Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric Brønsted Base-Catalyzed Aza-Michael Addition and [3+2] Cycloaddition Reactions of *N*-Ester Acylhydrazones and Enones

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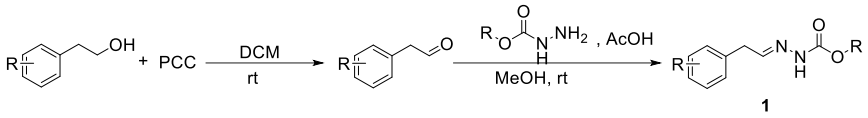
content

1. General information

All solvents and reagents were purchased from commercial sources and purified according to established procedures before use. ^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quaternary, m = multiplet), coupling constants (Hz), integration. $^{13}C\{^{1}H\}$ NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/IB/IC/ID/IF/IG/IH/MD/OD–H/OJ–H in comparison with the authentic racemates. Chiral HPLC analysis was operated at Thermo scientific Dionex Ultimate 3000. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was obtained by an ABI/Sciex QStar Mass Spectrometer (ESI). All melting points were conducted on a digital melting point apparatus and were uncorrected. TLC was performed on glass-backed silica plate.

2. Synthesis of substrates

General procedure for the synthesis of substrates **1**



1

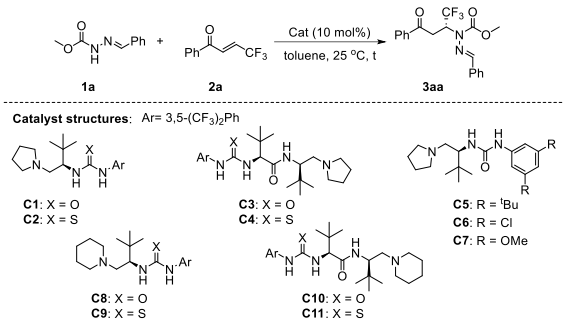
Pyridinium chlorochromate (7.5 mmol, 1.5 eq) and respective phenylethanol (5 mmol, 1.0 eq) dissolved in 25 mL dichloromethane, the resultant mixture was stirred for 5 h. Following this, the reaction was filtered through a silica plug and washed through with diethyl ether, and the solvent was removed to give the crude phenylacetaldehyde product (Colorless oil, 40-60% yields).

To a solution of methyl carbazate (10 mmol, 1.0 eq) in MeOH (30 mL) was added the respective phenylacetaldehyde (10 mmol, 1.0 eq) and glacial aceticacid (0.3 mL). The mixture was stirred at room temperature for 30 min and then concentrated. The resulting white solid obtained was dried in a vacuum oven and used without further purification.

3. Optimization of Asymmetric Reaction Conditions

3.1 The optimization of the enantioselective aza-Michael addition reaction catalyzed by organocatalyst

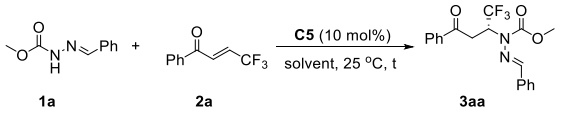
Table S1. The effect of catalyst[a]



entry	Cat.	time (h)	yield (%)[b]	ee (%)[c]
1	**C1**	96	40	95
2	**C2**	96	20	95
3	**C3**	96	5	83
4	**C4**	96	trace	N.A.
5	**C5**	30	80	98
6	**C6**	60	40	97
7	**C7**	30	70	98
8	**C8**	96	20	94
9	**C9**	96	15	93
10	**C10**	96	30	93
11	**C11**	96	trace	N.A.

[a] Reaction conditions: **1a** (0.1 mmol), Cat. (0.01 mmol), **2a** (0.2 mmol), and toluene (0.5 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

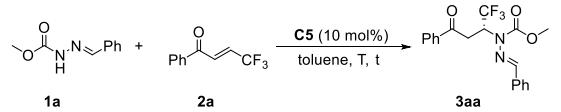
Table S2. The effect of solvents[a]



entry	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	THF	96	10	85
2	DCM	44	60	95
3	MeCN	96	10	73
4	Et_2O	96	10	95
5	PhCl	30	60	97
6	mesitylene	30	63	97
7	*m*-xylene	30	65	96
8	*o*-xylene	30	64	96
9	$PhCF_3$	30	58	97
10	C_6HF_5	96	20	92
11	PhBr	30	45	97

[a] Reaction conditions: **1a** (0.1 mmol), **C5** (0.01 mmol), **2a** (0.2 mmol), and solvent (0.5 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S3. The effect of temperature[a]

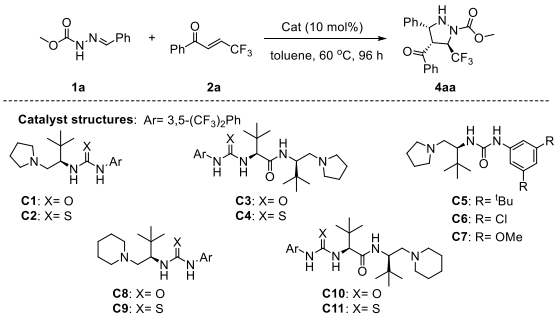


entry	T (°C)	time (h)	yield (%)[b]	ee (%)[c]
1	30	23	83	98
2	15	60	77	98
3	40	18	60	94

[a] Reaction conditions: **1a** (0.1 mmol), **C5** (0.01 mmol), **2a** (0.2 mmol), and toluene (0.5 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

3.2 The optimization of the enantioselective [3+2] cycloaddition reaction catalyzed by organocatalyst

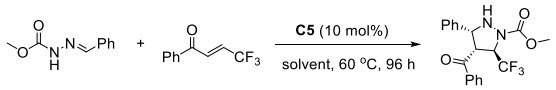
Table S4. The effect of catalyst[a]



Entry	Cat.	yield (%)[b]	ee (%)[c]	dr[d]
1	**C1**	69	86	>20:1
2	**C2**	56	83	>20:1
3	**C3**	30	61	>20:1
4	**C4**	30	58	>20:1
5	**C5**	83	92	>20:1
6	**C6**	80	85	>20:1
7	**C7**	81	91	>20:1
8	**C8**	35	80	>20:1
9	**C9**	55	89	>20:1
10	**C10**	45	8	>20:1
11	**C11**	30	27	>20:1

[a] Reaction conditions: **1a** (0.1 mmol), Cat. (0.01 mmol), **2a** (0.2 mmol), and toluene (0.5 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The dr was determined by ^{1}H NMR analysis of the reaction mixture.

Table S5. The effect of solvents[a]

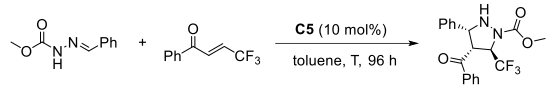


1a 2a 4aa

entry	solvent	yield (%)[b]	ee (%)[c]	dr[d]
1	THF	59	84	>20:1
2	DCM	53	85	>20:1
3	MeCN	48	61	>20:1
4	PhCl	84	86	>20:1
5	mesitylene	53	92	>20:1
6	*m*-xylene	59	86	>20:1
7	*o*-xylene	75	87	>20:1
8	$PhCF_3$	53	81	>20:1
9	C_6HF_5	53	80	>20:1
10	PhBr	64	85	>20:1

[a] Reaction conditions: **1a** (0.1 mmol), **C5** (0.01 mmol), **2a** (0.2 mmol), and solvent (0.5 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The dr was determined by ^{1}H NMR analysis of the reaction mixture.

Table S6. The effect of temperature[a]



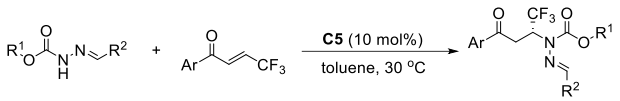
1a 2a 4aa

entry	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	50	53	93	>20:1
2	70	58	88	>20:1

[a] Reaction conditions: **1a** (0.1 mmol), **C5** (0.01 mmol), **2a** (0.2 mmol), and toluene (0.5 mL). [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The dr was determined by ^{1}H NMR analysis of the reaction mixture.

4. General procedure for the catalytic asymmetric reaction

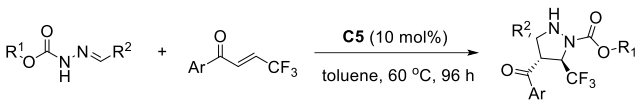
4.1 General procedure for the asymmetric aza-Michael addition catalyzed by organocatalyst



1 2 3

Acylhydrazone **1** (0.1 mmol, 1 eq), **C5** (4.0 mg, 0.1 eq) were dissolved in toluene (0.5 mL), Then *β*-trifluoromethyl-*α,β*-unsaturated ketone **2** (0.2 mmol, 2.0 eq) was added. The reaction mixture was stirred at 30 °C and monitored by TLC. Upon complete consumption acylhydrazone **1**, the organic solvent was removed and the residue was purified by column chromatography to give the product**,** which was then directly analyzd by HPLC to determine to enantiomeric excess.

4.2 General procedure for the asymmetric [3+2] cycloaddition catalyzed by organocatalyst

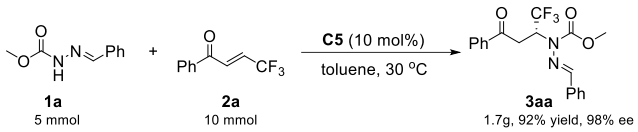


1 2 4

Acylhydrazone **1** (0.1 mmol, 1.0 eq), **C5** (4.0 mg, 0.1 eq) were dissolved in toluene (0.5 mL), Then *β*-trifluoromethyl-*α,β*-unsaturated ketone **2** (0.2 mmol, 2.0 eq) was added. The reaction mixture was stirred at 60 °C and monitored by TLC. Upon complete consumption acylhydrazone **1**, the organic solvent was removed and the residue was purified by column chromatography to give the product**,** which was then directly analyzd by HPLC to determine to enantiomeric excess.

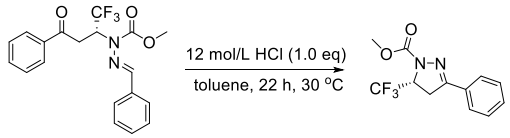
5. Synthetic application of the asymmetric reaction

5.1 Gram-Scale Synthesis of **3aa**



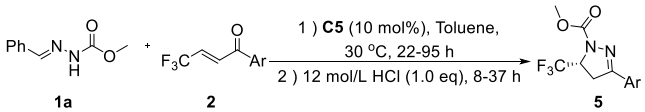
(*E*)-methyl 2-benzylidenehydrazinecarboxylate **1a** (0.89 g, 5 mmol) and **C5** (200 mg, 0.5 mmol) were dissolved in toluene (25 mL) at 30 °C, the (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **2a** (2 g, 10 mmol) was added and stirred for 28 h until the reaction was completed, as monitored by TLC analysis. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **3aa** in 92% yield with 98% ee.

5.2 General experimental procedure for transforming **3aa** to **5aa**



HCl (8.3 μL, 12 mol/L, 1.0 eq) was added to a solution of **5aa** (37.8 mg, 0.1 mmol) in toluene at 30 °C. After stirring at the same temperature for 22 hours, the mixture was removed under reduced pressure. Then the residue was purified by silica gel chromatography (PE/EA = 10/1-5/1) to afford compound 10aa as a white solid in 84% yield and 98% ee.

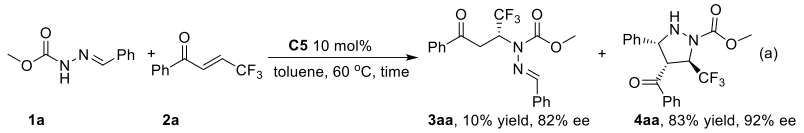
5.3 One-pot strategy for the synthesis of **5** from **1** and **2**



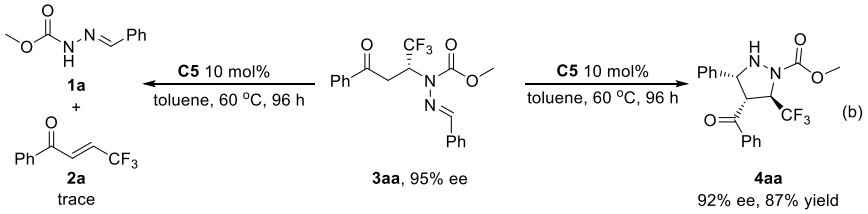
(*E*)-methyl 2-benzylidenehydrazinecarboxylate **1a** (0.1 mmol, 1.0 eq) and **C5** (4 mg, 0.1 eq) were dissolved in toluene (0.5 mL) at 30 °C, the *β*-trifluoromethyl-*α,β*-

unsaturated ketone **2** (0.2 mmol, 2.0 eq) was added and stirred for 22−95 h. The resulting mixture was monitored by TLC. Upon complete consumption of (*E*)-methyl 2-benzylidenehydrazinecarboxylate **3a**, HCl (8.3 μL, 1.0 eq) was added. The reaction mixture was stirred at the 30 °C for 8−37 h until the reaction was completed, as monitored by TLC analysis. The concentrated reaction residue was purified by flash column chromatography on silica gel to afford desired product **5**.

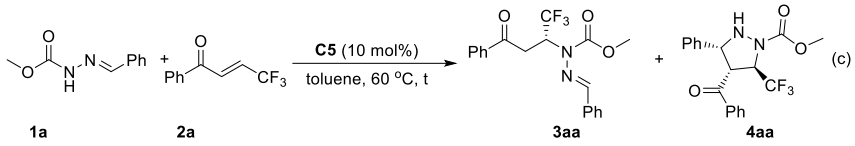
6. Control experiments



a) (*E*)-methyl 2-benzylidenehydrazinecarboxylate **1a** (17.8 g, 0.1 mmol) and **Cat 5** (4 mg, 0.01 mmol) were dissolved in toluene (0.5 mL) at 60 °C, the (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **2a** (40 g, 0.2 mmol) was added and stirred for 96 h. The reaction mixture was directly ladaed onto a short silica gel column, followed by gradient elution with PE/EA (10/1-3/1). Removing the solvent in vacuo, afforded products **3aa** (10% yield, 82% ee) and **4aa** (83% yield, 92% ee).



b) **3aa** (0.1 mmol, 1.0 eq), **C5** (4.0 mg, 0.1 eq) were dissolved in toluene (0.5 mL) at 60 °C. After stirring at the same temperature for 96 h, the mixture was removed under reduced pressure. Then the residue was purified by silica gel chromatography (PE/EA = 20/1 - 3/1) to afford compound **4aa** (87% yield, 92% ee), **1a** (trace) and **2a** (trace).

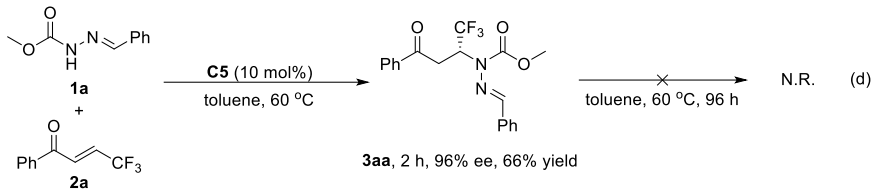


c) (*E*)-methyl 2-benzylidenehydrazinecarboxylate **1a** (17.8 g, 0.1 mmol) and **C5** (4 mg, 0.01 mmol) were dissolved in toluene (0.5 mL) at 60 °C, the (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **2a** (40 g, 0.2 mmol) was added and stirred for 96 h. With the passage of reaction time, the ee of products **3aa** and **4aa** changed as shown in the table below.

entry	reaction time	**3aa**	**4aa**

	(h)	ee (%)[b]	ee (%)[b]	dr[c]
1	2	96	N.D.	N.D.
2	14	94	96	>20:1
3	26	92	95	>20:1
4	40	90	95	>20:1
5	52	88	94	>20:1
6	65	86	94	>20:1
7	72	84	93	>20:1
8	96	82	92	>20:1

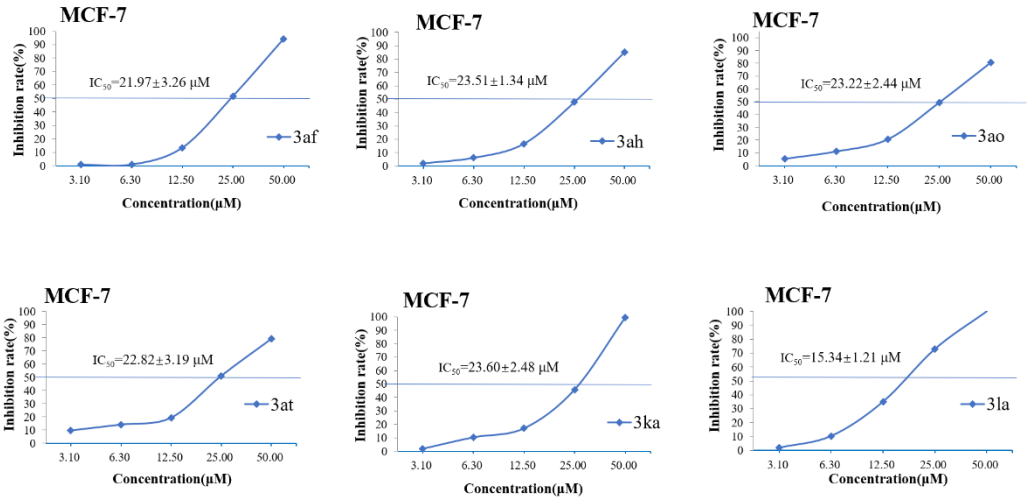
[a] Reaction conditions: **1a** (0.1 mmol), **C5** (0.01 mmol), **2a** (0.2 mmol), and solvent (0.5 mL). [b] Determined by HPLC analysis on a chiral stationary phase. [c] The dr was determined by ^{1}H NMR analysis of the reaction mixture.



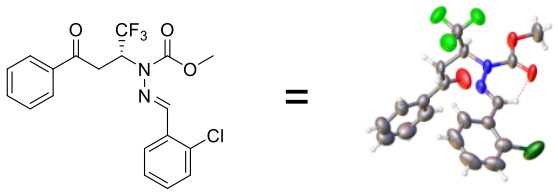
d) (*E*)-methyl 2-benzylidenehydrazinecarboxylate **1a** (17.8 g, 0.1 mmol) and **C5** (4 mg, 0.01 mmol) were dissolved in toluene (0.5 mL) at 60 °C, the (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **2a** (40 g, 0.2 mmol) was added and stirred for 2 h. The resulting mixture was monitored by TLC and purified by silica gel column using eluent: PE:EA = 10:1 to afford **3aa** with 66 % yield and 96% ee. Subsequently, **3aa** (0.66 mmol, 1 eq) was dissolved in toluene (0.3 mL) at 60 °C. After stirring at the same temperature for 96 h, the mixture was removed under reduced pressure. Then the residue was purified by silica gel chromatography (PE/EA = 10/1) to recover the material **3aa**.

7. Cell Culture and Cytotoxicity (CCK-8) assay

HepG2, A549 and MCF-7 cells were cultured in DMEM. CFPAC-1 cells were cultured in IMDM. All cells were purchased from American Type Culture Collection (ATCC). Cells were cultured with 10% fetal bovine serum (FBS) at 37 °C in a humidified atmosphere with 5% CO_2. And also added 1% penicillin-streptomycin solution (10 000 U/mL penicillin and 10 000 μg/mL streptomycin) to the culture medium in case of potential contamination. HepG2 (3.0×10^3 cells/well), A549 (3.0×10^3 cells/well), MCF-7 (3.0×10^3 cells/well), CFPAC-1 (5.0×10^3 cells/well) were seeded in 96-well tissue culture plates and cultured under 37 °C in a humidified atmosphere overnight. Cells were treated with various concentrations (3-50 μM) of each compound. After 48 h, cell viability was determined using CCK-8 assay according to the instruction manual. The reaction product of CCK-8 assay was measured at 450 nm and quantified using a Synergy Neo2 Multi-Mode Microplate Reader. Data were analyzed by GraphPad Prism 9.0. and presented as mean ± SD of three independent experiments.



8. Determination of the absolute configuration of products 3la and 4aa



3la

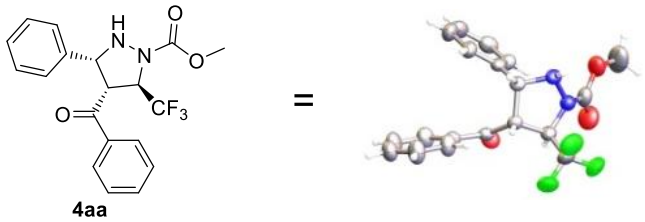
CCDC 2169815 (**3ia**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Displacement ellipsoids are drawn at the 50% probability level (solvent: PE/DCM =2:1)

Table 1 Crystal data and structure refinement for 3la.

Identification code	3la
Empirical formula	$C_{3.45}H_{0.09}Cl_{0.18}F_{0.55}N_{0.36}O_{0.55}$
Formula weight	72.21
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.9325(3)
b/Å	10.1011(2)
c/Å	12.3118(3)
α/°	98.974(2)
β/°	91.487(2)
γ/°	97.911(2)
Volume/Å^3	964.02(5)
Z	11
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	2.220
F(000)	393.0
Crystal size/mm^3	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.278 to 176.63

Index ranges	$-9 \le h \le 9, -12 \le k \le 13, -14 \le l \le 15$
Reflections collected	33914
Independent reflections	3817 [R_{int} = 0.0802, R_{sigma} = 0.0371]
Data/restraints/parameters	3817/0/254
Goodness-of-fit on F^2	1.982
Final R indexes [I>=2σ (I)]	R_1 = 0.0985, wR_2 = 0.2660
Final R indexes [all data]	R_1 = 0.1170, wR_2 = 0.3020
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.59



CCDC 2169816 (**4aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

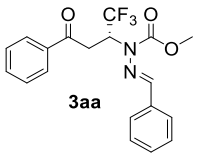
Displacement ellipsoids are drawn at the 50% probability level (solvent: PE/DCM =2:1)

Table 1 Crystal data and structure refinement for 4aa.

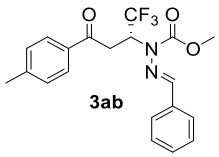
Identification code	4aa
Empirical formula	$C_{19}H_{17}F_3N_2O_3$
Formula weight	378.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.6089(2)
b/Å	5.61820(10)
c/Å	13.0437(2)
α/°	90
β/°	104.762(2)
γ/°	90
Volume/$Å^3$	893.51(3)
Z	2
ρ_{calc}g/cm^3	1.406

μ/mm^{-1}	1.001
F(000)	392.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.008 to 169.064
Index ranges	$-15 \leq h \leq 15$, $-6 \leq k \leq 6$, $-16 \leq l \leq 16$
Reflections collected	23354
Independent reflections	3255 [R_{int} = 0.0341, R_{sigma} = 0.0204]
Data/restraints/parameters	3255/1/245
Goodness-of-fit on F^2	1.140
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1046
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.1082
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.17
Flack parameter	0.10(7)

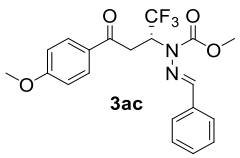
9. Characterization data of the praducts



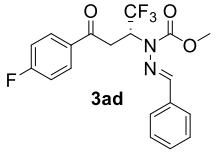
(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3aa): White solid; 83% yield, 98% ee; m.p.: 42.5 − 42.9 ºC; $[\alpha]_D^{18}$ = 71.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.855 min (major), 6.783 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.11 – 7.85 (m, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.53 (m, 2H), 7.50 – 7.45 (m, 2H), 7.39 – 7.30 (m, 3H), 5.86 – 5.62 (m, 1H), 4.27 (dd, J = 17.6, 10.3 Hz, 1H), 3.92 (s, 3H), 3.25 (dd, J = 17.6, 3.2 Hz, 1H): **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 195.3, 155.9, 154.3, 136.4, 134.7, 133.8, 130.6, 128.9, 128.7, 128.3, 127.7, 125.2 (q, J =281.1 Hz), 56.7 (q, J =30.5 Hz), 53.8, 34.8; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -73.50; **HRMS** (ESI) calcd. for $C_{19}H_{17}F_3N_2O_3Na$ ($[M+Na]^+$): 401.1083, found: 401.1074.



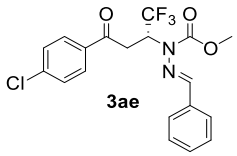
(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-(p-tolyl)butan-2-yl)hydrazinecarboxylate (3ab): White solid; 78% yield, 98% ee; m.p.: 40.4 − 41.3 ºC; $[\alpha]_D^{17}$ = 88.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.187 min (major), 6.877 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.99 – 7.81 (m, 2H), 7.62 – 7.47 (m, 2H), 7.40 – 7.30 (m, 3H), 7.28 – 7.19 (m, 2H), 5.78 – 5.62 (m, 1H), 4.22 (dd, J = 17.5, 10.2 Hz, 1H), 3.91 (s, 3H), 3.21 (dd, J = 17.6, 3.2 Hz, 1H), 2.40 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.9, 155.8, 154.3, 144.7, 134.8, 134.0, 130.5, 129.6, 128.7, 128.4, 127.7, 125.3 (q, J =281.0 Hz), 56.8 (q, J =30.7 Hz), 53.8, 34.7, 21.8;**^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.44; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1237.



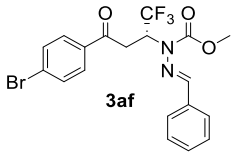
(*R,E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ac): White solid; 82% yield, 98% ee; m.p.: 65.0 − 65.6 °C; $[\alpha]_D^{15}$ = 91.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.017 min (major), 8.143 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.05 – 7.89 (m, 2H), 7.66 – 7.50 (m, 2H), 7.42 – 7.30 (m, 3H), 7.04 – 6.85 (m, 2H), 5.88 – 5.61 (m, 1H), 4.22 (dd, J = 17.5, 10.3 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.19 (dd, J = 17.4, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 193.7, 164.0, 155.6, 154.3, 134.8, 130.6, 130.5, 129.5, 128.7, 127.7, 125.2 (q, J =280.9 Hz), 114.0, 56.7 (q, J =30.1 Hz), 55.6, 53.8, 34.4; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.42; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_4Na$ ($[M+Na]^+$): 431.1189, found: 431.1181.



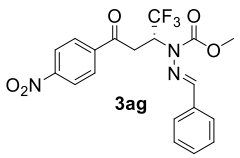
(*R,E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(4-fluorophenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ad): White solid; 66% yield, 97% ee; m.p.: 53.6 − 54.4 °C; $[\alpha]_D^{15}$ = 91.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.477 min (major), 6.772 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.13 – 7.91 (m, 2H), 7.61 – 7.46 (m, 2H), 7.43 – 7.29 (m, 3H), 7.20 – 7.07 (m, 2H), 5.81 – 5.62 (m, 1H), 4.23 (dd, J = 17.5, 10.3 Hz, 1H), 3.91 (s, 3H), 3.21 (dd, J = 17.5, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 193.7, 166.2 (d, J =254.1 Hz), 156.2, 154.3, 134.7, 132.9 (d, J =3.0 Hz), 131.0 (d, J =9.2 Hz), 130.7, 128.7, 127.7, 125.2 (q, J =281.1 Hz), 116.0 (d, J =21.7 Hz), 56.7 (q, J =30.4 Hz), 53.8, 34.7; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.54, -104.14; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0982.



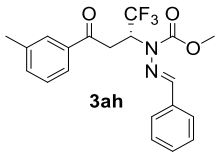
(*R*,*E*)-methyl 2-benzylidene-1-(4-(4-chlorophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)hydrazinecarboxylate (3ae): White solid; 66% yield, 96% ee; m.p.: 54.4 − 55.0 °C; $[\alpha]_D^{18}$ = 55.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.315 min (major), 5.930 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.99 – 7.87 (m, 2H), 7.59 – 7.49 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.29 (m, 3H), 5.79 – 5.62 (m, 1H), 4.22 (dd, J = 17.5, 10.3 Hz, 1H), 3.91 (s, 3H), 3.20 (dd, J = 17.5, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.1, 156.3, 154.3, 140.3, 134.8, 134.7, 130.7, 129.7, 129.2, 128.7, 127.7, 125.1 (q, J =281.4 Hz), 56.7 (q, J =30.9 Hz), 53.8, 34.7; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.55; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0689.



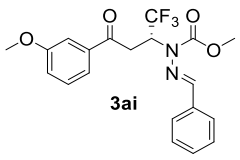
(*R*,*E*)-methyl 2-benzylidene-1-(4-(4-bromophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)hydrazinecarboxylate (3af): White solid; 65% yield, 97% ee; m.p.: 55.1 − 56.0 °C; $[\alpha]_D^{18}$ = 69.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.217 min (major), 6.840 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.98 – 7.77 (m, 2H), 7.66 – 7.56 (m, 2H), 7.57 – 7.49 (m, 2H), 7.41 – 7.31 (m, 3H), 5.80 – 5.61 (m, 1H), 4.21 (dd, J = 17.5, 10.3 Hz, 1H), 3.91 (s, 3H), 3.19 (dd, J = 17.5, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.3, 156.4, 154.3, 135.2, 134.6, 132.2, 130.7, 129.8, 129.1, 128.7, 127.7, 125.1 (q, J =281.0 Hz), 56.7 (q, J =30.5 Hz), 53.8, 34.7; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.56; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0186.



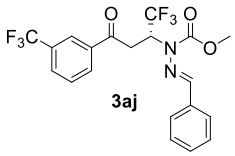
(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(4-nitrophenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ag): Colorless oil; 81% yield, 96% ee; $[\alpha]_D^{17}$ = 95.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.647 min (major), 11.640 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.39 – 8.23 (m, 2H), 8.21 – 8.07 (m, 2H), 7.58 – 7.47 (m, 2H), 7.42 – 7.28 (m, 3H), 5.79 – 5.65 (m, 1H), 4.29 (dd, J = 17.6, 10.3 Hz, 1H), 3.93 (s, 3H), 3.27 (dd, J = 17.6, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.0, 156.8, 154.3, 150.8, 140.8, 134.4, 130.9, 129.4, 128.8, 127.6, 125.0 (q, J =280.9 Hz), 124.1, 56.7 (q, J =31.0 Hz), 53.9, 35.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.65; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_3N_3O_5Na$ ($[M+Na]^+$): 446.0934, found: 446.0923.



(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-(m-tolyl)butan-2-yl)hydrazinecarboxylate (3ah): White solid; 75% yield, 98% ee; m.p.: 37.1 − 37.5 ºC; $[\alpha]_D^{17}$ = 104.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.460 min (major), 6.730 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.85 – 7.73 (m, 2H), 7.61 – 7.52 (m, 2H), 7.47 – 7.29 (m, 5H), 5.82 – 5.64 (m, 1H), 4.26 (dd, J = 17.6, 10.4 Hz, 1H), 3.92 (s, 3H), 3.21 (dd, J = 17.6, 3.2 Hz, 1H), 2.38 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.6, 155.8, 154.3, 138.7, 136.4, 134.7, 134.5, 130.6, 128.8, 128.7 (two peaks), 127.7, 125.5, 125.2 (q, J =280.9 Hz), 56.7 (q, J =30.6 Hz), 53.8, 34.8, 21.4; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.47; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1233.

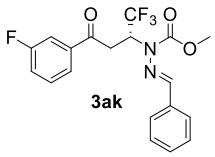


(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(3-methoxyphenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ai): Colorless oil; 77% yield, 98% ee; $[\alpha]_D^{21}$ = 77.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IB, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.057 min (major), 7.287 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.62 – 7.51 (m, 3H), 7.52 – 7.46 (m, 1H), 7.40 – 7.29 (m, 4H), 7.17 – 7.10 (m, 1H), 5.81 – 5.62 (m, 1H), 4.25 (dd, J = 17.6, 10.3 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 3.23 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 160.1, 156.0, 154.3, 137.8, 134.7, 130.6, 129.9, 128.7, 127.7, 125.2 (q, J =280.1 Hz), 121.0, 120.5, 112.3, 56.7 (q, J =30.6 Hz), 55.6, 53.8, 34.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.51; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_4Na$ ($[M+Na]^+$): 431.1189, found: 431.1188.



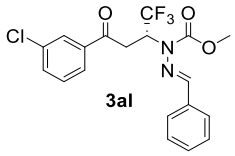
3aj

(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-(3-(trifluoromethyl)phenyl)butan-2-yl)hydrazinecarboxylate (3aj): Colorless oil; 77% yield, 98% ee; $[\alpha]_D^{21}$ = 76.8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.813 min (major), 5.803 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.24 (s, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.29 (m, 3H), 5.84 – 5.55 (m, 1H), 4.30 (dd, J = 17.5, 10.4 Hz, 1H), 3.92 (s, 3H), 3.23 (dd, J = 17.5, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.2, 156.7, 154.3, 137.0, 134.5, 131.7 (q, J =32.6 Hz), 131.5, 130.8, 130.2 (q, J =3.6 Hz), 130.0, 128.8, 127.7, 125.2 (q, J =4.2 Hz), 125.1 (q, J =280.9 Hz), 122.4, 56.7 (q, J =30.9 Hz), 53.9, 34.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -62.87, -73.61; **HRMS** (ESI) calcd. for $C_{20}H_{16}F_6N_2O_3Na$ ($[M+Na]^+$): 469.0957, found: 469.0952.



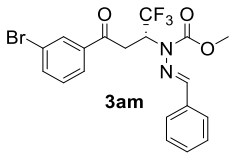
3ak

(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(3-fluorophenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ak): White solid; 61% yield, 96% ee; m.p.: 44.1 − 44.5 °C; $[\alpha]_D^{17}$ = 103.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.450 min (major), 6.022 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.86 – 7.73 (m, 1H), 7.71 – 7.62 (m, 1H), 7.59 – 7.51 (m, 2H), 7.49 – 7.40 (m, 1H), 7.39 – 7.27 (m, 4H), 5.78 – 5.63 (m, 1H), 4.23 (dd, J = 17.6, 10.2 Hz, 1H), 3.92 (s, 3H), 3.22 (dd, J = 17.6, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.1 (d, J =2.2 Hz), 164.1 (d, J =247.0 Hz), 156.3, 154.3, 138.5 (d, J =5.9 Hz), 134.7, 130.7, 130.6 (d, J =7.8 Hz), 128.7, 127.7, 125.1 (q, J =280.9 Hz), 124.1 (d, J =3.1 Hz), 120.8 (d, J =21.6 Hz), 115.1 (d, J =22.3 Hz), 56.7 (q, J =30.5 Hz), 53.8, 35.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.57, -111.40; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0985.



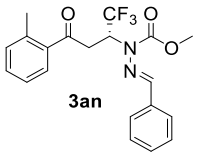
3al

(*R*,*E*)-methyl 2-benzylidene-1-(4-(3-chlorophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)hydrazinecarboxylate (3al): Colorless oil; 57% yield, 95% ee; $[\alpha]_D^{17}$ = 105.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.082 min (major), 9.600 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.02 – 7.92 (m, 1H), 7.91 – 7.82 (m, 1H), 7.61 – 7.51 (m, 3H), 7.48 – 7.30 (m, 4H), 5.85 – 5.60 (m, 1H), 4.23 (dd, J = 17.5, 10.4 Hz, 1H), 3.92 (s, 3H), 3.20 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.2, 156.6, 154.3, 138.0, 135.3, 134.6, 133.7, 130.7, 130.2, 128.8, 128.5, 127.7, 126.4, 125.1 (q, J =281.1 Hz), 56.7 (q, J =30.6 Hz), 53.9, 34.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.57; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0694.



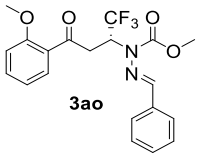
3am

(*R*,*E*)-methyl 2-benzylidene-1-(4-(3-bromophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)hydrazinecarboxylate (3am): Colorless oil; 64% yield, 98% ee; $[\alpha]_D^{22}$ = 69.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IB, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.837 min (major), 6.720 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.17 – 8.03 (m, 1H), 7.95 – 7.85 (m, 1H), 7.75 – 7.67 (m, 1H), 7.60 – 7.51 (m, 2H), 7.40 – 7.32 (m, 4H), 5.86 – 5.45 (m, 1H), 4.22 (dd, J = 17.5, 10.4 Hz, 1H), 3.91 (s, 3H), 3.19 (dd, J = 17.5, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.1, 156.6, 154.3, 138.2, 136.6, 134.6, 131.4, 130.7, 130.5, 128.8, 127.7, 126.8, 125.1 (q, J =281.1 Hz), 123.3, 56.7 (q, J =30.9 Hz), 53.9, 34.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.57; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0183.



3an

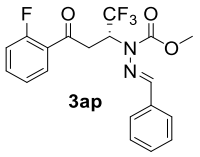
(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-(o-tolyl)butan-2-yl)hydrazinecarboxylate (3an): Colorless oil; 87% yield, 97% ee; $[\alpha]_D^{18}$ = 141.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.827 min (major), 15.425 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.77 – 7.62 (m, 1H), 7.57 – 7.47 (m, 2H), 7.43 – 7.28 (m, 4H), 7.27 – 7.18 (m, 2H), 5.76 – 5.60 (m, 1H), 4.12 (dd, J = 17.2, 10.4 Hz, 1H), 3.90 (s, 3H), 3.20 (dd, J = 17.2, 3.7 Hz, 1H), 2.42 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.8, 156.3, 154.4, 138.6, 137.4, 134.7, 132.2, 131.9, 130.6, 128.7, 128.6, 127.7, 125.9, 125.2 (q, J =281.3 Hz), 57.1 (q, J =30.5 Hz), 53.9, 37.6, 21.2; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.65; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1239.



