Supporting Information

Formal (4+2) cycloaddition of azoalkenes with trifluoromethylimidoyl sulfoxonium ylides: synthesis of trifluoromethyl pyridazine derivatives

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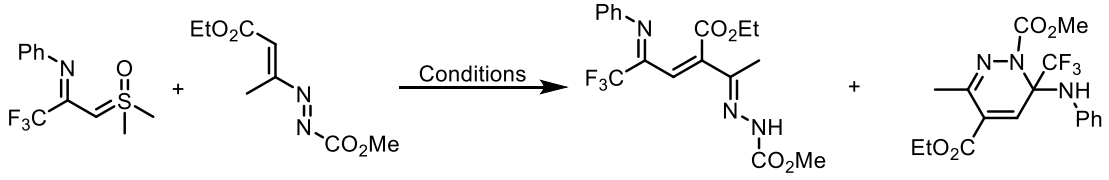
1. General information

Unless otherwise noted, all reactions were carried out under air. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 ℃) and ethyl acetate as eluent. Chemical shifts (δ, ppm) in the ^{1}H NMR spectra were recorded using TMS as internal standard or internally referenced to $CDCl_3$ (δ = 7.26 ppm), while the ^{13}C NMR spectra were internally $CDCl_3$ (δ = 77.16 ppm). All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. HRMS all data were obtained using ESI-TOF (Electrospray ionization-time of flight) or Waters GCT Premier mass spectrometerusing EI-TOF (electronionization-time of flight). The X-ray diffraction patterns was recorded on a Bruker D8 Venture (Ga) Single Crystal XRD system. All melting points were measured with the samples after column chromatography and uncorrected.

2. Optimization of the reaction conditions

Table S1. Optimization of direct (4+2) cycloaddition conditions[a]



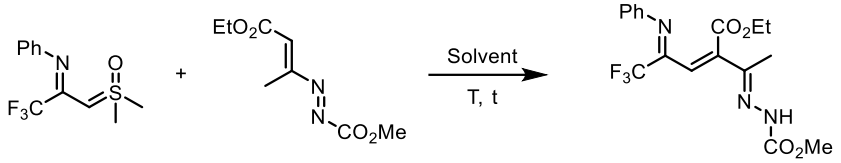
1a **2a** **3a** **4a**

Entry	Base	Solvent	Yield[b] (**3a**, %)	Yield (**4a**, %)
1	Na_2CO_3	DCM	21	ND
2	K_2CO_3	DCM	17	ND
3	Cs_2CO_3	THF	5	ND
4	KOH	THF	ND	ND
5	Et_3N	DCM	25	ND
6	DIPEA	DCM	23	ND

7	DMAP	DCM	16	ND
8	KOtBu	THF	12	ND
9	KHMDS	THF	7	ND
10	Et_3N	THF	22	ND
11	Et_3N	Toluene	26	ND
12	Et_3N	CCl_4	24	ND
13	Et_3N	DMSO	11	ND

[a] Reaction conditions: **1a** (0.025 mmol), **2a** (2.0 equiv.), base (3.0 equiv.), solvent (1.0 mL), 50 °C, under air for 24 h. [b] Yields based on ^1H NMR analysis using phenyltrimethylsilane as the internal standard.

Table S2. Optimization of conjugate addition reaction conditions [a]



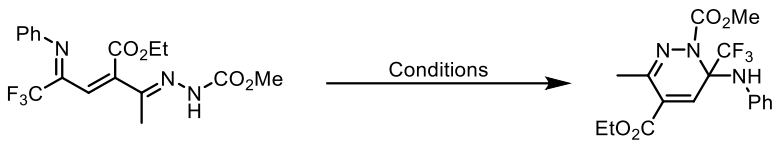
1a **2a** **3a**

Entry	Solvent	Time (h)	Temp. (°C)	Yield[b] (%)
1	Toluene	12	rt	60
2	Chlorobenzene	12	rt	29
3	Et_2O	12	rt	65
4	THF	12	rt	66
5	DCM	12	rt	74
6	DCE	12	rt	67
7	$CHCl_3$	12	rt	72
8	**CCl_4**	**12**	**rt**	**77(71)** [c]
9	EtOAc	12	rt	34
10	MeCN	12	rt	62
11	DMF	12	rt	59
12	DMSO	12	rt	25
13	MeOH	12	rt	47
14	HFIP	12	rt	72
15[d]	CCl_4	12	rt	48
16	CCl_4	36	10	30
17	CCl_4	8	50	35

[a] Reaction conditions: **1a** (0.025 mmol), **2a** (2.0 equiv.), solvent (1.0 mL), rt, under air.

[b] Yields based on ^{1}H NMR analysis using phenyltrimethylsilane as the internal standard. [c] Isolated yield in parentheses. [d] The reaction performed with **1a** (0.025 mmol), **2a** (1.5 equiv.).

Table S3. Optimization of intramolecular cyclization conditions[a]



3a **4a**

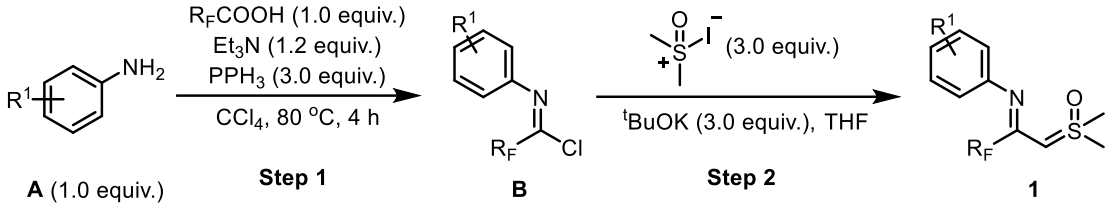
Entry	Base	Solvent	Temp (°C)	Yield[b] (%)
1	Na_2CO_3	Acetone	70	30
2	**Et_3N**	**CCl_4**	**70**	**65(56)** [c]
3	K_2CO_3	CCl_4	70	40
4	DIPEA	CCl_4	70	50
5	Et_3N	DMF	70	Mess
6	Et_3N	HFIP	70	Mess
7	Et_3N	MeCN	70	27
8	Et_3N	Acetone	70	54
9	Et_3N	Toluene	70	50
10	Et_3N	Chlorobenzene	70	61
11	Et_3N	Et_2O	70	58
12	Et_3N	THF	70	51
13	Et_3N	DCM	70	30
14	Et_3N	DCE	70	51

[a] Reaction conditions: **3a** (0.025 mmol), solvent (1.0 mL), base (3.0 equiv.), 70 °C, under air for 24 h. [b] Yields based on ^{1}H NMR analysis using phenyltrimethylsilane as the internal standard. [c] Isolated yield in parentheses.

3. Synthesis of the substrates and products

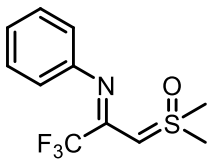
The imidoyl sulfoxonium ylides **1a-n**,[1] were synthesized according to the published procedures, the azoalkenes **2a-b**,[2] **2c**,[3] and **2d-g**,[2] were synthesized according to the published procedures.

General Procedure A: the preparation of imidoyl sulfoxonium ylides 2a-l



Step 1: To a solution of triphenylphosphine (60 mmol, 3.0 equiv.) in CCl_4 (100 mL), triethylamine (24 mmol, 1.2 equiv.) and fluorinated carboxylic acid (20 mmol, 1.0 equiv.) were added dropwise at 0 ℃. After stirring for 10 min at 0 ℃, aniline (20 mmol, 1.0 equiv.) was added. The mixture was refluxed on an oil bath for 4 h and then cooled at room temperature, and then filtered under reduced pressure. The filtrate was concentrated under vacuum, and the resulting residue was purified by flash chromatography on silica gel with petroleum ether.

Step 2: Trimethylsulfoxonium iodide (3.0 equiv.) was suspended in THF (150 mL) in a 250 mL round bottom flask. *t*-BuOK (3.0 equiv.) was added and the mixture was stirred at room temperature for 2 hours. After, fluorinated acetimidoyl chloride (1.0 equiv.) was added. The mixture was stirred at room temperature for 3 hours and then filtered through a plug of celite before all volatiles were removed under vacuum. Purification by flash chromatography (PE/EA = 3:1) afforded products.

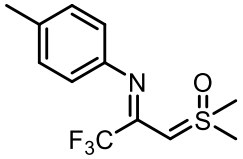


1a

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (1a) was prepared from aniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 59% yield (3.1 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 2H), 4.10 (s, 1H), 3.44 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63.

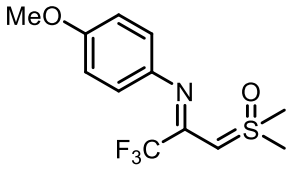


1b

(*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*p*-tolyl)propan-2-imine (1b) was prepared from *p*-toluidine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 63% yield (3.5 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 7.4 Hz, 2H), 4.08 (s, 1H), 3.43 (s, 6H), 2.30 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.58.

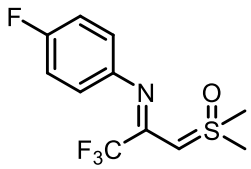


1c

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-methoxyphenyl)propan-2-imine (1c) was prepared from 4-methoxyaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 66% yield (3.9 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.70 (m, 4H), 4.08 (s, 1H), 3.78 (s, 3H), 3.43 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56.



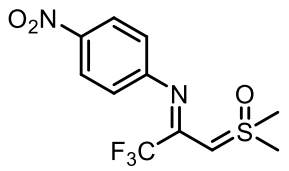
1d

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-fluorophenyl)propan-2-imine (1d) was prepared from 4-fluoroaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as

colorless crystal in 56% yield (3.1 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (t, *J* = 7.8 Hz, 2H), 6.74 (t, *J* = 7.6 Hz, 2H), 4.15 (s, 1H), 3.46 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56, -75.61.

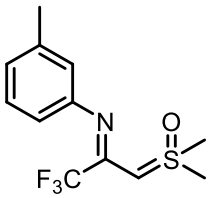


1e

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-nitrophenyl)propan-2-imine (1e) was prepared from 4-nitroaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 51% yield (3.1 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.31 (s, 1H), 3.51 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.27.

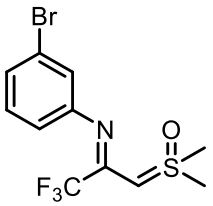


1f

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*m*-tolyl)propan-2-imine (1f) was prepared from *m*-toluidine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 64% yield (3.5 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.67 – 6.58 (m, 2H), 4.09 (s, 1H), 3.44 (s, 6H), 2.31 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63.

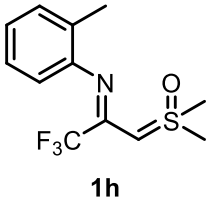


1g

(*E*)-*N*-(3-bromophenyl)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine (1g) was prepared from 3-bromoaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 41% yield (2.8 g, 2 steps).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, *J* = 3.6 Hz, 2H), 6.96 (s, 1H), 6.72 (t, *J* = 3.2 Hz, 1H), 4.15 (s, 1H), 3.45 (s, 6H).

^{19}F NMR (376 MHz, CDCl$_3$) δ -62.65.

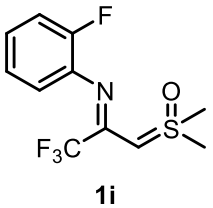


1h

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*o*-tolyl)propan-2-imine (1h) was prepared from *o*-toluidine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 59% yield (3.3 g, 2 steps).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.04 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.66 (s, 1H), 4.11 (s, 1H), 3.49 (s, 6H), 2.12 (s, 3H).

^{19}F NMR (376 MHz, CDCl$_3$) δ -64.33.

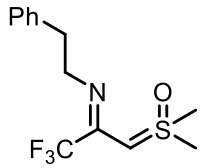


1i

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(2-fluorophenyl)propan-2-imine (1i) was prepared from 2-fluoroaniline and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 44% yield (2.3 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.97 (m, 2H), 6.96 – 6.91 (m, 1H), 6.87 (t, *J* = 8.0 Hz, 1H), 4.21 (s, 1H), 3.52 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.93.

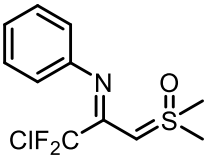


1j

(*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenethylpropan-2-imine (2j) was prepared from 2-phenylethan-1-amine and 2,2,2-trifluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 46% yield (2.7 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.17 (m, 5H), 3.86 (s, 1H), 3.78 (t, *J* = 7.2 Hz, 2H), 3.19 (s, 6H), 2.92 (t, *J* = 6.8 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.93.

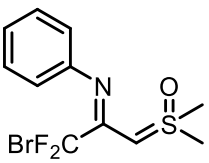


1k

(*Z*)-1-chloro-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1-difluoro-*N*-phenylpropan-2-imine (1k) was prepared from aniline and 2-chloro-2,2-difluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 42% yield (2.3 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.2 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 4.08 (s, 1H), 3.42 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -51.20.



1l

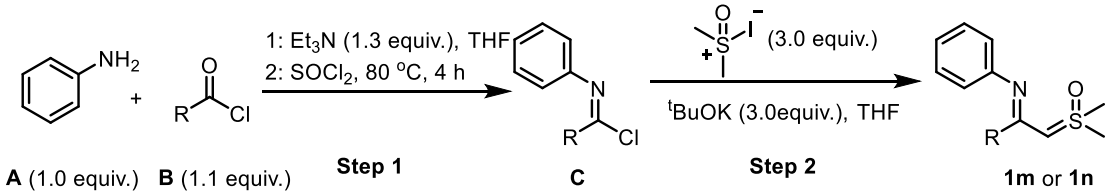
(*Z*)-1-bromo-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1-difluoro-*N*-phenylpropan-

2-imine (1l) was prepared from aniline and 2-bromo-2,2-difluoroacetic acid according to the General Procedure A (eluent: PE/EA = 3:1) as colorless crystal in 48% yield (3.1 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 4.03 (s, 1H), 3.41 (s, 6H).

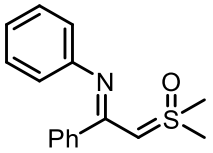
^{19}F NMR (376 MHz, $CDCl_3$) δ -47.19.

General Procedure B: the preparation of imidoyl sulfoxonium ylides 2m and 2n.



Step 1: To a dry round-bottom flask containing aniline solution (20 mmol, 1 equiv.) in THF (100 mL) and triethylamine (26 mmol, 1.3 equiv.) at 0 ℃ was added the acyl chloride substrates (22 mmol, 1.1 equiv.) dropwise. The reaction mixture was increased to room temperature, and stirred for 12 h. The resulting mixture was filtered to remove NH_4Cl salt, and the solvent was evaporated. The resulting solid was washed with hexane to obtain the *N*-phenylbenzamide or *N*-phenylpivalamide in quantitative yield. *N*-phenylbenzamide or *N*-phenylpivalamide (1.0 equiv.) was then added to a flask coupled to a reflux system. This substrate was dissolved in thionyl chloride (10 mL) and heated in a preheated oil bath at 80 ℃ for 4 h. At the end of the reaction, the thionyl chloride was evaporated and the resulting mixture was washed with hexane, filtered, and concentrated on a rotary evaporator. The *N*-phenylbenzimidoyl chloride or *N*-phenylpivalimidoyl chloride obtained was then used directly in the next step without further purification.

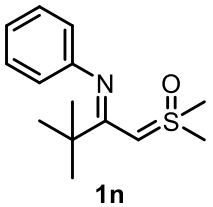
Step 2: Trimethylsulfoxonium iodide (3.0 equiv.) was suspended in THF (100 mL) in a 250 mL round bottom flask, *t*-BuOK (3.0 equiv.) was added and the mixture was stirred at room temperature for 2 hours. After, fluorinated acetimidoyl chloride (1.0 equiv.) was added. The mixture was stirred at room temperature for 3 hours and then filtered through a plug of celite before all volatiles were removed under vacuum. Purification by flash chromatography (PE/EA = 3:1) afforded products.



1m

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-*N*,1-diphenylethan-1-imine (1m) was prepared from aniline and benzoyl chloride according to the General Procedure B (eluent: PE/EA = 3:1) as colorless crystal in 42% yield (2.3 g, 2 steps).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 (s, 5H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 2H), 3.87 (s, 1H), 3.55 (s, 6H).

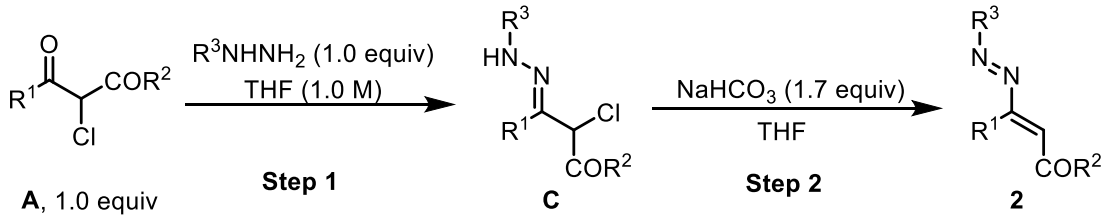


1n

(*E*)-1-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,3-dimethyl-*N*-phenylbutan-2-imine (1n) was prepared from aniline and pivaloyl chloride according to the General Procedure B (eluent: PE/EA = 3:1) as colorless crystal in 38% yield (1.9 g, 2 steps).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 – 7.16 (m, 2H), 6.88 (tt, *J* = 7.6, 1.4 Hz, 1H), 6.75 – 6.72 (m, 2H), 3.75 (s, 1H), 3.25 (s, 6H), 1.14 (s, 9H).

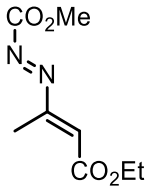
General procedure C: the preparation of azoalkenes 2a-g



Step 1: To a stirred solution of **A** (20 mmol, 1.0 equiv.) in dry THF (100 mL, 1.0 M) was added hydrazine (20 mmol, 1.0 equiv.). After that, the suspension was stirred at room temperature under N_2 for 48 h; the solid was filtered and washed with petroleum ether to give **C**.

Step 2: To a suspension of hydrazone **C** (1.0 equiv.) in THF (20 mL) was added a 1 N sodium bicarbonate solution (1.7 equiv.). After stirring at room temperature for 45 min, the red organic phase was separated and dried over anhydrous magnesium sulfate.

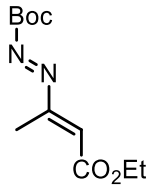
The mixture was evaporated under reduced pressure and purified by column chromatography (PE/EA = 10:1) to afford the pure product **2** as a bright red liquid.



2a

Methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (2a) was prepared from ethyl 2-chloro-3-oxobutanoate and methyl hydrazinecarboxylate according to the General Procedure C (eluent: PE/EA = 10:1) as red liquid in 78% yield (3.1 g, 2 steps).

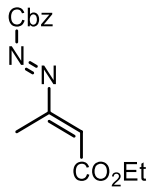
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.05 (s, 3H), 2.26 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).



2b

***Tert*-butyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (2b)** was prepared from ethyl 2-chloro-3-oxobutanoate and *tert*-butyl hydrazinecarboxylate according to the General Procedure C (eluent: PE/EA = 10:1) as red liquid in 71% yield (3.4 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.63 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H).

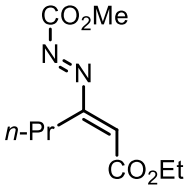


2c

Benzyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (2c) was

prepared from ethyl 2-chloro-3-oxobutanoate and benzyl hydrazinecarboxylate according to the General Procedure C (eluent: PE/EA = 10:1) as red liquid in 62% yield (3.4 g, 2 steps).

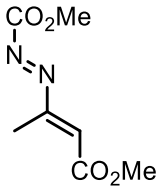
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 5H), 6.97 (s, 1H), 5.43 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).



2d

Methyl (*E*)-2-((*E*)-1-ethoxy-1-oxohex-2-en-3-yl)diazene-1-carboxylate (2d) was prepared from ethyl 2-chloro-3-oxohexanoate and methyl hydrazinecarboxylate according to the General Procedure C (eluent: PE/EA = 10:1) as red liquid in 21% yield (957.6 mg, 2 steps).

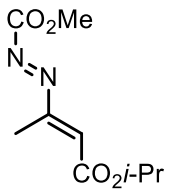
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.22 (t, *J* = 7.8 Hz, 2H), 1.28 – 1.25 (m, 5H), 0.88 (t, *J* = 6.6 Hz, 3H).



2e

Methyl (*E*)-2-((*E*)-4-methoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (2e) was prepared from methyl 2-chloro-3-oxobutanoate and methyl hydrazinecarboxylate according to the General Procedure C (eluent: PE/EA = 10:1) as red liquid in 54% yield (2.0 g, 2 steps).

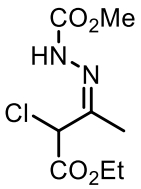
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 4.05 (s, 3H), 3.85 (s, 3H), 2.26 (s, 3H).



2f

Methyl (*E*)-2-((*E*)-4-isopropoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (2f) was prepared from isopropyl 2-chloro-3-oxobutanoate and methyl hydrazinecarboxylate according to the General Procedure C (eluent: PE/EA = 10:1) as red liquid in 55% yield (2.4 g, 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 5.19 – 5.13 (m, 1H), 4.05 (s, 3H), 2.24 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H).

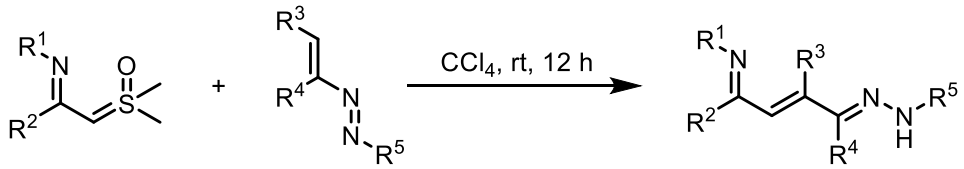


2g

Methyl (*Z*)-2-(3-chloro-4-ethoxy-4-oxobutan-2-ylidene)hydrazine-1-carboxylate (2g) was prepared from ethyl 2-chloro-3-oxobutanoate and methyl hydrazinecarboxylate according to the General Procedure C Step 1 (eluent: PE/EA = 3:1) as white solid in 89% yield (4.2 g).

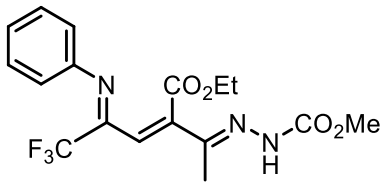
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 5.12 (s, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 1.94 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H).

General Procedure D



1 **2** **3**

To a stirred solution of imidoyl sulfoxonium ylides **1** (0.3 mmol, 1 equiv.), 1,2-diaza-1,3-dienes **2** (0.6 mmol, 2 equiv.) in CCl_4 (3 mL) and the reaction mixture was stirred at room temperature for 12 h, which was monitored by TLC. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3**.



3a

Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3a) was prepared as pale yellow solid from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 71% yield (82 mg).

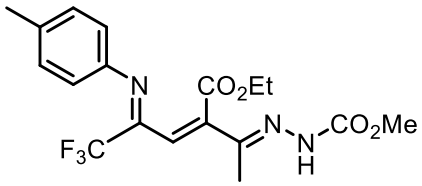
Mp: 100-101 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.48 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.86 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 154.1 (q, $J_{C\text{-}F}$ = 39.0 Hz), 146.8, 144.9, 141.7, 129.1 (2C), 128.7, 126.8, 125.6, 120.8 (2C), 116.1 (q, $J_{C\text{-}F}$ = 302.2 Hz), 62.4, 53.4, 13.8, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.32.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}F_3N_3NaO_4$ 408.1142, found: 408.1149.



3b

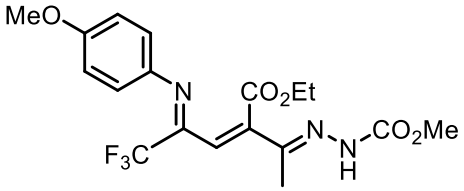
Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(*p*-tolylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3b) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*p*-tolyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 63% yield (75 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 2.33 (s, 3H), 1.89 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 153.3 (q, J_{C-F} = 36.9 Hz), 145.1, 144.1, 141.6, 137.0, 129.7 (2C), 129.3, 126.0, 121.3 (2C), 119.3 (q, J_{C-F} = 267.3 Hz), 62.3, 53.3, 21.2, 13.8, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.10.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_4$ 399.1406, found 399.1404.



3c

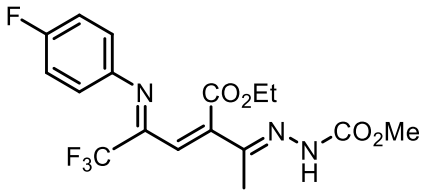
Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((4-methoxyphenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3c) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-methoxyphenyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 53% yield (66 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 9.2 Hz, 2H), 6.49 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.79 (s, 3H), 1.92 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.0, 152.0 (q, J_{C-F} = 34.6 Hz), 145.3, 141.6, 139.5, 125.9, 123.8 (2C), 120.4, 119.4 (q, J_{C-F} = 276.9 Hz), 114.3 (2C), 62.2, 55.5, 53.3, 13.8, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.84.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_5$ 415.1355, found 415.1357



3d

Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((4-fluorophenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3d) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-fluorophenyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-

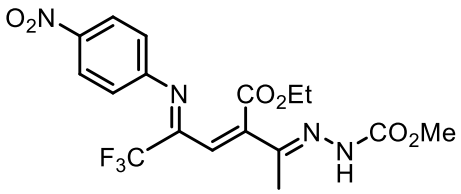
en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 60% yield (73 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.02 – 7.00 (m, 4H), 6.44 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.90 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 161.4 (d, $J_{C\text{-}F}$ = 245.4 Hz), 154.1 (q, $J_{C\text{-}F}$ = 35.7 Hz), 144.7, 142.6, 141.9, 125.4, 122.9 (d, $J_{C\text{-}F}$ = 8.4 Hz, 2C), 119.0 (q, $J_{C\text{-}F}$ = 277.3 Hz), 119.3 (d, $J_{C\text{-}F}$ = 19.3 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.7 Hz, 2C), 62.3, 53.2, 13.7, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.39, -115.25.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}F_4N_3NaO_4$ 426.1047, found 426.1055.



3e

Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((4-nitrophenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3e) was prepared as pale yellow solid from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(4-nitrophenyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 43% yield (56 mg).

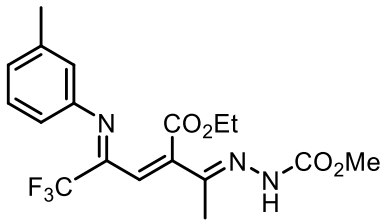
Mp: 108-109 ^{o}C**.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 6.97 (bs, 2H) , 6.46 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.92 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.8, 155.1 (q, $J_{C\text{-}F}$ = 34.6 Hz), 154.3, 152.7, 145.5, 144.6, 134.3, 124.9 (2C), 118.6 (q, $J_{C\text{-}F}$ = 299.9 Hz), 110.7 (2C), 62.3, 60.4, 53.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.85.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{17}H_{17}F_3N_4O_6$ 430.1100, found 430.1097.



3f

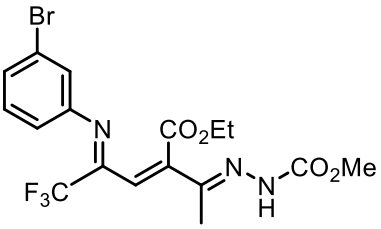
Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(*m*-tolylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3f) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*m*-tolyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 72% yield (86 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.78 (s, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.44 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.31 (s, 3H), 1.87 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 153.8 (q, $J_{C\text{-}F}$ = 36.3 Hz), 146.6, 144.9, 141.3, 138.9, 128.8, 128.4, 127.4, 126.0, 121.5, 118.0 (q, $J_{C\text{-}F}$ = 287.3 Hz), 117.5, 62.2, 53.2, 21.3, 13.7, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.29.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}F_3N_3NaO_4$ 422.1298, found 422.1305.



3g

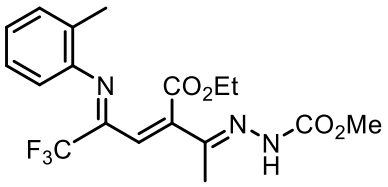
Methyl (*E*)-2-((3*Z*,5*Z*)-5-((3-bromophenyl)imino)-3-(ethoxycarbonyl)-6,6,6-trifluorohex-3-en-2-ylidene)hydrazine-1-carboxylate (3g) was prepared as pale yellow oil from (*E*)-*N*-(3-bromophenyl)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoropropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 54% yield (75 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.88 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 155.5 (q, $J_{C\text{-}F}$ = 36.3 Hz), 148.1, 144.7, 142.4, 130.5, 130.2, 129.4, 125.1, 123.6, 122.7, 118.9 (q, $J_{C\text{-}F}$ = 277.6 Hz), 118.9, 62.5, 53.4, 13.9, 13.7

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.64.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{17}H_{17}BrF_3N_3O_4$ 463.0355, found 463.0350.



3h

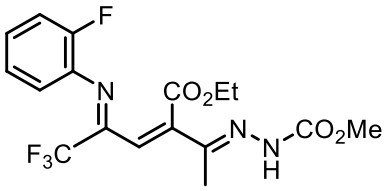
Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(*o*-tolylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3h) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*o*-tolyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 42% yield (50 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.20 (d, *J* = 6.0 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.77 (d, *J* = 6.0 Hz, 1H), 6.40 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.21 (s, 3H), 1.85 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 153.6 (q, $J_{C\text{-}F}$ = 34.7 Hz), 145.5, 145.2, 141.8, 130.8, 129.8, 126.6, 126.3, 125.9, 125.0, 119.1 (q, $J_{C\text{-}F}$ = 288.3 Hz), 118.7, 62.2, 53.6, 17.6, 13.8, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.80.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_4$ 399.1406, found: 399.1404.



3i

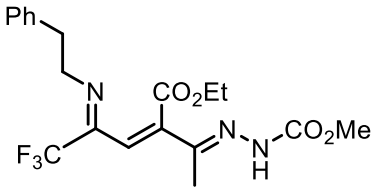
Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((2-fluorophenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3i) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(2-fluorophenyl)propan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 61% yield (77 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.15 – 7.05 (m, 3H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.48 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 1.87 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 157.7 (q, $J_{C\text{-}F}$ = 36.1 Hz), 151.6 (d, $J_{C\text{-}F}$ = 249.0 Hz), 144.9, 142.0, 134.4 (d, $J_{C\text{-}F}$ = 12.5 Hz), 127.9 (d, $J_{C\text{-}F}$ = 7.8 Hz), 124.5 (d, $J_{C\text{-}F}$ = 4.5 Hz), 124.1, 122.9, 118.9 (q, $J_{C\text{-}F}$ = 277.7 Hz), 116.4 (d, $J_{C\text{-}F}$ = 20.1 Hz), 115.8 (d, $J_{C\text{-}F}$ = 12.8 Hz), 62.3, 53.2, 13.7, 13.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.00, -123.42.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}F_4N_3NaO_4$ 426.1047, found: 426.1052.



3j

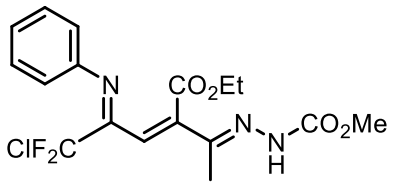
Methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenethylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3j) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenethylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 63% yield (78 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 5.82 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.79 – 3.75 (m, 5H), 2.97 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 154.6 (q, $J_{C\text{-}F}$ = 34.8 Hz), 145.0, 142.1, 139.1, 129.1 (2C), 128.8, 128.5 (2C), 126.4, 123.4, 118.9 (q, $J_{C\text{-}F}$ = 277.1 Hz), 62.0, 55.2, 53.2, 36.0, 13.7, 12.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.53.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}F_3N_3NaO_4$ 436.1455, found: 436.1462.



3k

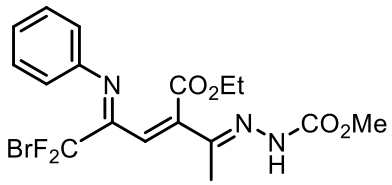
Methyl (*E*)-2-((3*Z*,5*Z*)-6-chloro-3-(ethoxycarbonyl)-6,6-difluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3k) was prepared as pale yellow oil from (*Z*)-1-chloro-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1-difluoro-*N*-phenylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 62% yield (75 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.58 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.86 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 156.7 (t, $J_{C\text{-}F}$ = 29.7 Hz), 146.6, 145.0, 141.6, 129.0 (2C), 126.5, 125.8, 122.9, 121.4 (t, $J_{C\text{-}F}$ = 276.2 Hz), 120.7 (2C), 62.2, 53.3, 13.8, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.53.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}ClF_2N_3O_4$ 401.0954, found: 401.0956.



3l

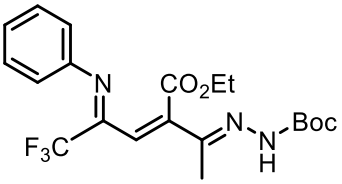
Methyl (*E*)-2-((3*Z*,5*Z*)-6-bromo-3-(ethoxycarbonyl)-6,6-difluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3l) was prepared as pale yellow oil from (*Z*)-1-bromo-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1-difluoro-*N*-phenylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 59% yield (79 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.59 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.87 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 157.6 (t, $J_{C\text{-}F}$ = 26.85 Hz), 146.4, 144.9, 141.5, 128.9 (2C), 128.5, 126.4, 125.5, 120.6 (2C), 118.3 (t, $J_{C\text{-}F}$ = 292.6 Hz), 62.1, 53.2, 13.7, 13.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -53.54.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}BrF_2N_3NaO_4$ 468.0341, found 468.0345.



3m

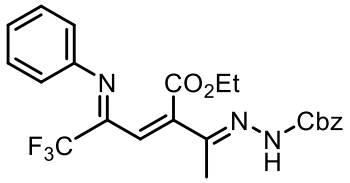
***Tert*-butyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3m)** was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (0.3 mmol) and *tert*-butyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 60% yield (77 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.48 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.85 (s, 3H), 1.49 (s, 9H), 1.29 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 154.3 (q, $J_{C\text{-}F}$ = 34.2 Hz), 146.8, 143.9, 141.9, 129.1 (2C), 128.7, 126.7, 125.0, 120.8 (2C), 120.6 (q, $J_{C\text{-}F}$= 256.4 Hz), 82.1, 62.3, 28.3 (3C), 14.5, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.38.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{20}H_{24}F_3N_3O_4$ 427.1719, found: 427.1721.



3n

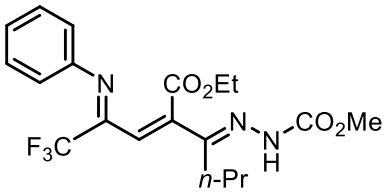
Benzyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3n) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (0.3 mmol) and benzyl (*E*)-2-((*E*)-4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 55% yield (76 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.38 – 7.30 (m, 7H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.49 (s, 1H), 5.23 (s, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.85 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 164.6, 153.7 (q, $J_{C\text{-}F}$ = 34.2 Hz), 146.7, 144.9, 141.8, 135.6, 129.1 (2C), 128.7 (2C), 128.6 (2C), 126.8, 125.6, 120.8 (2C), 119.1 (q, $J_{C\text{-}F}$ = 295.5 Hz), 68.0, 62.3, 14.3, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.36.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{23}H_{22}F_3N_3O_4$ 461.1562, found 461.1560.



3o

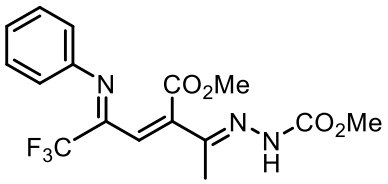
Methyl (*E*)-2-((4*Z*,6*Z*)-4-(ethoxycarbonyl)-7,7,7-trifluoro-6-(phenylimino)hept-4-en-3-ylidene)hydrazine-1-carboxylate (3o) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-1-ethoxy-1-oxohex-2-en-3-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 58% yield (70 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.38 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.24 (t, *J* = 8.0 Hz, 2H) ,1.32 – 1.26 (m, 5H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 154.6 (q, $J_{C\text{-}F}$ = 33.0 Hz), 147.1, 146.4, 141.2, 129.1 (2C), 126.6, 125.0, 123.3, 120.5 (2C), 116.2 (q, $J_{C\text{-}F}$ = 286.4 Hz), 62.3, 53.4, 28.6, 18.8, 14.0, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.26.

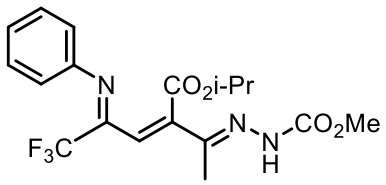
HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}F_3N_3NaO_4$ 436.1455, found: 436.1462.



3p

Methyl (*E*)-2-((3*Z*,5*Z*)-6,6,6-trifluoro-3-(methoxycarbonyl)-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3p) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-methoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 64% yield (71 mg).

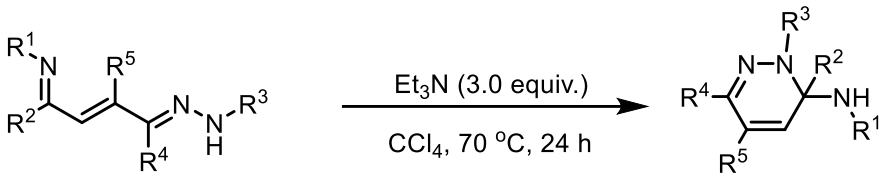
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.49 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 1.87 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0, 154.1 (t, $J_{C\text{-}F}$ = 35.25 Hz), 146.7, 144.8, 141.4, 129.1 (2C), 128.8, 126.9, 126.0, 120.8 (2C), 119.1 (t, $J_{C\text{-}F}$ = 277.2 Hz), 52.8, 29.8, 13.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -69.31.
HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{16}H_{16}F_3N_3O_4$ 371.1093, found: 371.1090.



3q

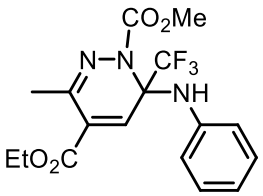
Methyl (*E*)-2-((3*Z*,5*Z*)-6,6,6-trifluoro-3-(isopropoxycarbonyl)-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (3q) was prepared as pale yellow oil from (*E*)-3-(dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine (0.3 mmol) and methyl (*E*)-2-((*E*)-4-isopropoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (0.6 mmol) according to the General Procedure D (12 h, eluent: PE/EA = 3:1) in 63% yield (75 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.40 (s, 1H), 5.09 (p, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 1.85 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 154.1 (q, $J_{C\text{-}F}$ = 34.9 Hz), 146.8, 145.0, 142.2, 129.1 (2C), 128.7, 126.8, 125.0, 120.8 (2C), 119.1 (q, $J_{C\text{-}F}$ = 296.8 Hz), 70.6, 53.3, 21.5 (2C), 13.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -69.12.
HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_4$ 399.1406, found: 399.1403.

General Procedure E



3 **4**

To a stirred solution of alkenyl imines **3** (0.3 mmol, 1.0 equiv.) in CCl_4 (3.0 mL) was added Et_3N (0.75 mmol, 3.0 equiv.) and the reaction mixture was stirred in a preheated oil bath at 70 °C, which was monitored by TLC. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 10:1) to afford the pure product **4**.



4a

4-Ethyl 1-methyl 3-methyl-6-(phenylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4a) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 56% yield (65 mg).

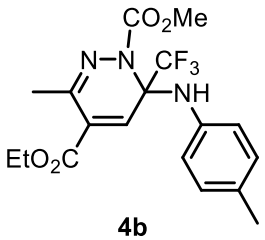
Mp: 133-134 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 6.77 (s, 1H), 5.75 (s, 1H), 4.35 – 4.23 (m, 2H), 3.81 (s, 3H), 2.32 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 154.6, 141.9, 139.8, 134.2, 129.4 (2C), 128.0, 123.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 122.8, 120.0 (2C), 74.1 (q, $J_{C\text{-}F}$ = 30.9 Hz), 62.2, 54.3, 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.87.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}F_3N_3NaO_4$ 408.1142, found: 408.1148.



4b

4-Ethyl 1-methyl 3-methyl-6-(p-tolylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4b) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(*p*-tolylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 53% yield (64 mg).

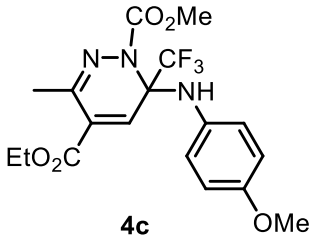
Mp: 136-137 ^{o}C

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.00 (d, *J* = 8.0 Hz, 2H), 6.76 – 6.74 (m, 3H), 5.70 (s, 1H), 4.34 – 4.23 (m, 2H), 3.83 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 163.1, 154.7, 139.8, 139.1, 134.3, 132.7, 129.9 (2C), 127.9, 123.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 120.8 (2C), 74.5 (q, $J_{C\text{-}F}$ = 31.6 Hz), 62.2, 54.3, 21.4, 20.7, 14.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -77.70.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}F_3N_3NaO_4$ 422.1298, found: 422.1306.



4c

4-Ethyl 1-methyl 6-((4-methoxyphenyl)amino)-3-methyl-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4c) was prepared as pale yellow oil from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((4-methoxyphenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol)

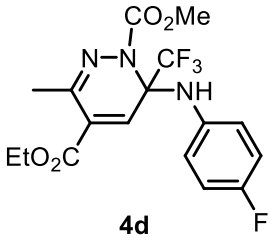
according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 51% yield (64 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 9.2 Hz, 2H), 6.77 – 6.72 (m, 3H), 5.69 (s, 1H), 4.31 – 4.24 (m, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 2.26 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 156.4, 155.0, 139.7, 134.5, 134.0, 127.6, 124.4 (q, $J_{C\text{-}F}$ = 289.7 Hz) 124.1 (2C), 114.6 (2C), 75.3 (q, $J_{C\text{-}F}$ = 30.6 Hz), 62.1, 55.5, 54.4, 21.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.36.

HRMS (ESI, TOF) m/z: $[M]^-$ calcd for $C_{18}H_{19}F_3N_3O_5$ 414.1282, found: 414.1276.



4d

4-Ethyl 1-methyl 6-((4-fluorophenyl)amino)-3-methyl-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4d) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((4-fluorophenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 65% yield (79 mg).

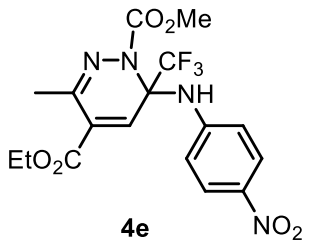
Mp: 133-134 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (t, *J* = 8.6 Hz, 2H), 6.85 – 6.81 (m, 2H), 6.72 (s, 1H), 5.75 (s, 1H), 4.35 – 4.24 (m, 2H), 3.85 (s, 3H), 2.29 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 159.3 (d, $J_{C\text{-}F}$ = 241.1 Hz), 154.9, 139.8, 137.7 (d, $J_{C\text{-}F}$ = 29 Hz), 133.7, 128.1, 123.3 (q, $J_{C\text{-}F}$ = 289.5 Hz), 123.0 (d, $J_{C\text{-}F}$ = 79.0 Hz, 2C) 116.1 (d, $J_{C\text{-}F}$ = 22.3 Hz, 2C), 74.6 (q, $J_{C\text{-}F}$ = 30.6 Hz), 62.3, 54.4, 21.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.59, -119.92.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{17}H_{17}F_4N_3O_4$ 403.1155, found: 403.1159.



4e

4-Ethyl 1-methyl 3-methyl-6-((4-nitrophenyl)amino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4e) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((4-nitrophenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 64% yield (83 mg).

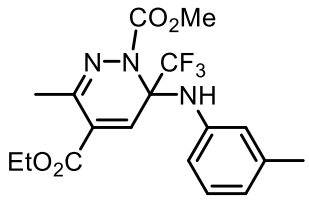
Mp: 143-144 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.2 Hz, 2H), 6.83 (d, *J* = 9.2 Hz, 2H), 6.71 (s, 1H), 6.06 (s, 1H), 4.39 – 4,27 (m, 2H), 3.78 (s, 3H), 2.38 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 154.1, 148.2, 142.1, 140.1, 132.8, 129.1, 125.7 (2C), 123.1 (q, $J_{C\text{-}F}$ = 290.5 Hz), 116.9 (2C), 72.9 (q, $J_{C\text{-}F}$ = 31.6 Hz), 62.6, 54.6, 21.4, 14.2.

^{19}F NMR (400 MHz, $CDCl_3$) δ -78.08.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}F_3N_4NaO_6$ 453.0992, found: 453.0999.



4f

4-Ethyl 1-methyl 3-methyl-6-(m-tolylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4f) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(*m*-tolylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 55% yield (66 mg).

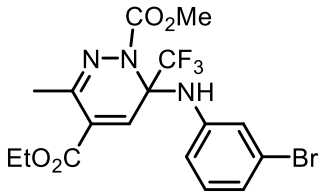
Mp: 89-90 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.76 (s, 1H), 6.68 (s, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 4.33 – 4.25 (m, 2H), 3.82 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 154.6, 141.8, 139.9, 139.3, 134.2, 129.1, 128.0, 126.3 (q, $J_{C\text{-}F}$ = 289.7 Hz), 123.7, 121.2, 116.6, 74.1 (q, $J_{C\text{-}F}$ = 30.8 Hz), 62.2, 54.4, 21.6, 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.86.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_4$ 399.1406, found: 399.1402.



4g

4-Ethyl 1-methyl 6-((3-bromophenyl)amino)-3-methyl-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4g) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-5-((3-bromophenyl)imino)-3-(ethoxycarbonyl)-6,6,6-trifluorohex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 56% yield (78 mg).

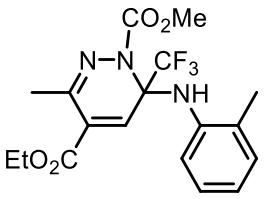
Mp: 95-96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 6.96 (m, 3H), 6.79 – 6.66 (m, 2H), 5.79 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.33 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 154.6, 143.3, 140.0, 133.4, 130.6, 128.3, 125.8, 123.3 (q, $J_{C\text{-}F}$ = 290.3 Hz), 123.2, 123.0, 118.0, 73.9 (q, $J_{C\text{-}F}$ = 31.3 Hz), 62.3, 54.5, 21.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.82.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}BrF_3N_3NaO_4$ 486.0247, found: 486.0239.



4h

4-Ethyl 1-methyl 3-methyl-6-(o-tolylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4h) was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(*o*-tolylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 51% yield (61 mg).

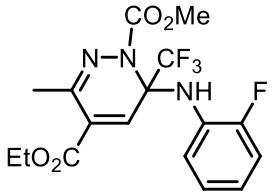
Mp: 95-96 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 5.45 (s, 1H), 4.32 – 4.20 (m, 2H), 3.79 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 154.4, 140.3, 140.1, 134.4, 131.1, 129.0, 128.4, 126.6, 123.6 (q, $J_{C\text{-}F}$ = 290.2 Hz), 122.0, 116.6, 73.5 (q, $J_{C\text{-}F}$ = 30.9 Hz), 62.2, 54.3, 21.5, 17.9, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.70.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_4$ 399.1406, found: 399.1409.



