Supplementary Information

$Cs_2AgBiBr_6$-Photocatalytic Trifluoromethylation and Applications in Drug Modification

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1. General Information

All chemical reagents used in this study were procured from commercial suppliers and utilized without any modification. Thin-layer chromatography (TLC) was performed on GF254 silica gel plates with a mesh size of 200-300. Product purification was accomplished through column chromatography, employing silica gel (200-300 mesh) obtained from Qingdao Haiyang Chemical Co., Ltd. NMR analyses, including ^{1}H, ^{13}C, and ^{19}F NMR, were conducted on a Bruker Avance 400 MHz spectrometer. Proton chemical shifts were reported in parts per million (ppm), with tetramethylsilane (TMS) as the internal standard, measured at a controlled room temperature of 20 ± 3°C. The high-resolution mass spectra (HR-MS) were obtained using an Agilent 6546 LC/Q-TOF equipped with an electrospray ionization (ESI) source. X-ray diffraction (XRD) measurements were conducted on an XRD-6000 with Cu Kα radiation (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Fisher K-Alpha spectrometer, with binding energies calibrated against the carbon C 1s peak (284.8 eV). Absorption spectra were recorded on a UV-2600 UV–Vis spectrometer. Transient photocurrent responses were measured using a CHI-660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). Fluorescence spectra were acquired using an F-4600 FL Spectrophotometer with an excitation wavelength of 330.0 nm.

Photochemical reaction was carried out under visible light irradiation by a blue LED at 25ºC. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. wasused in this system. Eight 10 W blue LEDs were equipped in this Photo reactor. The blue LED'senergy peak wavelength is 430 nm, peak width at half-height is 18.4 nm.

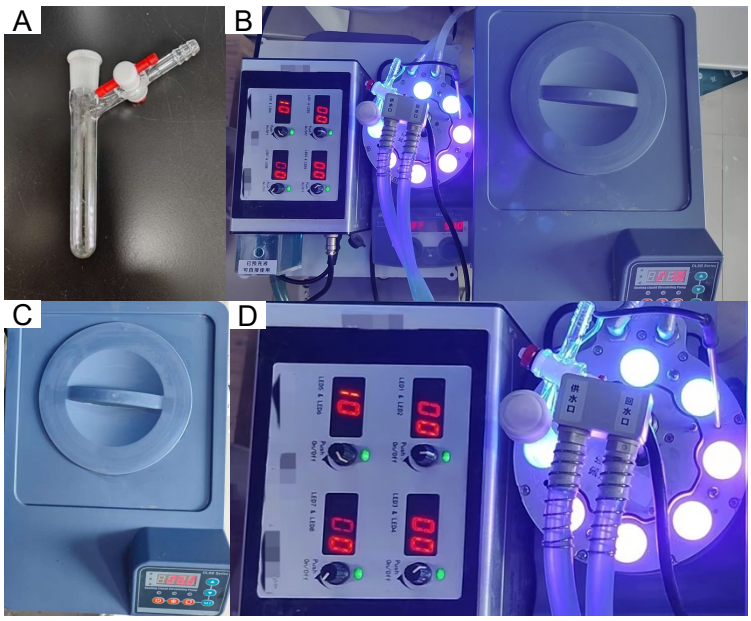


Figure S1. A: Schlenk tube; **B:** Total reaction system; **C**: Cooling water circuit; **D**: Photoreactor

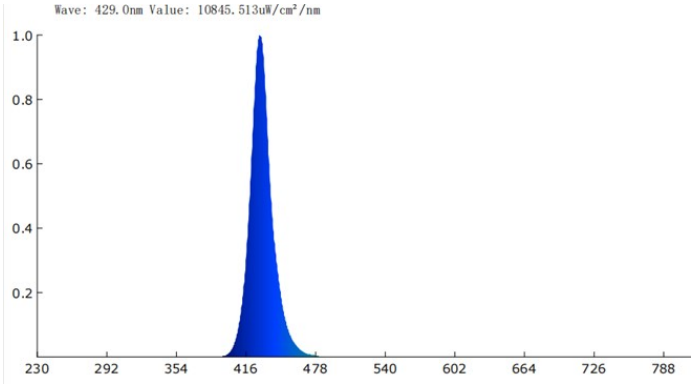
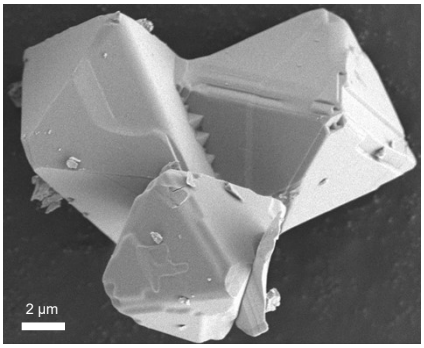


Figure S2. The spectrum of our lamp (430 nm LED)

2. Experimental Procedures

2.1 The Preparation and Characterization of $Cs_2AgBiBr_6$

$Cs_2AgBiBr_6$ was synthesized following the previously reported methods.[1] In a typical procedure, CsBr (0.426 g), $BiBr_3$ (0.449 g), AgBr (0.188 g) and 10 mL of 40% HBr were mixed in a 50 mL round-bottom flask. The reaction mixture was heated to 110 ℃ under stirring and maintained at this temperature for 2 hours, which then cooled to room temperature. An orange solid precipitated from the solution. The $Cs_2AgBiBr_6$ precipitate was separated by centrifugation at 10,000 rpm for 10 minutes. After centrifugation, the product was dried overnight in a vacuum oven at 60°C to yield 745 mg of $Cs_2AgBiBr_6$ (70% yield). The scanning electron microscope (SEM) analysis reveals that the sample consists of irregularly shaped octahedral particles.



According to the related curve of $(\alpha h\nu)^2$ versus photon energy ($(\alpha h\nu)^2 = A(h\nu - E_g)$) and UV-vis absorption results, the potentials of $Cs_2AgBiBr_6$ vs normal hydrogen electrode (NHE) are determined using the following equation:

$$E_{VB} = \chi - E_e + 0.5E_g,$$

$$E_{CB} = E_{VB} - E_g.$$

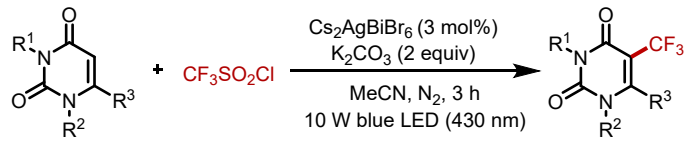
Where χ ($\chi \approx 5.34$ eV) is the absolute electronegativity of the semiconductor $Cs_2AgBiBr_6$, defined as the geometric mean of the absolute electronegativity of the constituent atoms; E_e is the energy of free electrons on the hydrogen scale (ca. 4.5 eV); and E_g is the band gap energy value (ca. 2.09 eV). Therefore, the potentials of $Cs_2AgBiBr_6$ vs NHE are calculated to be +1.86 eV and -0.23 eV. After relevant conversions, the values of the valence band (VB) and

conduction band (CB) relative to the saturated calomel electrode (SCE) are +1.61 eV and -0.48 eV, respectively.

2.2 The Preparation of $CsPbBr_3$

$CsPbBr_3$ was synthesized following a previously reported method.[2] First, two precursor solutions were prepared: 1.0 mmol of CsBr dissolved in 1.0 mL of H_2O and 1.0 mmol of $PbBr_2$ dissolved in 1.5 mL of DMF. The DMF solution of $PbBr_2$ and the H_2O solution of CsBr were then slowly added dropwise into a vigorously stirred mixture of 250 mL hexane, 4 mL oleic acid, and 0.75 mL n-octylamine. After the addition, 200 mL of acetone was introduced to decompose the emulsion. The $CsPbBr_3$ precipitate was separated by centrifugation at 7000 rpm for 10 minutes. Finally, the collected precipitate was dried overnight in a vacuum oven to yield 485 mg of $CsPbBr_3$ (82% yield).

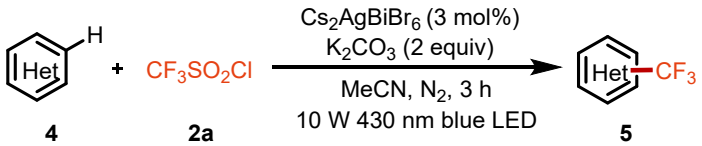
2.3 General Experimental Procedures for Trifluoromethylation of Uracils



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

Uracils (**1**, 0.1 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), and MeCN (1.0 mL) were sequentially added to a 25 mL reaction flask. The flask was then irradiated with a 10 W blue LED light (430 nm) at room temperature under a nitrogen atmosphere for 3 hours. After the reaction, the mixture was extracted with ethyl acetate (3 × 3 mL). The organic extracts were combined, dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography using a petroleum ether/ethyl acetate mixture as the eluent, yielding the desired product **3**.

2.4 General Experimental Procedures for Trifluoromethylation of (Hetero)arenes

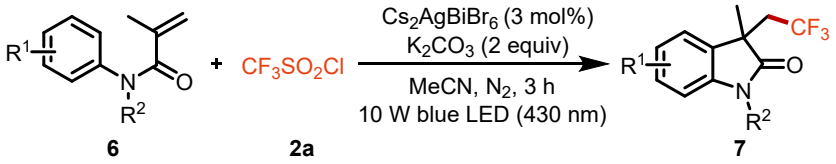


4 **2a** **5**

(Hetero)arenes (**4**, 0.1 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), and MeCN (1.0 mL) were sequentially added to a 25 mL reaction flask. The flask was then irradiated with a 10 W blue LED light (430 nm) at room temperature under a nitrogen atmosphere for 3 hours. After the reaction, the mixture was extracted with ethyl acetate (3 × 3 mL). The organic extracts were combined, dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography using a petroleum ether/ethyl acetate mixture as the eluent, yielding

the desired product **5**.

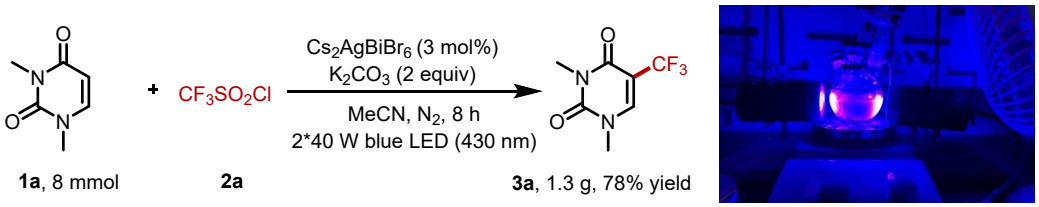
2.5 General Experimental Procedures for Trifluoromethylation/cyclization reaction



6 **2a** **7**

N-arylacrylamides (**6**, 0.1 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), and MeCN (1.0 mL) were sequentially added to a 25 mL reaction flask. The flask was then irradiated with a 10 W blue LED light (430 nm) at room temperature under a nitrogen atmosphere for 3 hours. After the reaction, the mixture was extracted with ethyl acetate (3 × 3 mL). The organic extracts were combined, dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography using a petroleum ether/ethyl acetate mixture as the eluent, yielding the desired product **7**.

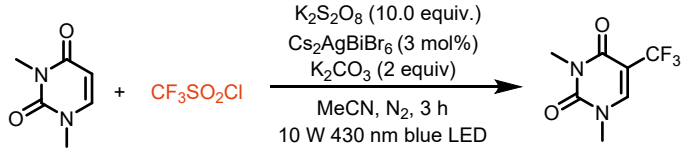
2.6 Scale-up Synthesis



1a, 8 mmol **2a** **3a**, 1.3 g, 78% yield

Uracil (**1a**, 8 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), and MeCN (80.0 mL) were sequentially added to a 250 mL reaction flask. The flask was then irradiated with 2*40 W blue LED light (430 nm) at room temperature under a nitrogen atmosphere for 8 hours. After the reaction, the mixture was extracted with ethyl acetate (3 × 30 mL). The organic extracts were combined, dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography using a petroleum ether/ethyl acetate mixture as the eluent, yielding the 1.3 g desired product **3a**.

2.7 Control expriments



1a **2a** N.D.

Uracils (**1a**, 0.1 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), $K_2S_2O_8$ (10 equiv.) and MeCN (1.0 mL) were sequentially added to a 25 mL reaction flask. The flask was then irradiated with a 10 W blue LED light (430 nm) at room

temperature under a nitrogen atmosphere for 3 hours. No desired product was detected. We performed additional tests to ensure that the photocatalyst remained unaltered during the reactions with $K_2S_2O_8$ and ammonium oxalate. For the reaction with $K_2S_2O_8$, we mixed $Cs_2AgBiBr_6$ with $K_2S_2O_8$ (1 equiv) in CH_3CN and stirred the mixture for 3 hours. The resulting solid was filtered, washed with deionized water, and dried before being analyzed by X-ray diffraction (XRD). The XRD pattern showed significant changes in the catalyst during the stirring process with $K_2S_2O_8$. However, the reaction proceeded smoothly with this modified catalyst, and product **3a** was obtained in 80% yield. Based on these results, we believed that $K_2S_2O_8$ primarily acts as an electron inhibitor, preventing the photogenerated electrons to participate in the reaction.

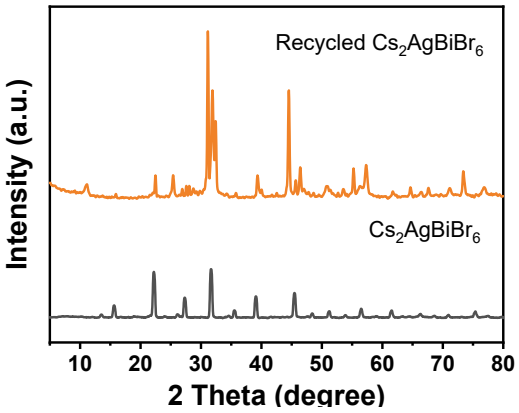
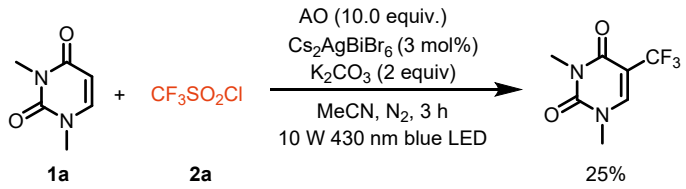


Figure S3. Yellow line: XRD of the recycled $Cs_2AgBiBr_6$ from mixture of $Cs_2AgBiBr_6$ and $K_2S_2O_8$; Black line: freshly prepared $Cs_2AgBiBr_6$



Uracils (**1a**, 0.1 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), ammonium oxalate (10 equiv.) and MeCN (1.0 mL) were sequentially added to a 25 mL reaction flask. The flask was then irradiated with a 10 W blue LED light (430 nm) at room temperature under a nitrogen atmosphere for 3 hours. desired product was obtained in 25% yield. Similarly, for the reaction with ammonium oxalate, we mixed $Cs_2AgBiBr_6$ with ammonium oxalate (1 equiv) in CH_3CN and stirred the mixture for 3 hours. The solid was again filtered, washed with deionized water, and dried before being analyzed by XRD. The XRD pattern showed significant changes in the catalyst during this process as well. Nonetheless, the reaction proceeded smoothly, and product **3a** was obtained in 82% yield. We believe that ammonium oxalate acts primarily as a hole inhibitor, preventing the photogenerated holes from participating in the reaction.

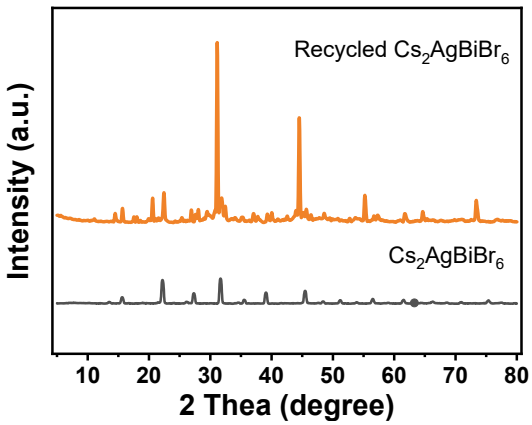


Figure S4. Yellow line: XRD of the recycled $Cs_2AgBiBr_6$ from mixture of $Cs_2AgBiBr_6$ and ammonium oxalate; Black line: freshly prepared $Cs_2AgBiBr_6$

2.8 Sensitivity Assessment of Reaction

Table S1. Sensitivity assessment of reaction

Parameter	Variation		Description	Yield [b]	Deviation[c]
Concentration (c)	High c	c + 10% c	0.9 mL CH_3CN	90%	-6%
	Low c	c - 10% c	1.1 mL CH_3CN	87%	-9%
H_2O level	High H_2O	+ H_2O; V (H_2O) = 1%V_{rxn}	10 μL H_2O in 1 mL CH_3CN	76%	-20%
O_2 level	High O_2	O_2 balloon	O_2 instead of N_2	0%	-96%
Temperature (T)	High T	T + 10 ℃	35 ℃	87%	-9%
	Low T	T – 10 ℃	15 ℃	77%	-19%
Light intensity (W)	Low W	W/16	0.6 W	0%	-96%
Base dosage	High base	+ 1 equiv	3 equiv K_2CO_3	91%	-5%
	Low base	- 1 equiv	1 equiv K_2CO_3	60%	-36%
Scale	Big scale	n·20	2 mmol of **1a**	78%	-18%

2.9 Recycling Experiments

N-arylacrylamides (**6**, 0.1 mmol), CF_3SO_2Cl (**2a**, 2 equiv.), $Cs_2AgBiBr_6$ (3 mol%), K_2CO_3 (2 equiv.), and MeCN (1.0 mL) were sequentially added to a 25 mL reaction flask. The flask was then irradiated with a 10 W blue LED light (430 nm) at room temperature under a nitrogen atmosphere for 3 hours. After the reaction, the $Cs_2AgBiBr_6$ previously used was

simply centrifuged (10000 rpm, 8 min), and washed with ethanol three times (3×5 mL). Subsequently, the recycled $Cs_2AgBiBr_6$ was dried under vacuum and directly reused for the next cycle without any further purification. We observed differences in the XRD patterns of the recycled $Cs_2AgBiBr_6$ samples compared to the freshly prepared $Cs_2AgBiBr_6$.

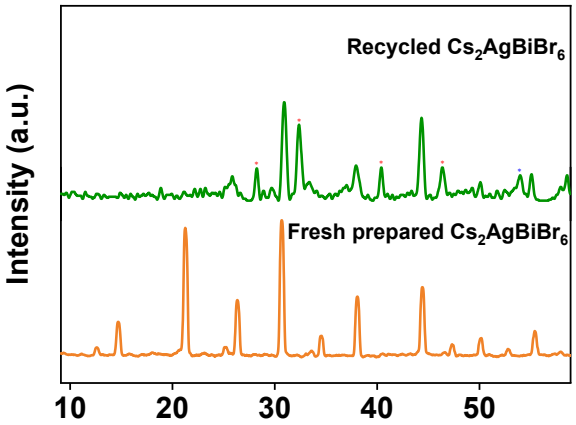


Figure S5. XRD of the recycled $Cs_2AgBiBr_6$ (5th) and the freshly prepared $Cs_2AgBiBr_6$

Interestingly, we demonstrated that the reaction could also be performed under base-free conditions, achieving a 28% yield. The XRD patterns of the $Cs_2AgBiBr_6$ samples recycled from these base-free conditions were similar to those of the freshly prepared samples.

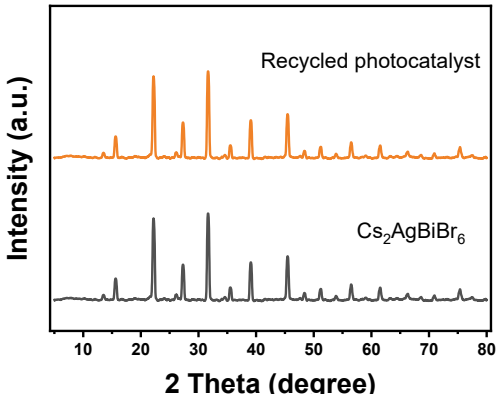


Figure S6. XRD of the recycled $Cs_2AgBiBr_6$ from based-free conditions and the freshly prepared $Cs_2AgBiBr_6$

We have conducted additional characterizations, including UV-Vis and photoluminescence (PL) spectroscopy, on the material post-reaction. We observed changes in the UV-Vis and PL spectra, indicating the formation of $Cs_2AgBiBr_6$-*x*Cl*x* during the reaction. Both the recycled $Cs_2AgBiBr_6$ and the newly prepared $Cs_2AgBiBr_6$-*x*Cl*x* according to the methods reported by Woodward[3] exhibited excellent photocatalytic activity, yielding the desired product **3a** in 90% and 92% yield, respectively. This indicates that both forms of the catalyst are indeed viable

for the model reaction.

