Electron Donor-Acceptor Complex-Initiated C-H Trifluoromethylation and Perfluoroalkylation of Enamides and Quinoxalinones

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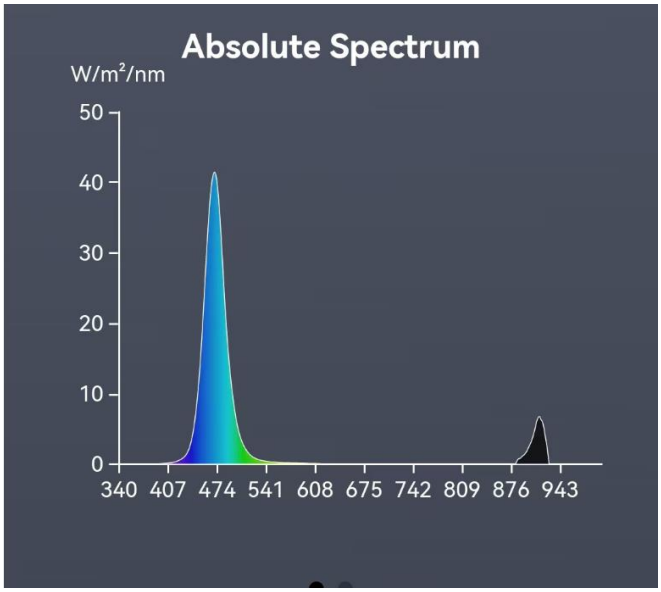
Column chromatography was carried out on silica gel. Unless noted ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$, ^{19}F NMR spectra were recorded on 376 MHz in $CDCl_3$ using a Bruker-400 spectrometer. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. UV-vis spectra were recorded on a TU-1950 UV spectrometer and are reported in 200-700 nm. Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are provided. All reagents were used as received unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh).

I. Experimental setup: The light source used for illuminating the reaction vessel (commercial supplier Synthware) consists of 40W blue LEDs (λ_{max} = 450 nm) and Kessil A 160WE TUNA BLUE 40W (λ_{max} = 471 nm).

Figure S1. Typical experimental setup for photoredox catalytic reactions

Spectral Illuminance Test Report:

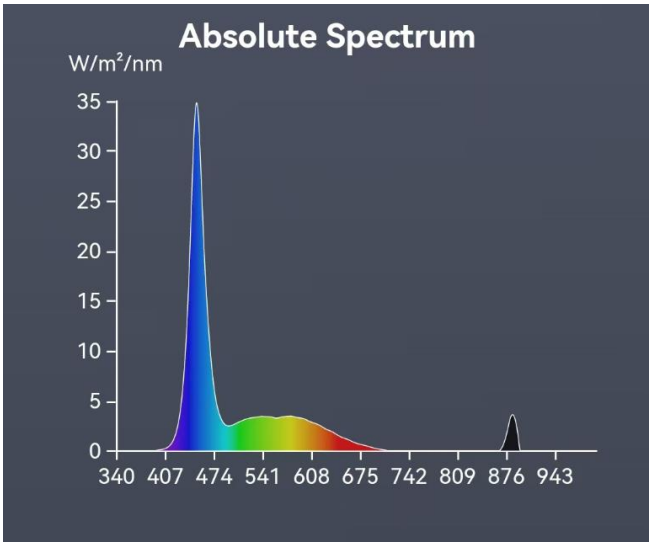
Kessil A 160WE TUNA BLUE 40 W:



Data analysis:

Peak wavelength LP (nm): 471. Half-peak width HW (nm): 31. Dominant wavelength LD (nm): 474. Color purity (%); 94.8.

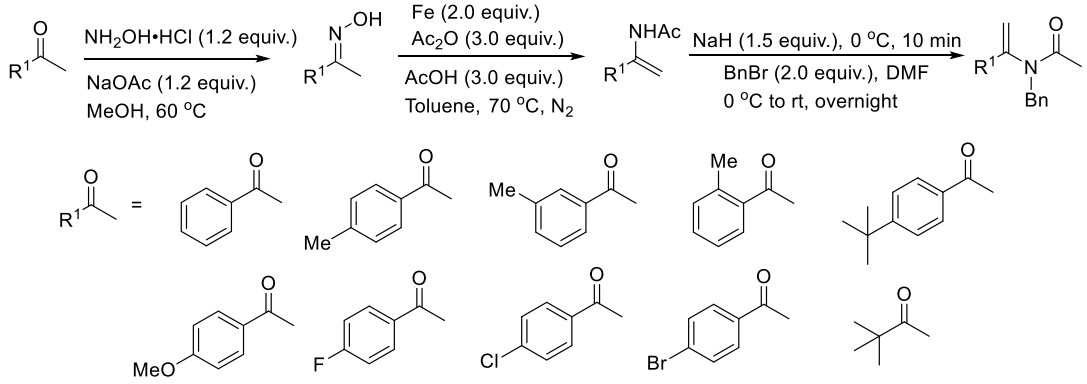
40W blue LED: LINBA, PAR 40 LED spotlight:



Peak wavelength LP (nm): 450. Half-peak width HW (nm): 23. Dominant wavelength LD (nm): 460. Color purity (%): 60.9.

II. Preparation of Starting Materials 1, 4

II.I Procedures for the Synthesis of Starting Material Enamides (1a-1n)

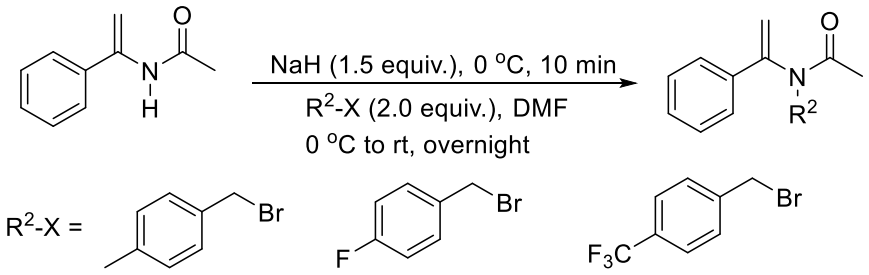


Synthetic procedure: a) A mixture of ketone (1.0 equiv.), NaOAc (1.2 equiv.) and hydroxylamine hydrochloride (1.2 equiv.) in methanol (0.5 M) was stirred for 2 h at 60 °C. Add water after cooling down to room temperature, then the mixture was extracted with ethyl acetate twice. The organic layer was collected, dried over $MgSO_4$ and vacuo to afford the ketoxime which was used without further purification for the next step.

b) To an oven-dried 50 mL two-neck round-bottom flask assembled with condenser was added the above ketoxime. The flask was vacuumed and back filled with N_2 for three times. Anhydrous toluene (0.5 M) was added followed by acetic anhydride (3.0 equiv.), acetic acid (3.0 equiv.) and iron powder (2.0 equiv.). The reaction flask was put into a 70 °C preheated oil bath and allowed to stir under nitrogen atmosphere. After the

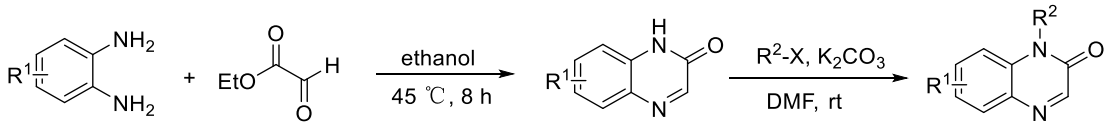
reaction completed and cooled to room temperature, ethyl acetate was added and the mixture was filtered through a short pad of celite. The solution thus was evaporated to get the crude enamide, which was directly purified by column chromatography.

c) 10 mmol (1.0 equiv.) of the *N*-acyl enamides was dissolved in 30 mL dry DMF in a dry two-necked round-bottom flask under nitrogen. The solution was cooled to 0 °C and 15 mmol (1.5 equiv.) sodium hydride was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then 20 mmol (2.0 equiv.) BnBr was added dropwise and the final solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding 10 mL water at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure product.



Synthetic procedure: 10 mmol (1.0 equiv.) of the *N*-acyl enamides was dissolved in 30 mL dry DMF in a dry two-necked round-bottom flask under nitrogen. The solution was cooled to 0 °C and 15 mmol (1.5 equiv.) sodium hydride was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then 20 mmol (2.0 equiv.) R^2-X was added dropwise and the final solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding 10 mL water at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure product.

II.II Synthesis of quinoline-2 (*1H*)-ketone by *N*-alkylation reaction



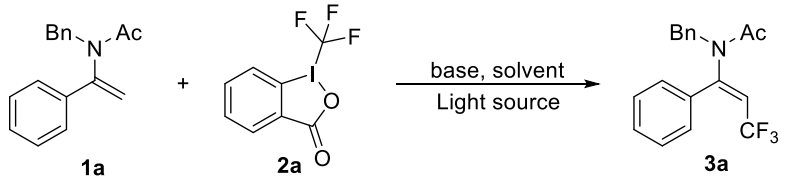
a) In a 100 mL round bottom flask, ethyl-2-oxoacetate (18.5 mmol, 1.2 equiv.) was added to a solution of 1,2-diaminobenzene (1.00 g, 1 equiv.) in ethanol (40 mL). The reaction mixture was heated to 45 °C on a heating block using a magnetic stirrer/heater for 8 hours. The formed precipitate was filtered, washed with water and dried under vacuum to afford the quinoxalin-2 (*1H*)-ones.

b) To a 100 mL round bottom flask with a stir bar was added quinoxalin-2(*1H*)-one

derivatives (6.8 mmol), DMF (15 mL) and K_2CO_3 (8.2 mmol), followed by dropwise addition of alkyl halide (10.9 mmol). The reaction mixture was stirred for 1-12 h at room temperature. Then reaction mixture was partitioned in water and EtOAc, and extracted with EtOAc twice. The combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (PET ether/ EtOAc) to afford the desired quinoxalin-2(*1H*)-ones.

III. Optimization conditions for the synthesis of products 3, 5, 7, 8

Table S1. Screening of reaction conditions for **3a**

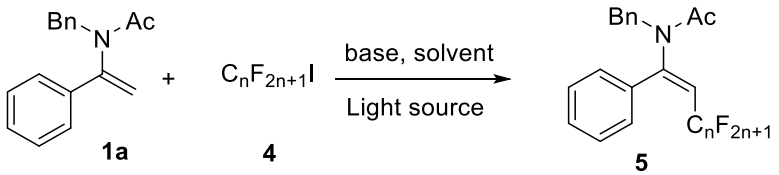


1a **2a** **3a**

Entry[a]	Solvent (mL)	Base (eq.)	Light source	Yield (%)[b]
1	Acetone (2)	Na_2CO_3 (3)	Blue LED 40W	28
2	Acetone (2)	Na_2CO_3 (3)	Kessil 40W+15 W Purple LED	36
3	**Acetone (2)**	**Na_2CO_3 (3)**	Kessil 40W×2	**53**
4	Acetone (2)	Na_2CO_3 (3)	49W Blue LED	45
5	**THF (2)**	Na_2CO_3 (3)	Kessil 40W×2	30
6	**CH_3CN (2)**	Na_2CO_3 (3)	Kessil 40W×2	<5
7	**DCE (2)**	Na_2CO_3 (3)	Kessil 40W×2	N.R
8	**DMSO (2)**	Na_2CO_3 (3)	Kessil 40W×2	N.R
9	**Toluene (2)**	Na_2CO_3 (3)	Kessil 40W×2	N.R
10	**Acetone : THF (1.5 : 0.5)**	**Na_2CO_3 (3)**	Kessil 40W×2	**68**
11	**Acetone : THF (1.2 : 0.8)**	**Na_2CO_3 (3)**	Kessil 40W×2	**73**
12	Acetone : THF (1.5 : 0.5)	Na_2CO_3 (2)	Kessil 40W×2	64
13	Acetone : THF (1 : 1)	Na_2CO_3 (3)	Kessil 40W×2	55
14	**Acetone : THF (1.2 : 0.8)**	–	Kessil 40W×2	59
15	**Acetone : THF (1.2 : 0.8)**	0.3	Kessil 40W×2	61

[a] Reaction conditions: **1a** (1.0 equiv., 0.1 mmol), **2a** (2 equiv., 0.2 mmol) irradiated under argon atmosphere for 12 h, rt. [b]Isolated yields of the **3a**. Kessil A 160WE TUNA BLUE 40W (λ_{max} = 471 nm).

Table S2. Screening of reaction conditions for **5**

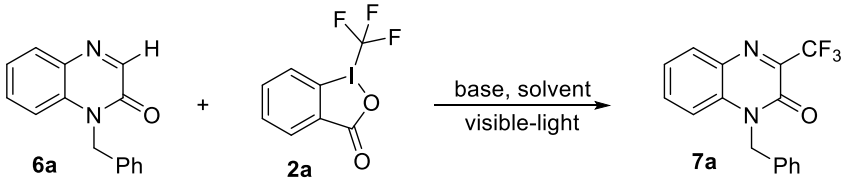


1a **4** **5**

Entry[a]	Alkyl iodides	Solvent	Base	Time (h)	Yield (%)
1	C_4F_9I	CH_3CN	Na_2CO_3	6	63
2	**C_4F_9I**	**CH_3CN**	**Cs_2CO_3**	**6**	**72**
3	C_4F_9I	CH_3CN	K_2CO_3	6	40
4	C_4F_9I	Acetone	Na_2CO_3	6	27
5	$C_6F_{13}I$	CH_3CN	Cs_2CO_3	6	70
6	C_3F_7I	CH_3CN	Cs_2CO_3	6	63
7	C_4F_9I	CH_3CN	—	6	N.D.

[a]Reaction conditions: **1a** (0.1 mmol,1.0 equiv.), **4** (0.3 mmol, 3.0 equiv.), base (0.3 mmol, 3.0 equiv.), solvent (2 mL), and Kessil A 160WE TUNA BLUE 40W (λ_{max} = 471 nm) under Ar at room temperature.

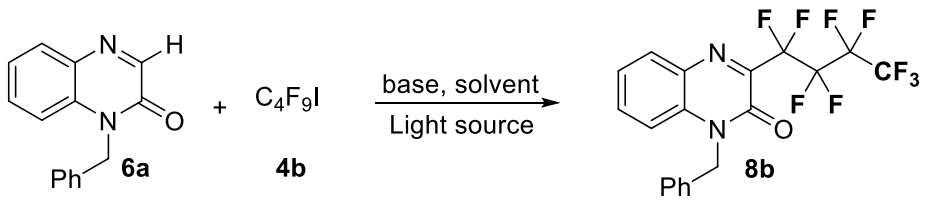
Table S3. Screening of reaction conditions for **7a**



Entry[a]	Solvent (mL)	Base (eq.)	Light source	Yield (%)
1	Acetone (2)	Na_2CO_3 (3)	Kessil 40W	61
2	Acetone (2)	K_2CO_3 (3)	Kessil 40W	39
3	Acetone (2)	K_3PO_4 (3)	Kessil 40W	28
4	Acetone (2)	DABCO (2)	Kessil 40W	43
5	Acetone (2)	PMDETA (2)	Kessil 40W	37
6	Acetone (2)	DBU (2)	Kessil 40W	31
7	Acetone (2)	Et_3N (2)	Kessil 40W	26
8	**Acetone (2)**	**Na_2CO_3 (3)**	**Blue LED 40W**	**68**
9	CH_3CN (2)	Na_2CO_3 (3)	Blue LED 40W	64
10	DCE (2)	Na_2CO_3 (3)	Blue LED 40W	52
11	Acetone (2)	-	Blue LED 40W	N.R.
12	Acetone (2)	Na_2CO_3 (0.3)	Blue LED 40W	N.R.

[a] Reaction conditions: **6a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), 1.0 equiv. Na_2SO_4 was added to the reaction using Kessil A 160WE TUNA BLUE 40 W (λ_{max} = 471 nm) or 40W blue LEDs (λ_{max} = 450 nm).

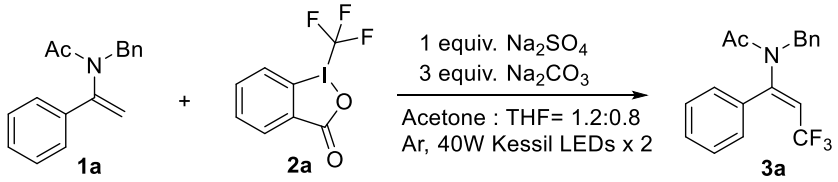
Table S4. Screening of reaction conditions for **8b**



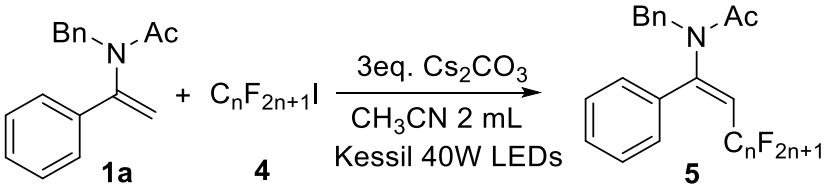
Entry	Solvent (mL)	Base (eq.)	Light source	Yield (%)
1	Acetone (2)	Na_2CO_3 (2)	Blue LED 40W	41
2	CH_3CN (2)	Na_2CO_3 (2)	Blue LED 40W	33
3	DCM (2)	Na_2CO_3 (2)	Blue LED 40W	N.R.
4	DMSO (2)	Na_2CO_3 (2)	Blue LED 40W	N.R.
5	DMF (2)	Na_2CO_3 (2)	Blue LED 40W	N.R.
6	DCE (2)	Na_2CO_3 (2)	Blue LED 40W	N.R.
7	THF (2)	Na_2CO_3 (2)	Blue LED 40W	Trace
8	Acetone (2)	Na_2CO_3 (2)	Blue LED 30W	31
9	Acetone (2)	Na_2CO_3 (2)	Blue LED 15W	29
10	Acetone (2)	Na_2CO_3 (2)	Kessil 40W	37
11	Acetone (2)	Cs_2CO_3 (2)	Blue LED 40W	52
12	Acetone (2)	$NaHCO_3$ (2)	Blue LED 40W	26
13	Acetone (2)	K_2CO_3 (2)	Blue LED 40W	35
14	Acetone (2)	Et_3N (2)	Blue LED 40W	38
15	Acetone (2)	Cs_2CO_3 (1)	Blue LED 40W	16
16	**Acetone (2)**	**Cs_2CO_3 (3)**	**Blue LED 40W**	**66**

[a] Reaction conditions: **6a** (0.1 mmol, 1.0 equiv.), C_4F_9I (0.3 mmol, 3.0 equiv.). 40 W blue LEDs (λ_{max} = 450 nm).

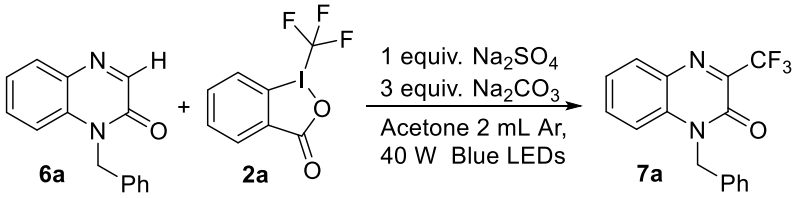
IV. General Procedure for the synthesis of products 3, 5, 7, 8, 10



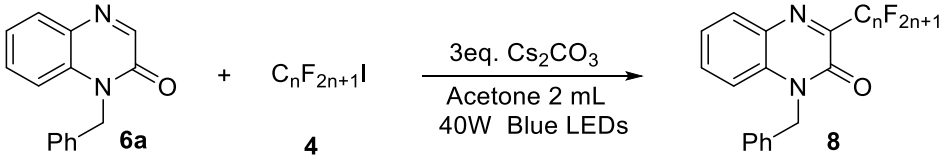
General Procedure A: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg), 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(*1H*)-one **2a** (0.2 mmol, 2 equiv., 63 mg). The flask was evacuated and backfilled with Ar for 3 times. Then *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.1 mmol, 1 equiv., 25 mg), acetone (1.2 mL) and THF (0.8 mL) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation from two light sources (40 W kessil). The Schlenk tube was positioned approximately 2 cm away from the light source. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (10:1)).



General Procedure B: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Cs_2CO_3 (0.3 mmol, 3 equiv., 98 mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL), perfluoroiodoalkane (0.3 mmol, 3 equiv.,) and *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.1 mmol, 1 equiv., 25.1 mg) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W, λ = 427 nm). The Schlenk tube was positioned approximately 2 cm away from the LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (8:1)).

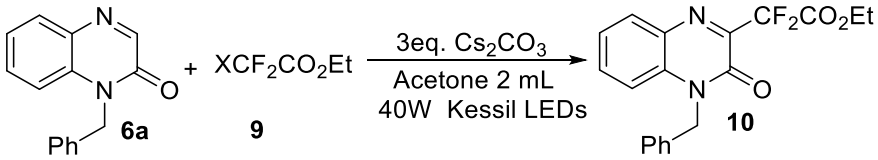


General Procedure C: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg), 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(*1H*)-one **2a** (0.3 mmol, 3 equiv., 98 mg) and 1-benzylquinoxalin-2(*1H*)-one **6a** (0.1mmol, 1 equiv., 23 mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL) was added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs. The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (6:1)).



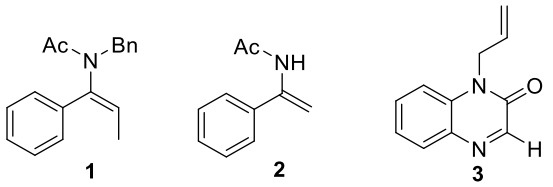
General Procedure D: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Cs_2CO_3 (0.3 mmol, 3 equiv., 98 mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL), perfluoroiodoalkane (0.3 mmol, 3 equiv.,) and 1-benzylquinoxalin-2(*1H*)-one **6a** (0.1 mmol, 1 equiv., 23.6 mg) were

added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs. The Schlenk tube was positioned approximately 2 cm away from the LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (6:1)).



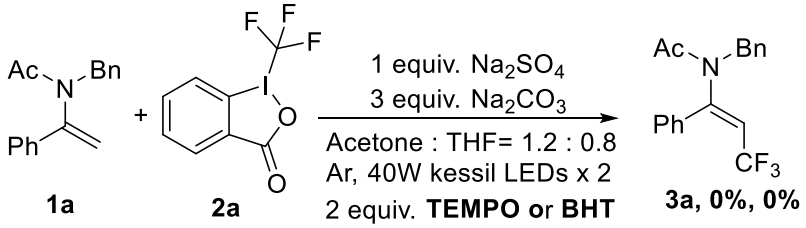
General Procedure E: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Cs_2CO_3 (0.3 mmol, 3 equiv., 98 mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL), perfluoroiodoalkane (0.3 mmol, 3 equiv.,) and 1-benzylquinoxalin-2(*1H*)-one **6a** (0.1 mmol, 1 equiv., 23.6 mg) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W, λ = 427 nm). The Schlenk tube was positioned approximately 2 cm away from the LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (6:1)).

Failed Substrates: The substrates (1, 2, 3) did not yield products under standard reaction conditions.



V. Mechanistic Studies

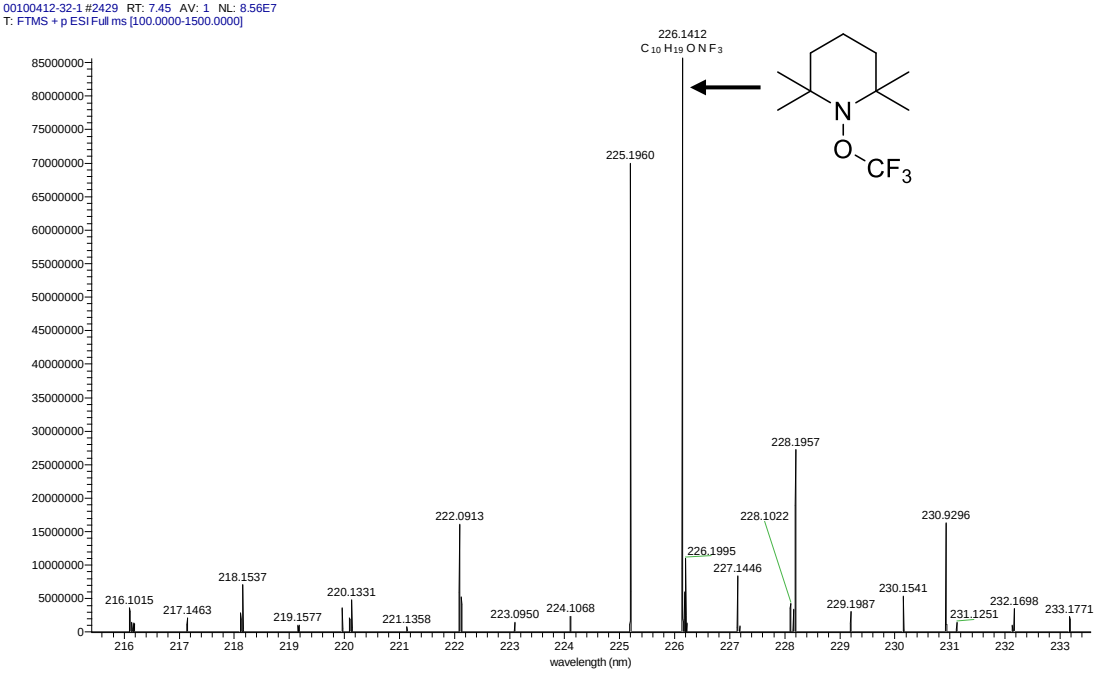
V. I Radical quenching experiment

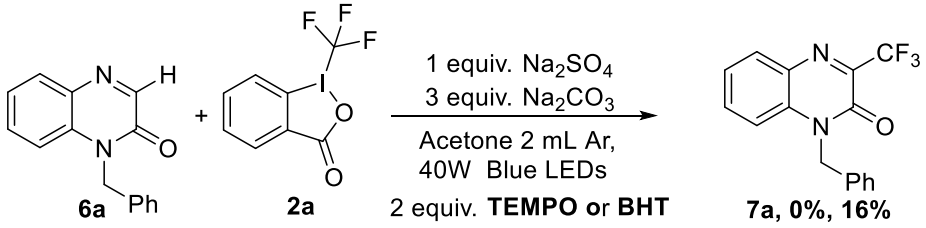


Scheme S1. Radical quenching experiment

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(*1H*)-one **2a** (0.2 mmol, 2 equiv., 63 mg) , Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg) and a

radical quencher (TEMPO or BHT, 0.2 mmol, 2 equiv., 31 mg or 44 mg). The flask was evacuated and backfilled with Ar for 3 times. Then *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.1 mmol, 1 equiv., 25 mg), acetone (1.2 mL) and THF (0.8 mL) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation from two light sources (40W Kessil LEDs). The Schlenk tube was positioned approximately 2 cm away from the light source. Stirring the reaction mixture at room temperature revealed that no product formation (monitored by TLC). After the reaction, the reaction system was checked by HRMS, and the signal of 2,2,6,6-tetramethyl-1-(trifluoromethoxy)piperidine was observed.

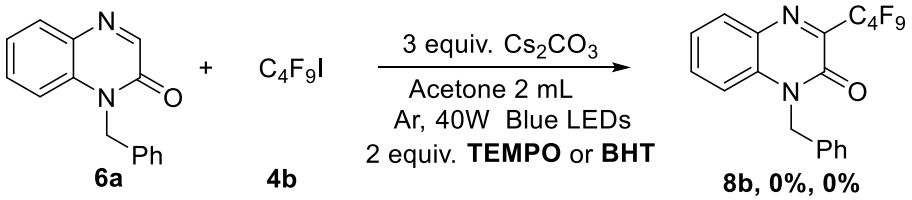




Scheme S2. Radical quenching experiment

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(*1H*)-one 2a (0.3 mmol, 3 equiv., 98 mg), 1-benzylquinoxalin-2(*1H*)-one **6a** (0.1mmol, 1 equiv., 23 mg)., Na_2SO_4 (0.1 mmol, 1 equiv, 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg) and a radical quencher (TEMPO or BHT, 0.2 mmol, 2 equiv., 31 mg or 44 mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL) was added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs. The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. Stirring the reaction mixture for a specified time at room temperature revealed that no product

formation (monitored by TLC). The product **7a** was significantly suppressed by radical quenchers, which indicated that a radical process was involved in this transformation.



Scheme S3. Radical quenching experiment

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Cs_2CO_3 (0.3 mmol, 3 equiv., 98 mg), 1-benzylquinoxalin-2(*1H*)-one **6a** (0.1 mmol, 1 equiv., 23.6 mg) and a radical quencher (TEMPO or BHT, 0.2 mmol, 2 equiv., 31 mg or 44 mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL) and perfluoroiodoalkane (0.3 mmol, 3 equiv.,) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs. The Schlenk tube was positioned approximately 2 cm away from the LEDs lamp. Stirring the reaction mixture for a specified time at room temperature revealed that no product formation (monitored by TLC). The product **8b** was significantly suppressed by radical quenchers, which indicated that a radical process was involved in this transformation.

V.II UV-vis absorbance experiment

Further to substantiate the formation of EDA complex, we have carried out UV-vis spectroscopic measurements with various combinations of **1a**, **2a**, and **1a** with **2a** (1:2) ratio in acetone medium, 2a with Na_2CO_3 (2:3) ratio in acetone medium, and **1a**, **2a** with Na_2CO_3 (1:2:3) ratio in acetone medium (Figure S1). As presented in Figure S1, when **1a**, **2a** and Na_2CO_3 were mixed in acetone in a 1:2:3 ratio, a new peak corresponding to the EDA complex was detected in the visible region (bathochromic shift). This result suggests the formation of EDA complex.

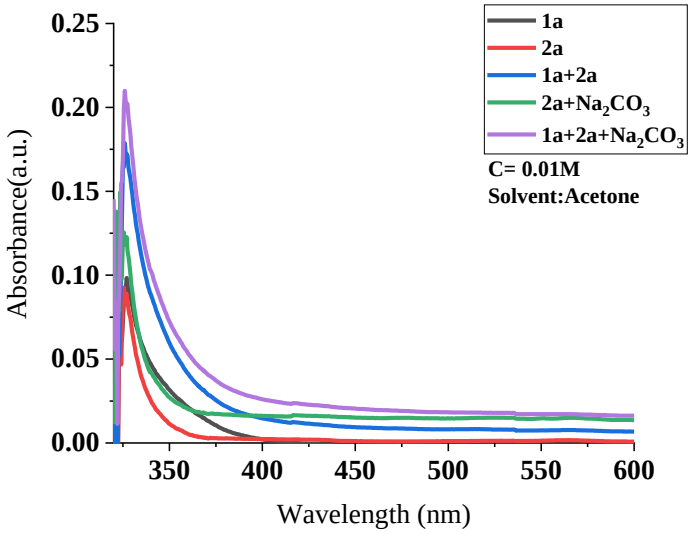


Figure S2. Comparison of the UV-vis spectra of **1a**, **2a** and the mixture of **1a**+ **2a** (1:2), **2a**+Na_2CO_3 (2:3), and **1a**+ **2a** +Na_2CO_3 (1:2:3) in 0.01M solution of acetone.

Further to substantiate the formation of EDA complex, we have carried out UV-vis spectroscopic measurements with various combinations of **1a**, $C_6F_{13}I$, and **1a** with $C_6F_{13}I$ (1:3) ratio in CH_3CN medium, $C_6F_{13}I$ with Cs_2CO_3 (3:3) ratio in CH_3CN medium, and **1a**, $C_6F_{13}I$ with Cs_2CO_3 (1:3:3) ratio in CH_3CN medium (Figure S2). As presented in Figure S2, when **1a**, $C_6F_{13}I$ and Cs_2CO_3 were mixed in acetone in a 1:3:3 ratio, a new peak corresponding to the EDA complex was detected in the visible region (bathochromic shift). This result suggests the formation of EDA complex.

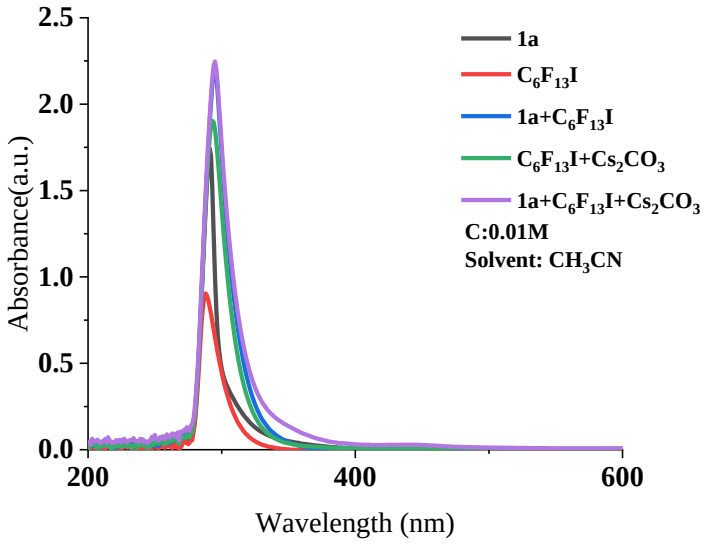
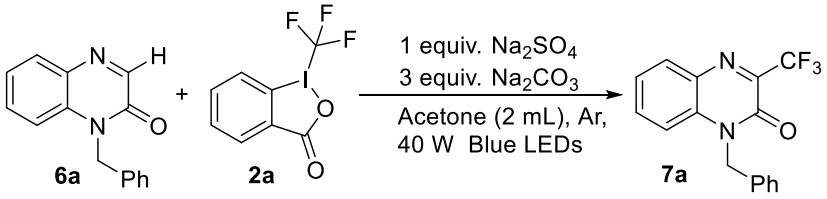


Figure S3. Comparison of the UV-vis spectra of **1a**, $C_6F_{13}I$ and the mixture of **1a**+ $C_6F_{13}I$ (1:3), $C_6F_{13}I$+Cs_2CO_3 (3:3), and **1a**+ $C_6F_{13}I$ +Cs_2CO_3 (1:3:3) in 0.01M solution of CH_3CN

In addition, we tested the CO_3^{2-} anion for its ability to induce the formation of the EDA complex with **2a** using UV-vis absorption spectroscopy. When Na_2CO_3 and **2a** were mixed in CH_3CN in a 2:3 ratio, the optical absorption spectrum of the mixture showed a significant bathochromic shift in the visible spectral region, and a new absorption peak (λ_{max}) appeared at about 346 nm ((Figure S3).



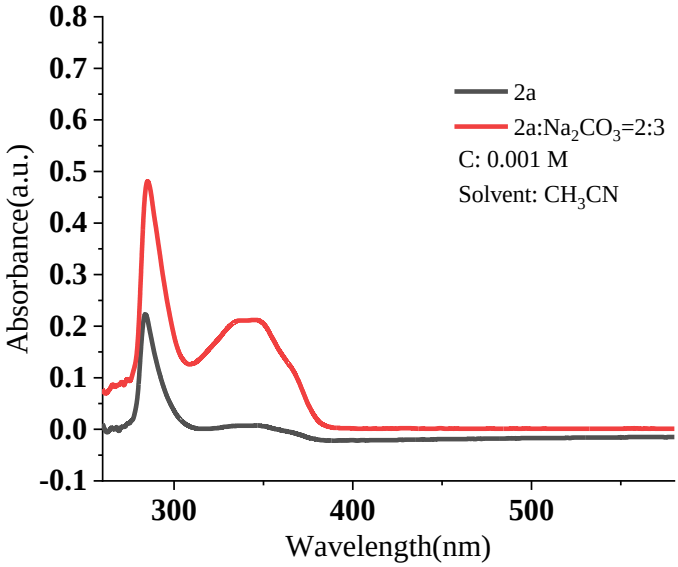
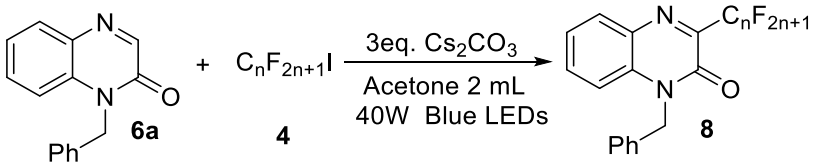


Figure S4. Comparison of the UV-vis spectra of **2a** and the mixture of **2a**+Cs_2CO_3 (2:3) in 0.001M solution of CH_3CN

A UV-vis absorbance experiment has been carried out for confirming the formation of EDA complex as illustrated below in Figure S4. As presented in Figure S4, when C_4F_9I and Cs_2CO_3 were mixed in acetone in a 1:1 ratio, an obvious bathochromic shift of the UV-vis absorbance was observed, strongly suggesting that C_4F_9I-Cs_2CO_3 EDA complex might be formed in the mixed solution.



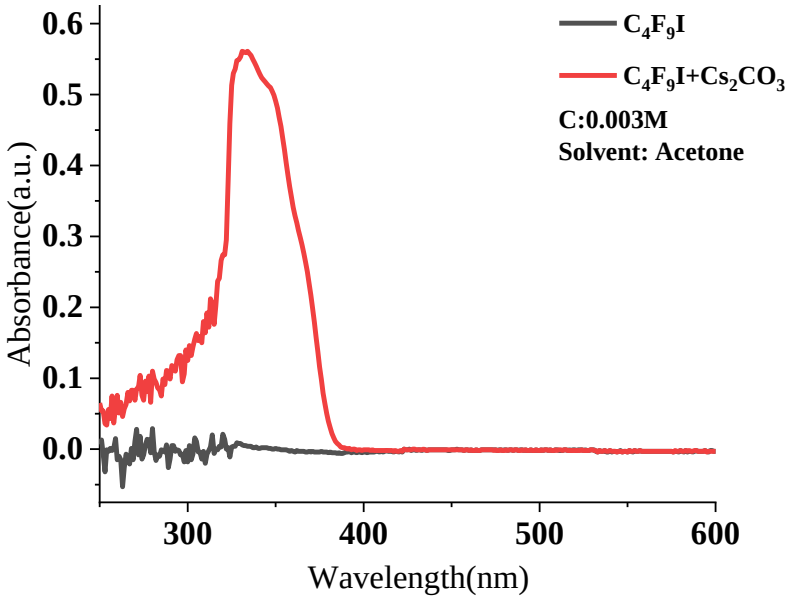


Figure S5. Comparison of the UV-vis spectra of C_4F_9I, and the mixture of C_4F_9I+ Cs_2CO_3 (1:1) in 0.003M solution of Acetone

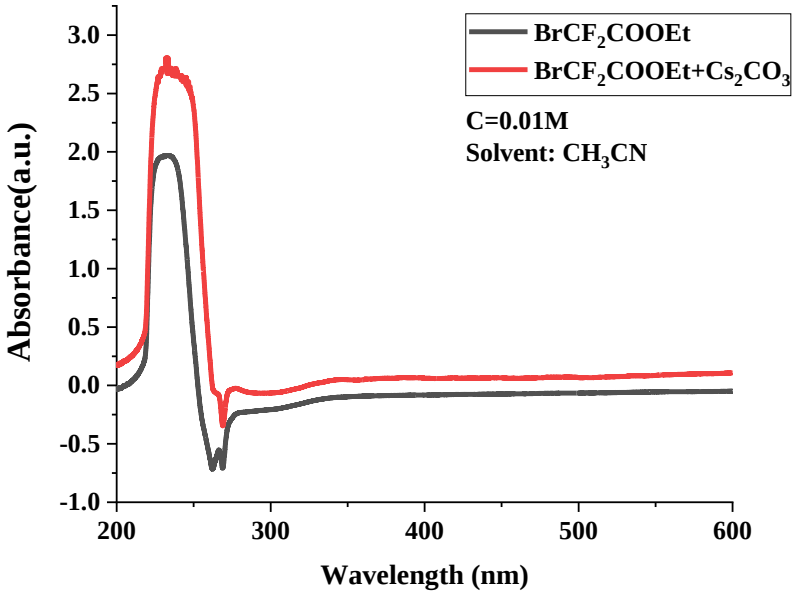


Figure S6. Comparison of the UV-vis spectra of $BrCF_2COOEt$, and the mixture of $BrCF_2COOEt$ + Cs_2CO_3 (1:1) in 0.01M solution of CH_3CN.

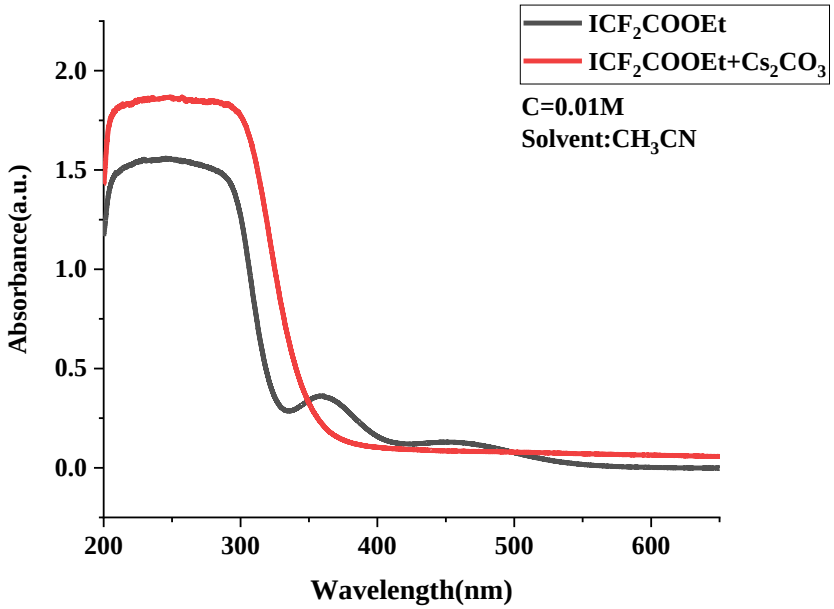
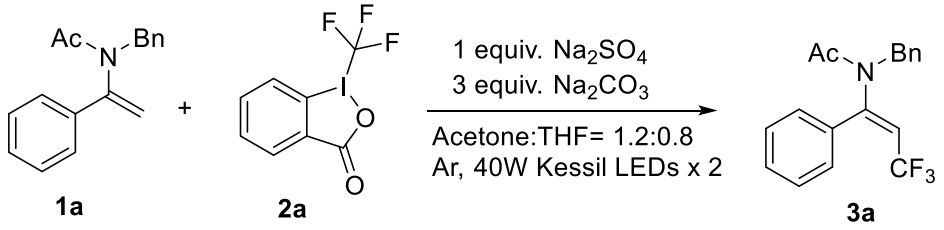


Figure S7. Comparison of the UV-vis spectra of ICF_2COOEt, and the mixture of ICF_2COOEt + Cs_2CO_3 (1:1) in 0.01M solution of CH_3CN.

From figure S6 and S7, we can see that no EDA complex was formed between $BrCF_2COOEt$ and Cs_2CO_3, or between ICF_2COOEt and Cs_2CO_3.

V. III Switch on-off experiment



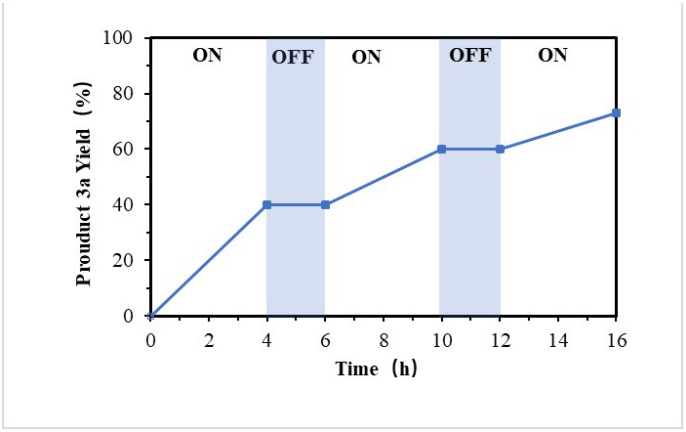
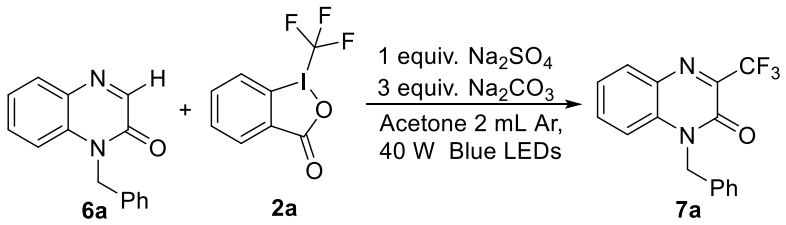


Figure S8. Graph for Switch on-off experiment

Two oven-dried Schlenk tubes (10 mL) were equally equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg), 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(*1H*)-one **2a** (0.2 mmol, 2 equiv., 63 mg). The flask was evacuated and backfilled with Ar for 3 times. Then *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.1 mmol, 1 equiv., 25 mg), acetone (1.2 mL) and THF (0.8 mL) were added with syringe. Two oven-dried Schlenk tubes were then stirred at room temperature under the irradiation from two light sources (40 W Kessil LEDs) at the same time. One tube stopped irradiation after 4 h of light irradiation, this resultant solution was further analyzed in GC to obtain the yield of the **3a**. The other tube stopped irradiation and continued stirred for two hours, and this resultant solution was analyzed similarly. The light was switched ON and OFF alternatively for a period and monitored the conversion of the product. This cycle was repeated and the yield of **3a** with respect to time was plotted (Figure S5).



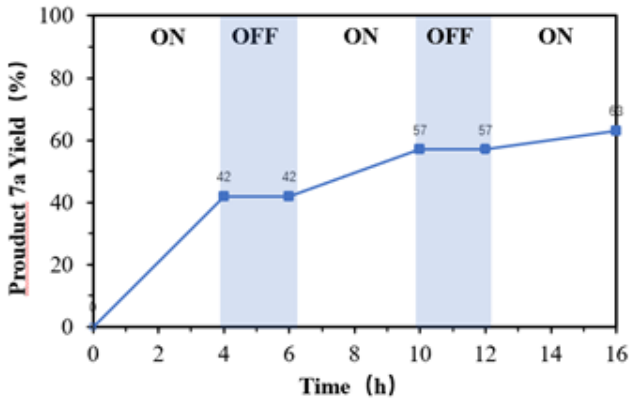
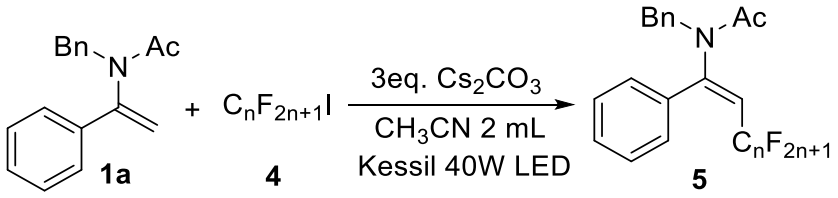


Figure S9. Graph for Switch on-off experiment

According to the switch on and off lamp experiment mentioned above, the same method was used to alternately switch on and off the lamp over a period of times, and the transformation of the product was monitored. The yield curve of **7a** over time was shown in Figure S6.



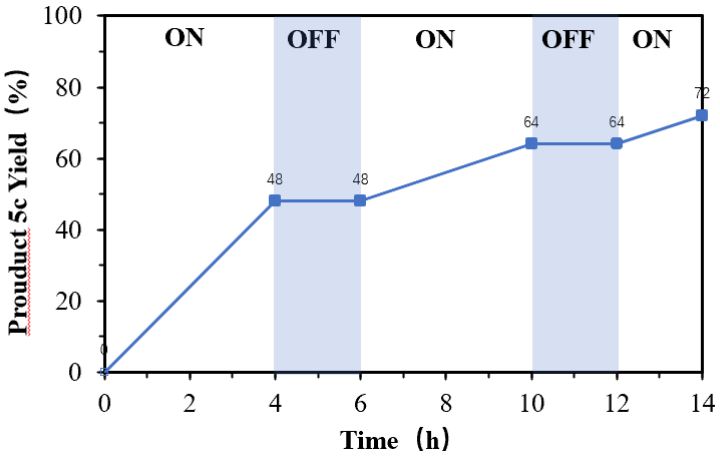
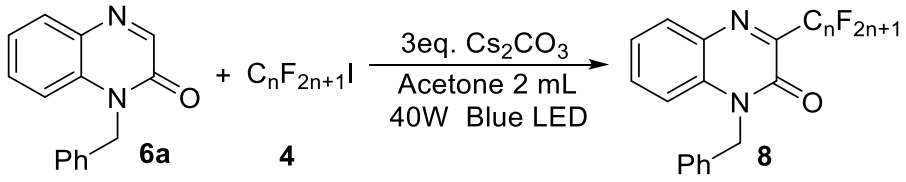


Figure S10. Graph for Switch on-off experiment

Similarly, Plot S7 of the yield of **5c** over time was obtained.



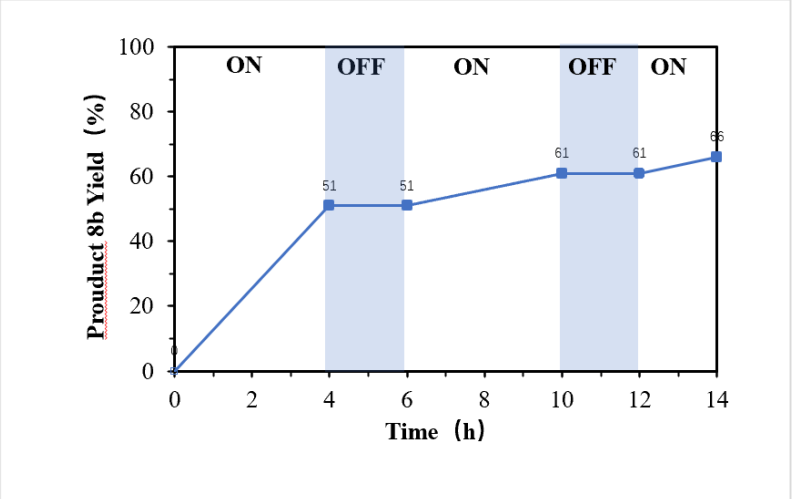


Figure S11. Graph for Switch on-off experiment

The variation curve of the yield of product **8b** over time was shown in Figure S8.

Quantum yield determination.

The photon flux was determined by ferrioxalate actinometry following the literature Procedure.[1]

Determination of photon flux:

A solution of ferrioxalate (0.15 M) was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of 1,10-phenanthroline was prepared by dissolving 25 mg of phenanthroline and 5.63 g of sodium acetate in 25 mL of 0.5 M H_2SO_4. Solutions were stored in the dark. While being careful to minimize exposure to background light, 3.0 mL of the 0.15 M ferrioxalate solution was added to a 4 mL vial. The vial was positioned 3 cm from LEDs (Kessil 40W, λ=471 nm). The ferrioxalate solution was irradiated for 60 seconds. After irradiation, 0.525 mL of the phenanthroline solution was added and the sample was allowed to rest for 1 hour for coordination. Next, the mixture was transferred to a quartz cuvette and the absorbance was measured at 510 nm. Non-irradiated samples as controls were also prepared. Photoconversion of Fe^{3+} to Fe^{2+} was calculated using eq 1.

$$\textbf{1.}\quad mol\ Fe^{2+} = \frac{V*\Delta A}{l*\varepsilon}$$

V is the total volume (0.003525L),ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1 cm) and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). After the mol Fe^{2+} was calculated from the eq1, the photo flux was determined using eq2.

$$\textbf{2.}\quad photo\ flux = \frac{mol\ Fe^{2+}}{\phi*t*f}$$

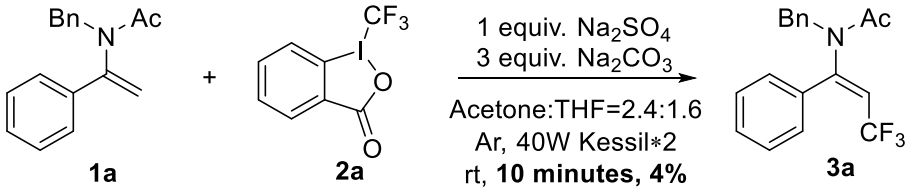
ϕ is the quantum yield for the ferrioxalate actinometer (0.92 for 0.15 M at λ = 468 nm),[2] t is the time (60 seconds), and f is the fraction of light absorbed by the ferrioxalate actinometer at λ = 471 nm (0.979). The fraction of light absorbed is calculated using eq 3.

$$\textbf{3.}\quad f = 1 - 10^{-A(at\ 471\ nm)}$$

The photon flux was determined to be 1.13 x 10^{-8} einsteins per second.

