Precise Electro-Reduction of Alkyl Halides for Radical Defluorinative Alkylation

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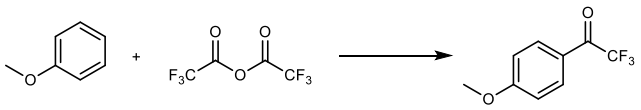
I. **General information**

Unless otherwise stated, analytical grade solvents and commercially available reagents were used without further purification. All solvents were analytical reagent or better and were degassed prior to use. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). The anode electrode was carbon rod and the cathode electrode was carbon rod. Cyclic voltammograms were obtained on a CHI 605E potentiostat. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60~90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. Gas chromatographic analyses were performed on SHIMADZU GC-2014 gas chromatography instrument with a FID detector and biphenyl was added as internal standard. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C). All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and Thermo Fisher Scientific LTQ FT Ultra.

II. The preparation of substrates

1. The synthesis of α-(trifluoromethyl)styrenes

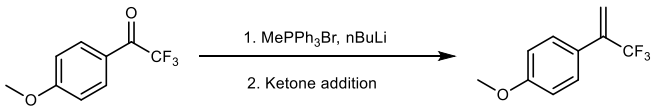
1) Method A



Scheme S1. The synthesis of 4'-methoxy-2,2,2-trifluoroacetophenone.

Step 1: The compounds were prepared according to a previously described procedure. [1]

To a solution mixture of anisole (20.0 g, 185 mmol) and dimethylaminopyridine (21.5 g, 176 mmol) in dry CH_2Cl_2 (20 mL), diluted trifluoroacetic anhydride (24.4 mL, 176 mmol) in dry CH_2Cl_2 (5 mL) was injected dropwise at 0 °C under a nitrogen atmosphere. Then, $AlCl_3$ (57.5 g, 431 mmol) was added to the mixture in 5 times under nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 13 h. The reaction mixture was poured into ice water, extracted with CH_2Cl_2, washed with brine, and the combined organic layers were dried over with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by distillation (93 °C, 11 torr).

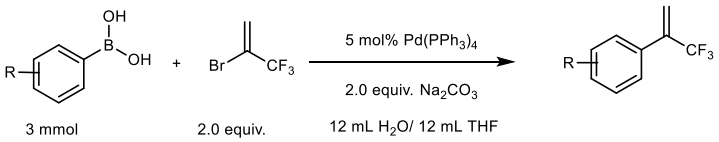


Scheme S2. The synthesis of 4'-Methoxy-2,2,2-trifluorostyrene.

Step 2: The compounds were prepared according to a previously described procedure.

A Schlenk flask was charged with THF (25 mL) and Ph_3PMeBr (8.9 g, 25 mmol, 1.25 equiv.). After cooling to 0 °C, *n*-BuLi (9.6 mL, 24 mmol, 1.2 equiv.) was added dropwise and the resulting yellow solution was stirred for 30 min. Next 20 mL THF was added to the Schlenk flask. Then the mixture was cooled to -78 °C, the *p*-Methoxyphenyl-2,2,2-trifluoroethanone (3 mL, 20 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was allowed to warm to room temperature and was stirred overnight. Saturated NH_4Cl solution was added to quench this reaction. And the organics were extracted with ether (3 x 20 mL). The combined organic layers were dried over with Na_2SO_4, the solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography (SiO_2, specified combination of solvents).

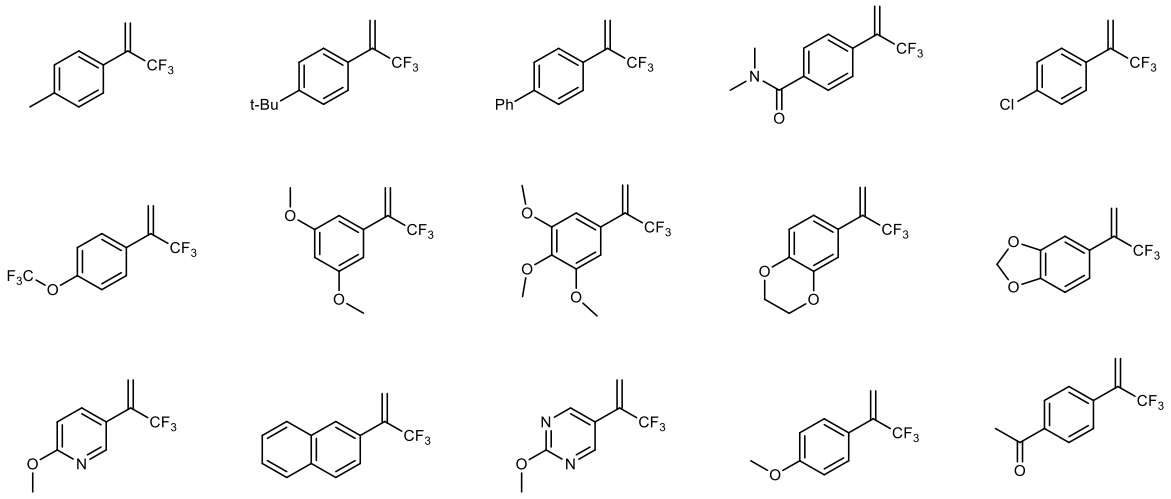
2) Method B[2]



Scheme S3. The synthesis of 2,2,2-trifluorostyrene derivatives.

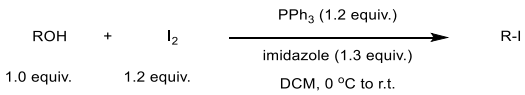
A 100 mL Schlenk flask was charged with a stir bar, arylboronic acid (3mmol), $Pd(PPh_3)_4$ (0.15 mmol, 173.0 mg) and Na_2CO_3 (6 mmol, 636.0 mg) were added into the Schlenk flask, then exchanged with nitrogen atmosphere. THF (12 mL), H_2O (12 mL) and 2-bromo-3,3,3-trifluoro-1-propene（0.7 mL，6 mmol）were added in turn. After stirring 1 h, the mixture was heated to 60 °C for 16 h. Next the mixture was cooled to room temperature. And the organics were extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography (SiO_2, specified combination of solvents).

The following substrates were prepared:



Scheme S4. The preparation of 2,2,2-trifluorostyrene substrates.

2. The synthesis of alkyl iodides



Scheme S5. The synthesis of alkyl iodides.

The alkyl iodides were synthesized according to literature report.[4]

A 100 mL oven-dried round-bottom flask equipped with a stir bar and rubber septum is cooled under a stream of nitrogen. The flask was opened to air, and triphenylphosphine (1.2 equiv.),

imidazole (1.3 equiv.), and DCM (non-anhydrous) were added under air. The rubber septum was replaced, and the flask was purged with nitrogen for 5 min. The flask was then placed in an ice-bath. After 5 min of stirring, the rubber septum was partly removed and iodine (1.2 equiv.) was added under a stream of nitrogen. The rubber septum was replaced and the reaction was stirred for another 15 min. The alcohol was then added. For solid alcohols, the rubber septum was partly removed, the alcohol was added under a stream of nitrogen, and the rubber septum was returned. For liquid alcohols, the alcohol was added via syringe through the rubber septum. The spectral data of the alkyl iodides are consistent with the literature data.[4]

III. Experimental procedures

1) General procedure for reaction operation

Graphical guide for the set-up:

As experiment set-up, two carbon rods (Φ = 5 mm) were fixed on electrode for anode and cathode. An undivided three-necked bottle with stir bar, and a dual display potentiostat (HJS-292B) were used.

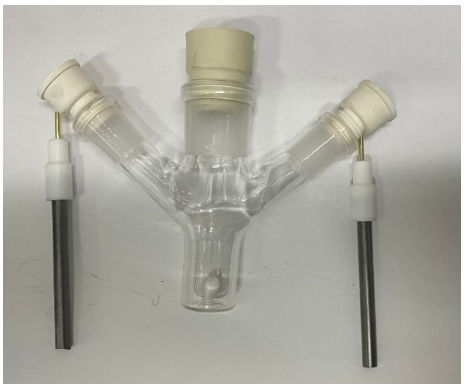


Figure S1. The equipments of this reaction.

General procedure:

Condition A:

For the 1° alkyl iodide derivate. An oven-dried 25 mL undivided three-necked bottle equipped with a stir bar and two carbon rods (Φ = 5 mm) as the anode and the cathode. Et_4NBr (63.0 mg, 0.3 mmol, 1.5 equiv.), DIPEA (0.4 mmol, 2.0 equiv.), Ph_3P (104.8 mg, 0.4 mmol, 2.0 equiv.) were

added into the undivided cell. After the cell was charged with nitrogen. Then the corresponding α-(trifluoromethyl)styrenes (0.2 mmol) and the 1° alkyl iodide derivate (0.8 mmol, 4.0 equiv.) were added. Finally, NMP (for iodoalkanes: 6.0 mL) or DMF (for iodoalkanes: 6.0 mL) was added. If any substrate was liquid, it would be added by using microsyringe before adding the solvent. The reaction mixture was stirred and electrolyzed at a constant current of 4.0 mA at room temperature for 8 h. Products were isolated by purification procedure A.

Condition B:

For the 2° and 3° alkyl iodide derivate. An oven-dried 25 mL undivided three-necked bottle equipped with a stir bar and two carbon rods (Φ = 5 mm) as the anode and the cathode. Et_4NBr (63.0 mg, 0.3 mmol, 1.5 equiv.), DABCO (0.4 mmol, 2.0 equiv.), Ph_3P (104.8 mg, 0.4 mmol, 2.0 equiv.) were added into the undivided cell. After the cell was charged with nitrogen. Then the corresponding α-(trifluoromethyl)styrenes (0.2 mmol) and the iodoalkanes were added. Finally, the NMP (6.0 mL) was added. If any substrate was liquid, it would be added by using microsyringe before adding the solvent. The reaction mixture was stirred and electrolyzed at a constant current of 4.0 mA at room temperature for 6 h. Products were isolated by purification procedure A.

Condition C:

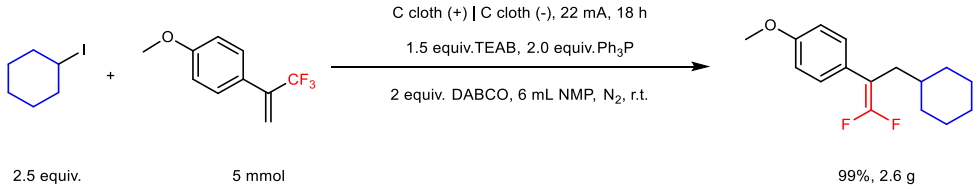
For the brominated alkanes. An oven-dried 25 mL undivided three-necked bottle equipped with a stir bar and two carbon rods (Φ = 5 mm) as the anode and the cathode. Et_4NBr (63.0 mg, 0.3 mmol, 1.5 equiv.), DBU (0.4 mmol, 2.0 equiv.), Ph_3P (262.0 mg, 1 mmol, 5.0 equiv.) were added into the undivided cell. After the cell was charged with nitrogen. Then the corresponding α-(trifluoromethyl)styrenes (0.2 mmol) and the brominated alkanes (0.8 mmol, 4.0 equiv.) were added. Finally, the DMF (6.0 mL) was added. If any substrate was liquid, it would be added by using microsyringe before adding the solvent. The reaction mixture was stirred and electrolyzed at a constant current of 4.0 mA at room temperature for 9 h. Products were isolated by purification procedure A.

Purification procedure A:

The reaction solution successively undergoes oxidation of the remaining Ph_3P by 30% H_2O_2 (aq.). Then $Na_2S_2O_3$ (aq.) was used to reduce iodine or bromine. The reaction was extraction with

saturated brine and dried with anhydrous sodium sulfate. Finally, this reaction was monitored by TLC. Solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

2) The gram-scale experiment



Scheme S6. The gram-scale experiment

An oven-dried 100 mL undivided three-necked bottle equipped with a stir bar and two pieces of carbon cloth (30 mm × 35 mm) as the anode and the cathode. Et_4NBr (7.5 mmol, 1.5 equiv., 1.8 g), DABCO (10 mmol, 2.0 equiv., 1.1 g), Ph_3P (10 mmol, 2.0 equiv., 2.6 g) were added into the undivided cell. And then the cell was charged with N_2. Then the 4'-Methoxy-2,2,2-trifluorostyrene (5.0 mmol, 1.0 g), the iodocyclohexane (12.5 mmol, 2.5 equiv., 2.6 g) were added. Finally, NMP (50.0 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 22.0 mA at room temperature for 18 h. The reaction solution successively undergoes oxidation of the remaining Ph_3P by 30% H_2O_2 (aq.). Then $Na_2S_2O_3$ (aq.) was used to reduce iodine or bromine. The reaction was extraced with saturated brine and dried with anhydrous sodium sulfate. Finally, this reaction was monitored by TLC. Solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. Finally, 2.6 g colorless product was obtained.

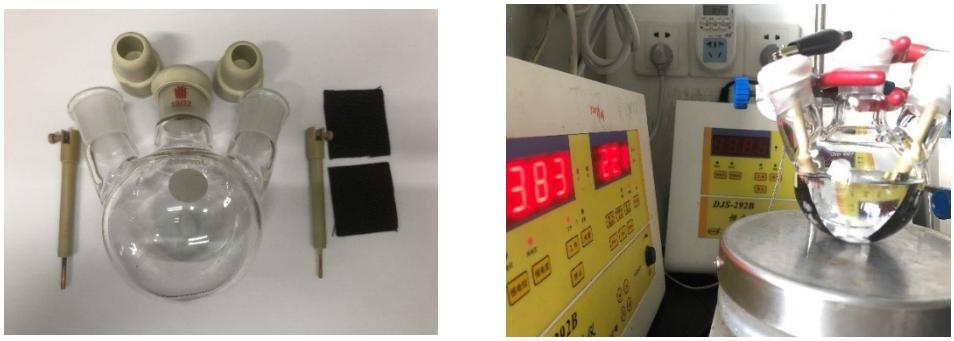
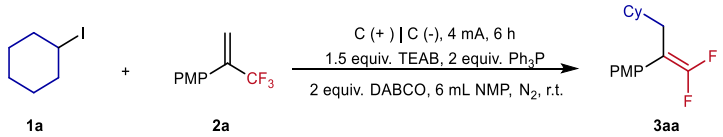


Figure S2. The equipments of the gram-scale experiment.

3) Optimization

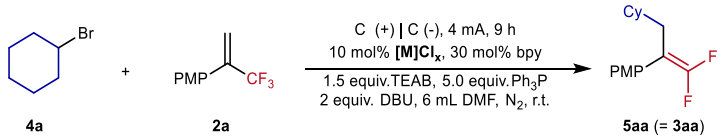
Optimization with alkyl iodide



Entry	Variation from the standard conditions	Yields of 3aa
1	none	98%
2	6 mA, 4 h instead of 4 mA, 6 h	72%
3	DBU instead of DABCO	94%
4	TEA instead of DABCO	97%
5	DIPEA instead of DABCO	71%
6	N(*n*-Bu)$_3$ instead of DABCO	75%
7	No current	N.d.
8	Without PPh_3	47%
9	Without DABCO	68%
10	Without PPh_3, Without DABCO	7%
11	1 equiv. DABCO	83%
12	Under air	47%

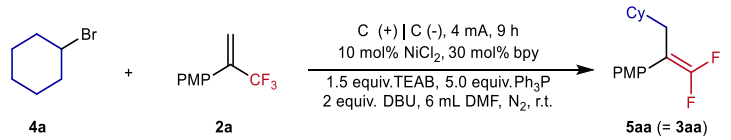
Table S1. Conditions: **2a** (0.2 mmol,), **1a** (0.5 mmol), TEAB (0.3 mmol), PPh_3 (0.4 mmol) and DABCO (0.4 mmol) and NMP (6 mL) were stirred under nitrogen atmosphere with carbon rod (Φ= 5 mm) anode and carbon rod (Φ= 5 mm) cathode at a constant current of 4.0 mA in an undivided cell at room temperature for 6 h. Yields were determined by ^{19}F NMR analysis with $PhCF_3$ as the internal standard.

Optimization with Alkyl bromide



Entry	$[M]Cl_x$	Con. of 2a	Yield of **5aa**
1	$CoCl_2$	89%	47%
2	$MnCl_2$	84%	33%
3	$FeCl_2$	78%	24%
4	$CeCl_3$	72%	24%
5	$CrCl_3$	78%	19%
6	$CuCl_2$	91%	32%
7	$Ni(bpy)_3Cl_2$	96%	90%

Table S2. Reaction results of alkyl bromides with different transition metal catalysts. Conditions: carbon rod electrode (Φ = 5 mm) as the anode and the cathode, **2a** (0.2 mmol), **4a** (0.8 mmol), TEAB (0.3 mmol), PPh_3 (1.0 mmol), metal chloride (0.02 mmol), 2,2'-bipyridine (0.06 mmol) and DBU (0.4 mmol) and DMF (6 mL) were stirred under nitrogen atmosphere with carbon rod (Φ= 5 mm) anode and carbon rod (Φ= 5 mm) cathode at a constant current of 4.0 mA in an undivided cell at room temperature for 9 h. Yields were determined by ^{19}F NMR analysis with $PhCF_3$ as the internal standard.

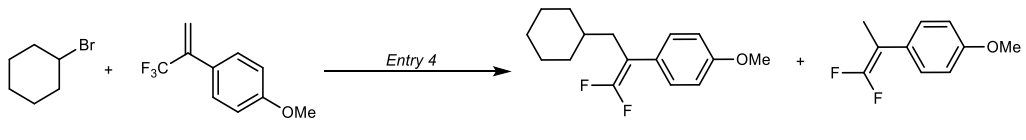


4a **2a** **5aa** (= **3aa**)

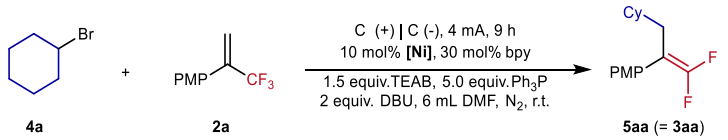
Entry	Variation from the standard conditions	Con. of 2a	Yield of **5aa**
1	Without current	7%	N.d.
2	Without $NiCl_2$	44%	26%
3	Without bpy	96%	39%
4	Without $NiCl_2$ & bpy	99%	36%
5	Without PPh_3	63%	42%
6	Without DBU	80%	24%

Table S3. Conditions: carbon rod electrode (Φ = 5 mm) as the anode and the cathode, **2a** (0.2 mmol), **4a** (0.8 mmol), TEAB (0.3 mmol), PPh_3 (1.0 mmol), metal chloride (0.02 mmol), 2,2'-bipyridine (0.06 mmol) and DBU (0.4 mmol) and DMF (6 mL) were stirred under nitrogen atmosphere with carbon rod (Φ= 5 mm) anode and carbon rod (Φ= 5 mm) cathode at a constant current of 4.0 mA in an undivided cell at room temperature for 9 h. Yield was determined by ^{19}F NMR analysis with $PhCF_3$ as the internal standard.

In entry 4, an obvious side reaction in this condition is defluorhydrogen of alkenes.



36% 55%



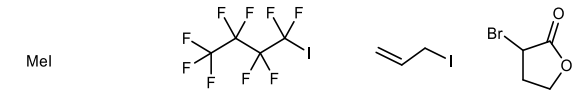
4a **2a** **5aa (= 3aa)**

Entry	[Ni]	Con. of 2a	Yield of **5aa**
1	NiF_2	66%	40%
2	$NiCl_2$	93%	82%
3	$NiBr_2$	87%	67%
4	$Ni(acac)_2$	99%	78%
5	$NiCl_2$·DME	93%	73%
6	$Ni(OTf)_2$	76%	64%
7	$Ni(OAc)_2$	100%	77%
8	$Ni(Ph_3P)_2Cl_2$	53%	30%
9	$NiClO_4 \cdot 6\ H_2O$	82%	61%
10	$Ni(bpy)_3Cl_2$	96%	90%

Table S4. Conditions: **2a** (0.2 mmol), **4a** (0.8 mmol), TEAB (0.3 mmol), Ph_3P (1.0 mmol), metal chloride (0.02 mmol), 2,2'-bipyridine (0.06 mmol) and DBU (0.4 mmol) and DMF (6 mL) were stirred under nitrogen atmosphere with carbon rod (Φ= 5 mm) anode and carbon rod (Φ= 5 mm) cathode at a constant current of 4.0 mA in an undivided cell at room temperature for 9 h. Yield was determined by ^{19}F NMR analysis with $PhCF_3$ as the internal standard.

4) Limitations of scope

With the respect to the limitations, this method has thus far not proven successful with iodomethane, perfluorobutyl iodide, allyl iodide and 3-bromodihydrofuran-2(3H)-one. Efforts to address these limitations are currently ongoing.



1%(trace) 10% N.d. N.d.

5) General procedure for cyclic voltammetry (CV)

General procedure for cyclic voltammetry (CV): Cyclic voltammetry experiment was performed in a three-electrode cell connected to an undivided three-necked bottle with stir bar under nitrogen at room temperature. The working electrode was a glass carbon electrode, the

counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. After adding 1.0 mmol TEAB, 0.1 mmol substrates, exchange the air into N_2, then liquid substrates were added, finally anhydrous degassed 10 mL NMP or DMF were injected into the electrochemical cell in all experiments. The scan rate was ranged from 10 mV/s to 100 mV/s, voltage range was 0 V ~ (-4 V). Data was analyzed using Origin by subtracting a background current prior to identifying the maximum current (Cp) and determining the potential (Ep) at this value (Cp). The obtained value was referenced to Ag/AgCl and converted to SCE by subtracting 0.03 V. A reduction peak of TEAB, NMP were not observed.

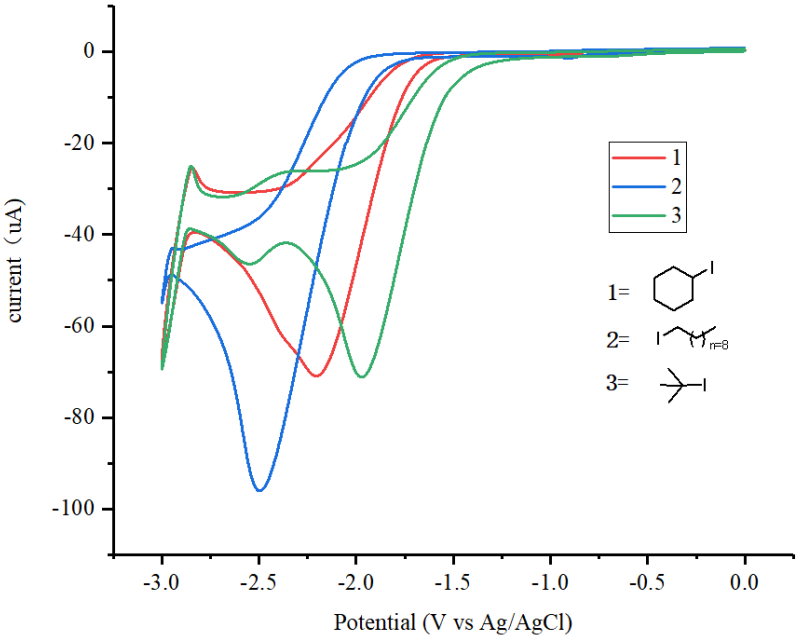


Figure S3. Cyclic voltammetry of Alkyl iodides in NMP. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of NMP containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Red line**: **1a** (CyI) (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). Ep = -2.26 V (*vs* Ag/AgCl). **Blue line**: $C_{10}H_{21}I$ (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). Ep = -2.47 V (*vs* Ag/AgCl). **Green line**: *t*-BuI (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). Ep = -2.05 V, -2.54V (*vs* Ag/AgCl).

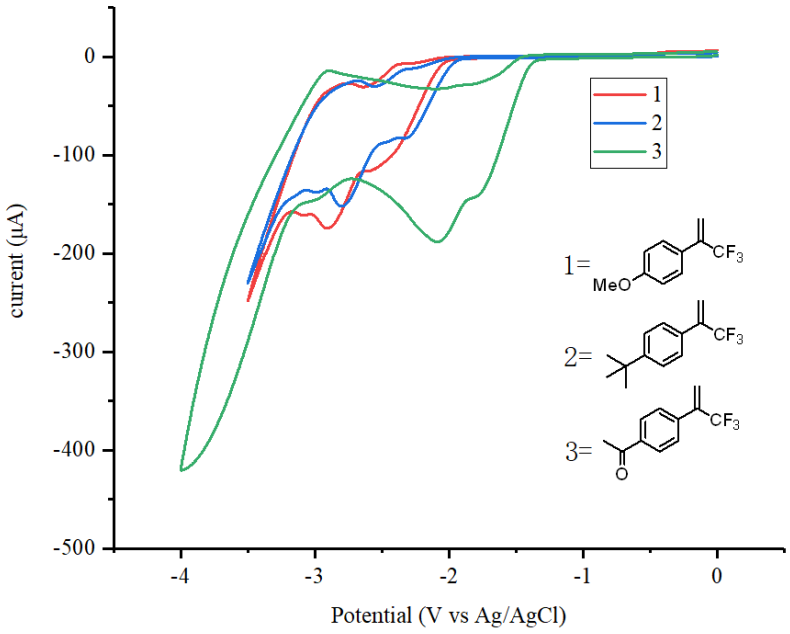


Figure S4. Cyclic voltammetry of alkenes in NMP. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of NMP containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Red line**: **2a** (1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene) (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). The reduction peaks of **red line** were observed at -2.55 V, -2.91 V (*vs* Ag/AgCl). **Blue line**: 1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). The reduction peaks of **blue line** were observed at -2.26 V, -2.79 V (*vs* Ag/AgCl). **Green line**: 1-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethan-1-one (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). The reduction peaks of **green line** were observed at -1.72 V, -2.07 V (*vs* Ag/AgCl).

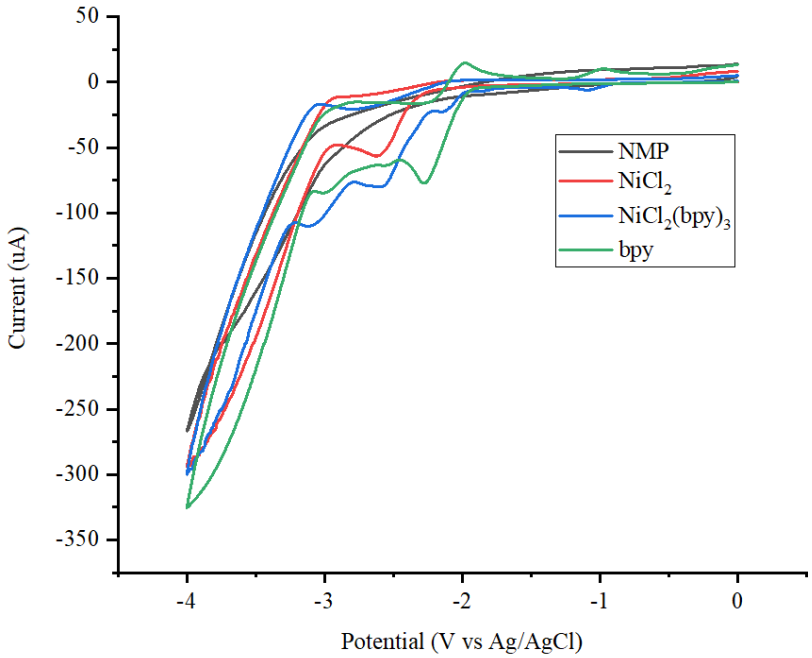


Figure S5. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of NMP containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line:** NMP (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** was not observed. **Red line:** $NiCl_2$ (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). Ep = -2.62 V (*vs* Ag/AgCl). **Blue line:** $NiCl_2(bpy)_3$ (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). The reduction peaks of **blue line** were observed at -1.10 V, -2.14 V, 2.58 V, 3.11 V (*vs* Ag/AgCl). **Green line:** bpy (0.1 mmol), NMP (10 mL), TEAB (1.0 mmol). The reduction peaks of **green line** were observed at -2.26 V, -2.56, -3.00 V (*vs* Ag/AgCl).

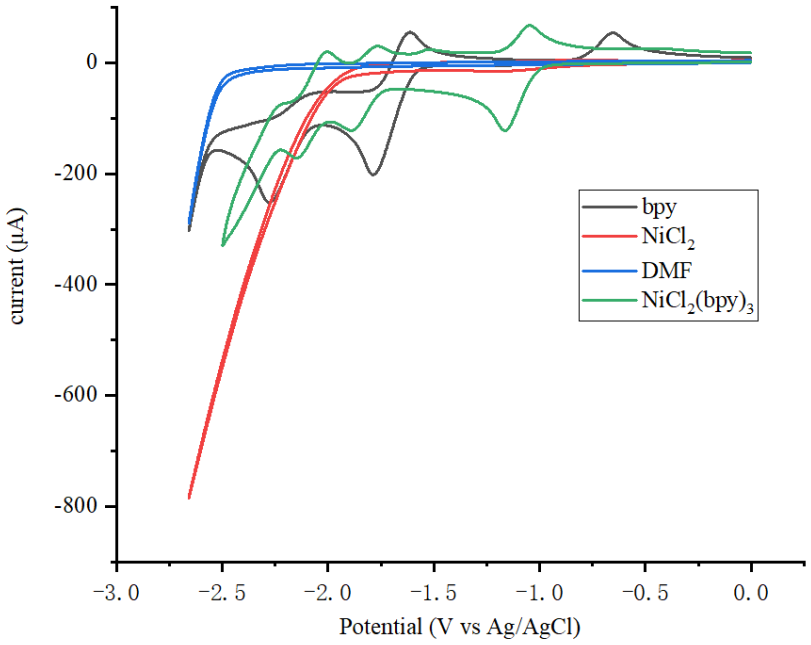


Figure S6. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line:** bpy (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** were observed at -1.79 V, -2.28 V (*vs* Ag/AgCl). **Red line:** $NiCl_2$ (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peak of **red line** was not observed. **Blue line:** DMF (10 mL), TEAB (1.0 mmol). The reduction peak of **blue line** was not observed. **Green line:** $NiCl_2(bpy)_3$ (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **green line** were observed at -1.17 V, -1.90 V, -2.16 V (*vs* Ag/AgCl).

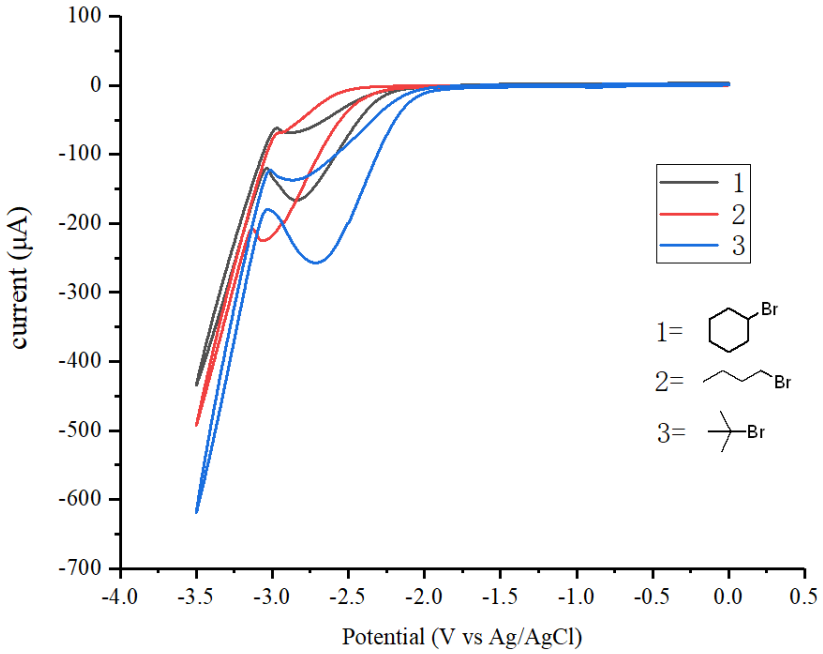


Figure S7. Cyclic voltammetry of Alkyl halides in DMF. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line:** CyBr (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). Ep = -2.62 V (*vs* Ag/AgCl). **Red line:** *n*-BuBr (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). Ep = -3.05 V (*vs* Ag/AgCl). **Blue line:** *t*-BuBr (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). Ep = -2.6 V (*vs* Ag/AgCl).

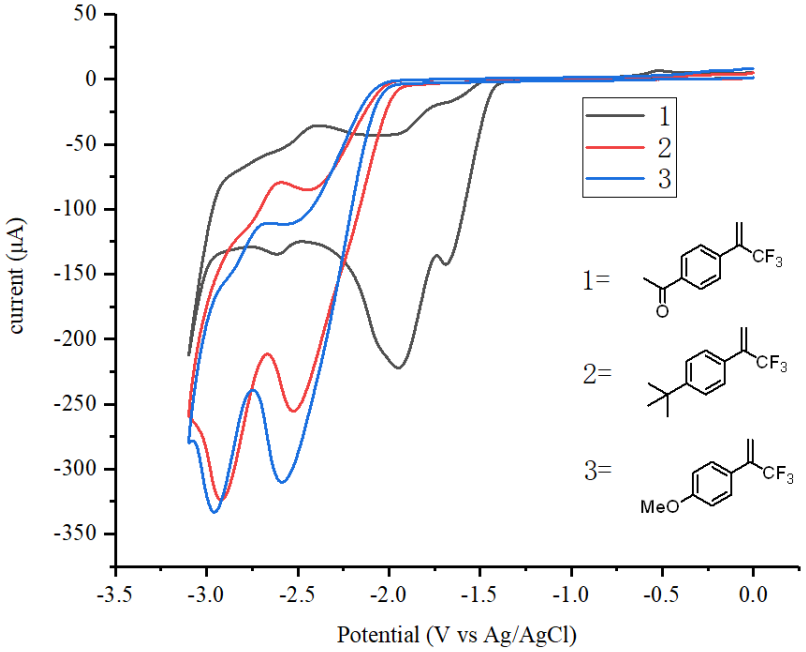


Figure S8. Cyclic voltammetry of alkenes in DMF. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line:** 1-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethan-1-one (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** were observed at -1.69 V, -1.95V (*vs* Ag/AgCl). **Red line:** 1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **red line** were observed at -2.52 V, -2.93 V (*vs* Ag/AgCl). **Blue line: 2a**(1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene) (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **blue line** were observed at -2.59 V, -2.96 V (*vs* Ag/AgCl).

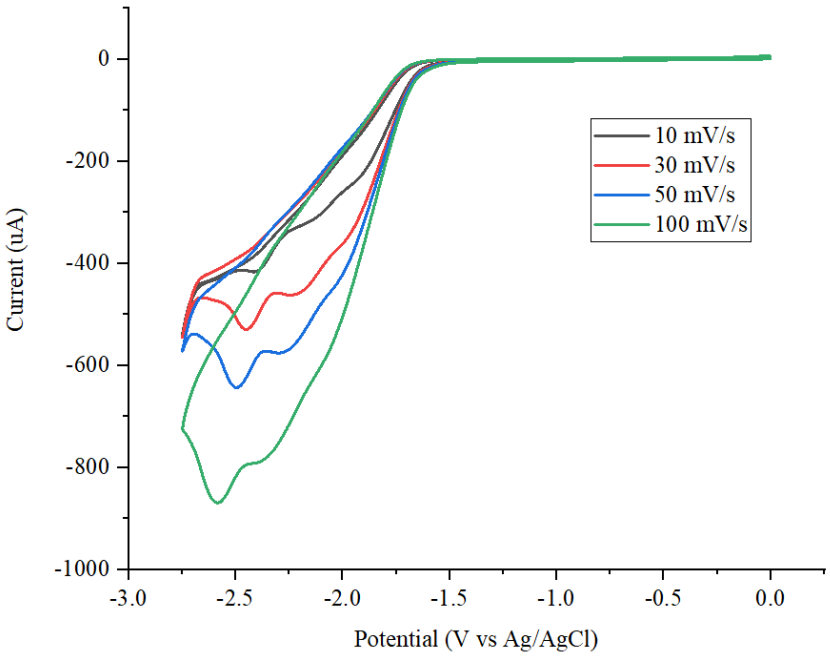


Figure S9. Cyclic voltammetry of **4a** and **2a** at different scan rates. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. **4a** (0.1 mmol), **2a** (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). **Black line:** The scan rate is 10 mV/s. **Red line:** The scan rate is 30 mV/s. **Blue line:** The scan rate is 50 mV/s. **Green line:** The scan rate is 100 mV/s. The reduction peaks of two substrates were observed at -2.38 V, -2.58 V (*vs* Ag/AgCl).

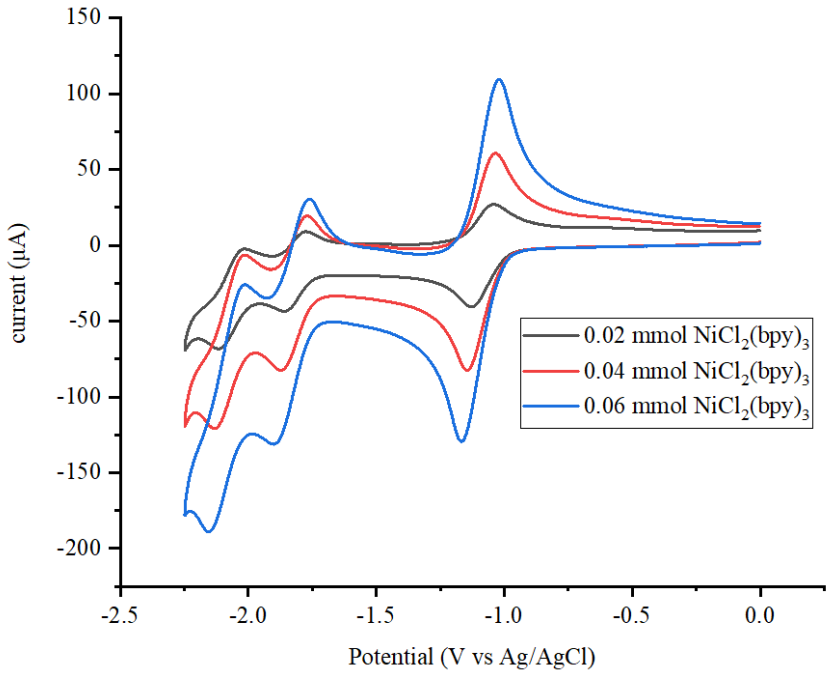


Figure S10. Cyclic voltammetry of $NiCl_2(bpy)_3$ at different concentrations. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. $NiCl_2(bpy)_3$ (x mmol), DMF (10 mL), TEAB (1.0 mmol). The scan rate is 0.1 V/s. **Black line:** $NiCl_2(bpy)_3$ (0.02 mmol). **Red line:** $NiCl_2(bpy)_3$ (0.04 mmol). **Blue line:** $NiCl_2(bpy)_3$ (0.06 mmol). The reduction peaks of $NiCl_2(bpy)_3$ were observed at -1.14 V, -1.87 V, -2.12 V (*vs* Ag/AgCl).

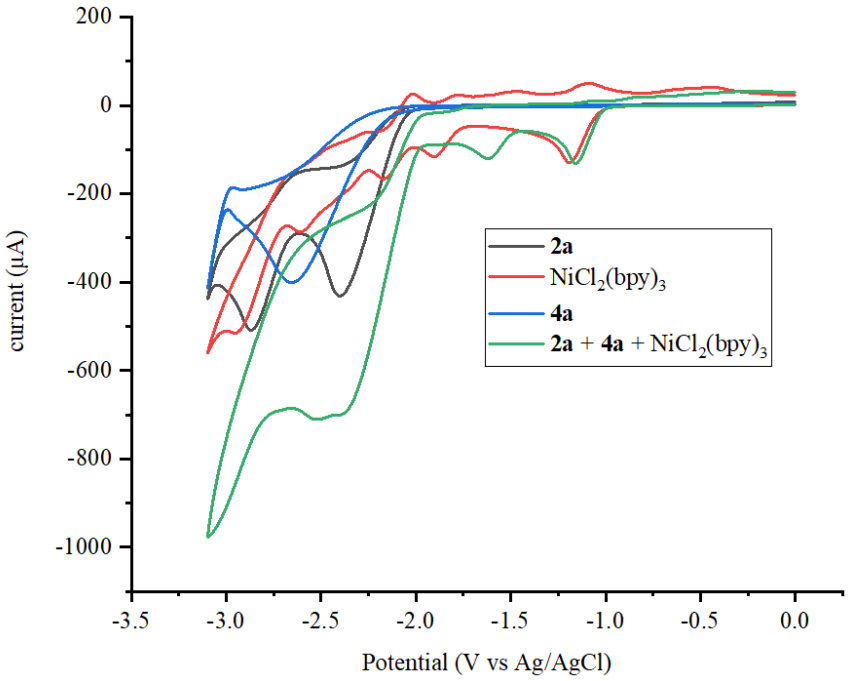


Figure S11. The interaction of alkene and CyBr with $NiCl_2(bpy)_3$. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line: 2a** (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** were observed at -2.40 V, -2.87 V (*vs* Ag/AgCl). **Red line:** $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **red line** were observed at -1.19 V, -1.90 V, -2.17 V, -2.60 V, -2.94 V (*vs* Ag/AgCl). **Blue line: 4a** (0.2 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peak of **blue line** was observed at -2.66 V (*vs* Ag/AgCl). **Green line: 2a** (0.1 mmol), **4a** (0.2 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peak of **green line** were observed at -1.16 V, -1.60 V, -2.38 V, -2.51 V (*vs* Ag/AgCl).

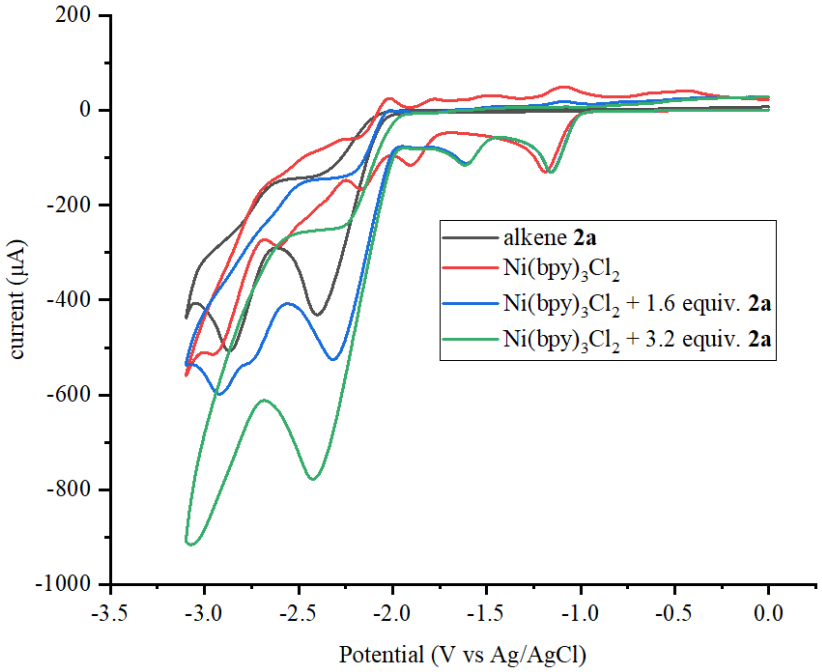


Figure S12. Different concentrations **2a** with $NiCl_2(bpy)_3$ in DMF. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line: 2a** (0.1 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** were observed at -2.40 V, -2.87 V (*vs* Ag/AgCl). **Red line:** $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **red line** were observed at -1.19 V, -1.90 V, -2.17 V, -2.60 V, -2.92 V (*vs* Ag/AgCl). **Blue line: 2a** (0.1 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **blue line** were observed at -1.16 V, -1.60 V, -2.31 V, -2.76 V, -2.92 V (*vs* Ag/AgCl). **Green line: 2a** (0.2 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **green line** were observed at -1.16 V, -1.60 V, -2.43 V, -3.07 V (*vs* Ag/AgCl).

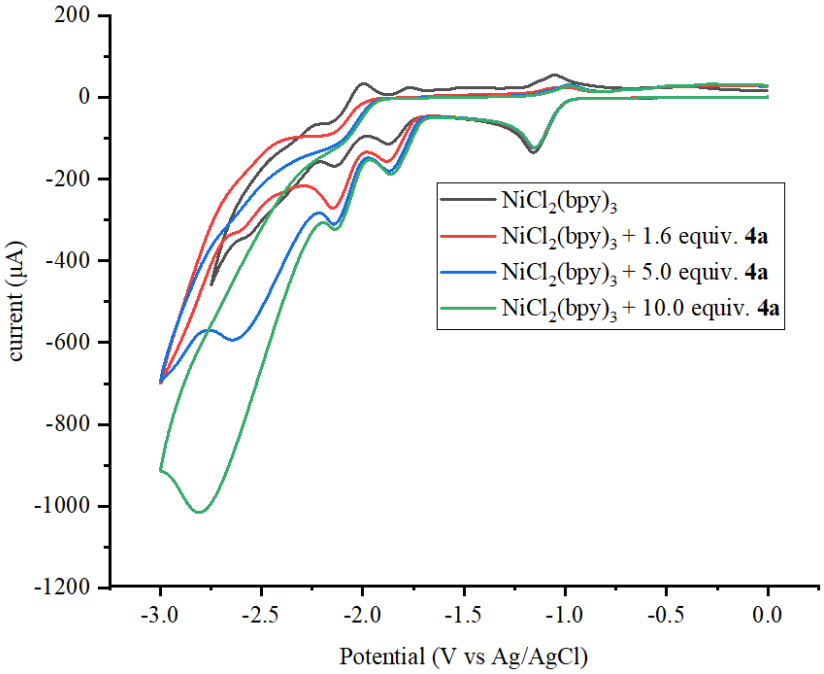


Figure S13. Different concentrations **4a** with $NiCl_2(bpy)_3$ in DMF. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line:** $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** were observed at -1.15 V, -1.87 V, -2.14 V, -2.58 V (*vs* Ag/AgCl). **Red line: 4a** (0.1 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **red line** were observed at -1.15 V, -1.87 V, -2.14 V, -2.62 V (*vs* Ag/AgCl). **Blue line: 4a** (0.3 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **blue line** were observed at -1.15 V, -1.87 V, -2.14 V, -2.64 V (*vs* Ag/AgCl). **Green line: 4a** (0.6 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **green line** were observed at -1.15 V, -1.87 V, -2.14 V, -2.80 V (*vs* Ag/AgCl).

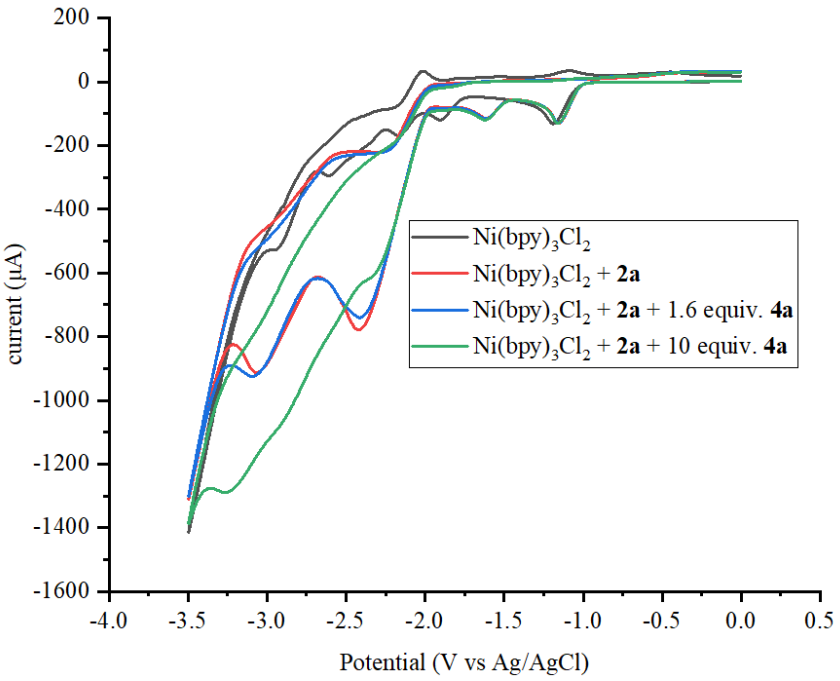


Figure S14. Different concentrations **4a** with $NiCl_2(bpy)_3$ and **2a** in DMF. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. 10 mL of DMF containing 0.1 M TEAB was poured into the electro chemical cell in all experiments. The scan rate is 0.1 V/s. **Black line:** $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **black line** were observed at -1.19 V, -1.90 V, -2.17 V, -2.61 V, -2.94 V (*vs* Ag/AgCl). **Red line: 2a** (0.2 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **red line** were observed at -1.15 V, -1.61 V, -2.42 V, -3.06 V (*vs* Ag/AgCl). **Blue line: 4a** (0.1mmol), **2a** (0.2 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **blue line** were observed at -1.15 V, -1.61 V, -2.41 V, -3.10 V (*vs* Ag/AgCl). **Green line: 4a** (0.6 mmol), **2a** (0.2 mmol), $NiCl_2(bpy)_3$ (0.06 mmol), DMF (10 mL), TEAB (1.0 mmol). The reduction peaks of **green line** were observed at -1.15 V, -1.61 V, -2.32 V, -3.26 V (*vs* Ag/AgCl).

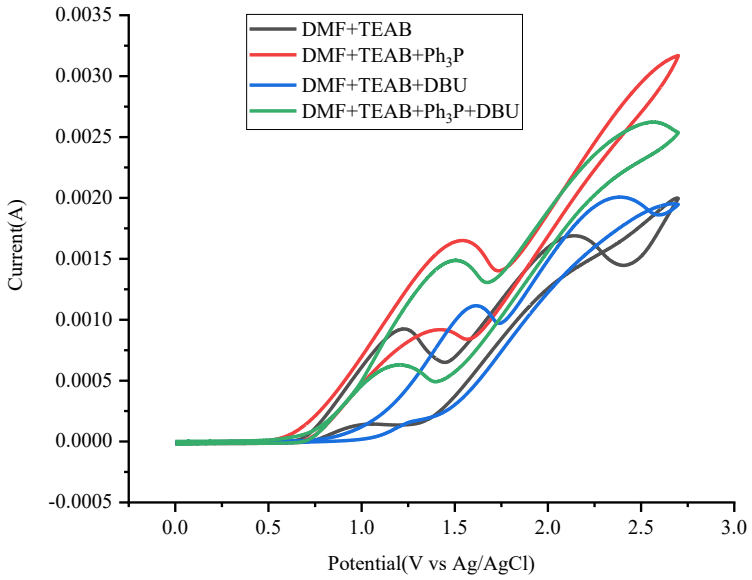


Figure S15. DBU, Ph_3P, TEAB in DMF. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. DBU (0.4 mmol), Ph_3P (0.4 mmol), DMF (10 mL), TEAB (1.0 mmol). The scan rate is 100 mV/s. **Black line**: DMF+TEAB. The peaks potential were observed at 1.22 V, 2.12 V. **Red line**: TEAB+DBU+Ph_3P. The oxidation peak was observed at 1.54 V. **Blue line**: TEAB+DBU. The oxidation peaks were observed at 1.61 V, 2.38 V. **Green line**: TEAB+Ph_3P+DBU. The oxidation peak was observed at 1.50 V (vs Ag/AgCl).

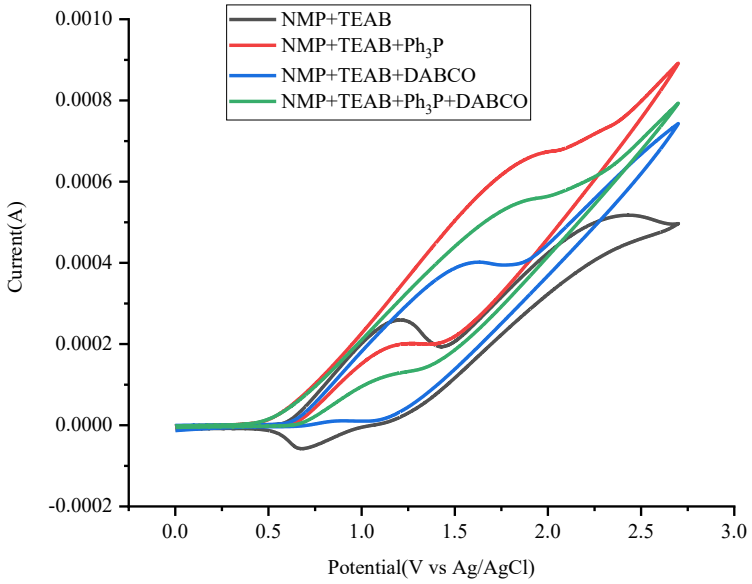
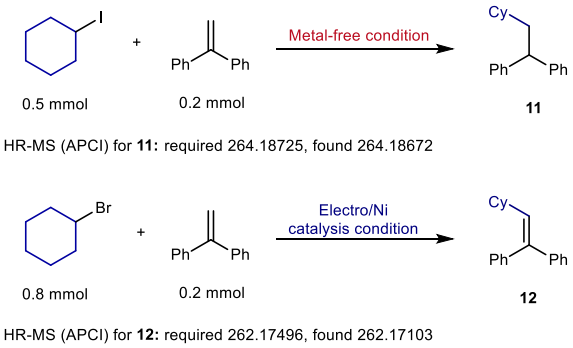


Figure S16. DABCO, Ph_3P, TEAB in NMP. Test conditions: A cyclic voltammograms in solvent (10 mL) by using glassy carbon as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode under N_2 at room temperature. DABCO (0.4 mmol), Ph_3P (0.4 mmol), NMP (10 mL), TEAB (1.0 mmol). The scan rate is 100 mV/s. **Black line**: DMF+TEAB. The peaks potential were observed at 1.20 V, 2.39 V. **Red line**: TEAB+DABCO+Ph_3P. The oxidation peak was observed at 1.95 V. **Blue line**: TEAB+DABCO. The oxidation peak was observed at 1.59 V. **Green line**: TEAB+Ph_3P+DABCO. The oxidation peak was observed at 1.86 V (vs Ag/AgCl).

6) Radical trapping experiment



Scheme S7. Free radical trapping experiment.

Condition of 11:

An oven-dried 25 mL undivided three-necked bottle equipped with a stir bar and two carbon rods (Φ = 5 mm) as the anode and the cathode. Et_4NBr (63.0 mg, 0.3 mmol, 1.5 equiv.), DABCO (0.4 mmol, 2.0 equiv.), Ph_3P (104.8 mg, 0.4 mmol, 2.0 equiv.) were added into the undivided cell. After the cell was charged with nitrogen. Then the 1,2-diphenylethylene (0.2 mmol) and the iodo-cyclohexan (0.5 mmol) were added. Finally, the NMP (6.0 mL) was added. If any substrate was liquid, it would be added by using microsyringe before adding the solvent. The reaction mixture was stirred and electrolyzed at a constant current of 4.0 mA at room temperature for 6 h. The result of the product was detected by HRMS.