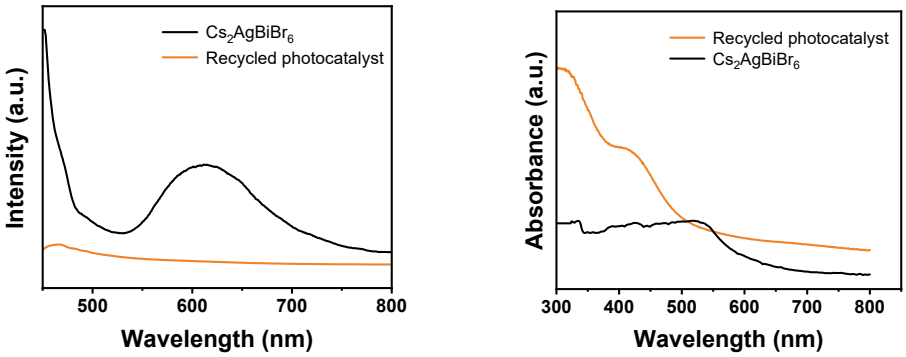


Figure S7. UV-Vis and PL spectra of recycled $Cs_2AgBiBr_6$ and the freshly prepared $Cs_2AgBiBr_6$

Afterward, we mixed $Cs_2AgBiBr_6$ with K_2CO_3 or K_2HPO_4 in CH_3CN and stirred the mixture for 3 hours. The solid was then filtered, washed with deionized water, and dried before being analyzed by XRD. The results showed that the XRD pattern of the catalyst underwent significant changes during the stirring process with K_2CO_3 or K_2HPO_4. Nevertheless, the reaction proceeded smoothly when this catalyst was used and product **3a** could also be obtained with a yield of over 85%. This suggests that despite the use of K_2CO_3 or K_2HPO_4 as a base, which could potentially undergo ion exchange with the photocatalyst, the photocatalyst can still be reused at least five times without significant loss of activity.

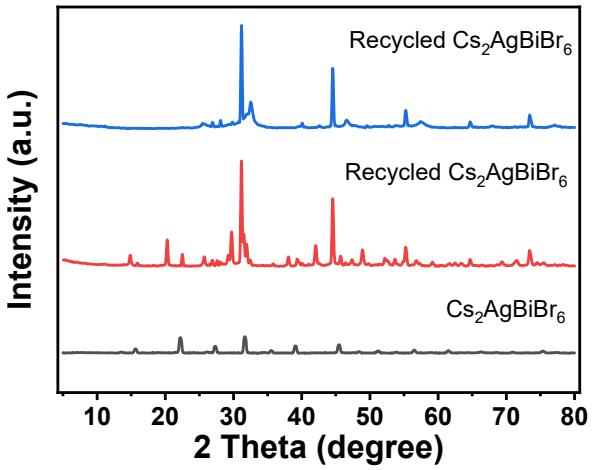
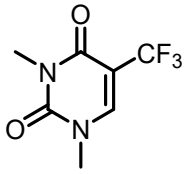


Fig. R5 Blue line: XRD of the recycled $Cs_2AgBiBr_6$ from mixture of $Cs_2AgBiBr_6$ and K_2CO_3; Blue line: XRD of the recycled $Cs_2AgBiBr_6$ from mixture of $Cs_2AgBiBr_6$ and K_2HPO_4, Black line: freshly prepared $Cs_2AgBiBr_6$

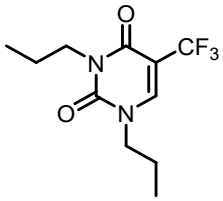
3. Characterization Data for Products

1,3-dimethyl-6-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3a)[4]



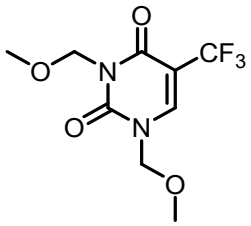
Purification by flash column chromatography to provide 16.2 mg of **3a** (78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 0.7 Hz, 1H), 3.52 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.8, 150.9, 144.1 (q, *J* = 5.8 Hz), 122.1 (q, *J* = 269.5 Hz), 103.5 (q, *J* = 32.8 Hz), 37.6, 27.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.85.

1,3-dipropyl-6-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3b)[5]



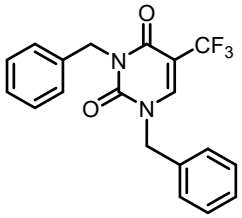
Purification by flash column chromatography to provide 24.6 mg of **3b** (93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 4.01 – 3.84 (m, 2H), 3.79 (t, *J* = 7.44 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.71 – 1.62 (m, 2H), 0.97 (dt, *J* = 15.3, 7.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.4, 150.4, 143.0 (q, *J* = 5.8 Hz), 122.1 (q, *J* = 269.8 Hz), 104.0 (q, *J* = 32.8 Hz), 52.1, 43.1, 22.3, 20.7, 11.2, 10.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.75.

1,3-bis(methoxymethyl)-6-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3c)[6]



Purification by flash column chromatography to provide 23.9 mg of **3c** (89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 5.39 (s, 2H), 5.21 (s, 2H), 3.45 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 150.8, 142.7 (q, *J* = 5.9 Hz), 121.7 (q, *J* = 270.3 Hz), 105.3 (q, *J* = 33.3 Hz), 79.5, 72.3, 58.2, 57.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.96.

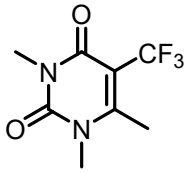
1,3-dibenzyl-6-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3d)[5]



Purification by flash column chromatography to provide 23.4 mg of **3d** (65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (s, 1H), 7.50 (d, J = 6.6 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.34 – 7.24 (m, 5H), 5.13

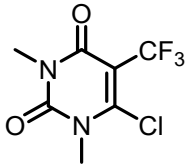
(s, 2H), 4.96 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 150.8, 142.5 (q, *J* = 5.7 Hz), 135.9, 134.1, 129.44, 129.39, 129.1, 128.5, 128.2, 128.0, 121.9 (q, *J* = 270.0 Hz), 104.8 (q, *J* = 33.1 Hz), 53.1, 44.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.70. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{16}F_3N_2O_2^+$ 361.1159; found 361.1151.

1,3,6-trimethyl-5-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3e)[5]



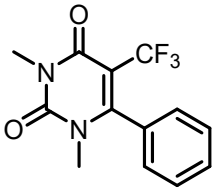
Purification by flash column chromatography to provide 19.1 mg of **3e** (86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.53 (s, 3H), 3.35 (s, 3H), 2.48 (q, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 155.2, 151.0, 123.5 (q, *J* = 272.4 Hz), 103.2 (q, *J* = 30.5 Hz), 32.4, 28.3, 17.5 (q, *J* = 4.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -54.89.

6-chloro-1,3-dimethyl-5-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3f)[5]



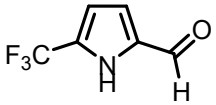
Purification by flash column chromatography to provide 19.9 mg of **3f** (82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.70 (d, *J* = 11.2 Hz, 2H), 3.38 (d, *J* = 10.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.0, 149.6, 148.7, 122.0 (q, *J* = 272.7 Hz), 103.3 (q, *J* = 32.0 Hz), 34.4, 28.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.25 (d, *J* = 10.8 Hz).

1,3-dimethyl-6-phenyl-5-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3g)[5]



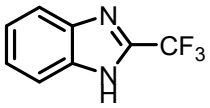
Purification by flash column chromatography to provide 24.2 mg of **3g** (85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 3H), 7.32 – 7.19 (m, 2H), 3.44 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.8, 155.6, 151.1, 131.3, 130.3, 129.1, 126.9 (q, *J* = 1.9 Hz), 122.4 (q, *J* = 272.3 Hz), 103. 9 (q, *J* = 30.5 Hz), 34.5, 28.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -55.59.

5-(trifluoromethyl)-1H-pyrrole-2-carbaldehyde (5a)[7]



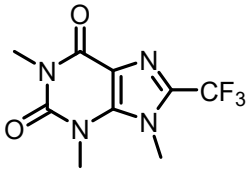
Purification by flash column chromatography to provide 8.5 mg of **5a** (52%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.47 (s, 1H), 9.66 (s, 1H), 7.00 (s, 1H), 6.68 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.6, 133.9, 127.4 (q, *J* = 40.4 Hz), 120.3 (q, *J* = 268.3 Hz), 120.1, 111.3 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.84.

2-(trifluoromethyl)-1H-benzo[d]imidazole (5b)[8]



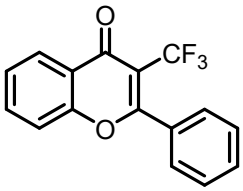
Purification by flash column chromatography to provide 13.4 mg of **5b** (72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.97 – 7.77 (m, 2H), 7.52 – 7.47 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 140.8, 130.9, 126.9, 126.3, 121.7, 119.2 (q, *J* = 322.8 Hz), 112.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.72.

1,3,9-trimethyl-8-(trifluoromethyl)-3,9-dihydro-1H-purine-2,6-dione (5c)[9]



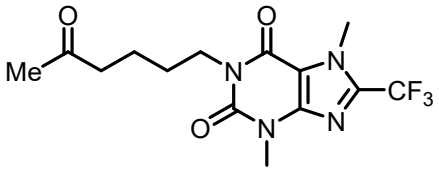
Purification by flash column chromatography to provide 14.9 mg of **5c** (57%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.16 (d, *J* = 1.2 Hz, 3H), 3.59 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.4, 151.3, 146.5, 138.9 (q, *J* = 40.0 Hz), 118.2 (q, *J* = 271.3 Hz), 109.6, 33.2 (q, *J* = 2.1 Hz), 29.9, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.41.

2-phenyl-3-(trifluoromethyl)-4H-chromen-4-one (5d)[4]



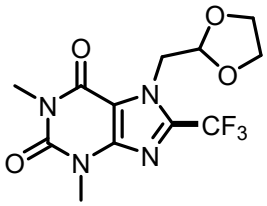
Purification by flash column chromatography to provide 16.8 mg of **5d** (58%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.63 – 7.56 (m, 3H), 7.56 – 7.45 (m, 4H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.4, 167.1 (q, *J* = 2.6 Hz), 155.5, 134.7, 132.5, 131.4, 128.6, 128.4, 126.19, 126.16, 123.4, 122.6 (q, *J* = 273.9 Hz), 118.0, 113.2 (q, *J* = 29.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.22.

3,7-dimethyl-1-(5-oxohexyl)-8-(trifluoromethyl)-3,7-dihydro-1H-purine-2,6-dione (5e)[4]



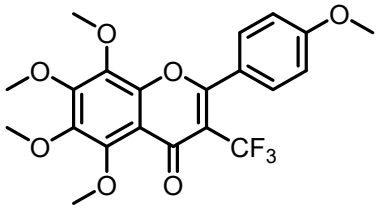
Purification by flash column chromatography to provide 13.2 mg of **5e** (38%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.16 (s, 3H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.58 (s, 3H), 2.51 (t, *J* = 6.6 Hz, 2H), 2.15 (s, 3H), 1.67 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.5, 155.3, 151.0, 146.5, 138.9 (q, *J* = 40.0 Hz), 118.2 (q, *J* = 271.5 Hz), 109.6, 43.0, 41.1, 33.1, 29.9, 29.8, 27.3, 20.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.32.

7-((1,3-dioxolan-2-yl)methyl)-1,3-dimethyl-8-(trifluoromethyl)-3,7-dihydro-1H-purine-2,6-dione (5f)[5]



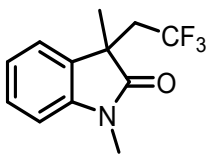
Purification by flash column chromatography to provide 26.1 mg of **5f** (78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.34 (t, *J* = 4.3 Hz, 1H), 4.67 (d, *J* = 4.2 Hz, 2H), 3.97 – 3.87 (m, 4H), 3.60 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.3, 151.3, 146.7, 139.1 (q, *J* = 40.2 Hz), 118.2 (q, *J* = 271.4 Hz), 109.5, 100. 9, 65.3, 48.7, 29.9, 28.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.75.

5,6,7,8-tetramethoxy-2-(4-methoxyphenyl)-3-(trifluoromethyl)-4H-chromen-4-one (5g)[5]



Purification by flash column chromatography to provide 32.6 mg of **5g** (78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 4.09 (s, 3H), 3.98 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.6, 164.9, 162.2, 152.1, 148.5, 146.8, 144.9, 137.7, 130.8, 124.3, 122.9 (q, *J* = 273.8 Hz), 114.3, 113.9, 112.3 (q, *J* = 28.4 Hz), 62.3, 62.0, 61.8, 61.7, 55.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.05.

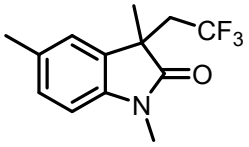
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7a)[10]



Purification by flash column chromatography to provide 20.7 mg of **7a** (78%). ^{1}H NMR (400 MHz,

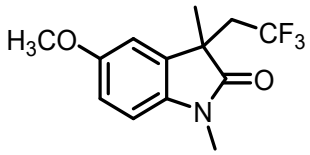
Chloroform-*d*) δ 7.47 – 7.22 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 2.92 – 2.79 (m, 1H), 2.71 – 2.61 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 142.9, 131.0, 128.5, 125.3 (q, *J* = 278.2 Hz), 123.5 (d, *J* = 1.6 Hz), 122.6, 108.4, 44.4 (q, *J* = 2.0 Hz), 40.6 (q, *J* = 28.3 Hz), 26.4, 25.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.95.

1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7b)[10]



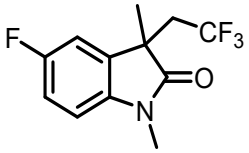
Purification by flash column chromatography to provide 23.9 mg of **7b** (93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 6.95 (m, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 3.21 (s, 3H), 2.86 – 2.72 (m, 1H), 2.69 – 2.59 (m, 1H), 2.35 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 140.5, 132.2, 131.1, 128.8, 125.3 (q, *J* = 278.2 Hz),124.3 (d, *J* = 1.6 Hz), 108.1, 44.4 (q, *J* = 2.0 Hz), 40.6 (q, *J* = 28.3 Hz), 26.4, 25.0, 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.91.

5-methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7c)[10]



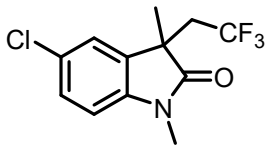
Purification by flash column chromatography to provide 23.5 mg of **7c** (86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 (d, *J* = 2.3 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.21 (s, 3H), 2.88 – 2.76 (m, 1H), 2.69 – 2.57 (m, 1H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.1, 156.1, 136.4, 132.4, 125.2 (q, *J* = 278.2 Hz), 112.6, 111.2 (d, *J* = 1.6 Hz), 108.7, 55.8, 44.8 (q, *J* = 2.1 Hz), 40.6 (q, *J* = 28.3 Hz), 26.5, 25.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.88.

5-fluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7d)[10]



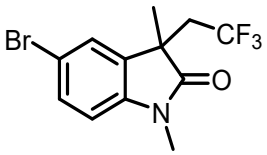
Purification by flash column chromatography to provide 19.3 mg of **7d** (74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.05 – 6.97 (m, 2H), 6.85 – 6.75 (m, 1H), 3.23 (s, 3H), 2.87 – 2.73 (m, 1H), 2.69 – 2.53 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.1, 159.3 (d, *J* = 240.9 Hz), 138.8 (d, *J* = 2.1 Hz), 132.6 (d, *J* = 8.0 Hz), 125.1 (q, *J* = 278.2 Hz), 114.8 (d, *J* = 23.5 Hz), 111.7 (dd, *J* = 24.9, 1.8 Hz), 108.9 (d, *J* = 8.1 Hz), 44.8 (q, *J* = 2.0 Hz), 40.5 (q, *J* = 28.5 Hz), 26.5, 24.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.00, -120.46.

5-chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7e)[10]



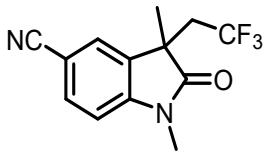
Purification by flash column chromatography to provide 20.3 mg of **7e** (73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.11 (m, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.22 (s, 3H), 2.90 – 2.79 (m, 1H), 2.71 – 2.60 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 141.5, 132.7, 128.5, 128.1, 125.1 (q, *J* = 278.2 Hz), 124.1 (d, *J* = 1.7 Hz), 109.4, 44.6 (q, *J* = 2.3 Hz), 40.5 (q, *J* = 28.4 Hz), 26.5, 24.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.96.

5-bromo-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7f)[10]



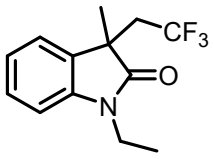
Purification by flash column chromatography to provide 25.1 mg of **7f** (78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.3, 1.9 Hz, 0H), 7.38 (d, *J* = 1.8 Hz, 0H), 6.77 (d, *J* = 8.3 Hz, 0H), 3.22 (s, 1H), 2.90 – 2.74 (m, 0H), 2.70 – 2.41 (m, 0H), 1.41 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.8, 142.0, 133.1, 131.4, 126.8 (d, *J* = 1.7 Hz), 125.1 (q, *J* = 278.1 Hz).115.3, 109.9, 44.5 (q, *J* = 2.0 Hz), 40.6 (q, *J* = 28.5 Hz), 26.6, 24.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.94.

1,3-dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (7g)[10]



Purification by flash column chromatography to provide 16.1 mg of **7g** (78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.54 (d, *J* = 1.3 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 3.28 (s, 3H), 2.93 – 2.81 (m, 1H), 2.76 – 2.64 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.1, 146.8, 133.9, 132.0, 127.01 (d, *J* = 1.5 Hz), 124.9 (q, *J* = 278.3 Hz), 119.0, 109.0, 105.9, 44.2 (q, *J* = 2.0 Hz), 40.5 (q, *J* = 28.5 Hz), 26.7, 24.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.04.

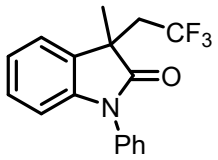
ethyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7h)[10]



Purification by flash column chromatography to provide 21.1 mg of **7h** (82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.21 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.73 – 3.64 (m, 1H), 2.90 – 2.78 (m, 3H), 2.70 – 2.58 (m, 3H), 1.39 (s, 1H), 1.25 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 141.9, 131.2, 128.4, 125.3 (q, *J* = 278.2 Hz), 123.7,

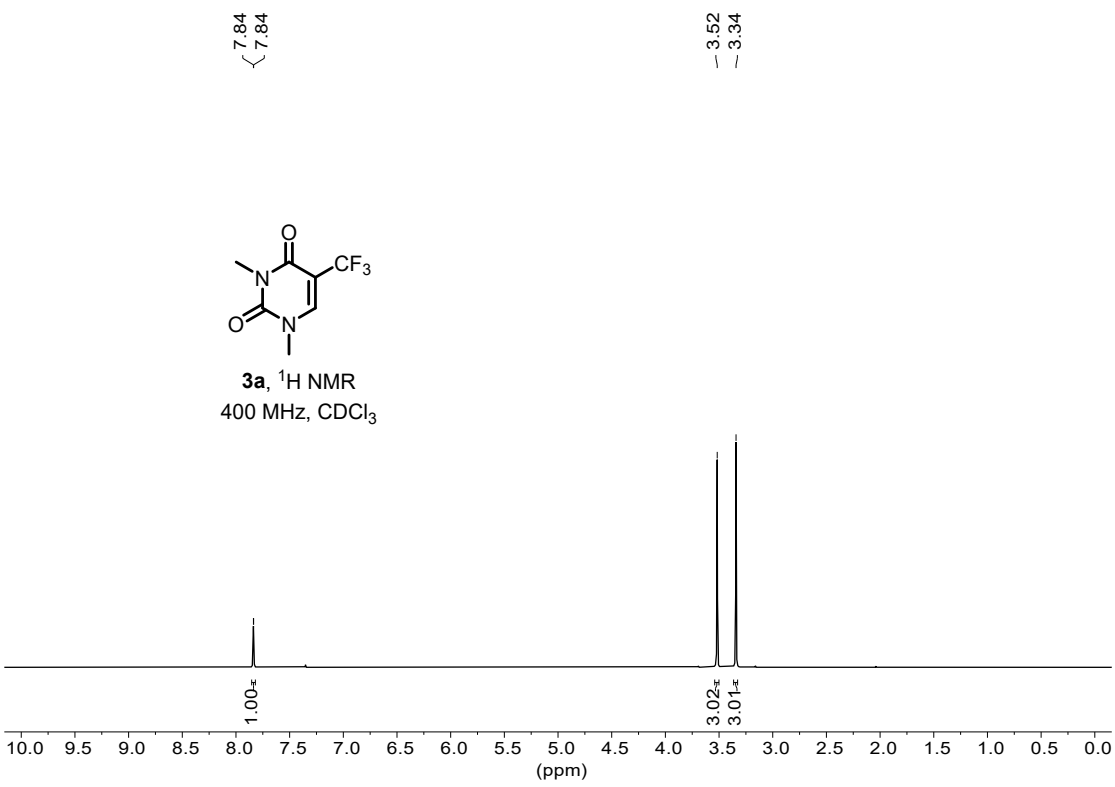
122.4, 108.6, 44.3 (q, J = 2.1 Hz), 40.7 (q, J = 28.2 Hz), 34.7, 25.1, 12.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.86.