4i

4-Ethyl 1-methyl 6-((2-fluorophenyl)amino)-3-methyl-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4i) was prepared as pale yellow solid from was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-((2-fluorophenyl)imino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 54% yield (65 mg).

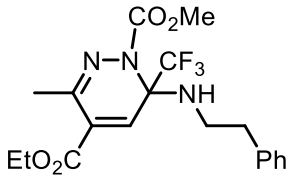
Mp: 91-92 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 1H), 6.93 – 6.89 (m, 2H), 6.80 – 6.75 (m, 2H), 5.80 (s, 1H), 4.35 – 4.24 (m, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 154.6 (d, $J_{C\text{-}F}$ = 242.4 Hz), 154.3, 139.9, 133.7, 130.3 (d, $J_{C\text{-}F}$ = 11.0 Hz), 128.3, 124.3 (d, $J_{C\text{-}F}$ = 3.9 Hz), 122.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 120.5 (q, $J_{C\text{-}F}$ = 267.3 Hz), 118.8 (d, $J_{C\text{-}F}$ = 1.2 Hz), 115.9 (d, $J_{C\text{-}F}$ = 19.4 Hz), 73.6 (q, $J_{C\text{-}F}$ = 30.0 Hz), 62.3, 54.4, 21.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.84, -129.27.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{17}H_{17}F_4N_3O_4$ 403.1155, found: 403.1160.



4j

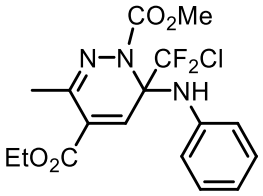
4-Ethyl 1-methyl 3-methyl-6-(phenethylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4j) was prepared as pale yellow solid from was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenethylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 44% yield (55 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.2 Hz, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.19 – 7.17 (m, 2H), 6.53 (s, 1H), 4.35 – 4.24 (m, 2H), 3.81 (s, 3H), 2.90 – 2.68 (m, 4H), 2.26 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 155.0, 140.2, 139.2, 133.7, 128.8 (2C), 128.6 (2C), 128.4, 126.6, 123.4 (q, $J_{C\text{-}F}$ = 288.7 Hz) 76.1 (q, $J_{C\text{-}F}$ = 30.6 Hz) 62.1, 54.2, 45.1, 36.4, 21.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.01.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}F_3N_3O_4$ 413.1562, found: 413.1553.



4k

4-Ethyl 1-methyl 6-(chlorodifluoromethyl)-3-methyl-6-(phenylamino)pyridazine-1,4(6H)-dicarboxylate (4k) was prepared as pale yellow solid from was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-6-chloro-3-(ethoxycarbonyl)-6,6-difluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 57% yield (69 mg).

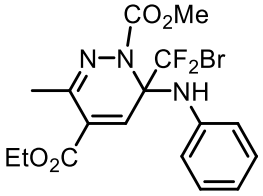
Mp: 124-125 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.2 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.83 – 6.82 (m, 3H), 5.77 (s, 1H), 4.35 – 4.24 (m, 2H), 3.80 (s, 3H), 2.35 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 154.5, 142.2, 140.6, 135.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 130.3 (t, $J_{C\text{-}F}$ = 308.6 Hz), 129.4 (2C), 127.9, 122.6, 119.7 (2C), 71.8 (t, $J_{C\text{-}F}$ = 29.9 Hz), 62.2, 54.4, 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82 (d, *J* = 160.2 Hz), -65.64 (d, *J* = 160.2 Hz)

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}ClF_2N_3O_4$ 401.0954, found: 401.0945.



4l

4-Ethyl 1-methyl 6-(bromodifluoromethyl)-3-methyl-6-(phenylamino)pyridazine-1,4(6H)-dicarboxylate (4l) was prepared as pale yellow solid from was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-6-bromo-3-(ethoxycarbonyl)-6,6-difluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 61% yield (81 mg).

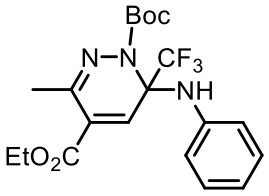
Mp: 94-95 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.82 (d, *J* = 7.6 Hz, 2H), 5.74 (s, 1H), 4.36 – 4.24 (m, 2H), 3.79 (s, 3H), 2.36 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 154.5, 142.1, 140.9, 135.6 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.4 (2C), 127.7, 125.6 (t, $J_{C\text{-}F}$ = 319.7 Hz), 122.5, 119.7 (2C), 77.8 (t, $J_{C\text{-}F}$ = 22.3 Hz), 62.2, 54.4, 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.40 (d, *J* = 158.3 Hz), -59.85 (d, *J* = 157.9 Hz).

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}BrF_2N_3NaO_4$ 468.0341, found: 468.0346.



4m

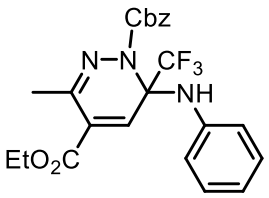
1-(*Tert*-butyl) 4-ethyl 3-methyl-6-(phenylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4m) was prepared as pale yellow solid from was prepared as pale yellow oil from *tert*-butyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 55% yield (47 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 5.48 (s, 1H), 4.34 – 4.23 (m, 2H), 2.32 (s, 3H), 1.40 (s, 9H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 152.5, 142.1, 139.2, 134.2, 129.4 (2C), 128.2, 123.5 (q, $J_{C\text{-}F}$ = 290.2 Hz), 122.3, 119.3 (2C), 83.8, 73.8 (q, $J_{C\text{-}F}$ = 30.7 Hz), 62.1, 27.9 (3C), 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.20.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}F_3N_3NaO_4$ 450.1611, found: 450.1618.



4n

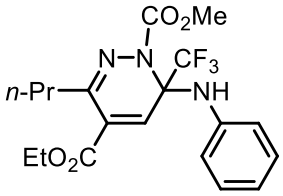
1-Benzyl 4-ethyl 3-methyl-6-(phenylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4n) was prepared as pale yellow solid from was prepared as pale yellow oil from benzyl (*E*)-2-((3*Z*,5*Z*)-3-(ethoxycarbonyl)-6,6,6-trifluoro-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 61% yield (84 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 3H), 7.23 – 7.21 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.77 – 6.74 (m, 3H) , 5.66 (s, 1H), 5.31 – 5.17 (m, 2H), 4.35 – 4.23 (m, 2H), 2.31 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 154.0, 141.8, 139.8, 135.6, 134.2, 129.4 (2C), 128.6 (2C), 128.3, 128.1, 127.9 (2C), 123.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 122.7, 119.9 (2C), 74.1 (q, $J_{C\text{-}F}$ = 31.0 Hz), 68.6, 62.2, 21.4, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.94.

HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{23}H_{22}F_3N_3O_4$ 461.1562, found: 461.1548.



4o

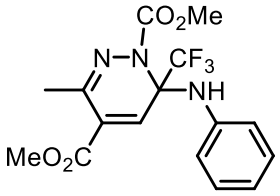
4-Ethyl 1-methyl 6-(phenylamino)-3-propyl-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4o) was prepared as pale yellow solid from was prepared as pale yellow oil from methyl (*E*)-2-((5*Z*,7*Z*)-5-(ethoxycarbonyl)-8,8,8-trifluoro-7-(phenylimino)oct-5-en-4-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 54% yield (67 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 H, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 5.74 (s, 1H), 4.35 – 4.23 (m, 2H), 3.79 (s, 3H), 2.85 – 2.78 (m, 1H), 2.58 – 2.51 (m, 1H), 1.54 – 1.42 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 154.7, 143.6, 141.9, 134.1, 129.4 (2C), 128.2, 123.5 (q, $J_{C\text{-}F}$ = 290.0 Hz), 122.7, 119.9 (2C), 73.9 (q, $J_{C\text{-}F}$ = 30.9 Hz), 62.2, 54.3, 35.7, 21.1, 14.2, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.13.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}F_3N_3NaO_4$ 436.1455, found: 436.1461.



4p

Dimethyl 3-methyl-6-(phenylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4p) was prepared as pale yellow solid from was prepared as pale yellow solid from methyl (*E*)-2-((3*Z*,5*Z*)-6,6,6-trifluoro-3-(methoxycarbonyl)-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 64% yield (71 mg).

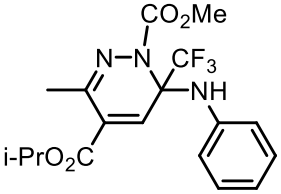
Mp: 145-146 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.79 (s, 1H), 5.74 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 154.6, 141.8, 139.8, 134.6, 129.4 (2C), 127.7, 123.4 (q, $J_{C\text{-}F}$ = 289.8 Hz), 122.8, 119.9 (2C), 74.0 (q, $J_{C\text{-}F}$ = 31.0 Hz), 54.4, 52.9, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.90.

HRMS (ESI, TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}F_3N_3NaO_4$ 394.0985, found: 394.0990.



4q

4-Isopropyl 1-methyl 3-methyl-6-(phenylamino)-6-(trifluoromethyl)pyridazine-1,4(6H)-dicarboxylate (4q) was prepared as pale yellow solid from was prepared as pale yellow oil from methyl (*E*)-2-((3*Z*,5*Z*)-6,6,6-trifluoro-3-(isopropoxycarbonyl)-5-(phenylimino)hex-3-en-2-ylidene)hydrazine-1-carboxylate (0.3 mmol) according to the General Procedure E (24 h, eluent: PE/EA = 10:1) in 58% yield (70 mg).

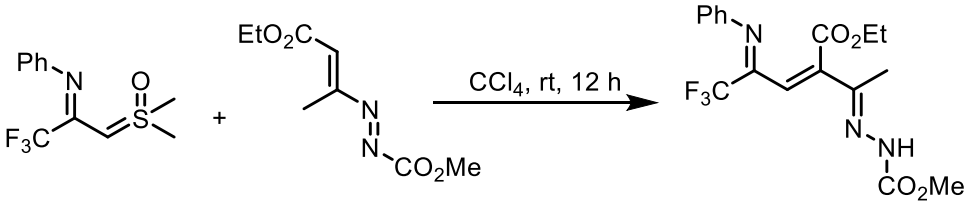
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.72 (s, 1H), 5.76 (s, 1H), 5.14 (p, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 2.31 (s, 3H), 1.31 (t, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 154.6, 141.9, 139.9, 133.8, 129.4 (2C), 128.4, 123.4 (q, $J_{C\text{-}F}$ = 289.8 Hz), 122.8, 120.1 (2C), 74.2 (q, $J_{C\text{-}F}$ = 31.0 Hz), 70.2, 54.3, 21.8 (2C), 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.84.

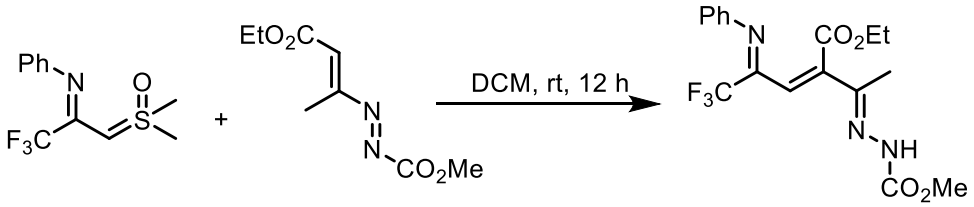
HRMS (EI, TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}F_3N_3O_4$ 399.1406, found: 399.1400.

4. Scale-up reactions and control experiments



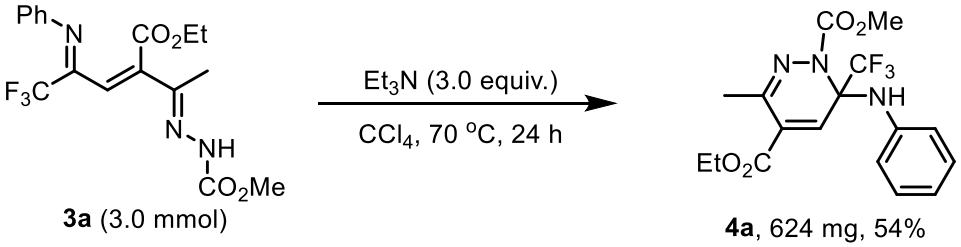
1a (3.0 mmol) **2a** (6.0 mmol) **3a**, 850 mg, 74%

To a stirred solution of imidoyl sulfoxonium ylides **1a** (3.0 mmol, 1 equiv.), 1,2-diaza-1,3-diene **2a** (6.0 mmol, 2 equiv.) in CCl_4 (30 mL) and the reaction mixture was stirred at room temperature for 12 h, which was monitored by TLC After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3a** (850 mg, 74%) as a pale yellow solid.



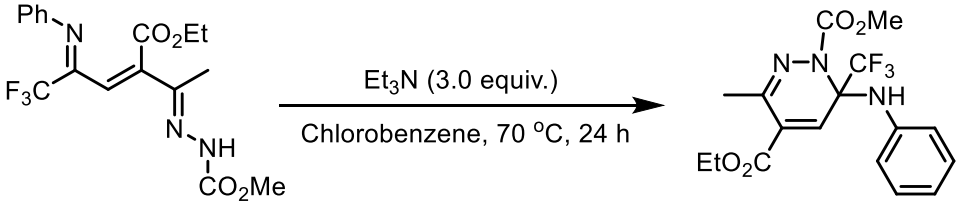
1a (1.0 mmol) **2a** (2.0 mmol) **3a**, 262 mg, 68%

To a stirred solution of imidoyl sulfoxonium ylides **1a** (1.0 mmol, 1 equiv.), 1,2-diaza-1,3-diene **2a** (2.0 mmol, 2 equiv.) in DCM(10 mL) and the reaction mixture was stirred at room temperature for 12 h, which was monitored by TLC After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3a** (262 mg, 74%) as a pale yellow solid.



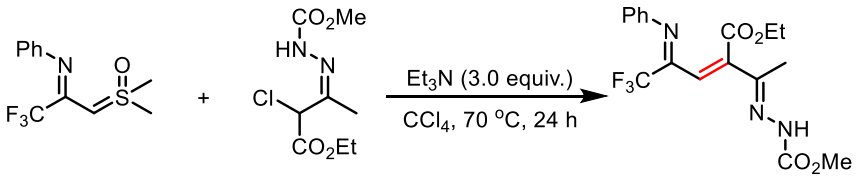
3a (3.0 mmol) **4a**, 624 mg, 54%

To a stirred solution of alkenyl imine **3a** (3.0 mmol, 1.0 equiv.) in CCl_4 (30 mL) was added Et_3N (9.0 mmol, 3.0 equiv.) and the reaction mixture was stirred in a preheated oil bath at 70 °C, which was monitored by TLC. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 10:1) to afford the pure product **4a** (624 mg, 54%) as a pale yellow solid.



3a (1.0 mmol) **4a**, 196 mg, 51%

To a stirred solution of alkenyl imine **3a** (1.0 mmol, 1.0 equiv.) in chlorobenzene (10 mL) was added Et_3N (3.0 mmol, 3.0 equiv.) and the reaction mixture was stirred in a preheated oil bath at 70 °C, which was monitored by TLC. After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 10:1) to afford the pure product **4a** (196 mg, 51%) as a pale yellow solid.



1a (0.3 mmol) **2g** (0.6 mmol) **3a**, 18%

To a stirred solution of imidoyl sulfoxonium ylides **1a** (0.3 mmol, 1 equiv.), **2a** (0.6 mmol, 2 equiv.) in CCl_4 (3 mL) was added Et_3N (0.9 mmol, 3.0 equiv.) and the reaction mixture was stirred at 70 ^oC (oil bath). After reaction finished, the reaction solution was evaporated under reduced pressure and purified by column chromatography (PE/EA = 3:1) to afford the pure product **3a** (21 mg, 18%) as a pale yellow solid.

5. Crystal data and structural refinement of compounds 3e and 4e

Single crystal of compound **3e** was obtained by slow evaporation from CH_2Cl_2 solution.

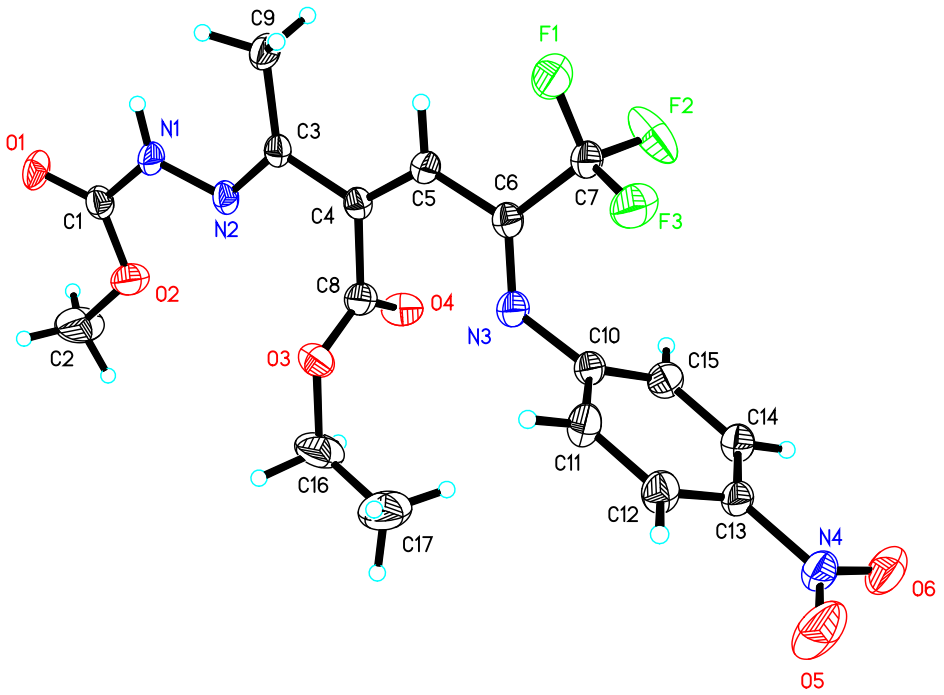


Figure S1. Crystal data and structure refinement of product **3e** (with thermal ellipsoils shown at the 50% probability level)

Table 1. Crystal data and structure refinement for **3e**.

Identification code	**3e**
CCDC	2272116
Empirical formula	C_{17} H_{17} F_3 N_4 O_6
Formula weight	430.34

Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.8993(5) Å	a= 113.990(2) °.
	b = 11.6888(7) Å	b= 103.914(2) °.
	c = 12.4066(8) Å	g = 90.572(2) °.
Volume	1008.35(11) $Å^3$	
Z	2	
Density (calculated)	1.417 Mg/m^3	
Absorption coefficient	0.126 mm^{-1}	
F(000)	444	
Crystal size	0.150 x 0.120 x 0.060 mm^3	
Theta range for data collection	1.865 to 24.995 °.	
Index ranges	-9<=h<=9, -13<=k<=13, -14<=l<=14	
Reflections collected	12518	
Independent reflections	3550 [R(int) = 0.0480]	
Completeness to theta = 25.242 °	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5861	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3550 / 56 / 324	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0661, wR2 = 0.1262	
R indices (all data)	R1 = 0.1088, wR2 = 0.1492	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.436 and -0.279 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3)

for **3e** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	6223(7)	3740(6)	10(5)	78(2)
F(2)	8925(10)	4138(6)	984(8)	90(2)
F(3)	7846(9)	5165(8)	4(7)	71(2)
F(1')	6922(13)	3508(8)	447(8)	77(2)
F(2')	9284(13)	4624(8)	1033(13)	75(3)
F(3')	7137(13)	4961(13)	-152(11)	74(3)
O(1)	842(3)	6162(2)	6492(2)	50(1)
O(2)	3154(4)	7479(2)	6752(2)	65(1)
O(3)	5446(3)	7984(2)	4169(2)	50(1)
O(4)	7542(3)	7112(2)	5038(2)	51(1)
O(5)	12105(4)	9849(3)	650(3)	95(1)
O(6)	14175(4)	9118(3)	1525(3)	78(1)
N(1)	2310(3)	5682(3)	5046(3)	40(1)
N(2)	3626(3)	6027(2)	4666(2)	37(1)
N(3)	7747(4)	6756(3)	2411(3)	48(1)
N(4)	12628(4)	9229(3)	1210(3)	52(1)
C(1)	2012(4)	6447(3)	6136(3)	42(1)
C(2)	2890(7)	8335(4)	7921(4)	98(2)
C(3)	3880(4)	5253(3)	3640(3)	34(1)
C(4)	5309(4)	5761(3)	3324(3)	34(1)
C(5)	5782(4)	5124(3)	2290(3)	37(1)
C(6)	7096(4)	5612(3)	1880(3)	40(1)
C(7)	7558(5)	4660(3)	754(3)	45(1)
C(8)	6181(5)	7055(3)	4239(3)	43(1)
C(9)	2901(4)	3973(3)	2812(3)	45(1)
C(10)	8977(4)	7317(3)	2058(3)	41(1)
C(11)	8401(5)	7998(3)	1379(3)	50(1)
C(12)	9587(5)	8614(3)	1087(3)	49(1)
C(13)	11354(4)	8562(3)	1508(3)	40(1)
C(14)	11955(4)	7923(3)	2207(3)	44(1)

C(15)	10762(5)	7301(3)	2484(3)	47(1)
C(16)	6307(13)	9237(7)	5091(8)	74(2)
C(17)	7299(14)	9809(8)	4534(9)	92(3)
C(17')	9419(10)	8940(7)	5577(7)	62(2)
C(16')	8167(9)	8368(6)	5995(6)	48(2)

Table 3. Bond lengths [Å] and angles [°] for **3e**.

F(1)-C(7)	1.351(6)
F(2)-C(7)	1.275(8)
F(3)-C(7)	1.346(8)
F(1')-C(7)	1.300(9)
F(2')-C(7)	1.329(11)
F(3')-C(7)	1.281(12)
O(1)-C(1)	1.212(4)
O(2)-C(1)	1.323(4)
O(2)-C(2)	1.455(4)
O(3)-C(8)	1.261(4)
O(3)-C(16)	1.470(8)
O(4)-C(8)	1.255(4)
O(4)-C(16')	1.447(7)
O(5)-N(4)	1.206(4)
O(6)-N(4)	1.215(4)
N(1)-N(2)	1.359(3)
N(1)-C(1)	1.363(4)
N(1)-H(1)	0.826(18)
N(2)-C(3)	1.292(4)
N(3)-C(6)	1.263(4)
N(3)-C(10)	1.410(4)
N(4)-C(13)	1.468(4)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(2)-H(2C)	0.9700
C(3)-C(4)	1.472(4)
C(3)-C(9)	1.496(4)
C(4)-C(5)	1.342(4)
C(4)-C(8)	1.503(4)
C(5)-C(6)	1.463(4)
C(5)-H(5)	0.9400
C(6)-C(7)	1.521(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(9)-H(9C)	0.9700

C(10)-C(11)	1.385(5)
C(10)-C(15)	1.385(5)
C(11)-C(12)	1.375(5)
C(11)-H(11)	0.9400
C(12)-C(13)	1.379(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.367(4)
C(14)-C(15)	1.372(4)
C(14)-H(14)	0.9400
C(15)-H(15)	0.9400
C(16)-C(17)	1.472(11)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700
C(17')-C(16')	1.487(9)
C(17')-H(17D)	0.9700
C(17')-H(17E)	0.9700
C(17')-H(17F)	0.9700
C(16')-H(16C)	0.9800
C(16')-H(16D)	0.9800

C(1)-O(2)-C(2)	115.3(3)
C(8)-O(3)-C(16)	116.2(4)
C(8)-O(4)-C(16')	114.1(4)
N(2)-N(1)-C(1)	120.7(3)
N(2)-N(1)-H(1)	128.2(16)
C(1)-N(1)-H(1)	111.0(15)
C(3)-N(2)-N(1)	118.2(3)
C(6)-N(3)-C(10)	125.5(3)
O(5)-N(4)-O(6)	122.5(3)
O(5)-N(4)-C(13)	119.1(3)
O(6)-N(4)-C(13)	118.3(3)
O(1)-C(1)-O(2)	125.1(3)
O(1)-C(1)-N(1)	121.9(3)
O(2)-C(1)-N(1)	113.0(3)
O(2)-C(2)-H(2A)	109.5

O(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
O(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	112.4(3)
N(2)-C(3)-C(9)	127.0(3)
C(4)-C(3)-C(9)	120.6(3)
C(5)-C(4)-C(3)	122.5(3)
C(5)-C(4)-C(8)	122.5(3)
C(3)-C(4)-C(8)	115.0(3)
C(4)-C(5)-C(6)	125.2(3)
C(4)-C(5)-H(5)	117.4
C(6)-C(5)-H(5)	117.4
N(3)-C(6)-C(5)	121.6(3)
N(3)-C(6)-C(7)	123.0(3)
C(5)-C(6)-C(7)	115.4(3)
F(3')-C(7)-F(1')	111.5(7)
F(3')-C(7)-F(2')	108.3(8)
F(1')-C(7)-F(2')	103.1(7)
F(2)-C(7)-F(3)	105.5(6)
F(2)-C(7)-F(1)	108.0(5)
F(3)-C(7)-F(1)	102.0(5)
F(2)-C(7)-C(6)	114.6(5)
F(3')-C(7)-C(6)	112.0(7)
F(1')-C(7)-C(6)	113.0(5)
F(2')-C(7)-C(6)	108.4(6)
F(3)-C(7)-C(6)	113.0(5)
F(1)-C(7)-C(6)	112.7(4)
O(4)-C(8)-O(3)	125.7(3)
O(4)-C(8)-C(4)	116.8(3)
O(3)-C(8)-C(4)	117.4(3)
C(3)-C(9)-H(9A)	109.5
C(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

C(11)-C(10)-C(15)	119.6(3)
C(11)-C(10)-N(3)	119.4(3)
C(15)-C(10)-N(3)	120.7(3)
C(12)-C(11)-C(10)	120.4(3)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(11)-C(12)-C(13)	118.6(3)
C(11)-C(12)-H(12)	120.7
C(13)-C(12)-H(12)	120.7
C(14)-C(13)-C(12)	122.1(3)
C(14)-C(13)-N(4)	119.0(3)
C(12)-C(13)-N(4)	118.9(3)
C(13)-C(14)-C(15)	118.9(3)
C(13)-C(14)-H(14)	120.5
C(15)-C(14)-H(14)	120.5
C(14)-C(15)-C(10)	120.4(3)
C(14)-C(15)-H(15)	119.8
C(10)-C(15)-H(15)	119.8
O(3)-C(16)-C(17)	109.0(6)
O(3)-C(16)-H(16A)	109.9
C(17)-C(16)-H(16A)	109.9
O(3)-C(16)-H(16B)	109.9
C(17)-C(16)-H(16B)	109.9
H(16A)-C(16)-H(16B)	108.3
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16')-C(17')-H(17D)	109.5
C(16')-C(17')-H(17E)	109.5
H(17D)-C(17')-H(17E)	109.5
C(16')-C(17')-H(17F)	109.5
H(17D)-C(17')-H(17F)	109.5
H(17E)-C(17')-H(17F)	109.5
O(4)-C(16')-C(17')	106.2(5)
O(4)-C(16')-H(16C)	110.5

C(17')-C(16')-H(16C)	110.5
O(4)-C(16')-H(16D)	110.5
C(17')-C(16')-H(16D)	110.5
H(16C)-C(16')-H(16D)	108.7

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3e** The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	70(3)	76(3)	52(3)	-15(2)	32(2)	-22(3)
F(2)	96(4)	88(5)	68(3)	13(4)	21(3)	57(4)
F(3)	99(5)	67(3)	46(3)	13(2)	37(3)	-15(3)
F(1')	104(5)	51(4)	67(5)	-1(3)	57(4)	-11(4)
F(2')	60(4)	57(5)	86(4)	-6(4)	43(3)	13(3)
F(3')	94(6)	84(5)	35(3)	18(3)	14(4)	11(5)
O(1)	37(1)	70(2)	47(2)	21(1)	24(1)	2(1)
O(2)	85(2)	44(2)	66(2)	5(1)	50(2)	-7(1)
O(3)	57(2)	39(1)	58(2)	19(1)	22(1)	14(1)
O(4)	59(2)	44(1)	44(2)	20(1)	1(1)	-1(1)
O(5)	83(2)	127(3)	128(3)	102(3)	36(2)	9(2)
O(6)	52(2)	85(2)	108(2)	48(2)	31(2)	-4(2)
N(1)	34(2)	47(2)	44(2)	17(2)	22(1)	4(1)
N(2)	36(1)	43(2)	41(2)	22(1)	21(1)	12(1)
N(3)	55(2)	44(2)	47(2)	14(2)	31(2)	2(2)
N(4)	56(2)	53(2)	54(2)	22(2)	26(2)	1(2)
C(1)	42(2)	44(2)	47(2)	21(2)	22(2)	12(2)
C(2)	145(5)	55(3)	86(4)	-6(3)	80(3)	-10(3)
C(3)	29(2)	40(2)	38(2)	21(2)	12(1)	9(1)
C(4)	33(2)	37(2)	36(2)	18(2)	12(1)	9(1)
C(5)	35(2)	38(2)	40(2)	16(2)	14(2)	3(2)
C(6)	40(2)	42(2)	38(2)	15(2)	16(2)	7(2)
C(7)	48(2)	46(2)	44(2)	16(2)	24(2)	4(2)
C(8)	56(2)	40(2)	40(2)	16(2)	27(2)	3(2)
C(9)	39(2)	52(2)	44(2)	15(2)	17(2)	-1(2)
C(10)	49(2)	37(2)	38(2)	11(2)	24(2)	3(2)
C(11)	40(2)	63(2)	57(2)	31(2)	19(2)	9(2)
C(12)	52(2)	58(2)	52(2)	33(2)	21(2)	13(2)
C(13)	45(2)	40(2)	37(2)	13(2)	20(2)	1(2)
C(14)	43(2)	50(2)	45(2)	22(2)	16(2)	8(2)
C(15)	55(2)	48(2)	51(2)	30(2)	21(2)	11(2)

C(16)	114(6)	41(4)	61(5)	7(4)	36(4)	10(4)
C(17)	122(7)	55(5)	80(6)	4(4)	41(5)	-18(5)
C(17')	74(5)	48(4)	54(4)	11(3)	18(4)	-18(4)
C(16')	56(4)	41(4)	41(4)	13(3)	11(3)	-5(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3e**

	x	y	z	U(eq)
H(2A)	1780	8670	7783	147
H(2B)	3841	9022	8338	147
H(2C)	2873	7881	8423	147
H(5)	5224	4298	1789	45
H(9A)	3619	3333	2905	68
H(9B)	2631	3867	1969	68
H(9C)	1817	3887	3025	68
H(11)	7192	8039	1117	60
H(12)	9201	9062	611	59
H(14)	13167	7911	2492	53
H(15)	11158	6861	2966	56
H(16A)	7106	9159	5790	89
H(16B)	5423	9773	5387	89
H(17A)	8340	9392	4422	137
H(17B)	7644	10699	5066	137
H(17C)	6567	9714	3746	137
H(17D)	10307	8385	5367	93
H(17E)	9978	9749	6229	93
H(17F)	8789	9060	4864	93
H(16C)	8758	8328	6768	58
H(16D)	7185	8868	6120	58
H(1)	1580(40)	5050(20)	4680(20)	61(13)

–

Table 6. Torsion angles [°] for **3e**.

C(1)-N(1)-N(2)-C(3)	178.3(3)
C(2)-O(2)-C(1)-O(1)	-2.5(5)
C(2)-O(2)-C(1)-N(1)	179.6(3)
N(2)-N(1)-C(1)-O(1)	179.7(3)
N(2)-N(1)-C(1)-O(2)	-2.4(4)
N(1)-N(2)-C(3)-C(4)	178.4(2)
N(1)-N(2)-C(3)-C(9)	-1.7(5)
N(2)-C(3)-C(4)-C(5)	-179.1(3)
C(9)-C(3)-C(4)-C(5)	1.0(4)
N(2)-C(3)-C(4)-C(8)	0.1(4)
C(9)-C(3)-C(4)-C(8)	-179.9(3)
C(3)-C(4)-C(5)-C(6)	175.2(3)
C(8)-C(4)-C(5)-C(6)	-3.9(5)
C(10)-N(3)-C(6)-C(5)	-178.0(3)
C(10)-N(3)-C(6)-C(7)	-0.3(6)
C(4)-C(5)-C(6)-N(3)	-9.0(5)
C(4)-C(5)-C(6)-C(7)	173.2(3)
N(3)-C(6)-C(7)-F(2)	86.1(6)
C(5)-C(6)-C(7)-F(2)	-96.1(5)
N(3)-C(6)-C(7)-F(3')	-61.4(6)
C(5)-C(6)-C(7)-F(3')	116.4(6)
N(3)-C(6)-C(7)-F(1')	171.7(5)
C(5)-C(6)-C(7)-F(1')	-10.5(6)
N(3)-C(6)-C(7)-F(2')	58.0(7)
C(5)-C(6)-C(7)-F(2')	-124.2(7)
N(3)-C(6)-C(7)-F(3)	-34.9(6)
C(5)-C(6)-C(7)-F(3)	142.9(4)
N(3)-C(6)-C(7)-F(1)	-149.8(4)
C(5)-C(6)-C(7)-F(1)	28.0(5)
C(16')-O(4)-C(8)-O(3)	5.7(5)
C(16')-O(4)-C(8)-C(4)	-171.2(4)
C(16)-O(3)-C(8)-O(4)	1.9(6)
C(16)-O(3)-C(8)-C(4)	178.7(4)
C(5)-C(4)-C(8)-O(4)	-86.7(4)
C(3)-C(4)-C(8)-O(4)	94.2(3)
C(5)-C(4)-C(8)-O(3)	96.2(4)

C(3)-C(4)-C(8)-O(3)	-83.0(3)
C(6)-N(3)-C(10)-C(11)	99.3(4)
C(6)-N(3)-C(10)-C(15)	-87.1(5)
C(15)-C(10)-C(11)-C(12)	2.5(5)
N(3)-C(10)-C(11)-C(12)	176.2(3)
C(10)-C(11)-C(12)-C(13)	-1.5(5)
C(11)-C(12)-C(13)-C(14)	-0.3(5)
C(11)-C(12)-C(13)-N(4)	-179.4(3)
O(5)-N(4)-C(13)-C(14)	-176.0(3)
O(6)-N(4)-C(13)-C(14)	4.9(5)
O(5)-N(4)-C(13)-C(12)	3.2(5)
O(6)-N(4)-C(13)-C(12)	-175.9(3)
C(12)-C(13)-C(14)-C(15)	0.9(5)
N(4)-C(13)-C(14)-C(15)	-180.0(3)
C(13)-C(14)-C(15)-C(10)	0.2(5)
C(11)-C(10)-C(15)-C(14)	-1.9(5)
N(3)-C(10)-C(15)-C(14)	-175.4(3)
C(8)-O(3)-C(16)-C(17)	101.3(7)
C(8)-O(4)-C(16')-C(17')	-90.6(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3e** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2B)...O(6)#1	0.97	2.59	3.486(5)	153.4
C(2)-H(2C)...F(1')#2	0.97	2.52	3.487(10)	172.0
C(9)-H(9C)...O(1)#3	0.97	2.33	3.293(4)	175.0
C(12)-H(12)...O(5)#4	0.94	2.45	3.387(5)	174.3
C(14)-H(14)...O(3)#5	0.94	2.37	3.188(4)	145.0
C(16)-H(16B)...O(3)#6	0.98	2.59	3.404(8)	141.0
N(1)-H(1)...O(1)#3	0.826(18)	2.17(2)	2.959(4)	160(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+2,-z+1 #2 -x+1,-y+1,-z+1 #3 -x,-y+1,-z+1
#4 -x+2,-y+2,-z #5 x+1,y,z #6 -x+1,-y+2,-z+1

Single crystal of compound **4e** was obtained by slow evaporation from CH_2Cl_2 solution.

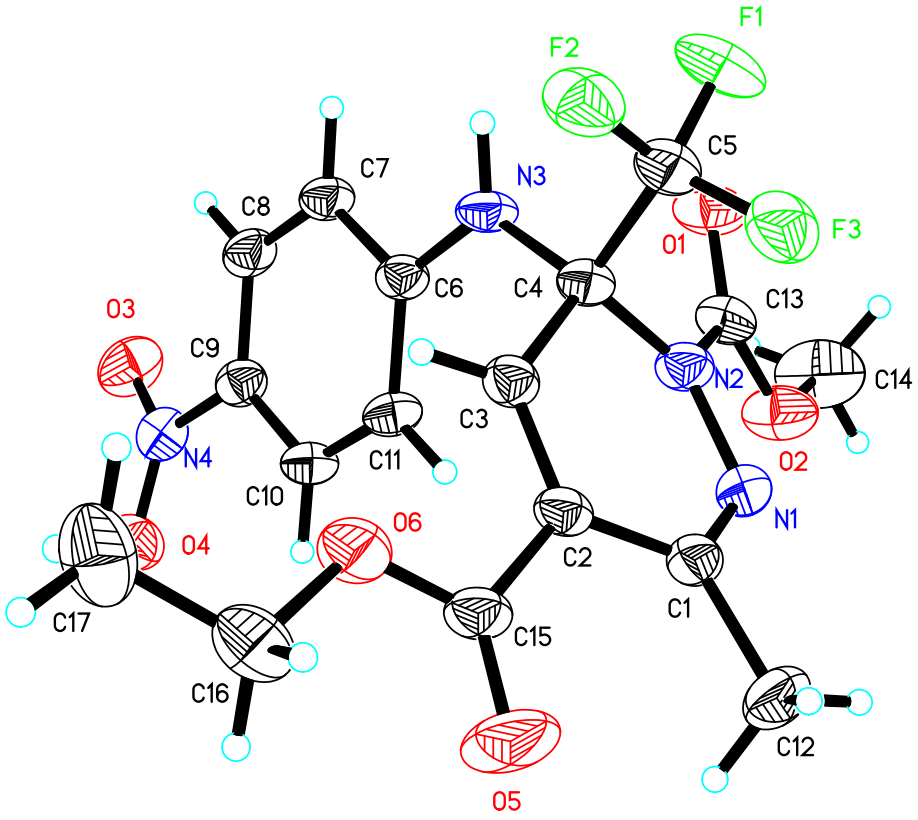


Figure S2. Crystal data and structure refinement of product **4e** (with thermal ellipsoils shown at the 50% probability level)

Table 1. Crystal data and structure refinement for **4e**.

Identification code	**4e**	
CCDC	2272117	
Empirical formula	$C_{17}H_{17}F_3N_4O_6$	
Formula weight	430.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.0815(8) Å	a= 95.562(3) °.
	b = 9.9989(9) Å	b= 100.951(3) °.
	c = 11.2070(10) Å	g = 93.877(3) °.

Volume	990.55(15) $Å^3$
Z	2
Density (calculated)	1.443 Mg/m^3
Absorption coefficient	0.128 mm^{-1}
F(000)	444
Crystal size	0.200 x 0.160 x 0.060 mm^3
Theta range for data collection	2.653 to 25.993 °.
Index ranges	-11<=h<=11, -12<=k<=12, -13<=l<=13
Reflections collected	17758
Independent reflections	3884 [R(int) = 0.0811]
Completeness to theta = 25.242 °	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5477
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3884 / 0 / 275
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.1288
R indices (all data)	R1 = 0.0989, wR2 = 0.1546
Extinction coefficient	0.051(6)
Largest diff. peak and hole	0.365 and -0.315 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4e** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	7082(2)	-208(2)	6654(2)	87(1)
F(2)	8634(2)	1503(2)	7327(2)	81(1)
F(3)	7635(2)	438(2)	8561(2)	81(1)
O(1)	3903(2)	-224(2)	6074(2)	71(1)
O(2)	2497(2)	66(2)	7500(2)	75(1)
O(3)	884(2)	5319(2)	3119(2)	78(1)
O(4)	940(2)	6316(2)	4922(2)	73(1)
O(5)	6795(4)	4936(3)	11072(2)	125(1)
O(6)	7946(2)	5335(2)	9602(2)	71(1)
N(1)	4593(2)	1382(2)	9024(2)	52(1)
N(2)	4787(2)	1187(2)	7825(2)	50(1)
N(3)	5721(2)	2115(2)	6134(2)	50(1)
N(4)	1358(3)	5473(2)	4229(2)	57(1)
C(1)	5389(3)	2348(3)	9759(2)	49(1)
C(2)	6411(3)	3314(2)	9340(2)	44(1)
C(3)	6685(3)	3083(2)	8221(2)	45(1)
C(4)	6079(3)	1815(2)	7376(2)	45(1)
C(5)	7361(3)	872(3)	7458(3)	57(1)
C(6)	4611(3)	2951(2)	5712(2)	44(1)
C(7)	4312(3)	3072(3)	4459(2)	50(1)
C(8)	3240(3)	3875(3)	3972(2)	53(1)
C(9)	2476(3)	4596(3)	4741(2)	48(1)
C(10)	2761(3)	4497(3)	5974(2)	50(1)
C(11)	3810(3)	3668(3)	6461(2)	49(1)
C(12)	5164(4)	2414(3)	11059(2)	73(1)
C(13)	3724(3)	280(3)	7044(3)	55(1)
C(14)	1318(4)	-866(4)	6747(4)	107(1)
C(15)	7068(3)	4595(3)	10117(2)	53(1)
C(16)	8708(4)	6583(3)	10303(3)	74(1)
C(17)	9374(4)	7357(4)	9433(4)	95(1)

Table 3. Bond lengths [Å] and angles [°] for **4e**.

F(1)-C(5)	1.315(3)
F(2)-C(5)	1.319(3)
F(3)-C(5)	1.334(3)
O(1)-C(13)	1.199(3)
O(2)-C(13)	1.324(3)
O(2)-C(14)	1.448(4)
O(3)-N(4)	1.227(3)
O(4)-N(4)	1.219(3)
O(5)-C(15)	1.169(3)
O(6)-C(15)	1.301(3)
O(6)-C(16)	1.462(3)
N(1)-C(1)	1.288(3)
N(1)-N(2)	1.384(3)
N(2)-C(13)	1.388(3)
N(2)-C(4)	1.487(3)
N(3)-C(6)	1.396(3)
N(3)-C(4)	1.433(3)
N(3)-H(3)	0.8600
N(4)-C(9)	1.458(3)
C(1)-C(2)	1.465(4)
C(1)-C(12)	1.506(3)
C(2)-C(3)	1.326(3)
C(2)-C(15)	1.496(4)
C(3)-C(4)	1.511(3)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.541(4)
C(6)-C(11)	1.391(3)
C(6)-C(7)	1.398(3)
C(7)-C(8)	1.371(4)
C(7)-H(7)	0.9300
C(8)-C(9)	1.385(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.371(3)
C(10)-C(11)	1.374(4)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300

C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(16)-C(17)	1.491(5)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600

C(13)-O(2)-C(14)	115.6(2)
C(15)-O(6)-C(16)	117.9(2)
C(1)-N(1)-N(2)	119.3(2)
N(1)-N(2)-C(13)	115.6(2)
N(1)-N(2)-C(4)	124.15(19)
C(13)-N(2)-C(4)	120.2(2)
C(6)-N(3)-C(4)	123.58(19)
C(6)-N(3)-H(3)	118.2
C(4)-N(3)-H(3)	118.2
O(4)-N(4)-O(3)	123.4(2)
O(4)-N(4)-C(9)	118.5(2)
O(3)-N(4)-C(9)	118.0(2)
N(1)-C(1)-C(2)	121.8(2)
N(1)-C(1)-C(12)	114.9(3)
C(2)-C(1)-C(12)	123.3(2)
C(3)-C(2)-C(1)	119.1(2)
C(3)-C(2)-C(15)	119.4(2)
C(1)-C(2)-C(15)	121.3(2)
C(2)-C(3)-C(4)	123.1(2)
C(2)-C(3)-H(3A)	118.5
C(4)-C(3)-H(3A)	118.5
N(3)-C(4)-N(2)	114.3(2)
N(3)-C(4)-C(3)	110.3(2)
N(2)-C(4)-C(3)	107.83(19)
N(3)-C(4)-C(5)	107.1(2)

N(2)-C(4)-C(5)	110.2(2)
C(3)-C(4)-C(5)	106.90(19)
F(1)-C(5)-F(2)	107.3(2)
F(1)-C(5)-F(3)	106.6(2)
F(2)-C(5)-F(3)	106.2(2)
F(1)-C(5)-C(4)	114.5(2)
F(2)-C(5)-C(4)	111.8(2)
F(3)-C(5)-C(4)	110.0(2)
C(11)-C(6)-N(3)	124.0(2)
C(11)-C(6)-C(7)	118.9(2)
N(3)-C(6)-C(7)	117.1(2)
C(8)-C(7)-C(6)	120.7(2)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	119.3(2)
C(7)-C(8)-H(8)	120.4
C(9)-C(8)-H(8)	120.4
C(10)-C(9)-C(8)	120.9(2)
C(10)-C(9)-N(4)	119.8(2)
C(8)-C(9)-N(4)	119.4(2)
C(9)-C(10)-C(11)	120.0(2)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(10)-C(11)-C(6)	120.3(2)
C(10)-C(11)-H(11)	119.9
C(6)-C(11)-H(11)	119.9
C(1)-C(12)-H(12A)	109.5
C(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-O(2)	124.9(3)
O(1)-C(13)-N(2)	123.5(3)
O(2)-C(13)-N(2)	111.6(2)
O(2)-C(14)-H(14A)	109.5
O(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

O(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(5)-C(15)-O(6)	122.4(3)
O(5)-C(15)-C(2)	124.4(3)
O(6)-C(15)-C(2)	113.2(2)
O(6)-C(16)-C(17)	106.8(3)
O(6)-C(16)-H(16A)	110.4
C(17)-C(16)-H(16A)	110.4
O(6)-C(16)-H(16B)	110.4
C(17)-C(16)-H(16B)	110.4
H(16A)-C(16)-H(16B)	108.6
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4e**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	81(1)	71(1)	97(1)	-36(1)	1(1)	26(1)
F(2)	57(1)	76(1)	113(2)	0(1)	28(1)	12(1)
F(3)	88(1)	80(1)	76(1)	15(1)	11(1)	35(1)
O(1)	71(1)	71(1)	63(1)	-28(1)	16(1)	-4(1)
O(2)	60(1)	84(2)	76(1)	-21(1)	21(1)	-9(1)
O(3)	76(1)	107(2)	50(1)	20(1)	5(1)	16(1)
O(4)	80(1)	65(1)	77(2)	6(1)	19(1)	19(1)
O(5)	192(3)	109(2)	71(2)	-47(2)	68(2)	-54(2)
O(6)	89(2)	58(1)	59(1)	-16(1)	17(1)	-12(1)
N(1)	64(1)	51(1)	43(1)	4(1)	15(1)	7(1)
N(2)	57(1)	49(1)	42(1)	-6(1)	12(1)	1(1)
N(3)	59(1)	57(1)	35(1)	-7(1)	15(1)	14(1)
N(4)	56(1)	62(2)	55(2)	11(1)	12(1)	3(1)
C(1)	62(2)	49(2)	37(1)	4(1)	10(1)	12(1)
C(2)	52(1)	45(1)	35(1)	-2(1)	5(1)	14(1)
C(3)	51(1)	43(1)	39(1)	-1(1)	7(1)	6(1)
C(4)	50(1)	46(1)	40(1)	-5(1)	10(1)	6(1)
C(5)	61(2)	52(2)	53(2)	-8(1)	8(1)	9(1)
C(6)	49(1)	44(1)	38(1)	-6(1)	11(1)	-1(1)
C(7)	62(2)	51(2)	36(1)	-6(1)	16(1)	3(1)
C(8)	65(2)	58(2)	34(1)	0(1)	11(1)	0(1)
C(9)	48(1)	52(2)	42(1)	1(1)	9(1)	1(1)
C(10)	53(2)	56(2)	40(1)	-5(1)	13(1)	9(1)
C(11)	53(2)	61(2)	32(1)	-3(1)	10(1)	6(1)
C(12)	100(2)	77(2)	42(2)	6(2)	21(2)	-3(2)
C(13)	58(2)	50(2)	55(2)	-8(1)	12(1)	7(1)
C(14)	67(2)	123(3)	114(3)	-35(3)	16(2)	-30(2)
C(15)	65(2)	55(2)	36(1)	-8(1)	8(1)	8(1)
C(16)	78(2)	60(2)	72(2)	-18(2)	-3(2)	-7(2)
C(17)	96(3)	70(2)	103(3)	7(2)	-8(2)	-17(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4e**.

	x	y	z	U(eq)
H(3)	6218	1761	5621	60
H(3A)	7278	3733	7943	54
H(7)	4846	2602	3949	60
H(8)	3029	3936	3135	63
H(10)	2244	4990	6481	60
H(11)	3984	3586	7294	59
H(12A)	4718	3229	11260	109
H(12B)	6119	2406	11600	109
H(12C)	4510	1650	11147	109
H(14A)	967	-512	5988	160
H(14B)	499	-984	7167	160
H(14C)	1708	-1720	6587	160
H(16A)	9490	6382	10963	89
H(16B)	7996	7101	10651	89
H(17A)	8585	7575	8801	142
H(17B)	10050	6821	9075	142
H(17C)	9917	8174	9864	142

Table 6. Torsion angles [°] for **4e**.