3ao

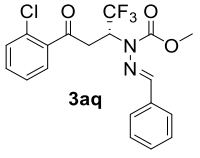
(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(2-methoxyphenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ao): Colorless oil; 78% yield, 97% ee; $[\alpha]_D^{16}$ = 79.4 (c 1.0,

$CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.180 min (major), 7.407 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.85 – 7.62 (m, 1H), 7.57 – 7.51 (m, 2H), 7.52 – 7.43 (m, 1H), 7.39 – 7.27 (m, 3H), 7.04 – 6.90 (m, 2H), 5.73 – 5.61 (m, 1H), 4.15 (dd, J = 18.0, 10.3 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.38 (dd, J = 18.0, 3.4 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 197.2, 158.7, 155.4, 154.3, 134.9, 134.2, 130.8, 130.4, 128.6, 127.7, 127.4, 125.2 (q, J =280.9 Hz), 120.9, 111.6, 56.9 (q, J =30.3 Hz), 55.7, 53.7, 40.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.49; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_4Na$ ($[M+Na]^+$): 431.1189, found: 431.1188.



3ap

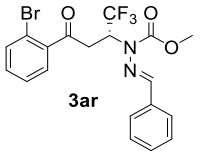
(*R,E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(2-fluorophenyl)-4-oxobutan-2-yl)hydrazinecarboxylate (3ap): Colorless oil; 63% yield, 89% ee; $[\alpha]_D^{17}$ = 101.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.373 min (major), 6.035 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.92 – 7.74 (m, 1H), 7.61 – 7.46 (m, 3H), 7.40 – 7.26 (m, 3H), 7.25 – 7.10 (m, 2H), 5.79 – 5.46 (m, 1H), 4.32 – 4.08 (m, 1H), 3.91 (s, 3H), 3.46 – 3.16 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 193.5 (d, J =3.9 Hz), 162.2 (d, J =252.9 Hz), 156.0, 154.4, 135.2 (d, J =8.9 Hz), 134.8, 130.9 (d, J =2.7 Hz), 130.6, 128.7, 127.7, 125.2 (d, J =12.8 Hz), 125.1 (q, J =280.9 Hz), 124.8 (d, J =3.6 Hz), 116.9 (d, J =23.7 Hz), 56.6 (q, J =30.0 Hz), 53.8, 39.5 (d, J =8.8 Hz); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.65, -109.22; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0993.



3aq

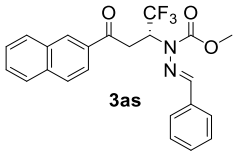
(*R,E*)-methyl 2-benzylidene-1-(4-(2-chlorophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)hydrazinecarboxylate (3aq): Colorless oil; 72% yield, 94% ee; $[\alpha]_D^{19}$ = 39.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0

mL/min, λ = 254 nm, retention time: 6.208 min (major), 6.748 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.61 – 7.43 (m, 3H), 7.43 – 7.18 (m, 6H), 5.76 – 5.53 (m, 1H), 4.14 (dd, J = 17.6, 10.4 Hz, 1H), 3.88 (s, 3H), 3.35 (dd, J = 17.6, 3.6 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.1, 156.2, 154.2, 138.5, 134.7, 132.4, 131.3, 130.7 (two peaks), 129.7, 128.7, 127.7, 127.2, 125.0 (q, J =281.4 Hz), 57.0 (q, J =31.0 Hz), 53.8, 39.2; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.70; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0687.



3ar

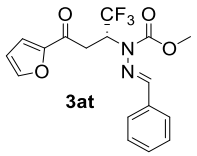
(*R,E*)-methyl 2-benzylidene-1-(4-(2-bromophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)hydrazinecarboxylate (3ar): White solid; 75% yield, 95% ee; m.p.: 41.2 − 42.0 °C; $[\alpha]_D^{17}$ = 86.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.820 min (major), 6.517 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.64 – 7.50 (m, 3H), 7.45 – 7.21 (m, 6H), 5.74 – 5.55 (m, 1H), 4.12 (dd, J = 17.6, 10.4 Hz, 1H), 3.89 (s, 3H), 3.35 (dd, J = 17.6, 3.6 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.9, 156.1, 154.2, 140.8, 134.7, 134.0, 132.2, 130.7, 129.3, 128.7, 127.7, 127.6, 124.9 (q, J =281.4 Hz), 118.9, 56.9 (q, J =30.9 Hz), 53.8, 39.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.64; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0187.



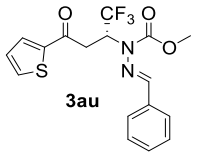
3as

(*R,E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(naphthalen-2-yl)-4-oxobutan-2-yl)hydrazinecarboxylate (3as): White solid; 66% yield, 98% ee; m.p.: 79.9 − 80.3 °C; $[\alpha]_D^{16}$ = 44.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.743 min (major), 8.340 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.59 – 8.43 (m, 1H), 8.14 – 7.98 (m, 1H), 7.95 – 7.83 (m, 3H), 7.68 – 7.56 (m, 1H), 7.57 – 7.50 (m, 3H), 7.39 – 7.30 (m, 3H), 5.85 – 5.67 (m, 1H), 4.42 (dd, J = 17.4, 10.4 Hz, 1H), 3.92 (s, 3H), 3.33 (dd, J =

17.4, 3.2 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 195.3, 156.0, 154.4, 135.9, 134.7, 133.8, 132.5, 130.6, 130.3, 129.7, 128.9, 128.8, 128.7, 127.9, 127.7, 127.1, 125.2 (q, J =281.2 Hz), 123.8, 56.7 (q, J =30.6 Hz), 53.8, 34.8; **$^{19}F\{^{1}H\}$ NMR** (376 MHz, $CDCl_3$) δ -73.40; **HRMS** (ESI) calcd. for $C_{23}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 451.1240, found: 451.1238.

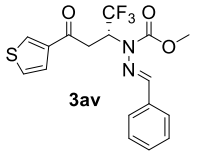


(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-(furan-2-yl)-4-oxobutan-2-yl)hydrazinecarboxylate (3at): White solid; 73% yield, 98% ee; m.p.: 124.4 − 124.8 °C; $[\alpha]_D^{22}$ = 94.8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.873 min (major), 8.473 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.66 – 7.52 (m, 3H), 7.41 – 7.32 (m, 3H), 7.29 – 7.15 (m, 1H), 6.53 (dd, J = 3.7, 1.7 Hz, 1H), 5.89 – 5.46 (m, 1H), 4.10 (dd, J = 17.3, 10.4 Hz, 1H), 3.88 (s, 3H), 3.14 (dd, J = 17.3, 3.5 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 184.2, 155.9, 154.2, 152.4, 146.9, 134.8, 130.6, 128.7, 127.7, 125.0 (q, J =281.0 Hz), 117.9, 112.7, 56.4 (q, J =30.8 Hz), 53.8, 34.8; **$^{19}F\{^{1}H\}$ NMR** (376 MHz, $CDCl_3$) δ -73.52; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_4Na$ ($[M+Na]^+$): 391.0876, found: 391.0873.

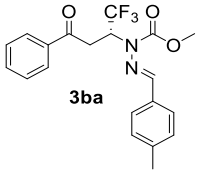


(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-(thiophen-2-yl)butan-2-yl)hydrazinecarboxylate (3au): White solid; 75% yield, 98% ee; m.p.: 120.1 − 120.5 °C; $[\alpha]_D^{17}$ = 68.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IB, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.507 min (major), 7.887 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.86 – 7.74 (m, 1H), 7.71 – 7.62 (m, 1H), 7.61 – 7.54 (m, 2H), 7.43 – 7.31 (m, 3H), 7.19 – 7.06 (m, 1H), 5.76 – 5.61 (m, 1H), 4.16 (dd, J = 17.1, 10.3 Hz, 1H), 3.89 (s, 3H), 3.22 (dd, J = 17.1, 3.3 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 188.0, 156.0, 154.2, 143.5, 134.8, 134.5, 132.7,

130.6, 128.7, 128.4, 127.7, 125.0 (q, J =281.5 Hz), 56.7 (q, J =30.5 Hz), 53.8, 35.6; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.40; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0647.

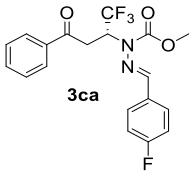


(*R*,*E*)-methyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-(thiophen-3-yl)butan-2-yl)hydrazinecarboxylate (3av): White solid; 75% yield, 99% ee; m.p.: 134.2 − 134.9 °C; $[\alpha]_D^{18}$ = 113.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OJ−H, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.530 min (major), 9.630 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.20 – 8.06 (m, 1H), 7.69 – 7.49 (m, 3H), 7.45 – 7.29 (m, 4H), 5.76 – 5.59 (m, 1H), 4.13 (dd, J = 17.3, 10.2 Hz, 1H), 3.90 (s, 3H), 3.19 (dd, J = 17.3, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 189.4, 156.0, 154.3, 141.7, 134.8, 132.8, 130.6, 128.7, 127.7, 127.0, 126.9, 125.1 (q, J =281.0 Hz), 56.6 (q, J =30.7 Hz), 53.8, 36.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.46; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0645.

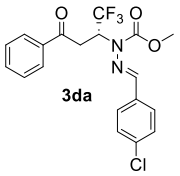


(*R*,*E*)-methyl 2-(4-methylbenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ba): Colorless oil; 85% yield, 98% ee; m.p.: $[\alpha]_D^{18}$ = 110.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.793 min (major), 7.147 min (minor); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 156.9, 154.4, 141.0, 136.4, 133.7, 131.9, 129.4, 128.9, 128.3, 127.7, 125.2 (q, J =281.4 Hz), 56.6 (q, J =30.5 Hz), 53.8, 34.7, 21.6; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.09 – 7.92 (m, 2H), 7.64 – 7.55 (m, 1H), 7.52 – 7.39 (m, 4H), 7.17 – 7.09 (m, 2H), 5.82 – 5.65 (m, 1H), 4.26 (dd, J = 17.6, 10.3 Hz, 1H), 3.91 (s, 3H), 3.22 (dd, J = 17.6, 3.2 Hz, 1H), 2.35 (s, 3H); **^{19}F{^{1}H} NMR**

(376 MHz, $CDCl_3$) δ -73.51; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1232.

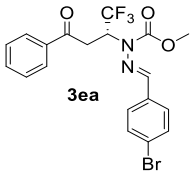


(*R,E*)-methyl 2-(4-fluorobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ca): Colorless oil; 75% yield, 96% ee; m.p.: $[\alpha]_D^{19}$ = 53.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.985 min (major), 8.240 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.05 – 7.92 (m, 2H), 7.67 – 7.56 (m, 1H), 7.55 – 7.43 (m, 4H), 7.10 – 6.92 (m, 2H), 5.79 – 5.55 (m, 1H), 4.23 (dd, J = 17.6, 10.3 Hz, 1H), 3.92 (s, 3H), 3.24 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 164.2 (d, J =249.8 Hz), 154.7, 154.3, 136.4, 133.8, 131.0 (d, J =2.9 Hz), 129.5 (d, J =8.6 Hz), 128.9, 128.3, 125.2 (q, J =281.0 Hz), 115.8 (d, J =21.7 Hz), 56.7 (q, J =30.4 Hz), 53.8, 34.7; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.55, -109.60; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0981.



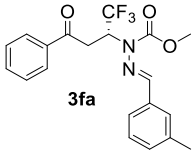
(*R,E*)-methyl 2-(4-chlorobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3da): White solid; 75% yield, 96% ee; m.p.: 54.4 − 55.0 ºC; $[\alpha]_D^{18}$ = 42.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.877 min (major), 8.593 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.04 – 7.95 (m, 2H), 7.68 – 7.56 (m, 1H), 7.52 – 7.42 (m, 4H), 7.31 – 7.25 (m, 2H), 5.82 – 5.59 (m, 1H), 4.23 (dd, J = 17.6, 10.3 Hz, 1H), 3.92 (s, 3H), 3.25 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 195.2, 154.2, 153.9, 136.4 (two peaks), 133.9, 133.3, 129.0, 128.9, 128.7, 128.3, 125.1 (q, J =281.1 Hz), 56.8 (q, J =30.6 Hz), 53.9, 34.9; **^{19}F{^{1}H} NMR**

(565 MHz, $CDCl_3$) δ -73.55; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0688.



3ea

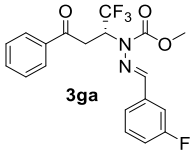
(*R,E*)-methyl 2-(4-bromobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ea): White solid; 70% yield, 96% ee; m.p.: 155.7 − 156.3 °C; $[\alpha]_D^{17}$ = 115.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.128 min (major), 8.813 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.09 – 7.91 (m, 2H), 7.71 – 7.55 (m, 1H), 7.53 – 7.40 (m, 4H), 7.42 – 7.33 (m, 2H), 5.77 – 5.64 (m, 1H), 4.23 (dd, J = 17.6, 10.3 Hz, 1H), 3.92 (s, 3H), 3.25 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 154.2, 153.8, 136.3, 133.9, 133.8, 131.9, 128.9 (two peaks), 128.3, 125.1 (q, J =281.5 Hz), 124.8, 56.8 (q, J =30.6 Hz), 53.9, 34.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.55; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0177.



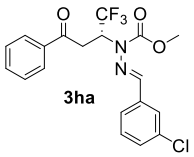
3fa

(*R,E*)-methyl 2-(3-methylbenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3fa): White solid; 75% yield, 98% ee; m.p.: 48.0 − 48.9 °C; $[\alpha]_D^{18}$ = 107.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.888 min (major), 8.178 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.08 – 7.94 (m, 2H), 7.65 – 7.54 (m, 1H), 7.53 – 7.43 (m, 2H), 7.37 – 7.29 (m, 2H), 7.24 – 7.12 (m, 2H), 5.81 – 5.66 (m, 1H), 4.27 (dd, J = 17.6, 10.4 Hz, 1H), 3.91 (s, 3H), 3.22 (dd, J = 17.5, 3.3 Hz, 1H), 2.28 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 156.9, 154.4, 138.3, 136.5, 134.5, 133.7, 131.5, 131.1, 128.9, 128.9, 128.7, 128.3, 128.1, 127.0, 125.2 (q, J =281.1 Hz), 125.1, 56.7 (q, J =30.5 Hz), 53.8, 34.7, 21.4; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ

-73.59; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1232.

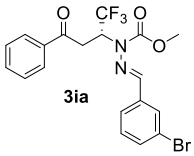


(*R,E*)-methyl 2-(3-fluorobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ga): Colorless oil; 55% yield, 96% ee; $[\alpha]_D^{18}$ = 97.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.170 min (major), 5.715 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.05 – 7.89 (m, 2H), 7.64 – 7.55 (m, 1H), 7.53 – 7.43 (m, 2H), 7.35 – 7.21 (m, 3H), 7.11 – 6.96 (m, 1H), 5.79 – 5.61 (m, 1H), 4.24 (dd, J = 17.7, 10.2 Hz, 1H), 3.93 (s, 3H), 3.26 (dd, J = 17.7, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 163.1 (d, J =244.3 Hz), 154.2, 153.3, 137.3(d, J =7.8 Hz), 136.4, 133.9, 130.2 (d, J =8.0 Hz), 128.9, 128.3, 125.1 (q, J =281.1 Hz), 124.1 (d, J =2.9 Hz), 117.4 (d, J =21.6 Hz), 113.2 (d, J =22.5 Hz), 56.8 (q, J =30.8 Hz), 53.9, 34.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.54, -112.81; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0985.



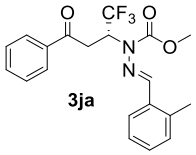
(*R,E*)-methyl 2-(3-chlorobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ha): White solid; 55% yield, 96% ee; m.p.: 98.7 − 99.4 °C; $[\alpha]_D^{19}$ = 64.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD‐H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.877 min (major), 8.677 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.11 – 7.91 (m, 2H), 7.66 – 7.55 (m, 1H), 7.55 – 7.44 (m, 3H), 7.43 – 7.33 (m, 1H), 7.34 – 7.27 (m, 1H), 7.29 – 7.22 (m, 1H), 5.82 – 5.63 (m, 1H), 4.26 (dd, J = 17.6, 10.4 Hz, 1H), 3.93 (s, 3H), 3.25 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 154.2, 153.2, 136.7, 136.3, 134.8, 133.9, 130.4, 129.9, 129.0, 128.3, 126.8, 126.2, 125.1 (q, J =281.4 Hz), 56.8 (q, J =30.5 Hz), 53.9, 34.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.57;

HRMS (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ([M+Na]$^+$): 435.0694, found: 435.0690.



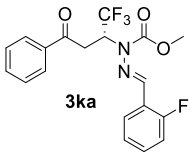
3ia

(*R*,*E*)-methyl 2-(3-bromobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ia): White solid; 70% yield, 97% ee; m.p.: 54.3 − 54.9 ºC; $[\alpha]_D^{19}$ = 80.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.628 min (major), 8.715 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.05 – 7.94 (m, 2H), 7.72 – 7.64 (m, 1H), 7.63 – 7.56 (m, 1H), 7.52 – 7.38 (m, 4H), 7.23 – 7.14 (m, 1H), 5.94 – 5.52 (m, 1H), 4.26 (dd, J = 17.6, 10.4 Hz, 1H), 3.93 (s, 3H), 3.24 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 154.1, 153.0, 136.9, 136.3, 133.9, 133.3, 130.2, 129.8, 129.0, 128.3, 126.6, 125.1 (q, J =281.1 Hz), 122.9, 56.8 (q, J =30.6 Hz), 53.9, 34.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.56; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ([M+Na]$^+$): 479.0189, found: 479.0199.

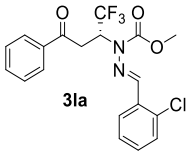


3ja

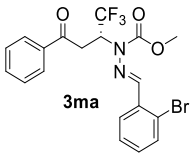
(*R*,*E*)-methyl 2-(2-methylbenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ja): Colorless oil; 65% yield, 98% ee; $[\alpha]_D^{19}$ = 81.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.840 min (major), 7.908 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.12 – 7.94 (m, 2H), 7.73 – 7.54 (m, 2H), 7.53 – 7.40 (m, 2H), 7.33 – 7.20 (m, 1H), 7.20 – 7.09 (m, 2H), 5.87 – 5.66 (m, 1H), 4.26 (dd, J = 17.7, 10.3 Hz, 1H), 3.92 (s, 3H), 3.25 (dd, J = 17.7, 3.2 Hz, 1H), 2.40 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 155.7, 154.4, 137.8, 136.4, 133.8, 132.7, 131.0, 130.3, 128.9, 128.3, 127.1, 126.12, 125.2 (q, J =281.0 Hz), 56.7 (q, J =30.4 Hz), 53.8, 34.8, 19.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.44; **HRMS** (ESI) calcd. for C20H19F3N2O3Na ([M+Na]$^+$): 415.1240, found: 415.1237.



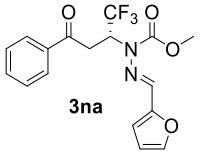
(*R*,*E*)-methyl 2-(2-fluorobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ka): Colorless oil; 60% yield, 96% ee; $[\alpha]_D^{19}$ = 83.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 17.937 min (major), 16.778 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.15 – 7.85 (m, 2H), 7.68 – 7.54 (m, 2H), 7.52 – 7.43 (m, 2H), 7.37 – 7.29 (m, 1H), 7.10 – 6.99 (m, 2H), 5.83 – 5.67 (m, 1H), 4.25 (dd, J = 17.7, 10.3 Hz, 1H), 3.93 (s, 3H), 3.26 (dd, J = 17.7, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 161.7 (d, J =252.0 Hz), 158.5, 154.2, 136.4, 133.8, 132.0 (d, J =8.6 Hz), 128.9, 128.3, 126.8 (d, J =2.8 Hz), 125.2 (q, J =281.0 Hz), 124.3 (d, J =3.4 Hz), 122.7 (d, J =9.5 Hz), 116.01 (d, J =20.9 Hz), 56.8 (q, J =30.6 Hz), 53.9, 34.8; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.53, -119.53; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0981.



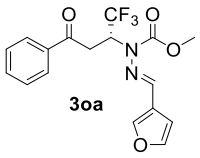
(*R*,*E*)-methyl 2-(2-chlorobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3la): White solid; 60% yield, 96% ee; m.p.: 135.5 − 136.2 °C; $[\alpha]_D^{18}$ = 71.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.607 min (major), 5,715 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.03 – 7.93 (m, 2H), 7.75 – 7.66 (m, 1H), 7.62 – 7.55 (m, 1H), 7.52 – 7.42 (m, 2H), 7.39 – 7.31 (m, 1H), 7.30 – 7.24 (m, 1H), 7.20 – 7.12 (m, 1H), 5.88 – 5.66 (m, 1H), 4.24 (dd, J = 17.7, 10.2 Hz, 1H), 3.94 (s, 3H), 3.28 (dd, J = 17.7, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.1, 154.1, 151.4, 136.3, 135.1, 133.8, 132.4, 131.3, 130.0, 128.9, 128.3, 127.1, 126.9, 125.1 (q, J =281.0 Hz), 56.8 (q, J =30.5 Hz), 54.0, 35.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.46; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0691.



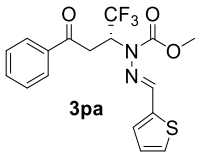
(*R,E)*-methyl 2-(2-bromobenzylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ma): White solid; 45% yield, 96% ee; m.p.: 115.3 − 116.9 °C; $[\alpha]_D^{18}$ = 41.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.797 min (major), 8.333 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.04 – 7.93 (m, 2H), 7.72 – 7.65 (m, 1H), 7.62 – 7.56 (m, 1H), 7.55 – 7.52 (m, 1H), 7.51 – 7.42 (m, 2H), 7.25 – 7.15 (m, 2H), 5.84 – 5.69 (m, 1H), 4.23 (dd, J = 17.7, 10.2 Hz, 1H), 3.94 (s, 3H), 3.28 (dd, J = 17.7, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.1, 154.1, 153.5, 136.3, 134.0, 133.8, 133.3, 131.5, 128.9, 128.3, 127.5, 125.1 (q, J =281.0 Hz), 125.1, 56.8 (q, J =30.7 Hz), 54.0, 35.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.44; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0177.



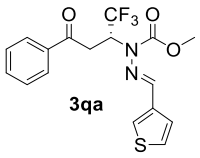
(*R,E*)-methyl 2-(furan-2-ylmethylene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3na): White solid; 52% yield, 96% ee; m.p.: 88.6 − 89.0 °C; $[\alpha]_D^{18}$ = 68.8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.393 min (major), 8.043 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.08 – 7.90 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.43 (m, 3H), 6.61 (d, J = 3.4 Hz, 1H), 6.42 (dd, J = 3.5, 1.8 Hz, 1H), 5.81 – 5.54 (m, 1H), 4.29 (dd, J = 17.6, 10.2 Hz, 1H), 3.90 (s, 3H), 3.20 (dd, J = 17.7, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 195.6, 154.2, 150.1, 144.8, 136.5, 133.7, 128.8, 128.4, 125.1 (q, J =281.1 Hz), 113.8, 111.9, 56.7 (q, J =30.5 Hz), 53.8, 34.7; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -73.53; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_4Na$ ($[M+Na]^+$): 391.0876, found: 391.0873.



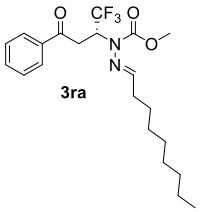
(*R*,*E*)-methyl 2-(furan-3-ylmethylene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3oa): White solid; 42% yield, 97% ee; m.p.: 90.1 − 90.7 °C; $[\alpha]_D^{18}$ = 50.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.310 min (major), 9.260 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.05 – 7.90 (m, 2H), 7.70 – 7.54 (m, 2H), 7.52 – 7.42 (m, 2H), 7.37 – 7.31 (m, 1H), 6.63 – 6.38 (m, 1H), 5.72 – 5.62 (m, 1H), 4.20 (dd, J = 17.5, 10.4 Hz, 1H), 3.89 (s, 3H), 3.18 (dd, J = 17.6, 3.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 154.5, 149.7, 145.1, 144.1, 136.5, 133.8, 129.0, 128.3, 125.2 (q, J =281.1 Hz), 123.2, 107.2, 56.5 (q, J =30.4 Hz), 53.8, 34.5; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.64; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_4Na$ ($[M+Na]^+$): 391.0876, found: 391.0875.



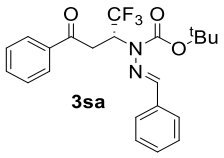
(*R*,*E*)-methyl 2-(thiophen-2-ylmethylene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3pa): White solid; 82% yield, 97% ee; m.p.: 93.9 − 94.8 °C; $[\alpha]_D^{18}$ = 82.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.827 min (major), 8.512 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.10 – 7.93 (m, 2H), 7.68 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.36 – 7.27 (m, 1H), 7.24 – 7.17 (m, 1H), 7.04 – 6.95 (m, 1H), 5.79 – 5.59 (m, 1H), 4.29 (dd, J = 17.7, 10.4 Hz, 1H), 3.91 (s, 3H), 3.17 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.5, 154.3, 149.5, 140.1, 136.4, 133.8, 130.8, 128.9, 128.7, 128.4, 127.5, 125.1 (q, J =281.0 Hz), 115.4, 56.6 (q, J =30.7 Hz), 53.9, 34.6; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.72; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0641.



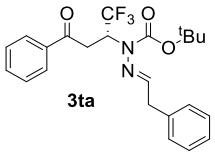
(*R*,*E*)-methyl 2-(thiophen-3-ylmethylene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3qa): White solid; 79% yield, 98% ee; m.p.: 101.2 − 101.8 °C; $[\alpha]_D^{19}$ = 61.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.427 min (major), 9.767 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.11 – 7.90 (m, 2H), 7.68 – 7.53 (m, 1H), 7.52 – 7.40 (m, 3H), 7.30 – 7.19 (m, 2H), 5.80 – 5.60 (m, 1H), 4.21 (dd, J = 17.6, 10.3 Hz, 1H), 3.89 (s, 3H), 3.20 (dd, J = 17.6, 3.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.2, 154.4, 151.8, 138.0, 136.4, 133.8, 128.9, 128.4, 128.26, 126.5, 125.2 (q, J =281.6 Hz), 125.0, 56.6 (q, J =30.7 Hz), 53.8, 34.6.; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.56; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0639.



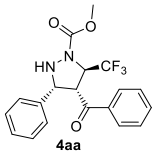
(*R*,*E*)-methyl 2-nonylidene-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3ra): White solid; 56% yield, 90% ee; m.p.: 91.4 − 92.6 °C; $[\alpha]_D^{19}$ = 61.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 3.660 min (major), 5.335 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 8.00 – 7.94 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.42 (m, 2H), 5.66 – 5.44 (m, 1H), 4.13 (dd, J = 17.6, 10.2 Hz, 1H), 3.84 (s, 3H), 3.13 (dd, J = 17.6, 3.4 Hz, 1H), 2.34 – 2.13 (m, 2H), 1.48 – 1.38 (m, 2H), 1.31 – 1.18 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 165.3, 154.8, 136.5, 133.6, 128.8, 128.3, 125.3 (q, J =281.0 Hz), 56.0 (q, J =30.6 Hz), 53.6, 34.4, 33.4, 32.0, 29.4, 29.3, 29.1, 25.9, 22.8, 14.2; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.60; **HRMS** (ESI) calcd. for $C_{21}H_{29}F_3N_2O_3Na$ ($[M+Na]^+$): 437.2022, found: 437.2013.



(*R*,*E*)-tert-butyl 2-benzylidene-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazinecarboxylate (3sa): White solid; 55% yield, 98% ee; m.p.: 101.4 − 102.3 ^{o}C; $[\alpha]_D^{19}$ = 50.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK MD, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 3.780 min (major), 4.250 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.01 – 7.97 (m, 2H), 7.61 – 7.51 (m, 3H), 7.50 – 7.42 (m, 2H), 7.36 – 7.28 (m, 3H), 5.75 – 5.65 (m, 1H), 4.25 (dd, J = 17.4, 10.2 Hz, 1H), 3.20 (dd, J = 17.4, 3.3 Hz, 1H), 1.59 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 154.8, 152.7, 136.6, 135.1, 133.6, 130.3, 128.8, 128.6, 128.3, 127.5, 125.4 (q, J =281.3 Hz), 83.2, 56.8 (q, J =30.4 Hz), 35.0, 28.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.47; **HRMS** (ESI) calcd. for $C_{22}H_{23}F_3N_2O_3Na$ ($[M+Na]^+$): 443.1553, found: 443.1560.

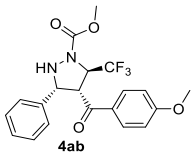


(*R*,*E*)-tert-butyl 2-(2-phenylethylidene)-1-(1,1,1-trifluoro-4-oxo-4-phenylbutan-2-yl)hydrazine-1-carboxylate (**3ta):** colorless oil; 58% yield, 87% ee; $[\alpha]_D^{25}$ = 15.2 (c 1.0 $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.018 min (major), 4.439 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.01 – 7.84 (m, 2H), 7.64 – 7.51 (m, 1H), 7.52 – 7.41 (m, 2H), 7.24 – 7.13 (m, 3H), 7.15 – 7.06 (m, 2H), 5.66 – 5.49 (m, 1H), 4.12 (dd, J = 17.4, 10.2 Hz, 1H), 3.54 (d, J = 5.5 Hz, 2H), 3.08 (dd, J = 17.4, 3.3 Hz, 1H), 1.51 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 160.0, 152.8, 136.7, 136.3, 133.5, 129.2, 128.8, 128.7, 128.3, 126.8, 125.4 (q, J = 281.1 Hz), 82.6, 56.2 (q, J = 30.2 Hz), 40.3, 34.7, 28.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -73.54; **HRMS** (ESI) calcd. for $C_{23}H_{25}F_3N_2O_3$ ($[M+Na]^+$): 457.1709, found: 457.1700.



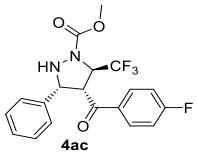
4aa

(*3R,4R,5R*)-methyl 4-benzoyl-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4aa): White solid; 83% yield, 92% ee, >20:1 dr; m.p.: 155.4 − 156.2 °C; $[\alpha]_D^{19}$ = -20.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.090 min (major), 12.903 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 – 7.59 (m, 2H), 7.57 – 7.45 (m, 1H), 7.41 – 7.30 (m, 2H), 7.14 – 6.99 (m, 3H), 6.87 – 6.77 (m, 2H), 5.73 – 5.63 (m, 1H), 5.16 (s, 1H), 4.98 (d, J = 8.2 Hz, 1H), 4.74 (dd, J = 8.2, 5.0 Hz, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 193.8, 157.1, 136.4, 135.9, 133.8, 128.9, 128.6, 128.3, 128.2, 127.4, 125.5 (q, J =279.9 Hz), 66.4, 61.8 (q, J =31.2 Hz), 56.2, 54.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -75.10; **HRMS** (ESI) calcd. for $C_{19}H_{17}F_3N_2O_3Na$ ($[M+Na]^+$): 401.1083, found: 401.1077.



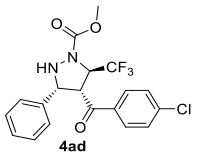
4ab

(*3R,4R,5R*)-methyl 4-(4-methoxybenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ab): White solid; 59% yield, 95% ee, >20:1 dr; m.p.: 134.9 − 135.6 °C; $[\alpha]_D^{19}$ = -12.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.070 min (major), 19.607 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 1H), 7.12 – 7.03 (m, 1H), 6.90 – 6.83 (m, 1H), 6.84 – 6.78 (m, 1H), 5.70 – 5.54 (m, 1H), 4.97 (d, J = 8.1 Hz, 1H), 4.69 (dd, J = 8.1, 5.0 Hz, 1H), 3.82 (s, 2H), 3.80 (s, 2H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 192.1, 164.0, 157.0, 135.9, 130.6, 129.3, 128.5, 128.2, 127.3, 125.5 (q, J =279.1 Hz), 114.0, 66.41, 62.0 (q, J =30.9 Hz), 55.6 (two peaks), 53.9; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.42; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_4Na$ ($[M+Na]^+$): 431.1189, found: 431.1183.



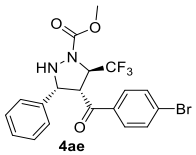
4ac

(*3R,4R,5R*)-methyl 4-(4-fluorobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ac): White solid; 68% yield, 93% ee, >20:1 dr; m.p.: 53.6 − 54.4 °C; $[\alpha]_D^{19}$ = -25.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.877 min (major), 9.975 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 – 7.55 (m, 2H), 7.14 – 7.02 (m, 3H), 7.06 – 6.96 (m, 2H), 6.87 – 6.73 (m, 2H), 5.65 (s, 1H), 5.27 – 5.16 (m, 1H), 5.03 – 4.90 (m, 1H), 4.77 – 4.62 (m, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 192.4, 166.0 (d, J =273.3 Hz), 157.1, 135.8, 132.8 (d, J =3.2 Hz), 130.9 (d, J =9.7 Hz), 128.6, 128.4, 127.3, 125.4 (q, J =281.6 Hz), 116.0 (d, J =22 Hz), 66.3, 61.9 (q, J =31.7 Hz), 56.1, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.49, -103.47; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0978.



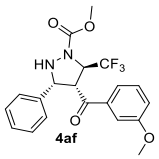
4ad

(*3R,4R,5R*)-methyl 4-(4-chlorobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ad): White solid; 73% yield, 91% ee, >20:1 dr; m.p.: 103.2 − 103.9 °C; $[\alpha]_D^{19}$ = -31.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.425 min (major), 10.962 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 – 7.46 (m, 2H), 7.38 – 7.25 (m, 2H), 7.15 – 7.02 (m, 3H), 6.93 – 6.75 (m, 2H), 5.65 (s, 1H), 5.28 – 5.09 (m, 1H), 5.06 – 4.80 (m, 1H), 4.76 – 4.60 (m, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 192.9, 157.1, 140.4, 135.7, 134.7, 129.5, 129.2, 128.7, 128.5, 127.4, 125.4 (q, J =281.7 Hz), 66.3, 61.9 (q, J =31.4 Hz) 56.1, 54.1; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.52; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0689.



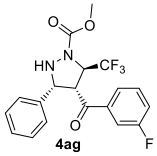
4ae

(*3R,4R,5R*)-methyl 4-(4-bromobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ae): White solid; 70% yield, 91% ee, >20:1 dr; m.p.: 159.4 − 159.9 °C; $[\alpha]_D^{22}$ = -52.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.527 min (major), 11.780 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 – 7.39 (m, 4H), 7.18 – 7.00 (m, 3H), 6.90 – 6.76 (m, 2H), 5.72 – 5.56 (m, 1H), 5.17 (s, 1H), 4.96 (d, J = 8.1 Hz, 1H), 4.67 (dd, J = 8.2, 4.9 Hz, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 193.0, 157.1, 135.7, 135.1, 132.1, 129.6, 129.1, 128.7, 128.5, 127.4, 125.4 (q, J =281.8 Hz), 66.3, 61.8 (q, J =31.6 Hz), 56.1, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.51; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0192.



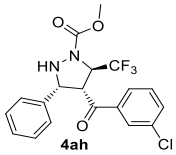
4af

(*3R,4R,5R*)-methyl 4-(3-methoxybenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4af): White solid; 73% yield, 94% ee, >20:1 dr; m.p.: 149.8 − 150.3 °C; $[\alpha]_D^{19}$ = -6.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.803 min (major), 12.667 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 2H), 7.12 – 6.99 (m, 5H), 6.88 – 6.75 (m, 2H), 5.73 – 5.56 (m, 1H), 5.19 (s, 1H), 4.97 (d, J = 8.2 Hz, 1H), 4.76 – 4.64 (m, 1H), 3.81 (s, 3H), 3.73 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 193.7, 159.9, 157.1, 137.8, 135.9, 129.7, 128.6, 128.3, 127.4, 125.5 (q, J =279.7 Hz), 120.6, 120.2, 112.6, 66.4, 61.8 (q, J =31.3 Hz), 56.4, 55.5, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.51; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_4Na$ ($[M+Na]^+$): 431.1189, found: 431.1184.



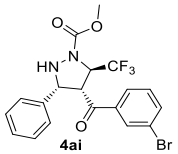
4ag

(*3R,4R,5R*)-methyl 4-(3-fluorobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ag): White solid; 76% yield, 90% ee, >20:1 dr; m.p.: 75.8 − 76.5 °C; $[\alpha]_D^{19}$ = -18.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.472 min (major), 9.578 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.30 – 7.22 (m, 1H), 7.23 – 7.12 (m, 1H), 7.14 – 7.03 (m, 3H), 6.85 – 6.76 (m, 2H), 5.72 – 5.59 (m, 1H), 5.17 (s, 1H), 4.98 (d, J = 8.2 Hz, 1H), 4.68 (dd, J = 8.2, 5.0 Hz, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 192.9, 162.8 (d, J =248.9 Hz), 157.0, 138.4 (d, J =6.6 Hz), 135.7, 130.5 (d, J =7.7 Hz), 128.7, 128.5, 127.4, 125.4 (q, J =281.6 Hz), 123.9 (d, J =2.5 Hz), 120.8 (d, J =21.8 Hz), 115.0 (d, J =22.3 Hz), 66.4, 61.8 (q, J =31.7 Hz), 56.4, 54.1; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.54, -111.15; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0985.