Determination of quantum yield.

The quantum yield was measured through the reaction of synthesis of **3a**.



In a 4-mL glass vial, Na_2SO_4 (0.1 mmol, 1 equiv., 28 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 63 mg), 1-(trifluoromethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(*1H*)-one **2a** (0.4 mmol, 2 equiv., 126 mg) were combined. Then *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.2 mmol, 1 equiv., 50 mg) was added with acetone (2.4 mL), then THF (1.6 mL) was added. The mixture was degassed with N_2 for 3 minutes. The reaction was exposed to two Kessil 40W blue LED at room temperature for 10 minutes. After irradiation, the yield was determined by ^{1}HNMR to be 4% (0.8×10^{-5} mol). f is the fraction of light absorbed by the reaction mixture in the conditions described (0.476).

$$quantum\ yield = \frac{mol\ product}{photon\ flux * t * f} = \frac{0.8 \times 10^{-5}}{1.13 \times 10^{-8} \times 600 \times 0.476} = 2.48$$

The quantum yield (Φ) was determined to be 2.48.

V. IV Cyclic voltammetry measurement of 1a, 2a, 6a.

Make: Shanghai Chenhua Instrument Co., Ltd.

Instrument Model: CHI760E.

The geometry of working electrode: cylinder.

The surface area of working electrode: 0.196 cm^2.

The polishing material and method: glassy carbon electrode; Polishing powder was used, then acetone, ethanol was cleaned, and deionized water was used for ultrasonication.

The solvent deoxygenation method: Blow nitrogen on the solvent using a clean needle for 10 min to expel air.

Temperature: room temperature.

Initial scan: positive.

The voltammograms were taken in a MeCN solution ([^{n}Bu$_4$NPF$_6$] = 0.1 M), scan rate: 100 mV s^{-1}. With ferrocene as the internal standard.

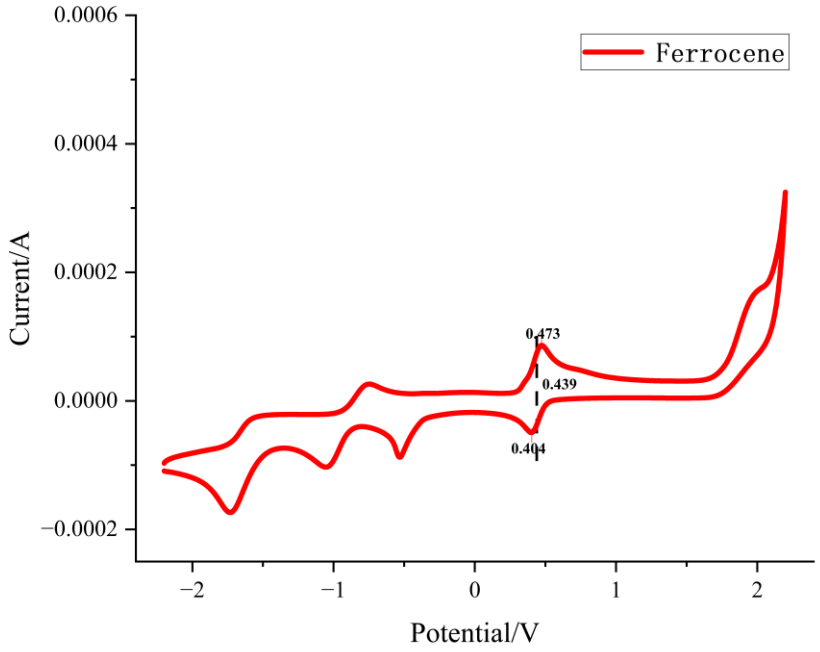


Figure S12. Cyclic voltammetry of **Ferrocene (0.001 M)**, $E_{1/2}$=0.439 V (vs Ag/AgCl).

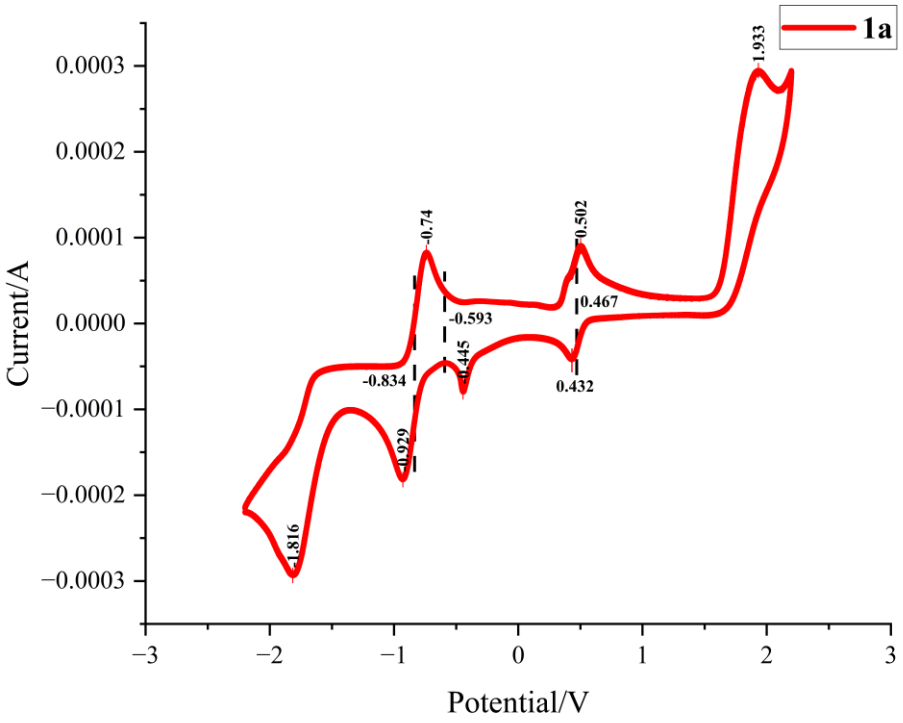


Figure S13. Cyclic voltammetry of **1a**

When the data measured with respect to Fc/Fc+ ($E_{1/2}$= 0.439 V vs. Ag/AgCl), $E_{1/2}$(**1a**)

= -0.862 V (vs Ag/AgCl) was obtained.

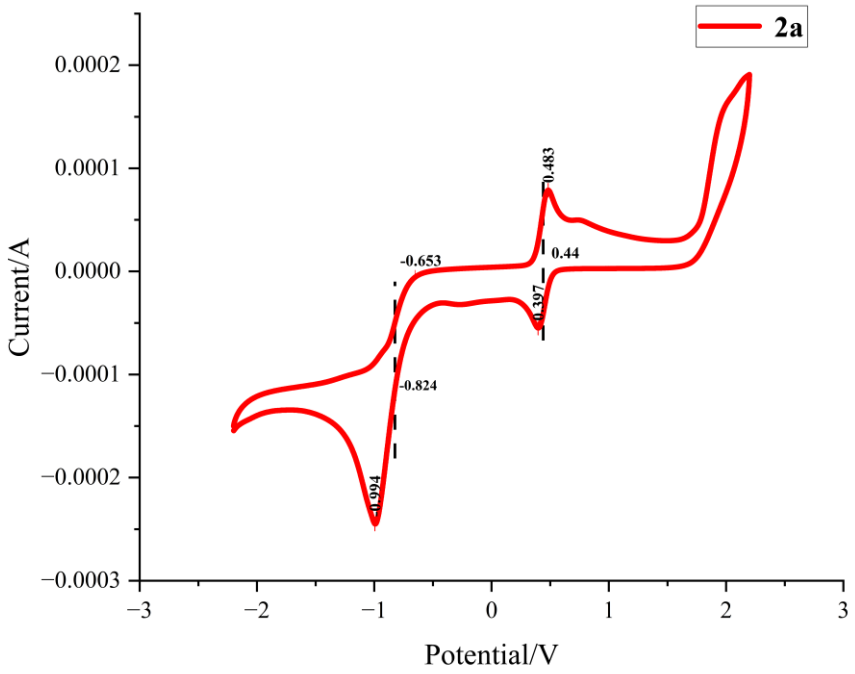


Figure S14. Cyclic voltammetry of **2a**

When the data measured with respect to Fc/Fc+ ($E_{1/2}$= 0.439 V vs. Ag/AgCl), $E_{1/2}$(**2a**) = -0.825 V (vs Ag/AgCl) was obtained.

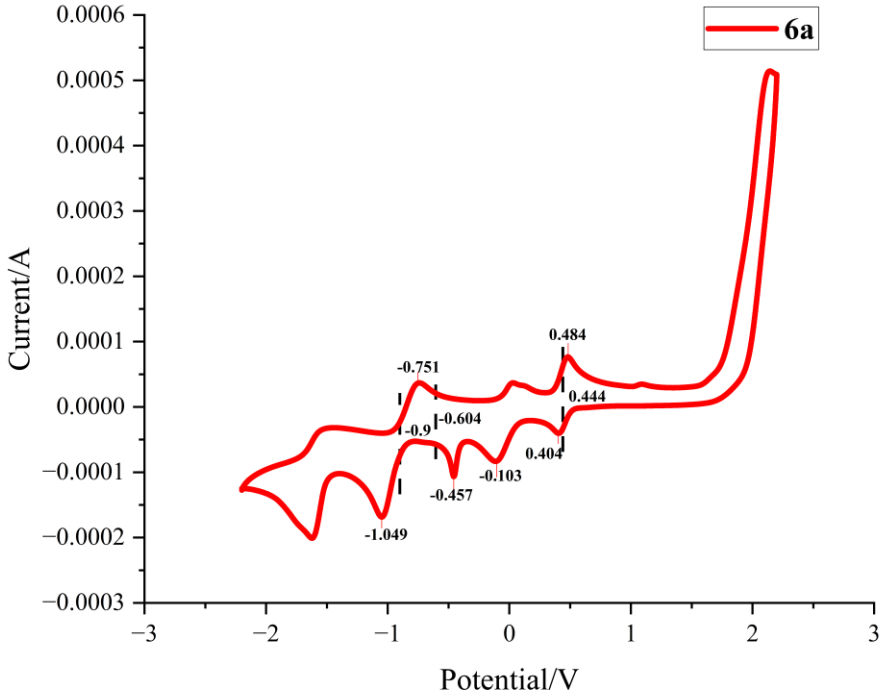


Figure S15. Cyclic voltammetry of **6a**

When the data measured with respect to Fc/Fc^+ ($E_{1/2}$= 0.439 V vs. Ag/AgCl), $E_{1/2}$(**6a**) = -0.905 V (vs Ag/AgCl) was obtained.

V. V An alternate mechanism for the synthesis of 3a

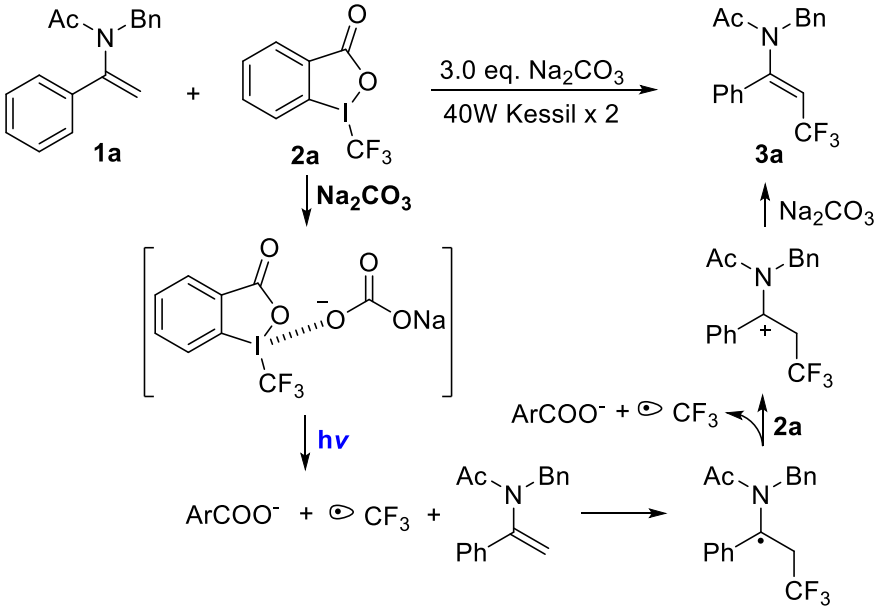
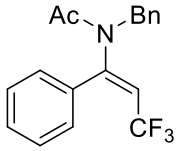
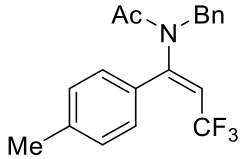


Figure S16. An alternate mechanism for the synthesis of **3a**.

VI The date of products 3, 5, 7, 8, 10

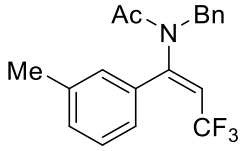


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl) acetamide (**3a**), 73%, 23.3 mg, yellow oil. CAS: 2699644-01-2.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.37 (dt, *J* = 14.6, 7.1 Hz, 3H), 7.28-7.20 (m, 5H), 7.11-7.06 (m, 2H), 5.38 (q, *J* = 8.2 Hz, 1H), 4.45 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.8 (q, *J* = 6.6 Hz), 136.5, 132.9, 130.8, 128.9, 128.7, 128.6, 127.7, 126.2 (q, *J* = 270 Hz), 117.4 (q, *J* = 33.3 Hz), 49.6, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -55.94. IR (cm^{-1}): 3064, 3030, 2926, 1673, 1446, 1379, 1272, 1126, 779, 699.

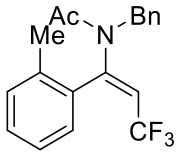


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl)acetamide (**3b)**, 69%, 23.0 mg, yellow oil. CAS: 2933938-20-4.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.24-7.13 (m, 7H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.32 (q, *J* = 8.2 Hz, 1H), 4.44 (s, 2H), 2.32 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.9 (q, *J* = 6.6 Hz), 141.2, 136.6, 129.9, 129.4, 128.8, 128.7, 128.5, 127.6, 126.2 (q, *J* = 270 Hz), 116.8 (q, *J* = 33.3 Hz), 49.5, 22.5, 21.4. ^{19}F NMR (376 MHz,

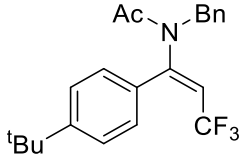
$CDCl_3$): -55.90. IR (cm^{-1}): 3064, 3030, 2926, 1672, 1512, 1378, 1271, 1126, 979, 834.



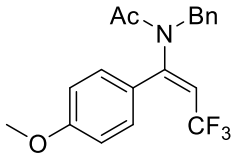
(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(m-tolyl)prop-1-en-1-yl)acetamide (**3c)**, 72%, 23.9 mg, yellow oil. Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.25-7.16 (m, 5H), 7.08 (d, *J* = 7.9 Hz, 3H), 7.01 (s, 1H), 5.36 (q, *J* = 8.2 Hz, 1H), 4.44 (s, 2H), 2.29 (s, 3H), 2.17 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 150.1 (q, *J* = 6.6 Hz), 138.5, 136.7, 132.8, 131.6, 129.2, 128.7, 128.5, 127.7, 126.3, 126.2 (q, *J* = 270 Hz), 117.2 (q, *J* = 33.3 Hz), 49.2, 22.6, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): -55.90. IR (cm^{-1}): 3063, 3030, 2927, 1672, 1494, 1378, 1126, 979, 702. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NO^+$ $(M+H)^+$ 334.1419, found 334.1414.



(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(o-tolyl)prop-1-en-1-yl)acetamide (**3d)**, 62%, 20.6 mg, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.23 (d, *J* = 21.2 Hz, 2H), 7.20-7.09 (m, 4H), 7.03-6.96 (m, 3H), 5.60 (q, *J* = 7.7 Hz, 1H), 4.39 (s, 2H), 2.30 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.7 (q, *J* = 6.6 Hz), 136.9, 136.8, 132.2, 130.7, 130.2, 128.6, 127.6, 127.4, 126.4 (q, *J* = 270 Hz), 125.7, 116.7 (q, *J* = 36.6 Hz), 49.1, 23.1, 19.5. ^{19}F NMR (376 MHz, $CDCl_3$): -56.87. IR (cm^{-1}): 3064, 3029, 2928, 1672, 1494, 1375, 1220, 1126, 981. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NO^+$ $(M+H)^+$ 334.1419, found 334.1410.

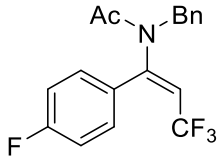


(*E*)-*N*-benzyl-*N*-(1-(4-(tert-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (**3e)**, 66%, 24.7 mg, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.43 (d, *J* = 6.5 Hz, 2H), 7.32-7.25 (m, 5H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.40 (q, *J* = 8.3 Hz, 1H), 4.52 (s, 2H), 2.24 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 154.2, 149.8 (q, *J* = 6.6 Hz), 129.7, 128.7, 128.5, 127.6, 126.2 (q, *J* = 270 Hz), 125.6, 116.9 (q, *J* = 36.6 Hz), 49.5, 34.9, 31.1, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -55.91. IR(cm^{-1}): 3031, 2963, 2869, 1673, 1494, 1380, 1271, 1127, 978, 847. HRMS (ESI) m/z calcd for $C_{22}H_{25}F_3NO^+$ $(M+H)^+$ 376.1888, found 376.1883.

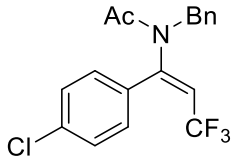


(E)-N-benzyl-N-(3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)acetamide **(3f)**,

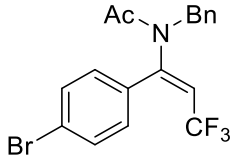
78%, 54.5 mg, oil. CAS: 2867534-02-7.[3] Column chromatography on silica gel (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (dt, *J* = 8.5, 3.4 Hz, 5H), 7.19 – 7.14 (m, 2H), 6.96 – 6.90 (m, 2H), 5.36 (q, *J* = 8.3 Hz, 1H), 4.53 (s, 2H), 3.85 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.09, 161.51, 149.61(dd, J_1=11.99 Hz, J_2=5.92 Hz), 136.59, 130.51(dd, J_1=4.06 Hz, J_2= 2.15 Hz), 128.66, 128.47, 127.59, 124.86, 123.65, 120.96, 116.01(q, *J*=35.00 Hz), 114.09, 55.30, 49.58, 22.48. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -55.89.



(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(4-fluorophenyl)prop-1-en-1-yl)acetamide (**3g**), 64%, 21.6 mg. CAS: 2867534-09-4.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.26 (m, 5H), 7.16-7.08 (m, 4H), 5.46 (q, *J* = 8.1 Hz, 1H), 4.53 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 165.2, 162.7, 148.8 (q, *J* = 6.6 Hz), 136.3, 131.0, 130.9, 128.6, 127.8, 126.1 (q, *J* = 270 Hz), 117.4 (q, *J* = 36.6 Hz), 116.0, 115.8, 49.6, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -55.94, -108.64. IR (cm^{-1}): 3066, 2935, 1673, 1603, 1509, 1379, 1127, 979, 848.

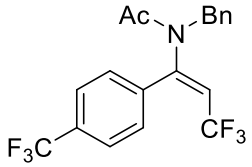


(*E*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (**3h**), 60%, 21.2 mg. CAS: 2867534-12-9.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (d, *J* = 8.6 Hz, 2H), 7.31-7.22 (m, 5H), 7.14 (d, *J* = 7.7 Hz, 2H), 5.48 (q, *J* = 8.1 Hz, 1H), 4.53 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 148.8 (q, *J* = 6.6 Hz), 137.0, 136.3, 131.4, 130.2, 129.1, 128.7, 128.6, 127.8, 126.0 (q, *J* = 270 Hz), 117.8 (q, *J* = 33.3 Hz), 49.7, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -55.94. IR (cm^{-1}): 3065, 3031, 2934, 1674, 1652, 1491, 1378, 1128, 1014, 843, 703.

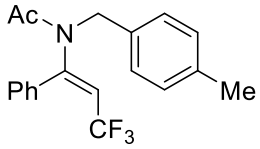


(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (**3i**), 54%, 21.4 mg, CAS: 2867534-15-2.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (d, *J* = 8.5 Hz, 2H), 7.25-7.18 (m, 3H), 7.12-7.03 (m, 4H), 5.41 (q, *J* = 8.1 Hz, 1H), 4.45 (s, 2H), 2.16 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 148.9 (q, *J* = 6.6 Hz), 136.3, 132.0, 131.9, 130.4, 128.7, 128.6, 127.8, 126.0 (q, *J* = 270 Hz), 125.3, 117.8 (q, *J* = 33.3 Hz), 49.7, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -55.91. IR (cm^{-1}): 3065, 3030, 2935, 2853, 1674, 1652, 1379, 1276, 1128,

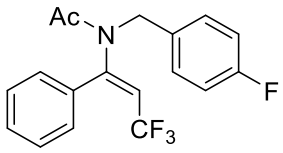
1029, 841.



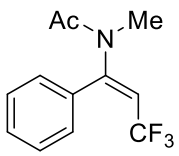
(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl) acetamide (**3j)**, 56%, 21.7 mg, oil. CAS: 2867534-06-1.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 3H), 7.05 (d, *J* = 5.5 Hz, 2H), 5.51 (q, *J* = 8.1 Hz, 1H), 4.46 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 148.6 (q, *J* = 6.6 Hz), 136.6, 136.2, 133.1 (q, *J* = 33.3 Hz), 129.3, 128.7, 128.5, 127.9, 125.7 (q, *J* = 3.3 Hz), 124.9 (q, *J* = 147 Hz), 118.7 (q, *J* = 33.3 Hz), 49.8, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -55.91, -62.98. IR (cm^{-1}): 3067, 3032, 2937, 1677, 1655, 1380, 1219, 1067, 979, 855.



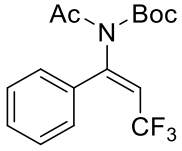
(*E*)-*N*-(4-methylbenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)-acetamide (**3k)**, 70%, 23.3 mg. CAS: 2699644-05-6.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.39 (m, 3H), 7.33 (d, *J* = 6.7 Hz, 2H), 7.13-7.02 (m, 4H), 5.45 (q, *J* = 8.2 Hz, 1H), 4.48 (s, 2H), 2.32 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.9 (q, *J* = 6.6 Hz), 137.4, 133.5, 133.0, 130.7, 129.2, 128.9, 128.7, 128.6, 126.2 (q, *J* = 270 Hz), 117.4 (q, *J* = 36.6 Hz), 22.6, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$): -55.87. IR (cm^{-1}): 3059, 3025, 2926, 1672, 1379, 1273, 1126, 977, 779, 699.



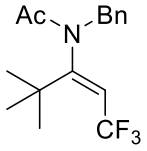
(*E*)-*N*-(4-fluorobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (**3l)**, 67%, 22.6 mg, oil. CAS: 2867534-19-6.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.39 (d, *J* = 22.7 Hz, 3H), 7.25 (d, *J* = 9.8 Hz, 2H), 7.08-7.03 (m, 2H), 6.90 (d, *J* = 17.3 Hz, 2H), 5.36 (q, *J* = 8.1 Hz, 1H), 4.39 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 163.4, 161.0, 149.7 (q, *J* = 6.6 Hz), 132.6, 132.3, 130.9, 130.5, 130.4, 128.8, 128.7, 126,0 (q, *J* = 270 Hz), 117.4 (q, *J* = 33.3 Hz), 115.5, 115.3, 48.6, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -55.94, -114.41. IR (cm^{-1}): 3066, 2937, 1672, 1651, 1509, 1379, 1273, 1126, 980, 779.



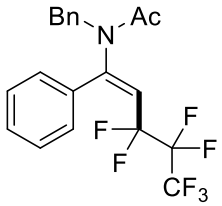
(*E*)-*N*-methyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (**3m)**, 45%, 11.0 mg, oil. CAS: 2699643-75-7.[3] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.29 (m, 5H), 5.64 (q, *J* = 8.1 Hz, 1H), 2.90 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.4, 151.8 (q, *J* = 6.6 Hz), 133.1, 130.7, 128.7, 126.5 (q, *J* = 270 Hz), 115.2 (q, *J* = 33.3 Hz), 35.3, 22.4. ^{19}F NMR (376 MHz, $CDCl_3$): -55.78. IR (cm^{-1}): 3063, 2959, 2852, 1674, 1651, 1370, 1269, 1130, 892, 699.



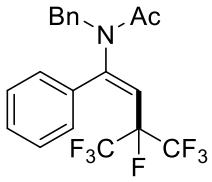
tert-butyl (*E*)-acetyl(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)carbamate (**3n)**, 42%, 13.8 mg, oil. CAS: 2867534-20-9.[3] Column chromatography on silica gel (PE/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.31 (dt, *J* = 17.7, 6.5 Hz, 7H), 5.70 (q, *J* = 8.0 Hz, 1H), 2.55 (s, 1H), 2.46 (s, 3H), 1.30 (s, 9H), 1.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.3, 151.5, 146.7 (q, *J* = 6.6 Hz), 134.5, 129.7, 128.8, 128.0, 126.1 (q, *J* = 270 Hz), 119.8 (q, *J* = 33.3 Hz), 84.3, 27.7, 26.2. ^{19}F NMR (376 MHz, $CDCl_3$): -55.90, -60.65. IR (cm^{-1}): 2980, 2934, 1746, 1713, 1369, 1253, 1133, 988, 773.



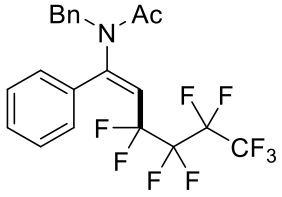
(E)-N-benzyl-N-(1,1,1-trifluoro-4,4-dimethylpent-2-en-3-yl)acetamide **(3o)**, 17%, 10 mg, oil. Column chromatography on silica gel (PE/EtOAc = 15:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 5H), 5.80 (q, *J* = 7.8 Hz, 1H), 5.02 (d, *J* = 15.2 Hz, 1H), 4.34 (d, *J* = 15.2 Hz, 1H), 2.07 (s, 3H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.25, 161.13(dd, J_1 = 11.16 Hz, J_2 = 5.54 Hz), 137.12, 128.79, 128.74, 128.26, 127.33, 116.60 (q, *J* = 33.67 Hz), 53.83, 53.81, 38.35, 30.18, 22.41. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.02, -60.35, -65.05.



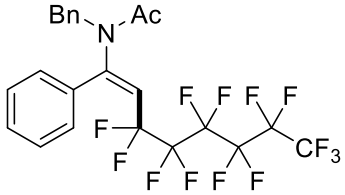
(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,5-heptafluoro-1-phenylpent-1-en-1-yl)acetamide (**5a)**, 67%, 28.0 mg, oil. CAS: 2649271-68-9.[4] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.36 (m, 3H), 7.35-7.22 (m, 5H), 7.15 (d, *J* = 5.8 Hz, 2H), 5.43 (t, *J* = 13.2 Hz, 1H), 4.50 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 151.6, 136.5, 133.2, 130.7, 129.1 (t, *J* = 3 Hz), 128.6, 128.5, 127.7, 114.0 (t, *J* = 22 Hz), 113.7, 49.4, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -80.19 (t, *J* = 9.8 Hz), -104.68 (q, *J* = 9.9 Hz), -126.72. IR (cm^{-1}): 3063, 3031, 2934, 1674, 1380, 1227, 1112, 949, 867, 699.



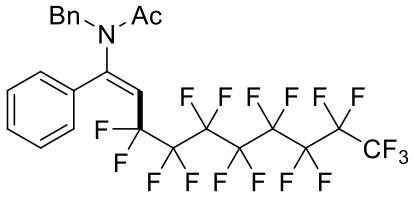
(*E*)-*N*-benzyl-*N*-(3,4,4,4-tetrafluoro-1-phenyl-3-(trifluoromethyl)but-1-en-1-yl) acetamide (**5b)**, 63%, 26.9 mg, yellow oil. Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.48-7.37 (m, 3H), 7.28 (t, *J* = 8.6 Hz, 5H), 7.16 (d, *J* = 6.0 Hz, 2H), 5.21 (d, *J* = 26.5 Hz, 1H), 4.45 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.4, 149.5, 136.4, 133.1 (d, *J* = 2 Hz), 130.2, 129.0 (d, *J* = 4 Hz), 128.8, 128.5, 128.2, 127.7, 112.8 (d, *J* = 14 Hz), 48.7, 22.4. ^{19}F NMR (376 MHz, $CDCl_3$): -76.42 (d, *J* = 7.5 Hz), -183.58. IR (cm^{-1}): 3062, 3031, 2934, 1672, 1494, 1381, 1227, 1037, 977, 699. HRMS (ESI) m/z calcd for $C_{20}H_{17}F_7NO^+$ $(M+H)^+$ 420.1198, found 420.1192.



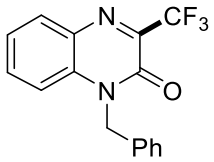
(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)acetamide (**5c)**, 72%, 33.7 mg, oil. CAS: 2649271-35-0.[4] Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (dt, *J* = 24.4, 7.1 Hz, 3H), 7.27 - 7.18 (m, 5H), 7.07 (d, *J* = 6.0 Hz, 2H), 5.36 (t, *J* = 14.4 Hz, 1H), 4.43 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 151.6, 136.5, 133.2, 130.7, 129.1 (t, *J* = 3 Hz), 128.6, 128.5, 127.7, 114.1 (t, *J* = 22 Hz), 49.4, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -81.06 – -81.12 (m), -104.00 (t, *J* = 12.9 Hz), -123.27 (q, *J* = 10.1 Hz), -125.71 – -125.82 (m). IR (cm^{-1}): 3060, 3030, 2936, 1670, 1496, 1384, 1227, 1037, 977, 699.



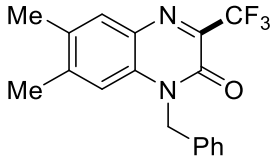
(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloct-1-en-1-yl) acetamide CAS: 2649271-69-0.[4] (**5d)**, 70%, 39.8 mg, oil. Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.39 (m, 3H), 7.34-7.24 (m, 5H), 7.15 (d, *J* = 5.9 Hz, 2H), 5.43 (t, *J* = 14.3 Hz, 1H), 4.51 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 151.5, 136.5, 133.2, 130.7, 129.1 (t, *J* = 3 Hz), 128.6, 128.5, 127.7, 114.3 (t, *J* = 22 Hz), 49.4, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -80.87 (t, *J* = 10.2 Hz), -103.77 – -103.98 (m), -121.55 – -121.76 (m), -122.40 (t, *J* = 11.7 Hz), -122.88, -126.11 – -126.20 (m). IR (cm^{-1}): 3064, 3032, 2935, 1673, 1644, 1381, 1239, 1144, 810, 699.



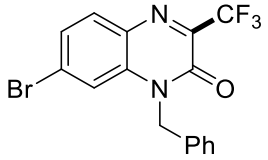
(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-phenyldec-1-en-1-yl)acetamide CAS: 2649271-70-3[4] (**5e)**, 68%, 45.5 mg, oil. Column chromatography on silica gel (PE/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.44 (dd, *J* = 16.9, 5.2 Hz, 3H), 7.36-7.22 (m, 5H), 7.16 (s, 2H), 5.43 (t, *J* = 14.1 Hz, 1H), 4.51 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 151.5, 136.5, 133.2, 130.7, 129.1 (t, *J* = 3 Hz), 128.6, 128.5, 127.7, 114.3 (t, *J* = 22 Hz), 49.4, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -80.85 (t, *J* = 10.0 Hz), -103.87 (t, *J* = 13.7 Hz), -121.43, -121.91, -122.37, -122.73, -126.13. IR (cm^{-1}): 3064, 3031, 2934, 1674, 1495, 1380, 1212, 1147, 976, 700.



1-benzyl-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7a)**, 68%, 20.6 mg, oil. CAS: 2244973-45-1.[6] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.1 Hz, 1H), 7.42-7.24 (m, 7 H), 5.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.8, 144.6 (q, *J* = 33.3 Hz), 134.5, 133.5, 131.9, 129.1, 128.1, 127.1, 124.5, 124.1 (q, *J* = 280 Hz), 114.8, 46.1. ^{19}F NMR (376 MHz, $CDCl_3$): -69.89. IR (cm^{-1}): 3033, 2925, 1672, 1606, 1564, 1361, 1142, 947, 757.

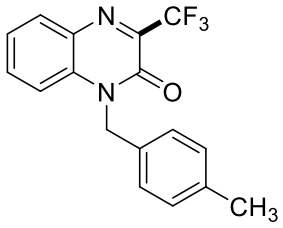


1-benzyl-6,7-dimethyl-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7b)**, 60%, 19.9 mg, M.P. = 158-160 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.73 (s, 1H), 7.36 -7.25 (m, 5H), 7.12 (s, 1H), 5.49 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 144.2, 143.2 (q, *J* = 33.3 Hz), 134.7, 133.9, 132.2, 131.6, 129.7, 129.1, 128.0, 127.1, 124.3 (q, *J* = 273 Hz), 115.1, 45.9, 21.0, 19.1. ^{19}F NMR (376 MHz, $CDCl_3$): -69.67. IR (cm^{-1}): 3064, 2948, 1660, 1620, 1549, 1373, 1190, 1133, 851, 721. HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3N_2O^+$ $(M+H)^+$ 333.1215, found 333.1208.

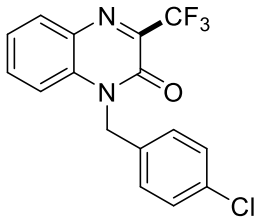


1-benzyl-7-bromo-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7c)**, 61%, 23.3 mg, M.P.>200 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc = 4:1).

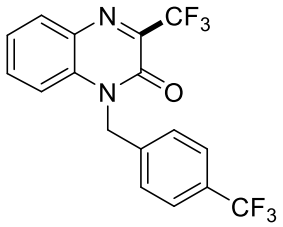
^{1}H NMR (400 MHz, $CDCl_3$): 7.83 (d, J = 8.5 Hz, 1H), 7.55-7.48 (m, 2H), 7.37-7.25 (m, 5H), 5.46 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.4, 144.8 (q, J = 33.3 Hz), 134.9, 133.9, 132.9, 130.0, 129.3, 128.3, 128.1, 127.1, 123.9 (q, J = 273 Hz), 46.2. ^{19}F NMR (376 MHz, $CDCl_3$): -69.95. IR (cm^{-1}): 3097, 2923, 1661, 1595, 1548, 1358, 1192, 1068, 943, 718. HRMS (ESI) m/z calcd for $C_{16}H_{11}BrF_3N_2O^+$ $(M+H)^+$ 383.0007, found 383.0002.



1-(4-methylbenzyl)-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7d**), 65%, 20.6 mg, oil. CAS: 2307774-59-8.[6] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (dd, J = 8.2, 1.5 Hz, 1H), 7.52 (t, J = 8.7 Hz, 1H), 7.34-7.28 (m, 2H), 7.07 (q, J = 8.1 Hz, 4H), 5.41 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.8, 144.6 (q, J = 33.3 Hz), 137.9, 134.1, 133.4, 131.9, 131.5, 131.2, 129.7, 127.1, 124.5, 124.0 (q, J = 273 Hz), 114.9, 45.9, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$): -69.90. IR (cm^{-1}): 3024, 2921, 1667, 1605, 1361, 1138, 930, 762, 731.

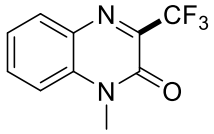


1-(4-chlorobenzyl)-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7e**), 53%, 17.9 mg, oil. CAS: 2350176-15-5.[5] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, J = 8.1 Hz, 1H), 7.58-7.52 (m, 1H), 7.37-7.31 (m, 1H), 7.26-7.21 (m, 3H), 7.15 (d, J = 8.5 Hz, 2H), 5.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.7, 144.3 (q, J = 33.3 Hz), 134.1, 133.8, 133.6, 133.0, 132.1, 131.2, 129.3, 128.6, 124.7, 124.0 (q, J = 273 Hz), 114.5, 45.5. ^{19}F NMR (376 MHz, $CDCl_3$): -69.88. IR (cm^{-1}): 3055, 2958, 1672, 1606, 1491, 1361, 1142, 1080, 933.

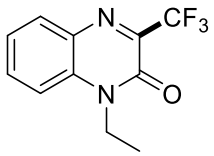


3-(trifluoromethyl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(*1H*)-one (**7f**), 56%, 20.8 mg, M.P.= 118-120 °C, yellow solid. CAS: 2815259-05-1.[5] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (d, J = 8.1 Hz, 1H), 7.62 (dd, J = 14.3, 7.5 Hz, 3H), 7.46-7.37 (m, 3H), 7.28 (d, J = 8.6 Hz,

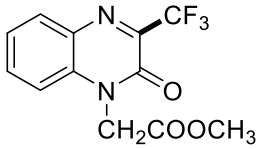
1H), 5.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.6, 144.3 (q, *J* = 33.3 Hz), 138.4, 133.8, 133.7, 132.2, 131.2, 130.7, 130.4, 127.4, 126.2 (q, *J* = 3.3 Hz), 125.2 (q, *J* = 233 Hz), 124.8, 114.4, 45.6. ^{19}F NMR (376 MHz, $CDCl_3$): -62.76, -69.93. IR (cm^{-1}): 3042, 2954, 1673, 1606, 1471, 1326, 1141, 1017, 939, 760.



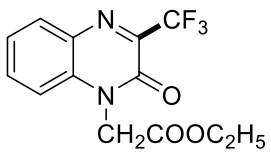
1-Methyl-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7g)**, 63%, 14.3 mg, oil. CAS: 109519-95-1.[5] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (d, *J* = 6.5 Hz, 1H), 7.66 (d, *J* = 17.3 Hz, 1H), 7.41-7.29 (m, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.6, 144.4 (q, *J* = 33.3 Hz), 134.6, 133.5, 131.8, 130.9, 124.5, 124.0 (q, *J* = 273 Hz), 114.0, 29.2. ^{19}F NMR (376 MHz, $CDCl_3$): -70.11. IR (cm^{-1}): 3432, 2921, 1667, 1605, 1565, 1361, 1138, 1079, 930, 762.



1-ethyl-3-(trifluoromethyl)quinoxalin-2(*1H*)-one (**7h)**, 59%, 14.3 mg, oil. CAS: 2244973-43-9.[5] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, *J* = 9.6 Hz, 1H), 7.75-7.70 (m, 1H), 7.46-7.40 (m, 2H), 4.39 (t, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.2, 144.1 (q, *J* = 33.3 Hz), 133.7, 133.4, 132.1, 131.3, 124.3, 121.3 (q, *J* = 273 Hz), 113.8, 37.7, 12.3. ^{19}F NMR (376 MHz, $CDCl_3$): -69.98. IR (cm^{-1}): 3111, 2922, 1664, 1605, 1470, 1145, 1071, 996, 764.

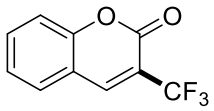


methyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(*2H*)-yl)acetate (**7i)**, 62%, 17.7 mg, oil. CAS: 1057224-82-4.[7] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 8.7 Hz, 1H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.16 (d, *J* = 9.6 Hz, 1H), 5.08 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.9, 151.2, 149.9, 144.0 (q, *J* = 33.3 Hz), 133.7, 132.1, 131.0, 124.8, 124.1 (q, *J* = 283 Hz), 113.5, 53.1, 43.3. ^{19}F NMR (376 MHz, $CDCl_3$): -69.98. IR (cm^{-1}): 3012, 2960, 1736, 1677, 1565, 1362, 1143, 1090, 755.

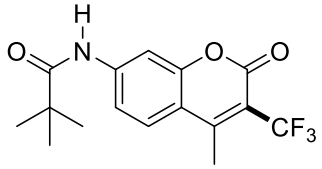


ethyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(*2H*)-yl)acetate (**7j)**, 62%, 18.6 mg, M.P.= 114-116 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc =

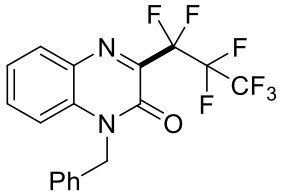
4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.70 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.49-7.42 (m, 1H), 7.16 (dd, *J* = 8.5, 1.1 Hz, 1H), 5.06 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 151.2, 144.0 (q, *J* = 33.3 Hz), 133.8, 133.7, 132.1, 131.0, 124.8, 123.9 (q, *J* = 273 Hz), 113.6, 62.4, 43.4, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): -70.00. IR (cm^{-1}): 3034, 2957, 1735, 1677, 1565, 1363, 1143, 1089, 957, 763. HRMS (ESI) m/z calcd for $C_{13}H_{12}F_3N_2O_3^+$ $(M+H)^+$ 301.0800, found 301.0792.



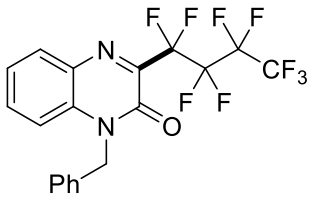
3-(trifluoromethyl)-*2H*-chromen-2-one (**7k)**, 52%, 11.2 mg, oil. CAS: 497959-34-9.[5] Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (s, 1H), 7.64-7.52 (m, 2H), 7.35-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 155.9, 154.7, 143.4 (q, *J* = 6.6 Hz), 134.4, 129.5, 125.3, 124.5 (q, *J* = 206 Hz), 118.3 (q, *J* = 33.3 Hz), 117.0, 116.8. ^{19}F NMR (376 MHz, $CDCl_3$): -66.18. IR (cm^{-1}): 3064, 2955, 1730, 1636, 1611, 1458, 1383, 1174, 975, 759.



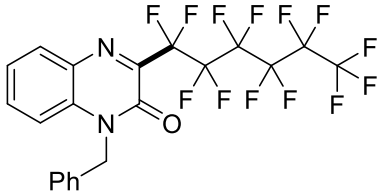
N-(4-methyl-2-oxo-3-(trifluoromethyl)-*2H*-chromen-7-yl)pivalamide (**7l)**, 57%, 18.6 mg, M.P.>200 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.74 (s, 2H), 2.66 (s, 3H), 1.36 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): 177.5, 156.5, 155.0, 153.9, 144.1, 126.8, 124.4 (q, *J* = 260 Hz), 116.5, 114.7, 106.7, 40.1, 27.4, 15.6 (q, *J* = 6.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): -56.48. IR (cm^{-1}): 3352, 2959, 1709, 1687, 1597, 1504, 1334, 1119, 948, 778. HRMS (ESI) m/z calcd for $C_{16}H_{17}F_3NO_3^+$ $(M+H)^+$ 328.1161, found 328.1154.



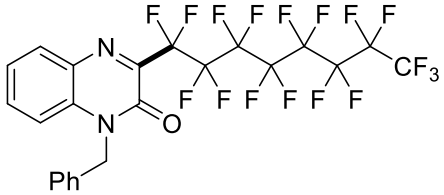
1-benzyl-3-(perfluoropropan-2-yl)quinoxalin-2(*1H*)-one (**8a)**, 61%, 24.6 mg, yellow oil. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 8.7 Hz, 1H), 7.35-7.13 (m, 7H), 5.45 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 144.3 (t, *J* = 20 Hz), 134.5, 133.9, 133.7, 132.0, 131.5, 129.1, 128.1, 127.0, 124.5, 114.8, 46.0. ^{19}F NMR (376 MHz, $CDCl_3$): -80.16 (t, *J* = 9.5 Hz), -113.57 (q, *J* = 9.4 Hz), -124.31 (t, *J* = 13.1 Hz). IR (cm^{-1}): 3034, 2959, 1673, 1605, 1352, 1229, 1118, 969, 756. HRMS (ESI) m/z calcd for $C_{18}H_{12}F_7N_2O^+$ $(M+H)^+$ 405.0838, found 405.0832.



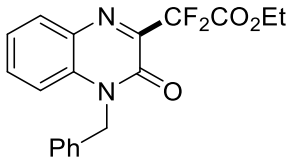
1-benzyl-3-(perfluorobutyl)quinoxalin-2(*1H*)-one (**8b)**, 66%, 29.9 mg, yellow oil. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.00 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.43-7.28 (m, 5H), 7.25 (d, *J* = 6.1 Hz, 2H), 5.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 144.3 (t, *J* = 30 Hz), 134.5, 133.9, 133.7, 132.0, 131.5, 129.1, 128.0, 127.0, 124.5, 114.8, 58.7, 46.1, 8.3. ^{19}F NMR (376 MHz, $CDCl_3$): -80.78 – -80.84 (m), -112.90 – -113.04 (m), -120.62 – -120.79 (m), -125.08 – -125.26 (m). IR (cm^{-1}): 3034, 2973, 1673, 1572, 1352, 1229, 1027, 969, 756. HRMS (ESI) m/z calcd for $C_{19}H_{12}F_9N_2O^+$ $(M+H)^+$ 455.0806, found 455.0801.



1-benzyl-3-(perfluorohexyl)quinoxalin-2(*1H*)-one **(8c)**, 62%, 34.3 mg, M.P.= 48-50 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 15.8 Hz, 1H), 7.42-7.24 (m, 7H), 5.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 167.1, 151.9, 144.4 (t, *J* = 30 Hz), 134.5, 133.9, 133.7, 131.5, 129.1, 128.0, 127.0, 124.5, 114.7, 62.0, 51.5, 46.1, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): -80.76 – -80.82 (m), -112.74 (t, *J* = 14.0 Hz), -119.78 – -119.87 (m), -121.08, -122.54, -125.97 – -126.06 (m). IR (cm^{-1}): 3034, 2983, 1740, 1674, 1559, 1238, 1145, 1028, 755. HRMS (ESI) m/z calcd for $C_{21}H_{12}F_{13}N_2O^+$ $(M+H)^+$ 555.0742, found 555.0737.



1-benzyl-3-(perfluorooctyl)quinoxalin-2(*1H*)-one (**8d)**, 67%, 43.8 mg, M.P.= 68-70 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.04-7.97 (m, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.45-7.25 (m, 7H), 5.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 144.4 (t, *J* = 30 Hz), 134.5, 133.9, 133.7, 132.0, 131.5, 129.1, 128.0, 127.0, 124.4, 114.7, 46.1. ^{19}F NMR (376 MHz, $CDCl_3$): -80.78 (t, *J* = 13.0 Hz), -112.48 – -112.99 (m), -119.50 – -120.03 (m), -120.86, -121.72 (d, *J* = 105.3 Hz), -122.68, -126.06 (t, *J* = 19.1 Hz). IR (cm^{-1}): 3032, 2924, 1674, 1606, 1241, 1211, 1149, 928, 756. HRMS (ESI) m/z calcd for $C_{23}H_{12}F_{17}N_2O^+$ $(M+H)^+$ 655.0678, found 655.0675.



ethyl 2-(4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2,2-difluoroacetate **10**, 58%, 42 mg, M.P.= 104-108 °C, yellow solid. Column chromatography on silica gel (PE/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, J = 9.5 Hz, 1H), 7.61-7.53 (m, 1H), 7.42-7.21 (m, 7H), 5.50 (s, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.3 (t, J = 30 Hz), 152.9, 148.1 (t, J = 20 Hz), 134.4, 133.4, 132.8, 132.0, 131.7, 129.0, 128.0, 126.9, 124.5, 114.8, 112.2, 109.7, 107.2, 63.3, 58.3, 53.4, 45.8, 13.9, 8.1. ^{19}F NMR (376 MHz, $CDCl_3$): -110.38. IR (cm^{-1}): 2928, 1780, 1677, 1663, 1605, 1349, 1118, 942, 758. HRMS (ESI) m/z calcd for $C_{19}H_{17}F_2N_2O_3^+$ $(M+H)^+$ 359.1207, found 359.1201.

