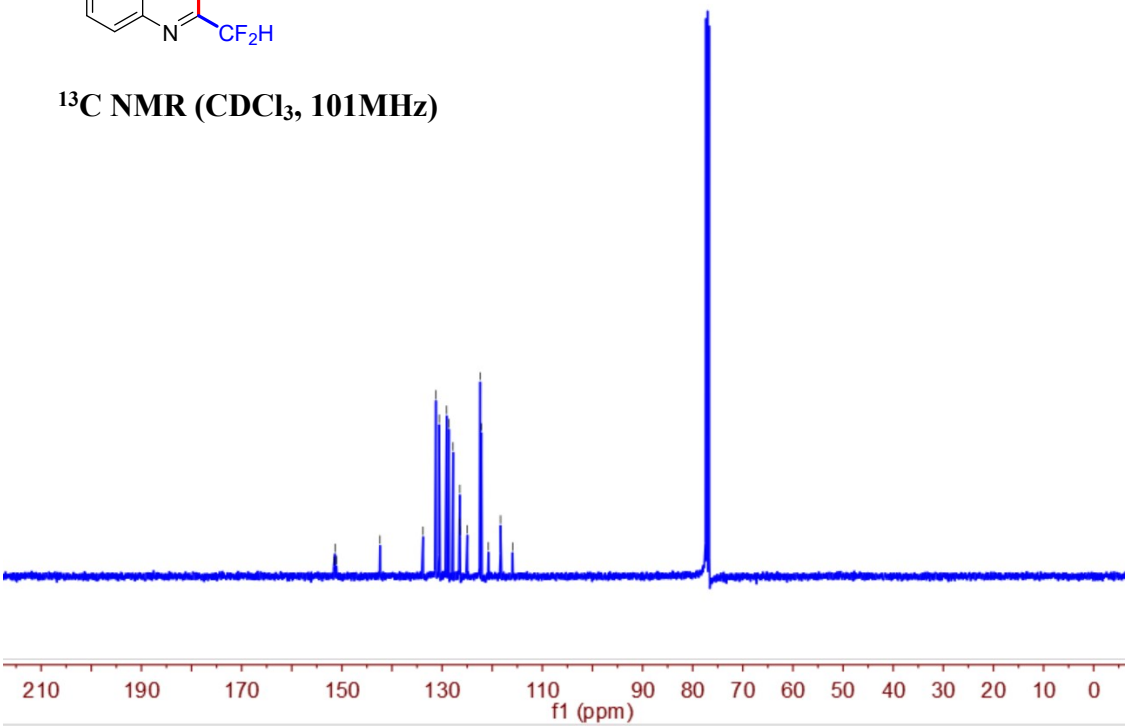
^{1}H NMR ($CDCl_3$, 400MHz)



^{1}H NMR Spectrum of Compound 5ae

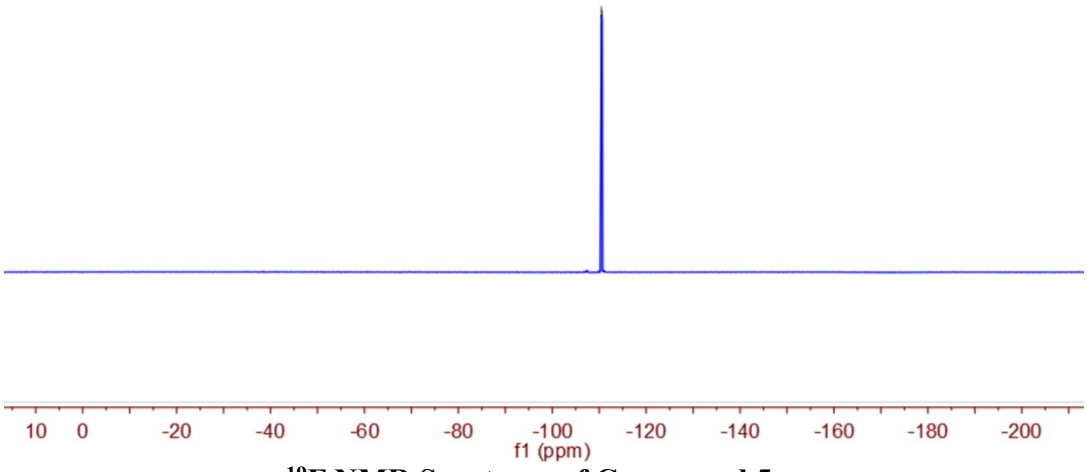


^{13}C NMR ($CDCl_3$, 101MHz)

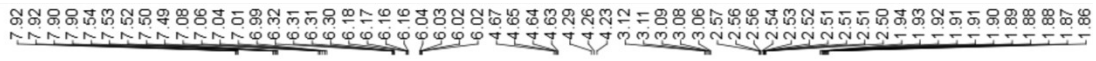


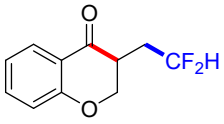
^{13}C NMR Spectrum of Compound 5ae

^{19}F NMR ($CDCl_3$, 376MHz)