C(1)-N(1)-N(2)-C(13)	-169.7(2)
C(1)-N(1)-N(2)-C(4)	14.1(3)
N(2)-N(1)-C(1)-C(2)	4.8(4)
N(2)-N(1)-C(1)-C(12)	-176.1(2)
N(1)-C(1)-C(2)-C(3)	-9.5(4)
C(12)-C(1)-C(2)-C(3)	171.5(3)
N(1)-C(1)-C(2)-C(15)	166.4(2)
C(12)-C(1)-C(2)-C(15)	-12.5(4)
C(1)-C(2)-C(3)-C(4)	-4.5(4)
C(15)-C(2)-C(3)-C(4)	179.5(2)
C(6)-N(3)-C(4)-N(2)	57.9(3)
C(6)-N(3)-C(4)-C(3)	-63.7(3)
C(6)-N(3)-C(4)-C(5)	-179.7(2)
N(1)-N(2)-C(4)-N(3)	-147.6(2)
C(13)-N(2)-C(4)-N(3)	36.3(3)
N(1)-N(2)-C(4)-C(3)	-24.6(3)
C(13)-N(2)-C(4)-C(3)	159.3(2)
N(1)-N(2)-C(4)-C(5)	91.8(3)
C(13)-N(2)-C(4)-C(5)	-84.3(3)
C(2)-C(3)-C(4)-N(3)	144.7(2)
C(2)-C(3)-C(4)-N(2)	19.3(3)
C(2)-C(3)-C(4)-C(5)	-99.2(3)
N(3)-C(4)-C(5)-F(1)	-53.3(3)
N(2)-C(4)-C(5)-F(1)	71.6(3)
C(3)-C(4)-C(5)-F(1)	-171.5(2)
N(3)-C(4)-C(5)-F(2)	69.0(3)
N(2)-C(4)-C(5)-F(2)	-166.1(2)
C(3)-C(4)-C(5)-F(2)	-49.2(3)
N(3)-C(4)-C(5)-F(3)	-173.3(2)
N(2)-C(4)-C(5)-F(3)	-48.4(3)
C(3)-C(4)-C(5)-F(3)	68.5(3)
C(4)-N(3)-C(6)-C(11)	5.2(4)
C(4)-N(3)-C(6)-C(7)	-175.4(2)
C(11)-C(6)-C(7)-C(8)	-0.5(4)
N(3)-C(6)-C(7)-C(8)	-179.9(2)
C(6)-C(7)-C(8)-C(9)	1.5(4)

C(7)-C(8)-C(9)-C(10)	-1.1(4)
C(7)-C(8)-C(9)-N(4)	178.7(2)
O(4)-N(4)-C(9)-C(10)	15.8(4)
O(3)-N(4)-C(9)-C(10)	-163.9(2)
O(4)-N(4)-C(9)-C(8)	-164.0(2)
O(3)-N(4)-C(9)-C(8)	16.2(4)
C(8)-C(9)-C(10)-C(11)	-0.4(4)
N(4)-C(9)-C(10)-C(11)	179.8(2)
C(9)-C(10)-C(11)-C(6)	1.5(4)
N(3)-C(6)-C(11)-C(10)	178.3(2)
C(7)-C(6)-C(11)-C(10)	-1.0(4)
C(14)-O(2)-C(13)-O(1)	0.7(5)
C(14)-O(2)-C(13)-N(2)	179.8(3)
N(1)-N(2)-C(13)-O(1)	-162.9(3)
C(4)-N(2)-C(13)-O(1)	13.5(4)
N(1)-N(2)-C(13)-O(2)	18.0(3)
C(4)-N(2)-C(13)-O(2)	-165.6(2)
C(16)-O(6)-C(15)-O(5)	5.2(5)
C(16)-O(6)-C(15)-C(2)	-177.2(2)
C(3)-C(2)-C(15)-O(5)	173.7(3)
C(1)-C(2)-C(15)-O(5)	-2.3(4)
C(3)-C(2)-C(15)-O(6)	-3.9(3)
C(1)-C(2)-C(15)-O(6)	-179.8(2)
C(15)-O(6)-C(16)-C(17)	-168.9(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **4e** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14C)...O(4)#1	0.96	2.54	3.275(4)	133.8
C(11)-H(11)...N(2)	0.93	2.64	3.130(4)	113.3
C(11)-H(11)...O(5)#2	0.93	2.48	3.135(3)	127.7
C(3)-H(3A)...O(3)#3	0.93	2.42	3.306(3)	159.0
N(3)-H(3)...O(1)#4	0.86	2.31	3.052(3)	145.3

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 -x+1,-y+1,-z+2 #3 -x+1,-y+1,-z+1
#4 -x+1,-y,-z+1

6. References

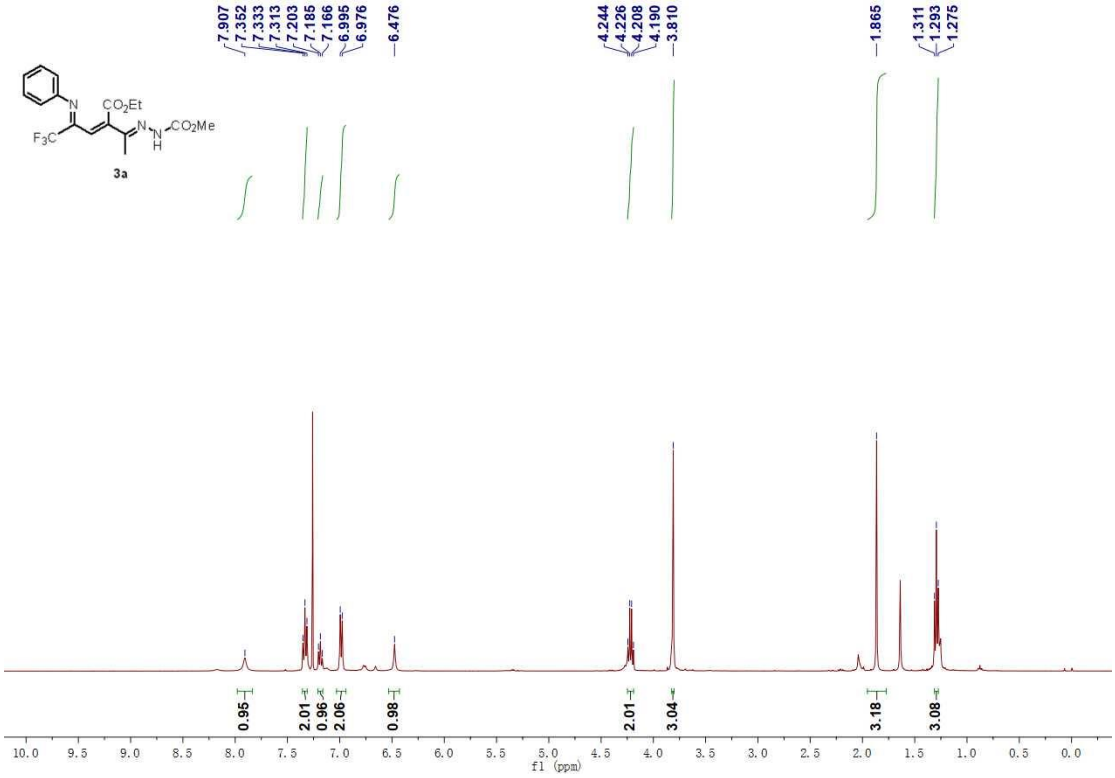
1 S. Wen, Y. Chen, Q. Tian, Y. Zhang and G. Cheng, *J. Org. Chem.*, 2022, **87**, 1124-1132.

2. A. G. Schultz and W. K. Hagmann, *J. Org. Chem.*, 1978, **43**, 3391-3393.

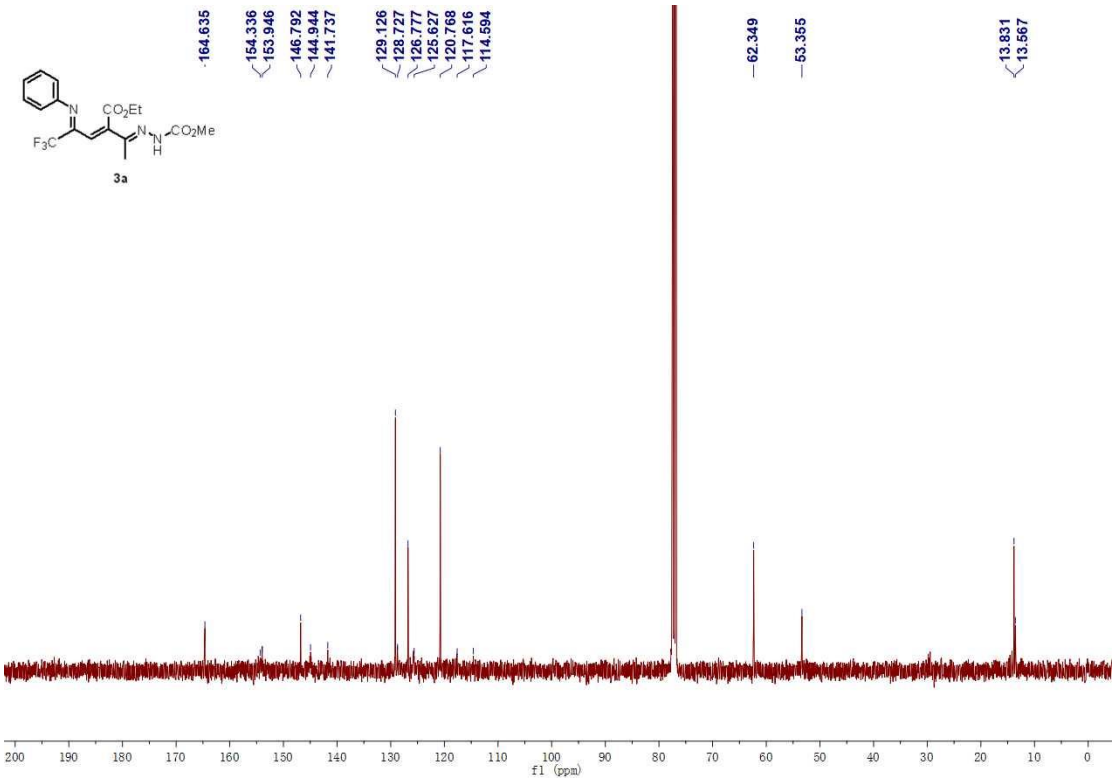
3. O. A. Attanasi, G. Favi, G. Giorgi, R. Majer, F. R. Perrulli and S. Santeusanio, *Org. Biomol. Chem.*, 2014, **12**, 4610-4619.

7. Copies of the NMR spectra

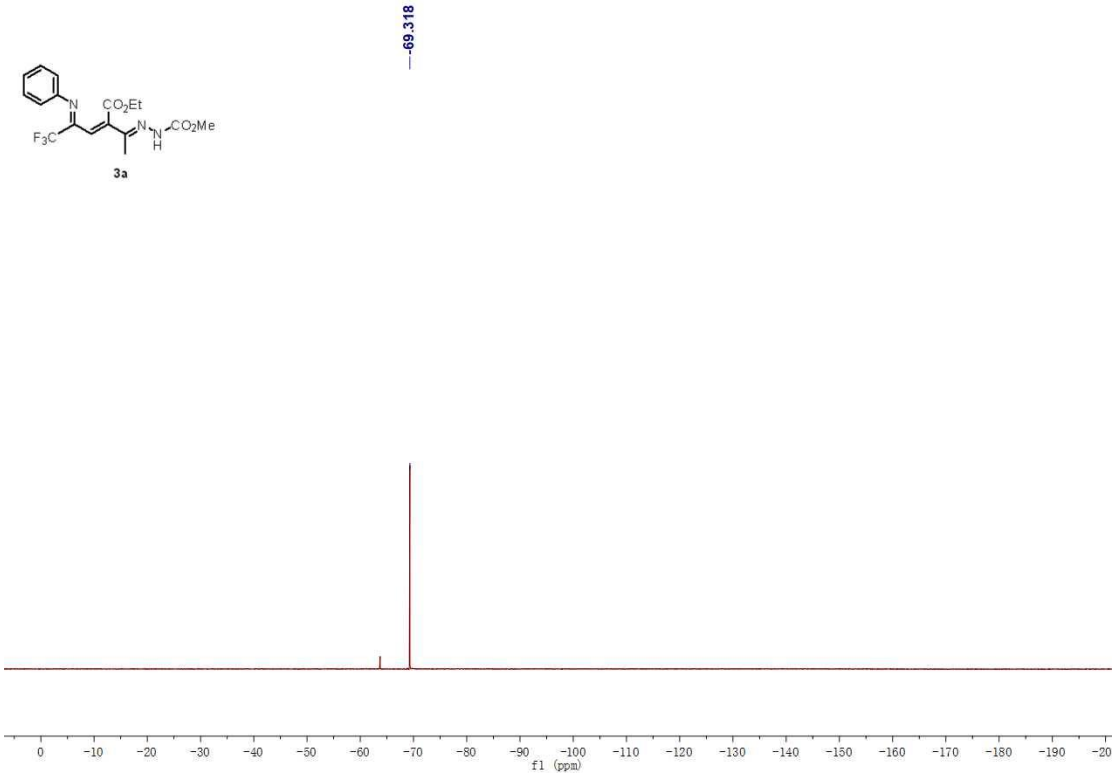
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a



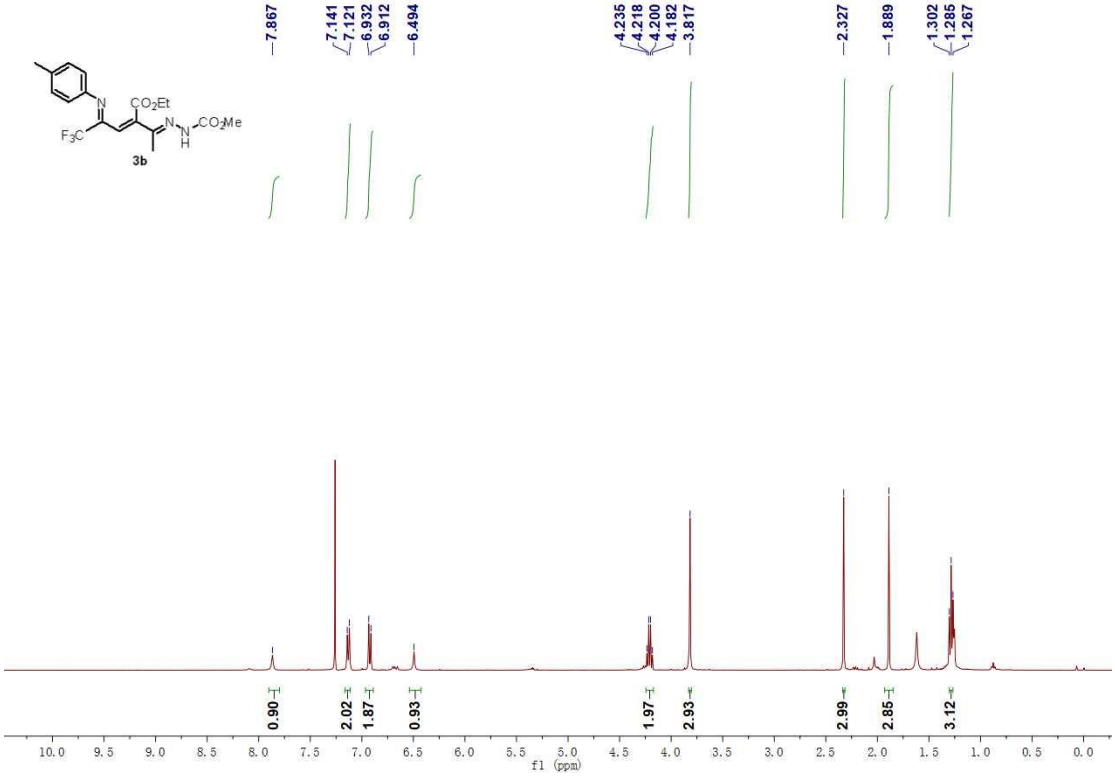
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3a



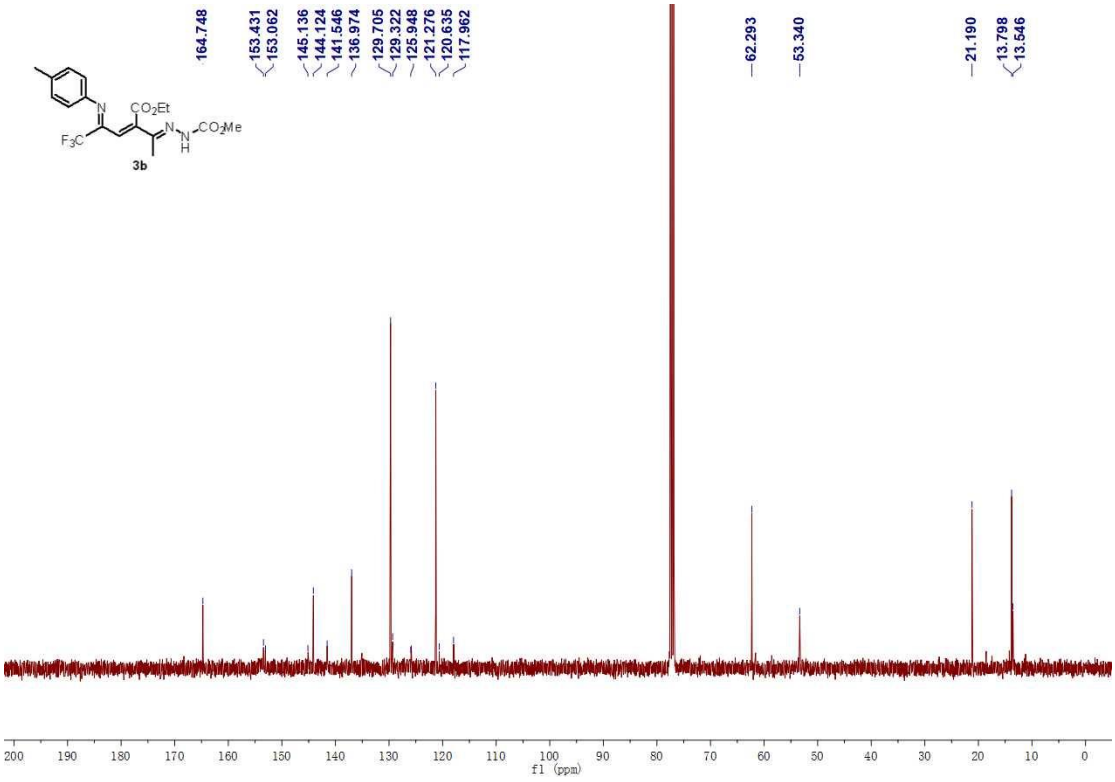
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3a



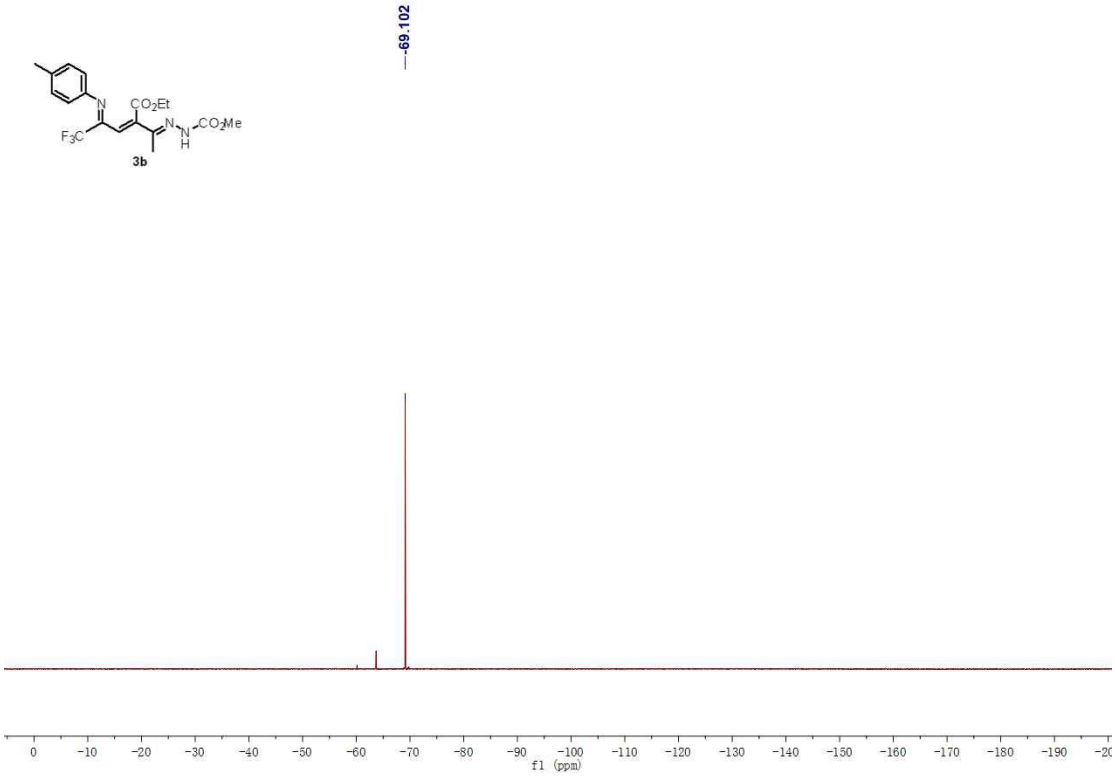
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



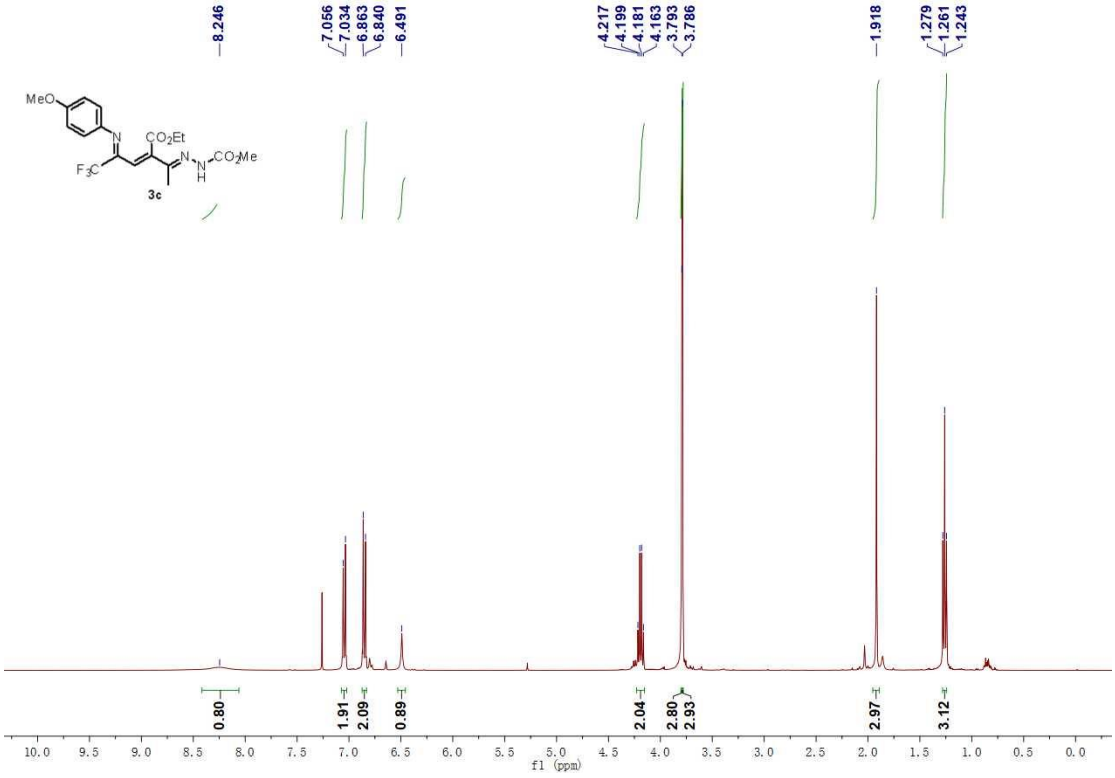
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3b



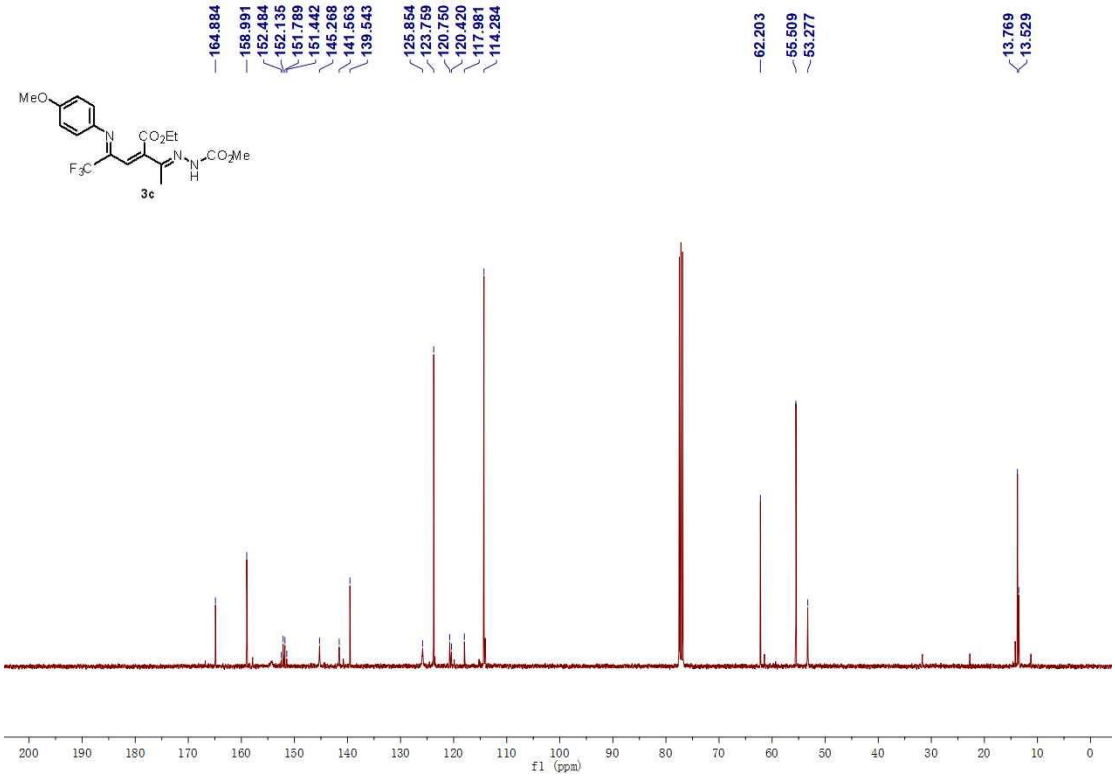
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3b



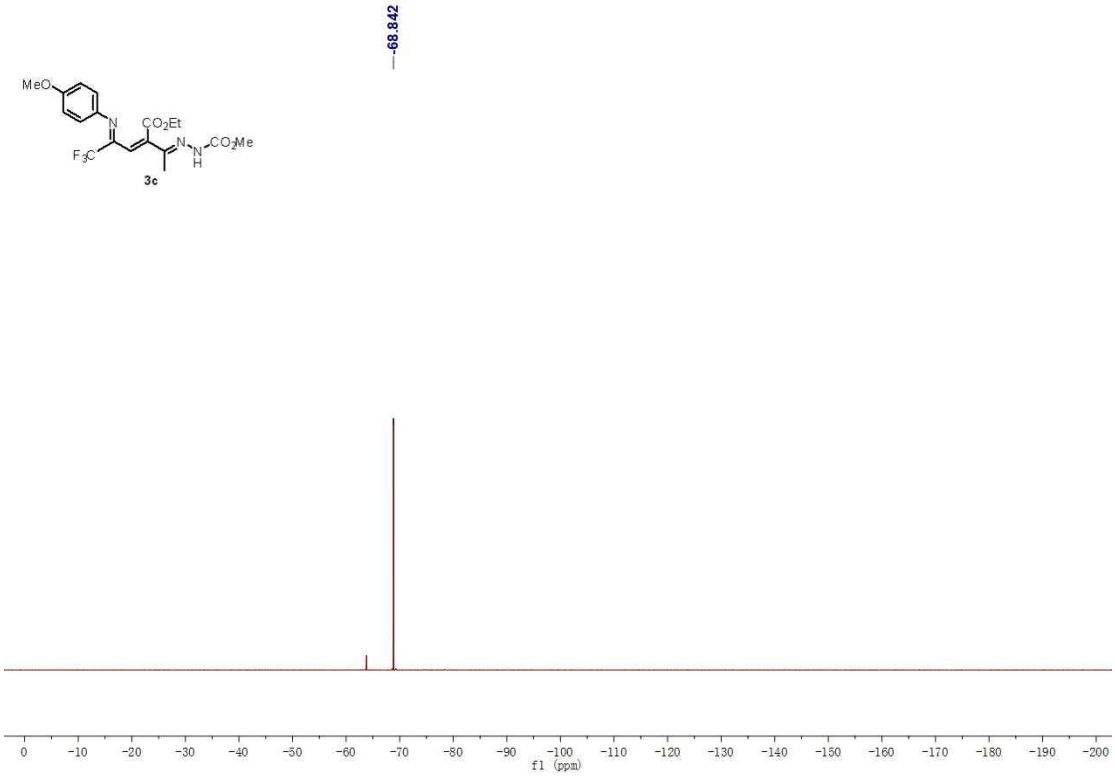
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c



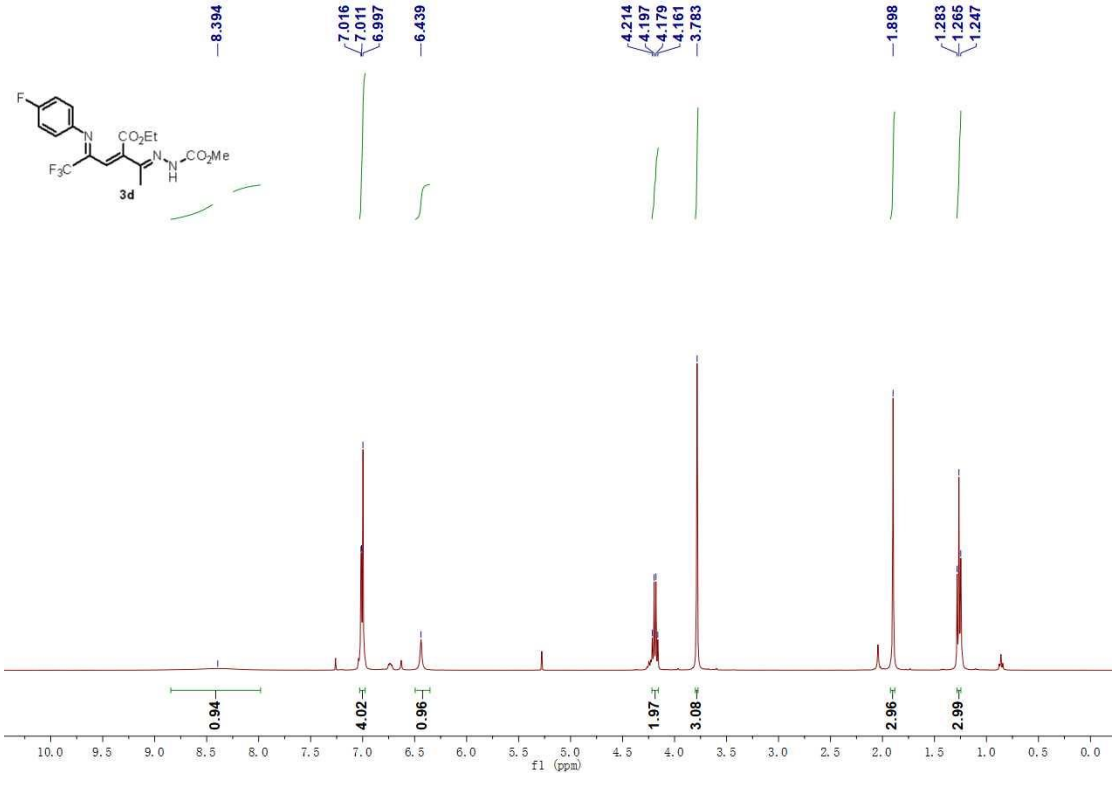
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3c



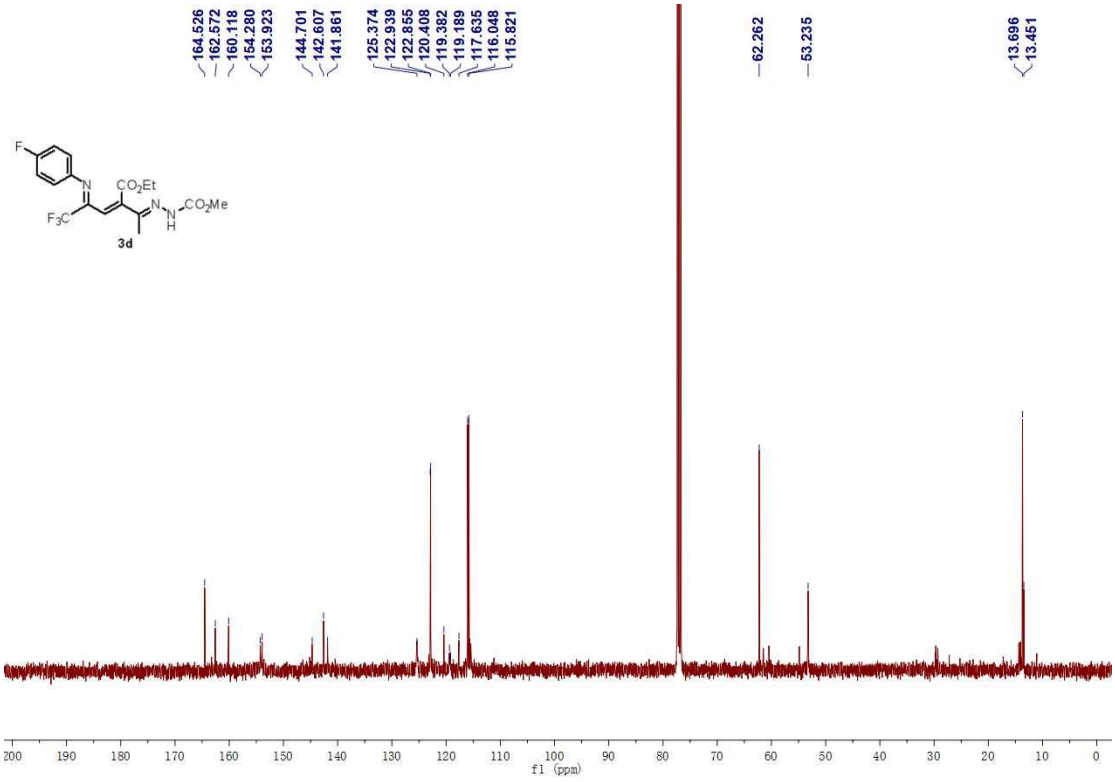
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3c



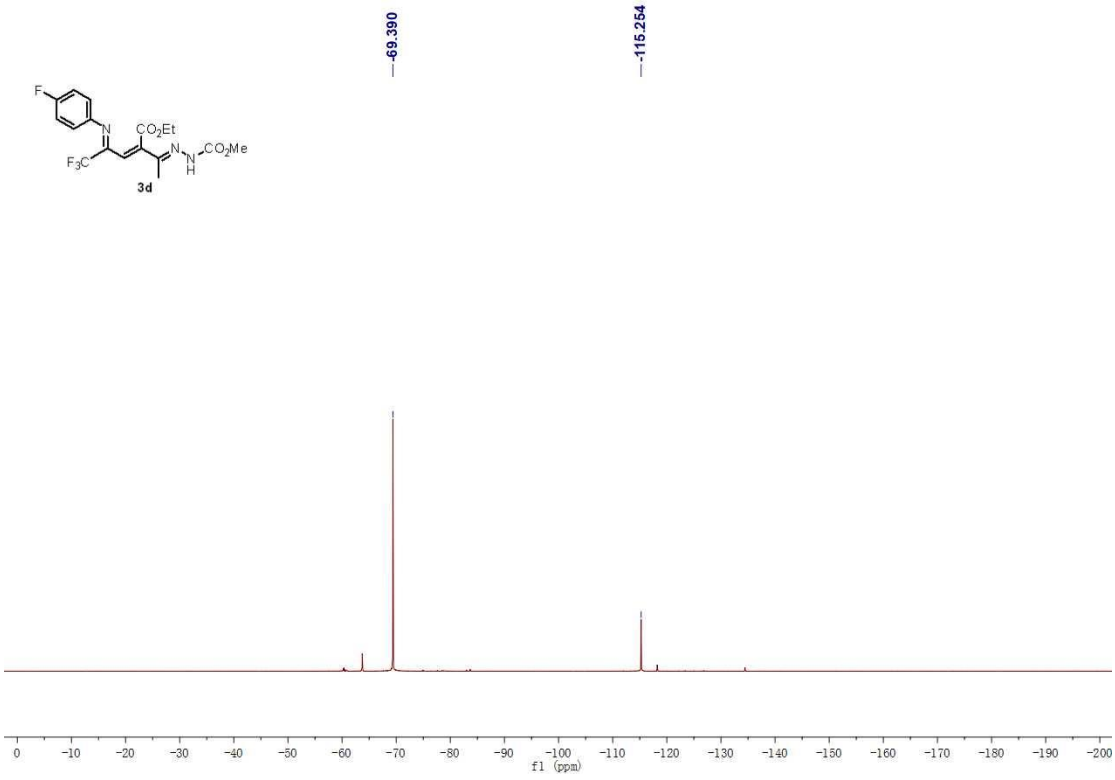
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3d



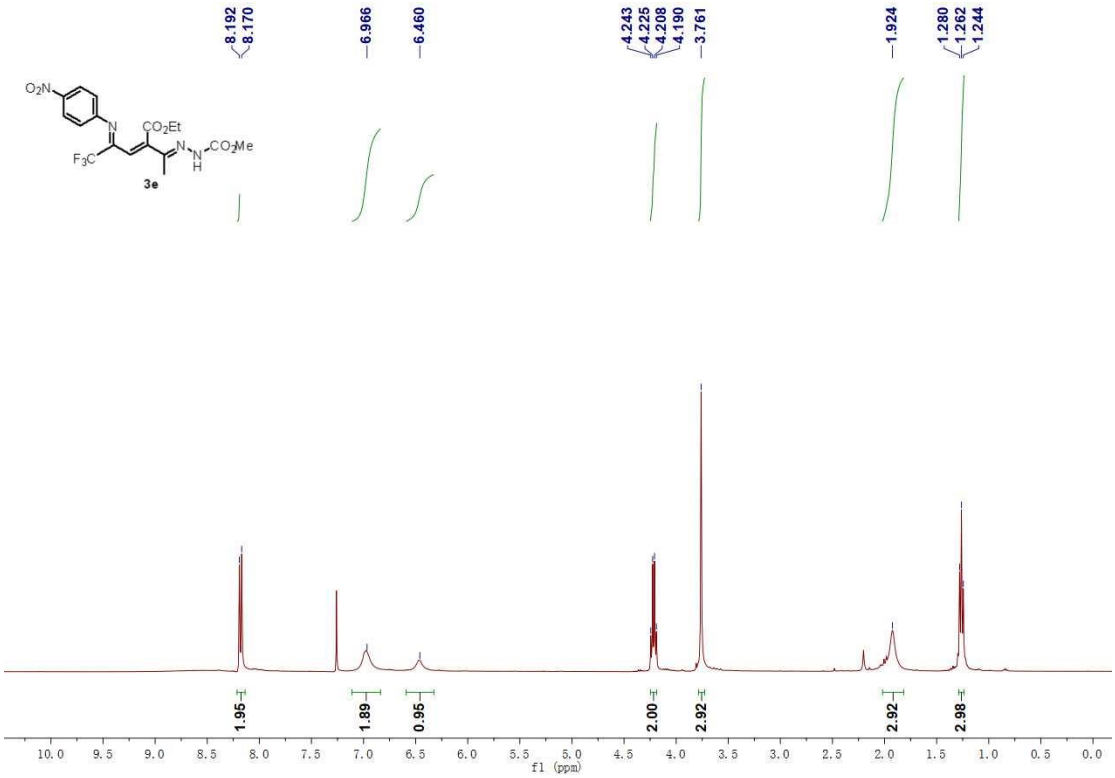
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3d



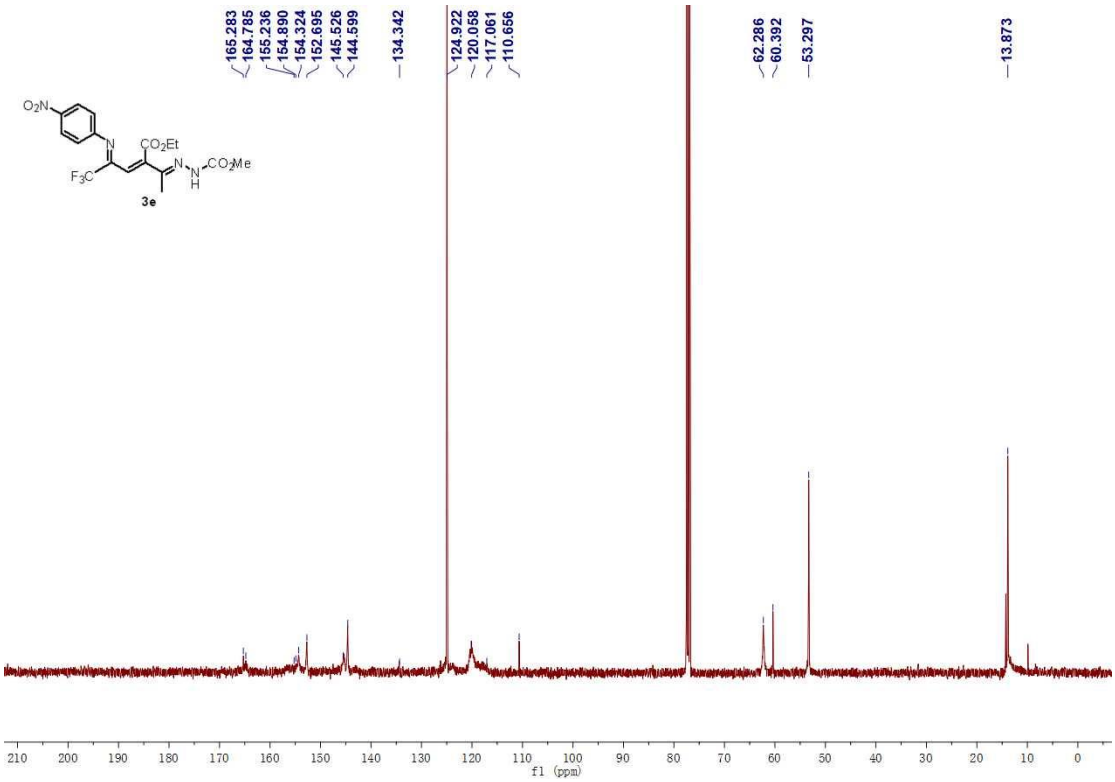
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3d



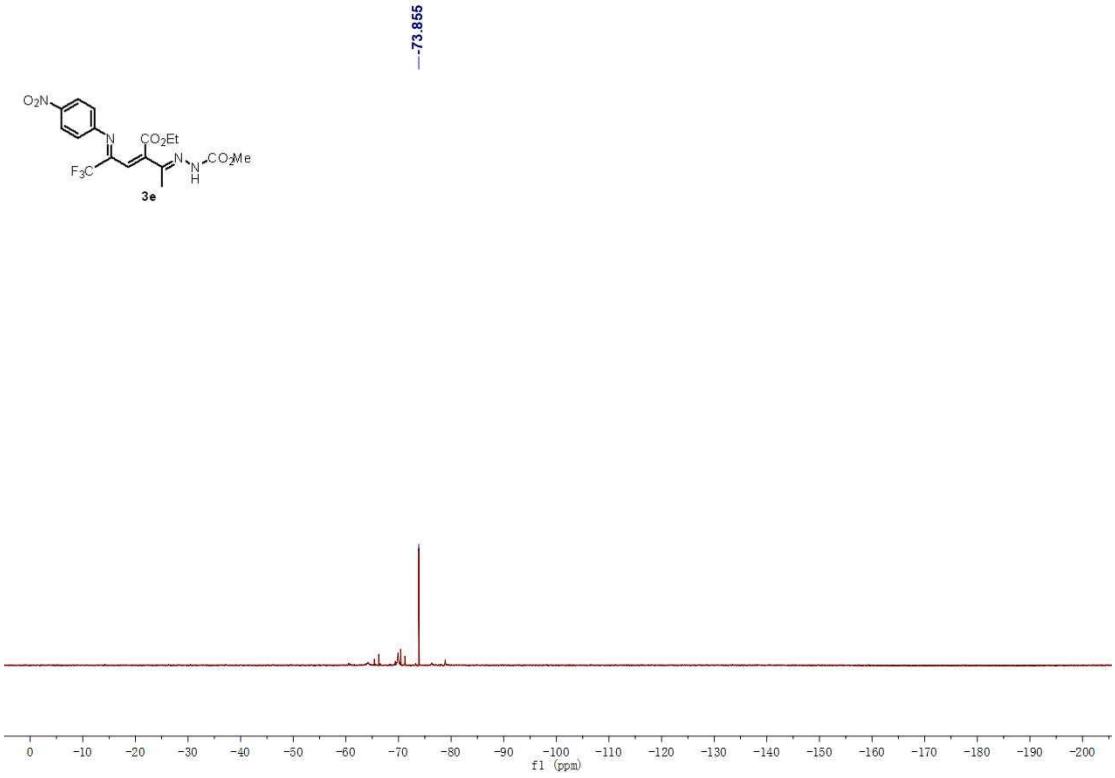
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3e