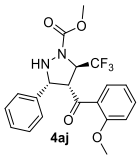
4ah

(*3R,4R,5R*)-methyl 4-(3-chlorobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ah): White solid; 70% yield, 87% ee, >20:1 dr; m.p.: 178.4 − 178.9 °C; $[\alpha]_D^{19}$ = -20.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.180 min (major), 10.003 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.50 (d, J = 7.7 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.32 – 7.24 (m, 1H), 7.16 – 7.02 (m, 3H), 6.85 – 6.78 (m, 2H), 5.78 – 5.61 (m, 2H), 5.17 (s, 1H), 4.98 (d, J = 8.2 Hz, 1H), 4.67 (dd, J = 8.2, 5.0 Hz, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 192.8, 157.4, 137.9, 135.7, 135.1, 133.6, 130.1, 128.7, 128.5, 128.2, 127.4, 126.2, 125.4 (q, J =279.4 Hz), 66.3, 61.8 (q, J =31.3 Hz), 56.4, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.51; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0688.



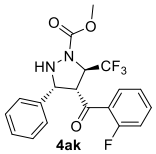
4ai

(*3R,4R,5R*)-methyl 4-(3-bromobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ai): White solid; 65% yield, 88% ee, >20:1 dr; m.p.: 94.7 − 95.5 ºC; $[\alpha]_D^{18}$ = -20.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.133 min (major), 10.093 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 – 7.52 (m, 1H), 7.27 – 7.18 (m, 1H), 7.14 – 7.05 (m, 3H), 6.88 – 6.78 (m, 2H), 5.64 (s, 1H), 5.17 (d, J = 6.6 Hz, 1H), 5.02 – 4.93 (m, 1H), 4.65 (dd, J = 8.3, 5.0 Hz, 1H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 192.8, 157.1, 138.1, 136.5, 135.7, 131.1, 130.3, 128.7, 128.5, 127.4, 126.6, 125.4 (q, J =281.6 Hz), 123.0, 66.3, 61.7 (q, J =31.5 Hz), 56.4, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.51; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0183.



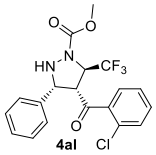
4aj

(*3R,4R,5R*)-methyl 4-(2-methoxybenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4aj): White solid; 56% yield, 95% ee, >20:1 dr; m.p.: 43.2 − 43.8 ºC; $[\alpha]_D^{18}$ = -11.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.953 min (major), 24.640 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 1H), 7.15 – 7.02 (m, 3H), 6.93 – 6.78 (m, 4H), 6.78 – 6.63 (m, 1H), 5.54 (s, 1H), 5.11 (d, J = 7.4 Hz, 1H), 4.98 (dd, J = 7.9, 4.7 Hz, 1H), 4.87 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.4, 157.7, 157.1, 136.6, 134.1, 130.8, 128.5, 128.1, 127.7, 127.2, 125.6 (q, J =279.8 Hz), 121.0, 111.3, 65.6, 62.0 (q, J =31.5 Hz), 59.9, 55.9, 53.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.57; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_4Na$ ($[M+Na]^+$): 431.1189, found: 431.1184.



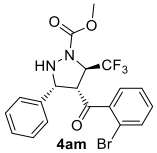
4ak

(*3R,4R,5R*)-methyl 4-(2-fluorobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ak): White solid; 73% yield, 90% ee, >20:1 dr; m.p.: 30.1 − 30.8 °C; $[\alpha]_D^{18}$ = -10.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.063 min (major), 14.752 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 1H), 7.25 – 7.16 (m, 1H), 7.11 – 7.02 (m, 4H), 7.01 – 6.92 (m, 1H), 6.87 – 6.77 (m, 2H), 5.73 (s, 1H), 5.16 – 5.06 (m, 1H), 5.04 – 4.87 (m, 1H), 4.81 – 4.68 (m, 1H), 3.79 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 191.7, 160.9 (d, J = 251.0 Hz), 157.2, 136.6, 135.2 (d, J = 9.4 Hz), 131.0 (d, J = 2.2 Hz), 128.6, 128.3, 127.2, 125.5 (q, J = 279.5 Hz), 125.0 (d, J = 12.0 Hz), 124.8 (d, J = 3.5 Hz), 116.4 (d, J = 23.4 Hz), 65.5, 61.4(q, J = 31.3 Hz), 60.7 (d, J = 7.4 Hz), 53.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.78, -111.69; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0982.



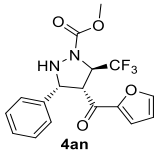
4al

(*3R,4R,5R*)-methyl 4-(2-chlorobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4al): White solid; 63% yield, 82% ee, >20:1 dr; m.p.: 106.4 − 107.2 °C; $[\alpha]_D^{18}$ = -34.8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.820 min (major), 13.813 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.09 (m, 3H), 7.05 – 6.93 (m, 1H), 6.88 – 6.80 (m, 2H), 6.51 – 6.35 (m, 1H), 5.68 – 5.51 (m, 1H), 5.10 (s, 1H), 4.98 (dd, J = 8.0, 4.9 Hz, 1H), 4.80 (d, J = 8.0 Hz, 1H), 3.77 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.7, 157.2, 137.8, 136.2, 132.4, 130.7, 130.3, 129.9, 128.9, 128.5, 127.4, 126.9, 125.4 (q, J =279.7 Hz), 65.4, 61.8 (q, J =31.7 Hz), 62.0, 59.3, 53.9; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.49; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0683.



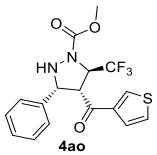
4am

(*3R,4R,5R*)-methyl 4-(2-bromobenzoyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4am): White solid; 62% yield, 88% ee, >20:1 dr; m.p.: 41.2 − 42.0 ºC; $[\alpha]_D^{18}$ = -20.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.397 min (major), 15.163 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 – 7.63 (m, 1H), 7.63 – 7.58 (m, 1H), 7.57 – 7.51 (m, 1H), 7.24 – 7.18 (m, 1H), 7.14 – 7.04 (m, 3H), 6.85 – 6.78 (m, 2H), 5.65 (s, 1H), 5.22 – 5.10 (m, 1H), 5.02 – 4.95 (m, 1H), 4.71 – 4.60 (m, 1H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 192.8, 157.0, 138.1, 136.5, 135.7, 131.2, 130.3, 128.7, 128.5, 127.3, 126.3, 125.4 (q, J =281.5 Hz), 123.1, 66.3, 61.8 (q, J =31.5 Hz) 56.4, 54.1; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.51; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0192.



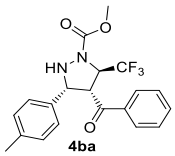
4an

(*3R,4R,5R*)-methyl 4-(furan-2-carbonyl)-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4an): White solid; 71% yield, 93% ee, >20:1 dr; m.p.: 130.4 − 130.9 ºC; $[\alpha]_D^{19}$ = -27.8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD–H, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.570 min (major), 6.525 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 1H), 7.10 – 7.03 (m, 3H), 6.98-6.89(m, 1H), 6.86 – 6.78 (m, 2H), 6.41-6.31 (m, 1H), 5.59 (s, 1H), 5.13 – 4.96 (m, 2H), 4.60-4.43 (m, 1H), 3.72 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 182.0, 157.4, 151.9, 146.5, 136.3, 128.7, 128.4, 127.0, 125.4 (q, J =281.1 Hz), 118.2, 113.2, 66.1, 60.8 (q, J =31.9 Hz), 56.8, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.70; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_4Na$ ($[M+Na]^+$): 391.0876, found: 391.0865.



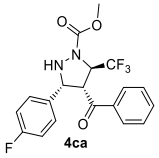
4ao

(*3R,4R,5R*)-methyl 3-phenyl-4-(thiophene-3-carbonyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ao): White solid; 65% yield, 95% ee, >20:1 dr; m.p.: 166.8 − 167.2 ºC; $[\alpha]_D^{17}$ = -35.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.708 min (major), 12.068 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 1H), 7.33 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 7.13 – 7.09 (m, 3H), 6.91 – 6.88 (m, 2H), 5.75 – 5.41 (m, 1H), 5.17 (s, 1H), 4.98 (d, J = 8.0 Hz, 1H), 4.52 (dd, J = 8.0, 4.7 Hz, 1H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 187.8, 157.2, 141.4, 135.6, 132.9, 128.6, 128.4, 127.3, 127.0, 126.8, 125.4 (q, J =281.8 Hz), 66.4, 61.8 (q, J =31.7 Hz), 57.2, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.43; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0647.

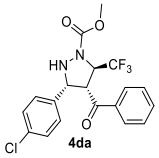


4ba

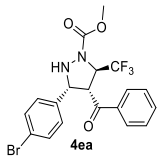
(*3R,4R,5R*)-methyl 4-benzoyl-3-(p-tolyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ba): White solid; 83% yield, 95% ee, >20:1 dr; m.p.: 192.4 − 193.3 ºC; $[\alpha]_D^{27}$ = -39.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.550 min (major), 17.032 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.56 (m, 2H), 7.56 – 7.42 (m, 1H), 7.35 (t, J = 7.7 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 6.69 (d, J = 7.9 Hz, 2H), 5.74 – 5.58 (m, 1H), 4.94 (d, J = 8.0 Hz, 1H), 4.71 (dd, J = 8.0, 5.3 Hz, 1H), 3.80 (s, 3H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 193.9, 157.2, 138.1, 136.4, 133.7, 132.7, 129.2, 128.8, 128.2, 127.2, 125.5 (q, J =282.4 Hz), 66.2, 61.8 (q, J =31.8 Hz), 56.3, 54.0, 21.1; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.53; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1232.



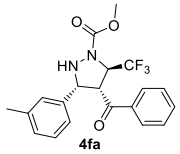
(*3R,4R,5R*)-methyl 4-benzoyl-3-(4-fluorophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ca): White solid; 63% yield, 92% ee, >20:1 dr; m.p.: 143.1 − 143.5 ^{o}C; $[\alpha]_D^{19}$ = -23.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.387 min (major), 12.130 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.58 (m, 2H), 7.56 – 7.48 (m, 1H), 7.41 – 7.32 (m, 2H), 6.89 – 6.67 (m, 4H), 5.79 – 5.59 (m, 1H), 4.98 (d, J = 8.3 Hz, 1H), 4.74 (dd, J = 8.3, 5.1 Hz, 1H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.7, 162.4 (d, J =248.7 Hz), 157.1, 136.2, 134.0, 132.0 (d, J =3.5 Hz), 129.2 (d, J =8.2 Hz), 128.9, 128.2, 125.5 (q, J =282.5 Hz), 115.5 (d, J =21.8 Hz), 65.7, 61.7 (q, J =31.7 Hz), 56.1, 54.1; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.58, -113.28; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0981.



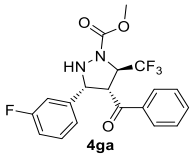
(*3R,4R,5R*)-methyl 4-benzoyl-3-(4-chlorophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4da): White solid; 63% yield, 92% ee, >20:1 dr; m.p.: 103.2 − 103.9 ^{o}C; $[\alpha]_D^{19}$ = -31.4 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.380 min (major), 13.887 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 2H), 7.58 – 7.48 (m, 1H), 7.42 – 7.32 (m, 2H), 7.11 – 6.96 (m, 2H), 6.81 – 6.69 (m, 2H), 5.74 – 5.54 (m, 1H), 5.17 (s, 1H), 4.97 (d, J = 8.3 Hz, 1H), 4.75 (dd, J = 8.3, 5.2 Hz, 1H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.5, 154.8, 136.2, 134.6, 134.3, 134.1, 129.0, 128.8, 128.8, 128.2, 125.4 (q, J =282.9 Hz), 65.7, 61.8 (q, J =32.2 Hz), 56.07, 54.11; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.55; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0689.



(*3R,4R,5R*)-methyl 4-benzoyl-3-(4-bromophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ea): White solid; 61% yield, 97% ee, >20:1 dr; m.p.: 197.0 − 197.9 ºC; $[\alpha]_D^{22}$ = -68.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.340 min (major), 10.197 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 5.65 (s, 1H), 5.17 – 5.18 (m, 1H), 4.95 (t, J = 7.5 Hz, 1H), 4.76 (dd, J = 8.1, 5.2 Hz, 1H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 193.5, 157.2, 136.2, 135.1, 134.1, 131.7, 129.1, 129.0, 128.2, 125.4 (q, J =279.7 Hz), 122.4, 65.75, 61.8 (q, J =31.5 Hz), 56.0, 54; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.55; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 443.0185.

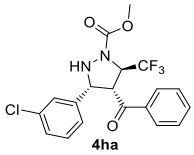


(*3R,4R,5R*)-methyl 4-benzoyl-3-(m-tolyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4fa): White solid; 53% yield, 93% ee, >20:1 dr; m.p.: 48.0 − 48.9 ºC; $[\alpha]_D^{22}$ = -34.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.660 min (major), 11.283 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.54 – 7.45 (m, 1H), 7.40 – 7.30 (m, 2H), 6.99 – 6.84 (m, 2H), 6.65 – 6.58 (m, 2H), 5.70 – 5.52 (m, 1H), 5.17 (s, 1H), 5.00 – 4.87 (m, 1H), 4.76 – 4.60 (m, 1H), 3.81 (s, 3H), 2.09 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 194.0, 157.1, 138.2, 136.5, 135.6, 133.7, 129.0, 128.7, 128.5, 128.3, 128.2, 125.5 (q, J =281.4 Hz), 124.2, 66.3, 61.7 (q, J =31.3 Hz), 56.0, 54.0, 21.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.48; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1230.



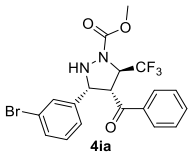
4ga

(*3R,4R,5R*)-methyl 4-benzoyl-3-(3-fluorophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ga): Colorless oil; 68% yield, 94% ee, >20:1 dr; $[\alpha]_D^{21}$ = -22.5 (c 0.5, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.023 min (major), 9.617 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.61 (m, 2H), 7.57 – 7.45 (m, 1H), 7.44 – 7.31 (m, 2H), 7.11 – 6.95 (m, 1H), 6.87 – 6.73 (m, 1H), 6.63 – 6.50 (m, 2H), 5.69 – 5.57 (m, 1H), 5.21 (s, 1H), 5.06 – 4.89 (m, 1H), 4.81 – 4.73 (m, 1H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.6, 162.6 (d, J =248.0 Hz), 156.9, 138.4 (d, J =7.2 Hz), 136.3, 134.1, 130.2 (d, J =8.7 Hz), 129.0, 128.2, 125.4 (q, J =283.0 Hz), 122.9 (d, J =3.1 Hz),115.3 (d, J =20.9 Hz), 114.8 (d, J =22.6 Hz), 65.8, 61.9 (q, J =31.6 Hz), 55.9, 54.1; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.53, -112.12; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0981.



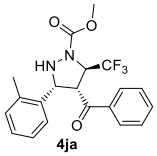
4ha

(*3R,4R,5R*)-methyl 4-benzoyl-3-(3-chlorophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ha): White solid; 51% yield, 93% ee, >20:1 dr; m.p.: 168.5 − 168.9 ^oC; $[\alpha]_D^{22}$ = -3.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.722 min (major), 13.908 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 2H), 7.57 – 7.49 (m, 1H), 7.43 – 7.34 (m, 2H), 7.09 – 6.95 (m, 2H), 6.86 – 6.80 (m, 1H), 6.77 – 6.66 (m, 1H), 5.62 (s, 1H), 5.17 (d, J =6.8 Hz, 1H), 4.95 (t, J =7.4 Hz, 1H), 4.76 (dd, J =8.3, 4.9 Hz, 1H), 3.85 (s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 193.7, 157.0, 138.0, 136.3, 134.4, 134.1, 130.0, 129.0, 128.5, 128.2, 128.0, 125.4 (q, J =281.8 Hz) 125.2, 65.7, 61.9 (q, J =31.3 Hz), 55.8, 54.1; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.50; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0683.



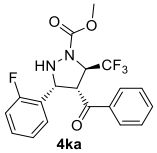
4ia

(*3R,4R,5R*)-methyl 4-benzoyl-3-(3-bromophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ia): White solid; 59% yield, 93% ee, >20:1 dr; m.p.: 119.8 − 120.5 ºC; $[\alpha]_D^{21}$ = -13.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.193 min (major), 9.143 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 2H), 7.58 – 7.50 (m, 1H), 7.45 – 7.35 (m, 2H), 7.25 – 7.18 (m, 1H), 7.01 – 6.90 (m, 2H), 6.82 – 6.73 (m, 1H), 5.62 (s, 1H), 5.21 – 5.10 (m, 1H), 5.00 – 4.89 (m, 1H), 4.82 – 4.67 (m, 1H), 3.85 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.7, 157.0, 138.3, 136.3, 134.1, 131.4, 130.9, 130.1, 129.0, 128.2, 125.6, 125.4 (q, J =282.4 Hz), 122.5, 65.6, 61.8 (q, J =31.8 Hz), 55.8, 54.1; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.52; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0177.



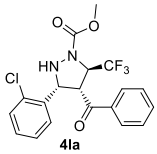
4ja

(*3R,4R,5R*)-methyl 4-benzoyl-3-(o-tolyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ja): White solid; 51% yield, 93% ee, >20:1 dr; m.p.: 172.3 − 172.8 ºC; $[\alpha]_D^{18}$ = -12.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.722 min (major), 13.908 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.37 (m, 3H), 7.31 – 7.21 (m, 2H), 7.05 – 6.89 (m, 2H), 6.87 – 6.76 (m, 2H), 5.70 – 5.52 (m, 1H), 5.39 – 5.05 (m, 2H), 4.91 – 4.59 (m, 1H), 3.77 (s, 3H), 2.07 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.1, 157.2, 136.6, 135.4, 133.8, 133.5, 130.6, 128.6, 128.2, 127.8, 126.4, 126.0, 125.5 (q, J =282.5 Hz), 62.3 (q, J =31.7 Hz), 61.4, 54.7, 53.9, 19.7; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.51; **HRMS** (ESI) calcd. for $C_{20}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 415.1240, found: 415.1238.



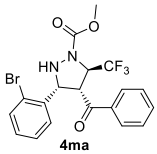
4ka

(*3R,4R,5R*)-methyl 4-benzoyl-3-(2-fluorophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ka): White solid; 78% yield, 92% ee, >20:1 dr; m.p.: 187.0 − 187.5 ^{o}C; $[\alpha]_D^{24}$ = -18.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.073 min (major), 9.003 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 – 7.54 (m, 2H), 7.54 – 7.37 (m, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.09 – 7.00 (m, 1H), 6.99 – 6.88 (m, 2H), 6.70 – 6.58 (m, 2H), 5.59 (s, 1H), 5.43 – 5.35 (m, 1H), 5.24 – 5.19 (m, 1H), 4.86 – 4.78 (m, 1H), 3.83 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 194.4, 159.6 (d, J =245.0 Hz), 157.05, 135.9, 133.9, 130.0 (d, J =8.6 Hz), 128.7, 128.1, 128.0, 125.5 (q, J =279.8 Hz), 124.5 (d, J =3.3 Hz), 123.8 (d, J =13.0 Hz), 115.1 (d, J =22.0 Hz), 62.4 (q, J =30.9 Hz), 58.6 (d, J =31.3 Hz), 54.5, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.48, -116.40; **HRMS** (ESI) calcd. for $C_{19}H_{16}F_4N_2O_3Na$ ($[M+Na]^+$): 419.0989, found: 419.0993.



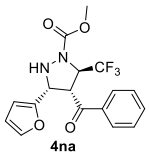
4la

(*3R,4R,5R*)-methyl 4-benzoyl-3-(2-chlorophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4la): White solid; 77% yield, 82% ee, >20:1 dr; m.p.: 133.7 − 134.5 ^{o}C; $[\alpha]_D^{22}$ = -30.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.090 min (major), 9.645 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 – 7.55 (m, 1H), 7.46 – 7.42 (m, 0H), 7.31 – 7.25 (m, 1H), 7.17 – 7.12 (m, 1H), 7.10 – 7.05 (m, 1H), 6.99 – 6.95 (m, 2H), 5.57 (d, J = 8.2 Hz, 1H), 5.49 – 5.39 (m, 1H), 5.19 (s, 1H), 4.88 (dd, J = 8.1, 3.0 Hz, 1H), 3.86 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 157.2, 136.0, 133.8 (two peaks), 133.2, 129.4, 129.30, 128.6, 128.4, 128.2, 127.2, 125.2 (q, J =279.0 Hz), 63.1 (q, J =31.5 Hz), 61.8, 54.0, 52.3; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.40; **HRMS** (ESI) calcd. for $C_{19}H_{16}ClF_3N_2O_3Na$ ($[M+Na]^+$): 435.0694, found: 435.0689.



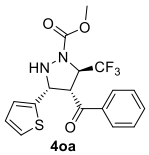
4ma

(*3R,4R,5R*)-methyl 4-benzoyl-3-(2-bromophenyl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ma): White solid; 77% yield, 84% ee, >20:1 dr; m.p.: 126.2 − 127.0 ºC; $[\alpha]_D^{27}$ = -16.7 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.637 min (major), 10.467 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 – 7.54 (m, 2H), 7.49 – 7.40 (m, 1H), 7.33 – 7.22 (m, 2H), 7.23 – 7.06 (m, 3H), 6.98 – 6.77 (m, 1H), 5.55 (d, J = 8.1 Hz, 1H), 5.48 – 5.36 (m, 1H), 5.15 (s, 1H), 4.89 (dd, J = 8.1, 2.8 Hz, 1H), 3.88 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.8, 157.2, 135.9, 135.2, 133.8, 132.6, 129.7, 128.6 (two peaks), 128.2, 127.8, 125.2 (q, J =282.6 Hz), 123.9, 64.4, 63.0 (q, J =31.8 Hz), 54.1, 52.1; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.39; **HRMS** (ESI) calcd. for $C_{19}H_{16}BrF_3N_2O_3Na$ ($[M+Na]^+$): 479.0189, found: 479.0180.



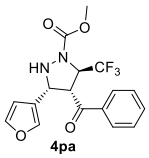
4na

(*3R,4R,5R*)-methyl 4-benzoyl-3-(furan-2-yl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4na): White solid; 81% yield, 94% ee, >20:1 dr; m.p.: 134.1 − 134.5 ºC; $[\alpha]_D^{19}$ = -55,8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.050 min (major), 10.410 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.12 (s, 1H), 6.10 – 6.00 (m, 1H), 5.89 – 5.82 (m, 1H), 5.82 – 5.69 (m, 1H), 5.25 – 4.99 (m, 2H), 4.63 (t, J = 7.0 Hz, 1H), 3.77 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 191.8, 158.3, 149.2, 142.8, 136.1, 133.9, 128.9, 128.1, 125.6 (q, J = 279.0 Hz),110.1, 109.0, 61.3 (q, J = 31.3 Hz), 59.9, 56.5, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.79; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_4Na$ ($[M+Na]^+$): 391.0876, found: 391.0873.



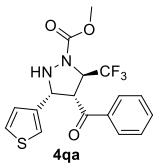
4oa

(*3R,4R,5R*)-methyl 4-benzoyl-3-(thiophen-2-yl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4oa): White solid; 52% yield, 95% ee, >20:1 dr; m.p.: 79.6 − 80.4 °C; $[\alpha]_D^{18}$ = -17.8 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.637 min (major), 12.610 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 – 7.68 (m, 2H), 7.60 – 7.54 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.06 (d, J = 5.0 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.37 (d, J = 3.5 Hz, 1H), 5.79 – 5.68 (m, 1H), 5.29 (d, J = 7.9 Hz, 1H), 5.21 (s, 1H), 4.70 (t, J = 7.1 Hz, 1H), 3.83 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 192.0, 157.0, 137.5, 136.2, 134.0, 129.0, 128.3, 126.8, 126.4, 125.7, 125.6 (q, J =278.7 Hz), 62.0, 60.6 (q, J =31.6 Hz), 57.6, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.55; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0639.



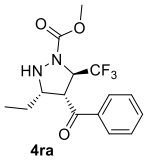
4pa

(*3R,4R,5R*)-methyl 4-benzoyl-3-(furan-3-yl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4pa): White solid; 70% yield, 95% ee, >20:1 dr; m.p.: 48.3 − 48.9 °C; $[\alpha]_D^{19}$ = -70.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.683 min (major), 12.083 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.22 – 7.11 (m, 1H), 6.98 (s, 1H), 5.85 (s, 1H), 5.75 – 5.62 (m, 1H), 4.98 (d, J = 7.7 Hz, 1H), 4.65 (t, J = 7.1 Hz, 1H), 3.80 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 192.4, 157.5, 143.6, 140.9, 136.2, 134.1, 129.2, 128.3, 125.5 (q, J =279.4 Hz), 120.2, 109.0, 61.1 (q, J =31.6 Hz), 58.8, 56.9, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.67; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_4Na$ ($[M+Na]^+$): 391.0876, found: 391.0873.



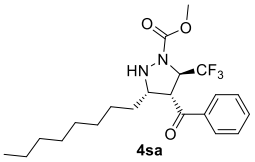
4qa

(*3R,4R,5R*)-methyl 4-benzoyl-3-(thiophen-3-yl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4qa): White solid; 55% yield, 93% ee, >20:1 dr; m.p.: 94.7 − 95.5 °C; $[\alpha]_D^{18}$ = -20.0 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.850 min (major), 14.100 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 – 7.63 (m, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.06 (dd, J = 5.0, 2.8 Hz, 1H), 6.80 – 6.70 (m, 1H), 6.51 (dd, J = 5.0, 1.3 Hz, 1H), 5.83 – 5.58 (m, 1H), 5.21 – 5.00 (m, 2H), 4.73 – 4.61 (m, 1H), 3.79 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 193.0, 157.4, 136.3, 136.1, 133.9, 129.0, 128.2, 126.5, 126.3, 125.5 (q, J =279.3 Hz), 123.9, 62.2, 61.3 (q, J =31.3 Hz), 56.8, 54.0; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.60; **HRMS** (ESI) calcd. for $C_{17}H_{15}F_3N_2O_3SNa$ ($[M+Na]^+$): 407.0648, found: 407.0638.



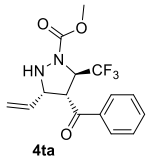
4ra

(*3S,4R,5R*)-methyl 4-benzoyl-3-ethyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ra): White solid; 68% yield, 92% ee, >20:1 dr; m.p.: 53.6 − 54.4 °C; $[\alpha]_D^{18}$ = -31.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.235 min (major), 8.057 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 – 7.93 (m, 2H), 7.68 – 7.61 (m, 1H), 7.56 – 7.48 (m, 2H), 5.59 – 5.44 (m, 1H), 4.59 (t, J = 6.9 Hz, 1H), 3.83 (s, 3H), 3.76 – 3.62 (m, 1H), 1.08 – 0.94 (m, 1H), 0.95 – 0.90 (m, 1H), 0.87 (t, J = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 192.8, 158.1, 135.9, 134.4, 129.3, 128.4, 125.7 (q, J =278.8 Hz), 64.4, 61.3 (q, J =31.2 Hz), 56.1, 53.9, 21.8, 11.3; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.86; **HRMS** (ESI) calcd. for $C_{15}H_{17}F_3N_2O_3Na$ ($[M+Na]^+$): 353.1083, found: 353.1080.



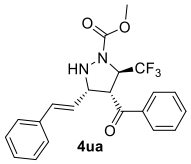
4sa

(*3S,4R,5R*)-methyl 4-benzoyl-3-octyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4sa): White solid; 77% yield, 96% ee, >20:1 dr; m.p.: 87.5 − 88.1 °C; $[\alpha]_D^{24}$ = -31.6 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.447 min (major), 10.890 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 – 7.91 (m, 2H), 7.68 – 7.61 (m, 1H), 7.52 (t, J = 7.7 Hz, 2H), 5.59 – 5.44 (m, 1H), 4.58 (s, 1H), 4.40 (t, J = 6.9 Hz, 1H), 3.87 – 3.76 (m, 4H), 1.55 – 1.39 (m, 1H), 1.26 – 0.98 (m, 12H), 0.88 – 0.78 (m, 4H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 192.8, 158.1, 136.0, 134.3, 129.3, 128.4, 125.7 (q, J =280.7 Hz), 62.8, 61.4 (q, J =31.6 Hz), 56.0, 53.9, 31.9, 29.3, 29.2, 29.0, 28.4, 26.5, 22.7, 14.2; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.84; **HRMS** (ESI) calcd. for $C_{21}H_{29}F_3N_2O_3Na$ ($[M+Na]^+$): 437.2022, found: 437.2012.

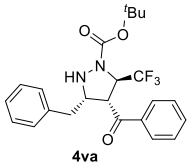


4ta

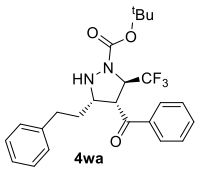
(*3S,4R,5R*)-methyl 4-benzoyl-5-(trifluoromethyl)-3-vinylpyrazolidine-1-carboxylate (4ta): White solid; 46% yield, 89% ee, >20:1 dr; m.p.: 36.4 − 36.8 °C; $[\alpha]_D^{18}$ = -50.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.958 min (major), 7.977 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.83 (m, 2H), 7.68 – 7.58 (m, 1H), 7.55 – 7.46 (m, 2H), 5.56 – 5.46 (m, 1H), 5.37 – 5.20 (m, 1H), 5.10 – 4.93 (m, 2H), 4.86 (d, J = 4.9 Hz, 1H), 4.58 – 4.49 (m, 1H), 4.45 – 4.33 (m, 1H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 192.5, 157.4, 136.1, 134.3, 130.7, 129.2, 128.6, 125.5 (q, J =278.9 Hz), 119.6, 64.9, 61.1 (q, J =31.5 Hz), 56.4, 54.0; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.67; **HRMS** (ESI) calcd. for $C_{15}H_{15}F_3N_2O_3Na$ ($[M+Na]^+$): 351.0927, found: 351.0918.



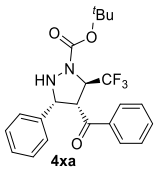
(*3S,4R,5R*)-methyl 4-benzoyl-3-((E)-styryl)-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4ua): White solid; 54% yield, 82% ee, >20:1 dr; m.p.: 54.3 − 54.9 °C; $[\alpha]_D^{17}$ = -71.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IG, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.493 min (major), 21.760 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 – 7.86 (m, 2H), 7.68 – 7.57 (m, 1H), 7.53 – 7.39 (m, 2H), 7.24 – 7.14 (m, 3H), 7.08 – 6.98 (m, 2H), 6.33 (d, J = 15.7 Hz, 1H), 5.69 – 5.42 (m, 2H), 4.91 (s, 1H), 4.70 – 4.50 (m, 2H), 3.86 (s, 3H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 192.6, 157.5, 136.3, 135.9, 134.6, 134.3, 129.3, 128.6, 128.5, 128.3, 126.7, 125.5 (q, J =278.8 Hz), 121.7, 64.5, 61.2 (q, J =31.5 Hz), 56.5, 54.1; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -74.57; **HRMS** (ESI) calcd. for $C_{21}H_{19}F_3N_2O_3Na$ ($[M+Na]^+$): 427.1240, found: 427.1232.



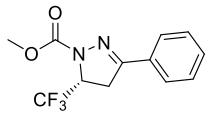
(*3S,4R,5R*)-tert-butyl 4-benzoyl-3-benzyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4va): White solid; 50% yield, 95% ee; >20:1 dr; m.p.: 164.7 − 165.6 °C; $[\alpha]_D^{17}$ = -43.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD−H, n−Hexane/2−propanol = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 17.597 min (major), 11.930 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.11 – 7.05 (m, 2H), 5.72 – 5.46 (m, 1H), 4.44 (t, J = 6.9 Hz, 1H), 4.15 – 3.86 (m, 1H), 2.39 (dd, J = 14.2, 10.6 Hz, 1H), 2.15 (dd, J = 14.2, 3.2 Hz, 1H), 1.57 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 193.2, 155.9, 138.0, 136.1, 134.4, 129.6, 129.3, 128.5, 128.3, 126.7, 125.8 (q, J =279.5 Hz), 82.3, 64.6, 61.4 (q, J =31.1 Hz), 55.9, 34.9, 28.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.87; **HRMS** (ESI) calcd. for $C_{23}H_{25}F_3N_2O_3Na$ ($[M+Na]^+$): 457.1709, found: 450.1702.



(*3S,4R,5R*)-tert-butyl 4-benzoyl-3-phenethyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4wa): White solid; 80% yield, 86% ee; >20:1 dr; m.p.: 77.1 − 77.4 °C; $[\alpha]_D^{18}$ = -26.1 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK OD‑H, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.107 min (major), 5.720 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.71 – 7.56 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.21 – 7.06 (m, 3H), 7.02 – 6.83 (m, 2H), 5.59 – 5.34 (m, 1H), 4.51 (s, 1H), 4.40 – 4.27 (m, 1H), 3.85 – 3.61 (m, 1H), 2.97 – 2.78 (m, 1H), 2.71 – 2.52 (m, 1H), 1.54 (s, 9H), 1.42 – 1.26 (m, 1H), 1.22 – 1.07 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 192.9, 156.4, 141.0, 136.0, 134.3, 129.3, 128.5, 128.4, 128.4, 126.01, 125.8 (q, J =279.3 Hz), 82.2, 61.7, 61.4 (q, J =30.5 Hz), 56.3, 32.4, 29.7, 28.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.98; **HRMS** (ESI) calcd. for $C_{24}H_{27}F_3N_2O_3Na$ ($[M+Na]^+$): 471.1866, found: 471.1851.

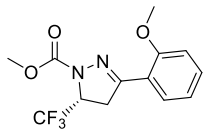


(*3R,4R,5R*)-tert-butyl 4-benzoyl-3-phenyl-5-(trifluoromethyl)pyrazolidine-1-carboxylate (4xa): White solid; 48% yield, 95% ee; >20:1 dr; m.p.: 158.4 − 159.3 °C; $[\alpha]_D^{24}$ = -20.2 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IH, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.627 min (major), 9.723 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.12 – 6.97 (m, 3H), 6.91 – 6.77 (m, 2H), 5.60 – 5.45 (m, 1H), 5.17 (s, 1H), 4.93 (d, J = 8.1 Hz, 1H), 4.81 – 4.65 (m, 1H), 1.52 (s, 9H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.2, 155.1, 136.6, 136.2, 133.7, 128.8, 128.4, 128.2, 128.1, 127.5, 125.6 (q, J = 279.5 Hz), 82.40, 66.1, 61.7 (q, J = 31.2 Hz), 56.3, 28.3; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -74.43; **HRMS** (ESI) calcd. for $C_{22}H_{23}F_3N_2O_3Na$ ($[M+Na]^+$): 443.1553, found: 443.1544.



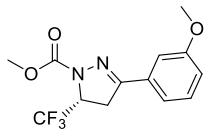
5aa

(*R*)-methyl 3-phenyl-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5aa): White solid; 84% yield, 98% ee; m.p.: 83.6 − 84.5 °C; $[\alpha]_D^{19}$ = 97.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.467 min (major), 4.850 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.68 (m, 2H), 7.50 – 7.36 (m, 3H), 5.11 – 4.98 (m, 1H), 3.92 (s, 3H), 3.56 (dd, J = 18.0, 11.7 Hz, 1H), 3.36 (dd, J = 18.0, 3.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 154.9, 153.9, 131.1, 130.2, 128.9, 127.0, 124.4 (q, J = 280.3 Hz), 58.2 (q, J = 32.6 Hz), 54.0, 34.6; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -77.21; **HRMS** (ESI) calcd. for $C_{12}H_{11}F_3N_2O_2Na$ ($[M+Na]^+$): 295.0665, found: 295.0662.



5ab

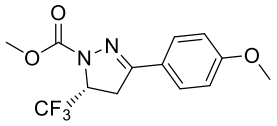
(*R*)-methyl 3-(2-methoxyphenyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5ab): White solid; 65% yield, 97% ee; m.p.: 94.7 − 95.5 °C; $[\alpha]_D^{19}$ = 97.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.752 min (major), 15.760 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1H), 7.50 – 7.33 (m, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 5.11 – 4.90 (m, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.73 (dd, J = 18.8, 11.7 Hz, 1H), 3.45 (dd, J = 18.9, 3.5 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 158.2, 155.4, 154.0, 132.3, 129.9, 124.5 (q, J =280.2 Hz), 121.1, 119.5, 111.4, 58.1 (q, J =32.0 Hz), 55.6, 53.9, 37.5; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -77.48; **HRMS** (ESI) calcd. for $C_{13}H_{13}F_3N_2O_3Na$ ($[M+Na]^+$): 325.0770, found: 325.0774.



5ac

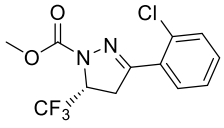
(*R*)-methyl 3-(3-methoxyphenyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5ac): White solid; 72% yield, 98% ee; m.p.: 73.0 − 73.8 °C; $[\alpha]_D^{19}$ = 92.0

(c 1.0, CHCl3); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.560 min (major), 17.085 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.30 – 7.22 (m, 1H), 7.05 – 6.95 (m, 1H), 5.09 – 4.94 (m, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.56 (dd, J = 17.9, 11.8 Hz, 1H), 3.34 (dd, J = 17.9, 3.7 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 160.0, 154.9, 153.8, 131.5, 129.9, 124.4 (q, J =280.8 Hz), 119.7, 117.4, 111.6, 58.1 (q, J =32.7 Hz), 55.6, 54.0, 34.8; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -77.24; **HRMS** (ESI) calcd. for $C_{13}H_{13}F_3N_2O_3Na$ ($[M+Na]^+$): 325.0770, found: 325.0772.



