www.sciencemag.org/content/360/6392/1010/suppl/DC1

Supplementary Materials for

A radical approach to the copper oxidative addition problem: Trifluoromethylation of bromoarenes

Chip Le*, Tiffany Q. Chen*, Tao Liang*, Patricia Zhang, David W. C. MacMillan[†]

*These authors contributed equally to this work.
[†]Corresponding author. Email: dmacmill@princeton.edu

Published 1 June 2018, *Science* **360**, 1010 (2018)
DOI: 10.1126/aat4133

This PDF file includes:

Materials and Methods
Figures S1 to S49
NMR Spectra
References

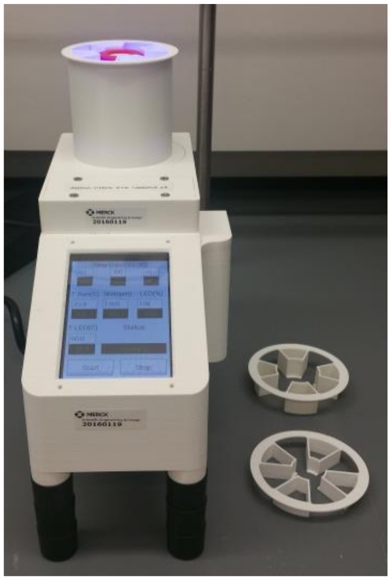
Table of Contents

1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego (*44*). All solvents were purified according to the method of Grubbs (*45*). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel according to the method of Still (*46*). Thin-layer chromatography (TLC) was performed on Analtech 250 micron silica gel plates. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and peaks are reported in terms of frequency of absorption (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-II 500 (500 and 125 MHz) instrument, and are internally referenced to residual protic solvent signals (note: $CDCl_3$ referenced at δ 7.26 and 77.16 ppm respectively). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities. Gas chromatography (GC) was performed on an Agilent 6850 Series chromatograph with splitless capillary injection and FID detection.

2) Reaction setup

1) Kessil blue LEDs setup: In a typical reaction, the reaction mixture is irradiated with 40W Kessil A160WE Tuna Blue from 5 cm away. Regular fans are employed to maintain the temperature at 35 °C. The reaction has been shown to be consistent within the range of 25 to 40 °C. Elevated temperature often results in diminished efficiency. Stirring rate for the reaction was set at 1000 rpm. In addition, it was found that pulverized inorganic bases (with mortar and pestle) provides more consistent results for the reaction.

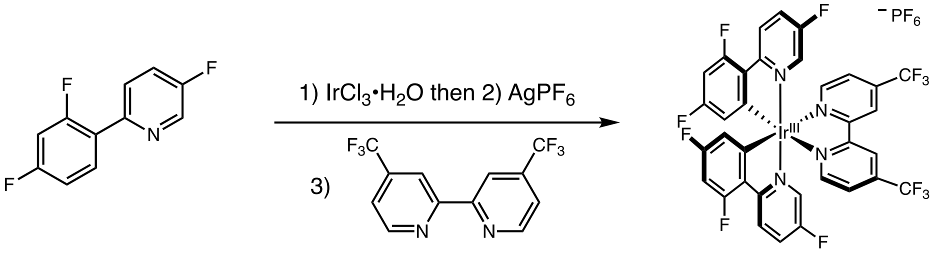


2) The Merck Integrated Photoreactor (*47*) can also be utilized to carry out this transformation. In a typical experiment with 450 nm LEDs module, the reaction vial was irradiated at 100% LED intensity, 1000 rpm stirring and 5000 rpm fan speed. The reaction temperature is kept at 25 °C under this setting. The photoreactor does provide accelerated rate using the optimized conditions. We typically observed a 2 to 3 times reduction in reaction time when the reactor was used in comparison to the standard setup.

3) Synthesis & Characterization of Photocatalysts

2-(2,4-difluorophenyl)-5-fluoropyridine, 2-(2,4-difluorophenyl)-5-methylpyridine, and 4,4'-ditrifluoromethyl-2,2'-bipyridyl were prepared according the reported procedure (*48*,*49*)

Ir[dFFppy]$_2$-(4,4'-dCF$_3$bpy)PF$_6$ (**1**)



(Step 1) **{Ir[dFFppy]$_2$Cl}$_2$** Under air, a three-neck round-bottom flask, equipped with a Teflon coated magnetic stir bar, was charged with 2-(2,4-difluorophenyl)-5-fluoropyridine (2.35 g, 11.3 mmol, 2.2 equiv) and IrCl$_3$•H$_2$O (1.58 g, 5.0 mmol, 1.0 equiv) and 2/1 mixture of 2-methoxyethanol/water (75 mL). The flask was equipped with a reflux condenser and nitrogen was bubbled through the solution with stirring for an hour before the mixture was heated at 120 ºC for 16 hours. Upon cooling to room temperature, water was added and the solid was isolated by filtration. Washing with cold Et$_2$O yielded {Ir[dFFppy]$_2$Cl}$_2$ as a bright yellow solid (2.5 g, 1.94 mmol, 78% yield). This complex was carried over to the next step without purification.

(Step 2) **Ir[dFFppy]$_2$-(MeCN)$_2$PF$_6$** Under air, a round-bottom flask, equipped with a Teflon coated magnetic stir bar, was charged with {Ir[dFFppy]$_2$Cl}$_2$ (1.28 g, 1.0 mmol, 1.0 equiv) and 5/1 mixture of DCM/MeCN (60 mL). AgPF$_6$ (0.53 g, 2.1 mmol, 2.1 equiv) was added in one portion. The reaction flask was protected from light with aluminum foil, then stirred at 55 ºC for 12 hours. Filtration of AgCl, followed by concentrating the filtrate yielded Ir[dFFppy]$_2$-(MeCN)$_2$PF$_6$ as a yellow solid (1.7 g, 2.00 mmol, >99% yield). This complex was carried over to the next step without purification.

(Step 3) **Ir[dFFppy]$_2$-(4,4'-dCF$_3$bpy)PF$_6$** Under air, a round-bottom flask, equipped with a Teflon coated magnetic stir bar, was charged with Ir[dFFppy]$_2$-(MeCN)$_2$PF$_6$ (1.7

g, 2.10 mmol, 1.0 equiv), 4,4’-ditrifluoromethyl-2,2’-bipyridyl (0.62 g, 2.1 mmol, 1.05 equiv) and 3/1 mixture of DCM/EtOH (12 mL). The solution was stirred under air at 45 ºC for 12 hours. Evaporation of solvent yielded a yellow crystalline solid. Column chromatography (silica gel, 0 to 0.25% MeOH in DCM), followed by recrystallization (layering, acetone/pentane at room temperature) yielded the pure product as a yellow crystalline solid (1.0 g, 1.00 mmol, 50% yield).

^{1}H NMR (500 MHz, acetone-*d$_6$*) δ 9.51 (s, 2H), 8.57 (d, *J* = 5.7 Hz, 2H), 8.49-8.43 (m, 2H), 8.13-8.11 (m, 2H), 8.02-7.98 (m, 4H), 6.84 (ddd, *J* = 12.7, 9.3, 2.4 Hz, 2H), 5.89 (dd, *J* = 8.5, 2.4 Hz, 2H).

^{13}C NMR (125 MHz, acetone-*d$_6$*) δ 165.4 (d, *J* = 12.6 Hz), 163.3 (d, *J* = 12.3 Hz), 162.8 (d, *J* = 12.8 Hz), 161.5 (dd, *J* = 7.1, 3.9 Hz), 160.7 (d, *J* = 13.1 Hz), 159.9 (d, *J* = 1.7 Hz), 158.0, 157.8 (d, *J* = 2.1 Hz), 154.1, 152.4 (d, *J* = 6.6 Hz), 141.4 (q, *J* = 35.3 Hz), 140.2 (d, *J* = 31.7 Hz), 128.4 (d, *J* = 18.9 Hz), 128.0 (dd, *J* = 4.9, 2.9 Hz), 126.5 (q, *J* = 3.6 Hz), 125.7 (dd, *J* = 20.7, 6.9 Hz), 124.3, 123.5 (q, *J* = 3.4 Hz), 123.19 (q, *J* = 273.6 Hz), 114.9 (dd, *J* = 18.3, 3.1 Hz), 100.2 (t, *J* = 27.1 Hz)

^{19}F NMR (282 MHz, acetone-*d$_6$*) δ -65.3 (s, 6F), -72.7 (d, *J* = 707.4 Hz, 6F), -107.3 (q, *J* = 9.0 Hz, 2F), -110.9 (q, *J* = 11.6 Hz, 2F), -124.8 (m, 2F).

^{31}P NMR (282 MHz, acetone-*d$_6$*) δ -144.29 (m)

IR (film) ν_{max} 3084, 1698, 1600, 1487, 1416, 1341, 1268, 1238, 1141, 1103, 830 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{34}H_{16}F_{12}IrN_4$ ([M-PF$_6$]$^+$) 899.0789, found 899.0784.

Cyclic Voltammogram: 1 μM solution in MeCN (with 100 equiv. of $TBAPF_6$ as electrolytes). Scan rate was set at 0.1 V/s.

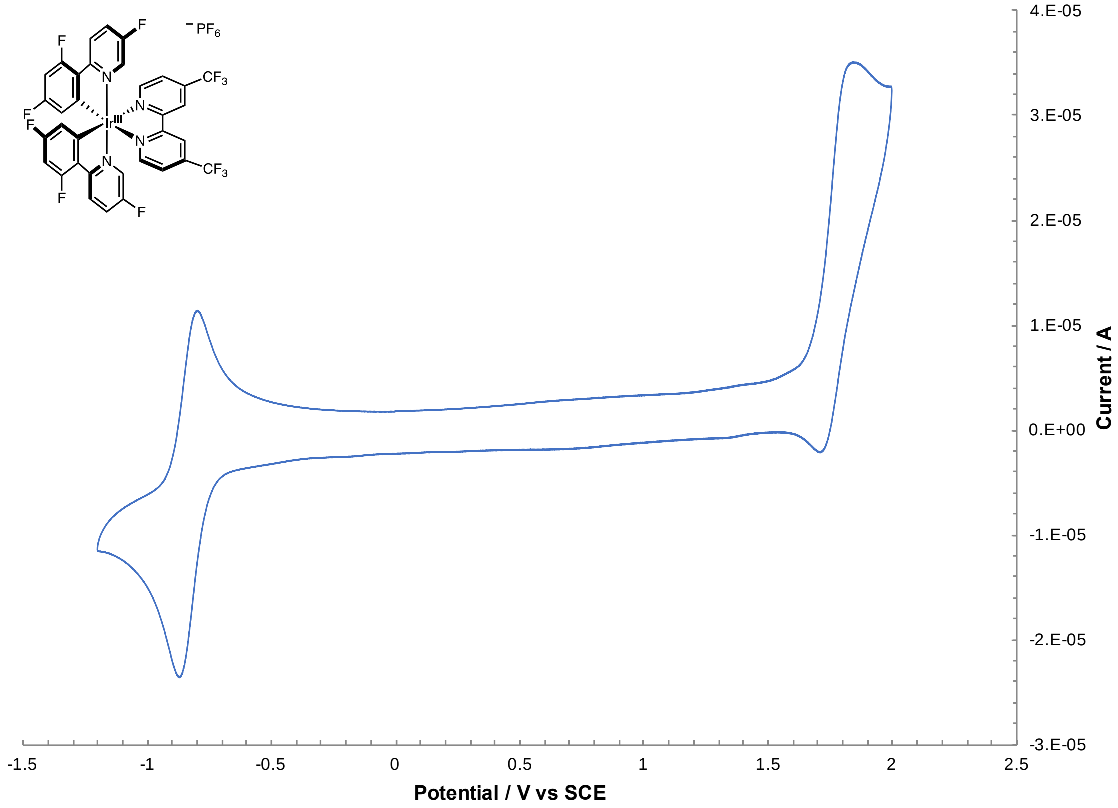


Figure S1. Cyclic voltammogram of photocatalyst **1** in MeCN.

Emission Data

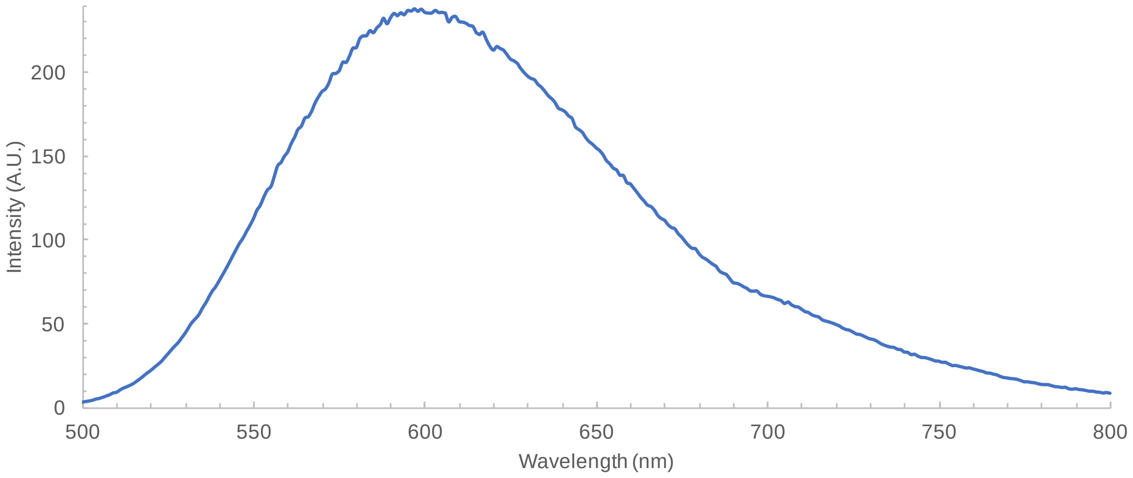
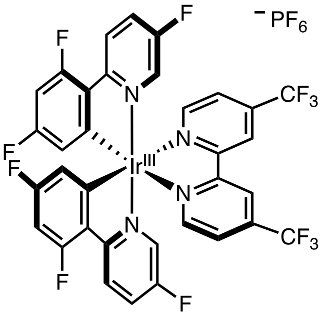


Figure S2. Emission spectra of photocatalyst **1** in MeCN.

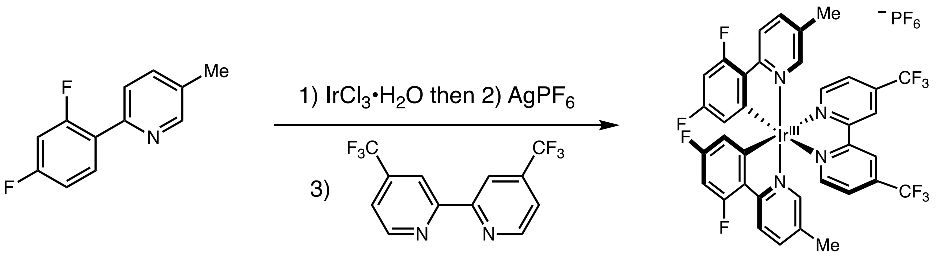
0.2 µM solution in MeCN and sparged with nitrogen. Excitation was set at 380 nm. The maxima was obtained at 603 nm (236.6 A.U.); the intensity is 10% of the emission maxima at 520 nm. Redox properties was calculated using the 10% rule (*50*)

Redox Properties



Ir(II)/Ir(III)*	E^* = 1.55V vs. SCE
Ir(II)/Ir(III)	$E_{1/2}$ = -0.83V vs. SCE
Ir(III)*/Ir(IV)	E^* = -0.54V vs. SCE
Ir(III)/Ir(IV)	E_p = 1.84V vs. SCE

Ir[dFMeppy]$_2$-(4,4’-dCF$_3$bpy)PF$_6$ (**14**)



(Step 1) **{Ir[dFMeppy]$_2$Cl}$_2$** Under air, a three-neck round-bottom flask, equipped with a Teflon coated magnetic stir bar, was charged with 2-(2,4-difluorophenyl)-5-methylpyridine (2.31 g, 11.3 mmol, 2.2 equiv) and IrCl$_3$•H$_2$O (1.58 g, 5.0 mmol, 1.0 equiv) and 2/1 mixture of 2-methoxyethanol/water (75 mL). The flask was equipped with a reflux condenser and nitrogen was bubbled through the solution with stirring for an hour before the mixture was heated at 120 ºC for 16 hours. Upon cooling to room temperature, water was added and the solid was isolated by filtration. Washing with cold Et$_2$O yielded {Ir[dFMeppy]$_2$Cl}$_2$ as a bright yellow solid (2.8 g, 2.2 mmol, 88% yield). This complex was carried over to the next step without purification.

(Step 2) **Ir[dFMeppy]$_2$-(MeCN)$_2$PF$_6$** Under air, a round-bottom flask, equipped with a Teflon coated magnetic stir bar, was charged with {Ir[dFMeppy]$_2$Cl}$_2$ (2.4 g, 1.9 mmol, 1.0 equiv) and 5/1 mixture of DCM/MeCN (60 mL). AgPF$_6$ (1.0 g, 4.1 mmol, 2.1 equiv) was added in one portion. The reaction flask was protected from light with aluminum foil, then stirred at 55 ºC for 12 hours. Filtration of AgCl, followed by concentrating the filtrate yielded Ir[dFMeppy]$_2$-(MeCN)$_2$PF$_6$ as a yellow solid (3.1 g, 3.75 mmol, 98% yield). This complex was carried over to the next step without purification.

(Step 3) **Ir[dFMeppy]$_2$-(4,4'-dCF$_3$bpy)PF$_6$** Under air, a round-bottom flask, equipped with a Teflon coated magnetic stir bar, was charged with Ir[dFMeppy]$_2$-(MeCN)$_2$PF$_6$ (3.1 g, 3.75 mmol, 1.0 equiv), 4,4'-ditrifluoromethyl-2,2'-bipyridyl (1.1 g, 3.9 mmol, 1.05 equiv) and 3/1 mixture of DCM/EtOH (40 mL). The solution was stirred under air at 45 ºC for 12 hours. Evaporation of solvent yielded a yellow crystalline solid. Column chromatography (silica gel, 0 to 0.25% MeOH in DCM), followed by recrystallization (layering, acetone/pentane at room temperature) yielded the pure product as a yellow crystalline solid (2.5 g, 2.4 mmol, 65% yield).

^{1}H NMR (500 MHz, CD$_3$CN) δ 8.97 (s, 2H), 8.23-8.20 (m, 4H), 7.81 (dd, *J* = 5.7, 1.7 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.40 (m, 2H), 6.71 (ddd, *J* = 12.8, 9.4, 2.4 Hz, 2H), 5.71 (dd, *J* = 8.7, 2.4 Hz, 2H).

^{13}C NMR (125 MHz, CD$_3$CN) δ 165.1 (d, *J* = 12.4 Hz), 163.1 (d, *J* = 12.4 Hz), 162.9 (d, *J* = 12.8 Hz), 161.6 (d, *J* = 6.8 Hz), 160.8 (d, *J* = 12.9 Hz), 157.4, 153.7, 153.0 (d, *J* = 6.7 Hz), 150.5, 141.5, 141.1 (q, *J* = 35.3 Hz), 135.9, 129.0 (dd, *J* = 4.9, 2.8 Hz), 126.2 (q, *J* = 3.6 Hz), 124.3, 124.2, 123.3 (q, *J* = 3.5 Hz), 123.2 (q, *J* = 273.4 Hz), 114.8 (dd, *J* = 18.1, 3.0 Hz), 100.0 (t, *J* = 27.1 Hz), 18.1.

^{19}F NMR (282 MHz, CD$_3$CN) δ -65.3 (s, 6F), -72.9 (d, *J* = 706.3 Hz, 6F), -108.8 (q, *J* = 9.5 Hz, 2F), -110.7 (t, *J* = 11.5 Hz, 2F)

^{31}P NMR (282 MHz, acetone-*d$_6$*) δ -144.65 (m)

IR (film) ν_{max} 3100, 1603, 1576, 1490, 1414, 1341, 1185, 1146, 1103, 833 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{36}H_{22}F_{10}IrN_4$ ($[M-PF_6]^+$) 891.1291, found 891.1254.

Cyclic Voltammogram: 1 μM solution in MeCN (with 100 equiv. of $TBAPF_6$ as electrolytes). Scan rate was set at 0.1 V/s.

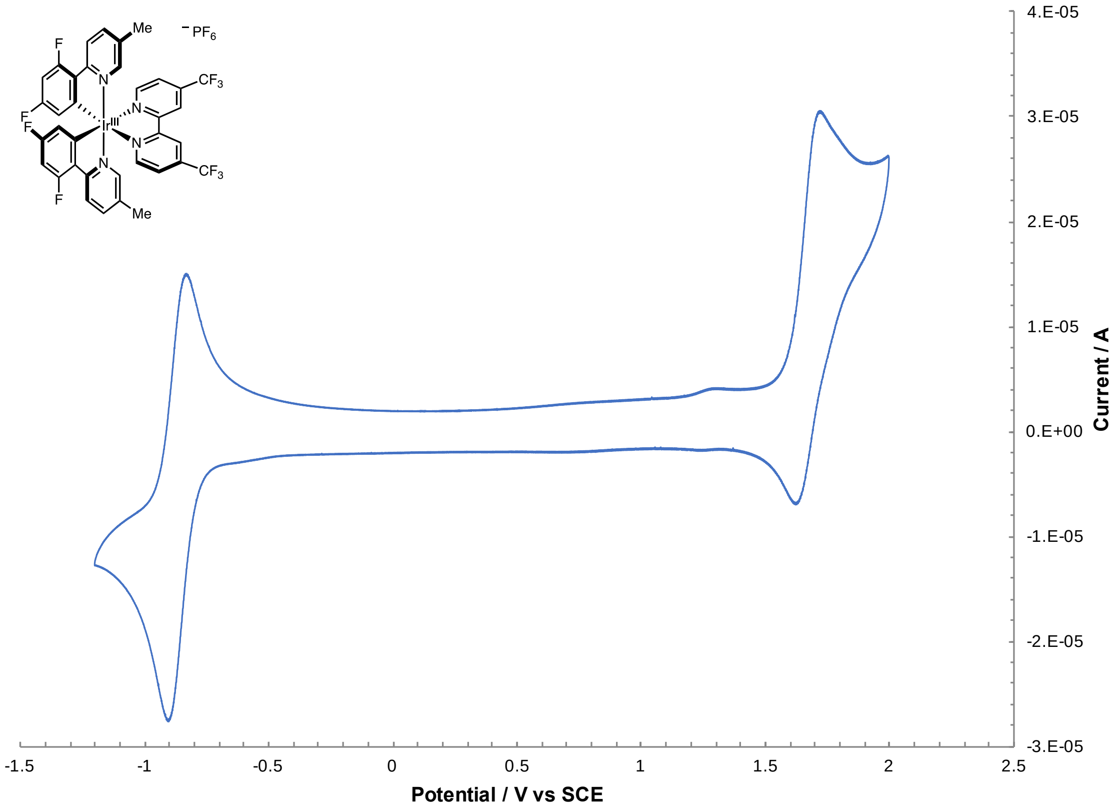


Figure S3. Cyclic voltammogram of photocatalyst **14** in MeCN.

Emission Data

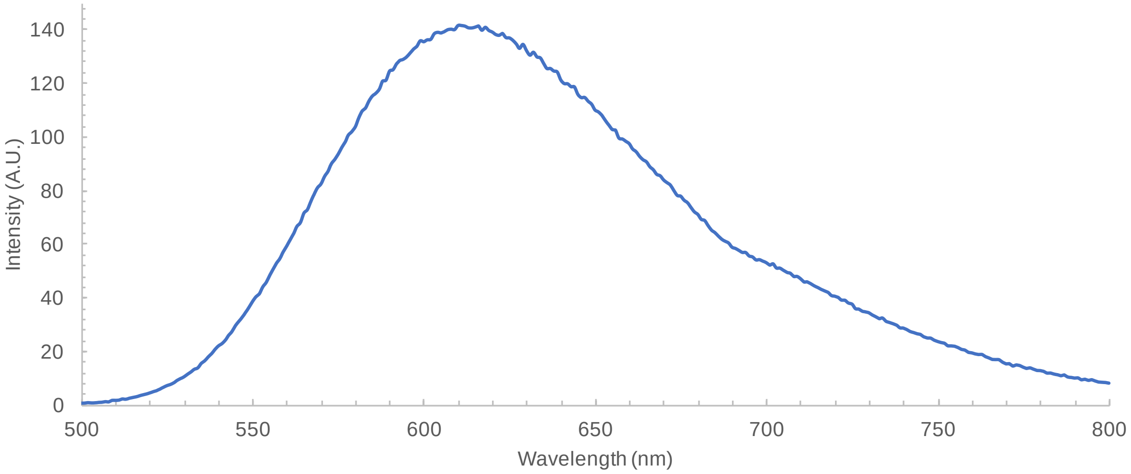
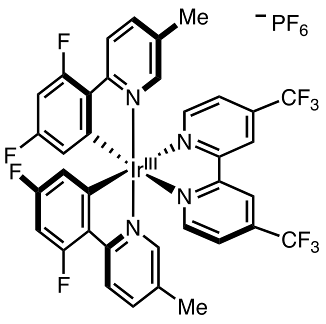


Figure S4. Emission spectra of photocatalyst **14** in MeCN.

0.2 µM solution in MeCN and sparged with nitrogen. Excitation was set at 380 nm. The maxima was obtained at 610 nm (141.5 A.U.); the intensity is 10% of the emission maxima at 534 nm. Redox properties was calculated using the 10% rule (*50*).

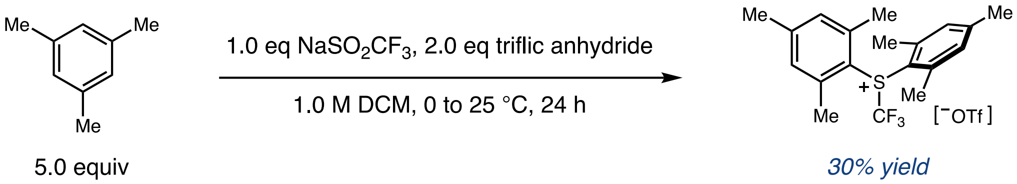
Redox Properties



Ir(II)/Ir(III)*	E^{*} = 1.46V vs. SCE
Ir(II)/Ir(III)	$E_{1/2}$ = -0.86V vs. SCE
Ir(III)*/Ir(IV)	E^{*} = -0.60V vs. SCE
Ir(III)/Ir(IV)	E_{p} = 1.72V vs. SCE

4) Synthesis & Characterization of CF_3 reagents (8)

Derivatives of diarylsulfonium-CF3 reagents were prepared using a modified version of previously reported protocol. (*51*)



Under air, a 2-neck round-bottom flask equipped with an additional funnel was charged with sodium trifluoromethanesulfinate (Langlois reagent, 150 mmol, 23.4 g), dichloromethane (150 mL) and mesitylene (5 equiv, 750 mmol, 104 mL). The reaction mixture was cooled down to 0 °C with an ice-water bath. The addition funnel was then charged with trifluoromethanesulfonic anhydride (2 equiv, 300 mmol, 51 mL) before the entire apparatus was placed under nitrogen. Trifluoromethanesulfonic anhydride was slowly added over the course of 15 minutes. The reaction mixture was allowed to warm up to room temperature on its own and stirred at this temperature for 24 hours. The final mixture was quenched with saturated aqueous sodium bicarbonate at 0 °C. Dichloromethane (500 mL) was added and the organic layer was separated. Concentration of the organic solution yielded a brown oil. Dichloromethane (20 mL) was added followed by diethyl ether (500 mL) to crash out the product as a white precipitate. This mixture was sonicated for 30 minutes and filtered to yield the product. The product was furthered purified by recrystallization via layering technique (diethyl ether over DCM at room temperature) to yield analytically pure *dMesSCF₃* as a white solid (22 g, 30% yield).

This reagent is air and moisture stable at room temperature but is typically kept in the freezer at -20 °C while not in use (no sign of decomposition has been observed after 6 months following this protocol).

This reagent is also available from Sigma Aldrich (Catalog #901466)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.21 (s, 4H), 2.53 (s, 12H), 2.39 (s, 6H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 147.8, 142.7, 133.9, 124.8 (q, *J* = 328.1 Hz), 121.0 (q, *J* = 320.9 Hz), 115.5, 21.4, 21.2 (q, *J* = 2.2 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ -41.4 (s, 3F), -78.3 (s, 3F) .

IR (film) ν_{max} 2958, 1598, 1457, 1385, 1262, 1150, 1070, 1029, 761, 729 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{22}F_3S$ ([M-OTf]$^+$) 339.1389, found 339.1375.

Cyclic Voltammogram: 1 μM solution in MeCN (with 100 equiv. of TBAOTf as electrolytes). Scan rate was set at 0.05 V/s.

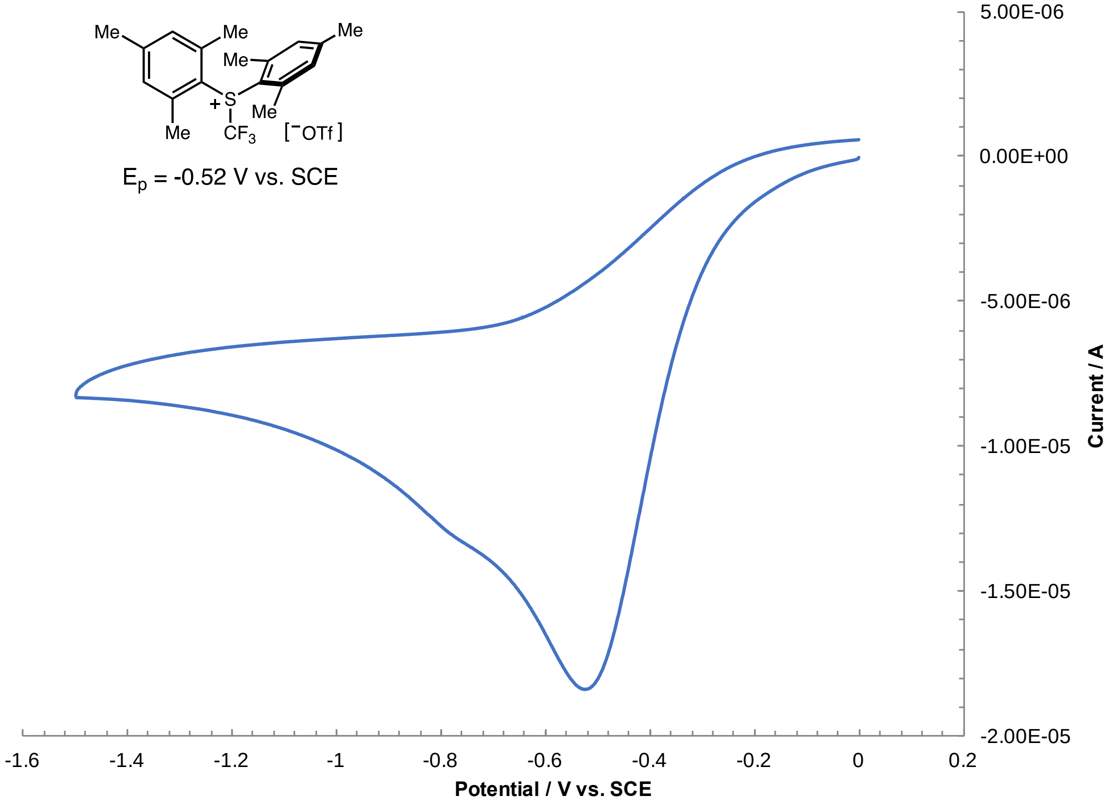


Figure S5. Cyclic voltammogram of dMesSCF$_3$(OTf) reagent ***(8)*** in MeCN.

X-Ray Structural Data for dMesSCF$_3$(OTf) *(8)*

Crystals suitable for X-Ray analysis was obtained via vapor diffusion (DCM/Et$_2$O) at room temperature.

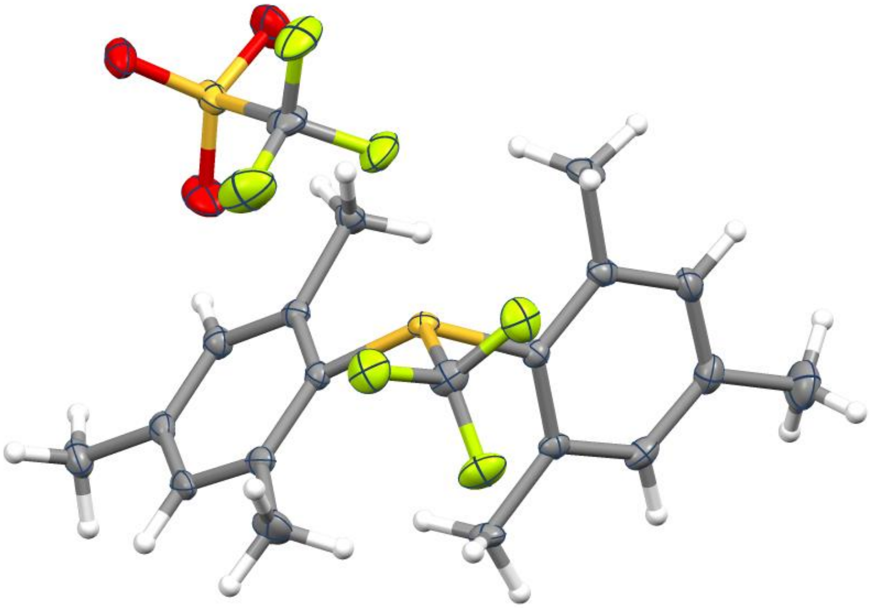


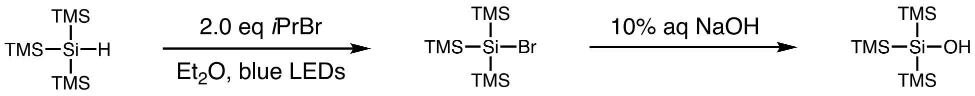
Figure S6. Representation of the solid-state of dMesSCF$_3$(OTf) ***(8)*** using 50% probability ellipsoids.

Table S1. Crystal data and structure refinement for dMesSCF$_3$(OTf) ***(8)***

Identification code	global	
Empirical formula	C60 H66 F18 O9 S6	
Formula weight	1465.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.7125(5) Å	a= 100.9223(13)°.
	b = 15.6802(6) Å	b= 90.8105(13)°.
	c = 18.0230(7) Å	g = 92.0309(13)°.

Volume	3247.3(2) Å3
Z	2
Density (calculated)	1.499 Mg/m3
Absorption coefficient	0.317 mm-1
F(000)	1512
Crystal size	0.195 x 0.112 x 0.061 mm3
Theta range for data collection	2.30 to 28.70°.
Index ranges	-15<=h<=15, -21<=k<=21, -24<=l<=24
Reflections collected	73759
Independent reflections	16760 [R(int) = 0.0364]
Completeness to theta = 28.70°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.98 and 0.92
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	16760 / 212 / 1002
Goodness-of-fit on F2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0963
R indices (all data)	R1 = 0.0583, wR2 = 0.1049
Largest diff. peak and hole	0.452 and -0.347 e.Å-3

5) Synthesis & characterization of TMS$_3$SiOH reagents (4)



Under air, a 40-mL vial equipped with a magnetic stir bar was charged with TMS$_3$SiH (3.6 mL, 12.5 mmol), 2-bromopropane (2.3 mL, 25.0 mmol, 2.0 eq) and Et$_2$O (4.0 mL). The reaction vial was capped under air and irradiated with Kessil 34 W blue LEDs (7 cm away, with fan cooling) for 12 hours. After irradiation, the reaction vial was slowly opened to allow for a slow gas evolution. After gas evolution completed, the organic solution was poured into a round-bottom flask containing a 10% aq NaOH solution (11 mL, 1.1 eq). More Et$_2$O is used to ensure complete transfer. This mixture was stirred at room temperature under air for 24 hours. Et$_2$O was then added and the organic layer was separated. The organic solution was dried with Na$_2$SO$_4$, followed by concentration to yield the crude silanol as a clear oil. Purification via distillation under high vac yielded the pure silanol as a clear oil. The purity of the silane reagent was confirmed by ^{1}H NMR and GC-MS.

^{1}H NMR (500 MHz, CD$_3$CN) δ 1.80 (s, 1H), 0.15 (s, 27H).

^{13}C NMR (125 MHz, CD$_3$CN) δ -0.25.

IR (film) ν_{max} 3651, 3434, 2949, 2894, 1395, 1243, 1057, 825 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{28}Si_4O$ ([M]$^{+*}$) 264.1212, found 264.1223.

Cyclic Voltammogram: 1 µM solution in MeCN (with 100 equiv. of TBAPF$_6$ as electrolytes). Scan rate was set at 0.05 V/s.

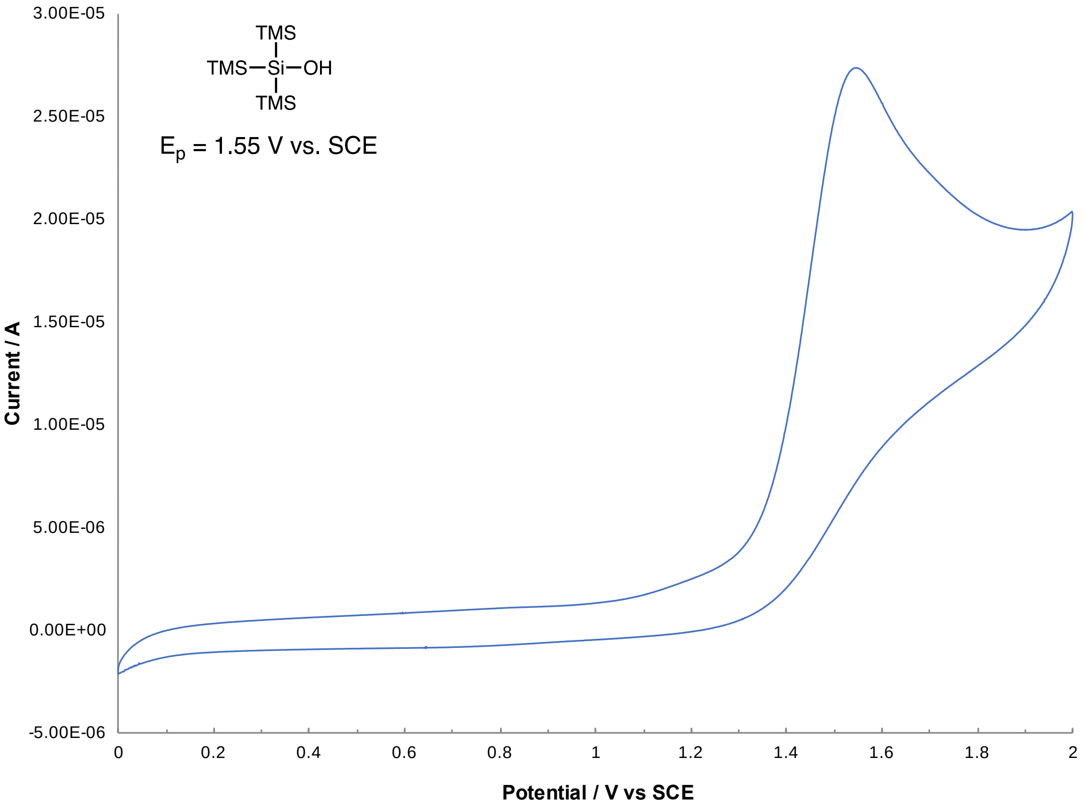


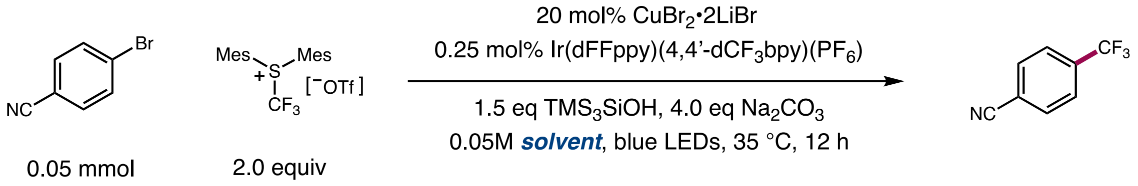
Figure S7. Cyclic voltammogram of TMS_3SiOH ***(4)*** in MeCN.

6) Reaction optimization

$CuBr_2$•2LiBr stock solution: Prepared fresh before each screen by dissolving $CuBr_2$ (67.0 mg, 0.03 mmol) and LiBr (52.1 mg, 0.06 mmol) in 15.0 mL of anhydrous acetone. This copper solution was stirred for 15 minutes before use.

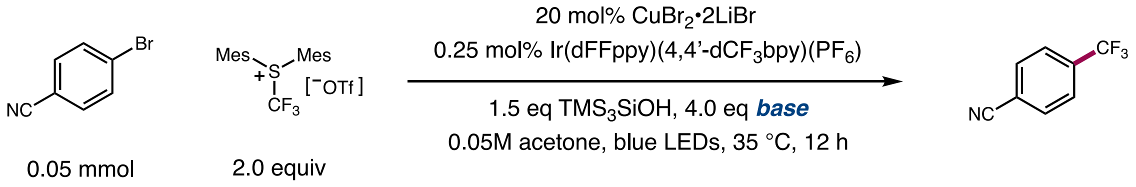
Photocatalyst stock solution: Prepared fresh before each screen by dissolving photocatalyst (1.25 µmol) in 5.0 mL of anhydrous acetone. This solution was sonicated for 5 minutes before use.

To an oven-dried 8-mL vial equipped with a magnetic stir bar was added 4-bromobenzonitrile (9.1 mg, 0.05 mmol), base (4.0 equiv.), and diarylsulfonium-CF_3 reagent (0.1 mmol, 2.0 equiv.). To this reaction vial was added $CuBr_2$•2LiBr stock solution (0.5 mL, 0.01 mmol, 20 mol%) and photocatalyst stock solution (0.5 mL, 0.125 µmol, 0.25 mol%), followed by silane source (0.075 mmol, 1.5 equiv.). The reaction mixture was sparged with nitrogen at 0 °C (ice water bath, to minimize solvent evaporation) for 15 mins. The reaction vial cap was then wrapped in parafilmed then irradiated with a 40W Kessil A160WE Tuna Blue (maximum blue setting & maximum intensity setting) from 5 cm away with fan cooling for 12 hours. The reaction was quenched by exposure to air with stirring for 15 minutes. Internal standard (1,3,5-triisopropylbenzene or 1,4-difluorobenzene, 1.0 equiv.) was added and an aliquot was taken for ^{1}H NMR analysis in DMSO-d_6. Formation of the desired product was confirmed by comparing the NMR & GC-MS data with sample of authentic product.



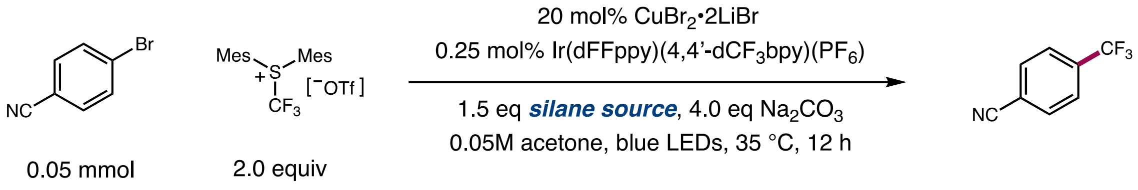
solvent	yield	***solvent***	yield
acetone	89%	$CHCl_3$	<1%
acetonitrile	55%	Et_2O	<1%
ethyl acetate	32%	THF	9%
toluene	0%	DME	27%
DMF	33%	Dioxane	2%
DCM	2%		

Figure S8. Evaluation of different solvents. Yields determined by ^{1}H NMR.



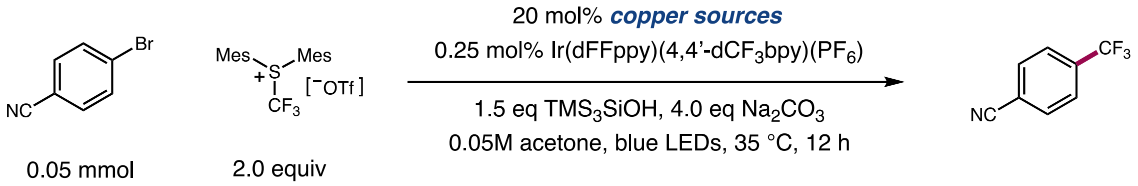
base	yield	***base***	yield
Na_2CO_3	89%	NaOAc	63%
Li_2CO_3	10%	KOAc	74%
K_2CO_3	80%	DBU	4%
Cs_2CO_3	80%	Hunig's base	10%
K_3PO_4	78%	2,6-lutidine	9%
$KHCO_3$	77%		

Figure S9. Evaluation of different bases. Yields determined by ^{1}H NMR.



silane	yield	***silane***	yield
TMS_3SiOH	89%	Me_2PhSiH	0%
TMS_3SiH	64%	Ph_3SiH	0%
$(TMSO)_3SiH$	0%	$i\text{Pr}_3SiH$	0%
Et_3SiH	0%	Me_3SiOH	0%

Figure S10. Evaluation of different silane sources. Yields determined by ^{1}H NMR.



copper source	yield	***copper source***	yield
$CuBr_2$•2LiBr	89%	CuCl	28%
$Cu(OAc)_2$	77%	CuBr	87%
$CuCl_2$	80%	CuI	28%
$Cu(acac)_2$	16%	CuCN	63%
$Cu(TFA)_2$	55%	$NH_4Cu(CF_3)_3$	3%
$Cu(MeCN)_4(PF_6)$	35%	$Cu(bpy)(CF_3)_3$	7%
CuTc	89%	$(phen)CuCF_3$	42%

Figure S11. Evaluation of different copper sources. Yields determined by ^{1}H NMR.

$CuBr_2$•2LiBr was chosen as the optimal source due to its solubility in acetone, thus providing high consistency in reaction efficiency.

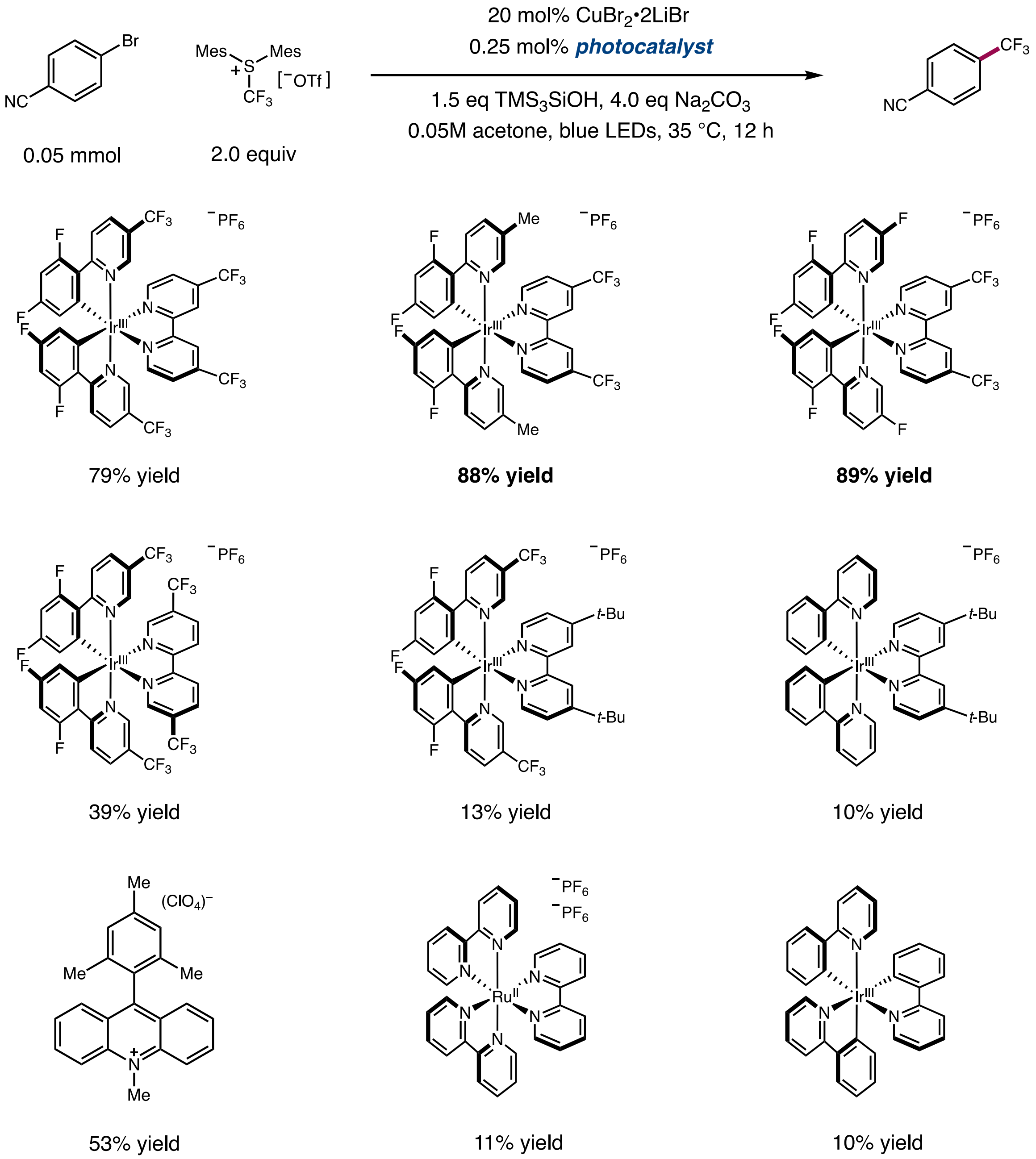


Figure S12. Evaluation of different photocatalysts. Yields determined by ^{1}H NMR.

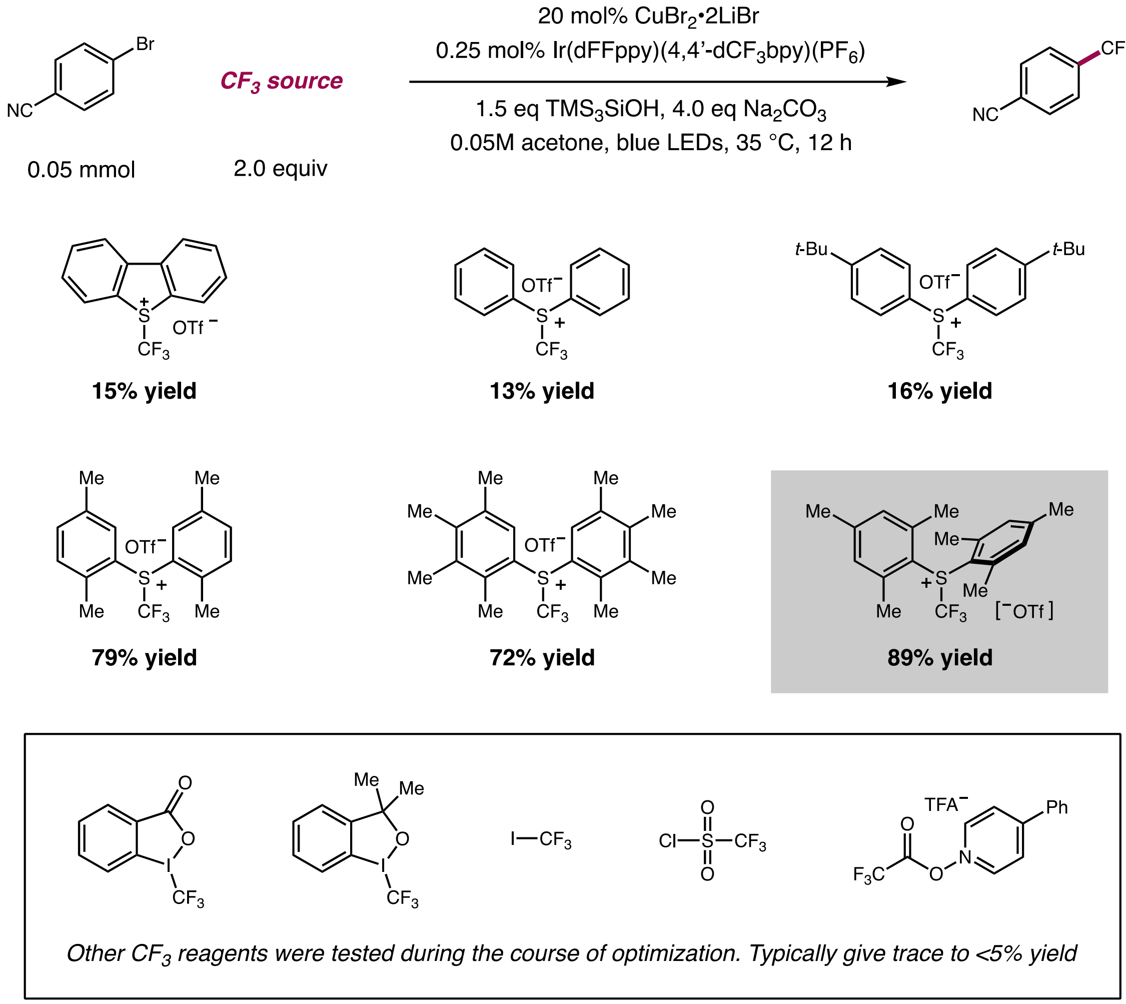
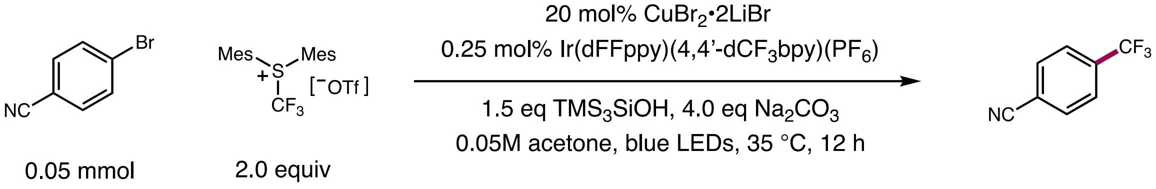


Figure S13. Evaluation of electrophilic CF3 sources. Yields determined by ^{1}H NMR.

7) Control experiments

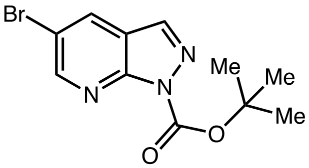


deviations	yield
none	89%
without base	40%
without silanol	0%
without copper	0%
without photocat	5%
without light	0%

Figure S14. Control experiments for the trifluoromethylation of aryl bromides.

*While yield was observed in the absence of the photocatalyst (5% yield), all trifluoromethylating reagent was consumed after 12 hours under this condition.

8) Synthesis of (hetero)aryl bromides



tert*-butyl 5-bromo-1*H*-pyrazolo[3,4-*b*]pyridine-1-carboxylate *(S1)

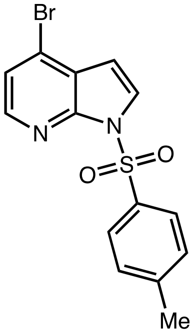
Under air, a 250-mL round-bottom flask equipped with a magnetic stir bar was charged with 5-bromo-1*H*-pyrazolo[3,4-*b*]pyridine-1-carboxylate (3.96 g, 20.0 mmol), *N*,*N*-dimethylpyridin-4-amine (DMAP, 49.0 mg, 0.4 mmol, 0.02 equiv.), and MeCN (100 mL). di-*tert*-butyl dicarbonate (5.24 g, 24.0 mmol, 1.2 equiv.) was slowly added then the reaction mixture was stirred at room temperature for 12 hours. The final mixture was diluted with EtOAc (200 mL) then the organic solution was washed with $NaHCO_3$ (saturated aqueous, 3 x 100 mL) and brine (2 x 100 mL). The organic solution was dried with $MgSO_4$ and filtered over celite. Concentration of the organic solution yielded the crude product as a thick oil. The desired product was purified via column chromatography (silica gel, gradient 5 to 10% EtOAc in hexanes) to yield a white crystalline solid (2.56 g, 8.6 mmol, 43% yield)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.78 (d, *J* = 2.3 Hz, 1H), 8.23 (d, *J* = 2.2 Hz, 1H), 8.13 (s, 1H), 1.73 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 151.7, 150.4, 147.6, 136.5, 132.4, 119.4, 115.5, 86.1, 28.2.

IR (film) ν_{max} 3081, 2982, 1752, 1485, 1386, 1253, 1148, 1052, 845 ν_{max} cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{12}BrN_3ONa$ ([M+Na]$^+$) 320.0005, found 319.9997.



4-bromo-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine *(S2)*

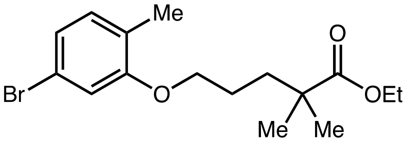
Under air, a 50-mL round-bottom flask equipped with a magnetic stir bar was charged with 4-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (2.96 g, 15.0 mmol) and DMF (30 mL). This mixture was cooled to 0 °C before NaH (60% weight, 720 mg, 18.0 mmol, 1.2 equiv.) was added in portions. The resulting mixture was stirred at 0 °C for 30 minutes before *p*-toluenesulfonyl chloride (3.15 g, 16.5 mmol, 1.1 equiv.) was added. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The final mixture was pour into a mixture of EtOAc (100 mL) and brine (200 mL) and stirred for 15 minutes. The organic layer was separated and washed with water (3 x 50 mL) then brine (3 x 50 mL) before it was dried with $MgSO_4$ and filtered over celite. Concentration of the organic solution yielded the crude product as an orange solid. The desired product was purified by column chromatography (silica gel, gradient 10 to 20% EtOAc in henxanes) to yield a white crystalline solid (4.20 g, 12.0 mmol, 80% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, *J* = 5.1 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 4.0 Hz, 1H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 4.0 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 146.9, 145.7, 145.2, 135.2, 129.9, 128.3, 127.1, 125.8, 124.5, 122.2, 105.0, 21.8.

IR (film) ν_{max} 3144, 1744, 1585, 1556, 1358, 1173, 678 ν_{max} cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{12}BrN_2O_2S$ ([M+H]$^+$) 350.9797, found 350.9784.



ethyl 5-(5-bromo-2-methylphenoxy)-2,2-dimethylpentanoate *(S3)*

To a 100mL round flask was added sodium hydride (95% w/w, 0.167 g, 6.60 mmol, 1.1 equiv.), followed by DMSO (10.00 ml). At room temperature a solution of 5-bromo-2-methylphenol (1.122 g, 6.00 mmol, 1.0 equiv.) in toluene (20mL, 0.3M) was added and the mixture was heated to 35 °C for 20 min. Then a solution of ethyl 5-bromo-2,2-dimethylpentanoate (1.423 g, 6.00 mmol, 1.0 equiv.) in toluene (10mL, 0.6M) was added and the mixture was stirred at 60 °C overnight.

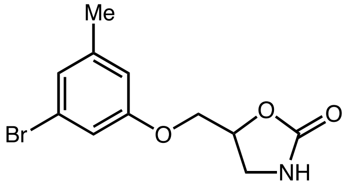
Water was added to the mixture and it was extracted by ether. The combined organic layer was washed by water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (7% EA in Hexane) to yield the pure product (1.50 g, 4.37 mmol, 73% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.01 – 6.93 (m, 2H), 6.89 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.91 (t, *J* = 5.3 Hz, 2H), 2.15 (s, 3H), 1.79 – 1.65 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 6H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 177.8, 157.8, 131.7, 125.9, 123.1, 119.6, 114.4, 68.4, 60.5, 42.1, 37.1, 25.3, 25.1, 16.0, 14.4.

IR (film) ν_{max} 1724, 1592, 1490, 1472, 1388, 1240, 1191, 1125, 1045, 1026, 992, 862, 836, 799, 772 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{23}BrO_3Na$ ([M+Na]$^+$) 365.0723, found 365.0728.



5-((3-bromo-5-methylphenoxy)methyl)oxazolidin-2-one *(S4)*

To a 100mL round flask was added pulverized sodium hydroxide (0.43 g, 10.69 mmol, 1.0 equiv.), 3-bromo-5-methylphenol (2.00 g, 10.69 mmol, 1.0 equiv.), 1,3,5-tris(oxiran-2-ylmethyl)-1,3,5-triazinane-2,4,6-trione (1.06 g, 3.56 mmol, 0.33 equiv.) and anhydrous acetone (30 mL, 0.36 M). The flask fitted with reflux condenser, and the yellow solution was gently refluxed for 24 hours.

The mixture was cooled to room temperature and diluted with EtOAc (50 mL) and water (50 mL). Organic layer was collected and aqueous layer was extracted twice with EtOAc (100 mL). Combined organic layer was washed with water, brine, and concentrated to yield the crude product as brown oil. The product was purified via silica gel column chromatography (50% EA in Hexane) to yield the pure product (1.0 g, 3.5 mmol, 33% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.96 (s, 1H), 6.87 (t, J = 2.0 Hz, 1H), 6.66 (s, 1H), 5.91 (s, 1H), 4.99 – 4.91 (m, 1H), 4.11 (d, J = 4.8 Hz, 2H), 3.77 (t, J = 8.8 Hz, 1H), 3.59 (dd, J = 8.7, 6.1 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 159.5, 158.8, 141.4, 125.6, 122.6, 115.0, 114.6, 74.1, 68.2, 42.7, 21.4.

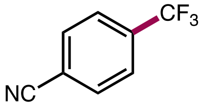
IR (film) ν_{max} 1598, 1570, 1489, 1443, 1382, 1208, 1275, 1241, 1161, 1072, 965, 826, 767, 730, 677 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}BrNO_3$ ([M+H]$^+$) 286.0073, found 286.0073.

9) Trifluoromethylation of (hetero)aryl bromides

General procedure: To an oven-dried 8-mL vial equipped with a stir bar was added Ir photocatalyst, inorganic base, *Mes*-Ume reagent, and aryl halide substrate (if solid). To an oven-dried 40-mL vial equipped with a stir bar, a solution of $CuBr_2$•2LiBr was prepared by dissolving $CuBr_2$ (67.0 mg, 0.03 mmol) and LiBr (52.1 mg, 0.06 mmol) in 15.0 mL of anhydrous acetone. This copper solution was stirred for 15 minutes before 5.0 mL was added to the reaction vial via syringe. Aryl halide (if oil) was added, followed by addition of TMS_3SiOH. The reaction mixture was sparged with nitrogen at 0 ºC for 15 minutes before the reaction vial was parafilmed to protect from air during the course of the reaction. The reaction vial was irradiated with two 40W Kessil A160WE (maximum blue with maximum intensity setting) from 6 cm away with fan cooling. Once the reaction is complete, the vial was quenched by exposure to air. Work up and purification for each substrate are described below.

Aryl iodides are also compatible with the reaction conditions to provide identical or 10-15% lower efficiency. Aryl chlorides are not competent substrates, giving trace to no reactivity under the optimized conditions.



4-(trifluoromethyl)benzonitrile (13)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 µmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 4-bromobenzonitrile (91.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

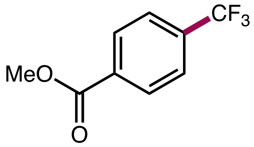
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed with Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (3% ether in pentane) to yield the pure product (75 mg, 0.445 mmol, 89% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 134.7 (q, *J* = 33.4 Hz), 132.8, 126.3 (q, *J* = 3.7 Hz) 123.2 (q, *J* = 273.0 Hz), 117.6, 116.2.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.5 (s, 3F).

Data are consistent with those reported in the literature: G. Shi, C. Shao, S. Pan, J. Yu, Y. Zhang, *Org. Lett.* **17**, 38–41 (2015).



Methyl 4-(trifluoromethyl)benzoate (15)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), methyl 4-(trifluoromethyl)benzoate (108.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

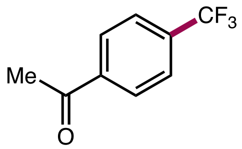
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (3% ether in pentane) to yield the pure product (89 mg, 0.435 mmol, 87% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.14 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 3.95 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 166.0, 134.5 (q, J = 32.7 Hz), 133.5, 130.1, 125.5 (q, J = 3.7 Hz), 123.8 (q, J = 272.7 Hz), 52.7.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.2 (s, 3F).

Data are consistent with those reported in the literature: C. A. Malapit, N. Ichiishi, M. S. Sanford, *Org. Lett.* **19**, 4142–4145 (2017).



1-(4-(trifluoromethyl)phenyl)ethanone (16)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-(4-bromophenyl)ethanone (100.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

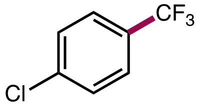
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (5% ether in pentane) to yield the pure product (84 mg, 0.445 mmol, 89% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 2.65 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 197.2, 139.8 (d, *J* = 1.3 Hz), 134.6 (q, *J* = 32.7 Hz), 128.8 , 125.8 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.7 Hz), 27.0.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.1 (s, 3F).

Data are consistent with those reported in the literature: J. Liu, K.–F. Hu, J.–P. Qu, Y.–B. Kang, *Org. Lett.* **19**, 5593–5596 (2017).

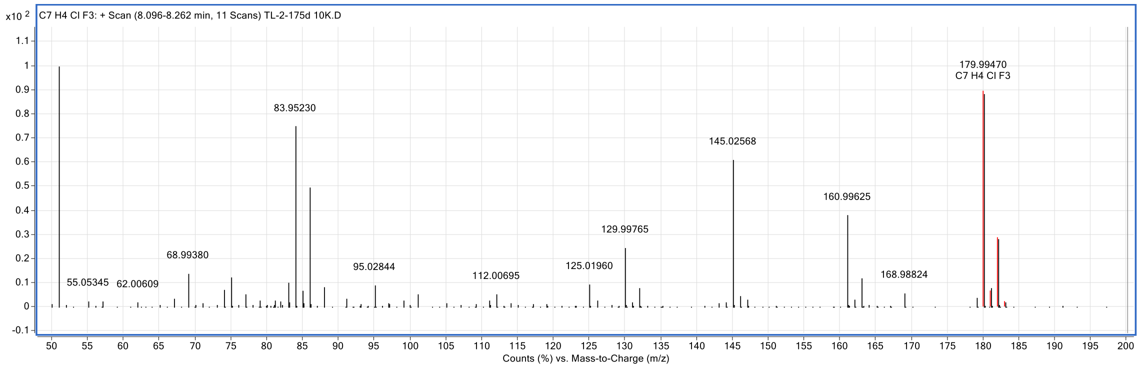


1-chloro-4-(trifluoromethyl)benzene (17)

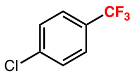
Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF₃* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-bromo-4-chlorobenzene (96.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

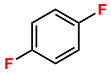
1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (96% yield – average of three trials: 97% yield, 96% yield, and 96% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_7H_4ClF_3$ ([M*]$^+$) 179.9948, found 179.9947.



-61.96 ppm



-120.00 ppm

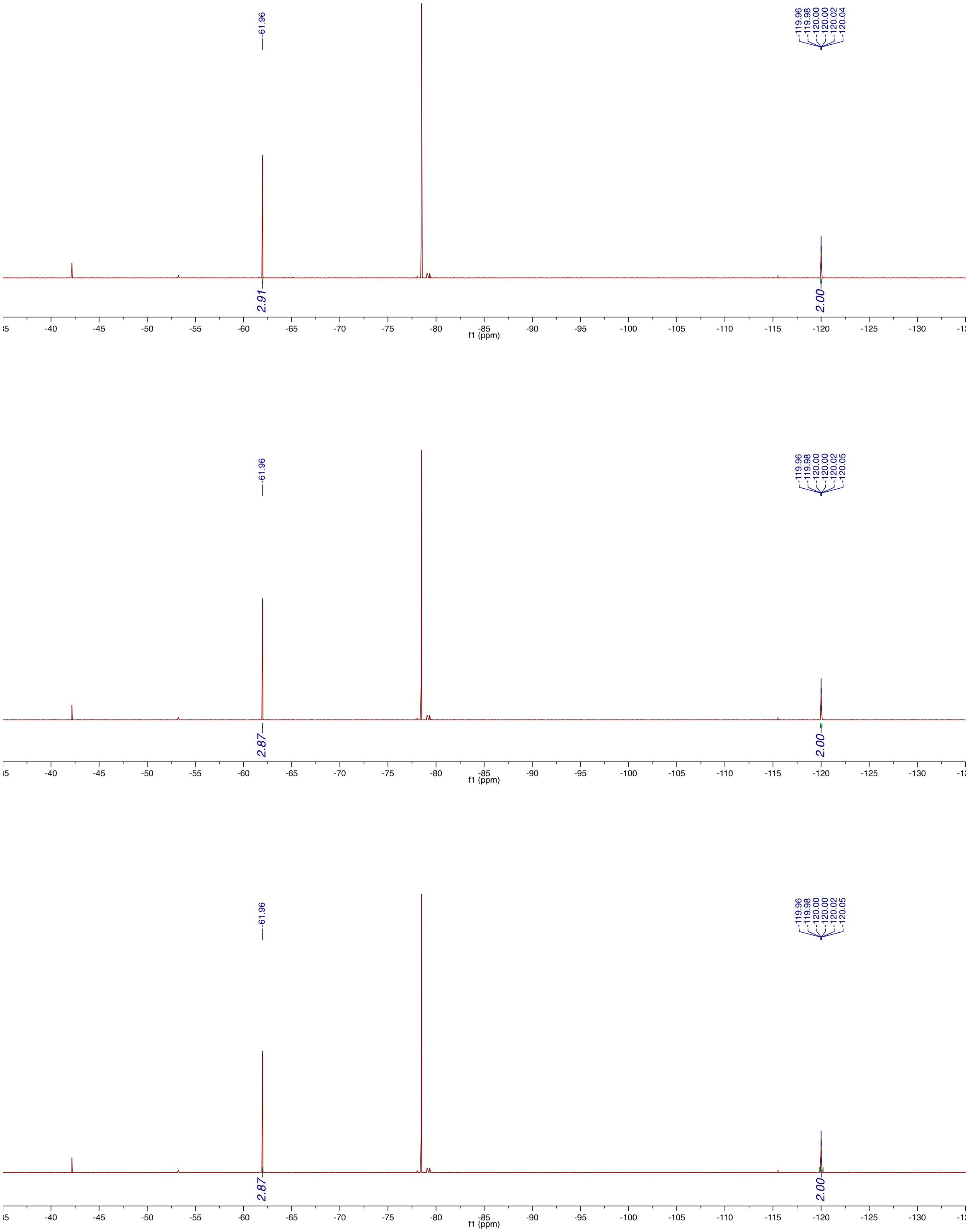
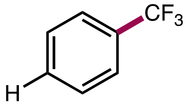


Figure S15. ^{19}F NMR assay for 1-chloro-4-(trifluoromethyl)benzene (**17**)

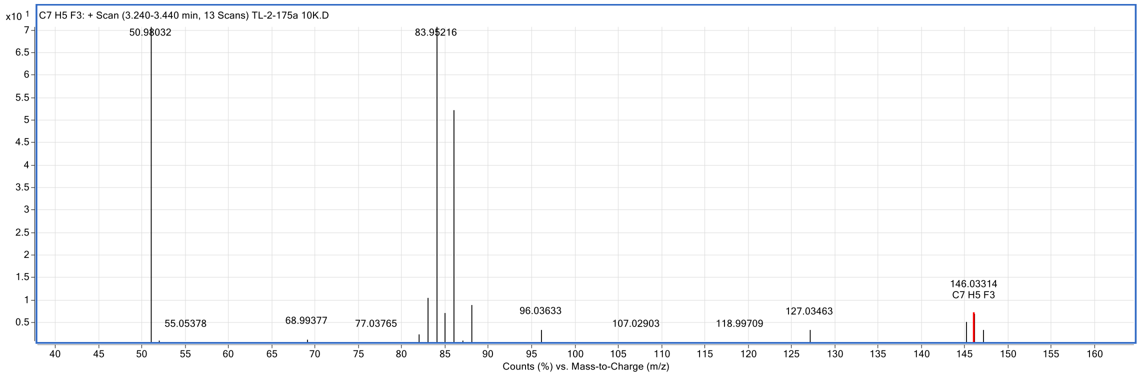


(trifluoromethyl)benzene (18)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), bromobenzene (79.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (82% yield – average of three trials: 81% yield, 82% yield, and 84% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_7H_5F_3$ ([M*]$^+$) 146.0338, found 146.0331.

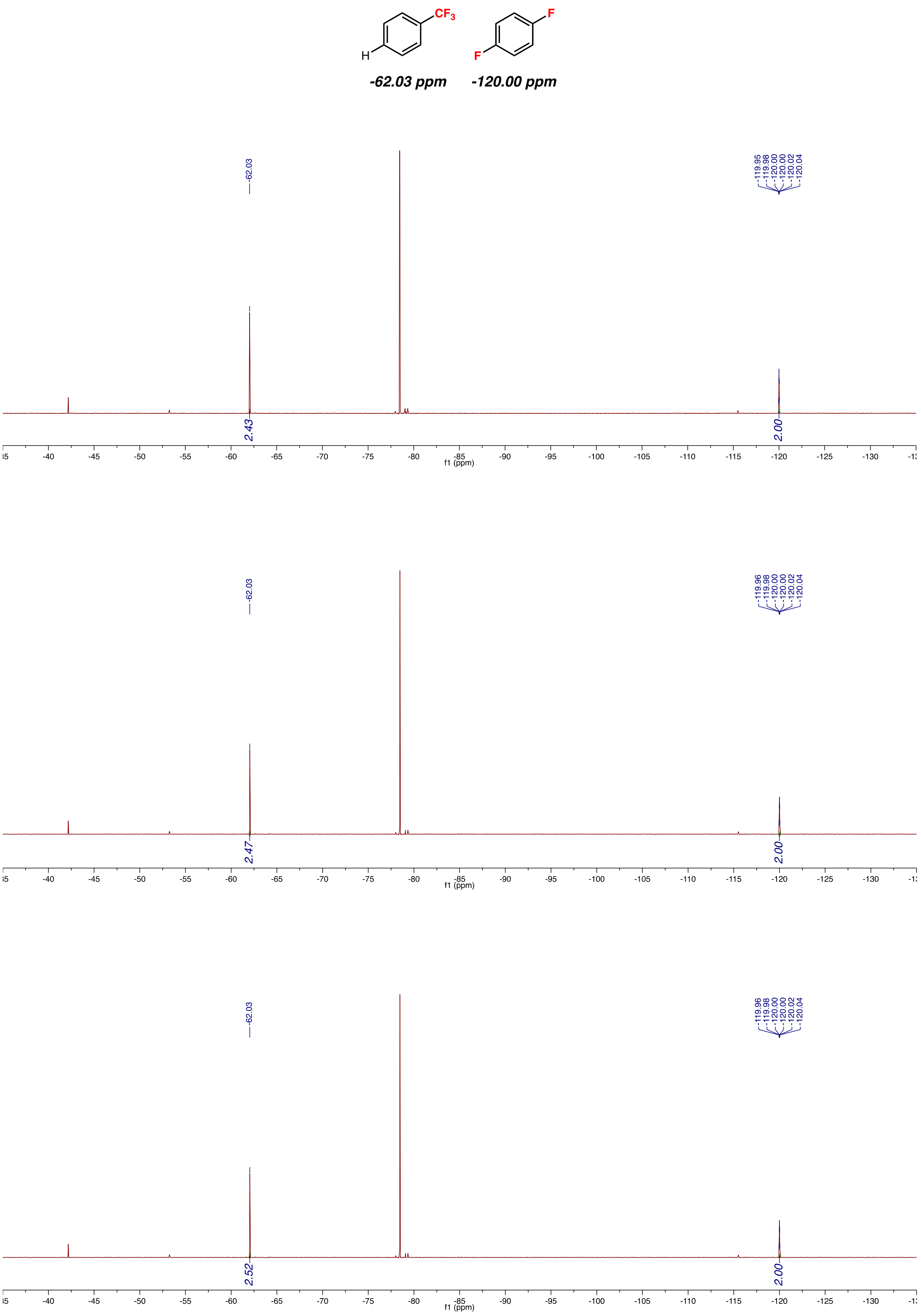
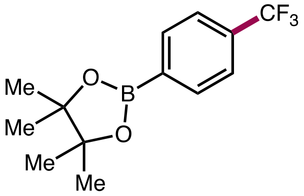


Figure S16. ^{19}F NMR assay for (trifluoromethyl)benzene (**18**)



4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (19)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (141.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

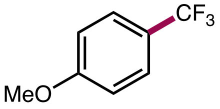
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (6% ether in hexane) to yield the pure product (106 mg, 0.390 mmol, 78% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 1.36 (s, 12H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 135.1, 133.0 (q, *J* = 32.1 Hz), 124.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.4 Hz), 84.4, 25.0.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.0 (s, 3F).

Data are consistent with those reported in the literature: X. Wang et al, *J. Am. Chem. Soc.* **135**, 10330–10333 (2013).

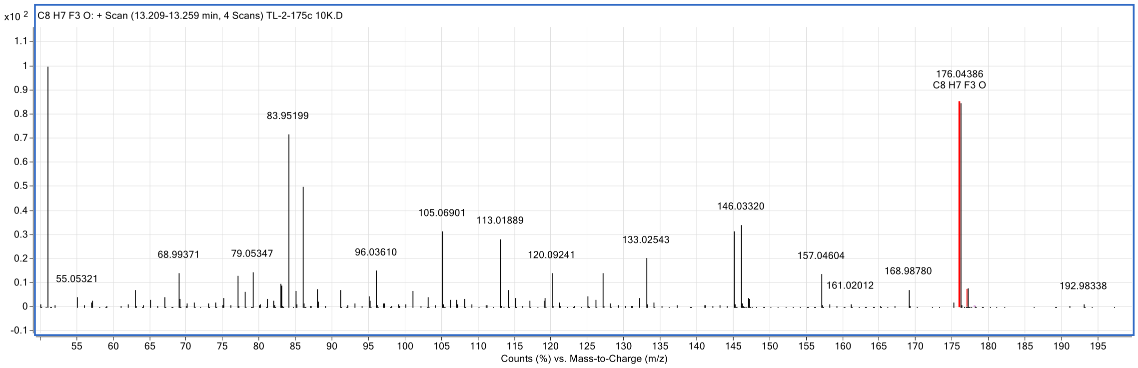


1-methoxy-4-(trifluoromethyl)benzene (20)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (429.0 mg, 0.875 mmol, 1.75 equiv.), 1-bromo-4-methoxybenzene (94.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (232 mg, 0.875 mmol, 1.75 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (80% yield – average of three trials: 79% yield, 80% yield, and 80% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_8H_7F_3O$ ($[M^*]^+$) 176.0444, found 176.0439.