Reference:

1. A. Delos Reyes, C. Nieves Escobar, A. Muñoz, M. Huffman and D. Tan. Direct conversion of amino acids to oxetanol bioisosteres via photoredox catalysis. Chem. Sci., **2023**, 14, 10524.
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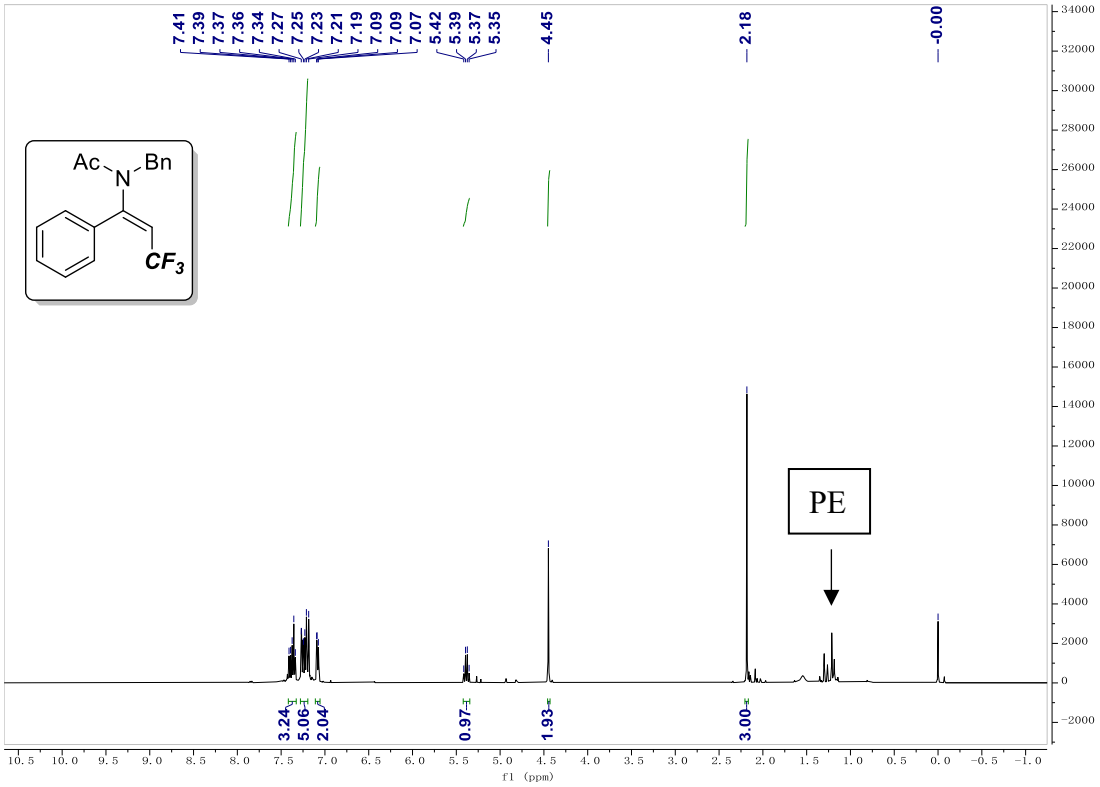
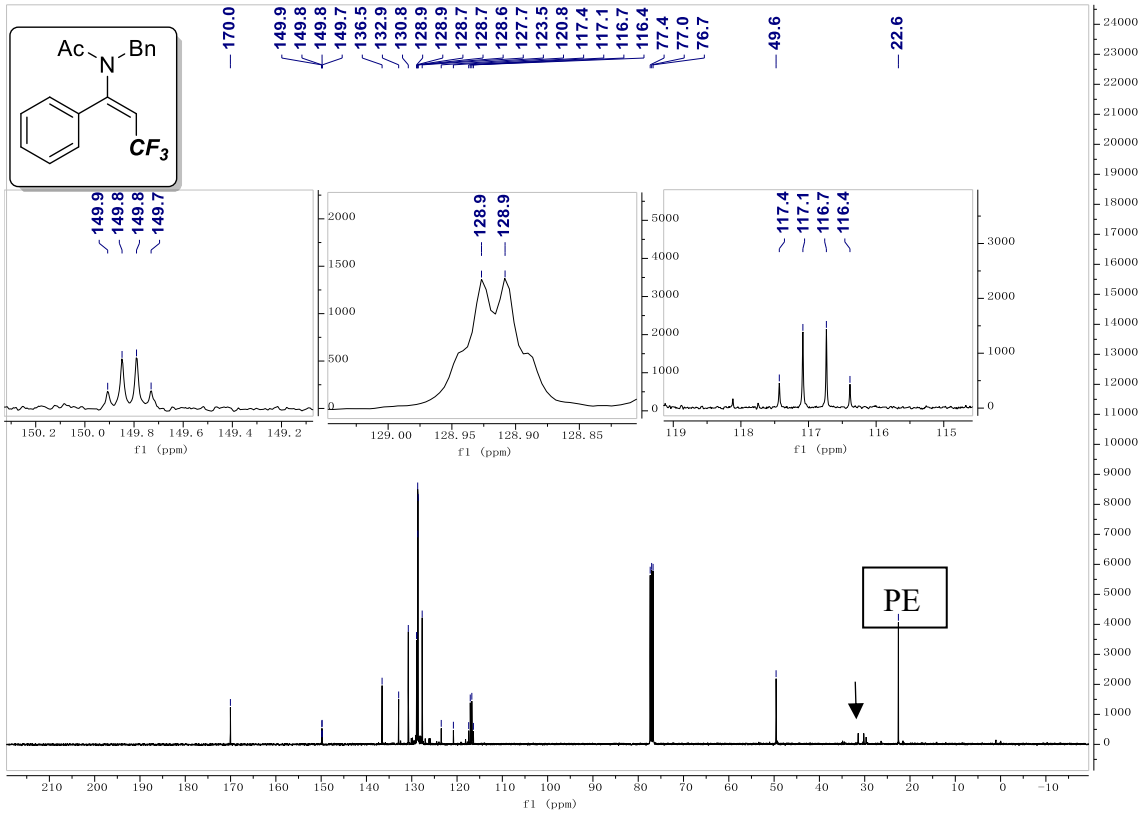
VI. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compounds 3, 5, 7, 8, 10

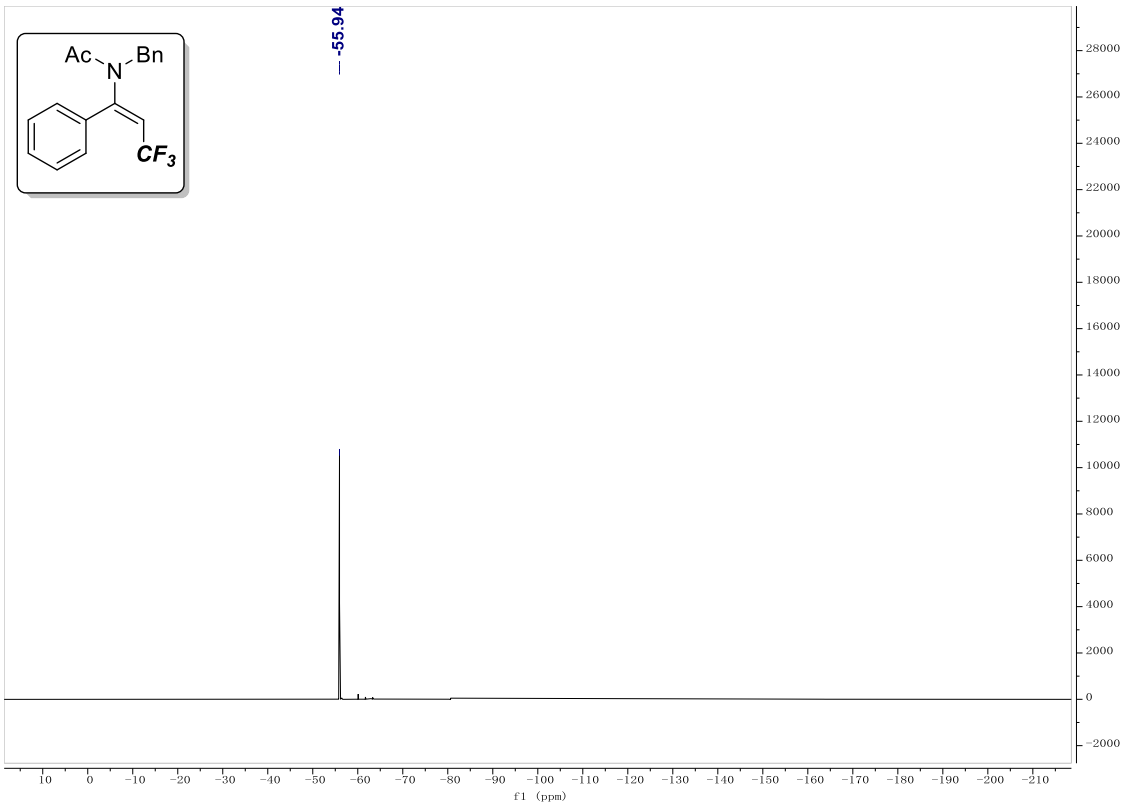
^{1}H NMR (400 MHz) Spectrum of **3a** in $CDCl_3$



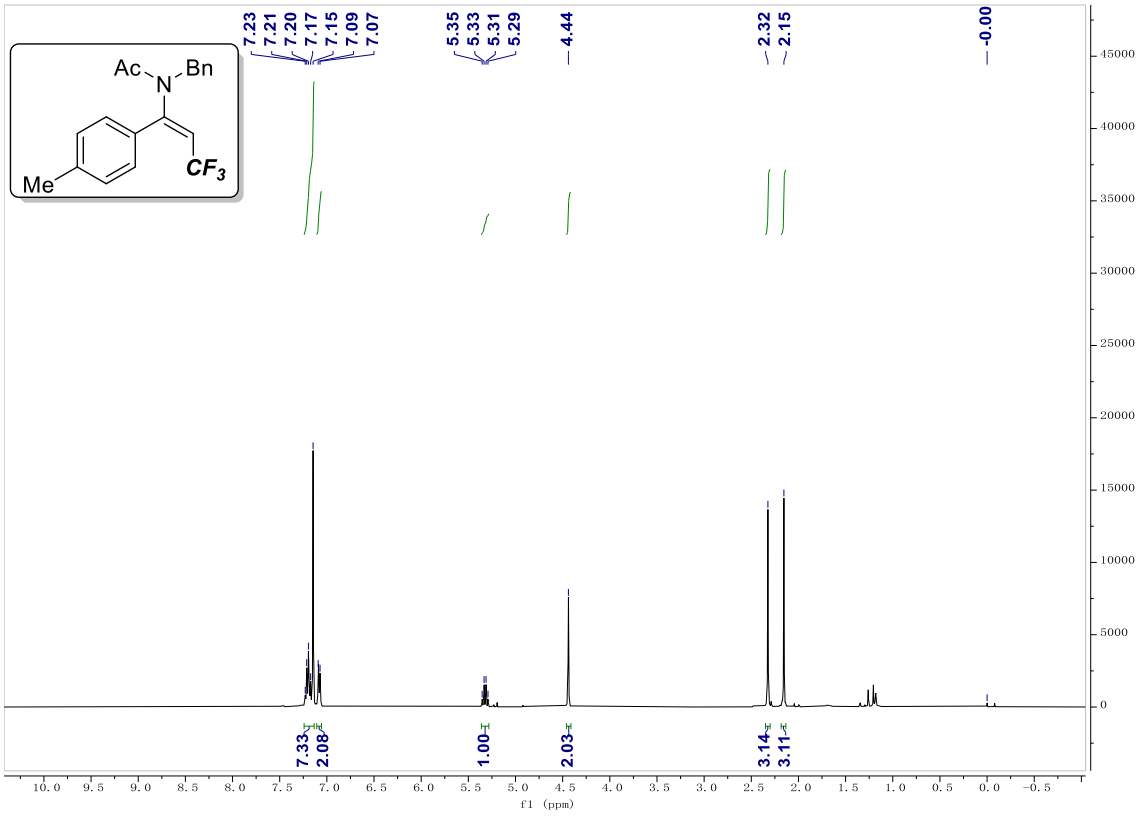
^{13}C NMR (100 MHz) Spectrum of **3a** in $CDCl_3$



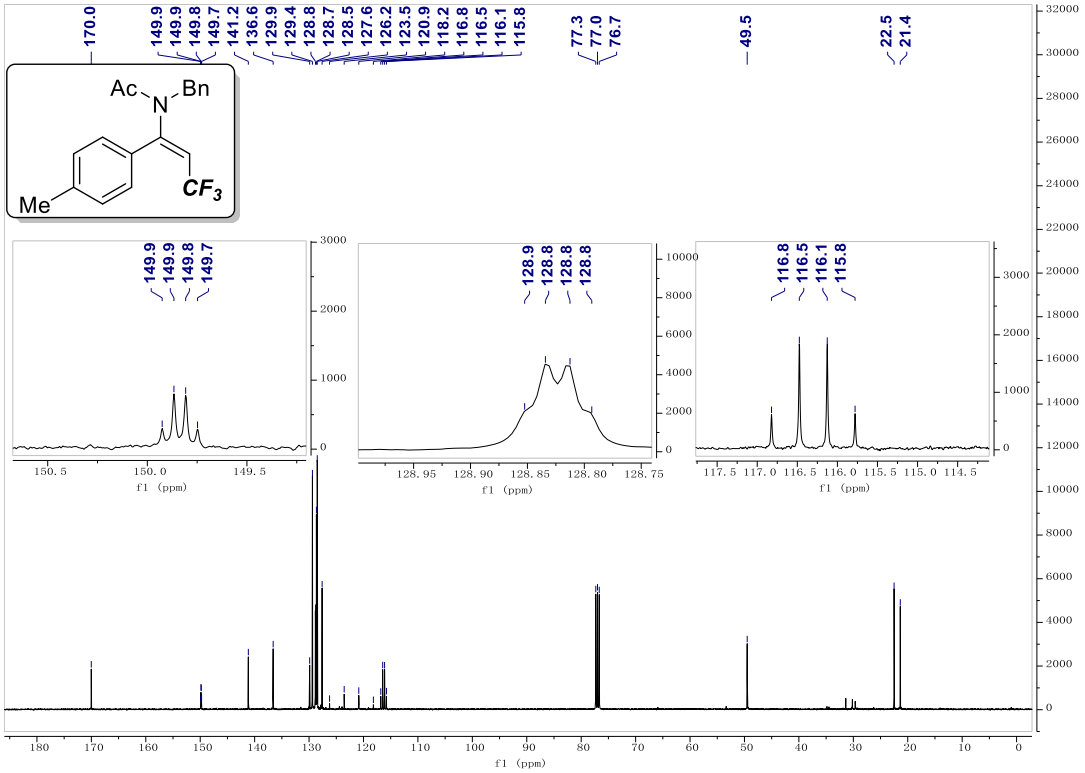
^{19}F NMR (376 MHz) Spectrum of **3a** in $CDCl_3$



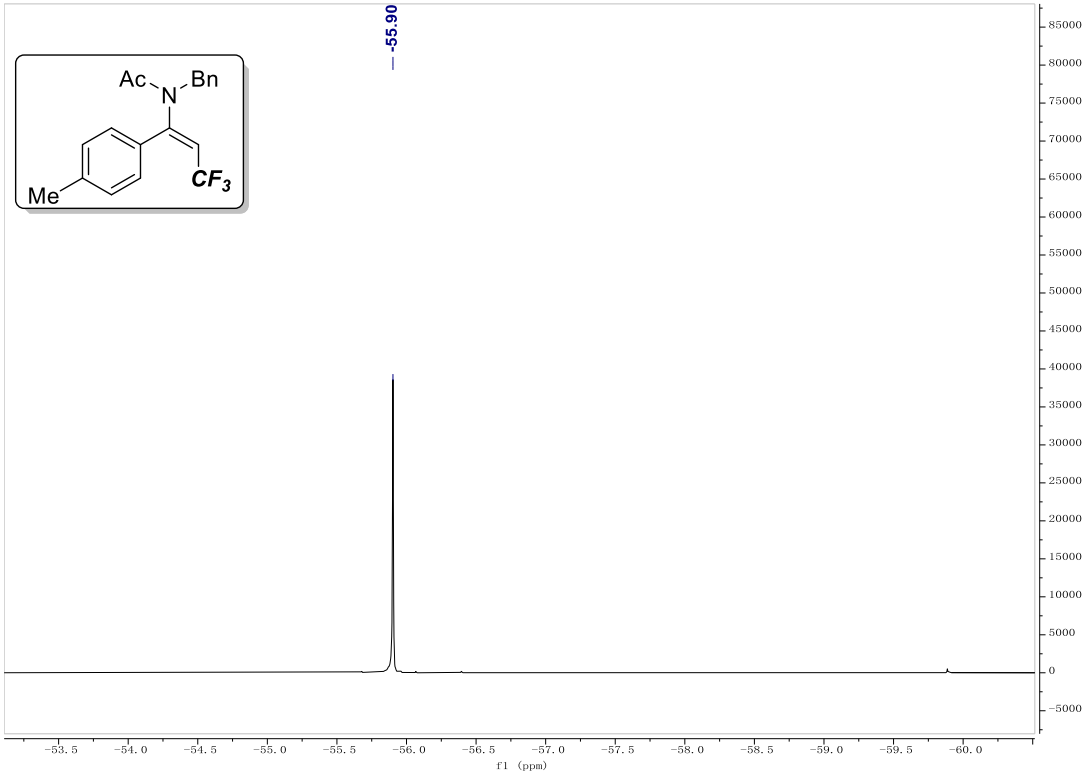
^{1}H NMR (400 MHz) Spectrum of **3b** in $CDCl_3$



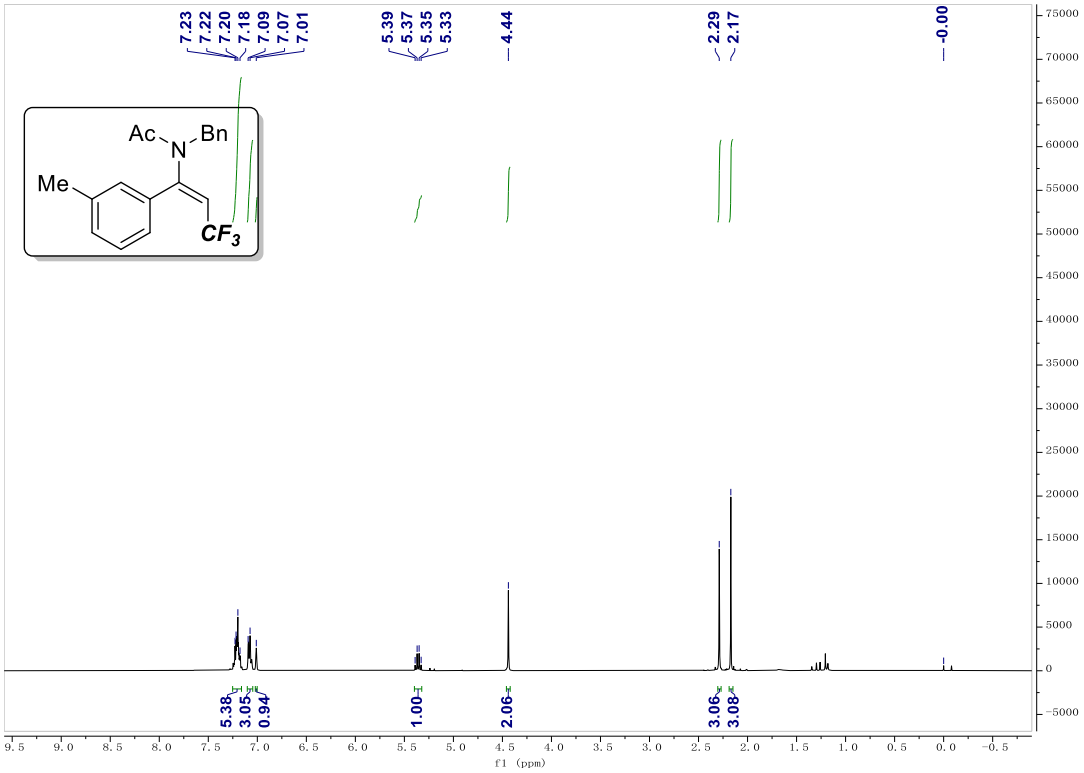
^{13}C NMR (100 MHz) Spectrum of **3b** in $CDCl_3$



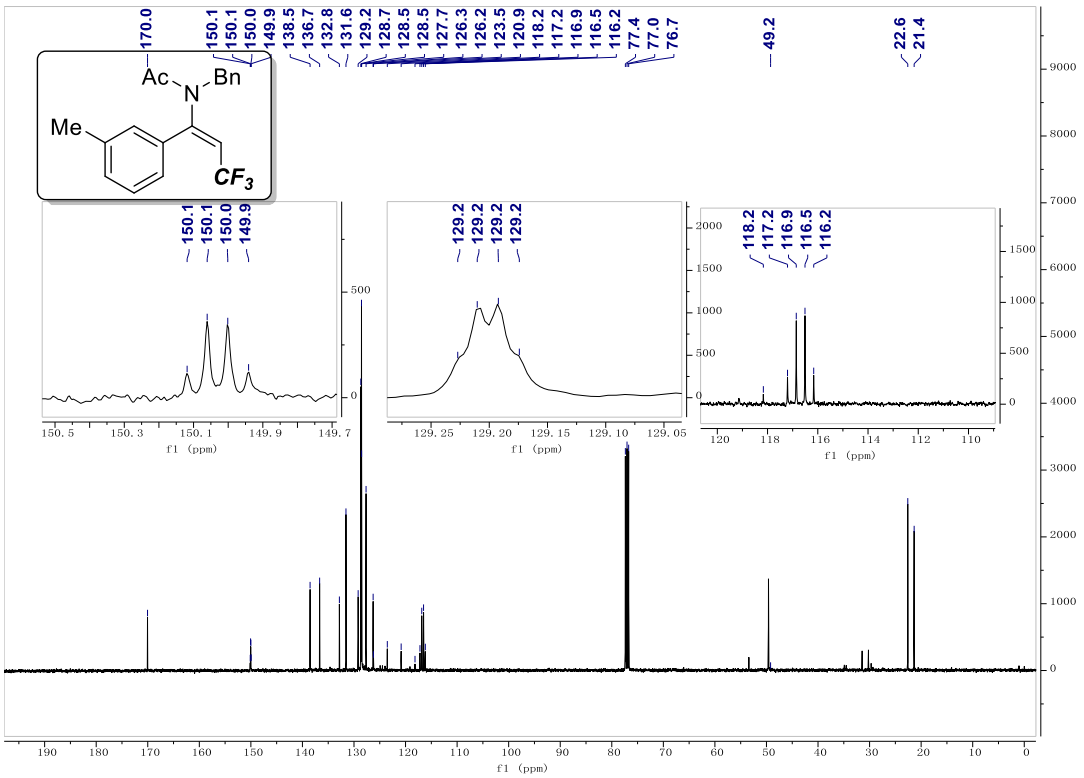
^{19}F NMR (376 MHz) Spectrum of **3b** in $CDCl_3$



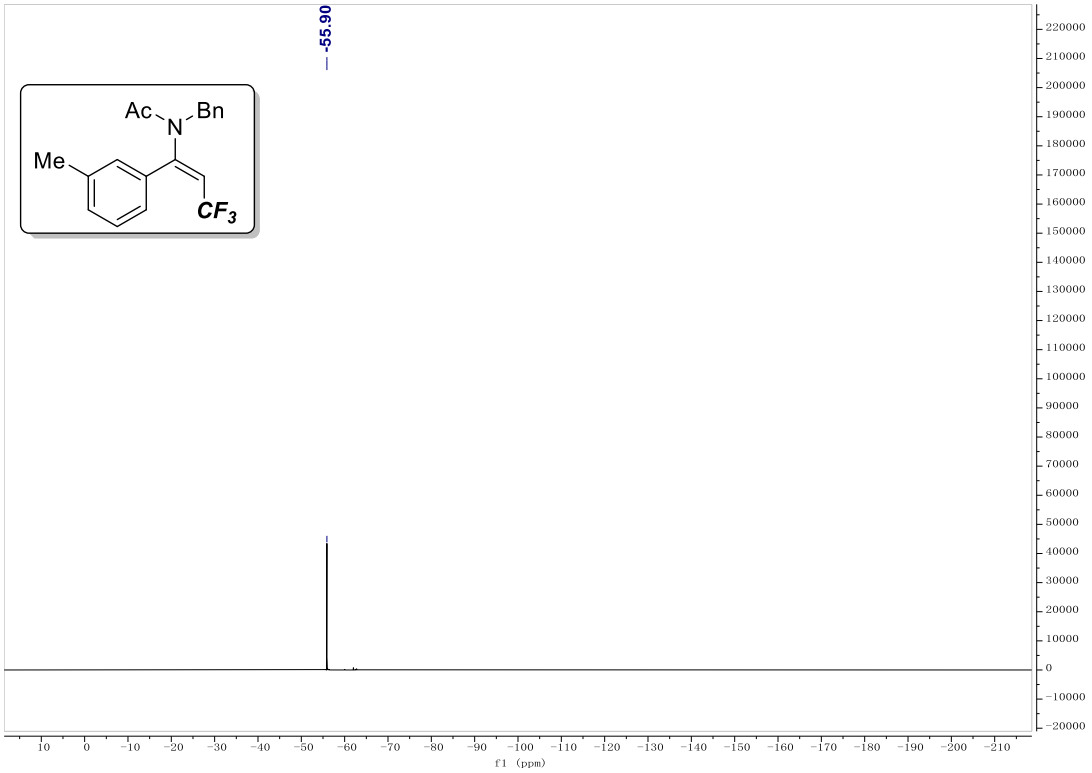
^{1}H NMR (400 MHz) Spectrum of **3c** in $CDCl_3$



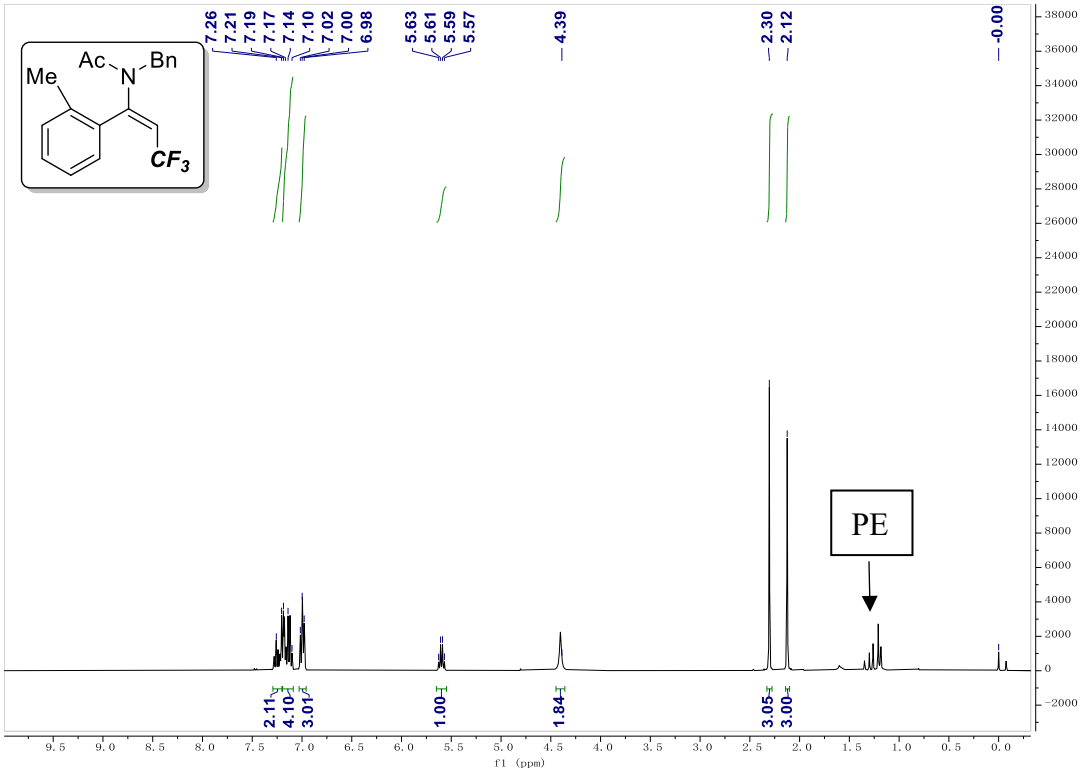
^{13}C NMR (100 MHz) Spectrum of **3c** in $CDCl_3$



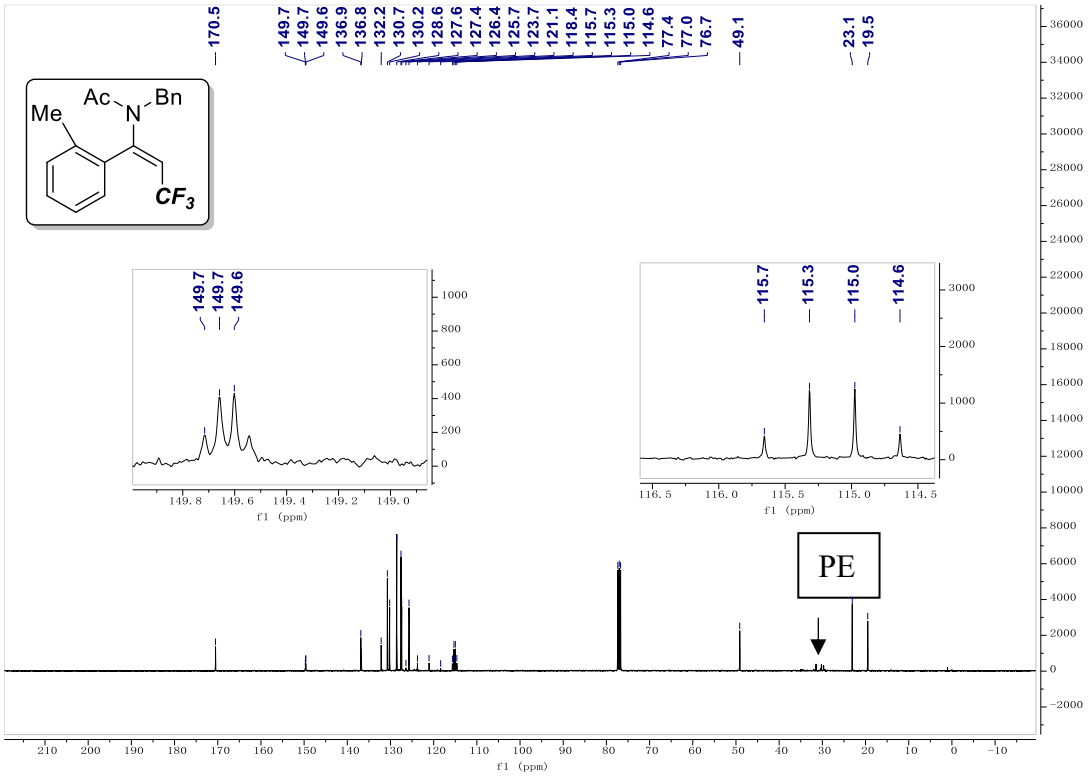
^{19}F NMR (376 MHz) Spectrum of **3c** in $CDCl_3$



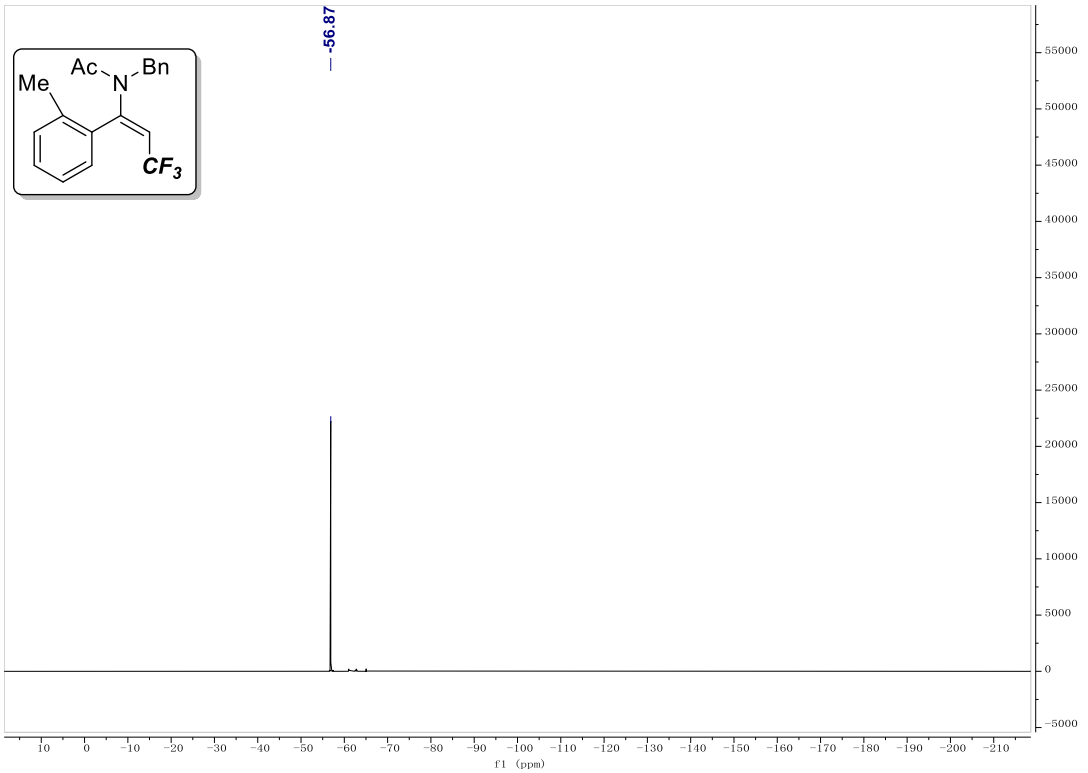
^{1}H NMR (400 MHz) Spectrum of **3d** in $CDCl_3$



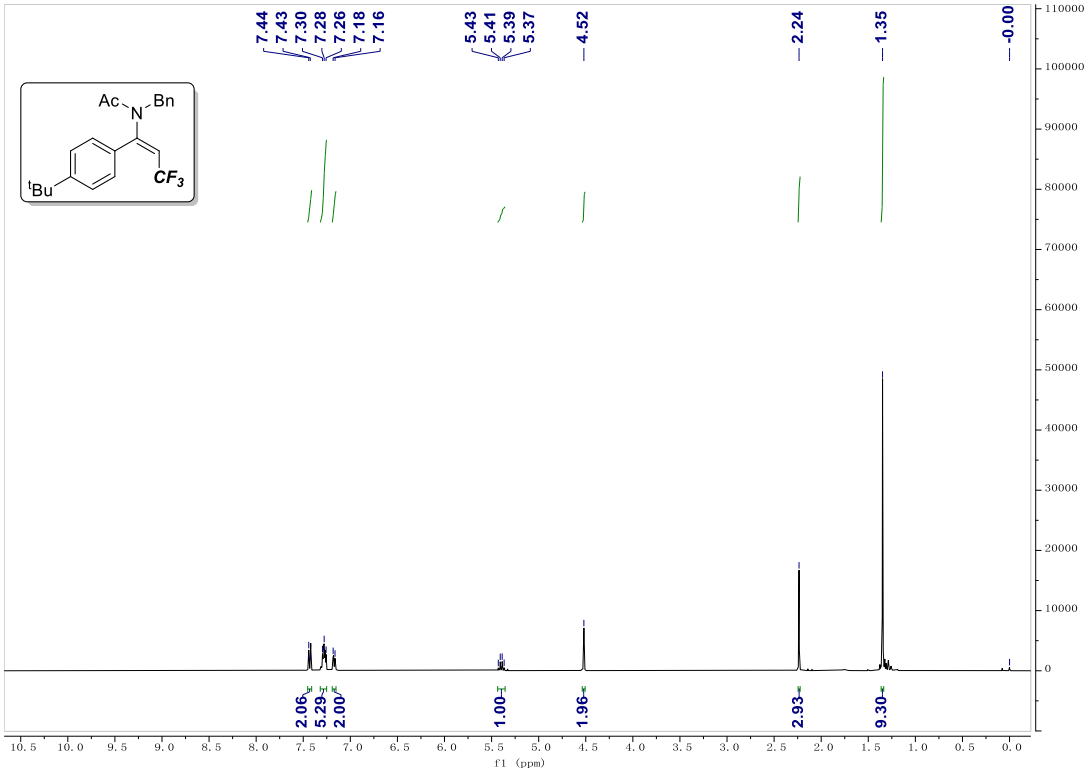
^{13}C NMR (100 MHz) Spectrum of **3d** in $CDCl_3$



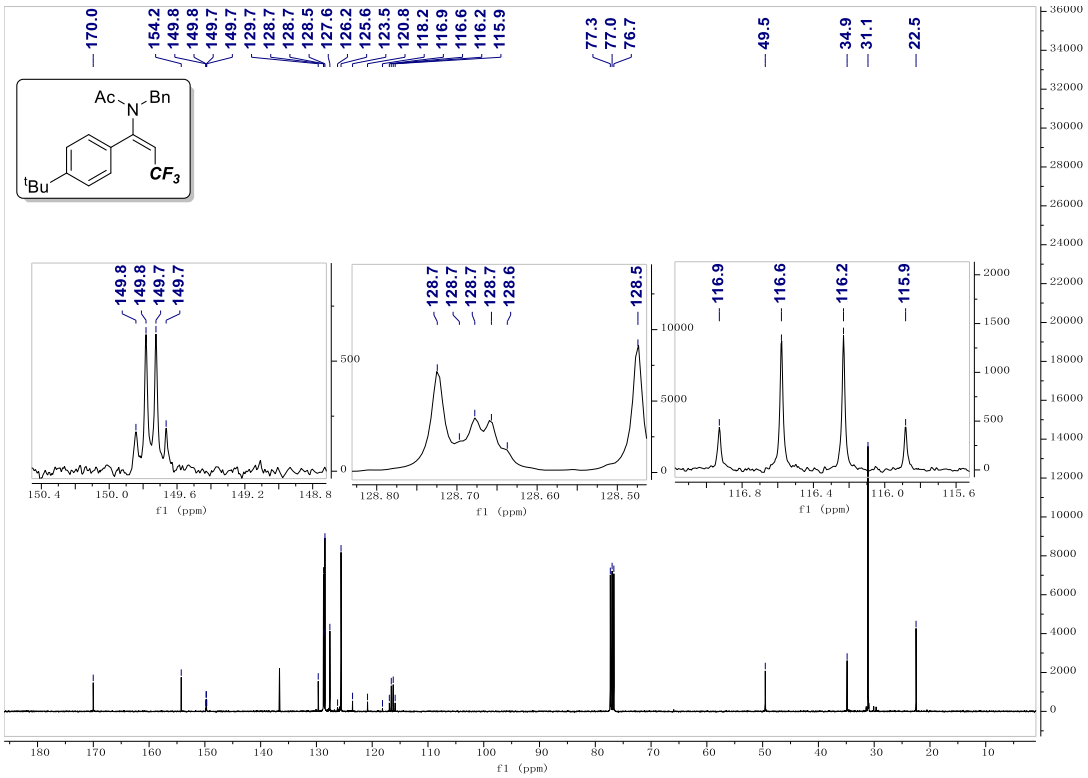
^{19}F NMR (376 MHz) Spectrum of **3d** in $CDCl_3$



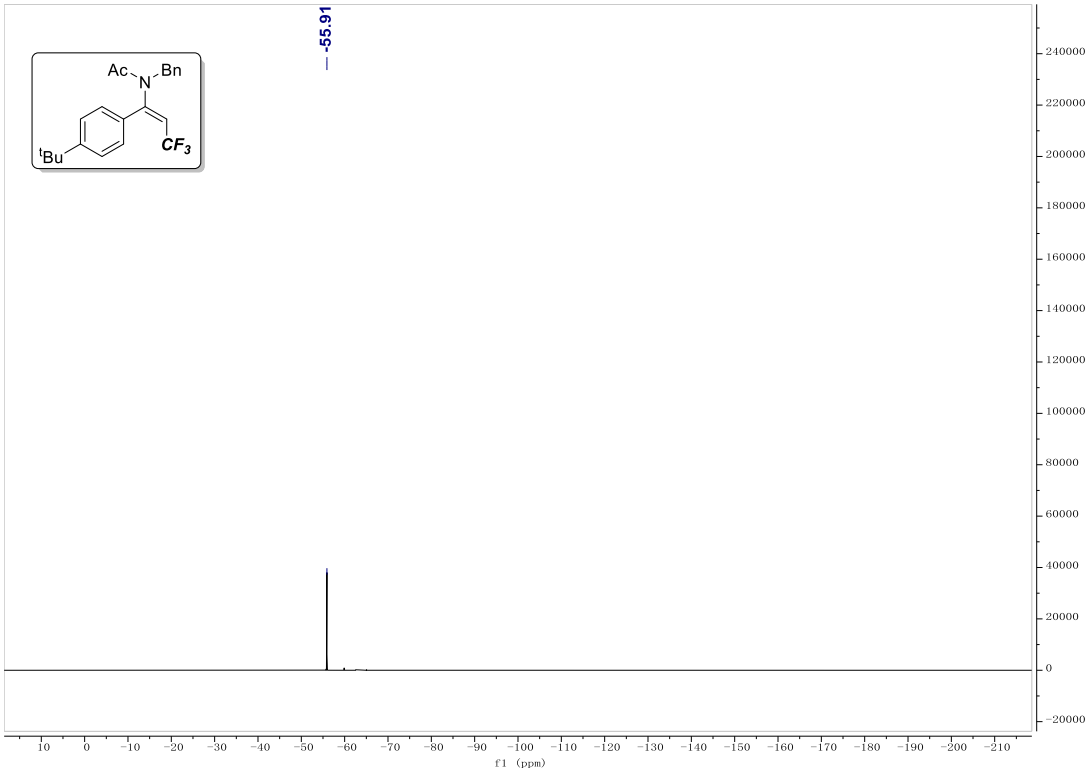
^{1}H NMR (400 MHz) Spectrum of **3e** in $CDCl_3$



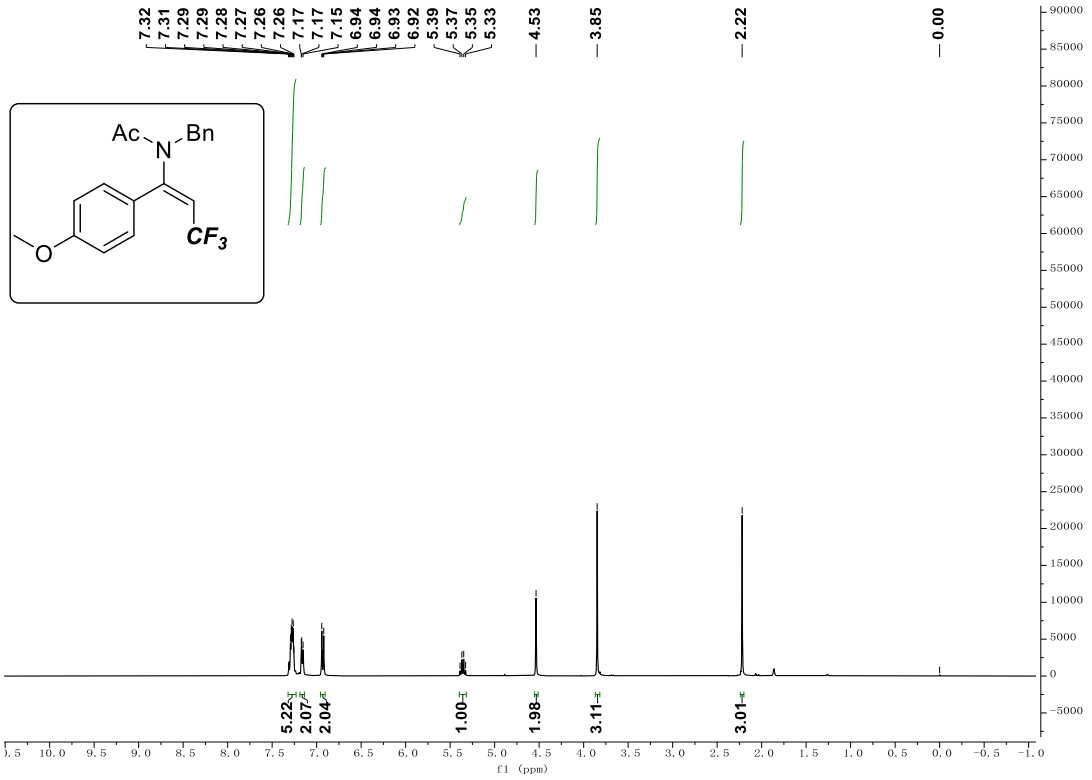
^{13}C NMR (100 MHz) Spectrum of **3e** in $CDCl_3$



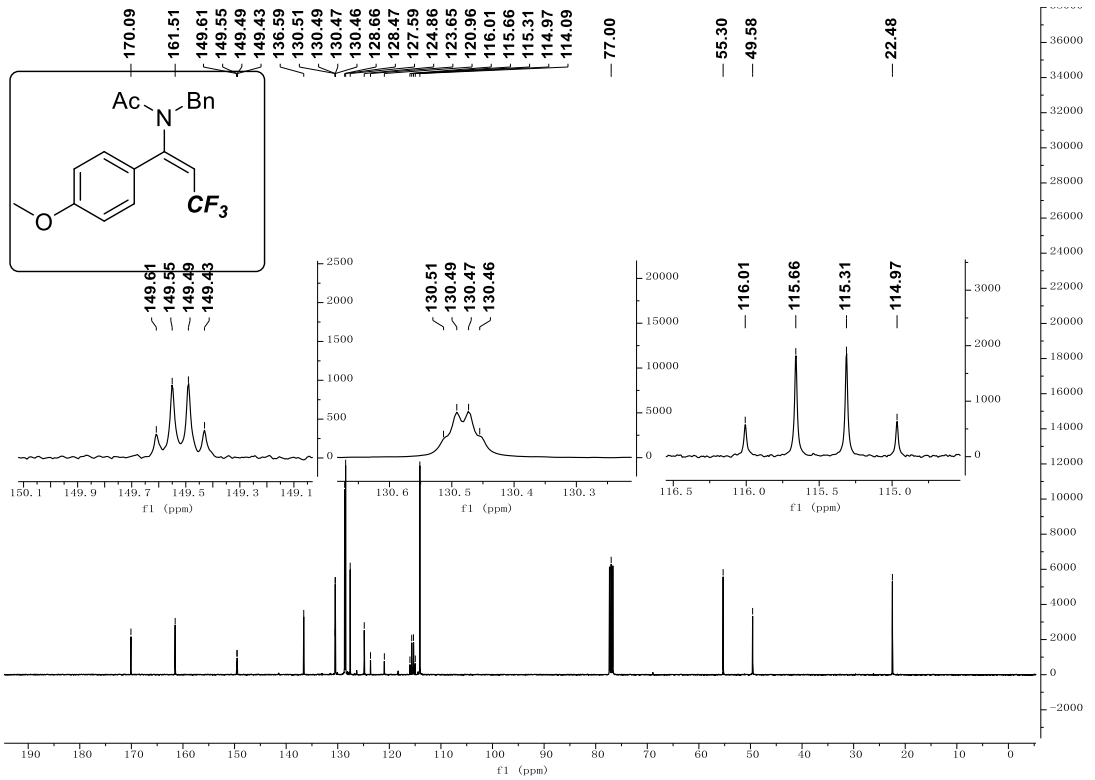
^{19}F NMR (376 MHz) Spectrum of **3e** in $CDCl_3$



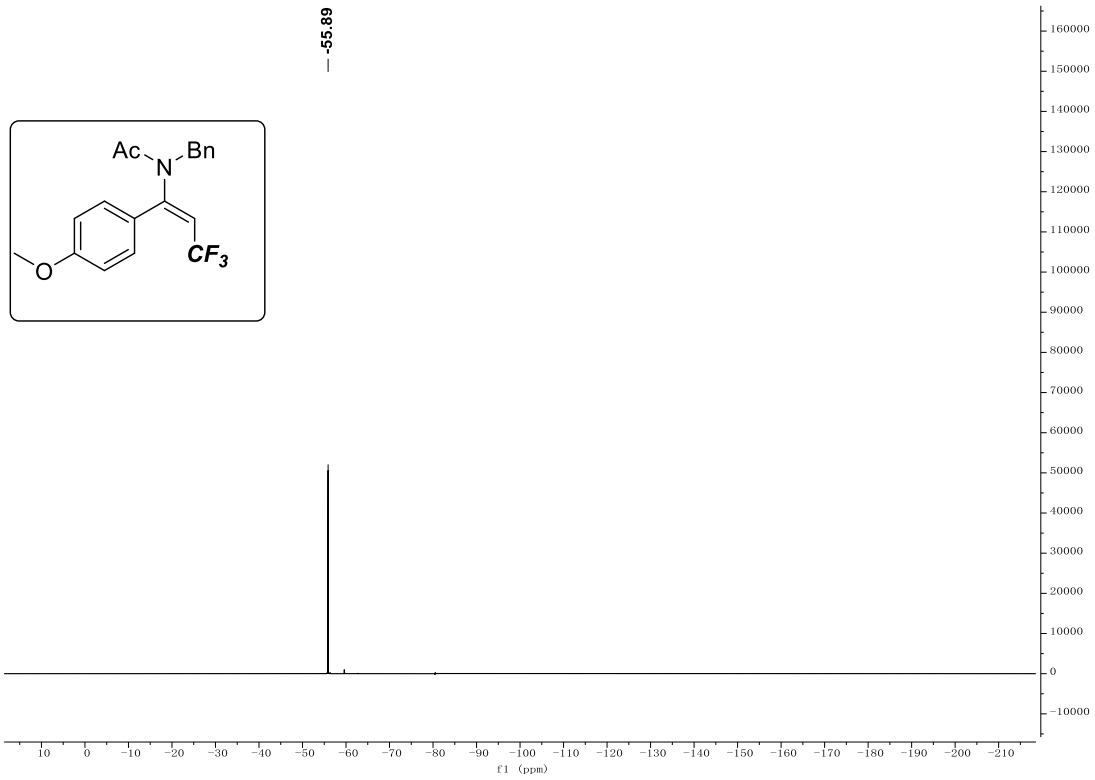
^{1}H NMR (400 MHz) Spectrum of **3f** in $CDCl_3$



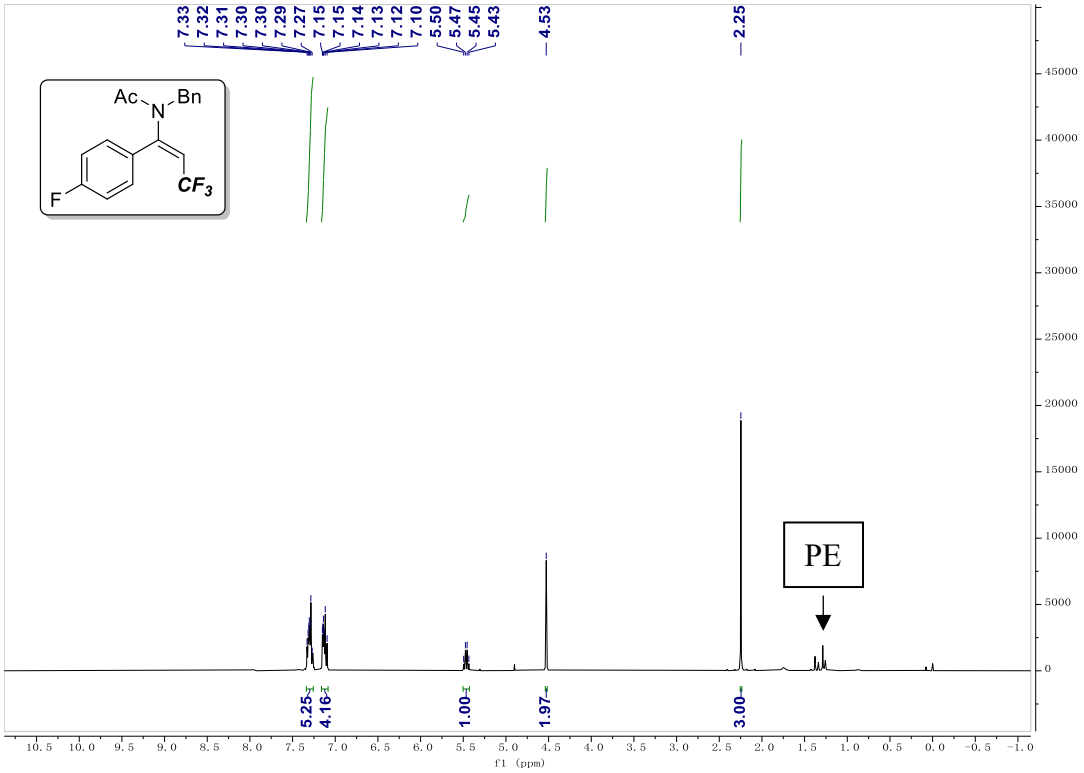
^{13}C NMR (100 MHz) Spectrum of **3f** in $CDCl_3$