5ad

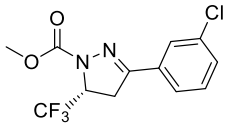
(*R*)-methyl 3-(4-methoxyphenyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5ad): White solid; 66% yield, 96% ee; m.p.: 146.7 − 147.3 °C; $[\alpha]_D^{19}$ = 83.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 18.097 min (major), 24.338 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 – 7.61 (m, 2H), 6.98 – 6.83 (m, 2H), 5.16 – 4.88 (m, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.53 (dd, J = 17.8, 11.7 Hz, 1H), 3.33 (dd, J = 17.8, 3.7 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 161.9, 154.6, 154.0, 128.7, 124.4 (q, J =280.6 Hz), 122.8, 114.3, 58.0 (q, J =32.7 Hz), 55.6, 53.9, 34.7; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -77.23; **HRMS** (ESI) calcd. for $C_{13}H_{13}F_3N_2O_3Na$ ($[M+Na]^+$): 325.0770, found: 325.0761.



5ae

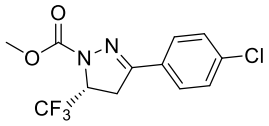
(*R*)-methyl 3-(2-chlorophenyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5ae): Colorless oil; 74% yield, 94% ee; $[\alpha]_D^{19}$ = 110.9 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 26.735 min (major), 25.118 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 – 7.67 (m, 1H), 7.44 – 7.39 (m, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.27 (m, 1H), 5.10 – 4.99 (m, 1H), 3.92 (s, 3H), 3.86 (dd, J = 18.5, 11.8 Hz, 1H), 3.46 (dd,

J = 18.4, 3.5 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 155.2, 153.6, 133.0, 131.6, 131.1, 130.7, 129.9, 127.3, 124.3 (q, J =281.0 Hz), 58.5 (q, J =32.8 Hz), 54.1, 37.3; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -77.50; **HRMS** (ESI) calcd. for $C_{12}H_{10}ClF_3N_2O_2Na$ ([M+Na]$^+$): 329.0275, found: 329.0277.



5af

(*R*)-methyl 3-(3-chlorophenyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5af): Colorless oil; 60% yield, 95% ee; $[\alpha]_D^{19}$ = 101.5 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.130 min (major), 9.552 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.65 – 7.57 (m, 1H), 7.46 – 7.39 (m, 1H), 7.39 – 7.33 (m, 1H), 5.13 – 4.98 (m, 1H), 3.92 (s, 3H), 3.54 (dd, J = 17.9, 11.8 Hz, 1H), 3.33 (dd, J = 17.9, 3.8 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 153.7, 153.7, 135.1, 131.9, 131.0, 130.2, 127.0, 125.1, 124.3 (q, J =281.0 Hz), 58.3 (q, J =32.8 Hz), 54.1, 34.6; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -77.23; **HRMS** (ESI) calcd. for $C_{12}H_{10}ClF_3N_2O_2Na$ ([M+Na]$^+$): 329.0275, found: 329.0275.

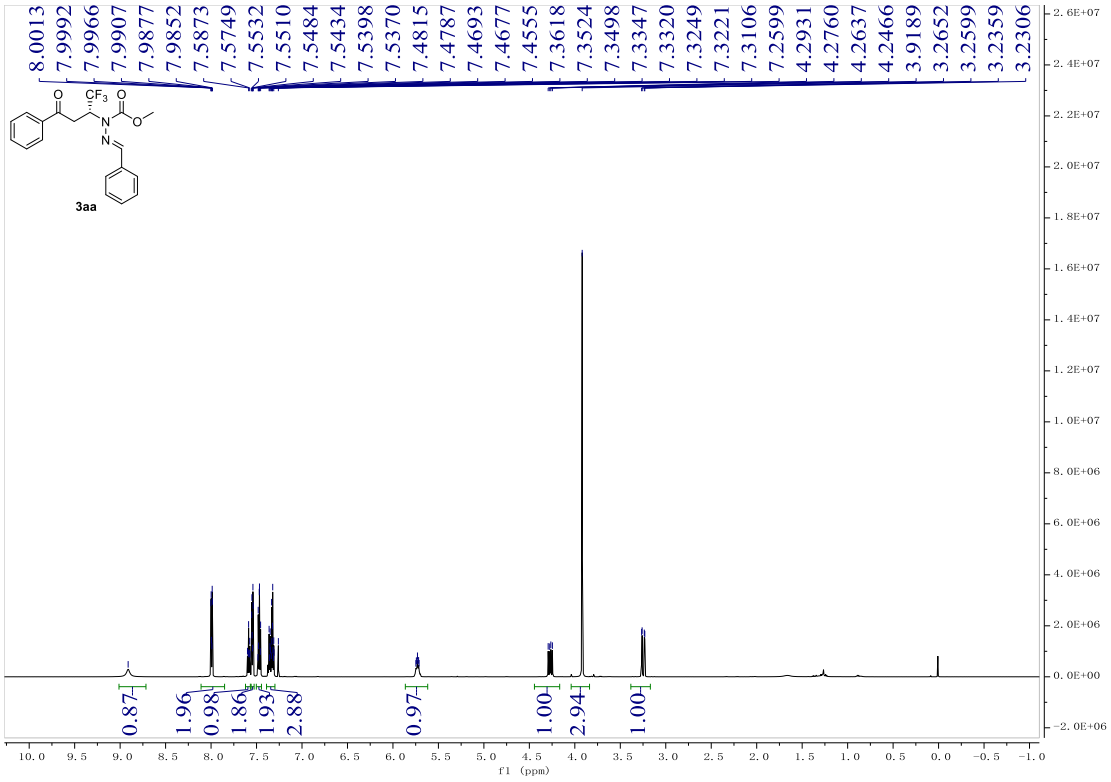


5ag

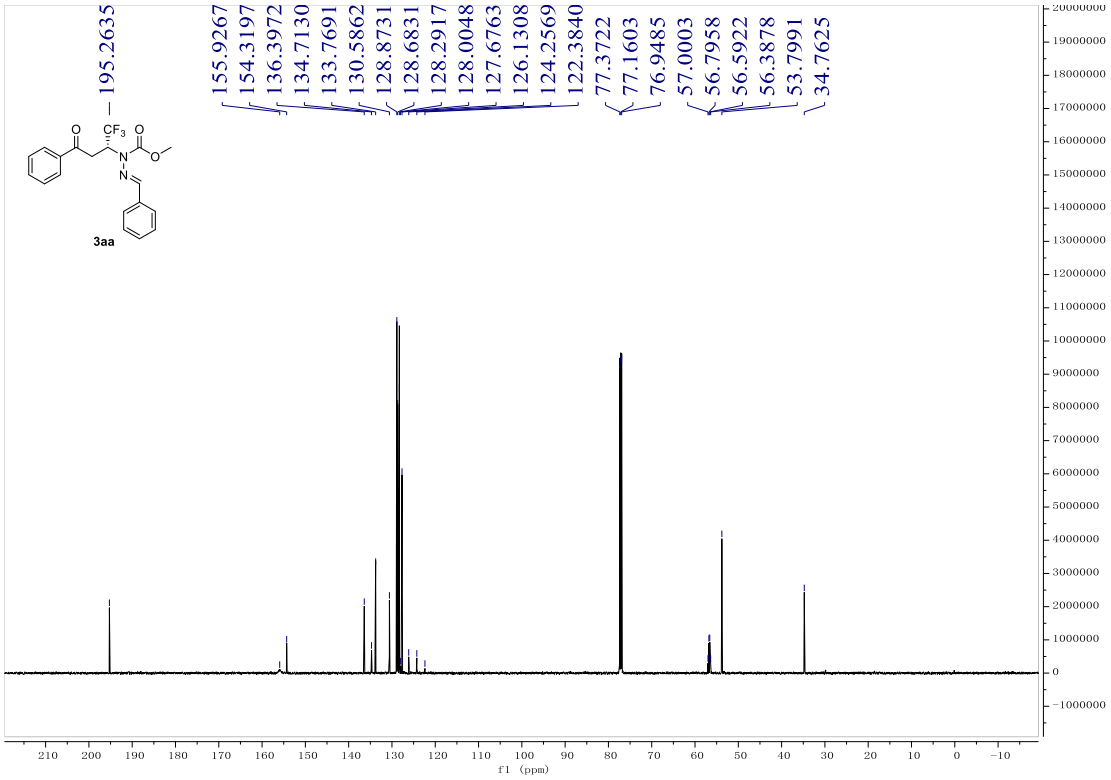
(*R*)-methyl 3-(4-chlorophenyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-1-carboxylate (5ag): Colorless oil; 70% yield, 97% ee; $[\alpha]_D^{19}$ = 105.3 (c 1.0, $CHCl_3$); **HPLC** CHIRALPAK IF, n−Hexane/2−propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.448 min (major), 9.908 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 2H), 7.48 – 7.35 (m, 2H), 5.11 – 4.98 (m, 1H), 3.92 (s, 3H), 3.54 (dd, J = 17.9, 11.8 Hz, 1H), 3.33 (dd, J = 17.9, 3.8 Hz, 1H); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 153.8, 153.7, 137.2, 129.3, 128.7, 128.3, 124.3 (q, J =280.3 Hz), 58.3 (q, J =33.0 Hz), 54.1, 34.6; **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -77.23; **HRMS** (ESI) calcd. for $C_{12}H_{10}ClF_3N_2O_2Na$ ([M+Na]$^+$): 329.0275, found: 329.0274.

10. Copies of NMR Spectra

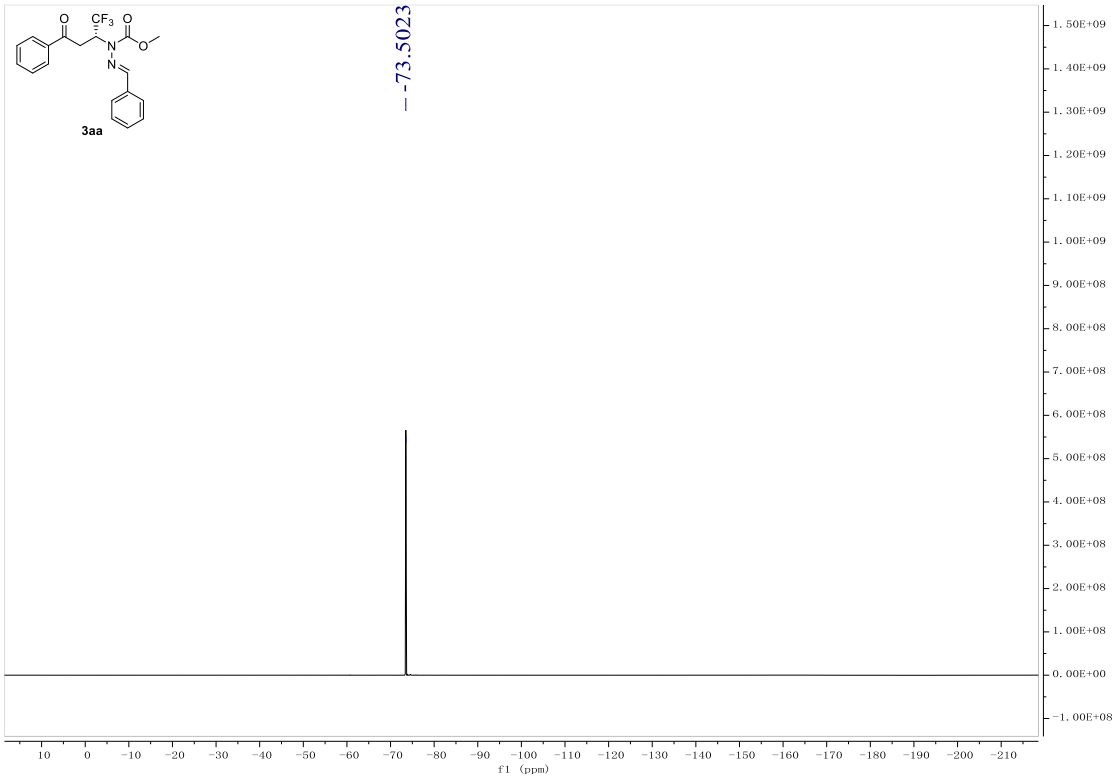
^{1}H NMR of 3aa (600 MHz, $CDCl_3$)



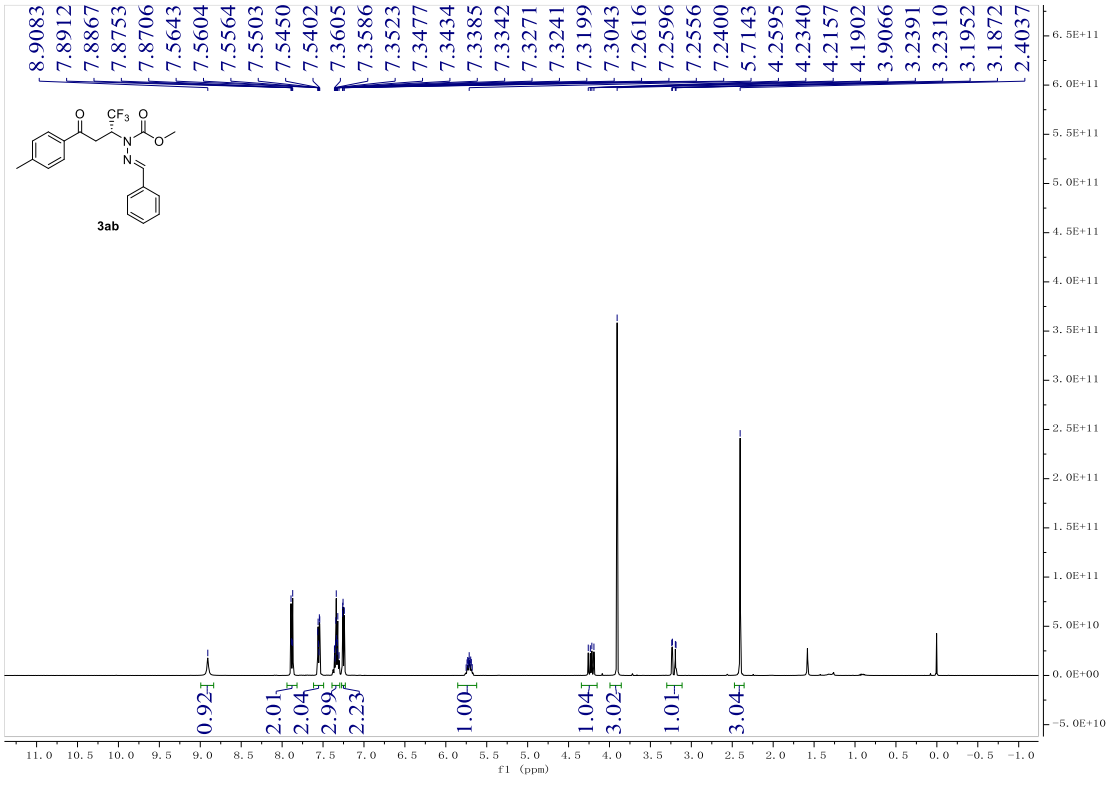
^{13}C{^{1}H} NMR of 3aa (150 MHz, $CDCl_3$)



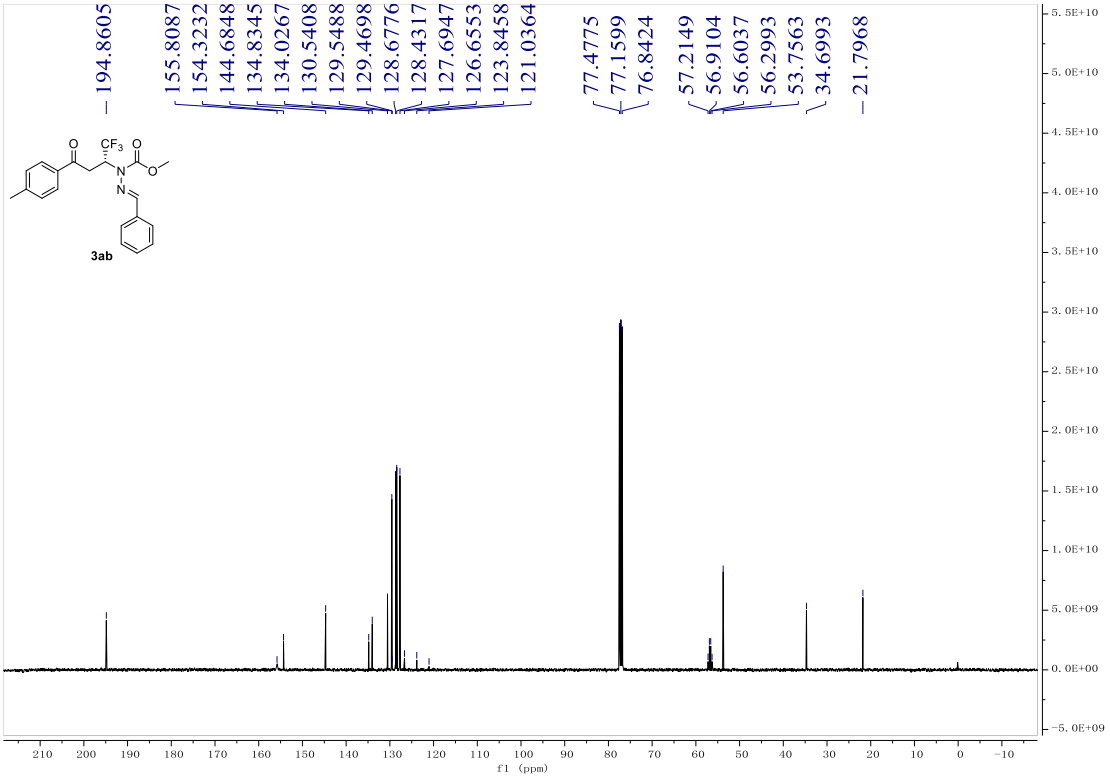
$^{19}F\{^{1}H\}$ NMR of 3aa (565 MHz, $CDCl_3$)



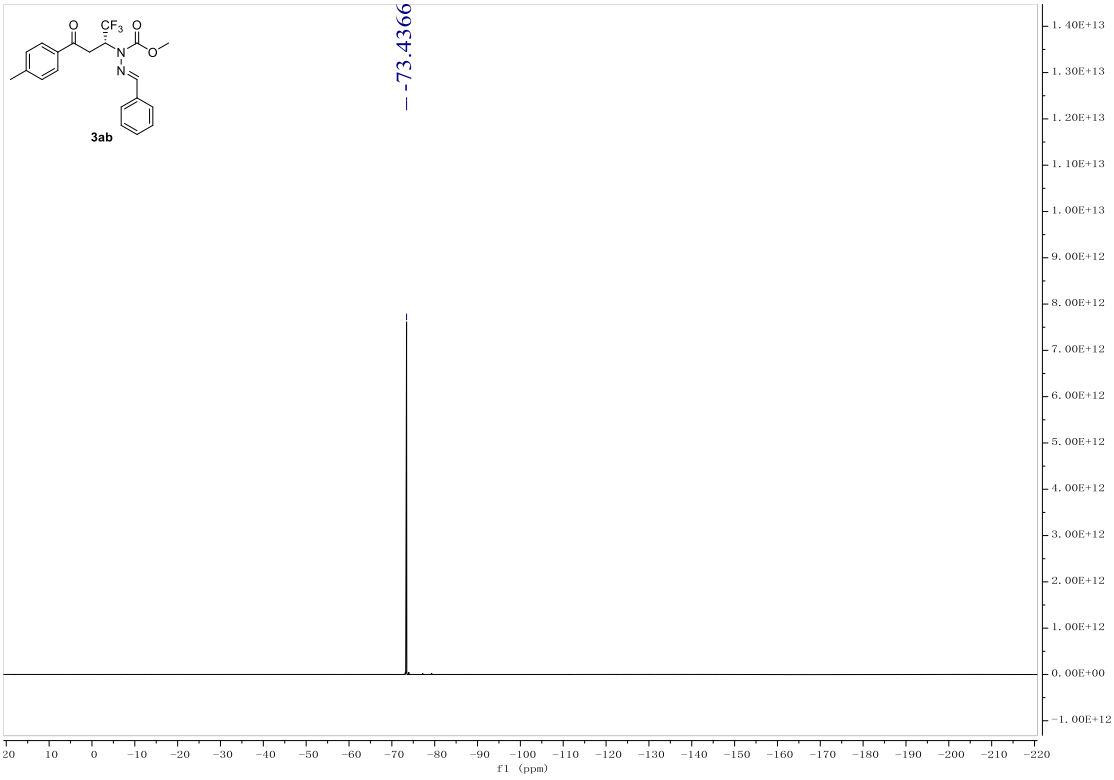
^{1}H NMR of 3ab (400 MHz, $CDCl_3$)



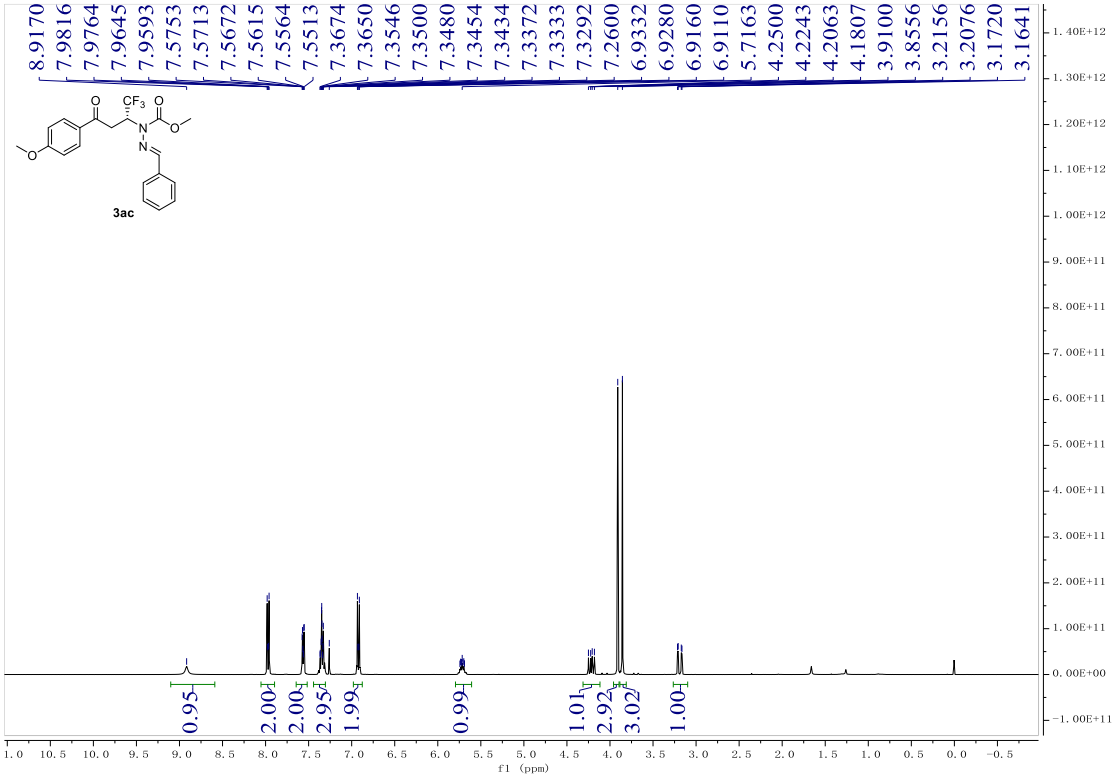
$^{13}C\{^{1}H\}$ NMR of 3ab (100 MHz, $CDCl_3$)



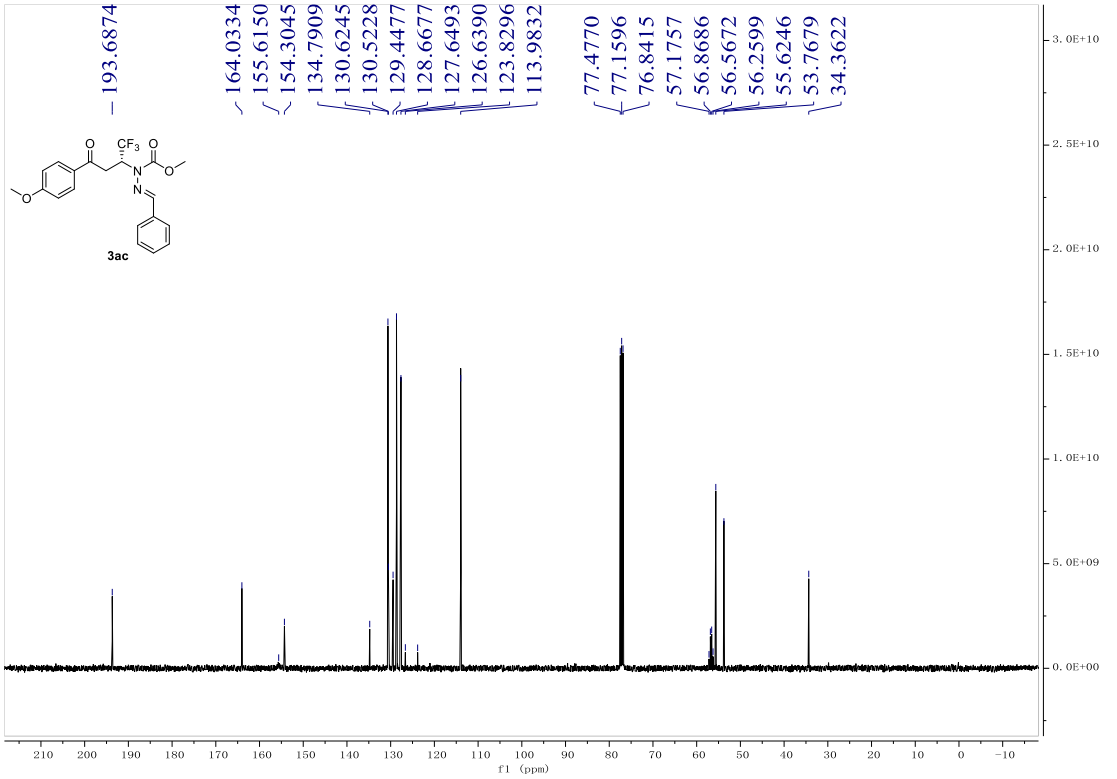
$^{19}F\{^{1}H\}$ NMR of 3ab (376 MHz, $CDCl_3$)



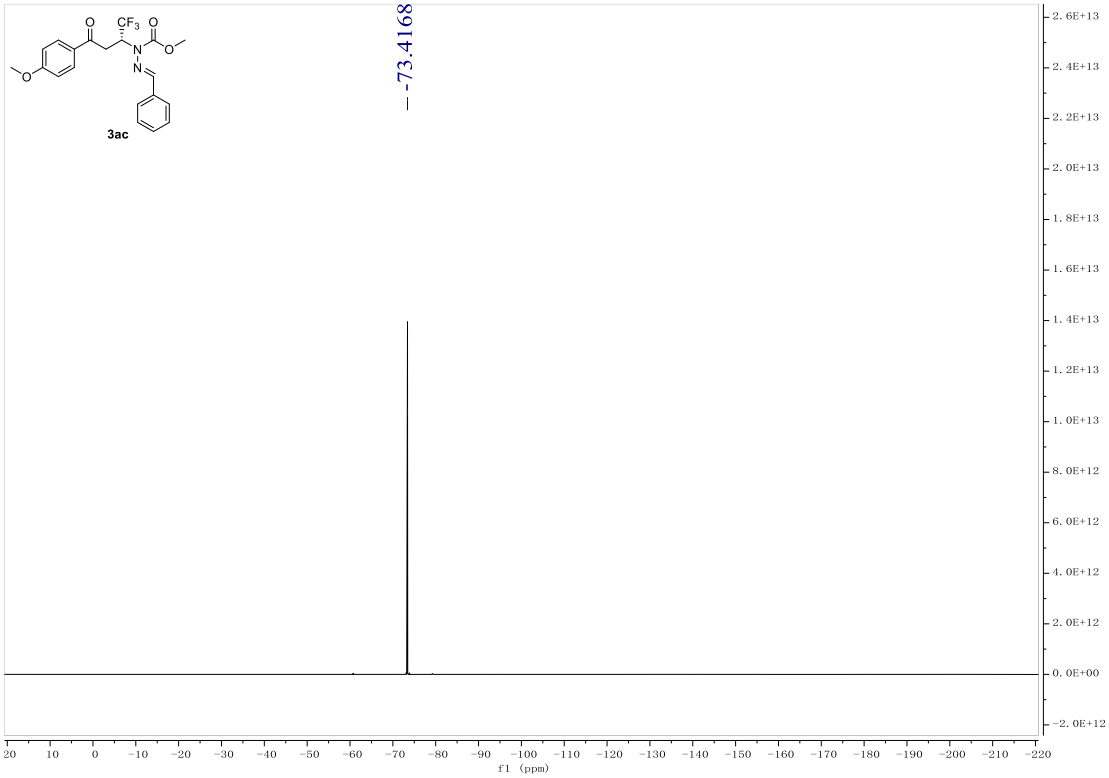
^{1}H NMR of 3ac (400 MHz, $CDCl_3$)



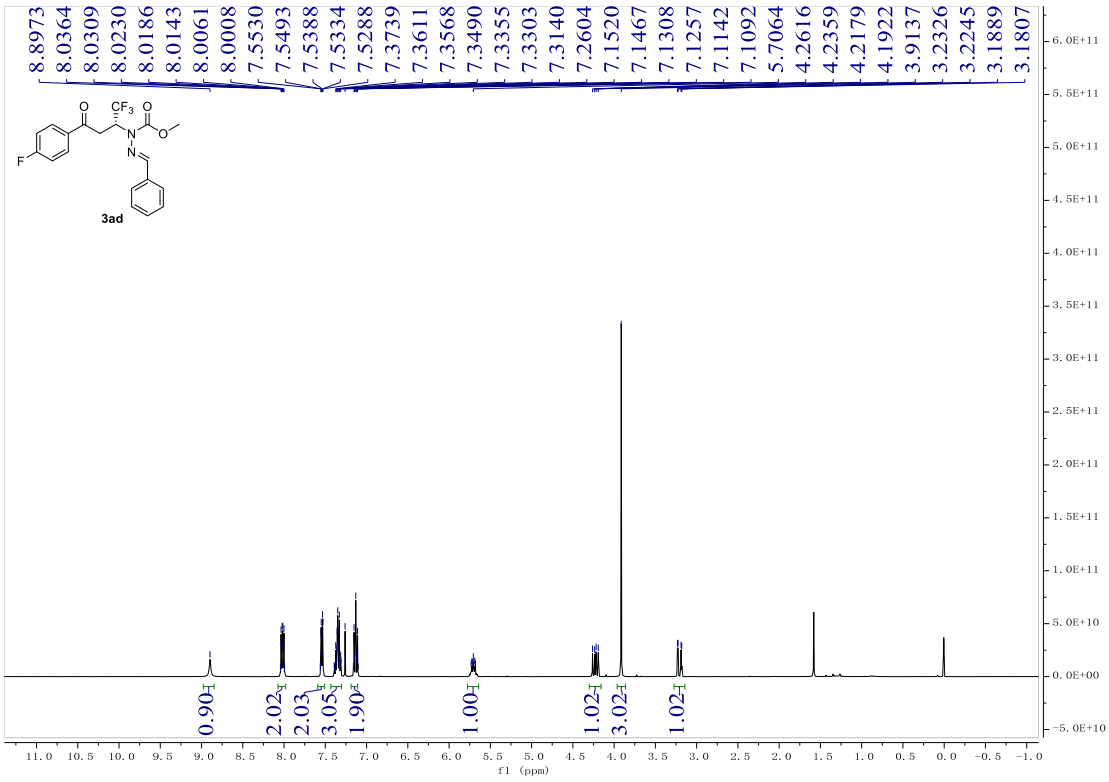
$^{13}C\{^{1}H\}$ NMR of 3ac (100 MHz, $CDCl_3$)



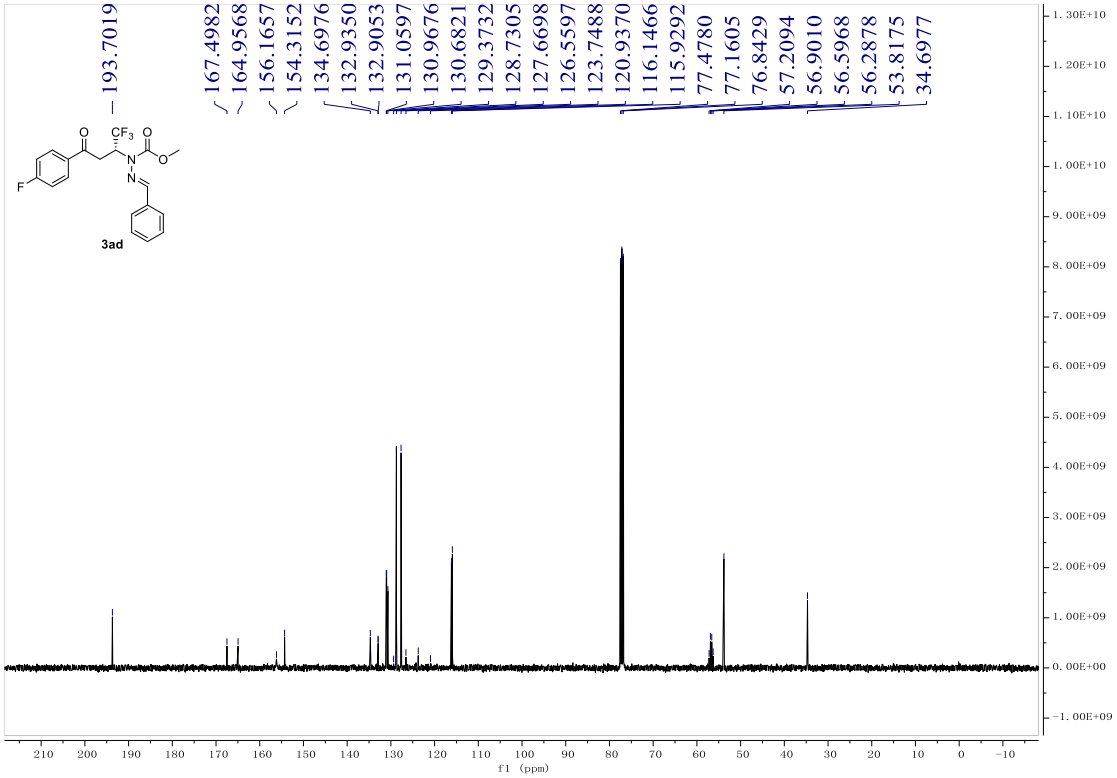
$^{19}F\{^{1}H\}$ NMR of 3ac (376 MHz, $CDCl_3$)



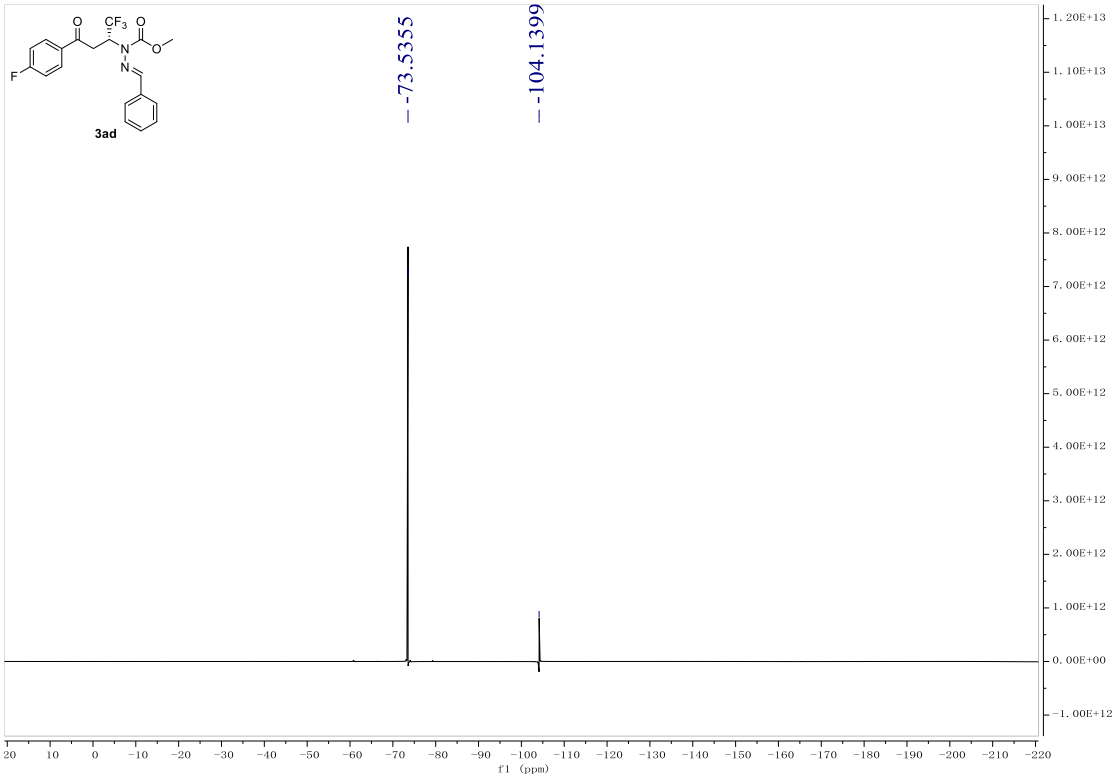
^{1}H NMR of 3ad (400 MHz, $CDCl_3$)