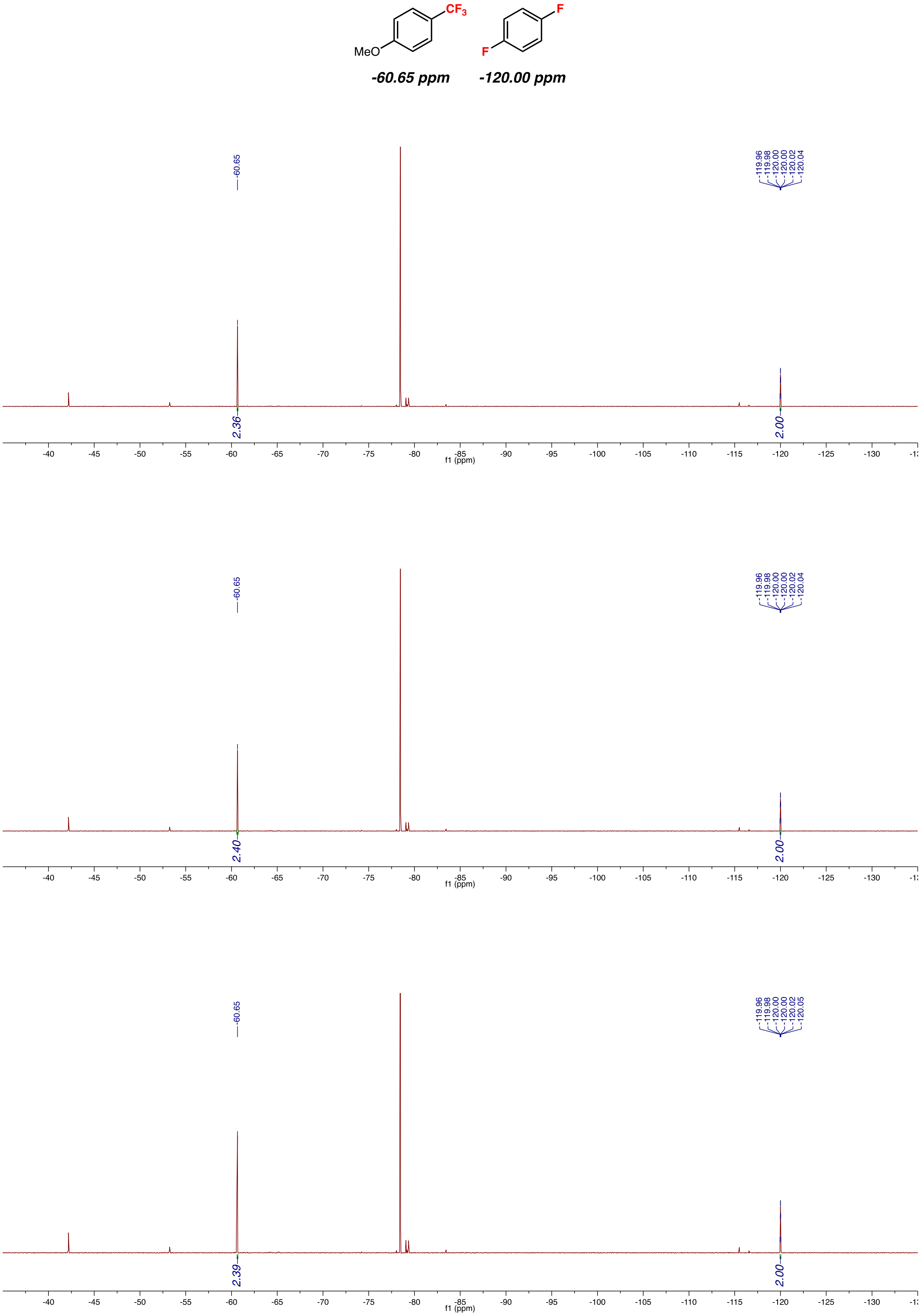
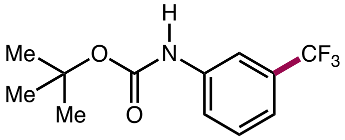


Figure S17. ^{19}F NMR assay for 1-methoxy-4-(trifluoromethyl)benzene (**20**)



tert-butyl (3-(trifluoromethyl)phenyl)carbamate (21)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF₃* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), *tert*-butyl-(3-bromophenyl)carbamate (136.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

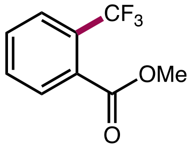
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (5% ether in pentane) to yield the pure product as a white solid (106 mg, 0.405 mmol, 81% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.60 (s, 1H), 1.53 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 152.6, 139.1, 131.6 (q, *J* = 32.4 Hz), 129.6, 124.1 (q, *J* = 272.4 Hz), 121.5, 119.7 (q, *J* = 3.9 Hz), 115.2, 81.3, 28.4.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.8 (s, 3F).

Data are consistent with those reported in the literature: Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura, M. Sodeoka, *J. Am. Chem. Soc.* **127**, 10164–10165 (2005).



methyl 2-(trifluoromethyl)benzoate (22)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), methyl 2-bromobenzoate (108.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

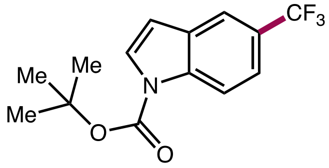
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (3% ether in pentane) to yield the pure product (71 mg, 0.350 mmol, 70% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 – 7.76 (m, 1H), 7.76 – 7.72 (m, 1H), 7.63 – 7.57 (m, 2H), 3.94 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 167.4, 131.9, 131.3, 131.2 (q, *J* = 2.1 Hz), 130.3, 128.9 (q, *J* = 32.5 Hz), 126.8 (q, *J* = 5.4 Hz), 123.5 (q, *J* = 273.4 Hz), 53.0.

^{19}F NMR (282 MHz, CDCl$_3$) δ –59.7 (s, 3F).

Data are consistent with those reported in the literature: A. Lishchynskyi et al, *J. Org. Chem.* **78**, 11126–11146 (2013).



tert-butyl 5-(trifluoromethyl)-1H-indole-1-carboxylate (23)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), *tert*-butyl 5-bromo-1H-indole-1-carboxylate (148.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 5 to 10% DCM in hexane) to yield the pure product (117 mg, 0.410 mmol, 82% yield).

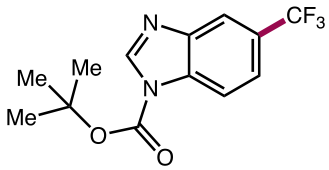
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.25 (d, *J* = 8.7 Hz, 1H), 7.85 (s, 1H), 7.69 (d, *J* = 3.6 Hz, 1H), 7.55 (dd, *J* = 8.7, 1.4 Hz, 1H), 6.64 (d, *J* = 3.5 Hz, 1H), 1.69 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 149.5, 136.9, 130.3, 127.7, 125.1 (q, *J* = 32.1 Hz), 124.9 (q, *J* = 271.7 Hz), 121.1 (q, *J* = 3.5 Hz), 118.5 (q, *J* = 4.1 Hz), 115.6, 107.5, 84.6, 28.3.

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.0 (s, 3F).

IR (film) ν_{max} 1732, 1480, 1371, 1358, 1340, 1289, 1247, 1152, 1113, 1083, 1055, 1024, 822, 769, 728, 671 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_6F_3N_2$ ([M+2H–Boc]$^+$) 186.0525, found 186.0513.



tert-butyl 5-(trifluoromethyl)-1H-benzo[d]imidazole-1-carboxylate (24)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (454.0 mg, 0.925 mmol, 1.85 equiv.), *tert*-butyl 5-bromo-1H-benzo[d]imidazole-1-carboxylate (149.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (7% EtOAc in hexane) to yield the pure product (107 mg, 0.375 mmol, 75% yield).

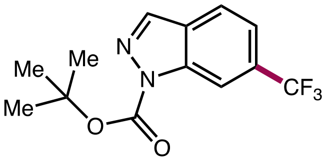
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (s, 1H), 8.15 – 8.11 (m, 2H), 7.77 (dd, J = 8.6, 1.3 Hz, 1H), 1.66 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 147.2, 145.1, 143.5, 133.6, 124.9 (q, J = 31.9 Hz), 124.5 (q, J = 271.8 Hz), 121.9 (q, J = 3.6 Hz), 117.5 (q, J = 4.0 Hz), 115.2, 86.2, 27.5.

^{19}F NMR (282 MHz, DMSO-d_6) δ –59.5 (s, 3F).

IR (film) ν_{max} 1748, 1368, 1326, 1262, 1234, 1152, 1064, 1050, 917, 888, 841, 821, 769, 674 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_6F_3N_2$ ([M+2H–Boc]$^+$) 187.0478, found 187.0470.



tert-butyl 6-(trifluoromethyl)-1H-indazole-1-carboxylate (25)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), *tert*-butyl 5-bromo-1*H*-indazole-1-carboxylate (148.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 10 to 40% DCM in hexane) to yield the pure product (110 mg, 0.385 mmol, 77% yield).

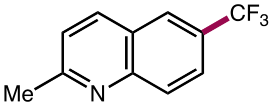
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.55 (s, 1H), 8.25 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 1.74 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 148.9, 139.2, 139.1, 131.0 (q, *J* = 32.3 Hz), 127.8, 124.3 (q, *J* = 272.7 Hz), 122.0, 120.5 (q, *J* = 3.3 Hz), 112.6 (q, *J* = 4.6 Hz), 86.0, 28.3.

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.8 (s, 3F).

IR (film) ν_{max} 1742, 1416, 1382, 1373, 1331, 1239, 1147, 1067, 1033, 924, 891, 857, 847, 816, 792, 762, 742, 665 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_6F_3N_2$ ([M+2H–Boc]$^+$) 186.0478, found 186.0473.



2-methyl-6-(trifluoromethyl)quinoline (26)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 6-bromo-2-methylquinoline (111.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

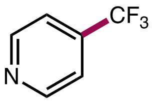
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (10% EtOAc in hexane) to yield the pure product (89 mg, 0.420 mmol, 84% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.15 – 8.10 (m, 2H), 8.10 – 8.08 (m, 1H), 7.85 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 2.79 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 161.7, 149.0, 137.0, 130.0, 127.7 (q, *J* = 32.5 Hz), 127.5, 125.62 (q, *J* = 4.5 Hz), 125.57, 125.3 (q, *J* = 3.1 Hz), 123.4, 25.7.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.2 (s, 3F).

Data are consistent with those reported in the literature: J. Li, J. Zhang, H. Yang, G. Jiang, *J. Org. Chem.* **82**, 3284–3290 (2017).

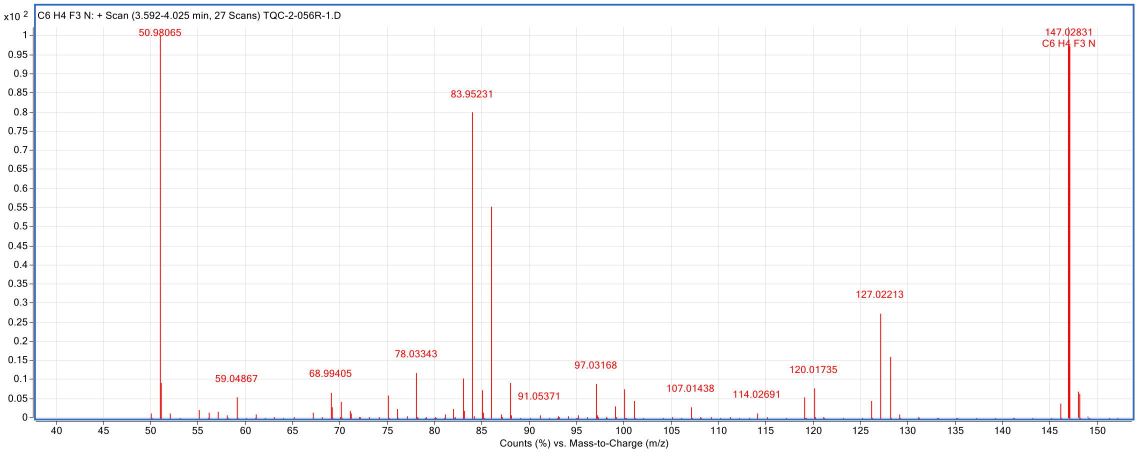


4-(trifluoromethyl)pyridine (27)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (2.6 mg, 2.50 µmol, 0.005 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 4-bromopyridine hydrochloride (97.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{1}H NMR in triplicate due to the high volatility of the desired product.

The reaction mixture was diluted with EtOAc (10 mL) and shaken with a mixture of NaHCO$_3$ (sat aq, 5 mL) and brine (sat aq, 1 mL). 1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{1}H-NMR analysis (DMSO-*d$_6$*). (76% yield – average of three trials: 76% yield, 78% yield, and 75% yield)



HRMS (ESI-TOF) m/z calcd. for C$_6$H$_4$F$_3$N ([M*]$^+$), 147.0296, found 147.0283.

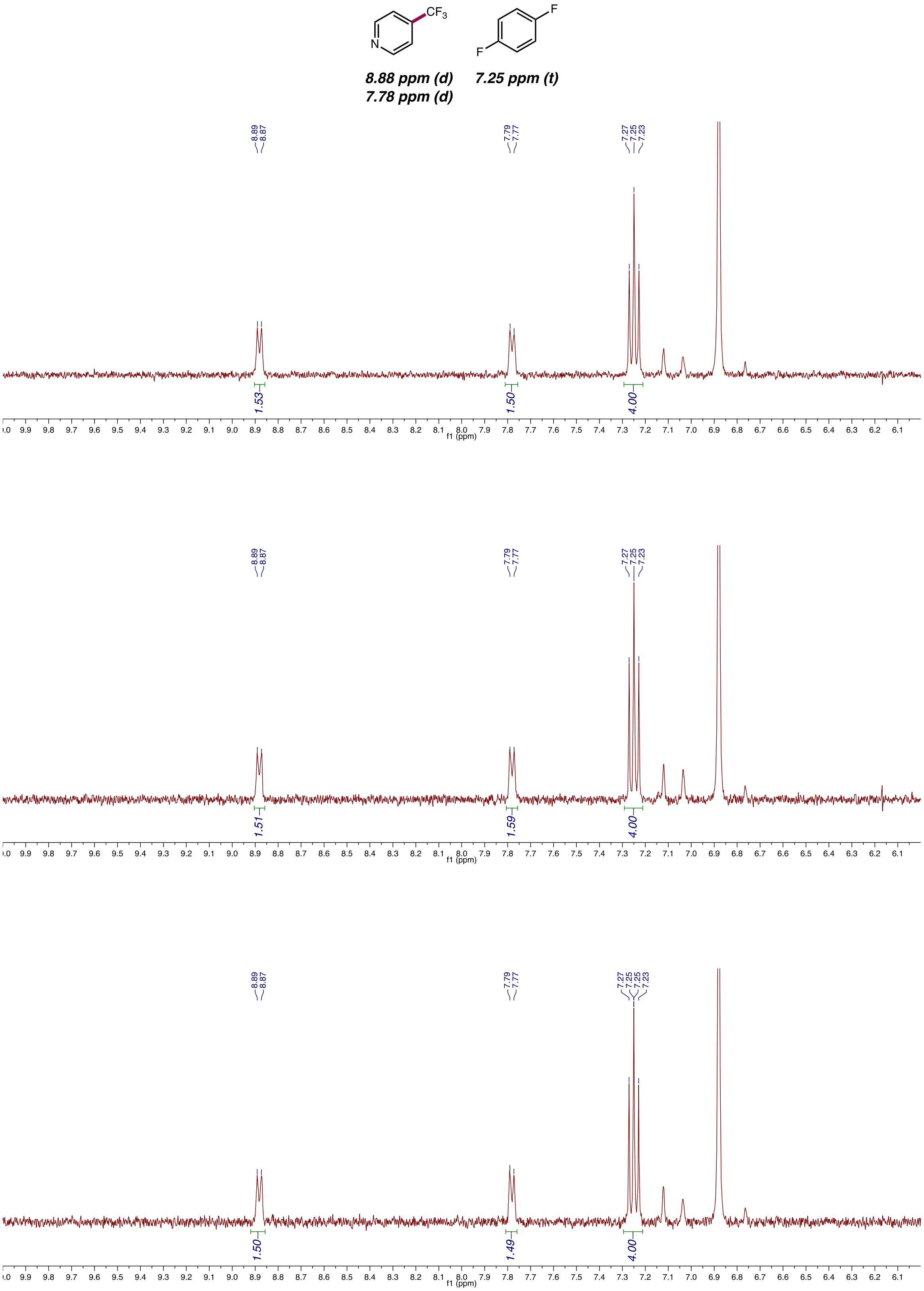
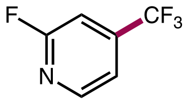


Figure S18. ^{1}H NMR assay for 4-(trifluoromethyl)pyridine (**27**)

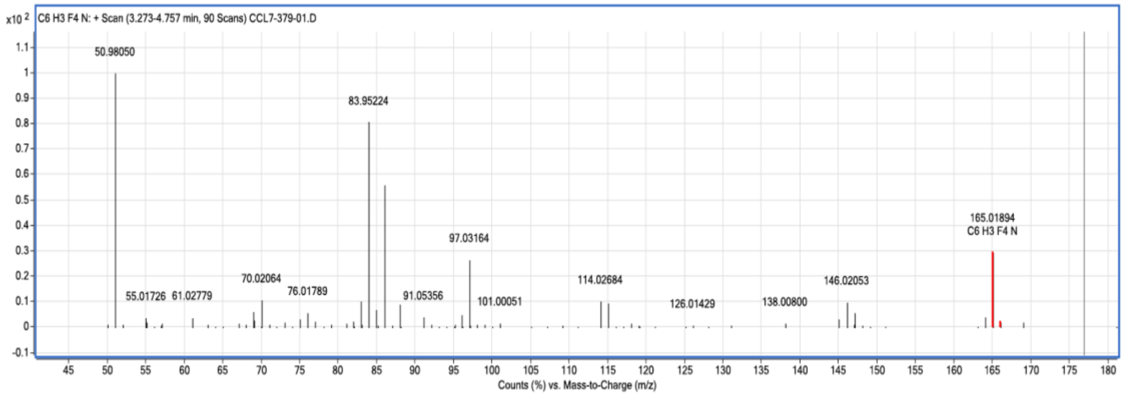


2-fluoro-4-(trifluoromethyl)pyridine (28)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-2-fluoropyridine (88.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

The reaction mixture was diluted with EtOAc (10 mL) and shaken with a mixture of $NaHCO_3$ (sat aq, 5 mL) and brine (sat aq, 1 mL). 1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (84% yield – average of three trials: 87% yield, 83% yield, and 83% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_6H_3F_4N$ ([M*]$^+$) 165.0196, found 165.0189.

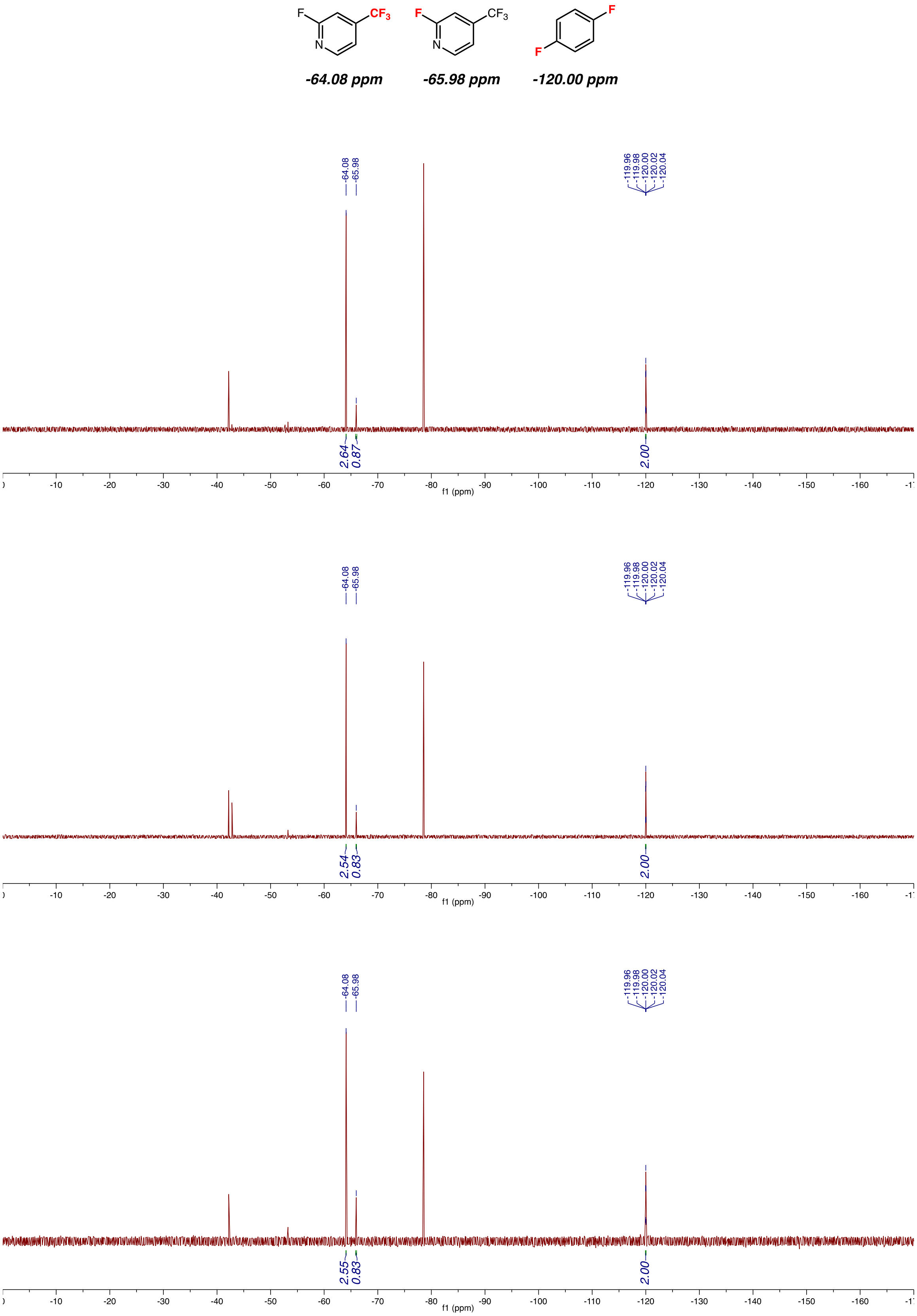
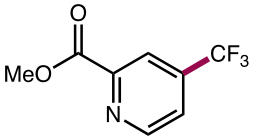


Figure S19. ^{19}F NMR assay for 2-fluoro-4-(trifluoromethyl)pyridine (**28**)

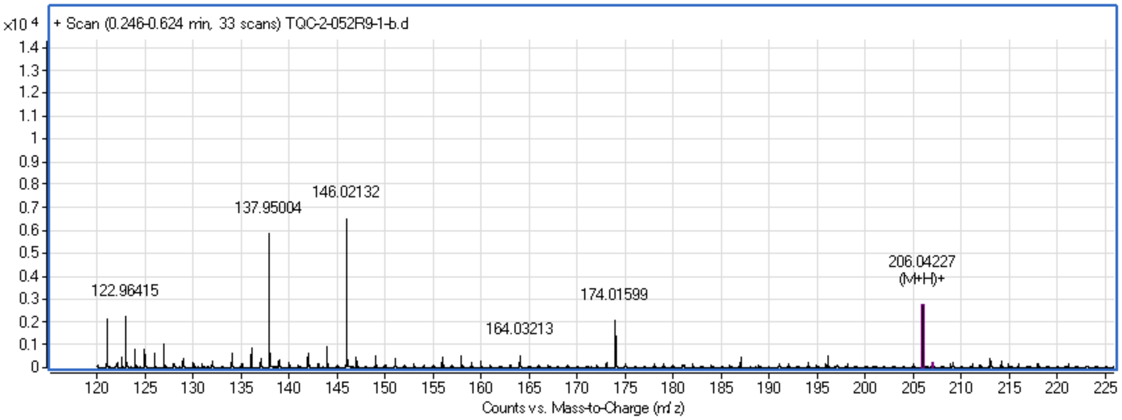


methyl 4-(trifluoromethyl)picolinate (29)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (2.6 mg, 2.50 µmol, 0.005 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), methyl 4-bromopicolinate (108.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{1}H NMR in triplicate due to the high volatility of the desired product.

The reaction mixture was diluted with EtOAc (10 mL) and shaken with a mixture of $NaHCO_3$ (sat aq, 5 mL) and brine (sat aq, 1 mL). 1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{1}H NMR analysis (DMSO-d_6). (65% yield – average of three trials: 63% yield, 66% yield, and 66% yield).



HRMS (LC-ESI-TOF) m/z calcd. for $C_8H_7F_3NO_2$ ($[M+H]^+$) 206.0423, found 206.0423.

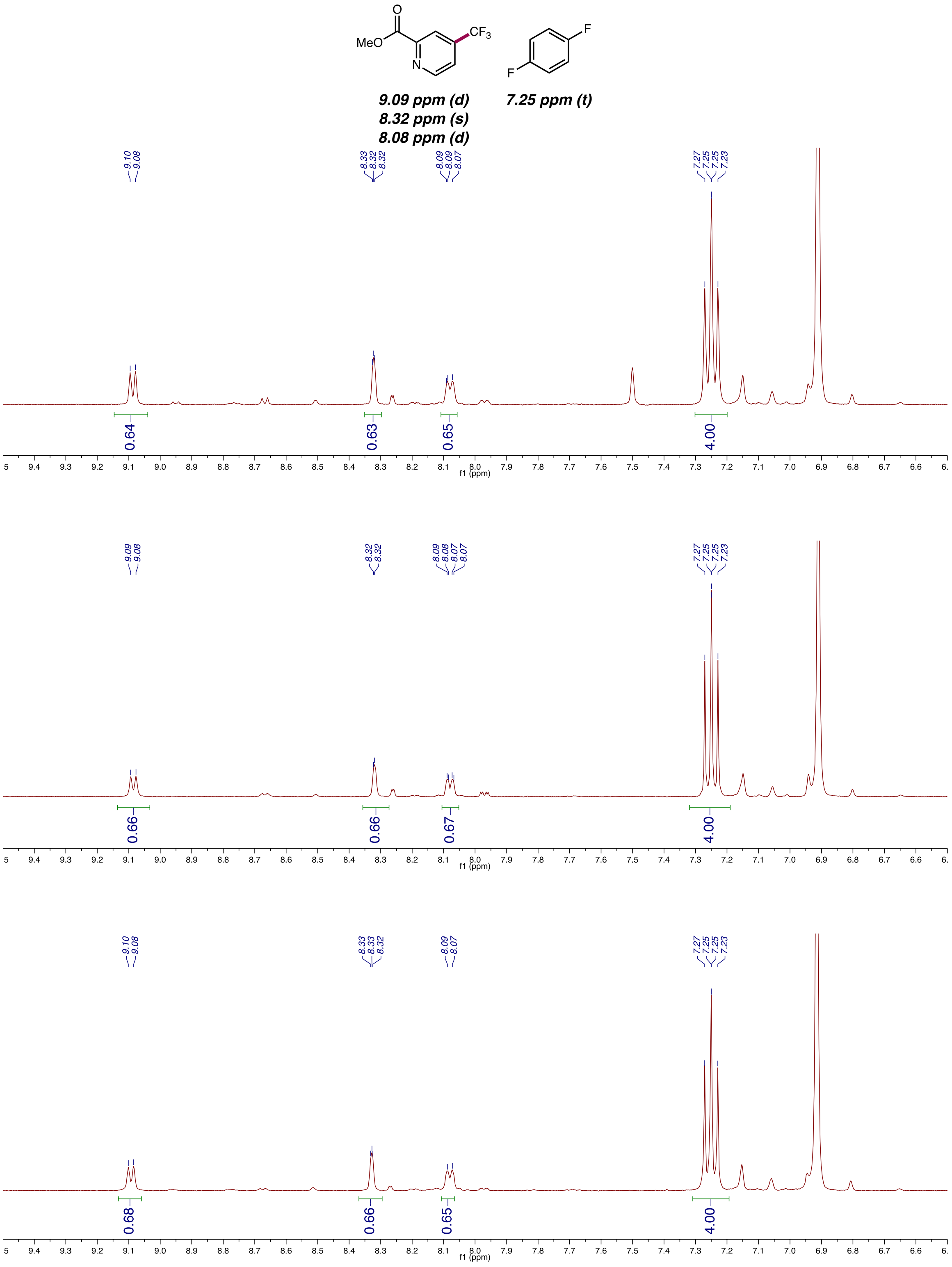
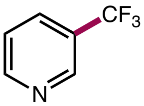


Figure S20. ^{1}H NMR assay for methyl 4-(trifluoromethyl)picolinate (**29**)

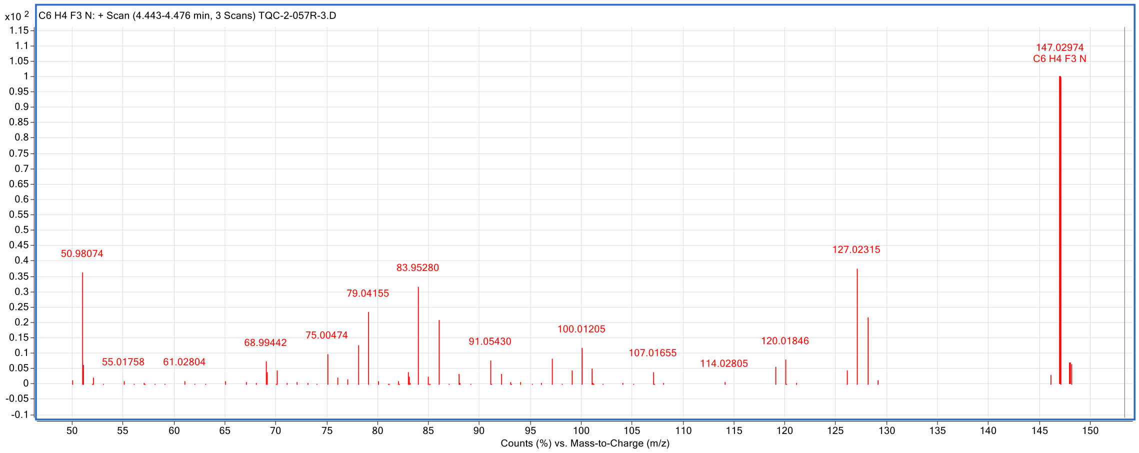


3-(trifluoromethyl)pyridine (30)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (2.6 mg, 2.50 μmol, 0.005 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 4-bromopyridine hydrochloride (97.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{1}H NMR in triplicate due to the high volatility of the desired product.

The reaction mixture was diluted with EtOAc (10 mL) and shaken with a mixture of NaHCO$_3$ (sat aq, 5 mL) and brine (sat aq, 1 mL). 1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{1}H-NMR analysis (DMSO-*d$_6$*). (68% yield – average of three trials: 67% yield, 67% yield, and 70% yield)



HRMS (GC-EI-TOF) m/z calcd. for $C_6H_4F_3N$ ([M*]$^+$), 147.0296, found 147.0297.

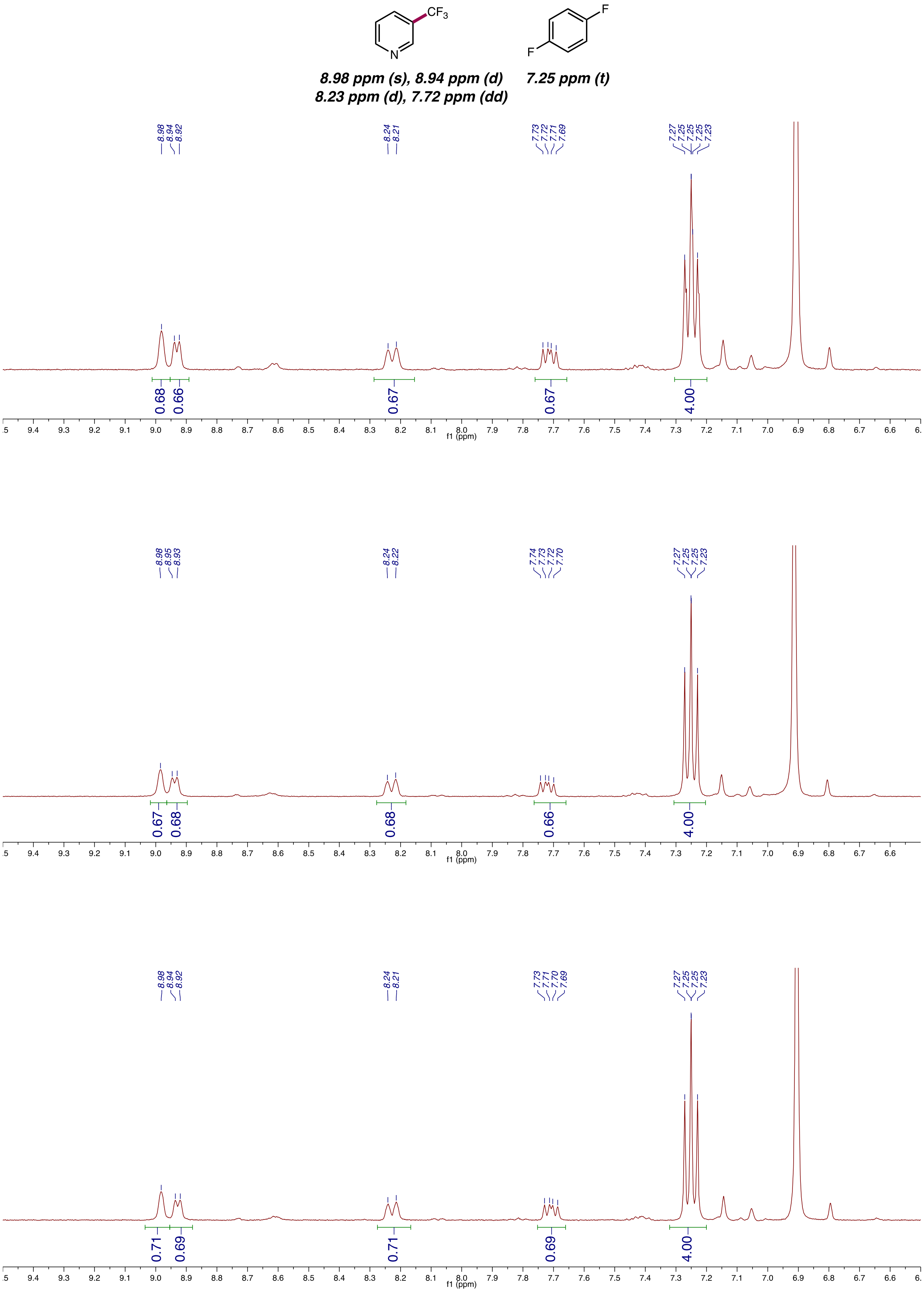
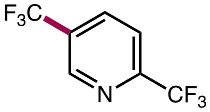


Figure S21. ^{1}H NMR assay for 3-(trifluoromethyl)pyridine (**30**)

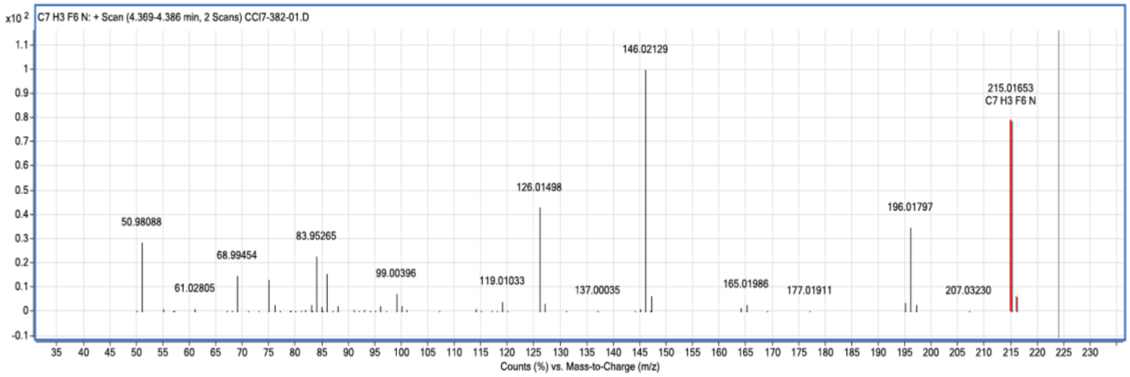


2,5-bis(trifluoromethyl)pyridine (31)

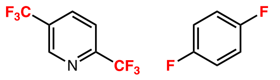
Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 5-bromo-2-(trifluoromethyl)pyridine (113.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

The reaction mixture was diluted with EtOAc (10 mL) and shaken with a mixture of $NaHCO_3$ (sat aq, 5 mL) and brine (sat aq, 1 mL). 1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (91% yield – average of three trials: 90% yield, 90% yield, and 92% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_7H_3F_6N$ ($[M^*]^+$) 215.0164, found 215.0165.



-62.16 ppm
-67.82 ppm

-120.00 ppm

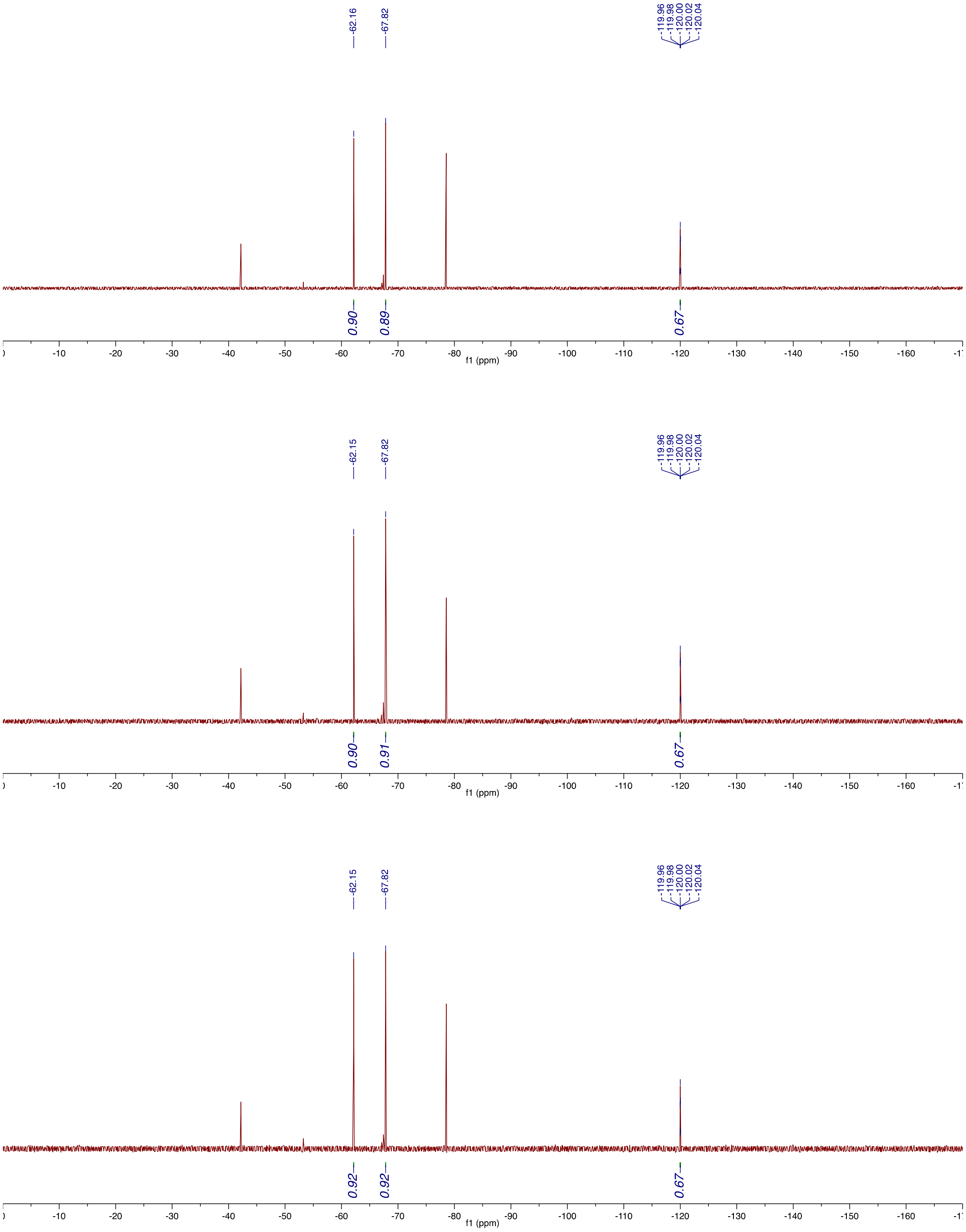
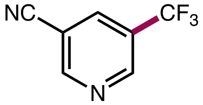


Figure S22. ^{19}F NMR assay for 2,5-bis(trifluoromethyl)pyridine (**31**)



5-(trifluoromethyl)nicotinonitrile (32)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 µmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF*$_3$ reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 5-bromonicotinonitrile (92.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

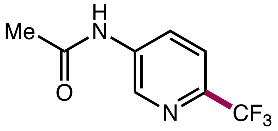
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (4% ether in pentane) to yield the pure product (60 mg, 0.350 mmol, 70% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.11 – 9.07 (m, 2H), 8.23 (s, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 155.4 (q, *J* = 1.5 Hz), 149.9 (q, *J* = 3.8 Hz), 136.6 (q, *J* = 3.6 Hz), 127.3 (q, *J* = 34.3 Hz), 122.4 (q, *J* = 273.2 Hz), 115.2, 110.6.

^{19}F NMR (282 MHz, CDCl$_3$) δ –67.5 (s, 3F).

Data are consistent with those reported in the literature: X. Lin, C. Hou, H. Li, Z. Weng, *Chem. Eur. J.* **22**, 2075-2084 (2016).



N-(6-(trifluoromethyl)pyridine-3-yl)acetamide (33)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (2.6 mg, 2.50 μmol, 0.005 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), methyl (6-bromopyridin-3-yl)carbamate (116.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 1 hour then filtered over celite. The organic solution was concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 20% to 50% EtOAc in hexanes) to yield the pure product as an off-white crystalline solid (90.1 mg, 0.41 mmol, 82% yield).

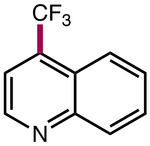
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.59 (d, *J* = 2.5 Hz, 1H), 8.46 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.45 (broad s, 1H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 168.95, 143.39 (q, *J* = 35.6 Hz), 140.60, 137.12, 127.24, 121.20 (q, *J* = 2.8 Hz), 121.59, (q, *J* = 273.2 Hz), 24.76.

^{19}F NMR (282 MHz, CDCl$_3$) δ –67.40 (s, 3F).

IR (film) ν_{max} 3269, 2924, 1680, 1589, 1545, 1378, 1338, 1132, 1088 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_8H_7F_3N_2O$ ([M*]$^+$) 204.0511, found 204.0510.



4-(trifluoromethyl)quinoline (34)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 4-bromoquinoline (104.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

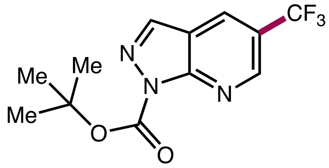
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in Ether (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (10% Ether in Pentane) and reverse phase column chromatography (gradient 20 to 75% MeCN in H_2O) to yield the pure product (71 mg, 0.360 mmol, 72% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.05 (d, *J* = 4.3 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.74 – 7.65 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 149.7, 149.1, 134.4 (q, *J* = 31.8 Hz), 130.6, 130.4, 128.5, 124.2 (q, *J* = 2.2 Hz), 123.6 (q, *J* = 274.6 Hz), 123.1 (d, *J* = 1.6 Hz), 118.1 (q, *J* = 5.3 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.5 (s, 3F).

Data are consistent with those reported in the literature: M. Nagase, Y. Kuninobu, M. Kanai, *J. Am. Chem. Soc.* **138**, 6103–6106 (2016).



tert-butyl 5-(trifluoromethyl)-1H-pyrazolo[3,4-b]pyridine-1-carboxylate (35)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), *tert*-butyl 5-bromo-1*H*-pyrazolo[3,4-*b*]pyridine-1-carboxylate (149.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was concentrated to yield the crude product as an oil. The product was purified via reverse phase column chromatography (gradient 20 to 75% MeCN in H_2O), followed by silica gel column chromatography (gradient 5 to 20% EtOAc in Hexanes) to yield the pure product as a white crystalline solid (94 mg, 0.33 mmol, 66% yield).

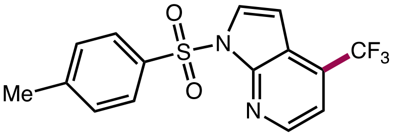
^{1}H NMR (500 MHz, acetone-*d$_6$*) δ 9.02 (d, *J* = 2.2 Hz, 1H), 8.76 (dd, *J* = 2.2, 0.9 Hz, 1H), 8.49 (s, 1H), 1.70 (s, 9H).

^{13}C NMR (125 MHz, acetone-*d$_6$*) δ 153.7, 148.0, 147.9 (q, *J* = 3.6 Hz), 139.0, 130.0 (q, *J* = 4.0 Hz), 125.3 (q, *J* = 271.4 Hz), 122.8 (q, *J* = 32.8 Hz), 118.1, 85.7, 28.3.

^{19}F NMR (282 MHz, acetone-*d$_6$*) δ –61.3 (s, 3F).

IR (film) ν_{max} 2986, 1761, 1618, 1573, 1342, 1252, 1076, 848 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_7H_4F_3N_3Na$ ([M-*Boc*+H+Na]$^+$) 210.0249, found 210.0249.



1-tosyl-4-(trifluoromethyl)-1*H*-pyrrolo[2,3-*b*]pyridine (36)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 μmol, 0.0025 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (176.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was concentrated to yield the crude product as an oil. The product was purified via reverse phase column chromatography (gradient 20 to 75% MeCN in H$_2$O), followed by silica gel column chromatography (gradient 5 to 20% EtOAc in Hexanes) to yield the pure product as a white crystalline solid (120 mg, 0.35 mmol, 71% yield).

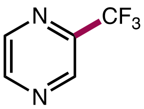
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.56 (d, *J* = 5.0 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 4.1 Hz, 1H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.77 (dd, *J* = 3.9, 1.7 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 147.9, 145.9, 145.0, 135.0, 130.8 (q, *J* = 34.6 Hz), 129.9, 128.7, 128.4, 123.2 (q, *J* = 273.3 Hz), 118.9 (d, *J* = 2.4 Hz), 114.9 (q, *J* = 4.2 Hz), 103.6 (d, *J* = 1.4 Hz), 21.8.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.8 (s, 3F).

IR (film) ν_{max} 3148, 2927, 1595, 1514, 1371, 1315, 1133, 1008, 680 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{11}F_3N_3O_2$ ([M+H]$^+$) 341.0568, found 341.0566.

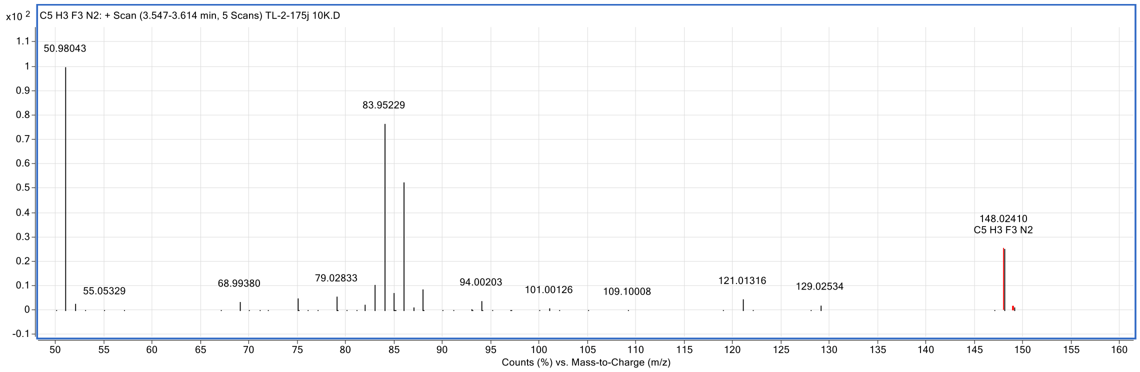


2-(trifluoromethyl)pyrazine (37)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 µmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF*$_3$ reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-bromopyrazine (79.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (70% yield – average of three trials: 70% yield, 71% yield, and 69% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_5H_3F_3N_2$ ([M*]$^+$) 148.0243, found 148.0241.

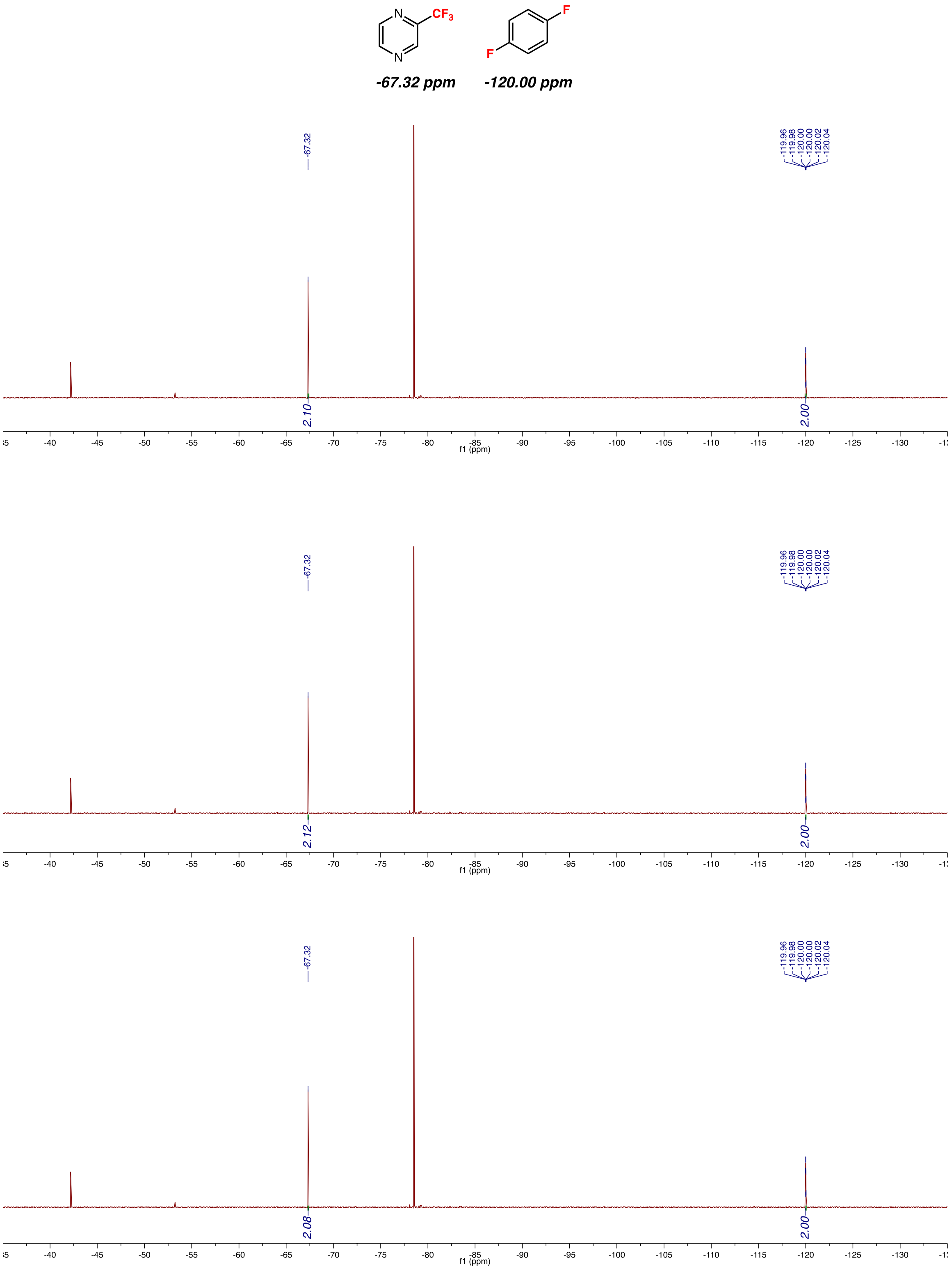
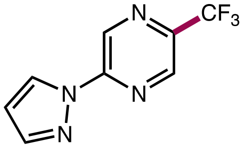


Figure S23. ^{19}F NMR assay for 2-(trifluoromethyl)pyrazine (**37**)



2-(1*H*-pyrazol-1-yl)-5-(trifluoromethyl)pyrazine (38)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (2.6 mg, 2.5 μmol, 0.005 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 2-bromo-5-(1H-pyrazol-1-yl)pyrazine (113.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 20 to 50% EtOAc in hexanes) to yield the pure product as a white crystalline solid (71 mg, 0.33 mmol, 66% yield).

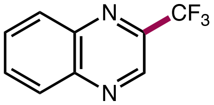
^{1}H NMR (500 MHz, CDCl$_3$) δ 9.42 (s, 1H), 8.71 (s, 1H), 8.55 (s, 1H), 7.85 (s, 1H), 6.57 (s, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 149.0, 144.4, 140.6 (q, *J* = 36.0 Hz), 139.5, (q, *J* = 3.3 Hz), 135.5, 128.2, 122.4 (q, *J* = 273.6 Hz), 109.8.

^{19}F NMR (282 MHz, CDCl$_3$) δ –67.1 (s, 3F).

IR (film) ν_{max} 3121, 1547, 1398, 1323, 1124, 1095, 1039, 1016, 920, 778 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_8H_5F_3N_4$ ([M*]$^+$) 214.0466, found 214.0464.



2-(trifluoromethyl)quinoxaline (39)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 µmol, 0.0025 equiv.), K_2CO_3 (276 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 2-bromoquinoxaline (105.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), 1,10-phenanthroline (18.0 mg, 0.1 mmol, 0.20 equiv.) and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

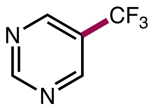
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 1 hour then filtered over celite. The organic solution was concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 1 to 3% EtOAc in hexanes) to yield the pure product as a white crystalline solid (90 mg, 0.45 mmol, 91% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.20 (s, 1H), 8.24 (td, *J* = 8.1, 1.6 Hz, 2H), 7.96-7.90 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 143.9, 142.9 (q, *J* = 35.3 Hz), 141.07, 141.05, 132.5, 131.7, 130.2, 129.7, 121.3 (q, *J* = 275.5 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –67.0 (s, 3F).

Data are consistent with those reported in the literature: M.G. Mormino, P. S. Fier, J. F. Hartwig, *Org. Lett,* **16**, 1744-1747 (2014).

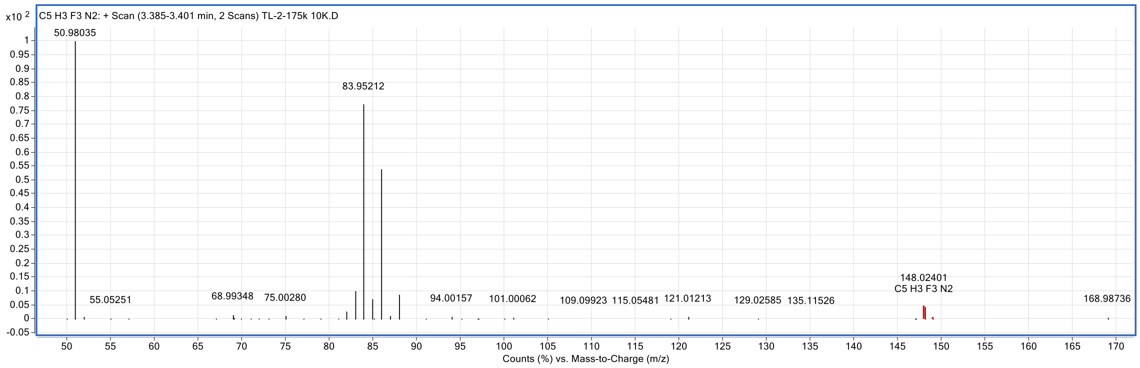


5-(trifluoromethyl)pyrimidine (40)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 5-bromopyrimidine (79.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d$_6$*). (90% yield – average of three trials: 89% yield, 92% yield, and 89% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_5H_3F_3N_2$ ($[M^*]^+$) 148.0243, found 148.0240.

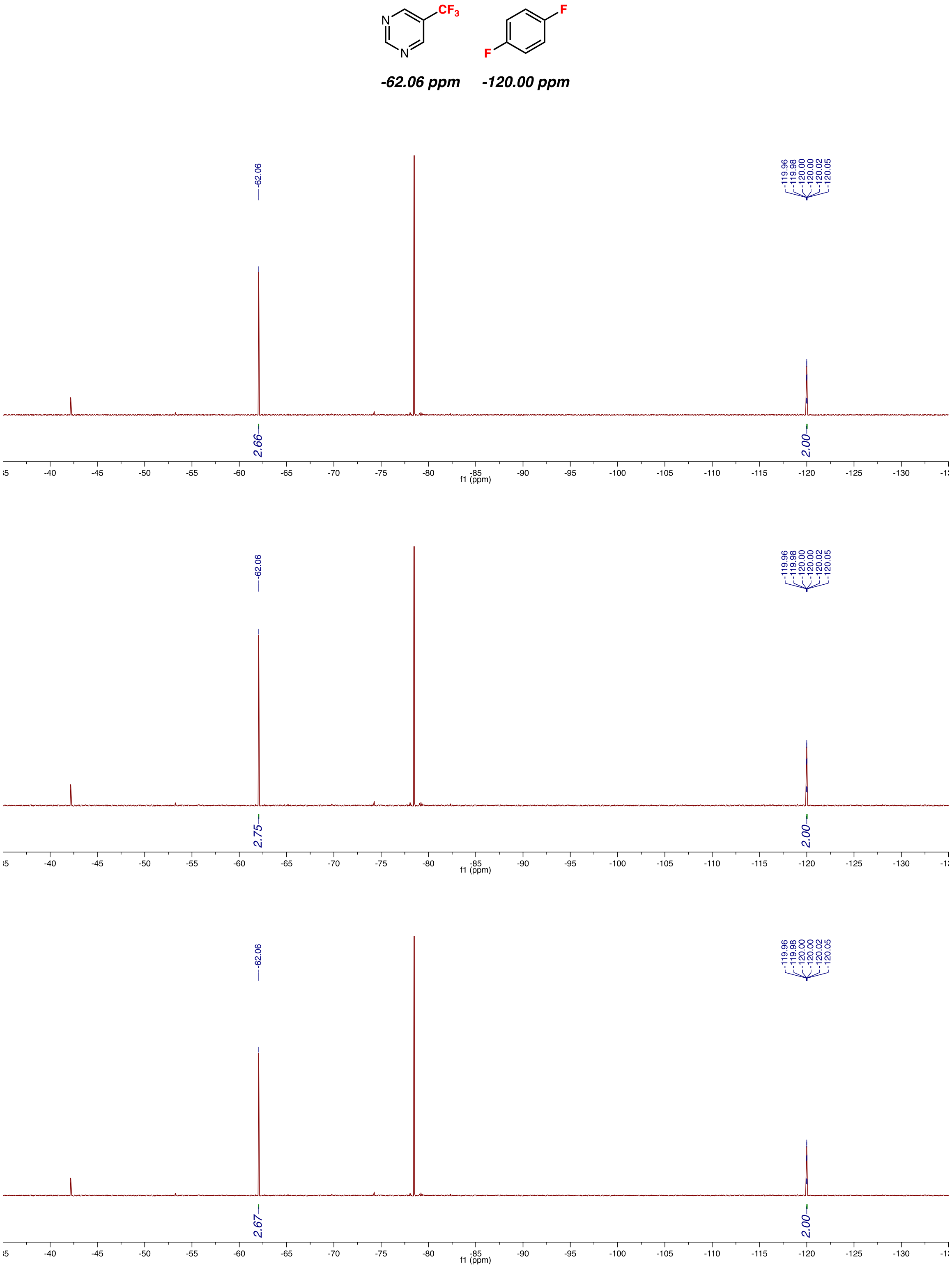
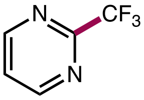


Figure S24. ^{19}F NMR assay for methyl 5-(trifluoromethyl)pyrimidine (**40**)

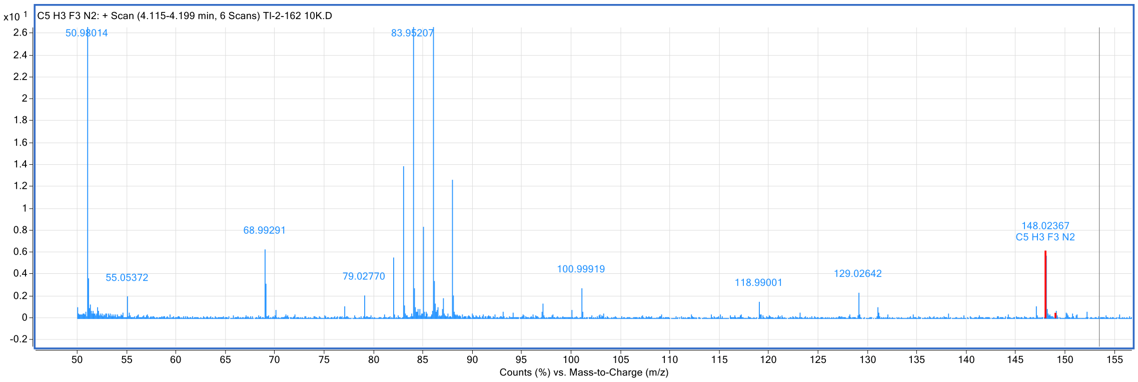


2-(trifluoromethyl)pyrimidine (41)

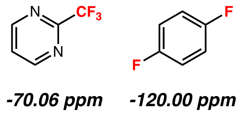
Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 µmol, 0.0025 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-bromopyrimidine (79.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (79% yield – average of three trials: 79% yield, 81% yield, and 78% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_5H_3F_3N_2$ ($[M^*]^+$) 148.0243, found 148.0237.



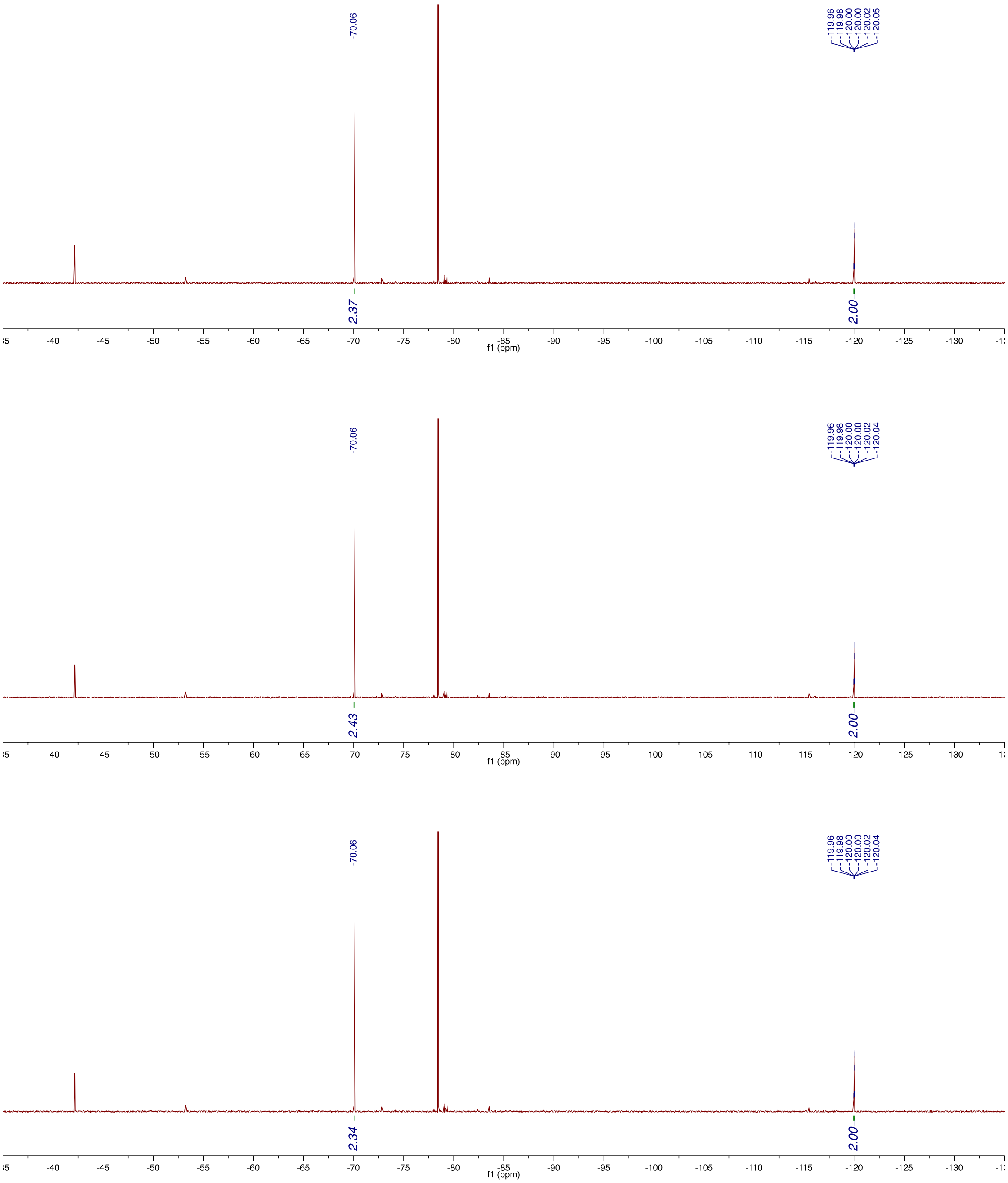
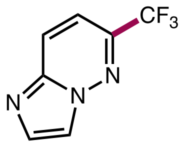


Figure S25. ^{19}F NMR assay for methyl 2-(trifluoromethyl)pyrimidine (**41**)



6-(trifluoromethyl)imidazo[1,2-b]pyridazine (42)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 µmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 6-bromoimidazo[1,2-b]pyridazine (99.0 mg, 0.5 mmol, 1.0 equiv.), CuTc (19.0 mg, 0.1 mmol, 0.2 equiv.), TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.), and acetone (10.0 mL, 0.05M).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in Ether (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 30 to 40% EA in hexanes) to yield the pure product (60 mg, 0.320 mmol, 64% yield).

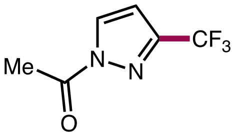
^{1}H NMR (500 MHz, acetone-*d$_6$*) δ 8.36 (s, 1H), 8.32 (d, *J* = 9.6 Hz, 1H), 8.00 (s, 1H), 7.59 (d, *J* = 9.5 Hz, 1H).

^{13}C NMR (125 MHz, acetone-*d$_6$*) δ 143.8 (q, *J* = 35.7 Hz), 139.7, 137.5, 128.4, 122.3 (q, *J* = 273.2 Hz), 119.0, 114.0 (q, *J* = 2.0 Hz).

^{19}F NMR (282 MHz, acetone-*d$_6$*) δ –67.1 (s, 3F).

IR (film) ν_{max} 3137, 3053, 1696, 1380, 1327, 1286, 1193, 1097, 827, 765 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_7H_5F_3N_3$ ($[M+H]^+$) 188.0430, found 188.0428.



1-(3-(trifluoromethyl)-1*H*-pyrazol-1-yl)ethanone (43)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-(3-bromo-1*H*-pyrazol-1-yl)ethanone (95.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product. The desired product was isolated for full characterizations.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (64% yield – average of three trials: 62% yield, 62% yield, and 67% yield).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in Ether (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (1% Methanol in DCM) to yield the pure product.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.33 – 8.29 (m, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 2.75 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 169.3, 146.6 (q, *J* = 38.8 Hz), 129.8, 120.5 (q, *J* = 269.7 Hz), 107.5 (q, *J* = 1.9 Hz), 21.7.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.3 (s, 3F).

IR (film) νmax 1754, 1468, 1378, 1279, 1239, 1177, 1131, 1102, 1045, 959, 945, 781, 745 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_6H_5F_3N_2O$ ([M*]$^+$) 178.0349, found 178.0349.

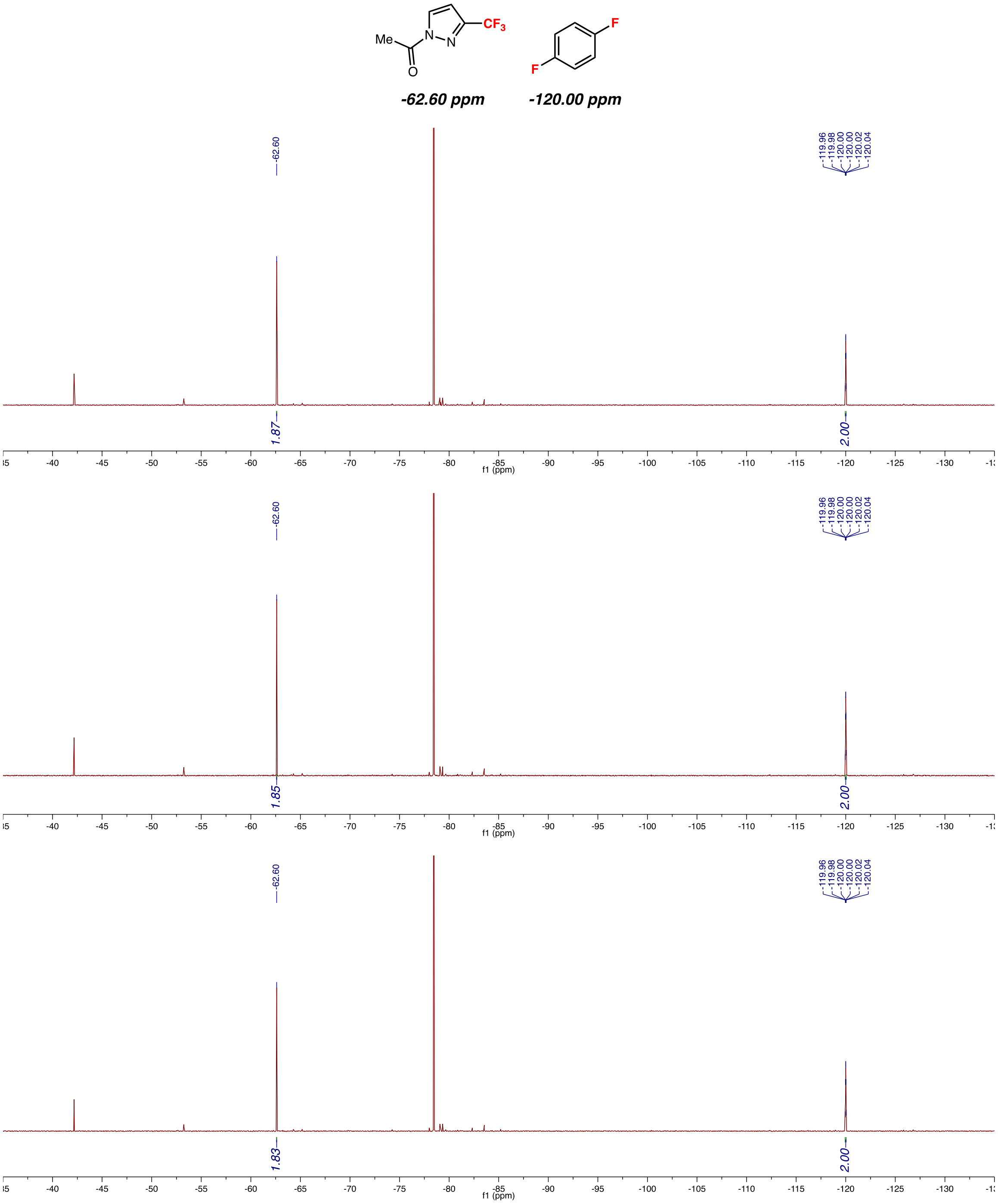
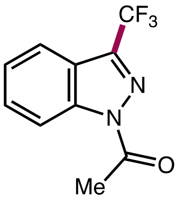


Figure S26. ^{19}F NMR assay for 1-(3-(trifluoromethyl)-1*H*-pyrazol-1-yl)ethanone (**43**)



1-(3-(trifluoromethyl)-1*H*-indazol-1-yl)ethanone (44)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-(3-bromo-1*H*-indazol-1-yl)ethanone (120.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 4 to 9% DCM in hexane) to yield the pure product (58 mg, 0.255 mmol, 51% yield).

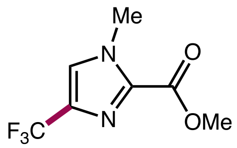
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.49 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.65 (td, *J* = 7.1, 1.0 Hz, 1H), 7.50 – 7.44 (m, 1H), 2.83 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 171.2, 140.2, 140.1 (q, *J* = 38.8 Hz), 130.7, 125.8, 122.0, 121.0 (q, *J* = 270.4 Hz), 120.3, 116.0, 23.1.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.6 (s, 3F).

IR (film) ν_{max} 1735, 1528, 1433, 1372, 1324, 1189, 1161, 1121, 1056, 986, 934, 843, 772, 750, 698, 688 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_{10}H_7F_3N_2O$ ([M*]$^+$) 228.0505, found 228.0504.

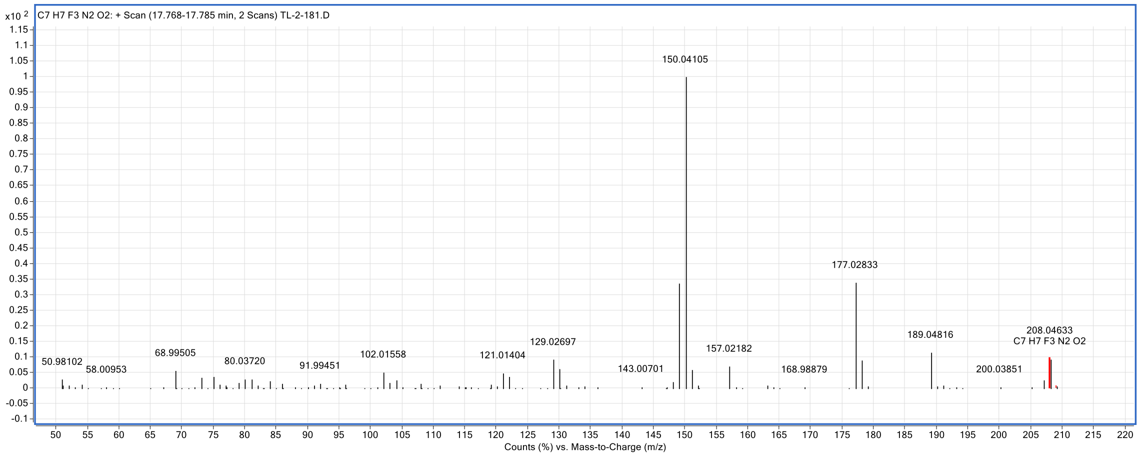


methyl 1-methyl-4-(trifluoromethyl)-1*H*-imidazole-2-carboxylate (45)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), methyl 4-bromo-1-methyl-1*H*-imidazole-2-carboxylate (110.0 mg, 0.5 mmol, 1.0 equiv.), CuTc (19.0 mg, 0.1 mmol, 0.20 equiv.), TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.), and acetone (5.0 mL, 0.1M).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (47% yield – average of three trials: 46% yield, 47% yield, and 47% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_7H_7F_3N_2O_2$ ([M*]$^+$) 208.0454, found 208.0463.

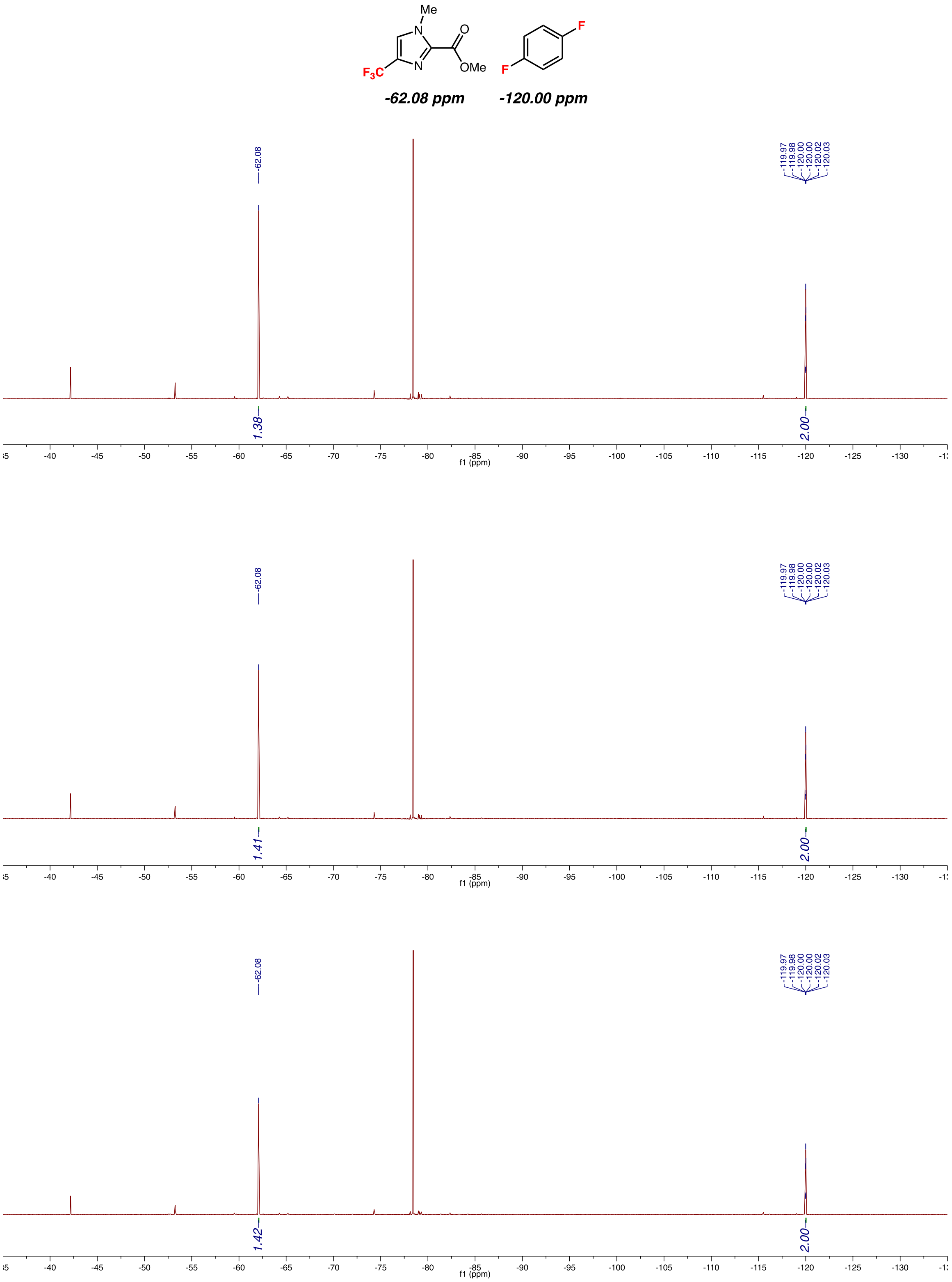
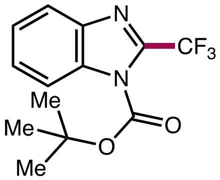


Figure S27. ^{19}F NMR assay for 1-methyl-4-(trifluoromethyl)-1*H*-imidazole-2-carboxylate (**45**)



tert-butyl 2-(trifluoromethyl)-1H-benzo[d]imidazole-1-carboxylate (46)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF*$_3$ reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), *tert*-butyl 2-bromo-1*H*-benzo[d]imidazole-1-carboxylate (149.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 10 to 50% DCM in hexane) to yield the pure product (54 mg, 0.190 mmol, 38% yield).

