Supplementary Information

Controllable atom transfer enables photoredox-catalyzed defluorinative alkylation of trifluoromethyl alkenes with polychloroalkanes

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from Energy Chemical, Bidepharm, Aladdin Bio-Chem, Meryer Biochemical and J&K Scientific, and were used without further purification.

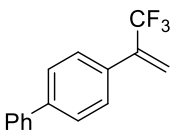
Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Futher visualization method was staining with a basic solution of potassium permanganate, followed by heating. Flash chromatography was performed using Nuotai silica gel (200 – 300 mesh) with distilled solvent. Column were typically packed as slurry and equilibrated with petroleum ether prior to use.

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 25 °C on JEOL 400M Hz spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of NMR solvent residual peak ($CDCl_3$: δ 7.26, triplet. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), and broad singlet (br s), etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet). To clarify the complete signal assignments, "× number" indicates the multiple carbons due to the superposition of chemical shifts.

High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2Q-TOF (Thermo Electron Corporation). Gas chromatography-mass spectrometry (GC-MS) analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Thermo Fisher Scientific GC column TG-5MS (30 m × 0.25 mm × 0.25 μm). PE = petroleum ether, EtOAc = ethyl acetate.

2. Preparation of the starting materials

2.1 Procedures for the synthesis of trifluoromethyl alkenes



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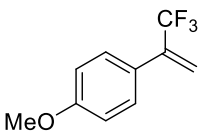

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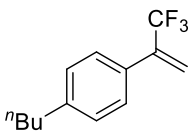

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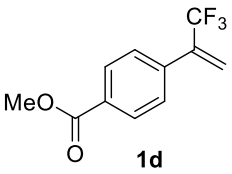

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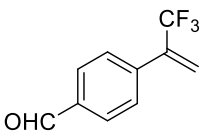

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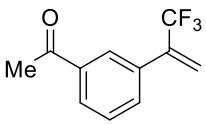

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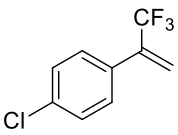

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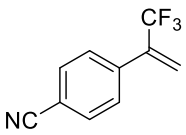

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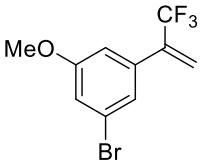

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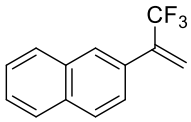

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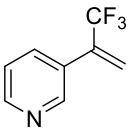

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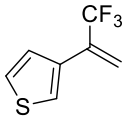

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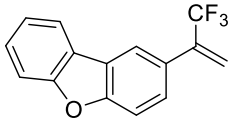

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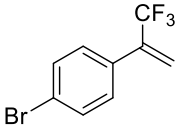

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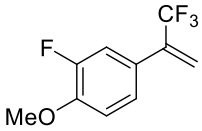

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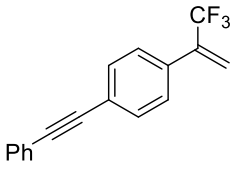

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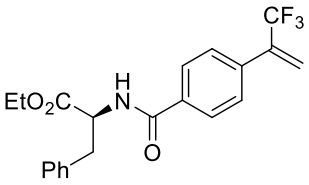

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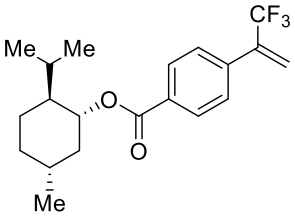

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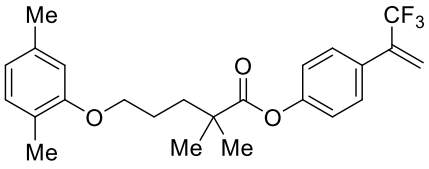

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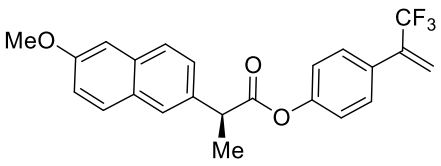

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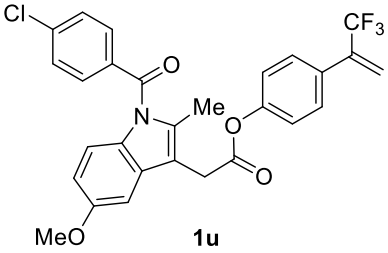

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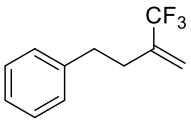
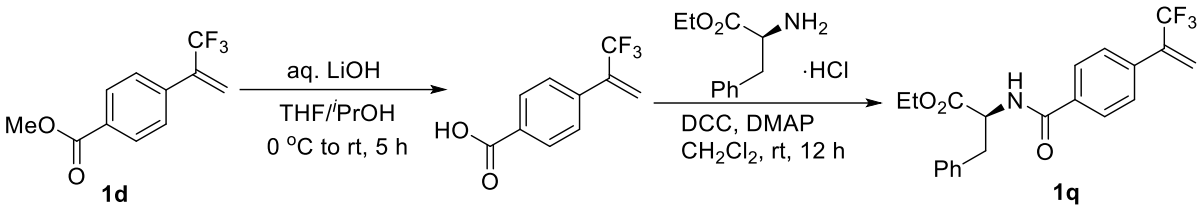


1v

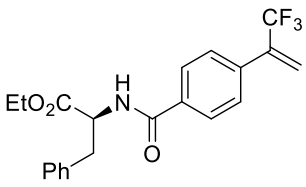
Trifluoromethyl alkenes **1a–1o**,[1] **1p**,[2] **1r**,[3] **1s–1u**,[4] and **1v**[5] are known compounds and could be prepared according to the existing methods reported in the literatures. ^{1}H NMR spectra data of all known compounds are in accordance with the corresponding reported data in the literatures. Trifluoromethyl alkene **1q** was prepared according to the following procedure.



To a 50 mL round bottom flask equipped with a stir bar was added methyl 3-(3,3,3-trifluoroprop1-en-2-yl)benzoate **1d** (1.15 g, 5 mmol, 1.0 equiv) and THF (10 mL) at 0 °C. After stirring for 10 min, aq. LiOH (1.0 M, 7.5 mL, 1.5 equiv) and ^{i}PrOH (2.2 mL) were successively added. Then, the solution was allowed to warm to room temperature and kept for 5 h. After the completion monitored by TLC, the crude mixture was concentrated in vacuo to give the residue which was dissolved in H_2O (10 mL). The aqueous solution was washed with Et_2O (10 mL × 3) and acidified with aq. HCl (1.0 M) to pH $\approx$ 1. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to give the corresponding benzoic acid (691.9 mg, 3.2 mmol, 64%), which was used directly in the next step without further purification.

To a stirred solution of 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid (432.3 mg, 2.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol, 10 mol%), and ethyl *L*-phenylalaninate hydrochloride (505.3 mg, 2.2 mmol, 1.1 equiv) in anhydrous CH_2Cl_2 (8 mL) was added *N*,*N*'-dicyclohexylcarbodiimide (DCC, 453.9 mg, 2.2 mmol, 1.1 equiv). The mixture was stirred at room temperature for 12 h. After the completion monitored by TLC, the reaction was quenched with H_2O (15 mL), extracted with CH_2Cl_2 (20 mL × 3). The combined organic phases were washed with sat. NaCl, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resultant residue was purified by column chromatography (PE/EtOAc = 8:1) to give the desired product **1q** (680.5 mg, 1.74 mmol, 87%) as a white solid.

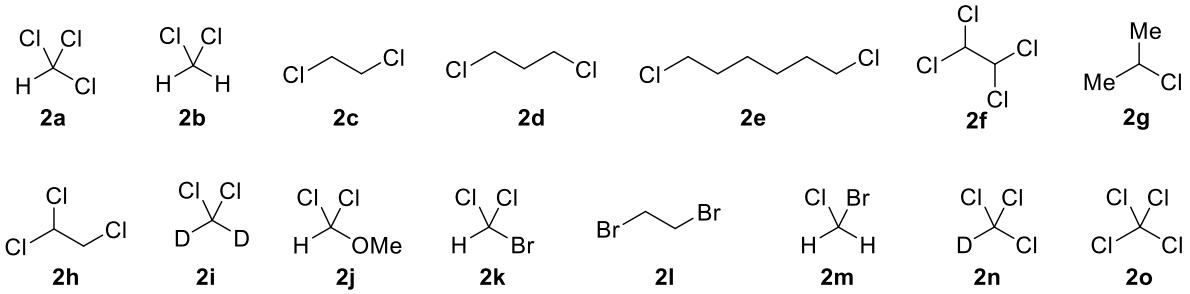
Ethyl (4-(3,3,3-trifluoroprop-1-en-2-yl)benzoyl)-*L*-phenylalaninate (1q)



M.p.: 66.8 – 67.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 – 7.72 (m, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.17 – 7.12 (m, 2H), 6.62 (d, J = 7.5 Hz, 1H), 6.04 (q, J = 1.4 Hz, 1H), 5.85 (q, J = 1.7 Hz, 1H), 5.07 (dt, J = 7.7, 5.6 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.35 – 3.19 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 166.2, 138.2 (q, J = 30.4 Hz), 136.9, 135.9, 134.4, 129.5 × 2, 128.7 × 2, 127.7 × 2, 127.4 × 2, 127.3, 125.9 (q, J = 274.5 Hz), 121.8 (q, J = 5.7 Hz),

61.9, 53.7, 38.0, 14.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -64.6 (s, 3F). **HRMS (ESI):** m/z calculated for $C_{21}H_{21}F_3NO_3^+$ $[M + H]^+$: 392.1468, found: 392.1473.

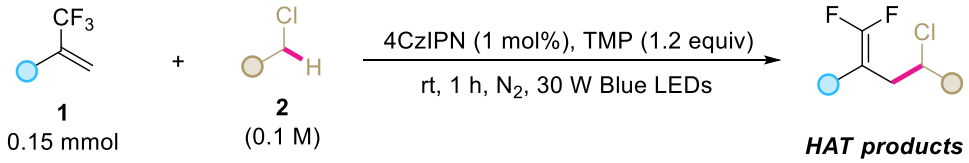
2.2 List of polychloroalkanes



Compounds **2a**–**2o** were purchased from commercial suppliers and used without further purification.

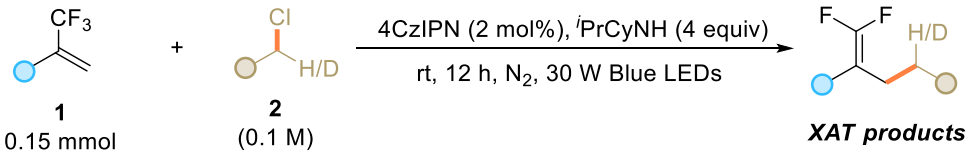
3. General procedures for the synthesis of *gem*-difluoroalkenes 3 and 4

General procedure 1 (GP1) for the synthesis of the HAT products



An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (1.2 mg, 0.0015 mmol, 1.0 mol%). Then the tube was evacuated and backfilled with N_2 for 3 times. α-Trifluoromethyl alkene **1** (0.15 mmol, 1.0 equiv), TMP (25.4 mg, 0.18 mmol, 1.2 equiv) and a specific polychloroalkane (1.5 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 1 h. Once the completion monitored by TLC, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE) to afford the desired HAT product.

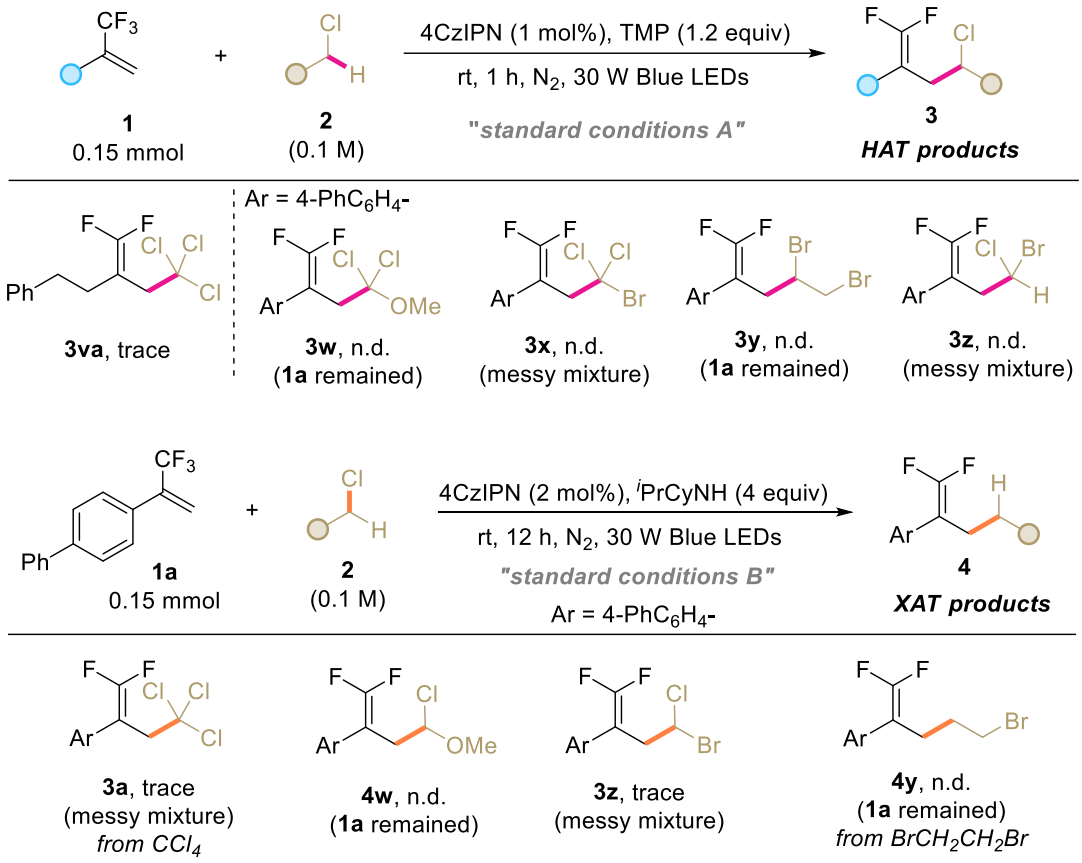
General procedure 2 (GP2) for the synthesis of the XAT products



An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (2.4 mg, 0.003 mmol, 2.0 mol%). Then the tube was evacuated and backfilled with N_2 for 3 times. α-

Trifluoromethyl alkene **1** (0.15 mmol, 1.0 equiv), *N*-isopropylcyclohexylamine (84.8 mg, 0.6 mmol, 4 equiv) and a specific polychloroalkane (1.5 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 12 h. Once the completion monitored by TLC, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE) to afford the desired XAT product.

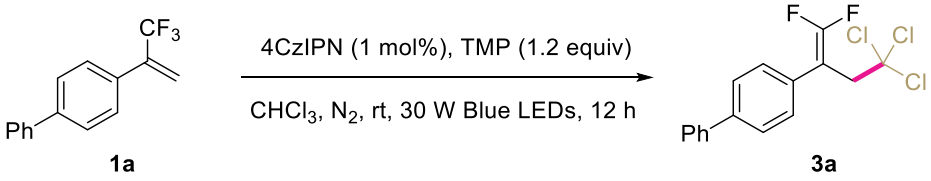
Limitations for the photocatalyzed defluorinative alkylation of trifluoromethyl alkenes



4. Derivatizations of the products 3a and 4a

4.1 Gram scale experiments

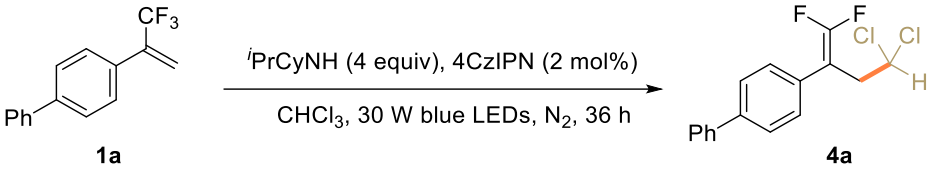
Scale-up synthesis of product 3a



An oven-dried 100 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (33.1 mg, 0.042 mmol, 1.0 mol%). Then the tube was evacuated and backfilled with N_2 for 3 times. Trifluoroprop-1-en-2-yl)-1,1'-biphenyl **1a** (1.04 g, 4.2 mmol, 1.0 equiv), TMP (711.9 mg, 5.04 mmol, 1.2 equiv) and

chloroform (42 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 12 h. Once the completion monitored by TLC, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE) to afford product **3a** (1.28 g, 3.7 mmol, 88%, **3a**/**4a** > 20:1) as a white solid.

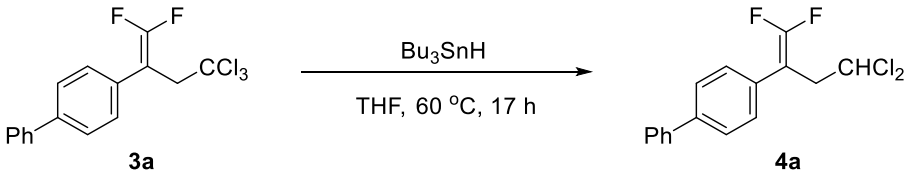
Scale-up synthesis of product 4a



An oven-dried 100 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (66.3 mg, 0.084 mmol, 2.0 mol%), then the tube was evacuated and backfilled with N_2 for 3 times. Trifluoroprop-1-en-2-yl)-1,1'-biphenyl **1a** (1.04 g, 4.2 mmol, 1.0 equiv), *N*-isopropylcyclohexylamine (2.37 g, 16.8 mmol, 4.0 equiv) and chloroform (42 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 36 h. Once the completion monitored by TLC, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE) to afford product **4a** (0.99 g, 3.2 mmol, 75%, **4a**/**3a** > 20:1).

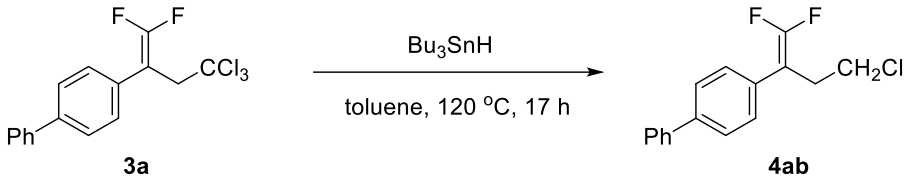
4.2 Transformations of product 3a

Synthesis of compound 4a from product 3a



According to the known procedure,[6] to a solution of compound **3a** (34.8 mg, 0.1 mmol, 1.0 equiv) in THF (1 mL) under N_2 atmosphere was added tributyltin hydride (87.3 mg, 0.3 mmol, 3.0 equiv) at room temperature. The reaction was warmed up to 60 °C with stirring for 17 h. The mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was dissolved in MeCN (2 mL) and washed with hexane (5 mL × 3) to remove all tin compounds. The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE) to give product **4a** (22.6 mg, 0.072 mmol, 72%) as a white solid.

Synthesis of compound 4ab from product 3a

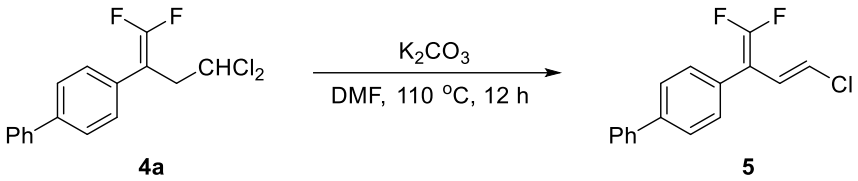


3a **4ab**

To a solution of compound **3a** (34.8 mg, 0.1 mmol, 1.0 equiv) in toluene (1 mL) under N_2 atmosphere was added tributyltin hydride (262.0 mg, 0.9 mmol, 9.0 equiv) at room temperature. The reaction was heated to reflux with stirring for 17 h. The mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was dissolved in MeCN (2 mL) and washed with hexane (5 mL × 3) to remove all tin compounds. The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE) to give product **4ab** (16.0 mg, 0.057 mmol, 57%) as a white solid.

4.3 Transformations of product 4a

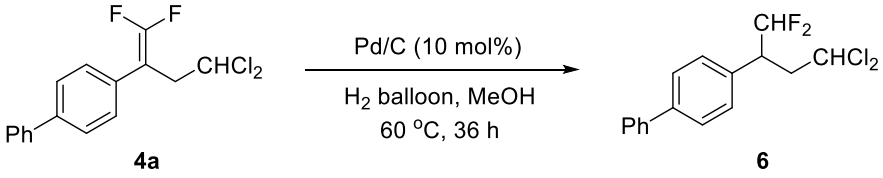
Synthesis of compound 5



4a **5**

To an oven-dried 10 mL Schlenk tube equipped with a stir bar under N_2 atmosphere was added K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv), compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv) and DMF (1 mL). The reaction was stirred at 110 ℃ for 12 h. After the completion monitored by TLC, the mixture was quenched with H_2O (10 mL) and extracted with EtOAc (10 mL × 3). The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE) to give the desired product **5** (14.3 mg, 0.052 mmol, 52%) as a white solid.

Synthesis of compound 6

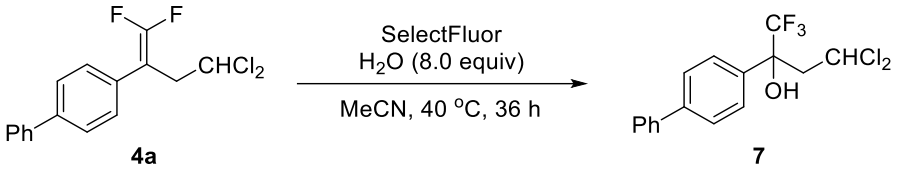


4a **6**

According to the known procedure,[7] to a 10 mL Schlenk tube equipped with a stir bar under an atmosphere of hydrogen balloon was added compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv), palladium on charcoal (5%, 21.3 mg, 0.01 mmol, 10 mol%) and MeOH (1 mL). The reaction was stirred at 60 °C

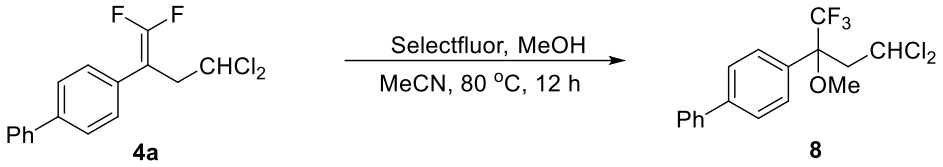
for 36 h. After cooling to room temperature, the reaction mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by column chromatography (PE) to give the desired product **6** (16.6 mg, 0.053 mmol, 53%) as a white solid.

Synthesis of compound 7



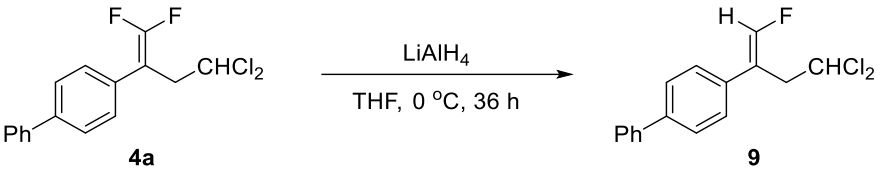
According to the known procedure,[8] to an oven-dried 10 mL Schlenk tube equipped with a stir bar under N_2 atmosphere were added SelectFluor (53.1 mg, 0.15 mmol, 1.5 equiv) and compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv). Then MeCN (1 mL) and H_2O (14.4 mg, 0.8 mmol, 8.0 equiv) were added. The reaction was stirred at 40 ℃ for 36 h. After the completion, the mixture was quenched with sat. NaCl (5 mL) and extracted with EtOAc (5 mL × 3). The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography (PE/ EtOAc = 20:1) to give the desired product **7** (31.5 mg, 0.090 mmol, 90%) as a white solid.

Synthesis of compound 8



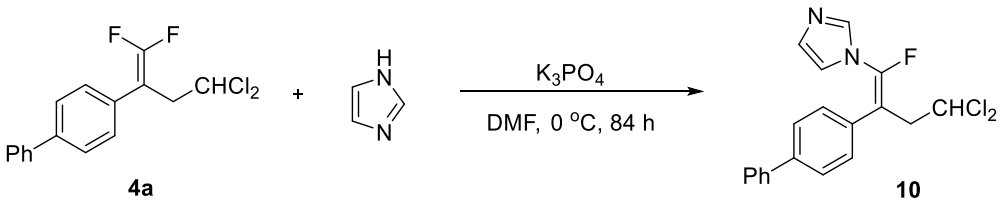
According to the known procedure,[8] to an oven-dried 10 mL Schlenk tube equipped with a stir bar under N_2 atmosphere, SelectFluor (53.1 mg, 0.15 mmol, 1.5 equiv) and compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv) were added. Then MeCN (1 mL) and MeOH (16.0 mg, 0.5 mmol, 5.0 equiv) were added. The reaction was stirred at 80 ℃ for 12 h. After the completion monitored by TLC, the mixture was quenched with sat. NaCl (5 mL) and extracted with EtOAc (5 mL × 3). The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography (PE) to give the desired product **8** (30.1 mg, 0.083 mmol, 83%) as a colorless oil.

Synthesis of compound 9



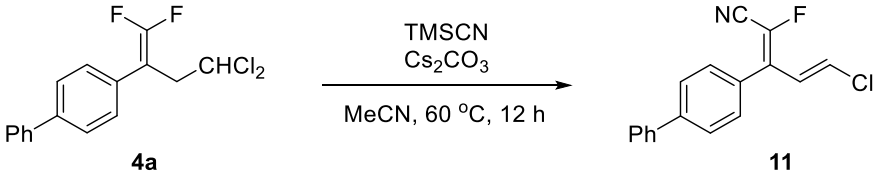
According to the known procedure,[9] to an oven-dried 10 mL Schlenk tube equipped with a stir bar under N_2 atmosphere was added lithium aluminum hydride (7.6 mg, 0.2 mmol, 2.0 equiv), compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv) and anhydrous THF (1.0 mL). The reaction was stirred at 0 ℃ for 36 h. After the completion monitored by TLC, the mixture was quenched with H_2O (5 mL) carefully and extracted with EtOAc (5 mL × 3). The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography (PE) to give the desired product **9** (24.1 mg, 0.082 mmol, 82%) as a white solid.

Synthesis of compound 10



According to the known procedure,[10] to an oven-dried 10 mL Schlenk tube equipped with a stir bar under N_2 atmosphere was added imidazole (17.0 mg, 0.25 mmol, 2.5 equiv), K_3PO_4 (53.1 mg, 0.25 mmol, 2.5 equiv), compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv) and DMF (1.0 mL). The reaction was stirred at 0 ℃ for 84 h. After the completion monitored by TLC, the mixture was then quenched with H_2O (5 mL) and extracted with EtOAc (10 mL × 3). The organic layers were combined and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 10:1) to give the desired product **10** (17.3 mg, 0.048 mmol, 48%) as a colorless oil.

Synthesis of compound 11

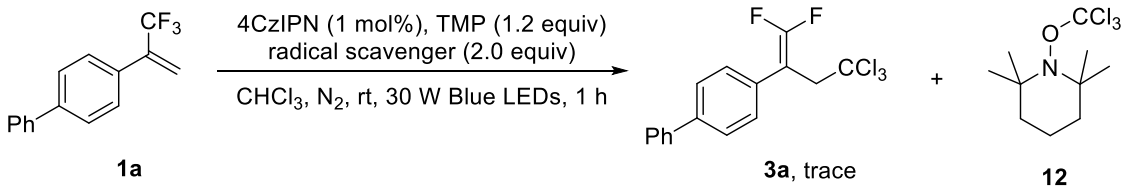


According to the known procedure,[11] to an oven-dried 10 mL Schlenk tube equipped with a stir bar under N_2 atmosphere was added Cs_2CO_3 (32.6 mg, 0.1 mmol, 1.0 equiv) and compound **4a** (31.3 mg, 0.1 mmol, 1.0 equiv). Then TMSCN (29.8 mg, 0.3 mmol, 3.0 equiv) was added, followed by the

addition of MeCN (1 mL). The reaction was stirred at 60 °C for 12 h. The resulting mixture was purified by column chromatography (PE) to give the desired product **11** (20.1 mg, 0.071 mmol, 71%, *E*/*Z* > 20:1) as a white solid.

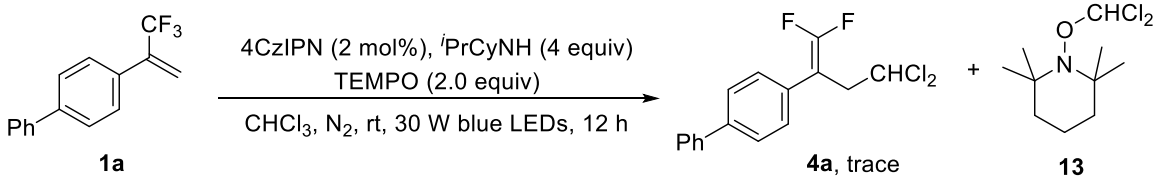
5. Mechanistic studies

5.1 Radical trapping experiments



1a **3a**, trace **12**

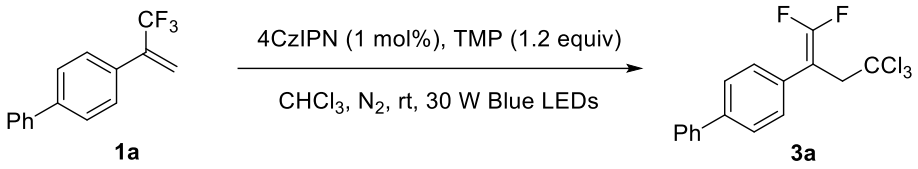
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (1.2 mg, 0.0015 mmol, 1.0 mol%) and a radical scavenger (TEMPO or BHT or 1,1-DPE, 2.0 equiv). Then the tube was evacuated and backfilled with N_2 for 3 times. Compound **1a** (37.2 mg, 0.15 mmol, 1.0 equiv), TMP (25.4 mg, 0.18 mmol, 1.2 equiv) and chloroform (1.5 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 1 h. After that, product **3a** was not observed by the crude ^{1}H NMR, instead adduct **12** from the coupling reaction of **2a** with TEMPO was detected by HRMS: $[M + H]^+$: 274.0527, found: 274.0532.



1a **4a**, trace **13**

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (2.4 mg, 0.003 mmol, 2.0 mol%) and TEMPO (46.9 mg, 0.3 mmol, 2.0 equiv). Then the tube was evacuated and backfilled with N_2 for 3 times. Compound **1a** (37.2 mg, 0.15 mmol, 1.0 equiv), *N*-isopropylcyclohexylamine (84.8 mg, 0.6 mmol, 4 equiv) and chloroform (1.5 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 12 h. After that, product **4a** was not observed by the crude ^{1}H NMR, instead adduct **13** from the coupling of **2a** with TEMPO was detected by HRMS: $[M + H]^+$: 240.0916, found: 240.0918.

5.2 Light on/off studies



The detailed procedures for light on/off experiments (Fig. S1): To a mixture of 4CzIPN (1.2 mg, 0.0015 mmol, 1.0 mol%), **1a** (37.2 mg, 0.15 mmol, 1.0 equiv), TMP (25.4 mg, 0.18 mmol, 1.2 equiv) and $CHCl_3$ (1.5 mL) were successively added into a 10 mL Schlenk tube with a stir bar. The reaction mixture was separately stirred and irradiated by 30 W blue LEDs (455 nm) at room temperature for 30 min, 45 min, 60 min. Product **3a** was isolated in 33%, 50%, 86%, respectively. Additionally, the reaction mixture was stirred and irradiated by 30 W blue LEDs at room temperature for 30 min, then the reaction mixture was continuously stirred in the dark for 15 min, product **3a** was also obtained in 33% yield. Additionally, when the reaction mixture was stirred and irradiated by 30 W blue LEDs at room temperature for 45 min, then the reaction mixture was continuously stirred in the dark for 15 min, product **3a** was obtained in 50% yield. Additionally, when the reaction mixture was stirred and irradiated by 30 W blue LEDs at room temperature for 60 min, then the reaction mixture was continuously stirred in the dark for 15 min, product **3a** was still obtained in 86% yield.

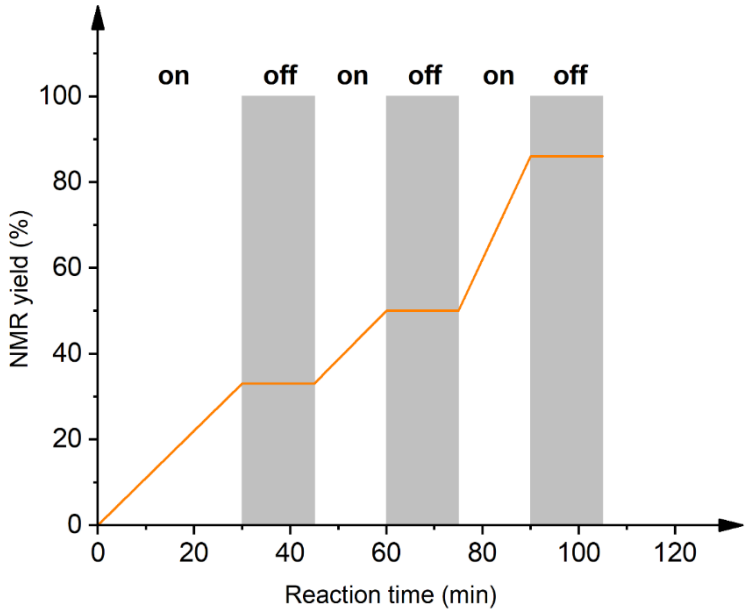
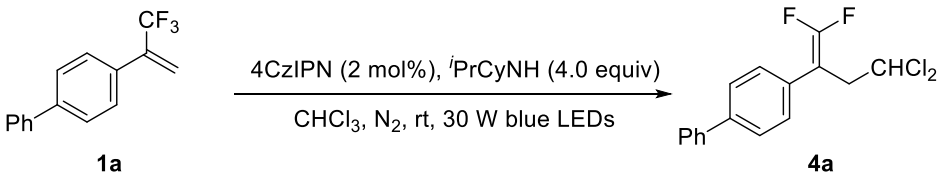


Fig. S1. Yield of light on-off experiments for product **3a**



The detailed procedures for light on/off experiments (Fig. S2): To a mixture of 4CzIPN (2.4 mg, 0.003 mmol, 2.0 mol%), **1a** (37.2 mg, 0.15 mmol, 1.0 equiv), *N*-isopropylcyclohexylamine (84.8 mg, 0.6 mmol, 4.0 equiv) and $CHCl_3$ (1.5 mL) were successively added into a 10 mL Schlenk tube with a stir bar. The reaction mixture was separately stirred and irradiated by 30 W blue LEDs (455 nm) at room temperature for 2 h, 3 h, 4 h. Product **4a** was isolated in 46%, 52%, 57%, respectively. Additionally, the reaction mixture was stirred and irradiated by 30 W blue LEDs at room temperature for 2 h, then the reaction mixture was continuously stirred in the dark for 1 h, product **4a** was also obtained in 46% yield. Additionally, when the reaction mixture was stirred and irradiated by 30 W blue LEDs at room temperature for 3 h, then the reaction mixture was continuously stirred in the dark for 1 h, product **4a** was obtained in 52% yield. Additionally, when the reaction mixture was stirred and irradiated by 30 W blue LEDs at room temperature for 4 h, then the reaction mixture was continuously stirred in the dark for 1 h, product **4a** was still obtained in 57% yield.

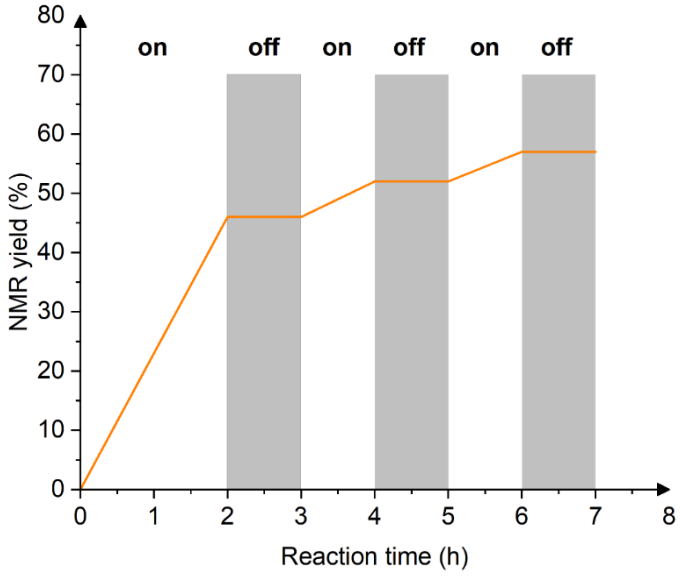


Fig. S2. Yield of light on-off experiments for product **4a**

5.3 Fluorescence quenching experiments

Quenched by substrate **2a**: For each quenching experiment, the emission intensity of photocatalyst 4CzIPN (1×10^{-4} M in MeCN) with different concentration of quencher **2a** (0, 1, 2, 3, 4, 5 mM) was collected. As shown in Fig. S3, substrate **2a** was capable of quenching the excited state of photocatalyst 4CzIPN slightly.

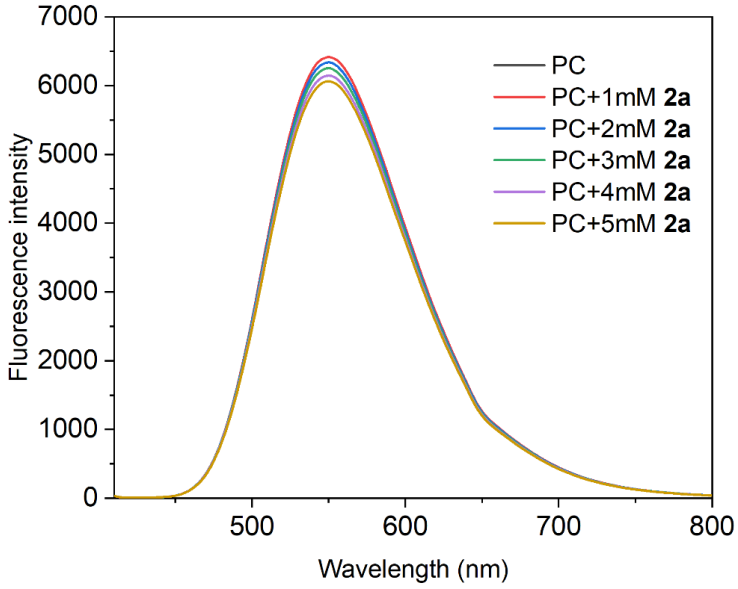


Fig. S3. The fluorescence emission spectra of a solution of 4CzIPN in MeCN containing different concentration of substrate **2a**

Quenched by TMP: For each quenching experiment, the emission intensity of photocatalyst 4CzIPN (1×10^{-4} M in MeCN) with different concentration of quencher TMP (0, 1, 2, 3, 4, 5 mM) was collected. As shown in Fig. S4 & S5, compound TMP was capable of quenching the excited state of photocatalyst 4CzIPN.

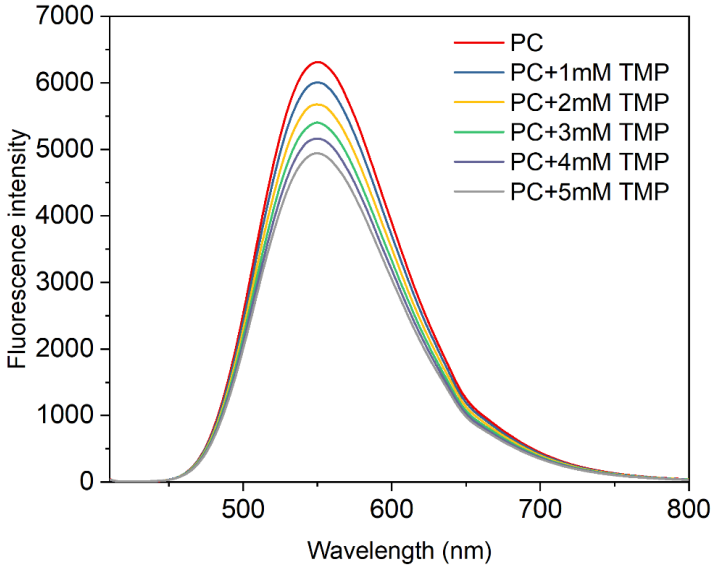


Fig. S4. The fluorescence emission spectra of a solution of 4CzIPN in MeCN containing different concentration of TMP

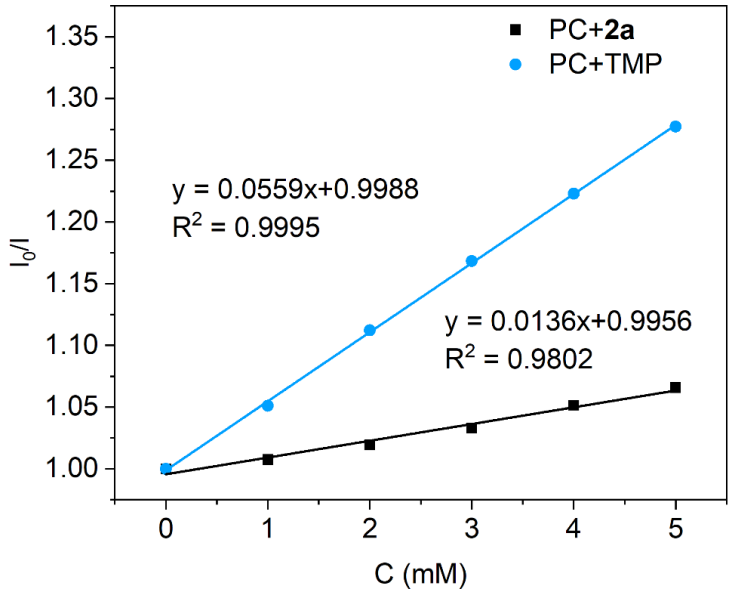


Fig. S5. Stern-Volmer plot of PC (1×10^{-4} M) at different concentrations of substrate **2a** and TMP

Quenched by ^{i}PrCyNH: For each quenching experiment, the emission intensity of photocatalyst 4CzIPN (1×10^{-4} M in MeCN) with different concentration of quencher ^{i}PrCyNH (0, 1, 2, 3, 4, 5 mM) was collected. As shown in Fig. S6 & S7, compound ^{i}PrCyNH was capable of quenching the excited state of photocatalyst 4CzIPN.

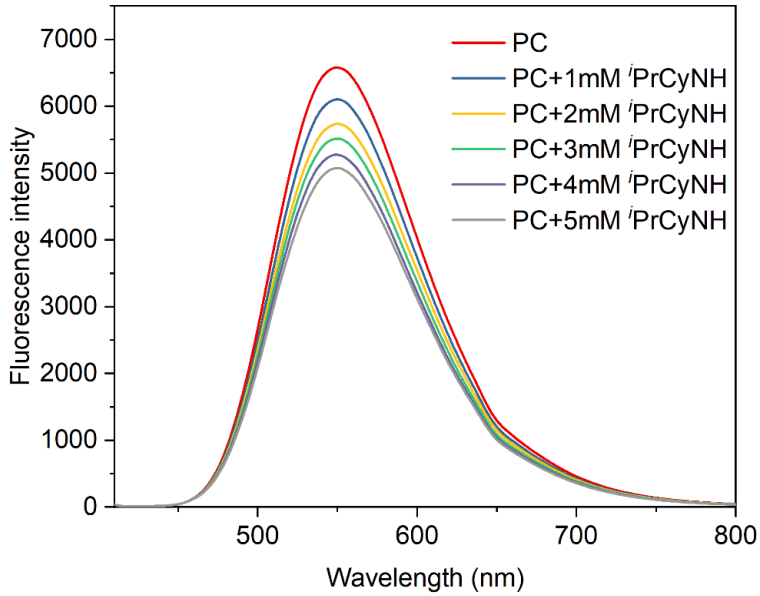


Fig. S6. The fluorescence emission spectra of a solution of 4CzIPN in MeCN containing different concentration of ^{i}PrCyNH

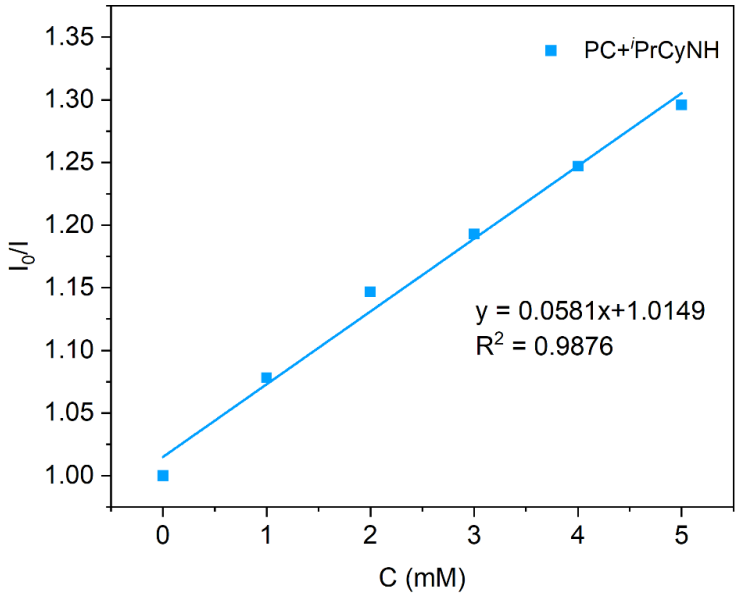
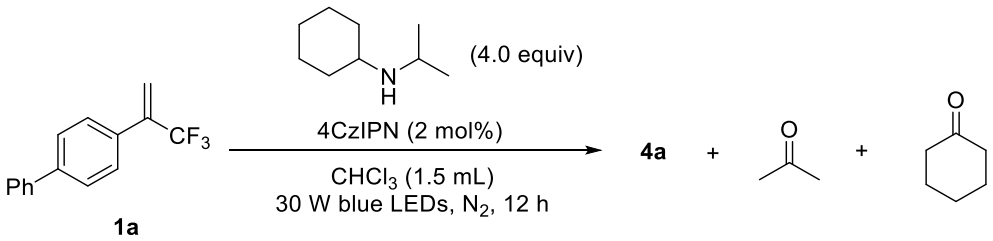


Fig. S7. Stern-Volmer plot of PC (1×10^{-4} M) at different concentrations of ^{i}PrCyNH

According to the results as well as the corresponding Stern-Volmer plots (Fig. S3–S7), substrate **2a** did not show an obvious quenching effect to the fluorescence intensity of 4CzIPN. While both TMP and ^{i}PrCyNH showed an obvious quenching effect to the fluorescence intensity of 4CzIPN.

5.4 Detection of acetone and cyclohexanone



An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4CzIPN (2.4 mg, 0.003 mmol, 2.0 mol%), then the tube was evacuated and backfilled with N_2 for 3 times. α-Trifluoromethyl alkene **1a** (37.2 mg, 0.15 mmol, 1.0 equiv), *N*-isopropylcyclohexylamine (84.8 mg, 0.6 mmol, 4 equiv) and chloroform (1.5 mL) were successively added via syringe under N_2 atmosphere. The sealed tube was stirred at room temperature under irradiation with 30 W blue LEDs for 12 h. After that, the precipitate was filtered off and then detected by ^{1}H NMR (Fig. S8) and GC-MS (Fig. S9) analyses.

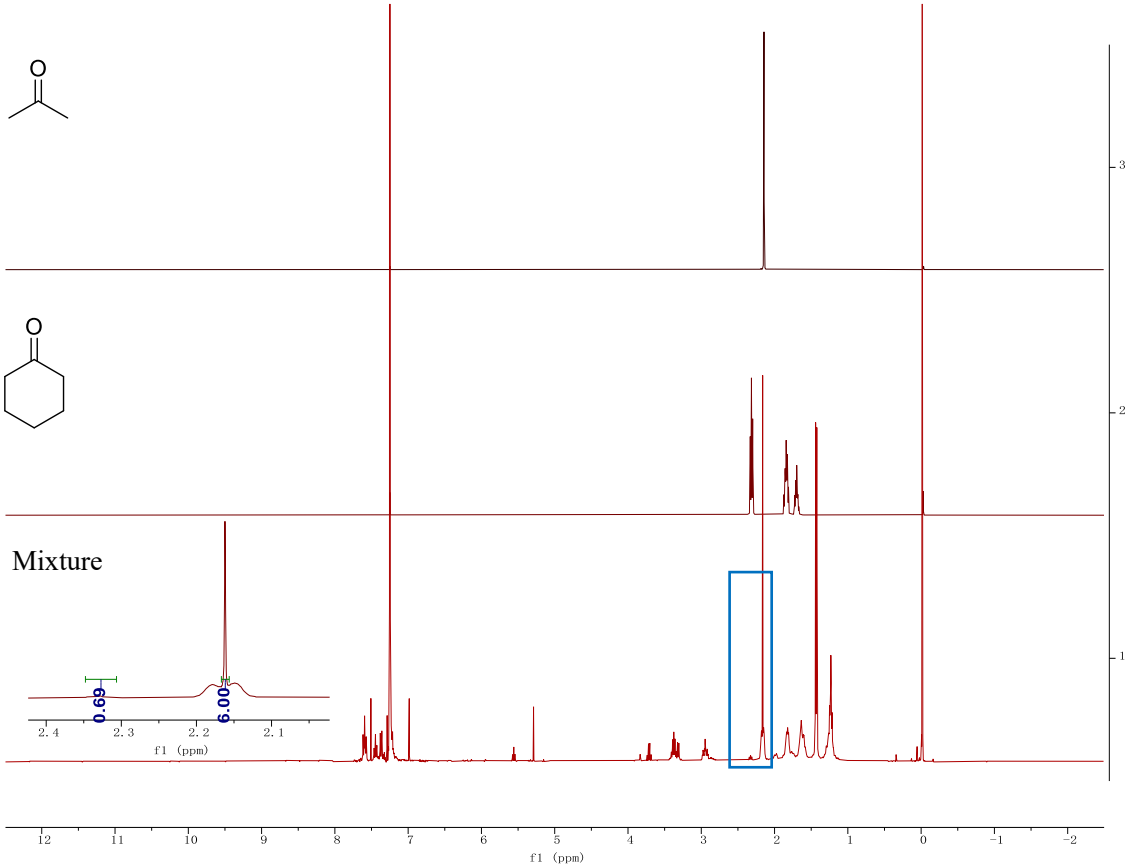


Fig. S8. ^{1}H NMR spectrum of the crude residue

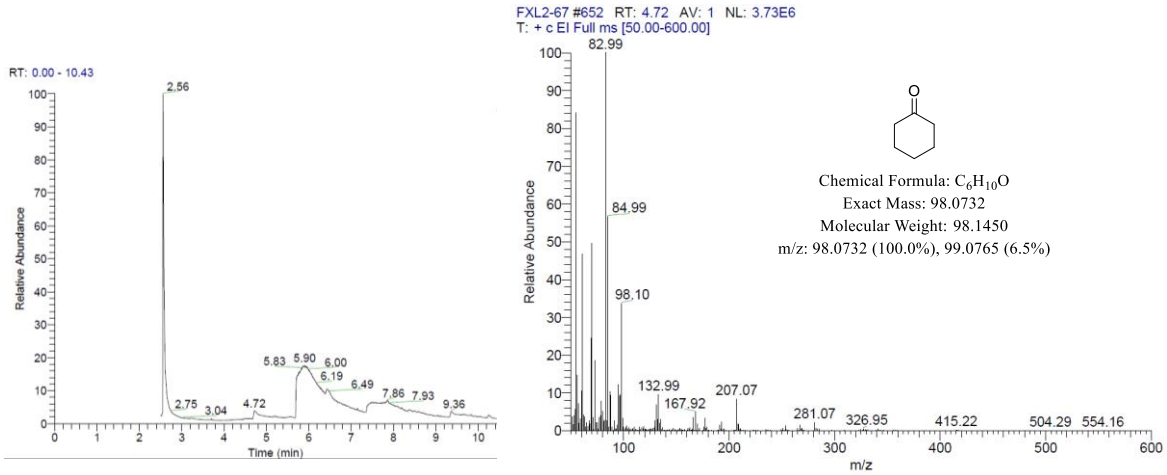
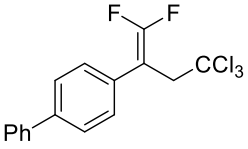


Fig. S9. GC-MS spectrum for the reaction mixture

6. NMR data of the products

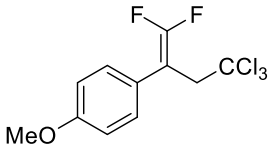
4-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (3a)



The title compound was prepared according to **GP1** and isolated as a white solid (46.6 mg, 0.134 mmol, 89%). M.p.: 71.7 – 72.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.59 (m, 4H), 7.49 – 7.33 (m, 5H), 3.85 (t, J = 1.9 Hz, 2H). **^{13}C NMR**

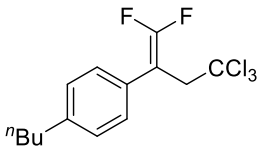
(101 MHz, $CDCl_3$) δ 156.3 (dd, J = 294.2, 293.3 Hz), 140.7, 140.4, 131.6 (dd, J = 3.6, 2.9 Hz), 129.2 (t, J = 2.8 Hz) × 2, 129.0 × 2, 127.7, 127.3 × 2, 127.2 × 2, 98.1 (dd, J = 7.5, 4.3 Hz), 88.7 (dd, J = 19.6, 18.9 Hz), 52.8 (d, J = 3.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -84.2 (d, J = 24.8 Hz), -86.2 (d, J = 24.8 Hz). **HRMS (ESI):** m/z calculated for $C_{16}H_{12}Cl_3F_2^+$ $[M + H]^+$: 346.9967, found: 346.9971.

1-Methoxy-4-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzene (3b)



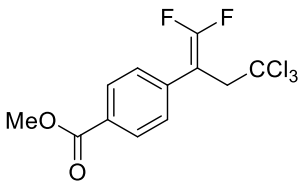
The title compound was prepared according to **GP1** and isolated as a white solid (30.5 mg, 0.101 mmol, 67%). M.p.: 50.2 – 51.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.24 (m, 2H), 6.94 – 6.88 (m, 2H), 3.82 (s, 3H), 3.77 (t, J = 1.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.2, 156.2 (dd, J = 293.6, 291.7 Hz), 130.0 (t, J = 2.9 Hz) × 2, 124.7 (dd, J = 3.9, 2.6 Hz), 114.1 × 2, 98.1 (dd, J = 7.1, 4.1 Hz), 88.5 (dd, J = 20.0, 18.7 Hz), 55.4, 53.0 (d, J = 4.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.7 (d, J = 27.8 Hz), -87.5 (d, J = 27.8 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_{10}Cl_3F_2O^+$ $[M + H]^+$: 300.9760, found: 300.9766.

1-Butyl-4-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzene (3c)



The title compound was prepared according to **GP1** and isolated as a colorless oil (40.6 mg, 0.124 mmol, 83%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 3.80 (t, J = 1.8 Hz, 2H), 2.61 (t, J = 7.9 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.36 (dq, J = 14.7, 7.3 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.2 (dd, J = 293.7, 292.5 Hz), 142.8, 129.8 (dd, J = 3.5, 2.8 Hz), 128.6 × 4, 98.1 (dd, J = 6.8, 4.4 Hz), 88.8 (dd, J = 19.8, 18.3 Hz), 52.9 (d, J = 3.3 Hz), 35.5, 33.6, 22.5, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.2 (d, J = 26.4 Hz), -87.0 (d, J = 26.4 Hz). **HRMS (ESI):** m/z calculated for $C_{14}H_{16}Cl_3F_2^+$ $[M + H]^+$: 327.0280, found: 327.0285.

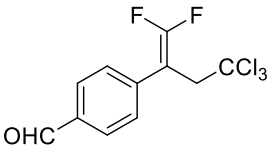
Methyl 4-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzoate (3d)



The title compound was prepared according to **GP1** and isolated as a colorless oil (40.7 mg, 0.124 mmol, 82%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (d, J = 8.0 Hz, 2H), 7.42 (dd, J = 8.0, 1.2 Hz, 2H), 3.92 (s, 3H), 3.84 (t, J = 1.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.7, 156.4 (t, J = 295.0 Hz), 137.5 (dd, J = 3.9, 3.2 Hz), 129.9 × 2, 129.7, 128.9 (t, J = 2.8 Hz) × 2, 97.8 (dd, J = 6.6, 4.4

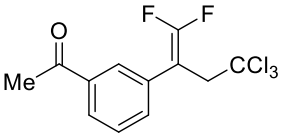
Hz), 88.7 (t, J = 19.1 Hz), 52.6 (d, J = 3.1 Hz), 52.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.8 (d, J = 20.8 Hz), -84.8 (d, J = 20.8 Hz). **HRMS (ESI):** m/z calculated for $C_{12}H_{10}Cl_3F_2O_2^+$ $[M + H]^+$: 328.9709, found: 328.9713.

4-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)benzaldehyde (3e)



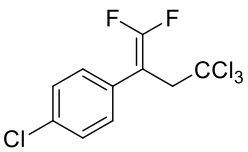
The title compound was prepared according to a modified **GP1** (run for 12 h) and isolated as a colorless oil (29.5 mg, 0.098 mmol, 66%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.02 (s, 1H), 7.92 – 7.88 (m, 2H), 7.55 – 7.51 (m, 2H), 3.86 (t, J = 1.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.7, 156.5 (t, J = 295.6 Hz), 139.1 (t, J = 3.7 Hz), 135.7, 130.0 × 2, 129.5 (t, J = 2.9 Hz) × 2, 97.7 (dd, J = 6.6, 4.6 Hz), 88.7 (t, J = 19.1 Hz), 52.5 (d, J = 3.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.1 (d, J = 19.4 Hz), -84.2 (d, J = 19.4 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_8Cl_3F_2O^+$ $[M + H]^+$: 298.9603, found: 298.9610.

1-(3-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)phenyl)ethan-1-one (3f)



The title compound was prepared according to a modified **GP1** (run for 24 h) and isolated as a colorless oil (35.7 mg, 0.114 mmol, 76%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 – 7.87 (m, 2H), 7.58 – 7.45 (m, 2H), 3.85 (t, J = 1.8 Hz, 2H), 2.63 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 156.5 (dd, J = 295.0, 293.6 Hz), 137.5, 133.6 (t, J = 2.9 Hz), 133.5 (dd, J = 4.2, 2.7 Hz), 129.0, 128.4 (t, J = 2.8 Hz), 128.1, 97.8 (dd, J = 7.2, 4.0 Hz), 88.5 (t, J = 19.4 Hz), 52. 8 (d, J = 3.3 Hz), 26.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -83.7 (d, J = 23.0 Hz), -85.7 (d, J = 23.0 Hz). **HRMS (ESI):** m/z calculated for $C_{12}H_{10}Cl_3F_2O^+$ $[M + H]^+$: 312.9760, found: 312.9770.

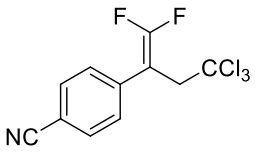
1-Chloro-4-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzene (3g)



The title compound was prepared according to **GP1** and isolated as a colorless oil (35.2 mg, 0.115 mmol, 77%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 3.77 (t, J = 1.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.3 (dd, J = 294.7, 293.4 Hz), 134.0, 131.2 (dd, J = 3.9, 2.9 Hz), 130.2 (t, J = 2.7 Hz) × 2, 128.9 × 2, 97.8 (dd, J = 6.4, 4.4 Hz), 88.2 (t, J = 19.5 Hz), 52. 8 (d, J = 3.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -83.9 (d, J = 22.8 Hz), -85.8 (d, J = 22.8 Hz). **HRMS (ESI):** m/z calculated for $C_{10}H_7Cl_4F_2^+$

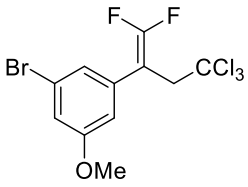
$[M + H]^+$: 304.9264, found: 304.9270.

4-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)benzonitrile (3h)



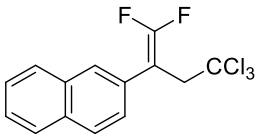
The title compound was prepared according to a modified **GP1** (run for 12 h) and isolated as a white solid (37.4 mg, 0.126 mmol, 84%). M.p.: 73.6 – 74.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 3.83 (t, J = 1.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.5 (t, J = 295.9 Hz), 137.7 (dd, J = 4.4, 3.2 Hz), 132.4 × 2, 129.6 (t, J = 3.1 Hz) × 2, 118.5, 111.8, 97.6 (dd, J = 7.3, 4.6 Hz), 88.3 (dd, J = 20.0, 18.6 Hz), 52.4 (d, J = 3.5 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.7 (d, J = 18.1 Hz), -83.9 (d, J = 18.1 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_7Cl_3F_2N^+$ $[M + H]^+$: 295.9607, found: 295.9614.

1-Bromo-3-methoxy-5-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzene (3i)



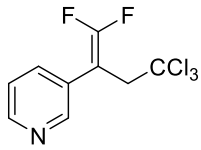
The title compound was prepared according to a modified **GP1** (run for 2 h) and isolated as a white solid (42.1 mg, 0.111 mmol, 74%). M.p.: 50.4 – 52.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (q, J = 1.5 Hz, 1H), 7.00 (t, J = 2.0 Hz, 1H), 6.81 (dt, J = 2.6, 1.4 Hz, 1H), 3.81 (s, 3H), 3.76 (t, J = 1.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.3, 155.0 (t, J = 294.6 Hz), 135.5 (dd, J = 4.3, 2.9 Hz), 124.1 (t, J = 3.0 Hz), 122.9, 116.4, 114.4 (t, J = 3.0 Hz), 97.8 (dd, J = 6.7, 4.6 Hz), 88.1 (t, J = 19.5 Hz), 55.7, 52.7 (d, J = 4.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -83.3 (d, J = 22.0 Hz), -84.5 (d, J = 22.0 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_9BrCl_3F_2O^+$ $[M + H]^+$: 378.8865, found: 378.8872.

2-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)naphthalene (3j)



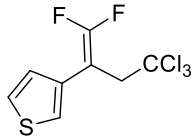
The title compound was prepared according to a modified **GP1** (run for 4 h) and isolated as a white solid (37.1 mg, 0.115 mmol, 77%). M.p.: 66.7 – 68.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.80 (m, 4H), 7.53 – 7.48 (m, 2H), 7.45 (dt, J = 8.6, 1.7 Hz, 1H), 3.93 (t, J = 1.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.5 (dd, J = 294.3, 293.3 Hz), 133.3, 132.8, 130.1 (dd, J = 3.5, 2.7 Hz), 128.3, 128.2 (t, J = 2.9 Hz), 128.1, 127.8, 126.6 × 2, 126.4 (t, J = 2.6 Hz), 98.1 (dd, J = 6.6, 4.7 Hz), 89.1 (dd, J = 19.4, 18.7 Hz), 53.0 (d, J = 3.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -84.2 (d, J = 24.0 Hz), -86.3 (d, J = 24.0 Hz). **HRMS (ESI):** m/z calculated for $C_{14}H_{10}Cl_3F_2^+$ $[M + H]^+$: 320.9811, found: 320.9815.

3-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)pyridine (3k)



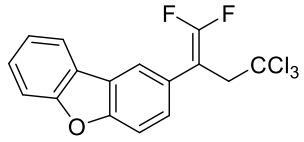
The title compound was prepared according to **GP1** and isolated as a colorless oil (23.3 mg, 0.086 mmol, 57%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (d, J = 22.7 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.0, 4.6 Hz, 1H), 3.82 (t, J = 1.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.7 (t, J = 295.0 Hz), 149.8, 149.1, 136.3, 129.0 (d, J = 4.4 Hz), 123.5, 97.6 (t, J = 5.6 Hz), 86.4 (d, J = 39.9 Hz), 52.5 (d, J = 2.4 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.4 (d, J = 21.0 Hz), -85.0 (d, J = 21.0 Hz). **HRMS (ESI):** m/z calculated for $C_9H_7Cl_3F_2N^+$ $[M + H]^+$: 271.9607, found: 271.9612.

3-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)thiophene (3l)



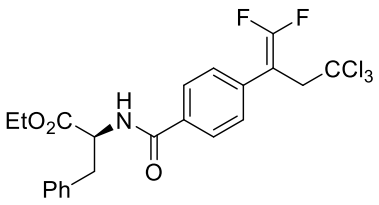
The title compound was prepared according to **GP1** and isolated as a colorless oil (27.8 mg, 0.100 mmol, 67%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (dd, J = 5.0, 3.0 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.16 (dt, J = 5.0, 1.6 Hz, 1H), 3.80 (t, J = 1.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.4 (dd, J = 294.9, 293.4 Hz), 132.3 (t, J = 3.7 Hz), 127.4 (dd, J = 4.0, 2.7 Hz), 125.7, 123.4 (t, J = 4.4 Hz), 98.0 (dd, J = 6.9, 4.2 Hz), 85.0 (dd, J = 20.6, 19.1 Hz), 52.6 (dd, J = 3.7, 0.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -83.4 (d, J = 23.3 Hz), -84.0 (d, J = 23.3 Hz). **HRMS (ESI):** m/z calculated for $C_8H_6Cl_3F_2S^+$ $[M + H]^+$: 276.9218, found: 276.9226.

2-(4,4,4-Trichloro-1,1-difluorobut-1-en-2-yl)dibenzo[*b*,*d*]furan (3m)



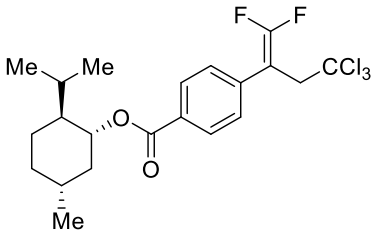
The title compound was prepared according to **GP1** and isolated as a white solid (39.9 mg, 0.110 mmol, 74%). M.p.: 68.8 – 69.3 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 – 7.89 (m, 2H), 7.63 (dt, J = 8.2, 0.9 Hz, 1H), 7.50 (m, 1H), 7.46 – 7.33 (m, 3H), 4.11 (t, J = 1.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.5 (dd, J = 294.8, 293.8 Hz), 156.1, 153.8 (d, J = 3.2 Hz), 128.6 (t, J = 2.5 Hz), 127.6, 124.8, 124.1, 123.2, 123.0, 120.9, 120.8, 117.0 (dd, J = 4.1, 2.5 Hz), 112.0, 98.2 (dd, J = 6.7, 4.4 Hz), 85.2 (dd, J = 21.2, 20.4 Hz), 52.0 (d, J = 3.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -83.3 (d, J = 20.7 Hz), -84.1 (d, J = 20.7 Hz). **HRMS (ESI):** m/z calculated for $C_{16}H_{10}Cl_3F_2O^+$ $[M + H]^+$: 360.9760, found: 360.9764.