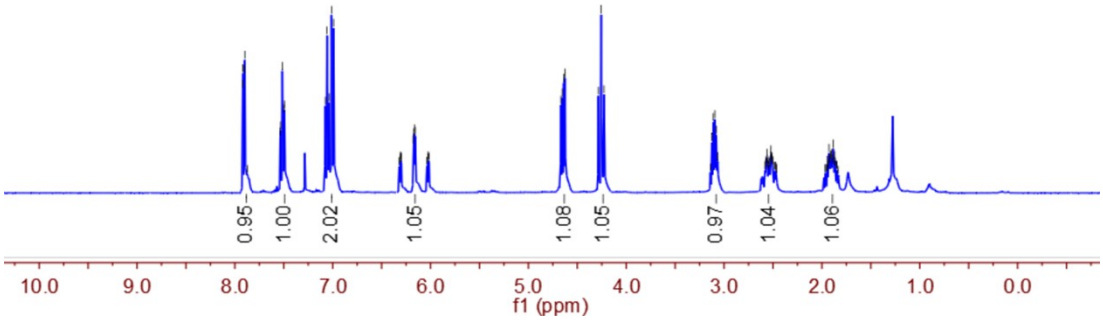


^{19}F NMR Spectrum of Compound 5ae

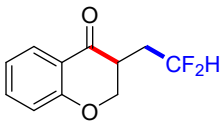




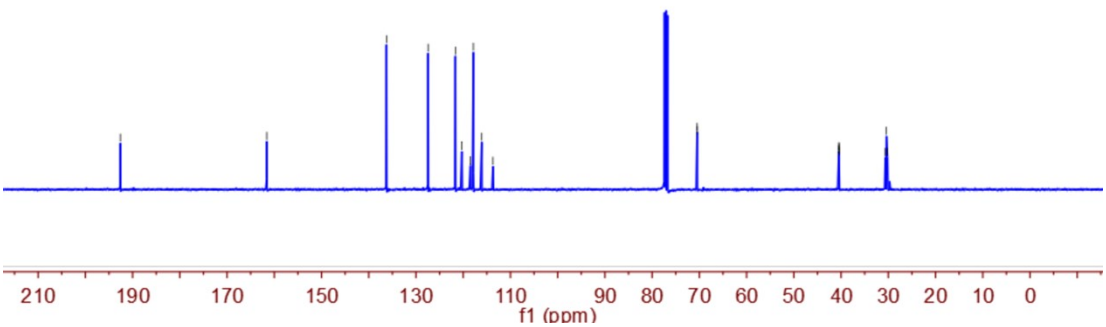
^{1}H NMR ($CDCl_3$, 400MHz)



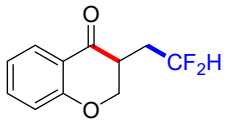
^{1}H NMR Spectrum of Compound 5af



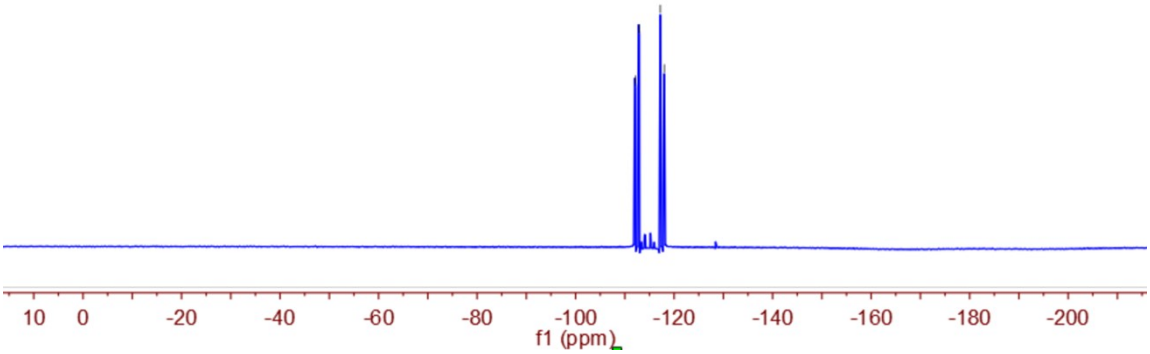
^{13}C NMR ($CDCl_3$, 101MHz)



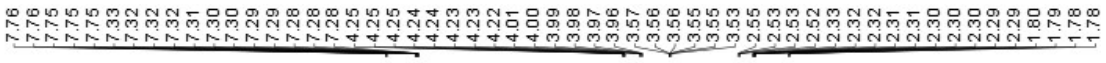
^{13}C NMR Spectrum of Compound 5af

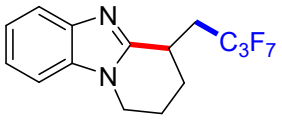


^{19}F NMR ($CDCl_3$, 376MHz)