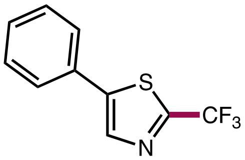
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.46 – 7.41 (m, 1H), 1.70 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 146.7, 140.6 (q, *J* = 40.3 Hz), 140.4, 133.9, 127.7, 125.4, 121.8, 118.6 (q, *J* = 271.1 Hz), 115.5, 87.6, 27.9.

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.9 (s, 3F).

IR (film) ν_{max} 1759, 1448, 1388, 1374, 1348, 1333, 1247, 1147, 1110, 1070, 928, 851, 760, 746, 737 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_8H_6F_3N_2$ ([M+2H–Boc]$^+$) 187.0478, found 187.0470.



5-phenyl-2-(trifluoromethyl)thiazole (47)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-bromo-5-phenylthiazole (120.0 mg, 0.5 mmol, 1.0 equiv.), 4,7-dimethoxy-1,10-phenanthroline (24.0 mg, 0.100 mmol, 0.2 equiv.), CuTc (19.0 mg, 0.1 mmol, 0.2 equiv.), TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.), and acetone (10.0 mL, 0.05M).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 2 to 10% DCM in hexanes) to yield the pure product (72 mg, 0.315 mmol, 63% yield).

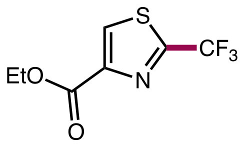
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.93 (m, 1H), 7.93 – 7.91 (m, 1H), 7.68 (s, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 154.2 (q, *J* = 40.9 Hz), 143.8, 139.2, 129.8, 129.7, 129.5, 127.3, 119.8 (q, *J* = 271.8 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.1 (s, 3F).

IR (film) ν_{max} 1455, 1434, 1324, 1305, 1296, 1192, 1138, 855, 755, 745, 687 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_{10}H_6F_3NS$ ([M*]$^+$) 229.0168, found 229.0173.



ethyl 2-(trifluoromethyl)thiazole-4-carboxylate (48)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), ethyl 2-bromothiazole-4-carboxylate (118.0 mg, 0.5 mmol, 1.0 equiv.), 4,7-dimethoxy-1,10-phenanthroline (24.0 mg, 0.100 mmol, 0.2 equiv.), CuTc (19.0 mg, 0.1 mmol, 0.2 equiv.), TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.), and acetone (10.0 mL, 0.05M).

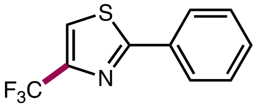
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (10% DCM in hexane) to yield the pure product (69 mg, 0.305 mmol, 61% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.39 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 160.4, 156.5 (q, *J* = 41.8 Hz), 148.7, 130.0, 119.3 (q, *J* = 272.9 Hz), 62.3, 14.4.

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.0 (s, 3F).

Data are consistent with those reported in the literature: MERCK SHARP and DOHME LIMITED, WO2006/120481, A2 (2006).



2-phenyl-4-(trifluoromethyl)thiazole (49)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 4-bromo-2-phenylthiazole (120.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS_3SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in ether (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 5 to 7% DCM in Hexane) to yield the pure product (71 mg, 0.310 mmol, 62% yield).

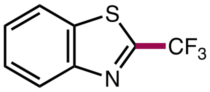
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.01 – 7.95 (m, 2H), 7.74 (s, 1H), 7.51 – 7.44 (m, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 170.6, 145.8 (q, *J* = 37.3 Hz), 132.6, 131.2, 129.2, 127.0, 120. 6 (q, *J* = 270.4 Hz), 120.4 (q, *J* = 3.5 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –64.0 (s, 3F).

IR (film) ν_{max} 1530, 1467, 1442, 1362, 1250, 1235, 1168, 1136, 1081, 1034, 985, 849, 772, 734, 688 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_{10}H_6F_3NS$ ([M*]$^+$) 229.0168, found 229.0163.



2-(trifluoromethyl)benzo[d]thiazole (50)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-bromobenzo[d]thiazole (107.0 mg, 0.5 mmol, 1.0 equiv.), 4,7-dimethoxy-1,10-phenanthroline (24.0 mg, 0.100 mmol, 0.2 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

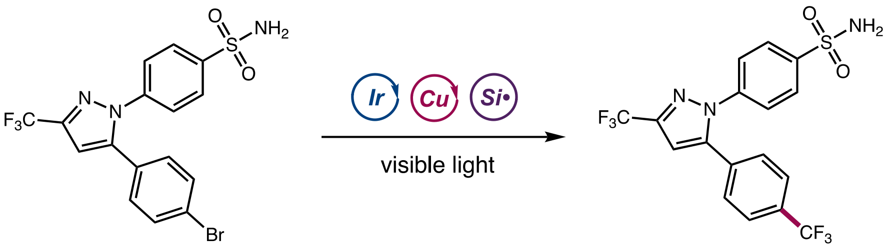
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (30% DCM in hexanes) to yield the pure product (61 mg, 0.300 mmol, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1 (q, *J* = 40.3 Hz), 152.2, 135.1, 127.6, 127.5, 125.1, 122.2, 119.9 (q, *J* = 273.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.7 (s, 3F).

Data are consistent with those reported in the literature: B. Bayarmagnai, C. Matheis, E. Risto, L. Goossen, *Adv. Synth. Catal.* **356**, 2343–2348 (2014).



4-(3-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (51)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 μmol, 0.0025 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.), 4-bromo-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (176.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution (0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (265 mg, 1.0 mmol, 2.0 equiv.).

The final reaction mixture was diluted with EtOAc (20 mL) and washed with NH$_4$Cl (1M aqueous) and brine. The organic solution was dried over Na$_2$SO$_4$ and filtered over celite, followed by removal of solvent to yield the crude product as a yellow solid. The product was purified via column chromatography (silica gel, gradient 5 to 45% EtOAc in hexanes) to yield the pure product as a white crystalline solid (168 mg, 0.39 mmol, 77% yield).

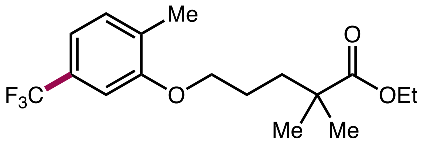
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 1H), 4.85 (s, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 144.6 (q, *J* = 38.9 Hz), 143.6, 142.2, 142.0, 132.2 (d, *J* = 1.5 Hz), 131.7 (q, *J* = 32.9 Hz), 129.3, 127.9, 126.3 (q, *J* = 3.7 Hz), 125.7, 123.7 (q, *J* = 272.5 Hz), 120.9 (q, *J* = 269.3 Hz), 107.3 (q, *J* = 2.1 Hz)

^{19}F NMR (282 MHz, CDCl$_3$) δ -62.51 (s, 3F), -62.92 (s, 3F).

IR (film) ν_{max} 3268, 1596, 1325, 1237, 1163, 1131, 846 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{12}F_6N_3O_2S$ ([M+H]$^+$) 436.0549, found 436.0541.



ethyl 2,2-dimethyl-5-(2-methyl-5-(trifluoromethyl)phenoxy)pentanoate (52)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), ethyl 5-(5-bromo-2-methylphenoxy)-2,2-dimethylpentanoate (172.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 2 to 6% EtOAc in hexanes) to yield the pure product (110 mg, 0.330 mmol, 66% yield).

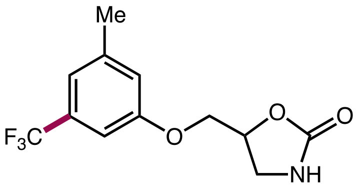
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.21 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 5.9 Hz, 2H), 2.26 (s, 3H), 1.80 – 1.69 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 6H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 177.8, 157.2, 131.1, 130.7, 129.1 (q, *J* = 32.1 Hz), 124.4 (q, *J* = 271.9 Hz), 117.1 (q, *J* = 4.0 Hz), 107.3 (q, *J* = 3.7 Hz), 68.4, 60.5, 42.1, 37.1, 25.3, 25.1, 16.4, 14.4.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.2 (s, 3F).

IR (film) ν_{max} 1726, 1422, 1330, 1243, 1193, 1163, 1118, 1078, 1045, 1027, 857, 818 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{24}F_3O_3$ ([M+H]$^+$) 332.1672, found 332.1668.



ethyl 2,2-dimethyl-5-(2-methyl-5-(trifluoromethyl)phenoxy)pentanoate (53)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 5-((3-bromo-5-methylphenoxy)methyl)oxazolidin-2-one (143.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 5 to 8% EtOAc in hexanes) to yield the pure product (99 mg, 0.360 mmol, 72% yield).

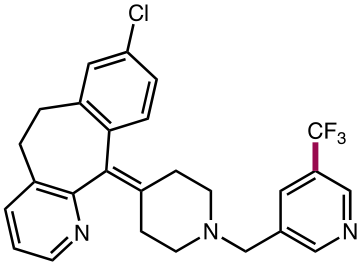
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.06 (s, 1H), 6.94 (s, 1H), 6.90 (s, 1H), 6.44 (br, 1H), 5.02 – 4.93 (m, 1H), 4.21 – 4.12 (m, 2H), 3.79 (t, *J* = 8.7 Hz, 1H), 3.61 (dd, *J* = 8.8, 5.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 158.3, 140.8, 131.8 (q, *J* = 32.6 Hz), 124.0 (q, *J* = 272.2 Hz), 119.3, 119.2, 118.9, 108.6 (q, *J* = 3.9 Hz), 74.2, 68.3, 42.7, 21.6.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.7 (s, 3F).

IR (film) ν_{max} 1742, 1603, 1461, 1349, 1316, 1391, 1349, 1316, 1248, 1167, 1095, 1031, 963, 931, 884, 856, 699 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{13}F_3NO_3$ ([M+H]$^+$) 276.0842, found 276.0852.



8-chloro-11-(1-((5-(trifluoromethyl)pyridin-3-yl)methyl)piperidin-4-ylidene)-6,11-dihydro-5*H*-benzo[5,6]cyclohepta[1,2-b]pyridine (54)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 11-(1-((5-bromopyridin-3-yl)methyl)piperidin-4-ylidene)-8-chloro-6,11-dihydro-5*H*-benzo[5,6]cyclohepta[1,2-b]pyridine (240.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (595 mg, 2.25 mmol, 4.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 4.0 g) and tetrabutylammonium bromide (2.0 g) in EtOAc (20 mL) for 5 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (1% methanol in DCM) to yield the pure product (99 mg, 0.210 mmol, 42% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.76 (s, 1H), 8.71 (s, 1H), 8.38 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.91 (s, 1H), 7.41 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.14 – 7.08 (m, 3H), 7.06 (dd, *J* = 7.7, 4.8 Hz, 1H), 3.55 (s, 2H), 3.43 – 3.29 (m, 2H), 2.86 – 2.74 (m, 2H), 2.73 – 2.65 (m, 2H), 2.53 (ddd, *J* = 14.0, 9.8, 4.3 Hz, 1H), 2.43 (ddd, *J* = 13.9, 9.7, 4.3 Hz, 1H), 2.33 (tt, *J* = 13.8, 3.9 Hz, 2H), 2.19 (qd, *J* = 10.6, 3.1 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 157.4, 153.4 (q, *J* = 1.4 Hz), 146.7, 145.4 (q, *J* = 4.1 Hz), 139.5, 138.3, 137.8, 137.3, 134.5, 133.38, 133.37 (q, *J* = 3.3 Hz), 133.1, 132.7, 130.8, 129.0, 126.5 (q, *J* = 32.8 Hz), 126.0, 123.6 (q, *J* = 272.7 Hz), 122.1, 59.5, 54.83, 54.76, 31.8, 31.5, 30.9, 30.7.

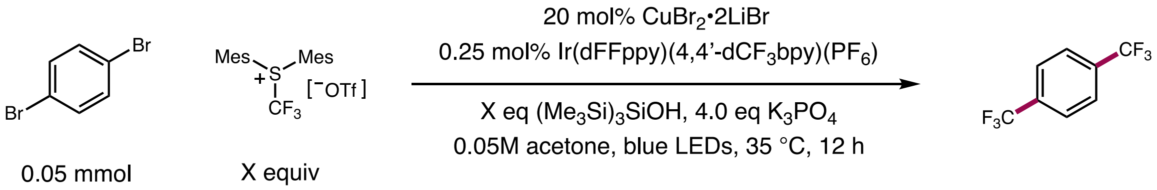
^{19}F NMR (282 MHz, CDCl$_3$) δ –62.3 (s, 3F).

IR (film) ν_{max} 1620, 1586, 1438, 1335, 1321, 1213, 1175, 1131, 1086, 1028, 909, 830, 732, 716 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{24}F_3N_3Cl$ ([M+H]$^+$) 469.1533, found 469.1545.

10) Trifluoromethylation of dibromoarenes

Performed following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.13 mg, 0.125 µmol, 0.0025 equiv.), K$_3$PO$_4$ (42.5 mg, 0.2 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (2.0 or 3.0 equiv.), dibromobenzene (12.0 mg, 0.05 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (1.0 mL acetone solution, 0.01M, 0.01 mmol, 0.20 equiv.), and TMS$_3$SiOH (2.0 or 3.0 equiv.). After the reaction was finished, 1,4-difluorobenzene (5.2 µL, 0.05 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-d6).



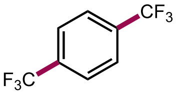
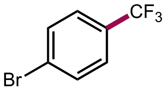
Reagent Loading		
2.0 equiv. SiOH and [CF$_3$]	**41%**	**45%**
3.0 equiv. SiOH and [CF$_3$]	**56%**	**15%**

Figure S28. Trifluoromethylation of 1,4-dibromobenzene.

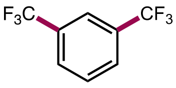
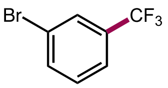
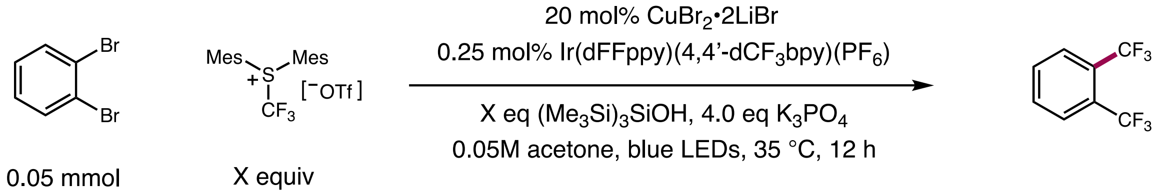
Reagent Loading		
2.0 equiv. SiOH and [CF$_3$]	**14%**	**55%**
3.0 equiv. SiOH and [CF$_3$]	**20%**	**56%**

Figure S29. Trifluoromethylation of 1,3-dibromobenzene.



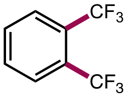
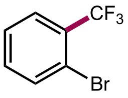
Reagent Loading		
2.0 equiv. SiOH and [CF_3]	**11%**	**38%**
3.0 equiv. SiOH and [CF_3]	**14%**	**36%**

Figure S30. Trifluoromethylation of 1,2-dibromobenzene.

11) Additional examples of (hetero)aryl bromides

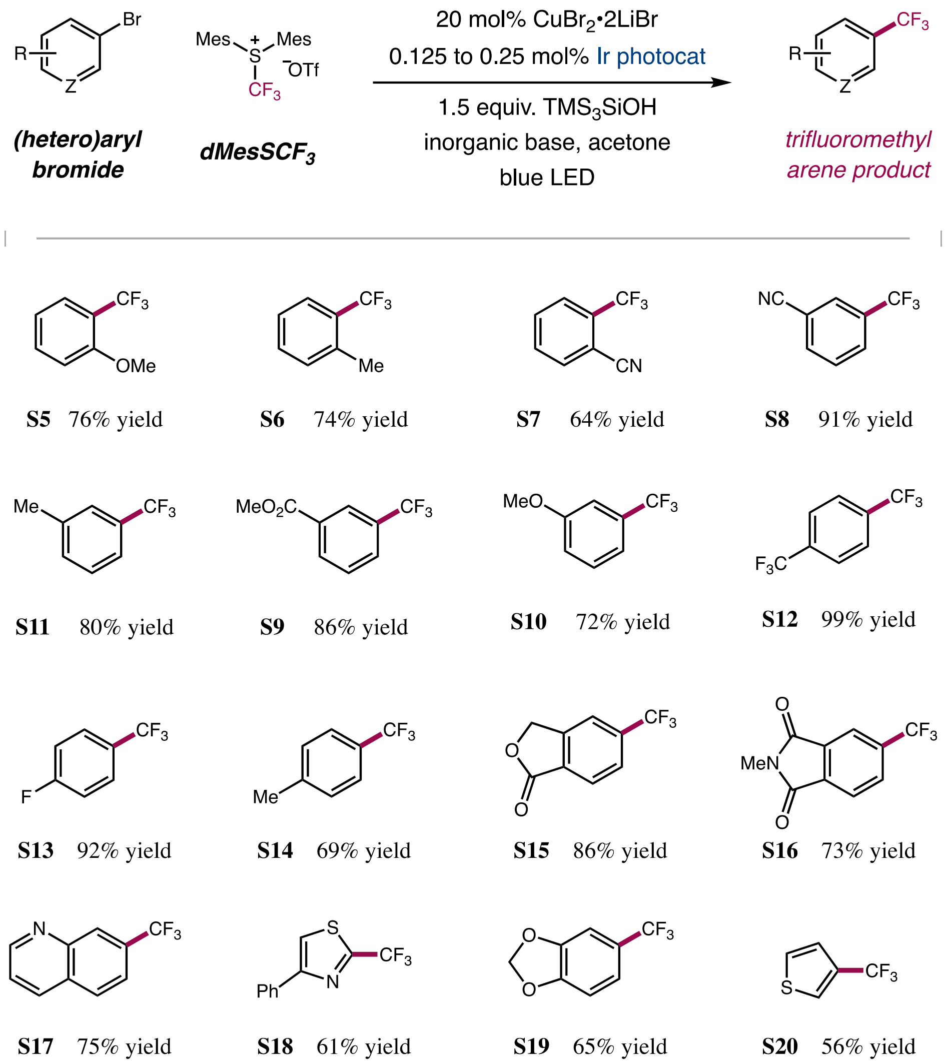
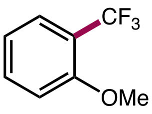


Figure S31. Additional examples for trifluoromethylation of (hetero)aryl halides.

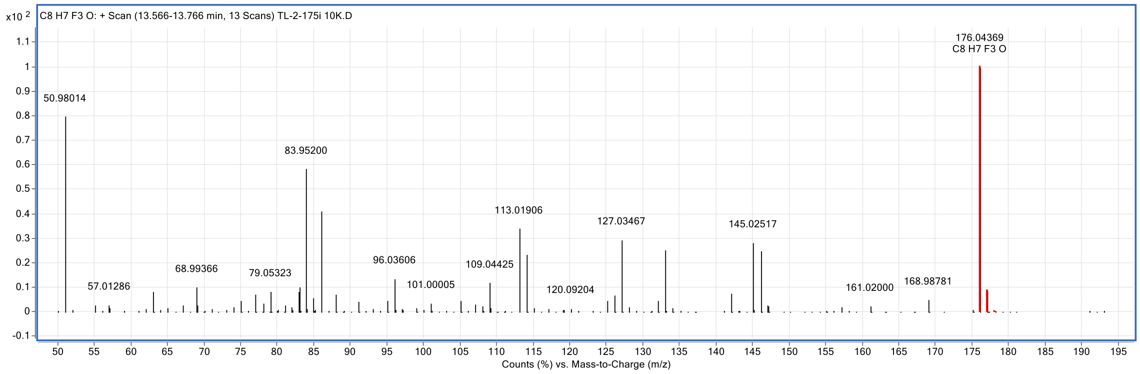


1-methoxy-2-(trifluoromethyl)benzene (S5)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 µmol, 0.0025 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.750 mmol, 1.5 equiv.), 1-bromo-2-methoxybenzene (94.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-d6). (76% yield – average of three trials: 75% yield, 76% yield, and 77% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_8H_7F_3O$ ([M*]$^+$) 176.0444, found 176.0437.

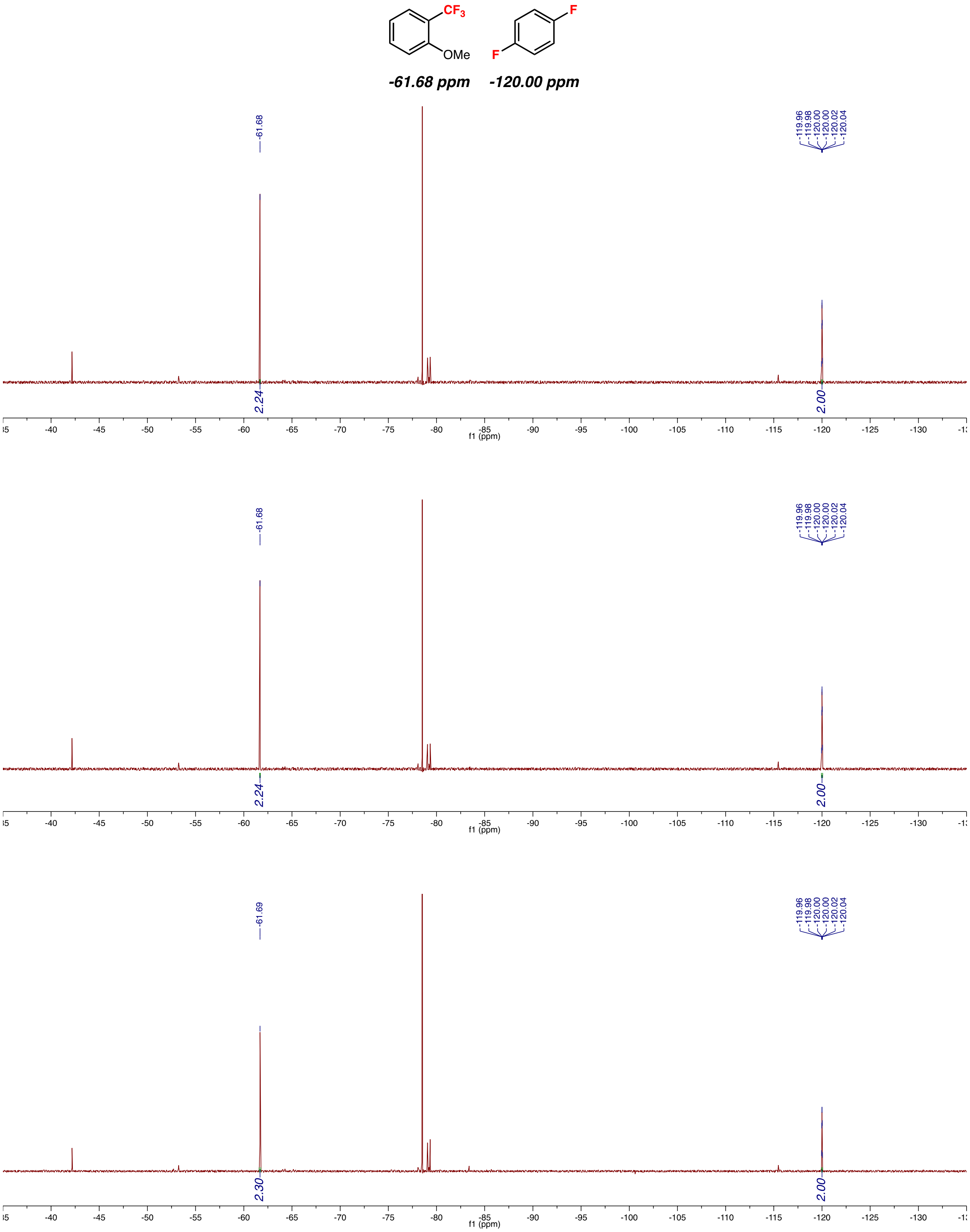
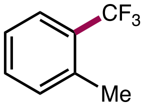


Figure S32. ^{19}F NMR assay for 1-methoxy-2-(trifluoromethyl)benzene (**S5**)

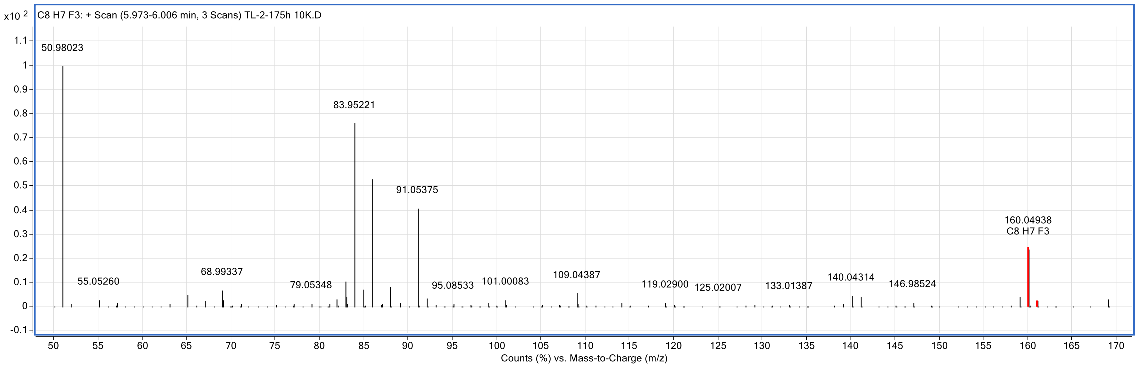


1-methyl-2-(trifluoromethyl)benzene (S6)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 µmol, 0.0025 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF*$_3$ reagent (454.0 mg, 0.925 mmol, 1.85 equiv.), 1-bromo-2-methylbenzene (86.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-d6). (74% yield – average of three trials: 76% yield, 74% yield, and 71% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_8H_7F_3$ ($[M^*]^+$) 160.0494, found 160.0494.

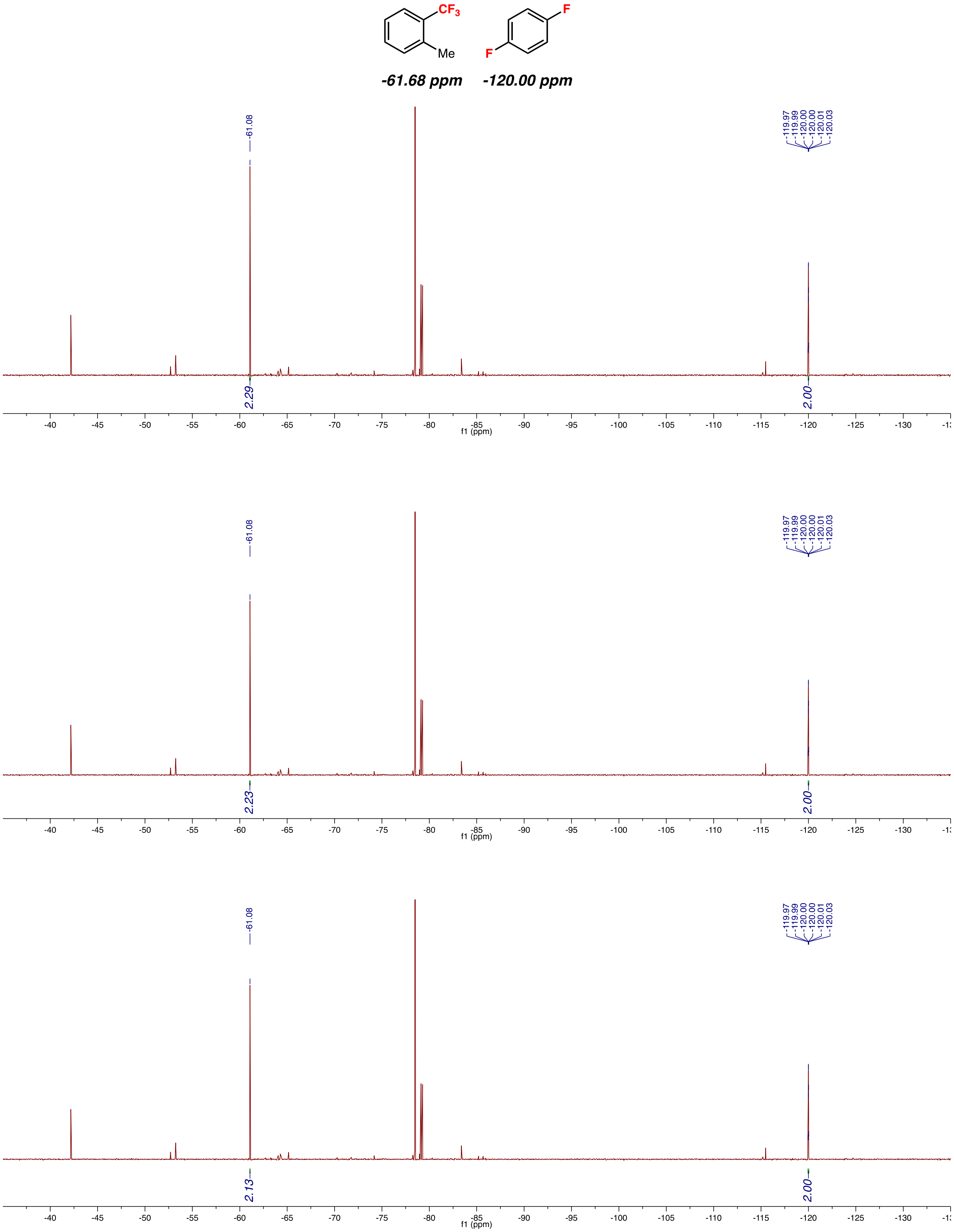
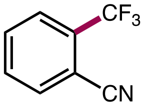


Figure S33. ^{19}F NMR assay for 1-methyl-2-(trifluoromethyl)benzene (**S6**)



2-(trifluoromethyl)benzonitrile (S7)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-bromobenzonitrile (91.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

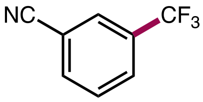
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 1 to 10% DCM in hexane) to yield the pure product (55 mg, 0.320 mmol, 64% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 134.8, 133.1, 132.8, 132.4, 126.8 (q, *J* = 4.7 Hz), 122.5 (q, *J* = 273.7 Hz), 115.6, 110.3.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.0 (s, 3F).

Data are consistent with those reported in the literature: X. Li, J. Zhao, L. Zhang, M. Hu, L. Wang, J. Hu, *Org. Lett.* **17**, 298–301 (2015).



3-(trifluoromethyl)benzonitrile (S8)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 3-bromobenzonitrile (91.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

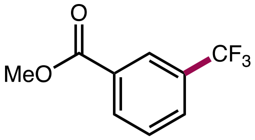
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (3% ether in pentane) to yield the pure product (78 mg, 0.455 mmol, 91% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.93 (s, 1H), 7.90 – 7.84 (m, 2H), 7.66 (t, *J* = 7.9 Hz, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 135.4, 132.1 (q, *J* = 33.7 Hz), 130.1, 129.6 (q, *J* = 3.6 Hz), 129.2 (q, *J* = 3.9 Hz), 123.0 (q, *J* = 272.7 Hz), 117.47, 113.60.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.2 (s, 3F).

Data are consistent with those reported in the literature: S. Shi, M. Szostak, *Org. Lett.* **19**, 3095–3098 (2017).



methyl 3-(trifluoromethyl)benzoate (S9)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), methyl 3-bromobenzoate (108.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

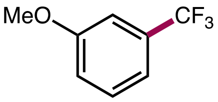
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (20% ether in pentane) to yield the pure product (88 mg, 0.430 mmol, 86% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.30 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 165.9, 132.9, 131.2 (q, *J* = 33.0 Hz), 131.1, 129.6 (q, *J* = 3.7 Hz), 129.2, 126.7 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 272.4 Hz), 52.6.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.9 (s, 3F).

Data are consistent with those reported in the literature: B. A. Khan et al., *Chem. Eur. J.* **18**, 1577–1581 (2012).



1-methoxy-3-(trifluoromethyl)benzene (S10)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-bromo-3-methoxybenzene (94.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

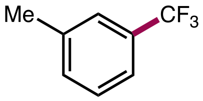
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (5% ether in pzentane) to yield the pure product (63 mg, 0.360 mmol, 72% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 1H), 7.07 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 159.8, 132.0 (q, *J* = 32.2 Hz), 130.1, 124.1 (q, *J* = 272.3 Hz), 117.7, 117.5 (q, *J* = 3.9 Hz), 110.7 (q, *J* = 3.9 Hz), 55.6.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.7 (s, 3F).

Data are consistent with those reported in the literature: S. Mizuta et al, *Org. Lett.* **15**, 2648–2651 (2013).

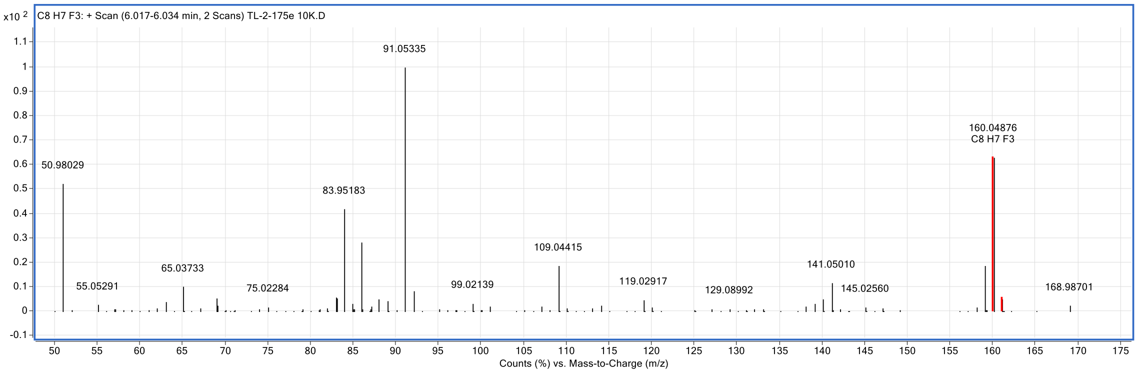


1-methyl-3-(trifluoromethyl)benzene (S11)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-bromo-3-methylbenzene (86.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-d6). (80% yield – average of three trials: 78% yield, 81% yield, and 80% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_8H_7F_3$ ($[M^*]^+$) 160.0494, found 160.0488.

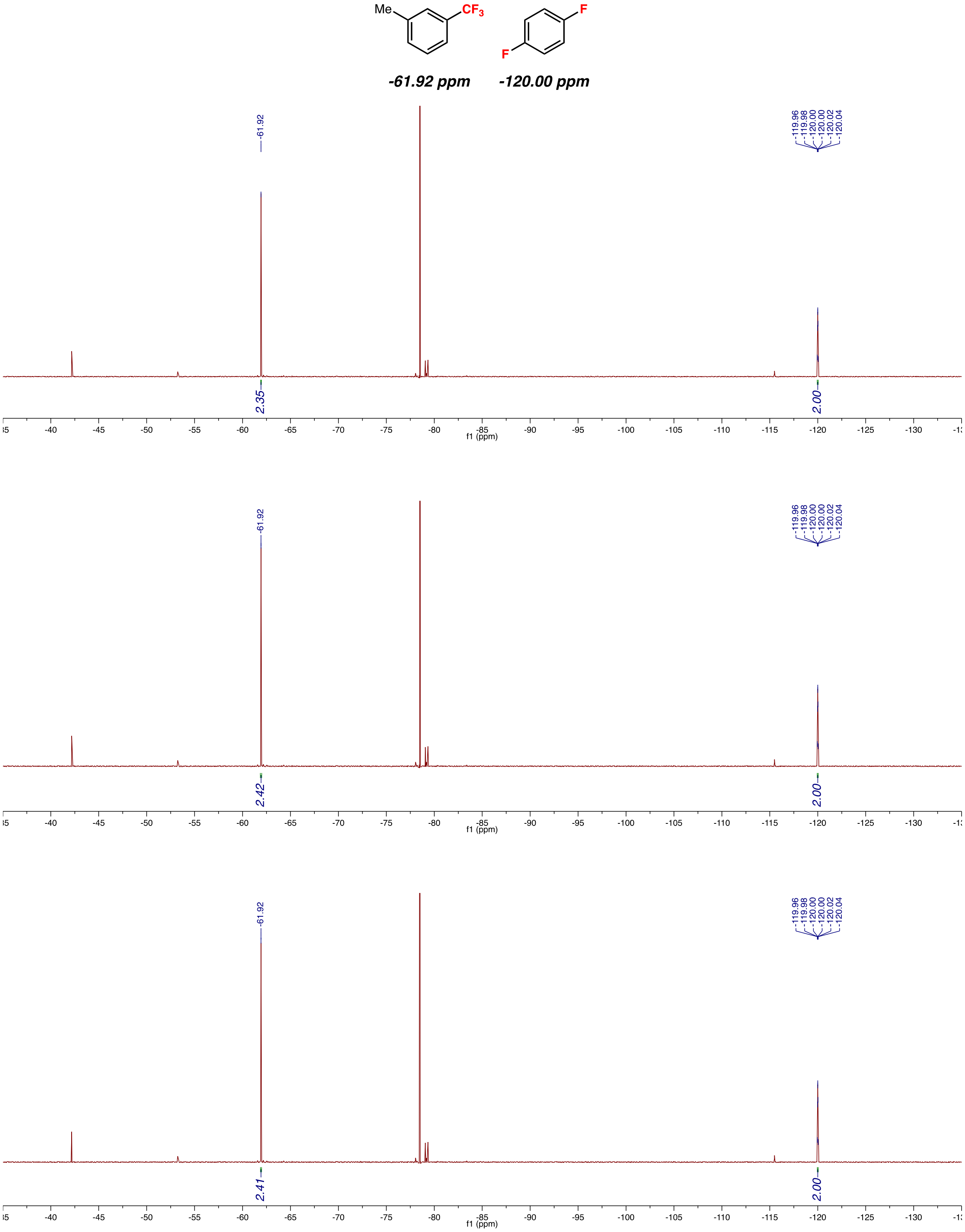
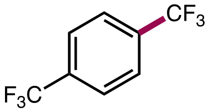


Figure S34. ^{19}F NMR assay for 1-methyl-3-(trifluoromethyl)benzene (**S11**)

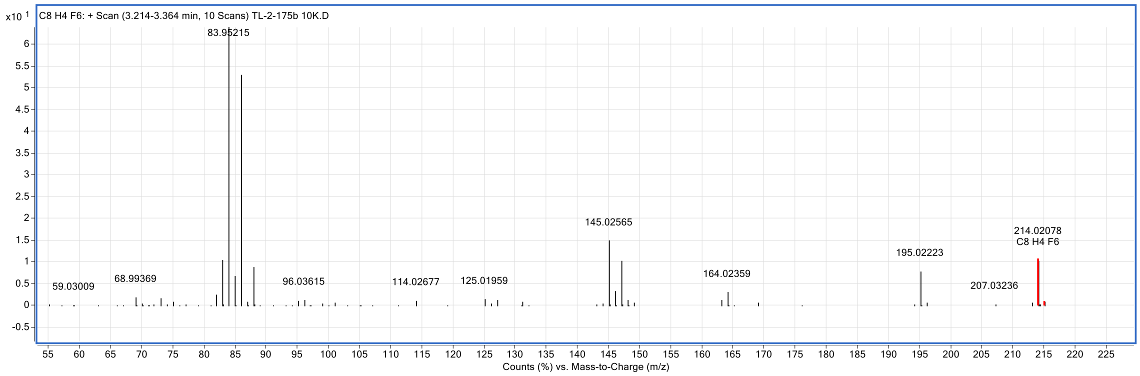


1,4-bis(trifluoromethyl)benzene (S12)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-bromo-4-(trifluoromethyl)benzene (113.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (99% yield – average of three trials: 99% yield, 99% yield, and 98% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_8H_4F_6$ ([M*]$^+$) 214.0212, found 214.0208.

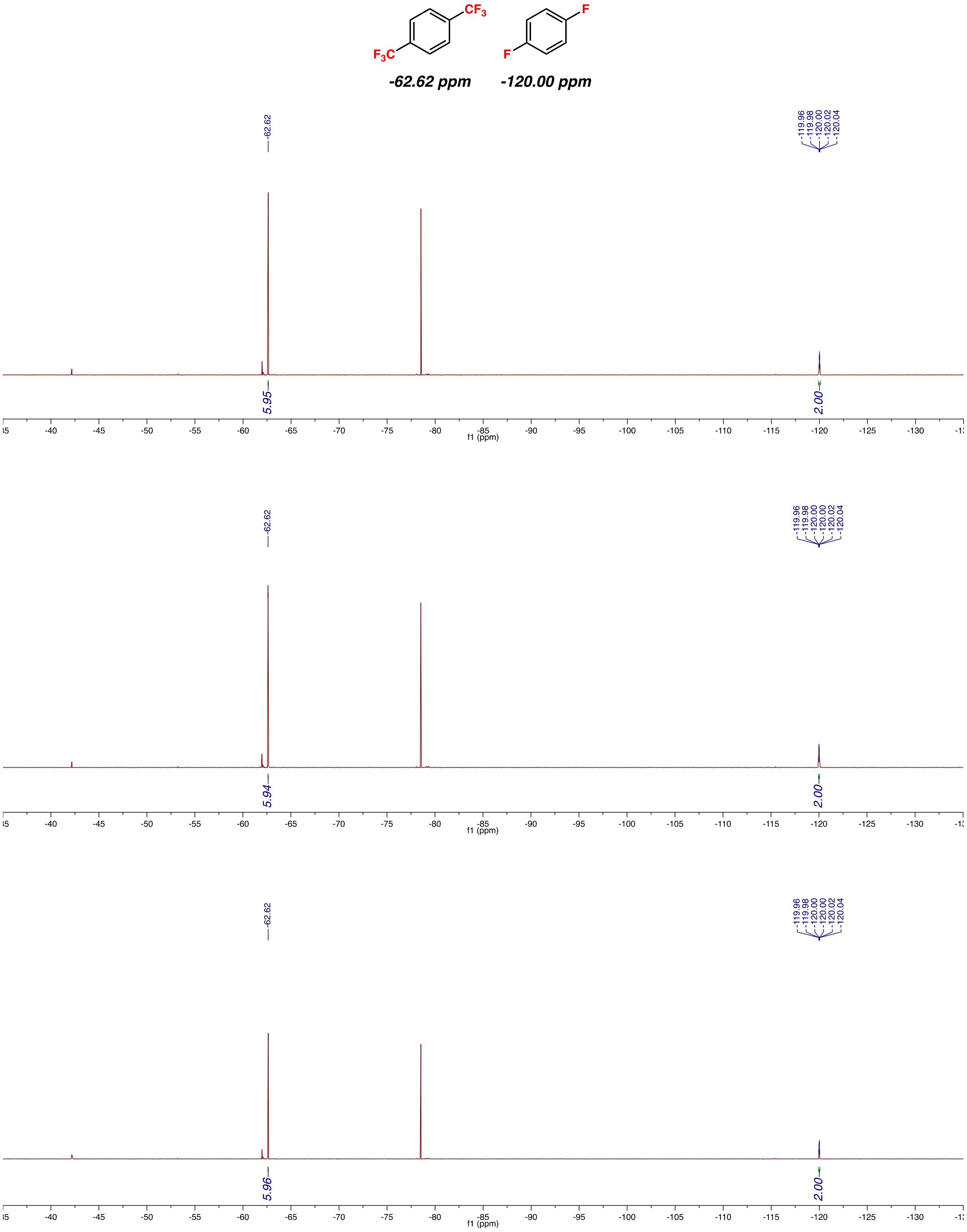
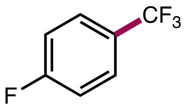


Figure S35. ^{19}F NMR assay for 1,4-bis(trifluoromethyl)benzene (**S12**)

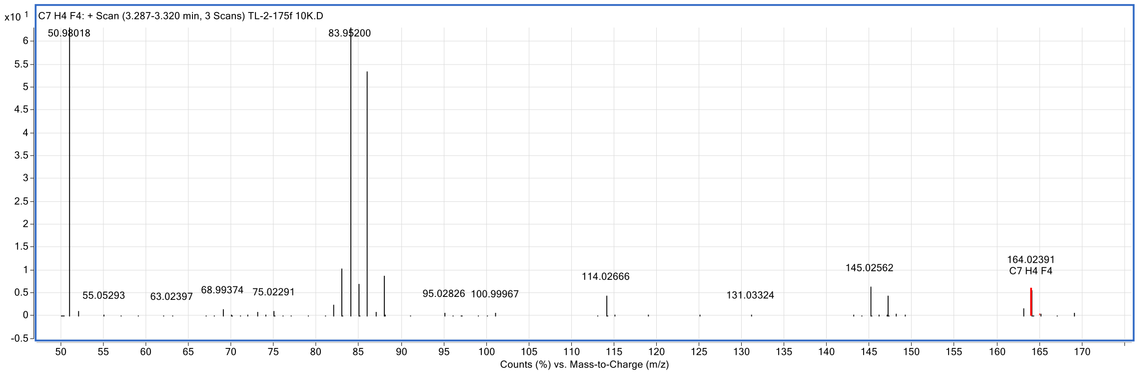


1-fluoro-4-(trifluoromethyl)benzene (S13)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-bromo-4-fluorobenzene (87.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d*$_6$). (92% yield – average of three trials: 92% yield, 93% yield, and 92% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_7H_4F_4$ ([M*]$^+$) 164.0244, found 164.0239.

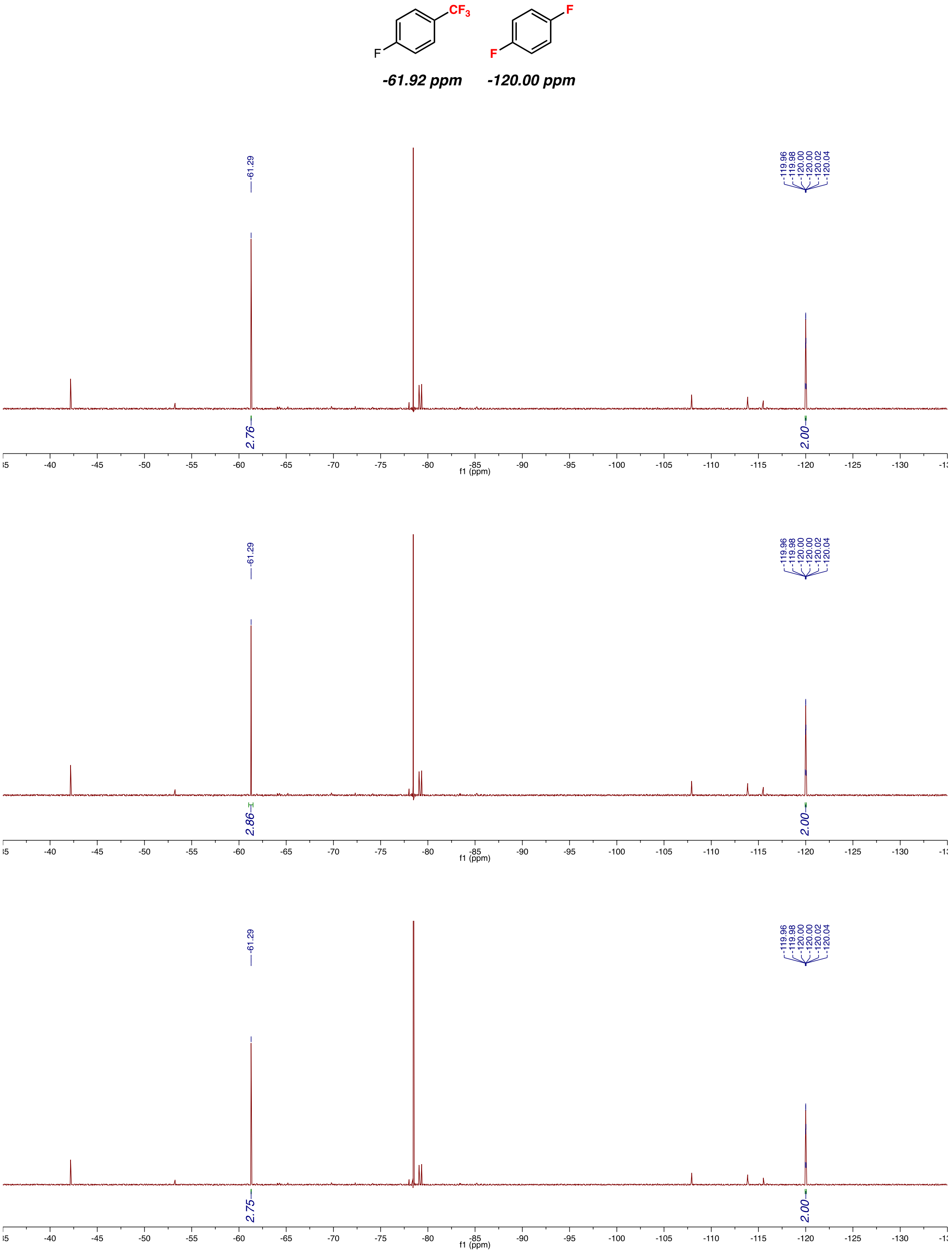
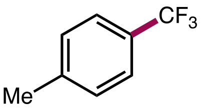


Figure S36. ^{19}F NMR assay for 1-fluoro-4-(trifluoromethyl)benzene **(S13)**

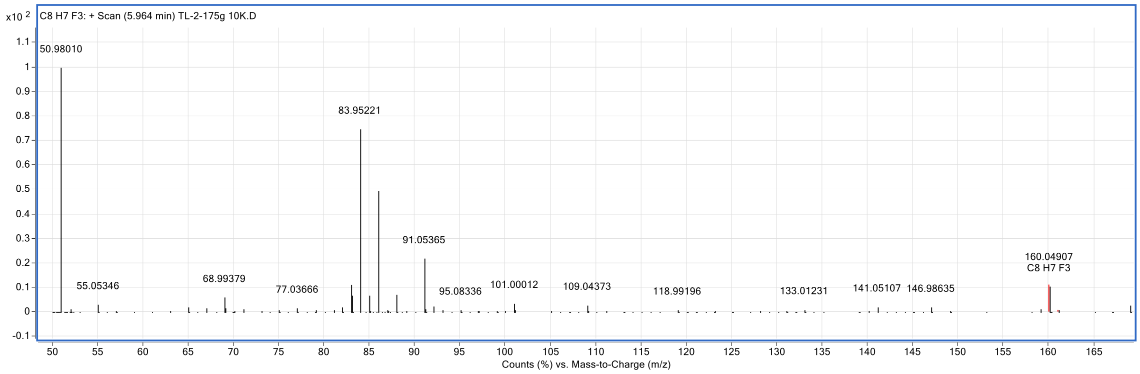


1-methyl-4-(trifluoromethyl)benzene (S14)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4’-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 1-bromo-4-methylbenzene (86.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-*d$_6$*). (69% yield – average of three trials: 70% yield, 68% yield, and 69% yield).



HRMS (GC-EI-TOF) m/z calcd. for C$_8$H$_7$F$_3$ ([M*]$^+$) 160.0494, found 160.0491.

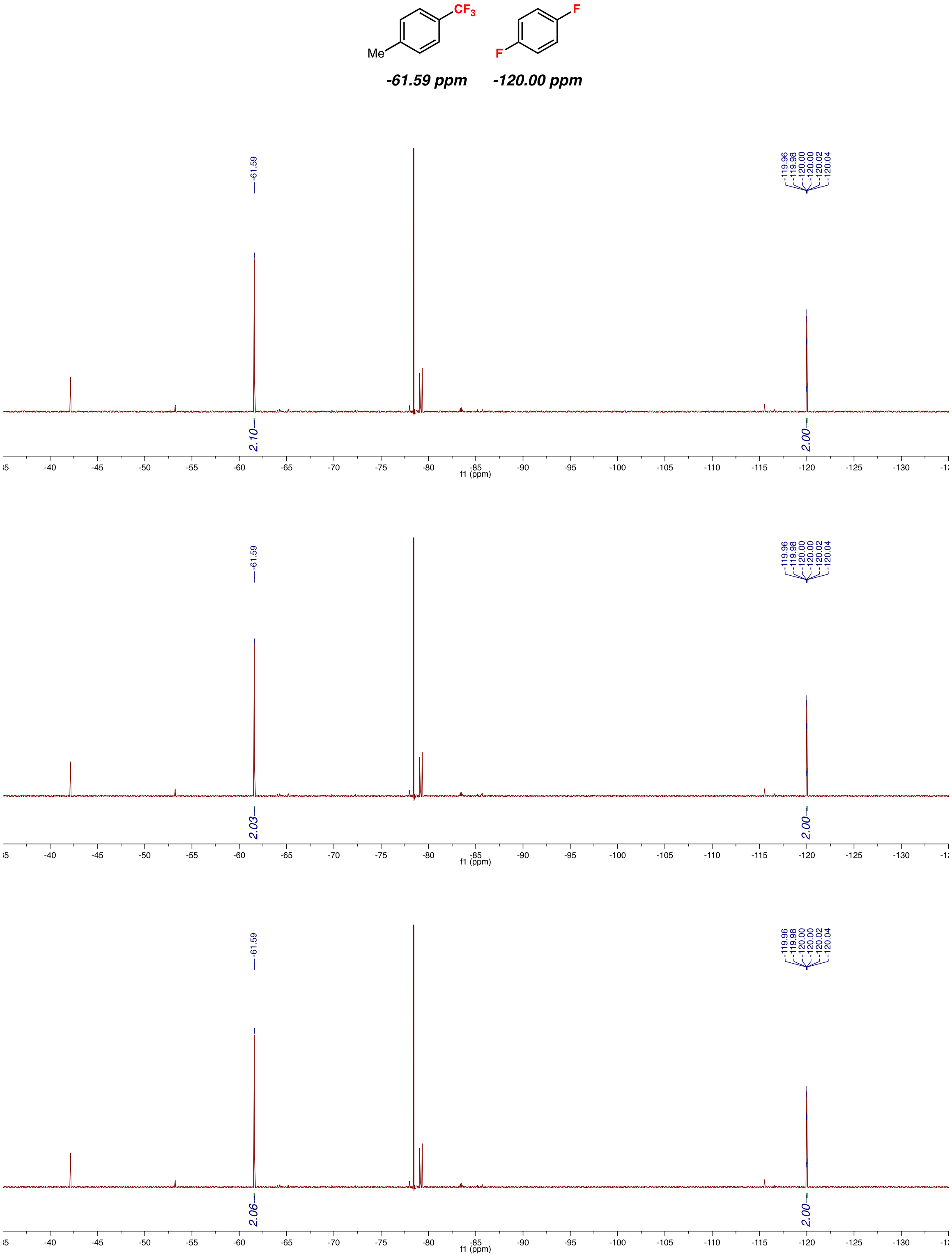
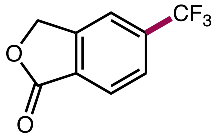


Figure S37. ^{19}F NMR assay for 1-methyl-4-(trifluoromethyl)benzene **(S14)**



5-(trifluoromethyl)isobenzofuran-1(3*H*)-one (S15)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 5-bromoisobenzofuran-1(3*H*)-one (107.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

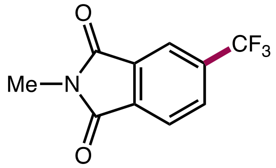
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na$_2$CO$_3$ (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (10% ether in hexane) to yield the pure product (87 mg, 0.430 mmol, 86% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.80 (s, 1H), 5.40 (s, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 169.6, 146.9, 136.0 (q, *J* = 32.9 Hz), 129.1, 126.7, 126.6 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 273.3 Hz), 119.8 (q, *J* = 3.9 Hz), 70.0.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.8 (s, 3F).

Data are consistent with those reported in the literature: Y.–H. Zhang et al, *Angew. Chem. Int. Ed.* **48**, 6097–6100 (2009).



2-methyl-5-(trifluoromethyl)isoindoline-1,3-dione (S16)

Prepared following the general procedure outlined above using Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.31 mg, 1.25 μmol, 0.0025 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF*$_3$ reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 5-bromo-2-methylisoindoline-1,3-dione (120.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3(aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (8% EA in Hexane) to yield the pure product (84 mg, 0.365 mmol, 73% yield).

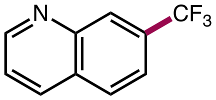
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, *J* = 1.4 Hz, 1H), 8.01 – 7.96 (m, 2H), 3.22 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 167.1 (d, *J* = 15.3 Hz), 136.1 (q, *J* = 33.4 Hz), 135.2, 133.0, 131.2 (q, *J* = 3.7 Hz), 123.9, 123.2 (q, *J* = 273.3 Hz), 120.6 (q, *J* = 3.8 Hz), 24.5.

^{19}F NMR (282 MHz, CDCl$_3$) δ –63.0 (s, 3F).

IR (film) ν_{max} 1700, 1430, 1387, 1325, 1272, 1256, 1165, 1125, 1100, 1006, 942, 869, 745, 694 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_{10}H_6F_3NO_2$ ([M*]$^+$) 229.0345, found 229.0341.



7-(trifluoromethyl)quinolone (S17)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.30 mg, 1.25 μmol, 0.0025 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 7-bromoquinoline (104.0 mg, 0.5 mmol, 1.0 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

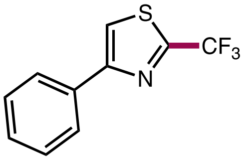
The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (9% EtOAc in hexane) to yield the pure product (74 mg, 0.375 mmol, 75% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.02 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.42 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.72 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.52 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 151.9, 147.4, 136.0, 131.4 (q, *J* = 32.7 Hz), 129.8, 129.2, 127.5 (q, *J* = 4.4 Hz), 124.0 (q, *J* = 272.4 Hz), 123.1, 122.4 (q, *J* = 3.2 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.7 (s, 3F).

Data are consistent with those reported in the literature: D. Jung, M. H. Kim, J. Kim, *Org. Lett.* **18**, 6300–6303 (2016).



4-phenyl-2-(trifluoromethyl)thiazole (S18)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 µmol, 0.00125 equiv.), Na_2CO_3 (212 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 2-bromo-4-phenylthiazole (120.0 mg, 0.5 mmol, 1.0 equiv.), 4,7-dimethoxy-1,10-phenanthroline (24.0 mg, 0.100 mmol, 0.2 equiv.), $CuBr_2$•2LiBr (10.0 mL acetone solution, 0.01M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

The final reaction mixture was treated with KF/alumina (40% wt, 2.0 g) and tetrabutylammonium bromide (1.0 g) in EtOAc (20 mL) for 45 minutes then filtered over celite. The organic solution was washed by Na_2CO_3 (aq), water, brine and concentrated to yield the crude product as an oil. The product was purified via silica gel column chromatography (gradient 2 to 7% DCM in hexane) to yield the pure product (70 mg, 0.305 mmol, 61% yield).

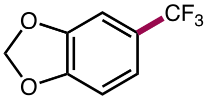
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.93 (m, 1H), 7.93 – 7.91 (m, 1H), 7.68 (s, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 157.2, 155.7 (q, J = 40.9 Hz), 133.2, 129.2, 129.1, 126.7, 119.9 (q, J = 272.0 Hz), 115.7 (q, J = 1.4 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.2 (s, 3F).

IR (film) ν_{max} 1740, 1499, 1456, 1445, 1302, 1211, 1138, 1073, 1060, 1033, 1025, 703, 690, 681 cm^{-1}.

HRMS (GC-EI-TOF) m/z calcd. for $C_{10}H_6F_3NS$ ([M*]$^+$) 229.0168, found 229.0167.

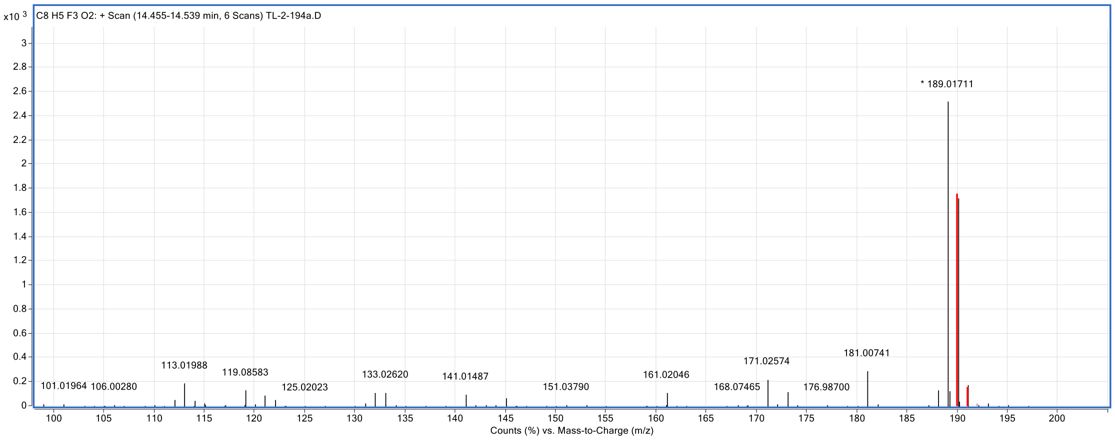


5-(trifluoromethyl)benzo[*d*][1,3]dioxole (S18)

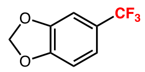
Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K$_3$PO$_4$ (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 5-bromobenzo[d][1,3]dioxole (100.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR in triplicate due to the high volatility of the desired product.

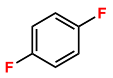
1,4-difluorobenzene (52 μL, 0.5 mmol, 1.0 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-d6). (65% yield – average of three trials: 66% yield, 64% yield, and 65% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_8H_5F_3O_2$ ($[M^*]^+$) 190.0236, found 190.0238.



-60.64 ppm



-120.00 ppm

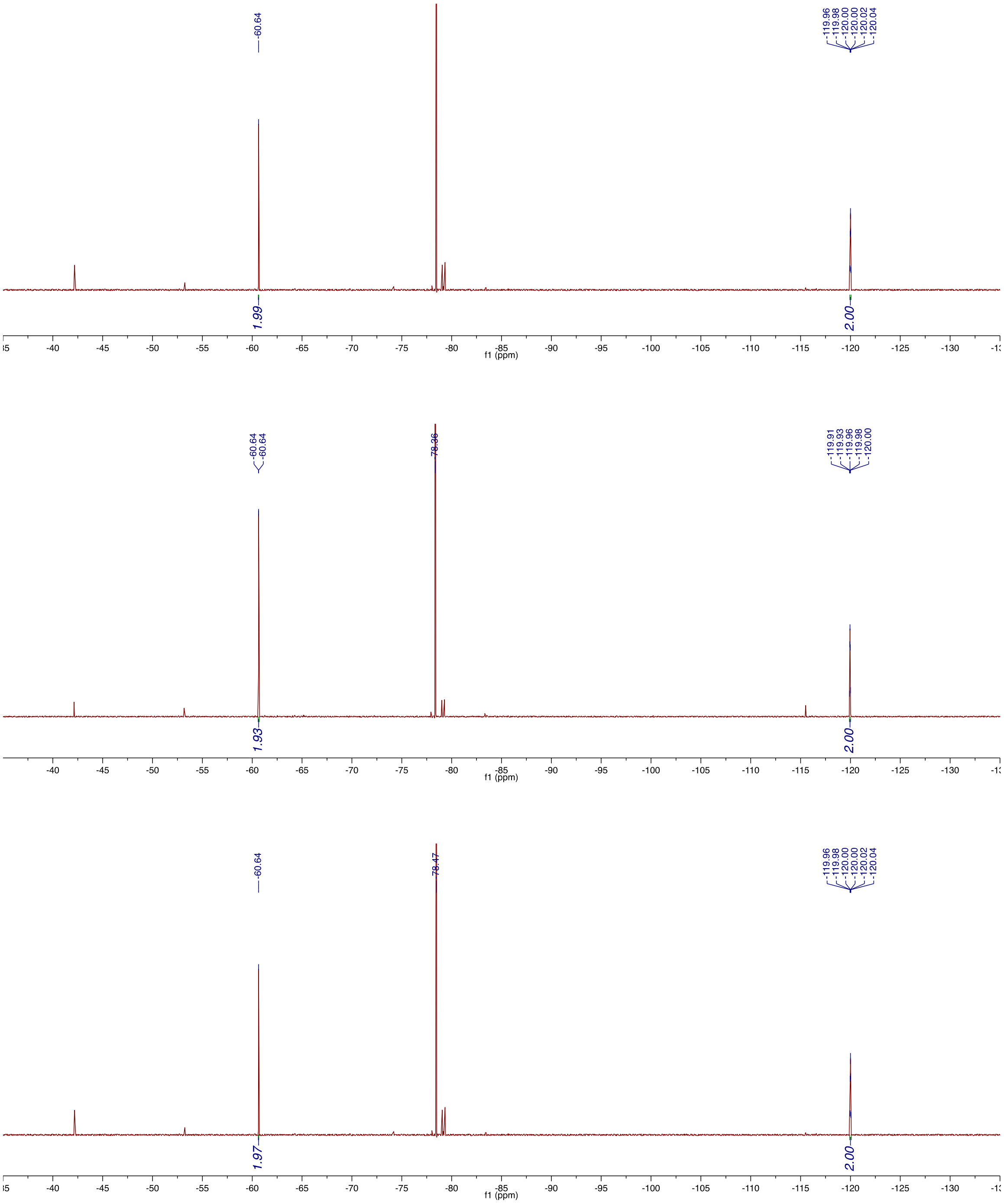
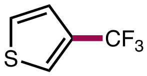


Figure S38. ^{19}F NMR assay for 5-(trifluoromethyl)benzo[*d*][1,3]dioxole **(S18)**

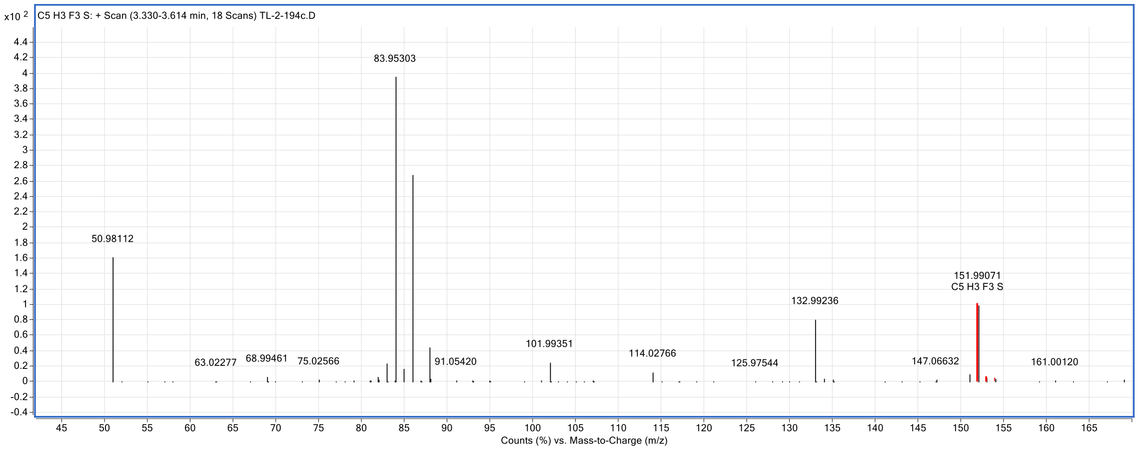


3-(trifluoromethyl)thiophene (S19)

Prepared following the general procedure outlined above using Ir[dFMeppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (0.65 mg, 0.625 μmol, 0.00125 equiv.), K_3PO_4 (425 mg, 2.0 mmol, 4.0 equiv.), *dMesSCF$_3$* reagent (368.0 mg, 0.75 mmol, 1.5 equiv.), 3-bromothiophene (80.0 mg, 0.5 mmol, 1.0 equiv.), CuBr$_2$•2LiBr (5.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.), and TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.).

Yield was determined by ^{19}F NMR due to the high volatility of the desired product.

1,4-difluorobenzene (26 μL, 0.25 mmol, 0.5 equiv.) was added as the internal standard for ^{19}F NMR analysis (DMSO-d6). (56% yield).



HRMS (GC-EI-TOF) m/z calcd. for $C_5H_3F_3S$ ($[M^*]^+$) 151.9902, found 151.9907.

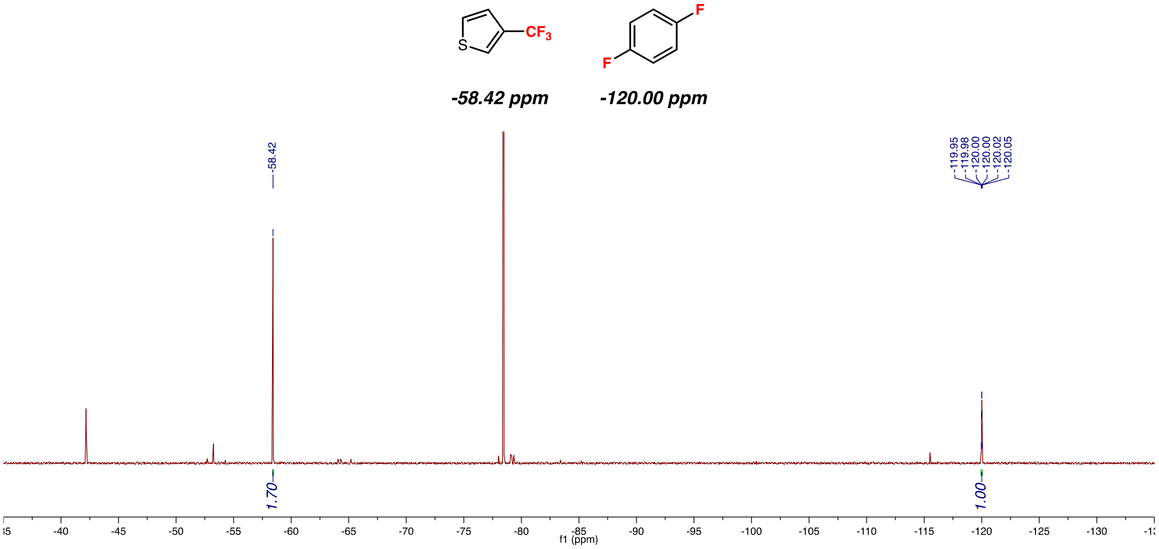


Figure S39. ^{19}F NMR assay for 5-(trifluoromethyl)benzo[*d*][1,3]dioxole **(S19)**

12) Stern-Volmer quenching experiments

Emission intensities were recorded using a Perkin Elmer LS50 luminescence spectrophotometer. All Ir[dFFppy]$_2$-(4,4'-dCF$_3$bpy)PF$_6$ solutions were excited at 380 nm and the emission intensity was collected at 400 to 800 nm. In a typical experiment, to a 3.06•10^{-4} M solution of Ir[dFFppy]$_2$-(4,4'-dCF$_3$bpy)PF$_6$ in acetone was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing the sample with a stream of nitrogen for 10 minutes, the emission of the sample was collected.

Stern-Volmer quenching experiment strongly indicate that oxidation of TMS$_3$SiOH by the excited photocatalyst is more likely to occur vs. reduction of the dMesSCF$_3$ reagent.

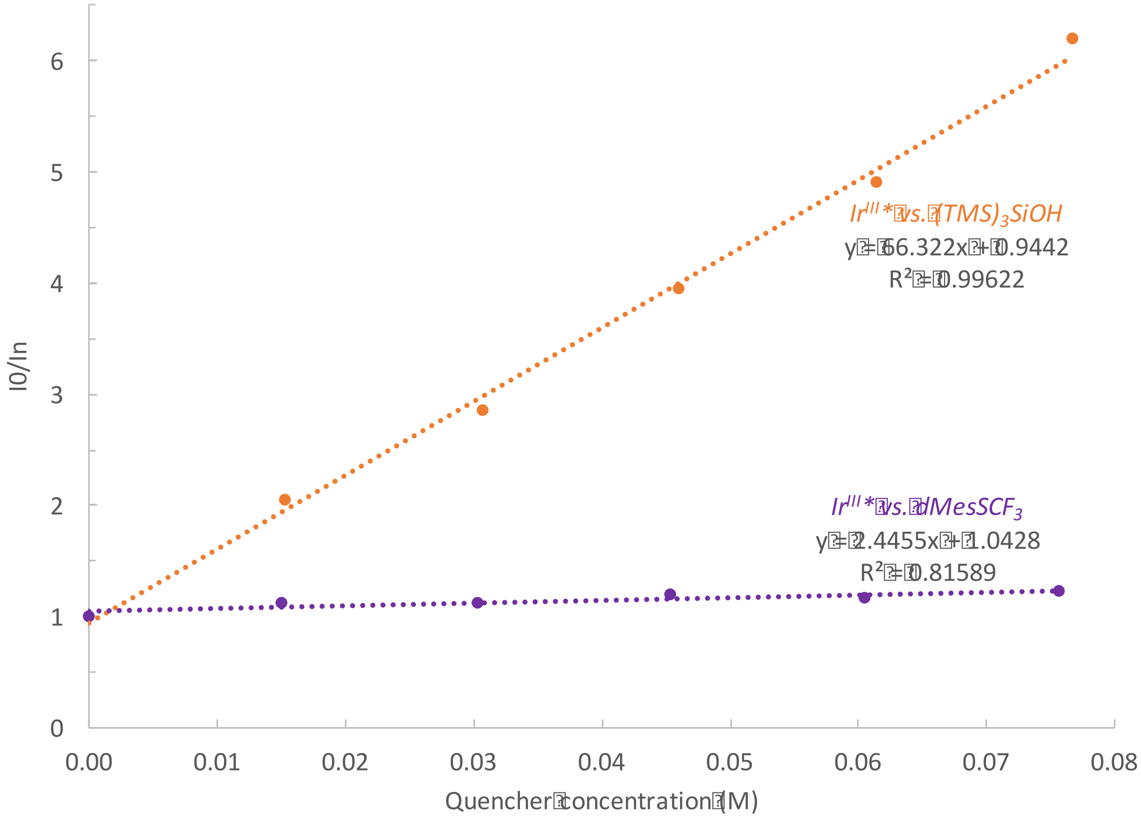
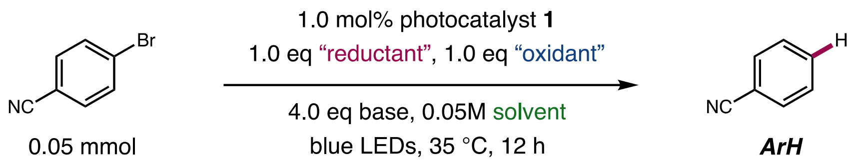


Figure S40. Stern-Volmer plot comparing quenching of excited photocatalyst Ir[dFFppy]$_2$-(4,4'-dCF$_3$bpy)PF$_6$ **(1)** against supersilanol **(4)** and dMesSCF$_3$ reagent **(8)**.

13) Radical probe experiments under copper-free conditions



entry	***"reductant"***	***"oxidant"***	***base***	***solvent***	***ArH***	ArBr	$ArCF_3$
1	TMS_3SiOH	$dMesSCF_3$	Na_2CO_3	acetone	***66%***	10%	0%
2	TMS_3SiOH	$dMesSCF_3$	Na_2CO_3	acetone-d_6	***51%*** ***(53% D)***	7%	0%
3	TMS_3SiOH	$dMesSCF_3$	none	acetone	***47%***	33%	0%
4	TMS_3SiOH	$K_2S_2O_8$	none	acetone	***45%***	50%	N/A
5	TMS_3SiOH	$K_2S_2O_8$	none	acetone-d_6	***40%*** ***(80% D)***	50%	N/A
6	NEt_3	$K_2S_2O_8$	none	acetone	***0%***	>99%	N/A
7	NEt_3	none	none	acetone	***0%***	>99%	N/A

Figure S41. Radical probe via aryl halide reduction under copper-free conditions.

General procedure: Under air, an 8-mL vial equipped with a magnetic stir bar was charged with all the solid components, followed by solvent and silanol. The reaction mixture was sparged with nitrogen for 15 minutes at 0 ºC. The reaction vial was then parafilmed and irradiated with 40W Kessil A160WE Tuna Blue from 5 cm away. Regular fans are employed to maintain the temperature at 35 °C. The final reaction mixture was quenched by exposure to air. Internal standard (1,4-difluorobenzene, 1 equiv) was added and the mixture was analyzed by ^{1}H NMR in DMSO-d_6.

