Supporting Information

Photoinduced transient activating strategy for late-stage chemoselective C(sp^3)-H trifluoromethylation of azines

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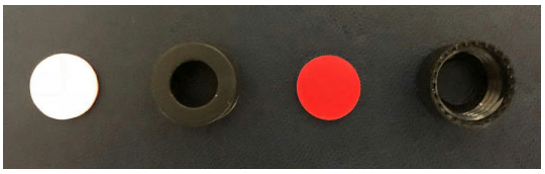
I. General Methods

All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica Gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was done using silica Gel (silica gel 60 F254). TLC plates were analyzed by an exposure to ultraviolet (UV) light and/or submersion in phosphomolybdic acid solution or submersion in $KMnO_4$ solution or in I_2. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out in chloroform-*d* ($CDCl_3$) or acetonitrile-d_3 (CD_3CN). ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers, respectively.^{19}F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as δ values relative to internal TMS (δ 0.00 for ^1H NMR), chloroform (δ 7.26 for ^1H NMR), acetonitrile (δ 1.94 for ^1H NMR), chloroform (δ 77.00 for ^{13}C NMR), and acetonitrile (δ 1.32 or 118.26 for ^{13}C NMR) in parts per million (ppm). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; Coupling constants (*J*) are reported in Hertz (Hz). Melting points were uncorrected. Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker miccOTOF-Q111. GC-MS spectra were performed on Agilent 5977B.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C)

Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)



II. Synthesis of Starting Materials

Substrates **S3-S6, S8-S9, S15, S16, S18-S21, S52, S53, S55, S57-S61** were purchased from commercial sources (Alfa, TCI, Energy and Macklin) and used as received.

Substrates **2a-2i** were prepared according to the literature.[1]

Substrates **S17** were prepared according to the literature.[2]

Substrates **S7, S10-S14, S22-S27** were prepared according to the literature.[3]

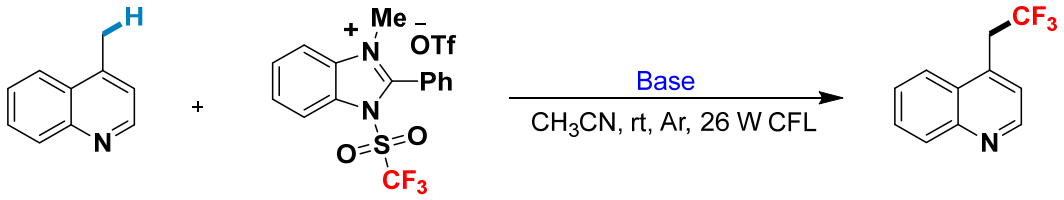
Substrates **S28-S40, S42-S51** were prepared according to the literature.[4]

Substrates **S41** were prepared according to the literature.[5]

Substrates **S54, S56, S62-S68** were prepared according to the literature.[6]

III. Optimizations of the Reaction Conditions

Table S1: Optimization of base [a]

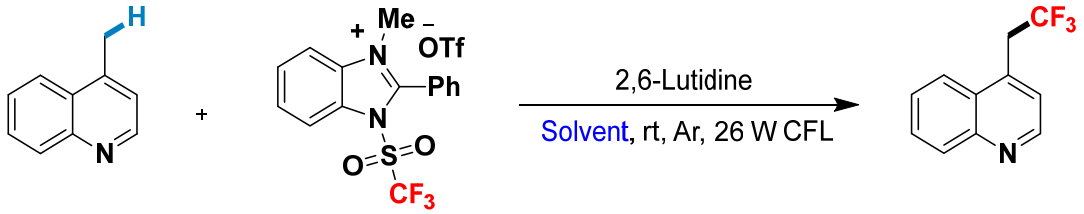


1, 0.2mmol **2a, IMDN-Tf** **3**

Entry	Base	pKa	Yield [b]
1	K_3PO_4	12.32	38% [c]
2	Na_2CO_3	10.33	29% [d]
3	Et_3N	10.75	40%
4	Pyridine	5.23	23%
5	4-tert-Butylpydrdine	5.99	40%
6	2,6-Lutidine	6.72	55%
7	4-Methoxypyridine	6.58	27%
8	DABCO	8.89	n.d.
9	DIPEA	10.98	30%

[a] All reactions were carried out with **1** (28.6 mg, 0.20 mmol), **2a** (0.30 mmol, 1.2 equiv) and Base (0.24 mmol, 1.2 equiv) in CH_3CN (2.0 mL) at rt under Ar and 26W CFL. [b] Yields determined by ^{19}F NMR spectroscopy using (trifluoromethoxy)benzene as an internal standard. [c] K_3PO_4 (0.2 equiv); [d] Na_2CO_3 (0.2 equiv). DABCO = Triethylenediamine; DIPEA = N,N-Diisopropylethylamine

Table S2: Optimization of solvent [a]

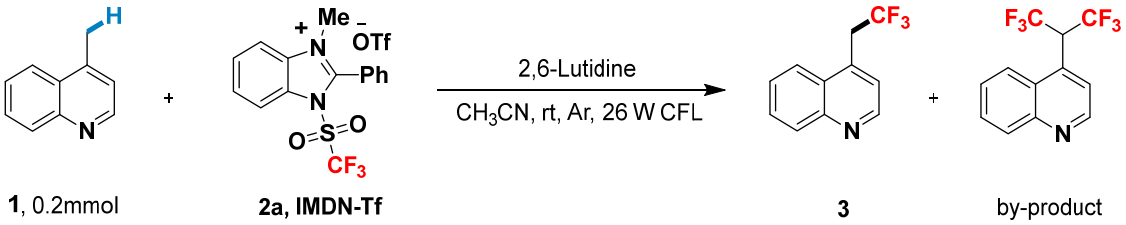


1, 0.2mmol **2a, IMDN-Tf** **3**

Entry	Solvent	Polarity	Yield [b]
1	Acetone	0.355	5%
2	DMF	0.386	n.d.
3	DMAc	0.392	n.d.
4	THF	0.207	28%
5	DMSO	0.444	n.d.
6	EtOAc	0.228	33%
7	CH_3CN	0.460	73%
8	CH_3CN:EtOAc = 1:3	≈0.25	69%

[a] All reactions were carried out with **1** (28.6 mg, 0.20 mmol), **2a** (0.36 mmol, 1.8 equiv) and 2,6-Lutidine (0.35 mmol, 1.75 equiv) in Solvent (2.0 mL) at rt under Ar and 26W CFL. [b] Yields determined by ^{19}F NMR spectroscopy using (trifluoromethoxy)benzene as an internal standard.

Table S3: Optimization of material ratio [a]

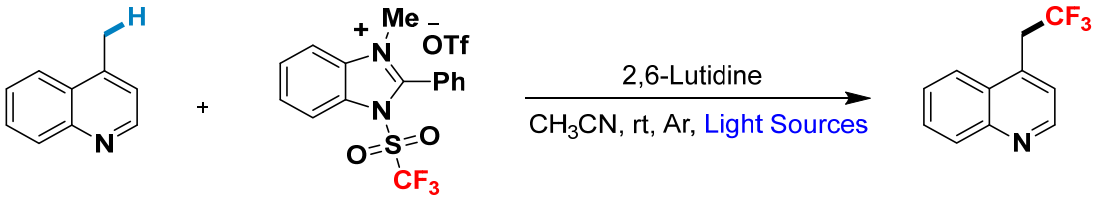


1, 0.2mmol **2a, IMDN-Tf** **3** by-product

Entry	**1** (equiv)	**2a** (equiv)	2,6-Lutidine (equiv)	Yield [b] (by-product)
1	1	1.5	0.5	56%(8%)
2	1	1.5	1.2	58%(5%)
3	1	1.5	1.5	63%(5%)
4	1	1.5	2	66%(6%)
5	1	1.5	3	52%(6%)
6	1	1.6	1.75/(0.35mmol)	65%(5%)
7	1	1.7	1.75/(0.35mmol)	67%(6%)
8	**1**	**1.8**	**1.75/(0.35mmol)**	**73%(6%)**
9	1	1.9	1.75/(0.35mmol)	48%(23%)
10	1	2	1.2	37%(32%)
11	1	2	1.5	31%(32%)
12	1	2	2	37%(32%)

[a] All reactions were carried out with **1** (28.6 mg, 0.20 mmol) in CH_3CN (2.0 mL) at rt under Ar and 26 W CFL. [b] Yields determined by ^{19}F NMR spectroscopy using (trifluoromethoxy)benzene as an internal standard.

Table S4: Optimization of light sources [a]

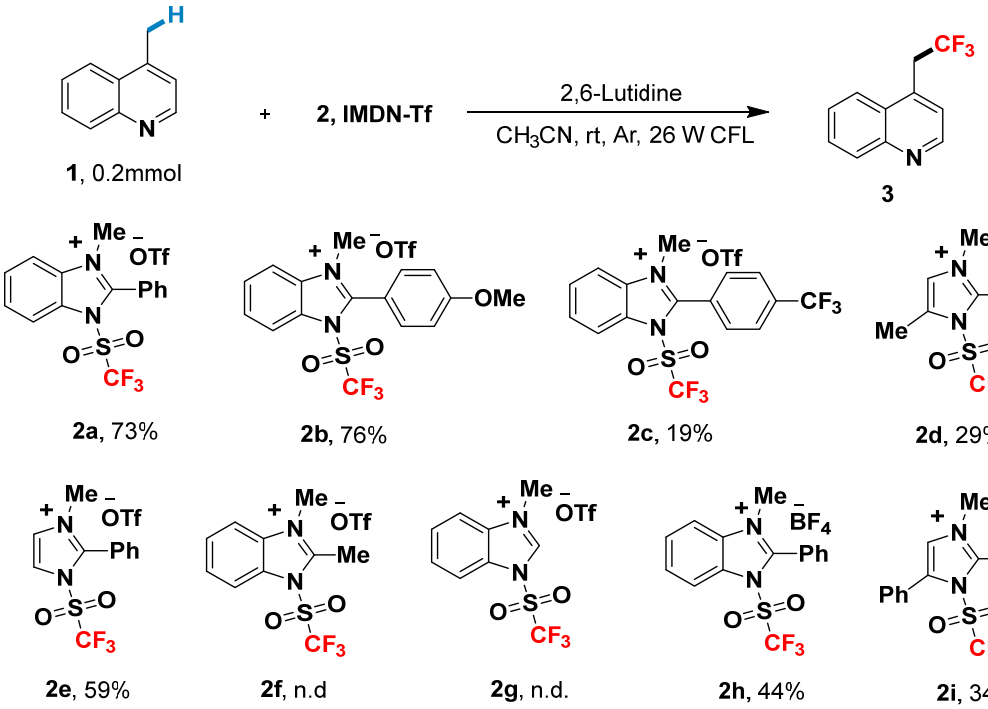


1, 0.2mmol **2a, IMDN-Tf** **3**

Entry	Light sources	Yield [b]
1	5 W CFL	63%
2	13 W CFL	67%
3	40 W CFL	65%
4	30 W blue LEDs	54%
5	60 W blue LEDs	53%

[a] All reactions were carried out with **1** (28.6 mg, 0.20 mmol), **2a** (0.36 mmol, 1.8 equiv) and 2,6-Lutidine (0.35 mmol, 1.75 eq.) in CH_3CN (2.0 mL) at rt under Ar. [b] Yields determined by ^{19}F NMR spectroscopy using (trifluoromethoxy)benzene as an internal standard.

Table S5: Optimization of imidazolium sulfonate reagents [a,b]



[a] All reactions were carried out with **1** (28.6 mg, 0.20 mmol), **2** (0.36 mmol, 1.8 equiv) and 2,6-Lutidine (0.35 mmol, 1.75 equiv) in CH_3CN (2.0 mL) at rt under Ar and 26W CFL. [b] Yields determined by ^{19}F NMR spectroscopy using (trifluoromethoxy)benzene as an internal standard.

IV. General Procedure for the Synthesis of the Products 3-68

General procedure for the synthesis of products 3-51

Condition A: Under argon, to a solution of **2a** (0.36 mmol, 1.8 equiv), 2,6-Lutidine (0.35 mmol, 1.75 eq.) in CH_3CN (2 mL) was added corresponding Substrates (0.2 mmol) at room temperature. After that, the tube was exposed to a 26 W compact fluorescent light at room temperature about 2-12 h until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired product.

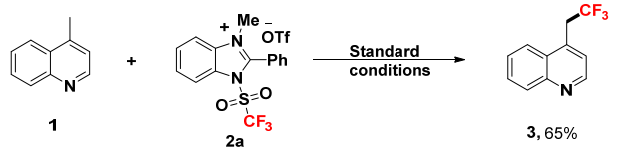
General procedure for the synthesis of products 52-68

Condition B: Under argon, to a solution of **2d** (0.3 mmol, 1.5 equiv) and alkenes (0.4 mmol, 2 equiv) in CH_3CN (2 mL) was added corresponding Substrates (0.2 mmol) at room temperature. After that, the tube was exposed to a 26 W compact fluorescent light at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired product.

V. Mechanistic studies

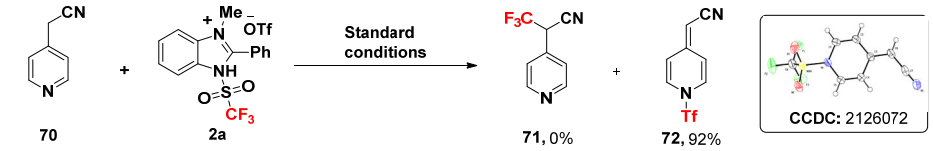
V-1. Control Experiment

I)



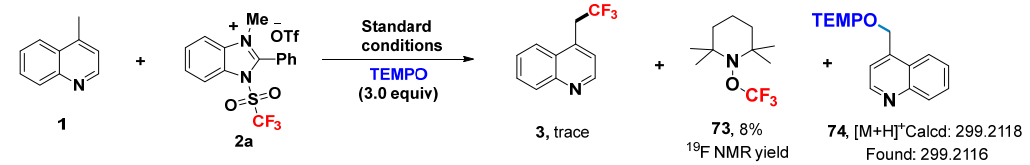
1 + **2a** → **3**, 65% + **69**, detected by GCMS

II)



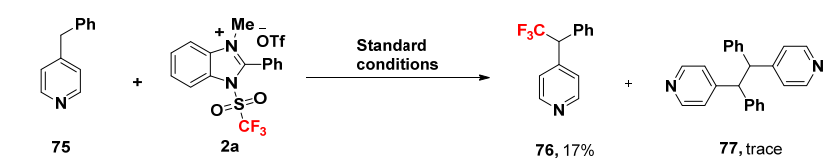
70 + **2a** → **71**, 0% + **72**, 92%

III)



1 + **2a** → **3**, trace + **73**, 8% ^{19}F NMR yield + **74**, $[M+H]^+$Calcd: 299.2118 Found: 299.2116

IV)



75 + **2a** → **76**, 17% + **77**, trace HRMS:$[M+H]^+$ Calcd: 337.1699 Found: 337.1689

Control Experiment (I):

Under argon, to a solution of **2a** (0.36 mmol, 1.8 equiv), 2,6-Lutidine (0.35 mmol, 1.75 eq.) in CH_3CN (2 mL) was added lepidine (0.2 mmol) at room temperature. After that, the tube was exposed to a 26 W compact fluorescent light at room temperature about 2 h until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC-MS. The reaction mixturewas evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired product **3**. At the same time, GC-MS analysis indicated that this Tf-shift product **69** was formed.

Control Experiment (II):

In order to verify the correctness of the Tf-shift process, we tried to introduce a cyano group at the benzyl position to enhance the acidity of the benzyl position, hoping to obtain a stable trifluoromethanesulfonyl transfer intermediate. Under argon, to a solution of **2a** (0.36 mmol, 1.8 equiv), 2,6-Lutidine (0.35 mmol, 1.75 eq.) in CH_3CN (2 mL) was added 4-Pyridineacetonitrile (0.2 mmol) at room temperature. After that, the tube was exposed to a 26 W compact fluorescent light at room temperature about 2-12 h until the reaction was completed as monitored by TLC analysis. Subsequently, The Tf-shift product were directly purified by flash chromatography on silica gel to give and confirmed its structure by single crystal diffraction.

Control Experiment (III):

Under argon, to a solution of **2a** (0.36 mmol, 1.8 equiv), TEMPO (3.0 equiv), 2,6-Lutidine (0.35 mmol, 1.75 eq.) in CH_3CN (2 mL) was added lepidine (0.2 mmol) at room temperature. After that, the tube was exposed to a 26 W compact fluorescent light at room temperature about 2-12 h until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC-MS. GC-MS analysis of this reaction mixture showed that the desired product was not formed.

Control Experiment (IV):

Under argon, to a solution of **2a** (0.3 mmol, 1.5 equiv), 2,6-Lutidine (0.35 mmol, 1.75 eq.) in CH_3CN (2 mL) was added 4-benzylpyridine (0.2 mmol) at standard conditions. After that, the tube was exposed to a 26 W compact fluorescent light at room temperature about 2-12 h until the reaction was completed as monitored by TLC analysis. Subsequently, add (trifluoromethoxy)benzene as an internal standard. ^{19}F NMR analysis of this reaction mixture showed that the yield of desired product was 17% and the dimeric product can be monitored by HRMS (ESI): caled for $C_{24}H_{21}N_2^+$ $[M + H]^+$ 337.1699; found 337.1689. In our reaction, there are only reagents, substrates, 2,6-Lutidine and acetonitrile present. It is difficult to explain the production of the dimer without the involvement of radicals.

V-2. UV/Vis Absorption Spectra

The UV/Vis absorption spectra of CH_3CN solutions of quinoline **1** ($5x10^{-5}$ M), IMDN-SO_2CF_3 **2a** ($5x10^{-5}$ M), a mixture of **1** ($5x10^{-5}$ M) and **2a** ($5x10^{-5}$ M) are shown in Figure S1. A strong absorption band of the mixture [**1**+**2a**] with a maximum absorption wavelength at 280 nm and there is a significant redshift relative to the respective absorption may indicate the formation of Tf-shift intermediate.

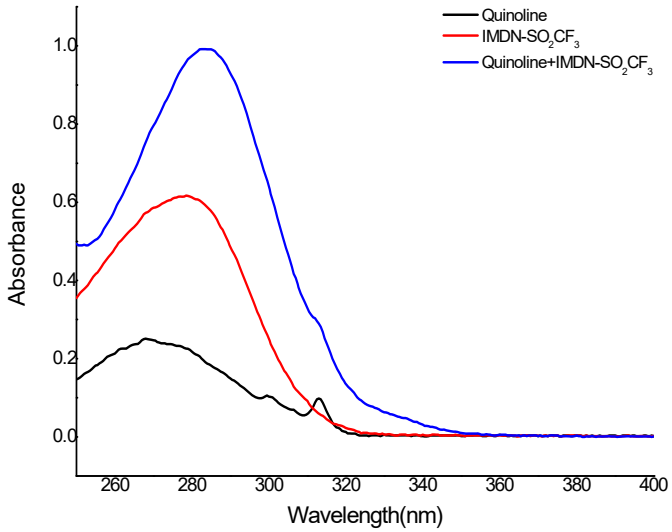


Figure S1. UV/Vis spectra **1**, **2a**, and a 1:1 mixture of **1** and **2a** in CH_3CN

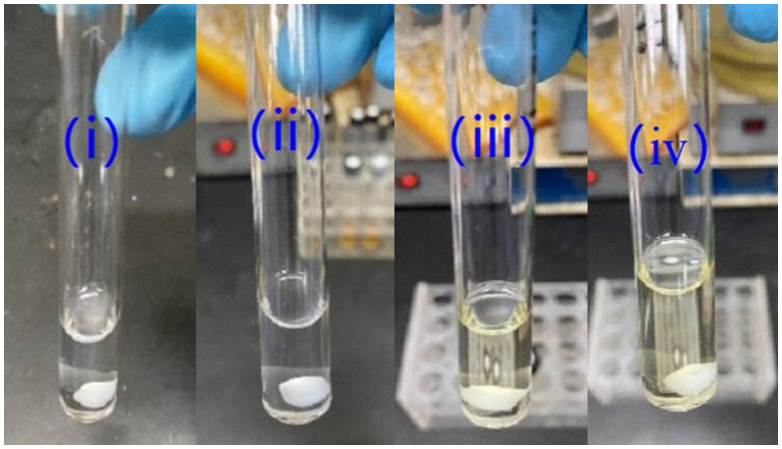


Figure S2. Comparison of the colors of CH_3CN solutions of (i) **1**, (ii) **2a**, (iii) a mixture of **1** and **2a** after 5 min irradiation, (iv) a mixture of **1**, **2a** and 2,6-Lutidine.

V-3. EPR Experiments

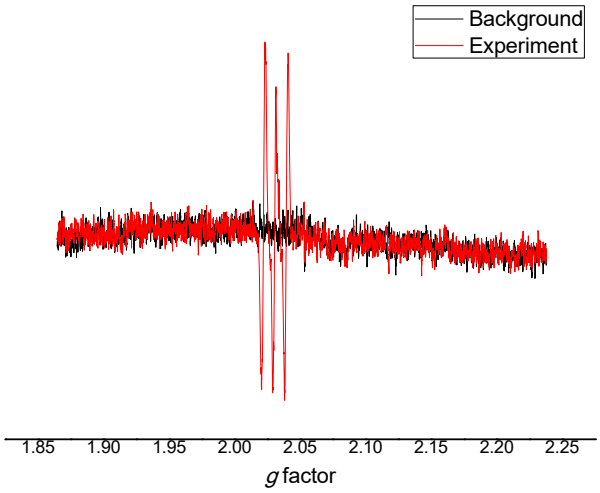


Figure S3. EPR experiments

To demonstrate the possible reaction mechanism, electron paramagnetic resonance (EPR) experiments with *N-tert*-butyl-*α*-phenylnitrone (PBN) as the electron-spin trapping reagent were carried out. A significant EPR signal was observed when the reaction was run under standard conditions, the measured g-factor value is 2.030428. Combining the above results indicating that the reaction probably proceeded via a radical process.

V-4. Quantum Yield Measurement

Determination of the light intensity at 395 nm:

According to the standard procedure for iron oxalate actinometry[7] and the works by Yoon and co-workers[8], the photon flux of the LED (λ_{max}= 395 nm) was first determined by standard ferrioxalate actinometry. For this, a 10 mL 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A 20 mL buffered solution of 1,10- phenanthroline was prepared by dissolving 1,10- phenanthroline (20 mg) and sodium acetate (4.5 g) in H_2SO_4 (20 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 5 seconds at λ_{max}= 395 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was stirred in the dark for 1.0 h to allow all the ferrous ions to be coordinated by phenanthroline. The absorption of the solution was measured at 510 nm. A nonirradiated sample was also prepared identically and the absorption at 510 nm was also measured. Each sample preparation and measurements were repeated two more times. The average of the absorption of the irradiated and non-irradiated samples were determined and used for the calculation of photon flux.

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A\ (510\ nm)}{l \times \varepsilon}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorption at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated based on the following equation:

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.13 for a 0.15 M solution at λ = 395 nm)[6], t is the irradiation time (5 s), and f is the fraction of light absorbed at λ = 395 nm. This value is calculated using the following equation where (395 nm) is the absorption of the ferrioxalate solution at 395 nm. The absorbance of the above ferrioxalate solution at 395 nm was measured to be 3.972.

$$f = 1 - 10^{-A\ (395\ nm)}$$

The average photon flux was thus calculated to be 9.276×10^{-8} einsteins s^{-1}

Determination of the reaction quantum yield:

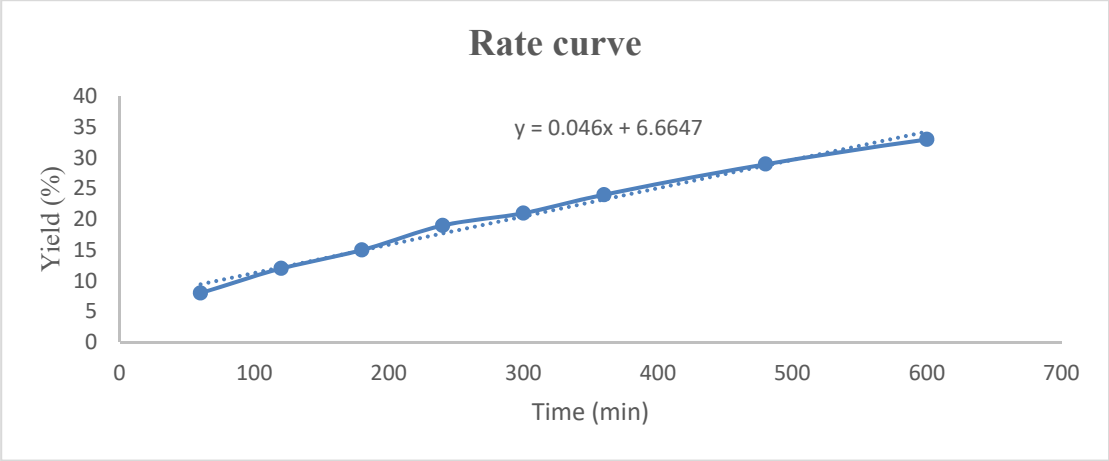


Figure S4. Determination of the reaction rate

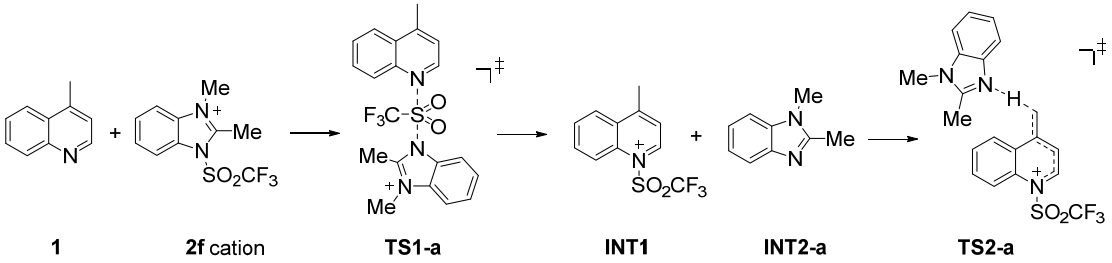
The reaction quantum yield (Φ) was determined with the following formula:

$$\Phi = \frac{\text{mole of product formation rate}}{photon\ flux \times f}$$

Where, f is the fraction of light absorbed at λ_{max} = 395 nm by the reaction mixture. An absorption spectrum gave an A (395 nm) value of > 3, indicating that the fraction of absorbed light (f) is >0.999. The reaction quantum yield (Φ) was thus determined to be Φ = 0.99.

V-5. Computational details

All calculations were performed with Gaussian 09 program[9]. Geometry optimizations were performed using (U)M06-2X functionals[10], while 6-31G(d,p) was used as basis set for all atoms. After optimization, frequency calculations were subsequently performed to confirm that all stationary points had correct number of imaginary frequencies (zero for minima and one for transition states) and to provide thermodynamic corrections at 298 K, 1 atm. For all transition states, Intrinsic Reaction Coordinate (IRC)[11] were calculated to confirm that they indeed connected between correct minima. Single-point energies of optimized structures were calculated using (U)M06-2X functionals, with 6-311+G(2d,p) as basis set. Methods M06-2X-D3[10,12], B3LYP-D3[12-15] and ωB97X-D[16] were also used for single-point energy calculations to evaluate the strength of π-π stacking (see Figure S7). SMD solvation model[17] (solvent = MeCN) was used in geometry optimizations and single-point energy calculations to consider solvent effect. The final Gibbs free energy was calculated as the sum of Gibbs free energy correction (from frequency calculation) and the single point energy in solution. For each species, extensive conformational search was done and the reported value is from the conformer with lowest Gibbs free energy. Graphics in Scheme 4 was rendered using CYLview[18]. See Table S6 for detailed energies and atom coordinates for all species involved.



Species	**1** + **2f** cation	**TS1-a**	**INT1** + **INT2-a**	**TS2-a**
Δ*G* (kcal/mol)	0.0	19.3	8.5	27.3

Figure S5. DFT study on the reaction using **2f** as imidazolium sulfonate reagent. Relative Gibbs free energies (kcal/mol) were computed with SMD(MeCN)-(U)M06-2X/6-311+G(2d,p)//SMD(MeCN)-(U)M06-2X/6-31G(d,p).

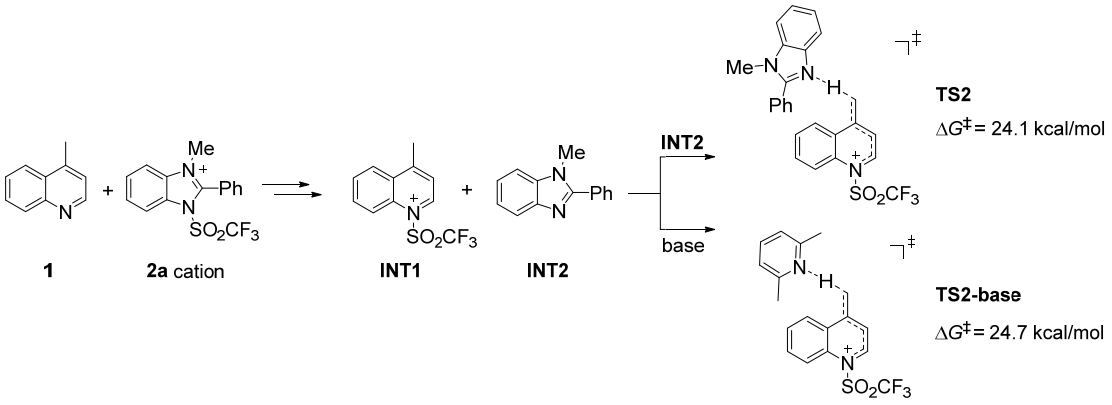
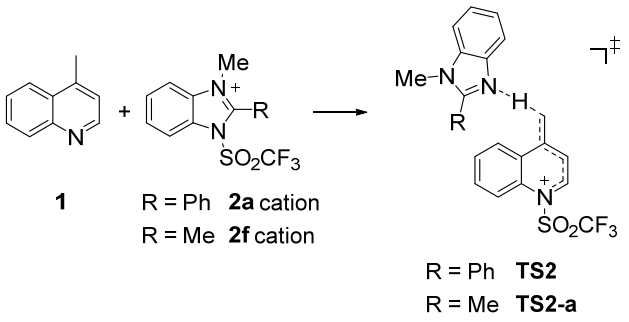


Figure S6. DFT study on the deprotonation process of **INT1**. Computed with SMD(MeCN)-(U)M06-2X/6-311+G(2d,p)//SMD(MeCN)-(U)M06-2X/6-31G(d,p).



Method	Δ*G*(**TS2**)	Δ*G*(**TS2-a**)	ΔΔ*G*
M06-2X	24.1	27.3	3.2
M06-2X-D3	22.4	26.0	3.6
B3LYP-D3	20.0	23.0	3.0
ωB97X-D	21.9	24.8	2.9

Figure S7. Relative free energies (kcal/mol) of the deprotonation transition states evaluated by different computational methods. Computed at SMD(MeCN)-(U)Method/6-311+G(2d,p)//SMD(MeCN)-(U)M06-2X/6-31G(d,p).

To explain the preference of CF_3 radical attacking **69**, the condensed nucleophilicity index of the respective carbons in **1** and **69** have been calculated. The condensed nucleophilicity index of atom *k* is defined[19] as:

$$N_k = N \cdot f_k^-$$

in which N is the global nucleophilicity index of the nucleophile. By definition[20],

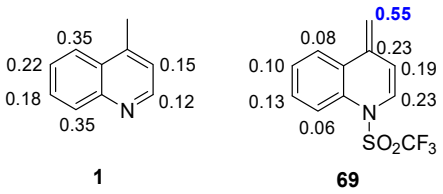
$$N = \varepsilon_{\mathrm{HOMO(Nu)}} - \varepsilon_{\mathrm{HOMO(TCE)}}$$ (TCE = tetracyanoethylene)

And f_k^- is the condensed Fukui function[21] of atom *k* :

$$f_k^- = q_{N-1}^k - q_N^k$$

Here *q* was obtained by Hirshfeld charges[22] of N and N-1 electrons states of the nucleophile[23]. All results were computed at SMD(MeCN)-M06-2X/6-31G(d,p).

The condensed nucleophilicity index of selected carbon atoms in **1** and **69** are shown in Fig. S8. The results show that the terminal alkenyl carbon has the largest nucleophilicity index than any other atoms. We believe the reduced aromaticity of **69** and the electron-donating conjugative effect from the N atom activates this site, resulting in the observed regioselectivity.



1 **69**

Figure S8. Condensed nucleophilicity index (*e*·eV) of selected carbon atoms in **1** and **69**. Computed at SMD(MeCN)-M06-2X/6-31G(d,p)

Table S6. Energies and Cartesian coordinates

1			
G (MeCN) = -441.064333 Hartree			

C	2.731840	-0.254115	0.000000
C	1.792962	-1.254839	0.000000
C	0.407885	-0.945476	0.000000
C	0.000000	0.417120	0.000000
C	0.994532	1.430070	0.000000
C	2.328365	1.102208	0.000000
H	3.789310	-0.499518	0.000000
H	2.078044	-2.302572	0.000000
C	-1.401382	0.703680	0.000000
H	0.691491	2.472561	0.000000
H	3.079497	1.886026	0.000000
C	-2.265044	-0.364279	0.000000
C	-1.756649	-1.684837	0.000000
H	-3.338960	-0.206359	0.000000
H	-2.453976	-2.521218	0.000000
N	-0.478963	-1.985733	0.000000
C	-1.901531	2.118860	0.000000
H	-1.542930	2.660231	0.881375
H	-1.542930	2.660231	-0.881375
H	-2.992671	2.140403	0.000000

2a cation			
G (MeCN) = -1536.006891 Hartree			

C	1.647795	-1.894689	-0.149803
C	1.807733	-0.541881	0.138428
C	-0.403282	-1.034917	-0.004373
N	0.276816	-2.144891	-0.231140
C	-0.274460	-3.457263	-0.575150
H	-1.334856	-3.354061	-0.792080
H	0.255399	-3.820978	-1.456253
H	-0.119965	-4.133673	0.266307
C	-1.869663	-0.929260	-0.019564
C	-2.611456	-1.643346	0.926102
C	-2.499521	-0.149058	-0.993056
C	-3.999027	-1.556877	0.903547
H	-2.104150	-2.247308	1.672505
C	-3.887383	-0.078134	-1.008632
H	-1.911004	0.376241	-1.737799
C	-4.634105	-0.775223	-0.059827
H	-4.582185	-2.100411	1.639128
H	-4.385311	0.518751	-1.765217
H	-5.717476	-0.712430	-0.074903
N	0.496463	-0.019777	0.224183
S	0.140393	1.530230	0.882443
O	-1.240778	1.553302	1.278319
O	1.231117	1.845657	1.767882
C	0.356775	2.581181	-0.636253
F	-0.703436	2.458060	-1.405259
F	1.440695	2.176558	-1.269686
F	0.495151	3.825024	-0.229709
C	3.069852	0.034577	0.262146
C	4.149803	-0.820264	0.091481
C	3.986647	-2.186911	-0.193649
C	2.728608	-2.754387	-0.322954
H	3.212699	1.084597	0.481339
H	5.151744	-0.415194	0.181213
H	4.865269	-2.810492	-0.316652
H	2.586313	-3.805779	-0.546360

3			
G (MeCN) = -778.125904 Hartree			

C	2.287977	0.991990	0.000000
C	1.872582	-1.256070	0.000000
C	0.465468	-1.051704	0.000000
C	-0.019625	0.294747	0.000000
C	0.906523	1.307732	0.000000
H	3.463498	-2.702964	0.000000
H	3.010184	1.806405	0.000000
C	2.384796	-2.579041	0.000000
C	-0.389291	-2.185716	0.000000
H	0.619198	2.352003	0.000000
C	0.133765	-3.455559	0.000000
C	1.534530	-3.655662	0.000000
H	-1.465946	-2.049059	0.000000
H	-0.530755	-4.313688	0.000000
H	1.932421	-4.665522	0.000000
C	-1.511738	0.518154	0.000000

H	-1.964988	0.051687	0.881047
H	-1.964988	0.051687	-0.881047
N	2.771360	-0.225759	0.000000
C	-1.948172	1.956330	0.000000
F	-1.511738	2.628969	1.079892
F	-3.287526	2.046345	0.000000
F	-1.511738	2.628969	-1.079892

69			
G (MeCN) = -1326.645764 Hartree			

S	-1.627444	-0.689641	-0.541935
O	-2.641041	-0.272642	-1.487688
O	-1.506170	-2.063465	-0.106692
C	-1.916104	0.295938	0.999960
F	-2.142203	1.561285	0.686543
F	-0.841268	0.211294	1.770548
F	-2.963507	-0.200630	1.638165
C	-0.202353	1.219117	-1.581322
C	1.065898	-0.582240	-0.486103
C	1.986412	0.365993	-0.010737
C	1.708546	1.813554	-0.172927
C	0.679601	2.129683	-1.168550
H	0.650465	-2.655769	-0.874169
H	-0.996564	1.416365	-2.289996
C	1.352453	-1.947745	-0.452591
C	3.190014	-0.102157	0.529216
H	0.625496	3.136162	-1.570417
C	3.460150	-1.460808	0.614371
C	2.541649	-2.384330	0.116396
H	3.929875	0.616111	0.867652
H	4.398408	-1.799852	1.041059
H	2.760317	-3.446567	0.145959
C	2.346130	2.783816	0.497959
H	3.081809	2.573244	1.266892
H	2.121250	3.826451	0.295665
N	-0.157977	-0.125072	-1.089711

69^{T}			
G (MeCN) = -1326.571492 Hartree			

S	-1.718263	-0.416385	-0.650970
O	-2.676820	0.327685	-1.440383
O	-1.768820	-1.858372	-0.553531
C	-1.873084	0.200911	1.089485
F	-1.821136	1.523214	1.101739
F	-0.876558	-0.291557	1.809722
F	-3.029476	-0.206001	1.588172
C	-0.098917	1.478651	-1.410665
C	0.977994	-0.562944	-0.571047
C	1.991819	0.240908	0.005716
C	1.931324	1.680575	-0.093822
C	0.914916	2.232648	-0.893723
H	0.360128	-2.536089	-1.152636
H	-0.891415	1.869698	-2.032988
C	1.113624	-1.947142	-0.646453
C	3.090792	-0.417984	0.592074
H	0.931906	3.292177	-1.129411
C	3.195289	-1.798786	0.571795
C	2.216505	-2.564744	-0.064724
H	3.869073	0.185366	1.050115
H	4.050844	-2.282205	1.032267
H	2.311991	-3.643980	-0.117910
C	2.963655	2.530661	0.510979
H	2.830176	2.953939	1.501241
H	3.877945	2.766401	-0.024808
N	-0.183186	0.090702	-1.113346

CF_3 radical			
G (MeCN) = -337.575339 Hartree			

C	-0.000000	0.000000	0.331513
F	0.000000	1.254185	-0.073669
F	-1.086156	-0.627093	-0.073669
F	1.086156	-0.627093	-0.073669

SO_2			
G (MeCN) = -548.620719 Hartree			

O	0.000000	1.239202	-0.373452
S	0.000000	-0.000000	0.373452
O	-0.000000	-1.239202	-0.373452

SO_2CF_3 radical			
G (MeCN) = -886.191616 Hartree			

S	-0.578431	-0.886186	-0.000000
O	-0.172103	-1.469968	1.284591
O	-0.172103	-1.469968	-1.284591
C	0.221755	0.837862	0.000000
F	1.530652	0.692821	0.000000
F	-0.172103	1.468662	1.083985
F	-0.172103	1.468662	-1.083985

B			
G (MeCN) = -326.766390 Hartree			

C	0.000000	1.155343	0.266119
C	0.000000	1.197915	-1.129881
C	0.000000	0.000000	-1.834979
C	-0.000000	-1.197915	-1.129881
C	-0.000000	-1.155343	0.266119
H	0.000000	2.153208	-1.644214
H	0.000000	0.000000	-2.921030
H	-0.000000	-2.153208	-1.644214
N	-0.000000	-0.000000	0.945591
C	0.000000	-2.413516	1.090797
H	-0.881281	-2.441278	1.738700
H	0.000000	-3.304751	0.460487
H	0.881281	-2.441278	1.738700
C	0.000000	2.413516	1.090797
H	0.000000	3.304751	0.460487
H	-0.881281	2.441278	1.738700
H	0.881281	2.441278	1.738700

BH^+			
G (MeCN) = -327.209682 Hartree			

C	0.000000	1.200327	0.224458
C	0.000000	1.208483	-1.161001
C	0.000000	0.000000	-1.851330
C	-0.000000	-1.208483	-1.161001
C	-0.000000	-1.200327	0.224458
H	0.000000	2.157876	-1.682189
H	0.000000	0.000000	-2.936452
H	-0.000000	-2.157876	-1.682189
N	-0.000000	-0.000000	0.844320
C	0.000000	-2.418352	1.085813
H	-0.885551	-2.426621	1.727737
H	0.000000	-3.313688	0.465379
H	0.885551	-2.426621	1.727737
C	0.000000	2.418352	1.085813
H	0.885551	2.426621	1.727737
H	0.000000	3.313688	0.465379
H	-0.885551	2.426621	1.727737
H	-0.000000	-0.000000	1.865624

INT1			
G (MeCN) = -1327.076601 Hartree			

S	1.728093	-0.382705	-0.781066
O	2.309566	-1.691979	-0.923125
O	1.807535	0.626552	-1.803135
C	2.344001	0.293512	0.859399
F	1.665371	-0.289187	1.823742
F	2.182659	1.596884	0.891775
F	3.617598	-0.020788	0.927679
C	-0.335710	-1.934639	-0.219500
C	-0.895793	0.404730	-0.281094
C	-2.241915	0.055848	0.020679
C	-2.615841	-1.310967	0.192284
C	-1.637797	-2.285919	0.069411
H	0.475128	2.056984	-0.674891
H	0.445555	-2.678394	-0.321402
C	-0.533964	1.755985	-0.437382
C	-3.197208	1.093905	0.149938
H	-1.871528	-3.335892	0.194870
C	-2.834847	2.407345	-0.006299
C	-1.497321	2.730795	-0.298771
H	-4.224272	0.835440	0.379066
H	-3.572802	3.194795	0.096487
H	-1.208058	3.768973	-0.421887
C	-4.024057	-1.694252	0.499972
H	-4.345527	-1.228474	1.437085
H	-4.692920	-1.336414	-0.289122
H	-4.118852	-2.776182	0.587764
N	0.022720	-0.647765	-0.394489

INT2			
G (MeCN) = -649.984243 Hartree			

C	-1.844316	0.497145	0.063726

C	-1.769046	-0.893831	-0.146802
C	0.249950	-0.186652	-0.024587
N	-0.536846	0.927558	0.144778
C	-0.144038	2.286220	0.485326
H	0.833289	2.274311	0.966707
H	-0.107191	2.920146	-0.404088
H	-0.874626	2.692408	1.187312
N	-0.448093	-1.291024	-0.195956
C	1.724643	-0.162069	-0.023667
C	2.409819	-1.248650	0.533244
C	2.450257	0.880857	-0.611094
C	3.799480	-1.281850	0.519509
H	1.842361	-2.059607	0.978742
C	3.842024	0.842773	-0.622734
H	1.931119	1.708694	-1.084091
C	4.518935	-0.234173	-0.054646
H	4.321838	-2.124742	0.961033
H	4.396136	1.652717	-1.086418
H	5.604106	-0.260418	-0.064028
C	-2.944502	-1.645986	-0.272111
C	-4.155006	-0.976709	-0.178088
C	-4.210970	0.415841	0.035953
C	-3.059213	1.179852	0.160435
H	-2.897774	-2.718085	-0.436210
H	-5.082931	-1.532295	-0.270500
H	-5.179195	0.901946	0.103253
H	-3.100665	2.252577	0.319749

INT3			
G (MeCN) = -650.424654 Hartree			

C	-1.847155	0.497995	0.074639
C	-1.810598	-0.881292	-0.149544
C	0.281624	-0.126538	-0.013205
N	-0.526278	0.927759	0.162898
C	-0.139816	2.299433	0.486840
H	0.854384	2.295924	0.930239
H	-0.150572	2.913392	-0.414858
H	-0.855522	2.688148	1.211341
N	-0.470264	-1.220229	-0.193664
C	1.746418	-0.138158	-0.016246
C	2.415318	-1.211166	0.585641
C	2.466559	0.881730	-0.649595
C	3.804116	-1.252194	0.563317
H	1.852765	-1.994942	1.084443
C	3.855666	0.828571	-0.667250
H	1.945904	1.693393	-1.147602
C	4.523587	-0.233566	-0.060028
H	4.324219	-2.077202	1.038210
H	4.414934	1.614484	-1.163493
H	5.608207	-0.269347	-0.075164
C	-2.973688	-1.637956	-0.285778
C	-4.170192	-0.946432	-0.184310
C	-4.208131	0.443857	0.042959
C	-3.050895	1.195098	0.176549
H	-2.934477	-2.706770	-0.461531
H	-5.104376	-1.488763	-0.283096
H	-5.170386	0.939371	0.114169
H	-3.075236	2.265578	0.346647
H	-0.090934	-2.142266	-0.387890

INT4			
G (MeCN) = -440.423995 Hartree			

C	-1.829348	-1.599223	0.000000
C	0.362764	-0.904778	0.000000
C	0.000000	0.469419	0.000000
C	-1.415411	0.800171	0.000000
C	-2.309985	-0.283791	0.000000
H	1.981429	-2.317580	0.000000
H	-2.540851	-2.423233	0.000000
C	1.735264	-1.260085	0.000000
C	1.024677	1.441943	0.000000
H	-3.379506	-0.099606	0.000000
C	2.351336	1.071526	0.000000
C	2.711234	-0.292989	0.000000
H	0.768281	2.496128	0.000000
H	3.124705	1.833312	0.000000
H	3.759450	-0.575053	0.000000
C	-1.902644	2.111440	0.000000
H	-1.257145	2.979775	0.000000
H	-2.973106	2.281271	0.000000
N	-0.550083	-1.928116	0.000000

INT5			
G (MeCN) = -1664.292152 Hartree			

S	2.188543	-0.589593	0.776560
O	2.250202	0.425774	1.804288
O	2.209250	-2.004375	1.082431
C	3.639667	-0.325113	-0.330736
F	3.693428	0.939474	-0.716590
F	3.516572	-1.110480	-1.388600
F	4.738862	-0.635812	0.335515
C	0.326613	-1.435463	-0.863447
C	0.177127	0.938974	-0.231845
C	-1.226169	0.879528	-0.437600
C	-1.843260	-0.357673	-0.845778
C	-1.013752	-1.458036	-1.108576
H	1.897194	2.197591	0.087439
H	0.989335	-2.264498	-1.067994
C	0.820250	2.154891	-0.011512
C	-1.947338	2.085580	-0.305135
H	-1.434115	-2.361039	-1.540071
C	-1.311090	3.284219	-0.033609
C	0.077732	3.324575	0.096419
H	-3.024703	2.072405	-0.422681
H	-1.894708	4.194098	0.061080
H	0.587862	4.264263	0.278280
C	-3.323776	-0.481246	-1.058318
H	-3.539387	-1.321290	-1.723893
H	-3.765785	0.416411	-1.499894
N	0.920168	-0.286408	-0.290632
C	-4.063120	-0.757505	0.227644
F	-3.661659	-1.905719	0.798708
F	-5.387000	-0.860901	0.024817
F	-3.880923	0.212640	1.141530

TS1			
G (MeCN) = -1977.039828 Hartree			

C	-3.450584	1.894517	-0.345444
C	-2.048949	1.864833	-0.329806
C	-2.766488	-0.202117	-0.193949
N	-3.865925	0.579337	-0.261553
C	-5.260481	0.158977	-0.248189
H	-5.308688	-0.925786	-0.321469
H	-5.733318	0.489127	0.679003
H	-5.772041	0.605809	-1.102404
C	-2.878776	-1.675369	-0.069017
C	-2.820497	-2.484288	-1.206217
C	-3.122573	-2.237802	1.185464
C	-2.987475	-3.859432	-1.081549
H	-2.638984	-2.035425	-2.177648
C	-3.284211	-3.616107	1.303683
H	-3.184978	-1.599616	2.061788
C	-3.215542	-4.425690	0.172318
H	-2.941885	-4.489258	-1.964095
H	-3.466724	-4.054945	2.279312
H	-3.344564	-5.499509	0.266289
N	-1.655228	0.532807	-0.230032
S	0.368952	-0.138184	-0.433389
O	-0.083423	-1.454115	-0.831066
O	0.600279	1.011758	-1.285043
C	0.290737	0.093886	1.464685
F	-0.644917	-0.714717	1.908732
F	-0.004113	1.353081	1.715784
F	1.433862	-0.213143	2.038694
C	-1.324814	3.063973	-0.385480
C	-2.049896	4.242206	-0.463933
C	-3.458572	4.253250	-0.485726
C	-4.187429	3.077401	-0.425196
H	-0.242159	3.075401	-0.376210
H	-1.515764	5.185632	-0.510144
H	-3.980858	5.202132	-0.548892
H	-5.272124	3.069077	-0.434531
C	3.952647	2.575576	0.469286
C	2.938274	1.671865	0.263465
C	3.243952	0.340593	-0.104036
C	4.604031	-0.056146	-0.224592
C	5.619796	0.911426	-0.016859
C	5.303646	2.202565	0.318723
H	3.702625	3.592434	0.752905
H	1.916847	2.003293	0.388514
C	4.924058	-1.416442	-0.527722
H	6.657210	0.613186	-0.118236
H	6.087355	2.934887	0.478172
C	3.884693	-2.305454	-0.681544
C	2.563723	-1.865771	-0.577133
H	4.066877	-3.350730	-0.900692
H	1.736625	-2.548728	-0.725487
N	2.252823	-0.605603	-0.313917

C	6.344335	-1.867118	-0.662473
H	6.847286	-1.315001	-1.462347
H	6.895562	-1.677918	0.263995
H	6.386823	-2.933026	-0.887664

TS2			
G (MeCN) = -1977.032896 Hartree			

S	3.854534	0.428503	-0.533813
O	4.242326	0.378083	-1.922638
O	3.766070	1.672231	0.189362
C	5.009346	-0.698844	0.381130
F	5.031249	-1.862360	-0.238298
F	4.585470	-0.848651	1.621692
F	6.203812	-0.142400	0.365860
C	2.044414	-1.207982	-1.489987
C	1.538131	-0.398042	0.744061
C	0.331530	-1.140276	0.698116
C	-0.024656	-1.932458	-0.466341
C	0.895564	-1.920673	-1.547853
H	2.781961	0.894463	1.976862
H	2.751379	-1.199490	-2.309720
C	1.859418	0.340761	1.896208
C	-0.542772	-1.070016	1.803415
H	0.689013	-2.497020	-2.441511
C	-0.236068	-0.320424	2.916748
C	0.978572	0.374194	2.959633
H	-1.478043	-1.616830	1.769974
H	-0.922819	-0.277348	3.754679
H	1.244585	0.953782	3.837245
C	-1.260030	-2.597426	-0.592362
H	-1.726990	-2.986015	0.310839
H	-2.093139	-1.561170	-0.772494
H	-1.351200	-3.249811	-1.458211
N	2.382680	-0.447116	-0.392533
C	-4.988399	0.331606	0.050902
C	-4.386946	-0.859574	-0.384367
C	-2.867654	0.701144	-0.447672
N	-4.001432	1.301525	-0.006365
C	-4.225166	2.714126	0.274856
H	-3.452001	3.306259	-0.212163
H	-5.198707	2.995624	-0.129716
H	-4.208754	2.895330	1.351529
N	-3.068569	-0.587609	-0.695275
C	-1.569598	1.365162	-0.638008
C	-0.823969	1.059712	-1.781683
C	-1.055239	2.245910	0.321610
C	0.416437	1.659023	-1.980179
H	-1.226536	0.367397	-2.515799
C	0.192656	2.828575	0.123051
H	-1.614951	2.453218	1.229047
C	0.921691	2.548127	-1.032872
H	0.987732	1.431263	-2.875479
H	0.596924	3.502683	0.871464
H	1.887160	3.018895	-1.189960
C	-5.116804	-2.051354	-0.444618
C	-6.448154	-1.995234	-0.063236
C	-7.045113	-0.792114	0.365440
C	-6.330031	0.394518	0.431366
H	-4.655595	-2.974240	-0.781018
H	-7.049317	-2.897969	-0.094973
H	-8.091384	-0.795899	0.652950
H	-6.785552	1.320778	0.765429

TS3^{S}			
G (MeCN) = -1326.606512 Hartree			

S	1.538367	-0.092130	0.909599
O	1.558452	1.228741	1.561924
O	2.009715	-1.291235	1.625212
C	2.740444	0.082376	-0.492395
F	2.413860	1.127821	-1.238673
F	2.713822	-1.017383	-1.233631
F	3.967196	0.254954	-0.014173
C	-0.362886	-1.785055	-0.608615
C	-1.172618	0.412923	-0.369911
C	-2.475934	-0.044291	-0.060344
C	-2.717444	-1.488868	-0.041193
C	-1.596278	-2.322776	-0.348723
H	0.101947	2.112512	-0.702626
H	0.486698	-2.423938	-0.833129
C	-0.904522	1.794895	-0.450436
C	-3.480876	0.911919	0.168282
H	-1.735261	-3.397901	-0.397830
C	-3.201566	2.264103	0.099930
C	-1.907023	2.710466	-0.212972

H	-4.491406	0.590358	0.396393
H	-3.991459	2.985666	0.281427
H	-1.698323	3.773397	-0.274228
C	-3.926987	-2.062720	0.240129
H	-4.808148	-1.486722	0.495430
H	-4.026981	-3.142626	0.218565
N	-0.116578	-0.451869	-0.628414

TS3^{T}			
G (MeCN) = -1326.564684 Hartree			

S	1.828536	0.094755	-0.676243
O	2.688594	-1.012163	-1.074572
O	2.166483	1.468896	-1.021407
C	1.740390	0.023957	1.192214
F	1.140715	-1.110132	1.528449
F	1.033390	1.050902	1.634731
F	2.955883	0.057248	1.715008
C	-0.122391	-1.706616	-1.352764
C	-0.945008	0.452920	-0.772528
C	-1.996313	-0.137709	-0.029435
C	-2.094013	-1.571304	0.048481
C	-1.167366	-2.315671	-0.668318
H	-0.089771	2.267790	-1.550409
H	0.622735	-2.280592	-1.890342
C	-0.885413	1.844365	-0.947704
C	-2.948536	0.717941	0.570063
H	-1.251429	-3.396930	-0.709554
C	-2.865399	2.085744	0.418503
C	-1.835513	2.652137	-0.352539
H	-3.753404	0.273583	1.148371
H	-3.605197	2.728242	0.885044
H	-1.788956	3.727283	-0.490158
C	-3.166507	-2.222632	0.812888
H	-2.967963	-2.659187	1.785299
H	-4.167616	-2.303667	0.403366
N	0.064420	-0.349632	-1.344393

TS4			
G (MeCN) = -886.183893 Hartree			

C	-1.204022	0.005268	0.004093
F	-1.366807	-0.740493	-1.057619
F	-1.556740	1.247873	-0.197536
F	-1.772165	-0.509545	1.063774
S	1.422324	0.000581	0.407501
O	1.686022	1.241242	-0.299469
O	1.655023	-1.243920	-0.303298

TS5			
G (MeCN) = -777.989734 Hartree			

C	-1.476817	2.254641	-0.904586
C	-1.589127	0.014303	-0.397759
C	-0.710872	0.151064	0.710947
C	-0.159391	1.468087	0.985312
C	-0.583172	2.510105	0.143953
H	-2.765314	-1.339292	-1.579893
H	-1.790763	3.077894	-1.543782
C	-2.100115	-1.266718	-0.724873
C	-0.384218	-0.999787	1.464684
H	-0.204937	3.515672	0.297288
C	-0.891953	-2.234156	1.124456
C	-1.755912	-2.370771	0.017325
H	0.278937	-0.916480	2.319291
H	-0.626292	-3.107369	1.711693
H	-2.148110	-3.348592	-0.244061
C	0.783290	1.713357	1.989770
H	1.160839	0.939427	2.645364
H	1.164069	2.718617	2.128647
N	-1.971414	1.064643	-1.192768
C	1.922982	-0.336709	-0.583878
F	1.439973	-1.335840	-1.296146
F	2.697970	-0.782342	0.387057
F	2.573535	0.516752	-1.350608

TS6			
G (MeCN) = -1664.211516 Hartree			

S	2.717848	-0.060469	-0.731645
O	3.275855	-1.010872	-1.669294
O	3.279575	1.259551	-0.553625
C	2.799364	-0.864161	0.937152
F	2.454598	-2.137325	0.840075
F	1.968052	-0.236978	1.757320
F	4.036965	-0.769997	1.395859

C	0.449882	-1.225377	-1.226426
C	0.302619	1.094596	-0.423256
C	-0.841890	0.755639	0.318511
C	-1.251616	-0.660094	0.433662
C	-0.655319	-1.556314	-0.554625
H	1.503656	2.665542	-1.267885
H	0.942965	-1.869307	-1.943635
C	0.648552	2.427502	-0.648282
C	-1.610572	1.797138	0.852979
H	-1.117260	-2.521069	-0.738462
C	-1.243795	3.123710	0.676384
C	-0.115502	3.438684	-0.080482
H	-2.520221	1.557485	1.393894
H	-1.852377	3.913467	1.104436
H	0.157980	4.474393	-0.252572
C	-2.159071	-1.113517	1.323629
H	-2.563900	-0.484970	2.110021
H	-2.425548	-2.166201	1.340947
N	1.078906	0.043907	-1.025538
C	-4.296890	-0.722955	-0.083194
F	-4.233299	0.549692	-0.435753
F	-5.483443	-1.001813	0.428563
F	-4.049675	-1.499994	-1.123244

TS7			
G (MeCN) = -1664.283765 Hartree			

S	2.730008	-0.533020	-0.677312
O	3.081238	-1.924672	-0.928200
O	3.546155	0.554169	-1.200882
C	2.723742	-0.346208	1.187395
F	1.708769	-1.053330	1.664849
F	2.569120	0.928235	1.503261
F	3.859573	-0.800629	1.691500
C	0.224181	-1.526865	-1.199821
C	0.266664	0.814452	-0.764068
C	-0.917951	0.709087	0.009646
C	-1.519639	-0.583009	0.184027
C	-0.951868	-1.660856	-0.474186
H	1.732098	2.113954	-1.652102
H	0.692497	-2.367939	-1.696255
C	0.846555	2.065904	-1.028414
C	-1.466424	1.903150	0.535753
H	-1.423846	-2.637457	-0.431151
C	-0.871689	3.123384	0.296494
C	0.285850	3.209350	-0.495465
H	-2.376481	1.860458	1.123010
H	-1.309291	4.025352	0.711656
H	0.735303	4.175707	-0.698295
C	-2.779603	-0.780320	0.982250
N	0.888667	-0.335946	-1.288130
C	-4.014911	-0.561141	0.143014
F	-4.078657	0.683403	-0.362059
F	-5.134618	-0.753523	0.857185
F	-4.062333	-1.405221	-0.901761
H	-2.841748	-0.110185	1.842922
H	-2.834586	-1.807924	1.350237

TS8			
G (MeCN) = -778.620833 Hartree			

C	2.997235	-1.707326	-0.215992
C	1.795839	-1.856539	0.430993
C	0.923619	-0.748596	0.602550
C	1.316794	0.528252	0.103341
C	2.562667	0.649719	-0.557646
C	3.384397	-0.442635	-0.715934
H	3.655648	-2.560510	-0.346504
H	1.473975	-2.816441	0.822999
C	0.435368	1.643585	0.313178
H	2.869619	1.617780	-0.940702
H	4.336953	-0.334976	-1.224907
C	-0.749589	1.401238	0.949255
C	-1.088434	0.067859	1.348993
H	-1.463160	2.199929	1.126966
H	-1.967474	-0.080658	1.976927
N	-0.250993	-0.963331	1.256369
C	0.817289	3.021076	-0.145148
H	1.754116	3.343244	0.320570
H	0.969148	3.041760	-1.229182
H	0.036477	3.740157	0.108676
C	-2.368071	-0.422970	-0.390070
F	-1.576151	-0.403152	-1.449392
F	-3.344528	0.459395	-0.530823
F	-2.864992	-1.635015	-0.214291

2f cation			
G (MeCN) = -1344.342418 Hartree			

C	2.208841	0.109759	0.072096
C	1.067774	-0.616061	-0.256799
C	0.560861	1.601275	-0.134429
N	1.847653	1.460248	0.123090
C	2.815180	2.516393	0.431365
H	2.410363	3.483438	0.147178
H	3.716315	2.317723	-0.148692
H	3.037879	2.488204	1.498672
N	0.042935	0.350771	-0.385147
S	-1.568752	-0.018238	-0.823121
O	-1.510112	-1.217172	-1.616550
O	-2.206725	1.195768	-1.257967
C	-2.251478	-0.474418	0.840797
F	-1.512334	-1.446268	1.339135
F	-2.210130	0.586445	1.620819
F	-3.492394	-0.875457	0.664636
C	1.092741	-2.003036	-0.381927
C	2.321003	-2.612511	-0.162614
C	3.472296	-1.879161	0.168929
C	3.439949	-0.498688	0.295618
H	0.214191	-2.580840	-0.637375
H	2.388644	-3.691268	-0.251279
H	4.406837	-2.404266	0.332195
H	4.319764	0.077134	0.558743
C	-0.194037	2.876966	-0.149546
H	-1.136606	2.764312	0.386219
H	-0.410828	3.168169	-1.180597
H	0.388989	3.657709	0.333150

4-methylpyridine			
G (MeCN) = -287.480214 Hartree			

C	1.215662	-1.139907	0.002198
C	1.219999	1.137229	0.002219
C	-0.170202	1.191430	-0.007746
C	-0.902013	0.002709	-0.010689
C	-0.173677	-1.189385	-0.007769
H	1.791919	-2.062725	0.003233
H	-0.683309	-2.148431	-0.015770
C	-2.404712	0.001431	0.006475
H	-2.770409	-0.113136	1.032567
N	1.919626	-0.002074	0.007478
H	-0.676331	2.152210	-0.015828
H	1.798880	2.058445	0.003290
H	-2.803256	-0.830580	-0.579444
H	-2.805225	0.937693	-0.388529

70			
G (MeCN) = -379.727865 Hartree			

C	-2.384112	0.175290	0.000000
C	-1.096114	-1.703739	0.000000
C	0.083835	-0.962226	0.000000
C	0.000000	0.426141	0.000000
C	-1.269693	1.004397	0.000000
H	-3.381782	0.608219	0.000000
H	-1.390615	2.083251	0.000000
C	1.210780	1.337602	0.000000
H	1.189226	1.988886	0.879859
N	-2.315353	-1.161369	0.000000
H	1.041912	-1.472393	0.000000
H	-1.048647	-2.790335	0.000000
C	2.485769	0.620535	0.000000
N	3.489338	0.047866	0.000000
H	1.189226	1.988886	-0.879859

72			
G (MeCN) = -1265.320528 Hartree			

S	1.786576	0.287516	-0.759312
O	1.995454	-0.635739	-1.849497
O	2.347711	1.617476	-0.724352
C	2.337154	-0.571172	0.782887
F	1.683903	-1.715548	0.887098
F	2.068757	0.201423	1.820470
F	3.635760	-0.792255	0.700392
C	-0.706474	-0.646207	-0.848194
C	-0.378358	1.514779	0.199579
C	-1.680954	1.571250	0.520771
C	-2.601629	0.502609	0.176055
C	-2.013114	-0.616110	-0.539485
H	-0.239050	-1.460890	-1.387298
H	-2.632223	-1.452694	-0.843521

C	-3.921222	0.577240	0.511921
H	-4.314959	1.434931	1.045282
N	0.134901	0.414438	-0.496596
H	-2.048668	2.444875	1.046981
H	0.331315	2.298756	0.432868
C	-4.834611	-0.455825	0.180078
N	-5.581687	-1.303169	-0.093094

INT2-a			
G (MeCN) = -458.316592 Hartree			

C	0.302296	0.477263	-0.006214
C	0.512231	-0.916528	0.000858
C	-1.610985	-0.624058	-0.003319
N	-1.067395	0.634244	-0.017322
C	-1.772898	1.902035	0.012921
H	-2.781591	1.766188	-0.377134
H	-1.246502	2.618083	-0.621199
H	-1.827278	2.293886	1.032223
N	-0.705037	-1.577275	0.003250
C	1.817173	-1.422495	0.003485
C	2.867224	-0.514454	0.002756
C	2.637001	0.875212	-0.000197
C	1.350482	1.398744	-0.003578
H	1.993454	-2.493831	0.006855
H	3.889612	-0.879181	0.005647
H	3.485615	1.552057	0.002048
H	1.169831	2.469023	-0.001560
C	-3.085123	-0.844395	0.001102
H	-3.280889	-1.915782	0.043462
H	-3.546850	-0.435657	-0.902983
H	-3.552785	-0.361513	0.864272

INT6			
G (MeCN) = -1173.062455 Hartree			

S	-0.845457	-1.194700	0.000000
O	-1.413738	-1.586877	1.270605
O	-1.413738	-1.586877	-1.270605
C	0.894762	-1.811054	0.000000
F	1.508393	-1.360337	1.082722
F	1.508393	-1.360337	-1.082722
F	0.890257	-3.132818	0.000000

C	-0.421290	1.127623	1.220825
C	-0.421290	1.127623	-1.220825
C	-0.026680	2.405150	-1.230254
C	0.214382	3.164245	0.000000
C	-0.026680	2.405150	1.230254
H	-0.620939	0.551016	2.115176
H	0.108353	2.893665	2.189476
C	0.614560	4.447125	0.000000
H	0.782171	4.980556	-0.930183
H	0.782171	4.980556	0.930183
N	-0.646002	0.448715	0.000000
H	0.108353	2.893665	-2.189476
H	-0.620939	0.551016	-2.115176

TS1-a			
G (MeCN) = -1785.375962 Hartree			

C	-4.178748	0.443944	-0.364679
C	-2.814020	0.755294	-0.258022
C	-3.013307	-1.409610	-0.046300
N	-4.265222	-0.930000	-0.237544
C	-5.503627	-1.693287	-0.269578
H	-5.287613	-2.726284	-0.537989
H	-5.997925	-1.658762	0.704149
H	-6.159117	-1.262351	-1.027568
N	-2.115012	-0.431099	-0.061039
S	0.110382	-0.624692	-0.366254
O	-0.099726	-2.000792	-0.761756
O	-0.001079	0.549198	-1.204048
C	-0.008489	-0.388137	1.528238
F	-0.715718	-1.384409	2.008674
F	-0.580665	0.772300	1.765337
F	1.190237	-0.407594	2.074165
C	-2.396716	2.090401	-0.331554
C	-3.373393	3.058582	-0.514801
C	-4.737389	2.727859	-0.622712
C	-5.166856	1.411869	-0.546875
H	-1.350657	2.361246	-0.253709
H	-3.077565	4.101040	-0.574299
H	-5.467026	3.518656	-0.762522
H	-6.216054	1.144771	-0.617859
C	3.019487	2.799191	0.428582
C	2.210736	1.702493	0.248143

C	2.779757	0.465501	-0.130243
C	4.188798	0.361161	-0.289100
C	4.984485	1.520113	-0.105742
C	4.413873	2.717472	0.241474
H	2.569291	3.741198	0.723508
H	1.146729	1.814011	0.403395
C	4.781139	-0.900902	-0.603967
H	6.058279	1.444594	-0.234424
H	5.030970	3.597743	0.384525
C	3.951603	-1.993960	-0.727948
C	2.573554	-1.846558	-0.586842
H	4.346066	-2.977406	-0.953704
H	1.905155	-2.688889	-0.712422
N	2.009255	-0.675547	-0.314921
C	6.258912	-1.038503	-0.784287
H	6.609492	-0.378102	-1.583412
H	6.784475	-0.751716	0.131960
H	6.519087	-2.067173	-1.033876
C	-2.757234	-2.862170	0.162256
H	-3.505448	-3.276297	0.841983
H	-2.822395	-3.399193	-0.789195
H	-1.768674	-3.019937	0.582626

TS2-a			
G (MeCN) = -1785.363218 Hartree			

S	-3.925873	-0.069047	-0.236835
O	-4.602351	-0.211896	-1.502539
O	-4.579537	-0.349710	1.016654
C	-3.262088	1.666569	-0.201907
F	-2.478119	1.825096	-1.251945
F	-2.583167	1.868587	0.910408
F	-4.293647	2.483095	-0.268203
C	-2.128105	-1.399804	-1.608025
C	-1.581642	-1.167314	0.748131
C	-0.351153	-1.822886	0.490862
C	0.012977	-2.237498	-0.852841
C	-0.952573	-2.017854	-1.871183
H	-2.807250	-0.225543	2.278489
H	-2.865354	-1.221527	-2.379773
C	-1.879474	-0.725743	2.048120
C	0.547720	-2.007825	1.563048
H	-0.750132	-2.331937	-2.887891
C	0.250612	-1.571301	2.834141
C	-0.970283	-0.928654	3.068444
H	1.494881	-2.500357	1.378520
H	0.956143	-1.722344	3.643226
H	-1.219926	-0.578924	4.064596
C	1.314141	-2.654533	-1.197088
H	1.433682	-3.034678	-2.208894
H	1.862443	-1.449235	-1.129983
H	1.918398	-3.163728	-0.449688
N	-2.458346	-0.960480	-0.346313
C	4.187053	1.073375	-0.034845
C	3.885638	-0.199297	-0.543473
C	2.026912	0.936449	-0.496124
N	2.987073	1.762612	-0.012993
C	2.826775	3.137350	0.434474
H	1.770548	3.343176	0.600893
H	3.365960	3.267843	1.374335
H	3.223694	3.826916	-0.313817
N	2.531028	-0.243620	-0.824537
C	4.886117	-1.164746	-0.690959
C	6.172711	-0.805602	-0.316136
C	6.464833	0.476793	0.188640
C	5.479359	1.442932	0.338806
H	4.660751	-2.150201	-1.085917
H	6.976317	-1.527854	-0.416813
H	7.486833	0.715229	0.464753
H	5.700332	2.433110	0.723627
C	0.594566	1.326658	-0.613907
H	0.134095	1.396888	0.377460
H	0.497502	2.297424	-1.106477
H	0.061698	0.580331	-1.204701

TS2-b			
G (MeCN) = -1823.452208 Hartree			

S	-3.825481	0.512425	0.082918
O	-4.058201	0.835500	1.469123
O	-3.718852	1.497075	-0.964917
C	-5.111509	-0.717251	-0.437800
F	-5.124458	-1.710697	0.430005
F	-4.800038	-1.158961	-1.640225
F	-6.277167	-0.103840	-0.457061
C	-2.106361	-1.265594	1.092429

C	-1.610694	-0.406433	-1.097879
C	-0.476223	-1.143927	-1.143392
C	-0.081743	-1.976049	-0.045750
C	-0.973249	-2.007243	1.075213
H	-2.794498	-1.248012	1.929777
H	-0.741344	-2.623499	1.936147
C	1.166461	-2.624641	-0.032263
H	1.601513	-2.854486	-1.005169
H	1.995552	-1.588492	0.280062
H	1.322896	-3.376850	0.738499
N	-2.424839	-0.464028	0.014701
C	4.947542	0.282222	-0.176355
C	4.297330	-0.921830	0.134145
C	2.798756	0.660408	0.174300
N	3.971829	1.265033	-0.136367
C	4.234052	2.688335	-0.310587
H	3.443757	3.262455	0.170518
H	5.186804	2.921765	0.167172
H	4.283637	2.939683	-1.372034
N	2.962352	-0.644479	0.356496
C	1.501829	1.339316	0.313773
C	0.671767	0.977074	1.380523
C	1.075025	2.297128	-0.613152
C	-0.565658	1.593343	1.536185
H	1.009627	0.228806	2.092125
C	-0.170150	2.899107	-0.459130
H	1.703049	2.554521	-1.460921
C	-0.985101	2.557573	0.620499
H	-1.202028	1.320746	2.373465
H	-0.504657	3.637247	-1.180746
H	-1.945958	3.047455	0.749020
C	5.001472	-2.129515	0.174823
C	6.359503	-2.075731	-0.096951
C	7.005914	-0.859952	-0.399867
C	6.315961	0.342315	-0.446272
H	4.500298	-3.062204	0.412400
H	6.943233	-2.990127	-0.075865
H	8.071462	-0.866355	-0.604390
H	6.810874	1.278287	-0.683008
H	0.151547	-1.079267	-2.025142
H	-1.931606	0.252790	-1.895485

TS2-c			

G (MeCN) = -1915.705033 Hartree			

S	4.035485	0.576880	-0.185193
O	4.253043	0.968393	-1.554179
O	3.961332	1.496944	0.920016
C	5.261941	-0.749442	0.253185
F	5.203768	-1.694356	-0.662195
F	4.944379	-1.226375	1.437976
F	6.452109	-0.190386	0.274755
C	2.178109	-1.004155	-1.300525
C	1.813319	-0.372228	0.978469
C	0.636120	-1.060599	0.996646
C	0.184965	-1.741709	-0.158955
C	1.002687	-1.694485	-1.313319
H	2.835712	-0.931451	-2.159290
H	0.703633	-2.202952	-2.222546
C	-1.116526	-2.370781	-0.220652
H	-1.929931	-1.362962	-0.514152
H	-1.244212	-3.088702	-1.030828
N	2.568232	-0.352962	-0.161812
C	-4.899130	0.524212	-0.013535
C	-4.255316	-0.640409	-0.458982
C	-2.728882	0.888856	-0.198154
N	-3.905129	1.476418	0.135110
C	-4.152211	2.868616	0.489460
H	-3.306971	3.477918	0.173356
H	-5.049398	3.202614	-0.034410
H	-4.298121	2.967064	1.567208
N	-2.903546	-0.371222	-0.574862
C	-1.415486	1.550661	-0.145617
C	-0.530587	1.397214	-1.218297
C	-1.037896	2.300839	0.973988
C	0.713160	2.020644	-1.183010
H	-0.830571	0.811600	-2.082635
C	0.213969	2.905898	1.010714
H	-1.715128	2.393801	1.817941
C	1.084853	2.777485	-0.071342
H	1.389302	1.923220	-2.027960
H	0.507373	3.483384	1.881197
H	2.051681	3.271336	-0.048953
C	-4.979514	-1.813086	-0.696064
C	-6.347879	-1.764562	-0.480094
C	-6.986263	-0.586658	-0.041058

C	-6.277227	0.580334	0.201580
H	-4.484644	-2.717470	-1.035132
H	-6.945181	-2.653756	-0.653600
H	-8.059957	-0.595371	0.115166
H	-6.764410	1.486155	0.546911
H	0.048325	-1.060101	1.907881
H	2.193615	0.182266	1.829016
C	-1.678450	-2.821902	1.026169
N	-2.172230	-3.139058	2.025671

TS3-b^{S}			
G (MeCN) = -1173.017514 Hartree			

S	1.072245	0.493558	0.722055
O	1.357472	1.928266	0.575357
O	1.307195	-0.200815	1.999357
C	2.231181	-0.345147	-0.454676
F	2.168053	0.234386	-1.642402
F	1.887990	-1.622635	-0.562722
F	3.472971	-0.265631	0.008454
C	-1.248281	-1.190556	0.041365
C	-1.386033	1.002132	-0.794368
C	-2.731662	1.042670	-0.583606
C	-3.412805	-0.094998	-0.029896
C	-2.588163	-1.229179	0.282798
H	-0.608239	-2.041623	0.254369
H	-3.040744	-2.132673	0.678605
C	-4.769910	-0.099330	0.184384
H	-5.374039	0.767253	-0.060992
H	-5.263255	-0.967462	0.607884
N	-0.623776	-0.105477	-0.520989
H	-3.298015	1.924098	-0.866632
H	-0.849620	1.843564	-1.222875

TS3-c^{S}			
G (MeCN) = -1265.270807 Hartree			

S	1.751813	0.307044	-0.568597
O	1.928417	-0.467086	-1.800417
O	2.218486	1.692872	-0.471482
C	2.895005	-0.598977	0.646714
F	2.513202	-1.863917	0.736468
F	2.812232	-0.020719	1.835240
F	4.148849	-0.546185	0.217247
C	-1.035931	-0.418512	-1.036979
C	-0.769924	1.573710	0.182170
C	-2.059188	1.512483	0.638746
C	-2.901272	0.437610	0.233884
C	-2.334694	-0.548280	-0.624917
H	-0.560869	-1.135365	-1.699559
H	-2.929651	-1.384904	-0.976054
C	-4.224192	0.382287	0.687218
H	-4.617419	1.152287	1.342310
N	-0.277189	0.646969	-0.676738
H	-2.445952	2.294752	1.282692
H	-0.093226	2.379535	0.449093
C	-5.097687	-0.667505	0.325984
N	-5.816862	-1.530514	0.027700

TS2-base			
G(MeCN) = -1653.814053 Hartree			

S	3.140957	-0.940283	-0.564720
O	3.456831	-2.253374	-0.057480
O	3.089906	-0.656224	-1.976726
C	4.342736	0.220618	0.249393
F	4.167345	0.142039	1.553729
F	4.139093	1.453385	-0.169427
F	5.552887	-0.183998	-0.079826
C	1.224558	-1.271596	1.198987
C	0.933022	0.693439	-0.197723
C	-0.267775	0.968672	0.503707
C	-0.722197	0.112852	1.584468
C	0.081194	-1.018072	1.880135
H	2.272377	1.385620	-1.767686
H	1.846983	-2.126877	1.428329
C	1.356513	1.555410	-1.223202
C	-1.032337	2.088769	0.112139
H	-0.207961	-1.696508	2.673579
C	-0.621493	2.918472	-0.906261
C	0.584701	2.649218	-1.563830
H	-1.964098	2.295698	0.626363
H	-1.222775	3.773897	-1.192623
H	0.928428	3.300826	-2.360143
C	-1.958850	0.295654	2.239174
H	-2.327441	1.313253	2.351117
H	-2.814925	-0.125884	1.313800
H	-2.114738	-0.330075	3.116058
N	1.665088	-0.459128	0.179875
C	-4.922232	0.308650	0.335843
C	-5.905480	0.065530	-0.619209
C	-5.699011	-0.936532	-1.560782
C	-4.521865	-1.675839	-1.531689
C	-3.569423	-1.391413	-0.556146
H	-6.814119	0.656938	-0.613824
H	-6.454344	-1.141640	-2.312856
H	-4.333964	-2.466879	-2.249053
N	-3.792779	-0.417317	0.339455
C	-2.267972	-2.132913	-0.455915
H	-2.097040	-2.472295	0.570044
H	-2.268242	-2.997944	-1.120429
H	-1.433832	-1.480056	-0.736894
C	-5.063728	1.371683	1.385681
H	-6.051366	1.831016	1.329833
H	-4.926212	0.947521	2.384447
H	-4.308177	2.151382	1.244912

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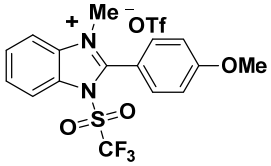
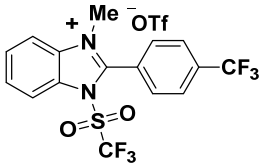
VII. Characteristic Data

2-(4-methoxyphenyl)-3-methyl-1-((trifluoromethyl)sulfonyl)-1H-benzo[d]imidazol-3-ium Trifluoromethanesulfonate (2b)



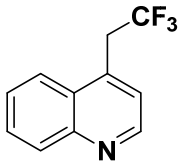
85%; white solid; mp 132.5-134.0 ℃; ^{1}H NMR (400 MHz, CD_3CN) δ 8.24 – 8.18 (m, 1H), 8.16 – 8.12 (m, 1H), 8.07 (s, 4H), 8.02 – 7.94 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 165.1, 155.9, 133.7, 133.2, 131.5, 131.0, 130.5, 122.0 (q, *J* = 320.9 Hz), δ 119.9 (q, *J* = 323.7 Hz). 116.3, 116.0, 115.7, 111.8, 56.7, 35.5. ^{19}F NMR (376 MHz, CD_3CN) δ -73.88, -79.30. HRMS (ESI): caled for $C_{16}H_{14}F_3N_2O_3S+$ $[M]^+$ 371.0672; found 377.0669.

3-methyl-2-(4-(trifluoromethyl)phenyl)-1-((trifluoromethyl)sulfonyl)-1H-benzo[d]imidazol -3-ium Trifluoromethanesulfonate (2c)



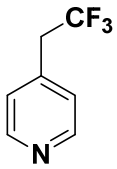
90%; white solid; mp 147.4-149.0 ℃; ^{1}H NMR (400 MHz, CD_3CN) δ 8.21 – 8.16 (m, 1H), 8.12 – 8.07 (m, 1H), 7.97 – 7.91 (m, 2H), 7.79 – 7.74 (m, 2H), 7.30 – 7.24 (m, 2H), 3.95 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 153.6, 135.7 (q, *J* = 33.0 Hz), 133.3, 132.7, 132.0, 131.2, 130.8, 127.3 (q, *J* = 3.8 Hz), 124.9 (m), 124.6 (q, *J* = 272.4 Hz), 122.0 (q, *J* = 320.6 Hz), 119.8 (q, *J* = 323.7 Hz), 118.4, 116.2, 35.7. ^{19}F NMR (376 MHz, CD_3CN) δ -63.95, -73.87, -79.37. HRMS (ESI): caled for $C_{16}H_{11}F_6N_2O_2S^+$ $[M]^+$ 409.0440; found 409.0437.

4-(2,2,2-trifluoroethyl)quinoline (3)

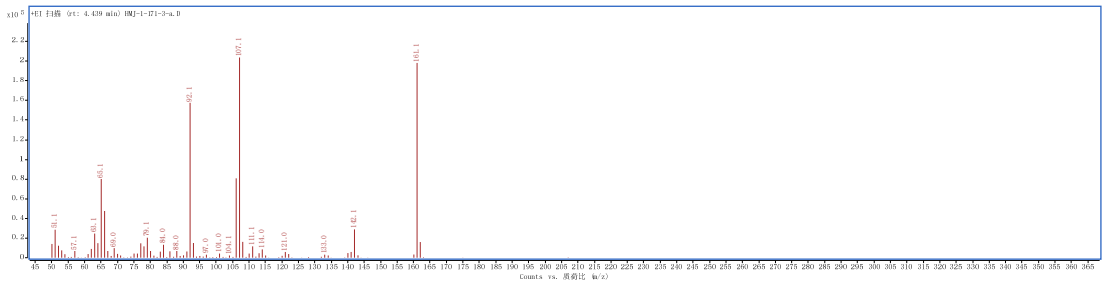


65% (27.5 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.3 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.70 (m, 1H), 7.68 – 7.57 (m, 1H), 7.38 (d, *J* = 4.3 Hz, 1H), 3.86 (q, *J* = 10.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 148.5, 135.9 (q, *J* = 2.7 Hz), 130.4, 129.6, 127.4, 127.2, 125.4(q, *J* = 277.6 Hz), 123.4, 123.2, 36.1 (q, *J* = 30.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.07 (t, *J* = 10.3 Hz). IR (neat) ν (cm^{-1}): 3041.5, 1595.3, 1511.4, 1354.9, 1250.5, 1133.1, 1095.8, 1030.6, 911.3, 825.6, 760.4, 598.2; HRMS (ESI): caled for $C_{11}H_9F_3N^+$ $[M + H]^+$ 212.0682; found 212.0681.

4-(2,2,2-trifluoroethyl)pyridine (4)

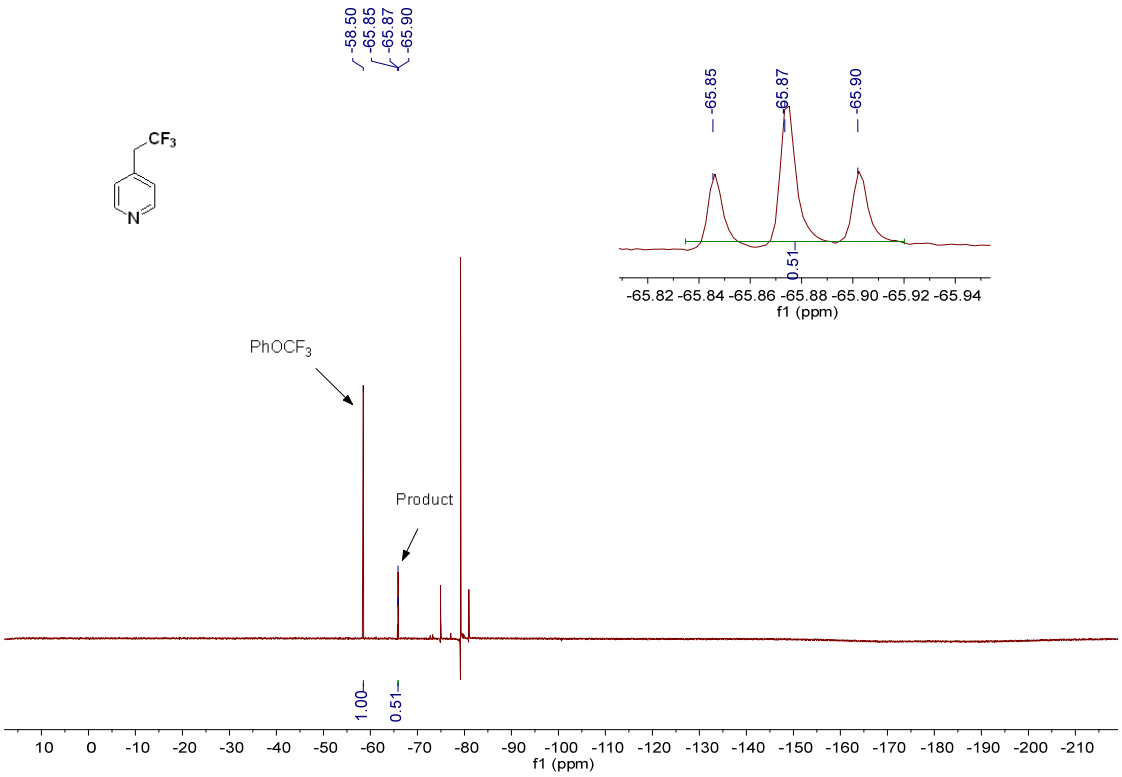


51% yield was determined by ^{19}F NMR with (Trifluoromethoxy)benzene (-58.50 ppm) as internal standard. The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.87 (t, *J* = 10.6 Hz). GC-MS m/z: 161.1, 142.1, 92.1, 65.1, 51.1.

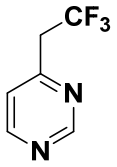


Gas chromatography-mass spectrometry of product **4**

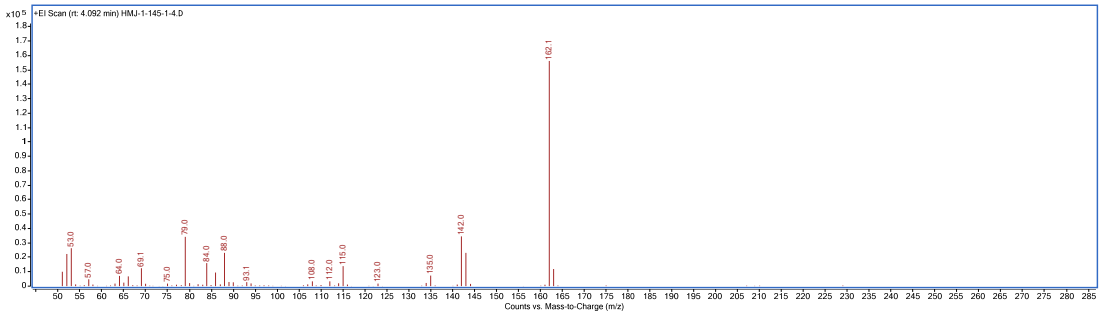
In situ ^{19}F NMR Spectra of product **4**:



4-(2,2,2-trifluoroethyl)pyrimidine (5)

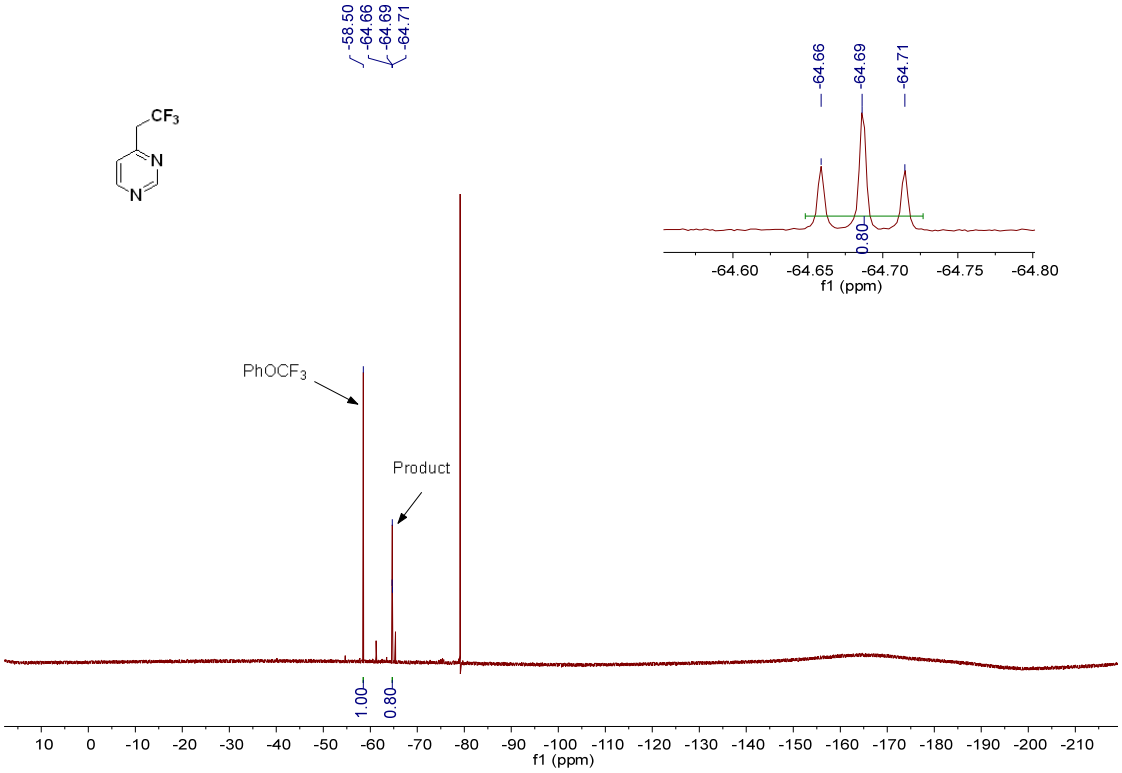


80% yield was determined by ^{19}F NMR with (Trifluoromethoxy)benzene (-58.50 ppm) as internal standard. The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.69 (t, *J* = 10.5 Hz). GC-MS m/z: 162.1, 143.1, 93.1, 79.0, 53.0.