Condition of 12:

An oven-dried 25 mL undivided three-necked bottle equipped with a stir bar and two carbon rods (Φ = 5 mm) as the anode and the cathode. Et_4NBr (63.0 mg, 0.3 mmol, 1.5 equiv.), DBU (0.4 mmol, 2.0 equiv.), Ph_3P (262.0 mg, 1.0 mmol, 2.0 equiv.), $NiCl_2(bpy)_3$ (11.9 mg, 0.02 mmol, 10 mol%) were added into the undivided cell. After the cell was charged with nitrogen. Then the 1,2-diphenylethylene (0.2 mmol) and the iodo-cyclohexan (0.5 mmol) were added. Finally, the DMF (6.0 mL) was added. If any substrate was liquid, it would be added by using microsyringe before adding the solvent. The reaction mixture was stirred and electrolyzed at a constant current of 4.0 mA at room temperature for 9 h. The result of the product was detected by HRMS.

7) Data analysis for anode oxidation

Control experiments proved that the addition of PPh_3 is necessary for this transformation. And triphenylphosphine oxide was confirmed by TLC and GC-MS, thereby supporting the oxidation of PPh_3 in the anode. Moreover, the addition of tertiary amines, one type of common reductants, increased the yields obviously. The oxidation of amines is also possible in the anode.[7]

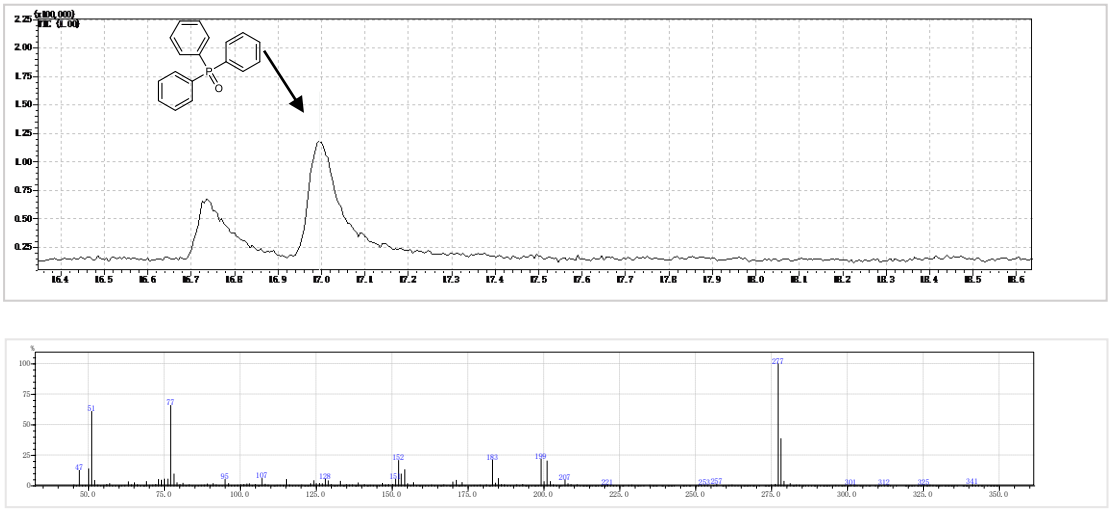
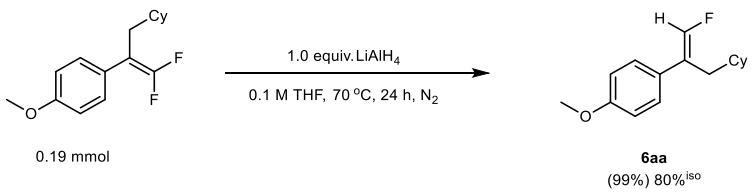


Figure S17. GC-MS data of reaction. **1a** (0.5 mmol), 2a (0.2 mmol), PPh_3 (0.4 mmol), DABCO (0.4 mmol), NMP (6 mL), 4 mA, 6 h, r.t., N_2. After this reaction finished, it was monitored by GC-MS.

8) Application

The product 3aa is a useful organic building block, it can be converted into other compounds.

1) Hydrodefluorination (HDF)[5]



0.19 mmol

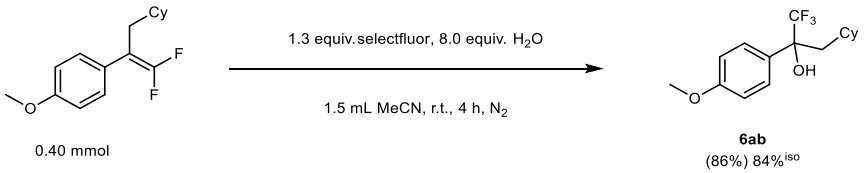
6aa
(99%) 80%^{iso}

Scheme S8. Hydrodefluorination (HDF).

An oven-dried 10 mL Schlenk tube with stir bar. $LiAlH_4$ (0.19 mmol, 1.0 equiv., 24.1 mg), was added into the tube. And then the tube was charged with N_2. Then **3aa** (0.19 mmol, 79.8 mg) was added. Finally, THF (3.0 mL) were added. The reaction mixture was stirred under 70 °C for 24 h.

$PhCF_3$ (11.0 mg) was added as an internal standard, the reaction was monitored by ^{19}F NMR. After recall the NMR sample, they were combined. Solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether as the eluent. Eventually, obtained as a colorless liquid, 37.5 mg HDF product (99% ^{19}FNMR yield, 80% isolated yield, r.r. = 95:5) was got.

2) Fluoro-hydroxylation of gem-difluoroalkenes [6]



Scheme S9. Fluoro-hydroxylation of gem-difluoroalkenes.

An oven-dried 10 mL Schlenk tube with stir bar. Selectfluor (0.5 mmol, 1.3 equiv., 184.2 mg), were added into the tube. And then the tube was charged with N_2. Then **3aa** (0.4 mmol, 106.4 mg), H_2O (8.0 equiv., 3.2 mmol, 57.6 μL). Finally, MeCN (1.5 mL) were added. The reaction mixture was stirred under r.t. for 4 h. $PhCF_3$ (11.0 mg) was added as an internal standard, the reaction was monitored by ^{19}F NMR. After recall the NMR sample, they were combined. Solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether/ EtOAc = 10:1 as the eluent. Eventually, obtained as a colorless liquid, 97.0 mg product (86% ^{19}FNMR yield, 84% isolated yield) was obtained.

IV. Density functional theory (DFT) studies

Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[7] Geometries were optimized using the B3LYP functional[8] and Grimme's D3(BJ) dispersion correction[9] with a mixed basis set of LANL2DZ for Ni and 6-31G(d) for other atoms. Vibrational frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. Solvation energy corrections were calculated in *N*, *N*-dimethylformamide solvent with the SMD continuum solvation model[10] based on the gas-phase

optimized geometries. The M06-L functional[11] with a mixed basis set of SDD for Ni and 6-311+G(d,p) for other atoms were used for single-point energy calculations.

Identifying the spin state of Ni(II) species

In this study, the electron configuration of Ni(II) is d^8 so both the singlet state and the triplet state of the Ni(II) species exists. The computational studies of the triplet and singlet state structures along the *β*-fluoride elimination pathway demonstrate that the singlet intermediates and transition state all have higher energies than the corresponding triplet structures. This conclusion is consistent with previous studies that this type of four-coordinated 16e Ni(II) complex prefers to be triplet.[12] Therefore, the *β*-fluoride elimination prefers to undergo the triplet free energy profile.

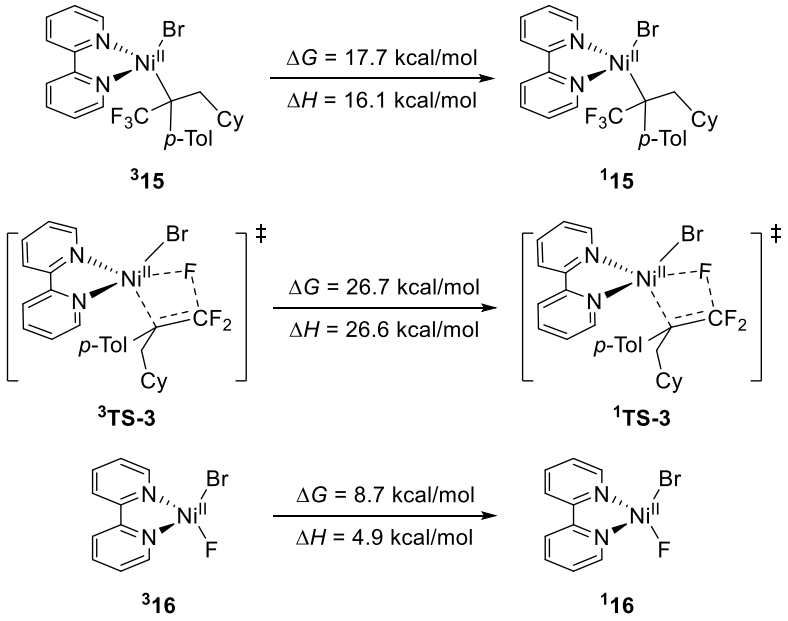


Figure S18. Identifying the spin state of Ni(II) species.

Computational results of the *β*-F elimination from Ni(I) complex

DFT calculations were also carried out to investigate the *β*-F elimination process from the Ni(I) complex. In this work, the cathodic reduction of alkyl-Ni(II) complex to anionic Ni(I) complex **19** followed by *β*-F elimination might be an alternative pathway for the formation of defluorinative coupling product. However, the computational results show that the energy barrier with respect to **19** is 11.5 kcal/mol (**Figure S19**), which is 3.5 kcal/mol higher than that of the same process from Ni(II) complex ^{3}**15**. The higher electron density at the anionic Ni(I) center might attribute to the higher energy barrier. Therefore, this possibility is disfavored than the *β*-F elimination from ^{3}**15**.

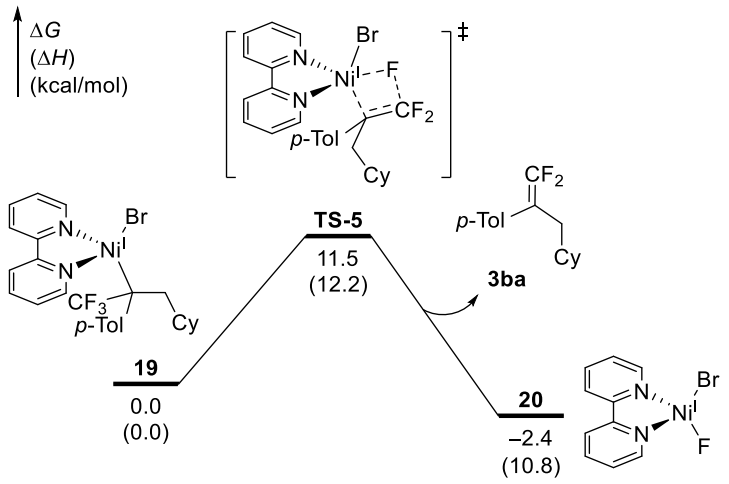


Figure S19. Calculated energy profiles of the *β*-F elimination process of the Ni(I) species **19**.

Identifying the most stable Ni(0) complex

To identify the most stable Ni(0) complex, DFT calculations were performed to investigate the dissociation of bpy ligand and alkene. The computational results show that the formation of Ni(0) complex **13** is favored over that of **22**, which manifests the higher tendency of the dissociation of bipyridine from **21**. These results are consistent with the CV experiments that *α*-trifluoromethylstyrene is coordinated to the nickel catalyst.

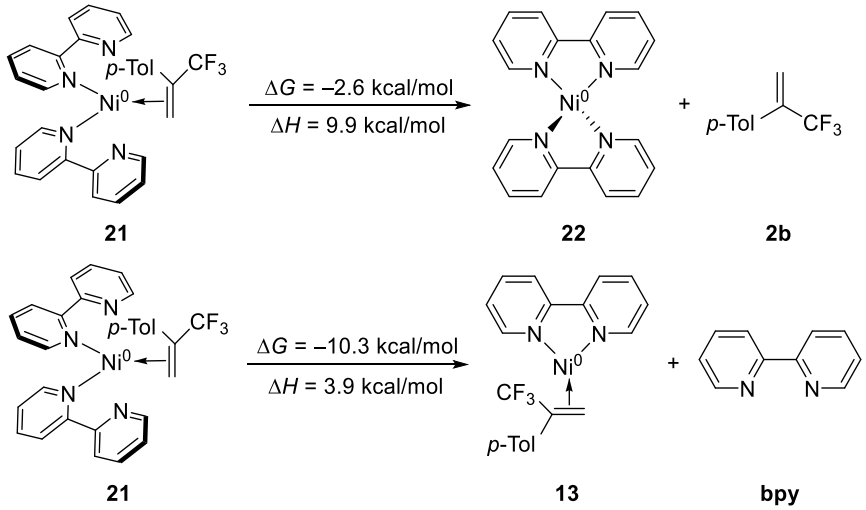


Figure S20. Identifying the most stable Ni(0) complex.

Giese radical addition to the alkene

Furthermore, we investigated the Giese radical addition between **4aR** and the alkene **2b**. The computational results show that the overall energy barrier is 17.1 kcal/mol compared with **13** and **4a**, which is 3.5 kcal/mol higher than that of the outer-sphere

radical addition mechanism. The coordination of alkene **2b** toward nickel bromide **17** is responsible for this higher energy barrier. Therefore, although the radical trapping of **2bR** by **17** is exergonic, this reaction pathway is less preferred due to the disfavored Giese addition step.

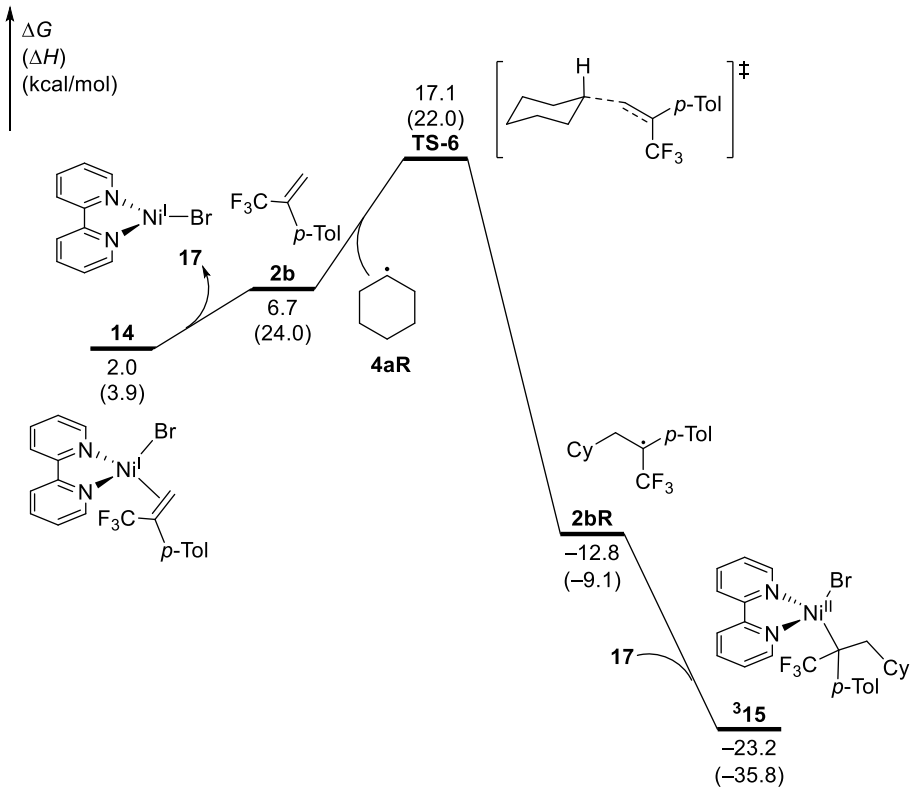


Fig. S21 Calculated energy profiles of the Giese radical addition process between **4aR** and **2b**. All energies are with respect to the energies of **13** and **4a**

Cartesian coordinates (Å) and energies of optimized structures

2b

B3LYP SCF energy: -686.03209580 a.u.

B3LYP enthalpy: -685.852349 a.u.

B3LYP free energy: -685.904772 a.u.

M06-L SCF energy in solution: -686.10972680 a.u.

M06-L enthalpy in solution: -685.929980 a.u.

M06-L free energy in solution: -685.982403 a.u.

Cartesian coordinates

ATOM X Y Z

C	-2.470675	1.120958	-0.324213
C	-1.109121	1.396493	-0.254774
C	-0.189322	0.406781	0.127471
C	-0.683486	-0.875972	0.413627
C	-2.047445	-1.144351	0.338394
C	-2.967401	-0.153836	-0.024198
H	-3.158900	1.904232	-0.632440
H	-0.747935	2.383044	-0.528717
H	-0.002152	-1.665827	0.705440
H	-2.404142	-2.145533	0.567360
C	1.252600	0.735826	0.220528
C	1.721981	1.933467	0.590205
H	1.048500	2.727579	0.894290
H	2.783679	2.147220	0.607491
C	2.239529	-0.351664	-0.133950
C	-4.446704	-0.444631	-0.075799
H	-4.639927	-1.497322	-0.306479
H	-4.925390	-0.228659	0.888668
H	-4.948960	0.167857	-0.831923
F	3.500474	0.109326	-0.258776
F	2.273926	-1.322362	0.817747
F	1.913988	-0.957076	-1.295354

2bR

B3LYP SCF energy: -921.33024321 a.u.

B3LYP enthalpy: -920.981459 a.u.

B3LYP free energy: -921.049057 a.u.

M06-L SCF energy in solution: -921.40851738 a.u.

M06-L enthalpy in solution: -921.059733 a.u.

M06-L free energy in solution: -921.127331 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.692361	-1.995443	-0.500938
C	1.557508	-1.244721	-0.764979
C	1.439634	0.106284	-0.332710
C	2.553659	0.641513	0.379320
C	3.678485	-0.122738	0.633139
C	3.778351	-1.458251	0.205616
H	2.741828	-3.023755	-0.850724
H	0.746434	-1.704746	-1.316716
H	2.528836	1.664691	0.729047
H	4.507532	0.323069	1.177712
C	0.260459	0.861617	-0.609704
C	-0.930443	0.270027	-1.307359
H	-1.547773	1.069273	-1.726486
H	-0.594516	-0.337945	-2.156430
C	0.157694	2.270333	-0.109596
C	5.000223	-2.282566	0.516166
H	5.920751	-1.710340	0.353555
H	5.004247	-2.605343	1.566101
H	5.044736	-3.182790	-0.104761
F	-1.017316	2.852650	-0.436078
F	0.259617	2.348675	1.248857
F	1.138056	3.073847	-0.601356
C	-1.822151	-0.609981	-0.393760

C	-2.410015	0.181586	0.785495
C	-2.941856	-1.270421	-1.212328
H	-1.189355	-1.407380	0.023760
C	-3.312677	-0.696608	1.661689
H	-2.991851	1.027541	0.391503
H	-1.603823	0.613078	1.388573
C	-3.847080	-2.149482	-0.338929
H	-2.509142	-1.863479	-2.029356
H	-3.547232	-0.481999	-1.684638
C	-4.427393	-1.354608	0.838279
H	-3.740770	-0.099434	2.476175
H	-2.702972	-1.480436	2.134575
H	-4.653289	-2.580322	-0.945638
H	-3.260742	-2.994550	0.050550
H	-5.097822	-0.573816	0.450132
H	-5.038843	-2.007102	1.473859

3ba

B3LYP SCF energy: -821.48758813 a.u.

B3LYP enthalpy: -821.142175 a.u.

B3LYP free energy: -821.206873 a.u.

M06-L SCF energy in solution: -821.54475336 a.u.

M06-L enthalpy in solution: -821.199340 a.u.

M06-L free energy in solution: -821.264038 a.u.

Cartesian coordinates

ATOM X Y Z

C	0.260122	1.061659	-0.372001
C	1.529435	0.309854	-0.239428
C	-0.908549	0.504403	-1.173659
C	0.082436	2.254893	0.200523
C	1.540920	-1.092106	-0.319259
C	2.769564	0.954714	-0.068350
H	-1.229472	1.259796	-1.901839
H	-0.559971	-0.351071	-1.760981
C	-2.139719	0.093637	-0.340143
F	-1.029800	2.979657	0.065674
F	0.942746	2.908513	0.976953
C	2.727909	-1.814154	-0.212795
H	0.612594	-1.633016	-0.457555
C	3.949889	0.227838	0.035226
H	2.813154	2.036232	-0.030008
C	-3.296040	-0.339460	-1.255550
C	-1.839154	-1.008658	0.686583
H	-2.471345	0.982447	0.214902
C	3.955513	-1.171927	-0.028986
H	2.696138	-2.899365	-0.274659
H	4.890274	0.760244	0.158820
C	-4.550031	-0.711766	-0.452617
H	-2.973508	-1.207508	-1.850949
H	-3.527425	0.461305	-1.970210
C	-3.085673	-1.369652	1.505449
H	-1.021923	-0.697878	1.348088
H	-1.492603	-1.908094	0.155019
C	5.239419	-1.951777	0.109921
C	-4.245812	-1.792056	0.594077

H	-5.346204	-1.047920	-1.128458
H	-4.928518	0.186472	0.056492
H	-2.850540	-2.168519	2.219611
H	-3.390893	-0.496230	2.099888
H	5.556626	-2.011920	1.159469
H	5.126483	-2.976593	-0.257954
H	6.056963	-1.479798	-0.446718
H	-3.976366	-2.726375	0.079734
H	-5.141358	-2.008387	1.189721

4a

B3LYP SCF energy: -2806.71528063 a.u.

B3LYP enthalpy: -2806.545497 a.u.

B3LYP free energy: -2806.585563 a.u.

M06-L SCF energy in solution: -2809.32881411 a.u.

M06-L enthalpy in solution: -2809.159030 a.u.

M06-L free energy in solution: -2809.199096 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.646172	1.267018	-0.135043
C	-0.006016	0.000000	0.406598
C	0.646172	-1.267018	-0.135042
C	2.150422	-1.264975	0.192728
C	2.837156	0.000000	-0.338970
C	2.150422	1.264975	0.192728
H	0.157394	-2.152550	0.283428

H	0.006146	0.000000	1.499416
H	0.504063	1.302104	-1.222579
H	0.157395	2.152551	0.283427
H	2.285288	-1.321474	1.282428
H	2.616590	-2.163928	-0.227759
H	3.898860	0.000000	-0.064520
H	2.793884	0.000000	-1.437521
H	2.285288	1.321474	1.282428
H	2.616590	2.163928	-0.227759
H	0.504062	-1.302105	-1.222578
Br	-1.953472	0.000000	-0.037897

4aR

B3LYP SCF energy: -235.23429288 a.u.

B3LYP enthalpy: -235.070823 a.u.

B3LYP free energy: -235.107545 a.u.

M06-L SCF energy in solution: -235.24054524 a.u.

M06-L enthalpy in solution: -235.077075 a.u.

M06-L free energy in solution: -235.113797 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.000012	1.408221	0.272879
C	1.265510	0.711905	-0.245193
C	1.288490	-0.776501	0.158938
C	0.000015	-1.462159	-0.169166
C	-1.288475	-0.776525	0.158934

C	-1.265526	0.711884	-0.245188
H	2.136173	-1.289381	-0.311970
H	1.291189	0.785914	-1.341000
H	2.164097	1.216345	0.131158
H	-0.000010	1.391162	1.373231
H	-0.000022	2.464234	-0.025050
H	-2.136146	-1.289420	-0.311980
H	-1.473213	-0.828152	1.250634
H	-1.291215	0.785900	-1.340994
H	-2.164119	1.216303	0.131174
H	1.473223	-0.828119	1.250639
H	0.000024	-2.525738	-0.393070

13

B3LYP SCF energy: -1350.84231186 a.u.

B3LYP enthalpy: -1350.489979 a.u.

B3LYP free energy: -1350.569233 a.u.

M06-L SCF energy in solution: -1352.62923191 a.u.

M06-L enthalpy in solution: -1352.276899 a.u.

M06-L free energy in solution: -1352.356153 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.612203	-0.796368	0.195401
N	2.493243	-0.505952	0.767443
C	3.199246	-1.298466	1.588948
C	3.097541	0.579869	0.217728

C	4.532530	-1.055446	1.906160
H	2.658740	-2.146723	1.993482
C	4.433617	0.882068	0.490631
C	5.160002	0.056665	1.345157
H	5.060863	-1.724837	2.576439
H	4.904939	1.746342	0.037236
H	6.199576	0.278004	1.565772
N	0.997152	0.858190	-0.875571
C	2.230640	1.383194	-0.672764
C	0.123758	1.510394	-1.657225
C	2.611545	2.591607	-1.260021
H	-0.842034	1.035053	-1.777830
C	1.702932	3.267109	-2.071825
H	3.596981	3.006646	-1.082080
H	1.980550	4.209020	-2.534734
C	0.437045	2.718703	-2.274696
H	-0.299653	3.213256	-2.898467
C	-2.191435	-0.434550	0.523977
C	-3.295484	-0.011596	-0.237675
C	-1.999660	0.207280	1.766551
C	-1.218232	-1.465632	0.059576
C	-4.150339	0.993287	0.218380
H	-3.505877	-0.471208	-1.194518
C	-2.857151	1.203950	2.214587
H	-1.148514	-0.068554	2.380242
C	-0.403453	-2.224958	0.991521
C	-1.489857	-2.099378	-1.269121
C	-3.955154	1.622252	1.449200
H	-4.994397	1.287276	-0.402229

H	-2.667505	1.672884	3.178268
H	-0.625012	-2.148099	2.055889
H	-0.087154	-3.222113	0.689322
F	-0.530938	-2.983546	-1.635223
F	-2.670379	-2.779437	-1.322619
F	-1.560059	-1.182425	-2.288880
C	-4.890571	2.696018	1.948554
H	-5.500413	2.339635	2.789474
H	-4.341186	3.576838	2.303123
H	-5.577088	3.023662	1.160946

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B3LYP SCF energy: -3922.31745231 a.u.

B3LYP enthalpy: -3921.961328 a.u.

B3LYP free energy: -3922.046862 a.u.

M06-L SCF energy in solution: -3926.70881888 a.u.

M06-L enthalpy in solution: -3926.352695 a.u.

M06-L free energy in solution: -3926.438229 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.445704	-0.956612	-0.089704
N	2.289678	-0.055101	-0.038088
C	3.356504	-0.459298	-0.734081
C	2.406444	0.964863	0.839508
C	4.606094	0.137716	-0.599752
H	3.189759	-1.289162	-1.412252

C	3.630782	1.612824	1.028145
C	4.740258	1.195635	0.298652
H	5.447001	-0.221084	-1.182839
H	3.721344	2.424490	1.740026
H	5.698312	1.687565	0.435241
N	0.119051	0.498006	1.338180
C	1.167965	1.312708	1.573189
C	-1.048534	0.719574	1.949748
C	1.058532	2.396083	2.449089
H	-1.847339	0.026461	1.710153
C	-0.158509	2.631272	3.084539
H	1.901711	3.052854	2.627737
H	-0.263517	3.470561	3.765191
C	-1.233257	1.780277	2.833307
H	-2.197805	1.930506	3.305583
C	-1.861621	0.040369	-1.246793
C	-2.435912	1.319915	-1.137640
C	-2.592361	-1.042507	-0.715863
C	-0.495153	-0.180793	-1.791765
C	-3.676589	1.501272	-0.531921
H	-1.915429	2.188160	-1.518875
C	-3.829336	-0.848027	-0.108645
H	-2.177104	-2.043569	-0.728650
C	0.016435	-1.452687	-2.068144
C	0.238374	1.008573	-2.355588
C	-4.401022	0.426307	-0.005334
H	-4.088268	2.505720	-0.465966
H	-4.354954	-1.707569	0.299880
H	-0.605069	-2.337233	-2.020923

H	0.932412	-1.551669	-2.637644
F	1.467005	0.691300	-2.823472
F	-0.437609	1.566481	-3.391461
F	0.421647	2.007580	-1.448722
C	-5.755140	0.626392	0.628271
H	-6.561191	0.471895	-0.101372
H	-5.922182	-0.080779	1.447934
H	-5.866227	1.641223	1.024719
Br	0.288703	-3.057561	1.021785

15-sing

B3LYP SCF energy: -4157.60955728 a.u.

B3LYP enthalpy: -4157.083022 a.u.

B3LYP free energy: -4157.179730 a.u.

M06-L SCF energy in solution: -4161.99385298 a.u.

M06-L enthalpy in solution: -4161.467318 a.u.

M06-L free energy in solution: -4161.564026 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	-1.213186	0.008501	-1.354346
C	-0.956128	1.056435	-2.146138
C	-2.321817	-0.730607	-1.596041
C	-1.792905	1.441884	-3.188797
H	-0.051673	1.602224	-1.929151
C	-3.214600	-0.398669	-2.617612
C	-2.951698	0.706620	-3.420947

H	-1.533398	2.302088	-3.795630
H	-4.091851	-1.008650	-2.796291
H	-3.633549	0.977577	-4.220900
N	-1.387380	-2.220206	0.001908
C	-2.476498	-1.919962	-0.740399
C	-1.410348	-3.302086	0.792535
C	-3.634411	-2.699140	-0.689227
H	-0.494083	-3.482647	1.344572
C	-3.659354	-3.819182	0.137893
H	-4.506446	-2.430370	-1.273544
H	-4.551557	-4.435056	0.196182
C	-2.526456	-4.130551	0.886353
H	-2.499910	-4.996339	1.539021
Ni	-0.013288	-0.699717	0.151603
Br	1.648337	-2.094984	1.023578
C	0.704040	1.058336	0.816706
C	-0.611686	1.818966	0.858141
C	1.812055	1.728969	-0.021817
C	1.205882	0.963962	2.259531
C	-0.803063	3.063009	0.241996
C	-1.741169	1.237193	1.473759
H	1.371394	2.237885	-0.885385
H	2.255024	2.537516	0.578802
C	2.939093	0.823029	-0.551412
F	2.481748	0.548797	2.375923
F	1.179006	2.200170	2.848736
F	0.446458	0.167108	3.052591
C	-2.063513	3.661032	0.179495
H	0.038369	3.586765	-0.197240

C	-2.995301	1.830934	1.404656
H	-1.631348	0.295381	1.999960
C	2.530964	0.087871	-1.836881
C	4.223142	1.629112	-0.801260
H	3.160067	0.064243	0.202409
C	-3.187837	3.050570	0.739163
H	-2.169935	4.625198	-0.312983
H	-3.842852	1.340242	1.878909
C	3.650924	-0.827589	-2.341316
H	2.286356	0.831390	-2.614453
H	1.625933	-0.504719	-1.657356
C	5.359716	0.732643	-1.311528
H	4.527834	2.132194	0.125747
H	4.021541	2.422832	-1.538932
C	-4.557716	3.675151	0.641707
C	4.947711	-0.040262	-2.571948
H	3.342390	-1.333592	-3.265489
H	3.819168	-1.611843	-1.591125
H	6.258545	1.331325	-1.507803
H	5.624224	0.015037	-0.521963
H	-5.220041	3.088968	-0.009208
H	-5.042920	3.732781	1.623326
H	-4.505690	4.689234	0.232906
H	4.794329	0.672283	-3.396773
H	5.755240	-0.714173	-2.885596

15-trip

B3LYP SCF energy: -4157.63425537 a.u.

B3LYP enthalpy: -4157.108106 a.u.

B3LYP free energy: -4157.207264 a.u.

M06-L SCF energy in solution: -4162.01915802 a.u.

M06-L enthalpy in solution: -4161.493009 a.u.

M06-L free energy in solution: -4161.592167 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	2.276157	0.941845	0.097958
C	2.251968	2.276797	0.173425
C	3.225844	0.319369	-0.634585
C	3.188594	3.070186	-0.484700
H	1.456227	2.707557	0.770376
C	4.196961	1.052124	-1.318788
C	4.175333	2.443552	-1.242233
H	3.133374	4.149937	-0.404317
H	4.956145	0.550972	-1.907111
H	4.921514	3.028030	-1.771560
N	2.128217	-1.683303	0.068795
C	3.140570	-1.159533	-0.652954
C	1.952153	-3.005959	0.130395
C	4.020236	-1.988898	-1.352728
H	1.122793	-3.340239	0.744375
C	3.837433	-3.368497	-1.297945
H	4.833009	-1.570028	-1.933813
H	4.510239	-4.026975	-1.838476
C	2.788059	-3.891622	-0.543019
H	2.617516	-4.960169	-0.474567

Ni	0.891435	-0.318538	0.935562
Br	0.435375	-0.989820	3.162475
C	-0.730492	-0.141479	-0.366636
C	-0.884897	1.327361	-0.189567
C	-1.808898	-1.043422	0.258123
C	-0.372286	-0.593761	-1.745863
C	-1.189210	1.841222	1.094016
C	-0.634960	2.279316	-1.202891
H	-1.399596	-2.053804	0.370068
H	-2.004893	-0.701459	1.277207
C	-3.158836	-1.163954	-0.485538
F	-0.221970	-1.944001	-1.811675
F	-1.299075	-0.283219	-2.708714
F	0.798212	-0.064721	-2.220276
C	-1.222986	3.210617	1.344092
H	-1.366809	1.157555	1.917229
C	-0.685863	3.646128	-0.943958
H	-0.402389	1.952149	-2.207534
C	-4.075434	-2.131338	0.283734
C	-3.863624	0.185369	-0.695150
H	-2.974054	-1.600526	-1.476699
C	-0.976265	4.146802	0.331515
H	-1.447580	3.556051	2.350688
H	-0.493569	4.342677	-1.757560
C	-5.438174	-2.305373	-0.398664
H	-4.227349	-1.741133	1.301615
H	-3.578722	-3.104397	0.395529
C	-5.229028	0.015752	-1.375478
H	-3.232488	0.849364	-1.292102

H	-3.997394	0.675673	0.280700
C	-1.054819	5.629809	0.596997
C	-6.132451	-0.952569	-0.601792
H	-6.074180	-2.978206	0.190773
H	-5.293164	-2.786209	-1.377341
H	-5.719052	0.991851	-1.483352
H	-5.075421	-0.371786	-2.393518
H	-0.426638	6.196276	-0.099255
H	-2.081727	6.002544	0.482791
H	-0.736178	5.872280	1.616821
H	-6.368482	-0.518380	0.381033
H	-7.088127	-1.087156	-1.124514

16-sing

B3LYP SCF energy: -3336.09941006 a.u.

B3LYP enthalpy: -3335.920013 a.u.

B3LYP free energy: -3335.974897 a.u.

M06-L SCF energy in solution: -3340.45702944 a.u.

M06-L enthalpy in solution: -3340.277632 a.u.

M06-L free energy in solution: -3340.332516 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	0.149389	1.159579	-0.000302
C	1.021764	2.178476	-0.000242
C	-1.184018	1.425886	-0.000071
C	0.606380	3.508184	0.000117

H	2.065622	1.882831	-0.000511
C	-1.664514	2.734652	0.000379
C	-0.756870	3.791216	0.000476
H	1.348671	4.298586	0.000139
H	-2.731279	2.925097	0.000712
H	-1.112743	4.816779	0.000849
N	-1.345022	-0.929143	0.000015
C	-2.040680	0.228434	-0.000164
C	-1.973202	-2.110156	0.000109
C	-3.435839	0.222674	-0.000422
H	-1.298974	-2.960574	0.000396
C	-4.101842	-1.001990	-0.000321
H	-3.993380	1.151930	-0.000720
H	-5.187104	-1.028559	-0.000496
C	-3.363640	-2.185508	0.000026
H	-3.851671	-3.153800	0.000204
Ni	0.595689	-0.774553	-0.000005
Br	2.899311	-0.512239	-0.000153
F	0.703319	-2.520079	0.000844

16-trip

B3LYP SCF energy: -3336.09880488 a.u.

B3LYP enthalpy: -3335.920156 a.u.

B3LYP free energy: -3335.981085 a.u.

M06-L SCF energy in solution: -3340.46411935 a.u.

M06-L enthalpy in solution: -3340.285470 a.u.

M06-L free energy in solution: -3340.346399 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	1.305905	-0.889300	0.001018
C	2.026770	-2.010139	-0.077602
C	1.879854	0.314930	-0.184137
C	3.380414	-1.985579	-0.406551
H	1.490597	-2.924869	0.149714
C	3.234560	0.417012	-0.509170
C	3.986463	-0.750088	-0.631656
H	3.941547	-2.910923	-0.473466
H	3.700752	1.384984	-0.649802
H	5.040235	-0.691539	-0.885975
N	-0.255297	1.163577	0.478755
C	0.975832	1.472413	0.019054
C	-1.159530	2.127168	0.680464
C	1.332606	2.797113	-0.243458
H	-2.140085	1.791608	0.998899
C	0.400771	3.806320	-0.011770
H	2.314691	3.038285	-0.632530
H	0.660574	4.841658	-0.209294
C	-0.867043	3.470823	0.460482
H	-1.622082	4.227341	0.642348
Ni	-0.669620	-0.870913	0.578561
Br	-2.567160	-0.728016	-0.849387
F	-0.364969	-2.085578	1.850731

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B3LYP SCF energy: -3236.25125066 a.u.

B3LYP enthalpy: -3236.076588 a.u.

B3LYP free energy: -3236.134348 a.u.

M06-L SCF energy in solution: -3240.56529517 a.u.

M06-L enthalpy in solution: -3240.390633 a.u.

M06-L free energy in solution: -3240.448393 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.000366	0.957339	0.000000
N	0.000291	-0.568400	1.298604
C	0.000201	-0.452413	2.635095
C	0.000168	-1.802764	0.738723
C	0.000016	-1.556645	3.481364
H	0.000317	0.563465	3.016835
C	-0.000009	-2.956173	1.527326
C	-0.000105	-2.831889	2.914048
H	-0.000038	-1.416141	4.556740
H	-0.000114	-3.938017	1.068350
H	-0.000256	-3.717671	3.541450
N	0.000291	-0.568400	-1.298604
C	0.000168	-1.802764	-0.738723
C	0.000201	-0.452413	-2.635095
C	-0.000009	-2.956173	-1.527326
H	0.000317	0.563465	-3.016835
C	-0.000105	-2.831889	-2.914048
H	-0.000114	-3.938017	-1.068350
H	-0.000256	-3.717671	-3.541450

C	0.000016	-1.556645	-3.481364
H	-0.000038	-1.416141	-4.556740
Br	0.000088	3.239070	0.000000

18-sing

B3LYP SCF energy: -3471.53153559 a.u.

B3LYP enthalpy: -3471.188596 a.u.

B3LYP free energy: -3471.256249 a.u.

M06-L SCF energy in solution: -3475.84927893 a.u.

M06-L enthalpy in solution: -3475.506339 a.u.

M06-L free energy in solution: -3475.573992 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.099212	-0.259863	0.037332
N	1.866227	-0.864721	-0.034446
C	2.307283	-2.126316	-0.126225
C	2.737270	0.153467	-0.205929
C	3.638824	-2.430029	-0.402117
H	1.548760	-2.885769	0.034380
C	4.084970	-0.073331	-0.496638
C	4.540390	-1.385403	-0.596931
H	3.952977	-3.466285	-0.465353
H	4.765443	0.755357	-0.653854
H	5.582710	-1.585289	-0.825899
N	0.783073	1.510272	0.047537
C	2.140200	1.490272	-0.042447

C	0.179953	2.686624	0.289827
C	2.898527	2.658120	0.068117
H	-0.897044	2.659139	0.379595
C	2.261591	3.873374	0.295772
H	3.978678	2.611905	-0.000536
H	2.838905	4.787728	0.389212
C	0.874295	3.884361	0.420032
H	0.328623	4.800651	0.616689
C	-2.681092	0.691593	0.941331
C	-1.870891	0.438885	-0.330405
C	-2.680759	-0.360364	-1.355279
C	-3.995213	0.372135	-1.690195
C	-4.821399	0.622082	-0.421142
C	-4.014260	1.399814	0.627013
H	-2.094602	-0.516935	-2.270303
H	-1.637329	1.400314	-0.815121
H	-2.880970	-0.271139	1.426106
H	-2.108986	1.286301	1.668699
H	-3.769330	1.336367	-2.170842
H	-4.578327	-0.211951	-2.414847
H	-5.747860	1.159206	-0.664286
H	-5.119977	-0.346224	0.005817
H	-3.806954	2.410533	0.241233
H	-4.602649	1.528617	1.545602
H	-2.912400	-1.352463	-0.957524
Br	-0.920142	-2.363270	0.627016

18-trip

B3LYP SCF energy: -3471.52700657 a.u.

B3LYP enthalpy: -3471.185561 a.u.

B3LYP free energy: -3471.258053 a.u.

M06-L SCF energy in solution: -3475.84910908 a.u.

M06-L enthalpy in solution: -3475.507664 a.u.

M06-L free energy in solution: -3475.580156 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.526991	-0.671151	-0.467980
N	1.186674	-1.223938	0.459707
C	1.281401	-2.233123	1.335016
C	2.239253	-0.400845	0.250019
C	2.443478	-2.471759	2.059903
H	0.392935	-2.849620	1.429666
C	3.439407	-0.583417	0.946112
C	3.539688	-1.627811	1.859312
H	2.488484	-3.299742	2.758714
H	4.283161	0.074964	0.775580
H	4.464112	-1.784903	2.406281
N	0.783805	0.630181	-1.341831
C	1.996750	0.670666	-0.734608
C	0.461435	1.577988	-2.234772
C	2.912636	1.687726	-1.023833
H	-0.523217	1.489275	-2.682151
C	2.574712	2.667844	-1.950236
H	3.873554	1.718869	-0.523817
H	3.274279	3.464444	-2.182676

C	1.323364	2.614233	-2.570765
H	1.021478	3.357058	-3.300850
C	-2.403397	1.420247	0.124155
C	-1.296483	0.662190	0.850689
C	-0.317935	1.605665	1.532896
C	-1.041795	2.574298	2.491608
C	-2.144538	3.348384	1.756728
C	-3.134462	2.397921	1.070838
H	0.449432	1.045097	2.083782
H	-1.733532	-0.030050	1.583815
H	-1.973444	2.010316	-0.702717
H	-3.121747	0.721308	-0.320600
H	-1.490264	1.997156	3.312696
H	-0.323710	3.270649	2.946927
H	-2.672617	4.013523	2.452458
H	-1.680994	3.995033	0.995748
H	-3.668017	1.816137	1.835511
H	-3.893306	2.968138	0.517865
H	0.213195	2.210422	0.781813
Br	-1.990242	-2.477165	-0.841946

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B3LYP SCF energy: -4157.68660288 a.u.

B3LYP enthalpy: -4157.163982 a.u.

B3LYP free energy: -4157.263624 a.u.

M06-L SCF energy in solution: -4162.12557564 a.u.

M06-L enthalpy in solution: -4161.602955 a.u.

M06-L free energy in solution: -4161.702597 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	2.332722	0.988935	0.245067
C	2.217209	2.329611	0.313619
C	3.312376	0.441988	-0.555510
C	3.053555	3.197969	-0.361874
H	1.406545	2.697141	0.934676
C	4.189260	1.280398	-1.275367
C	4.070093	2.652850	-1.178758
H	2.913780	4.269729	-0.266904
H	4.950499	0.842514	-1.913295
H	4.742716	3.302240	-1.733048
N	2.338129	-1.612236	0.130934
C	3.324935	-0.998661	-0.605177
C	2.257048	-2.954226	0.142158
C	4.238948	-1.780602	-1.345229
H	1.449891	-3.357696	0.747001
C	4.149405	-3.157538	-1.319315
H	5.010733	-1.295031	-1.933928
H	4.852362	-3.762702	-1.885890
C	3.132181	-3.769902	-0.549795
H	3.031283	-4.849198	-0.500185
Ni	0.981929	-0.358105	0.899616
Br	0.245677	-1.042384	3.136093
C	-0.718414	-0.184742	-0.336013
C	-0.923677	1.278477	-0.165672
C	-1.805377	-1.105989	0.246121

C	-0.335793	-0.617474	-1.708334
C	-1.331405	1.786074	1.093620
C	-0.655642	2.244813	-1.161169
H	-1.386975	-2.112315	0.356557
H	-2.024159	-0.785602	1.267112
C	-3.137213	-1.238194	-0.527838
F	-0.171867	-1.966942	-1.794787
F	-1.268263	-0.320940	-2.698273
F	0.818440	-0.065510	-2.183000
C	-1.456113	3.149538	1.330998
H	-1.494406	1.094570	1.913112
C	-0.789314	3.609596	-0.912644
H	-0.327938	1.930501	-2.142995
C	-4.067202	-2.215364	0.212246
C	-3.853584	0.101805	-0.757330
H	-2.924541	-1.669391	-1.516271
C	-1.193425	4.099061	0.332399
H	-1.755328	3.485218	2.322992
H	-0.564769	4.312549	-1.713863
C	-5.408801	-2.405975	-0.507420
H	-4.252610	-1.828233	1.226047
H	-3.563036	-3.182761	0.339171
C	-5.196259	-0.082176	-1.478095
H	-3.210026	0.770852	-1.333311
H	-4.021226	0.592013	0.213135
C	-1.358321	5.577244	0.589112
C	-6.112427	-1.060888	-0.731951
H	-6.057538	-3.086806	0.061341
H	-5.230260	-2.883198	-1.482908

H	-5.697228	0.887596	-1.602895
H	-5.008503	-0.470162	-2.490767
H	-0.805012	6.173172	-0.146248
H	-2.411333	5.891260	0.534006
H	-0.995693	5.856690	1.586405
H	-6.379077	-0.629391	0.244740
H	-7.053864	-1.205703	-1.280441

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B3LYP SCF energy: -3336.14788886 a.u.

B3LYP enthalpy: -3335.971617 a.u.

B3LYP free energy: -3336.027630 a.u.

M06-L SCF energy in solution: -3340.56271690 a.u.

M06-L enthalpy in solution: -3340.386445 a.u.

M06-L free energy in solution: -3340.442458 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	0.138240	1.151286	0.000044
C	0.984695	2.195617	0.000097
C	-1.235247	1.399479	-0.000004
C	0.569562	3.517352	0.000106
H	2.033813	1.920559	0.000126
C	-1.709480	2.737342	-0.000009
C	-0.822931	3.788070	0.000046
H	1.304840	4.315100	0.000154
H	-2.780427	2.917448	-0.000067

H	-1.187572	4.812873	0.000037
N	-1.332356	-0.949991	-0.000064
C	-2.046878	0.237261	-0.000042
C	-1.967193	-2.129551	-0.000101
C	-3.466460	0.183550	-0.000054
H	-1.288199	-2.976335	-0.000098
C	-4.109508	-1.033103	-0.000099
H	-4.035524	1.108433	-0.000016
H	-5.196634	-1.072999	-0.000104
C	-3.349023	-2.232747	-0.000127
H	-3.825493	-3.207436	-0.000164
Ni	0.584017	-0.764650	0.000011
Br	2.951418	-0.486813	0.000028
F	0.732966	-2.528631	0.000012

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B3LYP SCF energy: -1846.27753097 a.u.

B3LYP enthalpy: -1845.755397 a.u.

B3LYP free energy: -1845.856216 a.u.

M06-L SCF energy in solution: -1848.08502418 a.u.

M06-L enthalpy in solution: -1847.562890 a.u.

M06-L free energy in solution: -1847.663709 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.596312	0.245479	0.250277
N	2.045141	1.697796	0.311017

C	3.361225	1.393970	0.375891
C	1.683740	2.989606	0.411289
C	4.334180	2.379460	0.577451
C	2.595426	4.022142	0.610784
H	0.617402	3.163436	0.324380
C	3.950635	3.711170	0.704783
H	5.380798	2.096116	0.605042
H	2.242330	5.045493	0.687189
H	4.694525	4.487796	0.855961
N	3.136603	-0.719558	-0.767258
C	3.761030	-0.025682	0.201177
C	3.499888	-1.989015	-0.963818
C	4.760486	-0.589327	1.001600
C	4.493886	-2.631941	-0.225022
H	2.953094	-2.523113	-1.736574
C	5.131219	-1.915637	0.783801
H	5.217678	-0.005411	1.793597
H	4.742120	-3.668740	-0.427227
H	5.896125	-2.380323	1.399124
N	-0.158237	0.467435	-1.631224
C	0.522233	-0.070294	-2.658695
C	-1.396142	0.967691	-1.857799
C	0.003048	-0.161375	-3.945357
H	1.514233	-0.426372	-2.403927
C	-1.974537	0.919230	-3.132907
C	-1.276215	0.339890	-4.186155
H	0.592949	-0.612911	-4.736269
H	-2.953822	1.354241	-3.296533
H	-1.715649	0.295881	-5.178318

N	-1.349715	2.115385	0.261256
C	-2.111708	1.587320	-0.714922
C	-1.957913	2.674789	1.311073
C	-3.510698	1.620776	-0.658600
H	-1.298403	3.075985	2.078928
C	-4.131570	2.220264	0.431770
H	-4.101656	1.139276	-1.427915
H	-5.214867	2.238869	0.501177
C	-3.341440	2.762286	1.444026
H	-3.782554	3.228596	2.319187
C	-1.776374	-1.254614	0.965422
C	-2.483411	-1.714018	-0.165045
C	-2.541309	-0.747512	2.028462
C	-0.290661	-1.324957	1.021912
C	-3.872543	-1.676044	-0.216636
H	-1.931184	-2.113466	-1.007647
C	-3.931338	-0.700304	1.965235
H	-2.039450	-0.404738	2.927168
C	0.517397	-0.596811	1.975612
C	0.271745	-2.619938	0.502383
C	-4.628296	-1.160754	0.843277
H	-4.381139	-2.049355	-1.103864
H	-4.488011	-0.301226	2.811023
H	0.016303	0.036149	2.707827
H	1.429529	-1.055618	2.349992
F	1.543786	-2.855470	0.908533
F	-0.449082	-3.707038	0.892883
F	0.307189	-2.699690	-0.871957
C	-6.131978	-1.067962	0.761586

H	-6.590260	-1.092495	1.756423
H	-6.455024	-0.132486	0.281189
H	-6.555424	-1.891092	0.175163

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B3LYP SCF energy: -1160.21132826 a.u.

B3LYP enthalpy: -1159.871088 a.u.

B3LYP free energy: -1159.939309 a.u.

M06-L SCF energy in solution: -1161.95739206 a.u.

M06-L enthalpy in solution: -1161.617152 a.u.

M06-L free energy in solution: -1161.685373 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.000000	0.000000	0.000355
N	-0.793610	1.735179	-0.490837
C	0.000000	2.824754	-0.207208
C	-2.066220	1.963503	-0.894077
C	-0.502665	4.133649	-0.309772
C	-2.607106	3.227092	-1.028453
H	-2.646093	1.076807	-1.128896
C	-1.805609	4.345653	-0.722366
H	0.131896	4.972968	-0.045392
H	-3.626749	3.343817	-1.380810
H	-2.203232	5.352512	-0.801700
N	1.522697	1.149918	0.491480
C	1.342206	2.485570	0.206964

C	2.750955	0.746321	0.894942
C	2.406548	3.398380	0.308689
C	3.827383	1.601139	1.028534
H	2.839761	-0.309233	1.130615
C	3.653764	2.965978	0.721396
H	2.247077	4.438246	0.043616
H	4.780022	1.219526	1.381102
H	4.482154	3.662929	0.800086
N	-1.522697	-1.149918	0.491480
C	-2.750955	-0.746321	0.894942
C	-1.342206	-2.485570	0.206964
C	-3.827383	-1.601139	1.028534
H	-2.839761	0.309233	1.130615
C	-2.406548	-3.398380	0.308689
C	-3.653764	-2.965978	0.721396
H	-4.780022	-1.219526	1.381102
H	-2.247077	-4.438246	0.043616
H	-4.482154	-3.662929	0.800086
N	0.793610	-1.735179	-0.490837
C	0.000000	-2.824754	-0.207208
C	2.066220	-1.963503	-0.894077
C	0.502665	-4.133649	-0.309772
H	2.646093	-1.076807	-1.128896
C	1.805609	-4.345653	-0.722366
H	-0.131896	-4.972968	-0.045392
H	2.203232	-5.352512	-0.801700
C	2.607106	-3.227092	-1.028453
H	3.626749	-3.343817	-1.380810

bpy

B3LYP SCF energy: -495.40633208 a.u.

B3LYP enthalpy: -495.238430 a.u.

B3LYP free energy: -495.282675 a.u.

M06-L SCF energy in solution: -495.44765901 a.u.

M06-L enthalpy in solution: -495.279757 a.u.

M06-L free energy in solution: -495.324002 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	-1.355902	-1.143399	0.353583
C	-2.689947	-1.162385	0.362142
C	-0.745391	0.000007	-0.000954
C	-3.488679	-0.067294	0.023760
H	-3.148642	-2.104507	0.658749
C	-1.461253	1.150876	-0.363880
C	-2.853305	1.114779	-0.350023
H	-4.571107	-0.145643	0.049303
H	-0.935301	2.047177	-0.675866
H	-3.429078	1.990788	-0.635220
N	1.355910	-1.143390	-0.353603
C	0.745393	0.000010	0.000908
C	2.689961	-1.162387	-0.362113
C	1.461247	1.150881	0.363871
C	3.488677	-0.067291	-0.023741
H	3.148654	-2.104508	-0.658718
C	2.853292	1.114784	0.350040

H	0.935279	2.047167	0.675874
H	4.571106	-0.145622	-0.049285
H	3.429067	1.990791	0.635242

TS-1

B3LYP SCF energy: -4157.55368964 a.u.

B3LYP enthalpy: -4157.032263 a.u.

B3LYP free energy: -4157.131803 a.u.

M06-L SCF energy in solution: -4161.94435370 a.u.

M06-L enthalpy in solution: -4161.422927 a.u.

M06-L free energy in solution: -4161.522467 a.u.