Incomplete deuterium incorporation in entry 2 is ascribed to the presence of weak benzylic C–H in $dMesSCF_3$ reagent. Higher incorporation was observed when a different oxidant was used (see below). Substitution of $dMesSCF_3$ with an oxidant such as $K_2S_2O_8$ resulted in similar result. In addition, performing the reaction in acetone-d_6 resulted in high incorporation of deuterium (80% D, entry 5). The crucial role of TMS_3SiOH was demonstrated when triethylamine was used as a "reductant", resulted in no conversion of the starting material (entry 6). Finally, reduction of the aryl bromide by the photocatalyst (excited or ground state) does not seem to be feasible, as shown in entry 7.

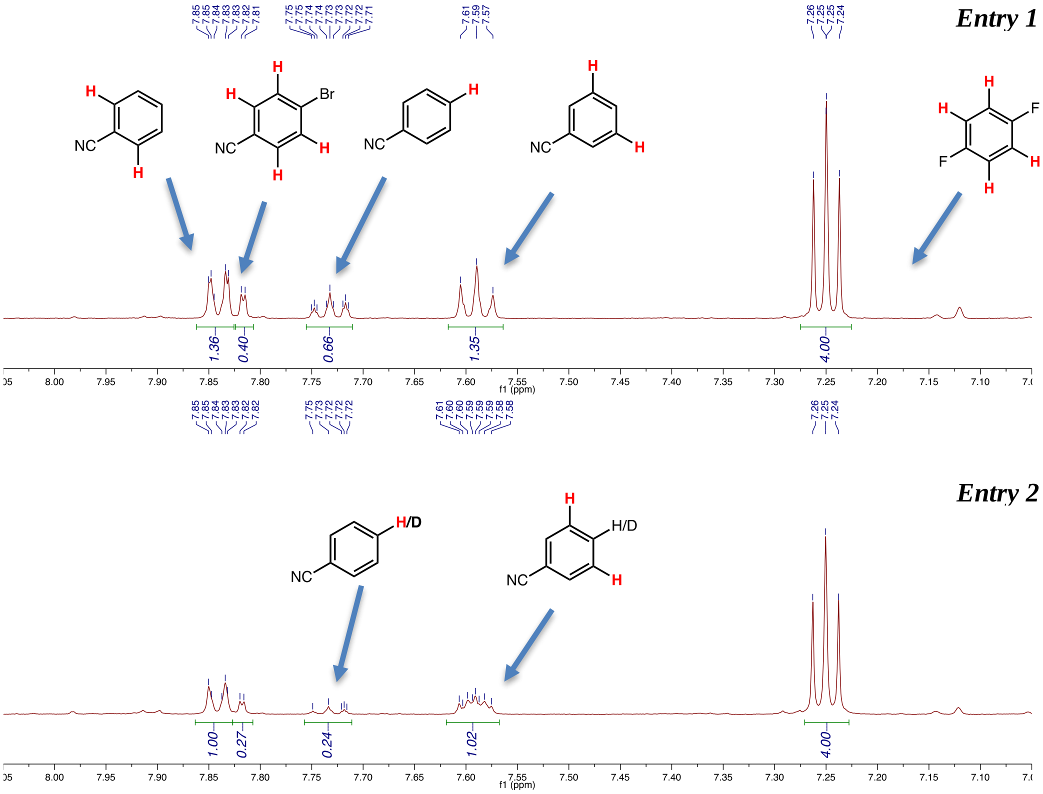
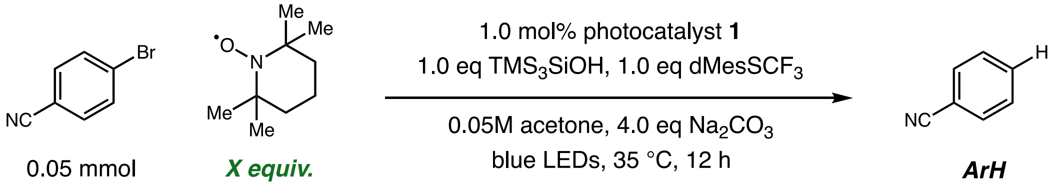


Figure S42. ^{1}H NMR analysis of entry 1 and entry 2 from figure ***S36***.

14) TEMPO trapping experiments



TEMPO	***ArH***	ArBr	***ArTEMPO***
none	***71%***	10%	***N/A***
1.0 equiv.	***43%***	45%	***10%***
2.0 equiv.	***31%***	40%	***15%***
4.0 equiv.	***0%***	84%	***10%***

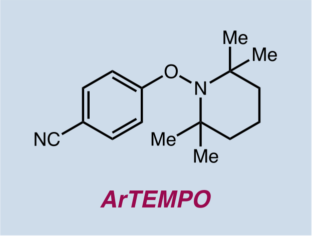
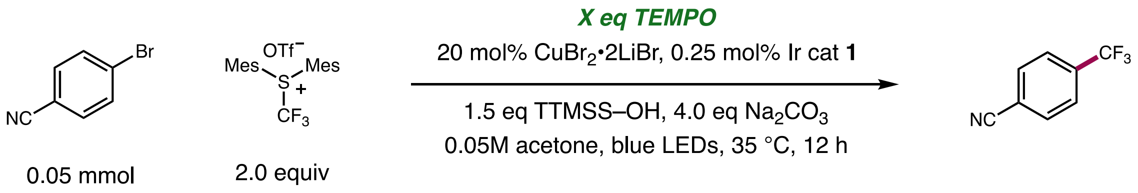


Figure S43. TEMPO trapping experiment under copper-free conditions.

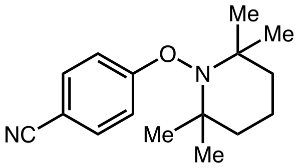
<u>*General procedure:*</u> Under air, an 8-mL vial equipped with a magnetic stir bar was charged with all the solid components, followed by solvent and silanol. The reaction mixture was sparged with nitrogen for 15 minutes at 0 ºC. The reaction vial was then parafilmed and irradiated with 40W Kessil A160WE Tuna Blue from 5 cm away. Regular fans are employed to maintain the temperature at 35 °C. The final reaction mixture was quenched by exposure to air. Internal standard (1,4-difluorobenzene, 1 equiv) was added and the mixture was analyzed by ^{1}H NMR in DMSO-*d*$_6$. ArTEMPO product yield was determined by isolation.



TEMPO	***ArCF3***	ArBr	ArH	***ArTEMPO***
none	***89%***	<1%	3%	***N/A***
1.0 equiv.	***55%***	25%	7%	***1%***
2.0 equiv.	***15%***	38%	23%	***7%***
4.0 equiv.	***0%***	92%	0%	***6%***

Figure S44. TEMPO trapping under Cu-catalyzed trifluoromethylation conditions.

General procedure: Under air, an 8-mL vial equipped with a magnetic stir bar was charged with all the solid components, followed by acetone solution of $CuBr_2$•2LiBr (1.0 mL acetone solution, 0.02M, 0.1 mmol, 0.20 equiv.) and silanol. The reaction mixture was sparged with nitrogen for 15 minutes at 0 ºC. The reaction vial was then parafilmed and irradiated with 40W Kessil A160WE Tuna Blue from 5 cm away. Regular fans are employed to maintain the temperature at 35 °C. The final reaction mixture was quenched by exposure to air. Internal standard (1,4-difluorobenzene, 1 equiv) was added and the mixture was analyzed by ^{1}H NMR in DMSO-d_6. ArTEMPO product yield was determined by isolation.



4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzonitrile (57)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.3 Hz, 2H), 7.25 (bs, 2H), 1.68-1.56 (m, 5H), 1.45-1.41 (m, 1H), 1.23 (s, 6H), 0.97 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 133.7, 119.8, 115.0, 103.3, 60.9, 39.8, 32.5, 20.6, 17.0.

Data are consistent with those reported in the literature: D. A. Leas, Y. Dong, J. L. Vennerstrom, D. E. Stack, *Org. Lett.* **19**, 2518–2521 (2017).

15) Radical cyclization experiments

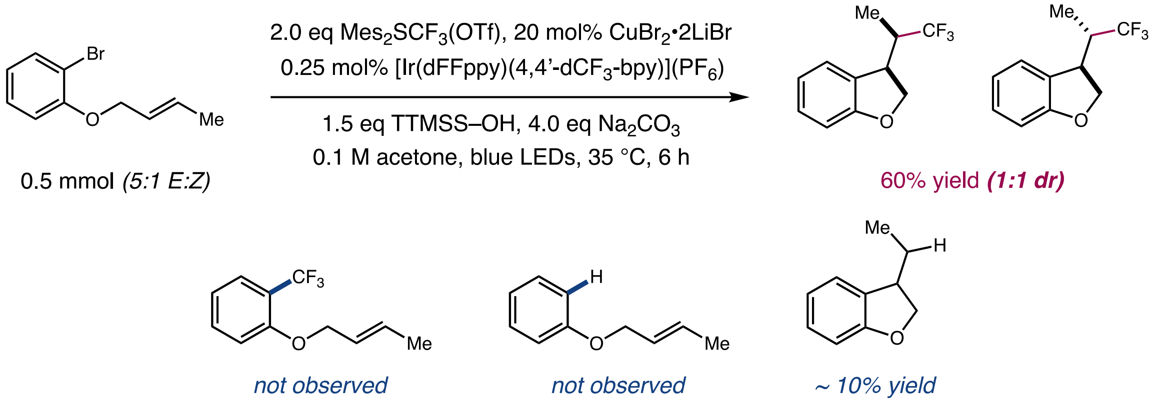


Figure S42. Summary of radical cyclization experiment.

To an oven-dried 8-mL vial equipped with a stir bar was added Ir[dFFppy]$_2$(4,4'-dCF$_3$bpy)PF$_6$ (1.3 mg, 1.25 µmol, 0.0025 equiv.), Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv.), and *dMesSCF$_3$* reagent (489.0 mg, 1.0 mmol, 2.0 equiv.). To an oven-dried 40-mL vial equipped with a stir bar, a solution of CuBr2•LiBr was prepared by dissolving CuBr$_2$ (67.0 mg, 0.03 mmol) and LiBr (52.1 mg, 0.06 mmol) in 15.0 mL of anhydrous acetone. This copper solution was stirred for 15 minutes before 5.0 mL was added to the reaction vial via syringe. 1-bromo-2-(but-2-en-1-yloxy)benzene (5 to 1 E/Z mixture, 114.0 mg, 0.5 mmol) was added, followed by addition of TMS$_3$SiOH (198 mg, 0.75 mmol, 1.5 equiv.). The reaction mixture was sparged with nitrogen at 0 ºC for 15 minutes before the reaction vial was parafilmed to protect from air during the course of the reaction. The reaction vial was irradiated with two 40W Kessil A160WE (maximum blue with maximum intensity setting) from 6 cm away with fan cooling. Once the reaction is complete, the vial was slowly vented then quenched by exposure to air. The reaction mixture was diluted with EtOAc (10 mL) and shaken with a mixture of NaHCO$_3$ (sat aq, 5 mL). 1,4-difluorobenzene (52 µL, 0.5 mmol, 1.0 equiv.) was added and an aliquot from the organic layer was taken for NMR analysis in DMSO-*d*$_6$. The remaining organic solution was dried with Na$_2$SO$_4$ then concentrated. The diastereomers of the desired product was isolated by multiple rounds of preparative TLC and SFC and they are fully characterized below.

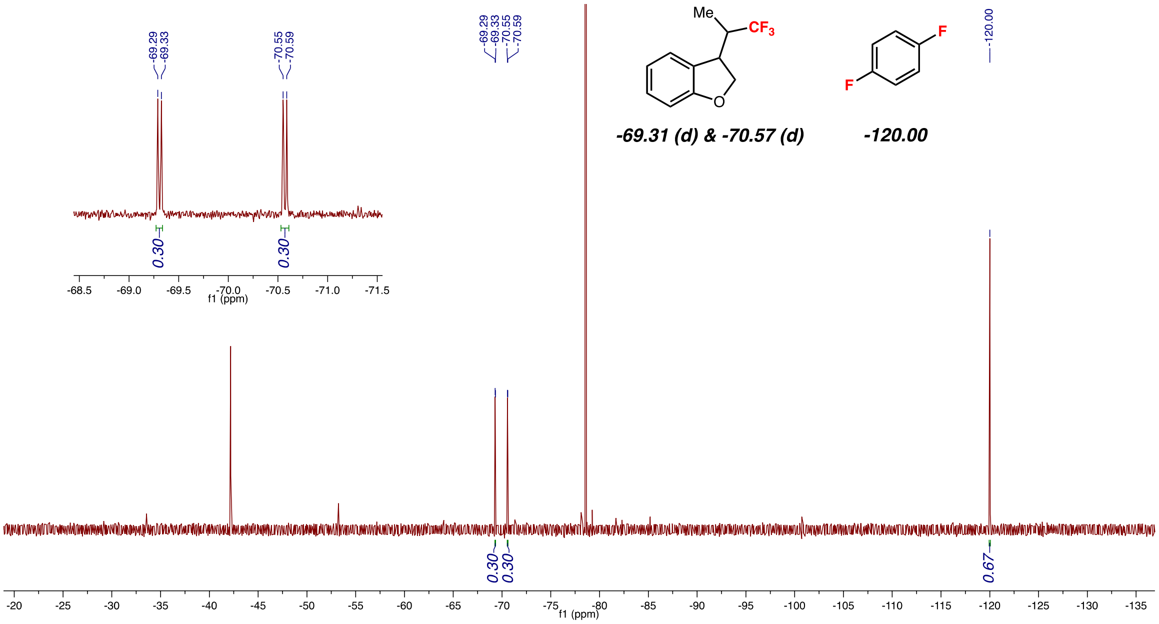
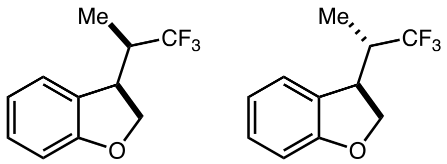


Figure S46. ^{19}F NMR analysis of radical cyclization experiment.

The E to Z ratio (5 to 1) of the starting material was monitored by 1H NMR and was shown to be constant during the course of the reaction. In addition, the remaining starting material was recovered during purification and the E to Z ratio was found to be 5 to 1.

time	**sm**	***prod.***
0 h	**98% (5:1 E:Z)**	***0%***
1 h	**60% (5:1 E:Z)**	***40% (1:1 dr)***
3 h	**20% (5:1 E:Z)**	***60% (1:1 dr)***
6 h	**15% (5:1 E:Z)**	***60% (1:1 dr)***



3-(1,1,1-trifluoropropan-2-yl)-2,3-dihydrobenzofuran (59)

<u>Diastereomer #1:</u>

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20-7.12 (m, 2H), 6.90 (td, *J* = 7.4, 1.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.60-4.49 (m, 2H), 3.97-3.90 (m, 1H), 2.71-2.58 (m, 1H), 0.98 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 160.2, 129.1, 128.0 (q, *J* = 280.3 Hz), 127.1, 124.0, 120.9, 109.9, 71.3 (d, *J* = 2.1 Hz), 40.8 (q, *J* = 25.3 Hz), 40.6 (q, *J* = 2.2 Hz), 7.4 (q, *J* = 2.7 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ -71.38 (d, *J* = 9.7 Hz, 3F).

IR (film) ν_{max} 2954, 2896, 1612, 1595, 1483, 1461, 1269, 1230, 750 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{11}F_3O$ ([M]$^{*+}$) 216.0756, found 216.0764.

<u>Diastereomer #2:</u>

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27-7.25 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.65 (t, *J* = 9.2 Hz, 1H), 4.38 (dd, *J* = 9.3, 4.4 Hz, 1H), 3.74 (dt, *J* = 9.3, 4.7 Hz, 1H), 2.49-2.38 (m, 1H), 1.07 (dt, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 160.9, 129.0, 127.9 (q, *J* = 280.2 Hz), 126.8 (q, *J* = 2.2 Hz), 125.4, 120.6, 110.0, 76.1 (q, *J* = 1.7 Hz), 42.0 (q, *J* = 25.3 Hz), 41.1 (q, *J* = 2.2 Hz), 9.7 (q, *J* = 2.9 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ -70.23 (d, *J* = 9.5 Hz, 3F).

IR (film) ν_{max} 2923, 1599, 1485, 1460, 1368, 1262, 1235, 1173, 1095, 1019, 750 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{11}F_3O$ ([M]$^{*+}$) 216.0756, found 216.0756.

16) Consideration of excited Cu(I)-CF_3 mechanism

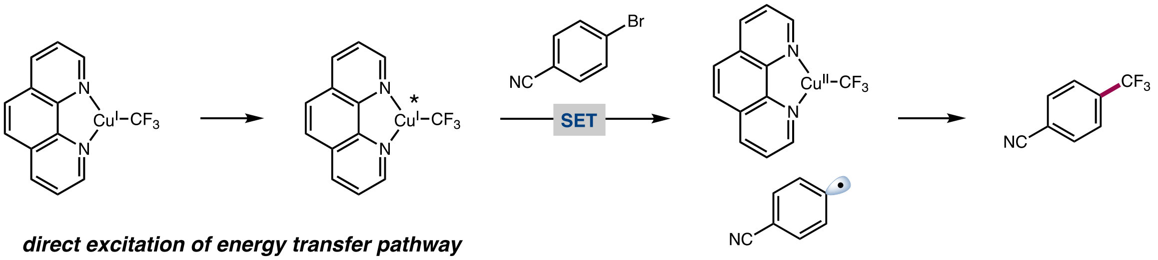


Figure S47. Possible photoexcited Cu(I)-CF_3 pathway.

While it is possible to postulate that a Cu(I)-CF_3 complex can undergo photoexcitation (direct excitation or energy transfer), followed by a rebound oxidative mechanism (ref 31 in the manuscript), to generate a Cu(III)-arene-CF_3 intermediate, which should undergo reductive elimination to give the desired trifluoromethylarene (Figure S42). Attempts to study such process using readily available (phen)Cu-CF_3 complex did not give sufficient yield with the standard substrate of 4-bromobenzonitrile. Moreover, when more electron-rich substrate such as 4-bromoanisole was used, this resulted in complete recovery of starting material. Given the high efficiency of the optimized conditions with silanol, regardless of the electronic properties of the arene substrate, it is highly unlikely that a mechanism involving excited Cu(I)-CF_3 is the major contributor to the formation of the desired product.

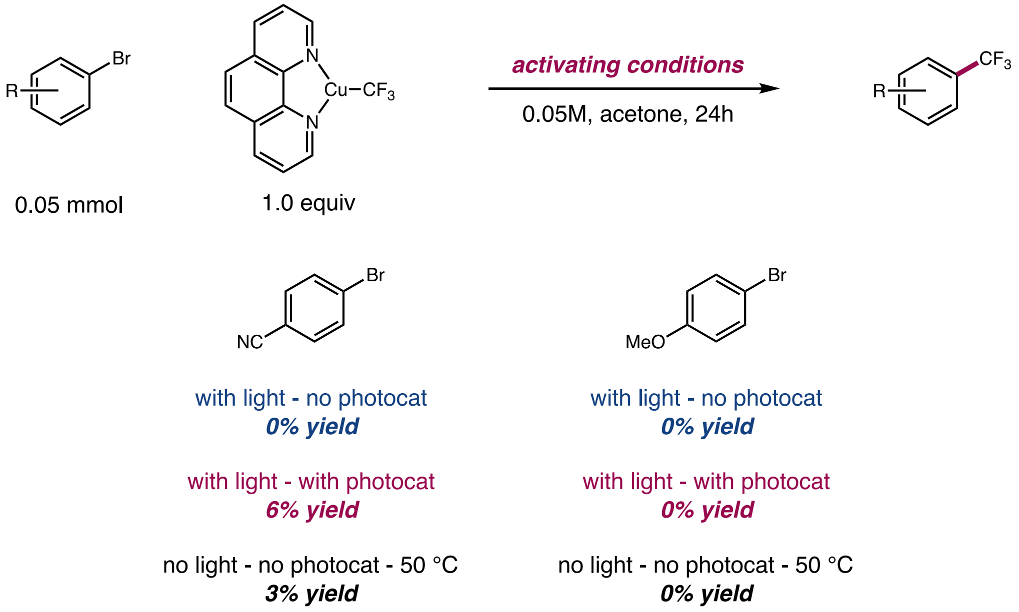


Figure S48. Stoichiometric studies of photoexcited Cu(I)-CF_3 complex.

17) Evidence for formation of radical CF_3

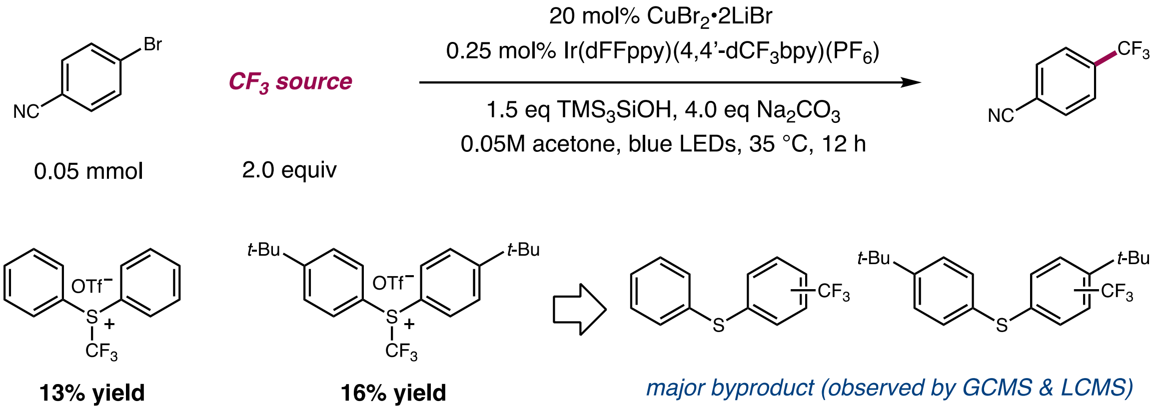
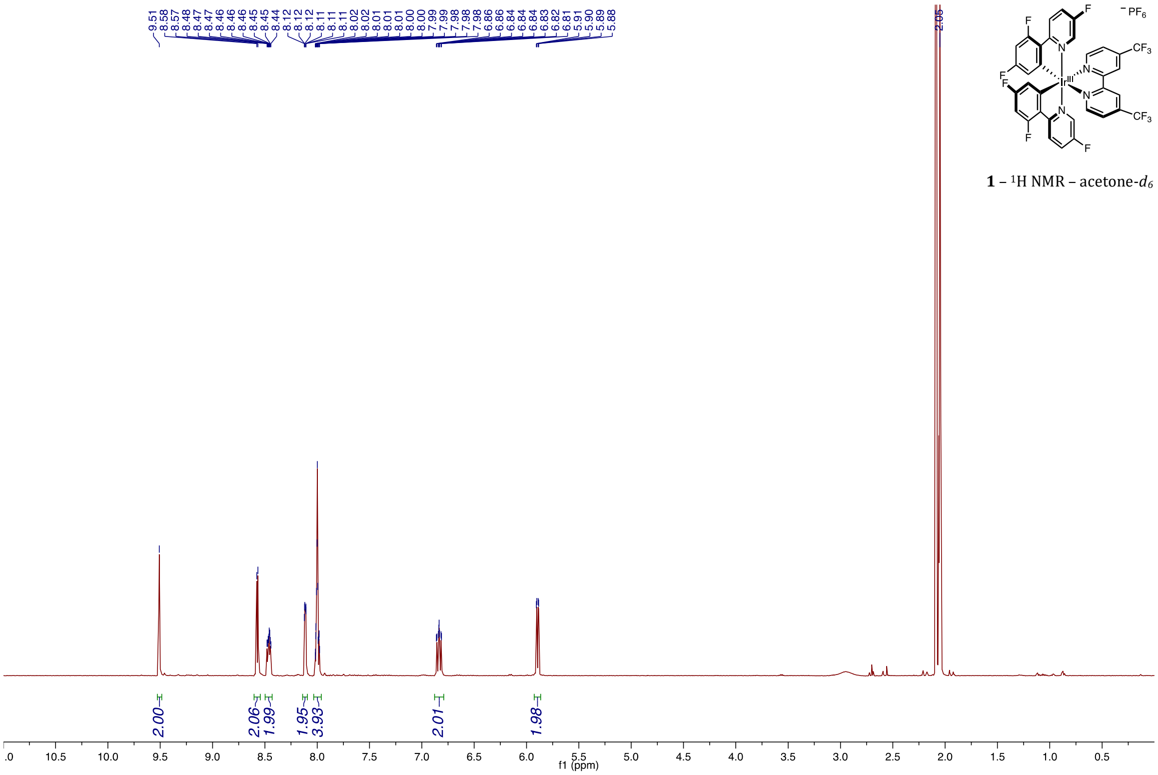


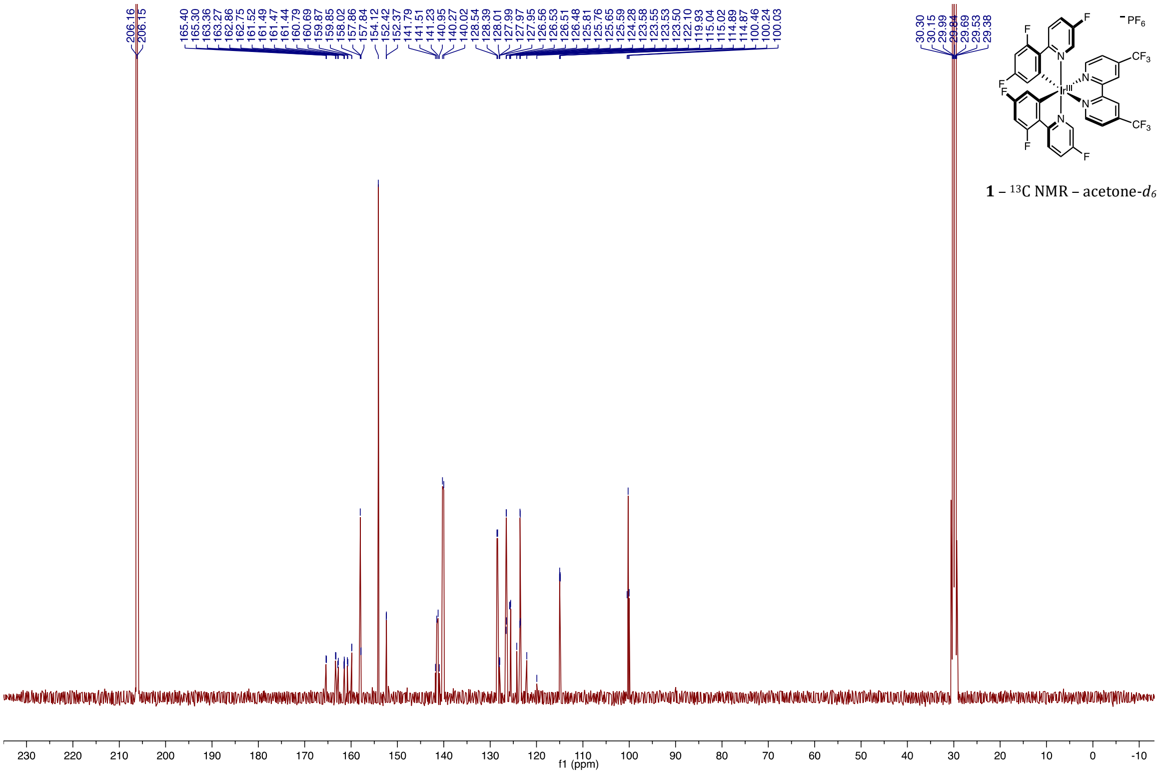
Figure S49. Evidence for radical CF_3 formation under reaction conditions.

While we were able to observe TEMPO-CF_3 adduct during the TEMPO trapping experiments, the background interaction between TEMPO and electrophilic CF_3 source to yield TEMPO-CF3 prevented us from making a conclusion based on this evidence. To date, the best evidence we have observed for formation of CF_3 radical has been the formation of trifluoromethylated diaryl sulfide (Figure S44).