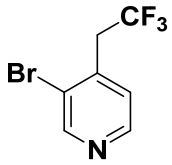


Gas chromatography-mass spectrometry of **5**

In situ ^{19}F NMR Spectra of product **5**:

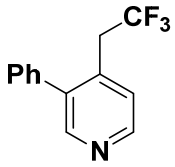


3-bromo-4-(2,2,2-trifluoroethyl)pyridine (6)



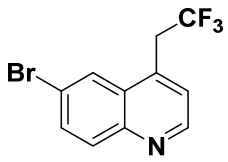
61% (29 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.52 (d, *J* = 5.0 Hz, 1H), 7.33 (d, *J* = 4.9 Hz, 1H), 3.62 (q, *J* = 10.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 148.4, 138.8 (q, *J* = 2.8 Hz), 126.1, 124.9 (q, *J* = 277.9 Hz), 123.9 (q, *J* = 2.5 Hz), 39.0 (q, *J* = 30.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.36 (t, *J* = 10.4 Hz). IR (neat) ν (cm^{-1}): 2918.5, 2849.5, 1463.0, 1377.3, 1261.7, 1092.1, 1090.6, 803.2, 719.4; HRMS (ESI): caled for $C_7H_6BrF_3N^+$ $[M + H]^+$ 239.9630; found 239.9620.

3-phenyl-4-(2,2,2-trifluoroethyl)pyridine (7)



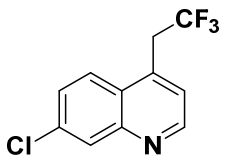
51% (24.2 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.2 Hz, 1H), 8.55 (s, 1H), 7.50 – 7.43 (m, 3H), 7.40 (d, *J* = 5.1 Hz, 1H), 7.28 (d, *J* = 6.6 Hz, 2H), 3.40 (q, *J* = 10.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 148.6, 138.9, 136.5, 129.4, 128.9, 128.7, 128.2, 125.3 (q, *J* = 277.4 Hz), 124.6, 36.1 (q, *J* = 30.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.87 (t, *J* = 10.6 Hz). IR (neat) ν (cm^{-1}): 3028.5, 2927.8, 1589.7, 1401.5, 1358.6, 1252.4, 1211.4, 1135.0, 1073.5, 911.3, 821.9, 702.6, 669.1, 602.0, 520.0; HRMS (ESI): caled for $C_{13}H_{11}F_3N^+$ $[M + H]^+$ 238.0838; found 238.0837.

6-bromo-4-(2,2,2-trifluoroethyl)quinoline (8)



75% (43.3 mg); white solid; mp 60.8-62.0 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.14 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.82 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.41 (d, *J* = 4.4 Hz, 1H), 3.82 (q, *J* = 10.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 147.1, 135.1 (q, *J* = 2.5 Hz), 133.2, 132.1, 125.7, 125.1 (q, *J* = 277.6 Hz), 124.2, 121.7, 36.1 (q, *J* = 30.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.04 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 3058.9, 2920.4, 2849.5, 1593.4, 1494.7, 1448.1, 1354.9, 1276.6, 1246.8, 1149.9, 1090.2, 1023.2, 915.1, 827.5, 585.2, 495.7; HRMS (ESI): caled for $C_{11}H_8BrF_3N^+$ $[M + H]^+$ 289.9787; found 289.9788.

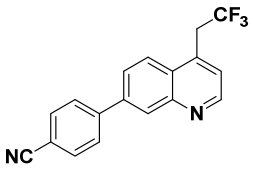
7-chloro-4-(2,2,2-trifluoroethyl)quinoline (9)



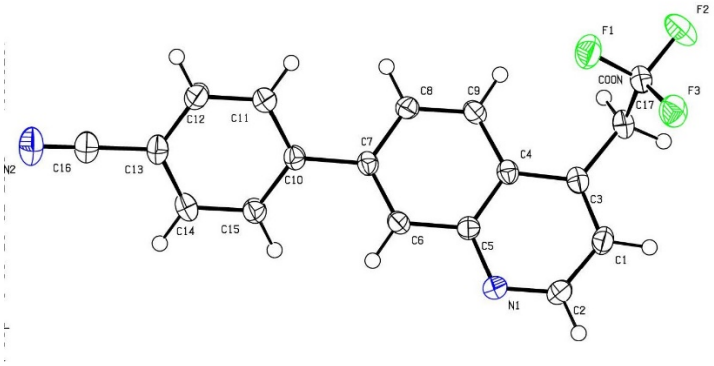
66% (32.3 mg); white solid; mp 84.6-85.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.4 Hz, 1H), 8.17 (d, *J* = 2.2 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.59 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.40 (d, *J* = 4.4 Hz, 1H), 3.86 (q, *J* = 10.3 Hz,

2H).[13]C NMR (126 MHz, $CDCl_3$) δ 150.9, 149.0, 136.0 (q, *J* = 2.6 Hz), 135.6, 129.3, 128.3, 125.8, 125.2 (q, *J* = 277.9 Hz), 124.7, 123.7, 36.2 (q, *J* = 30.7 Hz). [19]F NMR (376 MHz, $CDCl_3$) δ -64.10 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 3043.4, 2922.2, 2851.4, 1608.3, 1500.3, 1354.9, 1235.6, 1138.7, 1095.8, 911.3, 825.6, 773.4, 684.0, 598.2; HRMS (ESI): caled for $C_{11}H_8ClF_3N^+$ $[M + H]^+$ 246.0292; found 246.0291.

4-(4-(2,2,2-trifluoroethyl)quinolin-7-yl)benzonitrile (10)

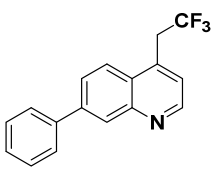


74% (46.2 mg); white solid; mp 158.4-159.8 ℃; [1]H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, *J* = 4.4 Hz, 1H), 8.39 (d, *J* = 1.9 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 7.89 – 7.76 (m, 5H), 7.44 (d, *J* = 4.4 Hz, 1H), 3.91 (q, *J* = 10.3 Hz, 2H). [13]C NMR (126 MHz, $CDCl_3$) δ 150.8, 148.7, 144.2, 140.1, 135.9 (q, *J* = 2.7 Hz), 132.8, 128.7, 128.0, 127.2, 126.2, 125.3 (q, *J* = 277.7 Hz), 124.4, 124.0, 118.7, 111.7, 36.2 (q, *J* = 30.6 Hz). [19]F NMR (376 MHz, $CDCl_3$) δ -64.05 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 2924.1, 2853.3, 2223.4, 1604.6, 1500.3, 1433.2, 1353.0, 1250.5, 1138.7, 1090.2, 896.4, 829.3, 739.9, 568.4; HRMS (ESI): caled for $C_{18}H_{12}F_3N_2^+$ $[M + H]^+$ 313.0947; found 313.0946.



X-ray crystallography for **10** (CCDC number: 2075782)

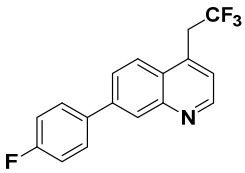
7-phenyl-4-(2,2,2-trifluoroethyl)quinoline (11)



53% (30.4 mg); white solid; mp 76.1-77.5 ℃; [1]H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 4.5 Hz, 1H), 8.39 (d, *J* = 1.9 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.37 (m, 2H), 3.90 (q, *J* = 10.3 Hz, 2H). [13]C NMR (101 MHz, $CDCl_3$) δ 150.3, 148.9,

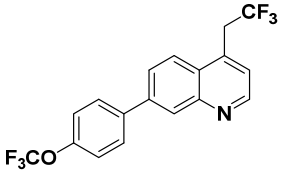
142.3, 139.7, 135.8 (q, *J* = 2.9 Hz), 129.0, 128.1, 127.9, 127.4, 126.9, 126.5, 125.4 (q, *J* = 278.8 Hz), 123.7, 123.3, 36.2 (q, *J* = 30.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.03 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 3058.3, 2963.2, 2920.4, 2849.5, 1595.3, 1492.8, 1425.7, 1347.4, 1246.8, 1127.5, 1090.2, 898.3, 829.3, 758.5, 691.4, 423.1; HRMS (ESI): caled for $C_{17}H_{13}F_3N^+$ $[M + H]^+$ 288.0995; found 288.0996.

7-(4-fluorophenyl)-4-(2,2,2-trifluoroethyl)quinoline (12)



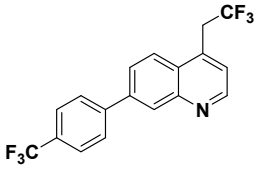
65% (39.7 mg); white solid; mp 131.6-132.4 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.34 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.85 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.40 (d, *J* = 4.2 Hz, 1H), 7.23 – 7.16 (m, 2H), 3.90 (q, *J* = 10.3 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 162.0, 150.4, 148.8, 141.3, 136.0 – 135.7 (m), 129.1 (d, *J* = 8.2 Hz), 127.7, 126.7, 125.3 (q, *J* = 277.9 Hz), 123.9, 123.5, 116.1, 115.9, 36.2 (q, *J* = 30.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.05 (t, *J* = 10.4 Hz), -114.24 – -114.34 (m). IR (neat) ν (cm^{-1}): 3058.3, 2920.4, 2851.4, 1593.4, 1504.0, 1356.8, 1250.5, 1135.0, 1092.1, 900.2, 829.3, 650.4, 503.2; HRMS (ESI): caled for $C_{17}H_{12}F_4N^+$ $[M + H]^+$ 306.0901; found 306.0900.

4-(2,2,2-trifluoroethyl)-7-(4-(trifluoromethoxy)phenyl)quinoline (13)



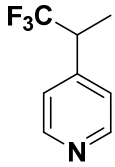
54% (40.1 mg); white solid; mp 107.3-108.4 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.4 Hz, 1H), 8.35 (d, *J* = 1.9 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.86 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.41 (d, *J* = 4.4 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 3.90 (q, *J* = 10.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 149.2 (q, *J* = 1.9 Hz), 148.8, 140.9, 138.5, 135.8 (q, *J* = 2.4 Hz), 128.8, 128.1, 126.7, 126.6, 125.3 (q, *J* = 277.6 Hz), 124.1, 123.6, 121.5, 120.5 (q, *J* = 257.1 Hz), 36.2 (q, *J* = 30.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.76, -64.06 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 3054.6, 1597.2 1505.8, 1354.9, 1248.7, 1209.5, 1176.0, 1138.7, 1094.0, 915.1, 831.2, 603.8; HRMS (ESI): caled for $C_{18}H_{12}F_6NO^+$ $[M + H]^+$ 372.0818; found 372.0819.

4-(2,2,2-trifluoroethyl)-7-(4-(trifluoromethyl)phenyl)quinoline (14)

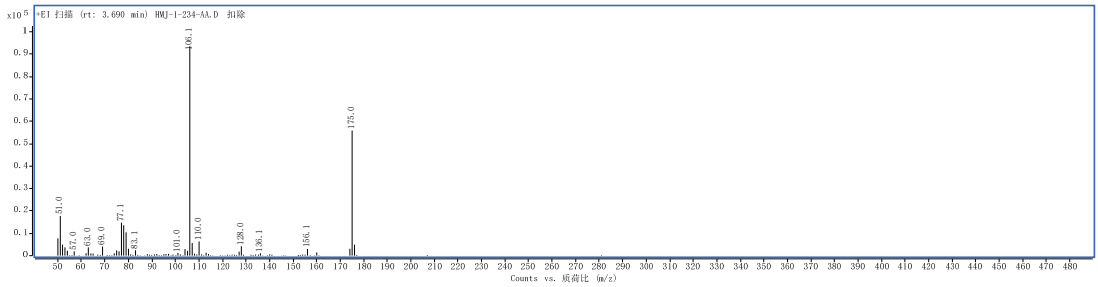


60% (42.6mg); white solid; mp 148.4-149.2 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, *J* = 4.4 Hz, 1H), 8.40 (d, *J* = 1.9 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.92 – 7.73 (m, 5H), 7.43 (d, *J* = 4.4 Hz, 1H), 3.91 (q, *J* = 10.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 148.8, 143.3, 140.8, 135.9 (q, *J* = 2.5 Hz), 130.1 (q, *J* = 32.7 Hz), 128.6, 128.5, 127.7, 127.0, 126.5, 126.4, 126.0 (q, *J* = 3.9 Hz), 124.2 (q, *J*= 1.0 HZ), 124.2 (q, *J* = 271.7 Hz), 123.8, 123.1 (q, *J* = 278.5 Hz), 36.2 (q, *J* = 30.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52, -64.05 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 3058.3, 2922.2, 1597.2, 1354.9, 1325.1, 1248.7, 1142.4, 1108.9, 1067.9, 1038.1, 831.2, 684.0, 600.1; HRMS (ESI): caled for $C_{18}H_{12}F_6N^+$ $[M + H]^+$ 356.0869; found 356.0868.

4-(1,1,1-trifluoropropan-2-yl)pyridine (15)

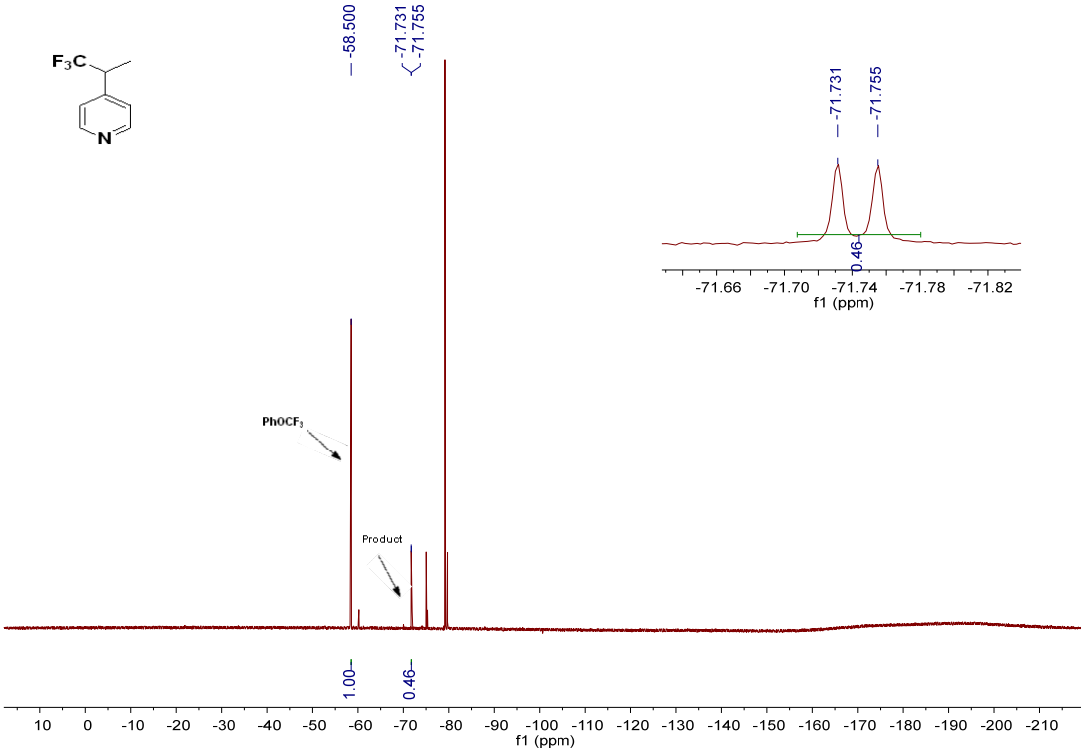


46% yield was determined by ^{19}F NMR with (Trifluoromethoxy)benzene (-58.50 ppm) as internal standard. The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.74 (d, *J* = 8.9 Hz). GC-MS m/z: 175.0, 156.1, 106.1, 78.1, 69.0.

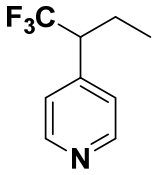


Gas chromatography-mass spectrometry of **15**

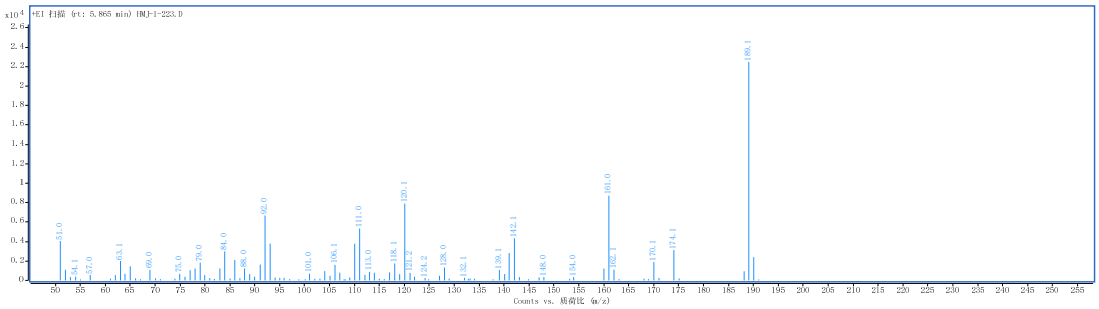
In situ ^{19}F NMR Spectra of product **15**:



4-(1,1,1-trifluorobutan-2-yl)pyridine (16)

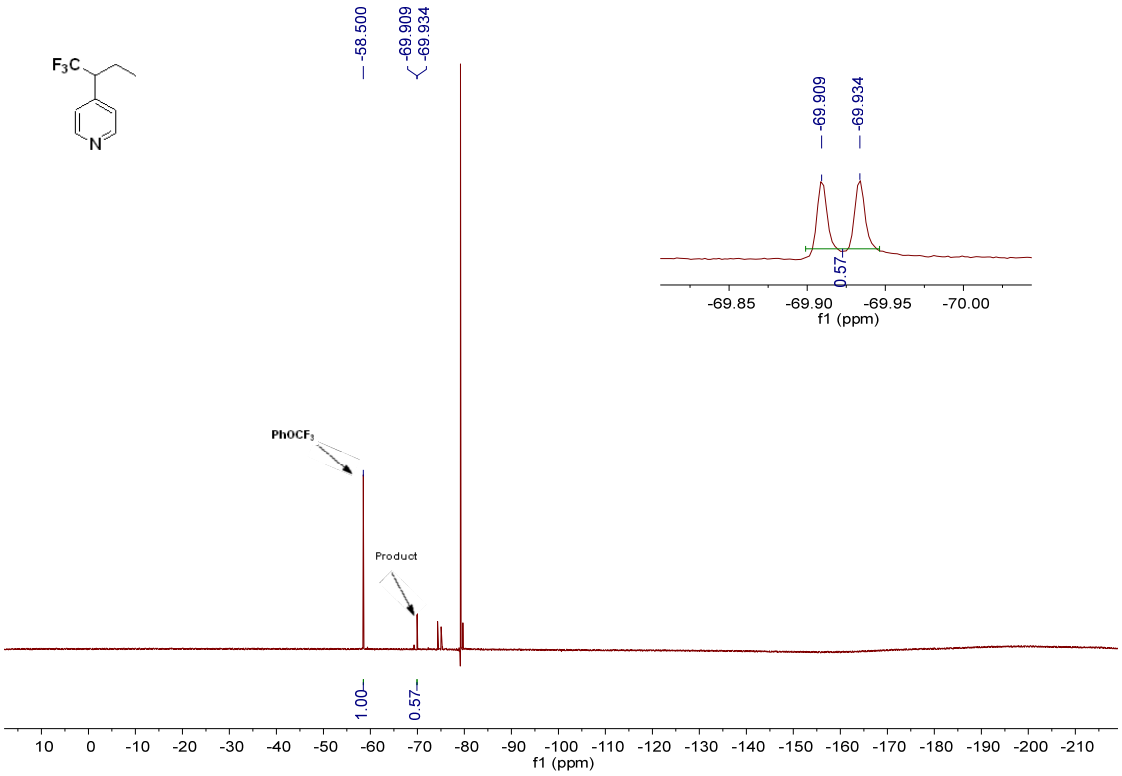


57% yield was determined by ^{19}F NMR with (Trifluoromethoxy)benzene (-58.50 ppm) as internal standard. The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained. ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.92 (d, *J* = 9.2 Hz). GC-MS m/z: 189.1, 174.1, 161.0, 142.1, 120.1, 111.0, 69.0.

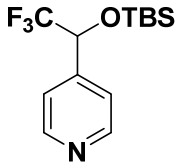


Gas chromatography-mass spectrometry of **16**

In situ ^{19}F NMR Spectra of product **16**:

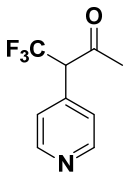


4-(1-((tert-butyldimethylsilyl)oxy)-2,2,2-trifluoroethyl)pyridine (17)

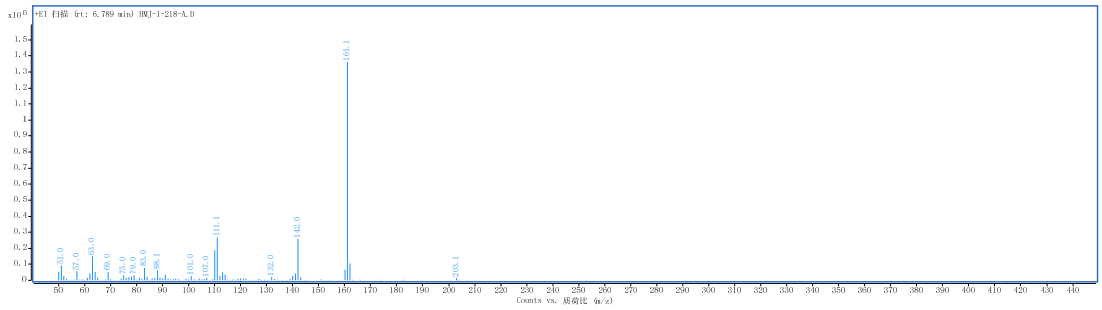


21% (12.3 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.3 Hz, 2H), 7.38 (d, *J* = 5.1 Hz, 2H), 4.91 (q, *J* = 6.3 Hz, 1H), 0.90 (s, 9H), 0.13 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 144.3, 123.6 (q, *J* = 282.8 Hz), 122.3, 72.6 (q, *J* = 32.4 Hz), 25.4, 18.1, -5.3 (d, *J* = 23.5 Hz). ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -78.13 . IR (neat) v (cm^{-1}): 2931.6, 2860.7, 1600.9, 1474.2, 1414.5, 1269.2, 1170.4, 1131.2, 1006.4, 836.8, 780.9, 670.9, 631.8; HRMS (ESI): caled for $C_{13}H_{21}F_3NOSi^+$ [M + H]$^+$ 292.1339; found 292.1337.

4,4,4-trifluoro-3-(pyridin-4-yl)butan-2-one (18)

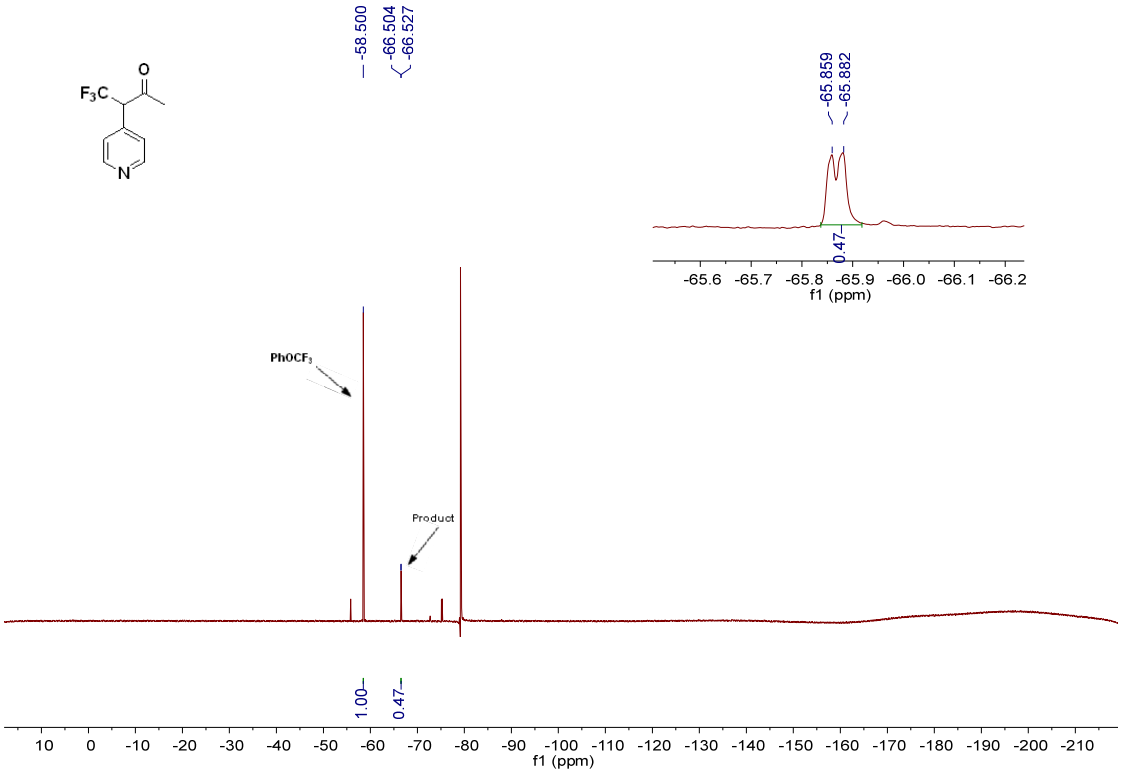


47% yield was determined by ^{19}F NMR with (Trifluoromethoxy)benzene (-58.50 ppm) as internal standard. The product could not be isolated due to its volatility. Consequently, ^{1}H NMR and ^{13}C NMR were not obtained. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.52 (d, *J* = 8.5 Hz). GC-MS m/z: 203.1, 161.1, 142.0, 111.1, 69.0.

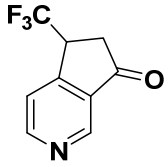


Gas chromatography-mass spectrometry of **18**

In situ ^{19}F NMR Spectra of product **18**:



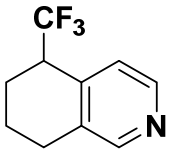
5-(trifluoromethyl)-5,6-dihydro-7H-cyclopenta[c]pyridin-7-one (19)



35% (14 mg); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.88 (d, *J* = 5.2 Hz, 1H), 7.70 – 7.66 (m, 1H), 4.20 – 4.08 (m, 1H), 3.03 – 2.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 154.9 (q, *J* = 2.3 Hz), 154.6, 146.9, 132.6, 125.6 (q, *J* = 278.2 Hz), 122.0, 42.7 (q, *J* = 30.3 Hz), 36.5 (q, *J* = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.79 (d, *J* = 8.4 Hz). IR (neat) ν (cm^{-1}): 3239.1, 3095.6, 2922.2, 2851.4,

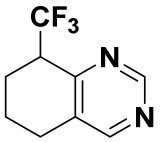
1727.6, 1597.2, 1448.1, 1351.2, 1261.7, 1159.2, 1107.0, 1021.3, 933.7, 836.8, 717.5, 661.6, 467.8; HRMS (ESI): caled for $C_9H_7F_3NO^+$ [M + H]$^+$ 202.0474; found 202.0473.

5-(trifluoromethyl)-5,6,7,8-tetrahydroisoquinoline (20)



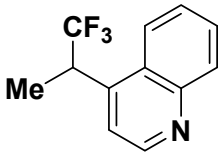
40% (16.1 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.29 (s, 1H), 3.57 – 3.44 (m, 1H), 2.88 – 2.70 (m, 2H), 2.16 – 1.95 (m, 2H), 1.87 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 146.9, 138.1, 134.3 – 134.1 (m), 126.8 (q, *J* = 281.0 Hz), 124.5 – 124.0 (m), 41.3 (q, *J* = 26.2 Hz), 26.0, 22.6 (q, *J* = 2.4 Hz), 19.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.53 (d, *J* = 9.9 Hz). IR (neat) ν (cm^{-1}): 2927.8, 2853.3, 1699.7, 1595.3, 1412.7, 1366.1, 1244.9, 1146.2, 1112.6, 1045.5, 833.1, 695.1, 611.3; HRMS (ESI): caled for $C_{10}H_{11}F_3N^+$ [M + H]$^+$ 202.0838; found 202.0839.

8-(trifluoromethyl)-5,6,7,8-tetrahydroquinazoline (21)



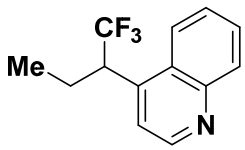
58% (23.4 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.54 (s, 1H), 3.67 – 3.57 (m, 1H), 2.88 – 2.72 (m, 2H), 2.22 – 2.00 (m, 2H), 1.85 – 1.75 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4 (q, *J* = 1.9 Hz), 157.9, 156.3, 131.7, 126.2 (q, *J* = 281.3 Hz), 44.3 (q, *J* = 25.9 Hz), 25.2, 22.7 (q, *J* = 2.4 Hz), 19.0. ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -66.23. IR (neat) ν (cm^{-1}): 2927.8, 2851.4, 1556.2, 1451.8, 1399.6, 1330.7, 1243.1, 1108.9, 1045.5, 950.5, 874.1, 695.1, 635.5, 542.3; HRMS (ESI): caled for $C_9H_{10}F_3N_2^+$ [M + H]$^+$ 203.0791; found 203.0788.

4-(1,1,1-trifluoropropan-2-yl)quinoline (22)



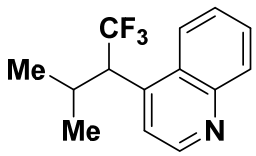
75% (33.8 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, 1H), 8.17 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.70 (m, 1H), 7.67 – 7.58 (m, 1H), 7.50 (d, *J* = 4.5 Hz, 1H), 4.45 – 4.32 (m, 1H), 1.64 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 148.5, 142.3 (q, *J* = 1.7 Hz), 130.6, 129.4, 127.2, 126.9, 126.8 (q, *J* = 280.2 Hz), 122.4, 119.6, 37.8 (q, *J* = 28.2 Hz), 14.8 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.98 (d, *J* = 8.7 Hz). IR (neat) ν (cm^{-1}): 2994.9, 2952.1, 1593.4, 1511.4, 1459.3, 1388.4, 1341.8, 1258.0, 1162.9, 1125.7, 1045.5, 1004.5, 848.0, 758.5, 616.9; HRMS (ESI): caled for $C_{12}H_{11}F_3N^+$ [M + H]$^+$ 226.0838; found 226.0839.

4-(1,1,1-trifluorobutan-2-yl)quinoline (23)



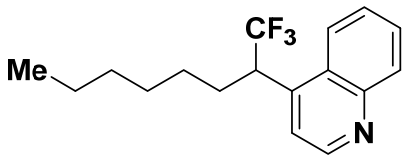
74% (35.4 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.6 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.66 – 7.59 (m, 1H), 7.48 (d, *J* = 4.5 Hz, 1H), 4.24 – 4.10 (m, 1H), 2.34 – 2.21 (m, 1H), 2.10 – 1.98 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 148.6, 140.9 (q, *J* =1.9 Hz), 130.6, 129.4, 128.0, 127.2, 126.5 (q, *J* = 280.4 Hz), 122.5, 119.7, 45.0 – 43.9 (m), 22.7 (q, *J* = 2.0 Hz), 11.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.41. IR (neat) ν (cm^{-1}): 3069.5, 2974.4, 2883.1, 1591.6, 1509.6, 1464.8, 1302.7, 1250.5, 1161.1, 1123.8, 1097.7, 1067.9, 833.1, 758.5, 622.5; HRMS (ESI): caled for $C_{13}H_{13}F_3N^+$ $[M + H]^+$ 240.0995; found 240.0994.

4-(1,1,1-trifluoro-3-methylbutan-2-yl)quinoline (24)



70% (35.5 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (d, *J* = 4.6 Hz, 1H), 8.17 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.65 – 7.60 (m, 1H), 7.48 (d, *J* = 4.5 Hz, 1H), 4.06 – 3.95 (m, 1H), 2.51 – 2.41 (m, 1H), 1.23 (dd, *J* = 6.6, 1.7 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.6, 141.9 (q, *J* = 2.8 Hz), 130.7, 129.3, 127.9, 127.1, 126.7 (q, *J* = 281.6 Hz), 122.5, 119.6, 49.1 (q, *J* = 25.6 Hz), 30.4, 21.3 (q, *J* = 2.1 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.11 (d, *J* = 9.2 Hz). IR (neat) ν (cm^{-1}): 3067.6, 2968.8, 2881.2, 1589.7, 1511.4, 1466.7, 1394.0, 1250.5, 1161.1, 1129.4, 1080.9, 844.2, 754.8, 631.8; HRMS (ESI): caled for $C_{14}H_{15}F_3N^+$ $[M + H]^+$ 254.1151; found 254.1150.

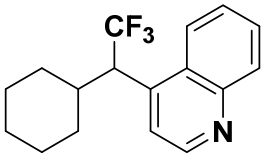
4-(1,1,1-trifluorooctan-2-yl)quinoline (25)



65% (38.2 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.6 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.66 – 7.60 (m, 1H), 7.48 (d, *J* = 4.6 Hz, 1H), 4.31 – 4.18 (m, 1H), 2.25 – 2.14 (m, 1H), 2.09 – 1.96 (m, 1H), 1.33 – 1.05 (m, 8H), 0.81 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 148.6, 141.2 (q, *J* = 1.7 Hz), 130.7, 129.4, 128.0, 127.2, 126.6 (q, *J* = 280.2 Hz), 122.4, 119.8, 42.8 (q, *J* =

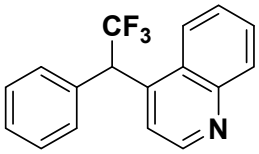
30.5 Hz), 31.3, 29.3 (d, *J* = 2.2 Hz), 28.9, 26.6, 22.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.58. IR (neat) v (cm−1): 3053.7, 2959.3, 2927.8, 2859.2, 1594.0, 1512.6, 1463.9, 1423.9, 1263.8, 1163.7, 1129.4, 1099.4, 896.4, 733.4, 700.5; HRMS (ESI): caled for $C_{17}H_{21}F_3N^+$ $[M + H]^+$ 295.1621; found 295.1613.

4-(1-cyclohexyl-2,2,2-trifluoroethyl)quinoline (26)



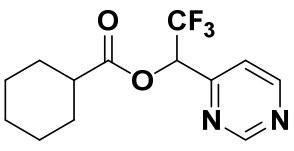
37% (21.7 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.62 (m, 1H), 7.50 (m, 1H), 4.14 – 4.00 (m, 1H), 2.21 – 2.06 (m, 2H), 1.85 – 1.77 (m, 1H), 1.67 – 1.52 (m, 2H), 1.38 – 1.21 (m, 3H), 1.16 – 1.06 (m, 2H), 0.94 – 0.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.6, 141.8, 130.7, 129.3, 127.1, 126.7 (q, *J* = 281.8 Hz), 122.5, 119.6, 48.4 (q, *J* = 25.5 Hz), 39.9, 31.3, 30.9, 26.0, 26.0, 25.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.33 (d, *J* = 9.5 Hz). IR (neat) v (cm^{-1}): 3055.1, 2986.5, 1422.5, 1263.8, 896.4, 733.4, 700.5; HRMS (ESI): caled for $C_{17}H_{19}F_3N^+$ $[M + H]^+$ 294.1464; found 294.1456.

4-(2,2,2-trifluoro-1-phenylethyl)quinoline (27)



70% (40.2 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.54 – 7.47 (m, 1H), 7.40 – 7.28 (m, 5H), 5.49 (q, *J* = 9.3 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.7, 140.2 (q, *J* = 1.0 Hz), 133.6 (q, *J* = 1.6 Hz), 130.7, 129.4, 129.3, 128.9, 128.6, 127.3, 126.4, 125.9 (q, *J* = 280.8 Hz), 122.8, 120.2 (q, *J* = 2.2 Hz), 50.6 (q, *J* = 27.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.00 (d, *J* = 9.5 Hz). IR (neat) v (cm^{-1}): 3065.7, 3035.9, 2926.0, 2853.3, 1591.6, 1509.6, 1354.9, 1252.4, 1151.7, 1112.6, 1030.6, 821.9, 751.1, 700.7, 631.8, 516.2; HRMS (ESI): caled for $C_{17}H_{13}F_3N^+$ $[M + H]^+$ 288.0995; found 288.0994.

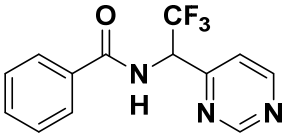
2,2,2-trifluoro-1-(pyrimidin-4-yl)ethyl cyclohexanecarboxylate (28)



25% (14.4 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.87 (s, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 6.16 (q, *J* = 6.7 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.04 – 1.94 (m, 2H), 1.83 – 1.75 (m, 2H),

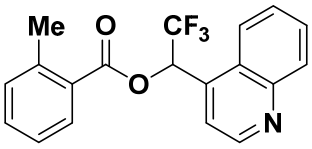
1.71 – 1.64 (m, 1H), 1.58 – 1.44 (m, 2H), 1.38 – 1.19 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 159.8, 158.8, 158.0, 122.4 (q, *J* = 281.5 Hz), 119.6 – 119.3 (m), 71.6 (q, *J* = 32.6 Hz), 42.6, 28.7 (d, *J* = 7.7 Hz), 25.5, 25.2 (d, *J* = 2.5 Hz). ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -74.52. IR (neat) v (cm^{-1}): 2935.3, 2858.9, 1753.7, 1578.5, 1451.8, 1388.4, 1261.7, 1187.2, 1123.8, 1064.2, 939.3, 844.2, 700.7, 641.1, 527.4; HRMS (ESI): caled for $C_{13}H_{16}F_3N_2O_2^+$ $[M + H]^+$ 289.1159; found 289.1160.

N-(2,2,2-trifluoro-1-(pyrimidin-4-yl)ethyl)benzamide (29)



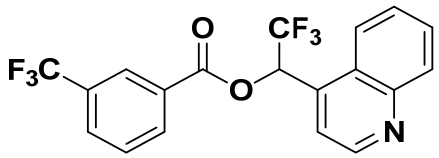
30% (16.9 mg); white solid; mp 67.9-70.9 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.87 (s, 1H), 7.93 – 7.89 (m, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.49 (m, 3H), 6.06 – 5.97 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 158.8, 158.8, 157.8, 132.9, 132.5, 128.8, 127.4, 123.6 (q, *J* = 283.3 Hz), 121.7 – 121.4 (m), 54.0 (q, *J* = 31.7 Hz). ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -73.58 . IR (neat) v (cm^{-1}): 3315.5, 3244.6, 3058.3, 2955.8, 2851.4, 1669.8, 1522.6, 1470.4, 1390.3, 1336.3, 1252.4, 1123.8, 997.1, 892.7, 821.9, 777.1, 684.0, 650.4, 609.4, 527.4, 456.6; HRMS (ESI): caled for $C_{13}H_{11}F_3N_3O^+$ $[M + H]^+$ 282.0849; found 282.0848.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 2-methylbenzoate (30)



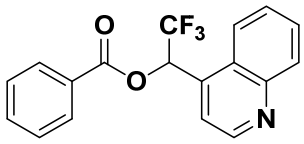
46% (31.7 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.5 Hz, 1H), 8.22 (t, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.73 – 7.68 (m, 2H), 7.52 – 7.47 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.20 (q, *J* = 6.4 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 149.8, 148.5, 141.5, 137.0, 133.3, 132.1, 131.1, 130.6, 129.8, 127.8, 127.1, 126.1, 125.9, 123.3 (q, *J* = 281.5 Hz), 122.8, 120.3, 67.6 (q, *J* = 33.8 Hz), 21.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.39 (d, *J* = 6.2 Hz). IR (neat) v (cm^{-1}): 3069.5, 2974.4, 1735.1, 1595.3, 1511.4, 1459.3, 1351.2, 1237.5, 1183.4, 1133.1, 1071.6, 915.1, 829.3, 734.3, 629.9; HRMS (ESI): caled for $C_{19}H_{15}F_3NO_2^+$ $[M + H]^+$ 346.1050; found 346.1049.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 3-(trifluoromethyl)benzoate (31)



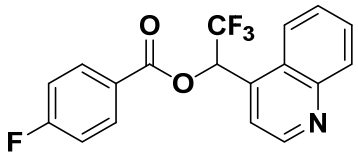
48% (38.3 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.5 Hz, 1H), 8.38 (s, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.76 – 7.62 (m, 3H), 7.22 (q, *J* = 6.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 149.8, 148.5, 136.3, 133.2, 131.6 (q, *J* = 33.5 Hz), 130.7 (q, *J* = 3.6 Hz), 130.7, 129.9, 129.6, 129.0, 127.9, 126.9 (q, *J* = 3.8 Hz), 125.7, 123.4 (q, *J* = 272.4 Hz), 123.0 (q, *J* = 281.5 Hz), 122.6, 120.2, 68.4 (q, *J* = 34.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.91, -74.44 (d, *J* = 6.2 Hz). IR (neat) ν (cm^{-1}): 3076.9, 1742.5, 1511.4, 1332.5, 1233.7, 1168.5, 1127.5, 1071.6, 918.8, 838.7, 751.1, 691.4, 629.9, 512.5; HRMS (ESI): caled for $C_{19}H_{12}F_6NO_2^+$ [M + H]$^+$ 400.0767; found 400.0766.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl benzoate (32)



68% (45.1 mg); white solid; mp 57.1-58.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.6 Hz, 1H), 8.22 (t, *J* = 8.7 Hz, 2H), 8.20 – 8.12 (m, 2H), 7.85 – 7.76 (m, 1H), 7.75 – 7.61 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.20 (q, *J* = 6.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 149.8, 148.5, 136.9, 134.2, 130.6, 130.1, 129.8, 128.8, 128.1, 127.8, 125.8, 123.2 (q, *J* = 281.5 Hz), 122.8, 120.2, 68.0 (q, *J* = 34.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.48 (d, *J* = 6.7 Hz). IR (neat) ν (cm^{-1}): 3067.6, 3037.8, 2991.2, 1738.8, 1597.2, 1511.4, 1453.7, 1340.0, 1261.7, 1164.8, 1094.0, 915.1, 866.6, 752.9, 698.9, 628.1, 508.8; HRMS (ESI): caled for $C_{18}H_{13}F_3NO_2^+$ [M + H]$^+$ 332.0893; found 332.0894.

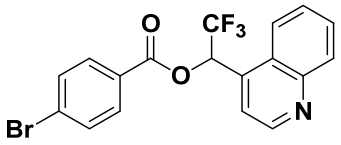
2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 4-fluorobenzoate (33)



53% (37.0 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.6 Hz, 1H), 8.24 – 8.13 (m, 4H), 7.82 – 7.77 (m, 1H), 7.72 – 7.67 (m, 2H), 7.21 – 7.14 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 165.4, 163.2, 149.8, 148.5, 136.7, 132.8 (d, *J* = 9.7 Hz), 130.6, 129.8, 127.8, 125.8, 124.3 (d, *J* = 3.1 Hz), 123.1 (q, *J* = 281.5 Hz), 122.7, 120.2, 116.2, 116.0, 68.1 (q, *J* = 34.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.49 (d, J = 6.6 Hz), -102.82 – -102.93 (m). IR

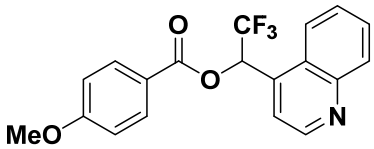
(neat) ν (cm^{-1}): 3075.1, 1736.9, 1599.0, 1507.7, 1250.5, 1183.4, 1135.0, 1080.9, 913.2, 851.7, 760.4, 598.2; HRMS (ESI): caled for $C_{18}H_{12}F_4NO_2^+$ $[M + H]^+$ 350.0799; found 350.0797.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 4-bromobenzoate (34)



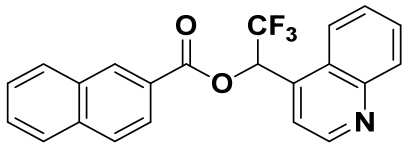
64% (52.4 mg); white solid; mp 102.0-102.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.5 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.5 Hz, 2H), 8.04 – 7.96 (m, 2H), 7.84 – 7.76 (m, 1H), 7.74 – 7.61 (m, 4H), 7.18 (q, *J* = 6.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 149.8, 148.6, 136.6, 132.2, 131.5, 130.7, 129.9, 129.7, 127.9, 127.0, 125.8, 123.1 (q, *J* = 281.6 Hz), 122.7, 120.2, 68.2 (q, *J* = 34.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.46 (d, *J* = 6.2 Hz). IR (neat) ν (cm^{-1}): 2983.7, 1735.1, 1593.4, 1511.4, 1340.0, 1254.2, 1170.4, 1135.0, 915.1, 844.2, 745.5, 680.2, 628.1; HRMS (ESI): caled for $C_{18}H_{12}BrF_3NO_2^+$ $[M + H]^+$ 409.9998; found 409.9999.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 4-methoxybenzoate (35)



60% (43.3 mg); white solid; mp 115.7-116.7 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 4.5 Hz, 1H), 8.28 – 8.17 (m, 2H), 8.15 – 8.07 (m, 2H), 7.82 – 7.75 (m, 1H), 7.73 – 7.66 (m, 2H), 7.17 (q, *J* = 6.4 Hz, 1H), 7.01 – 6.93 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 163.8, 149.8, 148.5, 137.1, 132.3, 130.5, 129.8, 127.7, 125.9, 123.3 (q, *J* = 281.5 Hz), 122.8, 120.3, 120.2, 114.1, 67.7 (q, *J* = 33.9 Hz), 55.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.47 (d, *J* = 6.4 Hz). IR (neat) ν (cm^{-1}): 3080.6, 2967.0, 2935.3, 2840.2, 1723.9, 1604.6, 1511.4, 1425.7, 1334.4, 1258.0, 1101.4, 1019.4, 916.9, 849.8, 752.9, 506.9; HRMS (ESI): caled for $C_{19}H_{15}F_3NO_3^+$ $[M + H]^+$ 362.0999; found 362.0999.

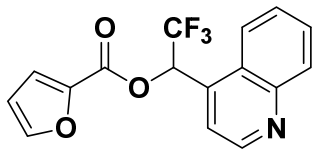
2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 2-naphthoate (36)



30% (22.9 mg); white solid; mp 109.4-110.7 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.6 Hz, 1H), 8.74 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.85 – 7.76 (m, 2H), 7.76 – 7.69 (m,

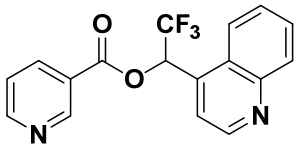
1H), 7.68 – 7.57 (m, 2H), 7.27 (q, *J* = 6.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 149.9, 148.5, 136.9, 136.0, 132.4, 132.1, 130.6, 129.8, 129.5, 129.0, 128.7, 127.9, 127.8, 127.1, 125.9, 125.2, 125.0, 123.3 (q, *J* = 281.5 Hz), 122.8, 1203, 68.1 (q, *J* = 33.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.36 (d, *J* = 6.2 Hz). IR (neat) ν (cm^{-1}): 3062.0, 2927.8, 2853.3, 1729.5, 1628.8, 1593.4, 1511.4, 1466.7, 1354.9, 1258.0, 1187.2, 1127.5, 1090.2, 905.7, 838.7, 758.5, 628.1, 473.4; HRMS (ESI): caled for $C_{22}H_{15}F_3NO_2^+$ $[M + H]^+$ 382.1050; found 382.1049.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl furan-2-carboxylate (37)



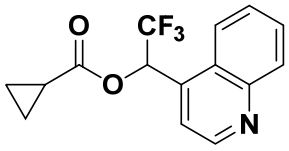
65% (41.7 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.5 Hz, 1H), 8.24 – 8.16 (m, 2H), 7.83 – 7.76 (m, 1H), 7.74 – 7.65 (m, 3H), 7.41 (dd, *J* = 3.5, 0.9 Hz, 1H), 7.16 (q, *J* = 6.3 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 149.8, 148.5, 147.8, 142.6, 136.4, 130.5, 129.8, 127.8, 125.7, 123.0 (q, *J* = 281.6 Hz), 122.8, 120.4, 112.4, 67.7 (q, *J* = 34.3 Hz). ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -74.51. IR (neat) ν (cm^{-1}): 3145.9, 2928.0, 2853.3, 1736.9, 1567.3, 1470.4, 1395.9, 1267.3, 1192.7, 1105.2, 1017.6, 903.9, 853.6, 756.6, 693.3, 628.1, 588.9; HRMS (ESI): caled for $C_{16}H_{11}F_3NO_3^+$ $[M + H]^+$ 322.0686; found 322.0685.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl nicotinate (38)



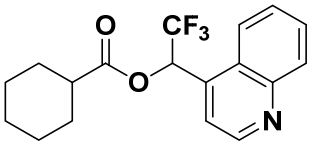
66% (43.8 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (d, *J* = 2.2 Hz, 1H), 9.00 (d, *J* = 4.5 Hz, 1H), 8.86 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.38 (dt, *J* = 8.0, 2.0 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.84 – 7.77 (m, 1H), 7.74 – 7.68 (m, 2H), 7.49 – 7.44 (m, 1H), 7.22 (q, *J* = 6.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 154.6, 151.2, 149.8, 148.5, 137.5, 136.3, 130.6, 129.9, 128.0, 125.7, 124.3, 123.6, 123.0 (q, *J* = 281.5 Hz), 122.6, 120.2, 68.3 (q, *J* = 34.2 Hz). ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -74.46. IR (neat) ν (cm^{-1}): 3043.4, 2926.0, 2855.1, 1742.5, 1591.6, 1511.4, 1422.0, 1354.9, 1256.1, 1183.4, 1135.0, 1099.6, 1021.3, 915.1, 823.7, 734.3, 698.9, 629.9; HRMS (ESI): caled for $C_{17}H_{12}F_3N_2O_2^+$ $[M + H]^+$ 333.0846; found 333.0845.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl cyclopropanecarboxylate (39)



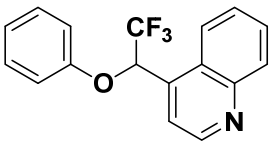
63% (37.2 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.6 Hz, 1H), 8.19 (m, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.69 – 7.62 (m, 2H), 6.97 (q, *J* = 6.4 Hz, 1H), 1.87 – 1.79 (m, 1H), 1.20 – 1.11 (m, 1H), 1.08 – 0.96 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 149.8, 148.6, 136.9, 130.5, 129.8, 127.7, 125.8, 123.1 (q, *J* = 281.4 Hz), 122.8, 120.3, 67.3 (q, *J* = 34.0 Hz), 12.6, 9.6. ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -74.69. IR (neat) ν (cm^{-1}): 3017.3, 2927.8, 1746.3, 1595.3, 1511.4, 1466.7, 1390.3, 1321.3, 1267.3, 1131.2, 941.2, 754.8, 628.1; HRMS (ESI): caled for $C_{15}H_{13}F_3NO_2^+$ $[M + H]^+$ 296.0893; found 296.0893.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl cyclohexanecarboxylate (40)



64% (43.2 mg); white solid; mp 54.5-55.3 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.5 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.70 – 7.64 (m, 1H), 7.61 (d, *J* = 4.4 Hz, 1H), 6.97 (q, *J* = 6.4 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.04 – 1.91 (m, 2H), 1.82 – 1.72 (m, 2H), 1.70 – 1.62 (m, 1H), 1.57 – 1.41 (m, 2H), 1.39 – 1.19 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 149.8, 148.5, 137.0, 130.5, 129.8, 127.7, 125.8, 123.1 (q, *J* = 281.6 Hz), 122.8, 120.2, 67.0 (q, *J* = 33.9 Hz), 42.7, 28.7 (d, *J* = 4.7 Hz), 25.5, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.71 (d, *J* = 6.6 Hz). IR (neat) ν (cm^{-1}): 2937.1, 2857.0, 1742.5, 1593.4, 1511.4, 1448.1, 1336.3, 1256.1, 1198.3, 1123.8, 1066.0, 939.3, 853.6, 756.6, 628.1, 508.8, 443.6; HRMS (ESI): caled for $C_{18}H_{19}F_3NO_2^+$ $[M + H]^+$ 338.1363; found 338.1363.

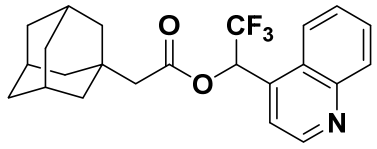
4-(2,2,2-trifluoro-1-phenoxyethyl)quinoline (41)



35% (21.2 mg); white solid; mp 65.1-66.7 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (d, *J* = 4.5 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.76 – 7.68 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.22 (q, *J* = 5.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 150.1, 148.5, 137.5, 130.8, 129.8, 129.7, 127.8, 125.9, 123.3 (q, *J* = 282.2 Hz), 122.9, 122.4, 120.7, 115.7, 73.9 (q, *J* = 32.9 Hz). ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -75.26. IR (neat) ν (cm^{-1}): 3071.3, 2944.6, 1591.6, 1485.3, 1366.1, 1271.0, 1224.4, 1138.7,

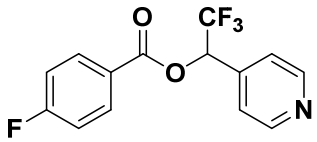
1095.8, 1002.7, 903.9, 851.7, 756.6, 691.4, 637.4, 553.5, 499.5, 423.1; HRMS (ESI): caled for $C_{17}H_{13}F_3NO^+$ $[M + H]^+$ 304.0944; found 304.0945.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)acetate (42)



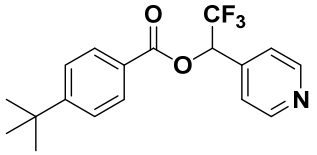
61% (49.2 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 4.5 Hz, 1H), 8.21 – 8.12 (m, 2H), 7.80 – 7.75 (m, 1H), 7.69 – 7.61 (m, 2H), 6.99 (q, *J* = 6.5 Hz, 1H), 2.32 – 2.20 (m, 2H), 1.98 – 1.93 (m, 3H), 1.72 – 1.57 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 149.7, 148.5, 136.9, 130.5, 129.7, 127.7, 125.8, 123.1 (q, *J* = 281.6 Hz), 122.8, 120.5, 66.9 (q, *J* = 33.9 Hz), 48.2, 42.2, 36.5, 33.2, 28.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.44 (d, *J* = 6.5 Hz). IR (neat) ν (cm^{-1}):2901.7, 2849.5, 1751.8, 1593.4, 1511.4, 1451.8, 1347.4, 1265.4, 1181.6, 1135.0, 1062.3, 1002.7, 913.2, 840.5, 754.8, 732.4, 628.1, 488.3; HRMS (ESI): caled for $C_{23}H_{25}F_3NO_2^+$ $[M + H]^+$ 404.1832; found 404.1829.

2,2,2-trifluoro-1-(pyridin-4-yl)ethyl 4-fluorobenzoate (43)



43% (25.7 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 8.20 – 8.11 (m, 2H), 7.45 (d, *J* = 5.1 Hz, 2H), 7.24 – 7.12 (m, 2H), 6.33 (q, *J* = 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 165.2, 163.1, 150.4, 139.8, 132.8 (d, *J* = 9.6 Hz), 122.7 (q, *J* = 281.0 Hz), 122.3, 116.1 (d, *J* = 22.2 Hz), 71.3 (q, *J* = 33.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.46 (d, *J* = 6.6 Hz), -102.78 – -102.91 (m). IR (neat) ν (cm^{-1}):3039.6, 2963.2, 1736.9, 1600.9, 1507.7, 1414.5, 1351.2, 1252.4, 1181.6, 1135.0, 1086.5, 1015.7, 915.1, 851.7, 810.7, 762.2, 596.4, 523.7; HRMS (ESI): caled for $C_{14}H_{10}F_4NO_2^+$ $[M + H]^+$ 300.0642; found 300.0642.

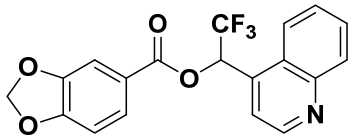
2,2,2-trifluoro-1-(pyridin-4-yl)ethyl 4-(tert-butyl)benzoate (44)



40% (26.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 2H), 8.09 – 8.01 (m, 2H), 7.55 – 7.51 (m, 2H), 7.47 (s, 2H), 6.34 (q, *J* = 6.7 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 158.2, 150.3, 140.1, 130.0, 125.8, 125.2, 122.8 (q, *J* = 281.1 Hz), 122.8 – 122.2 (m), 71.0 (q, *J* = 33.5 Hz), 35.3, 31.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.48 (d, *J* = 6.7 Hz). IR (neat)

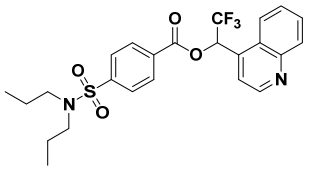
v (cm^{-1}):2965.1, 2871.9, 1735.1, 1606.5, 1410.8, 1351.2, 1258.0, 1181.6, 1135.0, 1086.5, 1026.9, 915.1, 851.7, 827.5, 771.6, 706.3, 633.6, 525.6; HRMS (ESI): caled for $C_{18}H_{19}F_3NO_2^+$ $[M + H]^+$ 338.1363; found 338.1362.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl benzo[*d*][1,3]dioxole-5-carboxylate (45)



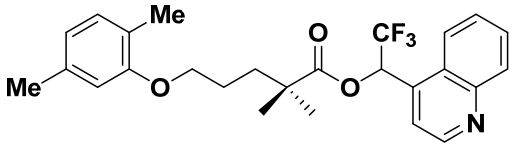
46% (34.6 mg); white solid; mp 128.6-129.8 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (d, *J* = 4.5 Hz, 1H), 8.25 – 8.20 (m, 2H), 7.85 – 7.78 (m, 2H), 7.75 – 7.69 (m, 2H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.18 (q, *J* = 6.4 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.10 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 152.7, 149.8, 148.5, 148.1, 137.0, 130.5, 129.8, 127.8, 126.4, 125.8, 123.2 (q, *J* = 281.4 Hz), 122.8, 121.8, 120.2, 109.7, 108.4, 102.1, 67.9 (q, *J* = 34.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.48 (d, *J* = 6.4 Hz). IR (neat) v (cm^{-1}):3080.6, 2905.5, 1727.6, 1606.5, 1489.1, 1442.5, 1366.1, 1254.2, 1183.4, 1135.0, 1036.2, 924.4, 846.1, 752.9, 732.4, 629.9, 510.6, 449.1; HRMS (ESI): caled for $C_{19}H_{13}F_3NO_4^+$ $[M + H]^+$ 376.0791; found 376.0792.

2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 4-(N,N-dipropylsulfamoyl)benzoate (46)



67% (66.2 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.5 Hz, 1H), 8.28 – 8.24 (m, 2H), 8.21 (d, *J* = 8.6 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.84 – 7.79 (m, 1H), 7.74 – 7.68 (m, 2H), 7.20 (q, *J* = 6.3 Hz, 1H), 3.15 – 3.06 (m, 4H), 1.62 – 1.49 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 149.8, 148.6, 145.6, 136.3, 131.2, 130.7, 130.7, 129.9, 127.9, 127.3, 125.7, 123.0 (q, *J* = 281.5 Hz), 122.6, 120.2, 68.5 (q, *J* = 34.2 Hz), 50.0, 22.0, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.44 (d, *J* = 6.2 Hz). IR (neat) v (cm^{-1}):2968.8, 2935.3, 2877.5, 1742.5, 1597.2, 1511.4, 1466.7, 1399.6, 1341.8, 1252.4, 1157.3, 1135.0, 1092.1, 991.5, 913.2, 866.6, 736.1, 600.1; HRMS (ESI): caled for $C_{24}H_{26}F_3N_2O_4S^+$ $[M + H]^+$ 495.1560; found 495.1558.

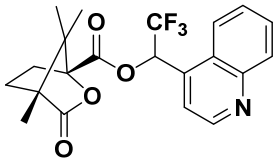
2,2,2-trifluoro-1-(quinolin-4-yl)ethyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (47)



48% (44.1 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 4.5 Hz, 1H), 8.24 – 8.11 (m, 2H), 7.83 – 7.75 (m, 1H), 7.72 – 7.60 (m, 2H), 7.06 – 6.95 (m, 2H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 3.98 – 3.86 (m, 2H), 2.31 (s, 3H), 2.19 (s, 3H), 1.92 – 1.65 (m, 4H), 1.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 156.8, 149.7, 148.5, 136.8, 136.5, 130.5, 130.3, 129.8, 127.7, 125.8, 123.5, 123.1 (q, *J* = 281.5 Hz), 122.8, 120.8, 120.2, 111.9, 67.6, 67.3 (q, *J* = 33.9 Hz), 42.3, 37.0 , 25.0 (d, *J* = 3.5 Hz), 24.8, 21.3, 15.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.65 (d, *J* = 6.4 Hz). IR (neat) ν (cm^{-1}): 2926.0, 2870.1, 1750.0, 1615.8, 1586.0, 1507.7, 1474.2, 1392.2, 1263.6, 1183.4, 1114.5, 1047.4, 926.2, 840.5, 754.8, 631.8; HRMS (ESI): caled for $C_{26}H_{29}F_3NO_3^+$ $[M + H]^+$ 460.2094; found 460.2092.

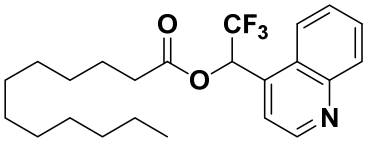
2,2,2-trifluoro-1-(quinolin-4-yl)ethyl

(1*R*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (48)



56% (45.6 mg); white solid; mp 153.7-155.2 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.73 – 7.67 (m, 1H), 7.63 (d, *J* = 4.4 Hz, 1H), 7.12 (q, *J* = 6.2 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.18 – 2.10 (m, 1H), 2.03 – 1.96 (m, 1H), 1.80 – 1.72 (m, 1H), 1.14 (s, 3H), 1.11 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 165.6, 149.8, 148.5, 135.7, 130.7, 130.0, 128.0, 125.5, 122.7 (q, *J* = 281.6 Hz), 122.6, 120.4, 90.4, 67.9 (q, *J* = 34.3 Hz), 54.8, 30.9, 29.7, 28.9, 16.6, 16.5, 9.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.50 (d, *J* = 6.2 Hz). IR (neat) ν (cm^{-1}): 3360.2, 2965.1, 2922.1, 2853.3, 1787.3, 1770.5, 1600.9, 1513.3, 1466.7, 1399.6, 1340.0, 1261.7, 1179.7, 1135.0, 1069.7, 1019.4, 935.6, 848.0, 758.5, 695.1, 628.1, 510.6; HRMS (ESI): caled for $C_{21}H_{21}F_3NO_4$+ $[M + H]^+$ 408.1417; found 408.1414.

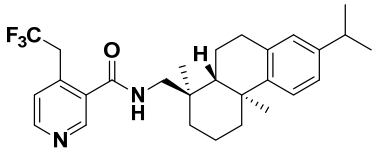
2,2,2-trifluoro-1-(quinolin-4-yl)ethyl dodecanoate (49)



42% (34.4 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H),

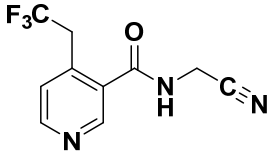
7.80 – 7.75 (m, 1H), 7.69 – 7.64 (m, 1H), 7.61 (d, *J* = 4.4 Hz, 1H), 6.98 (q, *J* = 6.4 Hz, 1H), 2.56 – 2.43 (m, 2H), 1.71 – 1.62 (m, 2H), 1.35 – 1.19 (m, 16H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 151.0, 149.7, 148.5, 136.8, 130.5, 129.7, 127.7, 123.1 (q, *J* = 281.5 Hz), 122.8, 120.4, 67.2 (q, *J* = 33.8 Hz), 33.8, 31.9, 29.5, 29.5, 29.4, 29.3, 29.1, 28.9, 24.7, 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.68 (d, *J* = 6.6 Hz). IR (neat) ν (cm^{-1}): 2924.1, 2855.1, 1759.3, 1595.3, 1511.4, 1466.7, 1351.2, 1267.3, 1183.4, 1135.0, 1064.2, 840.5, 756.6, 629.9, 424.9; HRMS (ESI): caled for $C_{23}H_{31}F_3NO_2^+$ $[M + H]^+$ 410.2302; found 410.2301.

N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-(2,2,2-trifluoroethyl)nicotinamide (50)



60% (58.4 mg) (dr=5:1); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.61 (d, *J* = 5.1 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.87 (d, 1H), 6.12 (t, *J* = 6.3 Hz, 1H), 3.92 – 3.67 (m, 2H), 3.47 – 3.25 (m, 2H), 2.98 – 2.75 (m, 2H), 2.32 (d, *J* = 12.7 Hz, 1H), 1.99 – 1.64 (m, 5H), 1.58 – 1.44 (m, 2H), 1.40 – 1.19 (m, 9H), 1.04 – 0.77 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 151.2, 147.7, 146.8, 145.7, 138.2 (q, *J* = 3.1 Hz), 134.4, 133.2, 126.9, 126.4, 125.1 (q, *J* = 277.3 Hz), 124.1, 123.9, 50.6, 46.0, 38.3, 37.5, 37.5, 36.3, 35.7 (q, *J* = 30.1 Hz), 33.4, 30.1, 25.2, 24.0 , 23.9, 19.1, 18.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.43 (t, *J* = 10.9 Hz), -64.47 (t, *J* = 10.8 Hz). IR (neat) ν (cm^{-1}): 3293.1, 2924.1, 2855.1, 1647.5, 1541.3, 1459.3, 1356.8, 1252.4, 1220.7, 1140.6, 1082.8, 825.6, 665.3, 605.7, 527.4; HRMS (ESI): caled for $C_{28}H_{36}F_3N_2O^+$ $[M + H]^+$ 473.2774; found 473.2769.

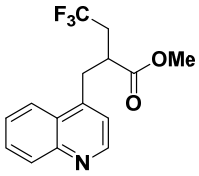
N-(cyanomethyl)-4-(2,2,2-trifluoroethyl)nicotinamide (51)



76% (36.9 mg); white solid; mp 187.4-189.1 ℃; ^{1}H NMR (400 MHz, CD_3CN) δ 8.81 – 8.61 (m, 2H), 7.56 (s, 1H), 7.45 (d, *J* = 5.0 Hz, 1H), 4.25 (d, *J* = 5.8 Hz, 2H), 3.91 (q, *J* = 11.0 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 168.0, 152.8, 149.5, 139.3 (q, *J* = 2.9 Hz), 132.1, 127.6, 126.7 (q, *J* = 276.4 Hz), 117.4, 36.0 (q, *J* = 29.8 Hz), 28.6. ^{19}F{H} NMR (471 MHz, CD_3CN) δ -65.37 . IR (neat) ν (cm^{-1}): 3285.6, 2912.9, 1641.9, 1535.7, 1408.9, 1354.9, 1310.2, 1248.7, 1218.8, 1131.2, 1080.9,

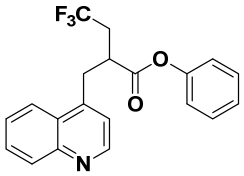
916.9, 833.1, 780.9, 708.2, 635.5, 609.4, 527.4; HRMS (ESI): caled for $C_{10}H_9F_3N_3O^+$ [M + H]$^+$ 244.0692; found 244.0691.

methyl 4,4,4-trifluoro-2-(quinolin-4-ylmethyl)butanoate (52)



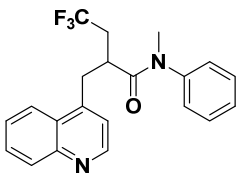
40% (23.8 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.4 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.66 – 7.59 (m, 1H), 7.22 (d, *J* = 4.4 Hz, 1H), 3.57 (s, 3H), 3.48 – 3.40 (m, 1H), 3.36 – 3.28 (m, 1H), 3.25 – 3.15 (m, 1H), 2.82 – 2.66 (m, 1H), 2.40 – 2.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 149.9, 148.4, 143.3, 130.5, 129.5, 127.1, 125.9 (q, *J* = 277.3 Hz), 122.8, 121.7, 52.3, 40.1 (q, *J* = 2.3 Hz), 35.9 (q, *J* = 29.2 Hz), 34.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.93 (t, *J* = 10.5 Hz). IR (neat) ν (cm^{-1}): 3055.1, 2957.9, 2925.0, 2853.6, 1741.3, 1676.9, 1595.5, 1511.1, 1435.4, 1383.9, 1263.8, 1208.0, 1143.7, 1110.8, 1073.7, 960.7, 897.8, 846.3, 736.3, 701.9; HRMS (ESI): caled for $C_{15}H_{15}F_3NO_2^+$ [M + H]$^+$ 298.1050; found 298.1043.

phenyl 4,4,4-trifluoro-2-(quinolin-4-ylmethyl)butanoate (53)



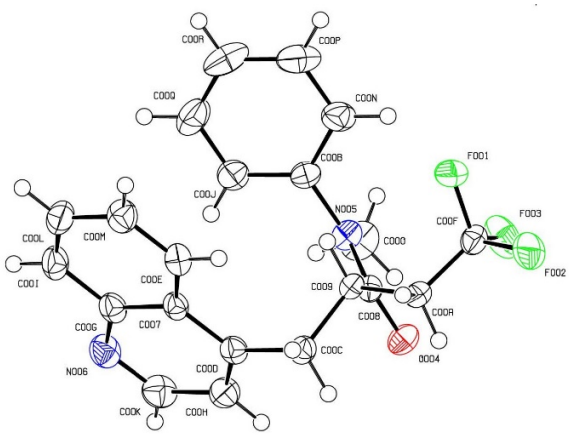
55% (39.5 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.68 – 7.62 (m, 1H), 7.33 – 7.28 (m, 3H), 7.22 – 7.17 (m, 1H), 6.74 – 6.69 (m, 2H), 3.59 – 3.52 (m, 1H), 3.50 – 3.42 (m, 2H), 2.96 – 2.82 (m, 1H), 2.53 – 2.41 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 150.0, 149.9, 148.5, 142.8, 130.6, 129.6, 129.4, 127.3, 127.0, 126.2, 125.9 (q, *J* = 277.2 Hz), 122.8, 121.9, 121.0, 40.3 (q, *J* = 2.3 Hz), 36.2 (q, *J* = 29.4 Hz), 34.6. ^{19}F{H} NMR (471 MHz, $CDCl_3$) δ -64.71. IR (neat) ν (cm^{-1}): 3053.7, 2985.1, 2929.3, 1759.9, 1594.0, 1488.3, 1429.6, 1383.9, 1263.8, 1193.7, 1142.3, 1108.0, 1067.9, 907.8, 734.8, 699.1; HRMS (ESI): caled for $C_{20}H_{17}F_3NO_2^+$ [M + H]$^+$ 360.1206; found 360.1198.

4,4,4-trifluoro-N-methyl-N-phenyl-2-(quinolin-4-ylmethyl)butanamide (54)



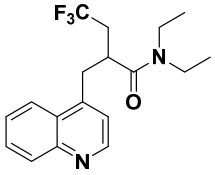
54% (40.2 mg); white solid; mp 121.0-122.2 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.2 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.13 – 7.07 (m, 2H),

3.32 – 3.23 (m, 1H), 3.21 – 3.13 (m, 2H), 3.07 (s, 3H), 2.91 – 2.77 (m, 1H), 2.22 – 2.09 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 149.9, 148.3, 143.7, 142.1, 130.2, 129.3, 129.3, 127.8, 127.4, 126.7, 126.7, 126.2 (q, *J* = 277.2 Hz), 122.7, 122.3, 37.4, 36.7 (q, *J* = 2.5 Hz), 36.5 (q, *J* = 28.6 Hz), 35.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.33 (t, *J* = 10.9 Hz). IR (neat) ν (cm^{-1}): 3055.1, 2923.6, 2853.6, 1422.5, 1263.8, 896.4, 734.8, 700.5; HRMS (ESI): caled for $C_{21}H_{20}F_3N_2O^+$ $[M + H]^+$ 373.1522; found 373.1520.



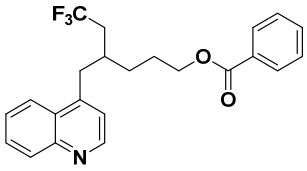
X-ray crystallography for **54** (CCDC number: 2075783)

N,N-diethyl-4,4,4-trifluoro-2-(quinolin-4-ylmethyl)butanamide (55)



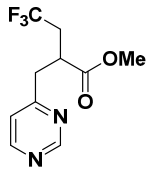
39% (26.4 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 3.6 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.65 – 7.59 (m, 1H), 7.25 (d, *J* = 4.3 Hz, 1H), 3.45 – 3.31 (m, 3H), 3.28 – 3.18 (m, 1H), 3.12 – 3.03 (m, 1H), 2.91 – 2.77 (m, 1H), 2.63 (q, *J* = 7.2 Hz, 2H), 2.44 – 2.32 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.55 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 150.0, 148.2, 144.0, 130.4, 129.4, 127.3, 127.1, 126.4 (q, *J* = 277.0 Hz), 122.9, 122.3, 41.5, 40.7, 37.3 (q, *J* = 28.4 Hz), 35.9 (q, *J* = 4.4 Hz), 35.5, 13.6, 12.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.50 (t, *J* = 10.9 Hz). IR (neat) ν (cm^{-1}): 3053.7, 2983.6, 2933.6, 1636.9, 1511.1, 1461.1, 1431.1, 1373.9, 1263.8, 1143.7, 1103.7, 907.8, 734.8, 700.5; HRMS (ESI): caled for $C_{18}H_{22}F_3N_2O^+$ $[M + H]^+$ 339.1679; found 339.1672.

6,6,6-trifluoro-4-(quinolin-4-ylmethyl)hexyl benzoate (56)



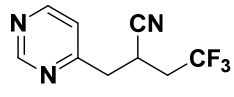
28% (22.5 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.10 – 7.98 (m, 3H), 7.82 – 7.74 (m, 1H), 7.68 – 7.61 (m, 1H), 7.60 – 7.52 (m, 1H), 7.49 – 7.40 (m, 3H), 4.82 – 4.68 (m, 2H), 4.42 – 4.27 (m, 2H), 3.46 – 3.36 (m, 1H), 3.03 – 2.87 (m, 1H), 2.64 – 2.46 (m, 1H), 2.30 – 2.17 (m, 1H), 2.14 – 1.89 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 149.7, 148.8, 133.1, 132.4, 130.6, 130.0, 129.9, 129.5, 128.5, 127.8, 127.2, 125.5 (q, *J* = 277.3 Hz), 124.4, 123.4, 63.7, 56.2 (q, *J* = 2.4 Hz), 53.9, 32.8 (q, *J* = 30.4 Hz), 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.54 (t, *J* = 10.5 Hz). IR (neat) ν (cm^{-1}): 3056.6, 2987.9, 2926.5, 2853.6, 1715.6, 1595.5, 1512.6, 1451.1, 1389.6, 1318.1, 1266.7, 1150.9, 1120.8, 1070.8, 1029.3, 907.8, 734.8, 704.8; HRMS (ESI): caled for $C_{23}H_{23}F_3NO_2^+$ $[M + H]^+$ 402.1676; found 402.1675.

methyl 4,4,4-trifluoro-2-(pyrimidin-4-ylmethyl)butanoate (57)



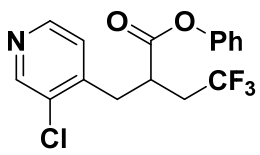
34% (16.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.65 (s, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 3.68 (s, 3H), 3.42 – 3.32 (m, 1H), 3.23 – 3.14 (m, 1H), 3.11 – 3.02 (m, 1H), 2.76 – 2.60 (m, 1H), 2.49 – 2.33 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 166.2, 158.7, 156.9, 126.1 (q, *J* = 276.9 Hz), 121.3 – 121.1 (m), 52.4, 38.4, 38.0 (q, *J* = 2.5 Hz), 35.1 (q, *J* = 29.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.59 (t, *J* = 10.8 Hz). IR (neat) ν (cm^{-1}): 3053.7, 2925.0, 2853.6, 1741.3, 1584.0, 1551.2, 1442.5, 1388.2, 1263.8, 1203.8, 1143.7, 1107.9, 899.2, 734.8, 701.9; HRMS (ESI): caled for $C_{10}H_{12}F_3N_2O_2^+$ $[M + H]^+$ 249.0846; found 249.0844.

(R)-4,4,4-trifluoro-2-(pyrimidin-4-ylmethyl)butanenitrile (58)



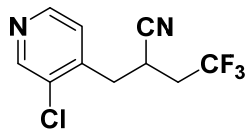
60% (25.8 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 1.1 Hz, 1H), 8.72 (d, *J* = 5.1 Hz, 1H), 7.29 – 7.27 (m, 1H), 3.72 – 3.61 (m, 1H), 3.24 – 3.10 (m, 2H), 2.70 – 2.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 158.9, 157.5, 125.0 (q, *J* = 277.5 Hz), 121.3, 119.0, 38.6, 35.7 (q, *J* = 30.1 Hz), 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.56 (t, *J* = 9.9 Hz). IR (neat) ν (cm^{-1}): 2920.4, 2851.4, 2249.4, 1584.1, 1552.4, 1388.4, 1259.8, 1144.3, 1108.9, 984.0, 840.5, 682.1, 568.4; HRMS (ESI): caled for $C_9H_9F_3N_3^+$ $[M + H]^+$ 216.0743; found 216.0744.

phenyl 2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (59)



41% (28.1 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.46 (d, *J* = 4.9 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.25 – 7.19 (m, 2H), 6.84 – 6.79 (m, 2H), 3.47 – 3.36 (m, 1H), 3.17 (d, *J* = 7.7 Hz, 2H), 2.91 – 2.74 (m, 1H), 2.50 – 2.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 150.0, 149.9, 148.0, 143.7, 132.4 – 132.2 (m), 129.5, 126.3, 125.8 (q, *J* = 277.0 Hz), 125.6, 121.0, 38.9 (q, *J* = 2.4 Hz), 36.1 (q, *J* = 29.5 Hz), 35.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.72 (t, *J* = 10.3 Hz). IR (neat) ν (cm^{-1}): 3047.1, 2935.3, 1757.4, 1587.8, 1492.8, 1377.3, 1254.2, 1189.0, 1136.8, 1105.2, 1038.1, 833.1, 749.2, 689.6, 534.9, 499.5; HRMS (ESI): caled for $C_{16}H_{14}ClF_3NO_2^+$ $[M + H]^+$ 344.0660; found 344.0660.

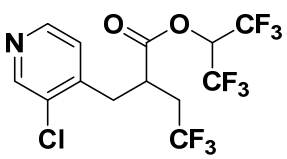
2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanenitrile (60)



39% (19.3 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.52 (d, *J* = 3.9 Hz, 1H), 7.30 (d, *J* = 4.8 Hz, 1H), 3.34 – 3.25 (m, 1H), 3.25 – 3.17 (m, 1H), 3.09 – 3.00 (m, 1H), 2.71 – 2.56 (m, 1H), 2.54 – 2.39 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.4, 141.7, 131.9 (q, *J* = 4.7 Hz), 125.7, 124.8 (q, *J* = 277.4 Hz), 118.2, 36.1 (q, *J* = 30.4 Hz), 34.9, 25.3 (q, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.52 (t, *J* = 9.8 Hz). IR (neat) ν (cm^{-1}): 3047.1, 2920.4, 2249.4, 1586.0, 1399.6, 1250.5, 1146.2, 1108.9, 1036.2, 836.8, 713.8, 637.4, 559.1; HRMS (ESI): caled for $C_{10}H_9ClF_3N_2^+$ $[M + H]^+$ 249.0401; found 249.0401.

1,1,1,3,3,3-hexafluoropropan-2-yl

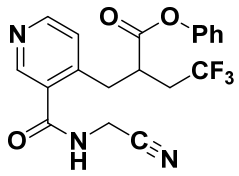
2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (61)



45% (37.5 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.43 (d, *J* = 4.9 Hz, 1H), 7.10 (d, *J* = 4.9 Hz, 1H), 5.82 – 5.62 (m, 1H), 3.43 – 3.33 (m, 1H), 3.16 – 3.04 (m, 2H), 2.81 – 2.65 (m, 1H), 2.44 – 2.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 145.0, 148.2, 142.4, 132.0, 125.2 (q, *J* = 276.9 Hz), 125.2, 121.6 – 121.3 (m), 118.8 – 118.4 (m), 67.0 (p, *J* = 35.1 Hz), 38.5 (q, *J* = 2.6 Hz), 35.7 (q, *J* = 30.2 Hz), 34.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.27 (t, *J* = 10.3 Hz), -73.10 –

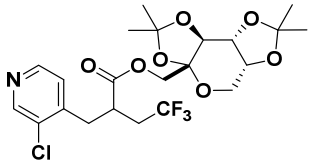
-73.92 (m). IR (neat) ν (cm^{-1}): 2974.4, 1779.8, 1587.8, 1384.7, 1287.8, 1226.3, 1198.3, 1107.0, 905.7, 836.8, 691.4, 542.3; HRMS (ESI): caled for $C_{13}H_{10}ClF_9NO_2^+$ $[M + H]^+$ 418.0251; found 418.0250.

phenyl 2-((3-((cyanomethyl)carbamoyl)pyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (62)



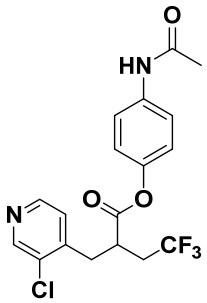
47% (36.8 mg) (dr=1:1); white solid; mp 158.7-160.0 ℃; ^1H NMR (400 MHz, CD_3CN) δ 8.71 – 8.60 (m, 3H), 7.68 (s, 1H), 7.43 (d, *J* = 5.1 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.29 – 7.22 (m, 1H), 6.87 – 6.81 (m, 1H), 4.29 – 4.24 (m, 2H), 3.91 (q, *J* = 11.0 Hz, 2H), 3.46 – 3.37 (m, 1H), 3.35 – 3.13 (m, 1H), 2.92 – 2.47 (m, 1H). ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 172.3, 168.0, 152.5 (d, *J* = 7.0 Hz), 149.4, 146.9, 139.3 (q, *J* = 3.2 Hz), 130.3, 127.6, 126.9, 126.7, 123.9 (q, *J* = 277.2 Hz), 122.2, 41.5 (q, *J* = 2.5 Hz), 37.0 – 35.2 (m), 35.9, 28.4 (d, *J* = 9.5 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -65.34 (t, *J* = 11.3 Hz), -65.41 (t, *J* = 11.1 Hz). IR (neat) ν (cm^{-1}): 3285.6, 2912.9, 1757.4, 1641.9, 1535.7, 1407.1, 1356.8, 1250.5, 1131.2, 916.9, 833.1, 751.1, 609.4, 527.4; HRMS (ESI): caled for $C_{19}H_{17}F_3N_3O_3^+$ $[M + H]^+$ 392.1217; found 392.1215.

((3aR,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (63)



37% (37.7 mg) (dr=1.4:1); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.3 Hz, 1H), 8.39 (d, *J* = 4.9 Hz, 1H), 7.16 – 7.09 (m, 1H), 4.57 – 4.47 (m, 1H), 4.25 – 4.16 (m, 2H), 4.11 – 4.04 (m, 1H), 3.91 (d, *J* = 11.6 Hz, 1H), 3.86 – 3.80 (m, 1H), 3.73 – 3.64 (m, 1H), 3.22 – 2.96 (m, 3H), 2.80 – 2.60 (m, 1H), 2.39 – 2.22 (m, 1H), 1.48 (d, *J* = 3.4 Hz, 3H), 1.44 (d, *J* = 3.8 Hz, 3H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.25 (d, *J* = 18.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 149.7, 148.2, 143.9, 132.0, 125.8 (q, *J* = 276.8 Hz), 125.4, 108.9 (d, *J* = 27.3 Hz), 100.9, 70.7, 70.5, 70.1, 66.0, 61.2 (d, *J* = 2.5 Hz), 39.0 – 38.7 (m), 35.8 (q, *J* = 29.4 Hz), 35.3, 29.7, 26.4 (d, *J* = 4.2 Hz), 25.8 (d, *J* = 2.9 Hz), 25.0, 24.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.77 (t, *J* = 10.5 Hz). IR (neat) ν (cm^{-1}): 2991.2, 2939.0, 1744.4, 1586.0, 1449.9, 1377.3, 1250.5, 1207.7, 1144.3, 1103.3, 1069.7, 982.2, 885.2, 756.6, 542.3; HRMS (ESI): caled for $C_{22}H_{28}ClF_3NO_7^+$ $[M + H]^+$ 510.1501; found 510.1500.

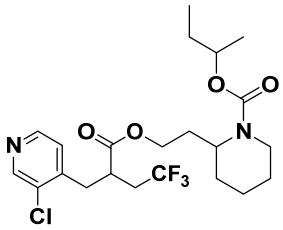
4-acetamidophenyl 2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (64)



47% (37.6 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.45 (d, *J* = 4.9 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.32 (s, 1H), 7.20 (d, *J* = 4.9 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 2H), 3.45 – 3.34 (m, 1H), 3.19 – 3.13 (m, 2H), 2.89 – 2.73 (m, 1H), 2.50 – 2.34 (m, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 168.2, 149.9, 148.0, 146.1, 143.7, 136.0 132.3, 125.8 (q, *J* = 277.0 Hz), 125.6, 121.5, 120.8, 38.9 (q, *J* = 2.5 Hz), 36.1 (q, *J* = 29.5 Hz), 35.3, 24.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.73 (t, *J* = 10.4 Hz). IR (neat) ν (cm^{-1}): 3268.9, 3060.1, 2924.1, 1753.7, 1669.8, 1612.1, 1543.1, 1505.8, 1373.5, 1254.2, 1190.9, 1135.0, 1105.2, 1015.7, 885.2, 821.9, 657.9, 516.2; HRMS (ESI): caled for $C_{18}H_{17}ClF_3N_2O_3^+$ $[M + H]^+$ 401.0875; found 401.0874.

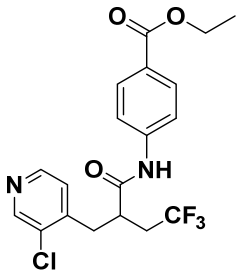
sec-butyl

2-(2-((2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoyl)oxy)ethyl)piperidine-1-carboxylate (65)



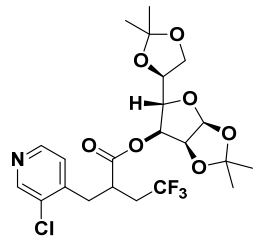
41% (39.2 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.40 (s, 1H), 7.14 (d, *J* = 4.5 Hz, 1H), 4.79 – 4.63 (m, 1H), 4.30 (d, *J* = 24.3 Hz, 1H), 4.10 – 3.89 (m, 3H), 3.16 – 2.97 (m, 2H), 2.78 – 2.59 (m, 2H), 2.34 – 2.17 (m, 1H), 2.00 – 1.86 (m, 2H), 1.64 – 1.30 (m, 9H), 1.21 – 1.12 (m, 3H), 0.94 – 0.81 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (d, *J* = 8.1 Hz), 155.4, 149.6, 147.8, 144.1, 132.5 – 131.9 (m), 125.8 (q, *J* = 277.9 Hz), 125.4, 73.4 – 71.8 (m), 63.0 (d, *J* = 14.0 Hz), 47.8 – 47.3 (m), 38.8, 35.7 (q, *J* = 29.2 Hz), 34.9 (d, *J* = 12.8 Hz), 29.6, 29.0 (d, *J* = 4.4 Hz), 28.6, 28.4 (d, *J* = 6.0 Hz), 25.4 (d, *J* = 5.6 Hz), 19.9 – 19.6 (m), 18.9, 9.7 – 9.4 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.81 (t, *J* = 10.5 Hz). IR (neat) ν (cm^{-1}): 2968.8, 2937.1, 2862.6, 1736.9, 1682.9, 1586.0, 1422.0, 1377.3, 1254.2, 1138.7, 1108.9, 1038.1, 833.1, 766.0, 544.2; HRMS (ESI): caled for $C_{22}H_{31}ClF_3N_2O_4^+$ $[M + H]^+$ 479.1919; found 479.1918.

ethyl 4-(2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanamido)benzoate (66)



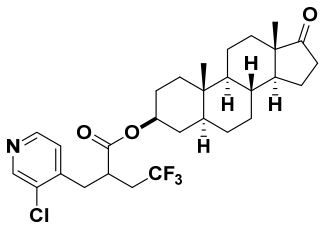
44% (36.4 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.30 (d, *J* = 4.7 Hz, 1H), 7.98 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 4.7 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.13 – 2.76 (m, 4H), 2.39 – 2.22 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 166.0, 149.5, 147.9, 144.4, 141.0, 132.0, 130.7, 126.6, 125.9 (q, *J* = 277.1 Hz), 125.9, 119.4, 61.0, 41.4 (q, *J* = 2.5 Hz), 36.3 (q, *J* = 29.3 Hz), 36.1, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.78 (t, *J* = 10.5 Hz). IR (neat) ν (cm^{-1}): 3322.9, 3049.0, 2983.7, 1686.6, 1599.0, 1533.8, 1408.9, 1367.9, 1256.1, 1140.6, 1101.4, 1017.6, 855.4, 769.7, 697.0, 546.1; HRMS (ESI): caled for $C_{19}H_{19}ClF_3N_2O_3^+$ [M + H]$^+$ 415.1031; found 415.1036.

(3aS,5S,6S,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (67)



48% (48.8 mg)(dr=1.5:1); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.41 (d, *J* = 4.6 Hz, 1H), 7.23 – 7.11 (m, 1H), 5.84 – 5.56 (m, 1H), 5.16 (d, *J* = 3.1 Hz, 1H), 4.40 – 3.89 (m, 6H), 3.22 – 3.09 (m, 1H), 3.09 – 2.88 (m, 1H), 2.79 – 2.60 (m, 1H), 2.39 – 2.16 (m, 1H), 1.47 (d, *J* = 9.3 Hz, 3H), 1.36 (d, *J* = 10.4 Hz, 3H), 1.29 – 1.22 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 149.8, 148.0 143.7, 125.7 (q, *J* = 277.3 Hz), 125.8 – 125.6 (m), 125.4, 112.4, 109.4, 105.0, 82.8, 79.5, 77.2, 72.2, 67.3, 38.6 (q, *J* = 2.5 Hz), 35.5 (q, *J* = 29.4 Hz), 34.8, 26.8, 26.6, 26.1, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.84(t, *J* = 10.2 Hz), -64.90 (t, *J* = 10.2 Hz). IR (neat) ν (cm^{-1}): 2989.3, 2939.0, 1746.3, 1586.0, 1373.5, 1254.2, 1215.1, 1146.2, 1073.5, 1019.4, 840.5, 732.4, 637.4, 534.9, 512.5; HRMS (ESI): caled for $C_{22}H_{28}ClF_3NO_7^+$ [M + H]$^+$ 510.1501; found 510.1501.