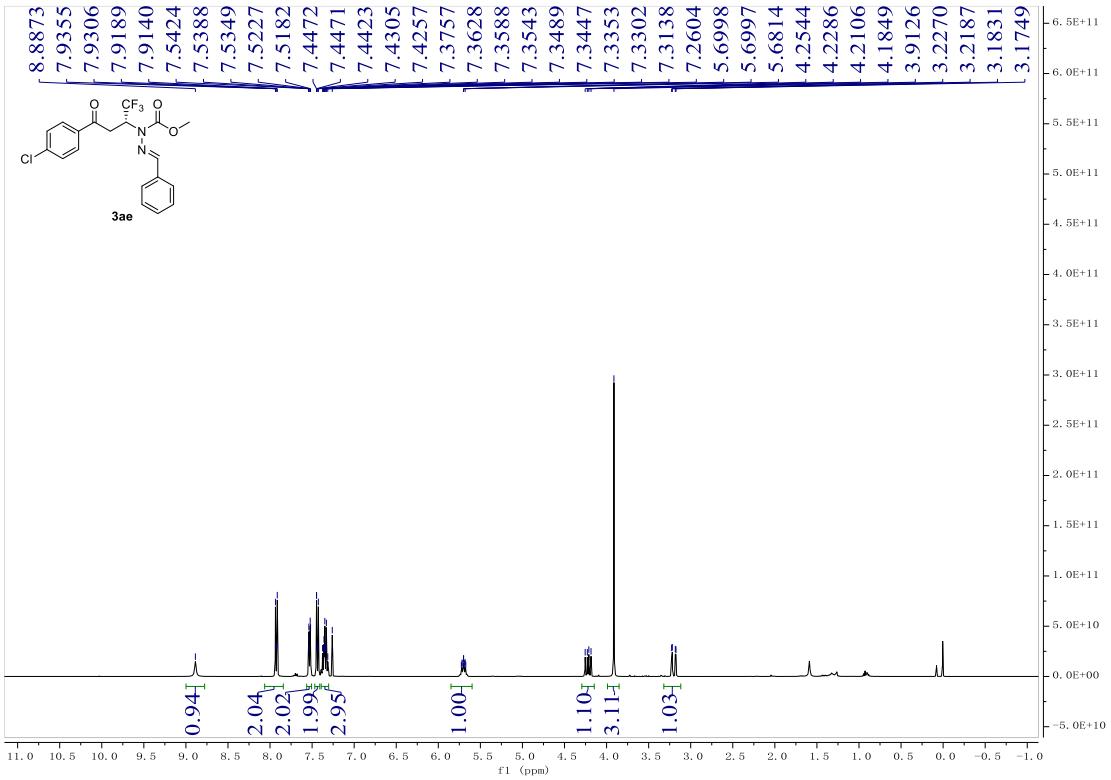
^{13}C{^{1}H} NMR of 3ad (100 MHz, $CDCl_3$)



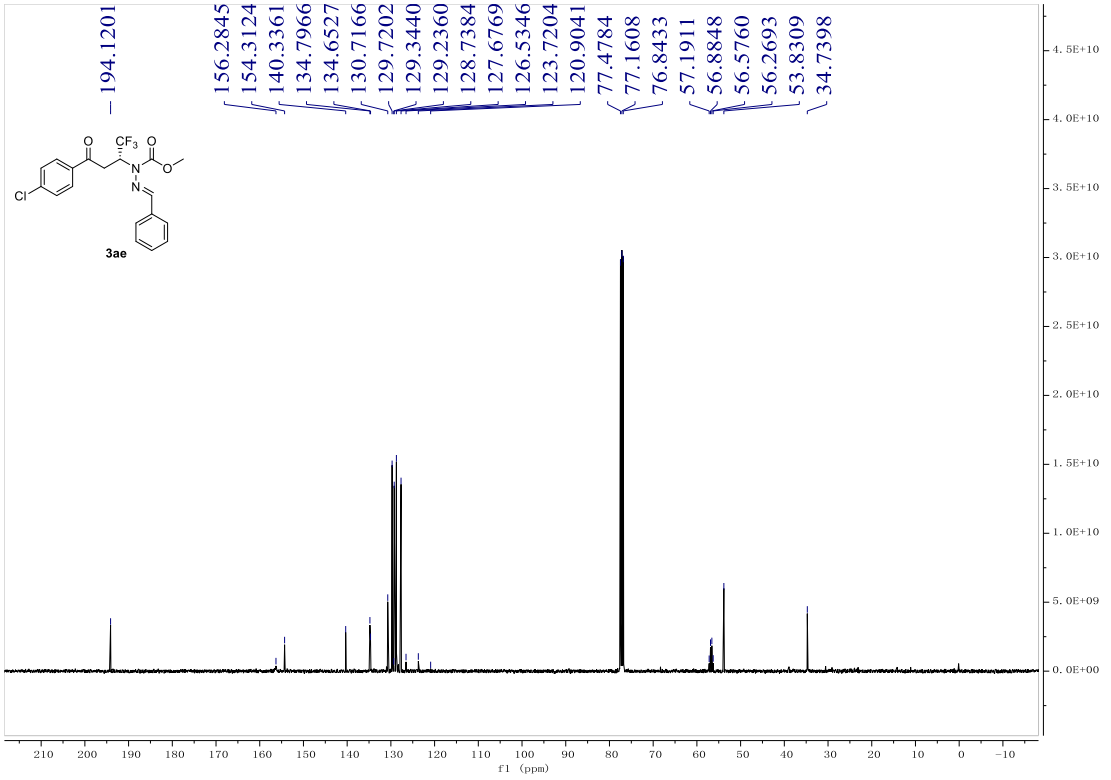
$^{19}F\{^{1}H\}$ NMR of 3ad (376 MHz, $CDCl_3$)



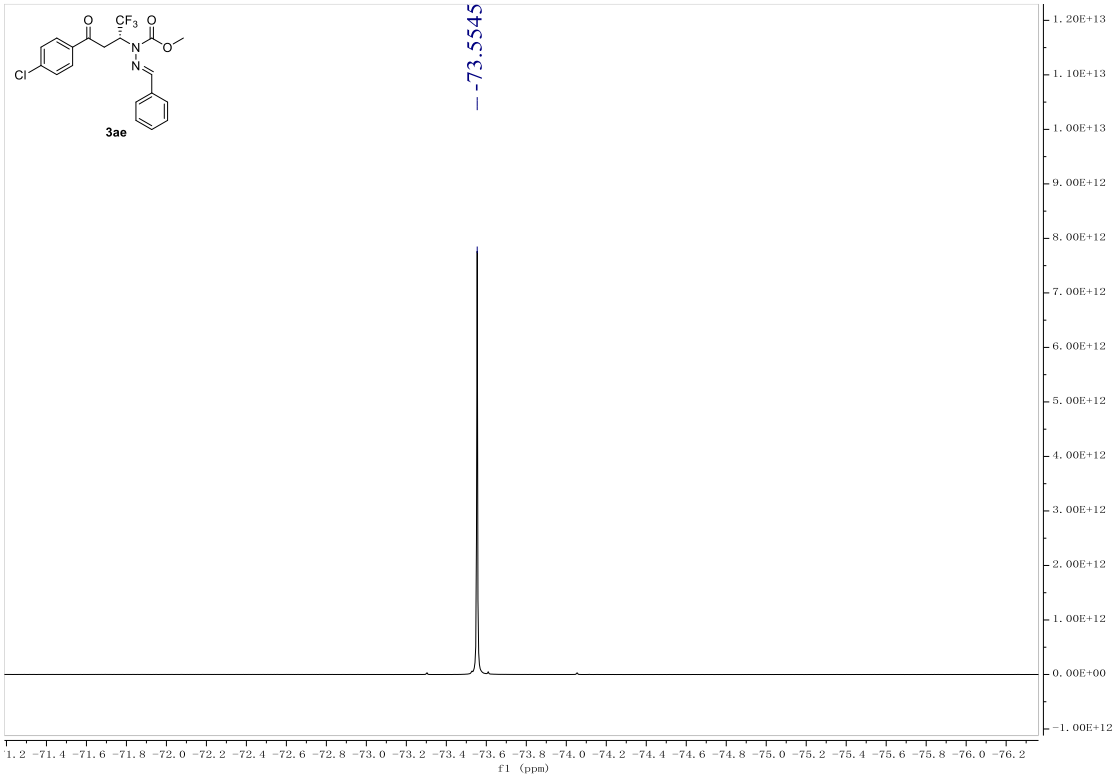
^{1}H NMR of 3ae (400 MHz, $CDCl_3$)



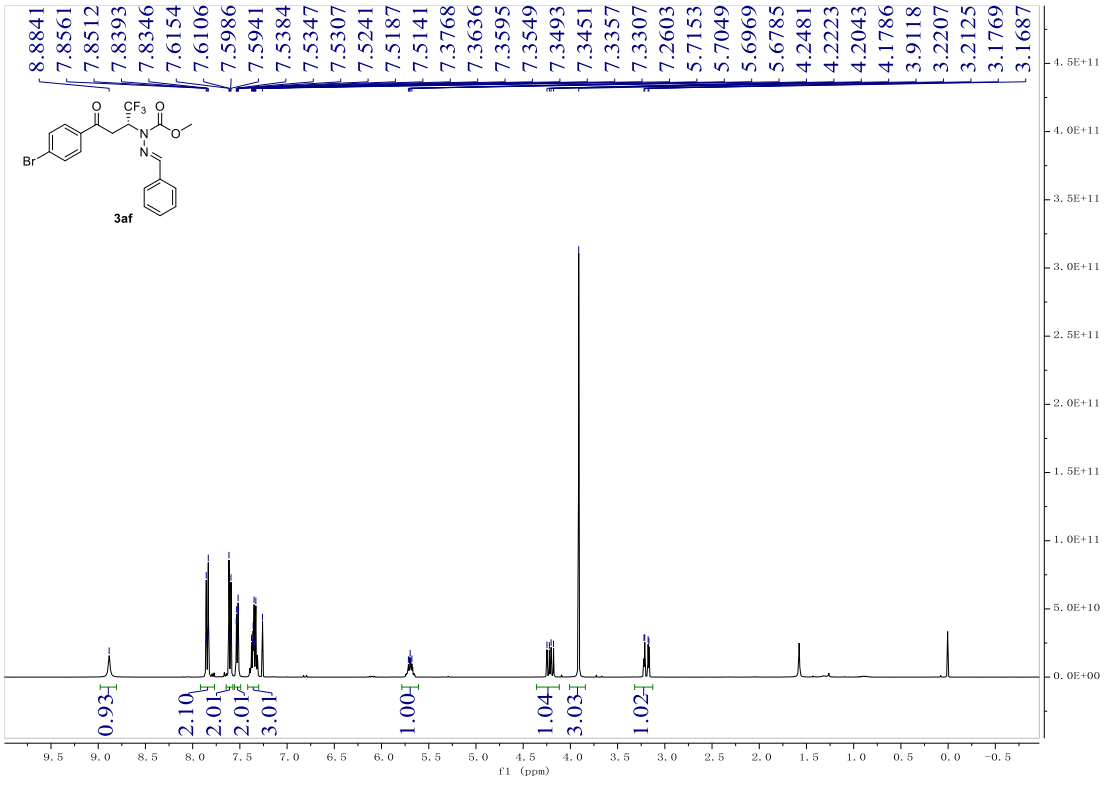
$^{13}C\{^{1}H\}$ NMR of 3ae (100 MHz, $CDCl_3$)



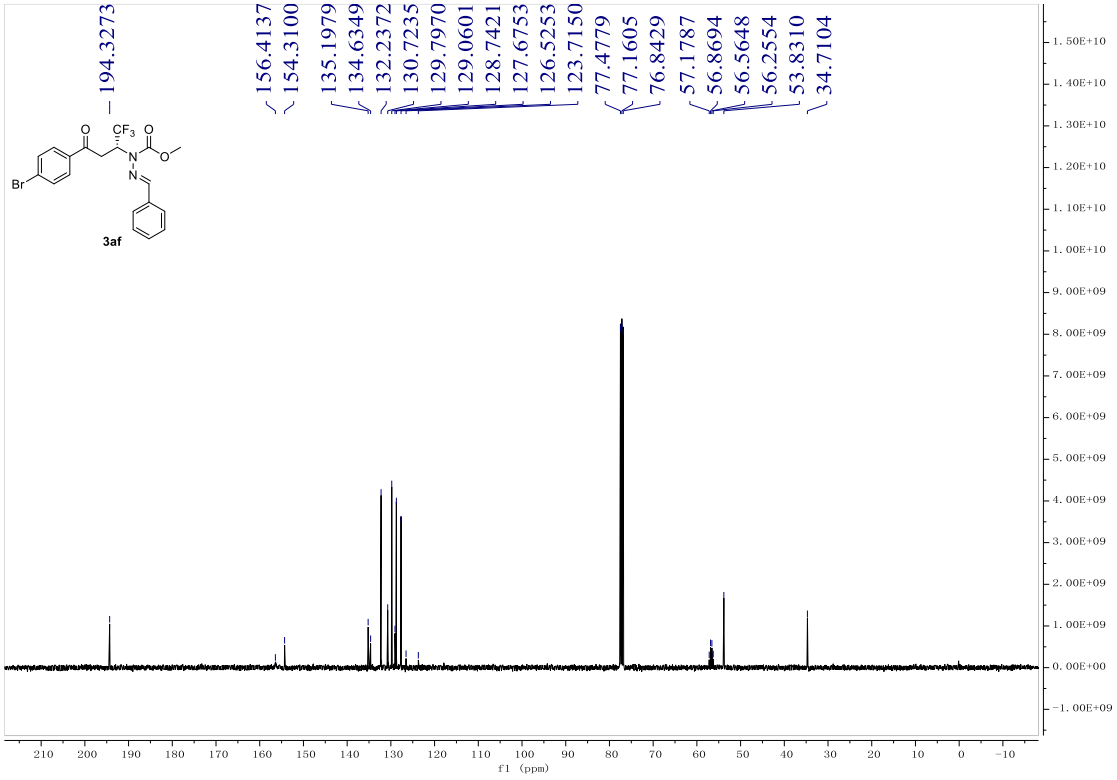
$^{19}F\{^{1}H\}$ NMR of 3ae (376 MHz, $CDCl_3$)



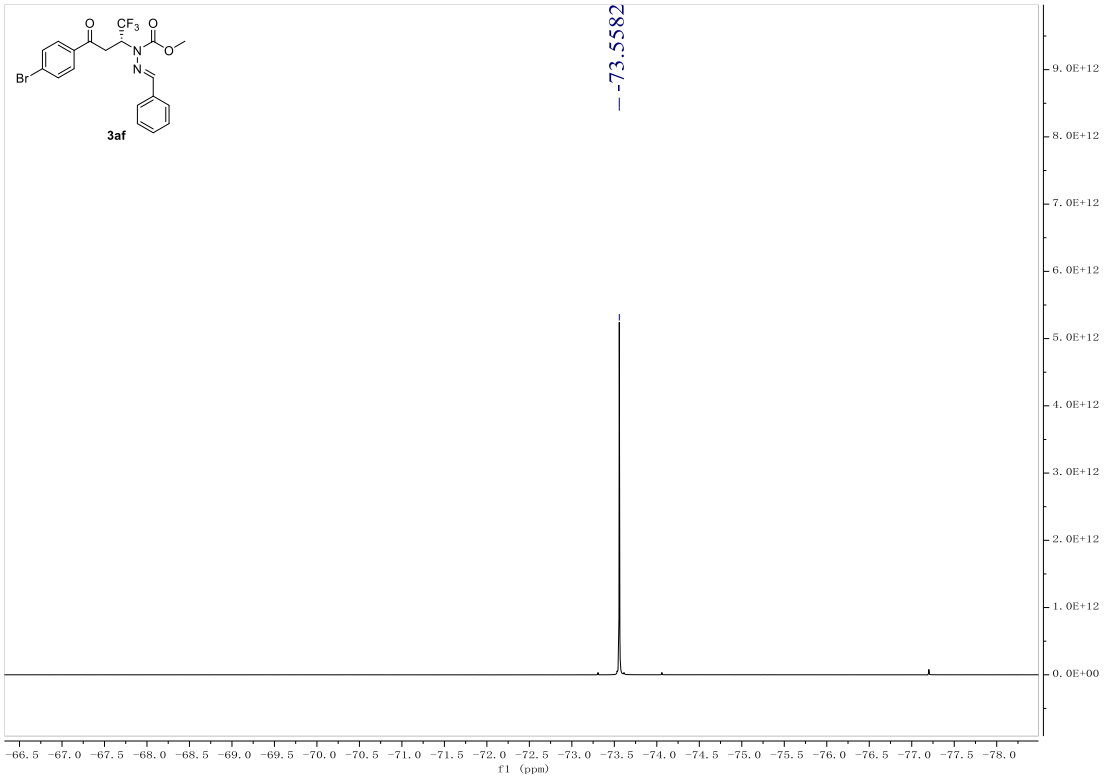
^{1}H NMR of 3af (400 MHz, $CDCl_3$)



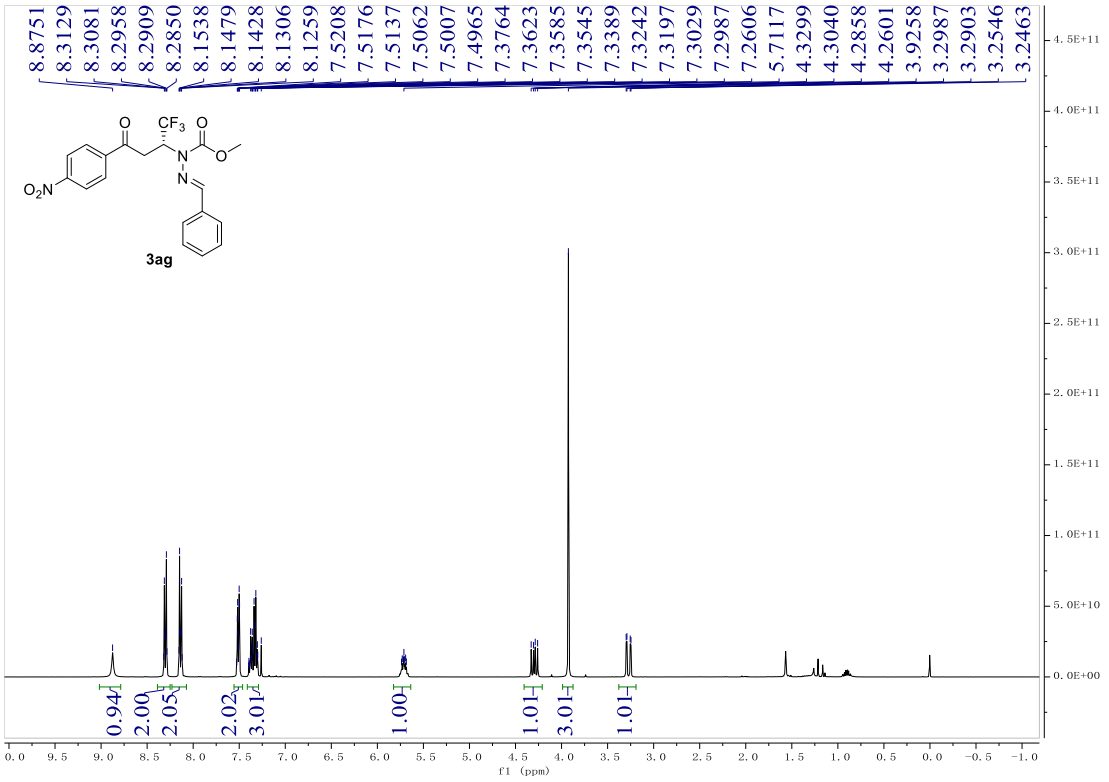
^{13}C{^{1}H} NMR of 3af (100 MHz, $CDCl_3$)



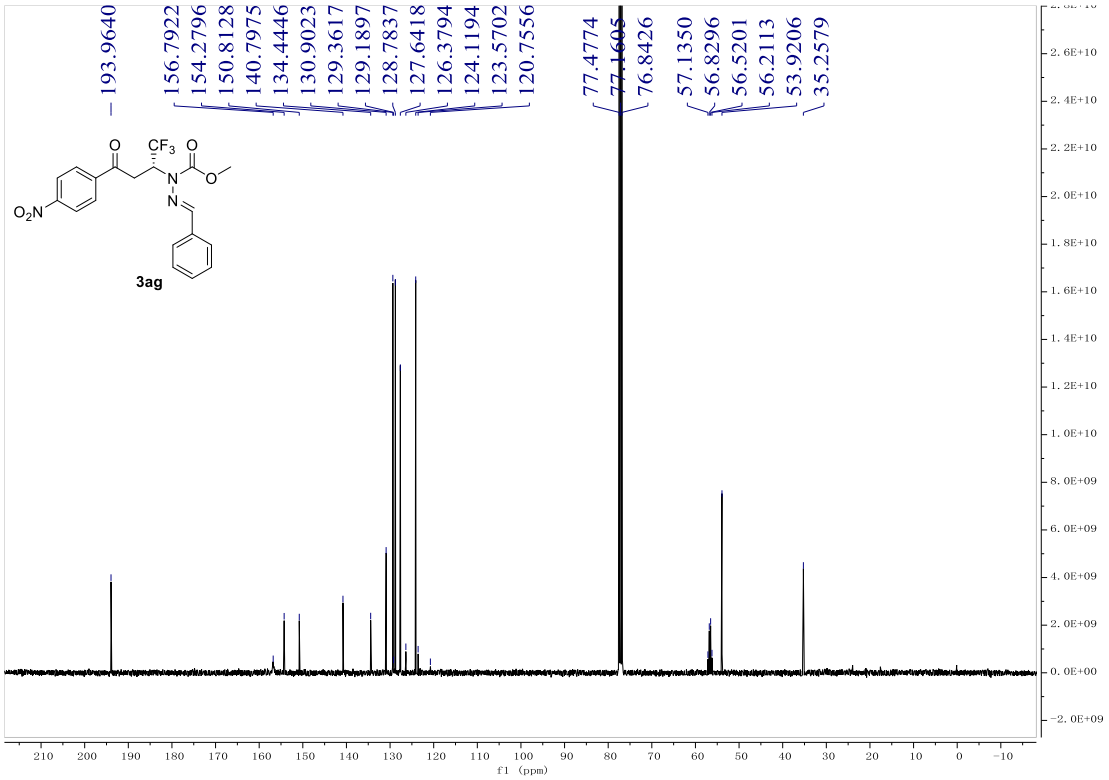
$^{19}F\{^{1}H\}$ NMR of 3af (376 MHz, $CDCl_3$)



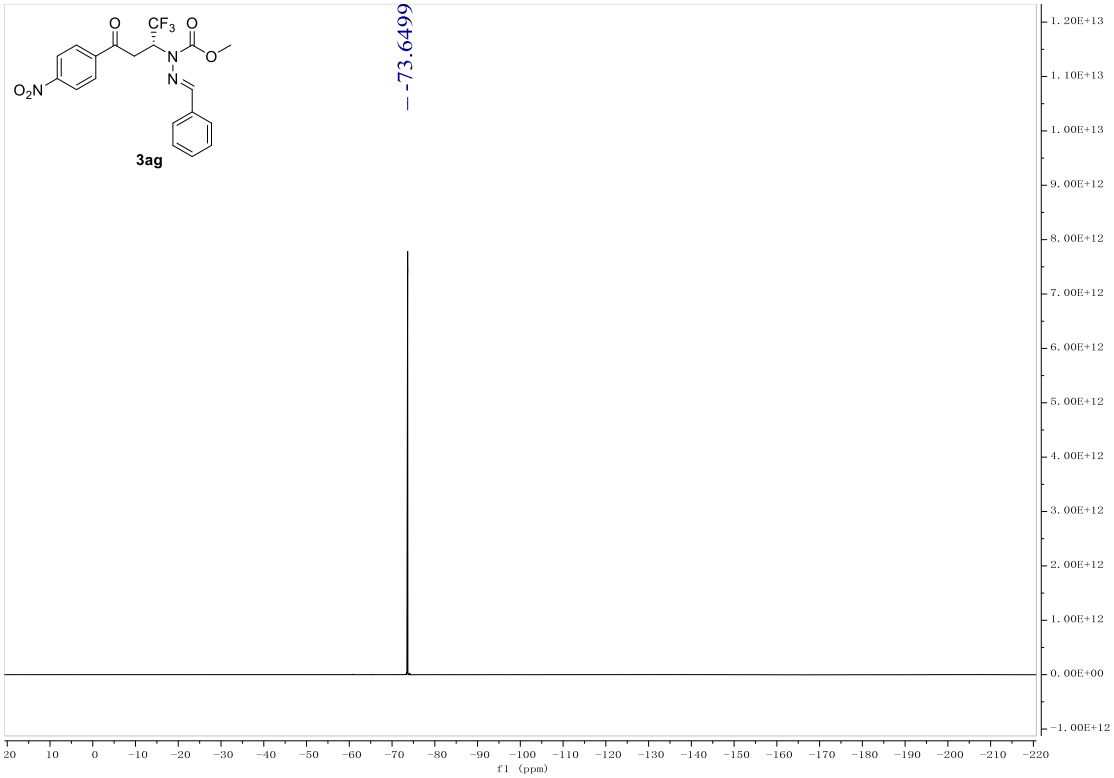
^{1}H NMR of 3ag (400 MHz, $CDCl_3$)



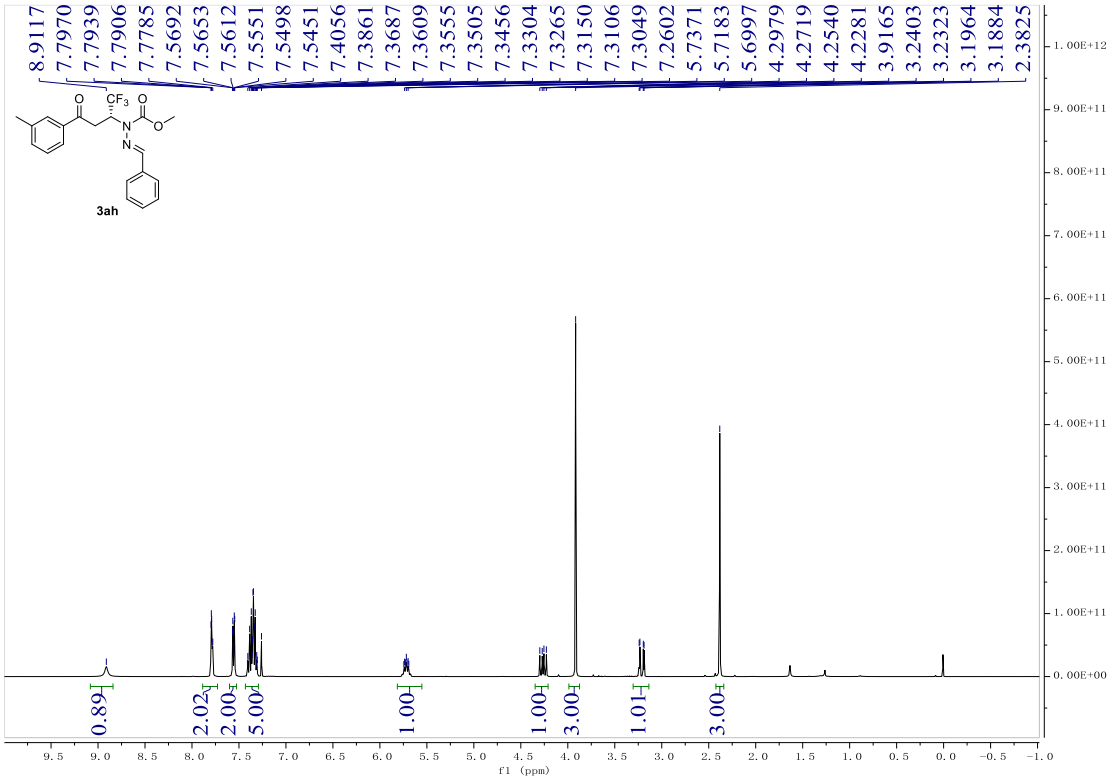
$^{13}C\{^{1}H\}$ NMR of 3ag (100 MHz, $CDCl_3$)



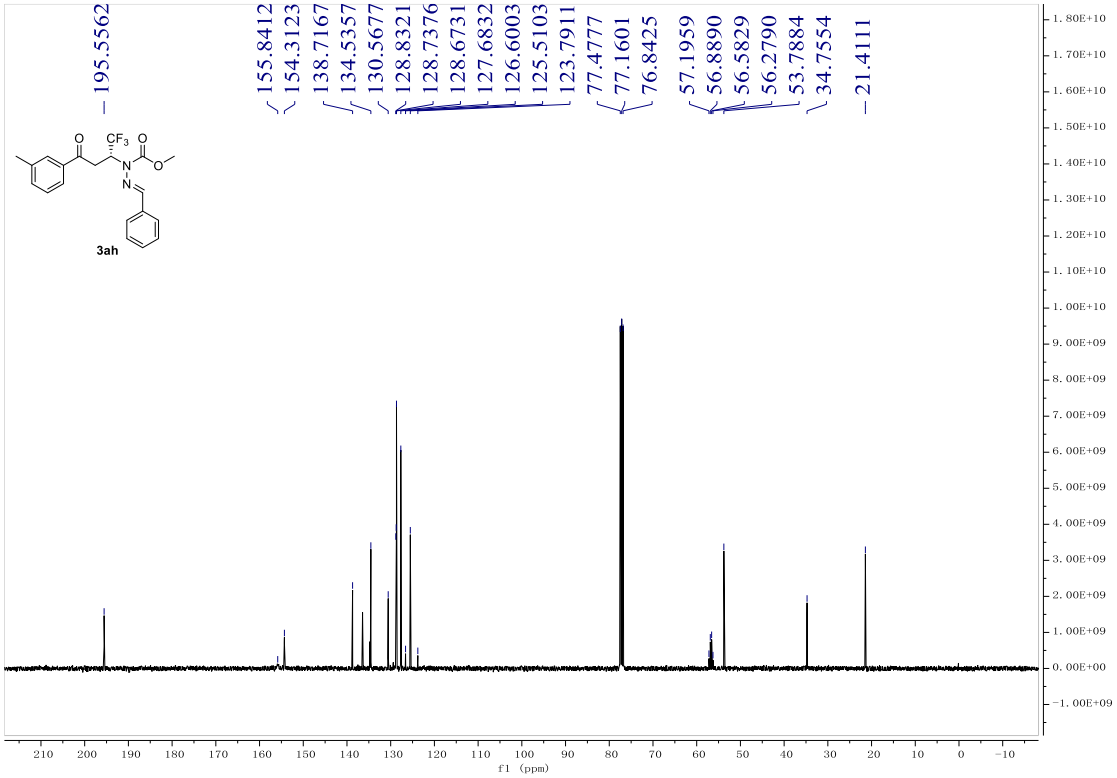
$^{19}F\{^{1}H\}$ NMR of 3ag (376 MHz, $CDCl_3$)



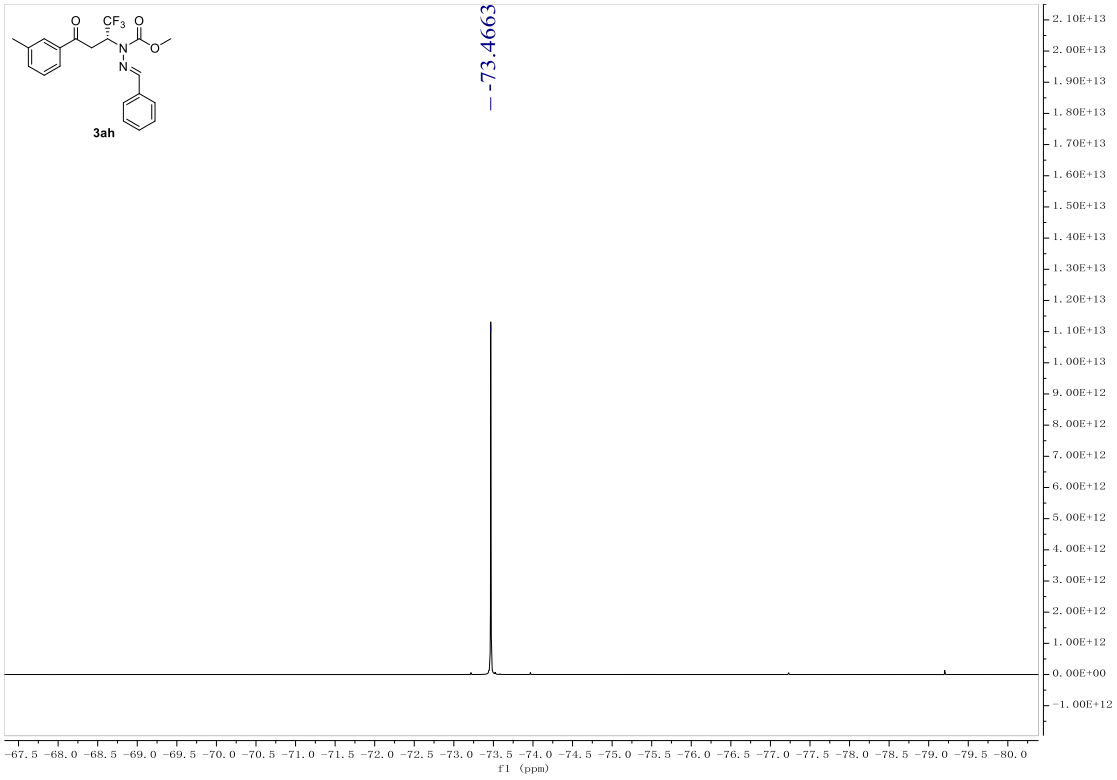
^{1}H NMR of 3ah (400 MHz, $CDCl_3$)



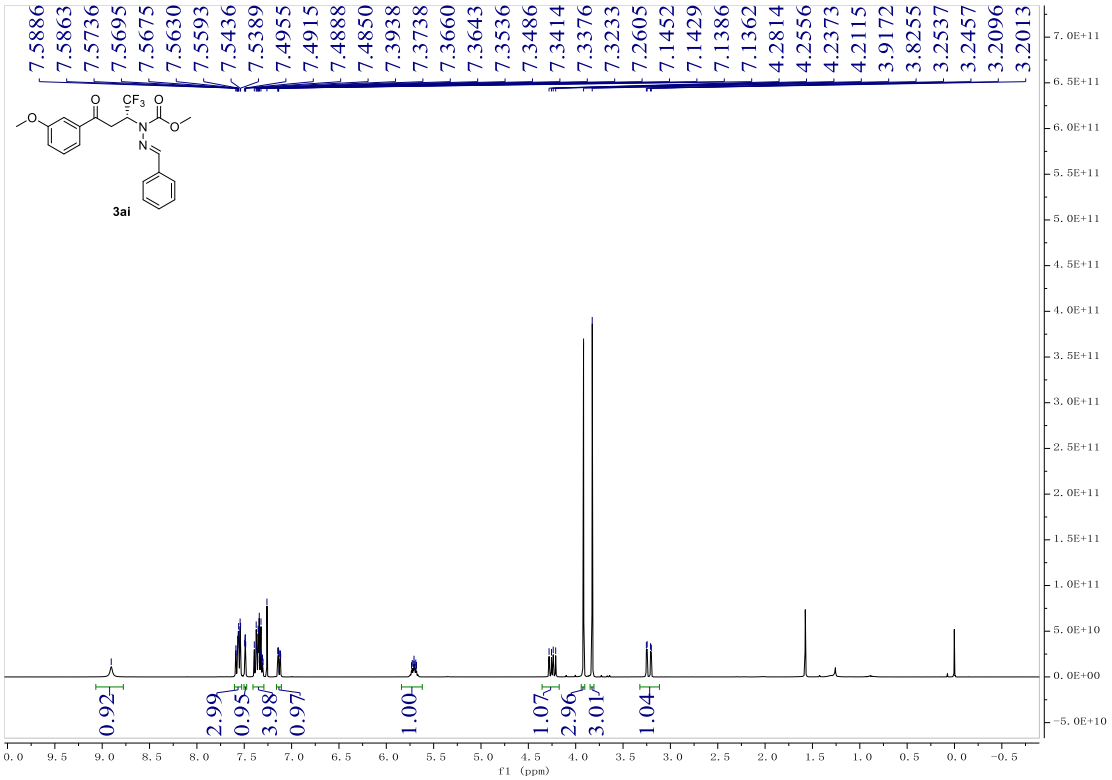
^{13}C{^{1}H} NMR of 3ah (100 MHz, $CDCl_3$)