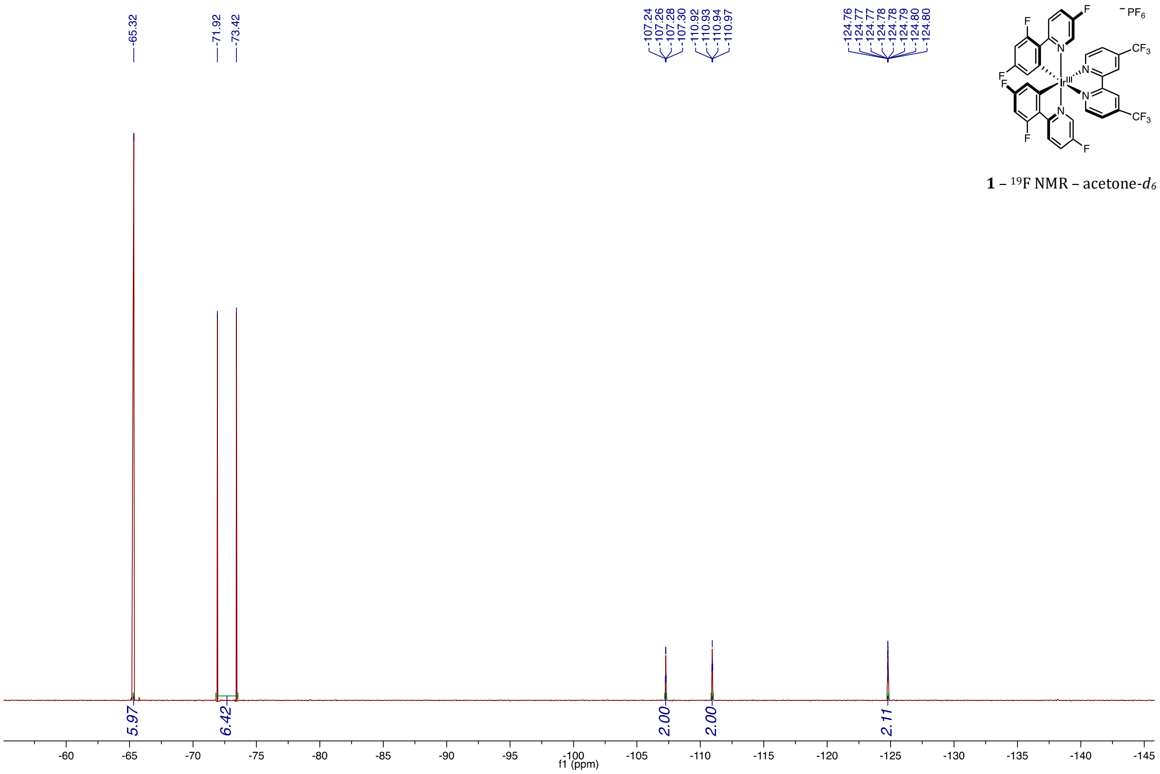
18) Spectral Data



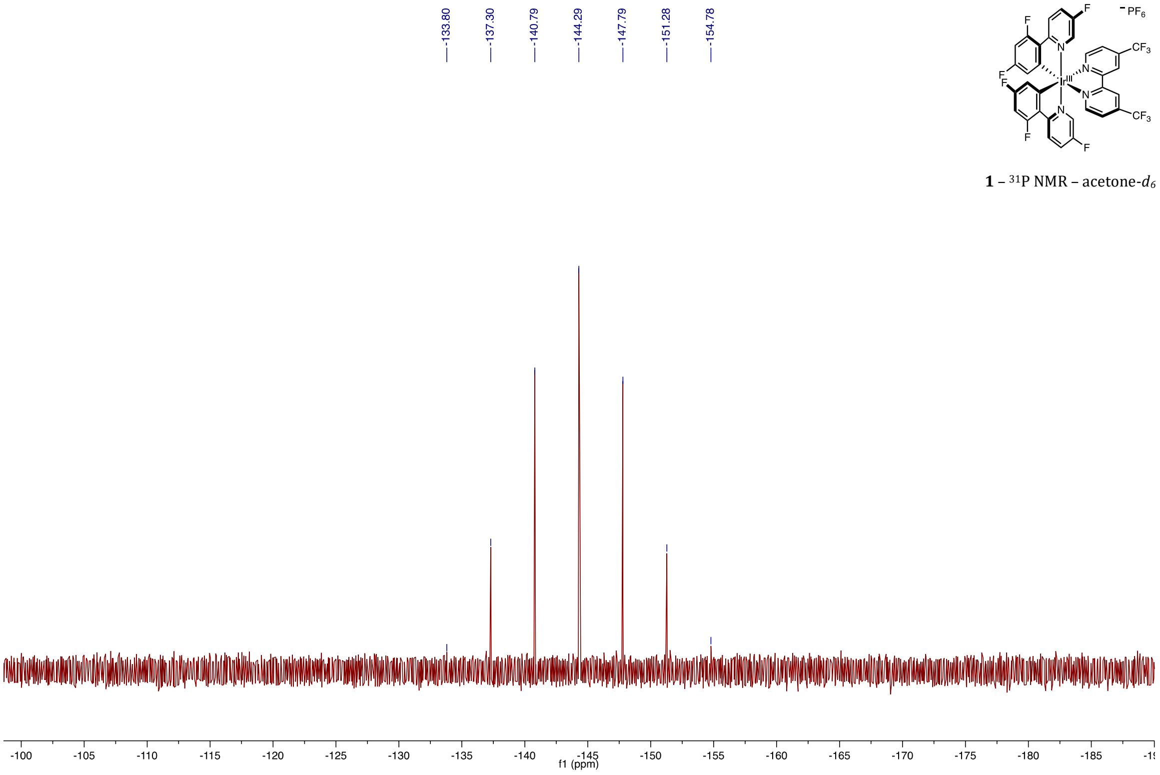
1 – ^{1}H NMR – acetone-d_6



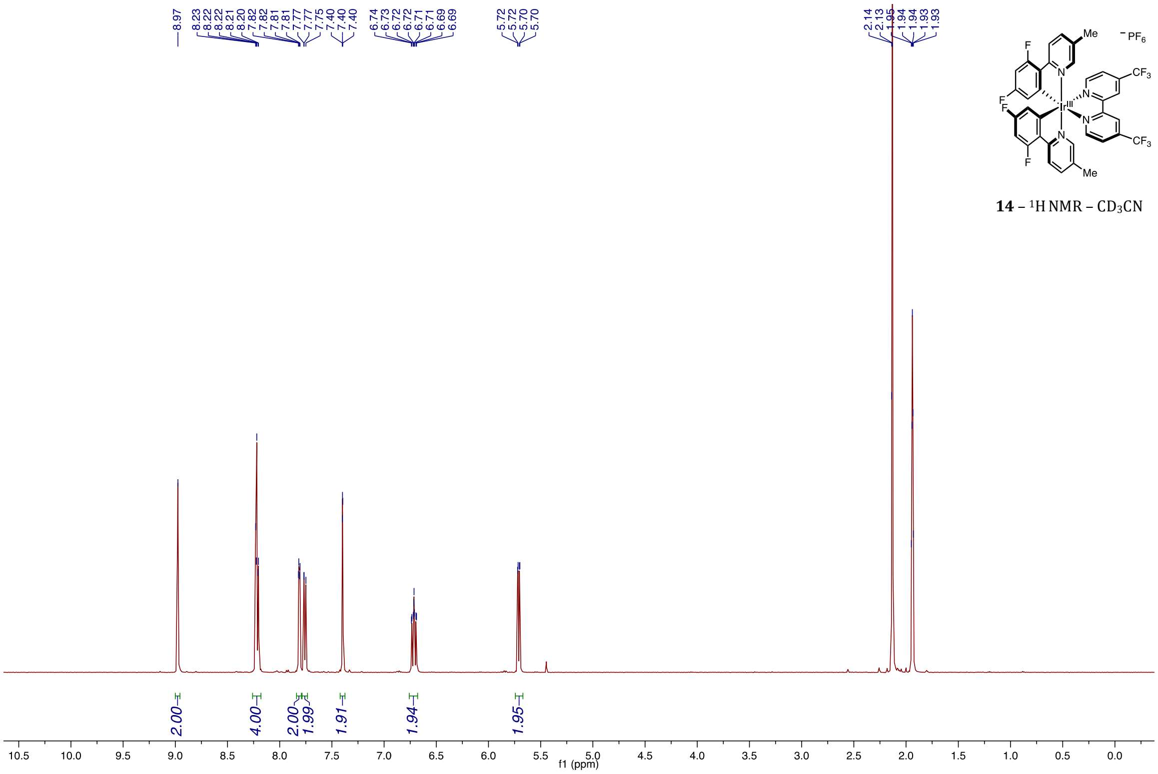
1 – ^{13}C NMR – acetone-d_6



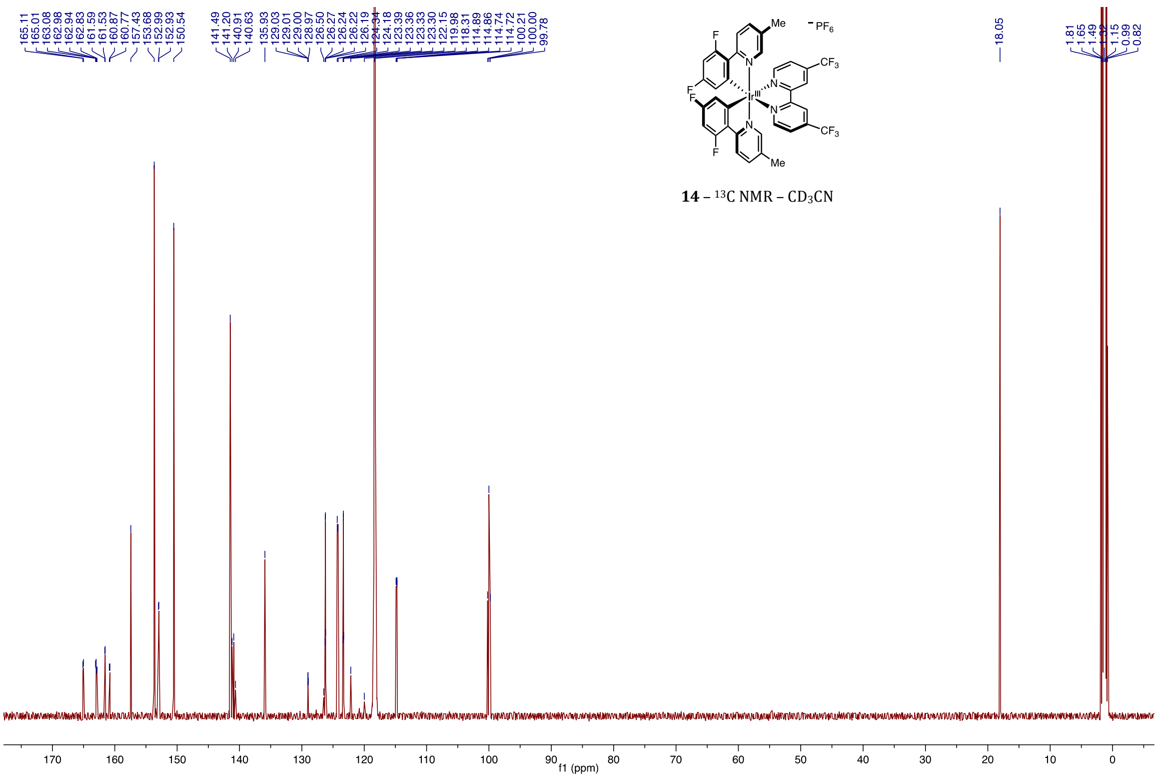
1 – ^{19}F NMR – acetone-d_6



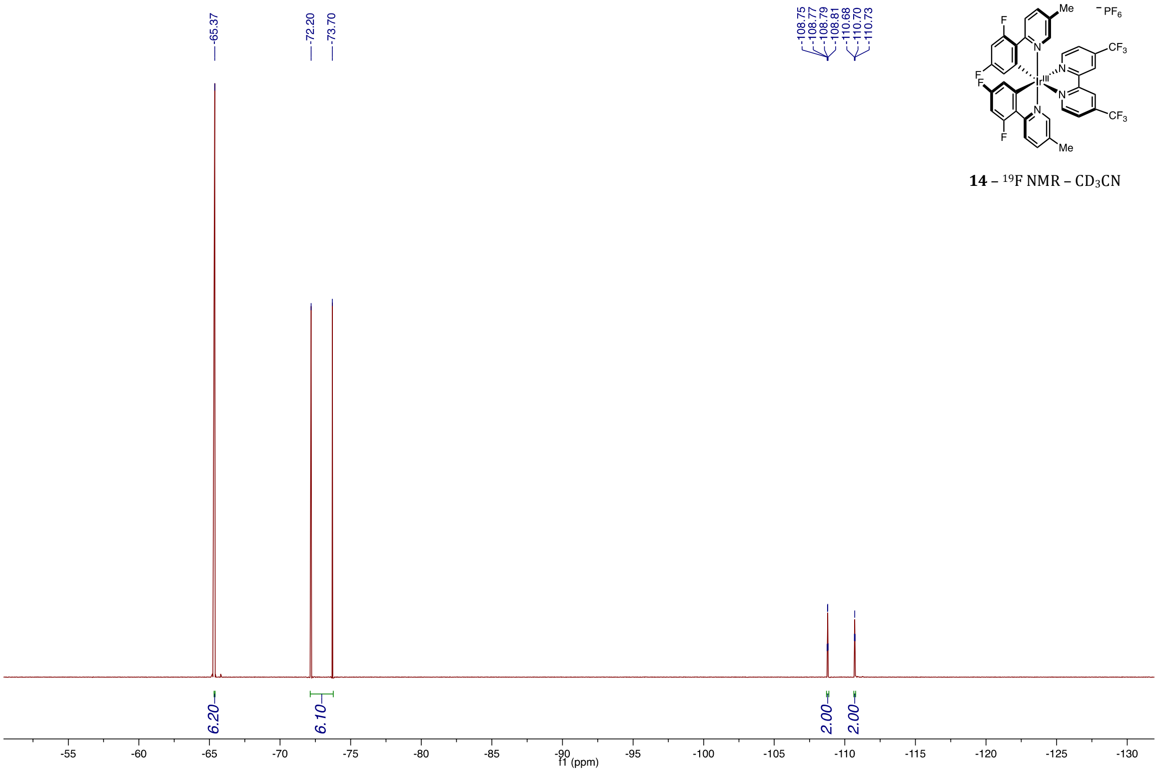
1 – ^{31}P NMR – acetone-d_6



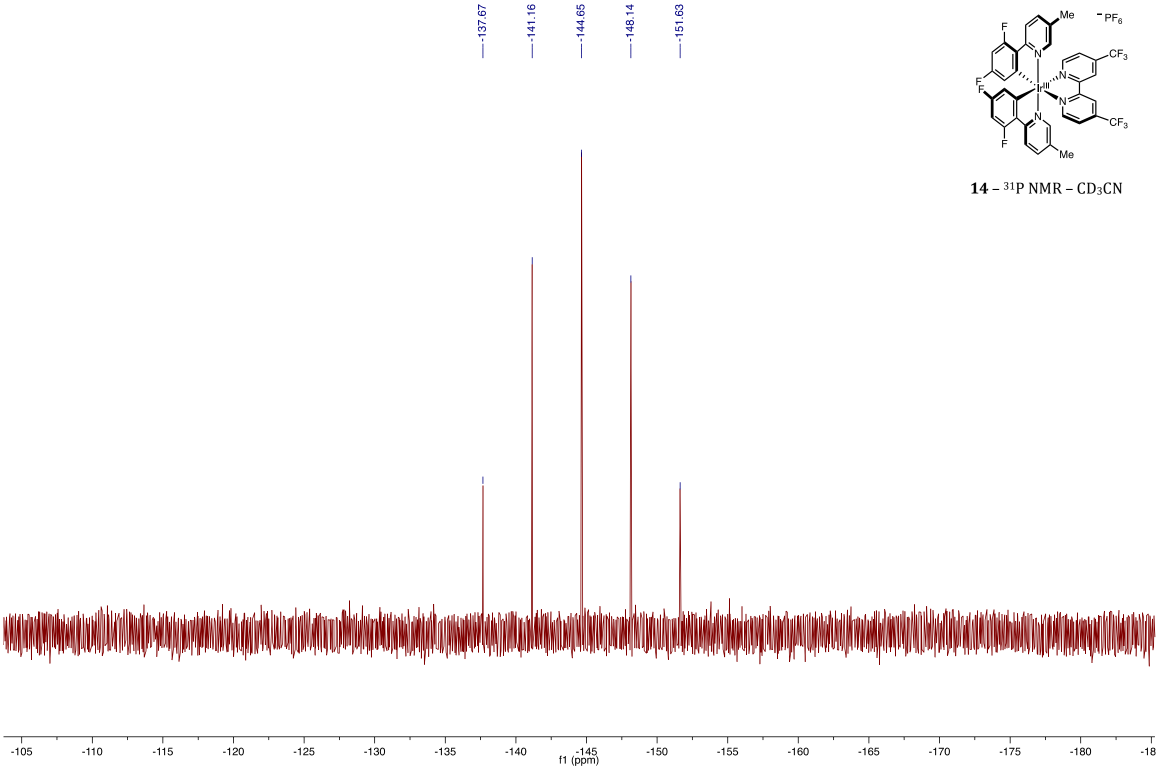
14 – ^{1}H NMR – CD$_3$CN



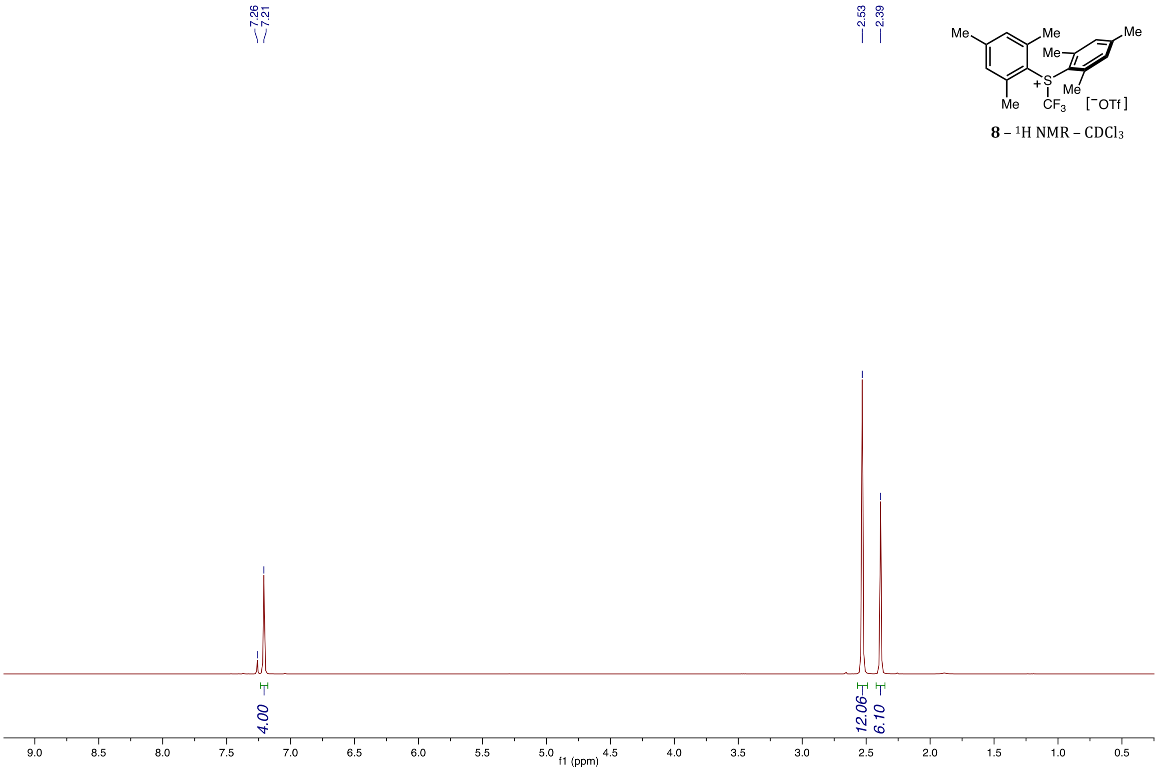
14 – ^{13}C NMR – CD$_3$CN



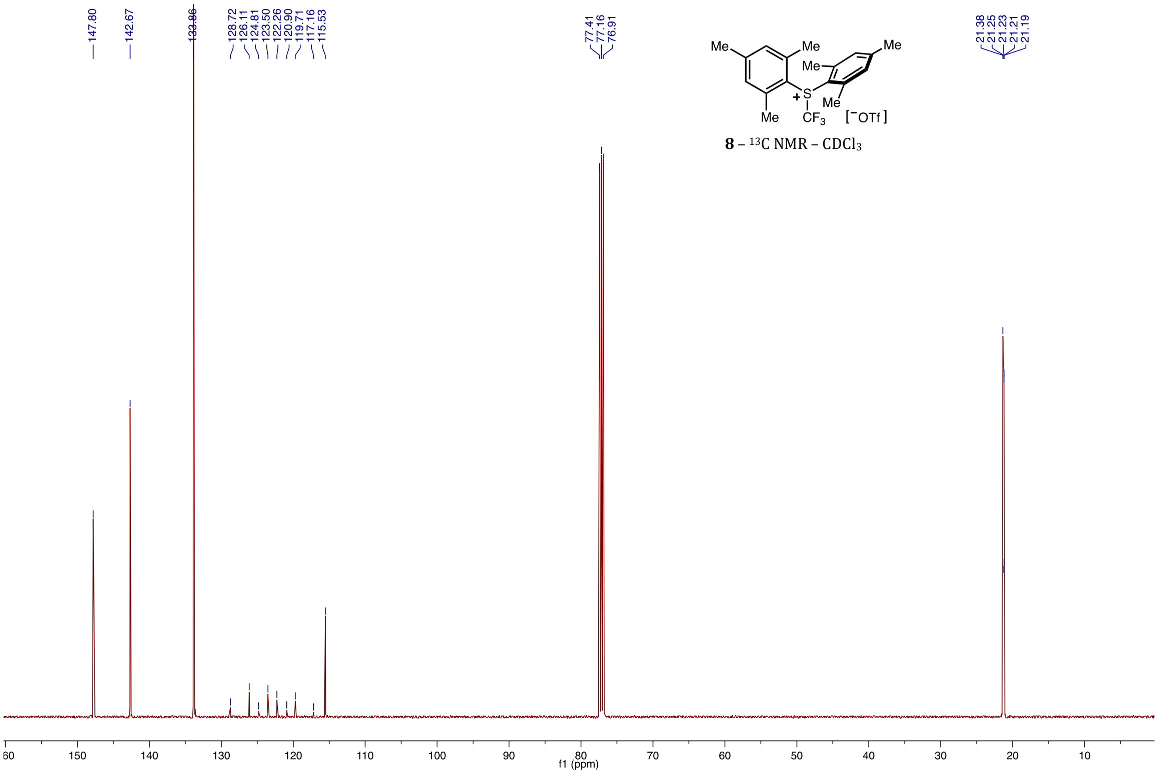
14 – ^{19}F NMR – CD_3CN



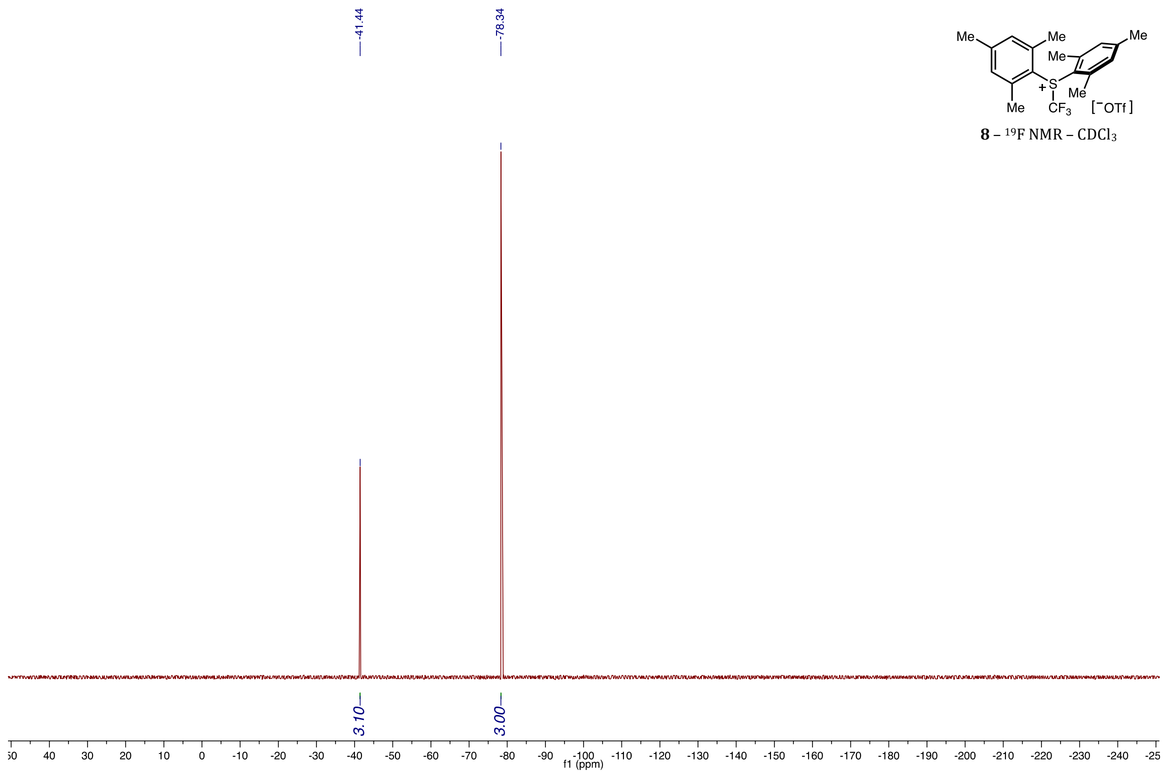
14 – ^{31}P NMR – CD_3CN



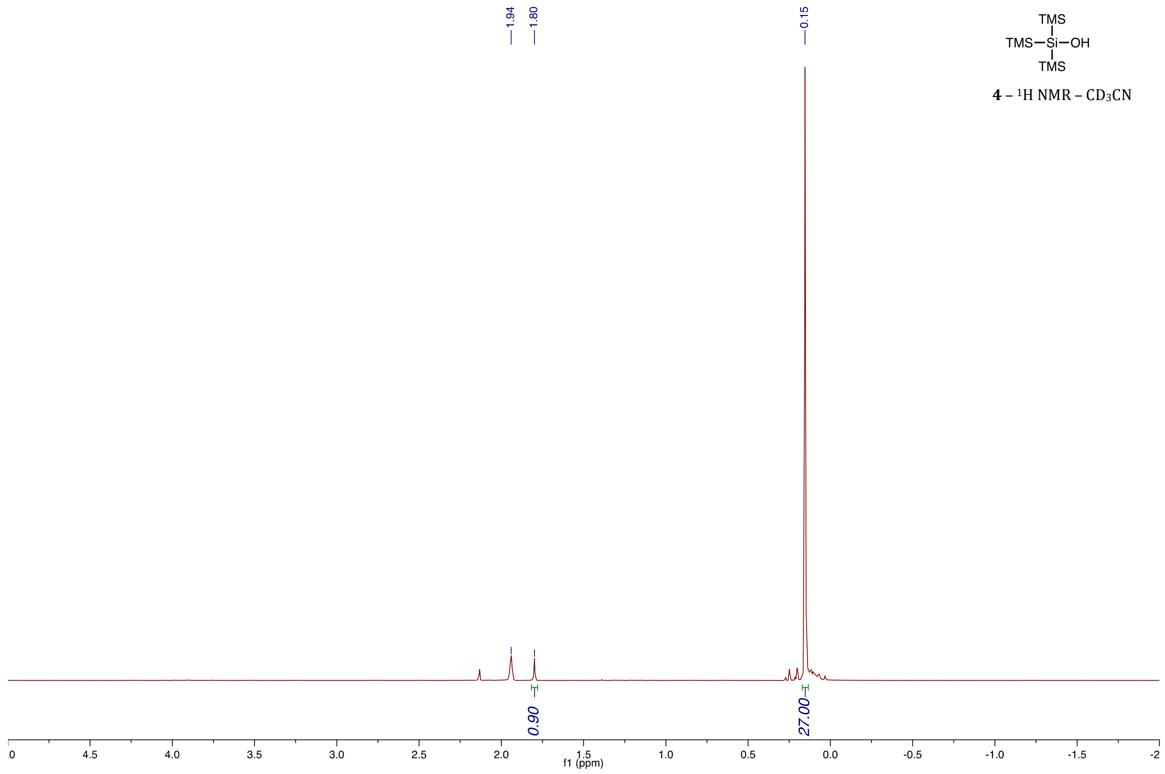
8 – ^{1}H NMR – CDCl$_3$



8 – ^{13}C NMR – CDCl$_3$

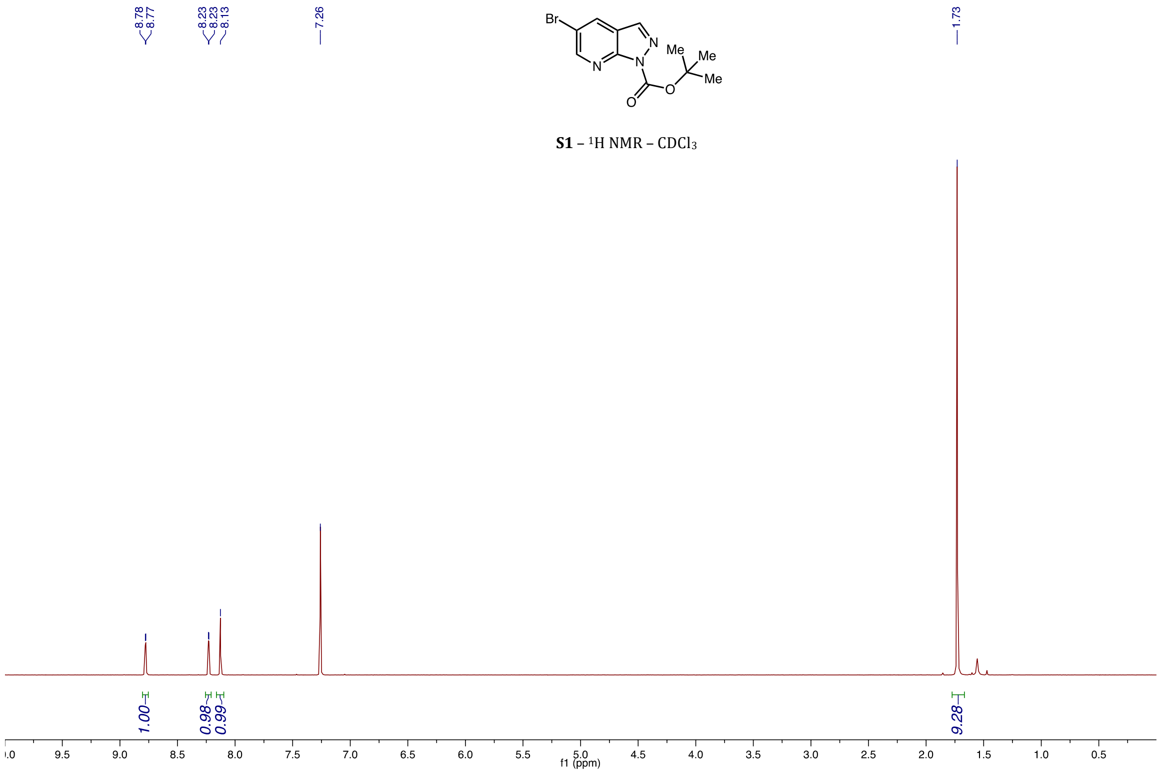


8 – ^{19}F NMR – $CDCl_3$

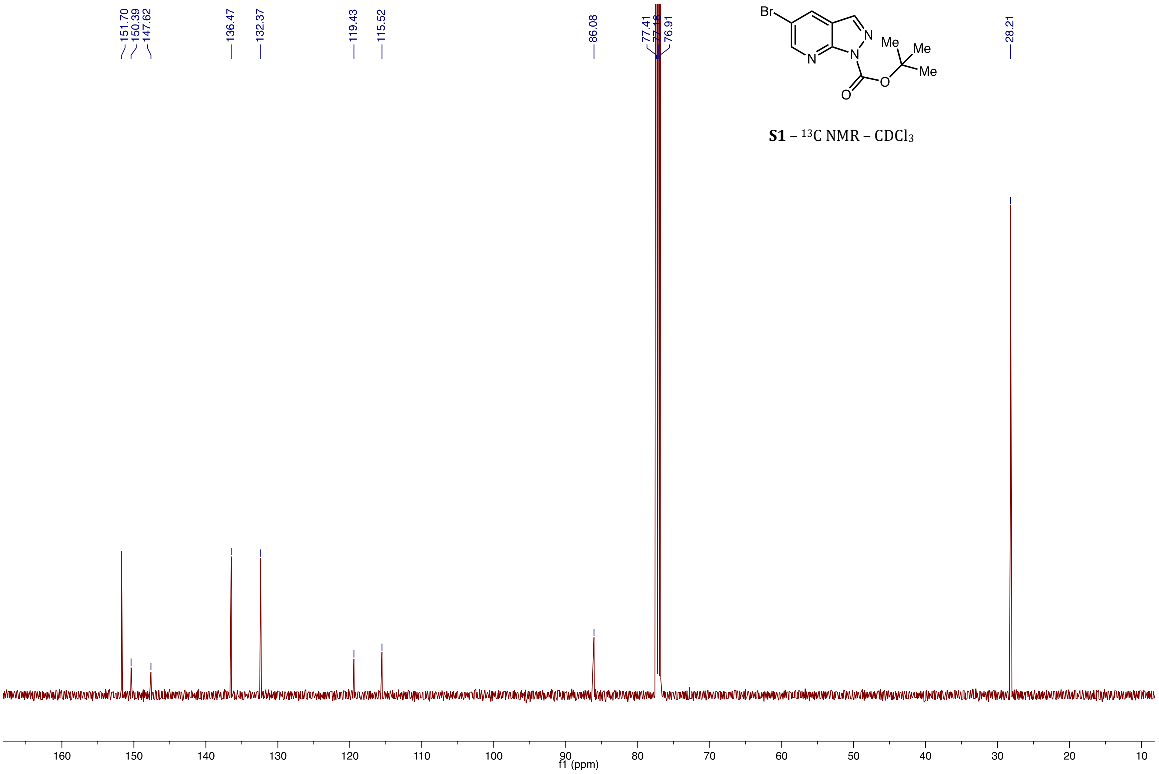


4 – ^{1}H NMR – CD_3CN

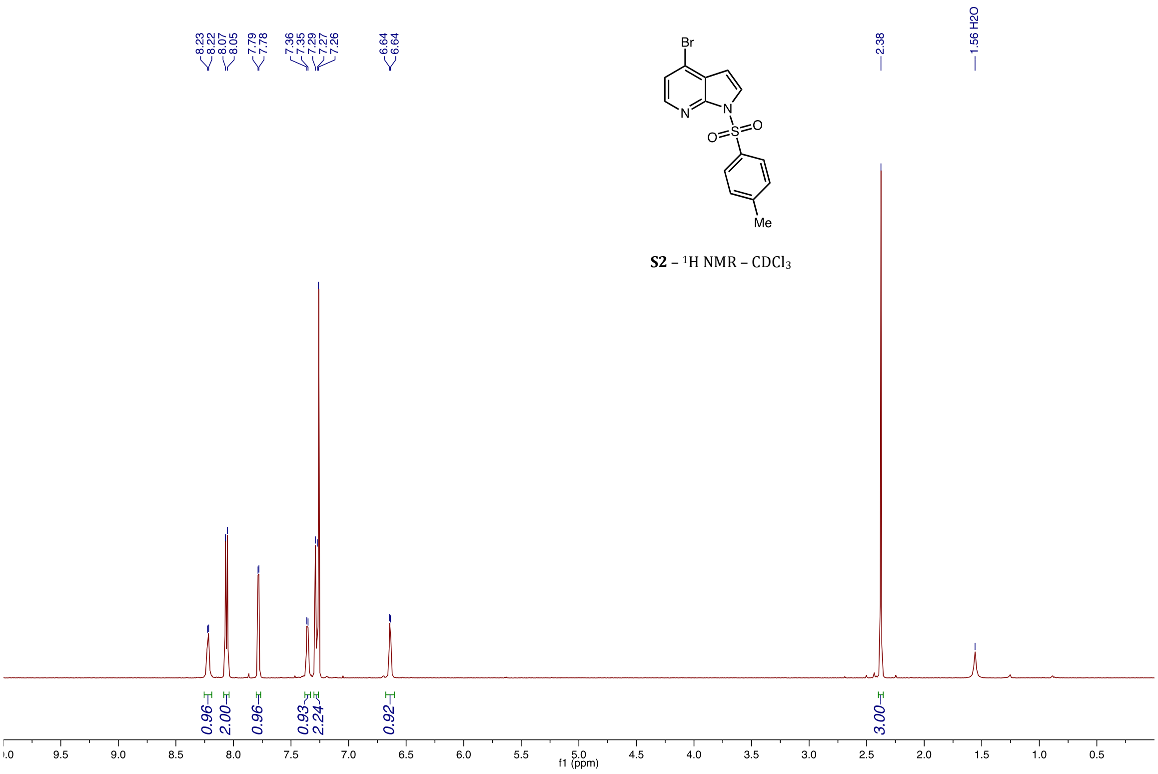
4 – ^{13}C NMR – CD_3CN



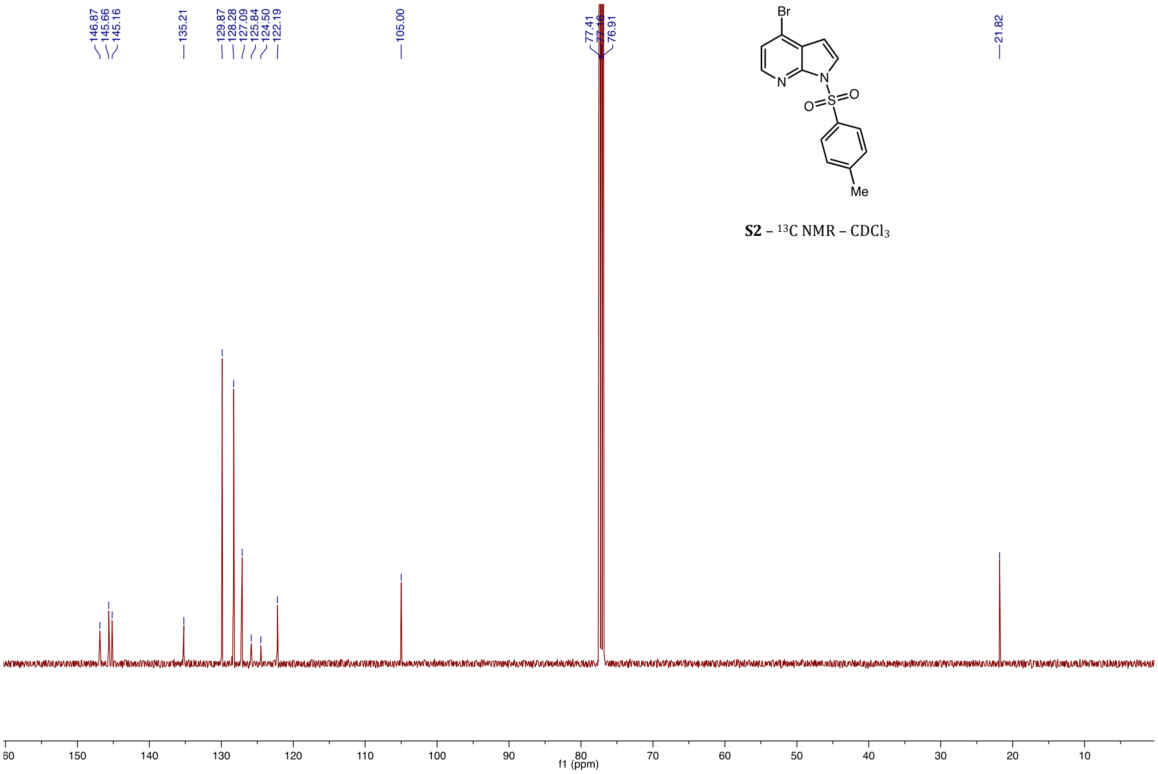
S1 – ^{1}H NMR – $CDCl_3$



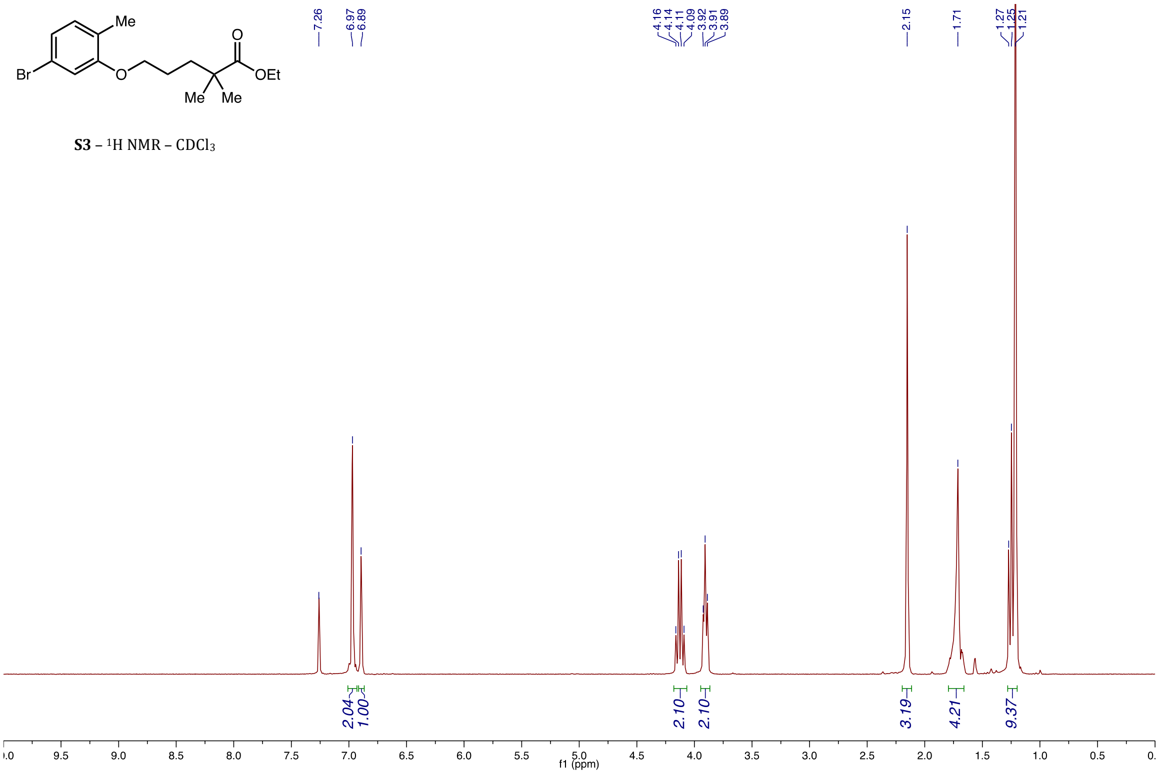
S1 – ^{13}C NMR – CDCl$_3$



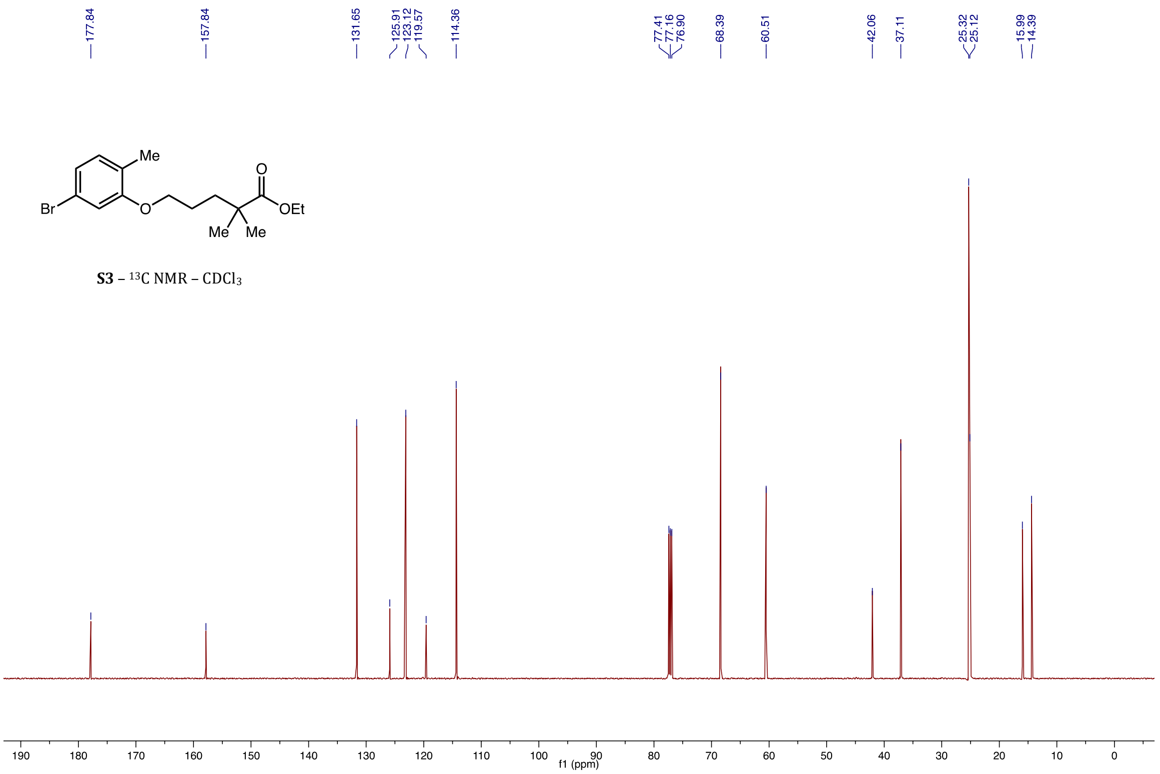
S2 – ^{1}H NMR – CDCl$_3$



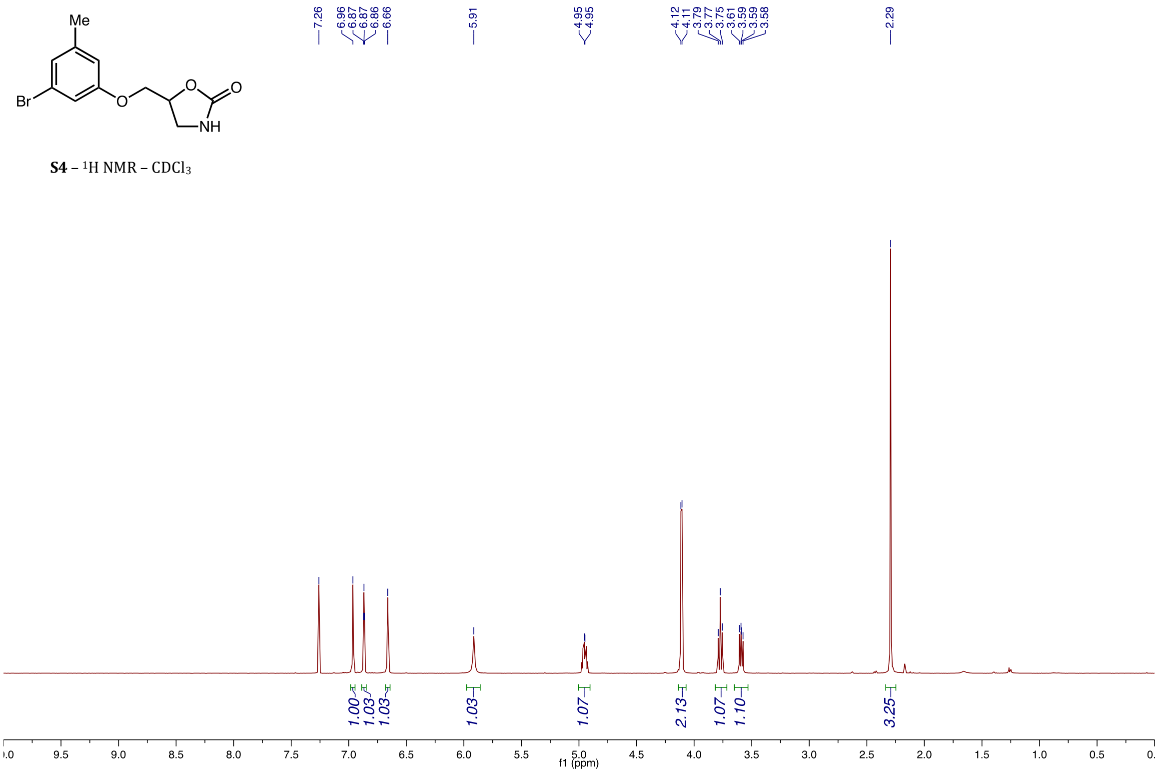
S2 – ^{13}C NMR – CDCl$_3$



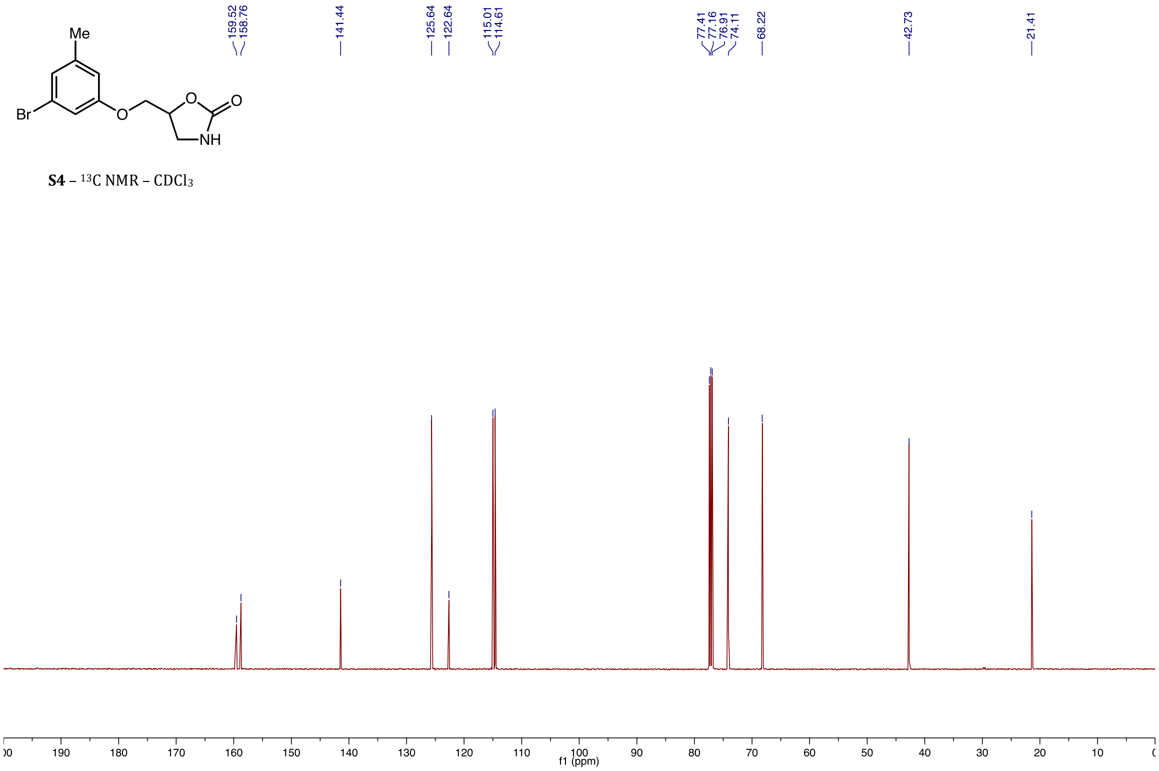
S3 – ^{1}H NMR – CDCl$_3$



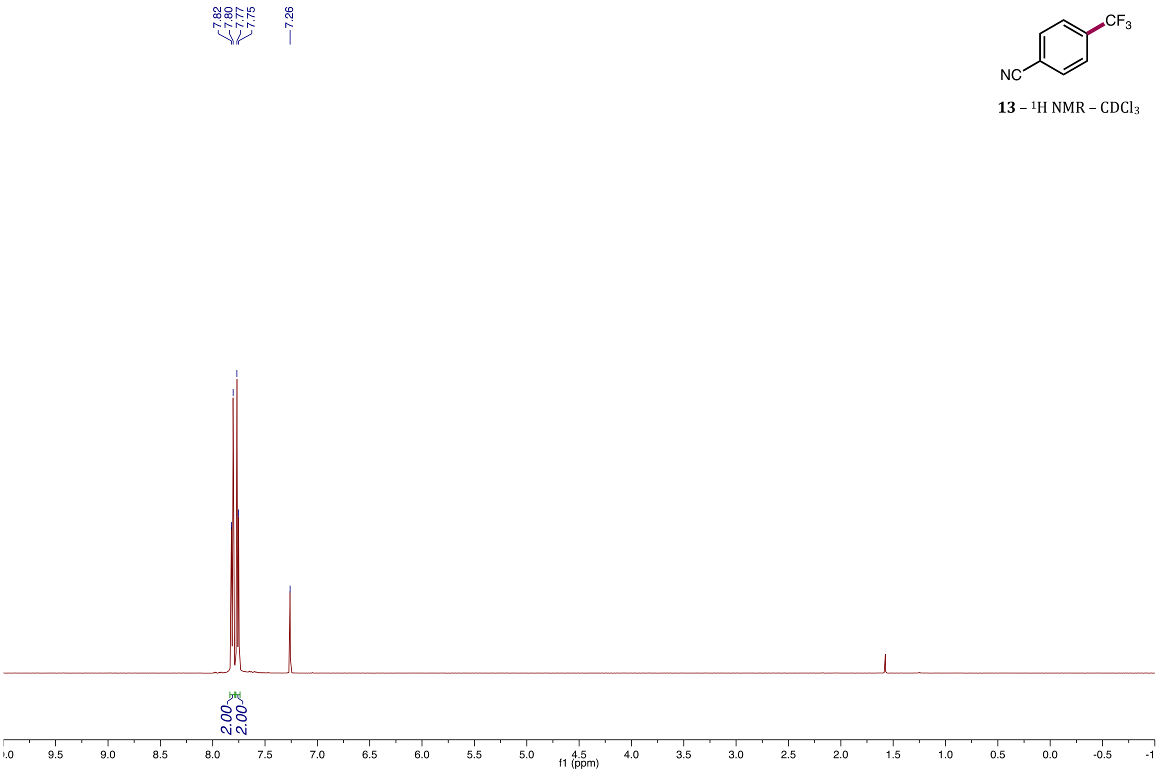
S3 – ^{13}C NMR – CDCl$_3$



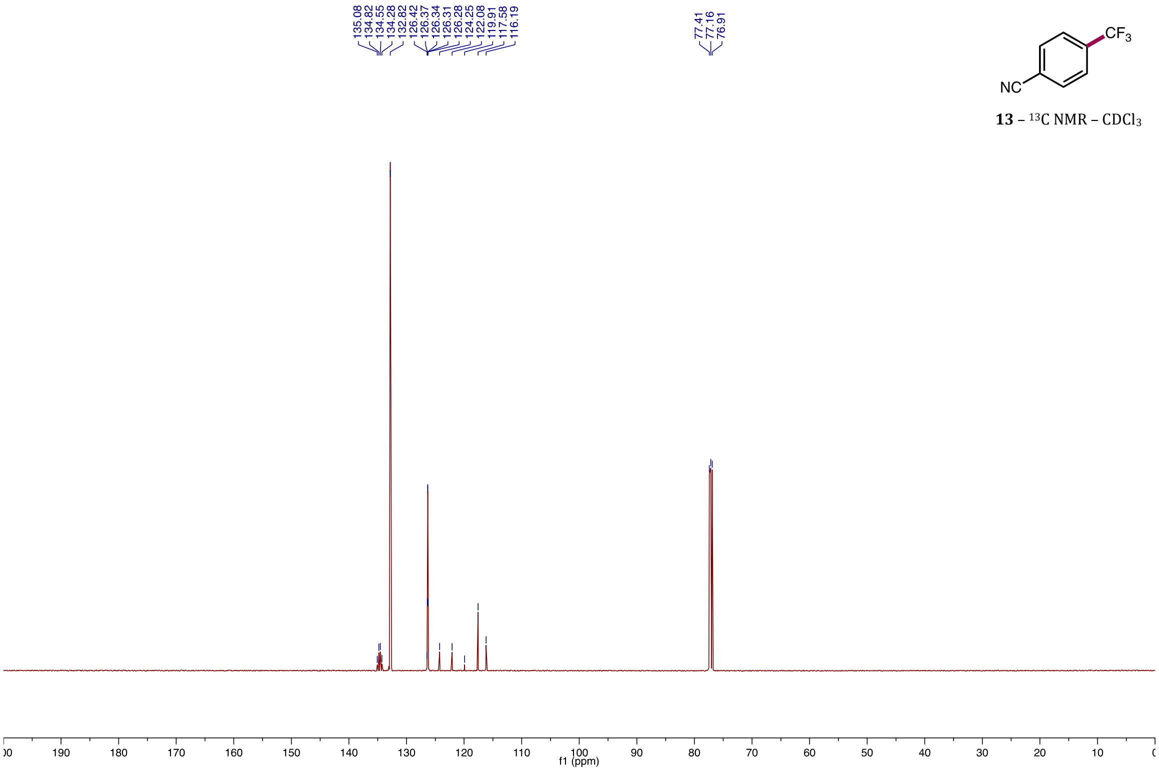
S4 – ^{1}H NMR – CDCl$_3$



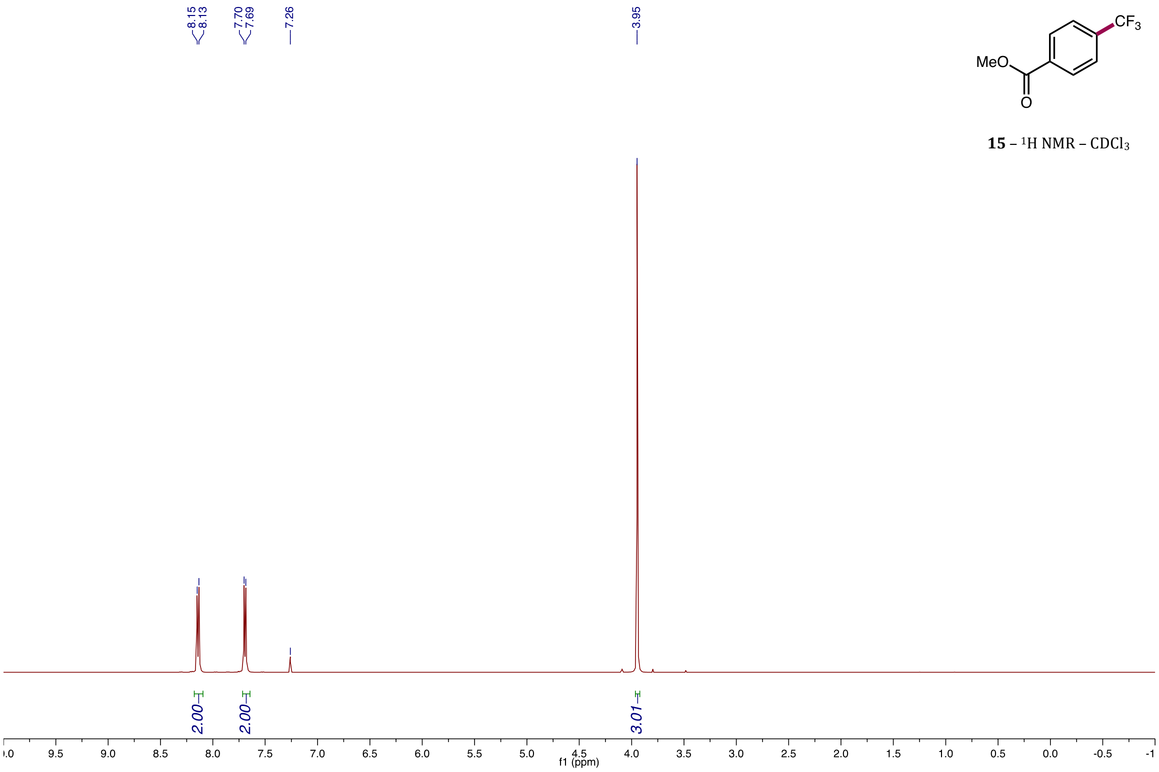
S4 – ^{13}C NMR – CDCl$_3$



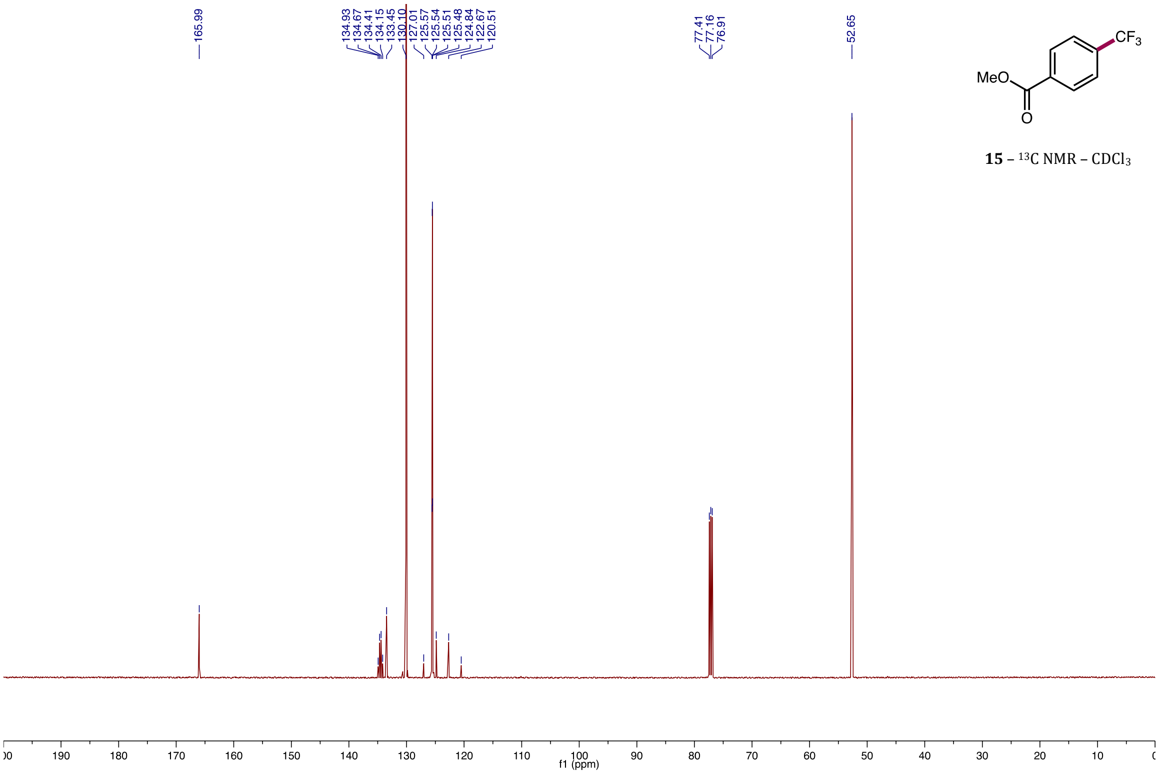
13 – ^{1}H NMR – CDCl$_3$



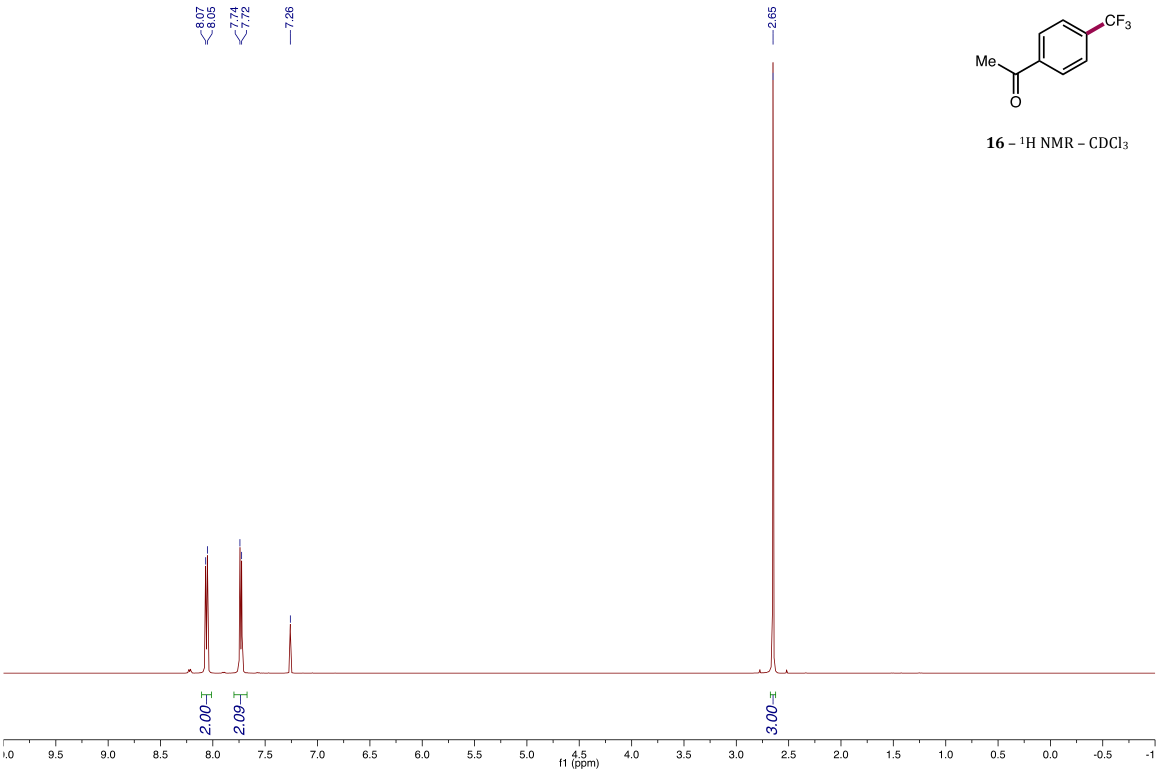
13 – ^{13}C NMR – CDCl$_3$



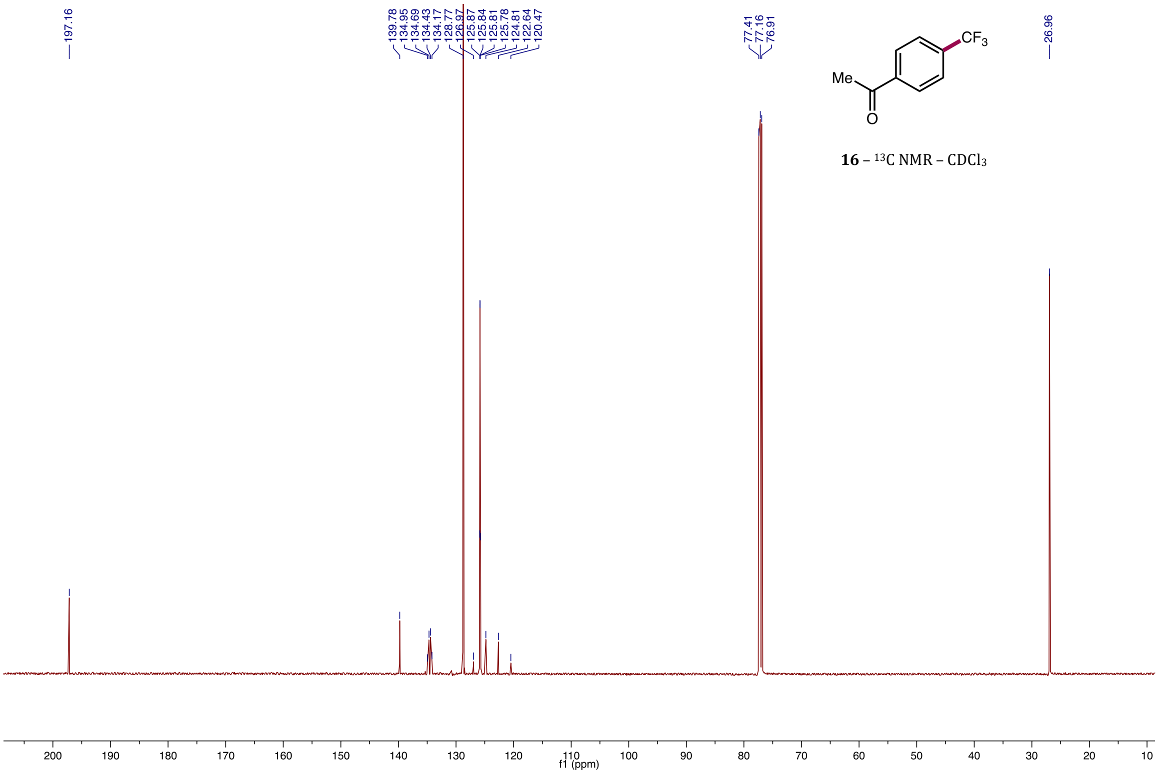
15 – ^{1}H NMR – CDCl$_3$



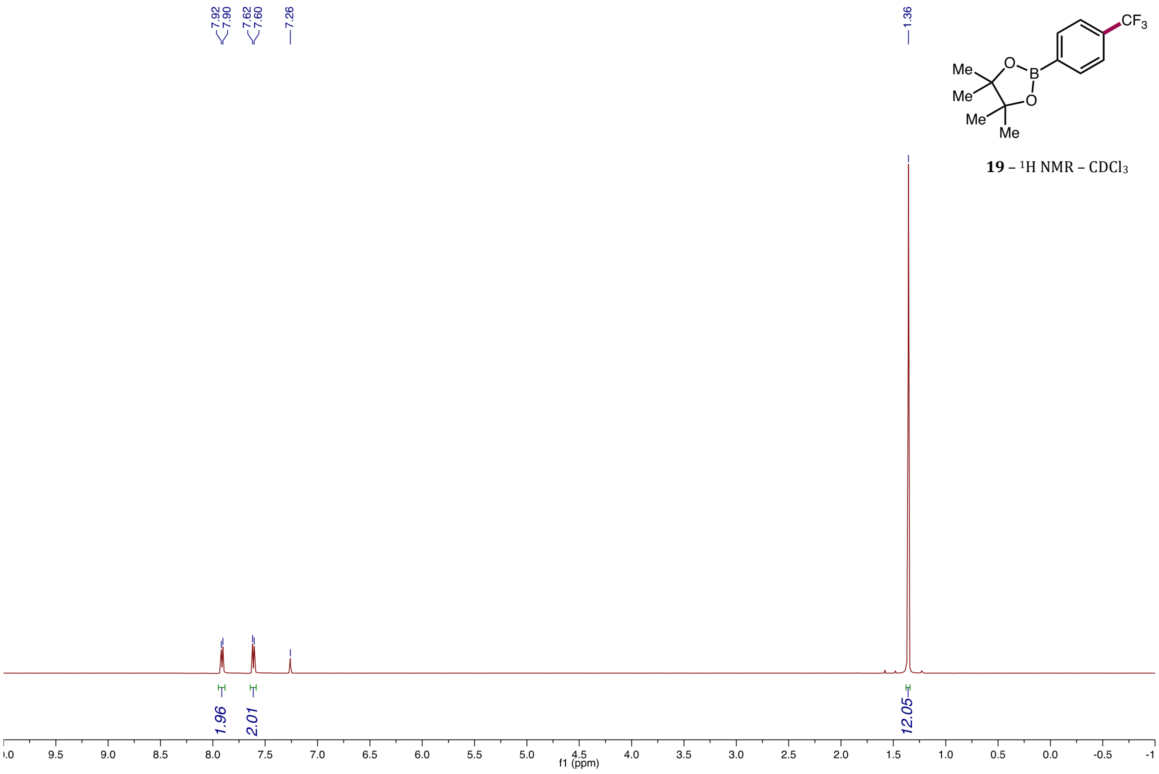
15 – ^{13}C NMR – CDCl$_3$



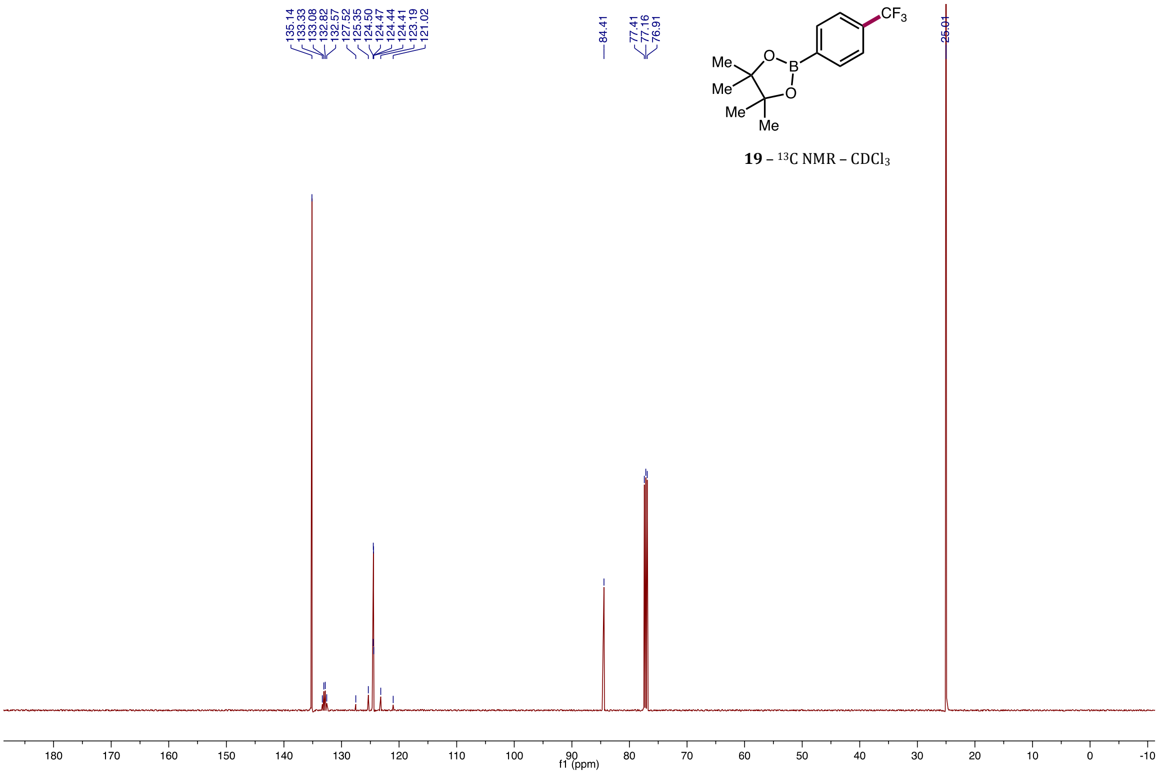
16 – ^{1}H NMR – CDCl$_3$



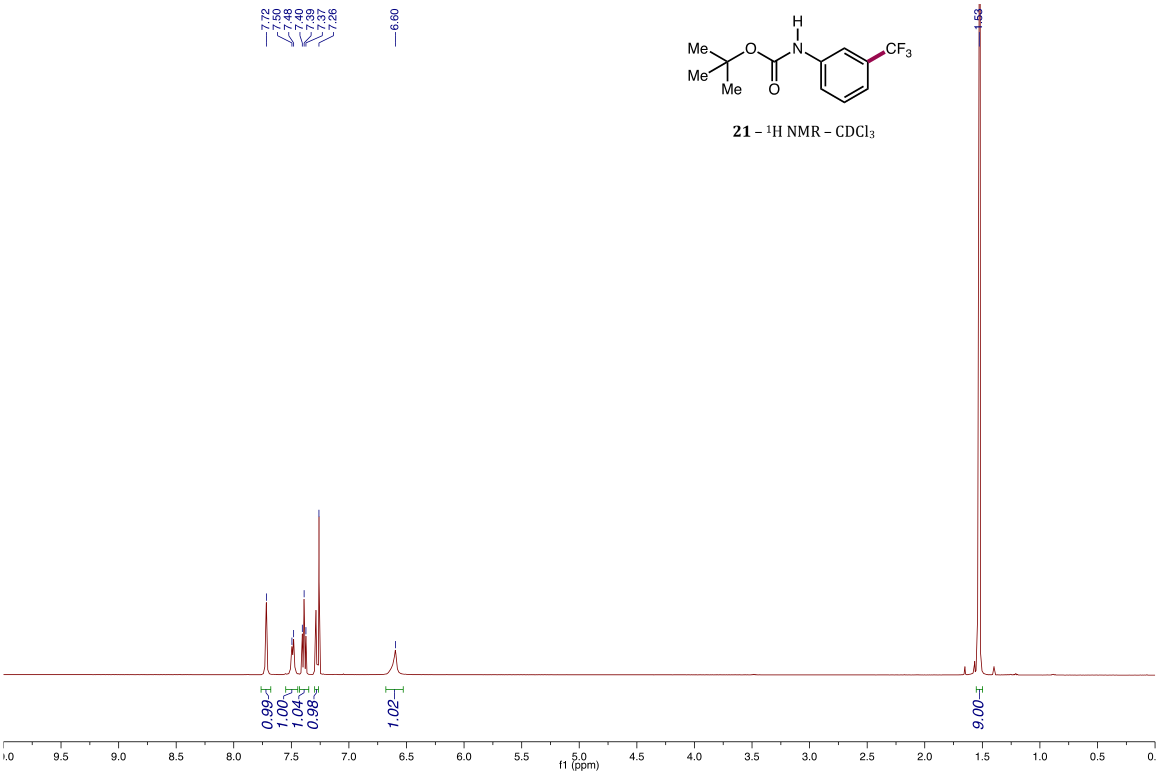
16 – ^{13}C NMR – CDCl$_3$



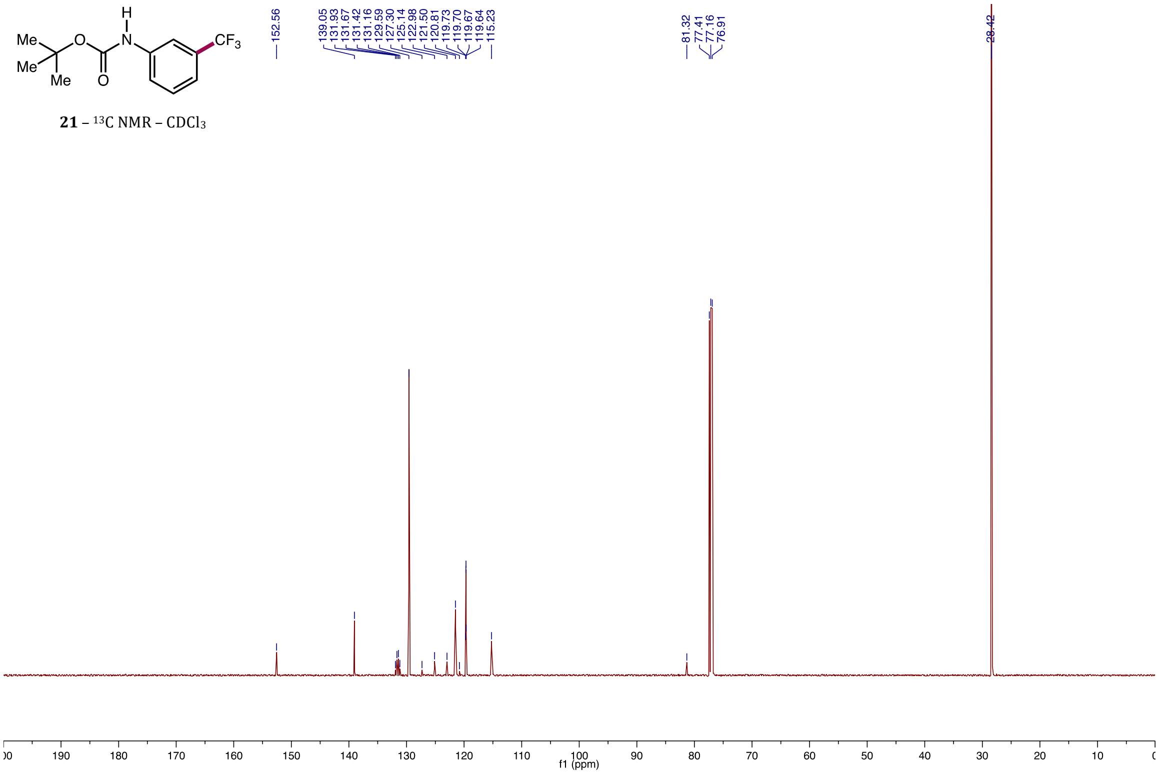
19 – ^{1}H NMR – CDCl$_3$



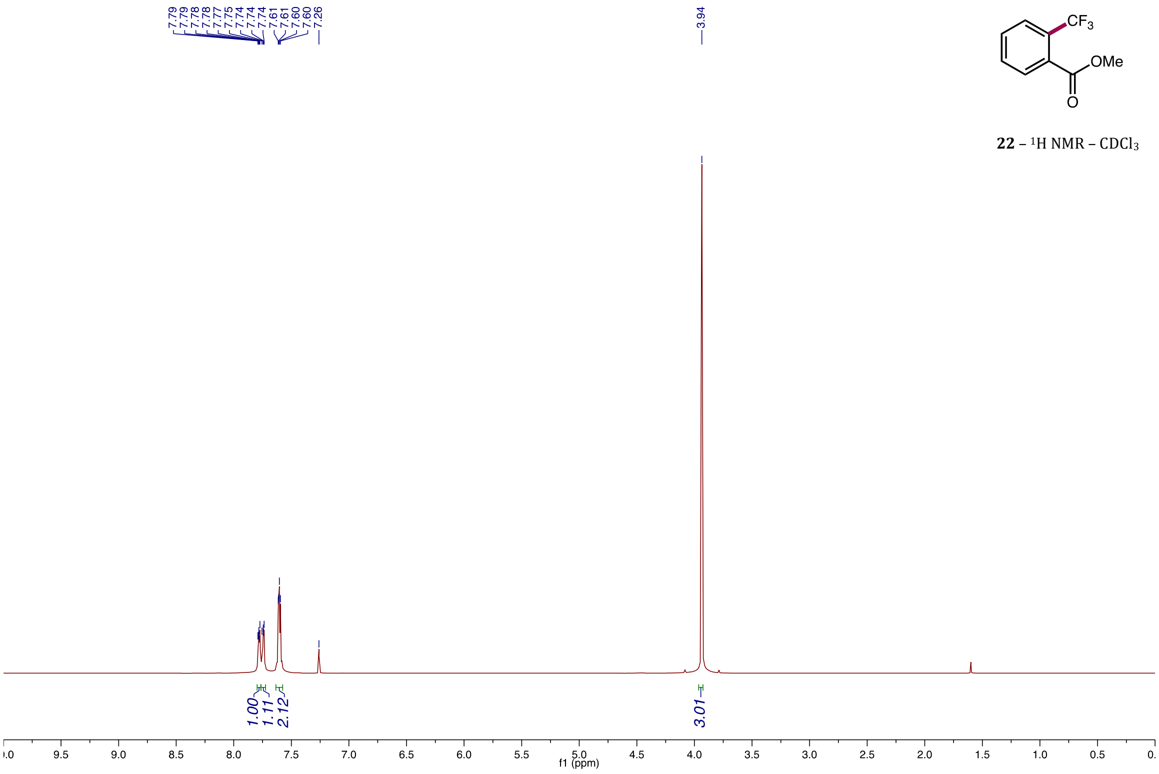
19 – ^{13}C NMR – CDCl$_3$



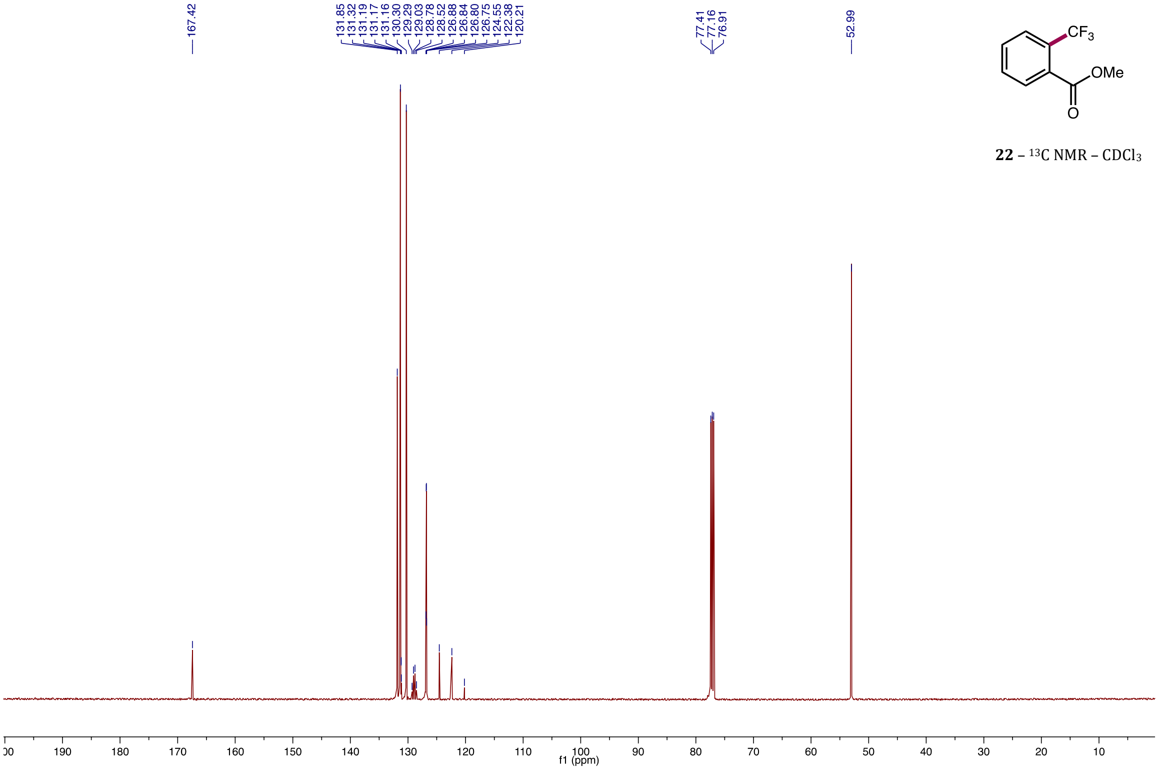
21 – ^{1}H NMR – CDCl$_3$



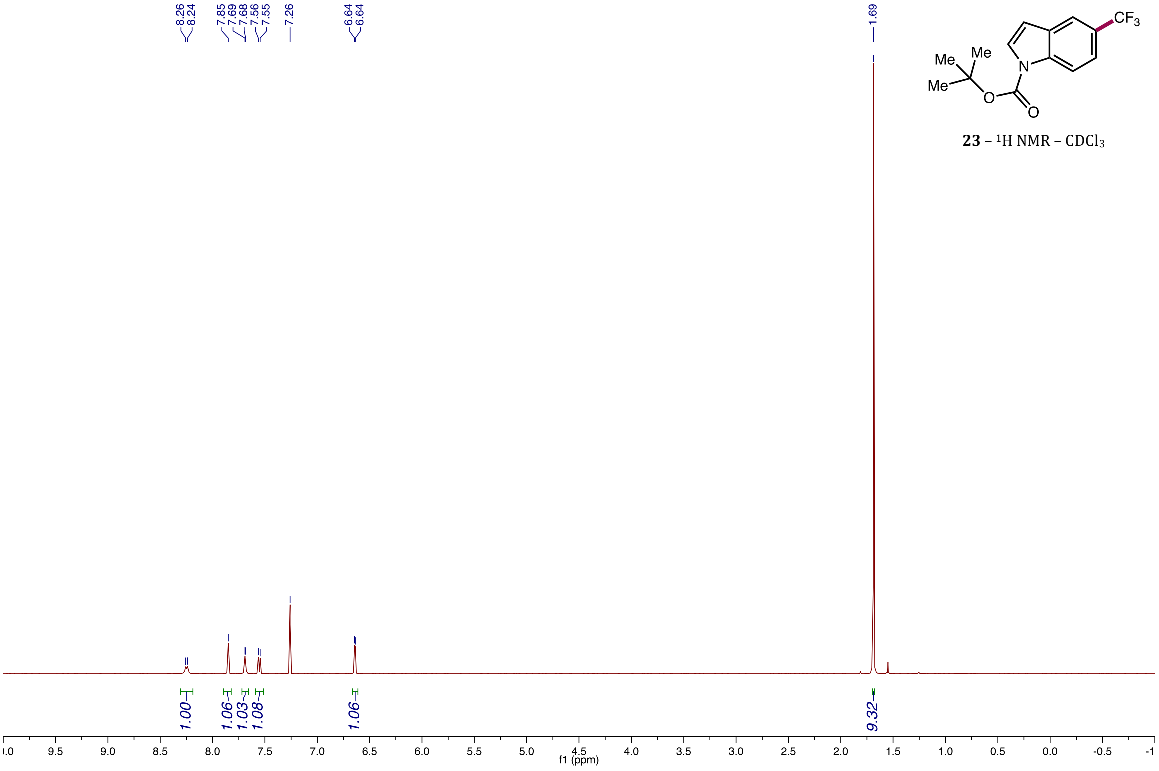
21 – ^{13}C NMR – CDCl$_3$



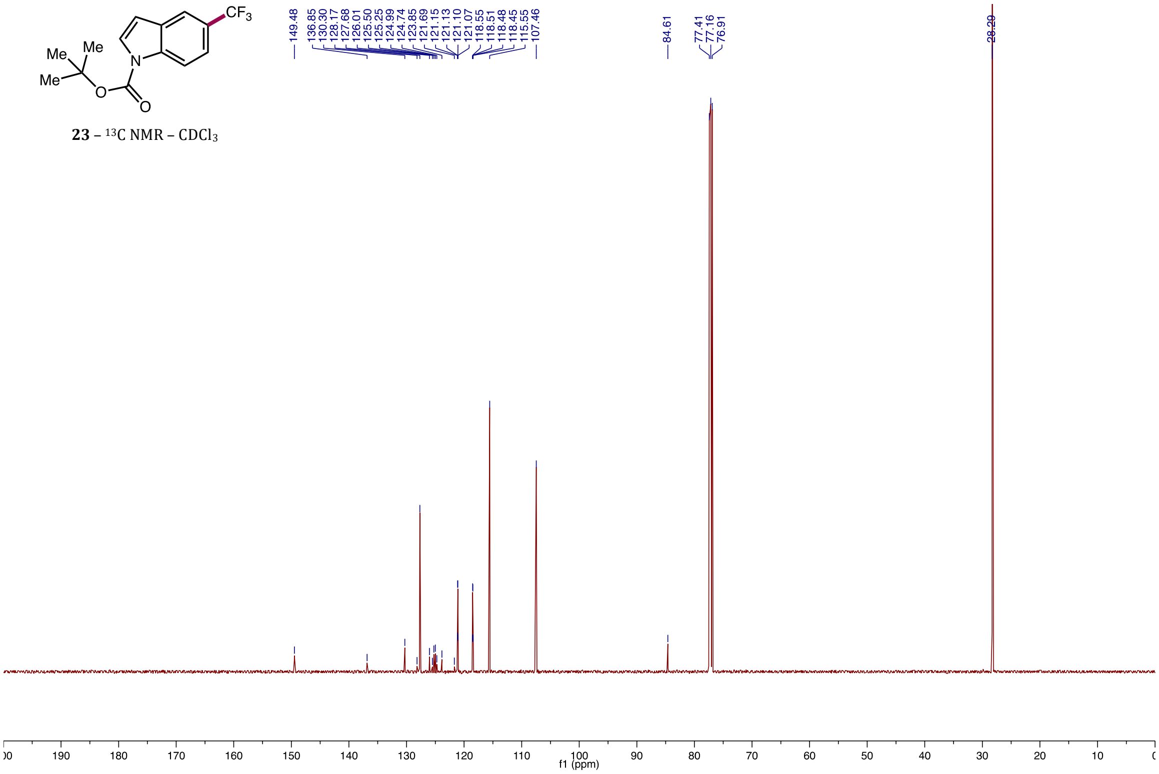
22 – ^{1}H NMR – CDCl$_3$



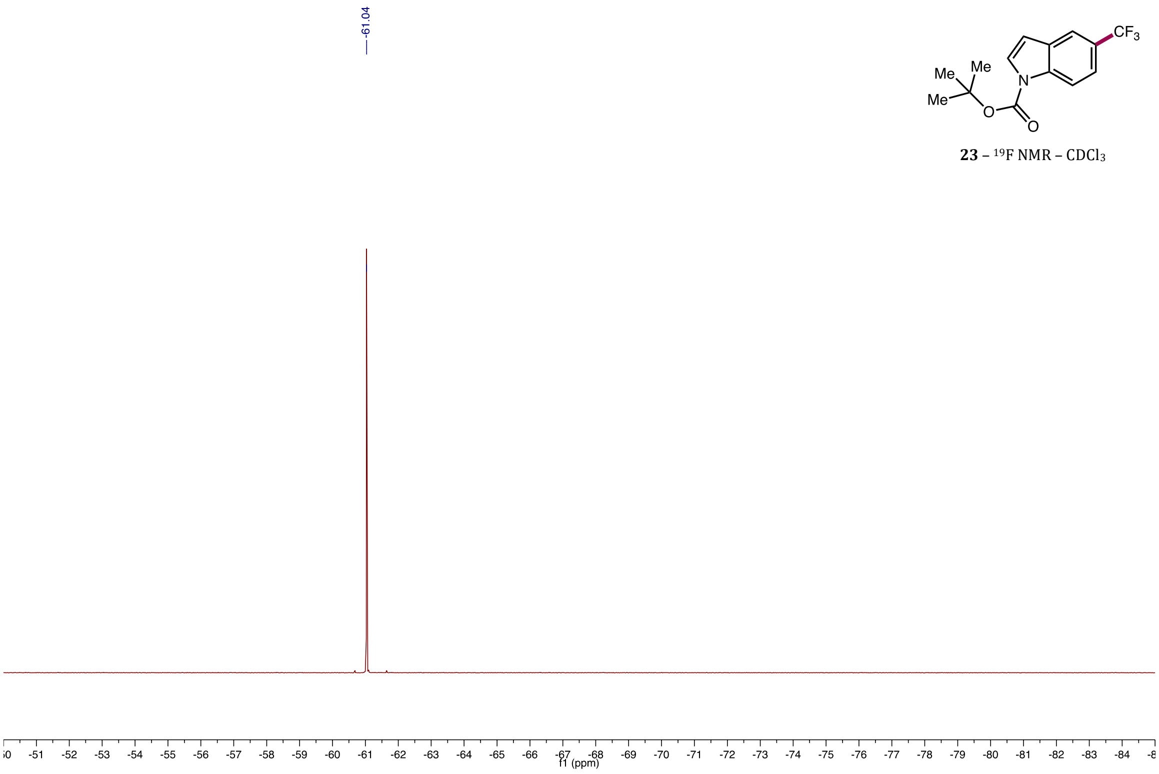
22 – ^{13}C NMR – CDCl$_3$



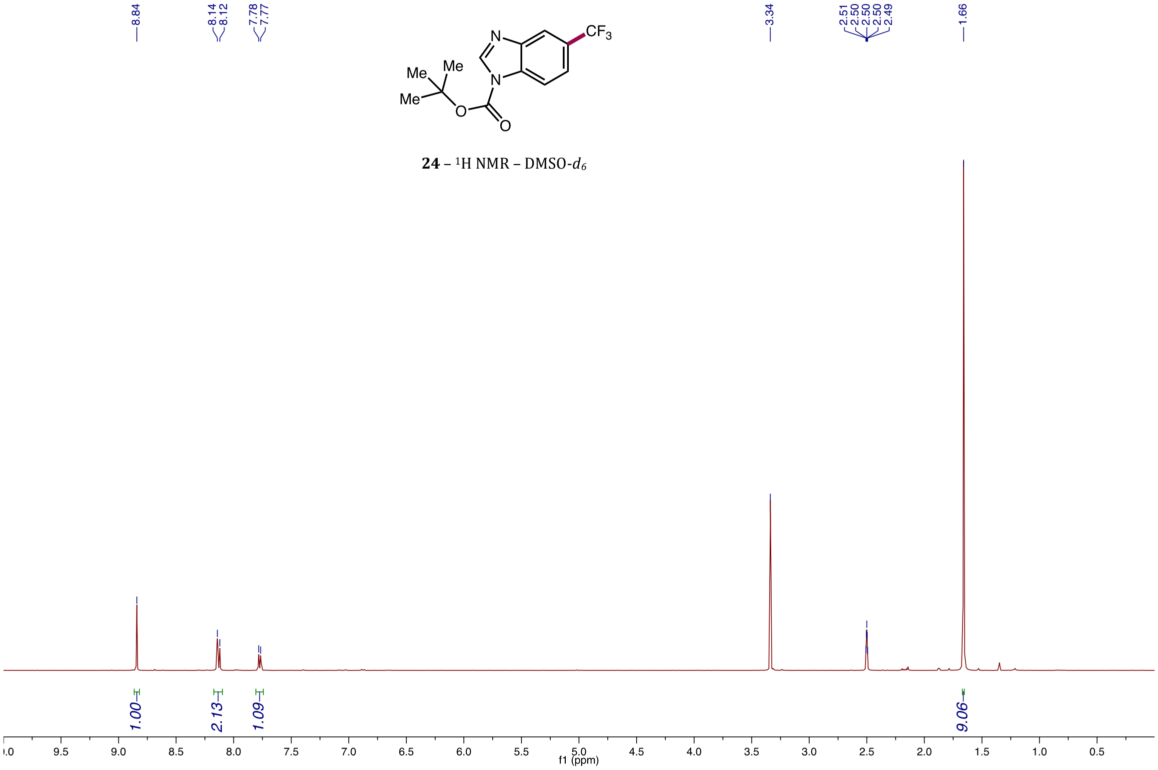
23 – ^{1}H NMR – CDCl$_3$



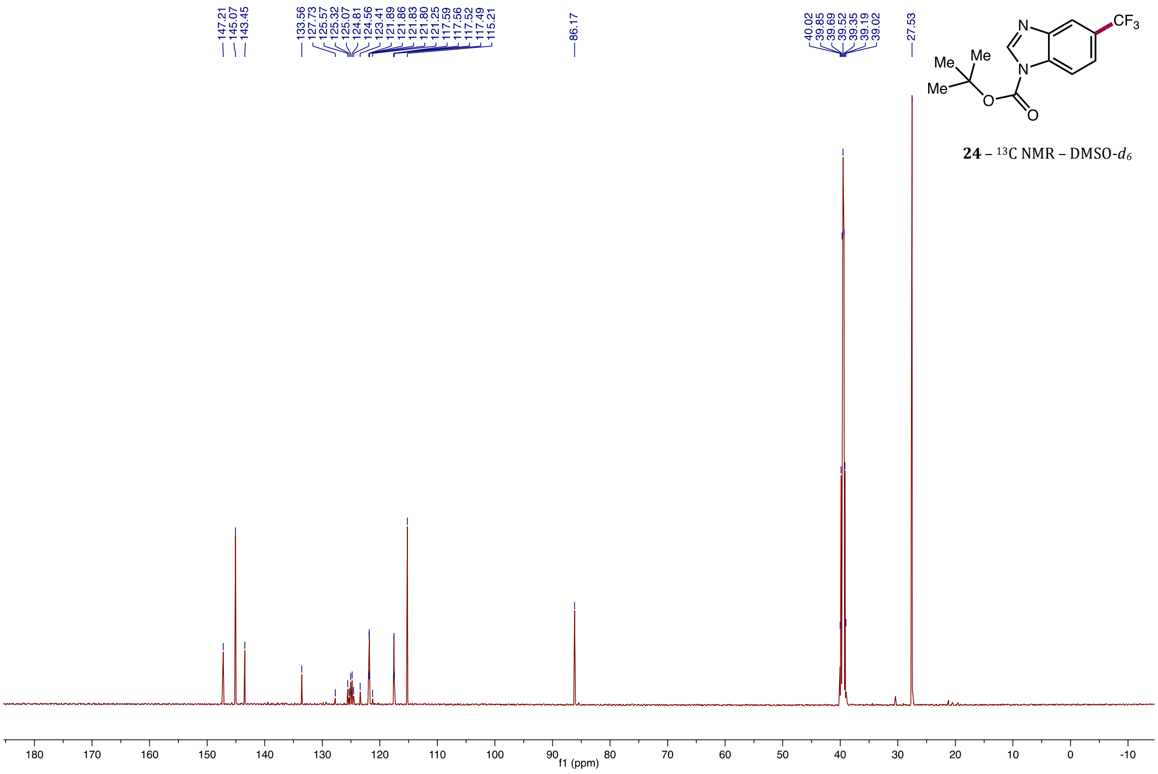
23 – ^{13}C NMR – CDCl$_3$



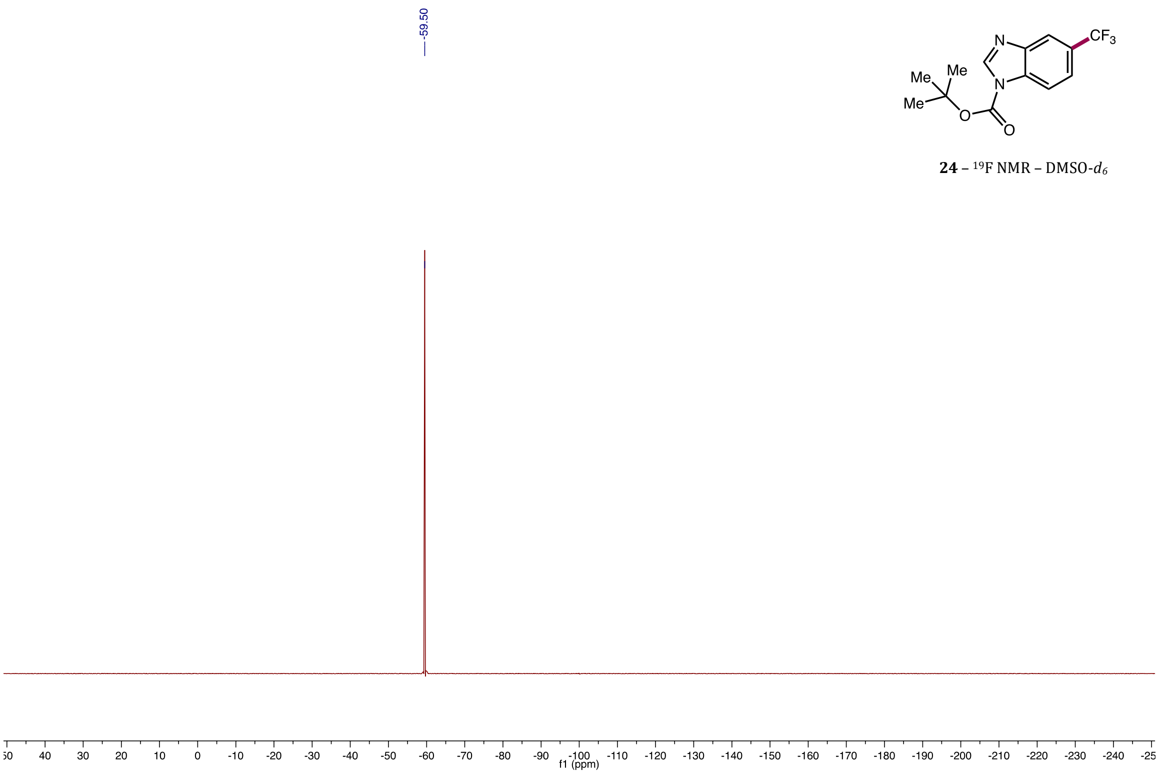
23 – ^{19}F NMR – CDCl$_3$



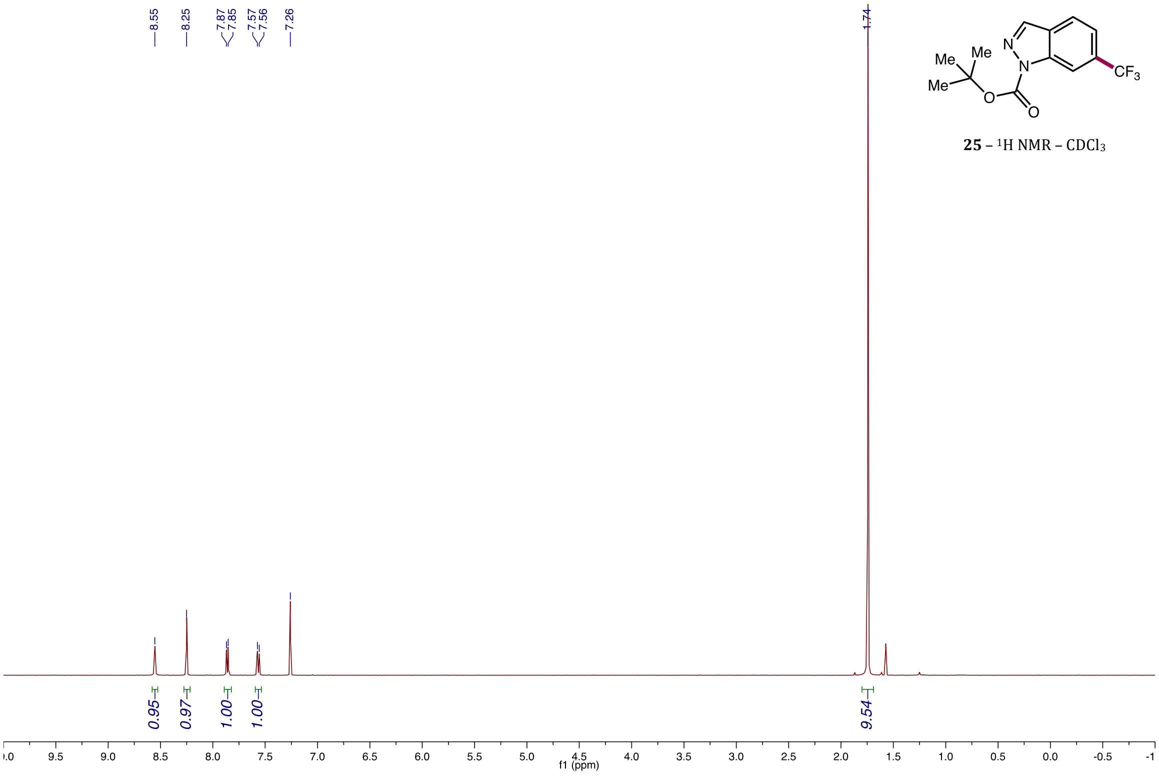
24 – ^{1}H NMR – DMSO-d_6



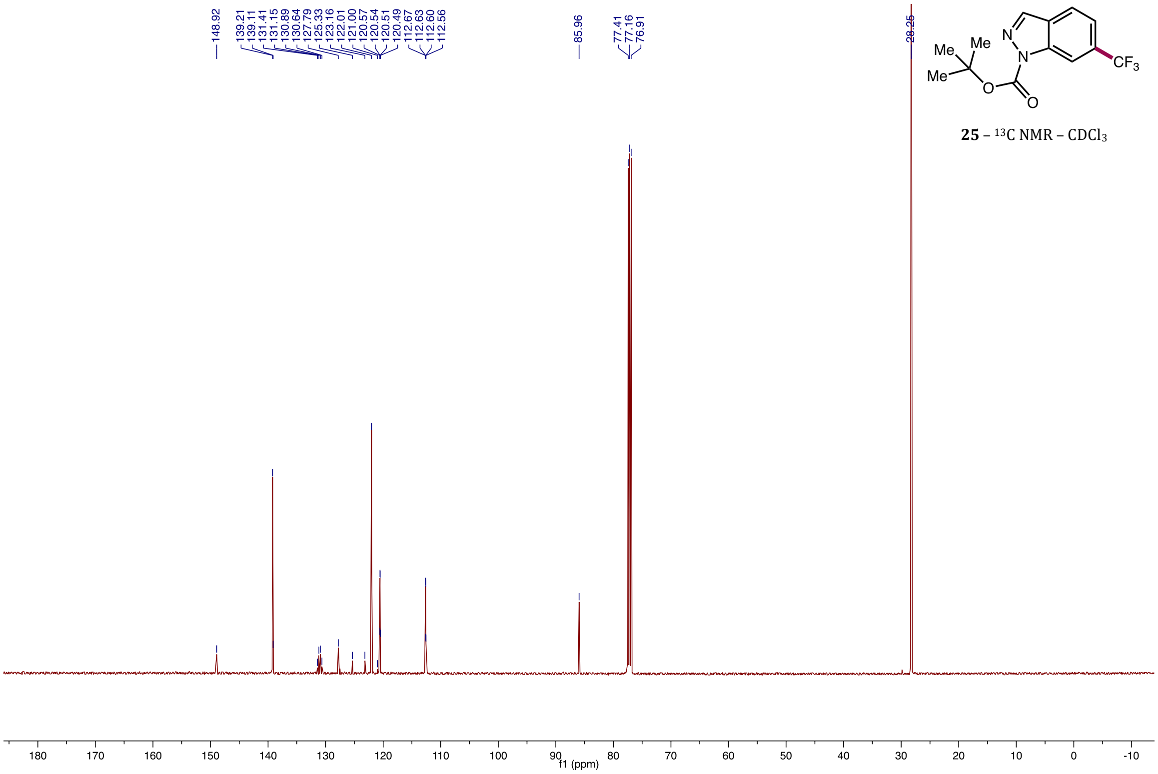
24 – ^{13}C NMR – DMSO-d_6



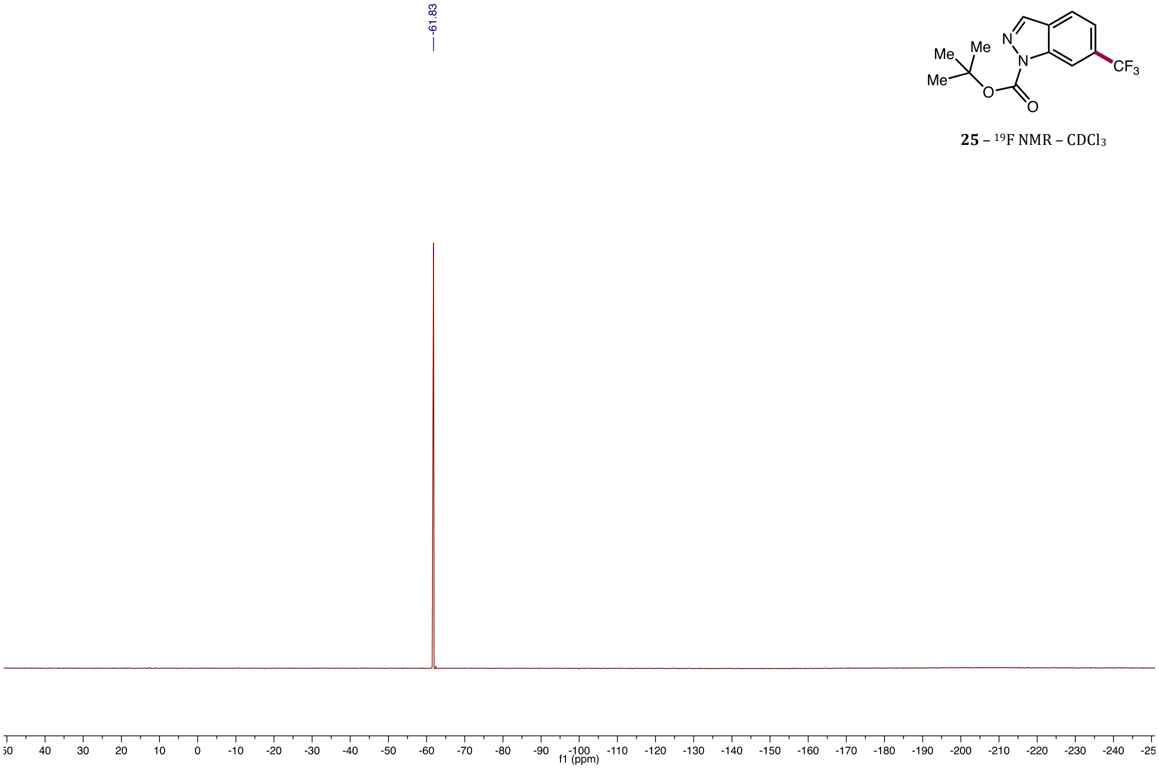
24 – ^{19}F NMR – DMSO-d_6



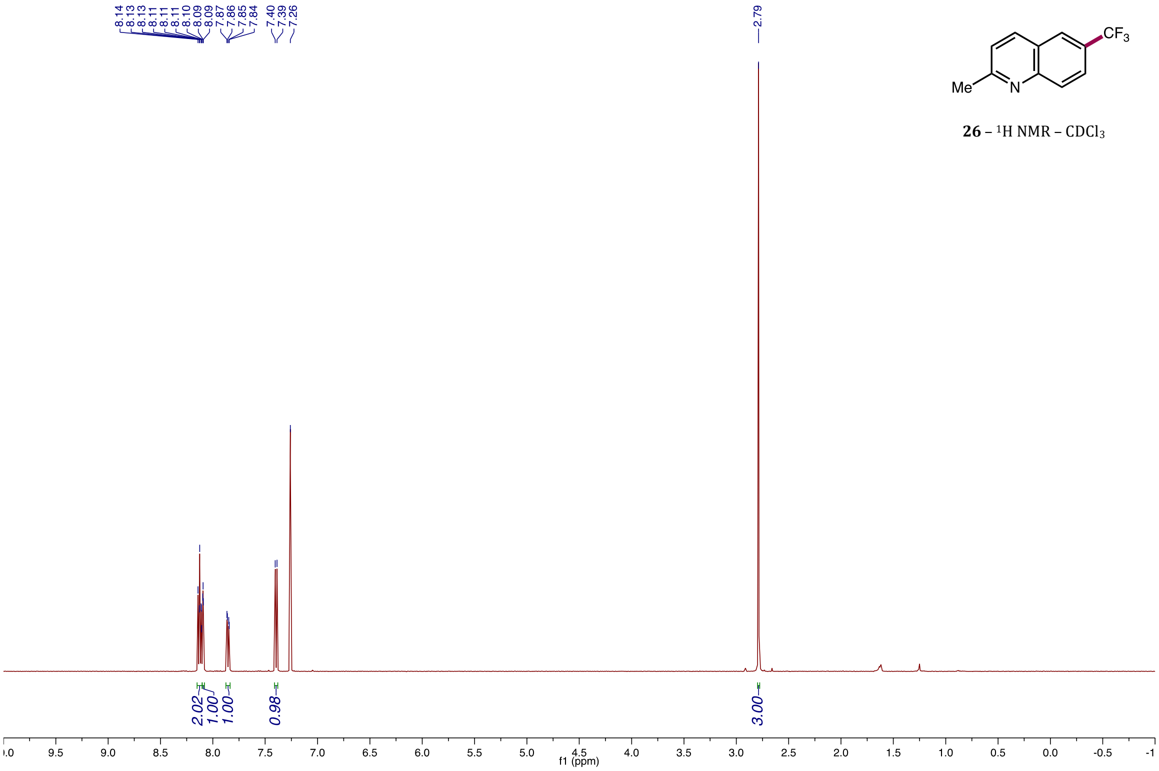
25 – ^{1}H NMR – CDCl$_3$



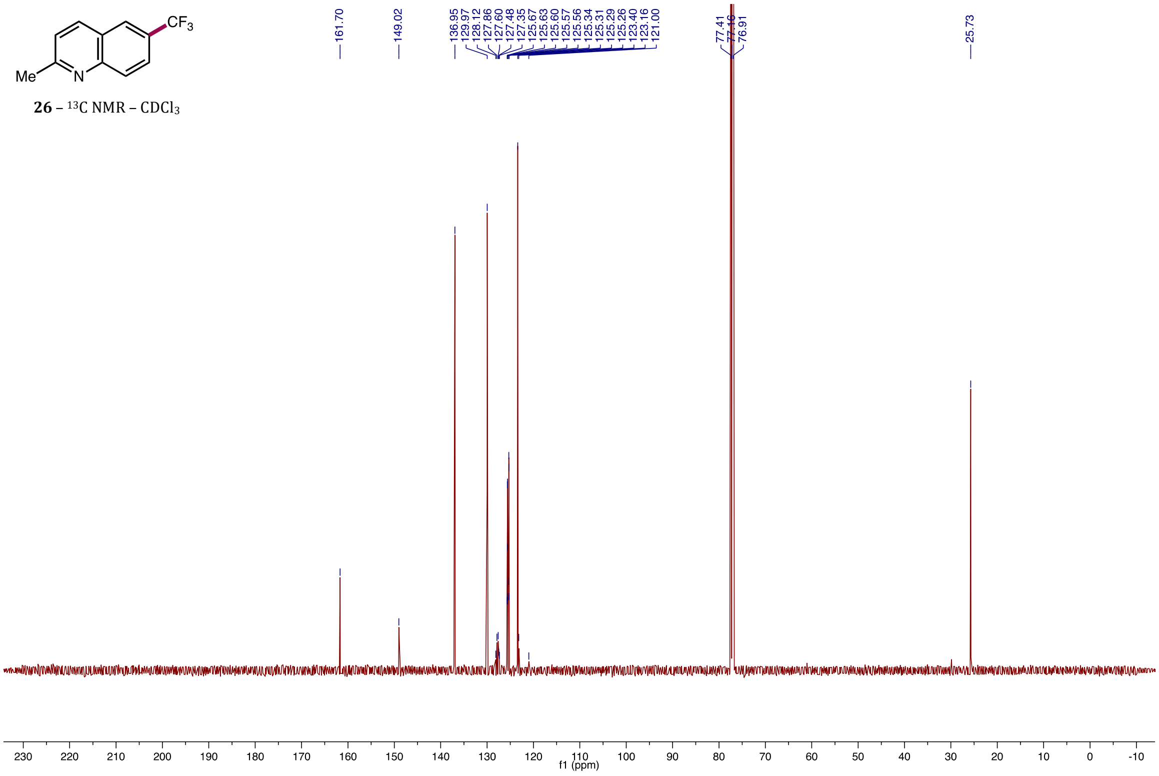
25 – ^{13}C NMR – CDCl$_3$



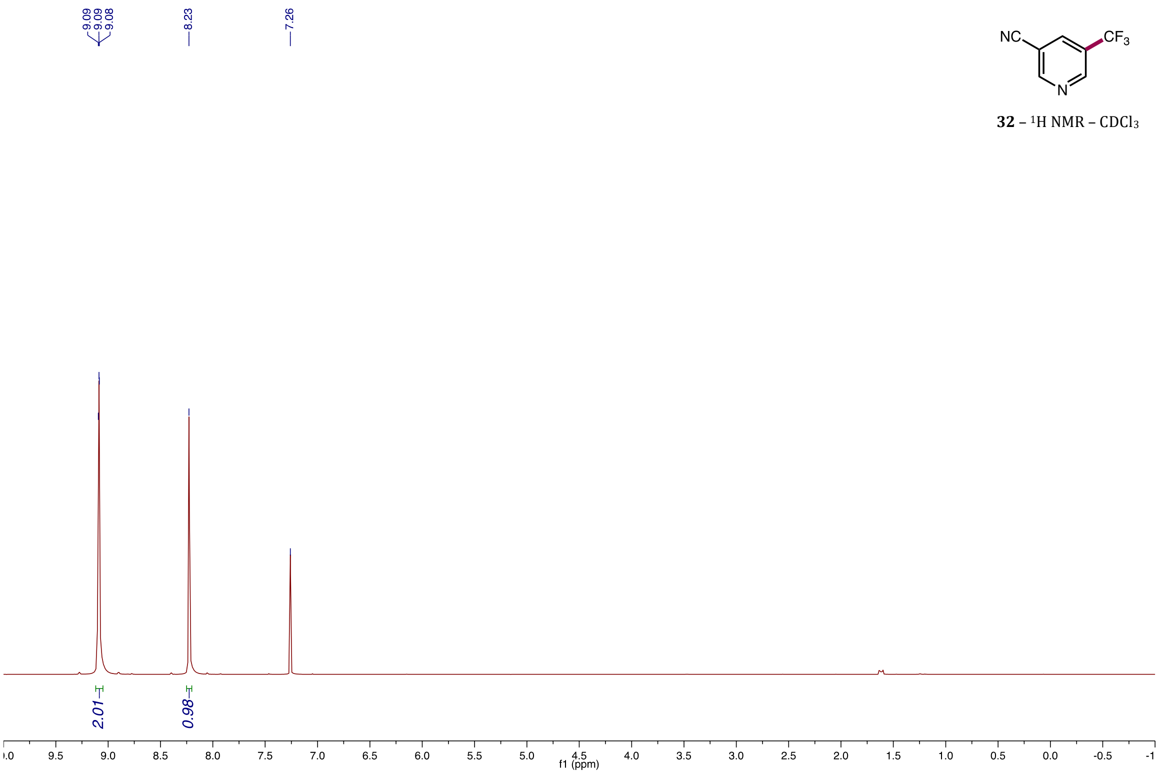
25 – ^{19}F NMR – CDCl$_3$



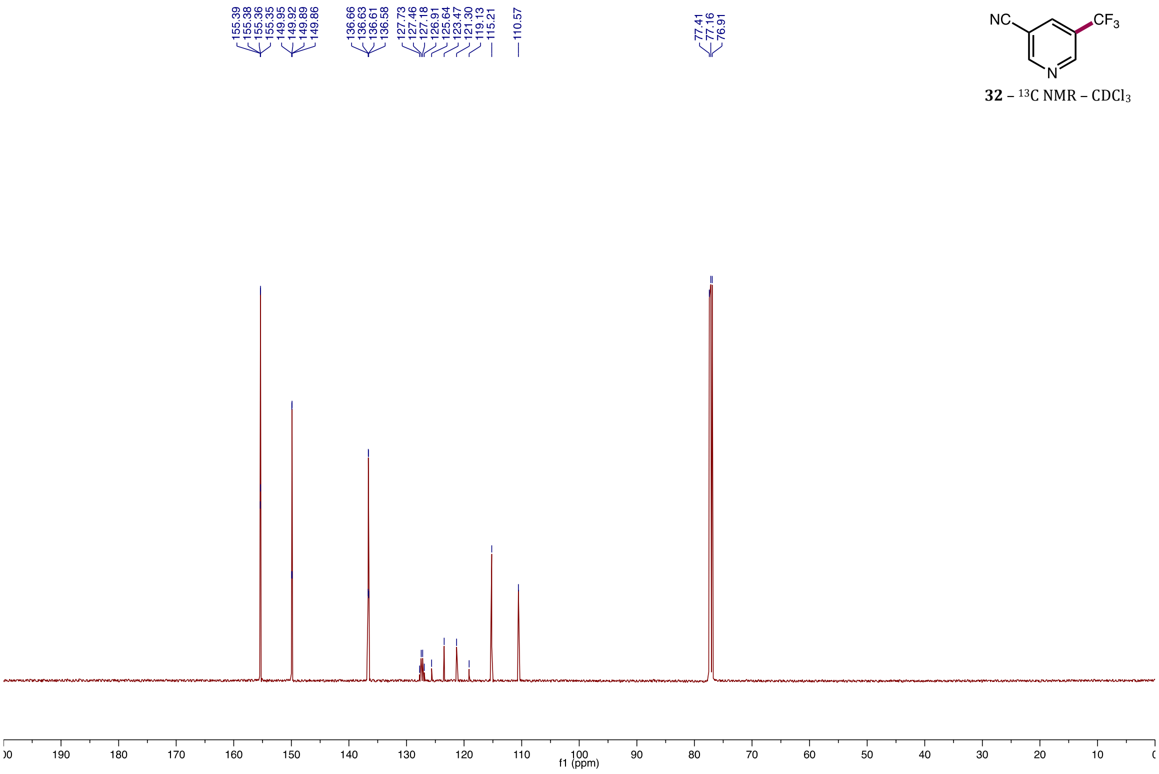
26 – ^{1}H NMR – CDCl$_3$



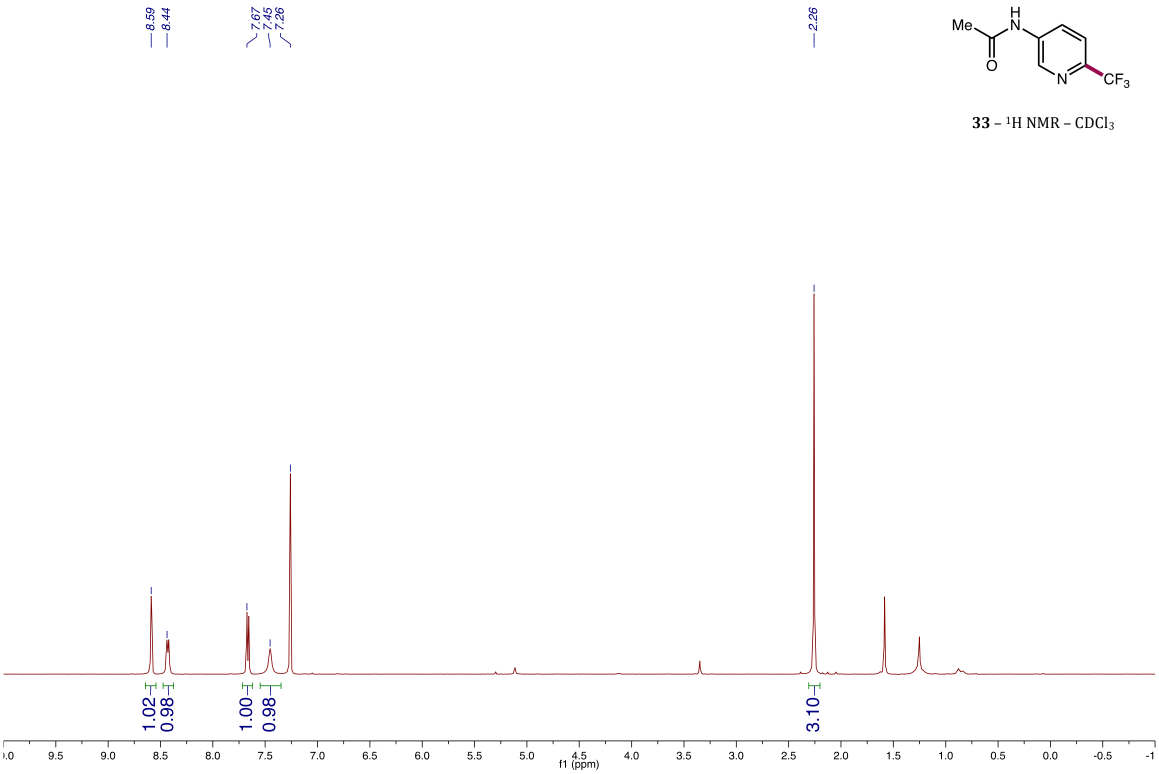
26 – ^{13}C NMR – CDCl$_3$



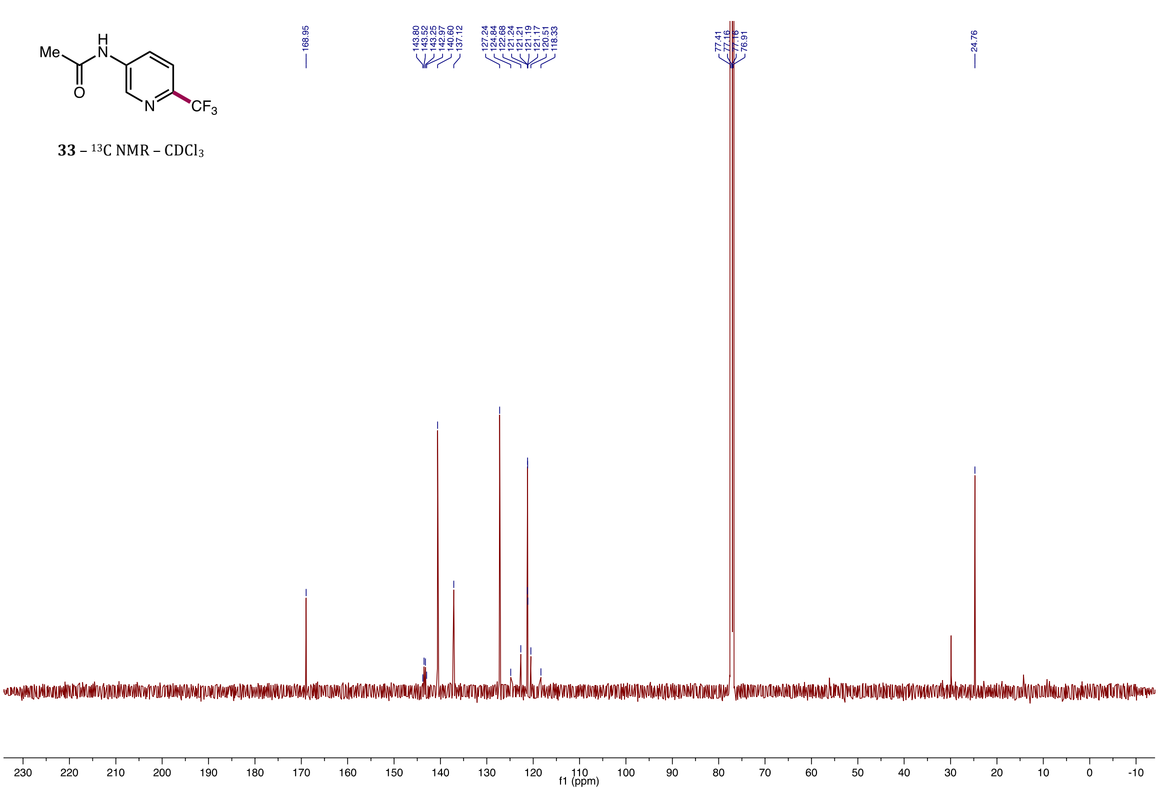
32 – ^{1}H NMR – CDCl$_3$



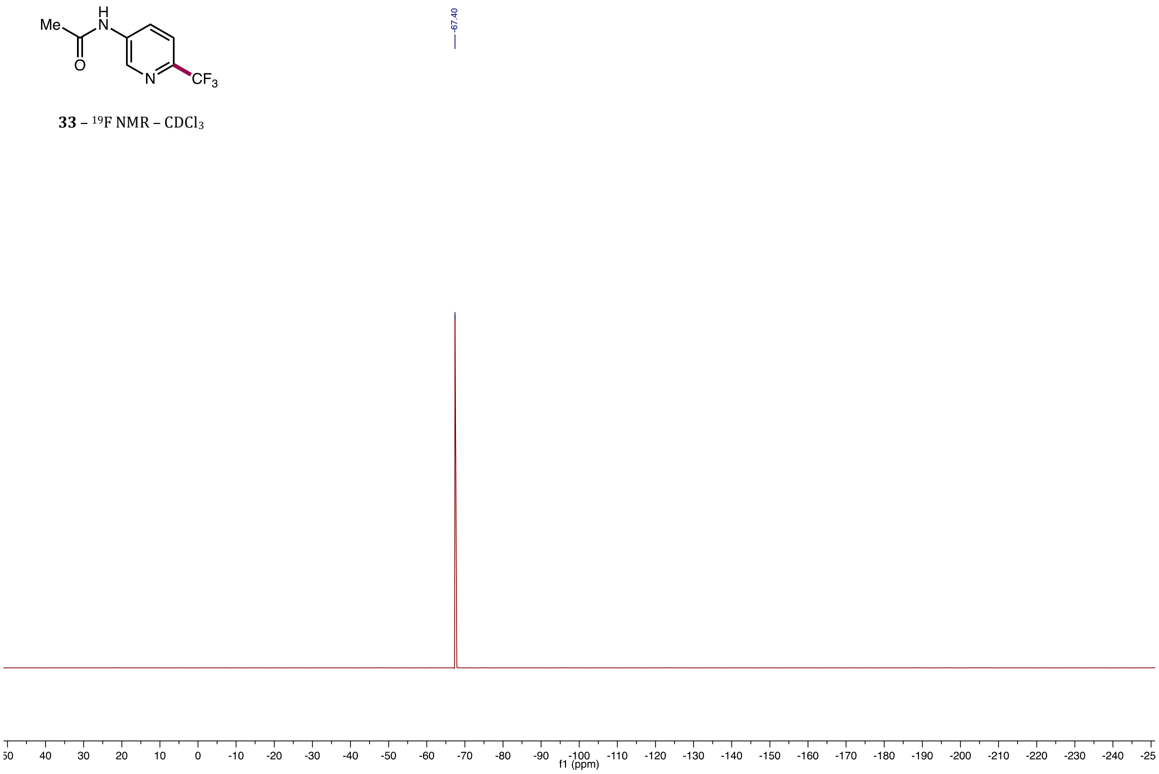
32 – ^{13}C NMR – CDCl$_3$



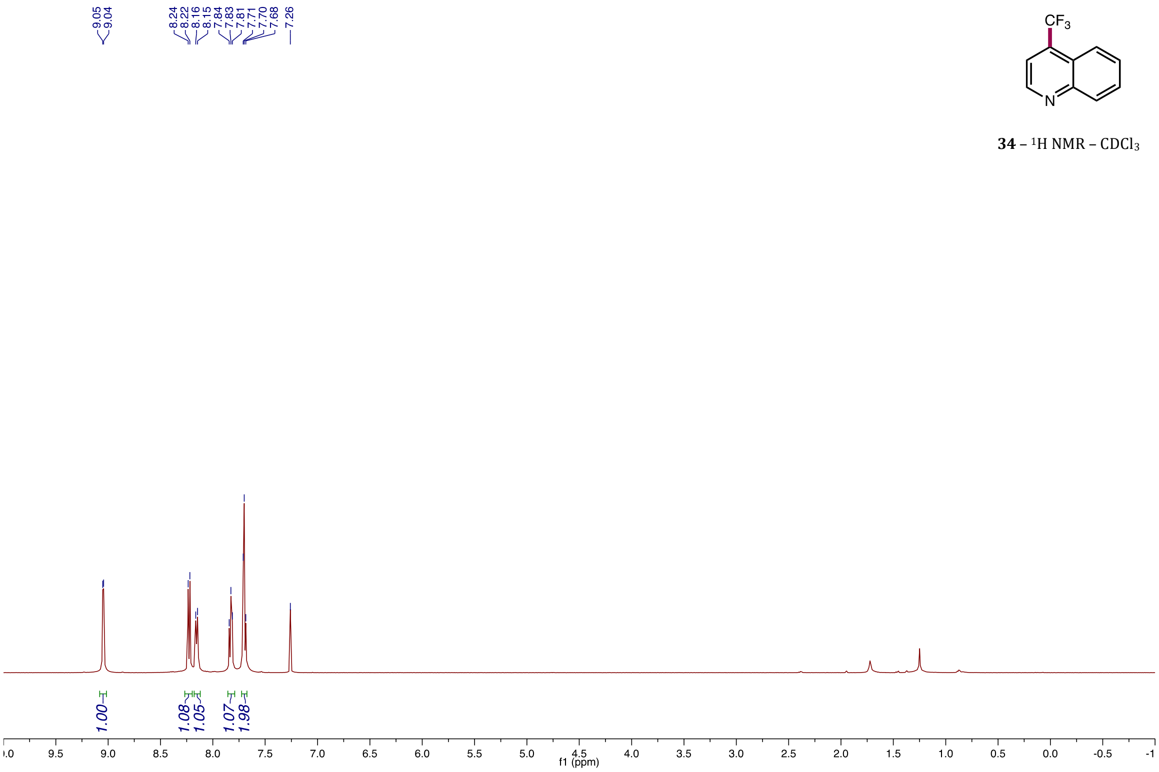
33 – ^{1}H NMR – CDCl$_3$



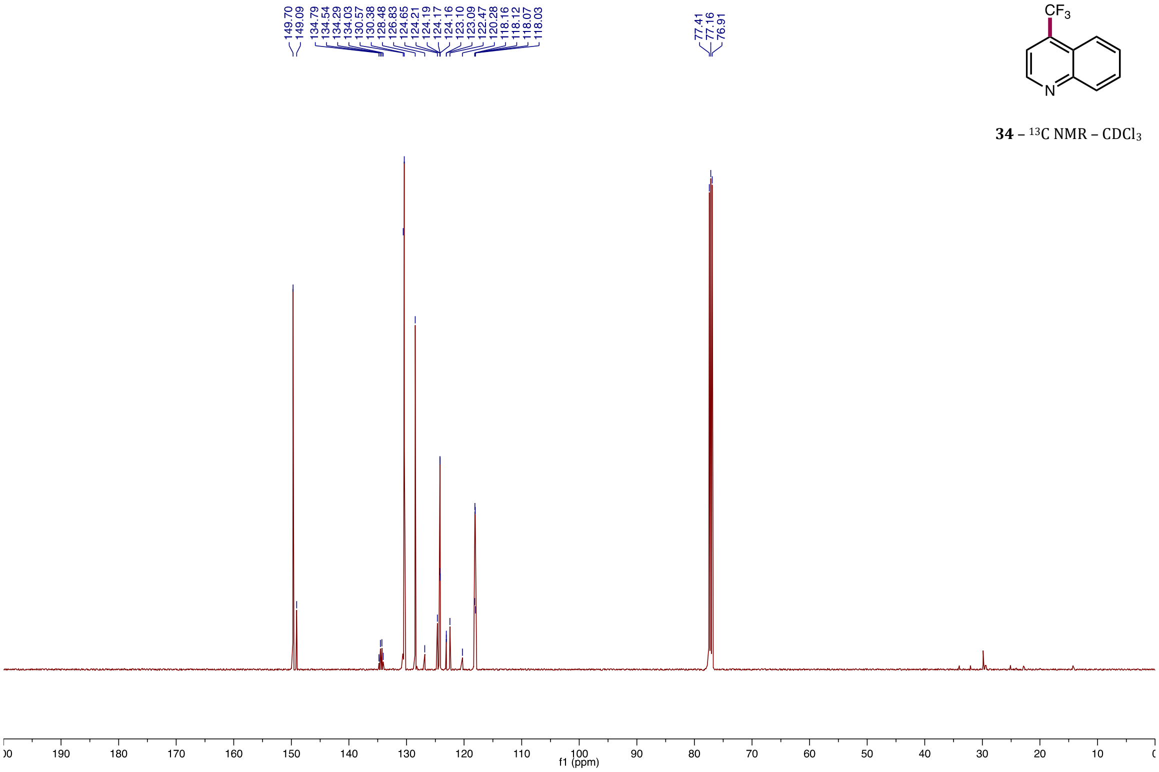
33 – ^{13}C NMR – CDCl$_3$



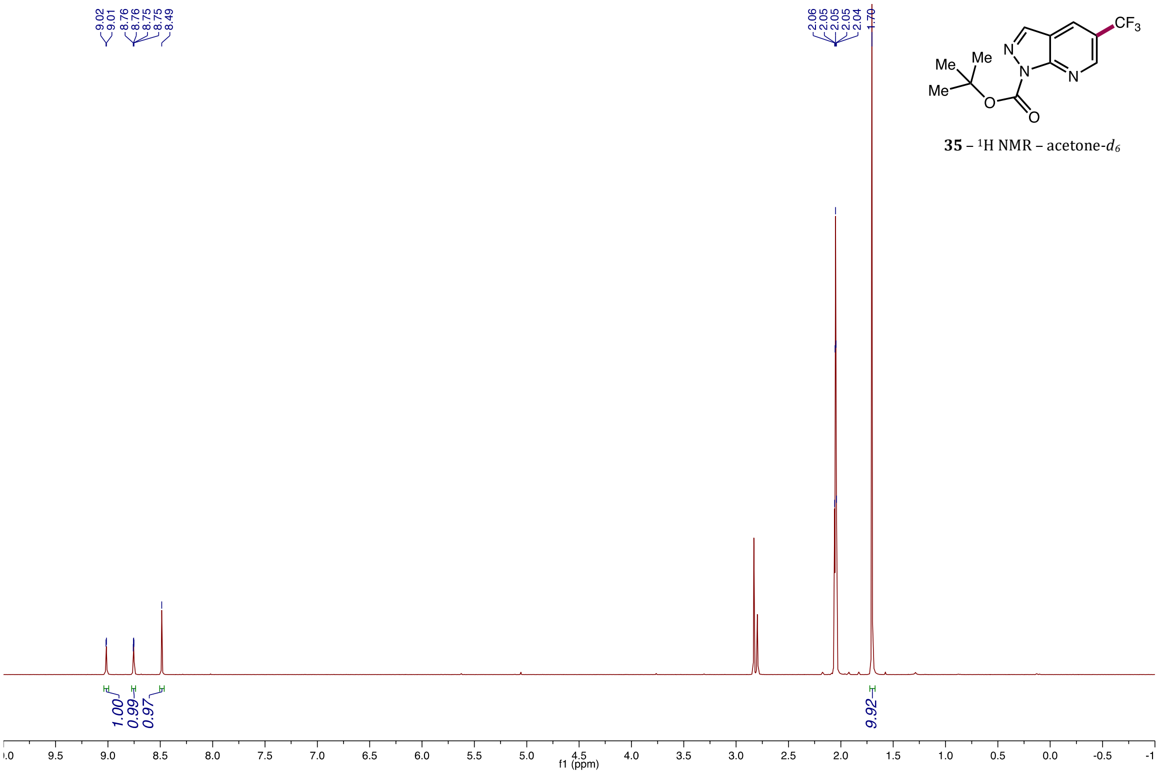
33 – ^{19}F NMR – CDCl$_3$



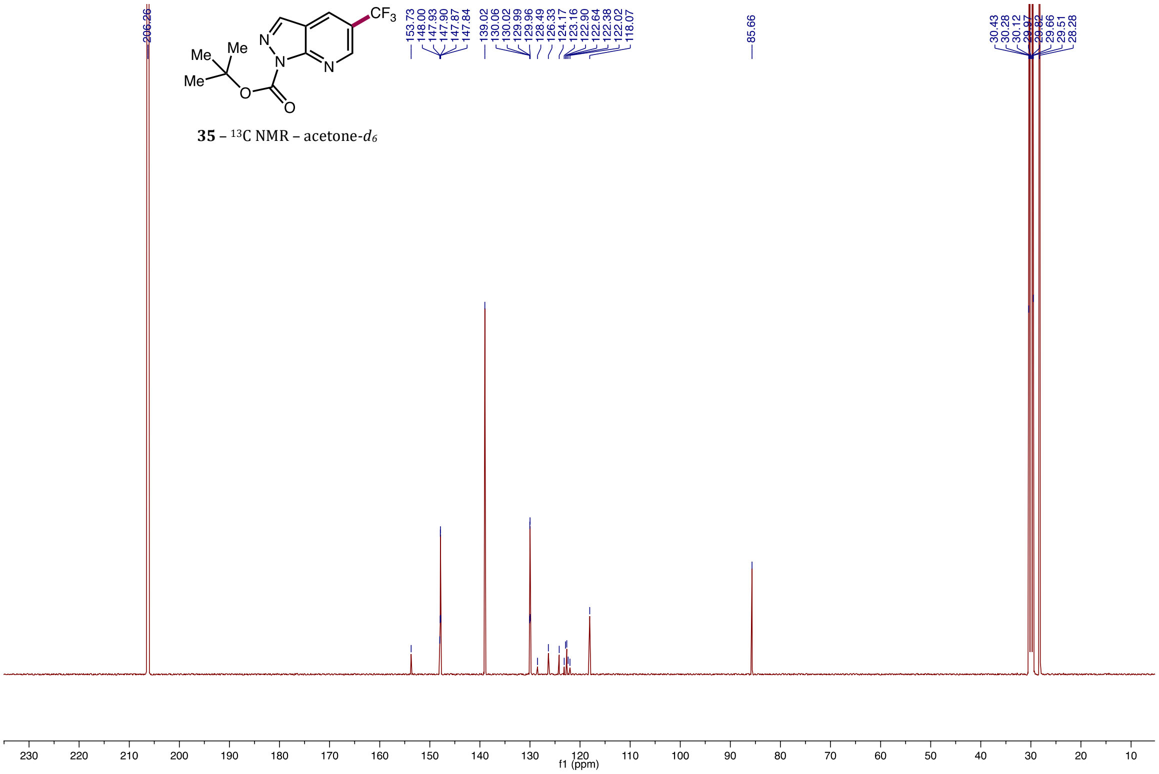
34 – ^{1}H NMR – CDCl$_3$



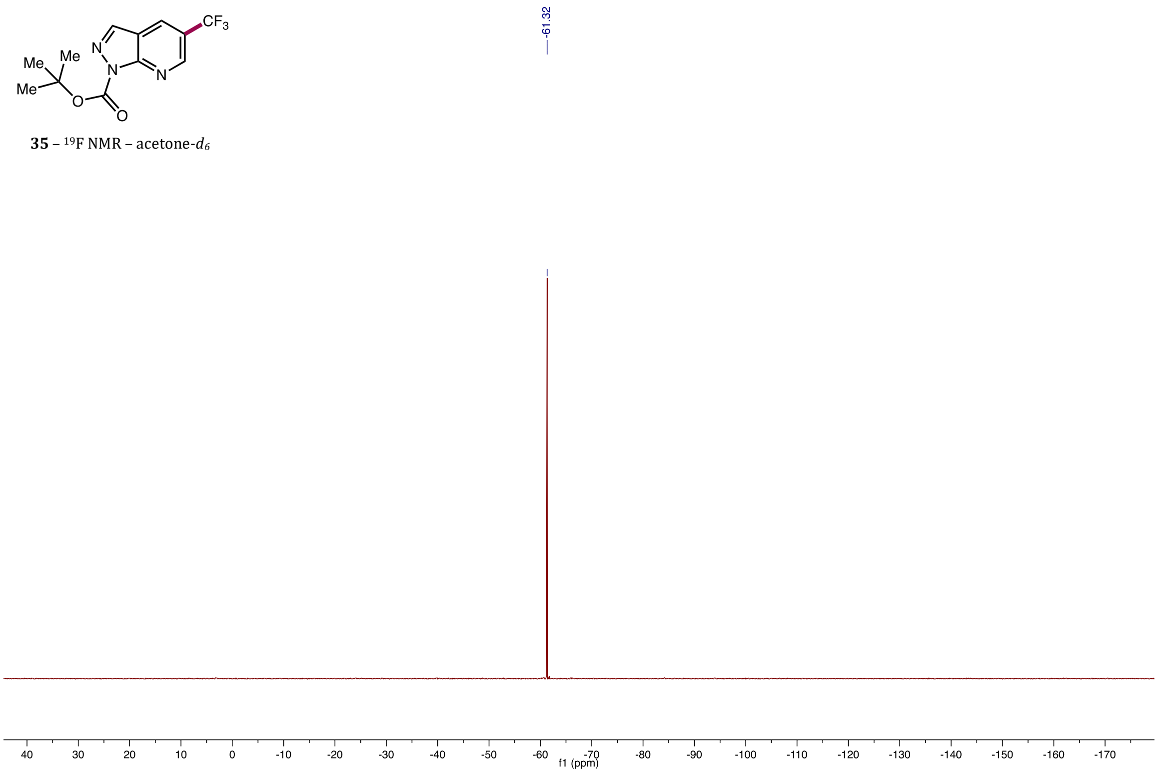
34 – ^{13}C NMR – CDCl$_3$



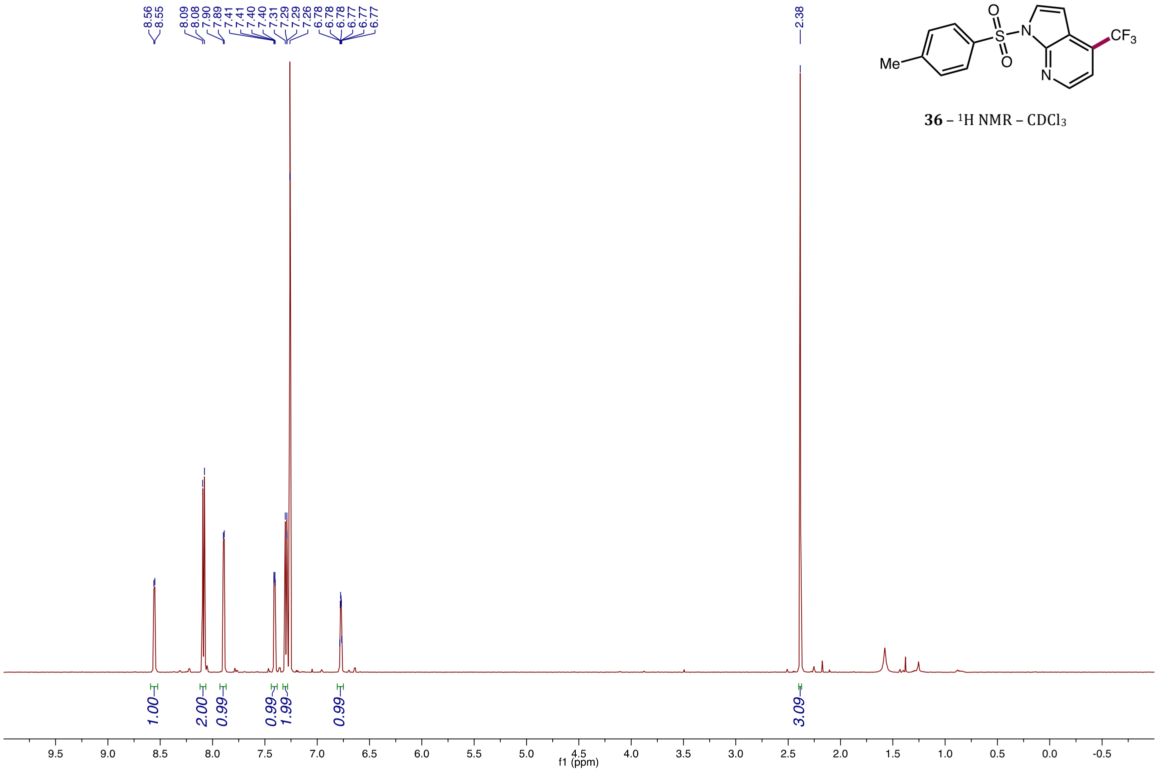
35 – ^{1}H NMR – acetone-d_6



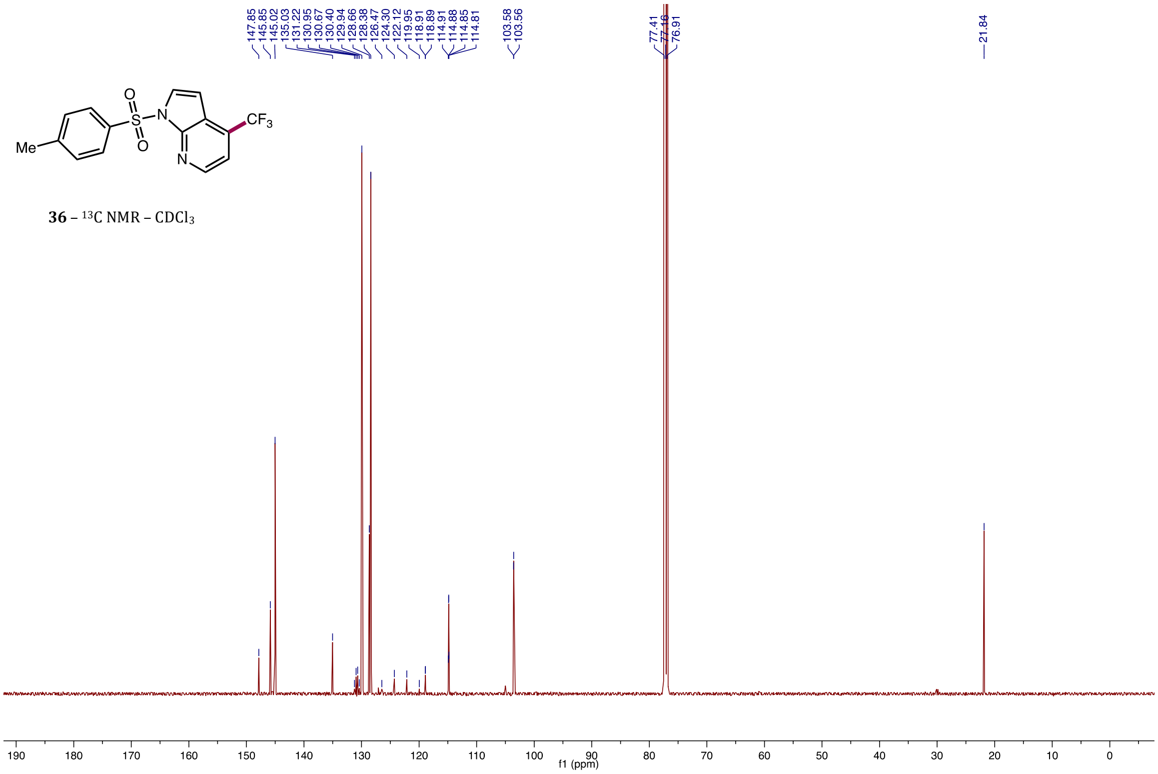
35 – ^{13}C NMR – acetone-*d*$_6$



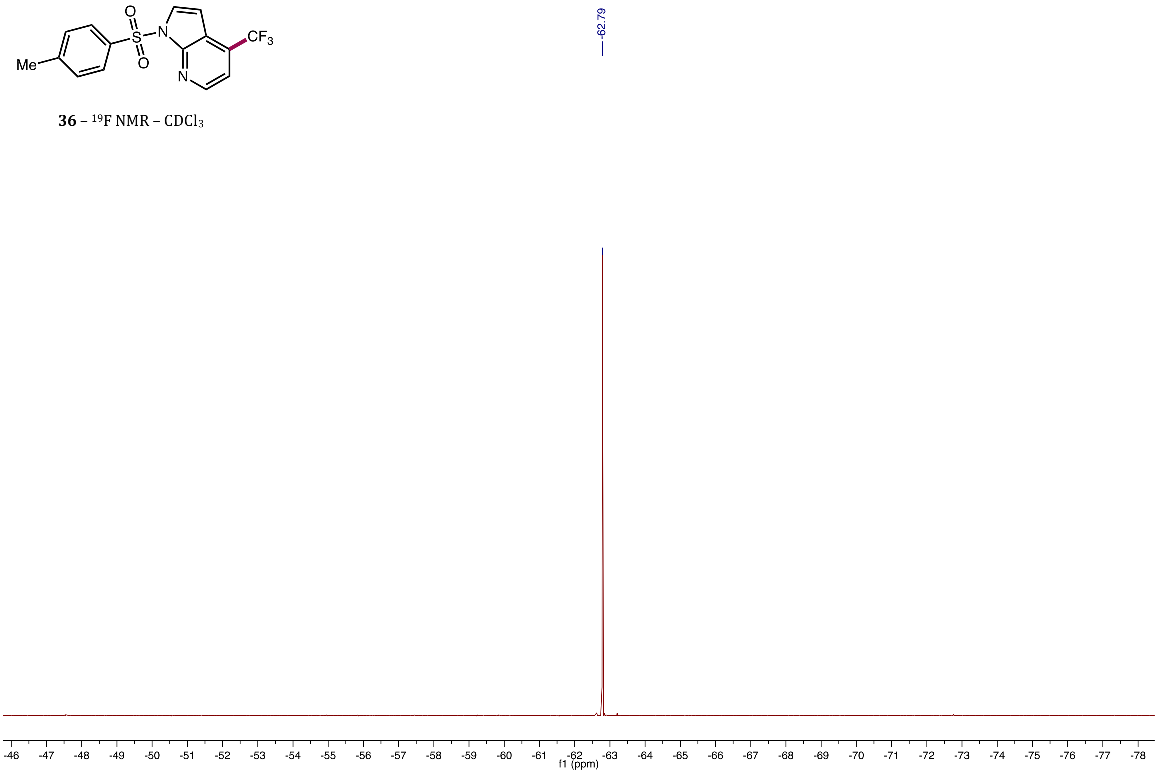
35 – ^{19}F NMR – acetone-*d*$_6$



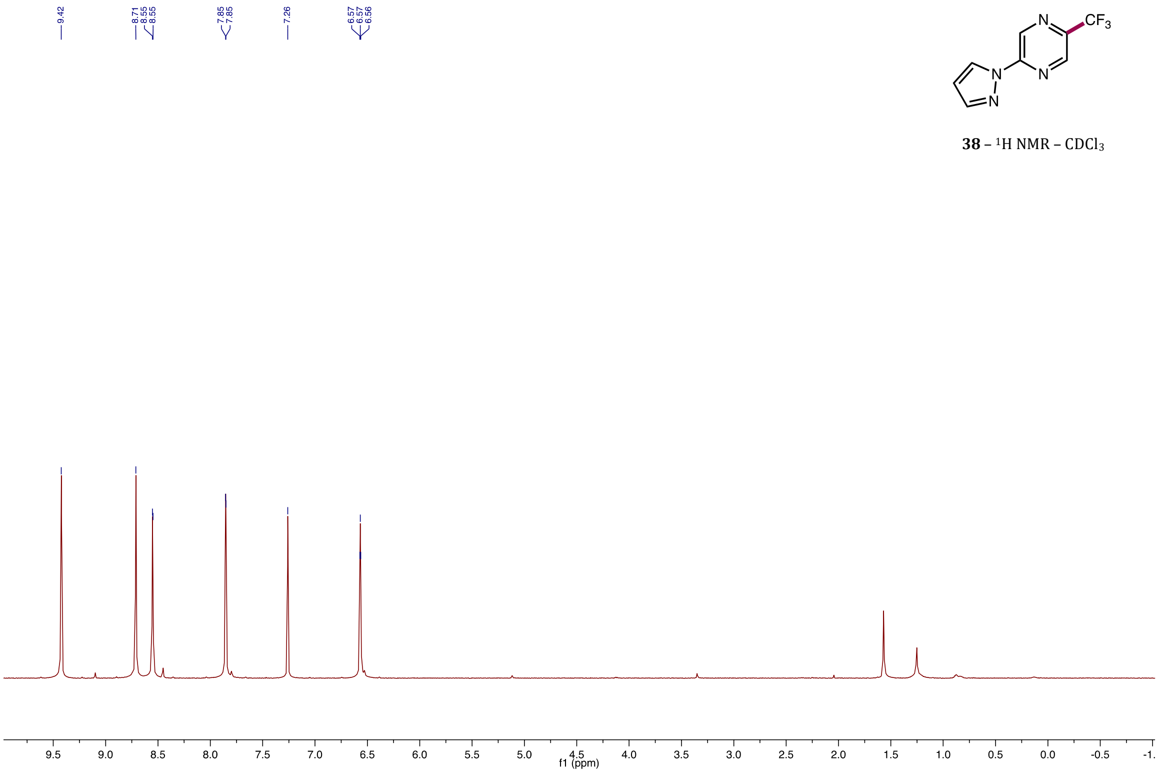
36 – ^{1}H NMR – CDCl$_3$



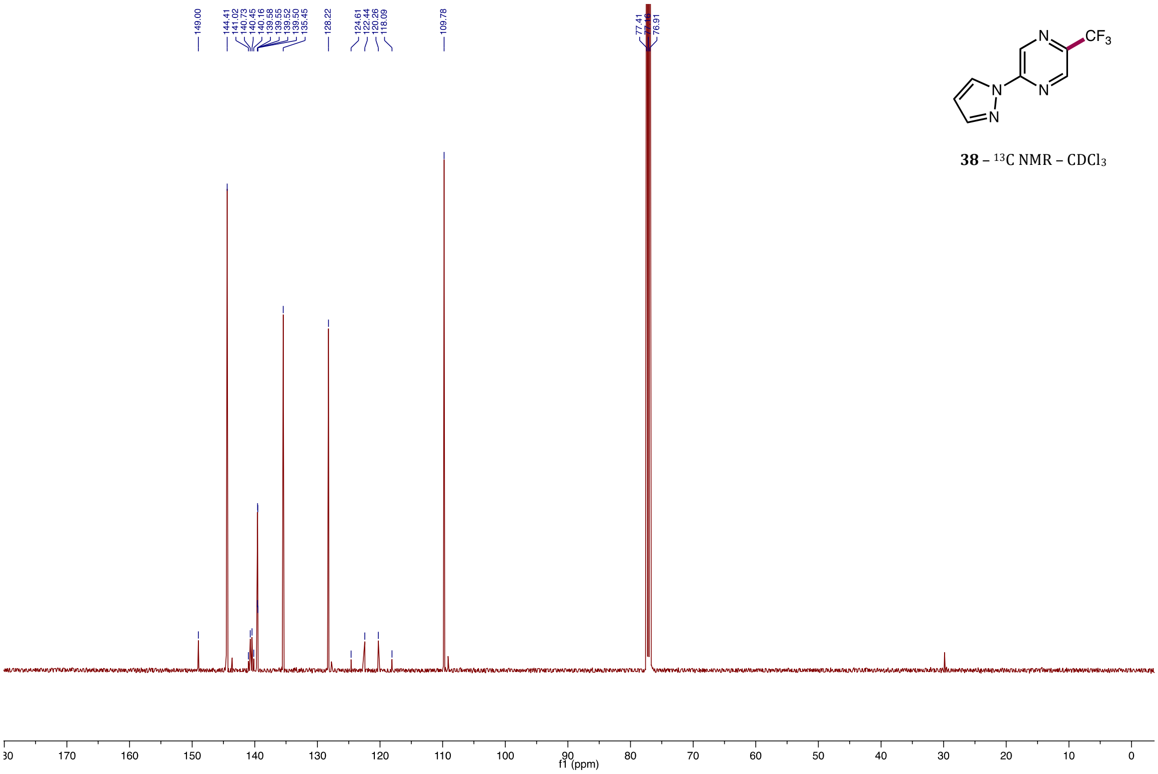
36 – ^{13}C NMR – CDCl$_3$



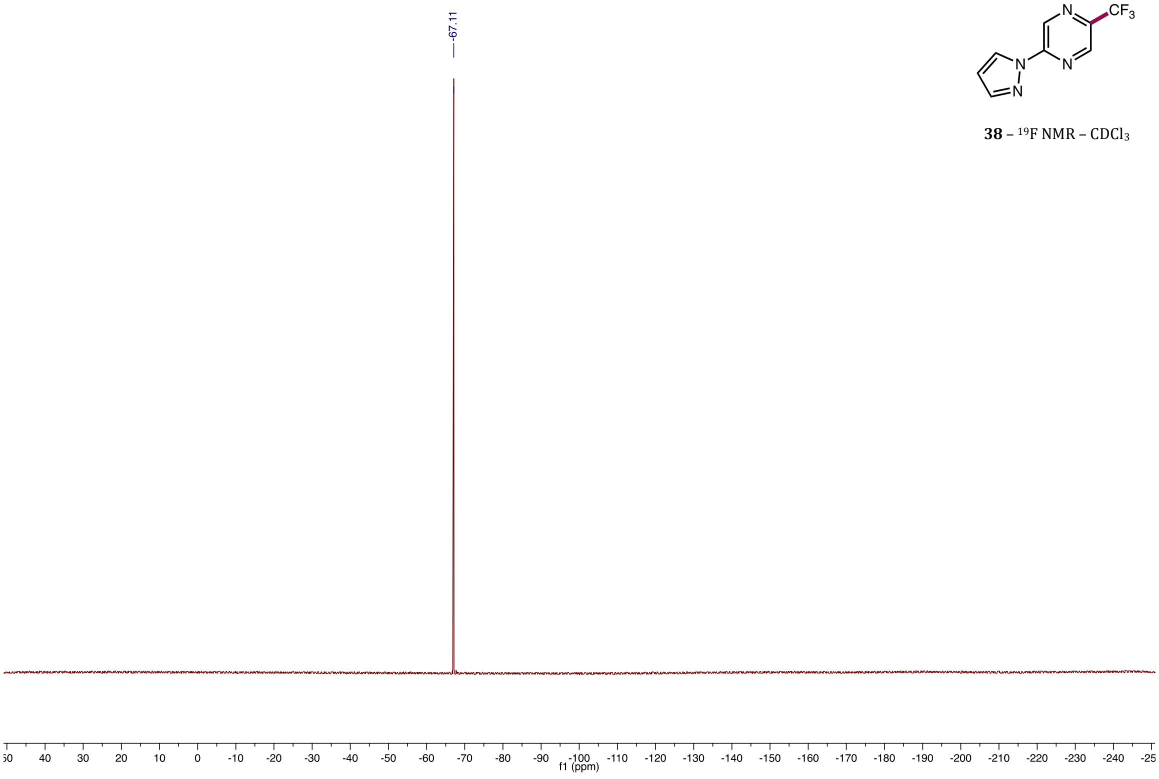
36 – ^{19}F NMR – CDCl$_3$



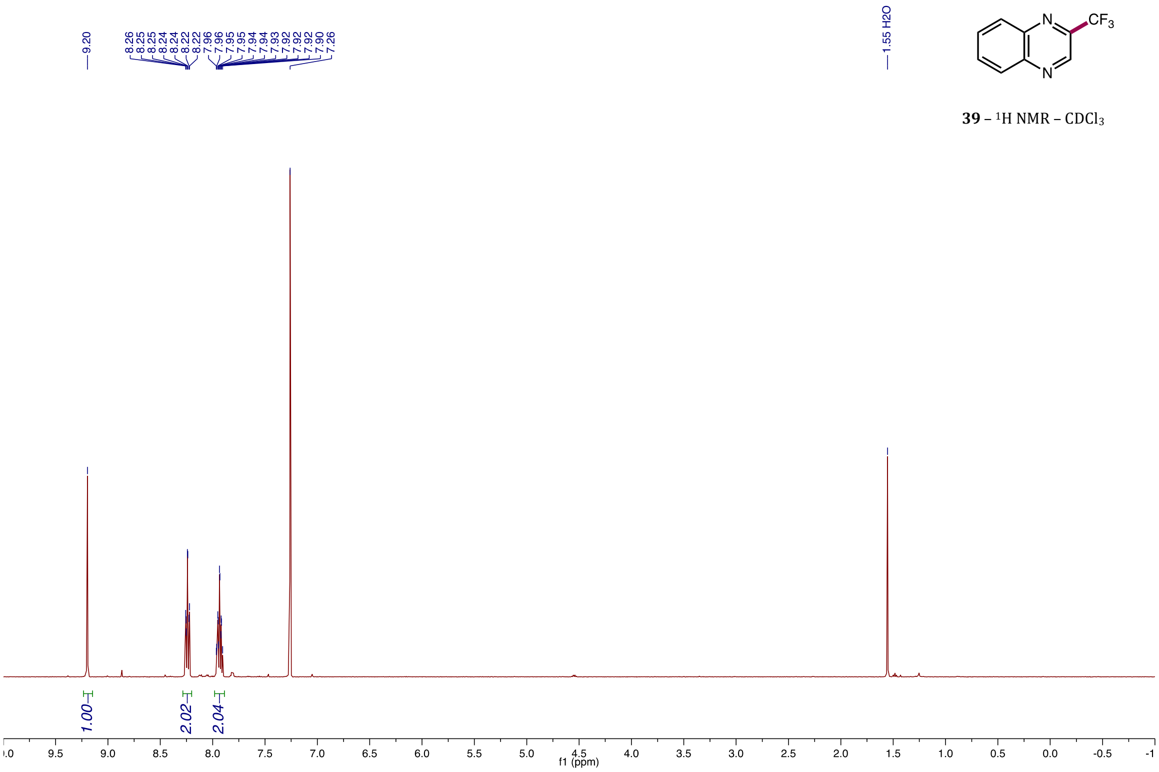
38 – ^{1}H NMR – CDCl$_3$



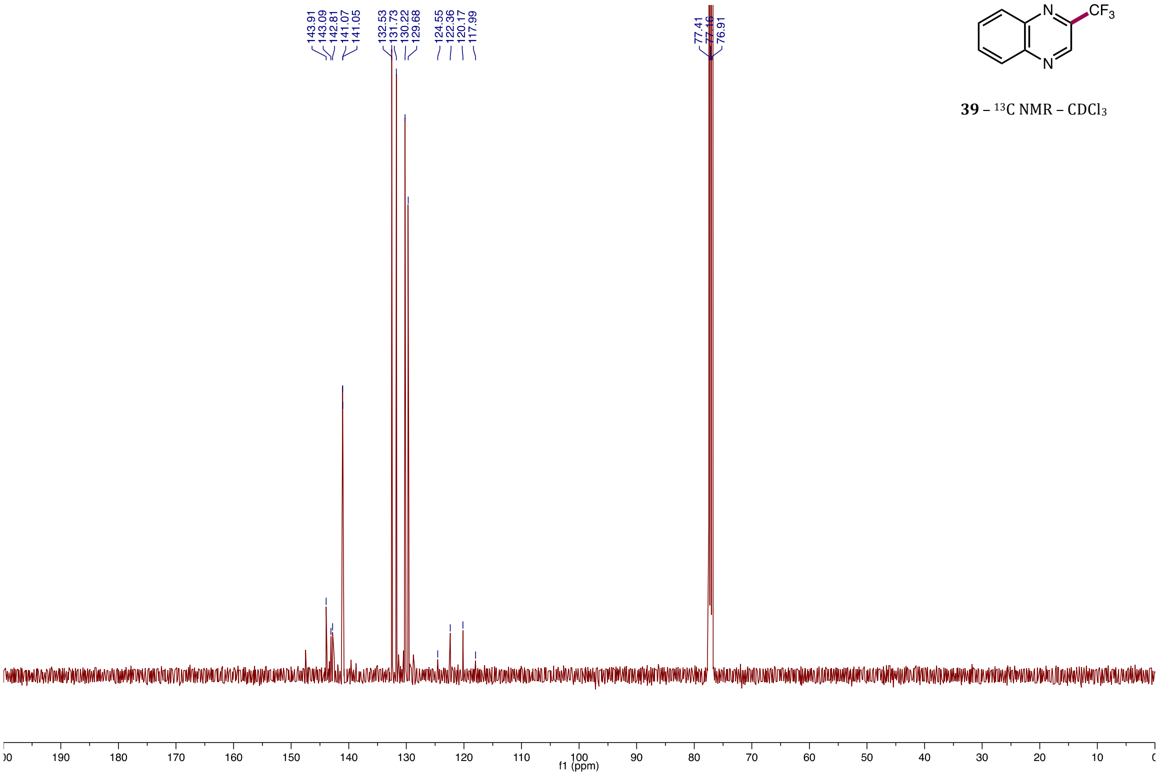
38 – ^{13}C NMR – CDCl$_3$



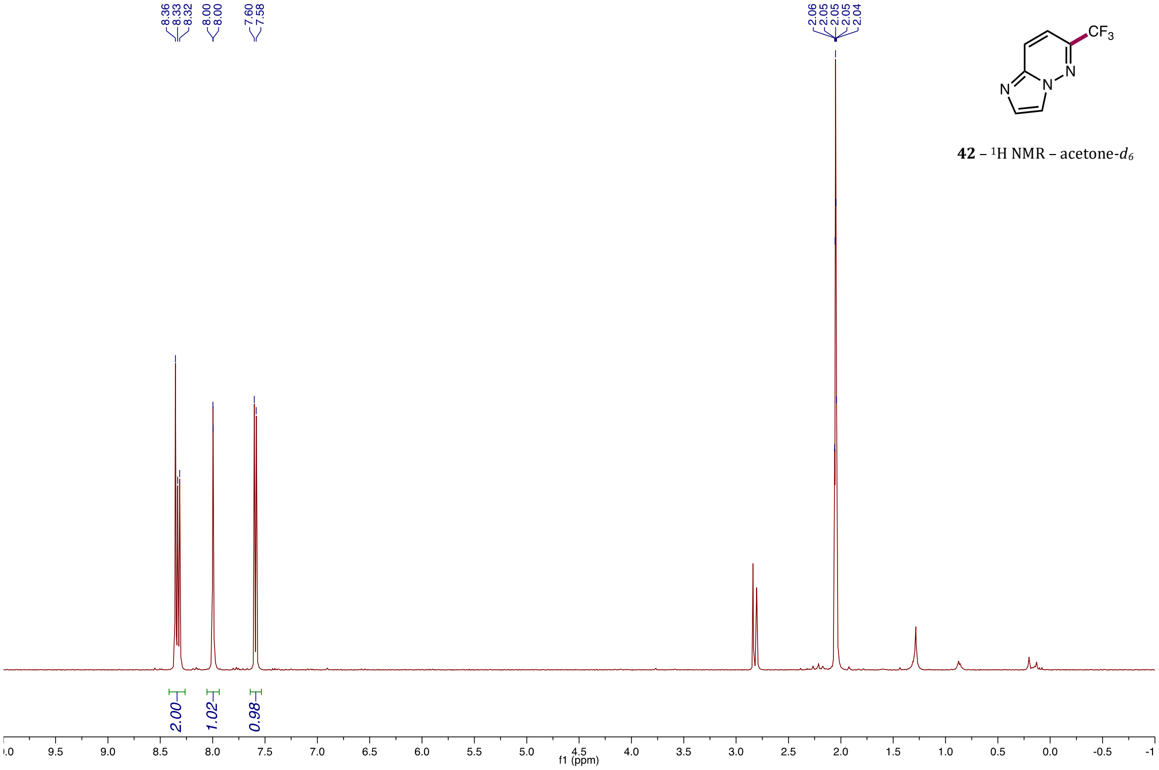
38 – ^{19}F NMR – CDCl$_3$



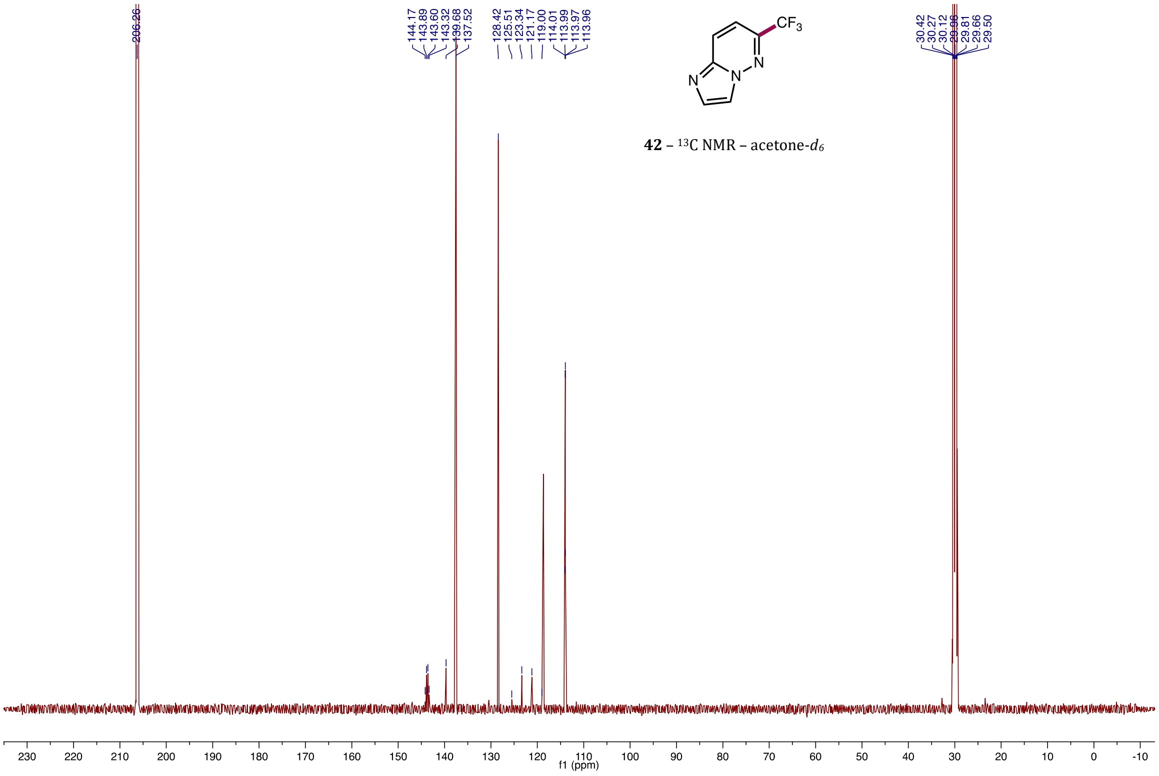
39 – ^{1}H NMR – CDCl$_3$



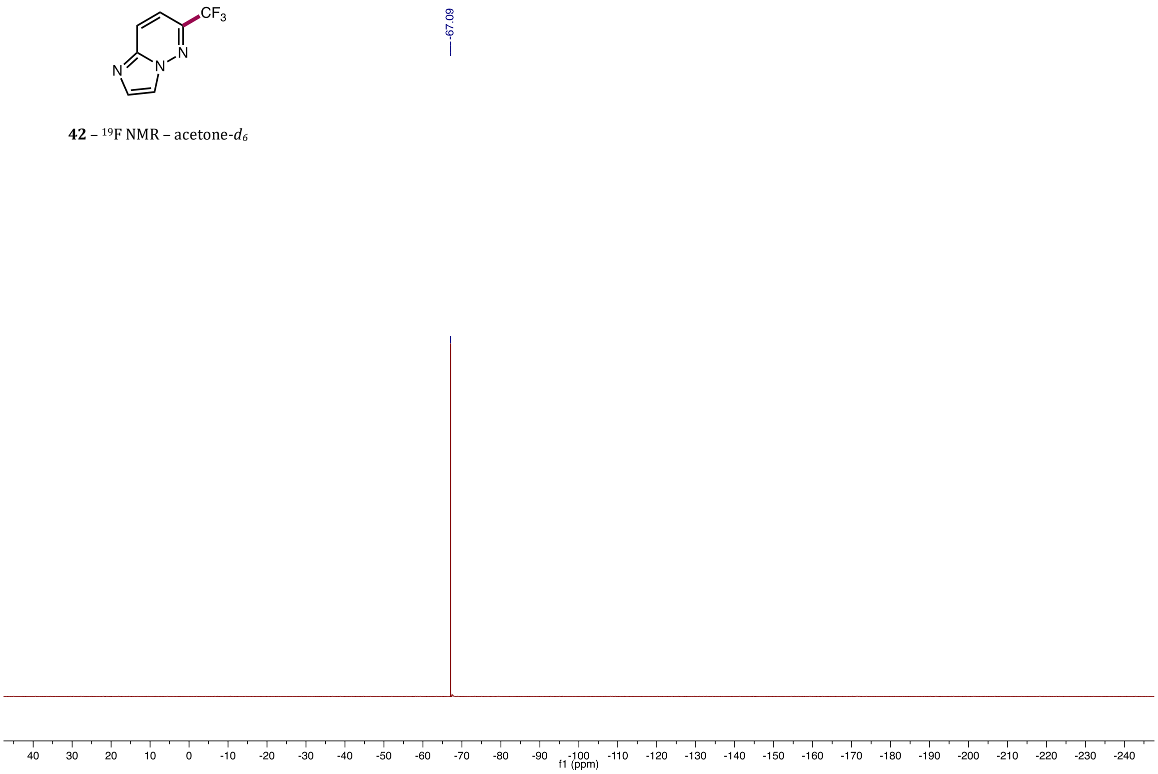
39 – ^{13}C NMR – CDCl$_3$



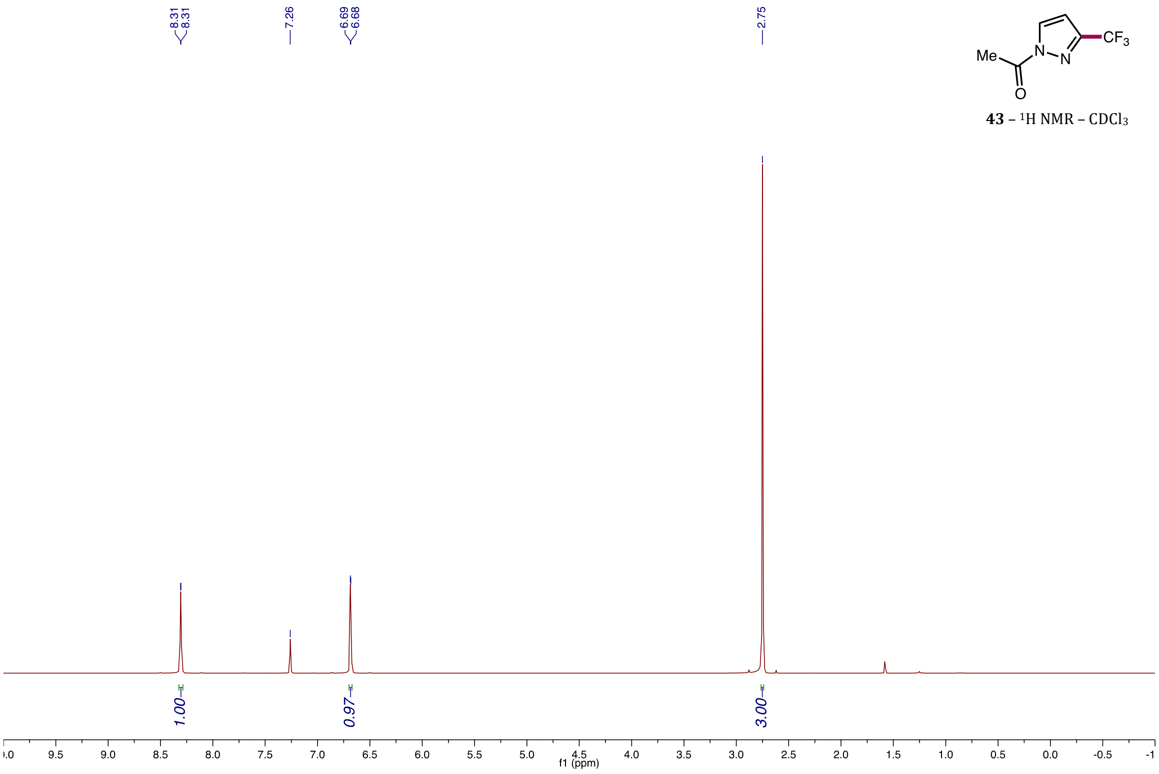
42 – ^{1}H NMR – acetone-d_6



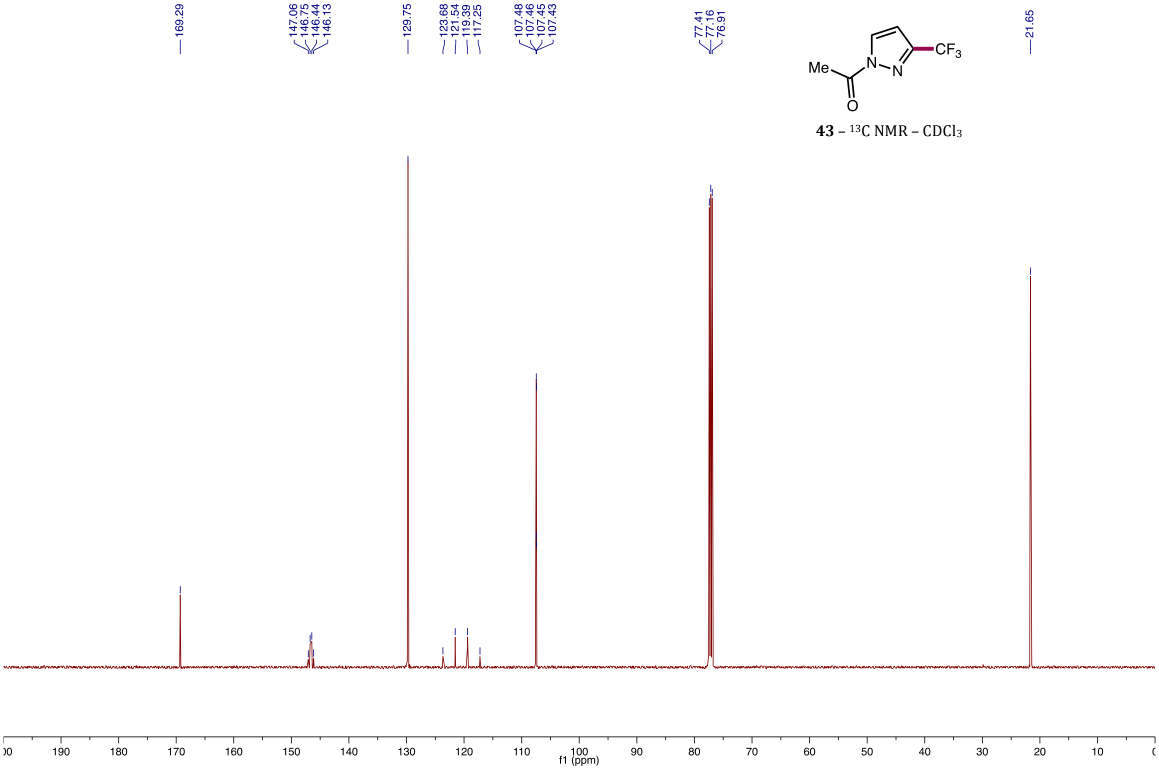
42 – ^{13}C NMR – acetone-d_6



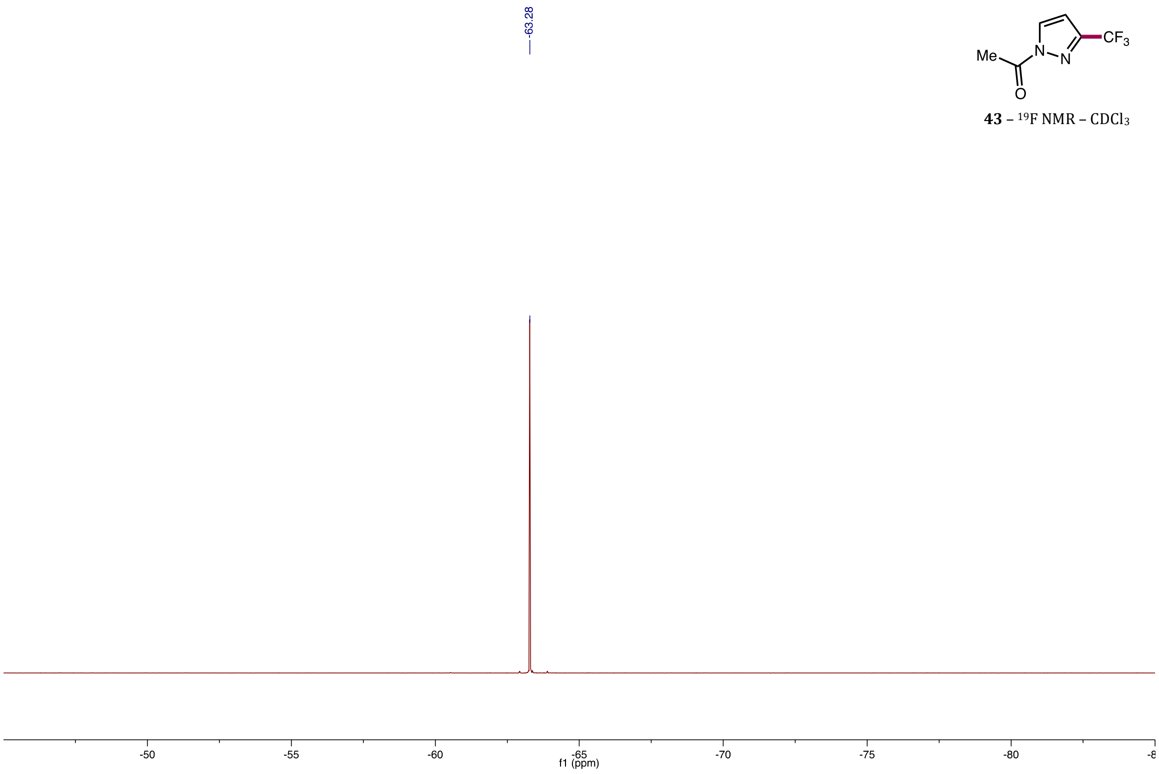
42 – ^{19}F NMR – acetone-*d*$_6$



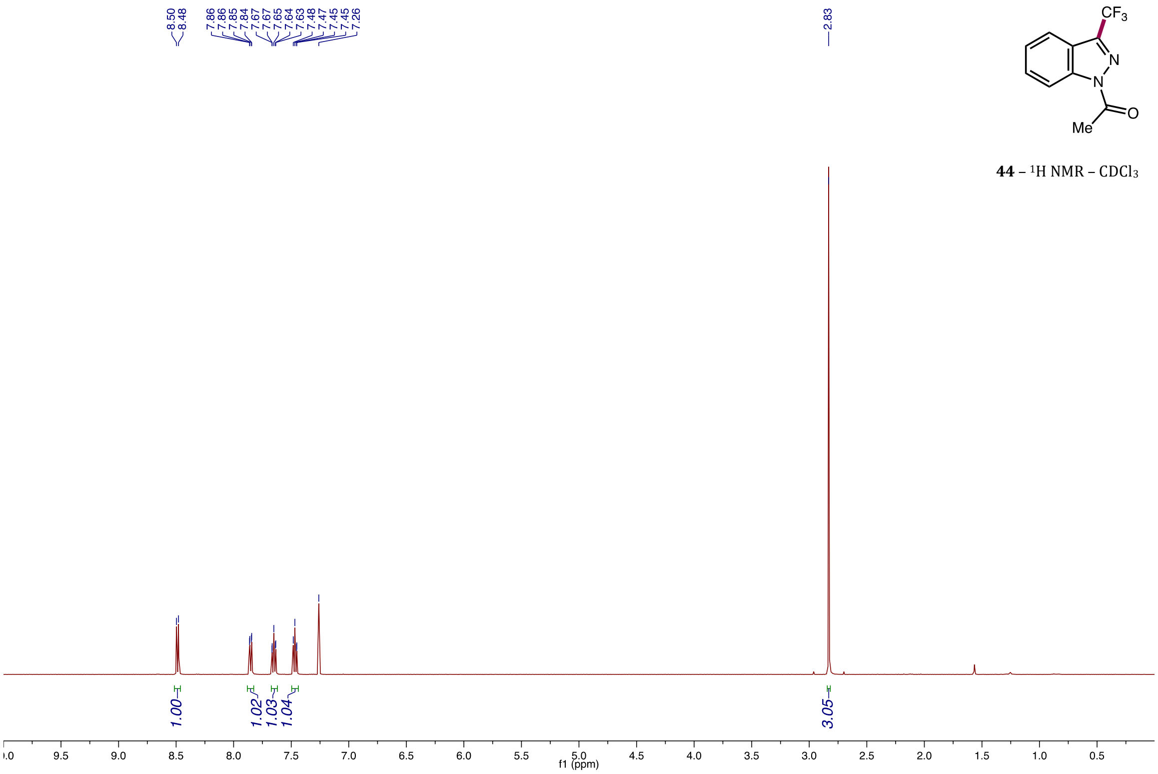
43 – ^{1}H NMR – CDCl$_3$



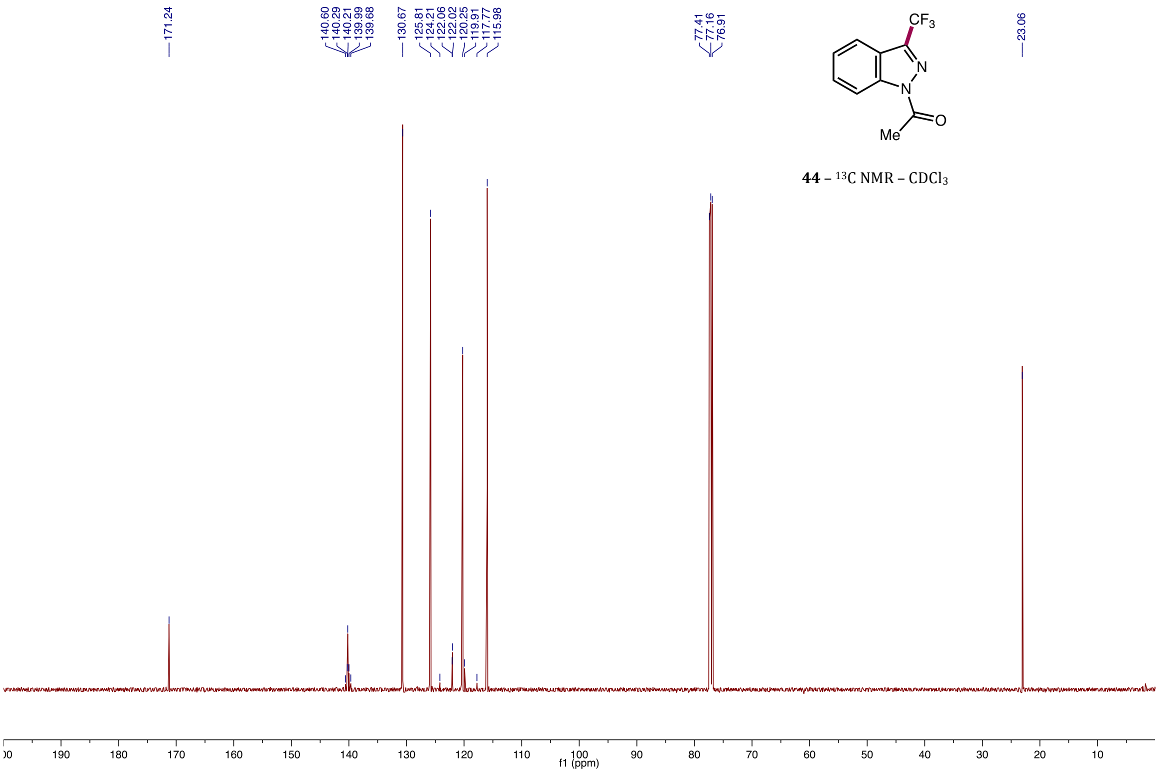
43 – ^{13}C NMR – CDCl$_3$



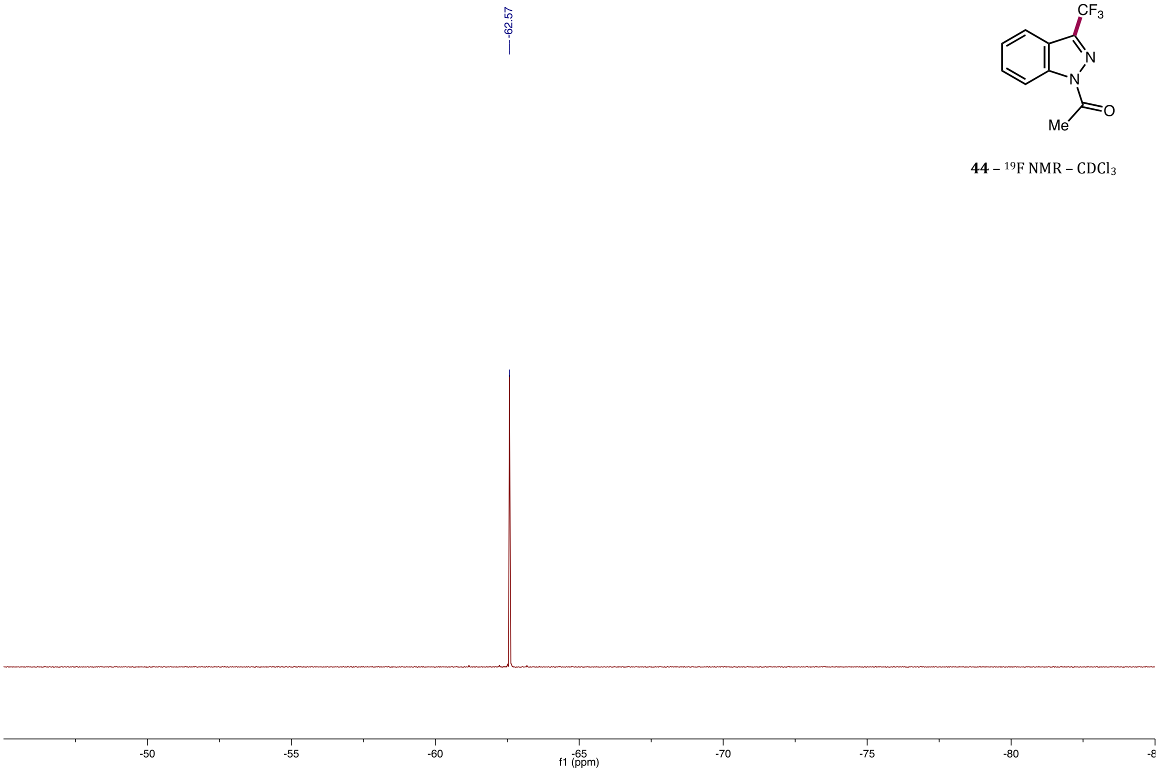
43 – ^{19}F NMR – CDCl$_3$



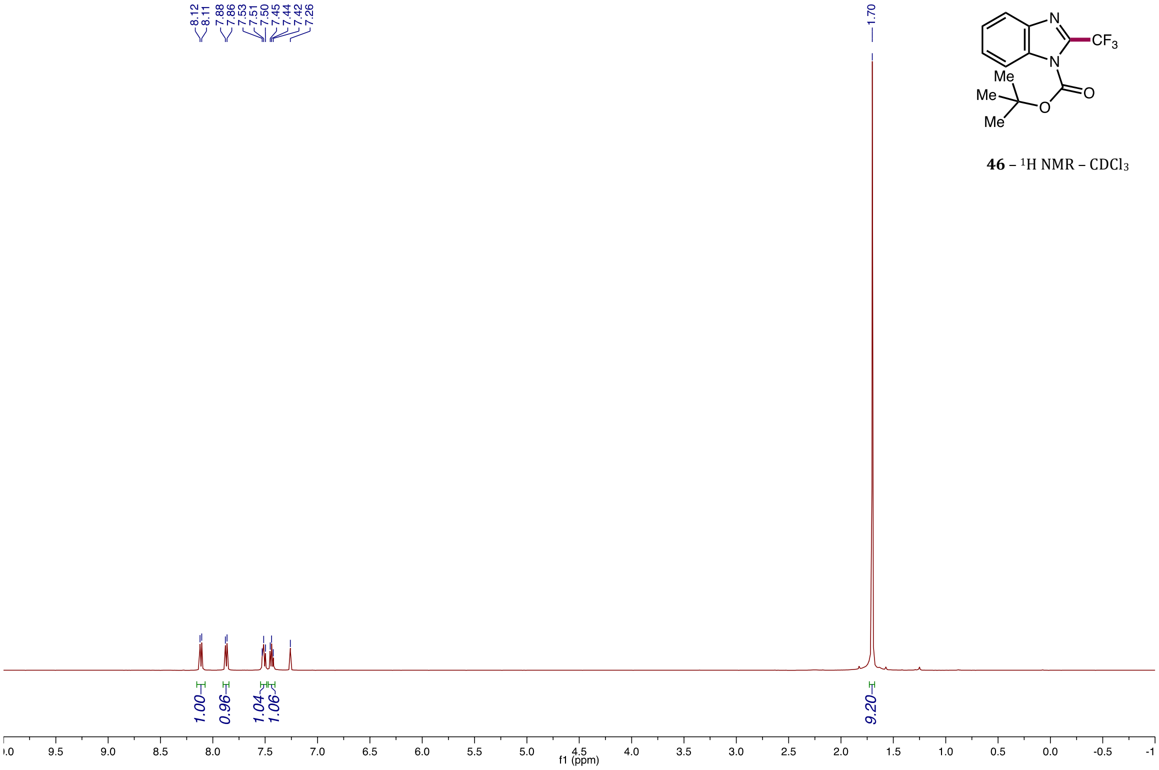
44 – ^{1}H NMR – CDCl$_3$



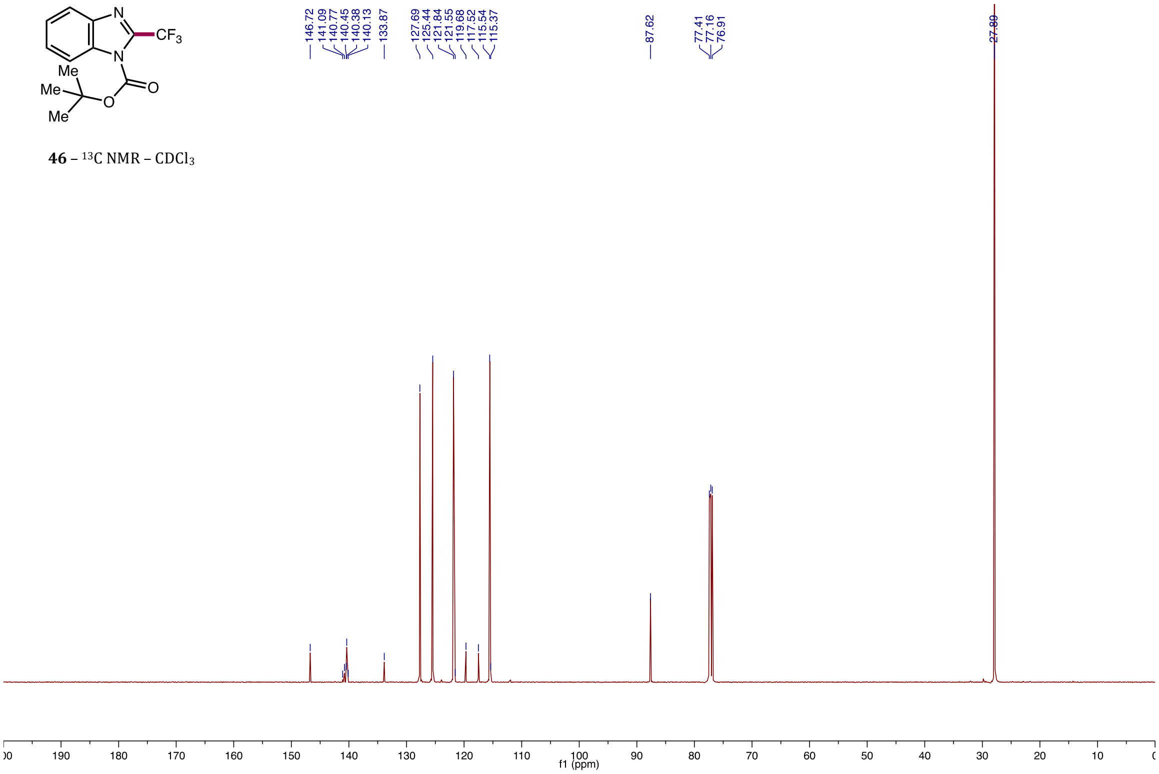
44 – ^{13}C NMR – CDCl$_3$



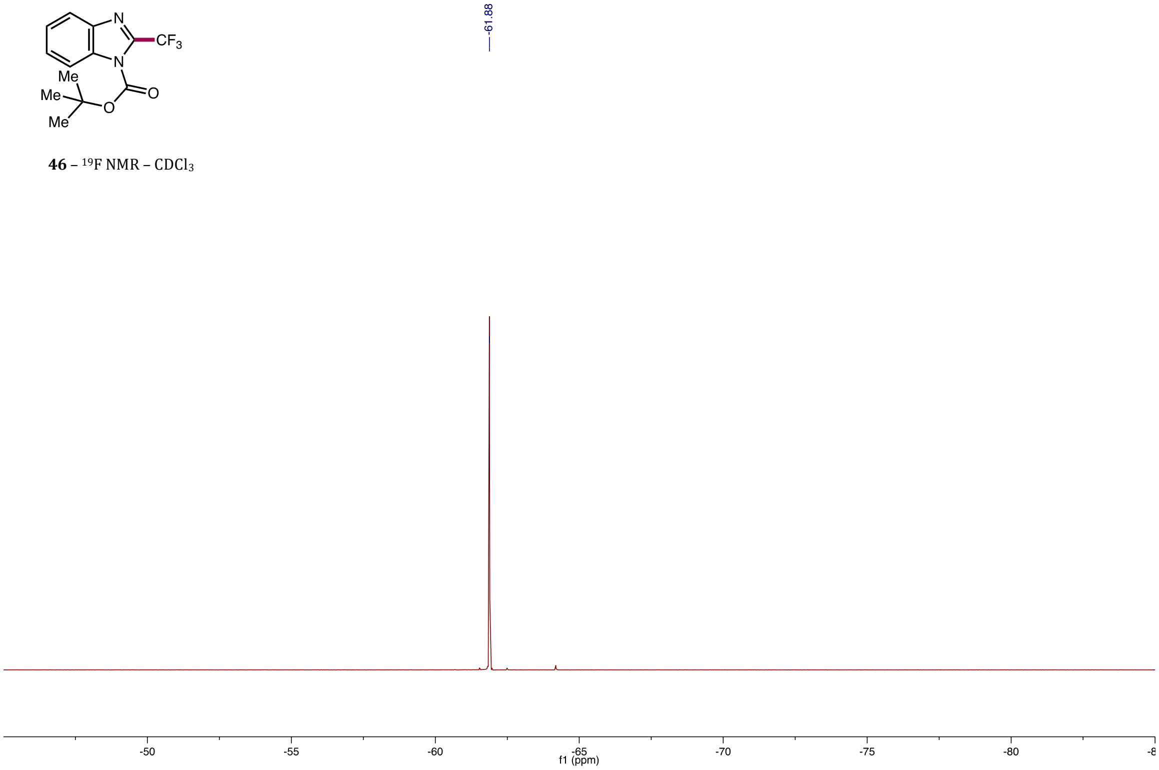
44 – ^{19}F NMR – CDCl$_3$



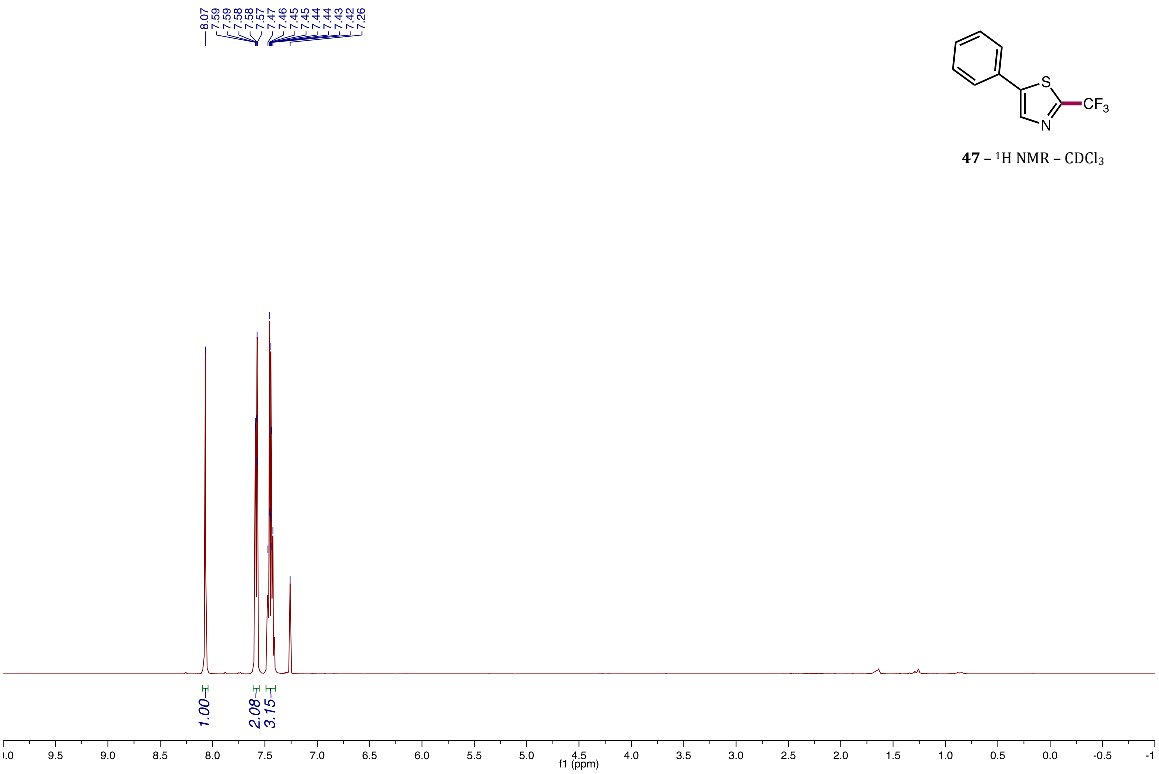
46 – ^{1}H NMR – CDCl$_3$



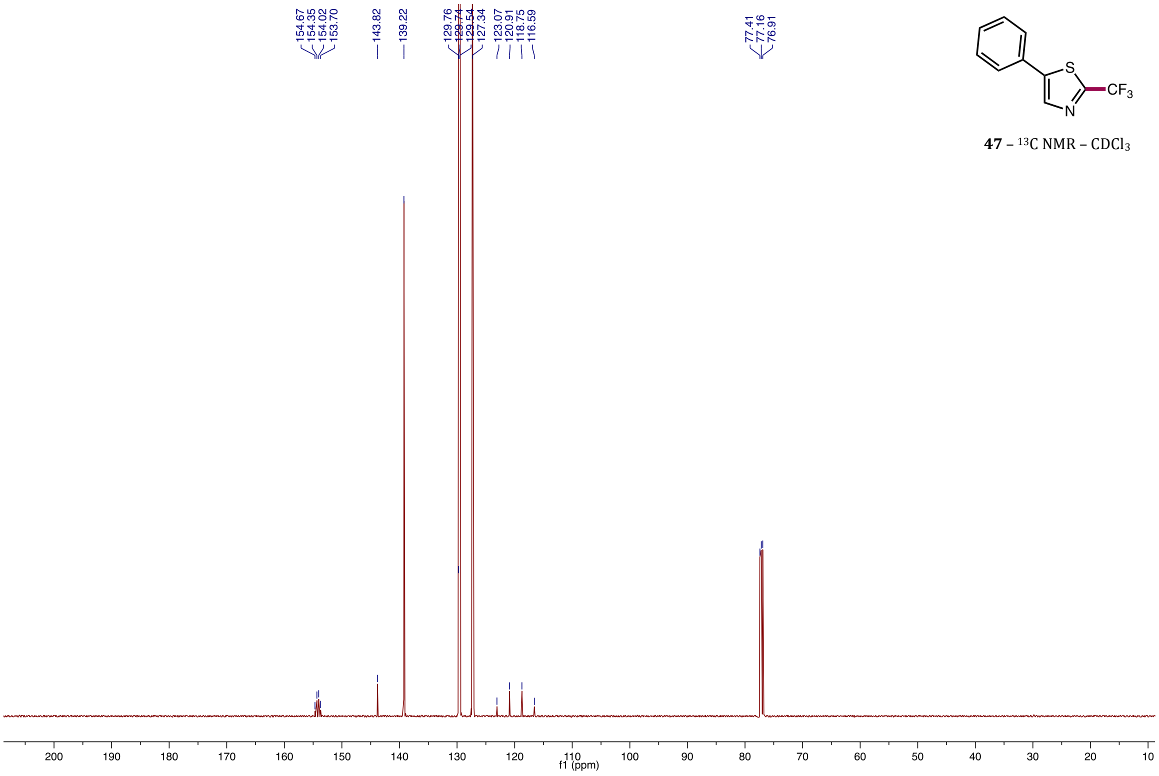
46 – ^{13}C NMR – CDCl$_3$



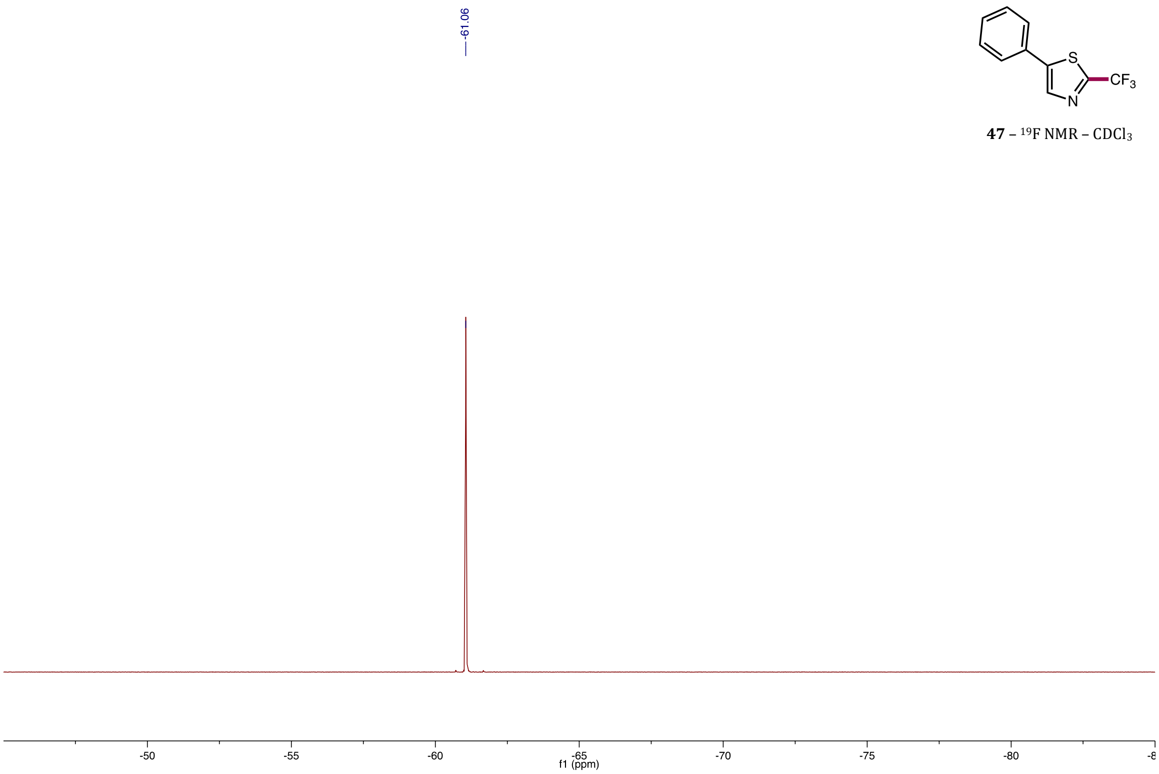
46 – ^{19}F NMR – CDCl$_3$



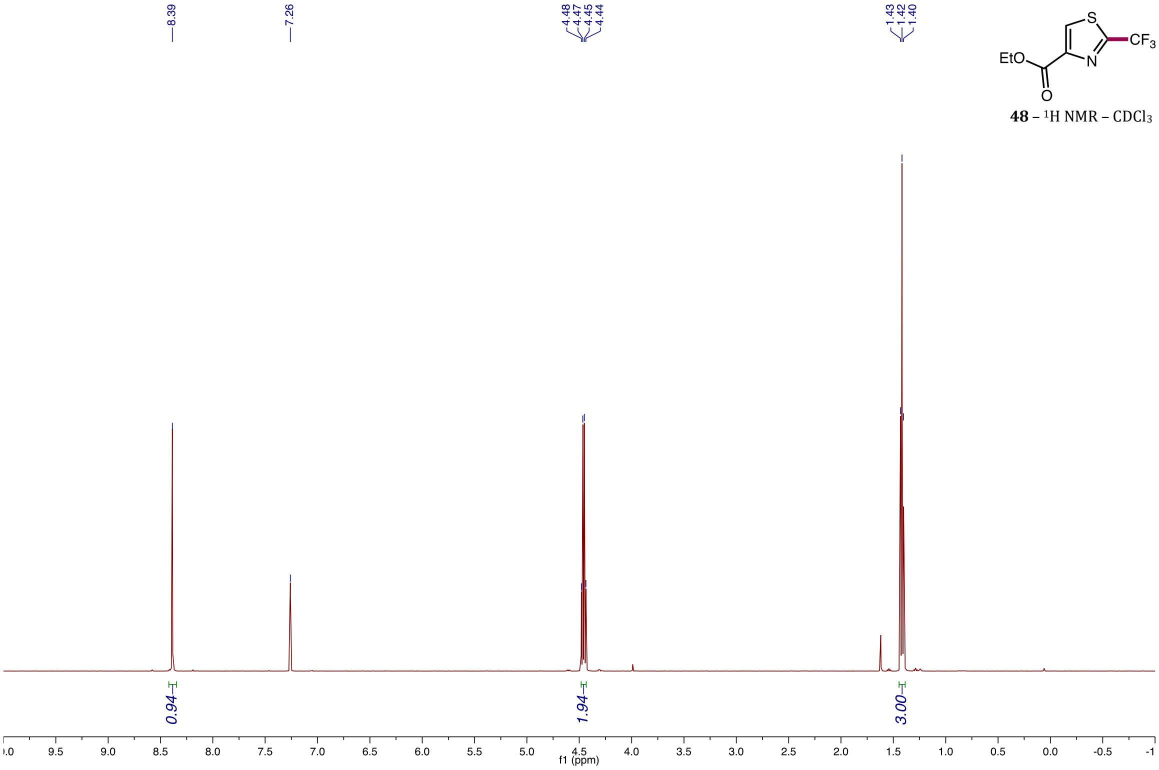
47 – ^{1}H NMR – CDCl$_3$



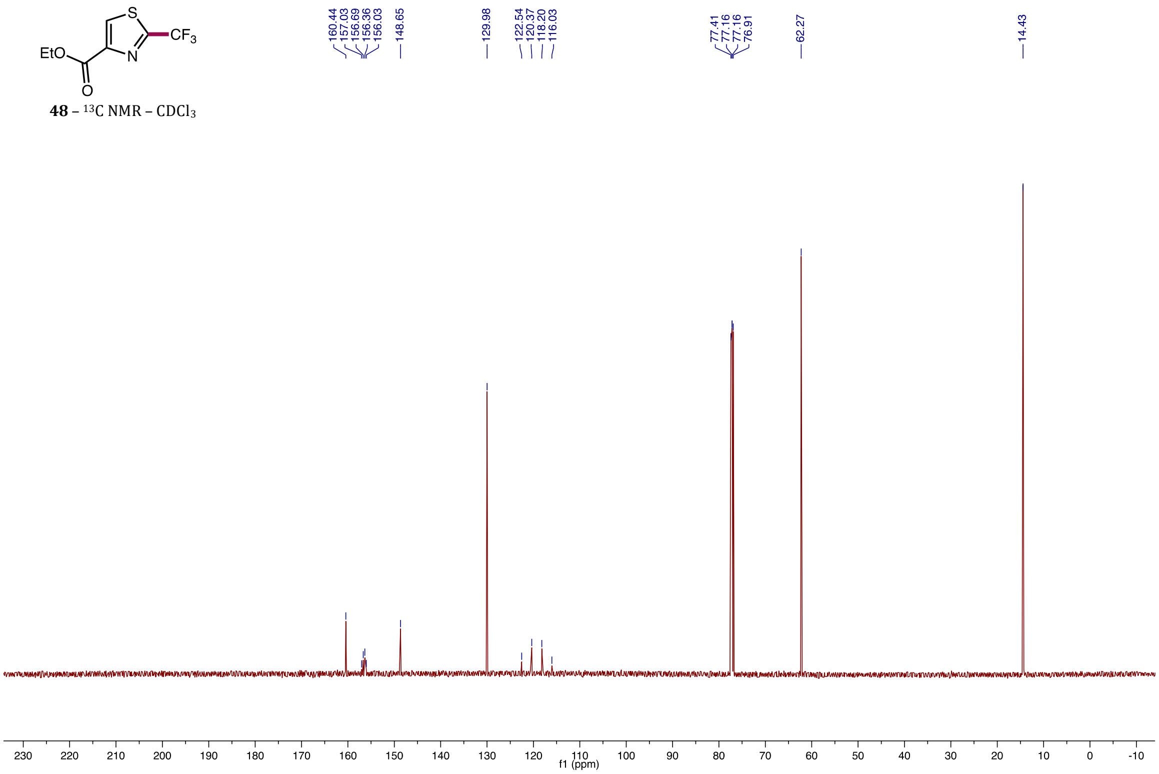
47 – ^{13}C NMR – CDCl$_3$



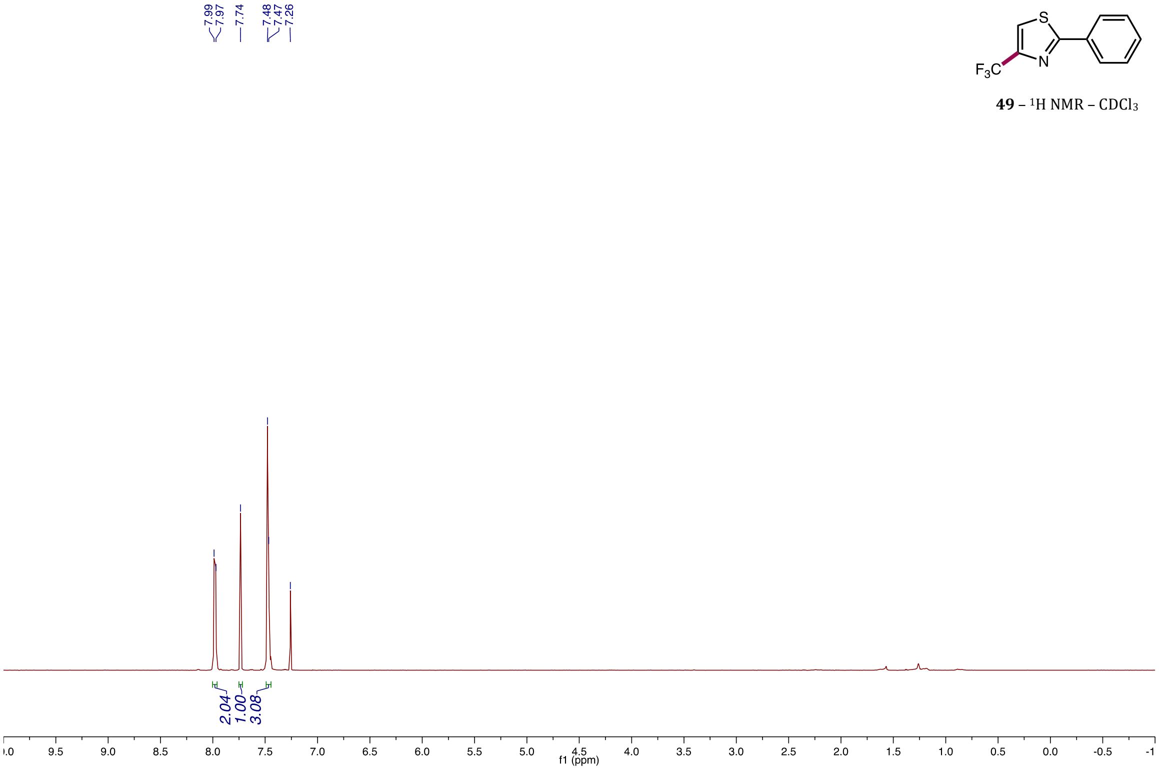
47 – ^{19}F NMR – CDCl$_3$



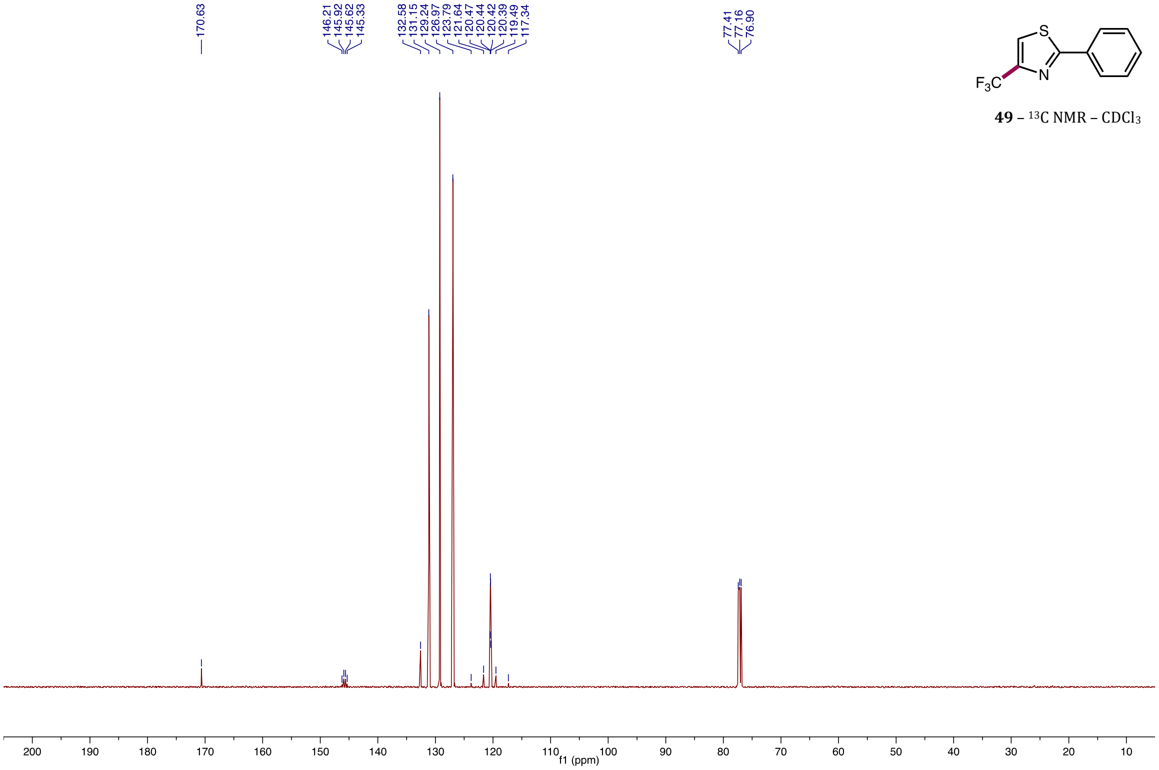
48 – ^{1}H NMR – CDCl$_3$



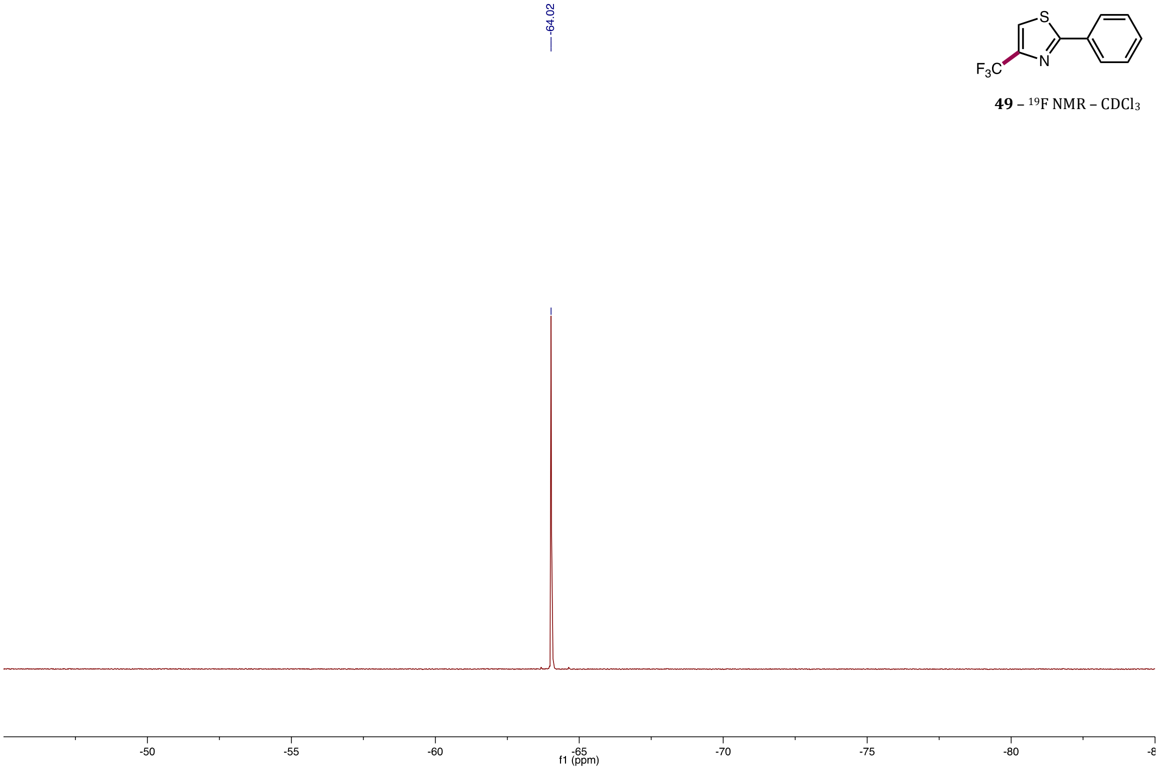
48 – ^{13}C NMR – CDCl$_3$



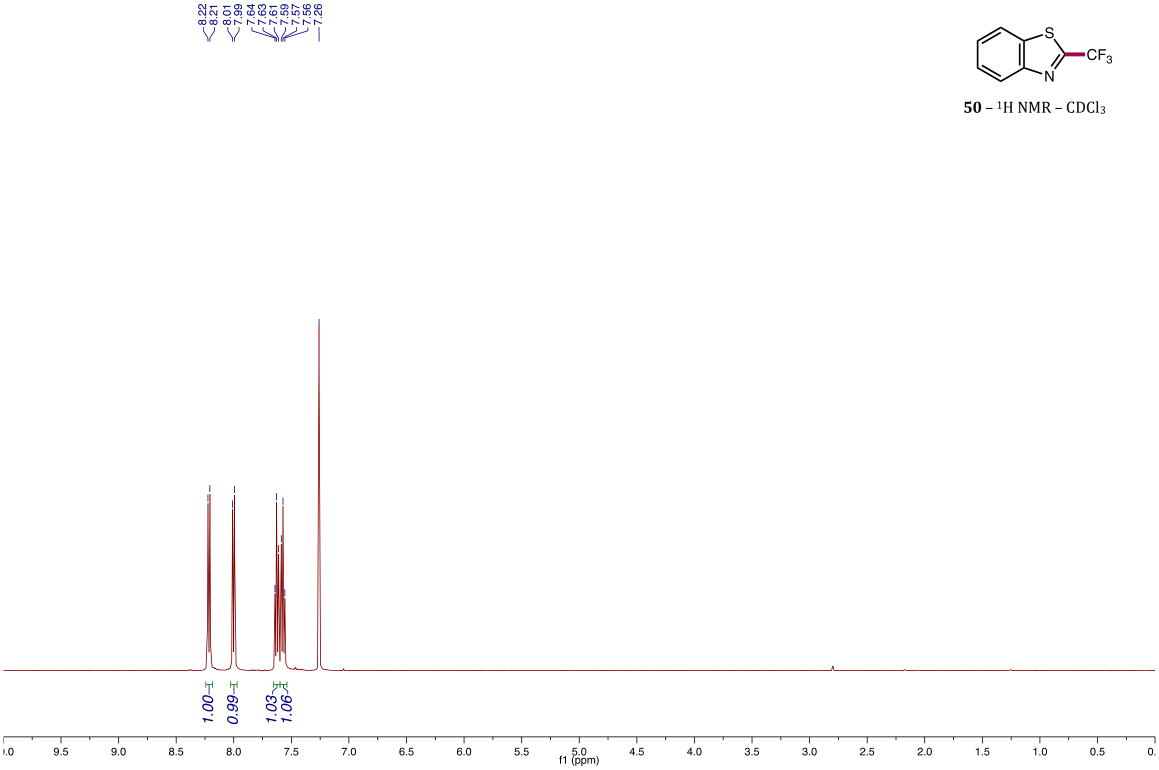
49 – ^{1}H NMR – CDCl$_3$



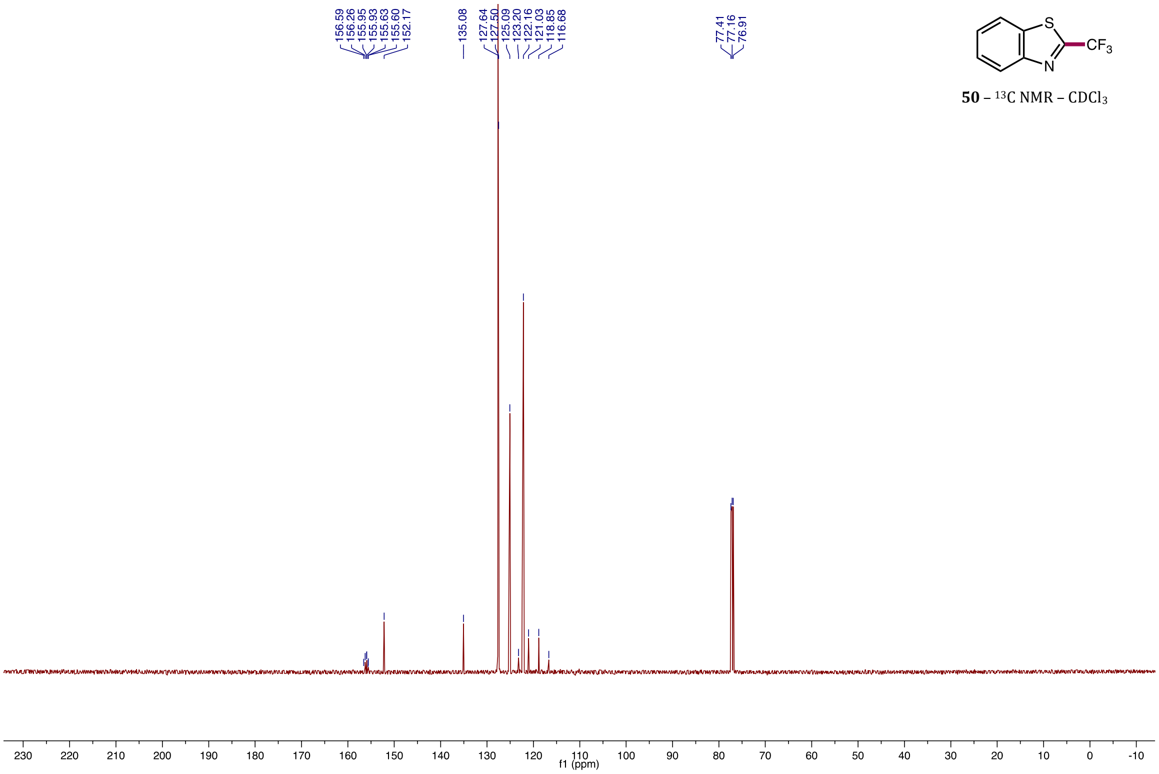
49 – ^{13}C NMR – CDCl$_3$



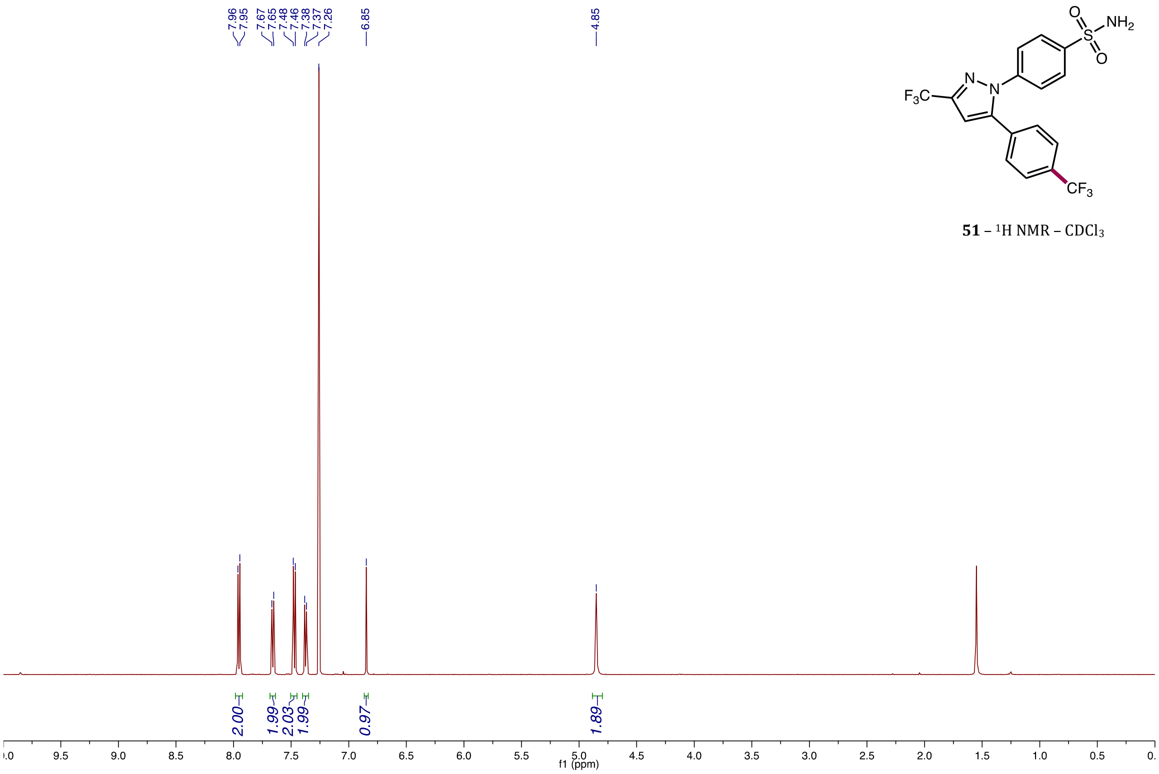