Ethyl (4-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzoyl)-*L*-phenylalaninate (3n)



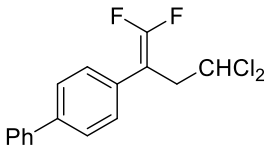
The title compound was prepared according to a modified **GP1** (run for 12 h) and isolated as a colorless oil (49.2 mg, 0.100 mmol, 67%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.68 (m, 2H), 7.45 – 7.35 (m, 2H), 7.35 – 7.20 (m, 3H), 7.20 – 7.11 (m, 2H), 6.65 (d, J = 7.5 Hz, 1H), 5.06 (dt, J = 7.5, 5.7 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.82 (t, J = 1.8 Hz, 2H), 3.34 – 3.17 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 166.3, 156.4 (t, J = 294.8 Hz), 136.3 (dd, J = 3.8, 3.0 Hz), 135.9, 133.4, 129.5 × 2, 129.1 (t, J = 2.7 Hz) × 2, 128.7 × 2, 127.4 × 2, 127.3, 97.8 (dd, J = 6.6, 4.6 Hz), 88.5 (t, J = 19.1 Hz), 61.8, 53.7, 52.6 (d, J = 3.1 Hz), 38.0, 14.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -83.0 (d, J = 21.1 Hz), -85.1 (d, J = 21.1 Hz). **HRMS (ESI):** m/z calculated for $C_{22}H_{21}Cl_3F_2NO_3^+$ $[M + H]^+$: 490.0550, found: 490.0555.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(4,4,4-trichloro-1,1-difluorobut-1-en-2-yl)benzoate (3o)



The title compound was prepared according to a modified **GP1** (run for 12 h) and isolated as a colorless oil (60.1 mg, 0.132 mmol, 86%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 – 8.00 (m, 2H), 7.50 – 7.35 (m, 2H), 4.94 (td, J = 10.9, 4.4 Hz, 1H), 3.84 (t, J = 1.8 Hz, 2H), 2.12 (dtd, J = 11.9, 3.9, 1.8 Hz, 1H), 2.04 – 1.89 (m, 1H), 1.77 – 1.71 (m, 2H), 1.62 – 1.48 (m, 2H), 1.22 – 1.02 (m, 2H), 0.92 (dd, J = 6.8, 1.4 Hz. 7H), 0.80 (d, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.7, 156.4 (t, J = 294.8 Hz), 137.3 (dd, J = 4.3, 3.0 Hz), 130.4, 129.8 × 2, 128.8 (t, J = 3.0 Hz) × 2, 97.8 (dd, J = 6.9, 4.7 Hz), 88.7 (t, J = 19.1 Hz), 75.1, 52.6 (d, J = 3.9 Hz), 47.3, 41.1, 34.4, 31.6, 26.5, 23.7, 22.2, 20.9, 16.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.9 (d, J = 22.0 Hz), -84.9 (d, J = 22.0 Hz). **HRMS (ESI):** m/z calculated for $C_{21}H_{26}Cl_3F_2O_2^+$ $[M + H]^+$: 453.0961, found: 453.0968.

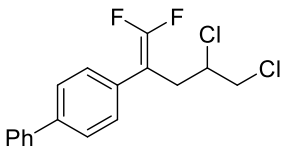
4-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (4a)



The title compound was prepared according to a modified **GP1** (run for 12 h) or **GP2** and isolated as a white solid (under **GP1**: 37.4 mg, 0.119 mmol, 80%, under **GP2**: 39.2 mg, 0.125 mmol, 83%). M.p.: 70.6 – 72.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 – 7.59 (m, 4H), 7.51 – 7.45 (m, 2H), 7.43 – 7.38 (m, 3H), 5.59 (t, J = 6.8 Hz, 1H),

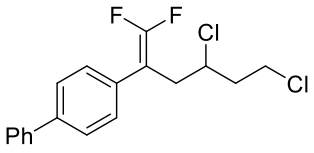
3.35 (dt, *J* = 6.9, 2.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (dd, *J* = 292.4, 291.1 Hz), 141.1, 140.4, 130.4 (t, *J* = 3.8 Hz), 129.0 × 2, 128.8 (t, *J* = 2.9 Hz) × 2, 127.8, 127.7 × 2, 88.7 (dd, *J* = 20.4, 18.1 Hz), 70.5 (t, *J* = 4.3 Hz), 42.3 (d, *J* = 2.6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -87.1 (d, *J* = 32.4 Hz), -87.9 (d, *J* = 32.4 Hz). **HRMS (ESI):** m/z calculated for $C_{16}H_{13}Cl_2F_2^+$ $[M + H]^+$: 313.0357, found: 313.0361.

4-(4,5-Dichloro-1,1-difluoropent-1-en-2-yl)-1,1'-biphenyl (3p)



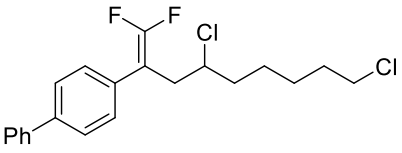
The title compound was prepared according to a modified **GP1** (run for 24 h) or **GP2** (run for 36 h) and isolated as a white solid (under **GP1**: 41.2 mg, 0.126 mmol, 84%, under **GP2**: 8.5 mg, 0.026 mmol, 17%). M.p.: 49.8 – 50.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.59 (m, 4H), 7.50 – 7.35 (m, 5H), 4.00 (ddt, *J* = 9.3, 7.3, 4.6 Hz, 1H), 3.78 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.68 (dd, *J* = 11.5, 7.3 Hz, 1H), 3.19 (ddt, *J* = 15.0, 4.6, 3.2 Hz, 1H), 2.87 (ddd, *J* = 15.0, 9.3, 1.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.8 (dd, *J* = 290.1, 289.8 Hz), 140.8, 140.4, 130.9 (q, *J* = 1.4 Hz), 129.0 × 2, 128.8 (t, *J* = 3.3 Hz) × 2, 127.7, 127.6 × 2, 127.2 × 2, 88.9 (dd, *J* = 19.9, 17.7 Hz), 58.1 (t, *J* = 3.5 Hz), 47.9, 33.9 (d, *J* = 2.8 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.3 (d, *J* = 35.6 Hz), -88.4 (d, *J* = 35.6 Hz). **HRMS (ESI):** m/z calculated for $C_{17}H_{15}Cl_2F_2^+$ $[M + H]^+$: 327.0513, found: 327.0520.

4-(4,6-Dichloro-1,1-difluorohex-1-en-2-yl)-1,1'-biphenyl (3q)



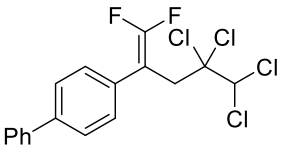
The title compound was prepared according to **GP1** and isolated as a colorless oil (38.5 mg, 0.113 mmol, 75%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.57 (m, 4H), 7.52 – 7.41 (m, 2H), 7.43 – 7.32 (m, 3H), 4.13 – 4.00 (m, 1H), 3.69 (td, *J* = 5.7, 3.6 Hz, 2H), 3.01 – 2.92 (m, 1H), 2.87 (ddt, *J* = 14.7, 6.4, 2.5 Hz, 1H), 2.29 – 2.03 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.8 (dd, *J* = 291.6, 289.1 Hz), 140.8, 140.5, 131.3 (dd, *J* = 4.4, 2.9 Hz), 129.0 × 2, 128.8 (t, *J* = 3.3 Hz) × 2, 127.7, 127.6 × 2, 127.2 × 2, 89.4 (dd, *J* = 21.1, 16.3 Hz), 57.0 (dd, *J* = 4.3, 2.8 Hz), 41.6, 40.4, 37.0 (d, *J* = 2.5 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.5 (d, *J* = 36.6 Hz), -88.9 (d, *J* = 36.6 Hz). **HRMS (ESI):** m/z calculated for $C_{18}H_{17}Cl_2F_2^+$ $[M + H]^+$: 341.0670, found: 341.0673.

4-(4,9-Dichloro-1,1-difluorononon-1-en-2-yl)-1,1'-biphenyl (3r)



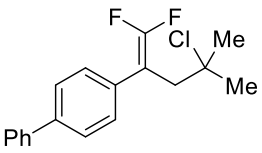
The title compound was prepared according to **GP1** and isolated as a colorless oil (21.2 mg, 0.055 mmol, 37%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.56 (m, 4H), 7.51 – 7.41 (m, 2H), 7.44 – 7.33 (m, 3H), 3.88 – 3.75 (m, 1H), 3.51 (t, J = 6.7 Hz, 2H), 2.97 – 2.75 (m, 2H), 1.83 – 1.66 (m, 4H), 1.41 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.7 (dd, J = 288.8, 288.4Hz), 140.7, 140.5, 131.6 (dd, J = 4.7, 2.9 Hz), 129.0 × 2, 128.9 (t, J = 3.2 Hz) × 2, 127.7, 127.5 × 2, 127.2 × 2, 89.8 (dd, J = 21.2, 15.9 Hz), 60.4 (dd, J = 4.0, 2.6 Hz), 45.0, 37.6, 37.1 (d, J = 2.4 Hz), 32.5, 26.4, 25.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -89.0 (d, J = 36.8 Hz), -89.5 (d, J = 39.0 Hz). **HRMS (ESI):** m/z calculated for $C_{21}H_{23}Cl_2F_2^+$ $[M + H]^+$: 383.1139, found: 383.1145.

4-(4,4,5,5-Tetrachloro-1,1-difluoropent-1-en-2-yl)-1,1'-biphenyl (3s)



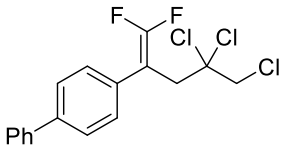
The title compound was prepared according to **GP1** and isolated as a colorless oil (18.9 mg, 0.048 mmol, 32%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.59 (m, 4H), 7.49 – 7.44 (m, 2H), 7.44 – 7.36 (m, 3H), 5.76 (s, 1H), 3.62 (t, J = 1.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.9 (dd, J = 292.2, 292.0 Hz), 140.9, 140.3, 131.3 (dd, J = 3.9, 2.8 Hz), 129.3 (t, J = 2.9 Hz) × 2, 129.0 × 2, 127.7, 127.4 × 2, 127.2 × 2, 92.8 (ddd, J = 6.5, 4.0, 1.7 Hz), 87.9 (d, J = 19.3 Hz), 78.0, 41.3 (dd, J = 3.3, 1.4 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -84.8 (d, J = 26.9 Hz), -86.4 (d, J = 26.9 Hz). **HRMS (ESI):** m/z calculated for $C_{17}H_{13}Cl_4F_2^+$ $[M + H]^+$: 394.9734, found: 394.9737.

4-(4-Chloro-1,1-difluoro-4-methylpent-1-en-2-yl)-1,1'-biphenyl (3t)



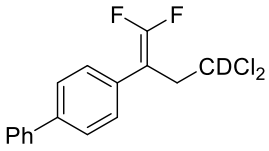
The title compound was prepared according to a modified **GP1** (2 mol% PC was used) and isolated as a white solid (17.9 mg, 0.058 mmol, 39%). M.p.: 53.7 – 55.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.58 (m, 4H), 7.49 – 7.36 (m, 5H), 3.00 (t, J = 2.3 Hz, 2H), 1.49 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (dd, J = 291.6, 290.1 Hz), 140.5, 140.3, 133.3 (dd, J = 4.2, 3.1 Hz), 129.0, 128.9 (t, J = 2.9 Hz) × 2, 127.6, 127.3 × 2, 127.1 × 2, 89.8 (dd, J = 20.7, 15.4 Hz), 70.0 (dd, J = 4.0, 2.9 Hz), 43.6 (d, J = 1.9 Hz), 32.7 × 2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -87.1 (d, J = 34.2 Hz), -89.7 (d, J = 34.2 Hz). **HRMS (ESI):** m/z calculated for $C_{18}H_{18}ClF_2^+$ $[M + H]^+$: 307.1060, found: 307.1067.

4-(4,4,5-Trichloro-1,1-difluoropent-1-en-2-yl)-1,1'-biphenyl (3u)



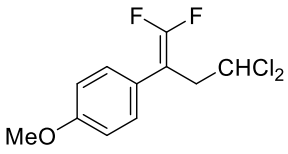
The title compound was prepared according to a modified **GP1** (run for 24 h) and isolated as a white solid (41.5 mg, 0.115 mmol, 77%). M.p.: 55.9 – 57.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.61 (m, 4H), 7.49 – 7.35 (m, 5H), 3.80 (s, 2H), 3.52 (t, J = 1.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.9 (d, J = 293.8, 292.4 Hz), 140.9, 140.4, 131.3 (dd, J = 4.0, 2.8 Hz), 129.2 (t, J = 2.9 Hz) × 2, 129.0 × 2, 127.7, 127.3 × 2, 127.2 × 2, 89.4 (dd, J = 6.4, 3.2 Hz), 88.3 (t, J = 19.0 Hz), 53.3, 42.2 (d, J = 3.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.0 (d, J = 27.8 Hz), -87.1 (d, J = 27.8 Hz). **HRMS (ESI):** m/z calculated for $C_{17}H_{14}Cl_3F_2^+$ $[M + H]^+$: 361.0124, found: 361.0128.

4-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)-1,1'-biphenyl (3v)



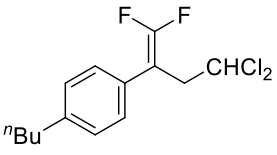
The title compound was prepared according to **GP1** or **GP2** and isolated as a white solid (under **GP1**: 37.2 mg, 0.118 mmol, 79%, under **GP2**: 42.3 mg, 0.135 mmol, 90%). M.p.: 73.7 – 74.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.54 (m, 4H), 7.51 – 7.40 (m, 2H), 7.40 – 7.34 (m, 3H), 3.32 (t, J = 2.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (dd, J = 292.4, 291.0 Hz), 141.1, 140.4, 130.4 (t, J = 3.5 Hz), 129.0 × 2, 128.8 (t, J = 3.0 Hz) × 2, 127.8, 127.7 × 2, 127.2 × 2, 88.7 (dd, J = 20.8, 18.0 Hz), 70.8 – 70.0 (m), 42.2 (d, J = 2.6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -87.1 (d, J = 32.6 Hz), -88.0 (d, J = 32.6 Hz). **HRMS (ESI):** m/z calculated for $C_{16}H_{12}DCl_2F_2^+$ $[M + H]^+$: 314.0420, found: 314.0426.

1-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl)-4-methoxybenzene (4b)



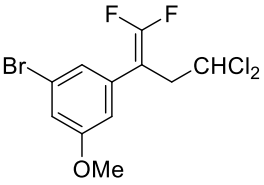
The title compound was prepared according to **GP2** and isolated as a colorless oil (29.3 mg, 0.110 mmol, 73%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.22 (m, 2H), 6.95 – 6.91 (m, 2H), 5.51 (td, J = 6.8, 0.6 Hz, 1H), 3.83 (s, 3H), 3.26 (dt, J = 6.8, 2.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.4, 155.1 (t, J = 290.5 Hz), 129.7 (t, J = 2.5 Hz) × 2, 123.5, 114.4 × 2, 88.5 (dd, J = 20.7, 19.3 Hz), 70.6 (dd, J = 3.4, 2.9 Hz), 55.4, 42.5 (d, J = 2.7 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.6 (d, J = 35.6 Hz), -89.4 (d, J = 35.6 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_{11}Cl_2F_2O^+$ $[M + H]^+$: 267.0150, found: 267.0158.

1-Butyl-4-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)benzene (4c)



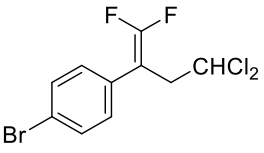
The title compound was prepared according to **GP2** and isolated as a colorless oil (36.5 mg, 0.124 mmol, 83%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 (s, 4H), 5.52 (t, J = 6.8 Hz, 1H), 3.28 (dd, J = 6.8, 1.9 Hz, 2H), 2.69 – 2.57 (m, 2H), 1.71 – 1.54 (m, 2H), 1.43 – 1.33 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.1 (t, J = 291.0 Hz), 143.2, 129.0 × 2, 128.6 (t, J = 4.0 Hz), 128.3 × 2, 88.8 (t, J = 19.5 Hz), 70.6 (t, J = 4.3 Hz), 42.4, 35.5, 33.6, 22.5, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.1 (d, J = 35.9 Hz), -88.8 (d, J = 35.9 Hz). **HRMS (ESI):** m/z calculated for $C_{14}H_{17}Cl_2F_2^+$ $[M + H]^+$: 293.0670, found: 293.0676.

1-Bromo-3-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)-5-methoxybenzene (4i)



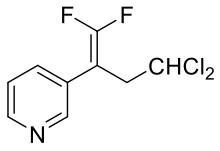
The title compound was prepared according to modified **GP2** (run for 18 h) and isolated as a colorless oil (36.3 mg, 0.105 mmol, 70%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.05 – 7.00 (m, 2H), 6.77 (s, 1H), 5.52 (t, J = 6.8 Hz, 1H), 3.81 (s, 3H), 3.24 (dt, J = 6.8, 2.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.6, 155.3 (dd, J = 293.2, 291.7 Hz), 134.4 (dd, J = 4.1, 2.6 Hz), 123.7 (t, J = 3.4 Hz), 123.4, 116.7, 114.0 (t, J = 3.2 Hz), 88.2 (dd, J = 21.4, 18.3 Hz), 70.2 (dd, J = 6.0, 3.9 Hz), 55.7, 42.2 (d, J = 2.5 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -86.2 (d, J = 29.8 Hz), -86.4 (d, J = 29.8 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_{10}BrCl_2F_2O^+$ $[M + H]^+$: 344.9255, found: 344.9260.

1-Bromo-4-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)benzene (4aa)



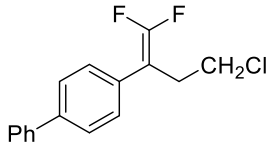
The title compound was prepared according to **GP2** and isolated as a colorless oil (40.5 mg, 0.128 mmol, 85%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (dt, J = 8.7, 2.6 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 5.51 (t, J = 6.8 Hz, 1H), 3.27 (dt, J = 6.7, 2.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (dd, J = 293.0, 291.5 Hz), 132.2 × 2, 130.6 (dd, J = 4.4, 2.8 Hz), 130.1 (t, J = 3.3 Hz) × 2, 122.4, 88.3 (dd, J = 21.4, 18.1 Hz), 70.3 (dd, J = 5.9, 3.7 Hz), 42.1 (d, J = 2.7 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -86.5 (d, J = 31.0 Hz), -87.4 (d, J = 31.0 Hz). **HRMS (ESI):** m/z calculated for $C_{10}H_8BrCl_2F_2^+$ $[M + H]^+$: 314.9149, found: 314.9156.

3-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl)pyridine (4k)



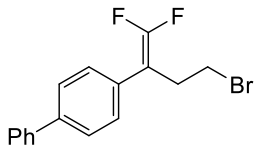
The title compound was prepared according to **GP2** and isolated as a colorless oil (24.6 mg, 0.103 mmol, 69%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (s, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 8.0, 4.6 Hz, 1H), 5.55 (t, J = 6.8 Hz, 1H), 3.30 (dt, J = 5.9, 1.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.6 (dd, J = 294.1, 293.1 Hz), 149.4 (t, J = 3.4 Hz), 149.4, 136.0 (t, J = 3.3 Hz), 128.1 (dd, J = 5.2, 3.7 Hz), 123.8, 86.4 (dd, J = 22.3, 18.1 Hz), 70.1 (dd, J = 5.6, 3.8 Hz), 41.9 (d, J = 2.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.1 (d, J = 23.7 Hz), -86.6 (d, J = 23.7 Hz). **HRMS (ESI):** m/z calculated for $C_9H_8Cl_2F_2N^+$ $[M + H]^+$: 237.9996, found: 237.9997.

4-(4-Chloro-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (4ab)



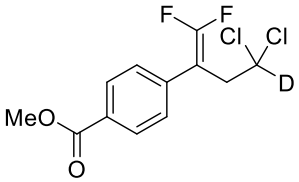
The title compound was prepared according to a modified **GP2** (3 mol% 4CzlPN and 3.0 equiv *i*PrCyNH were used in 0.05 M CH_2Cl_2 for 72 h) and isolated as a white solid (11.3 mg, 0.041 mmol, 27%). M.p.: 58.8 – 60.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.58 (m, 4H), 7.49 – 7.43 (m, 2H), 7.42 – 7.34 (m, 3H), 3.52 (t, J = 7.1 Hz, 2H), 2.91 (tt, J = 7.2, 2.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.6 (dd, J = 291.8, 289.4 Hz), 140.7, 140.5, 131.3 (dd, J = 4.4, 3.0 Hz), 128.9 × 2, 128.7 (t, J = 3.4 Hz) × 2, 127.6, 127.5 × 2, 127.1 × 2, 89.4 (dd, J = 21.4, 15.7 Hz), 41.9 (dd, J = 4.8, 2.9 Hz), 31.3 (d, J = 2.7 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.7 (d, J = 37.7 Hz), -89.0 (d, J = 37.7 Hz). **HRMS (ESI):** m/z calculated for $C_{16}H_{14}ClF_2^+$ $[M + H]^+$: 279.0747, found: 279.0749.

4-(4-Bromo-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (4z)



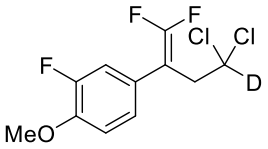
The title compound was prepared according to **GP2** and isolated as a colorless oil (33.8 mg, 0.105 mmol, 70%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.58 (m, 4H), 7.49 – 7.43 (m, 2H), 7.42 – 7.34 (m, 3H), 3.52 (t, J = 7.1 Hz, 2H), 2.91 (tt, J = 7.2, 2.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.7 (dd, J = 292.7, 290.5 Hz), 140.8, 140.5, 131.4 (t, J = 3.5 Hz), 129.0 × 2, 128.8 × 2 (t, J = 3.4 Hz), 127.7, 127.5 × 2, 127.2 × 2, 89.4 (dd, J = 21.4, 15.6 Hz), 41.9 (t, J = 3.6 Hz), 31.4 (d, J = 1.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.7 (d, J = 38.7 Hz), -89.1 (d, J = 38.7 Hz). **HRMS (ESI):** m/z calculated for $C_{16}H_{14}BrF_2^+$ $[M + H]^+$: 323.0241, found: 223.0245.

Methyl 4-(4,4-dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)benzoate (4ac)



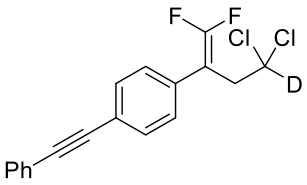
The title compound was prepared according to **GP2** and isolated as a colorless oil (26.6 mg, 0.090 mmol, 60%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 – 8.05 (m, 2H), 7.41 – 7.39 (m, 2H), 3.93 (s, 3H), 3.32 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 155.4 (t, J = 292.9 Hz), 136.5, 130.2 × 2, 129.9, 128.5 (t, J = 3.1 Hz) × 2, 88.7 (dd, J = 21.4, 17.6 Hz), 70.1 – 69.1 (m), 52.4, 41.9 (d, J = 2.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.3 (d, J = 28.4 Hz), -86.3 (d, J = 28.4 Hz). **HRMS (ESI):** m/z calculated for $C_{12}H_{10}DCl_2F_2O_2^+$ $[M + H]^+$: 296.0161, found: 296.0162.

4-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)-2-fluoro-1-methoxybenzene (4ad)



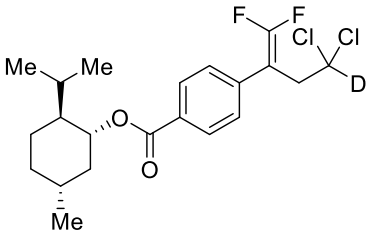
The title compound was prepared according to **GP2** and isolated as a colorless oil (29.2 mg, 0.102 mmol, 68%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12 – 6.87 (m, 3H), 3.91 (s, 3H), 3.23 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, J = 292.9 Hz), 152.4 (d, J = 247.1 Hz), 147.6 (d, J = 10.5 Hz), 124.5 (d, J = 3.3 Hz), 124.2, 116.3 (d, J = 19.7 Hz), 113.7 (d, J = 2.5 Hz), 88.0 (t, J = 20.2 Hz), 70.9 – 69.7 (m), 56.4, 42.2 (d, J = 2.4 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -87.4 (d, J = 33.8 Hz), -88.1 (d, J = 33.8 Hz), -133.9 (dd, J = 11.2, 8.2 Hz). **HRMS (ESI):** m/z calculated for $C_{11}H_9DCl_2F_3O^+$ $[M + H]^+$: 286.0118, found: 286.0117.

1-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)-4-(phenylethynyl)benzene (4ae)



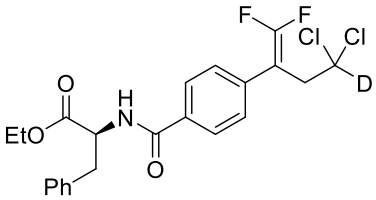
The title compound was prepared according to **GP2** and isolated as a colorless oil (40.2 mg, 0.119 mmol, 79%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.53 (m, 4H), 7.41 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 3.30 (t, J = 2.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, J = 292.9 Hz), 132.1 × 2, 131.8 × 2, 131.5 (t, J = 10.1 Hz), 128.6, 128.5 × 2, 128.4 (t, J = 3.1 Hz) × 2, 123.3, 123.1, 90.6, 88.8, 88.7 (dd, J = 20.2, 17.2 Hz), 70.2 – 70.0 (m), 42.0 (d, J = 2.4 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -86.3 (d, J = 31.3 Hz), -87.1 (d, J = 31.3 Hz). **HRMS (ESI):** m/z calculated for $C_{18}H_{12}DCl_2F_2^+$ $[M + H]^+$: 338.0420, found: 338.0422.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(4,4-dichloro-1,1-difluorobut-1-en-2-yl-4-*d*) benzoate (4af)



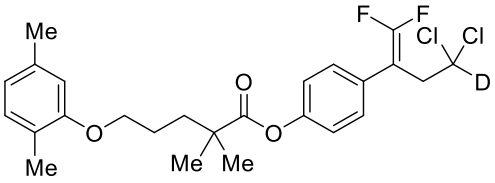
The title compound was prepared according to **GP2** and isolated as a colorless oil (45.0 mg, 0.107 mmol, 71%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 – 8.03 (m, 2H), 7.47 – 7.34 (m, 2H), 5.06 – 4.89 (m, 1H), 3.31 (t, J = 2.1 Hz, 2H), 2.15 – 2.10 (m, 1H), 2.00 – 1.92 (m, 1H), 1.79 – 1.68 (m, 2H), 1.64 – 1.48 (m, 2H), 1.22 – 1.04 (m, 2H), 0.93 (dd, J = 6.8, 3.7 Hz, 7H), 0.80 (d, J = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.6, 155.4 (t, J = 292.9 Hz), 136.2 (t, J = 4.0 Hz), 130.5, 130.2 × 2, 128.4 × 2, 88.8 (dd, J = 21.2, 17.6 Hz), 75.2, 70.8 – 69.2 (m), 47.4, 41.9, 41.1, 34.4, 31.6, 26.6, 23.7, 22.2, 20.9, 16.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.6 (d, J = 29.4 Hz), -86.6 (d, J = 29.4 Hz). **HRMS (ESI):** m/z calculated for $C_{21}H_{26}DCl_2F_2O_2^+$ $[M + H]^+$: 420.1413, found: 420.1417.

Ethyl (4-(4,4-dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)benzoyl)-*L*-phenylalaninate (4ag)



The title compound was prepared according to **GP2** and isolated as a colorless oil (48.8 mg, 0.107 mmol, 71%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 – 7.70 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.24 (m, 3H), 7.20 – 7.11 (m, 2H), 6.68 (d, J = 7.6 Hz, 1H), 5.07 (dt, J = 7.6, 5.7 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.36 – 3.19 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 166.2, 155.3 (t, J = 303 Hz), 135.9, 135.2 (t, J = 10.1 Hz), 133.7, 129.5 × 2, 128.7 × 2, 128.7 × 2, 127.7 × 2, 127.3, 88.6 (dd, J = 21.2, 17.7 Hz), 70.6 – 69.4 (m), 61.9, 53.7, 41.9, 38.0, 14.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.7 (d, J = 29.2 Hz), -86.7 (d, J = 29.2 Hz). **HRMS (ESI):** m/z calculated for $C_{22}H_{21}DCl_2F_2NO_3^+$ $[M + H]^+$: 457.1002, found: 457.1008.

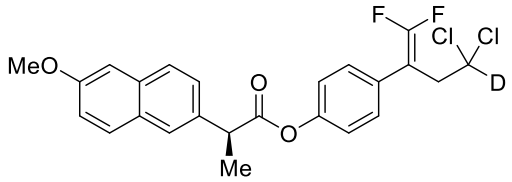
4-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4ah)



The title compound was prepared according to **GP2** and isolated as a colorless oil (46.7 mg, 0.096 mmol, 64%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (d, J = 7.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.65 (s, 1H), 4.01 (s, 2H), 3.28 (s, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 1.91 (s, 4H), 1.40 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.3, 156.9, 155.3 (t, J = 292.9 Hz), 150.8, 136.6, 130.5, 129.6 (t, J = 3.1 Hz) × 2, 129.0, 123.7, 122.2 × 2,

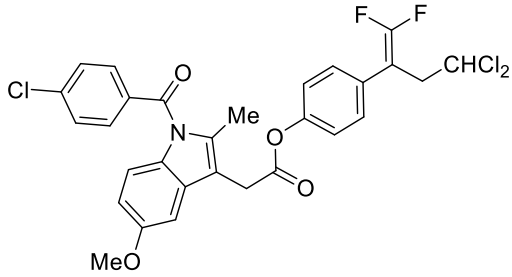
120.9, 112.0, 88.4 (dd, J = 21.2, 19.2 Hz), 70.5 – 69.7 (m), 67.8, 42.6, 42.3 (d, J = 2.9 Hz), 37.2, 25.4, 25.2 × 2, 21.5, 15.9. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -87.3 (d, J = 32.8 Hz), -88.0 (d, J = 32.8 Hz). **HRMS (ESI):** m/z calculated for $C_{25}H_{28}DCl_2F_2O_3^+$ $[M + H]^+$: 486.1519, found: 486.1516.

4-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl-4-*d*)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (4ai)



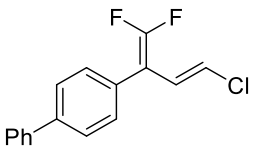
The title compound was prepared according to **GP2** and isolated as a colorless oil (39.1 mg, 0.084 mmol, 56%). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79 – 7.73 (m, 3H), 7.51 (dd, J = 8.4, 1.9 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.22 – 7.10 (m, 2H), 7.03 (d, J = 8.7 Hz, 2H), 4.11 (q, J = 7.1 Hz, 1H), 3.93 (s, 3H), 3.24 (s, 2H), 1.71 (d, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.2, 157.9, 155.2 (t, J = 292.9), 150.6, 135.0, 134.0, 129.5 (t, J = 3.0 Hz) × 2, 129.4, 129.1, 129.0, 127.6, 126.3, 126.2, 122.1 × 2, 119.3, 105.7, 88.3 (t, J = 22.2, 19.2 Hz), 70.6 – 69.6 (m), 55.5, 45.7, 42.2 (d, J = 2.9 Hz), 18.6. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -87.2 (d, J = 32.1 Hz), -88.0 (d, J = 32.1 Hz). **HRMS (ESI):** m/z calculated for $C_{24}H_{20}DCl_2F_2O_3^+$ $[M + H]^+$: 466.0893, found: 466.0892.

4-(4,4-Dichloro-1,1-difluorobut-1-en-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (4aj)



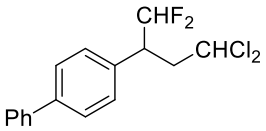
The title compound was prepared according to **GP2** and isolated as a colorless oil (63.5 mg, 0.107 mmol, 71%). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.72 – 7.66 (m, 2H), 7.51 – 7.45 (m, 2H), 7.33 – 7.28 (m, 2H), 7.14 – 7.09 (m, 2H), 7.07 (d, J = 2.5 Hz, 1H), 6.91 (d, J = 9.0 Hz, 1H), 6.71 (dd, J = 9.0, 2.5 Hz, 1H), 5.51 (td, J = 6.8, 0.8 Hz, 1H), 3.93 (s, 2H), 3.85 (s, 3H), 3.26 (dt, J = 6.8, 2.1 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.2, 168.4, 156.2, 155.2 (dd, J = 292.4, 291.1 Hz), 150.4, 139.5, 136.4, 133.8, 131.3 × 2, 130.9, 130.5, 129.6 (t, J = 3.2 Hz) × 2, 129.3 × 3, 122.0 × 2, 115.1, 111.9 × 2 (t, J = 1.2 Hz), 101.3, 88.3 (dd, J = 21.4, 18.3 Hz), 70.3 (dd, J = 5.9, 3.8 Hz), 55.8, 42.3 (d, J = 2.9 Hz), 30.6, 13.5. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -87.0 (d, J = 32.4 Hz), -87.9 (d, J = 32.4 Hz). **HRMS (ESI):** m/z calculated for $C_{29}H_{23}Cl_3F_2NO_4^+$ $[M + H]^+$: 592.0655, found: 592.0664.

(*E*)-4-(4-Chloro-1,1-difluorobuta-1,3-dien-2-yl)-1,1'-biphenyl (5)



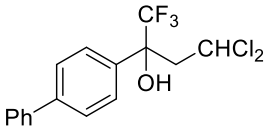
M.p.: 61.3 – 63.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.59 (m, 4H), 7.50 – 7.45 (m, 2H), 7.41 – 7.32 (m, 3H), 6.74 (dt, J = 13.5, 1.6 Hz, 1H), 5.91 (d, J = 13.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.5 (dd, J = 299.5, 293.3 Hz), 141.5, 140.5, 130.4 (d, J = 1.9 Hz), 130.4 (d, J = 1.9 Hz), 129.0 × 3, 127.8, 127.6 × 2, 127.2 × 2, 126.0 (d, J = 2.3 Hz), 120.9 (dd, J = 12.2, 4.3 Hz), 94.0 (dd, J = 23.0, 17.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -87.7 (d, J = 26.8 Hz, 1F), -88.4 (d, J = 26.8 Hz, 1F). **HRMS (ESI):** m/z calculated for $C_{16}H_{12}ClF_2^+$ $[M + H]^+$: 277.0590, found: 277.0594.

4-(4,4-Dichloro-1,1-difluorobutan-2-yl)-1,1'-biphenyl (6)



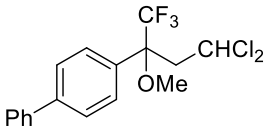
M.p.: 59.0 – 60.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.56 (m, 4H), 7.50 – 7.44 (m, 2H), 7.41 – 7.32 (m, 3H), 5.94 (td, J = 56.1, 3.3 Hz, 1H), 5.45 (dd, J = 9.6, 4.1 Hz, 1H), 3.66 – 3.35 (m, 1H), 2.89 – 2.68 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.6, 140.4, 133.2 (dd, J = 6.1, 2.5 Hz), 129.3 × 2, 129.0 × 2, 128.1 × 2, 127.8, 127.2 × 2, 117.0 (t, J = 245.9 Hz), 71.1, 47.3 (dd, J = 21.2, 19.7 Hz), 42.3 (dd, J = 5.6, 3.6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -117.6 (ddd, J = 278.4, 55.9, 12.6 Hz, 1F), -123.2 (ddd, J = 278.4, 56.5, 19.2 Hz, 1F). **HRMS (ESI):** m/z calculated for $C_{16}H_{15}Cl_2F_2^+$ $[M + H]^+$: 315.0513, found: 315.0521.

2-([1,1'-Biphenyl]-4-yl)-4,4-dichloro-1,1,1-trifluorobutan-2-ol (7)



M.p.: 64.1 – 64.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 – 7.58 (m, 6H), 7.48 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 5.67 (dd, J = 8.2, 4.1 Hz, 1H), 3.27 (dd, J = 15.6, 4.0 Hz, 1H), 3.24 (s, 1H), 3.11 (dd, J = 15.6, 8.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.3, 140.0, 133.5, 129.0 × 2, 127.9, 127.6 × 2, 127.3 × 2, 126.9 (t, J = 1.3 Hz) × 2, 124.7 (q, J = 285.8 Hz), 76.8 (q, J = 28.9 Hz), 68.2, 48.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.4 (s, 3F). **HRMS (ESI):** m/z calculated for $C_{16}H_{14}Cl_2F_3O^+$ $[M + H]^+$: 349.0368, found: 349.0369.

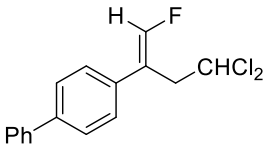
4-(4,4-Dichloro-1,1,1-trifluoro-2-methoxybutan-2-yl)-1,1'-biphenyl (8)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.55 (m, 6H), 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 5.81 (dd, J = 6.3, 4.4 Hz, 1H), 3.54 (q, J = 1.7 Hz, 3H), 3.34 (dd, J = 16.0, 6.3 Hz, 1H), 3.14 – 3.03 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)**

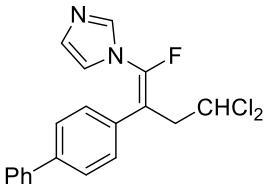
δ 142.0, 140.1, 133.0, 129.0 × 2, 127.9, 127.7 (q, J = 1.4 Hz) × 2, 127.4 × 2, 127.3 × 2, 124.9 (q, J = 290.5 Hz), 81.0 (d, J = 26.5 Hz), 67.5, 53.6, 46.8. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -72.1 (s, 3F). **HRMS (ESI):** m/z calculated for $C_{17}H_{16}Cl_2F_3O^+$ $[M + H]^+$: 363.0525, found: 363.0529.

(*E*)-4-(4,4-Dichloro-1-fluorobut-1-en-2-yl)-1,1'-biphenyl (9)



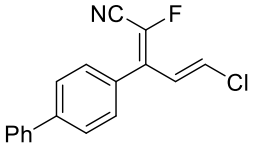
M.p.: 68.2 – 69.0 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.64 – 7.57 (m, 4H), 7.51 – 7.43 (m, 2H), 7.41 – 7.33 (m, 3H), 6.94 (d, J = 83.6 Hz, 1H), 5.71 (t, J = 6.9 Hz, 1H), 3.51 (ddd, J = 6.9, 2.5, 0.9 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.4 (d, J = 266.2 Hz), 141.3, 140.4, 133.4 (d, J = 7.9 Hz), 129.0 × 2, 127.8 × 2, 127.7, 127.5, 127.5, 127.1 × 2, 119.9 (d, J = 8.2 Hz), 70.6 (d, J = 4.4 Hz), 41.3 (d, J = 3.7 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -124.9 (d, J = 83.5 Hz, 1F). **HRMS (ESI):** m/z calculated for $C_{16}H_{14}Cl_2F^+$ $[M + H]^+$: 295.0451, found: 295.0458.

(*E*)-1-(2-([1,1'-Biphenyl]-4-yl)-4,4-dichloro-1-fluorobut-1-en-1-yl)-1*H*-imidazole (10)



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.51 (m, 4H), 7.48 – 7.40 (m, 3H), 7.40 – 7.33 (m, 1H), 7.20 – 7.12 (m, 2H), 7.00 (s, 1H), 6.92 (s, 1H), 5.62 (t, J = 6.8 Hz, 1H), 3.55 (dd, J = 6.9, 2.5 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.0 (d, J = 264.5 Hz), 141.7, 139.9, 131.8 (d, J = 4.0 Hz), 129.0 × 4, 128.8, 128.7, 128.1 × 2, 127.9 × 2, 127.1 × 2, 108.8 (d, J = 23.0 Hz), 70.1 (d, J = 4.9 Hz), 44.3. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -90.6 (s, 1F). **HRMS (ESI):** m/z calculated for $C_{19}H_{16}Cl_2FN_2^+$ $[M + H]^+$: 361.0669, found: 361.0676.

(2*E*,4*E*)-3-([1,1'-Biphenyl]-4-yl)-5-chloro-2-fluoropenta-2,4-dienenitrile (11)



M.p.: 68.5 – 69.8 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.74 – 7.67 (m, 2H), 7.65 – 7.59 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.37 (m, 3H), 7.12 (dd, J = 13.5, 1.4 Hz, 1H), 6.30 (dd, J = 13.5, 1.4 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.3, 139.9, 134.2 (d, J = 11.6 Hz), 131.1 (d, J = 6.1 Hz), 130.2, 130.2, 129.1 × 2, 128.4 (d, J = 3.1 Hz), 128.1, 128.0 × 2, 127.8 (d, J = 15.0 Hz), 127.3 × 2, 126.1 (d, J = 2.4 Hz), 112.4 (d, J = 44.9 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -123.5 (s, 1F). **HRMS (ESI):** m/z calculated for $C_{17}H_{12}ClFN^+$ $[M + H]^+$: 284.0637, found: 284.0640.

7. References

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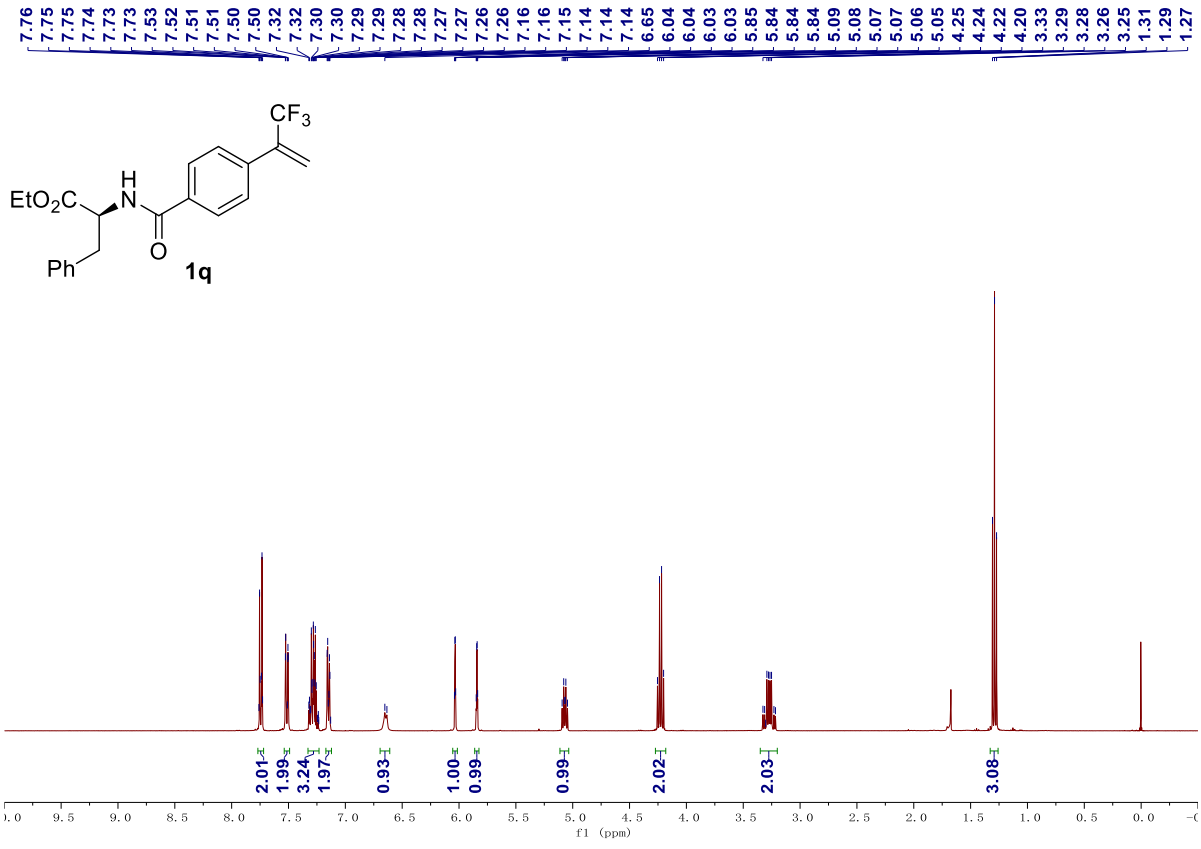
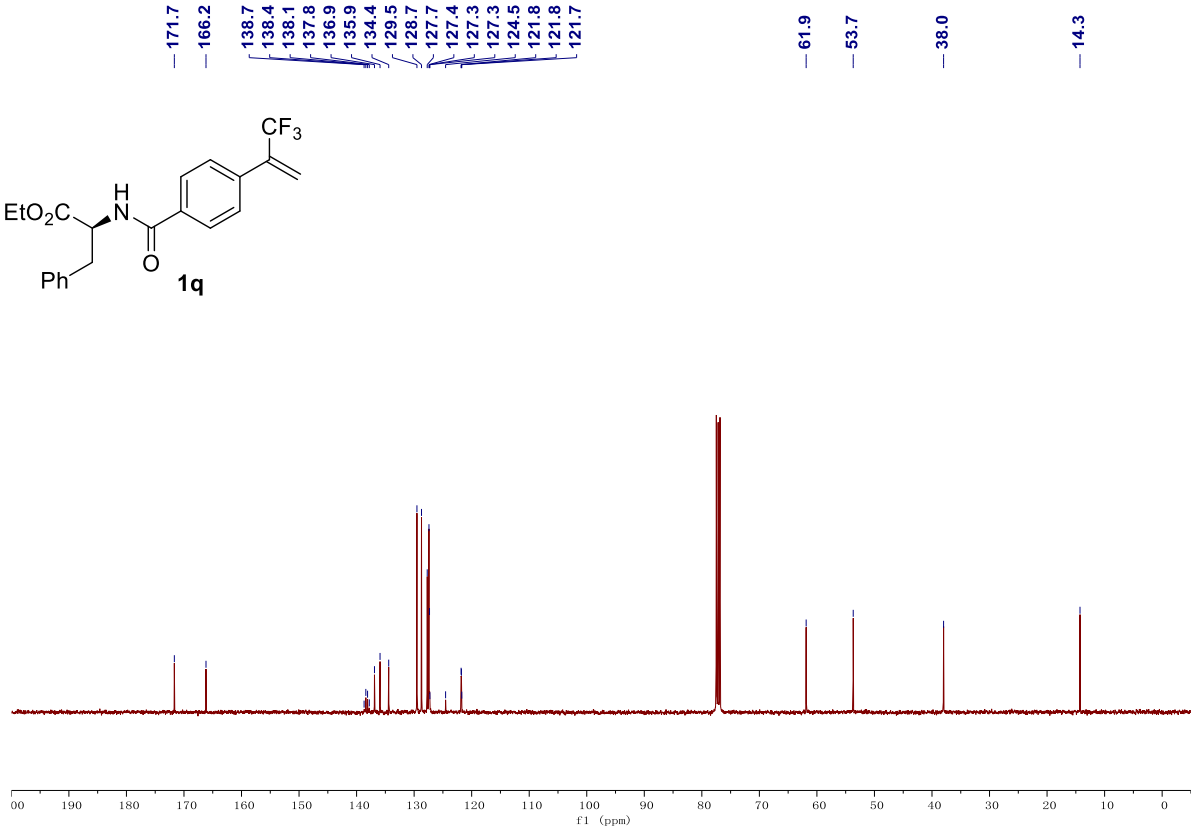
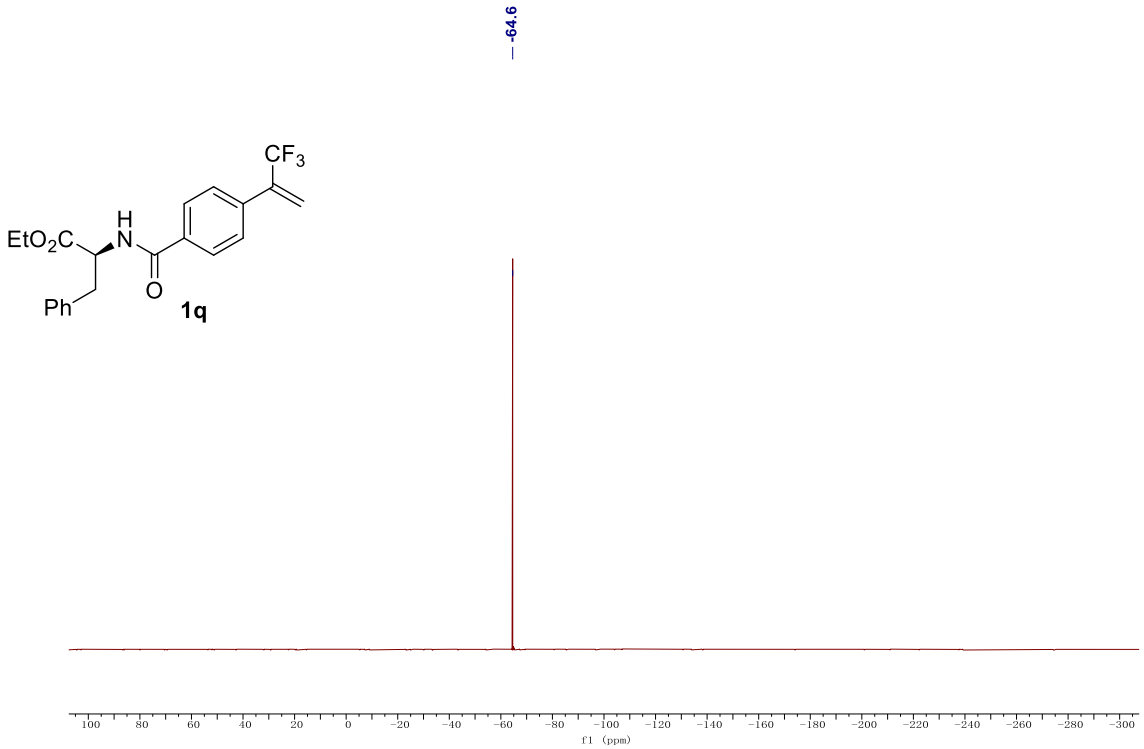
8. NMR spectra for substrate 1q



^{1}H NMR spectrum for substrate **1q** ($CDCl_3$)

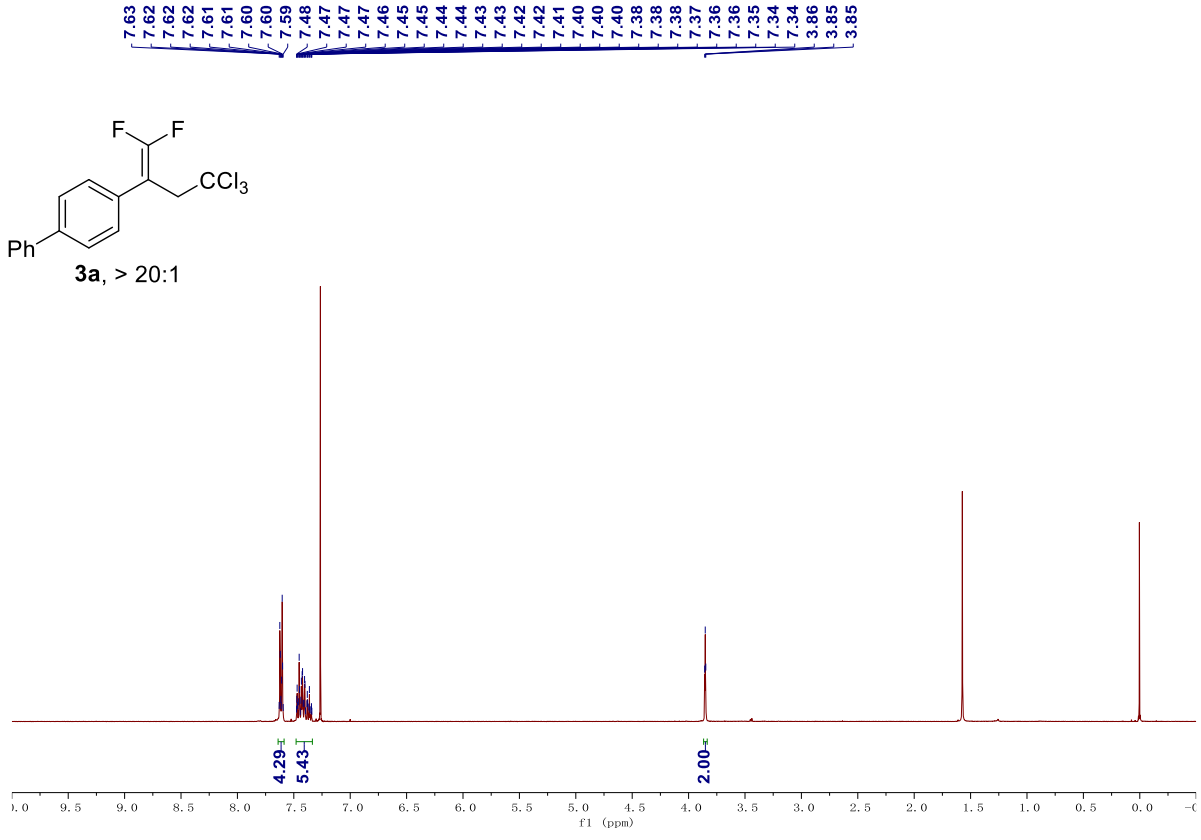


^{13}C NMR spectrum for substrate **1q** ($CDCl_3$)

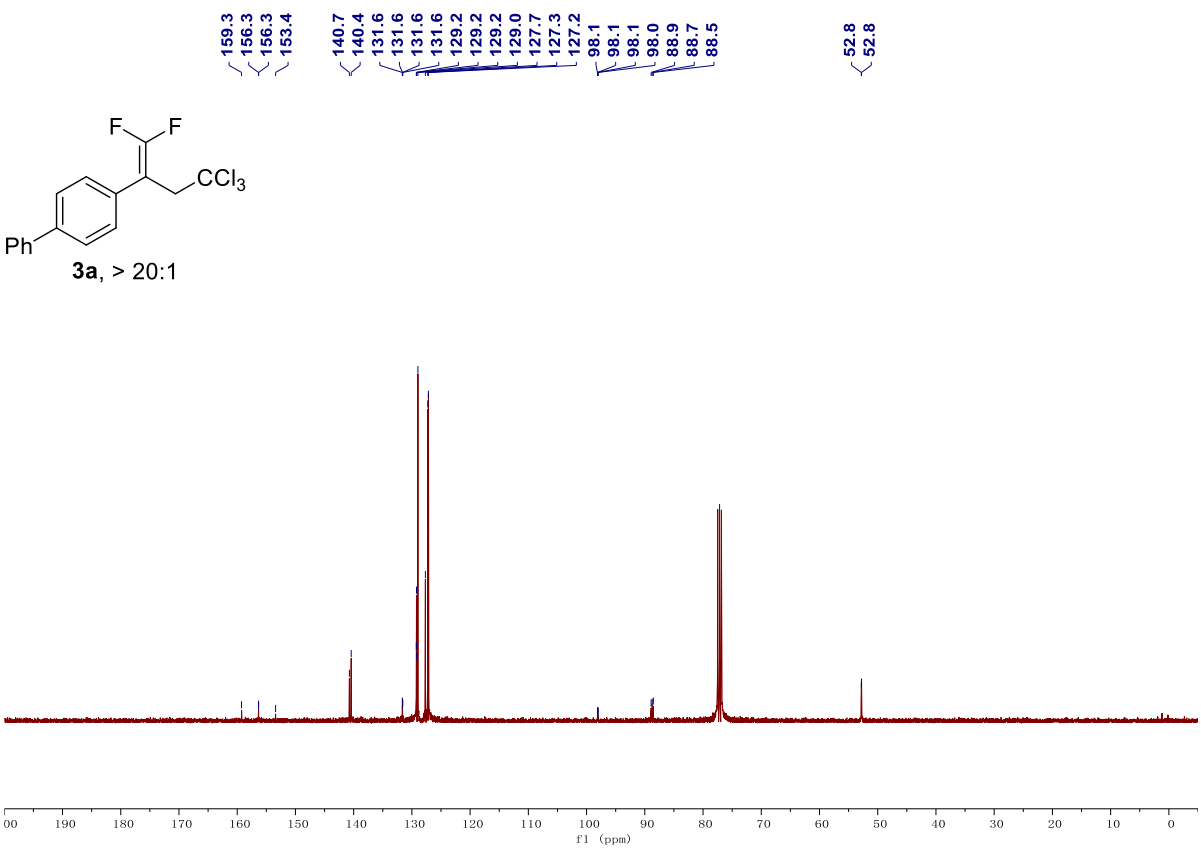


^{19}F NMR spectrum for substrate **1q** ($CDCl_3$)

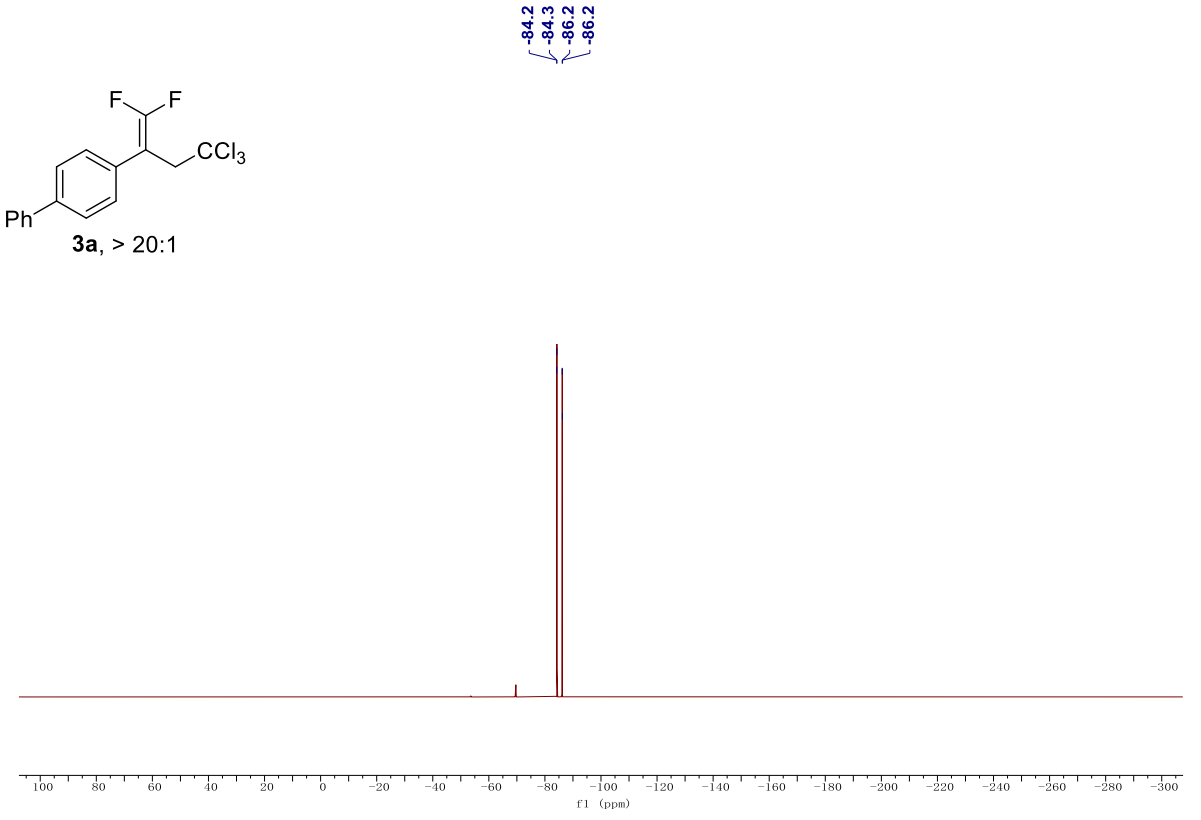
9. NMR spectra of the products



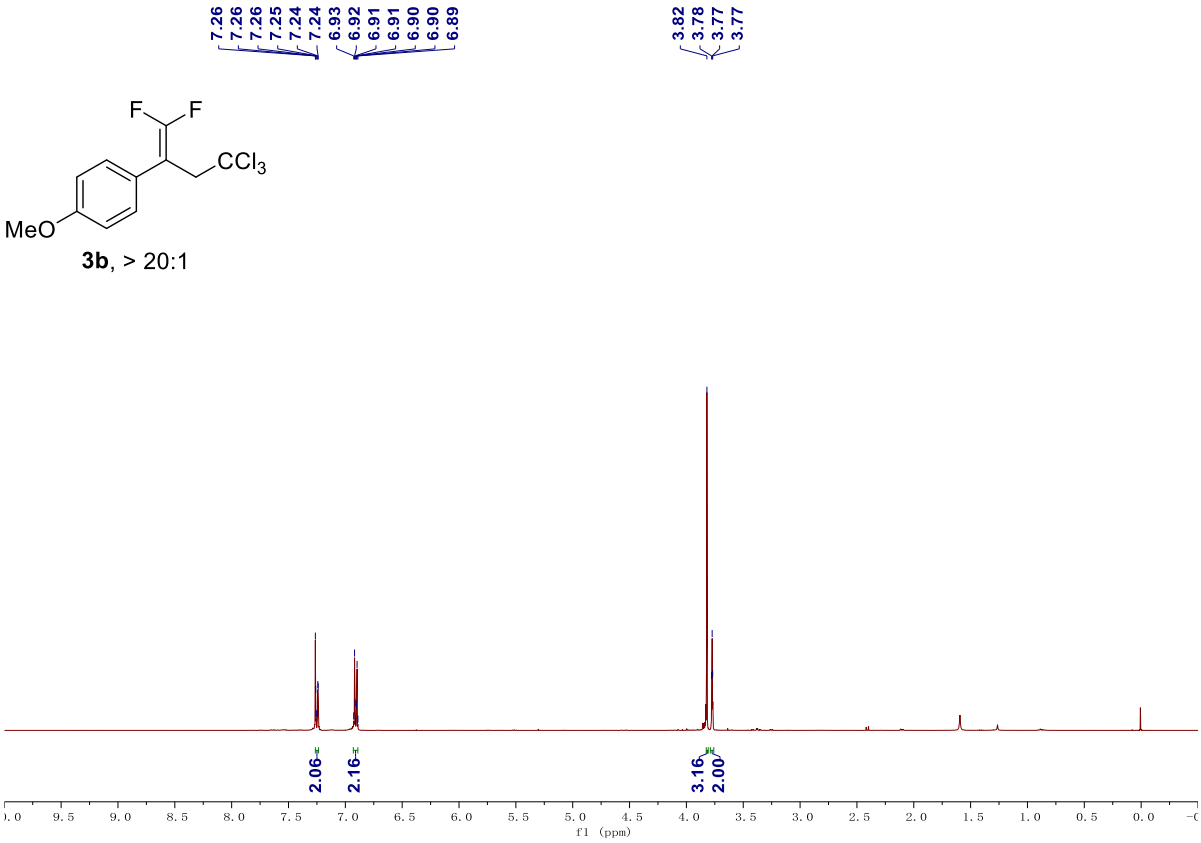
^{1}H NMR spectrum for compound **3a** ($CDCl_3$)



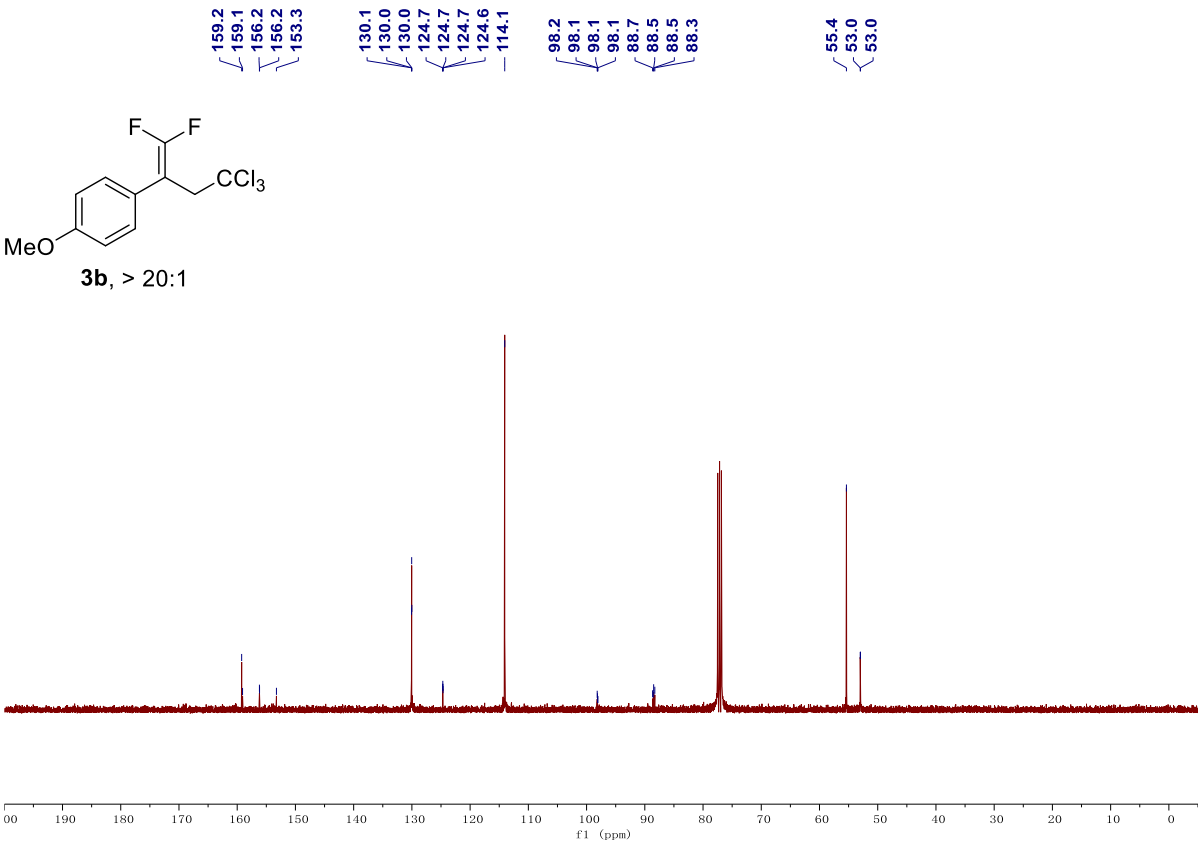
^{13}C NMR spectrum for compound **3a** ($CDCl_3$)



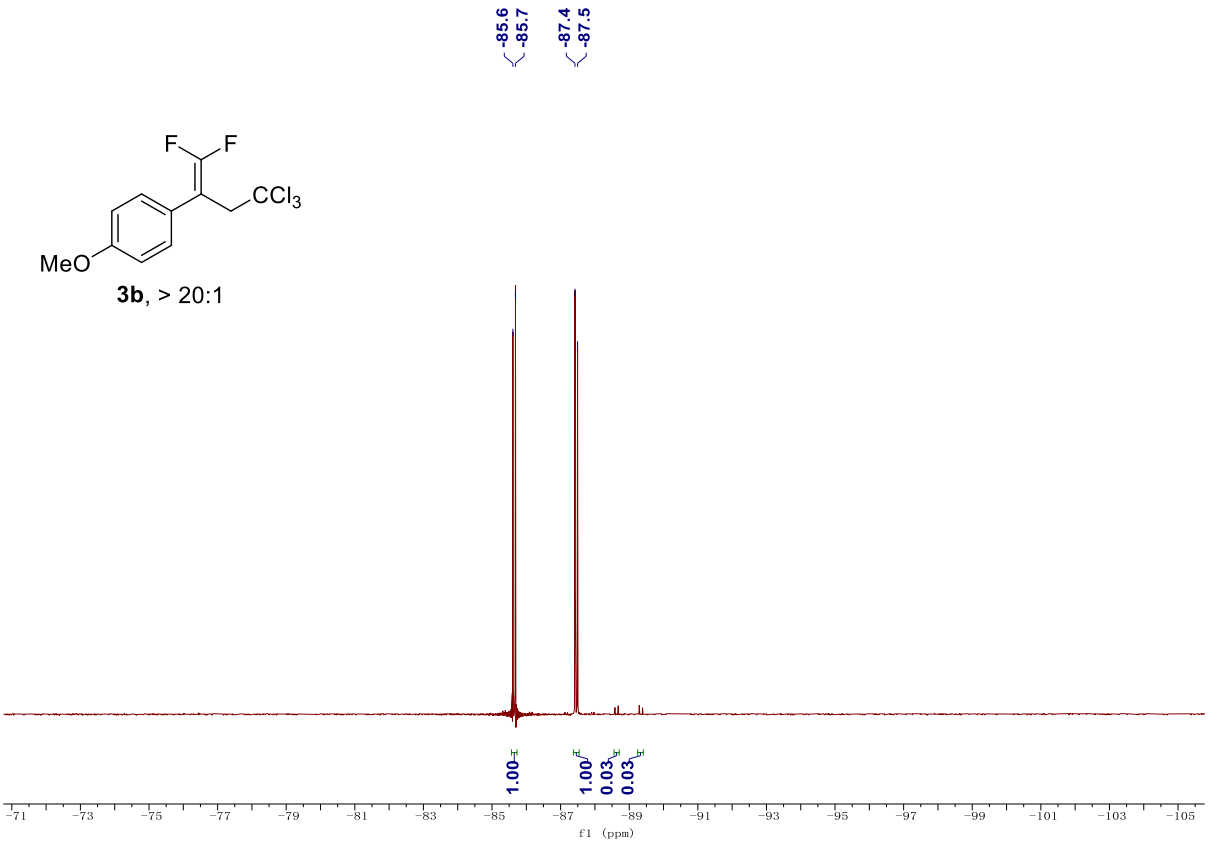
^{19}F NMR spectrum for compound **3a** ($CDCl_3$)