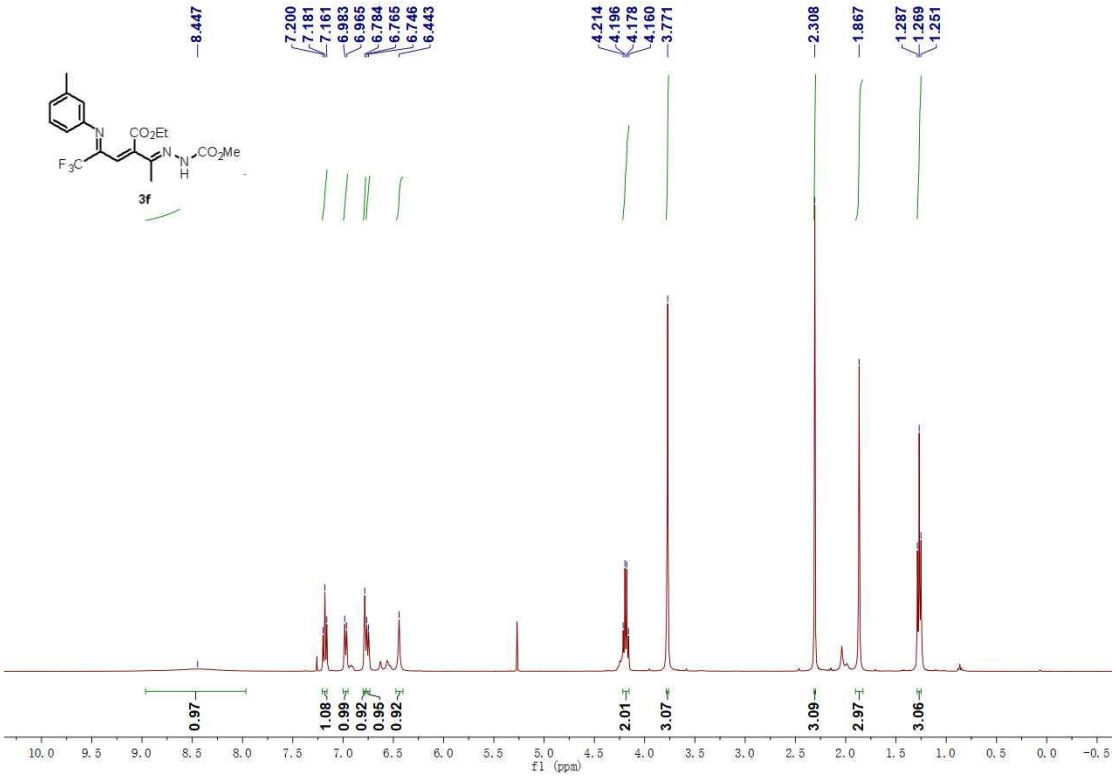
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3e



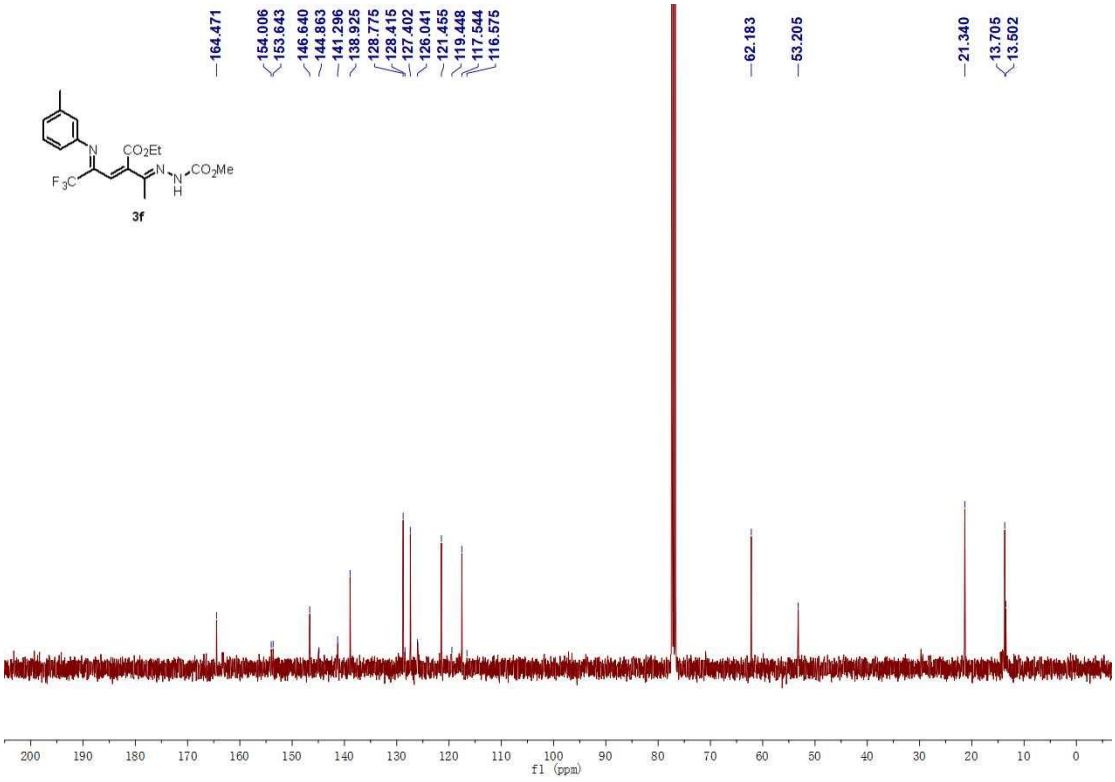
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3e



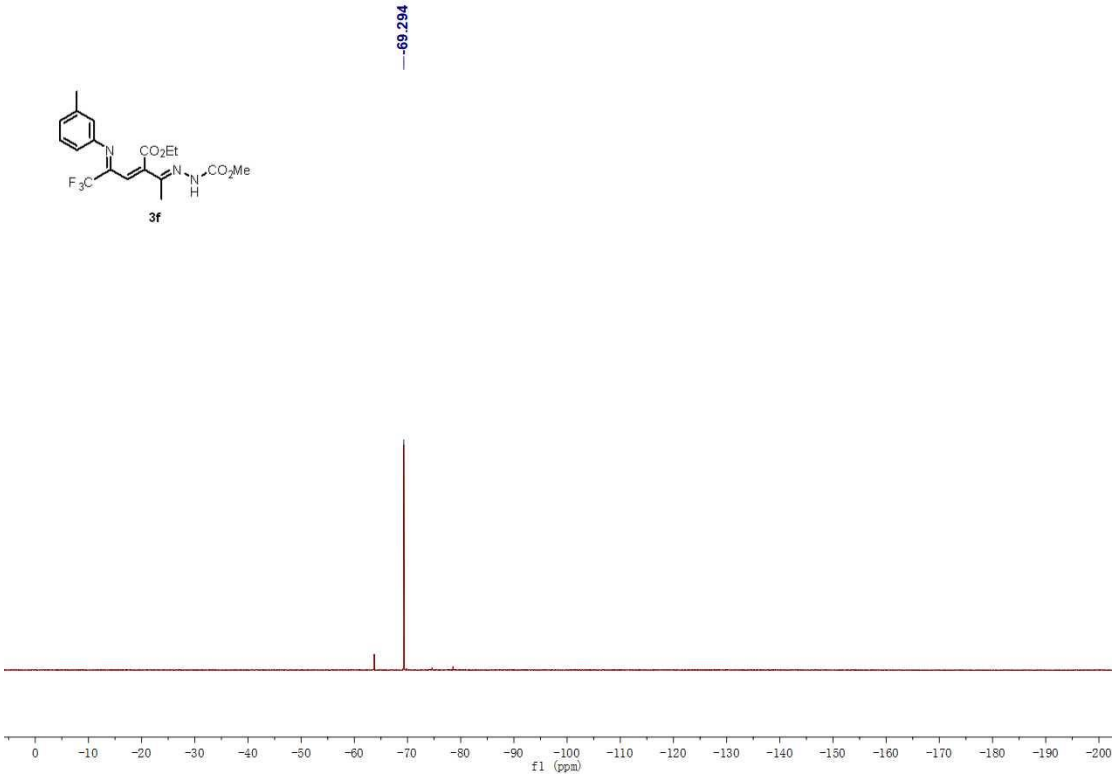
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3f



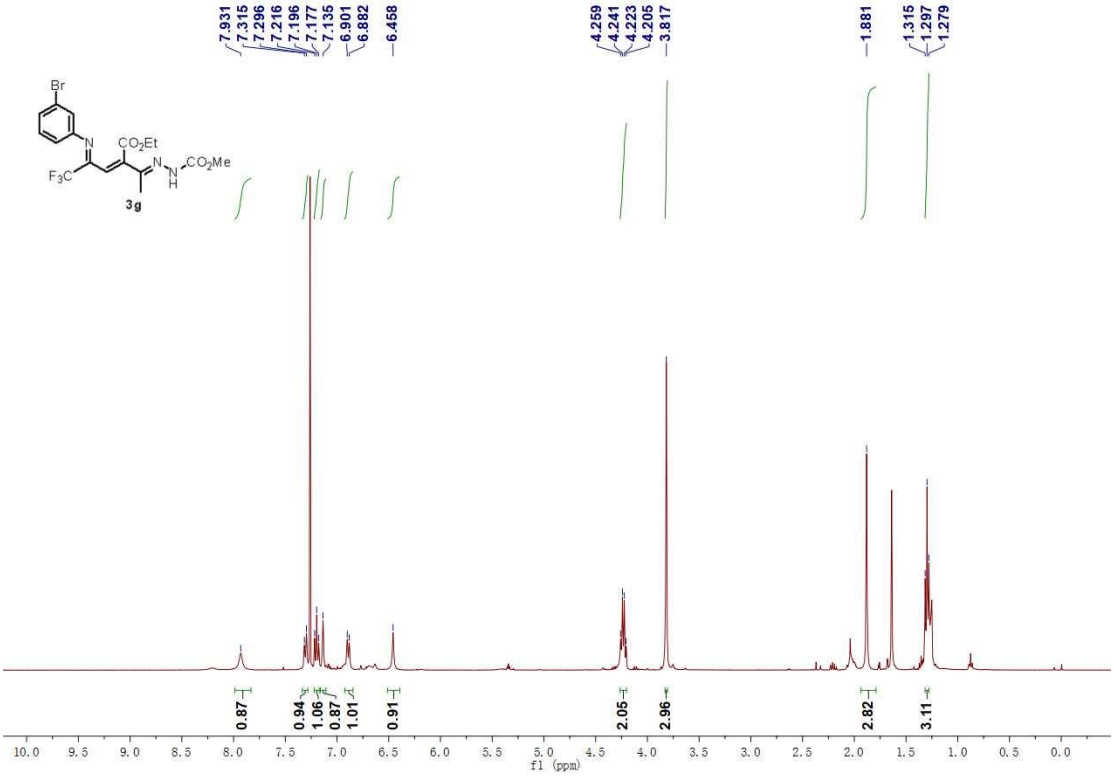
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f



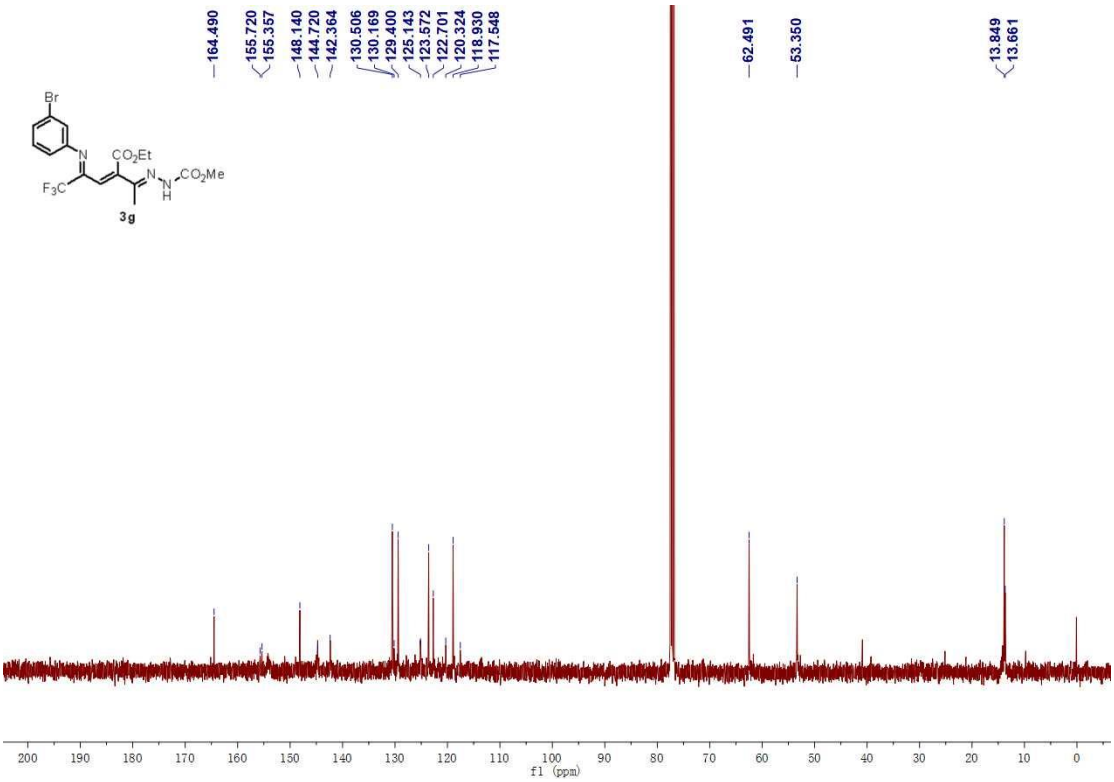
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3f



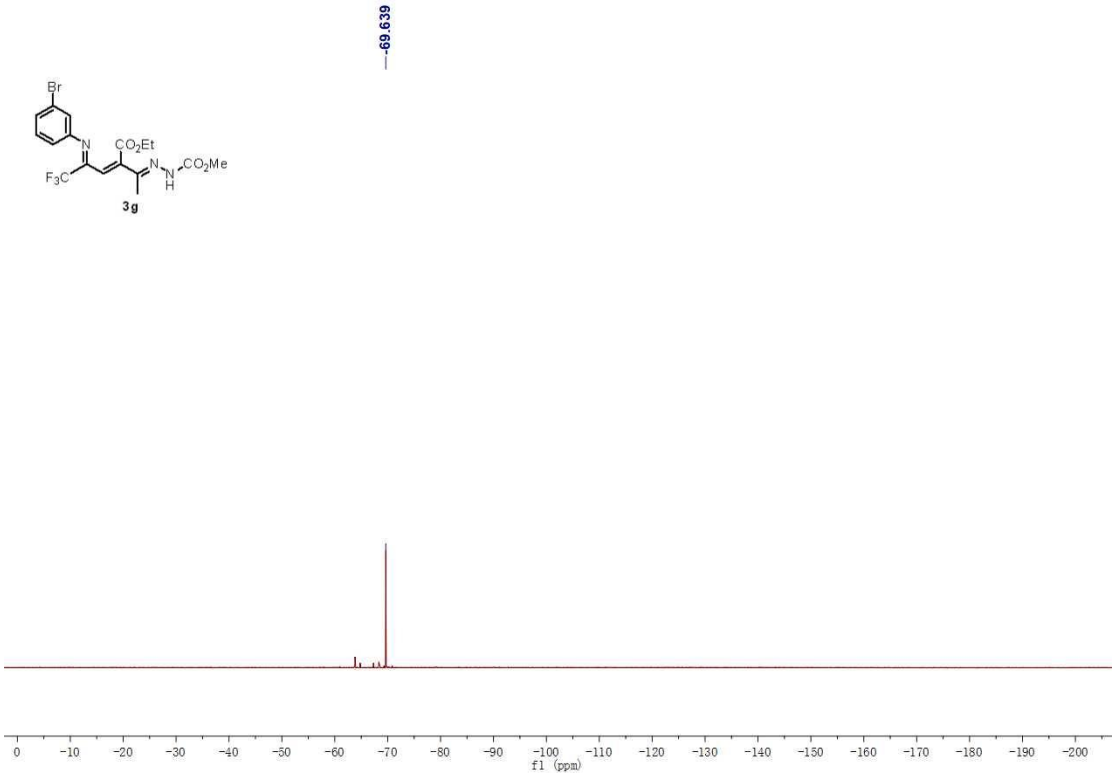
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3g



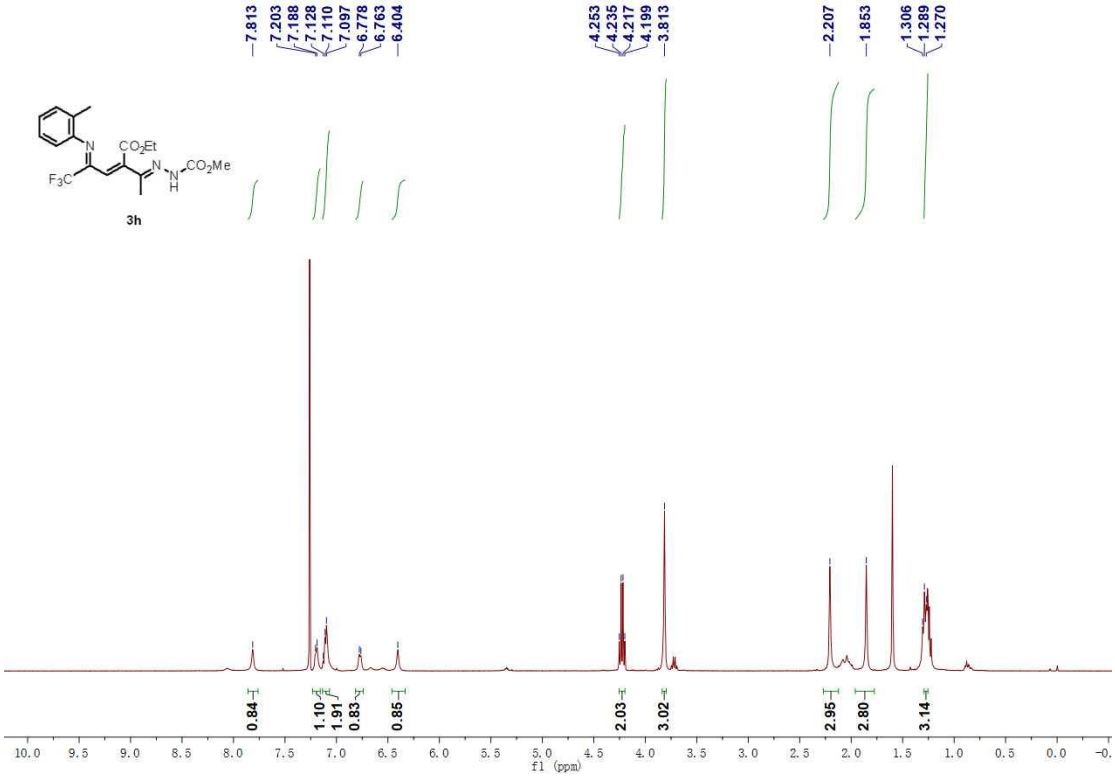
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



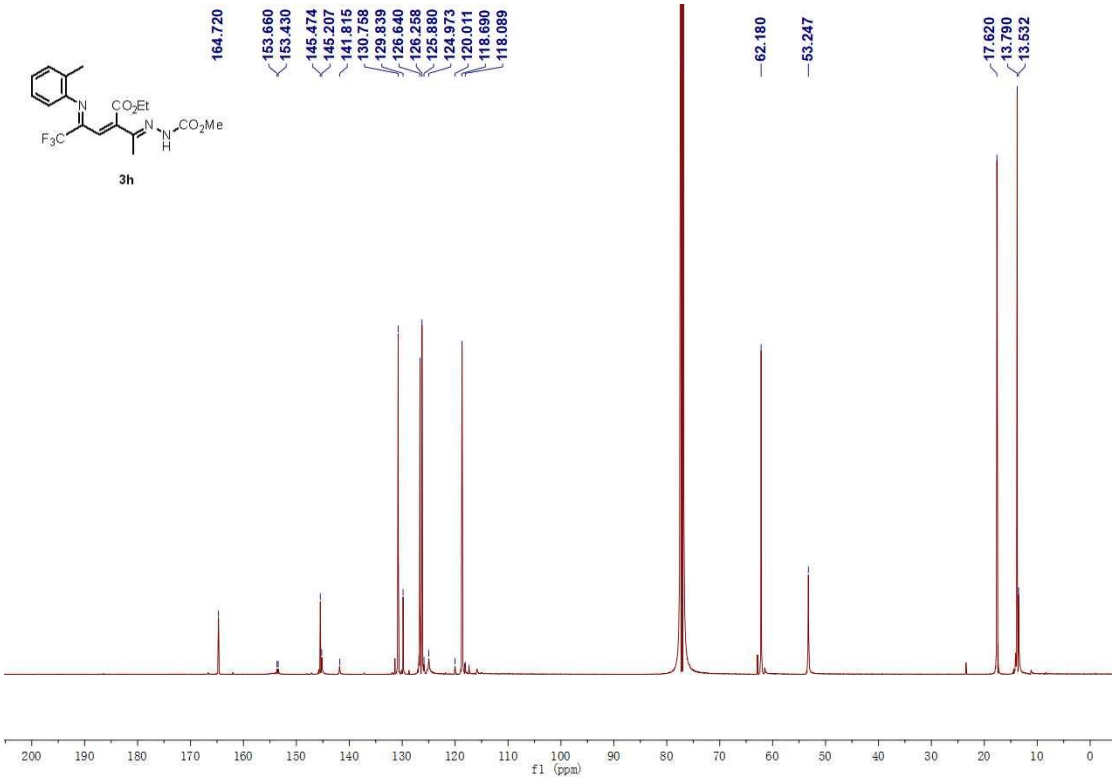
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3g



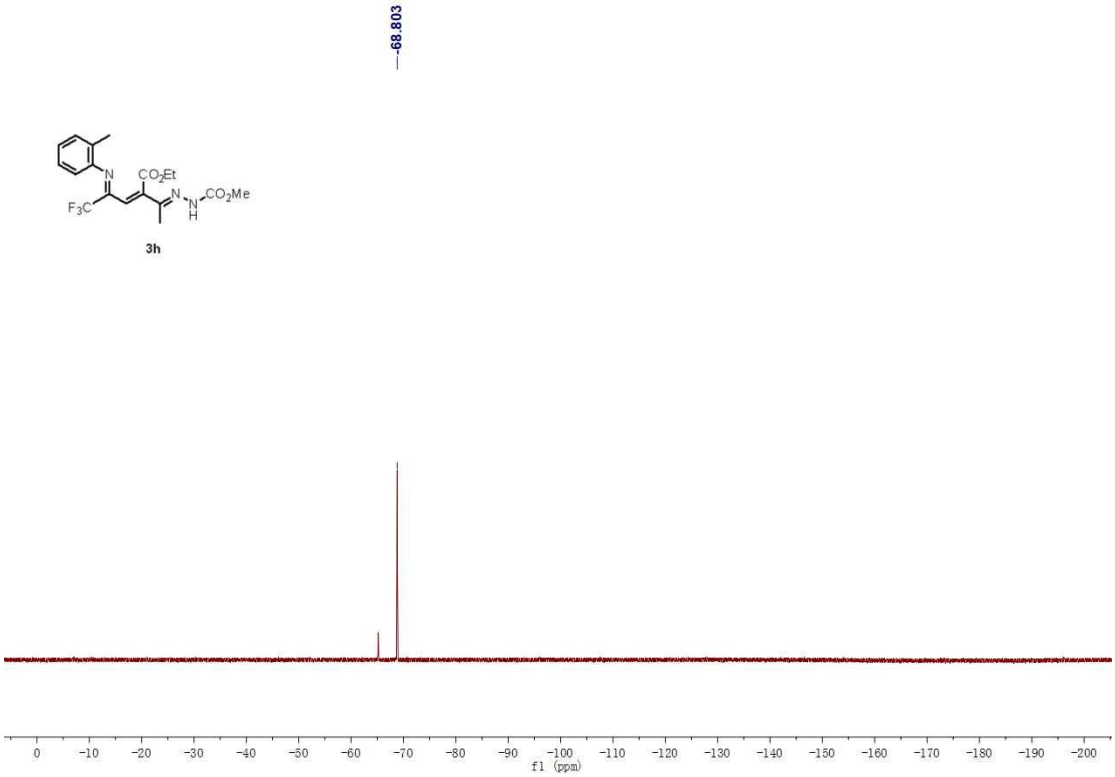
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3h



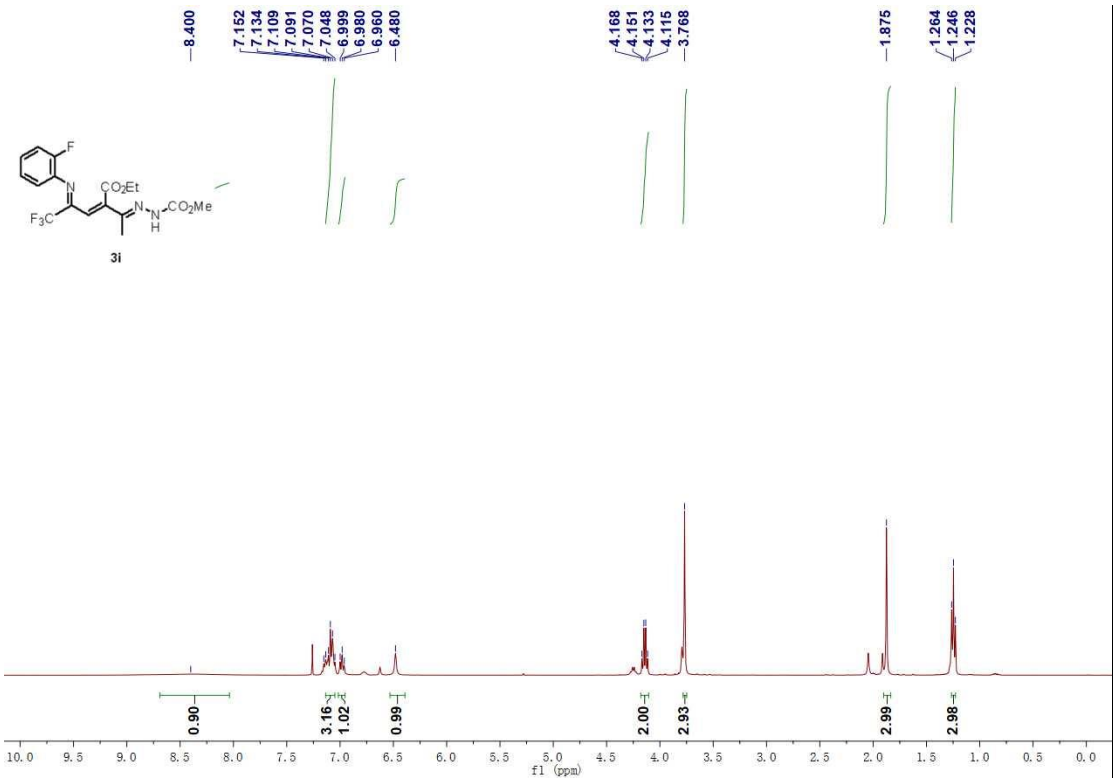
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3h



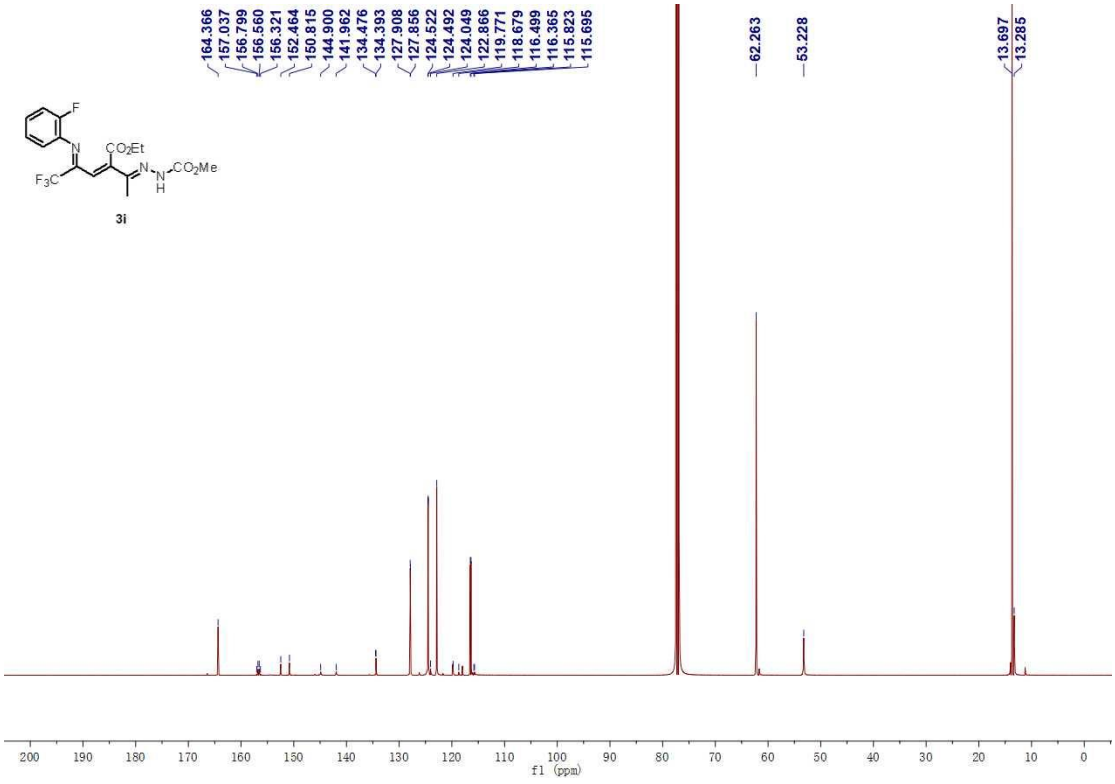
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3h



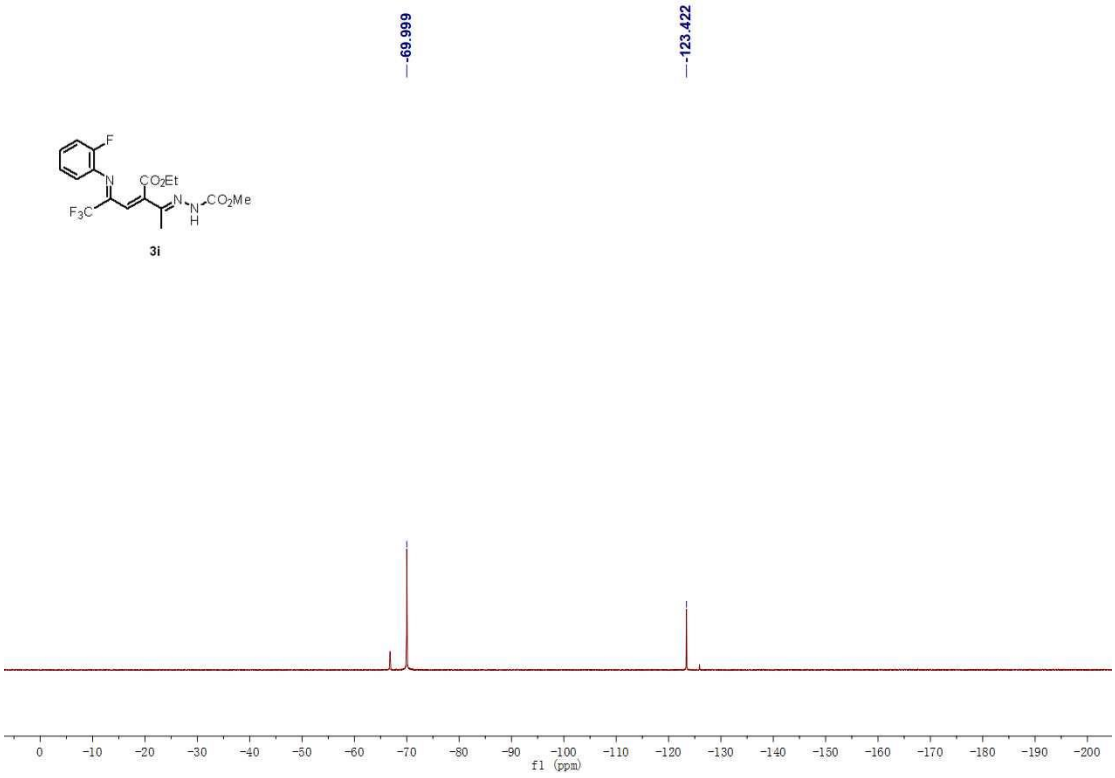
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3i



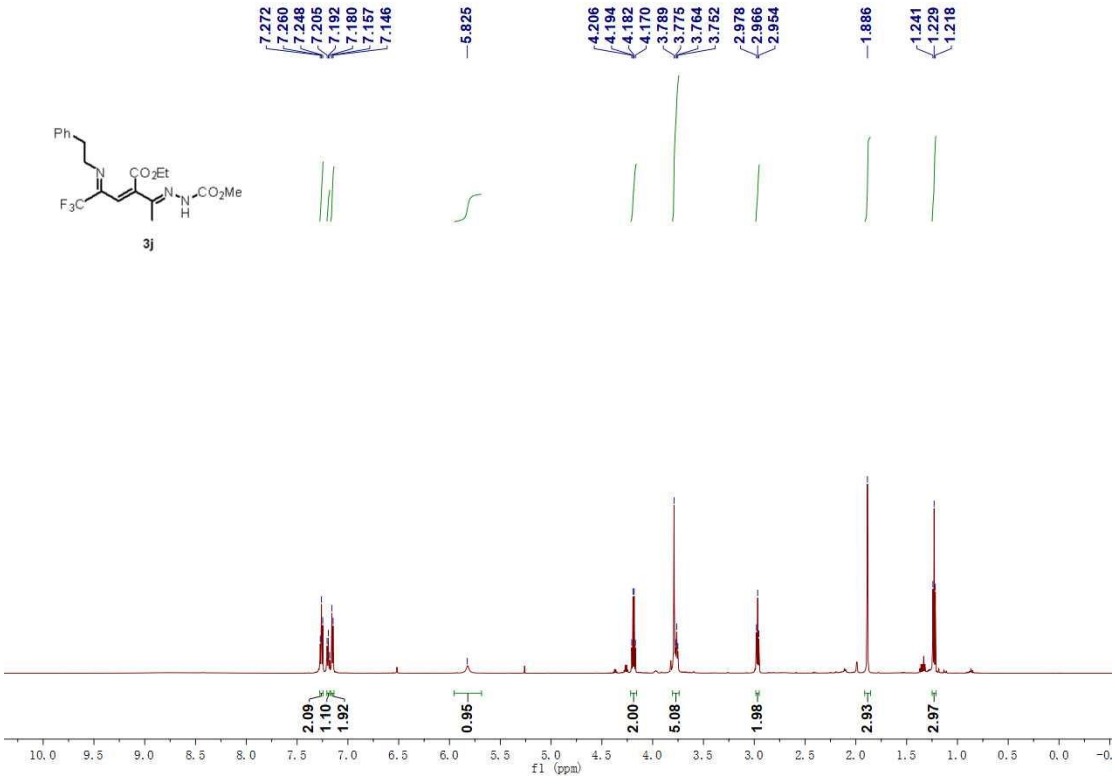
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3i



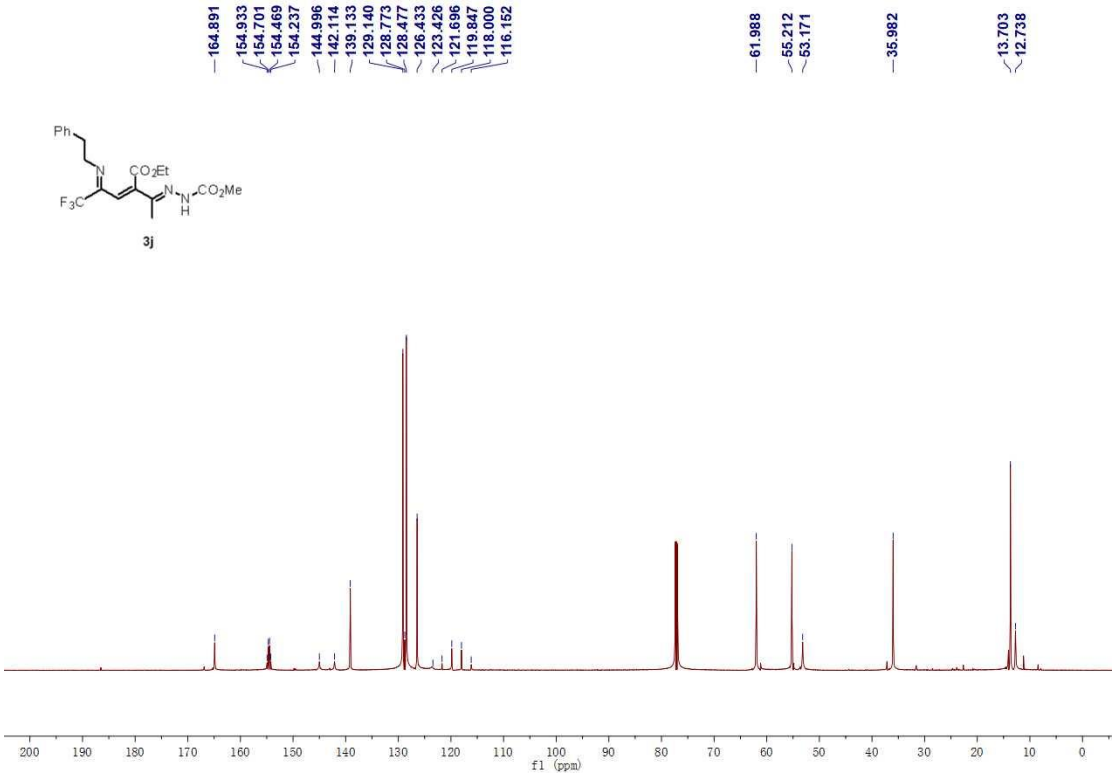
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3i



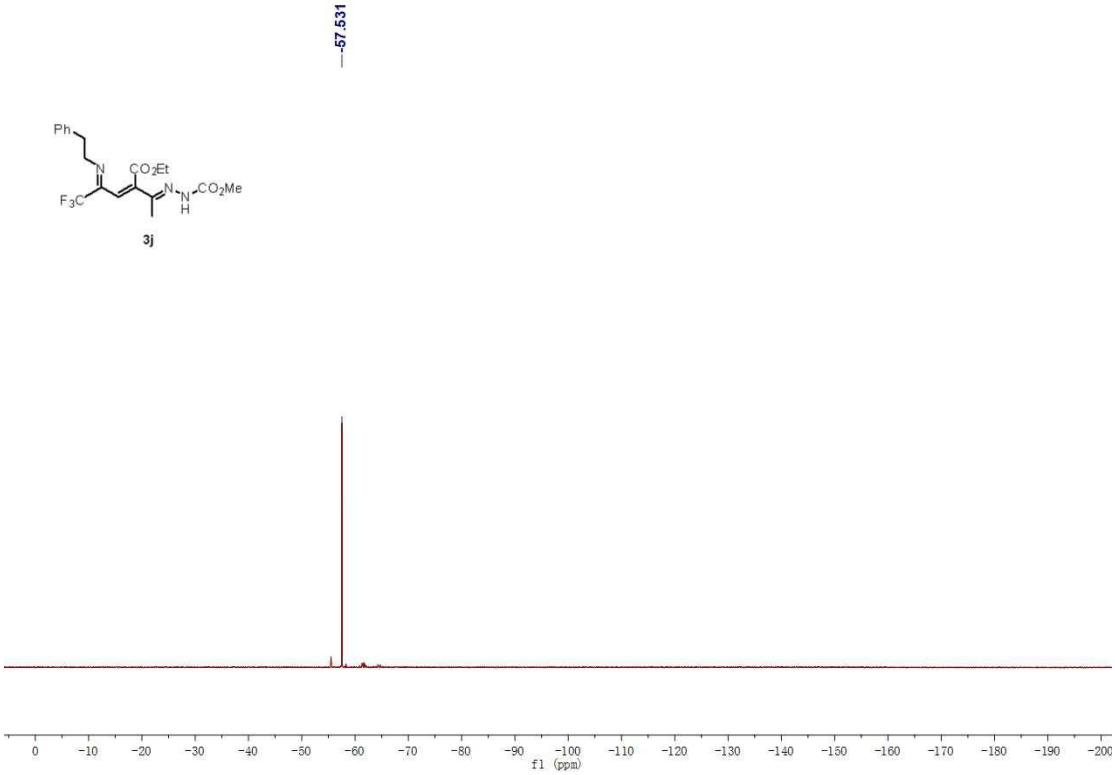
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3j



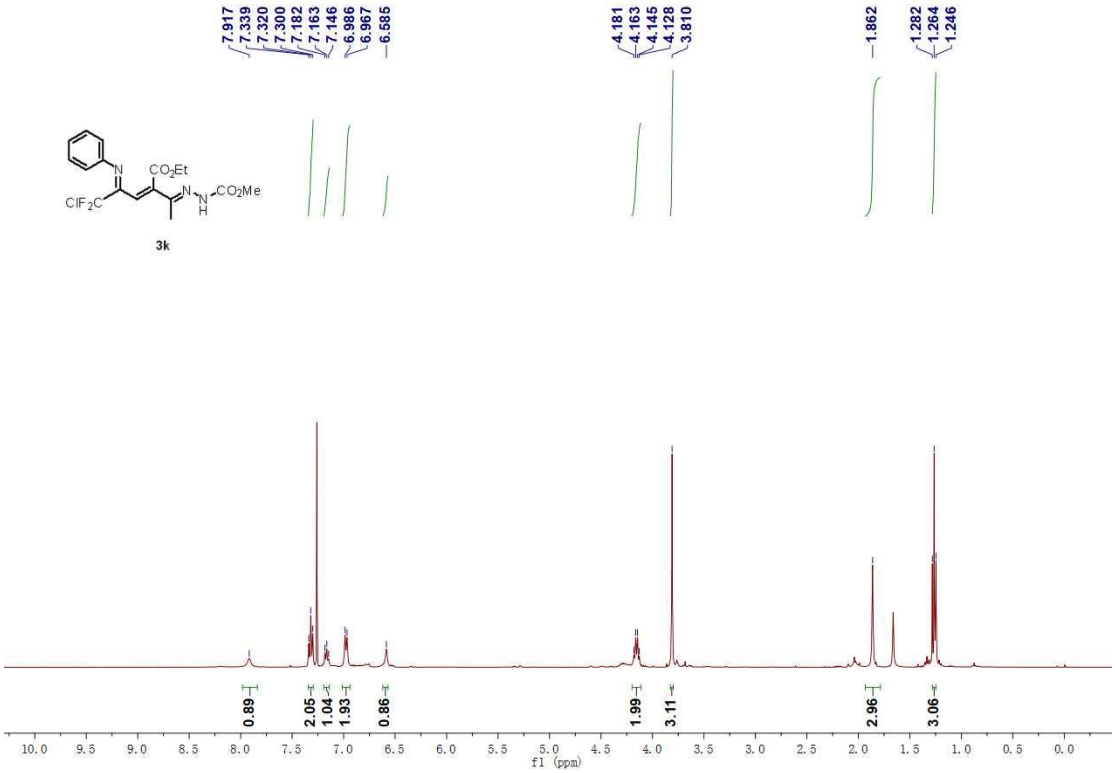
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3j



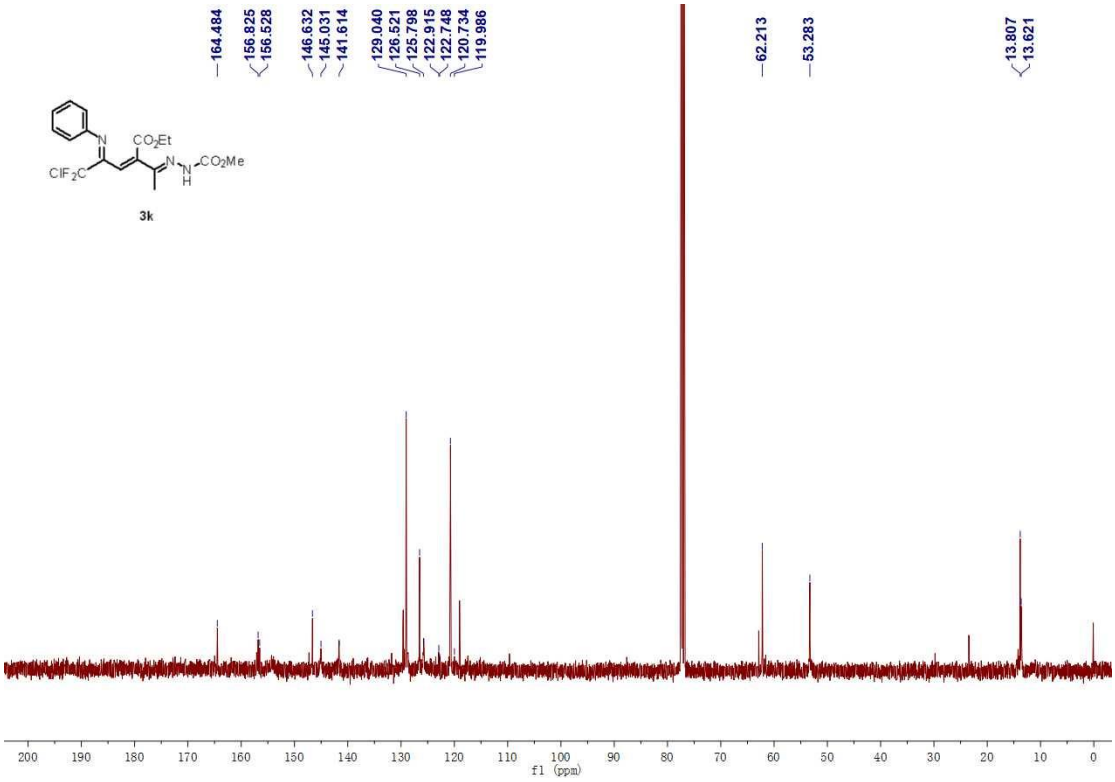
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3j