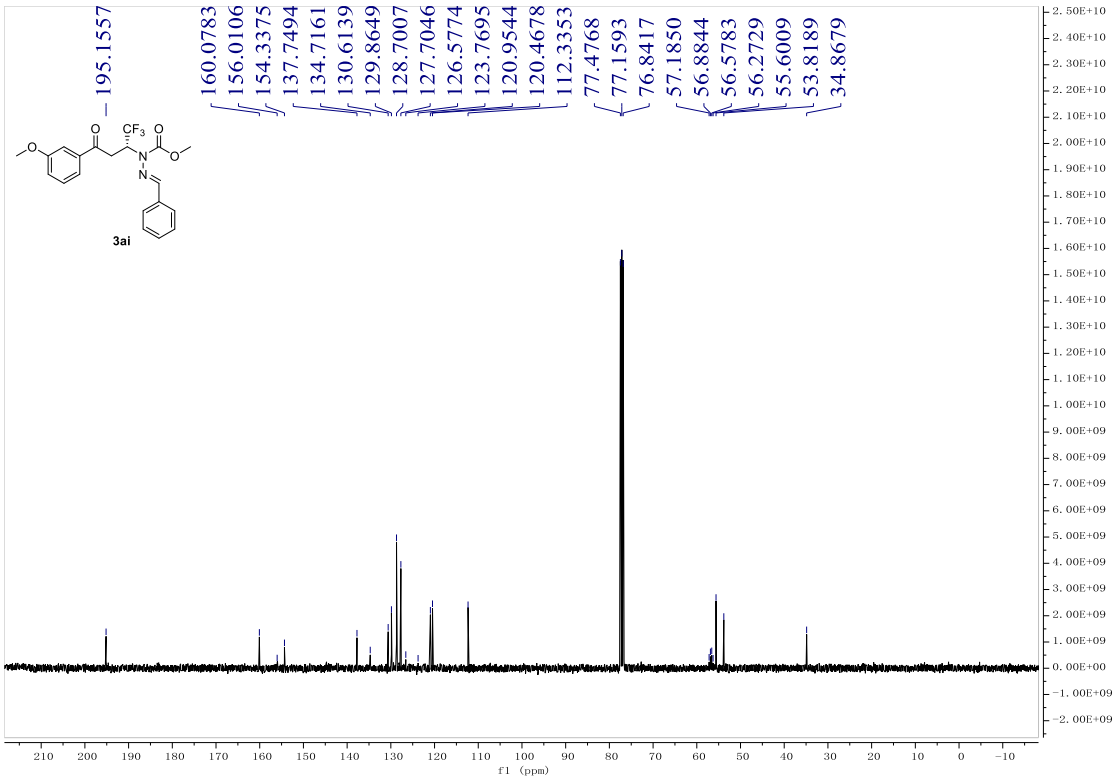
$^{19}F\{^{1}H\}$ NMR of 3ah (376 MHz, $CDCl_3$)



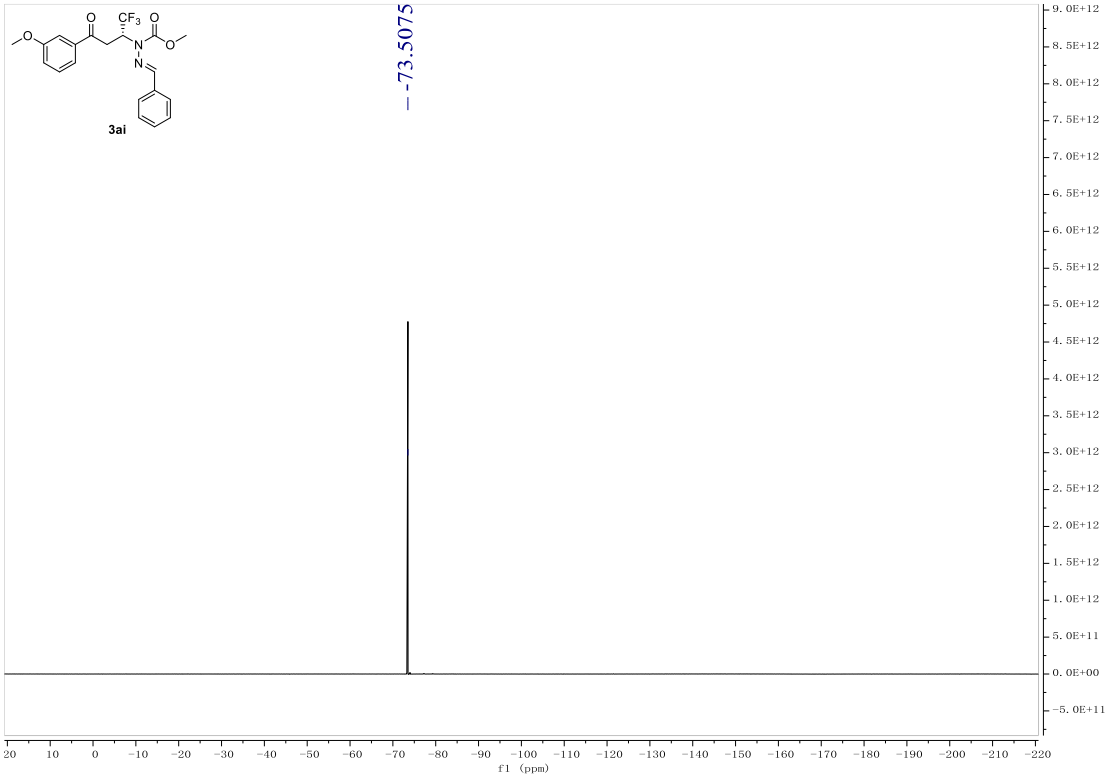
^{1}H NMR of 3ai (400 MHz, $CDCl_3$)



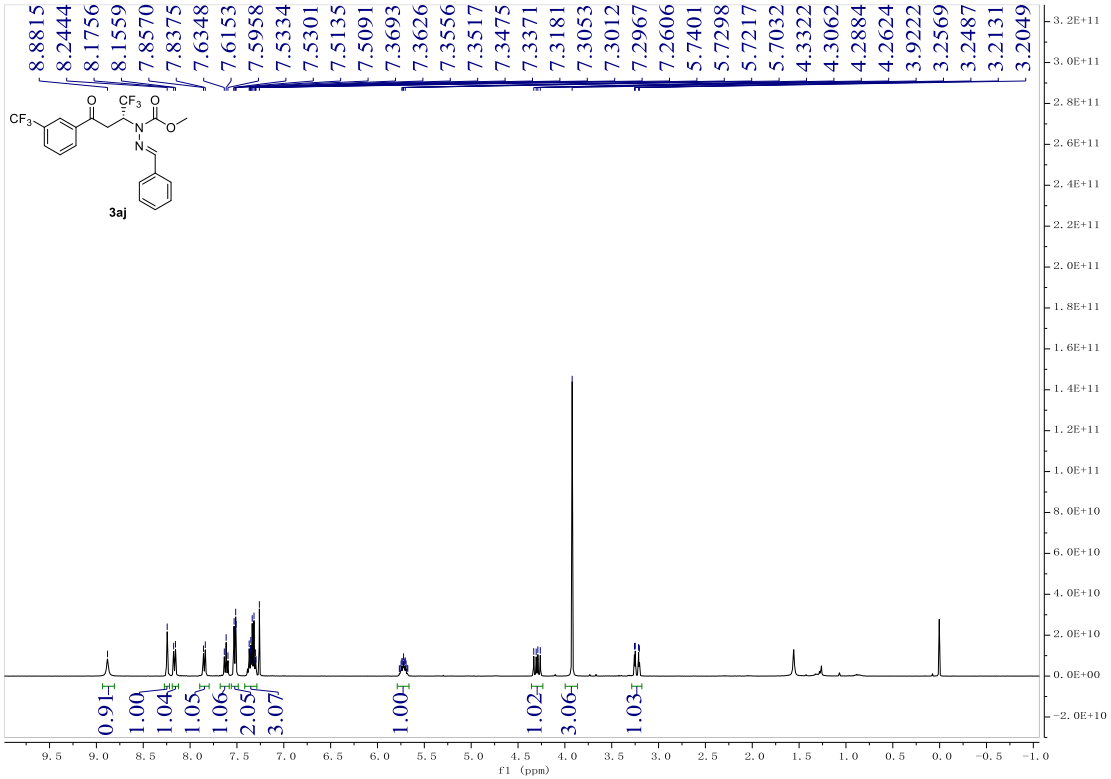
$^{13}C\{^{1}H\}$ NMR of 3ai (100 MHz, $CDCl_3$)



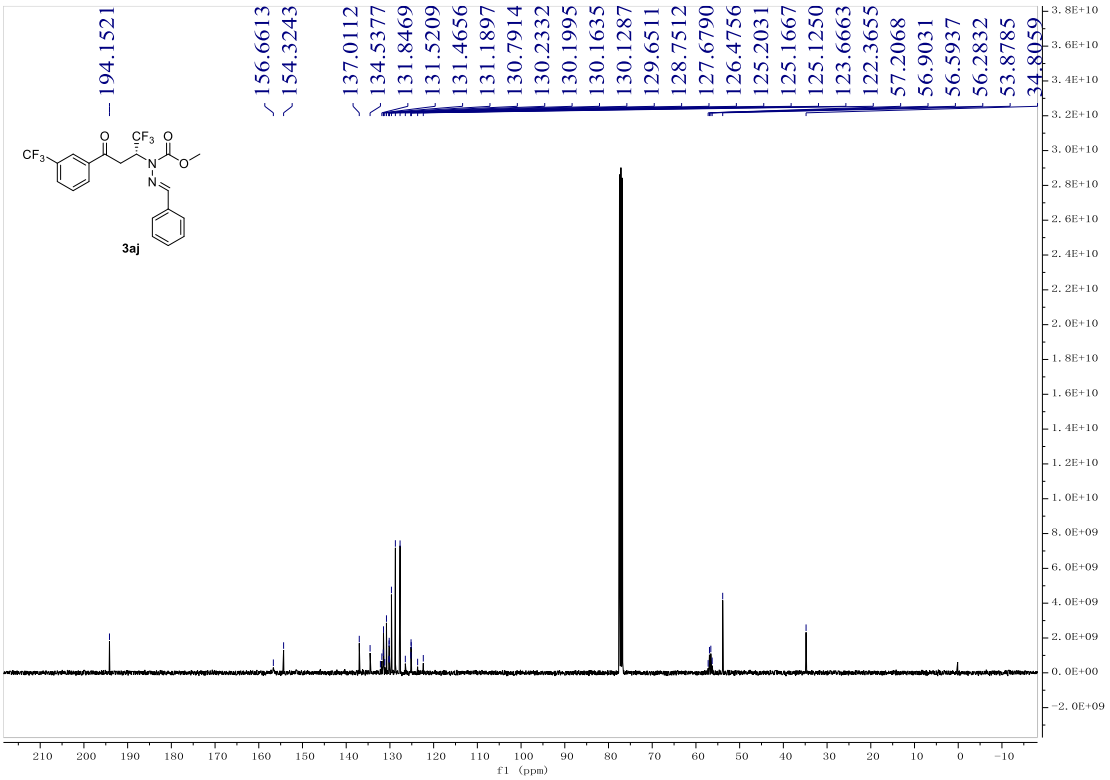
$^{19}F\{^{1}H\}$ NMR of 3ai (376 MHz, $CDCl_3$)



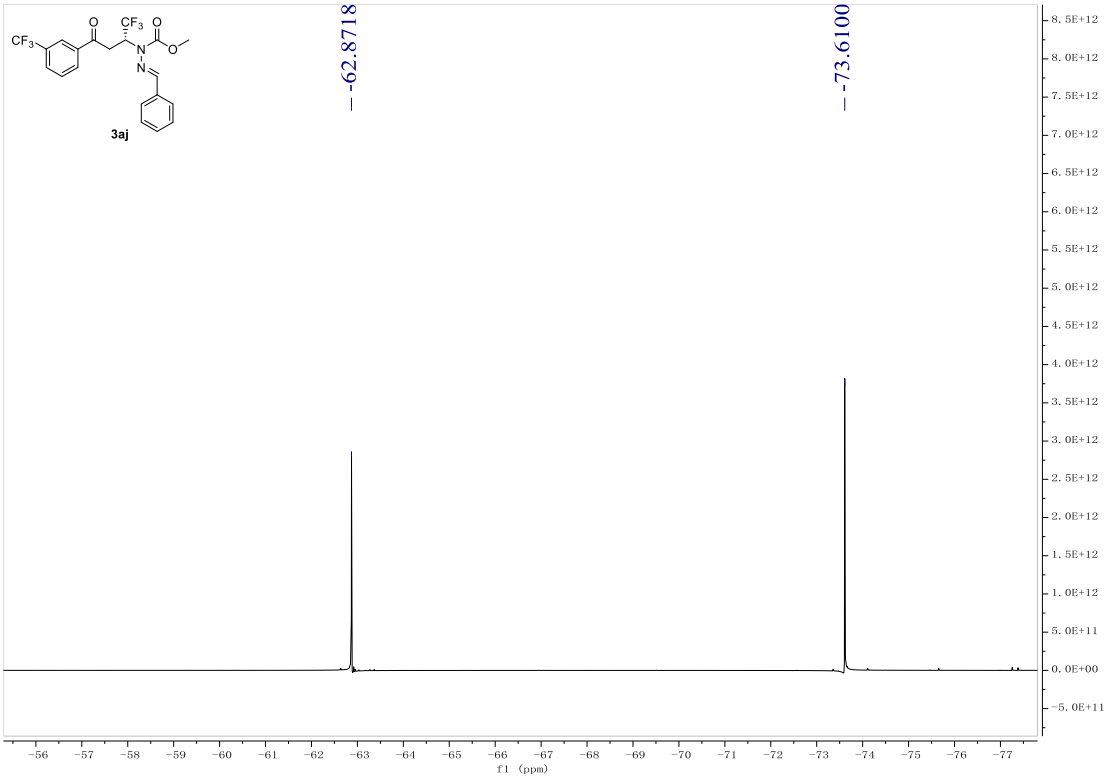
^{1}H NMR of 3aj (400 MHz, $CDCl_3$)



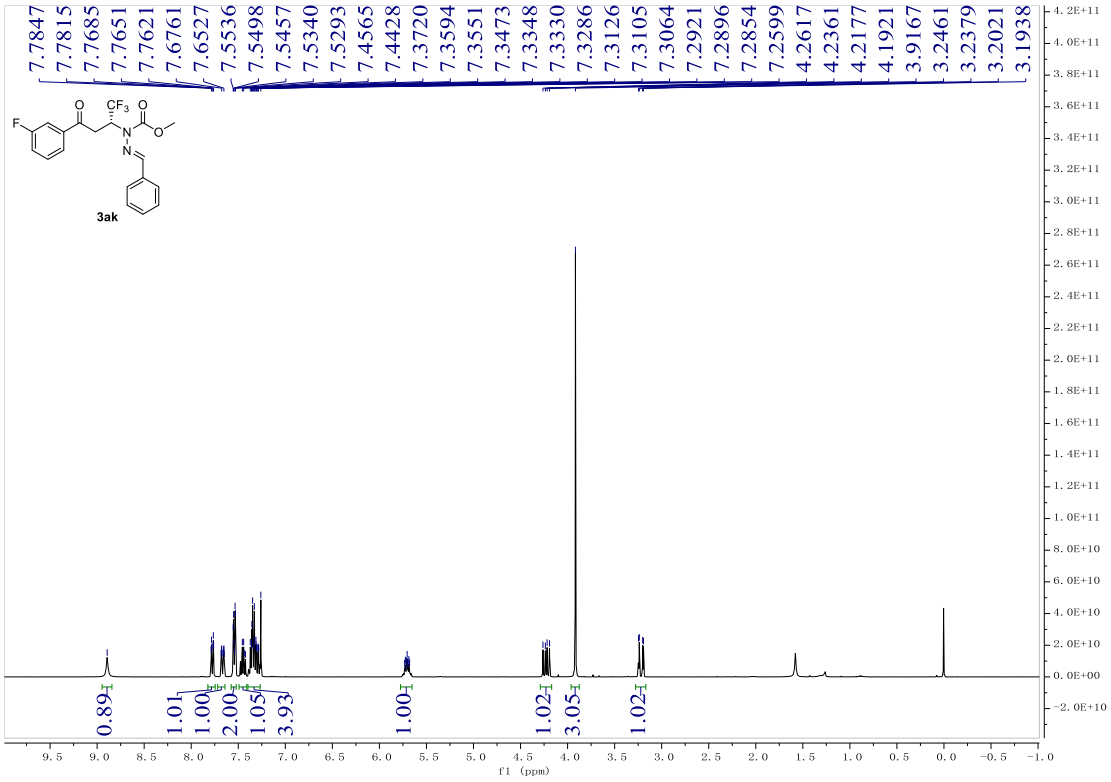
^{13}C{^{1}H} NMR of 3aj(100 MHz, $CDCl_3$)



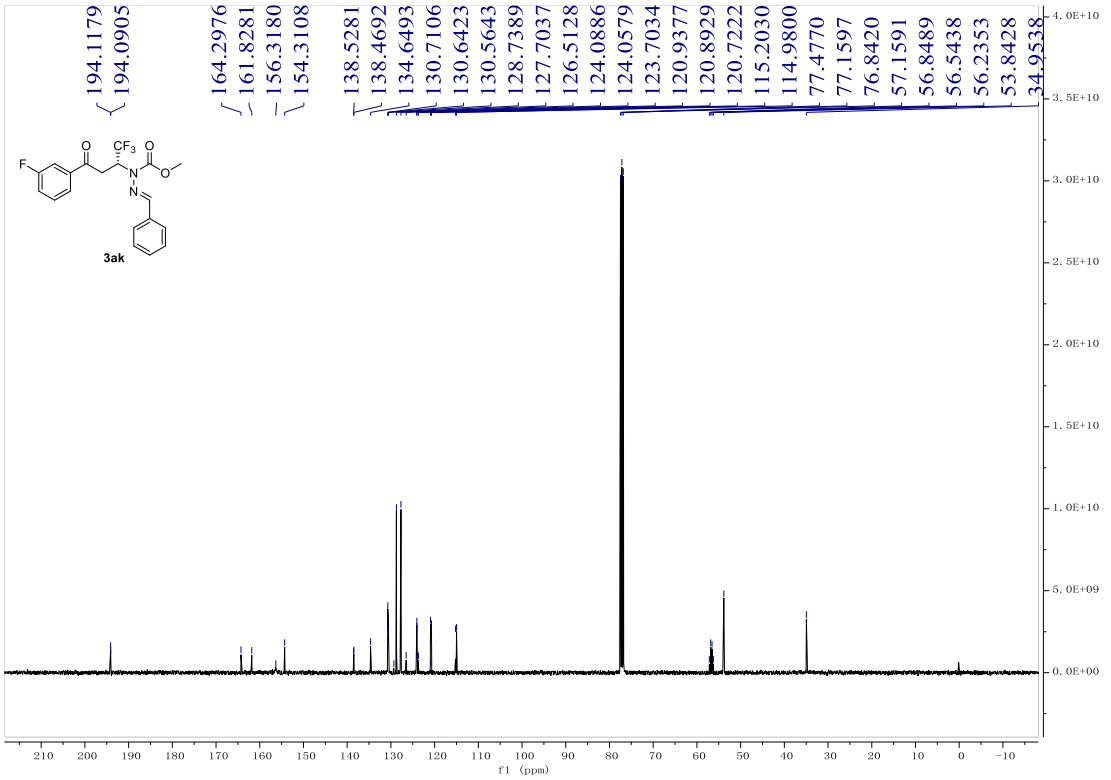
$^{19}F\{^{1}H\}$ NMR of 3aj(376 MHz, $CDCl_3$)



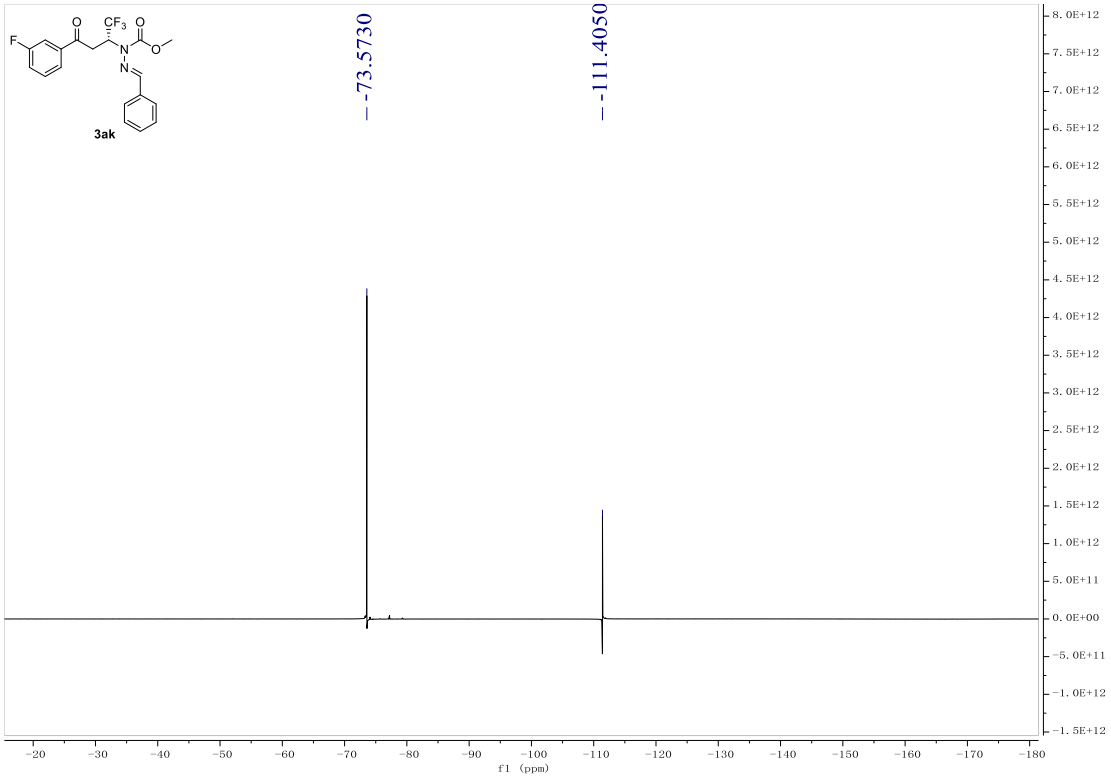
^{1}H NMR of 3ak (400 MHz, $CDCl_3$)



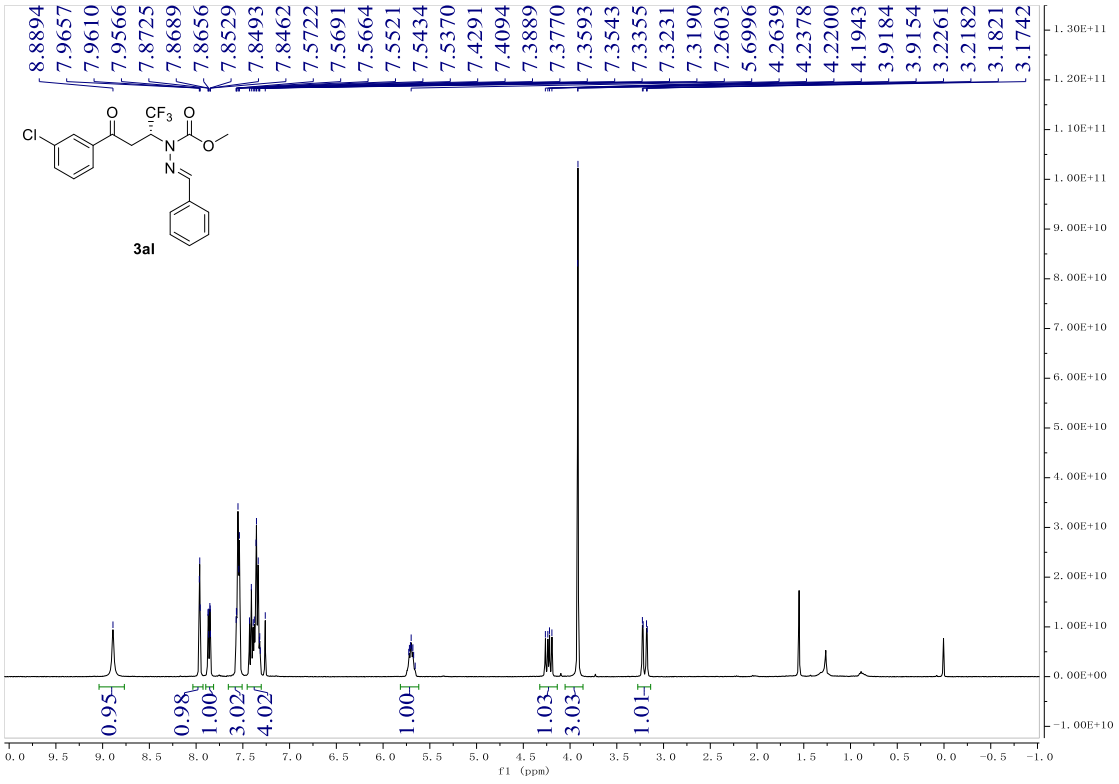
$^{13}C\{^{1}H\}$ NMR of 3ak (100 MHz, $CDCl_3$)



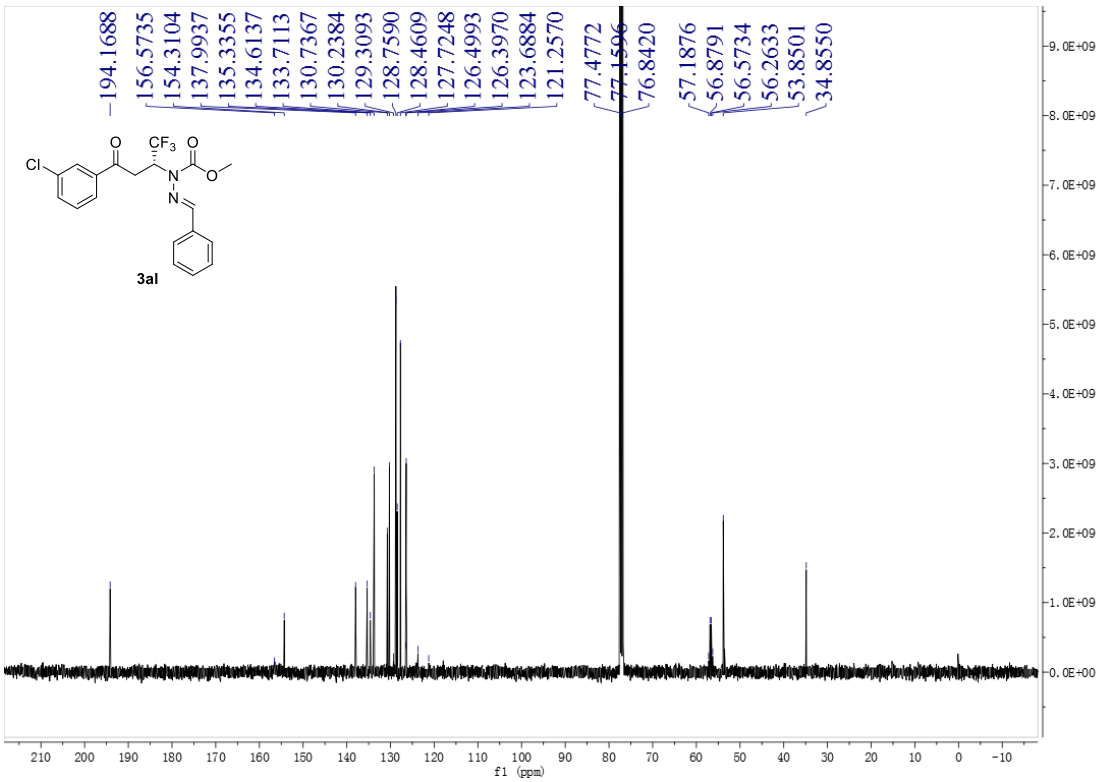
$^{19}F\{^{1}H\}$ NMR of 3ak (376 MHz, $CDCl_3$)



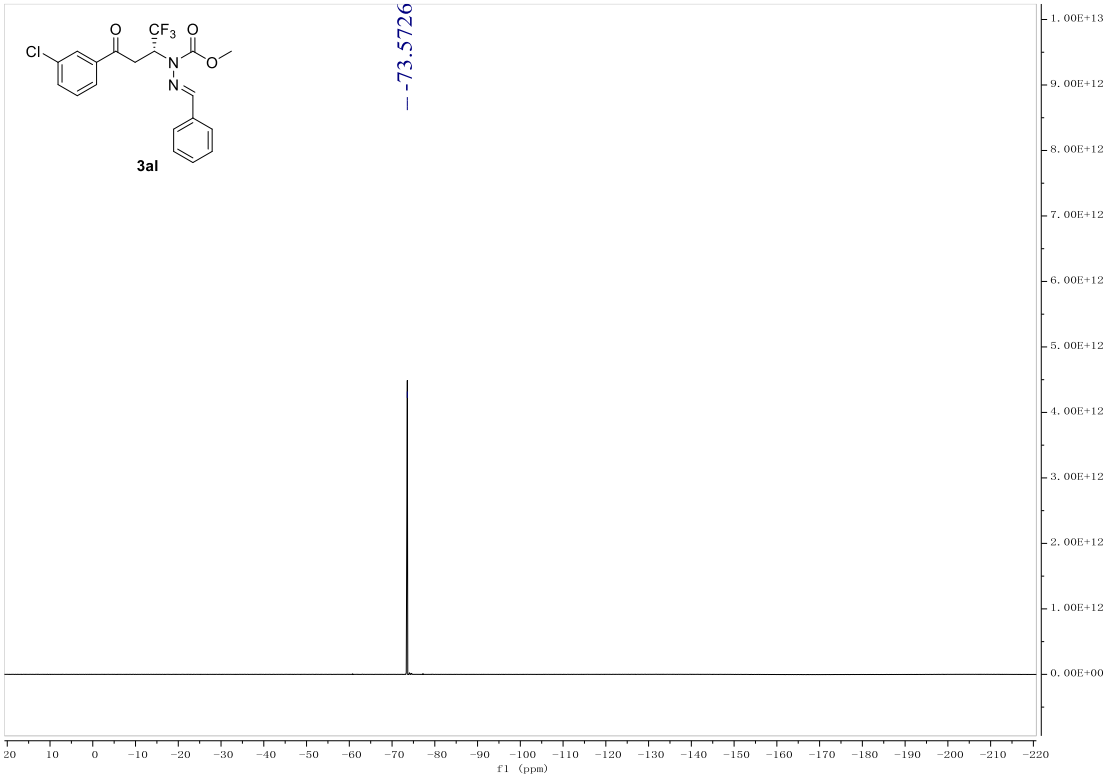
^{1}H NMR of 3al (400 MHz, $CDCl_3$)



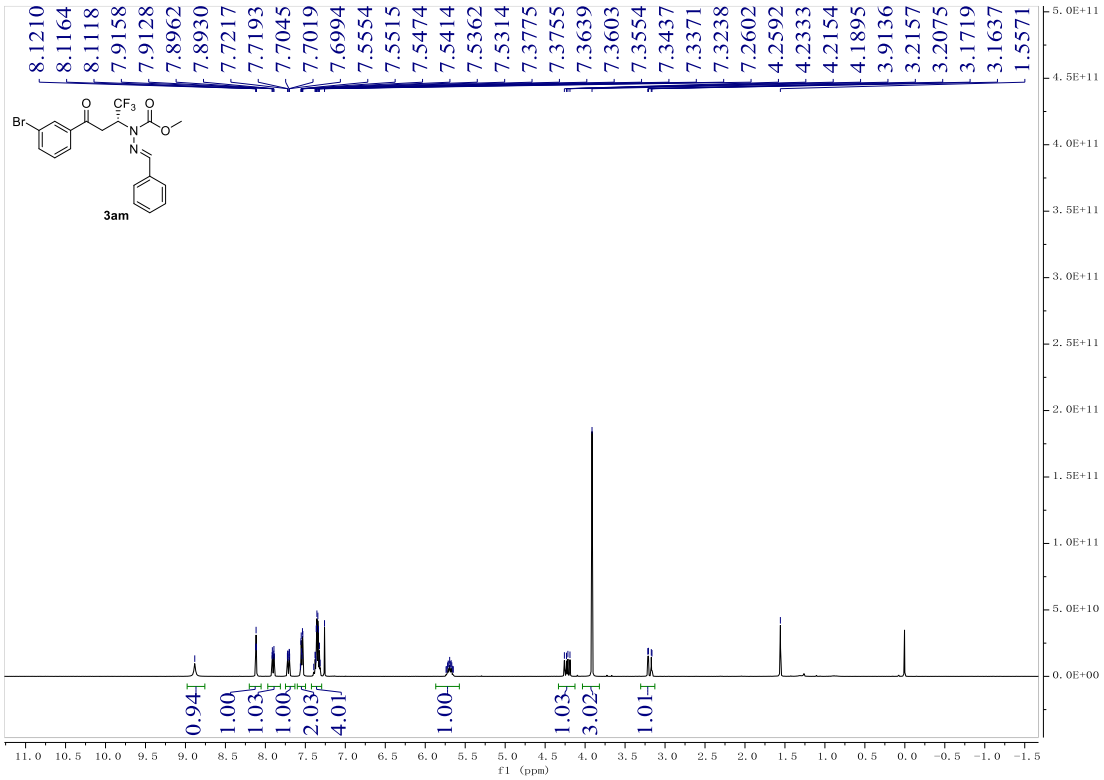
^{13}C{^{1}H} NMR of 3al (100 MHz, $CDCl_3$)



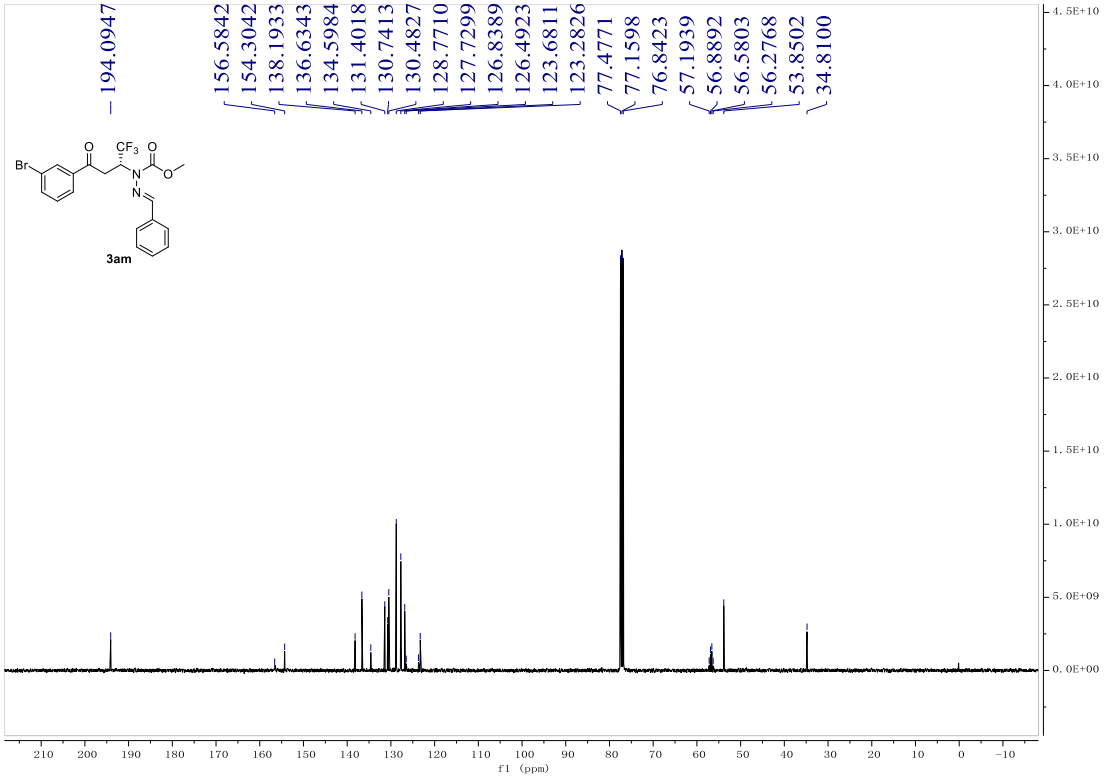
$^{19}F\{^{1}H\}$ NMR of 3al(376 MHz, $CDCl_3$)