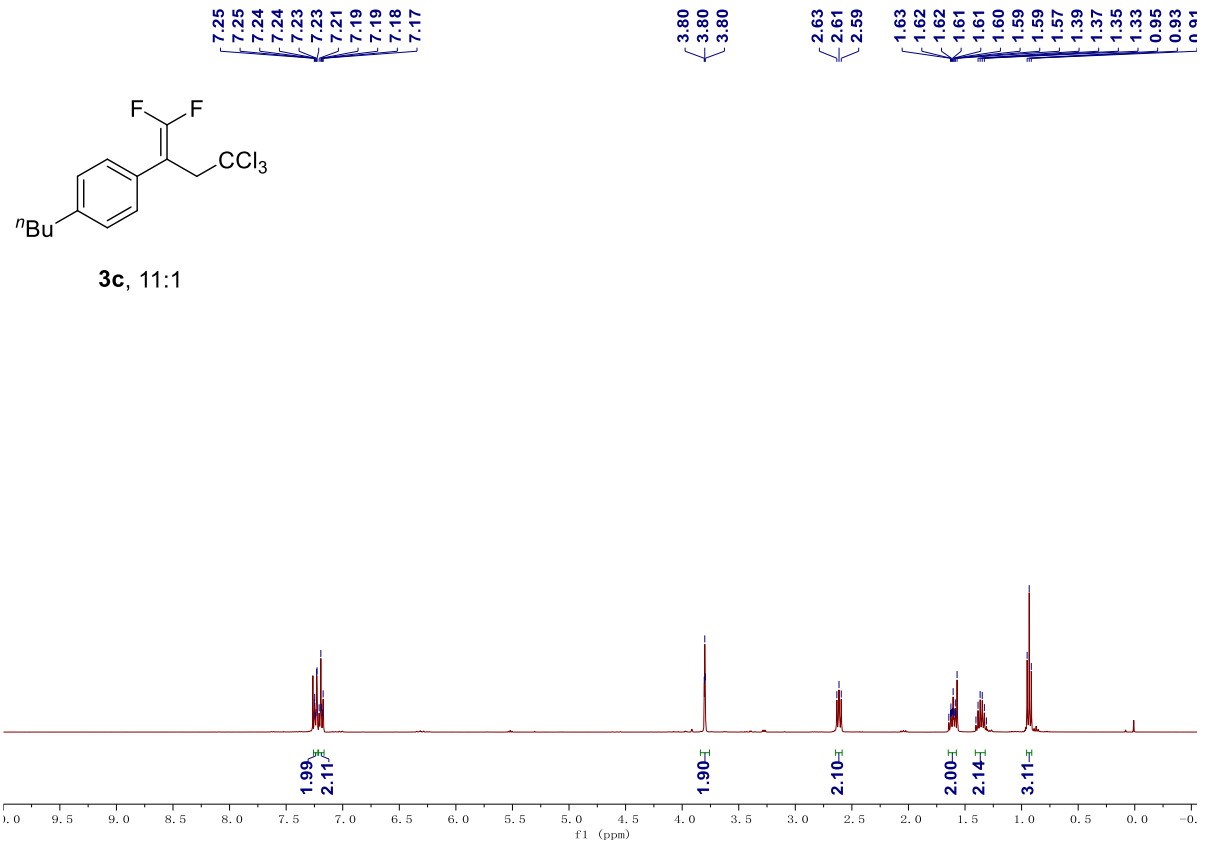
^{1}H NMR spectrum for compound **3b** ($CDCl_3$)



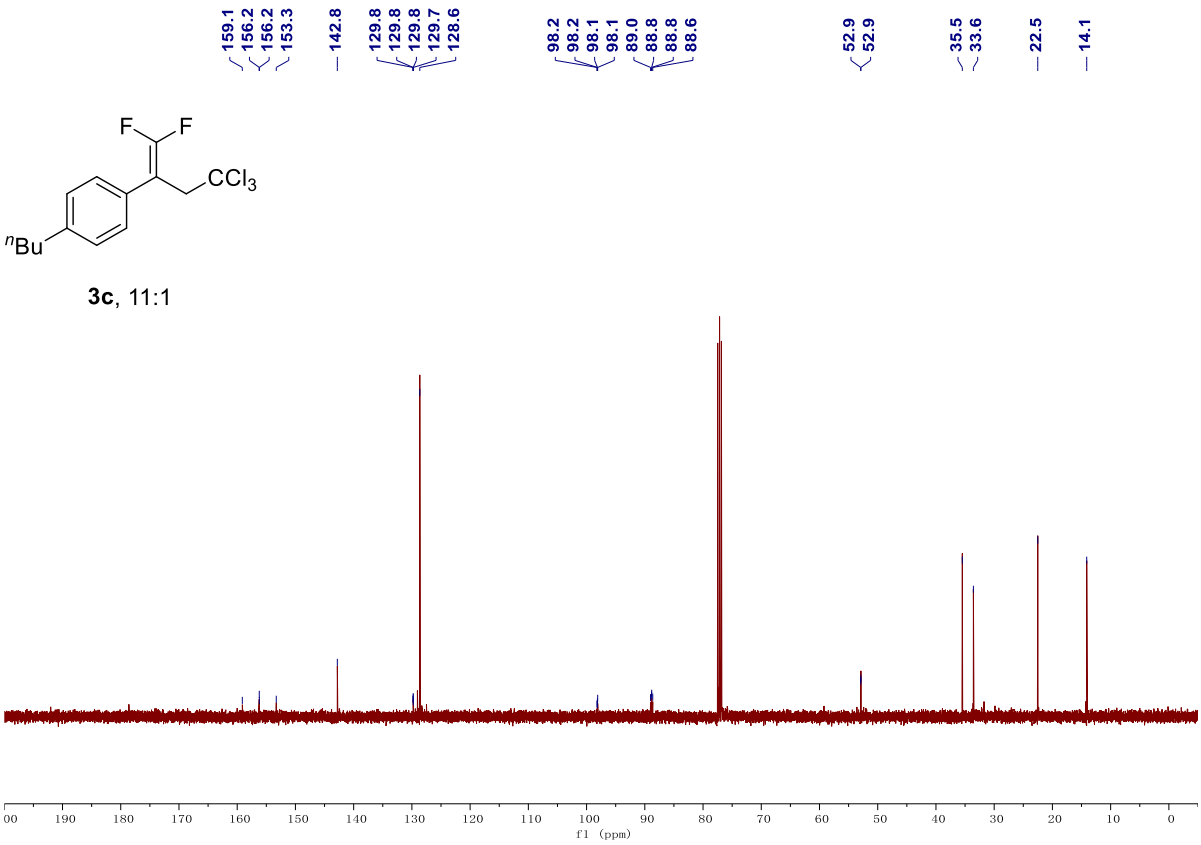
^{13}C NMR spectrum for compound **3b** ($CDCl_3$)



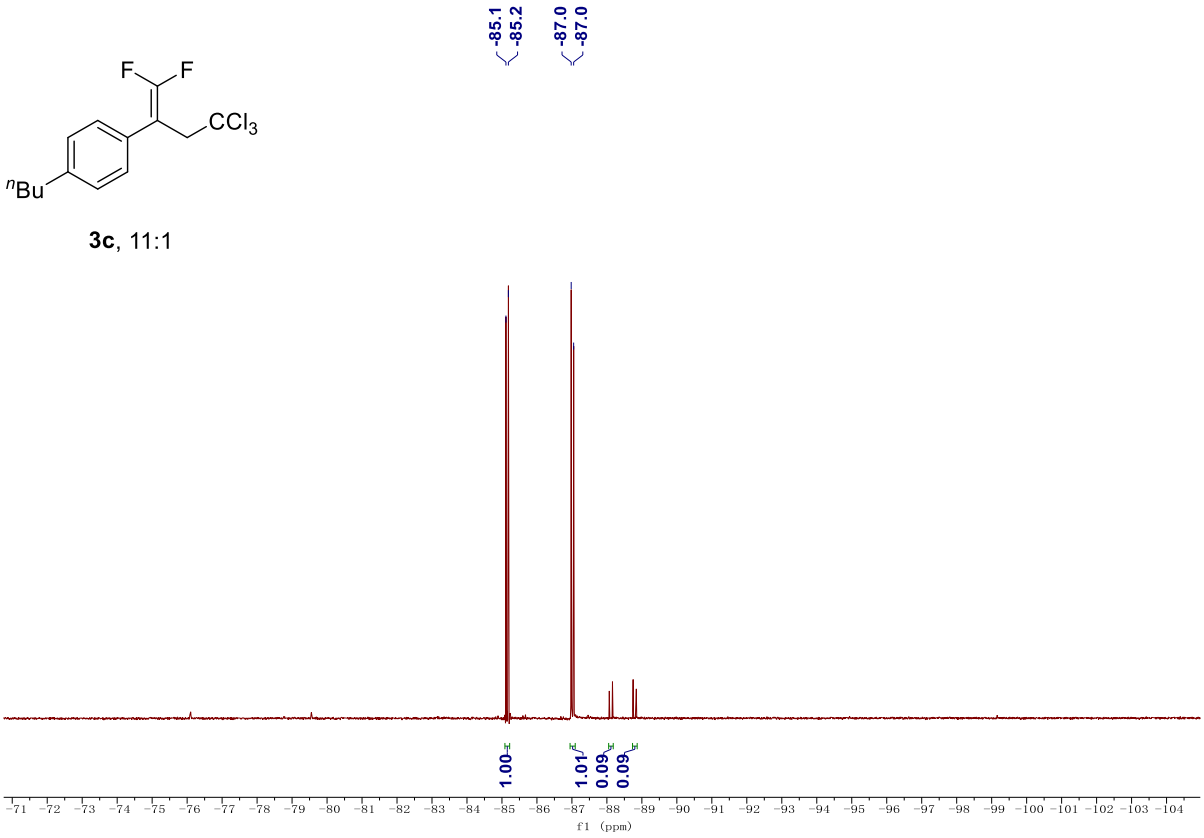
^{19}F NMR spectrum for compound **3b** ($CDCl_3$)



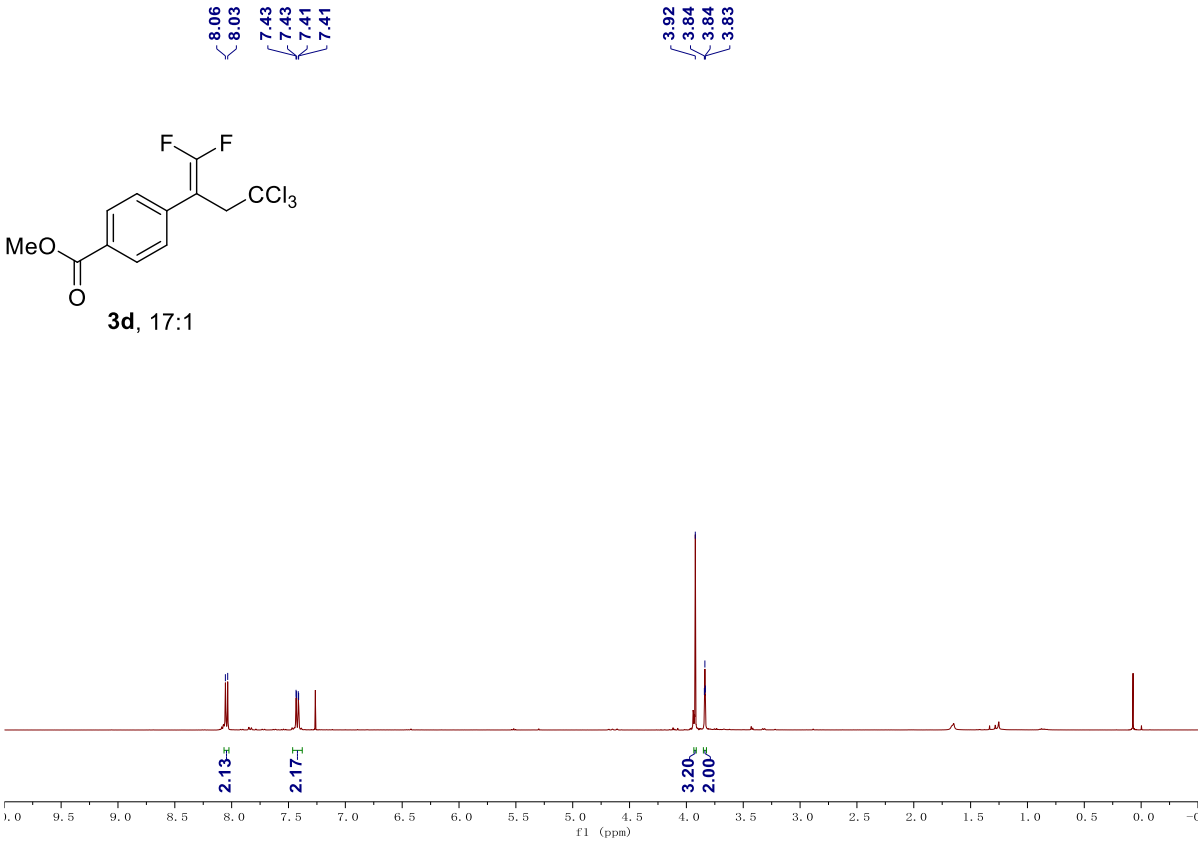
^{1}H NMR spectrum for compound **3c** ($CDCl_3$)



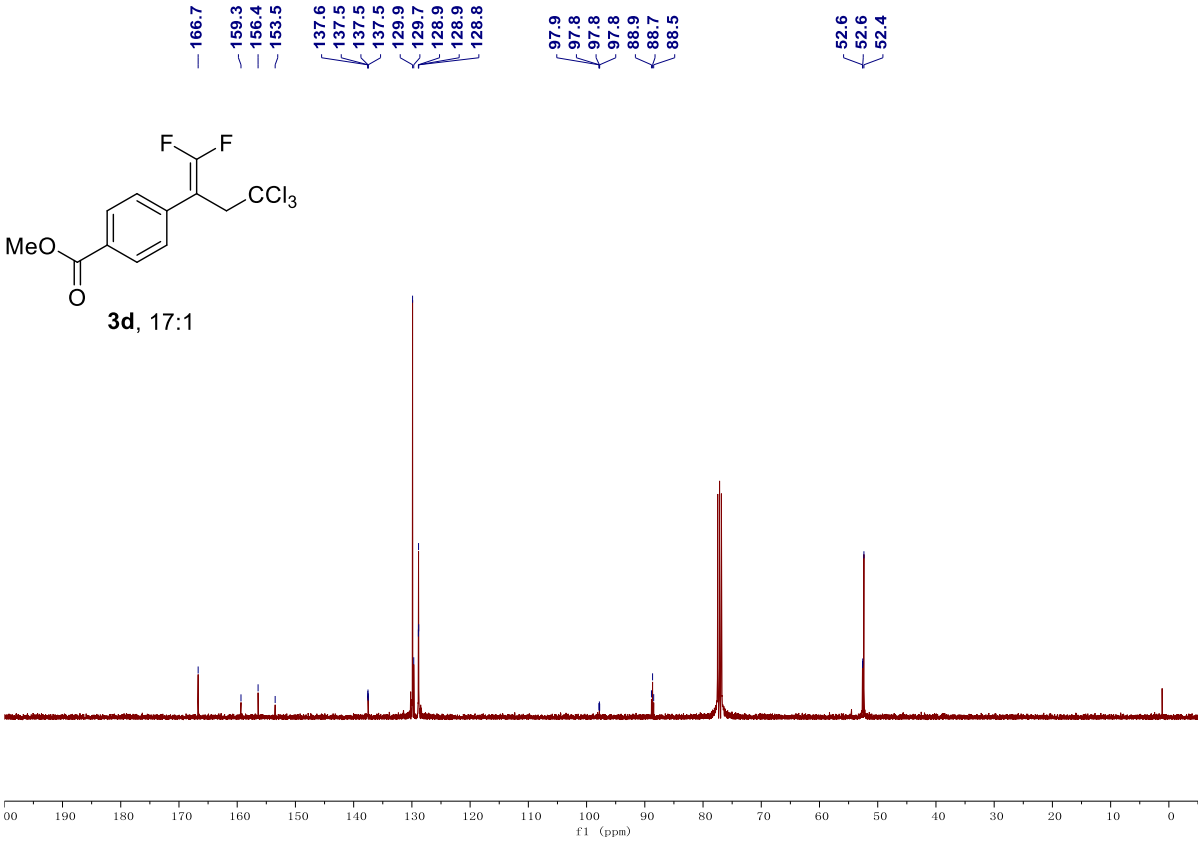
^{13}C NMR spectrum for compound **3c** ($CDCl_3$)



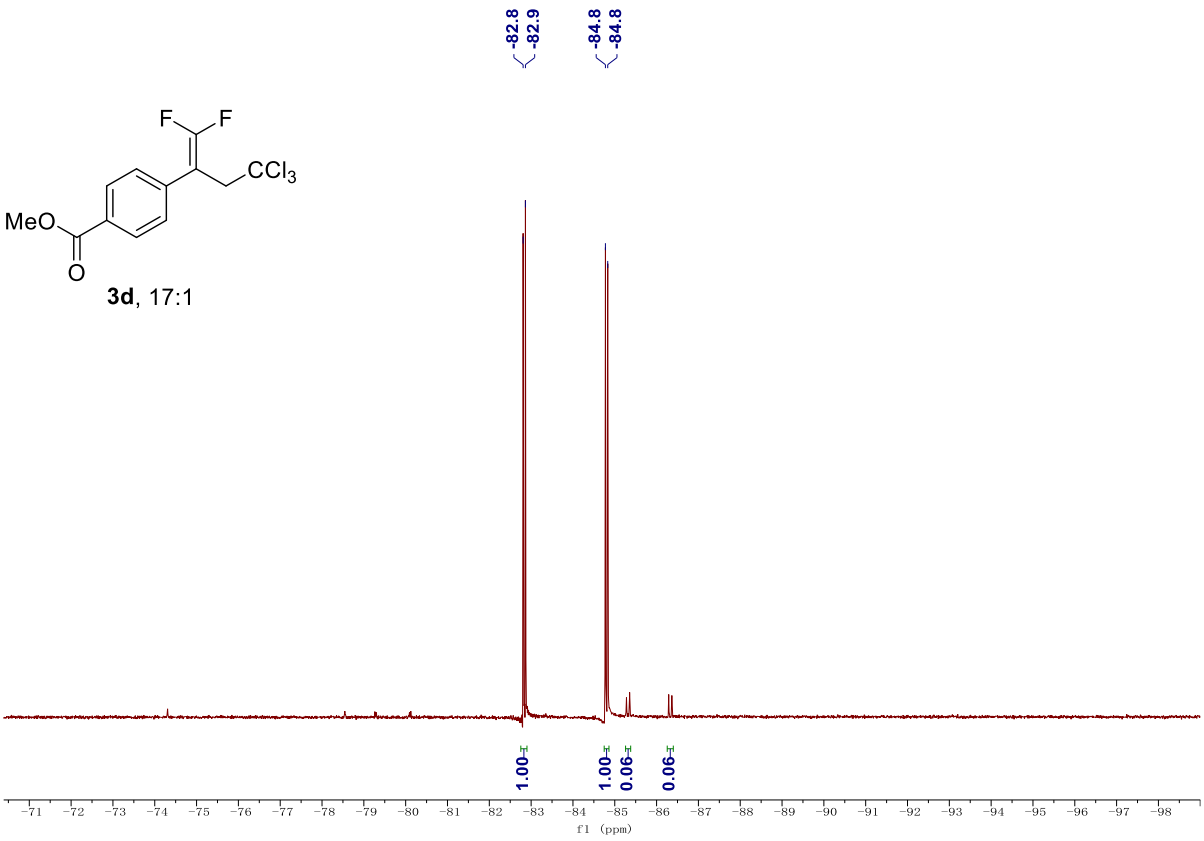
^{19}F NMR spectrum for compound **3c** ($CDCl_3$)



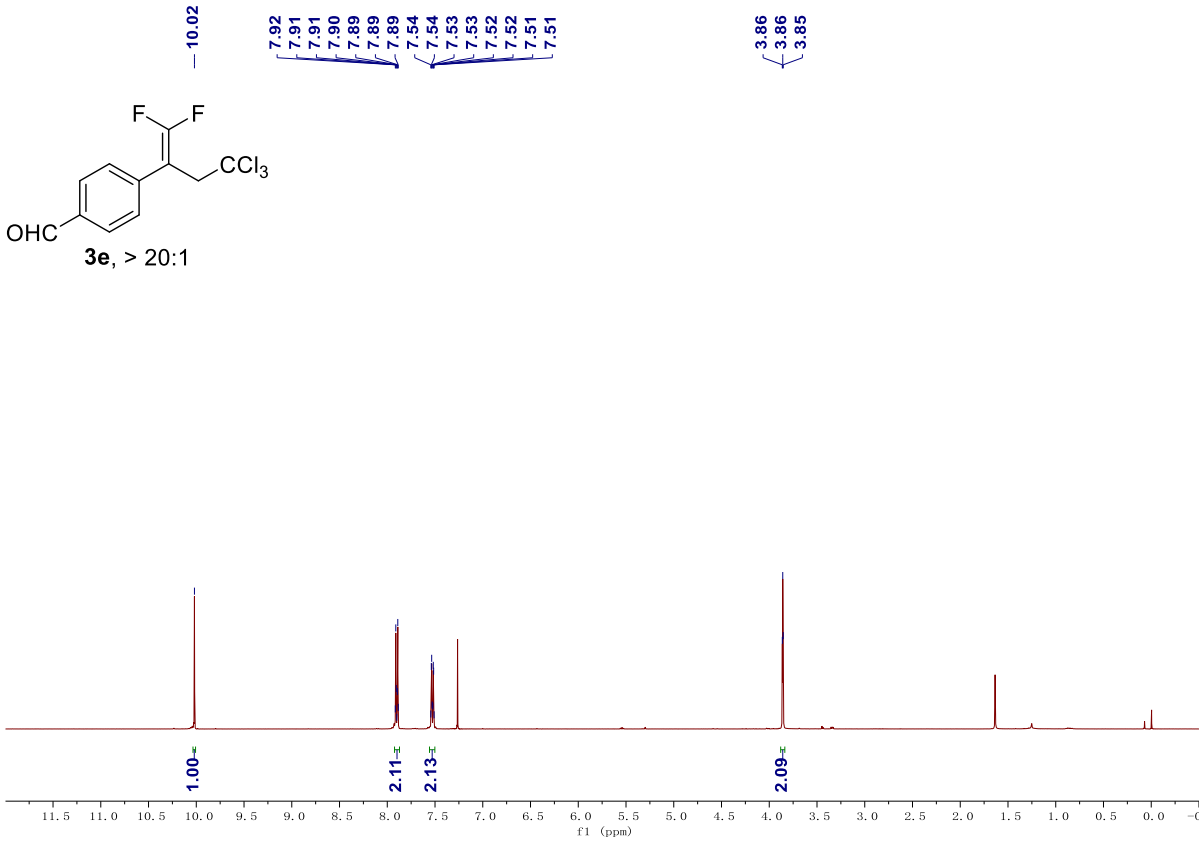
^{1}H NMR spectrum for compound **3d** ($CDCl_3$)



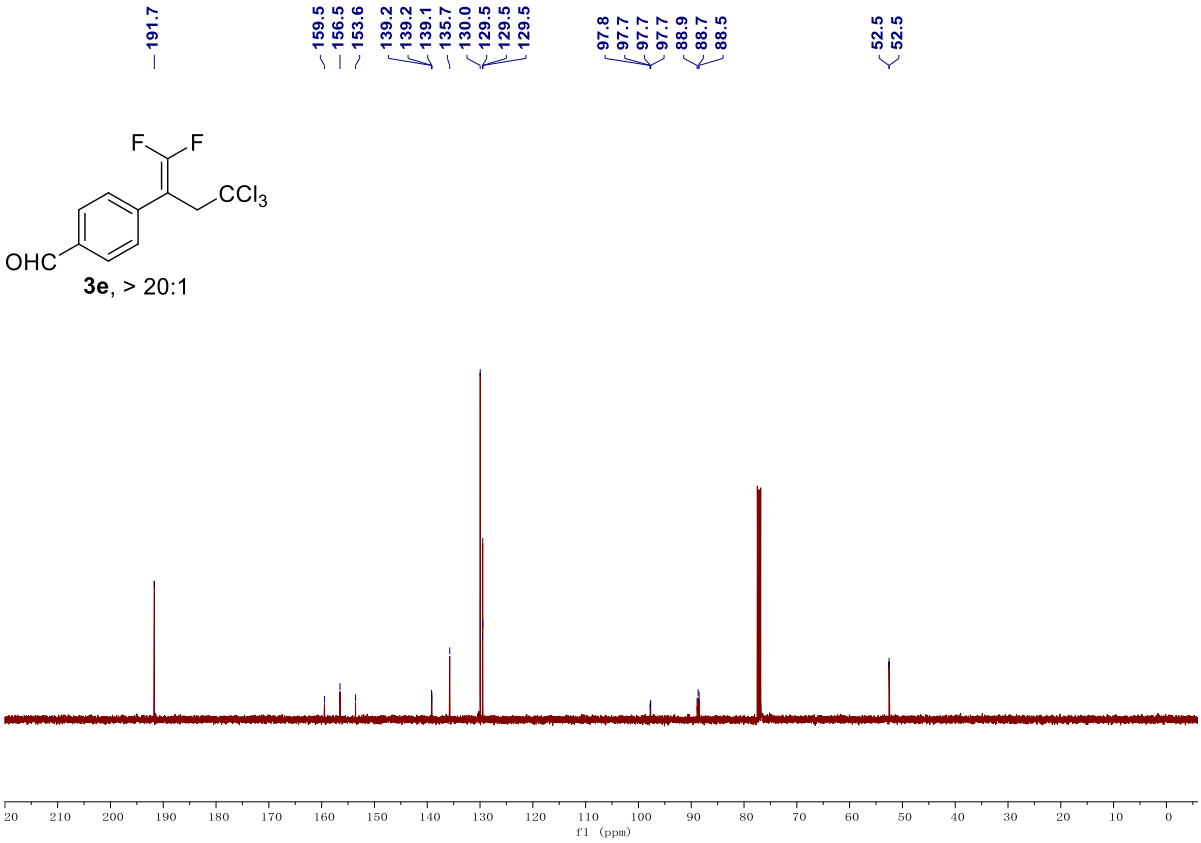
^{13}C NMR spectrum for compound **3d** ($CDCl_3$)



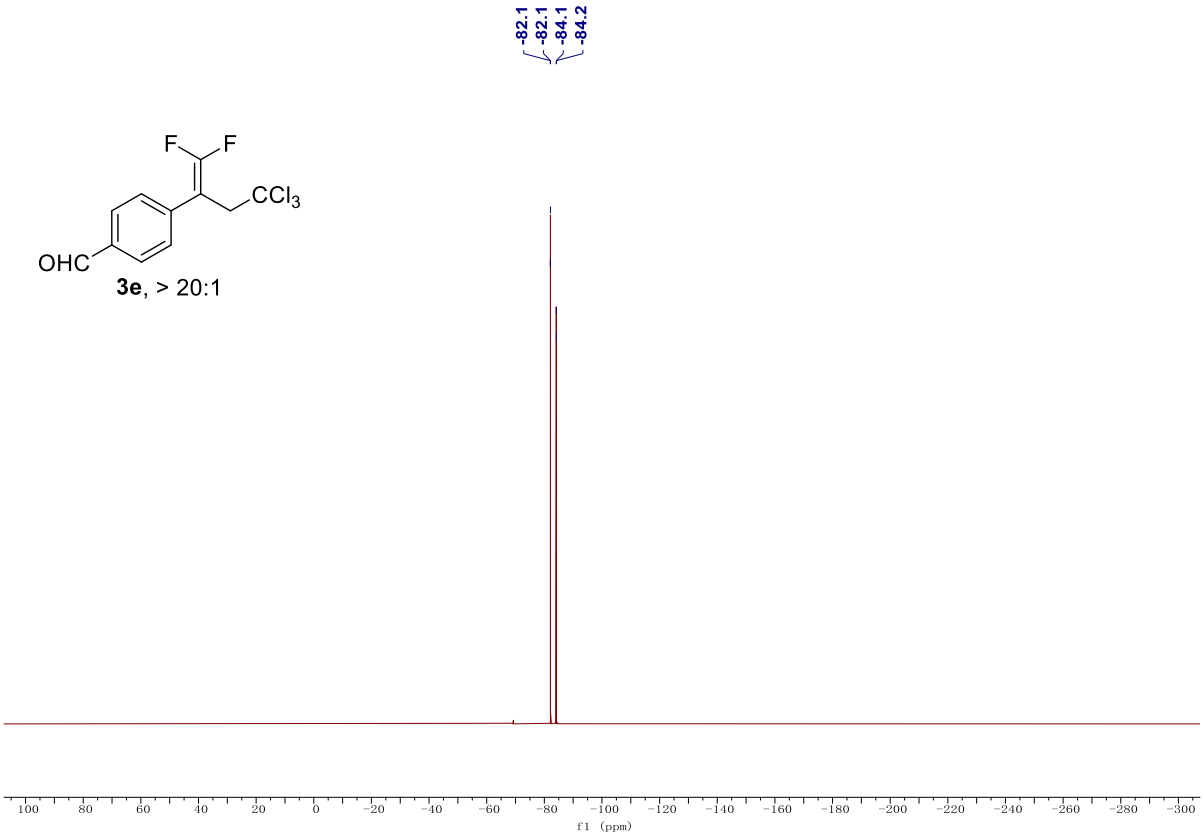
^{19}F NMR spectrum for compound **3d** ($CDCl_3$)



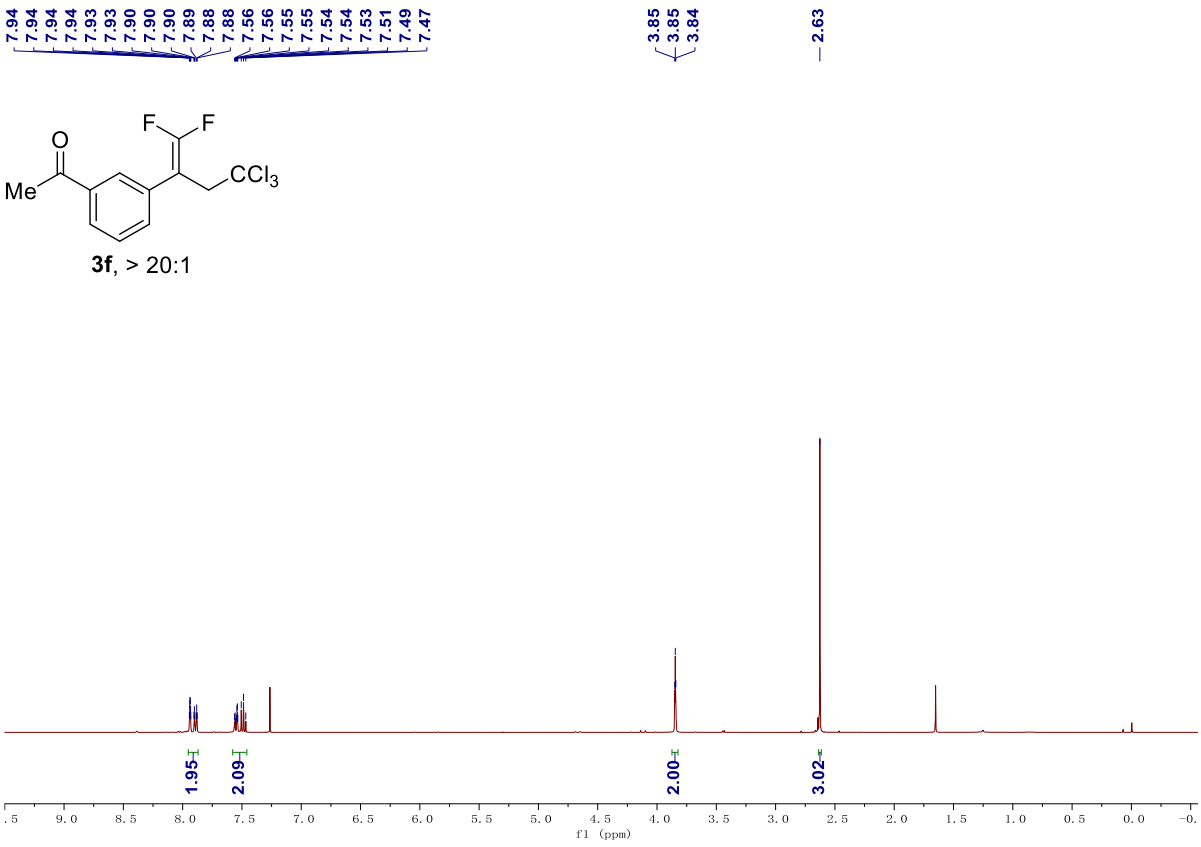
^{1}H NMR spectrum for compound **3e** ($CDCl_3$)



^{13}C NMR spectrum for compound **3e** ($CDCl_3$)

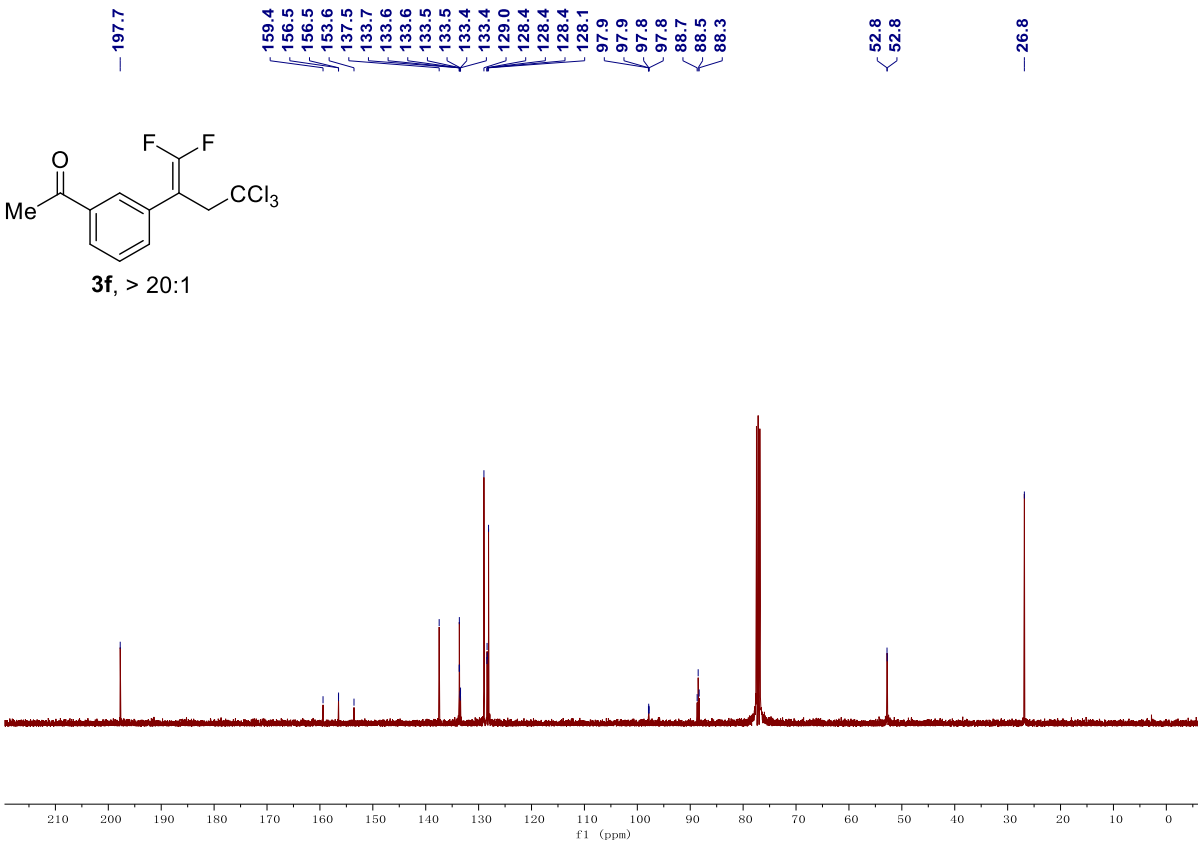


^{19}F NMR spectrum for compound **3e** ($CDCl_3$)



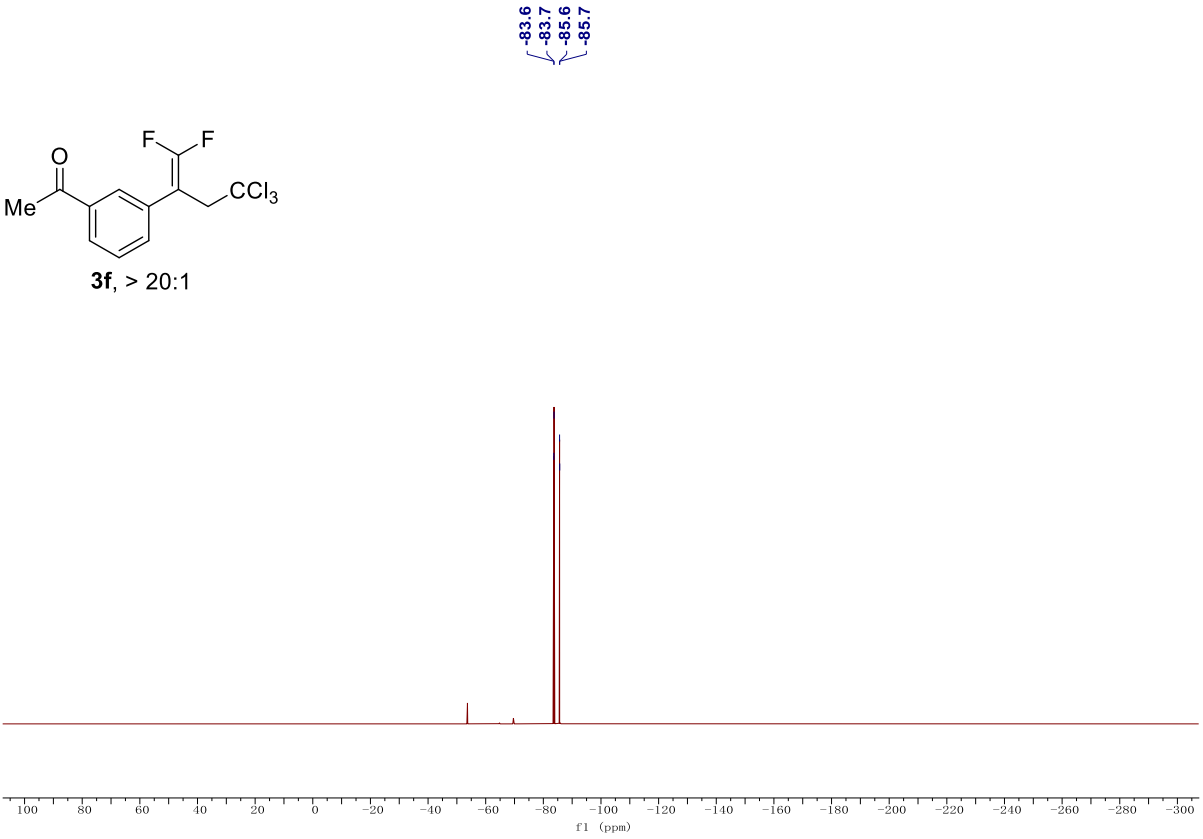
3f, > 20:1

^{1}H NMR spectrum for compound **3f** ($CDCl_3$)

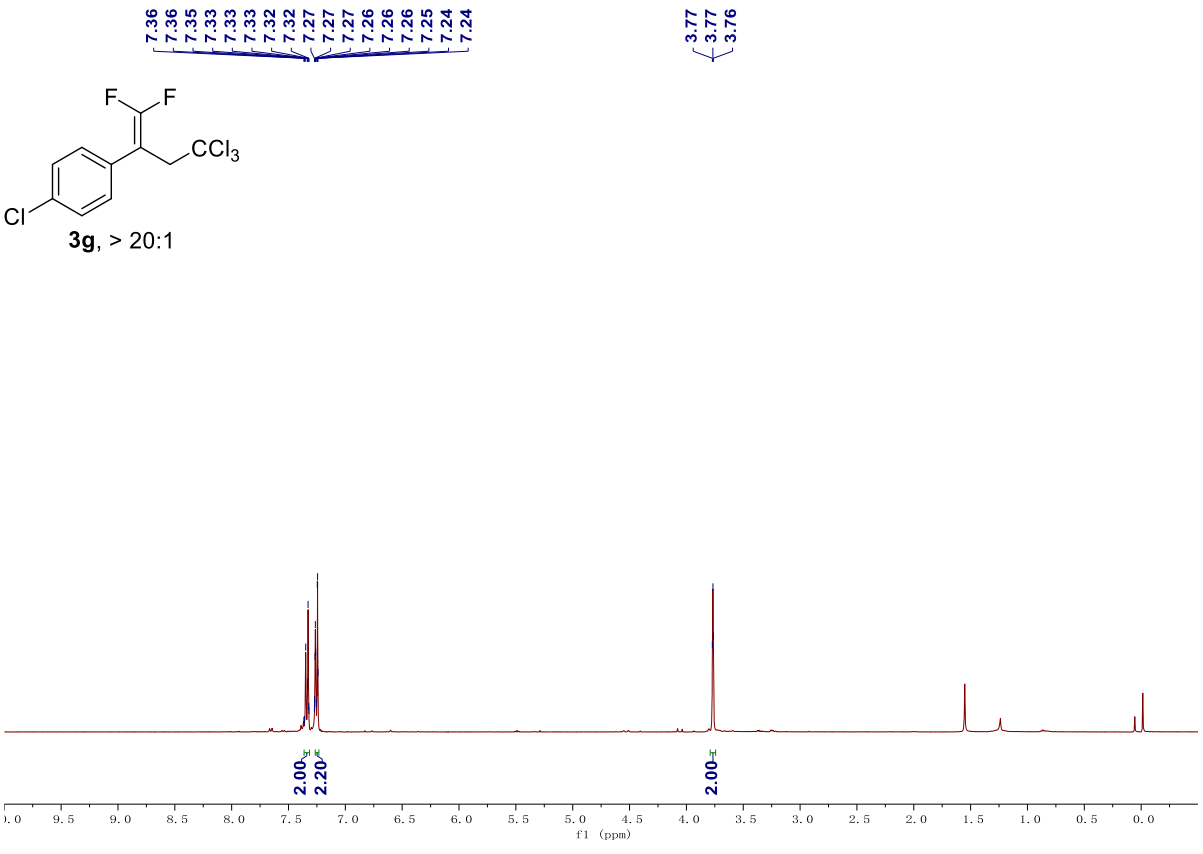


3f, > 20:1

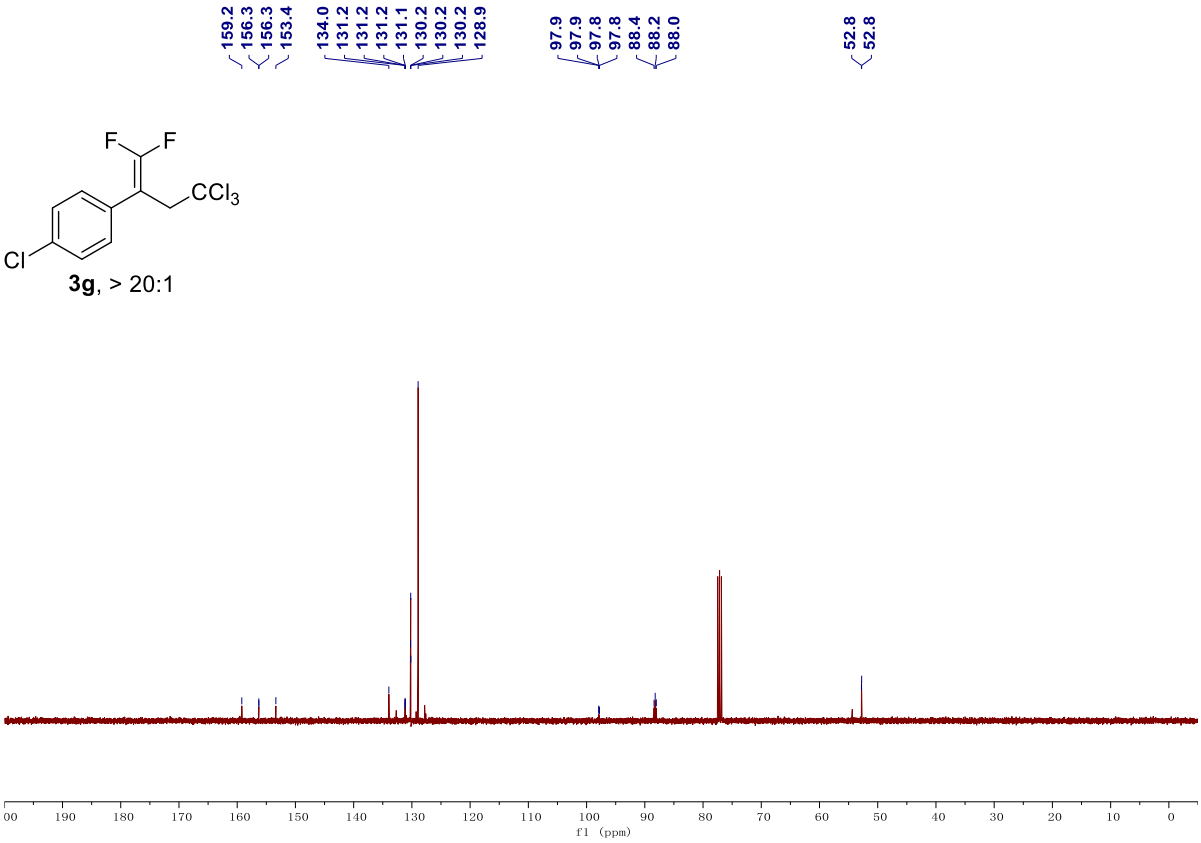
^{13}C NMR spectrum for compound **3f** ($CDCl_3$)



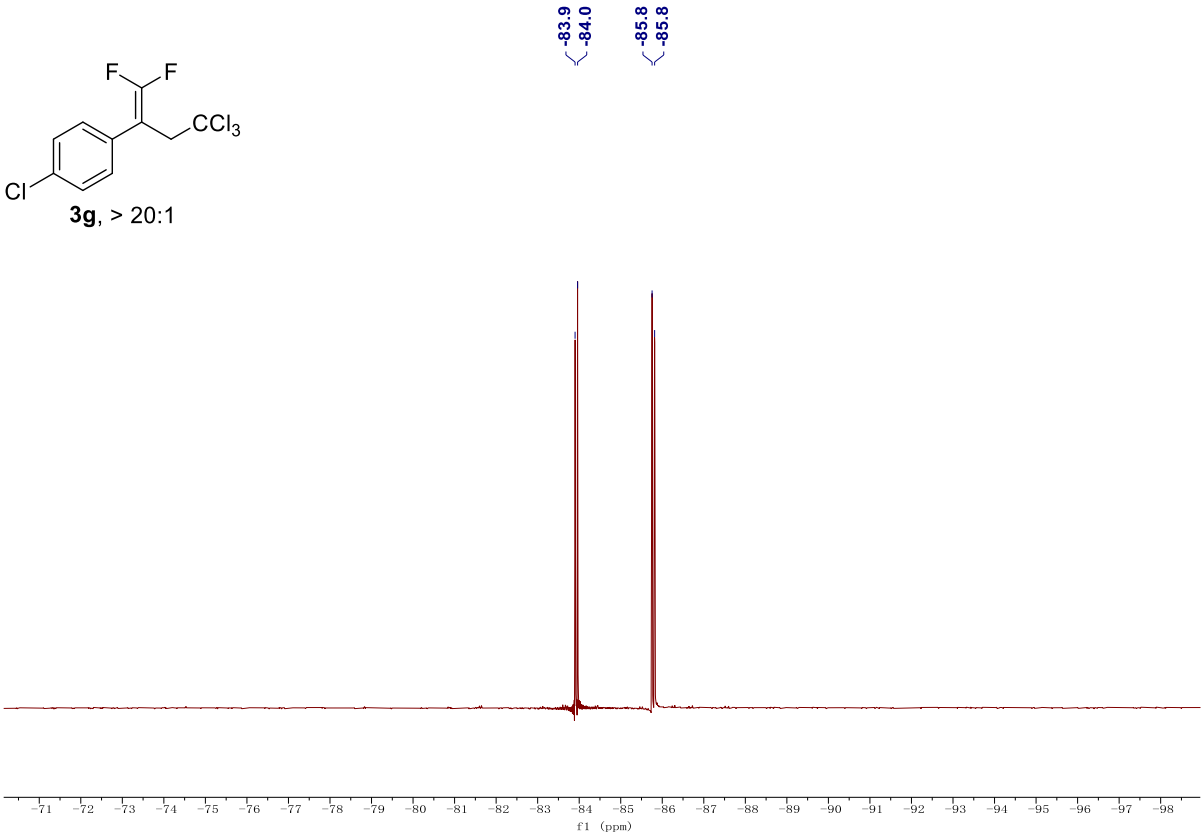
^{19}F NMR spectrum for compound **3f** ($CDCl_3$)



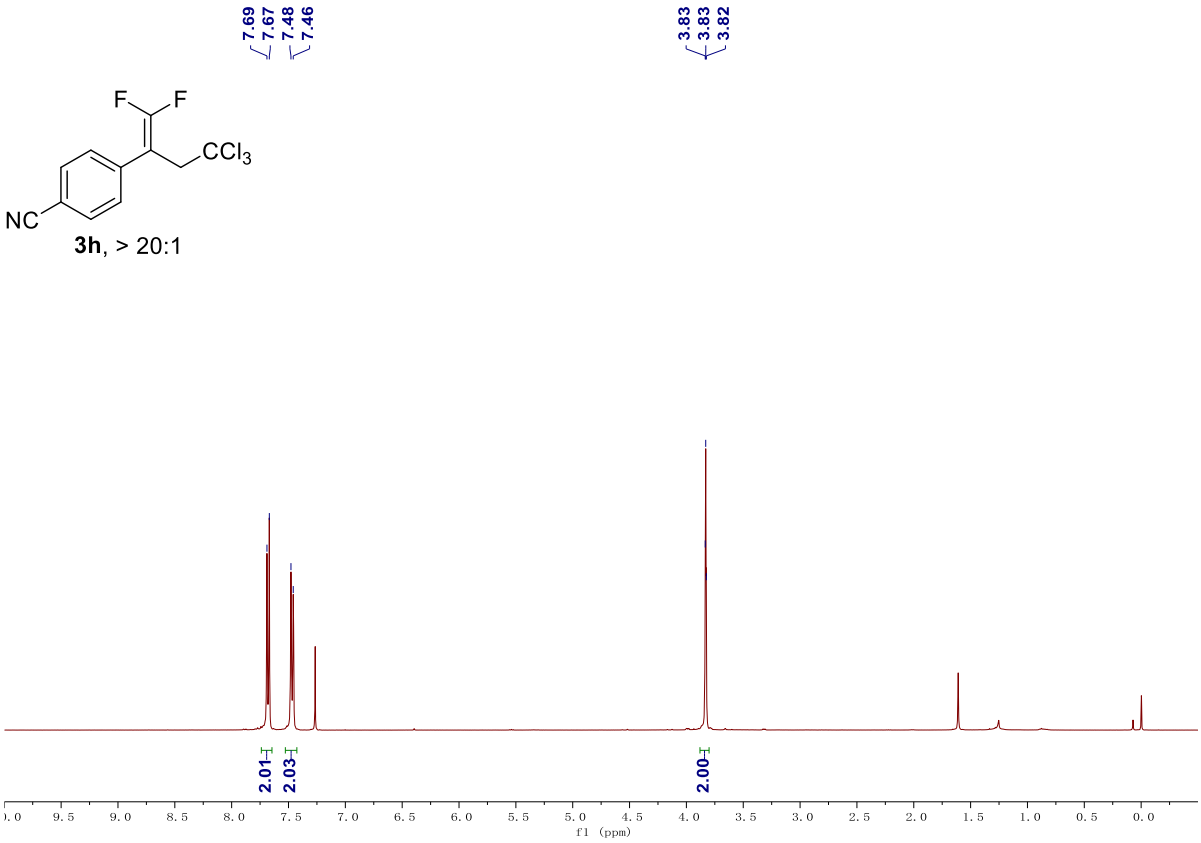
^{1}H NMR spectrum for compound **3g** ($CDCl_3$)



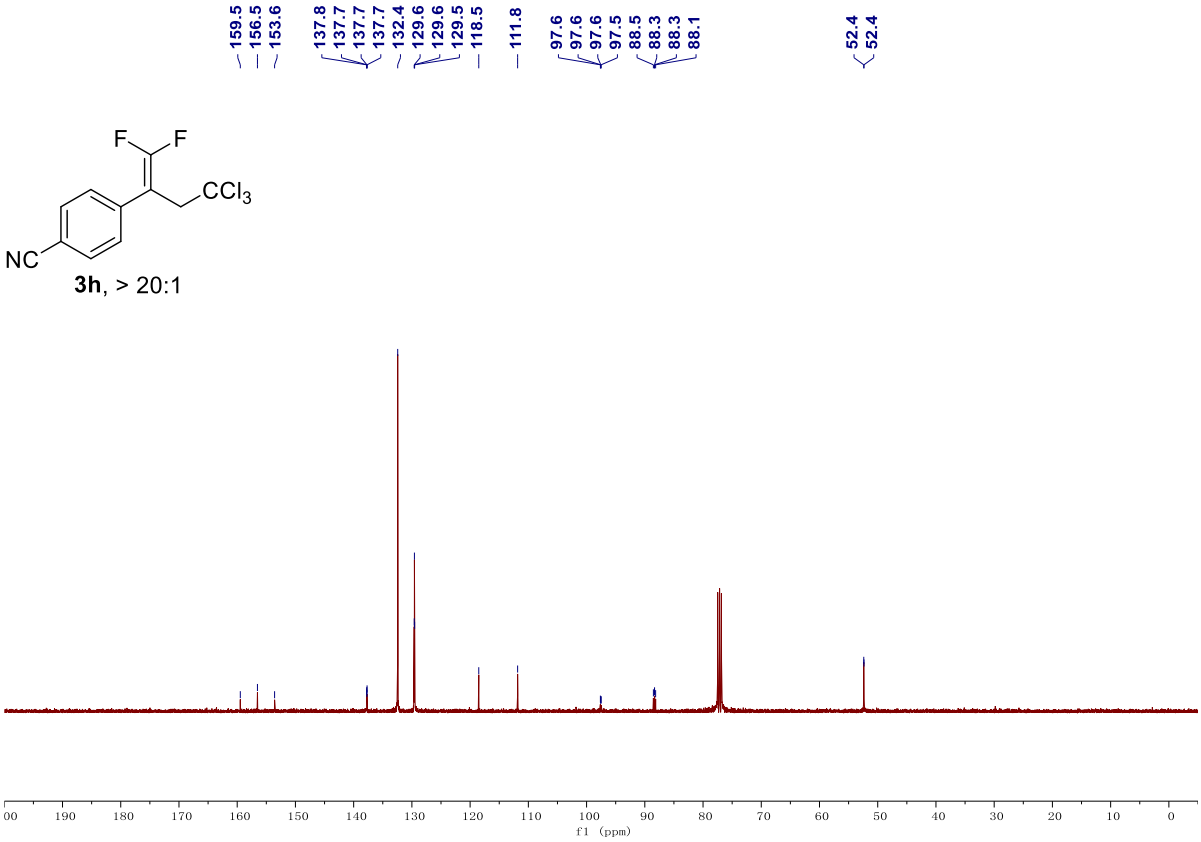
^{13}C NMR spectrum for compound **3g** ($CDCl_3$)



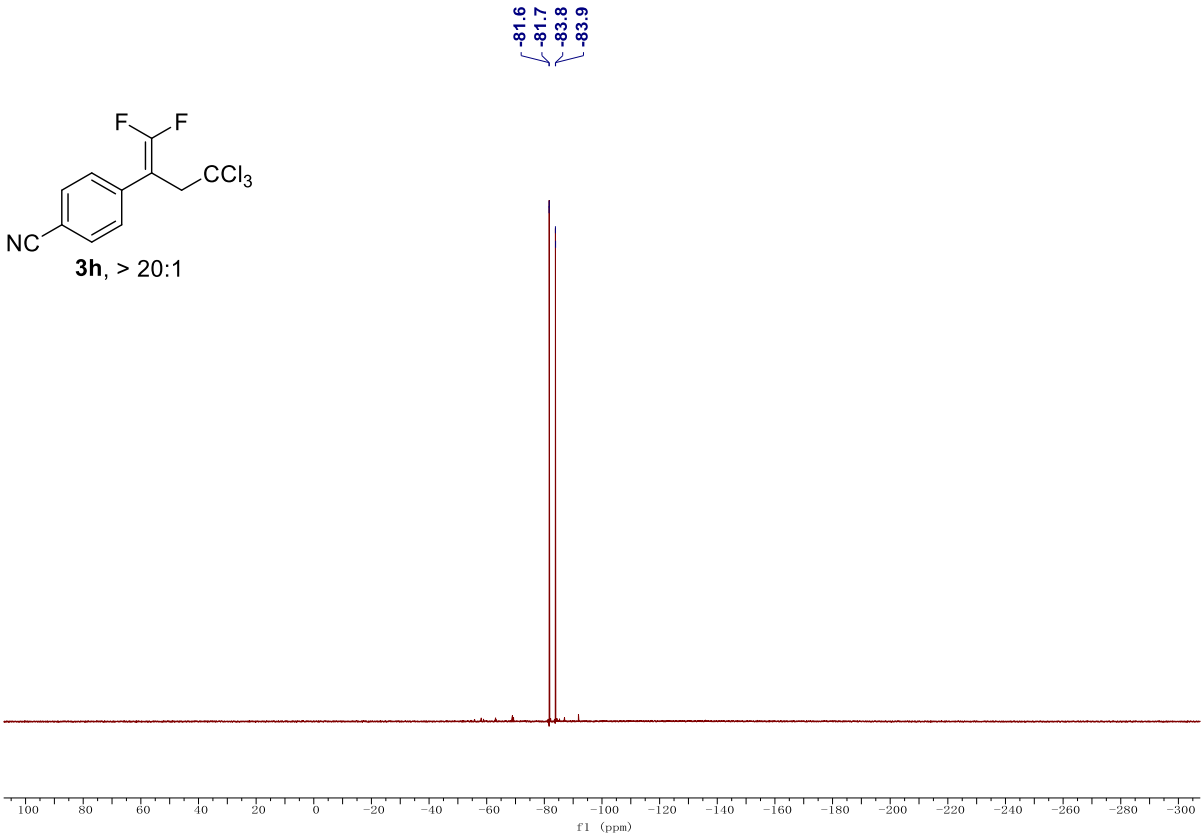
^{19}F NMR spectrum for compound **3g** ($CDCl_3$)



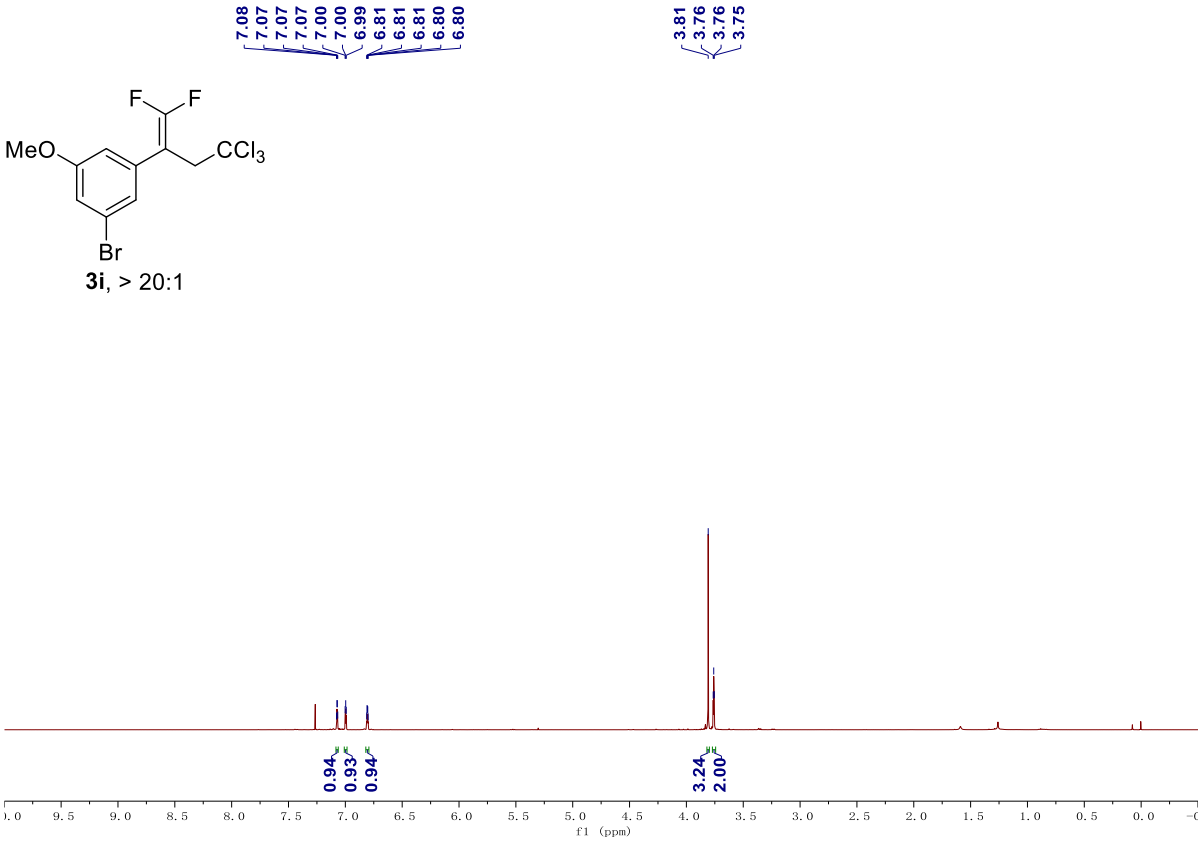
^{1}H NMR spectrum for compound **3h** ($CDCl_3$)



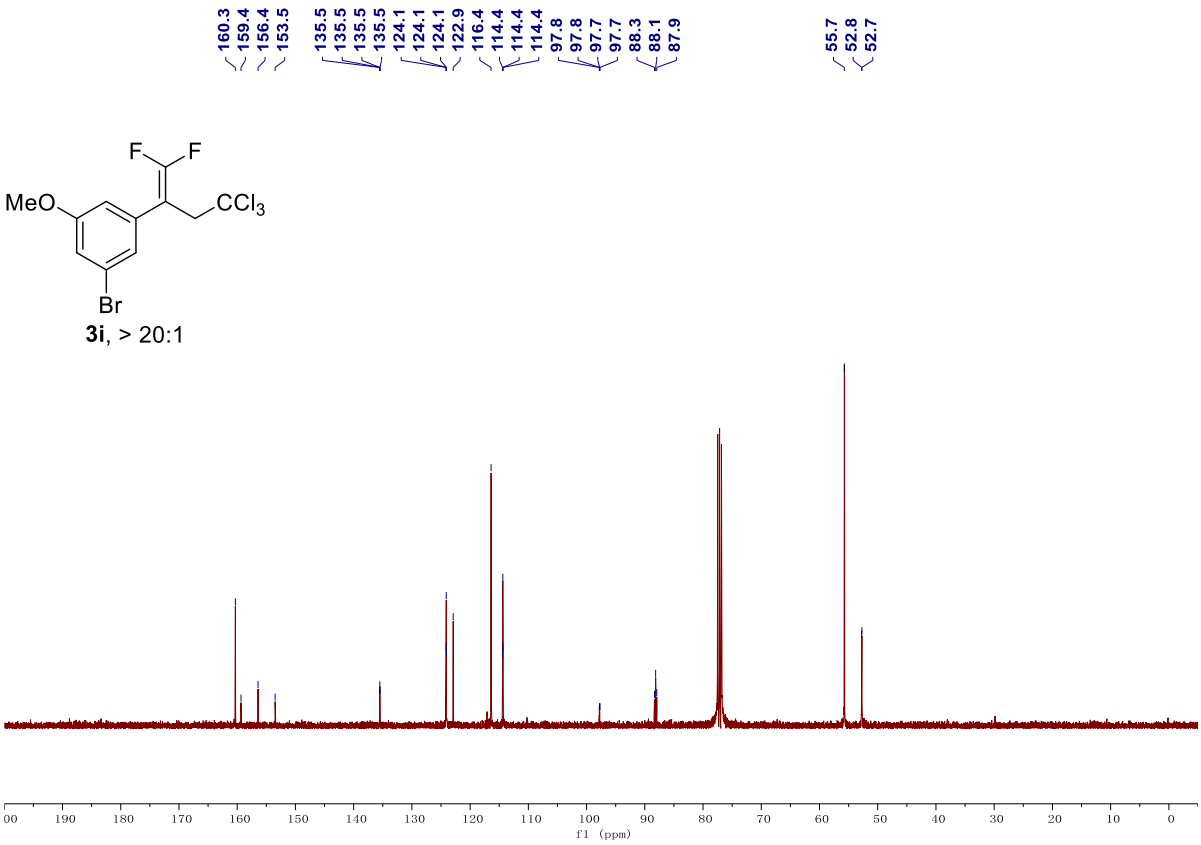
^{13}C NMR spectrum for compound **3h** ($CDCl_3$)



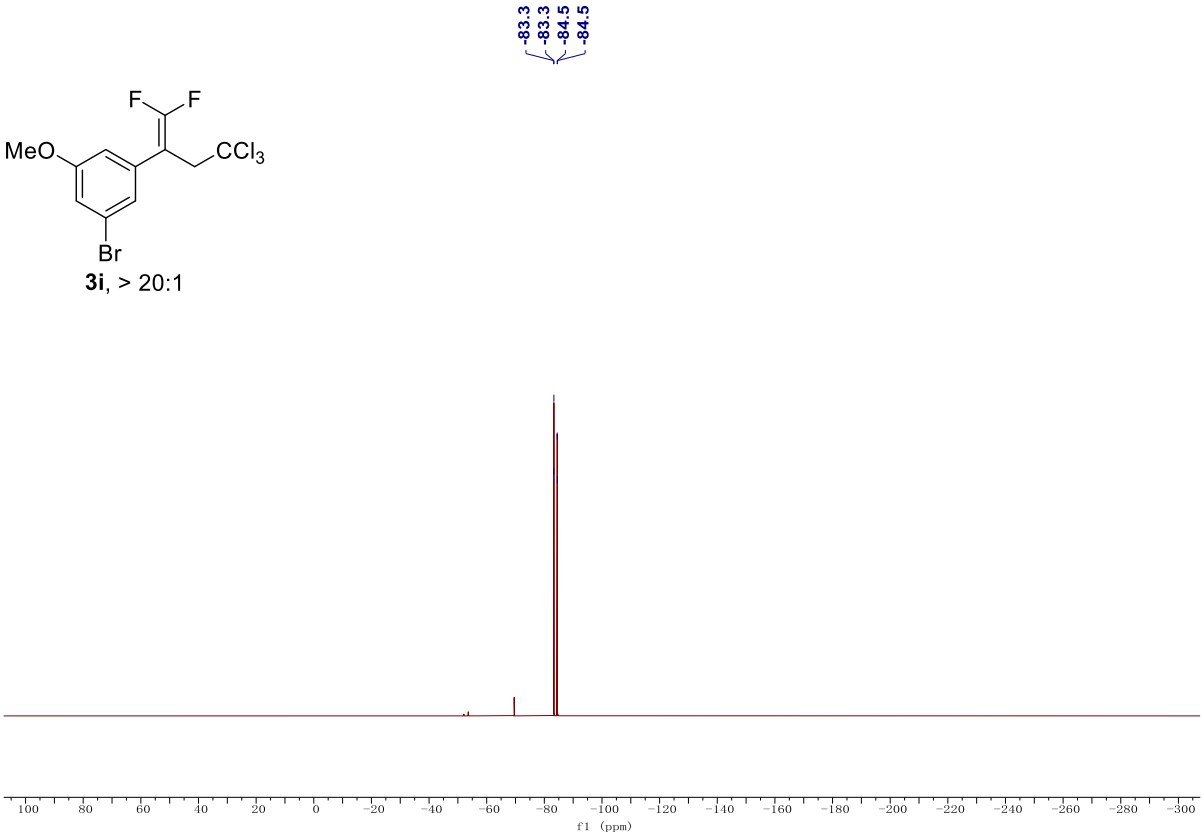
^{19}F NMR spectrum for compound **3h** ($CDCl_3$)