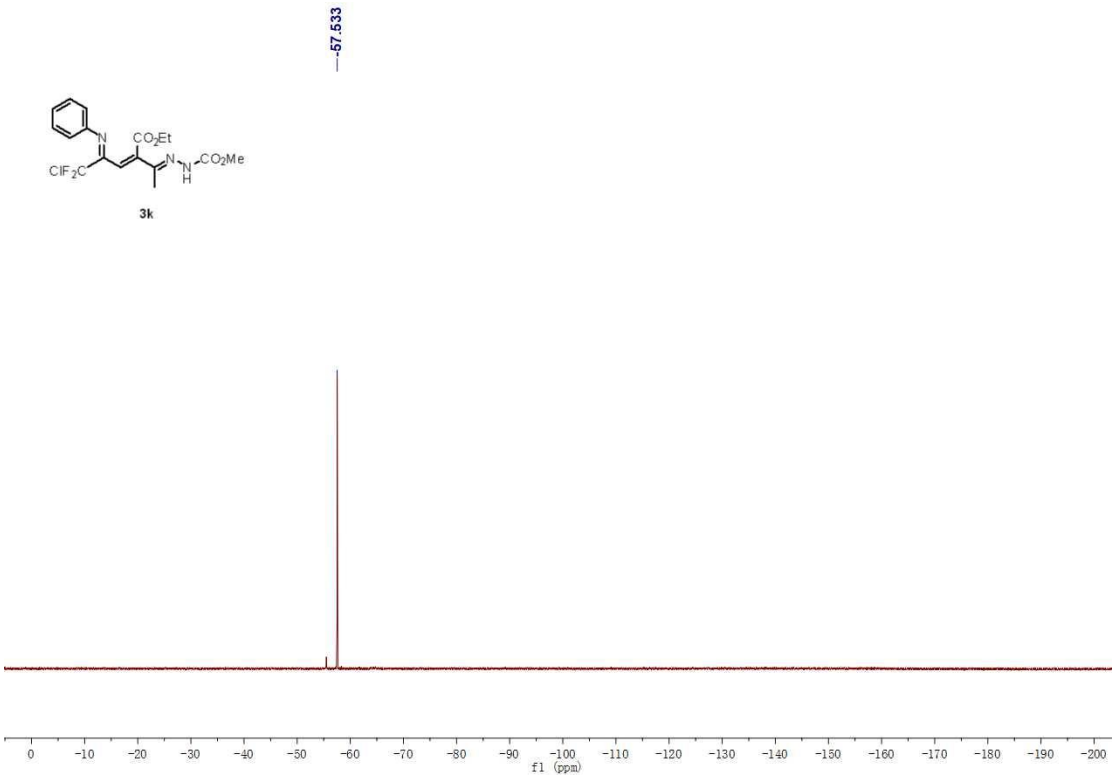
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k



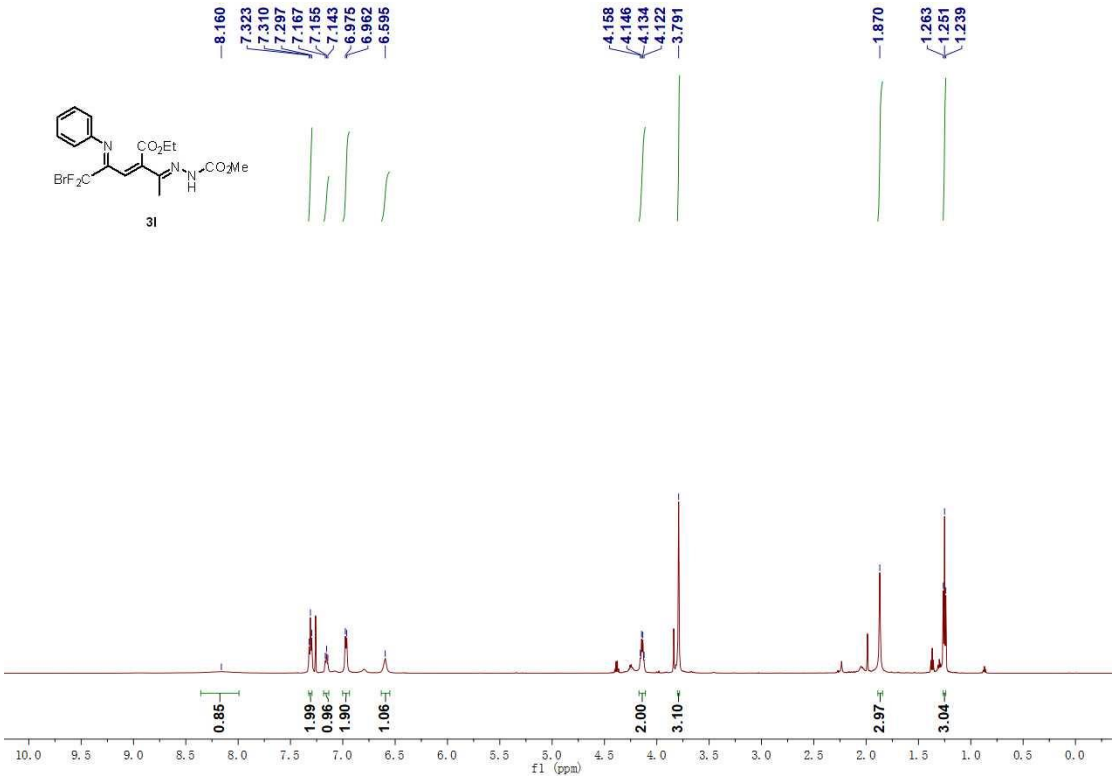
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3k



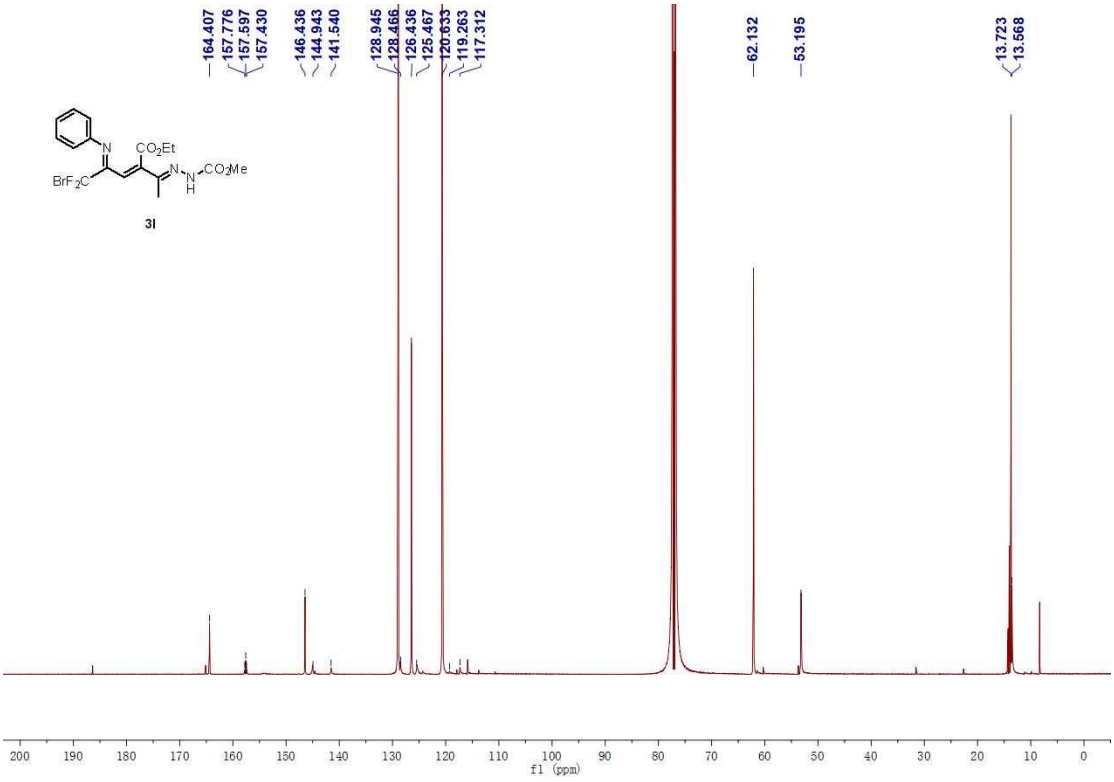
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3k



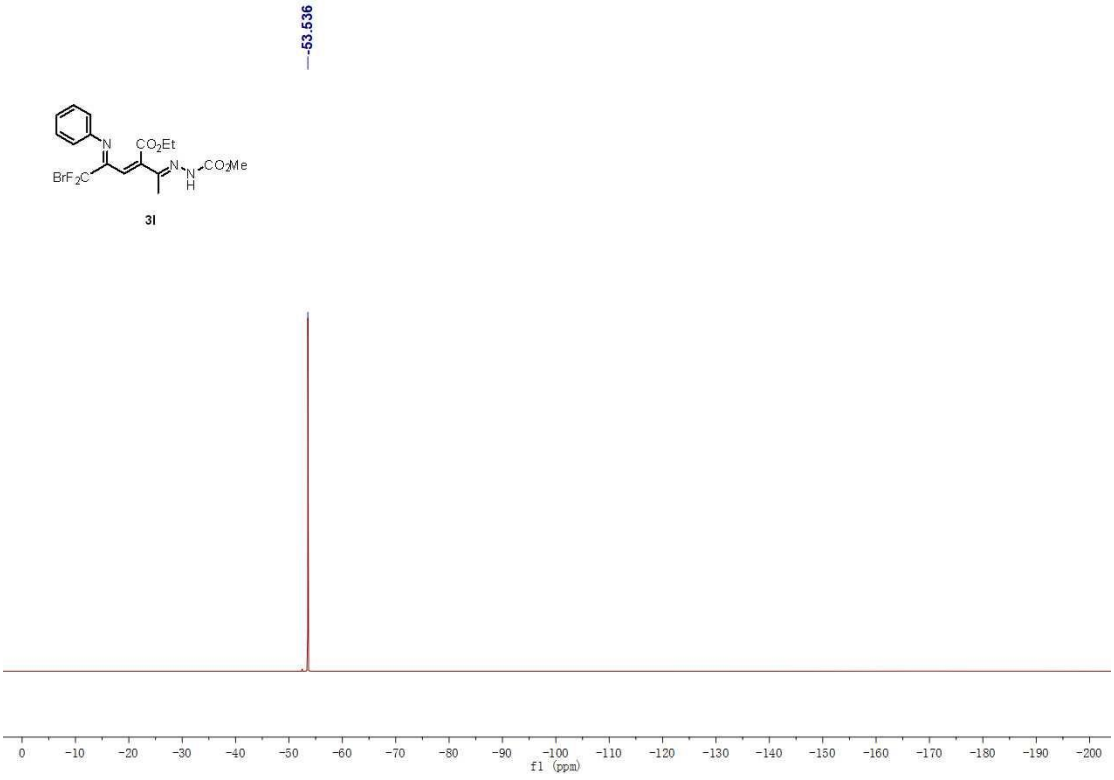
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3l



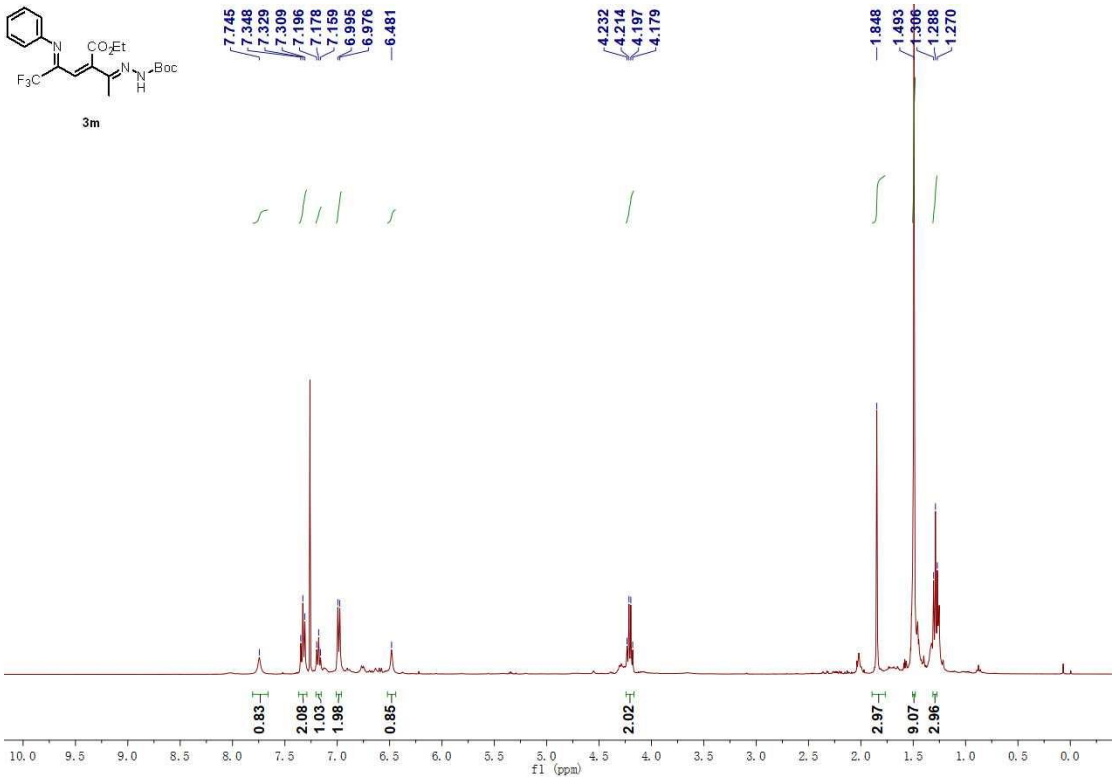
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3l



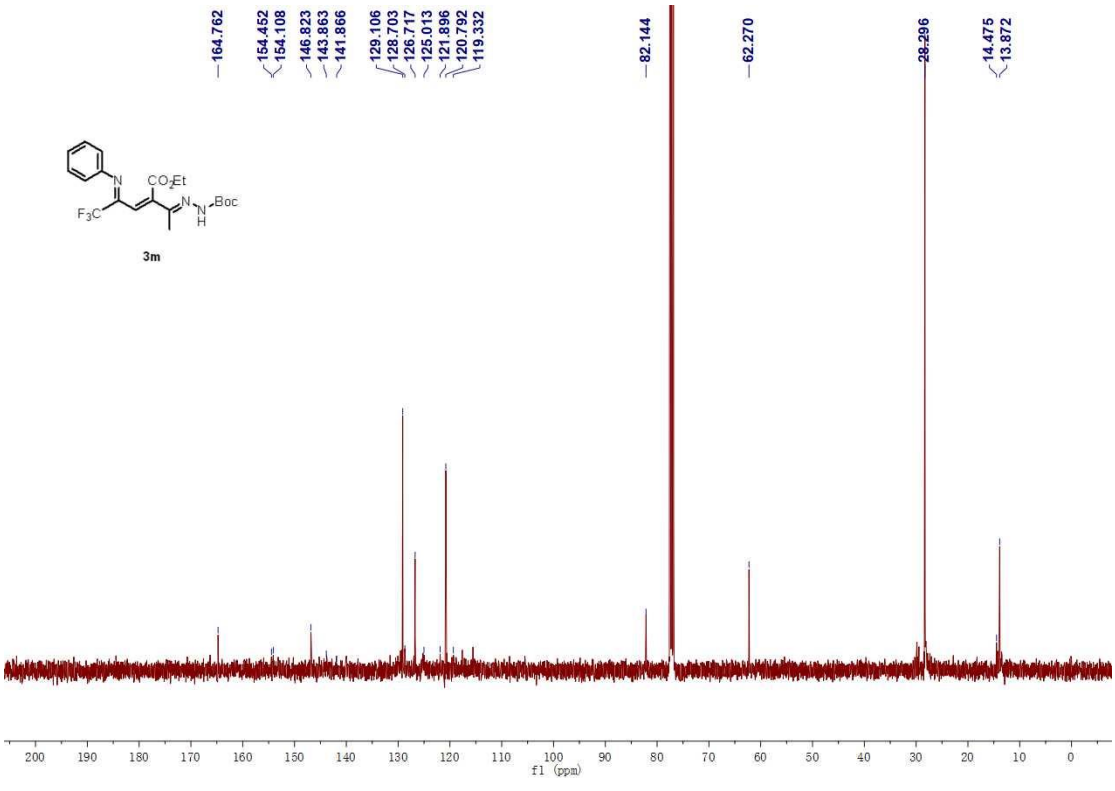
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3l



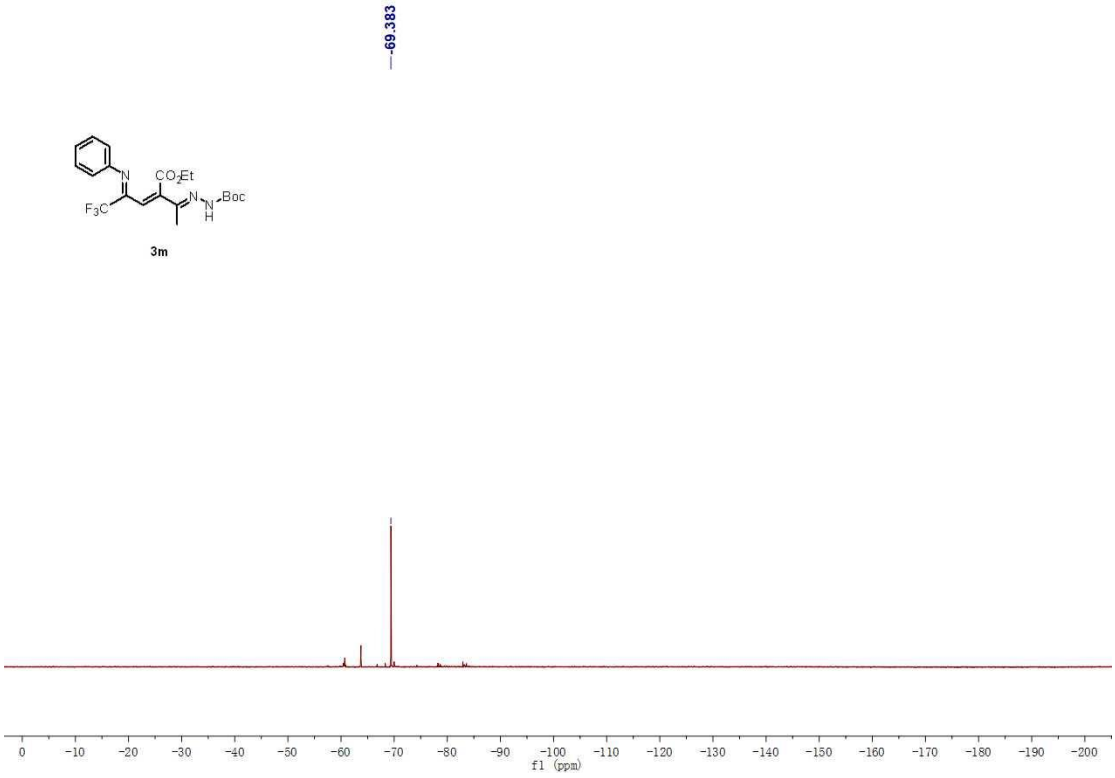
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3m



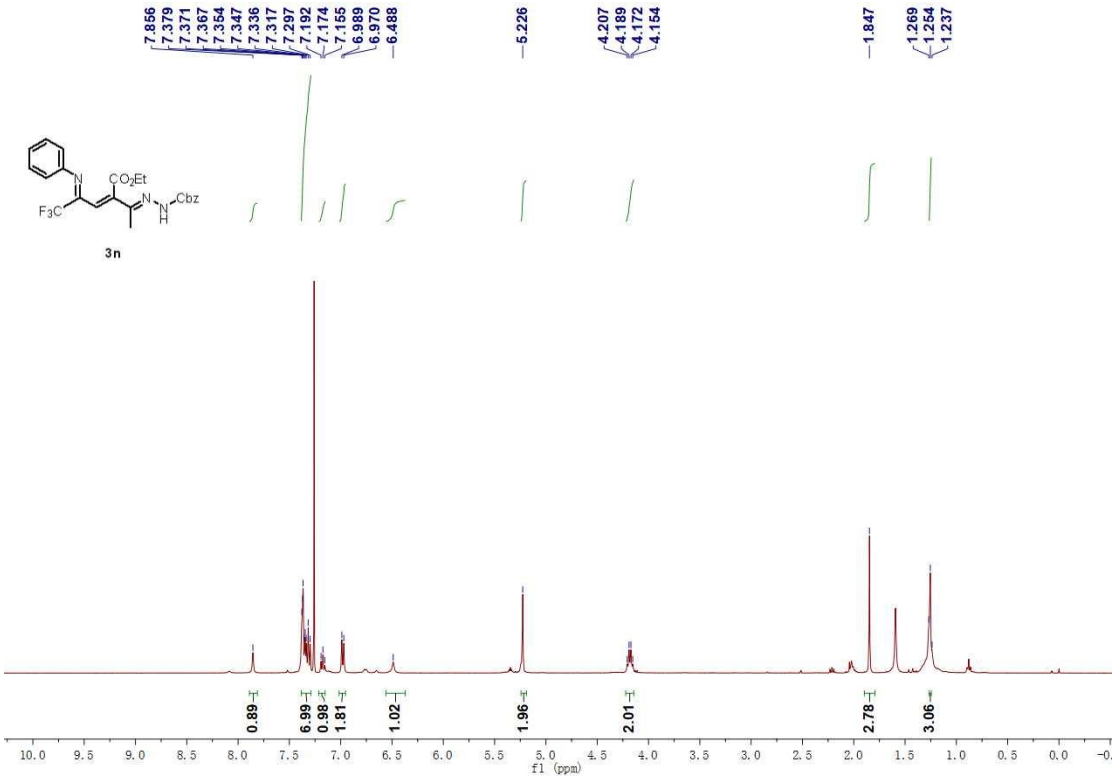
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3m



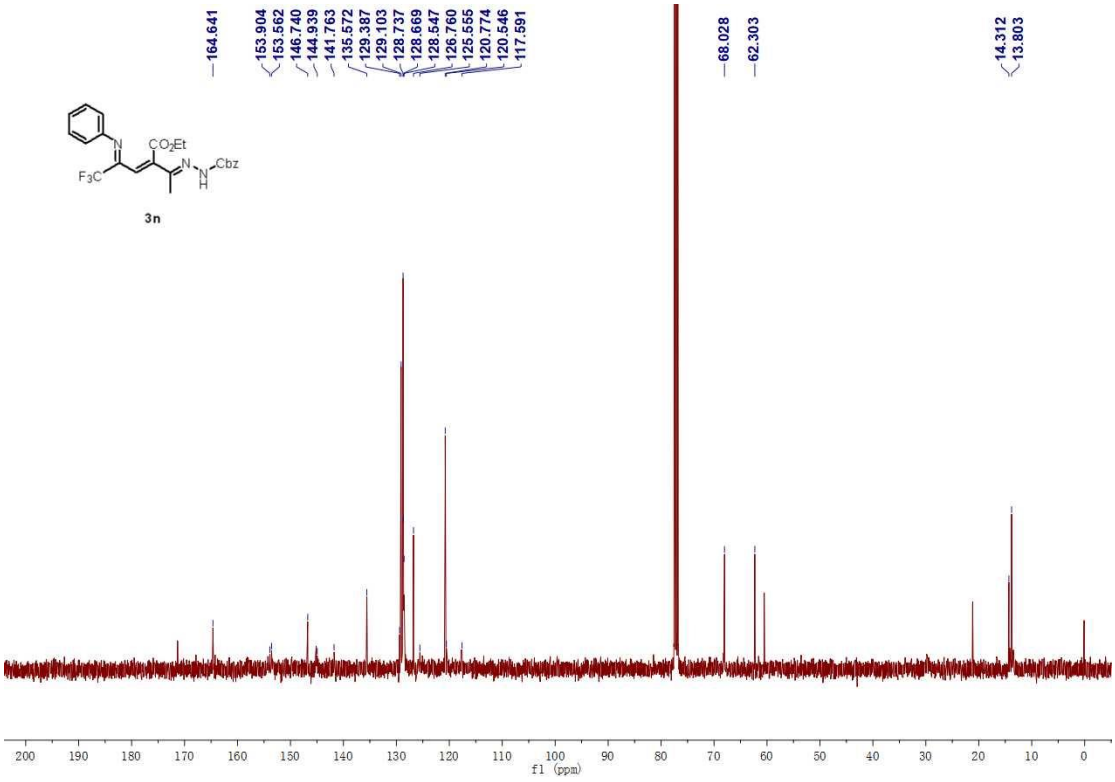
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3m



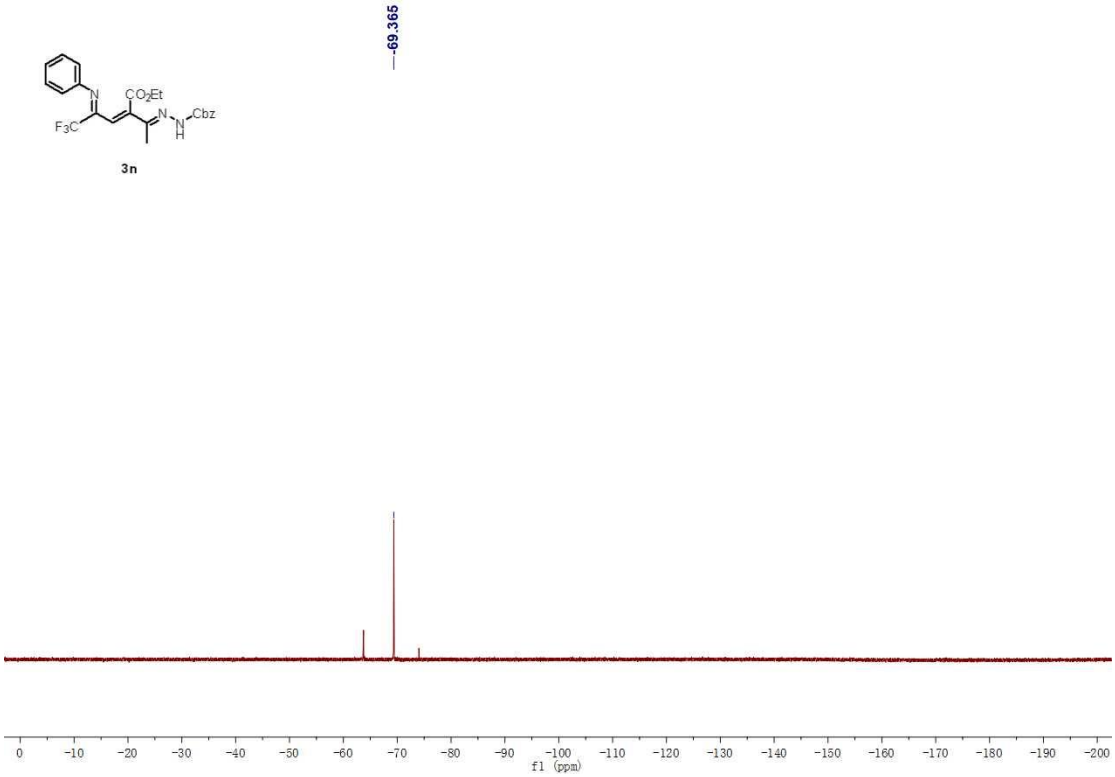
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3n



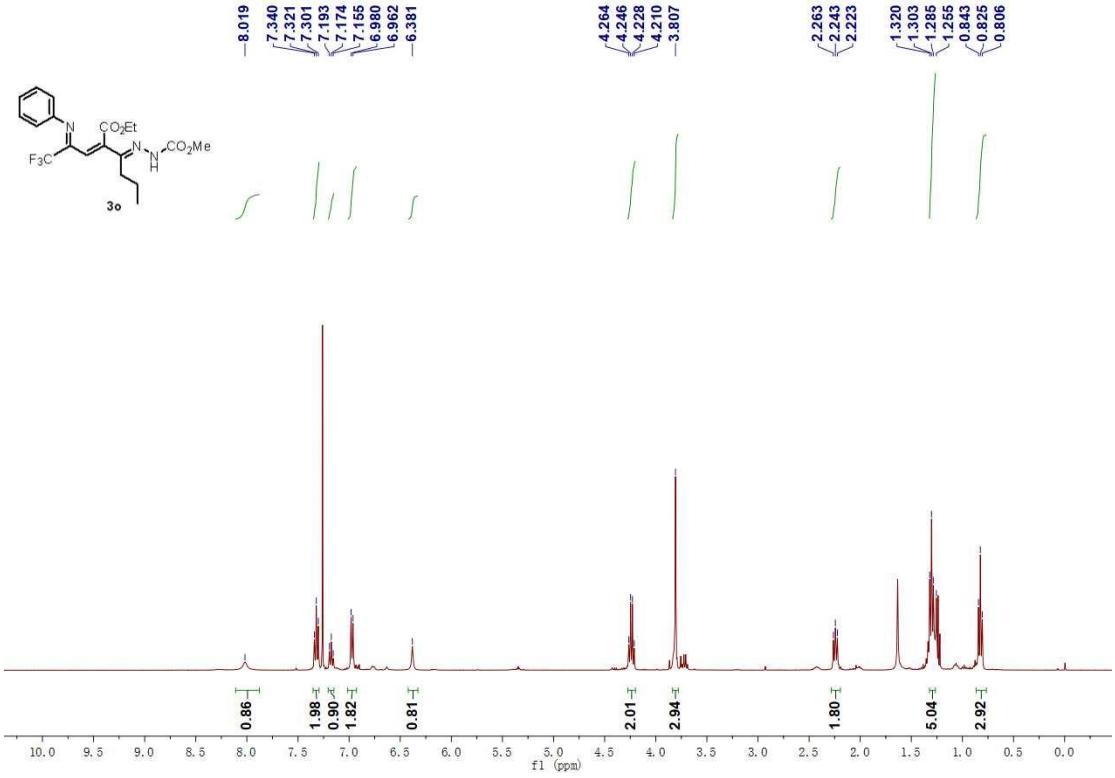
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3n



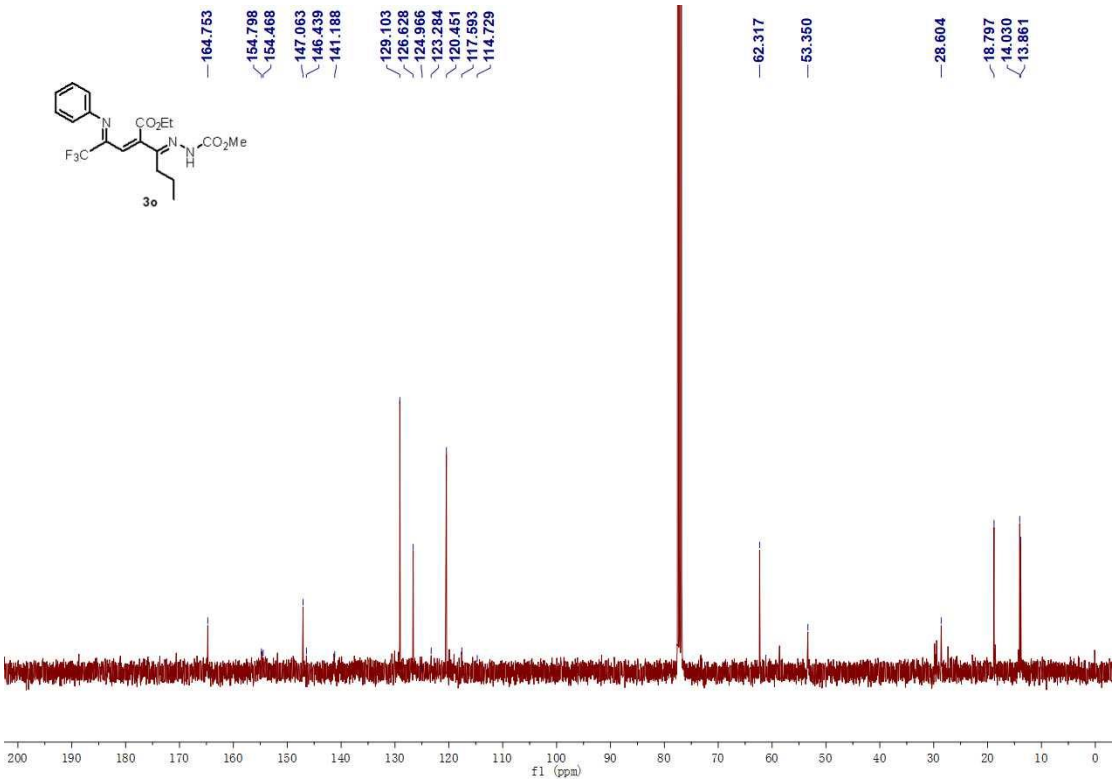
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3n



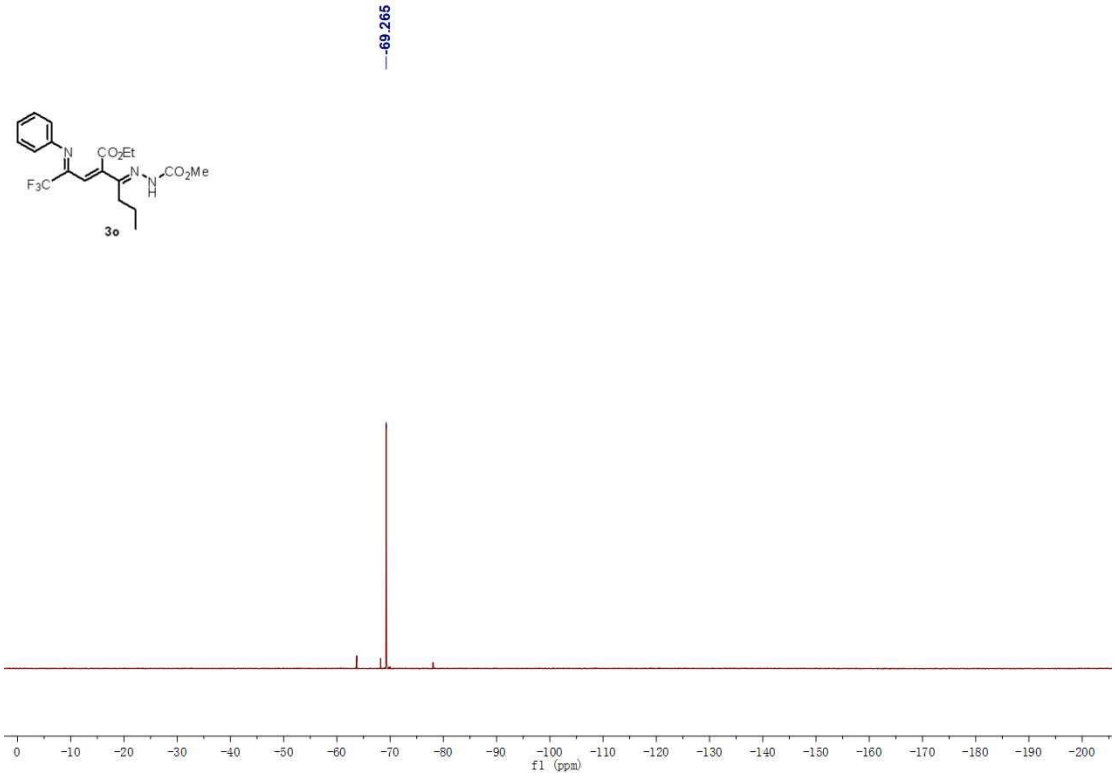
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3o



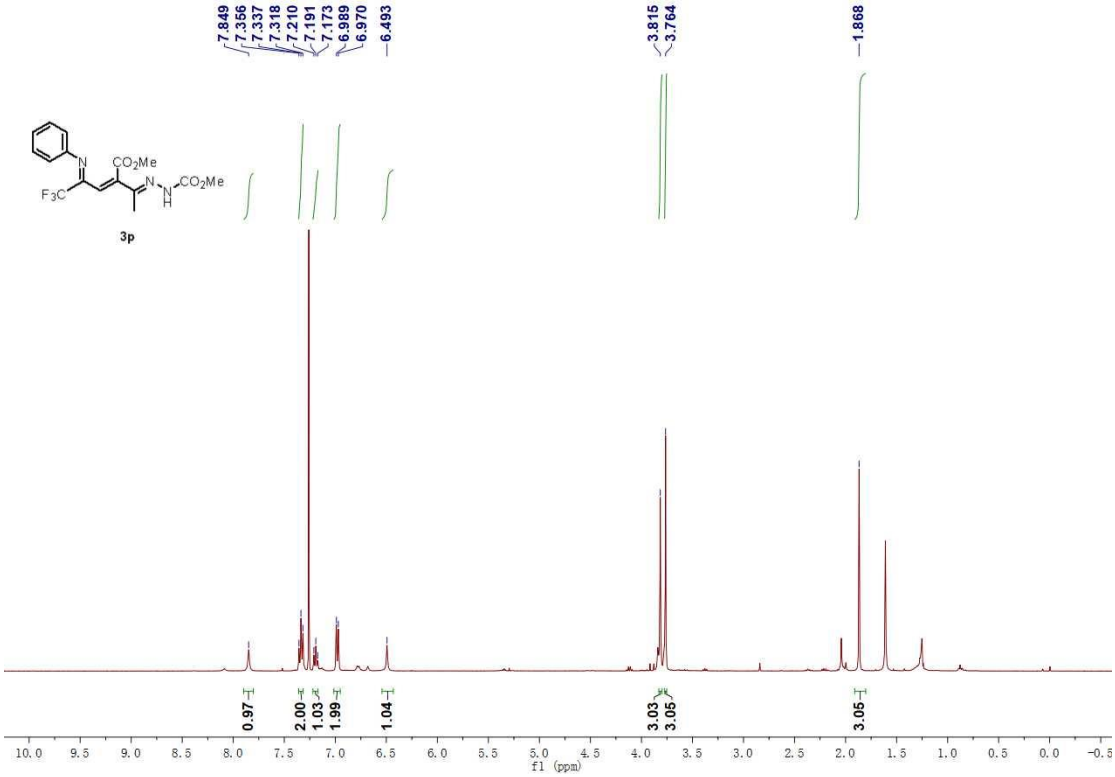
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3o



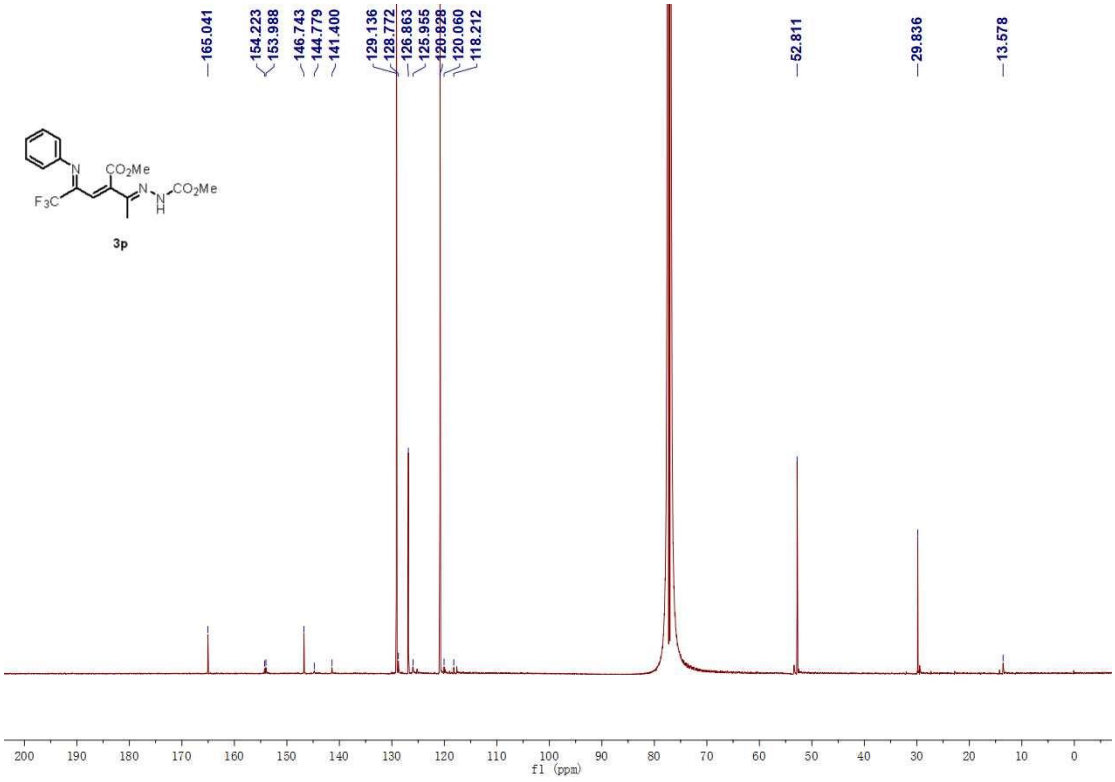
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3o



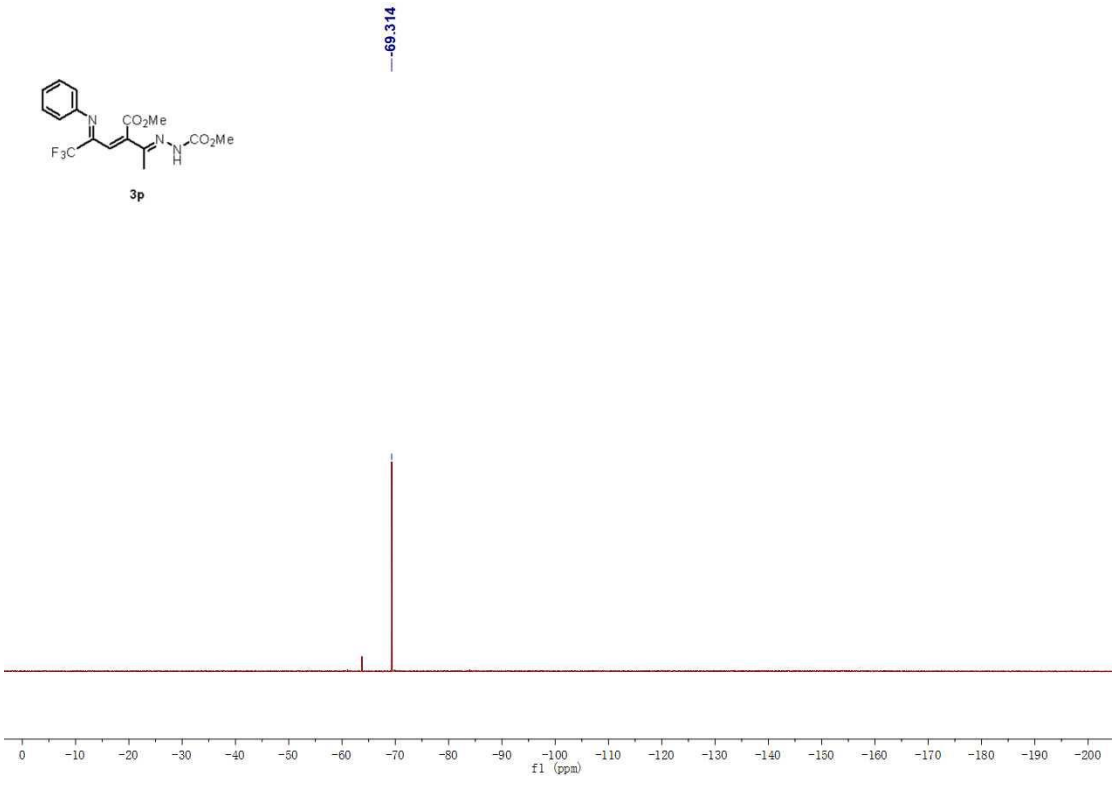
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p



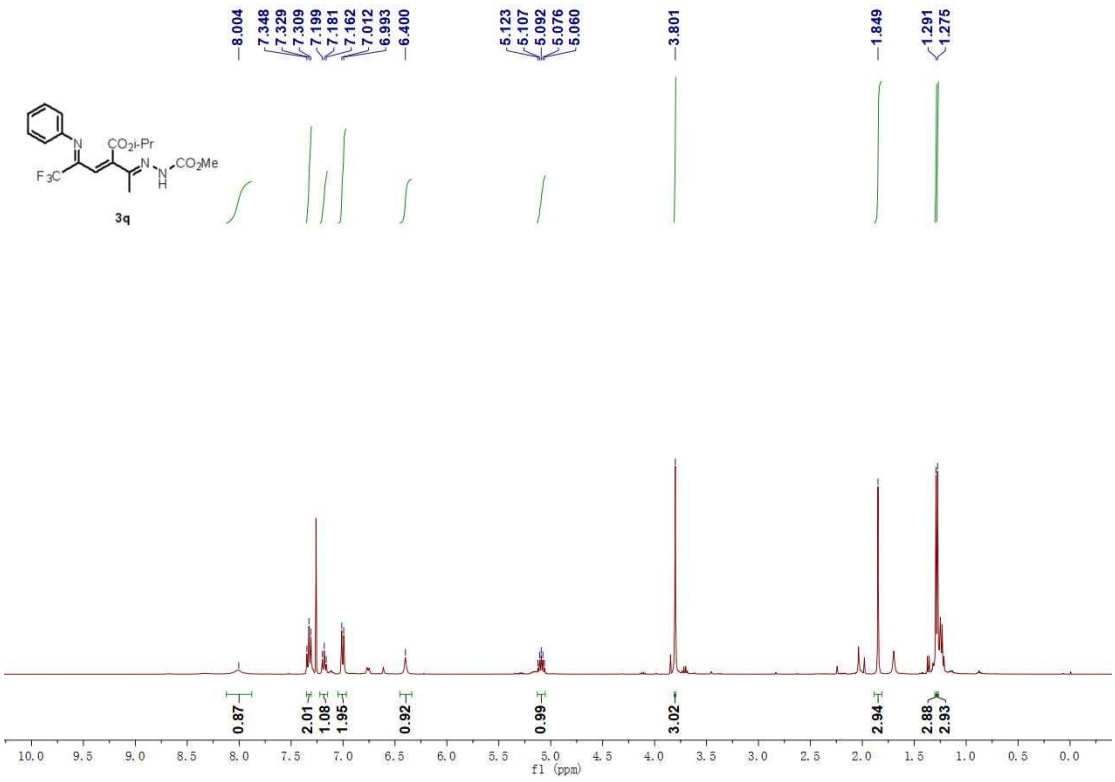
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3p