Imaginary frequency: -216.8591 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.928968	-0.278443	-0.562023
N	2.909302	-0.649011	-0.679613
C	3.658082	-0.667245	-1.797077
C	3.538355	-0.636788	0.530694
C	5.042711	-0.688164	-1.780437
H	3.103501	-0.670701	-2.729474
C	4.938253	-0.643665	0.618783
C	5.699033	-0.673801	-0.540147
H	5.597145	-0.714817	-2.712449
H	5.423286	-0.611393	1.587871
H	6.783112	-0.678563	-0.485587
N	1.325265	-0.451689	1.392894

C	2.644220	-0.613823	1.688521
C	0.425265	-0.451082	2.389961
C	3.068711	-0.766602	3.016612
H	-0.605953	-0.312620	2.088006
C	2.134093	-0.753138	4.042061
H	4.119992	-0.907678	3.240168
H	2.451406	-0.870940	5.073568
C	0.778244	-0.594800	3.723324
H	0.014089	-0.579517	4.493165
C	-0.968718	1.876797	-0.481432
C	-1.097810	2.188833	0.884156
C	-2.143060	1.873480	-1.255830
C	0.350101	1.566758	-1.099161
C	-2.344989	2.450185	1.447506
H	-0.212486	2.218771	1.506862
C	-3.383455	2.146866	-0.688387
H	-2.074877	1.679687	-2.321267
C	0.468914	0.726901	-2.234490
C	1.455200	2.548900	-0.819578
C	-3.514441	2.428728	0.678766
H	-2.409812	2.679778	2.508756
H	-4.266900	2.158128	-1.323174
H	-0.419727	0.291204	-2.678601
H	1.320354	0.835043	-2.898060
F	2.579472	2.288369	-1.527987
F	1.089654	3.820646	-1.126959
F	1.833533	2.581734	0.490475
C	-4.866798	2.702958	1.289089
H	-5.402673	3.486605	0.740021

H	-5.503619	1.809049	1.273339
H	-4.775029	3.026687	2.330625
Br	-0.432056	-2.366745	-0.800642
C	-2.743083	-2.366686	-0.303127
C	-2.928849	-1.416855	0.843226
C	-3.460854	-1.976442	-1.562240
H	-2.810566	-3.422619	-0.044471
C	-4.441034	-1.304083	1.160664
H	-2.546507	-0.428135	0.565552
H	-2.378117	-1.757068	1.725840
C	-4.977101	-1.900144	-1.252595
H	-3.263071	-2.687838	-2.369596
H	-3.110243	-0.989963	-1.888588
C	-5.252979	-0.937458	-0.089334
H	-4.585323	-0.552174	1.946430
H	-4.799453	-2.261303	1.564188
H	-5.517677	-1.582382	-2.152904
H	-5.345950	-2.903886	-0.999140
H	-4.983763	0.078388	-0.399636
H	-6.324242	-0.928876	0.147756

TS-2

B3LYP SCF energy: -4157.55976813 a.u.

B3LYP enthalpy: -4157.038536 a.u.

B3LYP free energy: -4157.142282 a.u.

M06-L SCF energy in solution: -4161.95101712 a.u.

M06-L enthalpy in solution: -4161.429785 a.u.

M06-L free energy in solution: -4161.533531 a.u.

Imaginary frequency: -239.1935 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
N	2.259979	0.883167	0.200852
C	2.184613	2.212997	0.315184
C	3.275222	0.322300	-0.488149
C	3.126828	3.060787	-0.261911
H	1.339000	2.592213	0.878187
C	4.259282	1.109378	-1.092272
C	4.181137	2.495406	-0.977165
H	3.027676	4.135096	-0.152430
H	5.067401	0.654309	-1.652779
H	4.934008	3.123314	-1.443693
N	2.156785	-1.735631	0.002170
C	3.246985	-1.156790	-0.547817
C	2.045990	-3.067919	0.011795
C	4.263578	-1.932403	-1.113143
H	1.148647	-3.462478	0.476345
C	4.144900	-3.319003	-1.107015
H	5.139829	-1.463004	-1.544060
H	4.926810	-3.934740	-1.540602
C	3.016179	-3.903045	-0.532684
H	2.887551	-4.979381	-0.503250
Ni	0.826777	-0.437082	0.863080
Br	0.722187	-0.306980	3.244779
C	-0.695606	-0.220296	-0.561578
C	-0.920647	1.245135	-0.473360

C	-1.220502	-1.118589	0.380663
C	-0.334274	-0.794588	-1.900937
C	-1.320500	1.827931	0.748083
C	-0.661204	2.119240	-1.545021
H	-1.117433	-2.185352	0.246323
H	-1.738374	-0.789071	1.268079
C	-3.552488	-1.572614	-0.475229
F	-0.165057	-2.137847	-1.865759
F	-1.302033	-0.561544	-2.832825
F	0.811471	-0.279156	-2.425686
C	-1.451832	3.206280	0.881450
H	-1.484141	1.208456	1.622040
C	-0.800242	3.497709	-1.400409
H	-0.341070	1.730462	-2.502414
C	-4.258480	-2.231612	0.670031
C	-4.042181	-0.207144	-0.848471
H	-3.186342	-2.208180	-1.279551
C	-1.198660	4.073434	-0.189610
H	-1.750117	3.614529	1.844086
H	-0.590682	4.139636	-2.253086
C	-5.784123	-2.276777	0.395040
H	-4.099441	-1.650614	1.592095
H	-3.873515	-3.240740	0.857558
C	-5.565074	-0.253905	-1.129856
H	-3.497400	0.186149	-1.711288
H	-3.870565	0.493055	-0.017611
C	-1.371474	5.564977	-0.045417
C	-6.320233	-0.879022	0.052401
H	-6.309765	-2.688641	1.266222

H	-5.976697	-2.956547	-0.446563
H	-5.939061	0.757755	-1.333623
H	-5.746924	-0.850612	-2.034563
H	-2.420287	5.859810	-0.184217
H	-1.069846	5.909038	0.950099
H	-0.779651	6.110443	-0.788120
H	-6.212175	-0.227536	0.932166
H	-7.393696	-0.931804	-0.169208

TS-3-sing

B3LYP SCF energy: -4157.57152641 a.u.

B3LYP enthalpy: -4157.046826 a.u.

B3LYP free energy: -4157.145628 a.u.

M06-L SCF energy in solution: -4161.96269425 a.u.

M06-L enthalpy in solution: -4161.437994 a.u.

M06-L free energy in solution: -4161.536796 a.u.

Imaginary frequency: -238.4209 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
N	-2.839160	0.729589	0.377677
C	-3.261550	1.980415	0.596738
C	-3.729119	-0.263900	0.178758
C	-4.611701	2.314915	0.614575
H	-2.484417	2.721153	0.746677
C	-5.101261	0.002371	0.192370
C	-5.547184	1.303593	0.405537

H	-4.912941	3.341888	0.788458
H	-5.807026	-0.809813	0.062156
H	-6.610700	1.521448	0.419252
N	-2.019003	-1.901077	0.571390
C	-3.190103	-1.631237	-0.028944
C	-1.491864	-3.116361	0.420715
C	-3.864334	-2.573922	-0.811992
H	-0.548803	-3.287360	0.933897
C	-3.298669	-3.836851	-0.973329
H	-4.788863	-2.314052	-1.315624
H	-3.791048	-4.581998	-1.590829
C	-2.089453	-4.120997	-0.342195
H	-1.614793	-5.091848	-0.440348
Ni	-0.927919	0.392905	0.356906
Br	-0.991197	0.288530	-1.993069
C	1.157146	0.189709	0.512566
C	1.578227	1.576472	0.133026
C	1.576430	-1.029714	-0.323668
C	1.007608	-0.079488	1.878060
C	2.317352	1.823407	-1.031693
C	1.172548	2.695881	0.888505
H	0.778854	-1.776177	-0.301227
H	1.624811	-0.717061	-1.367041
C	2.889705	-1.713103	0.107193
F	0.767776	-1.299317	2.304652
F	1.470801	0.654964	2.857059
F	-0.815701	0.657425	2.187646
C	2.659700	3.119921	-1.409564
H	2.619838	1.003001	-1.668644

C	1.519295	3.985875	0.504430
H	0.547247	2.552144	1.761498
C	3.197423	-2.890328	-0.833183
C	4.101963	-0.771973	0.190059
H	2.737033	-2.133777	1.113110
C	2.277192	4.227570	-0.648675
H	3.231750	3.269802	-2.322178
H	1.185064	4.825272	1.110509
C	4.463769	-3.646977	-0.410566
H	3.327014	-2.501993	-1.854532
H	2.338581	-3.574115	-0.868242
C	5.363867	-1.523823	0.633997
H	3.895204	0.059874	0.873447
H	4.280580	-0.322869	-0.796532
C	2.675762	5.628131	-1.042723
C	5.668264	-2.702405	-0.300199
H	4.676243	-4.456276	-1.120410
H	4.289009	-4.122954	0.565582
H	6.218192	-0.836719	0.672223
H	5.218474	-1.901447	1.656978
H	3.583307	5.949287	-0.513523
H	2.881990	5.697750	-2.115846
H	1.888796	6.351309	-0.801383
H	5.913568	-2.313910	-1.299552
H	6.551860	-3.250760	0.049701

TS-3-trip

B3LYP SCF energy: -4157.61014214 a.u.

B3LYP enthalpy: -4157.084890 a.u.

B3LYP free energy: -4157.183940 a.u.

M06-L SCF energy in solution: -4162.00557381 a.u.

M06-L enthalpy in solution: -4161.480322 a.u.

M06-L free energy in solution: -4161.579372 a.u.

Imaginary frequency: -331.7590 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
N	0.451031	-2.308854	-0.272719
C	-0.044498	-3.138257	-1.195377
C	0.383233	-2.608001	1.039914
C	-0.640690	-4.346500	-0.841970
H	0.041648	-2.788353	-2.218050
C	-0.206703	-3.800704	1.464709
C	-0.720338	-4.677110	0.510439
H	-1.034413	-5.003887	-1.609115
H	-0.273190	-4.041962	2.518907
H	-1.182543	-5.608166	0.823736
N	1.399555	-0.463763	1.350239
C	0.959963	-1.588002	1.950948
C	1.958974	0.515367	2.064175
C	1.066829	-1.747520	3.334508
H	2.307945	1.372689	1.501156
C	1.633810	-0.721757	4.088940
H	0.724949	-2.655422	3.817104
H	1.725530	-0.827824	5.165532
C	2.088281	0.429624	3.448905

H	2.540378	1.244596	4.003009
Ni	1.266581	-0.473083	-0.740966
Br	3.648513	-0.508223	-1.064467
C	-0.911638	0.658761	-0.793413
C	-0.145417	1.852610	-0.393768
C	-1.852060	-0.025637	0.181445
C	-0.990999	0.299659	-2.143790
C	-0.355459	2.473283	0.856400
C	0.936719	2.340285	-1.169521
H	-2.025836	-1.058361	-0.138872
H	-1.361642	-0.093066	1.160679
C	-3.228070	0.650335	0.375085
F	-1.808849	-0.684541	-2.501775
F	-0.899176	1.192205	-3.120405
F	0.547319	-0.546847	-2.627213
C	0.451536	3.519697	1.293525
H	-1.152714	2.127421	1.503368
C	1.746291	3.375687	-0.710893
H	1.160088	1.891807	-2.131038
C	-4.055751	0.712158	-0.917892
C	-4.015860	-0.070303	1.481123
H	-3.063925	1.687304	0.702082
C	1.521900	3.994242	0.524952
H	0.249517	3.972082	2.262295
H	2.580745	3.696936	-1.328801
C	-5.428426	1.355855	-0.681802
H	-4.192037	-0.307379	-1.306672
H	-3.508799	1.270533	-1.686034
C	-5.392420	0.563537	1.719993

H	-3.432179	-0.074233	2.412243
H	-4.146701	-1.124519	1.190792
C	2.386182	5.137490	0.996231
C	-6.207359	0.628343	0.421666
H	-6.005781	1.363981	-1.614537
H	-5.288160	2.407155	-0.390753
H	-5.939860	0.003790	2.488950
H	-5.255841	1.582522	2.110575
H	2.340097	5.252432	2.084576
H	3.434324	4.988202	0.714558
H	2.065574	6.090504	0.554371
H	-6.434773	-0.394794	0.087583
H	-7.170544	1.122285	0.600474

TS-4-sing

B3LYP SCF energy: -4157.54685999 a.u.

B3LYP enthalpy: -4157.022881 a.u.

B3LYP free energy: -4157.118822 a.u.

M06-L SCF energy in solution: -4161.93699792 a.u.

M06-L enthalpy in solution: -4161.413019 a.u.

M06-L free energy in solution: -4161.508960 a.u.

Imaginary frequency: -128.5270 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.859281	-0.272928	-0.066051
N	-0.582065	-1.488531	-0.634128

C	-0.498472	-2.802187	-0.369020
C	-1.601954	-1.026093	-1.388213
C	-1.449215	-3.714467	-0.805634
H	0.365789	-3.112825	0.199550
C	-2.572071	-1.899912	-1.894566
C	-2.505563	-3.252773	-1.589959
H	-1.344103	-4.763196	-0.551582
H	-3.355929	-1.521192	-2.538724
H	-3.254725	-3.938637	-1.973486
N	-0.470910	1.086382	-1.527827
C	-1.631880	0.424423	-1.684154
C	-0.432786	2.389873	-1.807453
C	-2.800635	1.073208	-2.102406
H	0.531481	2.872815	-1.676749
C	-2.751901	2.433874	-2.387886
H	-3.738034	0.534812	-2.167801
H	-3.648387	2.957659	-2.705919
C	-1.542404	3.111273	-2.247474
H	-1.456947	4.170846	-2.465301
C	3.700781	0.139821	0.784181
C	2.610538	0.940600	0.088406
C	2.804269	2.439970	0.295410
C	4.171359	2.857390	-0.283970
C	5.310763	2.064644	0.368988
C	5.083057	0.553881	0.239532
H	2.008068	3.018263	-0.190068
H	2.628789	0.755395	-0.985385
H	3.677051	0.325207	1.868642
H	3.551561	-0.929380	0.626415

H	4.173928	2.675979	-1.367670
H	4.319387	3.935820	-0.139877
H	6.272595	2.347986	-0.076976
H	5.366731	2.333053	1.434610
H	5.141001	0.257796	-0.815951
H	5.869371	0.000926	0.769366
H	2.789170	2.709116	1.360960
Br	2.179789	-1.622497	-1.716286
C	0.888704	1.020106	1.605943
C	-0.170665	0.100194	1.710102
H	0.660008	2.025330	1.287530
C	-1.590709	0.506184	1.493569
C	0.082357	-1.025649	2.687108
C	-1.937450	1.860421	1.325995
C	-2.638983	-0.427783	1.432936
F	1.397847	-1.318757	2.795149
F	-0.351864	-0.692105	3.927465
F	-0.538166	-2.196399	2.380018
C	-3.244332	2.250823	1.069084
H	-1.178572	2.630176	1.398176
C	-3.950916	-0.029336	1.182388
H	-2.433043	-1.480437	1.566491
C	-4.280943	1.312130	0.979181
H	-3.464682	3.307035	0.933798
H	-4.730329	-0.785974	1.133452
C	-5.690949	1.743365	0.663451
H	-6.033429	2.529818	1.346381
H	-5.763044	2.150468	-0.353986
H	-6.391597	0.905901	0.736963

H	1.725889	0.933161	2.283362

TS-4-trip

B3LYP SCF energy: -4157.55256052 a.u.

B3LYP enthalpy: -4157.029835 a.u.

B3LYP free energy: -4157.128271 a.u.

M06-L SCF energy in solution: -4161.94420043 a.u.

M06-L enthalpy in solution: -4161.421475 a.u.

M06-L free energy in solution: -4161.519911 a.u.

Imaginary frequency: -206.0197 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.817191	0.340132	-0.166591
N	0.798328	1.684052	-0.381534
C	0.830356	2.938736	0.073626
C	1.811635	1.210525	-1.128423
C	1.902850	3.789365	-0.175259
H	-0.033134	3.254724	0.646574
C	2.914466	2.012572	-1.439576
C	2.961889	3.312892	-0.948359
H	1.898471	4.799935	0.217917
H	3.718027	1.634035	-2.059463
H	3.811077	3.950104	-1.175376
N	0.447372	-0.745525	-1.385095
C	1.651280	-0.178575	-1.613472
C	0.196132	-1.977574	-1.834661

C	2.659347	-0.883723	-2.276620
H	-0.795705	-2.361753	-1.627682
C	2.402618	-2.172658	-2.732188
H	3.636232	-0.439837	-2.420232
H	3.178335	-2.733431	-3.244389
C	1.143383	-2.730690	-2.521358
H	0.898249	-3.728313	-2.868589
C	-3.718029	-0.093957	0.712931
C	-2.685111	-0.969630	0.018352
C	-3.000685	-2.448805	0.184393
C	-4.407946	-2.763758	-0.363128
C	-5.470689	-1.891423	0.317426
C	-5.134574	-0.401054	0.186801
H	-2.260596	-3.082568	-0.325181
H	-2.646688	-0.729522	-1.048731
H	-3.699402	-0.278185	1.798685
H	-3.495894	0.964414	0.555369
H	-4.422204	-2.576026	-1.445901
H	-4.634357	-3.828953	-0.220371
H	-6.460553	-2.101136	-0.107517
H	-5.523030	-2.159008	1.383501
H	-5.186509	-0.100451	-0.868067
H	-5.871990	0.206738	0.727223
H	-2.975110	-2.736409	1.246273
Br	-2.038311	1.843037	-1.729995
C	-0.954970	-1.144738	1.542824
C	0.202393	-0.361094	1.795441
H	-0.809787	-2.156652	1.196303
C	1.571597	-0.837962	1.519606

C	-0.087150	0.799970	2.696778
C	1.796046	-2.185077	1.150098
C	2.711754	-0.006926	1.536505
F	-1.189877	1.494533	2.244833
F	-0.402434	0.418404	3.961147
F	0.896173	1.720420	2.820183
C	3.048757	-2.647929	0.776305
H	0.973827	-2.891000	1.150792
C	3.969982	-0.484448	1.174067
H	2.620535	1.032435	1.812607
C	4.169153	-1.804689	0.766926
H	3.161143	-3.690738	0.487282
H	4.813776	0.201869	1.193278
C	5.521039	-2.309783	0.329969
H	5.835443	-3.182198	0.915929
H	5.511593	-2.620989	-0.723394
H	6.290031	-1.538779	0.441667
H	-1.797367	-1.025603	2.212795

TS-5

B3LYP SCF energy: -4157.66076002 a.u.

B3LYP enthalpy: -4157.140281 a.u.

B3LYP free energy: -4157.241074 a.u.

M06-L SCF energy in solution: -4162.10400971 a.u.

M06-L enthalpy in solution: -4161.583531 a.u.

M06-L free energy in solution: -4161.684324 a.u.

Imaginary frequency: -97.8251 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
N	0.432915	-2.260968	-0.185498
C	-0.168674	-3.114430	-1.034892
C	0.561510	-2.604255	1.136276
C	-0.672395	-4.339673	-0.637729
H	-0.246517	-2.757825	-2.056718
C	0.090304	-3.849758	1.594669
C	-0.529253	-4.718606	0.714920
H	-1.168101	-4.984584	-1.356081
H	0.211629	-4.123578	2.637784
H	-0.900586	-5.678679	1.062733
N	1.594371	-0.471423	1.309449
C	1.192909	-1.597693	1.970557
C	2.186695	0.525965	1.981020
C	1.399881	-1.713395	3.359819
H	2.482107	1.379310	1.381476
C	2.000531	-0.674624	4.049436
H	1.086416	-2.609933	3.884486
H	2.159320	-0.753047	5.121940
C	2.403877	0.477956	3.349813
H	2.870812	1.315997	3.856139
Ni	1.368349	-0.556609	-0.699058
Br	3.609289	-0.291704	-1.547544
C	-1.068757	0.725510	-0.820412
C	-0.258005	1.801990	-0.301851
C	-1.978812	-0.060448	0.094175
C	-0.995693	0.346495	-2.181891

C	-0.434749	2.288131	1.023496
C	0.818239	2.397620	-1.024638
H	-2.146825	-1.063605	-0.313857
H	-1.476286	-0.221454	1.059291
C	-3.360878	0.573269	0.372857
F	-1.922998	-0.547015	-2.602132
F	-0.904538	1.315913	-3.129789
F	0.308837	-0.440898	-2.563114
C	0.375127	3.280490	1.564047
H	-1.215359	1.866236	1.646204
C	1.624316	3.379845	-0.464052
H	1.040636	2.060143	-2.029281
C	-4.202447	0.725036	-0.901988
C	-4.133944	-0.232728	1.427759
H	-3.198763	1.584953	0.775523
C	1.426057	3.856767	0.840640
H	0.192483	3.606415	2.587924
H	2.449353	3.771628	-1.056486
C	-5.576795	1.340936	-0.610548
H	-4.336335	-0.265199	-1.362274
H	-3.651496	1.332829	-1.627528
C	-5.513694	0.369713	1.726202
H	-3.541726	-0.302564	2.350635
H	-4.259421	-1.264099	1.061977
C	2.293520	4.944382	1.425190
C	-6.341859	0.528130	0.443446
H	-6.167890	1.416148	-1.533562
H	-5.441393	2.368465	-0.240543
H	-6.055461	-0.247886	2.456197

H	-5.380670	1.358975	2.189414
H	1.985379	5.949501	1.097670
H	2.253598	4.939284	2.521527
H	3.343779	4.823960	1.130514
H	-6.562658	-0.469641	0.034778
H	-7.309699	0.997951	0.667516

TS-6

B3LYP SCF energy: -921.27617796 a.u.

B3LYP enthalpy: -920.931030 a.u.

B3LYP free energy: -921.000336 a.u.

M06-L SCF energy in solution: -921.35543303 a.u.

M06-L enthalpy in solution: -921.010285 a.u.

M06-L free energy in solution: -921.079591 a.u.

Imaginary frequency: -160.9091 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	2.937199	-1.613848	-0.783920
C	1.766450	-0.913956	-1.046664
C	1.509856	0.335865	-0.449730
C	2.483559	0.840800	0.431262
C	3.652537	0.130842	0.691563
C	3.905664	-1.108028	0.093995
H	3.099626	-2.577433	-1.261358
H	1.029934	-1.353900	-1.710448
H	2.339140	1.802213	0.907213
H	4.386613	0.553898	1.373080

C	0.265651	1.066024	-0.754460
C	-0.531685	0.795694	-1.816542
H	-1.412538	1.388279	-2.018976
H	-0.202476	0.129370	-2.603676
C	-0.198596	2.105279	0.229069
C	5.158288	-1.888588	0.404553
H	4.973950	-2.643142	1.181020
H	5.529574	-2.418841	-0.479328
H	5.956749	-1.234092	0.768678
F	-1.431623	2.584326	-0.055595
F	-0.254744	1.613983	1.493733
F	0.627086	3.183696	0.276005
C	-2.146452	-0.969786	-1.024246
C	-1.531291	-1.506210	0.231842
C	-3.396852	-0.161382	-0.844058
H	-2.059820	-1.570301	-1.928827
C	-2.580790	-2.311865	1.038803
H	-1.184667	-0.672555	0.858408
H	-0.653636	-2.125339	0.020123
C	-4.446101	-0.971652	-0.041416
H	-3.813903	0.154674	-1.807479
H	-3.165060	0.750621	-0.276034
C	-3.847748	-1.479047	1.277854
H	-2.145266	-2.633576	1.993274
H	-2.843869	-3.223263	0.484012
H	-5.329786	-0.349263	0.148903
H	-4.780660	-1.827595	-0.643817
H	-3.597413	-0.617672	1.914019
H	-4.591100	-2.070988	1.826488

V. References

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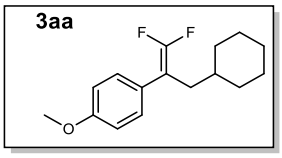
Badir, S. O.; Molander, G. A.; Gutierrez, O. On the Nature of C(sp^3)−C(sp^2) Bond Formation in Nickel-Catalyzed Tertiary Radical Cross-Couplings: A Case Study of Ni/Photoredox Catalytic Cross-Coupling of Alkyl Radicals and Aryl Halides. *J. Am. Chem. Soc.* **2020**, *142*, 7225-7234.

VI. Characterization of products



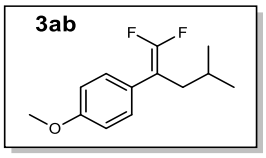
1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (3aa):

The reaction was carried out following the general procedure. Then 47.4 mg colorless oil was obtained in 89% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.21 (m, 2H), 6.91 – 6.86 (m, 2H), 3.81 (s, 3H), 2.29 – 2.12 (m, 2H), 1.70 – 1.58 (m, 5H), 1.30 – 1.20 (m, 1H), 1.17 – 1.04 (m, 3H), 0.97 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 153.8 (dd, *J* = 288.7, 285.4 Hz), 129.3 (t, *J* = 3.2 Hz), 126.2 (dd, *J* = 4.4, 3.0 Hz), 113.8, 90.4 (dd, *J* = 22.1, 13.0 Hz), 55.2, 35.6 (t, *J* = 2.4 Hz), 35.3, 32.8, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.34 (d, *J* = 46.0 Hz), -92.76 (d, *J* = 46.9 Hz).



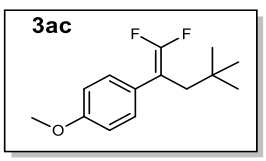
1-(1,1-difluoro-4-methylpent-1-en-2-yl)-4-methoxybenzene (3ab):

The reaction was carried out following the general procedure. Then 29.4 mg colorless oil was obtained in 65% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.2 Hz, 2H), 6.92 – 6.85 (m, 2H), 3.80 (s, 3H), 2.23 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.61 – 1.51 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 153.9 (dd, *J* = 288.9, 285.3 Hz), 129.4 (t, *J* = 3.2 Hz), 126.1 (dd, *J* = 4.3, 2.8 Hz), 113.8, 91.0 (dd, *J* = 21.8, 13.1 Hz), 55.2, 36.7 (d, *J* = 1.2 Hz), 26.3 (t, *J* = 2.4 Hz), 22.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.59 (d, *J* = 46.9 Hz), -92.99 (d, *J* = 46.9 Hz).



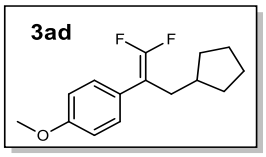
1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-methoxybenzene (3ac):

The reaction was carried out following the general procedure. Then 29.8 mg colorless oil was obtained in 62% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.19 (m, 2H), 6.91 – 6.83 (m, 2H), 3.80 (s, 3H), 2.29 (t, *J* = 2.4 Hz, 2H), 0.80 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4, 154.3 (dd, *J* = 288.8, 286.7 Hz), 129.5 (t, *J* = 2.8 Hz), 127.7 (dd, *J* = 4.7, 2.7 Hz), 113.7, 90.5 (dd, *J* = 21.6, 13.2 Hz), 55.2, 41.2, 32.6 (t, *J* = 2.6 Hz), 29.7.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.76 (d, *J* = 43.5 Hz), -93.33 (d, *J* = 43.6 Hz).



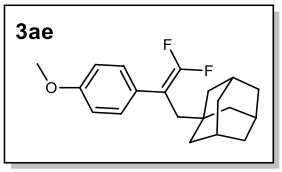
1-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (3ad):

The reaction was carried out following the general procedure. Then 30.3 mg colorless oil was obtained in 60% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.19 (m, 2H), 6.93 – 6.84 (m, 2H), 3.80 (s, 3H), 2.35 (dt, *J* = 7.6, 2.4 Hz, 2H), 1.86 – 1.71 (m, 1H), 1.71 – 1.55 (m, 4H), 1.53 – 1.38 (m, 2H), 1.20 – 1.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ158.6, 153.7 (dd, *J* = 288.3, 285.4 Hz), 129.4 (t, *J* = 3.1 Hz), 126.1 (dd, *J* = 4.3, 2.6 Hz), 113.8, 91.7 (dd, *J* = 21.7, 13.2 Hz), 55.2, 38.2 (t, *J* = 2.4 Hz), 33.7 (d, *J* = 1.4 Hz), 32.1, 25.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -93.08 (d, *J* = 47.7 Hz), -93.39 (d, *J* = 47.7 Hz).



(1*R*,3*R*,5*S*)-1-(3,3-difluoro-2-(4-methoxyphenyl)allyl)adamantane (3ae):

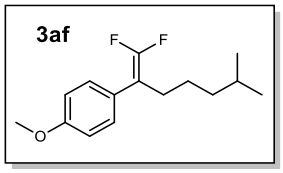
The reaction was carried out following the general procedure. Then 51.5 mg white solid was obtained in 81% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.6 Hz, 2H), 6.89 – 6.84 (m, 2H), 3.80 (s, 3H), 2.16 (t, *J* = 2.6 Hz, 2H), 1.89 – 1.83 (m, 3H), 1.69 – 1.59 (m, 3H), 1.56 – 1.49 (m, 3H), 1.37 (d, *J* = 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.3, 129.4 (t, *J* = 3.0 Hz), 113.6, 89.1 (dd, *J* = 22.0, 12.9 Hz), 55.1, 52.4, 42.6, 41.9, 35.6, 34.6 (t, *J* = 2.3 Hz), 33.1, 28.6.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.02 (d, *J* = 43.5 Hz), -93.05 (d, *J* = 43.3 Hz).

HR-MS (APCI+): m/z calculated for $C_{20}H_{24}F_2O$, $[M]^+$: 318.1789, measured: 318.1785.



1-(1,1-difluoro-6-methylhept-1-en-2-yl)-4-methoxybenzene (3af):

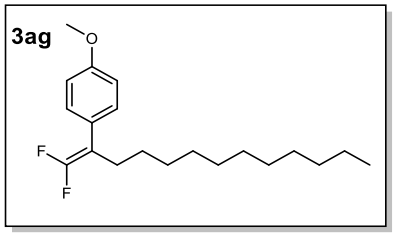
The reaction was carried out following the general procedure. Then 25.4 mg colorless oil was obtained in 50% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.93 – 6.85 (m, 2H), 3.81 (s, 3H), 2.37 – 2.28 (m, 2H), 1.56 – 1.43 (m, 1H), 1.40 – 1.26 (m, 2H), 1.20 – 1.13 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 153.4 (t, *J* = 287.2 Hz), 129.3 (t, *J* = 3.3 Hz), 126.0, 113.8, 91.8 (t, *J* = 17.4 Hz), 55.2, 38.2, 27.9, 27.7, 25.5 (t, *J* = 2.5 Hz), 22.6.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.98.

HR-MS (APCI+): m/z calculated for $C_{15}H_{20}F_2O$, $[M]^+$: 254.1477, measured: 254.1468.



1-(1,1-difluorotridec-1-en-2-yl)-4-methoxybenzene (3ag):

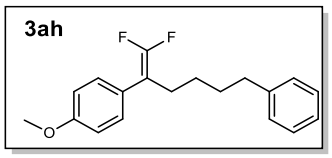
The reaction was carried out following the general procedure. Then 38.3 mg colorless oil was obtained in 59% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.92 – 6.85 (m, 2H), 3.81 (s, 3H), 2.39 – 2.29 (m, 2H), 1.23 (m, 18H), 0.88 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 153.4 (t, *J* = 287.3 Hz), 129.3 (t, *J* = 3.3 Hz), 126.0, 113.8, 91.9 (t, *J* = 17.4 Hz), 55.2, 53.4, 31.9, 29.6, 29.5, 29.3 (d, *J* = 4.0 Hz), 29.0, 27.7, 22.7, 14.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -93.00.

HR-MS (APCI+): m/z calculated for $C_{20}H_{30}F_2O$, $[M]^+$: 324.2259, measured: 324.2260.



1-(1,1-difluoro-6-phenylhex-1-en-2-yl)-4-methoxybenzene (3ah):

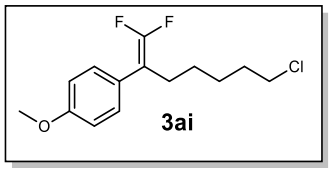
The reaction was carried out following the general procedure. Then 50.8 mg colorless oil was obtained in 84% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 7.15 – 7.10 (m, 2H), 6.90 – 6.85 (m, 2H), 3.80 (s, 3H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.43 – 2.34 (m, 2H), 1.65 – 1.58 (m, 2H), 1.46 – 1.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 153.4 (dd, *J* = 285.8, 285.6 Hz), 142.4, 129.3 (t, *J* = 3.2 Hz), 128.8, 128.3 (d, *J* = 8.4 Hz), 125.8 (d, *J* = 1.8 Hz), 125.6, 113.8, 91.6 (dd, *J* = 18.7, 16.1 Hz), 55.2, 35.5, 30.7, 27.4, 27.2 (t, *J* = 2.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.71 (d, *J* = 2.1 Hz).

HR-MS (APCI+): m/z calculated for $C_{19}H_{20}F_2O$, $[M]^+$: 302.1477, measured: 302.1467.



1-(7-chloro-1,1-difluorohept-1-en-2-yl)-4-methoxybenzene (3ai):

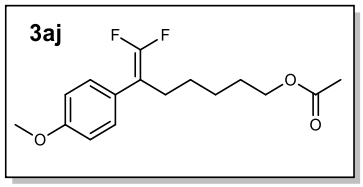
The reaction was carried out following the general procedure. Then 29.1 mg colorless oil was obtained in 53% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.18 (m, 2H), 6.93 – 6.85 (m, 2H), 3.81 (s, 3H), 3.53 – 3.09 (m, 2H), 2.42 – 2.33 (m, 2H), 1.86 – 1.68 (m, 2H), 1.48 – 1.32 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 153.4 (dd, *J* = 288.3, 286.6 Hz), 129.3 (t, *J* = 3.3 Hz), 125.7, 113.9, 91.5 (dd, *J* = 19.9, 15.3 Hz), 55.2, 44.9, 32.2, 27.5, 26.9 (t, *J* = 2.6 Hz), 26.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.59 (d, *J* = 47.1 Hz), -92.73(d, *J* = 46.7 Hz).

HR-MS (ESI): m/z calculated for $C_{14}H_{17}ClF_2O$ $[M]^+$: 274.0930, measured: 274.0929.



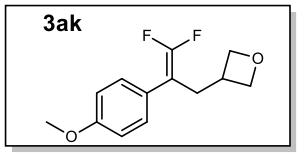
7,7-difluoro-6-(4-methoxyphenyl)hept-6-en-1-yl acetate (3aj):

The reaction was carried out following the general procedure. Then 35.2 mg colorless oil was obtained in 59% isolated yield using petroleum ether/ EtOAc =20:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 6.93 – 6.85 (m, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 2.42 – 2.32 (m, 2H), 2.03 (s, 3H), 1.64 – 1.53 (m, 2H), 1.44 – 1.29 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 158.6, 157.9 – 148.3 (m), 129.3 (t, *J* = 3.3 Hz), 125.7 (d, *J*= 2.2 Hz), 113.9, 91.6 (dd, *J* = 19.7, 15.4 Hz), 64.4, 55.2, 28.2, 27.5, 27.3 (t, *J* = 2.5 Hz), 25.3, 21.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ= –92.68 (d, *J*= 46.7 Hz), –92.82 (d, *J*= 47.1 Hz).



3-(3,3-difluoro-2-(4-methoxyphenyl)allyl)oxetane (3ak):

The reaction was carried out following the general procedure. Then 17.8 mg colorless oil was obtained in 37% isolated yield using petroleum ether/ EtOAc = 20:1 as eluent.

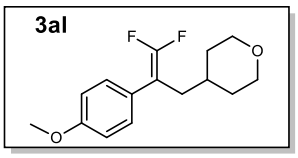
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 – 7.13 (m, 2H), 6.91 – 6.86 (m, 2H), 4.65 (dd, *J* = 7.6, 6.0 Hz,

2H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 3.07 – 2.94 (m, 1H), 2.75 (dt, *J* = 7.6, 2.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 153.8 (dd, *J* = 289.3, 286.8 Hz), 129.4 (t, *J* = 3.0 Hz), 125.0 (dd, *J* = 4.4, 2.7 Hz), 114.0, 89.8 (dd, *J* = 21.6, 15.0 Hz), 76.8, 55.2, 33.8 (t, *J* = 2.6 Hz), 31.9 (d, *J* = 1.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.58 (d, *J* = 45.1 Hz), -92.09 (d, *J* = 45.0 Hz).

HR-MS (ESI): m/z calculated for $C_{13}H_{14}F_2O_2$ $[M]^+$: 240.093, measured: 240.092.



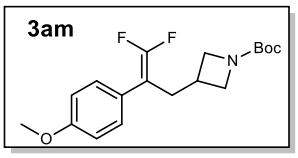
4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)tetrahydro-2*H*-pyran (3al):

The reaction was carried out following the general procedure. Then 27.4 mg colorless oil was obtained in 51% isolated yield using petroleum ether/ EtOAc = 20:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.95 – 3.86 (m, 2H), 3.82 (s, 3H), 3.31 – 3.20 (m, 2H), 2.35 – 2.27 (m, 2H), 1.60 – 1.50 (m, 2H), 1.50 – 1.43 (m, 1H), 1.37 – 1.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 157.0 – 150.8 (m), 129.3 (t, *J* = 3.3 Hz), 126.4 – 124.6 (m), 113.9, 89.7 (dd, *J* = 21.7, 13.8 Hz), 67.8, 55.2, 34.8 (d, *J* = 1.5 Hz), 33.1 (t, *J* = 2.6 Hz), 32.6.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.78 (d, *J* = 45.2 Hz), -92.09 (d, *J* = 45.5 Hz).



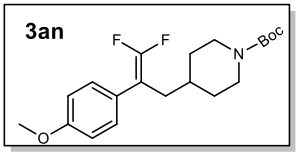
***tert*-butyl 3-(3,3-difluoro-2-(4-methoxyphenyl)allyl)azetidine-1-carboxylate (3am):**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 3.91 (t, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 3.55 (dd, *J* = 9.2, 6.0 Hz, 2H), 2.67 (d, *J* = 7.6 Hz, 2H), 2.59 – 2.46 (m, 1H), 1.45 (d, *J* = 2.0 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 156.3, 153.8 (dd, *J* = 289.4, 286.9 Hz), 129.3 (t, *J* = 3.0 Hz), 124.9 (dd, *J* = 4.4, 2.6 Hz), 114.0, 89.8 (dd, *J* = 21.5, 15.1 Hz), 79.3, 55.2, 53.6, 32.4 (d, *J* = 1.7 Hz), 29.6, 28.3, 27.3 (t, *J* = 2.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.42 (d, *J* = 44.6 Hz), -92.00 (d, *J* = 44.8 Hz).

HR-MS (ESI): m/z calculated for $[C_{18}H_{23}F_2NO_3+H]^+$: 340.1719, measured: 340.1712.



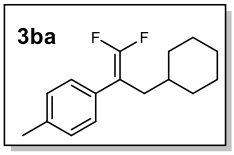
***tert*-butyl 4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)piperidine-1-carboxylate (3an):**

The reaction was carried out following the general procedure. Then 39.7 mg colorless oil was obtained in 54% isolated yield using petroleum ether/ EtOAc = 5:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.21 – 3.93 (m, 2H), 3.82 (s, 3H), 2.57 (t, *J* = 12.8 Hz, 1H), 2.30 (dt, *J* = 7.4, 2.4 Hz, 2H), 1.68 – 1.52 (m, 2H), 1.44 (s, 9H), 1.41 – 1.35 (m, 1H), 1.18 – 1.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 154.7, 153.8 (dd, *J* = 287.8, 284.2 Hz) 129.2 (t, *J* = 3.2 Hz), 125.6 (dd, *J* = 4.1, 3.0Hz), 113.9, 89.8 (dd, *J* = 21.9, 13.6 Hz), 79.2, 55.2, 43.6, 34.4 (d, *J* = 1.5 Hz), 34.1 (t, *J* = 2.5 Hz), 31.6, 28.4.

^{19}F NMR (377 MHz, $CDCl_3$): δ-91.72 (d, *J* = 45.5 Hz), -92.07 (d, *J* = 45.1 Hz).



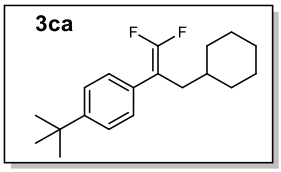
1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (3ba):

The reaction was carried out following the general procedure. Then 44.0 mg colorless oil was obtained in 88% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.12 (m, 4H), 2.35 (s, 3H), 2.30 – 2.19 (m, 2H), 1.72 – 1.56 (m, 5H), 1.32 – 1.19 (m, 1H), 1.17 – 1.05 (m, 3H), 0.97 – 0.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9 (dd, *J* = 289.4, 285.6 Hz), 136.8, 131.1 (dd, *J* = 4.3, 3.0 Hz), 129.1, 128.1 (t, *J* = 3.2 Hz), 90.8 (dd, *J* = 21.7, 13.0 Hz), 35.6 (t, *J* = 2.5 Hz), 35.2, 32.8, 26.4, 26.0, 21.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.86 (d, *J* = 45.6 Hz), -92.22 (d, *J* = 45.4 Hz).



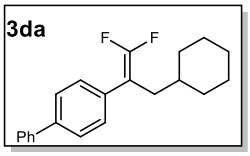
1-(*tert*-butyl)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (3ca):

The reaction was carried out following the general procedure. Then 49.4 mg colorless oil was obtained in 75% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 2H), 7.29 7.31 – 7.27 (m, 2H), 2.35 – 2.27 (m, 2H), 1.81 – 1.61 (m, 5H), 1.38 (s, 9H), 1.31 (s, 1H), 1.22 – 1.14 (m, 3H), 1.05 – 0.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0 (dd, *J* = 290.1, 285.5 Hz), 149.9, 131.0 (dd, *J* = 4.3, 3.5 Hz, 2H), 127.8 (t, *J* = 3.4 Hz), 125.2, 90.7 (dd, *J* = 21.8, 12.4 Hz), 35.6 (t, *J* = 2.5 Hz), 35.1, 34.5, 32.9, 31.3, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.33 (d, *J* = 44.9 Hz), -91.84 (d, *J* = 44.9 Hz).



4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (3da):

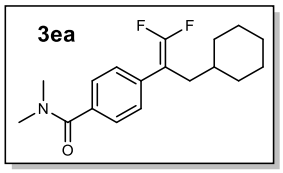
The reaction was carried out following the general procedure. Then 50.0 mg white solid was

obtained in 80% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1H NMR (400 MHz, Chloroform-d) δ 7.65 – 7.54 (m, 4H), 7.50 – 7.30 (m, 5H), 2.41 – 2.23 (m, 2H), 1.75 – 1.57 (m, 5H), 1.38 – 1.25 (m, 1H), 1.19 – 1.09 (m, 3H), 0.99 – 0.87 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1 (dd, *J* = 290.6, 286.3 Hz), 140.6, 139.8, 133.0 (dd, *J* = 4.4, 3.4 Hz), 128.8, 128.6 (t, *J* = 3.4 Hz), 127.3, 127.0, 127.0, 90.8 (dd, *J* = 22.3, 12.3 Hz), 35.7 (t, *J* = 2.4 Hz), 35.1, 32.9, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.64 (d, *J* = 43.4 Hz), -91.20 (d, *J* = 43.4 Hz).



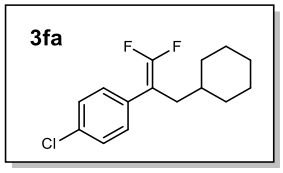
4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-*N*,*N*-dimethylbenzamide (3ea):

The reaction was carried out following the general procedure. Then 33.2 mg colorless oil was obtained in 54% isolated yield using petroleum ether/EtOAc = 1:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.12 (s, 3H), 3.01 (s, 3H), 2.28 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.72 – 1.61 (m, 5H), 1.25 – 1.18 (m, 1H), 1.16 – 1.04 (m, 3H), 0.98 – 0.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 154.0 (dd, *J* = 291.2, 286.7 Hz), 135.5 (dd, *J* = 4.7, 3.3 Hz), 134.9, 128.1 (t, *J* = 3.3 Hz), 127.2, 90.7 (dd, *J* = 22.6, 12.2 Hz), 39.5, 35.5 (t, *J* = 2.1 Hz), 35.3, 34.9, 32.7, 26.3, 25.9.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.20 (d, *J* = 41.8 Hz), -90.86 (d, *J* = 41.8 Hz).



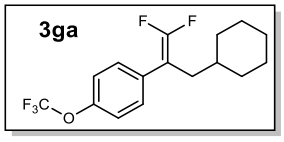
1-chloro-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (3fa):

The reaction was carried out following the general procedure. Then 32.4 mg colorless oil was obtained in 60% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 2.24 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.71 – 1.58 (m, 5H), 1.24 – 1.18 (m, 1H), 1.17 – 1.02 (m, 3H), 0.97 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0 (dd, *J* = 290.7, 286.6 Hz), 132.9, 132.6 (dd, *J* = 4.8, 3.2 Hz), 129.6 (t, *J* = 3.3 Hz), 128.6, 90.3 (dd, *J* = 22.8, 12.5 Hz), 35.7 (t, *J* = 2.4 Hz), 35.1, 32.8, 26.3, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.51 (d, *J* = 42.5 Hz), -91.05 (d, *J* = 42.8 Hz).



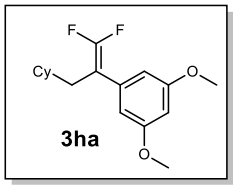
1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-(trifluoromethoxy)benzene (3ga):

The reaction was carried out following the general procedure. Then 35.8 mg colorless oil was obtained in 56% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.26 (dt, *J* = 7.6, 2.4 Hz, 2H), 1.75 – 1.58 (m, 5H), 1.27 – 1.18 (m, 1H), 1.16 – 1.08 (m, 3H), 1.00 – 0.82 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1 (dd, *J* = 290.7, 286.6 Hz), 148.9 – 147.8 (m), 132.8 (dd, *J* = 4.9, 3.2 Hz), 129.6 (t, *J* = 3.4 Hz), 120.8, 90.2 (dd, *J* = 23.1, 12.4 Hz), 35.6 (t, *J* = 2.1 Hz), 35.2, 32.8, 29.7, 26.3, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -57.82, -90.37 (d, *J* = 42.3 Hz), -91.06 (d, *J* = 42.5 Hz).



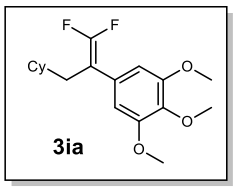
1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-(trifluoromethoxy)benzene (3ha):

The reaction was carried out following the general procedure. Then 43.2 mg colorless oil was obtained in 73% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (dd, *J* = 2.4, 1.2 Hz, 2H), 6.39 (t, *J* = 2.3 Hz, 2H), 3.80 (s, 6H), 2.23 (ddd, *J* = 7.2, 2.8, 2.0 Hz, 2H), 1.71 – 1.56 (m, 5H), 1.34 – 1.20 (m, 1H), 1.18 – 1.06 (m, 3H), 0.98 – 0.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6, 153.9 (dd, *J* = 290.4, 285.9 Hz), 136.1 (dd, *J* = 4.8, 2.9 Hz), 106.7 (t, *J* = 3.3 Hz), 98.9, 91.1 (dd, *J* = 22.4, 12.4 Hz), 55.3, 35.7 (t, *J* = 2.0 Hz), 35.3, 32.8, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.51 (d, *J* = 43.2 Hz), -91.01 (d, *J* = 43.3 Hz).



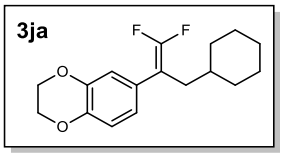
5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,2,3-trimethoxybenzene (3ia):

The reaction was carried out following the general procedure. Then 43.1 mg white solid was obtained in 66% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (s, 2H), 3.86 (d, *J* = 2.0 Hz, 9H), 2.32 – 2.19 (m, 2H), 1.76 – 1.60 (m, 5H), 1.35 – 1.23 (m, 1H), 1.14 (d, *J* = 8.8 Hz, 3H), 1.00 – 0.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9 (dd, *J* = 289.6, 286.0 Hz), 153.0, 137.2, 129.6 (dd, *J* = 4.6, 2.9 Hz), 105.6 (t, *J* = 3.3 Hz), 91.2 (dd, *J* = 22.2, 12.7 Hz), 60.8, 56.1, 35.7 (t, *J* = 2.5 Hz), 35.5, 32.9, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.12 (d, *J* = 44.6 Hz), -91.49 (d, *J* = 44.5 Hz).



6-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine (3ja):

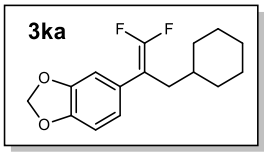
The reaction was carried out following the general procedure. Then 32.4 mg colorless oil was obtained in 55% isolated yield using petroleum ether/EtOAc=20/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 – 6.74 (m, 3H), 4.26 (s, 4H), 2.20 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.74 – 1.61 (m, 5H), 1.35 – 1.18 (m, 1H), 1.19 – 1.04 (m, 3H), 0.99 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9 (dd, *J* = 289.2, 285.7 Hz), 143.2, 142.6, 127.2 (dd, *J* = 3.8, 2.4 Hz), 121.4 (t, *J* = 3.4 Hz), 117.1 (d, *J* = 3.5 Hz), 90.4 (dd, *J* = 21.6, 13.5 Hz), 64.3 (d, *J* = 2.6 Hz), 35.6 (t, *J* = 2.4 Hz), 35.2, 32.8, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -91.87 (d, *J* = 45.6 Hz), -92.07 (d, *J* = 45.4 Hz).

HR-MS (APCI+): m/z calculated for $C_{17}H_{20}F_2O$, $[M]^+$: 294.1426, measured: 294.1417.



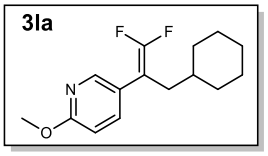
5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzo[*d*][1,3]dioxole (3ka):

The reaction was carried out following the general procedure. Then 43.7 mg colorless oil was obtained in 78% isolated yield using petroleum ether/EtOAc=20/1as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 – 6.74 (m, 3H), 5.96 (s, 2H), 2.20 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.72 – 1.59 (m, 5H), 1.33 – 1.18 (m, 1H), 1.17 – 1.08 (m, 3H), 0.98 – 0.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9 (dd, *J* = 285.9, 285.3 Hz), 147.6, 146.6, 127.7 (d, *J* = 2.0 Hz), 121.8 (t, *J* = 3.2 Hz), 108.8 (t, *J* = 3.4 Hz), 108.2, 101.1, 90.8 (dd, *J* = 19.2, 16.2 Hz), 35.6 (t, *J* = 2.4 Hz), 35.5, 32.8, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.06 (d, *J* = 1.9 Hz).



5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-methoxypyridine (3la):

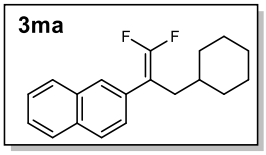
The reaction was carried out following the general procedure. Then 52.4 mg colorless oil was obtained in 98% isolated yield using petroleum ether/EtOAc=10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.52 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 2.27 – 2.20 (m, 2H), 1.71 – 1.62 (m, 5H), 1.31 – 1.20 (m, 1H), 1.12 (s, 3H), 0.98 – 0.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 154.0 (dd, *J* = 290.1, 286.6 Hz), 146.2 (t, *J* = 3.5 Hz), 138.4 (t, *J* = 3.2 Hz), 122.9 – 122.8 (m), 110.6, 88.0 (dd, *J* = 23.9, 12.9 Hz), 53.4, 35.9 – 35.4 (m),

34.9, 32.8, 26.3, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.71 (d, *J* = 44.3 Hz), -91.49 (d, *J* = 44.1 Hz).



2-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)naphthalene (3ma):

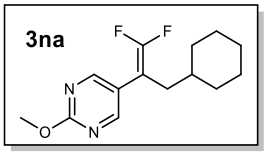
The reaction was carried out following the general procedure. Then 40.1 mg white solid was obtained in 70% isolated yield using petroleum ether as eluent.

According to the general procedure. Yellow oil (49.0 mg, 85%). Rf 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.72 (m, 4H), 7.53 – 7.37 (m, 3H), 2.37 (dt, *J* = 7.2, 2.8 Hz, 2H), 1.79 – 1.54 (m, 5H), 1.36 – 1.21 (m, 1H), 1.18 – 1.01 (m, 3H), 1.01 – 0.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.2 (dd, *J* = 290.4, 286.3 Hz), 133.2, 132.4, 131.5 (dd, *J* = 4.5, 3.3 Hz), 127.9, 127.9, 127.6, 127.3 (t, *J* = 3.4 Hz), 126.3, 126.2, 126.0, 91.2 (dd, *J* = 22.2, 12.5 Hz), 35.7, 35.3, 32.9, 26.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -90.84 (d, *J* = 43.2 Hz), -91.55 (d, *J* = 43.5 Hz).



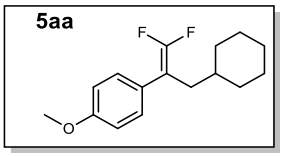
5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-methoxypyrimidine (3na):

The reaction was carried out following the general procedure. Then 30.6 mg colorless oil was obtained in 57% isolated yield using petroleum ether/EtOAc=10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 0.8 Hz, 2H), 4.03 (s, 3H), 2.25 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.74 – 1.59 (m, 5H), 1.31 – 1.21 (m, 1H), 1.18 – 1.08 (m, 3H), 1.00 – 0.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.5, 158.4 (t, *J* = 3.7 Hz), 157.4 – 150.8 (m), 121.6 – 121.5 (m), 85.4 (dd, *J* = 25.3, 12.9 Hz), 55.0, 35.6, 34.4, 32.7, 26.2, 25.9.

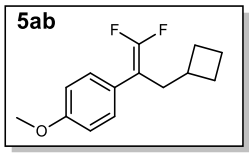
^{19}F NMR (377 MHz, $CDCl_3$): δ -88.71 (d, *J* = 40.2 Hz), -89.69 (d, *J* = 40.1 Hz).



1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (5aa):

The reaction was carried out following the general procedure. Then 48.4 mg colorless oil was obtained in 91% isolated yield using petroleum ether as eluent.

The spectral data of the **5aa** is consistent with the **3aa**.



1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (5ab):

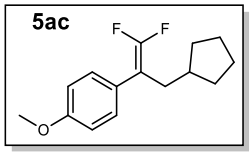
The reaction was carried out following the general procedure. Then 31.0 mg colorless oil was obtained in 65% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.16 (m, 2H), 6.92 – 6.83 (m, 2H), 3.81 (s, 3H), 2.43 (dt, *J* = 7.6, 2.4 Hz, 2H), 2.33 – 2.20 (m, 1H), 1.98 – 1.88 (m, 2H), 1.81 – 1.72 (m, 2H), 1.67 – 1.55 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 153.8 (dd, *J* = 288.2, 285.6 Hz), 129.4 (t, *J* = 3.2 Hz), 128.6, 126.1 (dd, *J* = 4.3, 2.4 Hz), 113.7, 90.7 (dd, *J* = 21.9, 13.6 Hz), 55.2, 34.7 (d, *J* = 1.2 Hz), 34.2 (t, *J* = 2.5 Hz), 27.9, 18.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -93.01 (d, *J* = 47.7 Hz), -93.30 (d, *J* = 47.7 Hz).

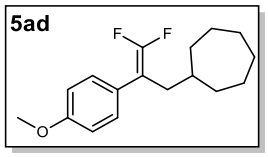
HR-MS (APCI+): m/z calculated for $C_{14}H_{16}F_2O$, $[M]^+$: 238.1164, measured: 238.1156.