3-methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (7i)[10]

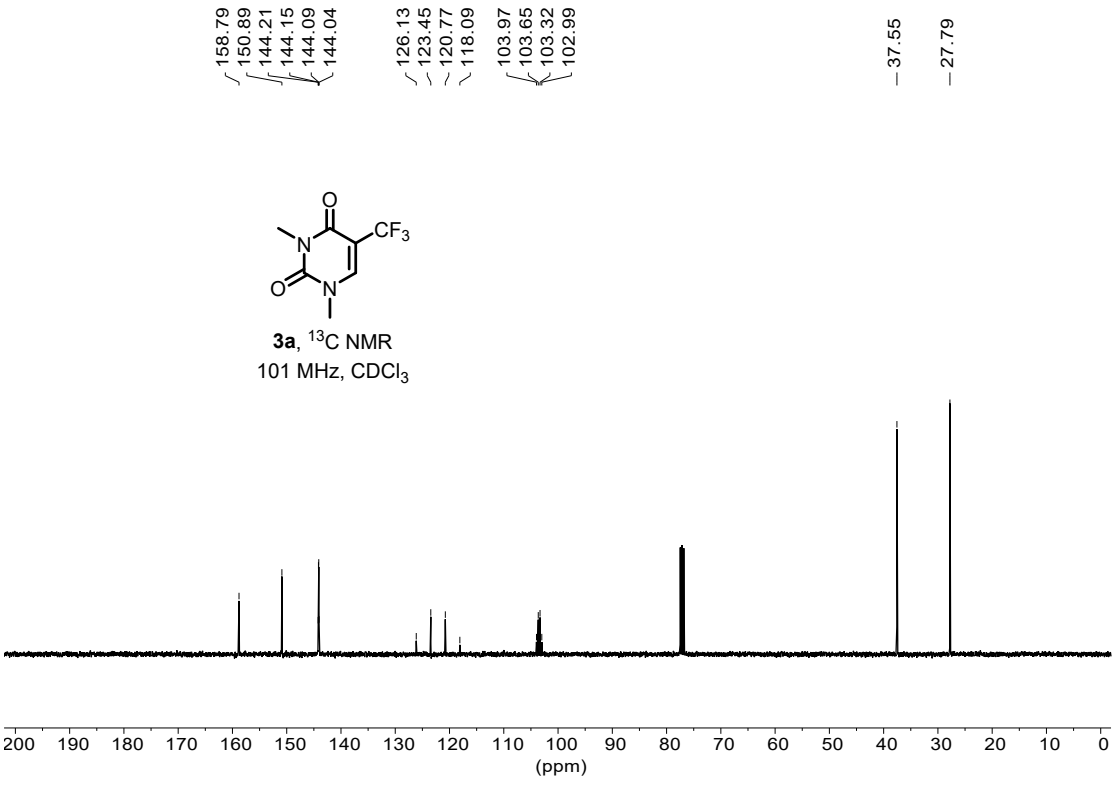


Purification by flash column chromatography to provide 25.6 mg of **7i** (84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (t, J = 7.6 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.32 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 7.9 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.78 – 2.66 (m, 1H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 142.9, 134.4, 130.7, 129.7, 128.5, 128.3, 126.6, 125.3 (q, J = 278.4 Hz), 123.8, 123.1, 109.8, 44.5 (q, J = 2.3 Hz), 41.1 (q, J = 28.2 Hz), 25.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.30.

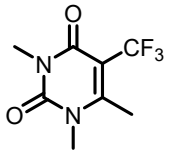
4. NMR Copies of Products



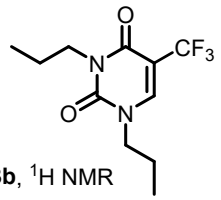
3a, ^{1}H NMR
400 MHz, $CDCl_3$



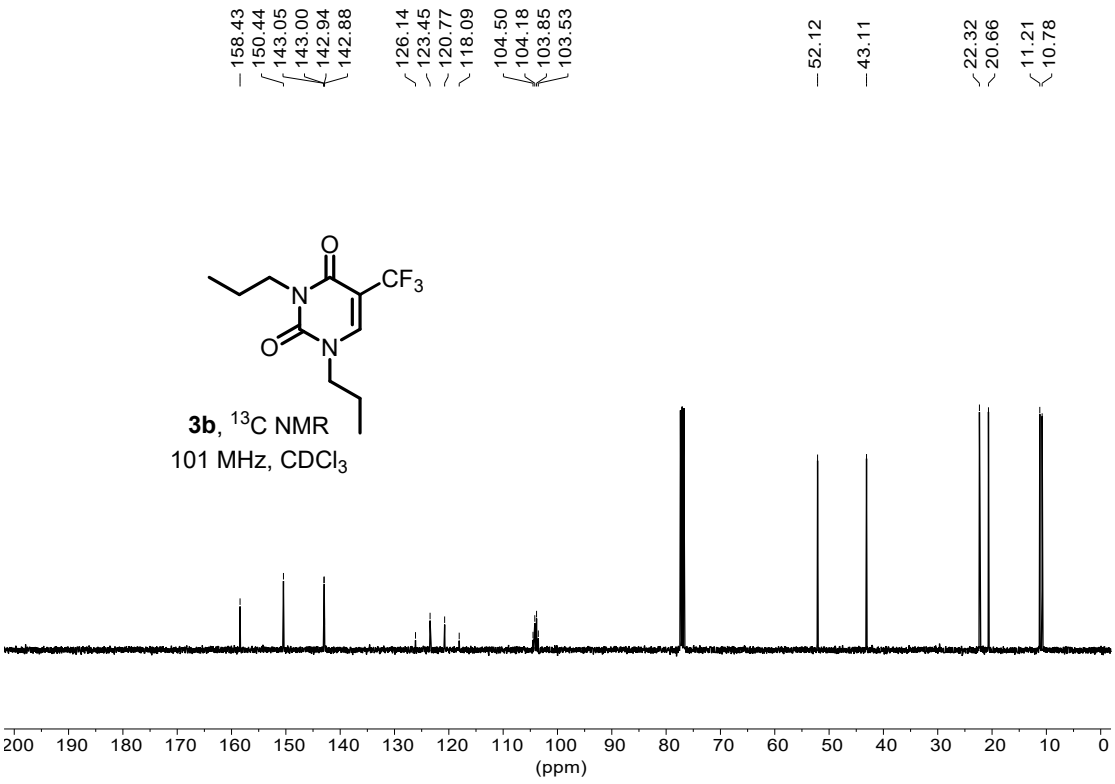
3a, ^{13}C NMR
101 MHz, $CDCl_3$



3a, ^{19}F NMR
376 MHz, $CDCl_3$



3b, ^{1}H NMR
400 MHz, $CDCl_3$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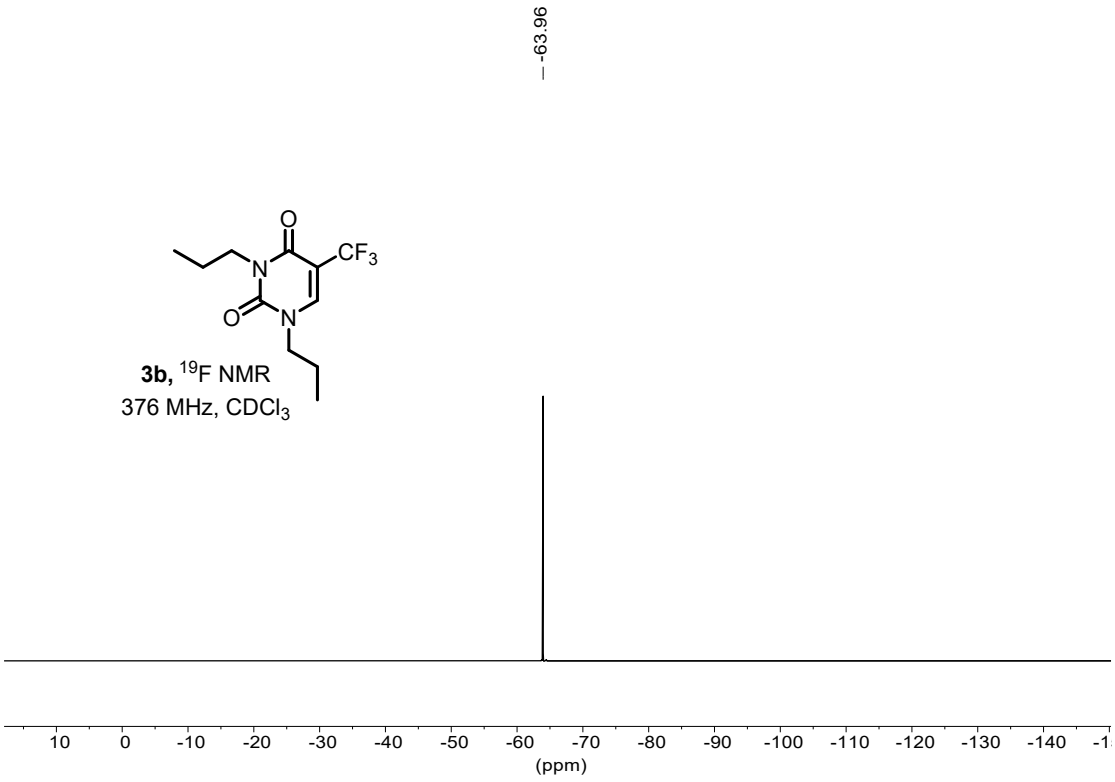
143.05
143.00
142.94
142.88
126.14
123.45
120.77
118.09
104.50
104.18
103.85
103.53
52.12
43.11
22.32
20.66
11.21
10.78
O
N
O
N
CF3
3b, 13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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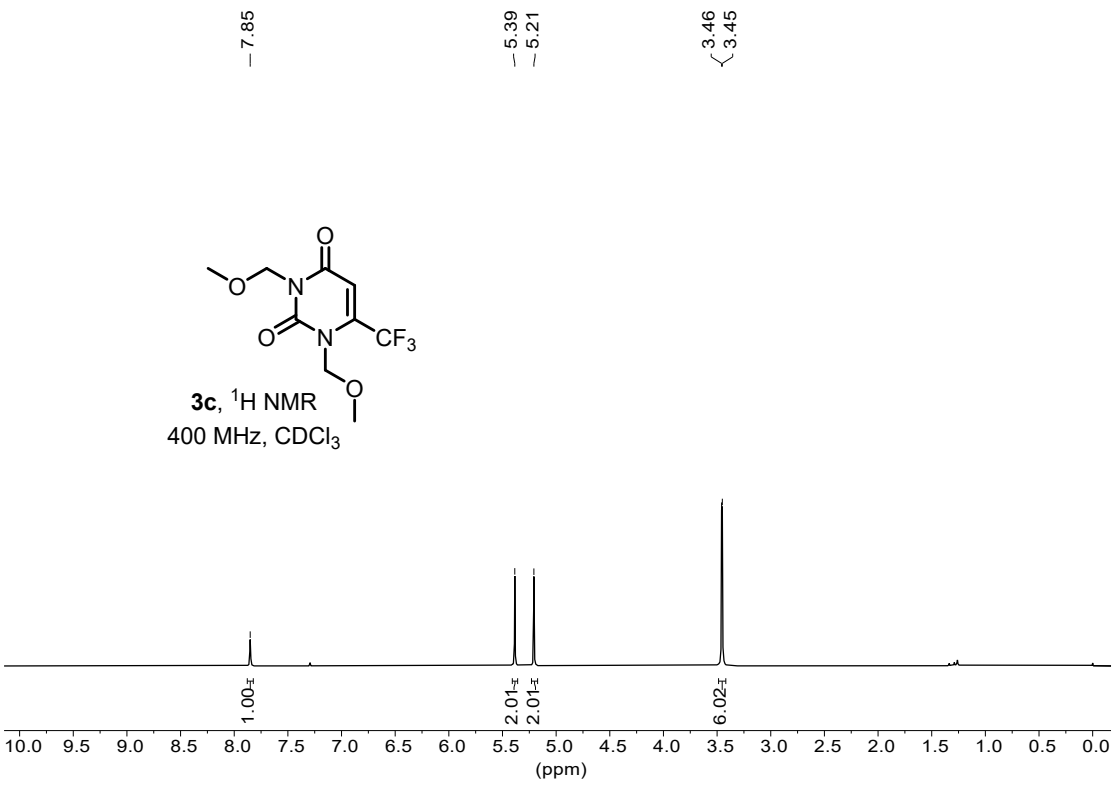
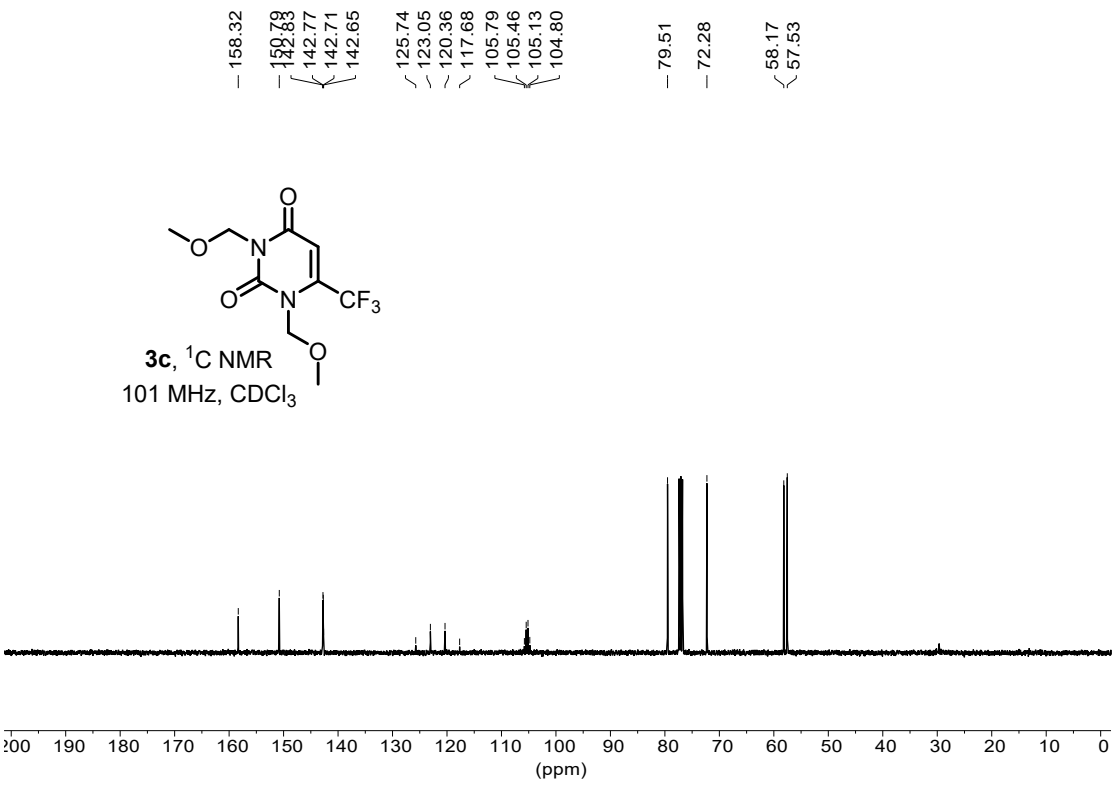
N
O
N
CF3
3b, 19F NMR
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
(ppm)


7.85
5.39
5.21
3.46
3.45
O
N
O
N
CF3
O
3c, 1H NMR
400 MHz, CDCl3
1.00
2.01
2.01
6.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)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142.77
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142.65
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123.05
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117.68
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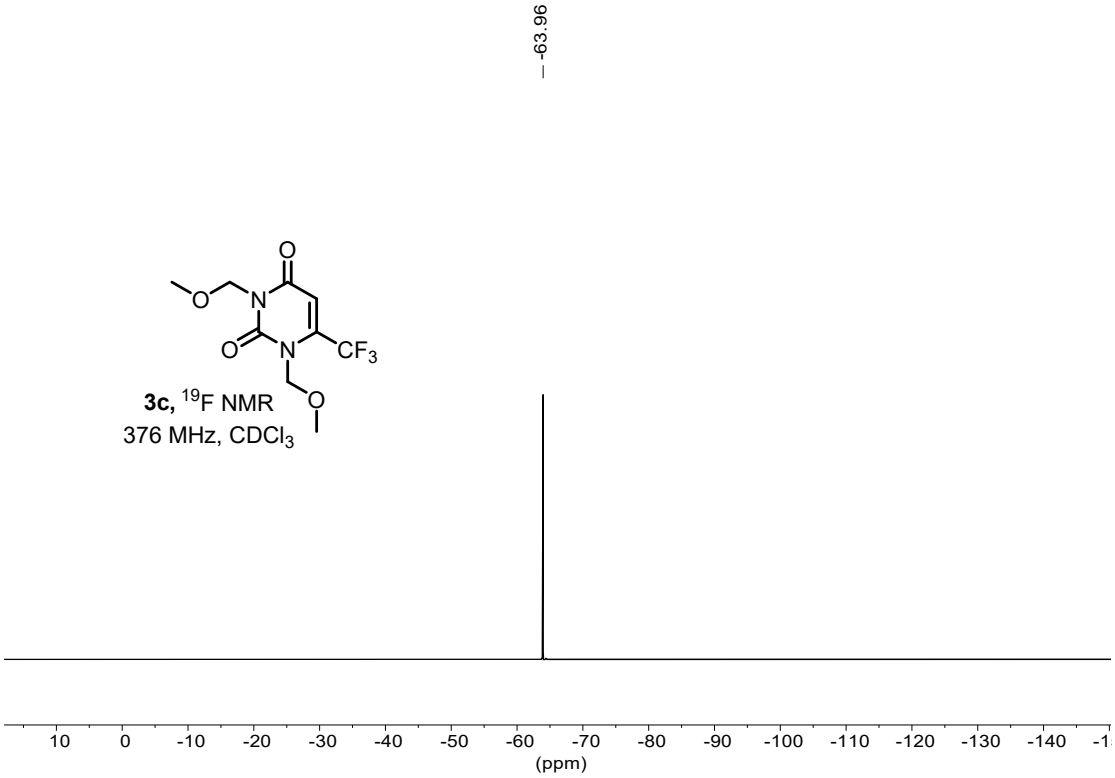
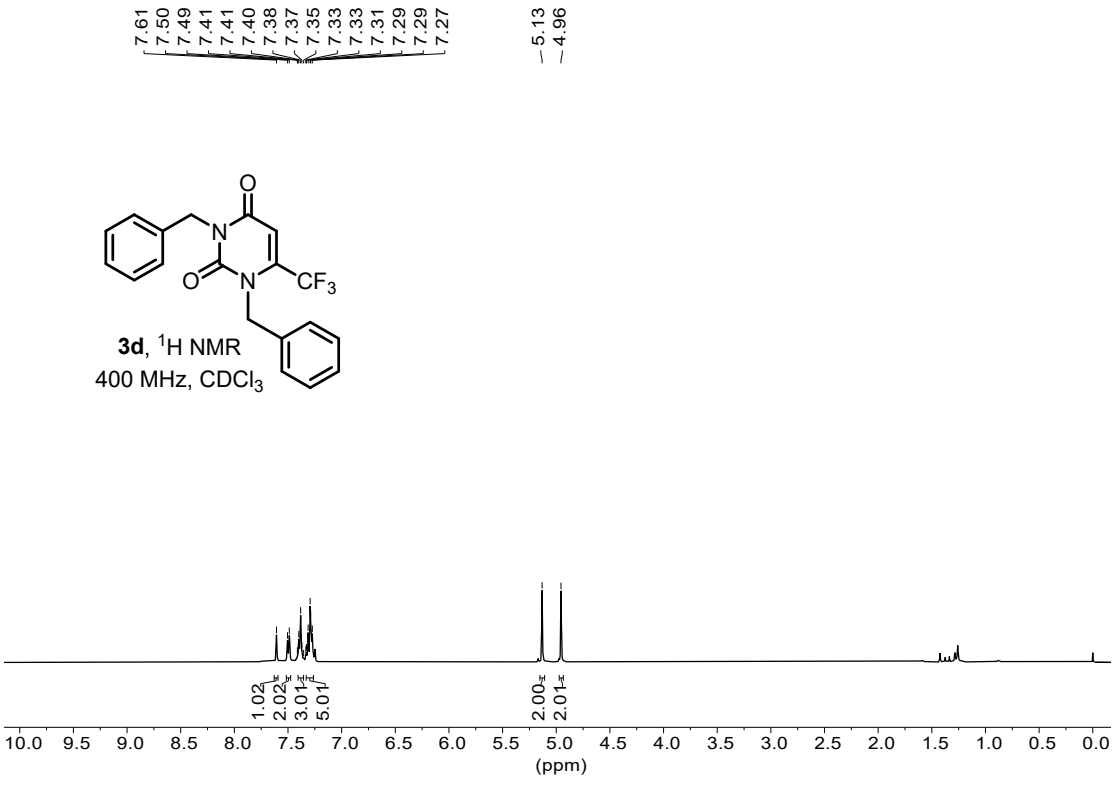
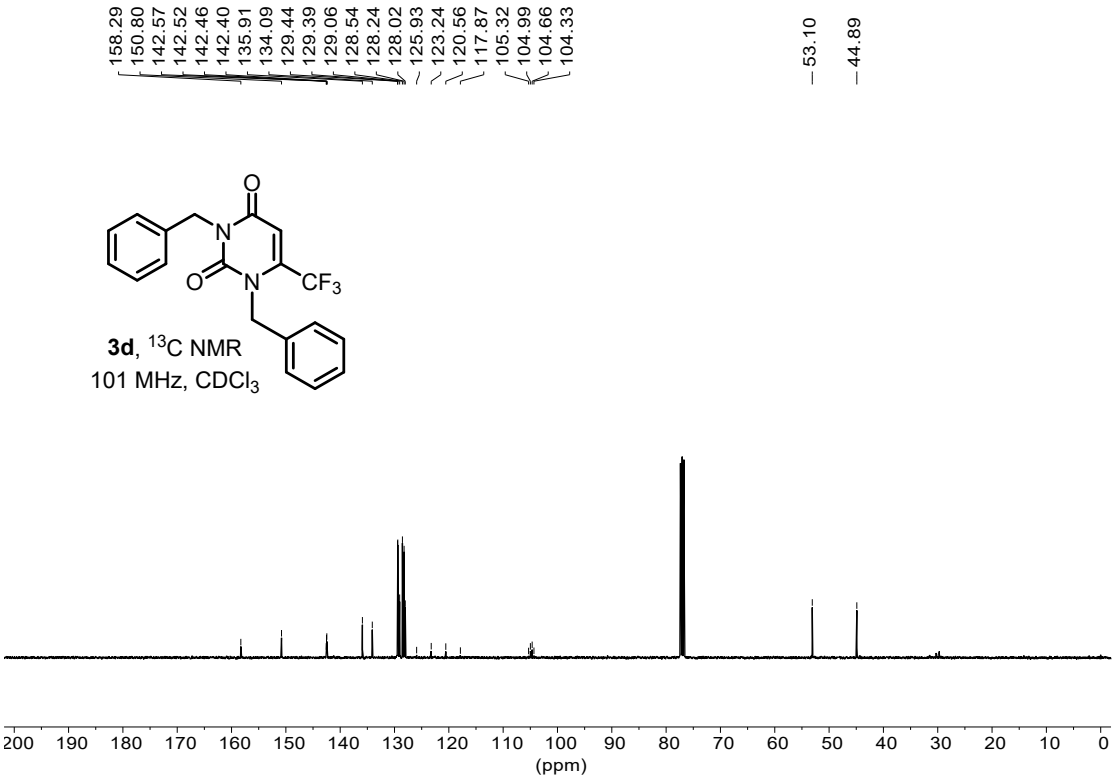
105.13
104.80
79.51
72.28
58.17
57.53
O
N
O
N
CF3
O
3c, 1C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)