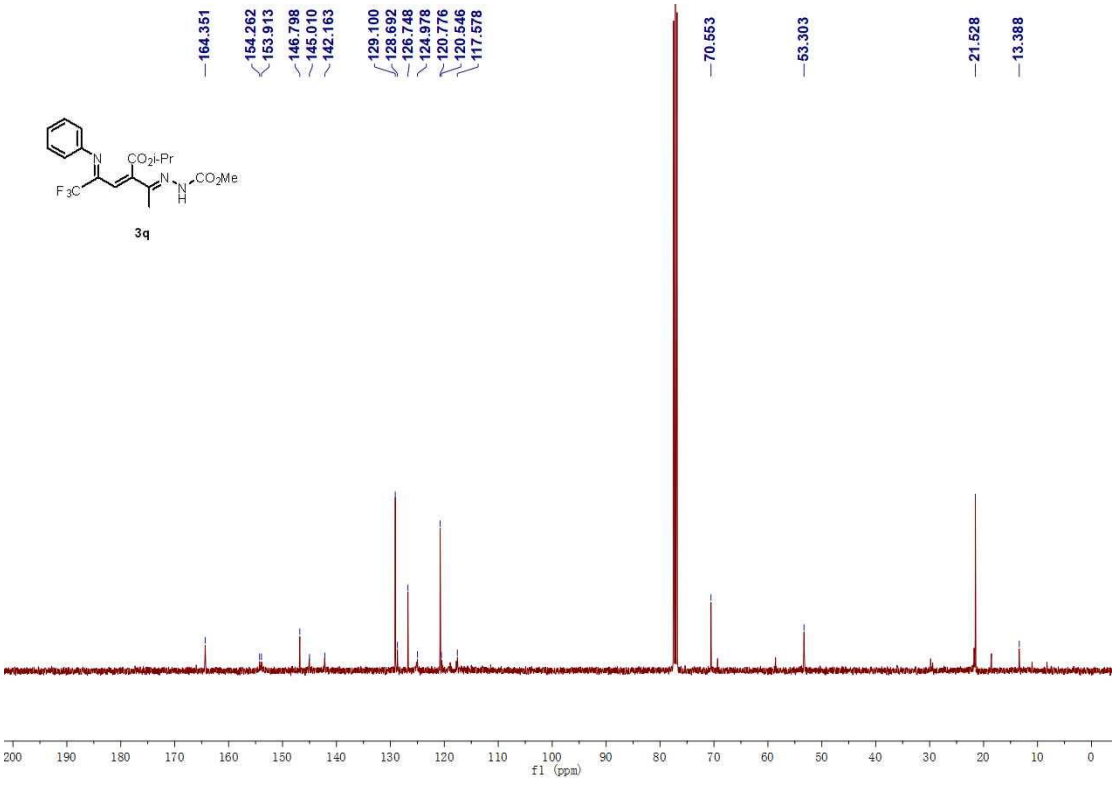
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3p



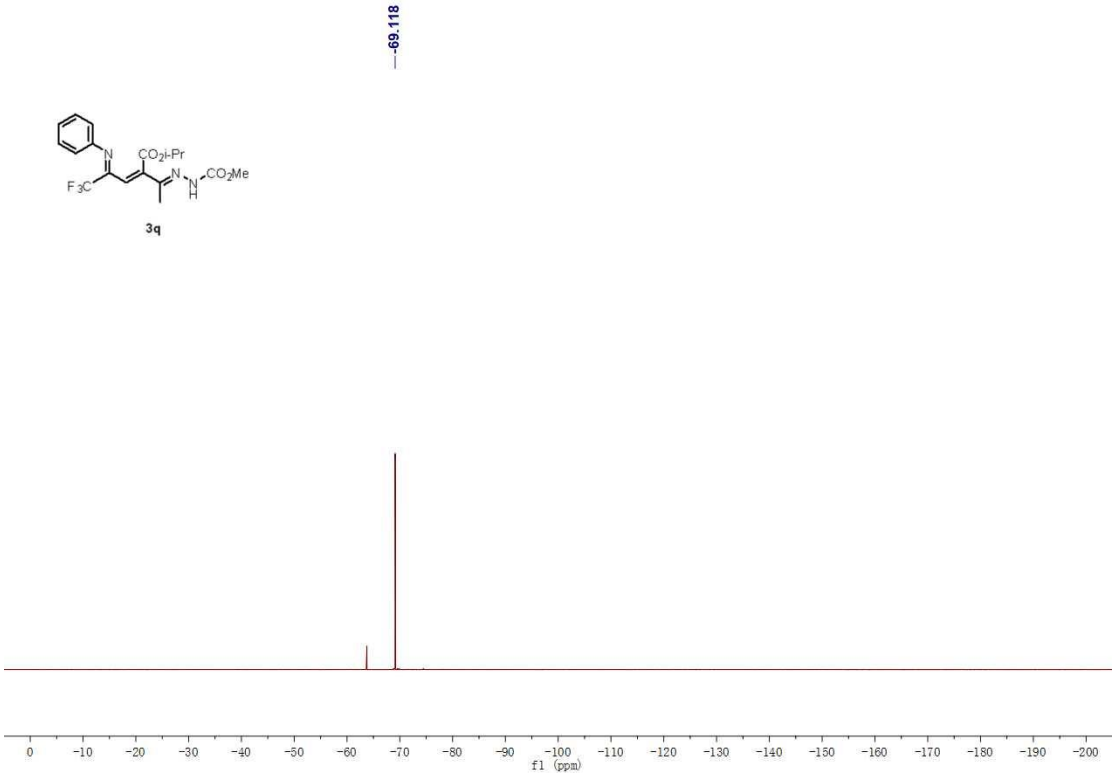
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3q



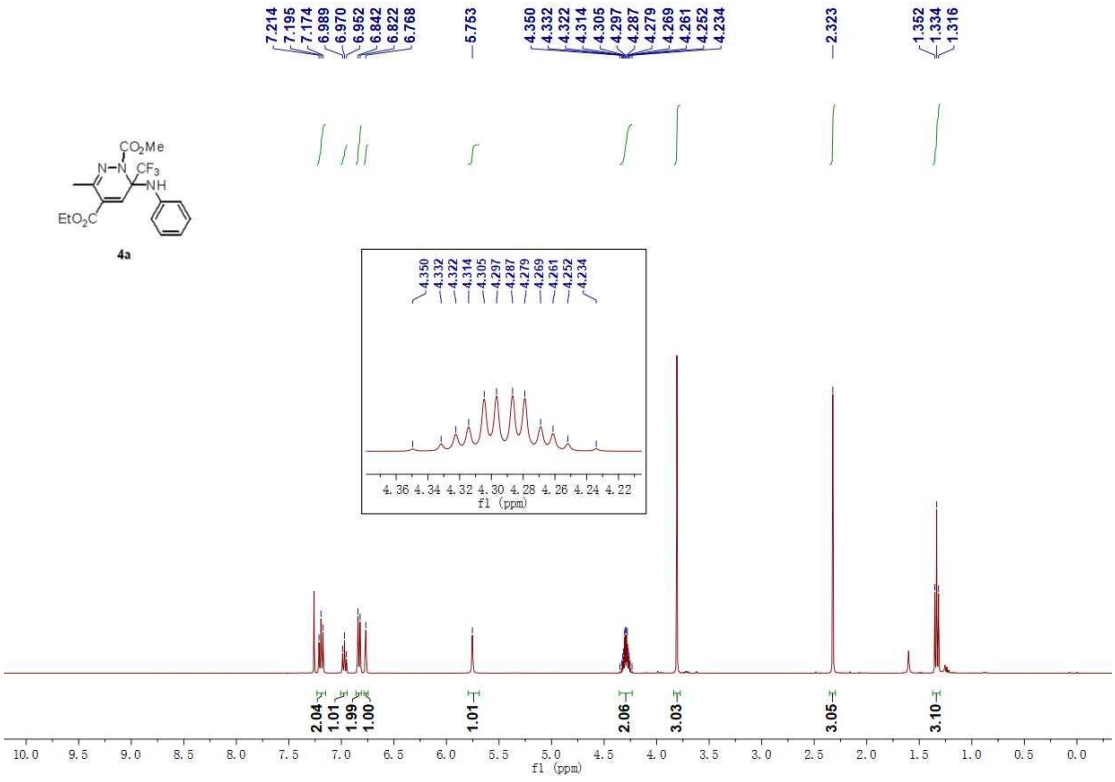
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3q



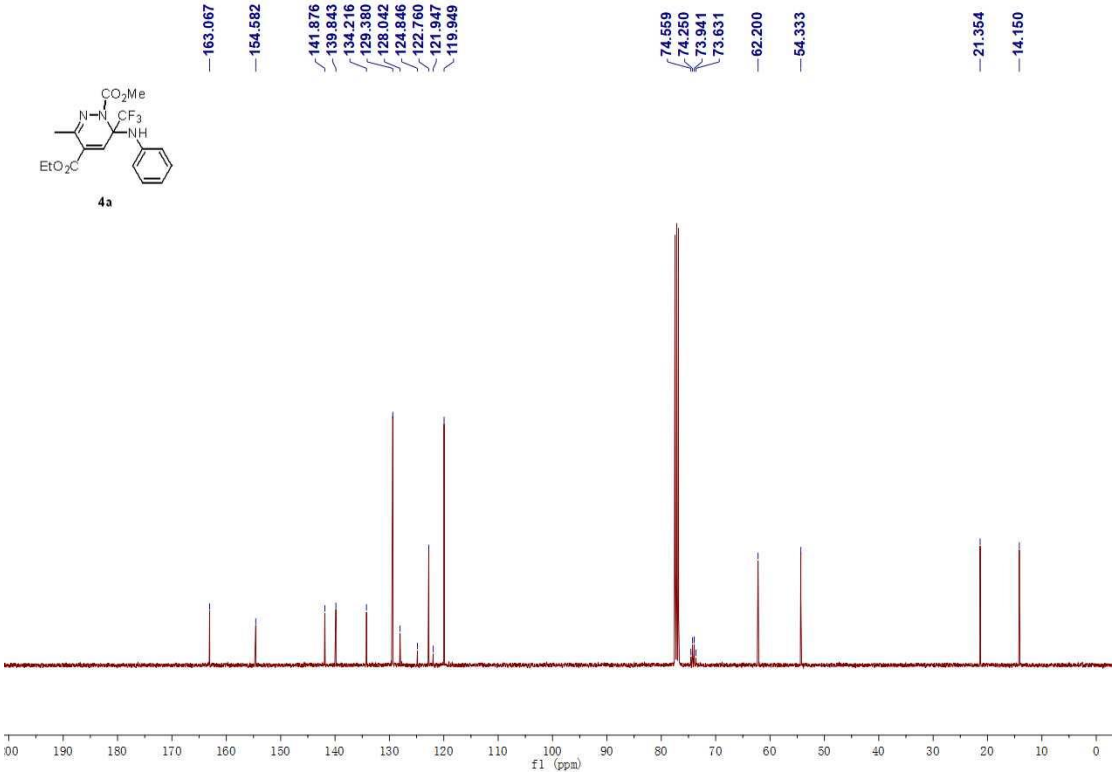
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3q



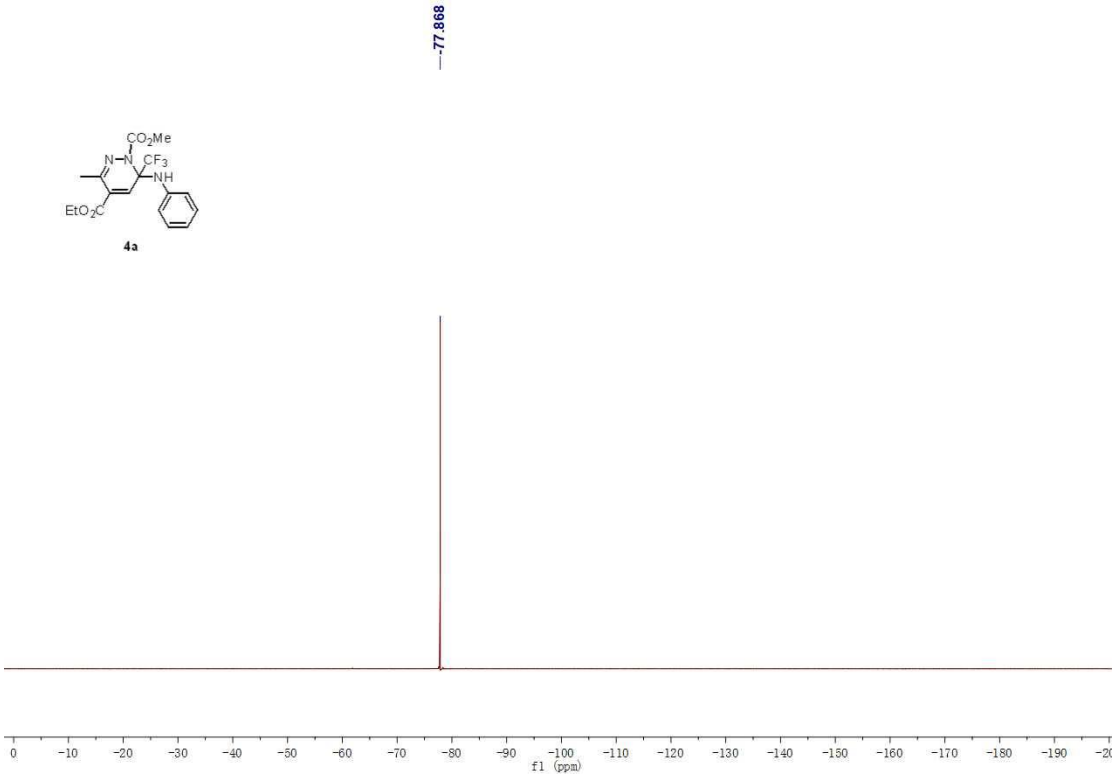
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a



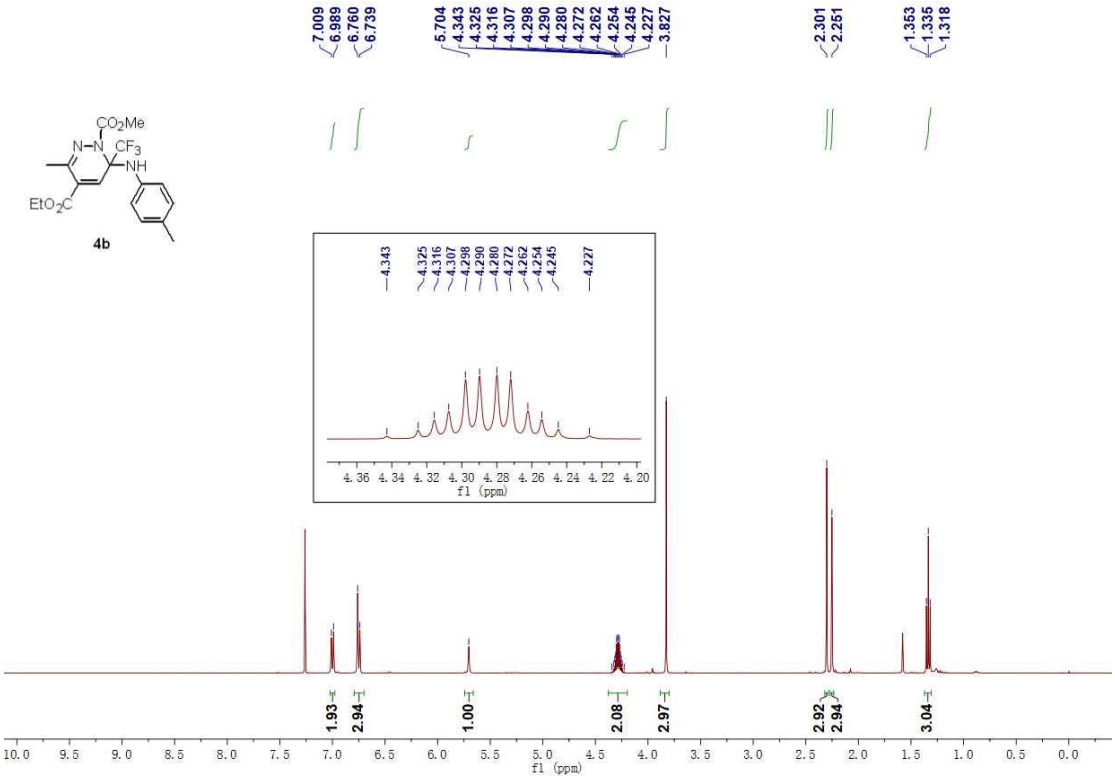
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4a



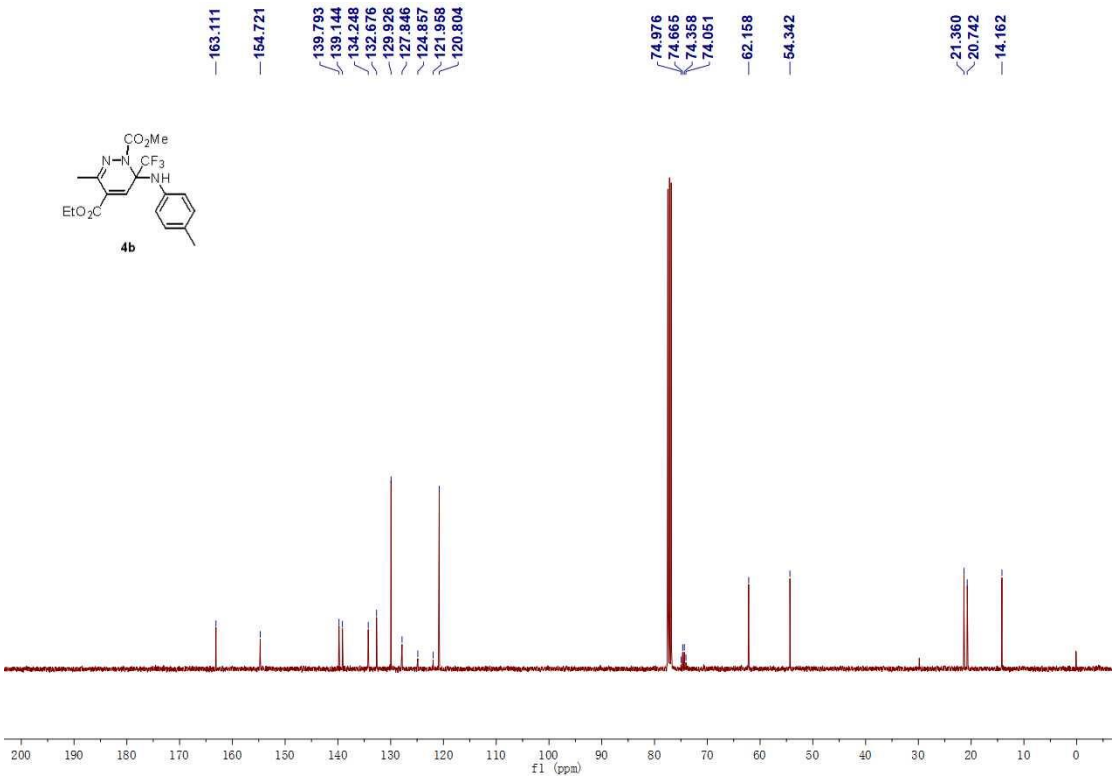
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4a



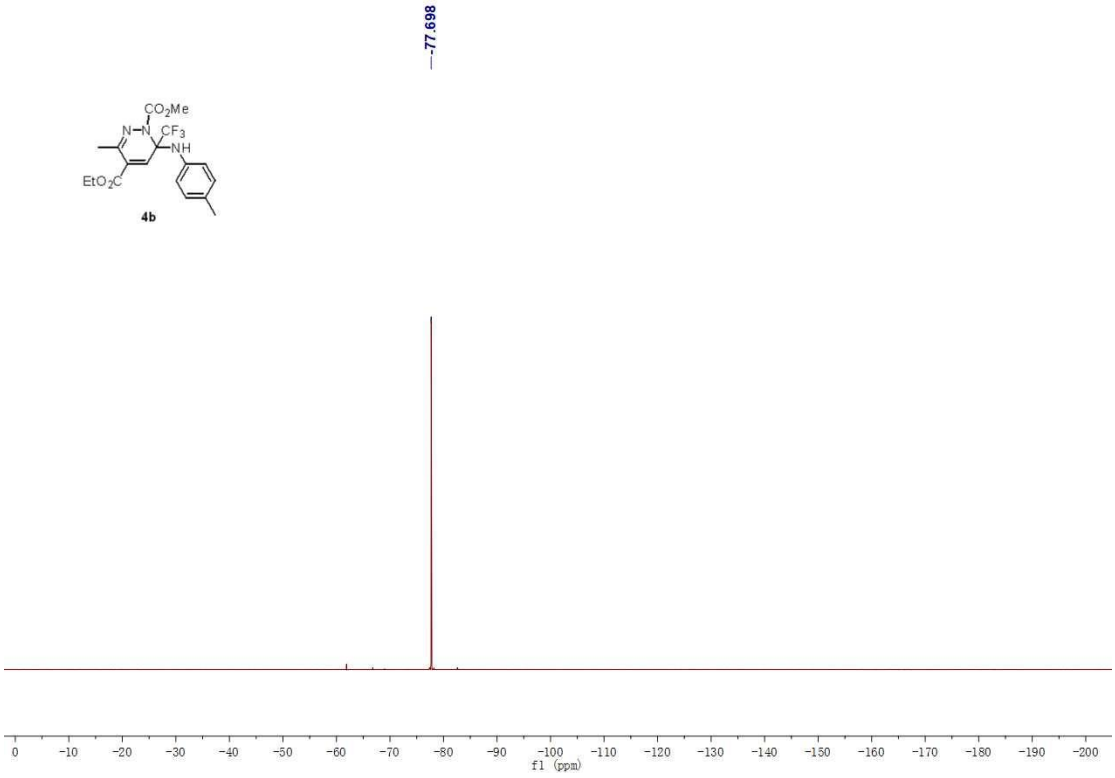
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4b



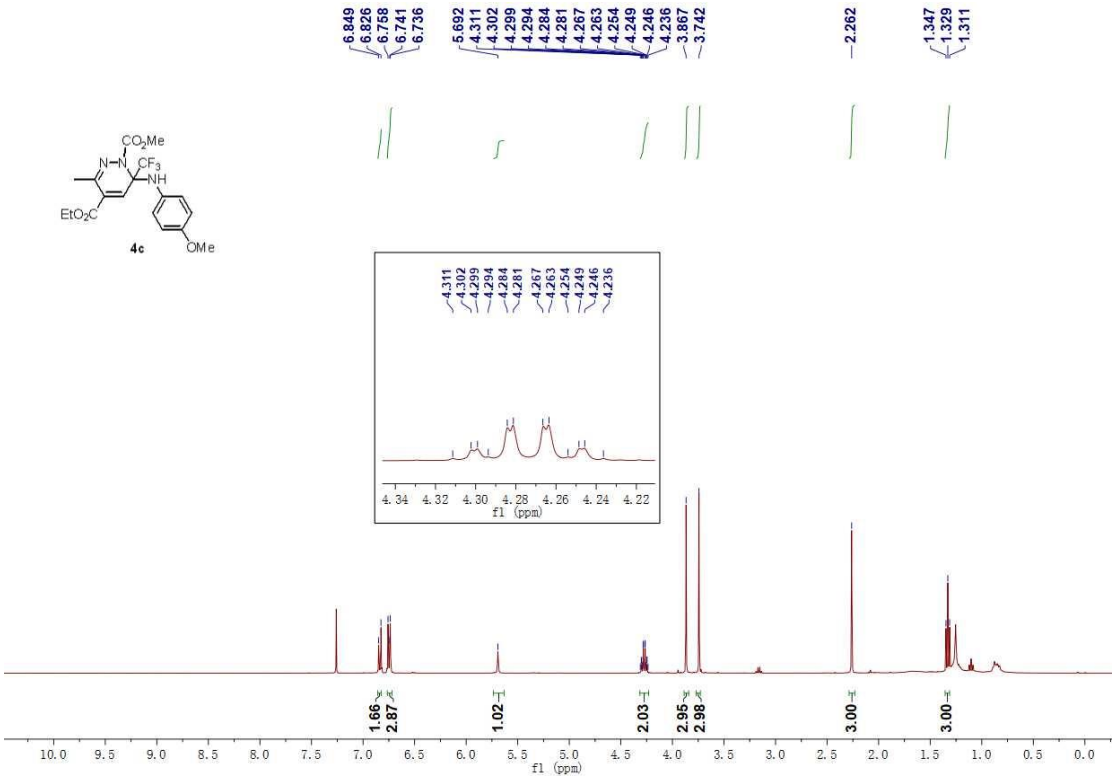
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4b



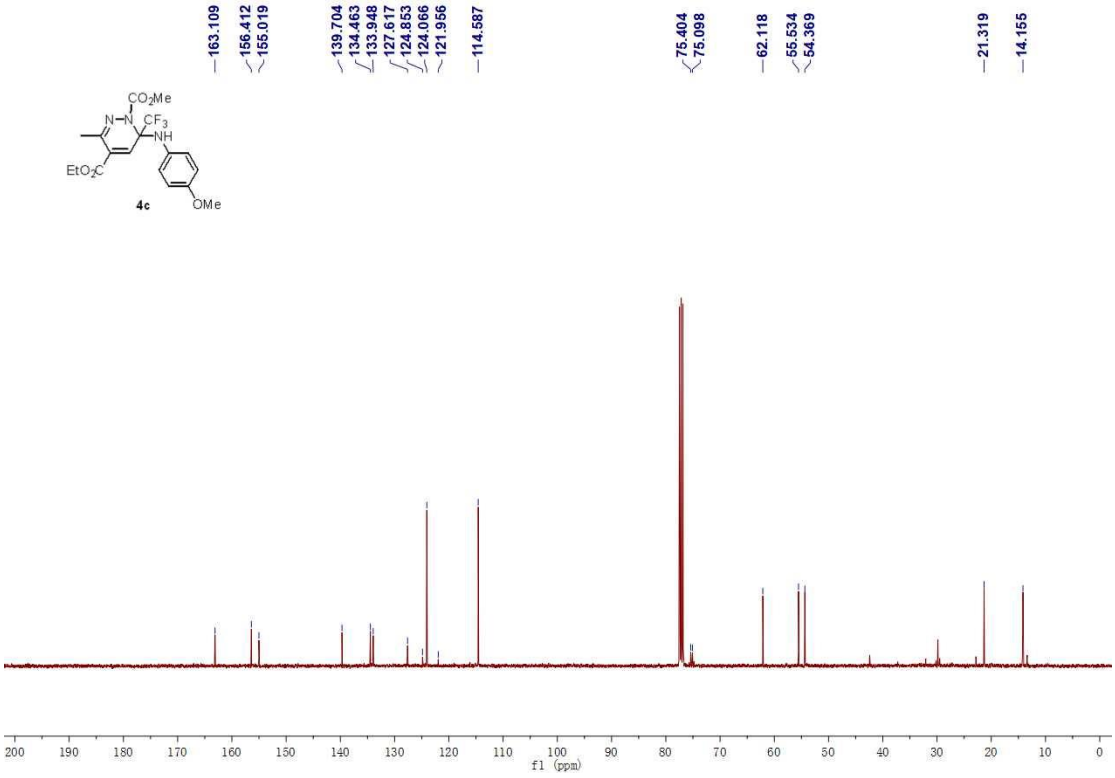
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4b



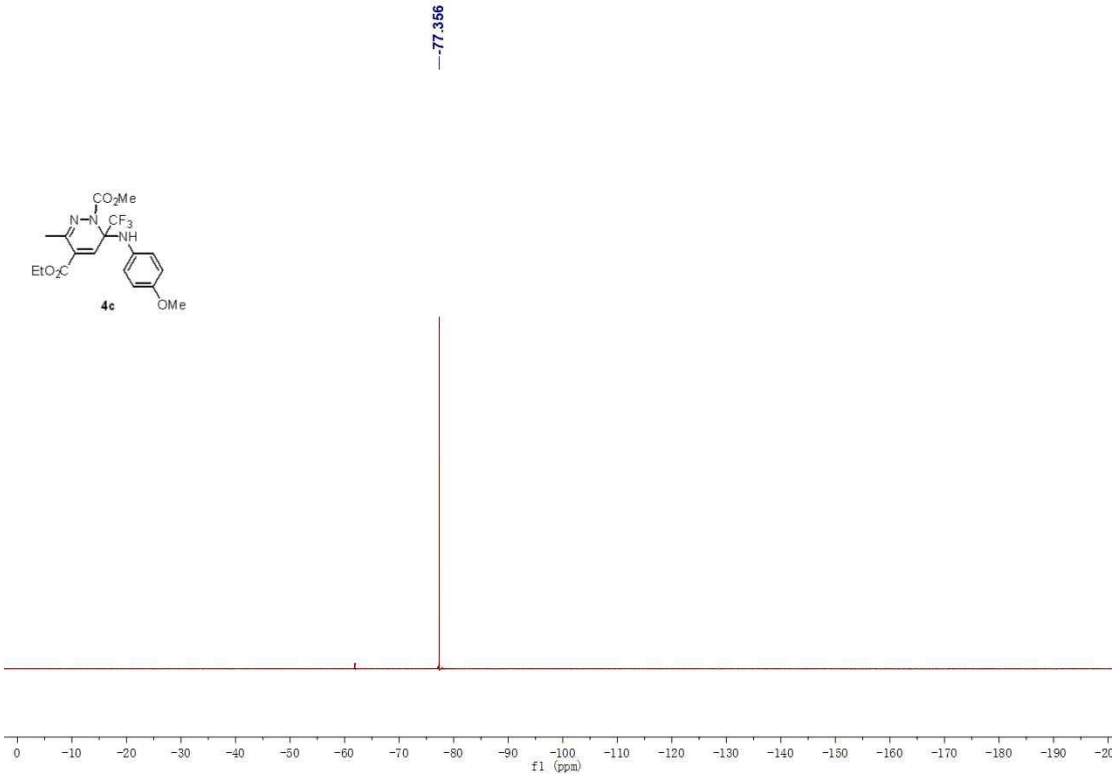
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4c



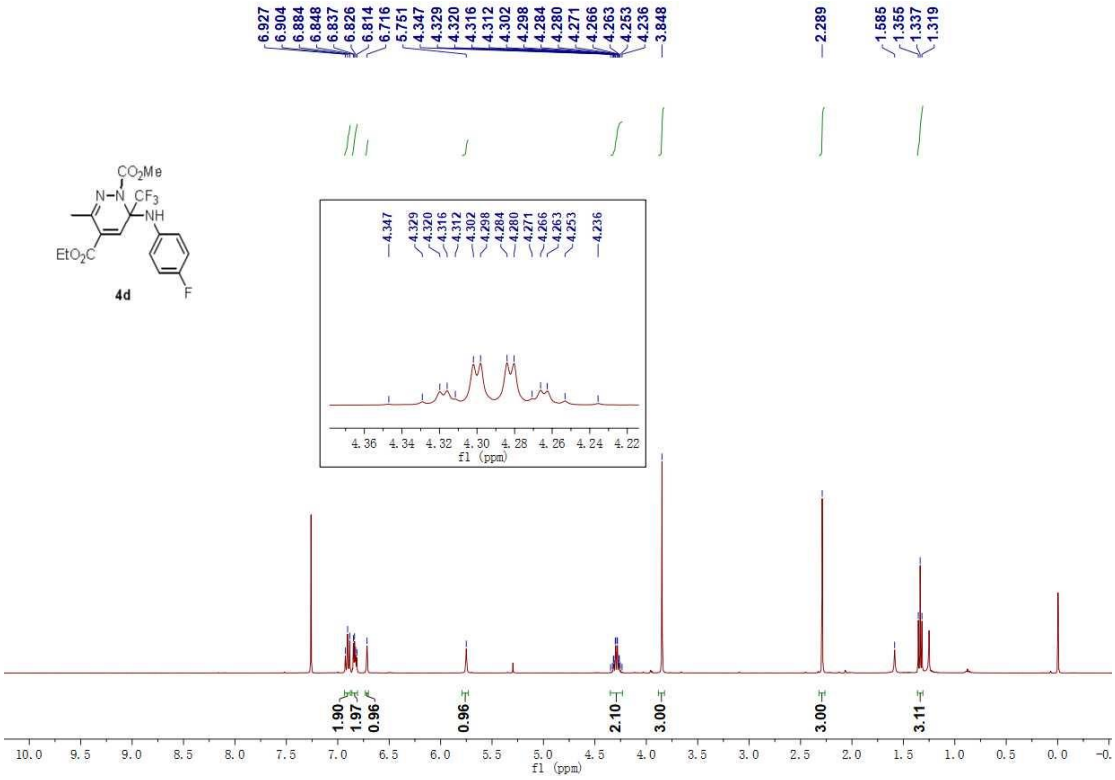
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4c



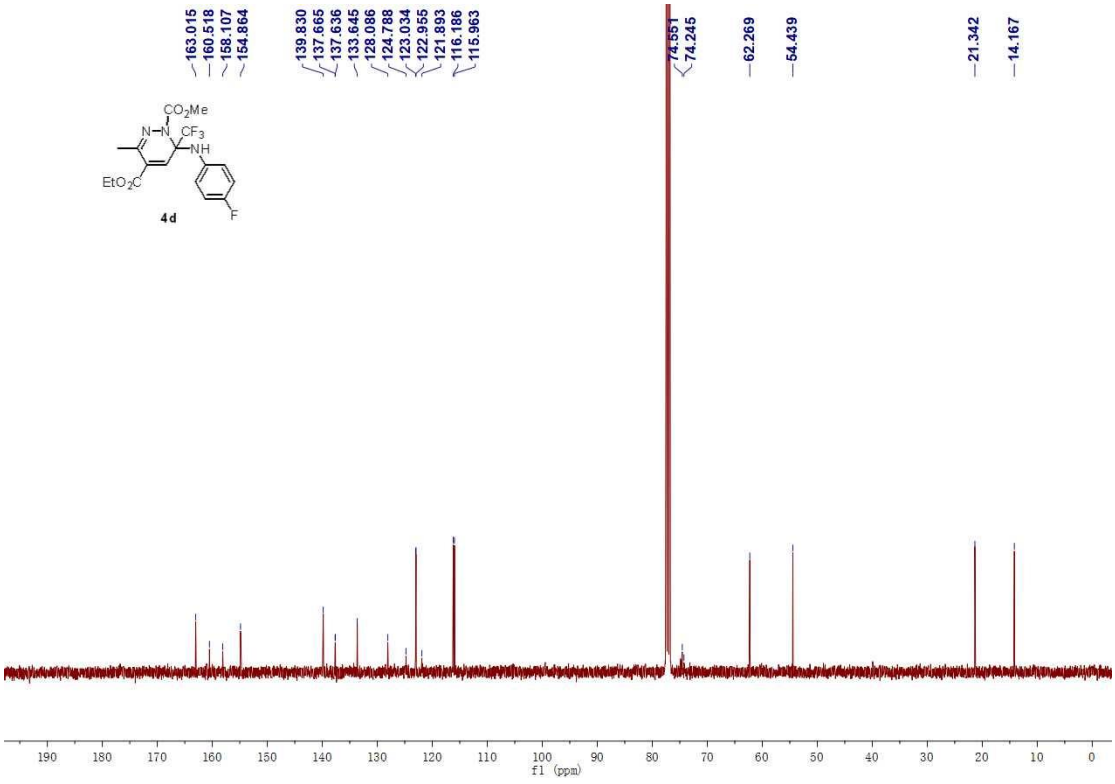
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4c



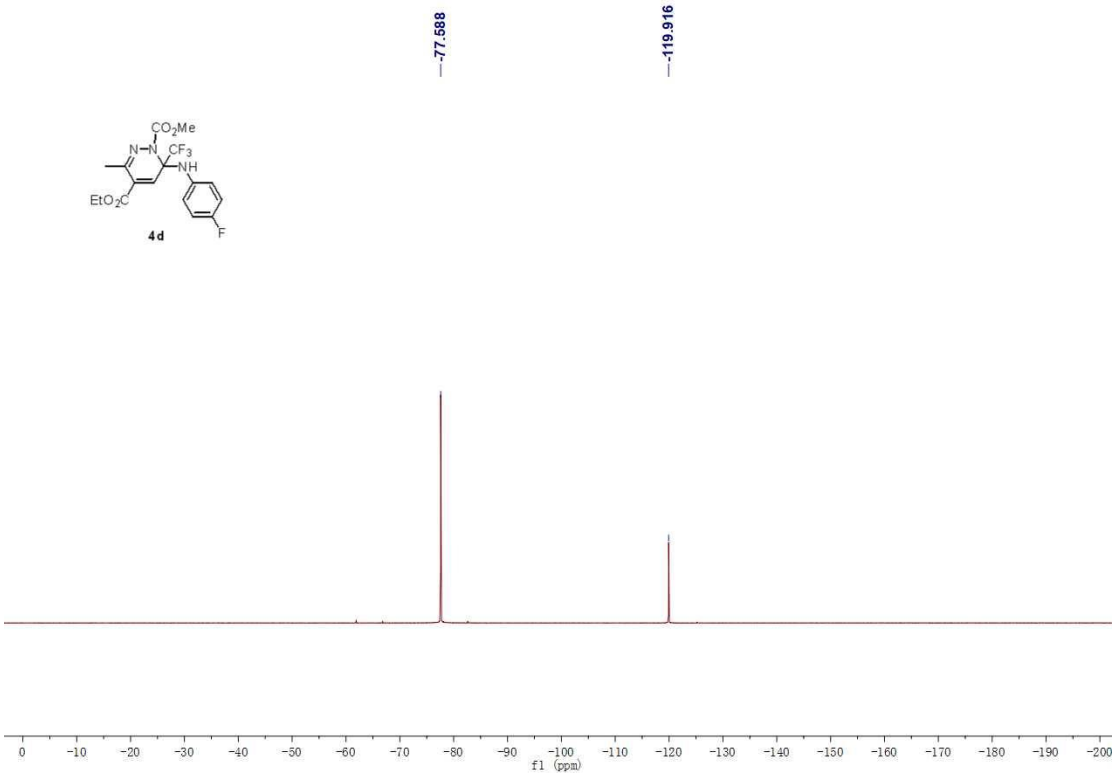
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4d



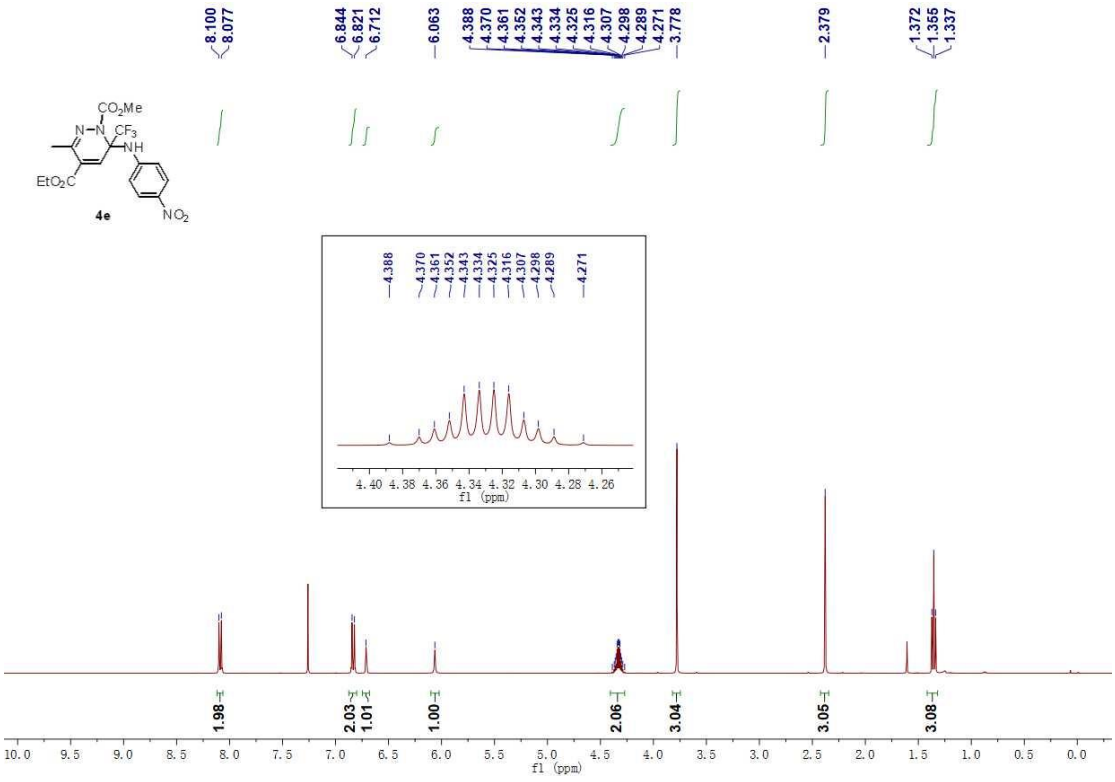
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4d



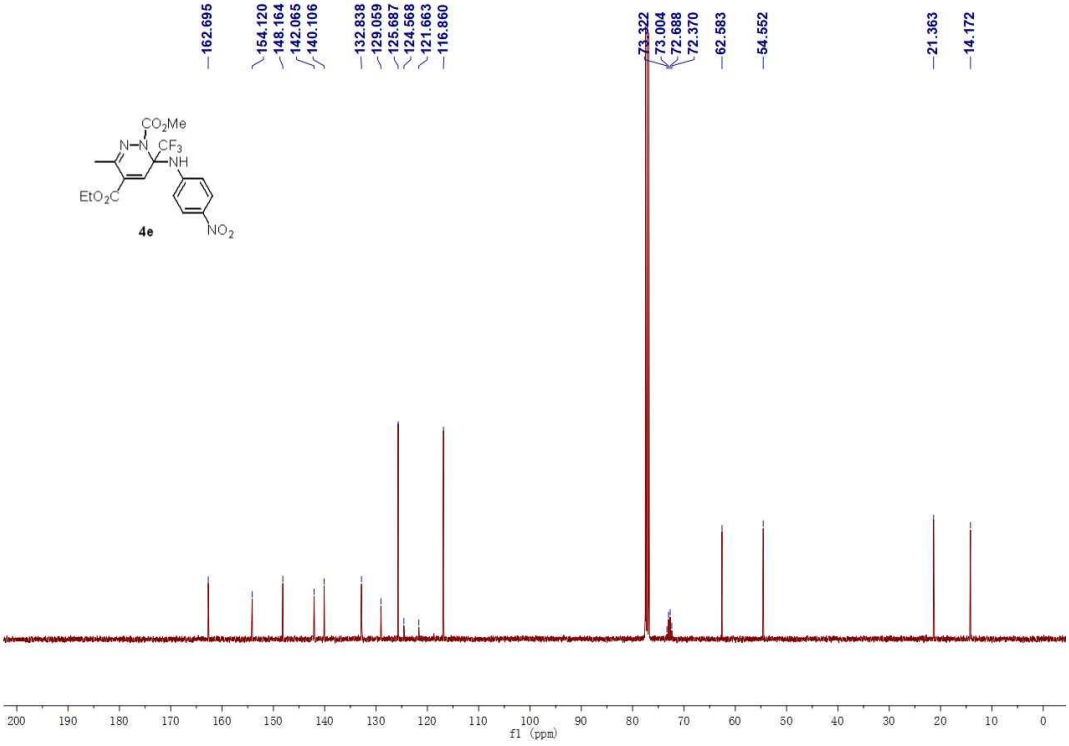
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4d



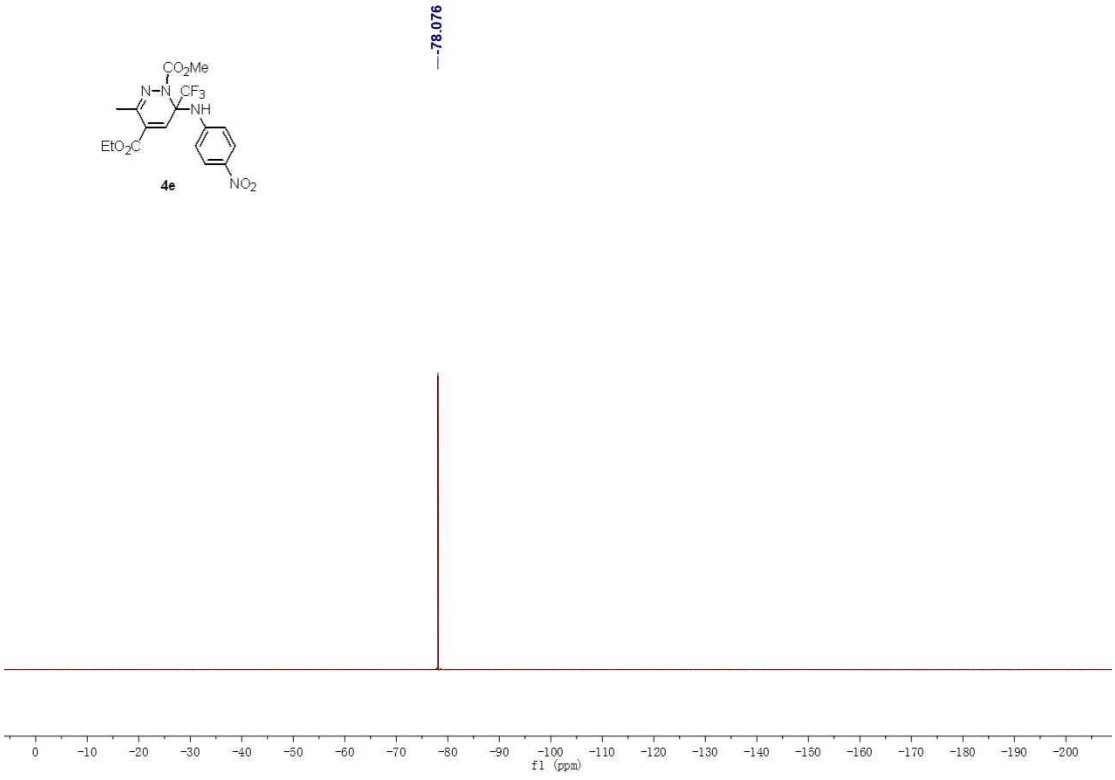
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4e