1-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (5ac):

The reaction was carried out following the general procedure. Then 39.3 mg colorless oil was obtained in 78% isolated yield using petroleum ether as eluent.

The spectral data of the **5ac** is consistent with the **3ad**.



(3,3-difluoro-2-(4-methoxyphenyl)allyl)cycloheptane (5ad):

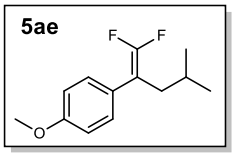
The reaction was carried out following the general procedure. Then 44.8 mg white solid was obtained in 80% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.25 (dt, *J* = 7.2, 2.8 Hz, 2H), 1.72 – 1.55 (m, 4H), 1.54 – 1.39 (m, 5H), 1.35 – 1.25 (m, 2H), 1.22 – 1.10 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 153.9 (dd, *J* = 288.5, 285.3 Hz), 129.4 (t, *J* = 3.2 Hz), 126.3 – 125.9 (m), 113.8, 91.0 (dd, *J* = 21.5, 13.3 Hz), 55.2, 36.9 (t, *J* = 2.2 Hz), 35.7, 34.0, 28.4, 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.61 (d, *J* = 46.9 Hz), -92.89 (d, *J* = 46.9 Hz).

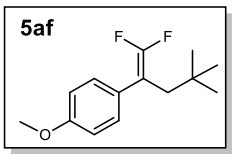
HR-MS (APCI+): m/z calculated for $C_{17}H_{22}F_2O$, $[M]^+$: 280.1633, measured: 280.1624.



1-(1,1-difluoro-4-methylpent-1-en-2-yl)-4-methoxybenzene (5ae):

The reaction was carried out following the general procedure. Then 29.9 mg colorless oil was obtained in 66% isolated yield using petroleum ether as eluent.

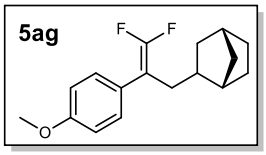
The spectral data of the **5ae** is consistent with the **3ab**.



1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-methoxybenzene (5cf):

The reaction was carried out following the general procedure. Then 36.0 mg colorless oil was obtained in 75% isolated yield using petroleum ether as eluent.

The spectral data of the **5af** is consistent with the **3ac**.



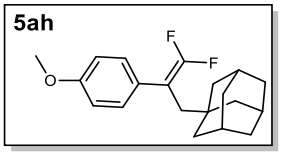
(1*S*,4*R*)-2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)bicyclo[2.2.1]heptane (5ag):

The reaction was carried out following the general procedure. Then 32.8 mg colorless oil was obtained in 59% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.17 (m, 2H), 6.93 – 6.85 (m, 2H), 3.81 (s, 3H), 2.35 – 2.24 (m, 1H), 2.19 (s, 1H), 2.17 – 2.09 (m, 1H), 1.95 (s, 1H), 1.47 – 1.33 (m, 4H), 1.32 – 1.24 (m, 1H), 1.14 – 0.98 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 157.0 – 150.8 (m), 129.5 (t, J = 3.1 Hz), 126.1, 113.8, 91.1 (t, J = 17.5 Hz), 55.2, 40.5, 39.8 (t, J = 2.4 Hz), 37.2, 36.7, 35.2, 34.3, 29.7, 28.7.

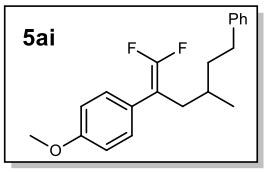
^{19}F NMR (377 MHz, $CDCl_3$): δ -93.09.



(1*R*,3*R*,5*S*)-1-(3,3-difluoro-2-(4-methoxyphenyl)allyl)adamantane (5ah):

The reaction was carried out following the general procedure. Then 17.0 mg white solid was obtained in 26% isolated yield using petroleum ether as eluent.

The spectral data of the **5ah** is consistent with the **3ae**.



1-(1,1-difluoro-4-methyl-6-phenylhex-1-en-2-yl)-4-methoxybenzene (5ai):

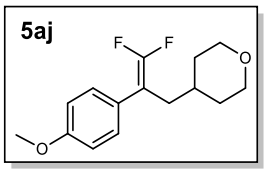
The reaction was carried out following the general procedure. Then 53.7 mg white solid was obtained in 85% isolated yield using petroleum ether as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.13 (m, 5H), 7.14 – 7.07 (m, 2H), 6.89 – 6.84 (m, 2H), 3.79 (s, 3H), 2.66 – 2.56 (m, 1H), 2.54 – 2.44 (m, 1H), 2.43 – 2.36 (m, 1H), 2.27 – 2.17 (m, 1H), 1.69 – 1.59 (m, 1H), 1.53 – 1.38 (m, 2H), 0.91 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 153.8 (dd, *J* = 288.3, 285.8 Hz), 142.6, 129.4 (t, *J* = 3.1 Hz), 128.3, 128.2, 125.9 (dd, *J* = 3.6, 1.9 Hz), 125.6, 113.8, 90.8 (dd, *J* = 20.7, 14.5 Hz), 55.2, 38.2, 34.8, 33.2, 30.7 (t, *J* = 2.4 Hz), 19.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -92.36 (d, *J* = 46.4 Hz), -92.54 (d, *J* = 46.6 Hz).

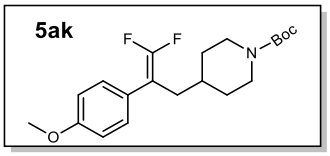
HR-MS (APCI+): m/z calculated for $C_{20}H_{22}F_2O$, $[M]^+$: 316.1633, measured: 316.1629.



4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)tetrahydro-2*H*-pyran (5aj):

The reaction was carried out following the general procedure. Then 38.1 mg colorless oil was obtained in 71% isolated yield using petroleum ether/EtOAc=20/1 as eluent.

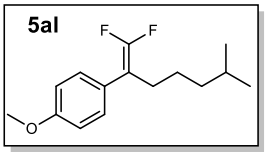
The spectral data of the **5aj** is consistent with the **3al**.



***tert*-butyl 4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)piperidine-1-carboxylate (5ak):**

The reaction was carried out following the general procedure. Then 68.3 mg colorless oil was obtained in 93% isolated yield using petroleum ether/EtOAc=10/1 as eluent.

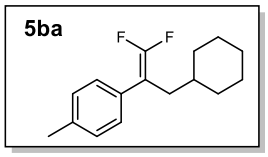
The spectral data of the **5ak** is consistent with the **3an**.



1-(1,1-difluoro-6-methylhept-1-en-2-yl)-4-methoxybenzene (5al):

The reaction was carried out following the general procedure. Then 31.0 mg colorless oil was obtained in 61% isolated yield using petroleum ether as eluent.

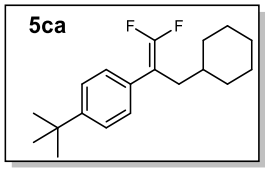
The spectral data of the **5al** is consistent with the **3af**.



1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (5ba):

The reaction was carried out following the general procedure. Then 37.5 mg colorless oil was obtained in 72% isolated yield using petroleum ether as eluent.

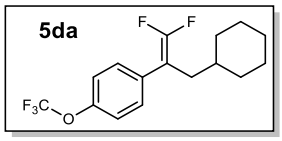
The spectral data of the **5ba** is consistent with the **3ba**.



1-(*tert*-butyl)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (5ca):

The reaction was carried out following the general procedure. Then 42.1 mg colorless oil was obtained in 72% isolated yield using petroleum ether as eluent.

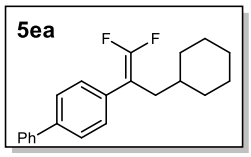
The spectral data of the **5ca** is consistent with the **3ca**.



1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-(trifluoromethoxy)benzene (5da):

The reaction was carried out following the general procedure. Then 35.9 mg colorless oil was obtained in 56% isolated yield using petroleum ether as eluent.

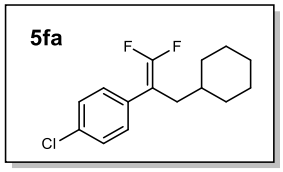
The spectral data of the **5da** is consistent with the **3ga**.



4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (5ea):

The reaction was carried out following the general procedure. Then 30.0 mg white solid was obtained in 48% isolated yield using petroleum ether as eluent.

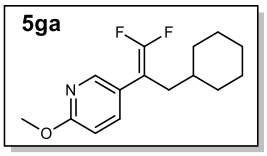
The spectral data of the **5ea** is consistent with the **3da**.



1-chloro-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (5fa):

The reaction was carried out following the general procedure. Then 25.9 mg colorless oil was obtained in 48% isolated yield using petroleum ether as eluent.

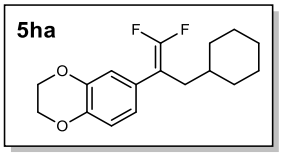
The spectral data of the **5fa** is consistent with the **3fa**.



5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-methoxypyridine (5ga):

The reaction was carried out following the general procedure. Then 21.4 mg colorless oil was obtained in 40% isolated yield using petroleum ether/EtOAc=5/1 as eluent.

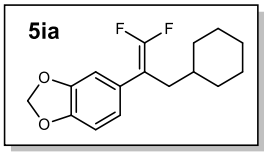
The spectral data of the **5ga** is consistent with the **3la**.



6-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine (5ha):

The reaction was carried out following the general procedure. Then 47.7 mg colorless oil was obtained in 81% isolated yield using petroleum ether/EtOAc=10/1 as eluent.

The spectral data of the **5ha** is consistent with the **3ja**.

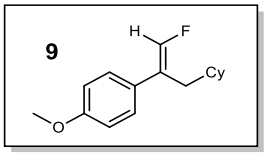


5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzo[*d*][1,3]dioxole (5ia):

The reaction was carried out following the general procedure. Then 42.1 mg colorless oil was obtained in 75% isolated yield using petroleum ether/EtOAc=10/1 as eluent.

The spectral data of the **5ia** is consistent with the **3ka**.

Application:



(*E*)-1-(3-cyclohexyl-1-fluoroprop-1-en-2-yl)-4-methoxybenzene (9):

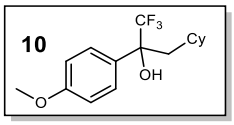
The reaction was carried out following the application procedure. 37.5 mg colorless oil was obtained in 80% isolated yield using petroleum ether/EtOAc=200/1 as eluent. (99% ^{19}F NMR yield, 80% isolated yield, 37.5 mg, r.r. = 95:5)

^{1}H NMR (400 MHz, $CDCl_3$): 7.23 – 7.15 (m, 2H), 6.89 – 6.83 (m, 2.5 H), 6.66 (s, 0.5 H), 3.80 (s, 3H), 2.66 – 2.08 (m, 2H), 1.85 – 1.52 (m, 5H), 1.33 – 1.21 (m, 1H), 1.17 – 1.05 (m, 3H), 1.01 – 0.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 145.5 (d, J = 257.4 Hz), 129.2 (d, J = 9.2 Hz), 127.8 (d, J = 2.9 Hz), 123.2 (d, J = 9.4 Hz), 113.9, 55.2, 35.6 (d, J = 2.3 Hz), 34.2 (d, J = 3.0 Hz), 33.0, 26.4, 26.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -131.81.

HR-MS (APCI+): m/z calculated for $C_{16}H_{21}FO$, $[M]^+$: 248.1571, measured: 248.1566.



3-cyclohexyl-1,1,1-trifluoro-2-(4-methoxyphenyl)propan-2-ol (10):

The reaction was carried out following the application procedure. 97.0 mg colorless oil was obtained in 80% isolated yield using petroleum ether/EtOAc=10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 7.49 – 7.42 (m, 2H), 6.95 – 6.87 (m, 2H), 3.81 (s, 3H), 2.40 (s, 1H), 2.12 (dd, *J* = 14.8, 4.6 Hz, 1H), 1.88 – 1.76 (m, 2H), 1.68 – 1.48 (m, 3H), 1.38 – 1.24 (m, 2H), 1.16 – 0.94 (m, 4H), 0.91 – 0.77 (m, 1H).

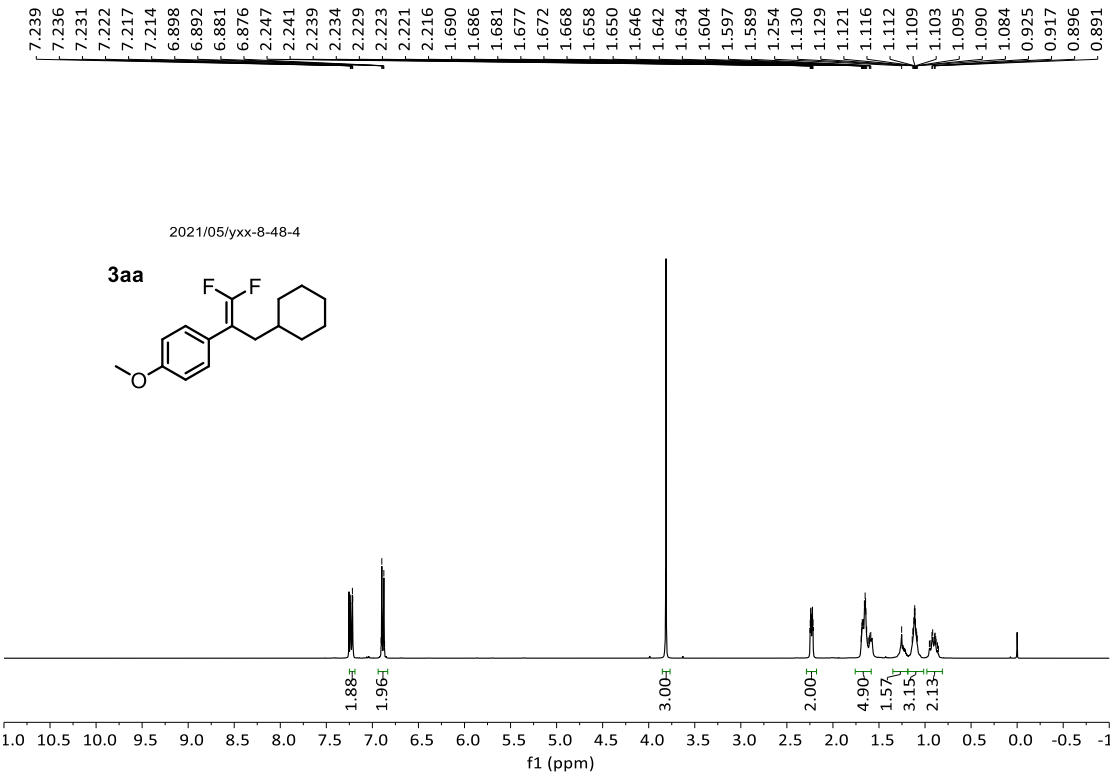
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 128.7, 127.6 (d, *J* = 1.5 Hz), 113.5, 78.1 – 77.2 (m), 56.1, 55.1, 41.8, 34.6 (d, *J* = 9.8 Hz), 32.5, 26.1 (d, *J* = 6.9 Hz), 26.0.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.97.

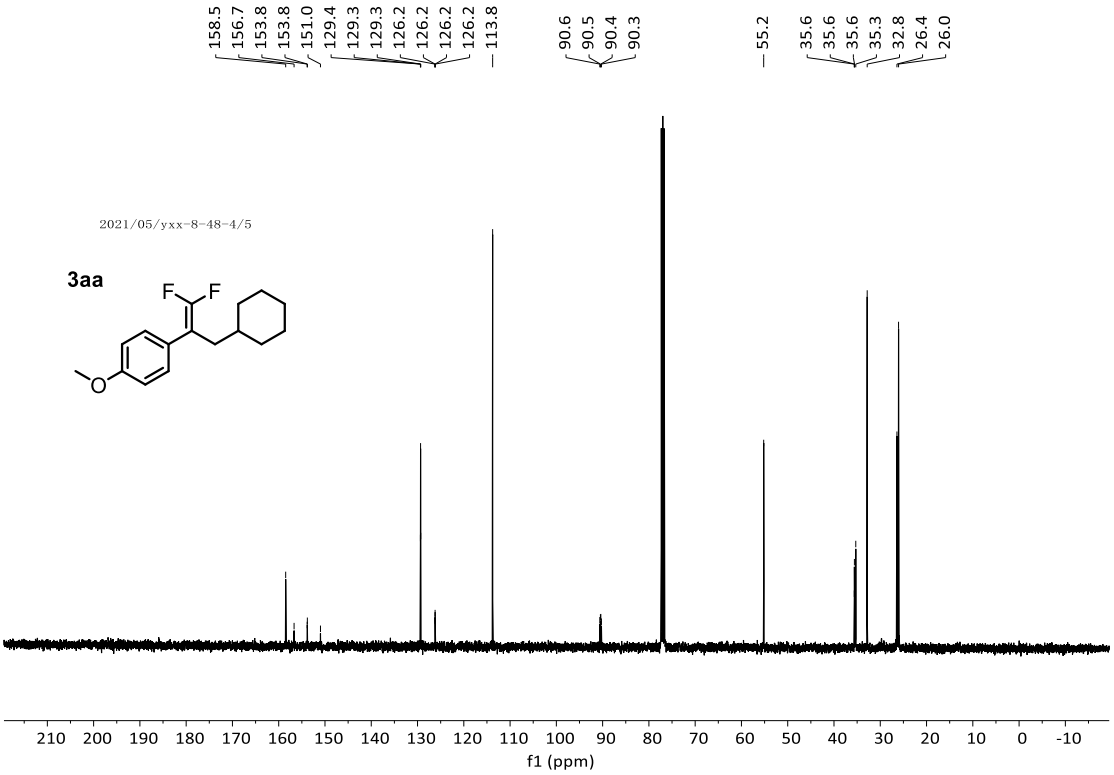
HR-MS (APCI+): m/z calculated for $C_{16}H_{21}F_3O_2$, $[M]^+$: 302.1488, measured: 302.1484.

VII. NMR spectra

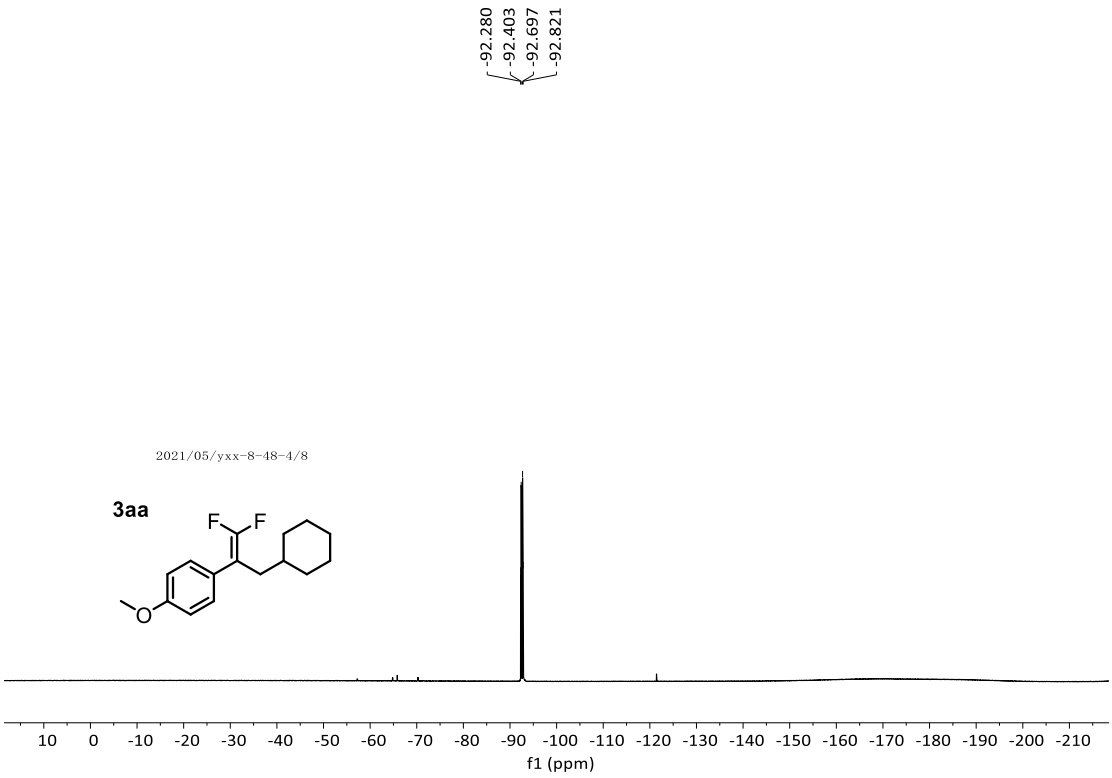
^{1}H NMR (400 MHz, $CDCl_3$):



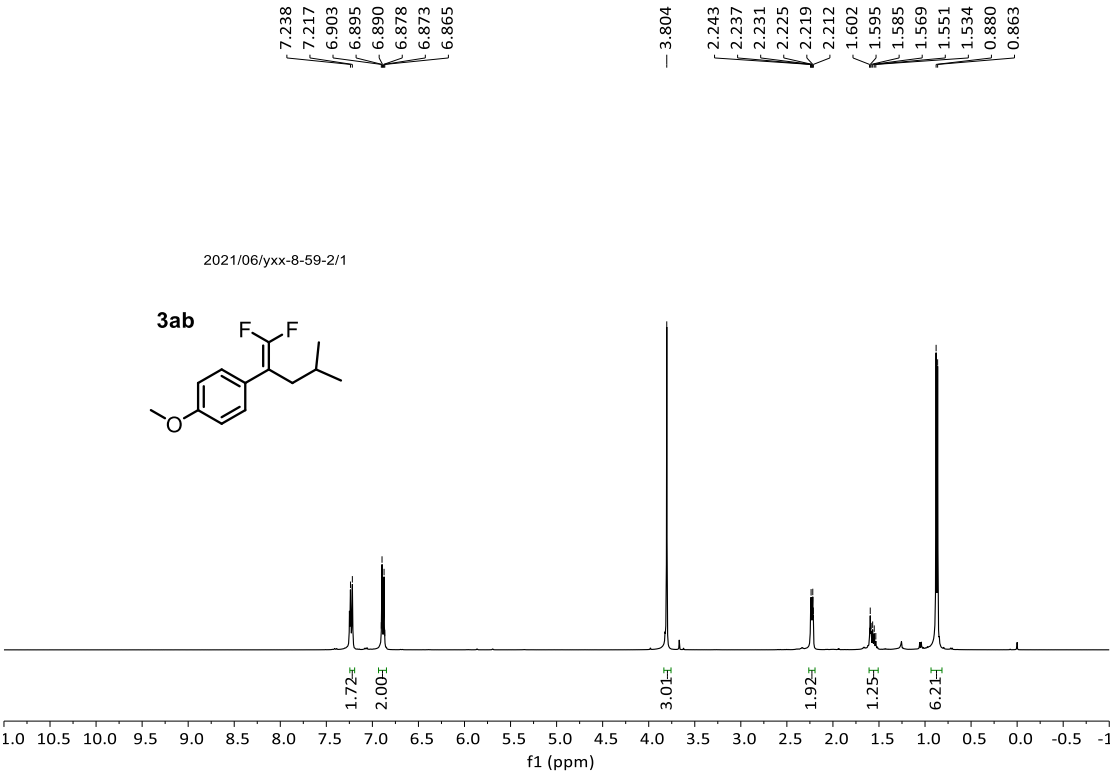
^{13}C NMR (101 MHz, $CDCl_3$):



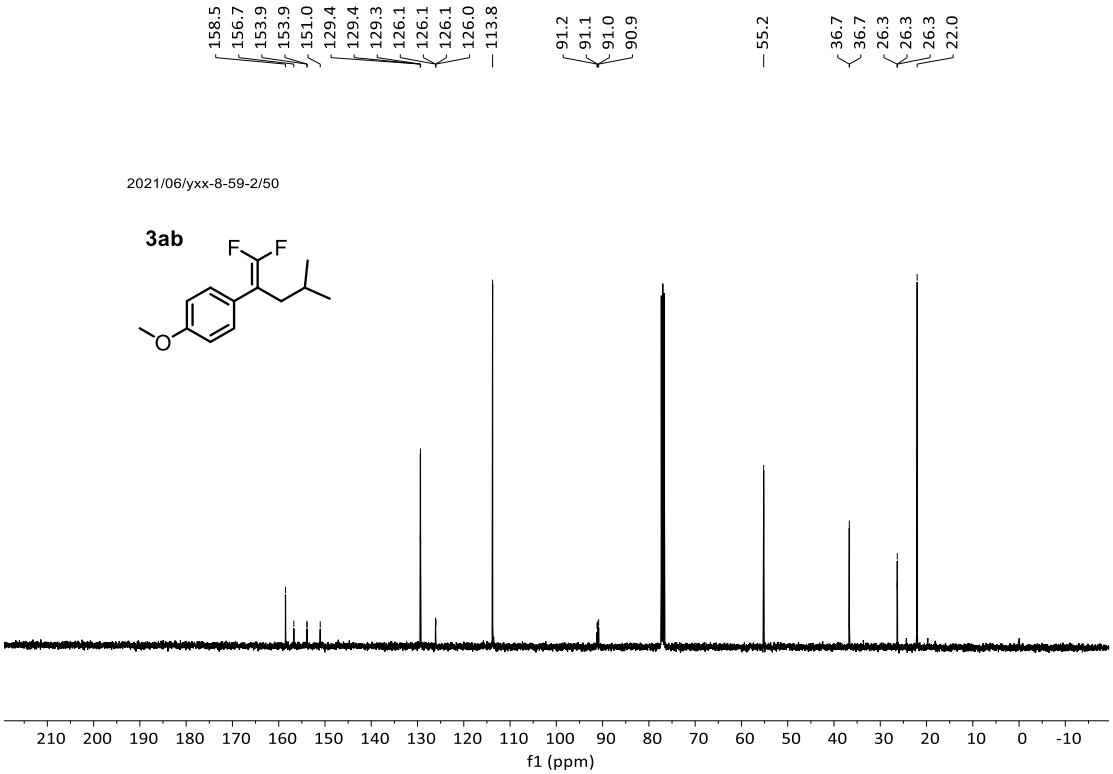
^{19}F NMR (377 MHz, $CDCl_3$):



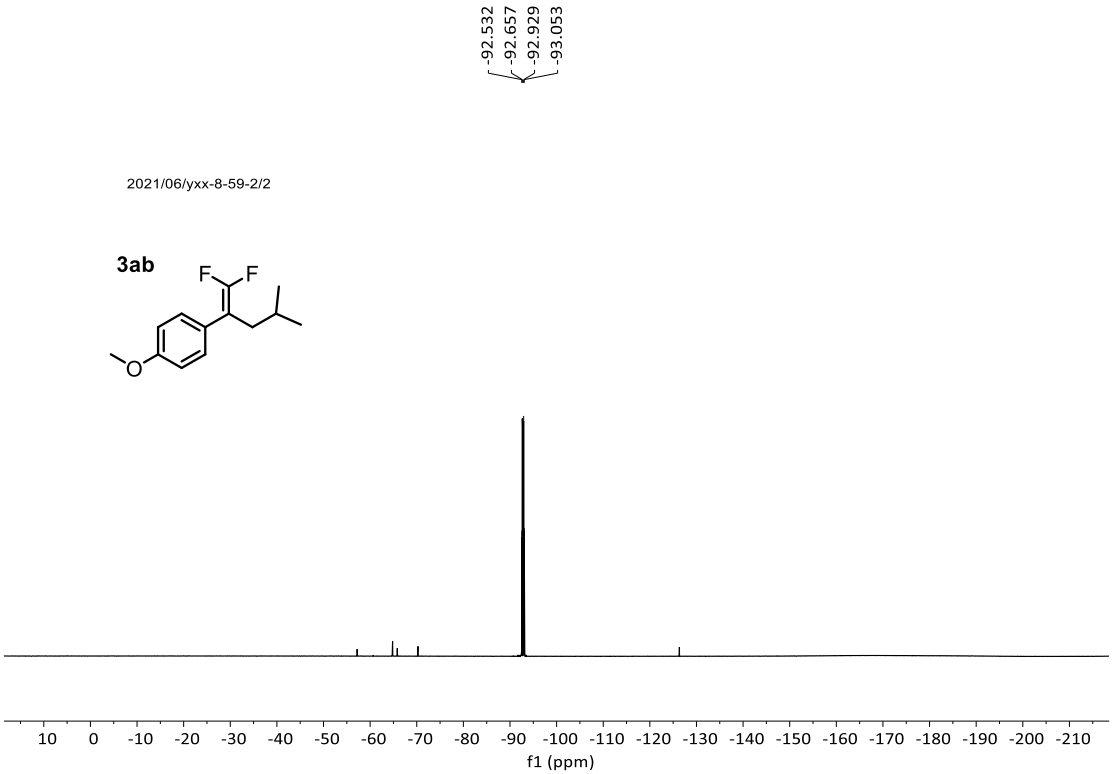
^{1}H NMR (400 MHz, $CDCl_3$):



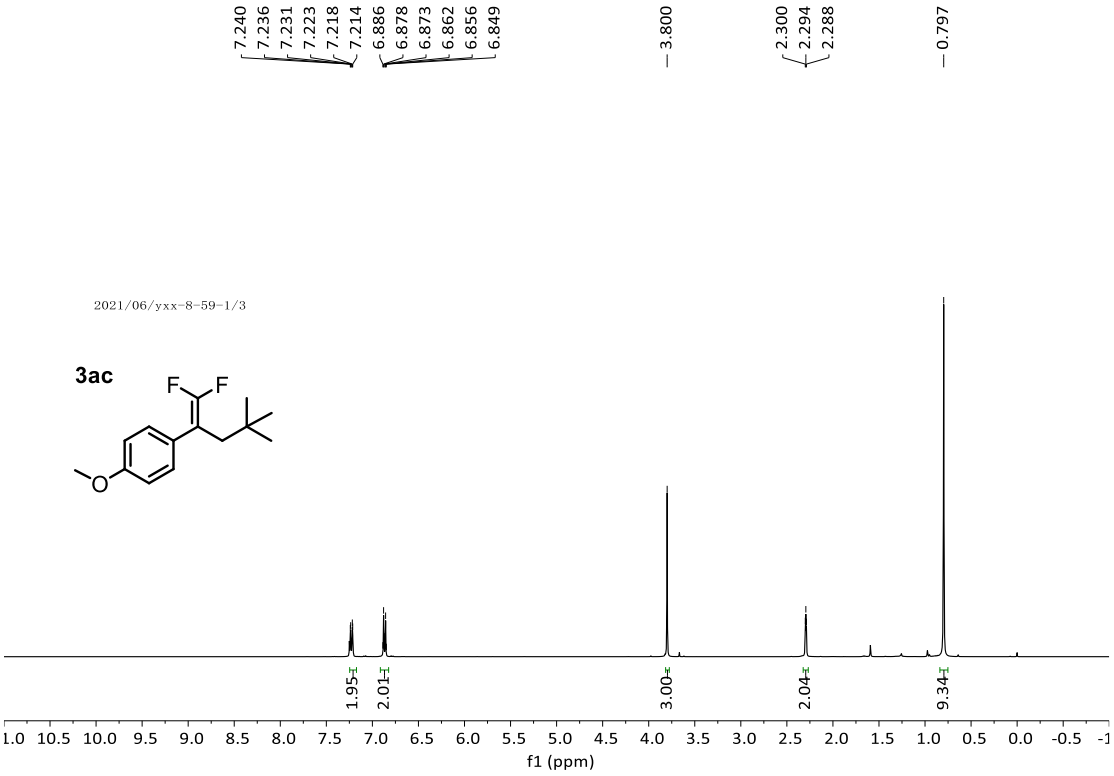
^{13}C NMR (101 MHz, $CDCl_3$):



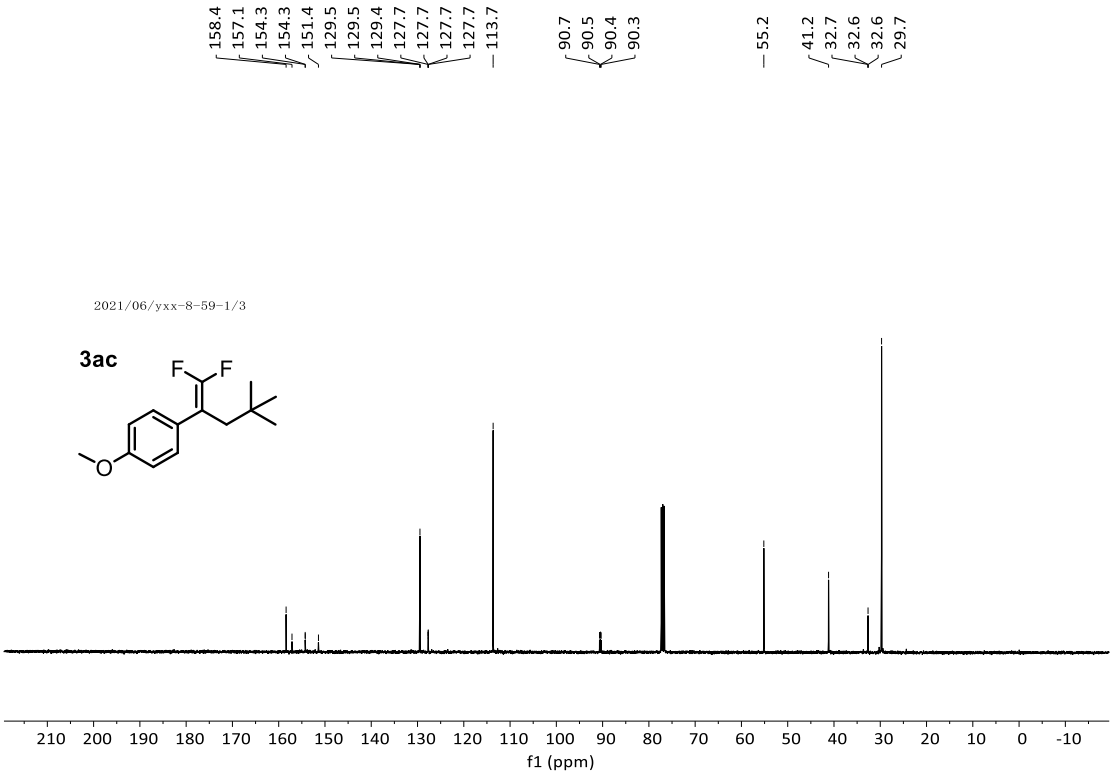
^{19}F NMR (377 MHz, $CDCl_3$):



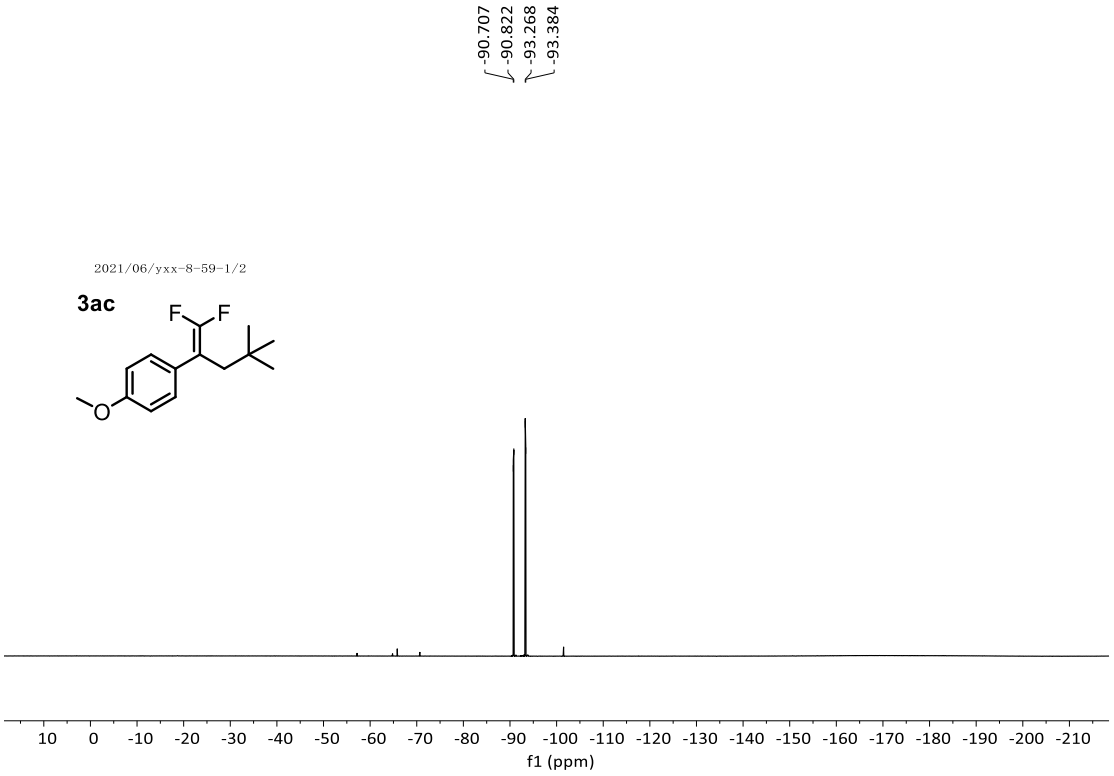
^{1}H NMR (400 MHz, $CDCl_3$):



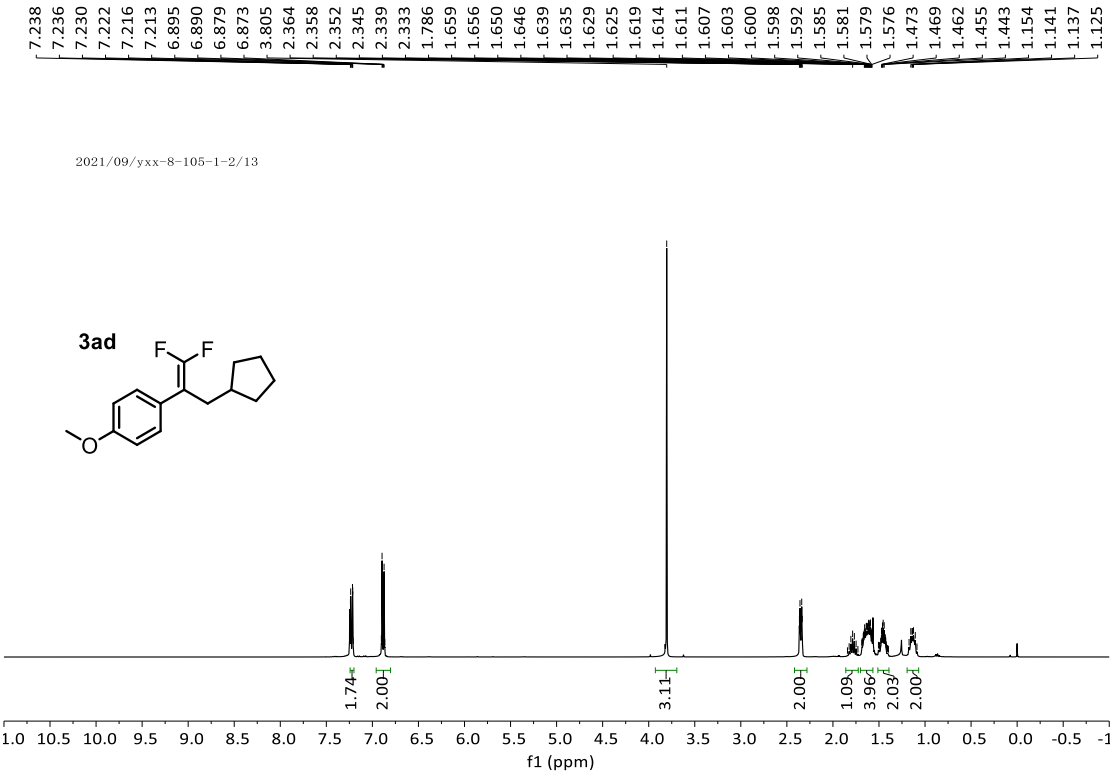
^{13}C NMR (101 MHz, $CDCl_3$):



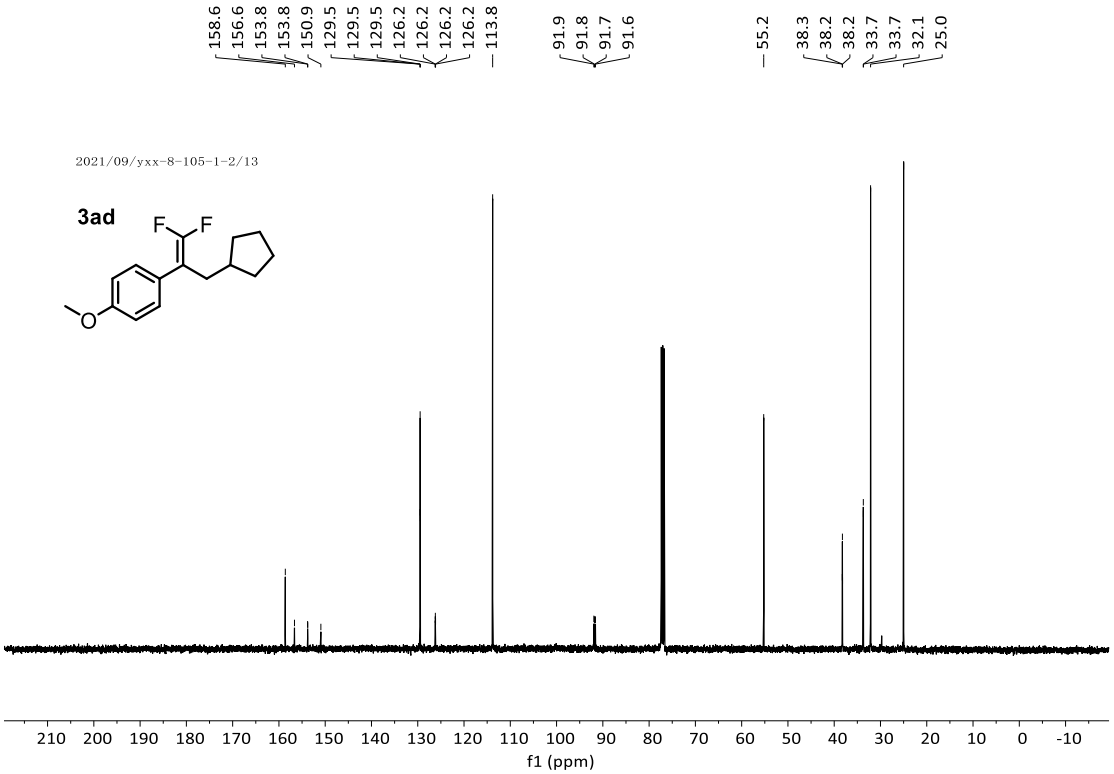
^{19}F NMR (377 MHz, $CDCl_3$):



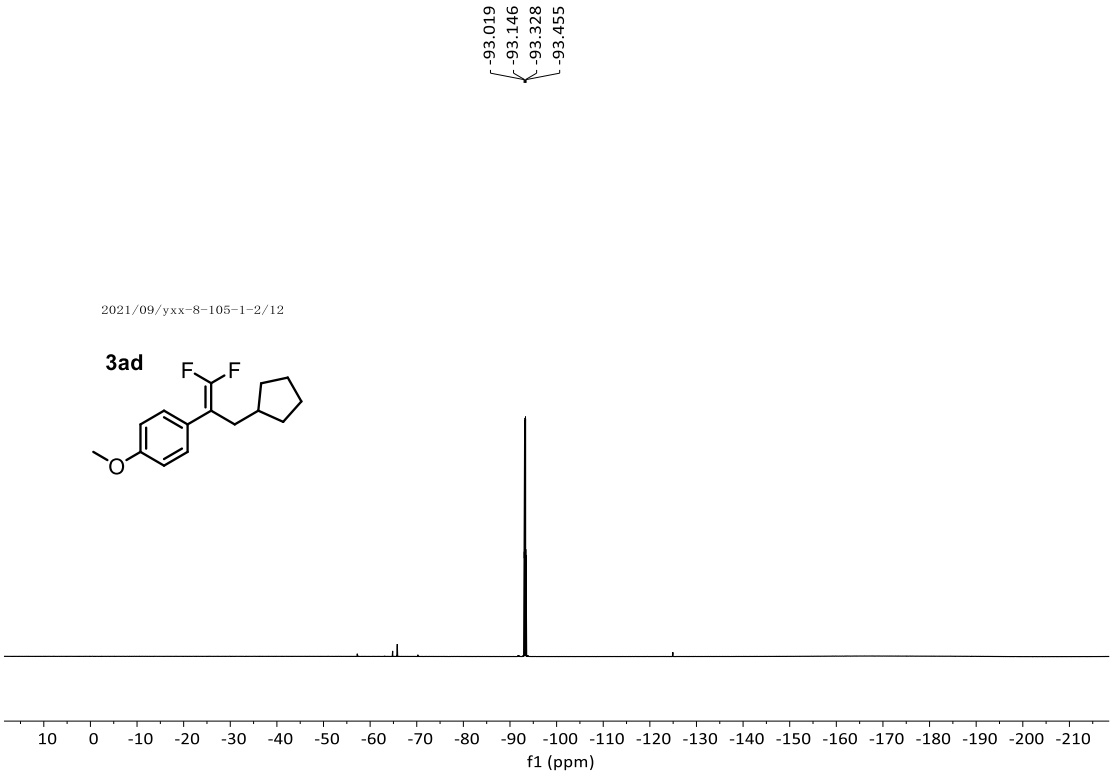
^{1}H NMR (400 MHz, $CDCl_3$):



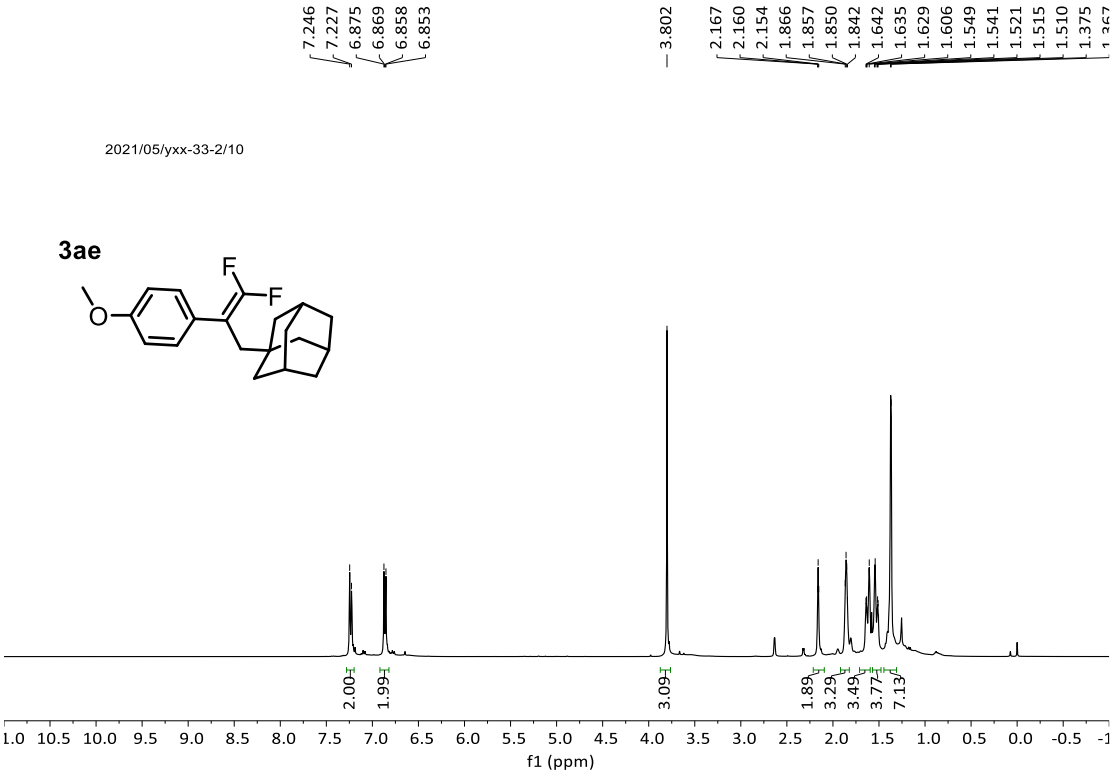
^{13}C NMR (101 MHz, $CDCl_3$):



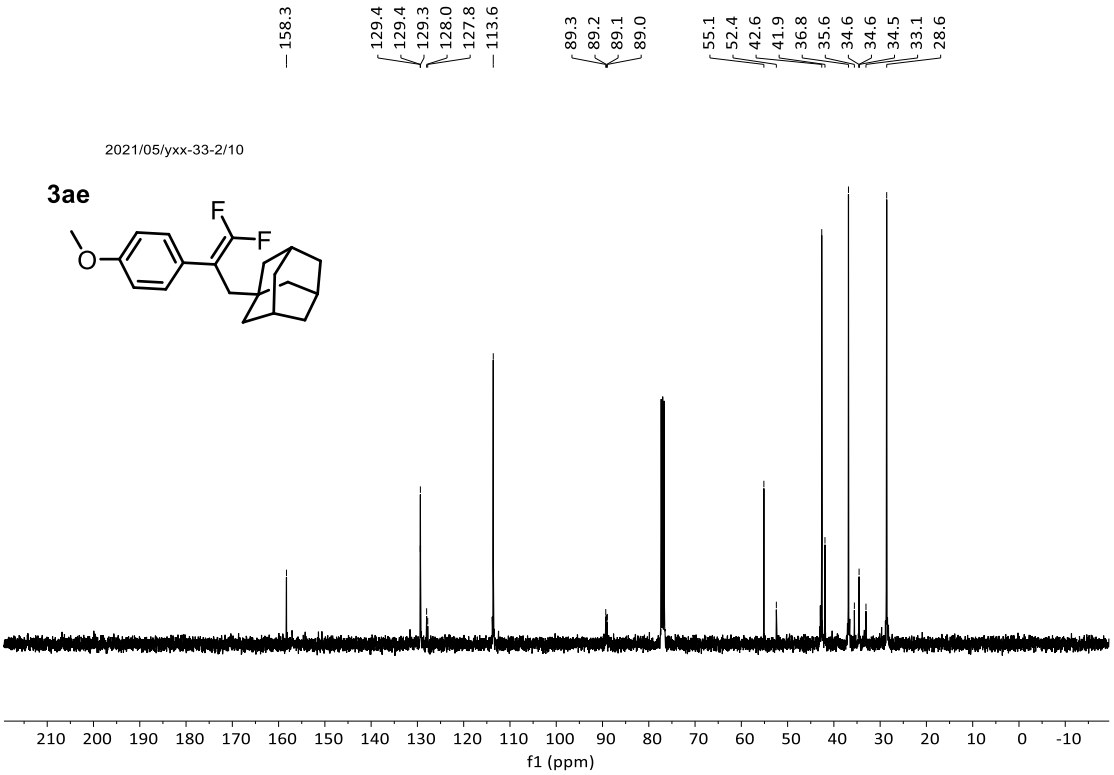
^{19}F NMR (377 MHz, $CDCl_3$):



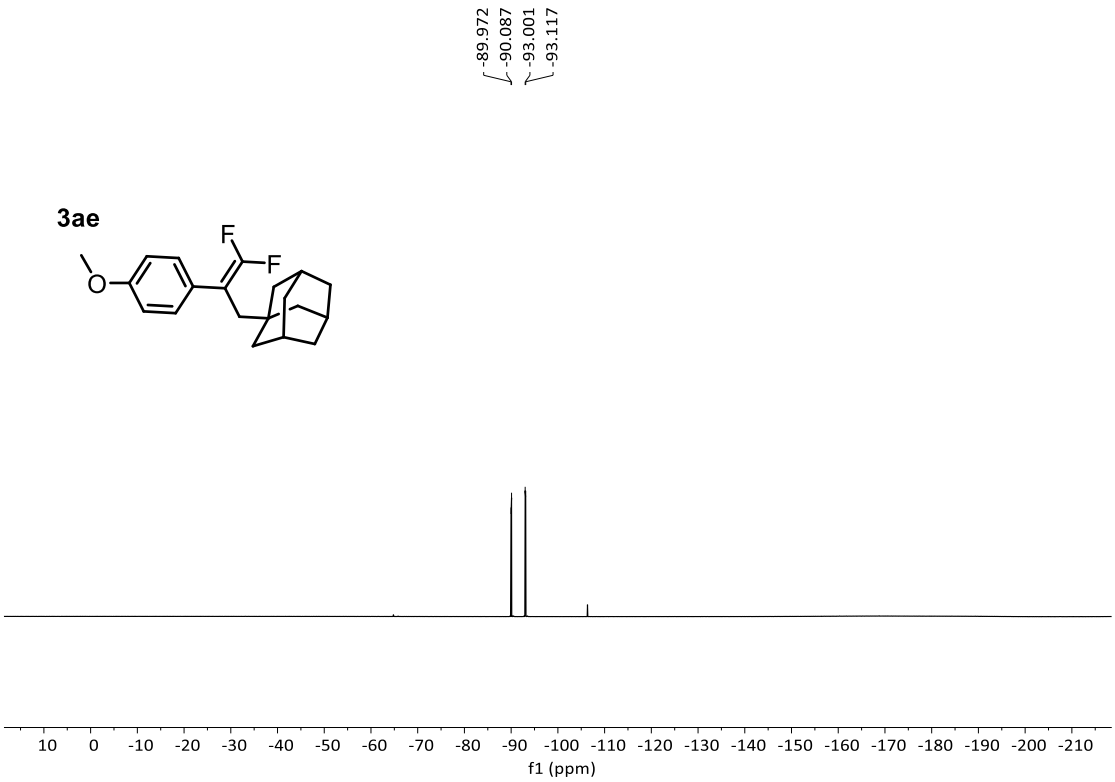
^{1}H NMR (400 MHz, $CDCl_3$):