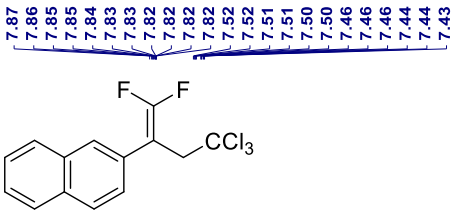
^{1}H NMR spectrum for compound **3i** ($CDCl_3$)



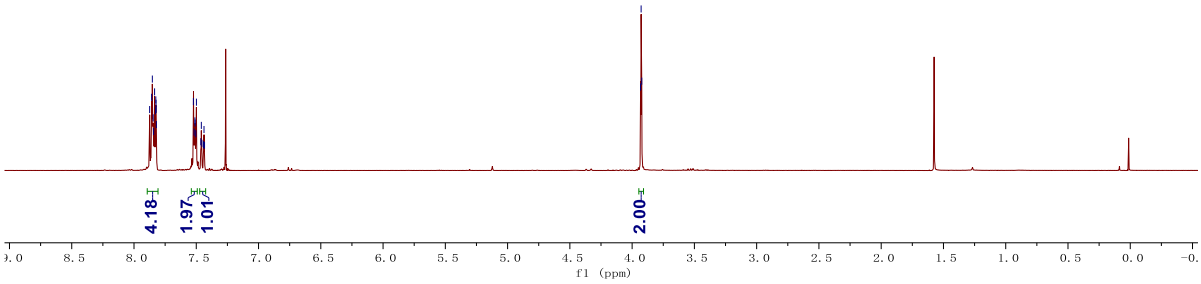
^{13}C NMR spectrum for compound **3i** ($CDCl_3$)



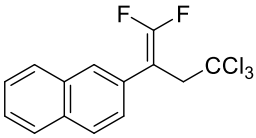
^{19}F NMR spectrum for compound **3i** ($CDCl_3$)



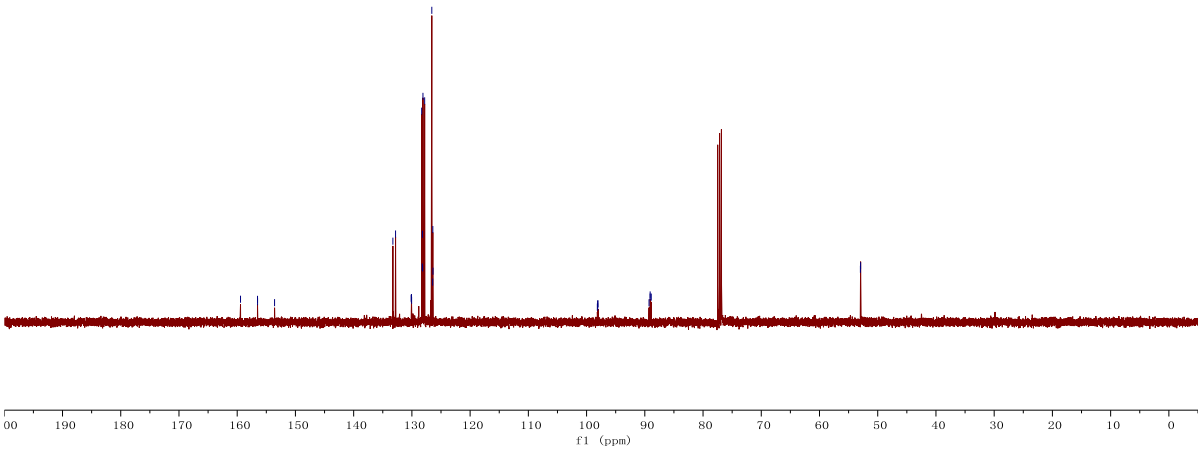
3j, > 20:1



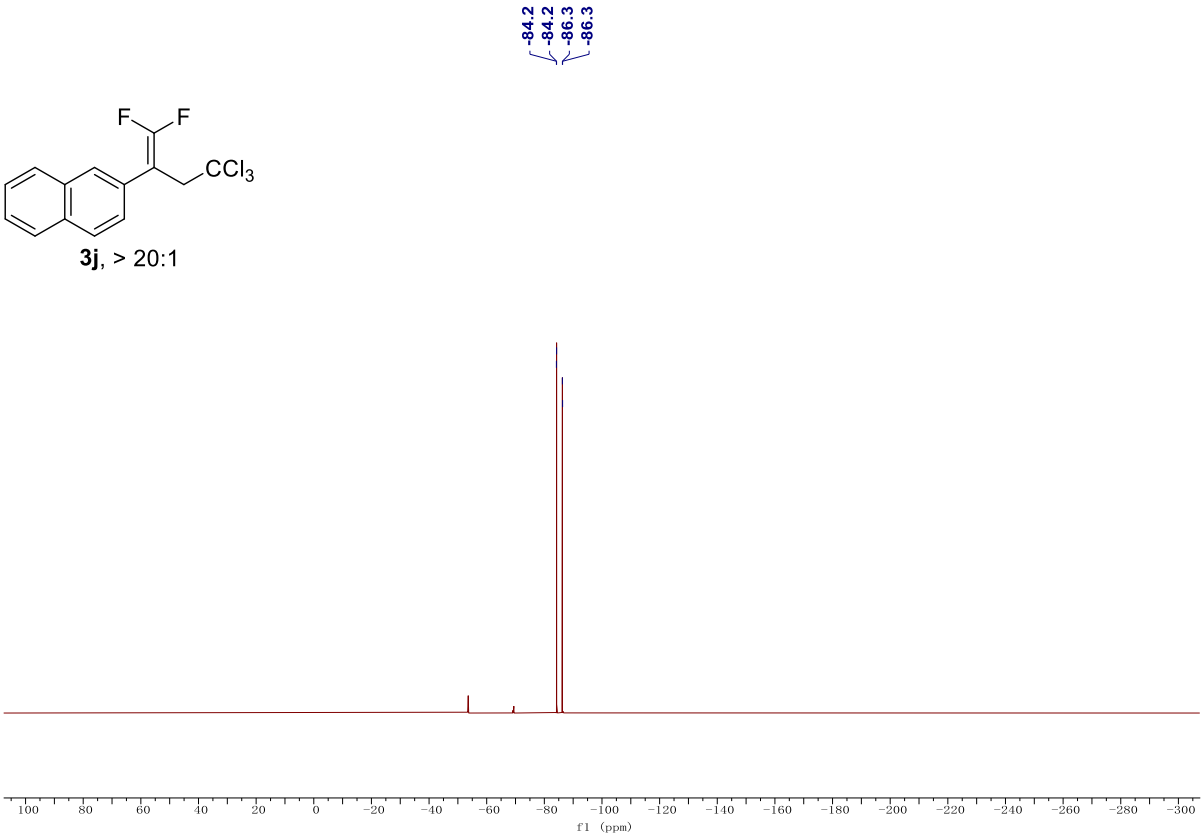
^{1}H NMR spectrum for compound **3j** ($CDCl_3$)



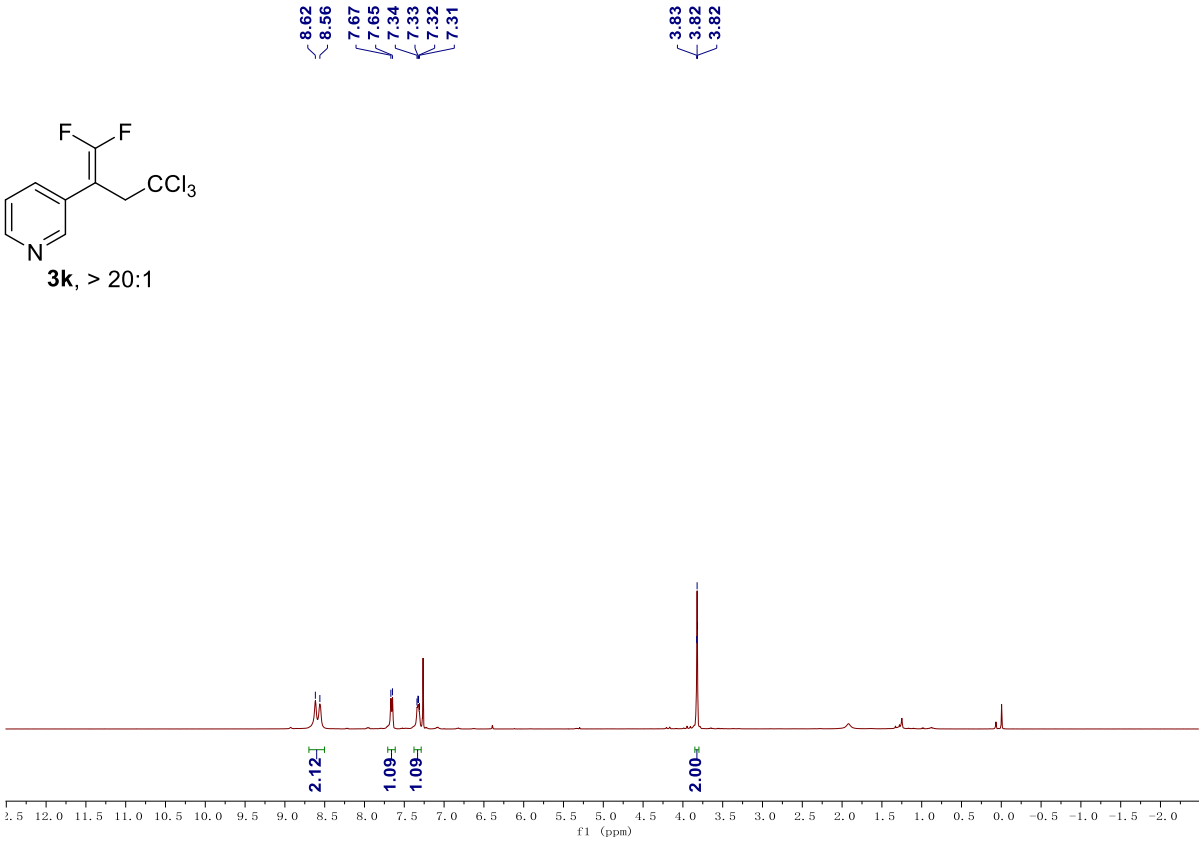
3j, > 20:1



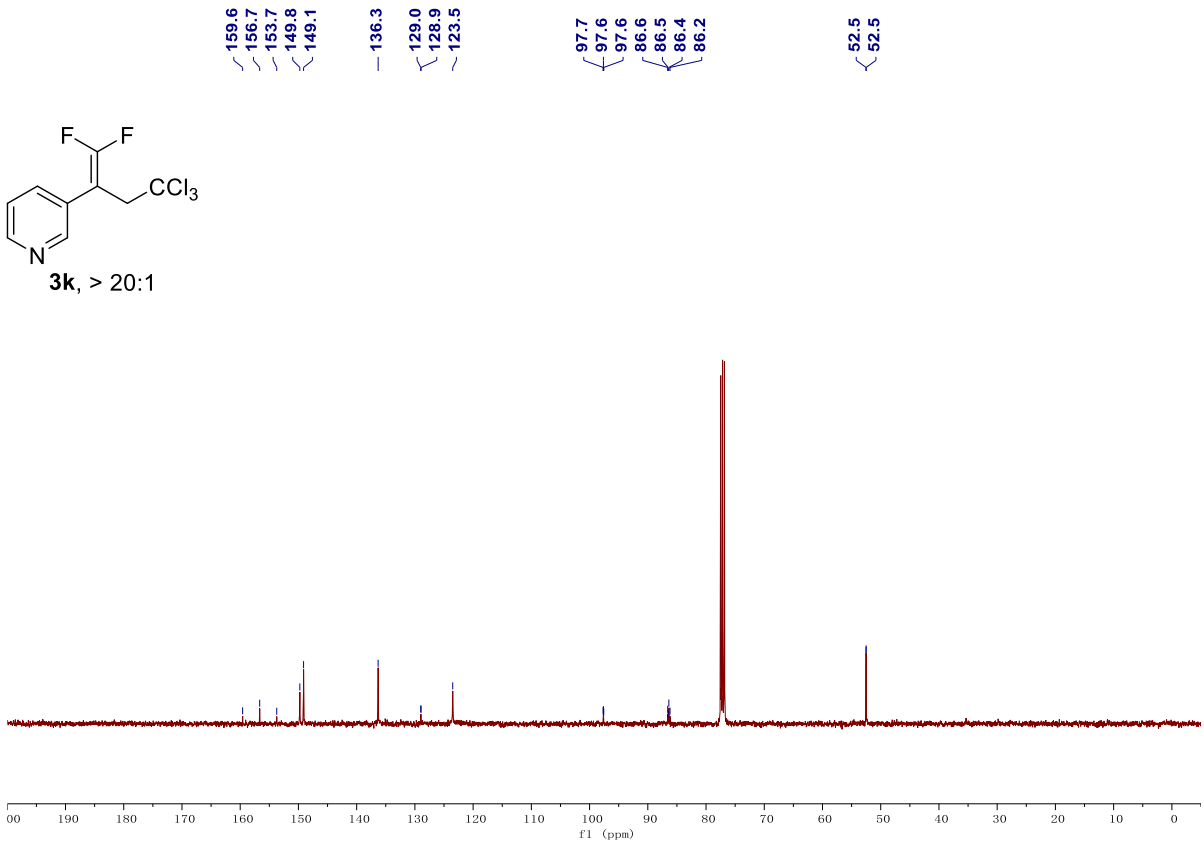
^{13}C NMR spectrum for compound **3j** ($CDCl_3$)



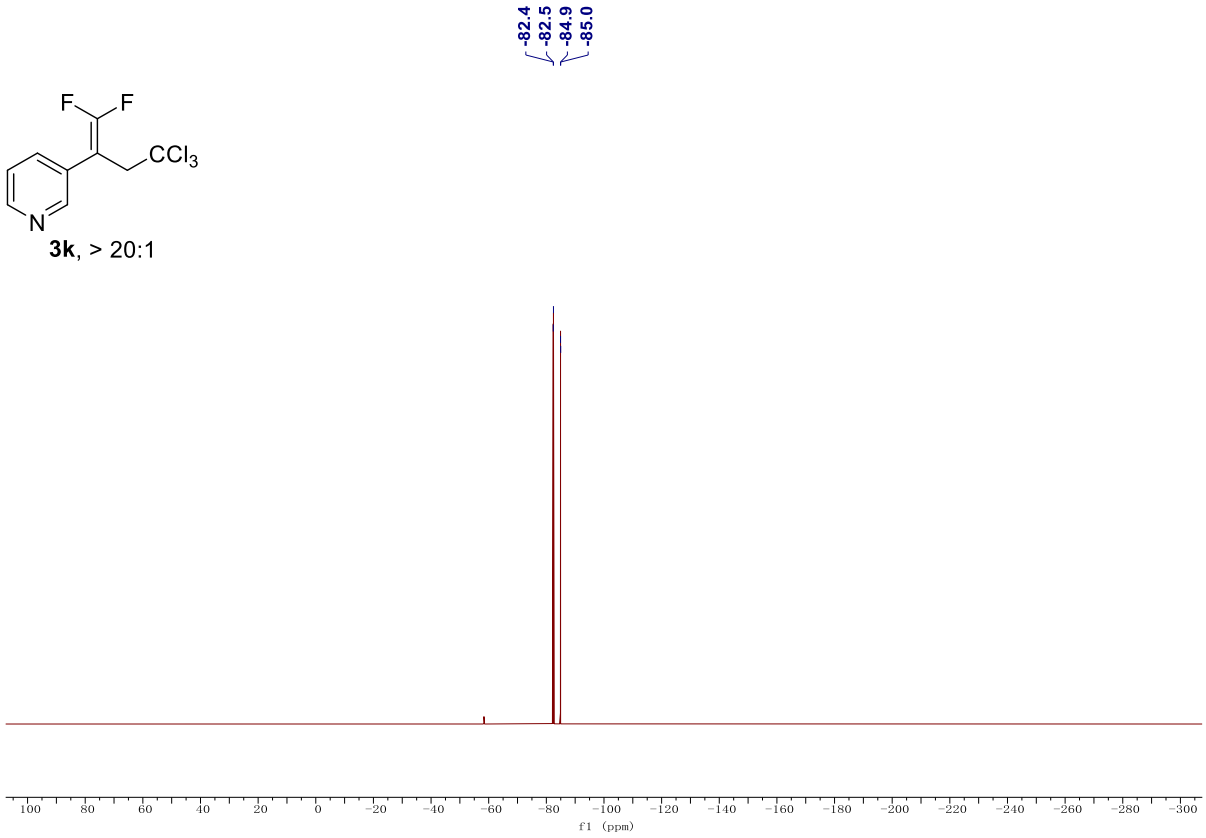
^{19}F NMR spectrum for compound **3j** ($CDCl_3$)



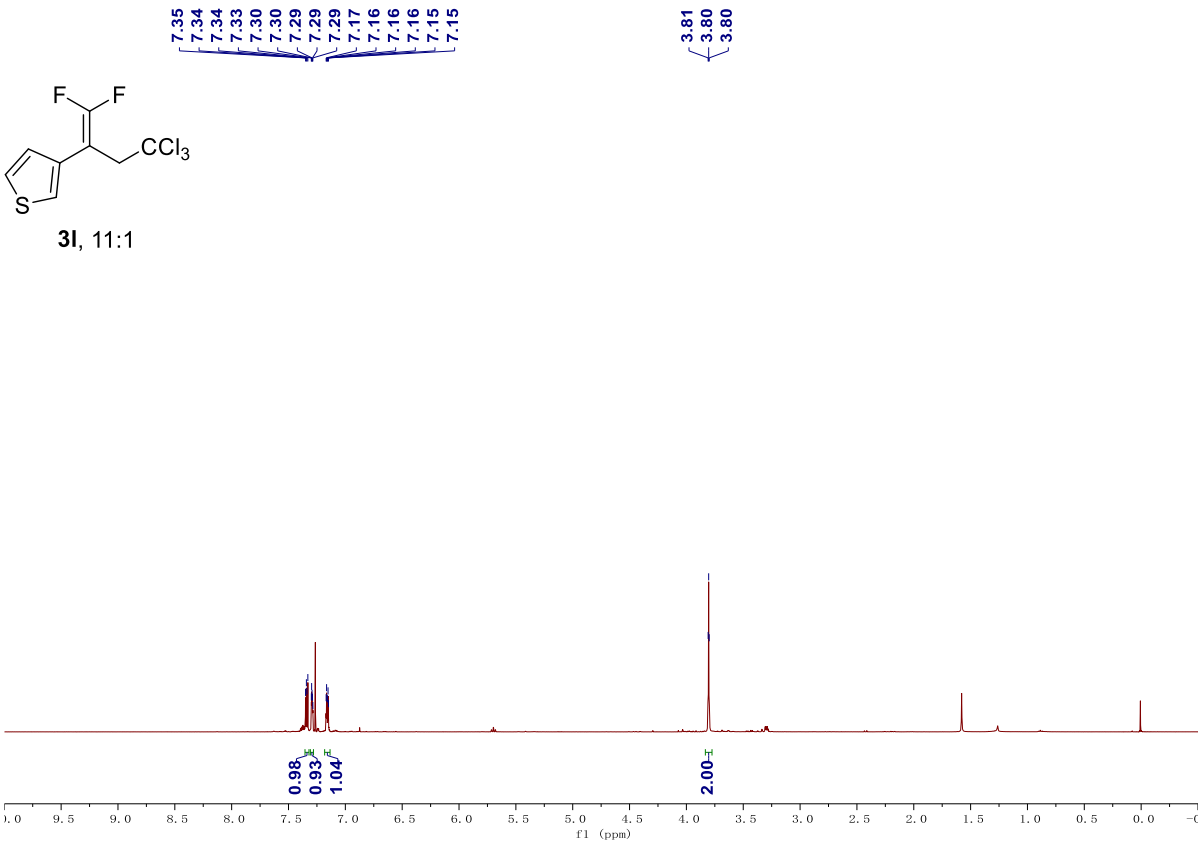
^{1}H NMR spectrum for compound **3k** ($CDCl_3$)



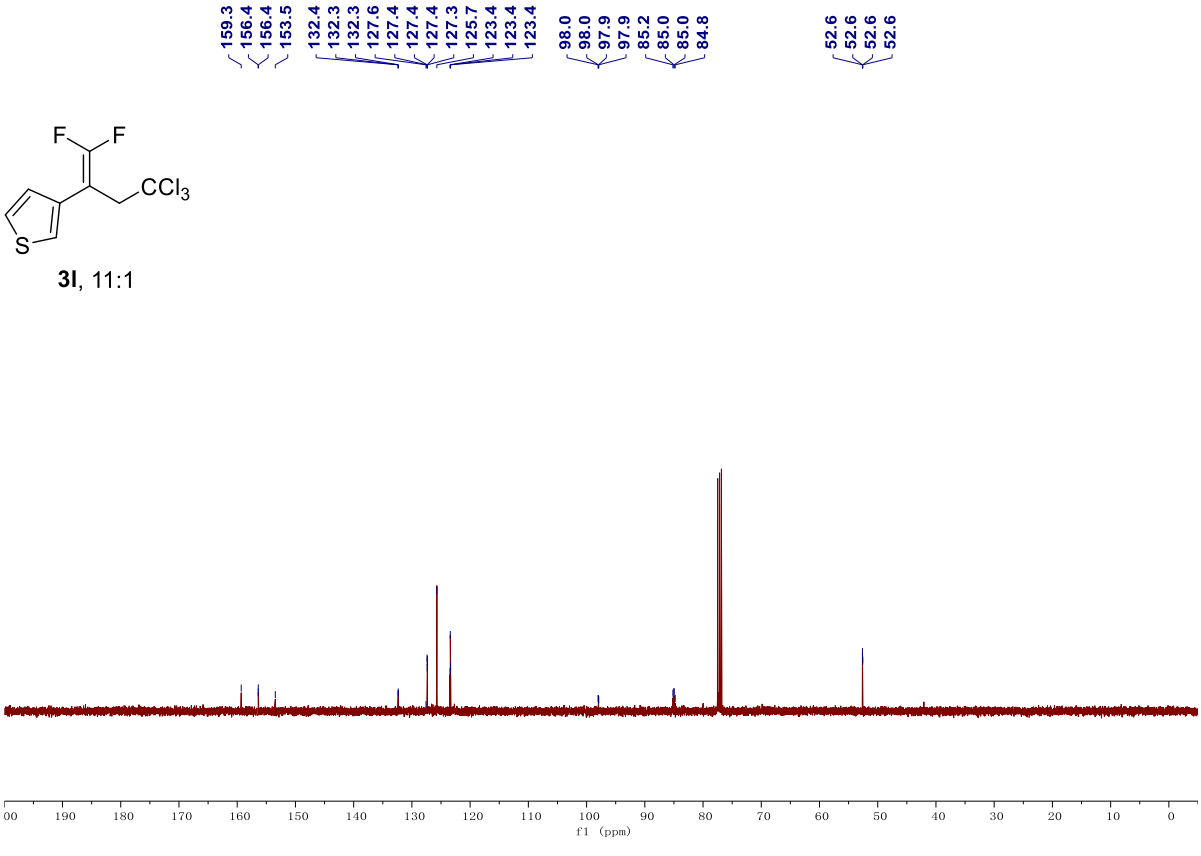
^{13}C NMR spectrum for compound **3k** ($CDCl_3$)



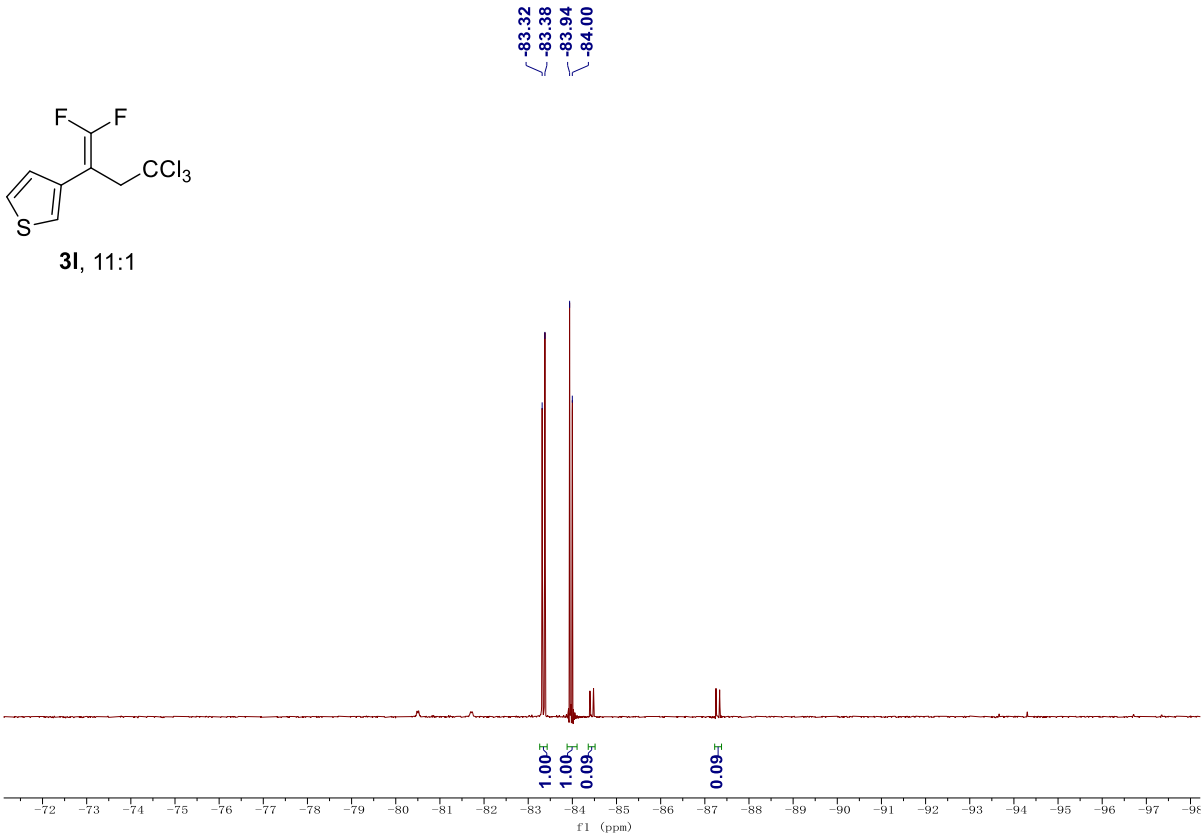
^{19}F NMR spectrum for compound **3k** ($CDCl_3$)



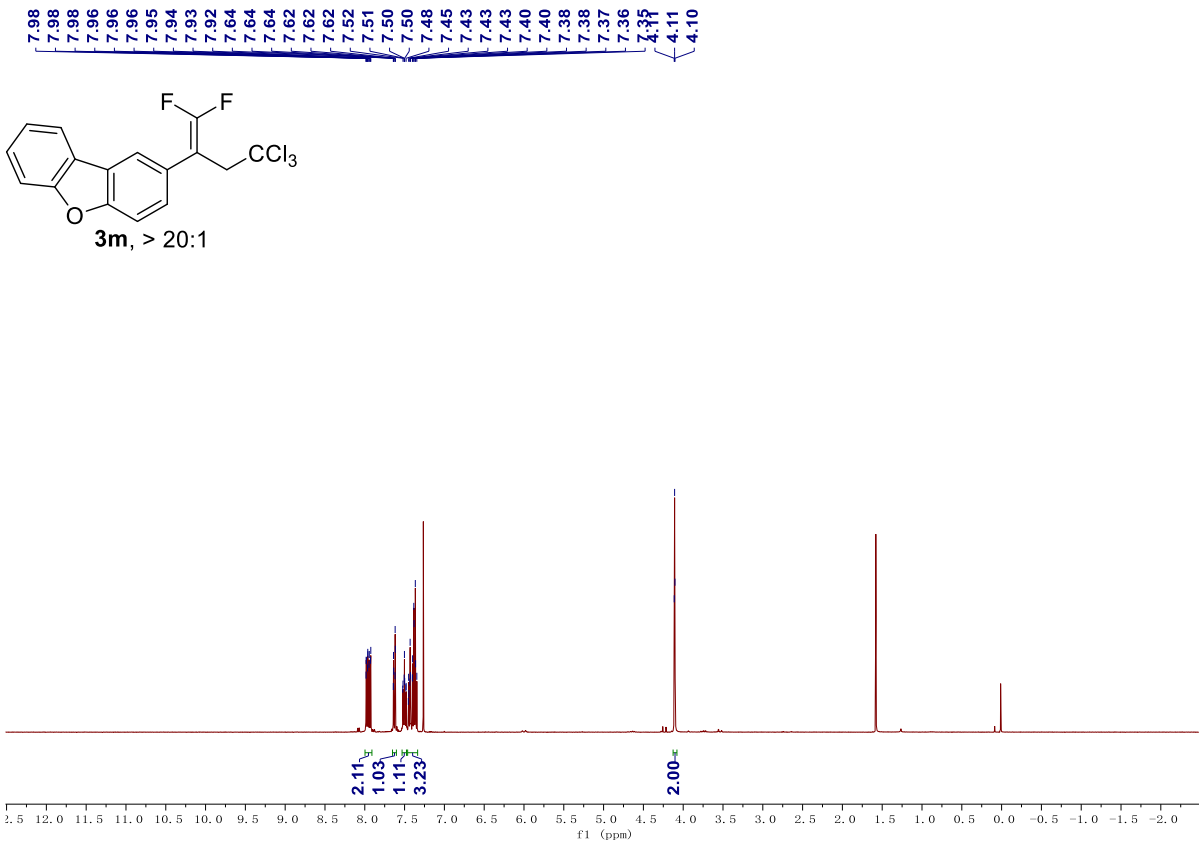
^{1}H NMR spectrum for compound **3l** ($CDCl_3$)



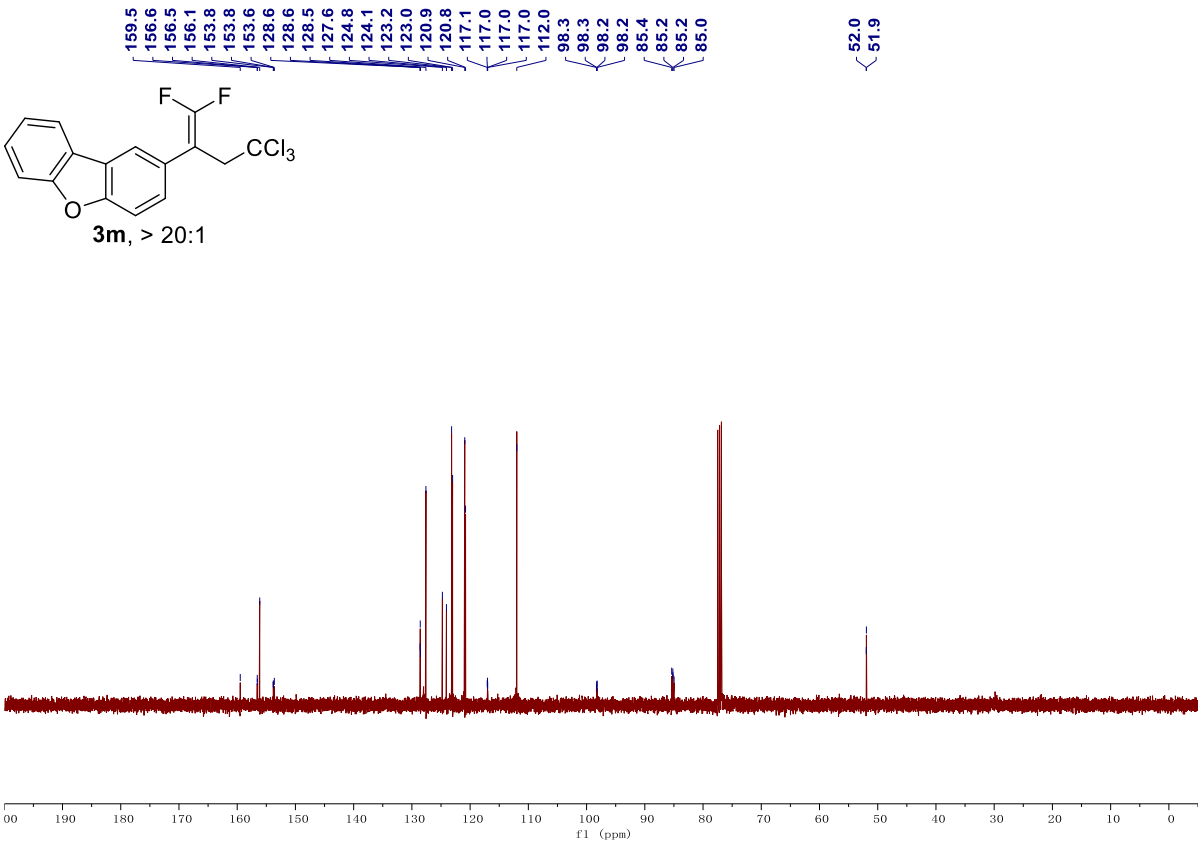
^{13}C NMR spectrum for compound **3l** ($CDCl_3$)



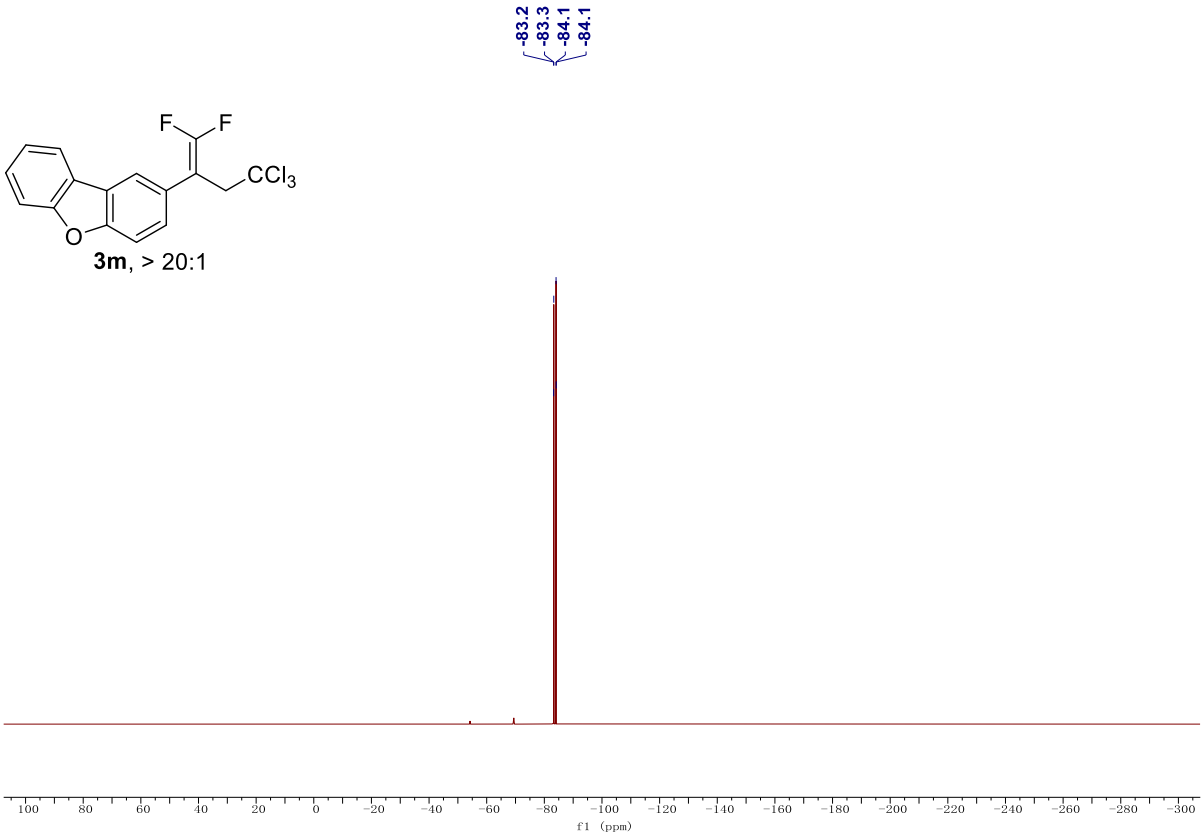
^{19}F NMR spectrum for compound **3l** ($CDCl_3$)



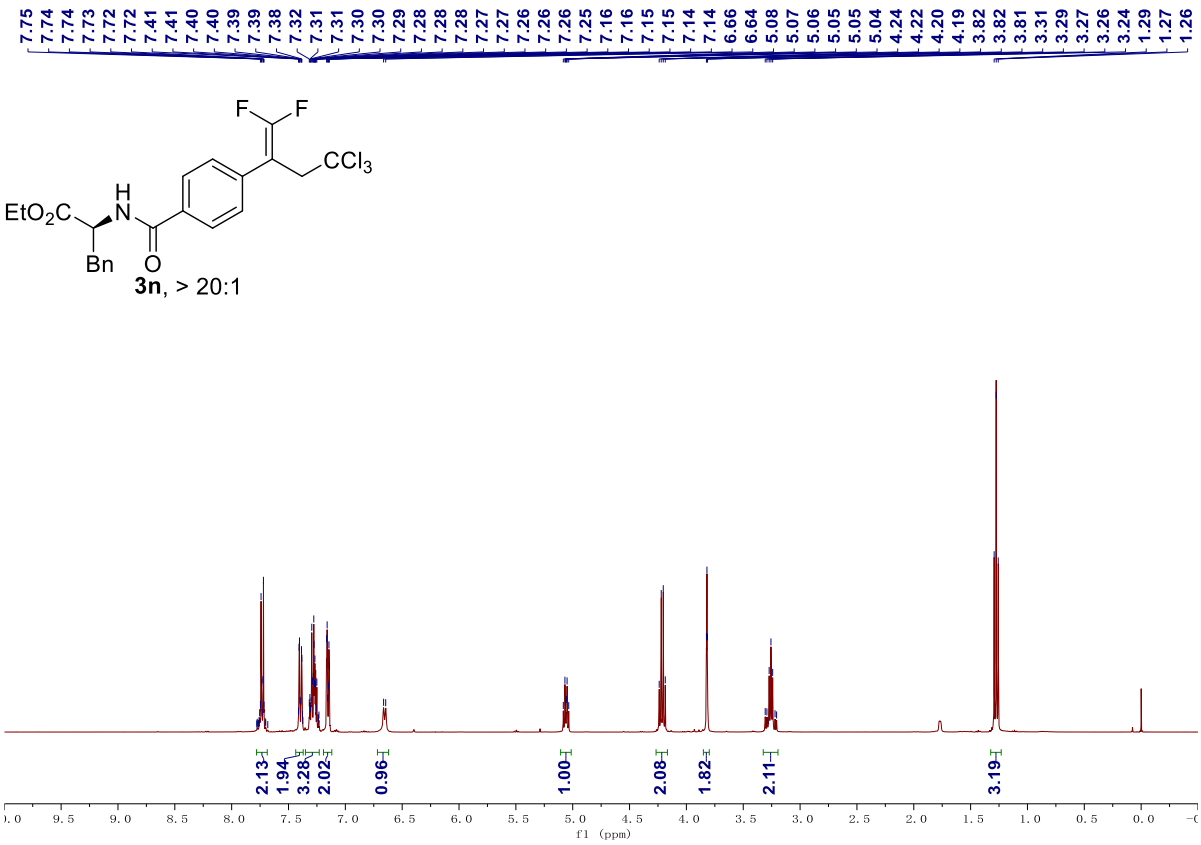
^{1}H NMR spectrum for compound **3m** ($CDCl_3$)



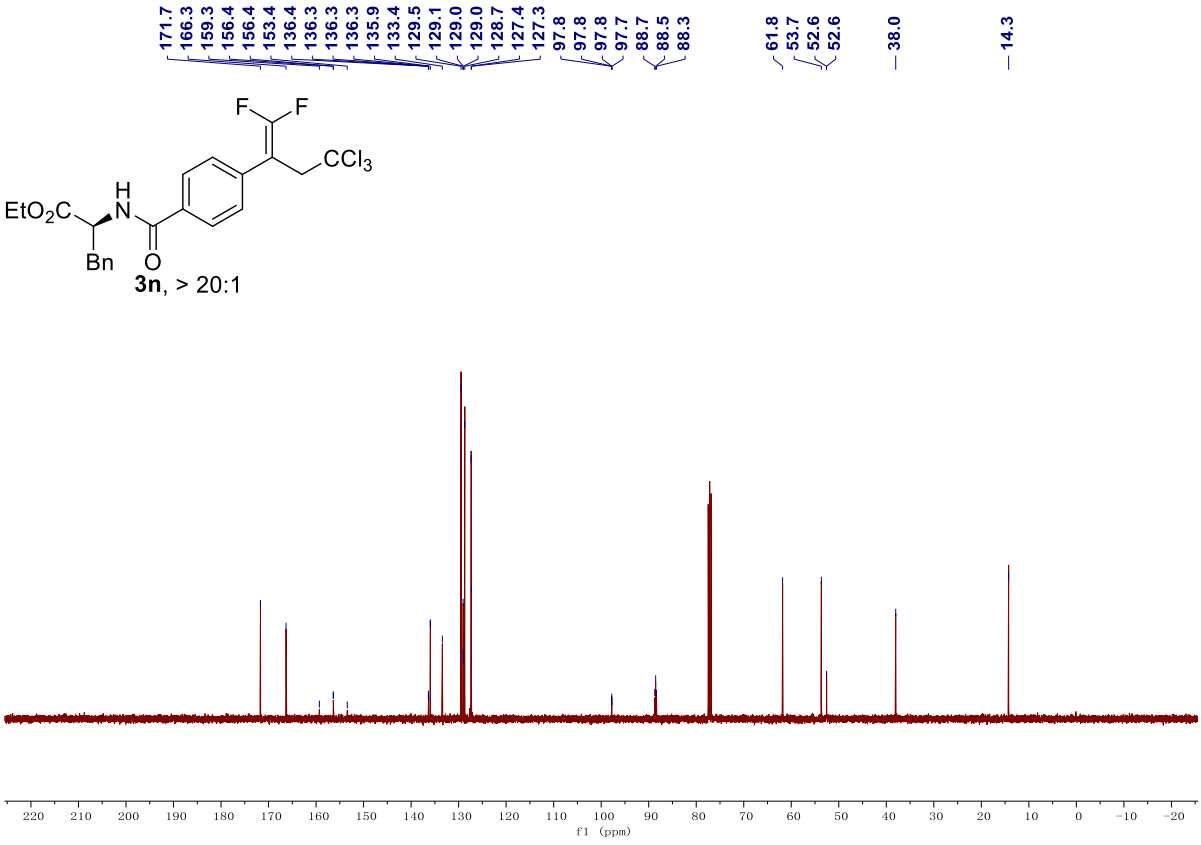
^{13}C NMR spectrum for compound **3m** ($CDCl_3$)



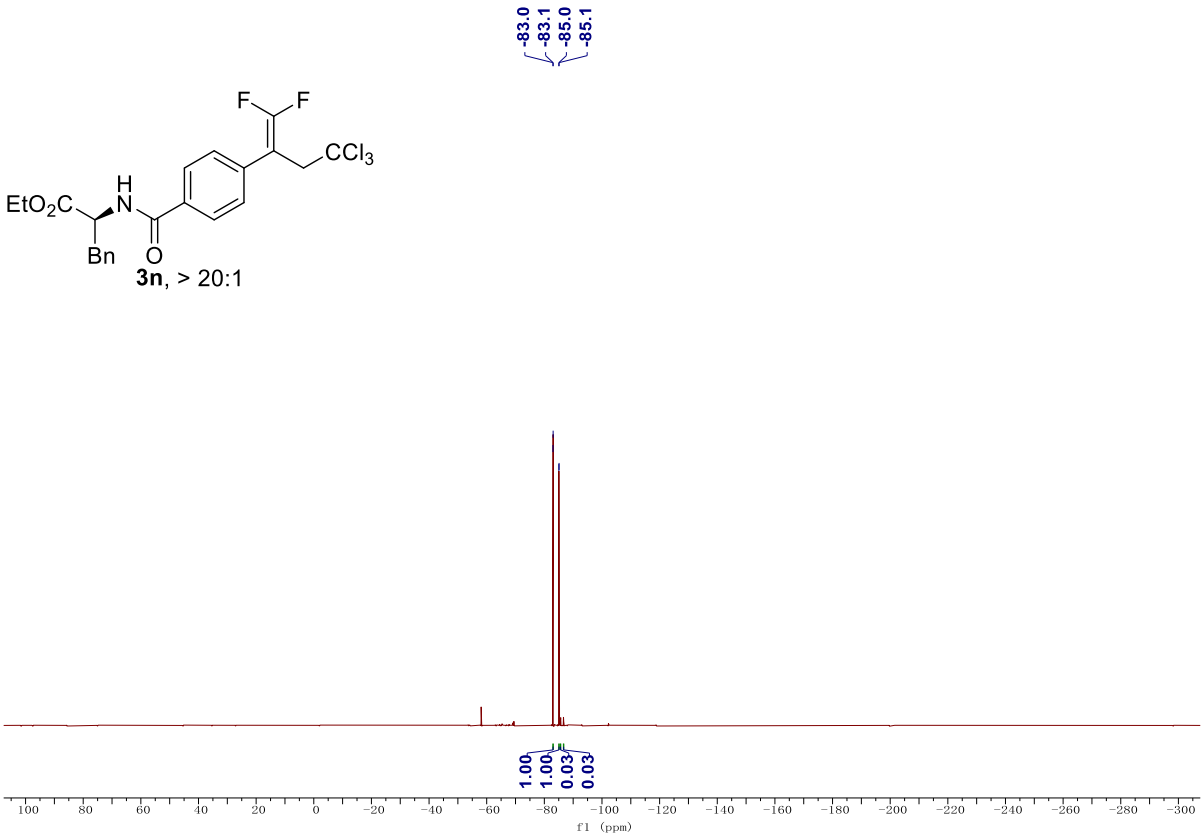
^{19}F NMR spectrum for compound **3m** ($CDCl_3$)



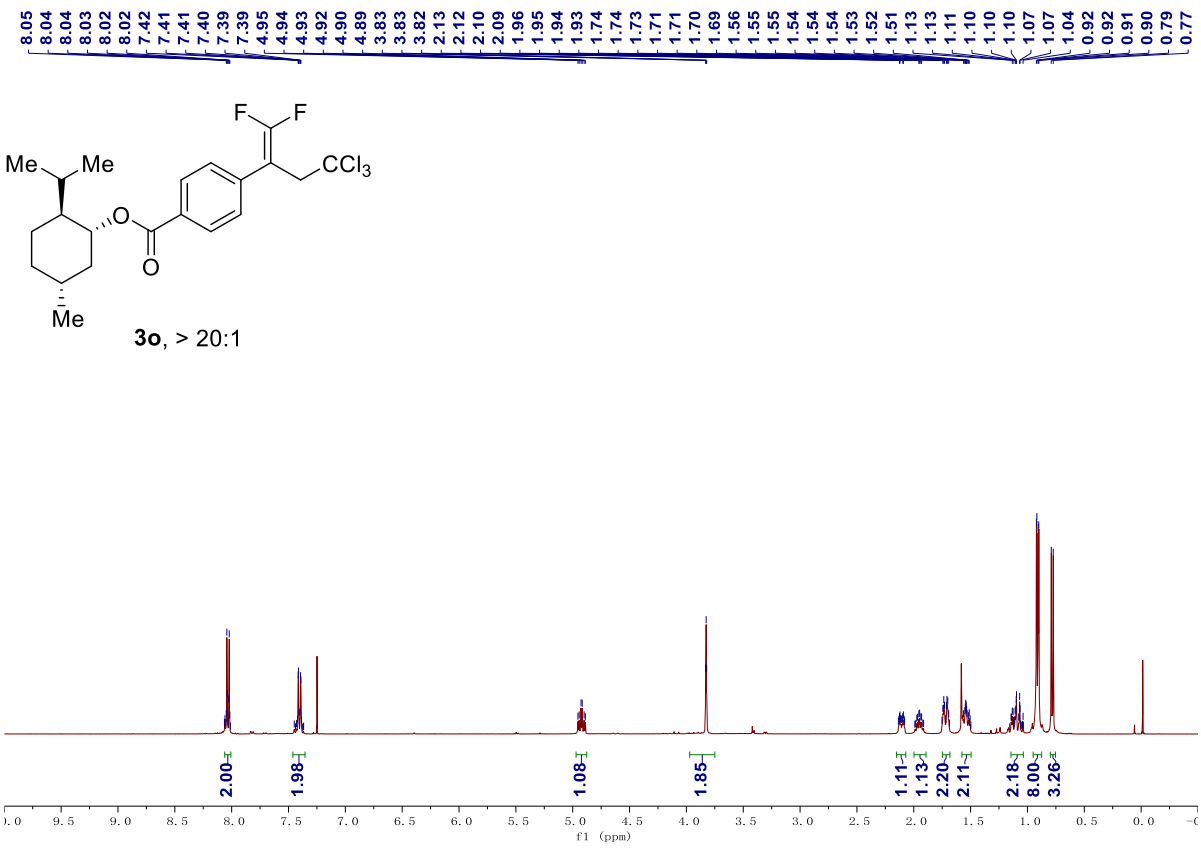
^{1}H NMR spectrum for compound **3n** ($CDCl_3$)



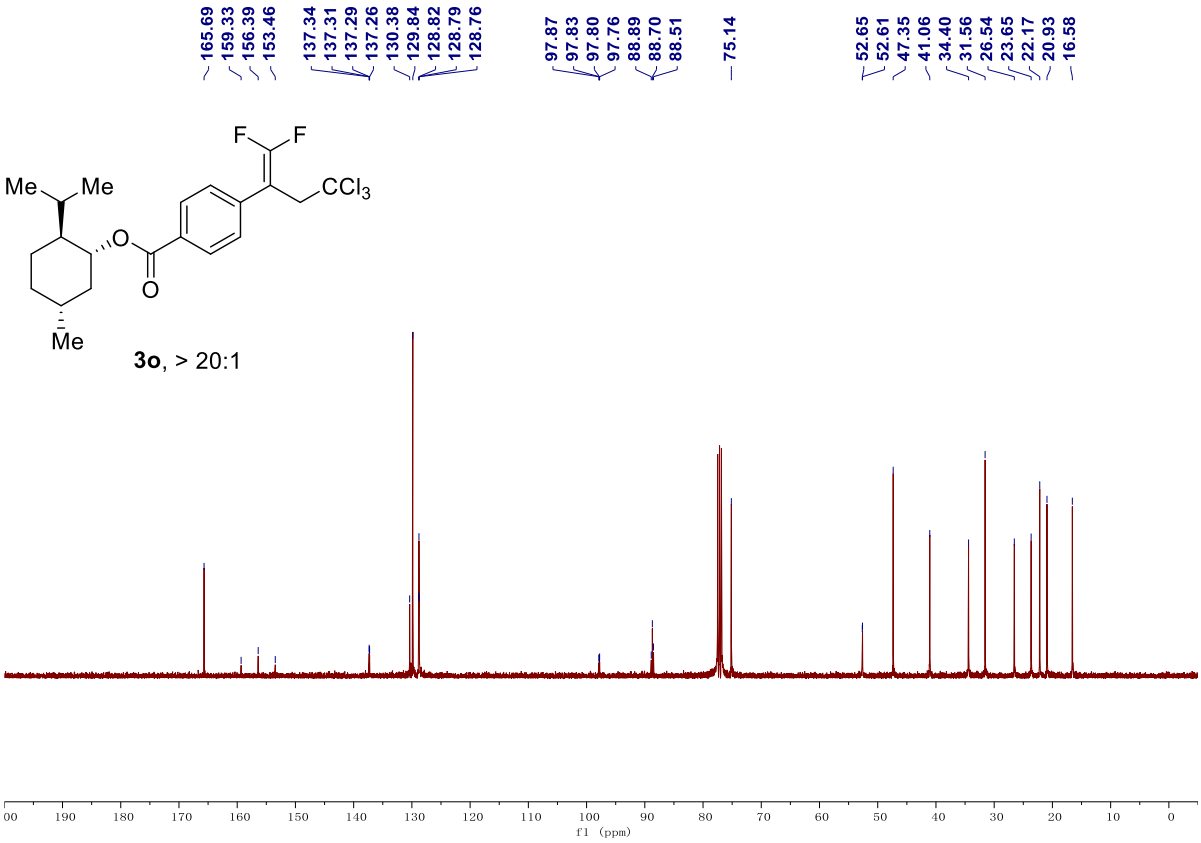
^{13}C NMR spectrum for compound **3n** ($CDCl_3$)



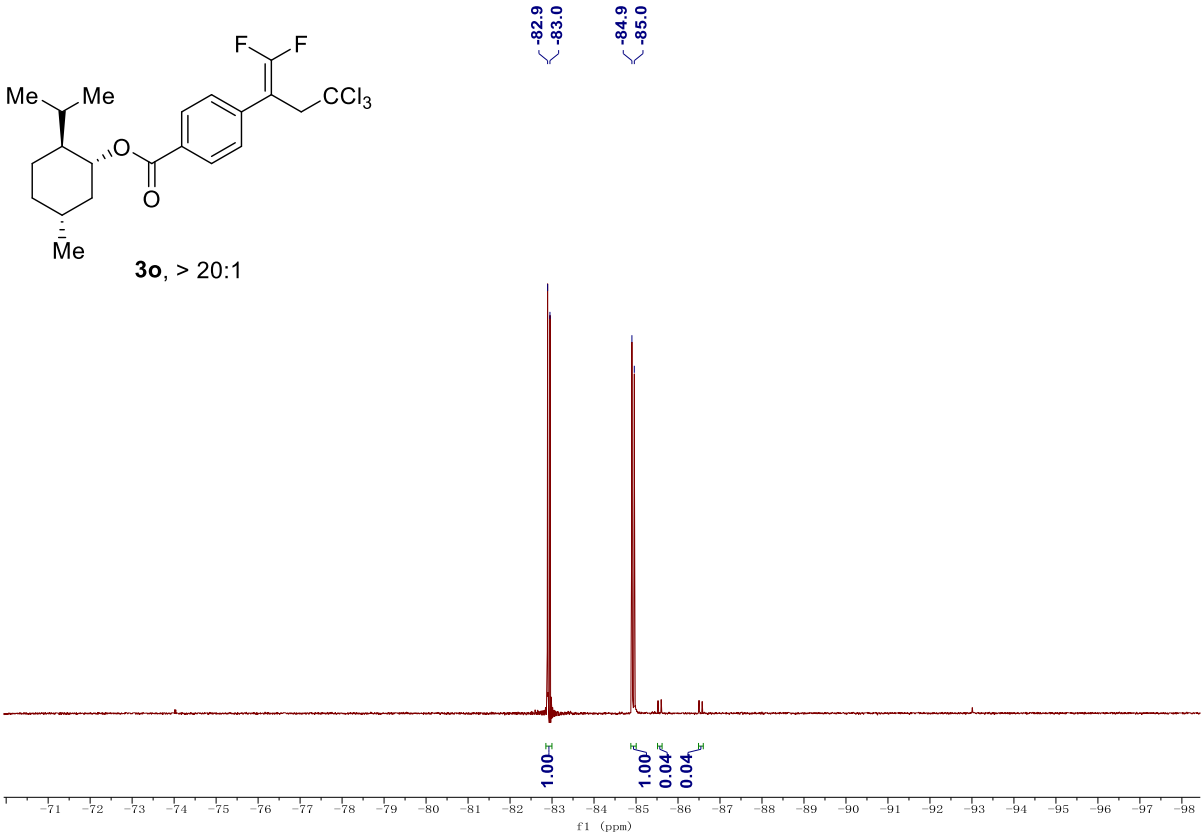
^{19}F NMR spectrum for compound **3n** ($CDCl_3$)



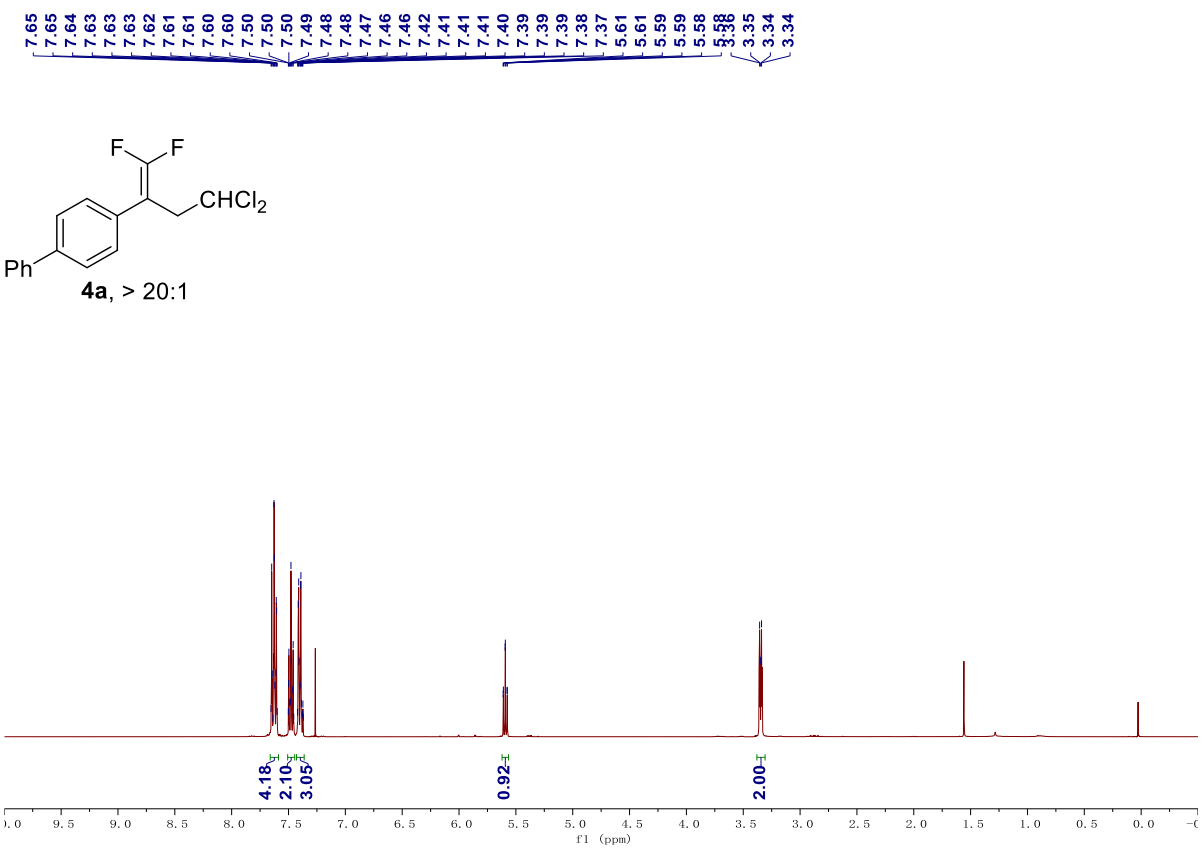
^{1}H NMR spectrum for compound **3o** ($CDCl_3$)



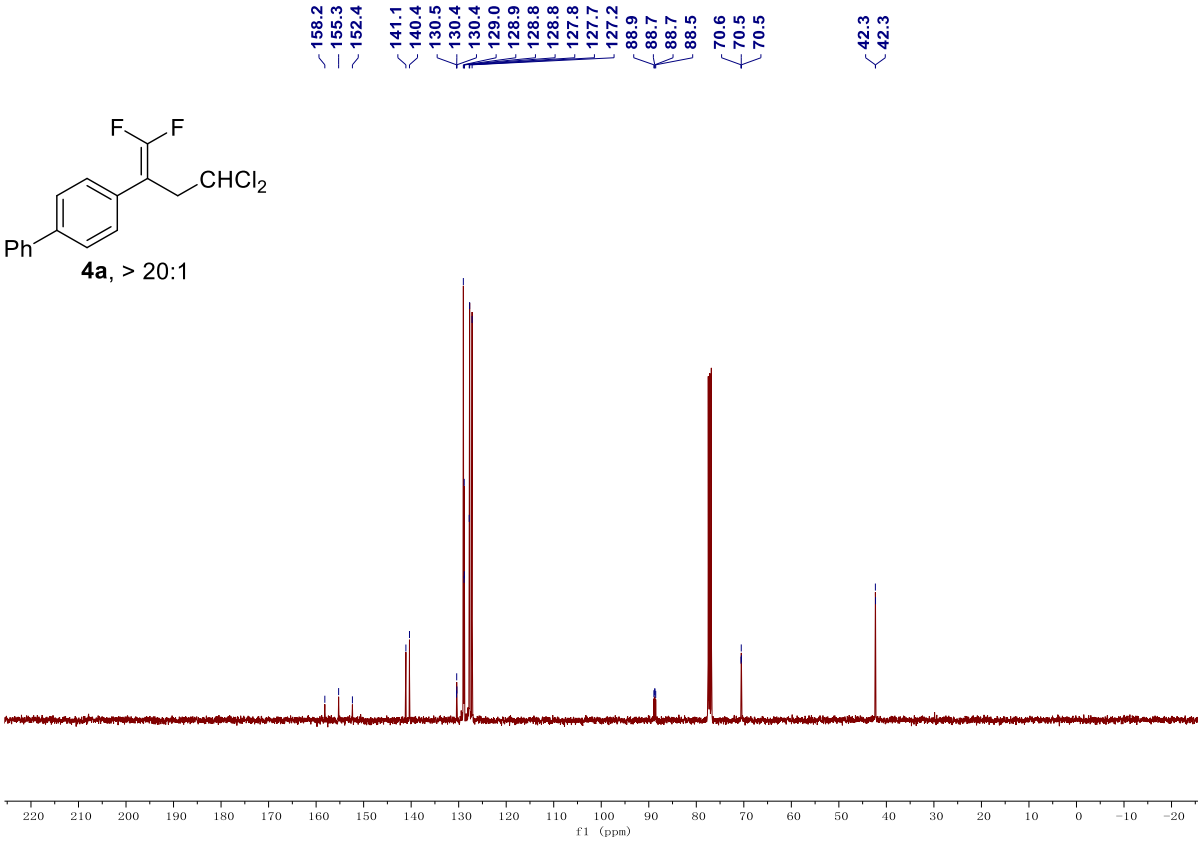
^{13}C NMR spectrum for compound **3o** ($CDCl_3$)



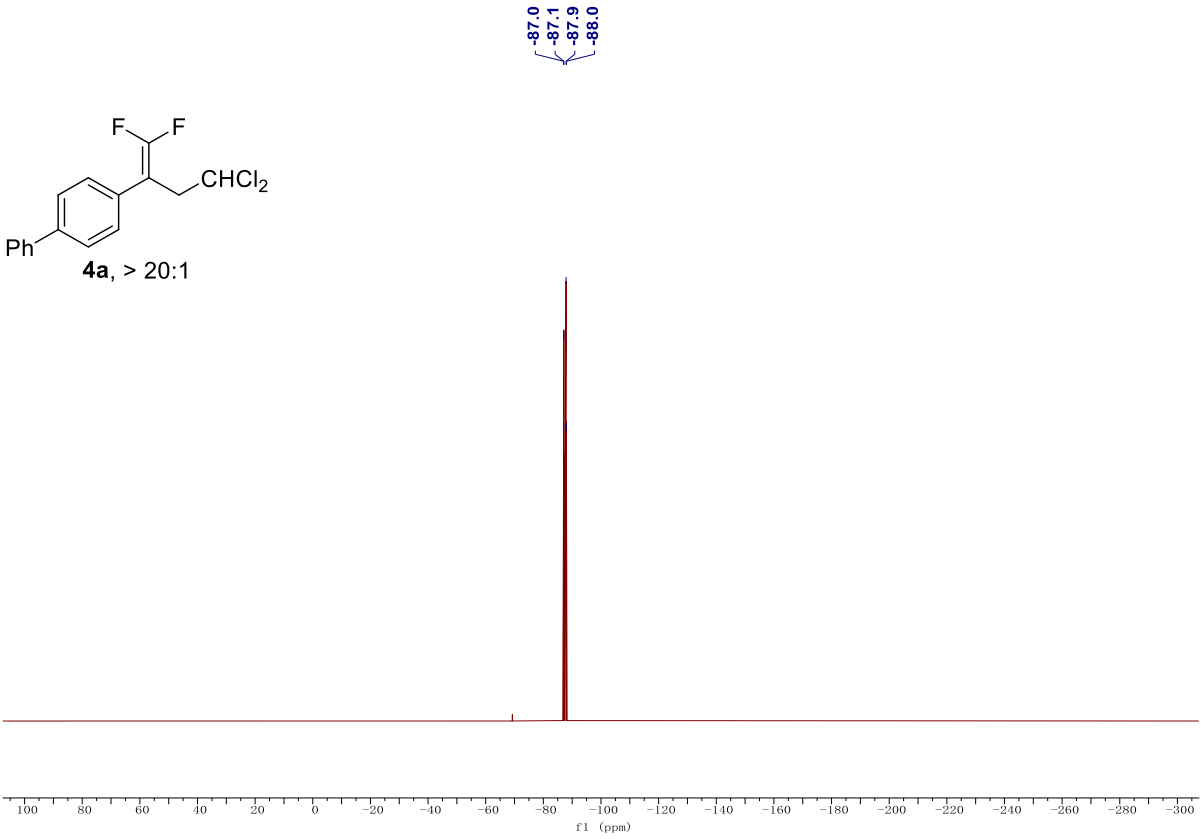
^{19}F NMR spectrum for compound **3o** ($CDCl_3$)