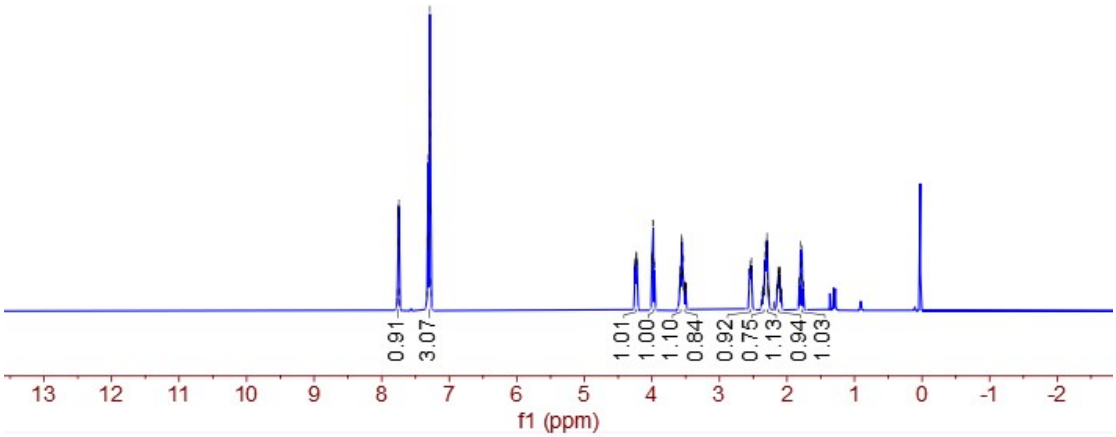


^{19}F NMR Spectrum of Compound 5af

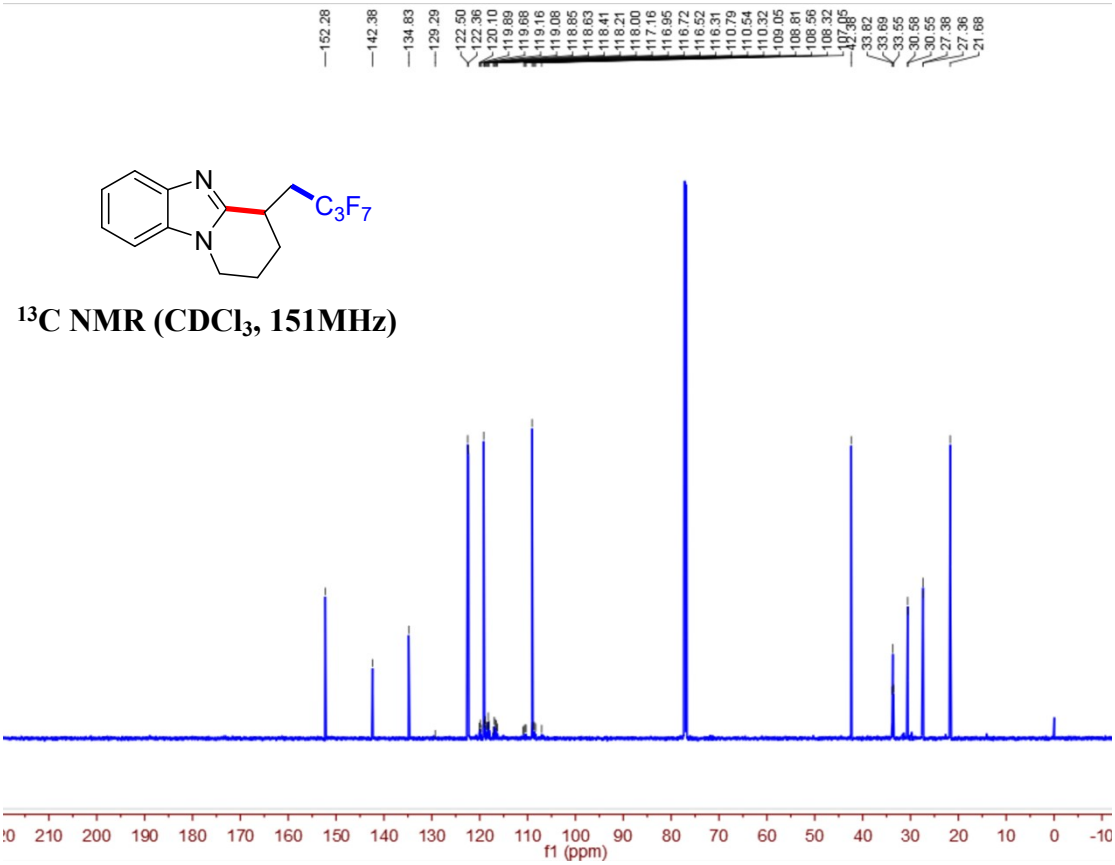




^{1}H NMR ($CDCl_3$, 600MHz)