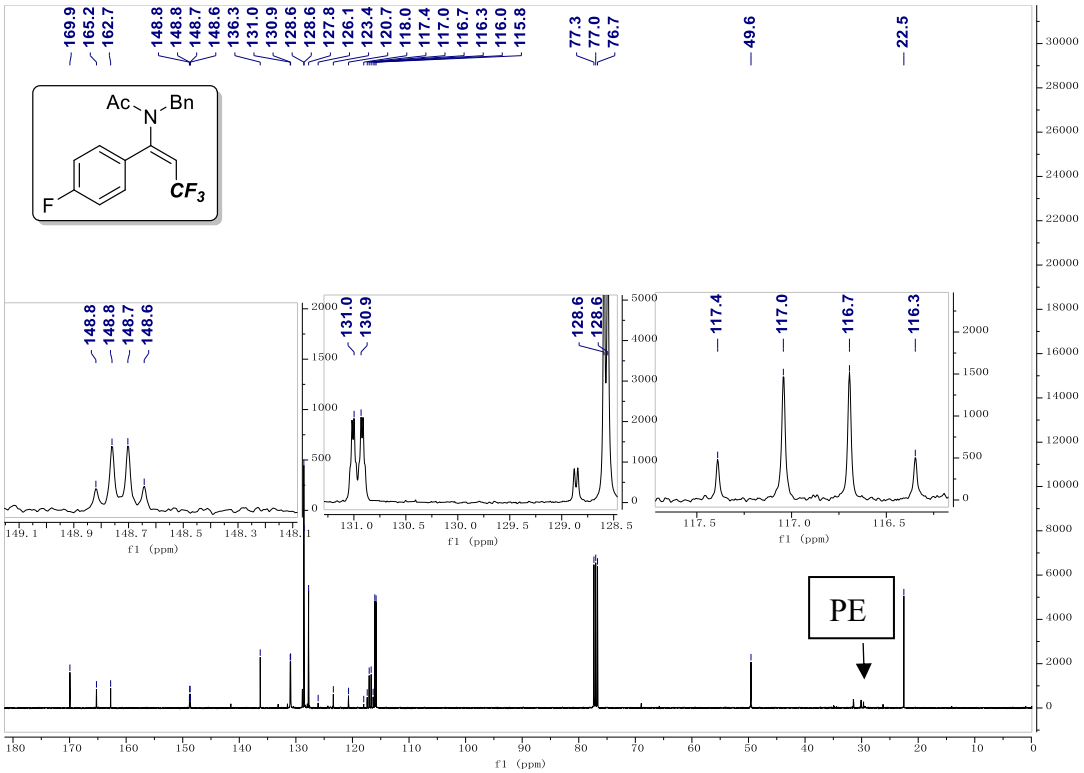
^{19}F NMR (376 MHz) Spectrum of **3f** in $CDCl_3$



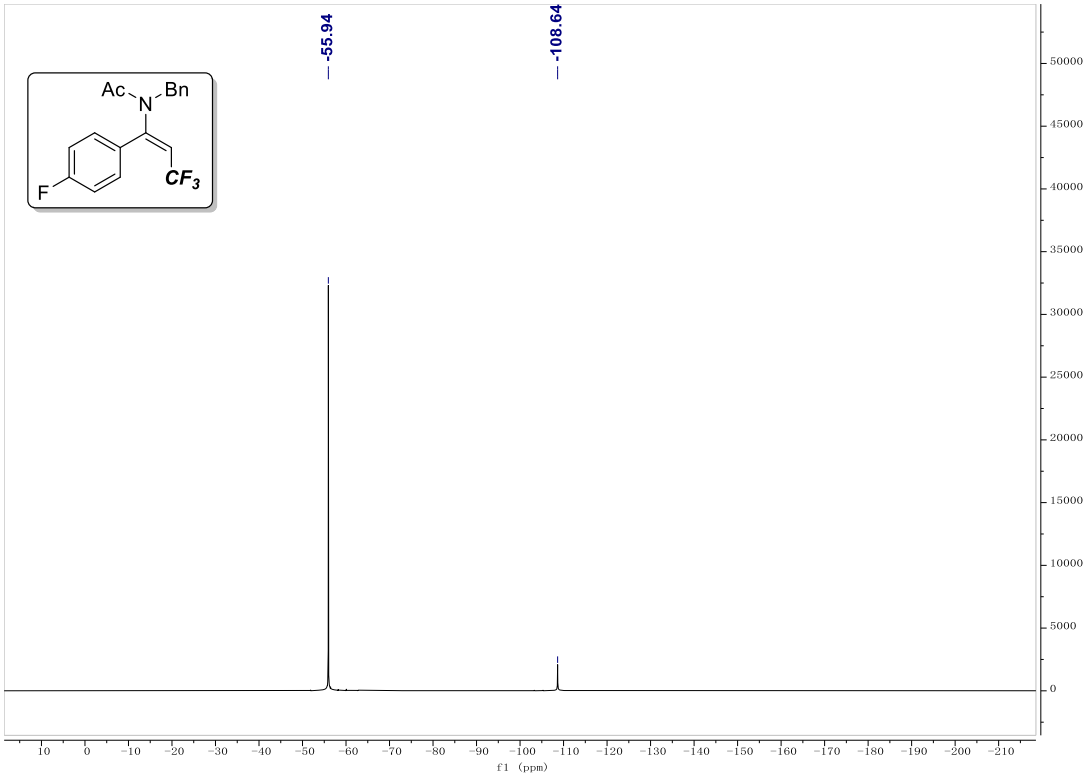
^{1}H NMR (400 MHz) Spectrum of **3g** in $CDCl_3$



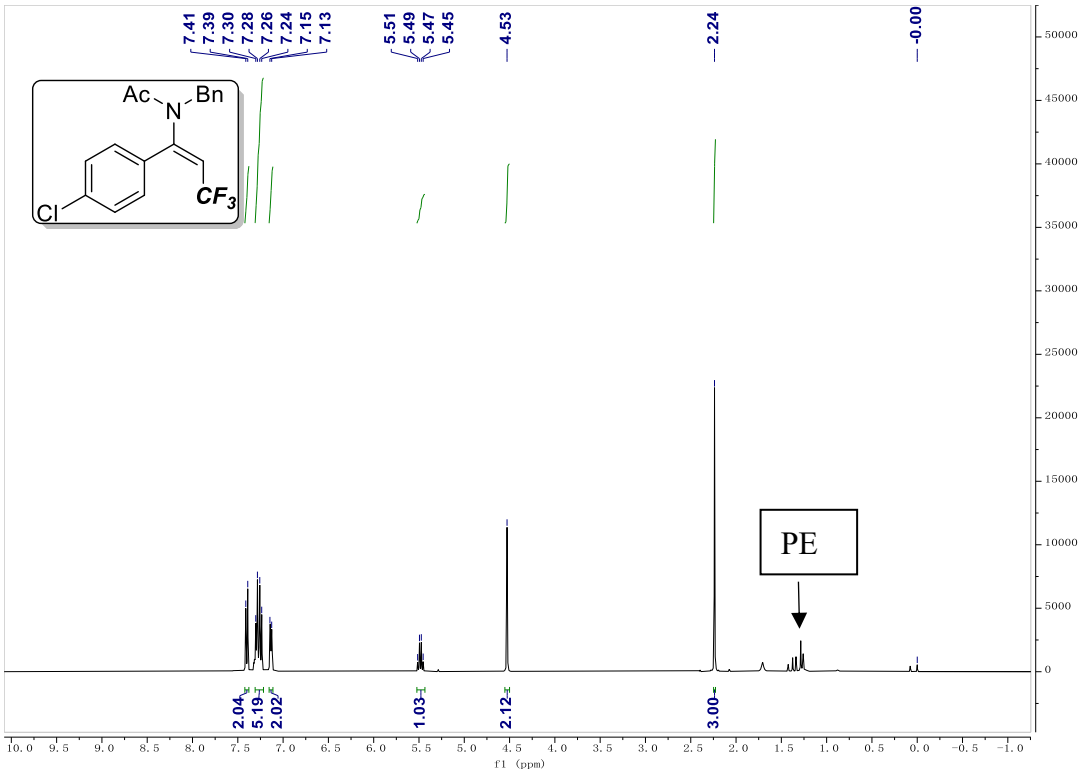
^{13}C NMR (100 MHz) Spectrum of **3g** in $CDCl_3$



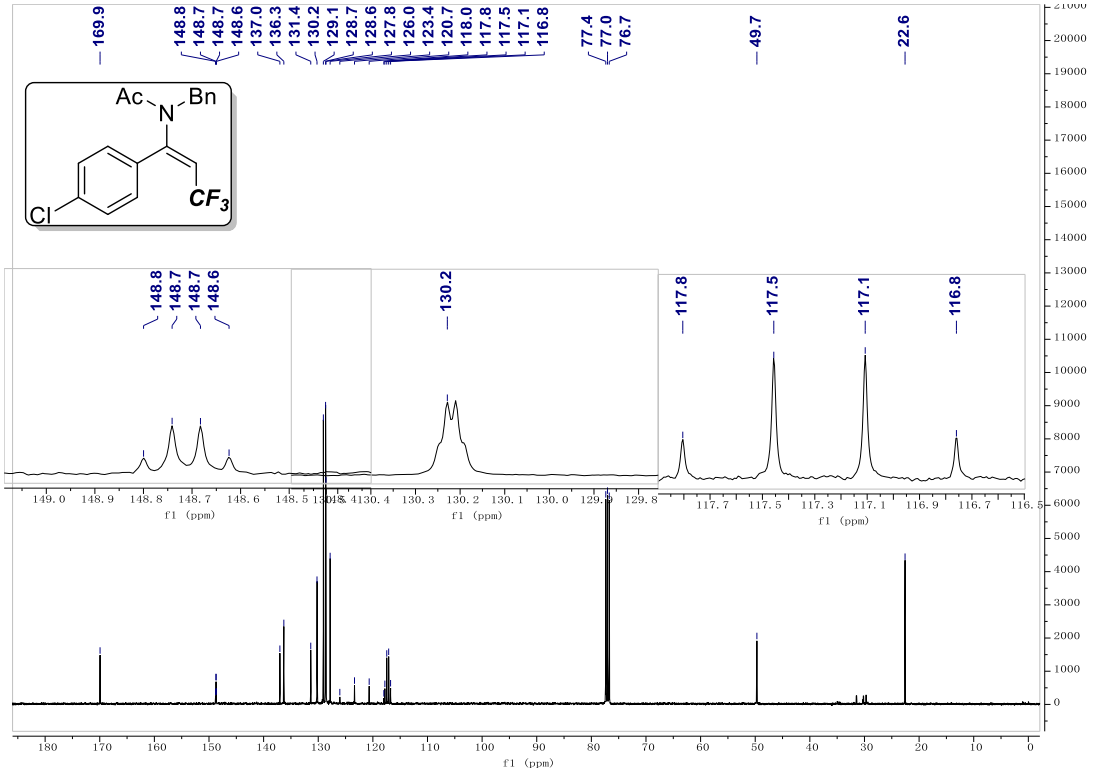
^{19}F NMR (376 MHz) Spectrum of **3g** in $CDCl_3$



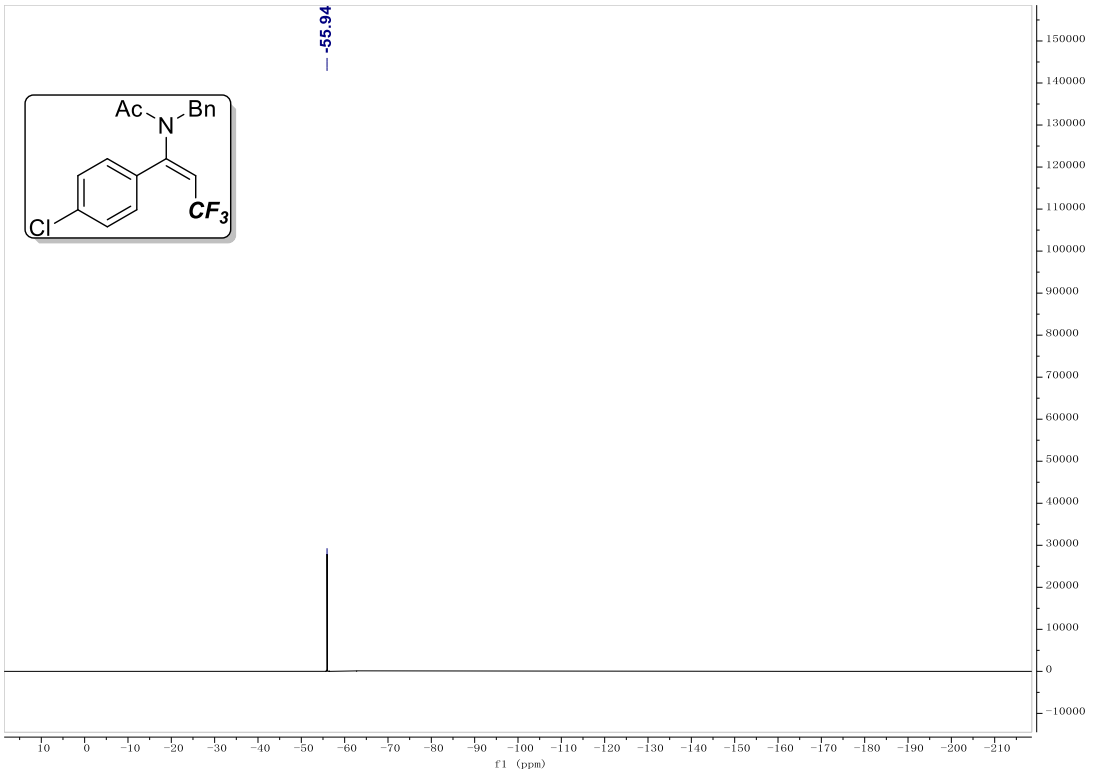
^{1}H NMR (400 MHz) Spectrum of **3h** in $CDCl_3$



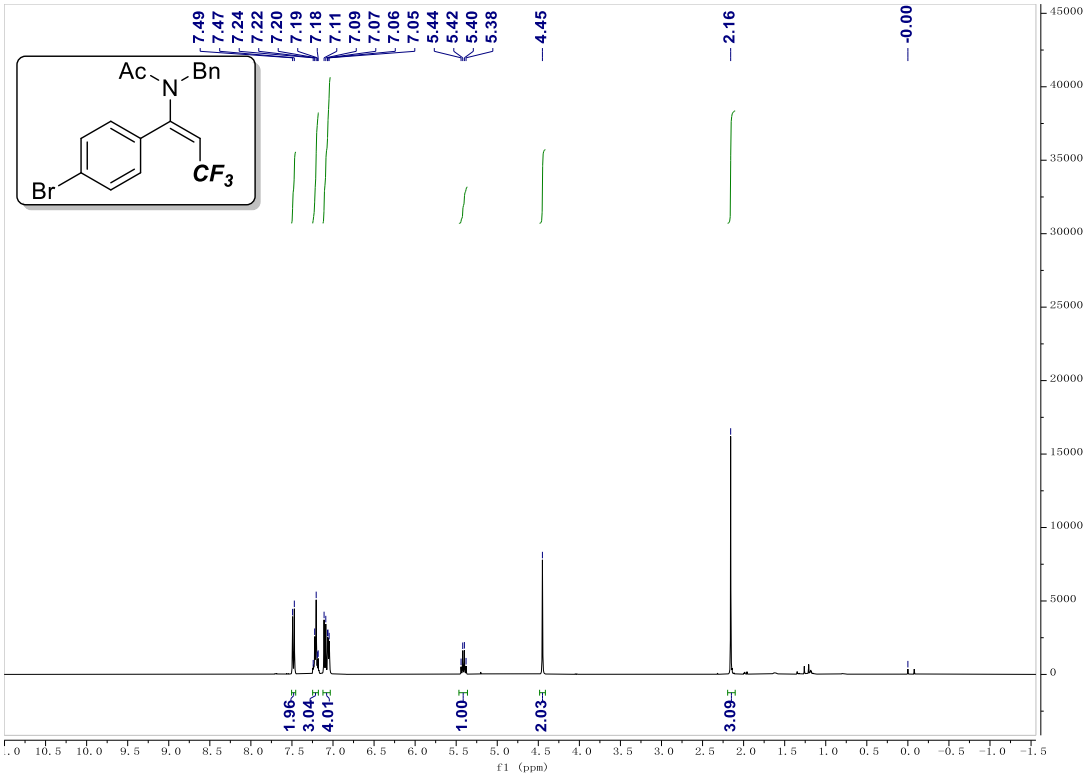
^{13}C NMR (100 MHz) Spectrum of **3h** in $CDCl_3$



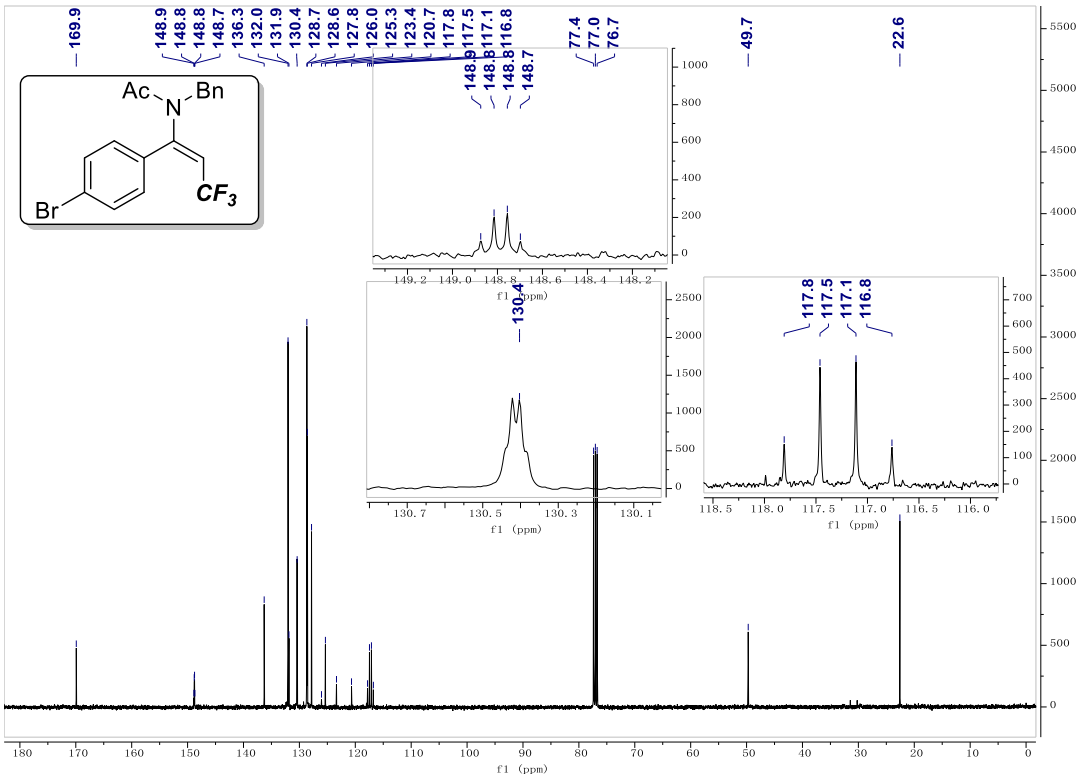
^{19}F NMR (376 MHz) Spectrum of **3h** in $CDCl_3$



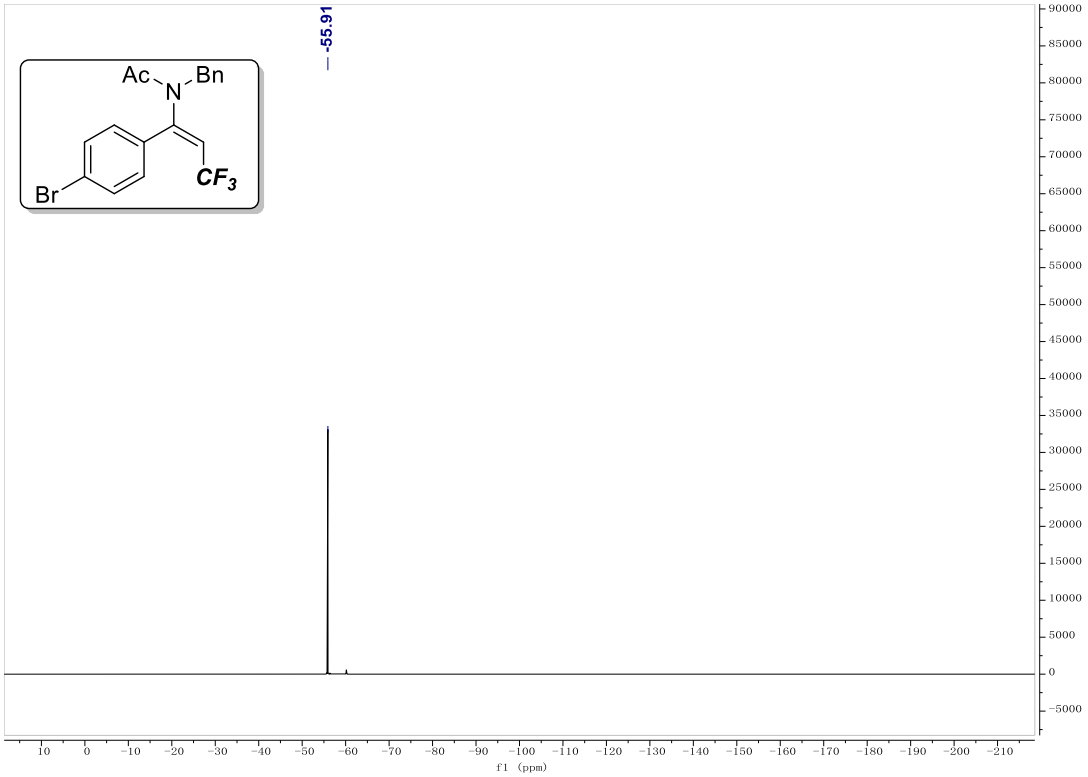
^{1}H NMR (400 MHz) Spectrum of **3i** in $CDCl_3$



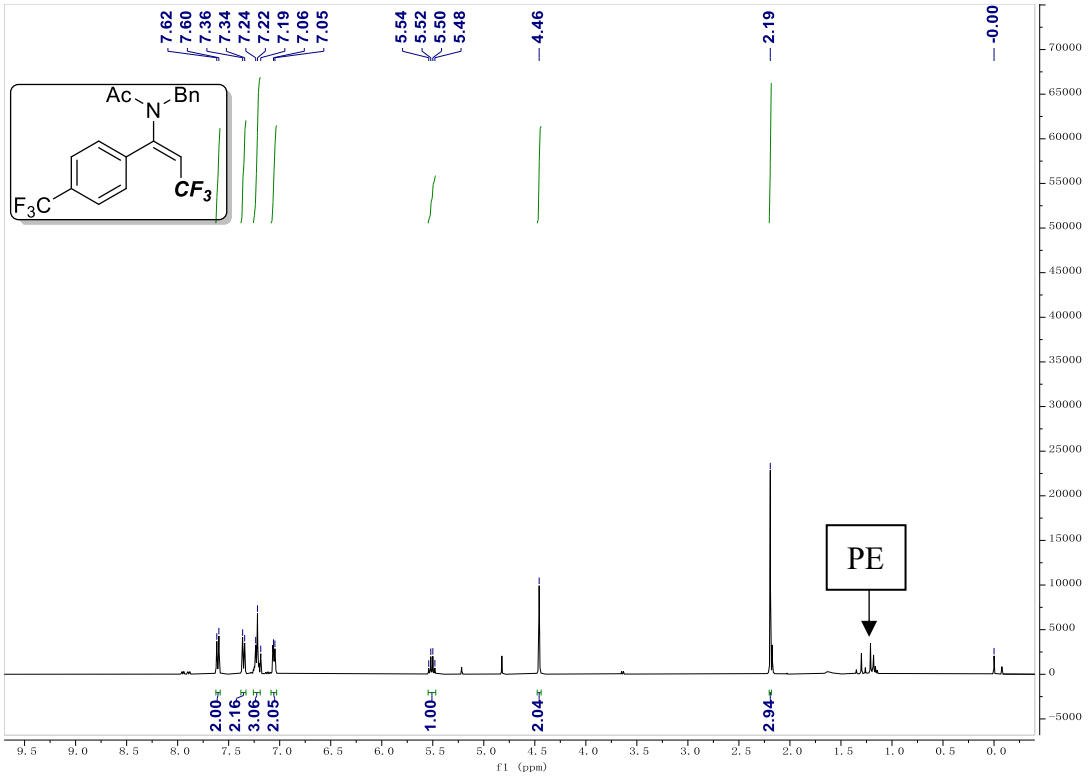
^{13}C NMR (100 MHz) Spectrum of **3i** in $CDCl_3$



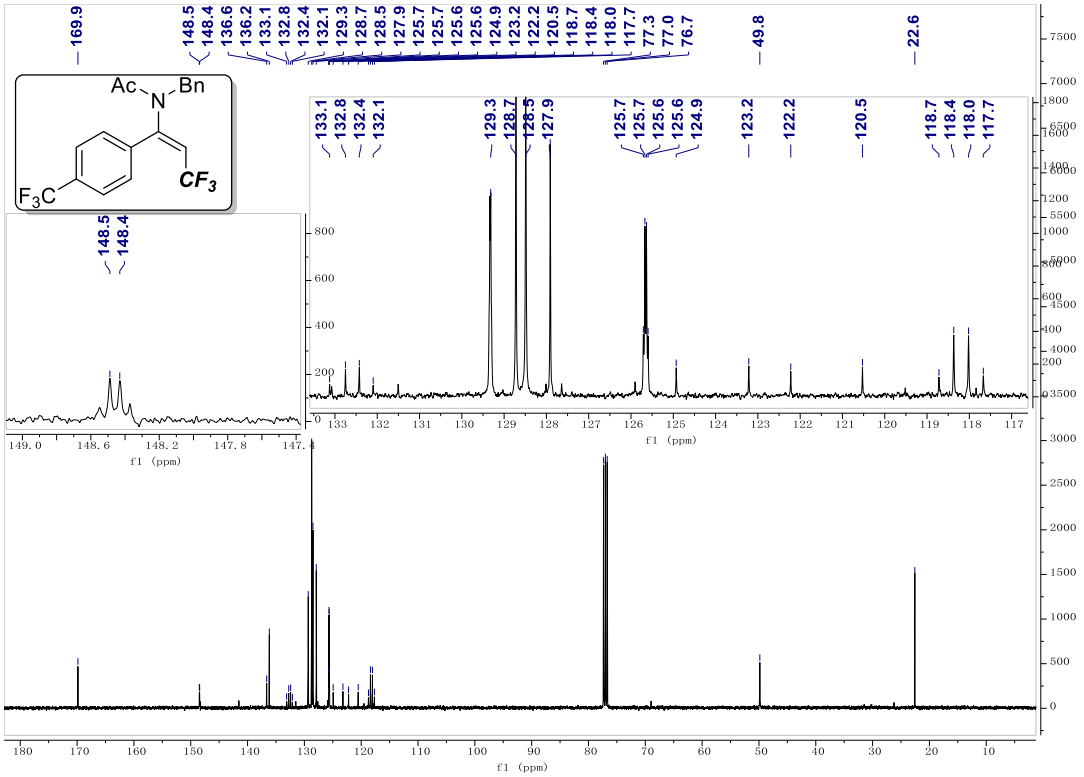
^{19}F NMR (376 MHz) Spectrum of **3i** in $CDCl_3$



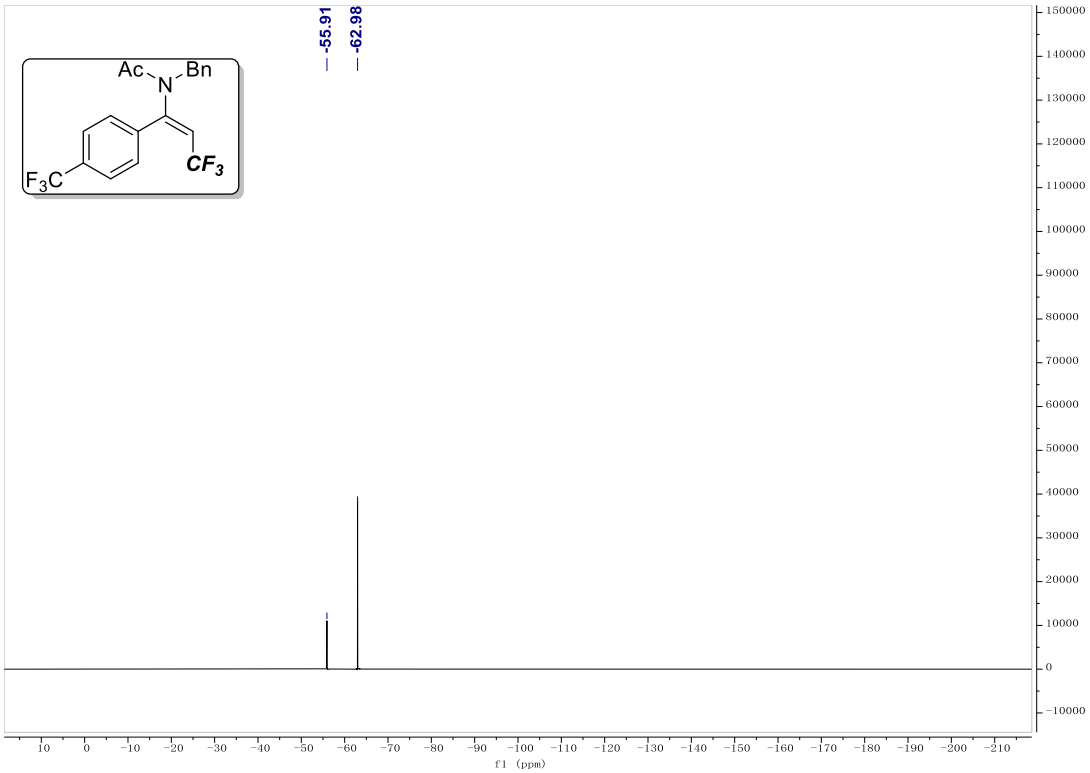
^{1}H NMR (400 MHz) Spectrum of **3j** in $CDCl_3$



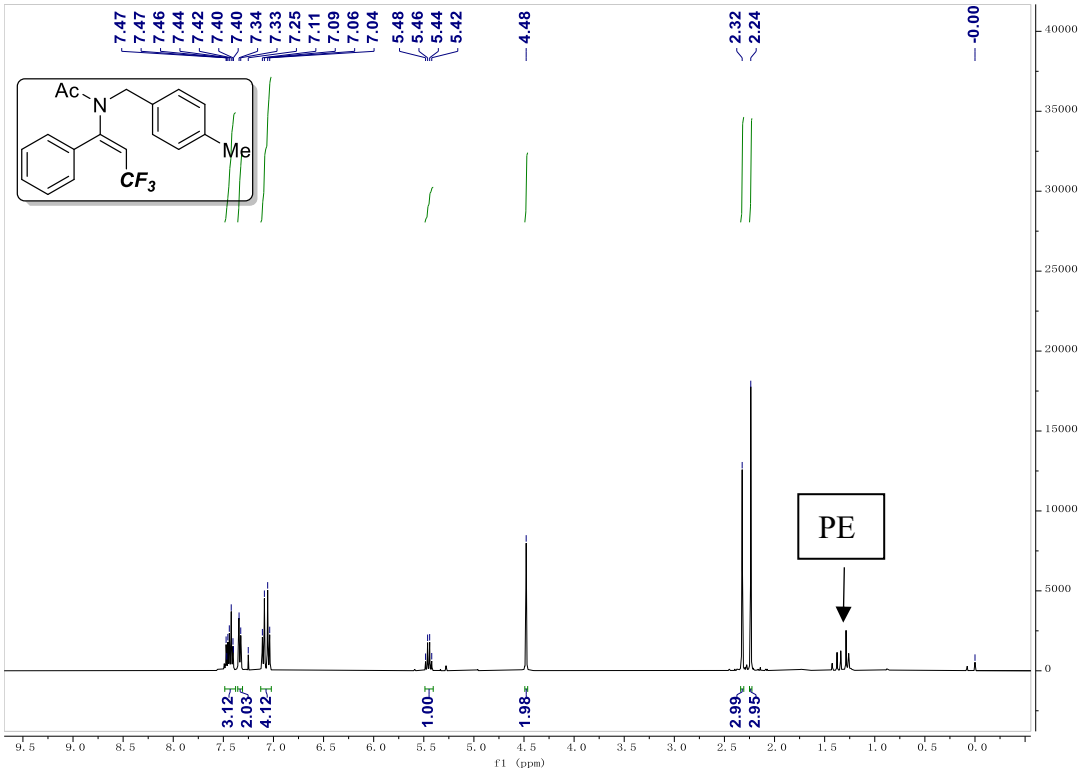
^{13}C NMR (100 MHz) Spectrum of **3j** in $CDCl_3$



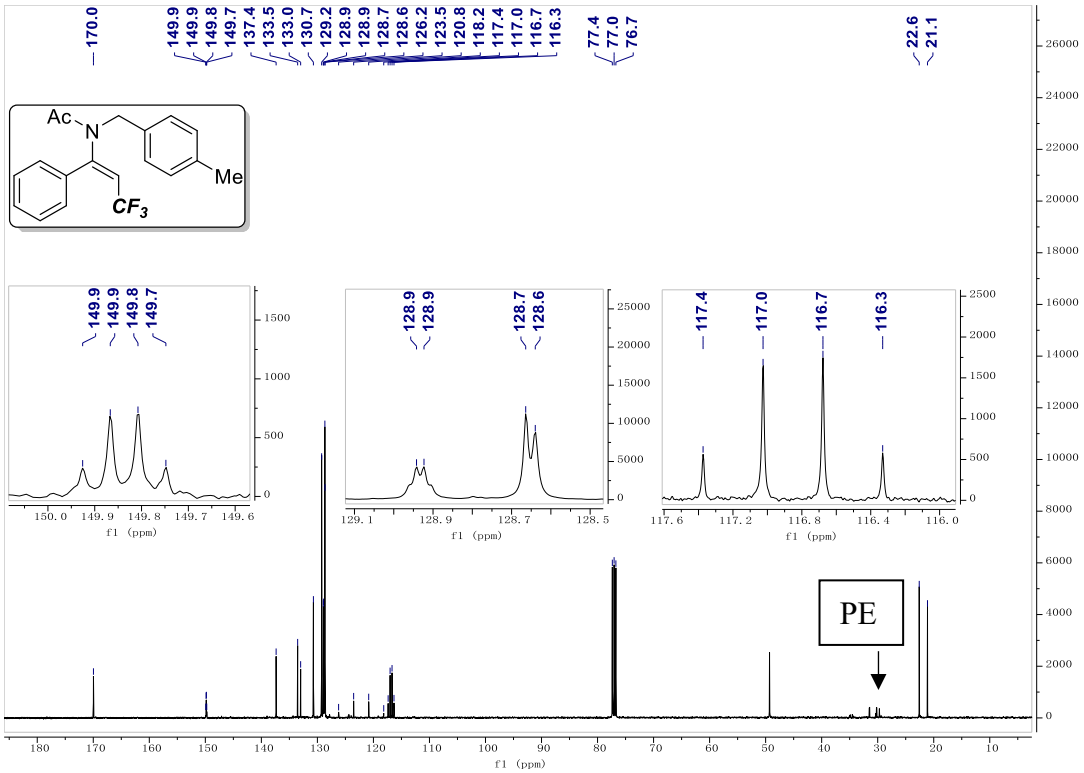
^{19}F NMR (376 MHz) Spectrum of **3j** in $CDCl_3$



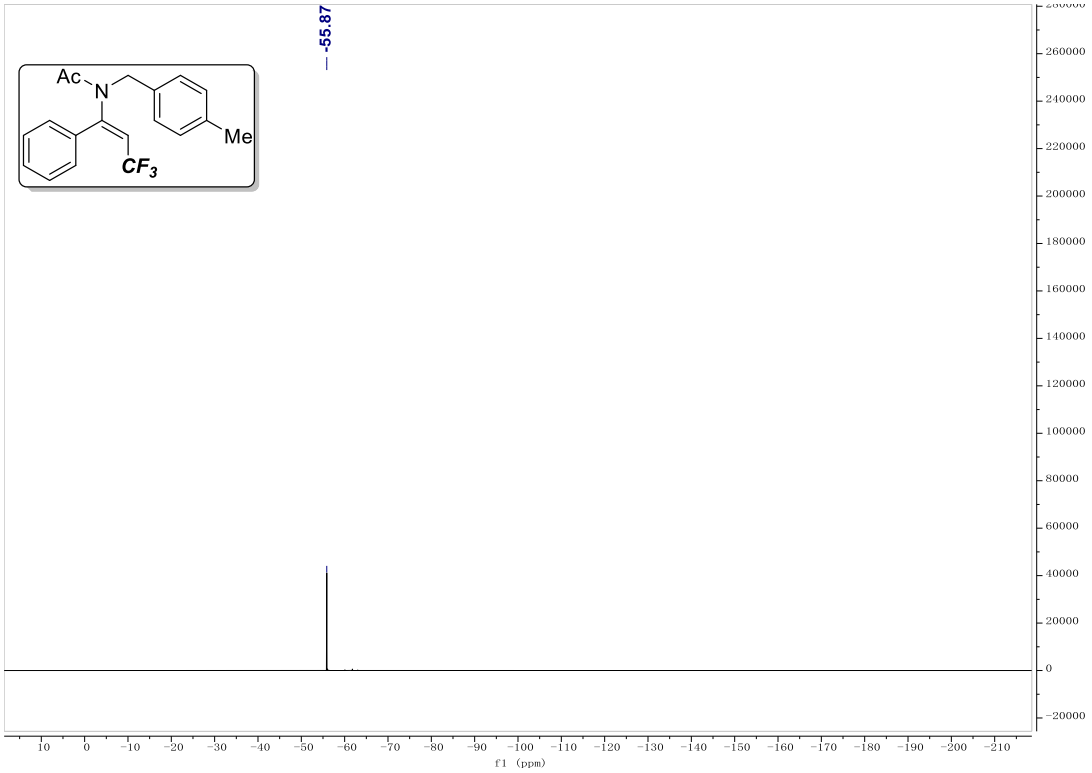
^{1}H NMR (400 MHz) Spectrum of **3k** in $CDCl_3$



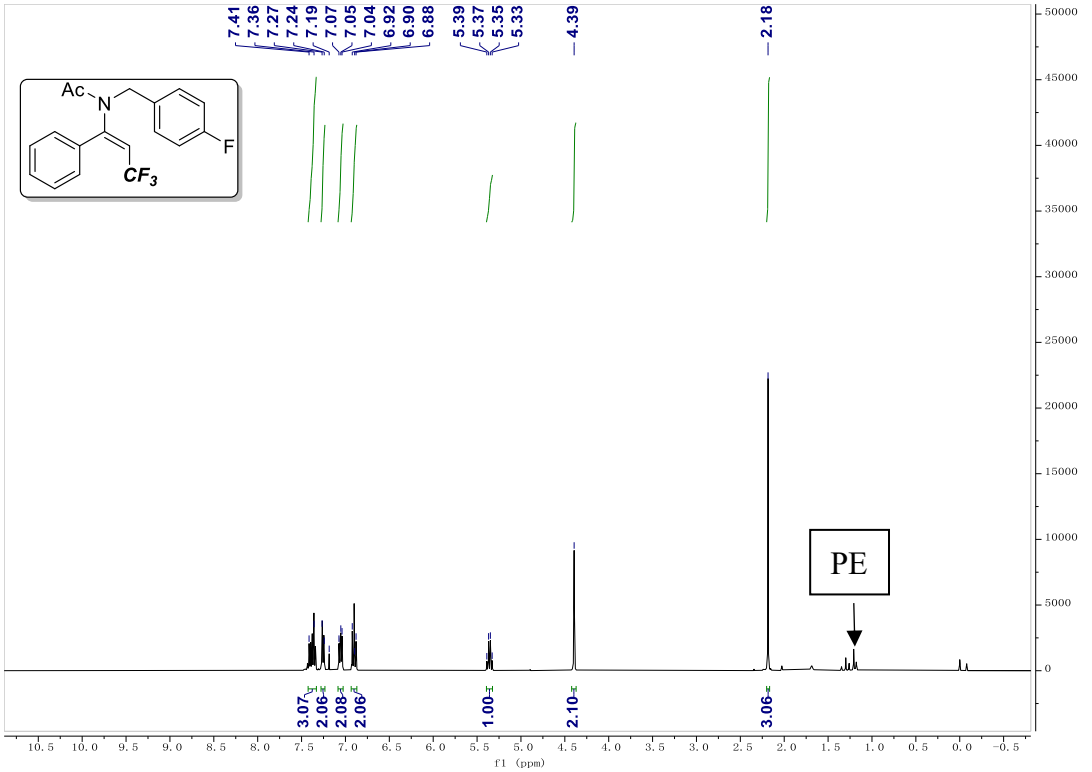
^{13}C NMR (100 MHz) Spectrum of **3k** in $CDCl_3$



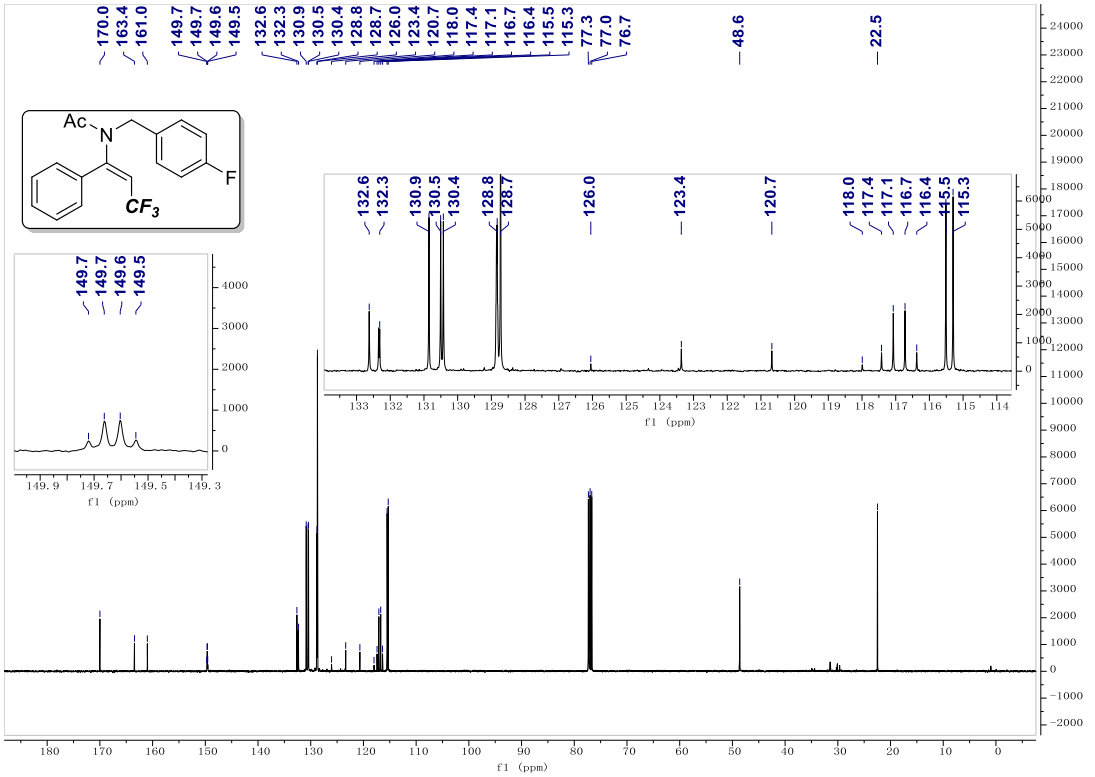
^{19}F NMR (376 MHz) Spectrum of **3k** in $CDCl_3$



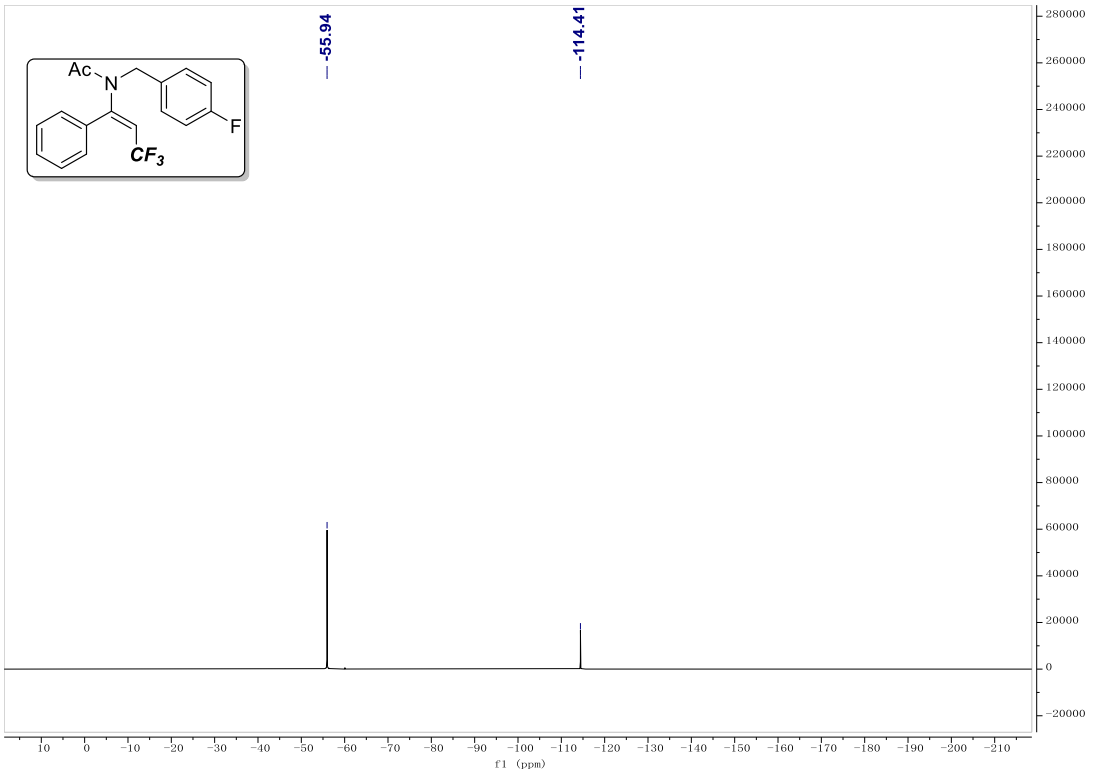
^{1}H NMR (400 MHz) Spectrum of **3l** in $CDCl_3$



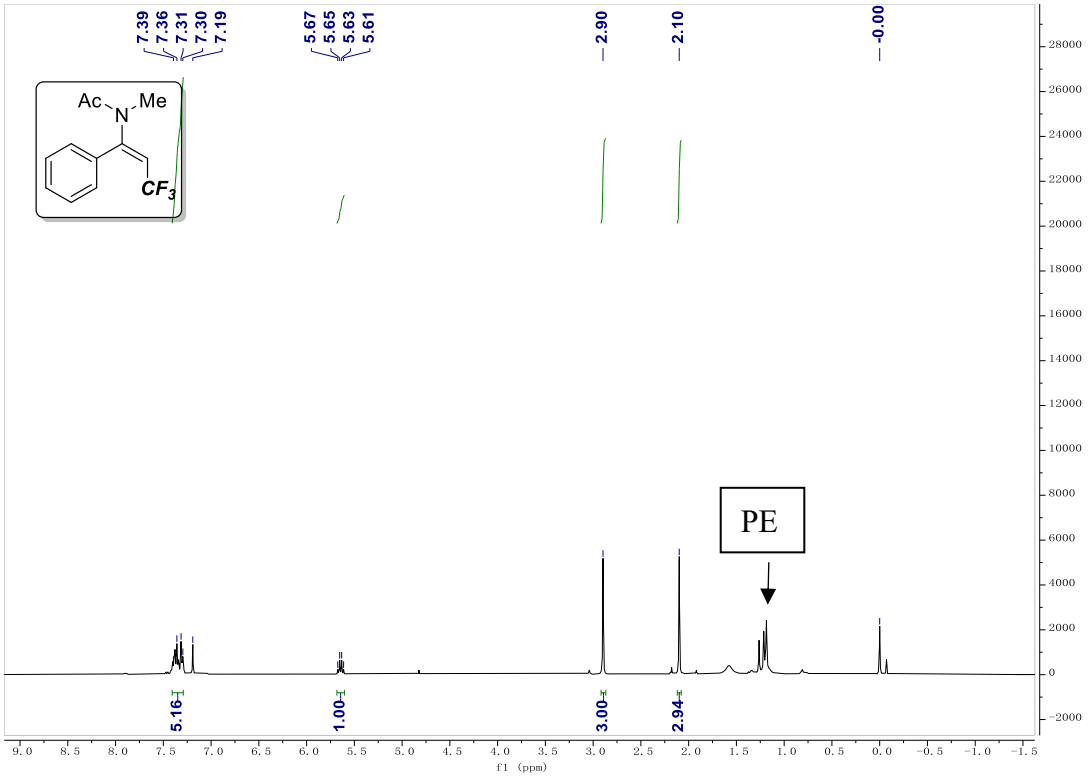
^{13}C NMR (100 MHz) Spectrum of **3l** in $CDCl_3$



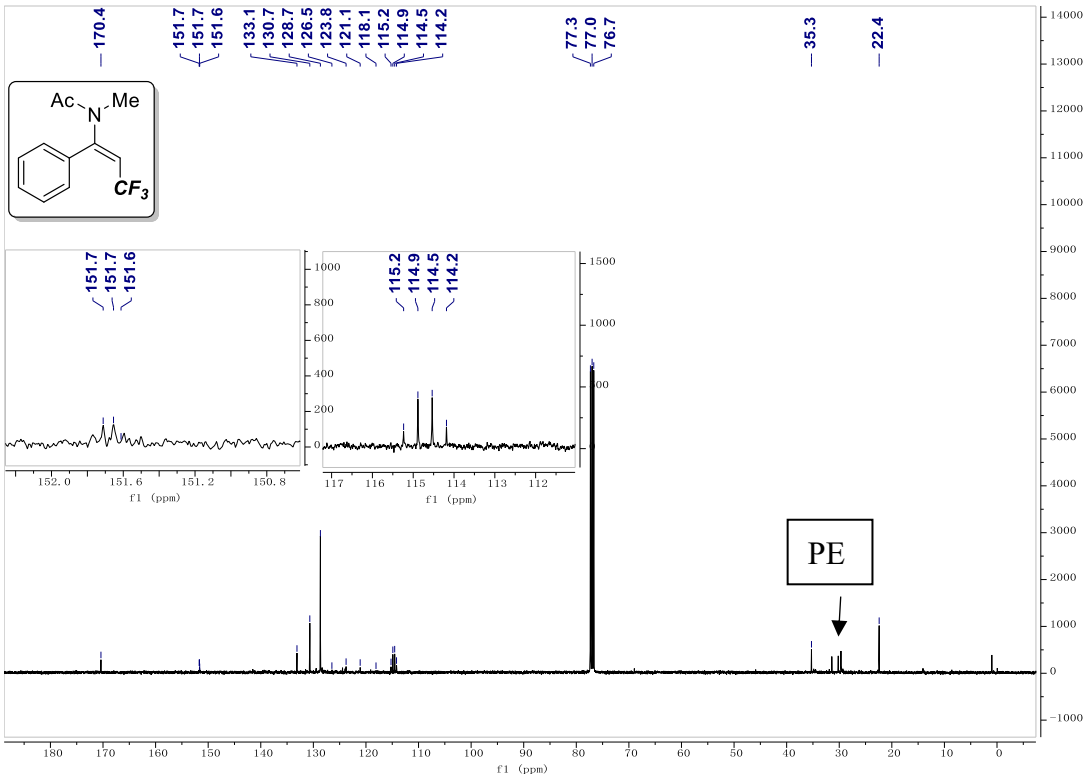
^{19}F NMR (376 MHz) Spectrum of **3l** in $CDCl_3$