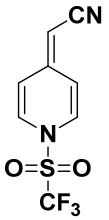
(3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-((3-chloropyridin-4-yl)methyl)-4,4,4-trifluorobutanoate (68)



41% (44.2 mg)(dr=1:1); white solid; mp 91.1-92.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.39 (d, *J* = 5.0 Hz, 1H), 7.13 (d,

J = 4.9 Hz, 1H), 4.65 – 4.55 (m, 1H), 3.11 – 2.96 (m, 3H), 2.76 – 2.58 (m, 1H), 2.46 – 2.36 (m, 1H), 2.33 – 2.17 (m, 1H), 2.10 – 1.98 (m, 1H), 1.95 – 1.85 (m, 2H), 1.80 – 1.08 (m, 15H), 1.01 – 0.89 (m, 2H), 0.83 (s, 3H), 0.78 (s, 3H), 0.71 – 0.60 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 221.2, 172.0 (d, *J* = 4.9 Hz), 149.6, 147.7, 144.1, 132.3, 125.8 (q, *J* = 277.1 Hz), 125.5, 74.6, 54.2, 51.3, 47.7, 44.5, 39.1 – 38.8 (m), 36.5, 36.0 (q, *J* = 29.3 Hz), 35.8, 35.5, 35.2 (d, *J* = 3.7 Hz), 34.9, 33.4, 31.4, 30.7 (d, *J* = 2.9 Hz), 28.1, 26.9 (d, *J* = 4.6 Hz), 21.7, 20.4, 13.8, 12.1 (d, *J* = 1.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.76 (t, *J* = 10.5 Hz), -64.77 (t, *J* = 10.5 Hz). IR (neat) ν (cm^{-1}): 2931.6, 2853.3, 1727.6, 1586.0, 1449.9, 1375.4, 1245.2, 1179.7, 1136.8, 1101.4, 1010.1, 823.7, 732.4, 587.1, 540.5; HRMS (ESI): caled for $C_{29}H_{38}ClF_3NO_3^+$ $[M + H]^+$ 540.2487; found 540.2487.

2-(1-((trifluoromethyl)sulfonyl)pyridin-4(1*H*)-ylidene)acetonitrile (72)



92% (46 mg); white solid; mp 77.1-78.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.56 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.17 (dd, *J* = 8.1, 2.3 Hz, 1H), 4.66 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 127.2, 126.3, 119.0 (q, *J* = 324.3 Hz), 117.8, 115.2, 113.7, 82.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.52. IR (neat) ν (cm^{-1}): 3114.2, 3065.7, 2922.2, 2853.3, 2195.4, 1660.5, 1429.4, 1306.4, 1215.1, 1142.4, 1053.0, 971.0, 810.7, 769.7, 702.6, 575.9, 484.6; HRMS (ESI): caled for $C_8H_6F_3N_2O_2S^+$ $[M + H]^+$ 251.0102; found 251.0098.

VIII. X-ray crystallography data for 10

Table 1 Crystal data and structure refinement

Identification code	**10**
Empirical formula	$C_{18}H_{11}F_3N_2$
Formula weight	312.29
Temperature/K	193
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.3732(4)
b/Å	7.0194(3)
c/Å	17.8991(6)
α/°	90
β/°	100.7770(10)
γ/°	90
Volume/Å^3	1403.74(9)
Z	4
ρ_{calc}g/cm^3	1.478
μ/mm^{-1}	0.116
F(000)	640.0
Crystal size/mm^3	0.17 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.67 to 55.006
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 7, -23 ≤ l ≤ 23

Reflections collected	12337
Independent reflections	3191 [R_{int} = 0.0267, R_{sigma} = 0.0236]
Data/restraints/parameters	3191/0/216
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0464, wR_2 = 0.1029
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.21

Crystal structure determination of 10

Crystal Data for $C_{18}H_{11}F_3N_2$ (*M* = 312.29 g/mol): monoclinic, space group $P2_1/n$ (no.14), *a* = 11.3732(4) Å, *b* = 7.0194(3) Å, *c* = 17.8991(6) Å, *β* = 100.7770(10)°, *V* = 1403.74(9) $Å^3$, *Z* = 4, *T* = 193 K, μ(MoKα)= 0.116 mm^{-1}, *Dcalc*= 1.478 g/cm^3, 12337 reflections measured (4.67° ≤ 2Θ ≤ 55.006°), 3191 unique (R_{int} = 0.0267, R_{sigma} = 0.0236) which were used in all calculations. The final R_1 was 0.0381 (I > 2σ(I)) and wR_2 was 0.1029 (all data).

X-ray crystallography data for 54

Table 1 Crystal data and structure refinement

Identification code	**54**
Empirical formula	$C_{21}H_{19}F_3N_2O$
Formula weight	372.38
Temperature/K	293.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.832(2)
b/Å	11.476(2)
c/Å	17.721(4)

α/°	90.00(3)
β/°	91.06(3)
γ/°	90.00(3)
Volume/Å^3	1796.0(7)
Z	4
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	0.107
F(000)	776.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.228 to 54.994
Index ranges	-10 ≤ h ≤ 11, -14 ≤ k ≤ 14, -23 ≤ l ≤ 20
Reflections collected	16006
Independent reflections	4117 [R_{int} = 0.0456, R_{sigma} = 0.0430]
Data/restraints/parameters	4117/0/245
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0462, wR_2 = 0.0976
Final R indexes [all data]	R_1 = 0.0775, wR_2 = 0.1138
Largest diff. peak/hole / e Å^{-3}	0.21/-0.22

Crystal structure determination of 54

Crystal Data for $C_{21}H_{19}F_3N_2O$ (*M* = 372.38 g/mol): monoclinic, space group $P2_1/n$ (no.14), *a* = 8.832(2) Å, *b* = 11.476(2) Å, *c* = 17.721(4) Å, *β* = 91.06(3)°, *V* = 1796.0(7) Å^3, *Z* = 4, *T* = 293.0 K, μ(MoKα)= 0.107 mm^{-1}, *Dcalc*= 1.377 g/cm^3, 16006 reflections measured (4.228° ≤ 2Θ ≤ 54.994°), 4117 unique (R_{int} = 0.0456, R_{sigma} = 0.0430) which were used in all calculations. The final R_1 was 0.0462 (I > 2σ(I)) and wR_2 was 0.1138 (all data).

X-ray crystallography data for 72

Table 1 Crystal data and structure refinement

Identification code	**72**
Empirical formula	$C_8H_5F_3N_2O_2S$
Formula weight	250.20
Temperature/K	193.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.810(2)
b/Å	5.693(2)
c/Å	16.013(3)
α/°	90.00(3)
β/°	93.45(3)
γ/°	90.00(3)
Volume/Å^3	983.7(4)
Z	4
ρ_{calc}g/cm^3	1.689
μ/mm^{-1}	0.360
F(000)	504.0
Crystal size/mm^3	0.17 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.1 to 54.98
Index ranges	-14 ≤ h ≤ 13, -7≤ k ≤ 7, -20 ≤ l ≤ 15

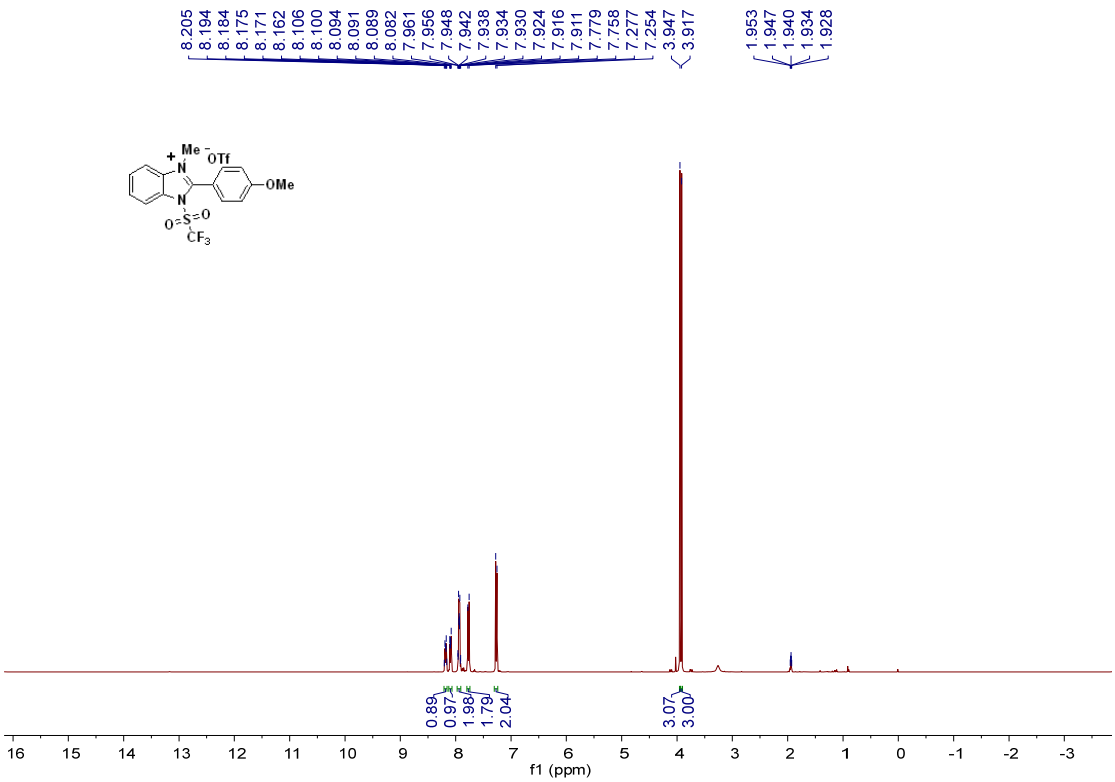
Reflections collected	8493
Independent reflections	2243 [R_{int} = 0.0499, R_{sigma} = 0.0472]
Data/restraints/parameters	2243/0/145
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0940
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.0987
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.25

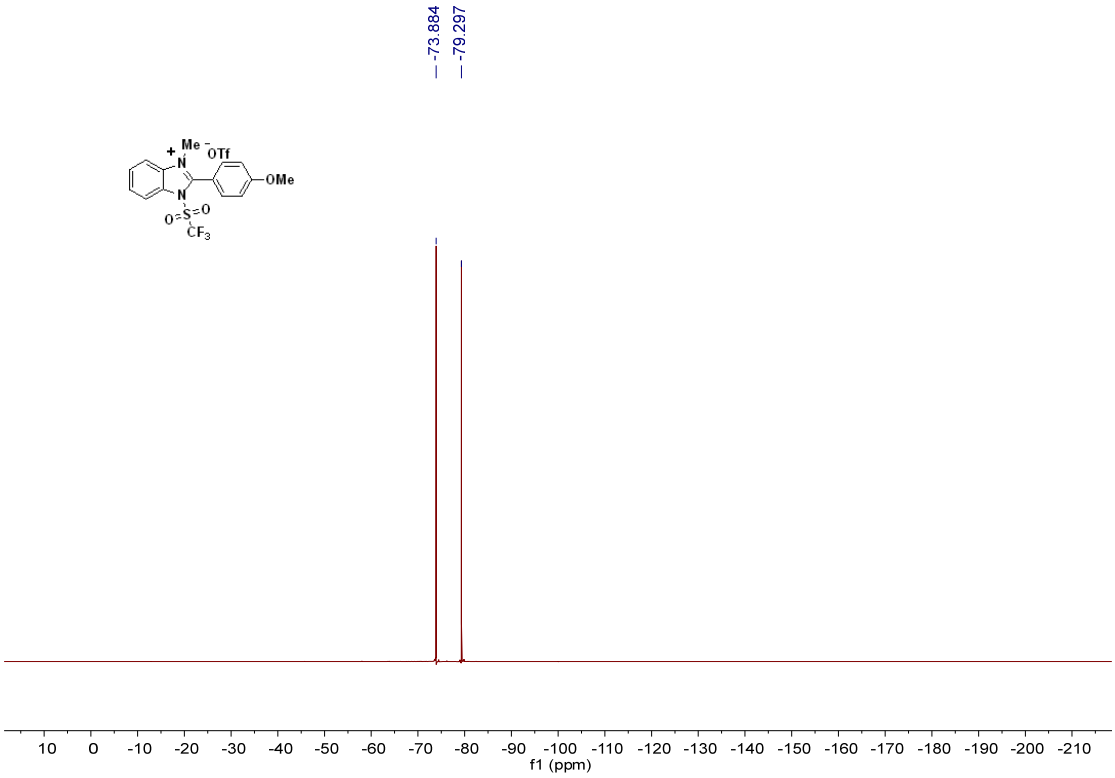
Crystal structure determination of 72

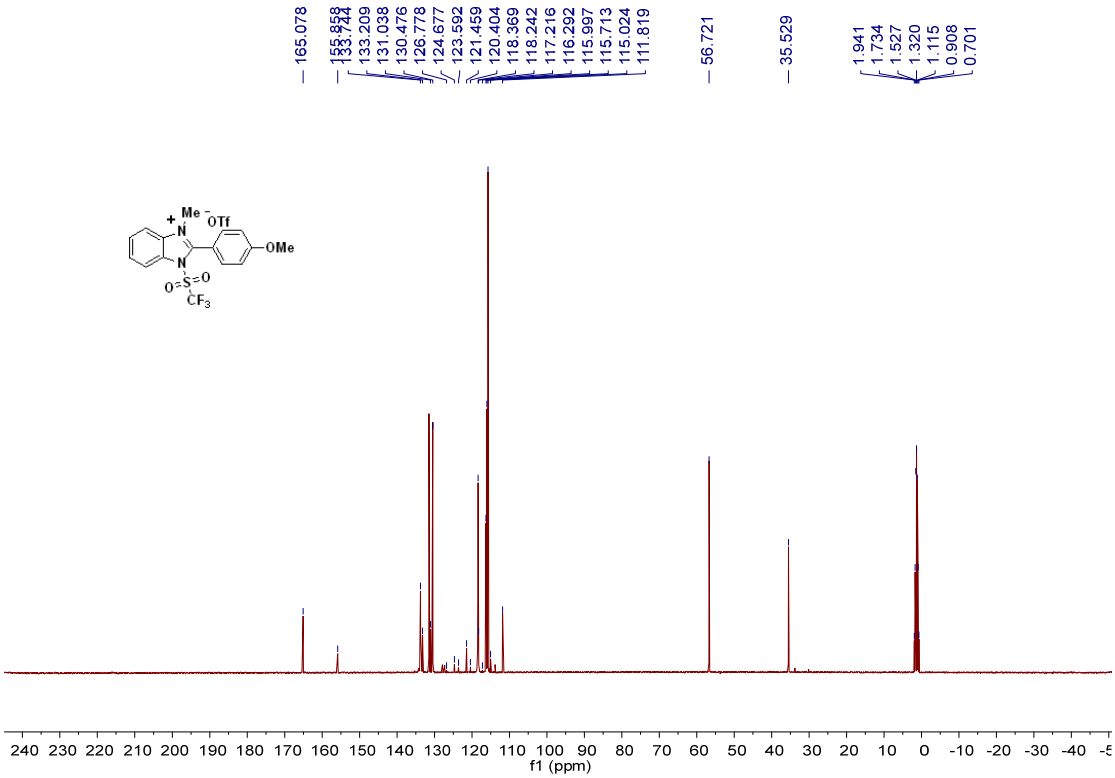
Crystal Data for $C_8H_5F_3N_2O_2S$ (*M* = 250.20 g/mol): monoclinic, space group $P2_1/c$ (no.14), *a* = 10.810(2) Å, *b* = 5.693(2) Å, *c* = 16.013(3) Å, *β* = 93.45(3)°, *V* = 987.3(4) $Å^3$, *Z* = 4, *T* = 193.0 K, μ(MoKα)= 0.360 mm^{-1}, *Dcalc*= 1.689 g/cm^3, 8493 reflections measured (5.1° ≤ 2Θ ≤ 54.98°), 2243 unique (R_{int} = 0.0499, R_{sigma} = 0.0472) which were used in all calculations. The final R_1 was 0.0364 (I > 2σ(I)) and wR_2 was 0.0987 (all data).

IX. NMR Spectra for compounds 2b, 2c, 3-68

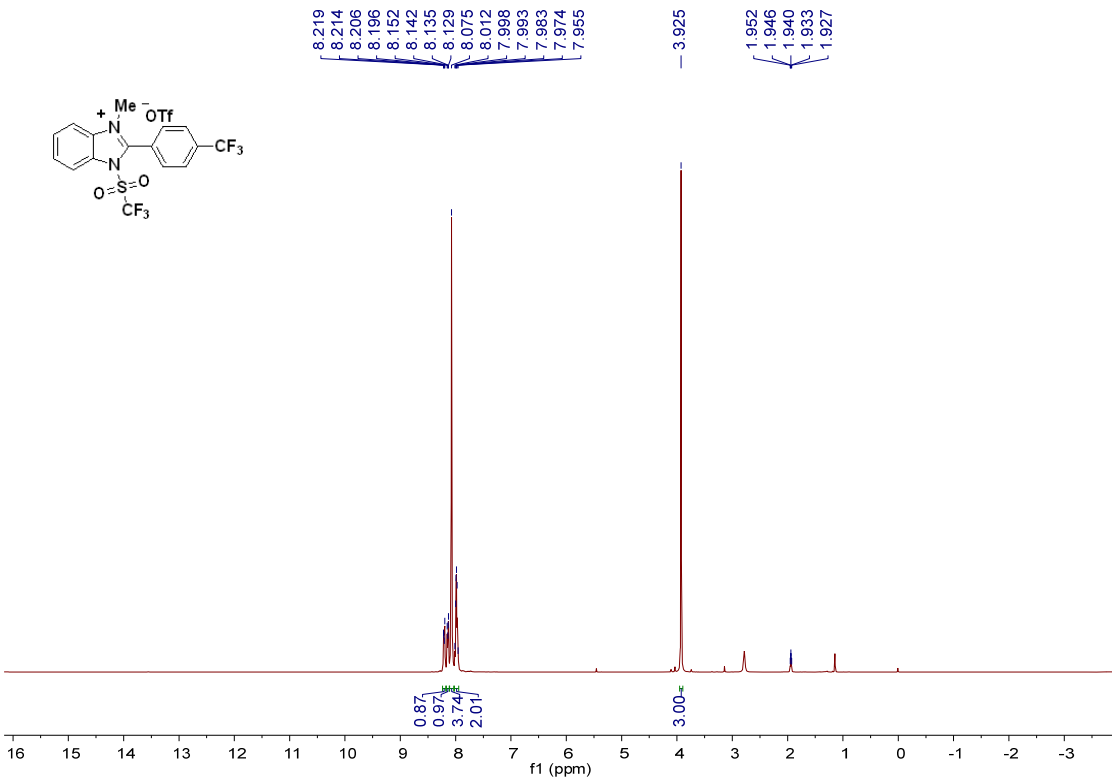
NMR Spectra of product **2b**:

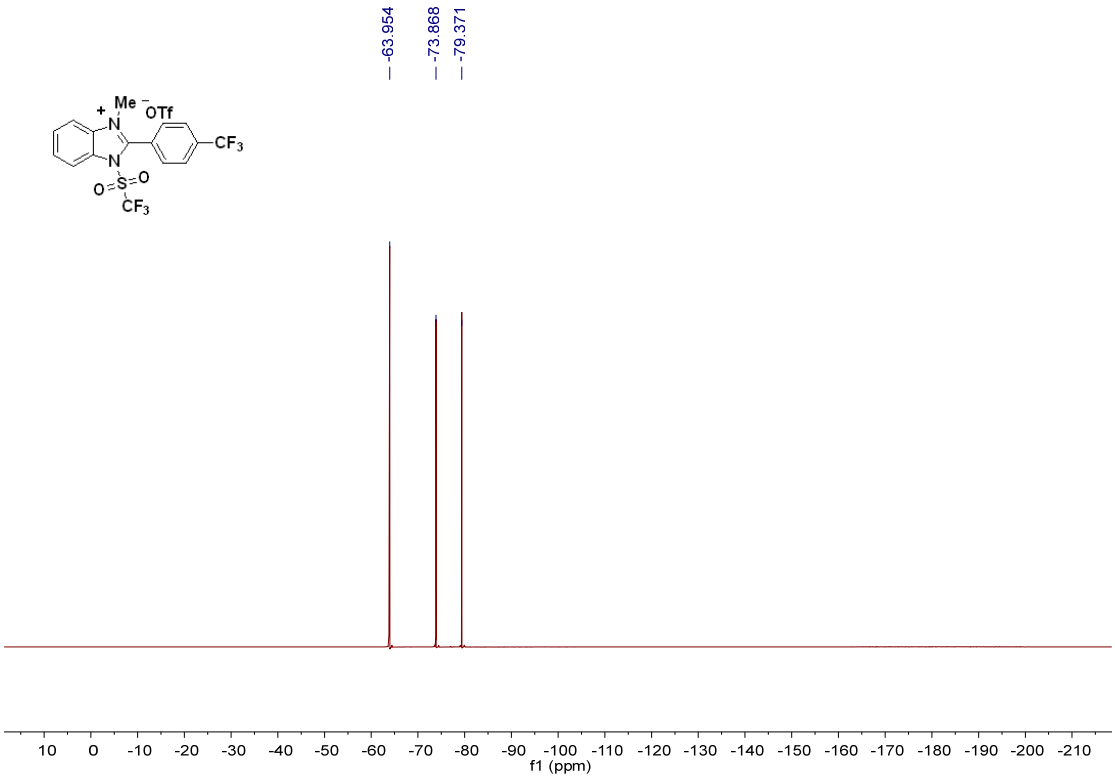


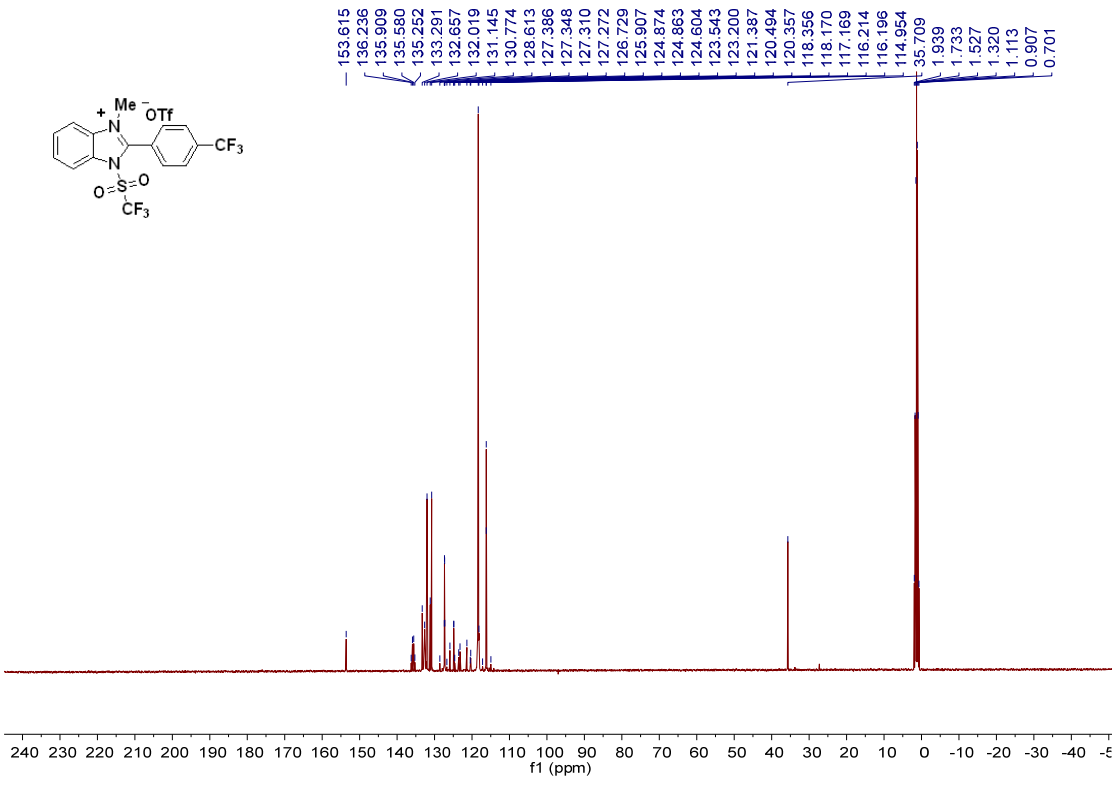




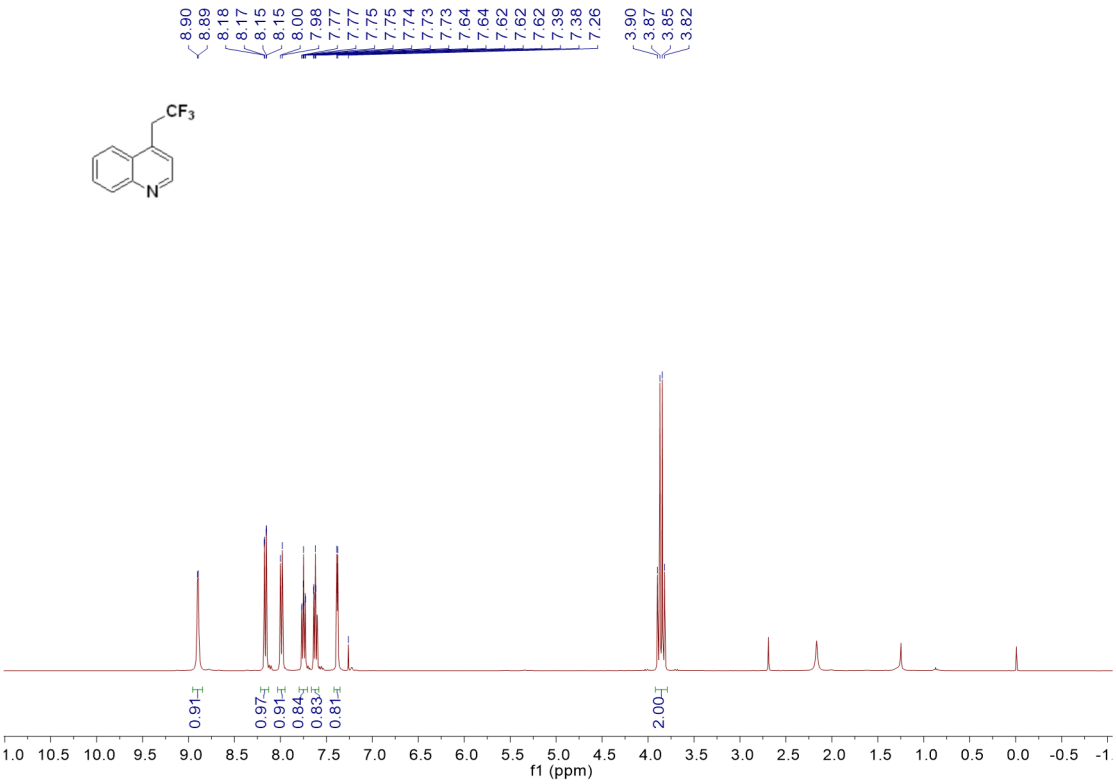
NMR Spectra of product **2c**:

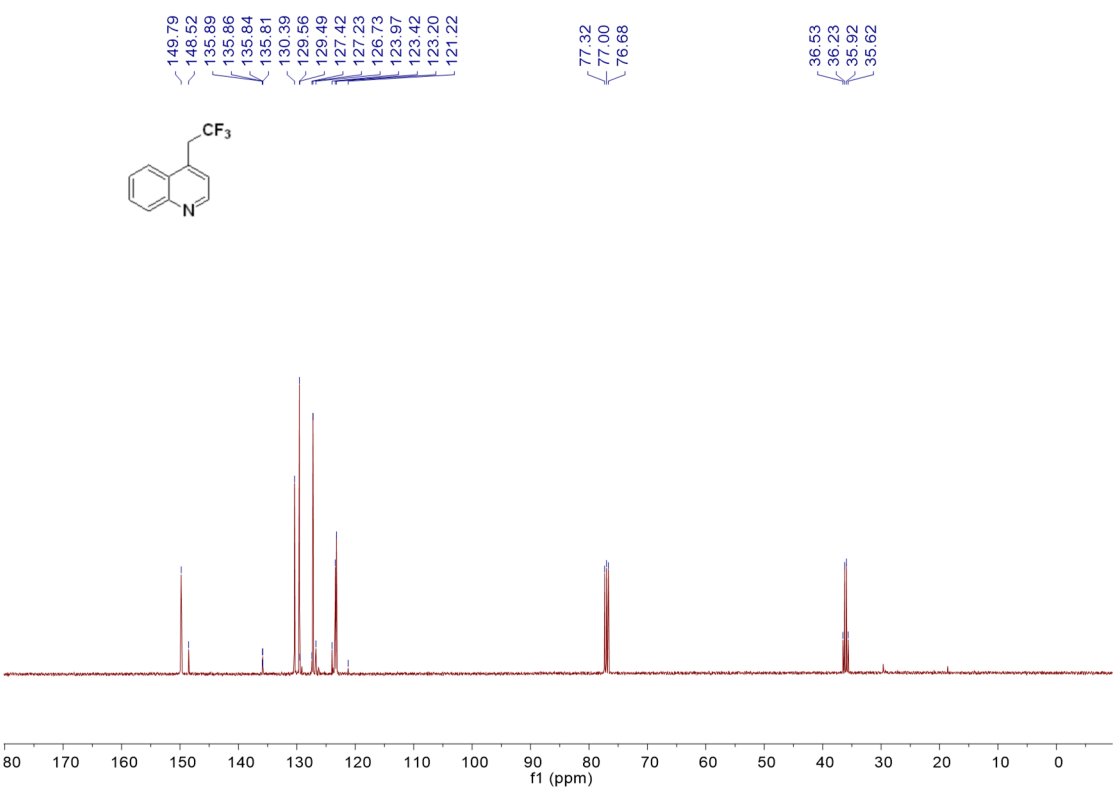


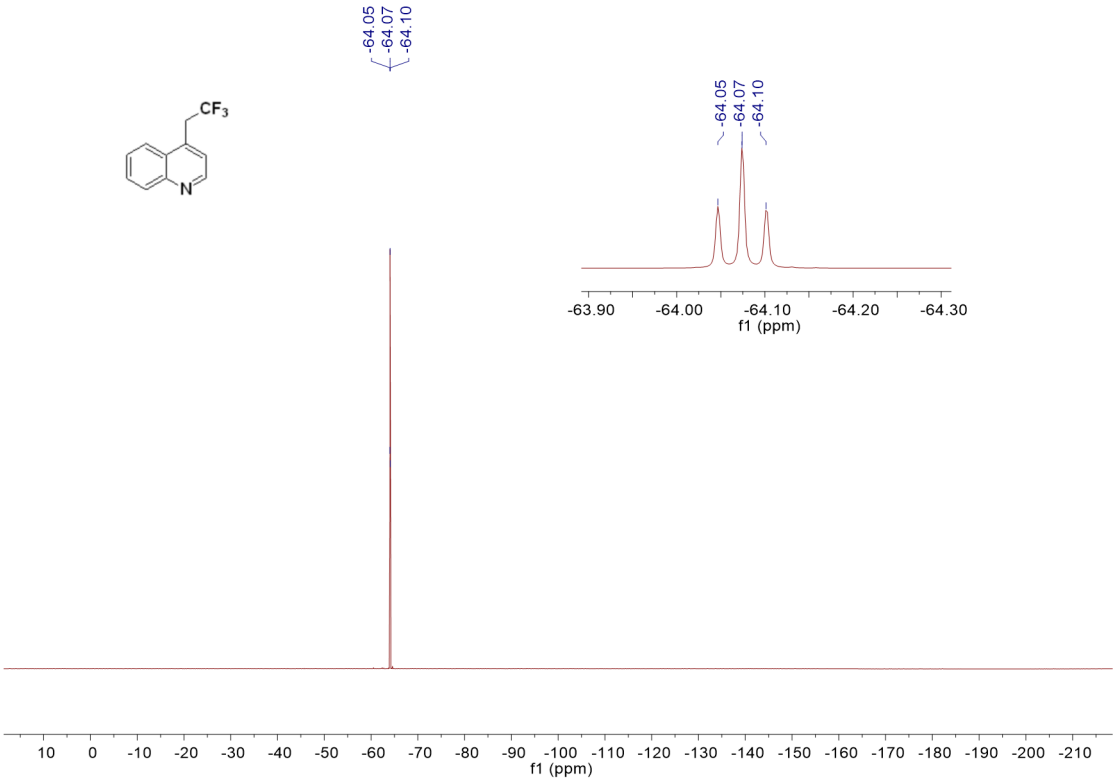




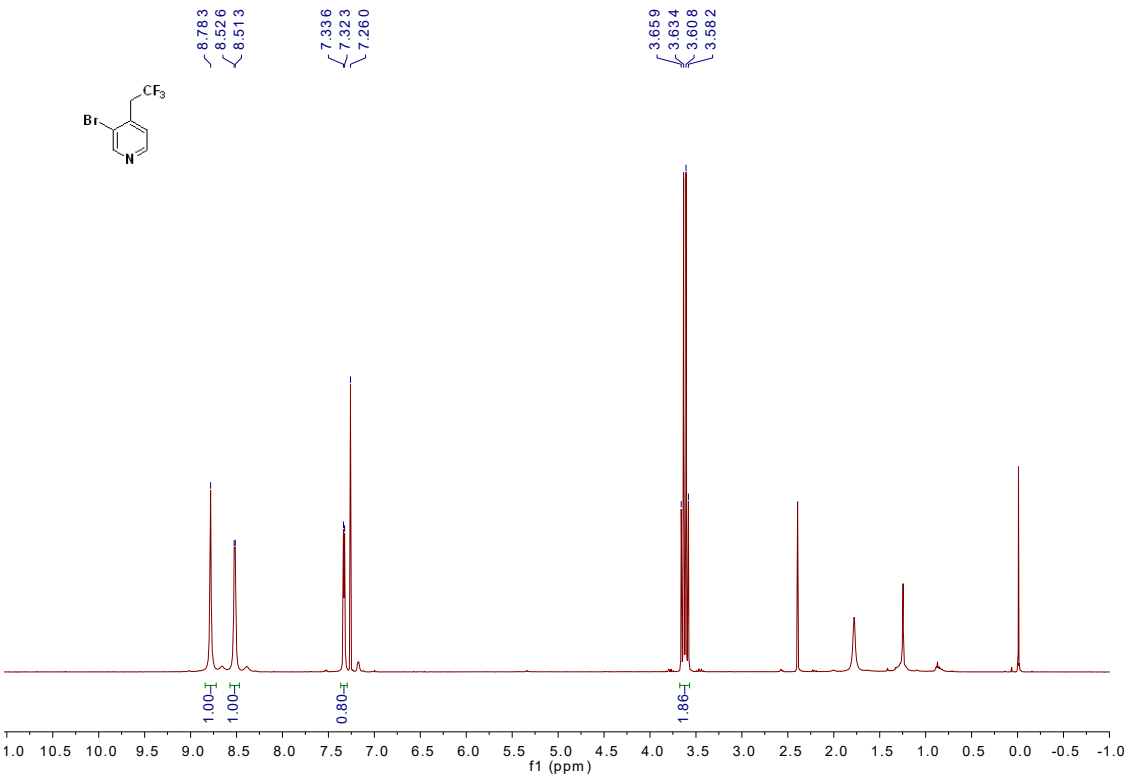
NMR Spectra of product **3**:

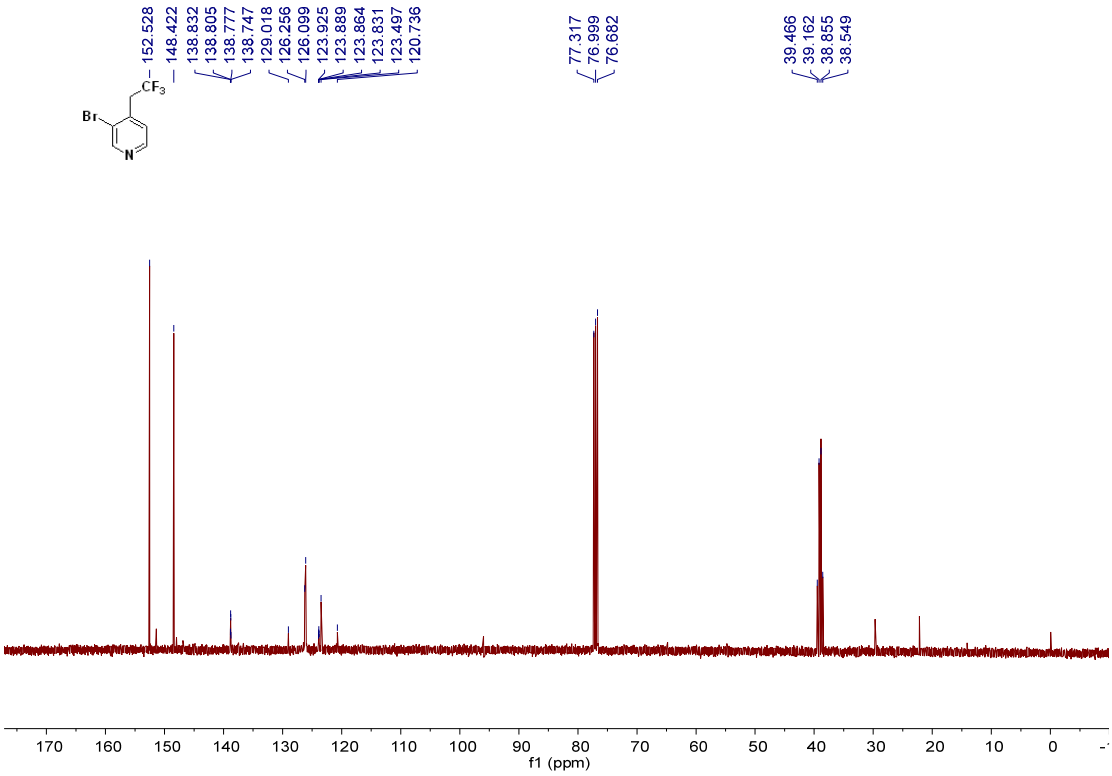

8.90
8.89
8.18
8.17
8.15
8.15
8.00
7.98
7.77
7.77
7.75
7.75
7.74
7.73
7.73
7.64
7.64
7.62
7.62
7.62
7.39
7.38
7.26
3.90
3.87
3.85
3.82
CF3
N
0.91
0.97
0.91
0.84
0.83
0.81
2.00
f1 (ppm)

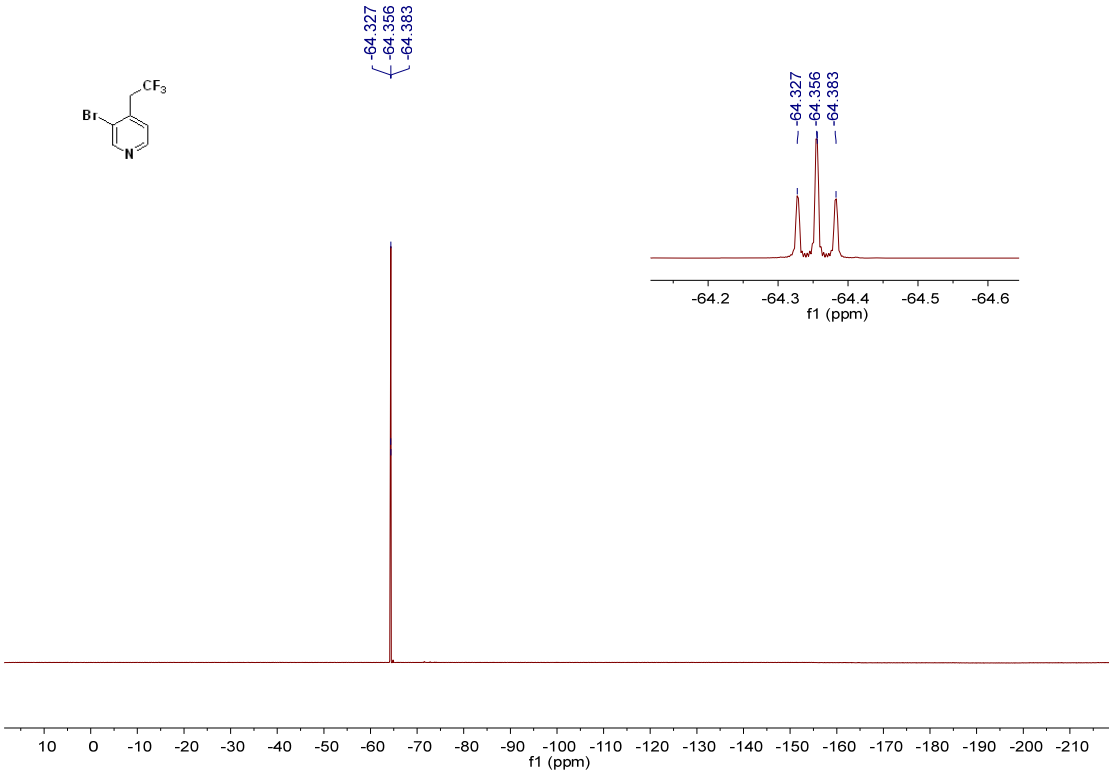

149.79
148.52
135.89
135.86
135.84
135.81
130.39
129.56
129.49
127.42
127.23
126.73
123.97
123.42
123.20
121.22
77.32
77.00
76.68
36.53
36.23
35.92
35.62
CF3
N
f1 (ppm)



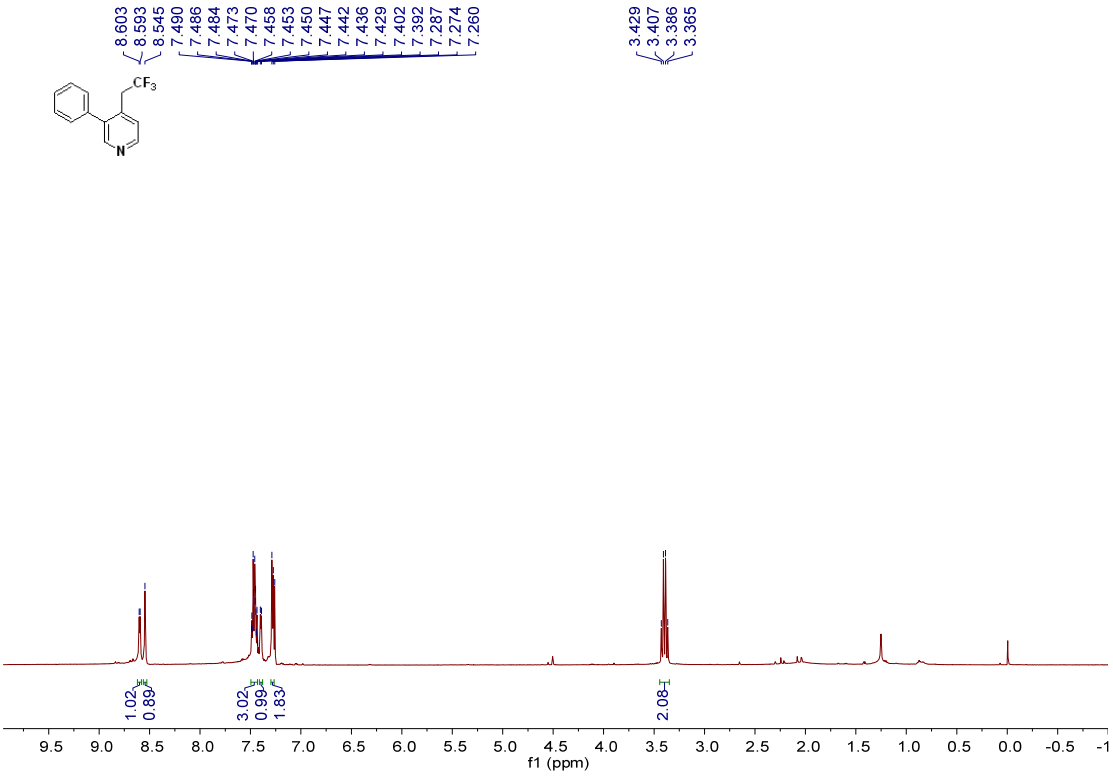
NMR Spectra of product **6**:

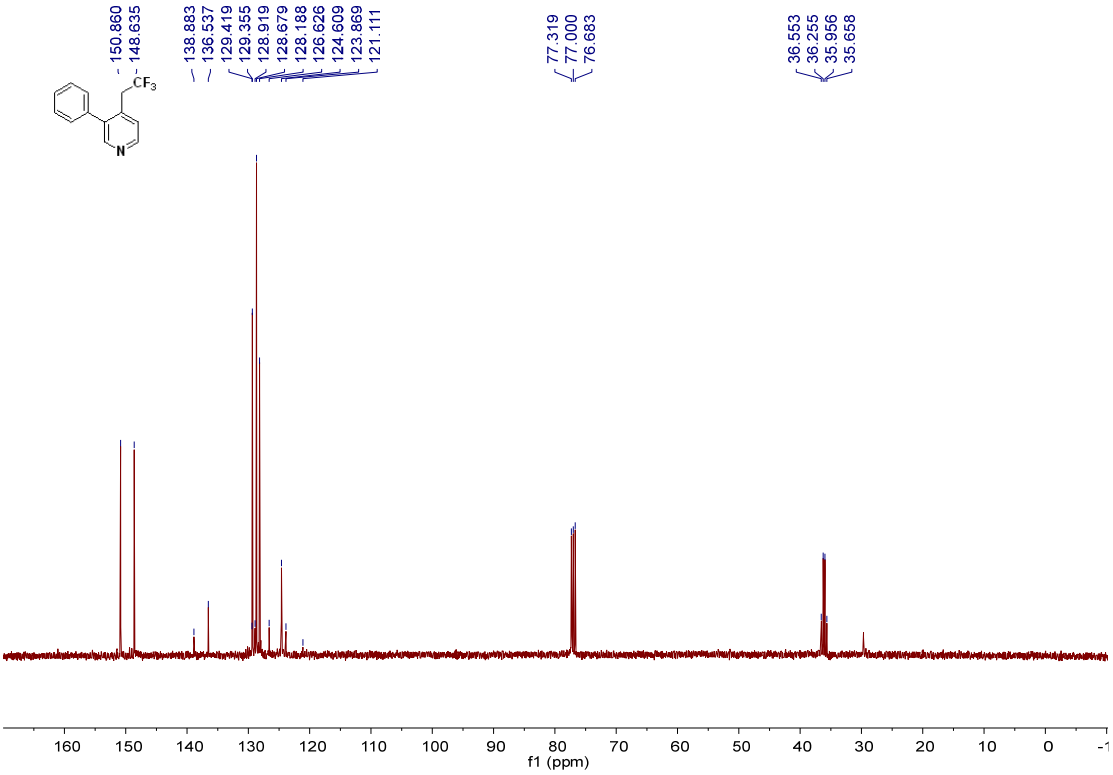


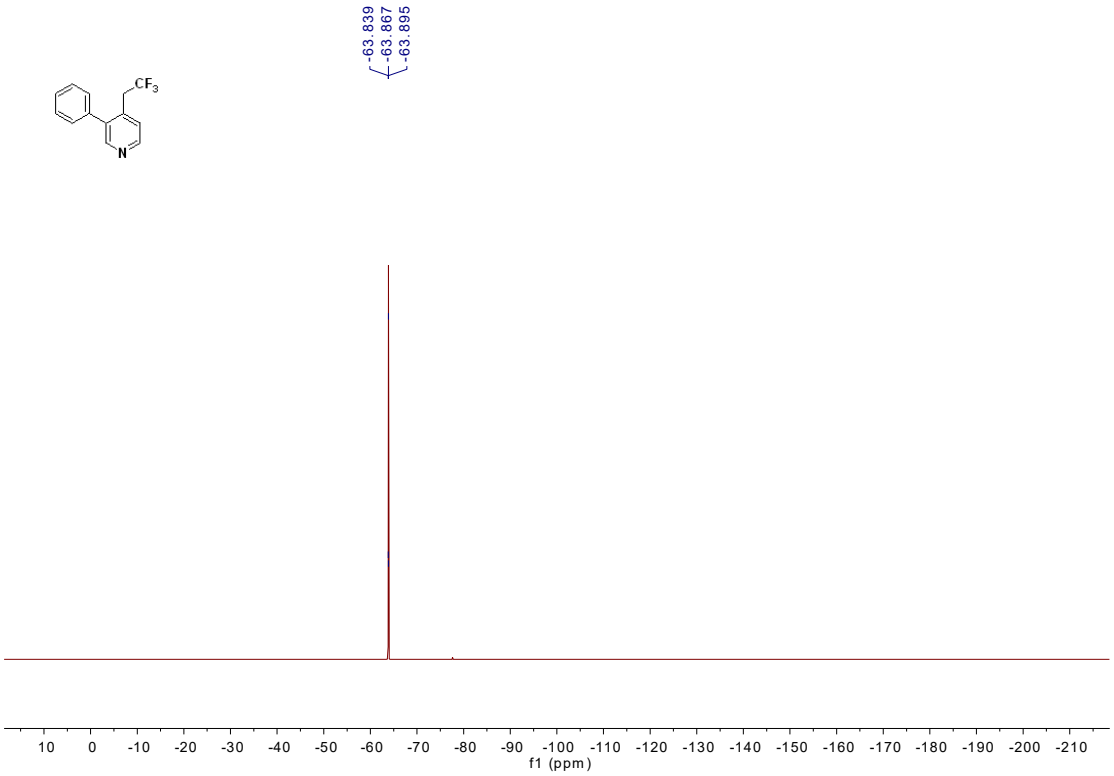




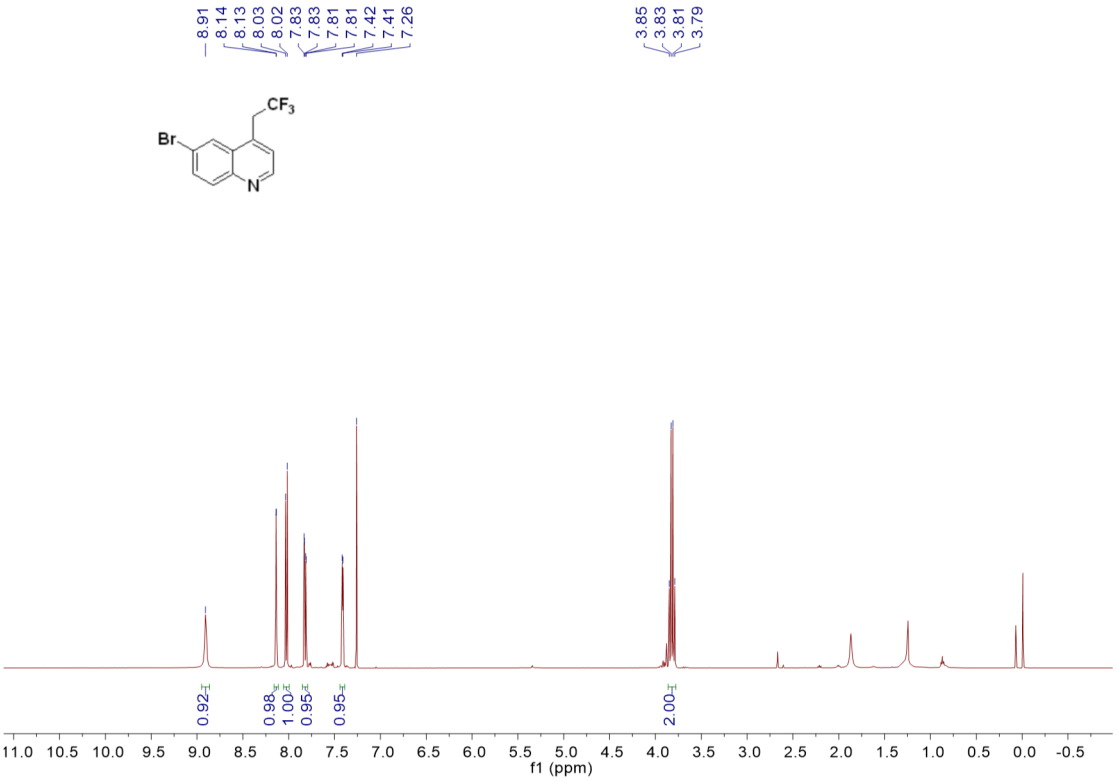
NMR Spectra of product **7**:

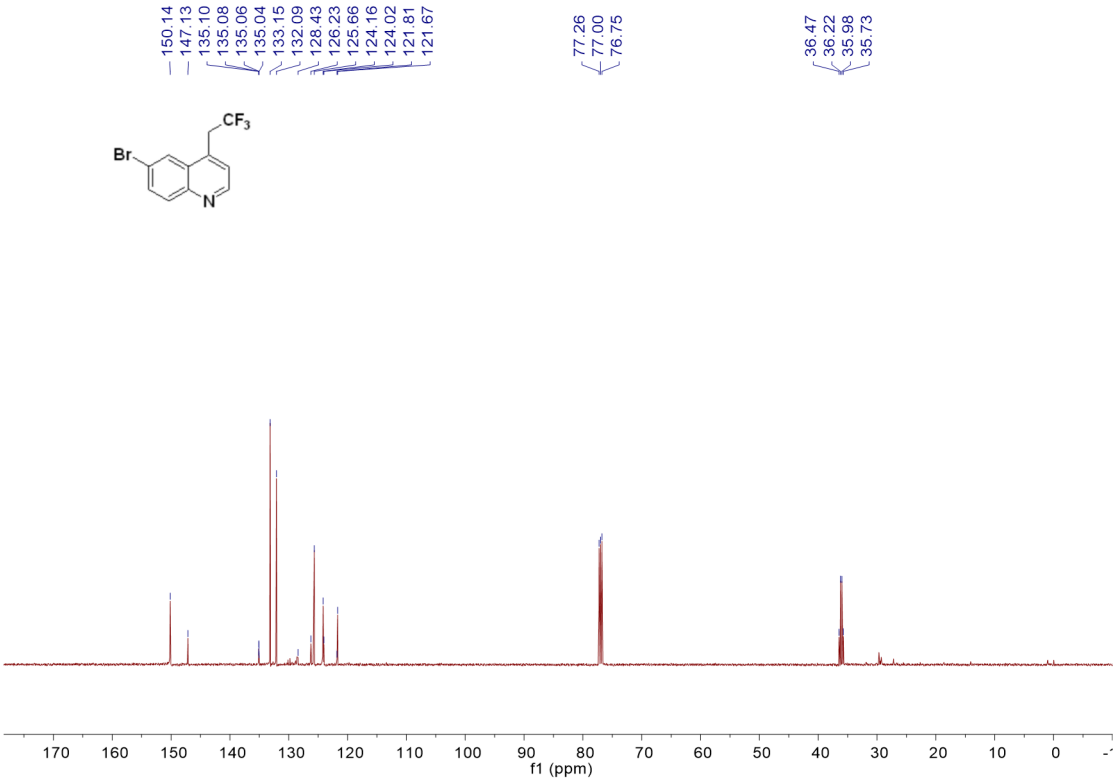

8.603
8.593
8.545
7.490
7.486
7.484
7.473
7.470
7.458
7.453
7.450
7.447
7.442
7.436
7.429
7.402
7.392
7.287
7.274
7.260
3.429
3.407
3.386
3.365
CF3
N
1.02
0.89
3.02
0.99
1.83
2.08
f1 (ppm)

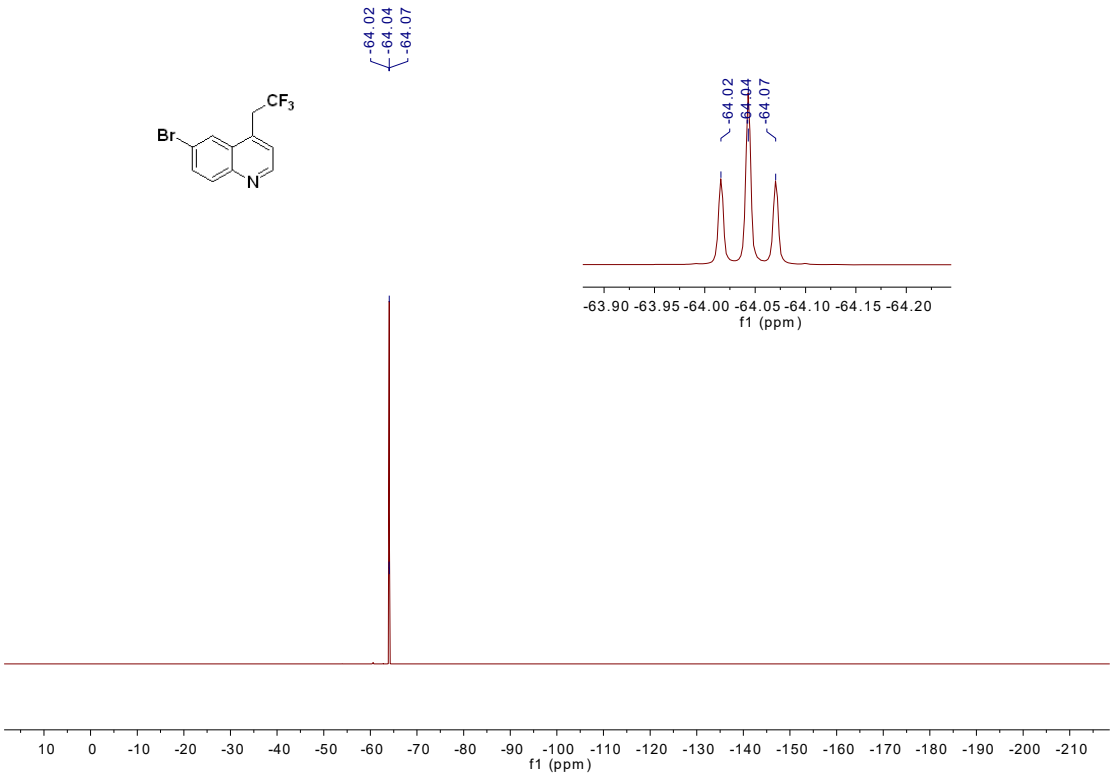

150.860
148.635
138.883
136.537
129.419
129.355
128.919
128.679
128.188
126.626
124.609
123.869
121.111
77.319
77.000
76.683
36.553
36.255
35.956
35.658
CF3
N
f1 (ppm)



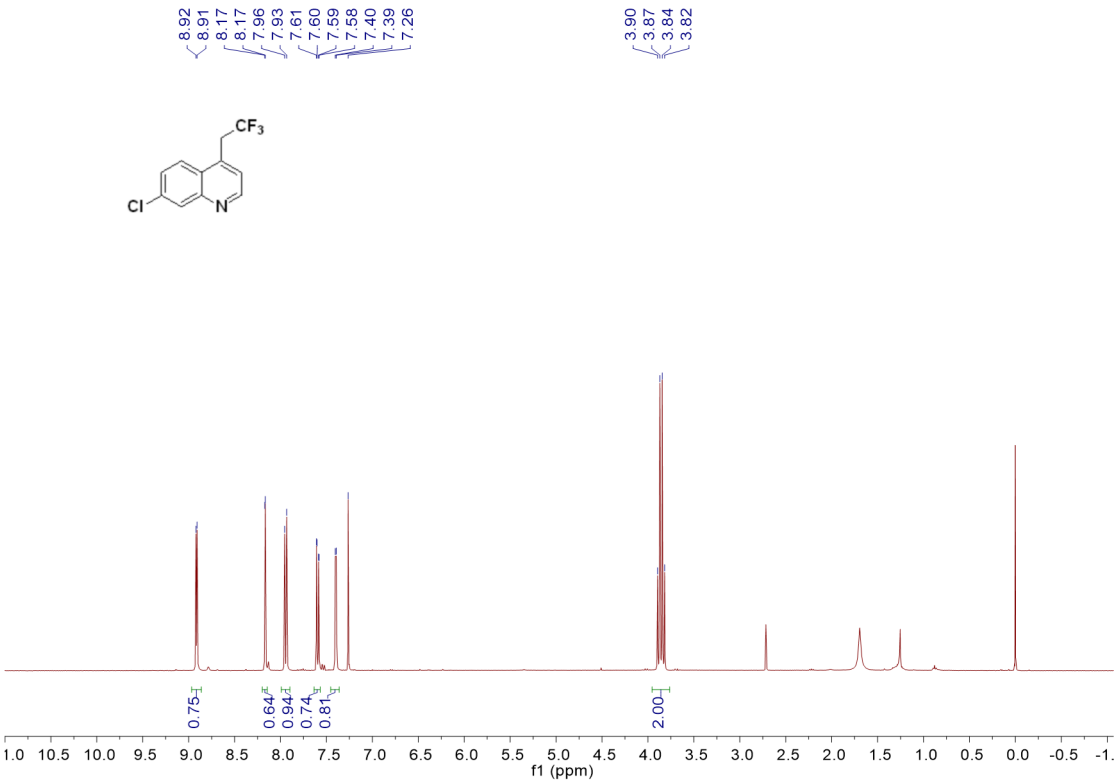
NMR Spectra of product **8**:

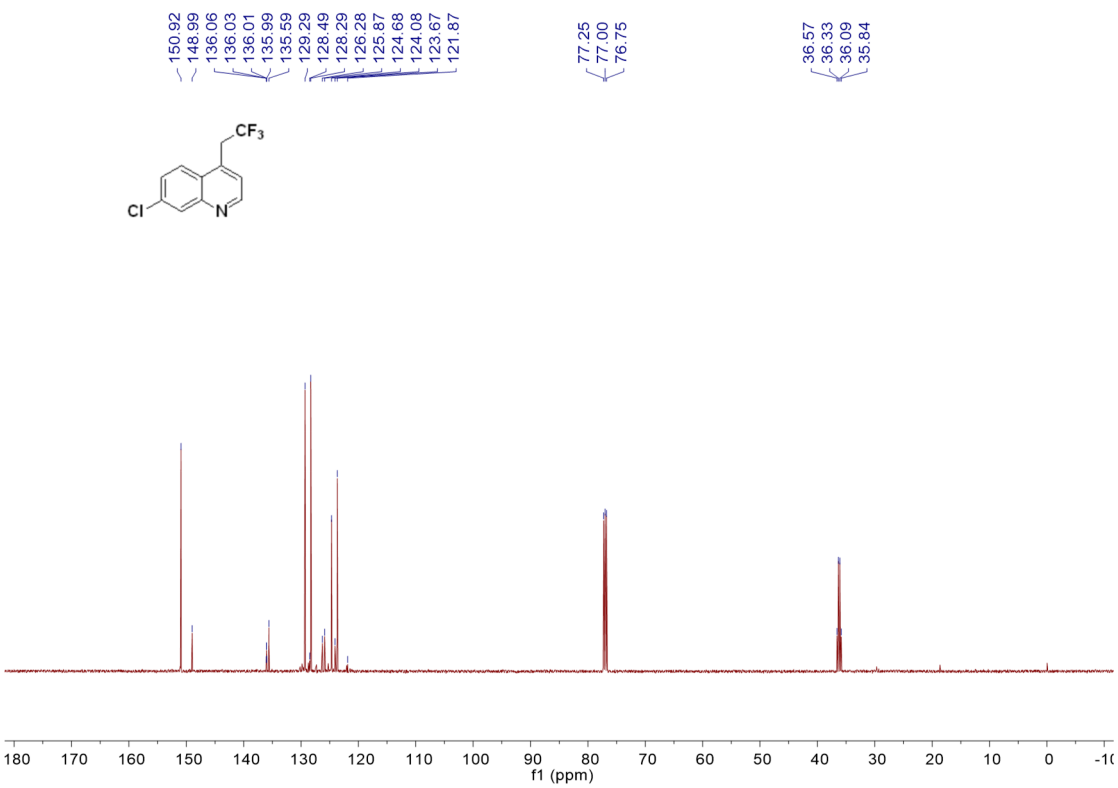


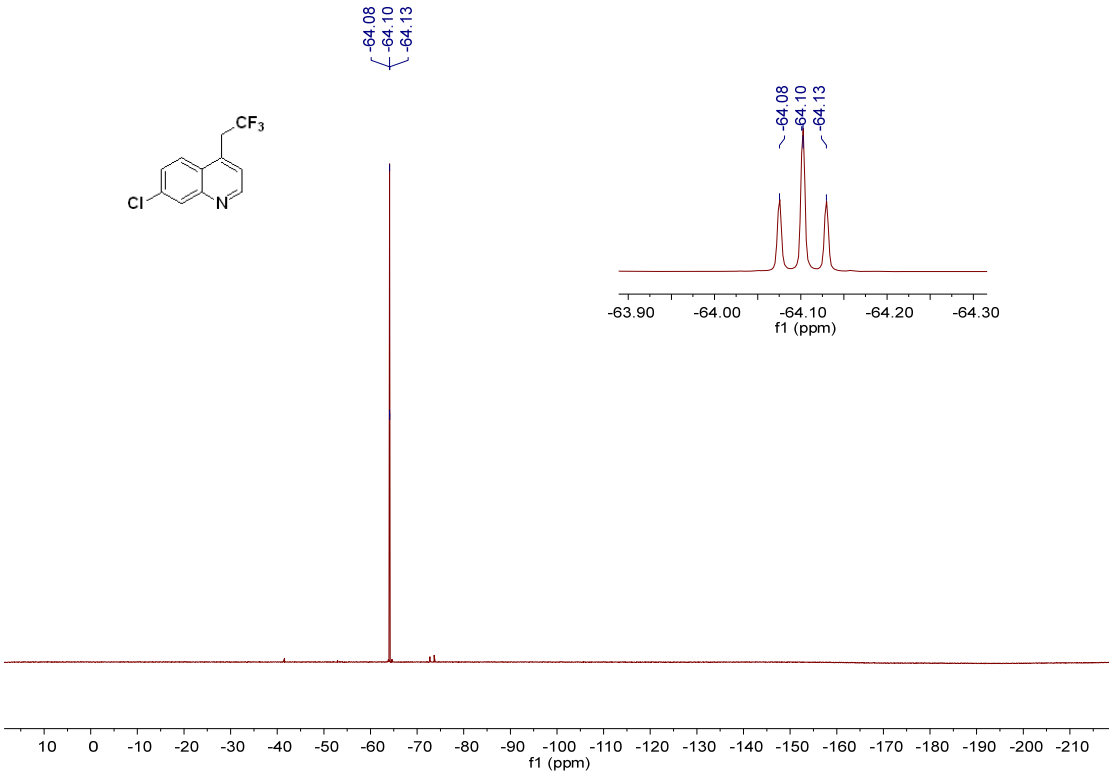




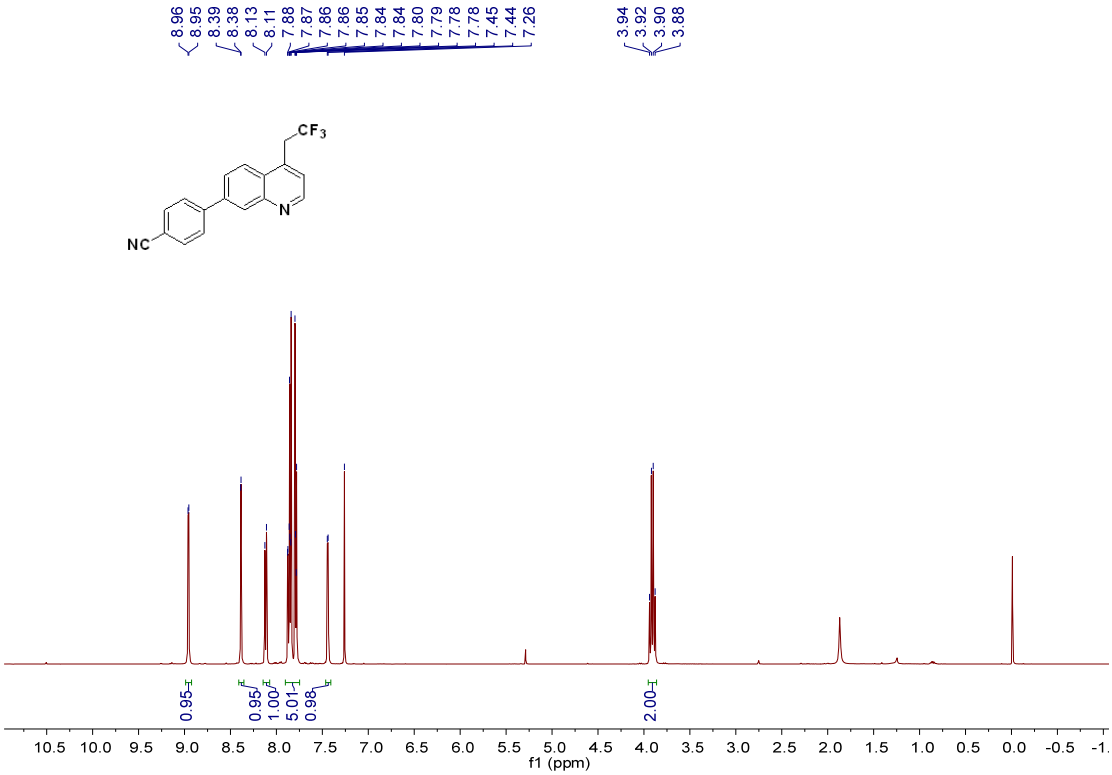
NMR Spectra of product **9**:

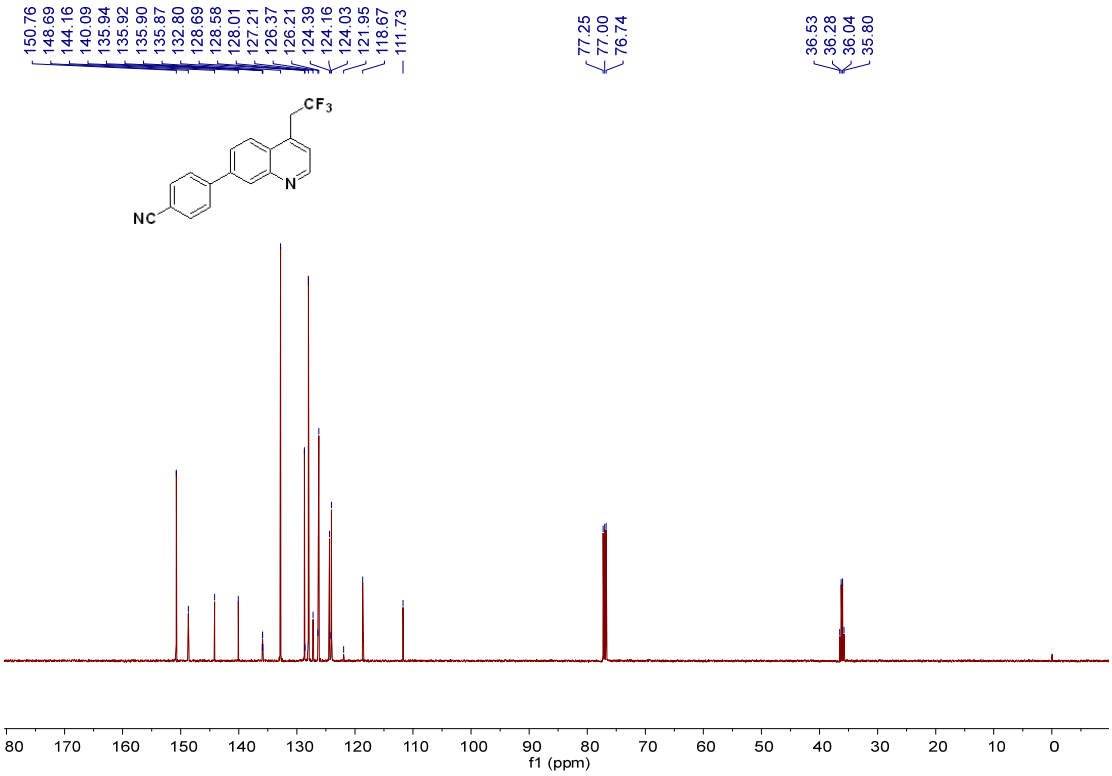

8.92
8.91
8.17
8.17
7.96
7.93
7.61
7.60
7.59
7.58
7.40
7.39
7.26
3.90
3.87
3.84
3.82
CF3
Cl
N
0.75
0.64
0.94
0.74
0.81
2.00
f1 (ppm)

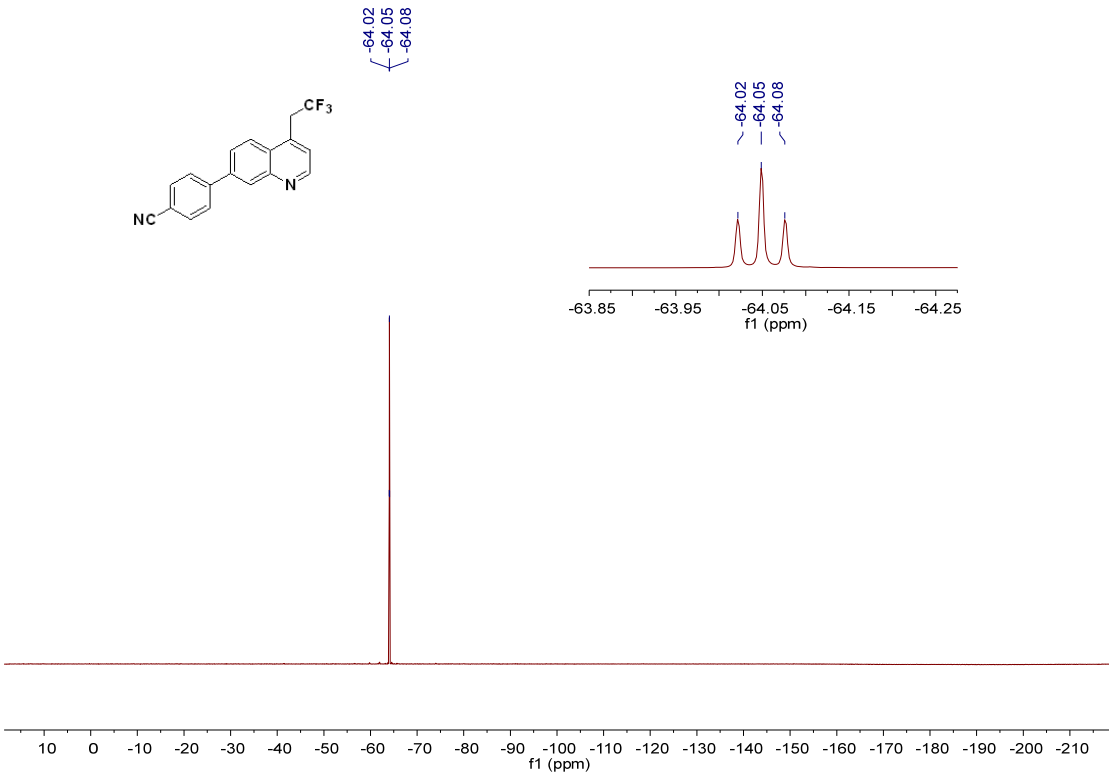

150.92
148.99
136.06
136.03
136.01
135.99
135.59
129.29
128.49
128.29
126.28
125.87
124.68
124.08
123.67
121.87
77.25
77.00
76.75
36.57
36.33
36.09
35.84
CF3
Cl
N
f1 (ppm)



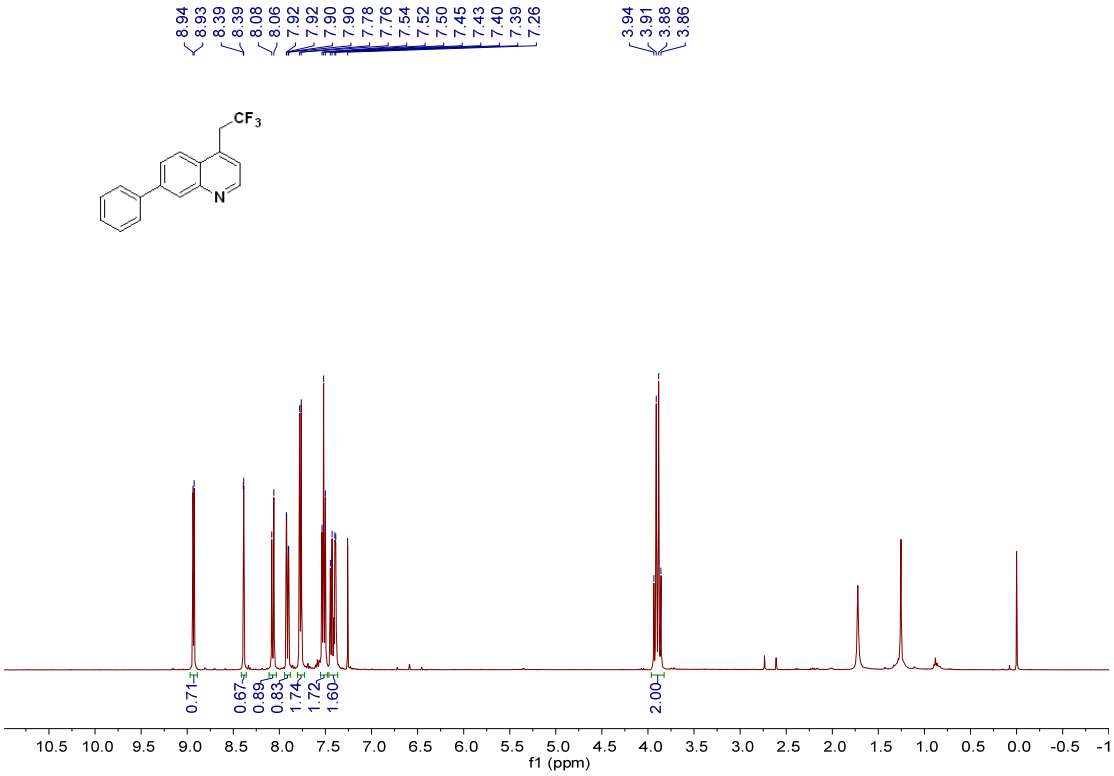
NMR Spectra of product **10**:

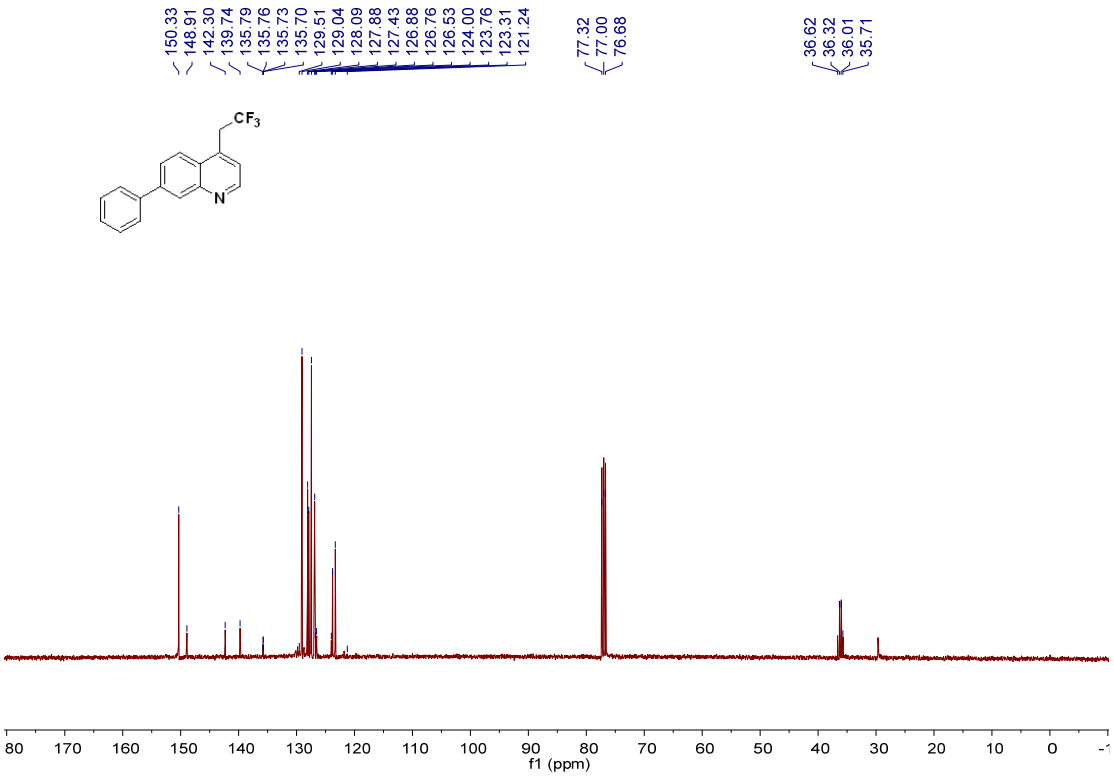


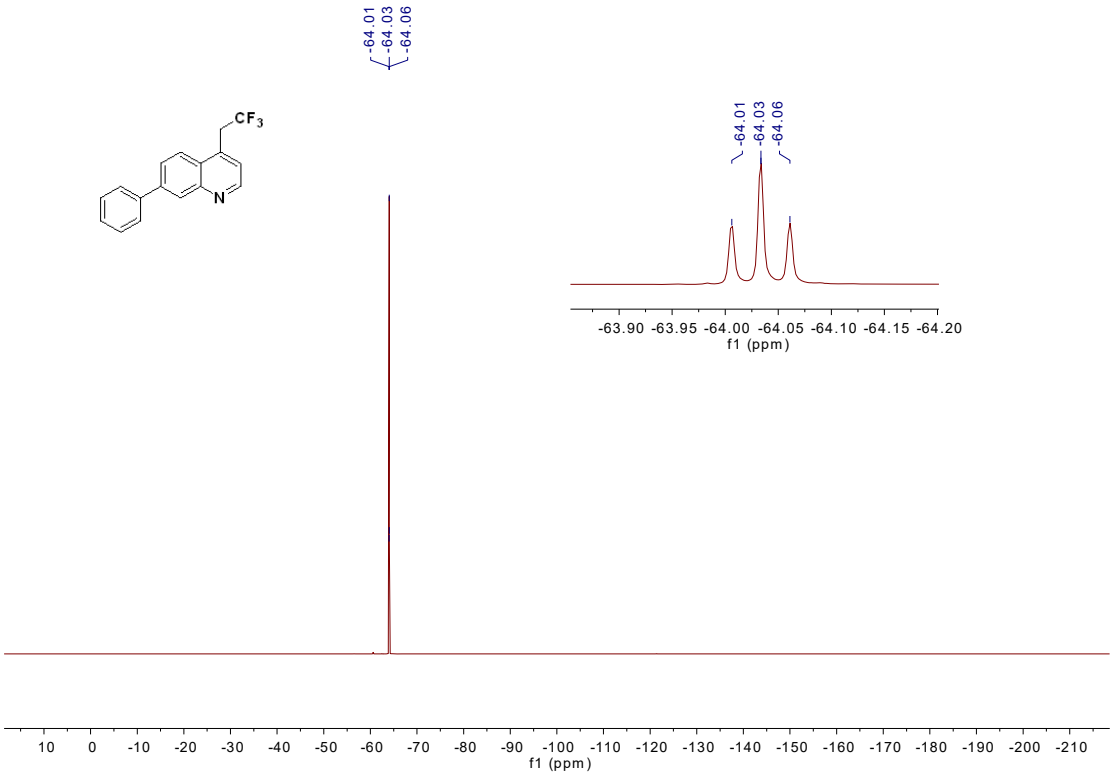




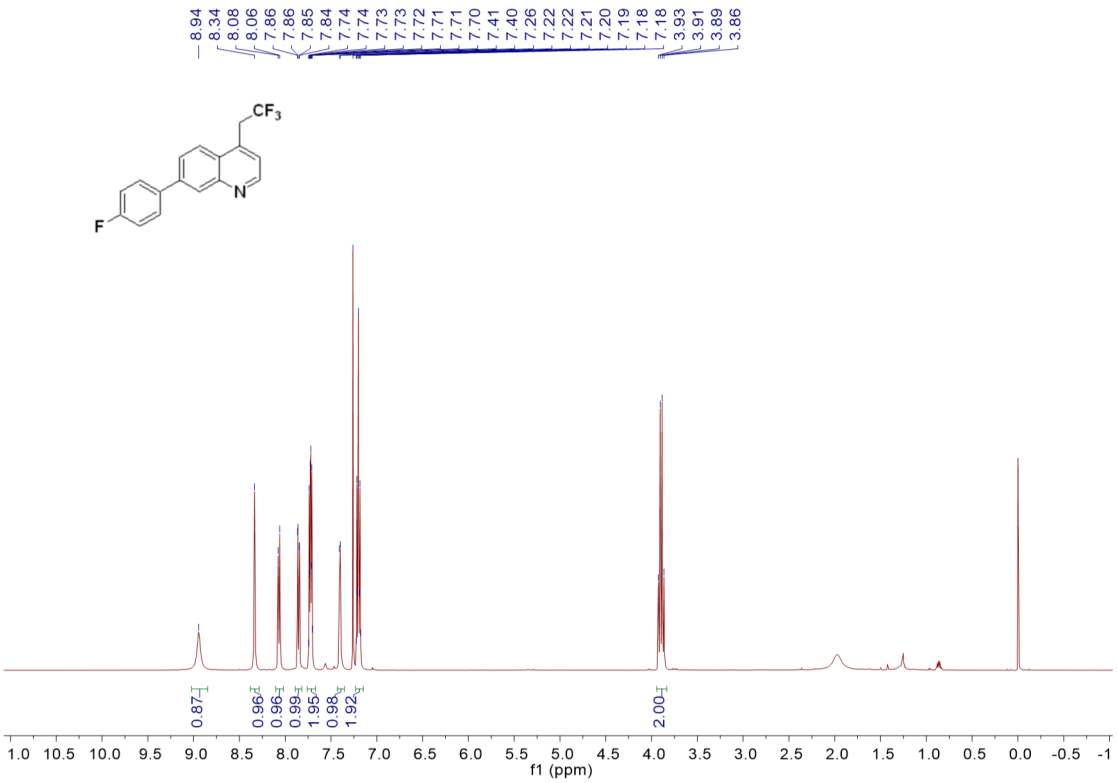
NMR Spectra of product **11**:

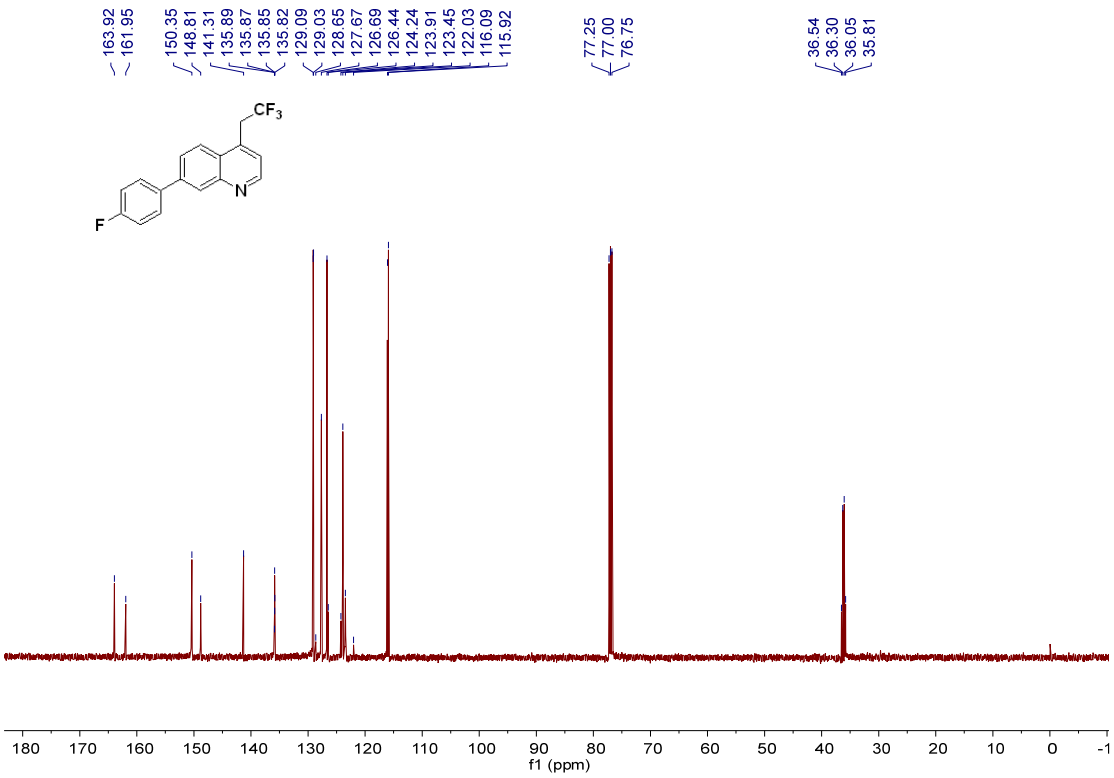

8.94
8.93
8.39
8.39
8.08
8.06
7.92
7.92
7.90
7.90
7.78
7.76
7.54
7.52
7.50
7.45
7.43
7.40
7.39
7.26
3.94
3.91
3.88
3.86
CF3
N
0.71
0.67
0.89
0.83
1.74
1.72
1.60
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

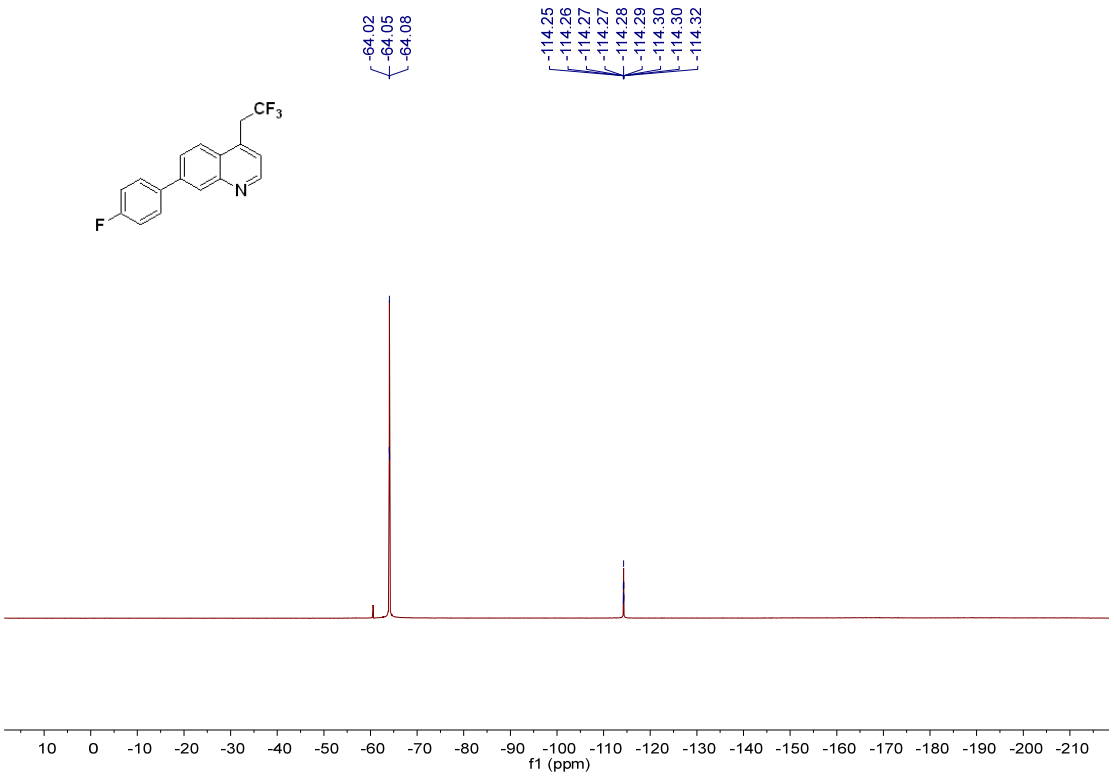

150.33
148.91
142.30
139.74
135.79
135.76
135.73
135.70
129.51
129.04
128.09
127.88
127.43
126.88
126.76
126.53
124.00
123.76
123.31
121.24
77.32
77.00
76.68
36.62
36.32
36.01
35.71
CF3
N
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