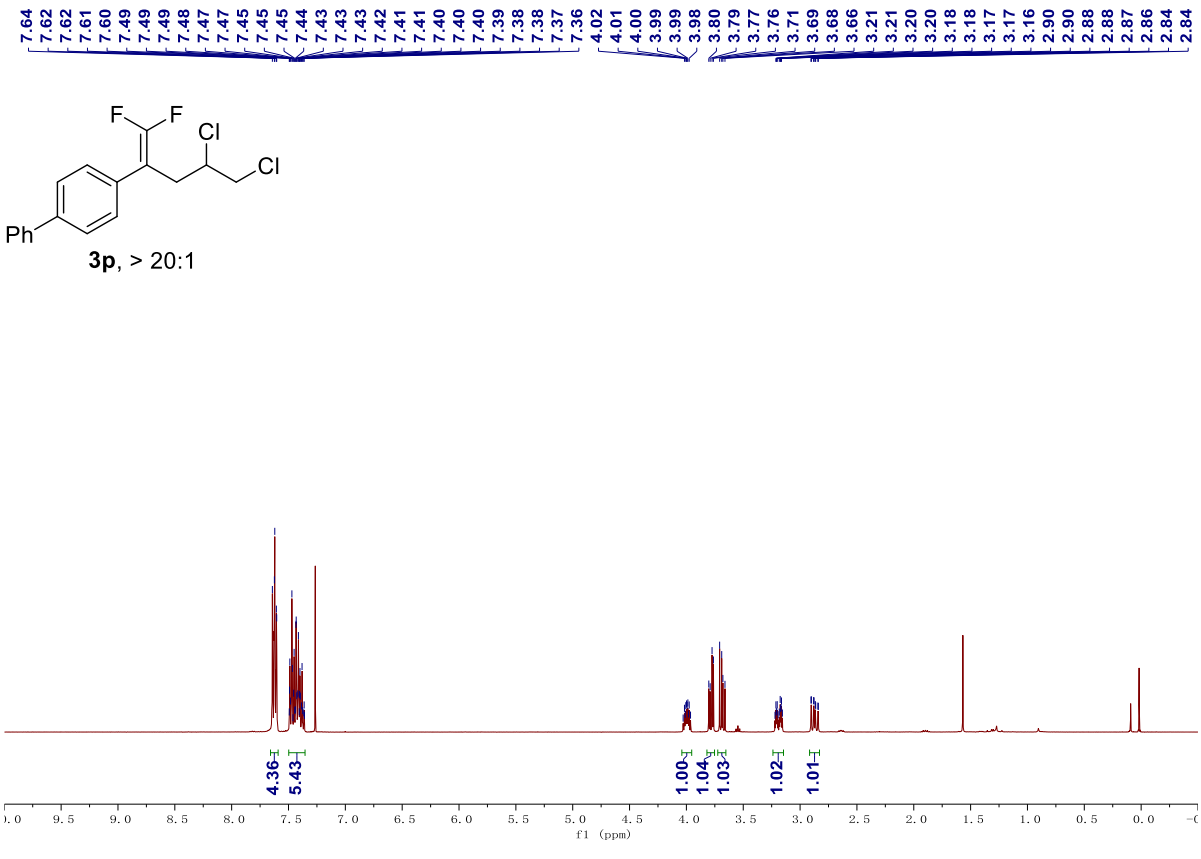
^{1}H NMR spectrum for compound **4a** ($CDCl_3$)



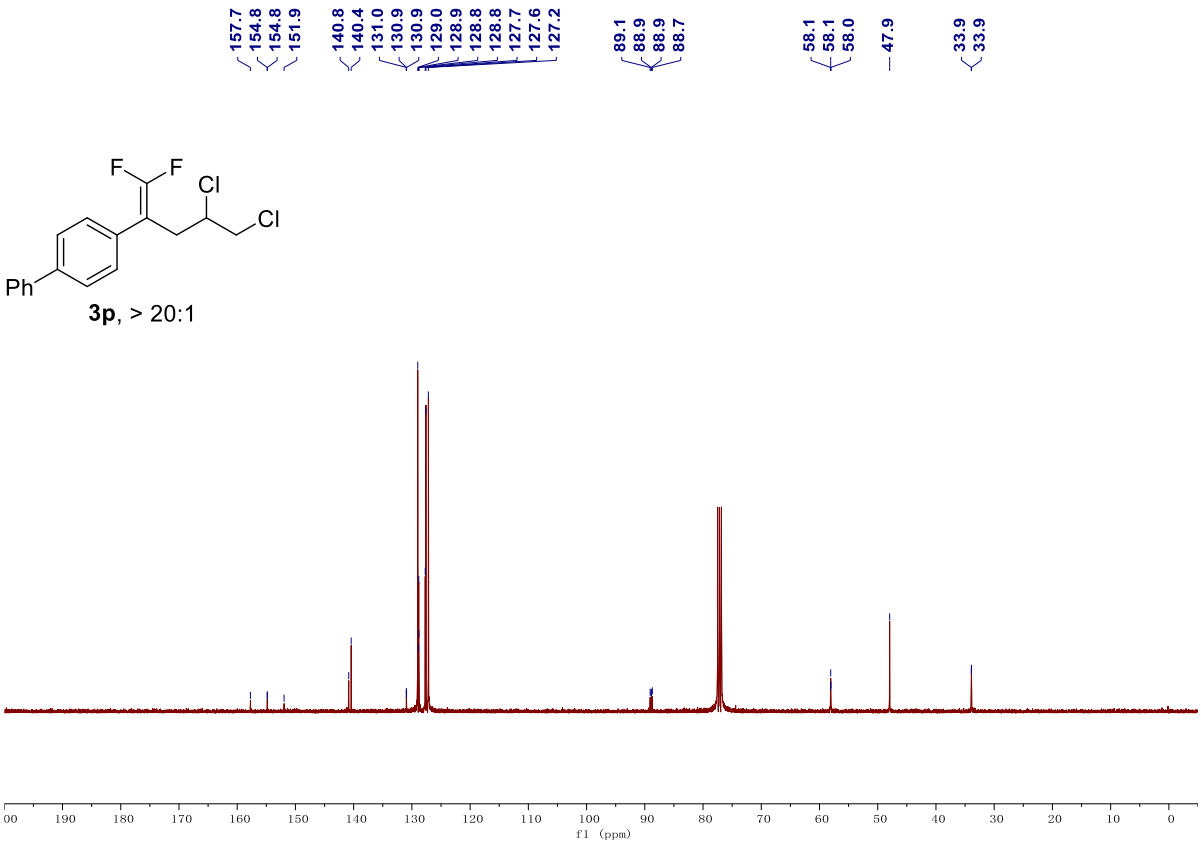
^{13}C NMR spectrum for compound **4a** ($CDCl_3$)



^{19}F NMR spectrum for compound **4a** ($CDCl_3$)

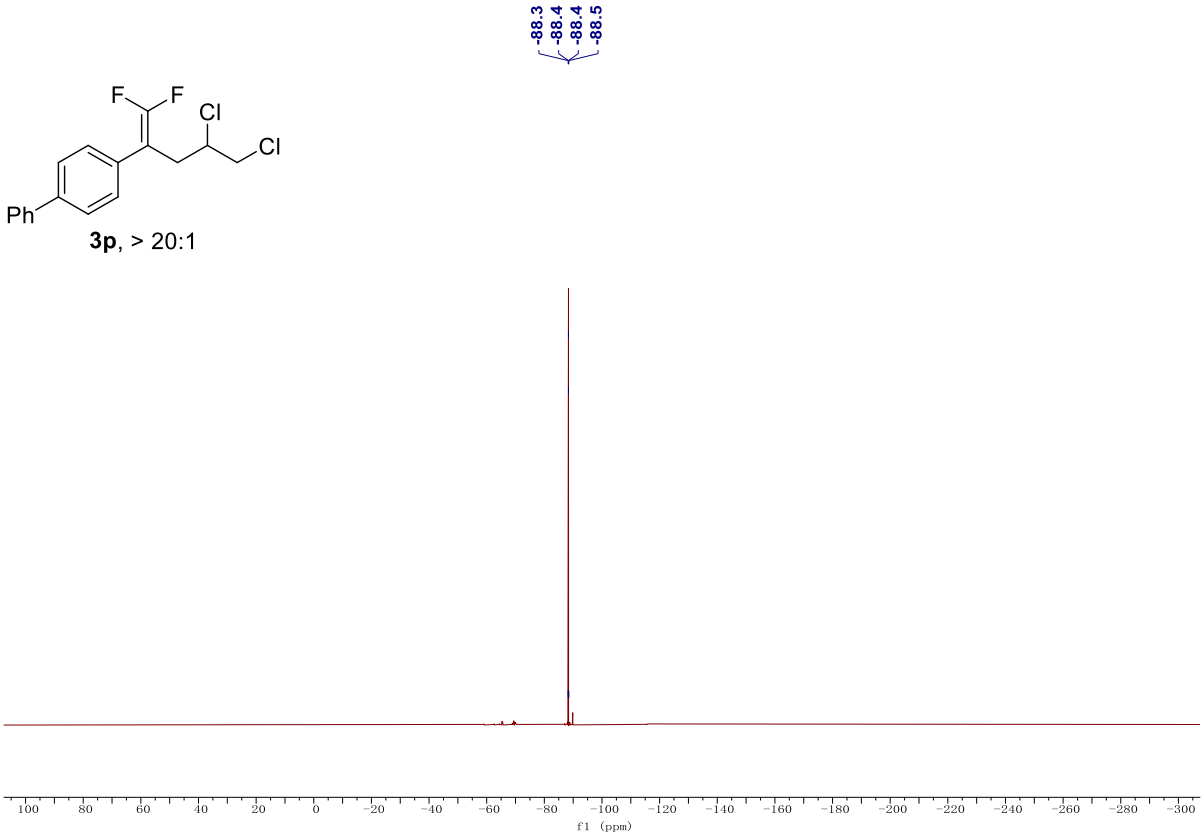


^{1}H NMR spectrum for compound **3p** ($CDCl_3$)



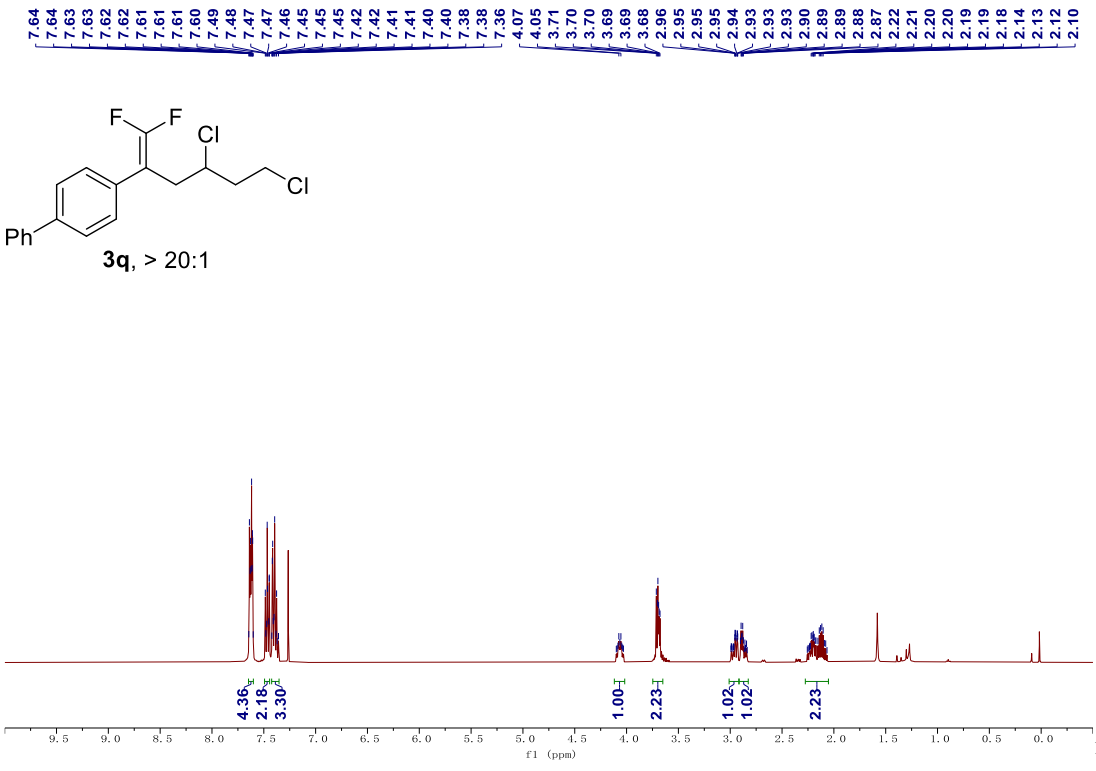
3p, > 20:1

^{13}C NMR spectrum for compound **3p** ($CDCl_3$)

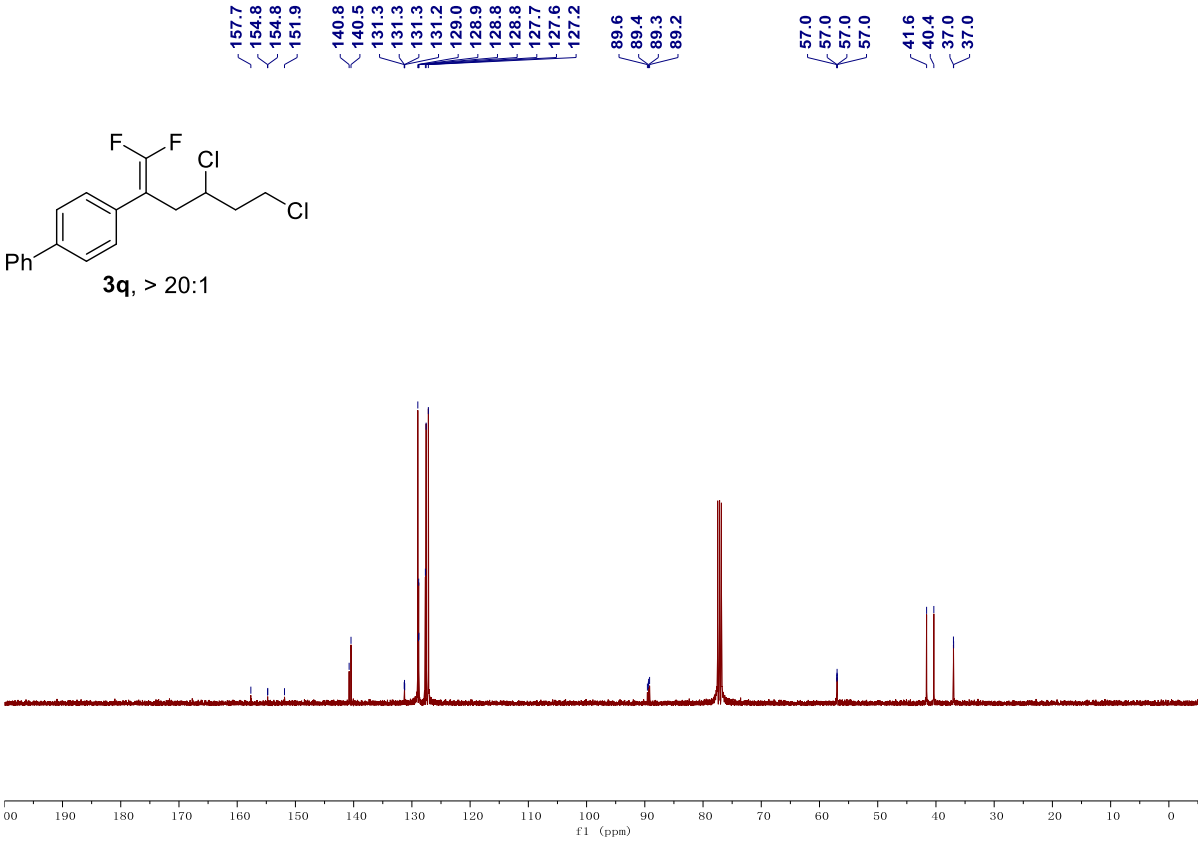


3p, > 20:1

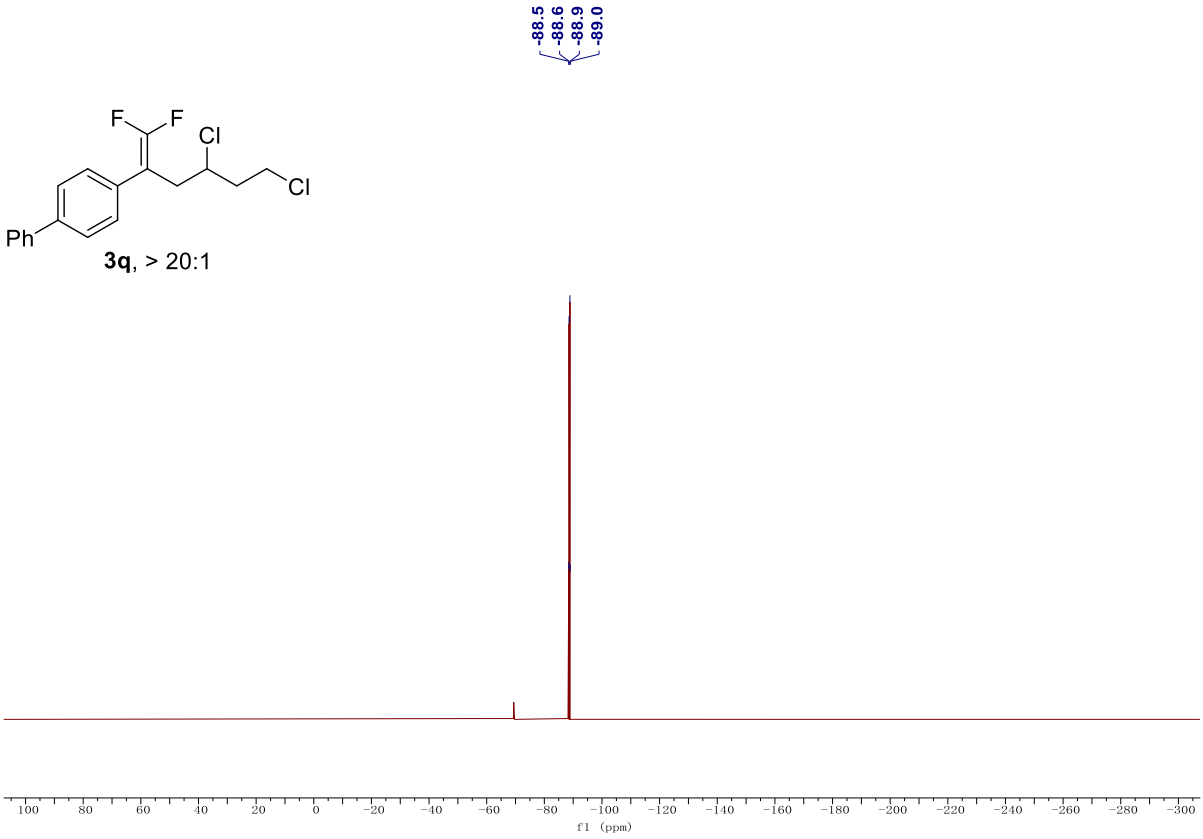
^{19}F NMR spectrum for compound **3p** ($CDCl_3$)



^{1}H NMR spectrum for compound **3q** ($CDCl_3$)

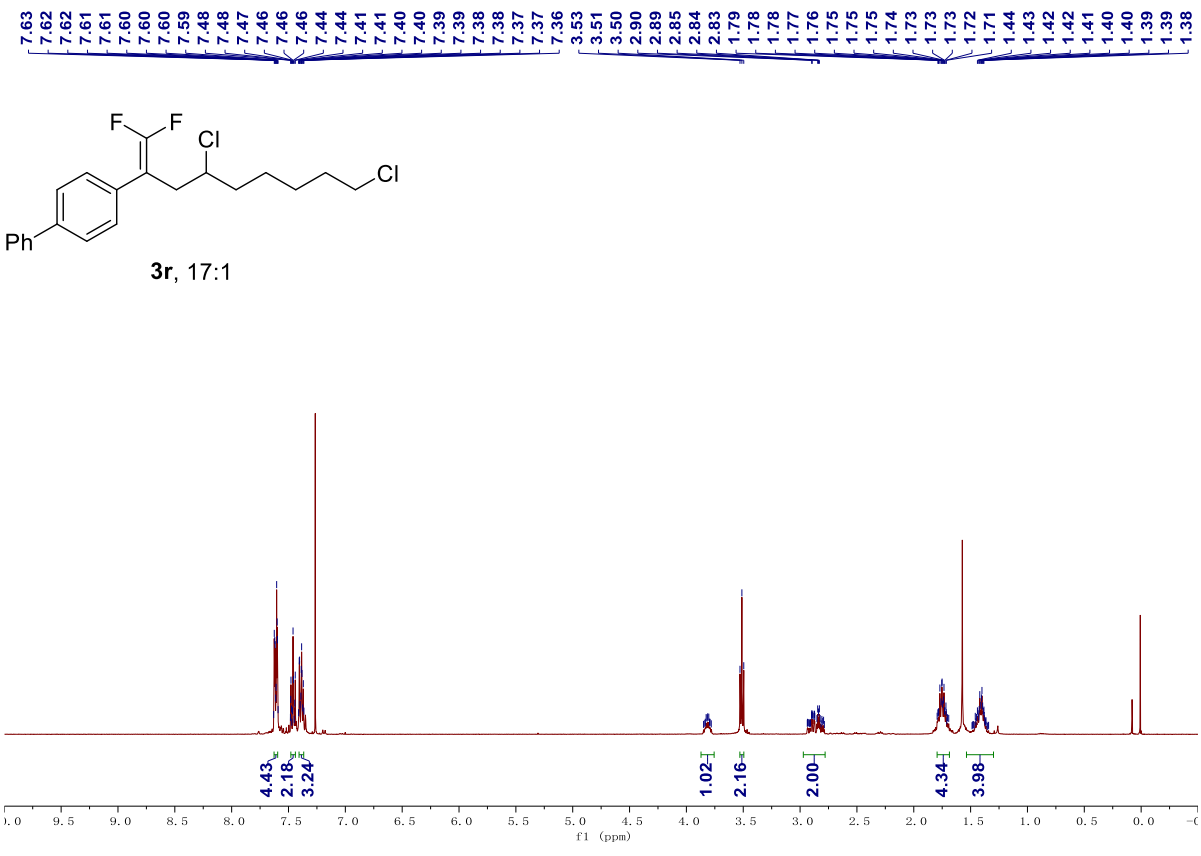


^{13}C NMR spectrum for compound **3q** ($CDCl_3$)



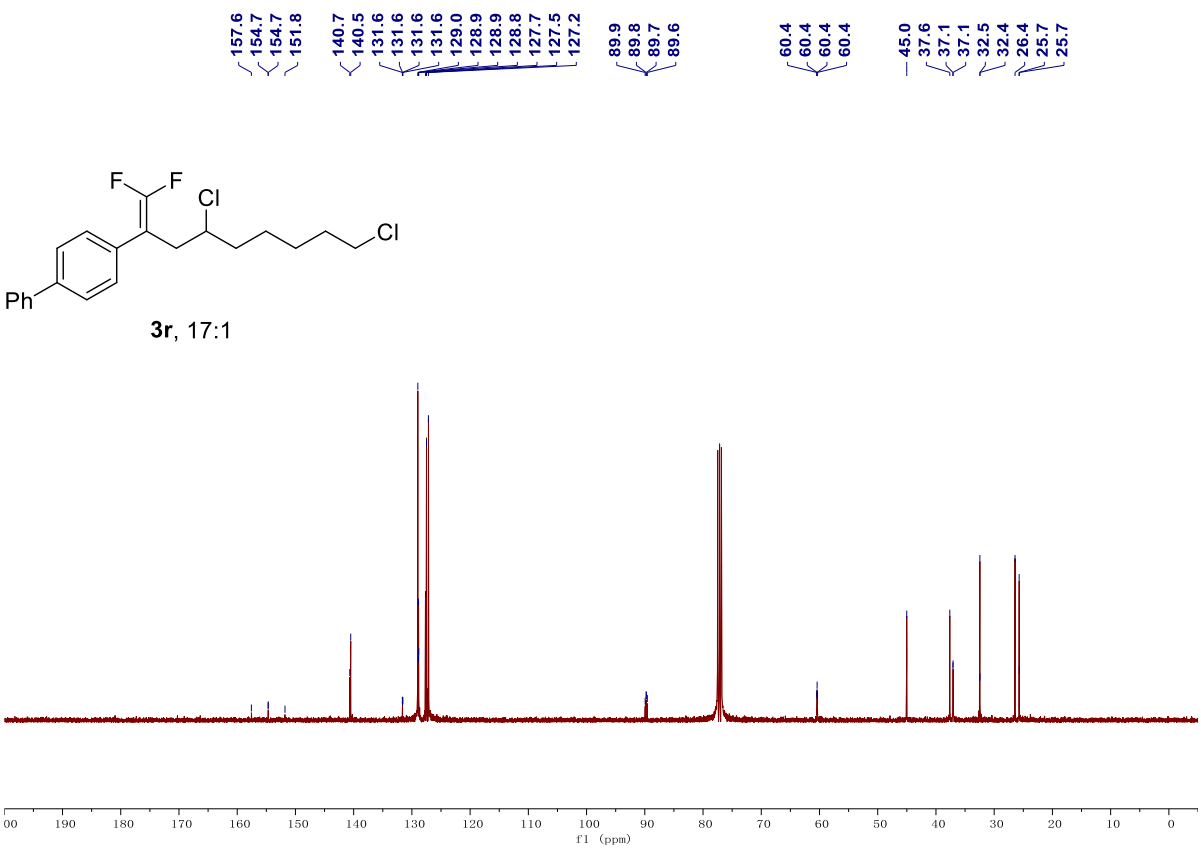
3q, > 20:1

^{19}F NMR spectrum for compound **3q** ($CDCl_3$)

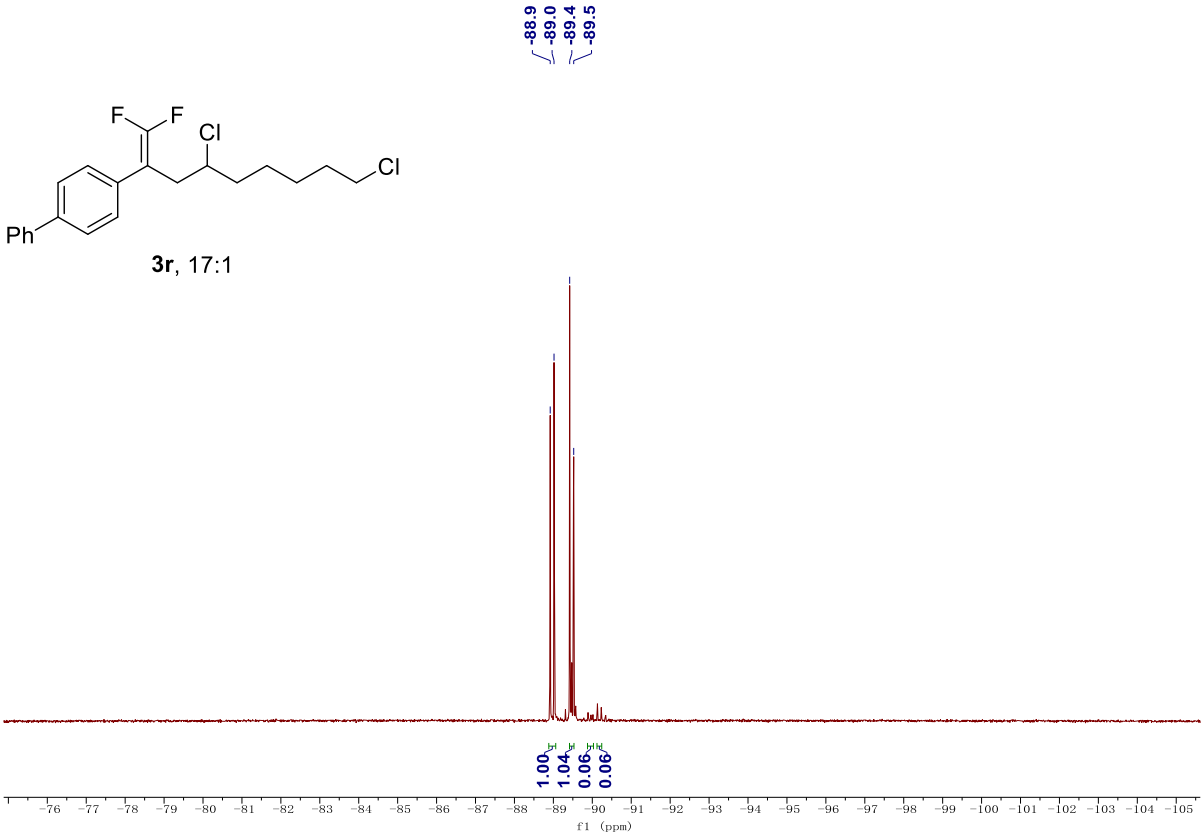


3r, 17:1

^{1}H NMR spectrum for compound **3r** ($CDCl_3$)

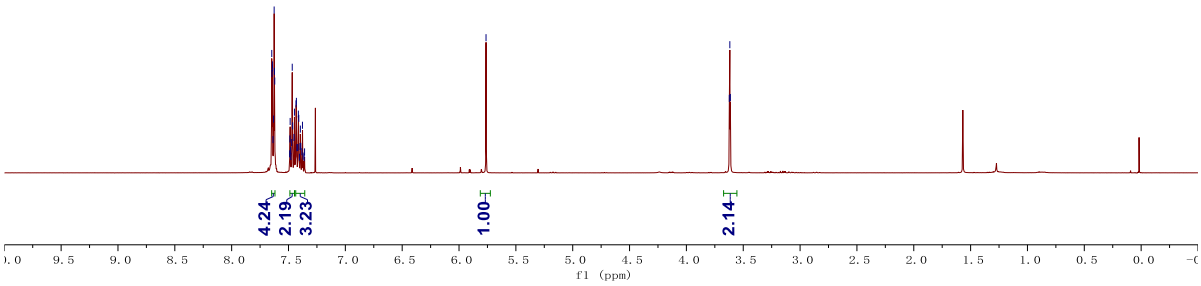


^{13}C NMR spectrum for compound **3r** ($CDCl_3$)

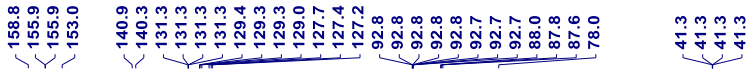


^{19}F NMR spectrum for compound **3r** ($CDCl_3$)

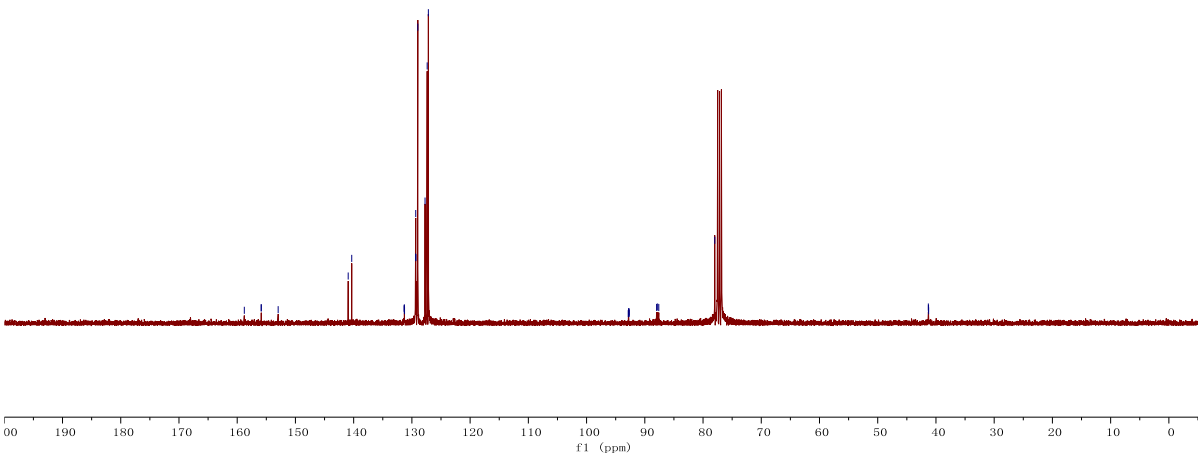
3s, 20:1



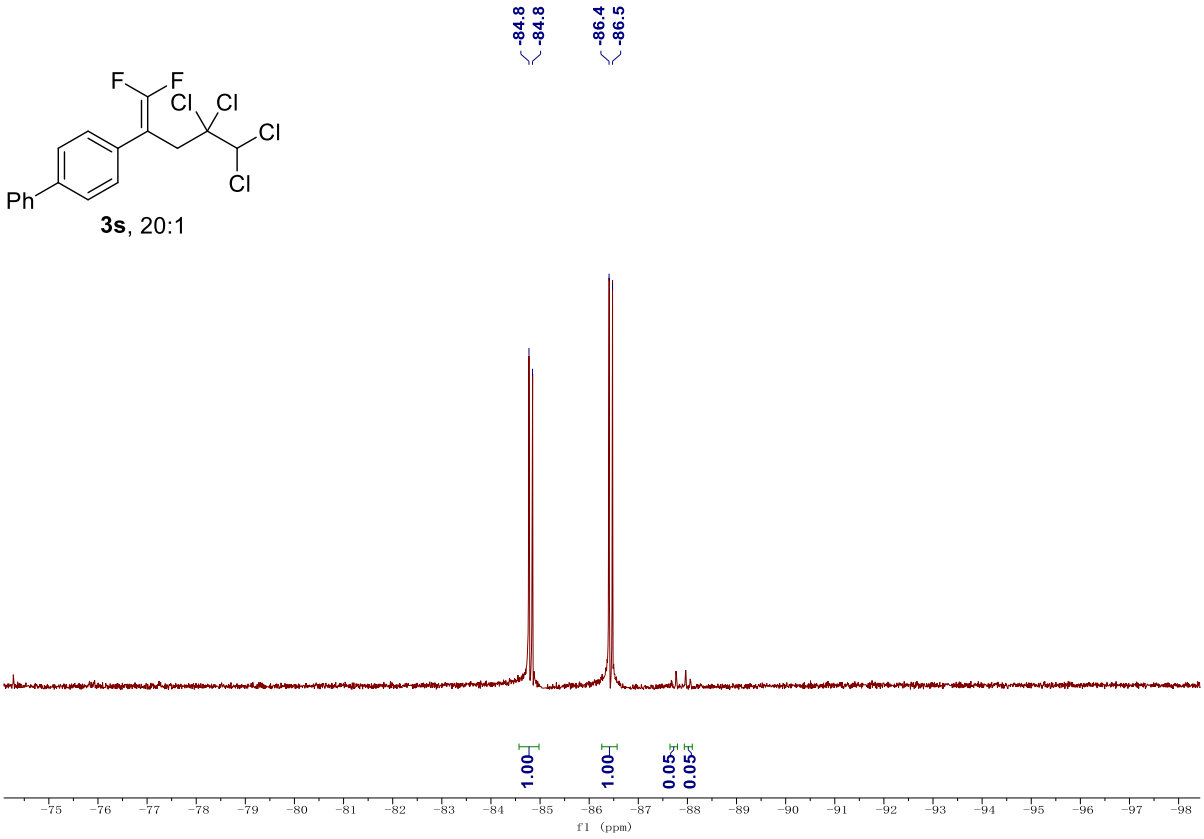
^{1}H NMR spectrum for compound **3s** ($CDCl_3$)



3s, 20:1

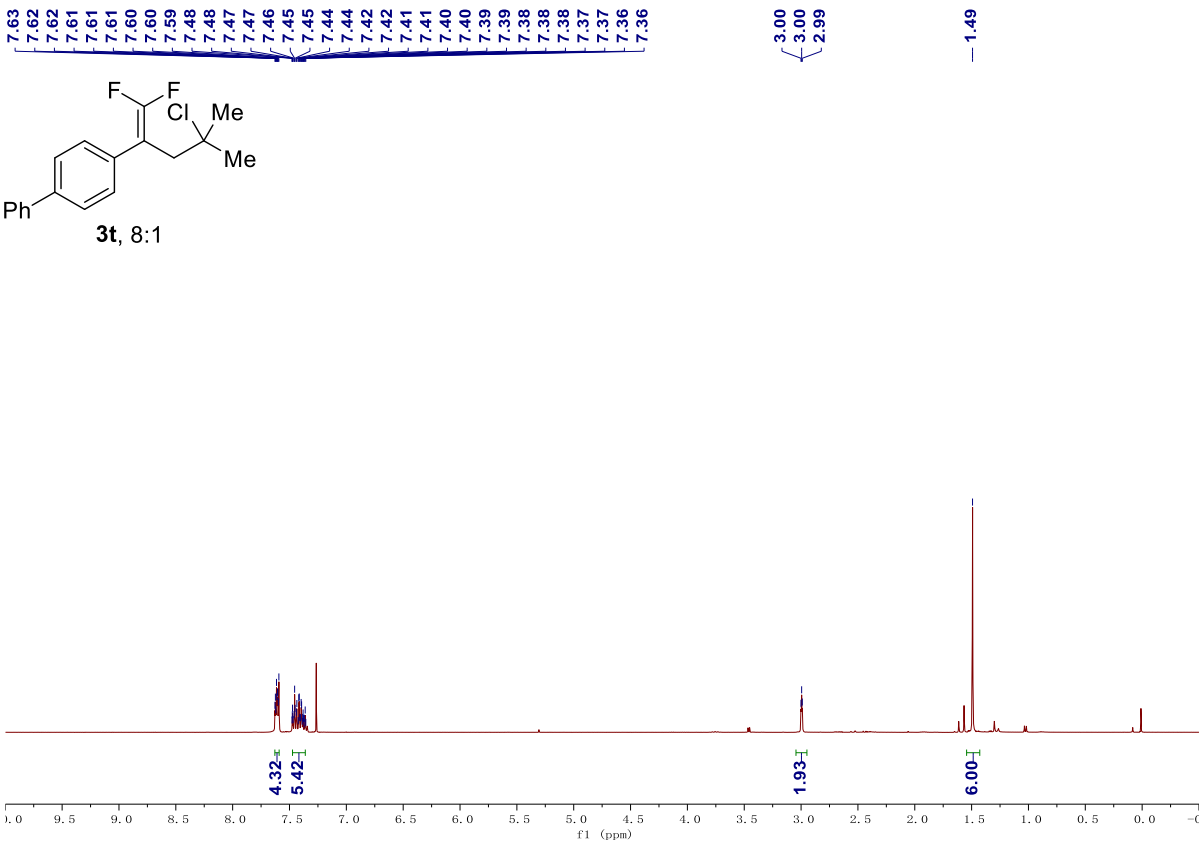


^{13}C NMR spectrum for compound **3s** ($CDCl_3$)



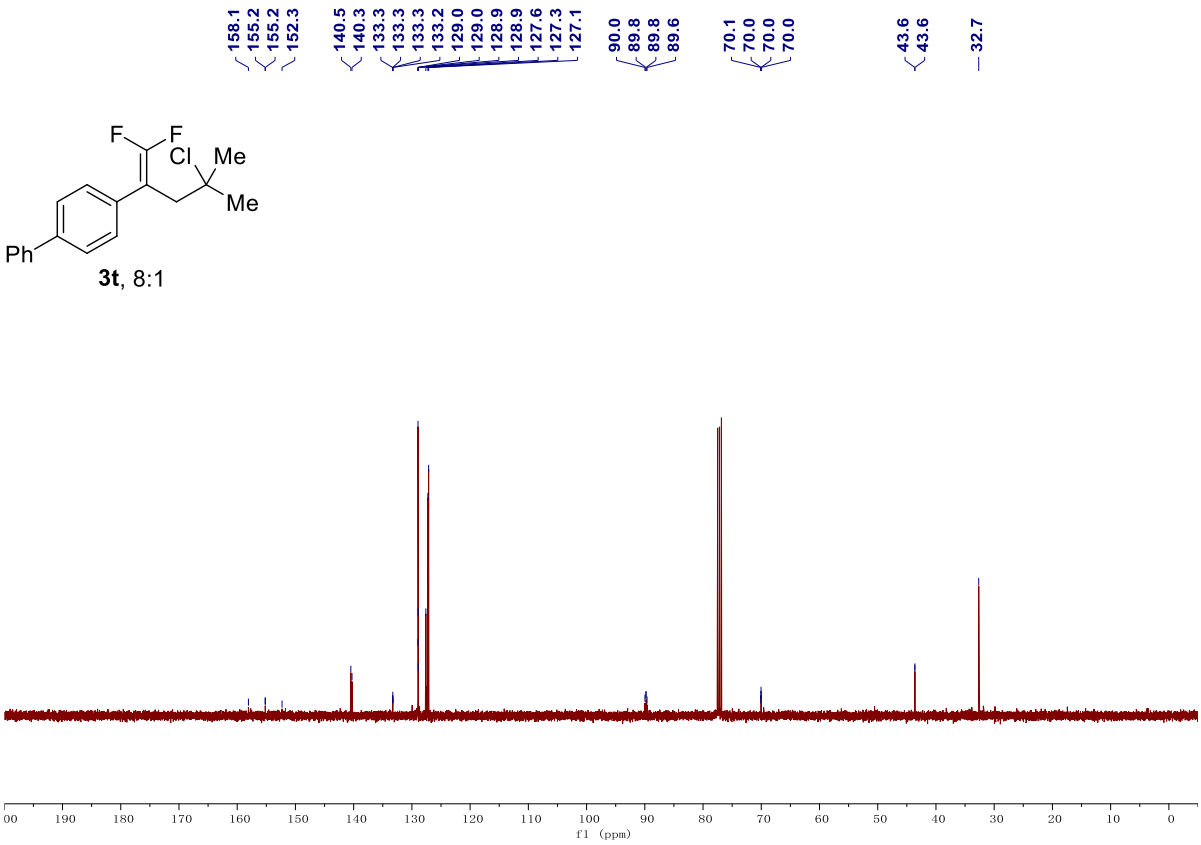
3s, 20:1

^{19}F NMR spectrum for compound **3s** ($CDCl_3$)

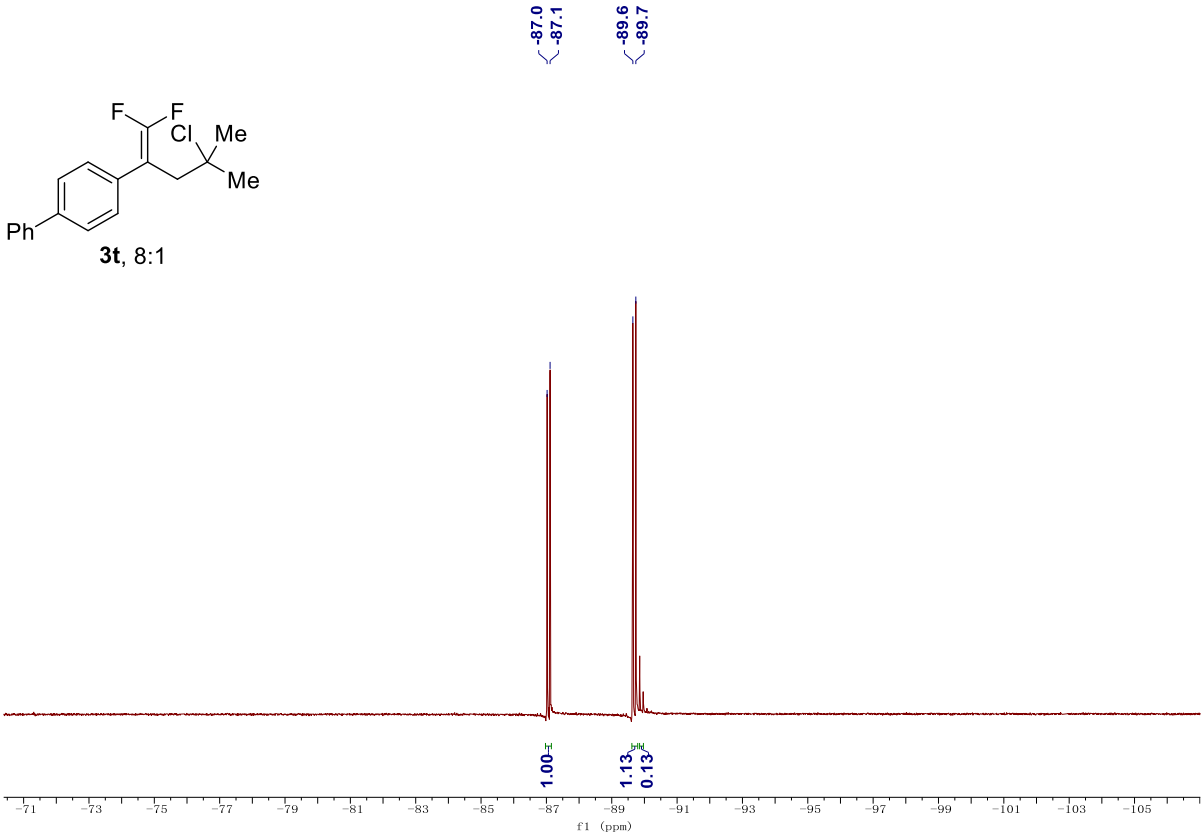


3t, 8:1

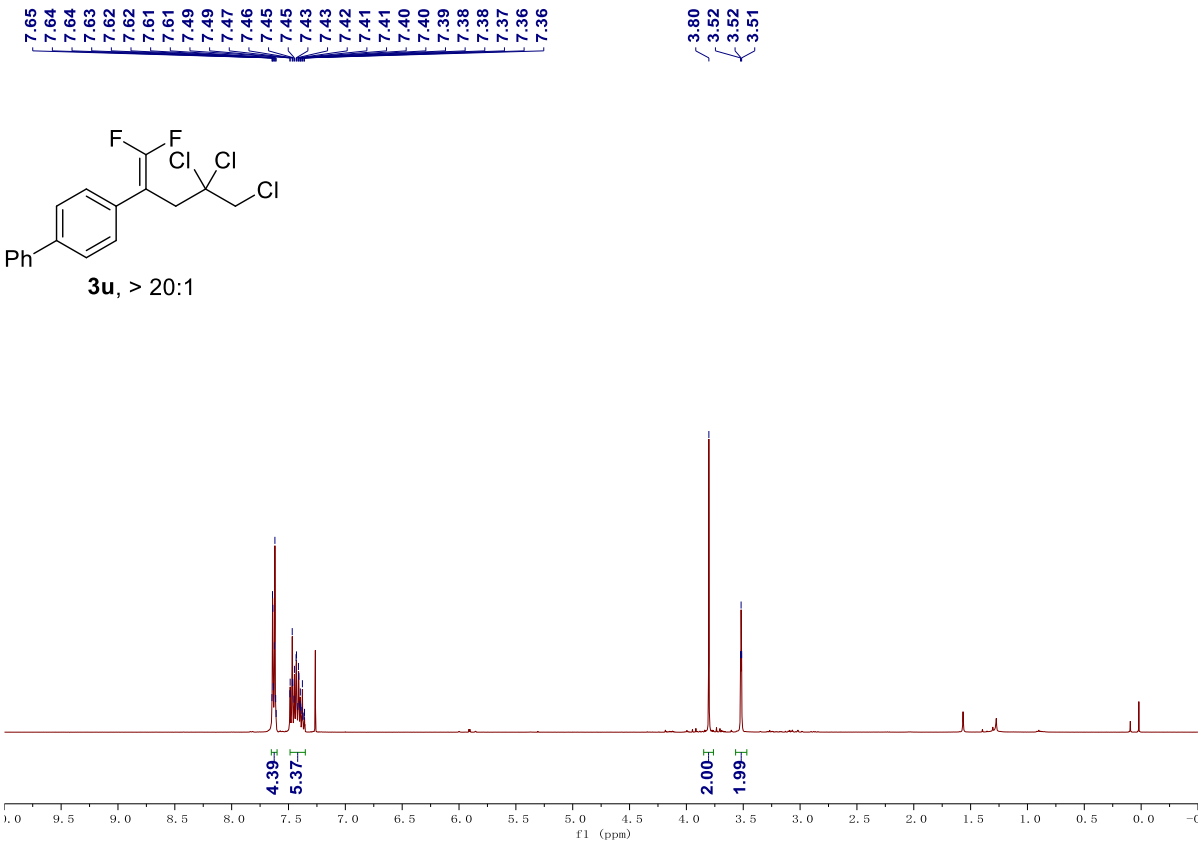
^{1}H NMR spectrum for compound **3t** ($CDCl_3$)



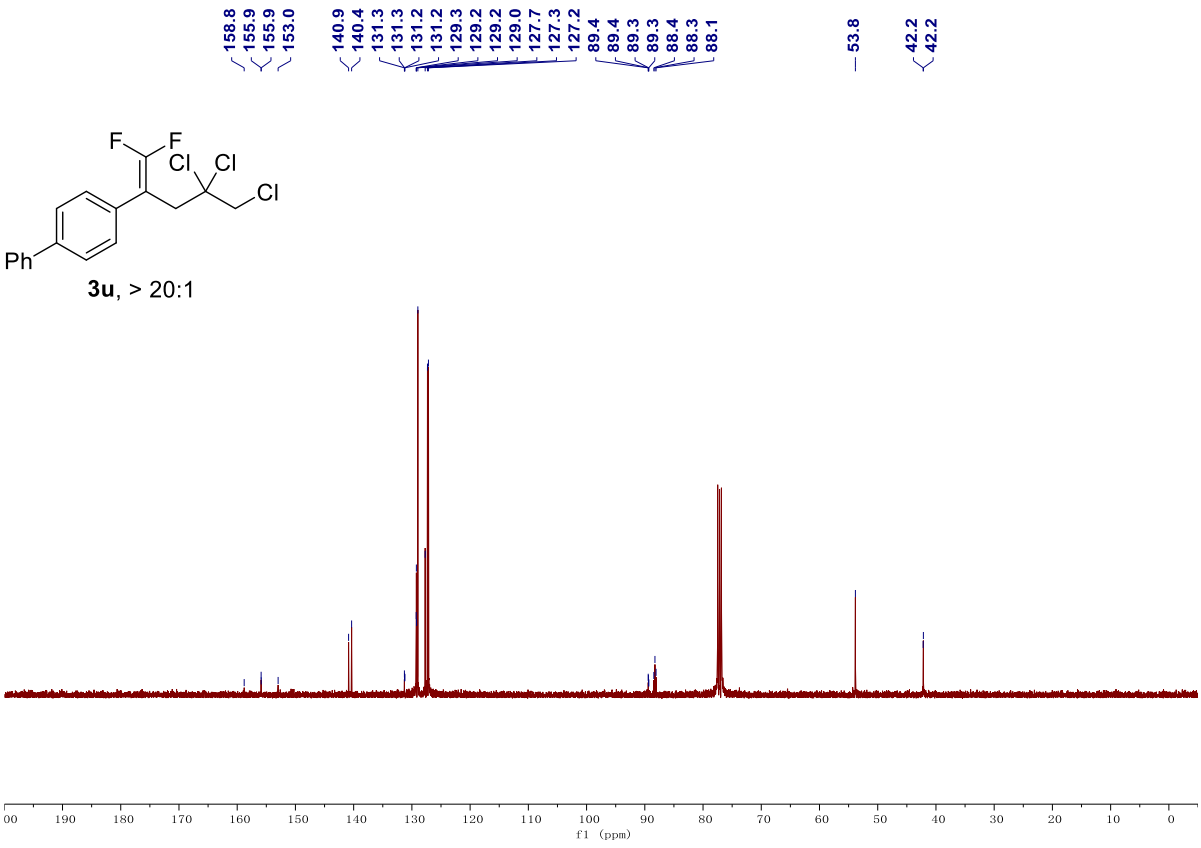
^{13}C NMR spectrum for compound **3t** ($CDCl_3$)



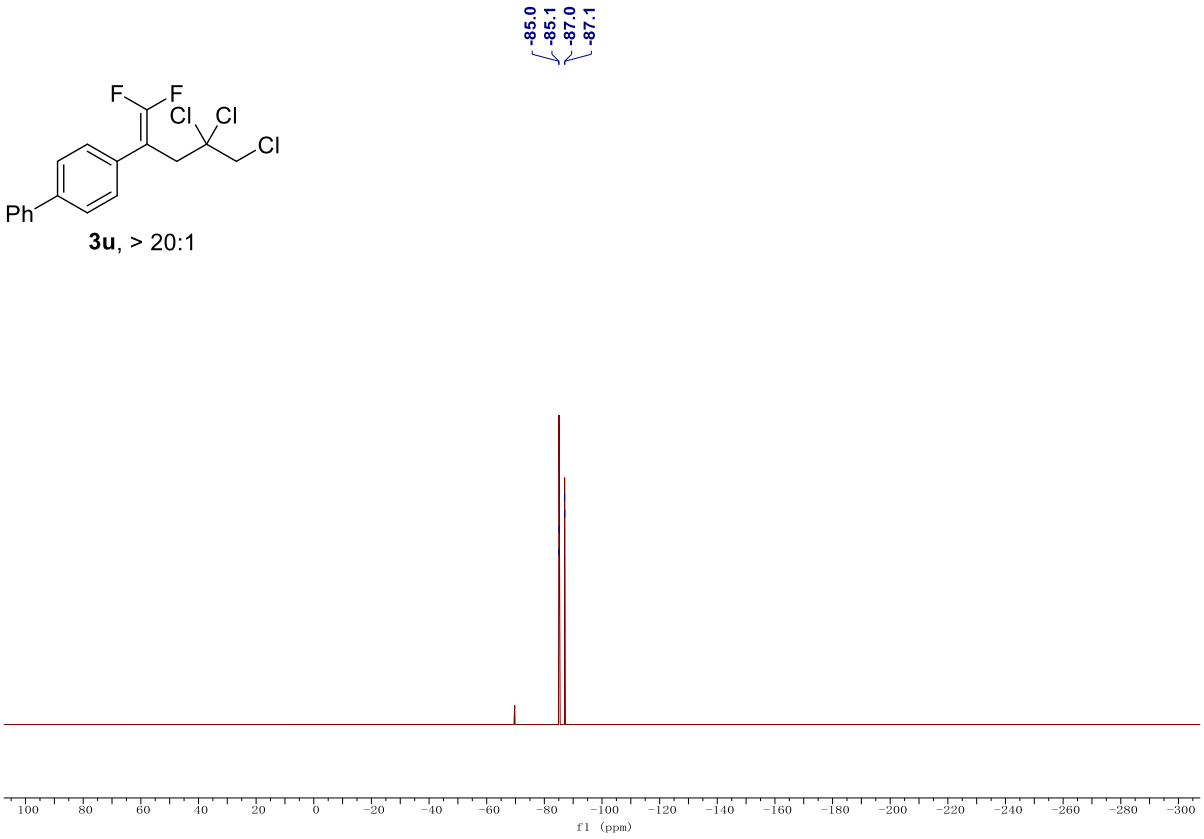
^{19}F NMR spectrum for compound **3t** ($CDCl_3$)



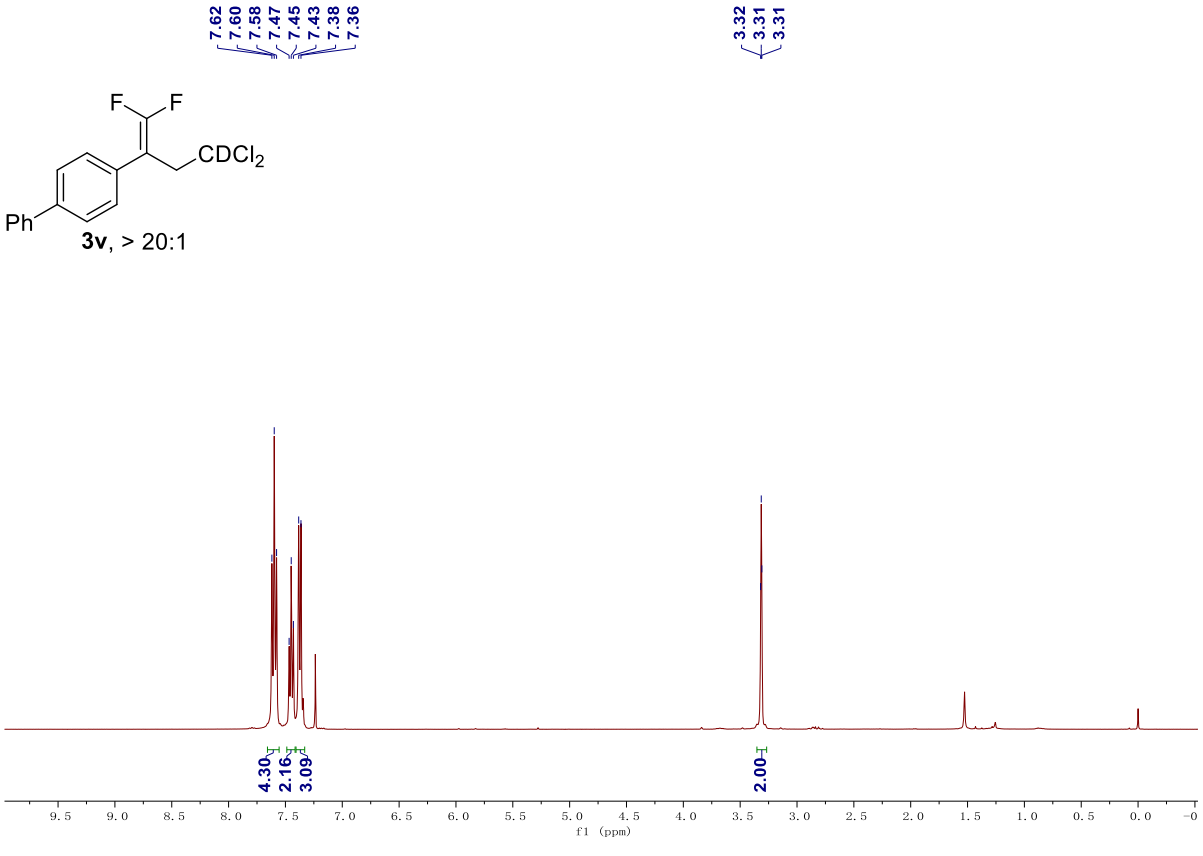
^{1}H NMR spectrum for compound **3u** ($CDCl_3$)



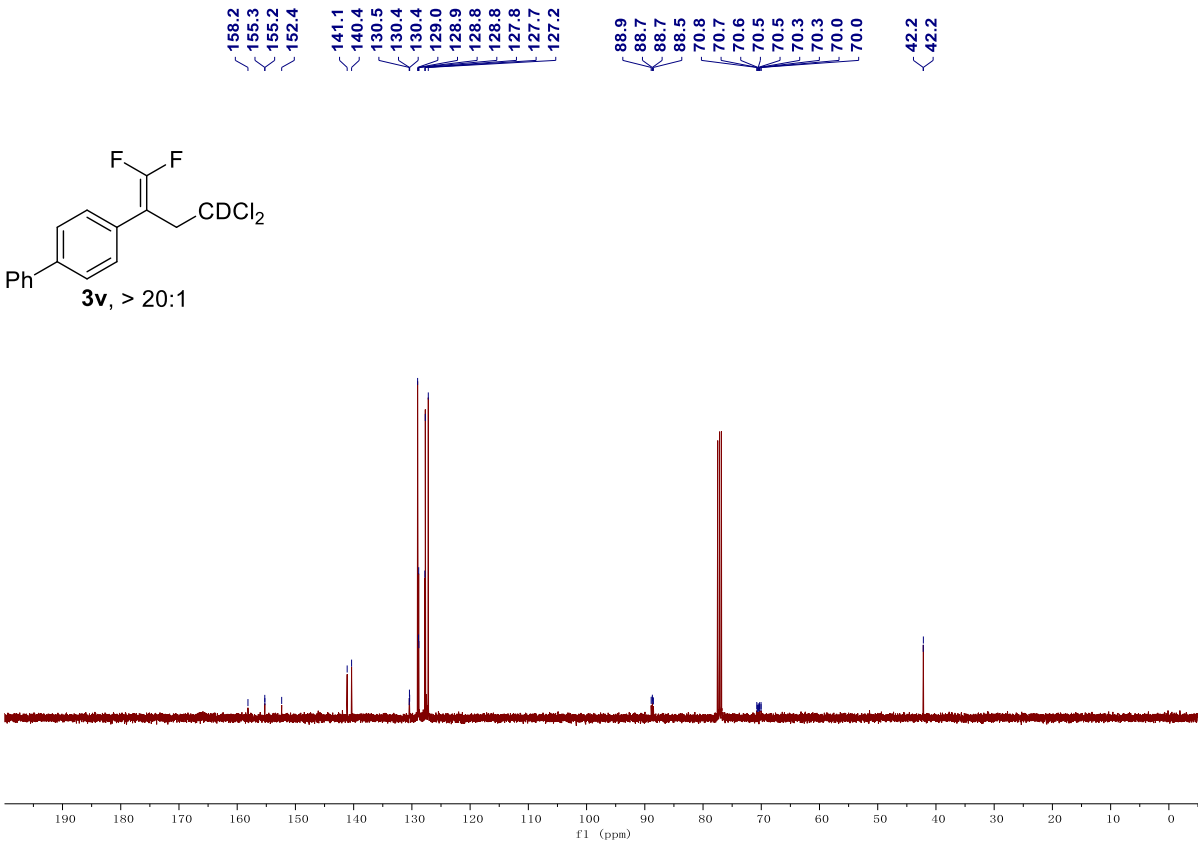
^{13}C NMR spectrum for compound **3u** ($CDCl_3$)



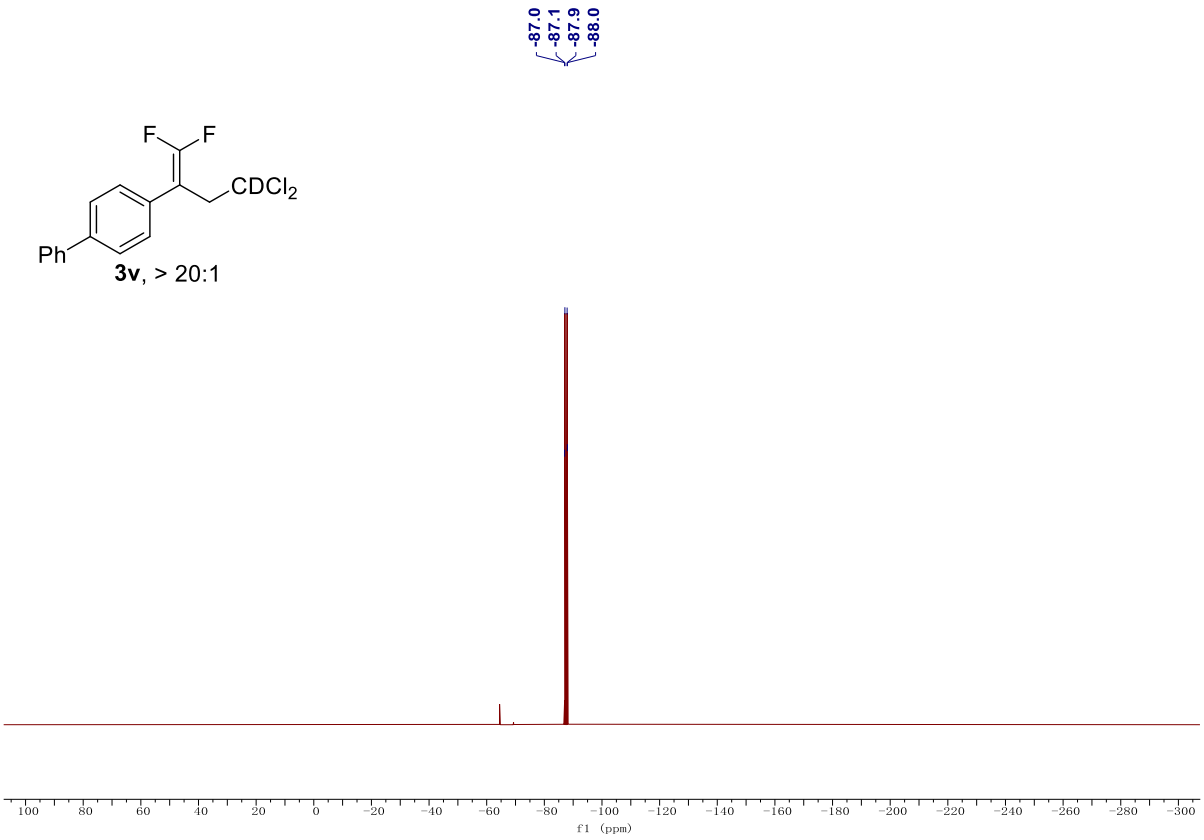
^{19}F NMR spectrum for compound **3u** ($CDCl_3$)



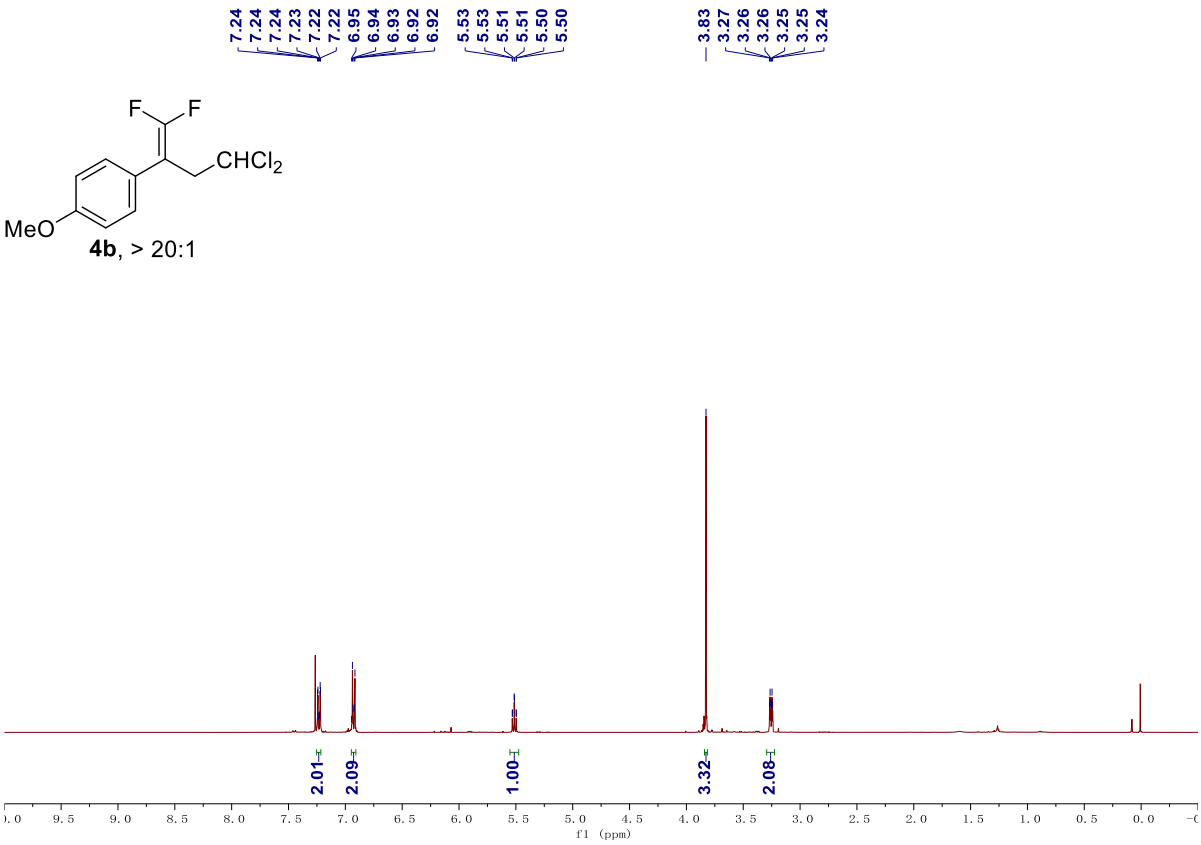
^{1}H NMR spectrum for compound **3v** ($CDCl_3$)