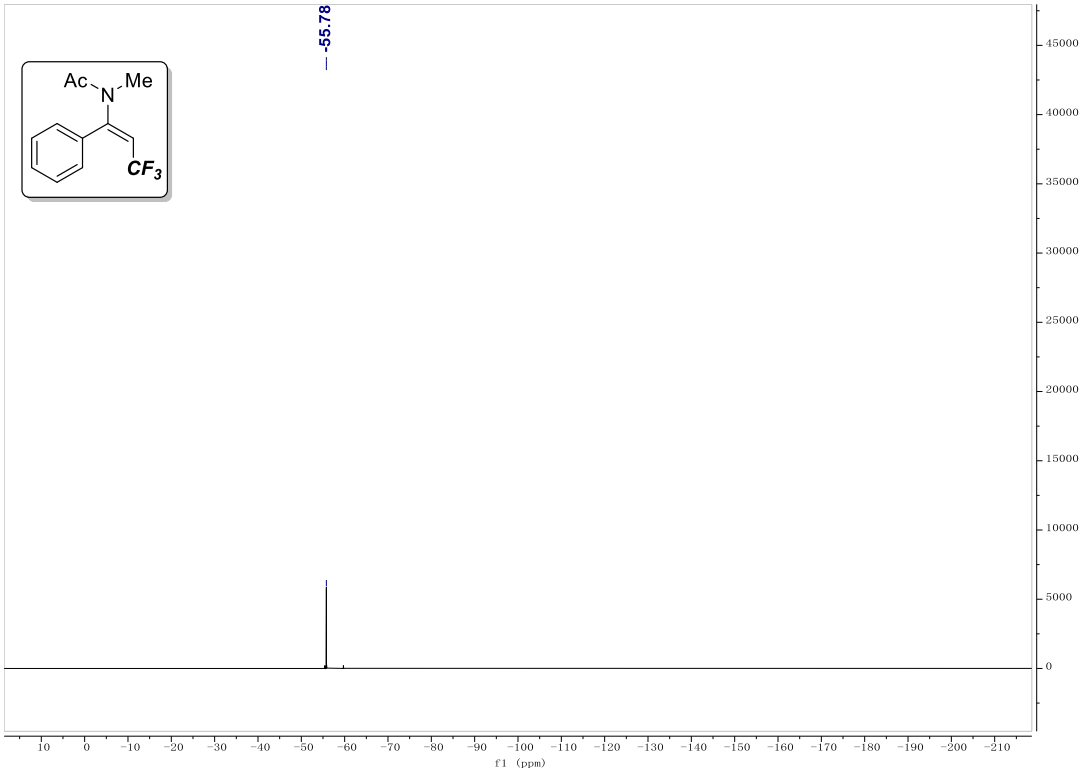
^{1}H NMR (400 MHz) Spectrum of **3m** in $CDCl_3$



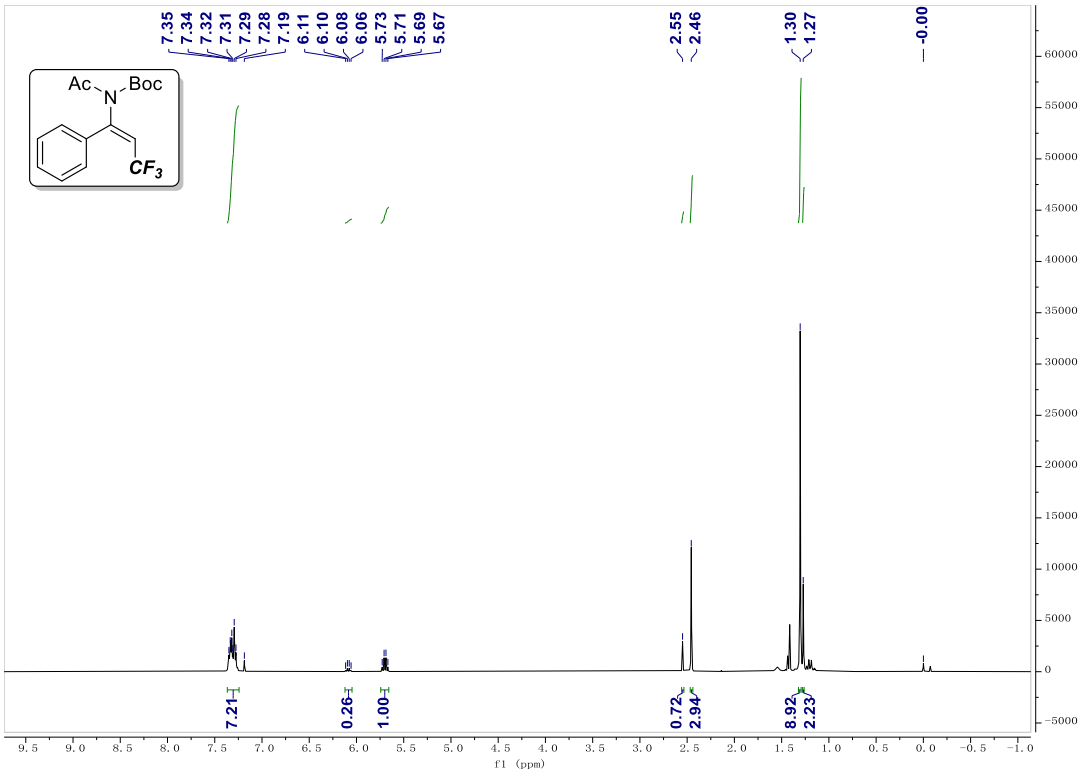
^{13}C NMR (100 MHz) Spectrum of **3m** in $CDCl_3$



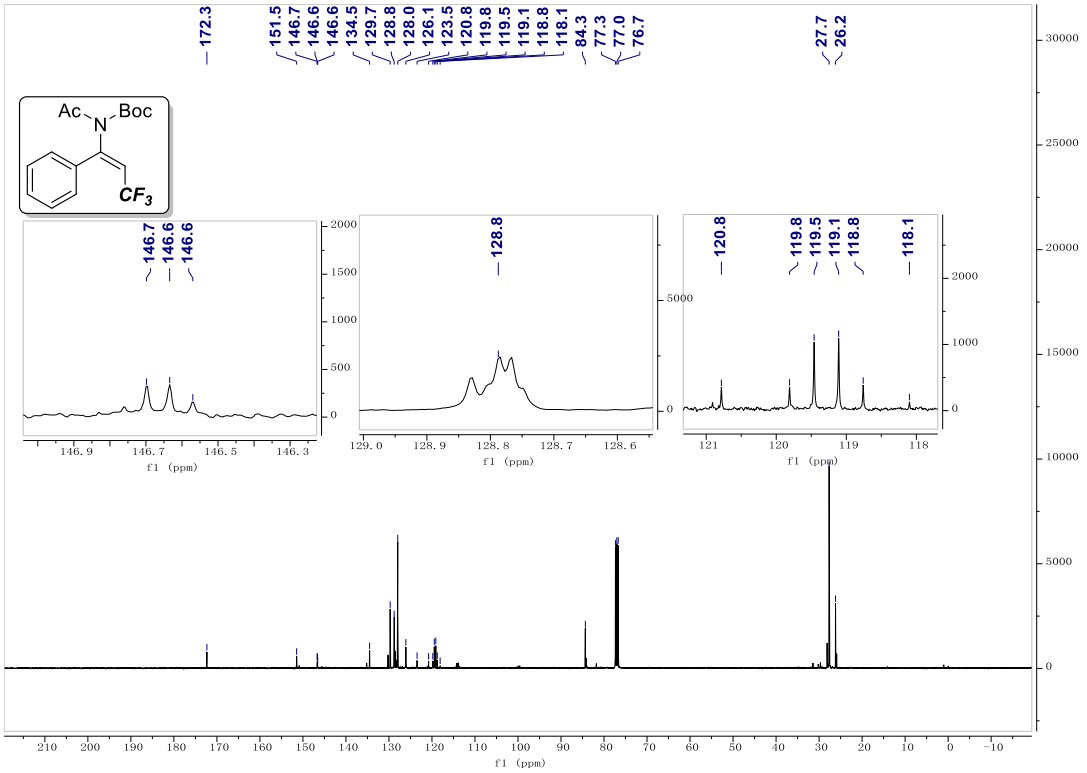
^{19}F NMR (376 MHz) Spectrum of **3m** in $CDCl_3$



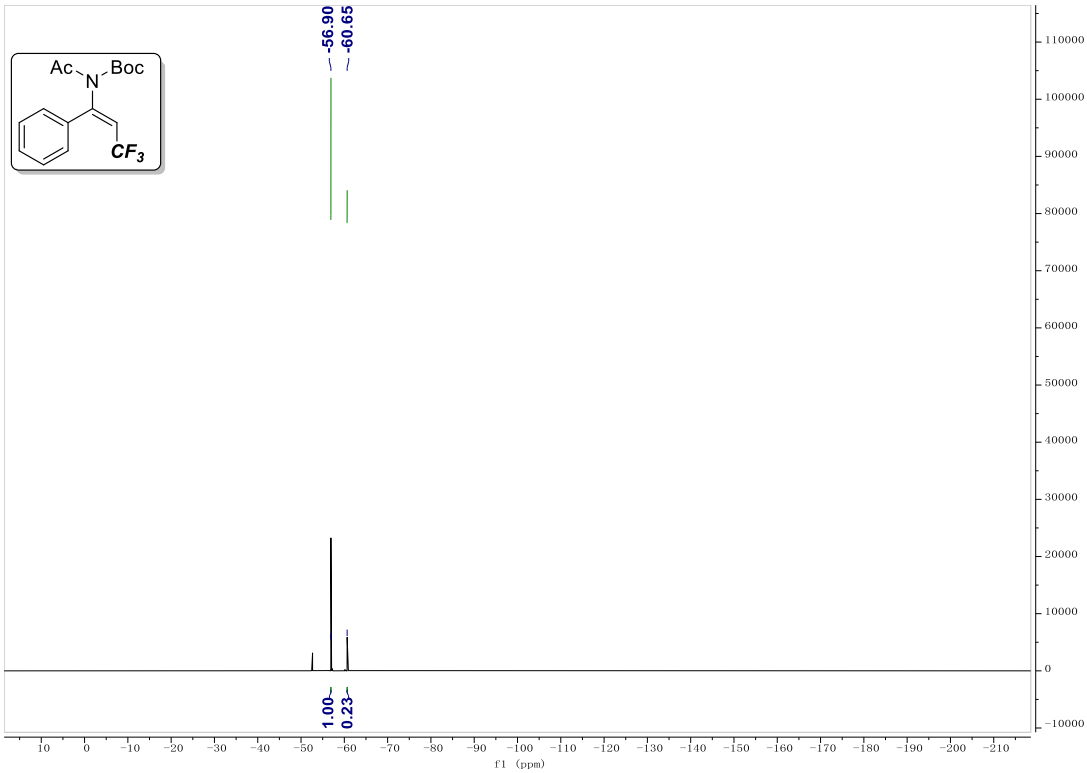
^{1}H NMR (400 MHz) Spectrum of **3n** in $CDCl_3$



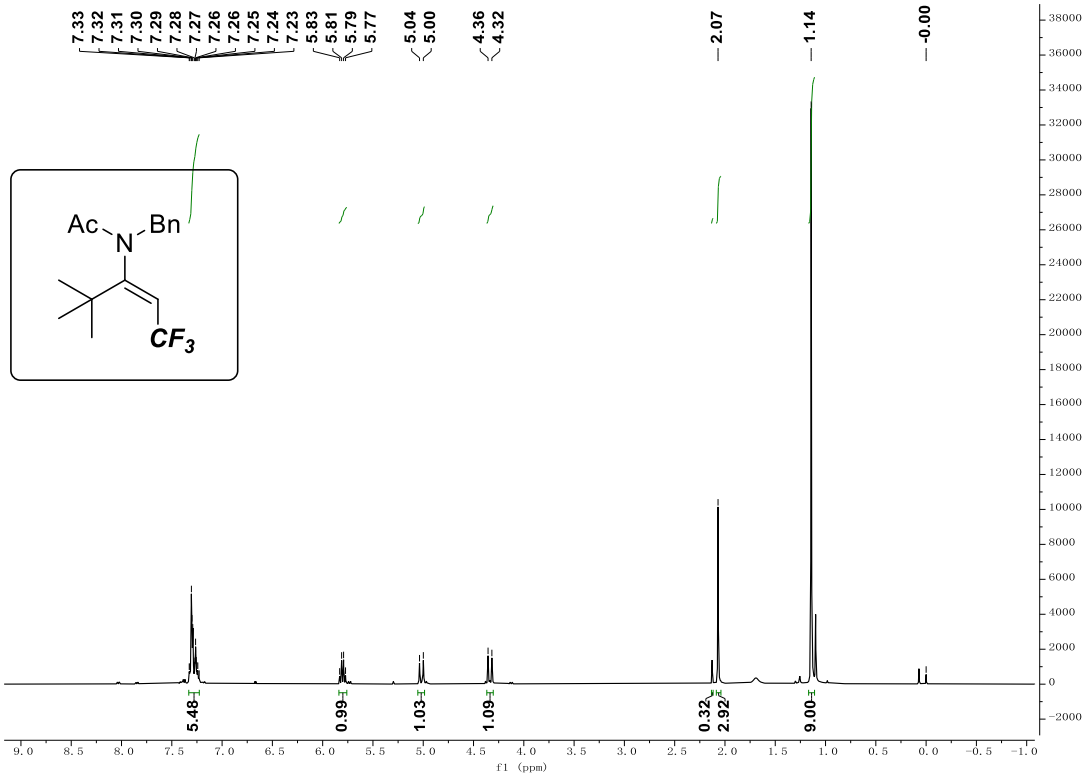
^{13}C NMR (100 MHz) Spectrum of **3n** in $CDCl_3$



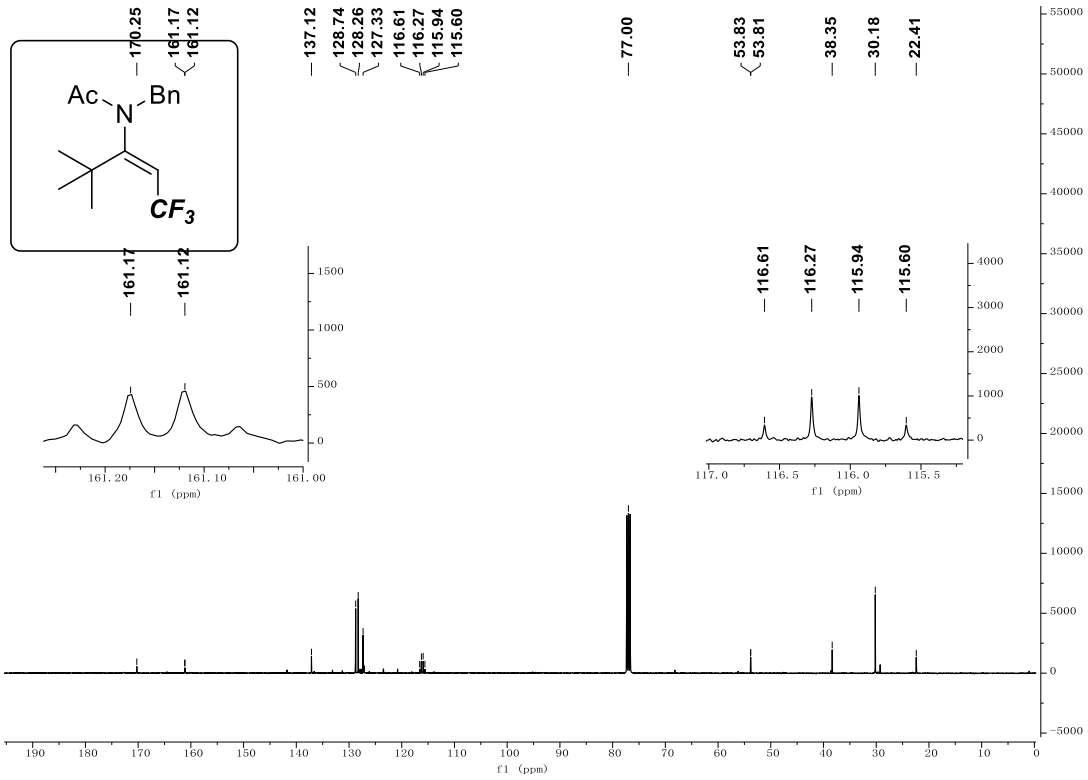
^{19}F NMR (376 MHz) Spectrum of **3n** in $CDCl_3$



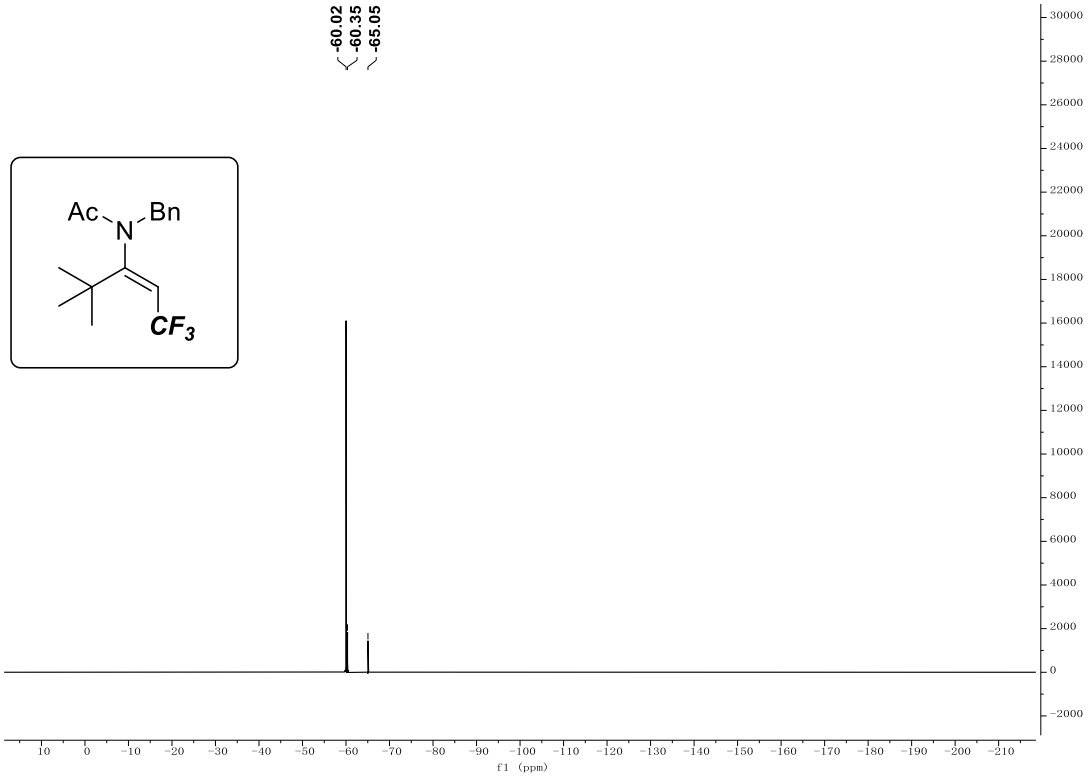
^{1}H NMR (400 MHz) Spectrum of **3o** in $CDCl_3$



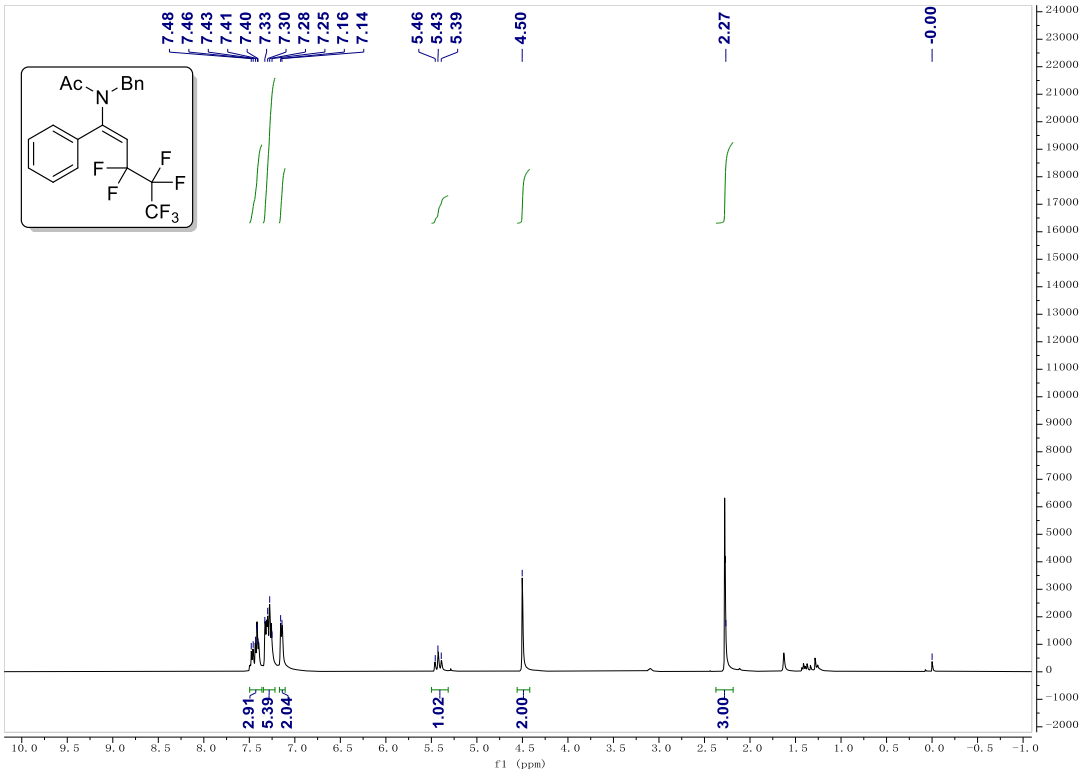
^{13}C NMR (100 MHz) Spectrum of **3o** in $CDCl_3$



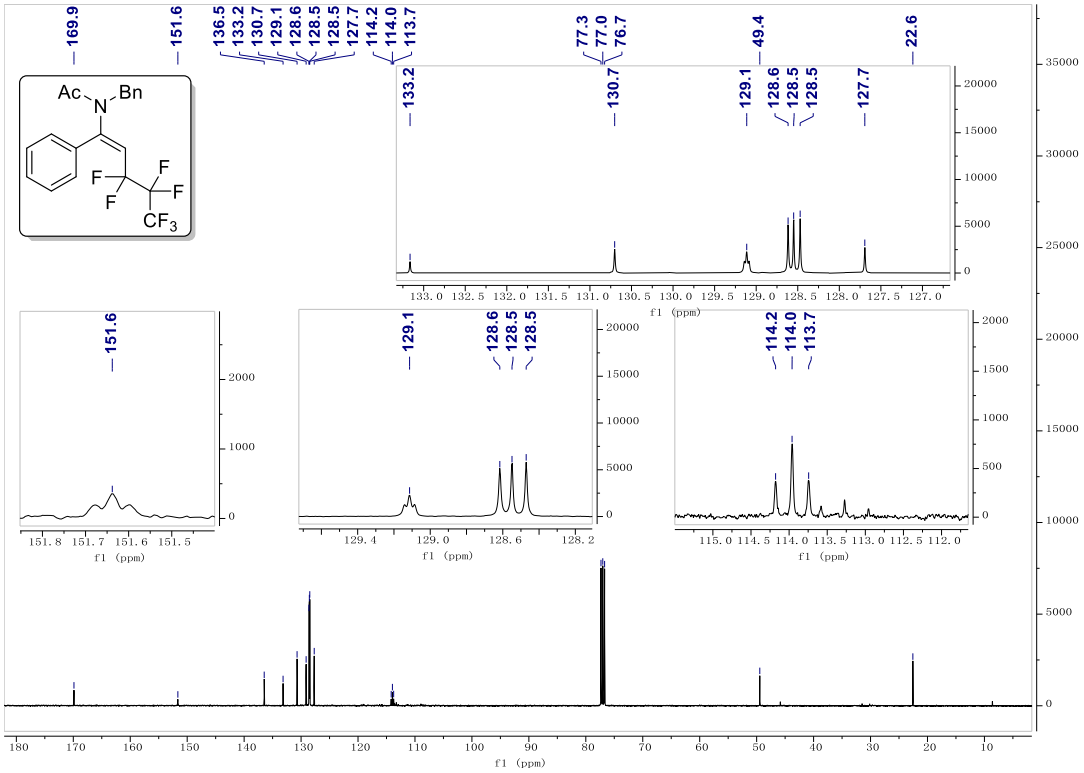
^{19}F NMR (376 MHz) Spectrum of **3o** in $CDCl_3$



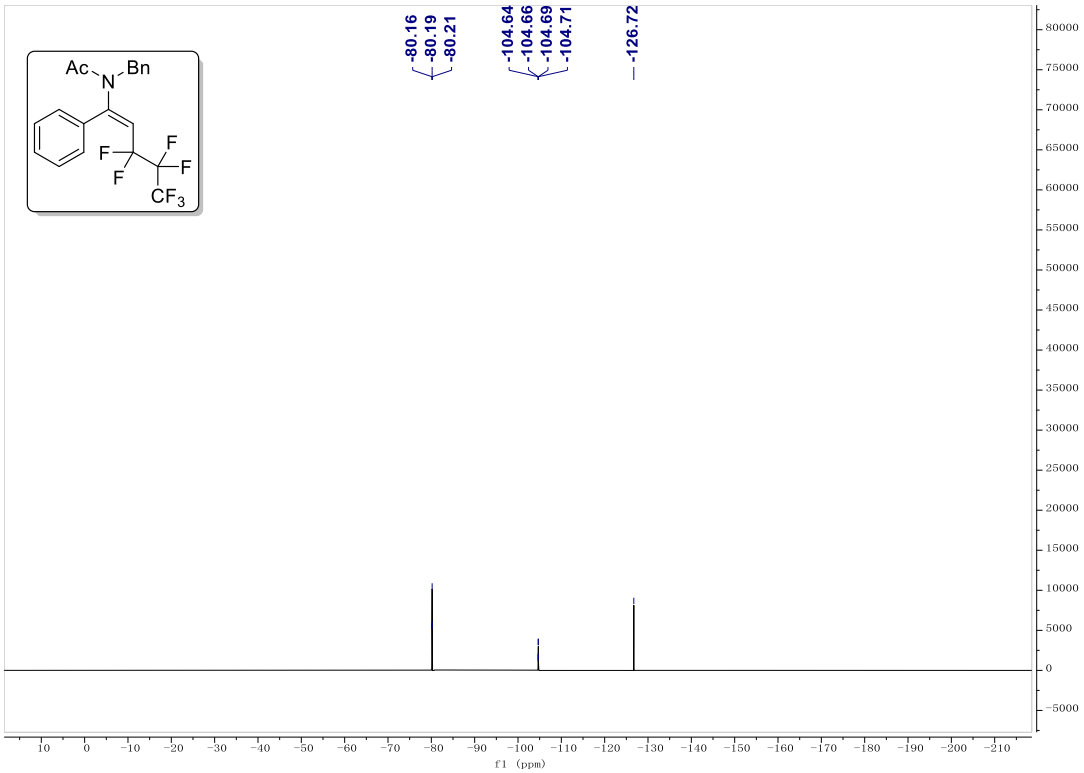
^{1}H NMR (400 MHz) Spectrum of **5a** in $CDCl_3$



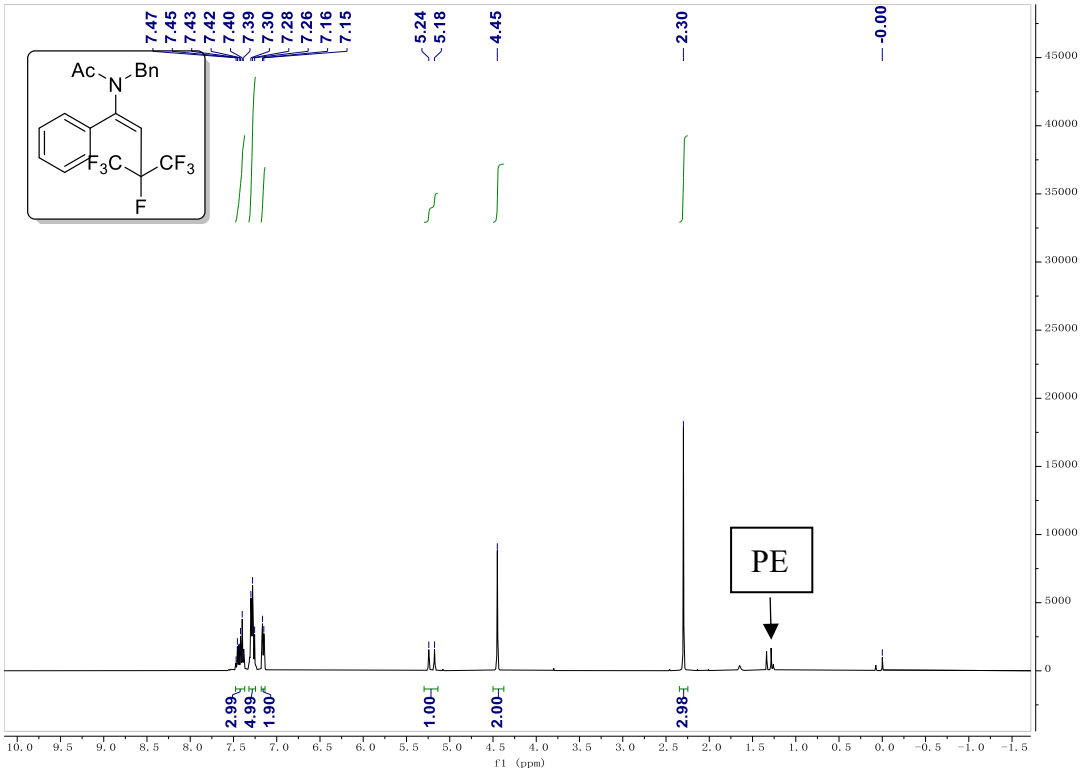
^{13}C NMR (100 MHz) Spectrum of **5a** in $CDCl_3$



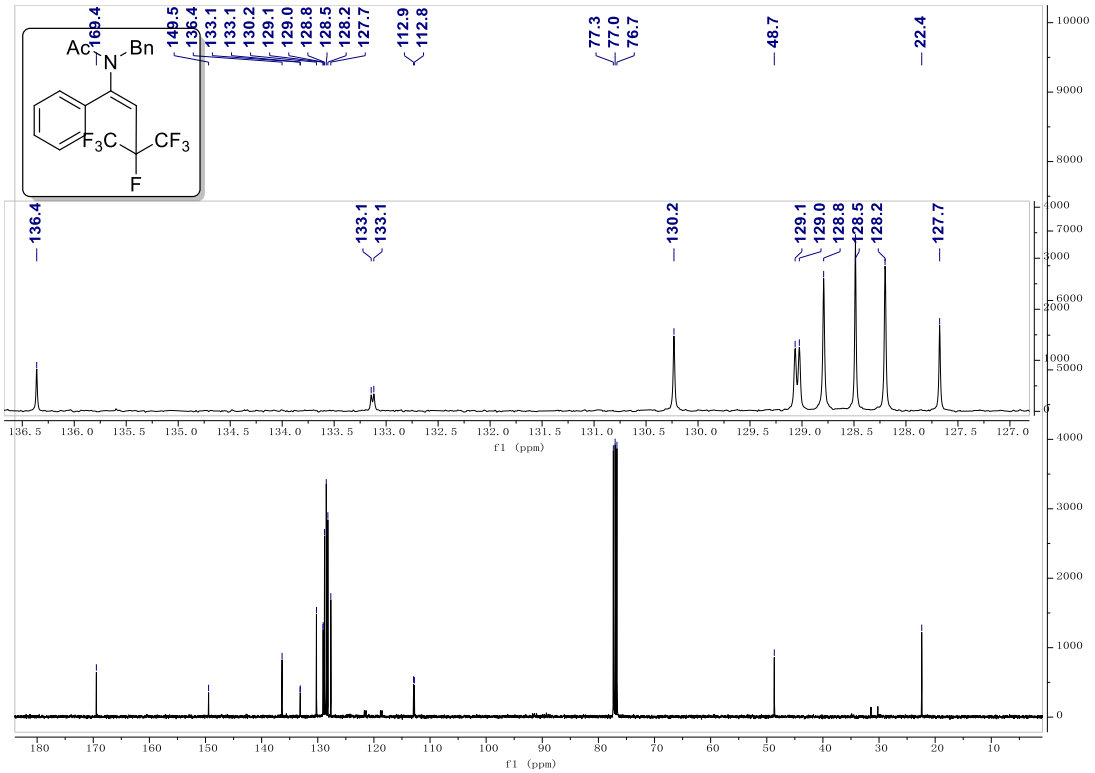
^{19}F NMR (376 MHz) Spectrum of **5a** in $CDCl_3$



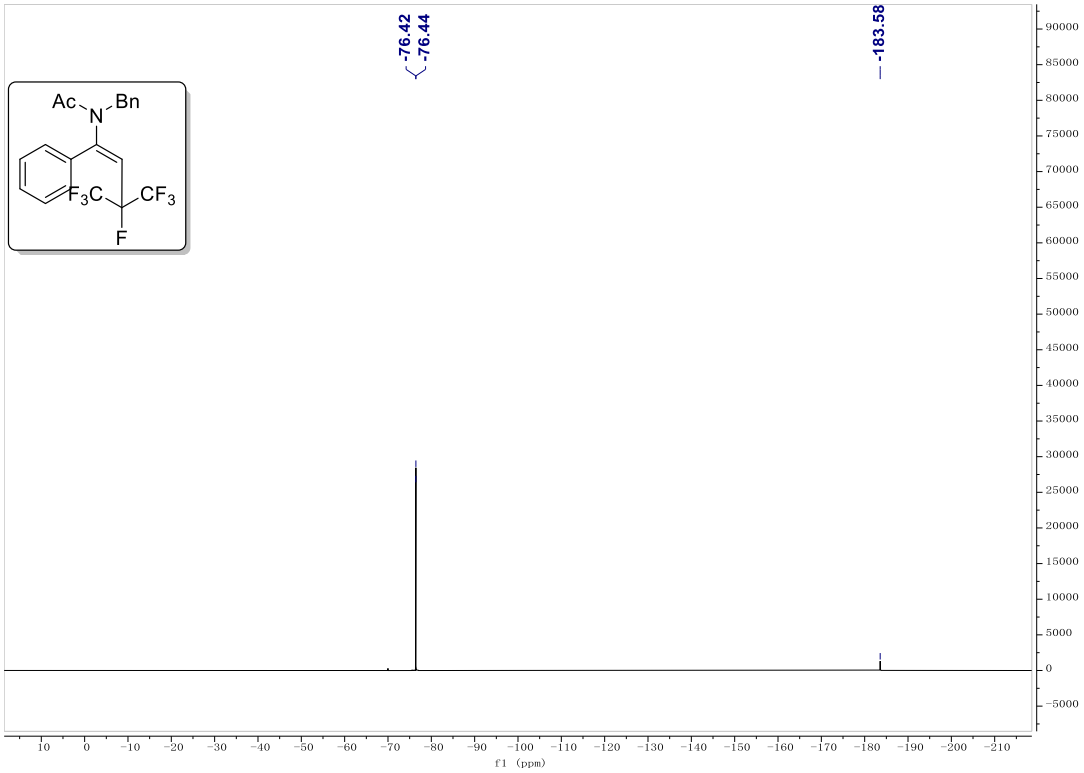
^{1}H NMR (400 MHz) Spectrum of **5b** in $CDCl_3$



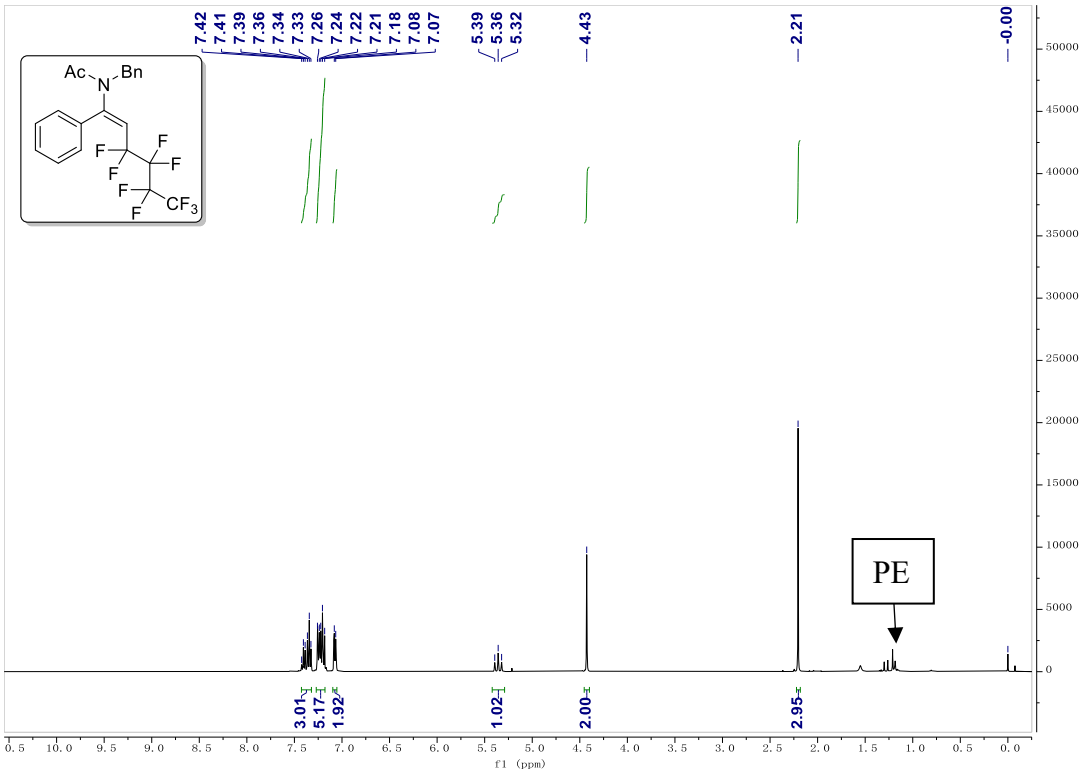
^{13}C NMR (100 MHz) Spectrum of **5b** in $CDCl_3$



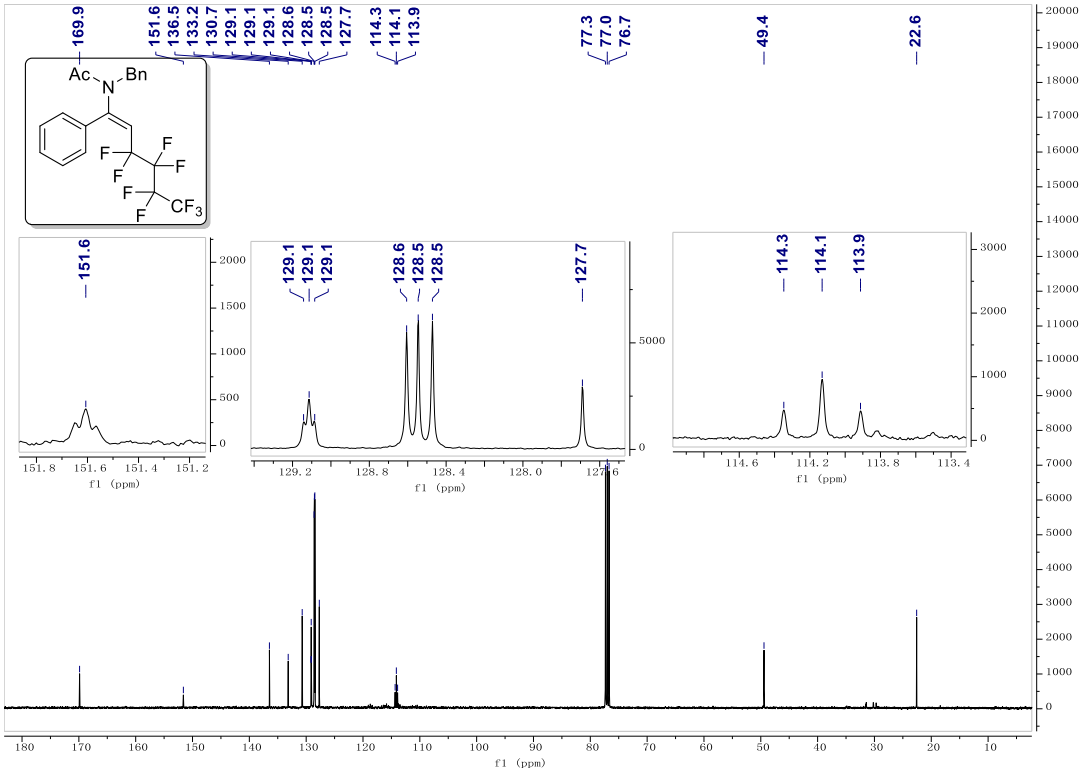
^{19}F NMR (376 MHz) Spectrum of **5b** in $CDCl_3$



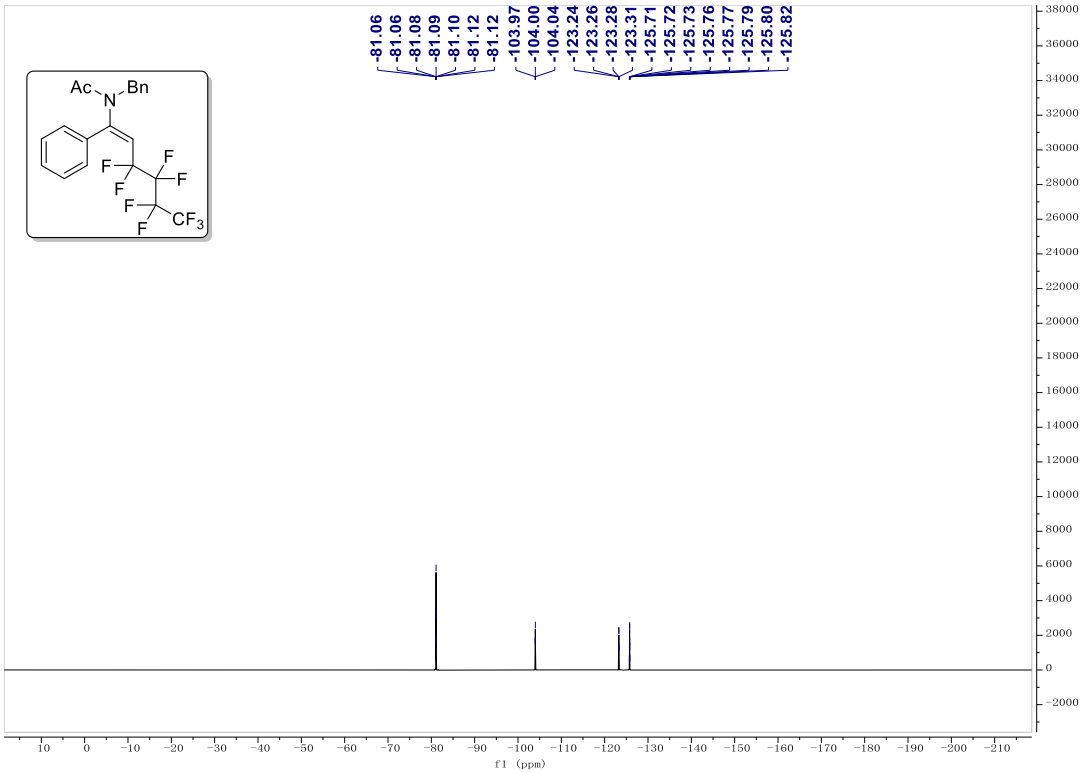
^{1}H NMR (400 MHz) Spectrum of **5c** in $CDCl_3$



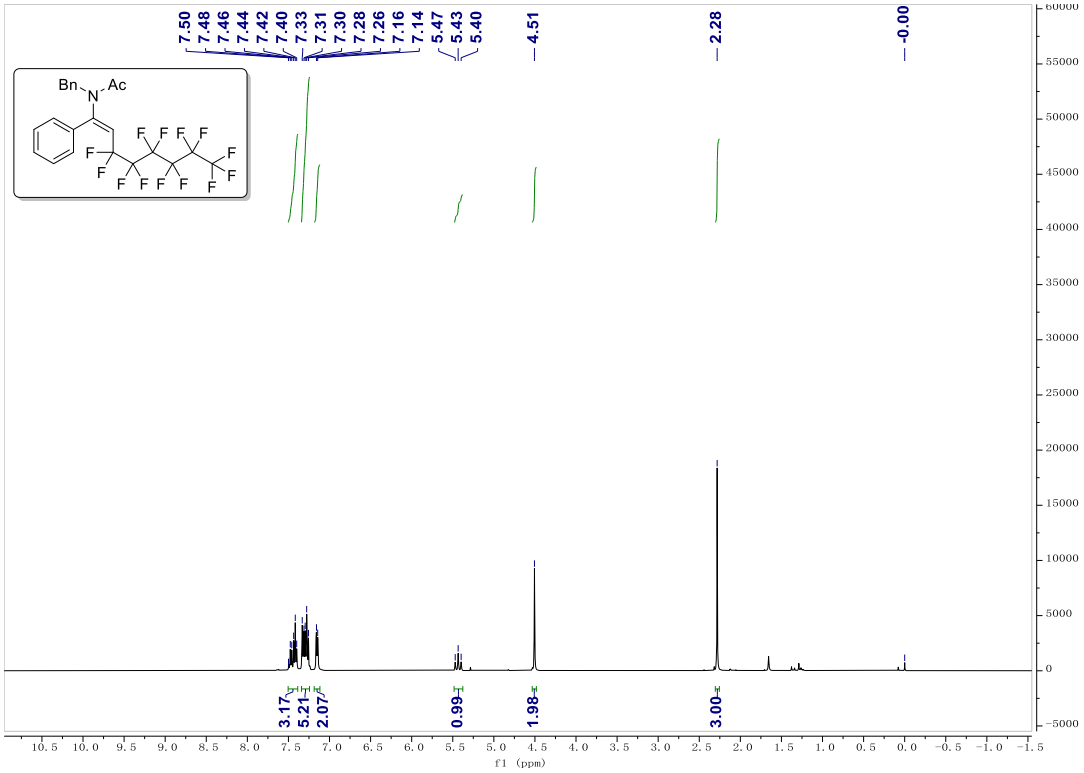
^{13}C NMR (100 MHz) Spectrum of **5c** in $CDCl_3$



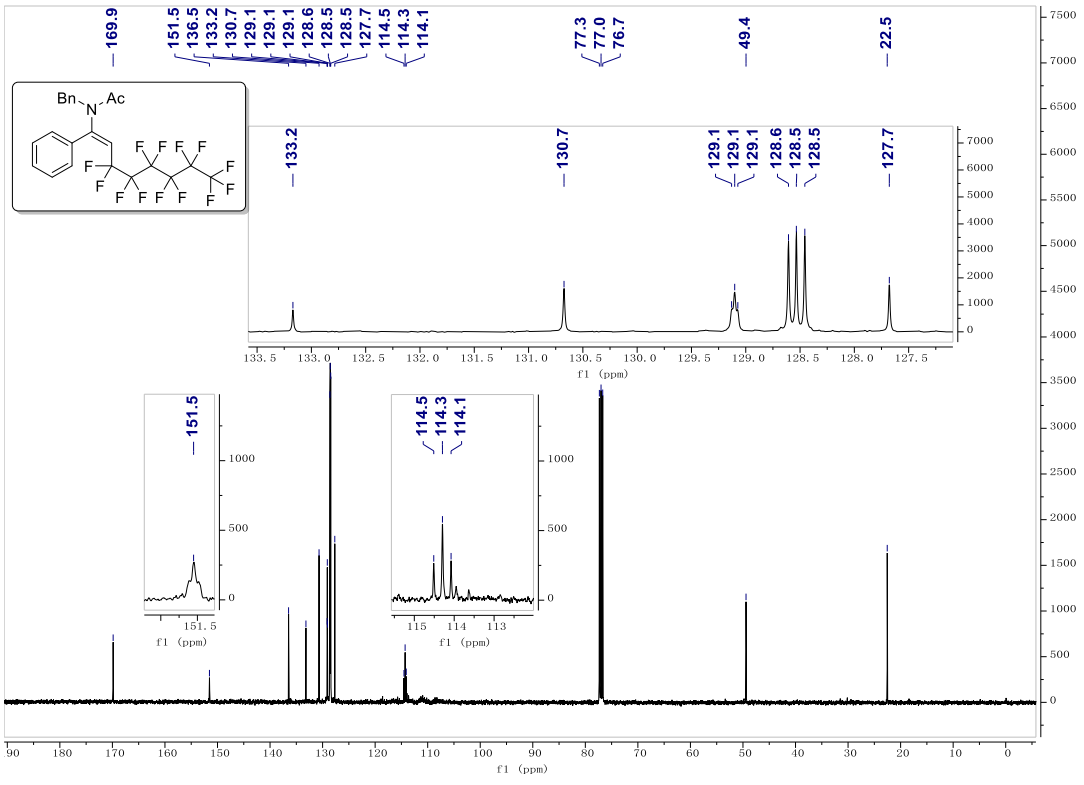
^{19}F NMR (376 MHz) Spectrum of **5c** in $CDCl_3$



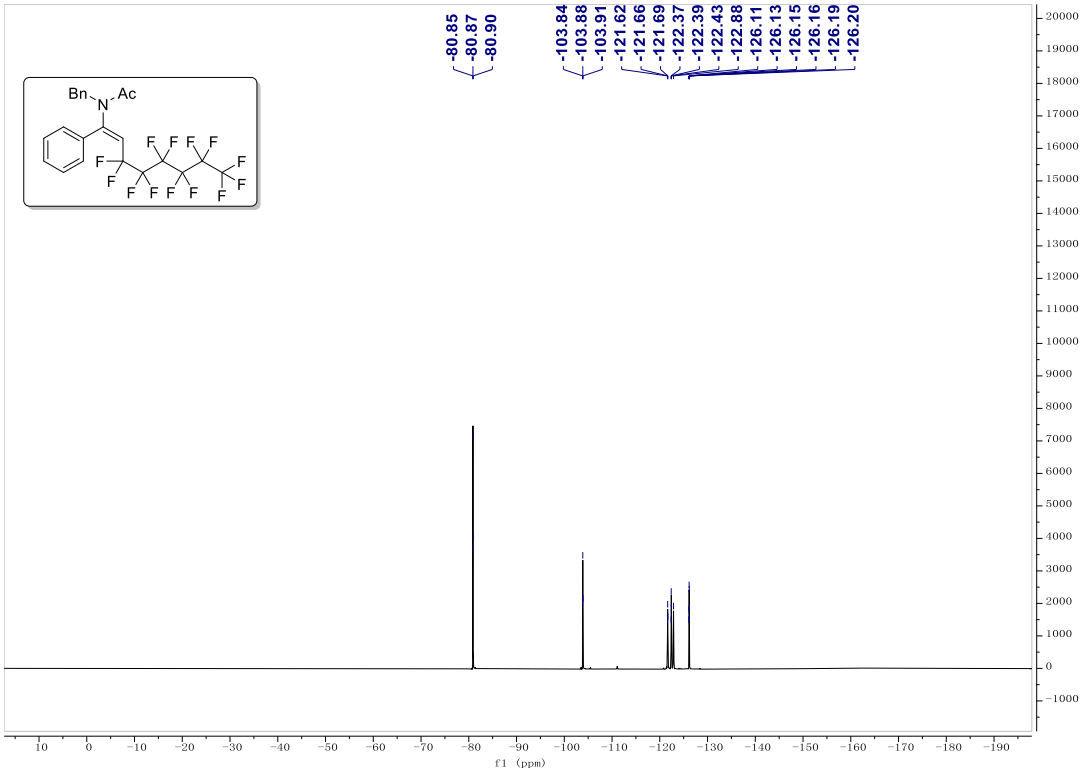
^{1}H NMR (400 MHz) Spectrum of **5d** in $CDCl_3$