3c, ^{19}F NMR
376 MHz, $CDCl_3$



3d, ^{1}H NMR
400 MHz, $CDCl_3$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134.09
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129.39
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128.54
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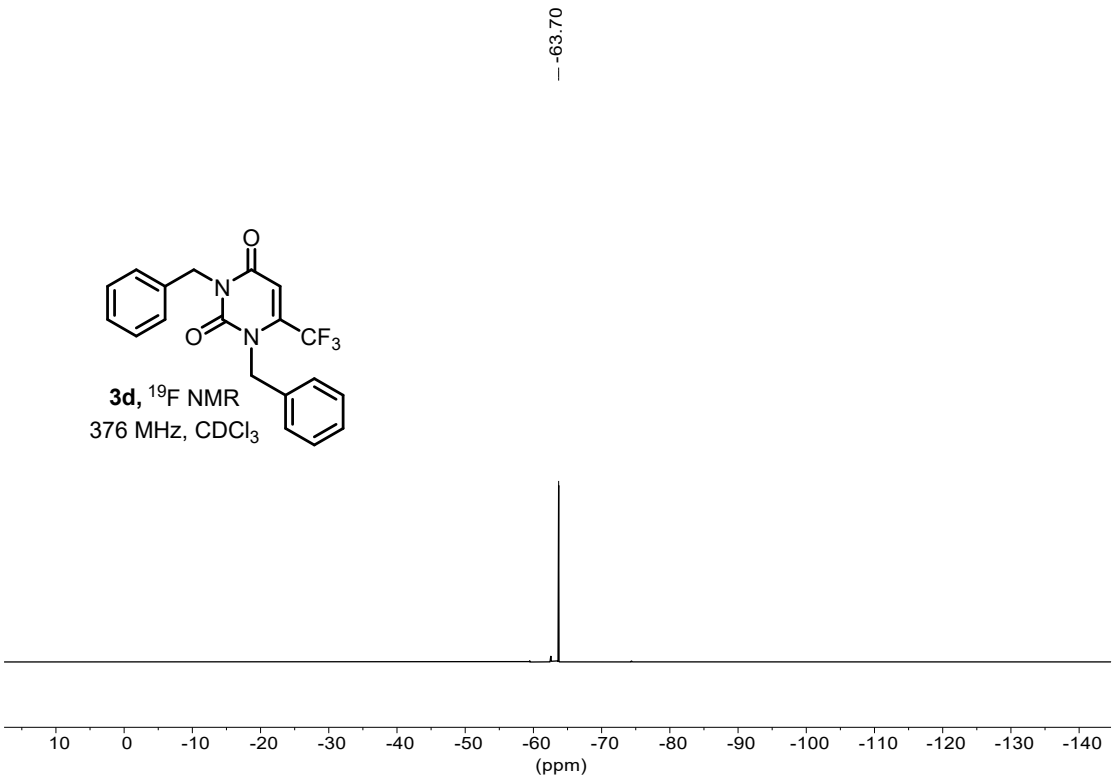
128.02
125.93
123.24
120.56
117.87
105.32
104.99
104.66
104.33
53.10
44.89
O
N
O
N
CF3
3d, 13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


-63.70
O
N
O
N
CF3
3d, 19F NMR
376 MHz, CDCl3
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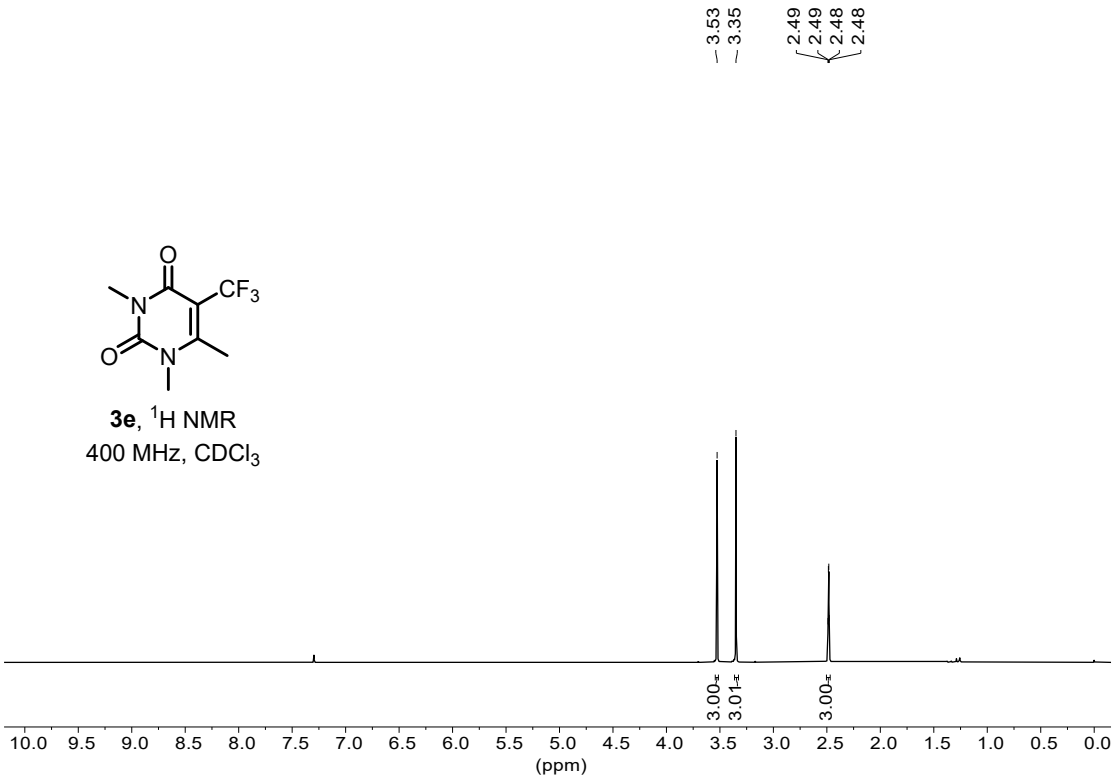
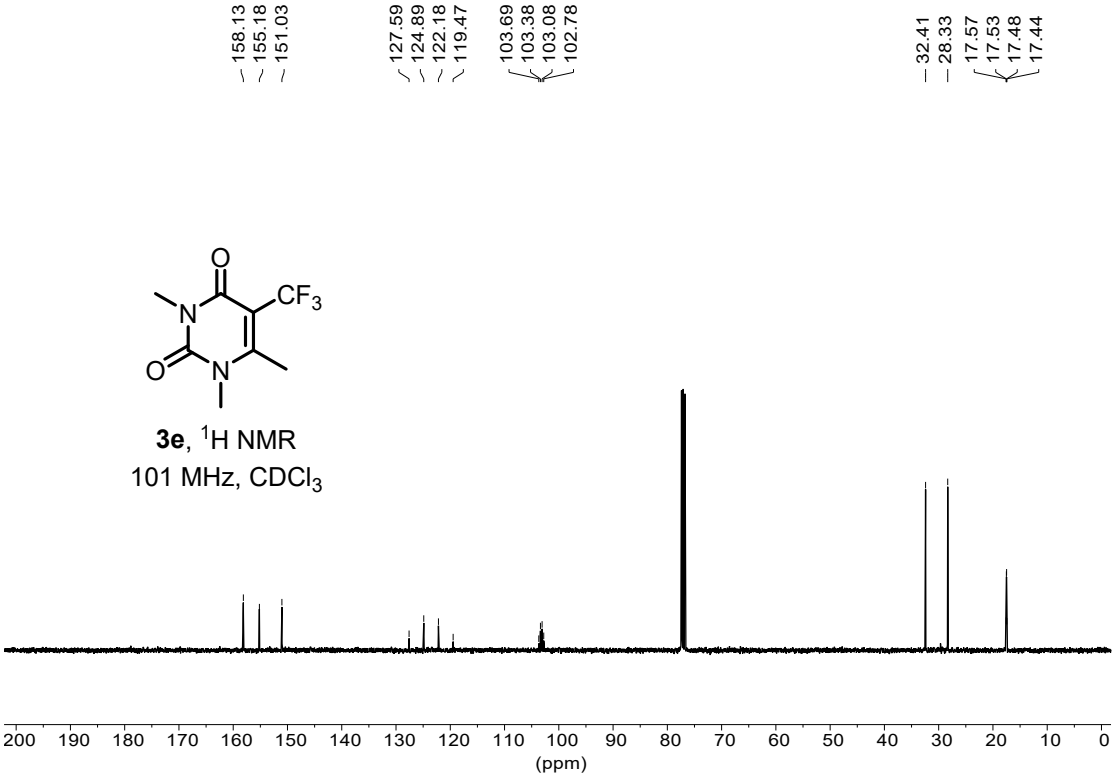
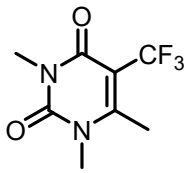
(ppm)