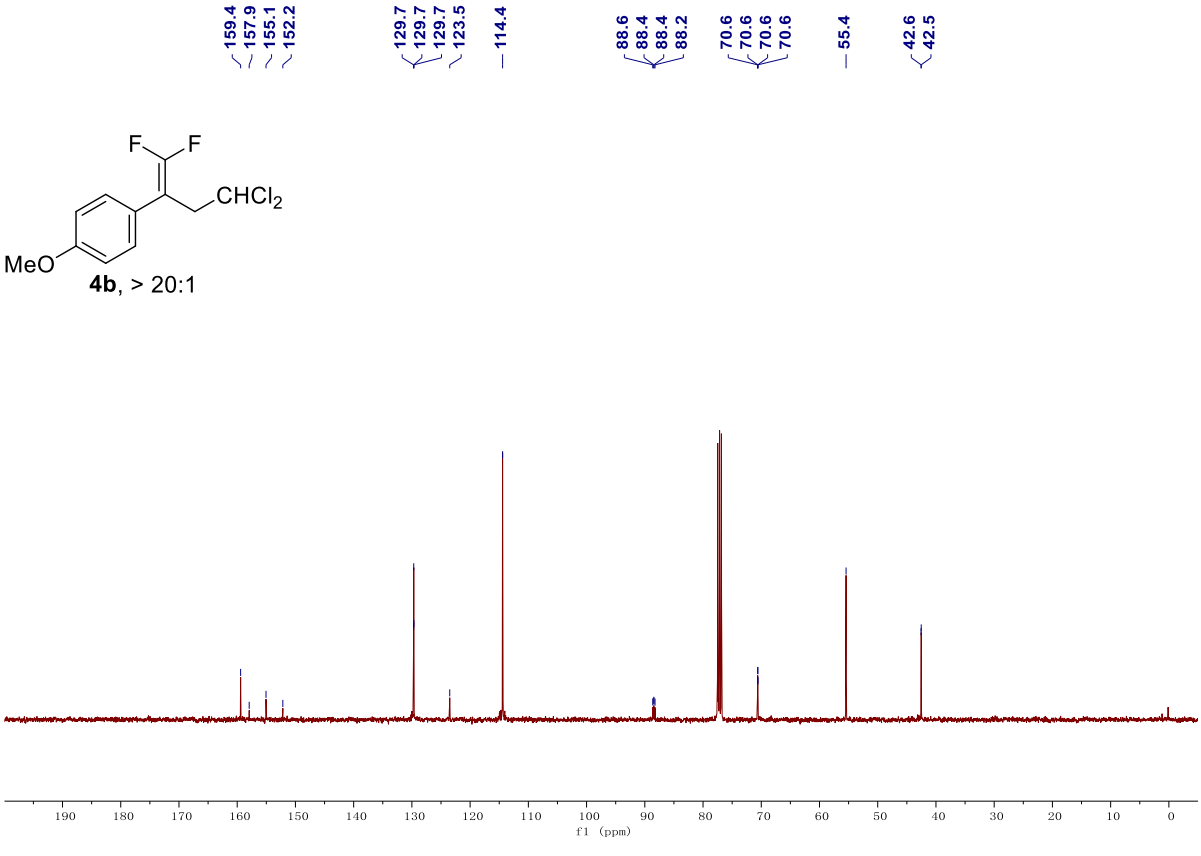
^{13}C NMR spectrum for compound **3v** ($CDCl_3$)



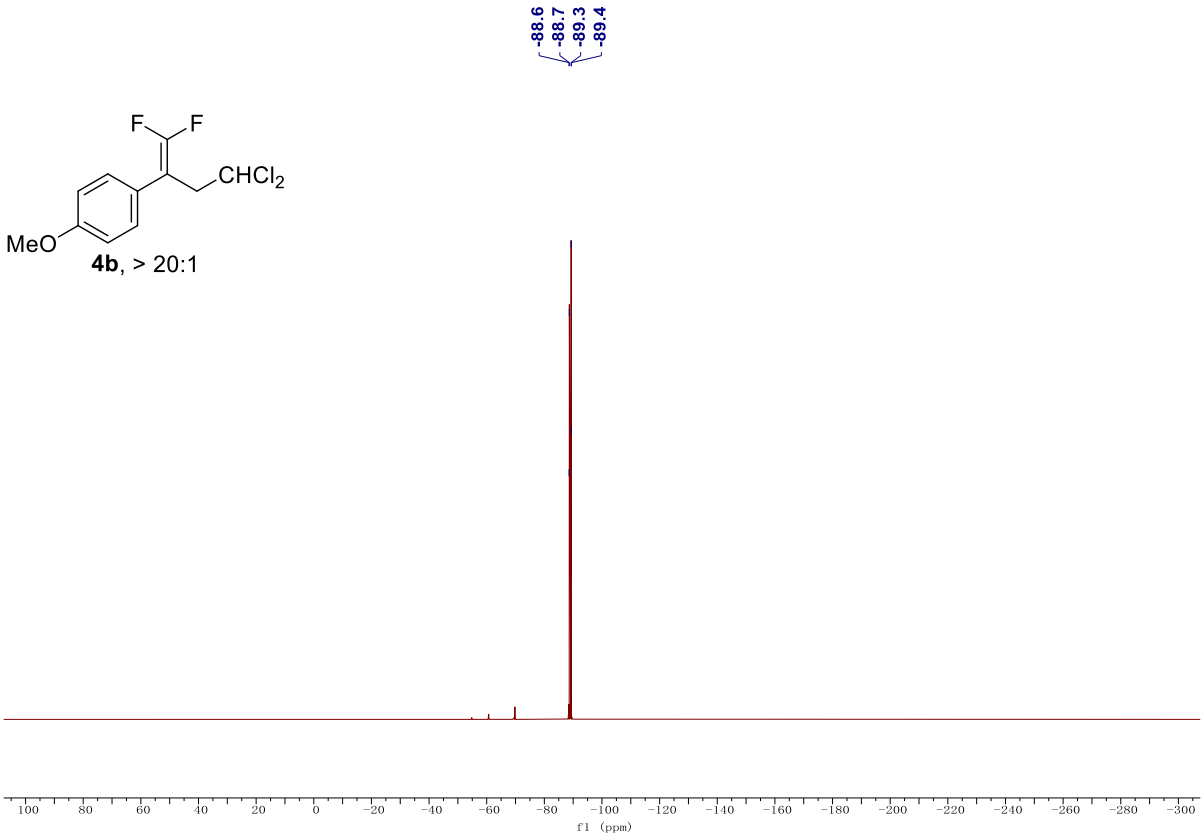
^{19}F NMR spectrum for compound **3v** ($CDCl_3$)



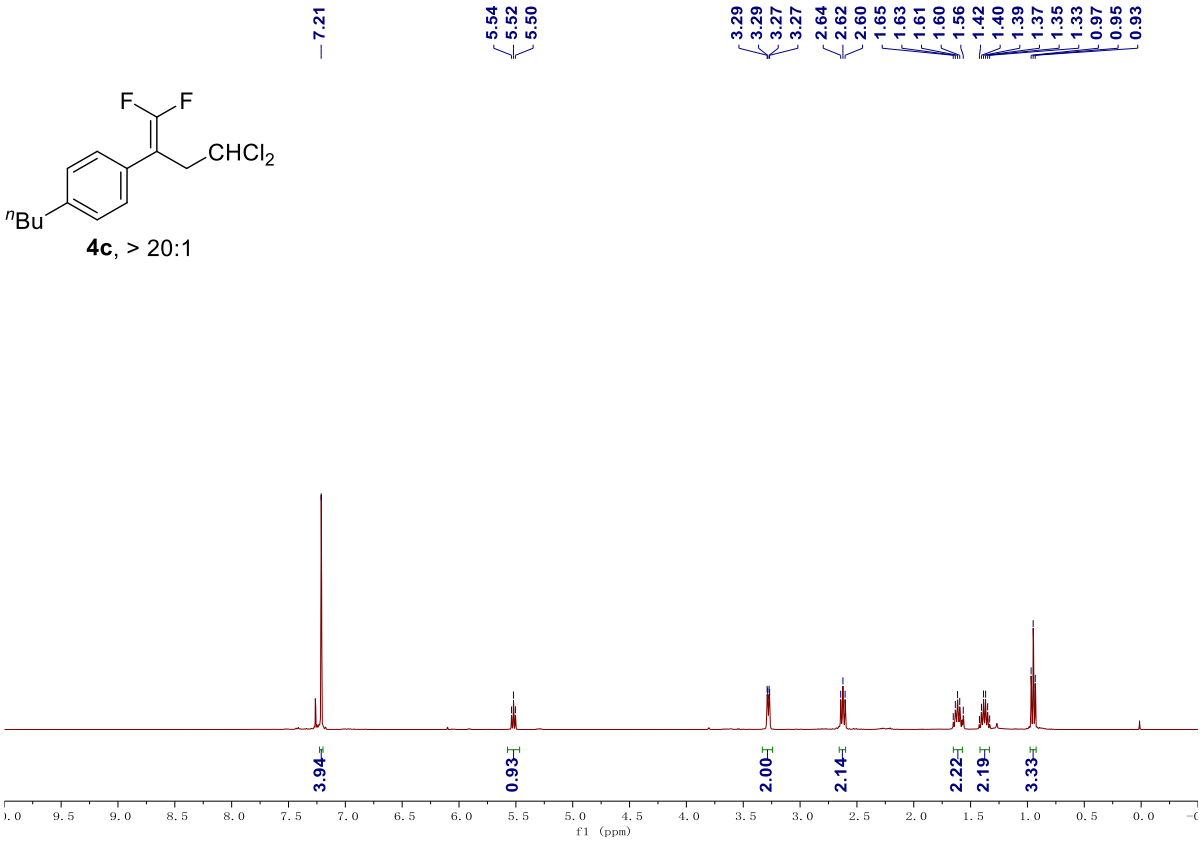
^{1}H NMR spectrum for compound **4b** ($CDCl_3$)



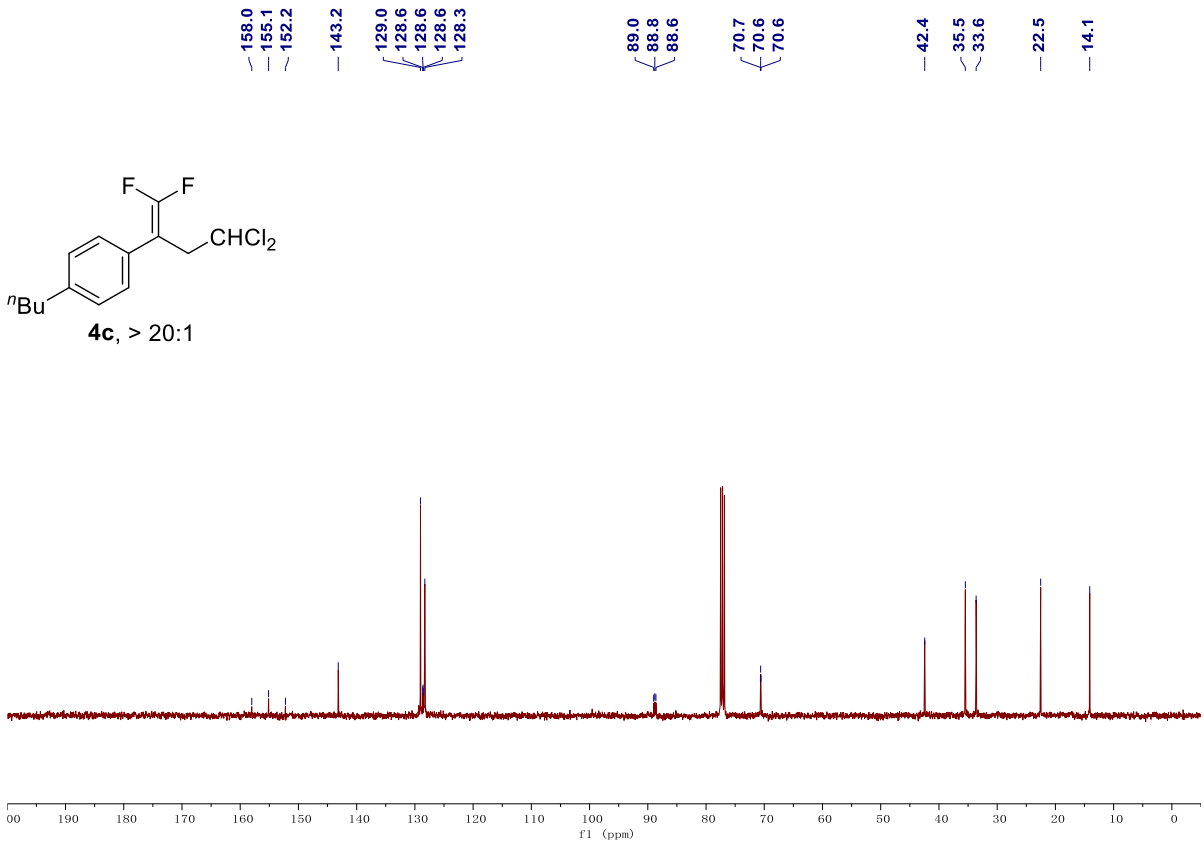
^{13}C NMR spectrum for compound **4b** ($CDCl_3$)



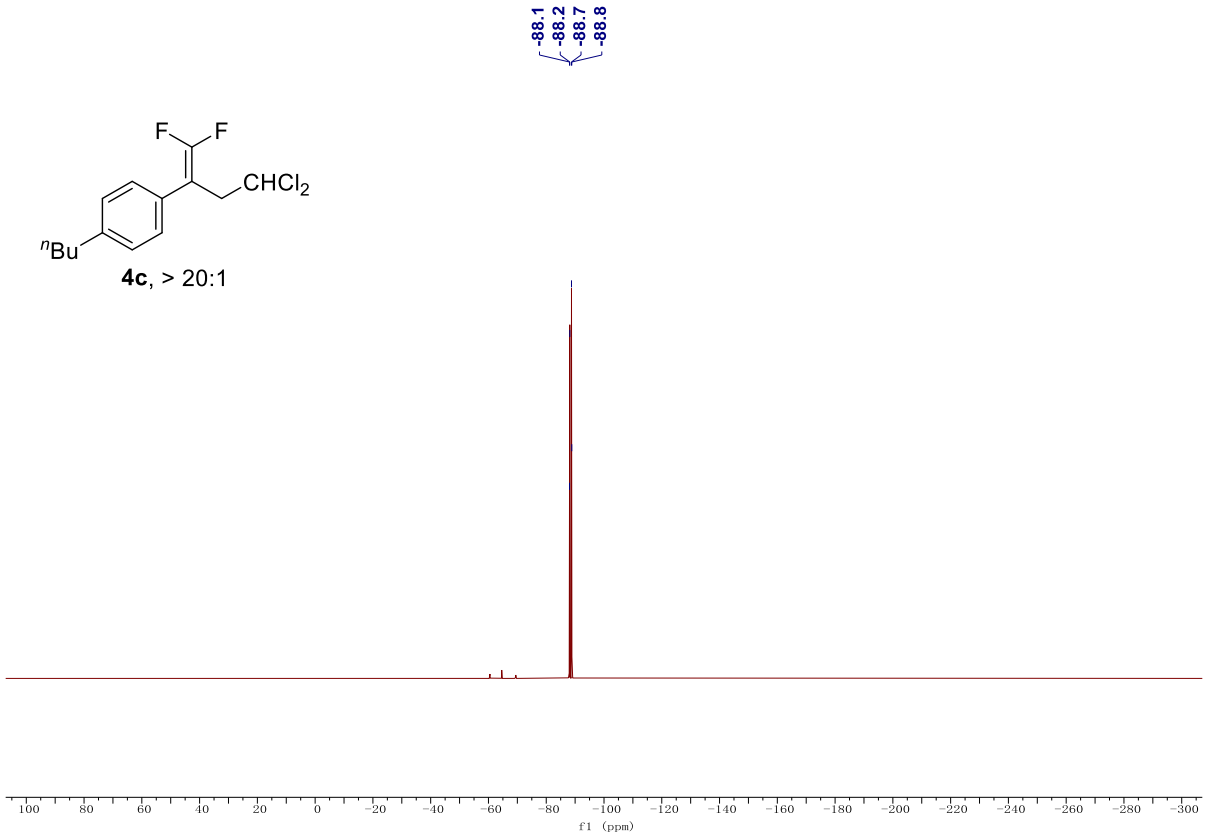
^{19}F NMR spectrum for compound **4b** ($CDCl_3$)



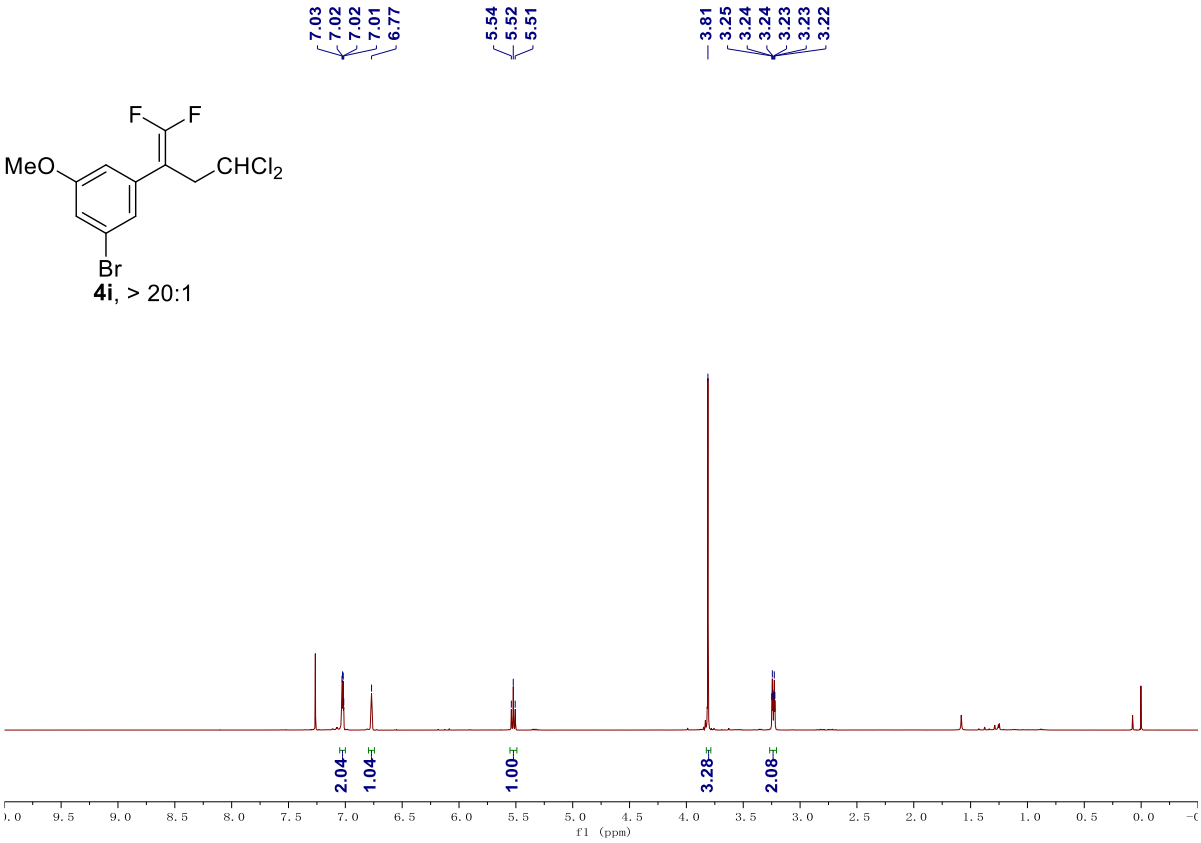
^{1}H NMR spectrum for compound **4c** ($CDCl_3$)



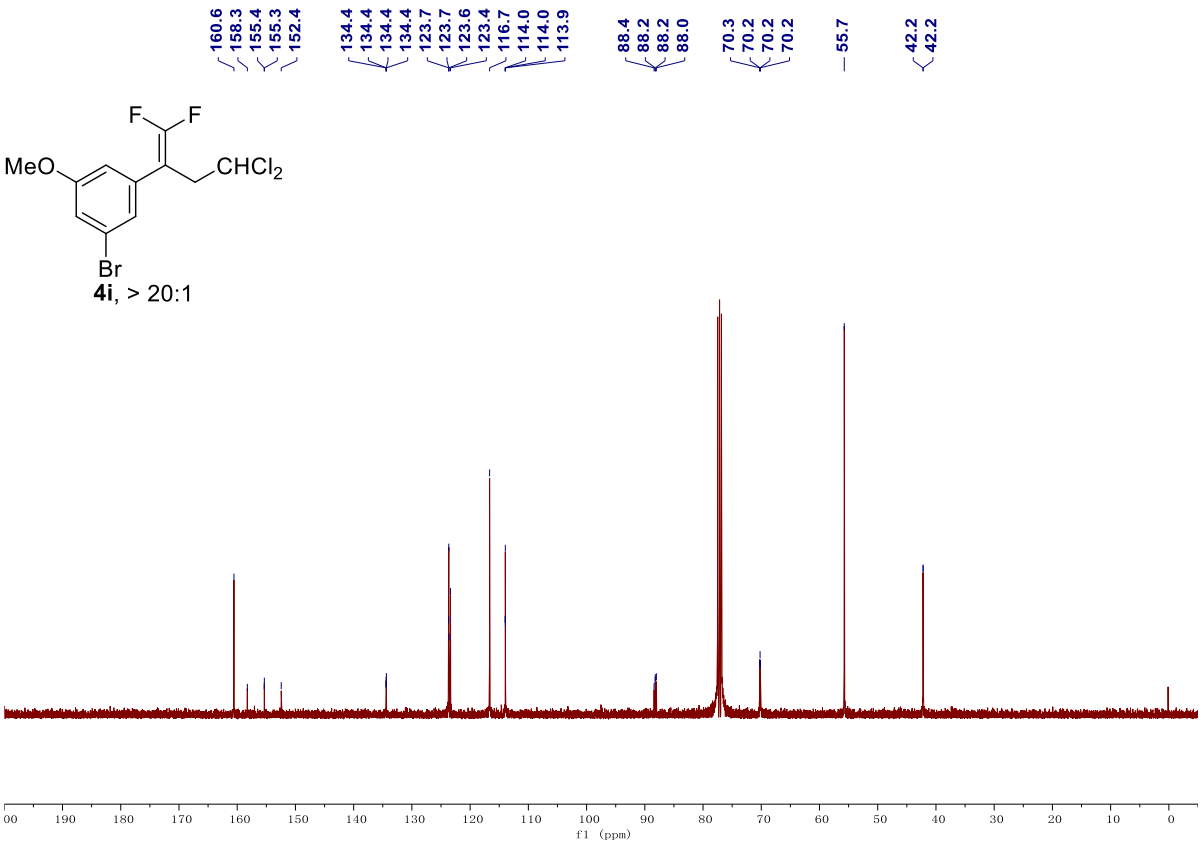
^{13}C NMR spectrum for compound **4c** ($CDCl_3$)



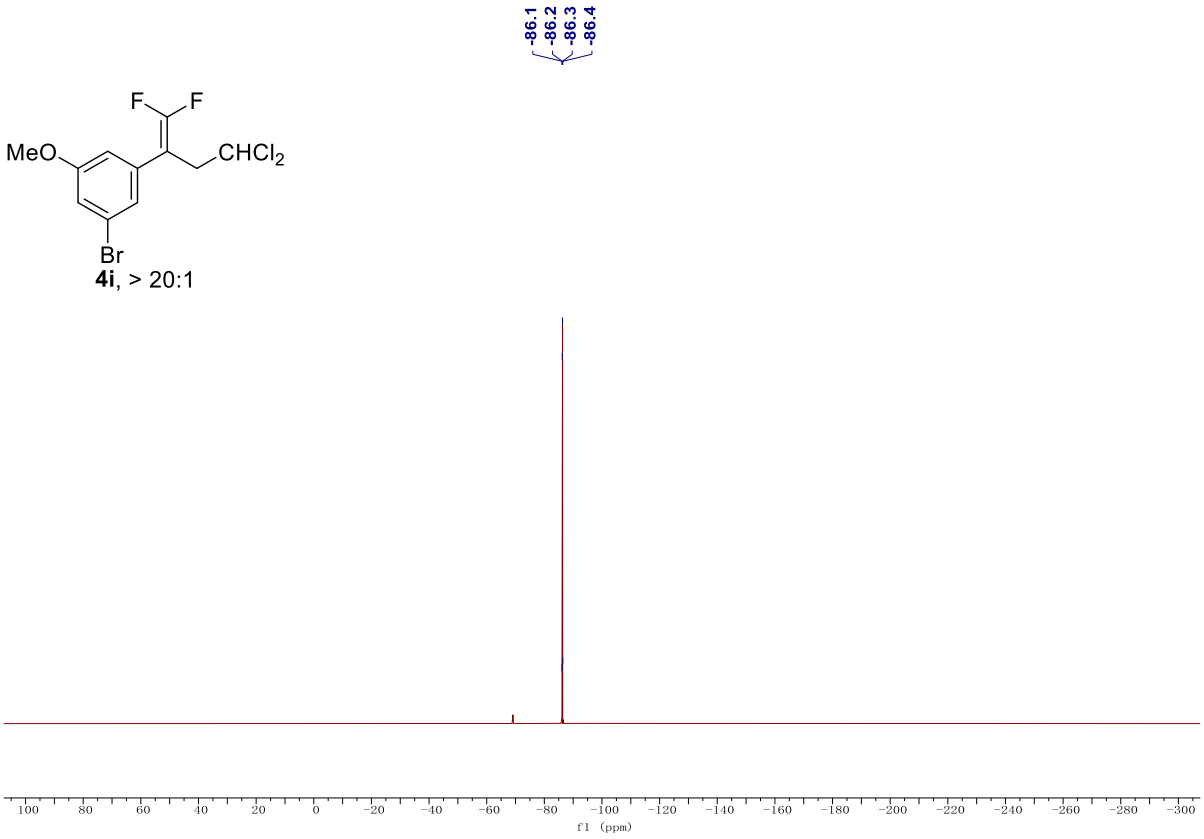
^{19}F NMR spectrum for compound **4c** ($CDCl_3$)



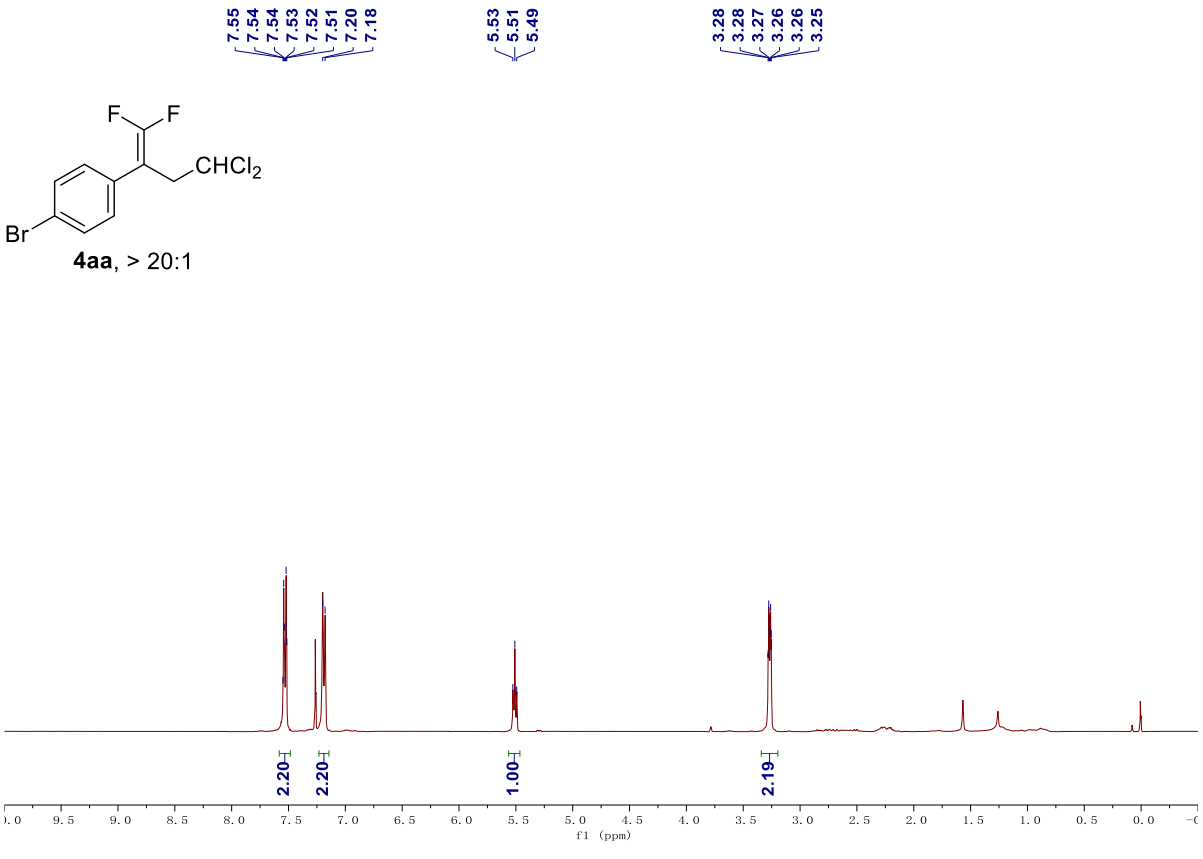
^{1}H NMR spectrum for compound **4i** ($CDCl_3$)



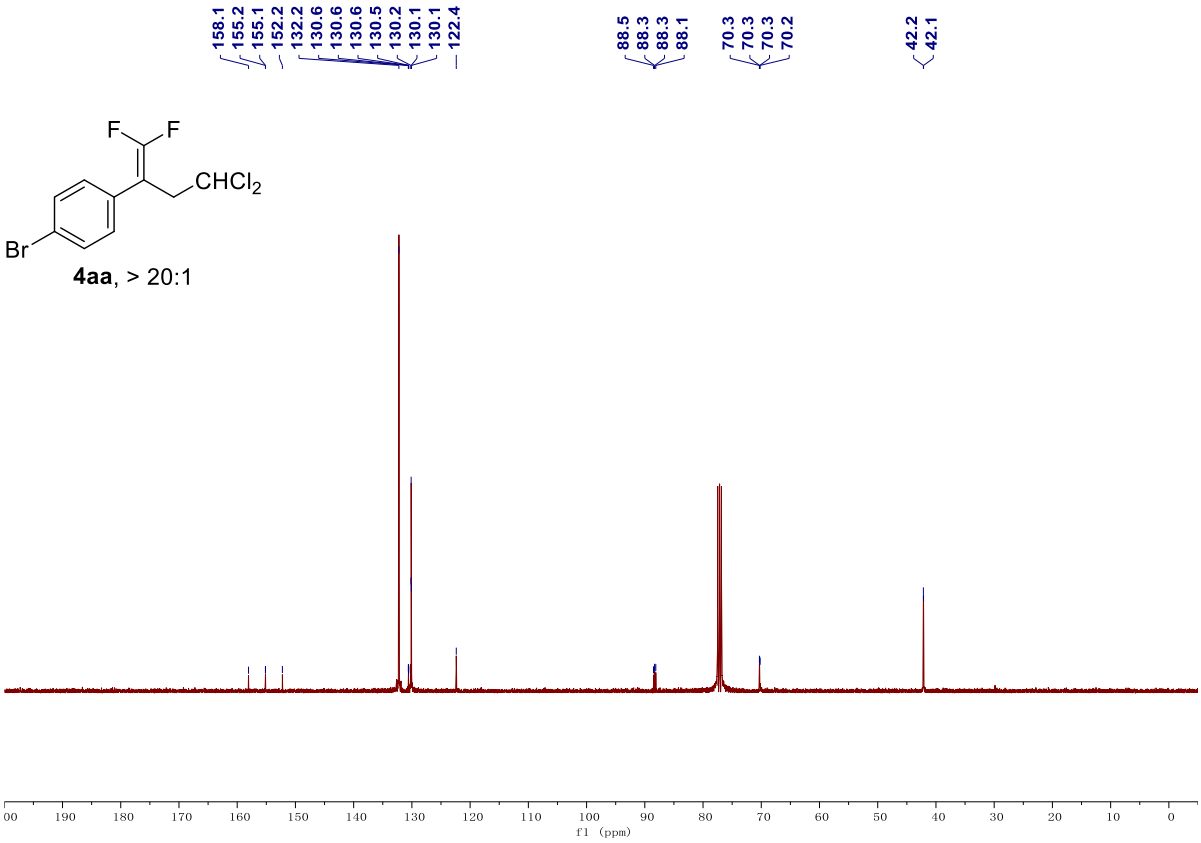
^{13}C NMR spectrum for compound **4i** ($CDCl_3$)



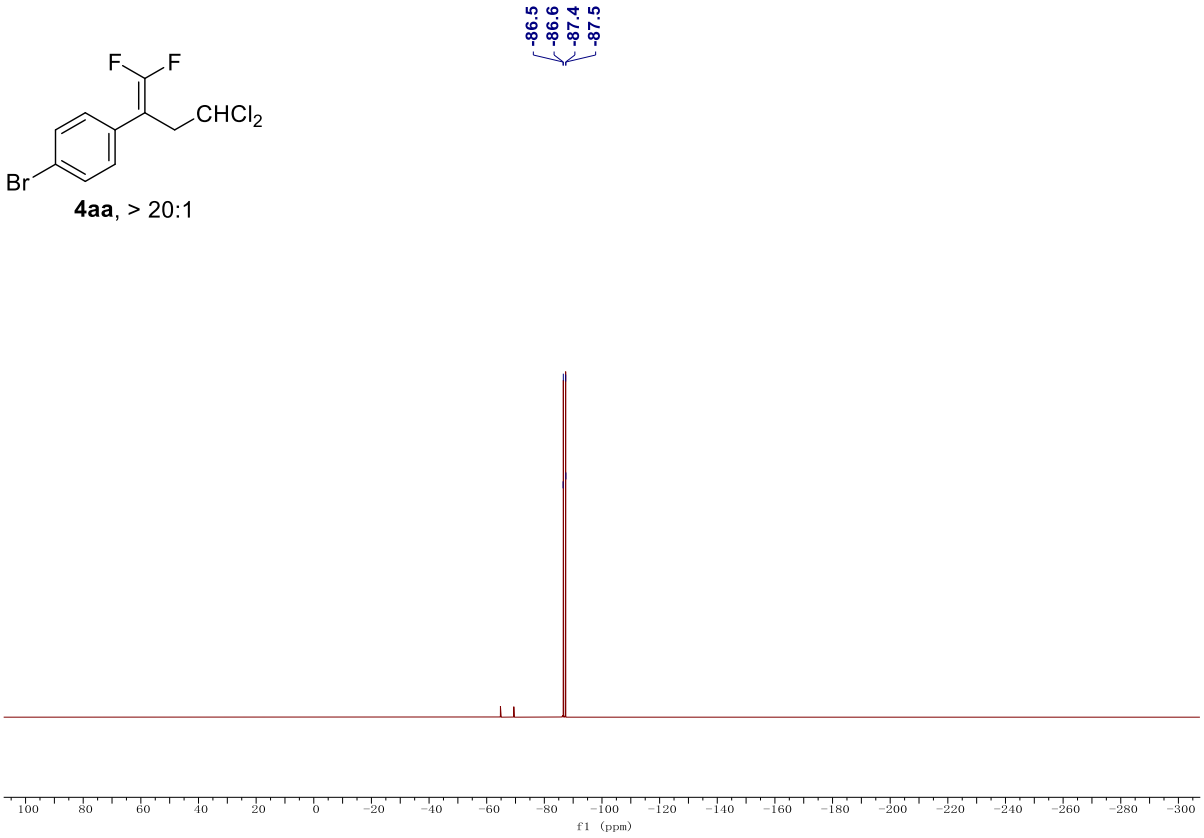
^{19}F NMR spectrum for compound **4i** ($CDCl_3$)



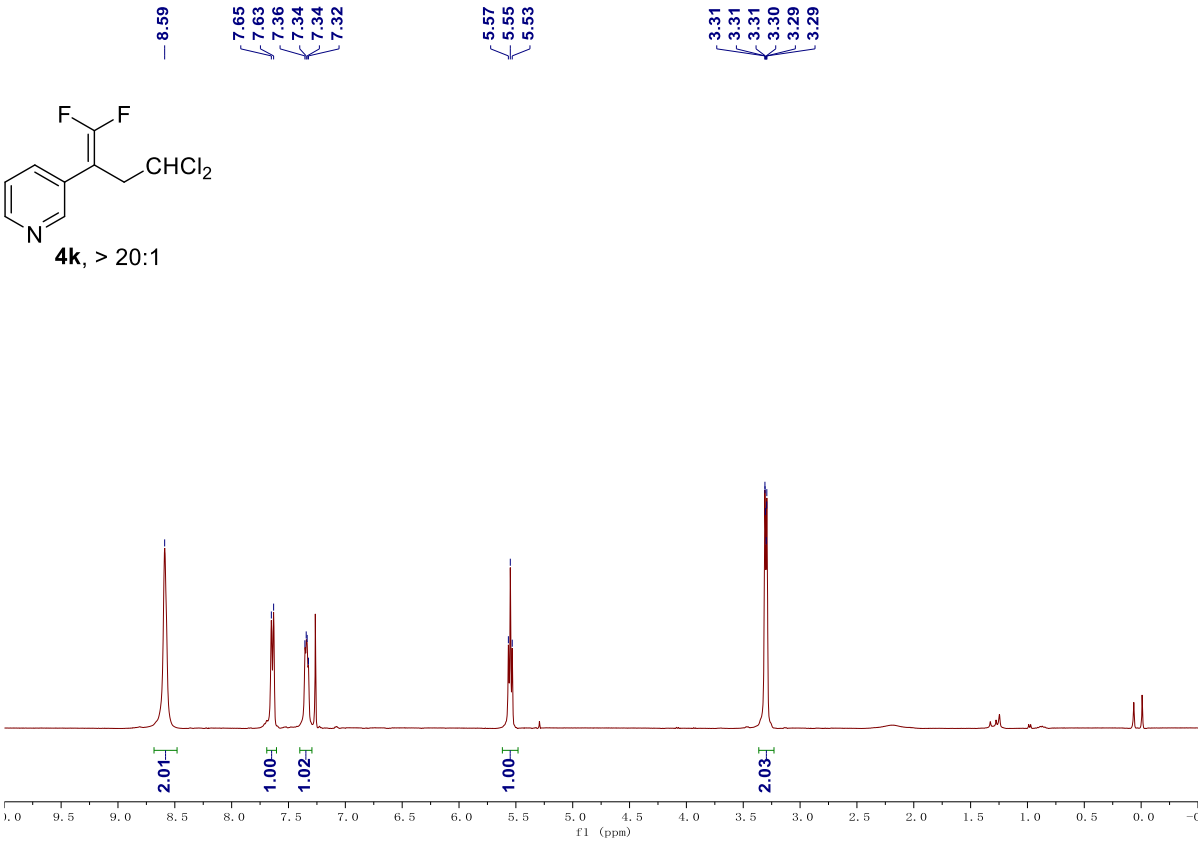
^{1}H NMR spectrum for compound **4aa** ($CDCl_3$)



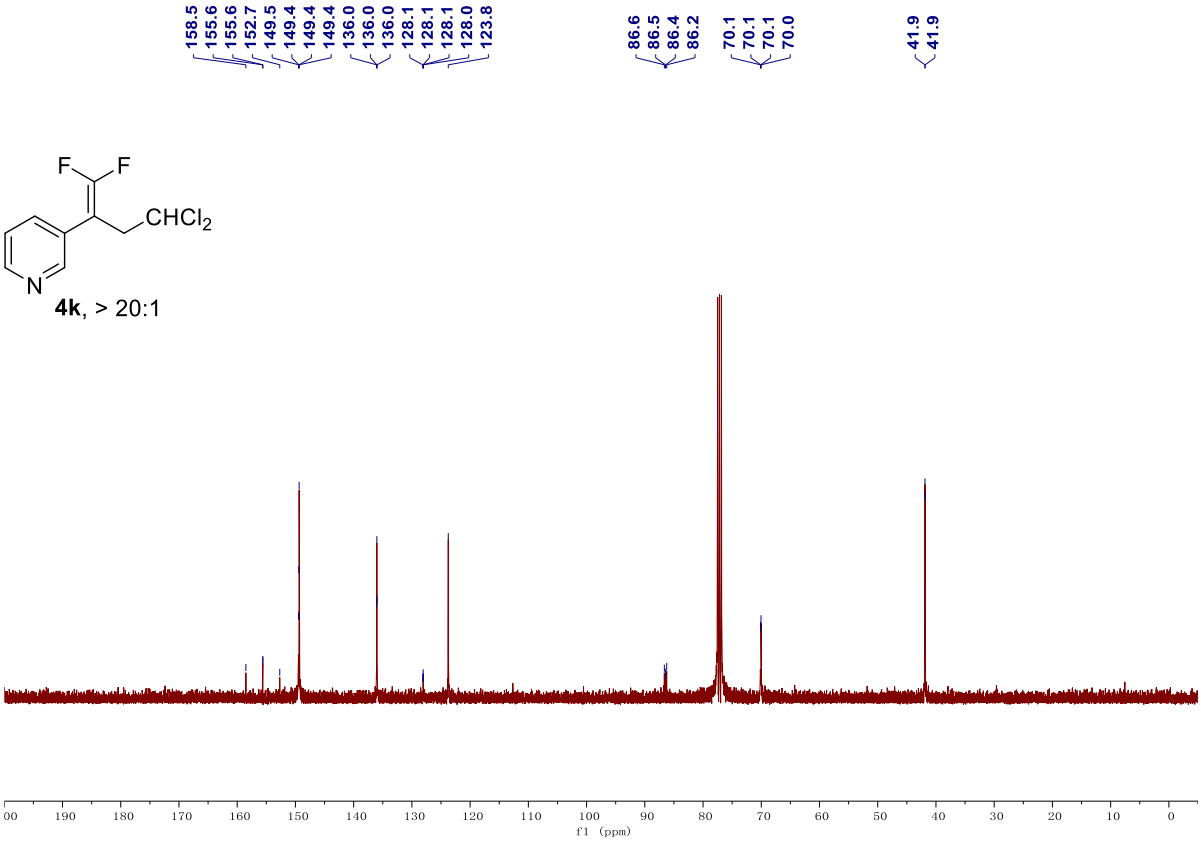
^{13}C NMR spectrum for compound **4aa** ($CDCl_3$)



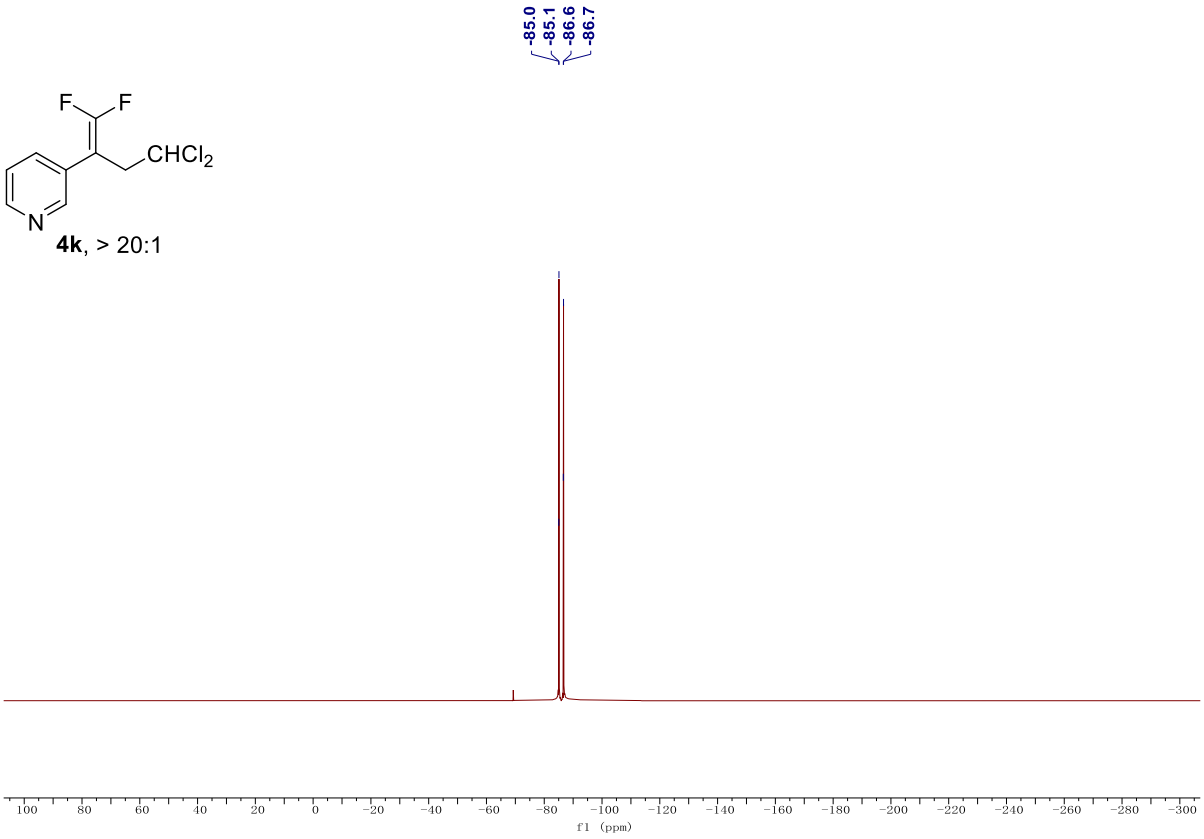
^{19}F NMR spectrum for compound **4aa** ($CDCl_3$)



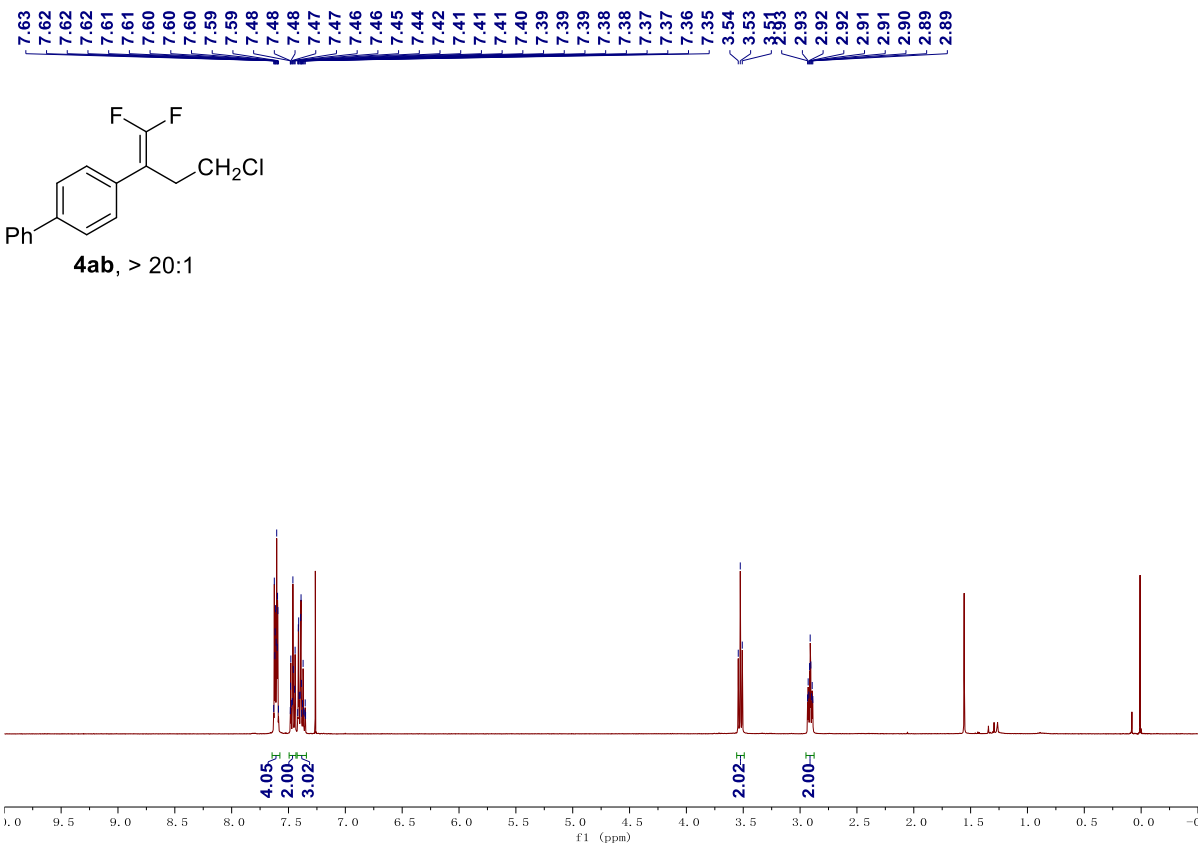
^{1}H NMR spectrum for compound **4k** ($CDCl_3$)



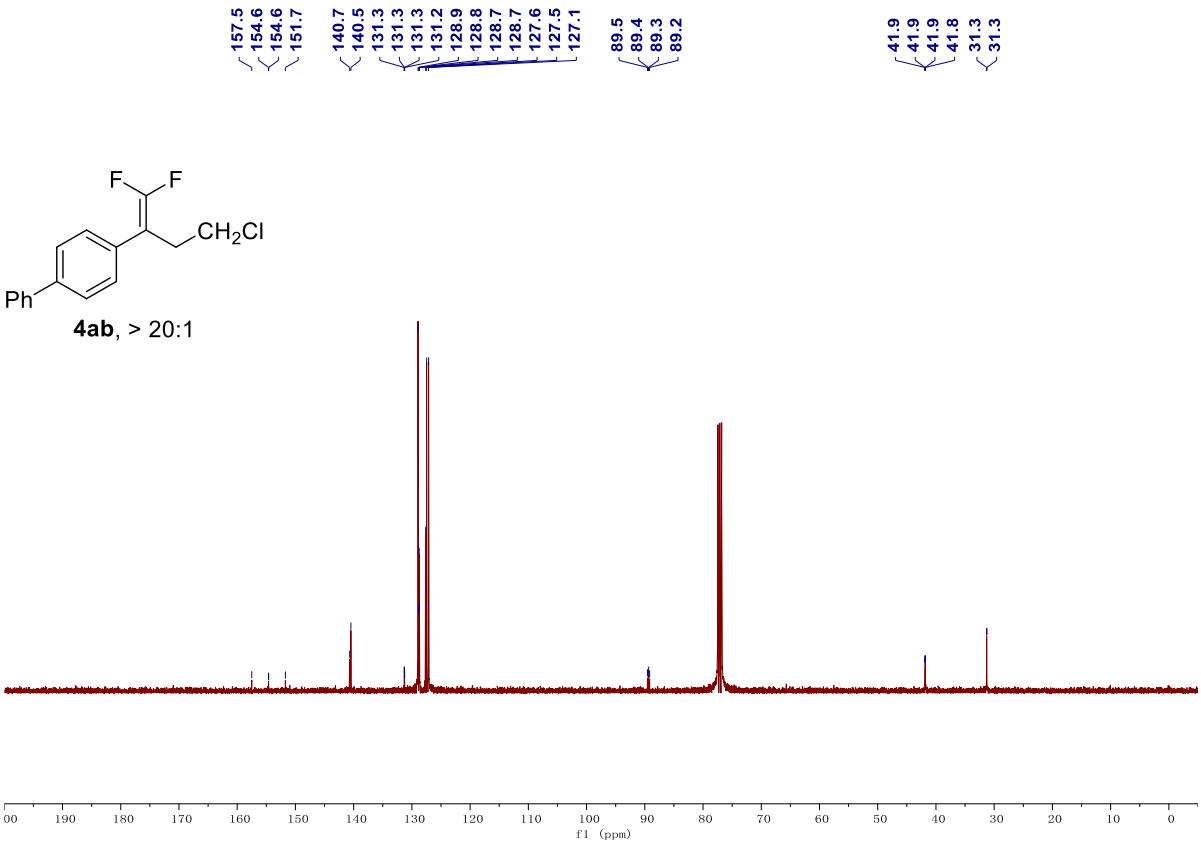
^{13}C NMR spectrum for compound **4k** ($CDCl_3$)



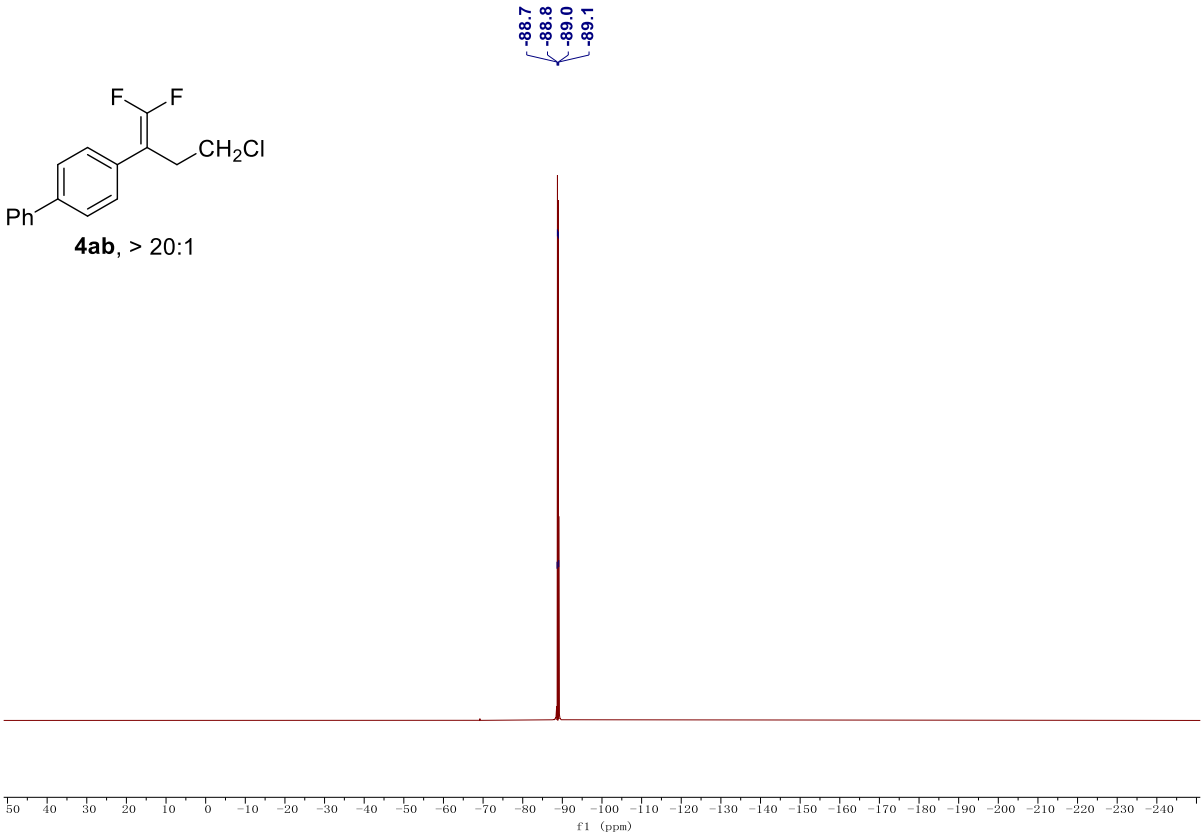
^{19}F NMR spectrum for compound **4k** ($CDCl_3$)



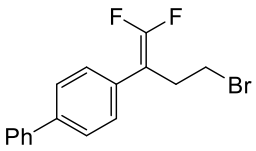
^{1}H NMR spectrum for compound **4ab** ($CDCl_3$)



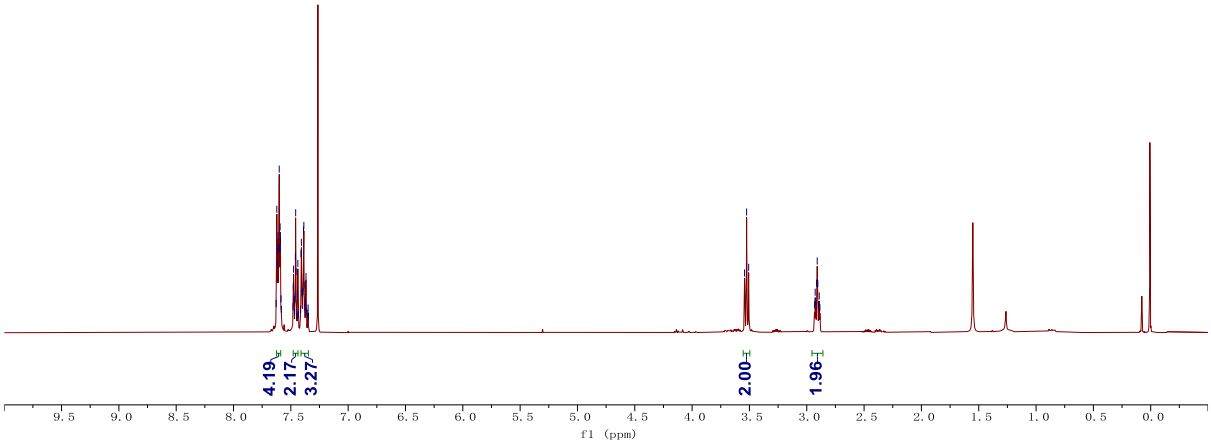
^{13}C NMR spectrum for compound **4ab** ($CDCl_3$)



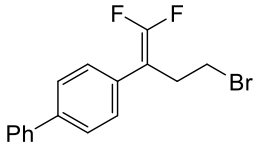
^{19}F NMR spectrum for compound **4ab** ($CDCl_3$)



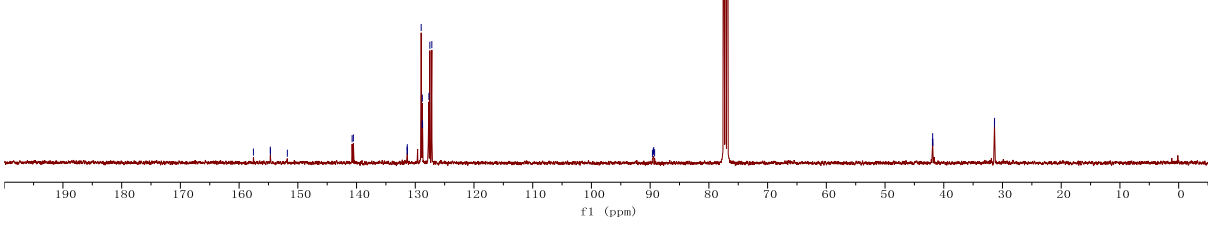
4z, > 20:1



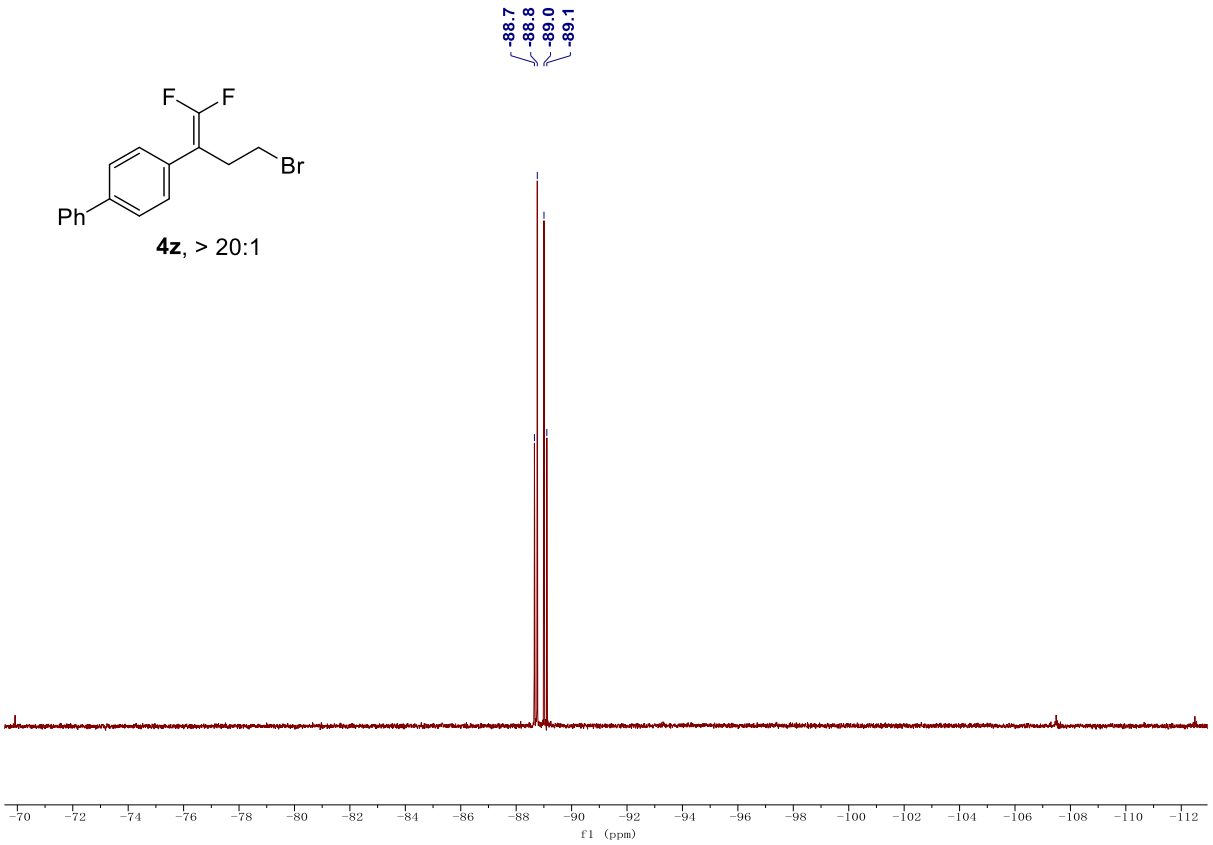
^{1}H NMR spectrum for compound **4z** ($CDCl_3$)



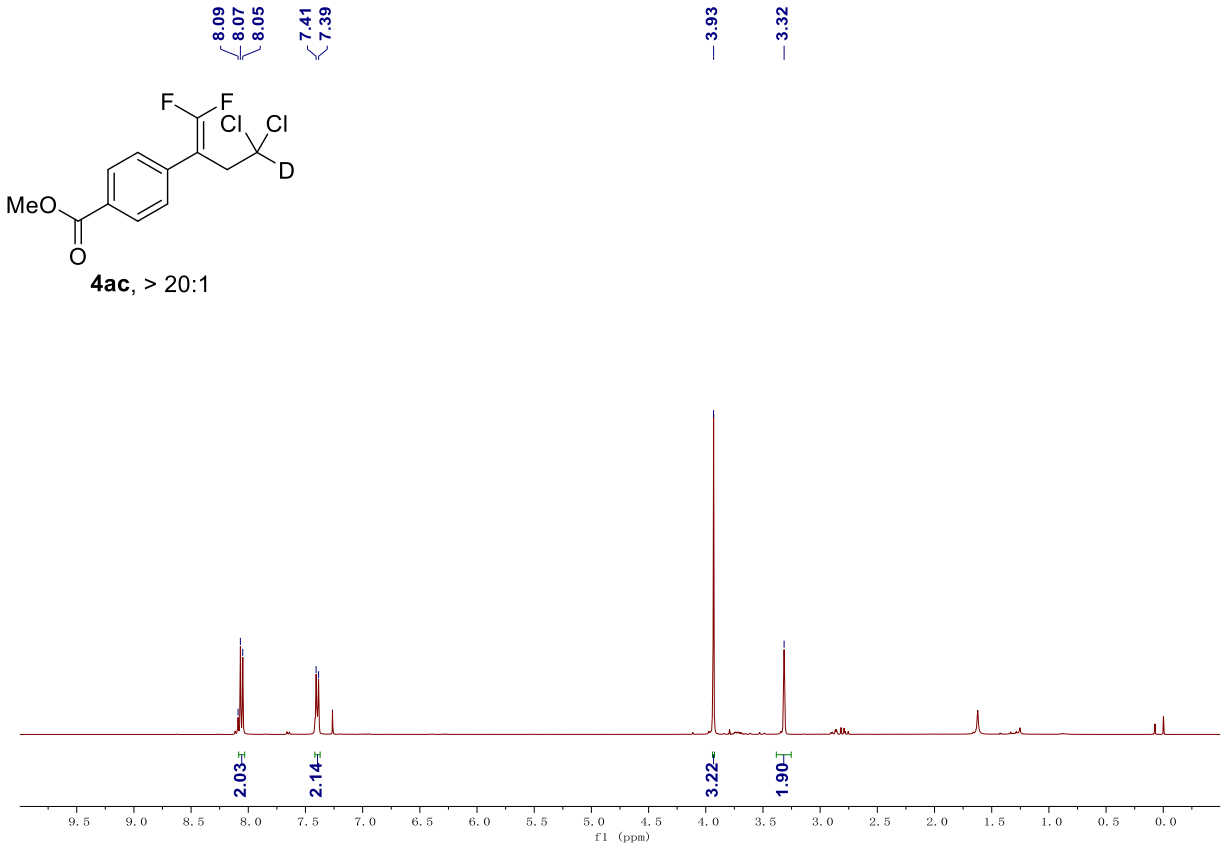
4z, > 20:1



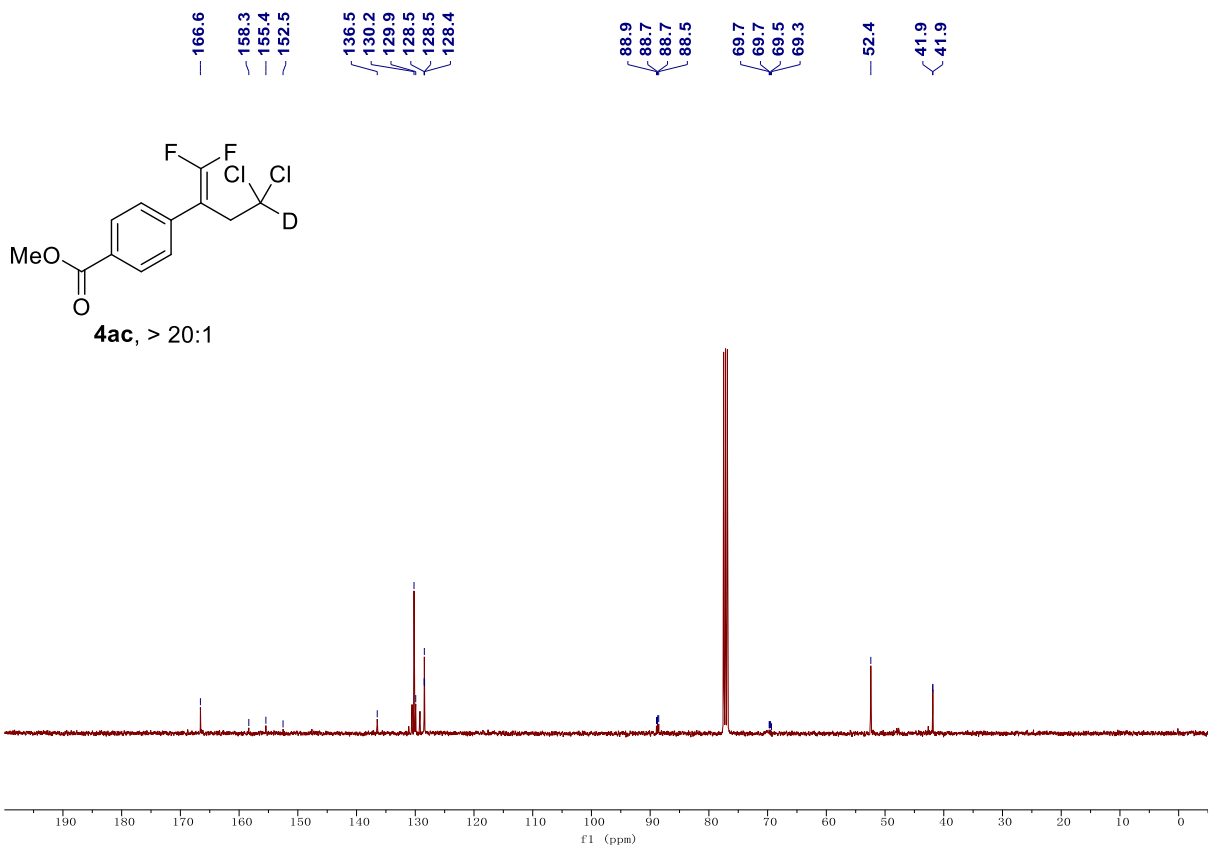
^{13}C NMR spectrum for compound **4z** ($CDCl_3$)