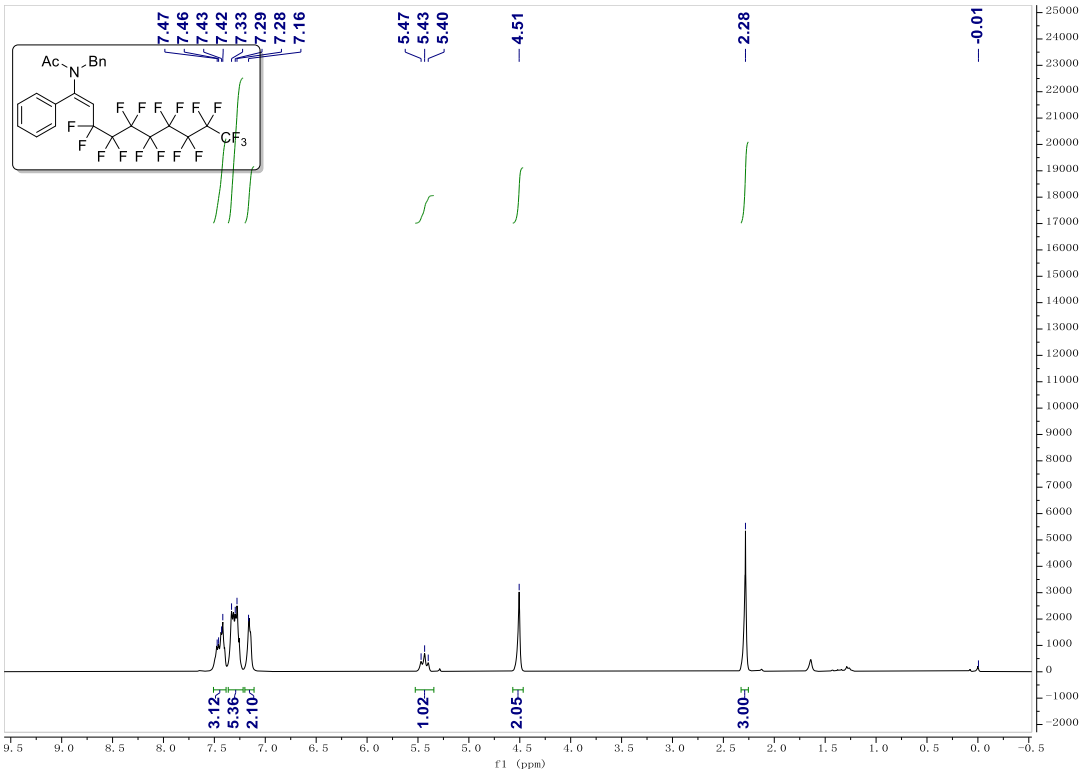
^{13}C NMR (100 MHz) Spectrum of **5d** in $CDCl_3$



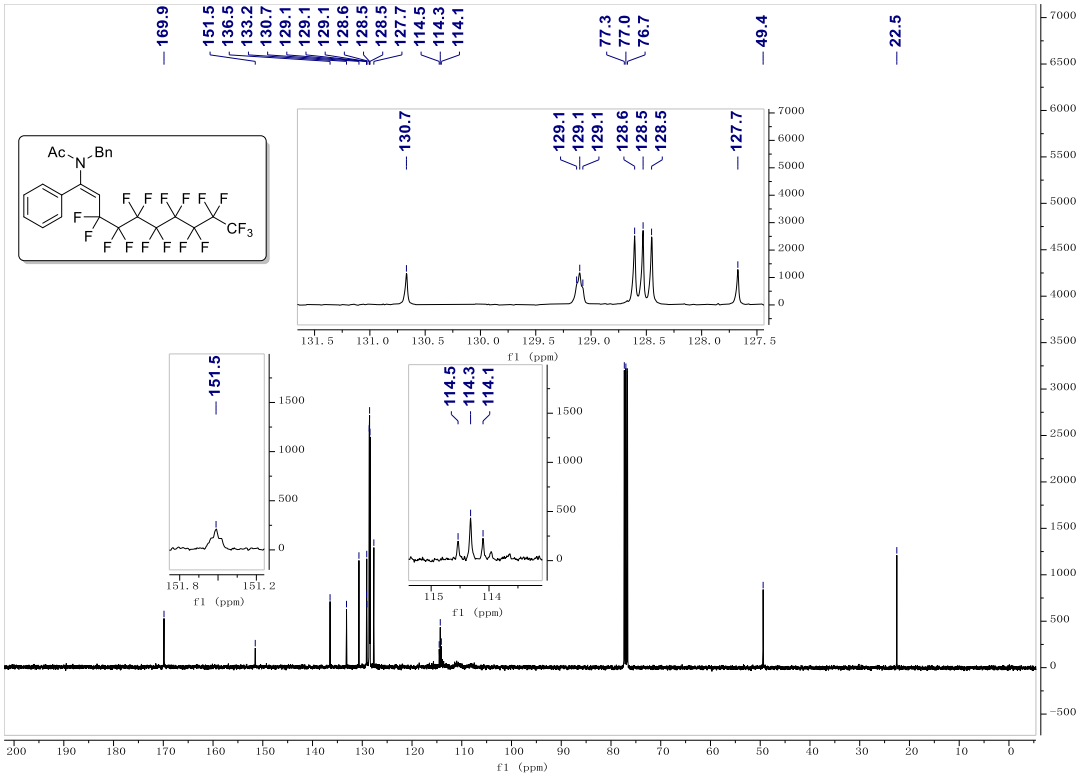
^{19}F NMR (376 MHz) Spectrum of **5d** in $CDCl_3$



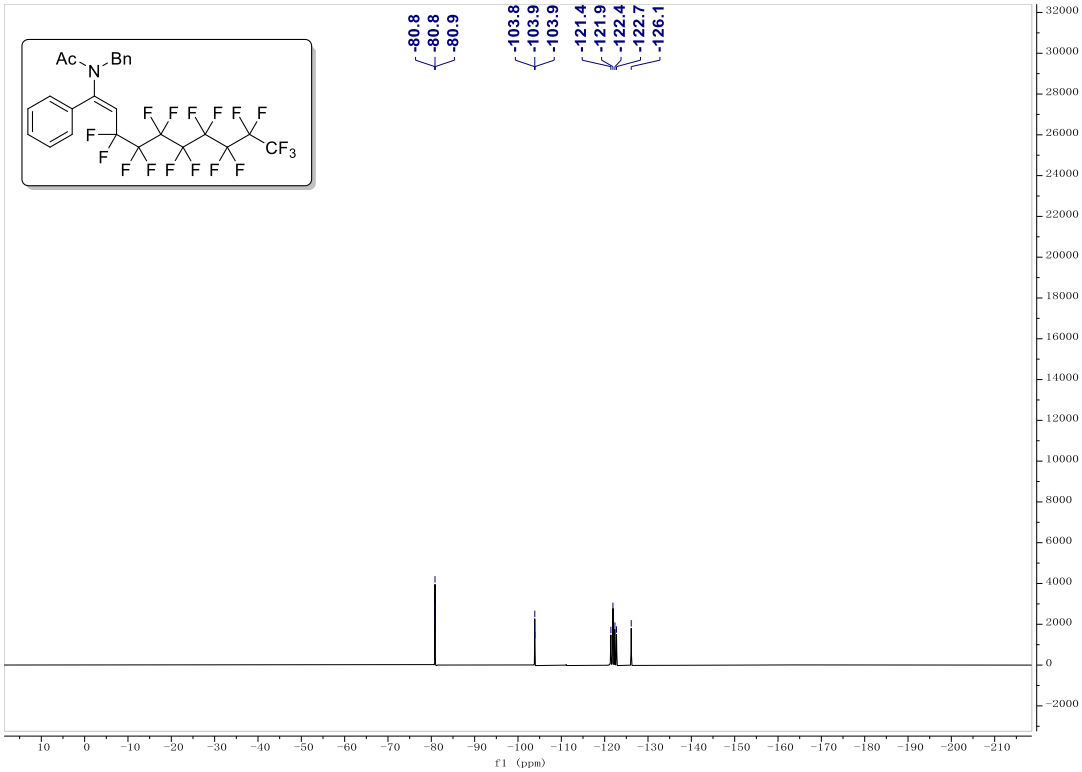
^{1}H NMR (400 MHz) Spectrum of **5e** in $CDCl_3$



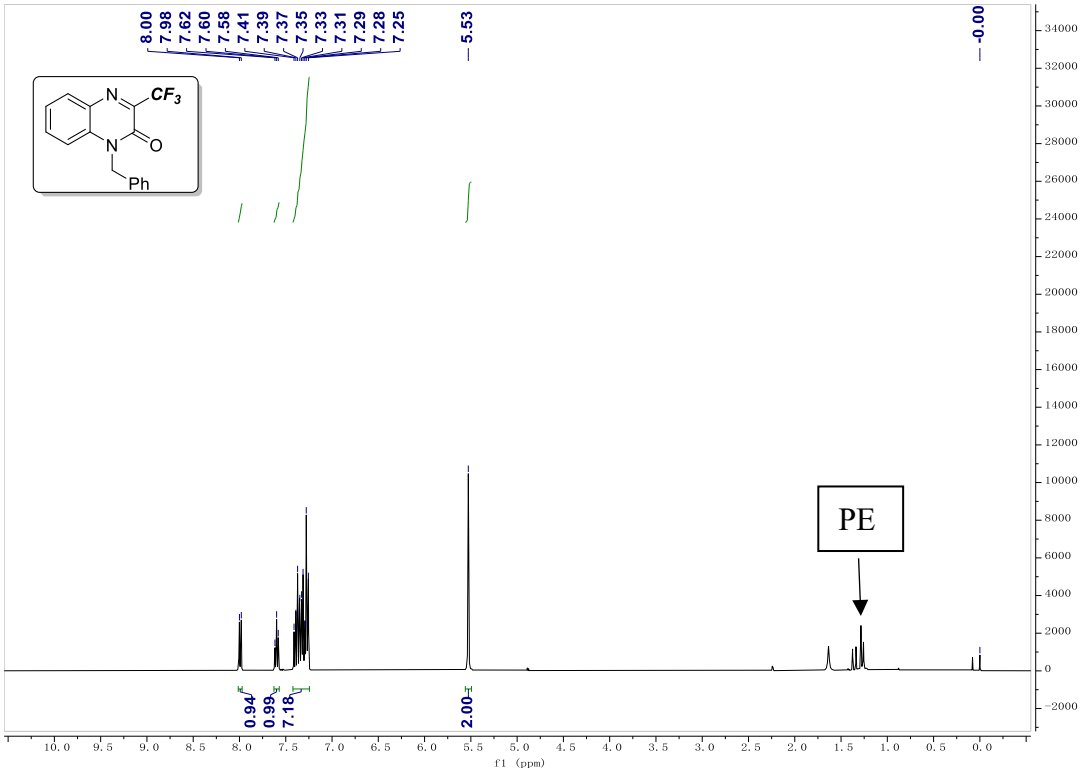
^{13}C NMR (100 MHz) Spectrum of **5e** in $CDCl_3$



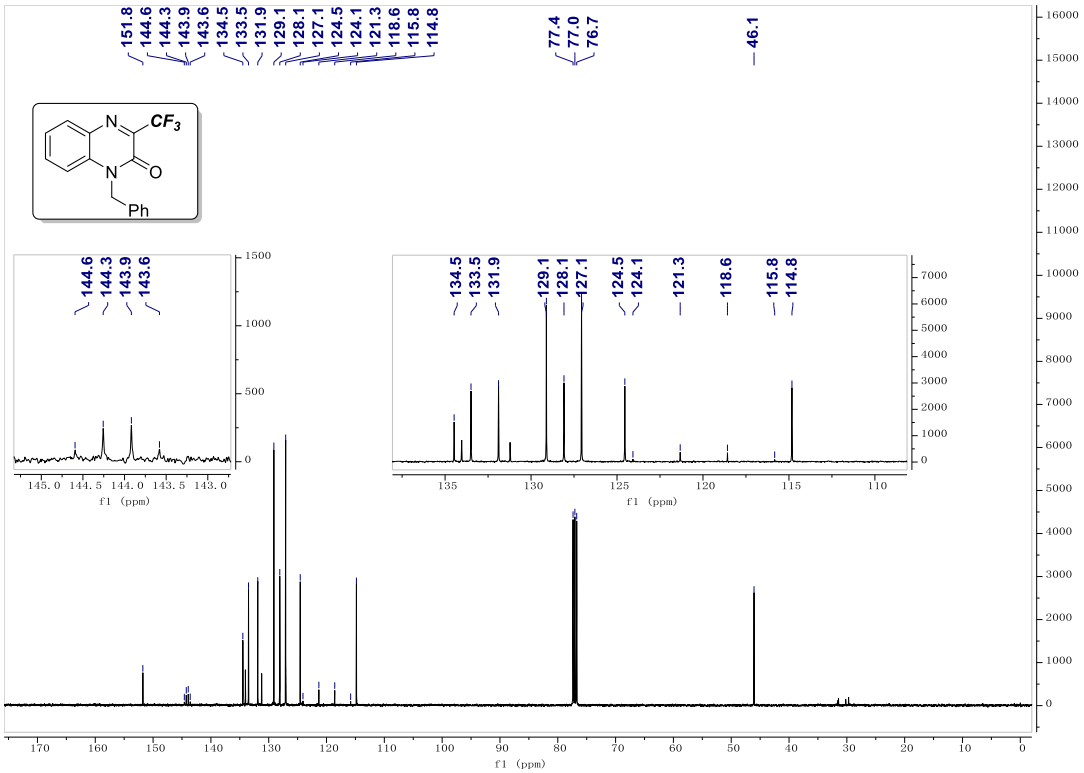
^{19}F NMR (376 MHz) Spectrum of **5e** in $CDCl_3$



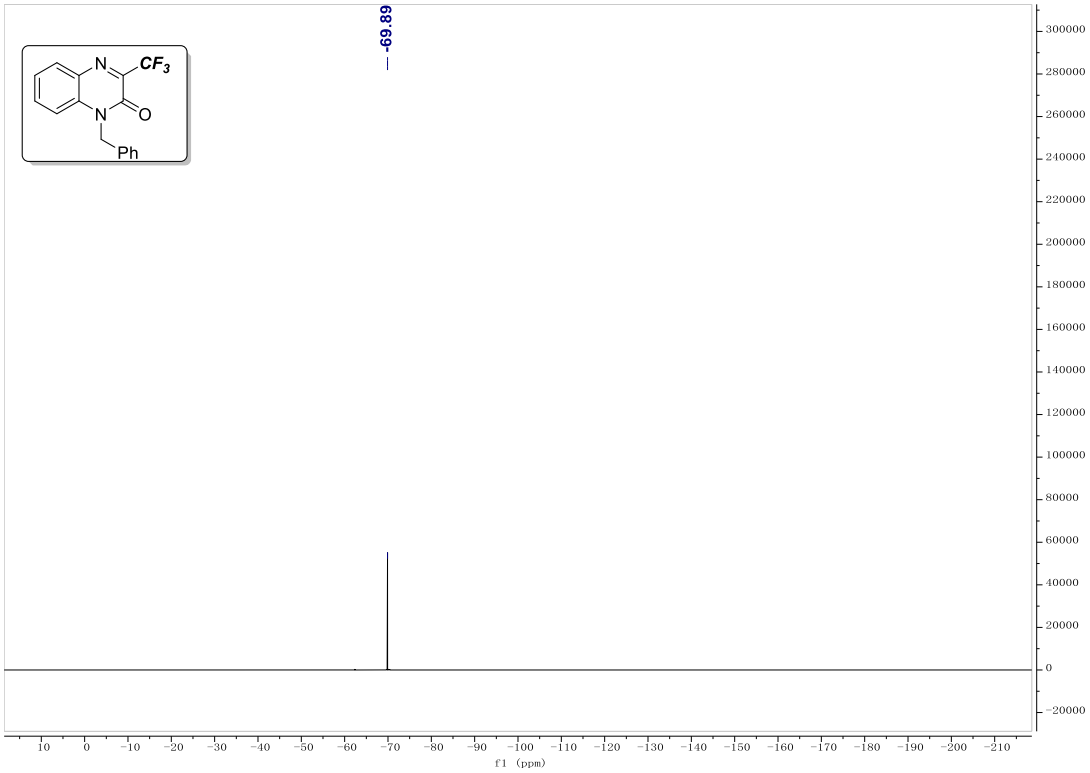
^{1}H NMR (400 MHz) Spectrum of **7a** in $CDCl_3$



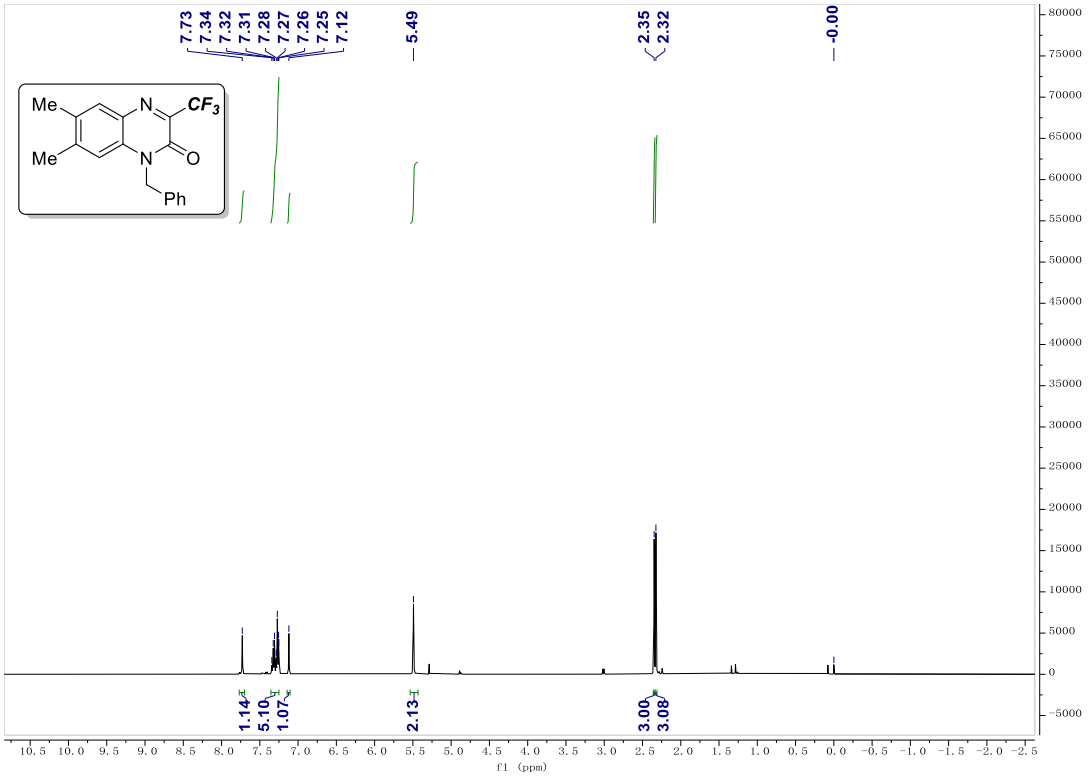
^{13}C NMR (100 MHz) Spectrum of **7a** in $CDCl_3$



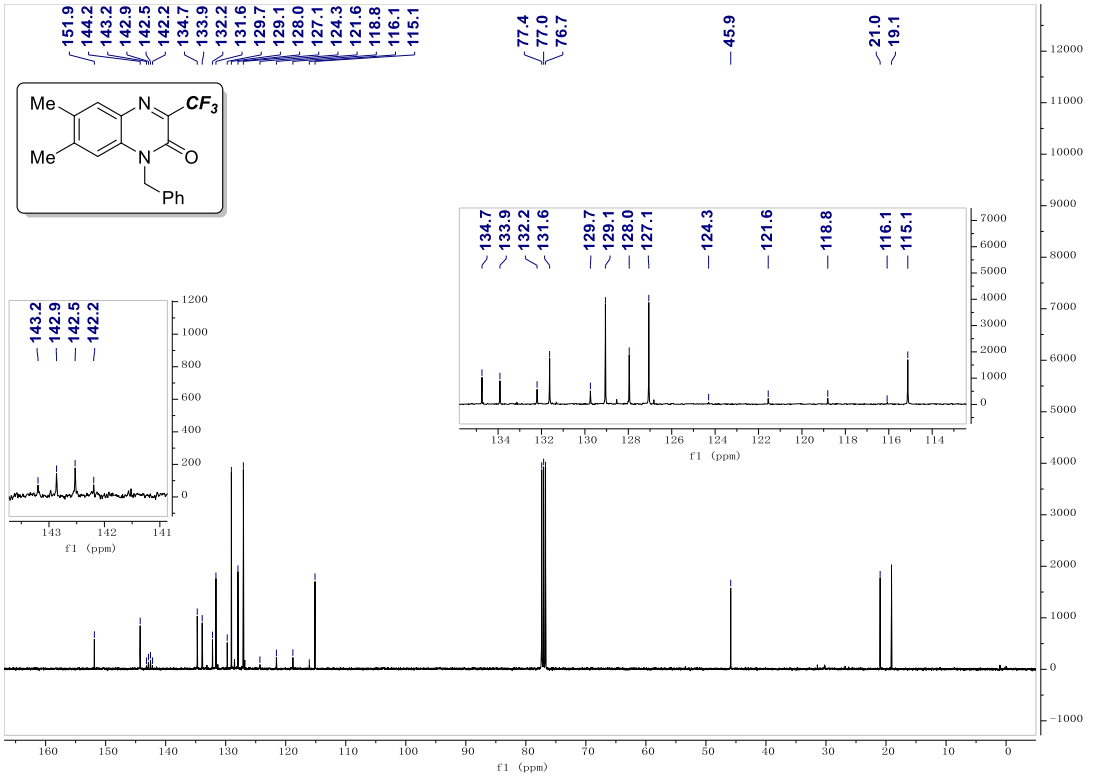
^{19}F NMR (376 MHz) Spectrum of **7a** in $CDCl_3$



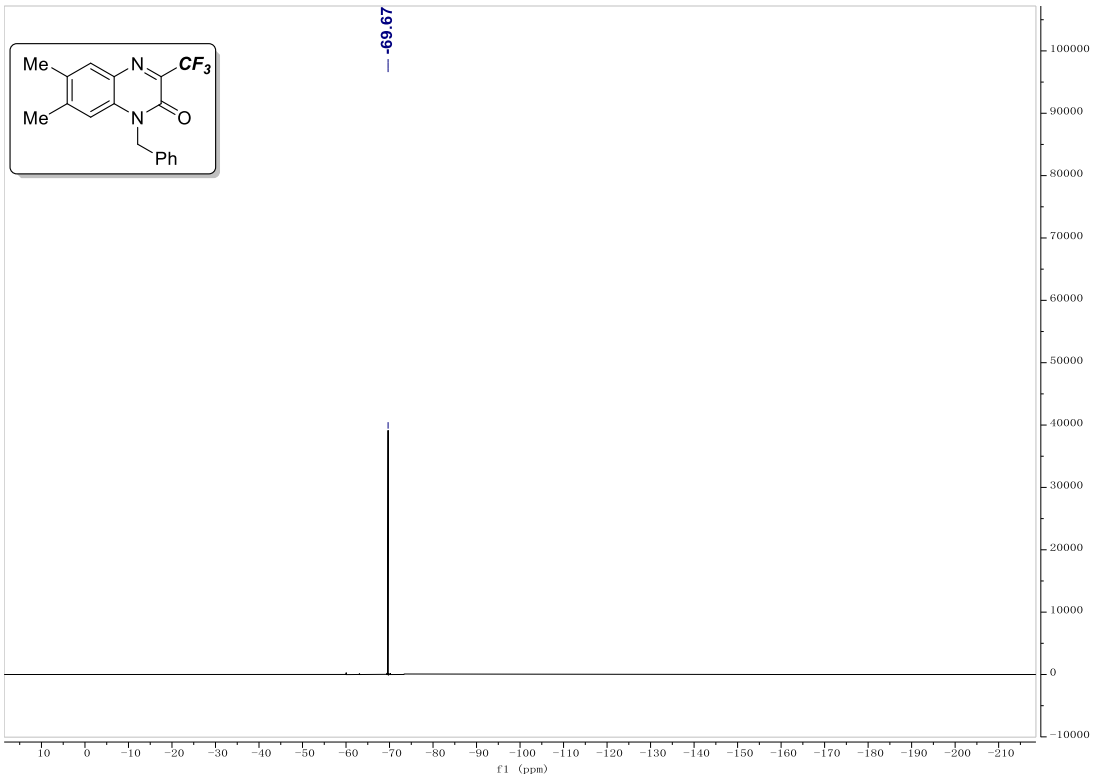
^{1}H NMR (400 MHz) Spectrum of **7b** in $CDCl_3$



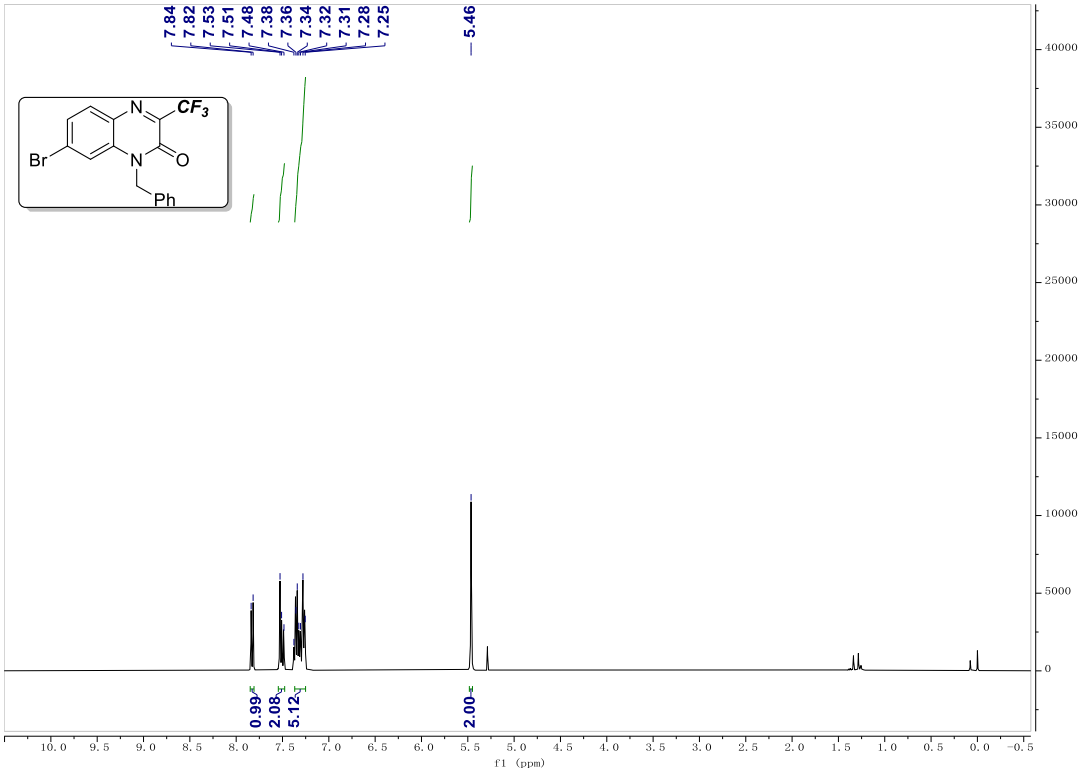
^{13}C NMR (100 MHz) Spectrum of **7b** in $CDCl_3$



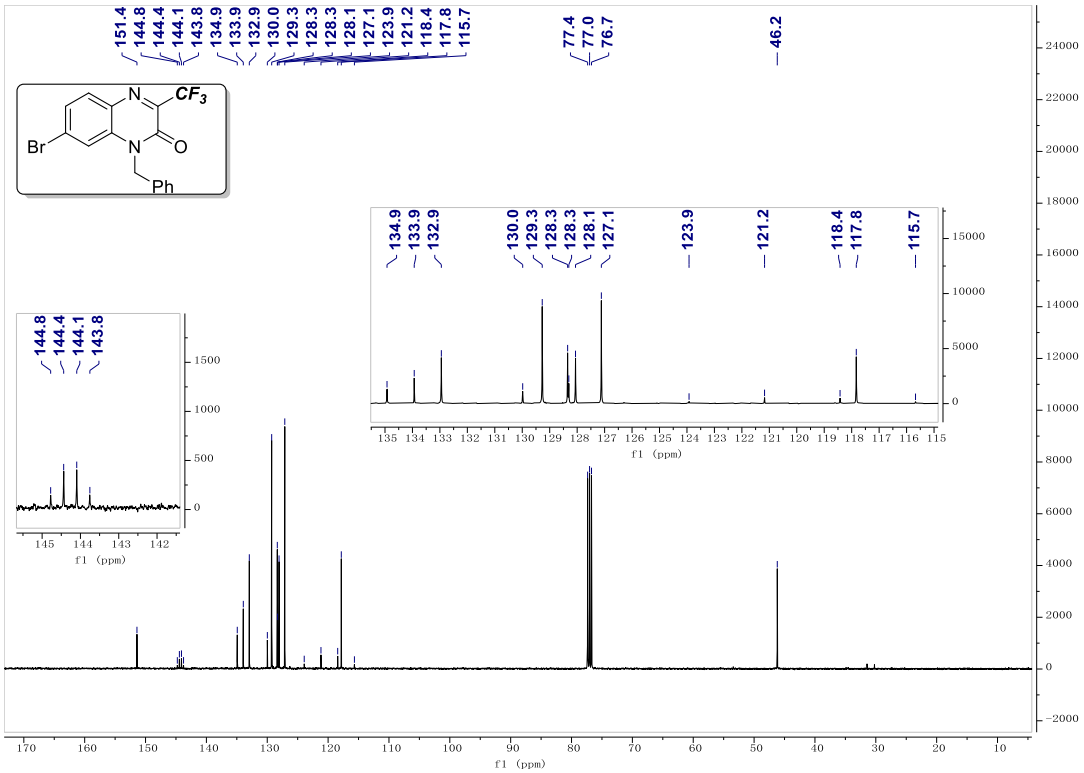
^{19}F NMR (376 MHz) Spectrum of **7b** in $CDCl_3$



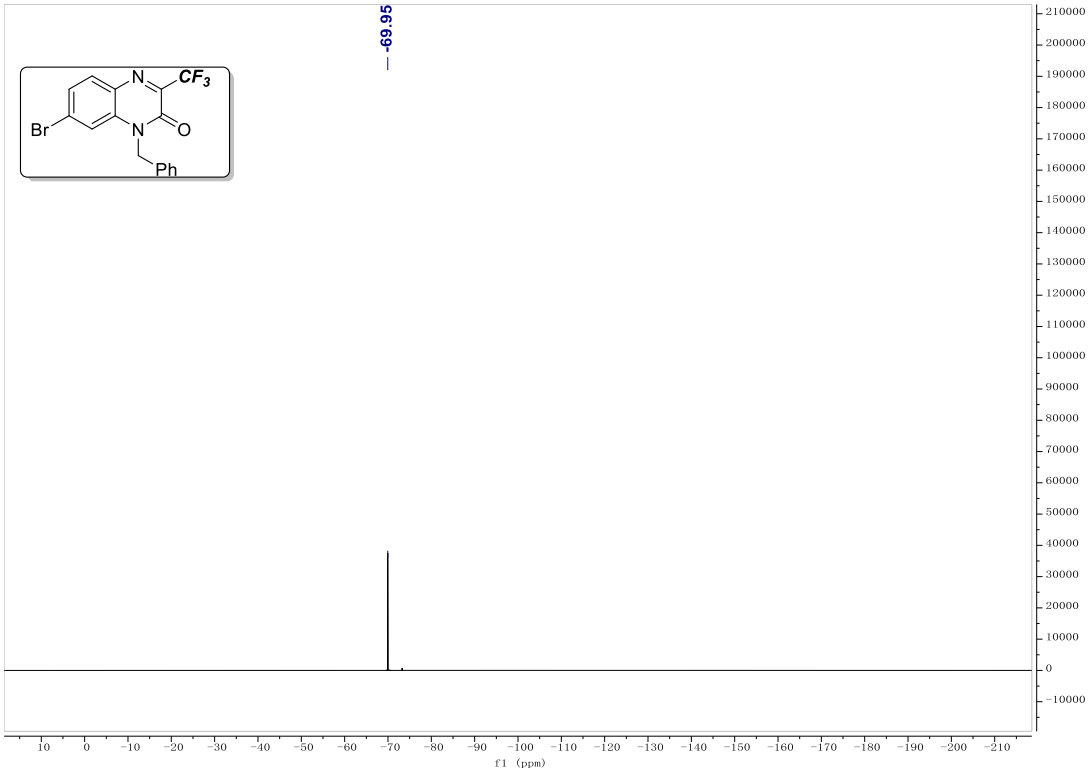
^{1}H NMR (400 MHz) Spectrum of **7c** in $CDCl_3$



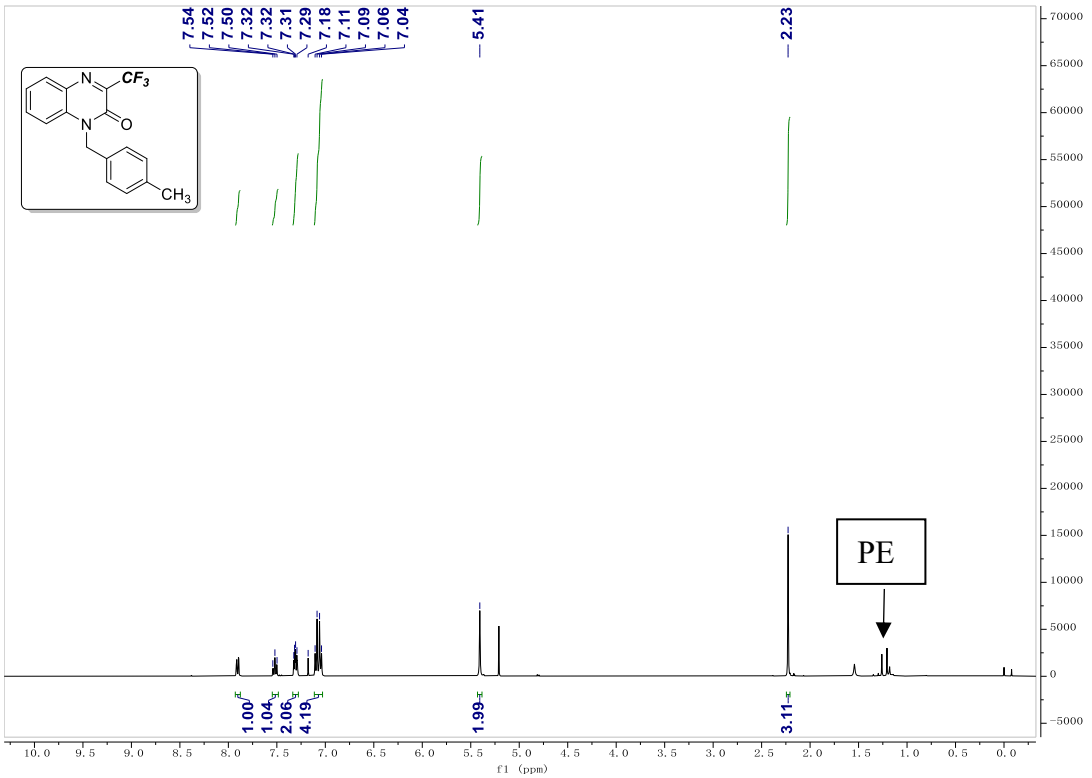
^{13}C NMR (100 MHz) Spectrum of **7c** in $CDCl_3$



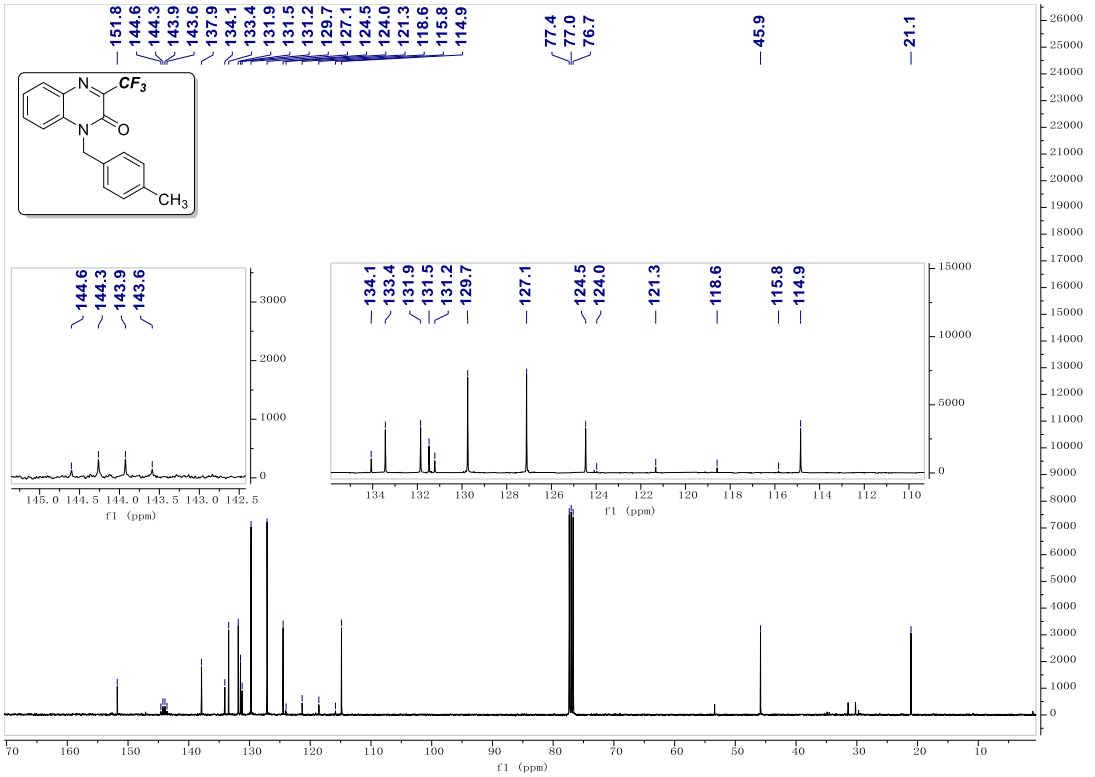
^{19}F NMR (376 MHz) Spectrum of **7c** in $CDCl_3$



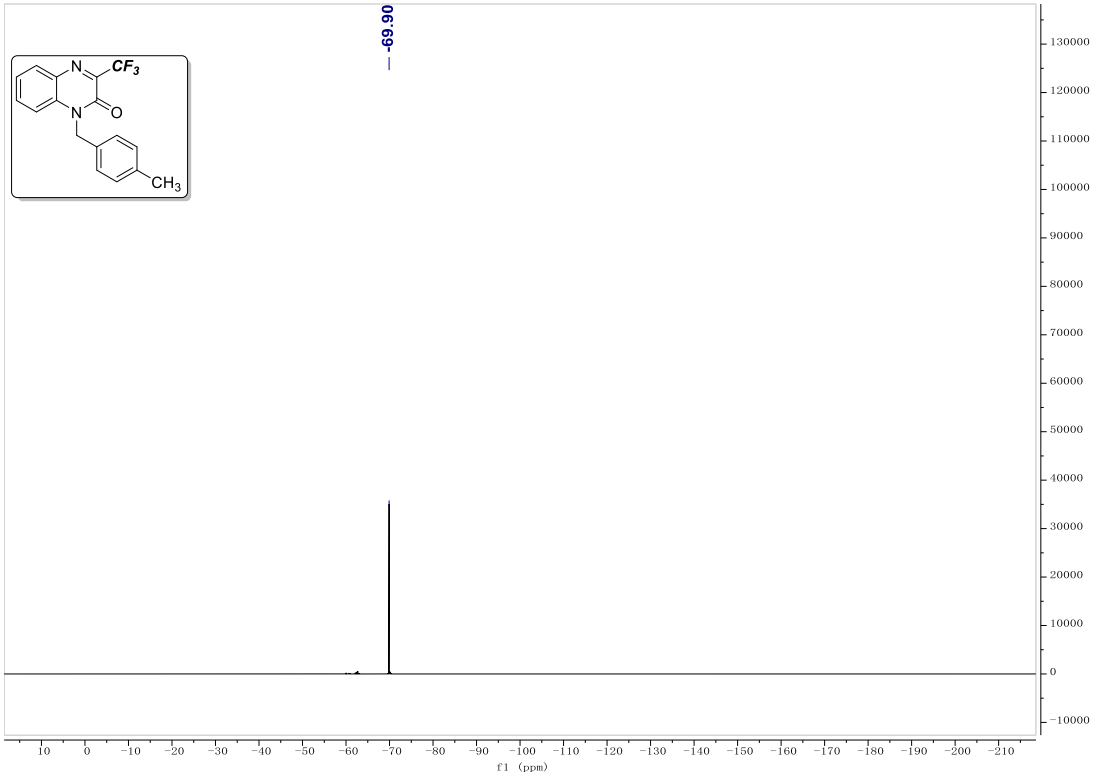
^{1}H NMR (400 MHz) Spectrum of **7d** in $CDCl_3$



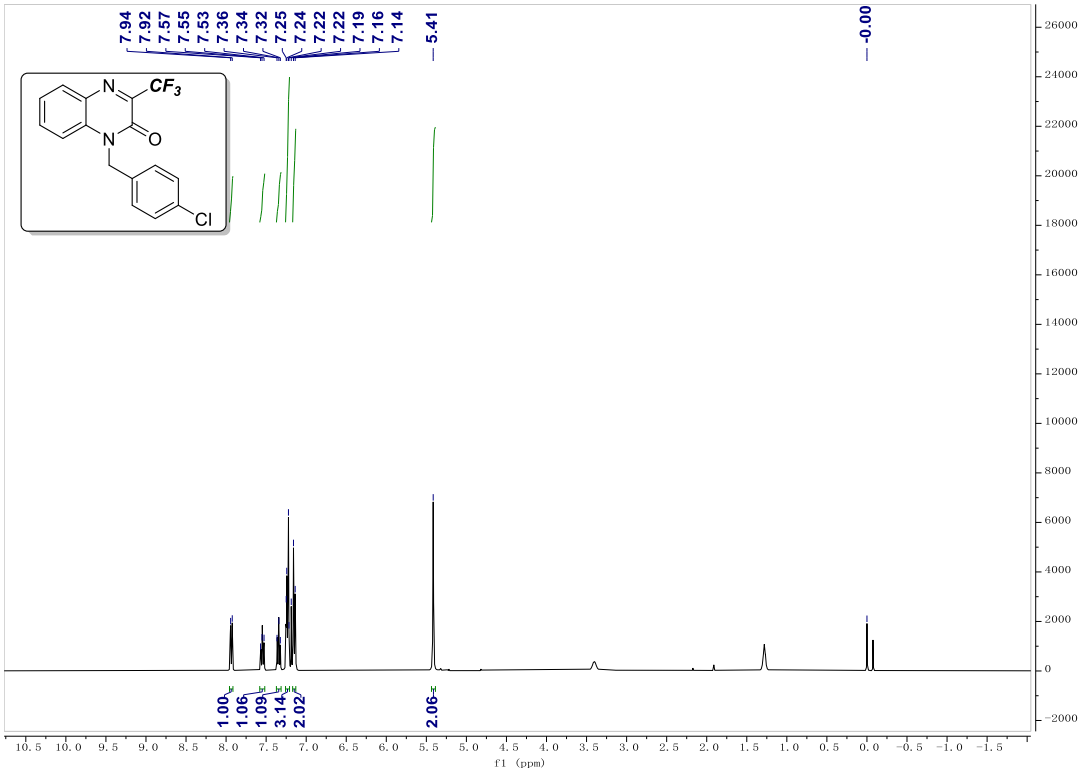
^{13}C NMR (100 MHz) Spectrum of **7d** in $CDCl_3$



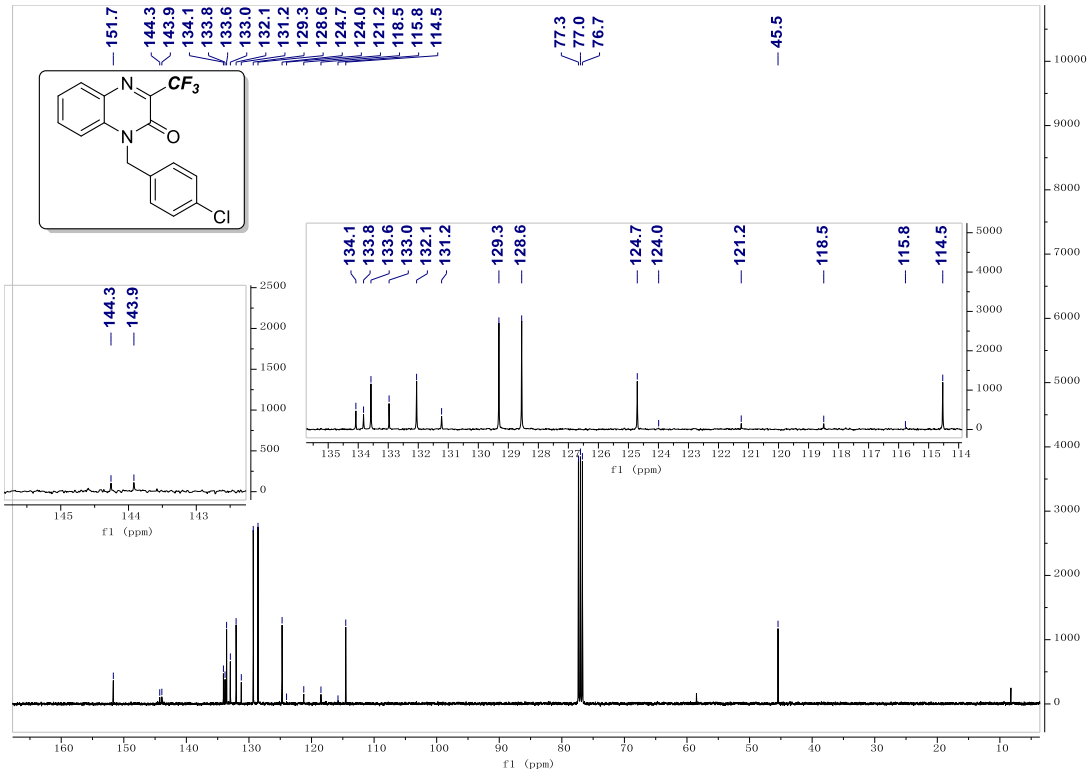
^{19}F NMR (376 MHz) Spectrum of **7d** in $CDCl_3$



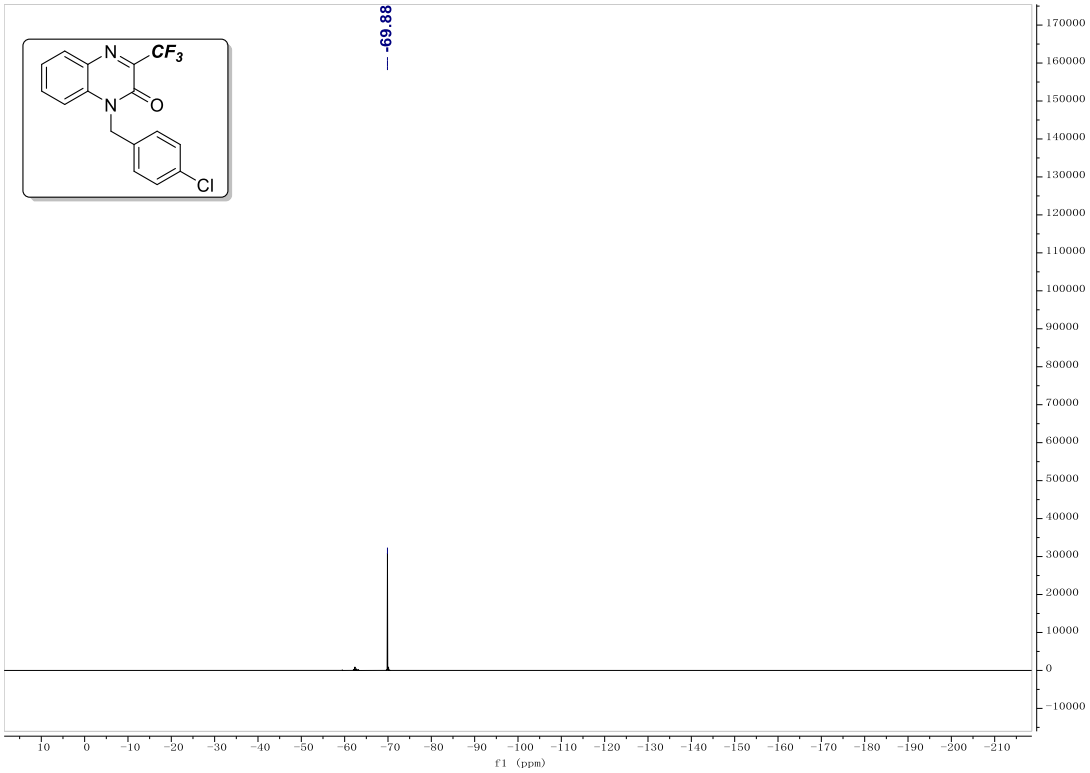
^{1}H NMR (400 MHz) Spectrum of **7e** in $CDCl_3$



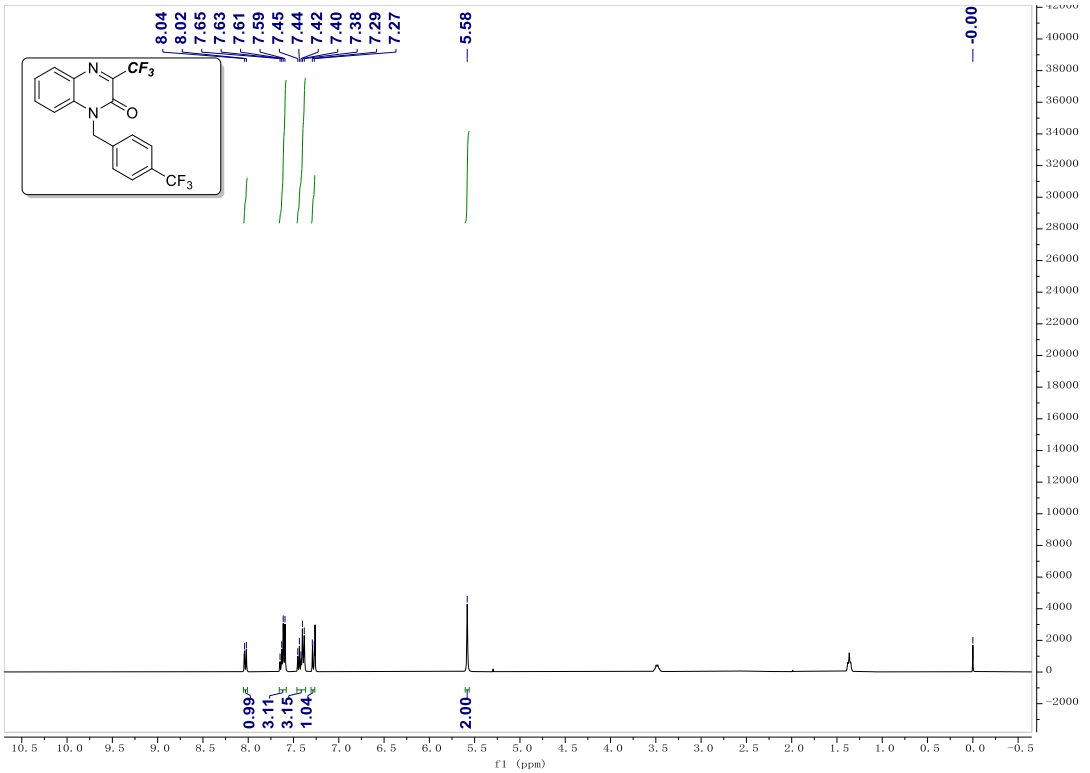
^{13}C NMR (100 MHz) Spectrum of **7e** in $CDCl_3$