49 – ^{19}F NMR – CDCl$_3$



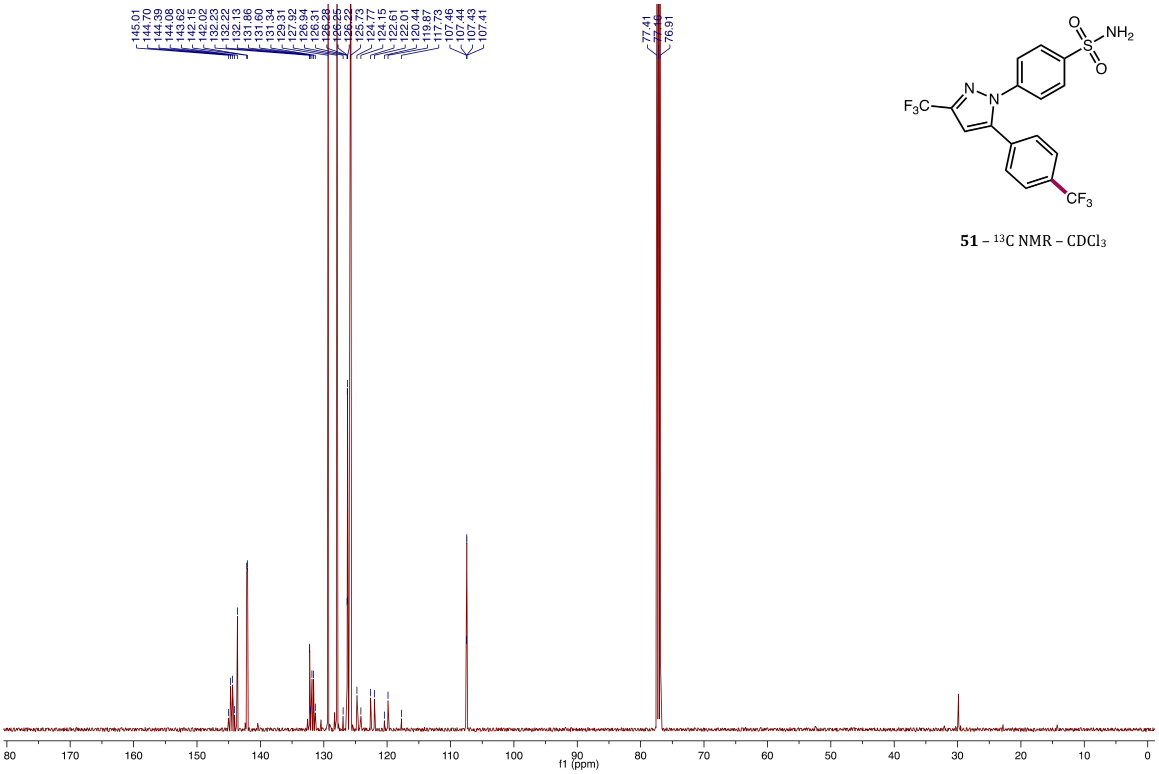
50 – ^{1}H NMR – CDCl$_3$



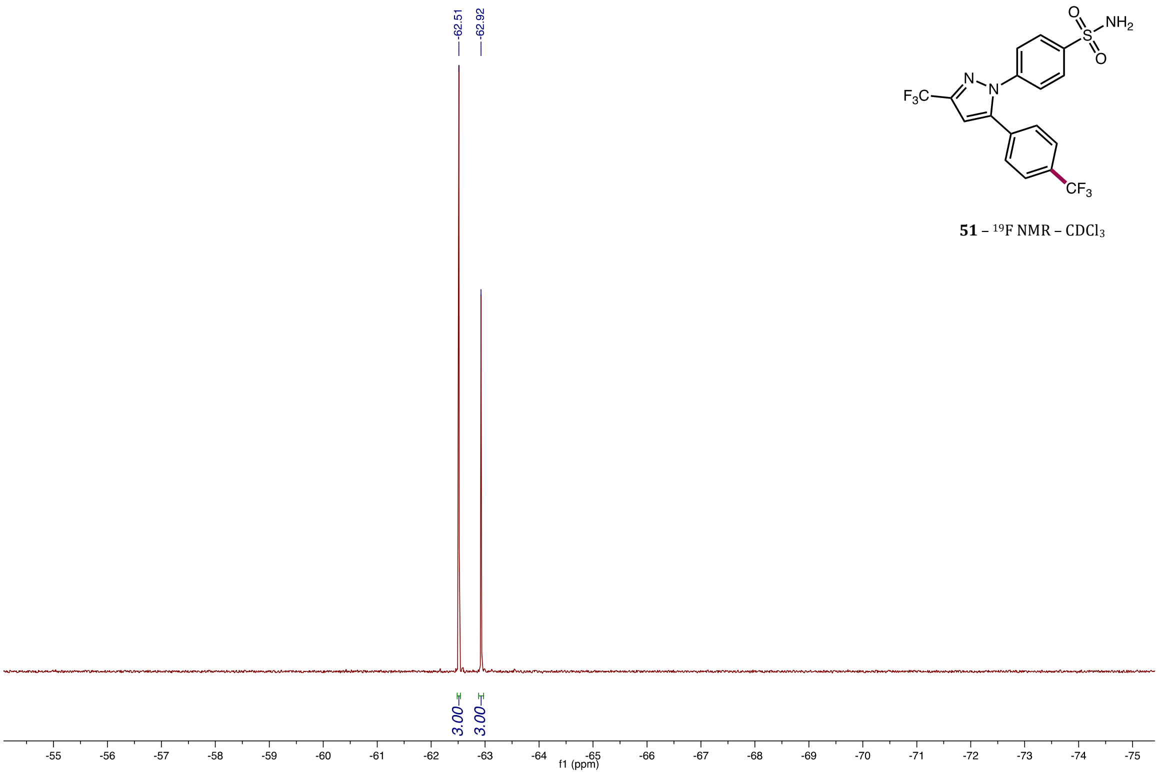
50 – ^{13}C NMR – CDCl$_3$



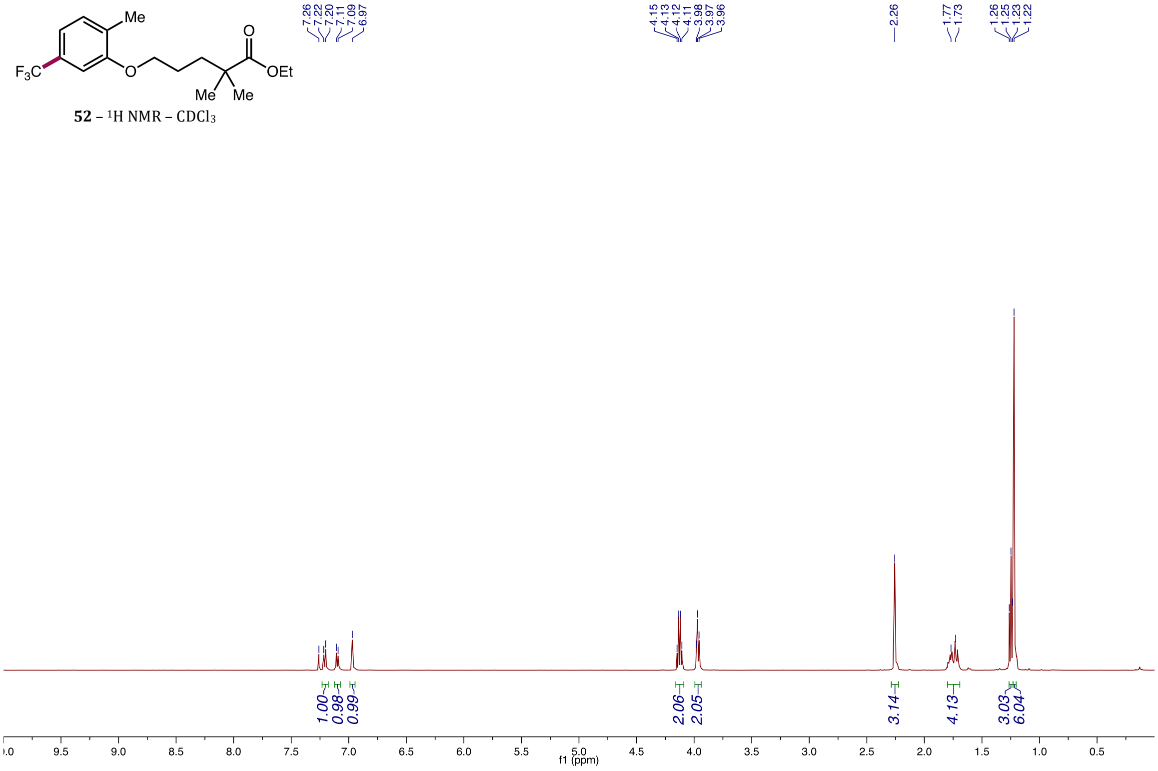
51 – ^{1}H NMR – CDCl$_3$



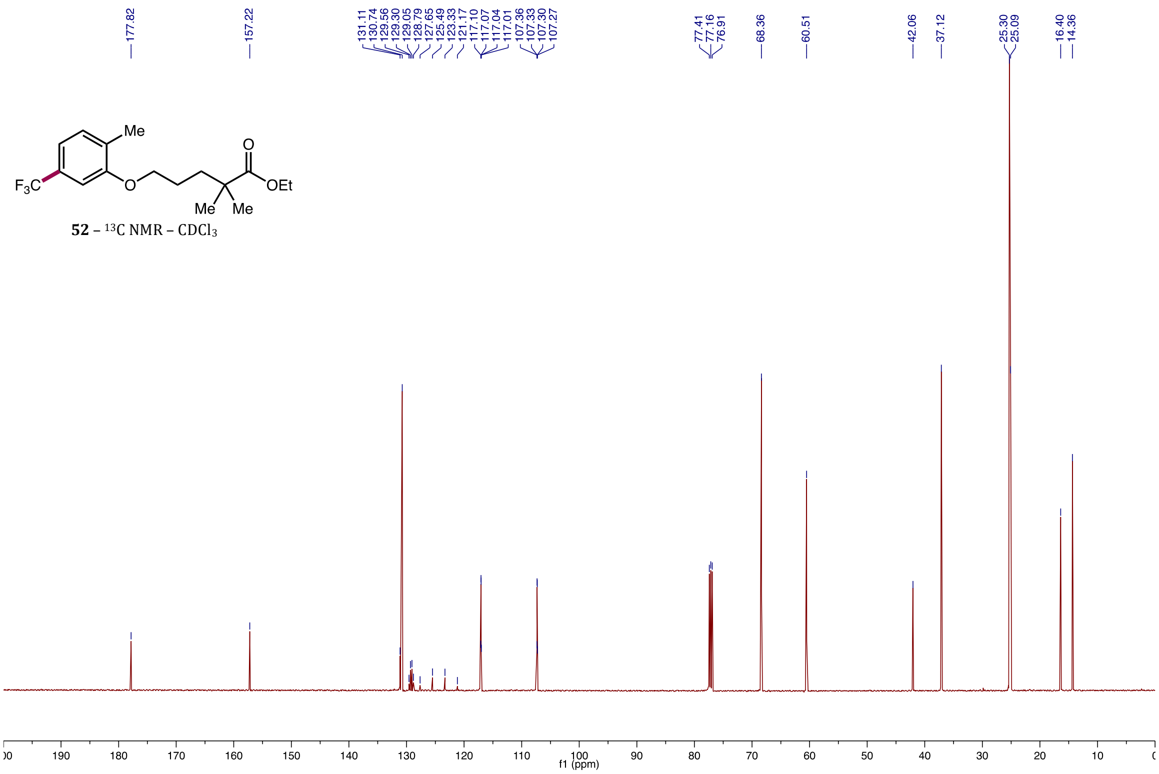
51 – ^{13}C NMR – CDCl$_3$



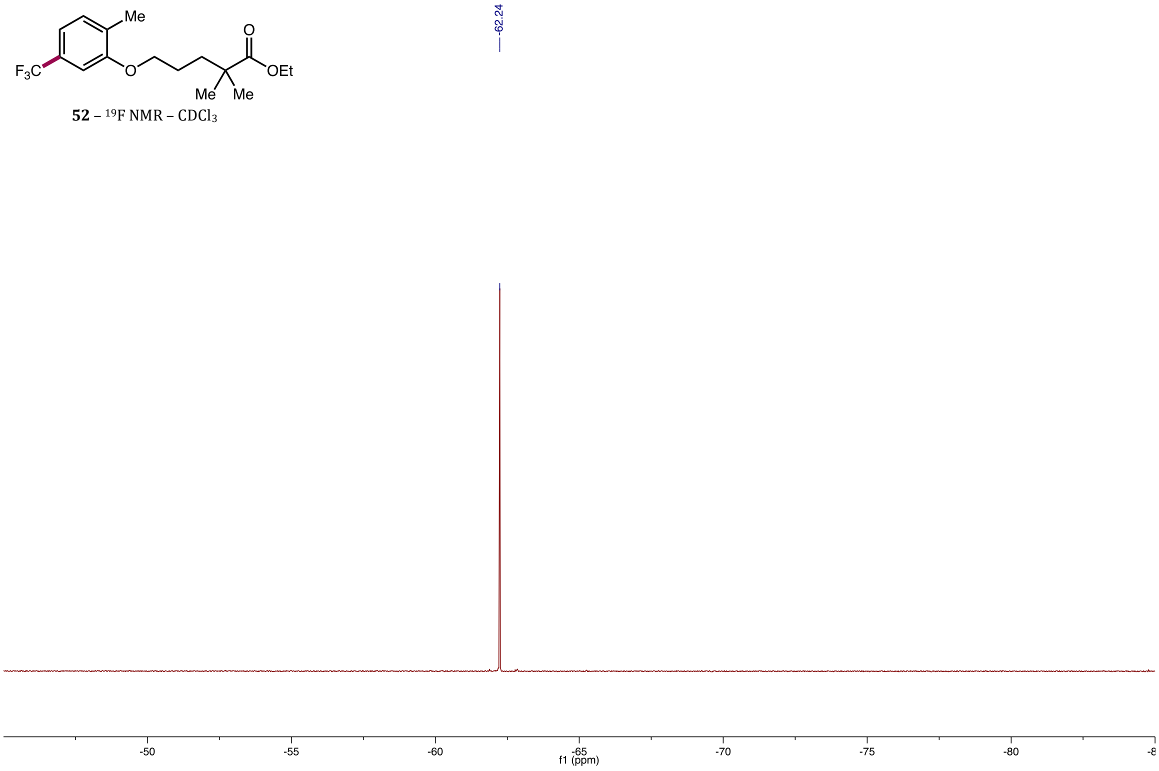
51 – ^{19}F NMR – CDCl$_3$



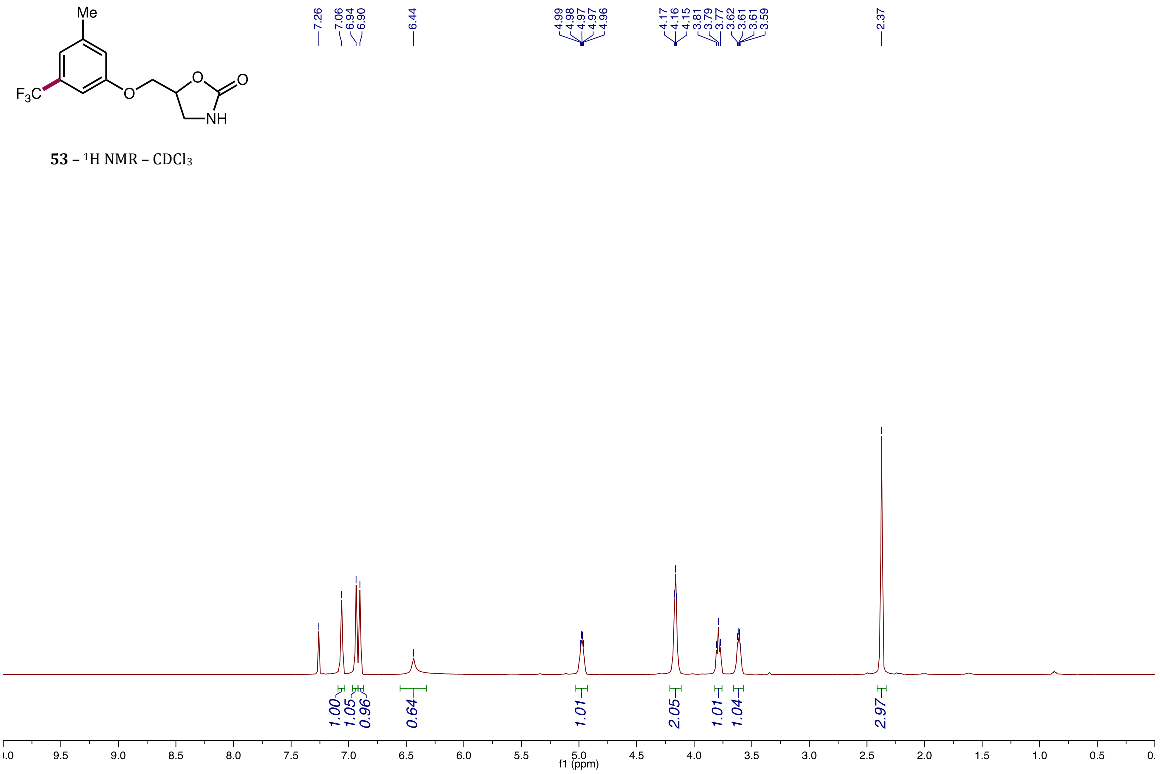
52 – ^{1}H NMR – CDCl$_3$



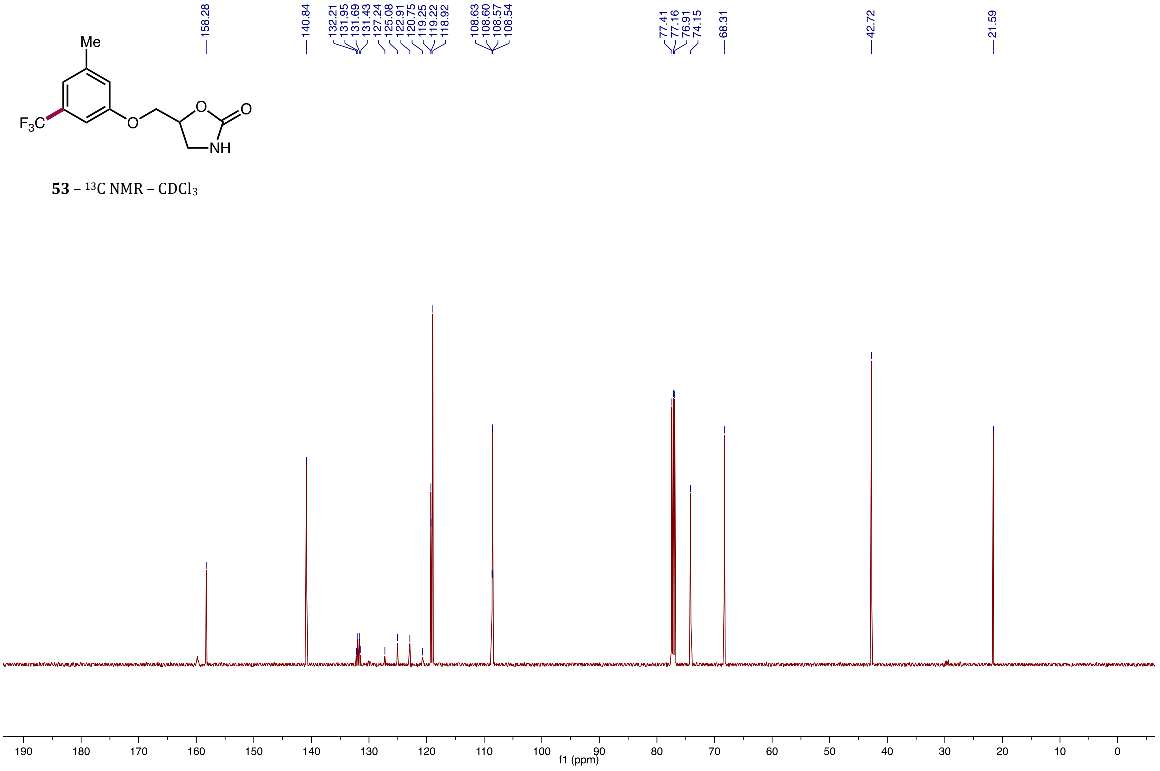
52 – ^{13}C NMR – CDCl$_3$



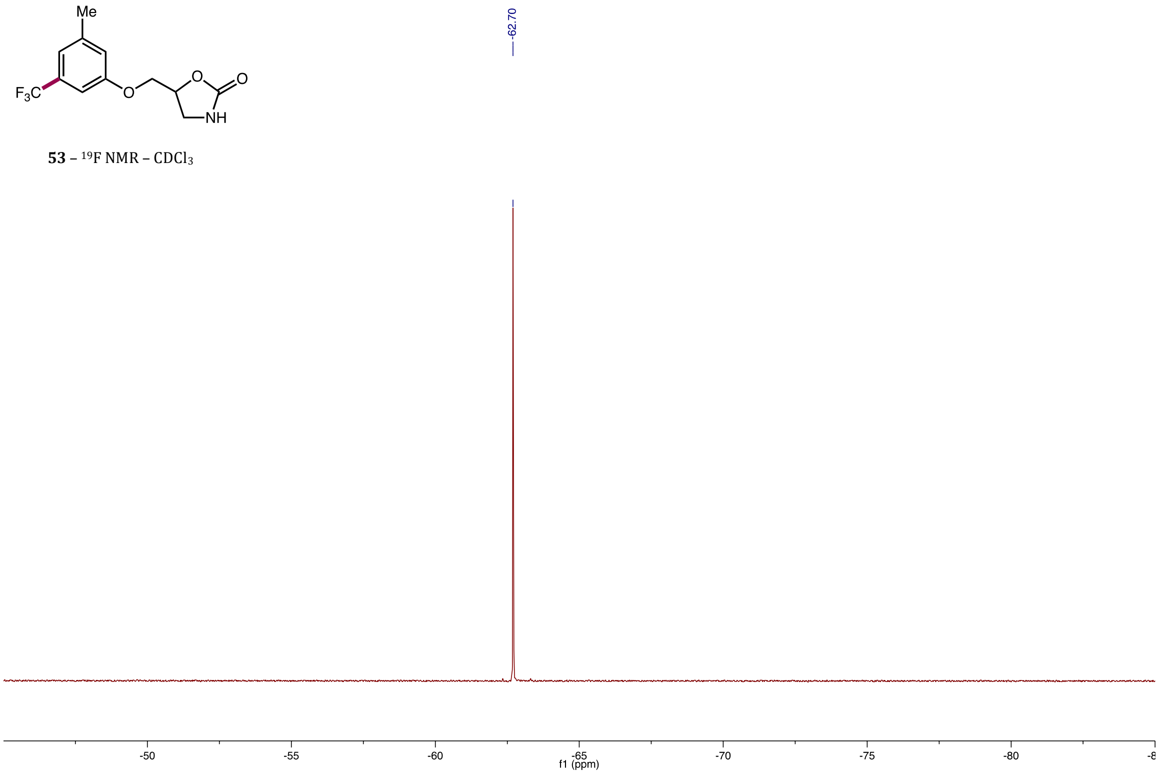
52 – ^{19}F NMR – CDCl$_3$



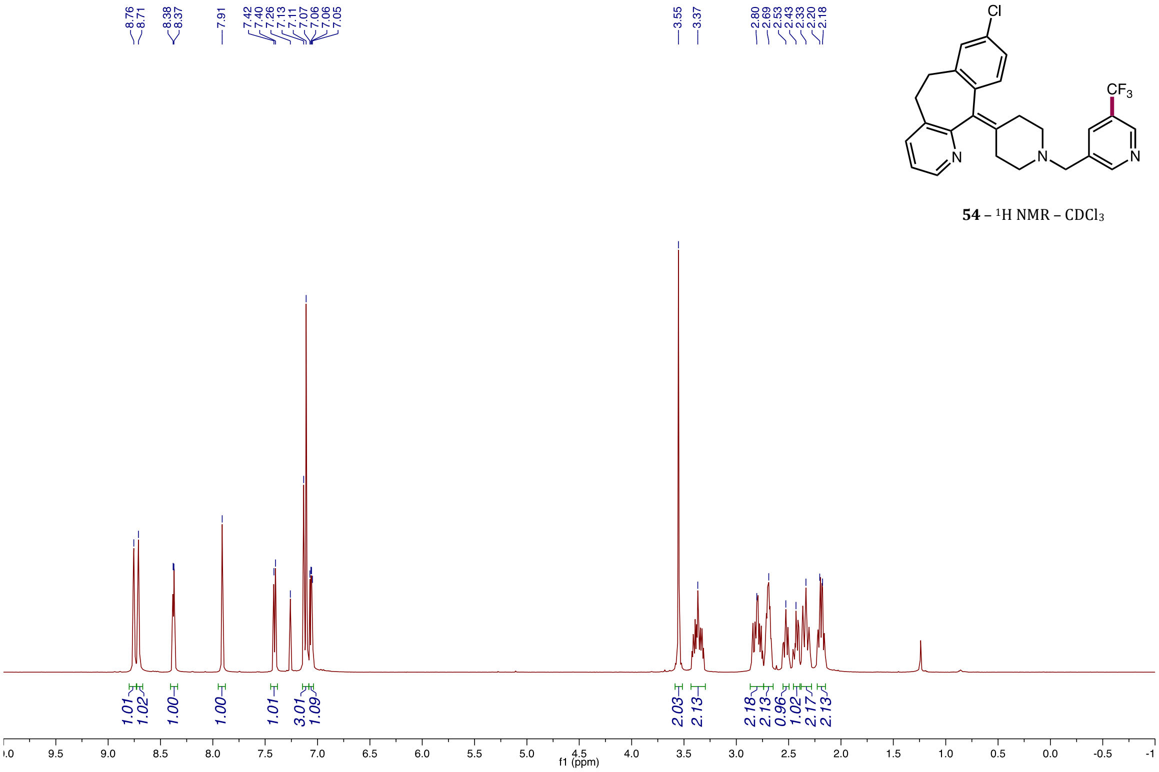
53 – ^{1}H NMR – CDCl$_3$



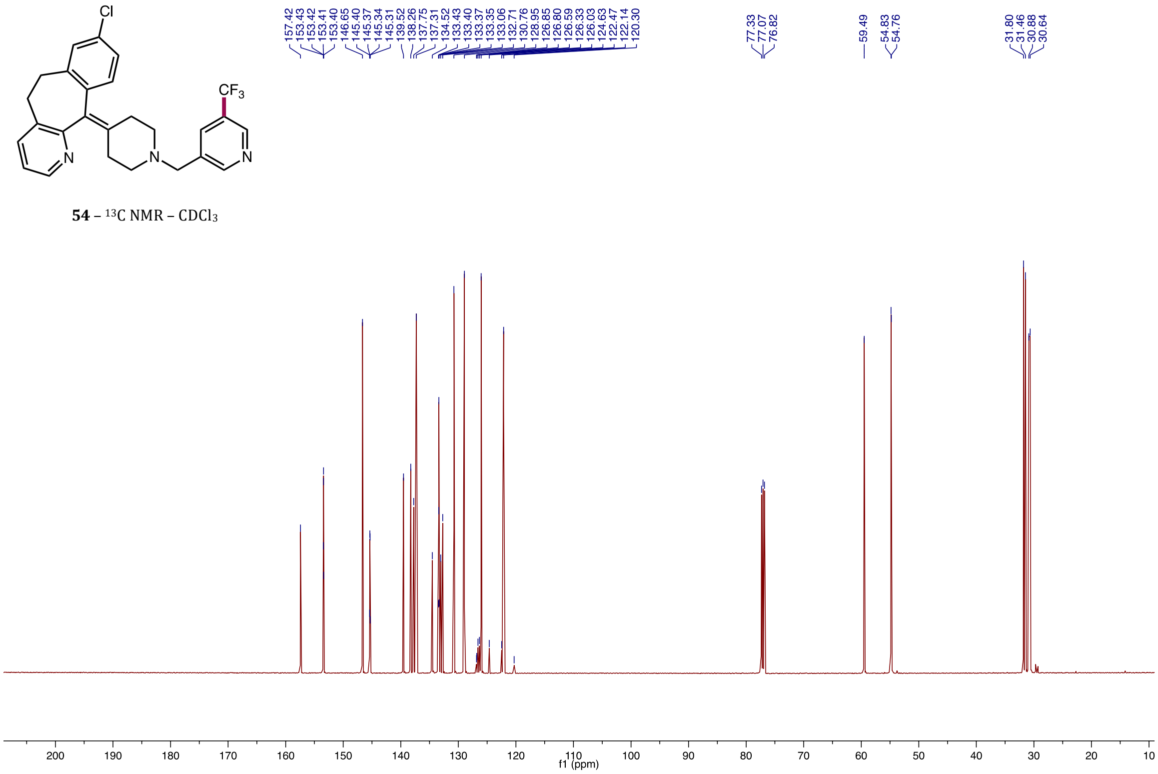
53 – ^{13}C NMR – CDCl$_3$



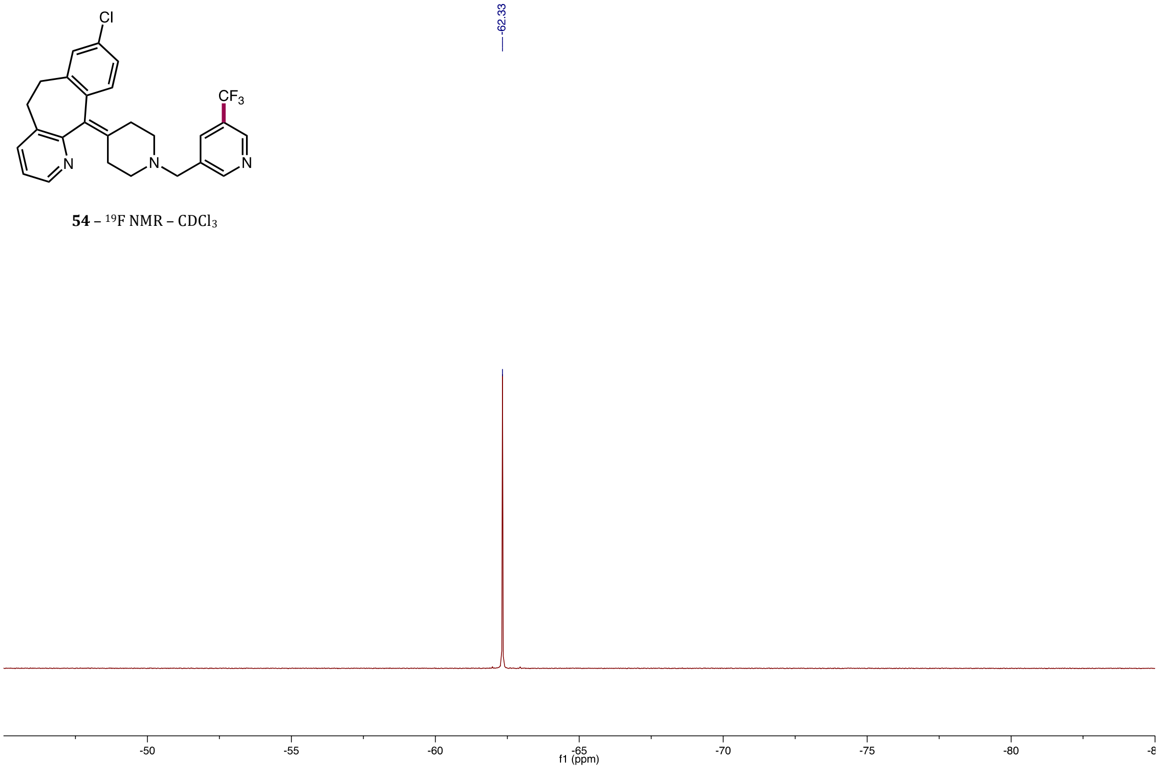
53 – ^{19}F NMR – CDCl$_3$



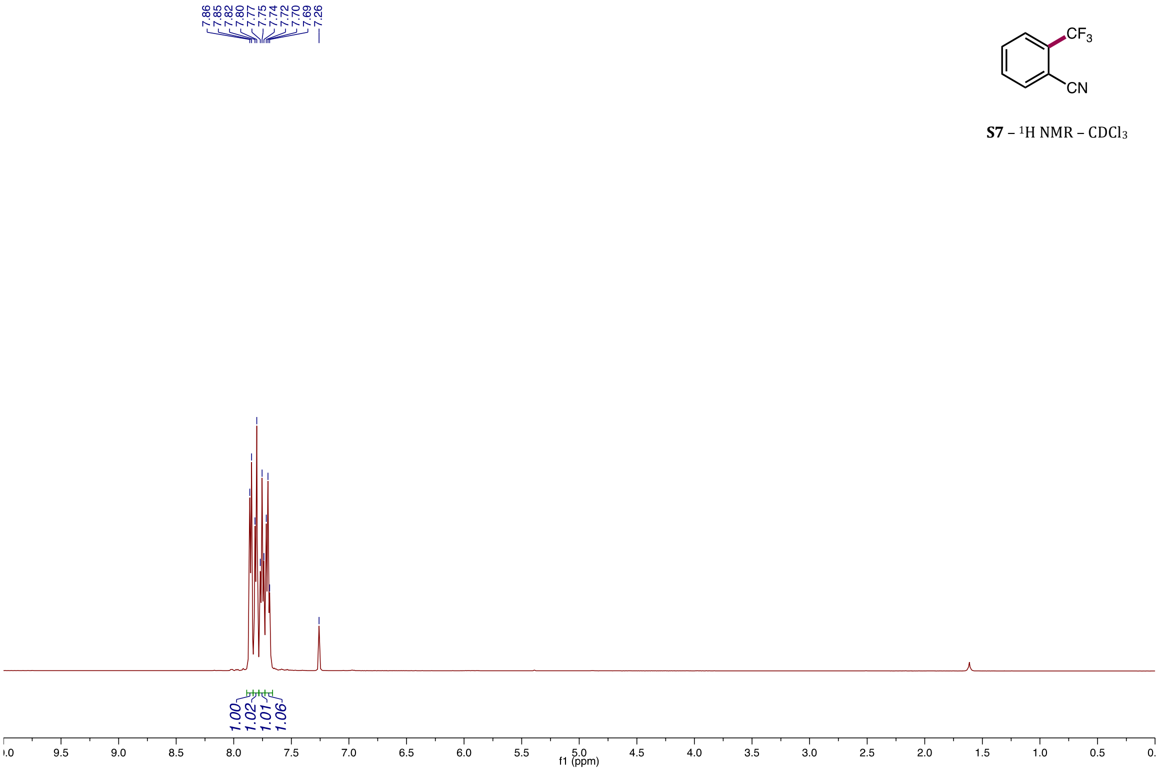
54 – ^{1}H NMR – CDCl$_3$



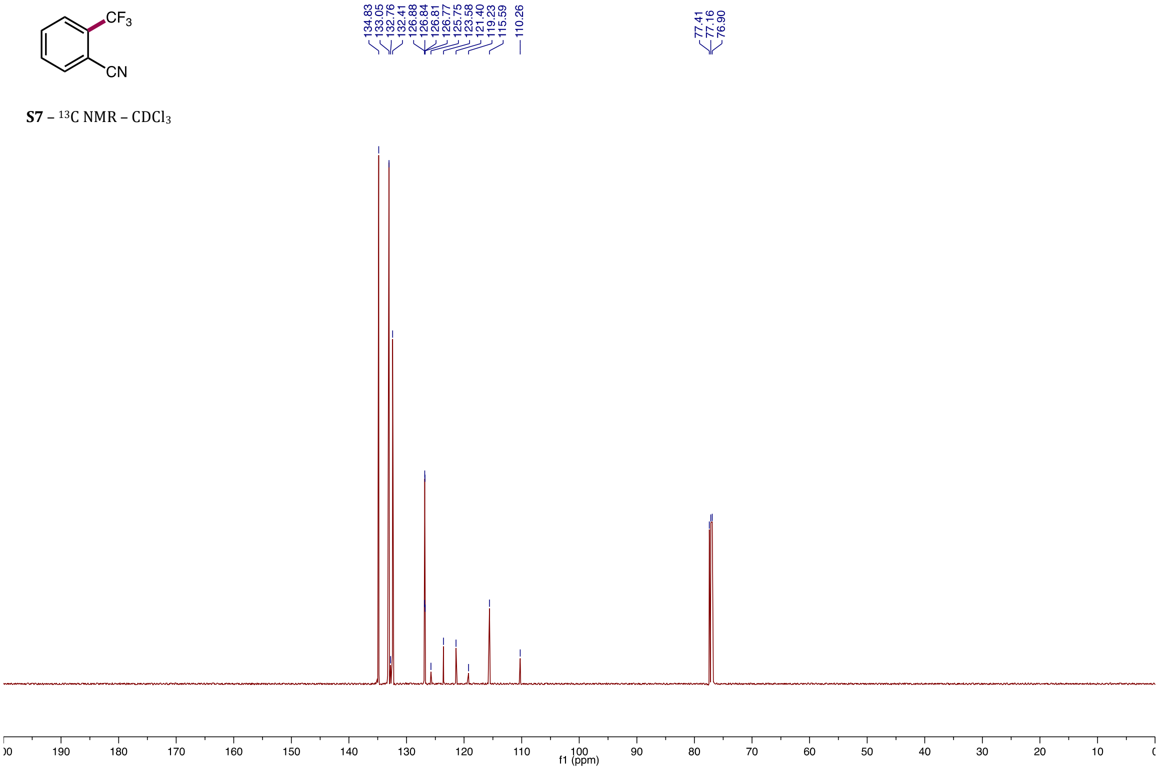
54 – ^{13}C NMR – CDCl$_3$



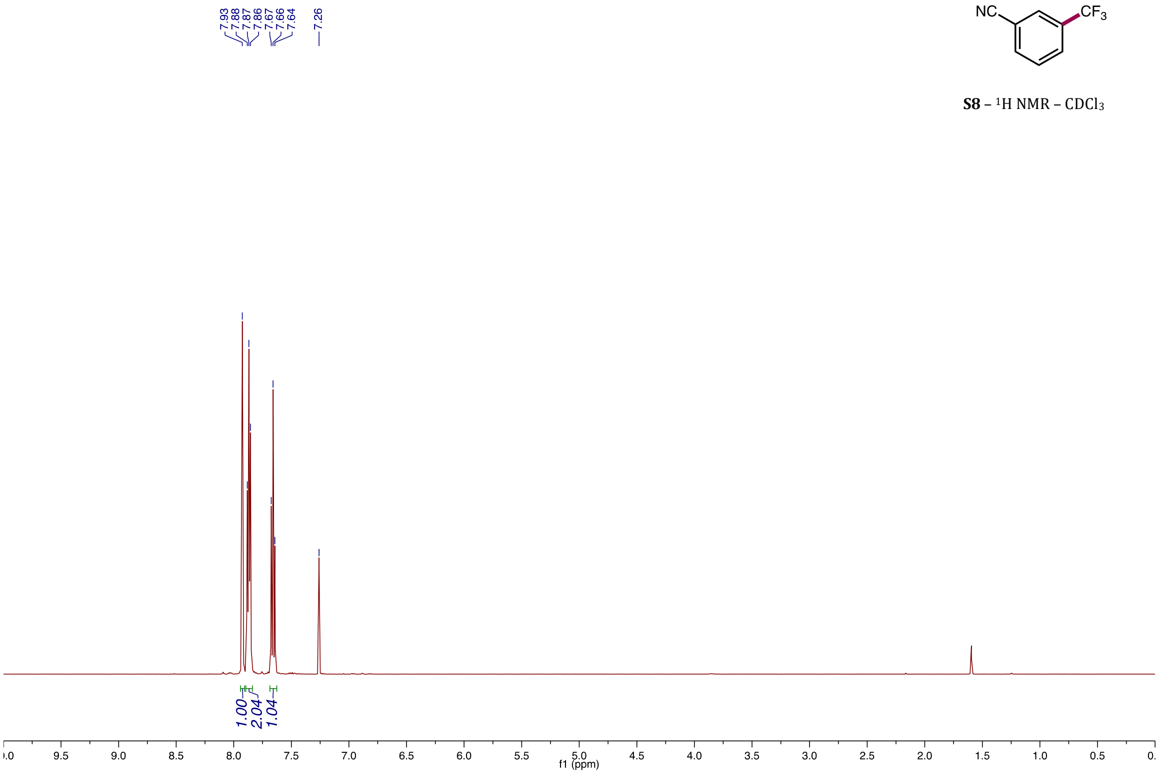
54 – ^{19}F NMR – CDCl$_3$



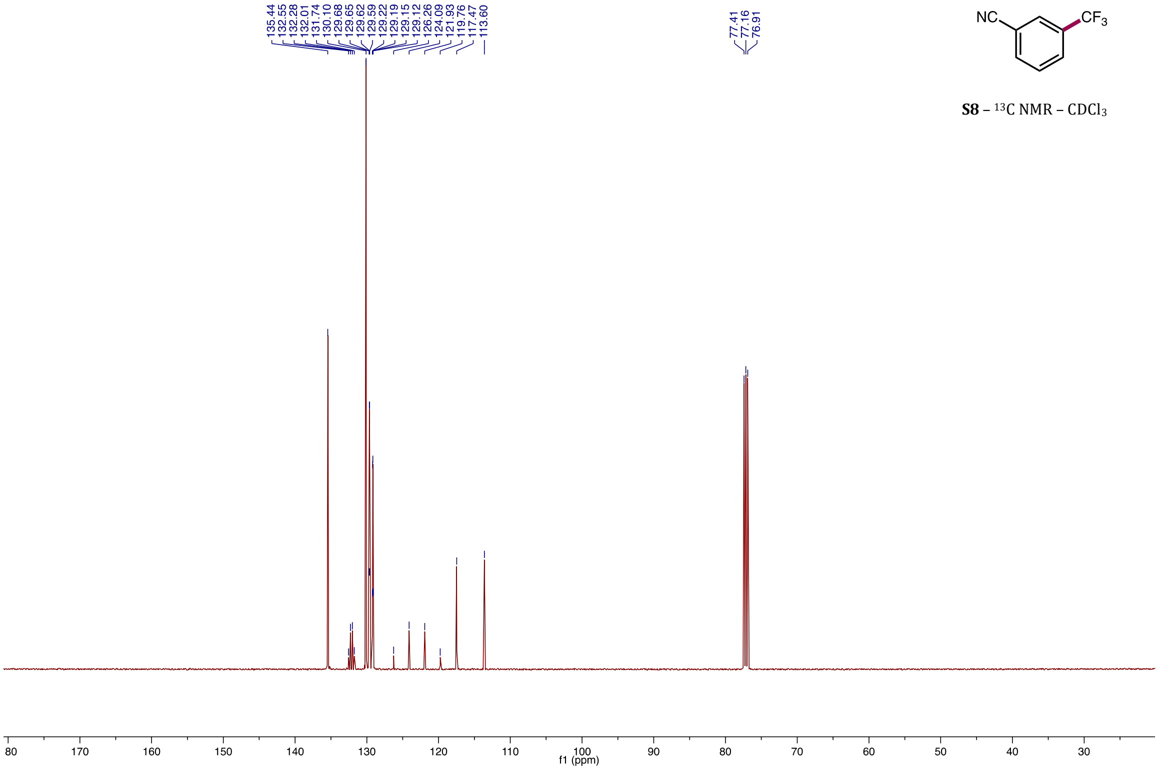
S7 – ^{1}H NMR – $CDCl_3$



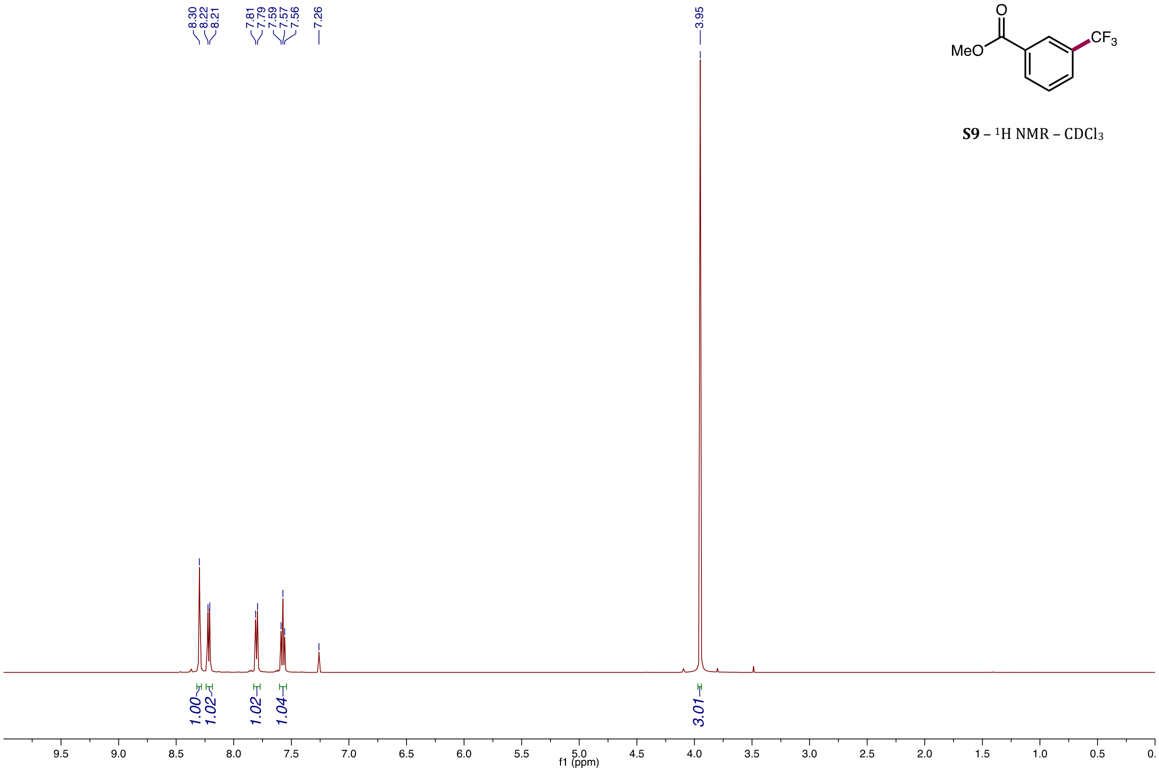
S7 – ^{13}C NMR – $CDCl_3$



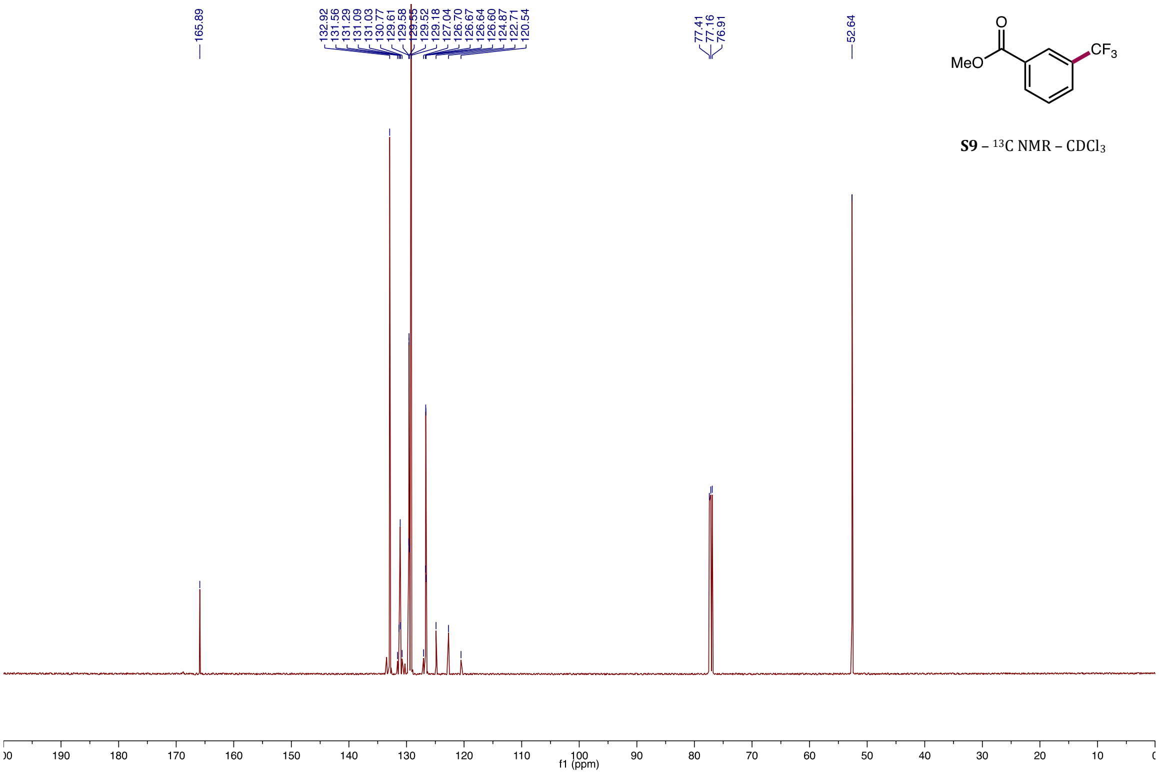
S8 – ^{1}H NMR – CDCl$_3$



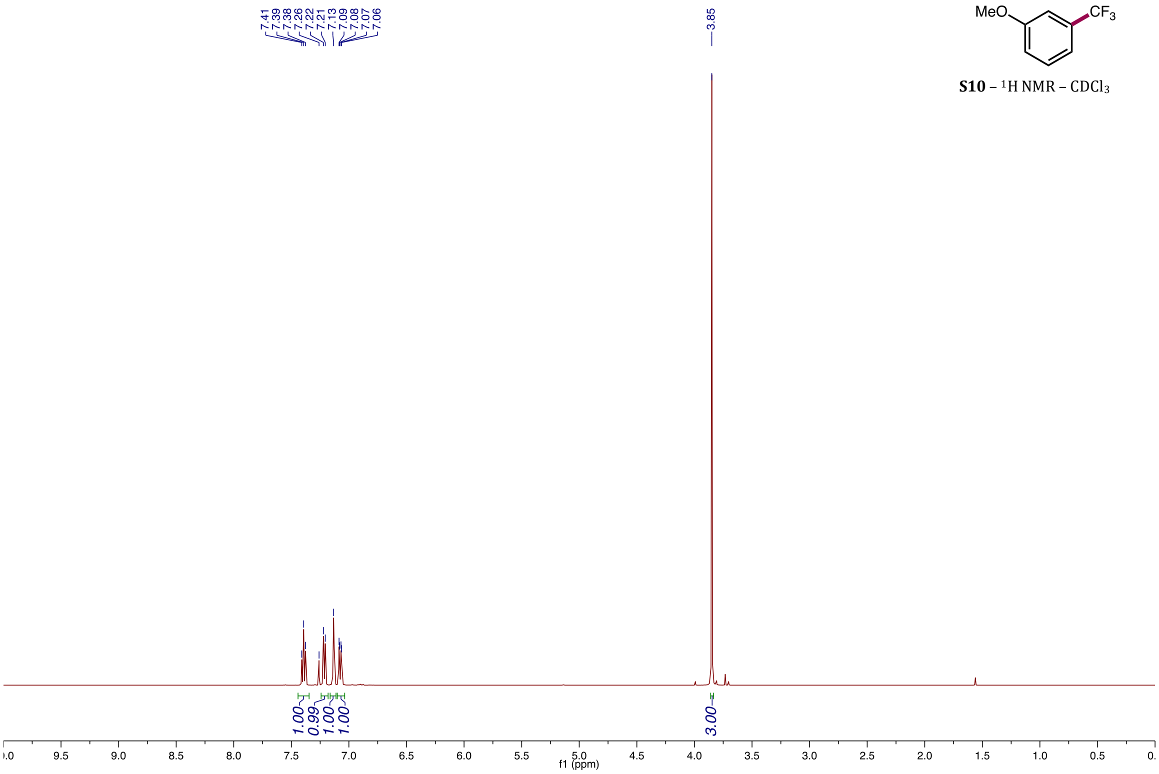
S8 – ^{13}C NMR – CDCl$_3$



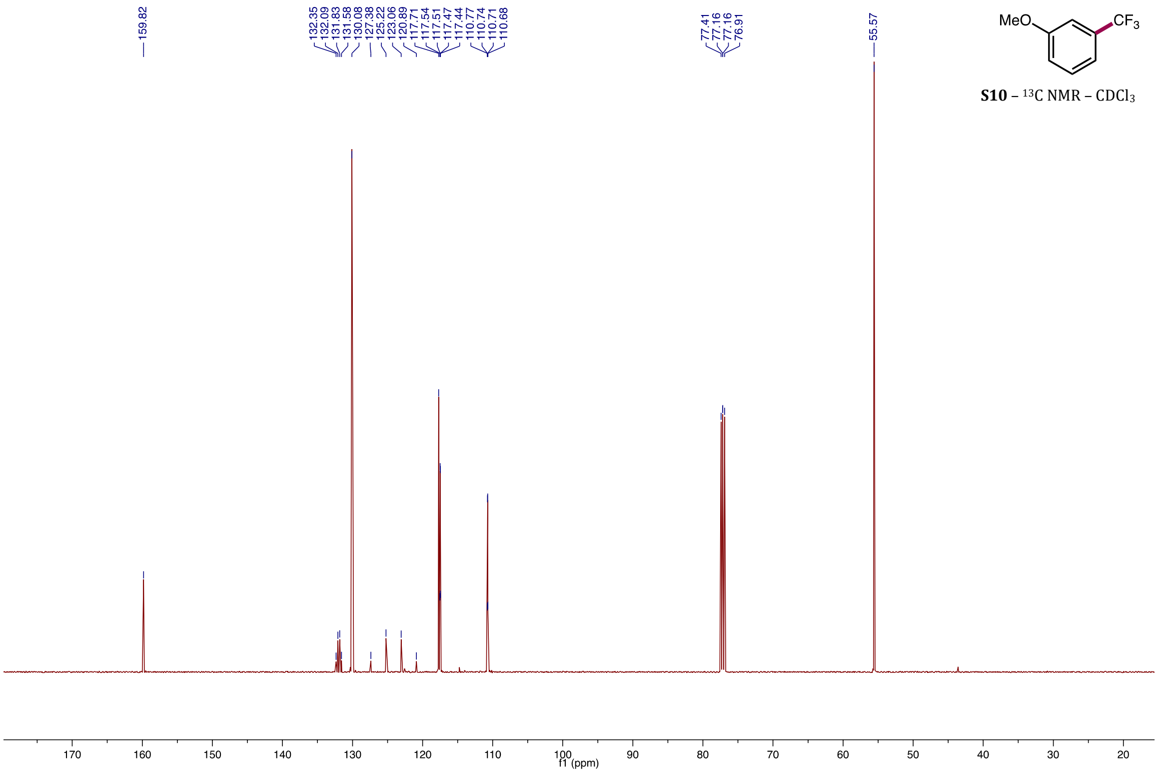
S9 – ^{1}H NMR – CDCl$_3$



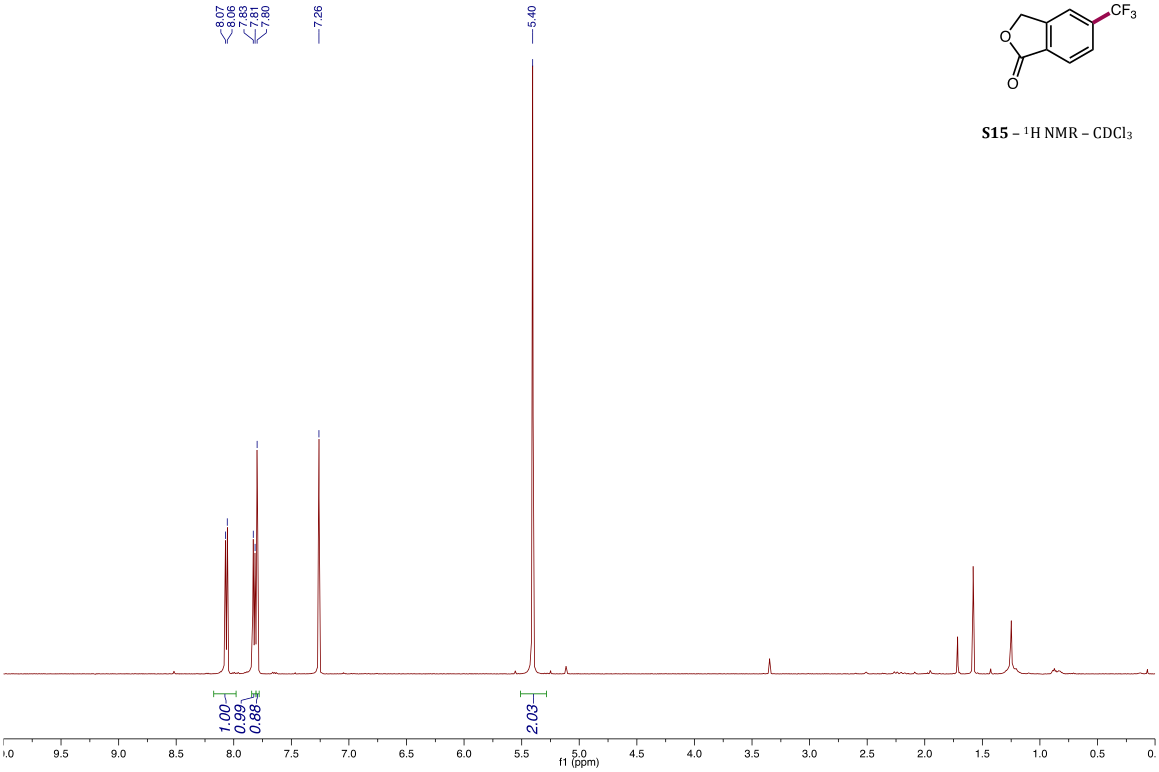
S9 – ^{13}C NMR – CDCl$_3$



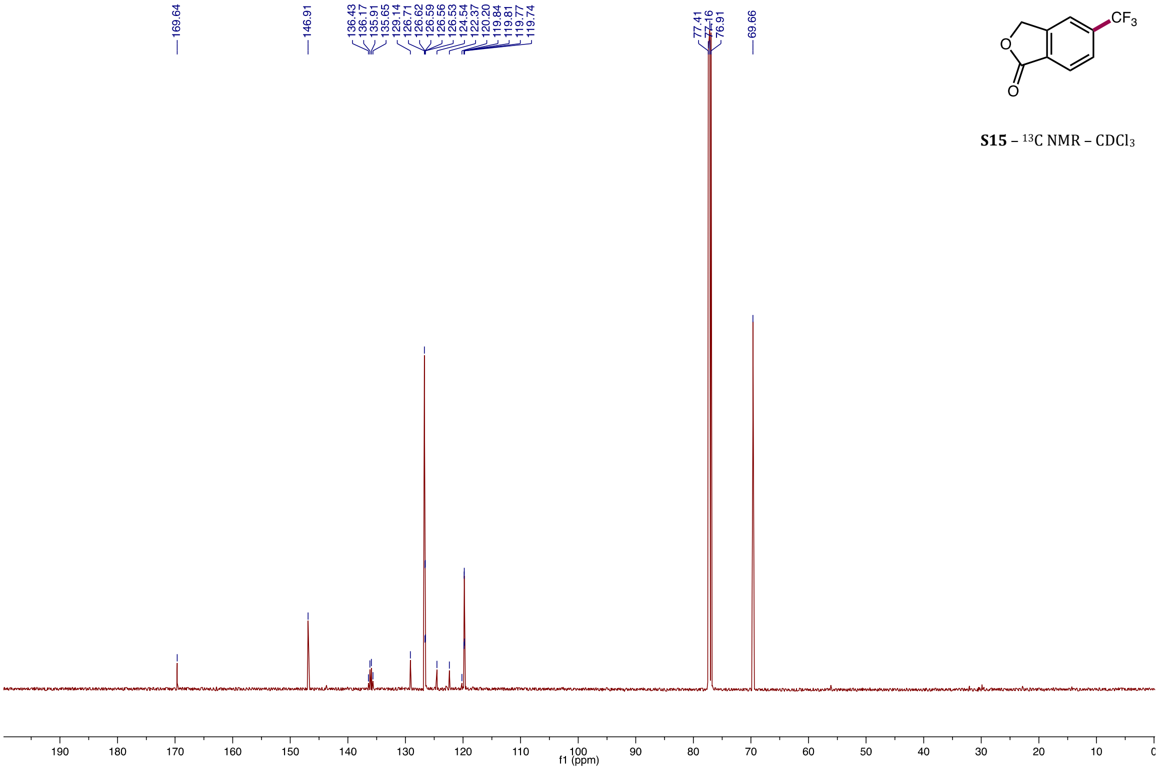
S10 – ^{1}H NMR – $CDCl_3$



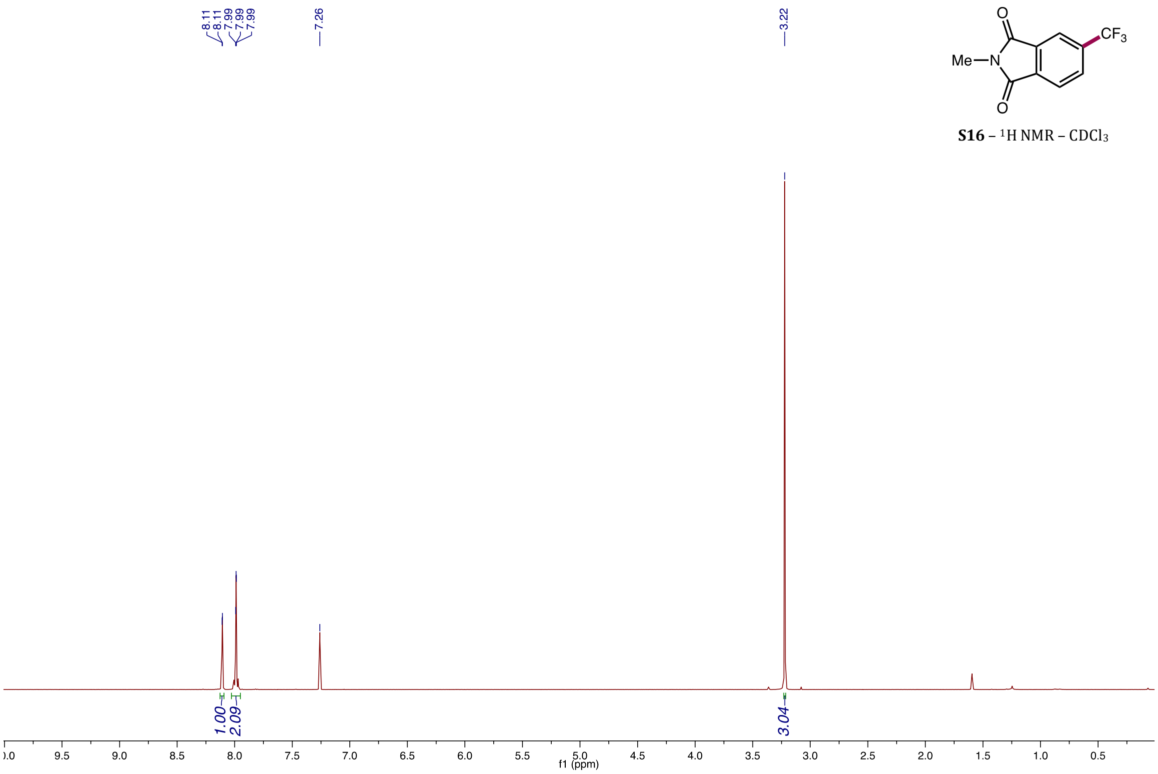
S10 – ^{13}C NMR – $CDCl_3$



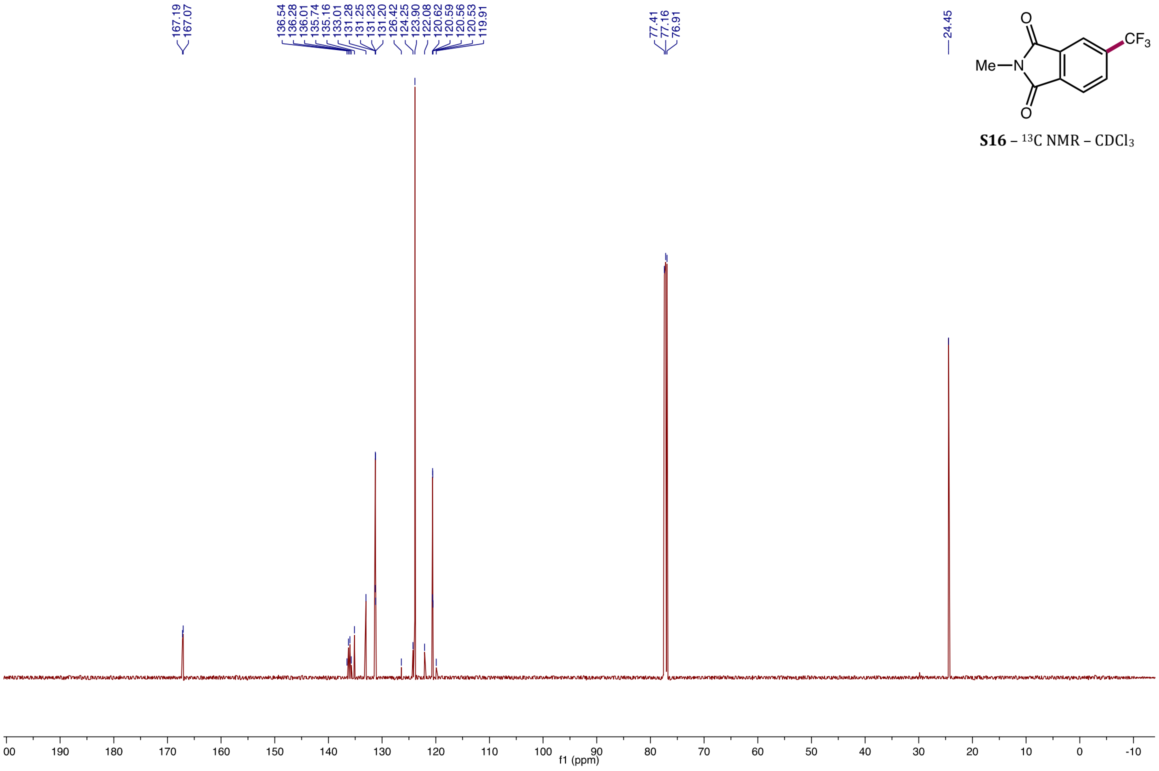
S15 – ^{1}H NMR – CDCl$_3$



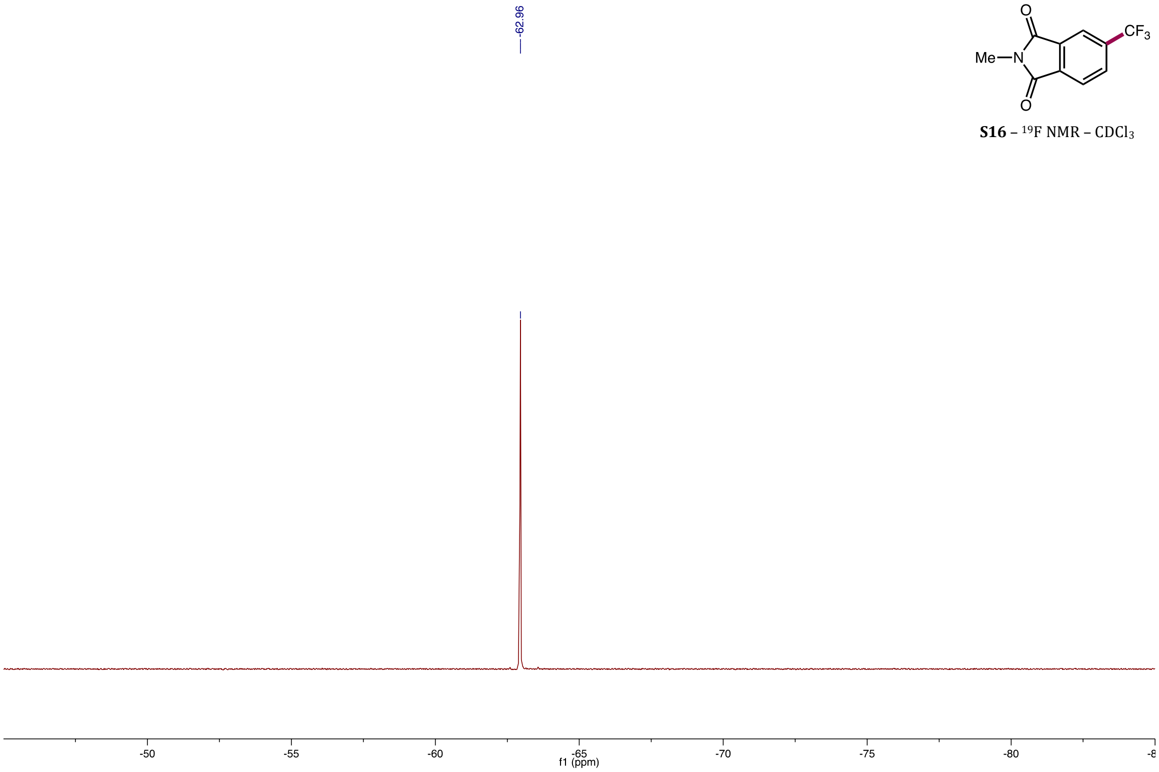
S15 – ^{13}C NMR – CDCl$_3$



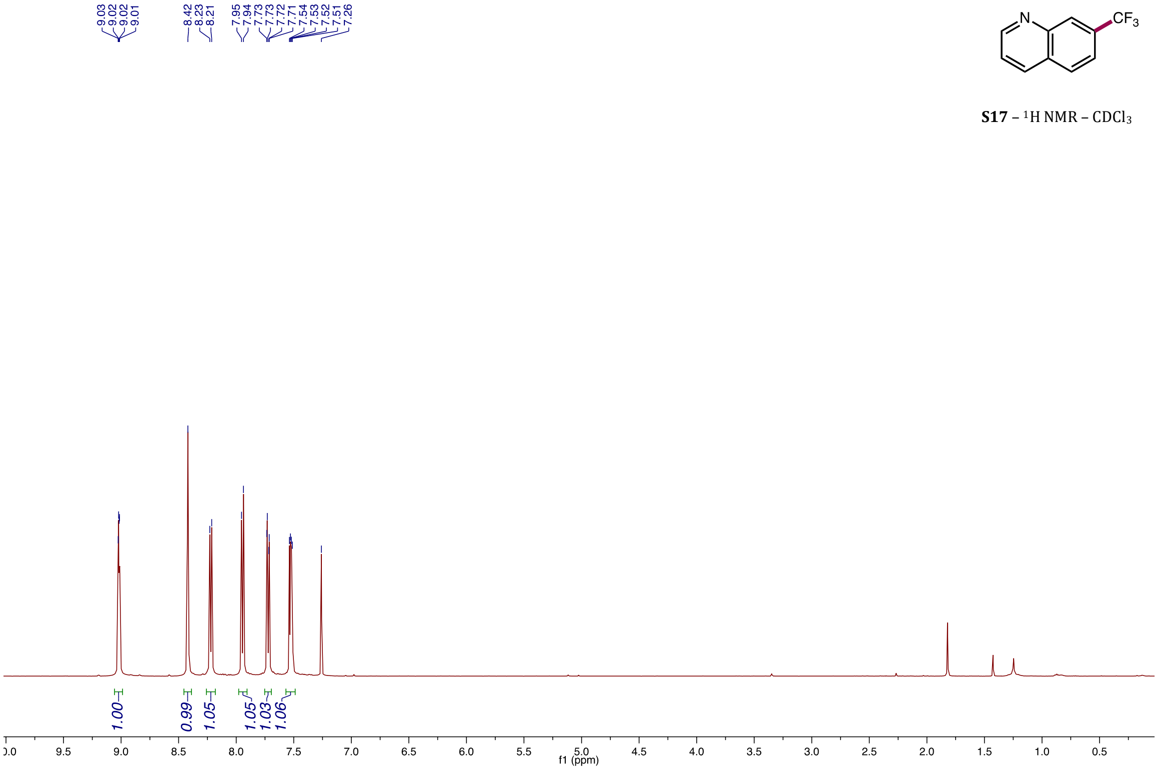
S16 – ^{1}H NMR – CDCl$_3$



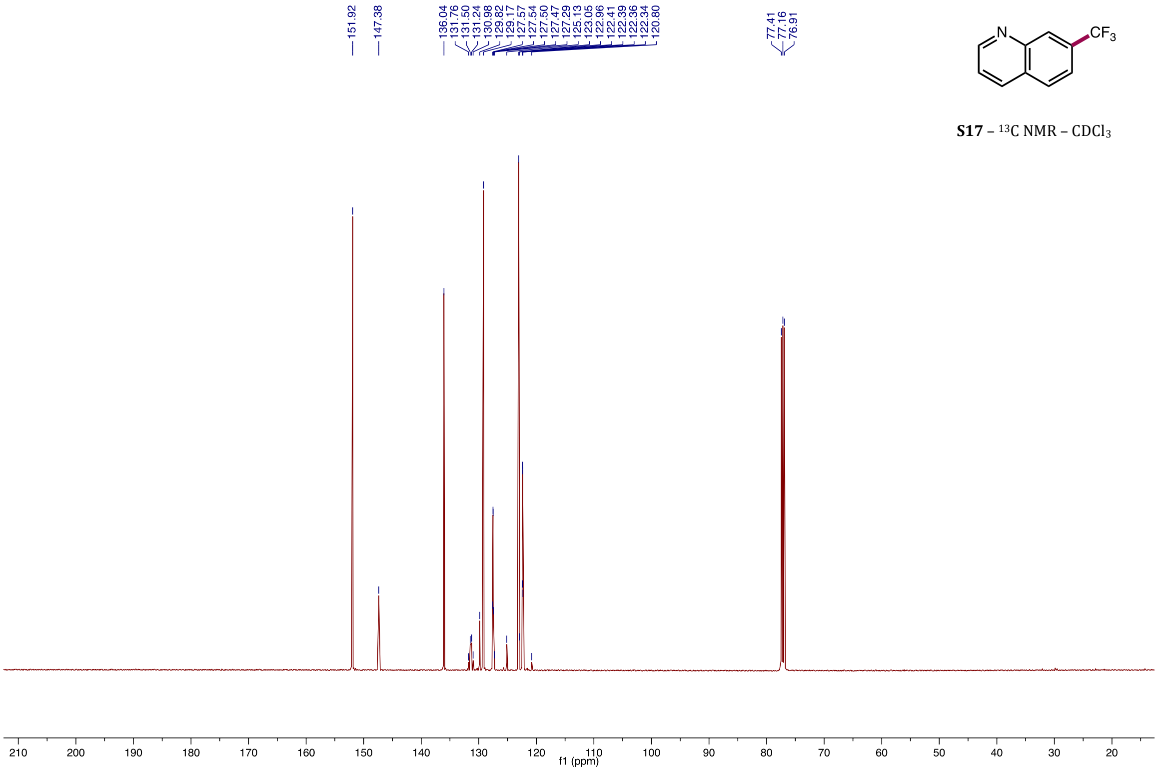
S16 – ^{13}C NMR – CDCl$_3$



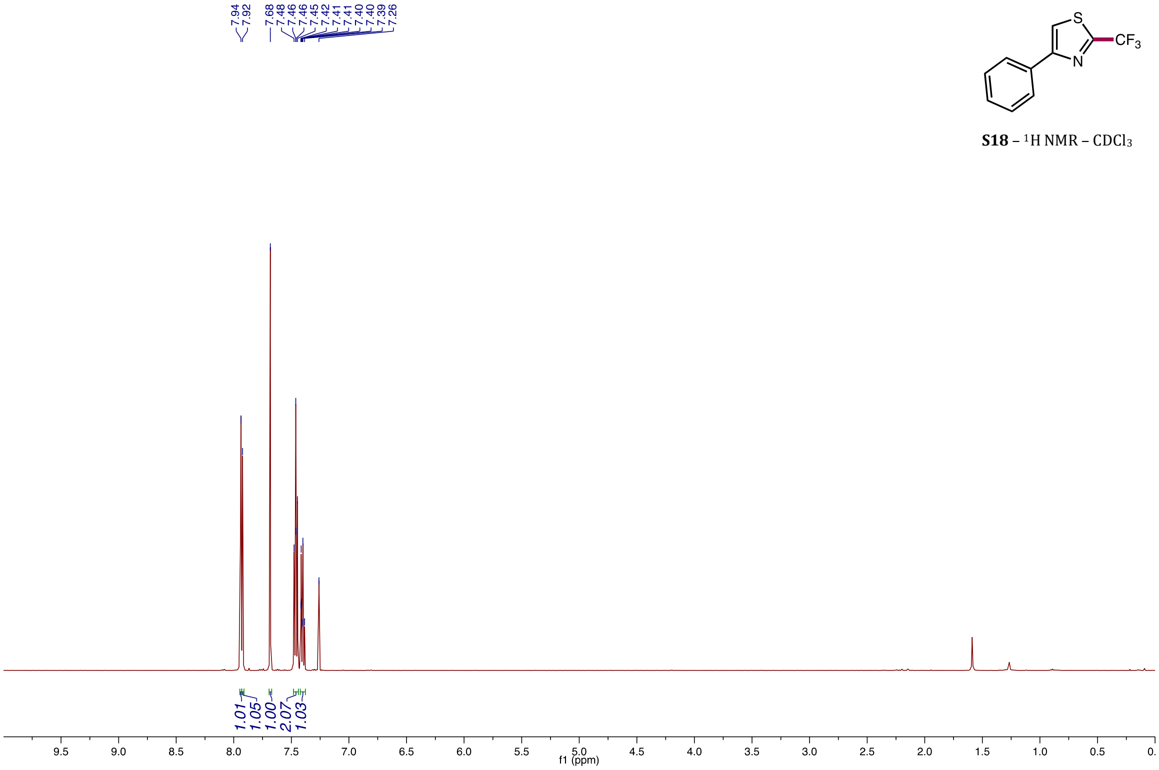
S16 – ^{19}F NMR – CDCl$_3$



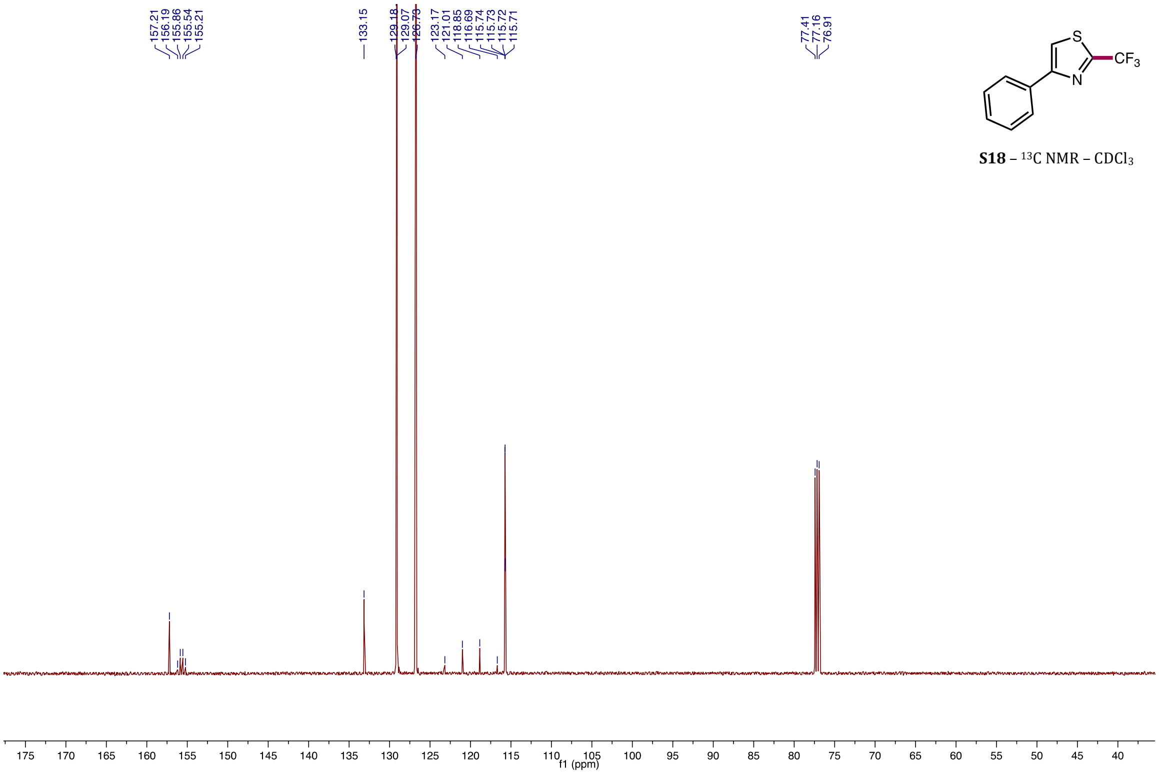
S17 – ^{1}H NMR – CDCl$_3$



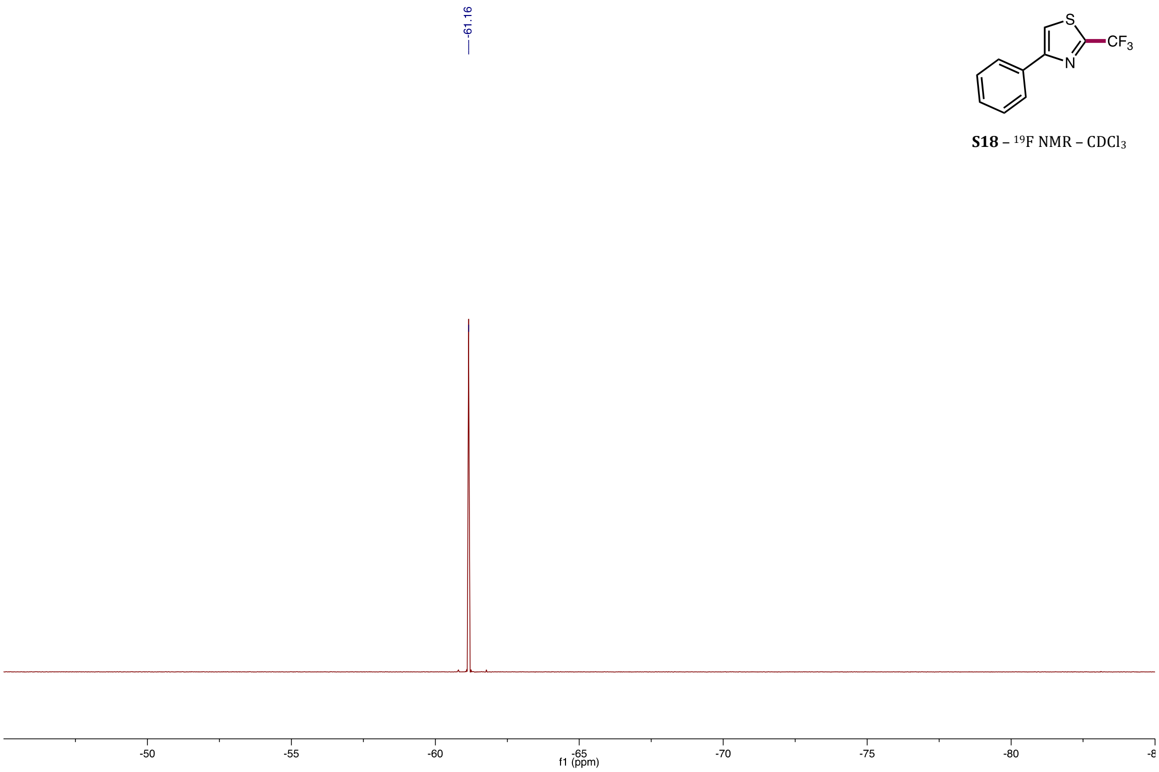
S17 – ^{13}C NMR – CDCl$_3$



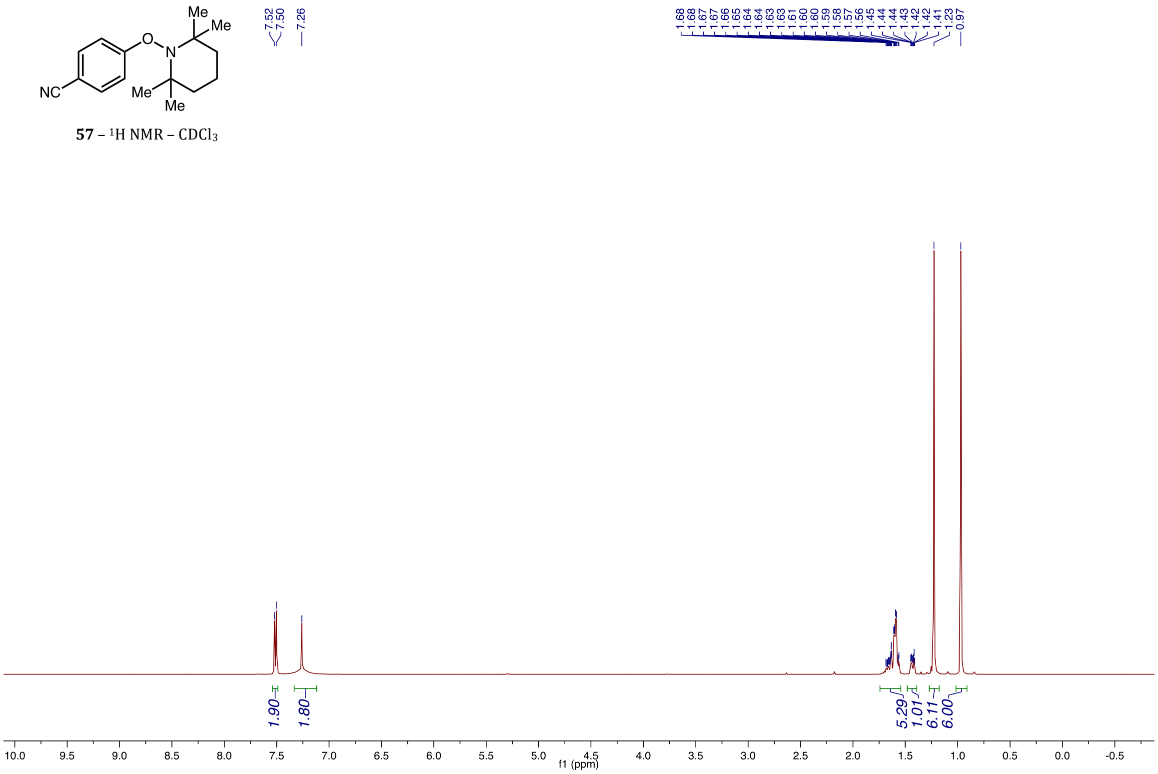
S18 – ^{1}H NMR – CDCl$_3$



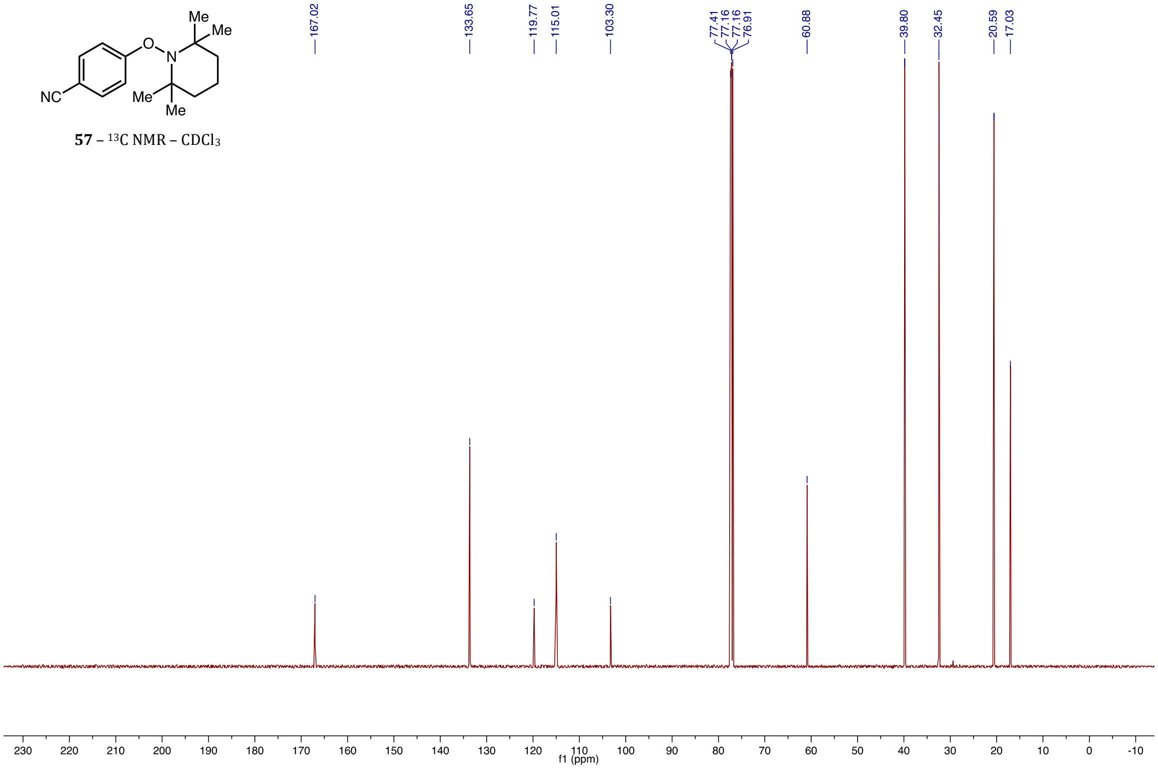
S18 – ^{13}C NMR – CDCl$_3$



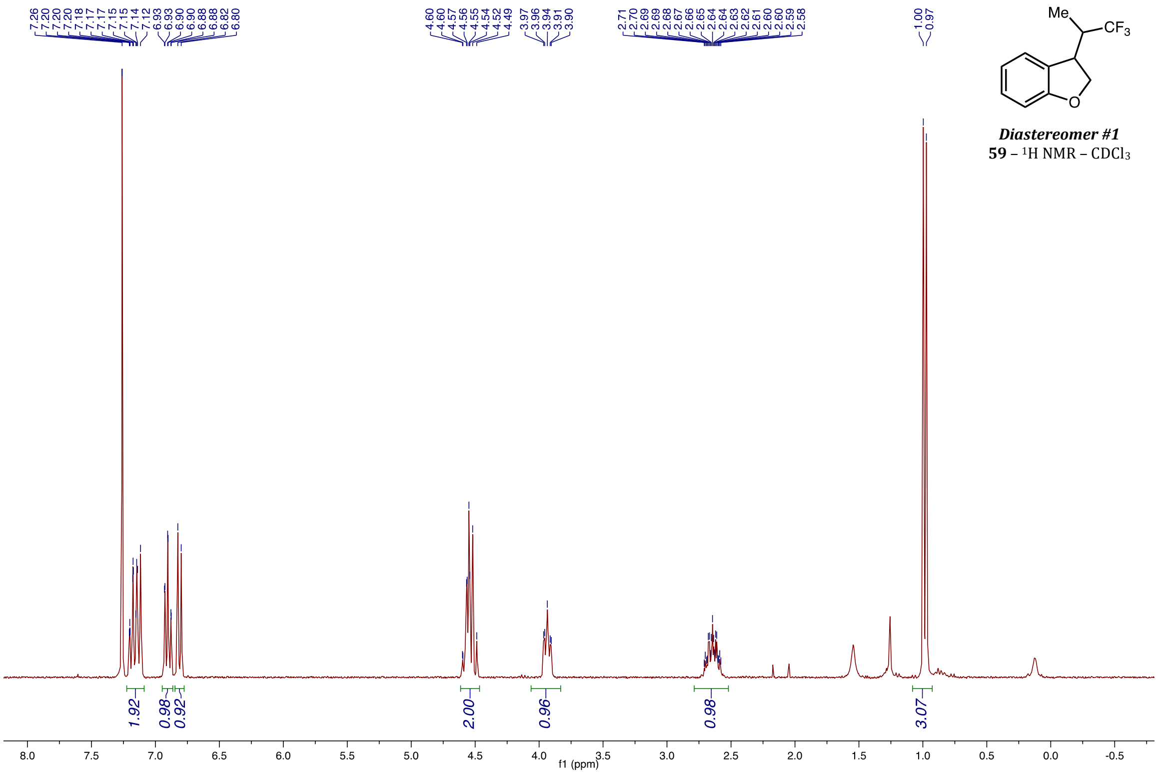
S18 – ^{19}F NMR – CDCl$_3$



57 – ^{1}H NMR – CDCl$_3$

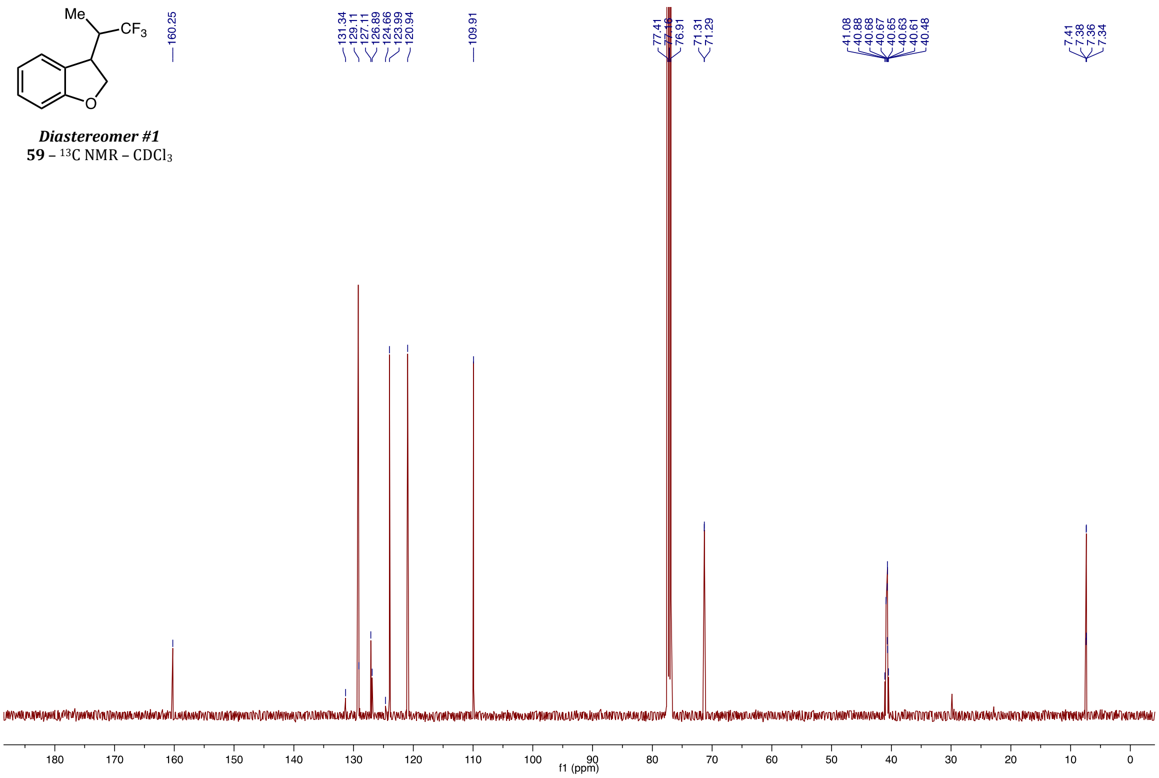


57 – ^{13}C NMR – CDCl$_3$



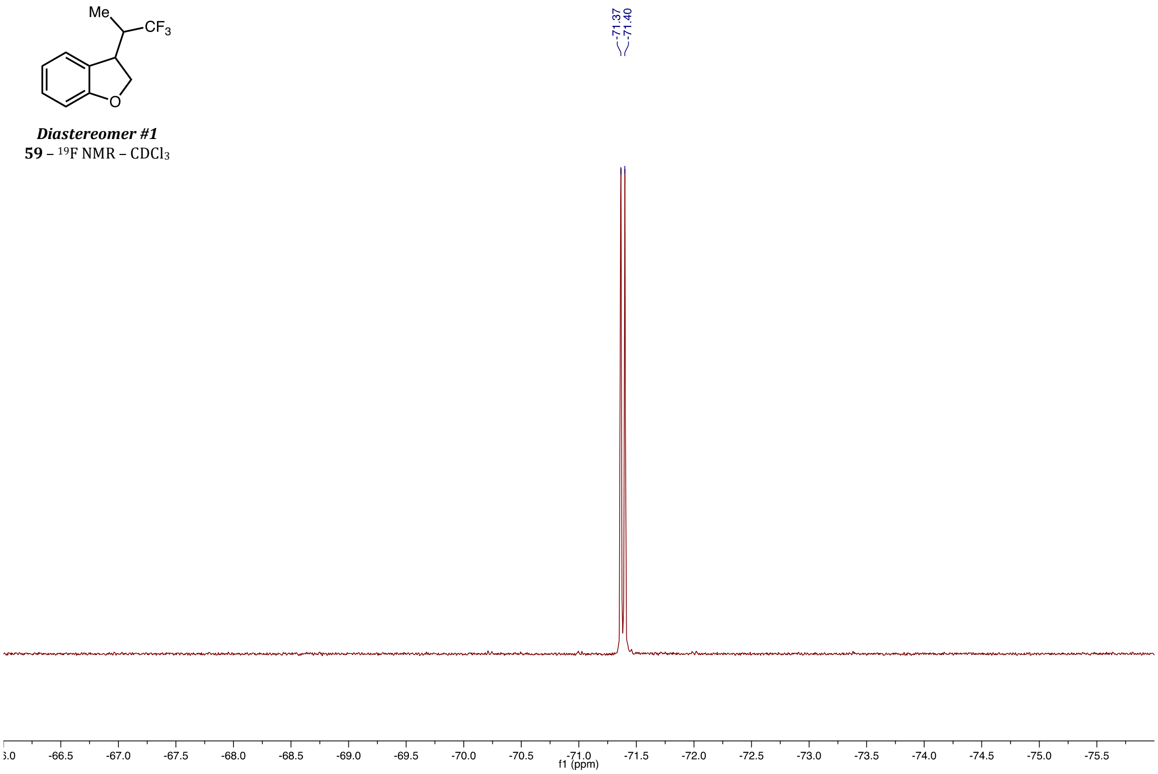
Diastereomer #1

59 – ^{1}H NMR – CDCl$_3$

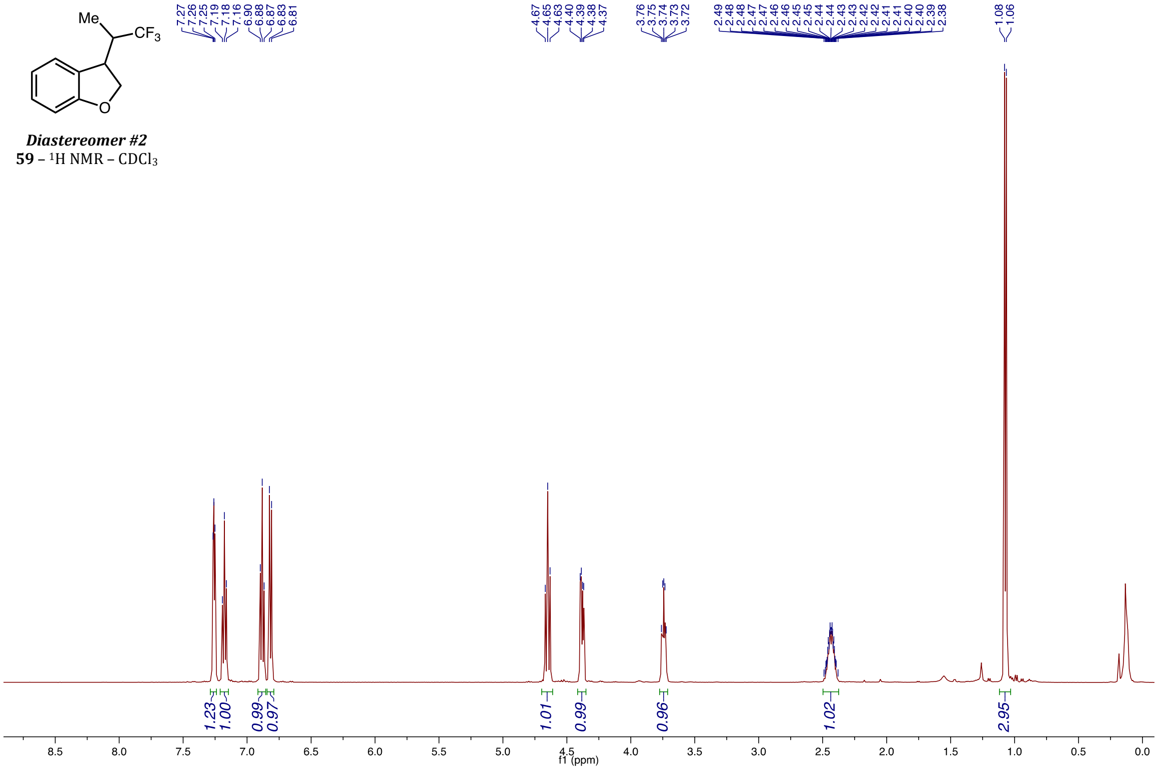


Diastereomer #1

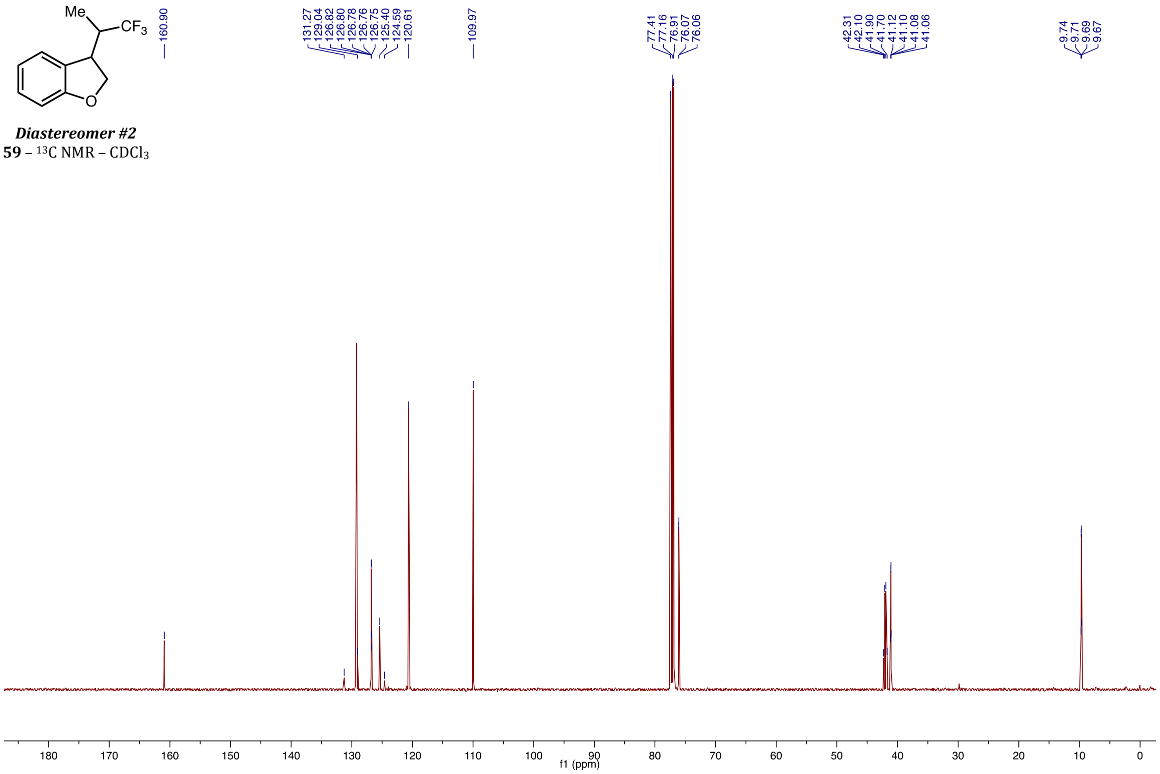
59 – ^{13}C NMR – CDCl$_3$



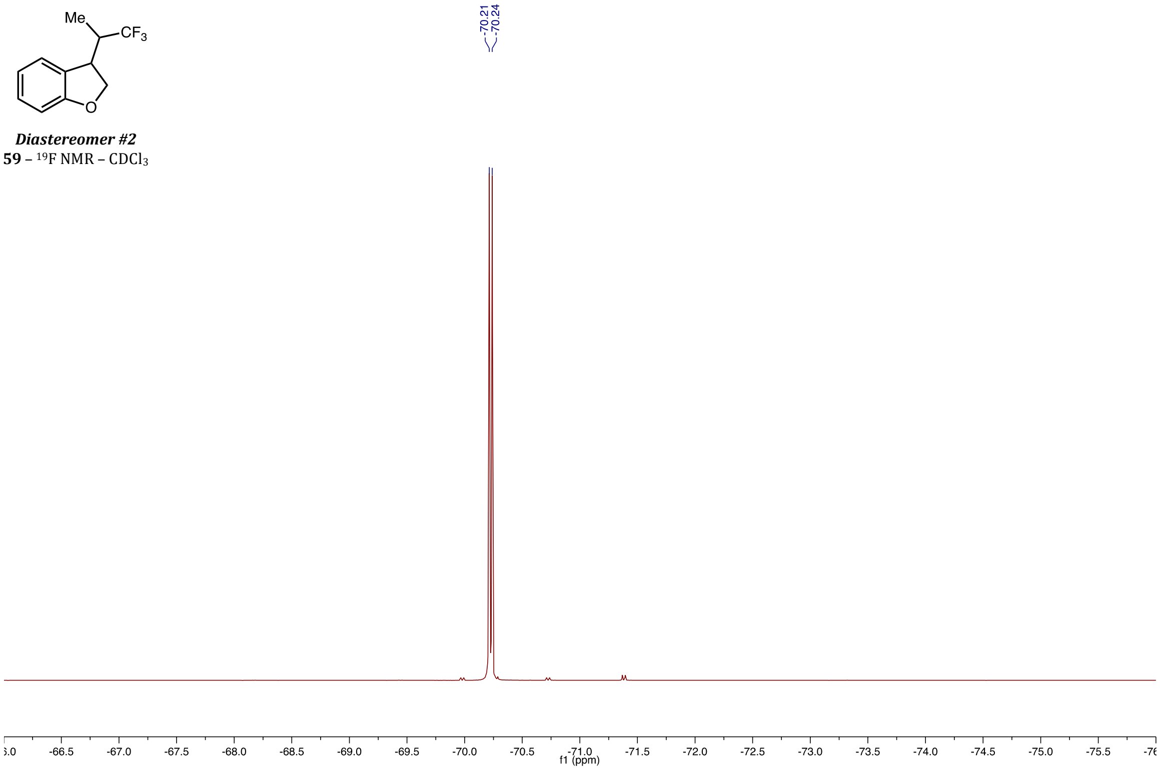
Diastereomer #1
59 – ^{19}F NMR – CDCl$_3$



Diastereomer #2
59 – ^{1}H NMR – CDCl$_3$



Diastereomer #2
59 – ^{13}C NMR – CDCl$_3$



Diastereomer #2
59 – ^{19}F NMR – CDCl$_3$

19) References

1. L. S. Hegedus, B. C. G. Söderberg, *Transition Metals in the Synthesis of Complex Organic Molecules* (University Science Books, United States, 3rd Edition, 2010).
2. D. A. Petrone, J. Ye, M. Lautens, *Chem. Rev.* **116**, 8003-8104 (2016).
3. J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century* (John Wiley & Sons, England, 2005).
4. S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* **509**, 299-309 (2014).
5. G. Evano, N. Blanchard, *Copper-Mediated Cross-Coupling Reactions* (John Wiley & Sons, England, 2014).
6. G. O. Jones, P. Liu, K. N. Houk, S. L. Buchwald, *J. Am. Chem. Soc.* **132**, 6205-6213 (2010).
7. H.-Z. Yu, Y.-Y. Jiang, Y. Fu, L. Liu, *J. Am. Chem. Soc.* **132**, 18078-18091 (2010).
8. R. Giri, A. Brusoe, K. Troshin, J. T. Wang, M. Font, J. F. Hartwig, *J. Am. Chem. Soc.* **140**, 793-806 (2018).
9. P. J. Amal Joseph, S. Priyadarshini, *Org. Process. Res. Dev.* **21**, 1889-1924 (2017).
10. Systems competent for aryl chloride oxidative addition have recently been reported. See (11).
11. S. Bhunia, G. G. Pawar, V. Kumar, Y. Jiang, D. Ma, Angew. Chem. Int. Ed. **56**, 161636-16179 (2017)
12. A. Casitas, X. Ribas, Chem. Sci. 4, 2301-2318 (2013).
13. T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **473**, 470-477 (2011).
14. A. J. Hickman, M. S. Sanford, *Nature* **484**, 177-185 (2012).
15. K. Uneyama, *Organofluorine Chemistry* (Blackwell, Oxford, UK, 2006).
16. W. K. Hagmann, *J. Med. Chem.* **51**, 4359-4369 (2008).
17. O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **111**, 4475-4521 (2011).
18. E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson, S. L. Buchwald, *Science* **328**, 1679-1681 (2010).
19. J. R. Bour, N. M. Camasso, M. S. Sanford, *J. Am. Chem. Soc.* **137**, 8034-8037 (2015).
20. A. Concepción, E. M. de Marigorta, G. Rubiales, F. Palacios, *Chem. Rev.* **115**, 1847-1935 (2015).

21. A. I. Konovalov, A. Lishchynskyi, V. V. Grushin, *J. Am. Chem. Soc.* **136**, 13410-13425 (2015).
22. J. Jover, *ACS Catal.* **4**, 4389-4397 (2014).
23. G. G. Dubinina, H. Furutachi, D. A. Vicic, *J. Am. Chem. Soc.* **130**, 8600-8601 (2008).
24. A. Zanardi, M. A. Novikov, E. Martin, J. Benet-Buchholz, V. V. Grushin, *J. Am. Chem. Soc.* **133**, 20901-20913 (2011).
25. H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig, *Angew. Chem. Int. Ed.* **50**, 3793-3798 (2011).
26. Q.-Y. Chen, S.-W. Wu, *J. Chem. Soc., Chem. Commun.* **11**, 705-706 (1989).
27. M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **14**, 1909-1911 (2009).
28. T. Schareina, X.-F. Wu, A. Zapf, A. Cotté, M. Gotta, M. Beller, *Top. Catal.* **55**, 426-431 (2012).
29. J. Twilton, C. C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nat. Rev. Chem.* **1**, 52 (2017).
30. P. Zhang, C. C. Le, D. W. C. MacMillan, *J. Am. Chem. Soc.* **138**, 8084-8087 (2016).
31. C. Chatgilialoglu, *Organosilanes in Radical Chemistry* (Wiley, Chichester, UK, 2014).