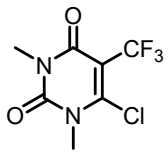
3e, ^{1}H NMR
400 MHz, $CDCl_3$



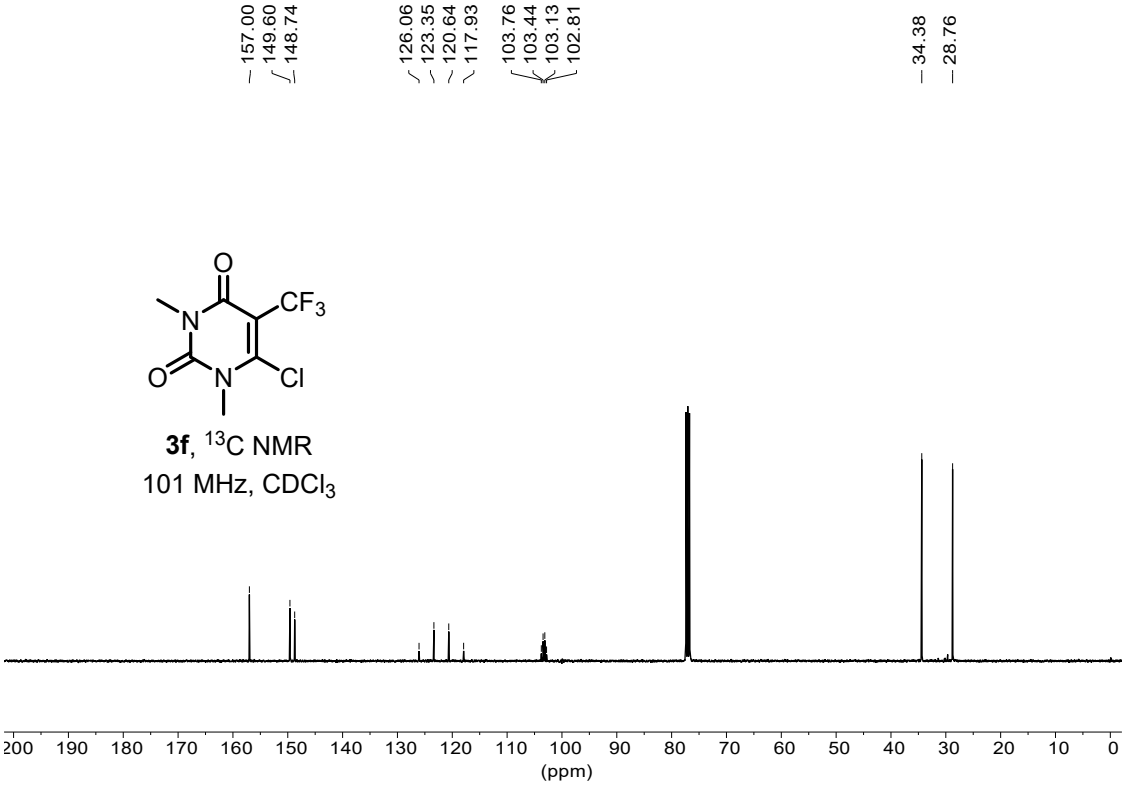
3e, ^{1}H NMR
101 MHz, $CDCl_3$



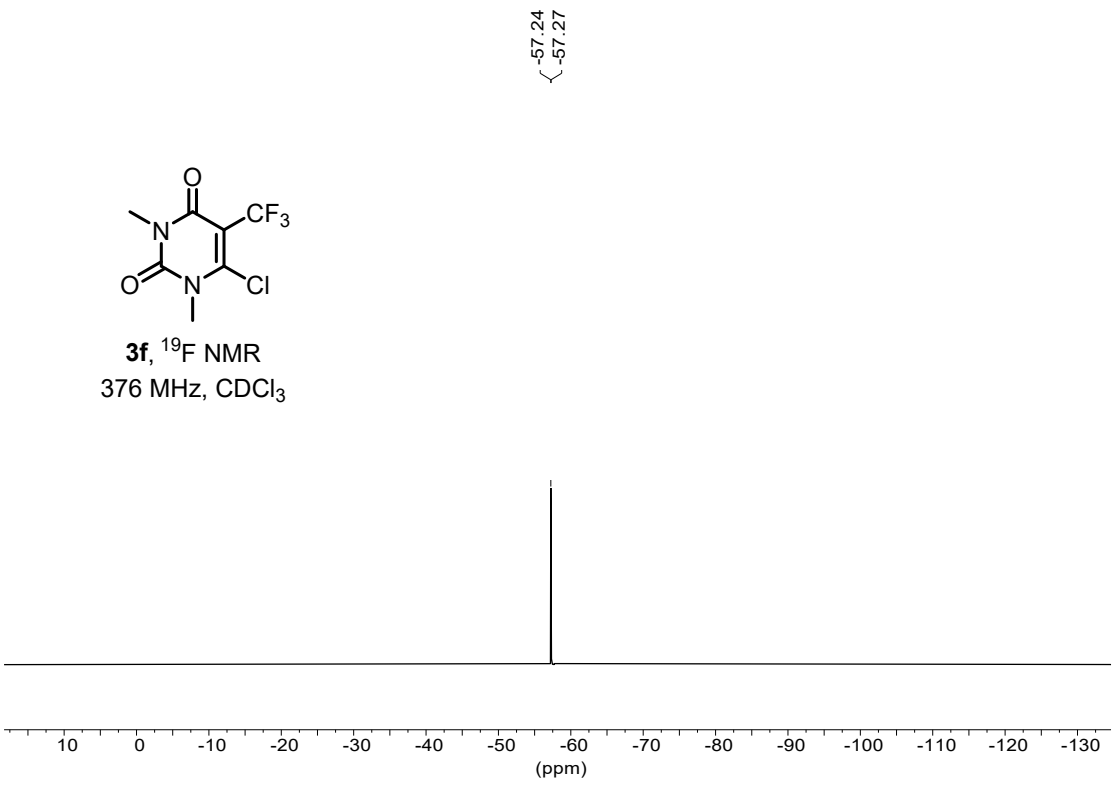
3e, ^{19}F NMR
376 MHz, $CDCl_3$



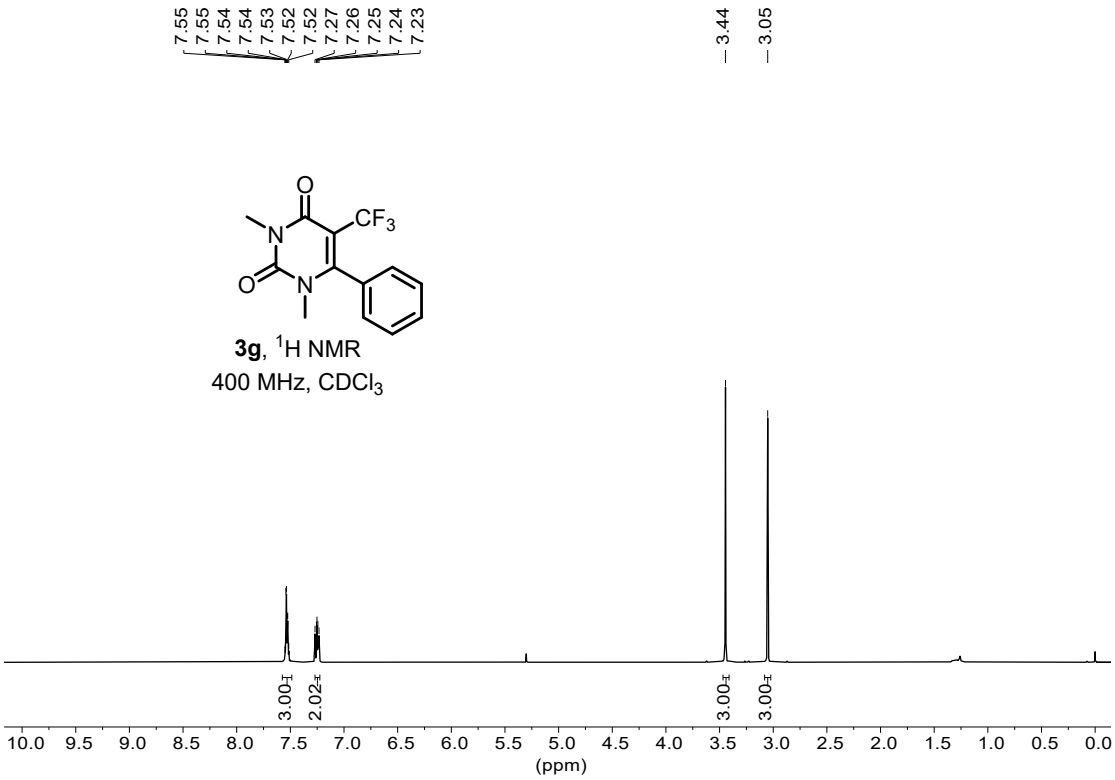
3f, ^{1}H NMR
400 MHz, $CDCl_3$



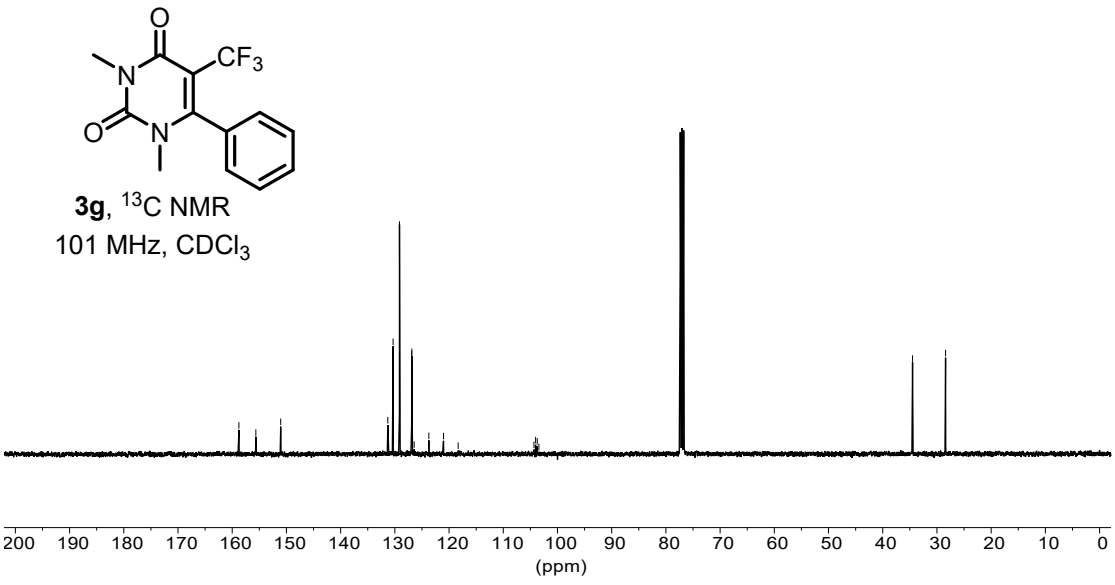
3f, ^{13}C NMR
101 MHz, $CDCl_3$



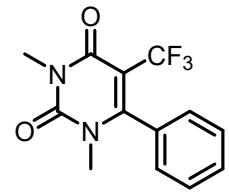
3f, ^{19}F NMR
376 MHz, $CDCl_3$



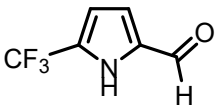
3g, ^{1}H NMR
400 MHz, $CDCl_3$



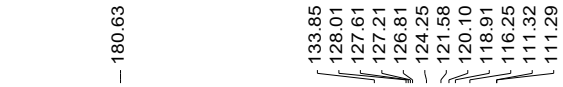
3g, ^{13}C NMR
101 MHz, $CDCl_3$

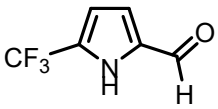


3g, ^{19}F NMR
376 MHz, $CDCl_3$

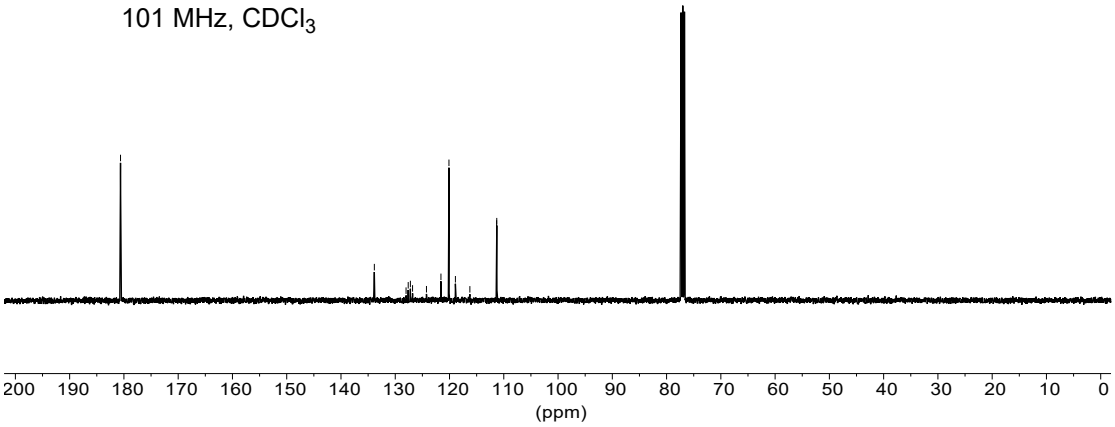


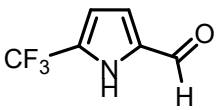
5a, ^{1}H NMR
400 MHz, $CDCl_3$



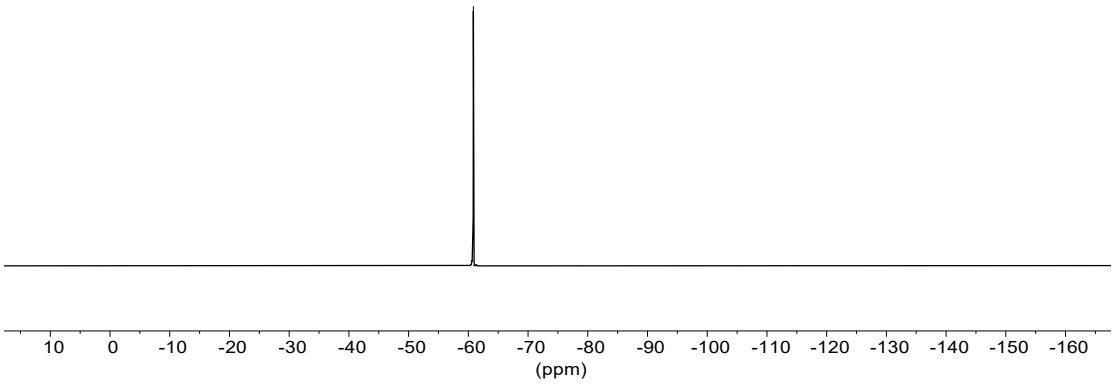


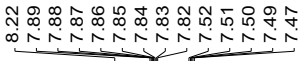
5a, ^{13}C NMR
101 MHz, $CDCl_3$

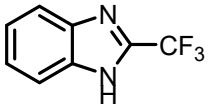




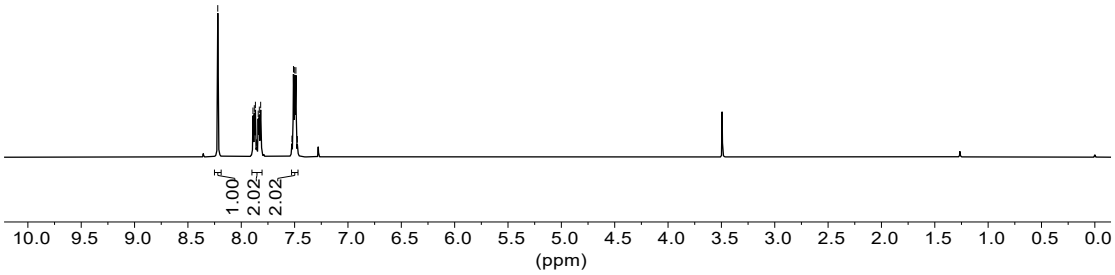
5a, ^{19}F NMR
376 MHz, $CDCl_3$

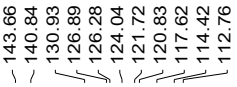


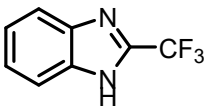




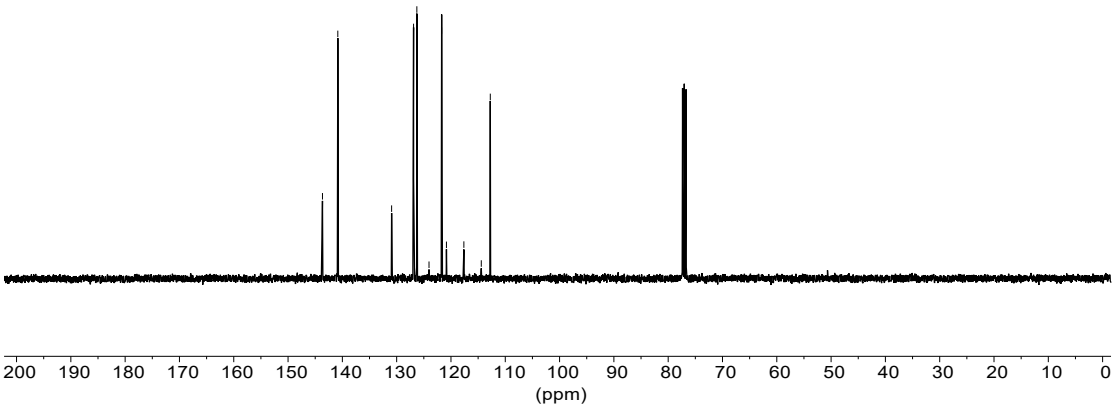
5b, ^{1}H NMR
400 MHz, $CDCl_3$

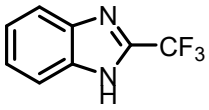




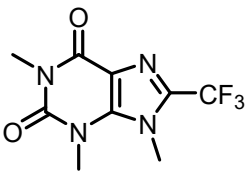


5b, ^{13}C NMR
101 MHz, $CDCl_3$

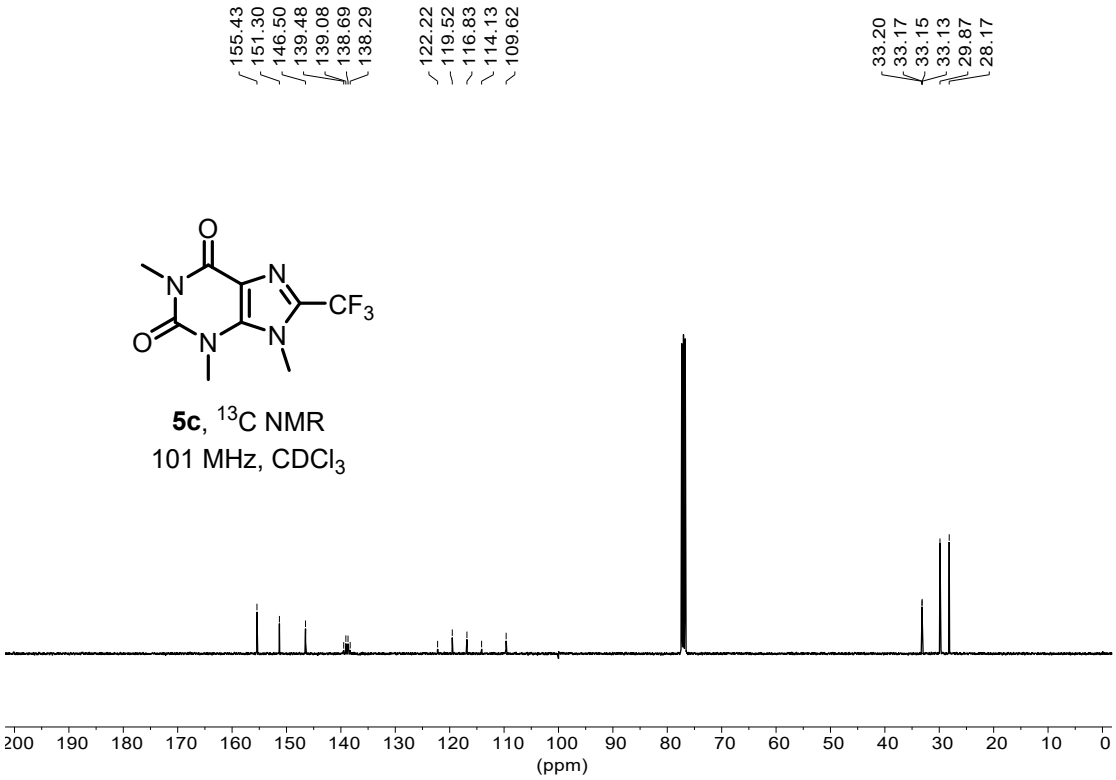




5b, ^{19}F NMR
376 MHz, $CDCl_3$



5c, ^{1}H NMR
400 MHz, $CDCl_3$



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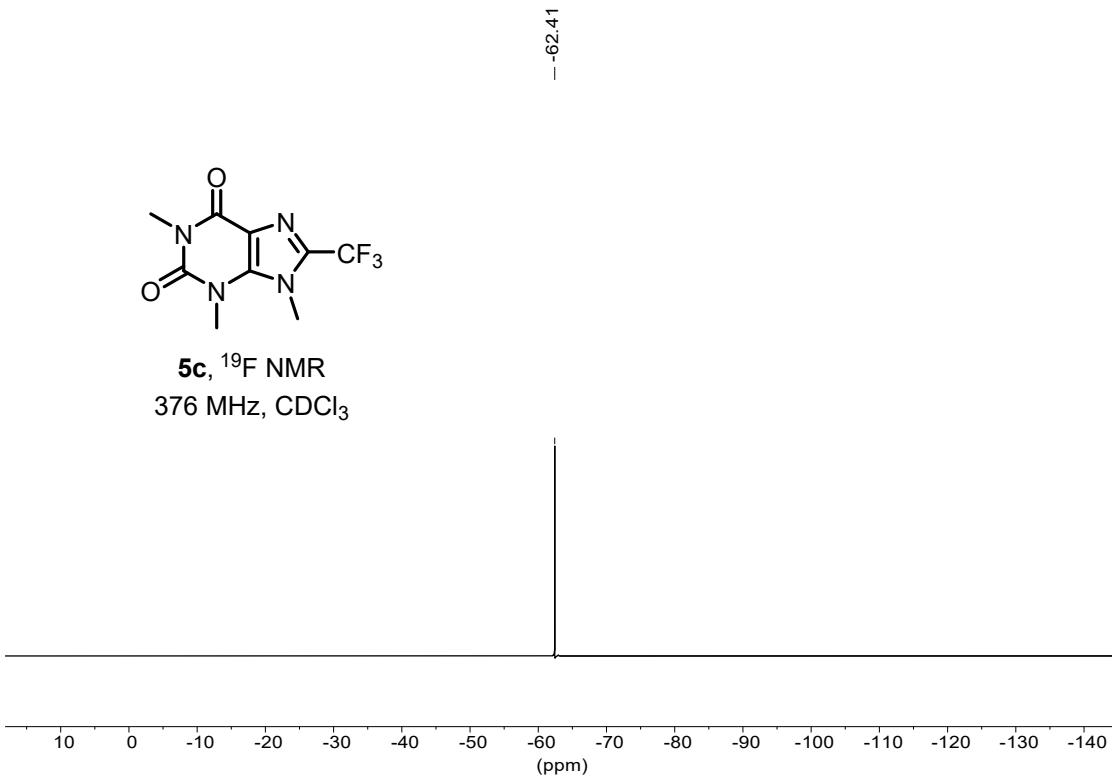
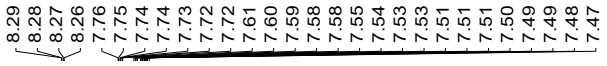
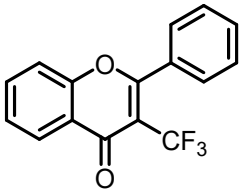
101 MHz, $CDCl_3$