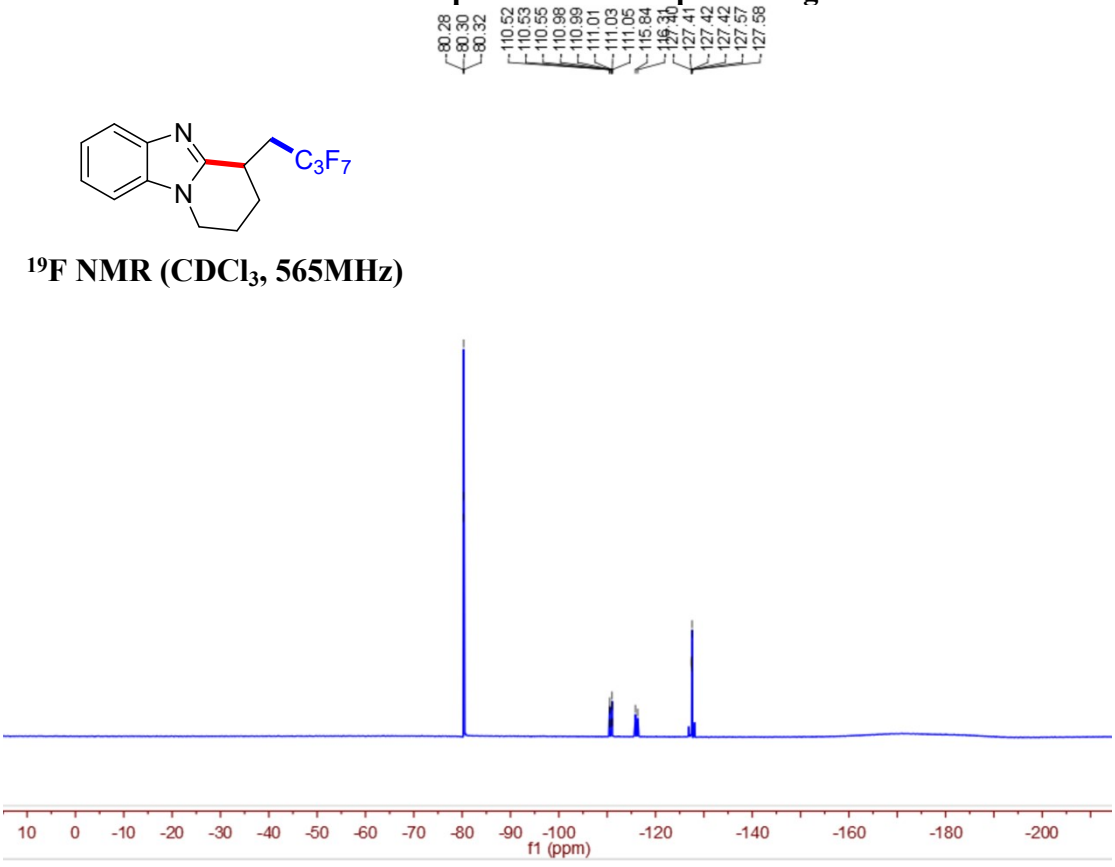


^{1}H NMR Spectrum of Compound 5ag



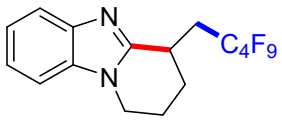
^{13}C NMR ($CDCl_3$, 151MHz)

^{13}C NMR Spectrum of Compound 5ag

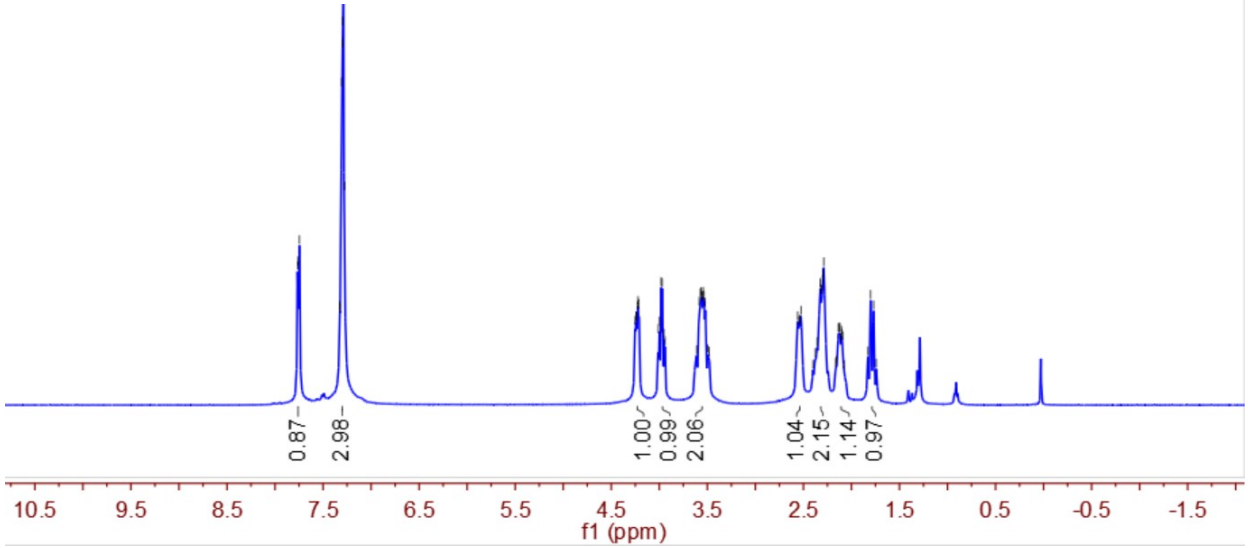


^{19}F NMR ($CDCl_3$, 565MHz)

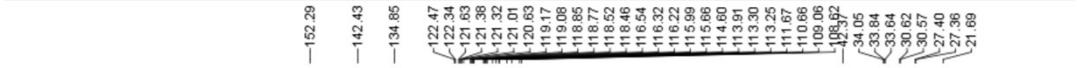
^{19}F NMR Spectrum of Compound 5ag

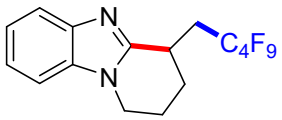


^{1}H NMR ($CDCl_3$, 400MHz)

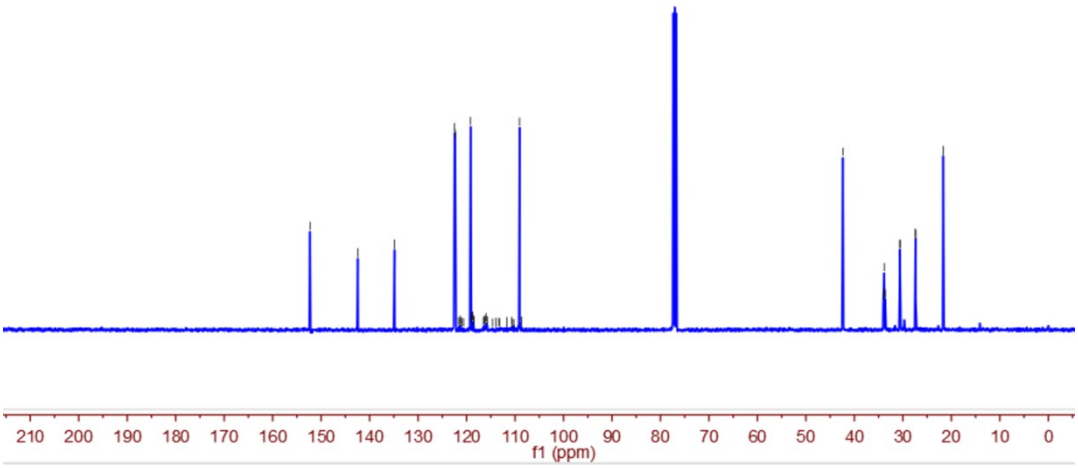


^{1}H NMR Spectrum of Compound 5ah

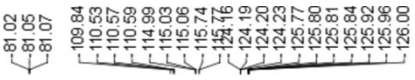


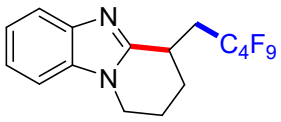


^{13}C NMR ($CDCl_3$, 101MHz)