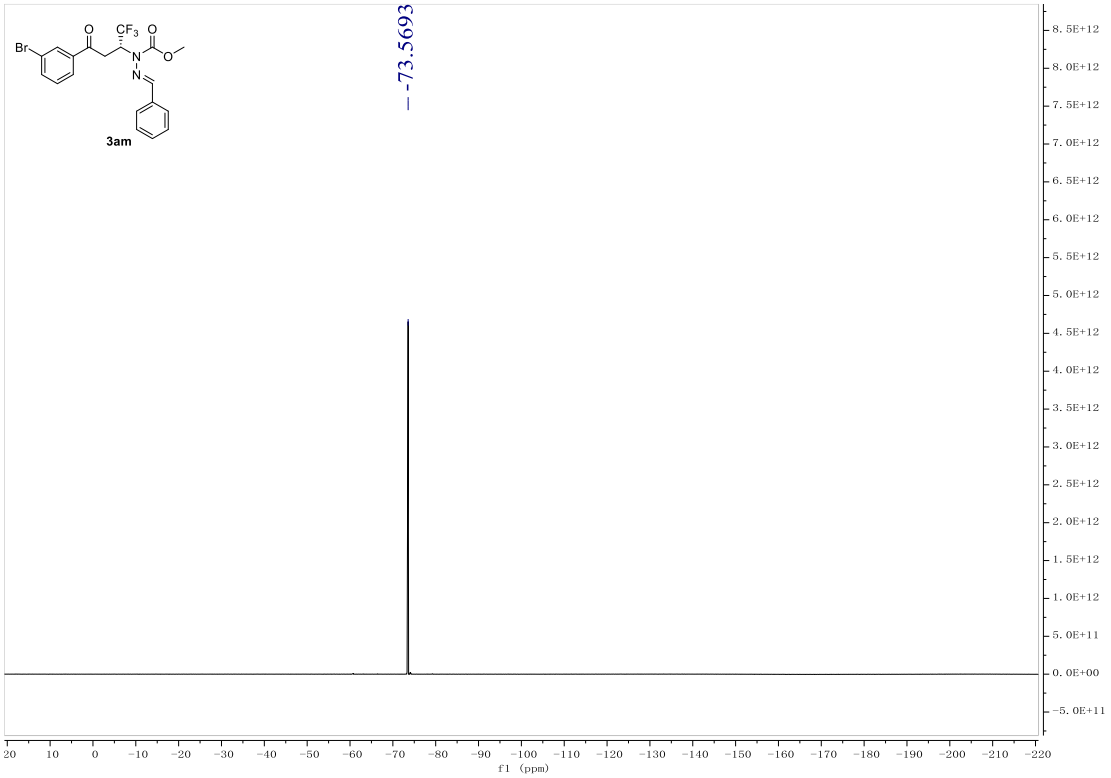
^{1}H NMR of 3am (400 MHz, $CDCl_3$)



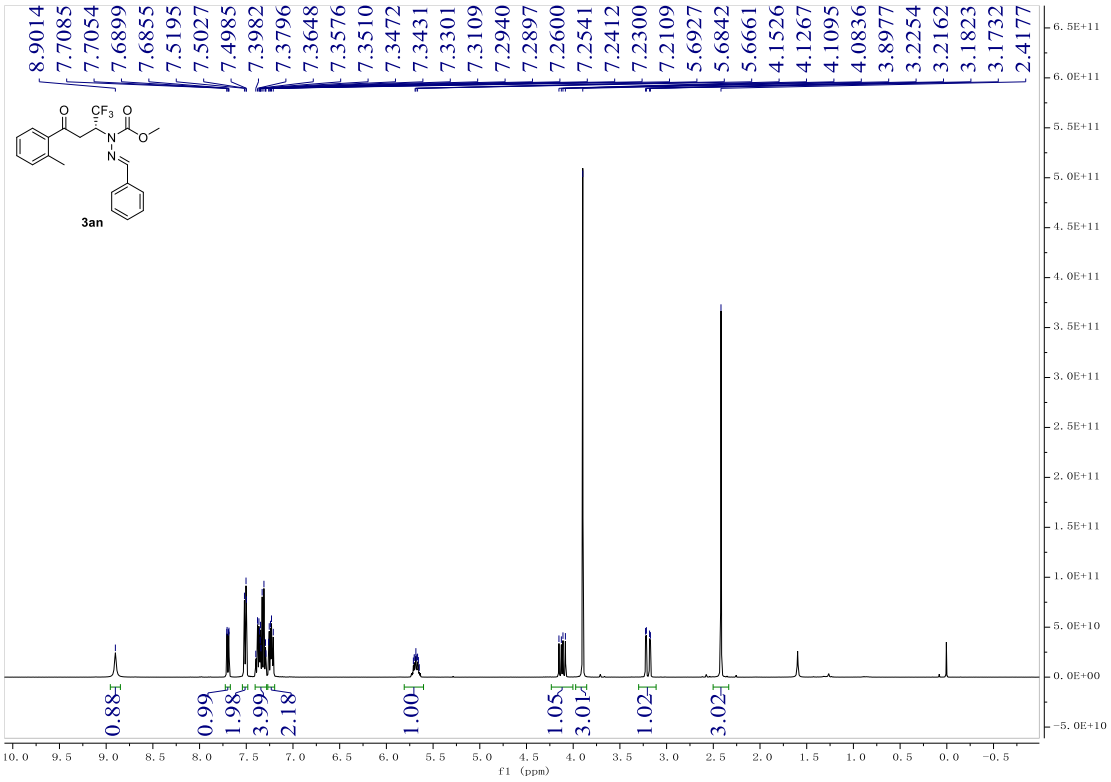
$^{13}C\{^{1}H\}$ NMR of 3am (100 MHz, $CDCl_3$)



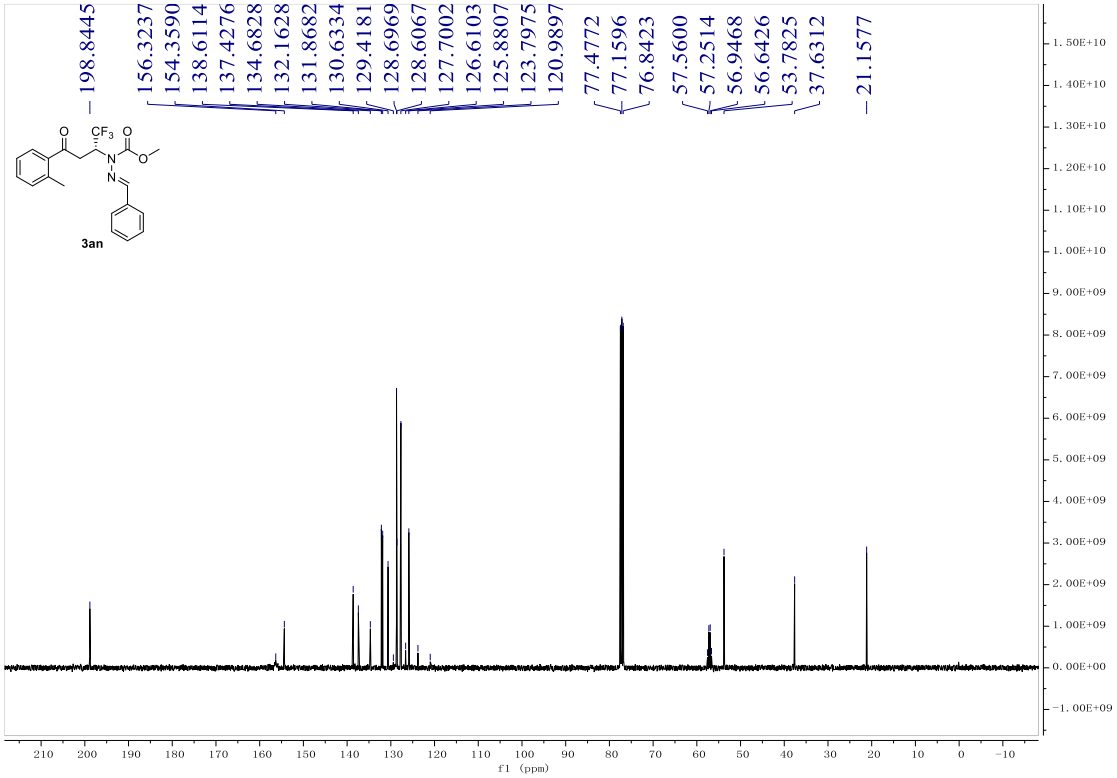
$^{19}F\{^{1}H\}$ NMR of 3am (376 MHz, $CDCl_3$)



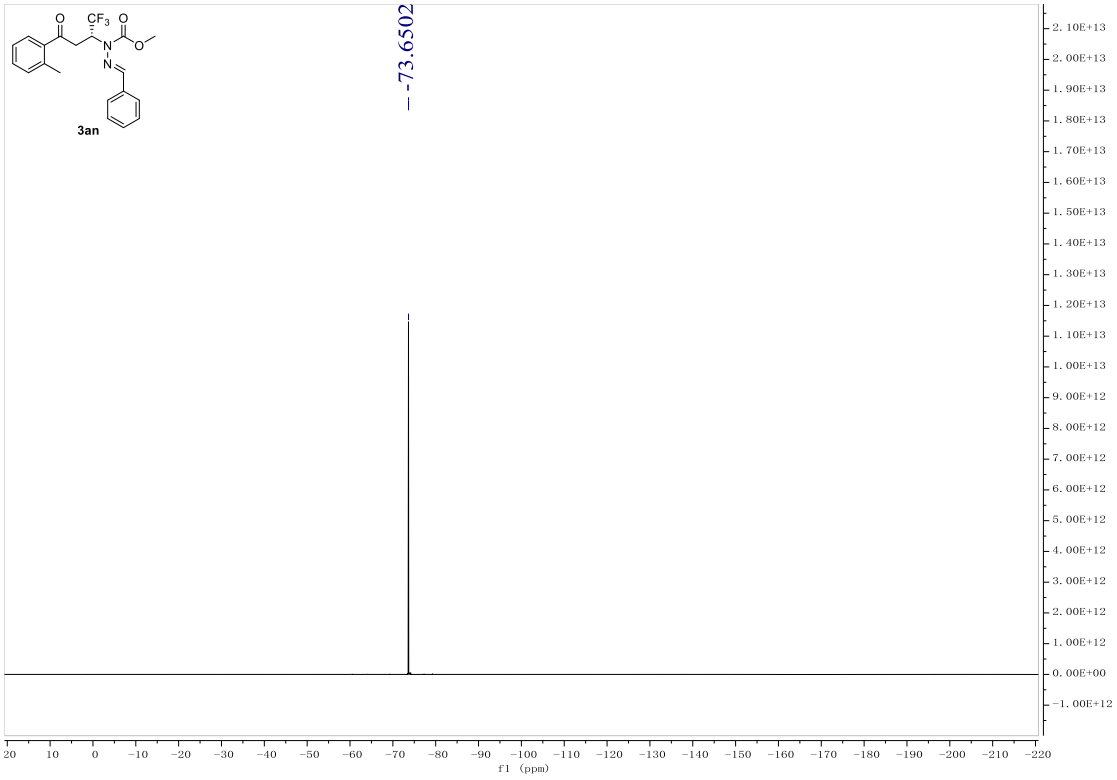
^{1}H NMR of 3an (400 MHz, $CDCl_3$)



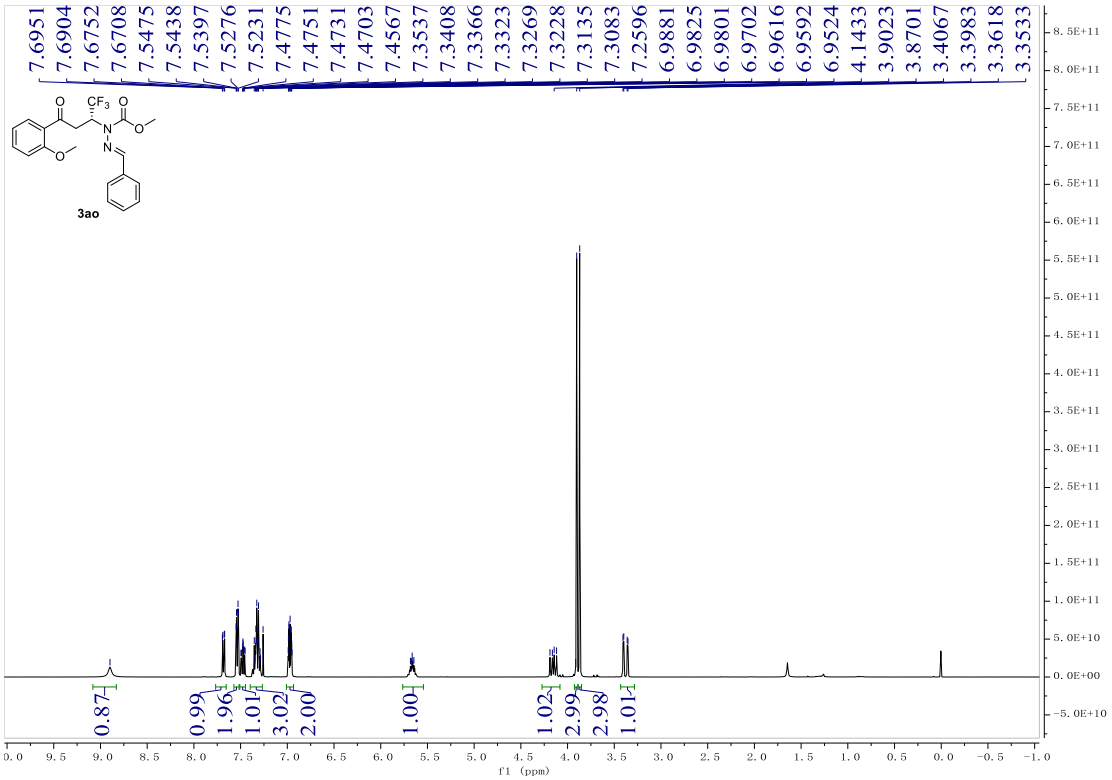
^{13}C{^{1}H} NMR of 3an (100 MHz, $CDCl_3$)



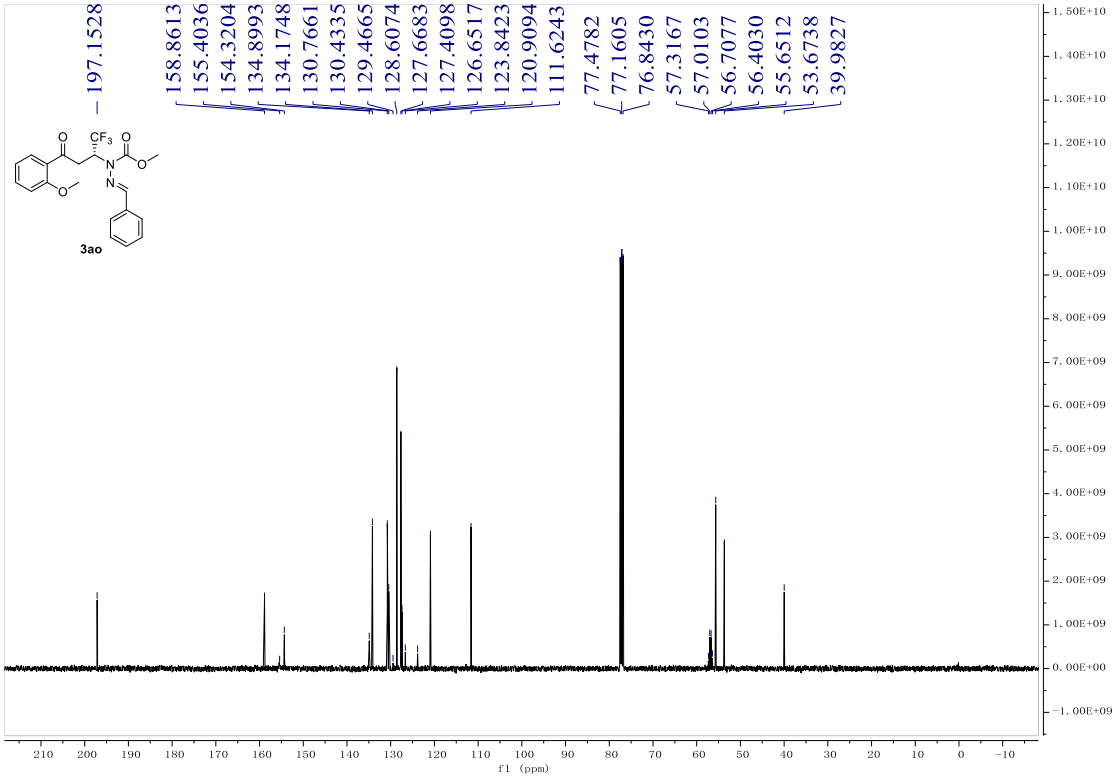
$^{19}F\{^{1}H\}$ NMR of 3an (376 MHz, $CDCl_3$)



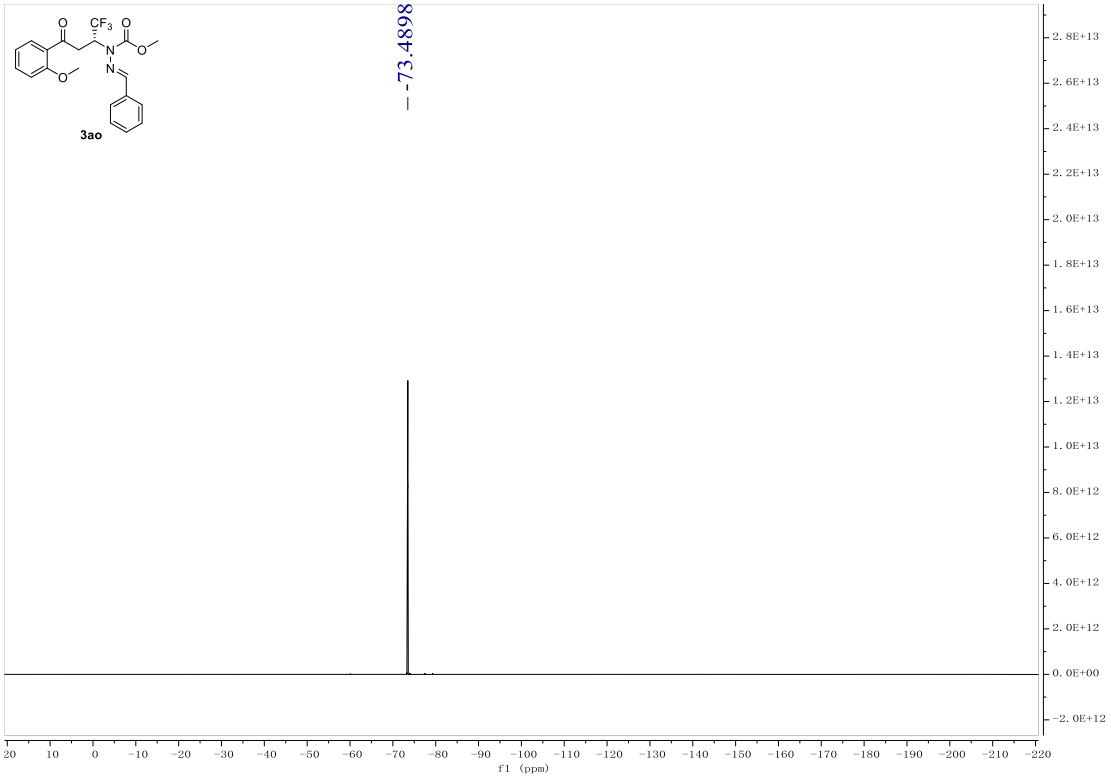
^{1}H NMR of 3ao (400 MHz, $CDCl_3$)



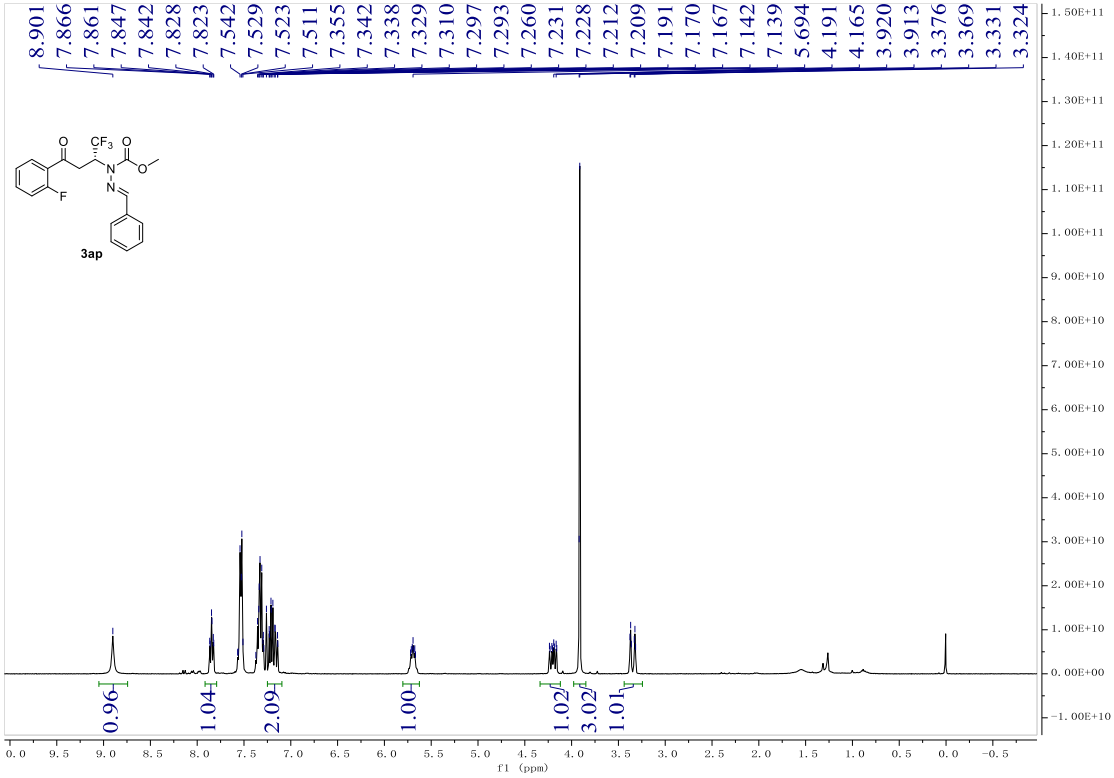
$^{13}C\{^{1}H\}$ NMR of 3ao (100 MHz, $CDCl_3$)



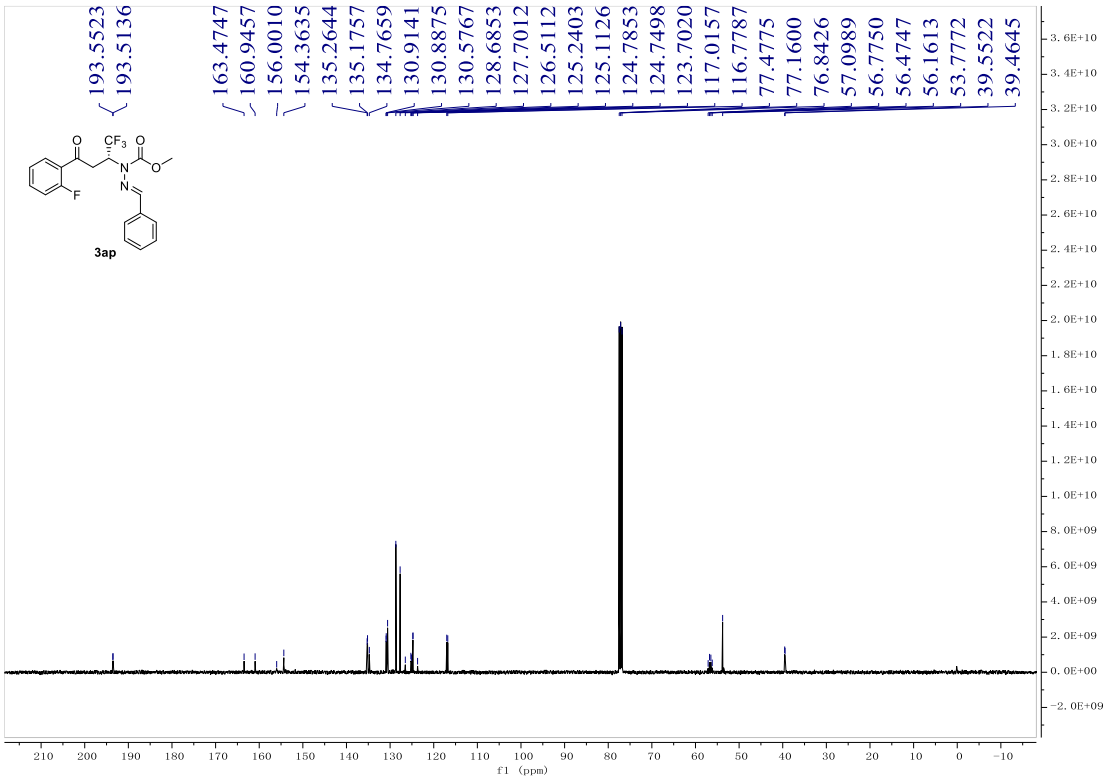
$^{19}F\{^{1}H\}$ NMR of 3ao (376 MHz, $CDCl_3$)



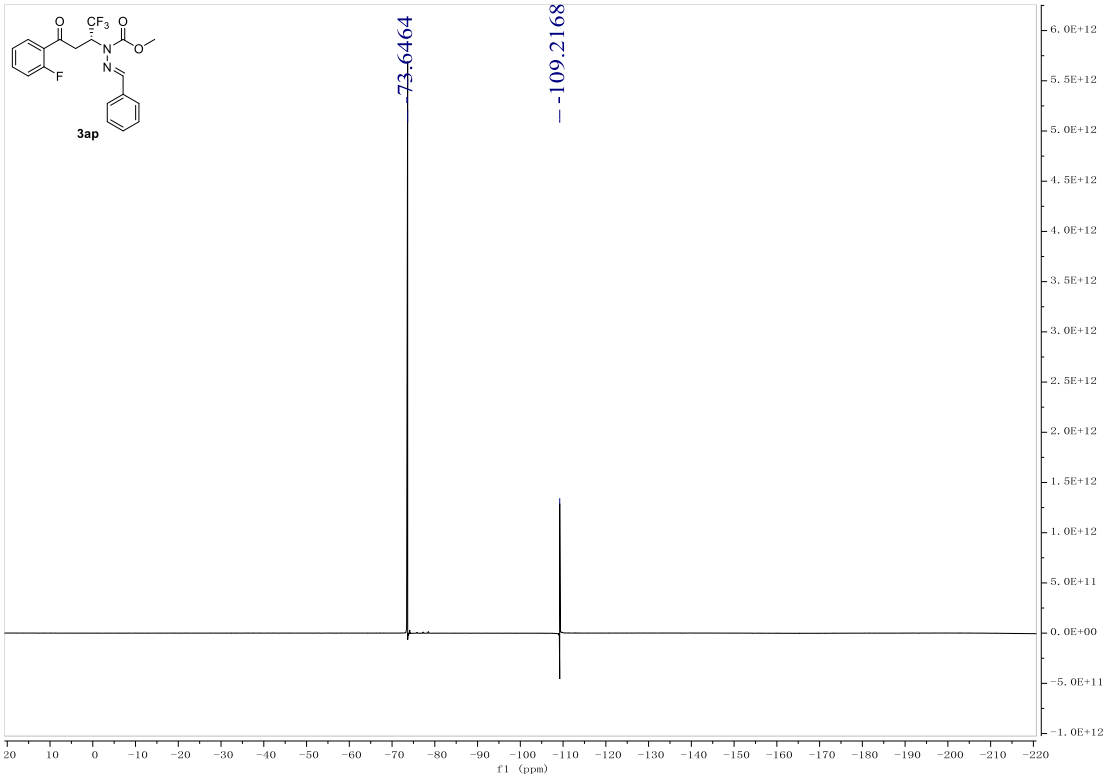
^{1}H NMR of 3ap (400 MHz, $CDCl_3$)



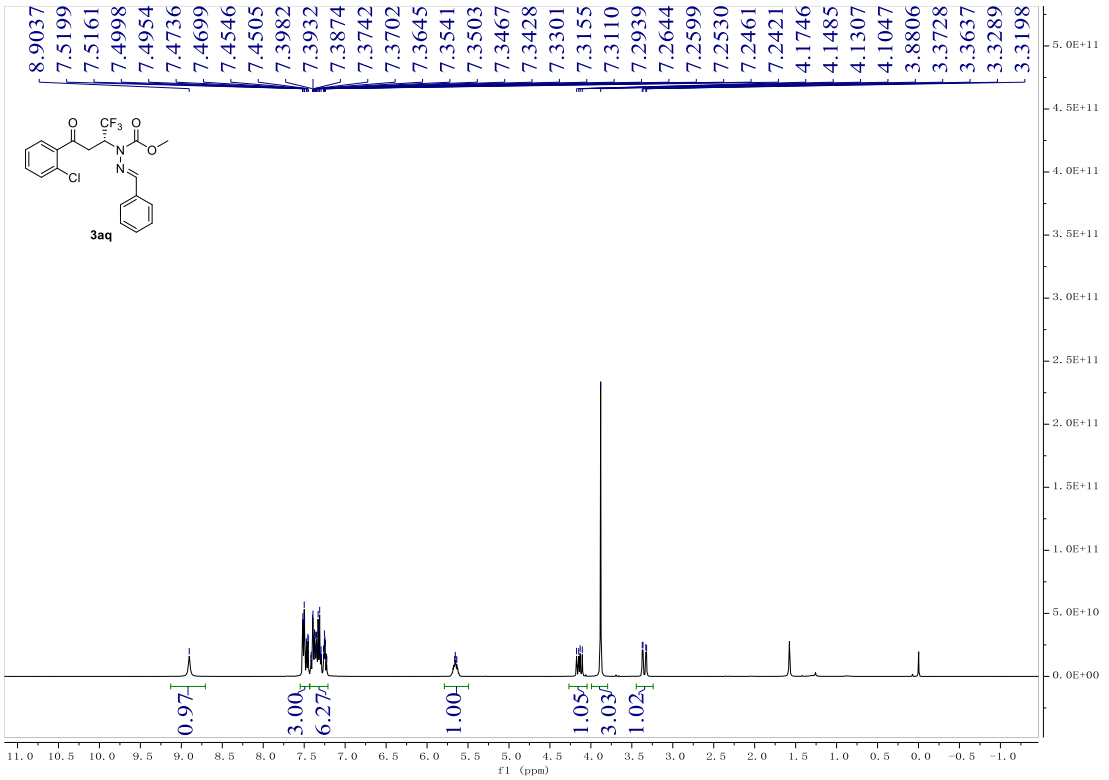
^{13}C{^{1}H} NMR of 3ap (100 MHz, $CDCl_3$)



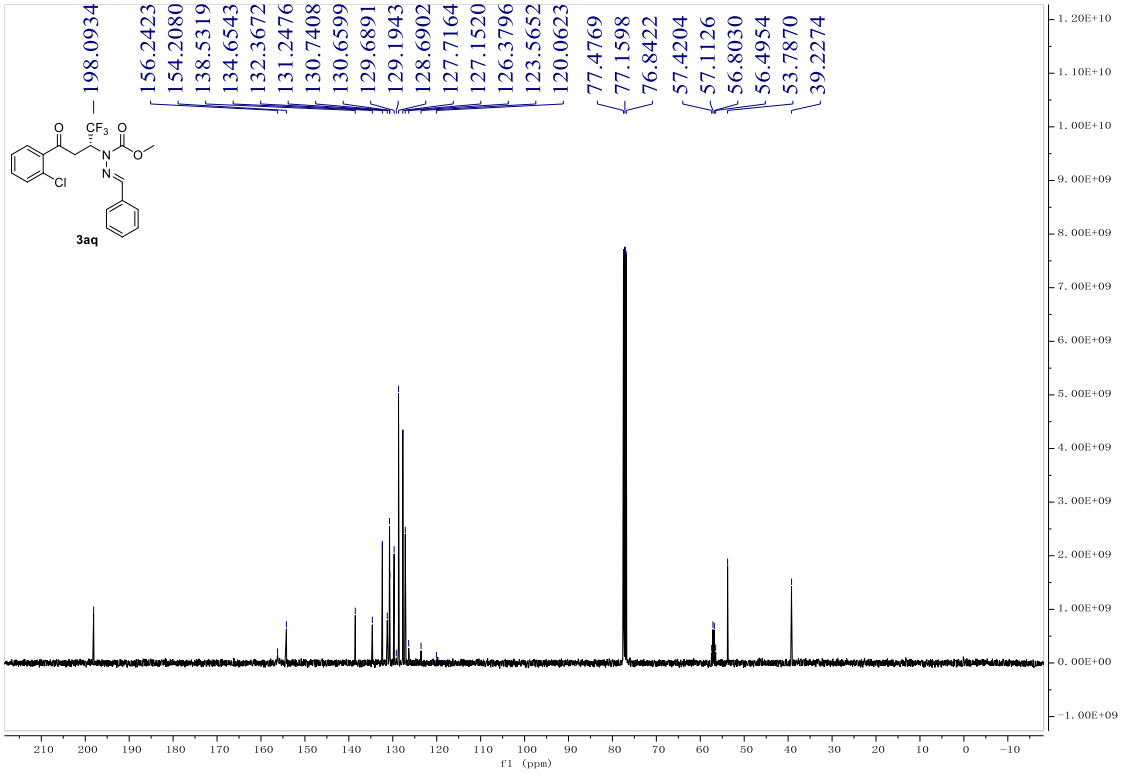
$^{19}F\{^{1}H\}$ NMR of 3ap (376 MHz, $CDCl_3$)



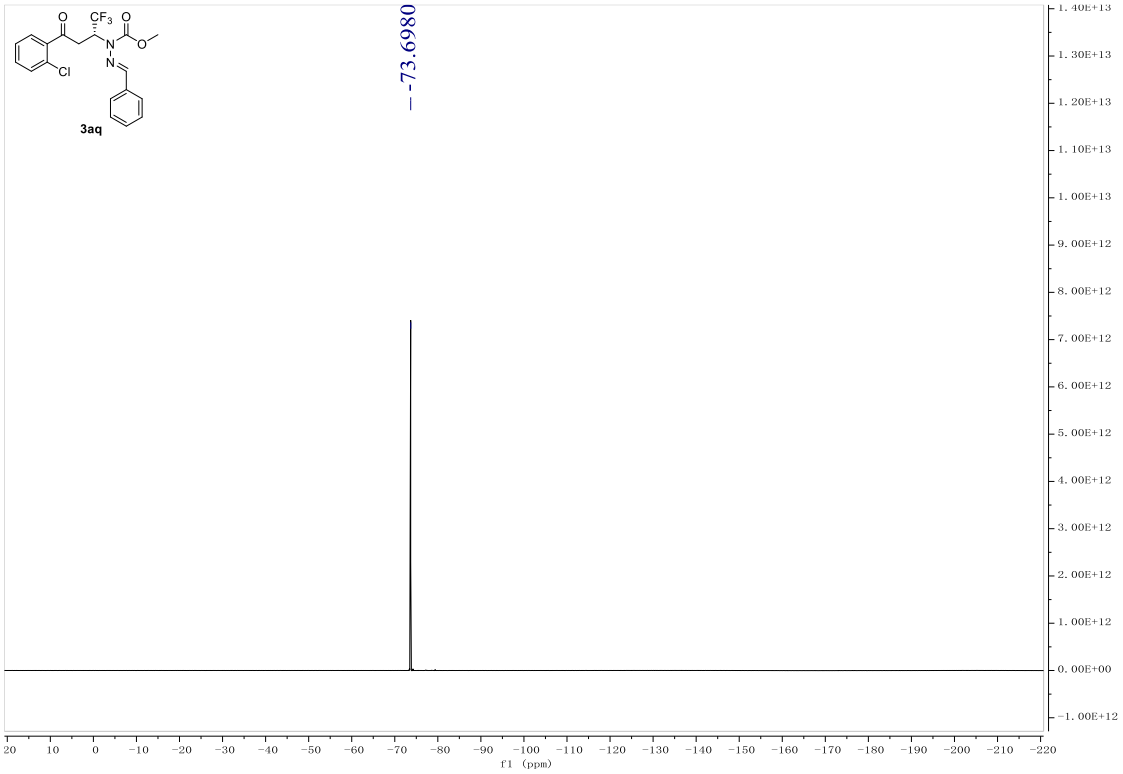
^{1}H NMR of 3aq (400 MHz, $CDCl_3$)



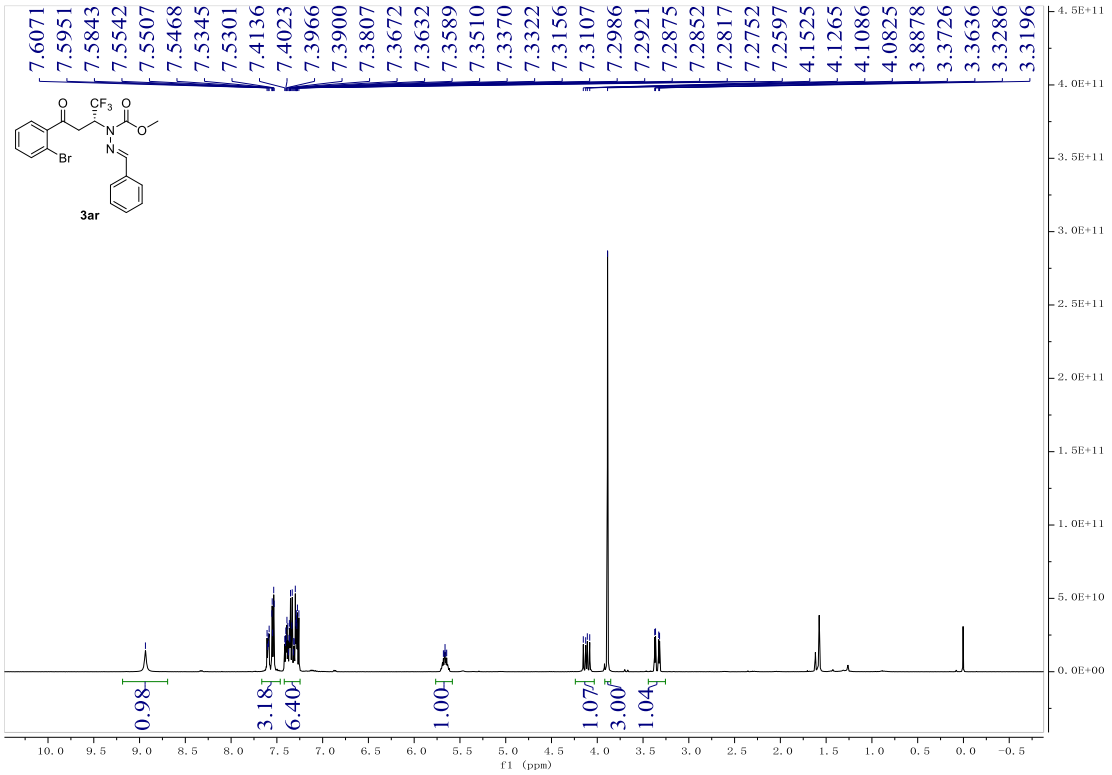
$^{13}C\{^{1}H\}$ NMR of 3aq (100 MHz, $CDCl_3$)