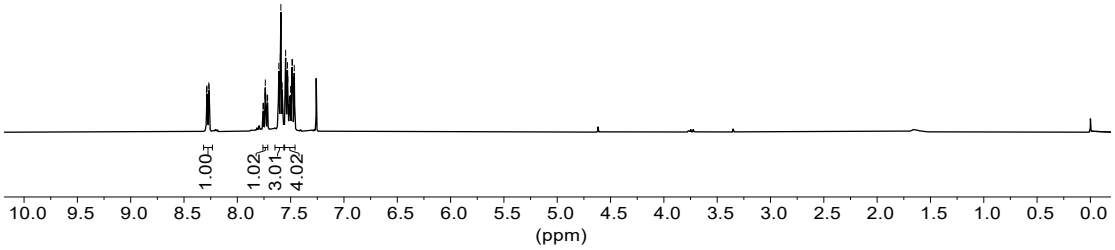


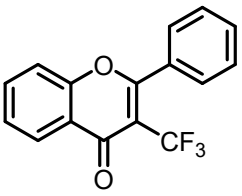
5c, ^{19}F NMR
376 MHz, $CDCl_3$



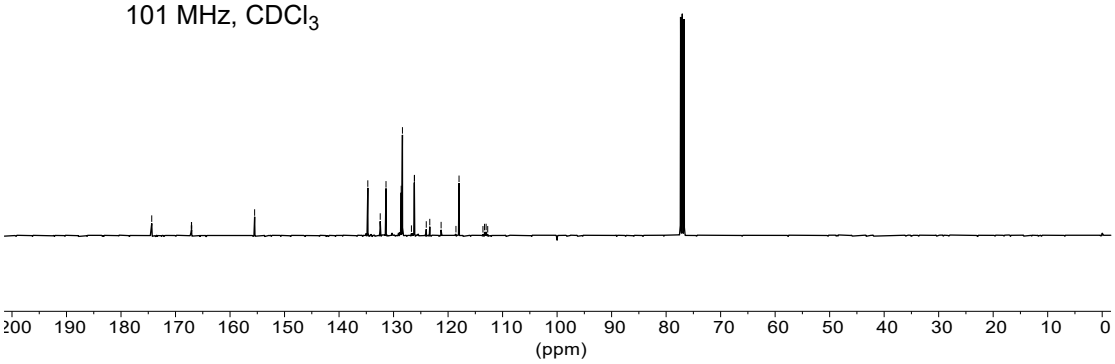


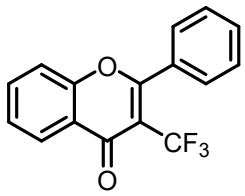
5d, ^{1}H NMR
400 MHz, $CDCl_3$



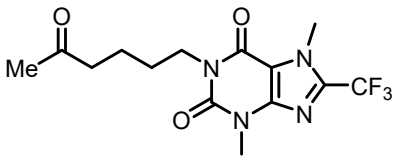


5d, ^{13}C NMR
101 MHz, $CDCl_3$

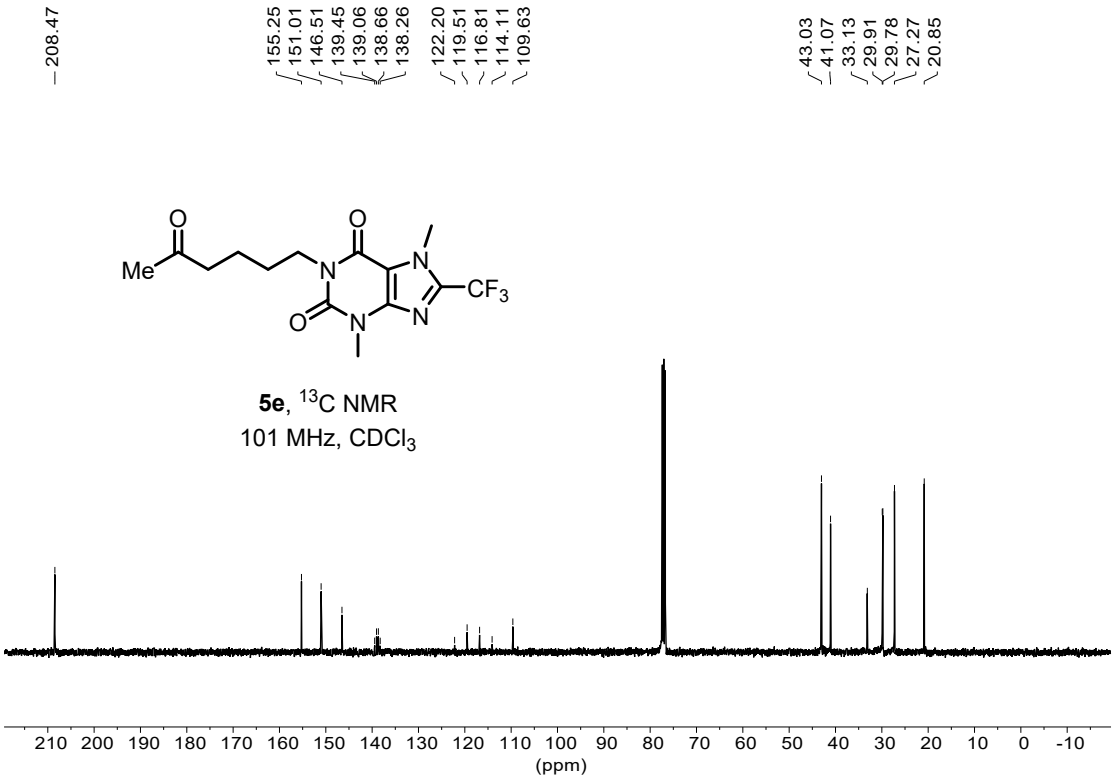




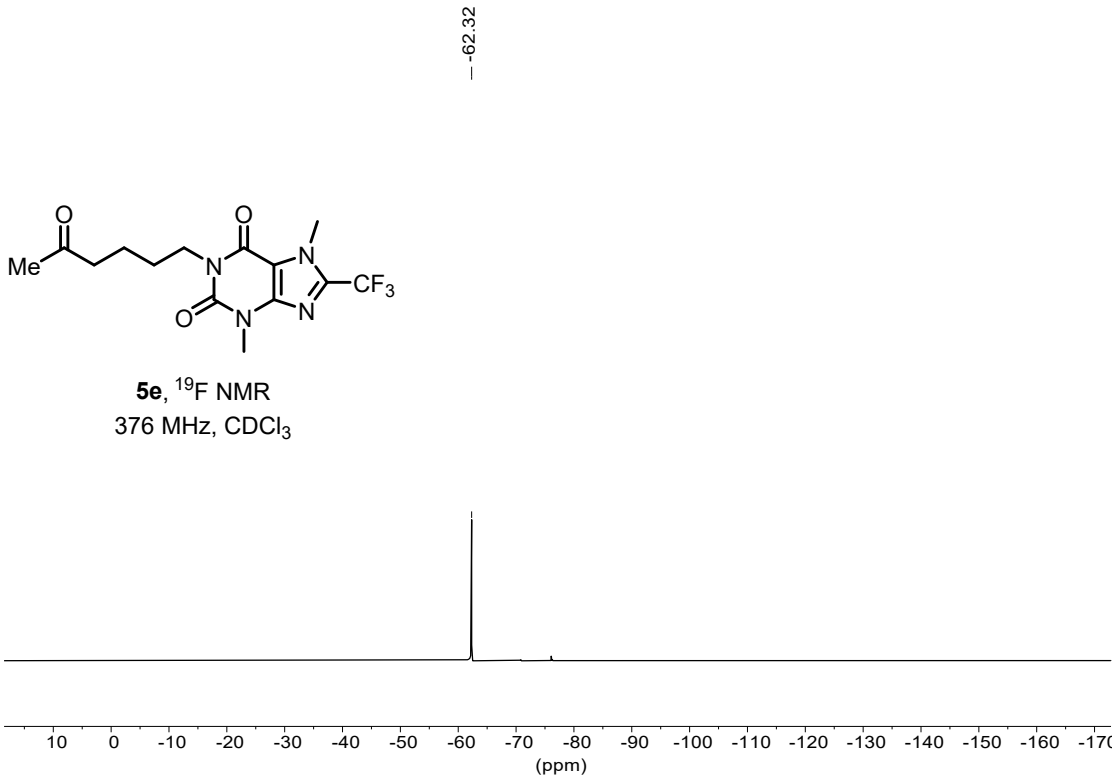
5d, ^{19}F NMR
376 MHz, $CDCl_3$



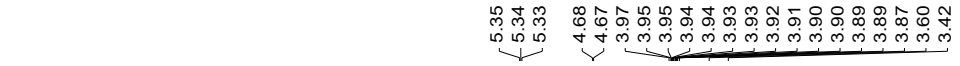
5e, ^{1}H NMR
400 MHz, $CDCl_3$

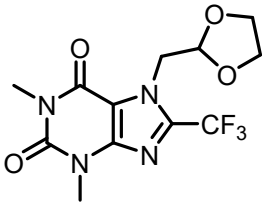


5e, ^{13}C NMR
101 MHz, $CDCl_3$

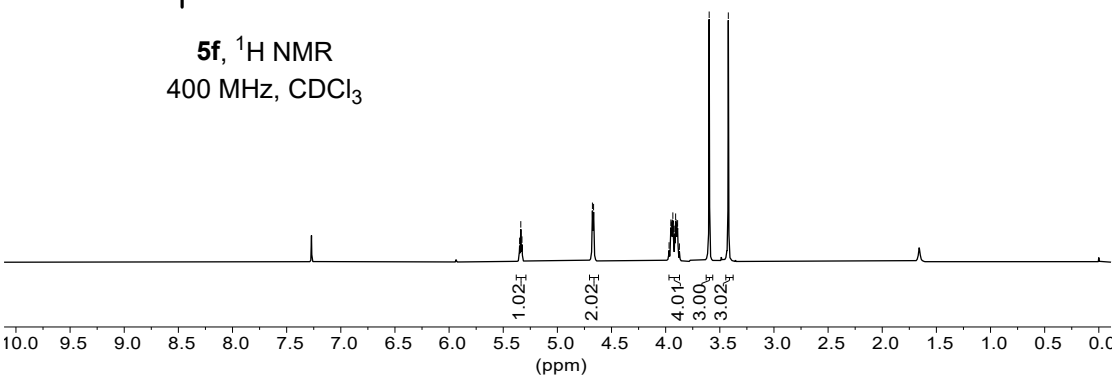


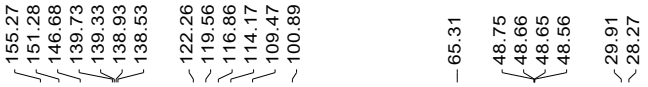
5e, ^{19}F NMR
376 MHz, $CDCl_3$

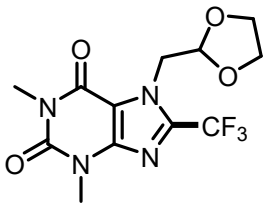




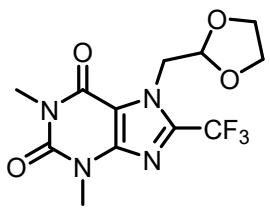
5f, ^{1}H NMR
400 MHz, $CDCl_3$



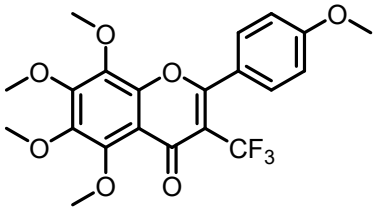




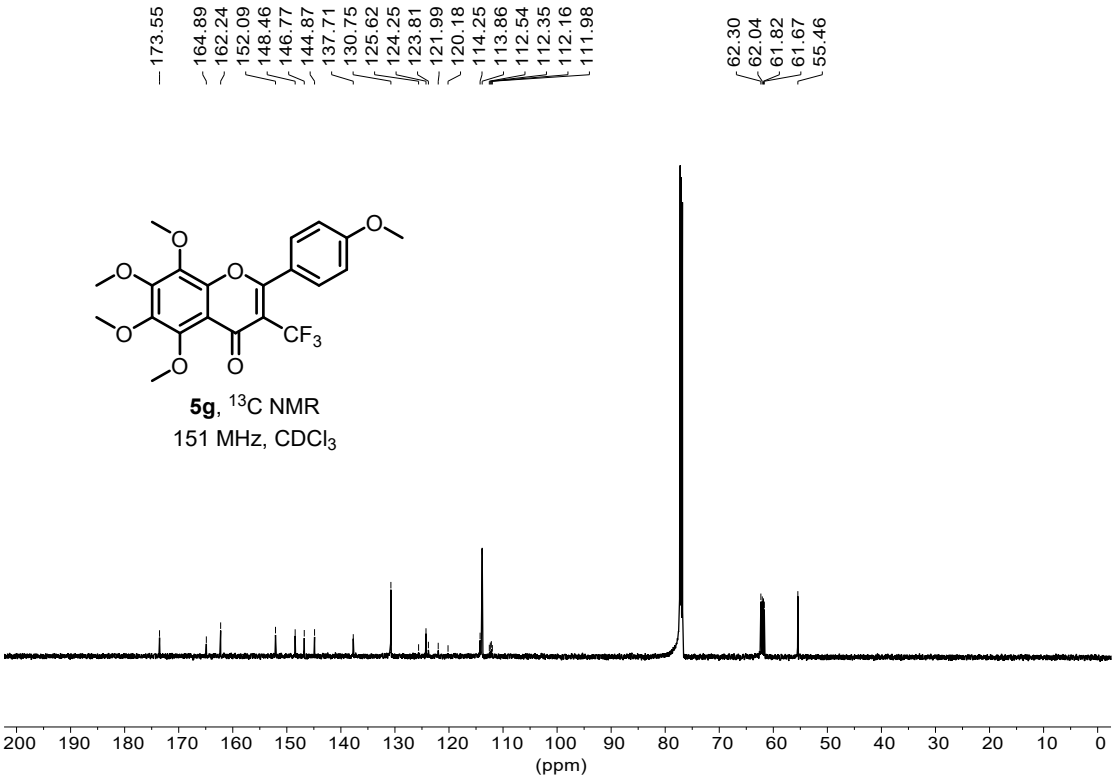
5f, ^{13}C NMR
101 MHz, $CDCl_3$



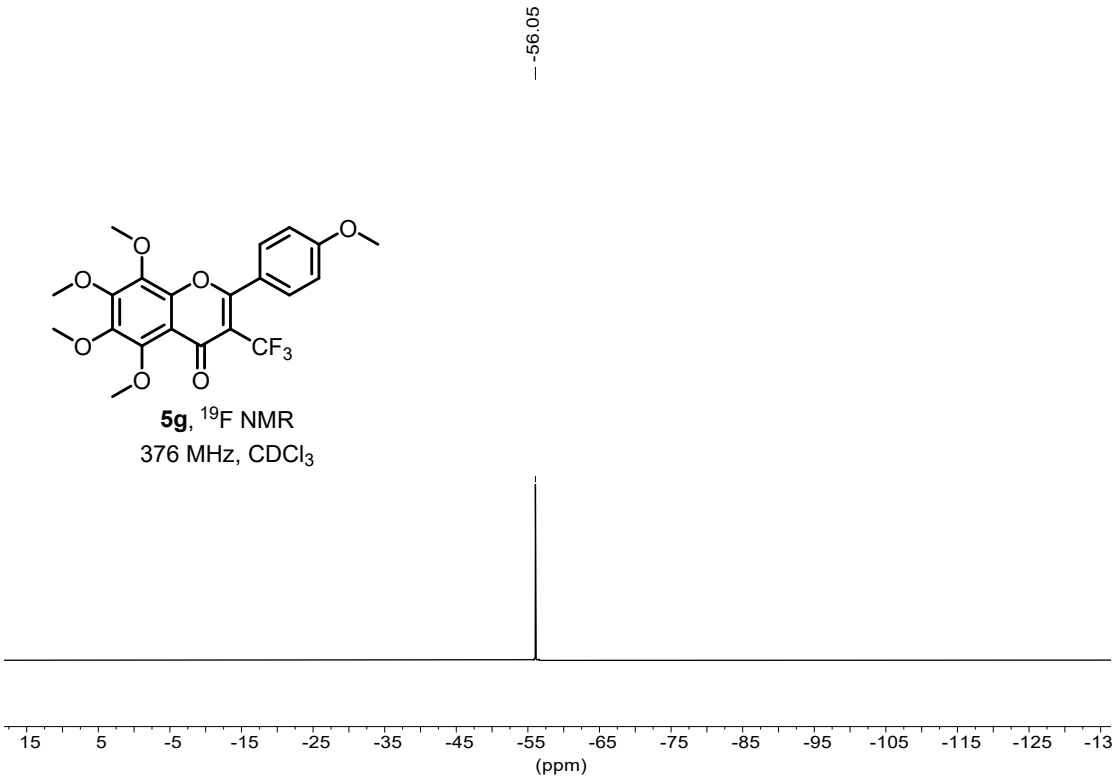
5f, ^{19}F NMR
376 MHz, $CDCl_3$



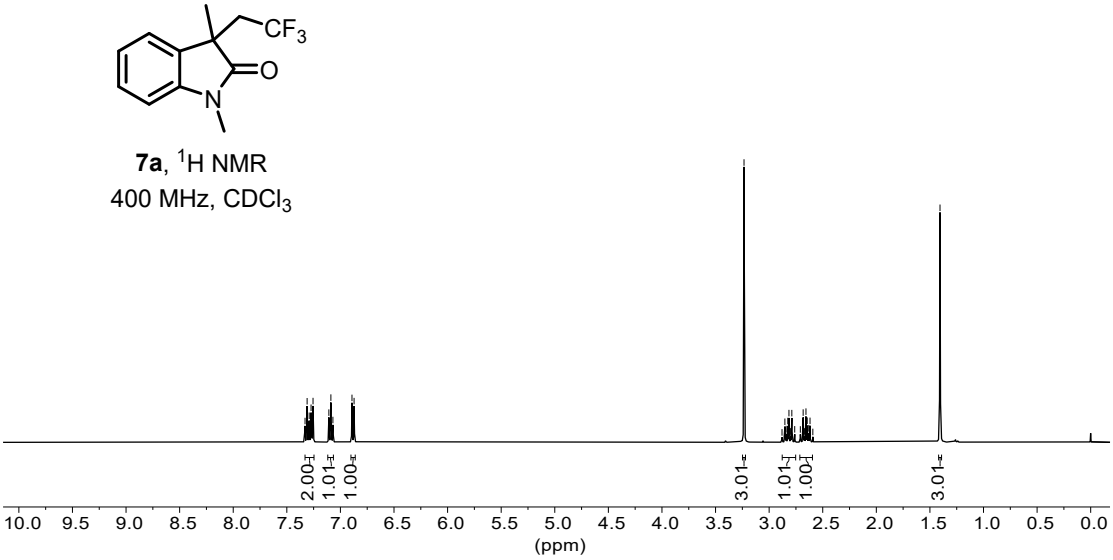
5g, ^{1}H NMR
400 MHz, $CDCl_3$



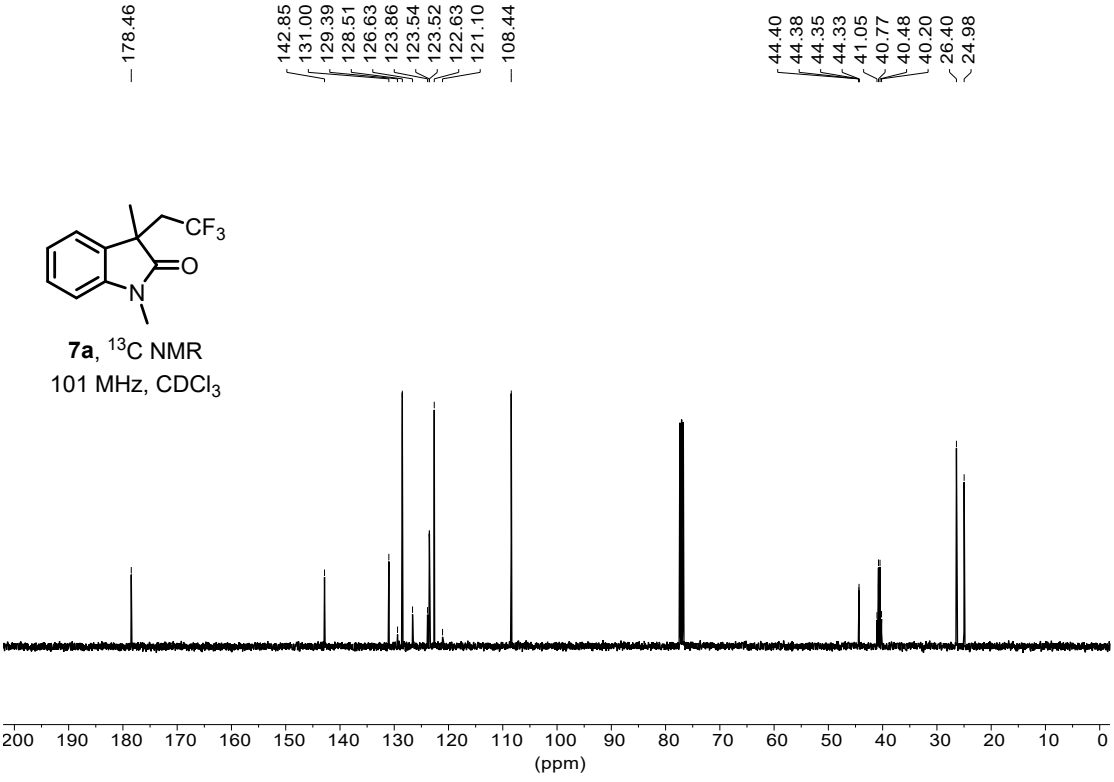
5g, ^{13}C NMR
151 MHz, $CDCl_3$



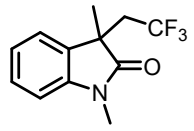
5g, ^{19}F NMR
376 MHz, $CDCl_3$



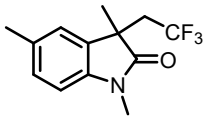
7a, ^{1}H NMR
400 MHz, $CDCl_3$



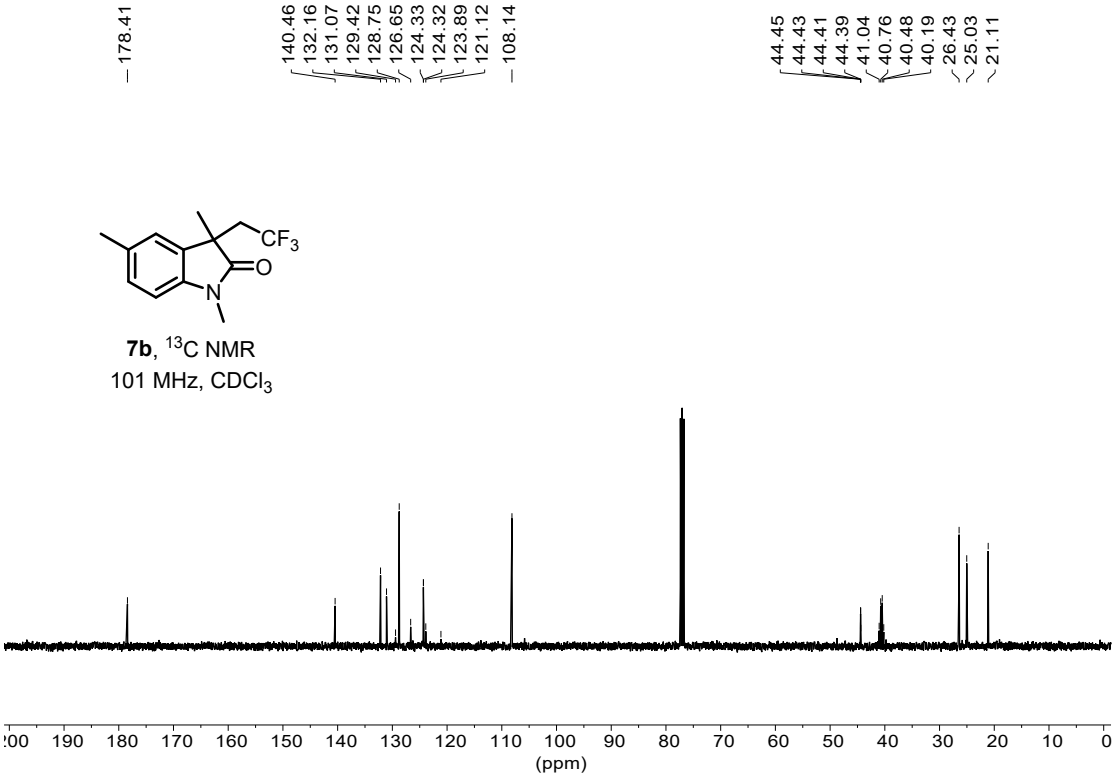
7a, ^{13}C NMR
101 MHz, $CDCl_3$



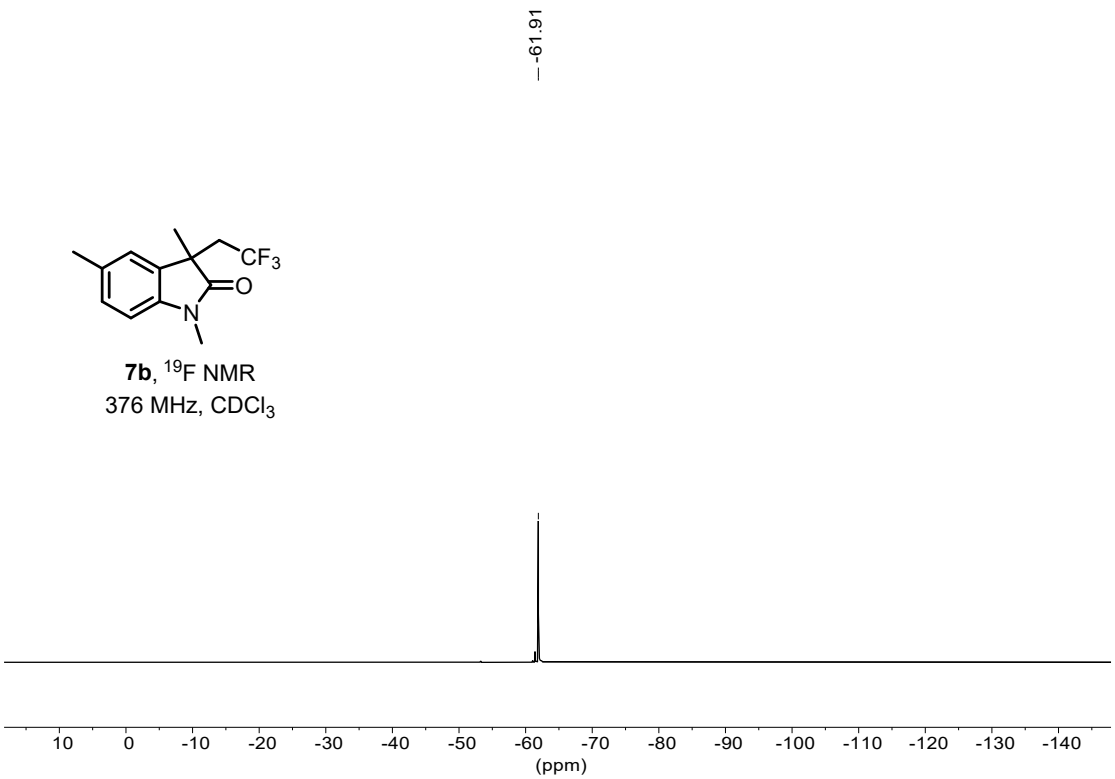
7a, ^{19}F NMR
376 MHz, $CDCl_3$



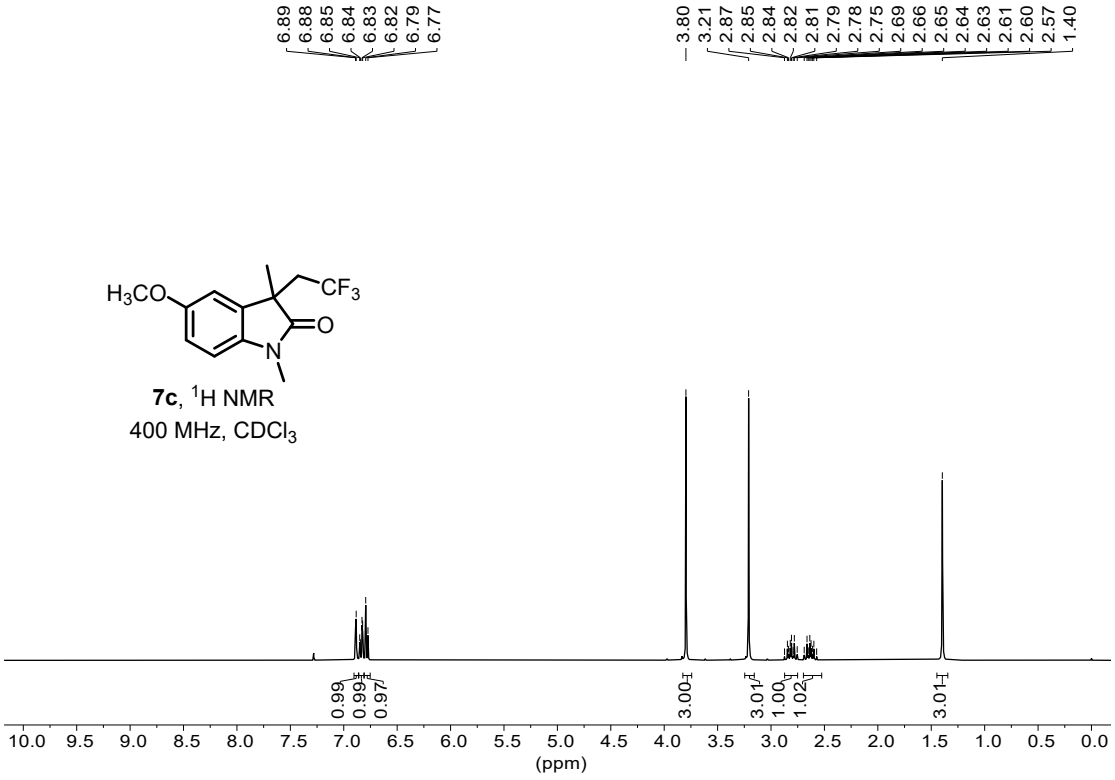
7b, ^{1}H NMR
400 MHz, $CDCl_3$

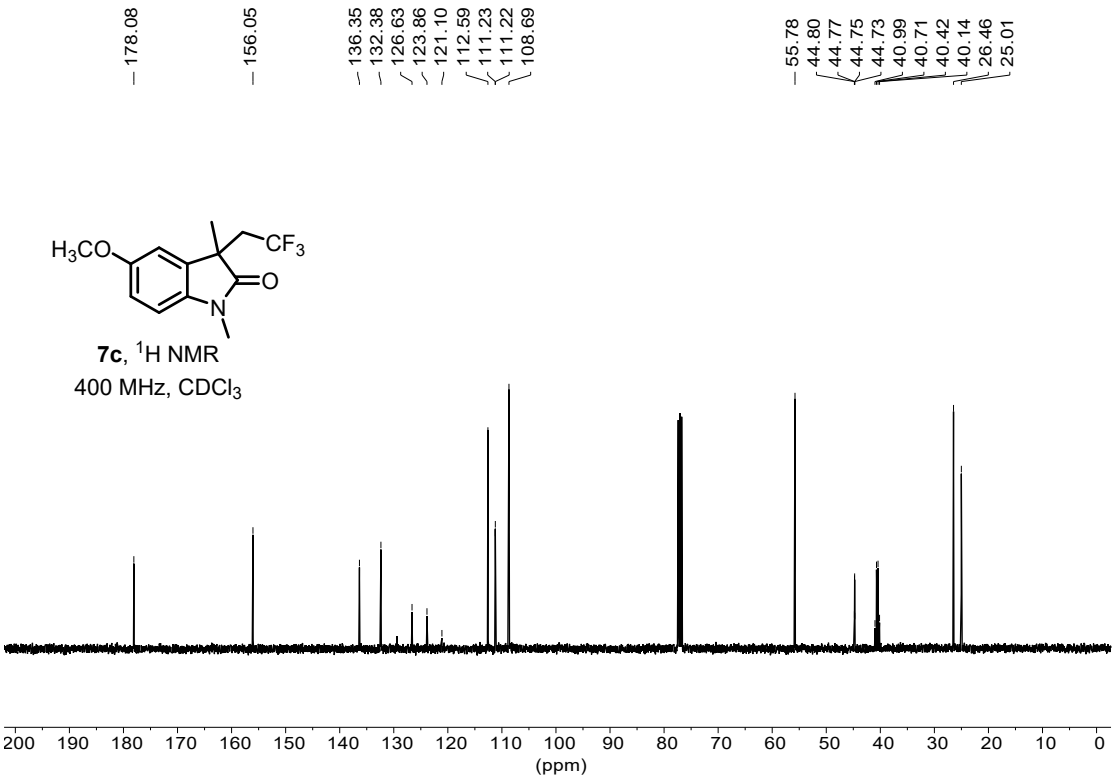


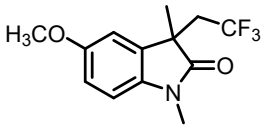
7b, ^{13}C NMR
101 MHz, $CDCl_3$



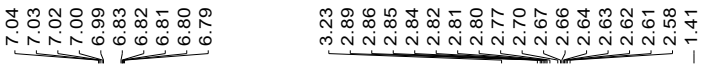
7b, ^{19}F NMR
376 MHz, $CDCl_3$

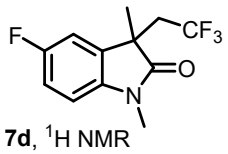

6.89
6.88
6.85
6.84
6.83
6.82
6.79
6.77
3.80
3.21
2.87
2.85
2.84
2.82
2.81
2.79
2.78
2.75
2.69
2.66
2.65
2.64
2.63
2.61
2.60
2.57
1.40
H3CO
CF3
O
N
7c, 1H NMR
400 MHz, CDCl3
0.99
0.99
0.97
3.00
3.01
1.00
1.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