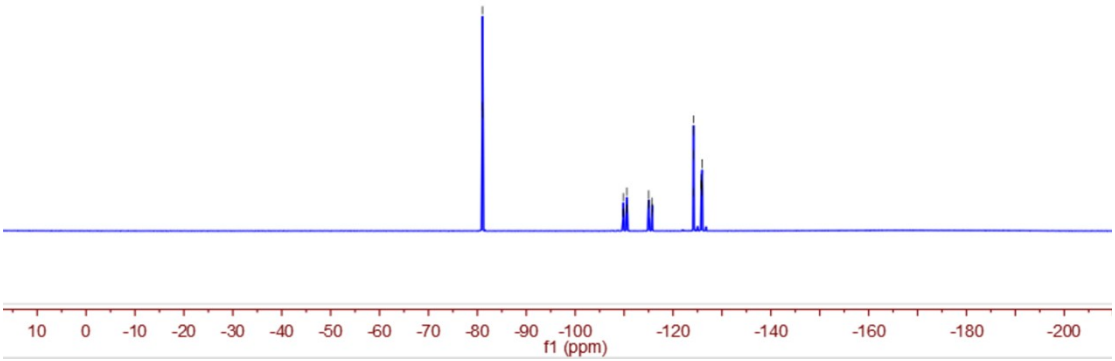


^{13}C NMR Spectrum of Compound 5ah

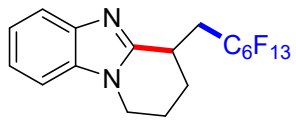




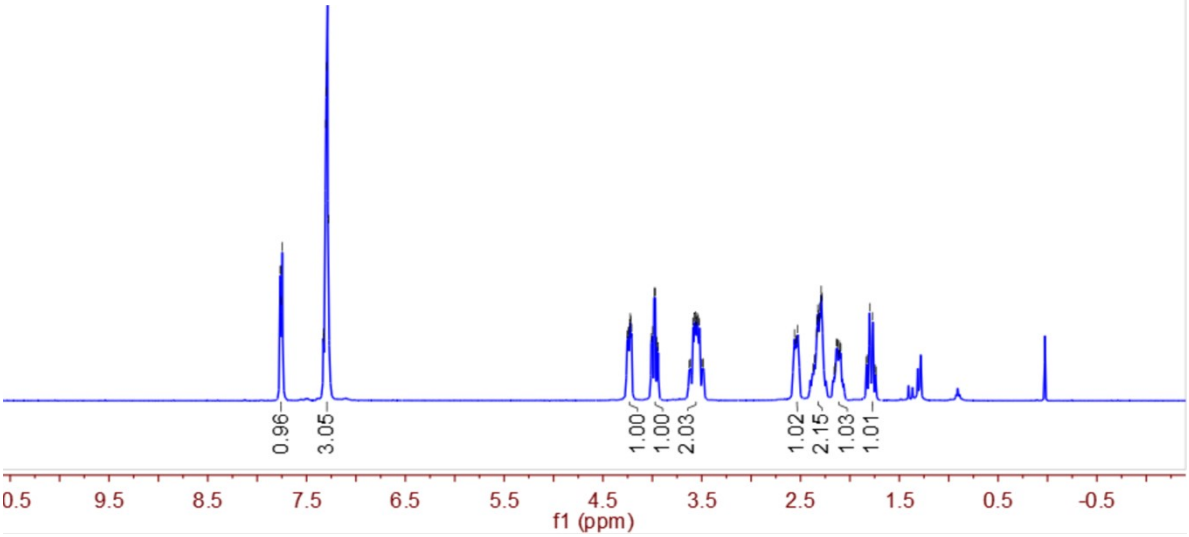
^{19}F NMR ($CDCl_3$, 376MHz)