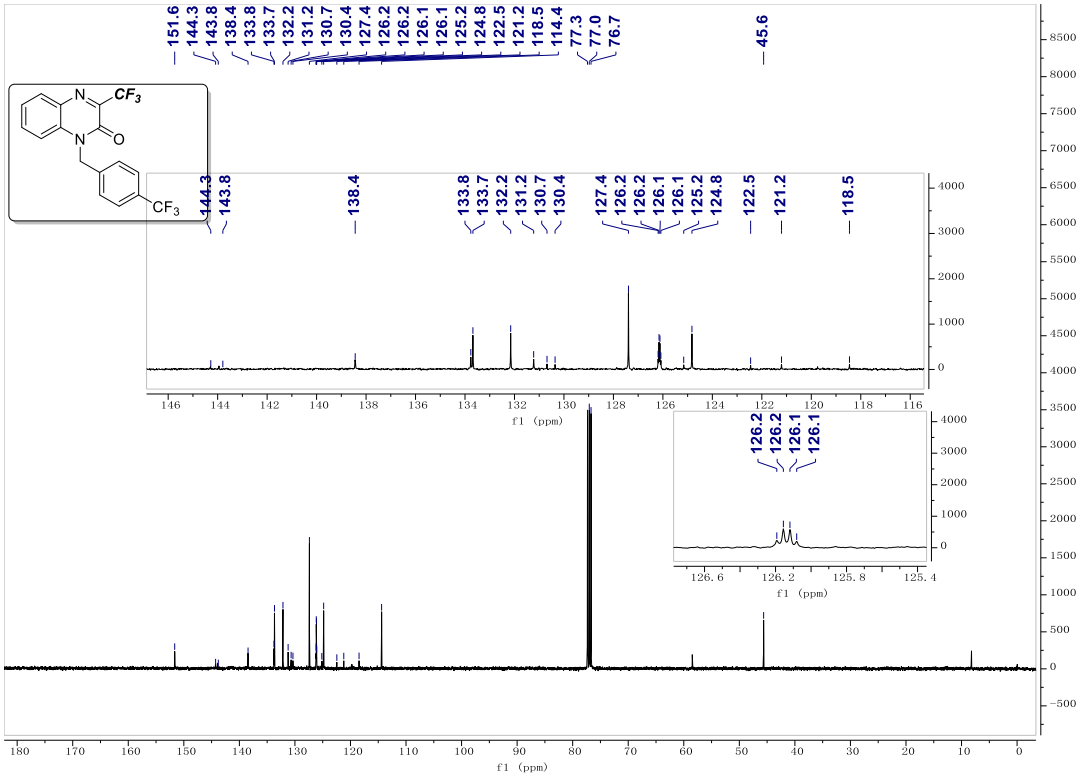
^{19}F NMR (376 MHz) Spectrum of **7e** in $CDCl_3$



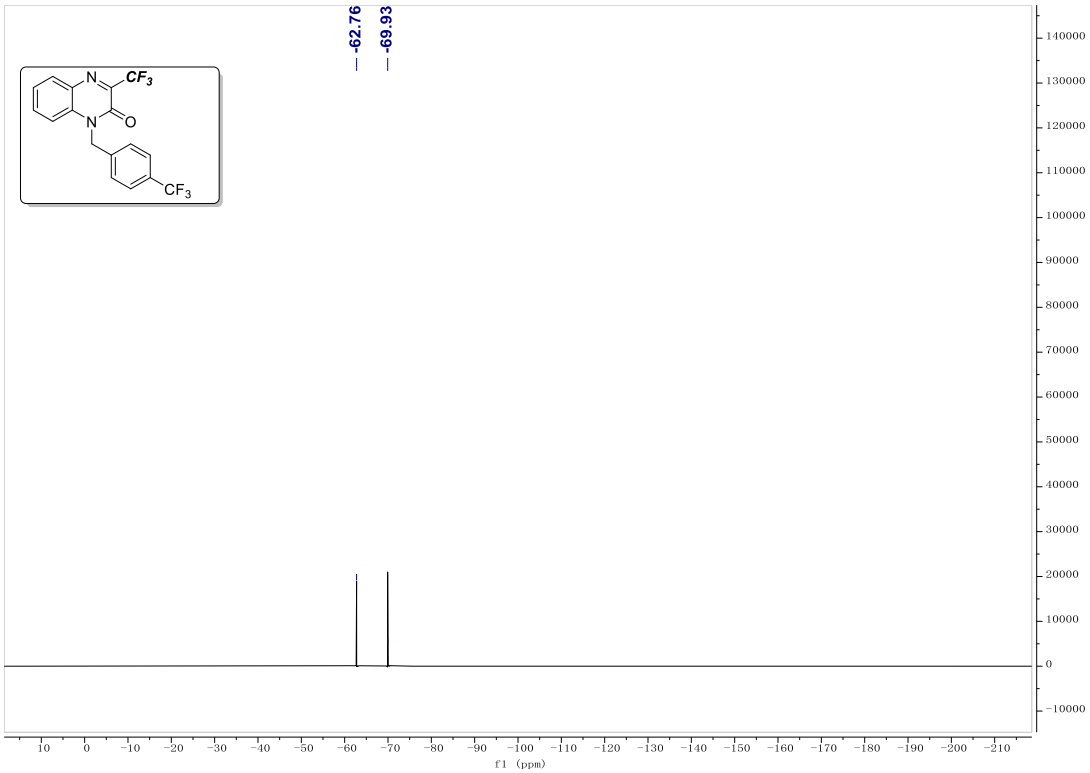
^{1}H NMR (400 MHz) Spectrum of **7f** in $CDCl_3$



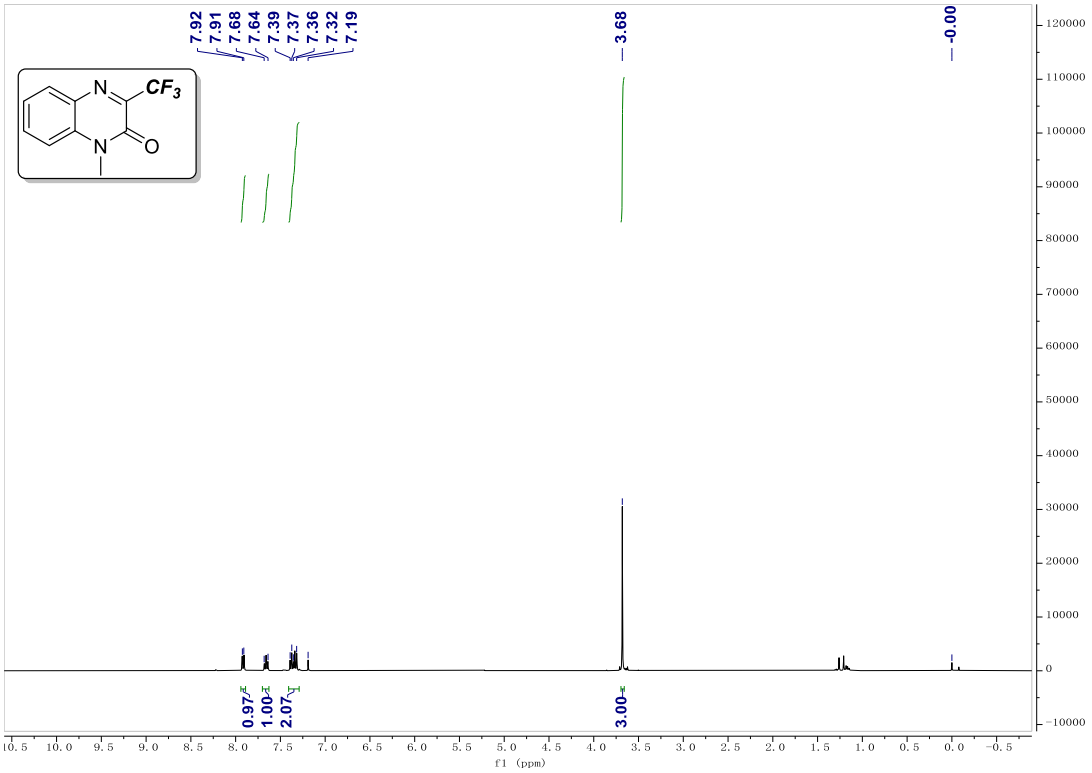
^{13}C NMR (100 MHz) Spectrum of **7f** in $CDCl_3$



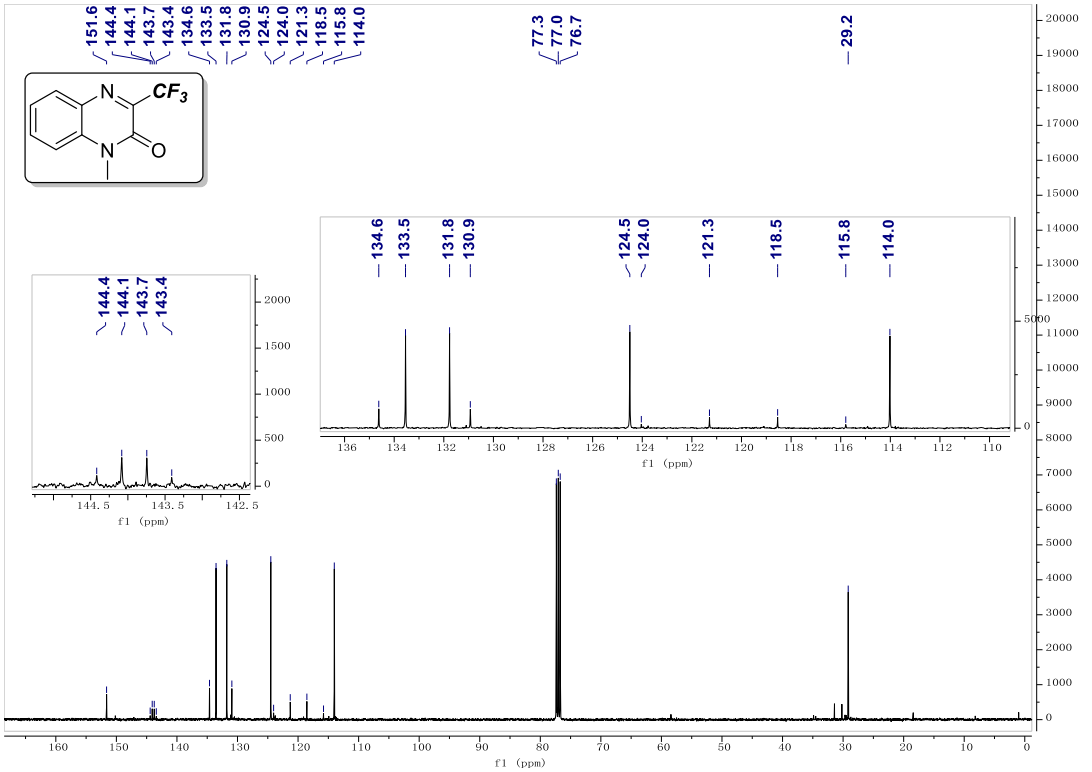
^{19}F NMR (376 MHz) Spectrum of **7f** in $CDCl_3$



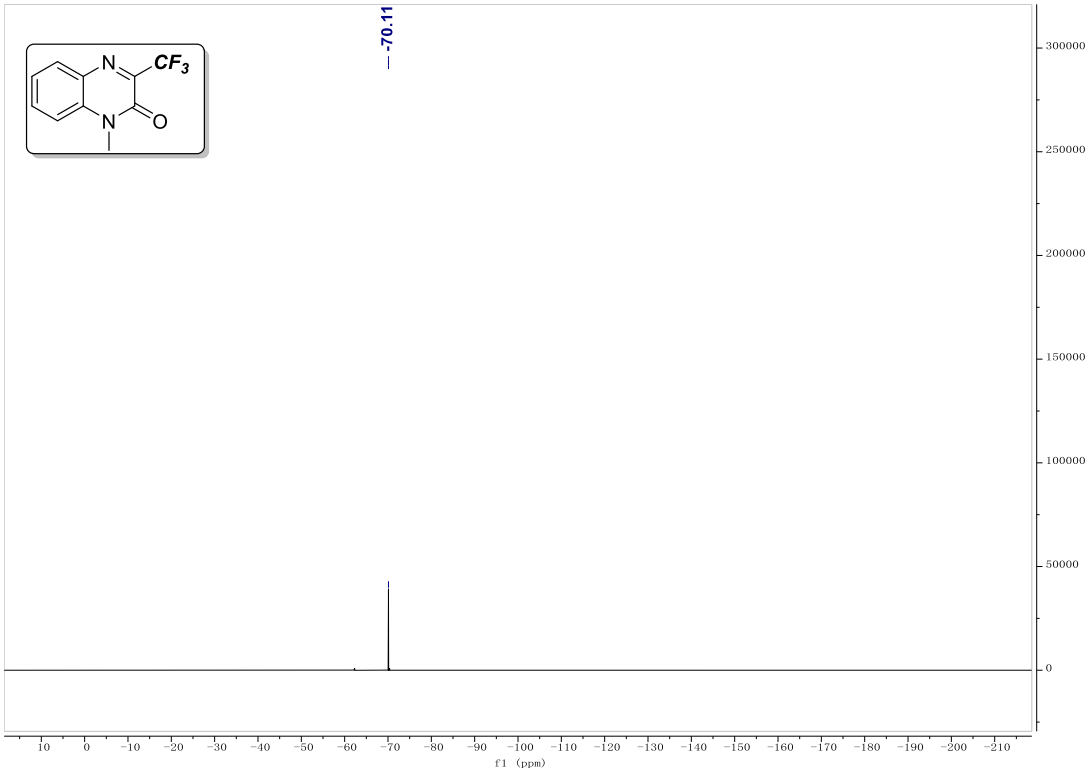
^{1}H NMR (400 MHz) Spectrum of **7g** in $CDCl_3$



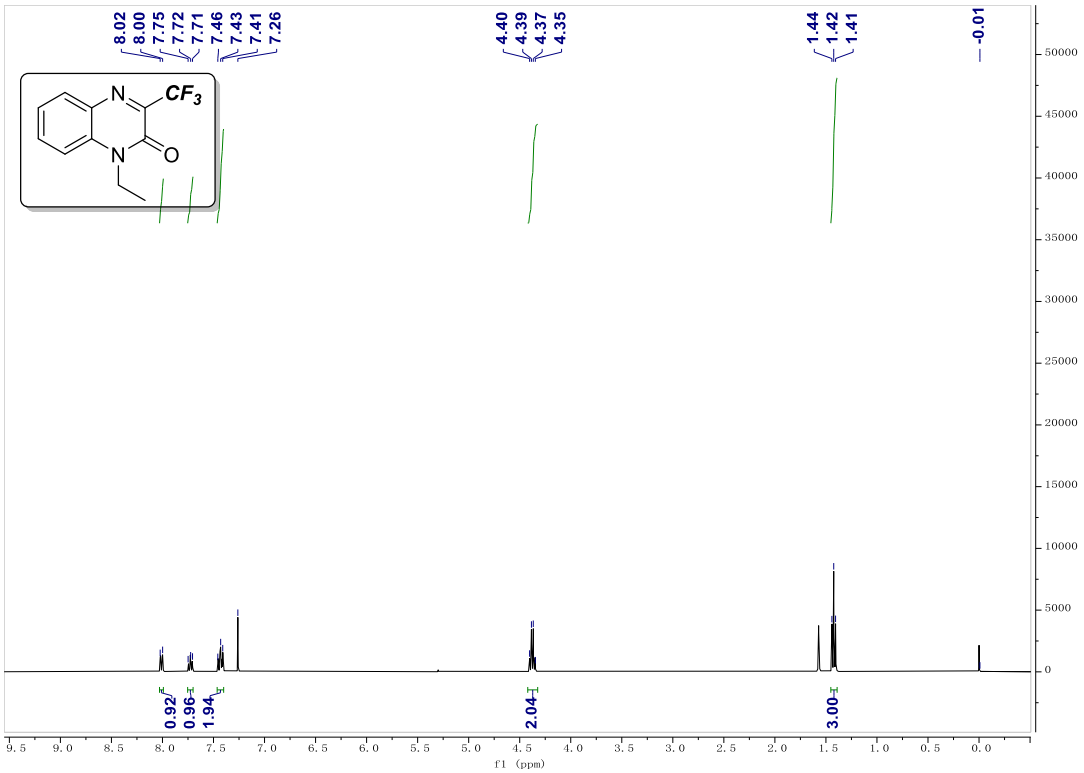
^{13}C NMR (100 MHz) Spectrum of **7g** in $CDCl_3$



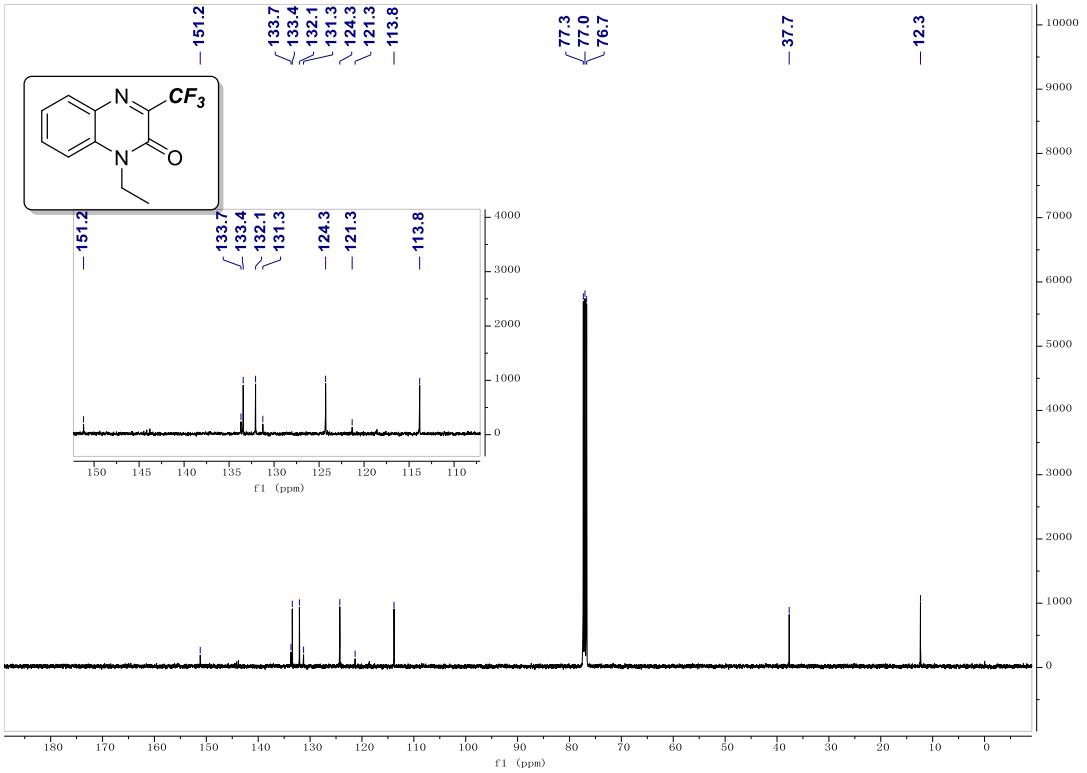
^{19}F NMR (376 MHz) Spectrum of **7g** in $CDCl_3$



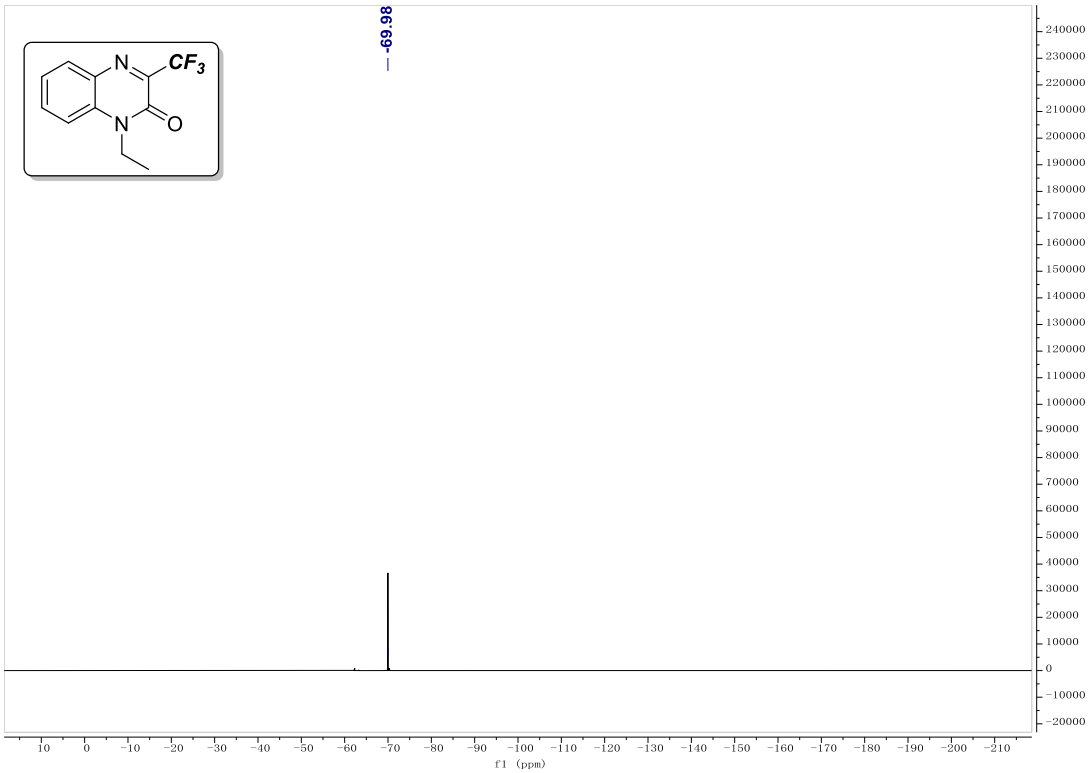
^{1}H NMR (400 MHz) Spectrum of **7h** in $CDCl_3$



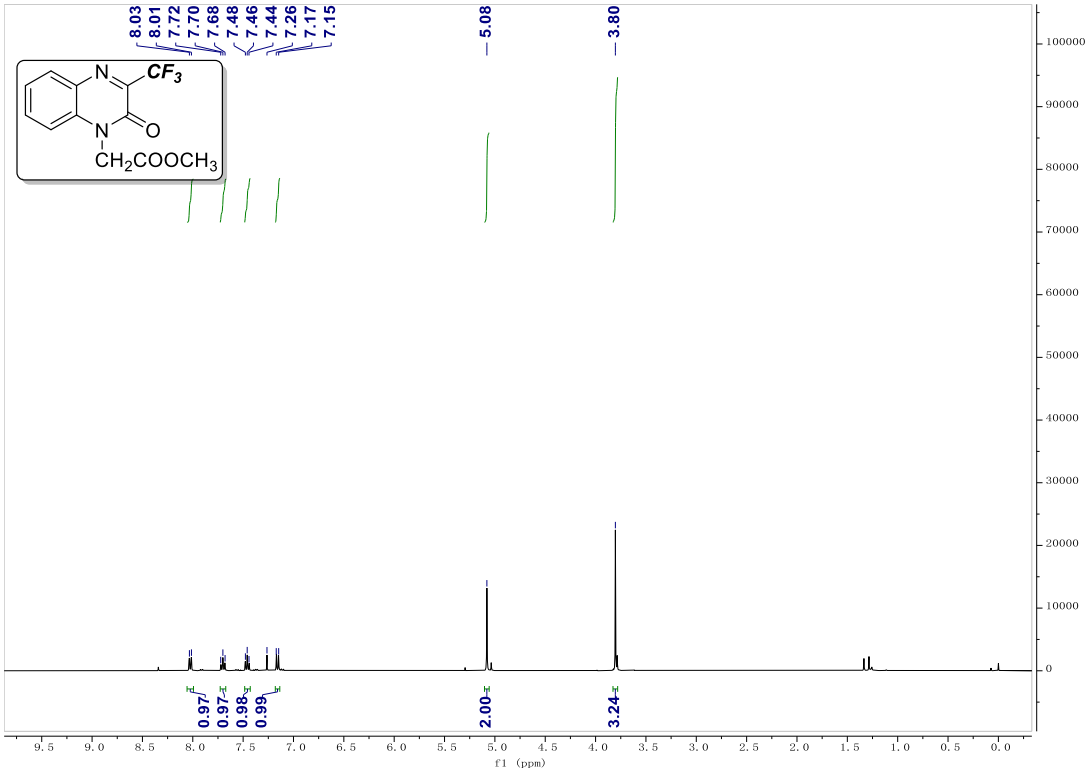
^{13}C NMR (100 MHz) Spectrum of **7h** in $CDCl_3$



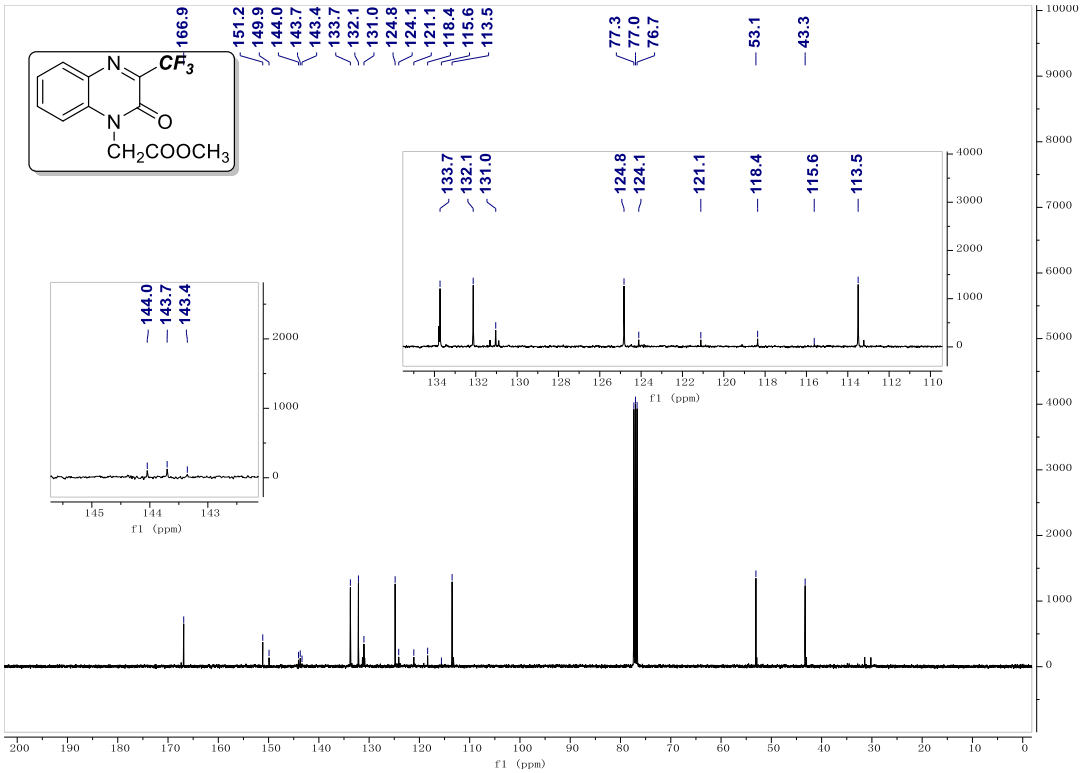
^{19}F NMR (376 MHz) Spectrum of **7h** in $CDCl_3$



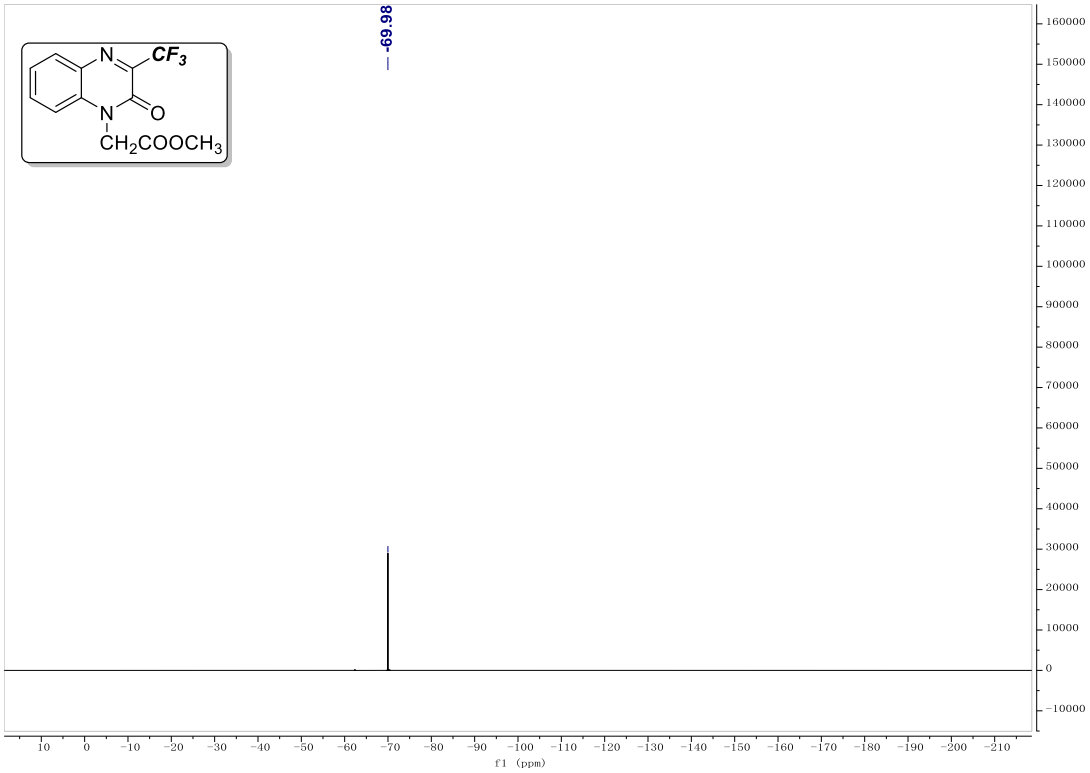
^{1}H NMR (400 MHz) Spectrum of **7i** in $CDCl_3$



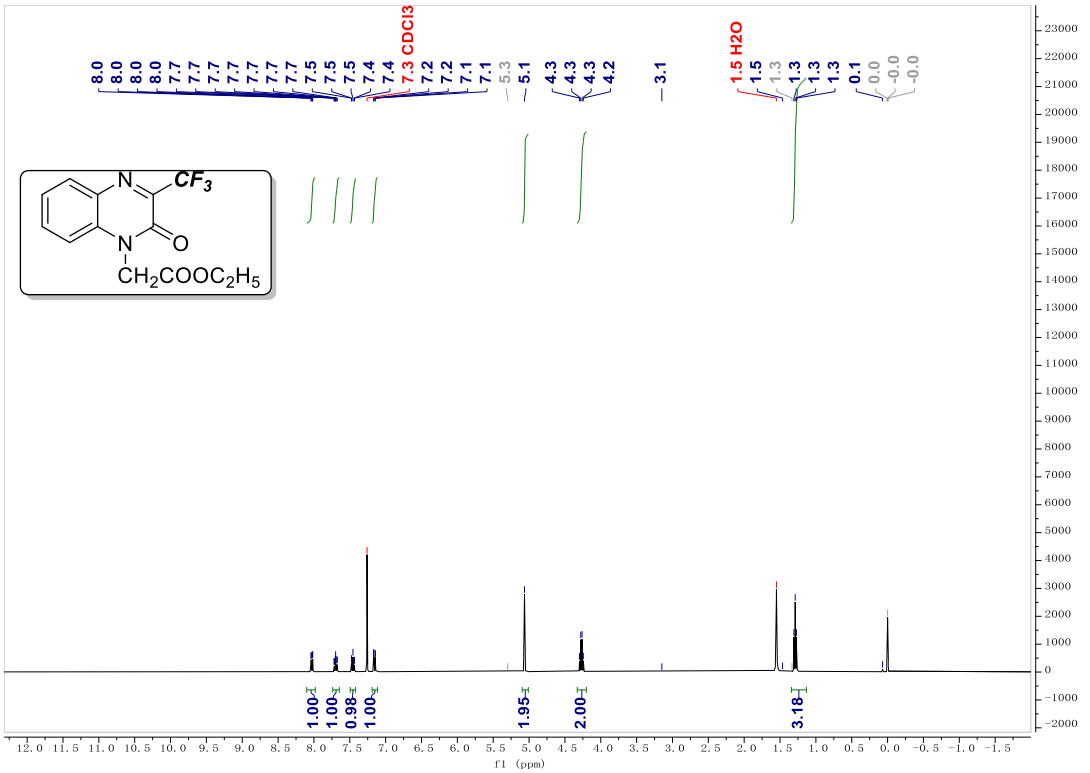
^{13}C NMR (100 MHz) Spectrum of **7i** in $CDCl_3$



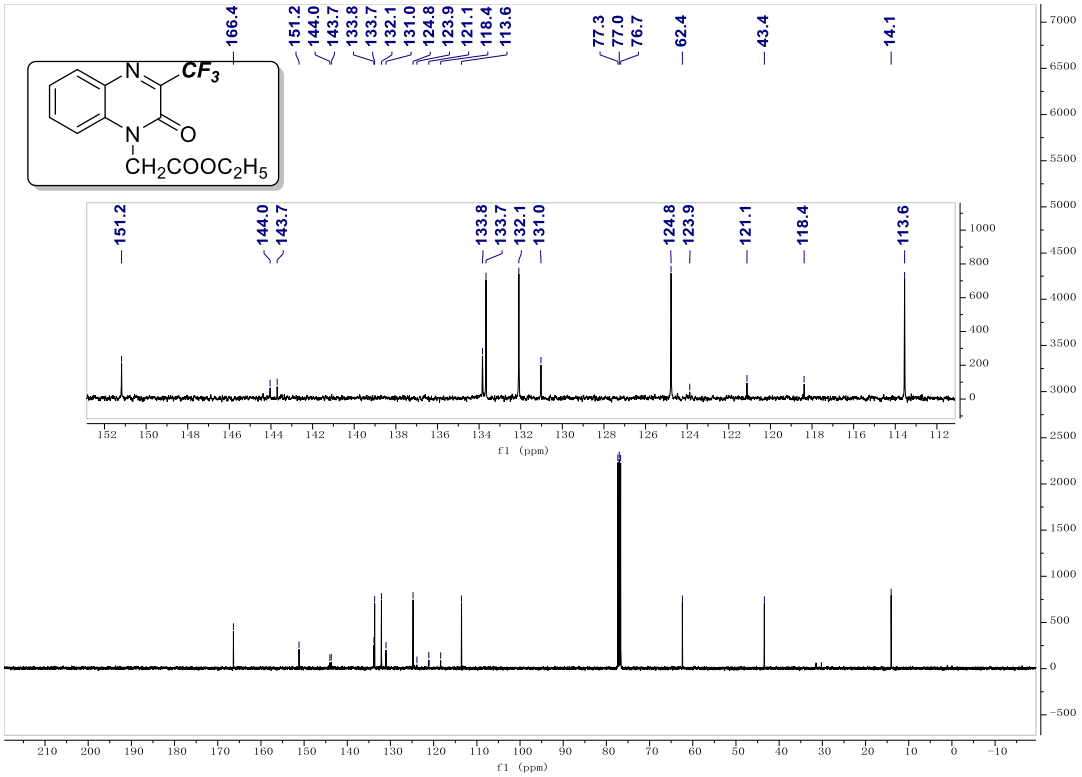
^{19}F NMR (376 MHz) Spectrum of **7i** in $CDCl_3$



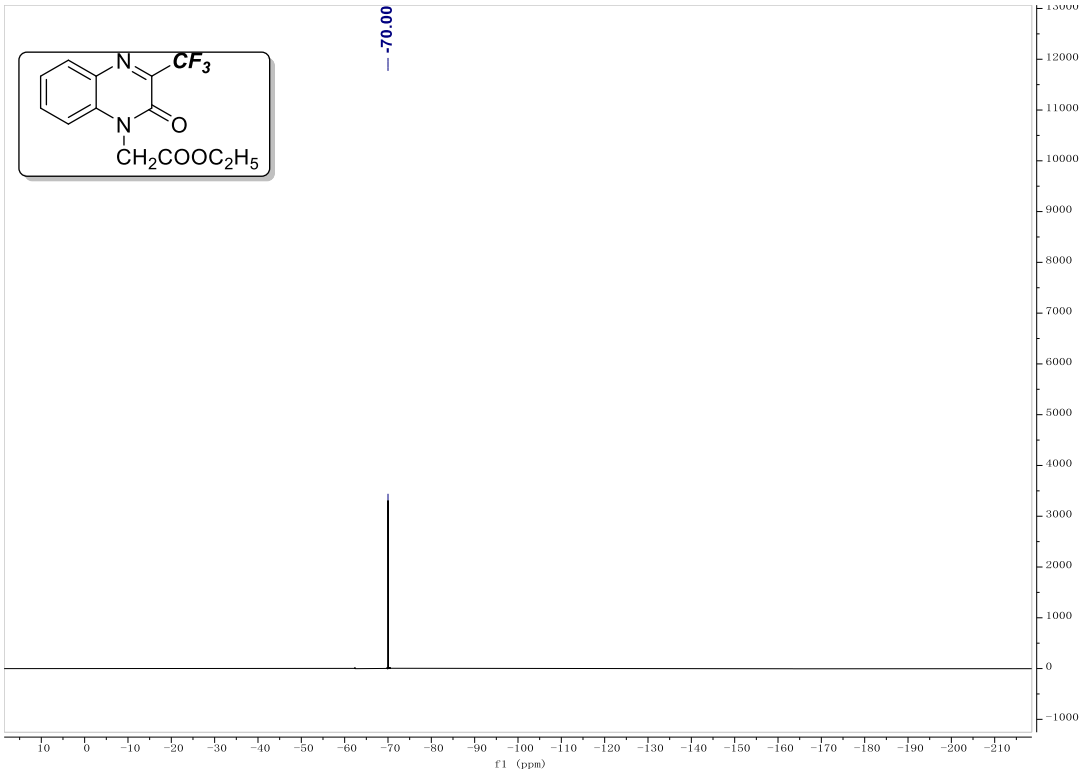
^{1}H NMR (400 MHz) Spectrum of **7j** in $CDCl_3$



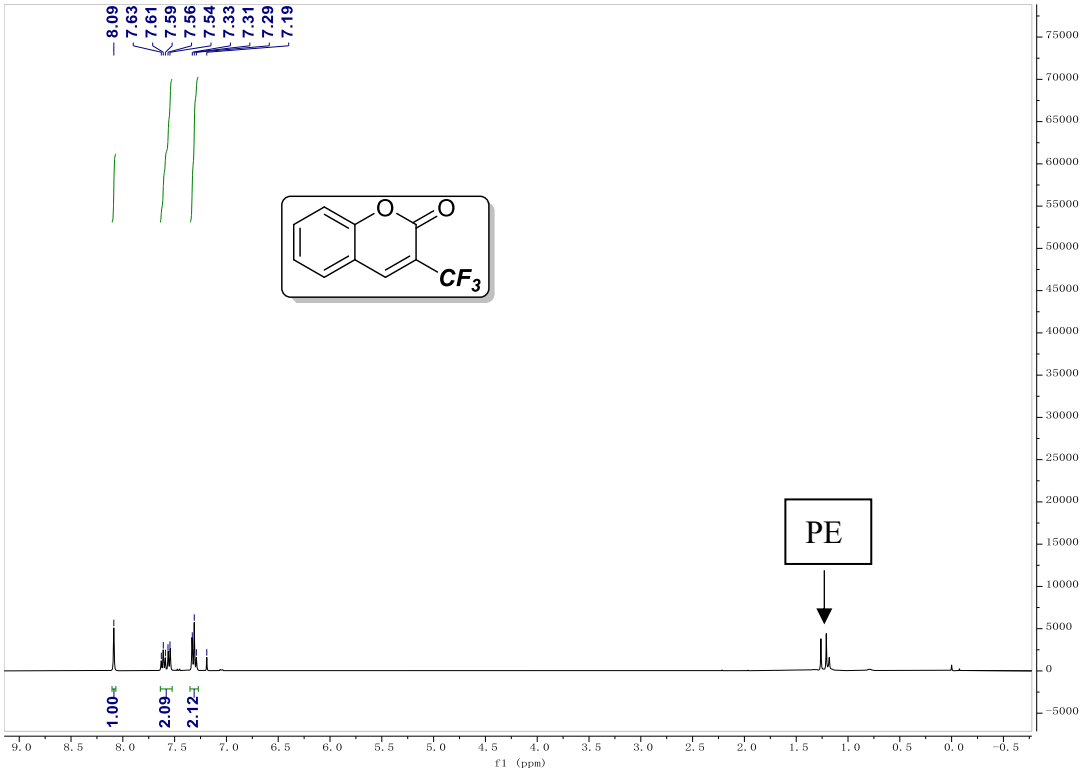
^{13}C NMR (100 MHz) Spectrum of **7j** in $CDCl_3$



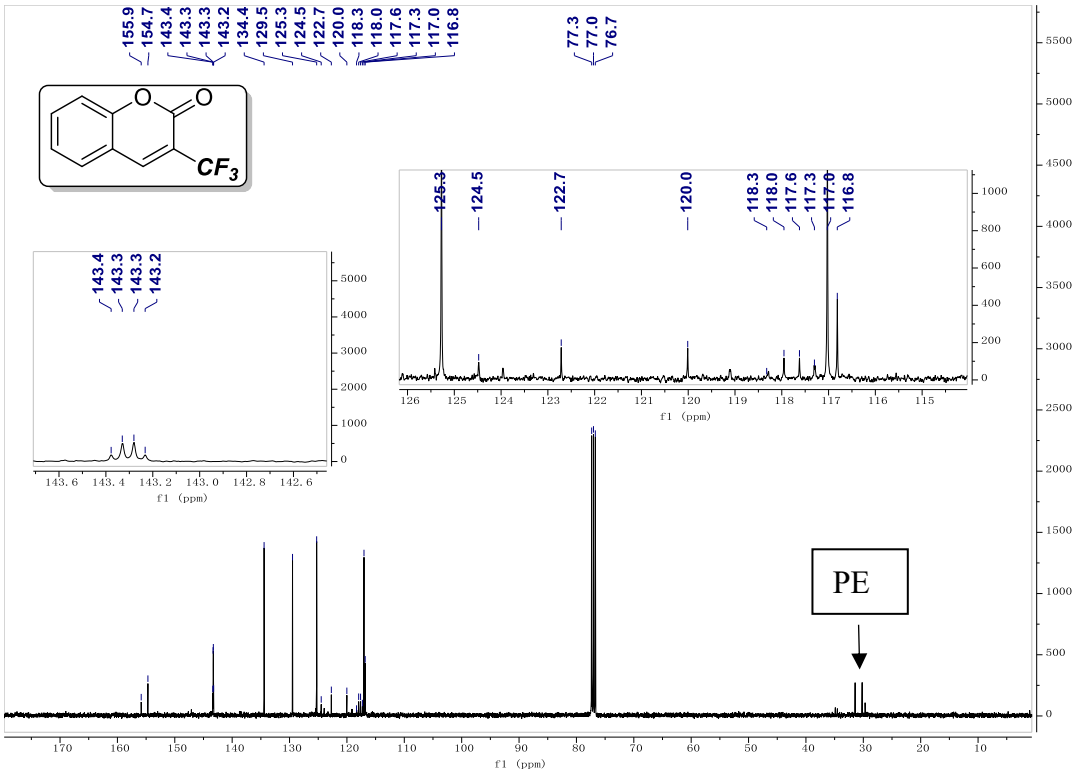
^{19}F NMR (376 MHz) Spectrum of **7j** in $CDCl_3$



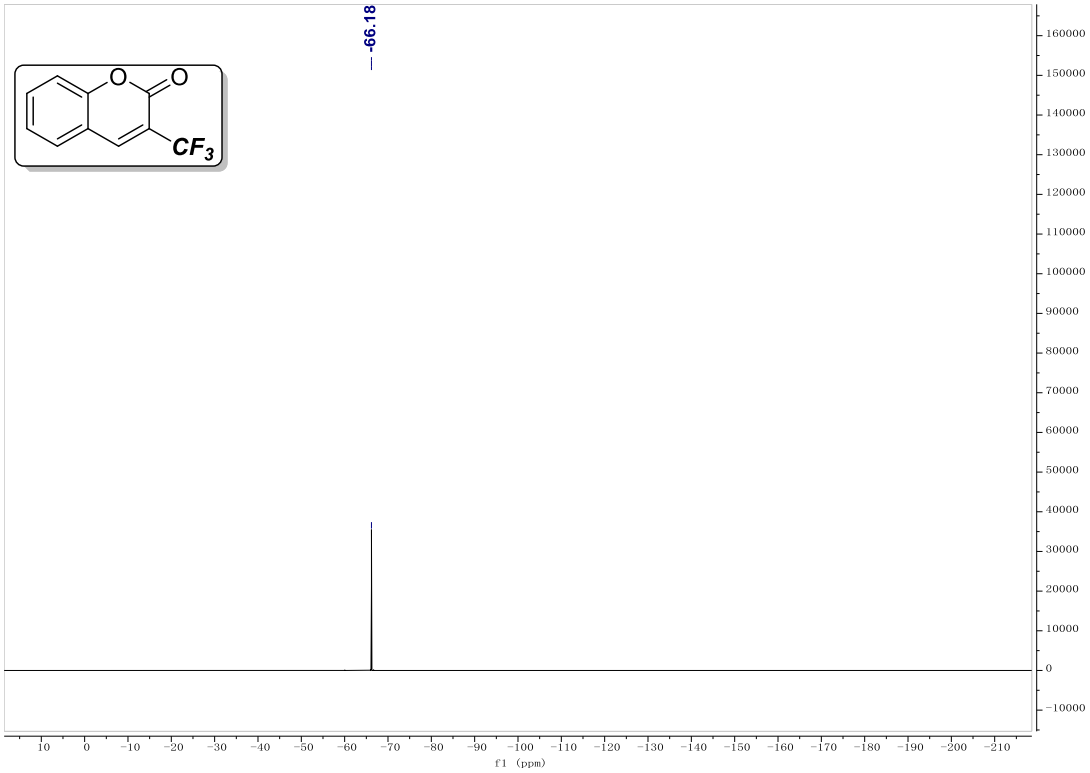
^{1}H NMR (400 MHz) Spectrum of **7k** in $CDCl_3$



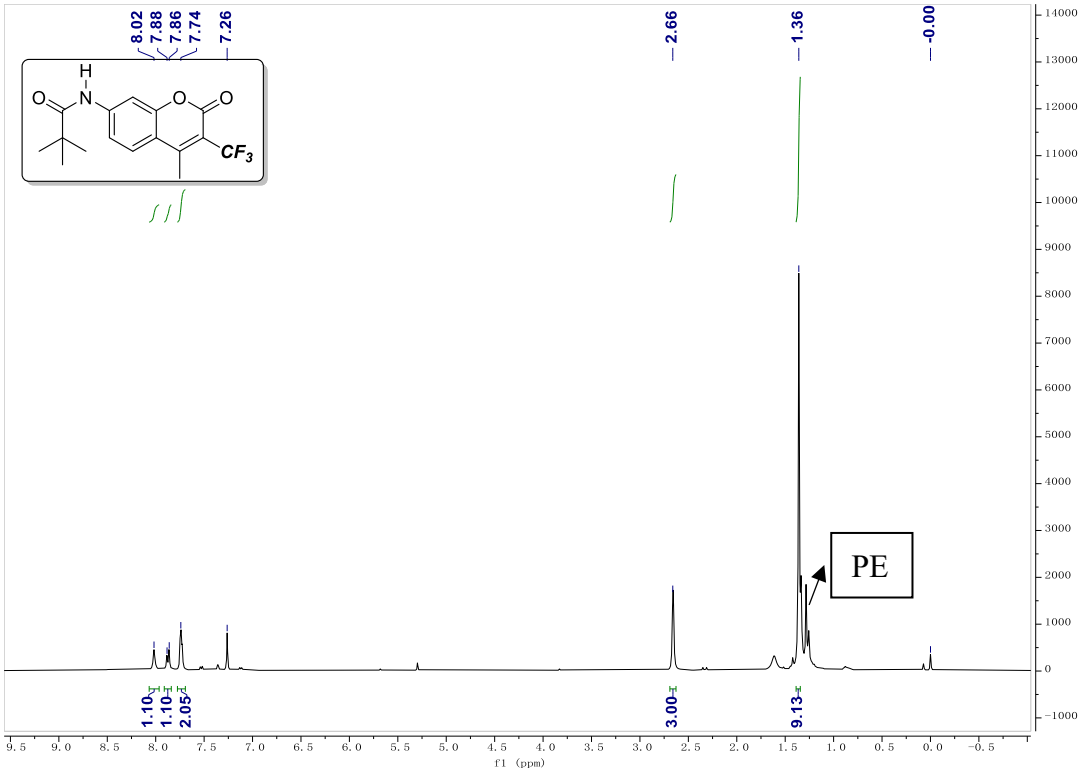
^{13}C NMR (100 MHz) Spectrum of **7k** in $CDCl_3$