178.08
156.05
136.35
132.38
126.63
123.86
121.10
112.59
111.23
111.22
108.69
55.78
44.80
44.77
44.75
44.73
40.99
40.71
40.42
40.14
26.46
25.01
H3CO
CF3
O
N
7c, 1H NMR
400 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

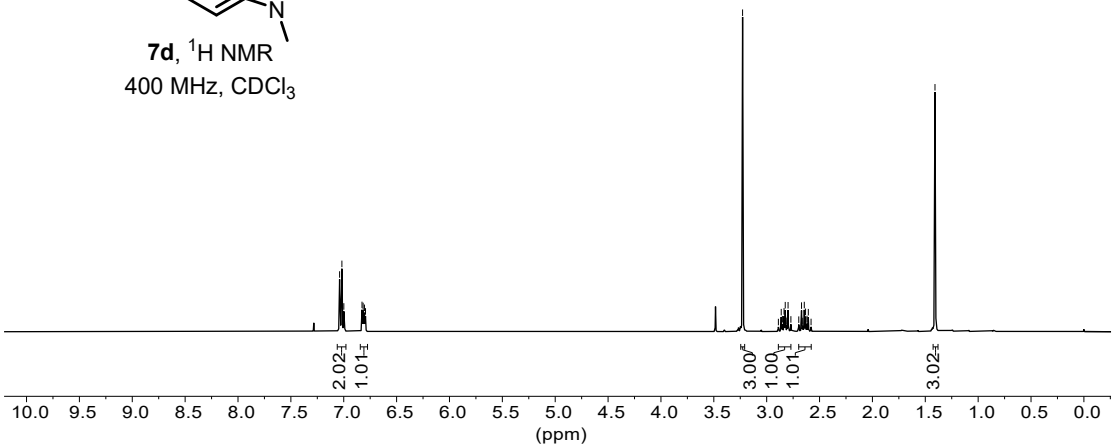


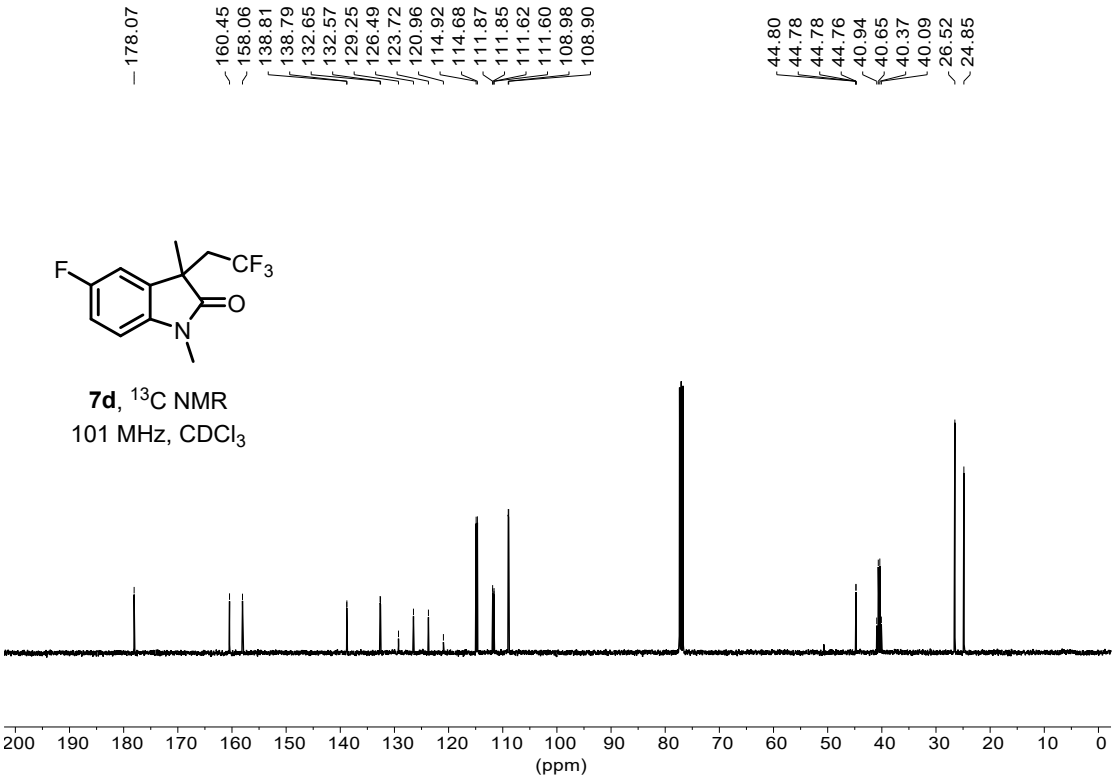
7c, ^{19}F NMR
376 MHz, $CDCl_3$

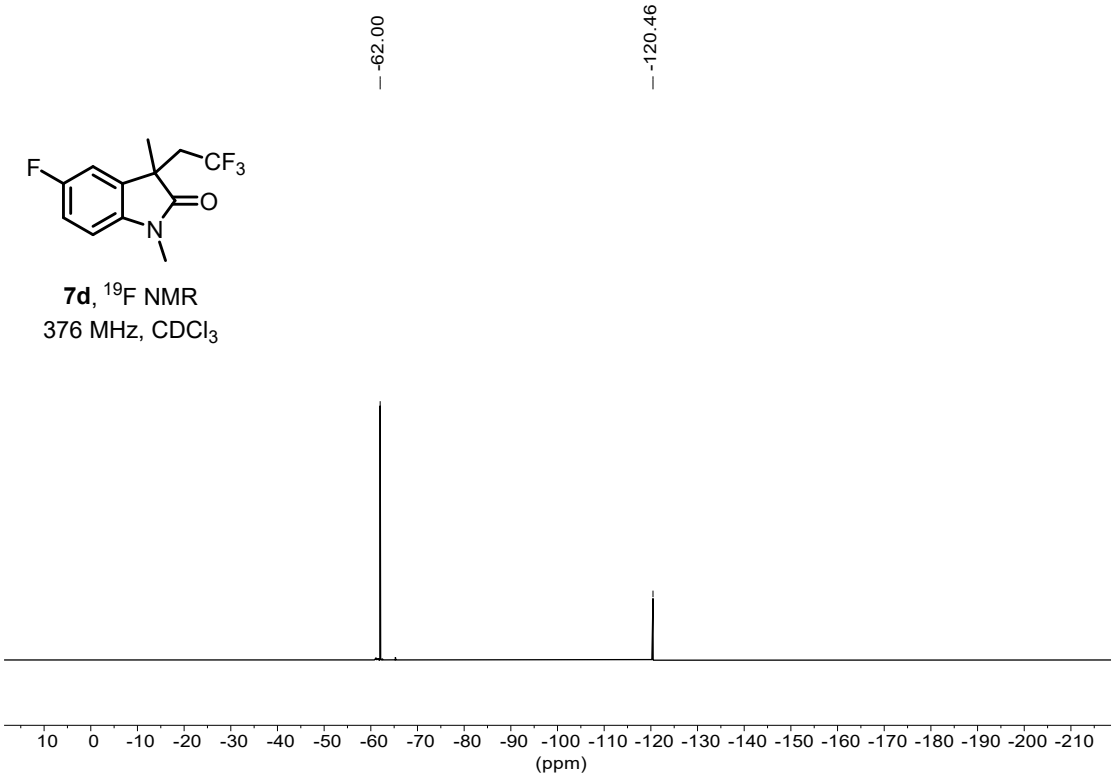


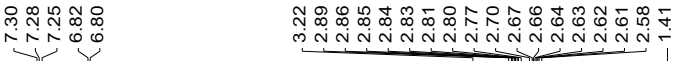


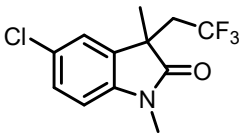
7d, ^{1}H NMR
400 MHz, $CDCl_3$



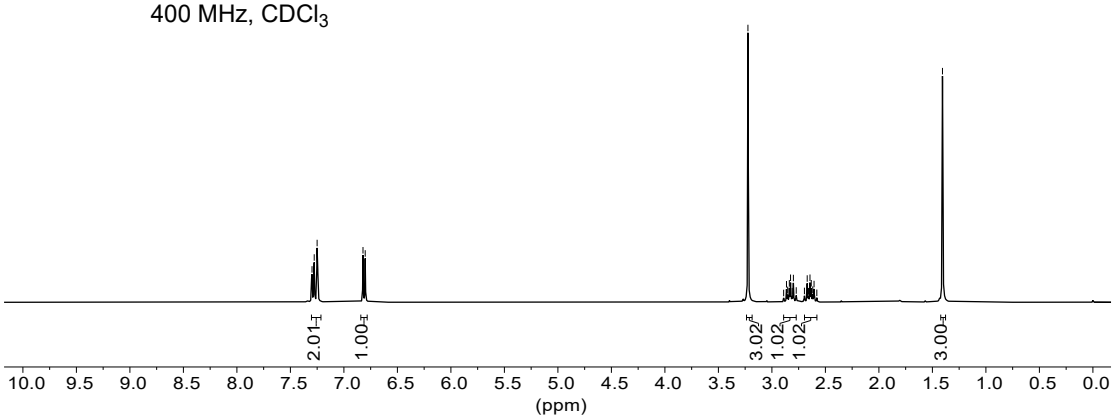

178.07
160.45
158.06
138.81
138.79
132.65
132.57
129.25
126.49
123.72
120.96
114.92
114.68
111.87
111.85
111.62
111.60
108.98
108.90
44.80
44.78
44.78
44.76
40.94
40.65
40.37
40.09
26.52
24.85
F
CF3
O
N
7d, 13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

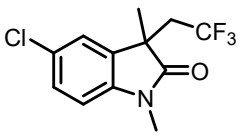

-62.00
-120.46
F
CF3
O
N
7d, 19F NMR
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
(ppm)