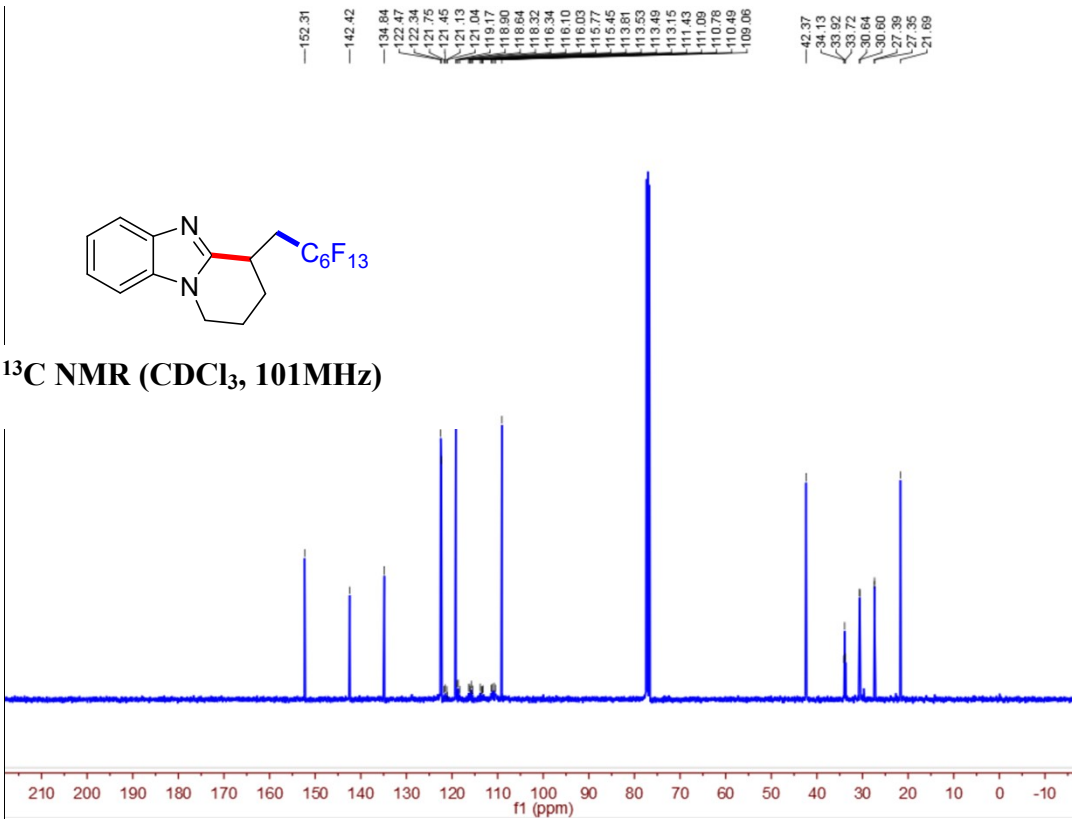
^{19}F NMR Spectrum of Compound 5ah



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

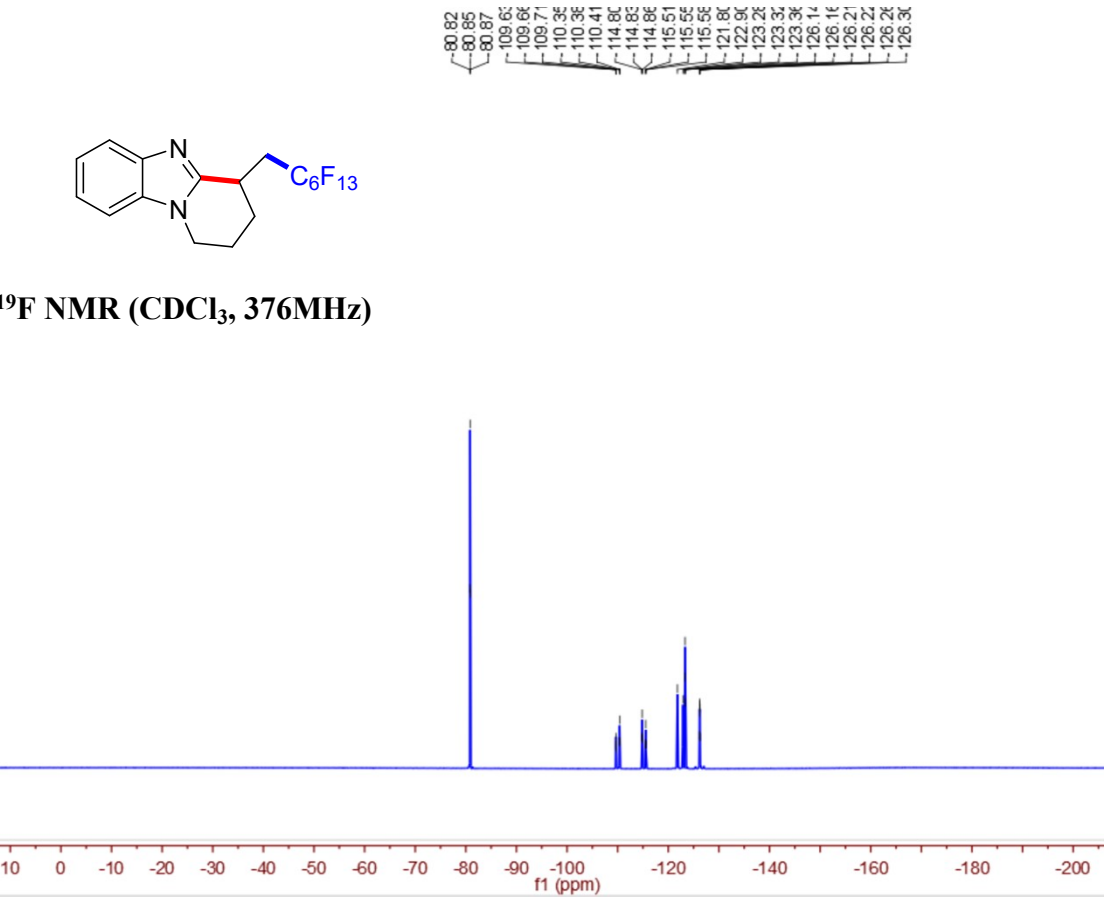


^{1}H NMR Spectrum of Compound 5ai



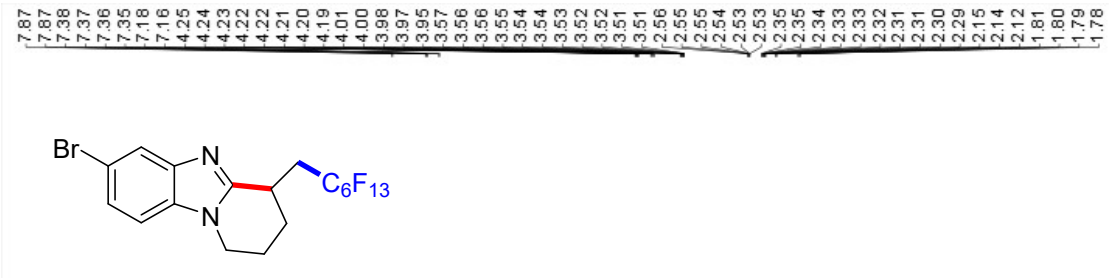
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 5ai