32. J. J. Devery III, J. D. Nguyen, C. Dai, C. R. J. Stephenson, *ACS Catal.* **6**, 5962-5967 (2016).
33. S. E. Creutz, K. J. Lotito, G. C. Fu, J. C. Peters, *Science* **338**, 647-651 (2012).
34. M. W. Johnson, K. I. Hannoun, Y. Tan, G. C. Fu, J. C. Peters, *Chem. Sci.* **7**, 4091-4100 (2016).
35. Stern-Volmer studies confirmed quenching interaction between supersilanol **4** and the excited photocatalyst. See figure S35 in supplementary materials.
36. M. Lucarini, E. Marchesi, G. F. Pedulli, C. Chatgilialoglu, *J. Org. Chem.* **63**, 1687-1693 (1998).
37. For reviews on radical-radical cross coupling in the presence of a transition metal catalyst see (*35*).
38. H. Yi; G. Zhang; H. Wang; Z, Huang; J. Wang; A. K. Singh; A. Lei, *Chem. Rev.* **117**, 9016-9085 (2017).

39. A. Lishchynskyi, G. Berthon, V. V. Grushin, *Chem. Commun.* **50**, 10237-10240 (2014).
40. See supplementary materials for optimization studies.
41. Z. Xia, Q. Zhu, *Org. Lett.* **15**, 4110-4113 (2013).
42. D. A. Leas, Y. Dong, J. L. Vennerstrom, D. E. Stack, *Org. Lett.* **19**, 2518-2521 (2017).
43. Studies were carried out to rule out an aryl bromide activation by an excited Cu(I)-CF_3 species as the major pathway under the standard conditions. See supplementary materials.
44. D. D. Perrin, W. L. F.Armarego, *Purification of Laboratory Chemicals* (Pergamon Press, Oxford, 1988) ed 3.
45. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **15**, 1518-1520 (1996).
46. W. C. Still, M. Kahn, A. J. Mitra, *J. Org. Chem.* **43**, 2923-2925 (1978).
47. C. C. Le, M. K. Wismer, Z.-C. Shi, R. Zhang, D. V. Conway, G. Li, P. Vachal, I. W. Davies, D. W. C. MacMillan *ACS Cen. Sci.* **3**, 647-653 (2017).
48. H. Yu, C. Liu, X. Lv, J. Xiu, J.-Z. Zhao, *Dyes Pigm.* **145**, 136-143 (2017).
49. D. M. Schultz, J. W. Sawicki, T. P. Yoon, *Beilstein J. Org. Chem.* **11**, 61-65 (2015).
50. G. J. Choi, Q. Zhu, D. C. Miller, C. J. Gu, R. R. Knowles, *Nature* **539**, 268-271 (2016).
51. S.-M. Wang, X.-Y. Wang, H.-L. Qin, C.-P. Zhang, *Chem. Eur. J.* **22**, 6542-6546 (2016).

References

1. L. S. Hegedus, B. C. G. Söderberg, *Transition Metals in the Synthesis of Complex Organic Molecules* (University Science Books, United States, 3rd Edition, 2010).

2. D. A. Petrone, J. Ye, M. Lautens, Modern Transition-Metal-Catalyzed Carbon-Halogen Bond Formation. *Chem. Rev.* **116**, 8003–8104 (2016). doi:10.1021/acs.chemrev.6b00089 Medline

3. J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century* (John Wiley & Sons, 2005).

4. S. Z. Tasker, E. A. Standley, T. F. Jamison, Recent advances in homogeneous nickel catalysis. *Nature* **509**, 299–309 (2014). doi:10.1038/nature13274 Medline

5. G. Evano, N. Blanchard, *Copper-Mediated Cross-Coupling Reactions* (John Wiley & Sons, 2014).

6. G. O. Jones, P. Liu, K. N. Houk, S. L. Buchwald, Computational explorations of mechanisms and ligand-directed selectivities of copper-catalyzed Ullmann-type reactions. *J. Am. Chem. Soc.* **132**, 6205–6213 (2010). doi:10.1021/ja100739h Medline

7. H.-Z. Yu, Y.-Y. Jiang, Y. Fu, L. Liu, Alternative mechanistic explanation for ligand-dependent selectivities in copper-catalyzed *N*- and *O*-arylation reactions. *J. Am. Chem. Soc.* **132**, 18078–18091 (2010). doi:10.1021/ja104264v Medline

8. R. Giri, A. Brusoe, K. Troshin, J. Y. Wang, M. Font, J. F. Hartwig, Mechanism of the Ullmann Biaryl Ether Synthesis Catalyzed by Complexes of Anionic Ligands: Evidence for the Reaction of Iodoarenes with Ligated Anionic Cu^I Intermediates. *J. Am. Chem. Soc.* **140**, 793–806 (2018). doi:10.1021/jacs.7b11853 Medline

9. P. J. Amal Joseph, S. Priyadarshini, Copper-Mediated C–X Functionalization of Aryl Halides. *Org. Process Res. Dev.* **21**, 1889–1924 (2017). doi:10.1021/acs.oprd.7b00285

10. Systems competent for aryl chloride oxidative addition have recently been reported. See (*11*).

11. S. Bhunia, G. G. Pawar, S. V. Kumar, Y. Jiang, D. Ma, Selected Copper-Based Reactions for C-N, C-O, C-S, and C-C Bond Formation. *Angew. Chem. Int. Ed.* **56**, 1636–16179 (2017). doi:10.1002/anie.201701690 Medline

12. A. Casitas, X. Ribas, The role of organometallic copper(iii) complexes in homogeneous catalysis. *Chem. Sci.* **4**, 2301–2318 (2013). doi:10.1039/c3sc21818j

13. T. Furuya, A. S. Kamlet, T. Ritter, Catalysis for fluorination and trifluoromethylation. *Nature* **473**, 470–477 (2011). doi:10.1038/nature10108 Medline

14. A. J. Hickman, M. S. Sanford, High-valent organometallic copper and palladium in catalysis. *Nature* **484**, 177–185 (2012). doi:10.1038/nature11008 Medline

15. K. Uneyama, *Organofluorine Chemistry* (Blackwell, Oxford, UK, 2006).

16. W. K. Hagmann, The many roles for fluorine in medicinal chemistry. *J. Med. Chem.* **51**, 4359–4369 (2008). doi:10.1021/jm800219f Medline

17. O. A. Tomashenko, V. V. Grushin, Aromatic trifluoromethylation with metal complexes. *Chem. Rev.* **111**, 4475–4521 (2011). doi:10.1021/cr1004293 Medline

18. E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson, S. L. Buchwald, The palladium-catalyzed trifluoromethylation of aryl chlorides. *Science* **328**, 1679–1681 (2010). doi:10.1126/science.1190524 Medline

19. J. R. Bour, N. M. Camasso, M. S. Sanford, Oxidation of Ni(II) to Ni(IV) with Aryl Electrophiles Enables Ni-Mediated Aryl-CF_3 Coupling. *J. Am. Chem. Soc.* **137**, 8034–8037 (2015). doi:10.1021/jacs.5b04892 Medline

20. C. Alonso, E. M. de Marigorta, G. Rubiales, F. Palacios, *Chem. Rev.* **115**, 1847–1935 (2015). doi:10.1021/cr500368h Medline

21. A. I. Konovalov, A. Lishchynskyi, V. V. Grushin, Mechanism of trifluoromethylation of aryl halides with $CuCF_3$ and the ortho effect. *J. Am. Chem. Soc.* **136**, 13410–13425 (2014). doi:10.1021/ja507564p Medline