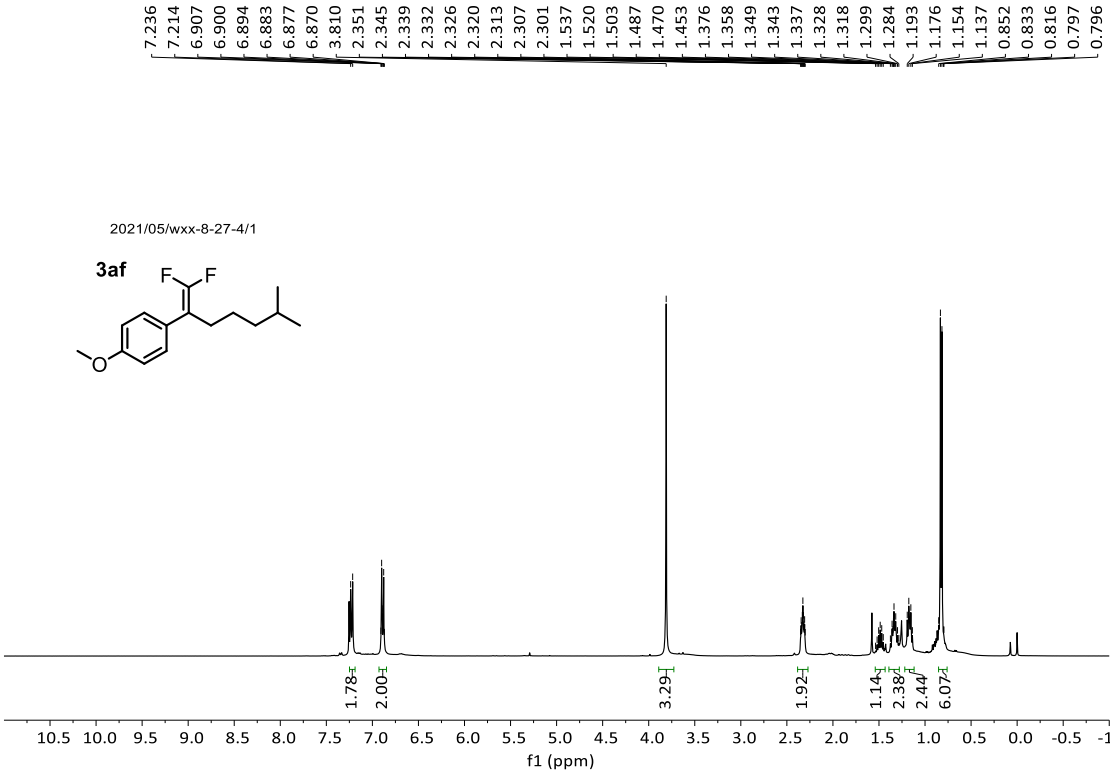
^{13}C NMR (101 MHz, $CDCl_3$):



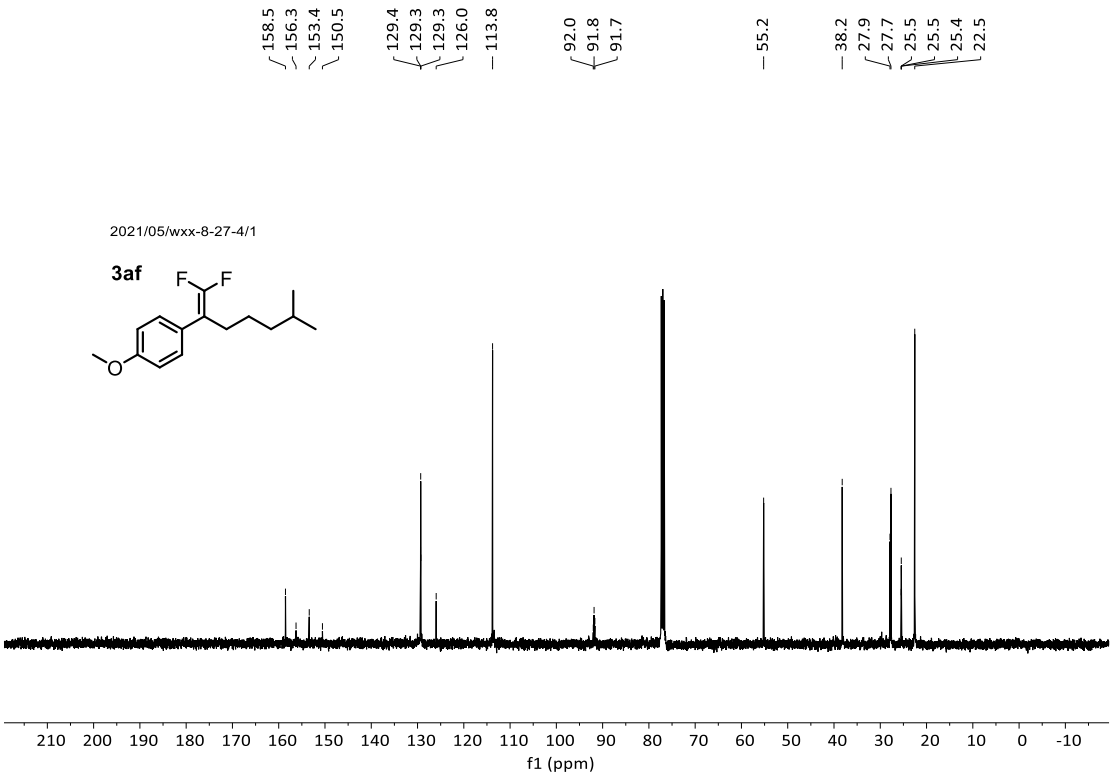
^{19}F NMR (377 MHz, $CDCl_3$):



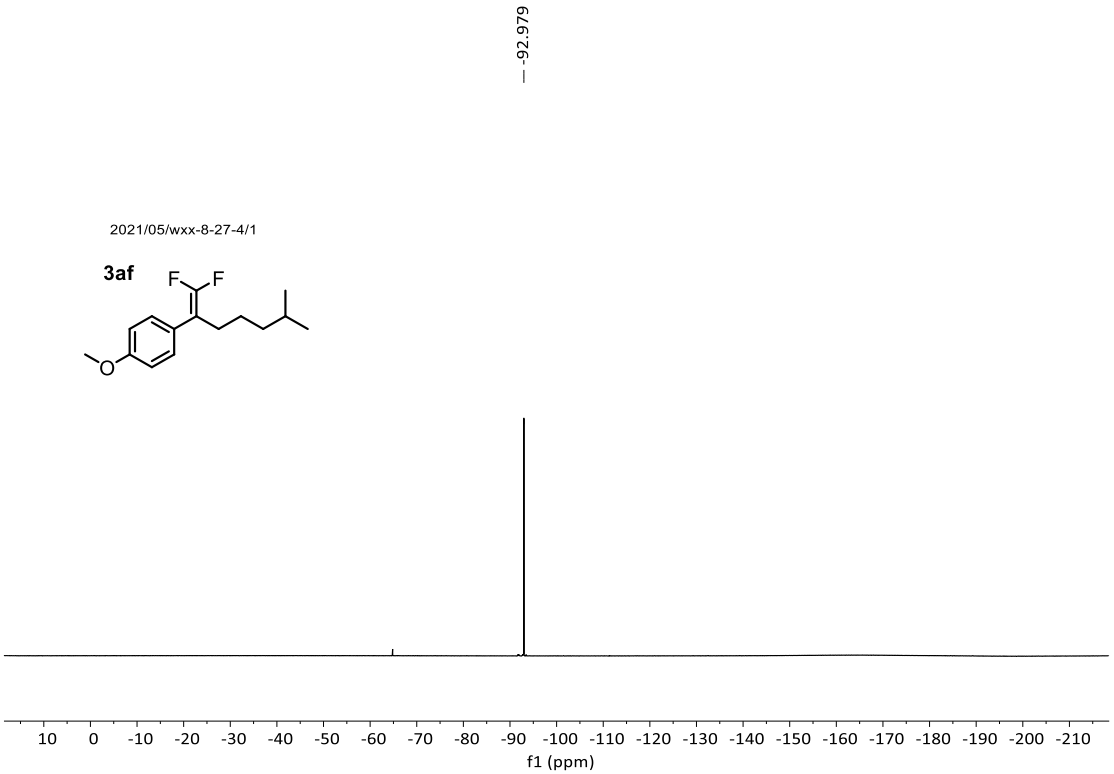
^{1}H NMR (400 MHz, $CDCl_3$):



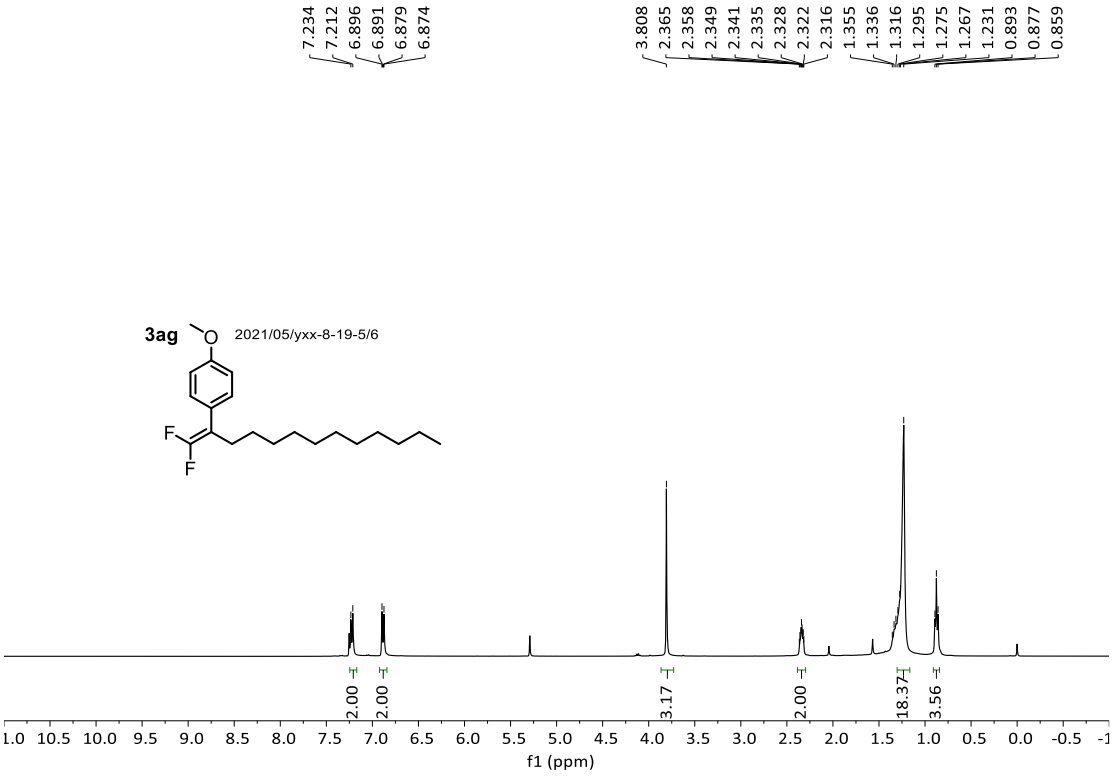
^{13}C NMR (101 MHz, $CDCl_3$):



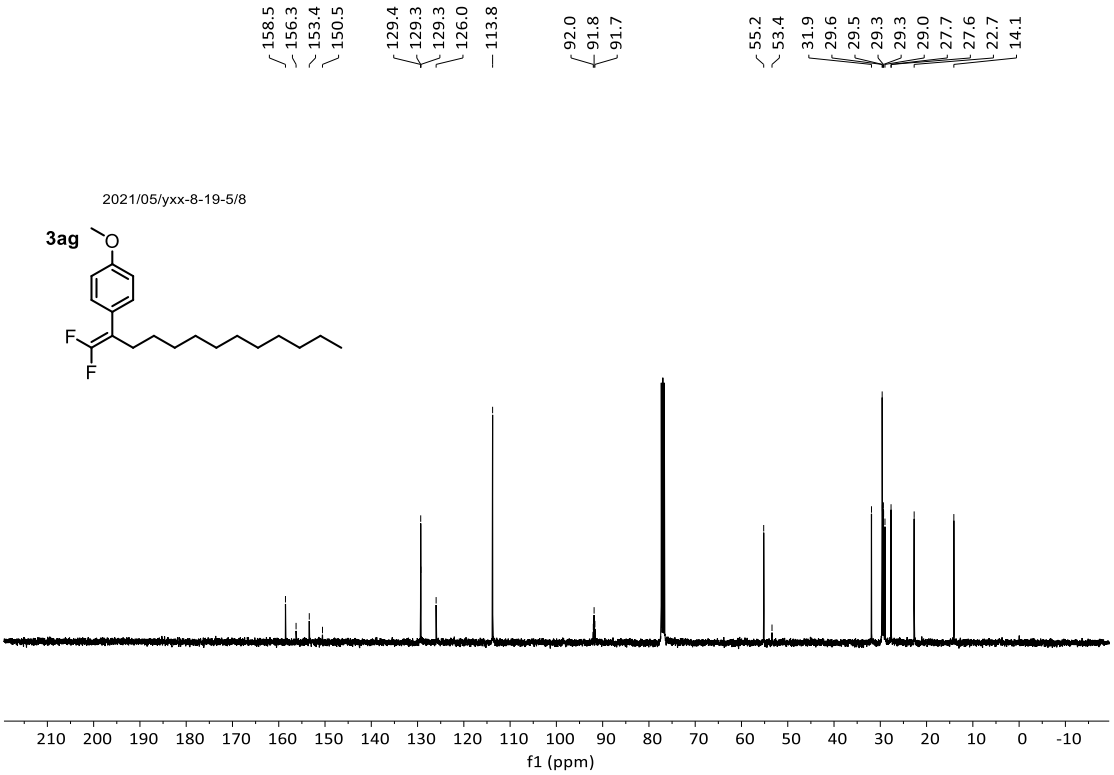
^{19}F NMR (377 MHz, $CDCl_3$):



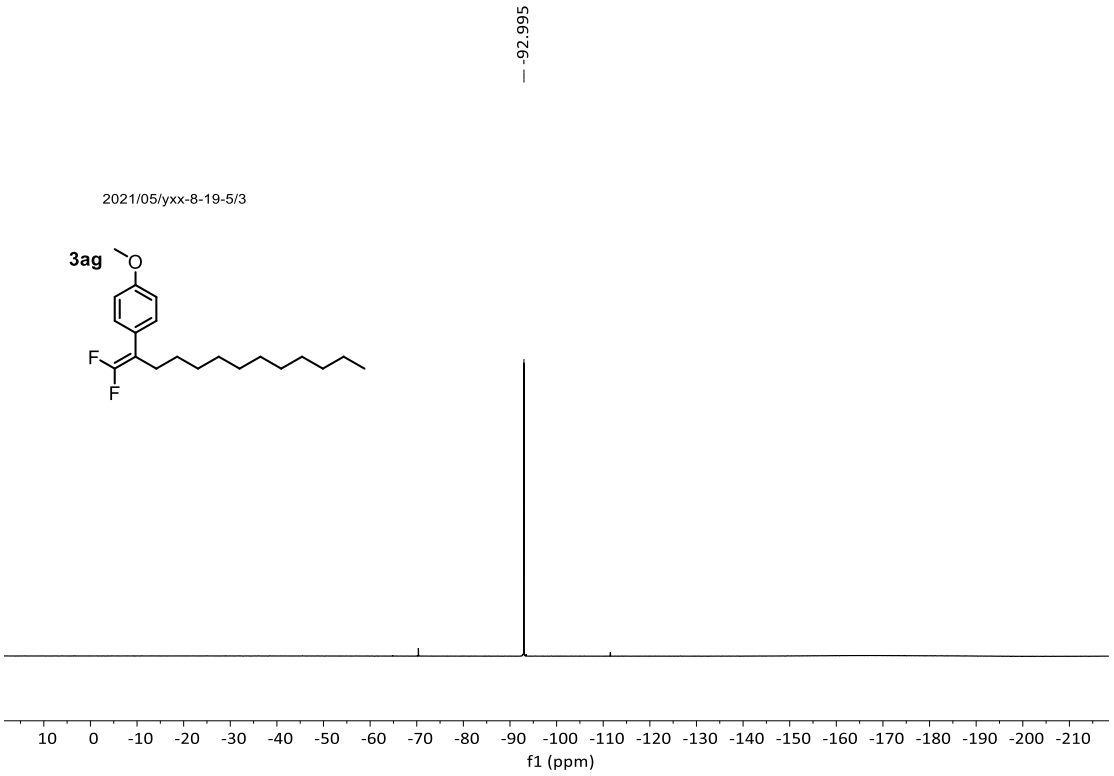
^{1}H NMR (400 MHz, $CDCl_3$):



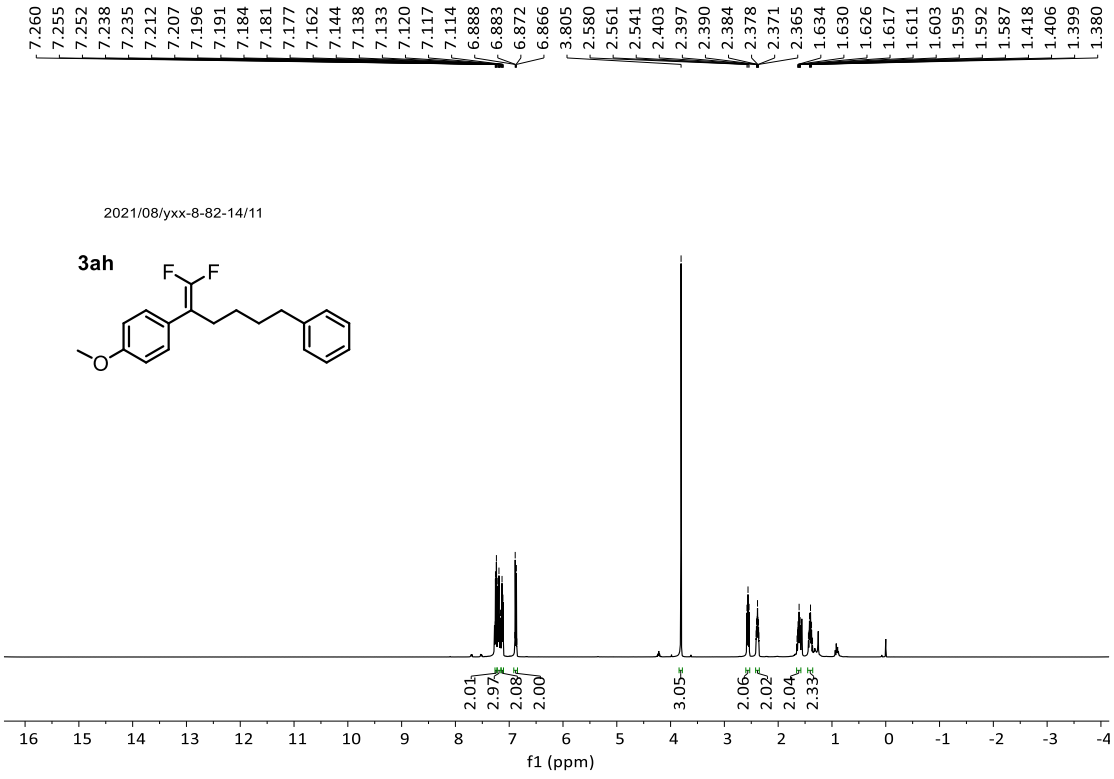
^{13}C NMR (101 MHz, $CDCl_3$):



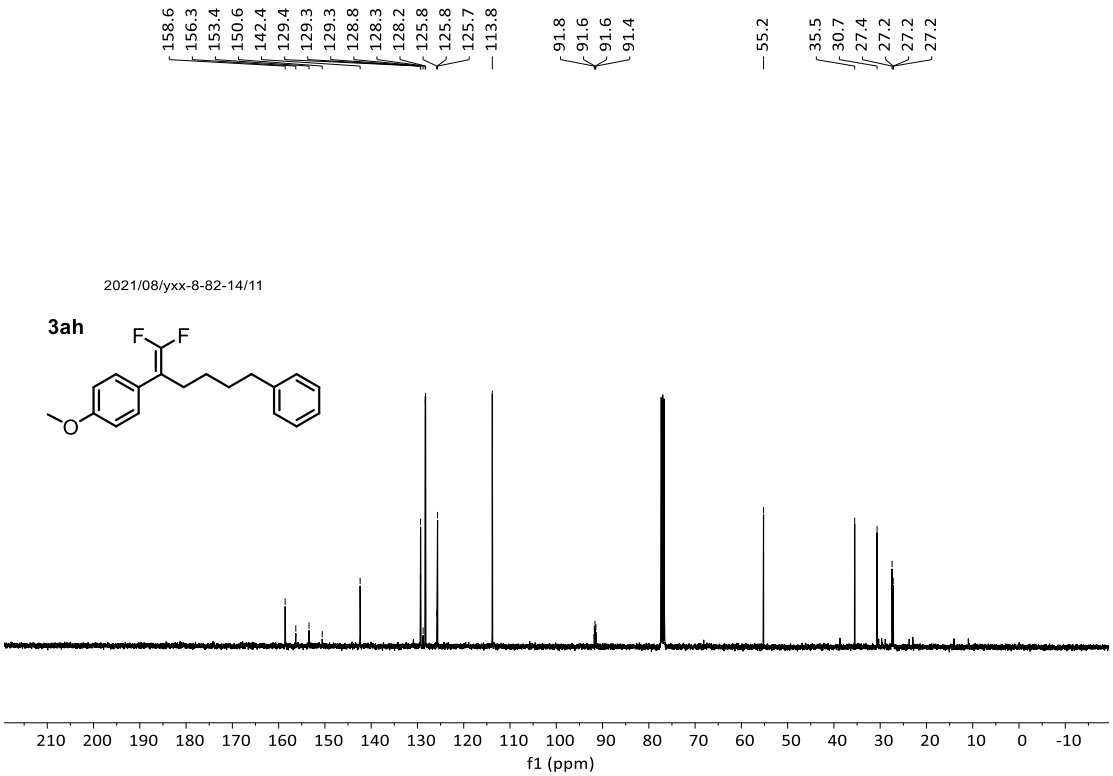
^{19}F NMR (377 MHz, $CDCl_3$):



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

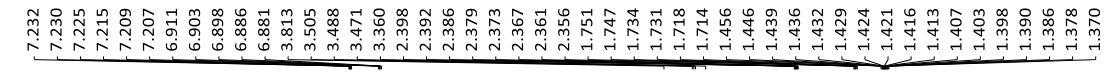


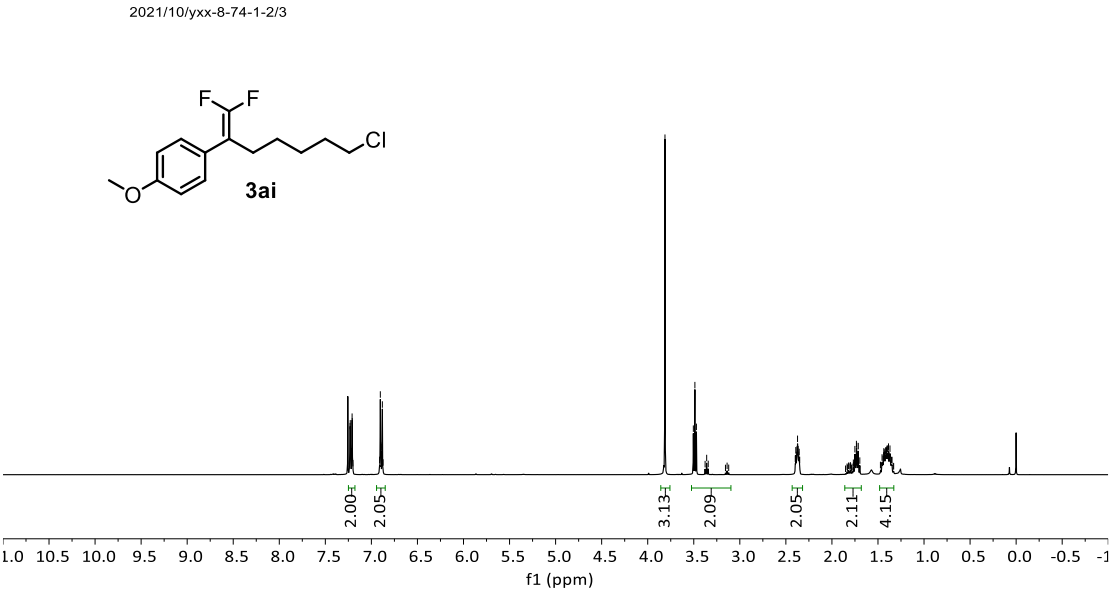
^{13}C NMR (101 MHz, $CDCl_3$):



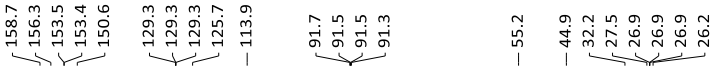
^{19}F NMR (377 MHz, $CDCl_3$):

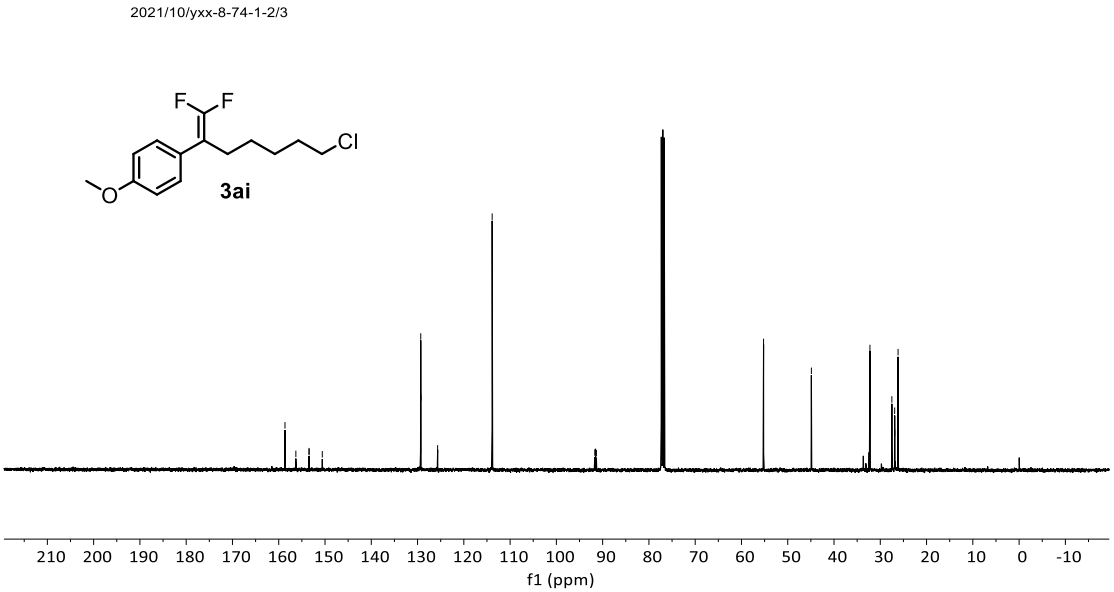
^{1}H NMR (400 MHz, $CDCl_3$):



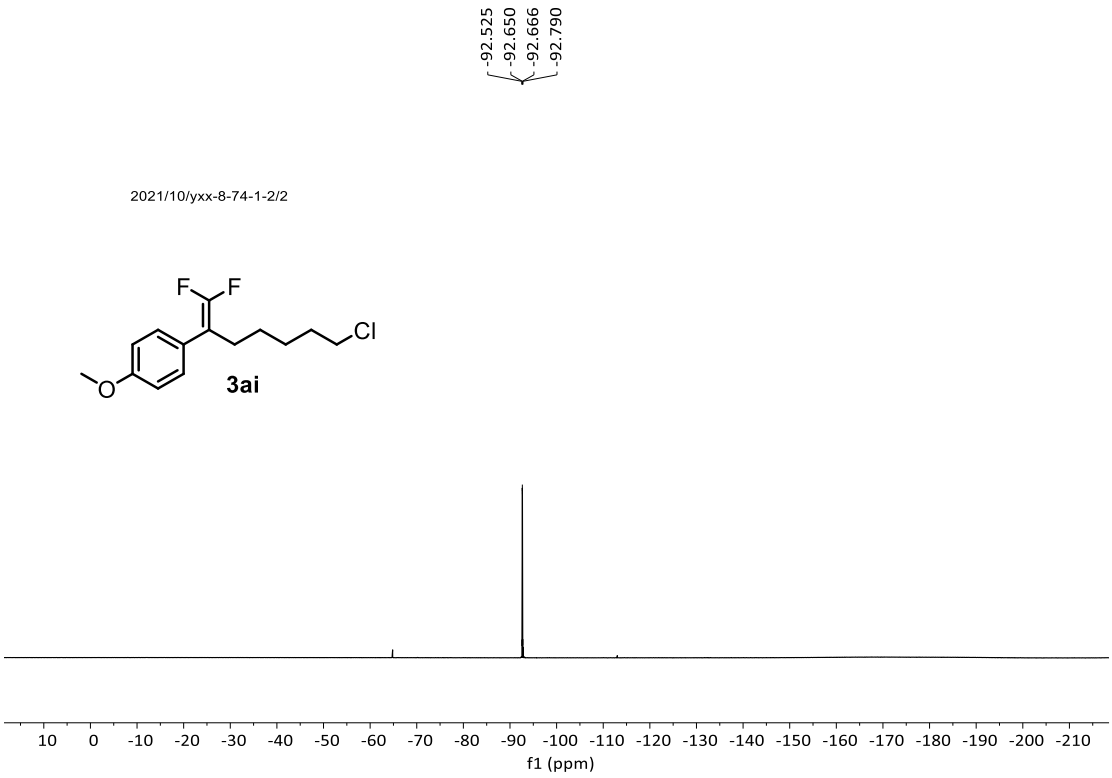


^{13}C NMR (101 MHz, $CDCl_3$):

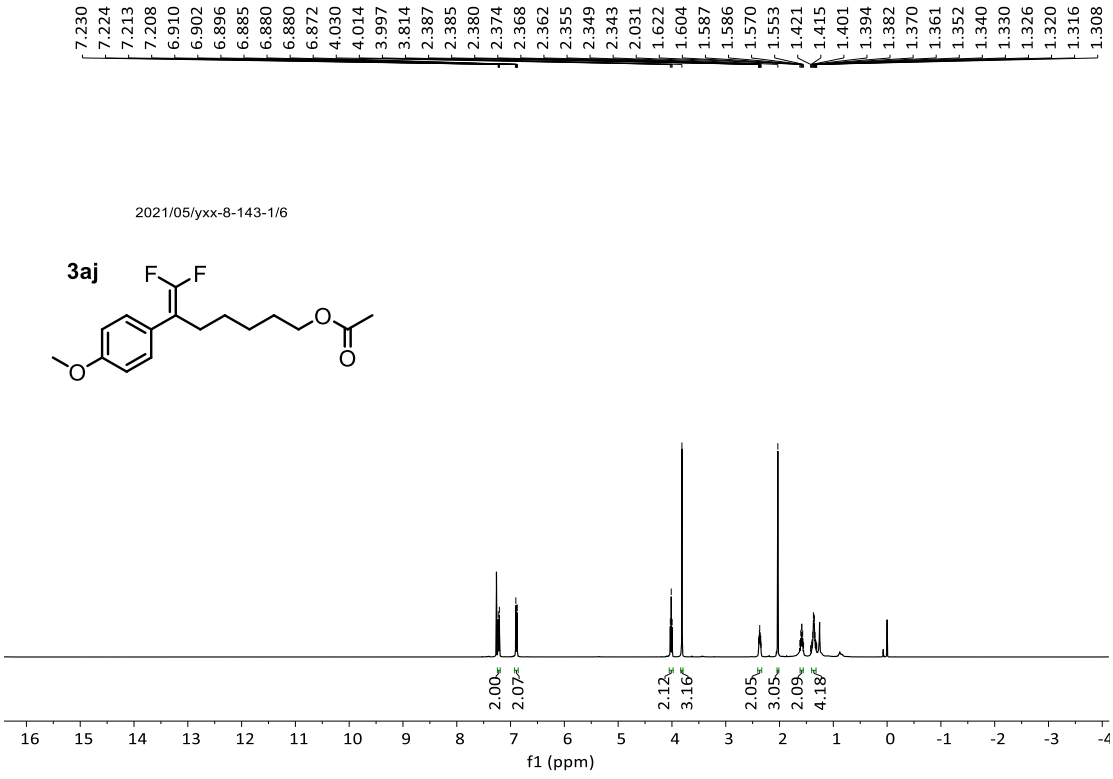




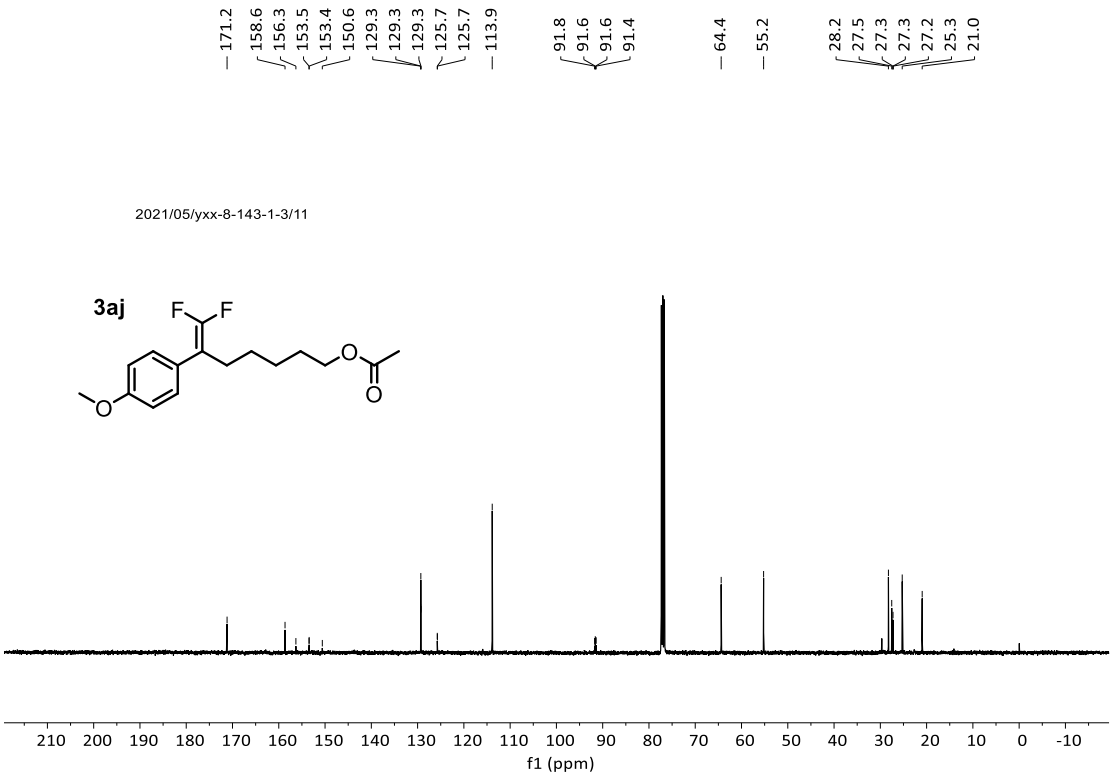
^{19}F NMR (377 MHz, $CDCl_3$):



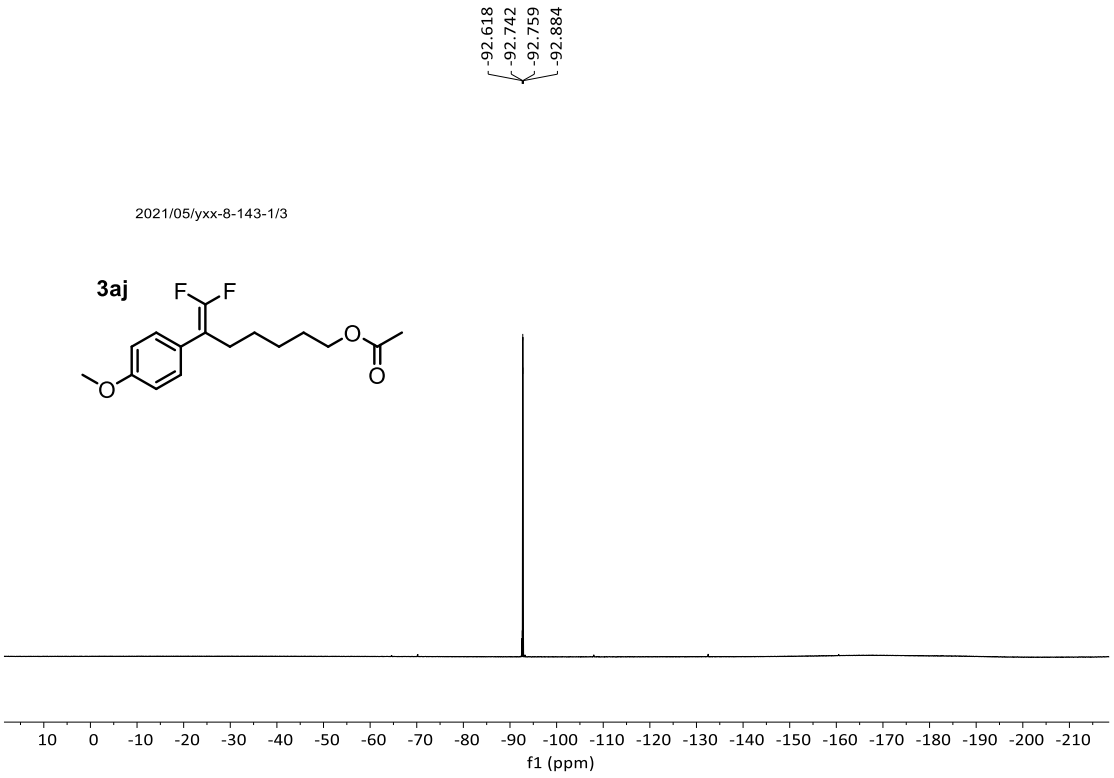
^{1}H NMR (400 MHz, $CDCl_3$):



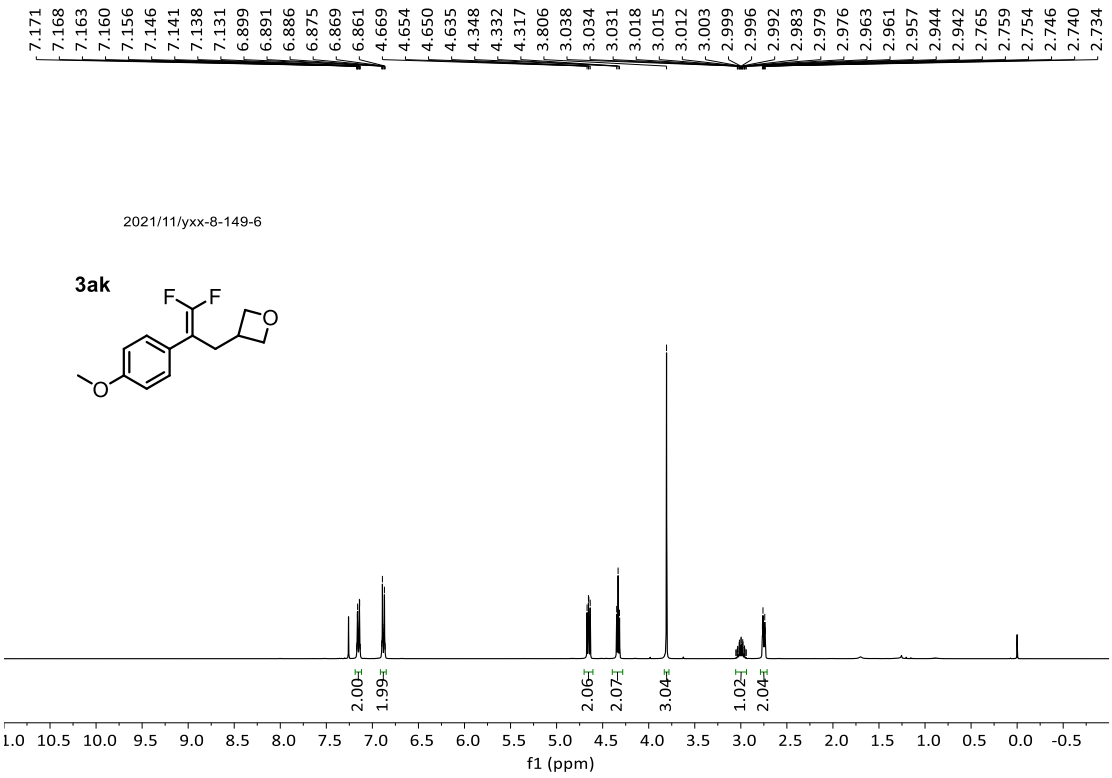
^{13}C NMR (101 MHz, $CDCl_3$):



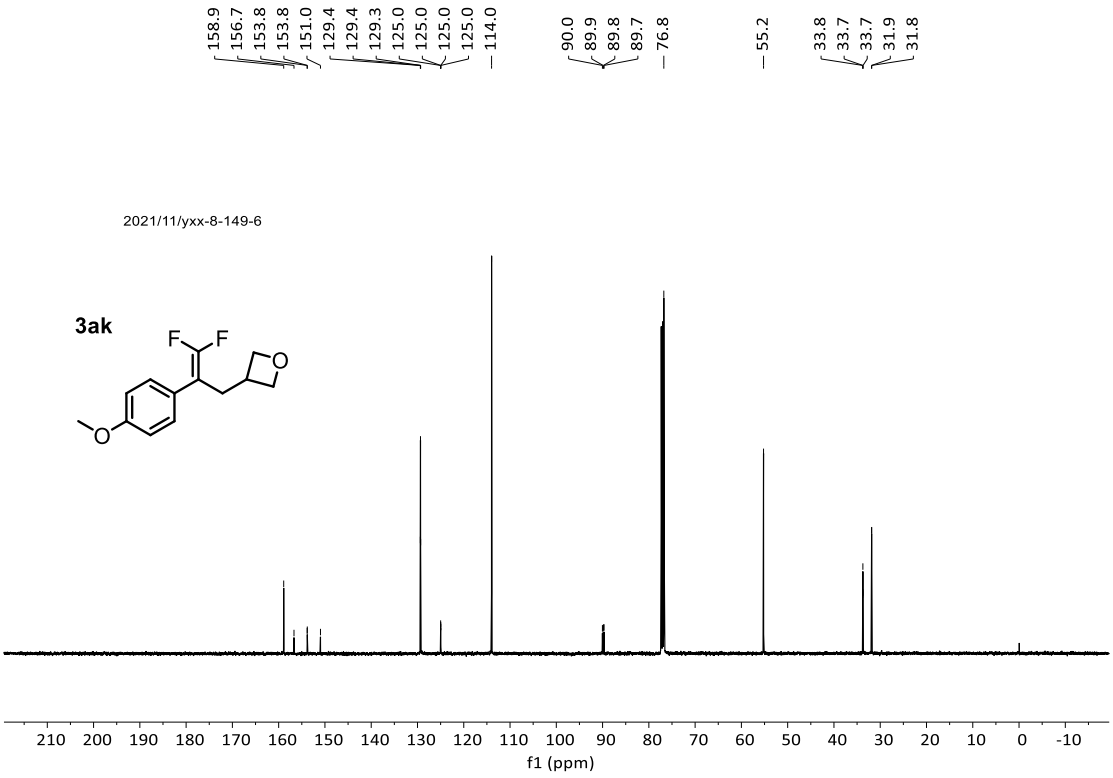
^{19}F NMR (377 MHz, $CDCl_3$):



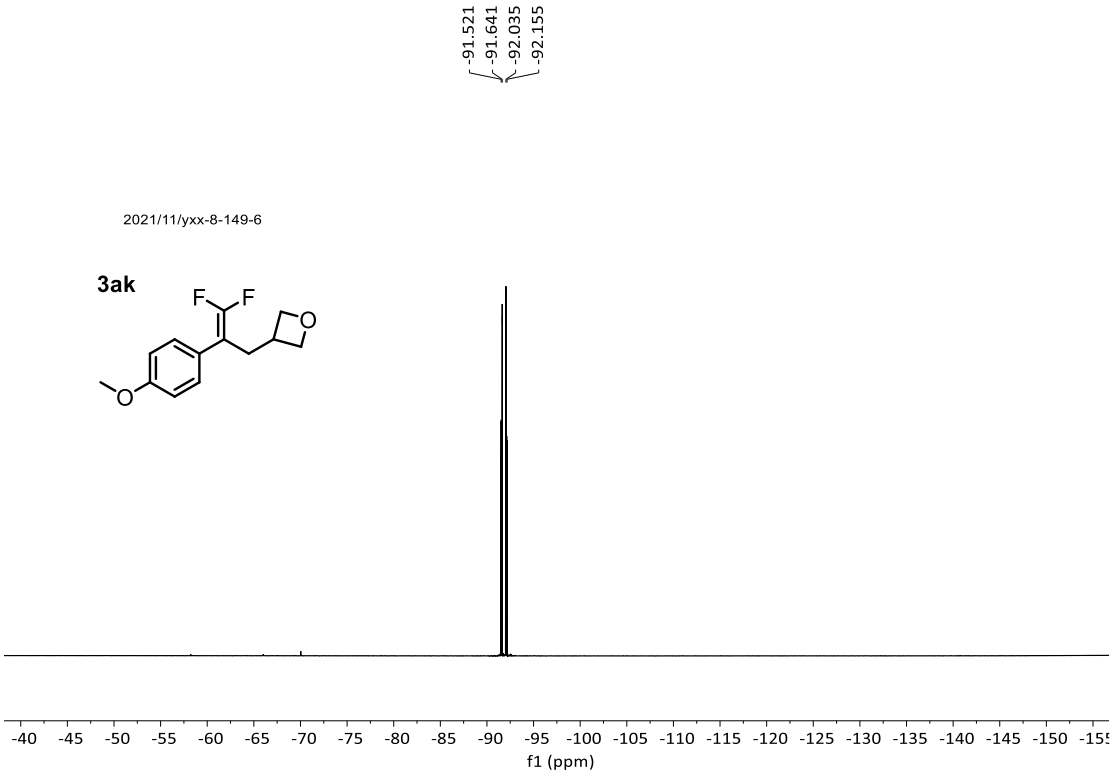
^{1}H NMR (400 MHz, $CDCl_3$):



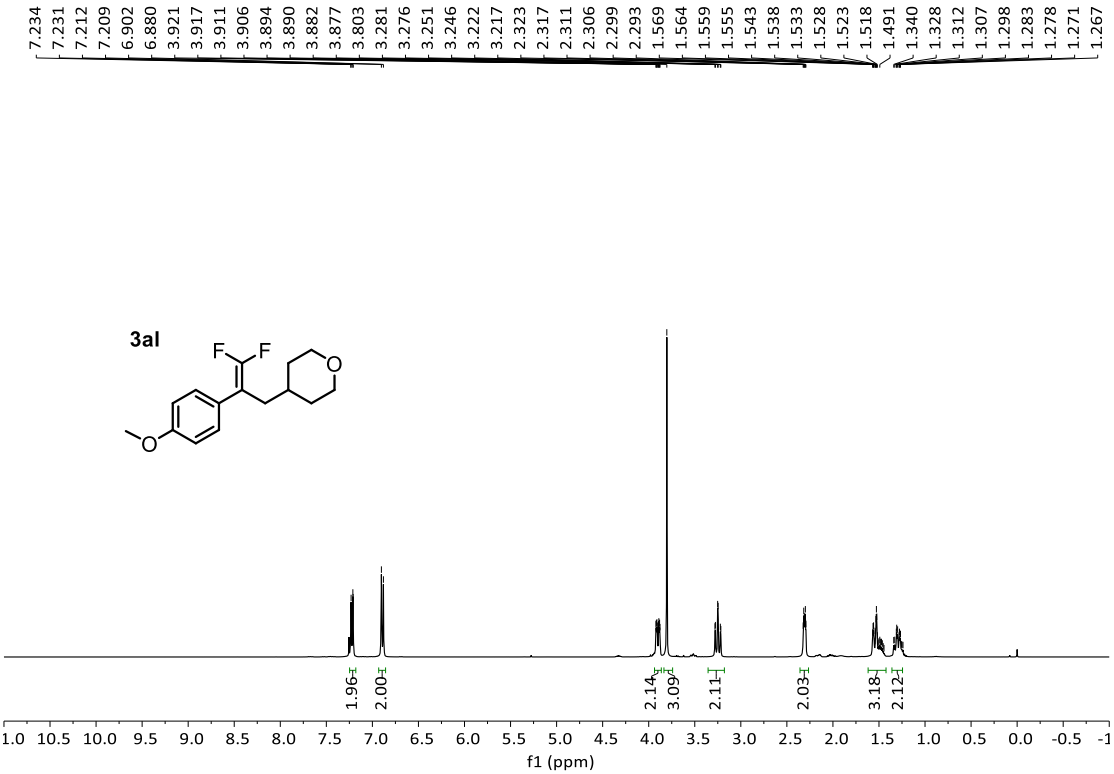
^{13}C NMR (101 MHz, $CDCl_3$):



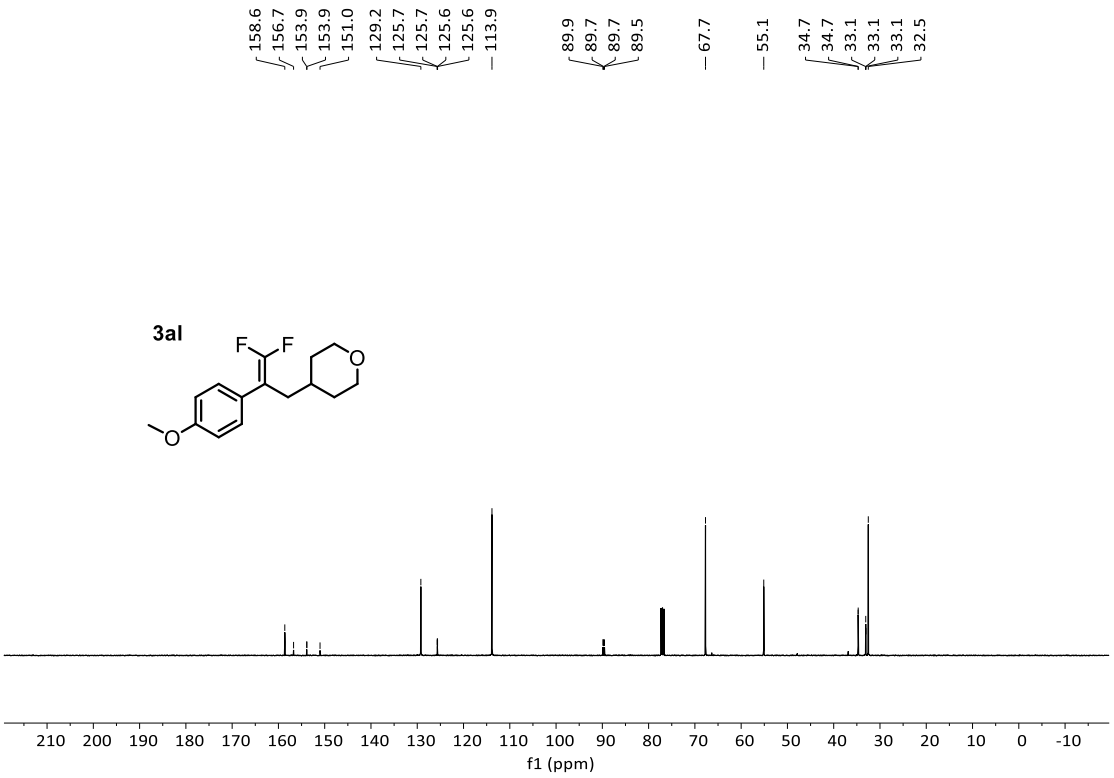
^{19}F NMR (377 MHz, $CDCl_3$):



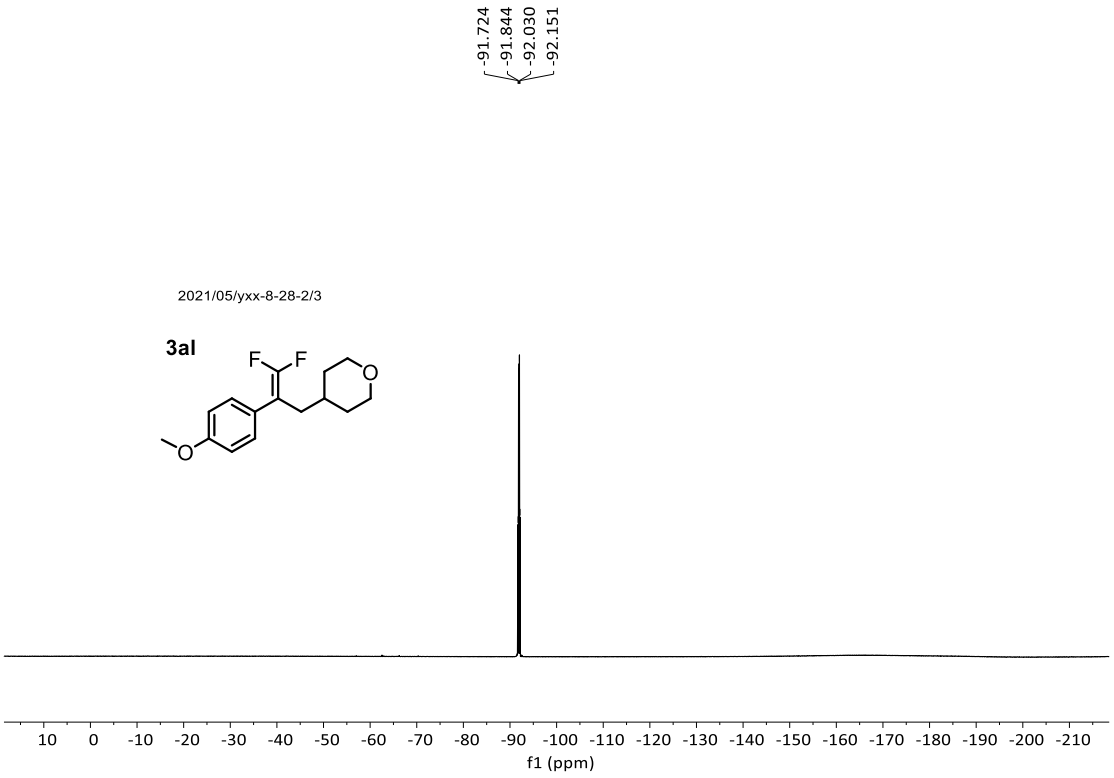
^{1}H NMR (400 MHz, $CDCl_3$):