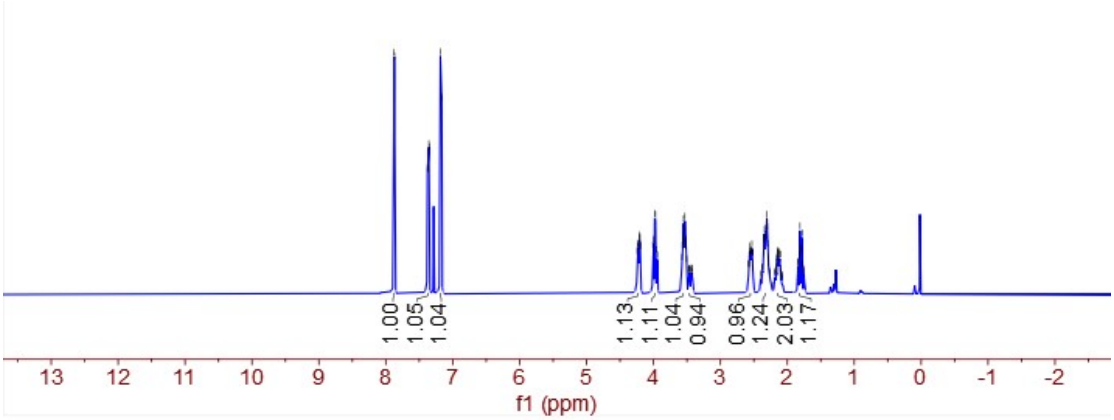


^{19}F NMR ($CDCl_3$, 376MHz)