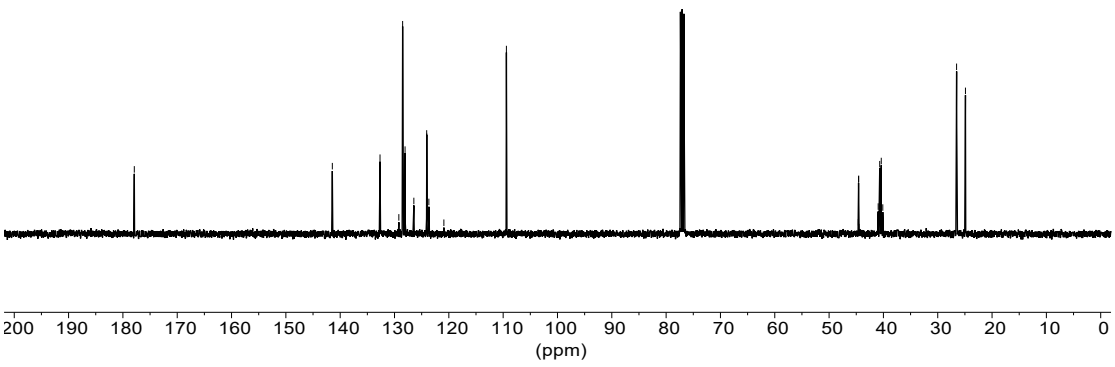


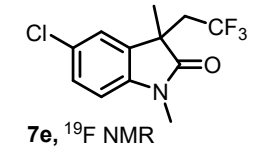
7e, ^{1}H NMR
400 MHz, $CDCl_3$



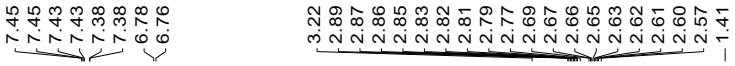


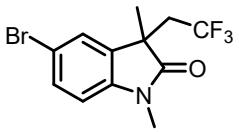
7e, ^{13}C NMR
101 MHz, $CDCl_3$



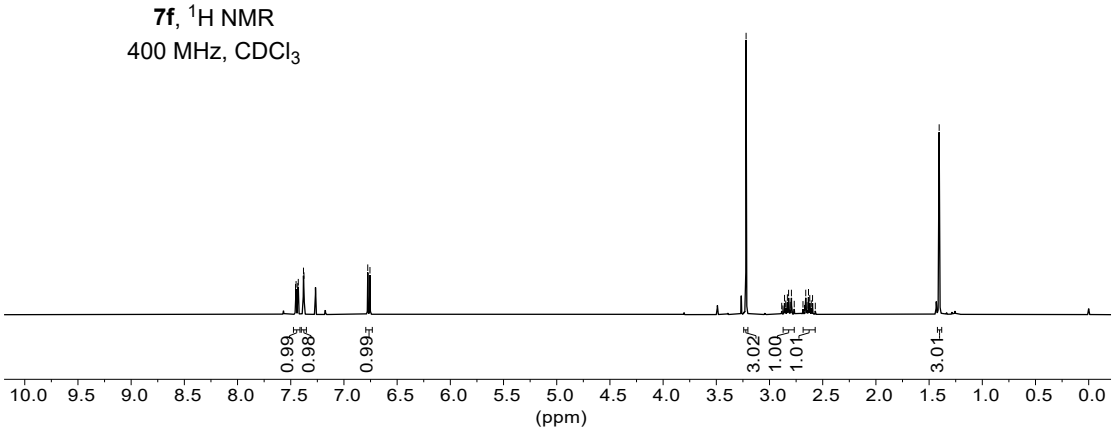


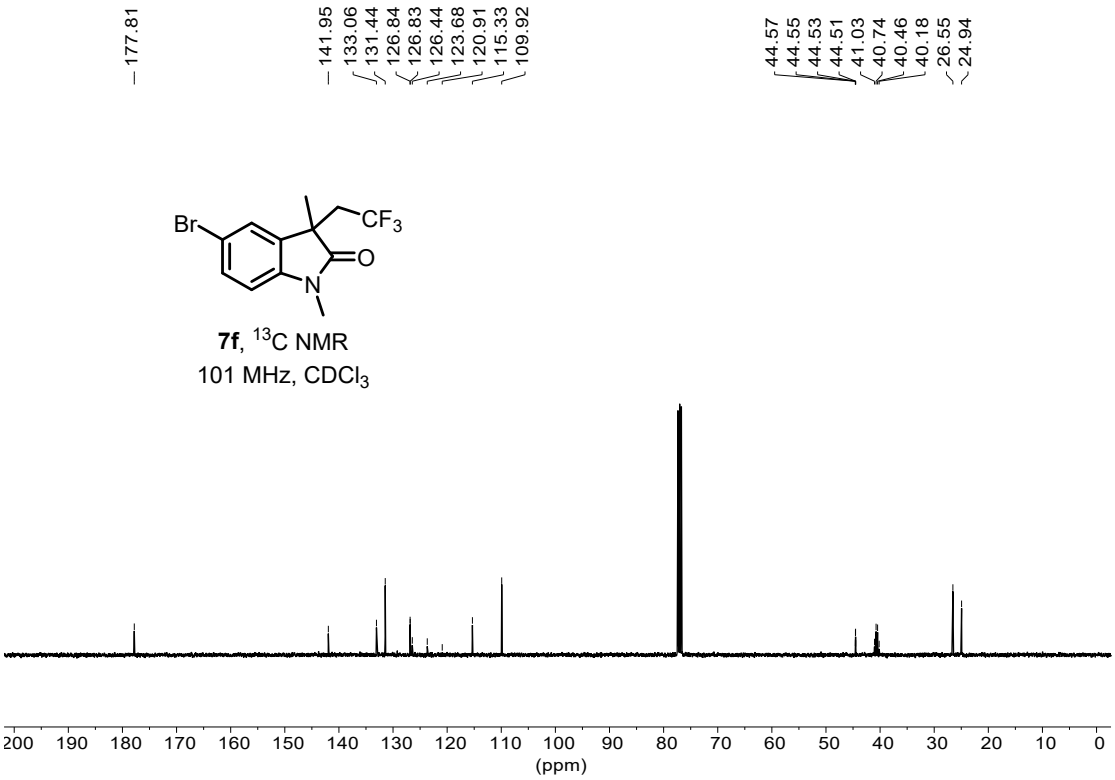
7e, ^{19}F NMR
376 MHz, $CDCl_3$



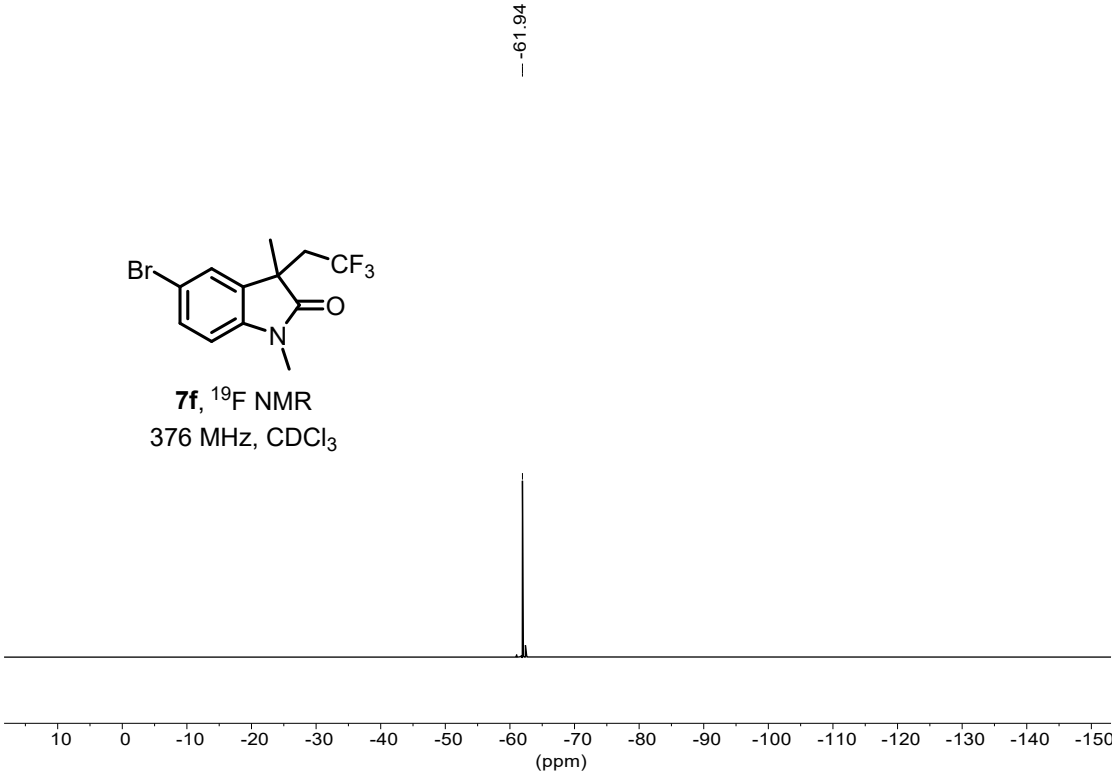


7f, ^{1}H NMR
400 MHz, $CDCl_3$

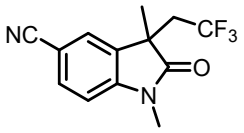




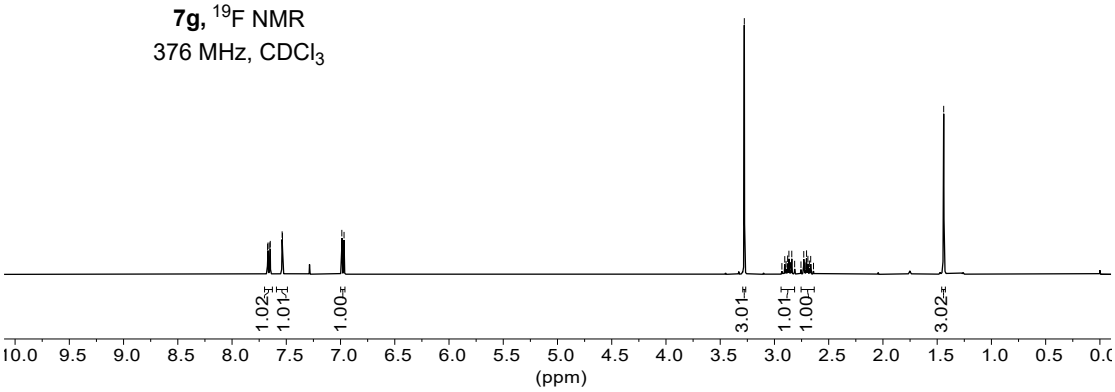
7f, ^{13}C NMR
101 MHz, $CDCl_3$

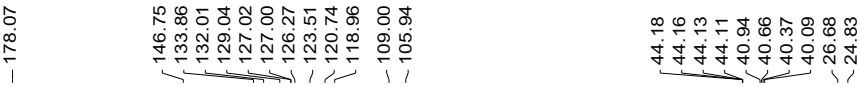


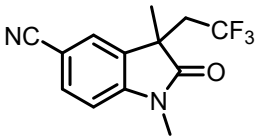
7f, ^{19}F NMR
376 MHz, $CDCl_3$



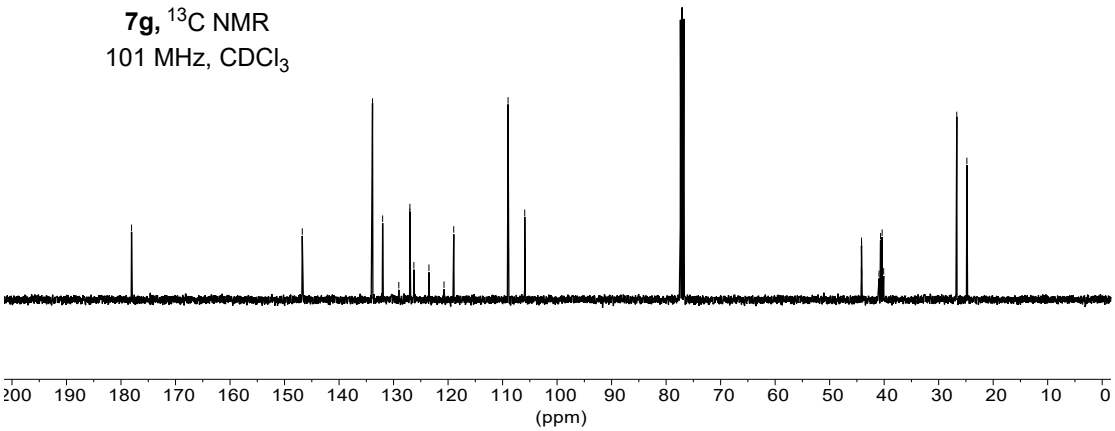
7g, ^{19}F NMR
376 MHz, $CDCl_3$

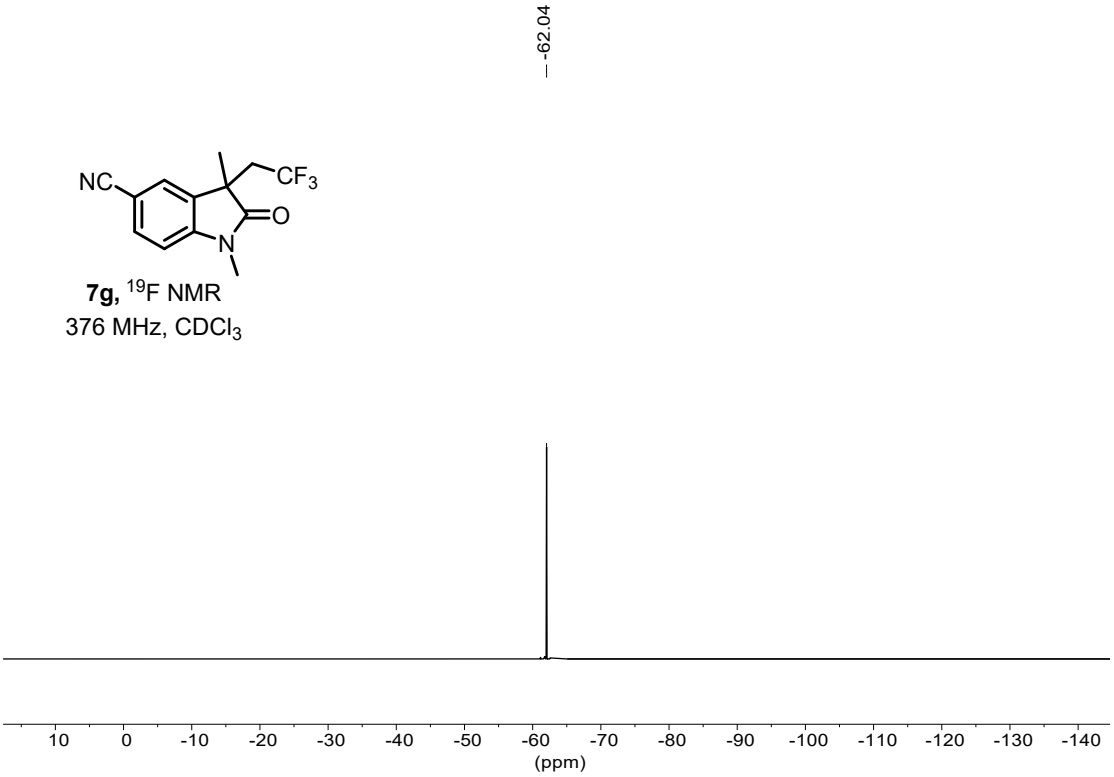




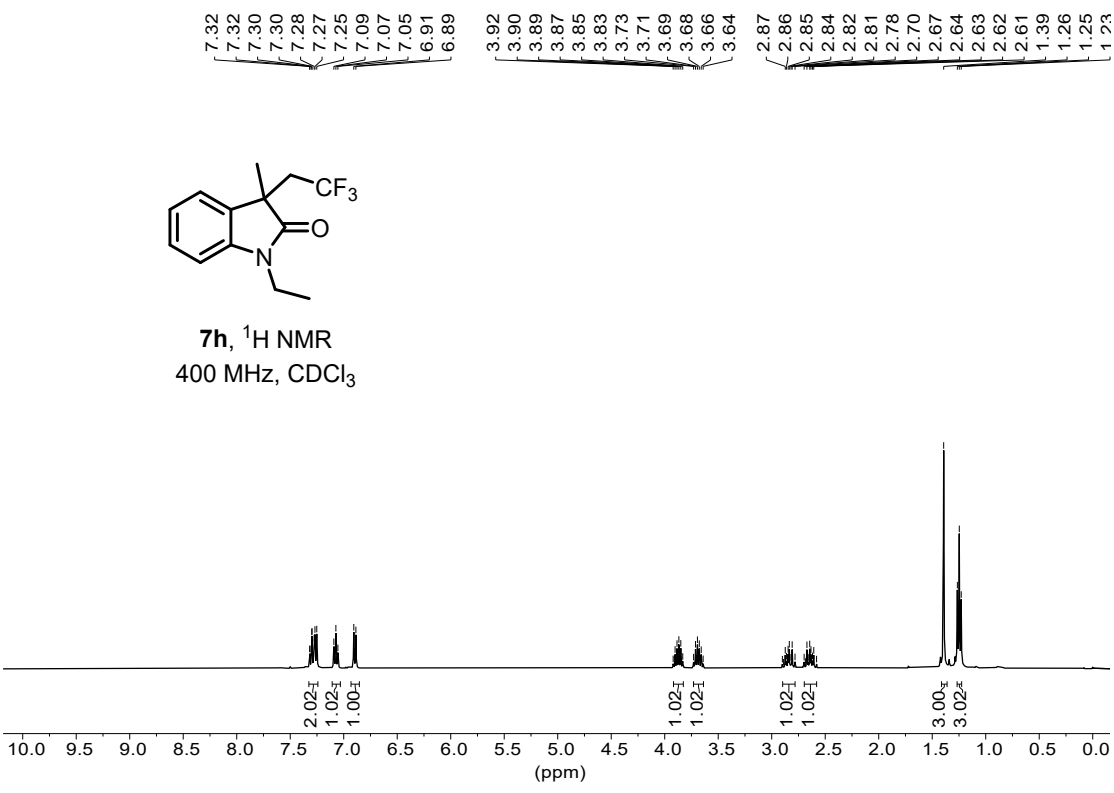


7g, ^{13}C NMR
101 MHz, $CDCl_3$

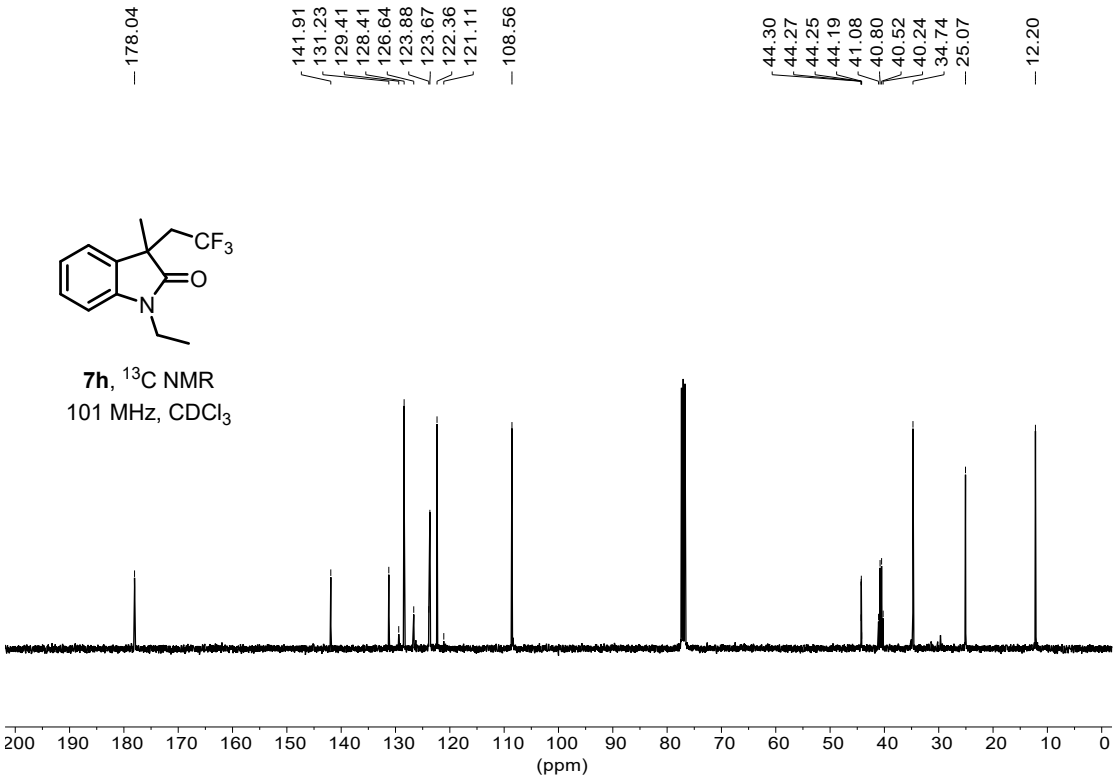




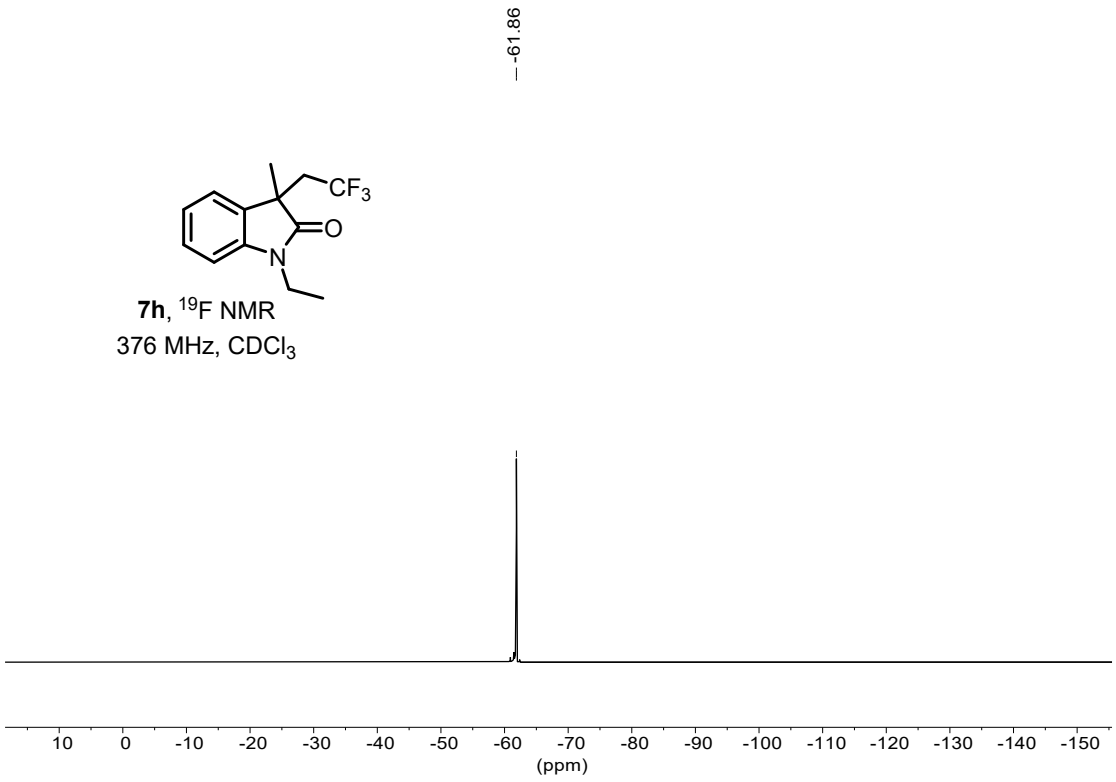
7g, ^{19}F NMR
376 MHz, $CDCl_3$



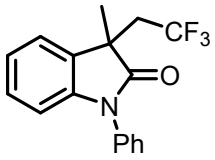
7h, ^{1}H NMR
400 MHz, $CDCl_3$



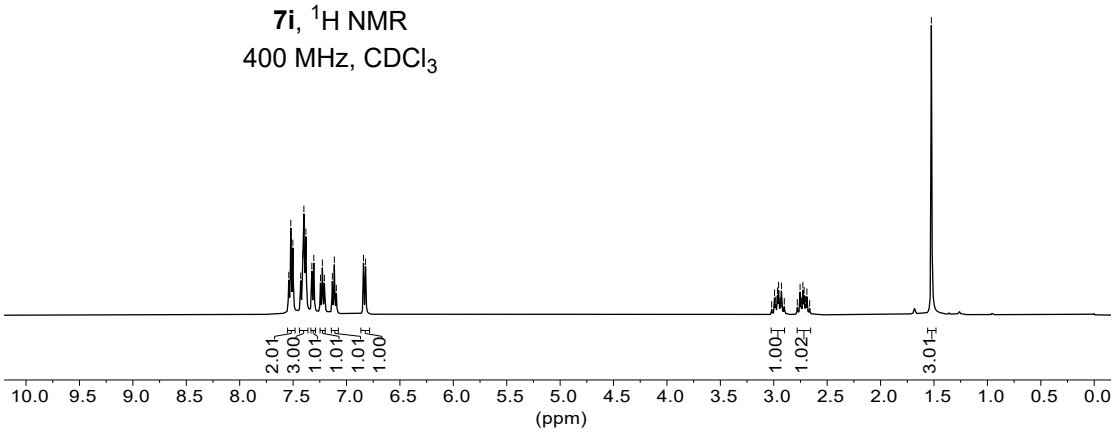
7h, ^{13}C NMR
101 MHz, $CDCl_3$

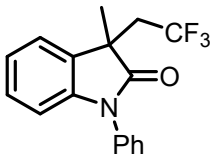


7h, ^{19}F NMR
376 MHz, $CDCl_3$

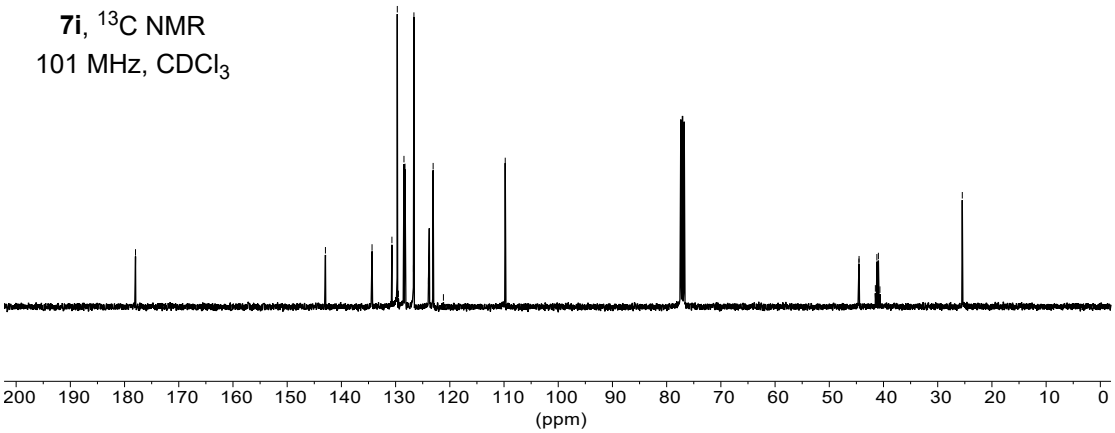


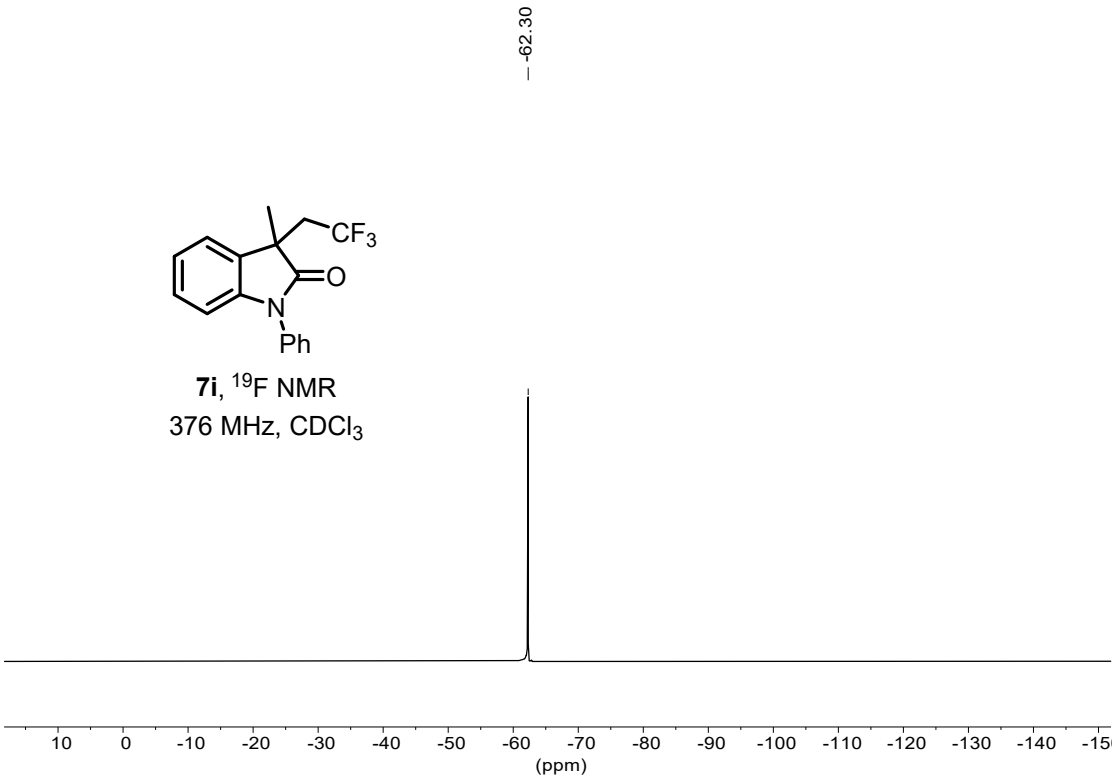
7i, ^{1}H NMR
400 MHz, $CDCl_3$





7i, ^{13}C NMR
101 MHz, $CDCl_3$





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