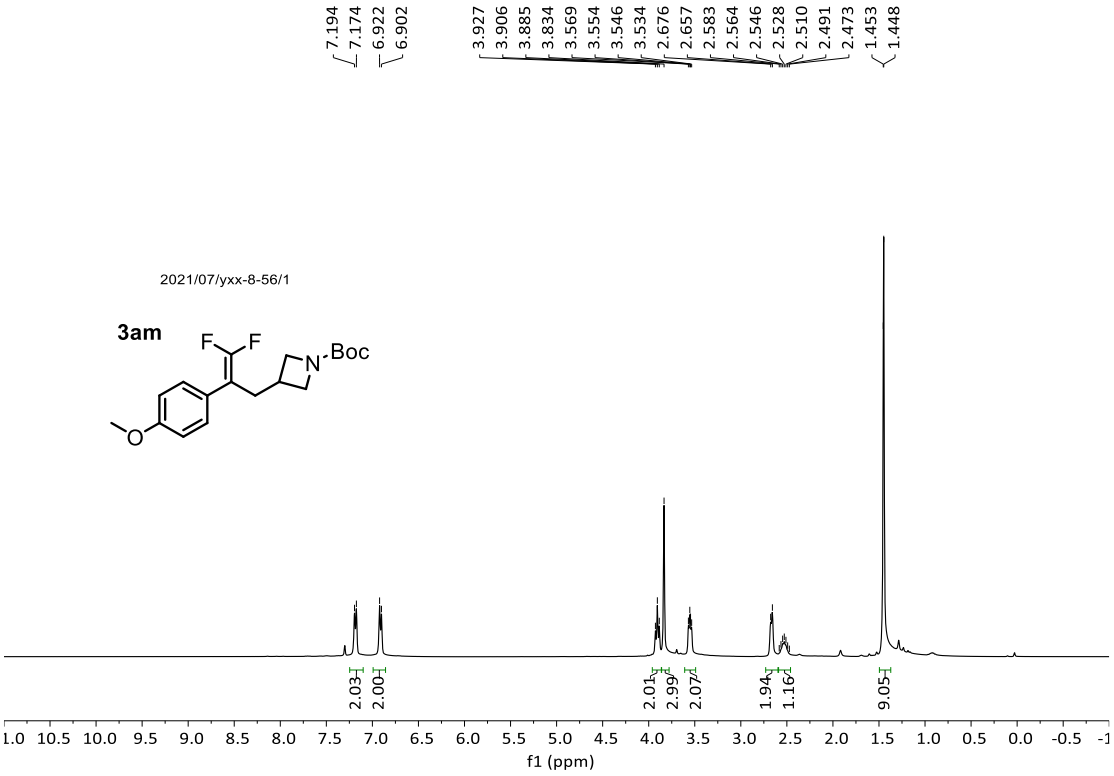
^{13}C NMR (101 MHz, $CDCl_3$):



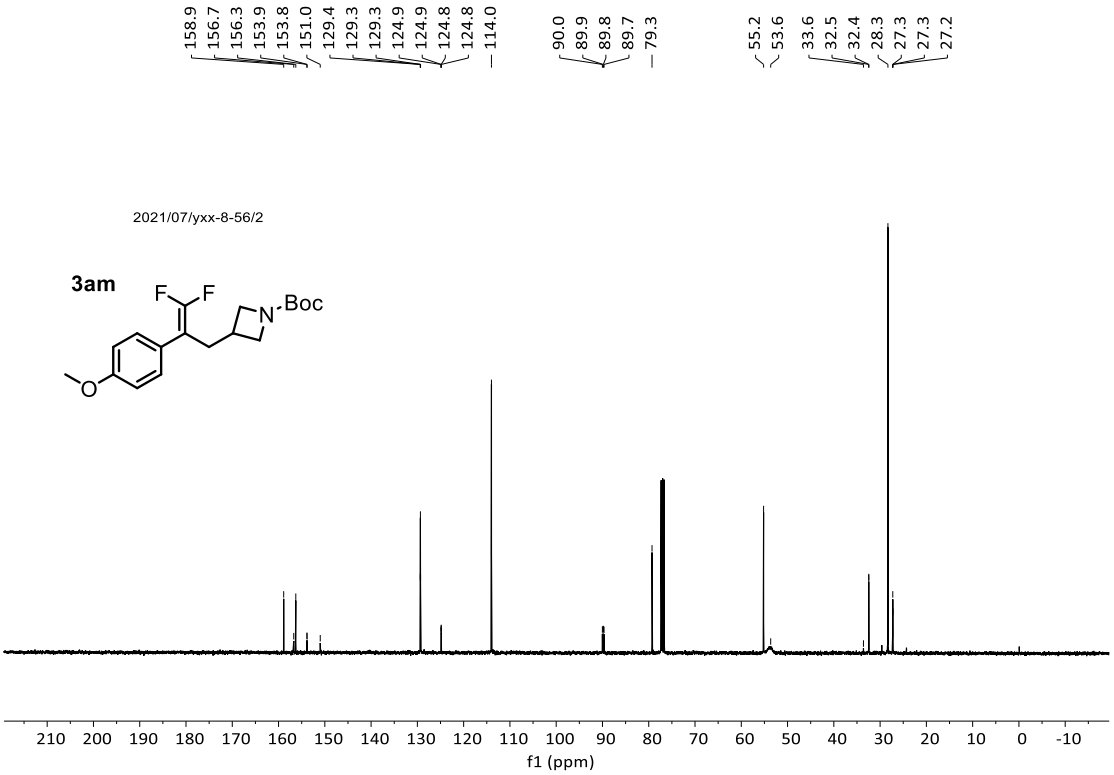
^{19}F NMR (377 MHz, $CDCl_3$):



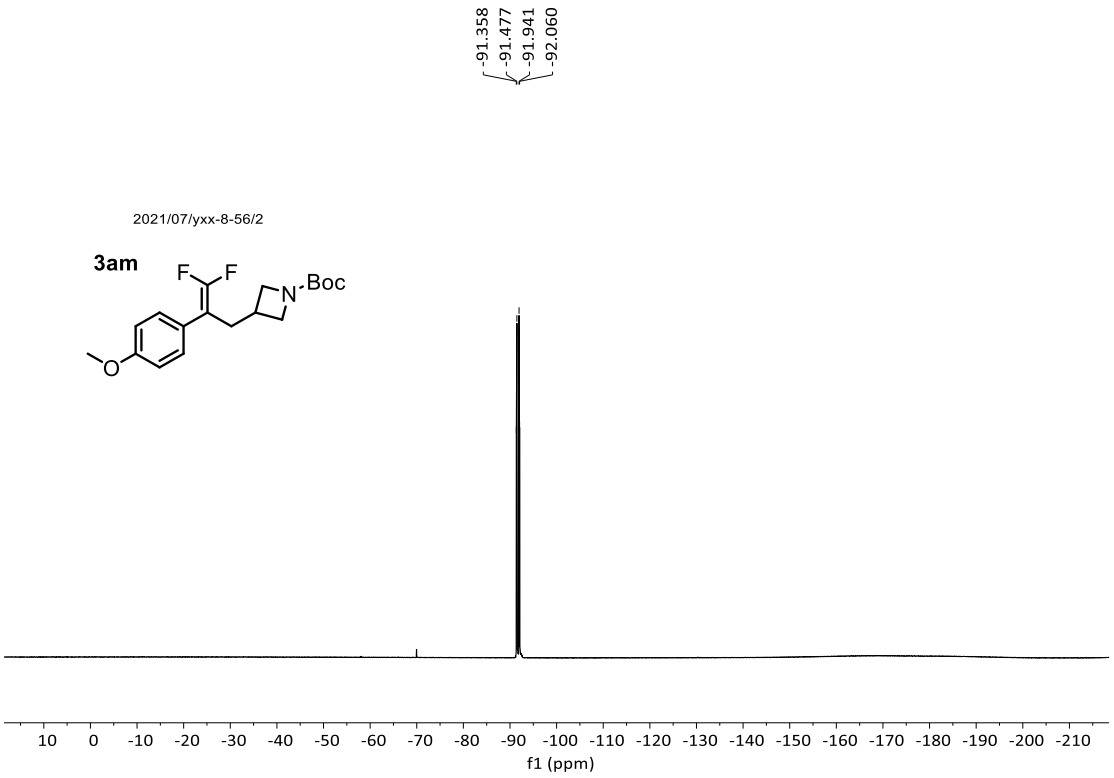
^{1}H NMR (400 MHz, $CDCl_3$):



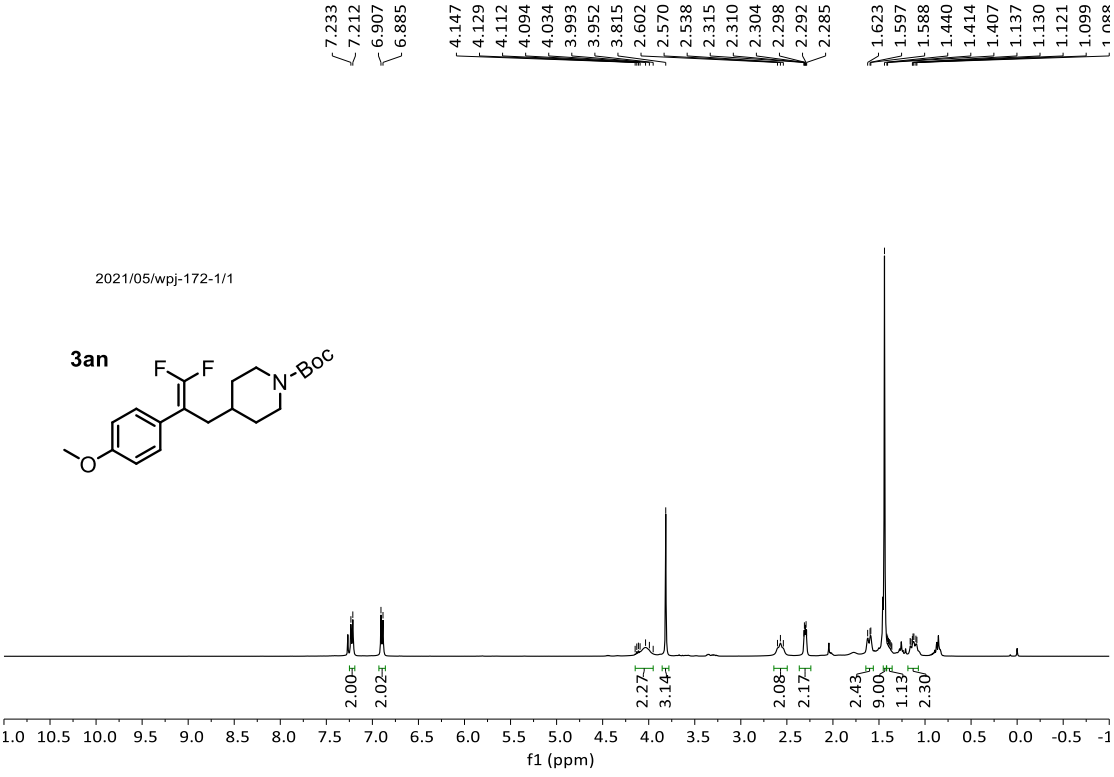
^{13}C NMR (101 MHz, $CDCl_3$):



^{19}F NMR (377 MHz, $CDCl_3$):



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



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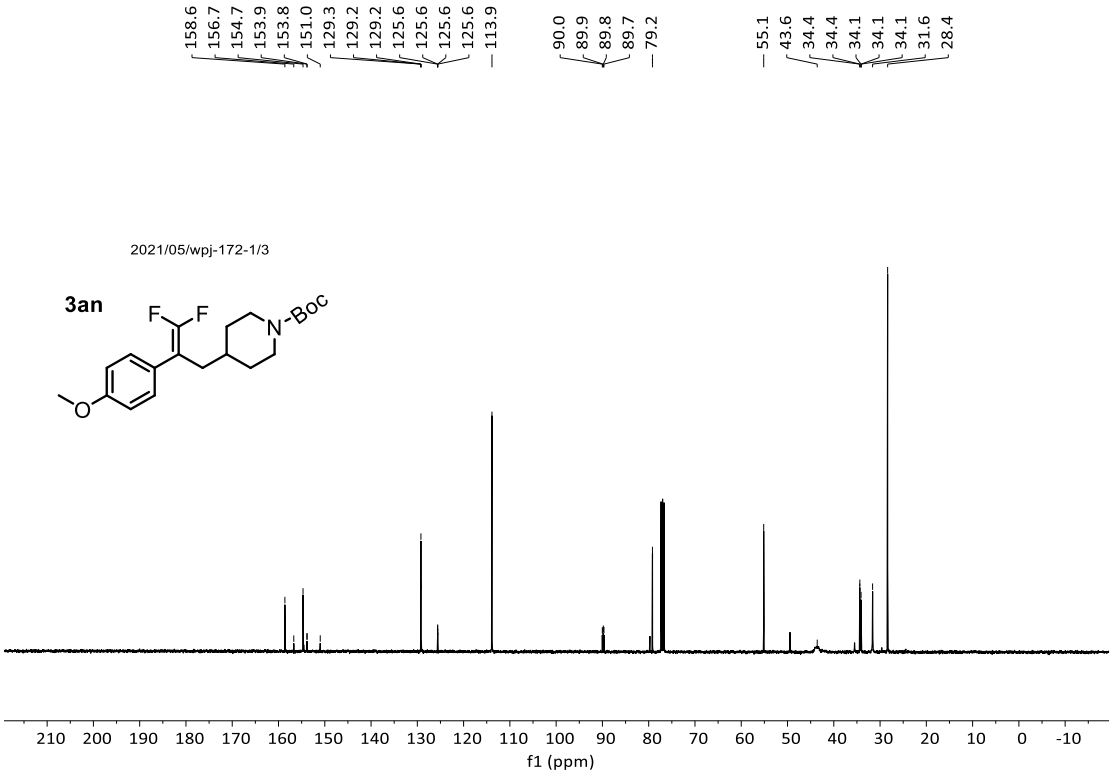
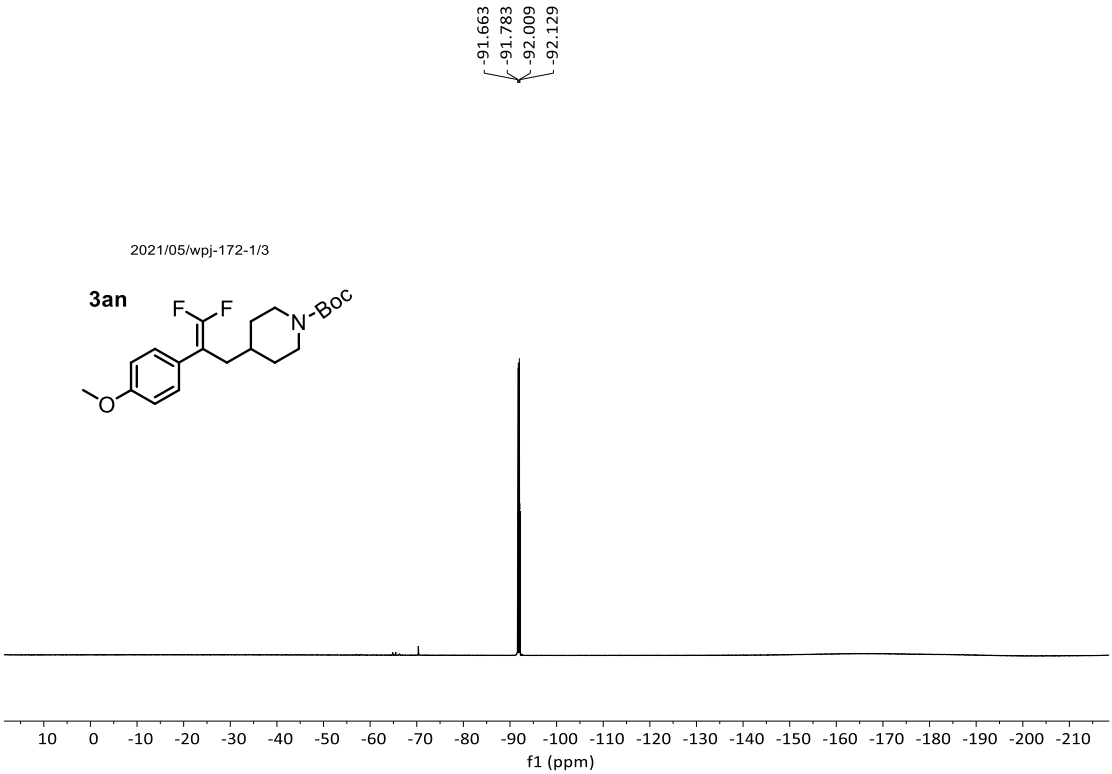


^{19}F NMR (377 MHz, $CDCl_3$):



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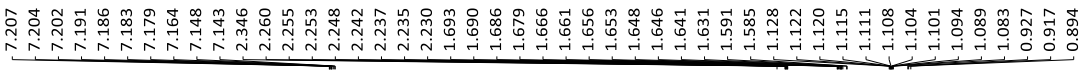

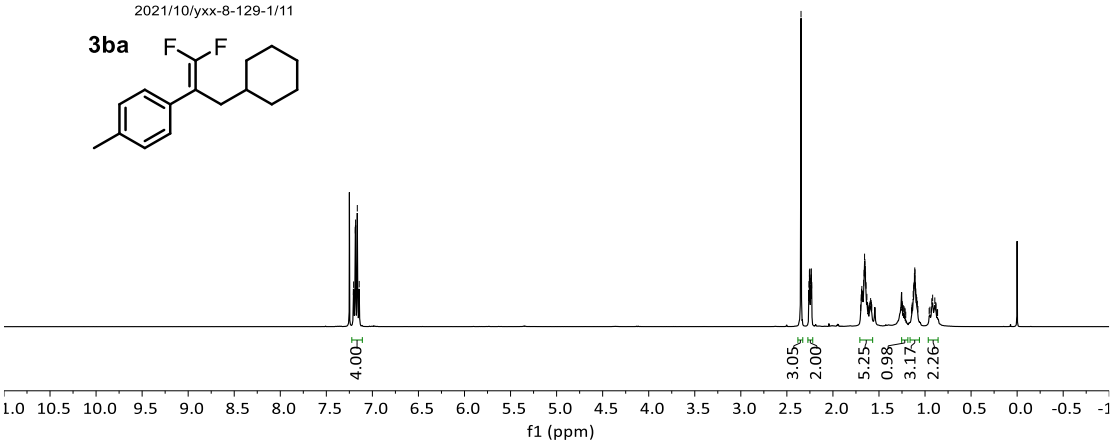

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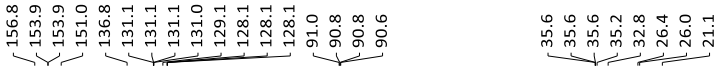

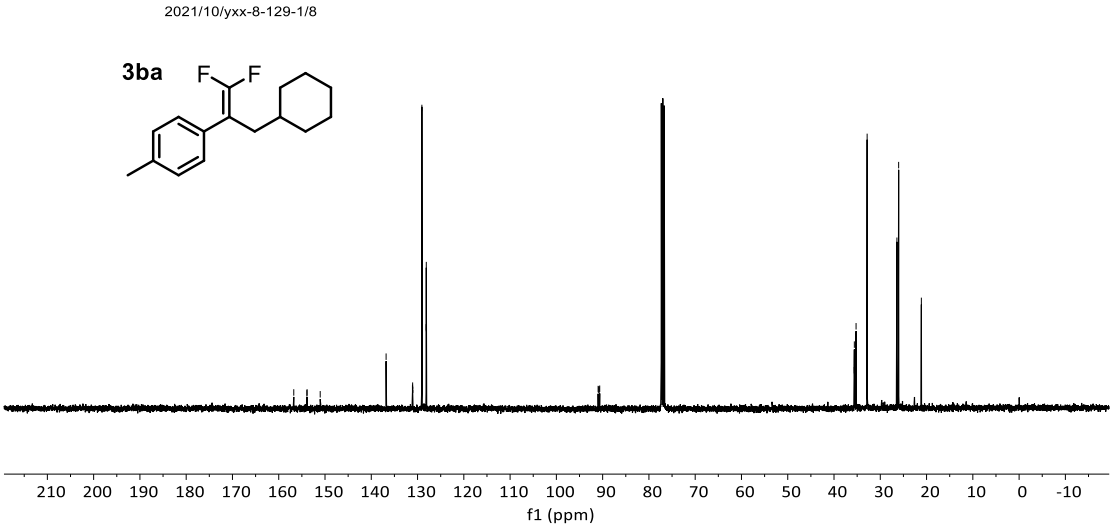

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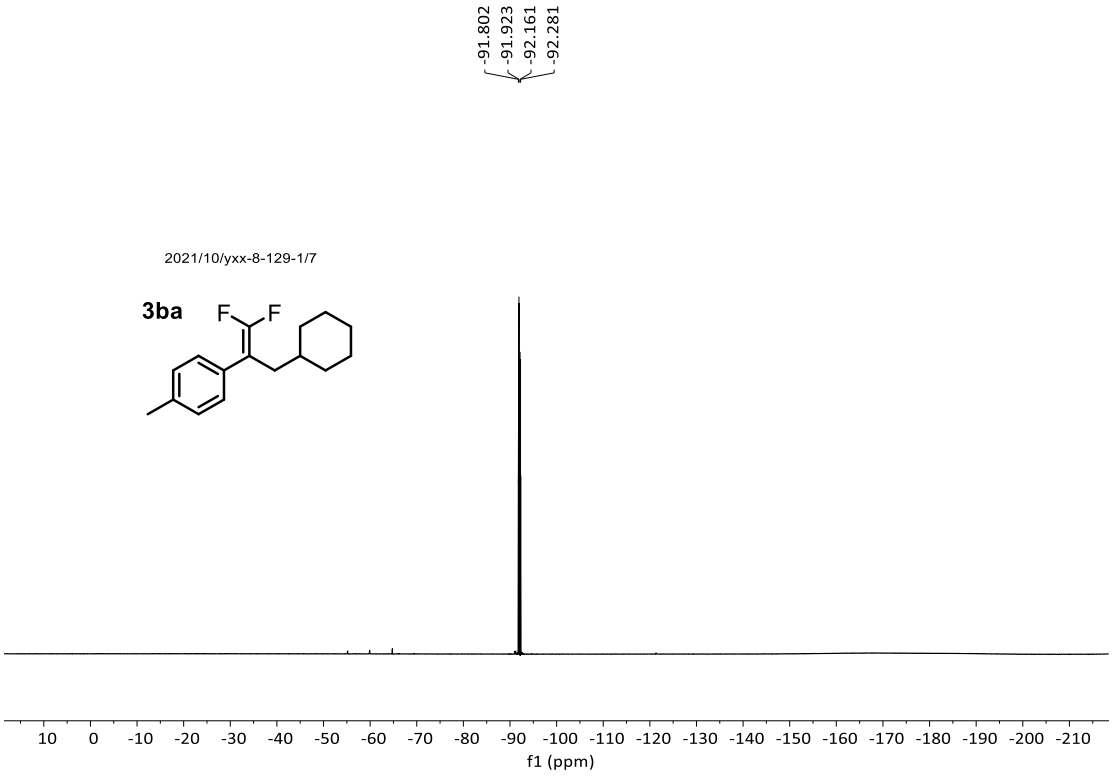
^{19}F NMR (377 MHz, $CDCl_3$):



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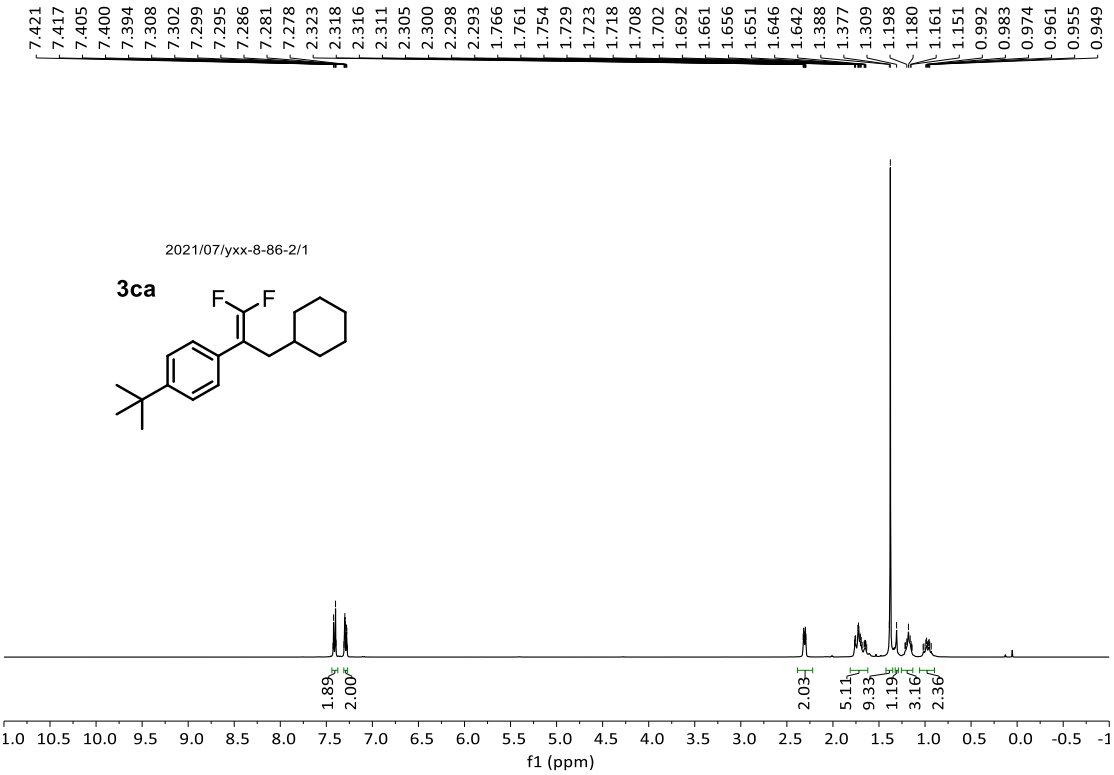

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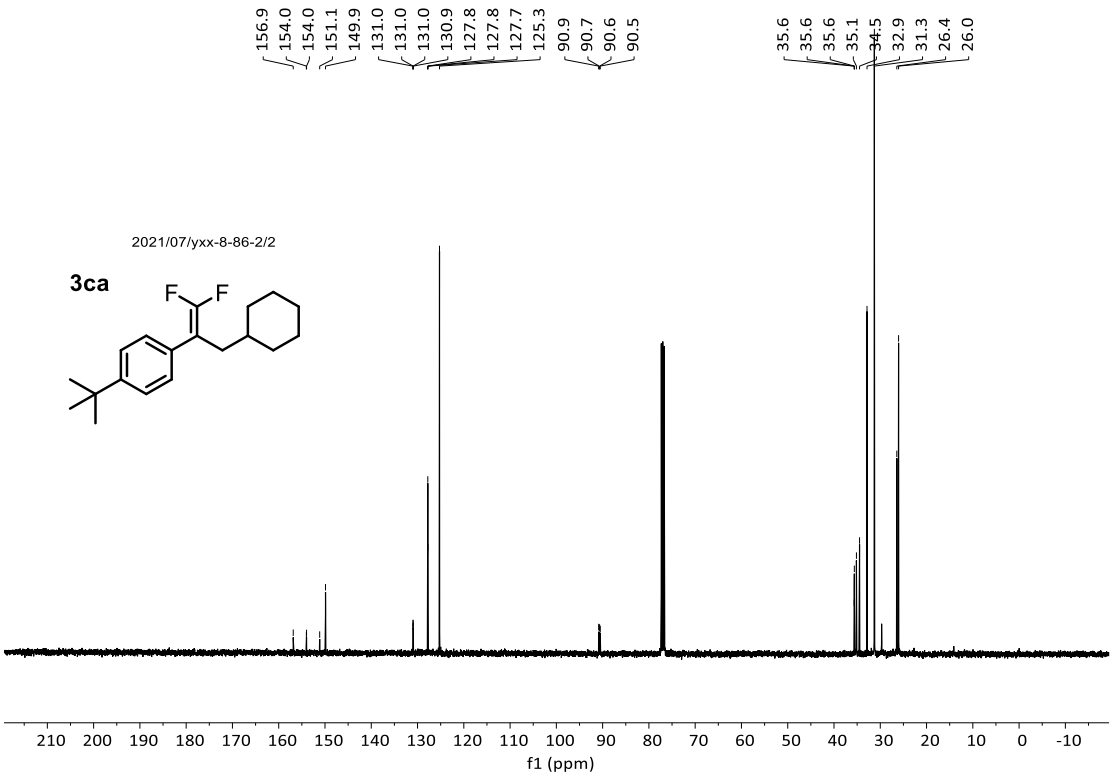

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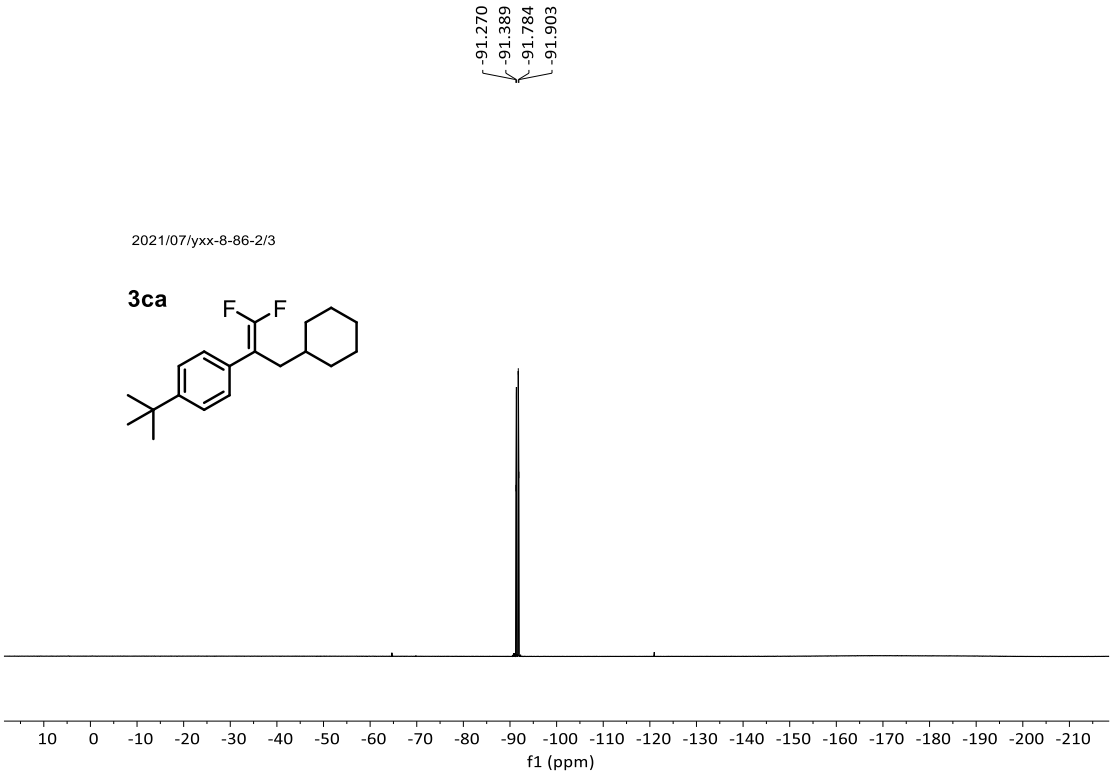

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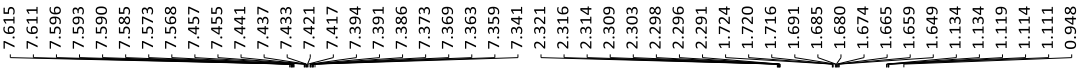

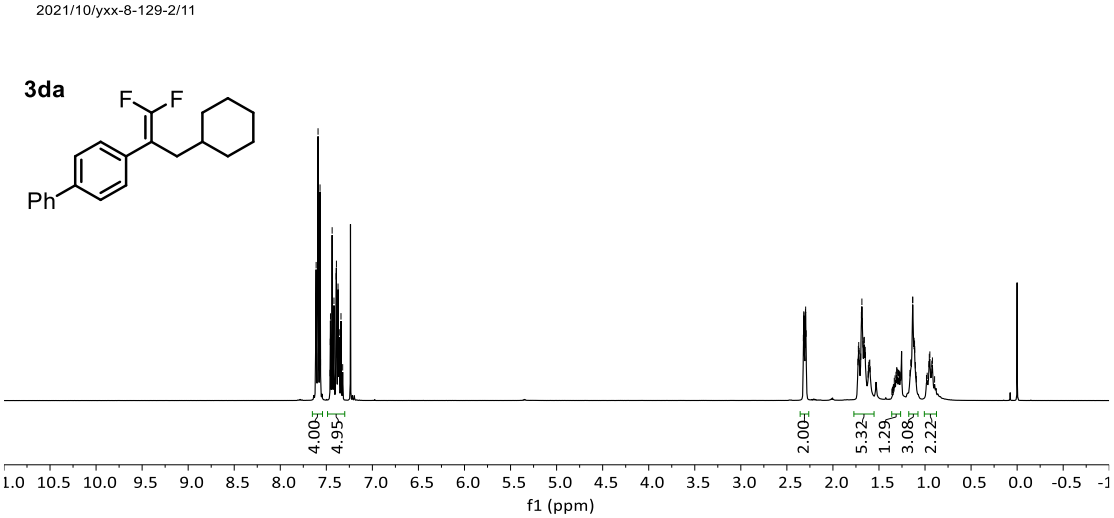

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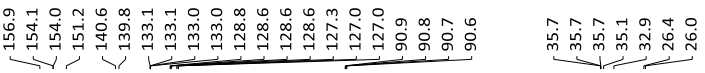

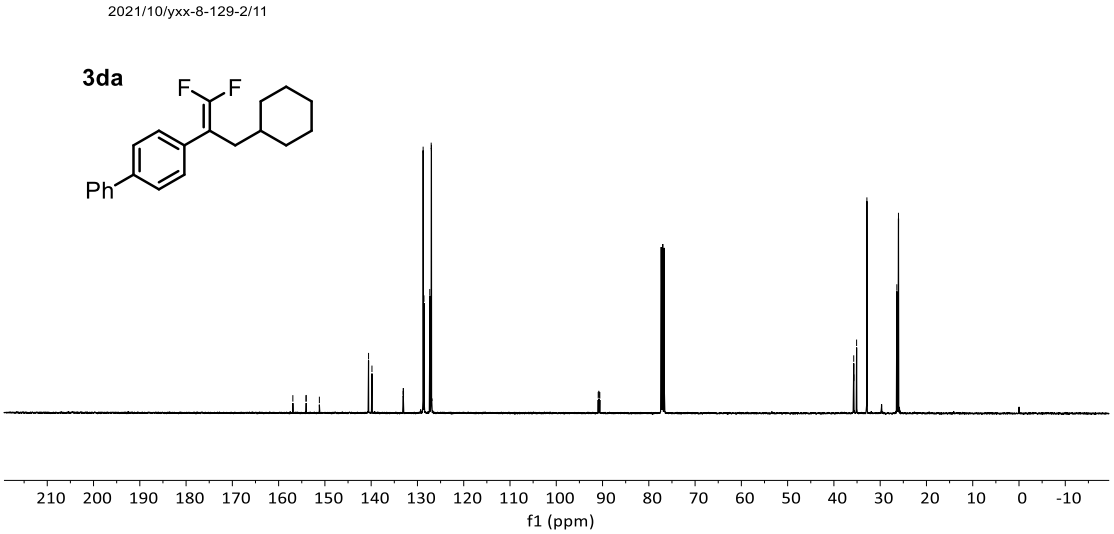

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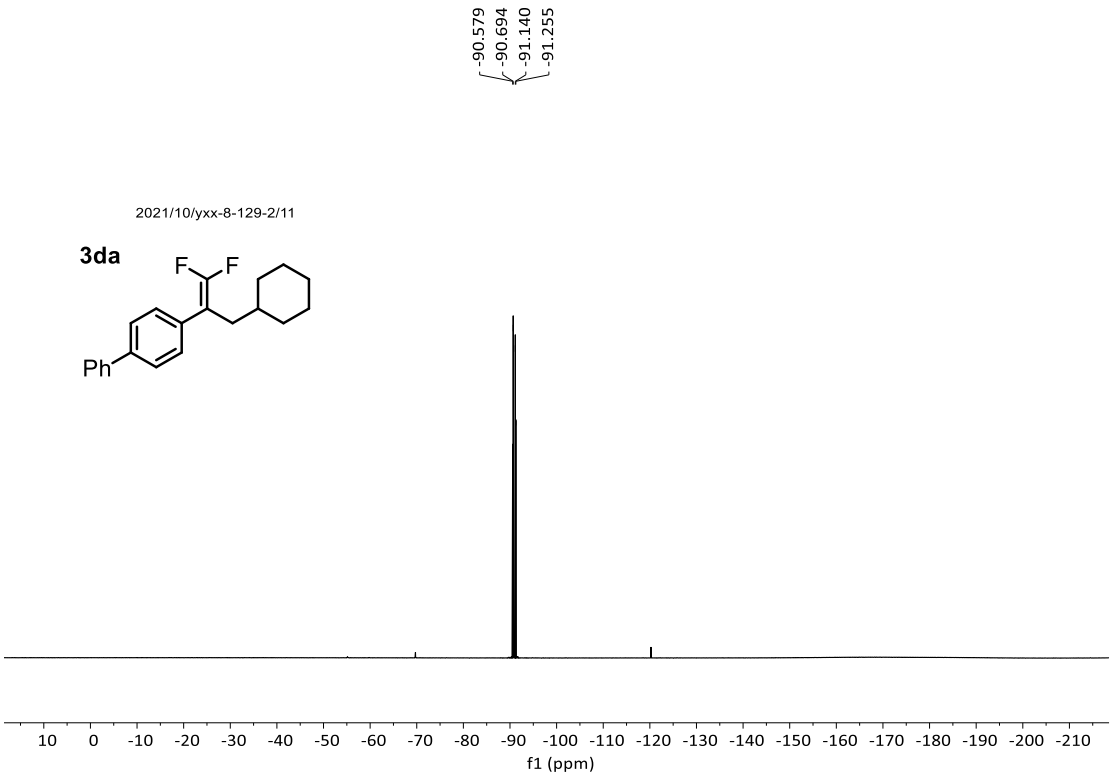

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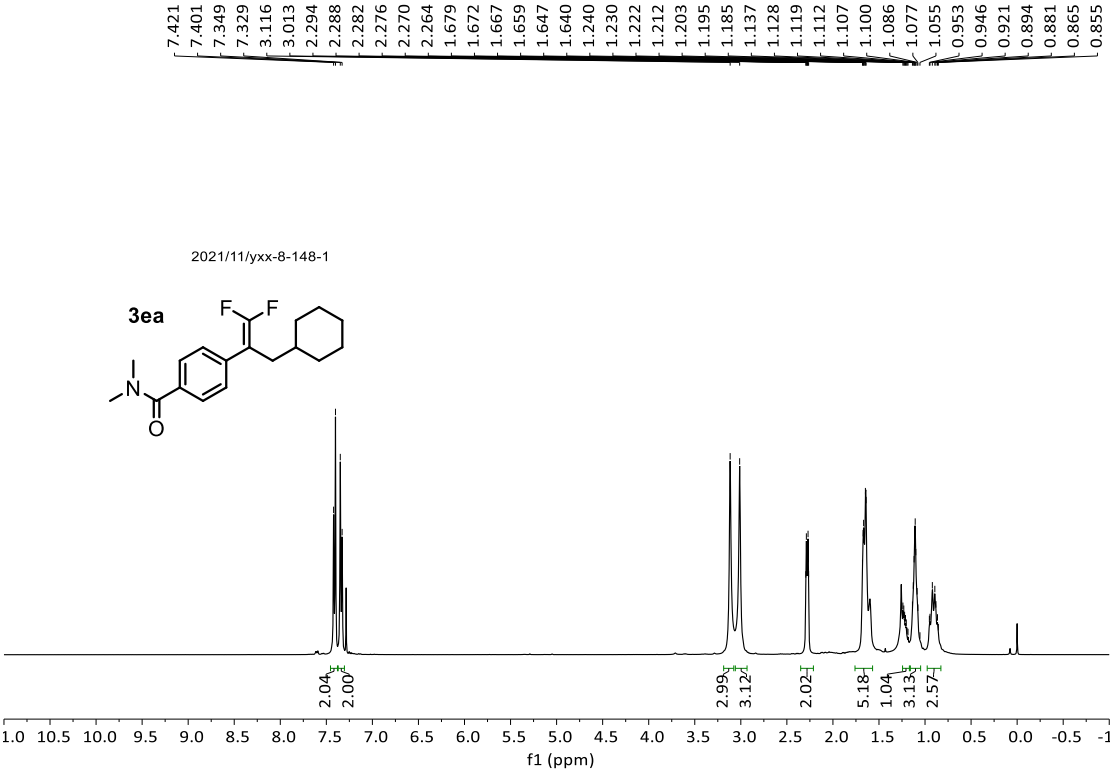

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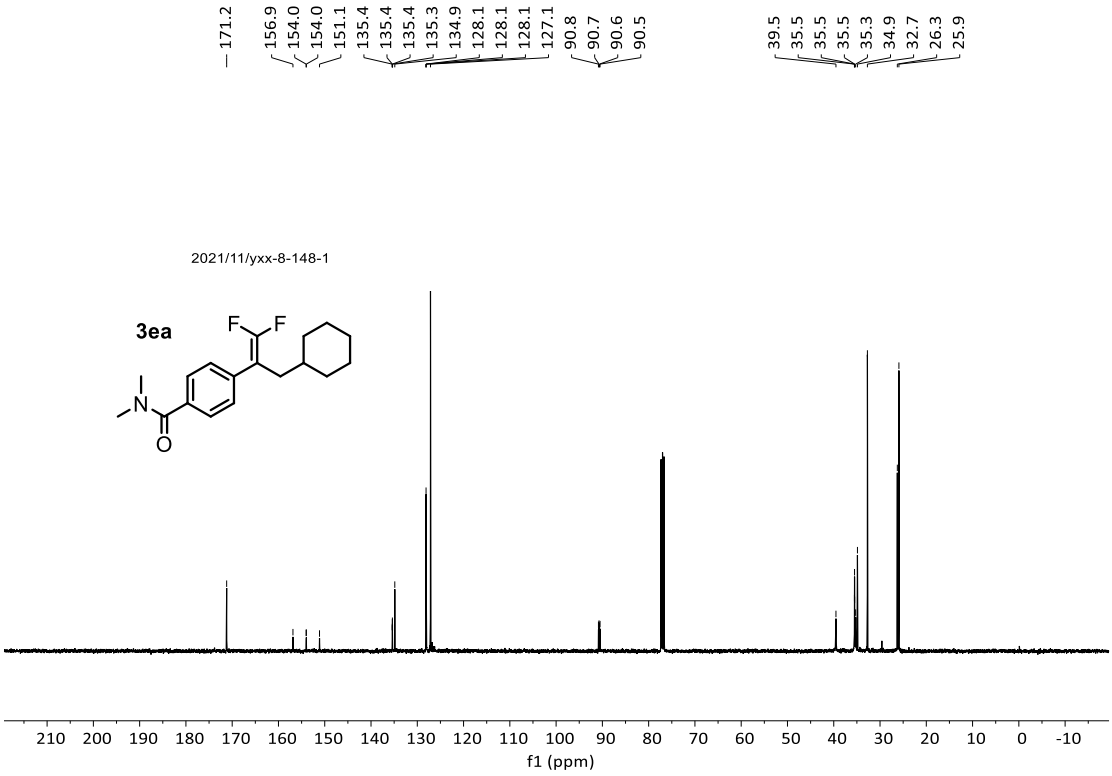

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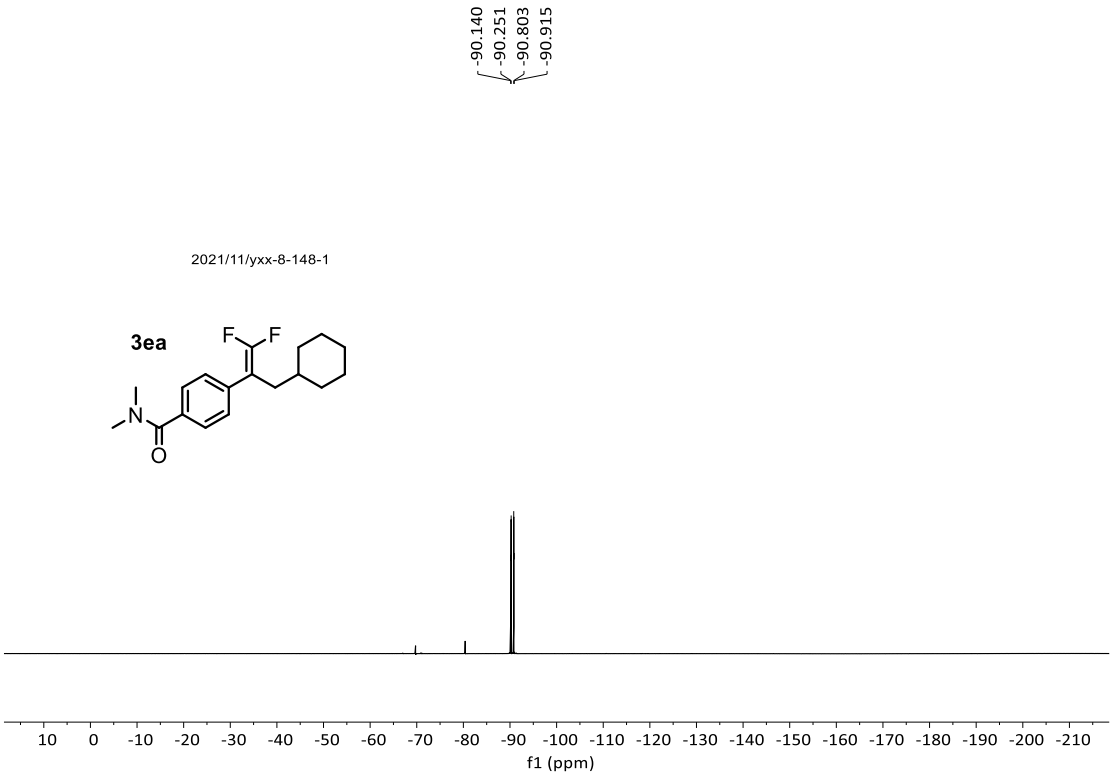

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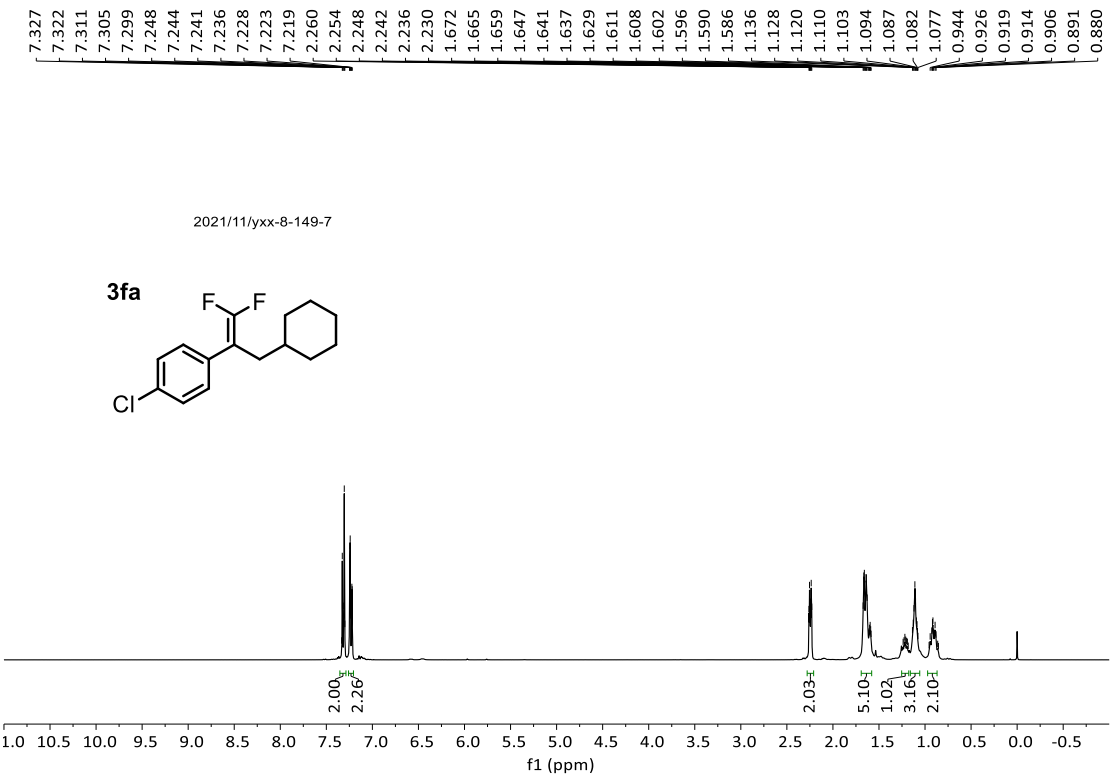

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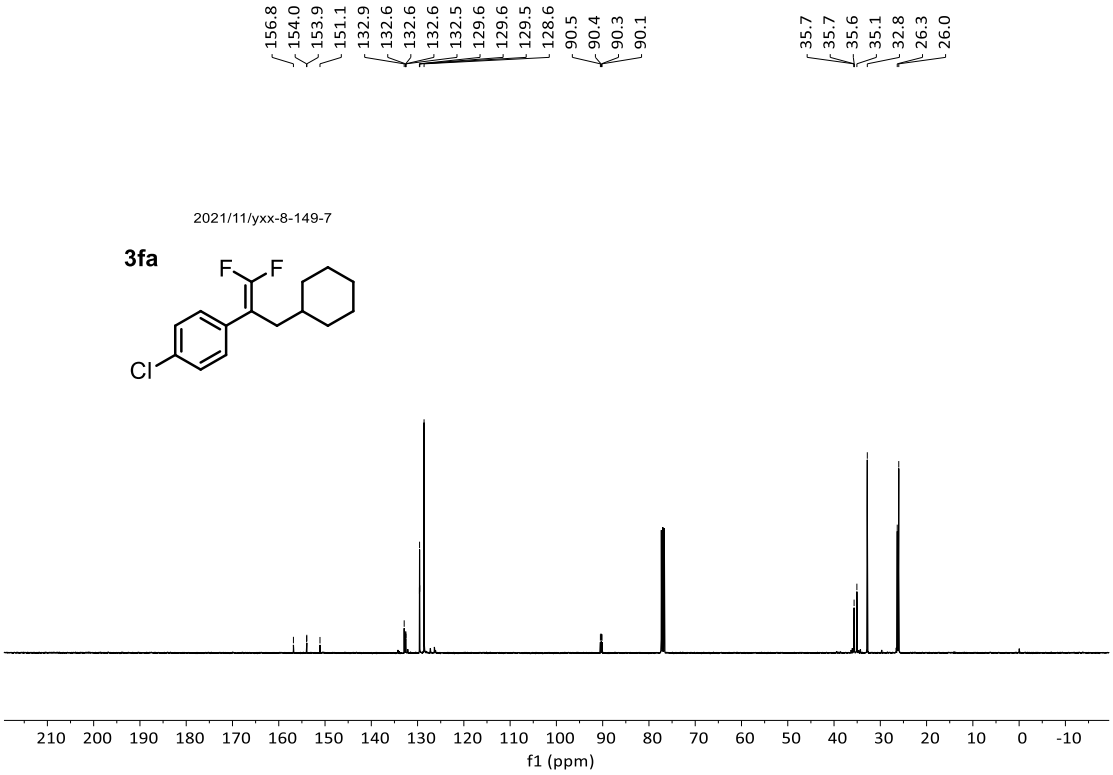

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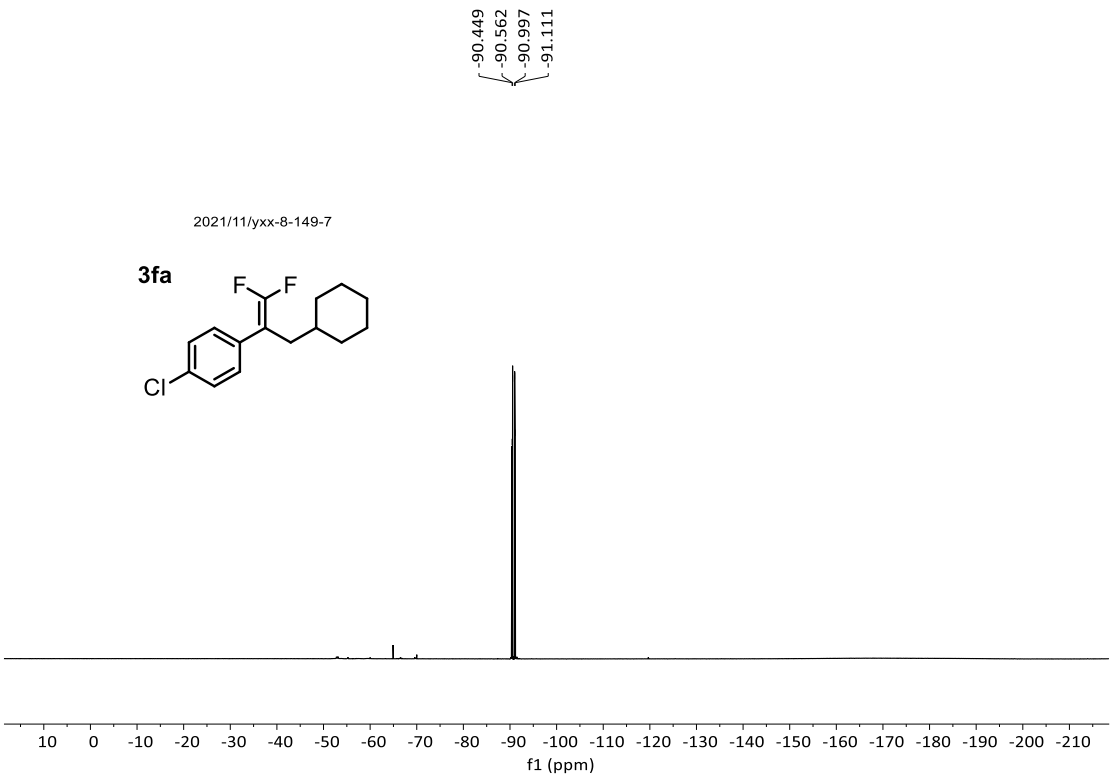