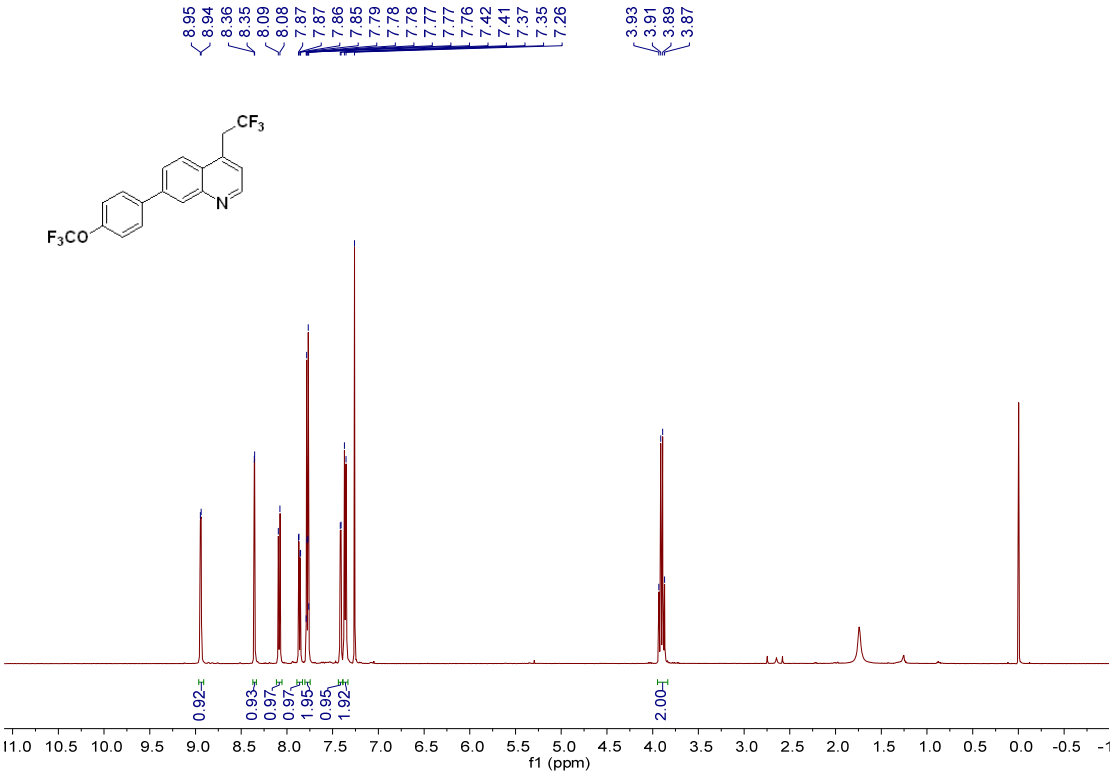
NMR Spectra of product **12**:

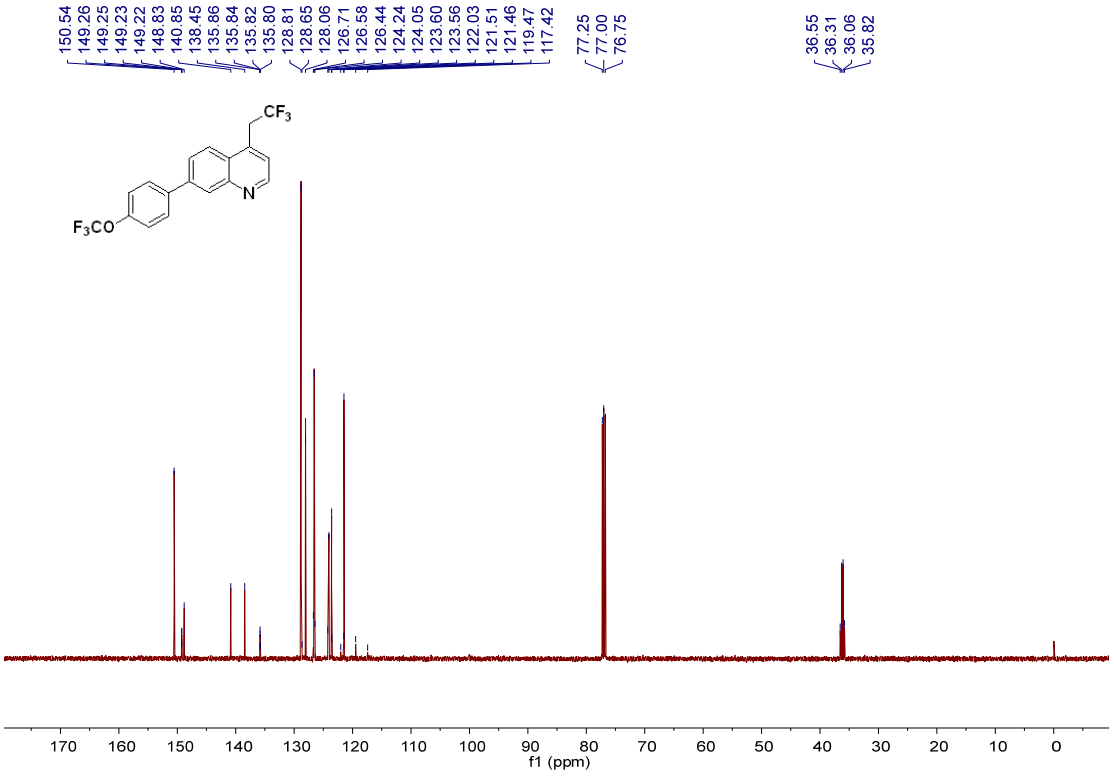


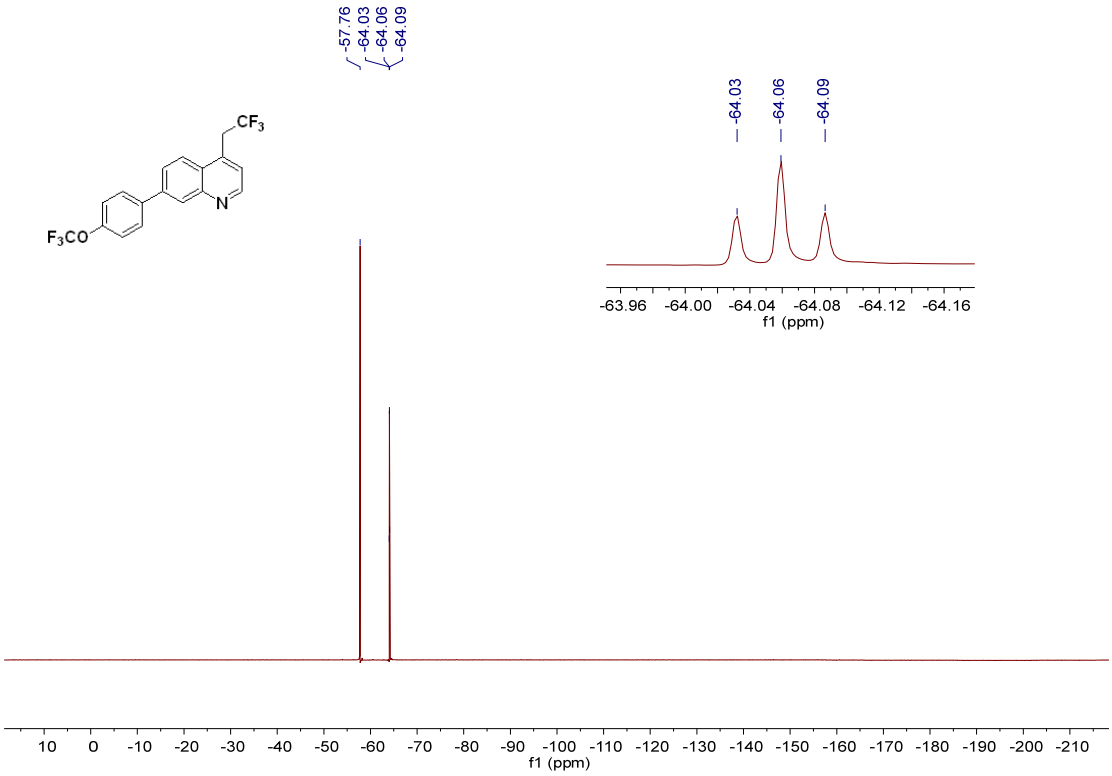




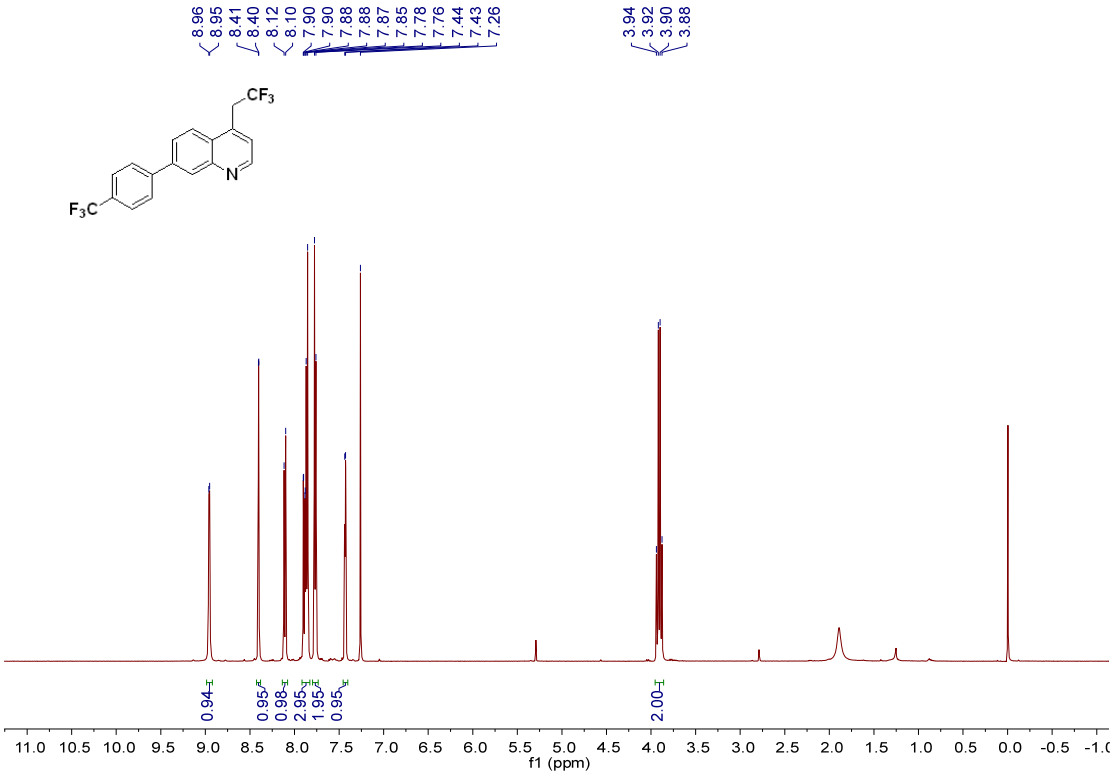
NMR Spectra of product **13**:

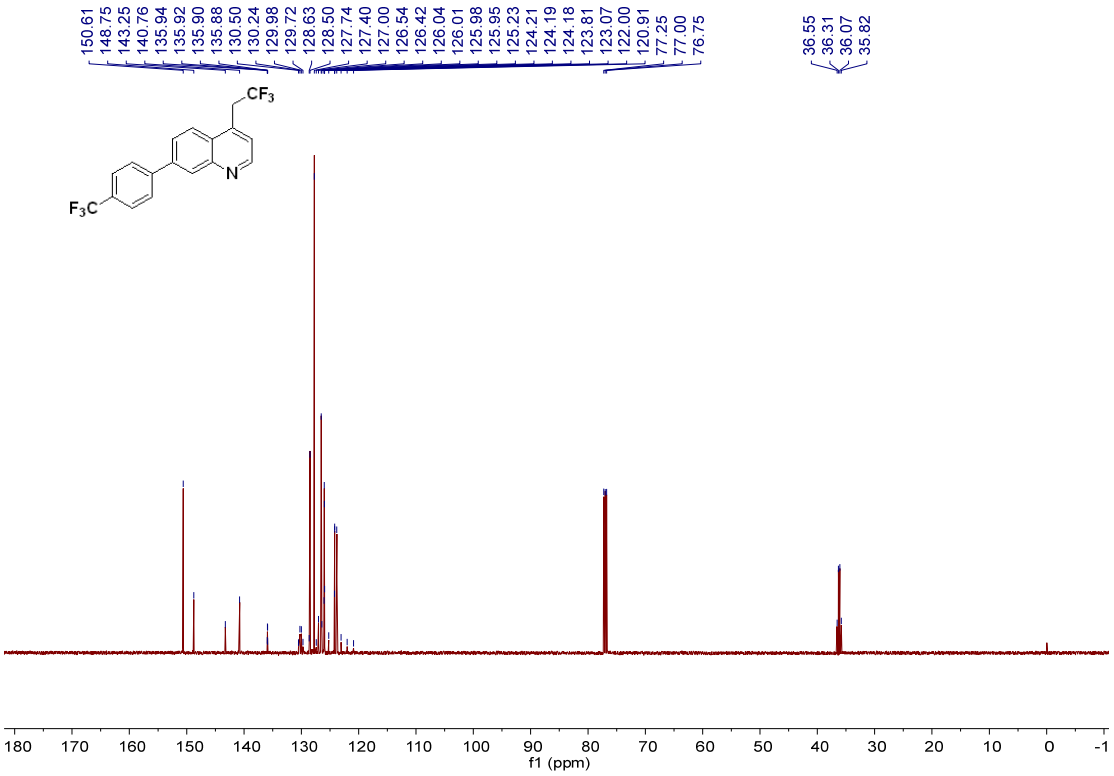

8.95
8.94
8.36
8.35
8.09
8.08
7.87
7.87
7.86
7.85
7.79
7.78
7.78
7.77
7.77
7.76
7.42
7.41
7.37
7.35
7.26
3.93
3.91
3.89
3.87
CF3
F3CO
N
0.92
0.93
0.97
0.97
1.95
0.95
1.92
2.00
f1 (ppm)

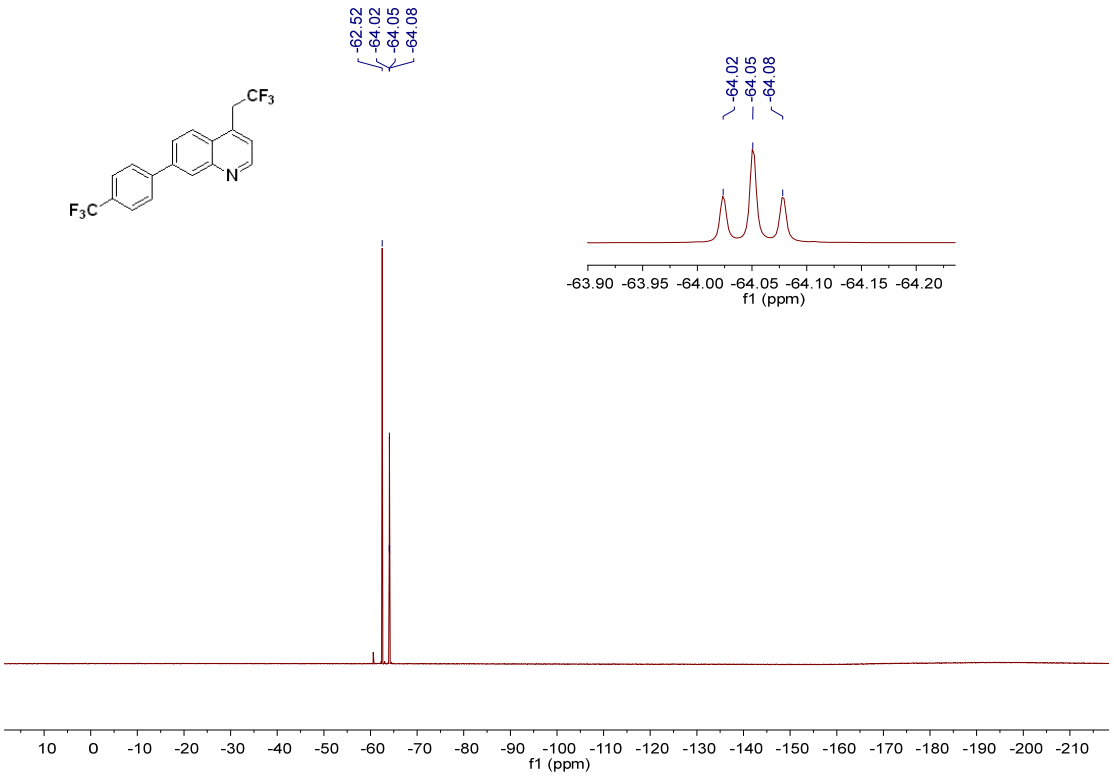

150.54
149.26
149.25
149.23
149.22
148.83
140.85
138.45
135.86
135.84
135.82
135.80
128.81
128.65
128.06
126.71
126.58
126.44
124.24
124.05
123.60
123.56
122.03
121.51
121.46
119.47
117.42
77.25
77.00
76.75
36.55
36.31
36.06
35.82
CF3
F3CO
N
f1 (ppm)



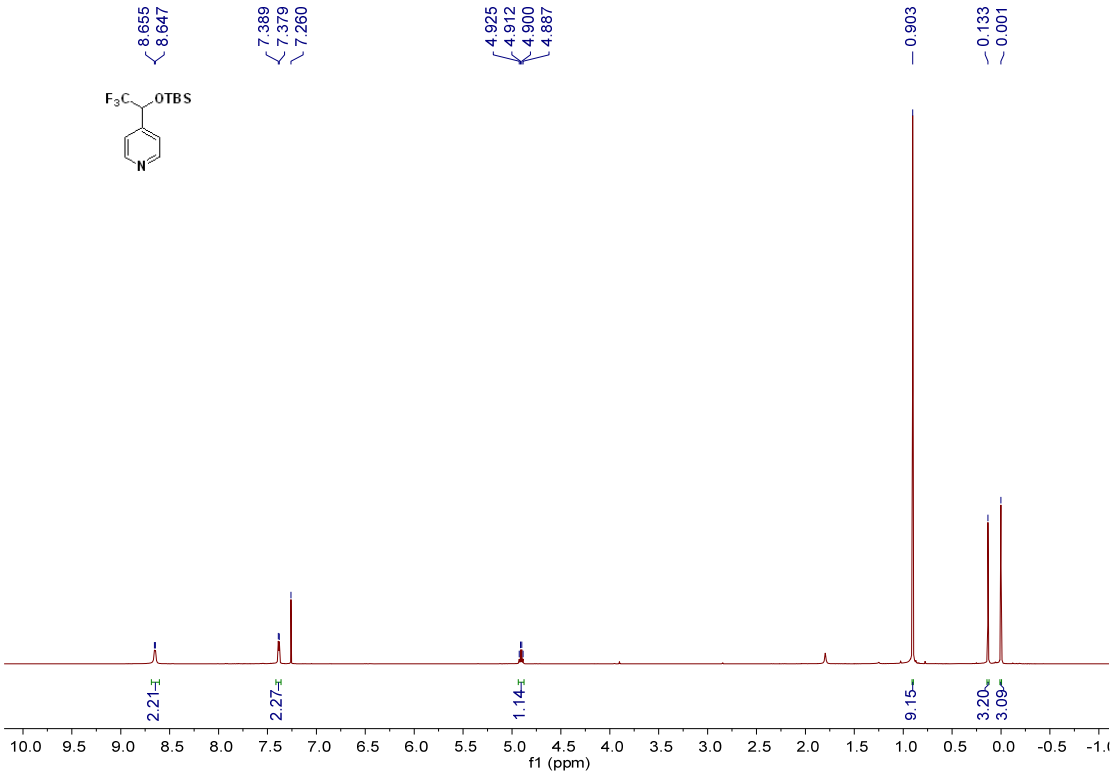
NMR Spectra of product **14**:

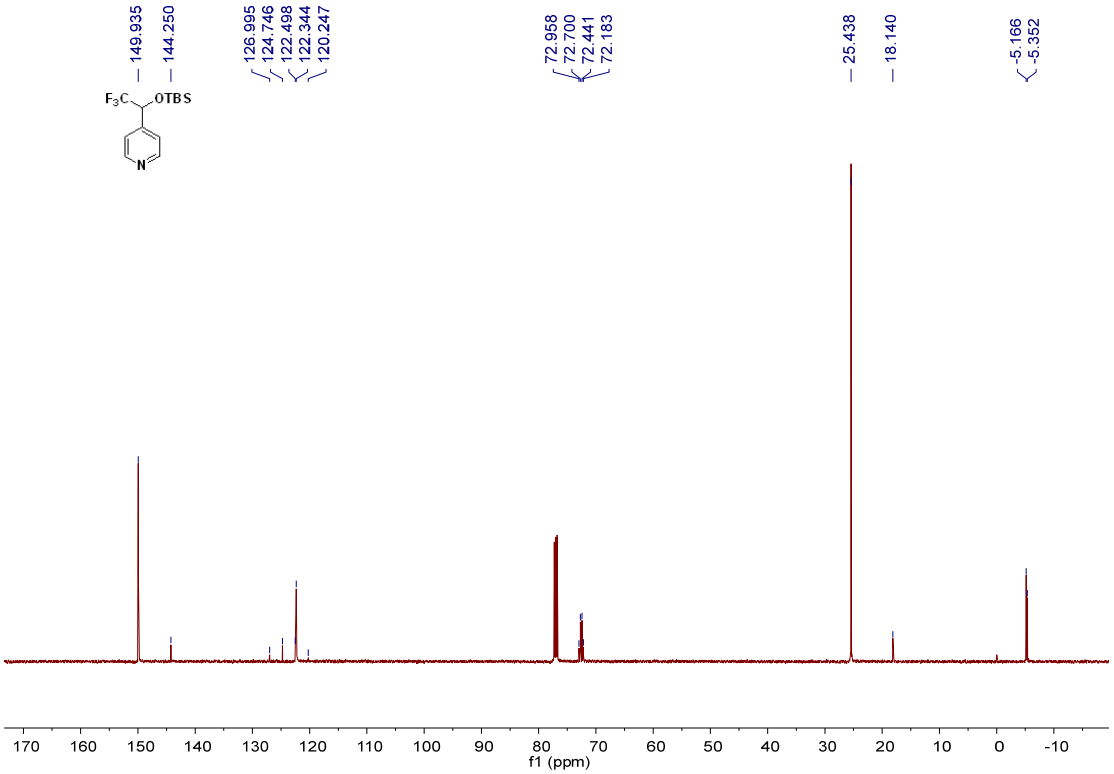


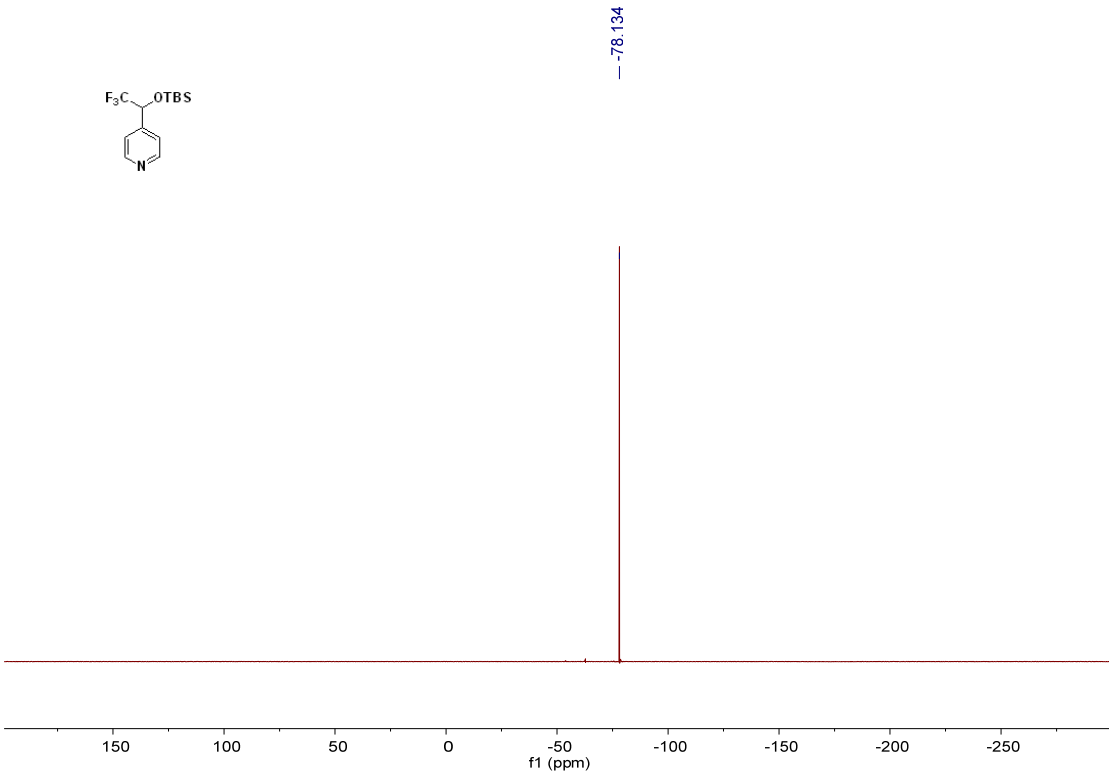




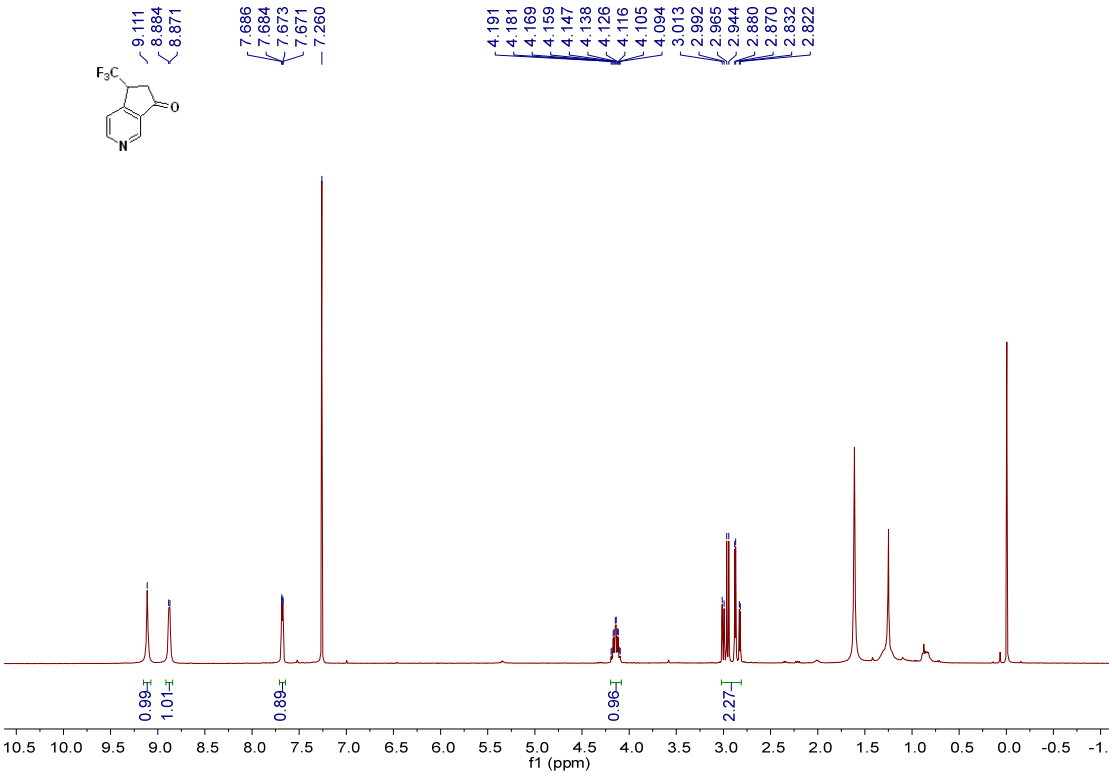
NMR Spectra of product **17**:

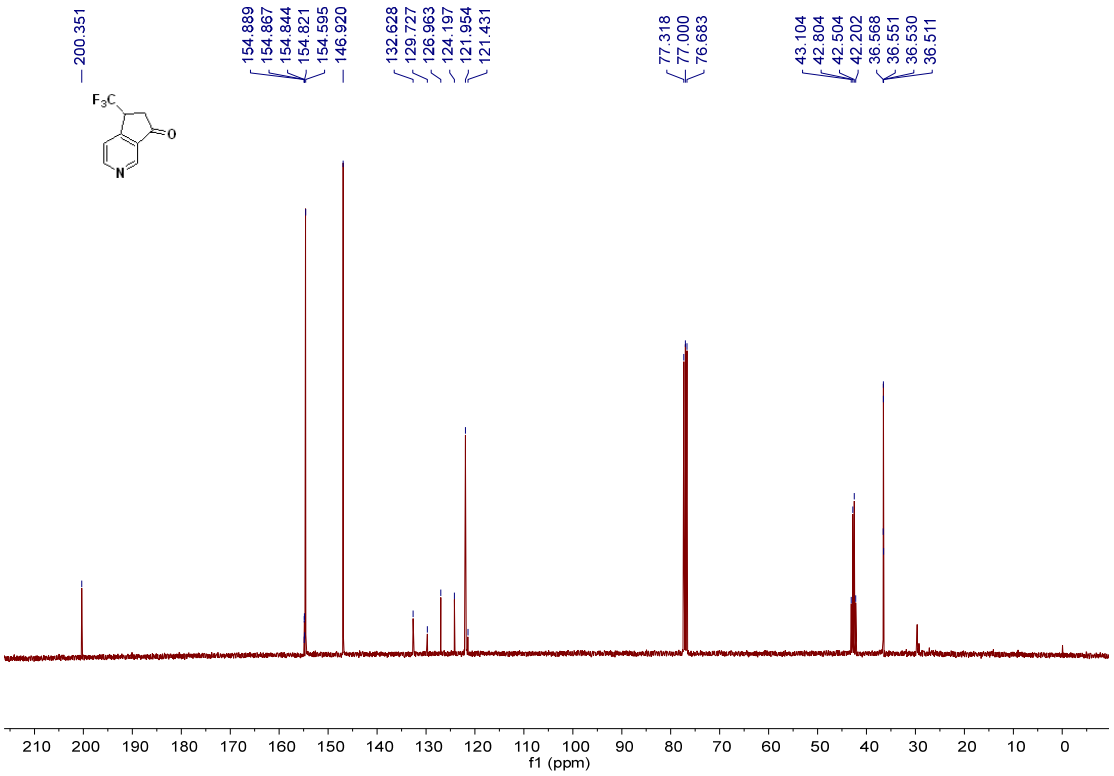

8.655
8.647
7.389
7.379
7.260
4.925
4.912
4.900
4.887
0.903
0.133
0.001
F3C
OTBS
N
2.21
2.27
1.14
9.15
3.20
3.09
f1 (ppm)

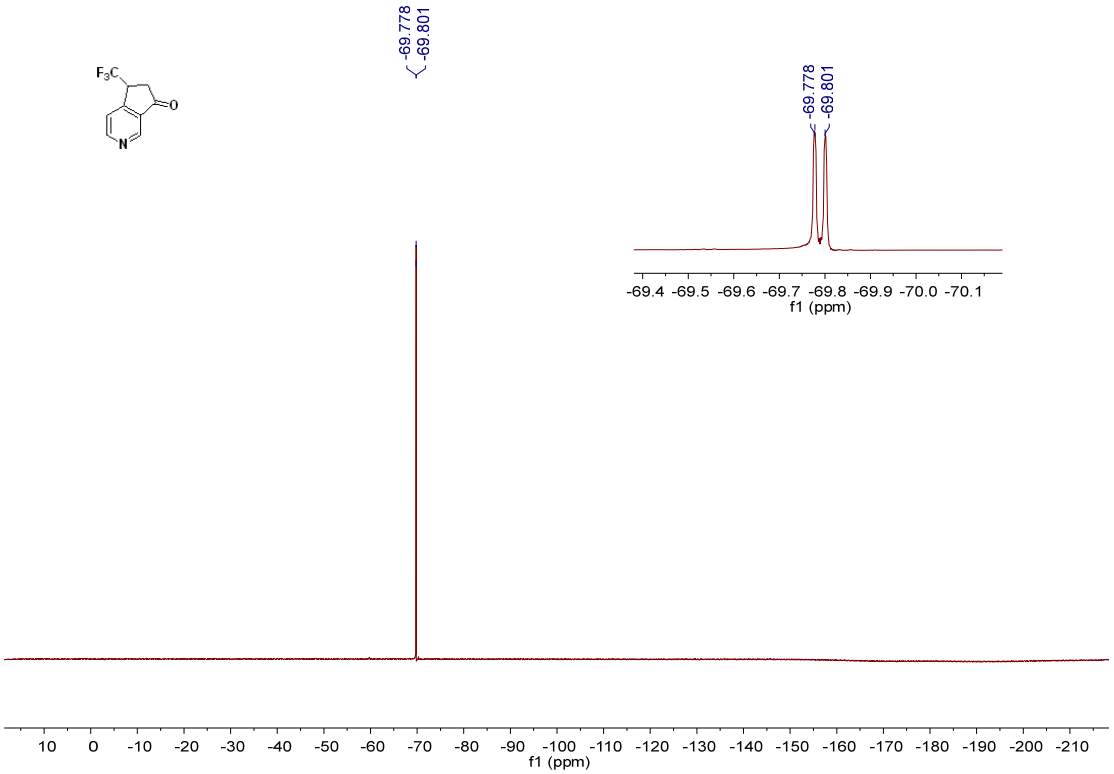

149.935
144.250
126.995
124.746
122.498
122.344
120.247
72.958
72.700
72.441
72.183
25.438
18.140
-5.166
-5.352
F3C
OTBS
N
f1 (ppm)



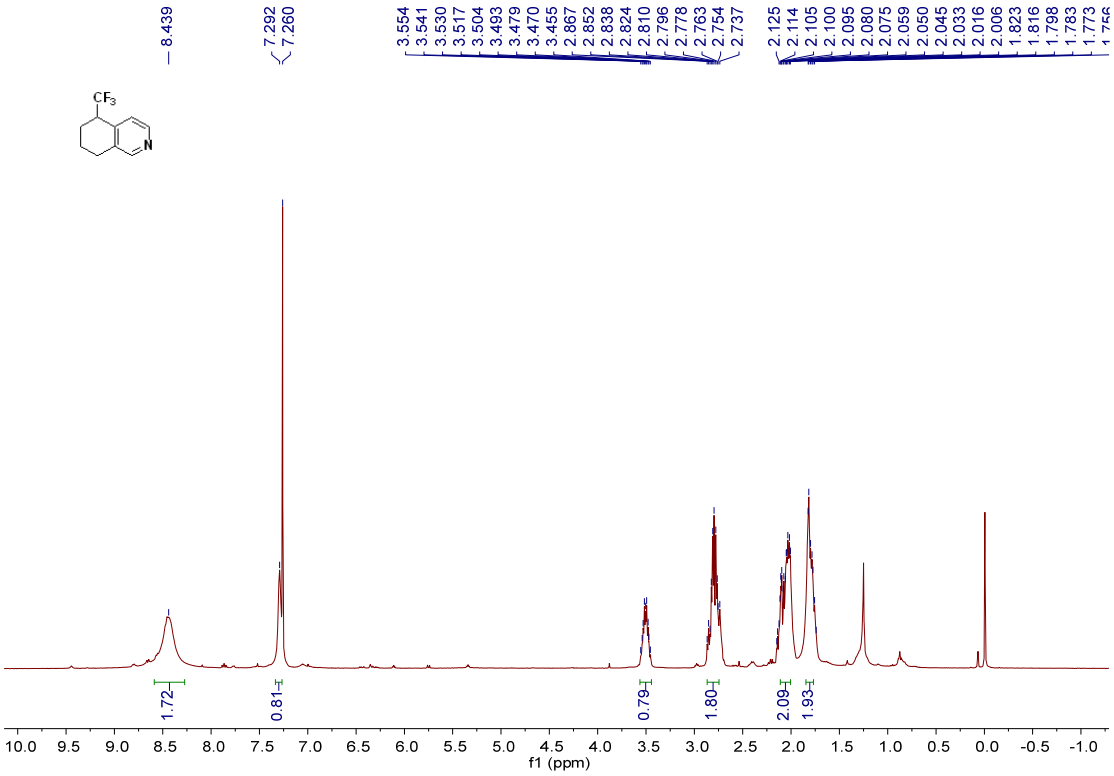
NMR Spectra of product **19**:

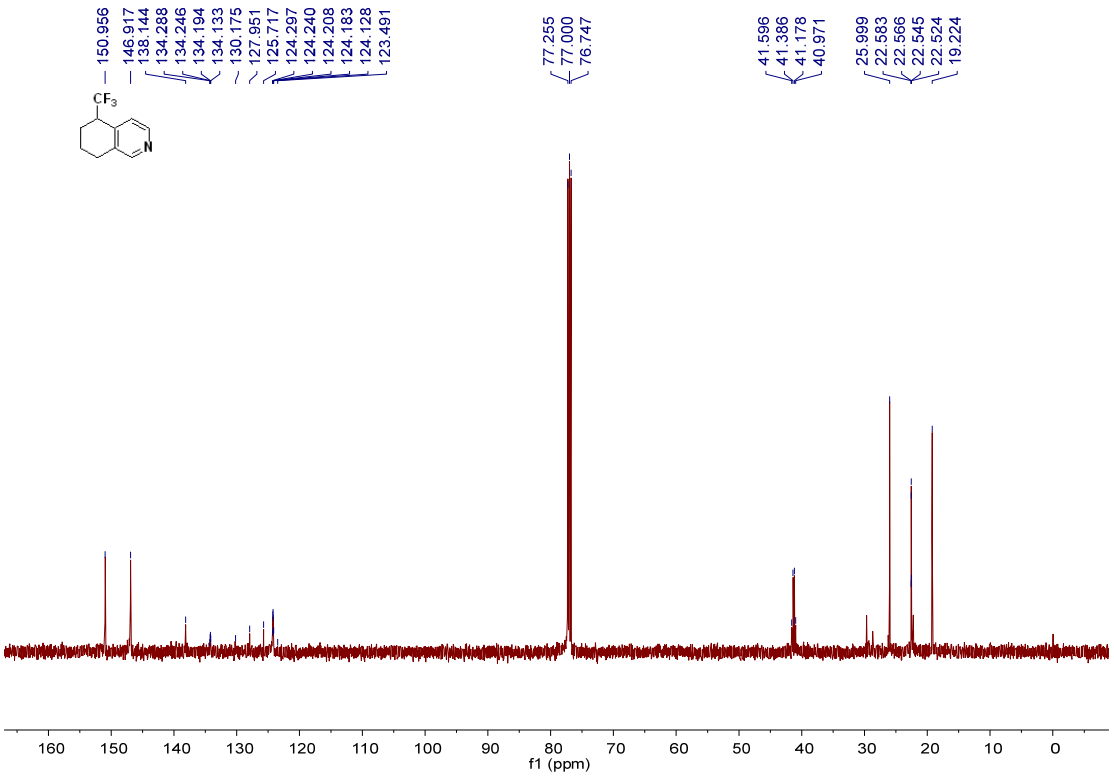


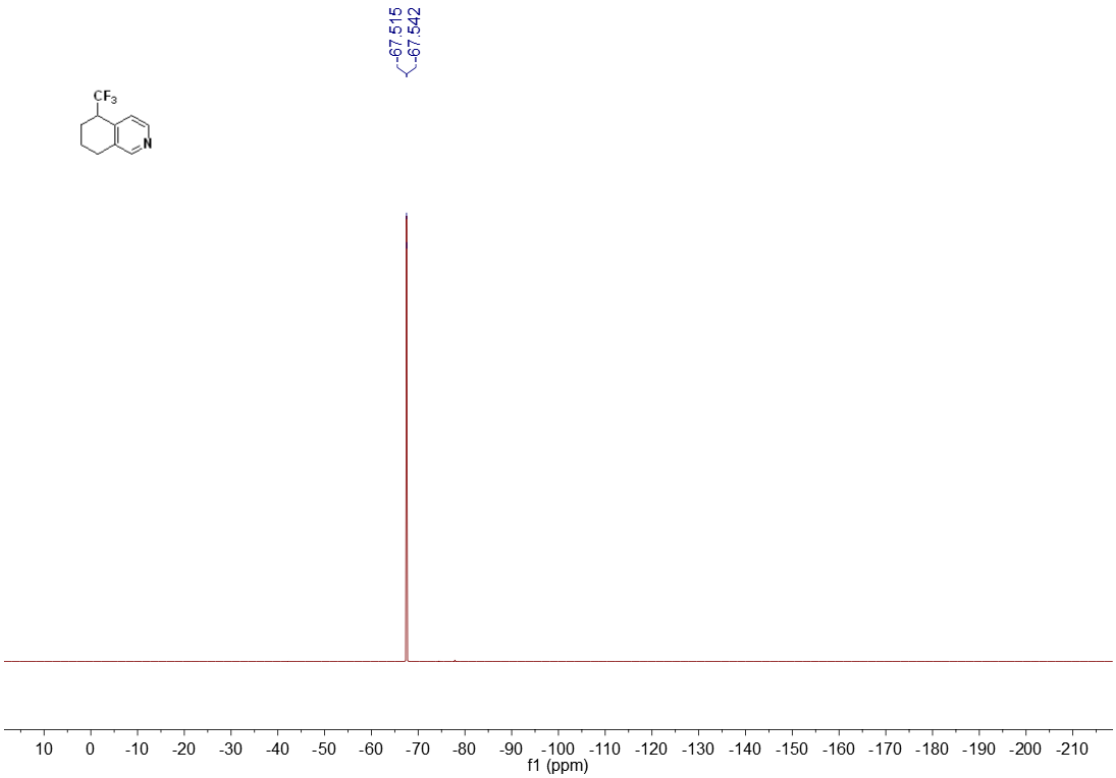




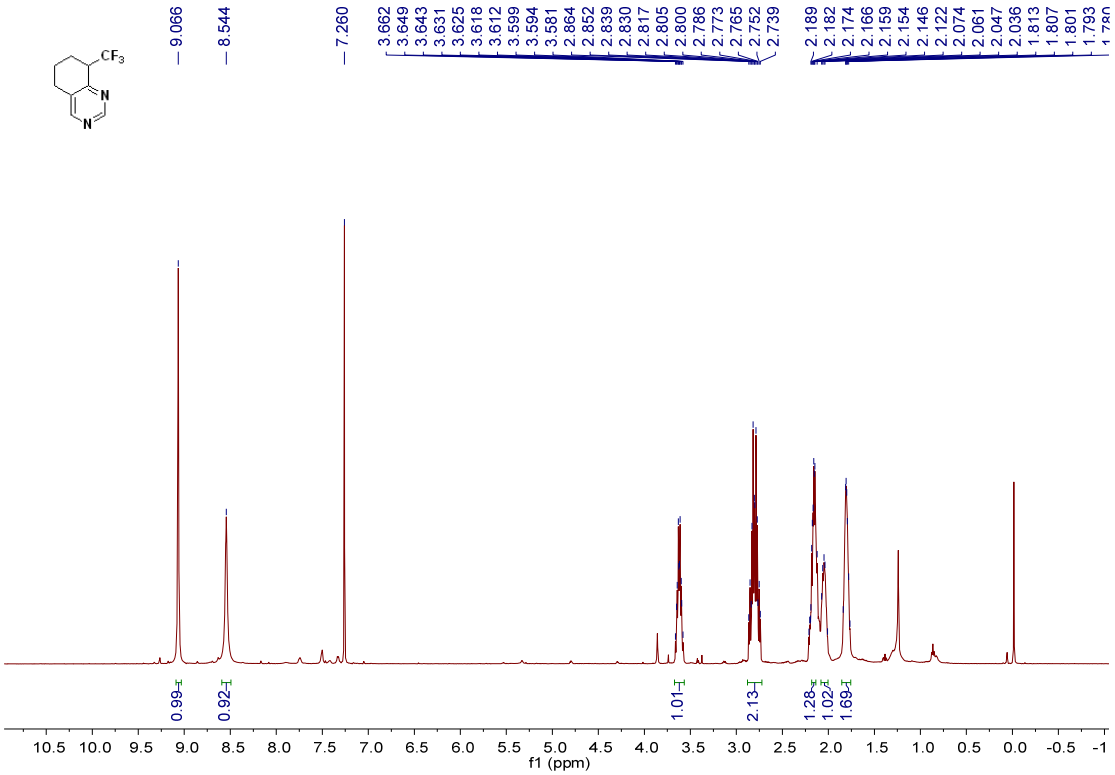
NMR Spectra of product **20**:

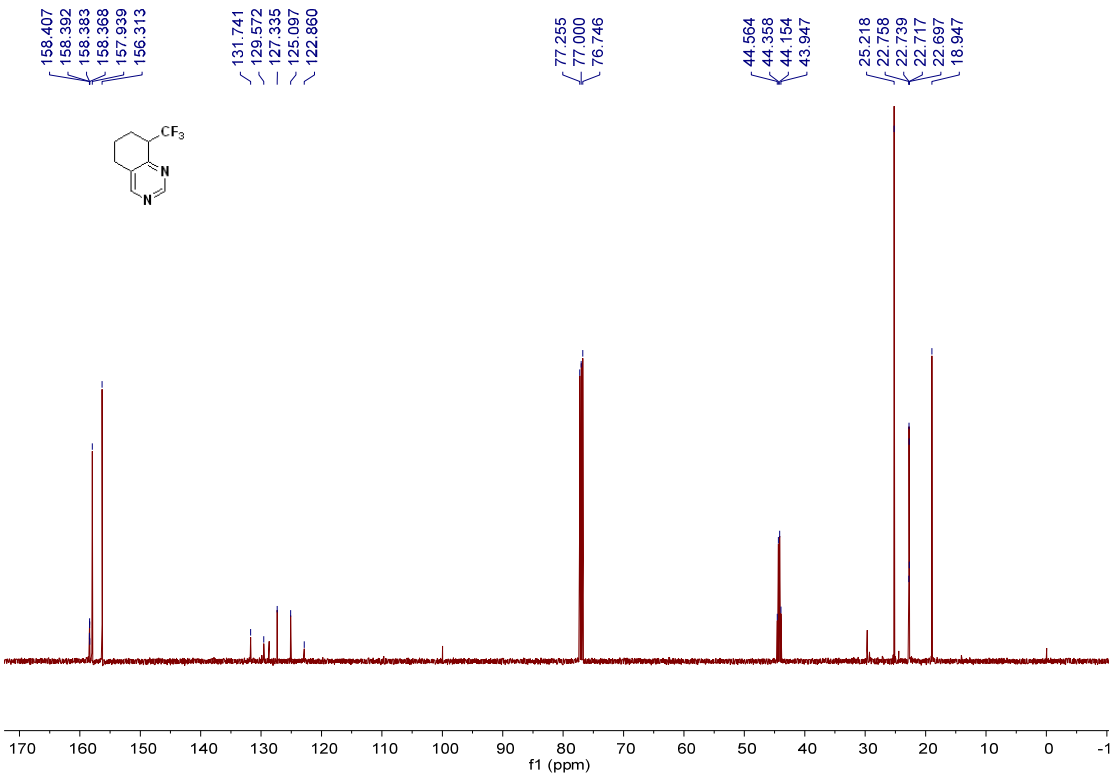

8.439
7.292
7.260
3.554
3.541
3.530
3.517
3.504
3.493
3.479
3.470
3.455
2.867
2.852
2.838
2.824
2.810
2.796
2.778
2.763
2.754
2.737
2.125
2.114
2.105
2.100
2.095
2.080
2.075
2.059
2.050
2.045
2.033
2.016
2.006
1.823
1.816
1.798
1.783
1.773
CF3
N
1.72
0.81
0.79
1.80
2.09
1.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

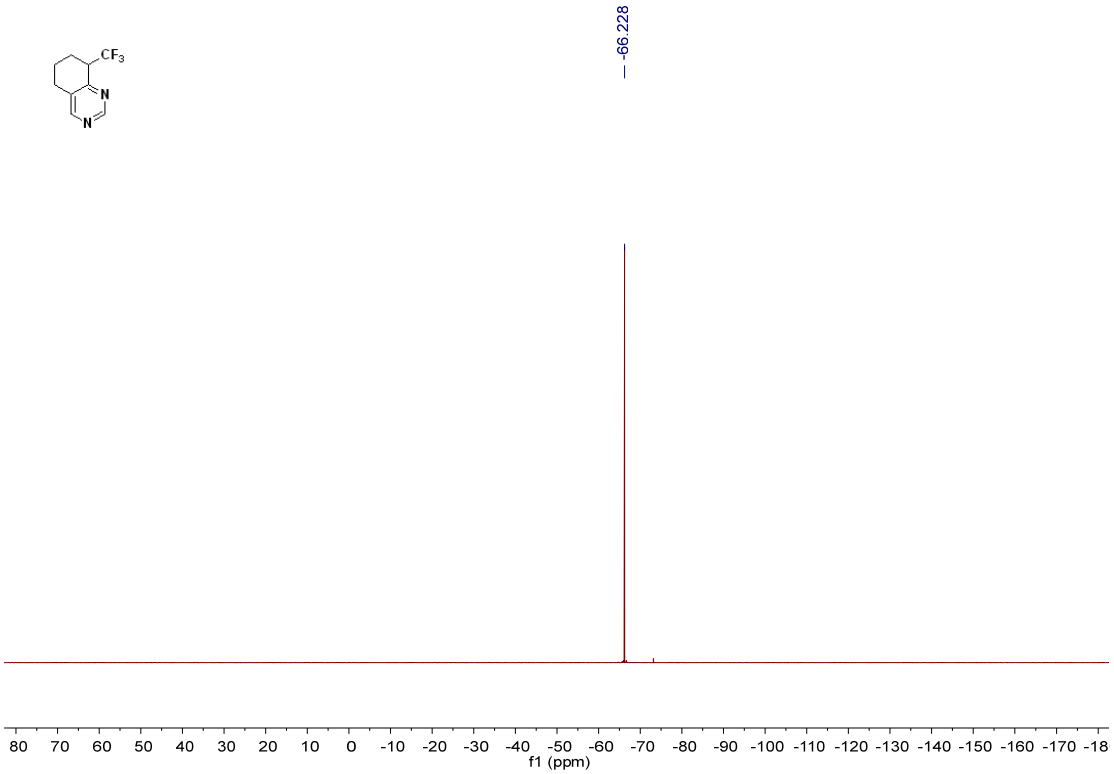

150.956
146.917
138.144
134.288
134.246
134.194
134.133
130.175
127.951
125.717
124.297
124.240
124.208
124.183
124.128
123.491
77.255
77.000
76.747
41.596
41.386
41.178
40.971
25.999
22.583
22.566
22.545
22.524
19.224
CF3
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



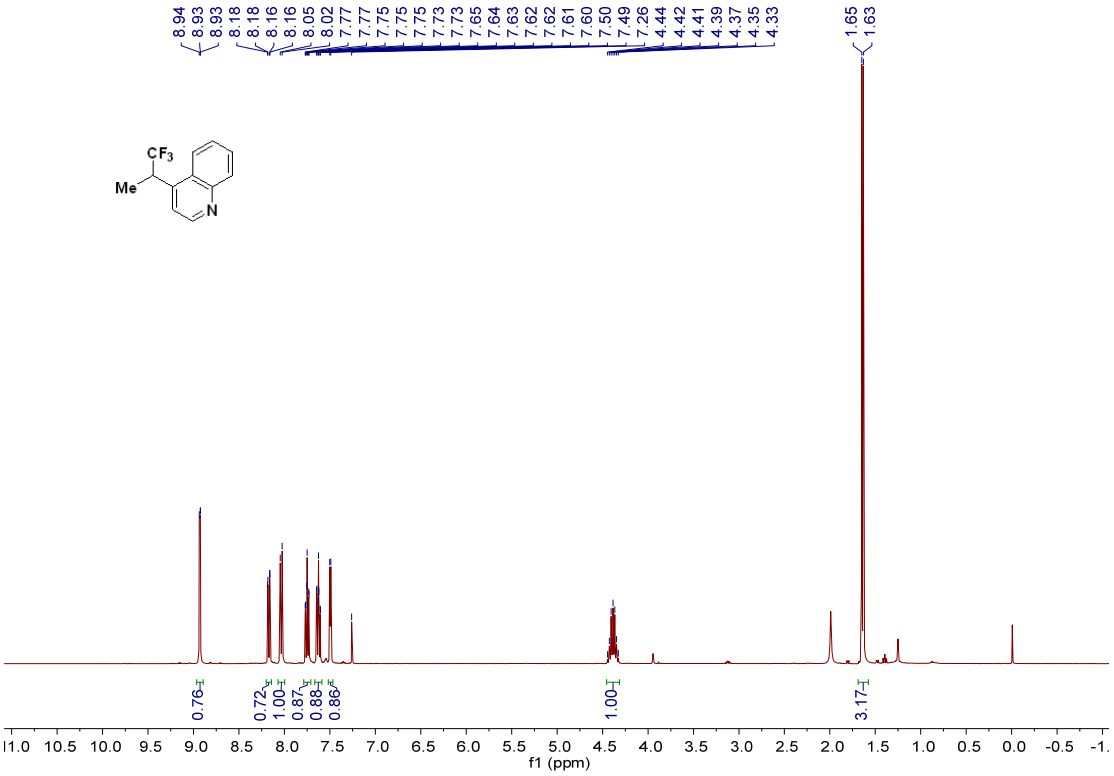
NMR Spectra of product **21**:

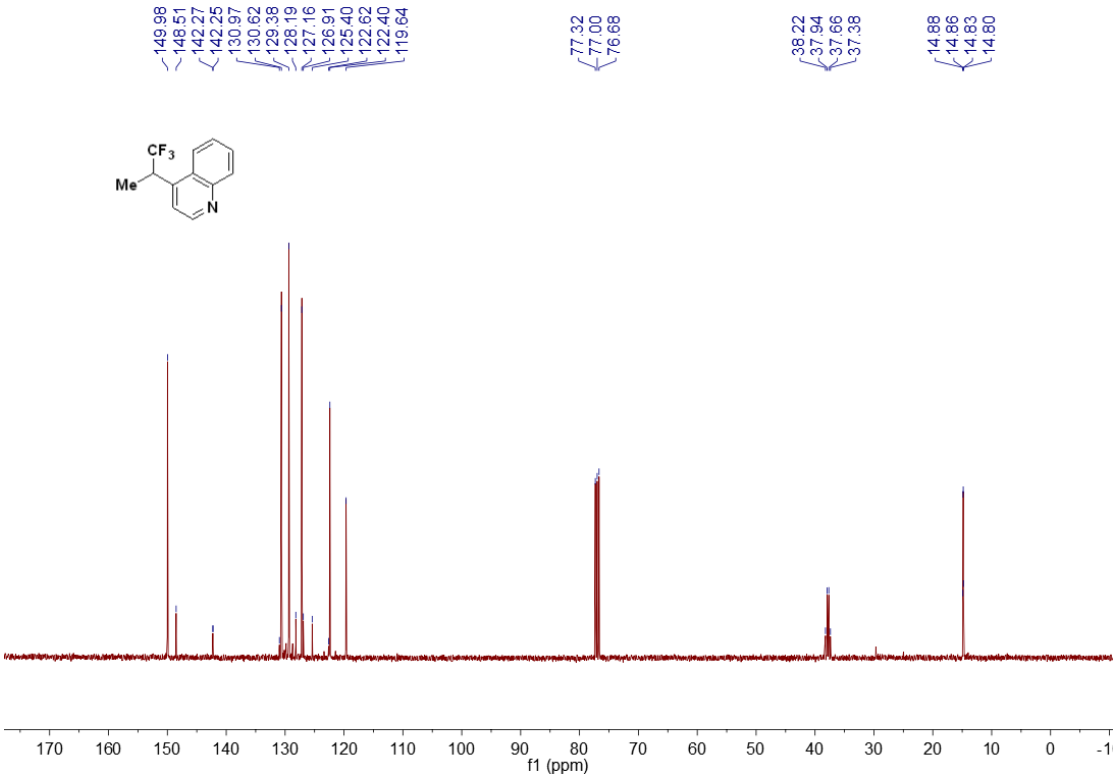


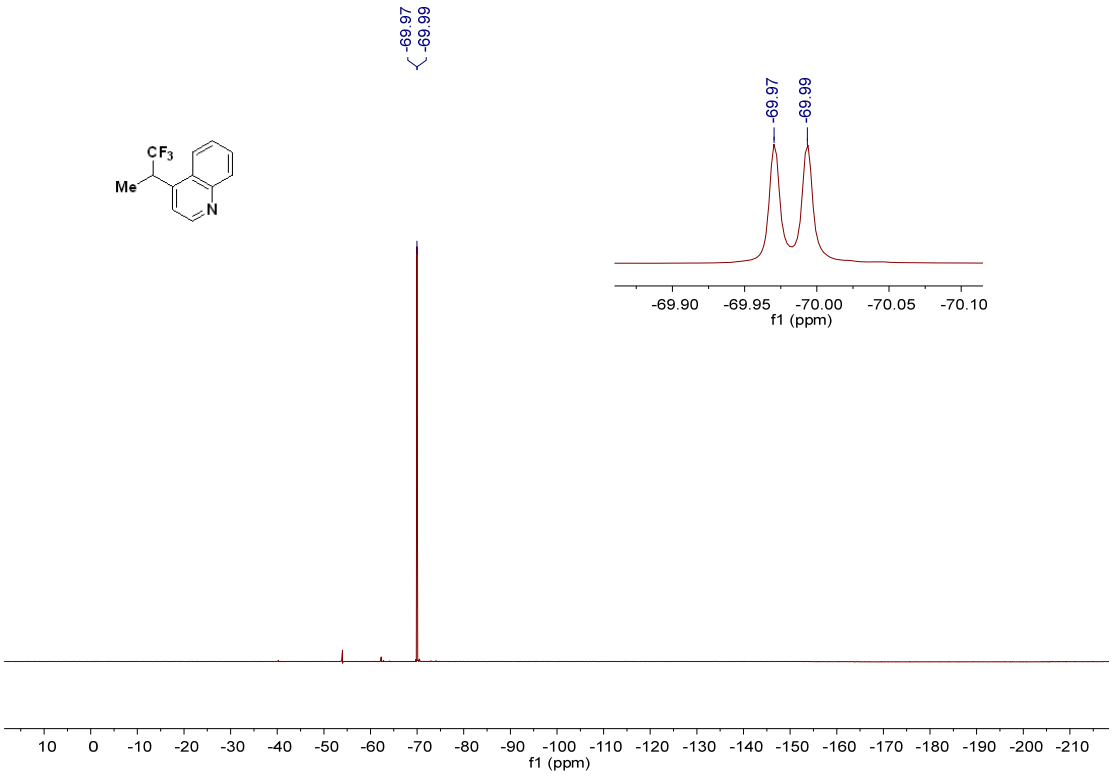




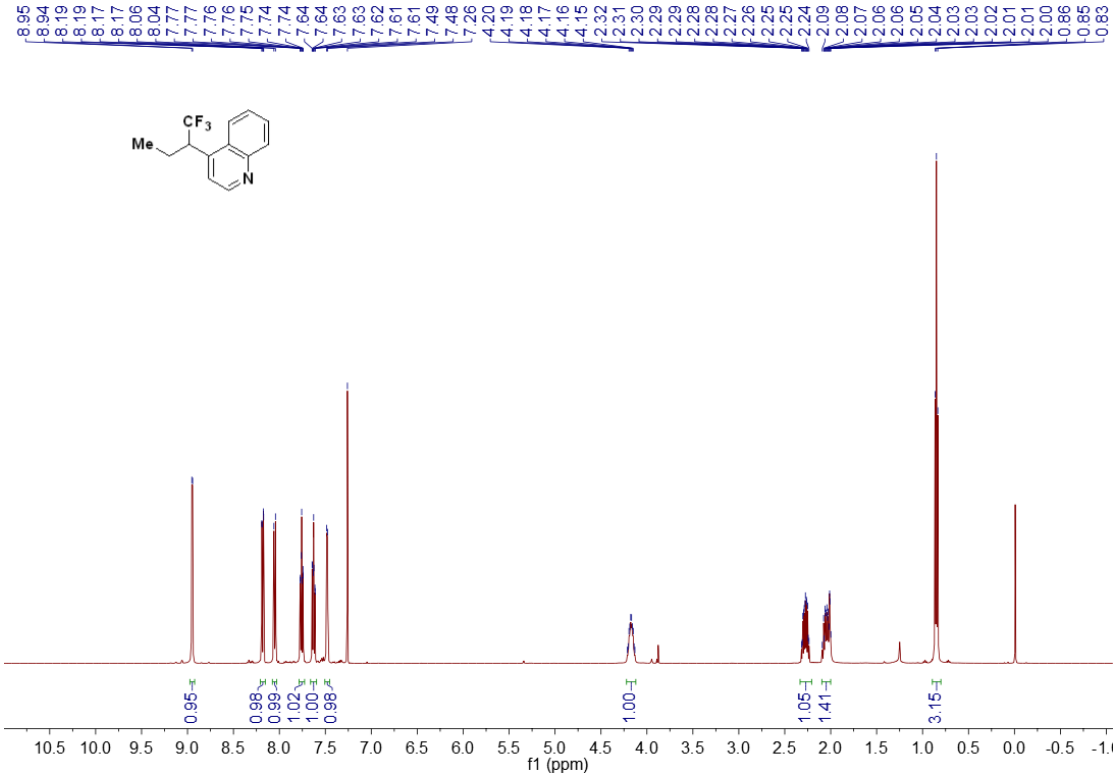
NMR Spectra of product **22**:

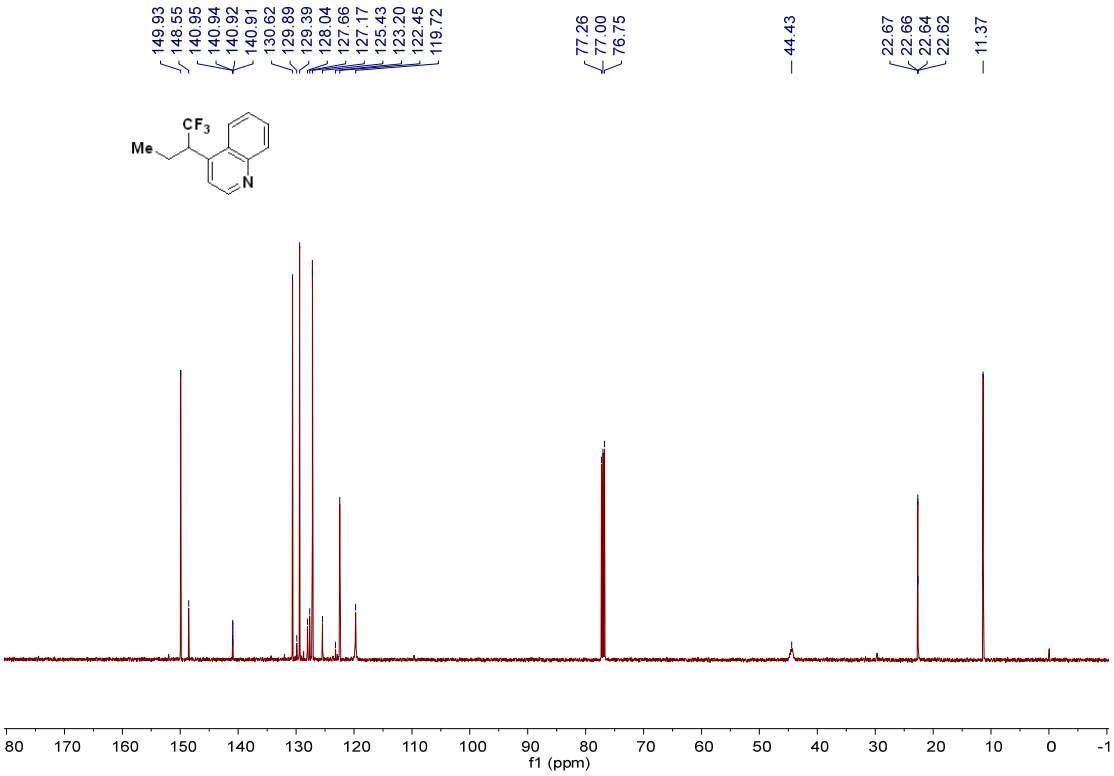

8.94
8.93
8.93
8.18
8.18
8.16
8.16
8.05
8.02
7.77
7.77
7.75
7.75
7.75
7.73
7.73
7.65
7.64
7.63
7.62
7.62
7.61
7.60
7.50
7.49
7.26
4.44
4.42
4.41
4.39
4.37
4.35
4.33
1.65
1.63
CF3
Me
N
0.76
0.72
1.00
0.87
0.88
0.86
1.00
3.17
f1 (ppm)

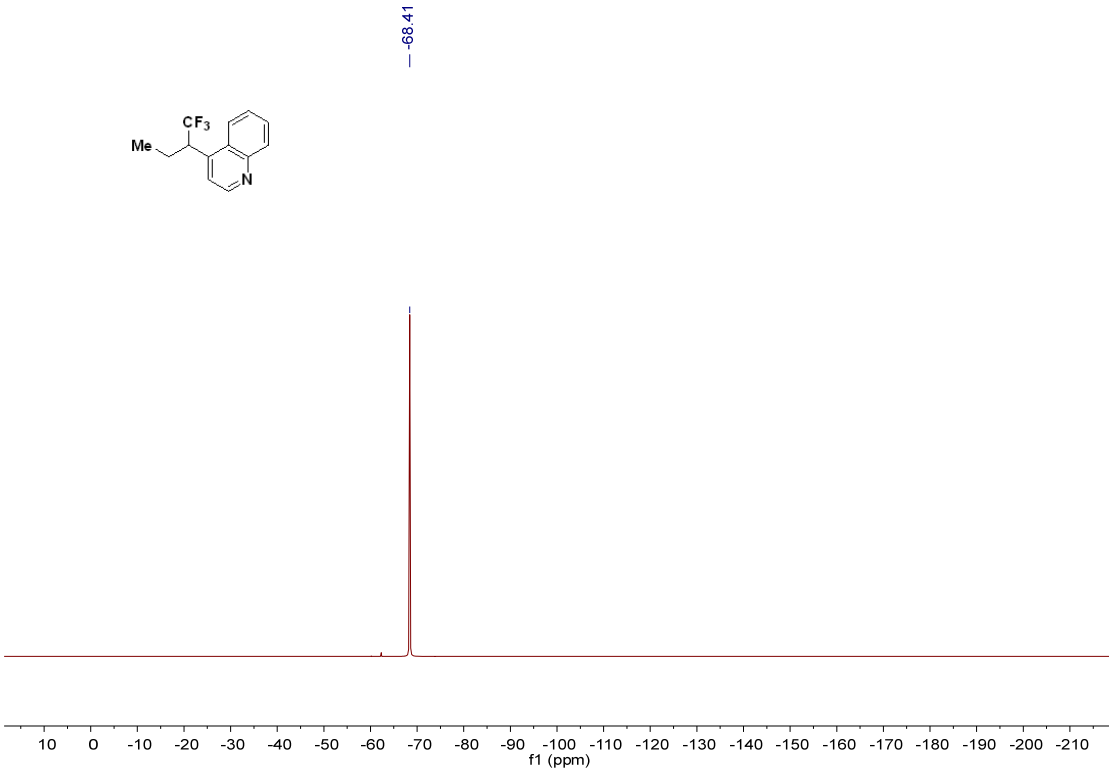

149.98
148.51
142.27
142.25
130.97
130.62
129.38
128.19
127.16
126.91
125.40
122.62
122.40
119.64
77.32
77.00
76.68
38.22
37.94
37.66
37.38
14.88
14.86
14.83
14.80
CF3
Me
N
f1 (ppm)



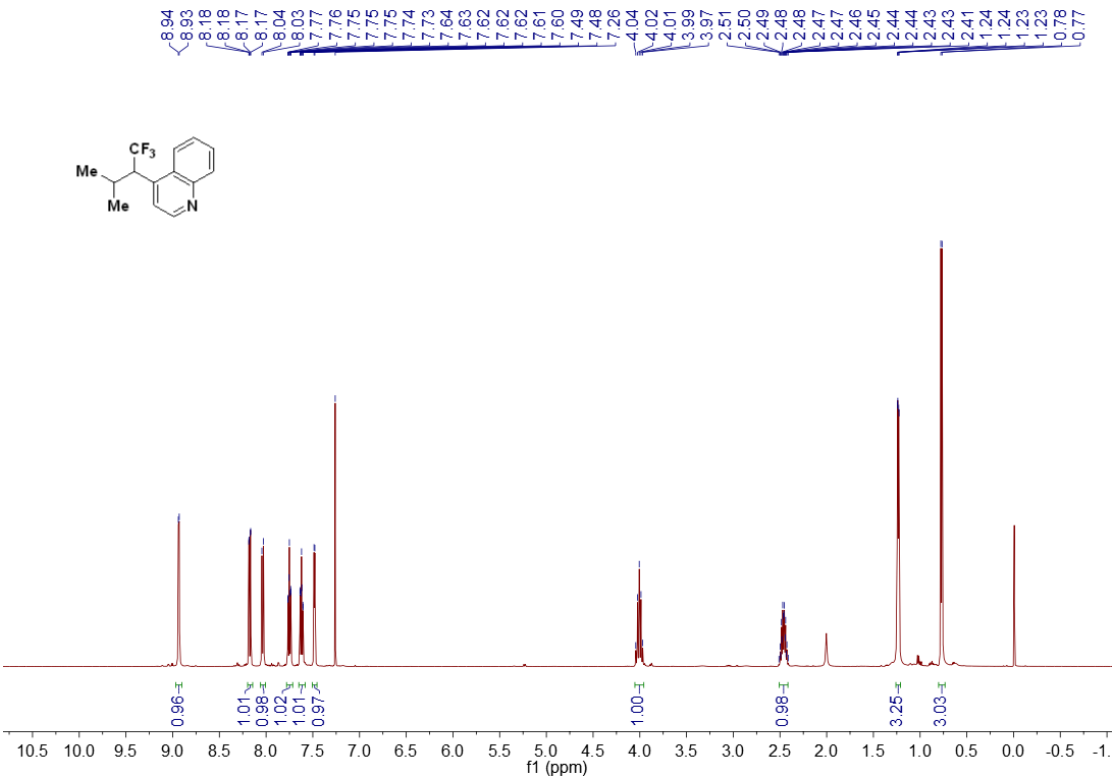
NMR Spectra of product **23**:

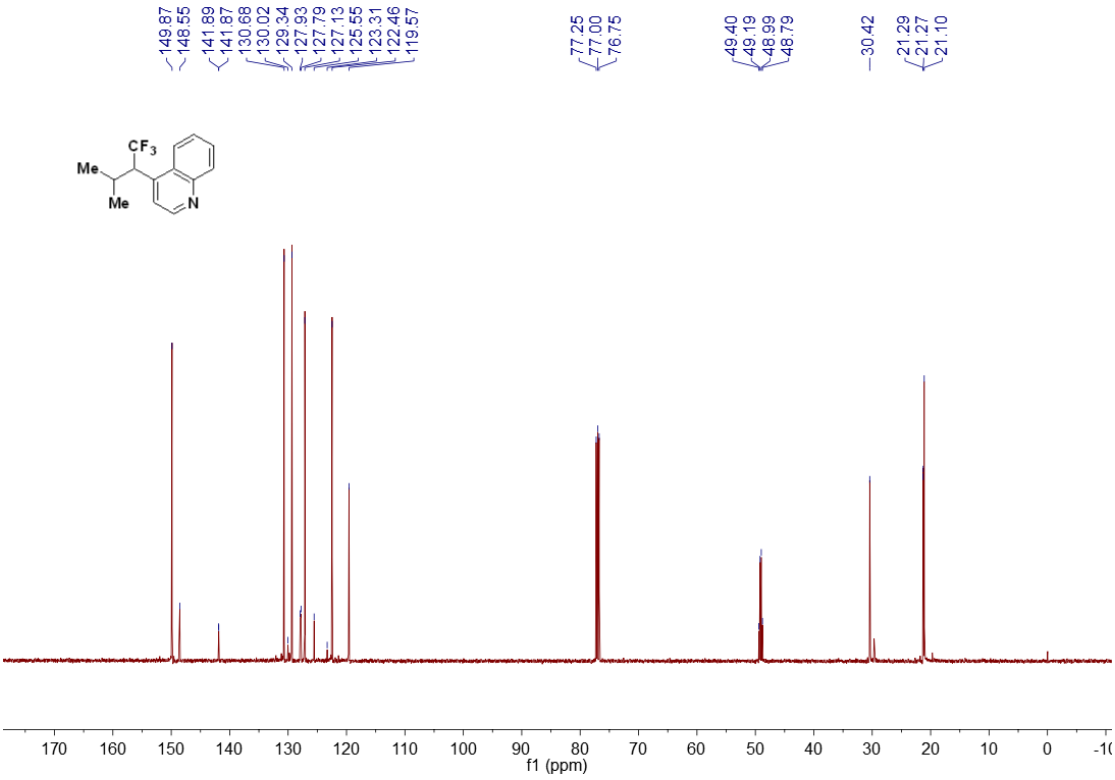


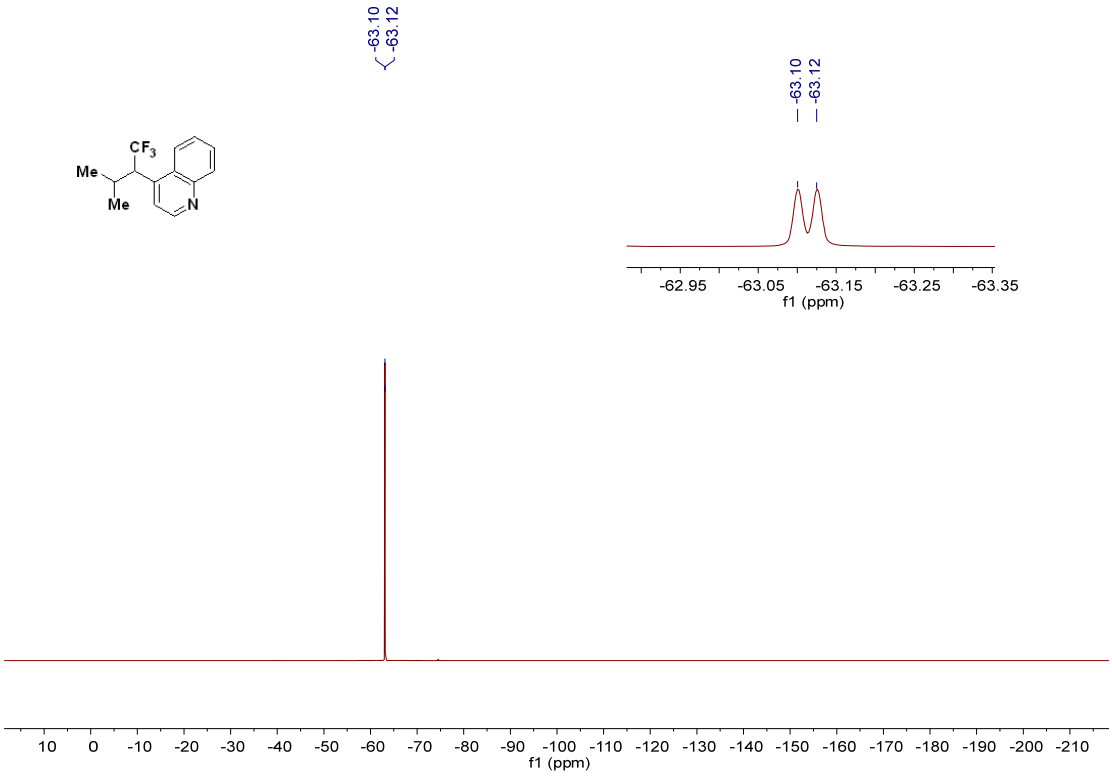




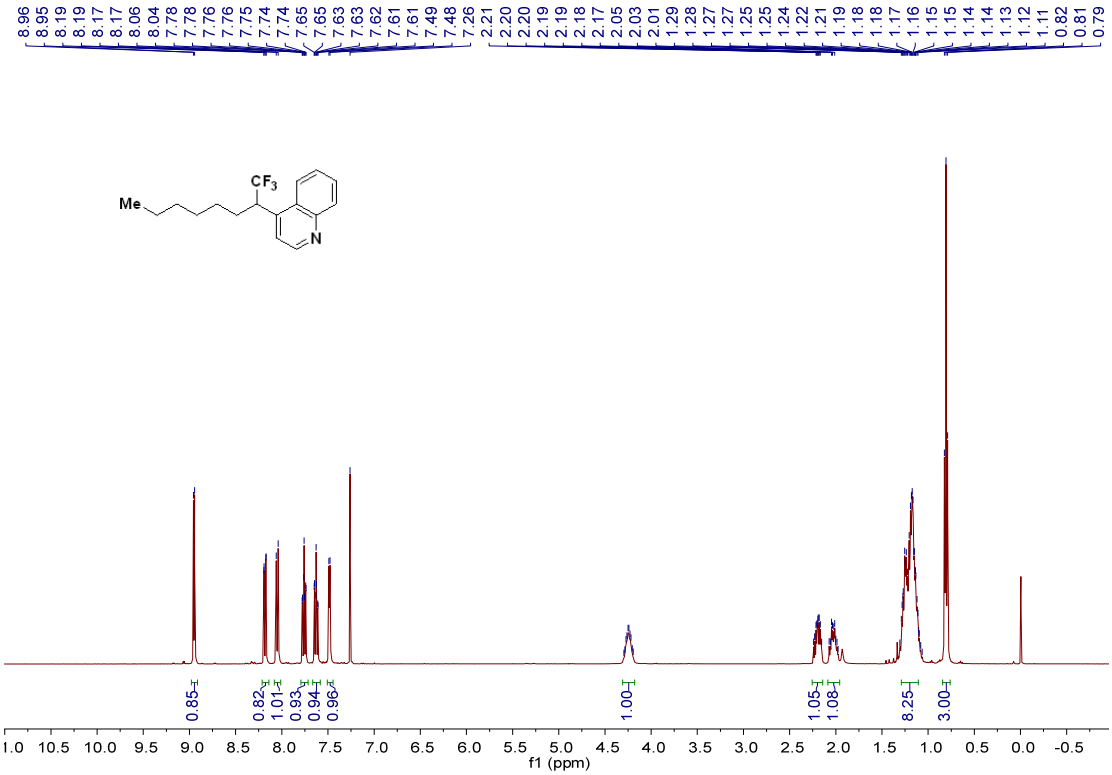
NMR Spectra of product **24**:

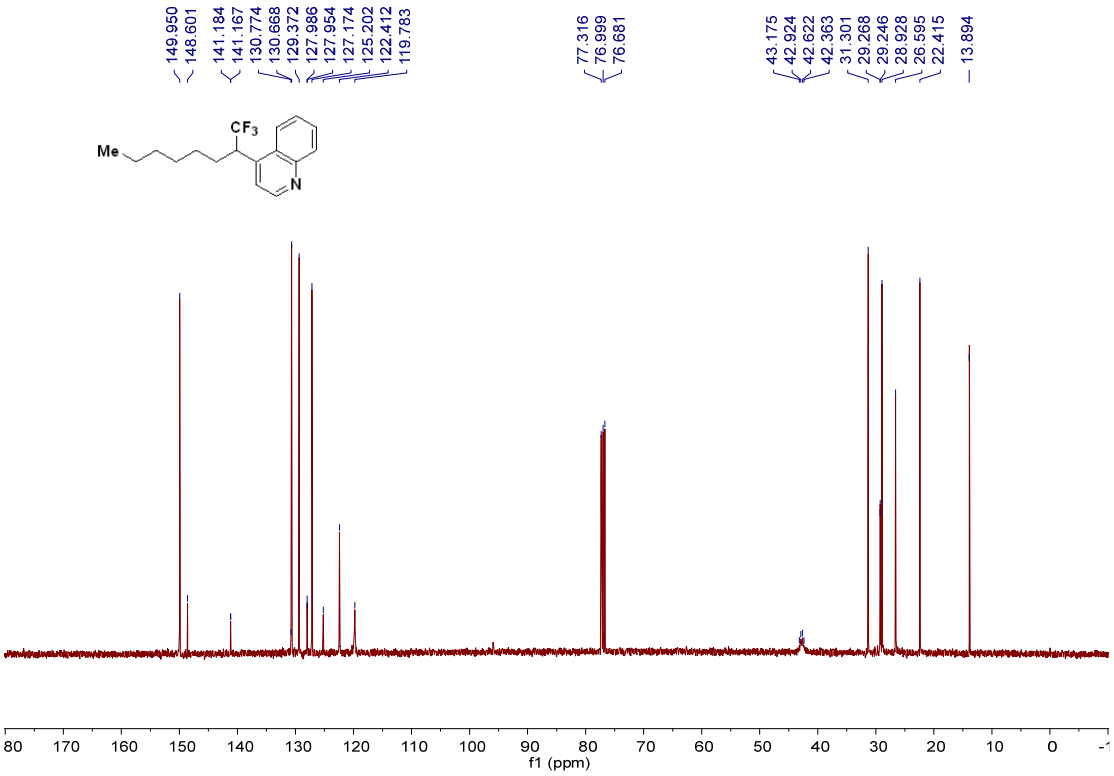

8.94
8.93
8.18
8.18
8.17
8.17
8.04
8.03
7.77
7.76
7.75
7.75
7.75
7.74
7.73
7.64
7.63
7.62
7.62
7.62
7.61
7.60
7.49
7.48
7.26
4.04
4.02
4.01
3.99
3.97
2.51
2.50
2.49
2.48
2.48
2.47
2.47
2.46
2.45
2.44
2.44
2.43
2.43
2.41
1.24
1.24
1.23
1.23
0.78
0.77
CF3
Me
Me
N
0.96
1.01
0.98
1.02
1.01
0.97
1.00
0.98
3.25
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

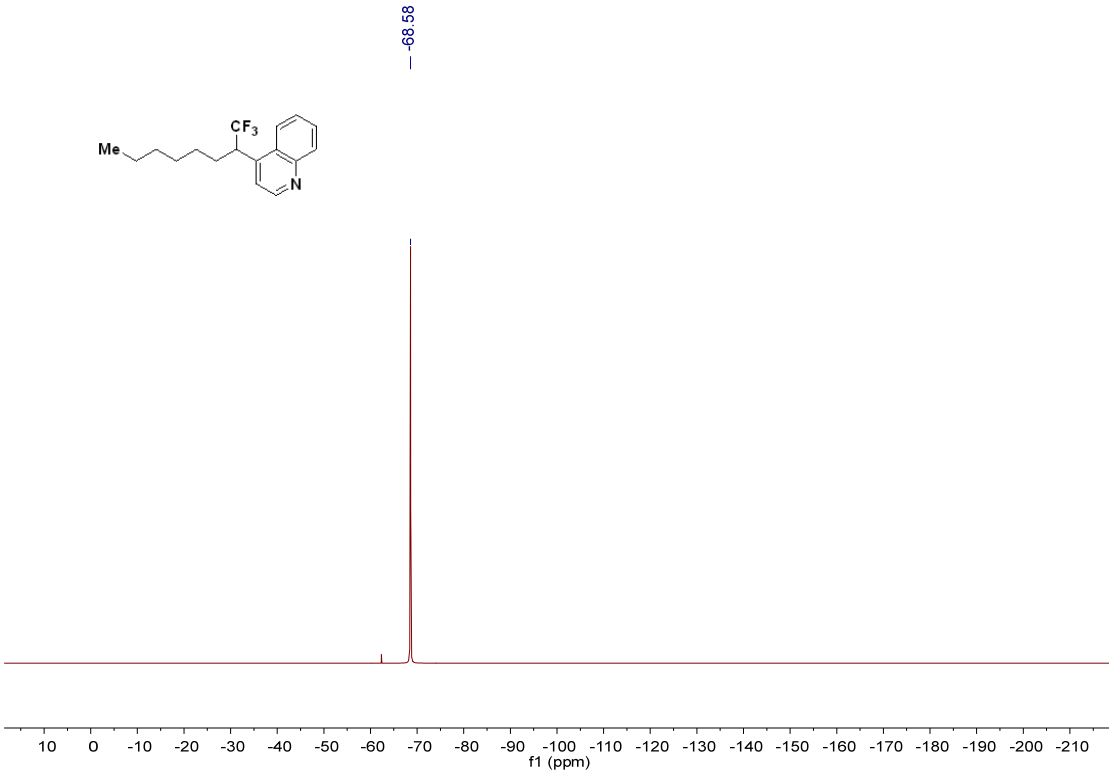

149.87
148.55
141.89
141.87
130.68
130.02
129.34
127.93
127.79
127.13
125.55
123.31
122.46
119.57
77.25
77.00
76.75
49.40
49.19
48.99
48.79
30.42
21.29
21.27
21.10
CF3
Me
Me
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1(
f1 (ppm)



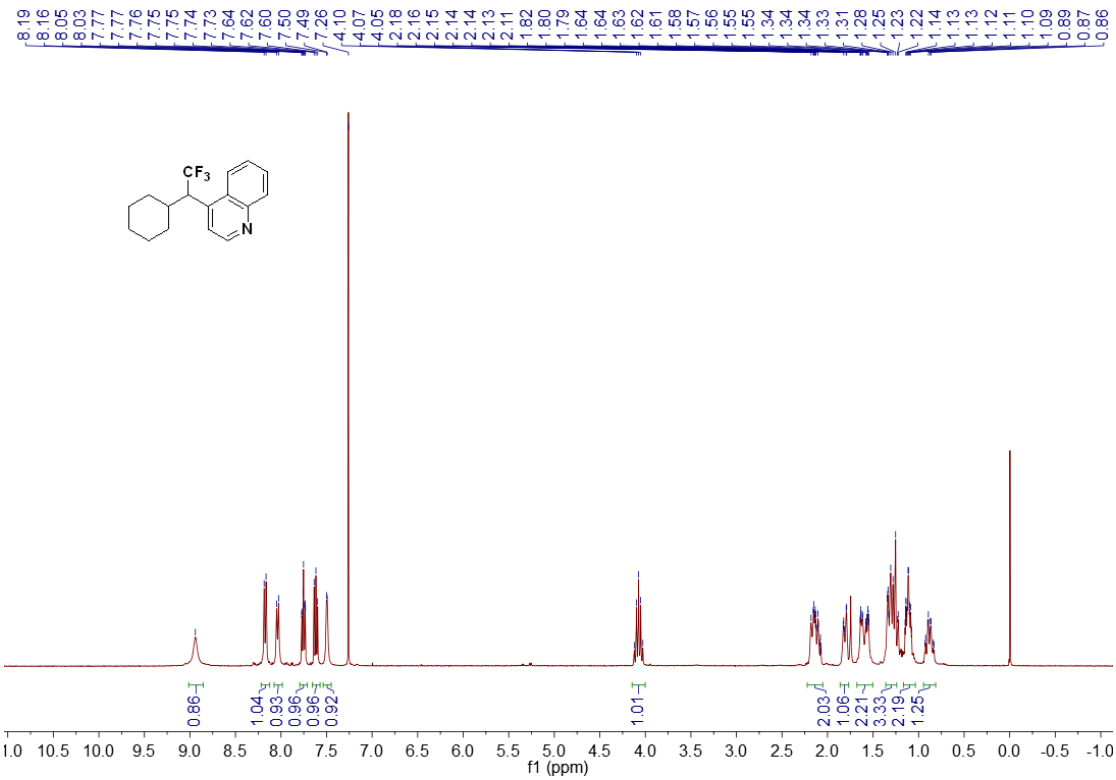
NMR Spectra of product **25**:

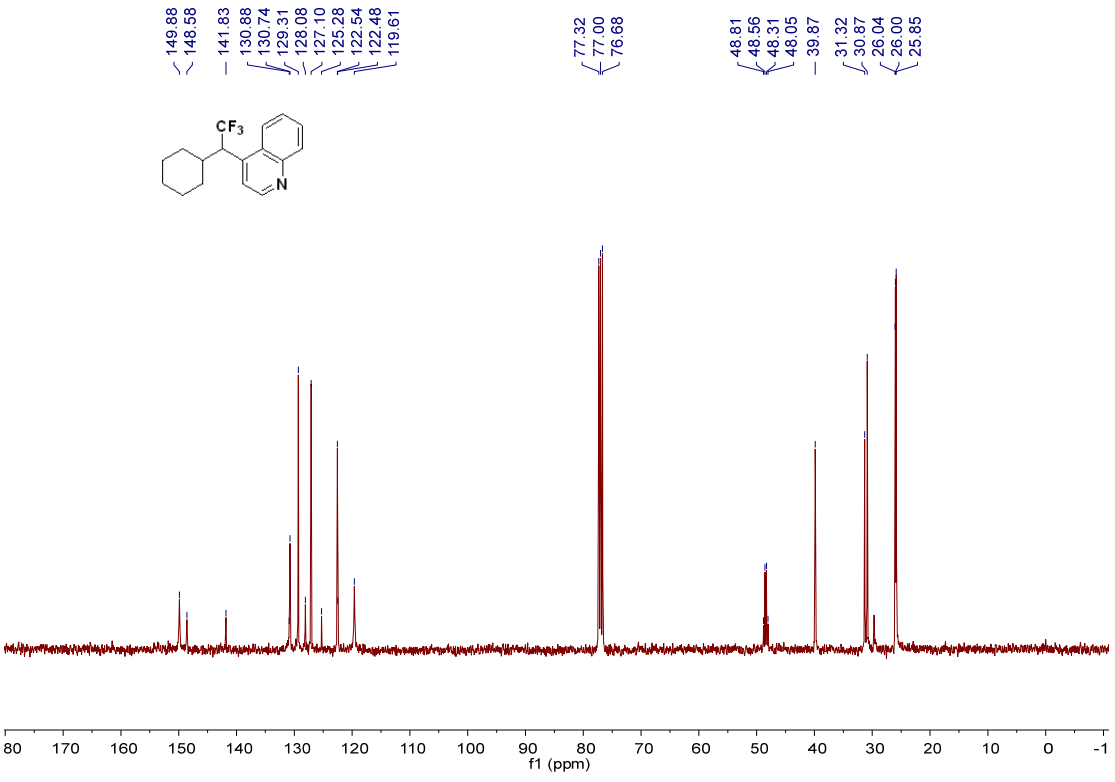


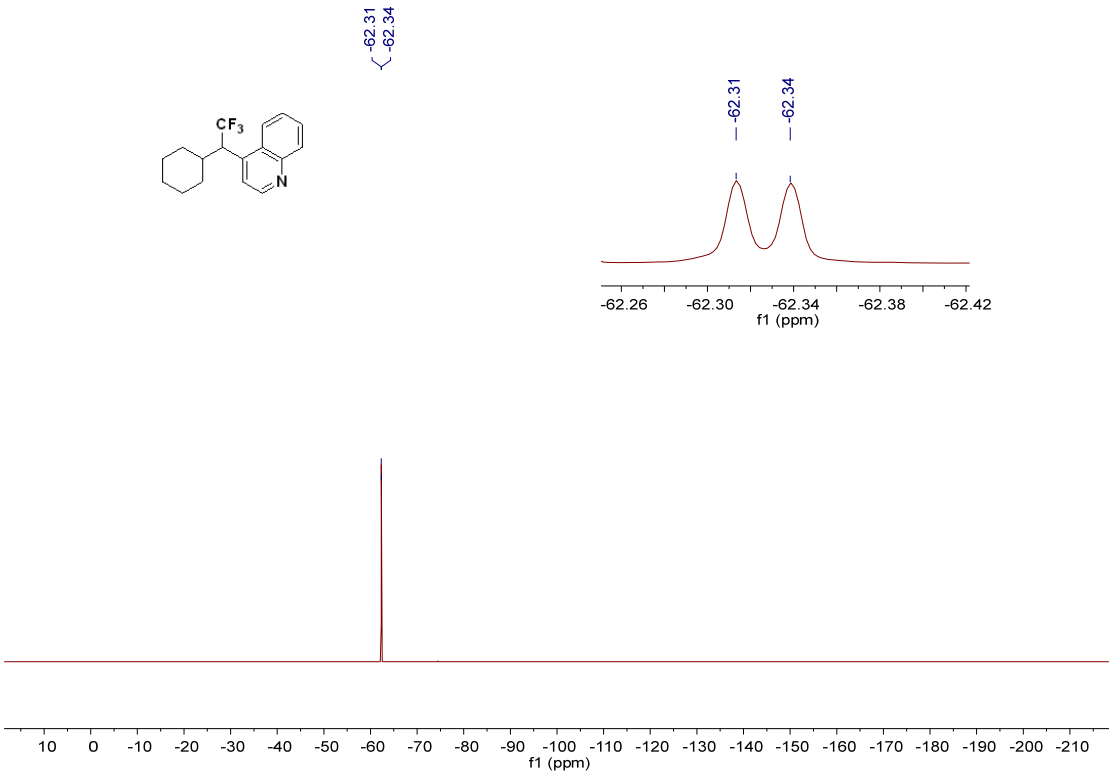




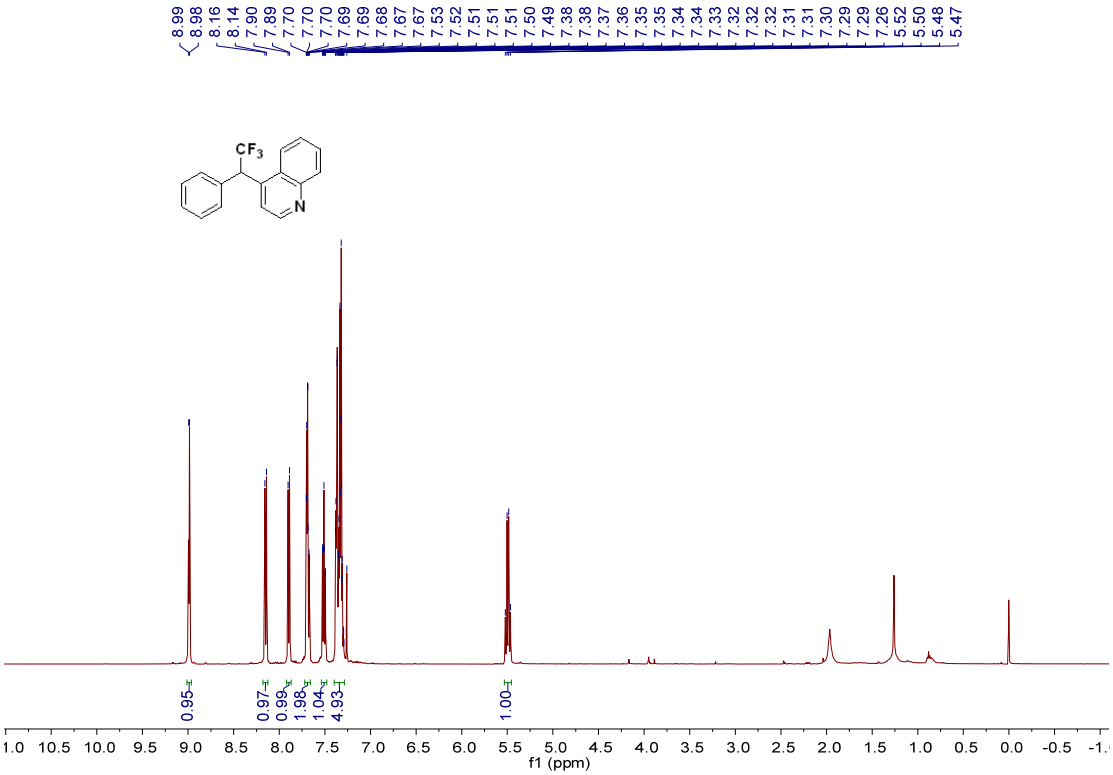
NMR Spectra of product **26**:

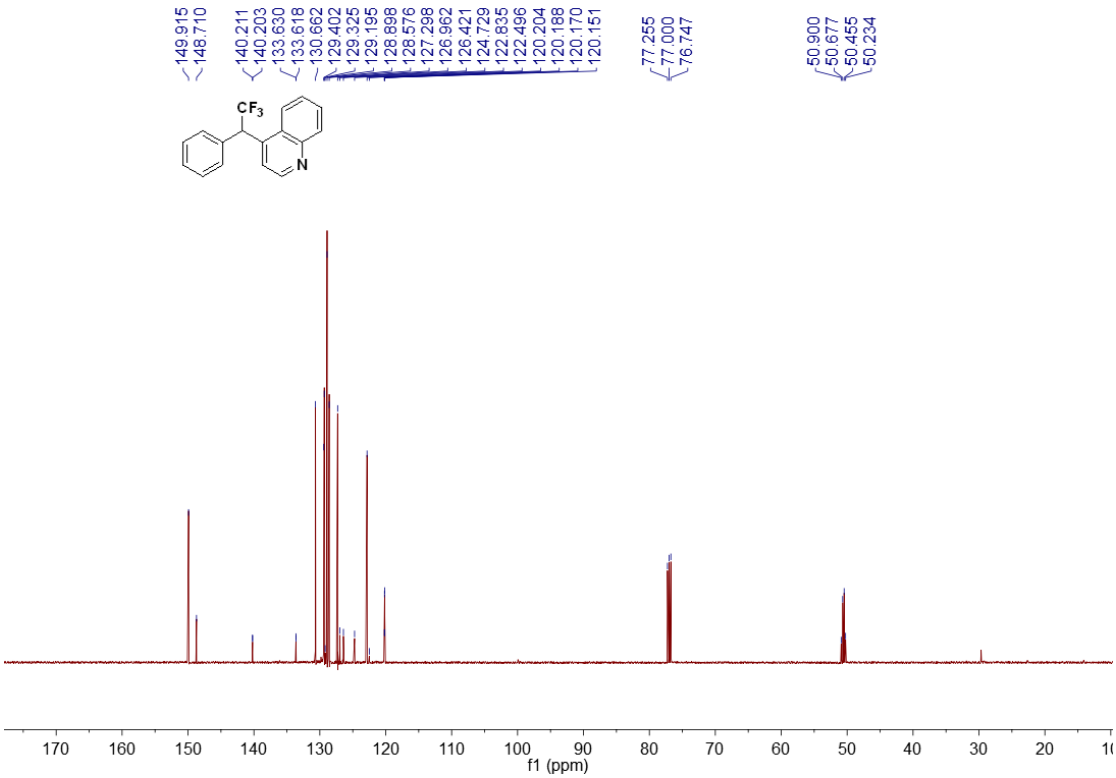

8.19 8.16 8.05 8.03 7.77 7.77 7.76 7.75 7.75 7.74 7.73 7.64 7.62 7.60 7.50 7.49 7.26 4.10 4.07 4.05 2.18 2.16 2.15 2.14 2.14 2.13 2.11 1.82 1.80 1.79 1.64 1.64 1.63 1.62 1.61 1.58 1.57 1.56 1.55 1.55 1.34 1.34 1.33 1.31 1.28 1.25 1.23 1.22 1.14 1.13 1.13 1.12 1.11 1.10 1.09 0.89 0.87 0.86
CF3
N
0.86 1.04 0.93 0.96 0.96 0.92 1.01 2.03 1.06 2.21 3.33 2.19 1.25
f1 (ppm)

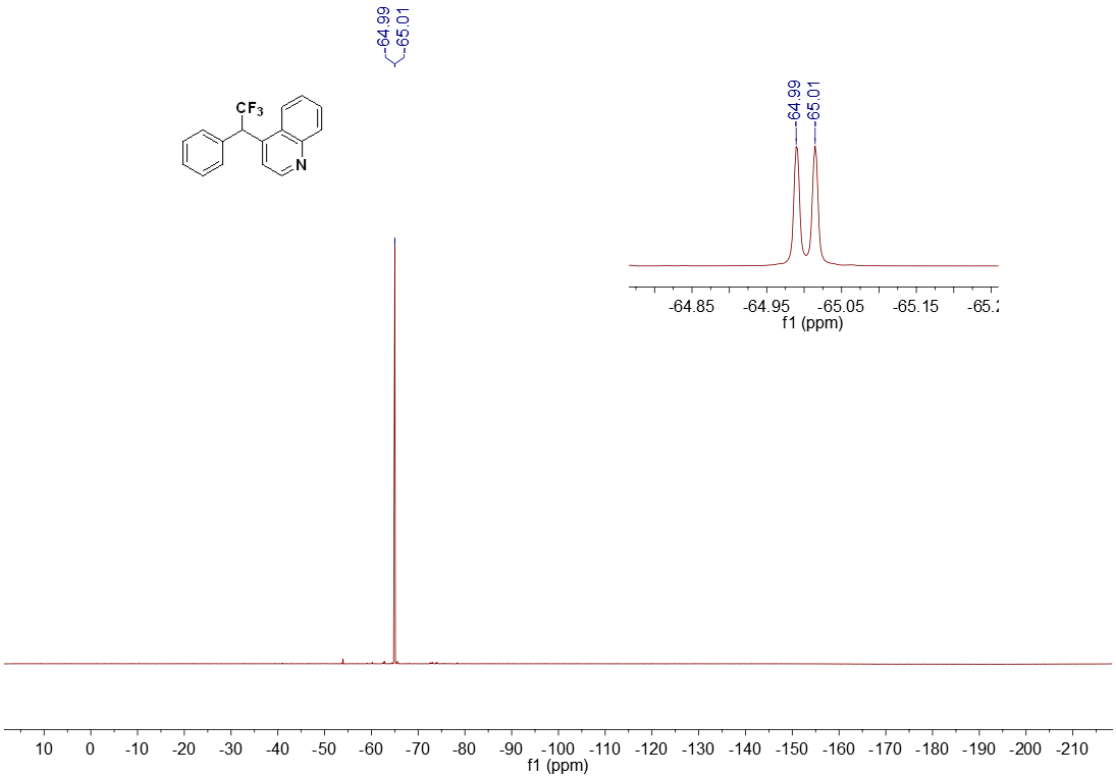

149.88 148.58 141.83 130.88 130.74 129.31 128.08 127.10 125.28 122.54 122.48 119.61 77.32 77.00 76.68 48.81 48.56 48.31 48.05 39.87 31.32 30.87 26.04 26.00 25.85
CF3
N
f1 (ppm)



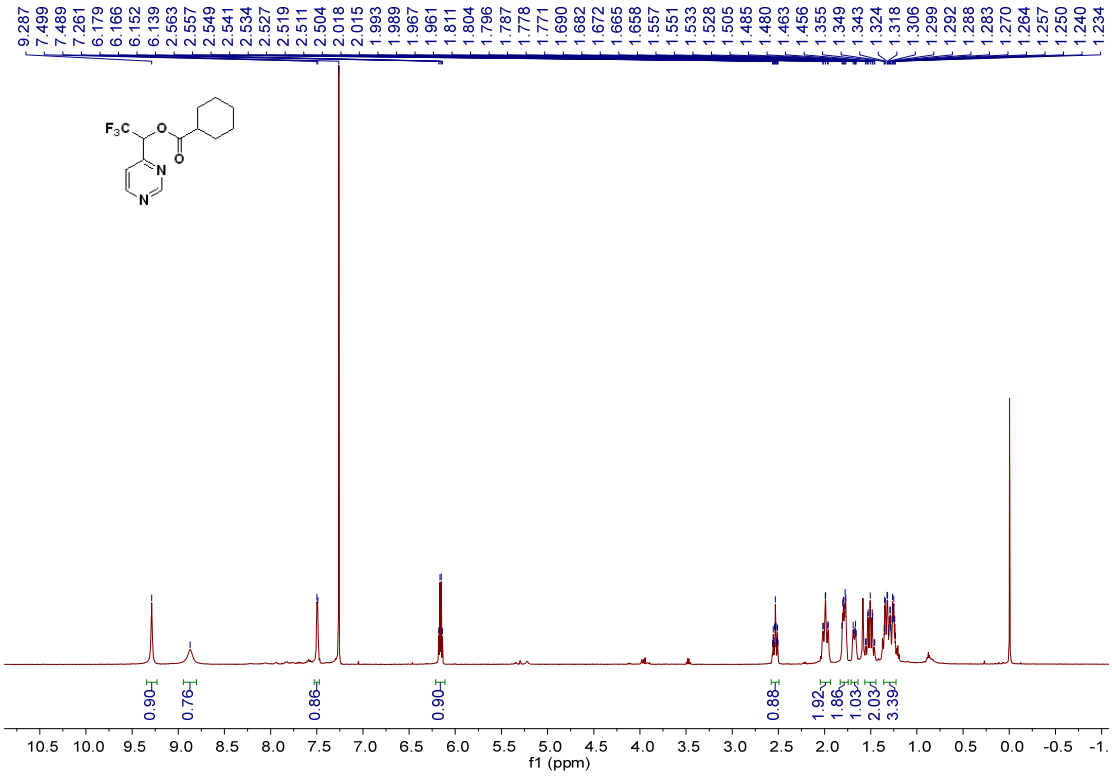
NMR Spectra of product **27**:

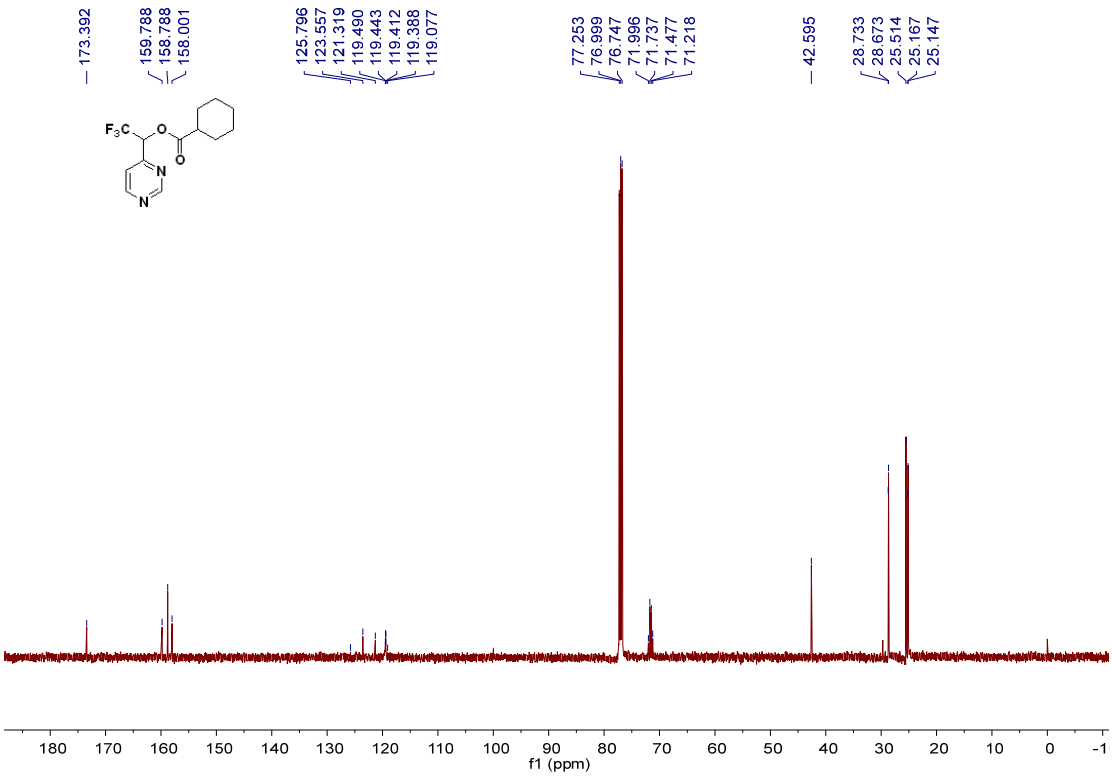


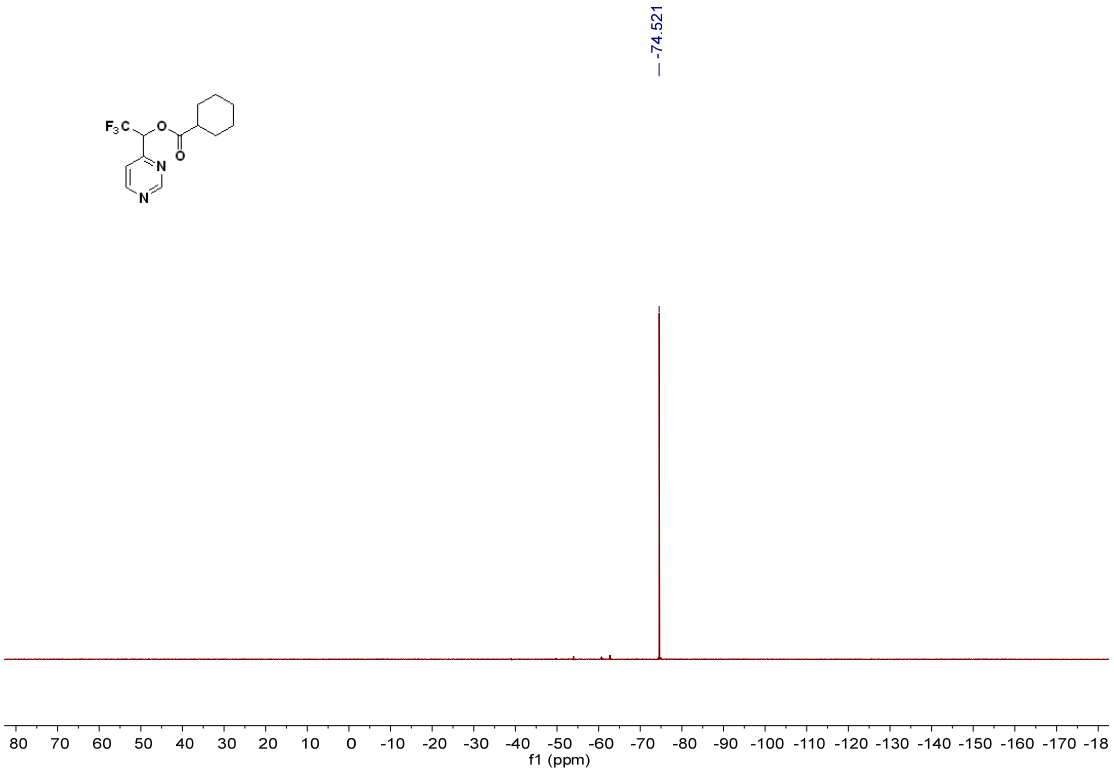




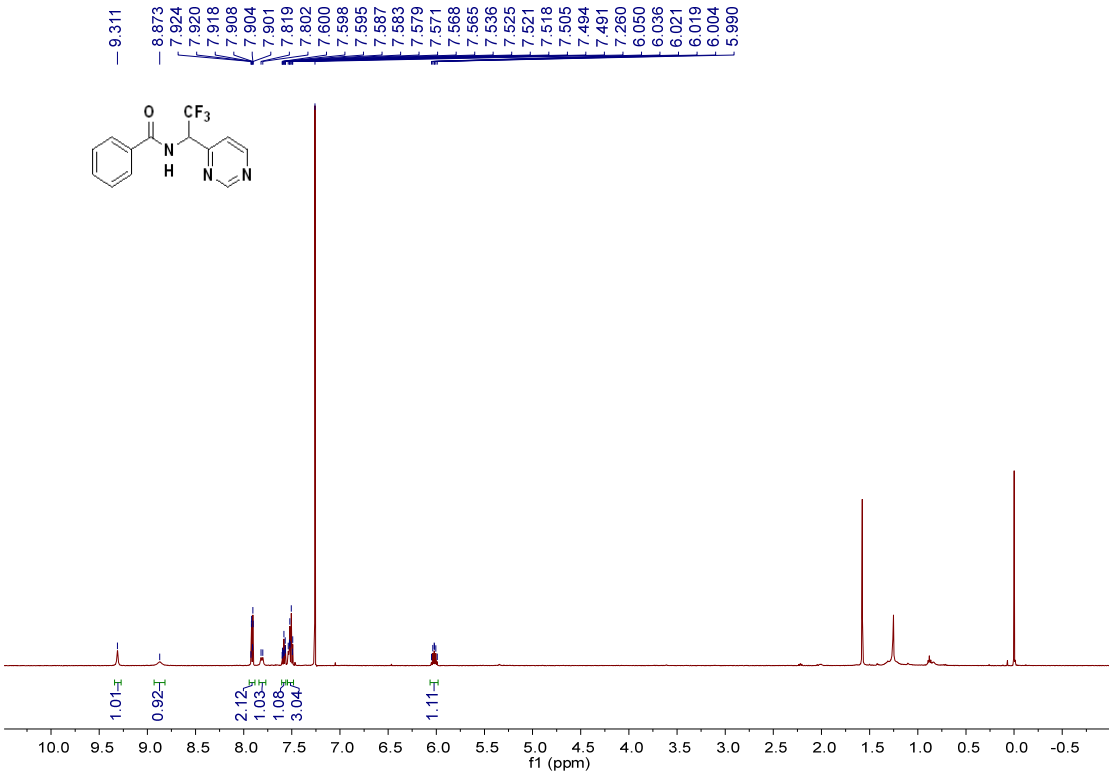
NMR Spectra of product **28**:

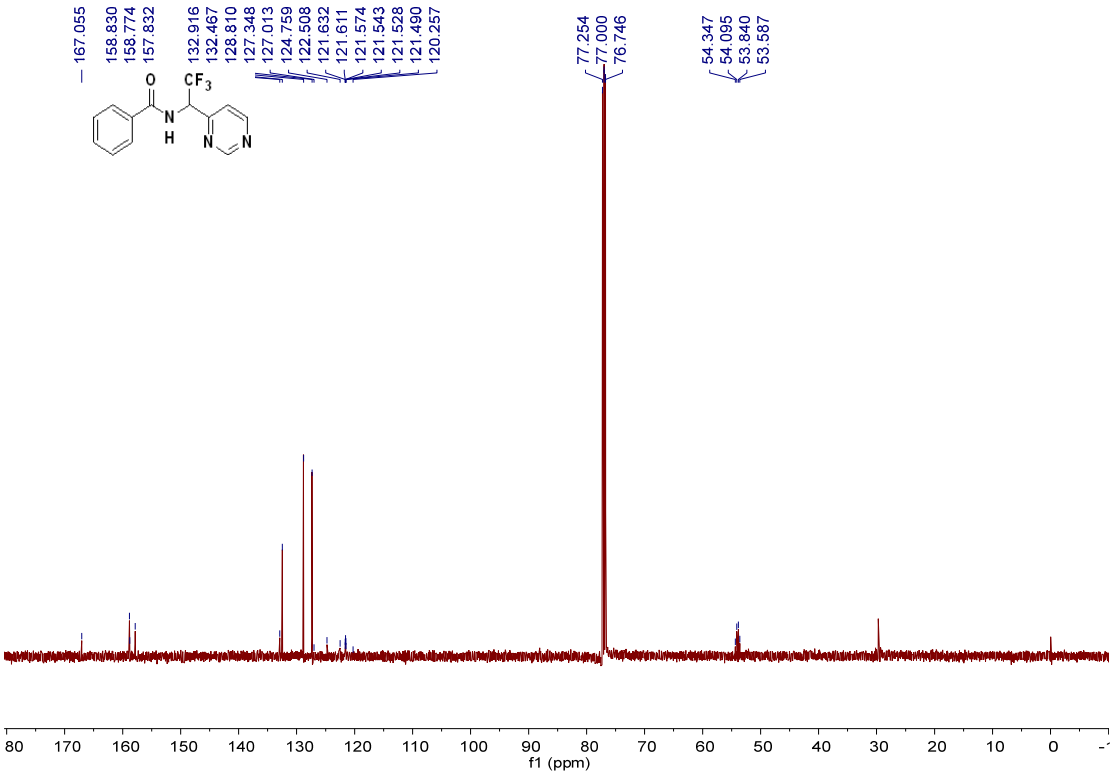

9.287
7.499
7.489
7.261
6.179
6.166
6.152
6.139
2.563
2.557
2.549
2.541
2.534
2.527
2.519
2.511
2.504
2.018
2.015
1.993
1.989
1.967
1.961
1.811
1.804
1.796
1.787
1.778
1.771
1.690
1.682
1.672
1.665
1.658
1.557
1.551
1.533
1.528
1.505
1.485
1.480
1.463
1.456
1.355
1.349
1.343
1.324
1.318
1.306
1.299
1.292
1.288
1.283
1.270
1.264
1.257
1.250
1.240
1.234
F3C
O
O
N
N
0.90
0.76
0.86
0.90
0.88
1.92
1.86
1.03
2.03
3.39
f1 (ppm)

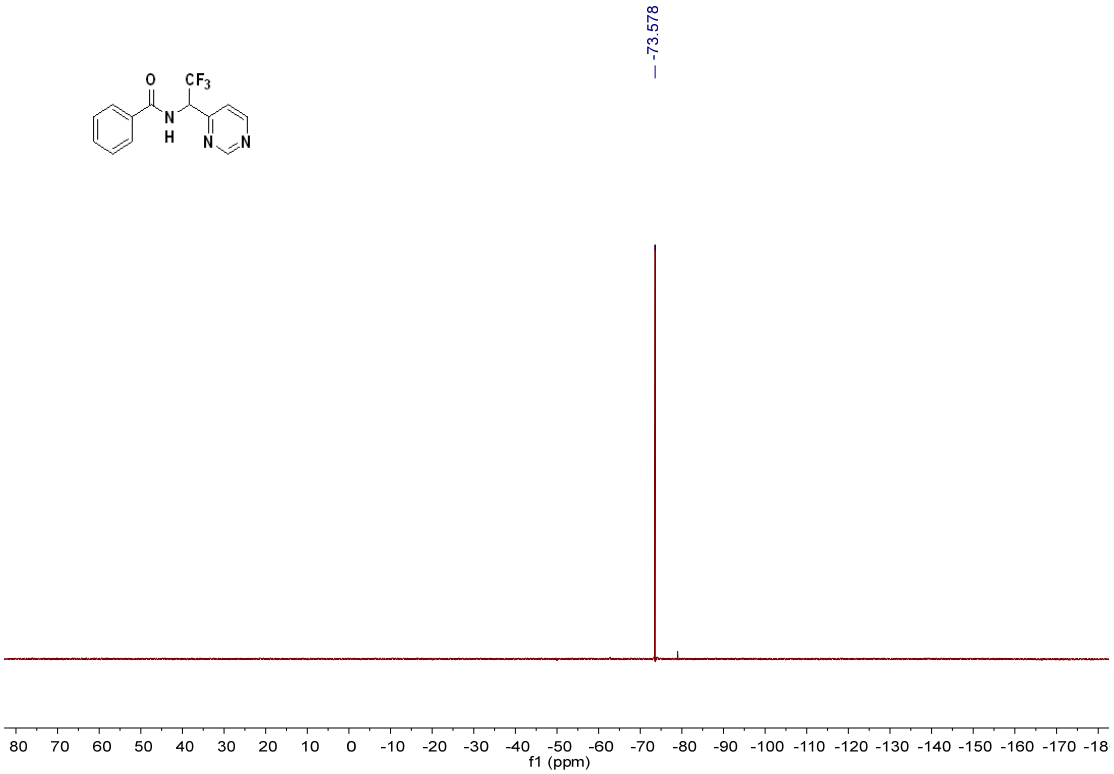

173.392
159.788
158.788
158.001
125.796
123.557
121.319
119.490
119.443
119.412
119.388
119.077
77.253
76.999
76.747
71.996
71.737
71.477
71.218
42.595
28.733
28.673
25.514
25.167
25.147
F3C
O
O
N
N
f1 (ppm)



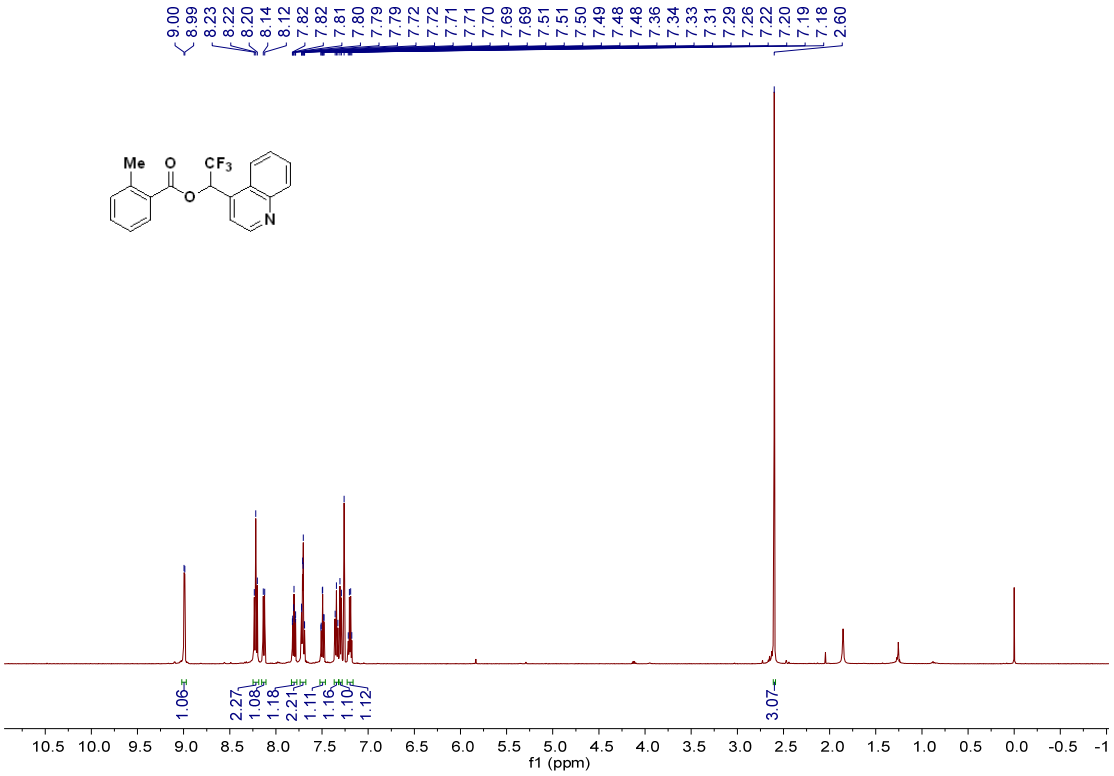
NMR Spectra of product **29**:

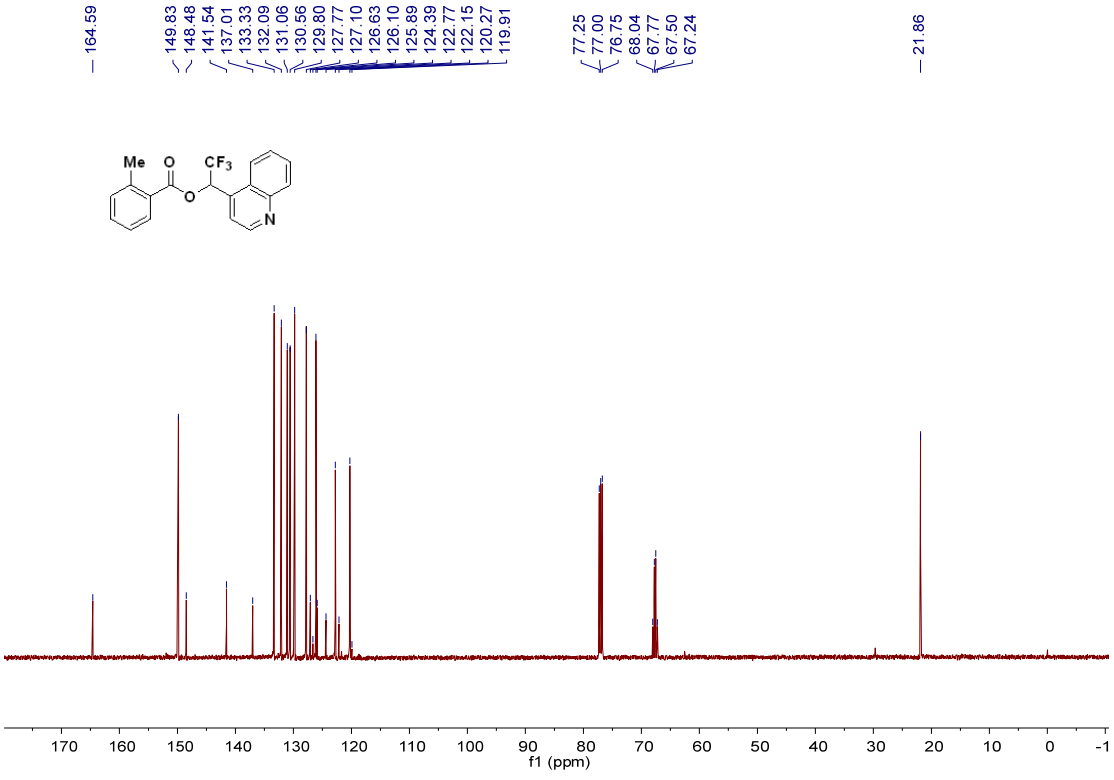


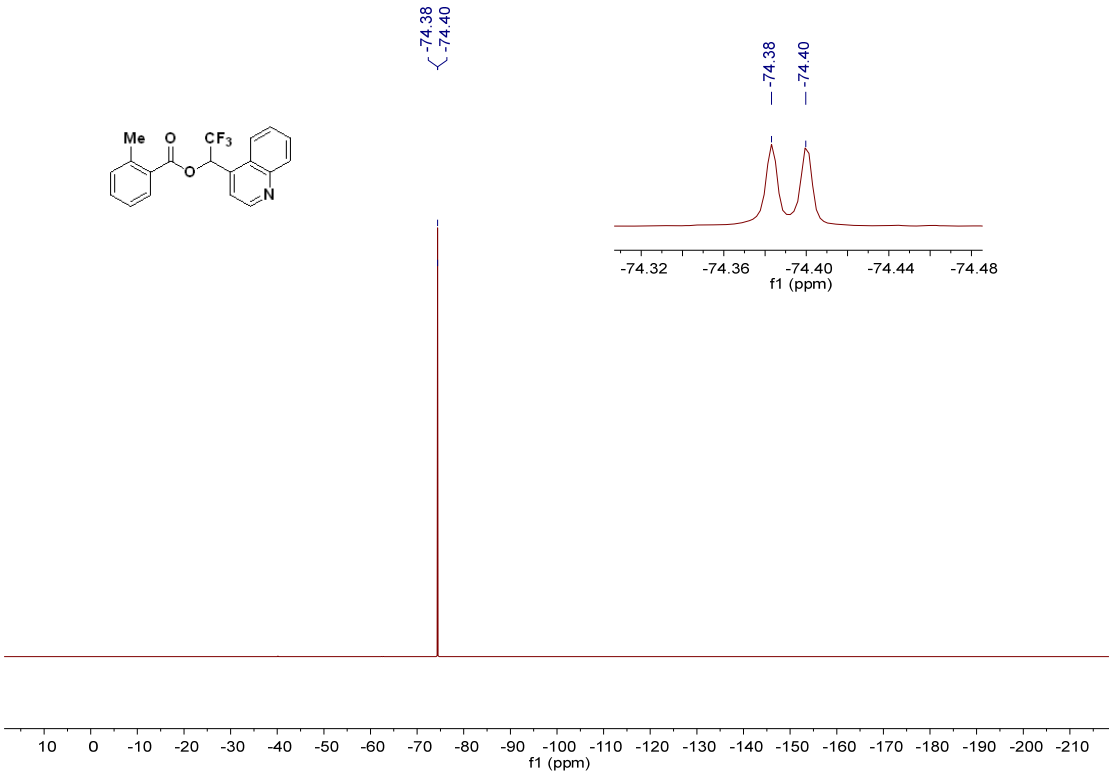




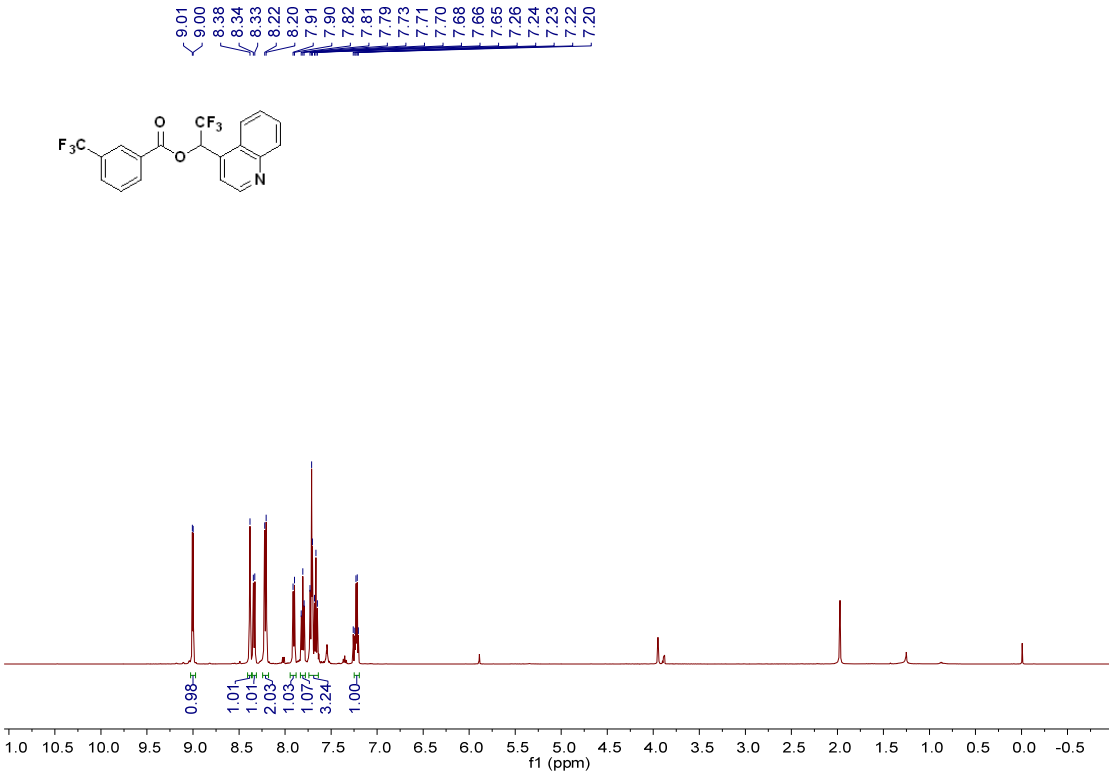
NMR Spectra of product **30**:

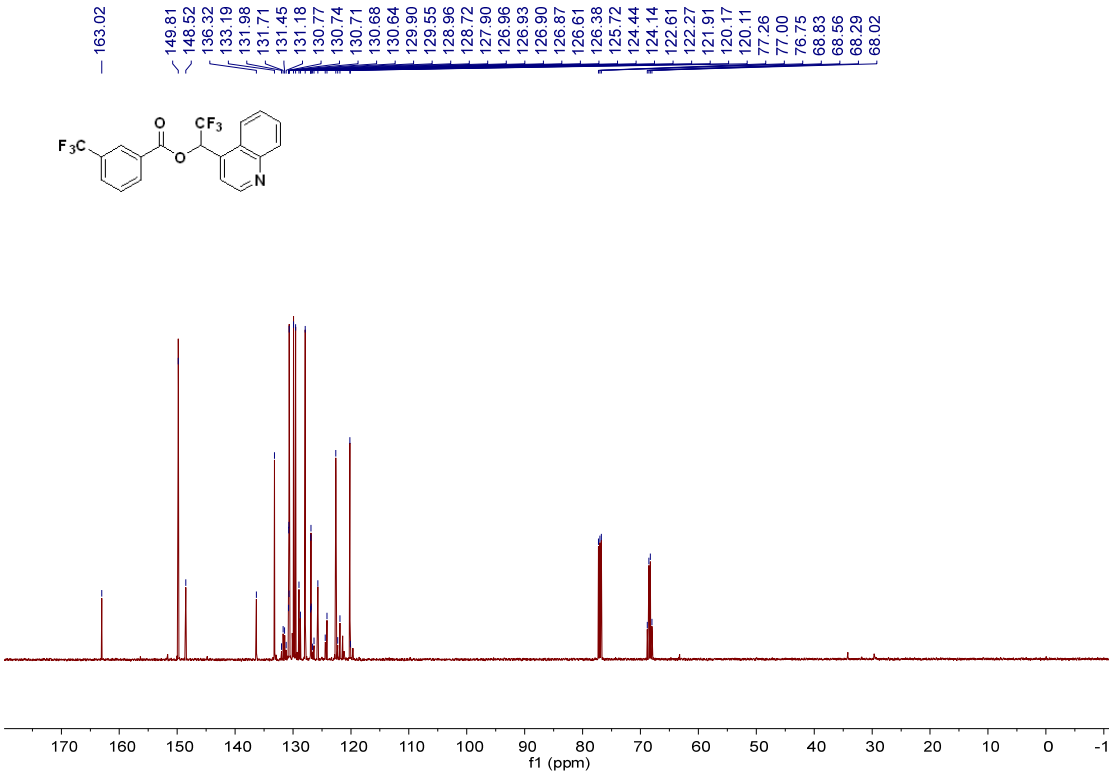

9.00
8.99
8.23
8.22
8.20
8.14
8.12
7.82
7.82
7.81
7.80
7.79
7.79
7.72
7.72
7.71
7.71
7.70
7.69
7.69
7.51
7.51
7.50
7.49
7.48
7.48
7.36
7.34
7.33
7.31
7.29
7.26
7.22
7.20
7.19
7.18
2.60
Me
O
CF3
O
N
1.06
2.27
1.08
1.18
2.21
1.11
1.16
1.10
1.12
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

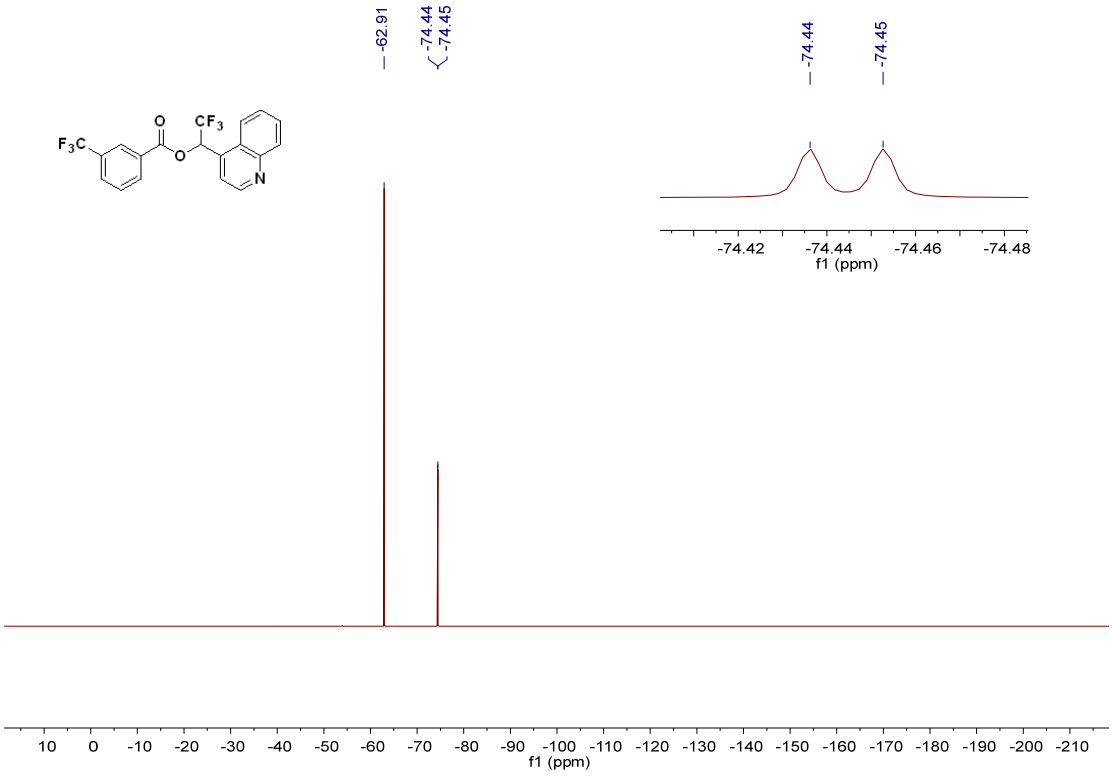

164.59
149.83
148.48
141.54
137.01
133.33
132.09
131.06
130.56
129.80
127.77
127.10
126.63
126.10
125.89
124.39
122.77
122.15
120.27
119.91
77.25
77.00
76.75
68.04
67.77
67.50
67.24
21.86
Me
O
CF3
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



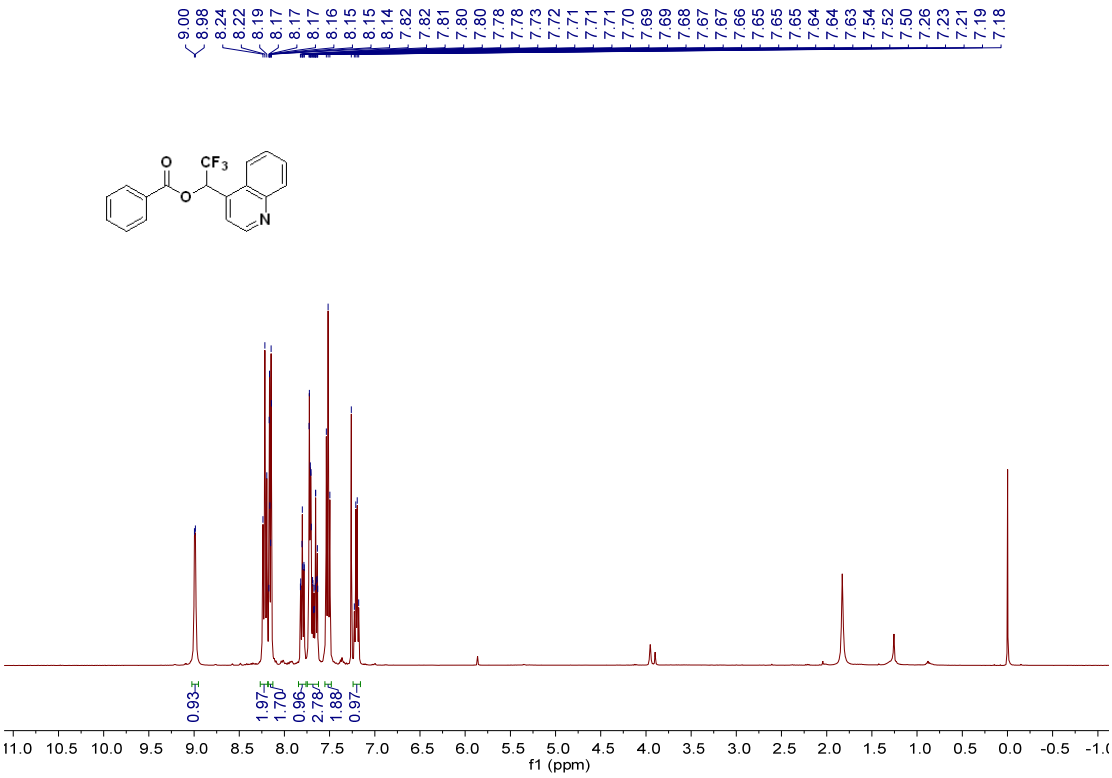
NMR Spectra of product **31**:

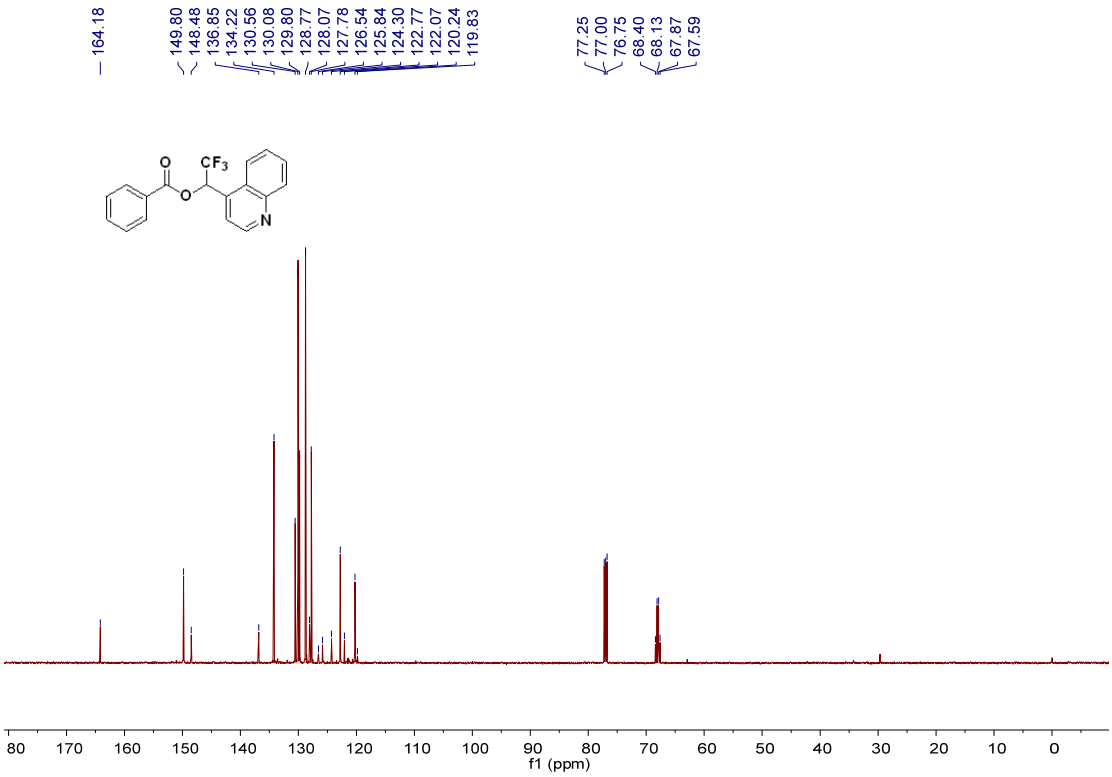


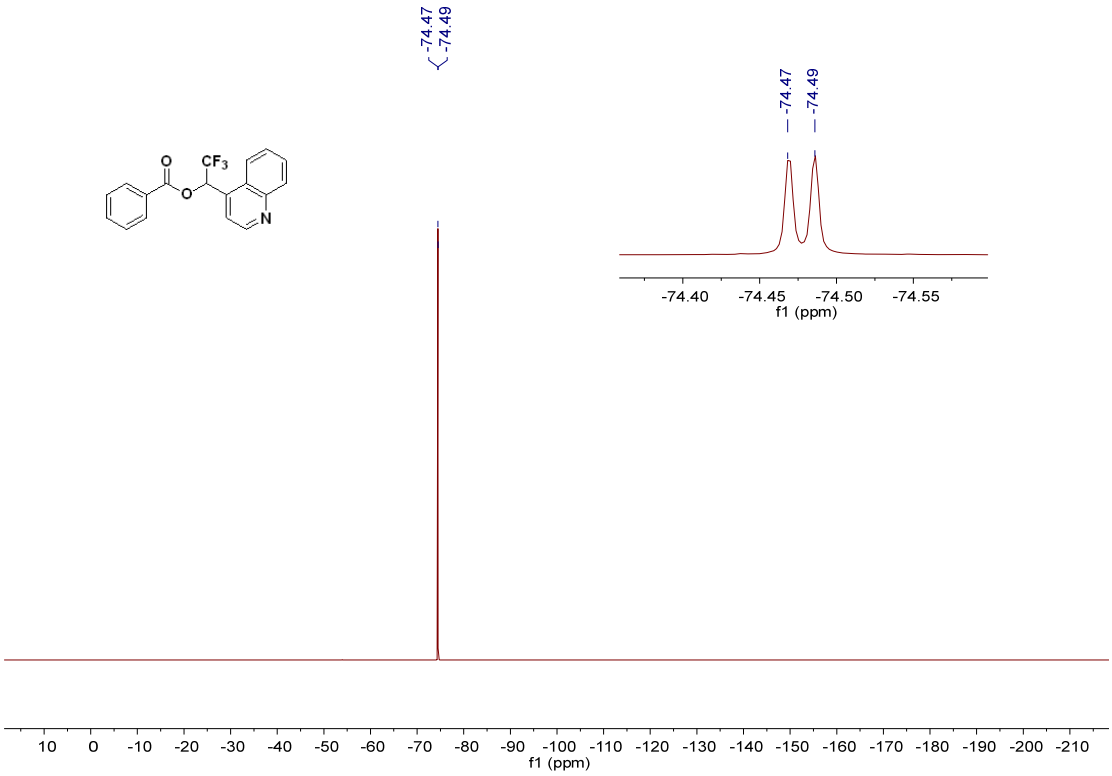




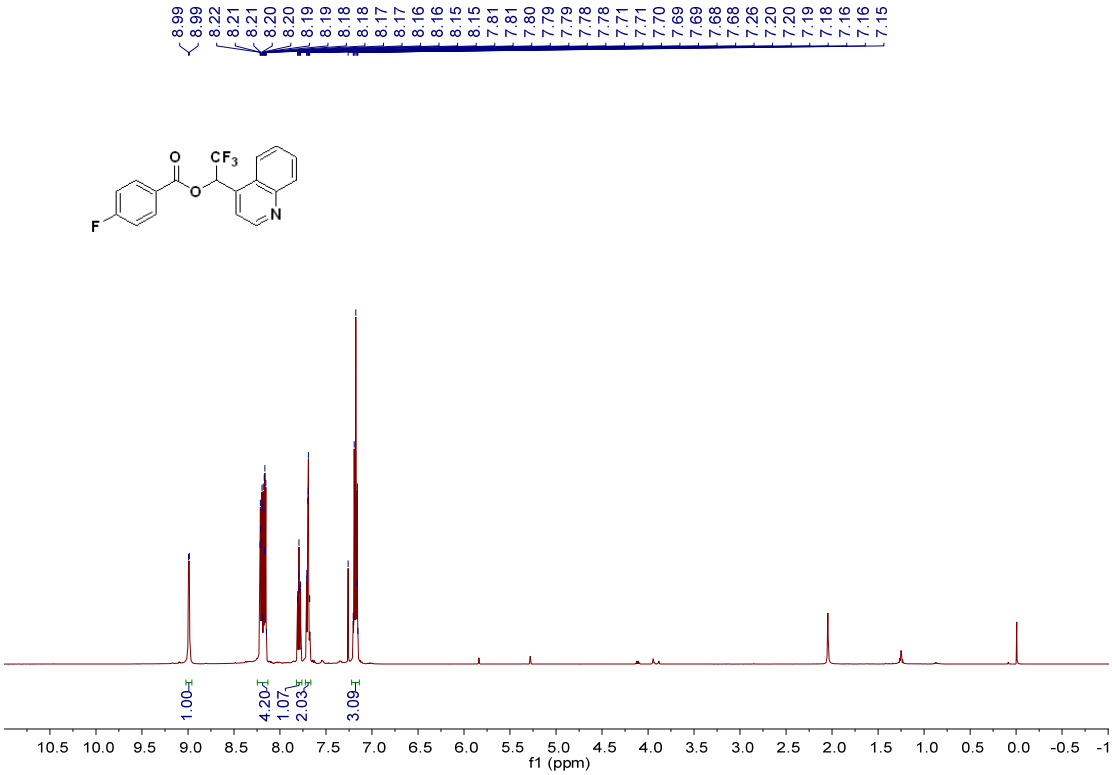
NMR Spectra of product **32**:

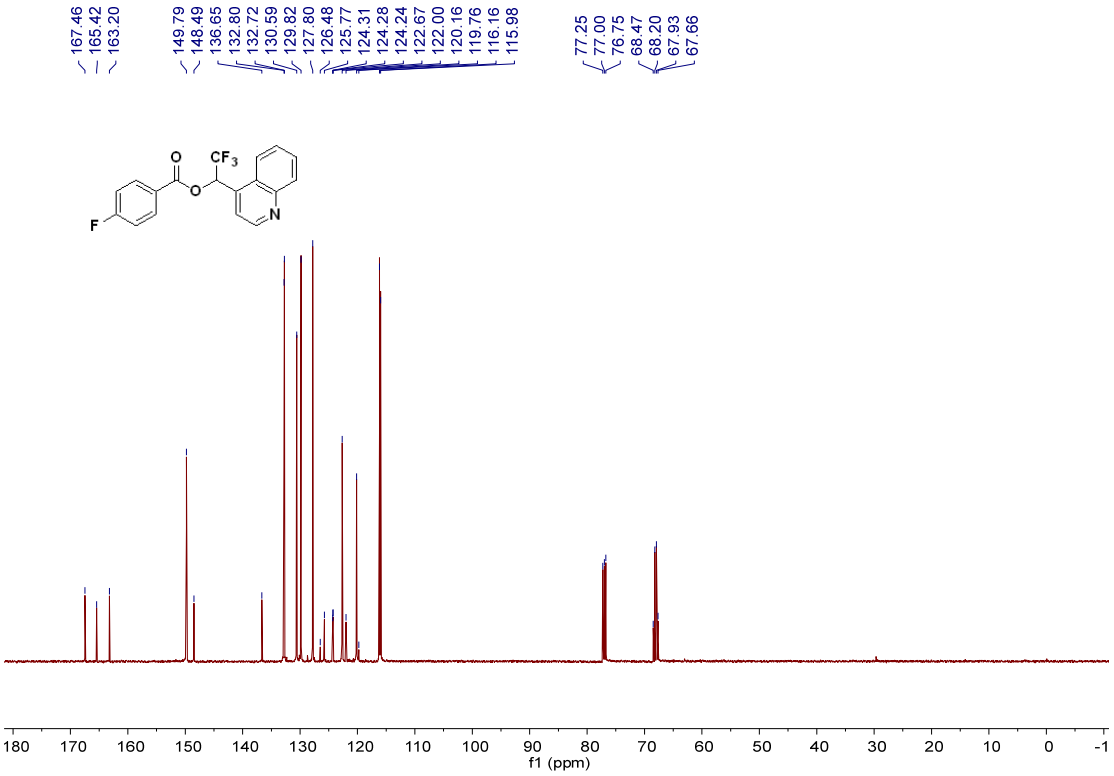

9.00
8.98
8.24
8.22
8.19
8.17
8.17
8.17
8.16
8.15
8.15
8.14
7.82
7.82
7.81
7.80
7.80
7.78
7.78
7.73
7.72
7.71
7.71
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.65
7.65
7.64
7.64
7.63
7.54
7.52
7.50
7.26
7.23
7.21
7.19
7.18
O
CF3
O
N
0.93
1.97
1.70
0.96
2.78
1.88
0.97
f1 (ppm)

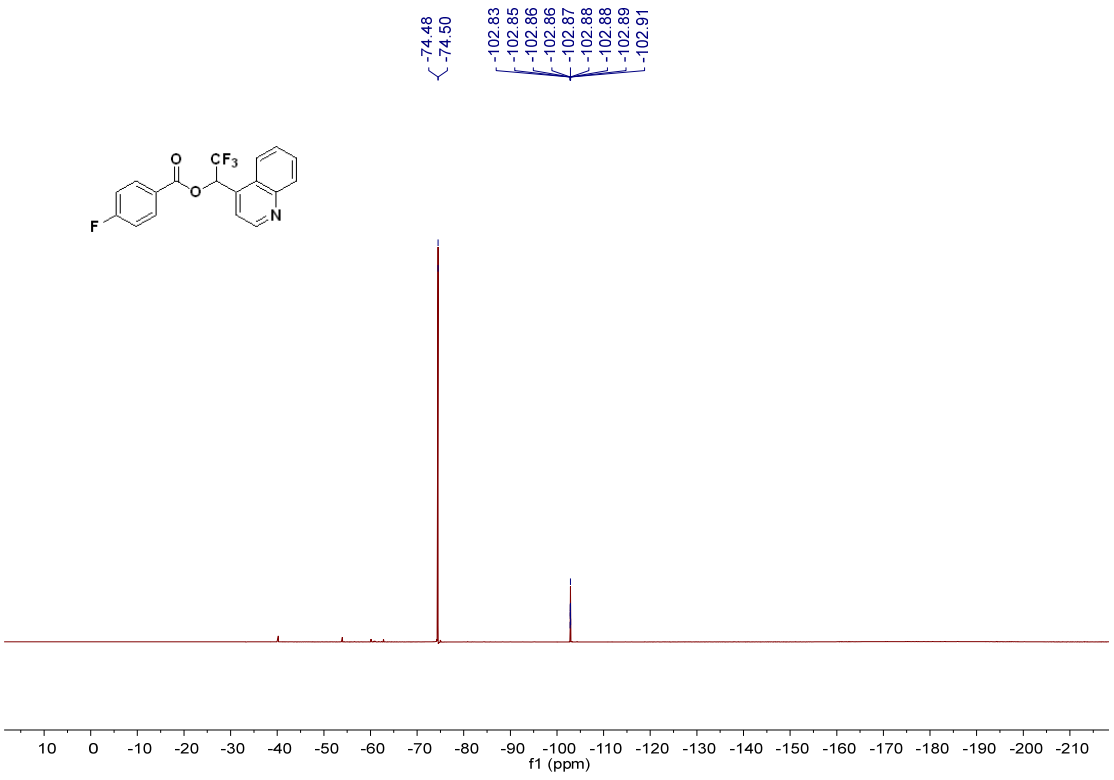

164.18
149.80
148.48
136.85
134.22
130.56
130.08
129.80
128.77
128.07
127.78
126.54
125.84
124.30
122.77
122.07
120.24
119.83
77.25
77.00
76.75
68.40
68.13
67.87
67.59
O
CF3
O
N
f1 (ppm)



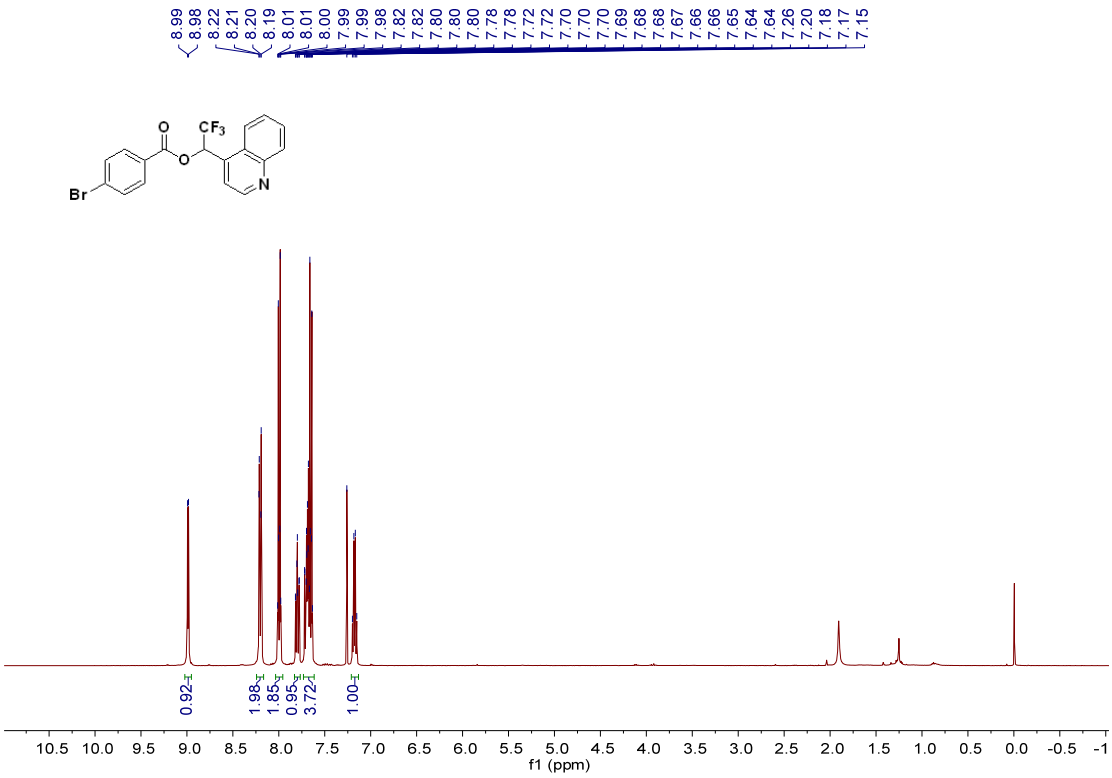
NMR Spectra of product **33**:

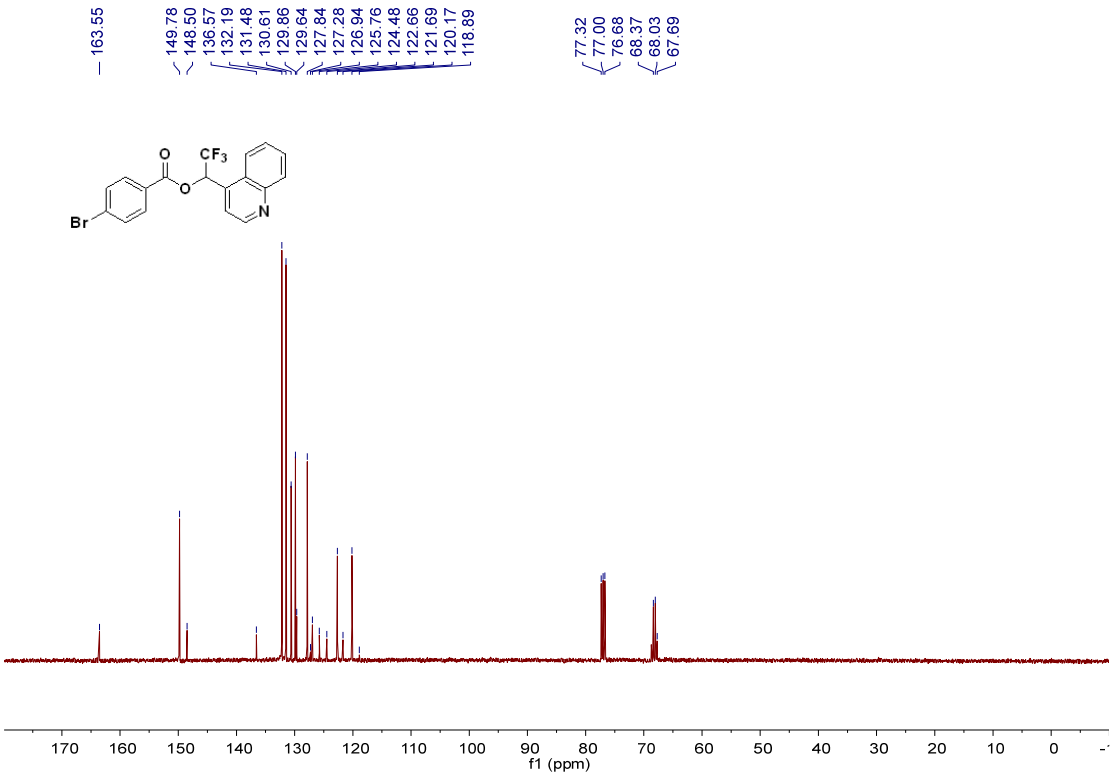


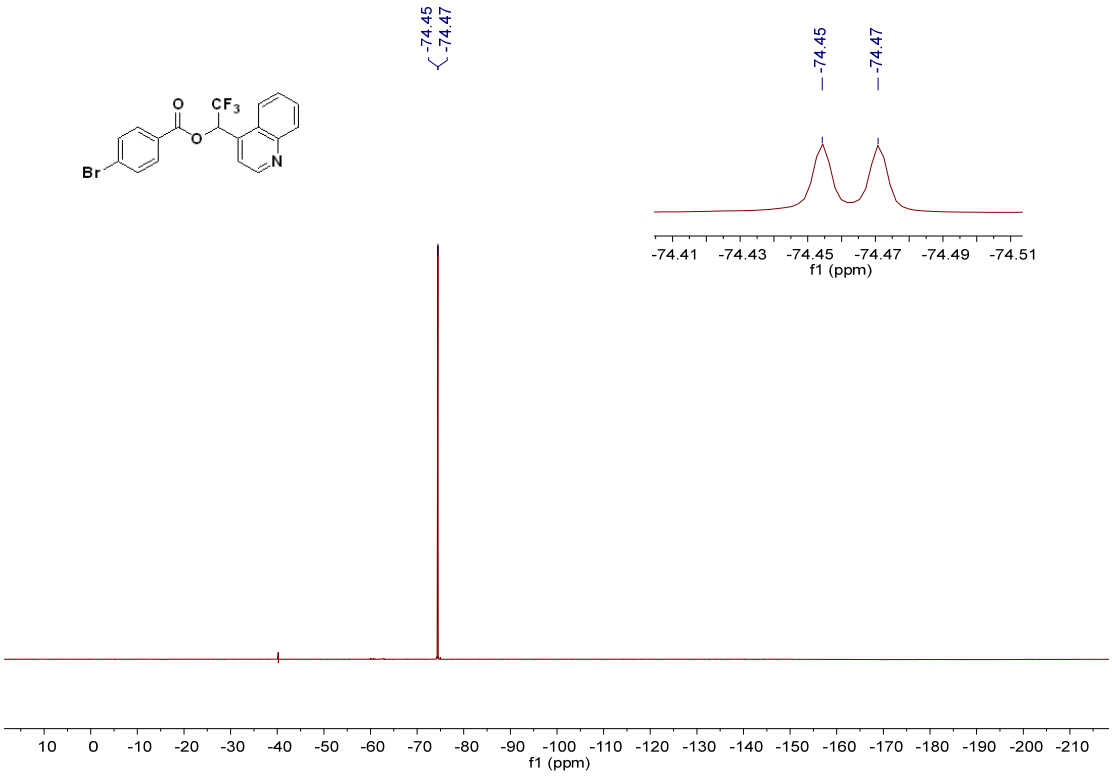




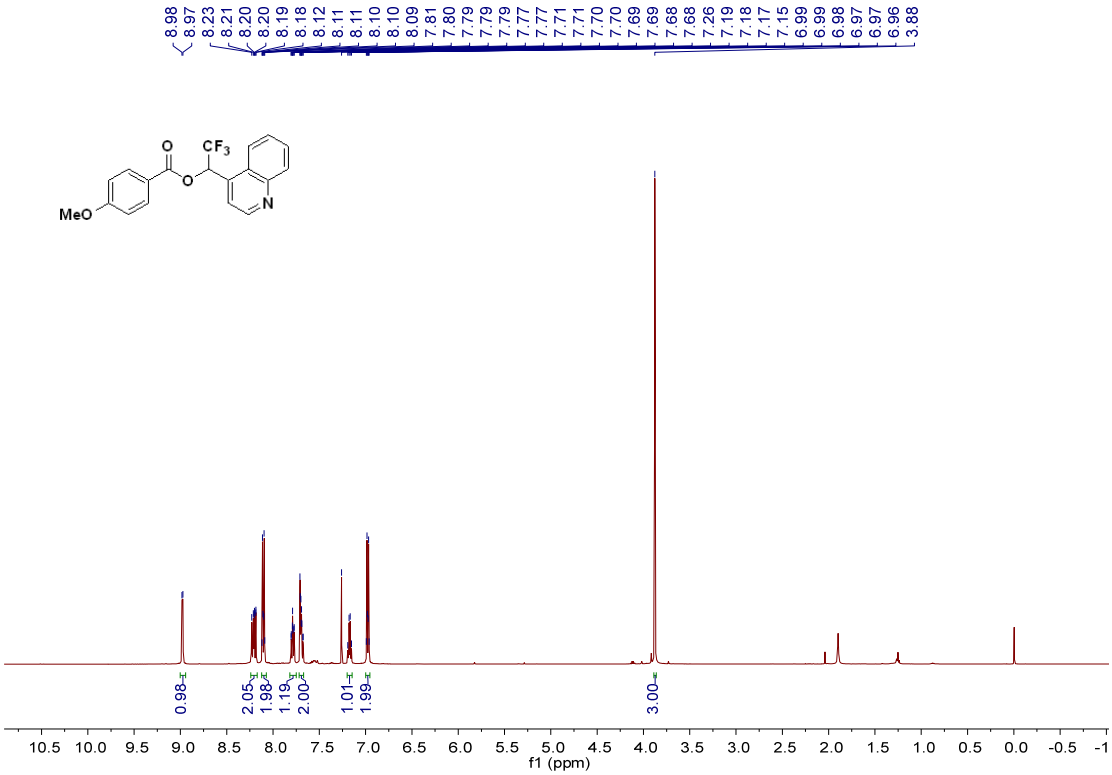
NMR Spectra of product **34**:

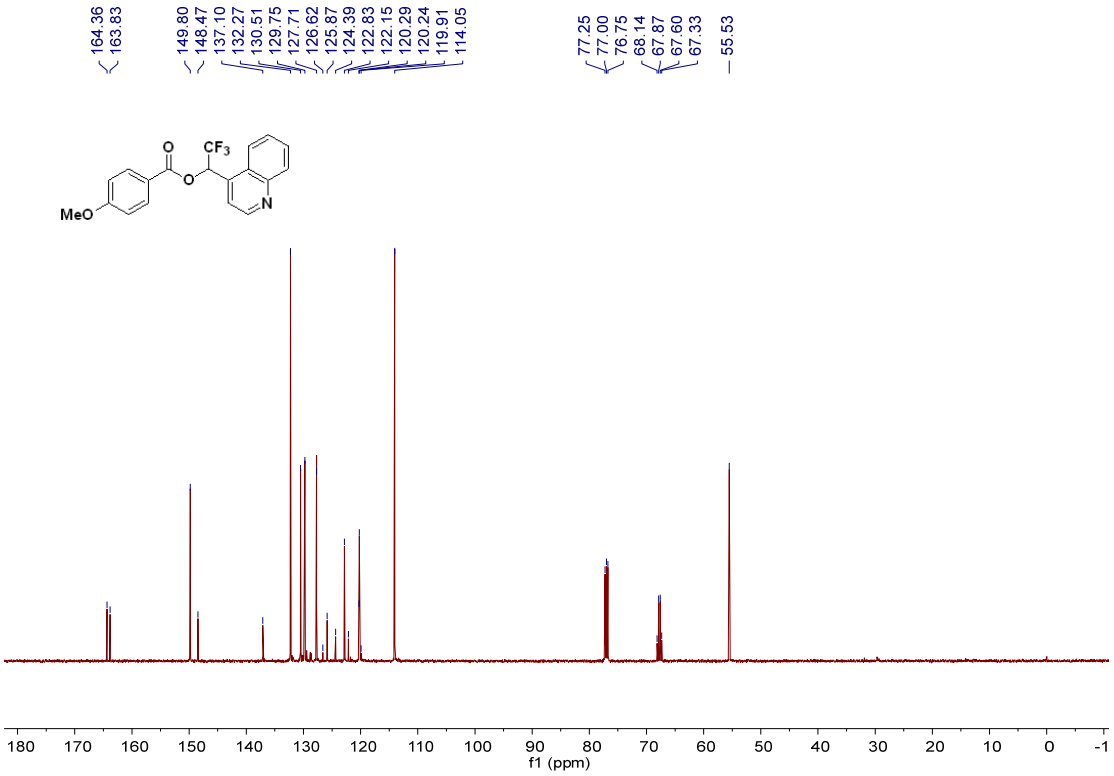

8.99
8.98
8.22
8.21
8.20
8.19
8.01
8.01
8.00
7.99
7.99
7.98
7.82
7.82
7.80
7.80
7.80
7.78
7.78
7.72
7.72
7.70
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.65
7.64
7.64
7.26
7.20
7.18
7.17
7.15
O
CF3
O
Br
N
0.92
1.98
1.85
0.95
3.72
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

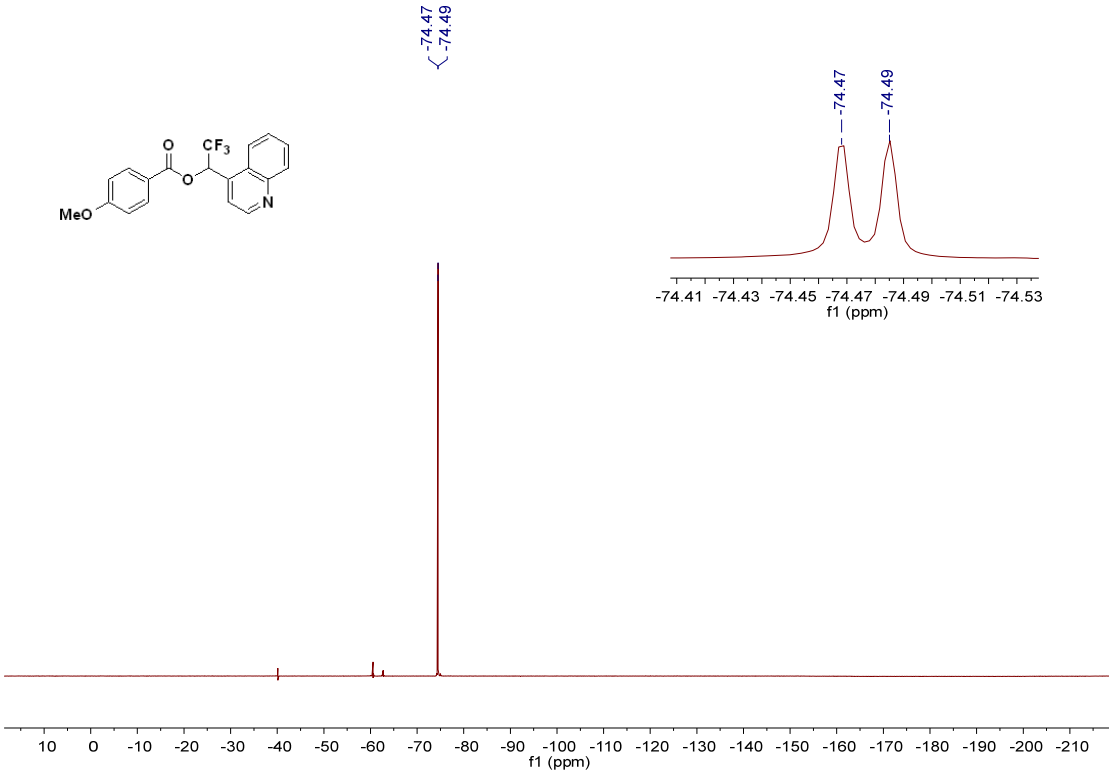

163.55
149.78
148.50
136.57
132.19
131.48
130.61
129.86
129.64
127.84
127.28
126.94
125.76
124.48
122.66
121.69
120.17
118.89
77.32
77.00
76.68
68.37
68.03
67.69
O
CF3
O
Br
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



NMR Spectra of product **35**:

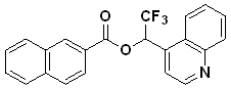


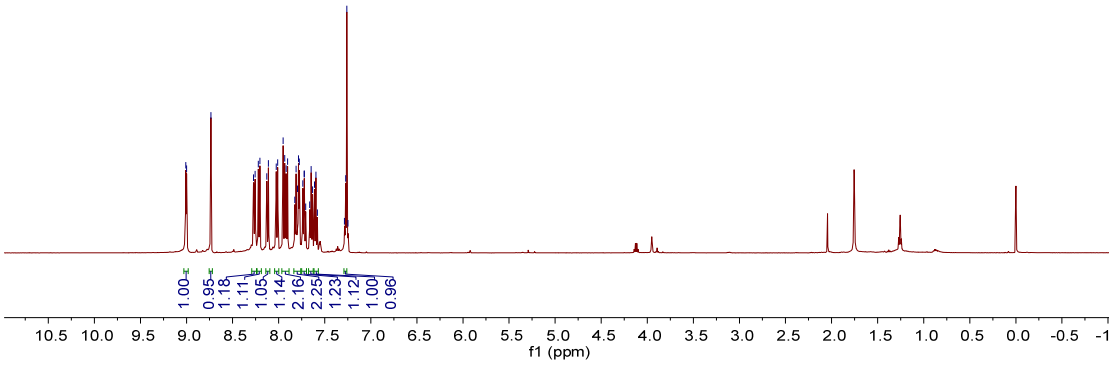




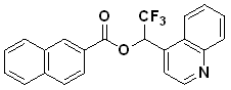
NMR Spectra of product **36**:

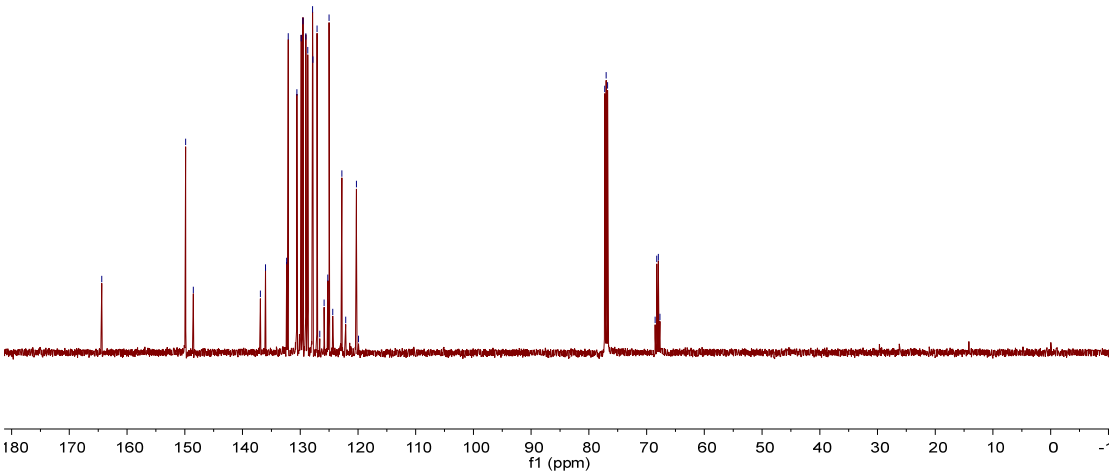

9.01
9.00
8.74
8.27
8.26
8.22
8.20
8.13
8.11
8.03
8.01
7.95
7.93
7.92
7.90
7.83
7.81
7.80
7.79
7.78
7.74
7.72
7.72
7.71
7.66
7.65
7.63
7.61
7.60
7.58
7.29
7.27
7.26
7.25

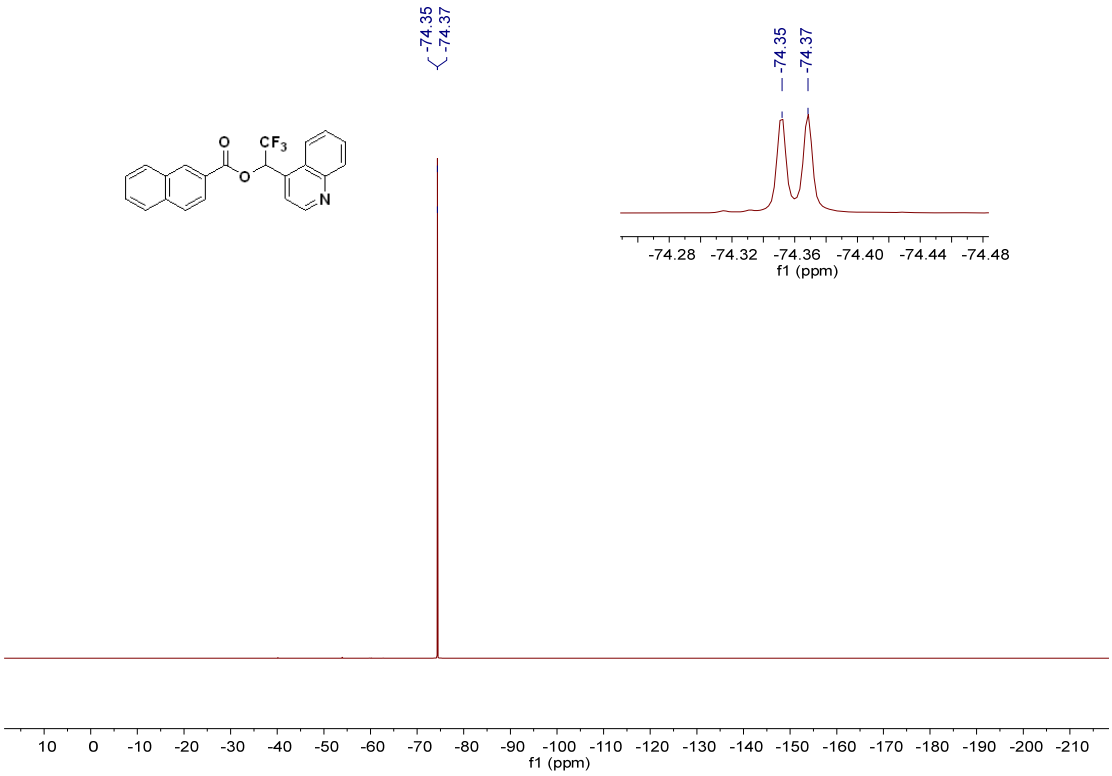

O
CF3
O
N


1.00
0.95
1.18
1.11
1.05
1.14
2.16
2.25
1.23
1.12
1.00
0.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

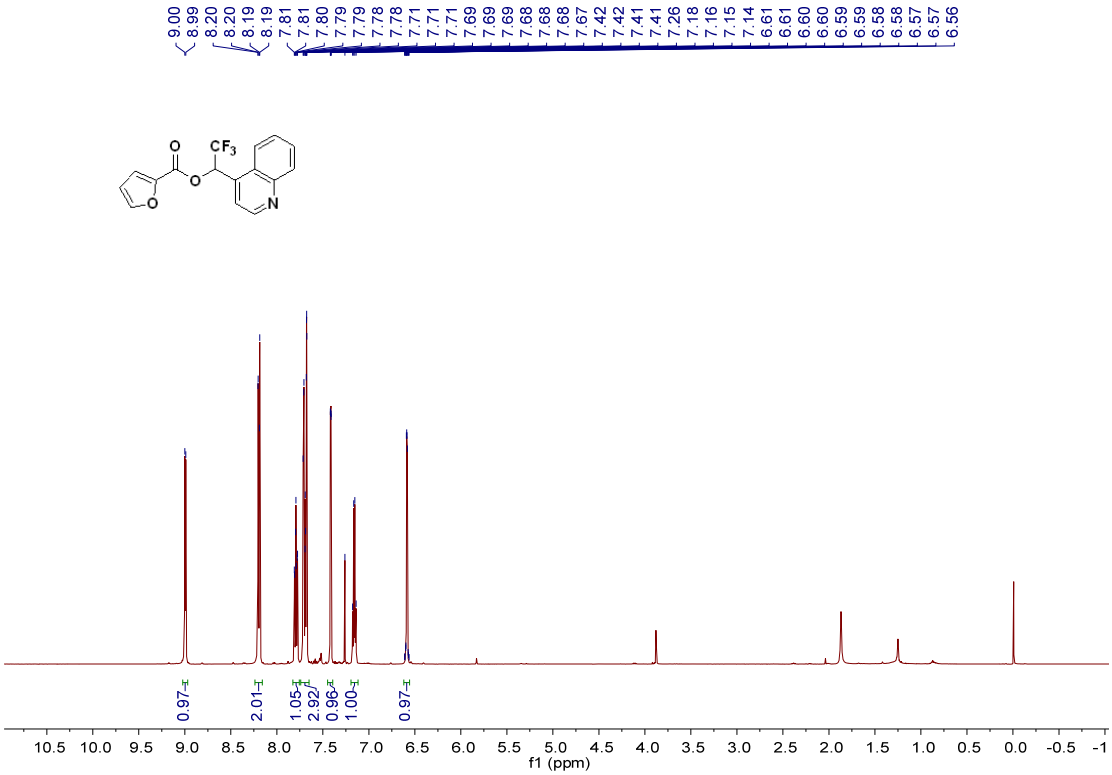

164.38
149.85
148.51
136.90
136.00
132.35
132.08
130.58
129.82
129.52
129.03
128.69
127.85
127.79
127.08
126.61
125.87
125.22
125.00
124.37
122.80
122.13
120.26
119.89
77.25
77.00
76.75
68.51
68.24
67.97
67.70