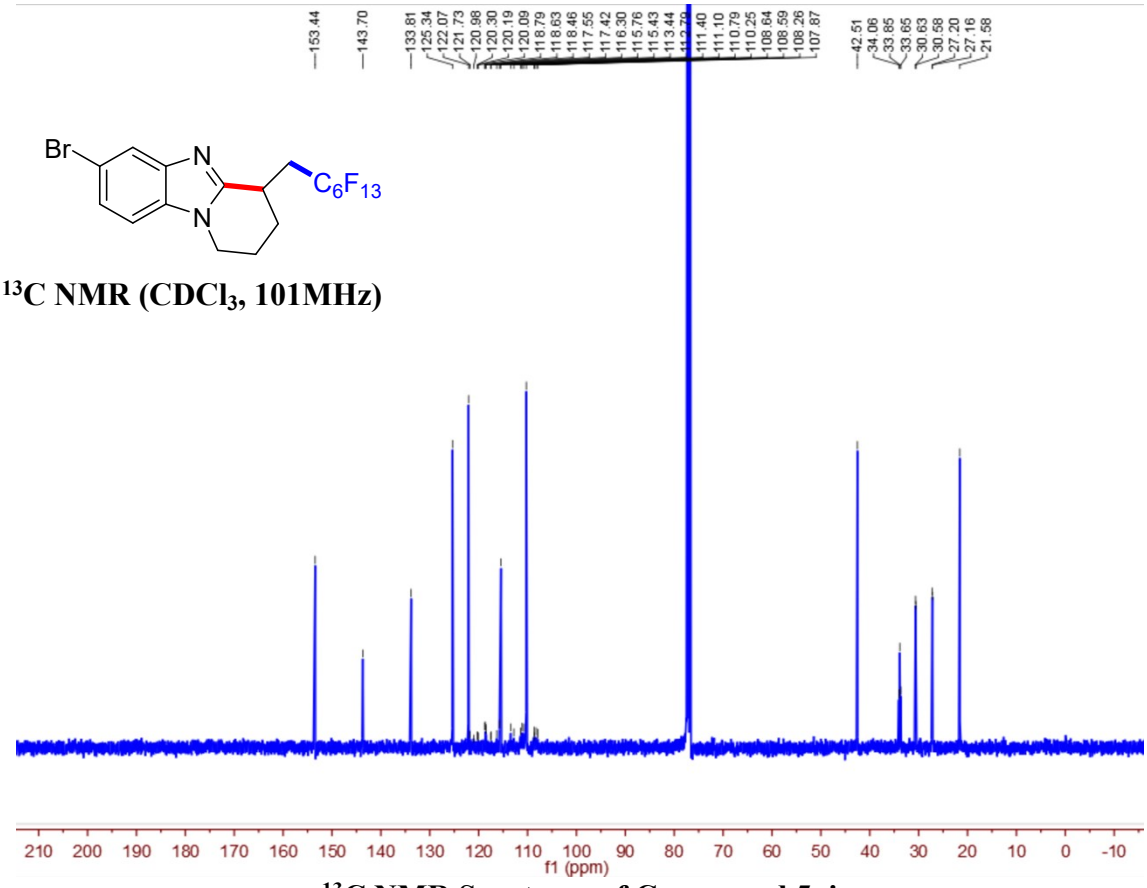
^{19}F NMR Spectrum of Compound 5ai



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

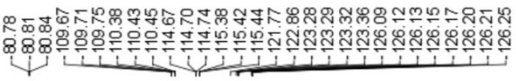


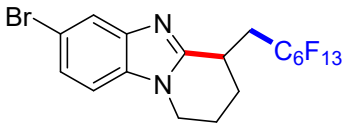
^{1}H NMR Spectrum of Compound 5aj



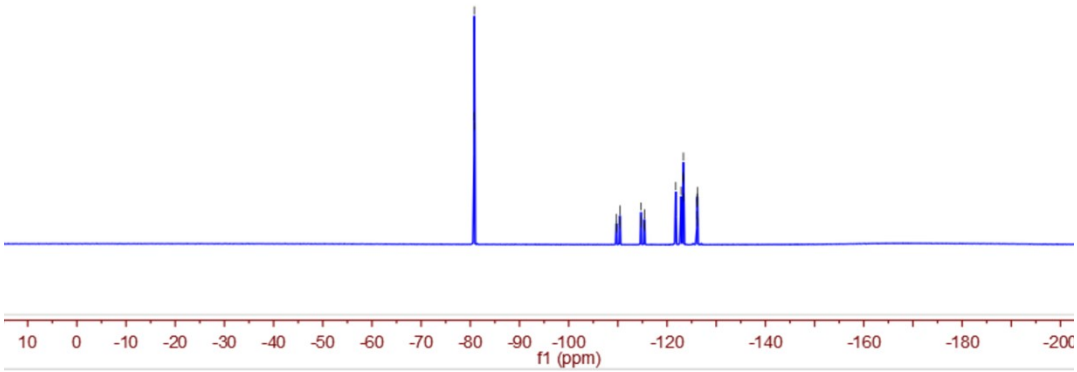
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 5aj

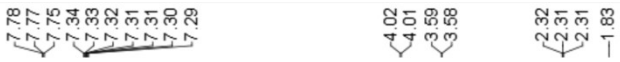


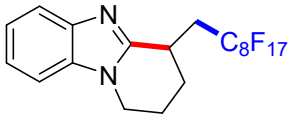


^{19}F NMR ($CDCl_3$, 376MHz)

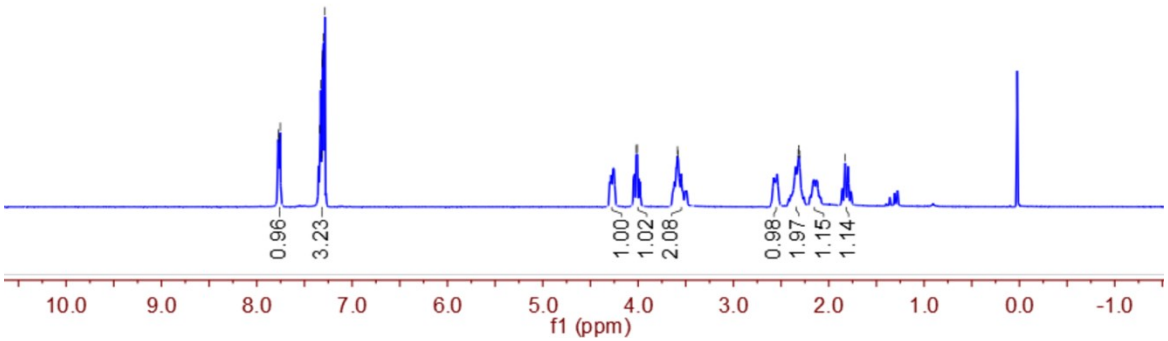


^{19}F NMR Spectrum of Compound 5aj

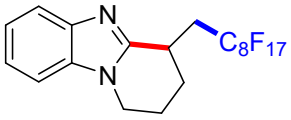




^{1}H NMR ($CDCl_3$, 400MHz)

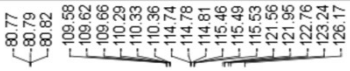


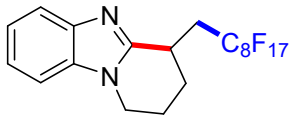
^{1}H NMR Spectrum of Compound 5ak



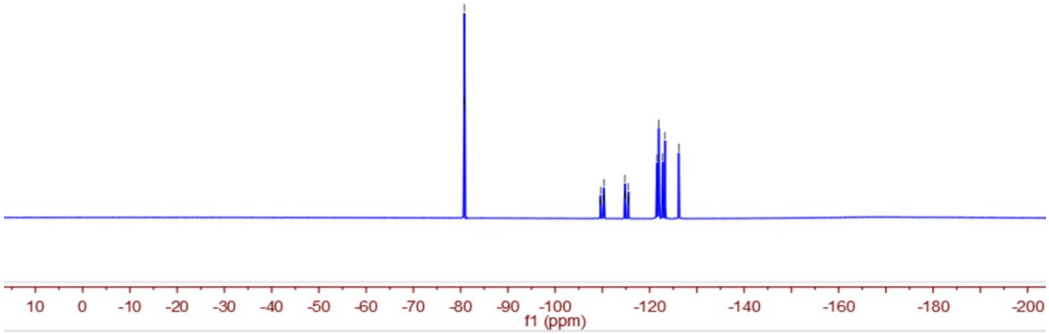
^{13}C NMR ($CDCl_3$, 101MHz)

^{13}C NMR Spectrum of Compound 5ak





^{19}F NMR ($CDCl_3$, 376MHz)



^{19}F NMR Spectrum of Compound 5ak