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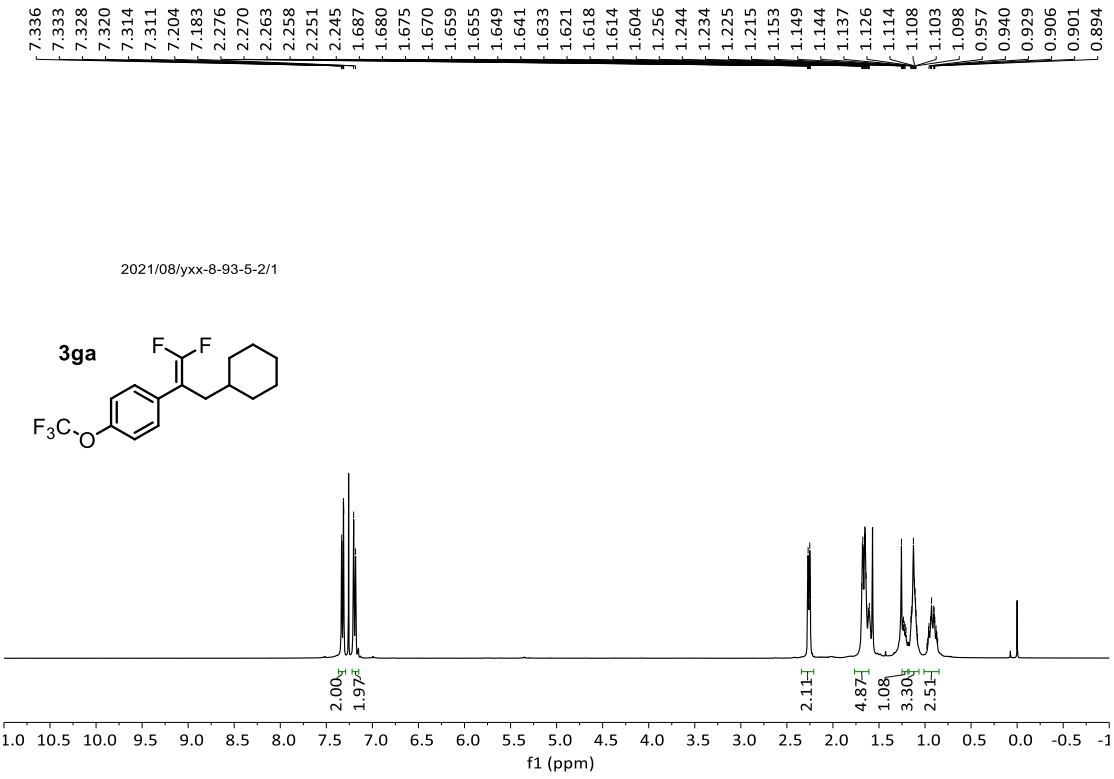

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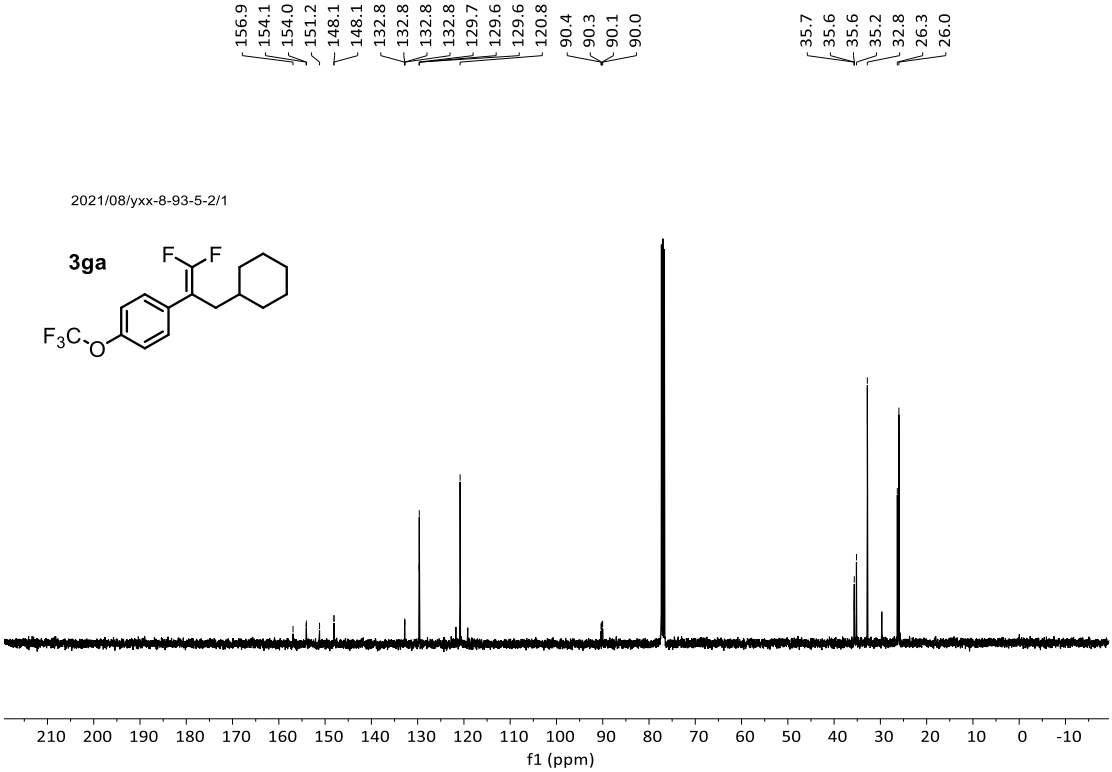

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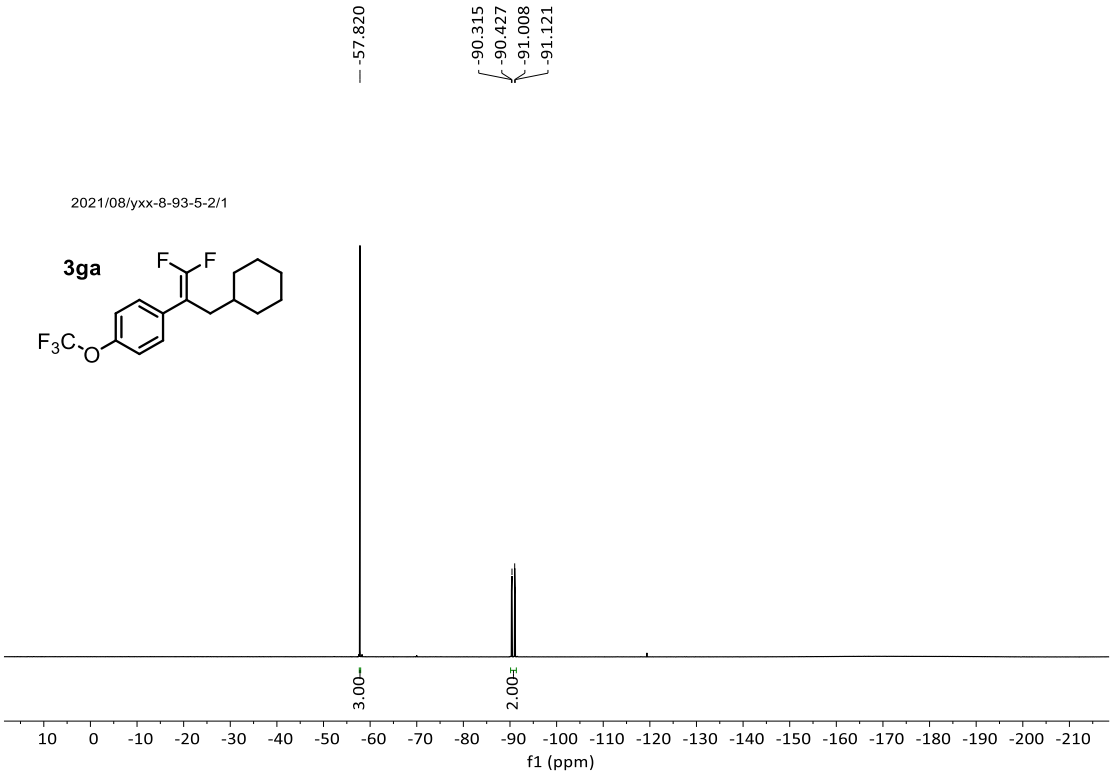

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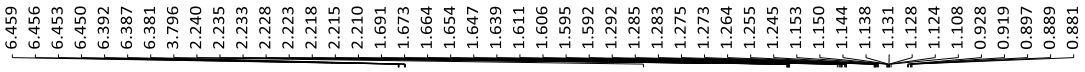

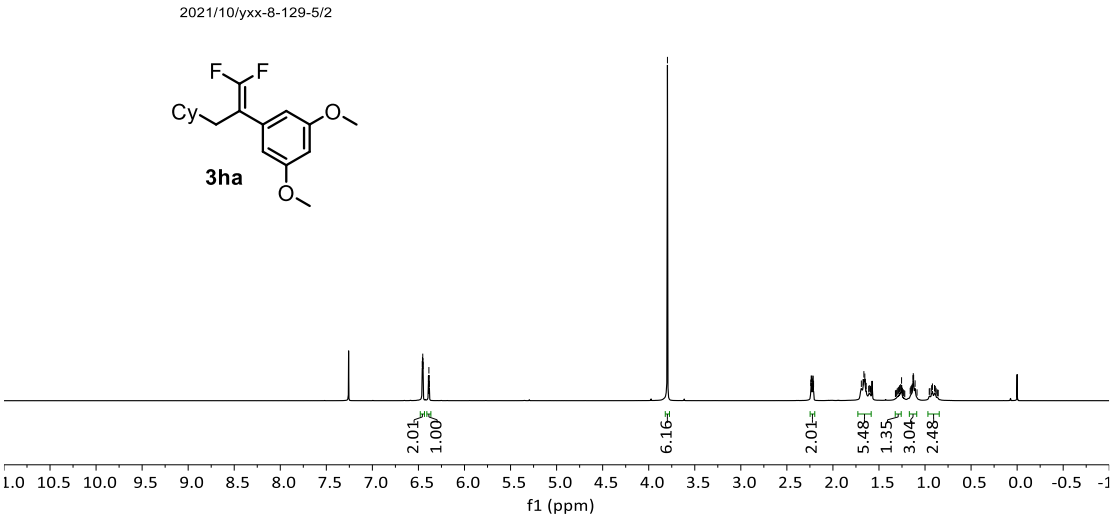

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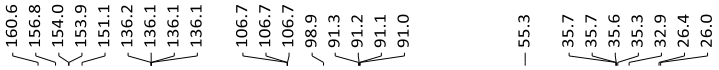

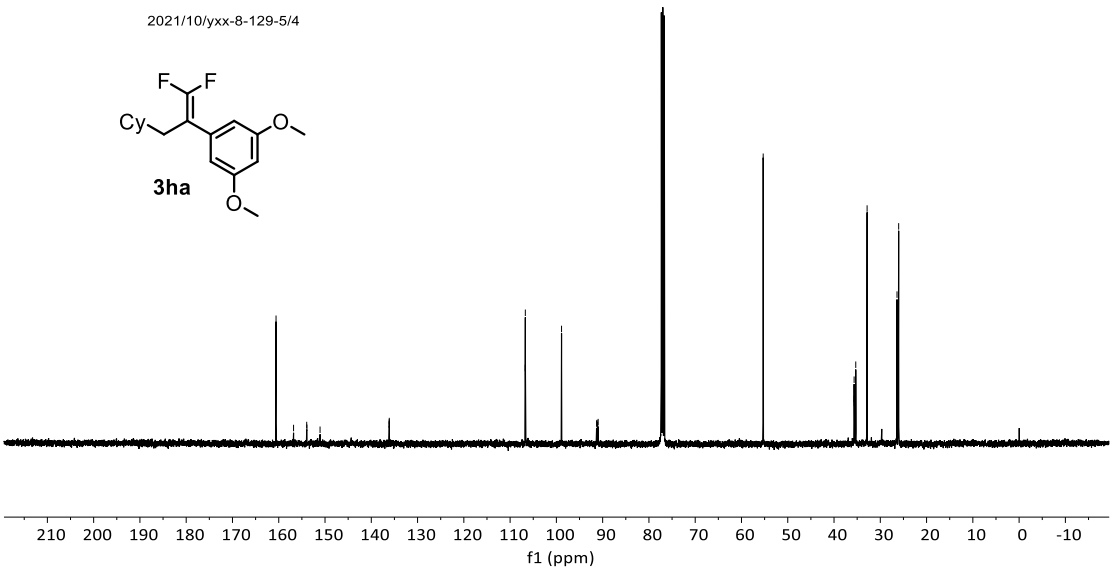

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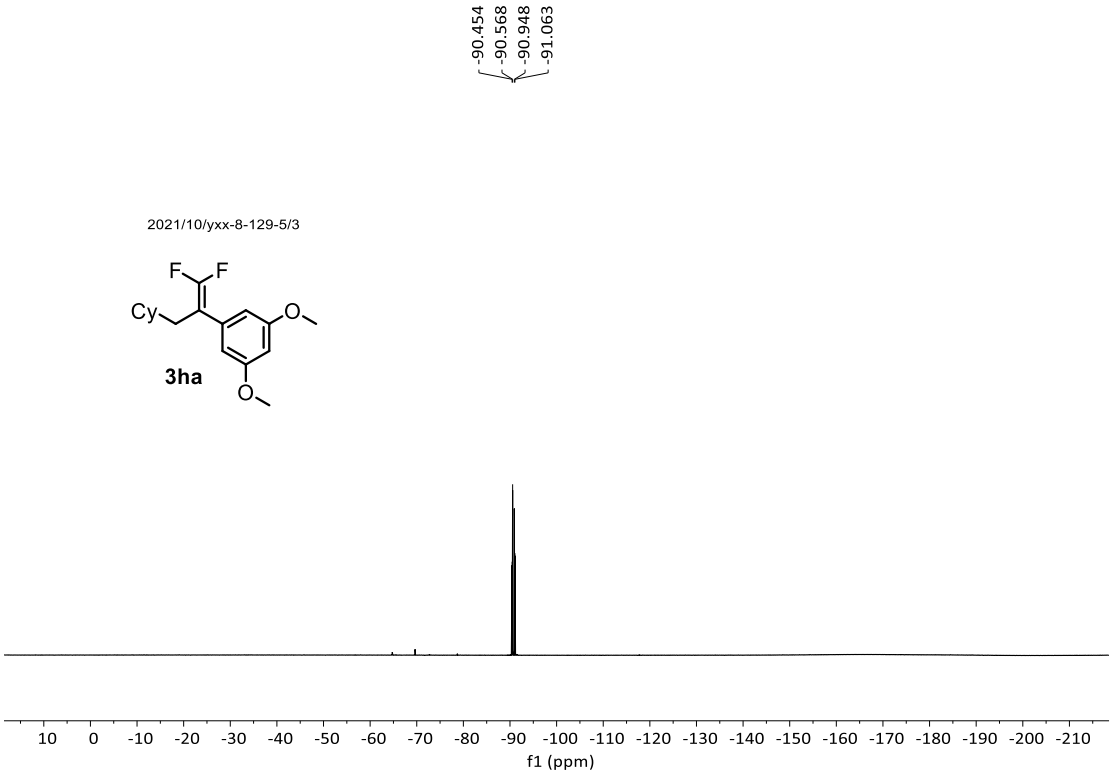

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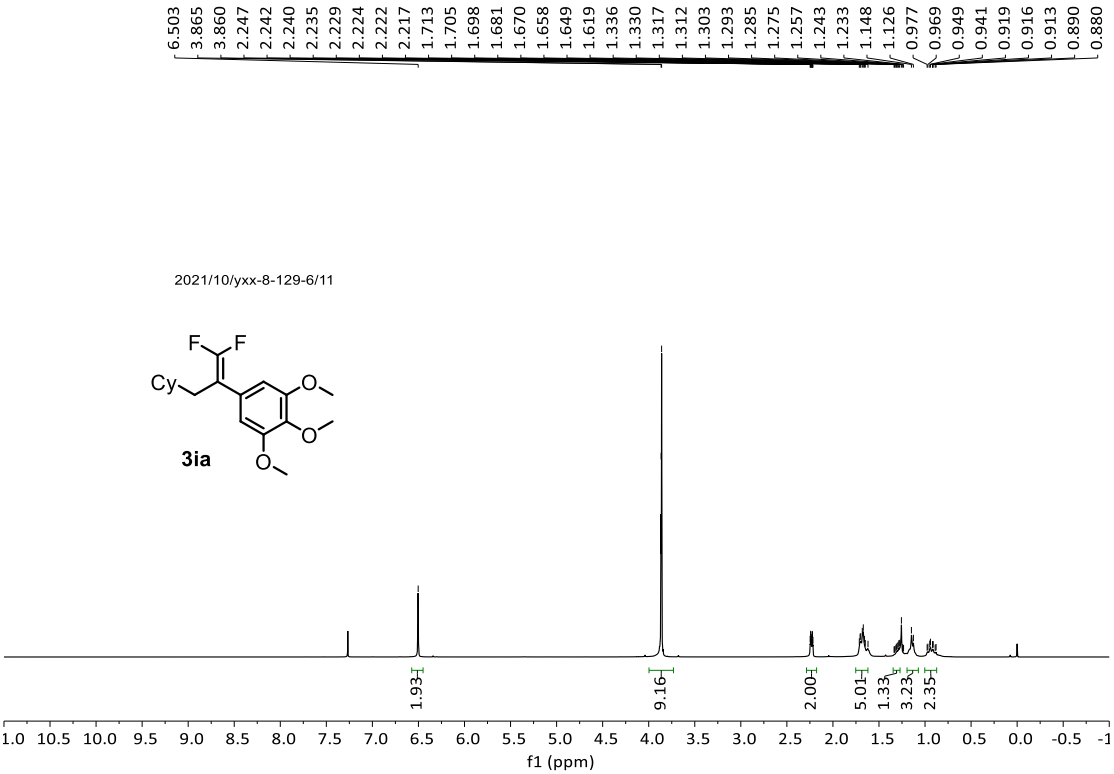

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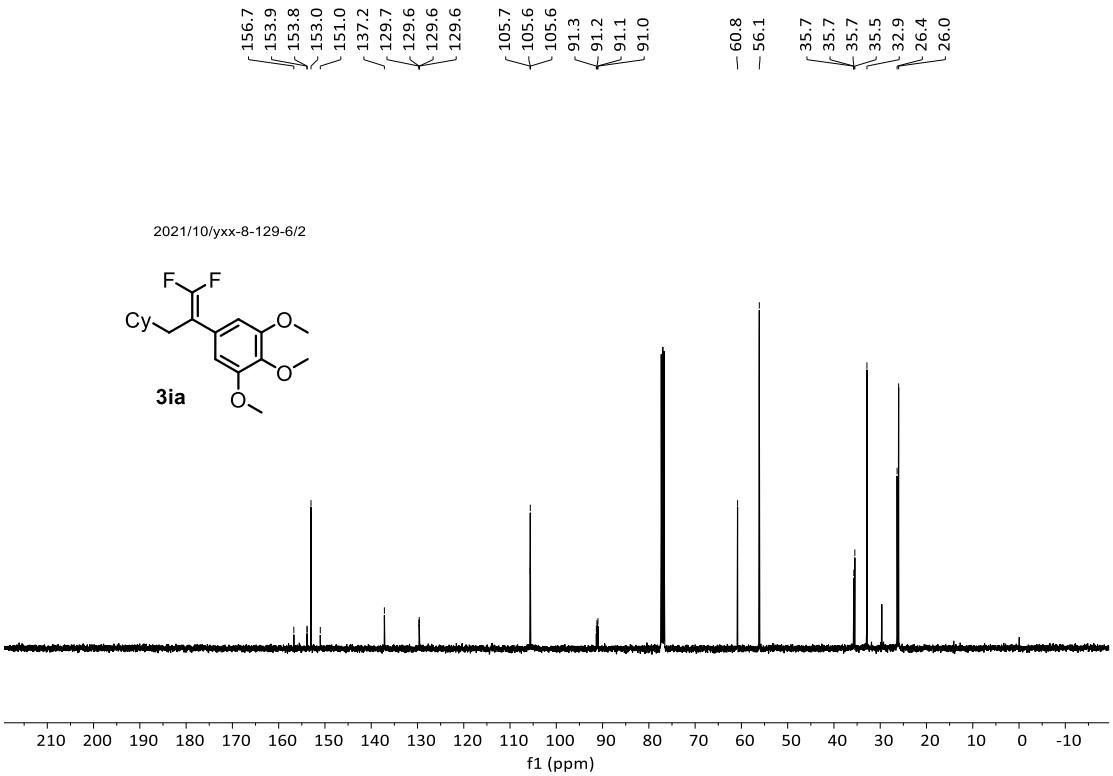

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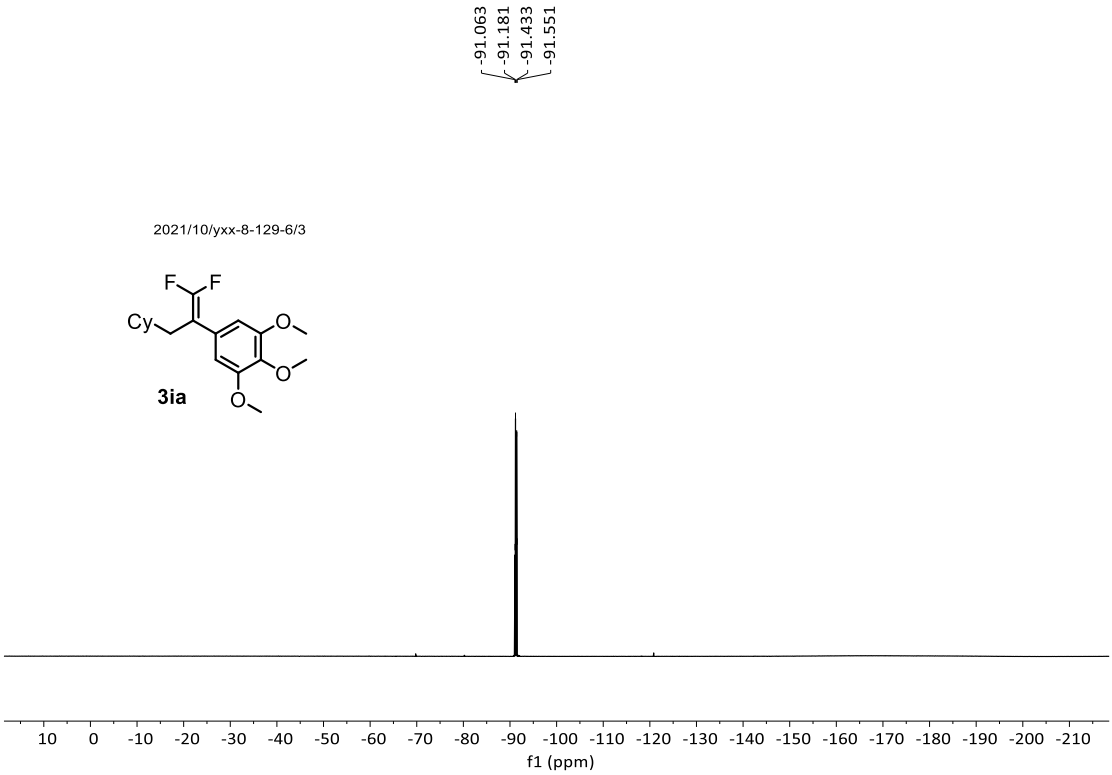

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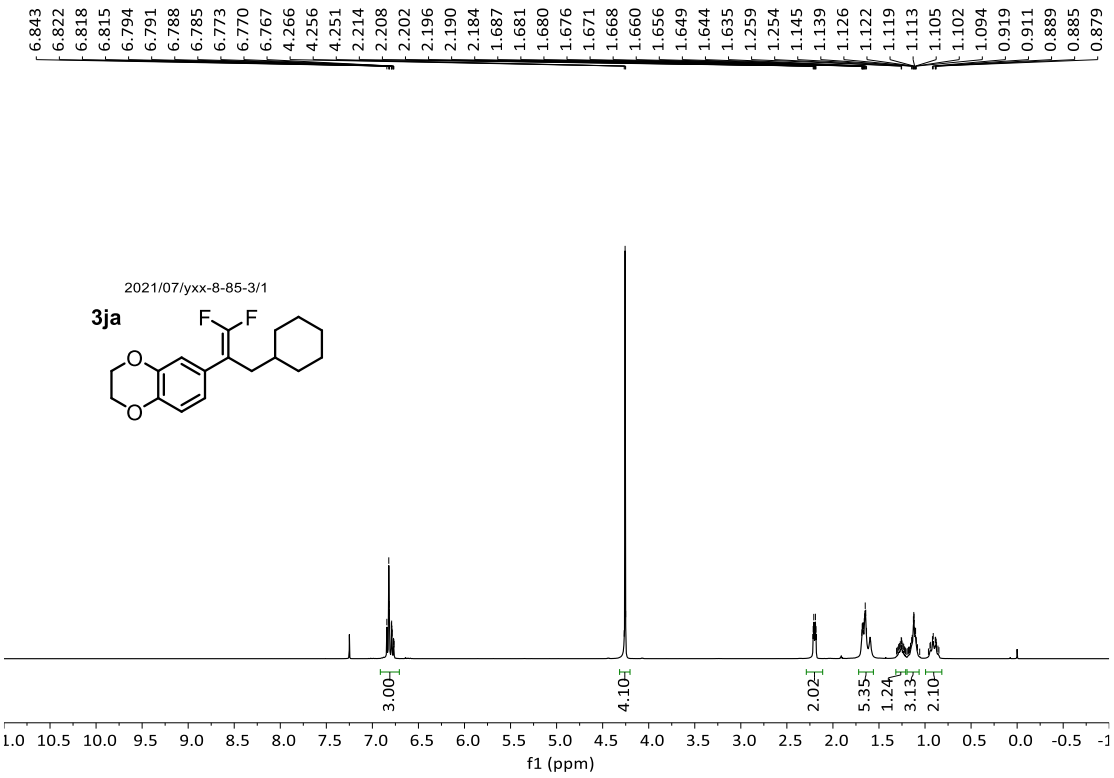

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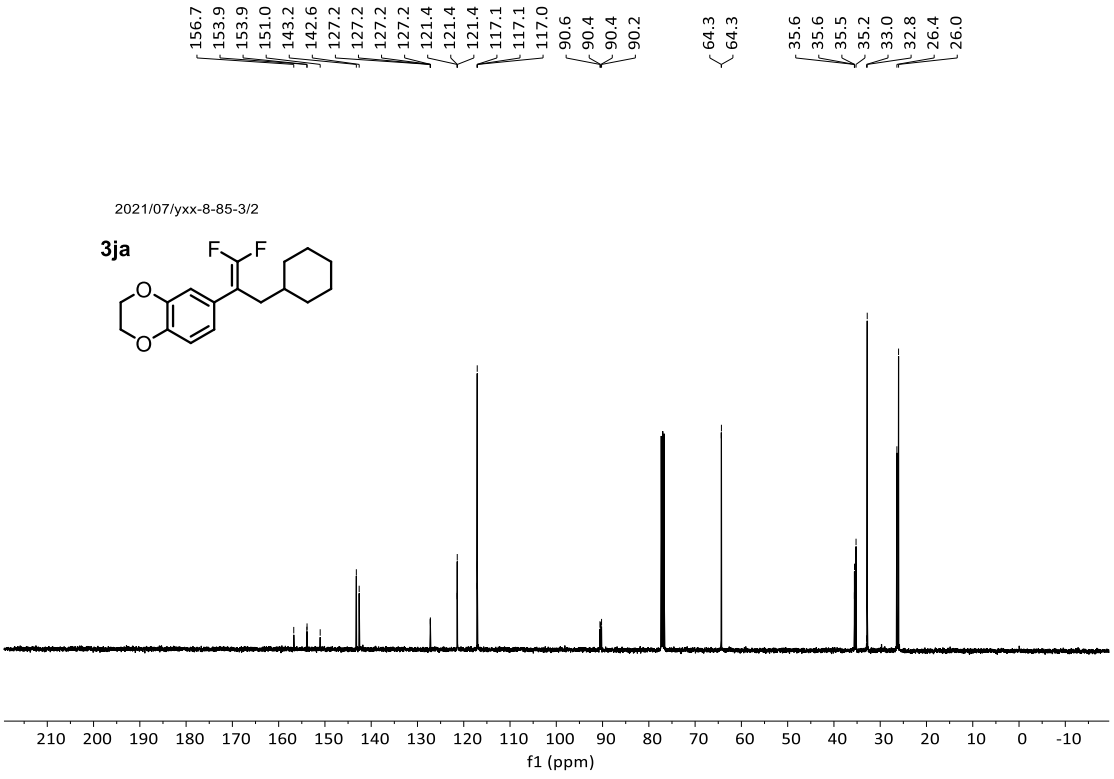

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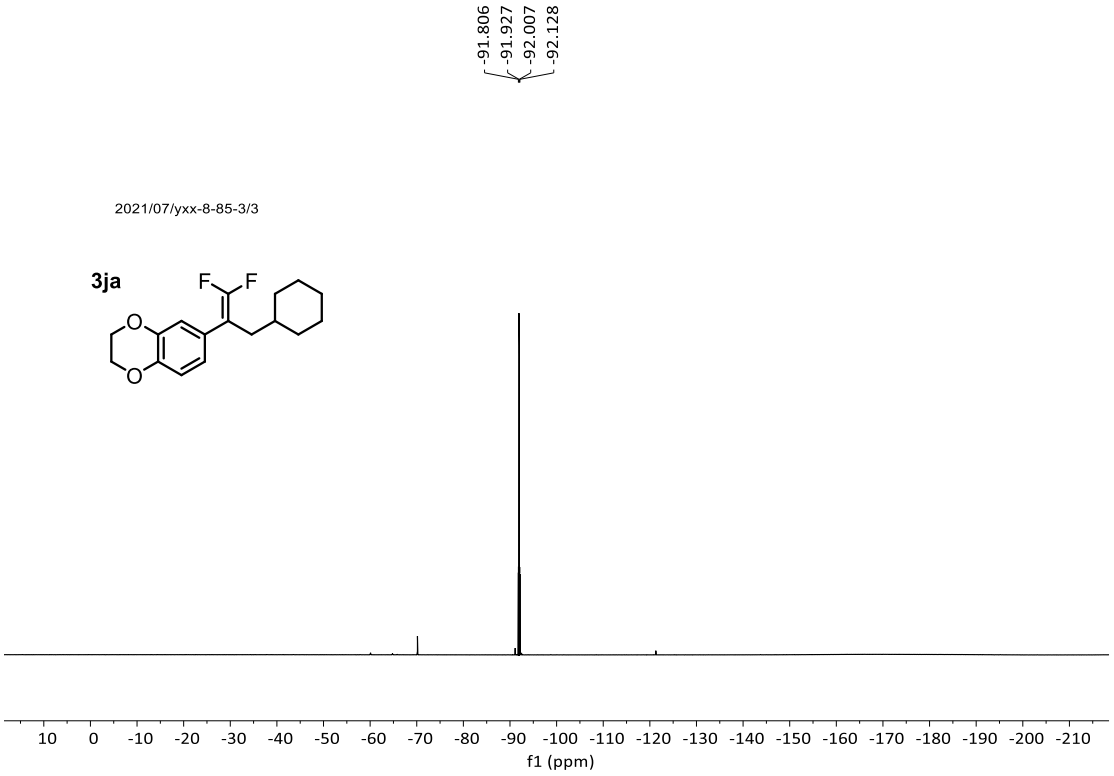

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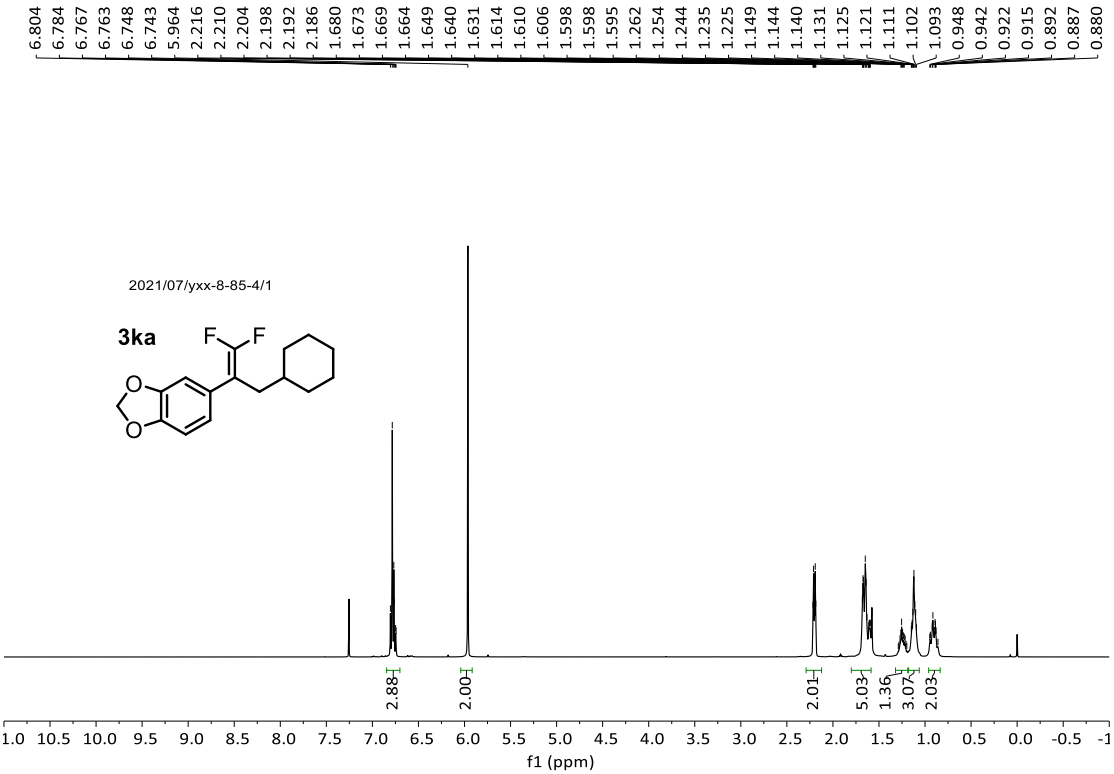

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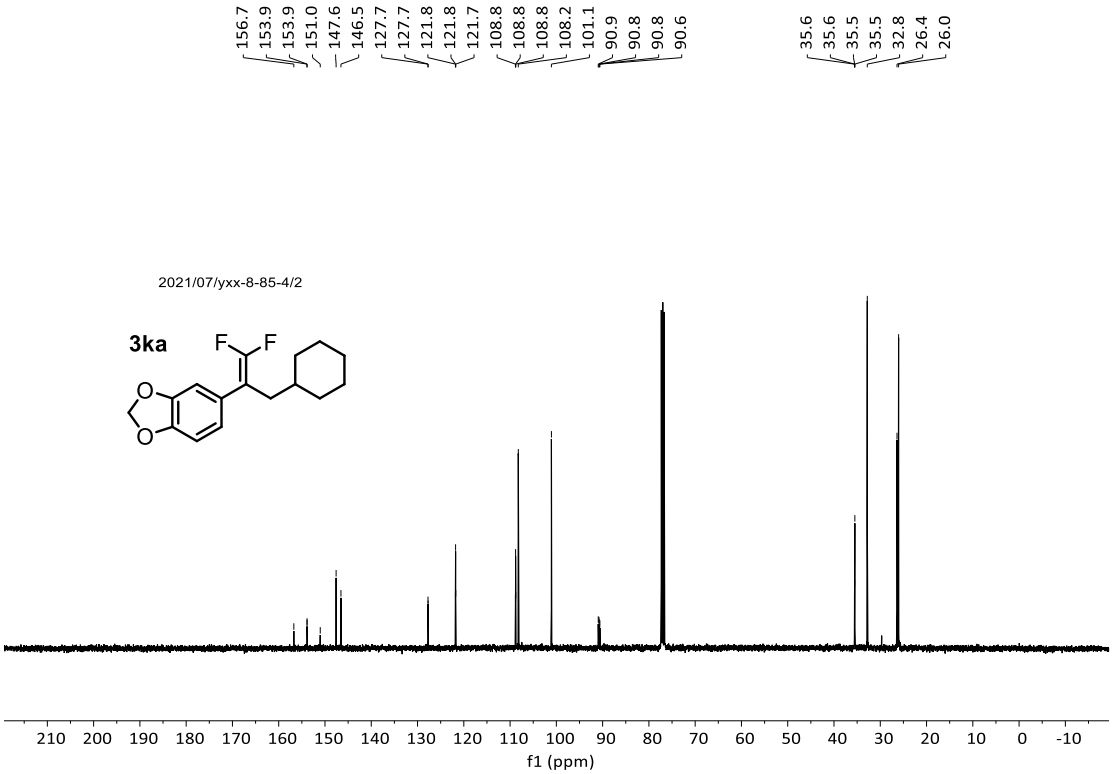

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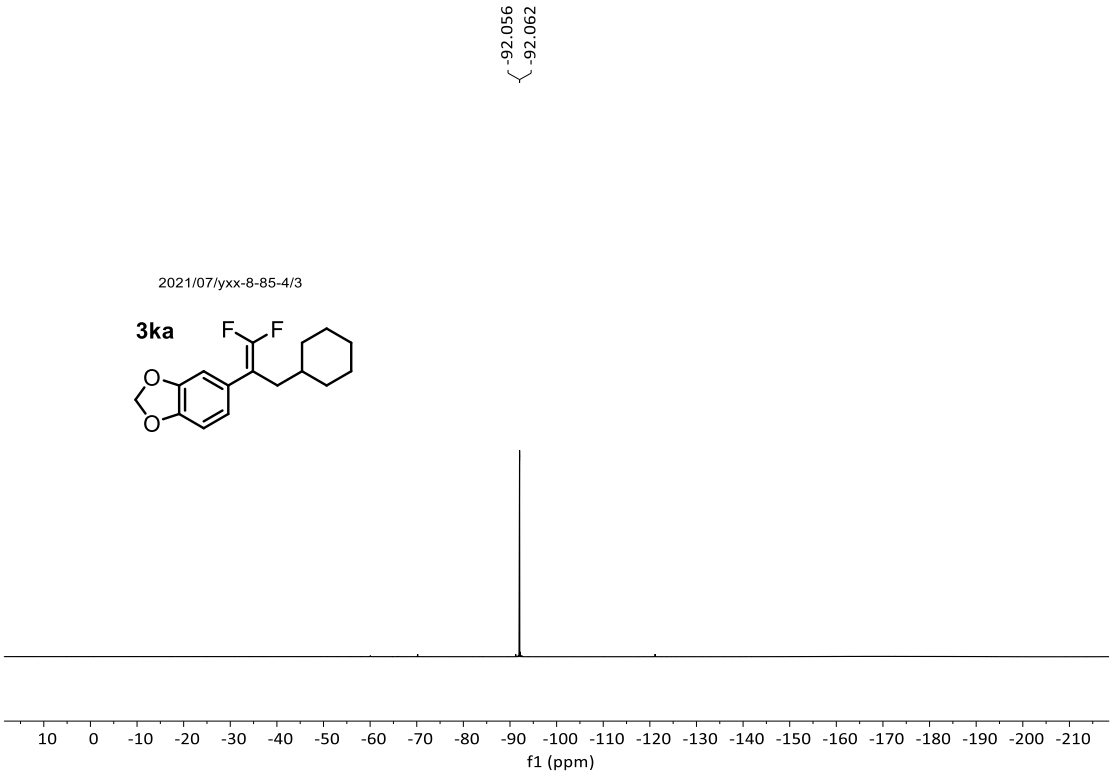

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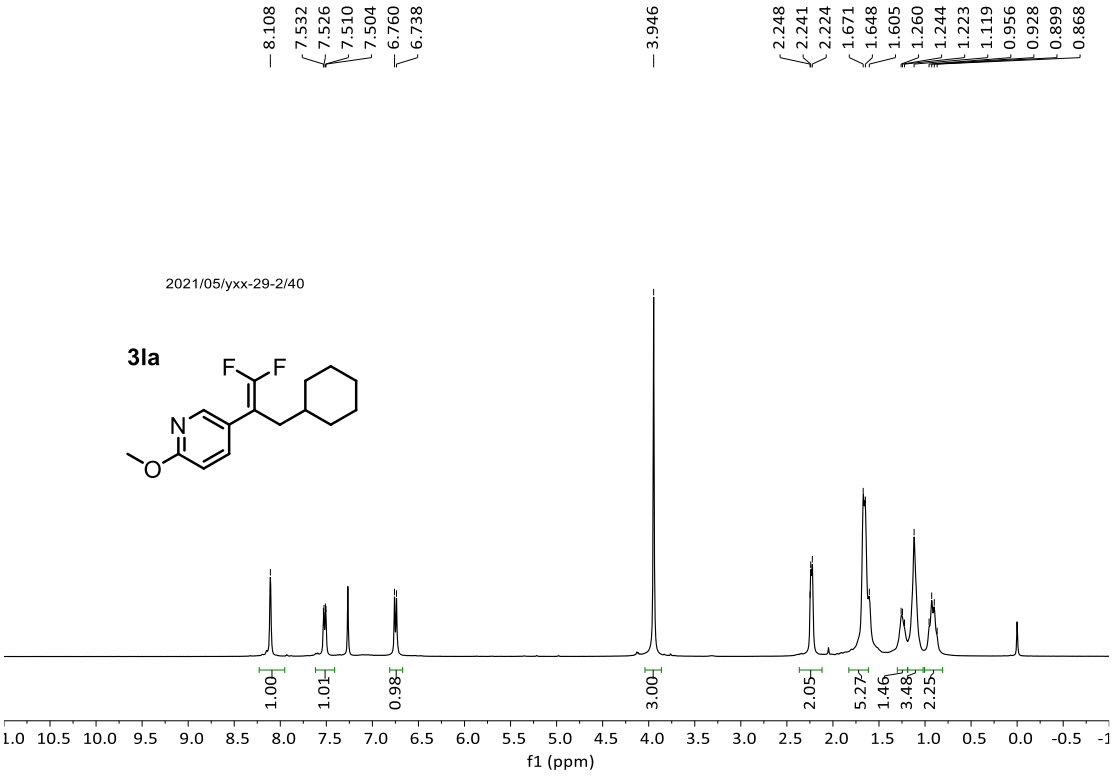

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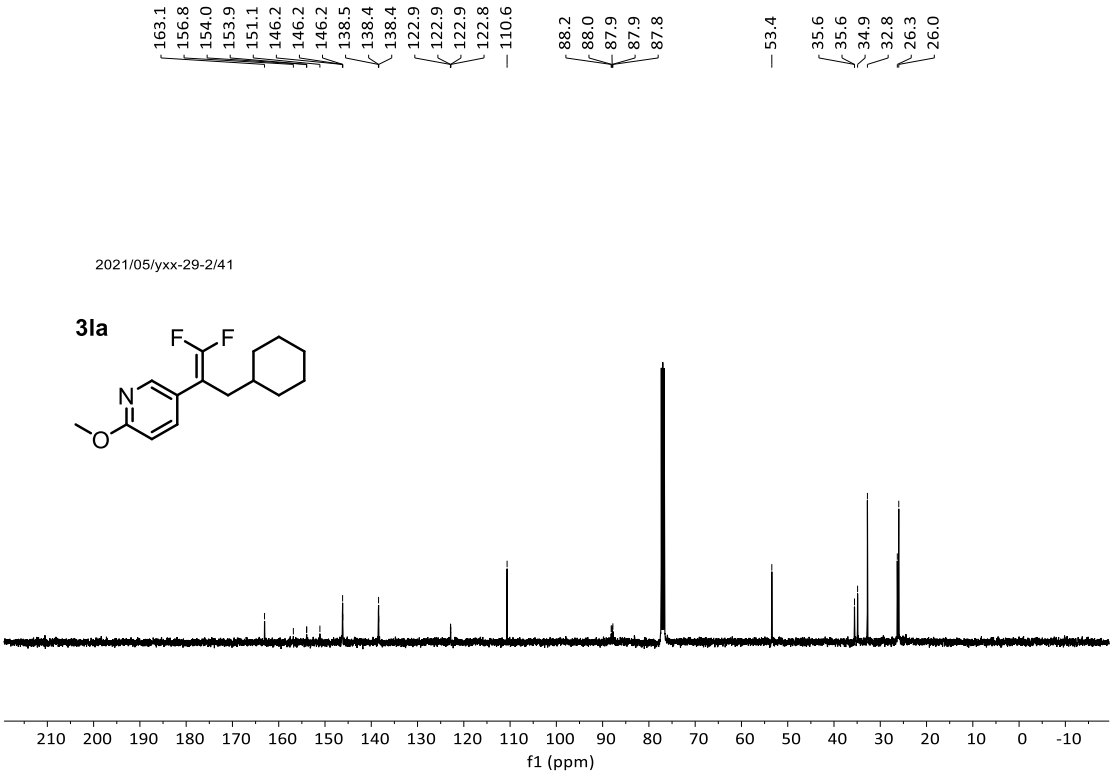

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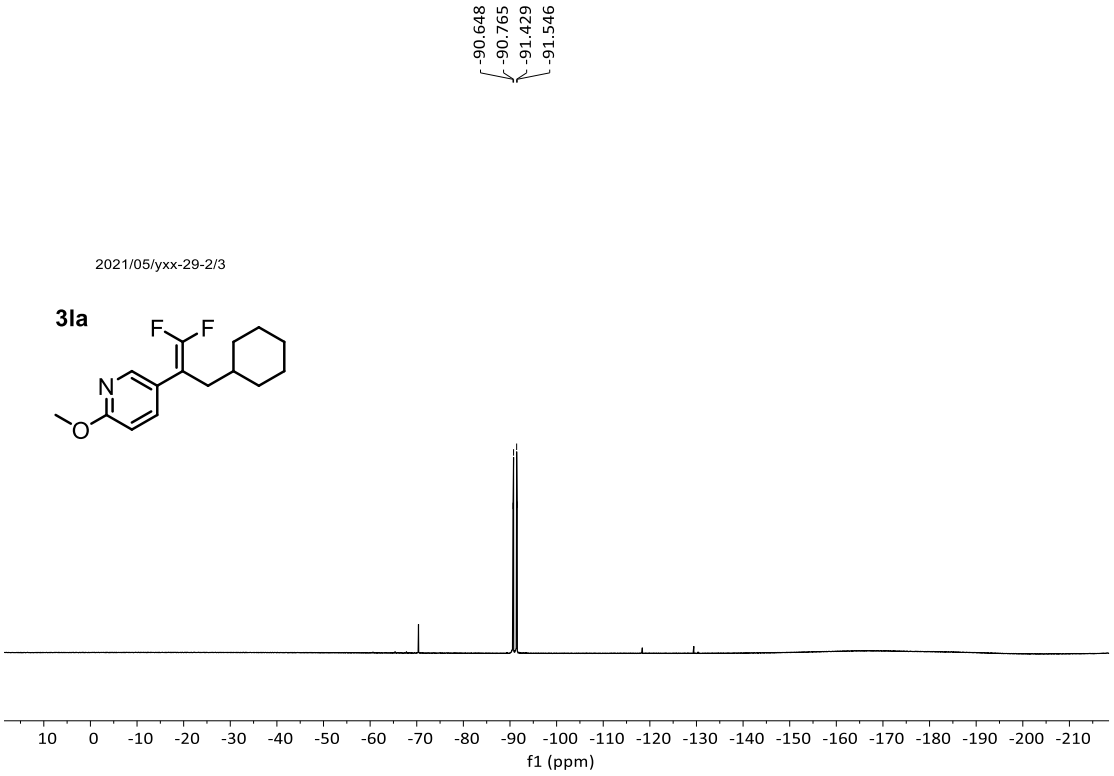

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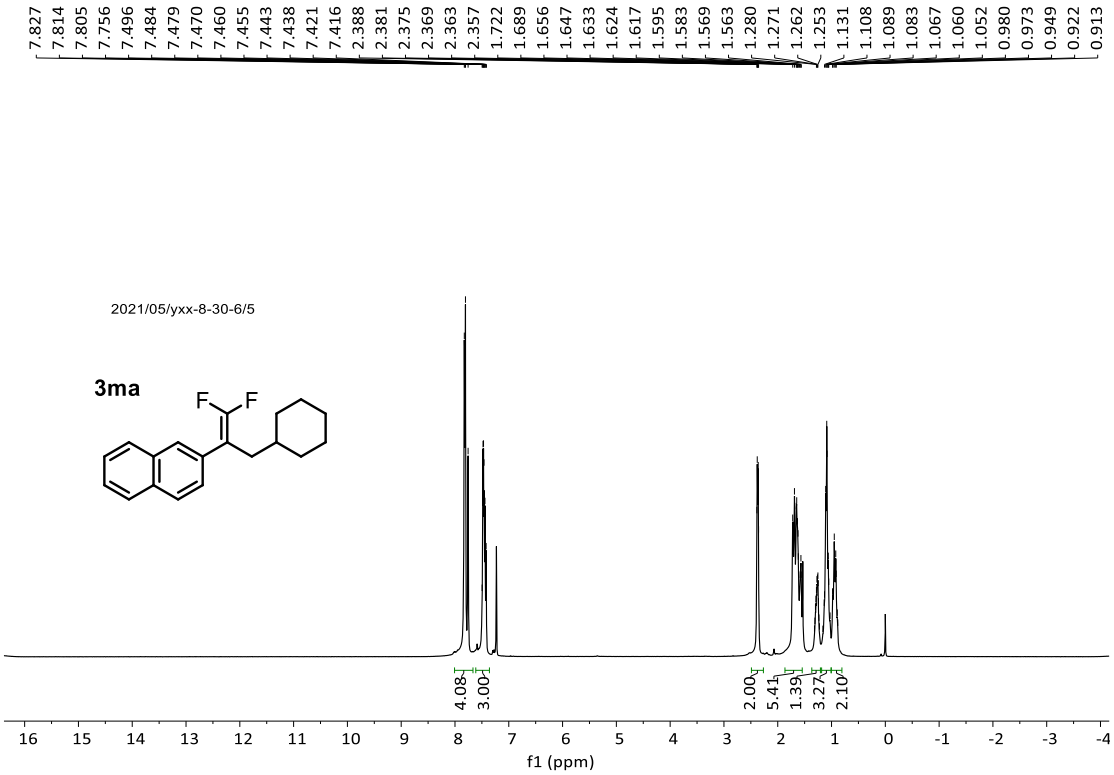

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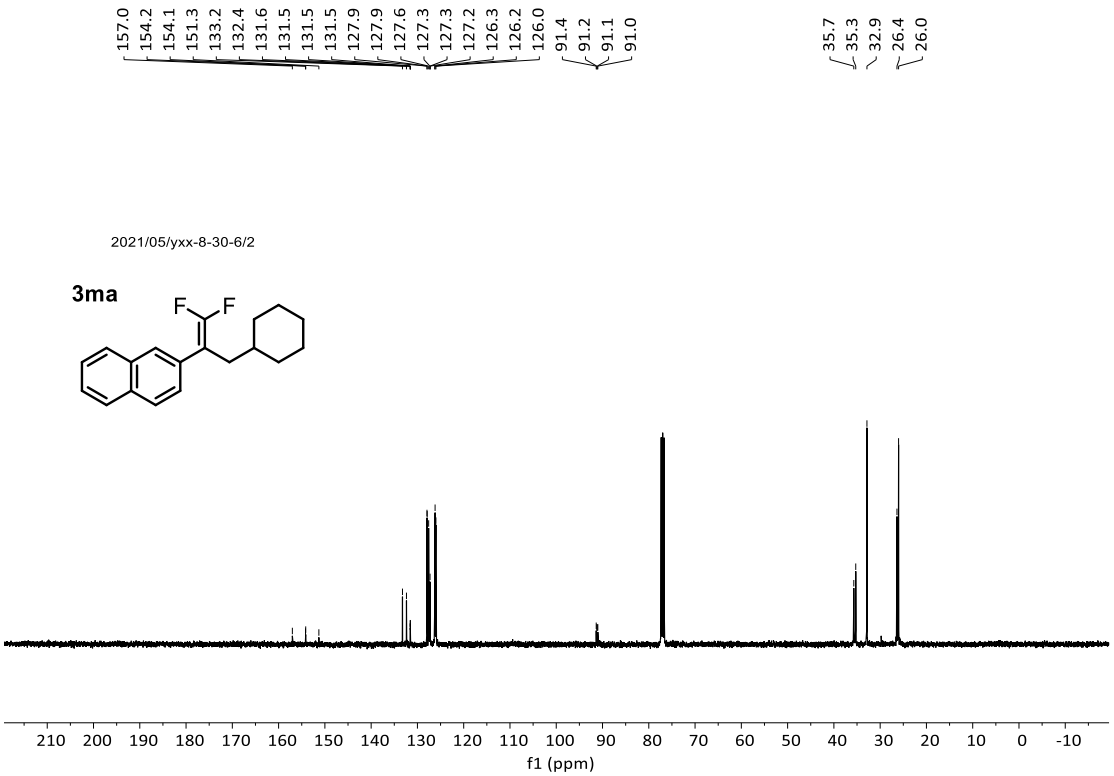

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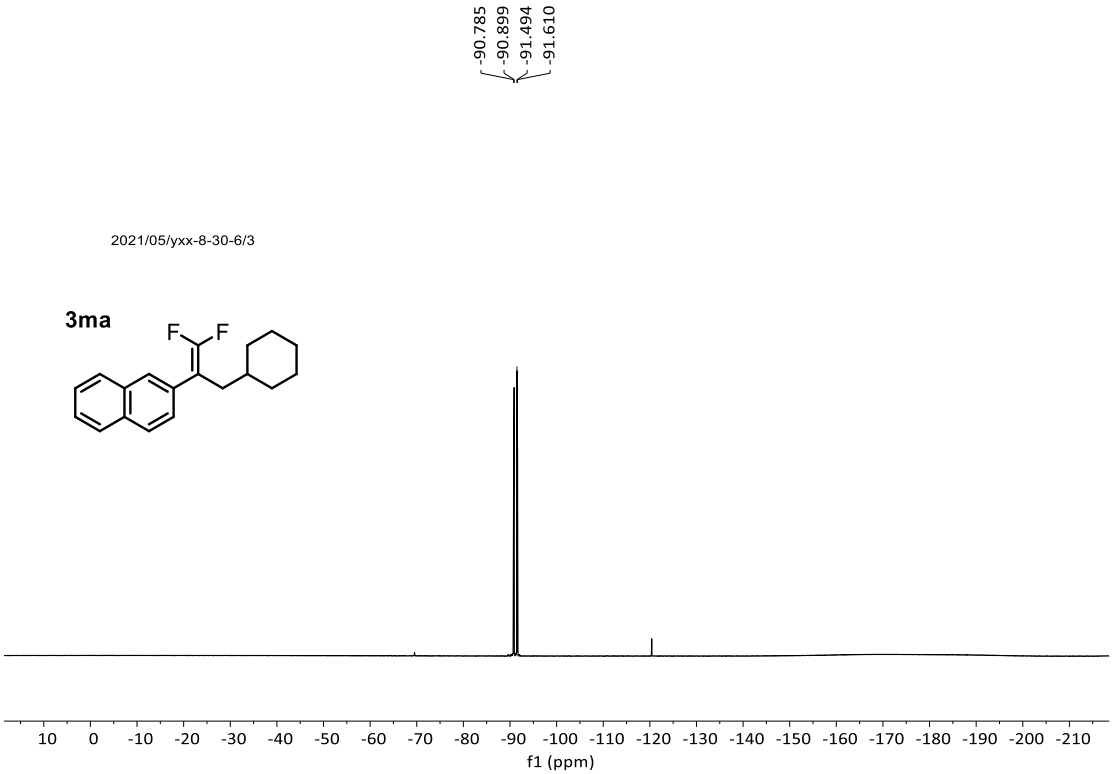