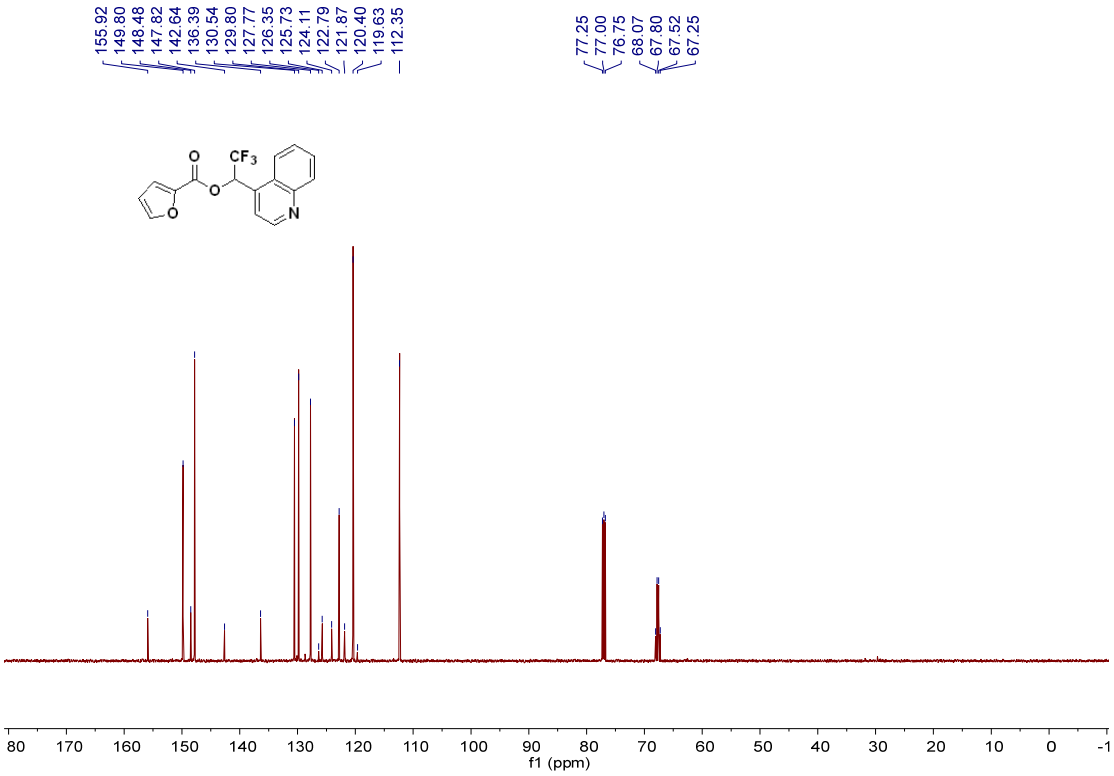

O
CF3
O
N

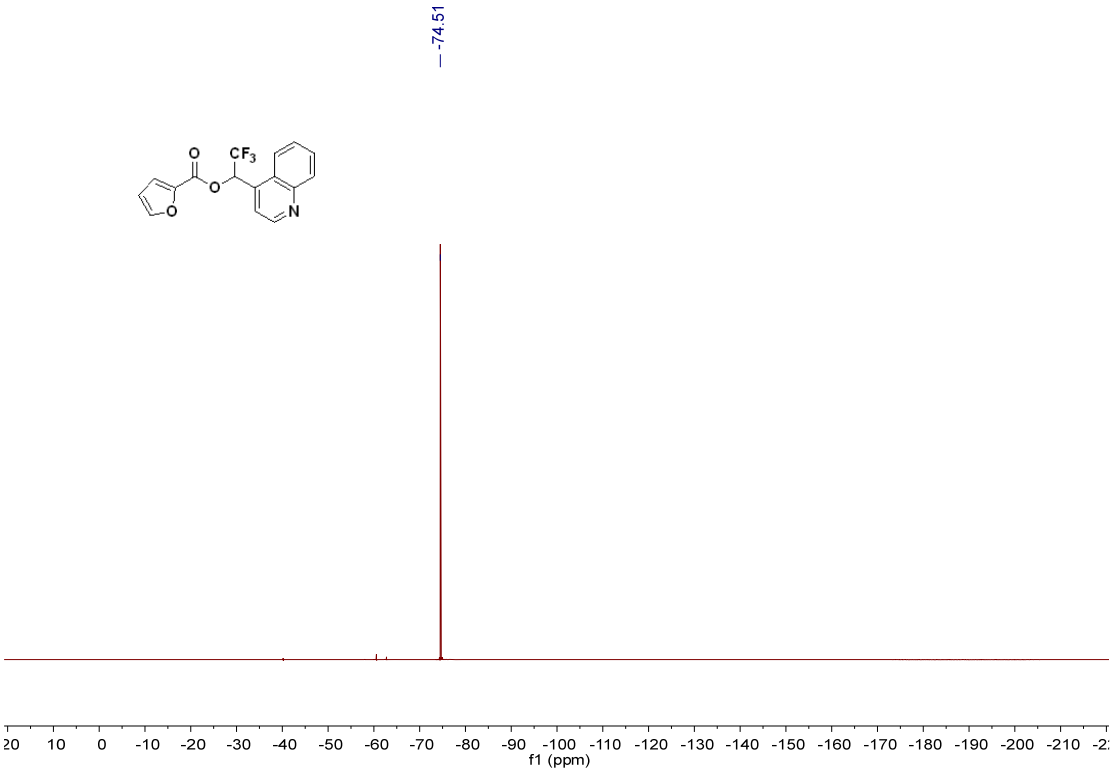

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



NMR Spectra of product **37**:

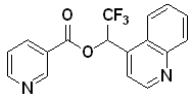


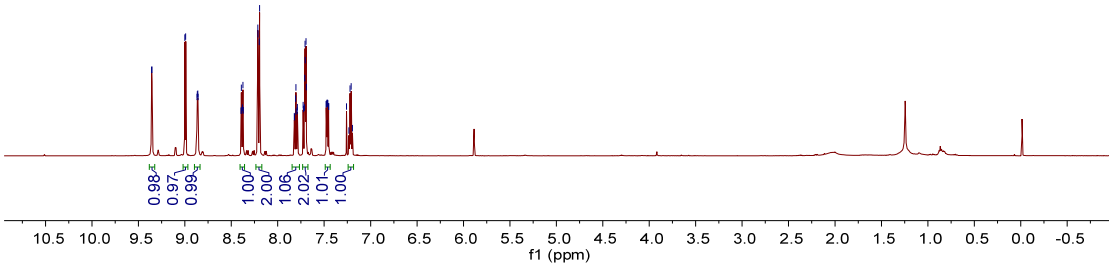




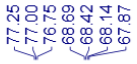
NMR Spectra of product **38**:

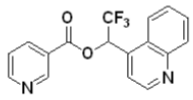

9.36
9.35
9.00
8.99
8.87
8.87
8.86
8.86
8.40
8.39
8.39
8.38
8.38
8.37
8.21
8.21
8.20
8.19
7.82
7.82
7.81
7.80
7.80
7.79
7.79
7.73
7.72
7.71
7.71
7.71
7.70
7.70
7.69
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.26
7.23
7.22
7.21
7.20

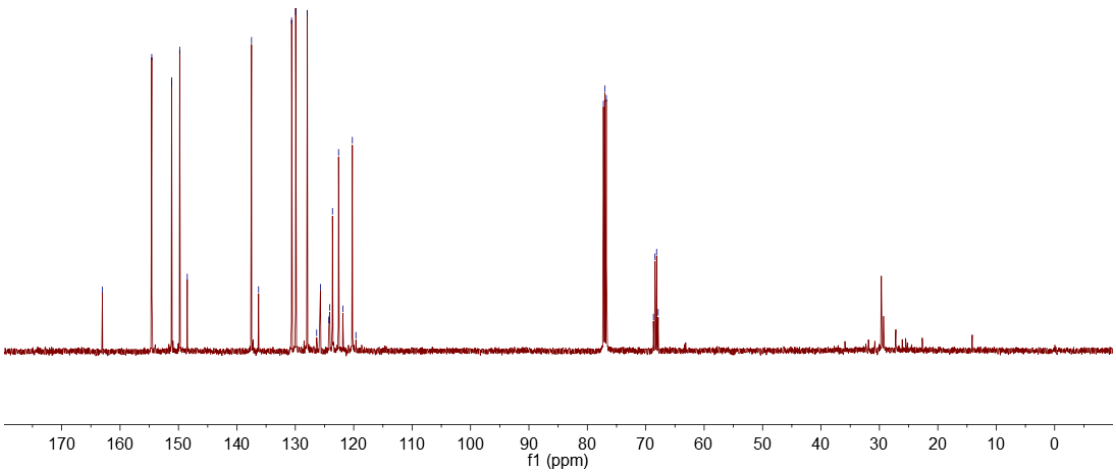

O
CF3
O
N
N

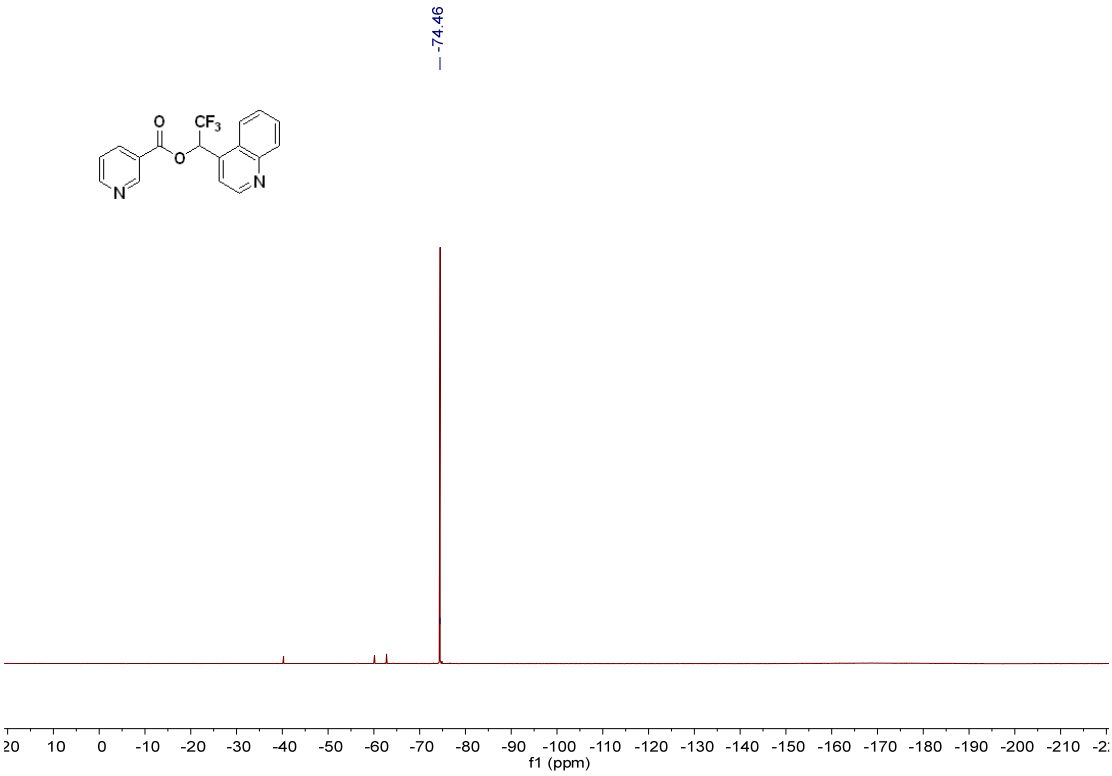

0.98
0.97
0.99
1.00
2.00
1.06
2.02
1.01
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.03
154.58
151.17
149.79
148.50
137.50
136.29
130.63
129.94
127.94
126.34
125.71
124.25
124.10
123.64
122.59
121.86
120.23
119.63

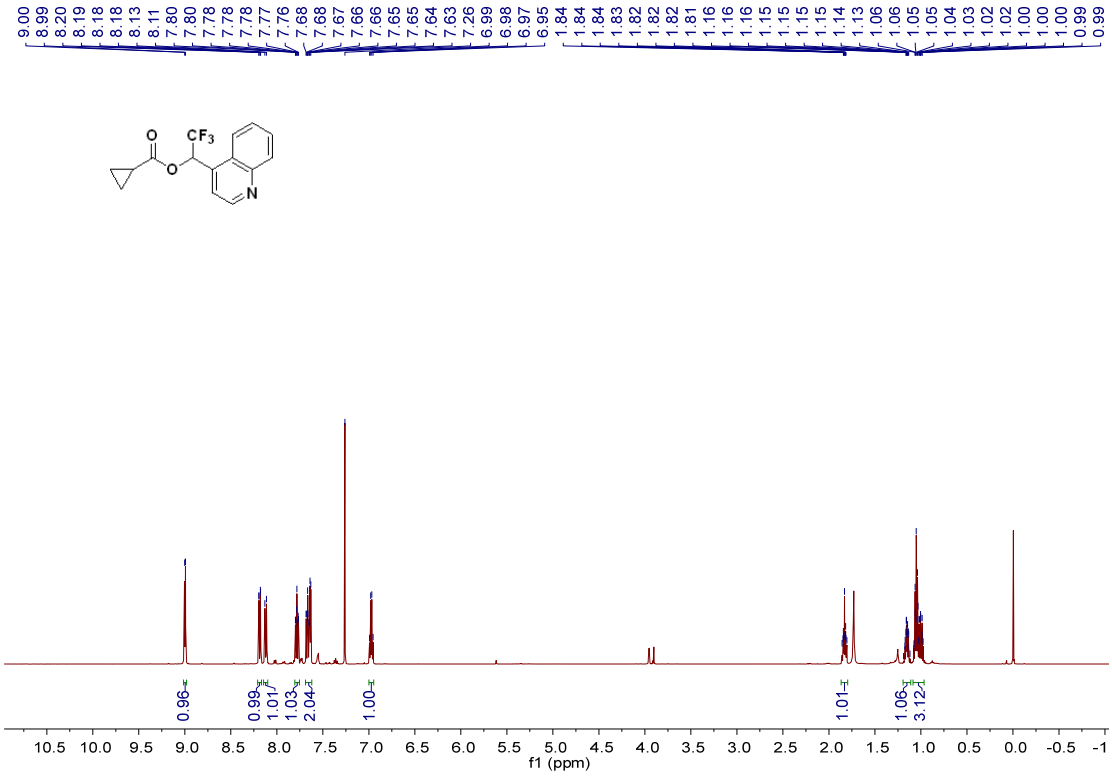

77.25
77.00
76.75
68.69
68.42
68.14
67.87

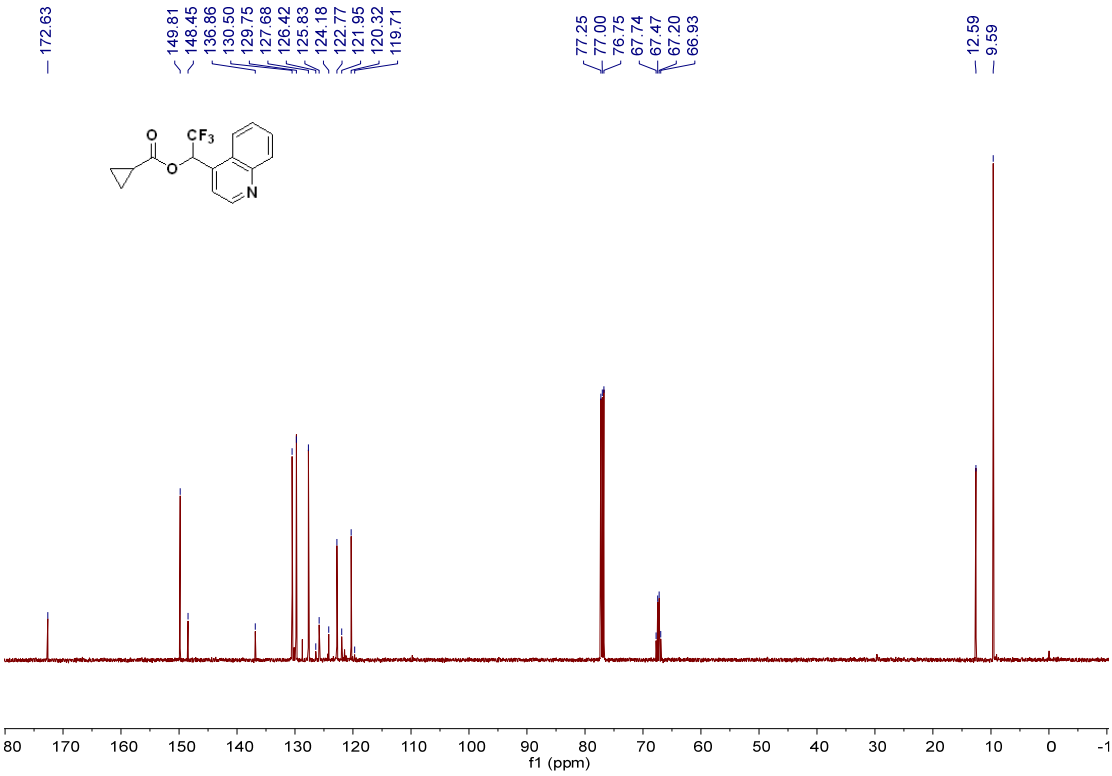

O
CF3
O
N
N

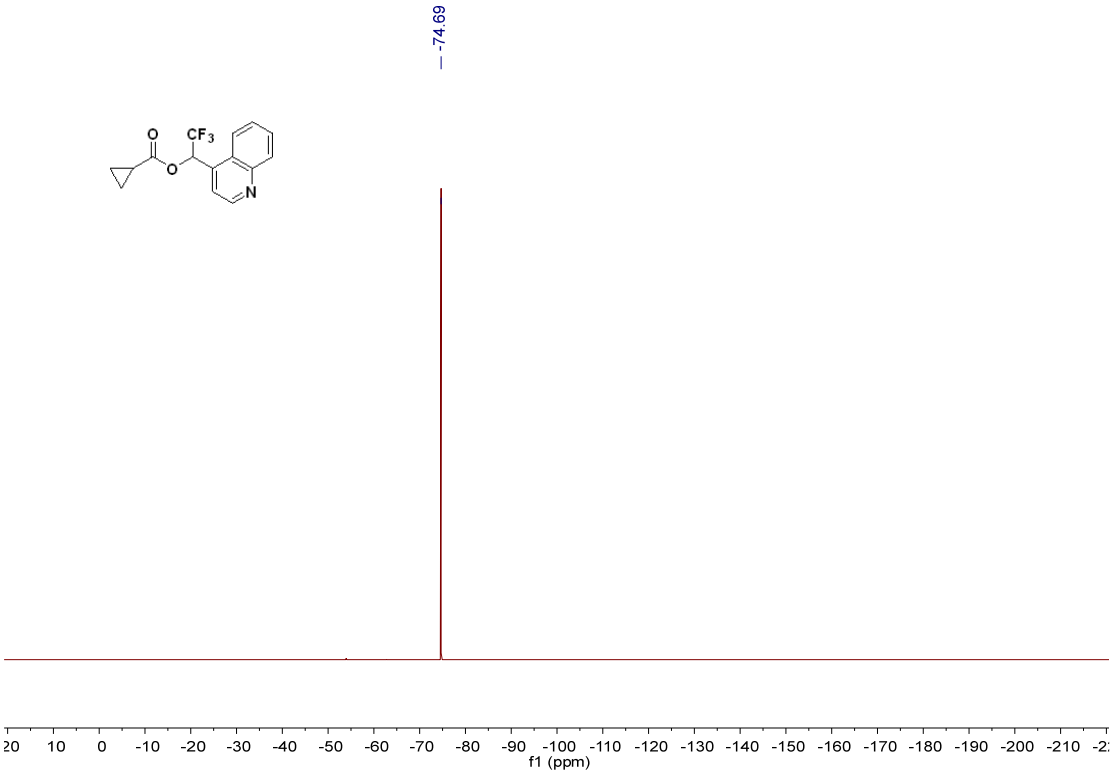

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



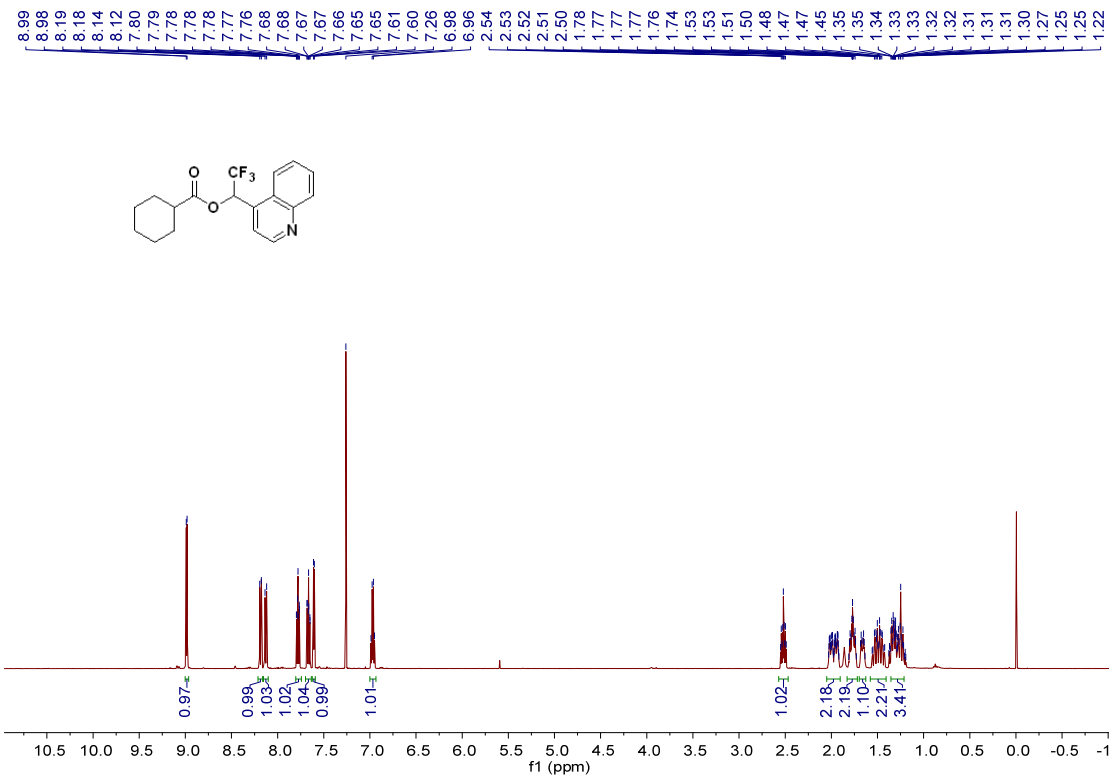
NMR Spectra of product **39**:

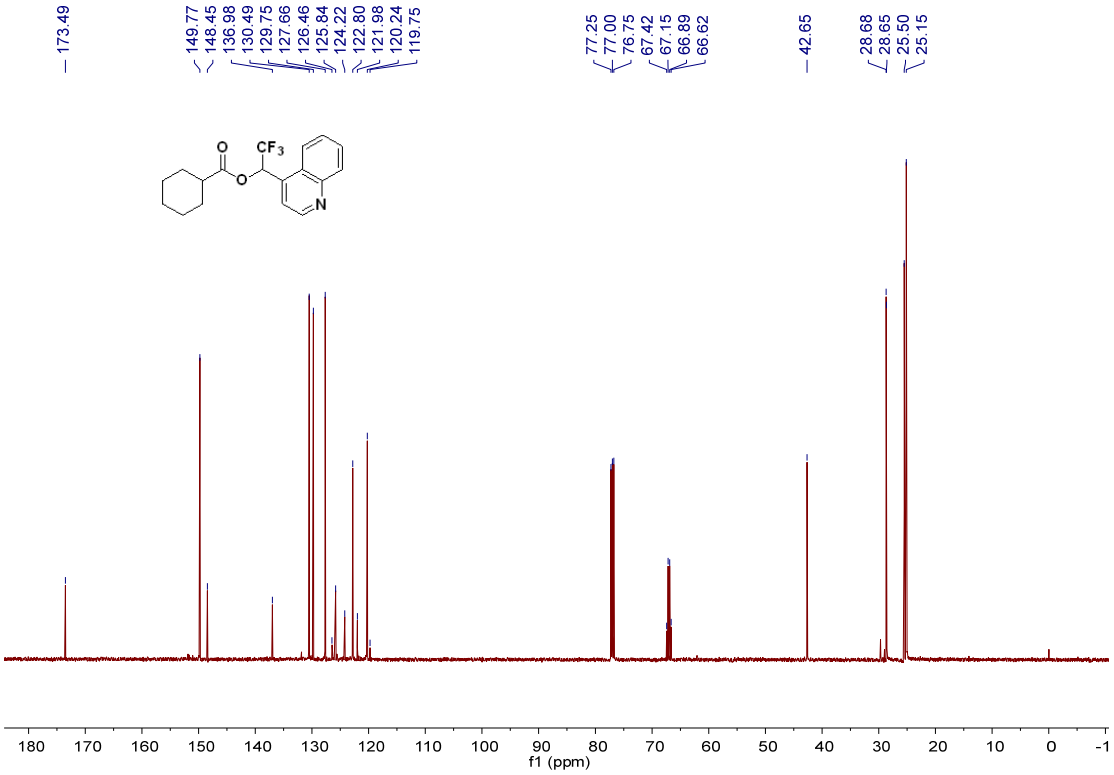


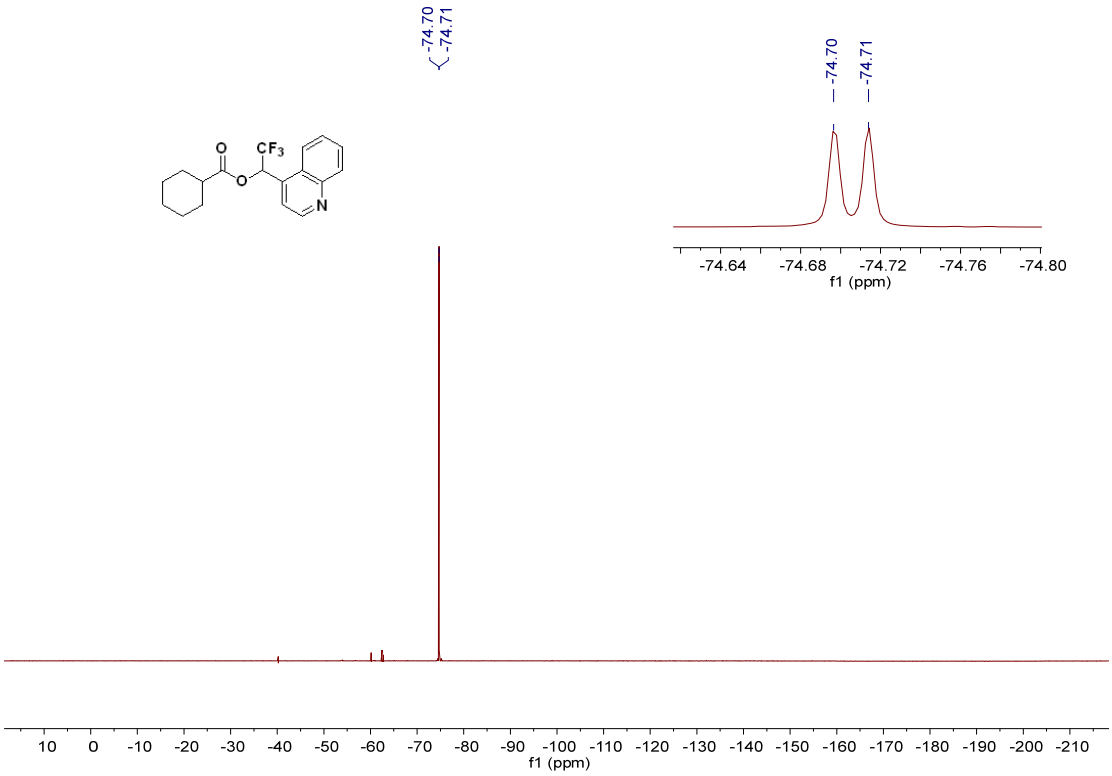




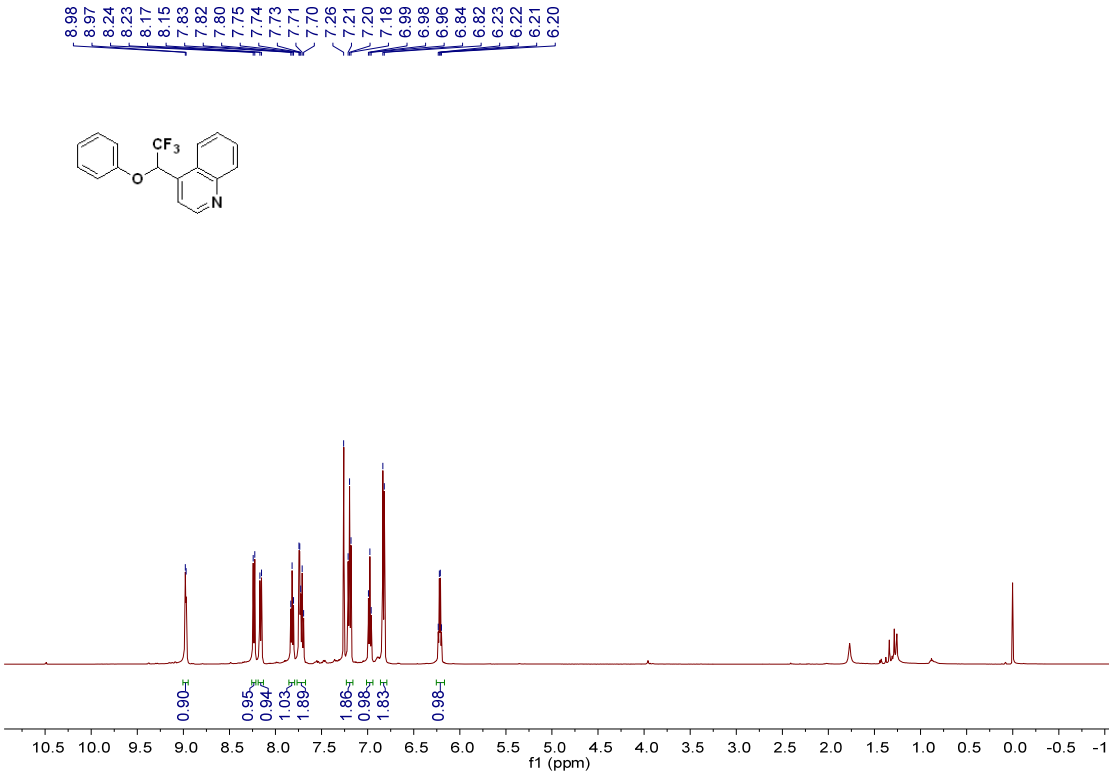
NMR Spectra of product **40**:

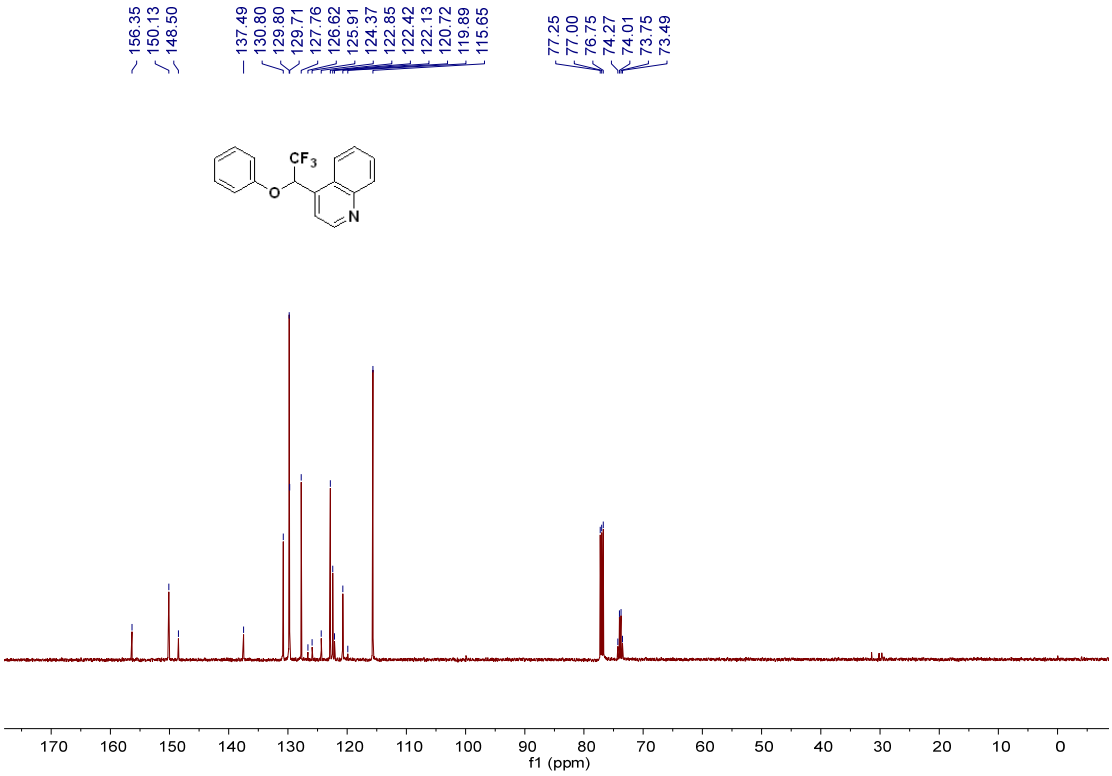

8.99 8.98 8.19 8.18 8.14 8.12 7.80 7.79 7.78 7.78 7.78 7.77 7.76 7.68 7.68 7.67 7.67 7.66 7.65 7.65 7.61 7.60 7.26 6.98 6.96
2.54 2.53 2.52 2.51 2.50 1.78 1.77 1.77 1.77 1.76 1.74 1.53 1.53 1.51 1.50 1.48 1.47 1.47 1.45 1.35 1.35 1.34 1.33 1.33 1.32 1.32 1.31 1.31 1.31 1.30 1.27 1.25 1.25 1.22
O
CF3
O
N
0.97 0.99 1.03 1.02 1.04 0.99 1.01 1.02 2.18 2.19 1.10 2.21 3.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

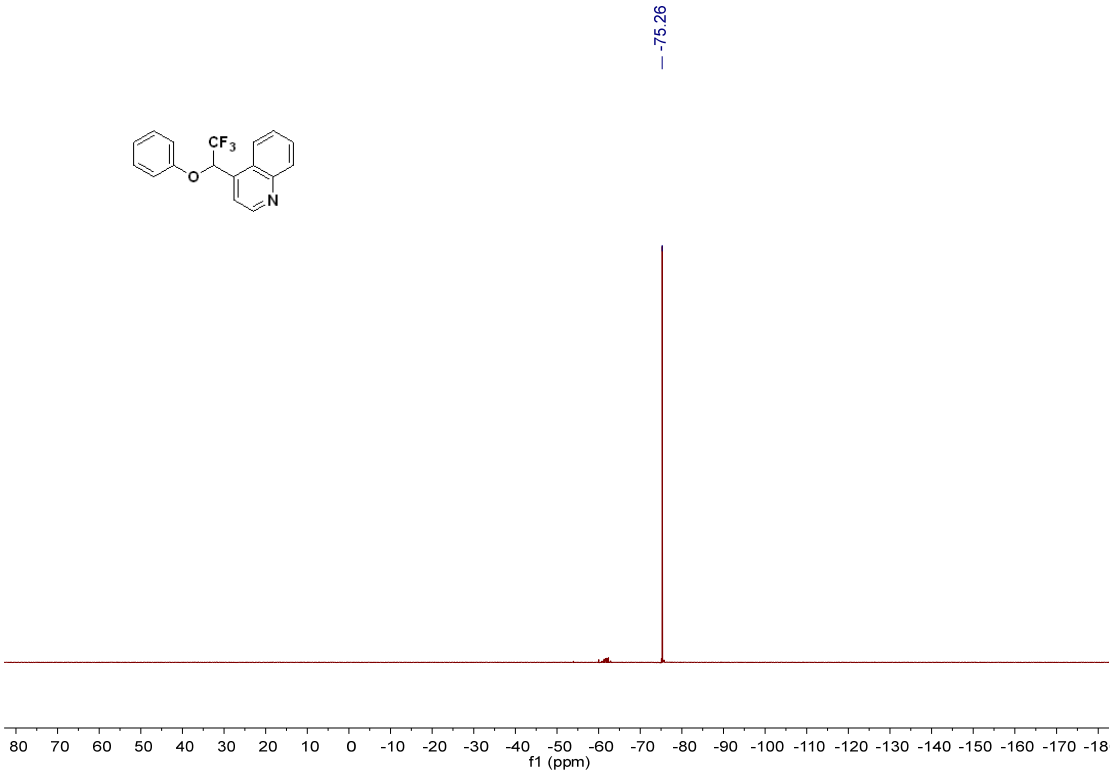

173.49
149.77 148.45 136.98 130.49 129.75 127.66 126.46 125.84 124.22 122.80 121.98 120.24 119.75
77.25 77.00 76.75 67.42 67.15 66.89 66.62
42.65
28.68 28.65 25.50 25.15
O
CF3
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



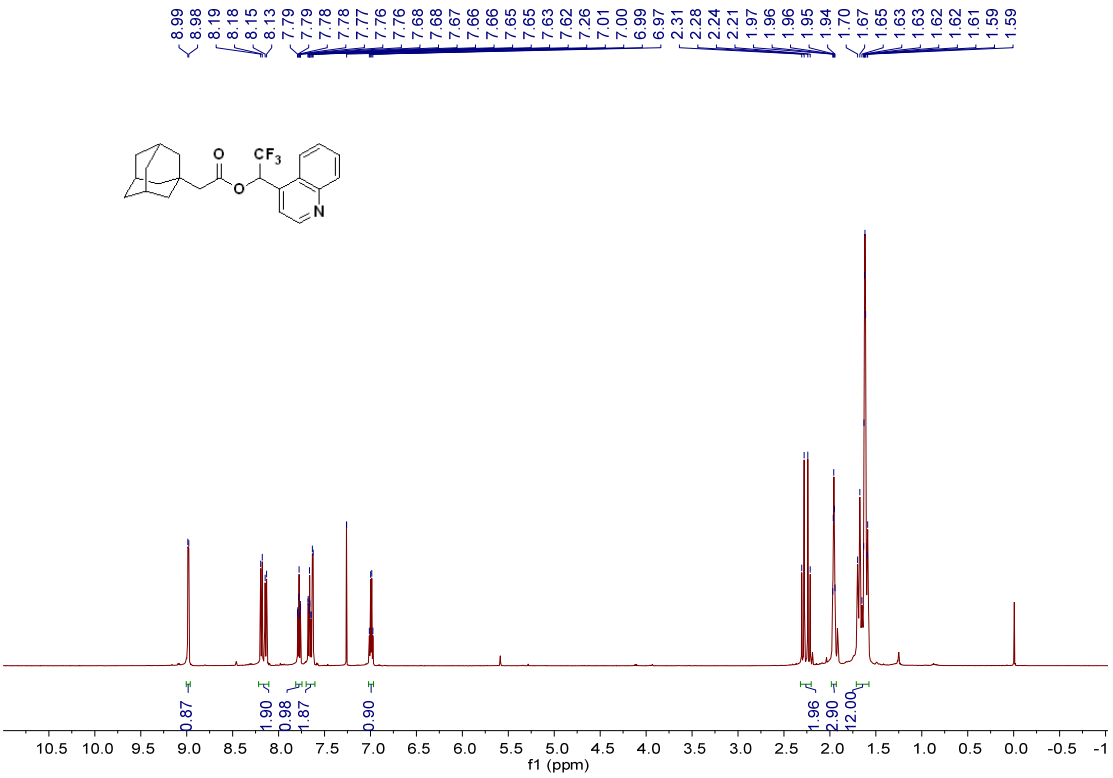
NMR Spectra of product **41**:

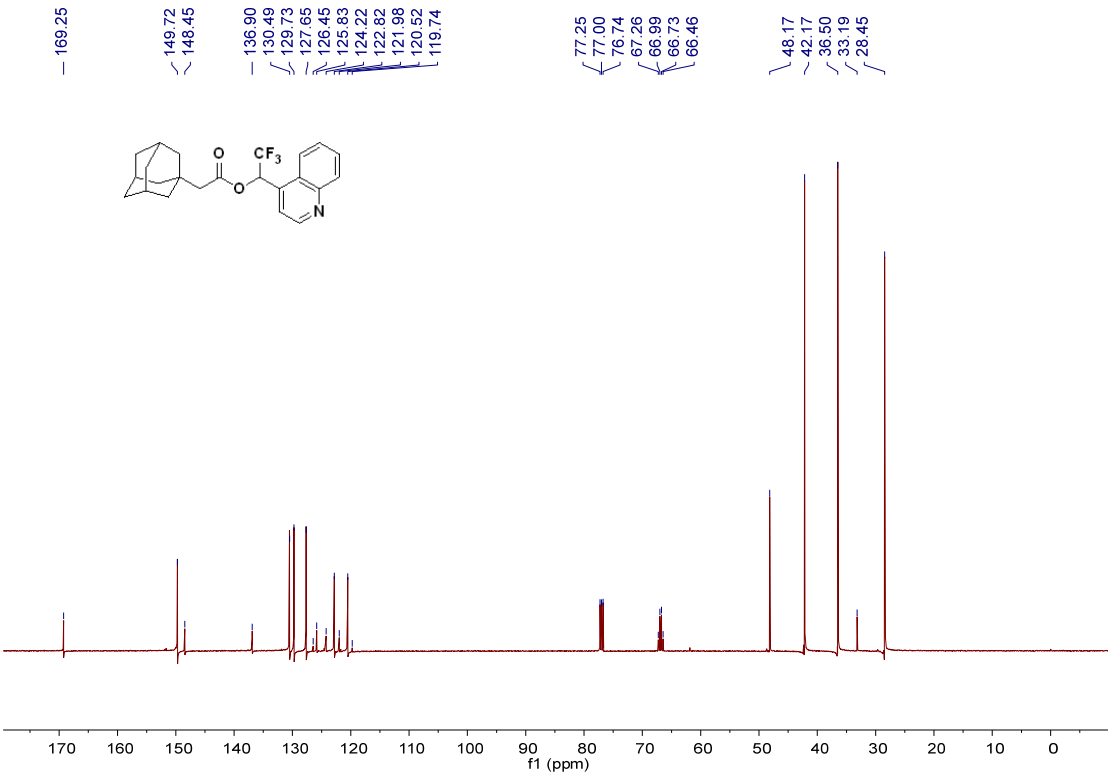


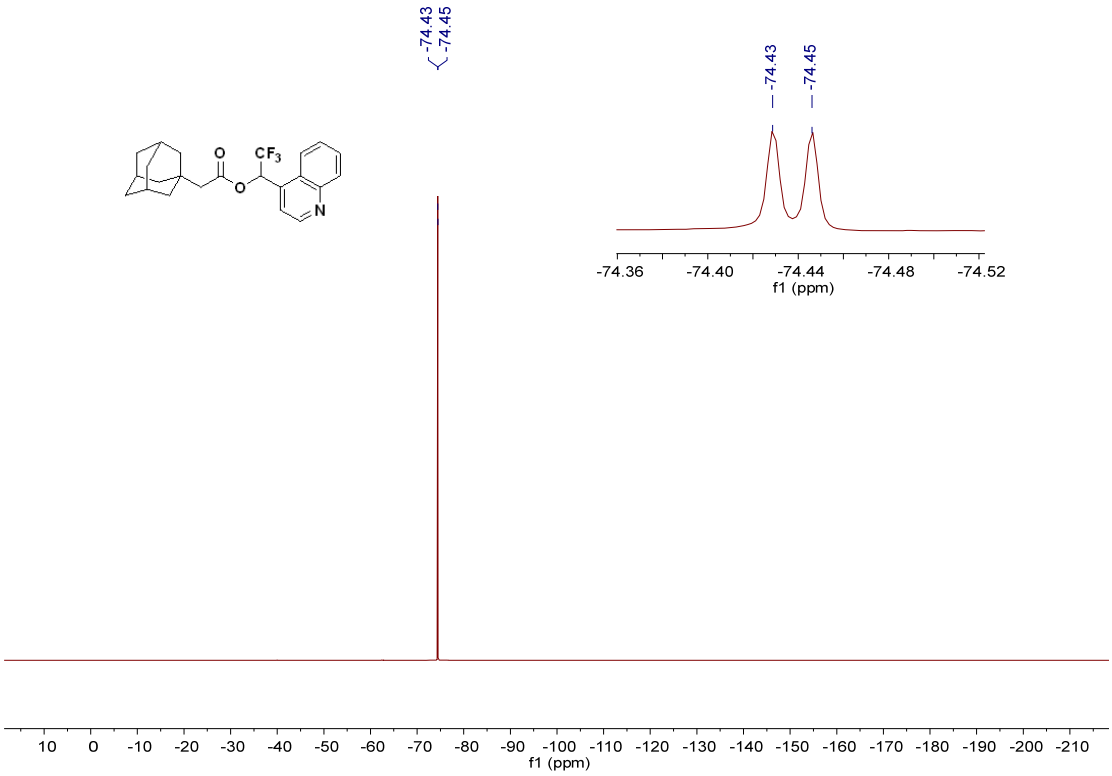




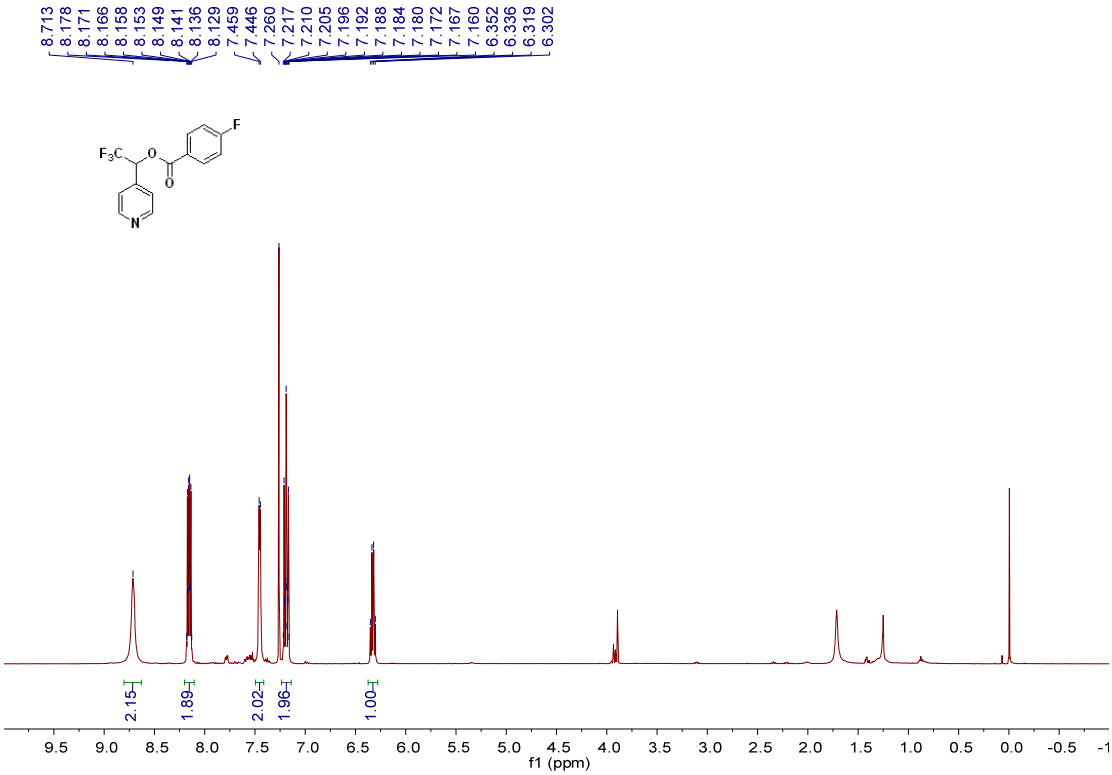
NMR Spectra of product **42**:

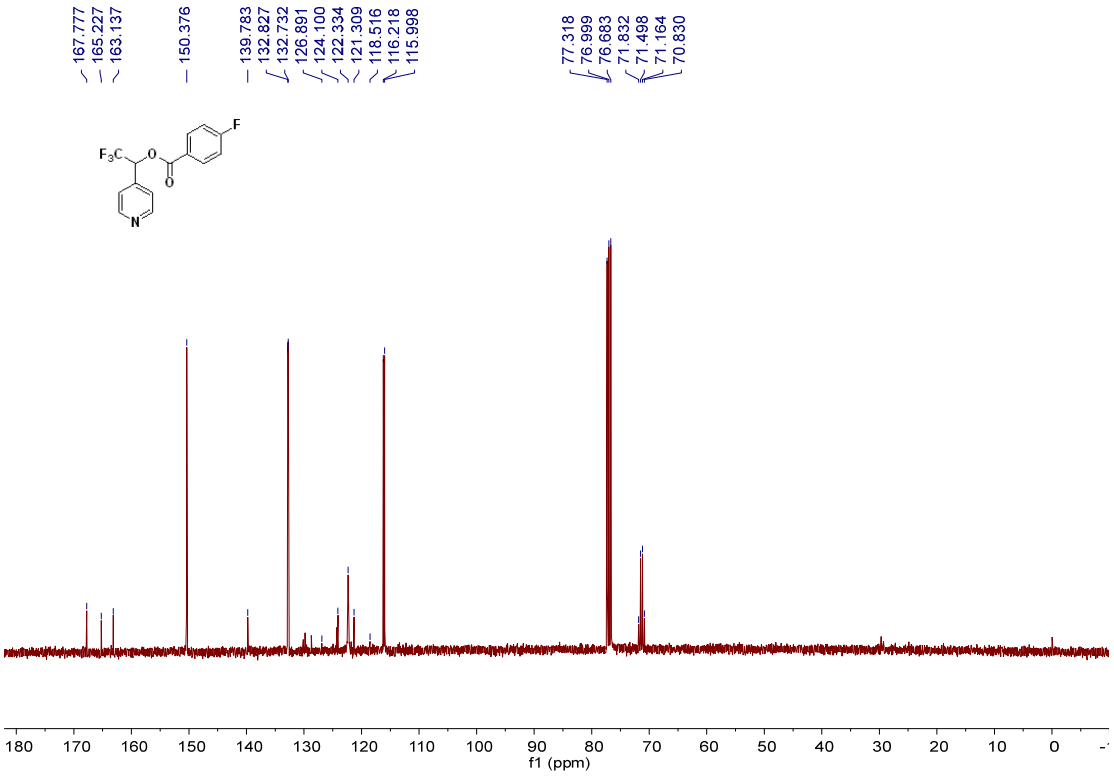

8.99
8.98
8.19
8.18
8.15
8.13
7.79
7.79
7.78
7.78
7.77
7.76
7.76
7.68
7.68
7.67
7.66
7.66
7.65
7.65
7.63
7.62
7.26
7.01
7.00
6.99
6.97
2.31
2.28
2.24
2.21
1.97
1.96
1.96
1.95
1.94
1.70
1.67
1.65
1.63
1.63
1.62
1.62
1.61
1.59
1.59
O
CF3
O
N
0.87
1.90
0.98
1.87
0.90
1.96
2.90
12.00
f1 (ppm)

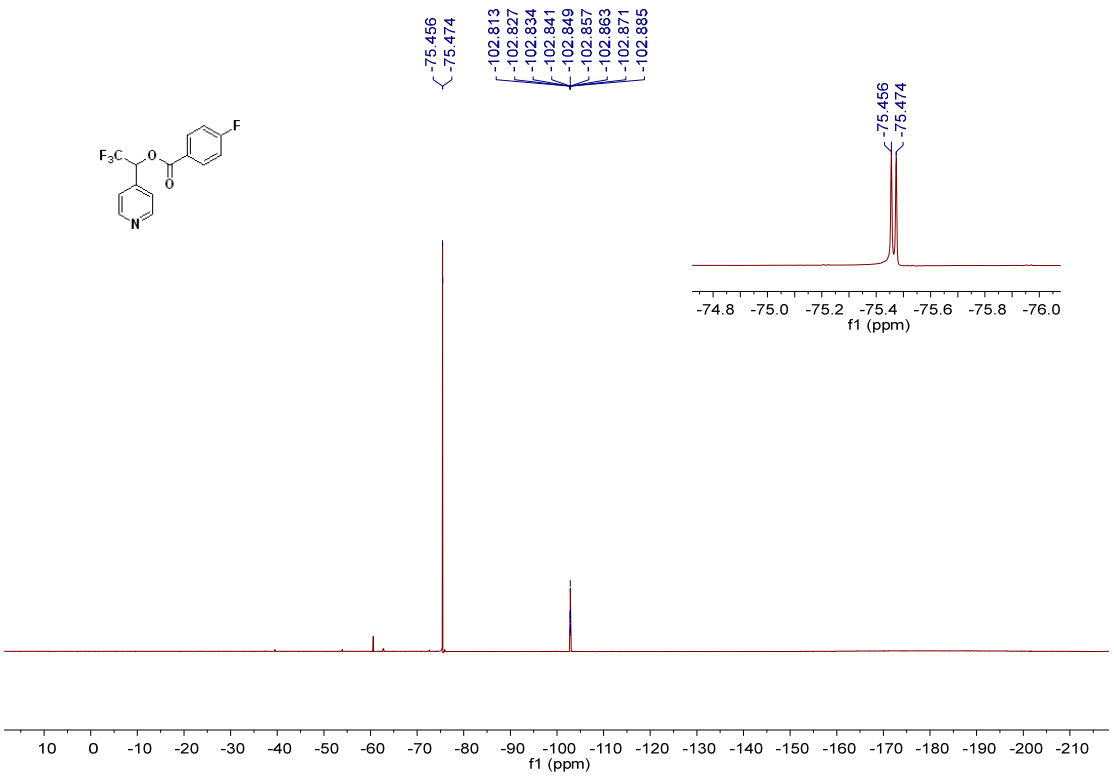

169.25
149.72
148.45
136.90
130.49
129.73
127.65
126.45
125.83
124.22
122.82
121.98
120.52
119.74
77.25
77.00
76.74
67.26
66.99
66.73
66.46
48.17
42.17
36.50
33.19
28.45
O
CF3
O
N
f1 (ppm)



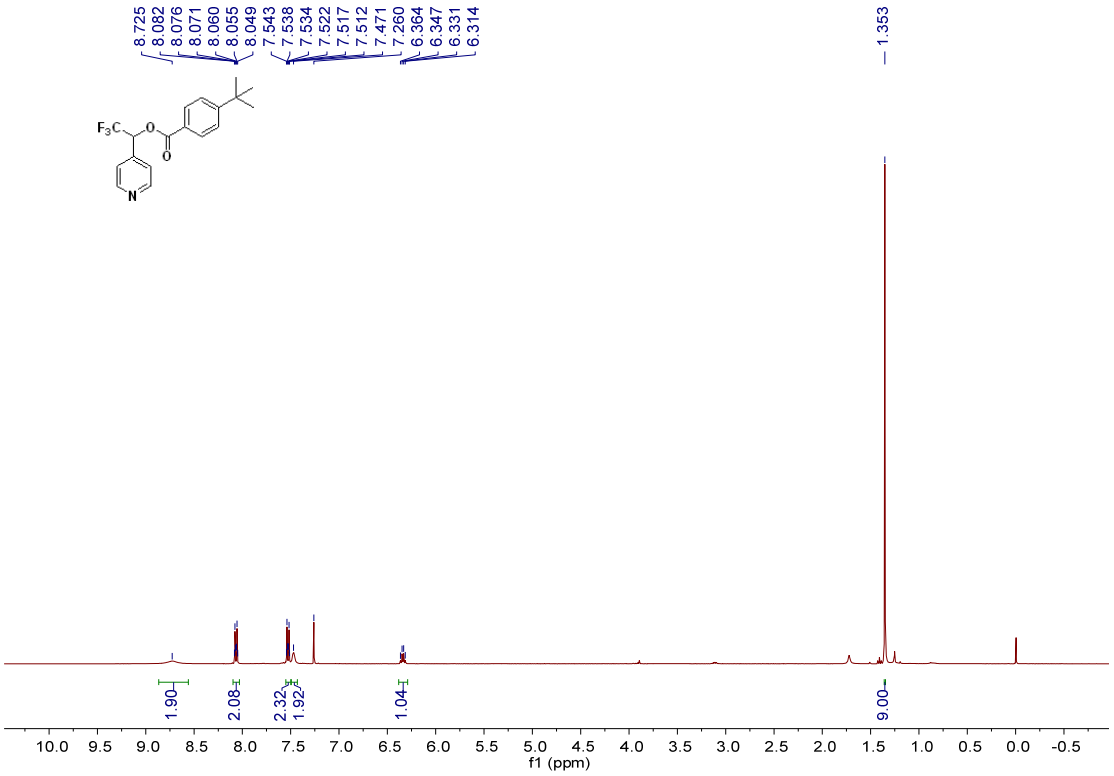
NMR Spectra of product **43**:

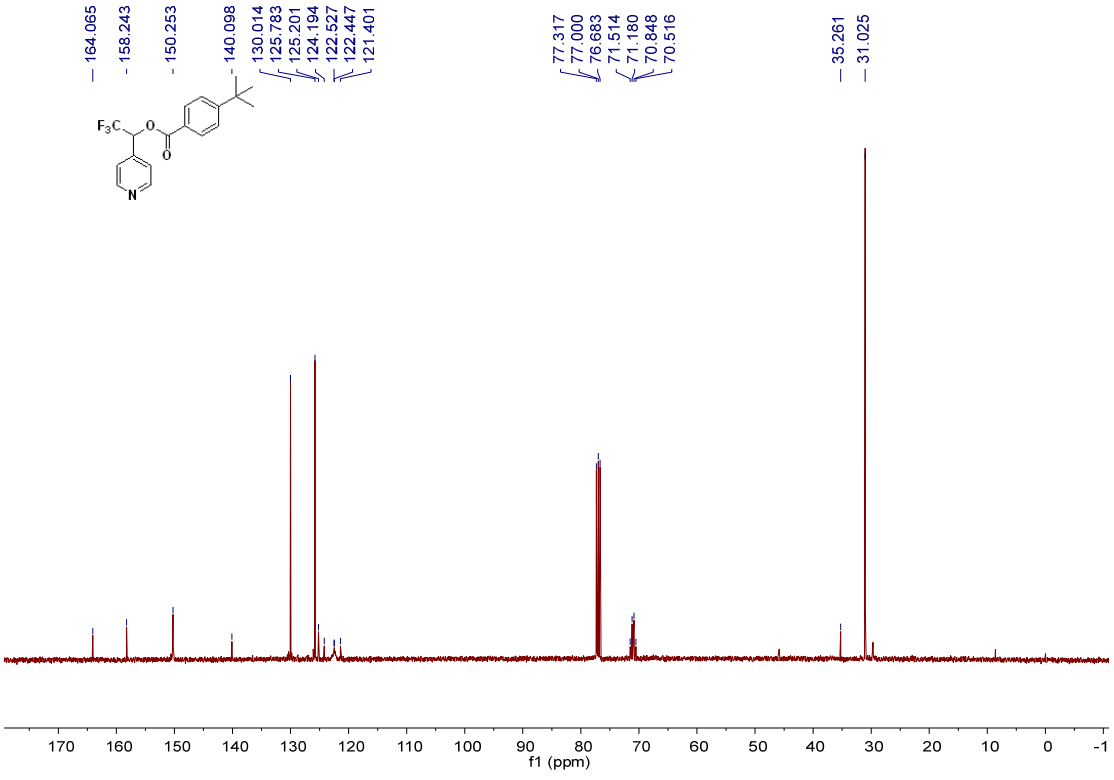


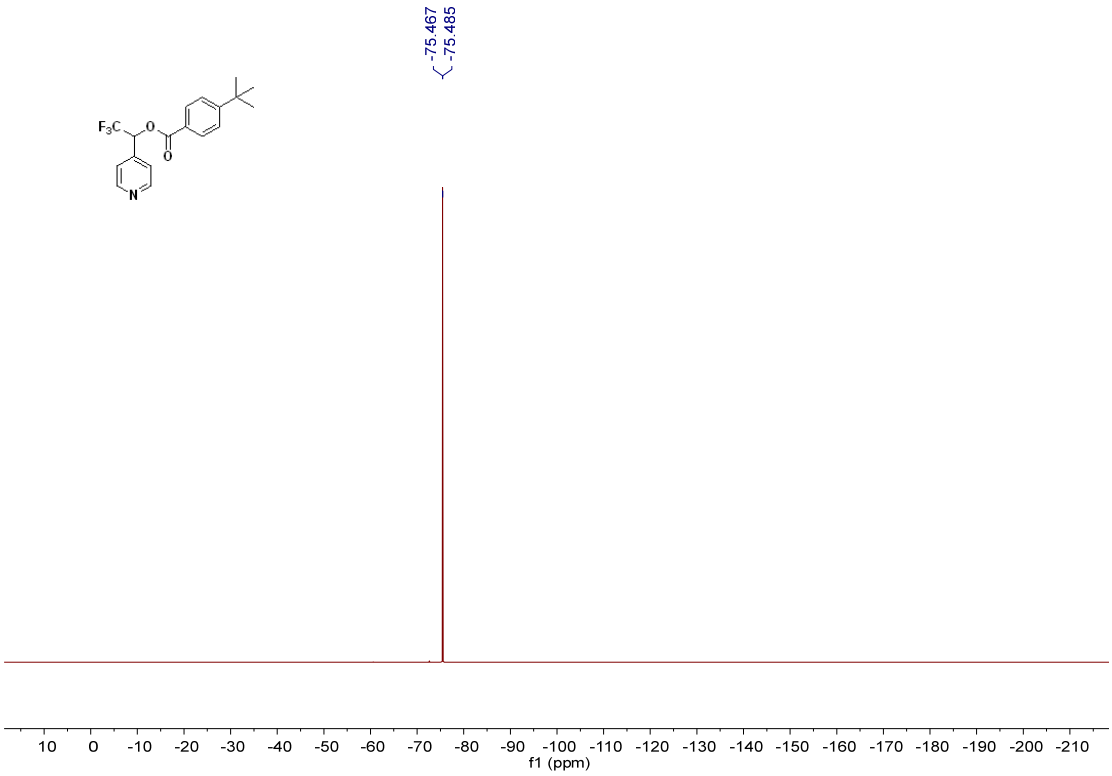




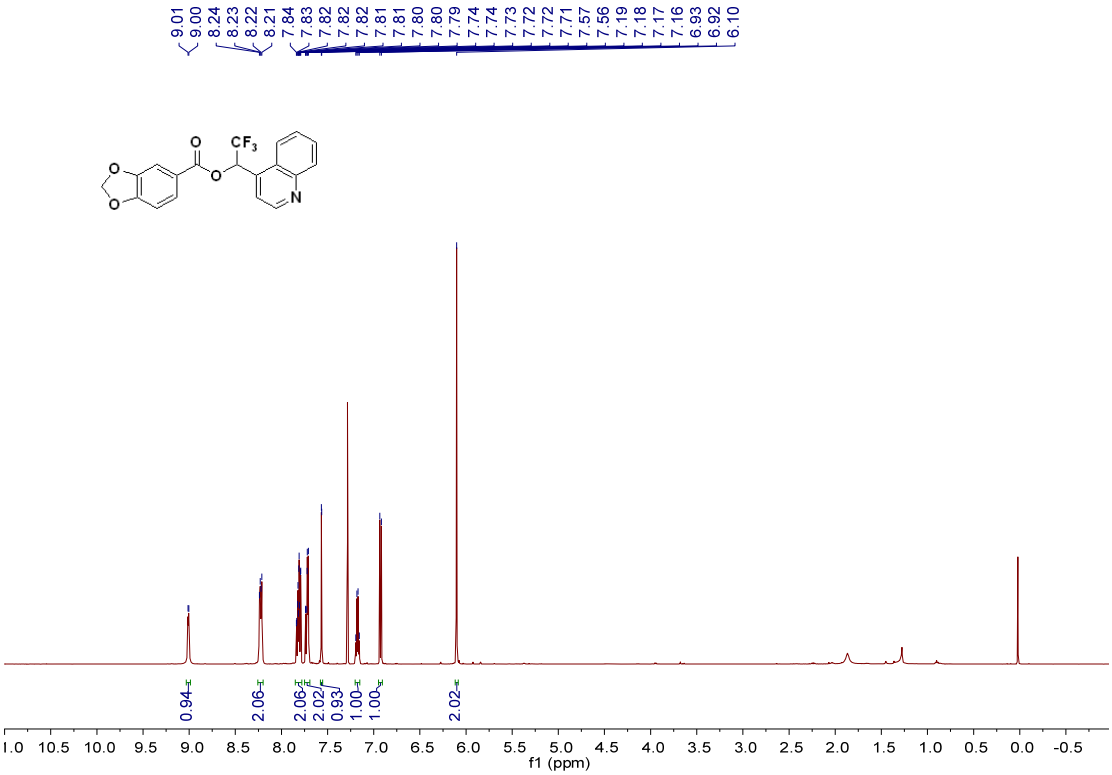
NMR Spectra of product **44**:

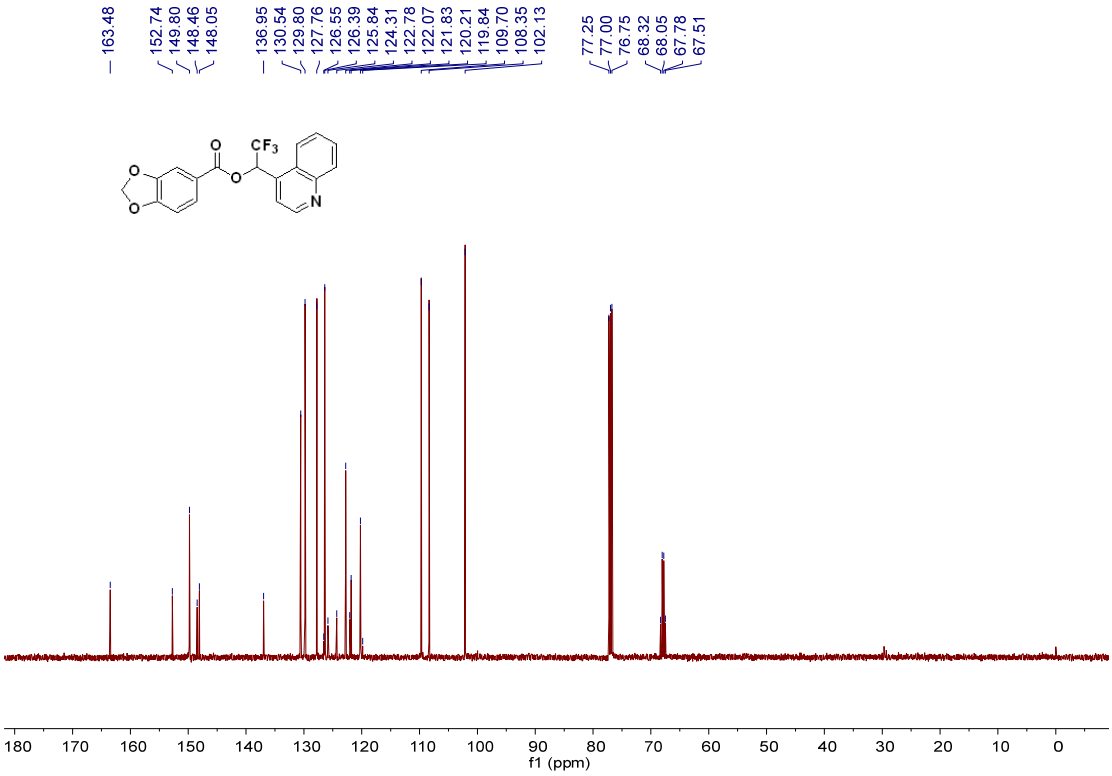

8.725
8.082
8.076
8.071
8.060
8.055
8.049
7.543
7.538
7.534
7.522
7.517
7.512
7.471
7.260
6.364
6.347
6.331
6.314
1.353
F3C
O
O
N
1.90
2.08
2.32
1.92
1.04
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

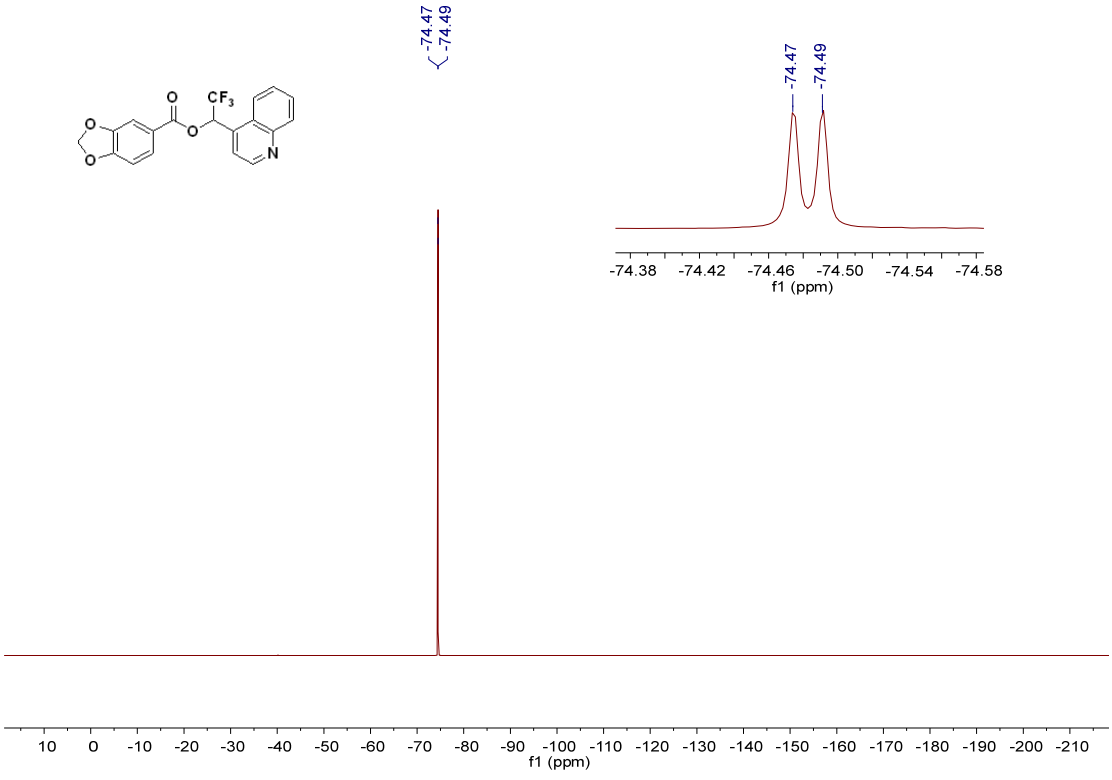

164.065
158.243
150.253
140.098
130.014
125.783
125.201
124.194
122.527
122.447
121.401
77.317
77.000
76.683
71.514
71.180
70.848
70.516
35.261
31.025
F3C
O
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



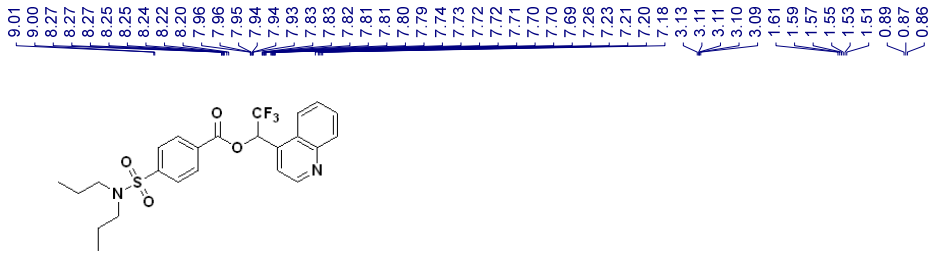
NMR Spectra of product **45**:



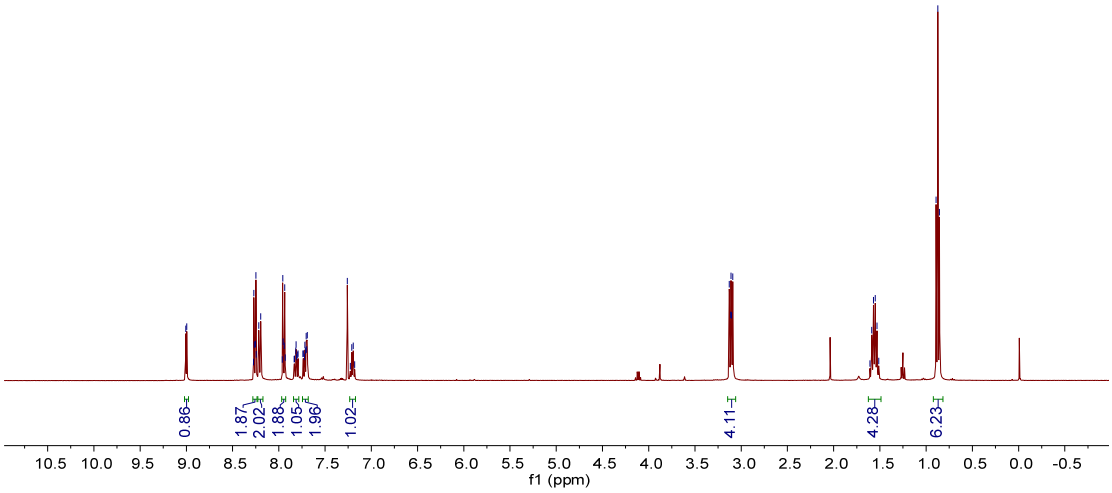


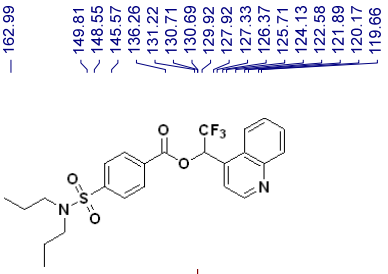


NMR Spectra of product **46**:

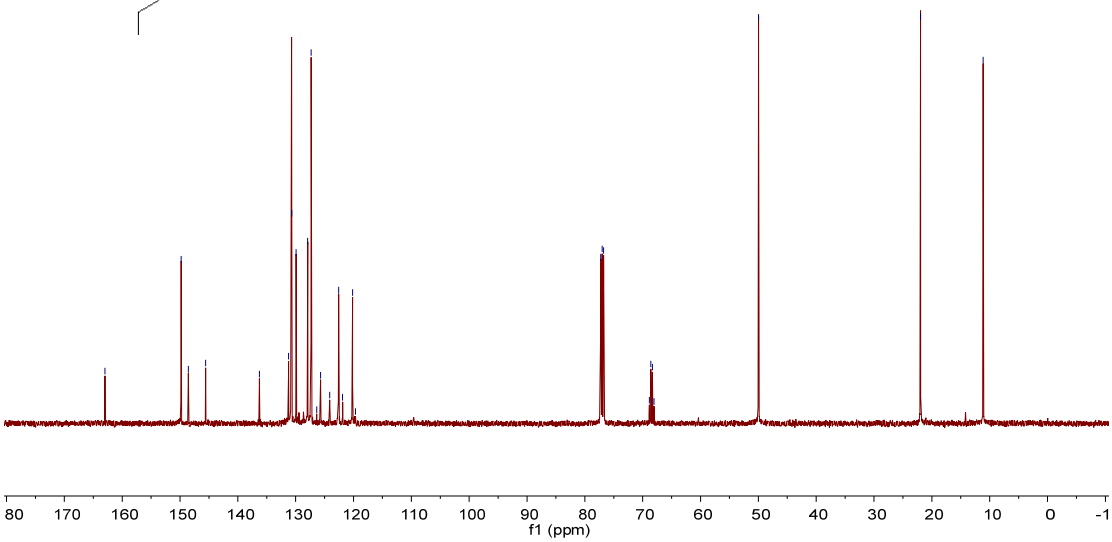

9.01
9.00
8.27
8.27
8.27
8.25
8.25
8.24
8.22
8.20
7.96
7.96
7.95
7.94
7.94
7.93
7.83
7.83
7.82
7.81
7.81
7.80
7.79
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.26
7.23
7.21
7.20
7.18
3.13
3.11
3.11
3.10
3.09
1.61
1.59
1.57
1.55
1.53
1.51
0.89
0.87
0.86

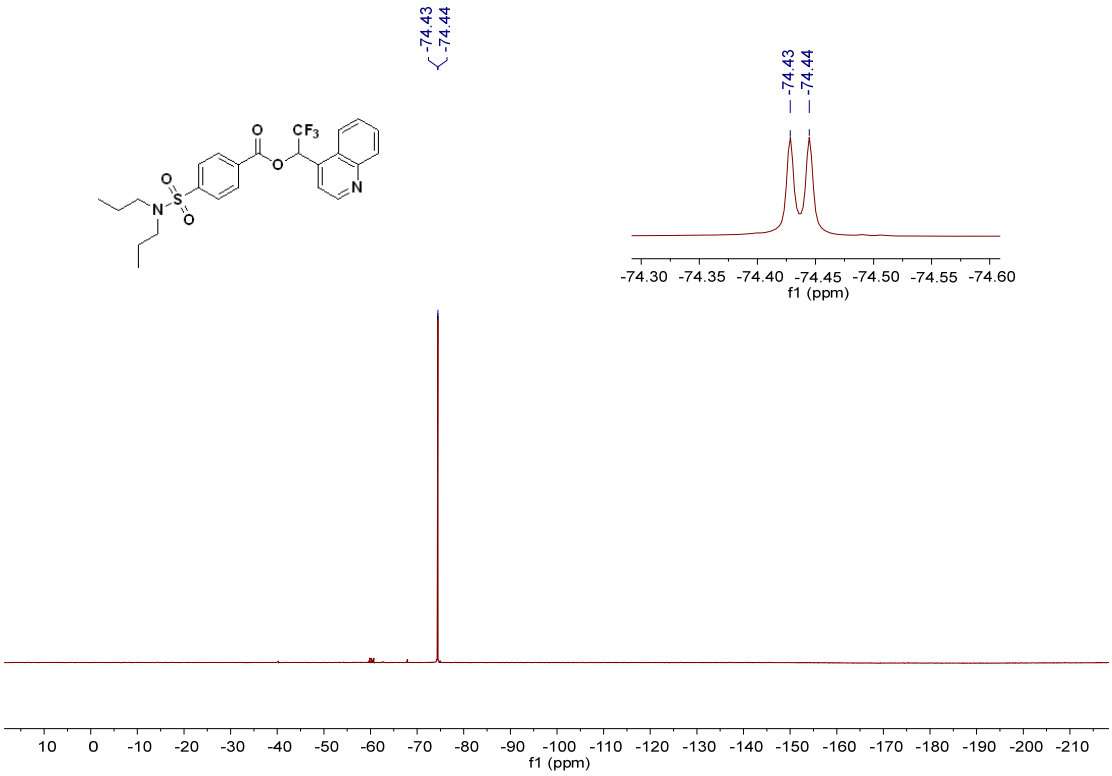
O
CF3
O
O
S
O
N
O
N


0.86
1.87
2.02
1.88
1.05
1.96
1.02
4.11
4.28
6.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

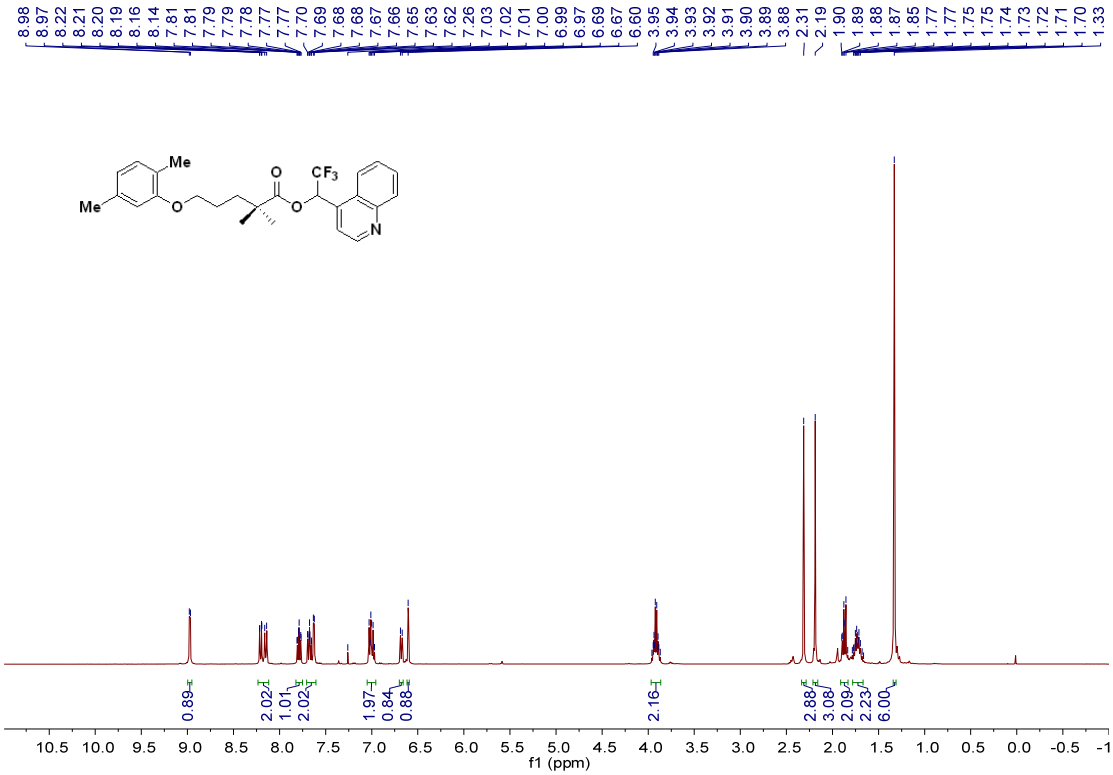

162.99
149.81
148.55
145.57
136.26
131.22
130.71
130.69
129.92
127.92
127.33
126.37
125.71
124.13
122.58
121.89
120.17
119.66
77.26
77.00
76.75
68.86
68.59
68.31
68.04
49.97
21.96
11.13

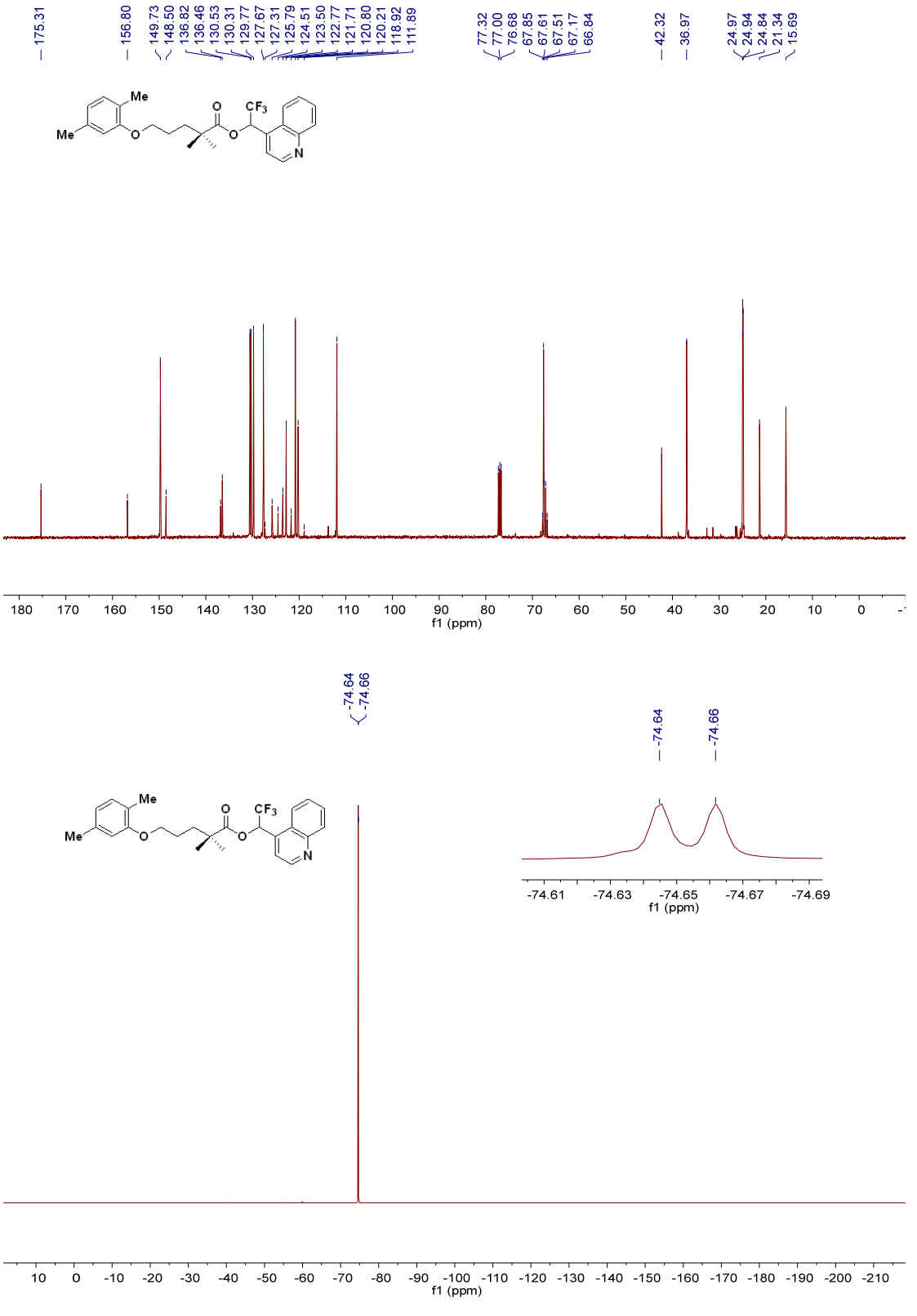
O
CF3
O
O
S
O
N
O
N


80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

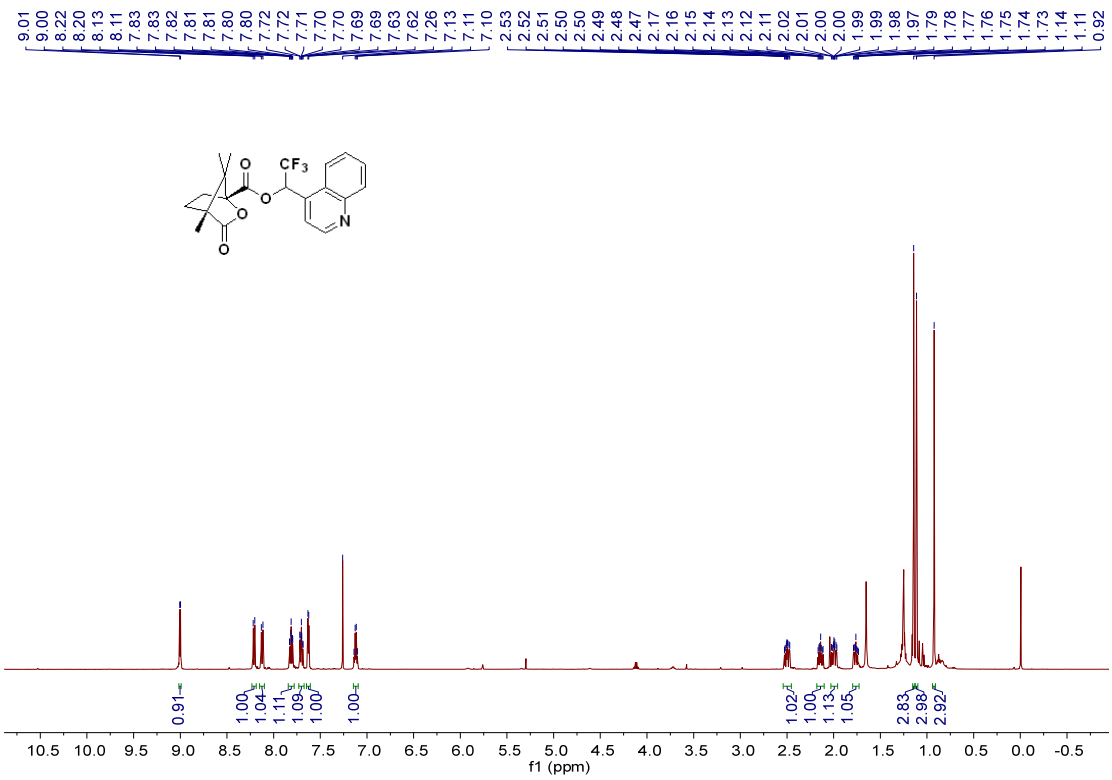


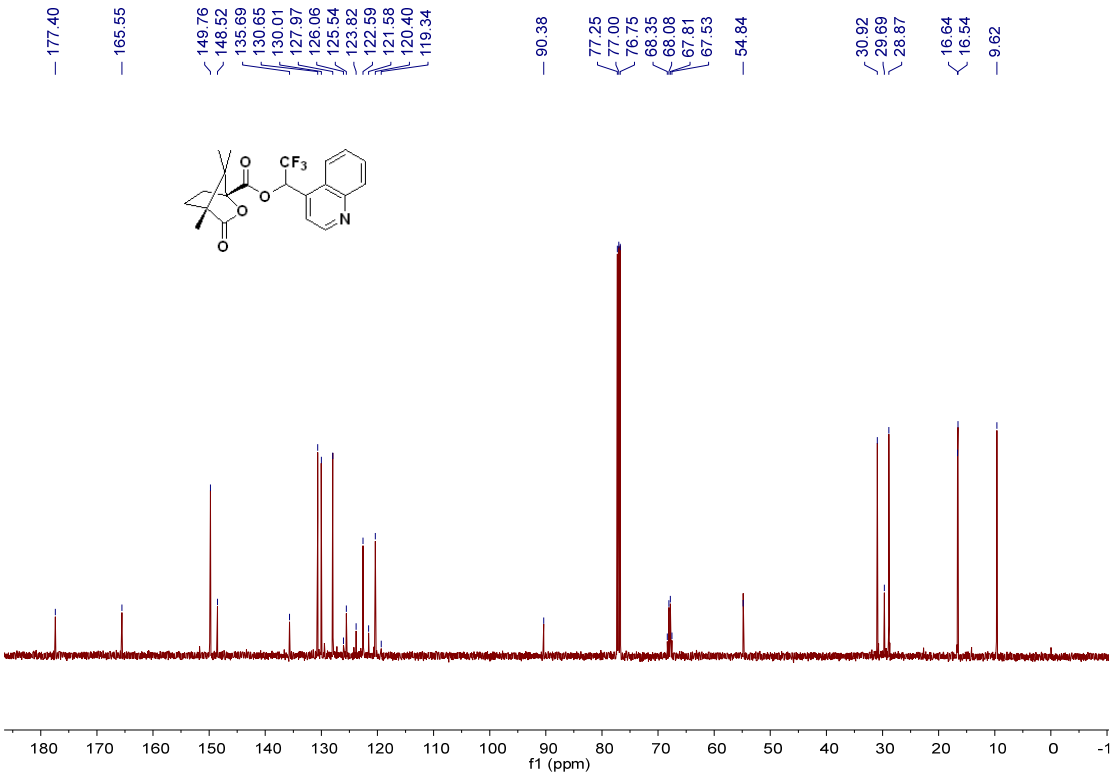
NMR Spectra of product **47**:

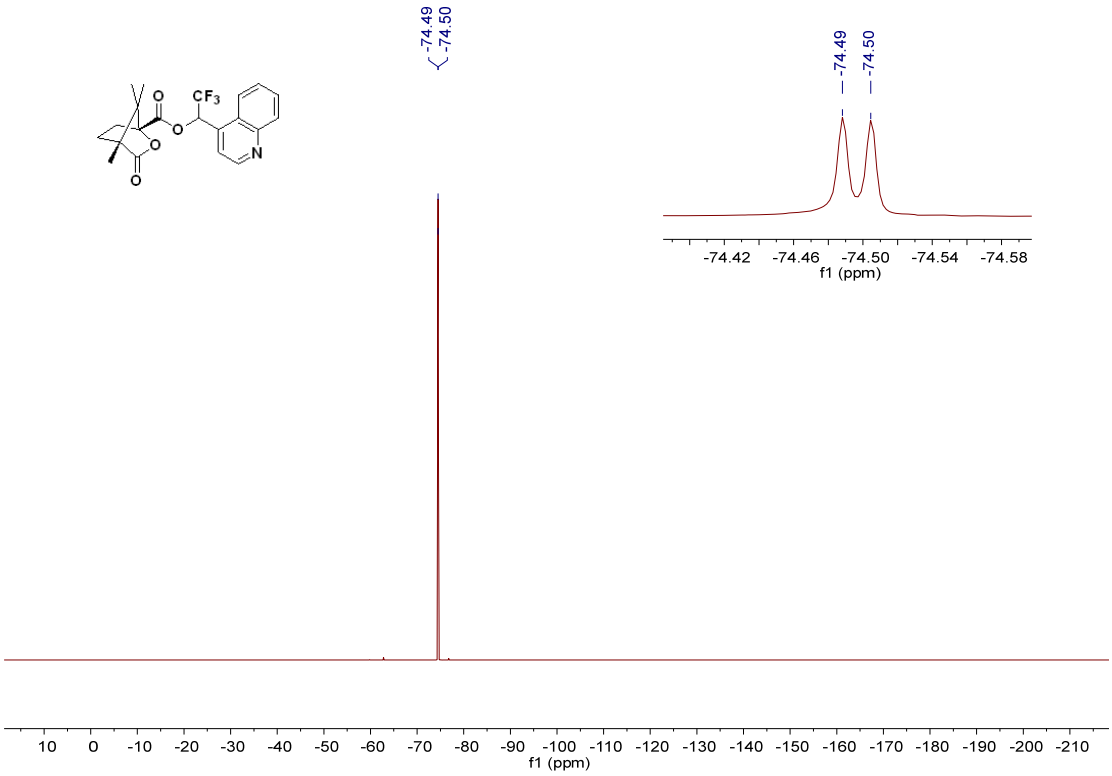




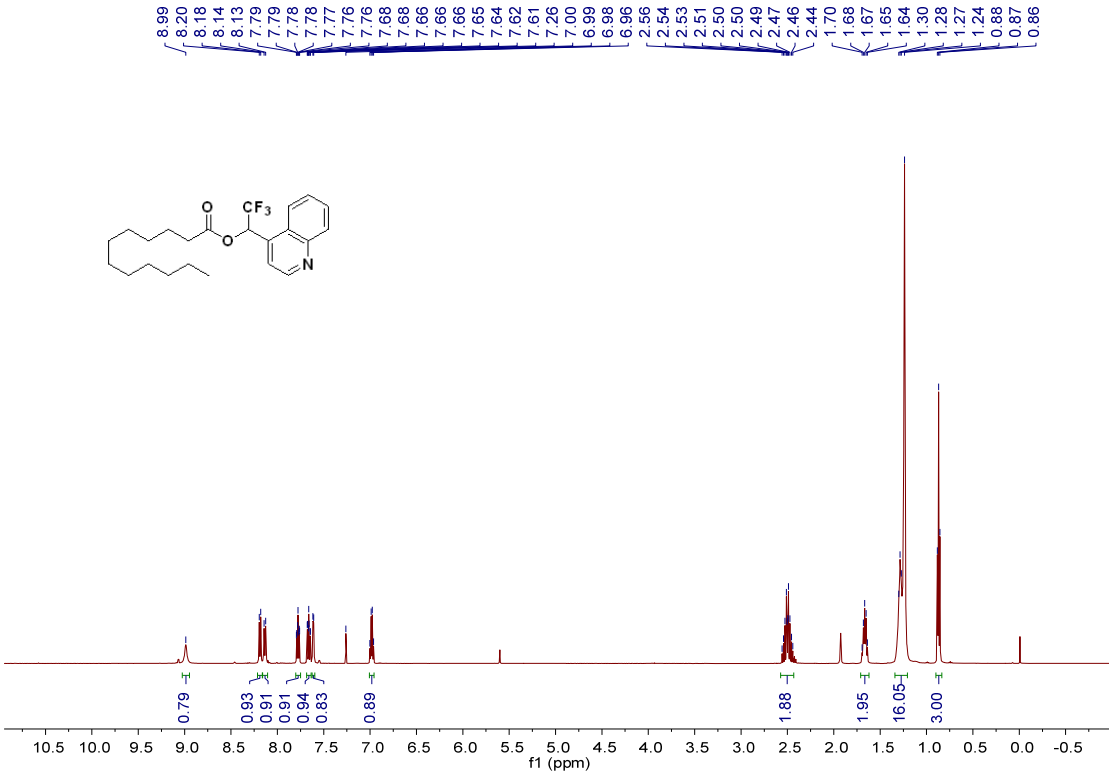
NMR Spectra of product **48**:

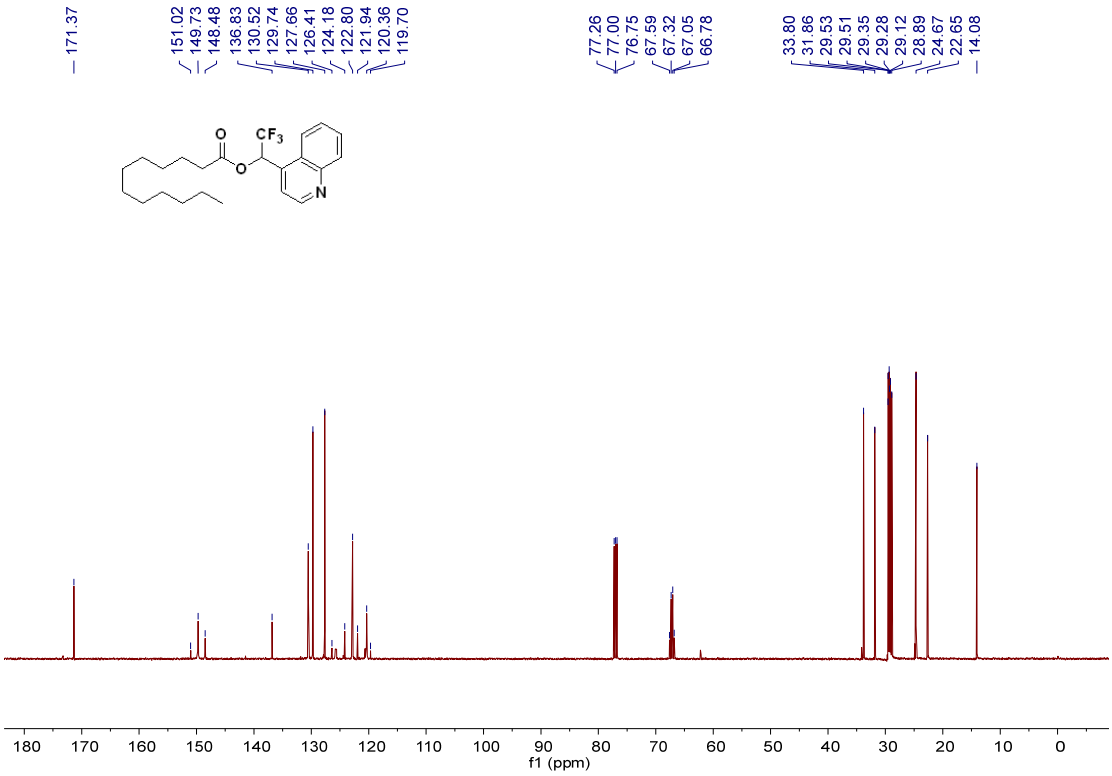

9.01 9.00 8.22 8.20 8.13 8.11 7.83 7.83 7.82 7.81 7.81 7.80 7.80 7.72 7.72 7.71 7.70 7.70 7.69 7.69 7.63 7.62 7.26 7.13 7.11 7.10
2.53 2.52 2.51 2.50 2.50 2.49 2.48 2.47 2.17 2.16 2.15 2.14 2.13 2.12 2.11 2.02 2.01 2.00 2.00 1.99 1.99 1.98 1.97 1.79 1.78 1.77 1.76 1.75 1.74 1.73 1.14 1.11 0.92
O
CF3
O
O
O
N
0.91 1.00 1.04 1.11 1.09 1.00 1.00 1.02 1.00 1.13 1.05 2.83 2.98 2.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

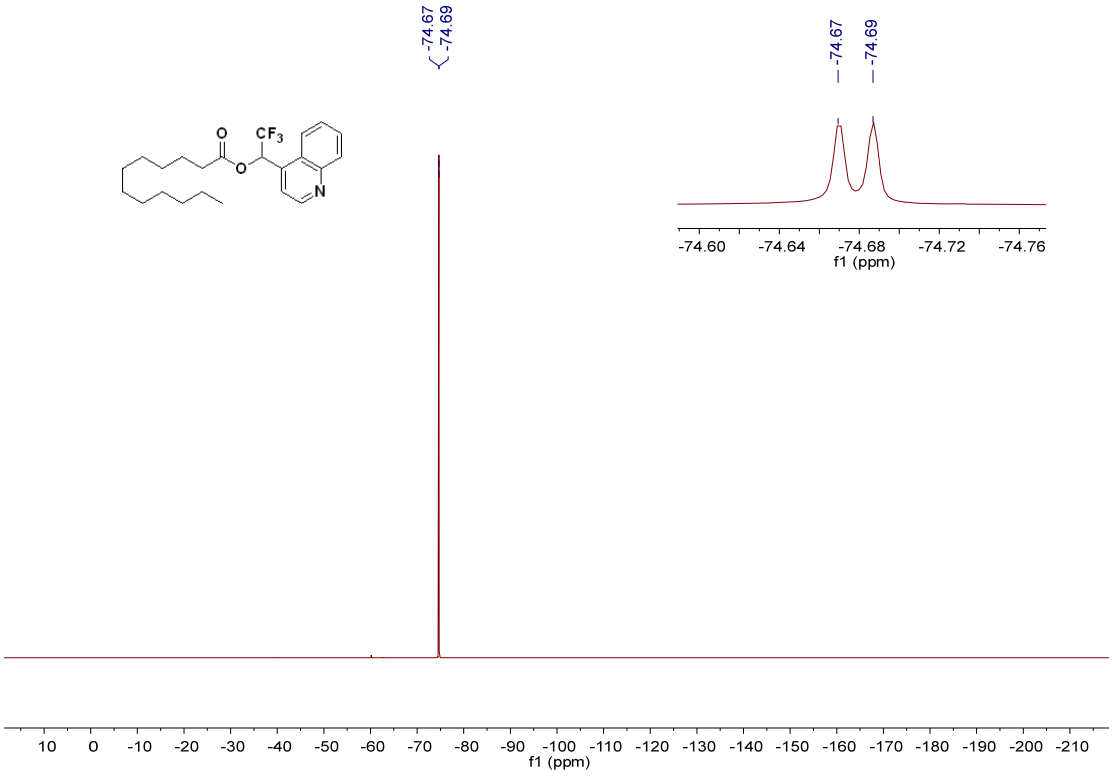

177.40 165.55 149.76 148.52 135.69 130.65 130.01 127.97 126.06 125.54 123.82 122.59 121.58 120.40 119.34 90.38 77.25 77.00 76.75 68.35 68.08 67.81 67.53 54.84 30.92 29.69 28.87 16.64 16.54 9.62
O
CF3
O
O
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



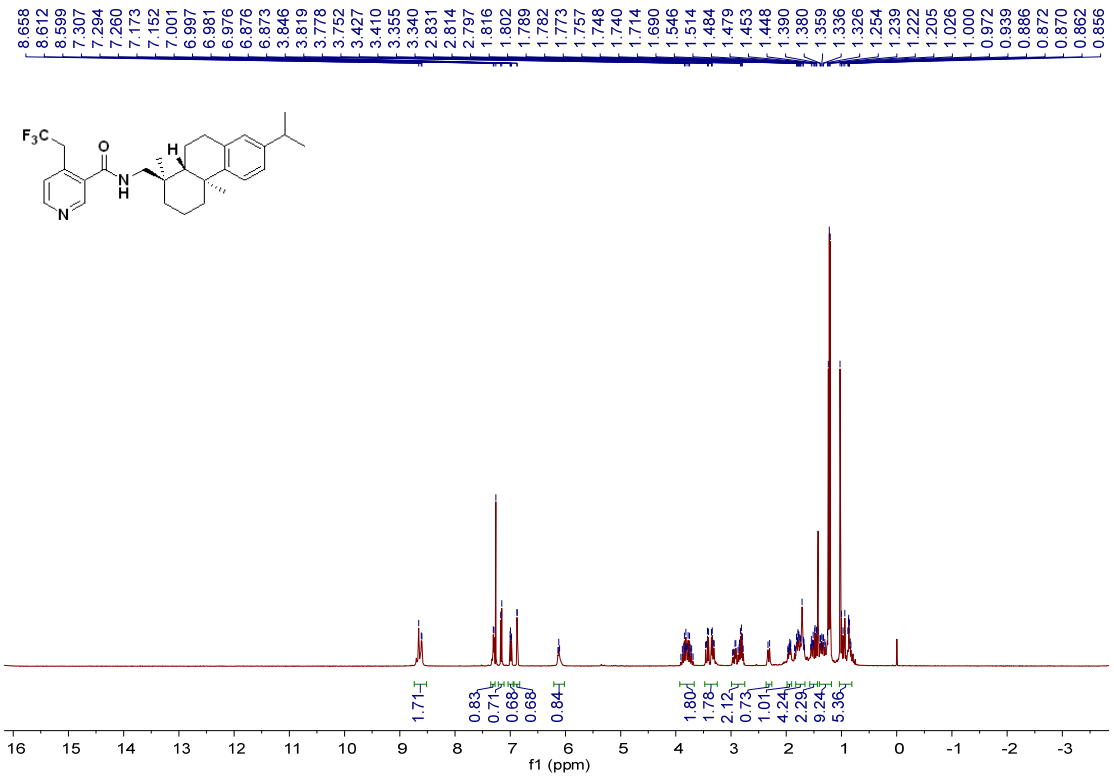
NMR Spectra of product **49**:

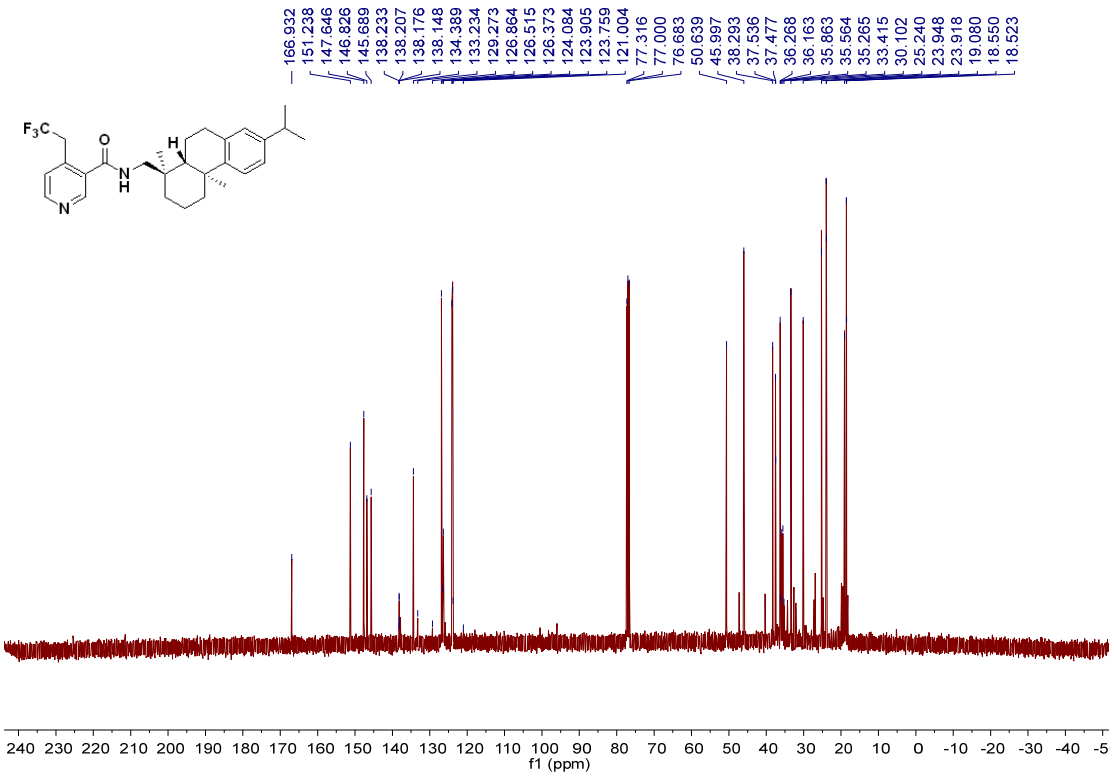


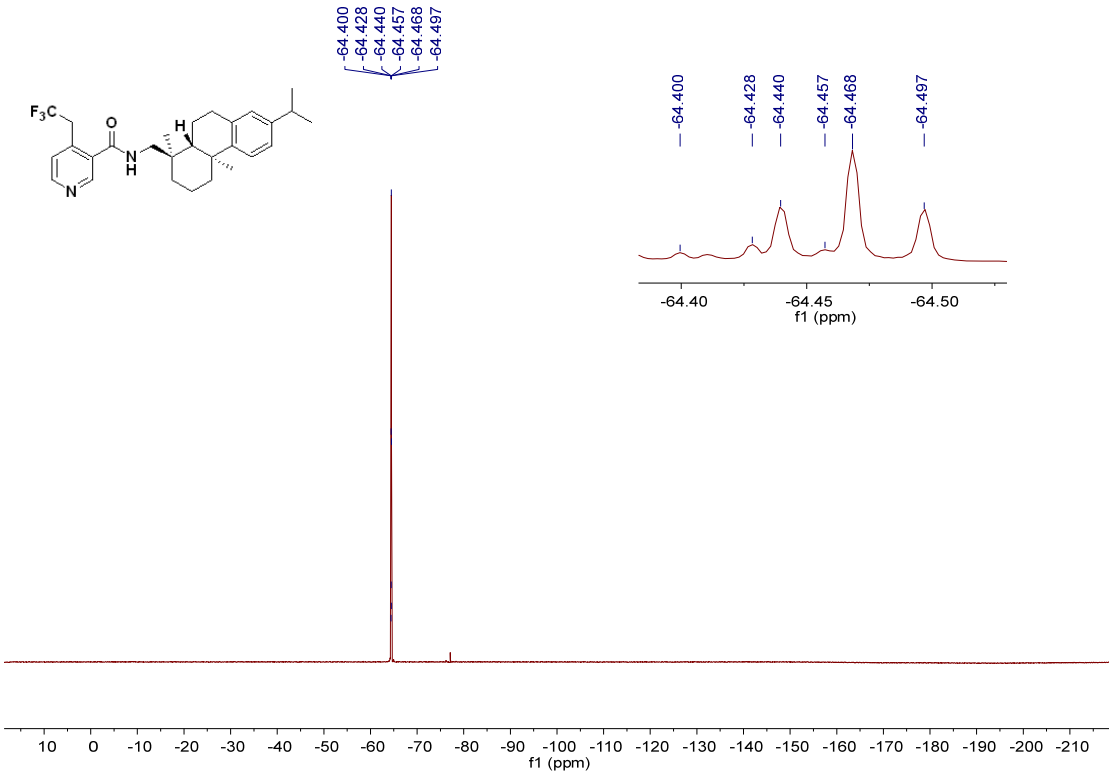




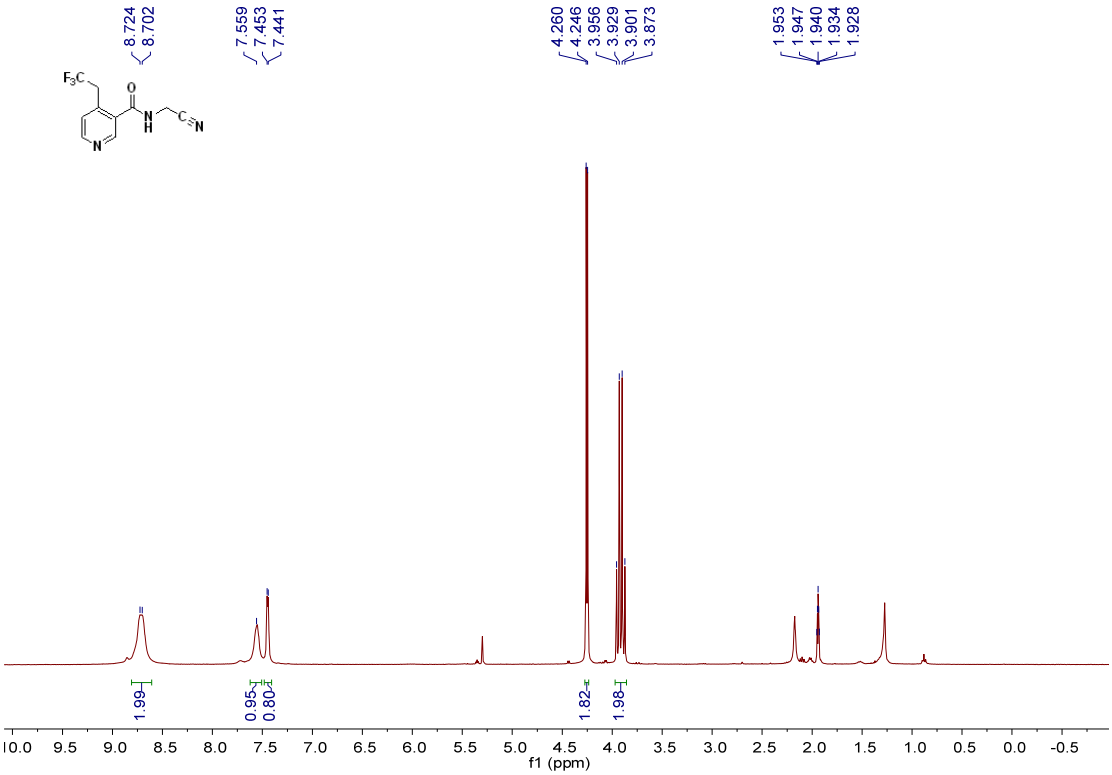
NMR Spectra of product **50**:

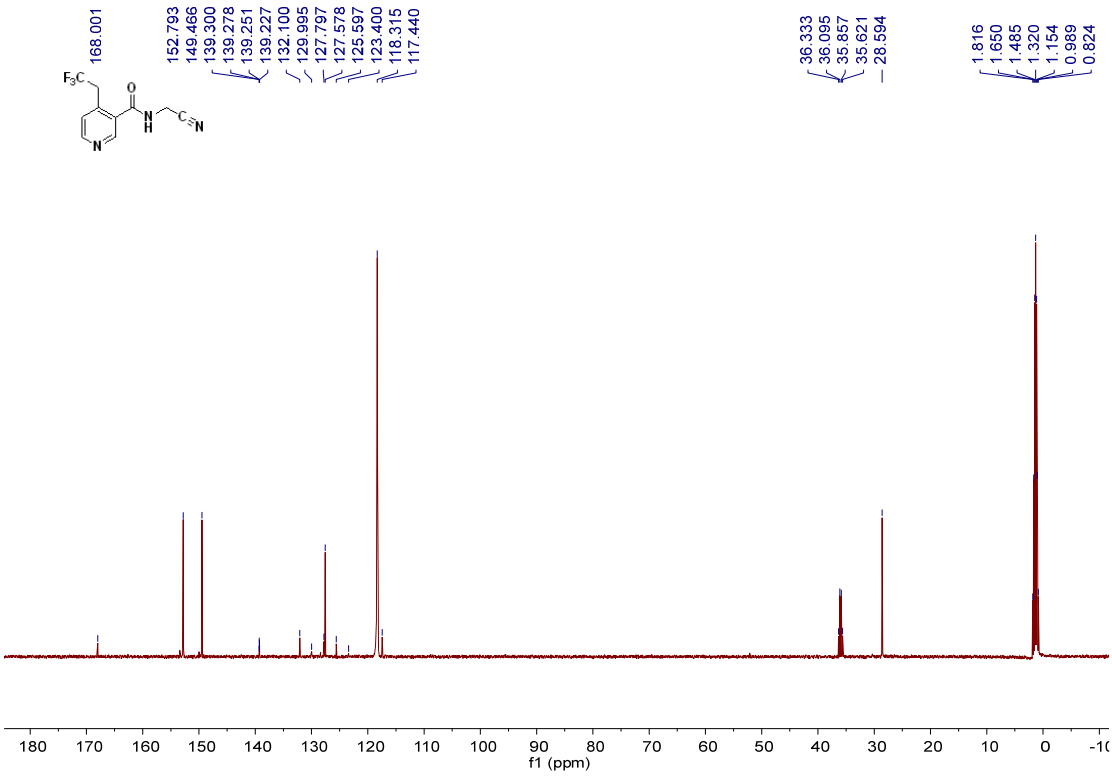

8.658
8.612
8.599
7.307
7.294
7.260
7.173
7.152
7.001
6.997
6.981
6.976
6.876
6.873
3.846
3.819
3.778
3.752
3.427
3.410
3.355
3.340
2.831
2.814
2.797
1.816
1.802
1.789
1.782
1.773
1.757
1.748
1.740
1.714
1.690
1.546
1.514
1.484
1.479
1.453
1.448
1.390
1.380
1.359
1.336
1.326
1.254
1.239
1.222
1.205
1.026
1.000
0.972
0.939
0.886
0.872
0.870
0.862
0.856
F3C
O
N
H
H
N
1.71
0.83
0.71
0.68
0.68
0.84
1.80
1.78
2.12
0.73
1.01
4.24
2.29
9.24
5.36
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

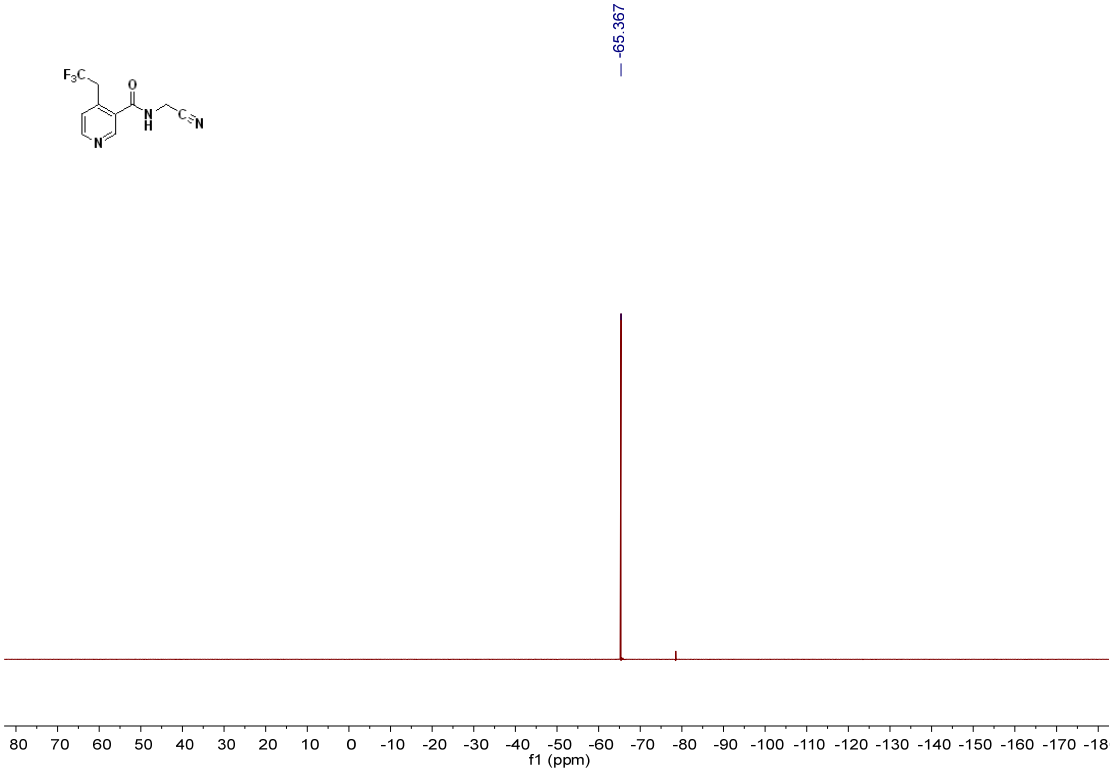

166.932
151.238
147.646
146.826
145.689
138.233
138.207
138.176
138.148
134.389
133.234
129.273
126.864
126.515
126.373
124.084
123.905
123.759
121.004
77.316
77.000
76.683
50.639
45.997
38.293
37.536
37.477
36.268
36.163
35.863
35.564
35.265
33.415
30.102
25.240
23.948
23.918
19.080
18.550
18.523
F3C
O
N
H
H
N
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
f1 (ppm)



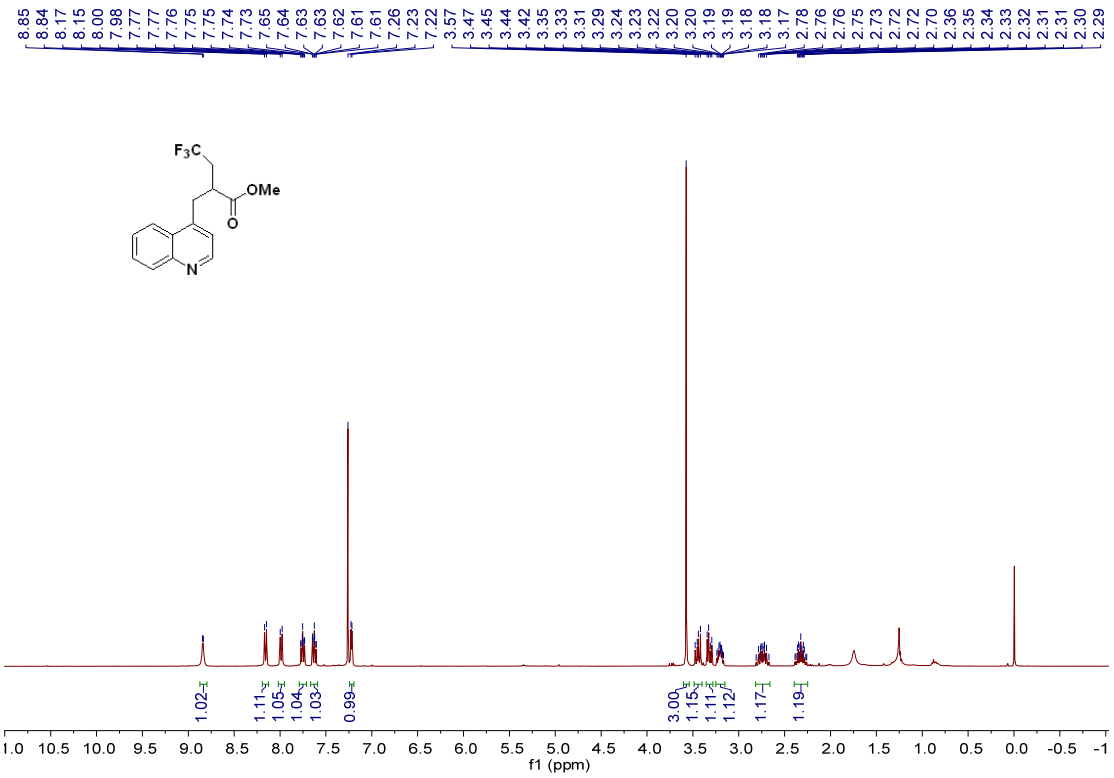
NMR Spectra of product **51**:

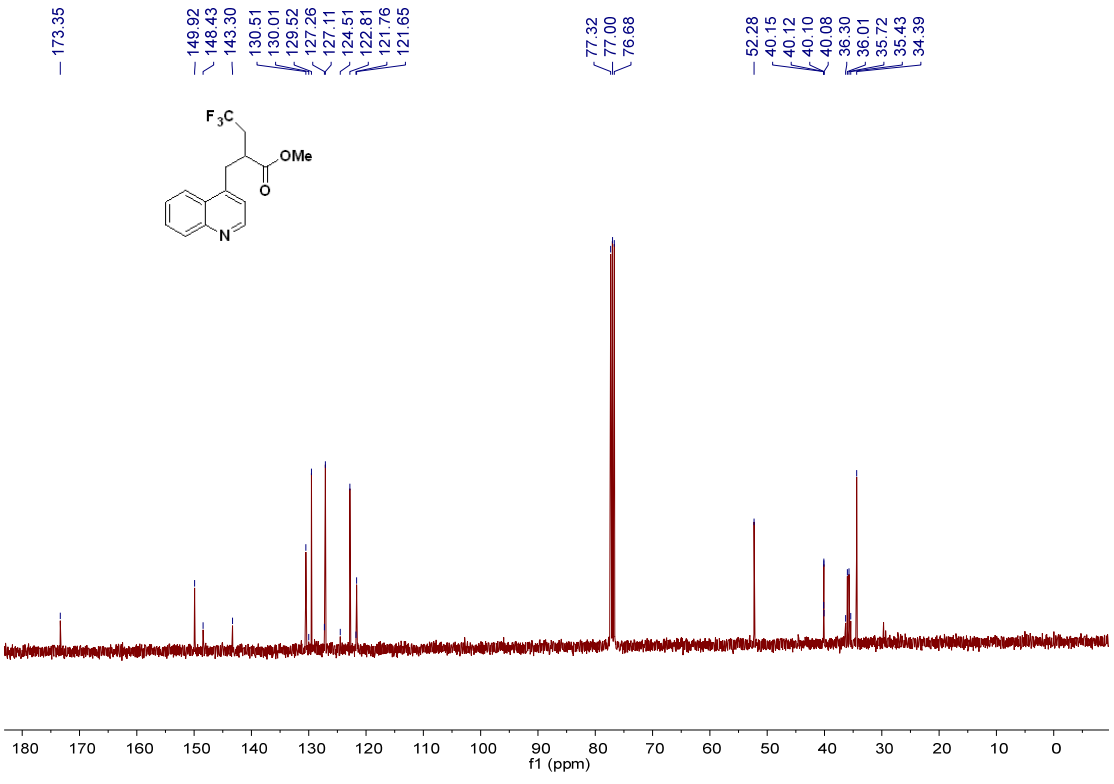


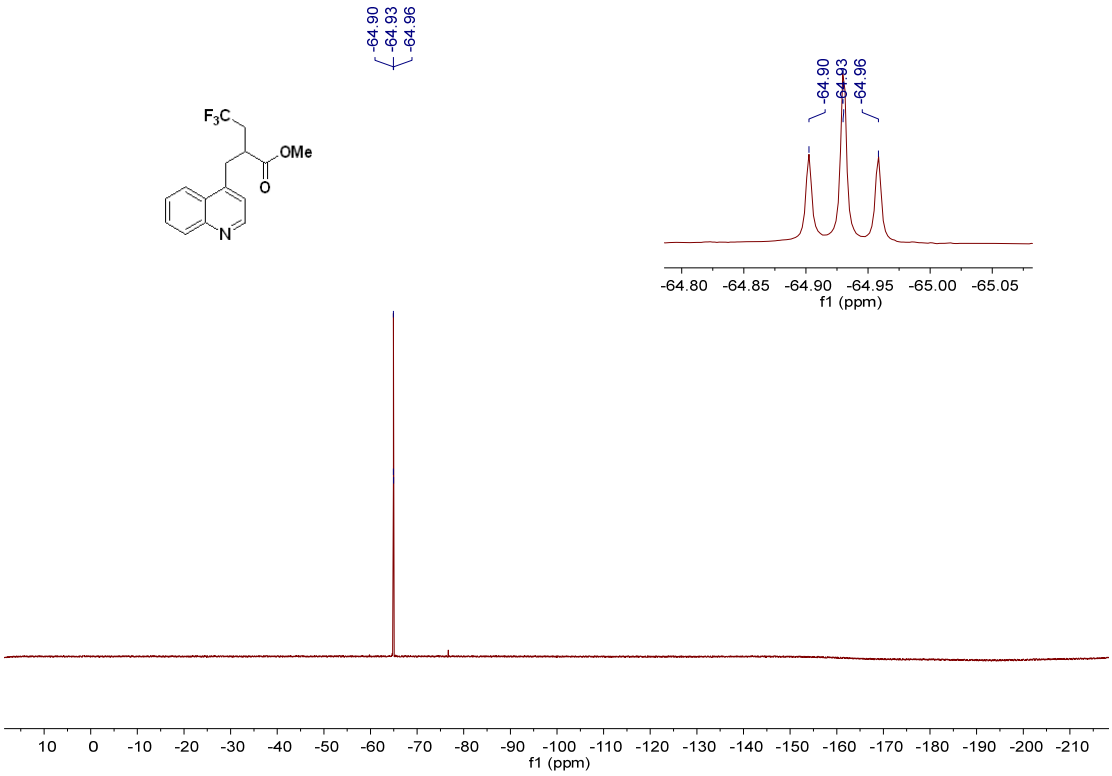




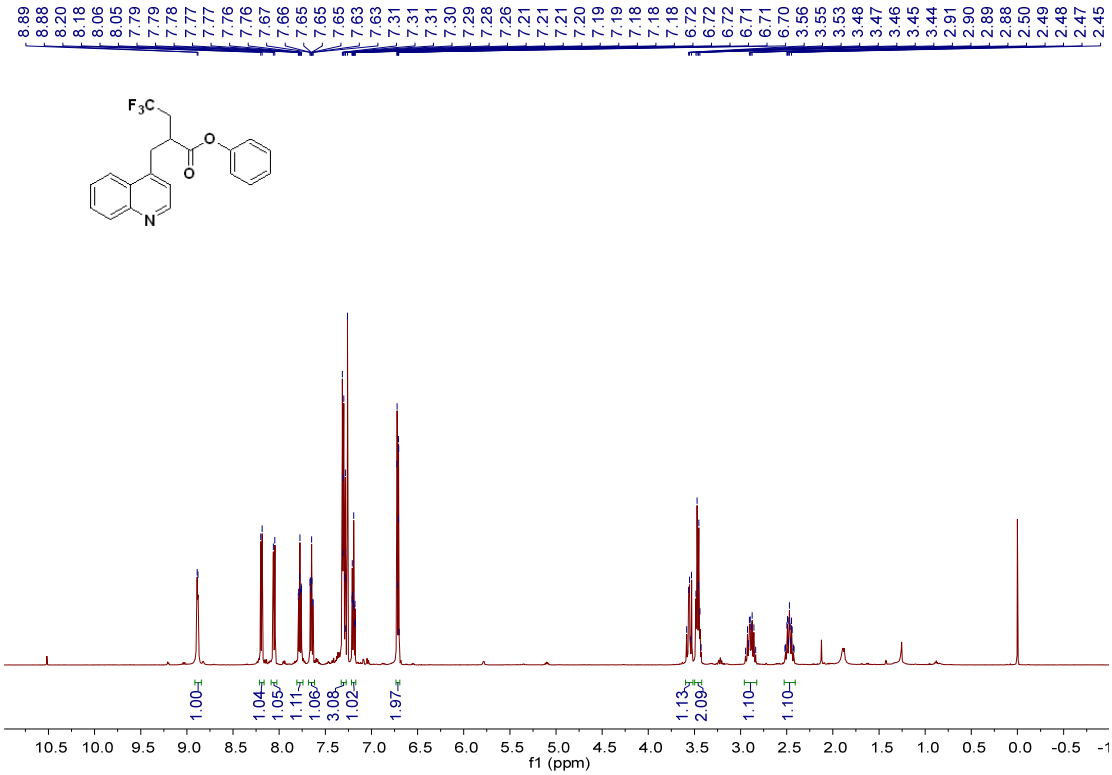
NMR Spectra of product **52**:

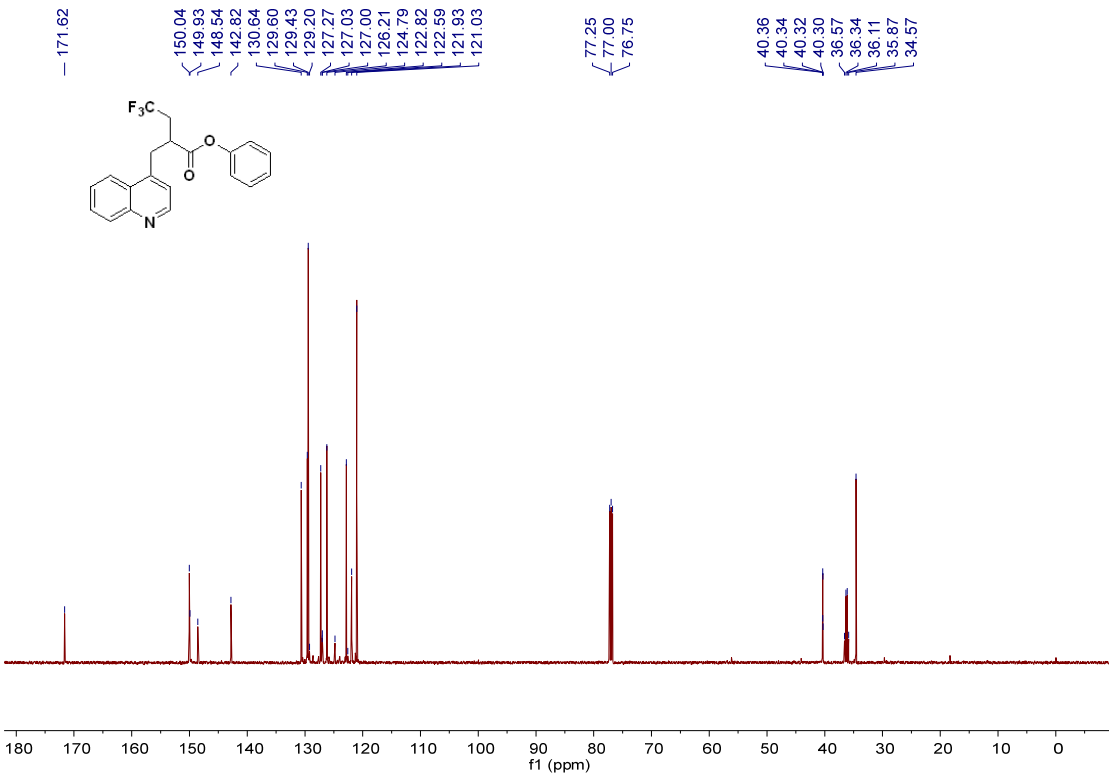

8.85 8.84 8.17 8.15 8.00 7.98 7.77 7.77 7.76 7.75 7.75 7.74 7.73 7.65 7.64 7.63 7.63 7.62 7.61 7.61 7.26 7.23 7.22
3.57 3.47 3.45 3.44 3.42 3.35 3.33 3.31 3.29 3.24 3.23 3.22 3.20 3.20 3.19 3.19 3.18 3.18 3.17 2.78 2.76 2.76 2.75 2.73 2.72 2.72 2.70 2.36 2.35 2.34 2.33 2.32 2.31 2.31 2.30 2.29
F3C
OMe
O
N
1.02 1.11 1.05 1.04 1.03 0.99 3.00 1.15 1.11 1.12 1.17 1.19
f1 (ppm)

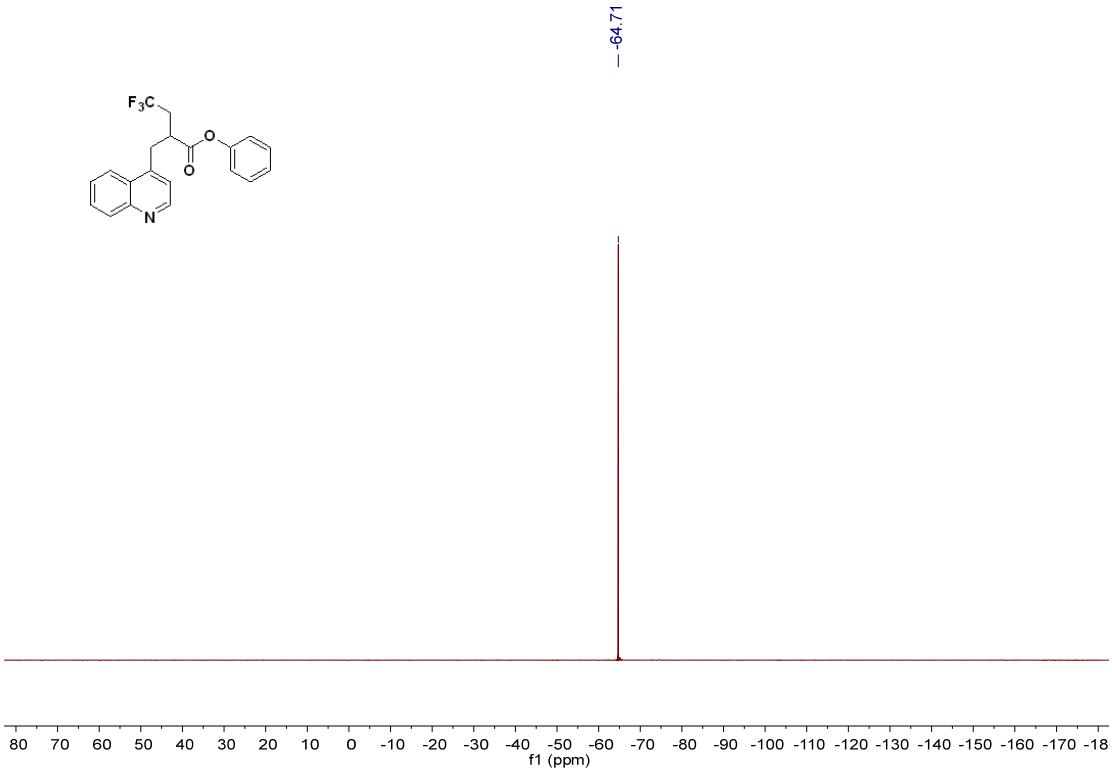

173.35
149.92 148.43 143.30 130.51 130.01 129.52 127.26 127.11 124.51 122.81 121.76 121.65
77.32 77.00 76.68
52.28 40.15 40.12 40.10 40.08 36.30 36.01 35.72 35.43 34.39
F3C
OMe
O
N
f1 (ppm)



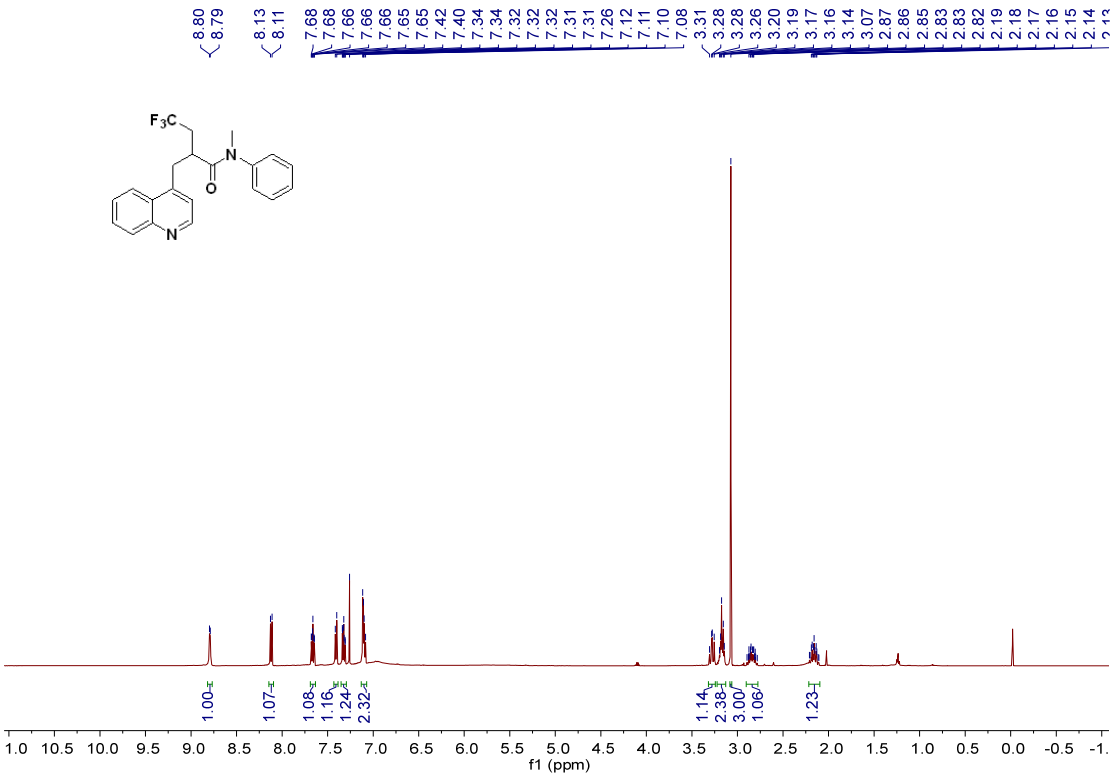
NMR Spectra of product **53**:

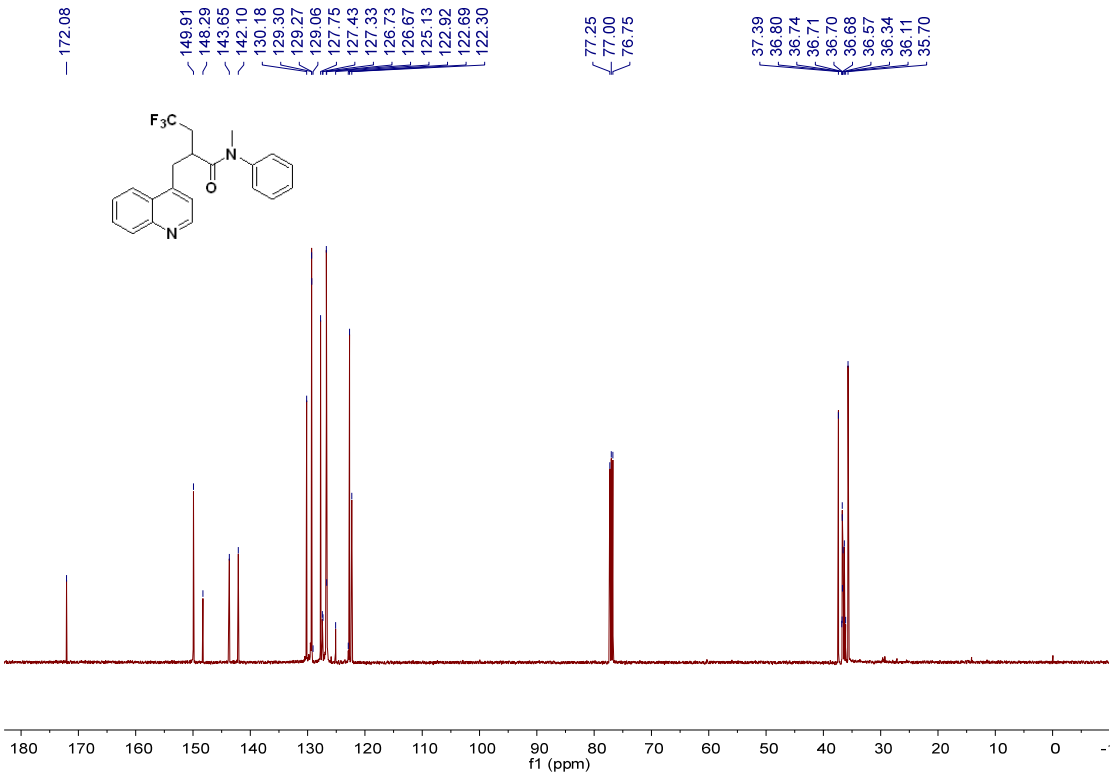


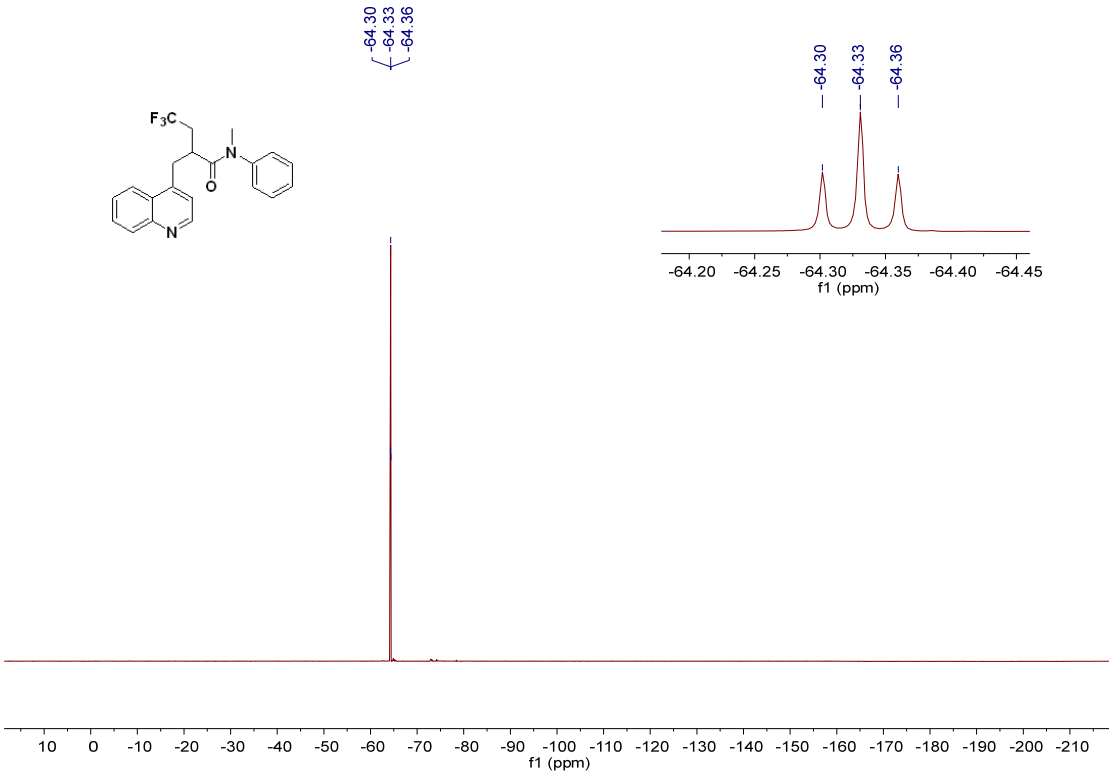




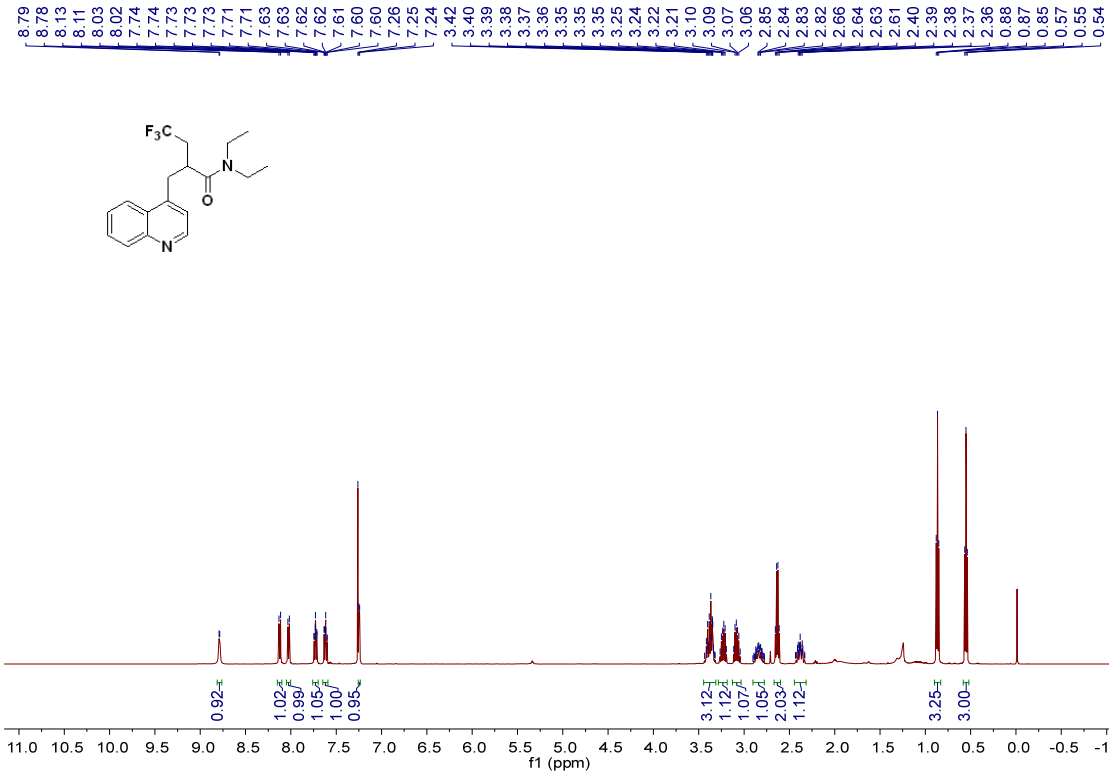
NMR Spectra of product **54**:

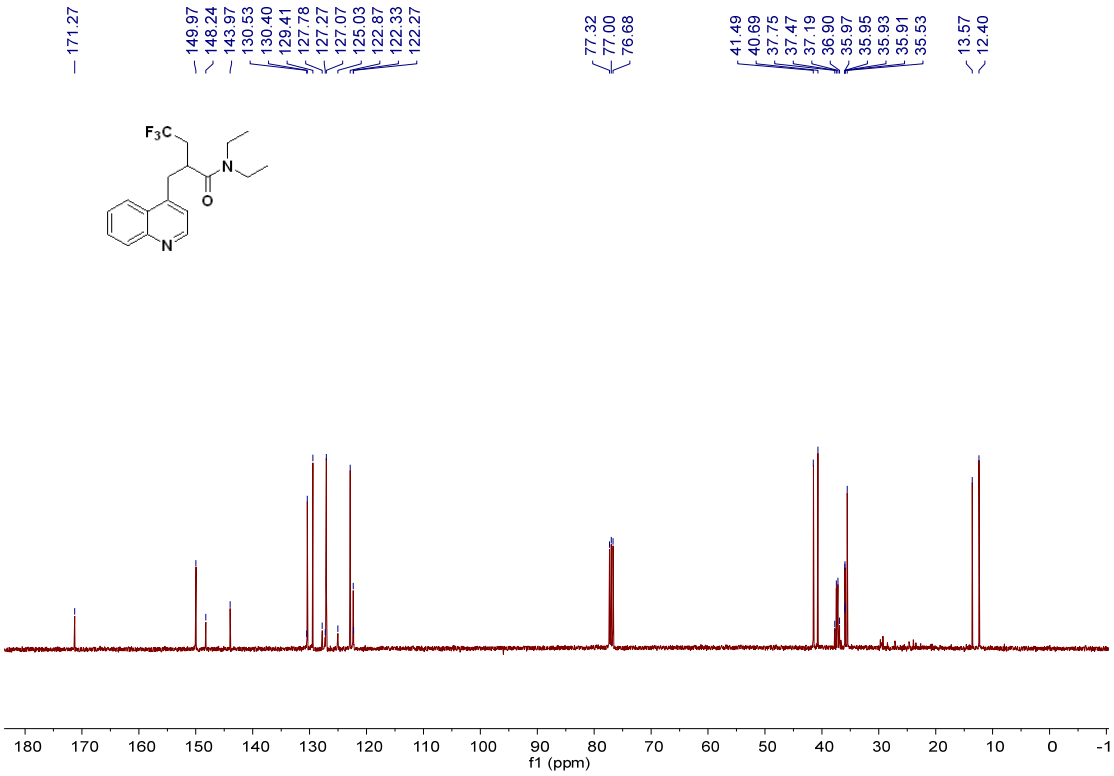

8.80
8.79
8.13
8.11
7.68
7.68
7.66
7.66
7.66
7.65
7.65
7.42
7.40
7.34
7.34
7.32
7.32
7.31
7.31
7.26
7.12
7.11
7.10
7.08
3.31
3.28
3.28
3.26
3.20
3.19
3.17
3.16
3.14
3.07
2.87
2.86
2.85
2.83
2.83
2.82
2.19
2.18
2.17
2.16
2.15
2.14
F3C
N
O
N
1.00
1.07
1.08
1.16
1.24
2.32
1.14
2.38
3.00
1.06
1.23
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

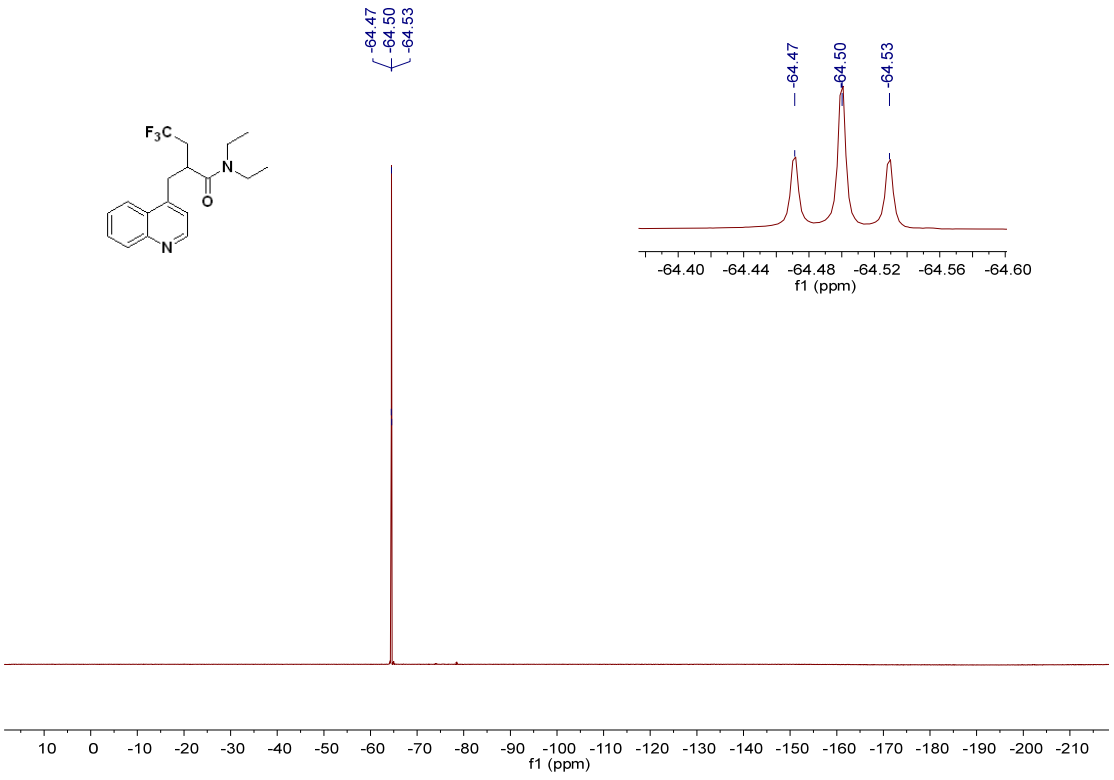

172.08
149.91
148.29
143.65
142.10
130.18
129.30
129.27
129.06
127.75
127.43
127.33
126.73
126.67
125.13
122.92
122.69
122.30
77.25
77.00
76.75
37.39
36.80
36.74
36.71
36.70
36.68
36.57
36.34
36.11
35.70
F3C
N
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



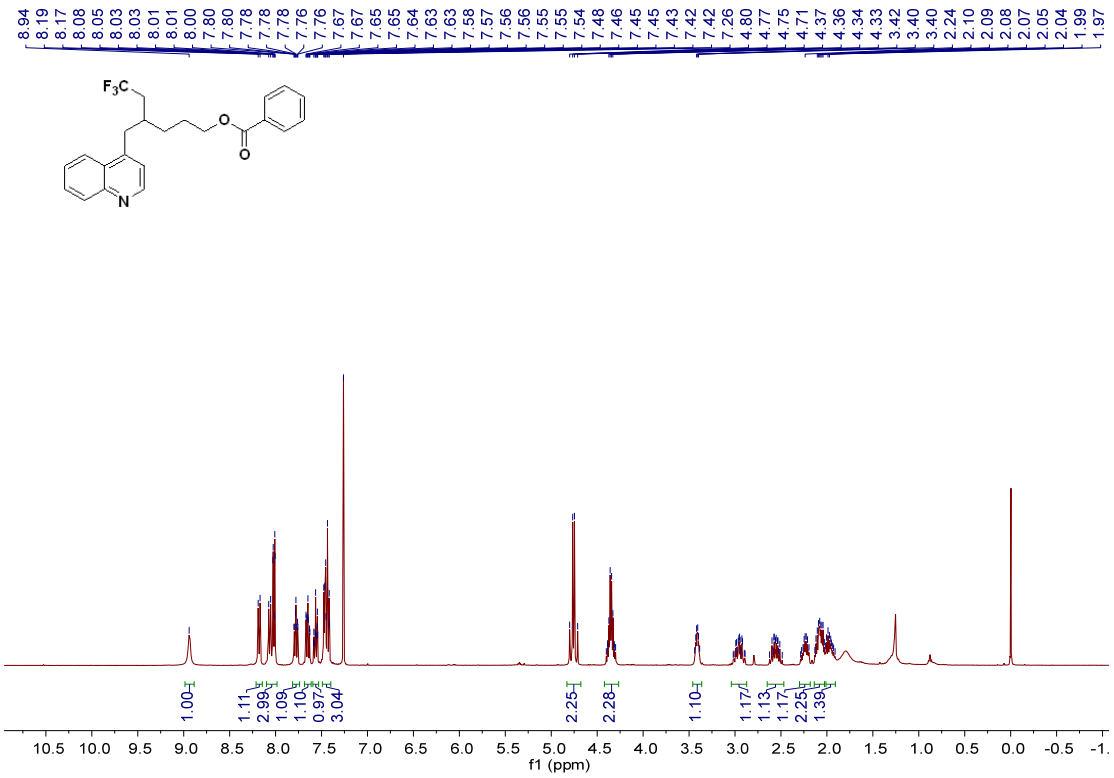
NMR Spectra of product **55**:

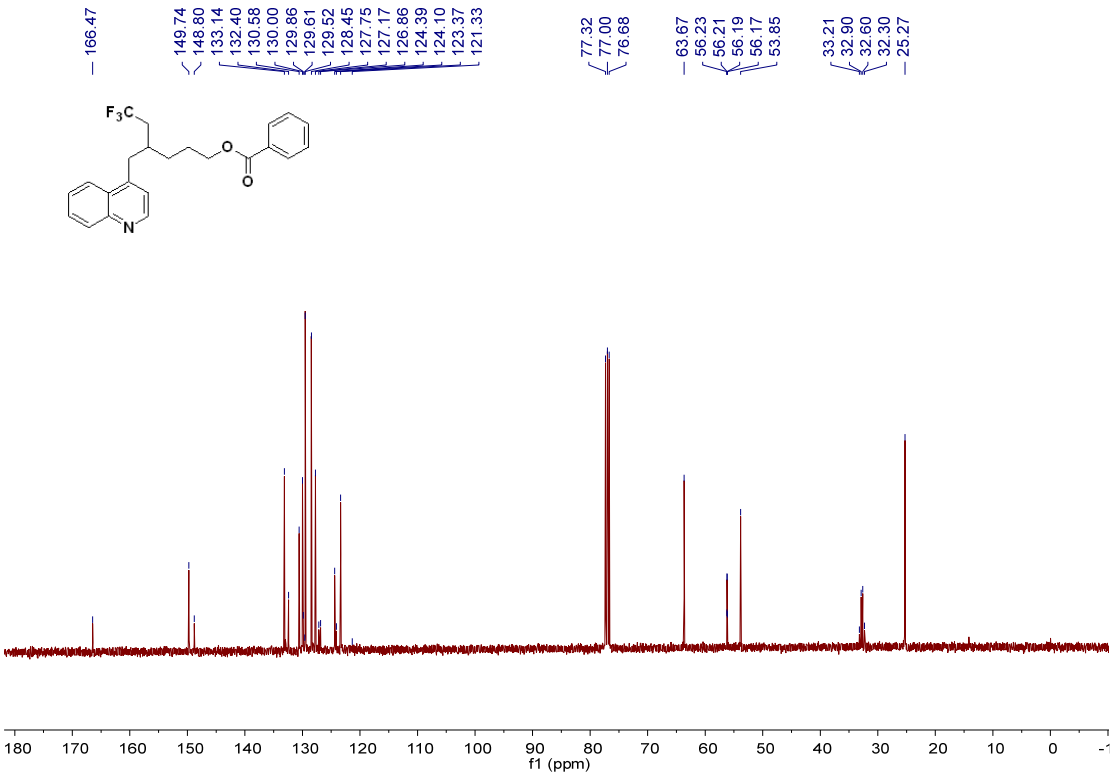


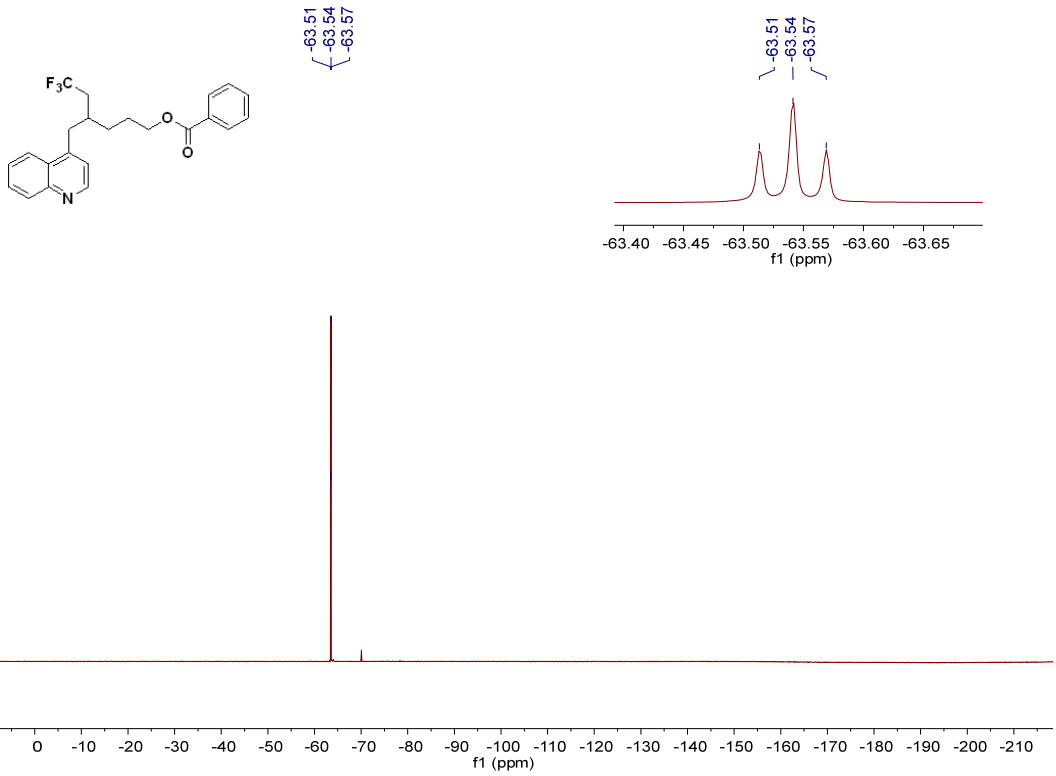




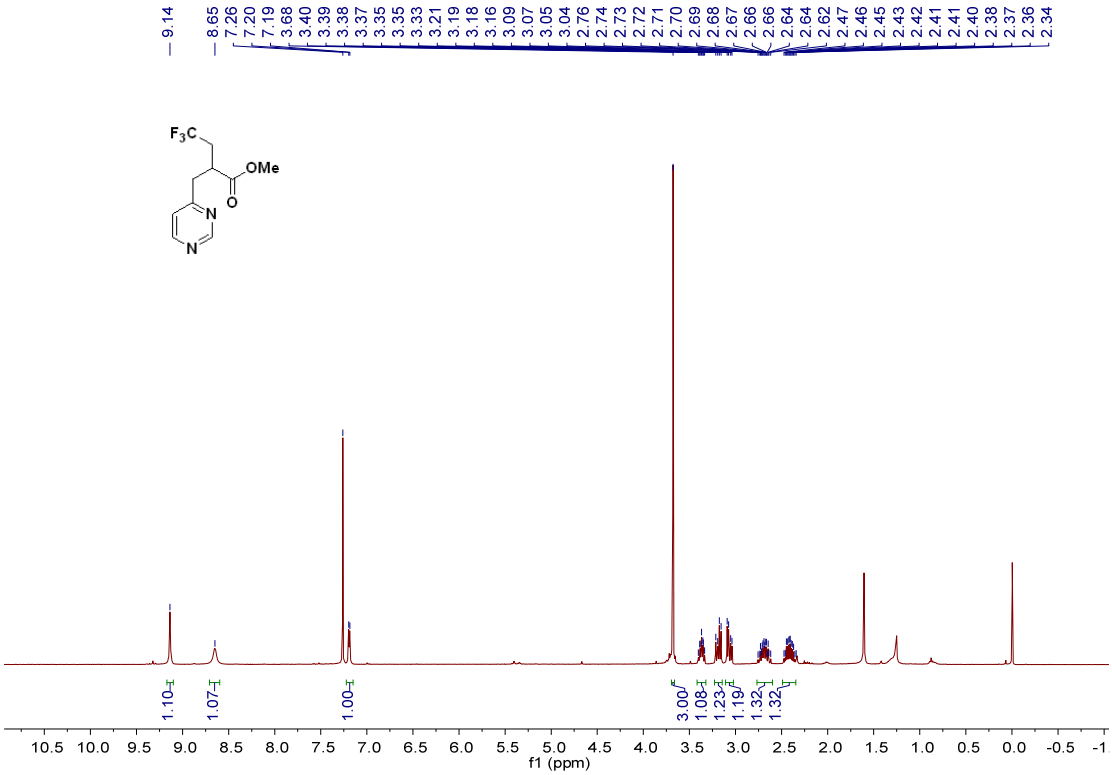
NMR Spectra of product **56**:

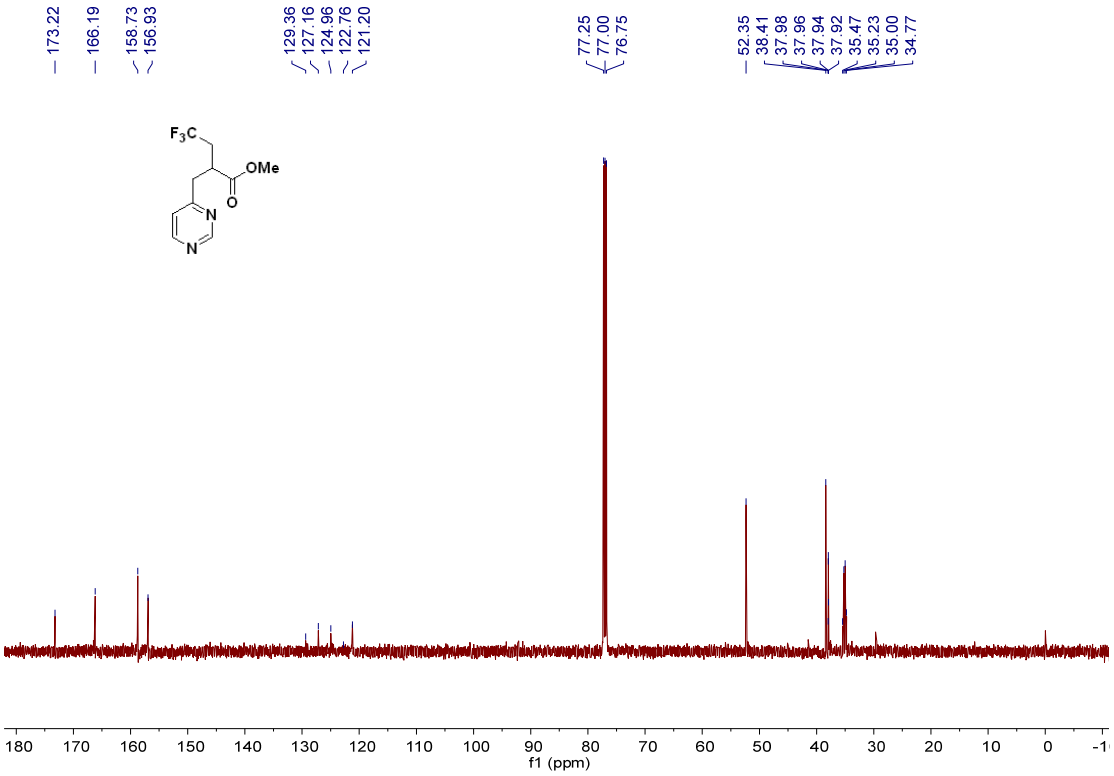

8.94 8.19 8.17 8.08 8.05 8.03 8.03 8.01 8.01 8.00 7.80 7.80 7.78 7.78 7.78 7.76 7.76 7.67 7.67 7.65 7.65 7.64 7.63 7.63 7.58 7.57 7.56 7.56 7.55 7.55 7.54 7.48 7.46 7.45 7.45 7.43 7.42 7.42 7.26 4.80 4.77 4.75 4.71 4.37 4.36 4.34 4.33 3.42 3.40 3.40 2.24 2.10 2.09 2.08 2.07 2.05 2.04 1.99 1.97
F3C
O
O
N
1.00 1.11 2.99 1.09 1.10 0.97 3.04 2.25 2.28 1.10 1.17 1.13 1.17 2.25 1.39
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

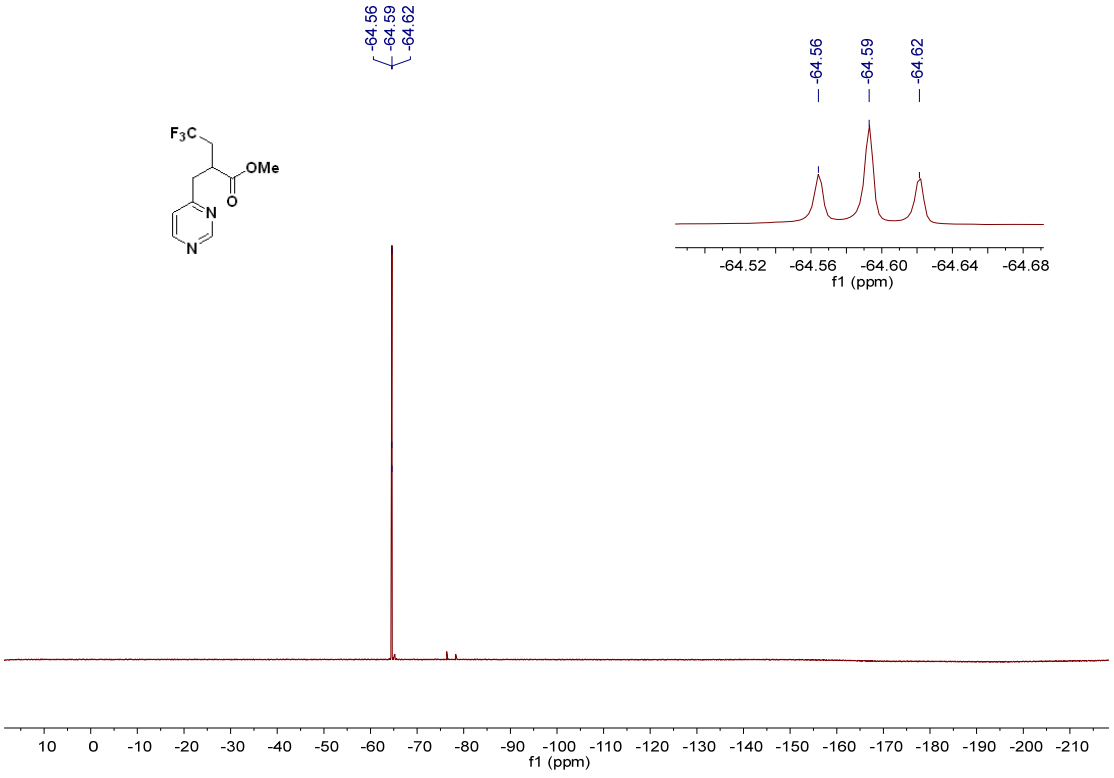

166.47
149.74 148.80 133.14 132.40 130.58 130.00 129.86 129.61 129.52 128.45 127.75 127.17 126.86 124.39 124.10 123.37 121.33
77.32 77.00 76.68
63.67 56.23 56.21 56.19 56.17 53.85
33.21 32.90 32.60 32.30 25.27
F3C
O
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



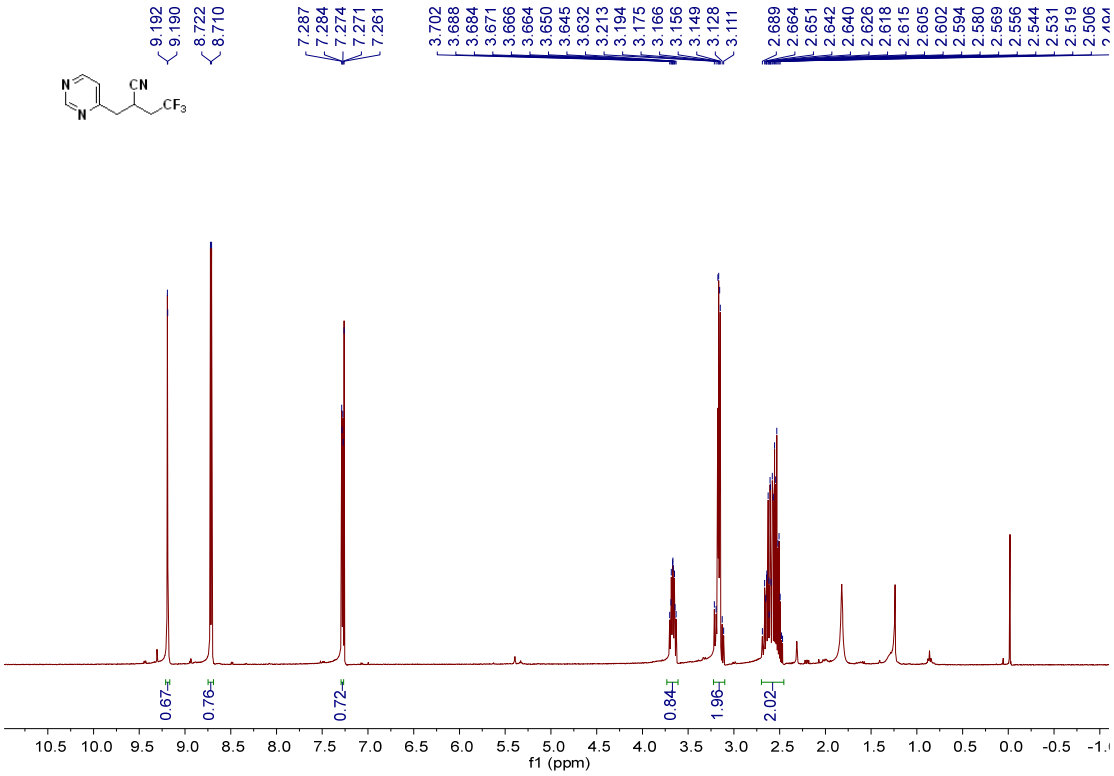
NMR Spectra of product **57**:

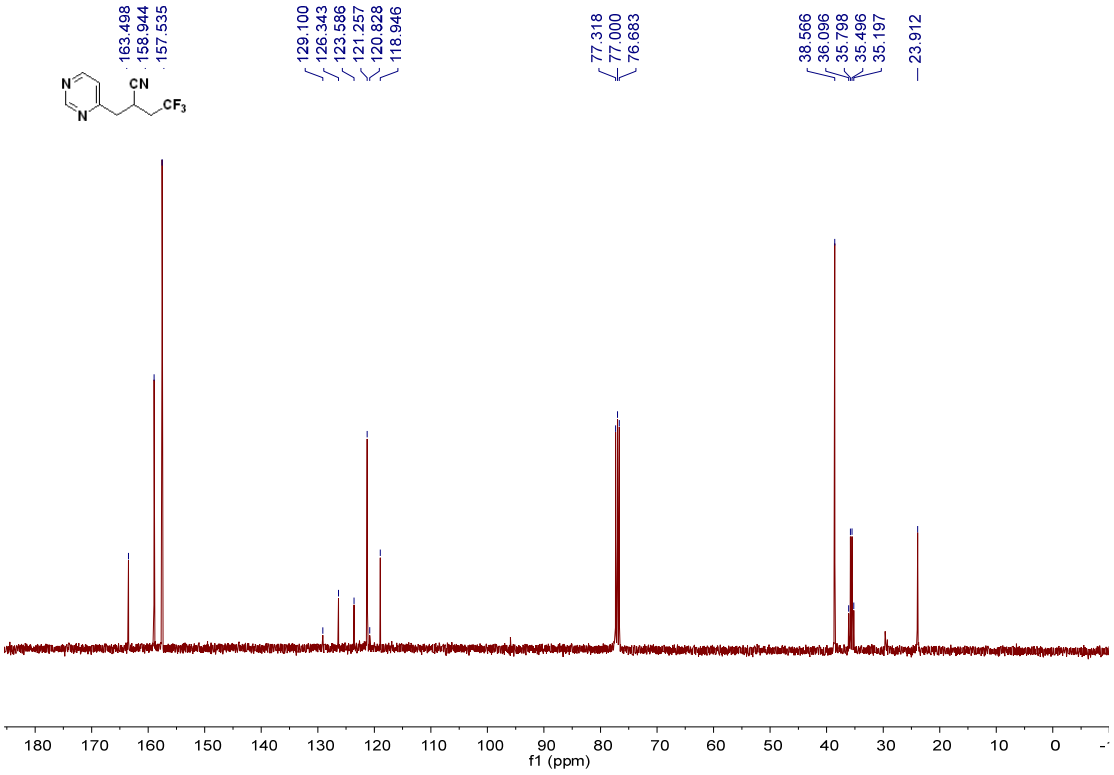


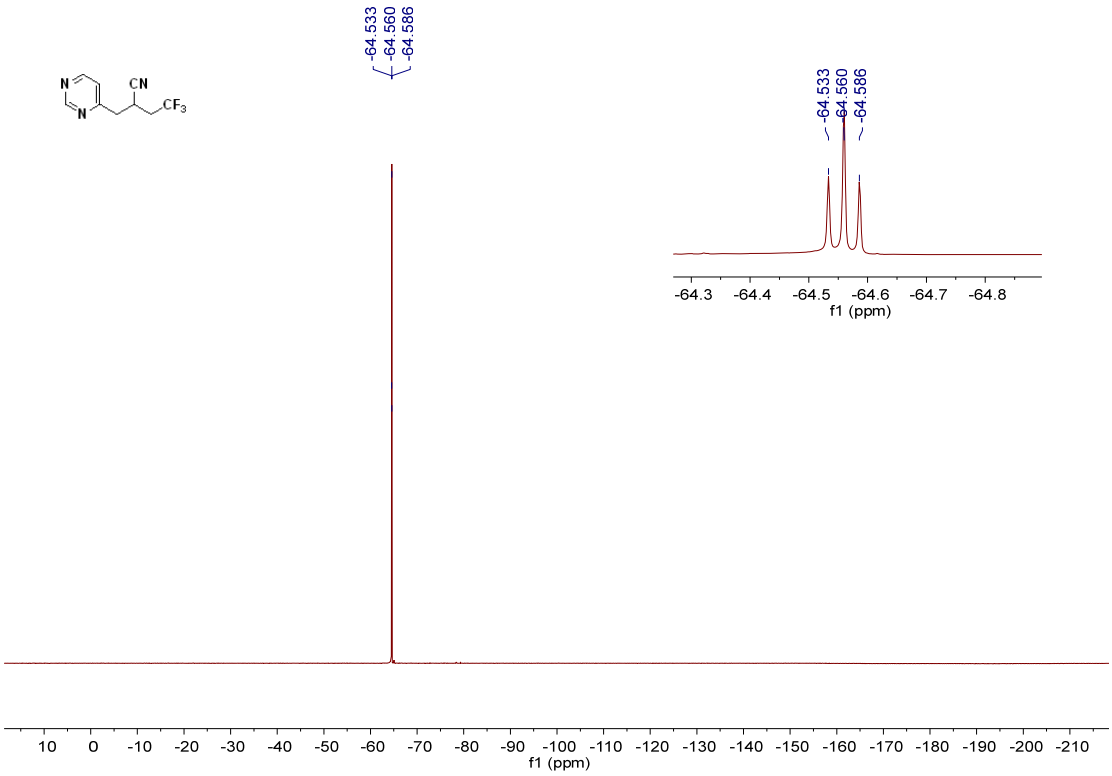




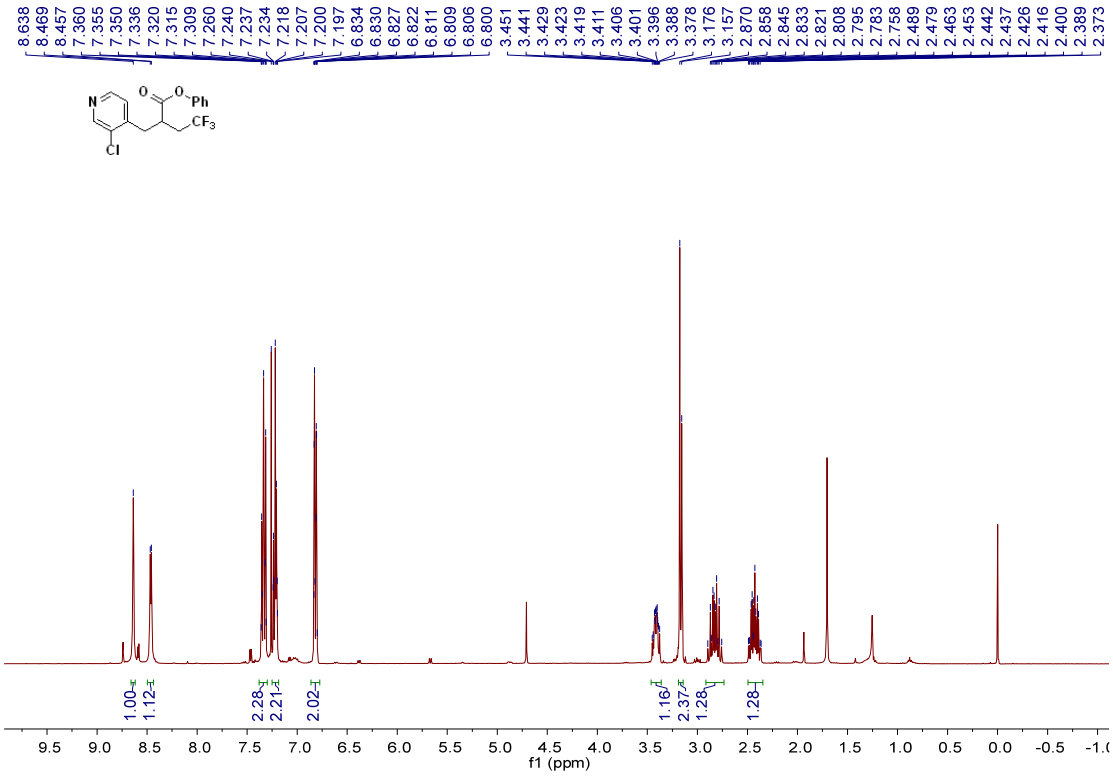
NMR Spectra of product **58**:

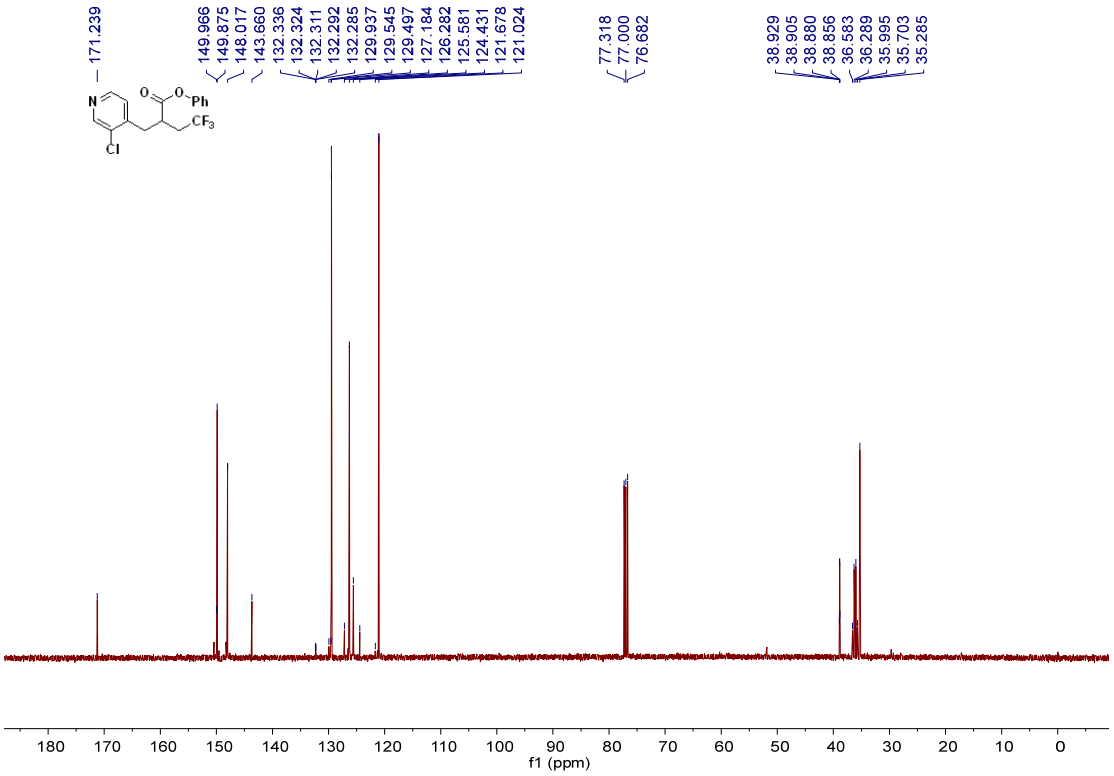

9.192
9.190
8.722
8.710
7.287
7.284
7.274
7.271
7.261
3.702
3.688
3.684
3.671
3.666
3.664
3.650
3.645
3.632
3.213
3.194
3.175
3.166
3.156
3.149
3.128
3.111
2.689
2.664
2.651
2.642
2.640
2.626
2.618
2.615
2.605
2.602
2.594
2.580
2.569
2.556
2.544
2.531
2.519
2.506
CN
CF3
0.67
0.76
0.72
0.84
1.96
2.02
f1 (ppm)