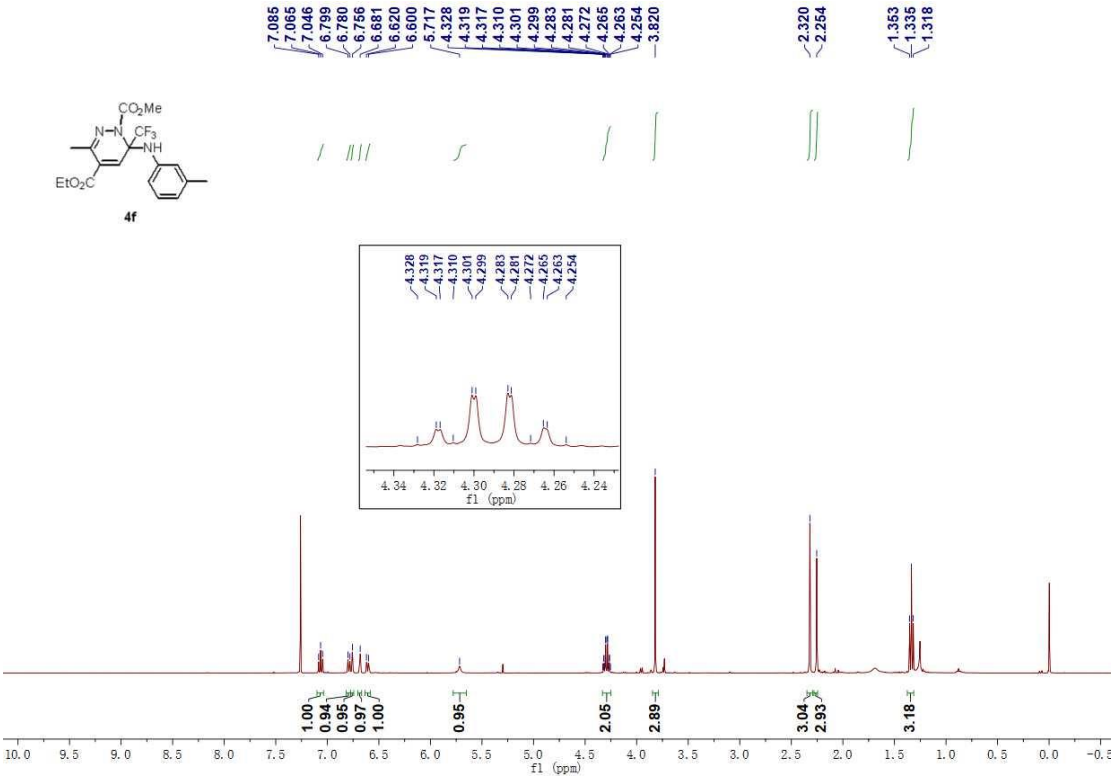
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4e



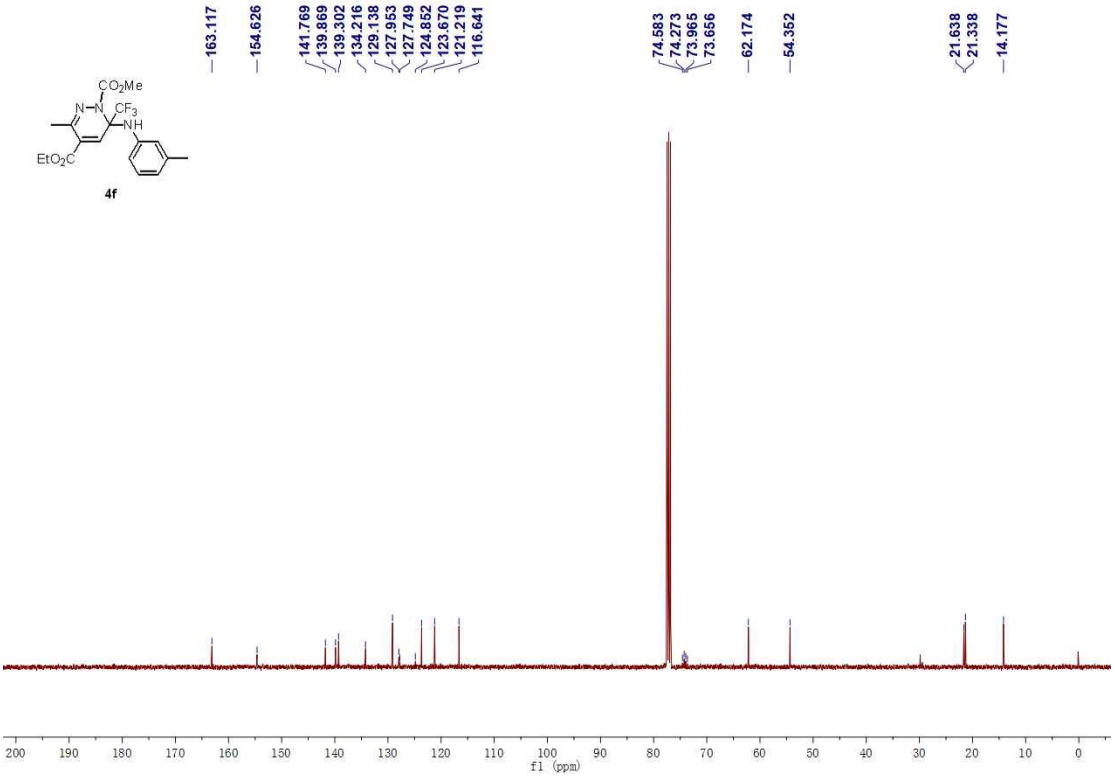
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4e



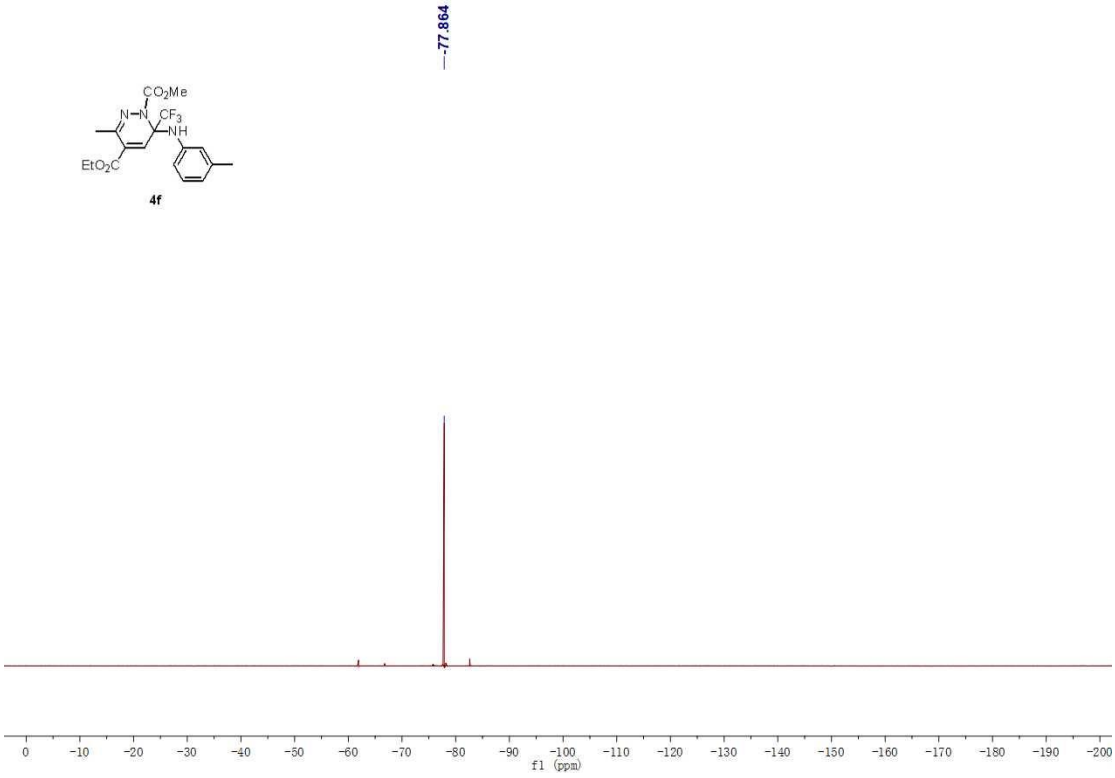
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4f



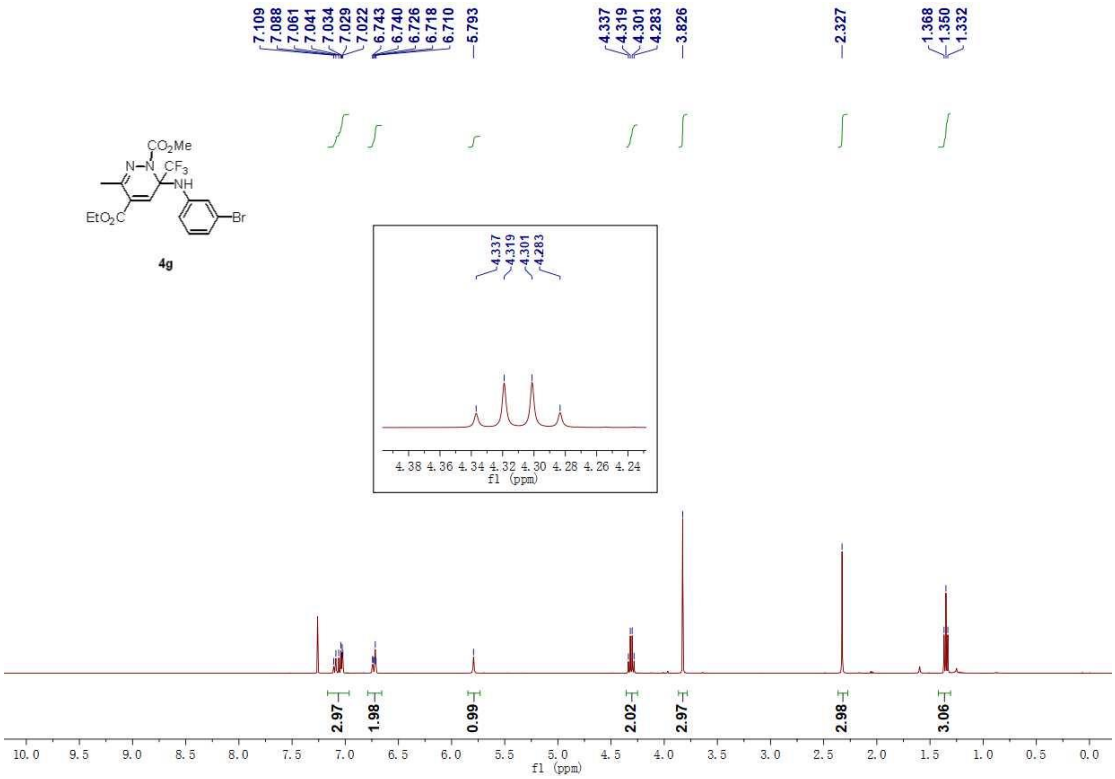
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4f



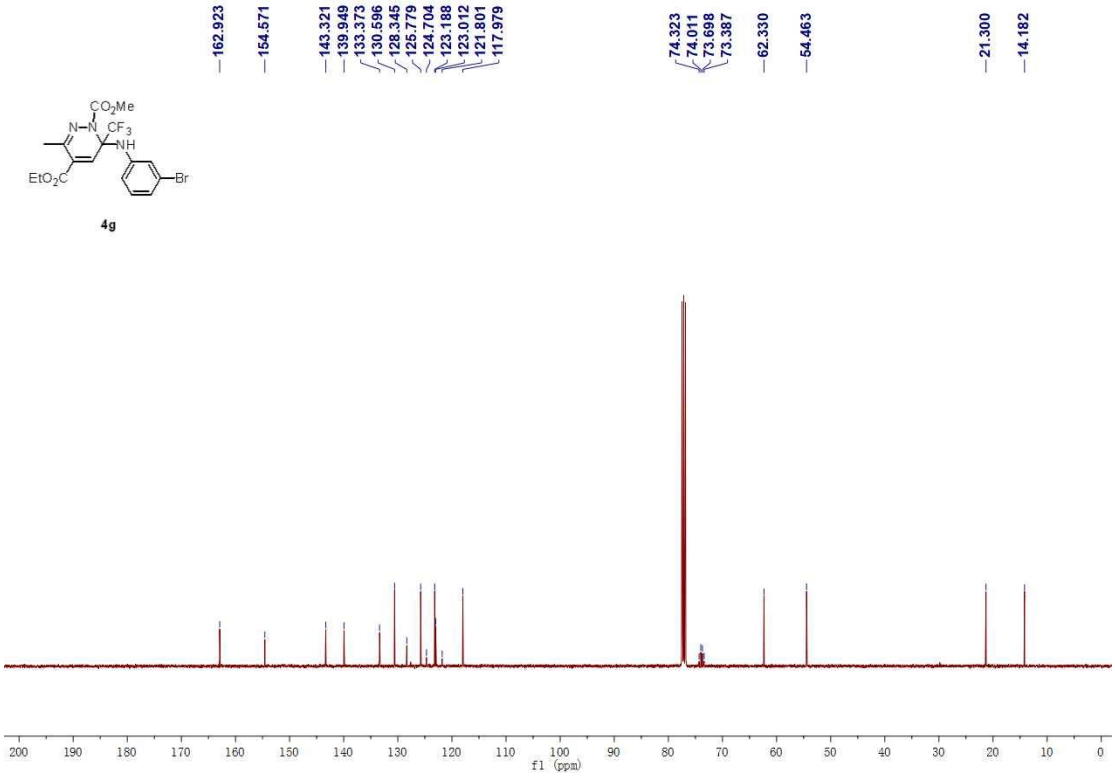
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4f



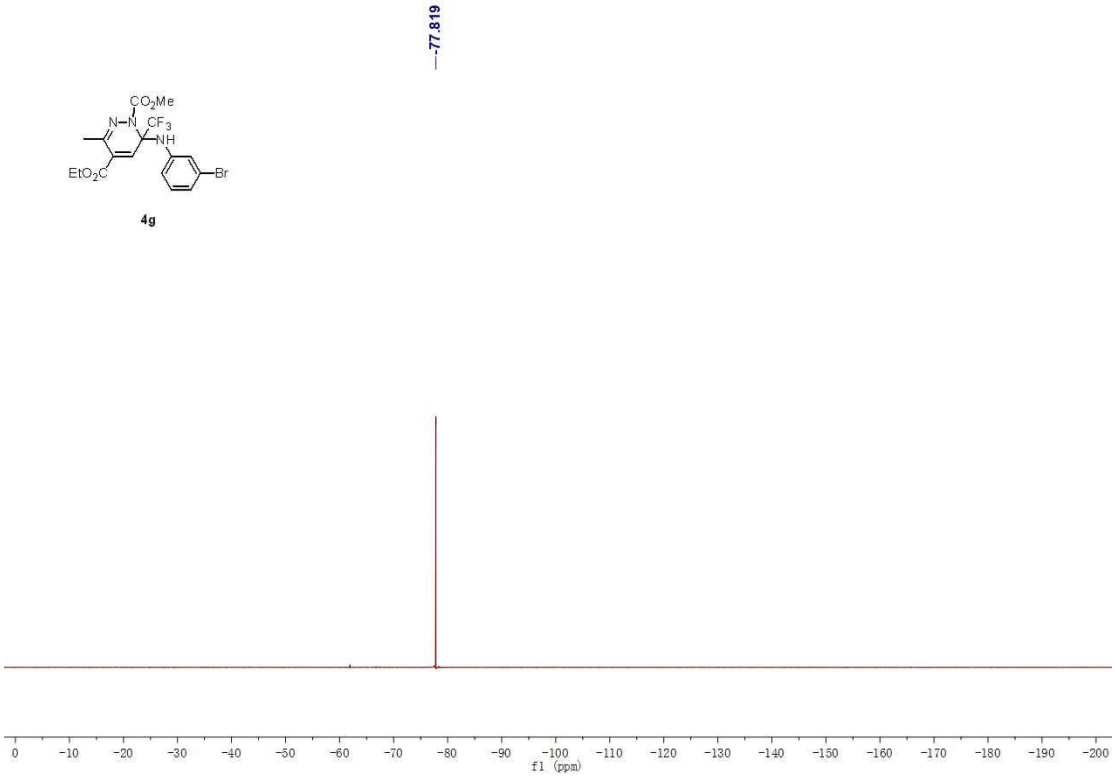
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4g



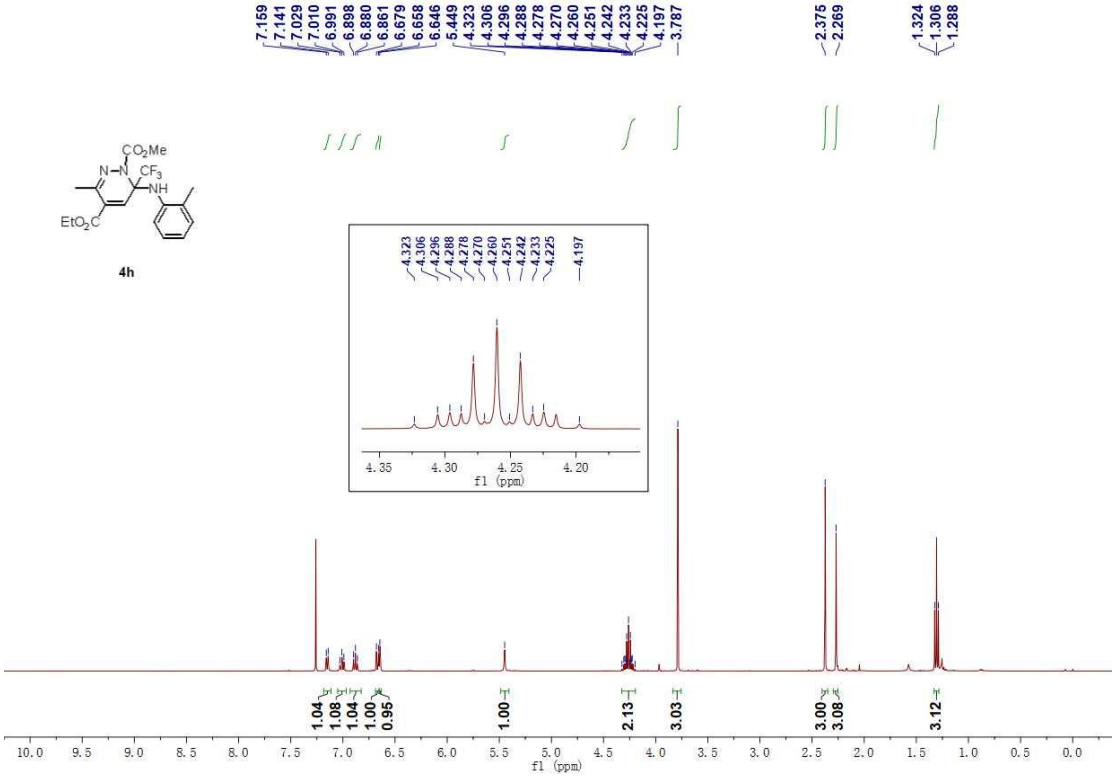
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4g



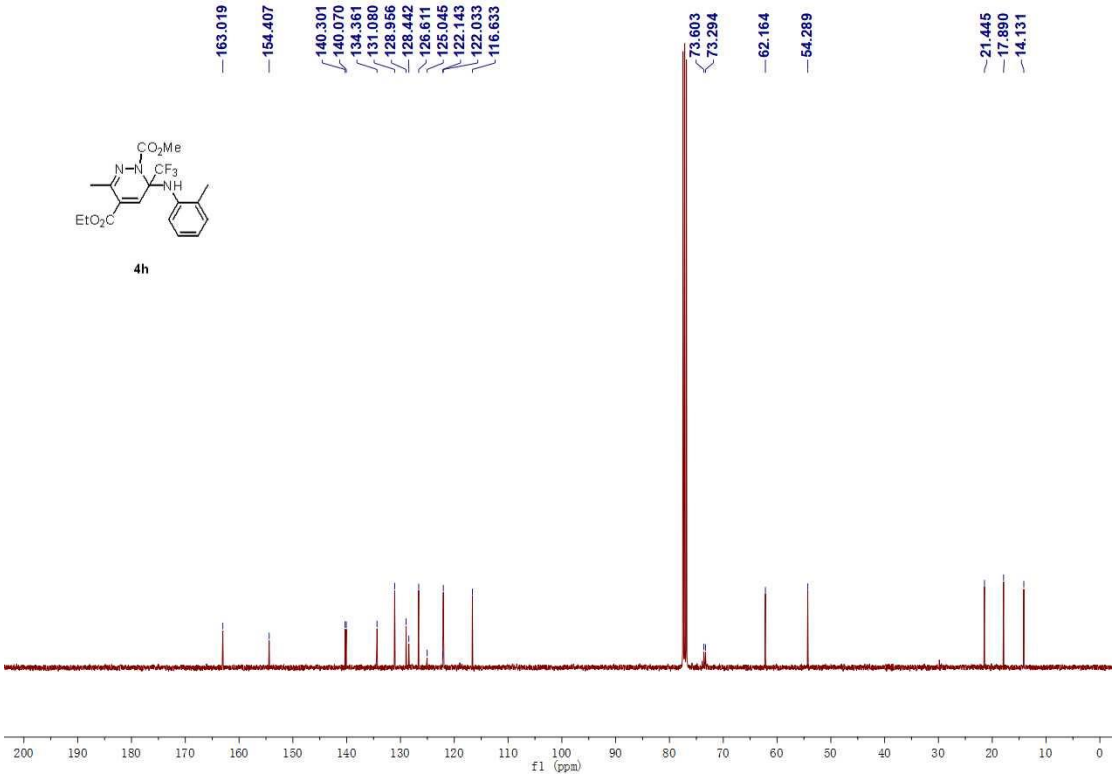
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4g



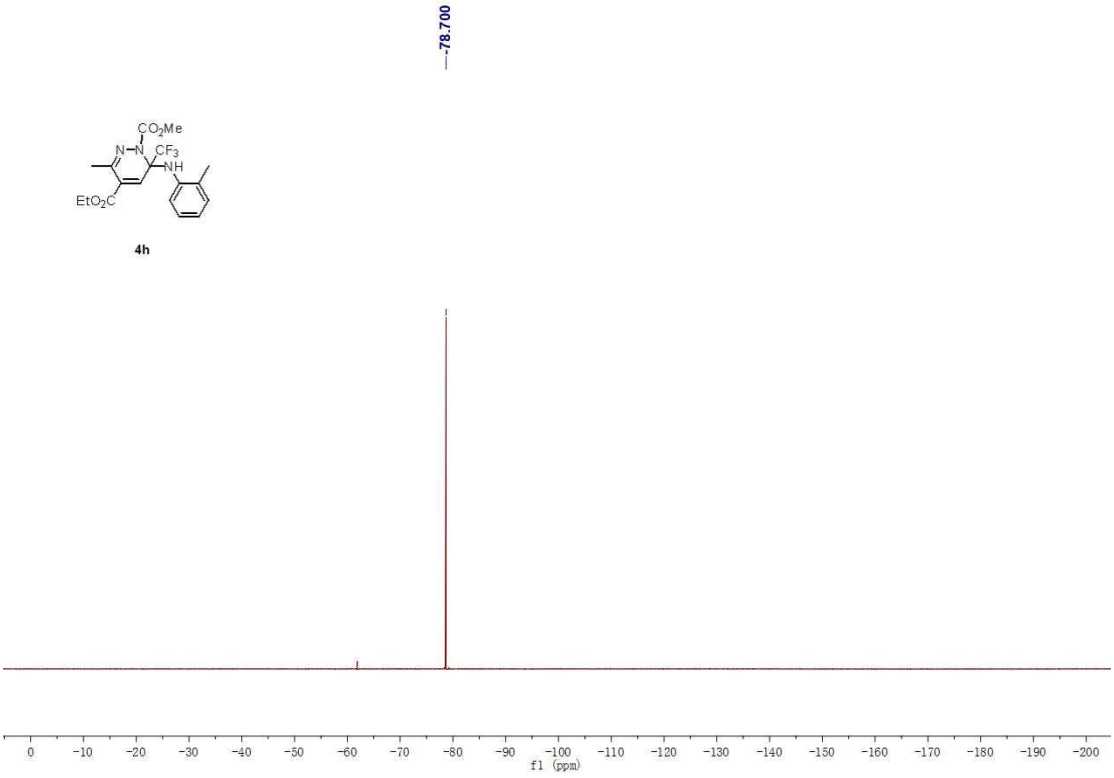
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4h



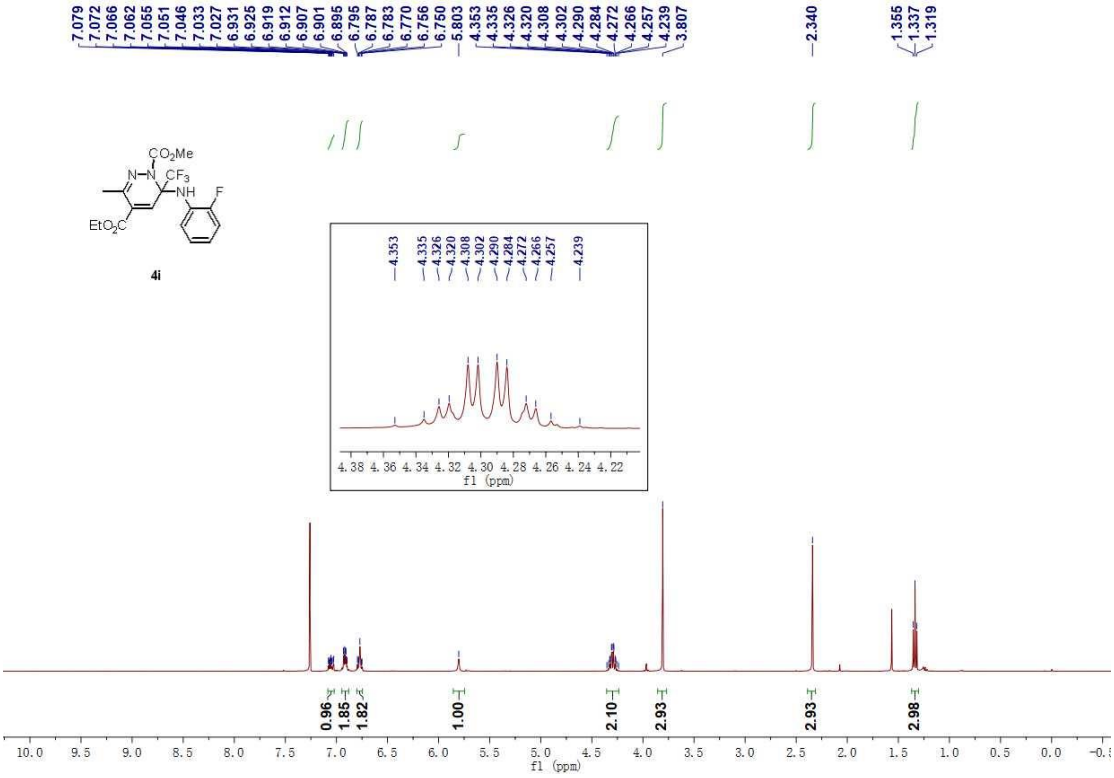
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4h



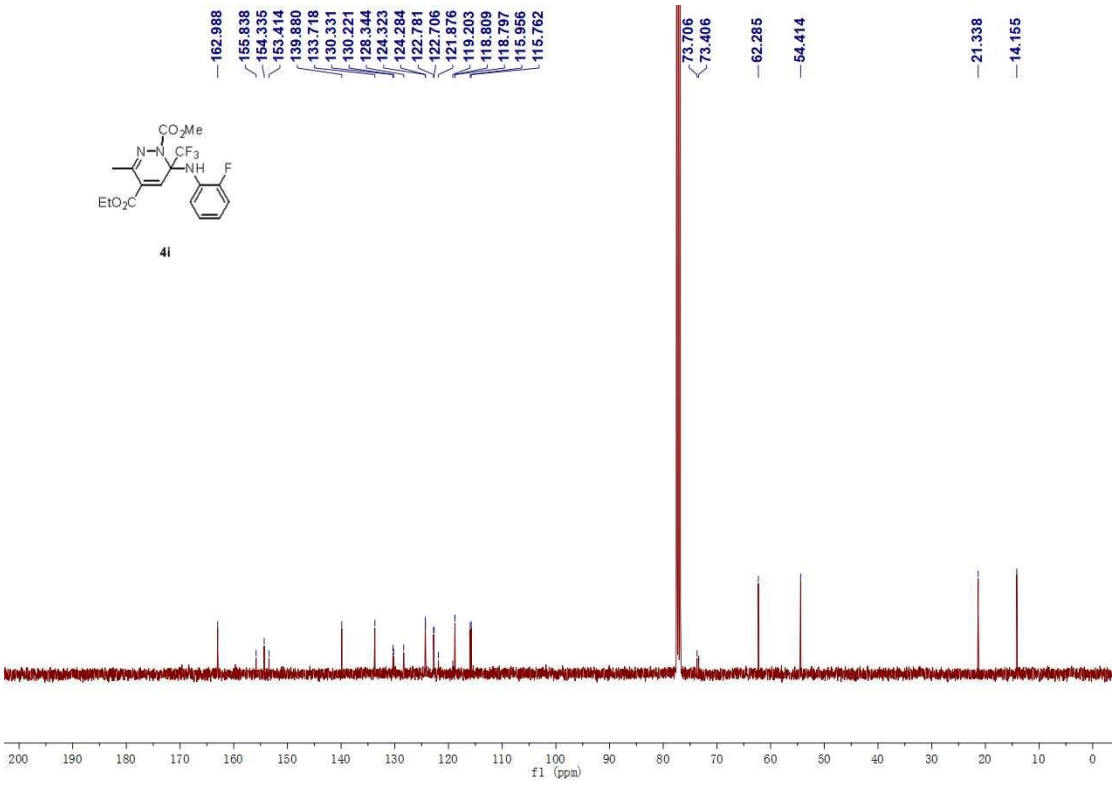
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4h



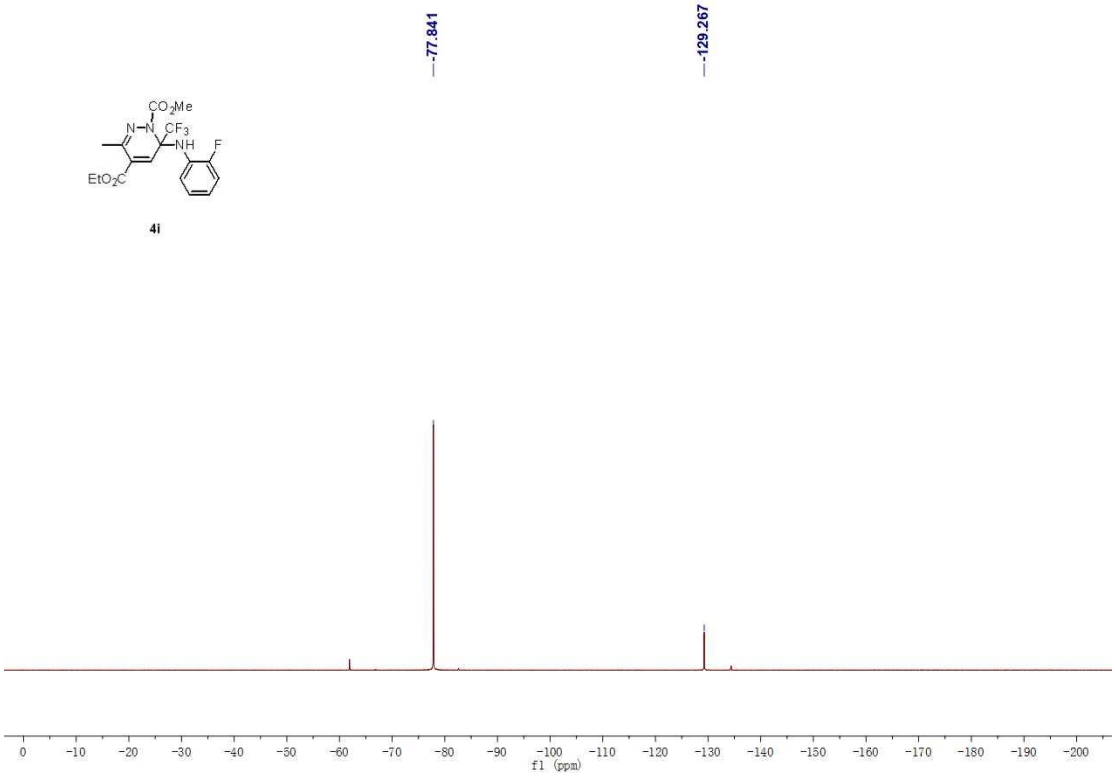
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4i



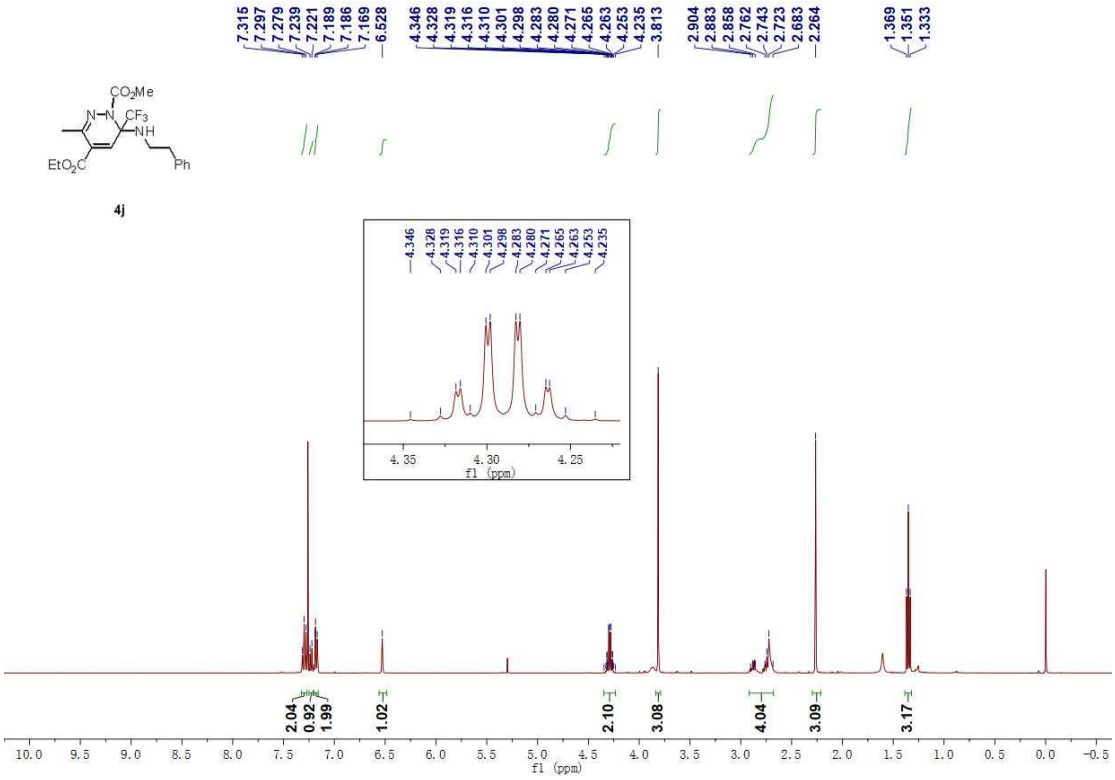
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4i



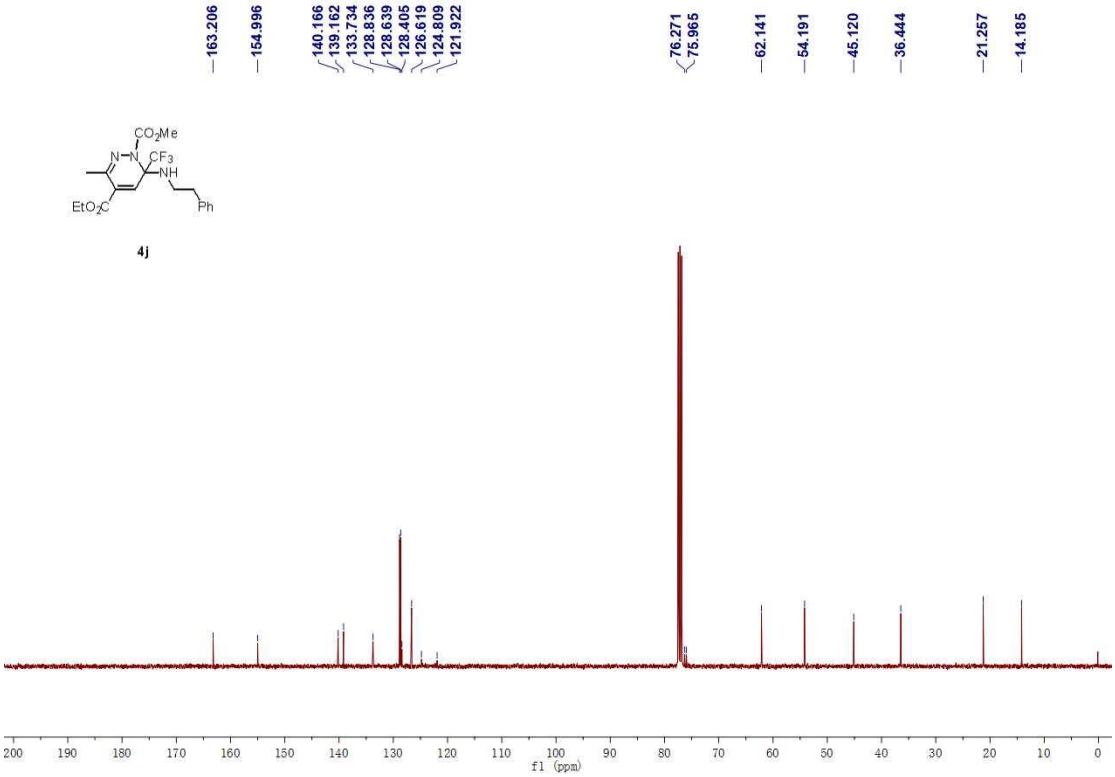
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4i



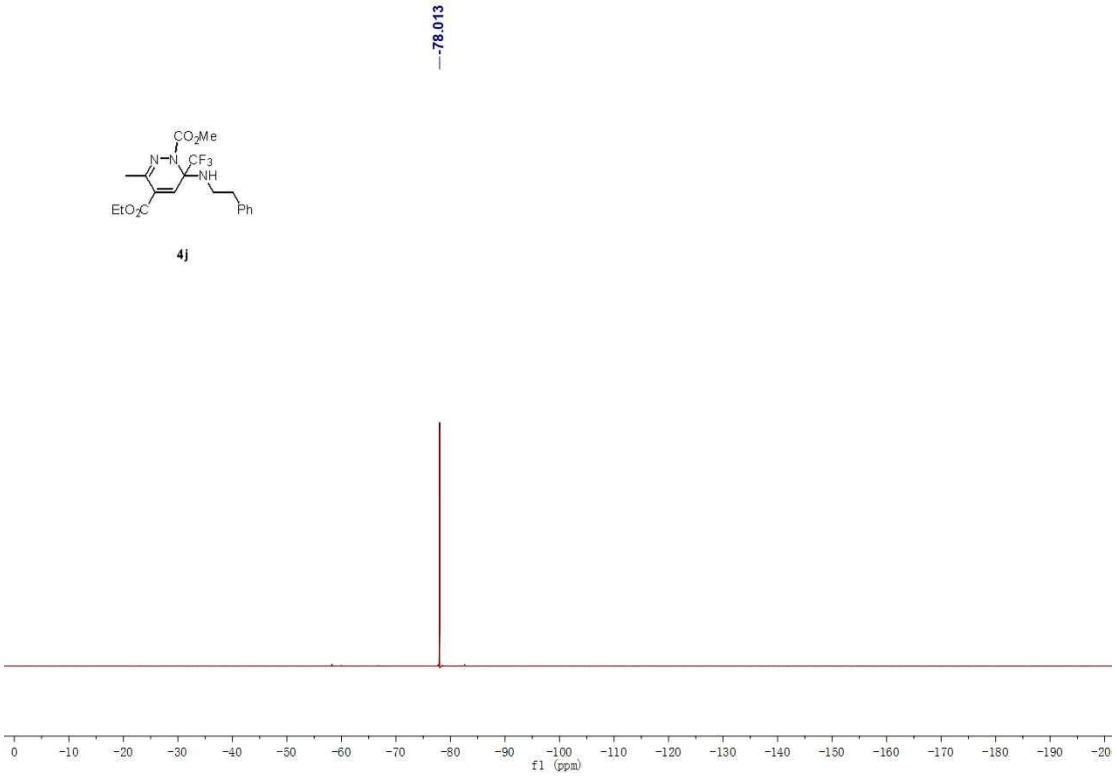
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4j



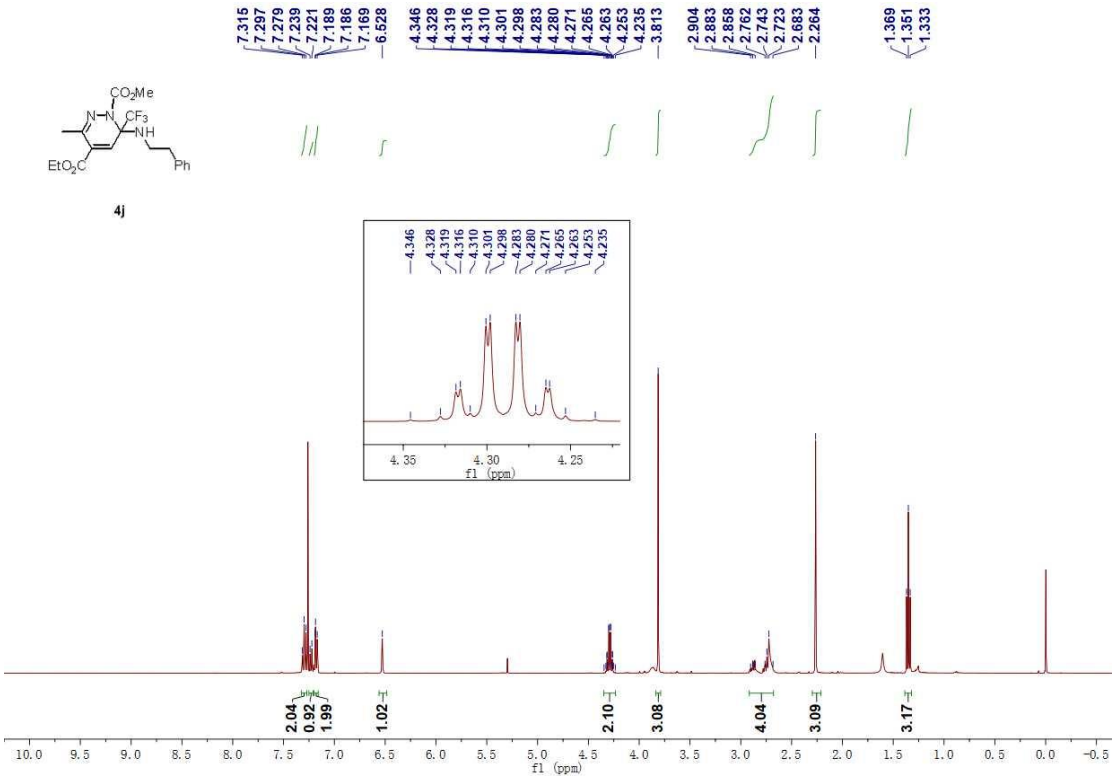
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4j



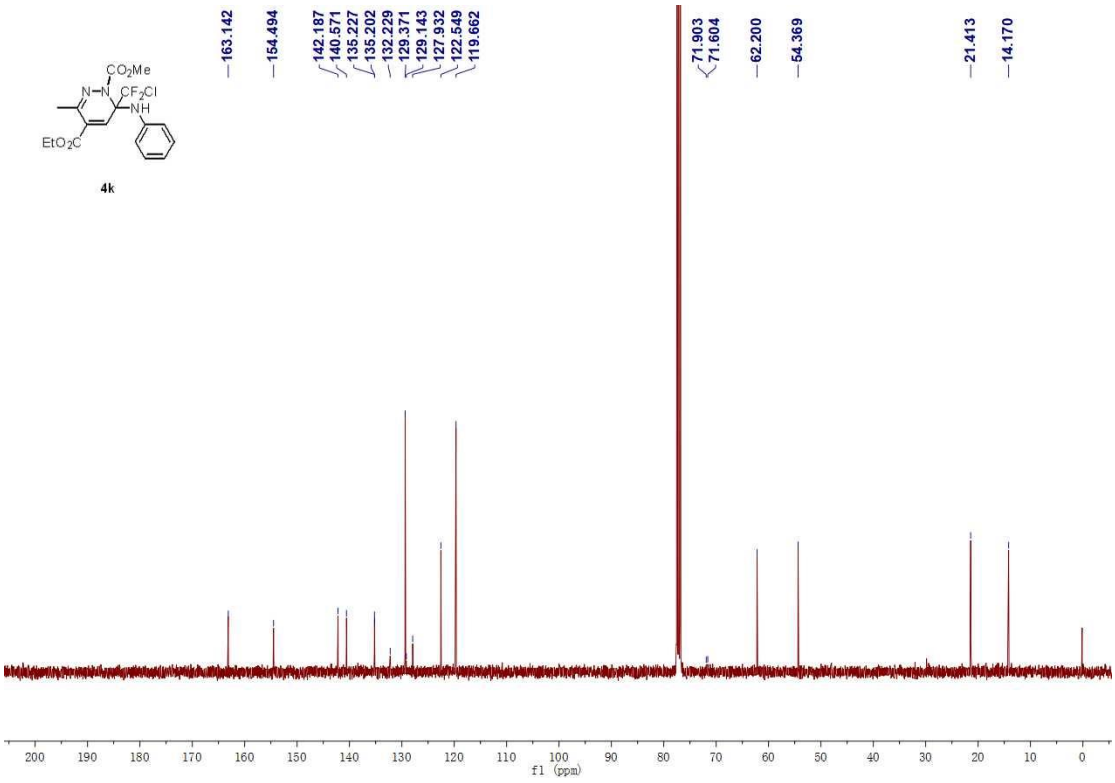
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4j



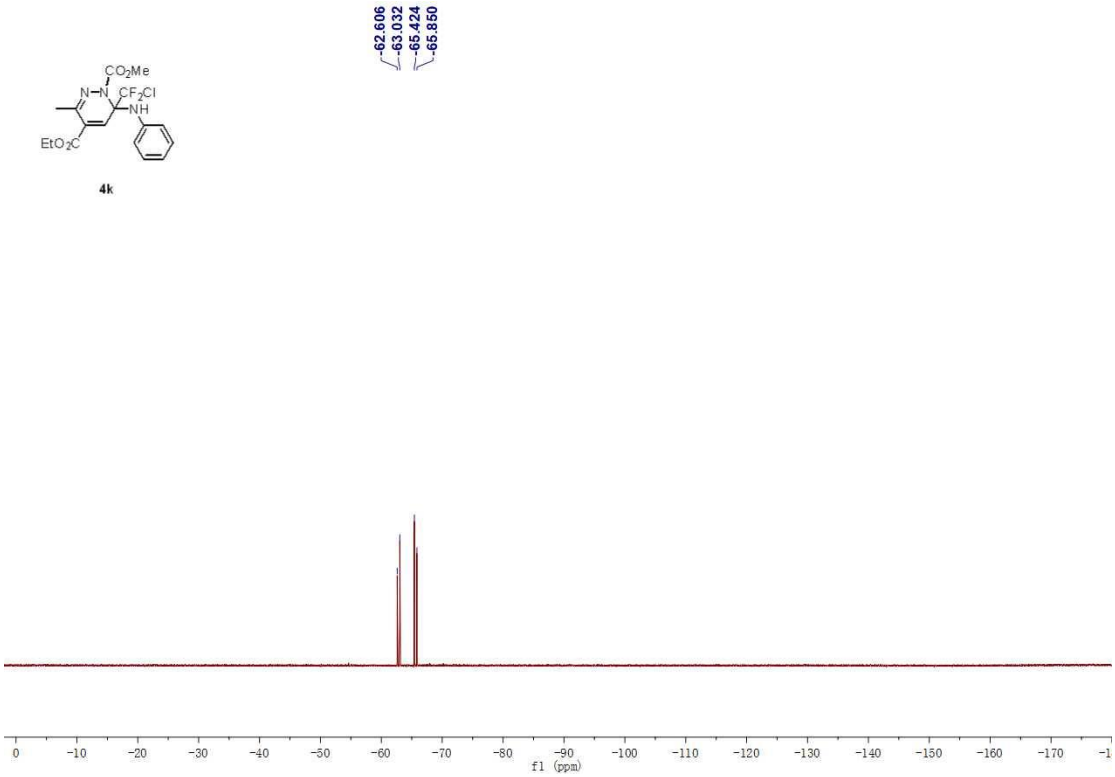
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4k