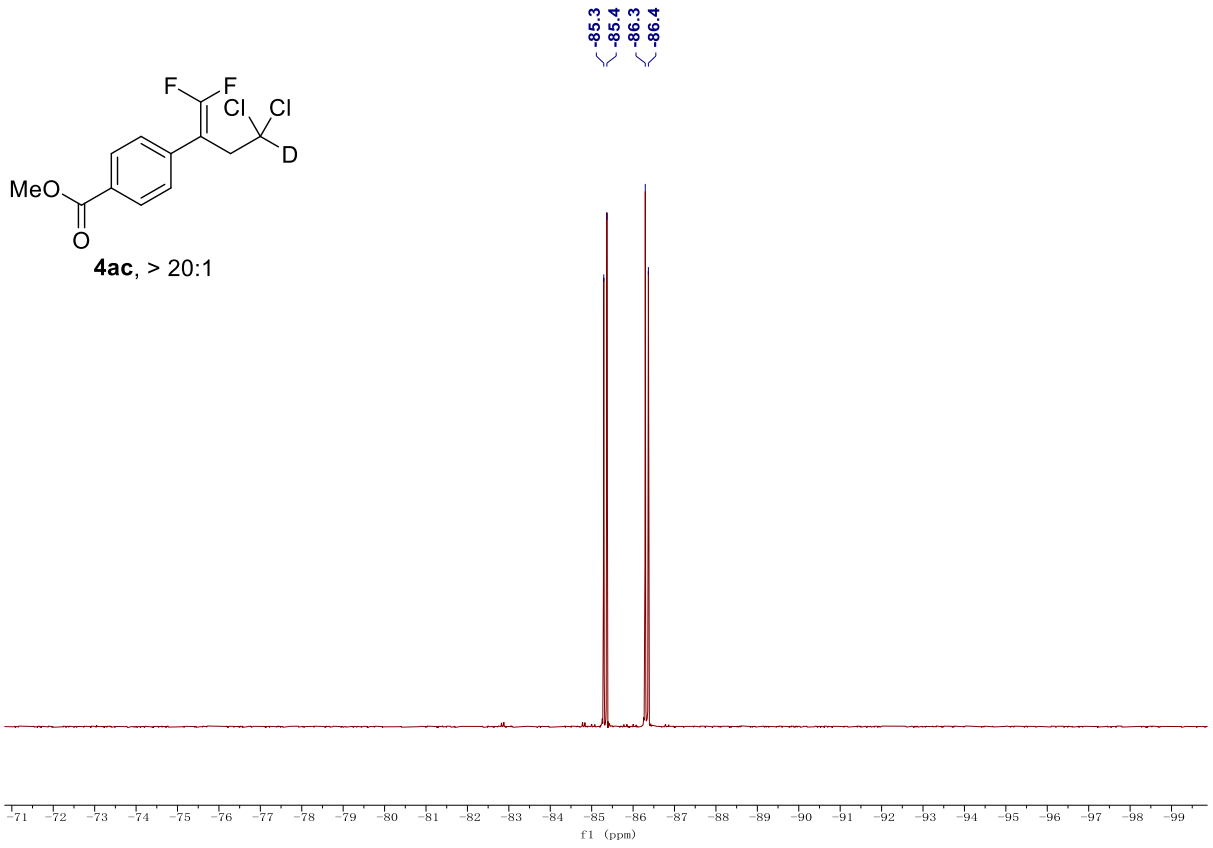
^{19}F NMR spectrum for compound **4z** ($CDCl_3$)



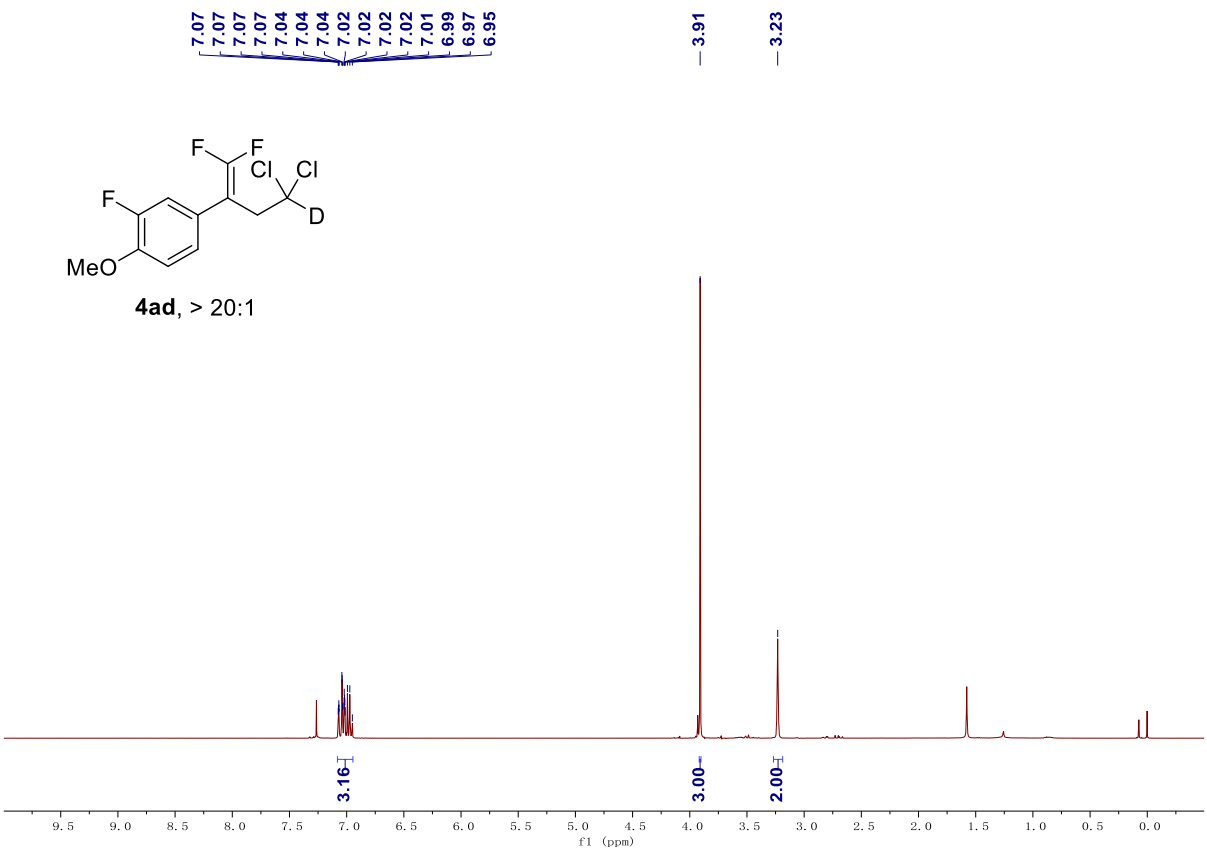
^{1}H NMR spectrum for compound **4ac** ($CDCl_3$)



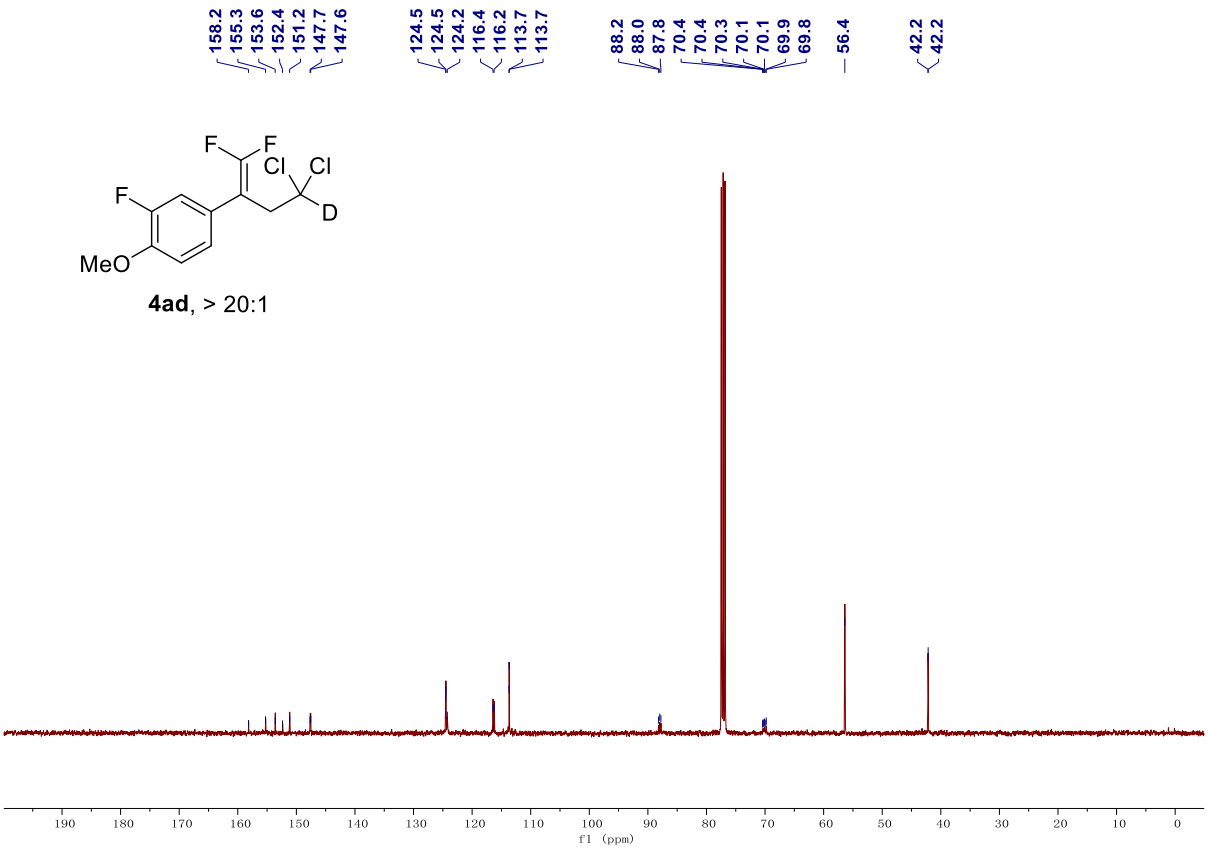
^{13}C NMR spectrum for compound **4ac** ($CDCl_3$)



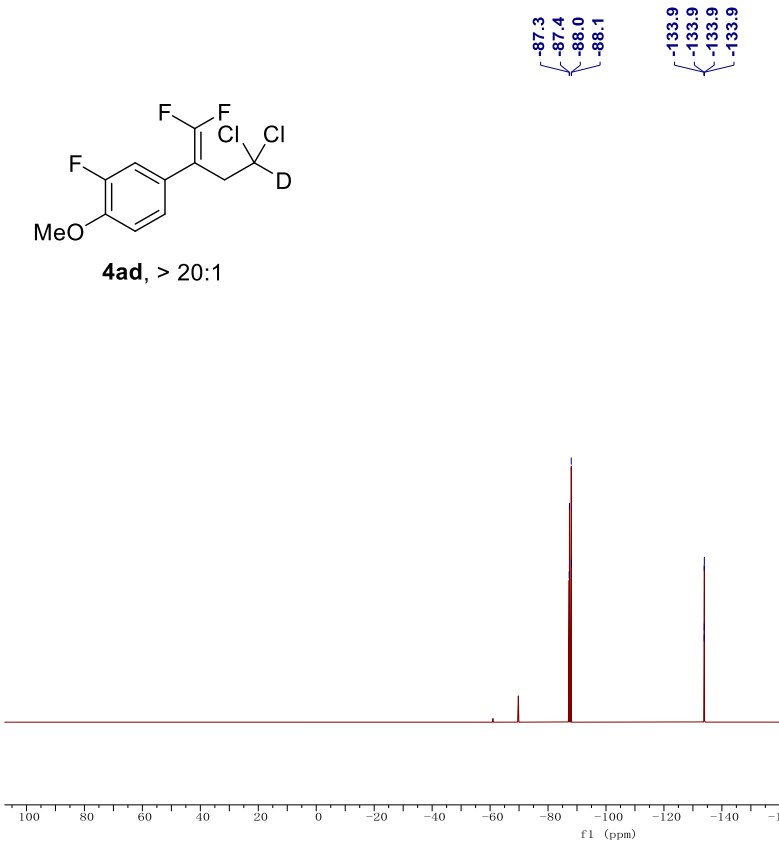
^{19}F NMR spectrum for compound **4ac** ($CDCl_3$)



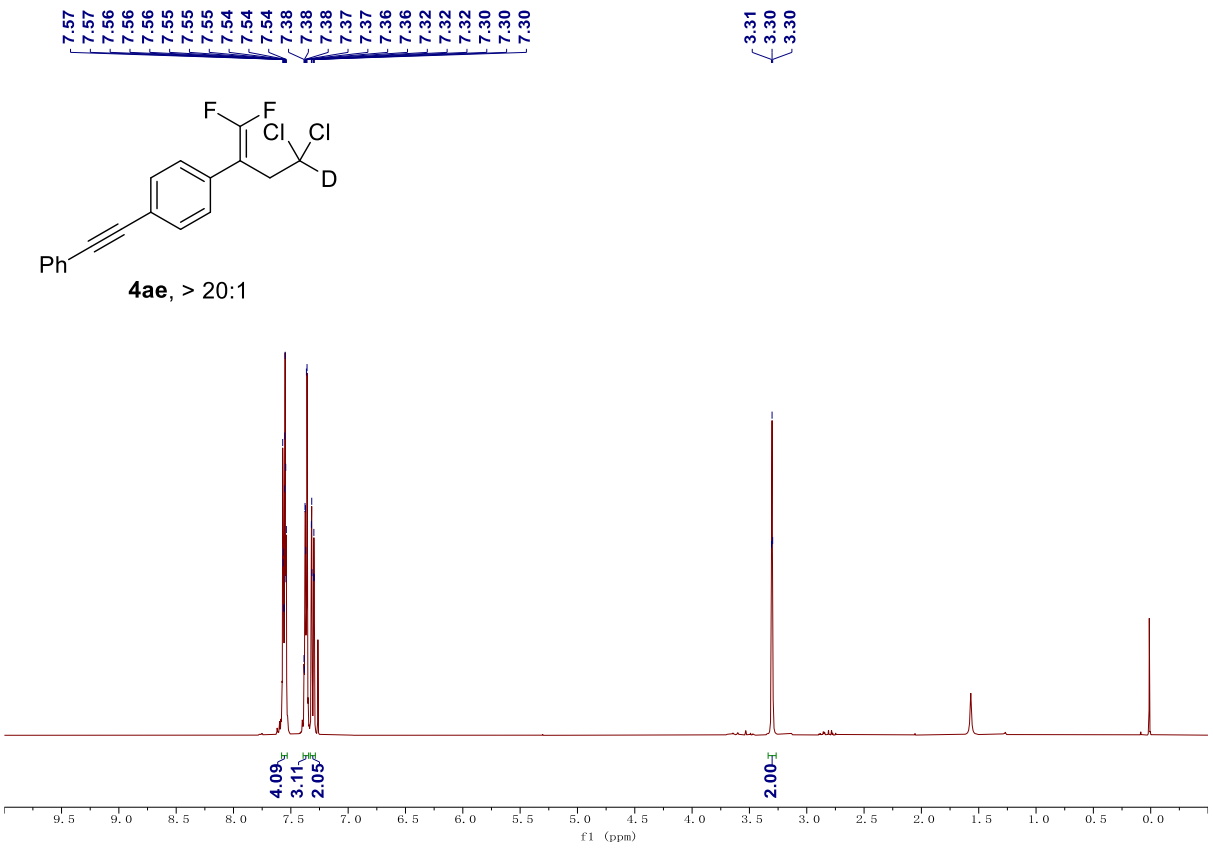
^{1}H NMR spectrum for compound **4ad** ($CDCl_3$)



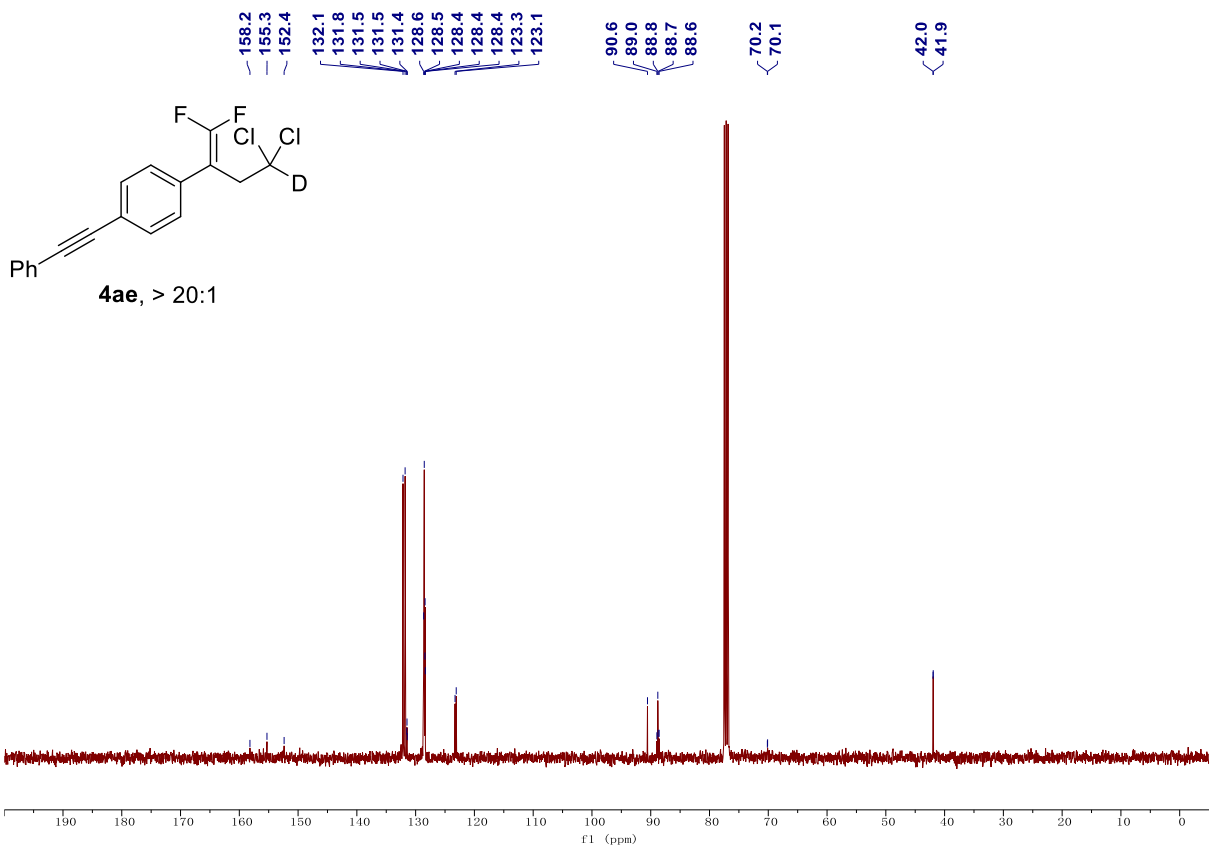
^{13}C NMR spectrum for compound **4ad** ($CDCl_3$)



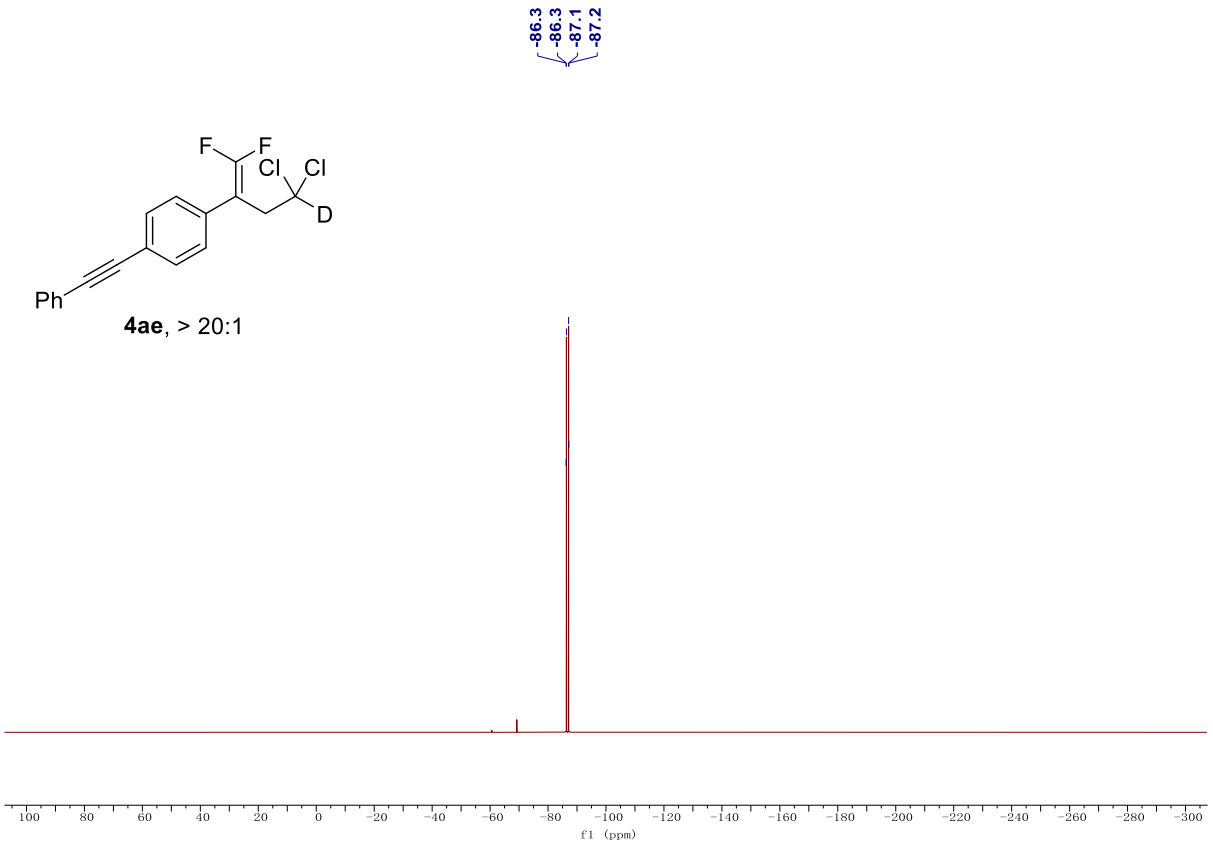
^{19}F NMR spectrum for compound **4ad** ($CDCl_3$)



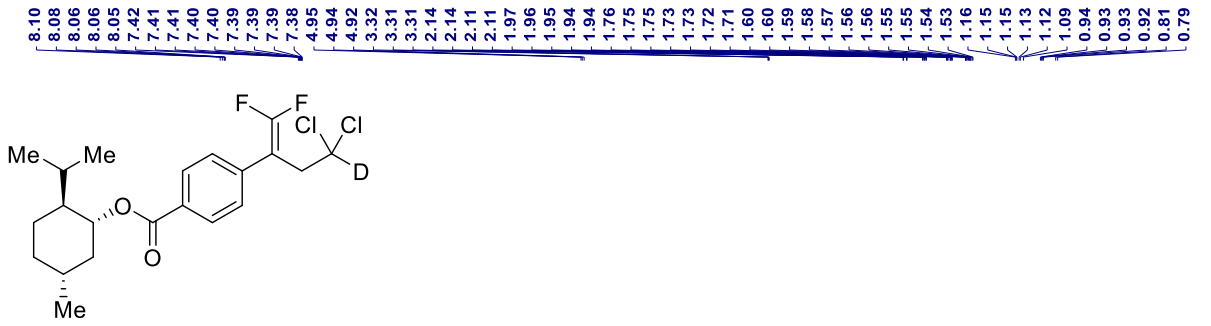
^{1}H NMR spectrum for compound **4ae** ($CDCl_3$)



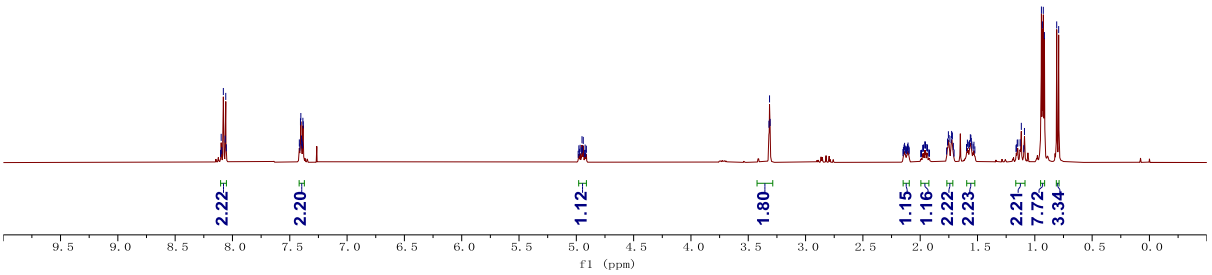
^{13}C NMR spectrum for compound **4ae** ($CDCl_3$)



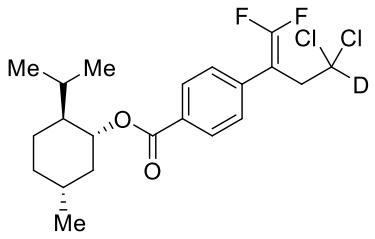
^{19}F NMR spectrum for compound **4ae** ($CDCl_3$)



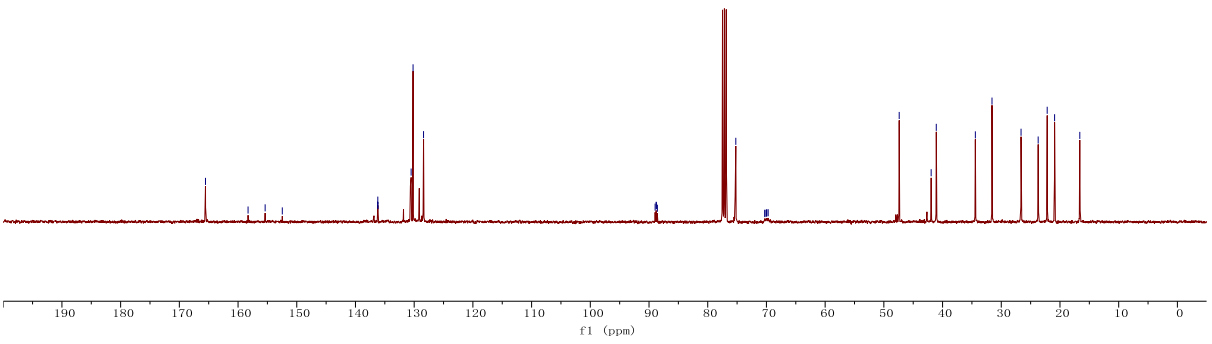
4af, > 20:1



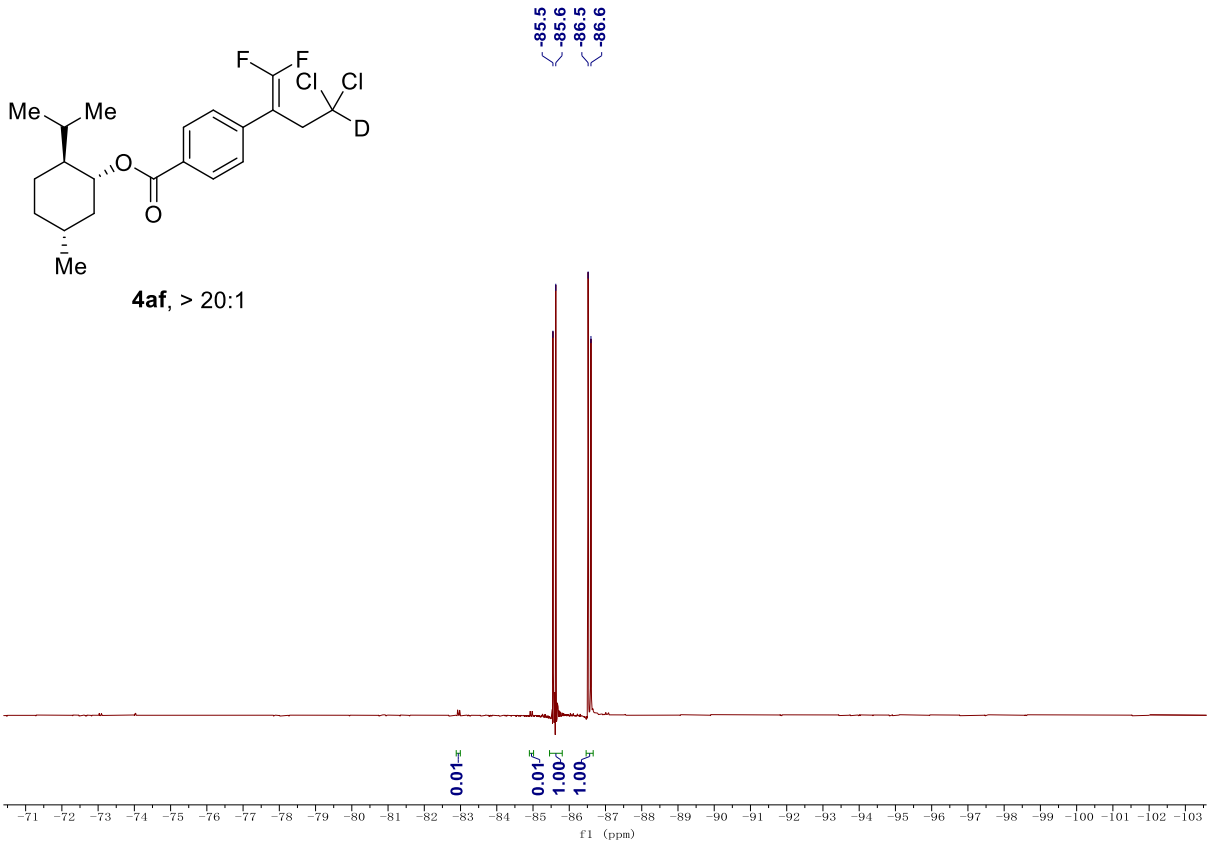
^{1}H NMR spectrum for compound **4af** ($CDCl_3$)



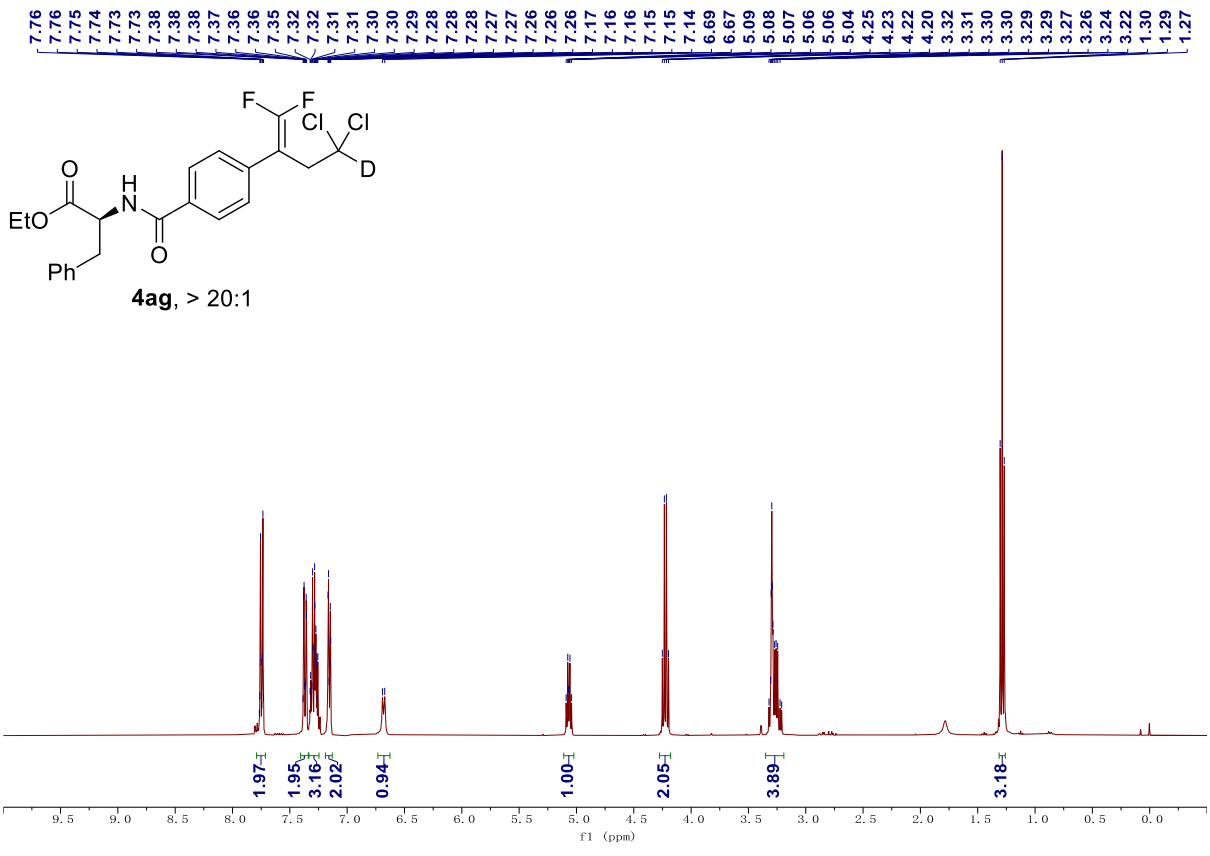
4af, > 20:1



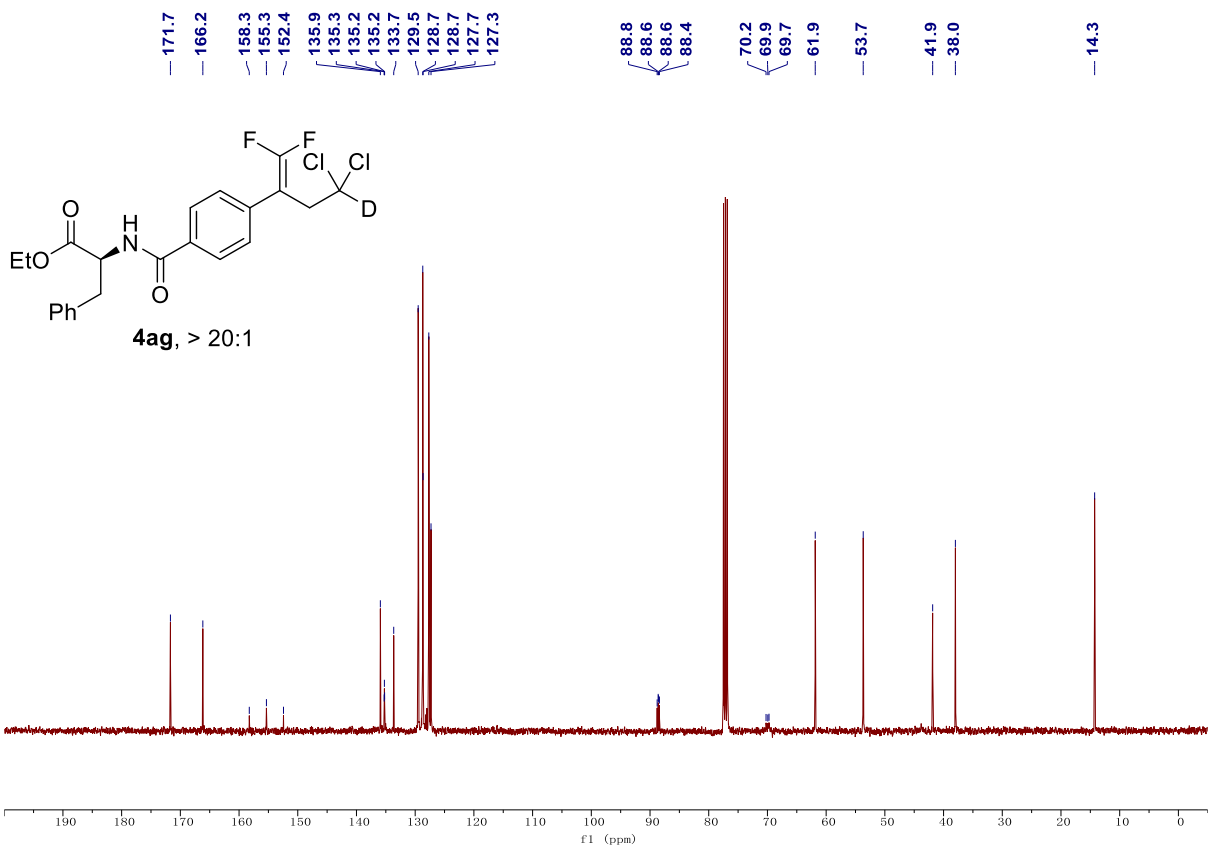
^{13}C NMR spectrum for compound **4af** ($CDCl_3$)



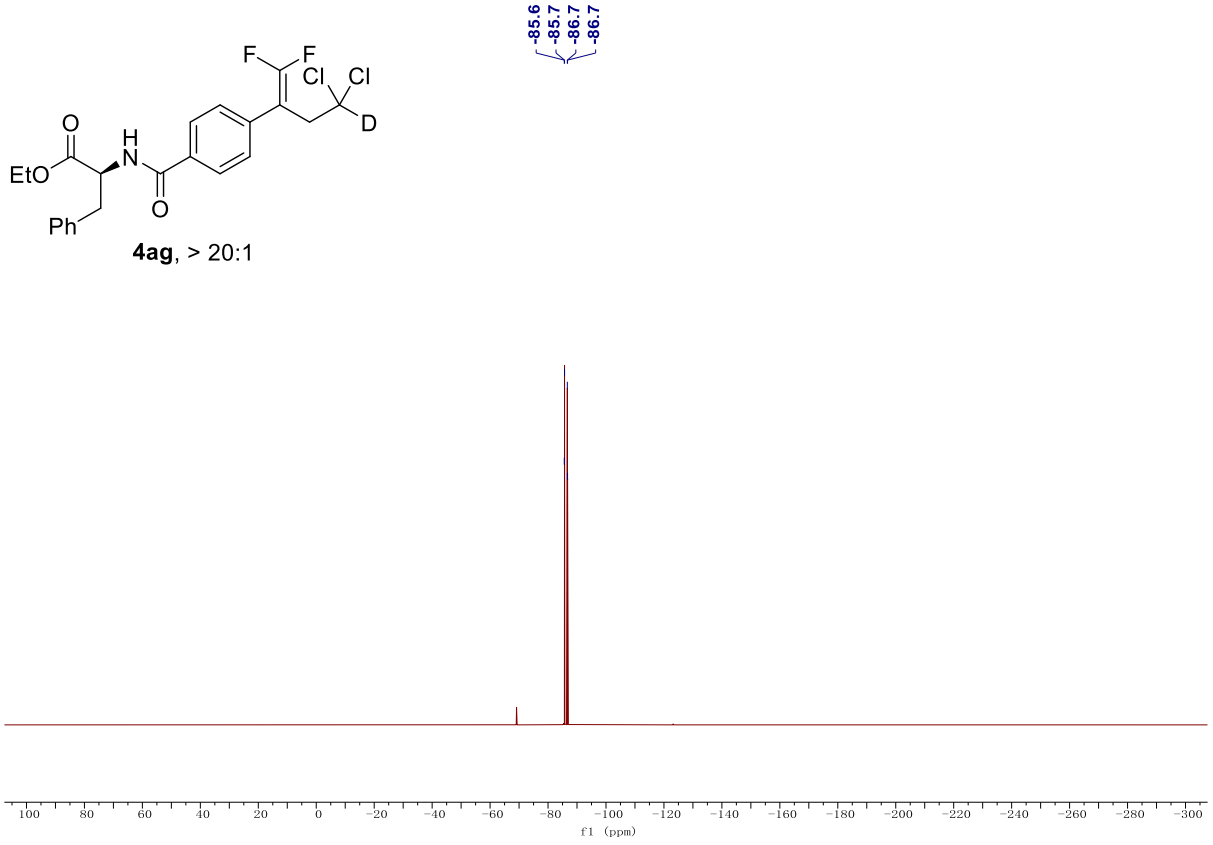
^{19}F NMR spectrum for compound **4af** ($CDCl_3$)



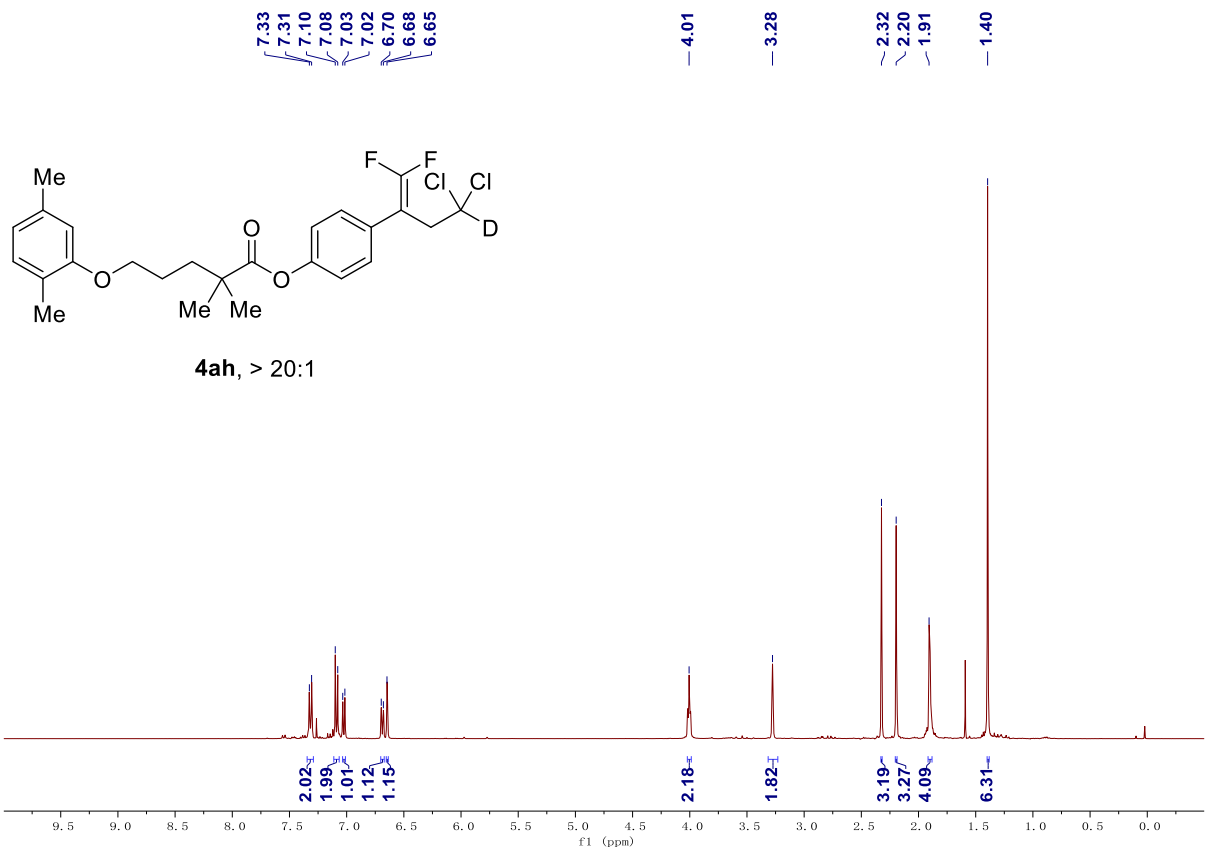
^{1}H NMR spectrum for compound **4ag** ($CDCl_3$)



^{13}C NMR spectrum for compound **4ag** ($CDCl_3$)

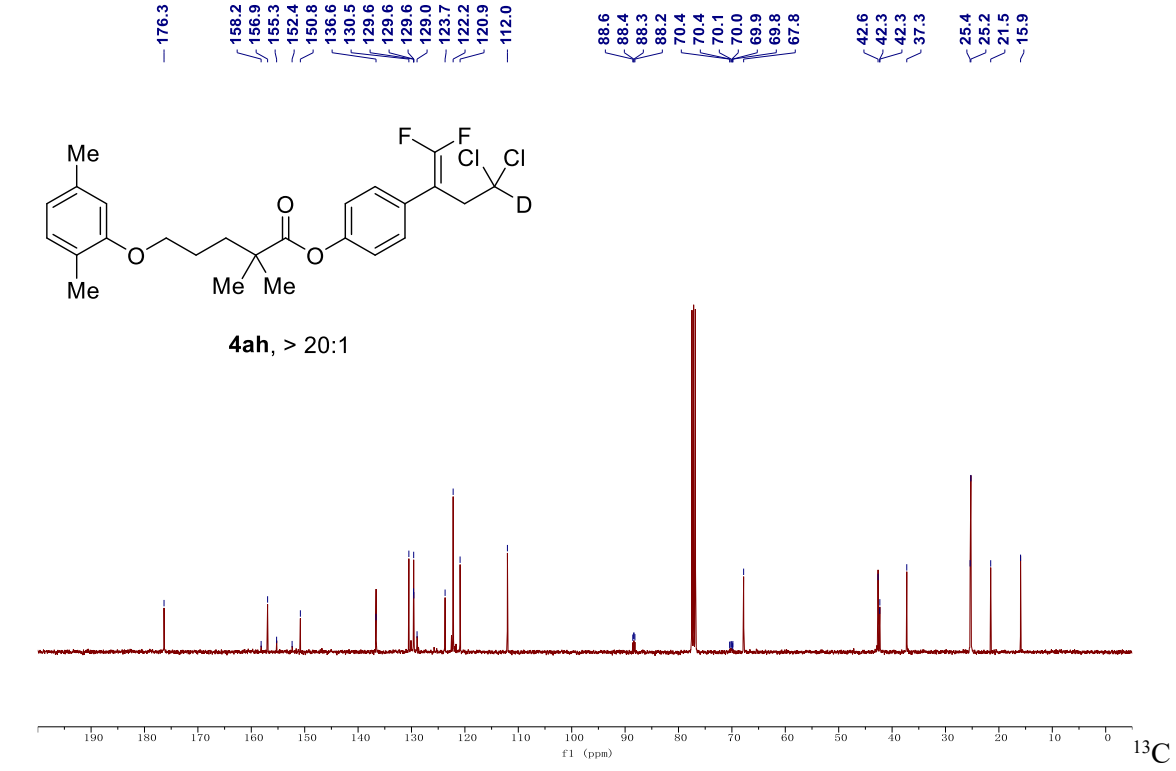


^{19}F NMR spectrum for compound **4ag** ($CDCl_3$)



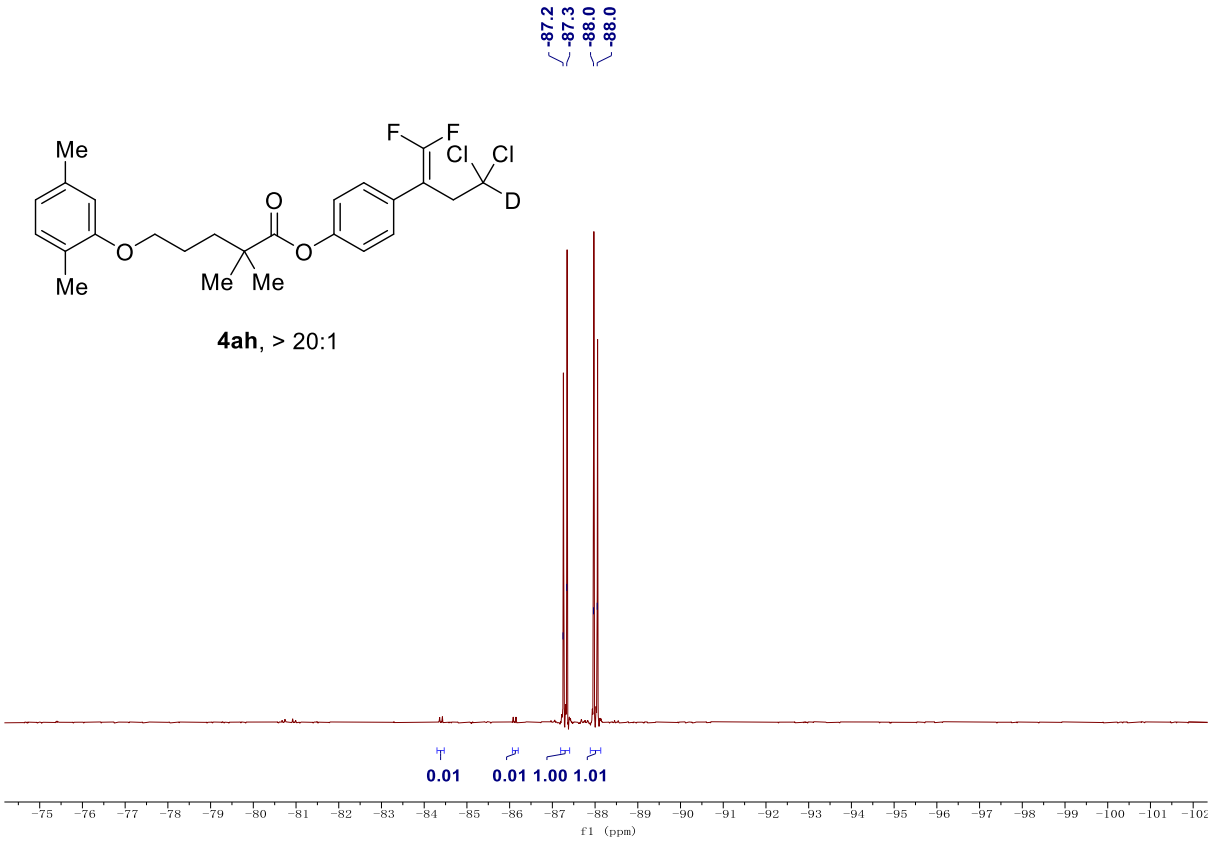
4ah, > 20:1

^{1}H NMR spectrum for compound **4ah** ($CDCl_3$)



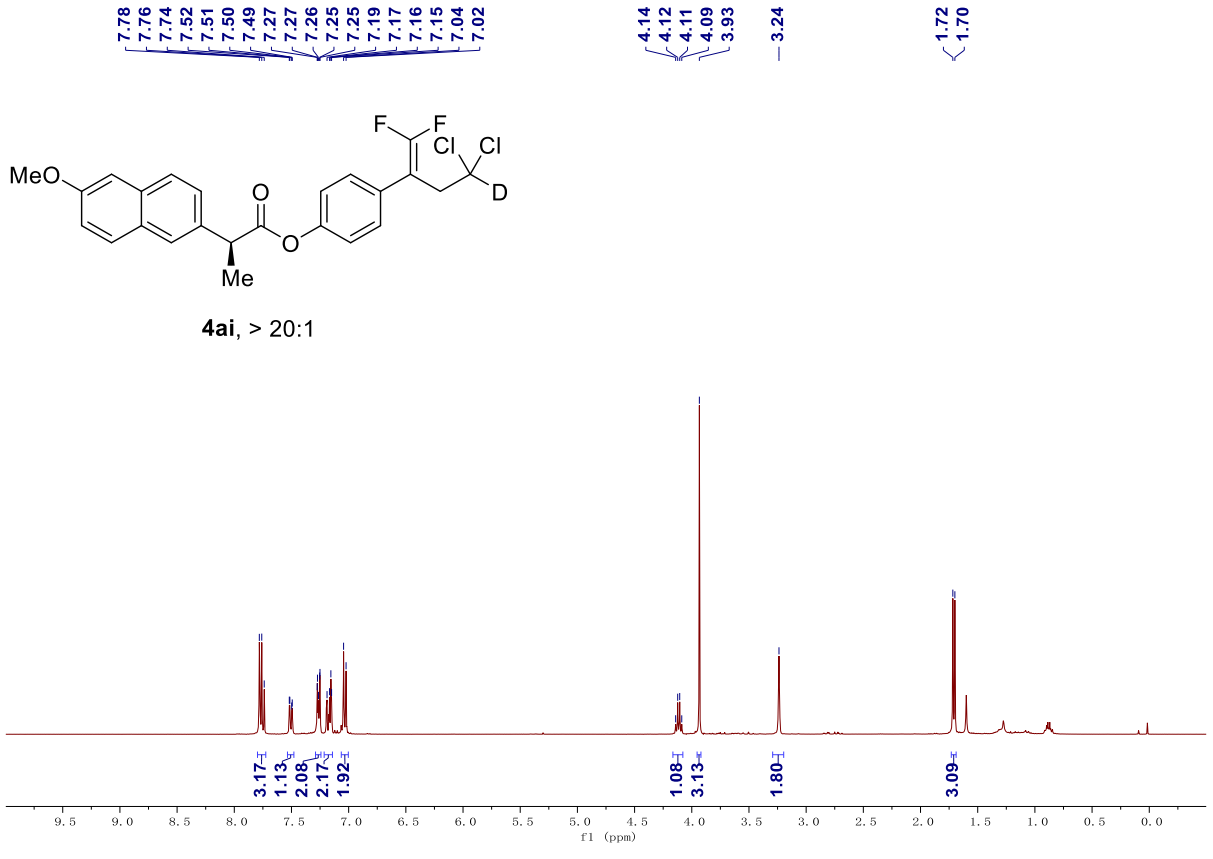
4ah, > 20:1

^{13}C NMR spectrum for compound **4ah** ($CDCl_3$)



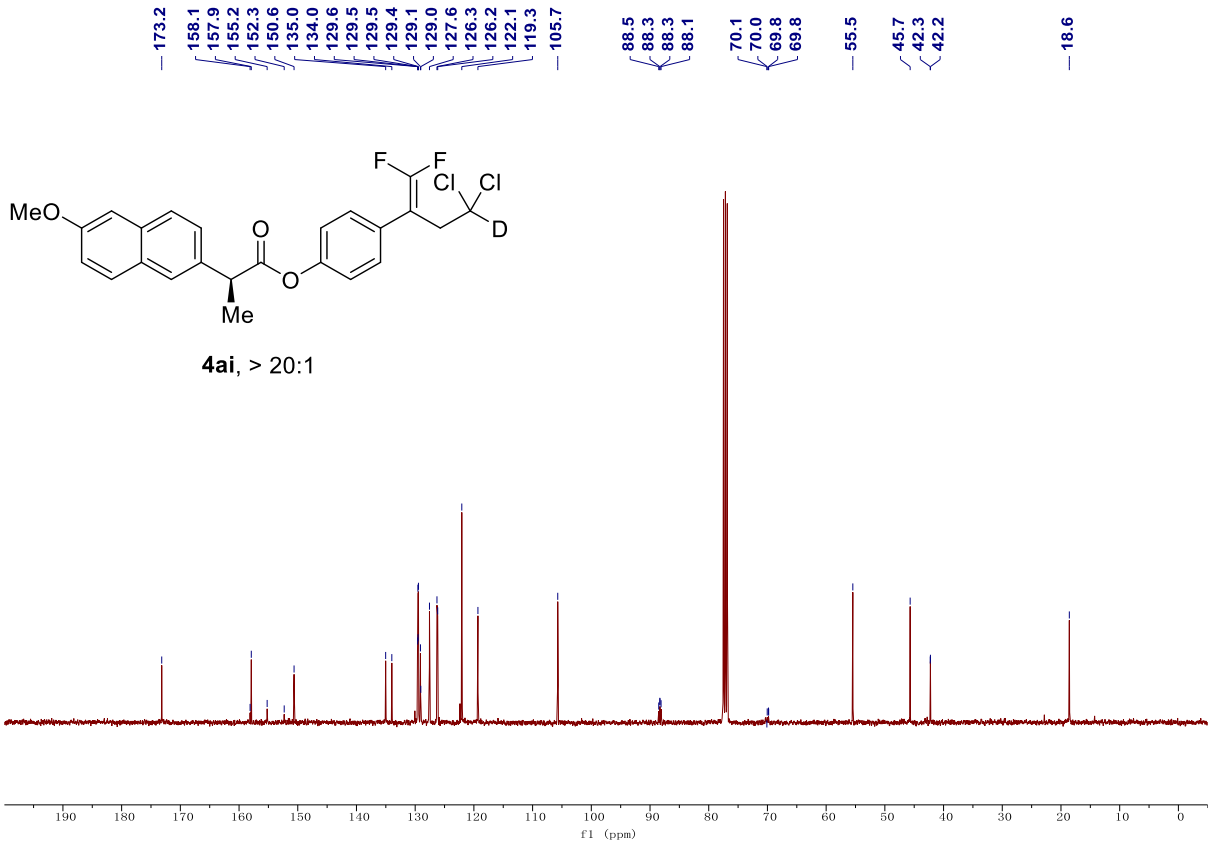
4ah, > 20:1

^{19}F NMR spectrum for compound **4ah** ($CDCl_3$)

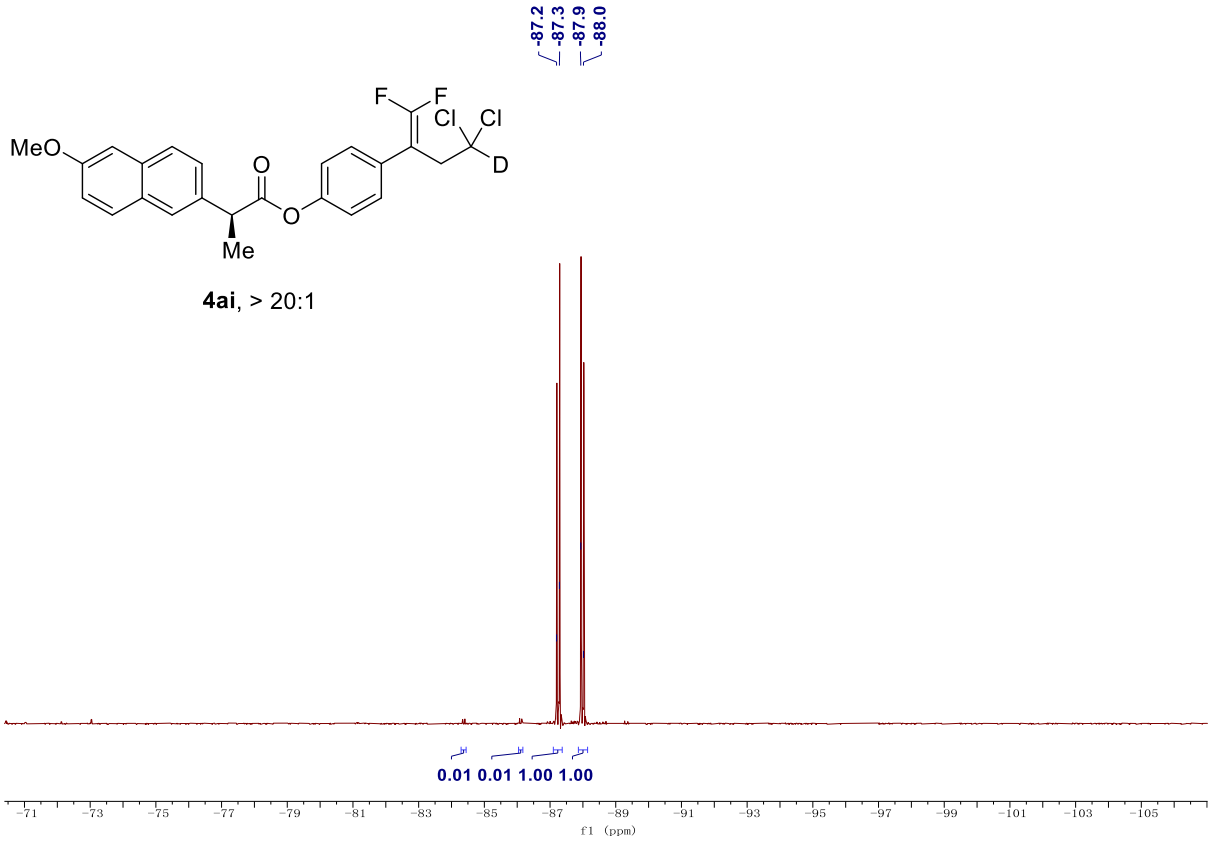


4ai, > 20:1

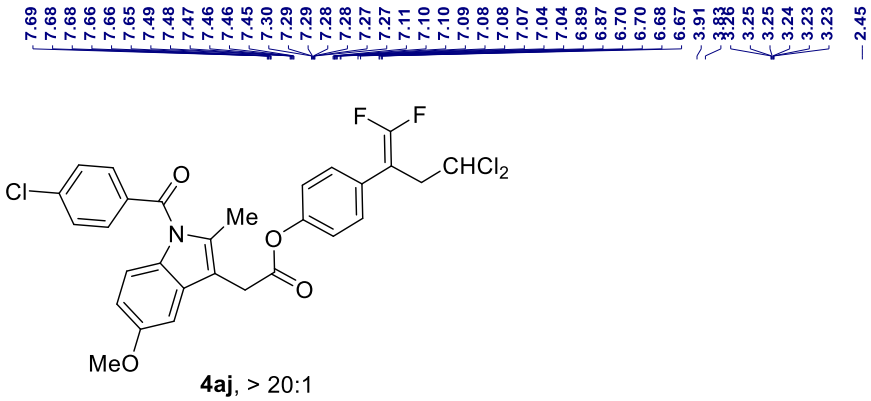
^{1}H NMR spectrum for compound **4ai** ($CDCl_3$)



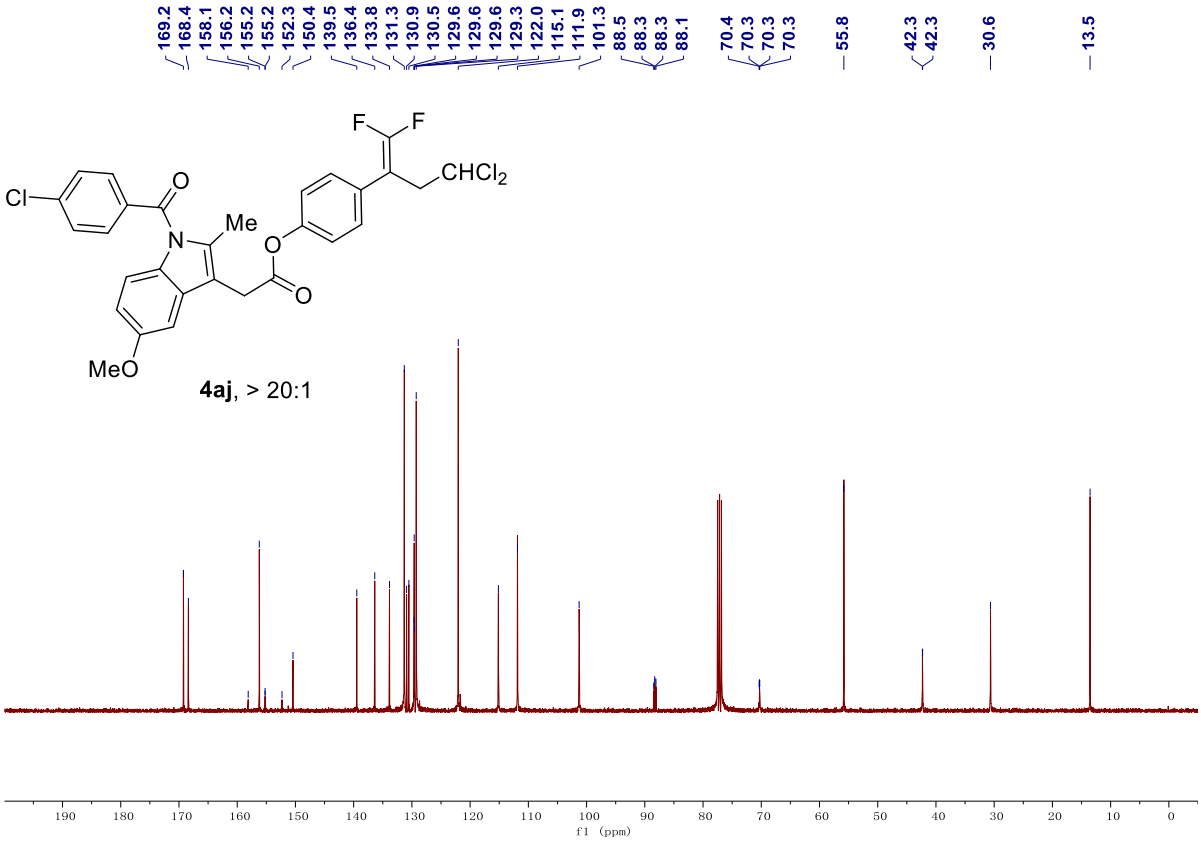
^{13}C NMR spectrum for compound **4ai** ($CDCl_3$)



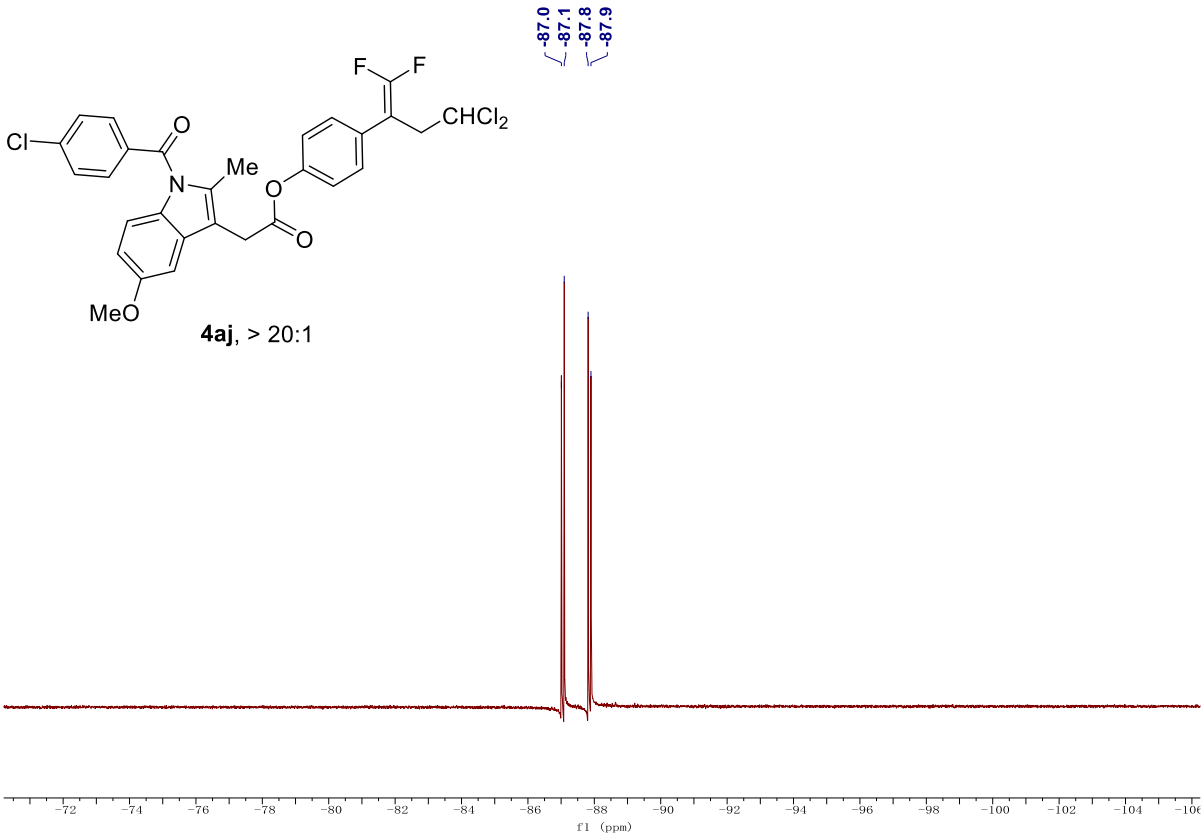
^{19}F NMR spectrum for compound **4ai** ($CDCl_3$)