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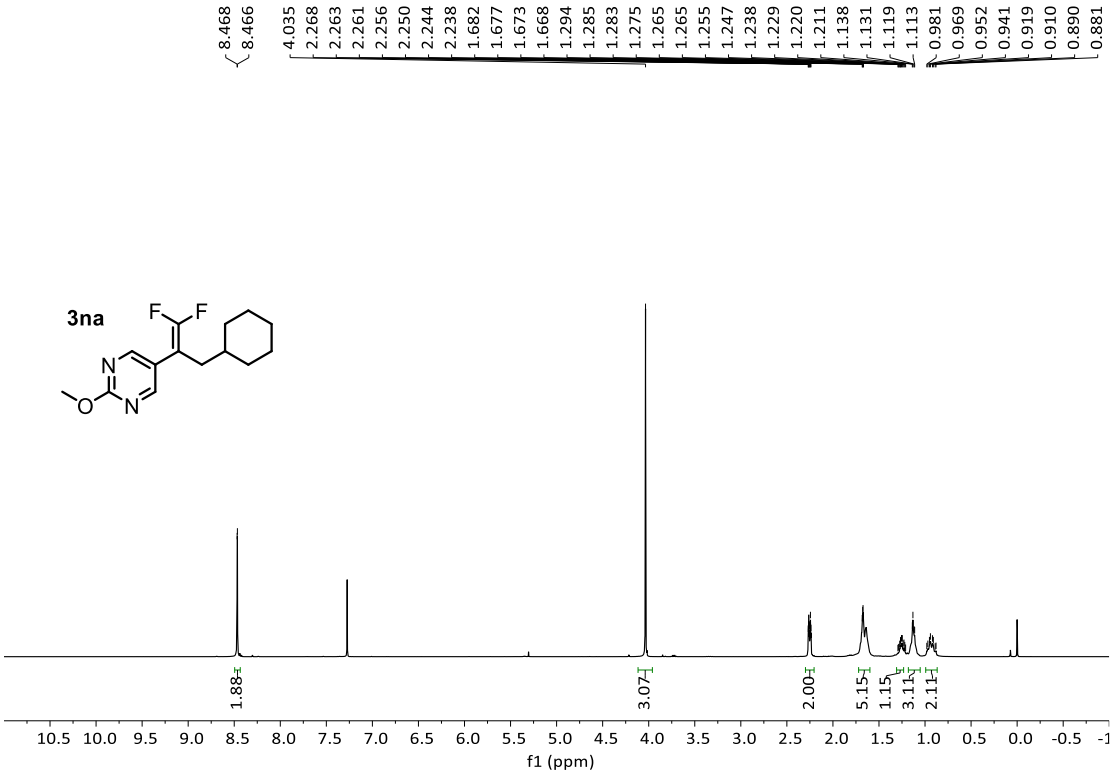

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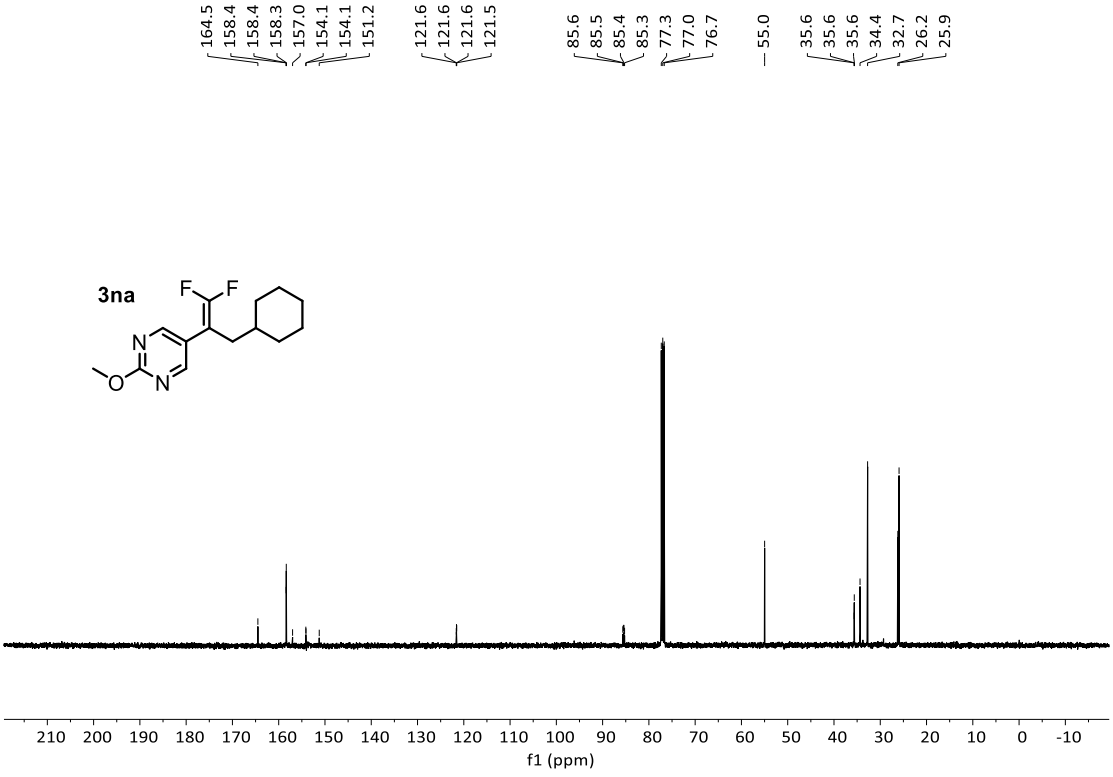

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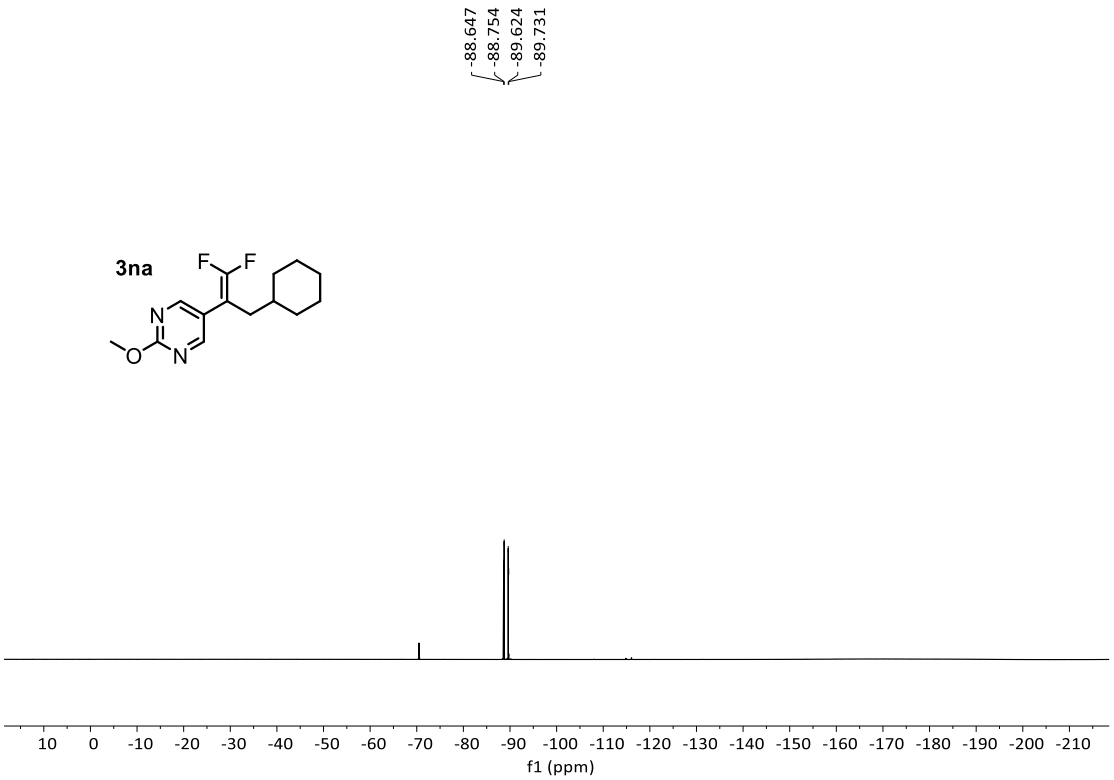
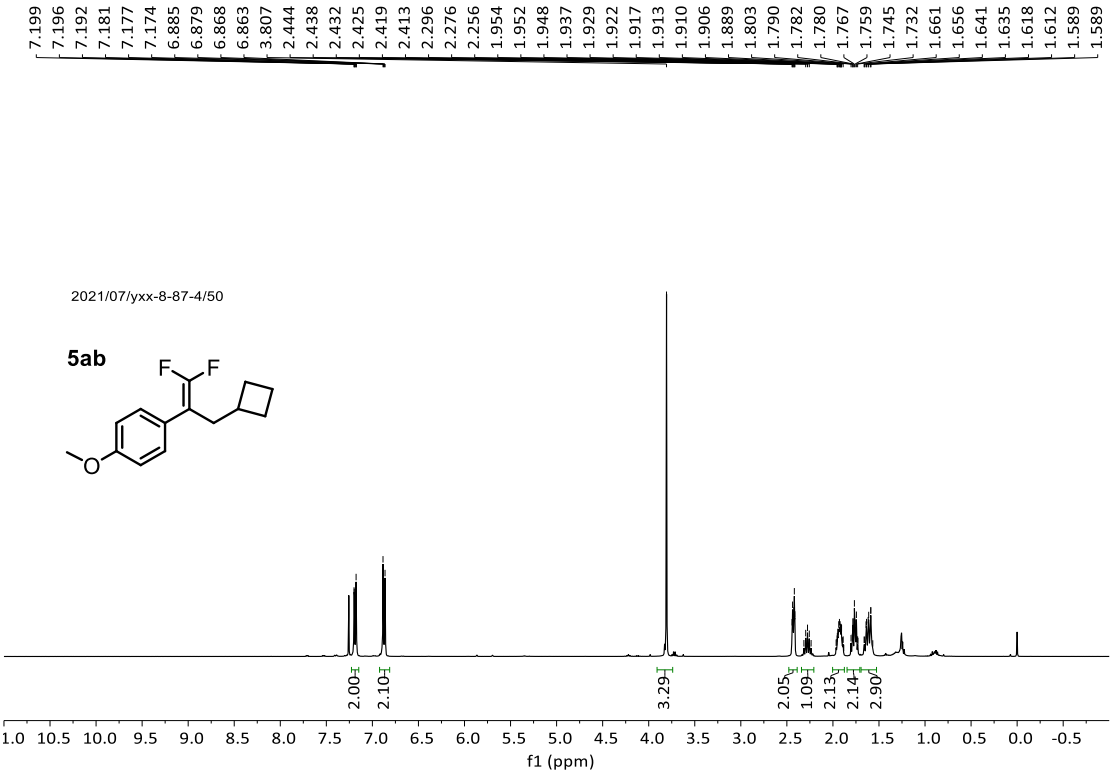
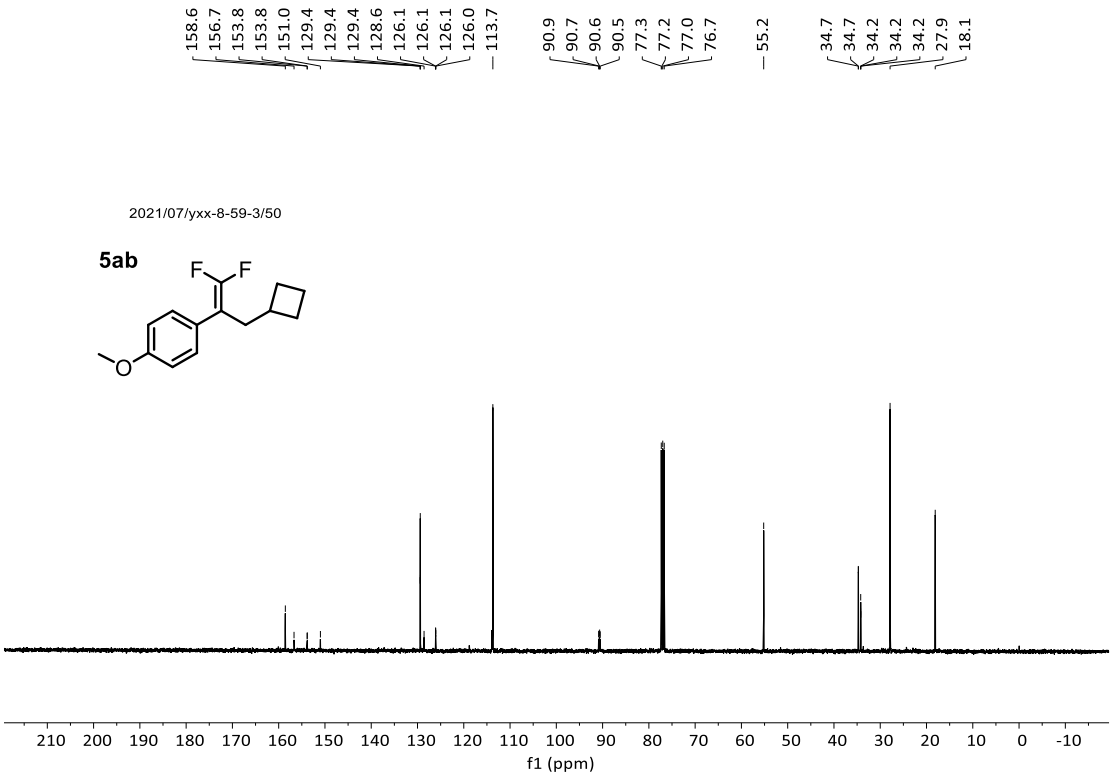


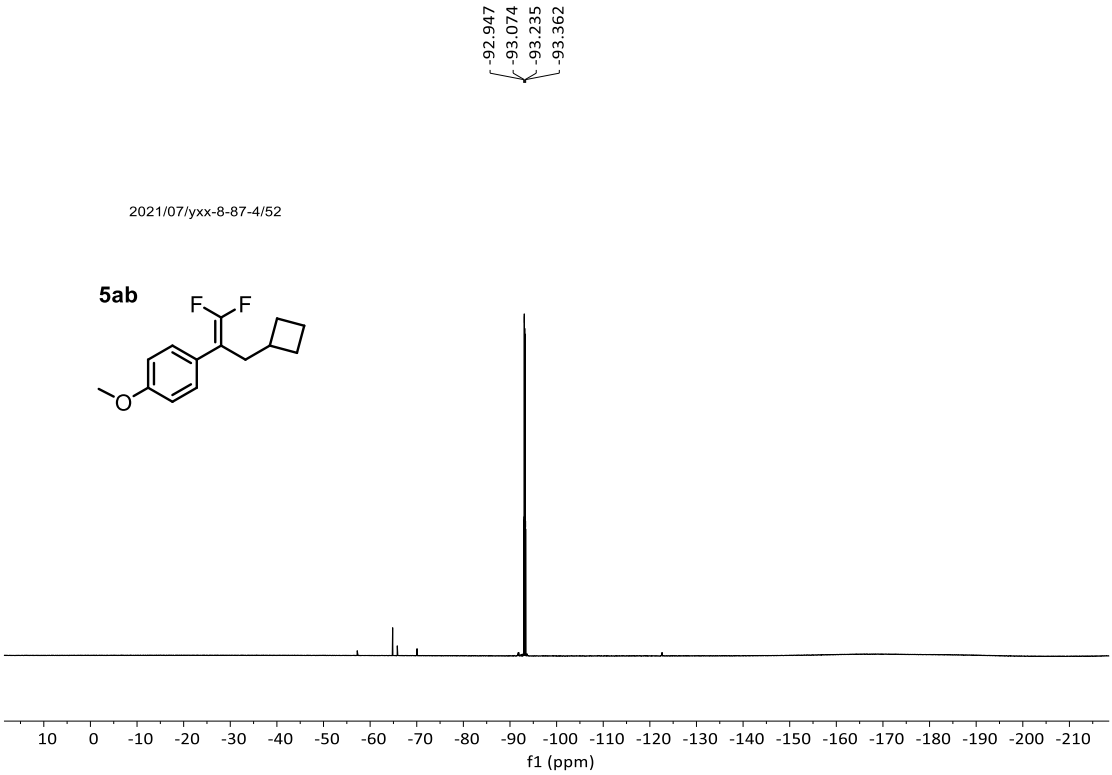
^{1}H NMR (400 MHz, $CDCl_3$):



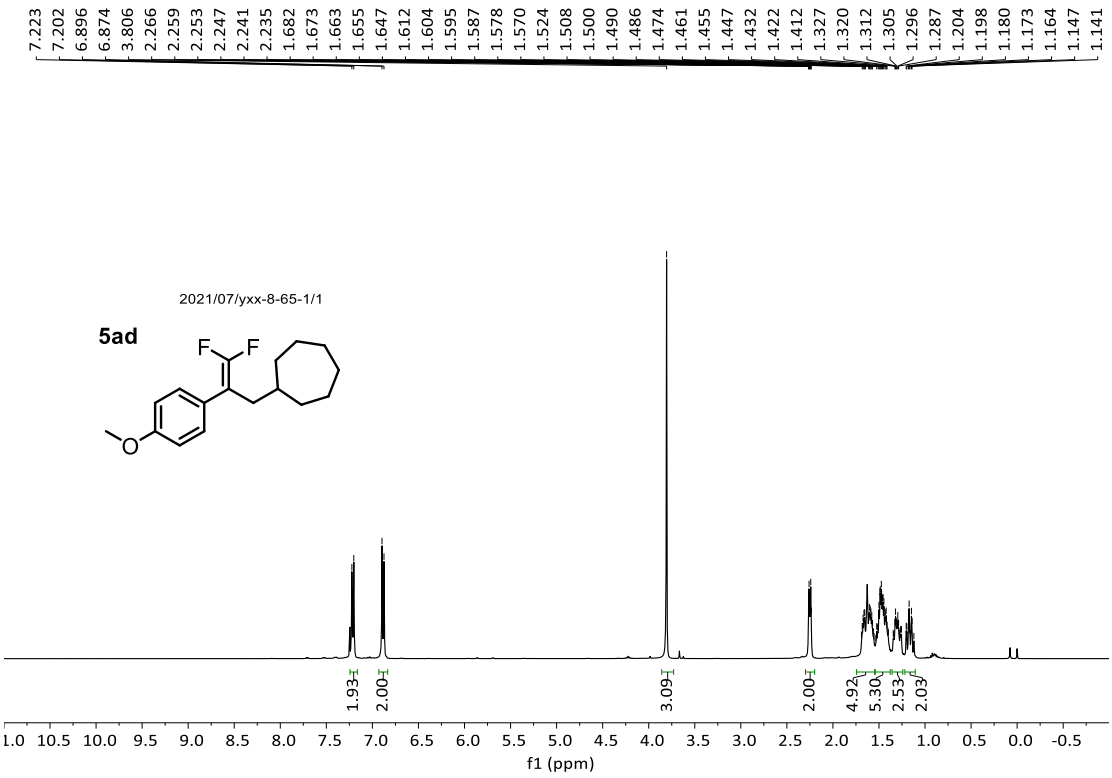
^{13}C NMR (101MHz, $CDCl_3$):



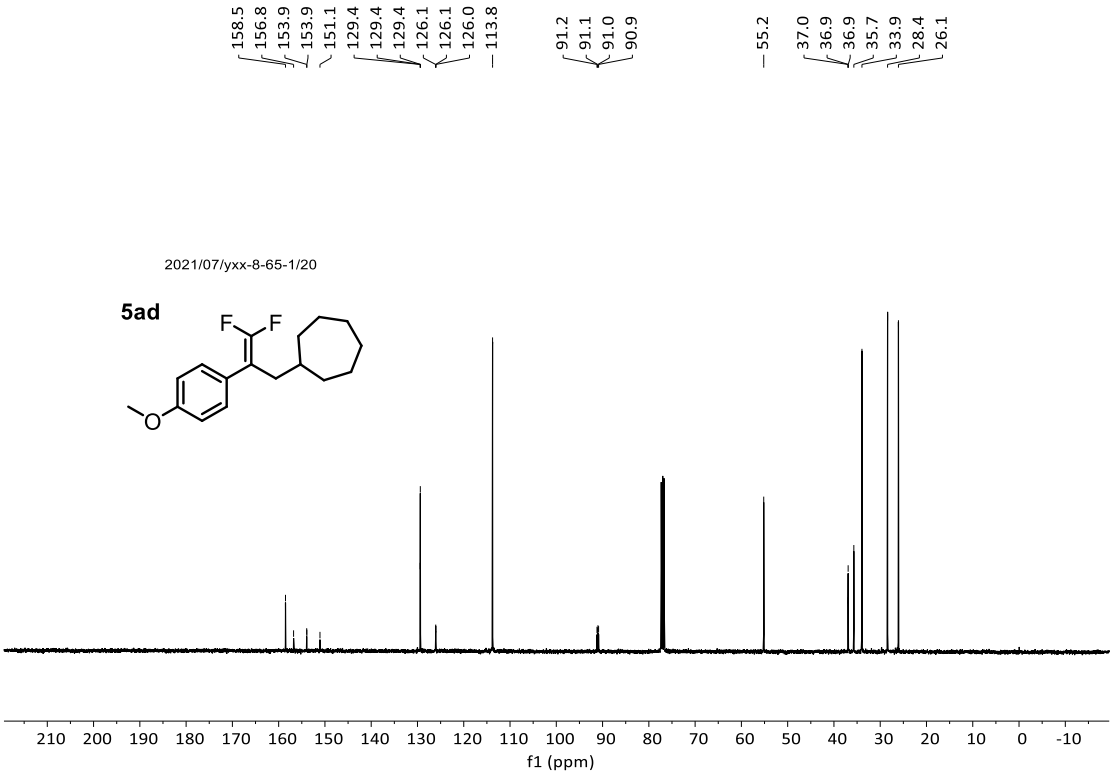
^{19}F NMR (377 MHz, $CDCl_3$):



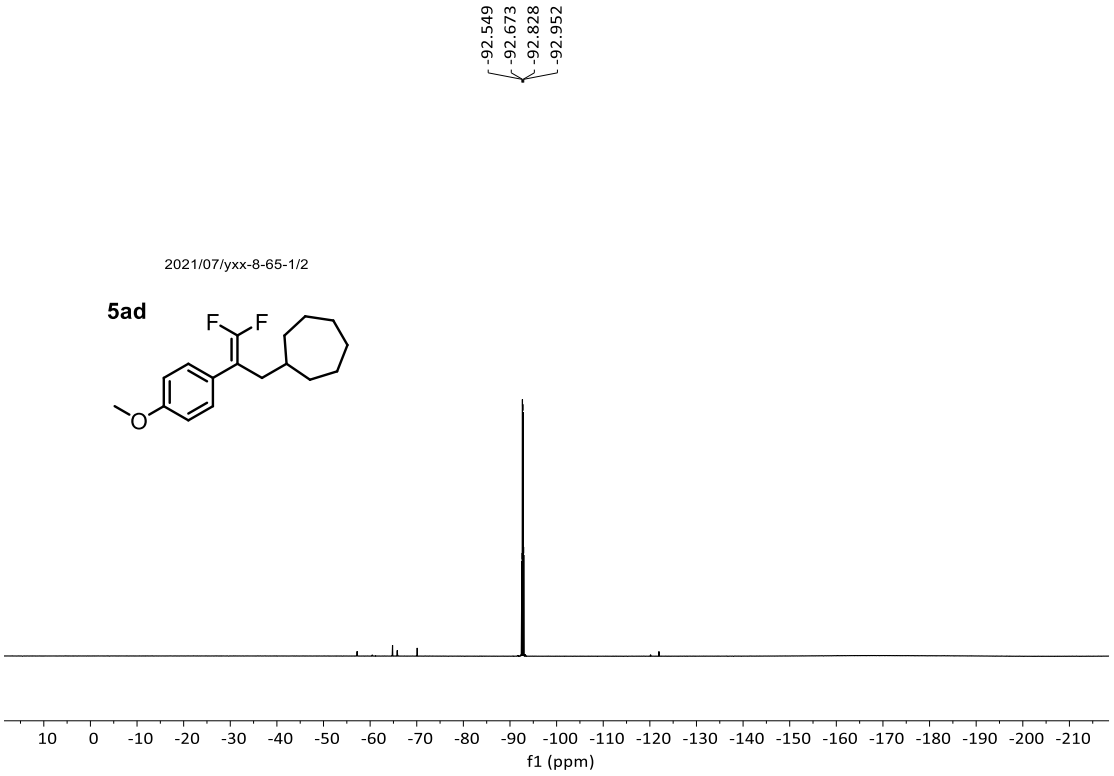
^{1}H NMR (400 MHz, $CDCl_3$):



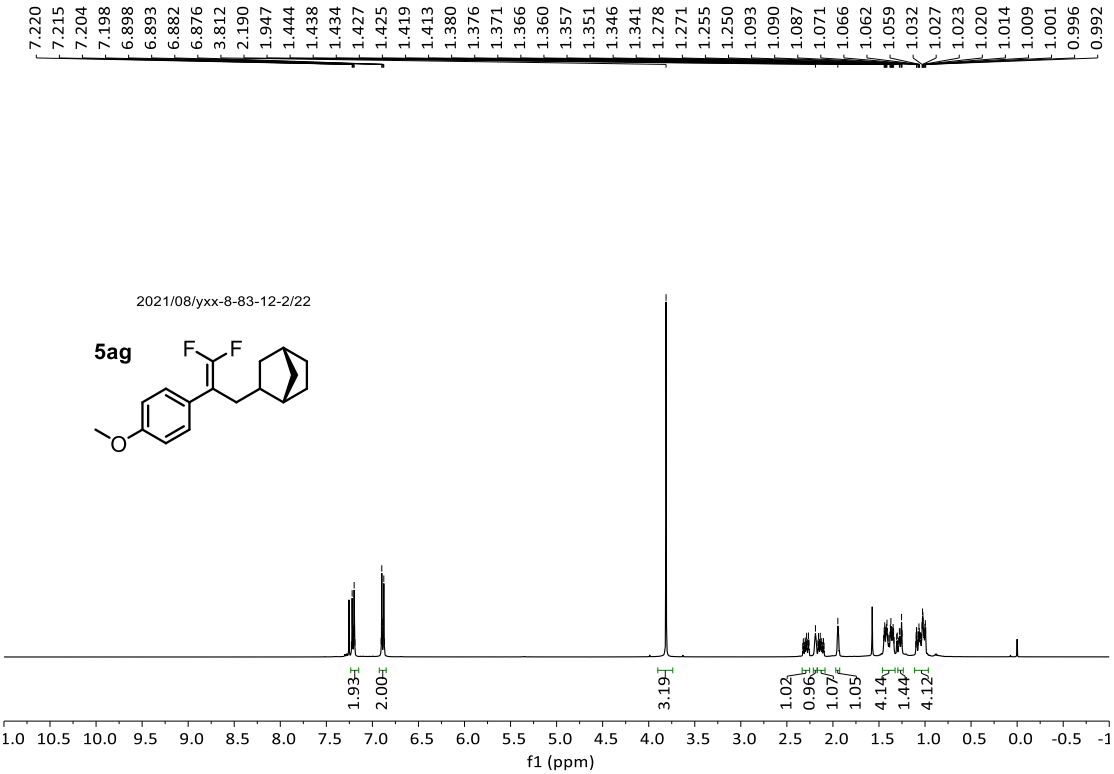
^{13}C NMR (101 MHz, $CDCl_3$):



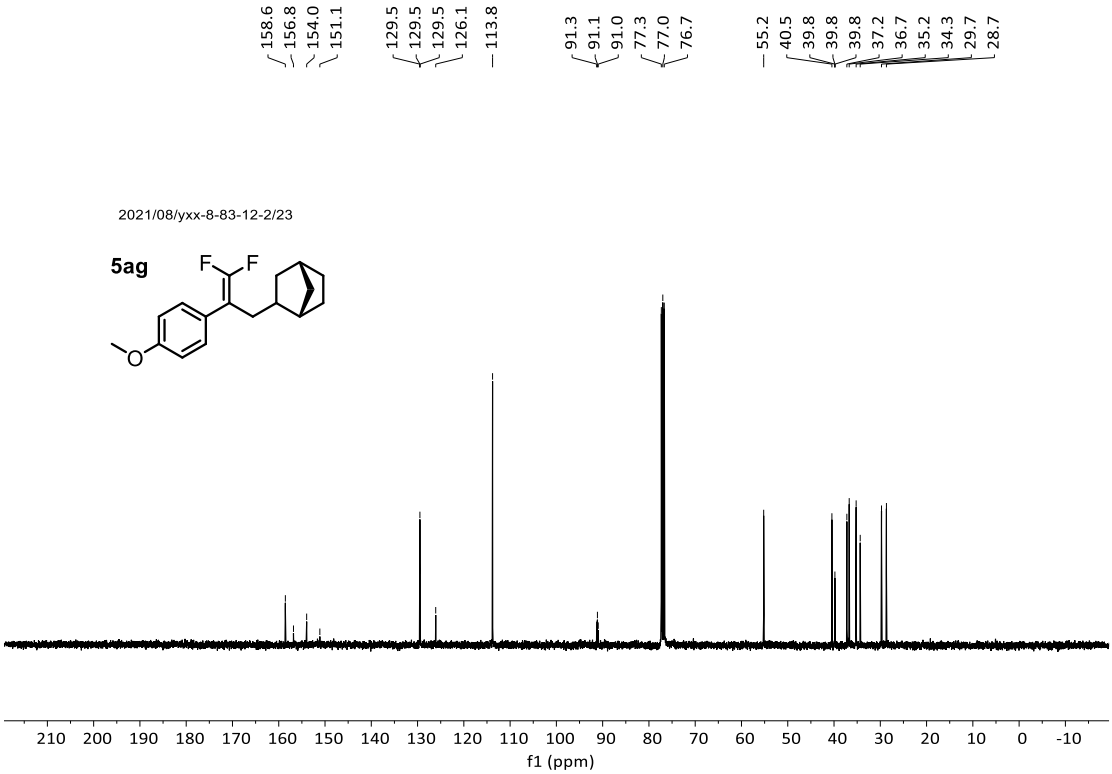
^{19}F NMR (377 MHz, $CDCl_3$):



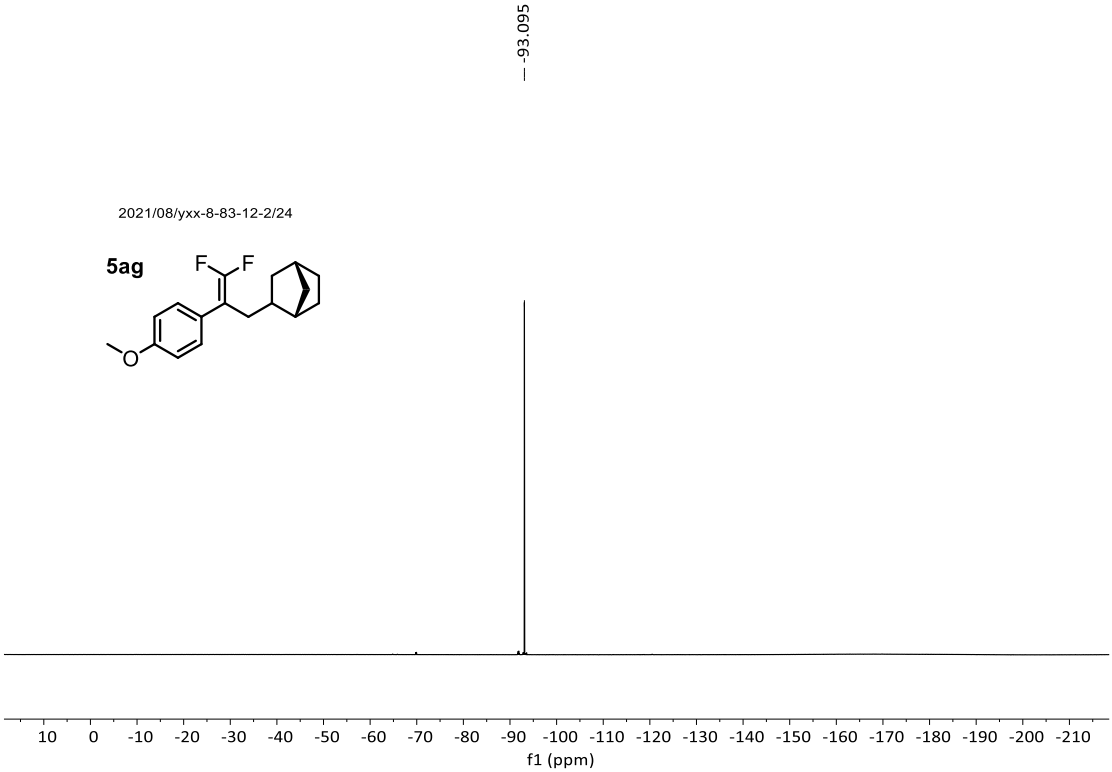
^{1}H NMR (400 MHz, $CDCl_3$):



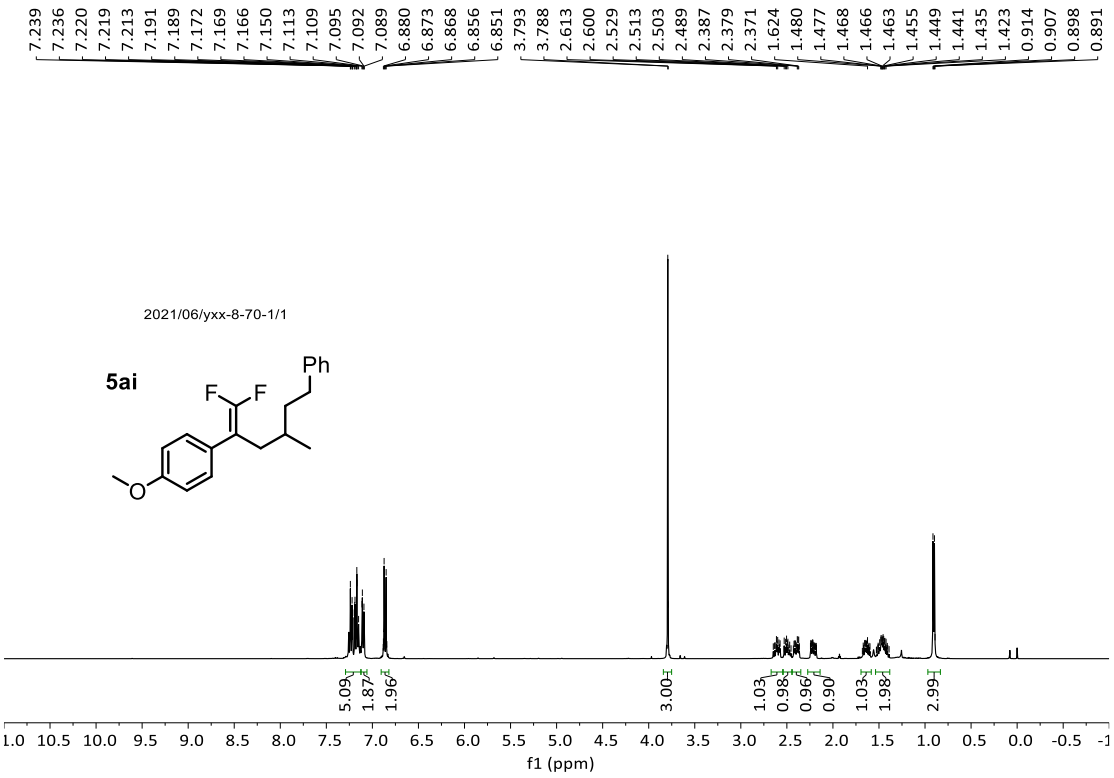
^{13}C NMR (101 MHz, $CDCl_3$):



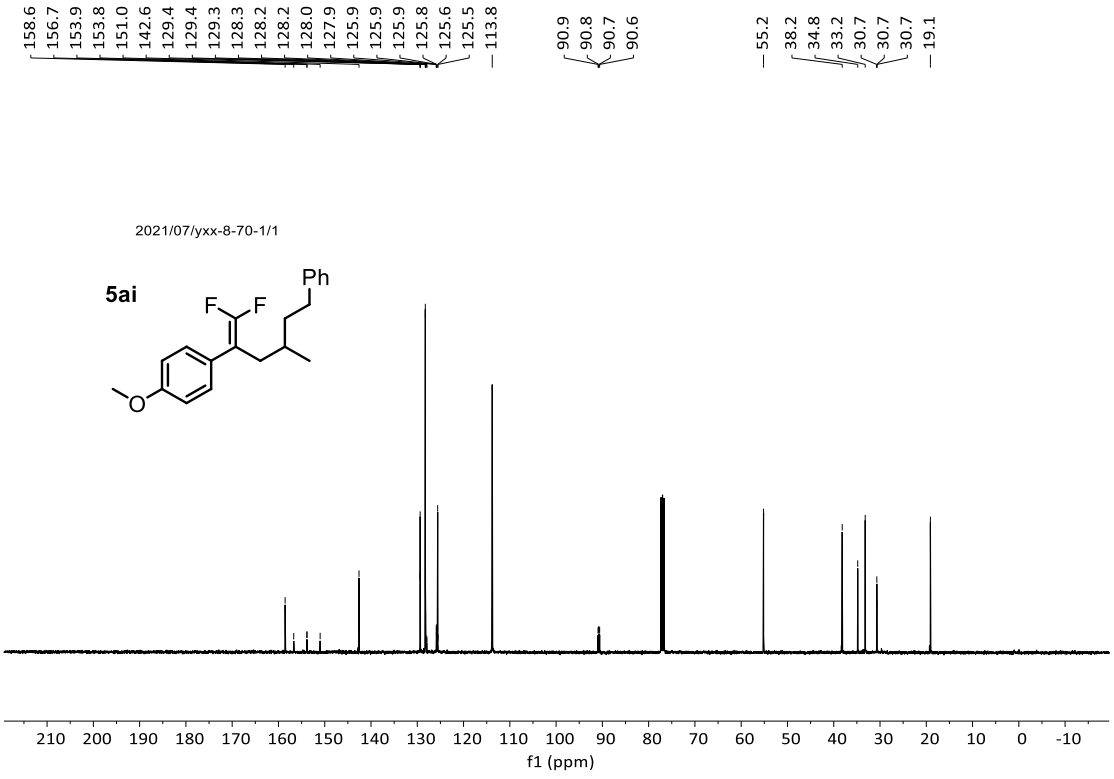
^{19}F NMR (377 MHz, $CDCl_3$):



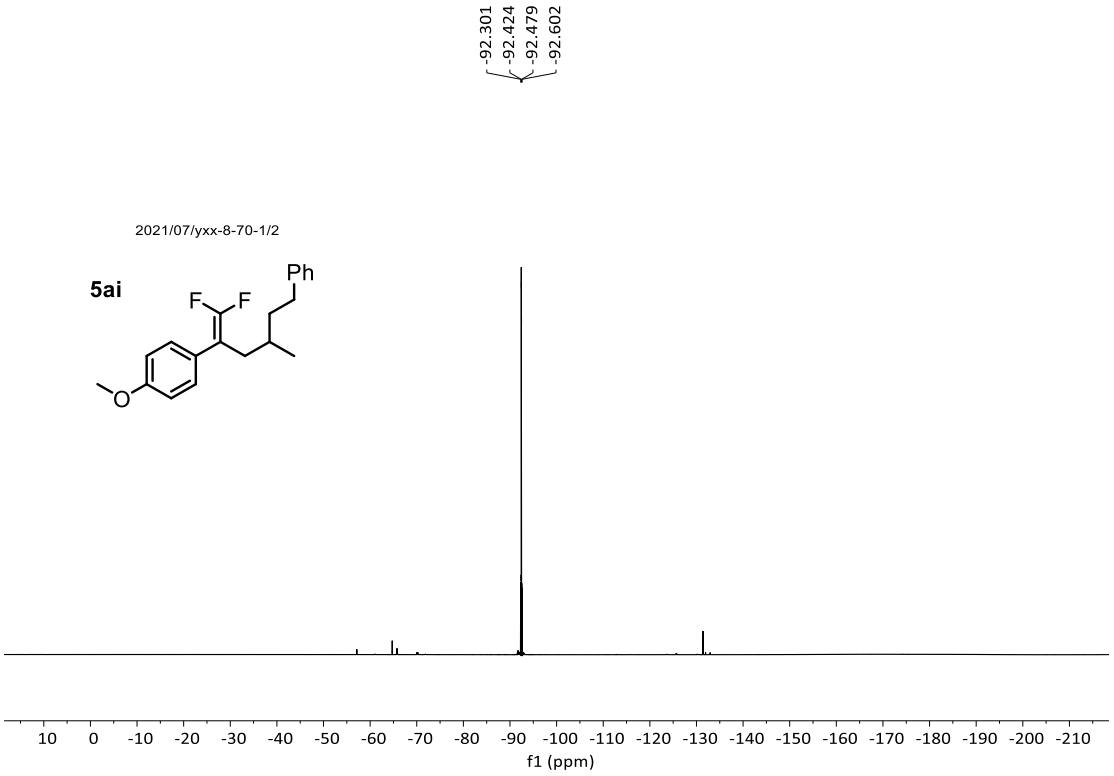
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (400 MHz, $CDCl_3$):

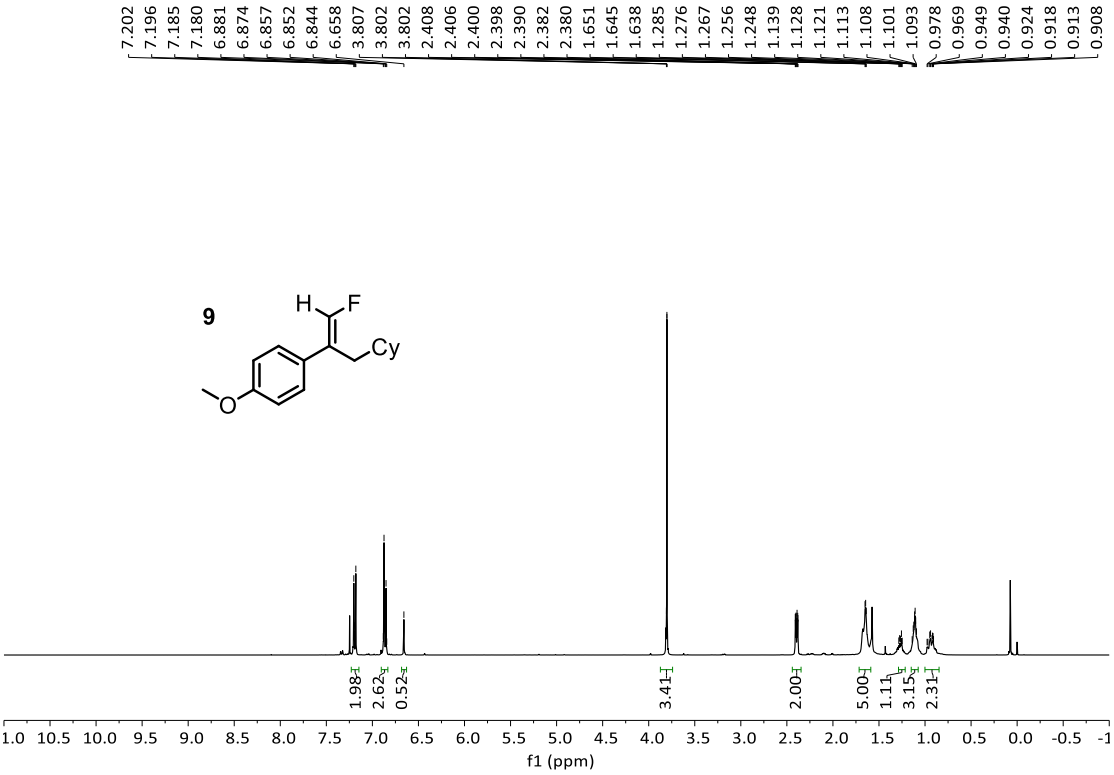


^{19}F NMR (400 MHz, $CDCl_3$):

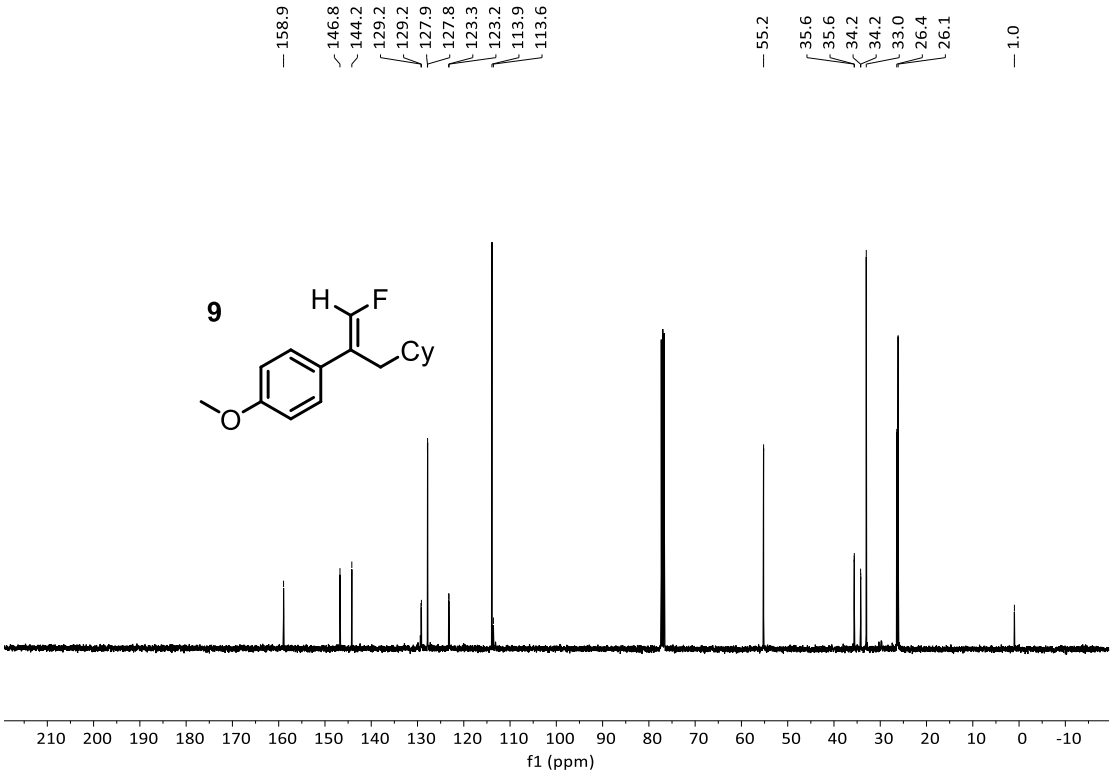


Application:

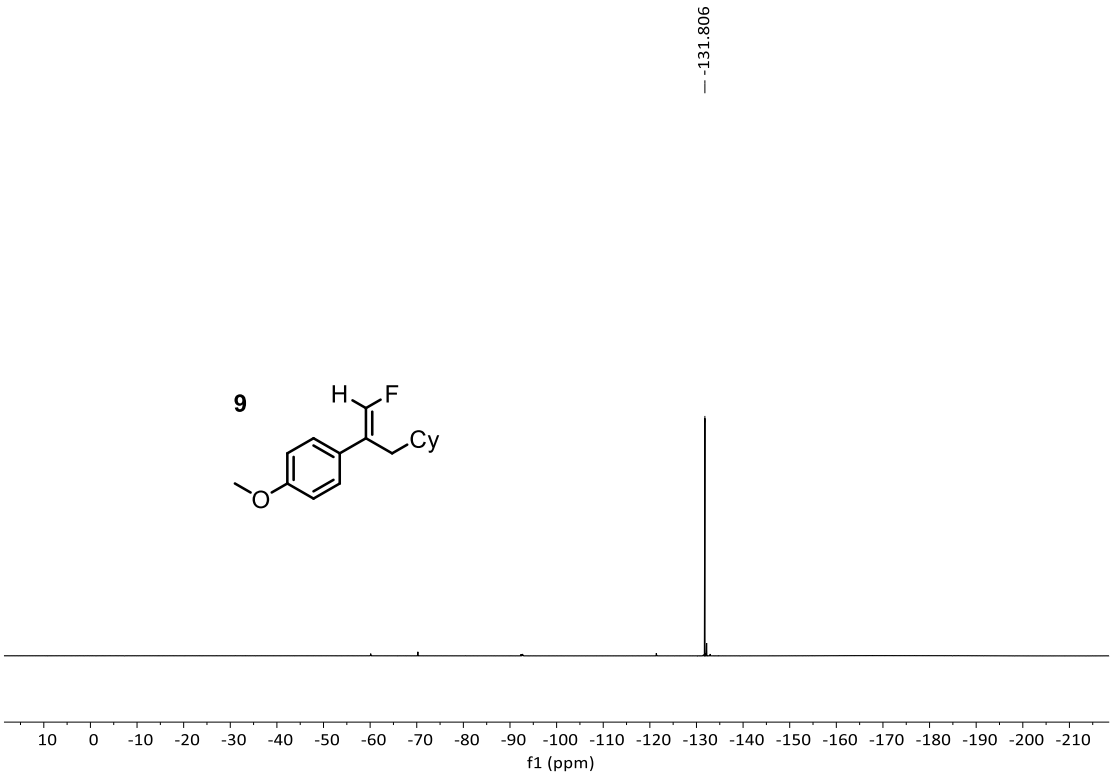
^{1}H NMR (400 MHz, $CDCl_3$):



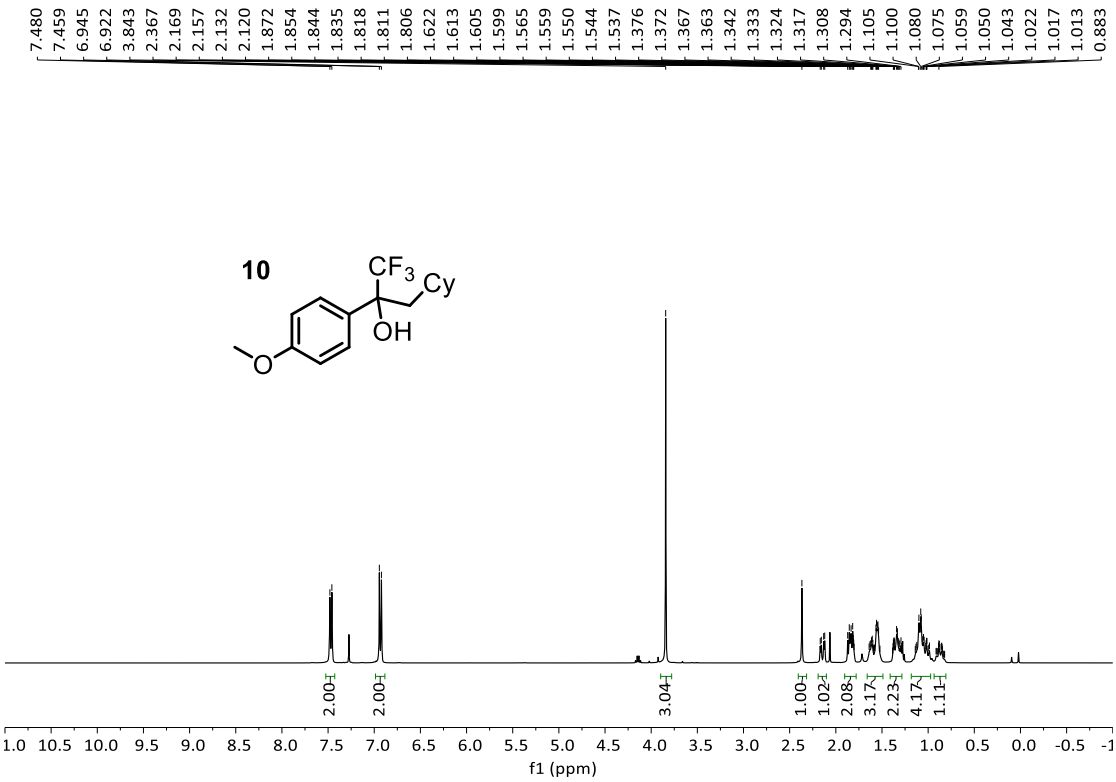
^{13}C NMR (101 MHz, $CDCl_3$):



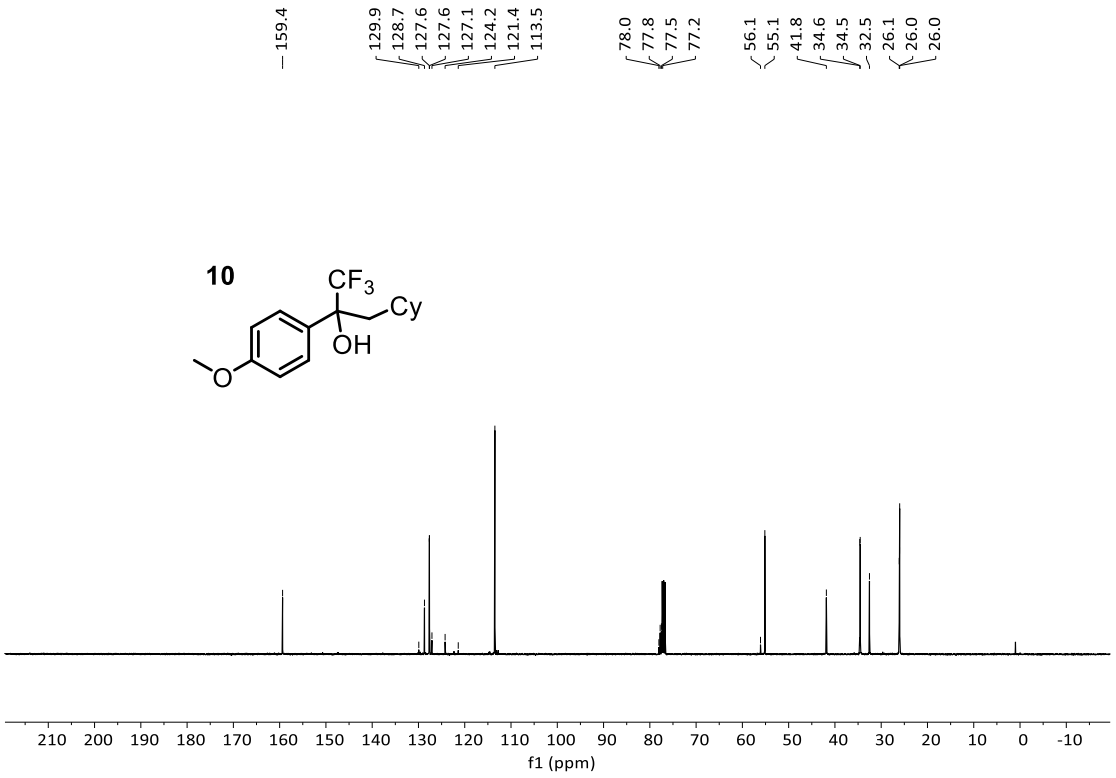
^{19}F NMR (377 MHz, $CDCl_3$):



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



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



^{19}F NMR (377 MHz, $CDCl_3$):