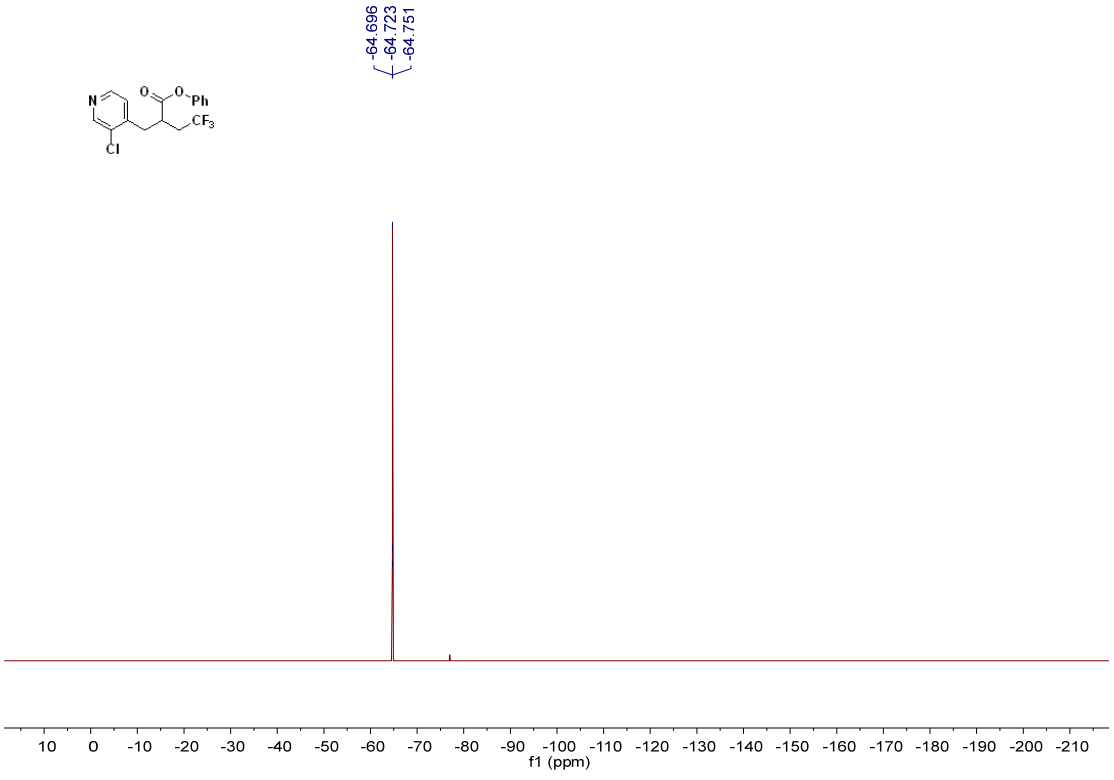

163.498
158.944
157.535
129.100
126.343
123.586
121.257
120.828
118.946
77.318
77.000
76.683
38.566
36.096
35.798
35.496
35.197
23.912
CN
CF3
f1 (ppm)



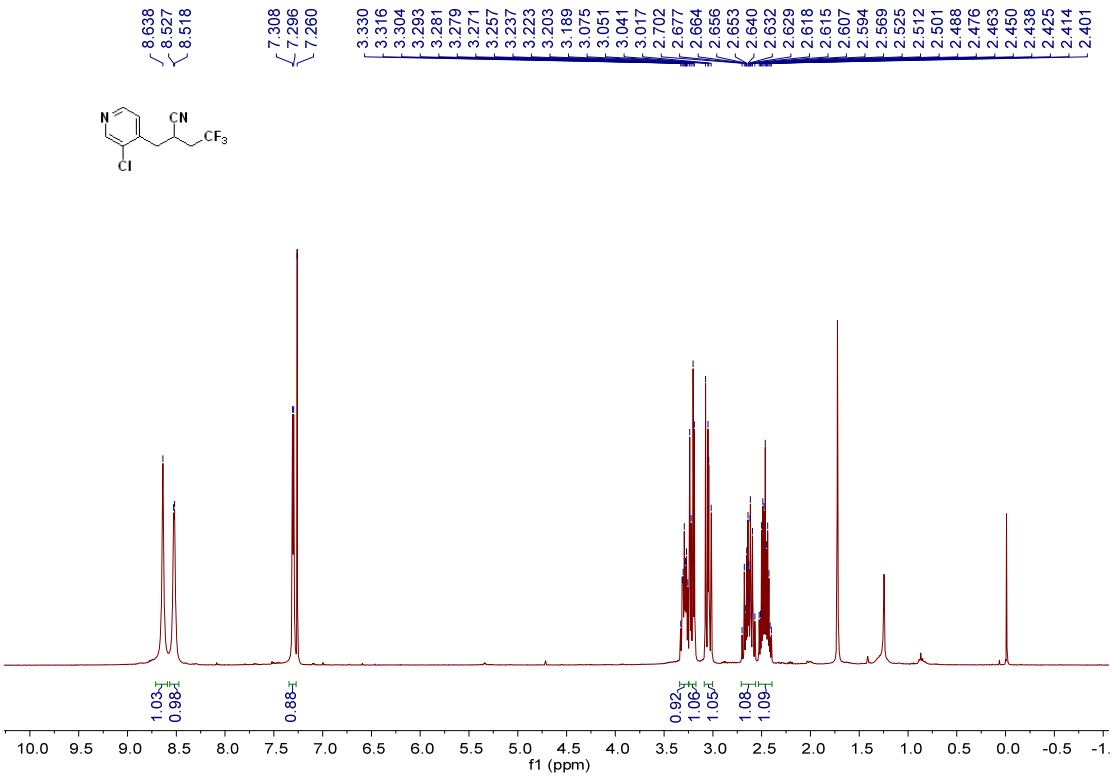
NMR Spectra of product **59**:

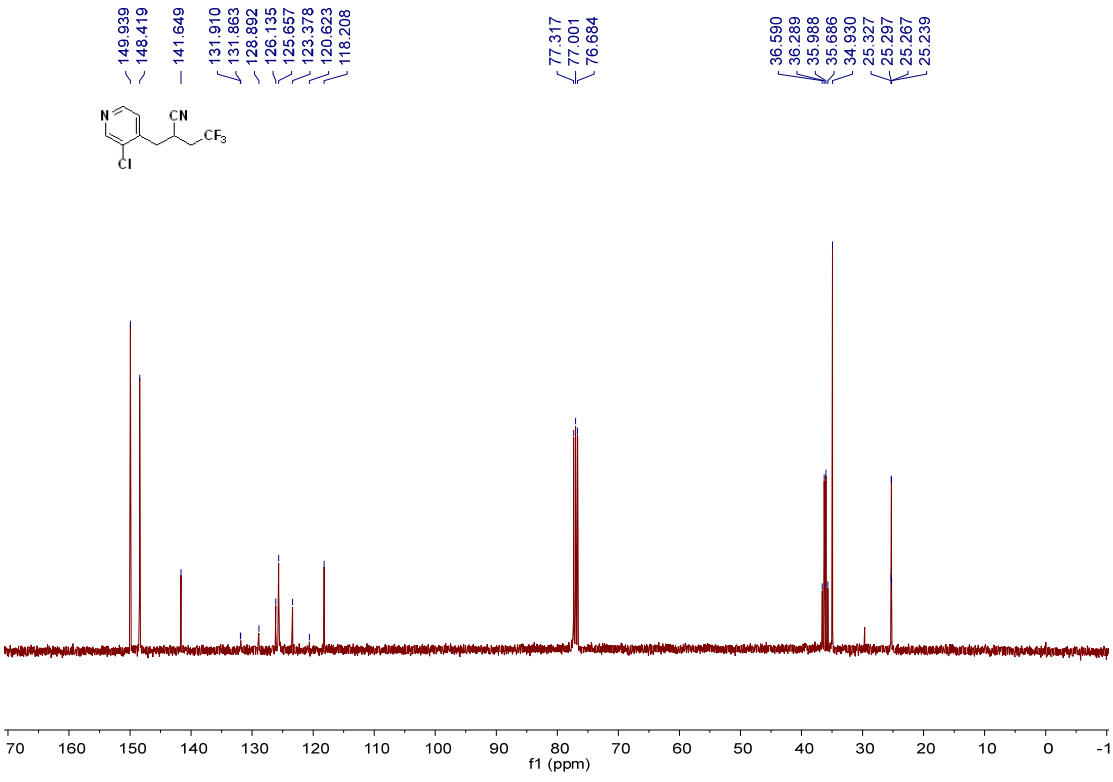


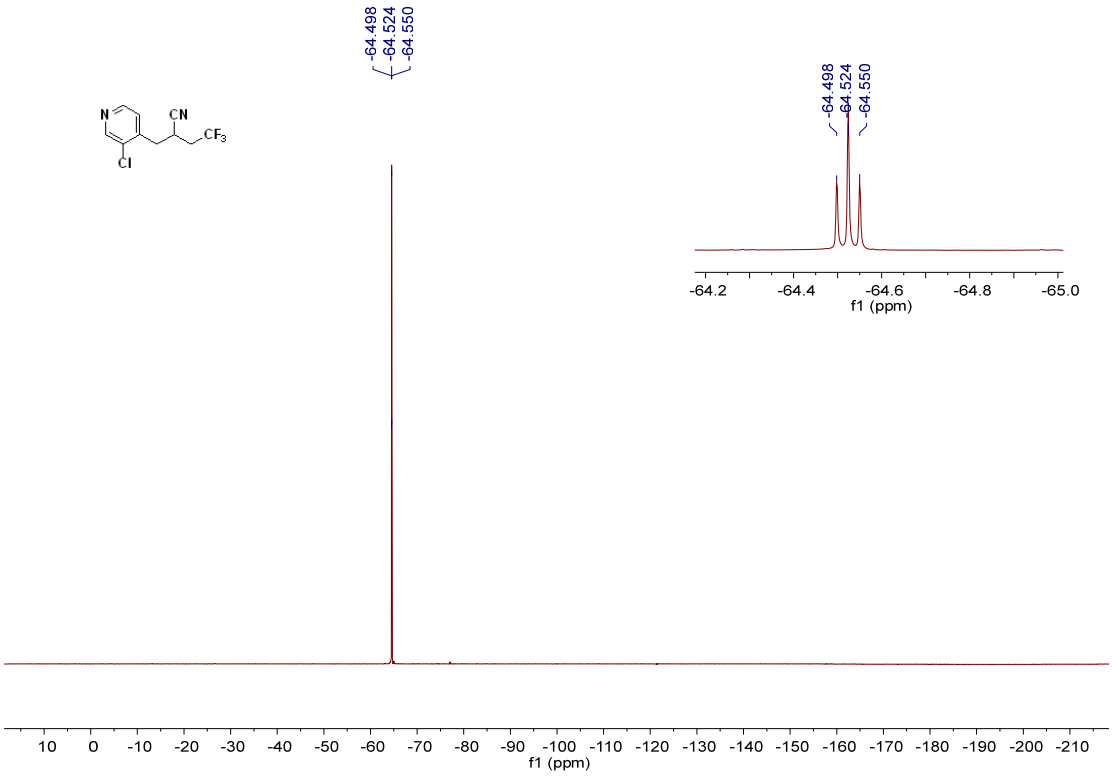




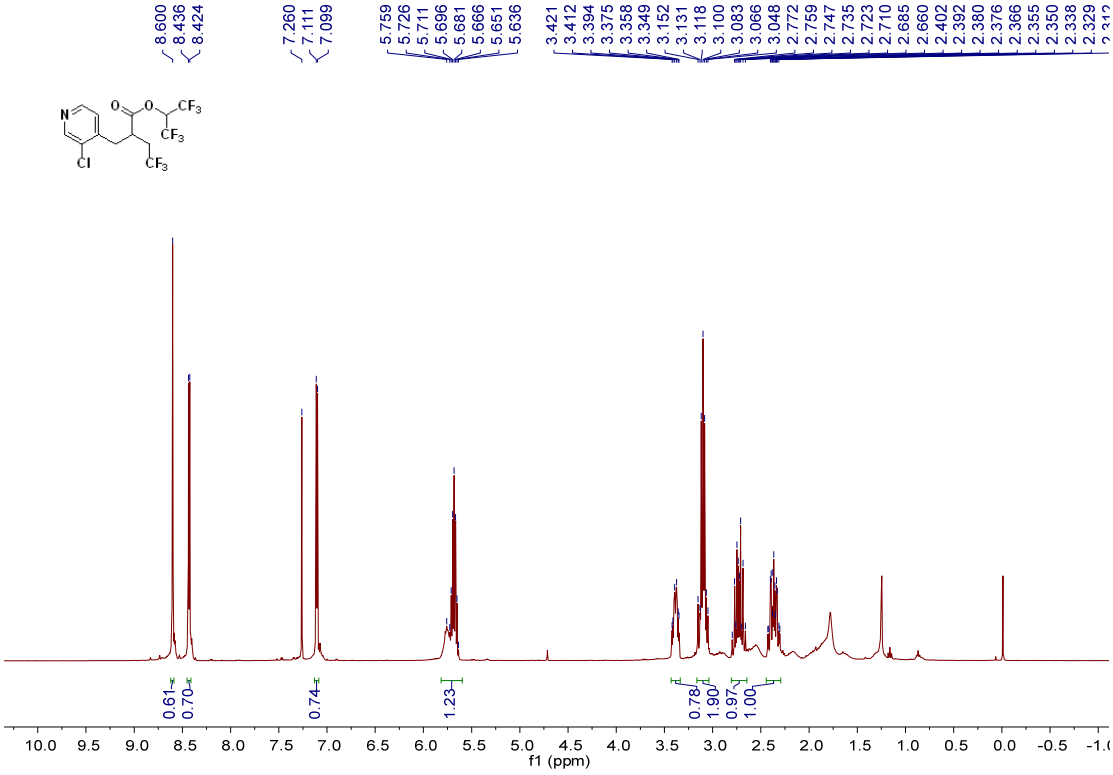
NMR Spectra of product **60**:

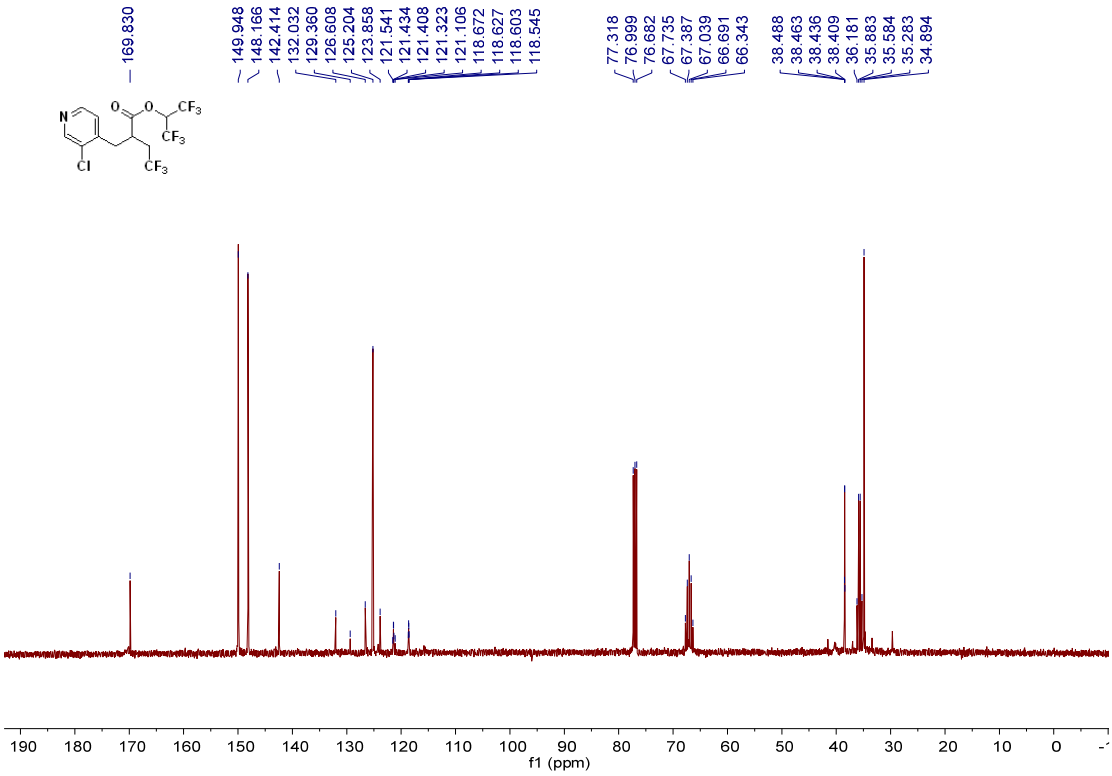

8.638
8.527
8.518
7.308
7.296
7.260
3.330
3.316
3.304
3.293
3.281
3.279
3.271
3.257
3.237
3.223
3.203
3.189
3.075
3.051
3.041
3.017
2.702
2.677
2.664
2.656
2.653
2.640
2.632
2.629
2.618
2.615
2.607
2.594
2.569
2.525
2.512
2.501
2.488
2.476
2.463
2.450
2.438
2.425
2.414
2.401
N
CN
CF3
Cl
1.03
0.98
0.88
0.92
1.06
1.05
1.08
1.09
f1 (ppm)

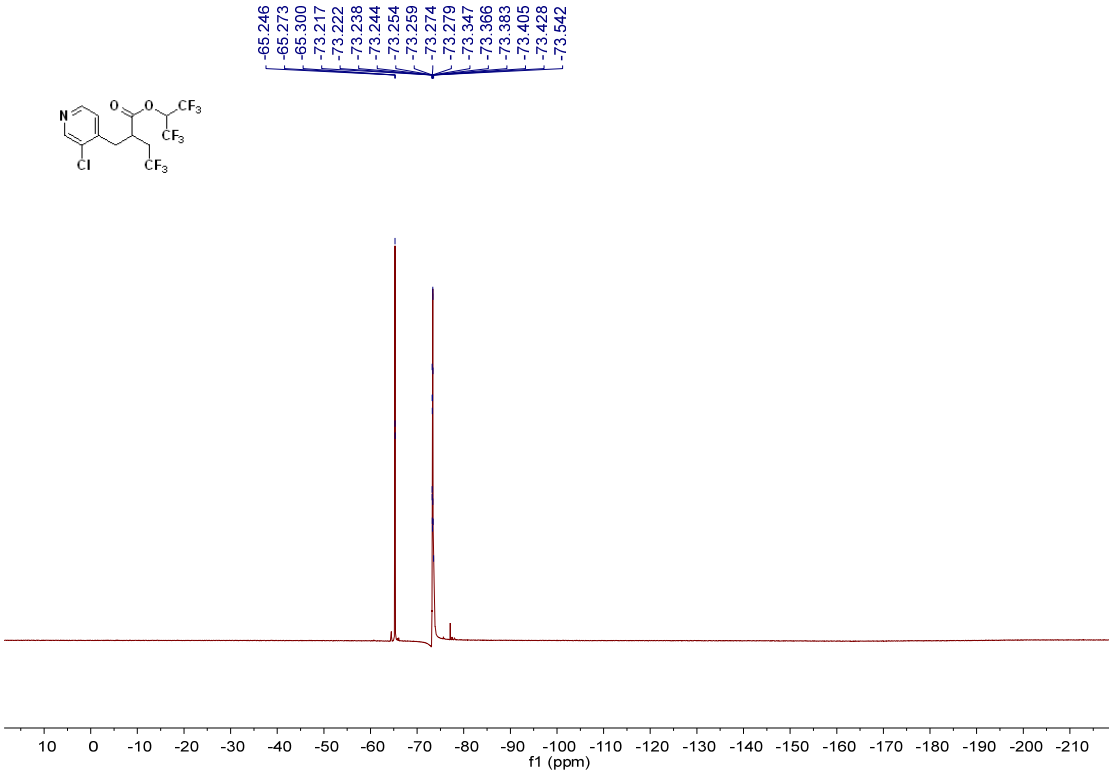

149.939
148.419
141.649
131.910
131.863
128.892
126.135
125.657
123.378
120.623
118.208
77.317
77.001
76.684
36.590
36.289
35.988
35.686
34.930
25.327
25.297
25.267
25.239
N
CN
CF3
Cl
f1 (ppm)



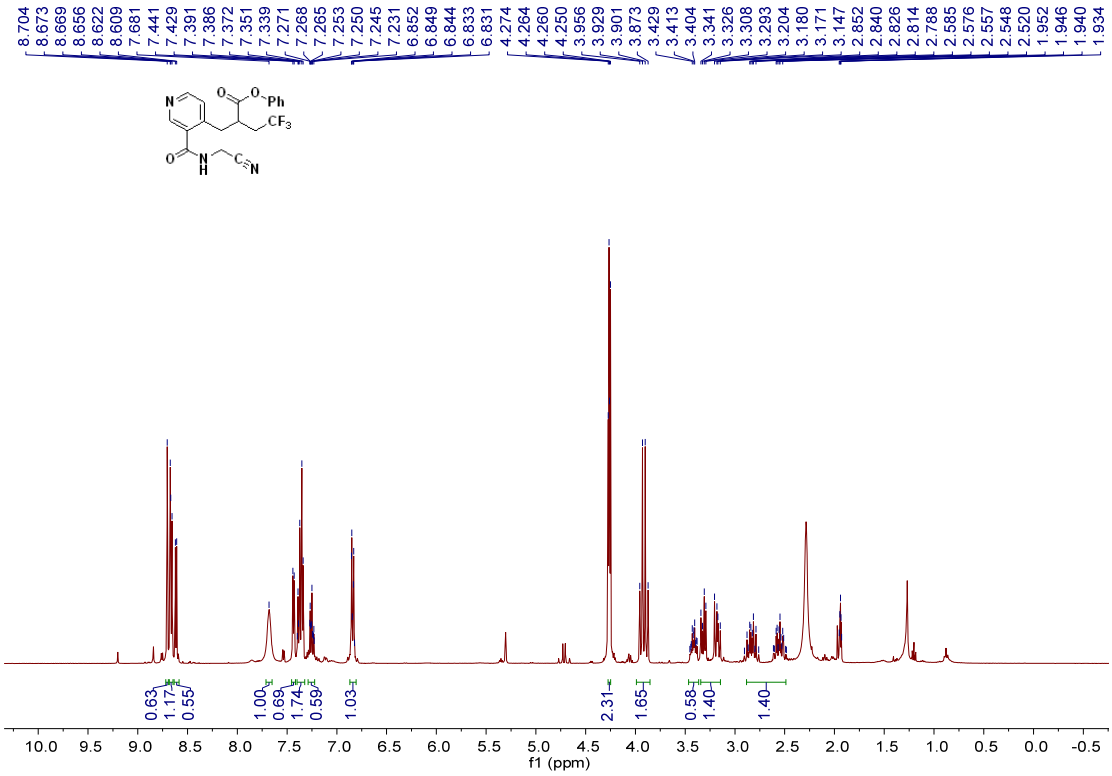
NMR Spectra of product **61**:

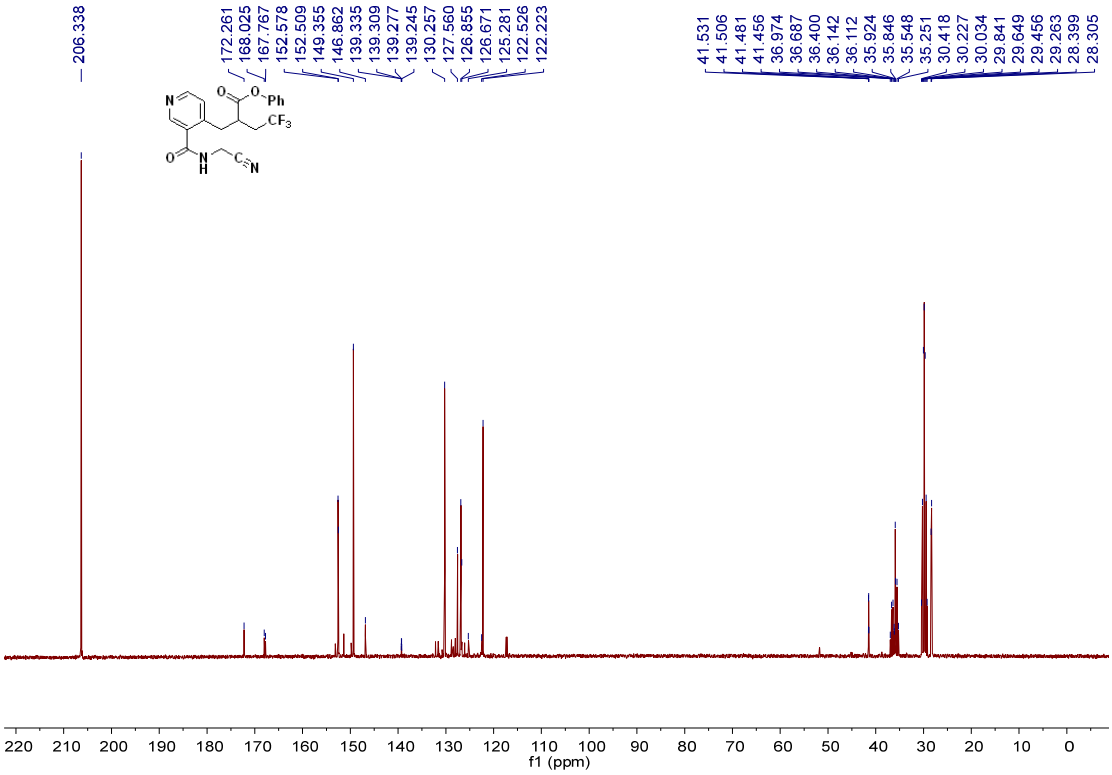


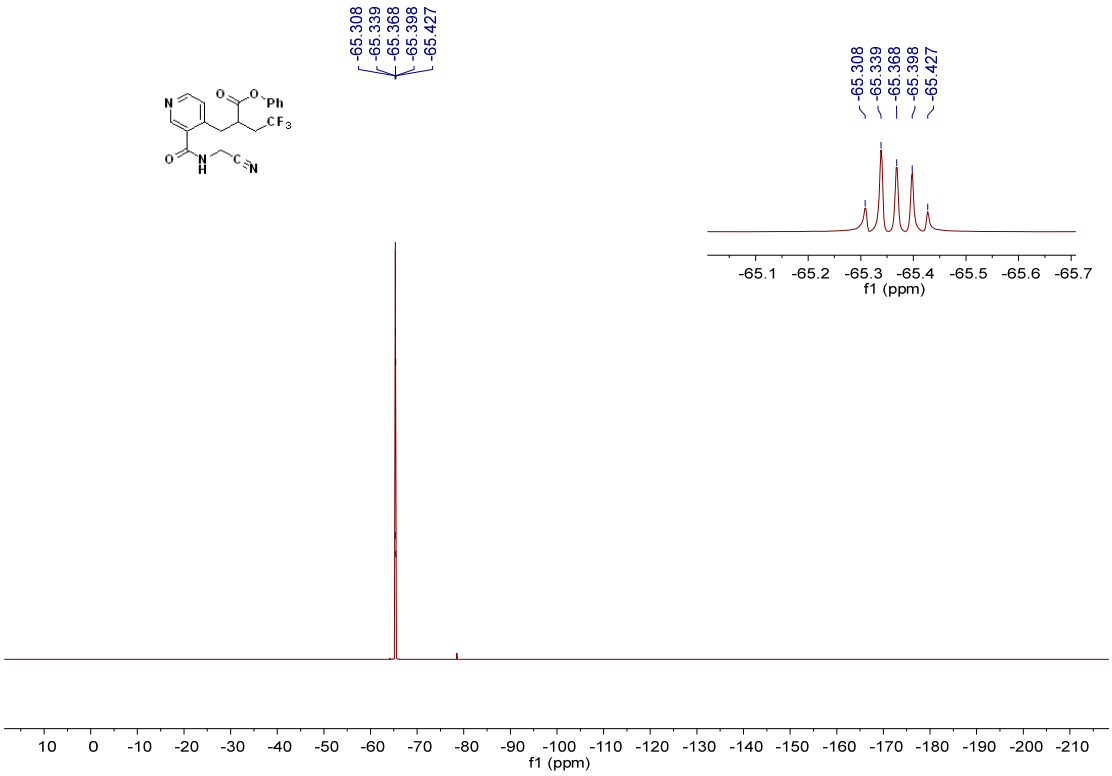




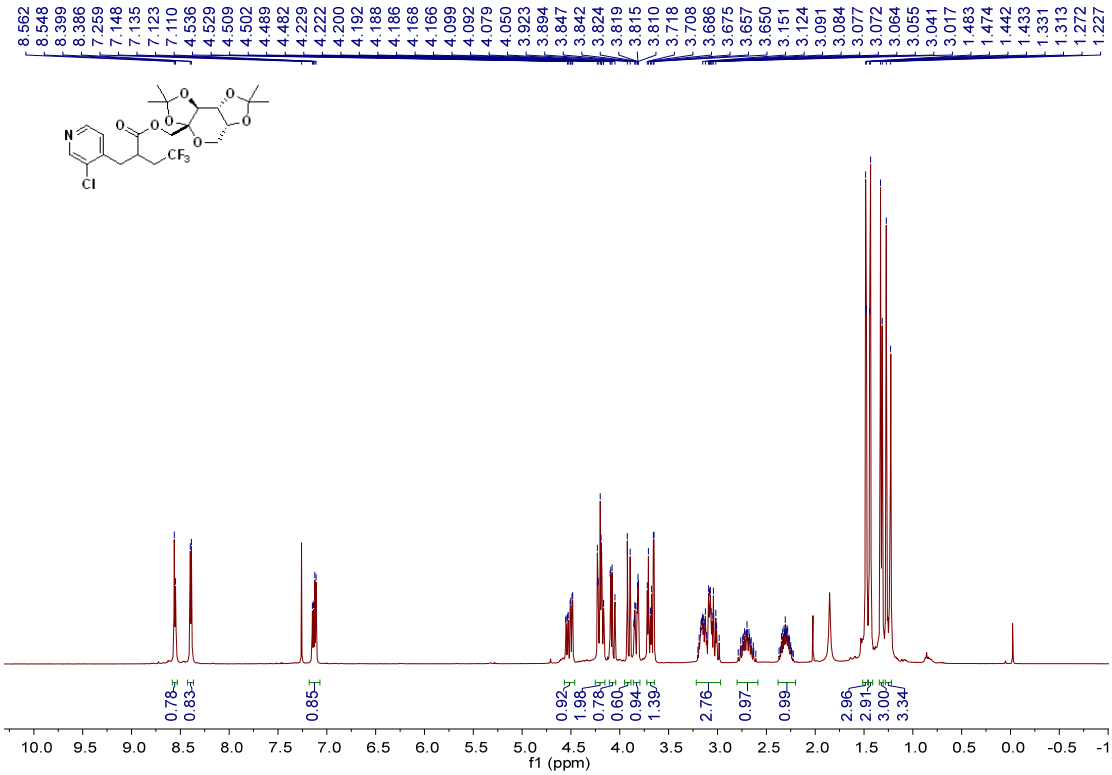
NMR Spectra of product **62**:

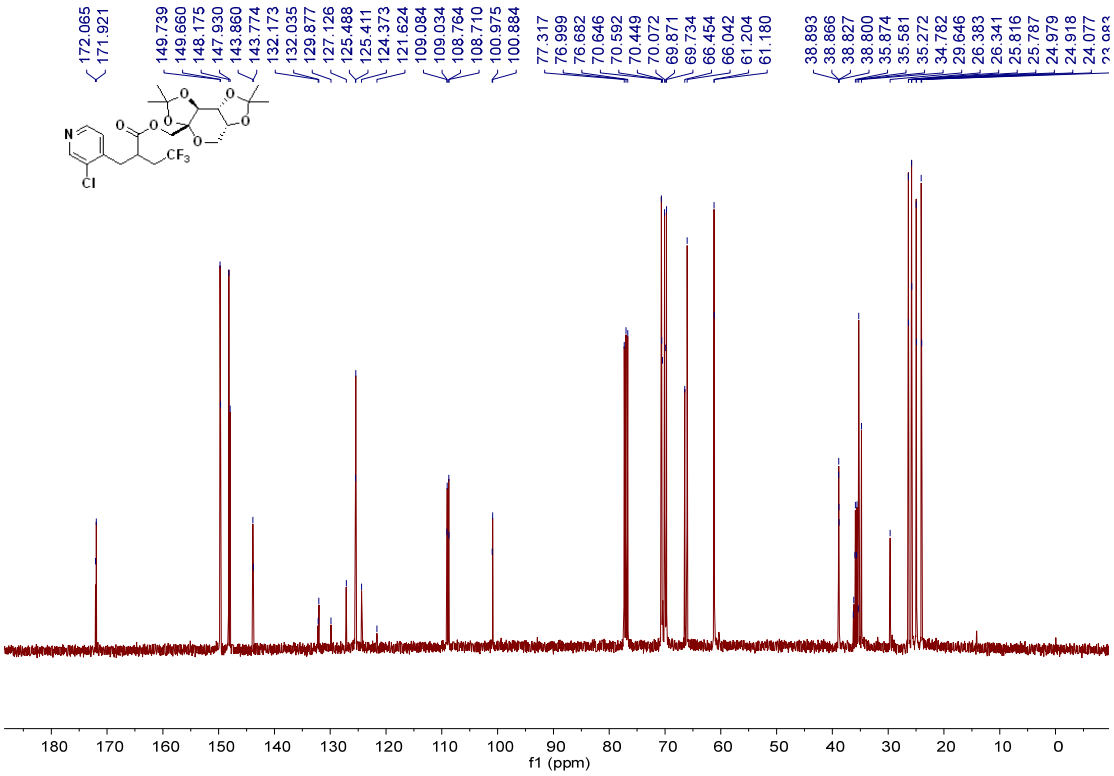

8.704
8.673
8.669
8.656
8.622
8.609
7.681
7.441
7.429
7.391
7.386
7.372
7.351
7.339
7.271
7.268
7.265
7.253
7.250
7.245
7.231
6.852
6.849
6.844
6.833
6.831
4.274
4.264
4.260
4.250
3.956
3.929
3.901
3.873
3.429
3.413
3.404
3.341
3.326
3.308
3.293
3.204
3.180
3.171
3.147
2.852
2.840
2.826
2.814
2.788
2.585
2.576
2.557
2.548
2.520
1.952
1.946
1.940
1.934
Ph
CF3
0.63
1.17
0.55
1.00
0.69
1.74
0.59
1.03
2.31
1.65
0.58
1.40
1.40
f1 (ppm)

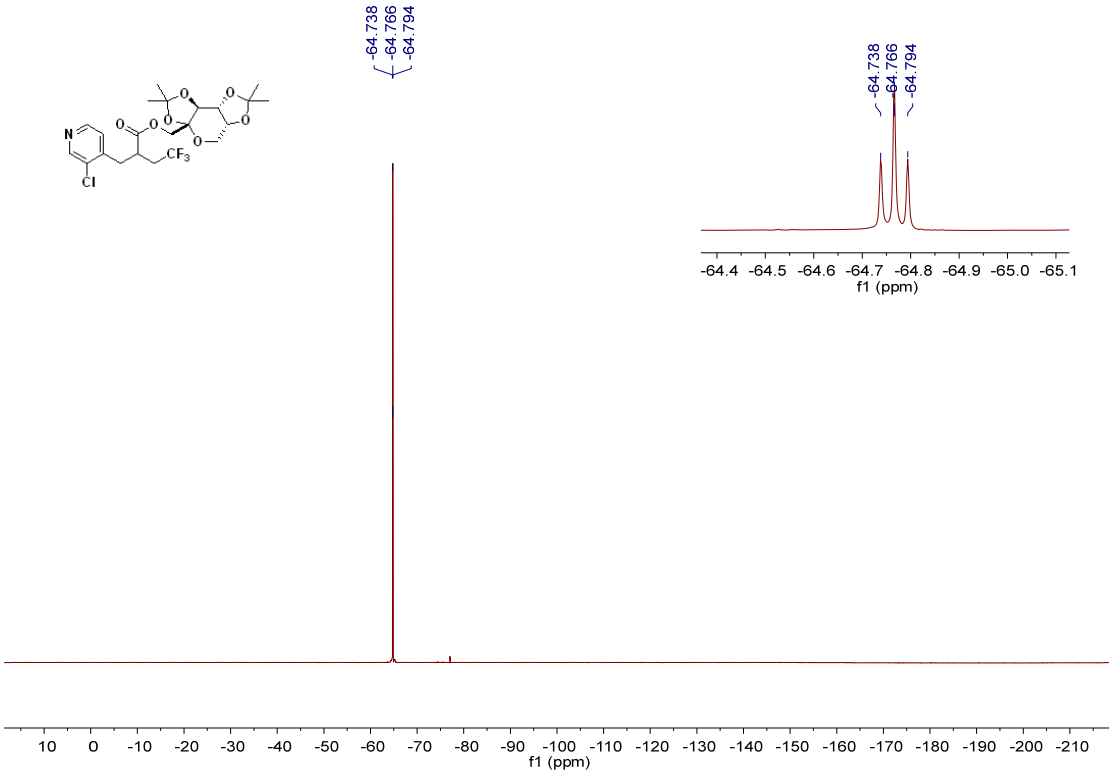

206.338
172.261
168.025
167.767
152.578
152.509
149.355
146.882
139.335
139.309
139.277
139.245
130.257
127.560
126.855
126.671
125.281
122.526
122.223
41.531
41.506
41.481
41.456
36.974
36.687
36.400
36.142
36.112
35.924
35.846
35.548
35.251
30.418
30.227
30.034
29.841
29.649
29.456
29.263
28.399
28.305
Ph
CF3
f1 (ppm)



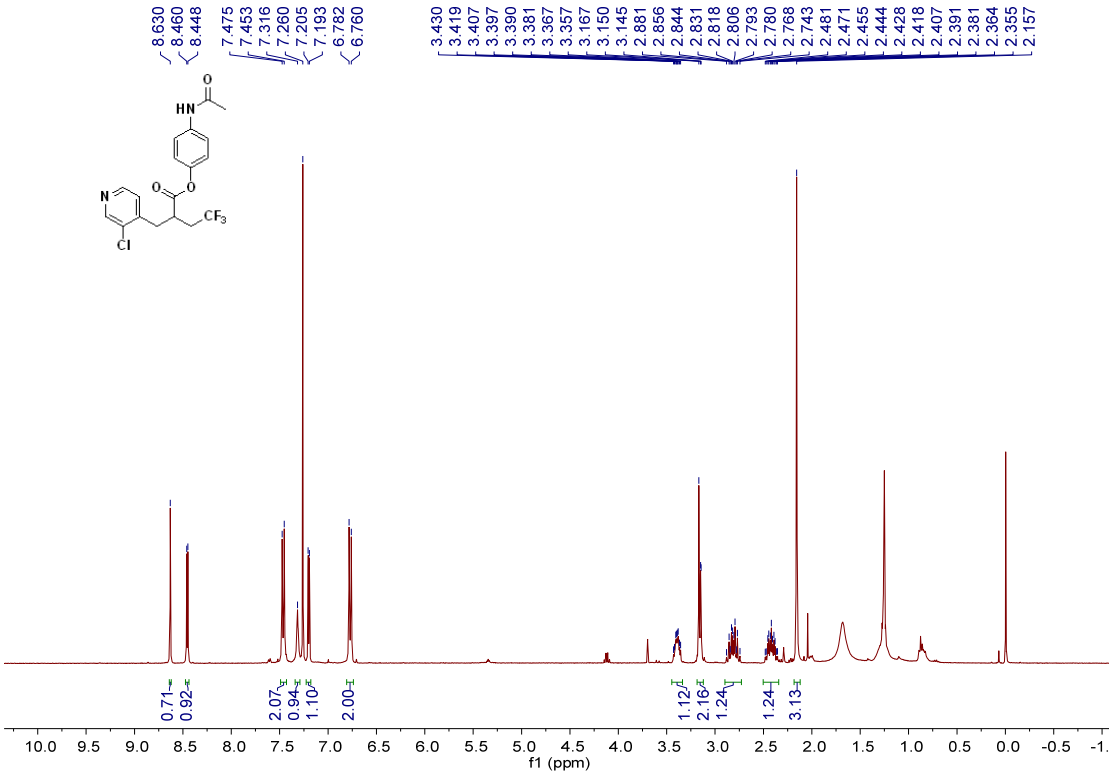
NMR Spectra of product **63**:

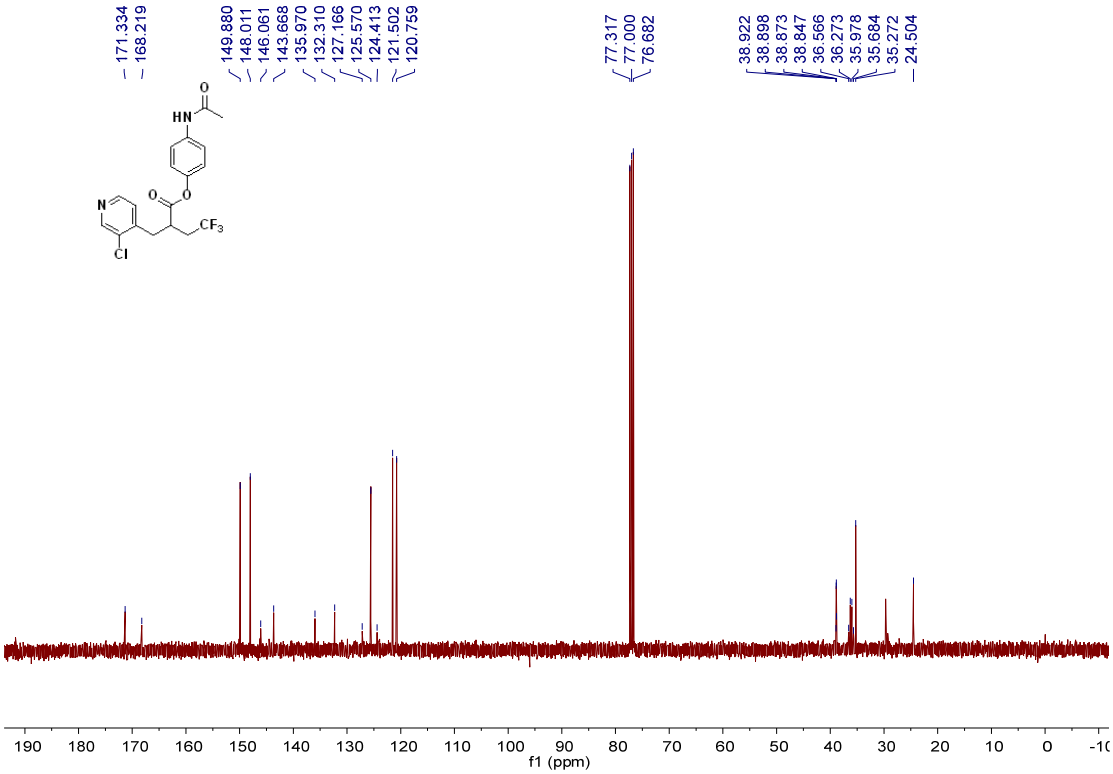


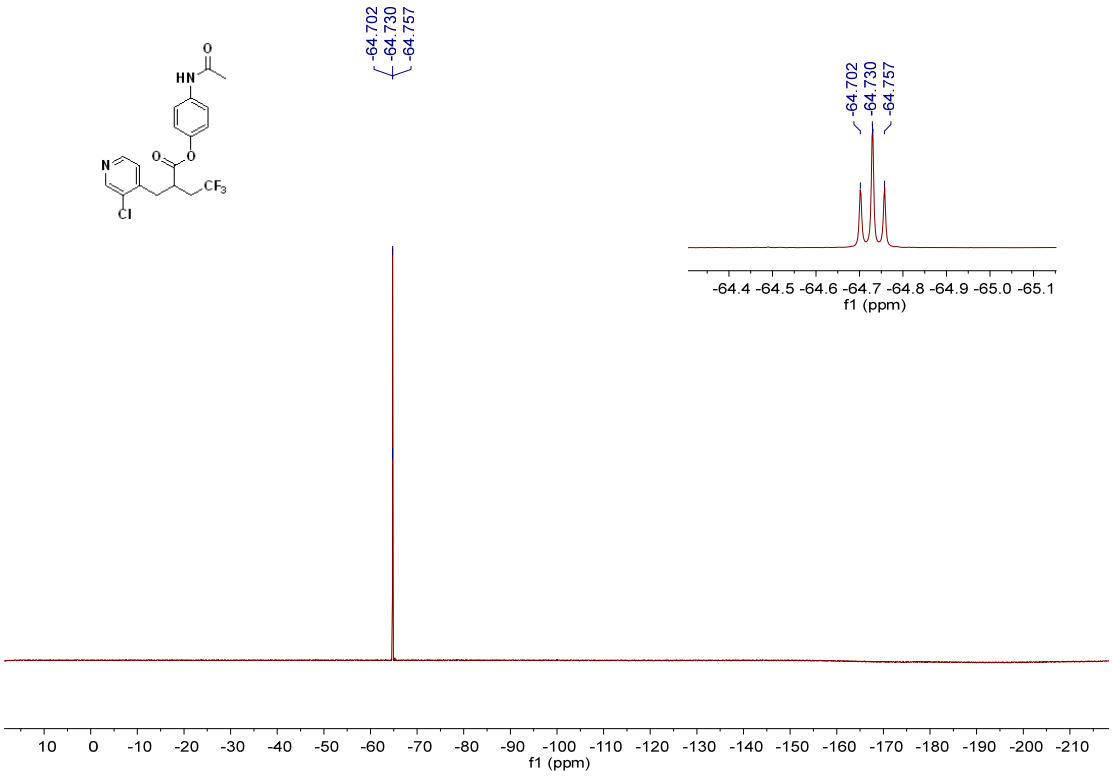




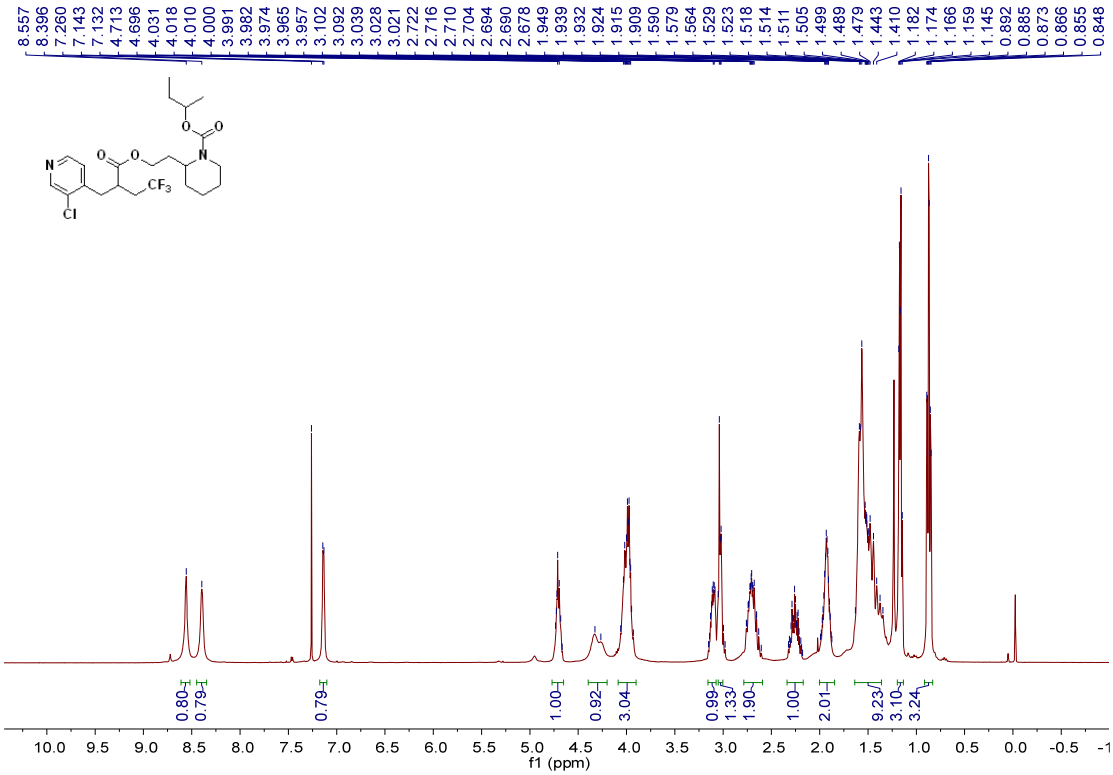
NMR Spectra of product **64**:

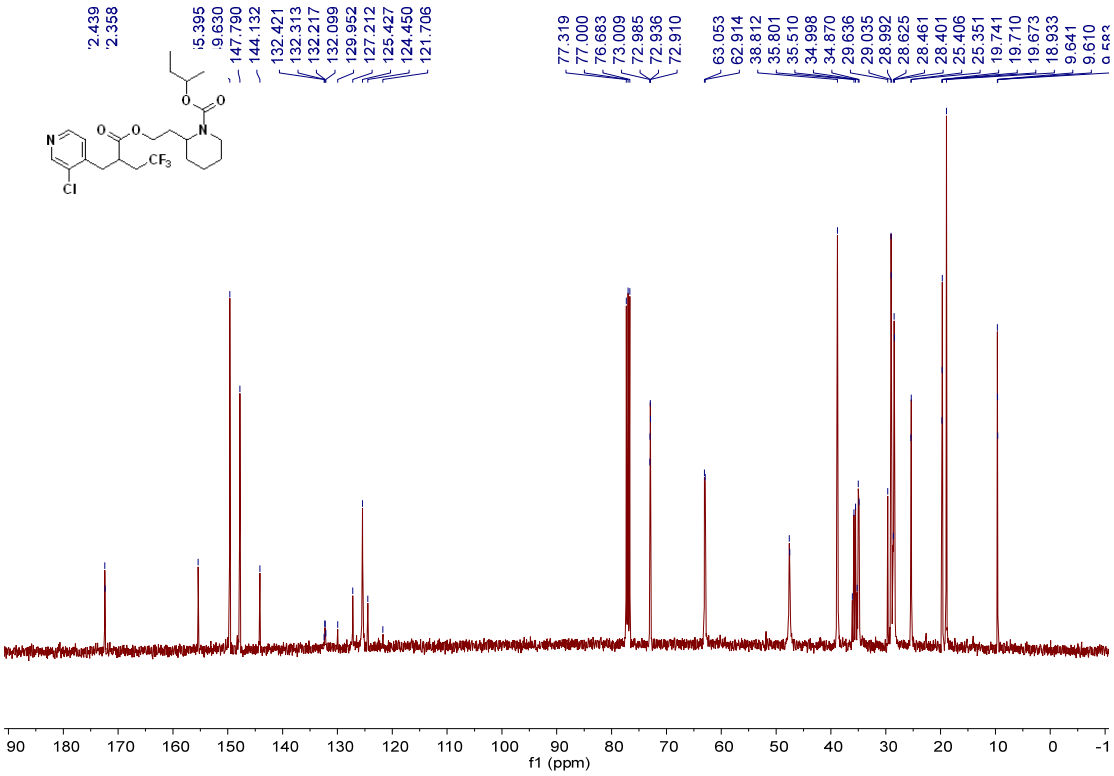

8.630
8.460
8.448
7.475
7.453
7.316
7.260
7.205
7.193
6.782
6.760
3.430
3.419
3.407
3.397
3.390
3.381
3.367
3.357
3.167
3.150
3.145
2.881
2.856
2.844
2.831
2.818
2.806
2.793
2.780
2.768
2.743
2.481
2.471
2.455
2.444
2.428
2.418
2.407
2.391
2.381
2.364
2.355
2.157
HN
O
O
O
N
Cl
CF3
0.71
0.92
2.07
0.94
1.10
2.00
1.12
2.16
1.24
1.24
3.13
f1 (ppm)

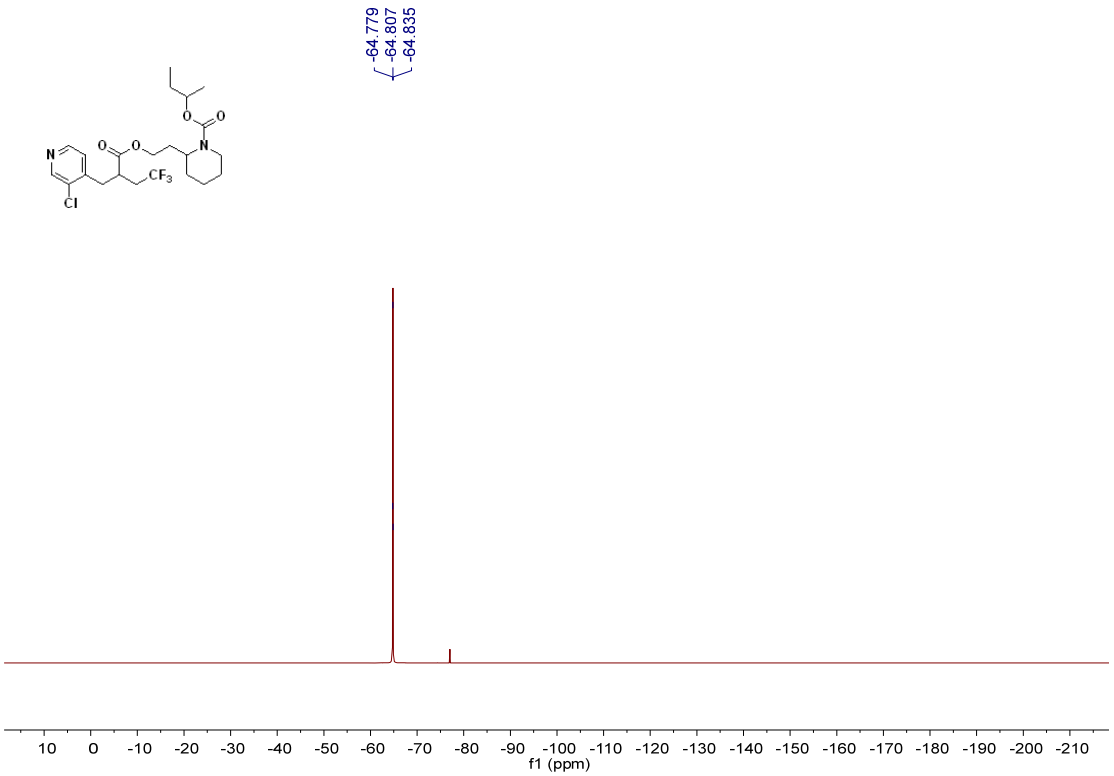

171.334
168.219
149.880
148.011
146.061
143.668
135.970
132.310
127.166
125.570
124.413
121.502
120.759
77.317
77.000
76.682
38.922
38.898
38.873
38.847
36.566
36.273
35.978
35.684
35.272
24.504
HN
O
O
O
N
Cl
CF3
f1 (ppm)



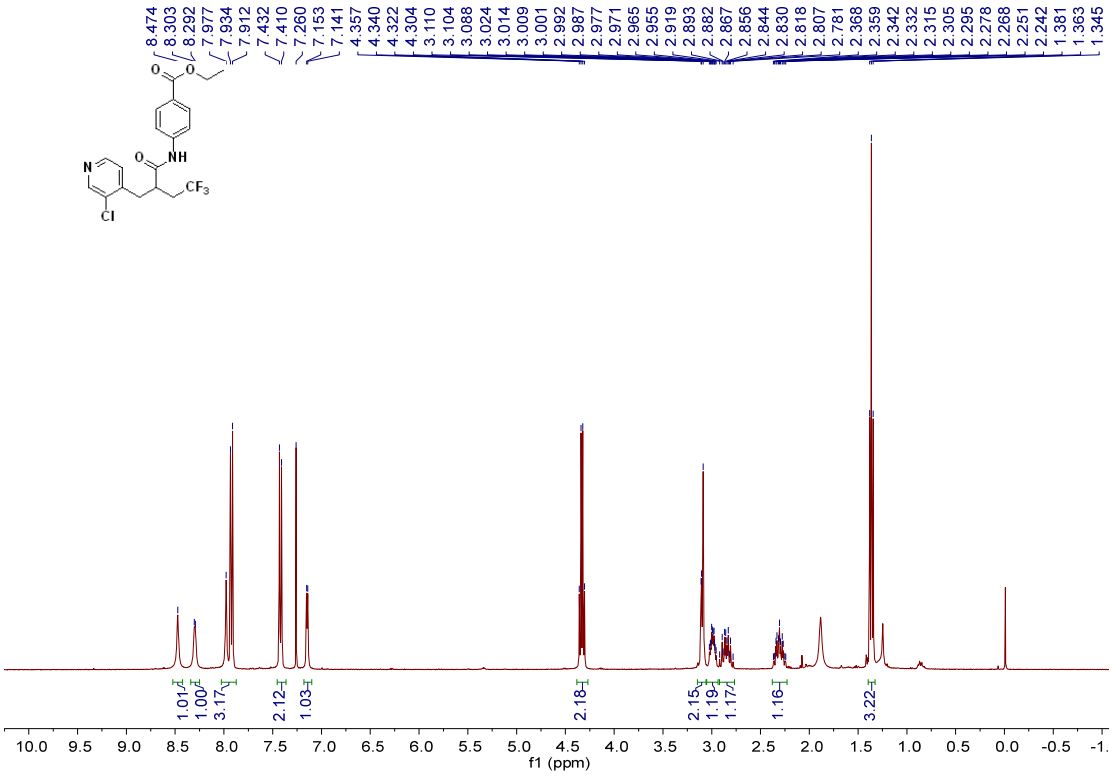
NMR Spectra of product **65**:

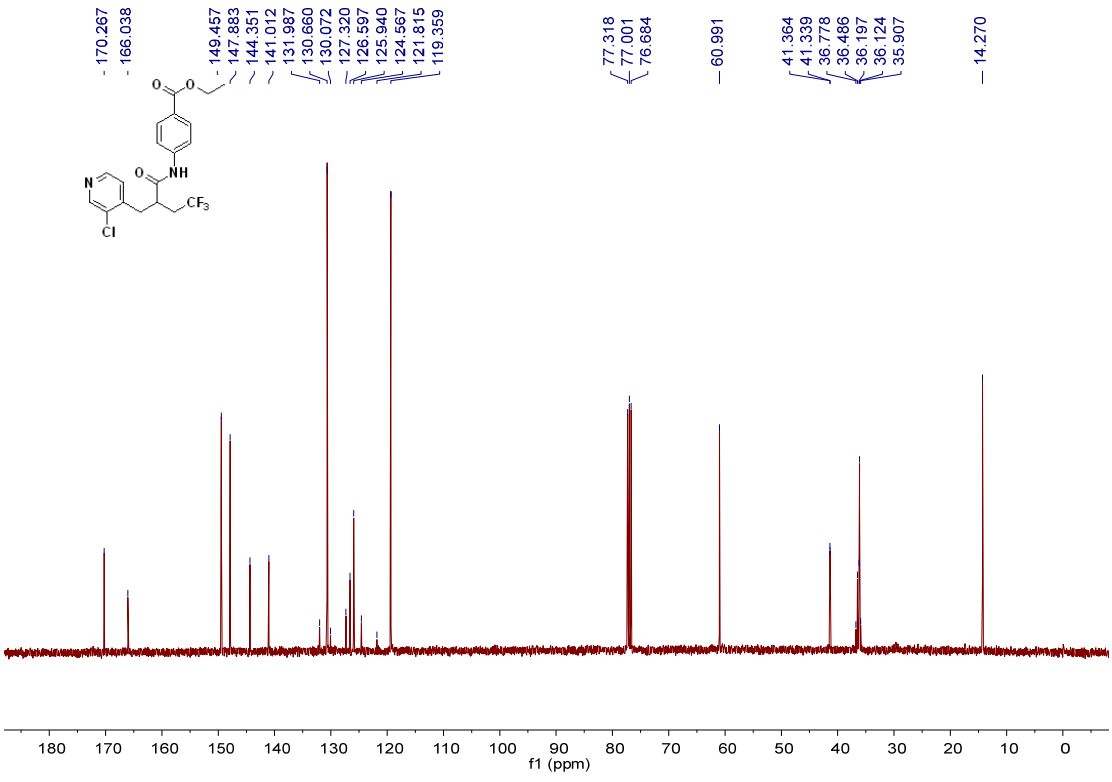


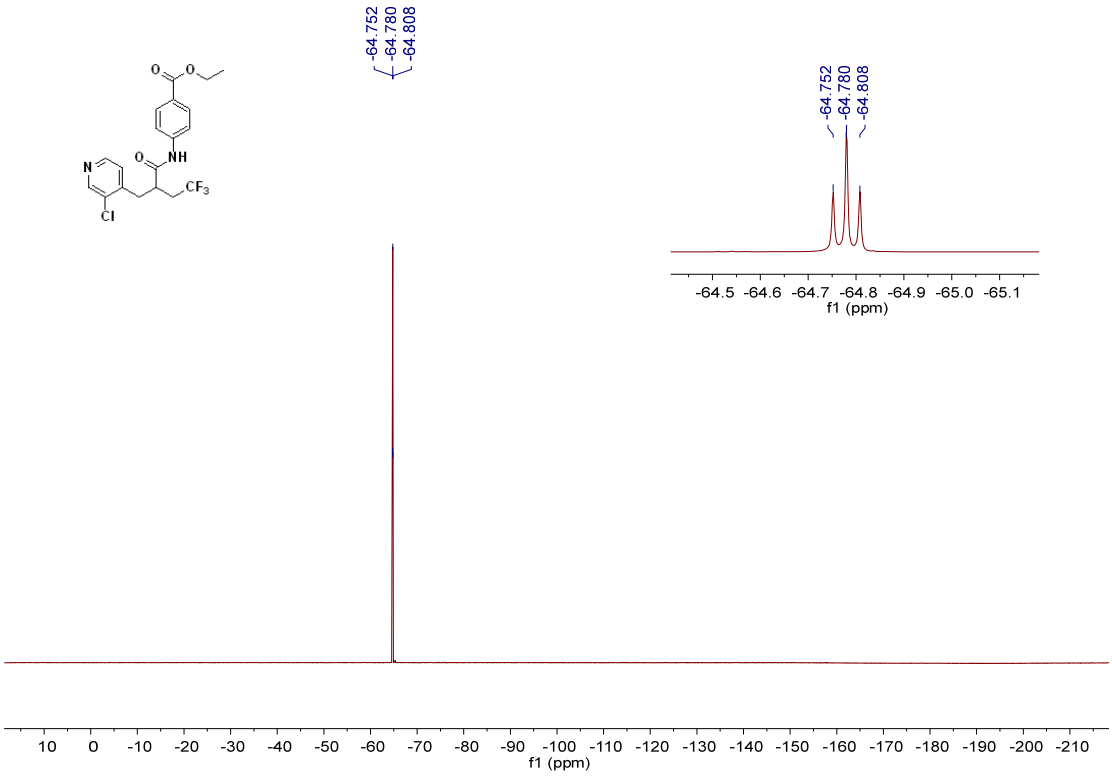




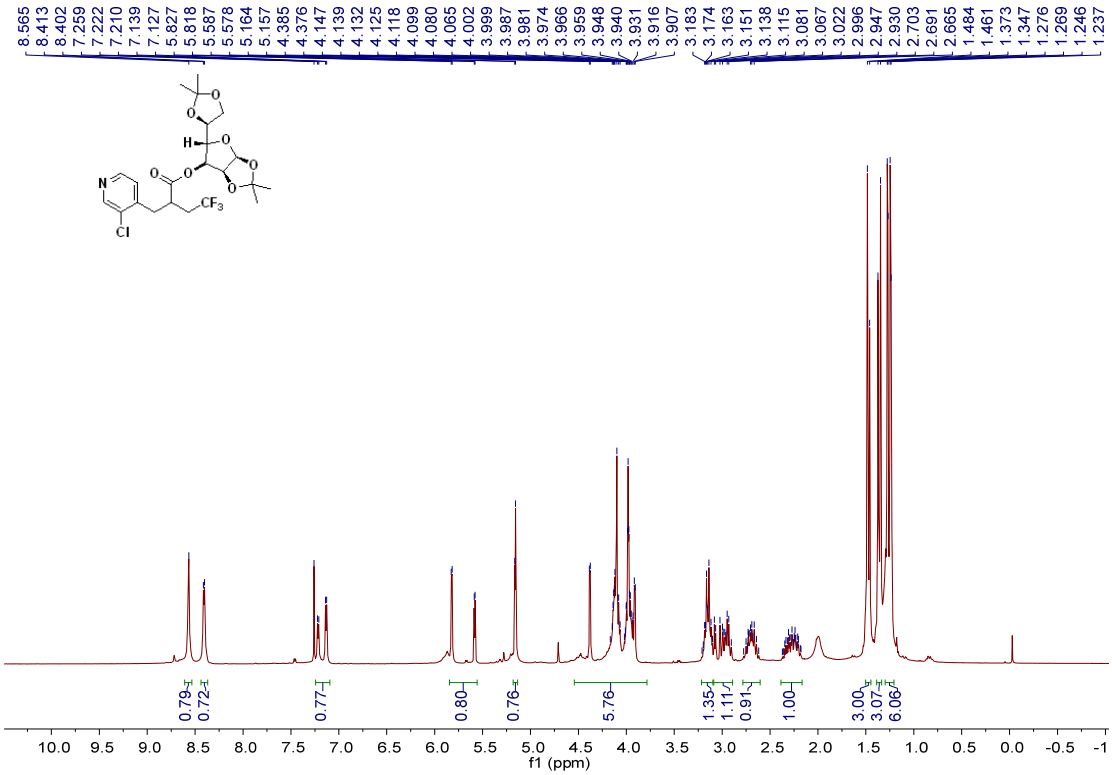
NMR Spectra of product **66**:

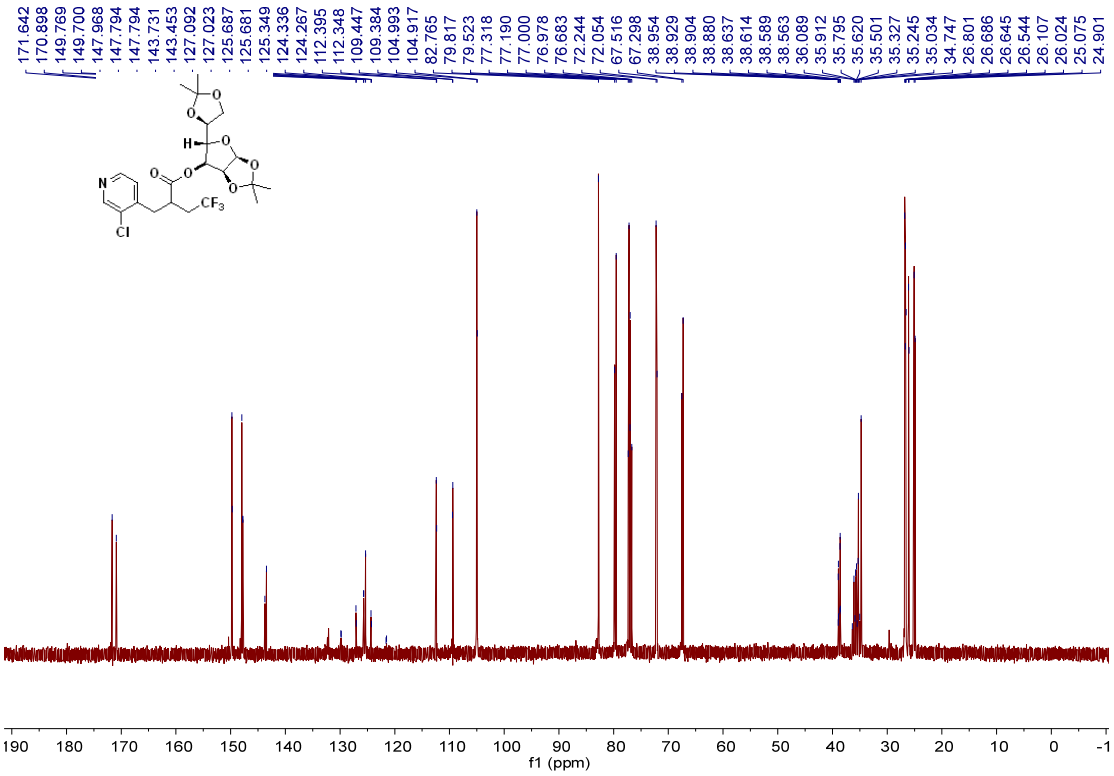

8.474
8.303
8.292
7.977
7.934
7.912
7.432
7.410
7.260
7.153
7.141
4.357
4.340
4.322
4.304
3.110
3.104
3.088
3.024
3.014
3.009
3.001
2.992
2.987
2.977
2.971
2.965
2.955
2.919
2.893
2.882
2.867
2.856
2.844
2.830
2.818
2.807
2.781
2.368
2.359
2.342
2.332
2.315
2.305
2.295
2.278
2.268
2.251
2.242
1.381
1.363
1.345
1.01
1.00
3.17
2.12
1.03
2.18
2.15
1.19
1.17
1.16
3.22
f1 (ppm)

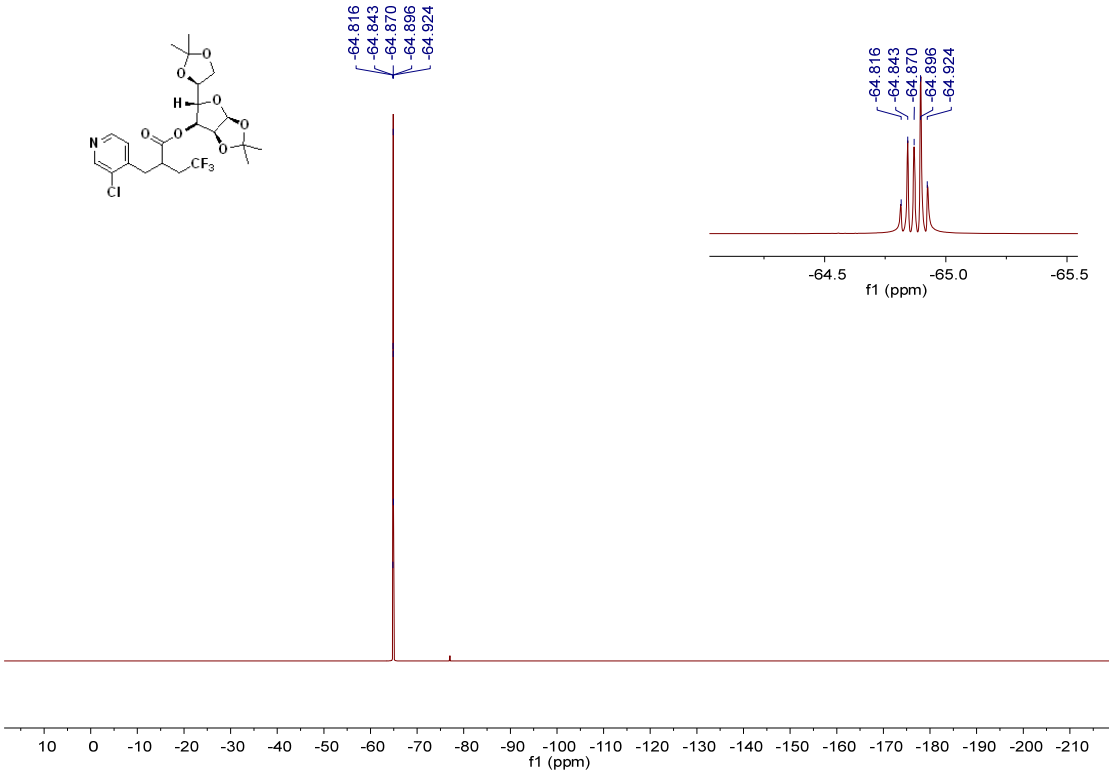

170.267
166.038
149.457
147.883
144.351
141.012
131.987
130.660
130.072
127.320
126.597
125.940
124.567
121.815
119.359
77.318
77.001
76.684
60.991
41.364
41.339
36.778
36.486
36.197
36.124
35.907
14.270
f1 (ppm)



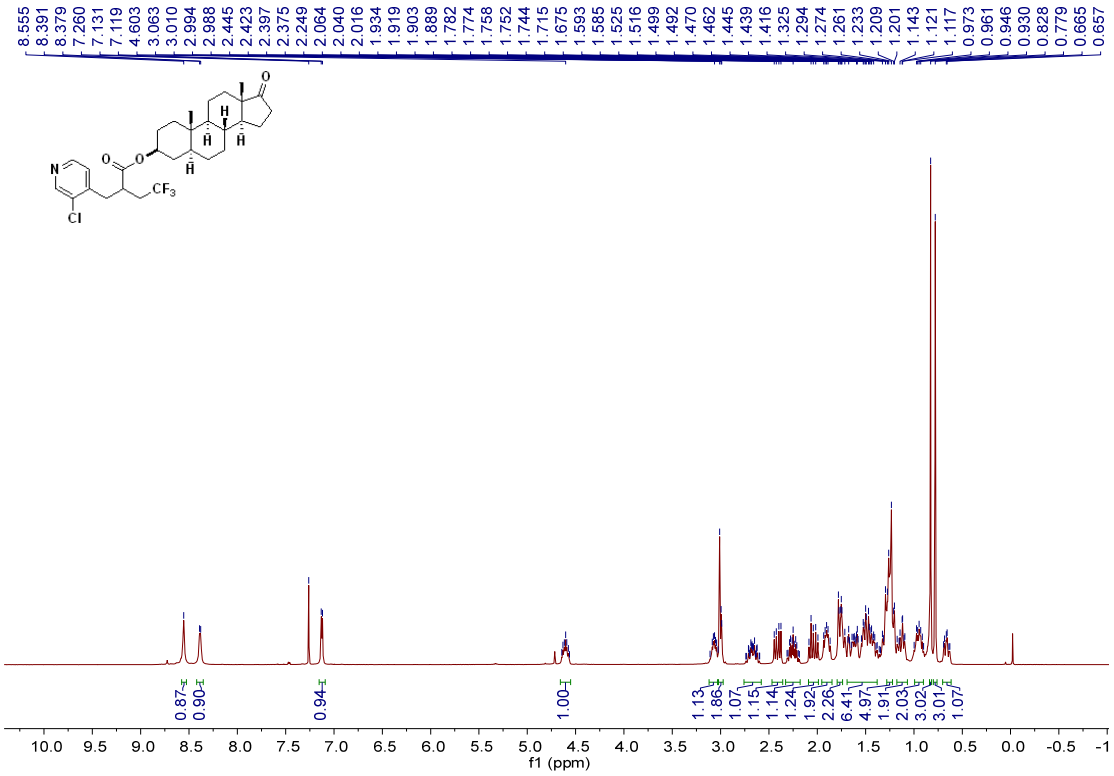
NMR Spectra of product **67**:

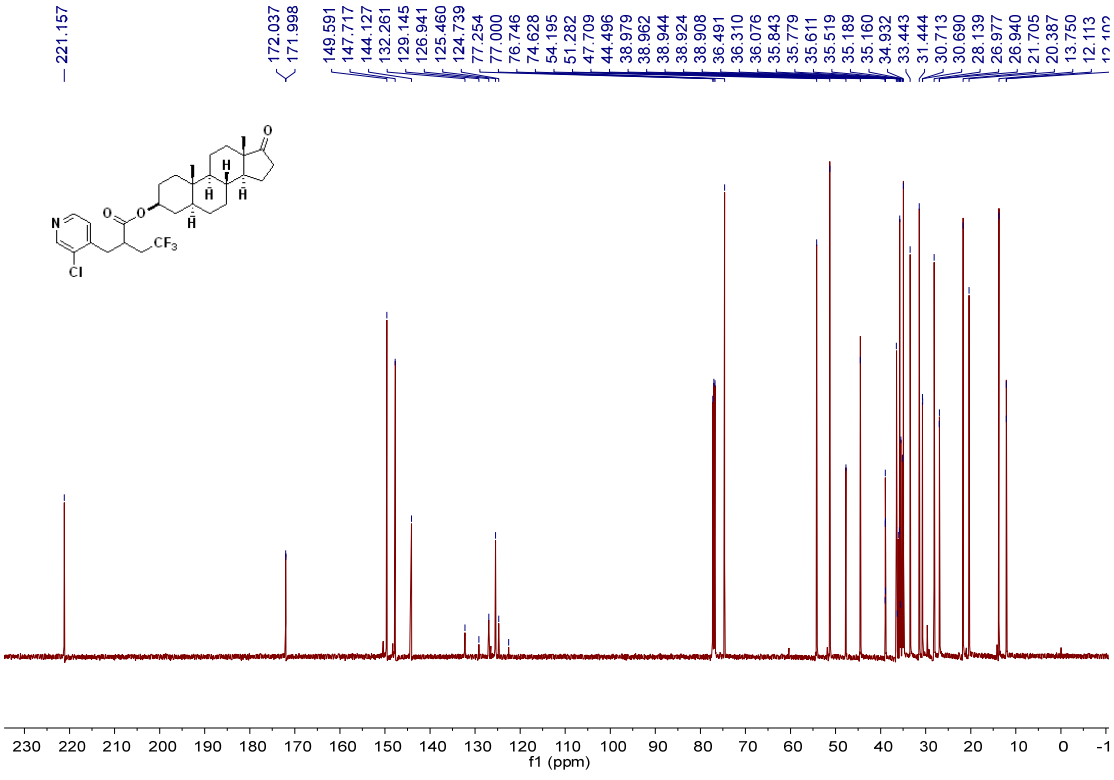


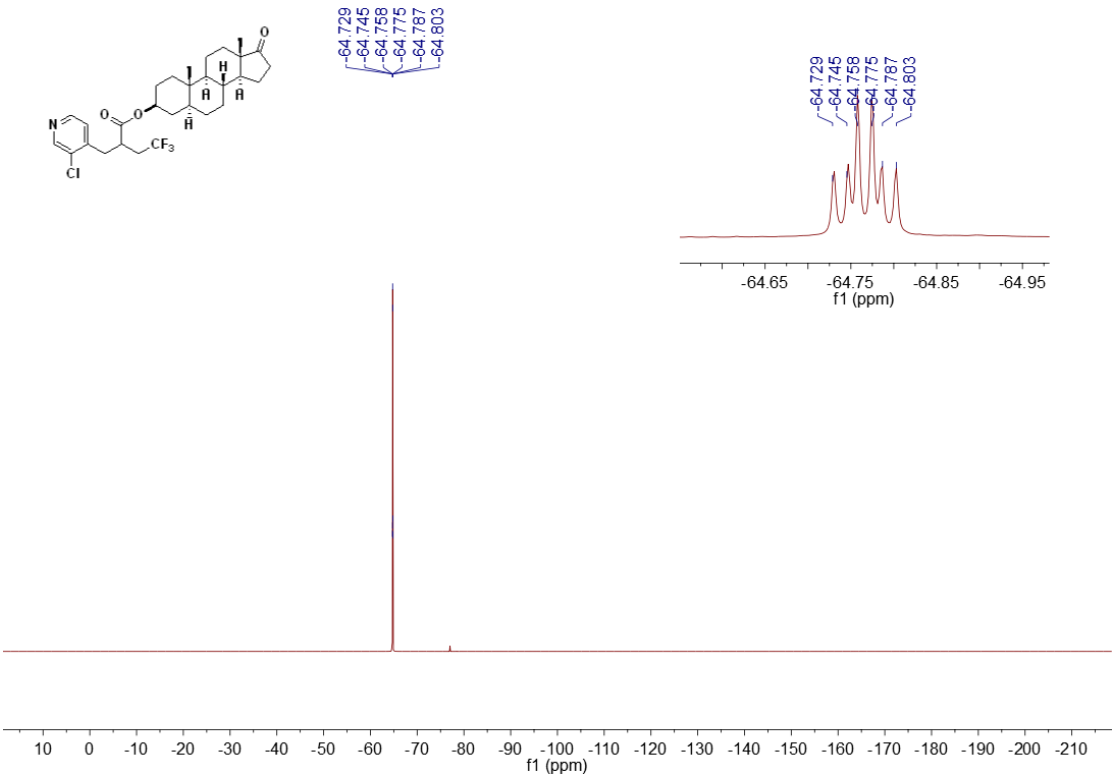




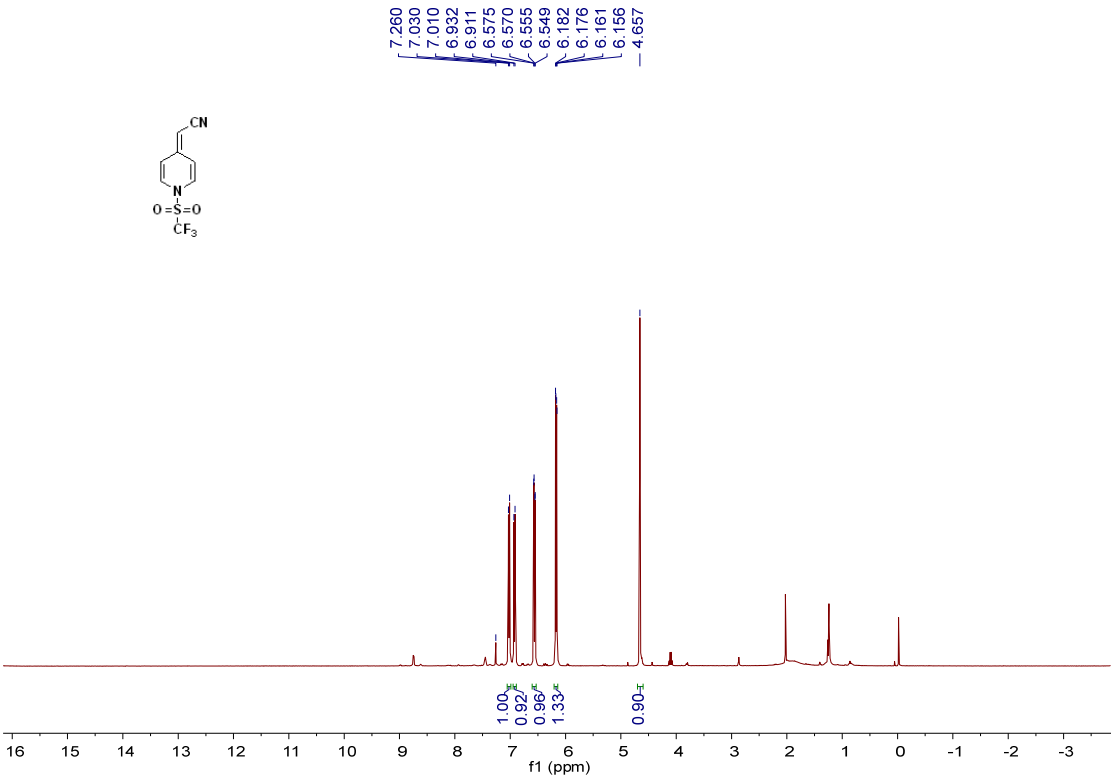
NMR Spectra of product **68**:

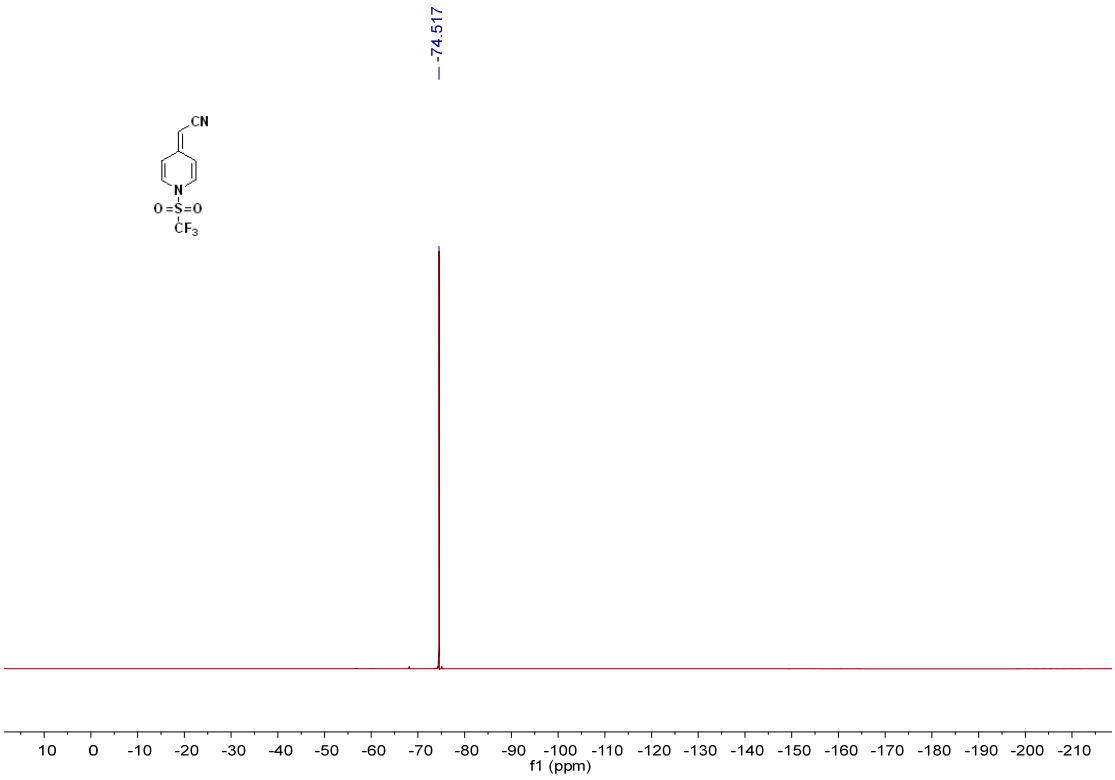

8.555
8.391
8.379
7.260
7.131
7.119
4.603
3.063
3.010
2.994
2.988
2.445
2.423
2.397
2.375
2.249
2.064
2.040
2.016
1.934
1.919
1.903
1.889
1.782
1.774
1.758
1.752
1.744
1.715
1.675
1.593
1.585
1.525
1.516
1.499
1.492
1.470
1.462
1.445
1.439
1.416
1.325
1.294
1.274
1.261
1.233
1.209
1.201
1.143
1.121
1.117
0.973
0.961
0.946
0.930
0.828
0.779
0.665
0.657
O
H
H
H
O
O
H
N
CF3
Cl
0.87
0.90
0.94
1.00
1.13
1.86
1.07
1.15
1.14
1.24
1.92
2.26
6.41
4.97
1.91
2.03
3.02
3.01
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

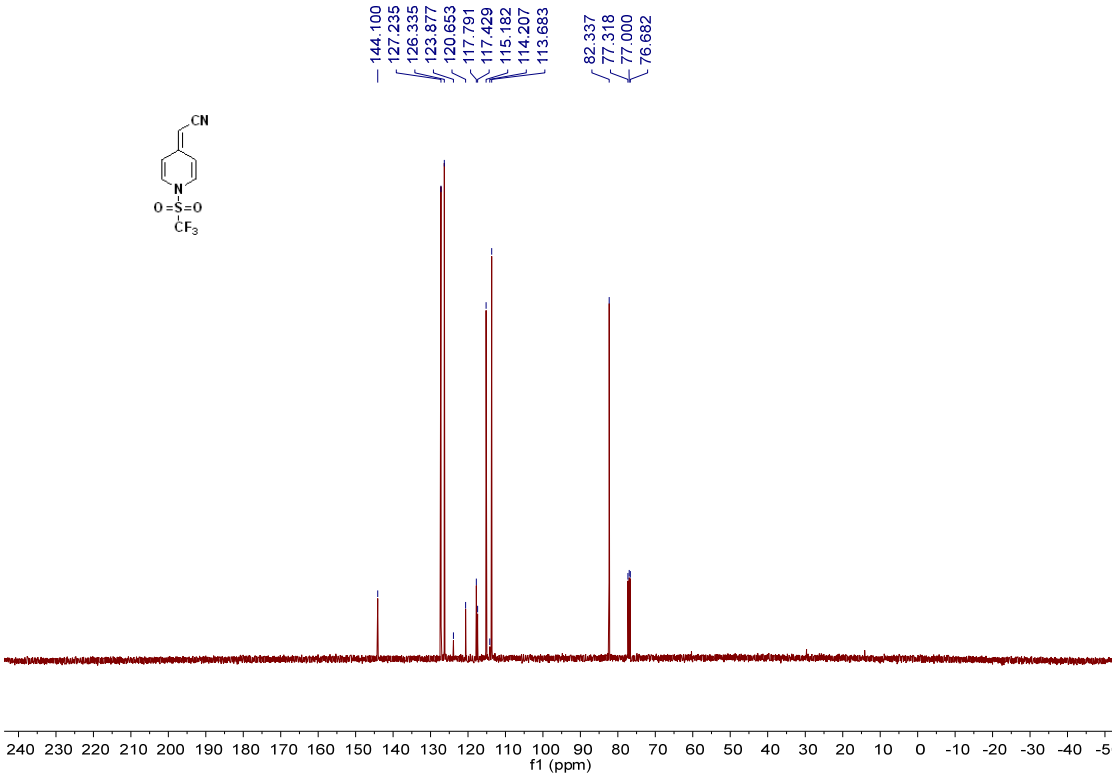

221.157
172.037
171.998
149.591
147.717
144.127
132.261
129.145
126.941
125.460
124.739
77.254
77.000
76.746
74.628
54.195
51.282
47.709
44.496
38.979
38.962
38.944
38.924
38.908
36.491
36.310
36.076
35.843
35.779
35.611
35.519
35.189
35.160
34.932
33.443
31.444
30.713
30.690
28.139
26.977
26.940
21.705
20.387
13.750
12.113
O
H
H
H
O
O
H
N
CF3
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



NMR Spectra of product **72**:




-74.517
CN
N
O=S=O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


144.100
127.235
126.335
123.877
120.653
117.791
117.429
115.182
114.207
113.683
82.337
77.318
77.000
76.682
CN
N
O=S=O
CF3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
f1 (ppm)