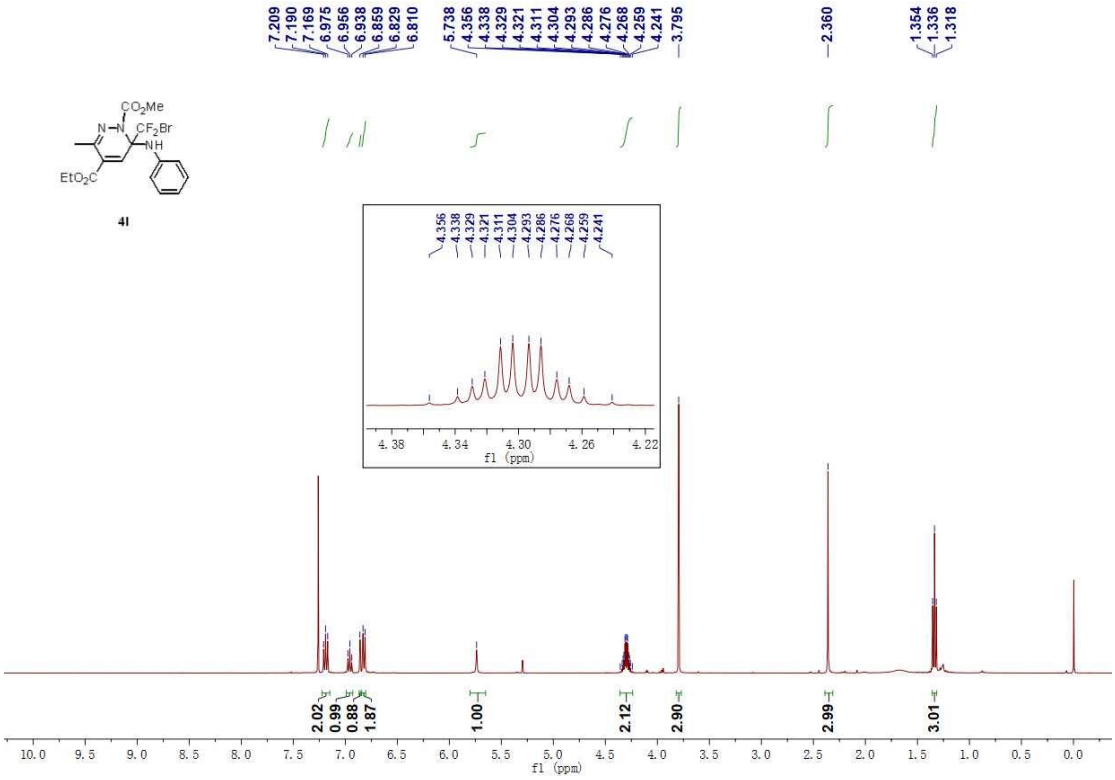
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4k



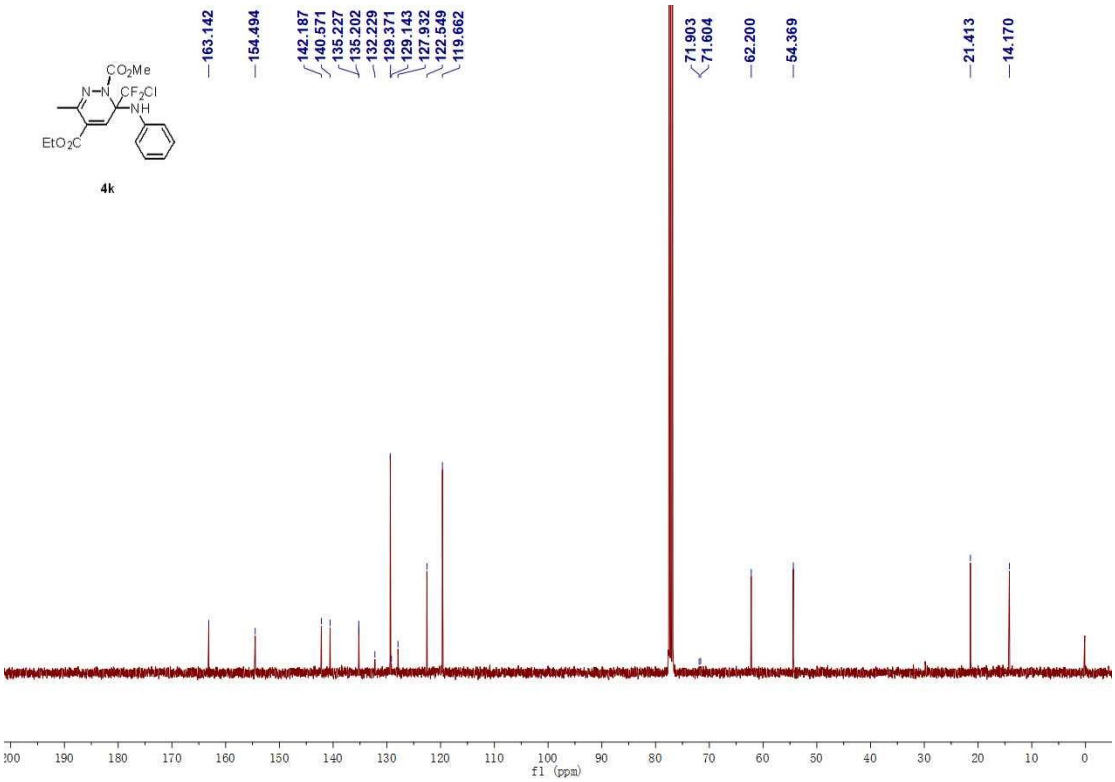
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4k



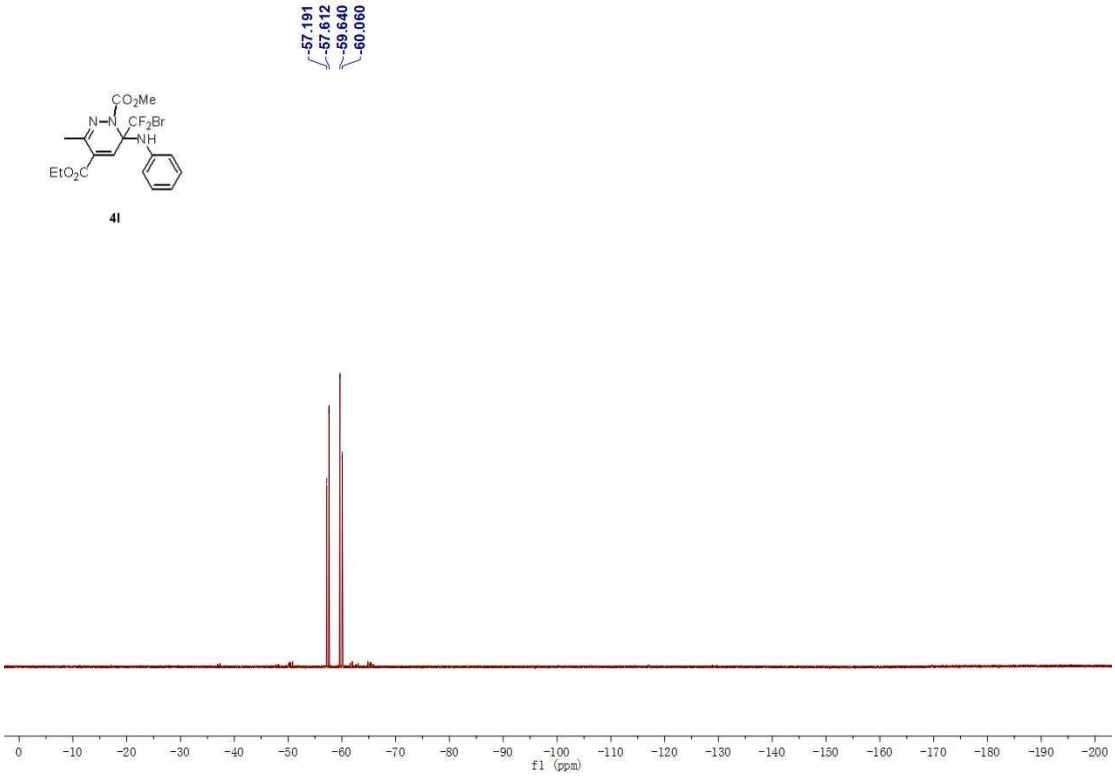
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4l



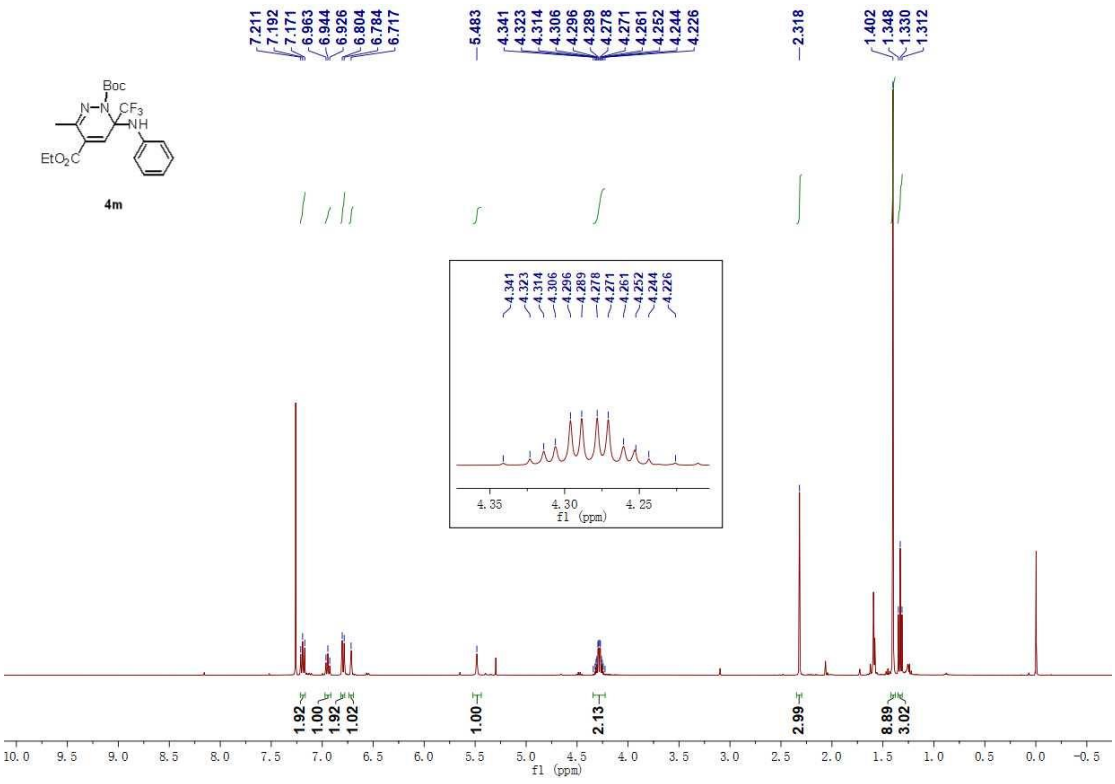
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4l



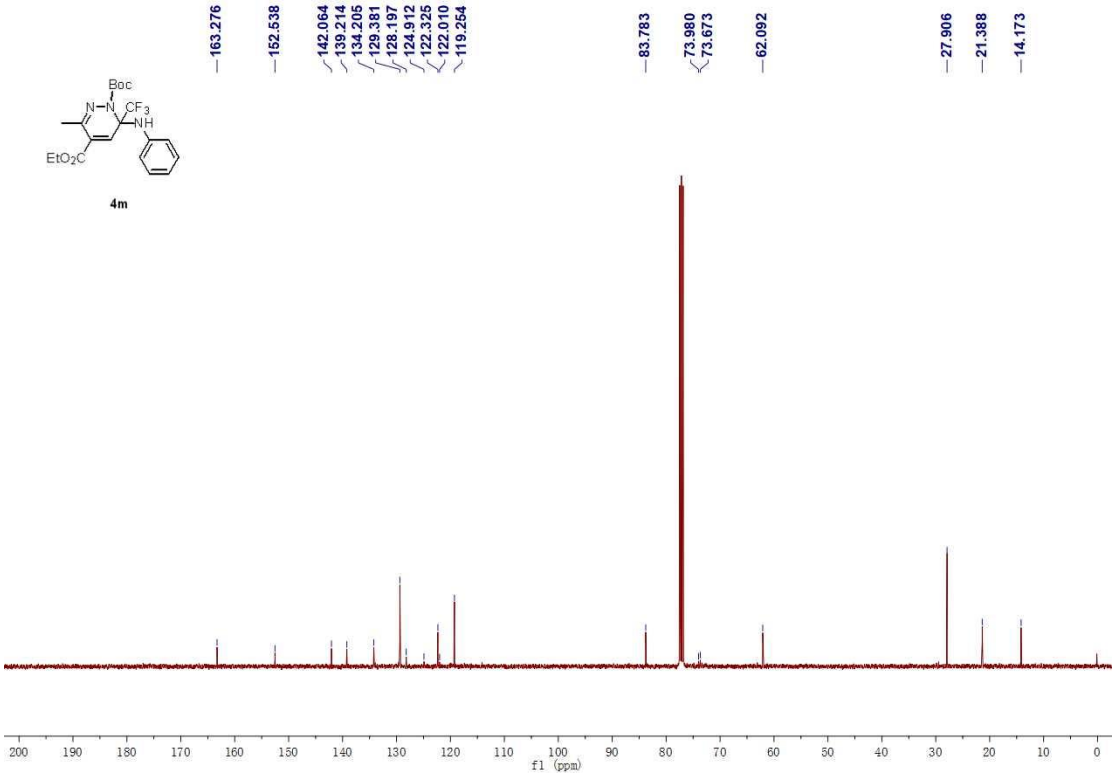
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4l



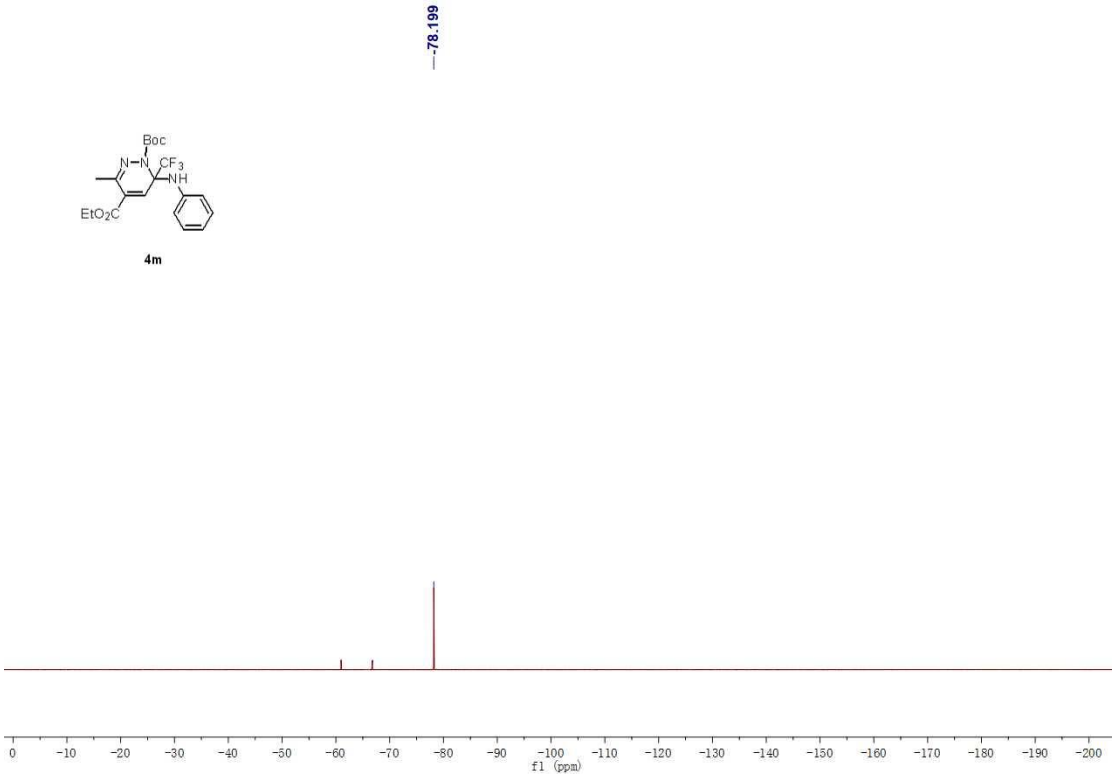
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4m



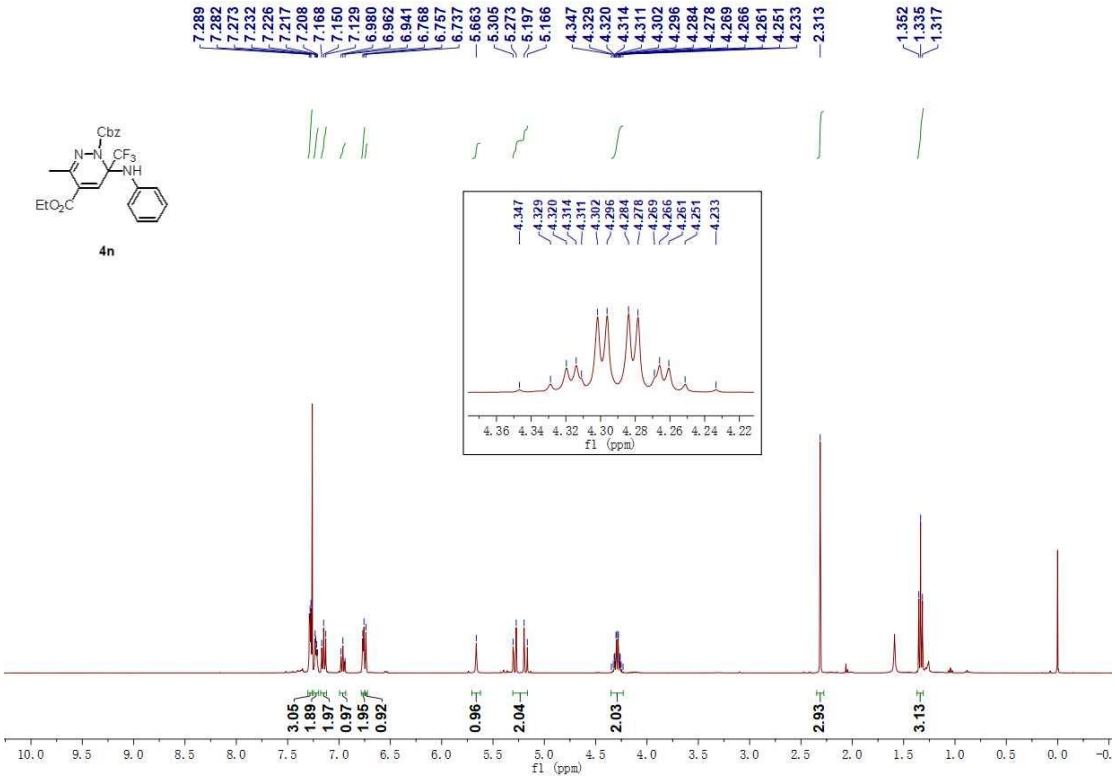
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4m



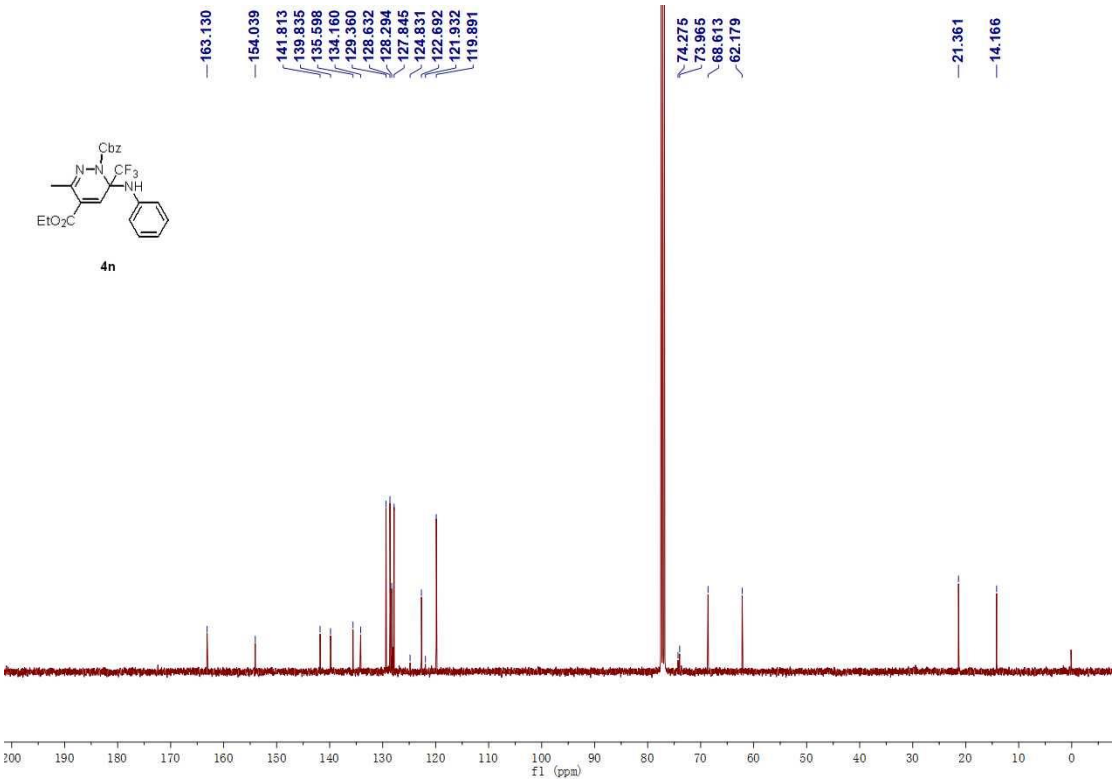
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4m



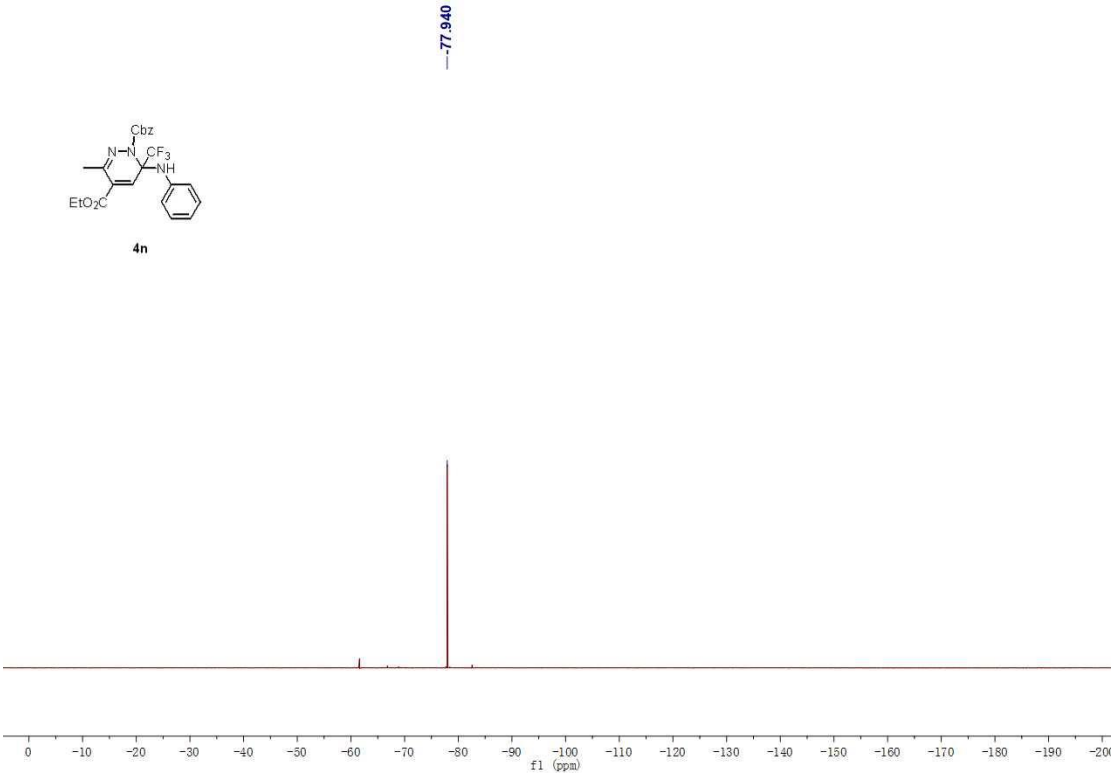
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4n



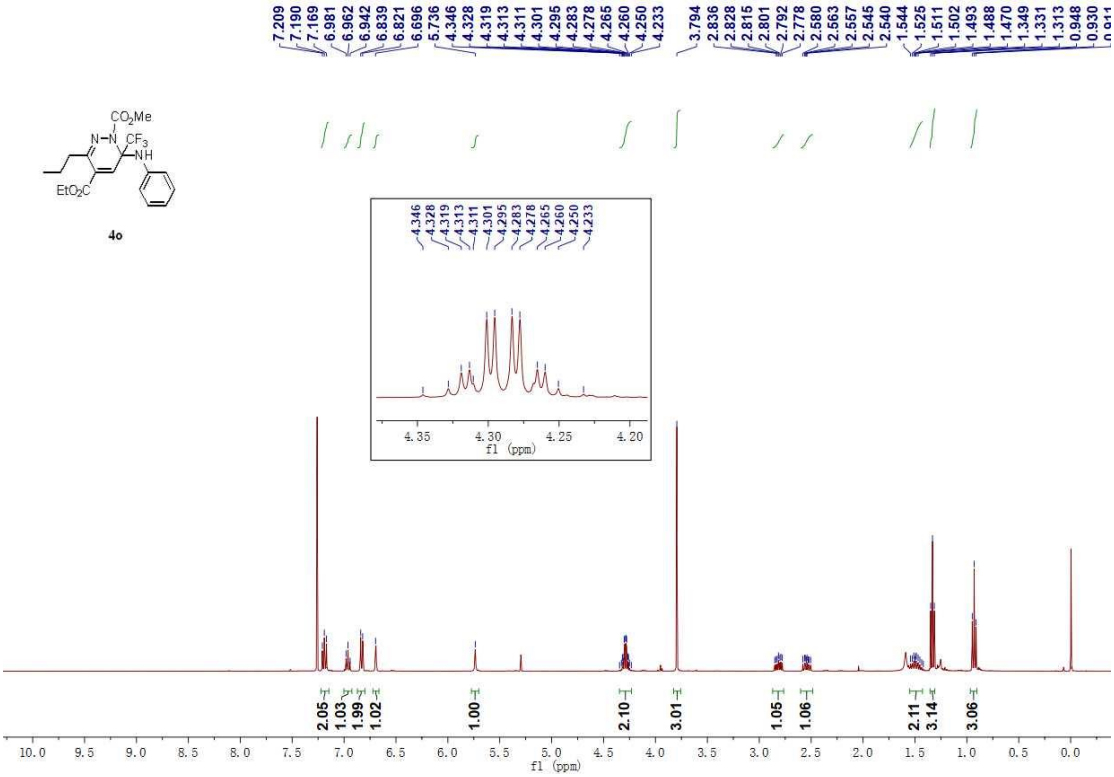
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4n



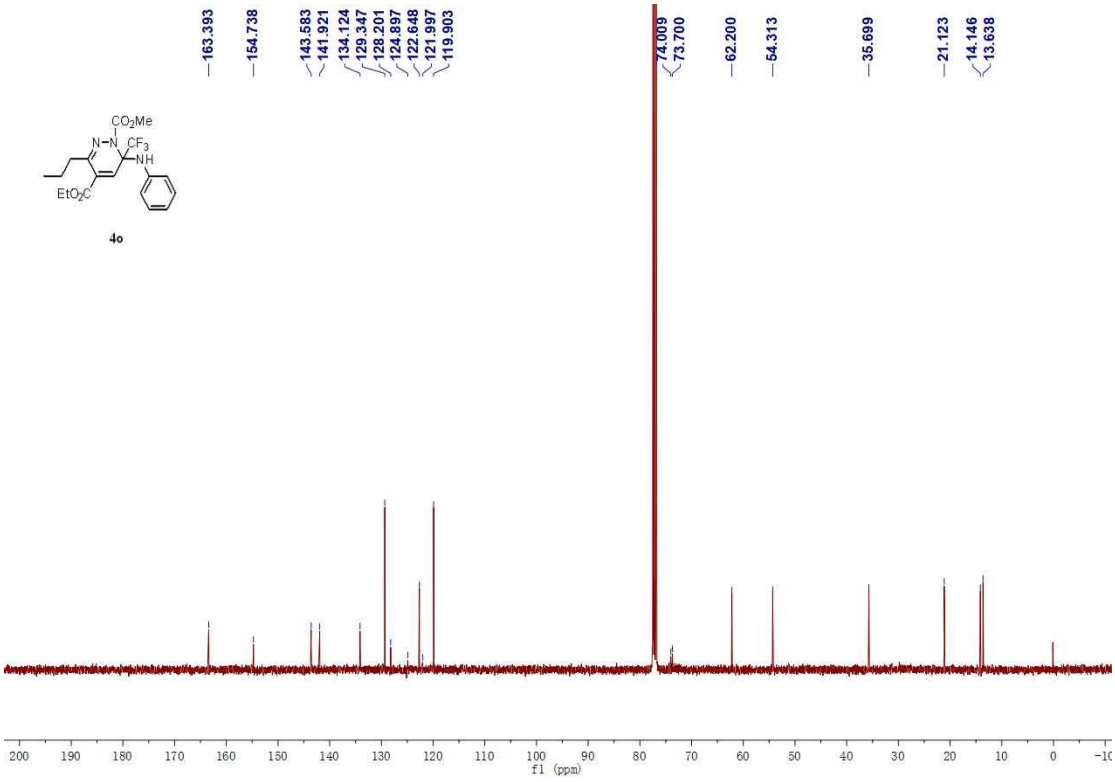
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4n



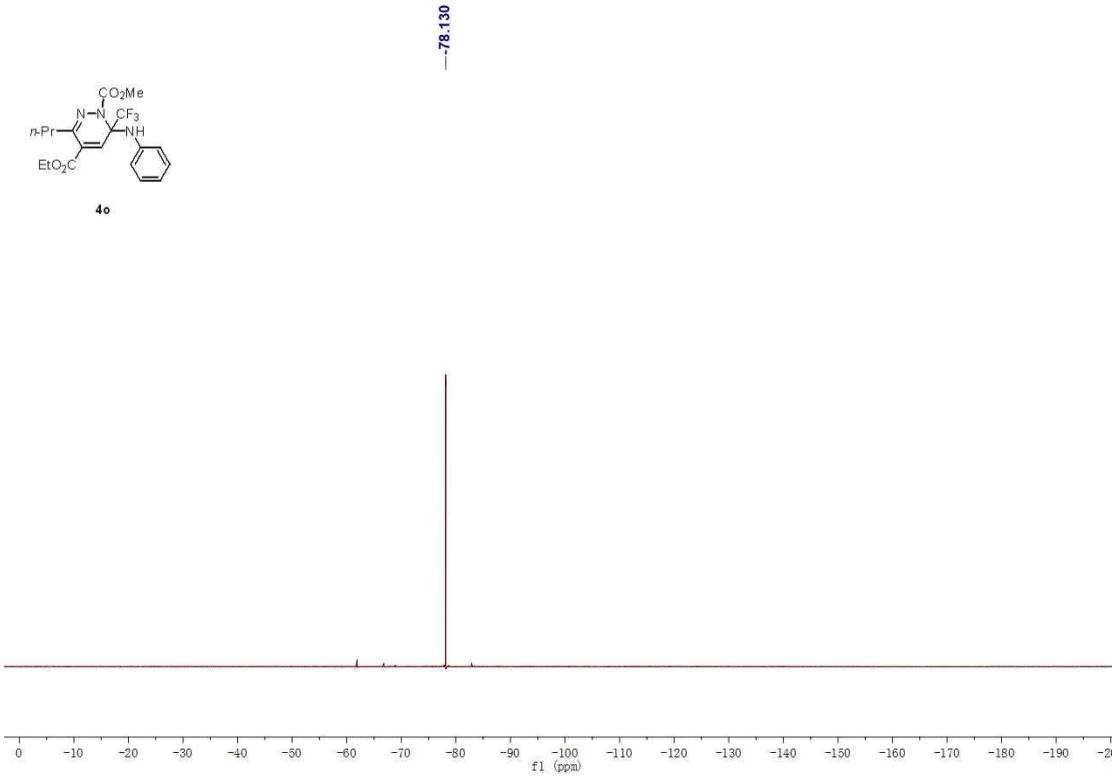
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4o



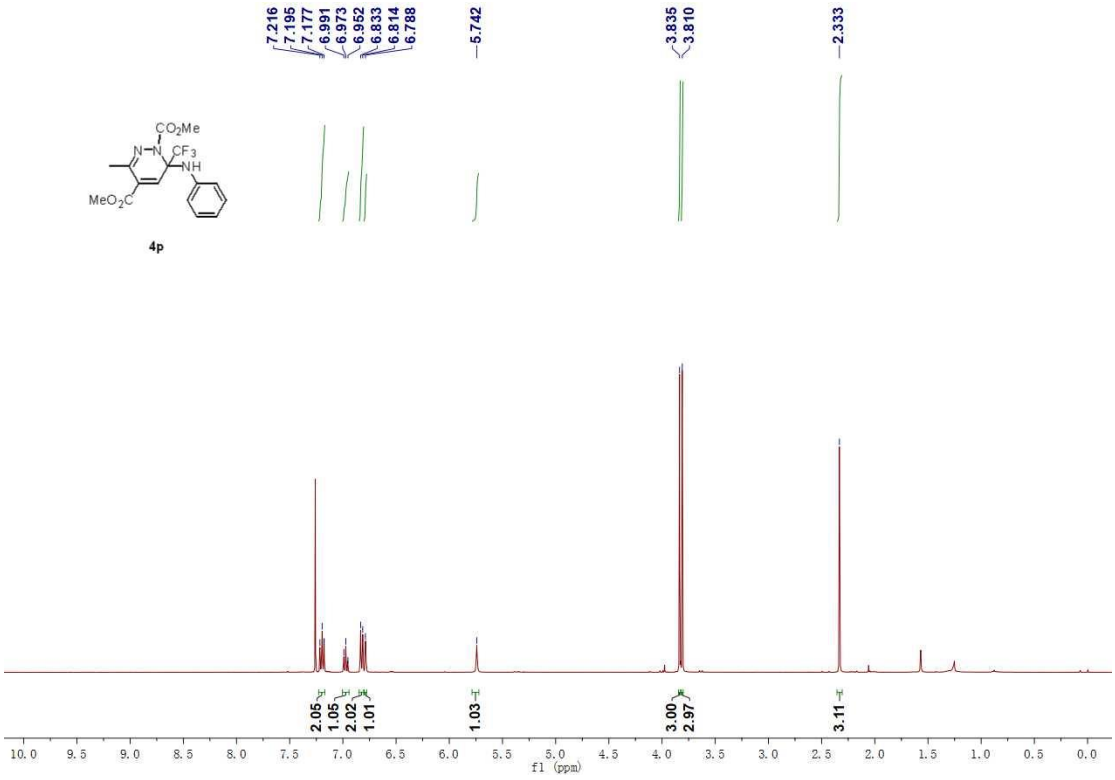
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4o



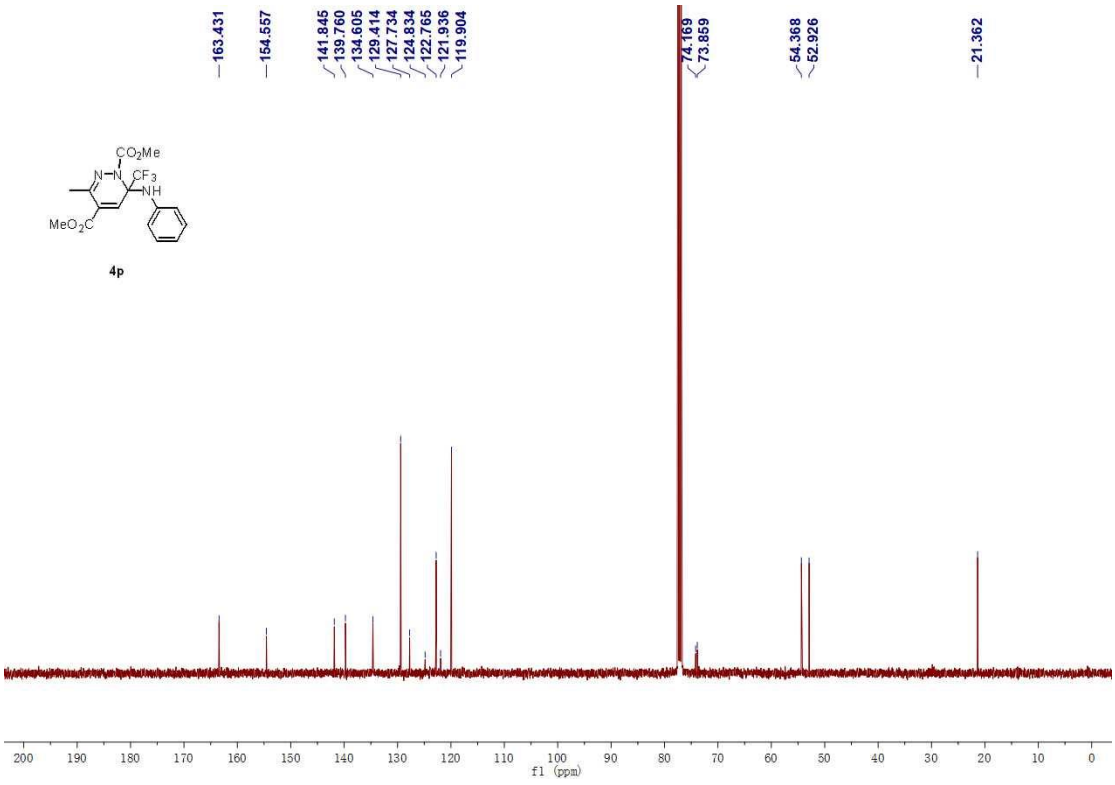
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4o



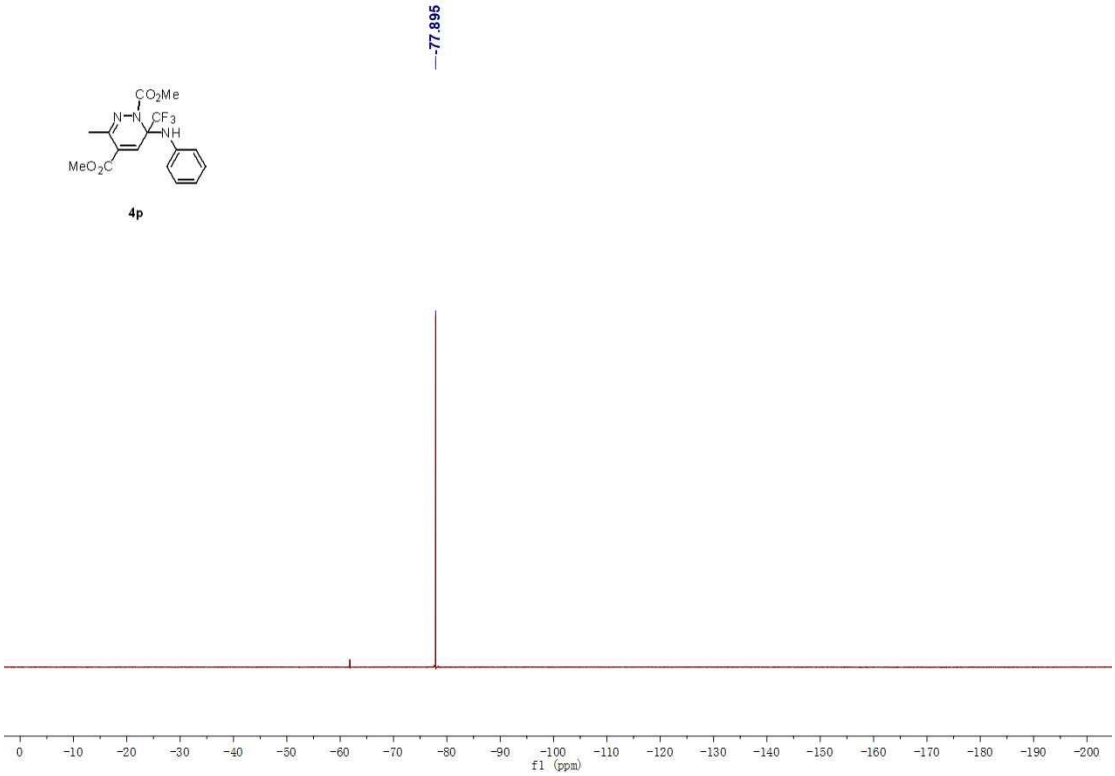
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4p



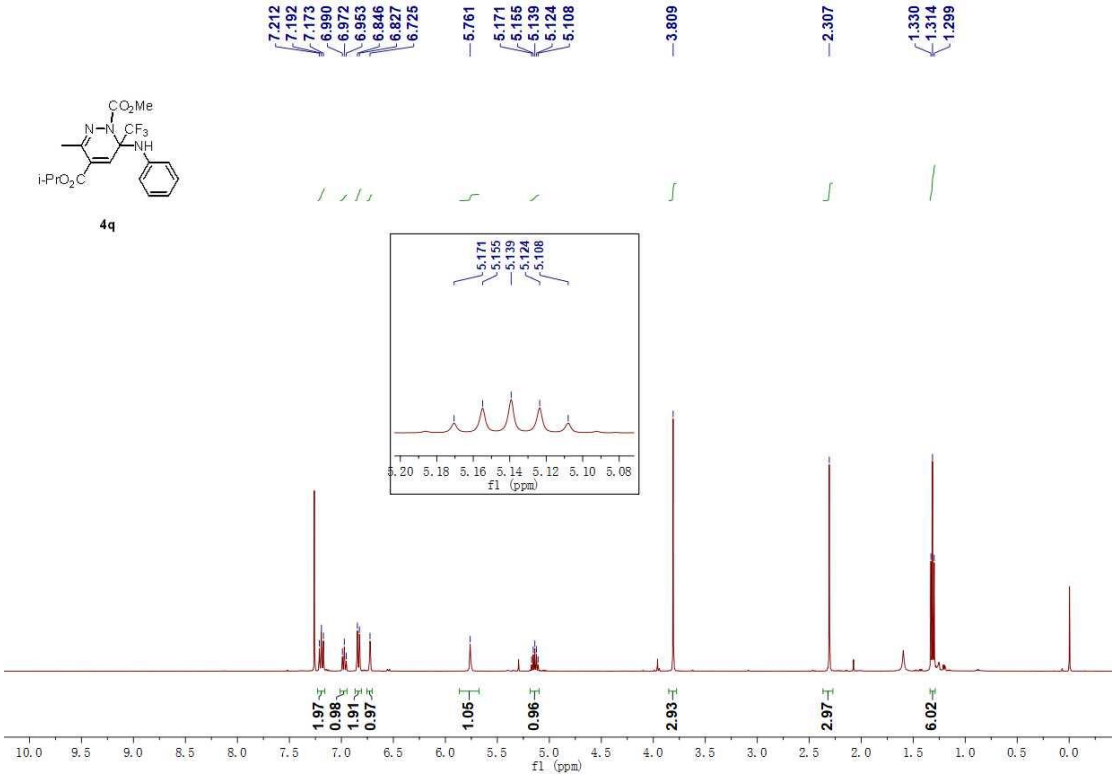
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4p



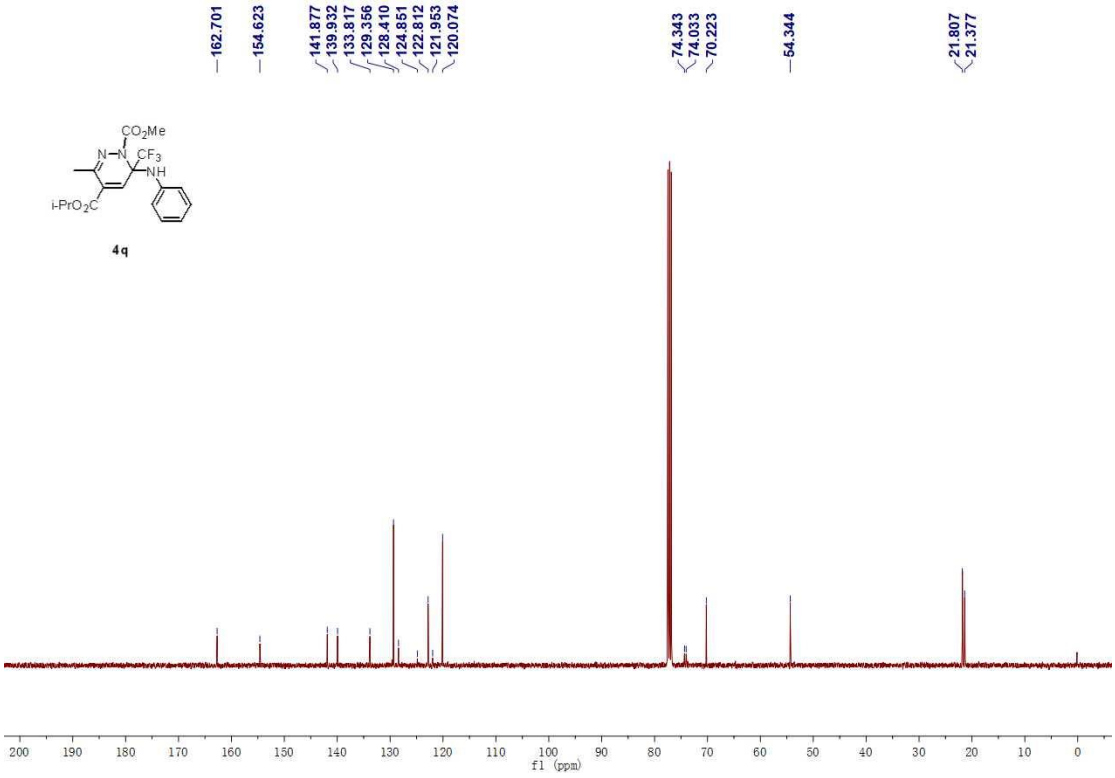
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4p



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4q



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4q



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4q