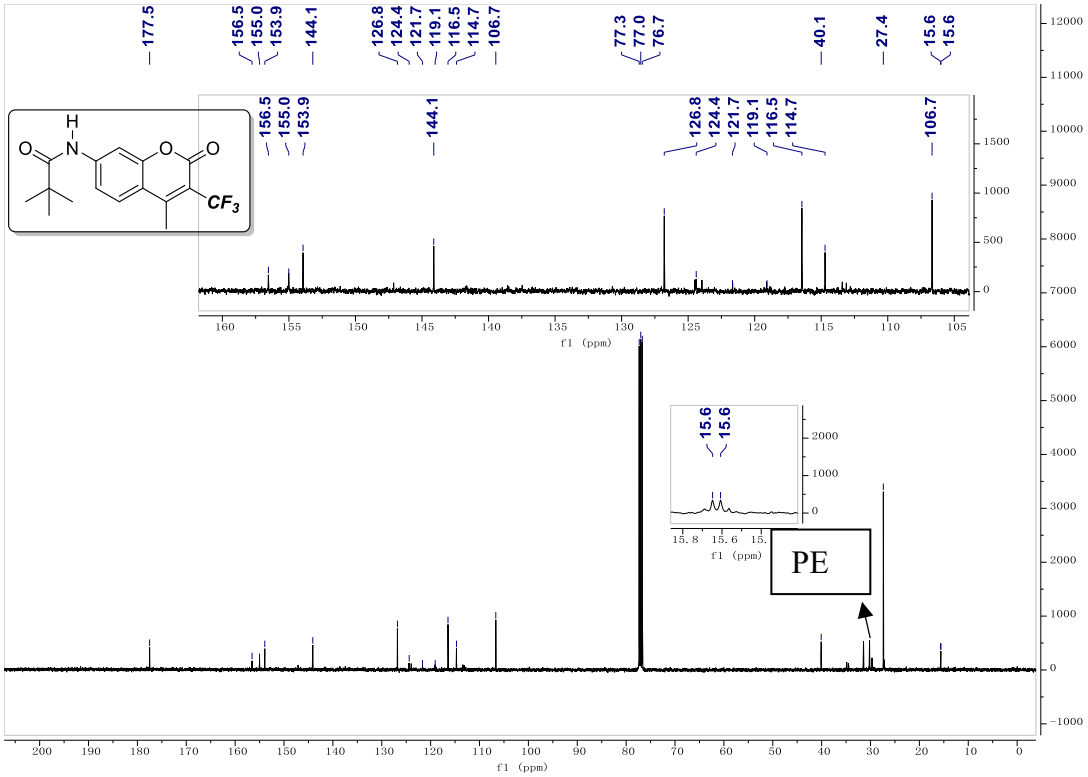
^{19}F NMR (376 MHz) Spectrum of **7k** in $CDCl_3$



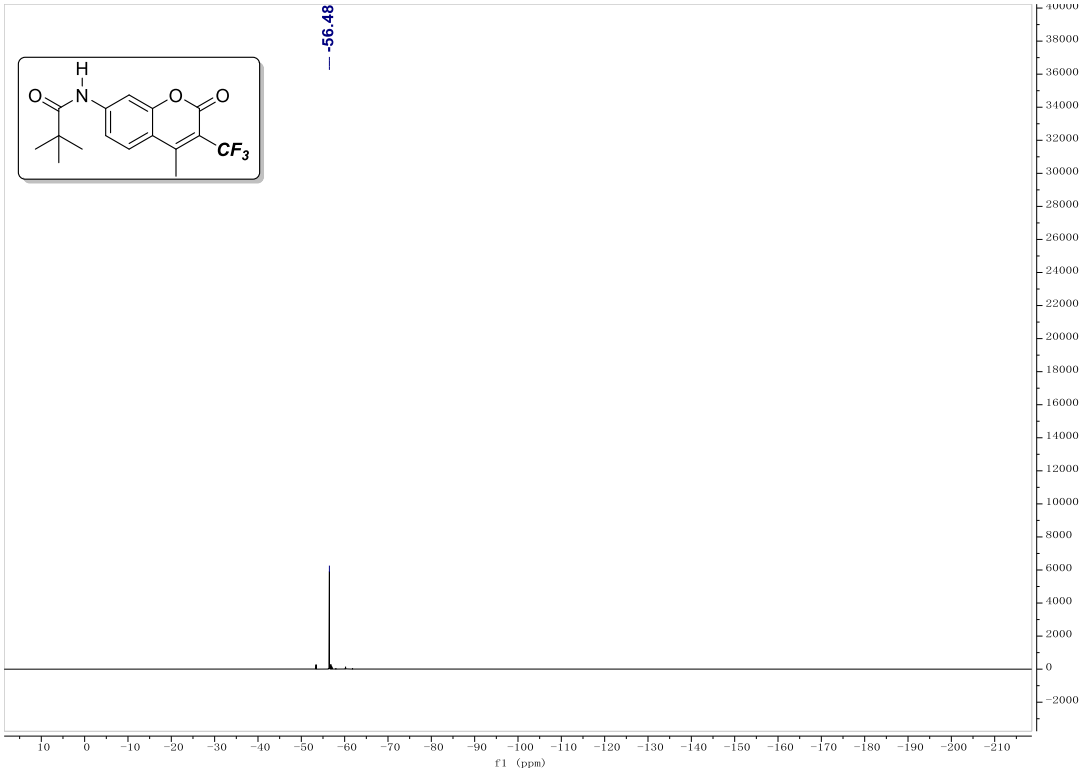
^{1}H NMR (400 MHz) Spectrum of **7l** in $CDCl_3$



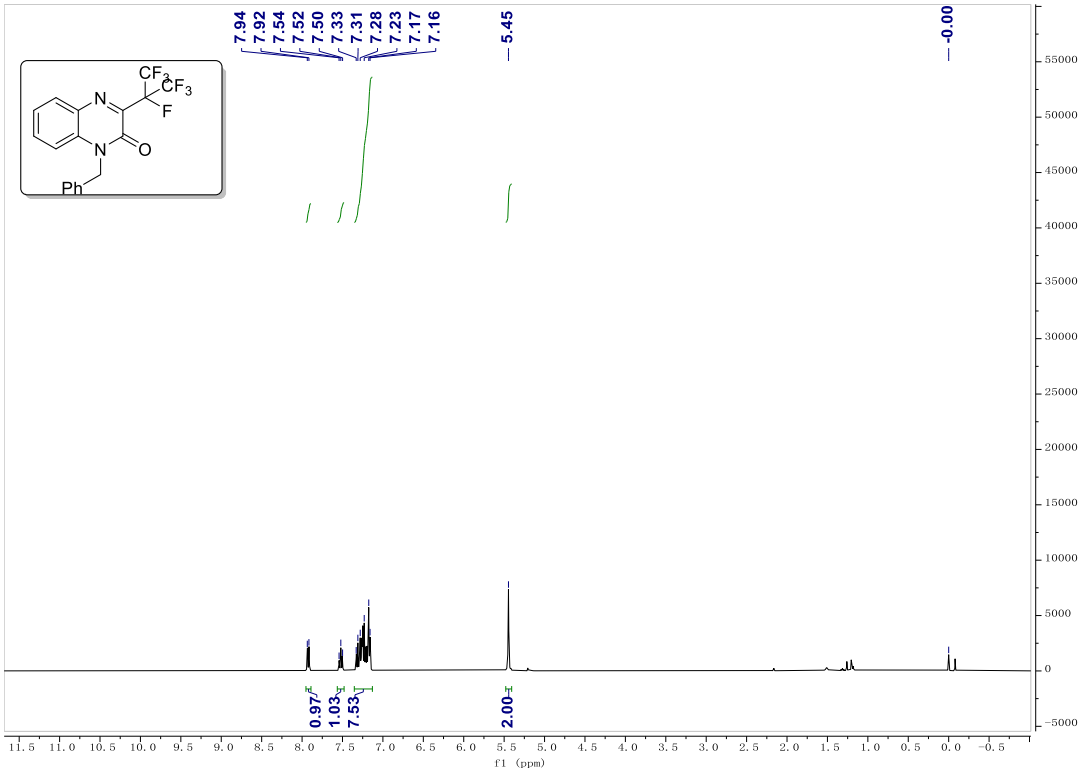
^{13}C NMR (100 MHz) Spectrum of **7l** in $CDCl_3$



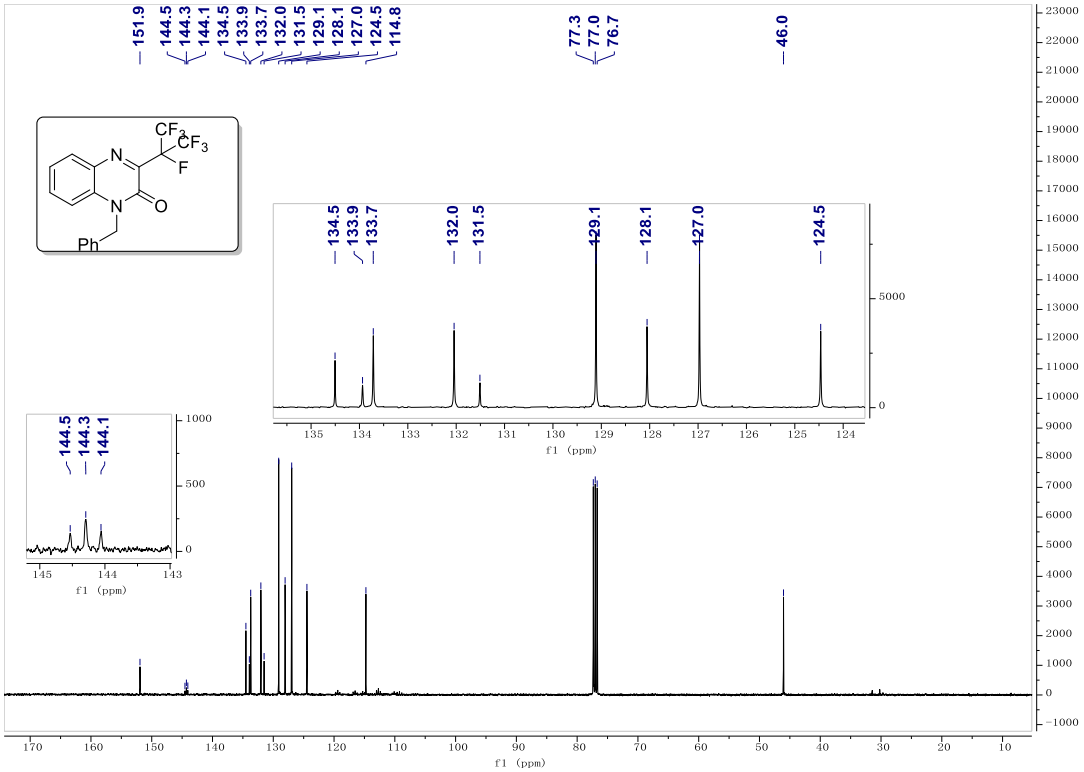
^{19}F NMR (376 MHz) Spectrum of **7l** in $CDCl_3$



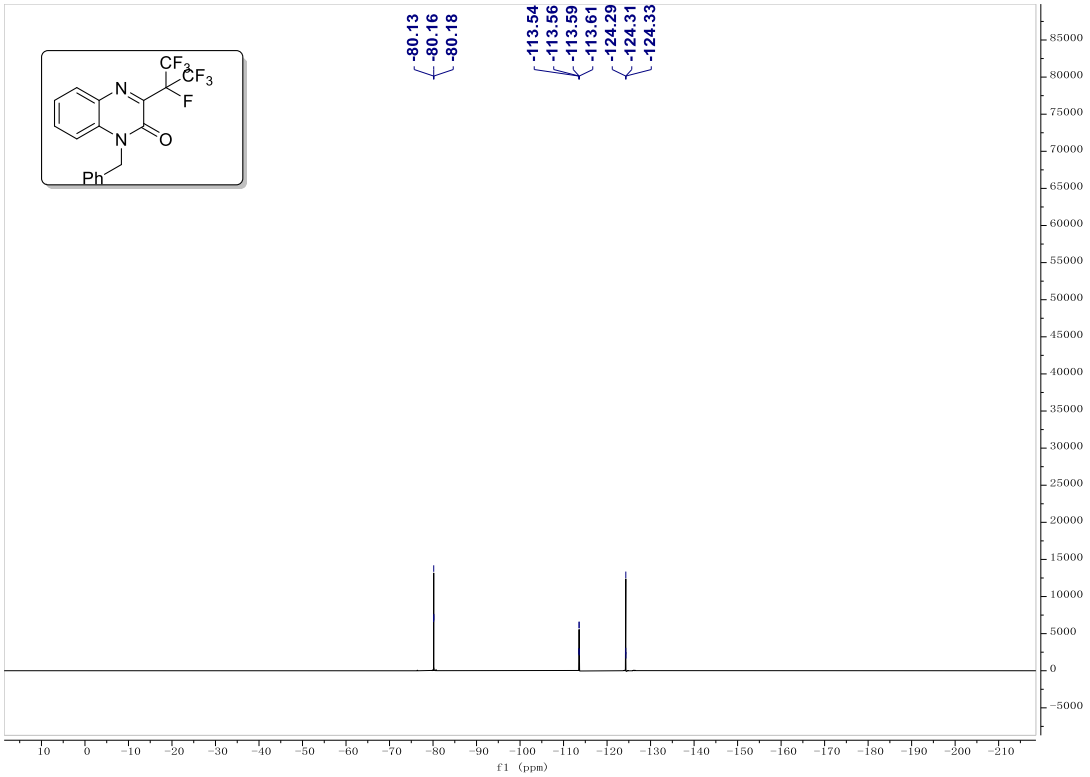
^{1}H NMR (400 MHz) Spectrum of **8a** in $CDCl_3$



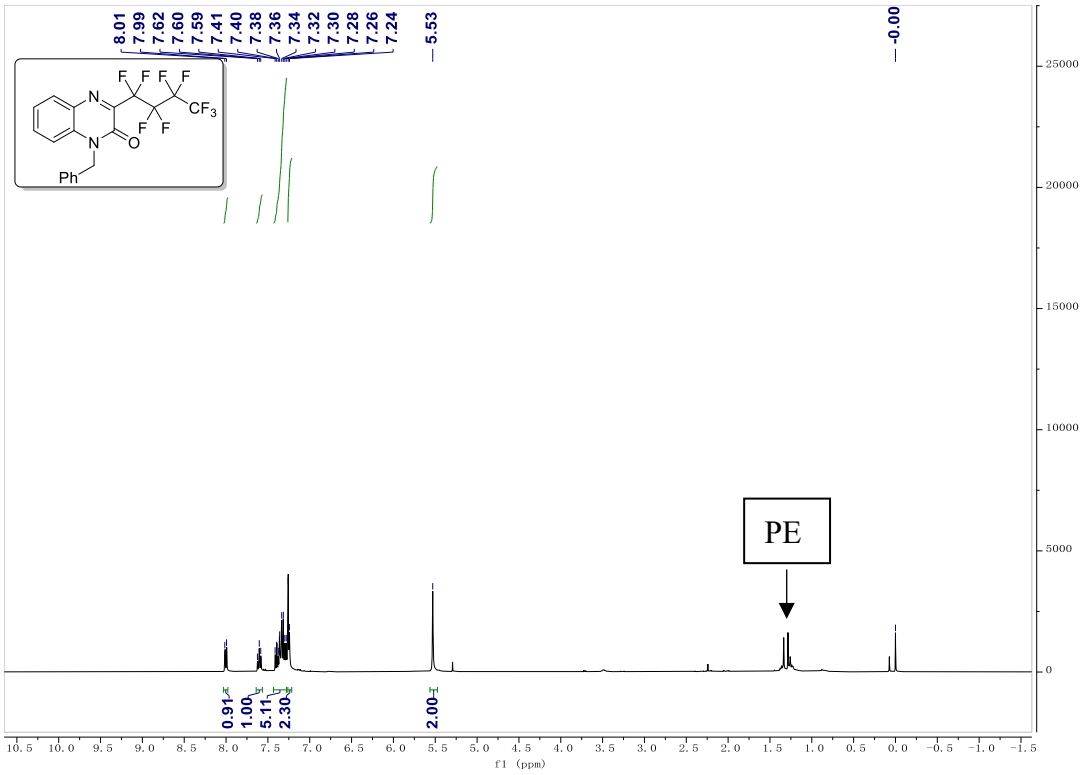
^{13}C NMR (100 MHz) Spectrum of **8a** in $CDCl_3$



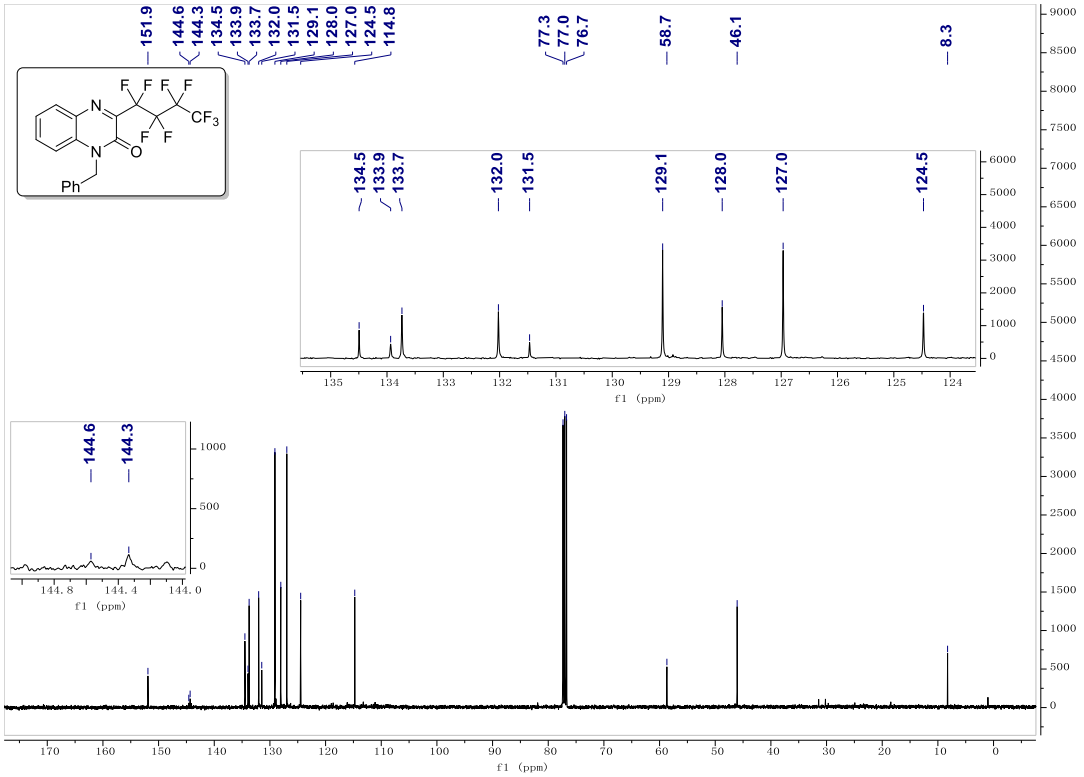
^{19}F NMR (376 MHz) Spectrum of **8a** in $CDCl_3$



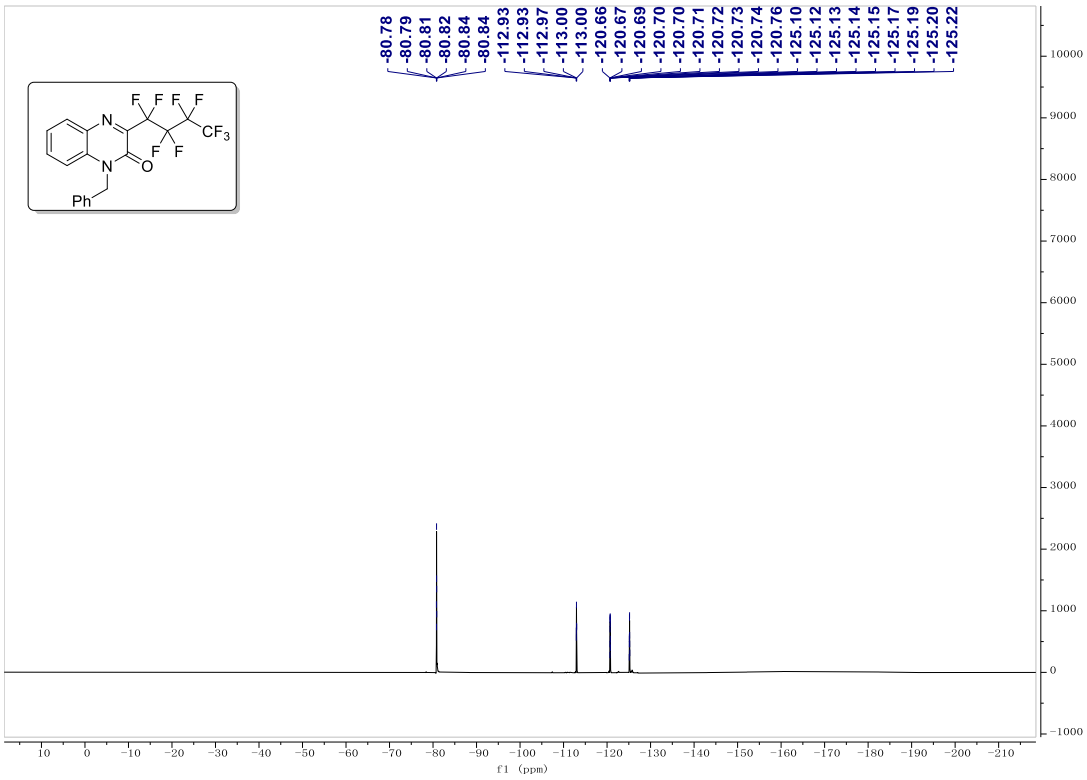
^{1}H NMR (400 MHz) Spectrum of **8b** in $CDCl_3$



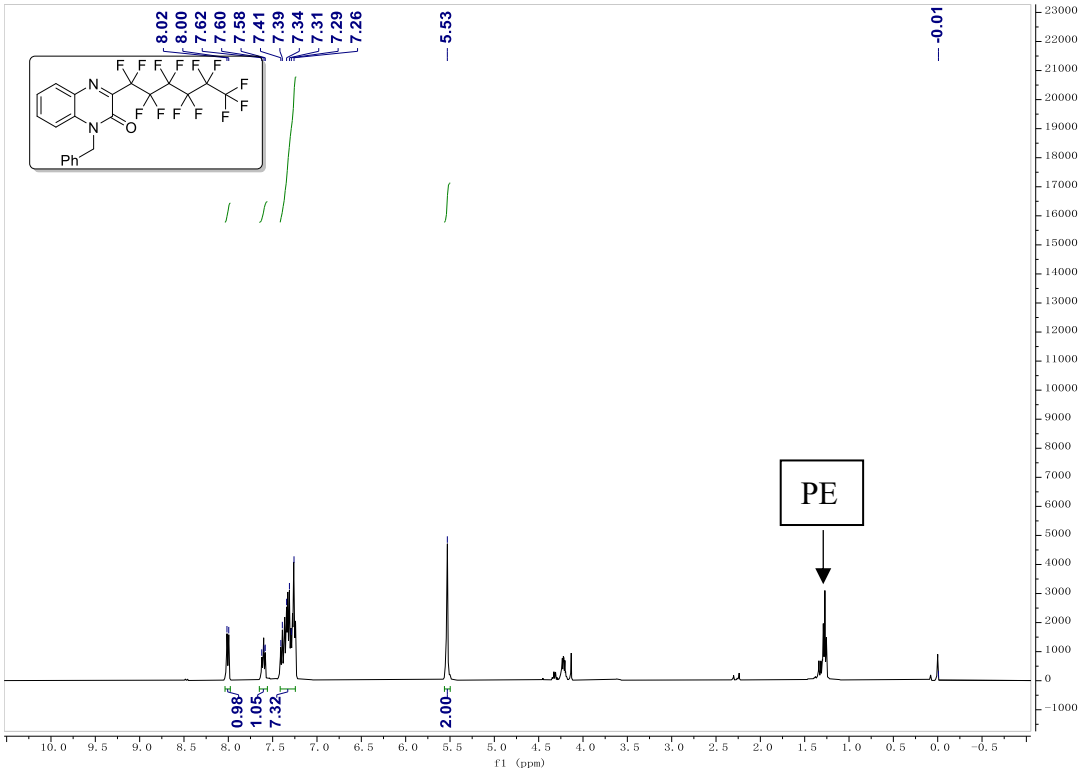
^{13}C NMR (100 MHz) Spectrum of **8b** in $CDCl_3$



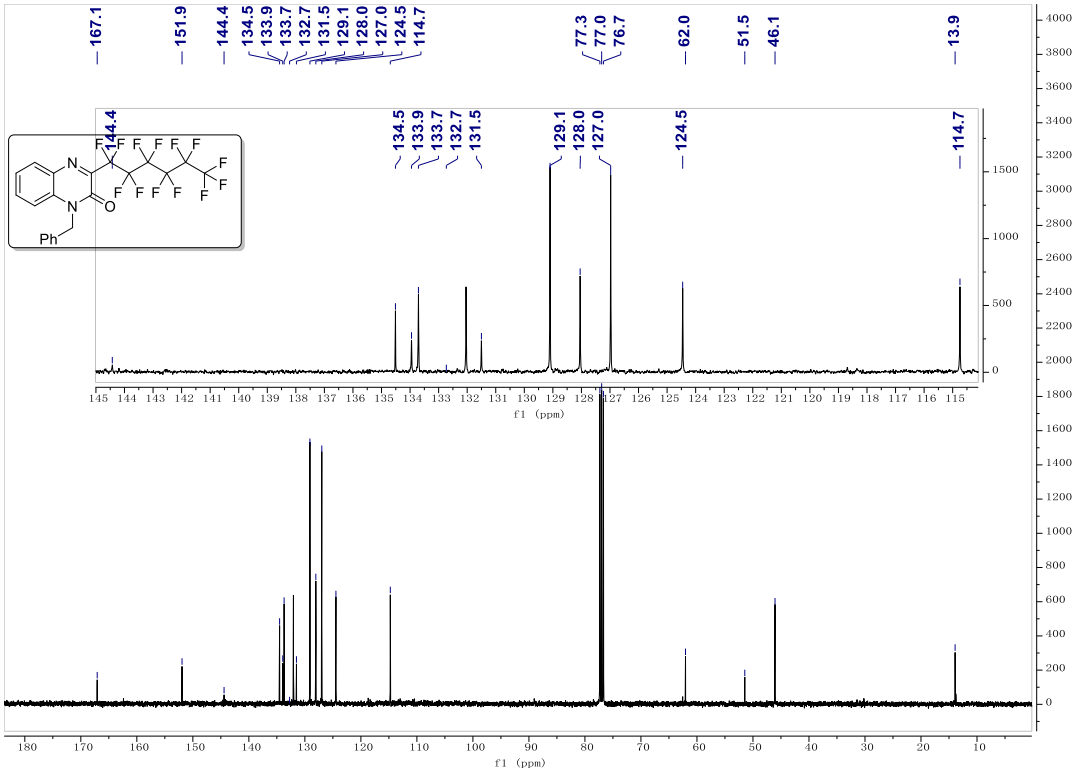
^{19}F NMR (376 MHz) Spectrum of **8b** in $CDCl_3$



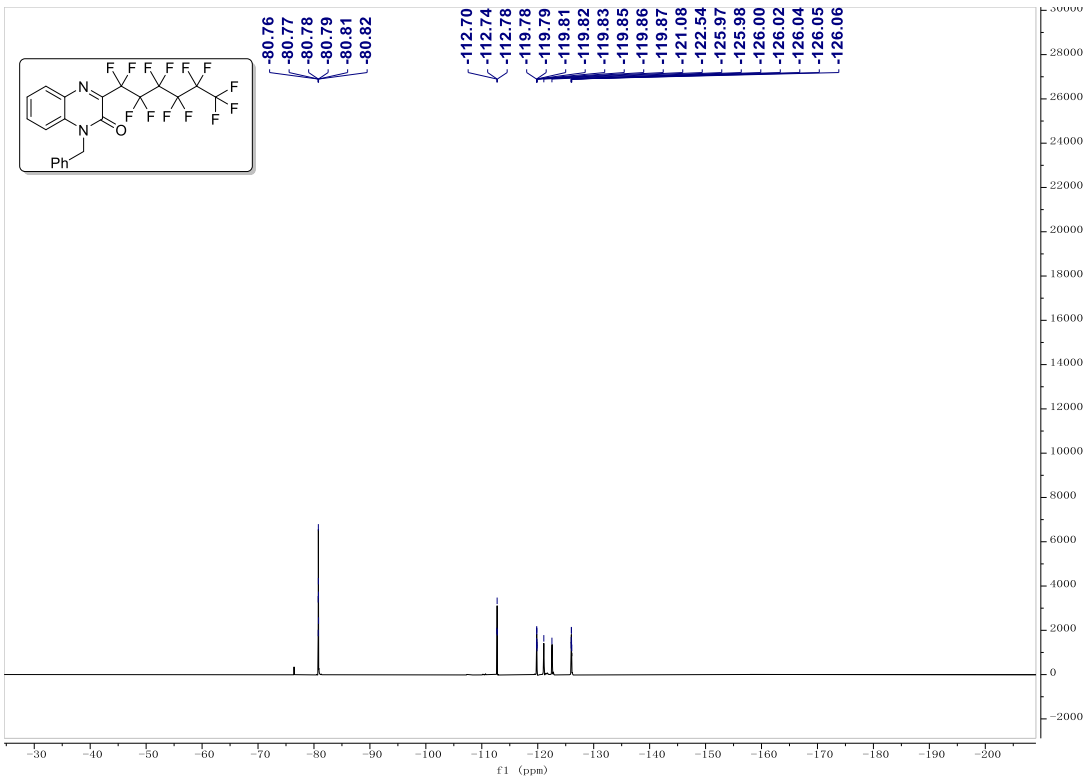
^{1}H NMR (400 MHz) Spectrum of **8c** in $CDCl_3$



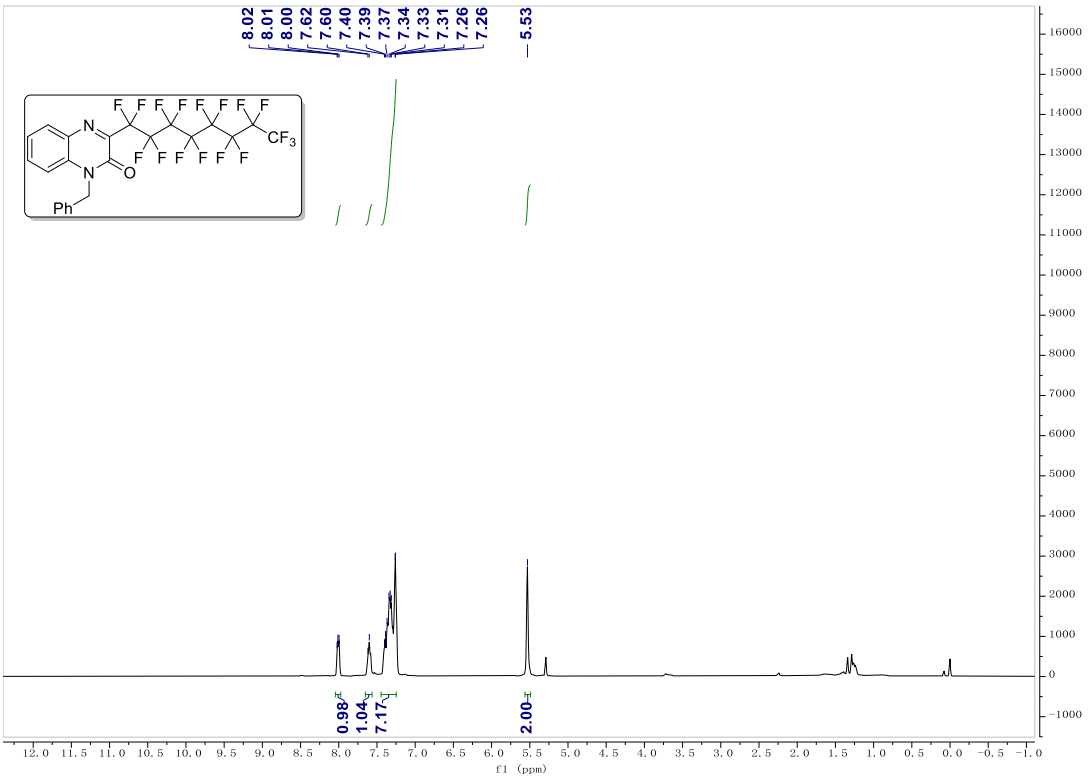
^{13}C NMR (100 MHz) Spectrum of **8c** in $CDCl_3$



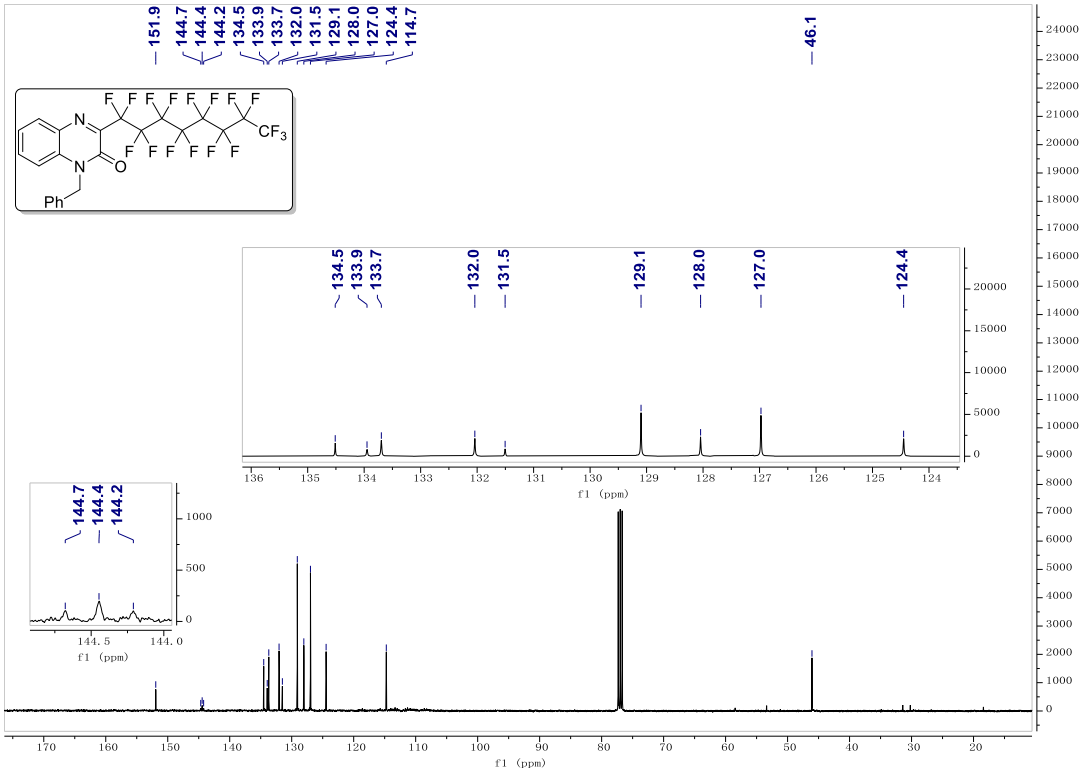
^{19}F NMR (376 MHz) Spectrum of **8c** in $CDCl_3$



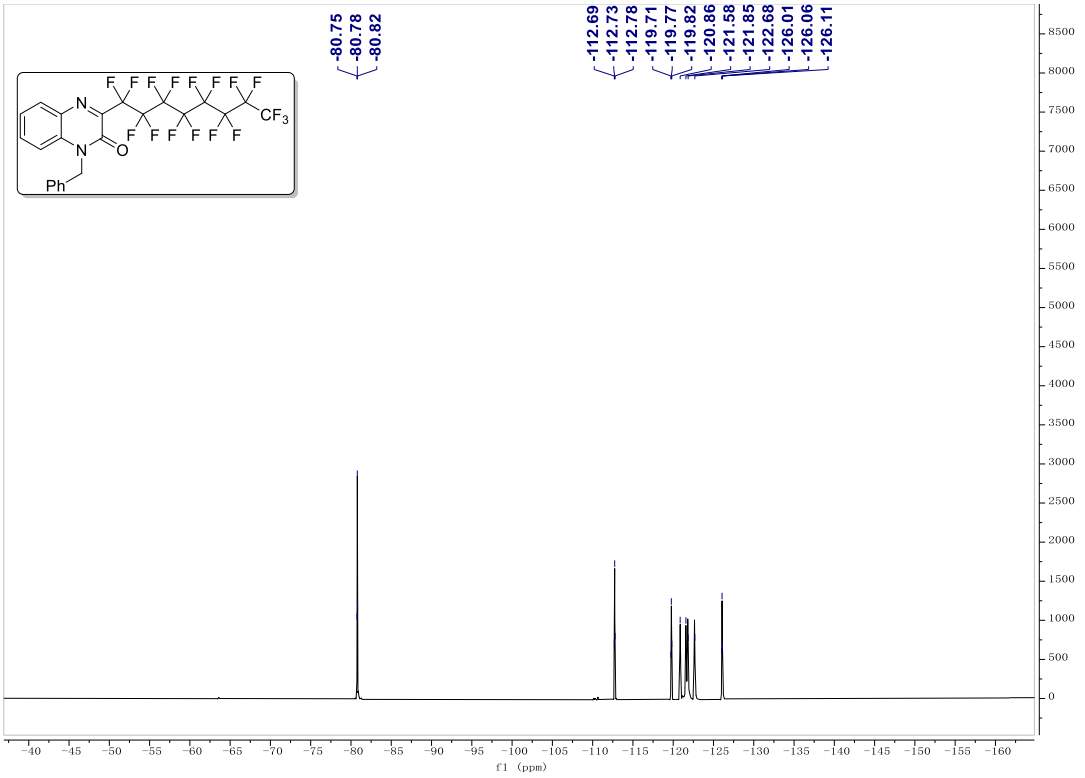
^{1}H NMR (400 MHz) Spectrum of **8d** in $CDCl_3$



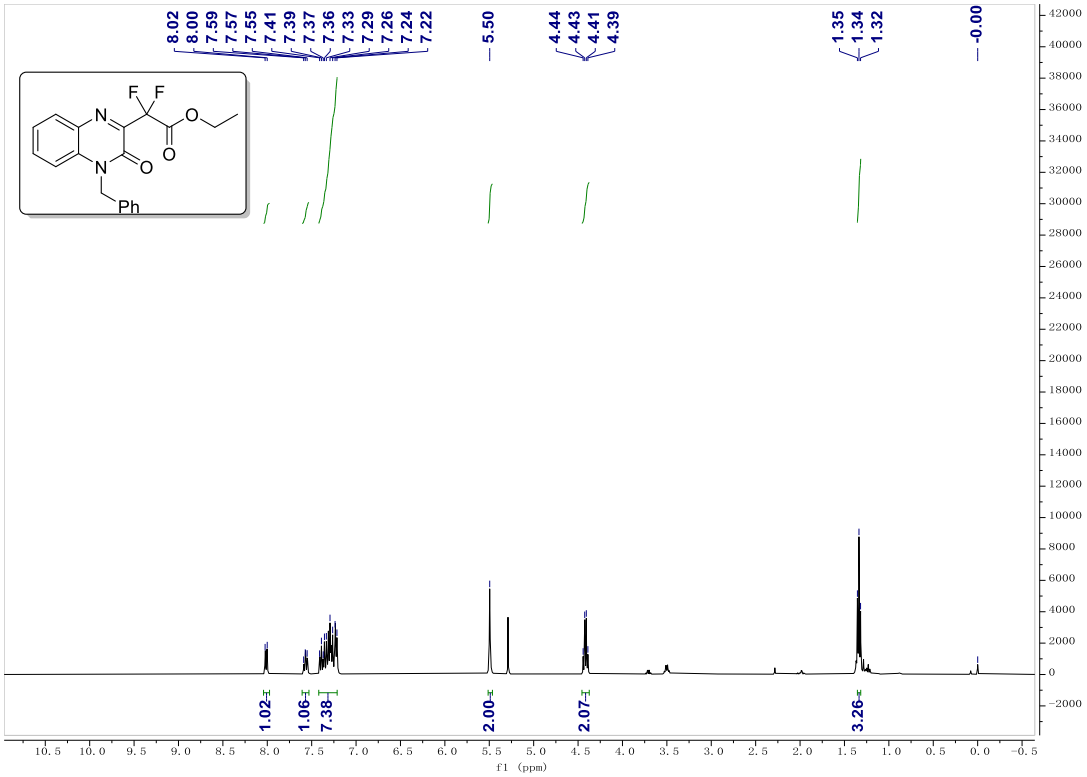
^{13}C NMR (100 MHz) Spectrum of **8d** in $CDCl_3$



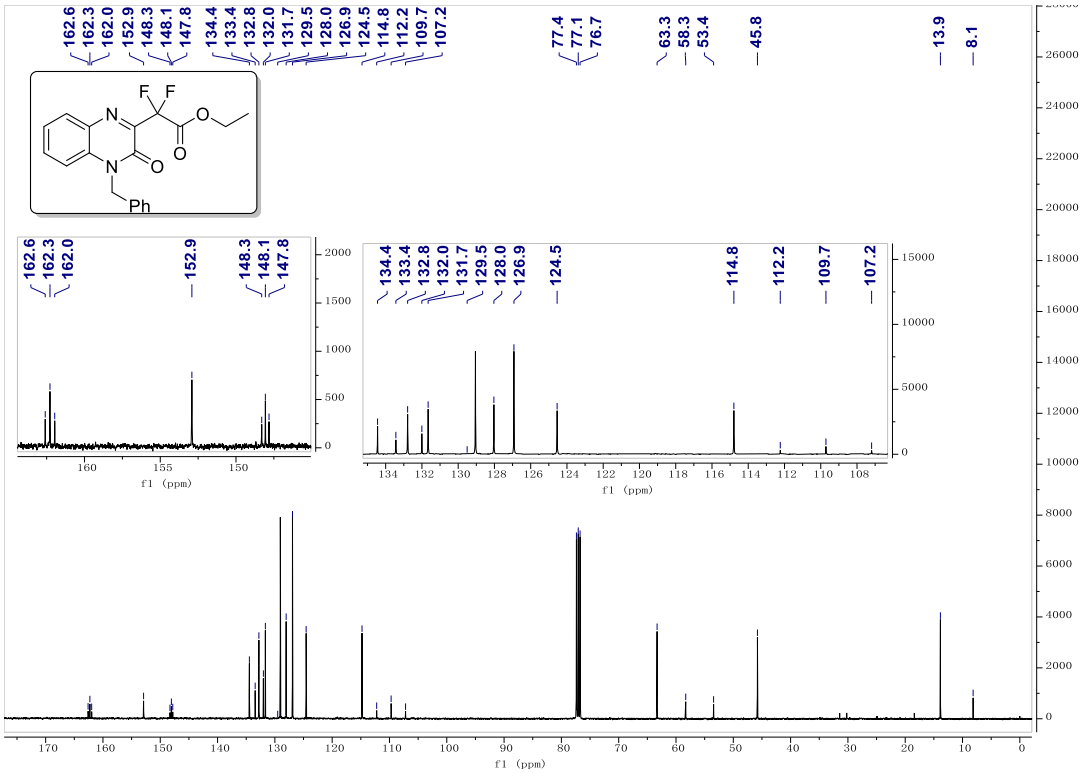
^{19}F NMR (376 MHz) Spectrum of **8d** in $CDCl_3$



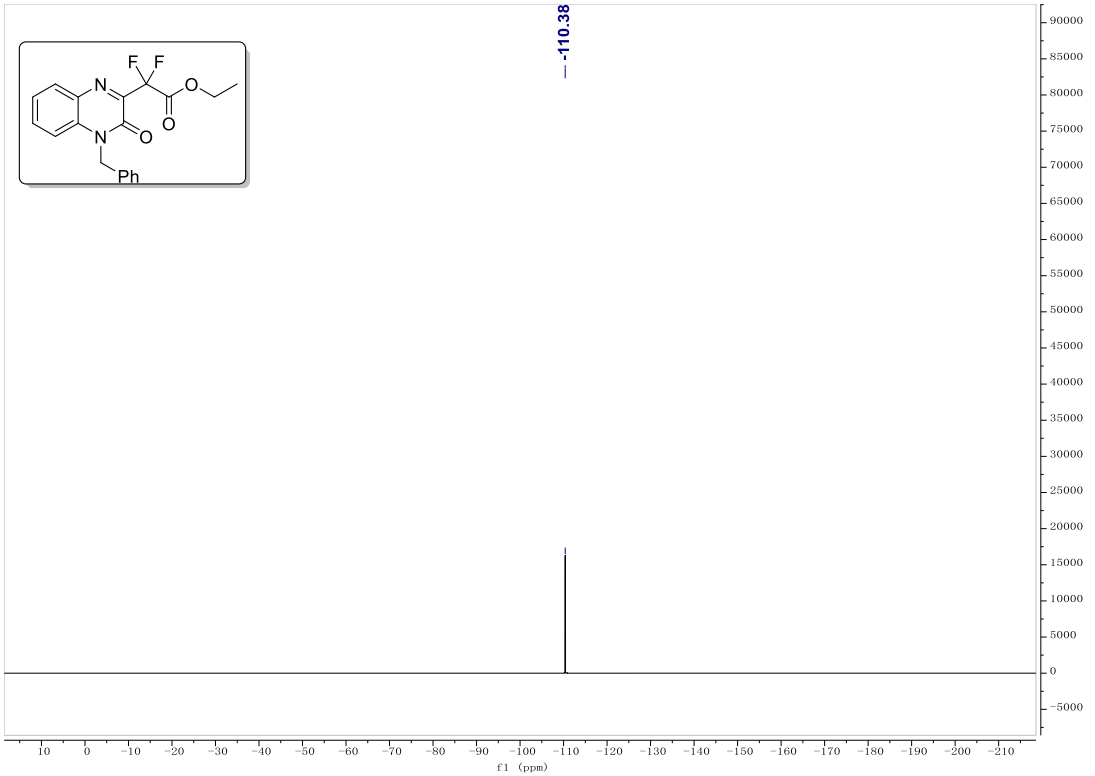
^{1}H NMR (400 MHz) Spectrum of **10** in $CDCl_3$

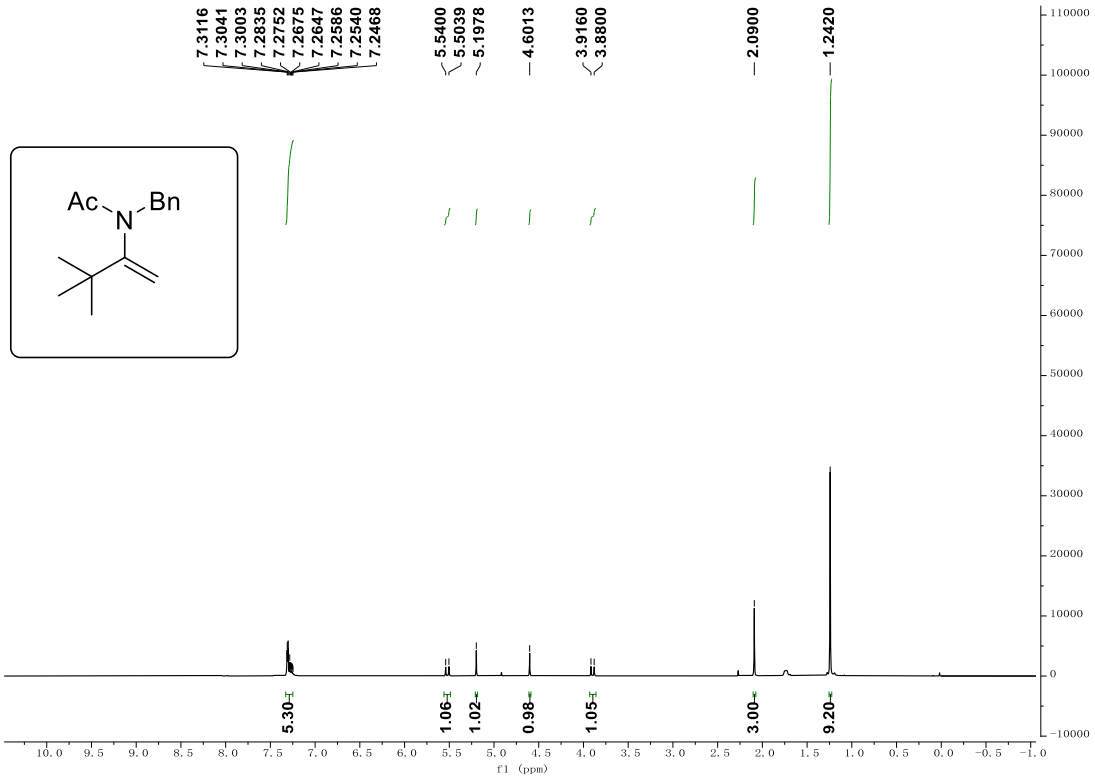


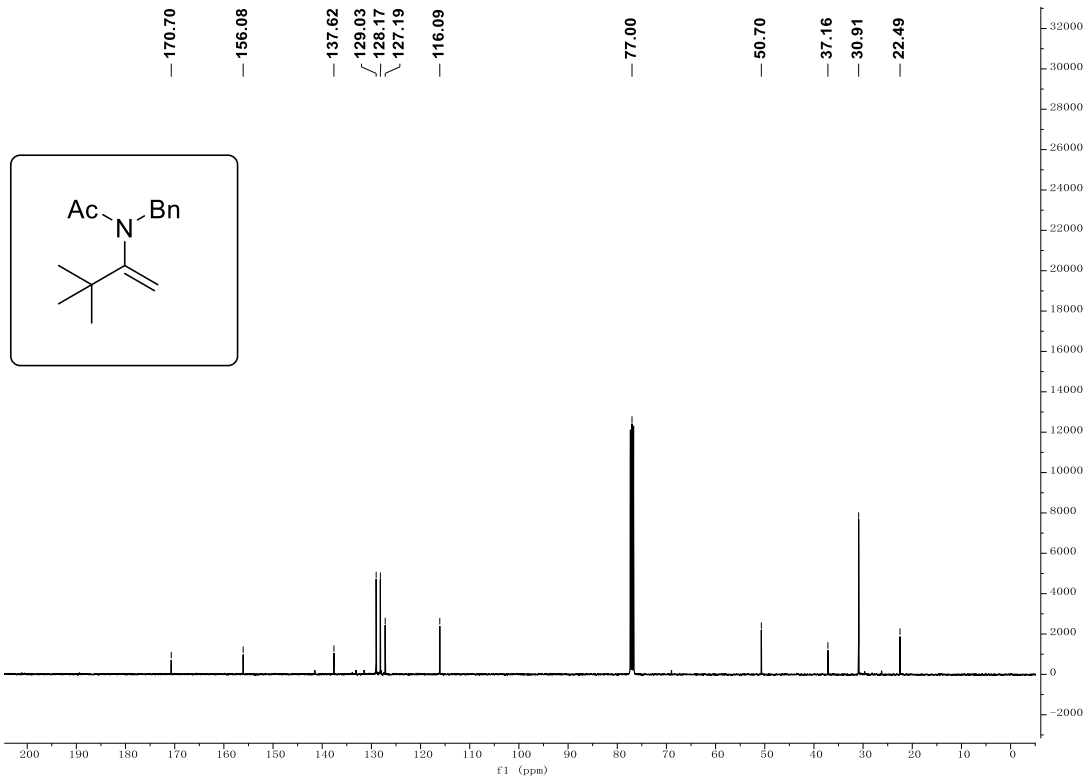
^{13}C NMR (100 MHz) Spectrum of **10** in $CDCl_3$



^{19}F NMR (376 MHz) Spectrum of **10** in $CDCl_3$


-110.38
F
F
N
O
O
N
O
Ph
f1 (ppm)


7.3116
7.3041
7.3003
7.2835
7.2752
7.2675
7.2647
7.2586
7.2540
7.2468
5.5400
5.5039
5.1978
4.6013
3.9160
3.8800
2.0900
1.2420
Ac
N
Bn
5.30
1.06
1.02
0.98
1.05
3.00
9.20
f1 (ppm)


170.70
156.08
137.62
129.03
128.17
127.19
116.09
77.00
50.70
37.16
30.91
22.49
Ac
N
Bn
f1 (ppm)