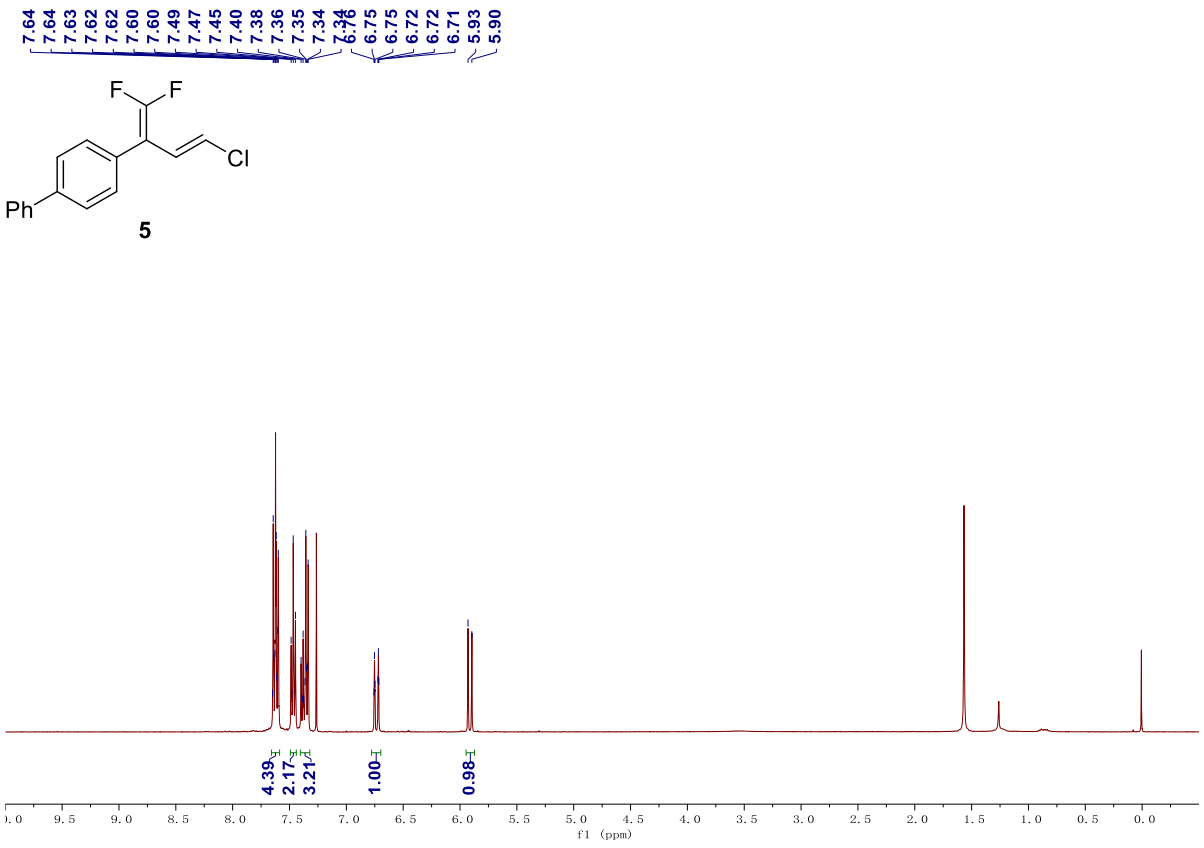
^{1}H NMR spectrum for compound **4aj** ($CDCl_3$)



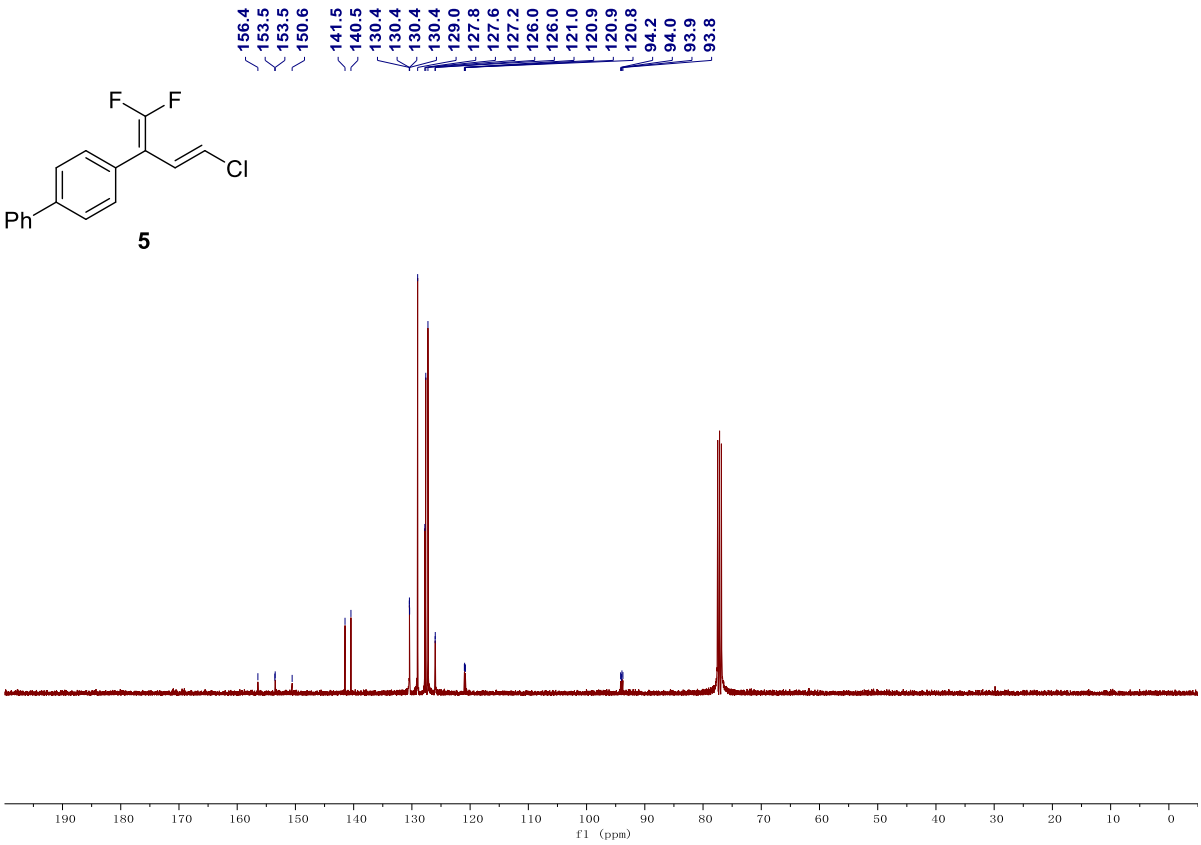
^{13}C NMR spectrum for compound **4aj** ($CDCl_3$)



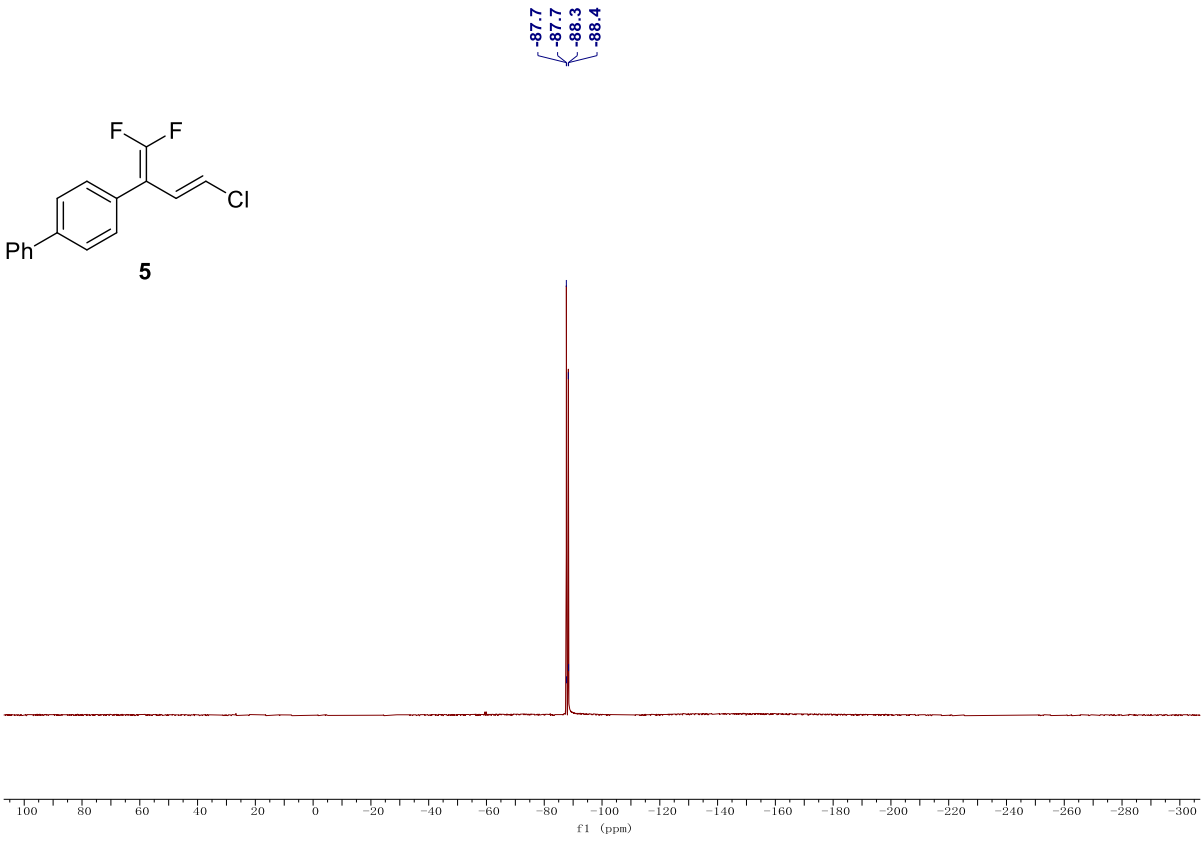
^{19}F NMR spectrum for compound **4aj** ($CDCl_3$)



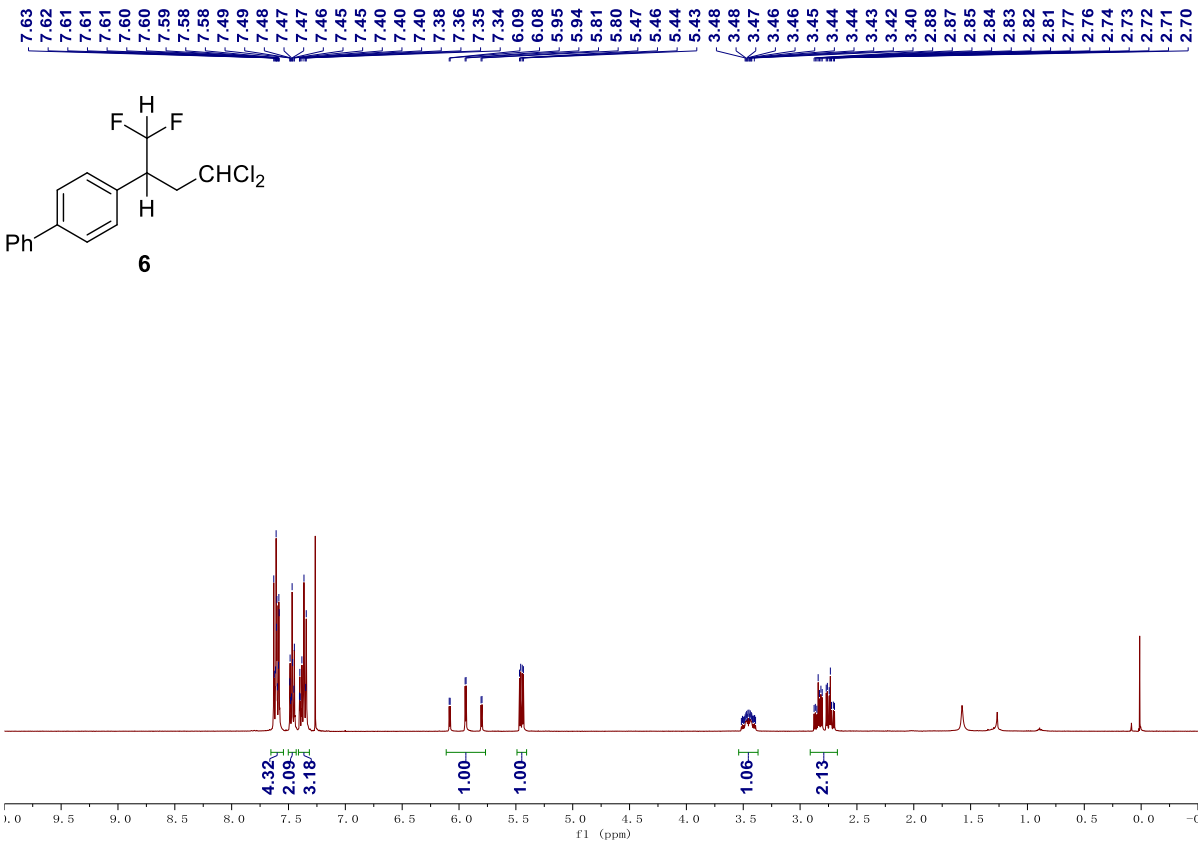
^{1}H NMR spectrum for compound **5** ($CDCl_3$)



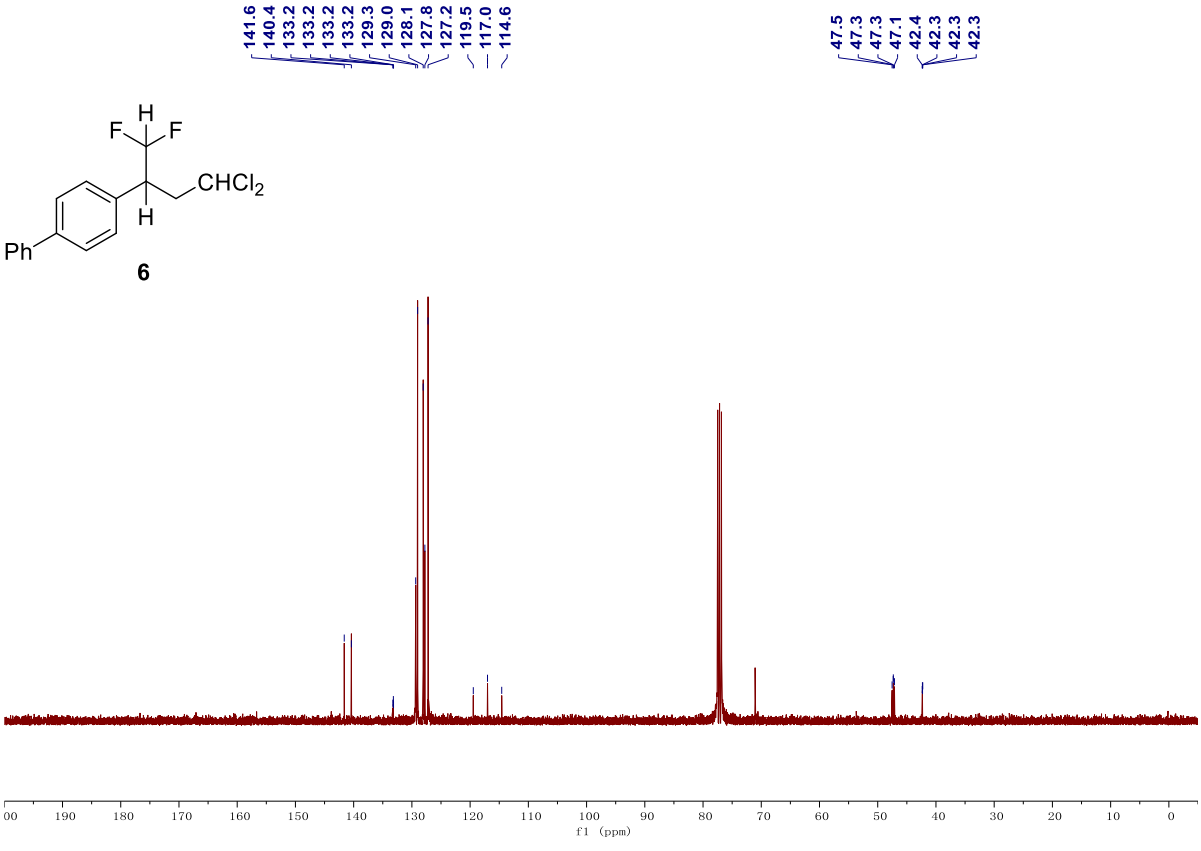
^{13}C NMR spectrum for compound **5** ($CDCl_3$)



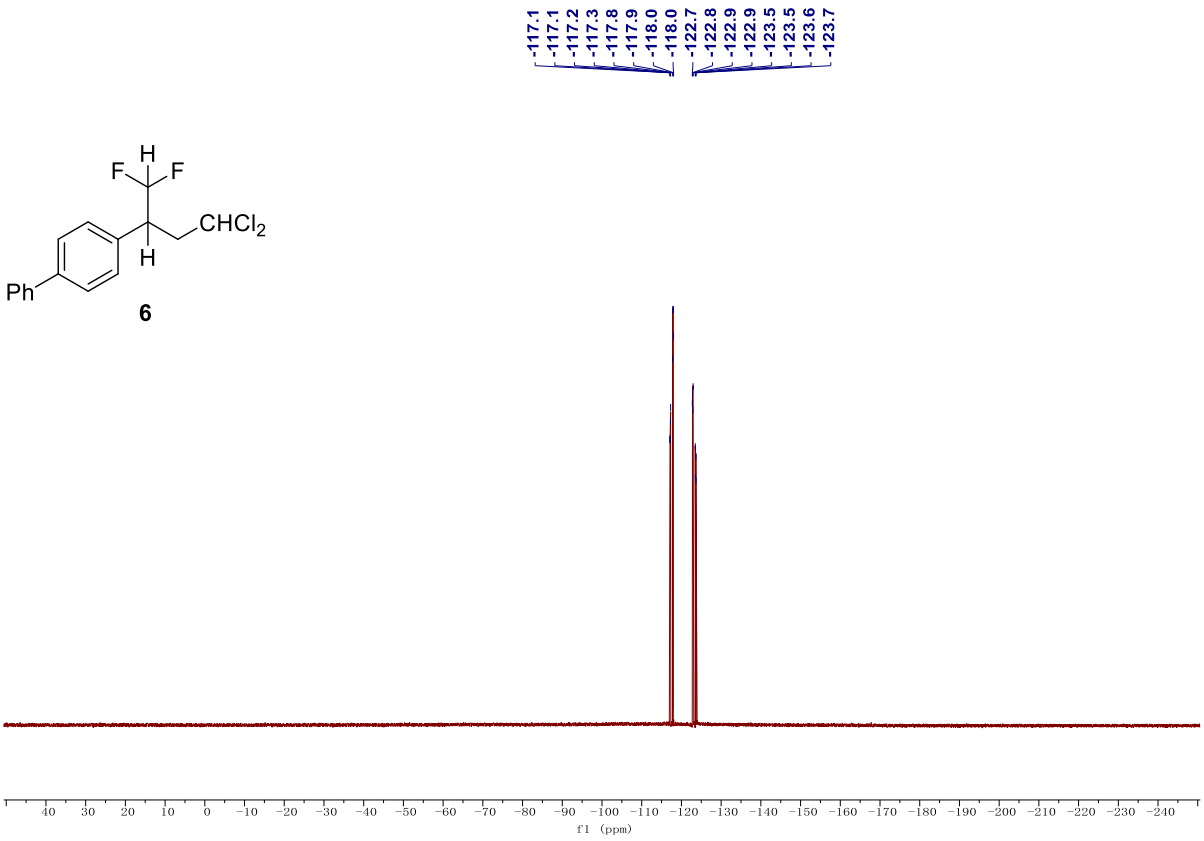
^{19}F NMR spectrum for compound **5** ($CDCl_3$)



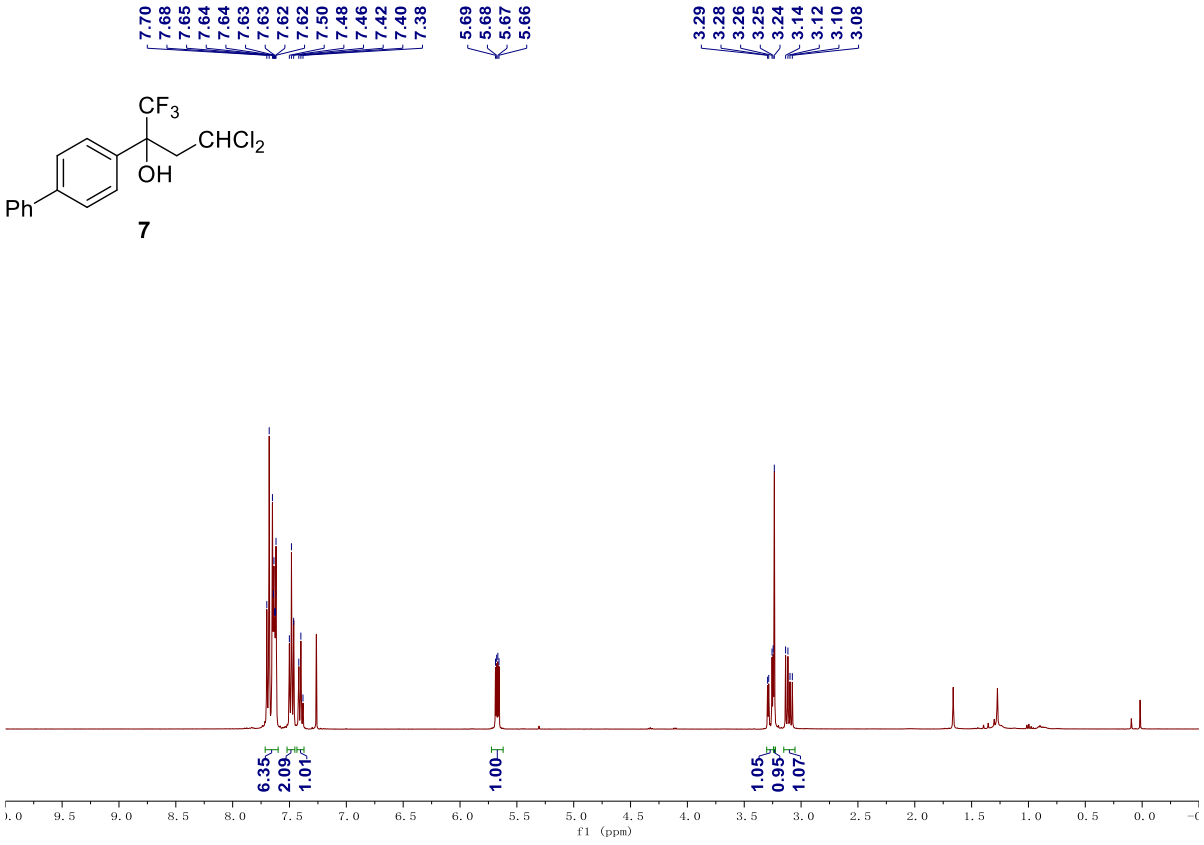
^{1}H NMR spectrum for compound **6** ($CDCl_3$)



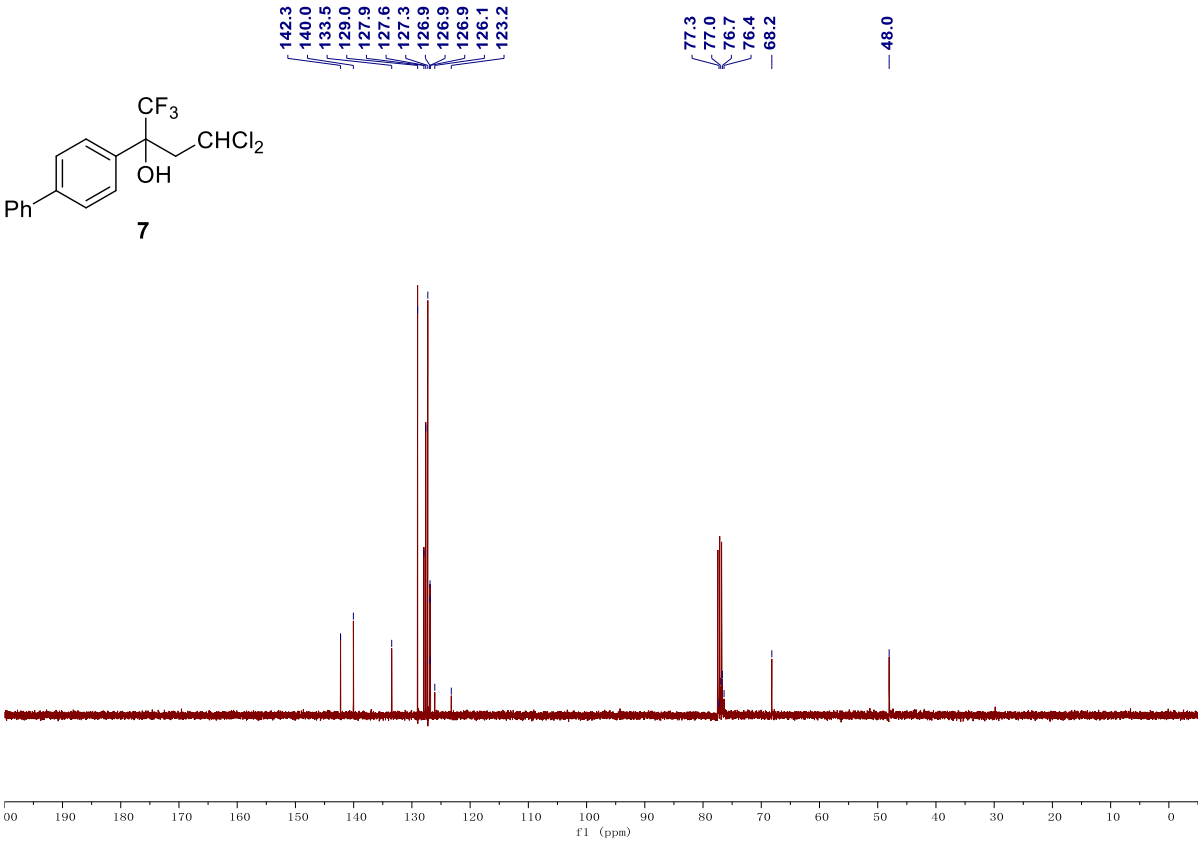
^{13}C NMR spectrum for compound **6** ($CDCl_3$)



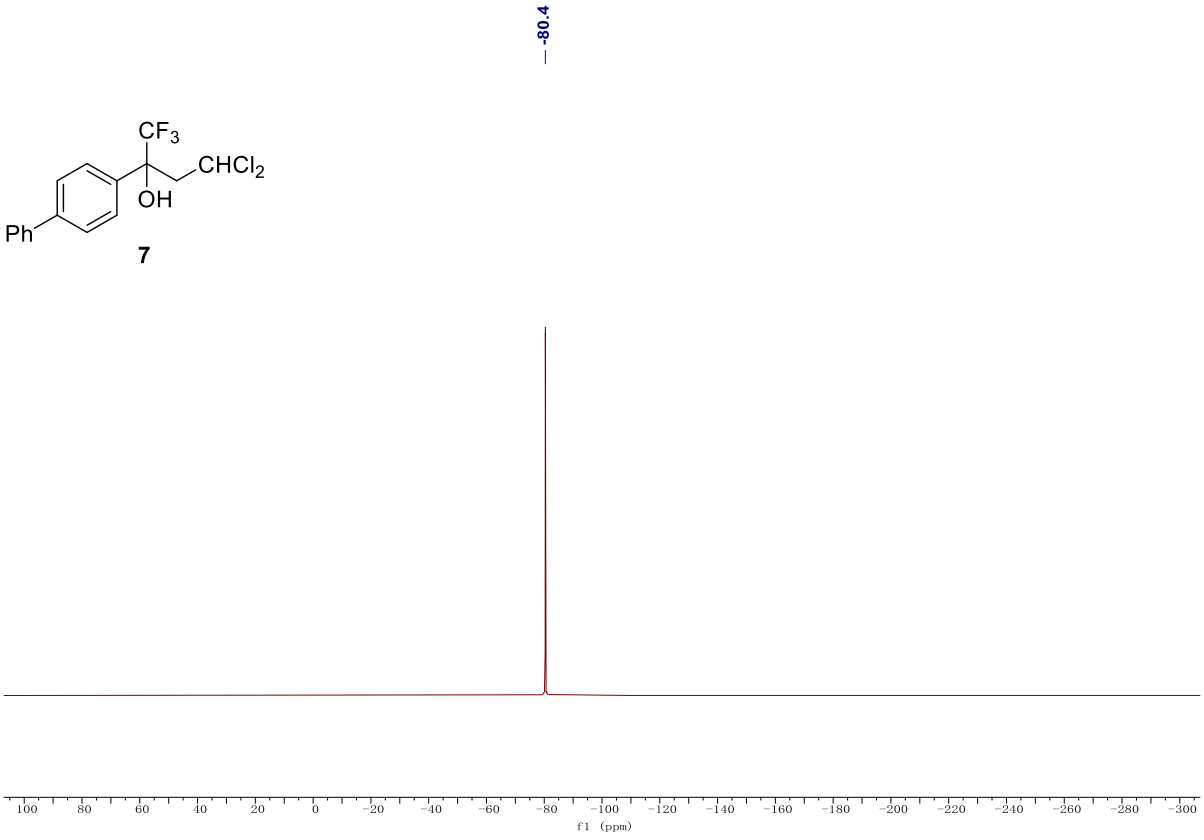
^{19}F NMR spectrum for compound **6** ($CDCl_3$)



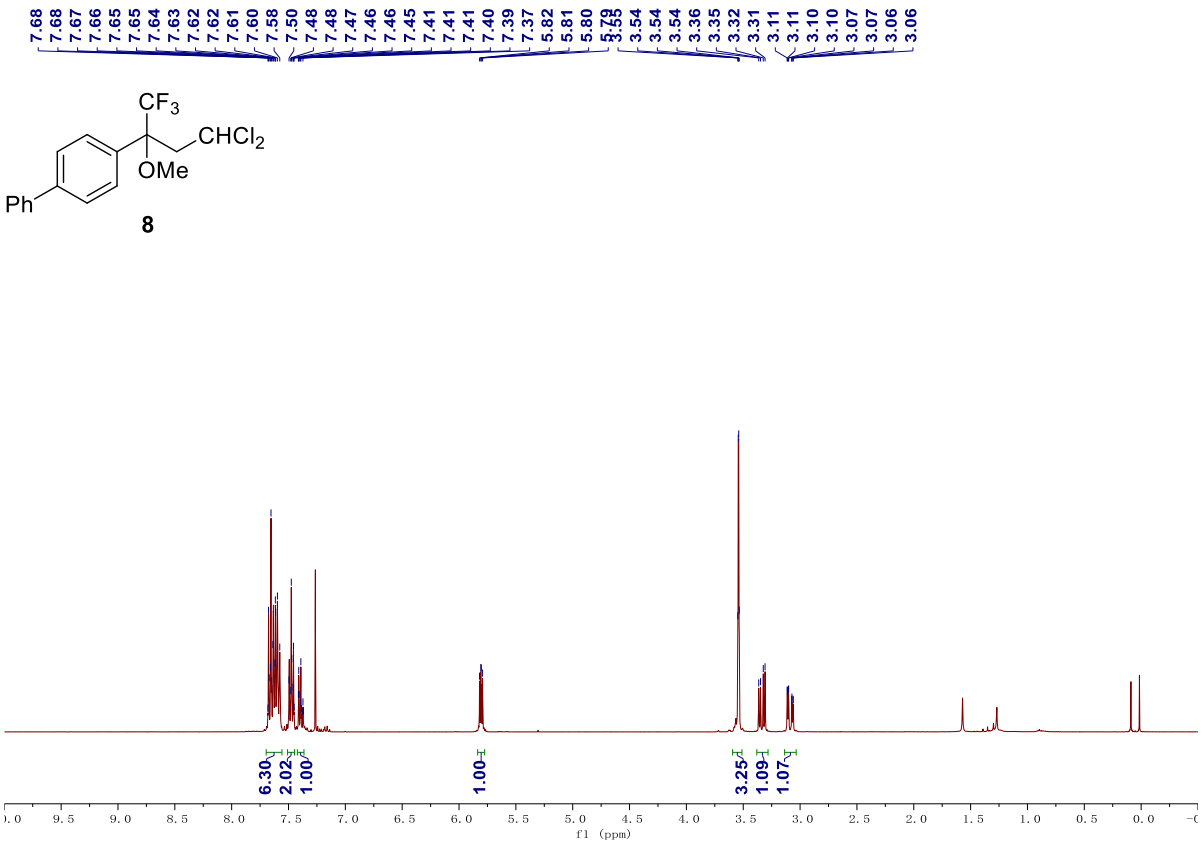
^{1}H NMR spectrum for compound **7** ($CDCl_3$)



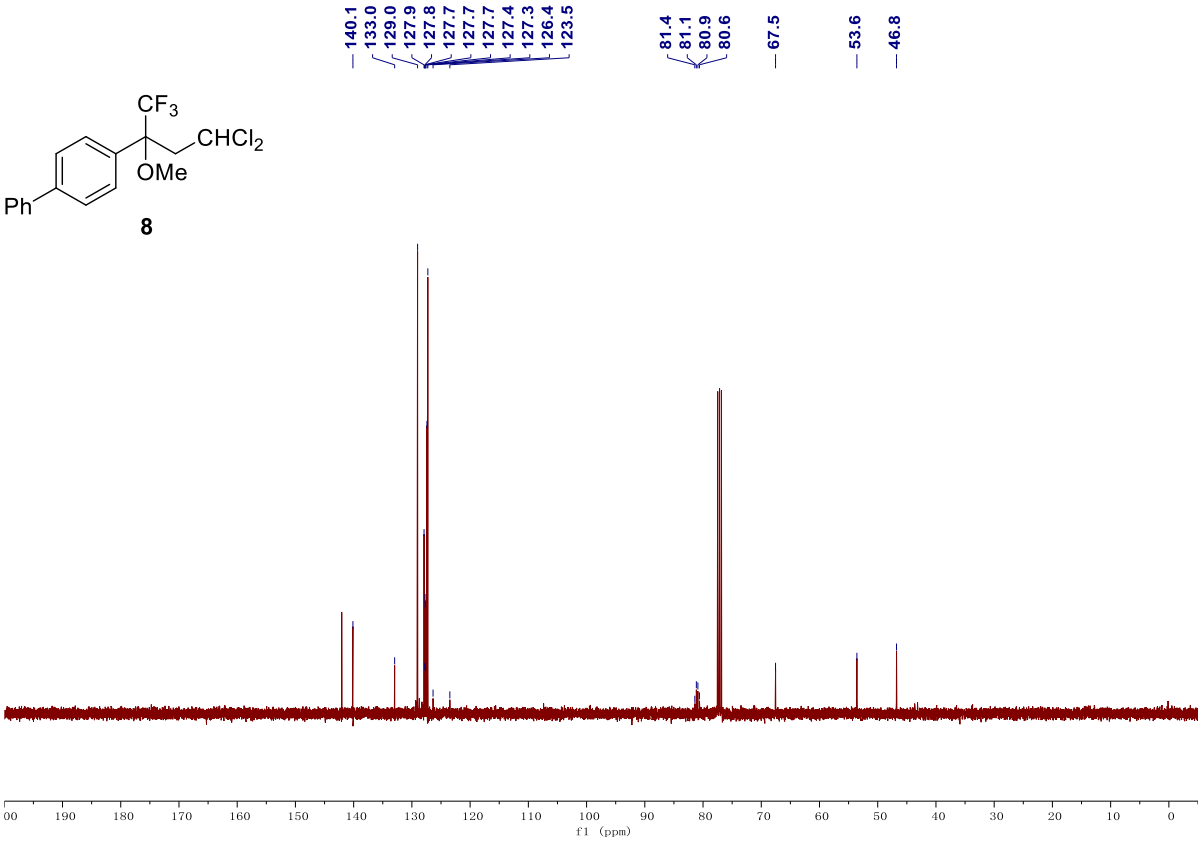
^{13}C NMR spectrum for compound **7** ($CDCl_3$)



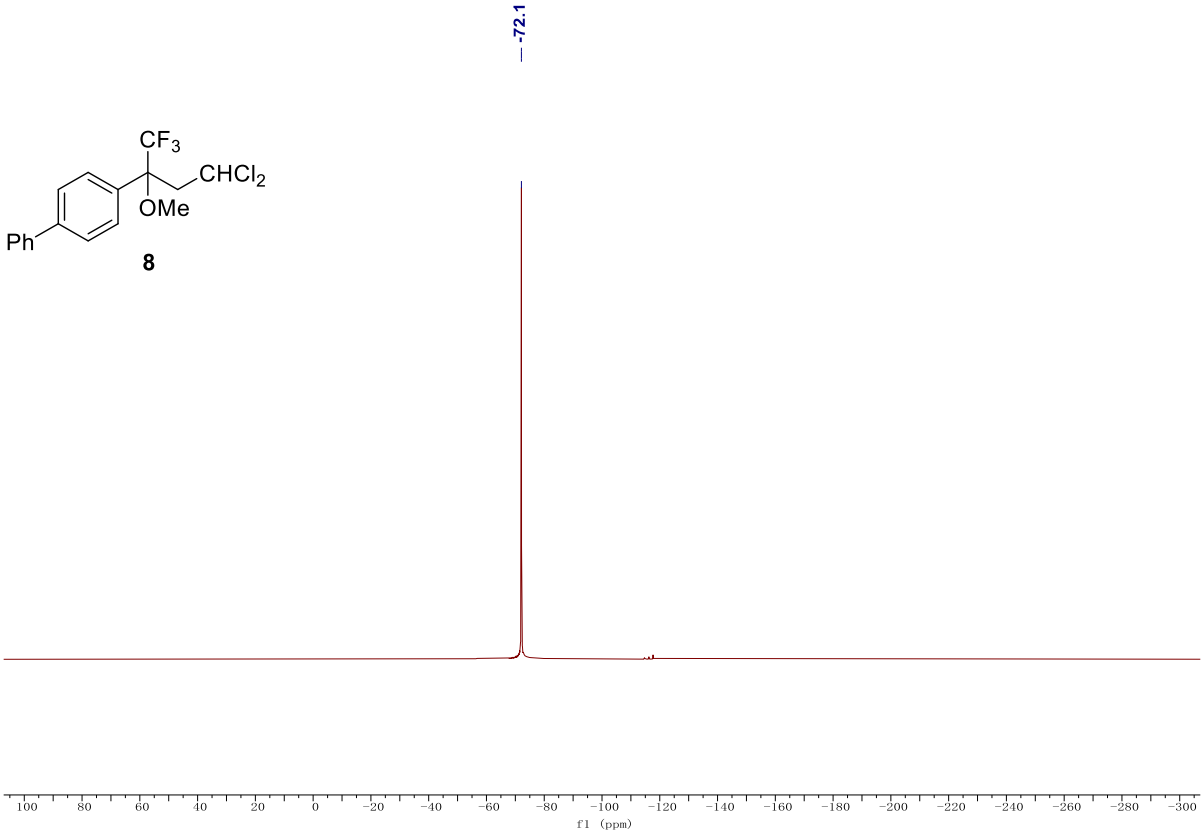
^{19}F NMR spectrum for compound **7** ($CDCl_3$)



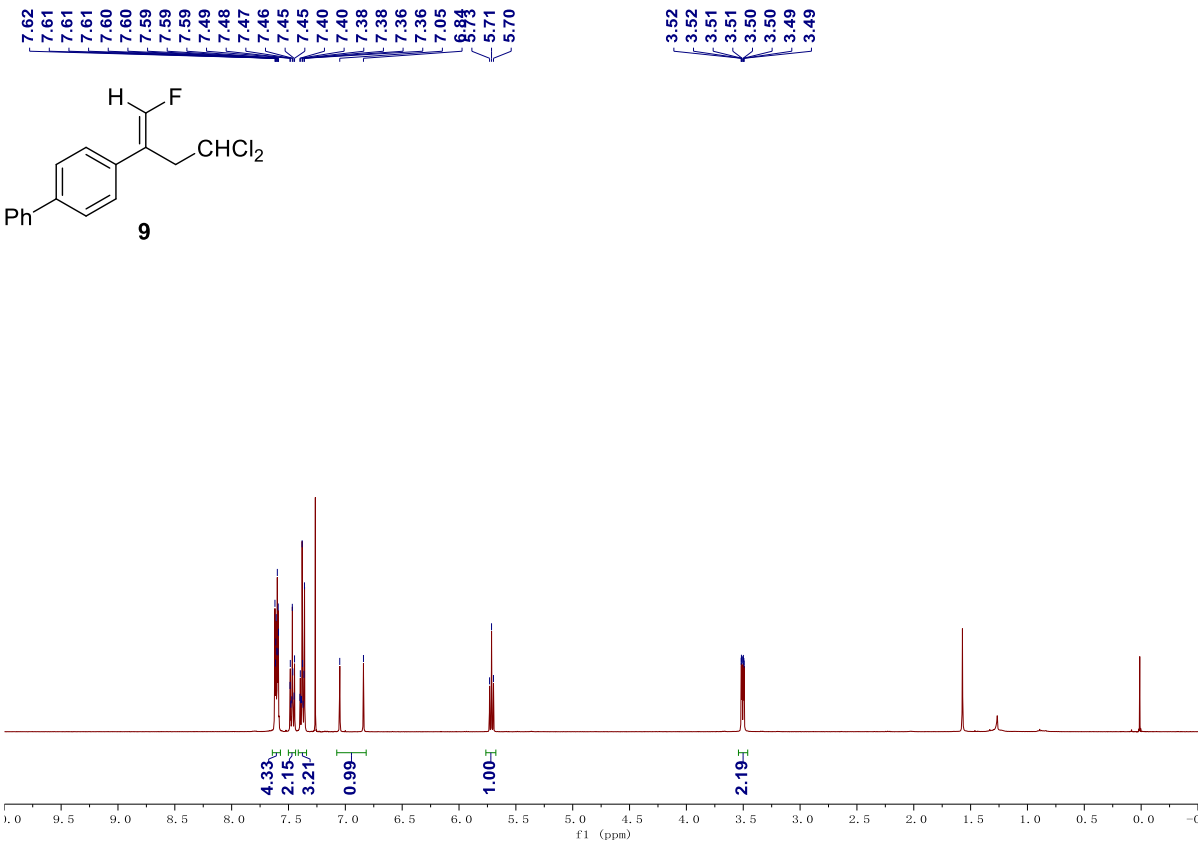
^{1}H NMR spectrum for compound **8** ($CDCl_3$)



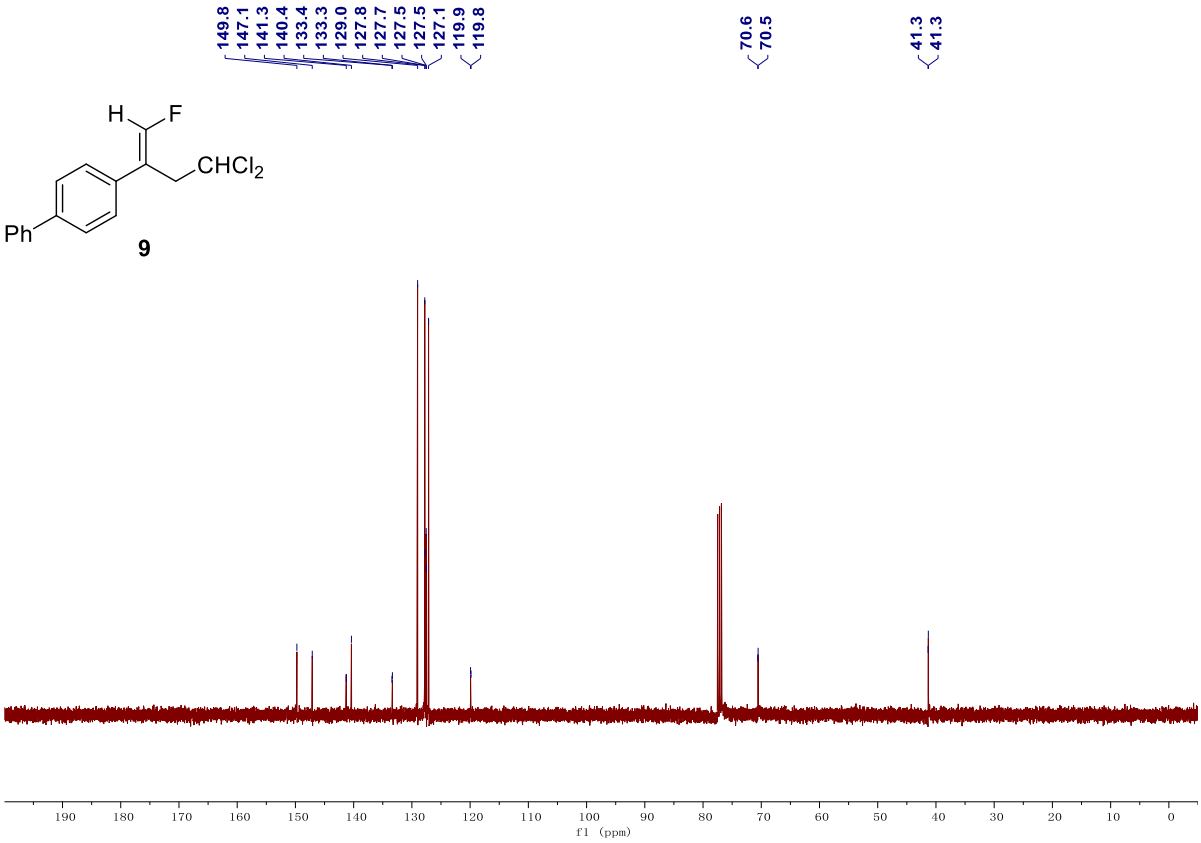
^{13}C NMR spectrum for compound **8** ($CDCl_3$)



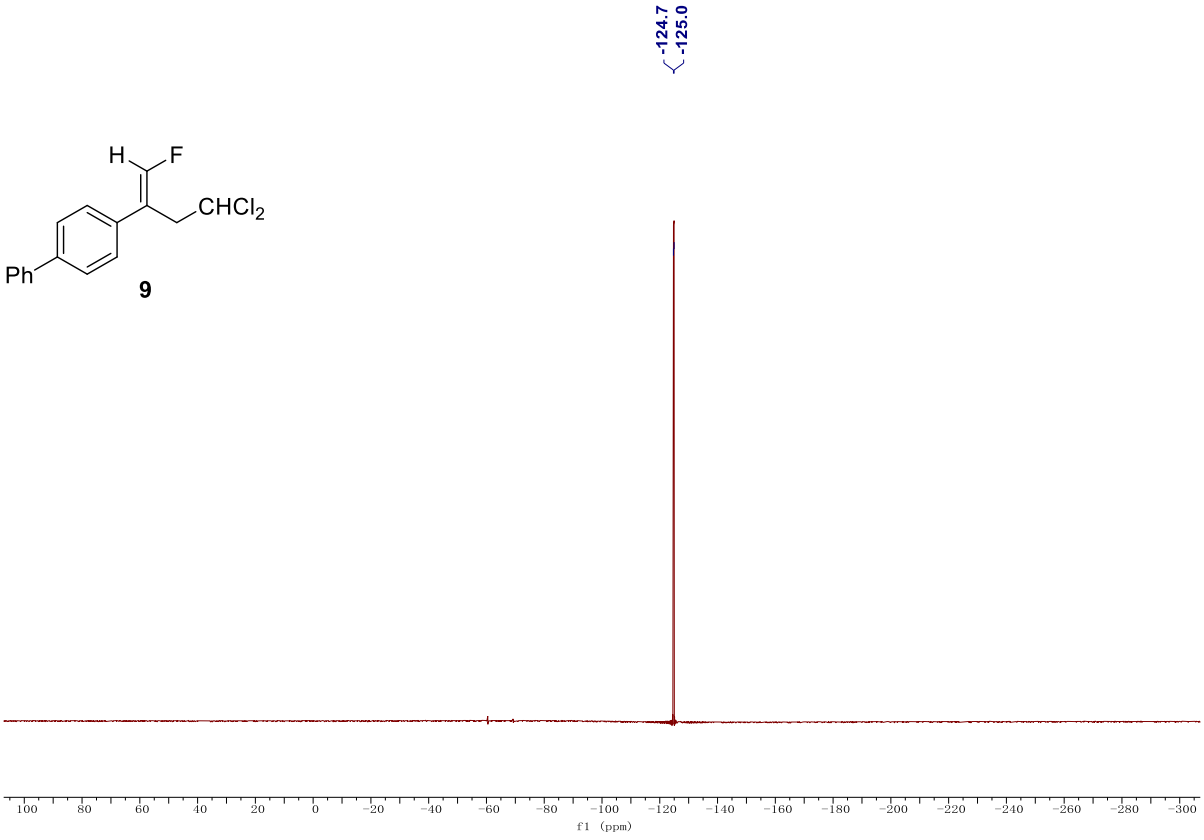
^{19}F NMR spectrum for compound **8** ($CDCl_3$)



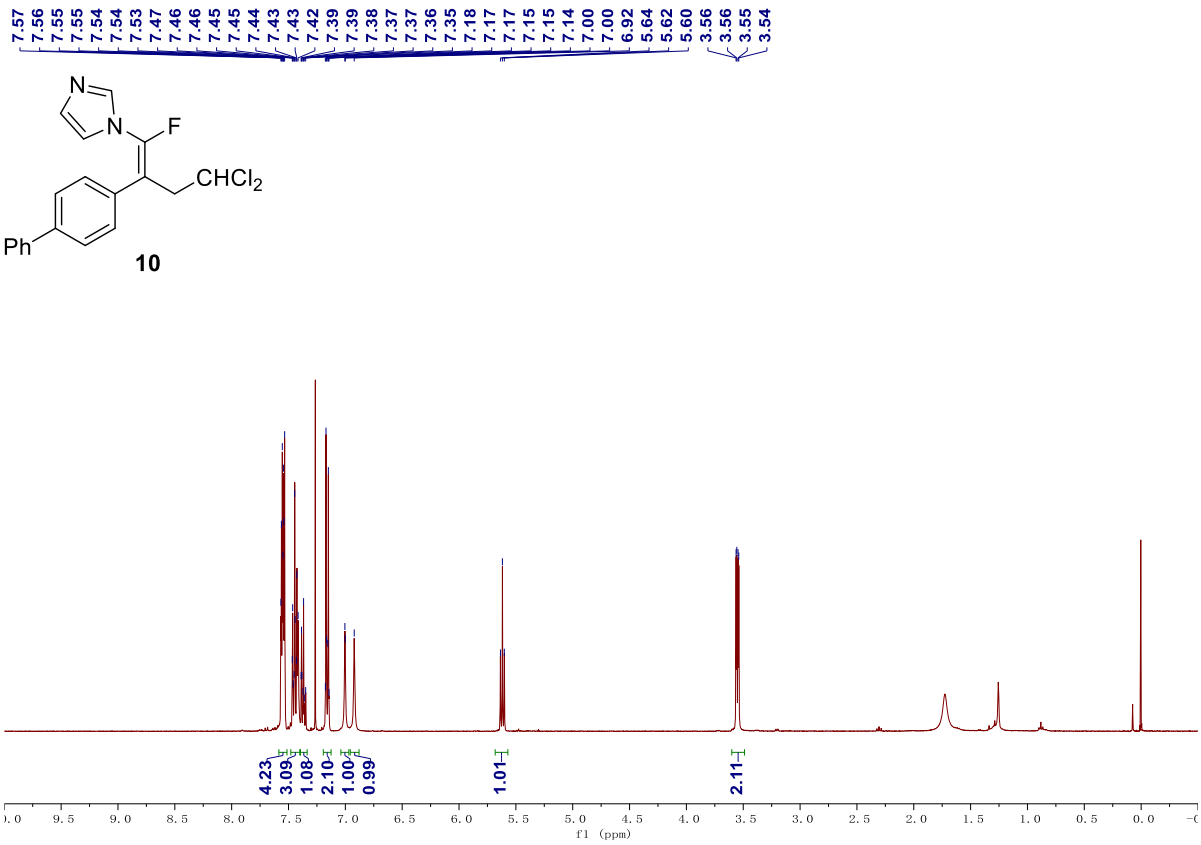
^{1}H NMR spectrum for compound **9** ($CDCl_3$)



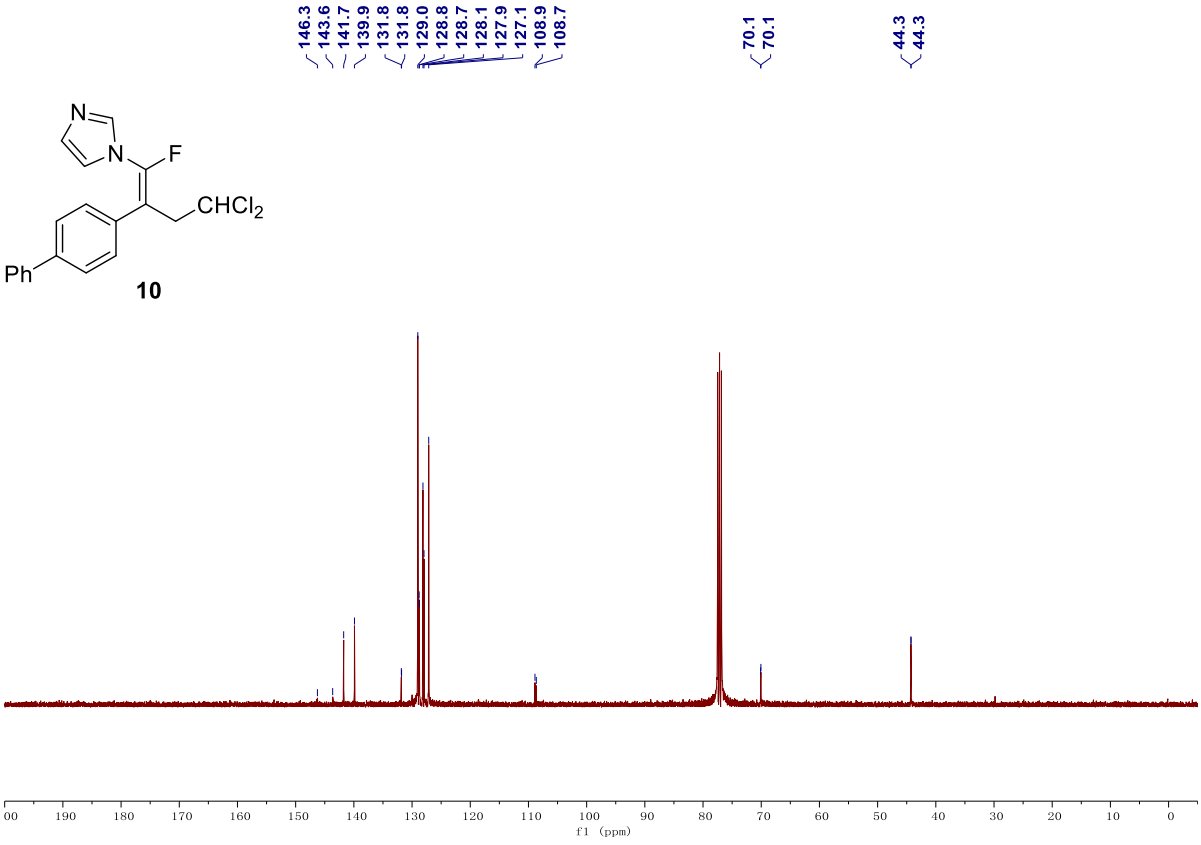
^{13}C NMR spectrum for compound **9** ($CDCl_3$)



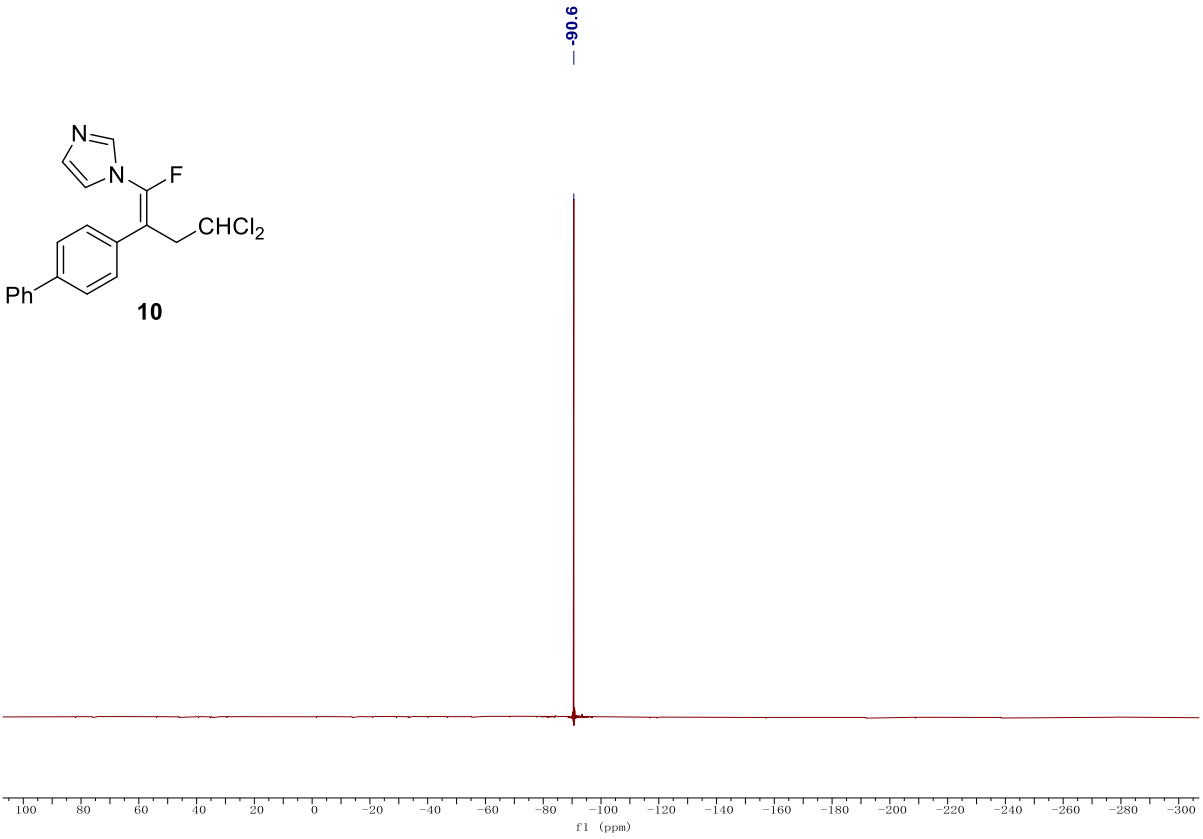
^{19}F NMR spectrum for compound **9** ($CDCl_3$)



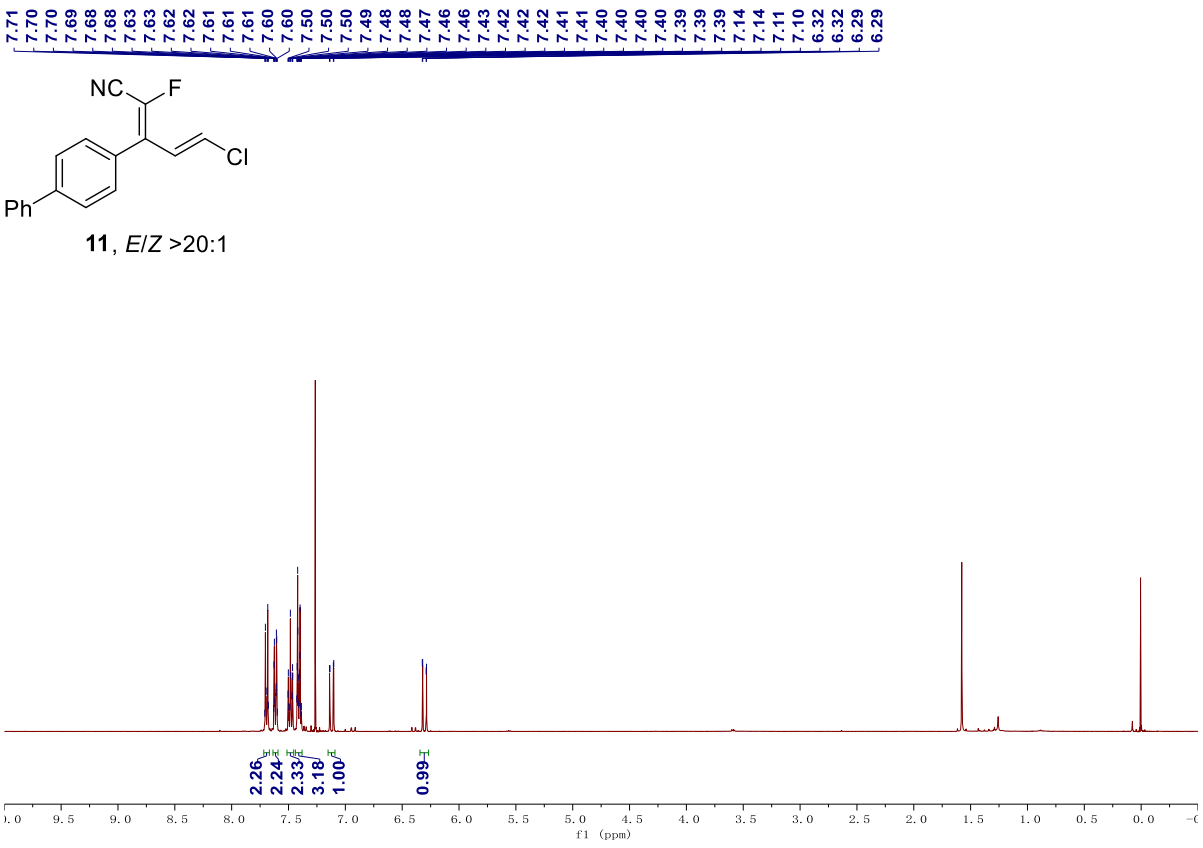
^{1}H NMR spectrum for compound **10** ($CDCl_3$)



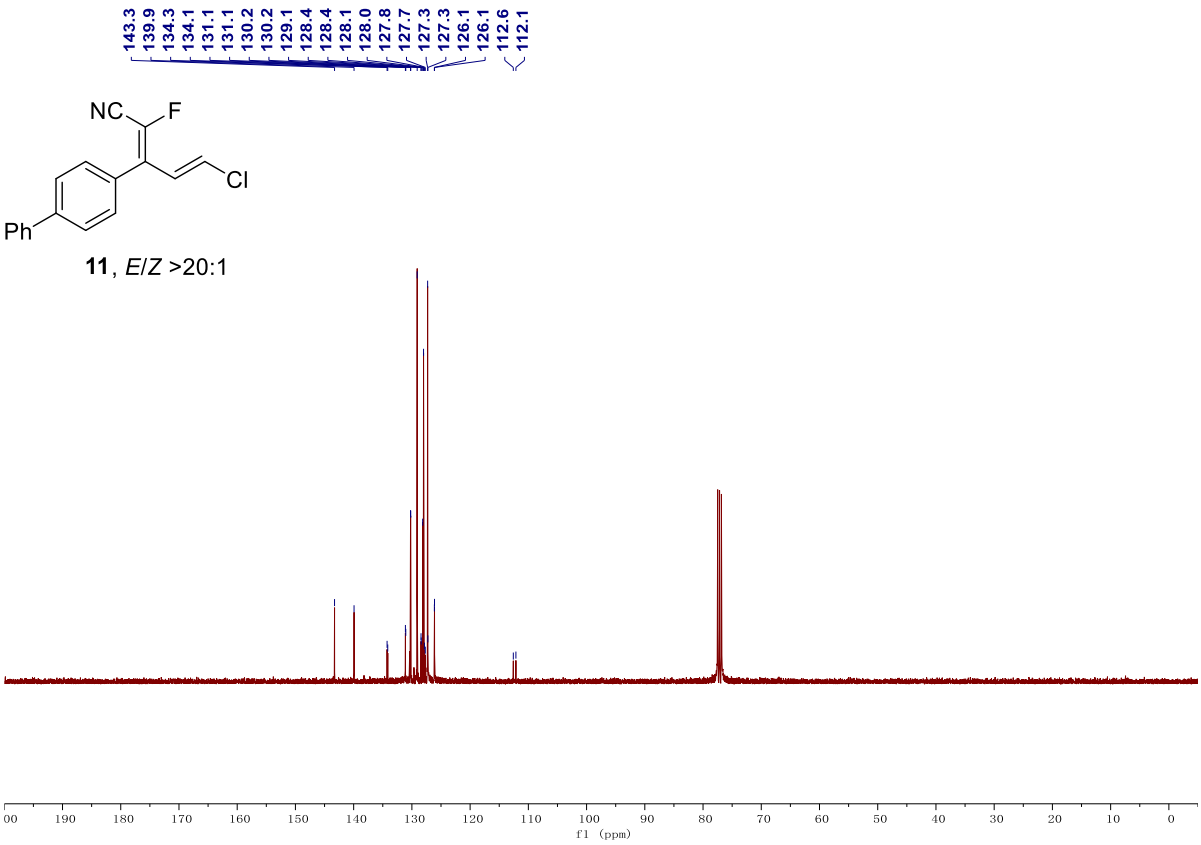
^{13}C NMR spectrum for compound **10** ($CDCl_3$)



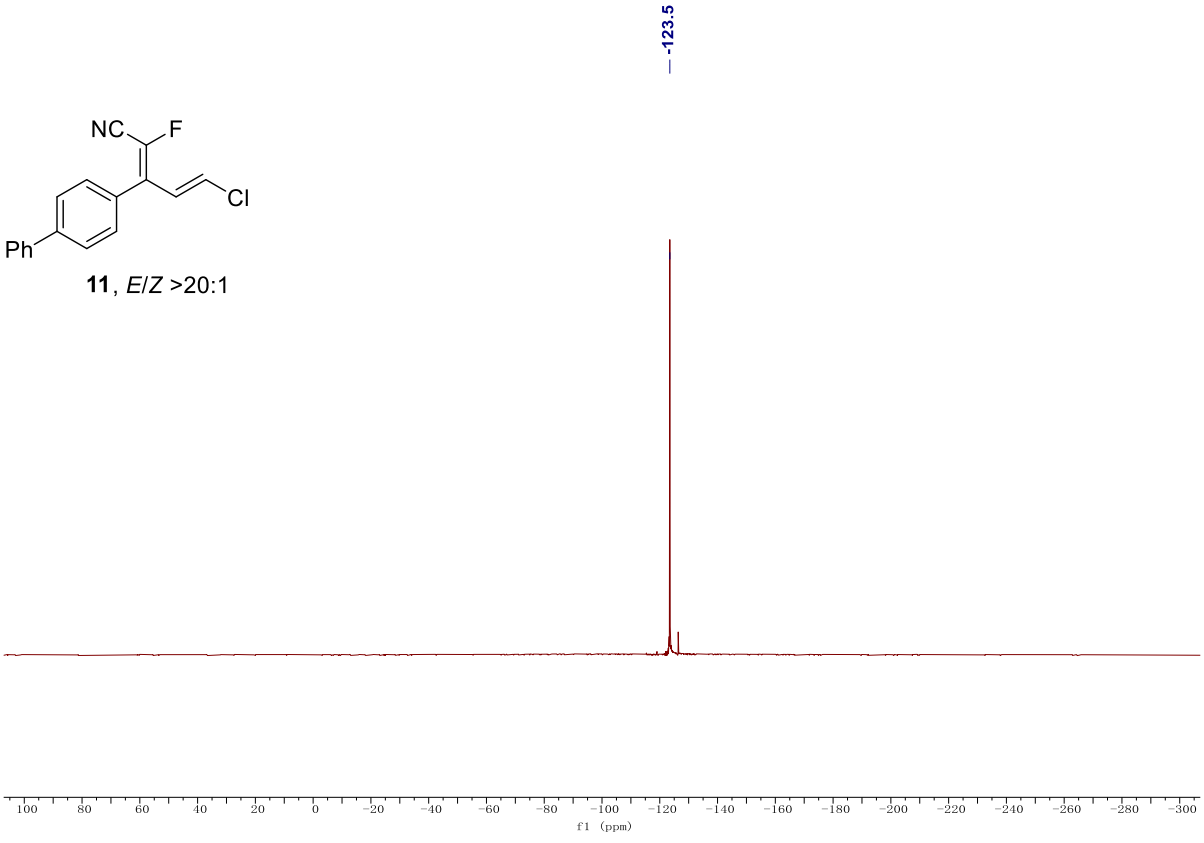
^{19}F NMR spectrum for compound **10** ($CDCl_3$)



^{1}H NMR spectrum for compound **11** ($CDCl_3$)



^{13}C NMR spectrum for compound **11** ($CDCl_3$)



^{19}F NMR spectrum for compound **11** ($CDCl_3$)