22. J. Jover, Computational Insights into Nucleophilic Copper-Catalyzed Trifluoromethylation of Aryl Halides. *ACS Catal.* **4**, 4389–4397 (2014). doi:10.1021/cs500872m

23. G. G. Dubinina, H. Furutachi, D. A. Vicic, Active trifluoromethylating agents from well-defined Copper(I)-CF_3 complexes. *J. Am. Chem. Soc.* **130**, 8600–8601 (2008). doi:10.1021/ja802946s Medline

24. A. Zanardi, M. A. Novikov, E. Martin, J. Benet-Buchholz, V. V. Grushin, Direct cupration of fluoroform. *J. Am. Chem. Soc.* **133**, 20901–20913 (2011). doi:10.1021/ja2081026 Medline

25. H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig, A broadly applicable copper reagent for trifluoromethylations and perfluoroalkylations of aryl iodides and bromides. *Angew. Chem. Int. Ed.* **50**, 3793–3798 (2011). doi:10.1002/anie.201100633 Medline

26. Q.-Y. Chen, S.-W. Wu, Methyl fluorosulphonyldifluoroacetate; a new trifluoromethylating agent. *J. Chem. Soc. Chem. Commun.* **11**, 705–706 (1989). doi:10.1039/c39890000705

27. M. Oishi, H. Kondo, H. Amii, Aromatic trifluoromethylation catalytic in copper. *Chem. Commun. (Camb.)* **14**, 1909–1911 (2009). doi:10.1039/b823249k Medline

28. T. Schareina, X.-F. Wu, A. Zapf, A. Cotté, M. Gotta, M. Beller, Towards a Practical and Efficient Copper-Catalyzed Trifluoromethylation of Aryl Halides. *Top. Catal.* **55**, 426–431 (2012). doi:10.1007/s11244-012-9824-0

29. J. Twilton, C. C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, The merger of transition metal and photocatalysis. *Nat. Rev. Chem.* **1**, 0052 (2017). doi:10.1038/s41570-017-0052

30. P. Zhang, C. C. Le, D. W. C. MacMillan, Silyl Radical Activation of Alkyl Halides in Metallaphotoredox Catalysis: A Unique Pathway for Cross-Electrophile Coupling. *J. Am. Chem. Soc.* **138**, 8084–8087 (2016). doi:10.1021/jacs.6b04818 Medline

31. C. Chatgilialoglu, *Organosilanes in Radical Chemistry* (Wiley, Chichester, UK, 2014).

32. J. J. Devery III, J. D. Nguyen, C. Dai, C. R. J. Stephenson, Light-Mediated Reductive Debromination of Unactivated Alkyl and Aryl Bromides. *ACS Catal.* **6**, 5962–5967 (2016). doi:10.1021/acscatal.6b01914

33. S. E. Creutz, K. J. Lotito, G. C. Fu, J. C. Peters, Photoinduced Ullmann C-N coupling: Demonstrating the viability of a radical pathway. *Science* **338**, 647–651 (2012). doi:10.1126/science.1226458 Medline

34. M. W. Johnson, K. I. Hannoun, Y. Tan, G. C. Fu, J. C. Peters, A mechanistic investigation of the photoinduced, copper-mediated cross-coupling of an aryl thiol with an aryl halide. *Chem. Sci.* **7**, 4091–4100 (2016). doi:10.1039/C5SC04709A Medline

35. Stern-Volmer studies confirmed quenching interaction between supersilanol **4** and the excited photocatalyst. See fig. S40.

36. M. Lucarini, E. Marchesi, G. F. Pedulli, C. Chatgilialoglu, Homolytic Reactivity of Group 14 Organometallic Hydrides toward Nitroxides. *J. Org. Chem.* **63**, 1687–1693 (1998). doi:10.1021/jo972178i

37. For reviews on radical-radical cross coupling in the presence of a transition metal catalyst, see (*38*).

38. H. Yi, G. Zhang, H. Wang, Z. Huang, J. Wang, A. K. Singh, A. Lei, Recent Advances in Radical C-H Activation/Radical Cross-Coupling. *Chem. Rev.* **117**, 9016–9085 (2017). doi:10.1021/acs.chemrev.6b00620 Medline

39. A. Lishchynskyi, G. Berthon, V. V. Grushin, Trifluoromethylation of arenediazonium salts with fluoroform-derived $CuCF_3$ in aqueous media. *Chem. Commun. (Camb.)* **50**, 10237–10240 (2014). doi:10.1039/C4CC04930F Medline

40. See the supplementary materials for optimization studies.

41. Z. Xia, Q. Zhu, A transition-metal-free synthesis of arylcarboxyamides from aryl diazonium salts and isocyanides. *Org. Lett.* **15**, 4110–4113 (2013). doi:10.1021/ol4017244 Medline

42. D. A. Leas, Y. Dong, J. L. Vennerstrom, D. E. Stack, One-Pot, Metal-Free Conversion of Anilines to Aryl Bromides and Iodides. *Org. Lett.* **19**, 2518–2521 (2017). doi:10.1021/acs.orglett.7b00771 Medline

43. Studies were carried out to rule out an aryl bromide activation by an excited Cu(I)-CF_3 species as the major pathway under the standard conditions. See the supplementary materials.

44. D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals* (Pergamon Press, Oxford, 1988) ed. 3.

45. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, Safe and Convenient Procedure for Solvent Purification. *Organometallics* **15**, 1518–1520 (1996). doi:10.1021/om9503712

46. W. C. Still, M. Kahn, A. J. Mitra, Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **43**, 2923–2925 (1978). doi:10.1021/jo00408a041

47. C. C. Le, M. K. Wismer, Z.-C. Shi, R. Zhang, D. V. Conway, G. Li, P. Vachal, I. W. Davies, D. W. C. MacMillan, A General Small-Scale Reactor to Enable Standardization and Acceleration of Photocatalytic Reactions. *ACS Cent. Sci.* **3**, 647–653 (2017). doi:10.1021/acscentsci.7b00159 Medline

48. H. Yu, C. Liu, X. Lv, J. Xiu, J.-Z. Zhao, Effect of substituents on properties of diphenylphosphoryl-substituted bis-cyclometalated Ir(III) complexes with a picolinic acid as ancillary ligand. *Dyes Pigm.* **145**, 136–143 (2017). doi:10.1016/j.dyepig.2017.05.056

49. D. M. Schultz, J. W. Sawicki, T. P. Yoon, An improved procedure for the preparation of $Ru(bpz)_3(PF_6)_2$ via a high-yielding synthesis of 2,2′-bipyrazine. *Beilstein J. Org. Chem.* **11**, 61–65 (2015). doi:10.3762/bjoc.11.9 Medline

50. G. J. Choi, Q. Zhu, D. C. Miller, C. J. Gu, R. R. Knowles, Catalytic alkylation of remote C-H bonds enabled by proton-coupled electron transfer. *Nature* **539**, 268–271 (2016). doi:10.1038/nature19811 Medline

51. S.-M. Wang, X.-Y. Wang, H.-L. Qin, C.-P. Zhang, Palladium-Catalyzed Arylation of Arylboronic Acids with Yagupolskii-Umemoto Reagents. *Chemistry* **22**, 6542–6546 (2016). doi:10.1002/chem.201600991 Medline