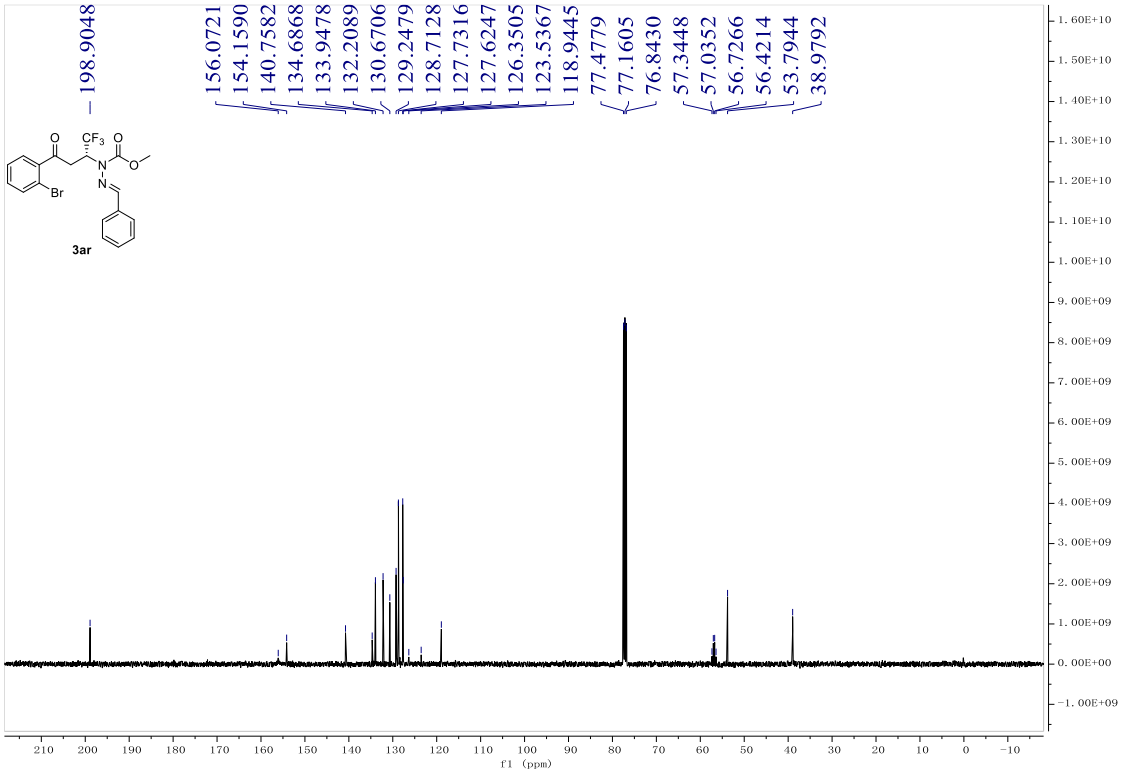
$^{19}F\{^{1}H\}$ NMR of 3aq (376 MHz, $CDCl_3$)



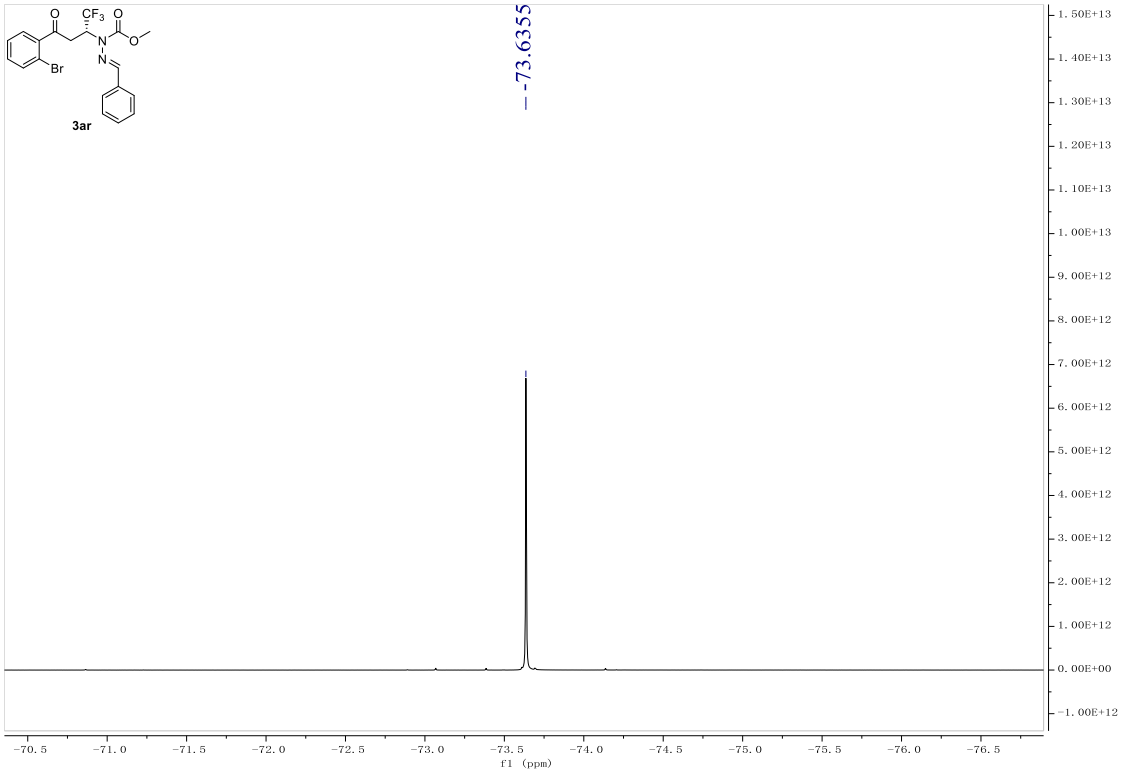
^{1}H NMR of 3ar (400 MHz, $CDCl_3$)



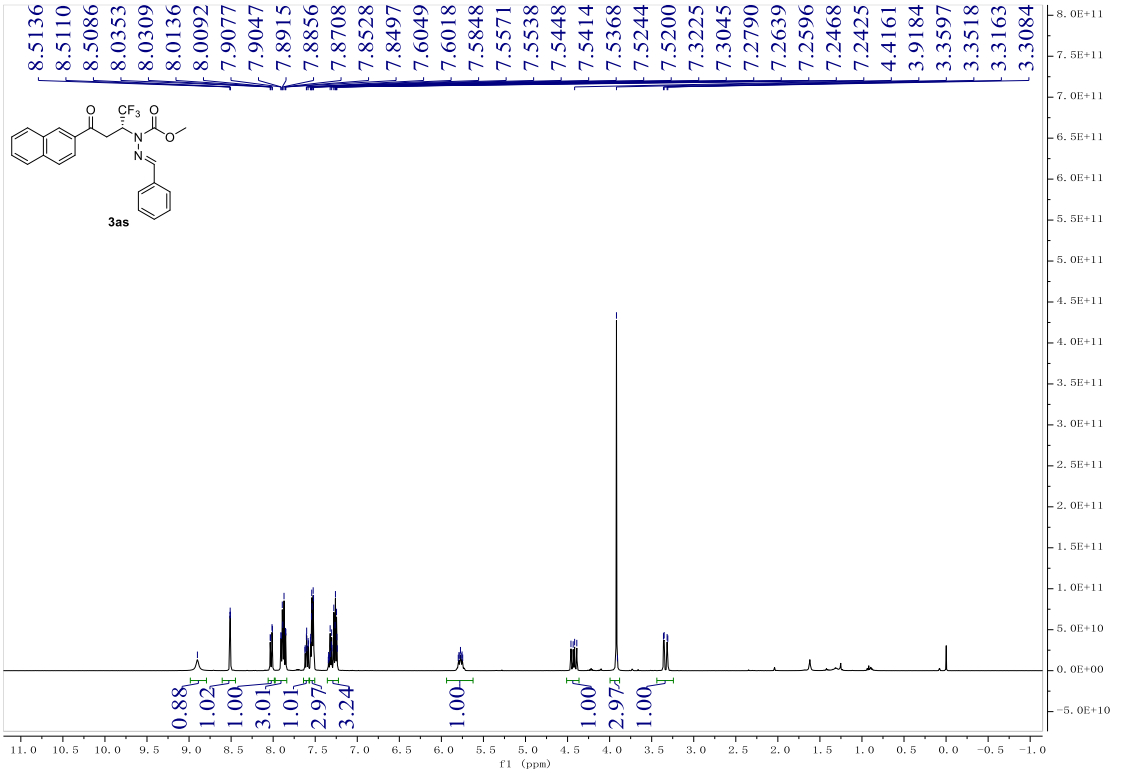
^{13}C{^{1}H} NMR of 3ar (100 MHz, $CDCl_3$)



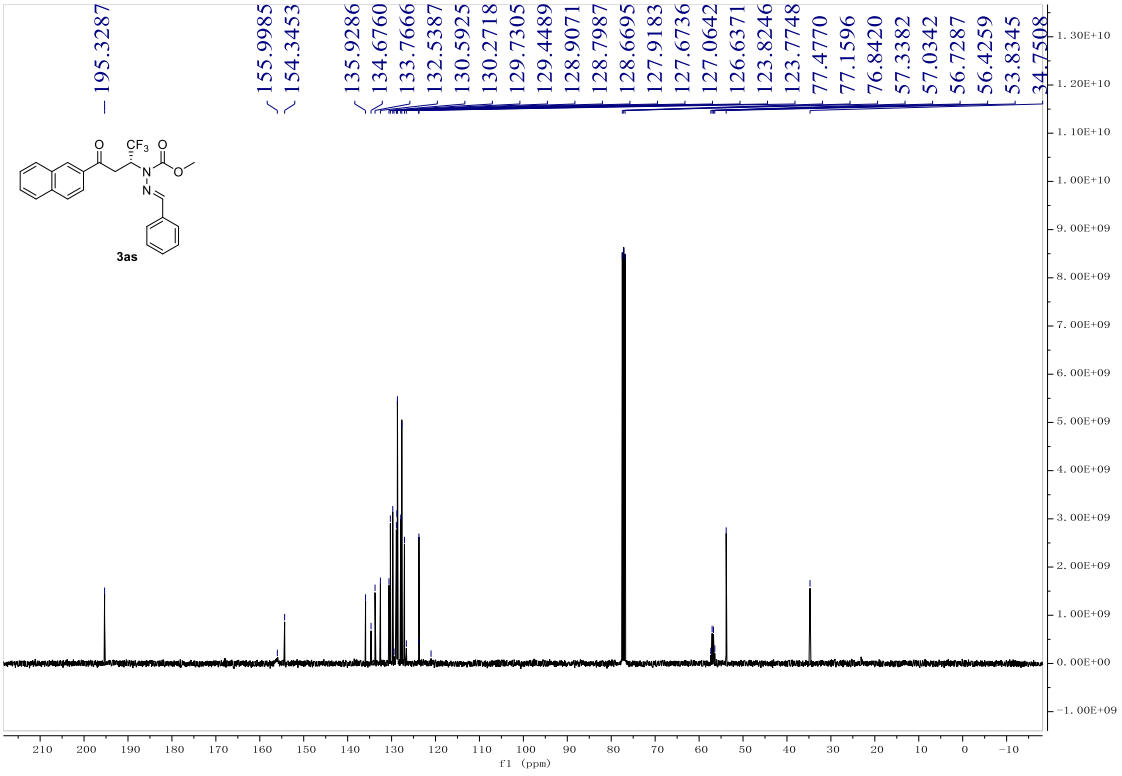
$^{19}F\{^{1}H\}$ NMR of 3ar (376 MHz, $CDCl_3$)



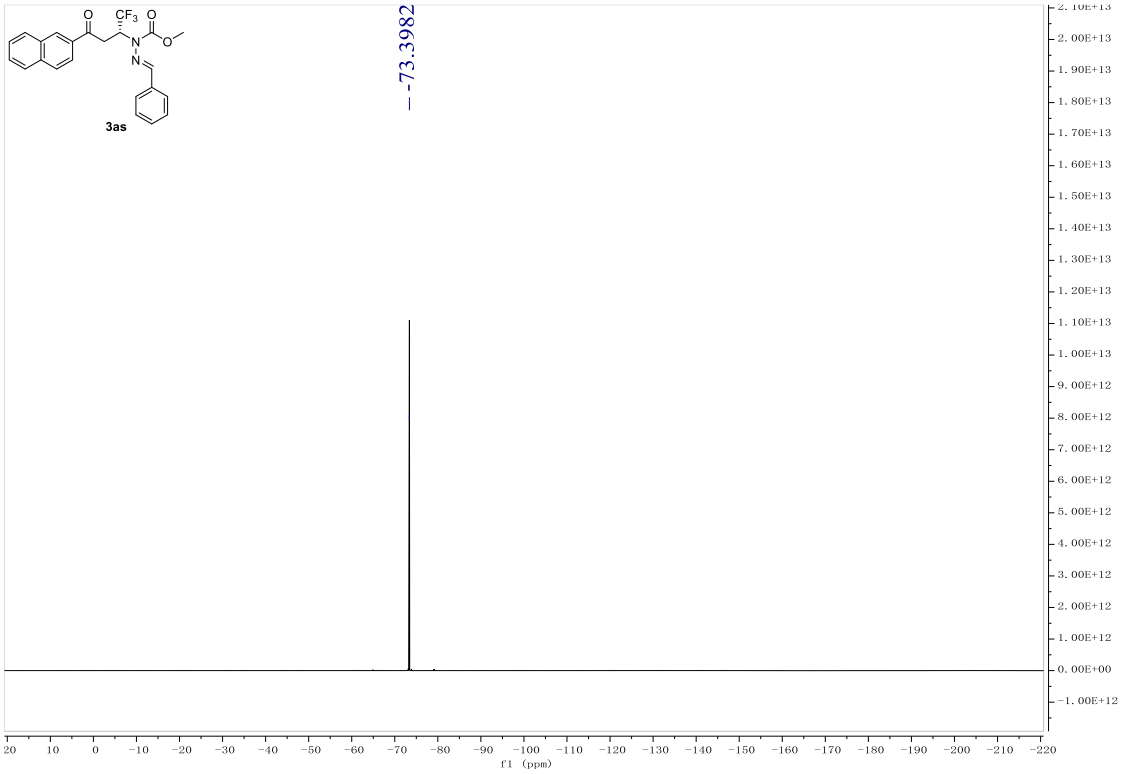
^{1}H NMR of 3as (400 MHz, $CDCl_3$)



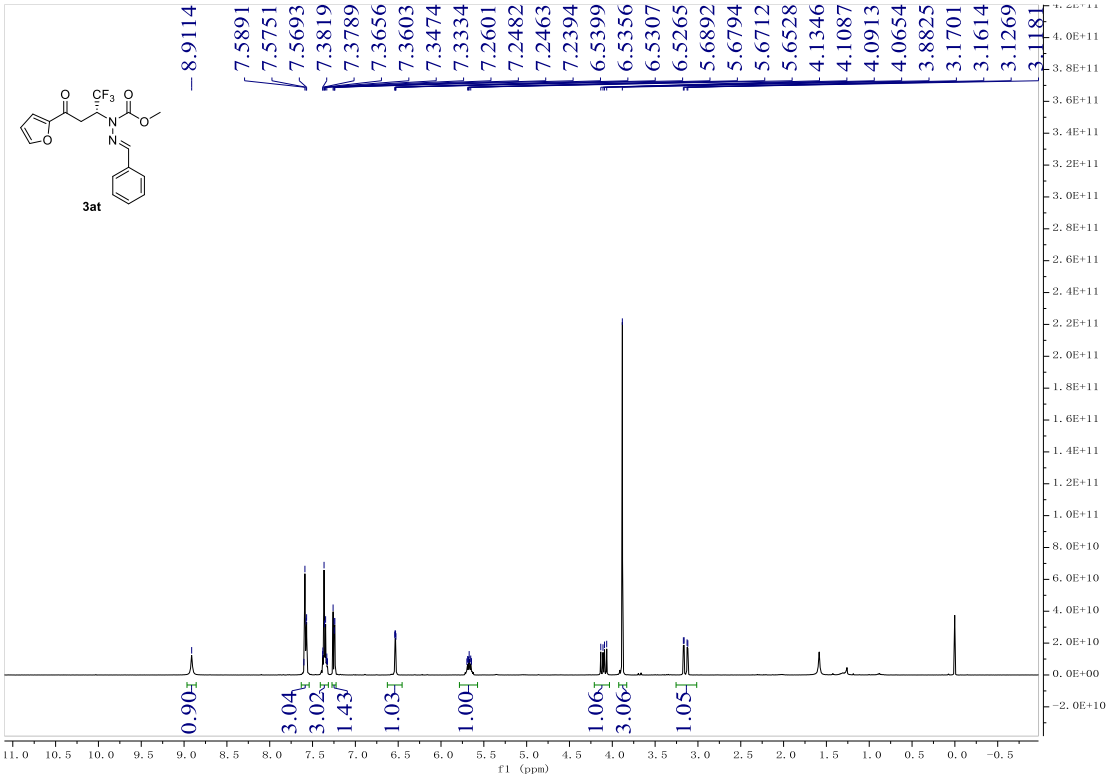
$^{13}C\{^{1}H\}$ NMR of 3as (100 MHz, $CDCl_3$)



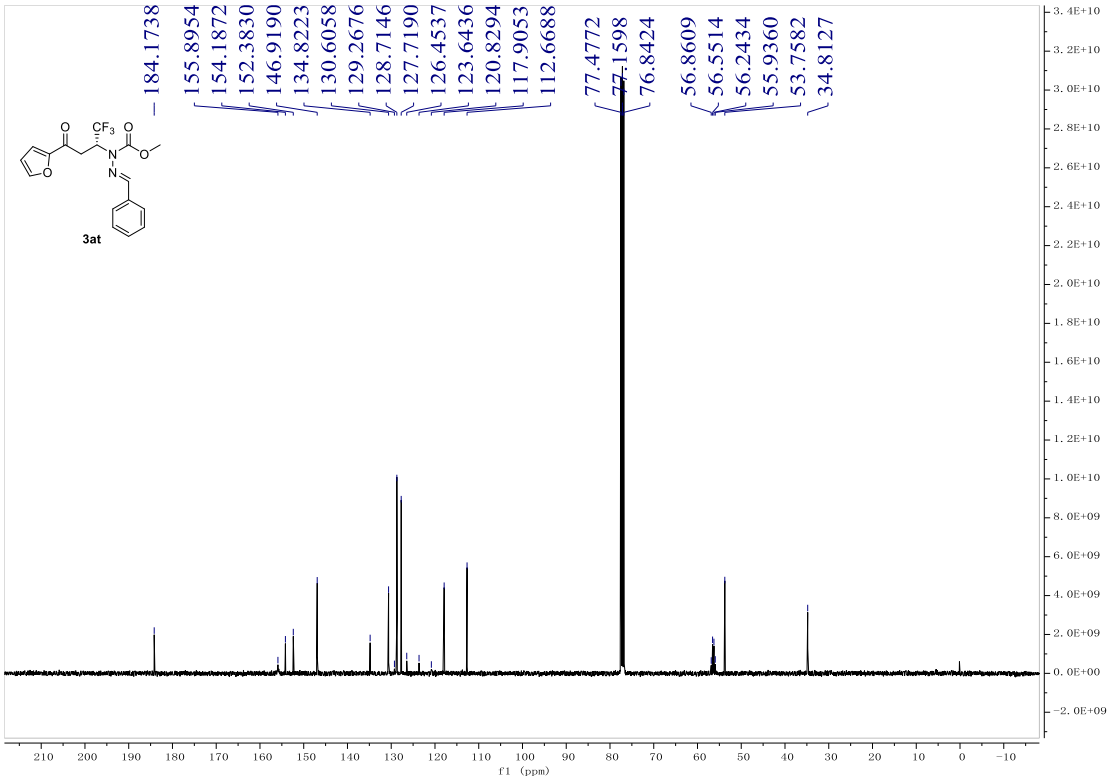
$^{19}F\{^{1}H\}$ NMR of 3as (376 MHz, $CDCl_3$)



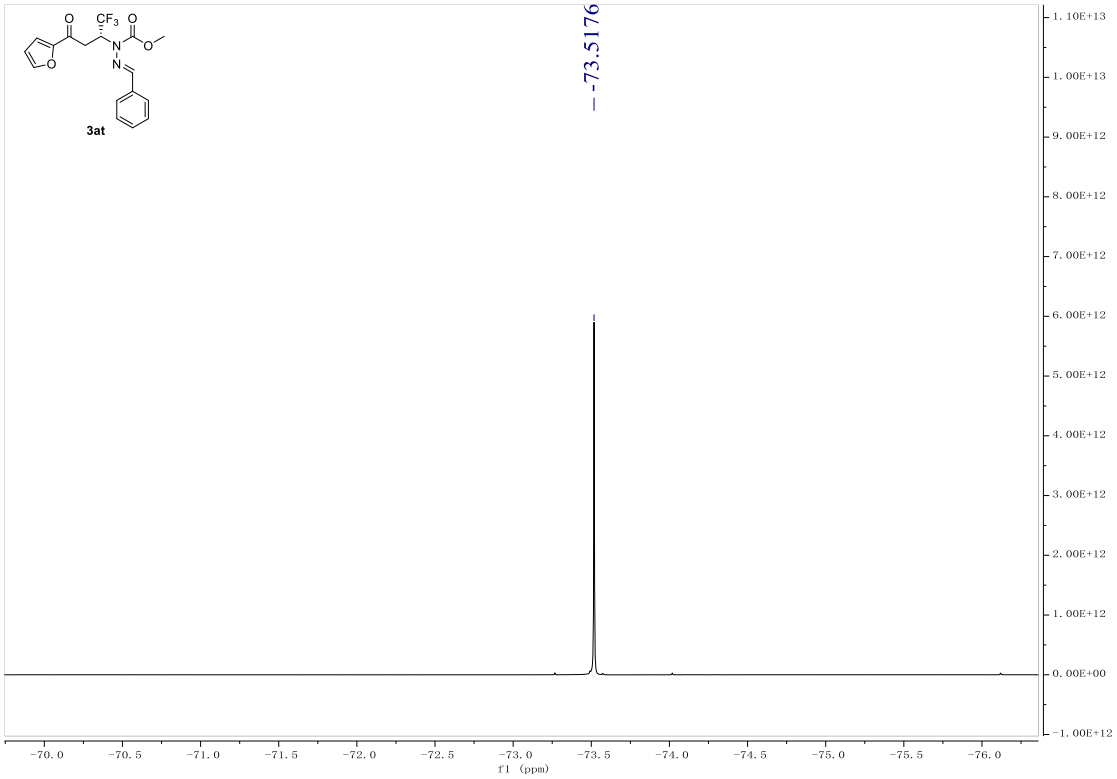
^{1}H NMR of 3at (400 MHz, $CDCl_3$)



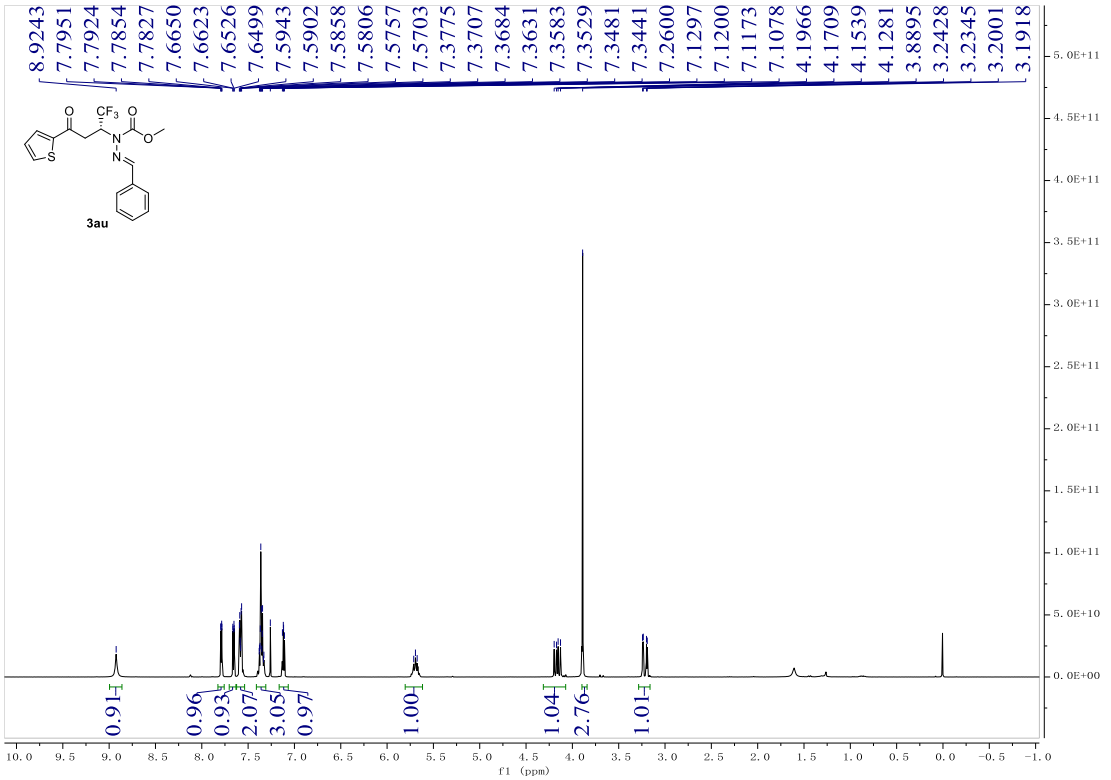
^{13}C{^{1}H} NMR of 3at (100 MHz, $CDCl_3$)



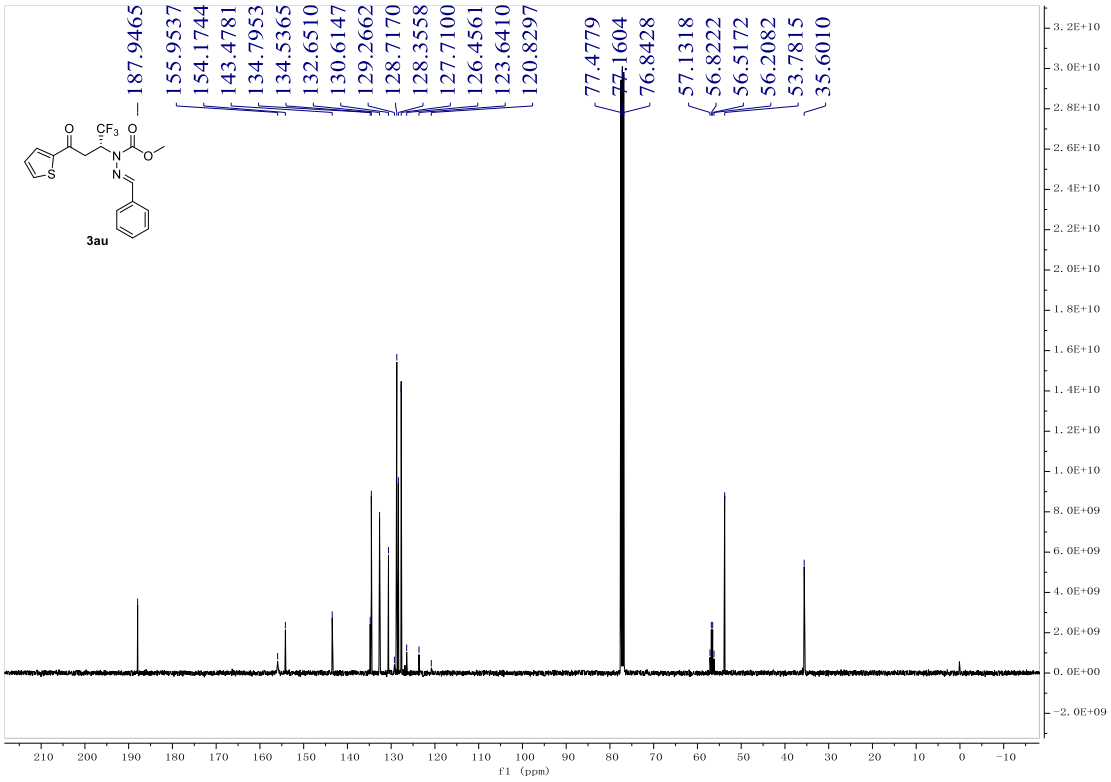
$^{19}F\{^{1}H\}$ NMR of 3at (376 MHz, $CDCl_3$)



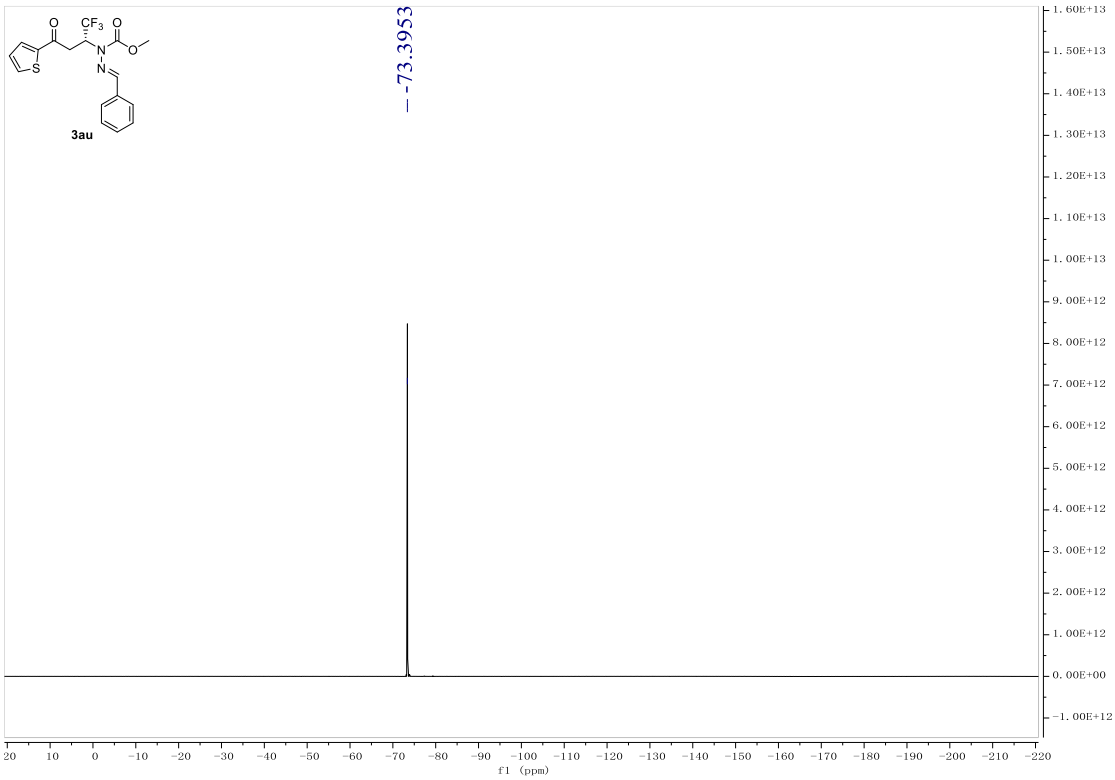
^{1}H NMR of 3au (400 MHz, $CDCl_3$)



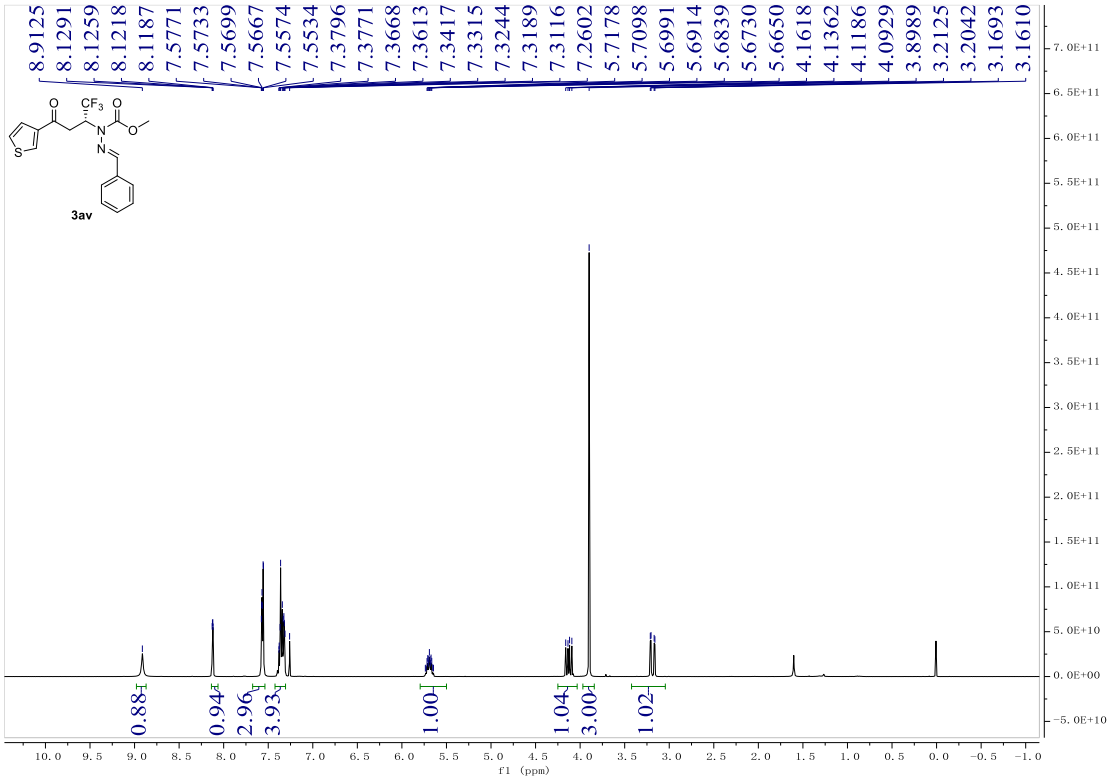
$^{13}C\{^{1}H\}$ NMR of 3au (100 MHz, $CDCl_3$)



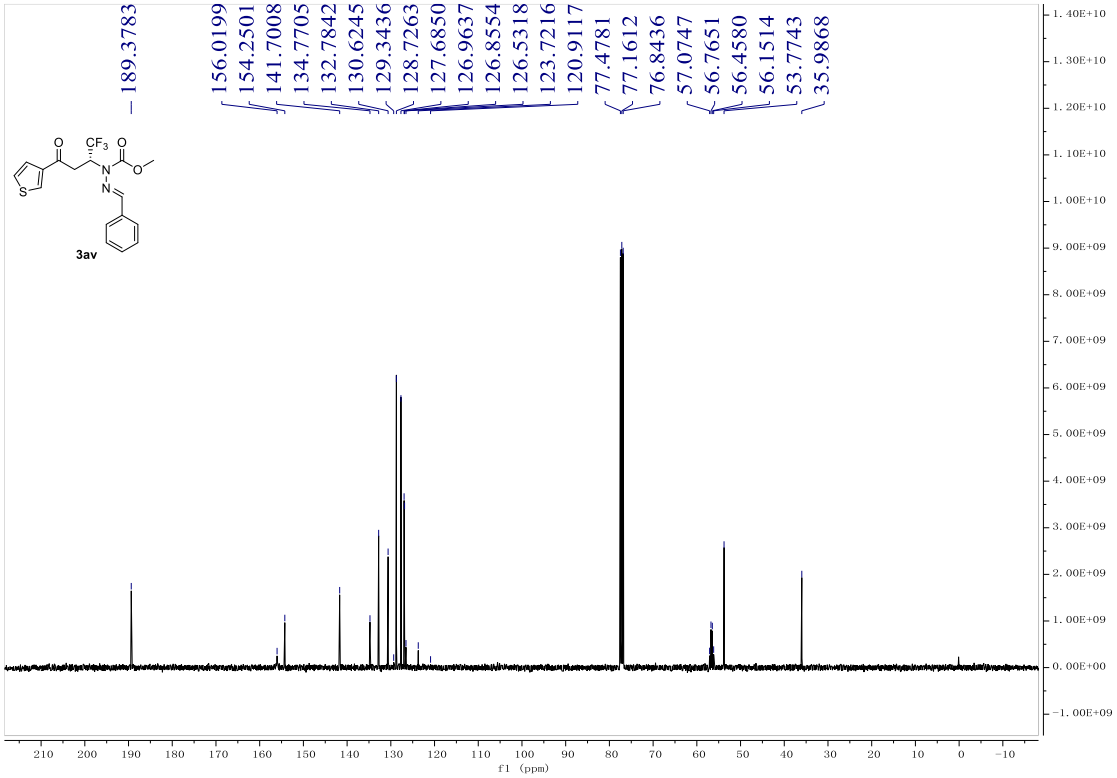
$^{19}F\{^{1}H\}$ NMR of 3au (376 MHz, $CDCl_3$)



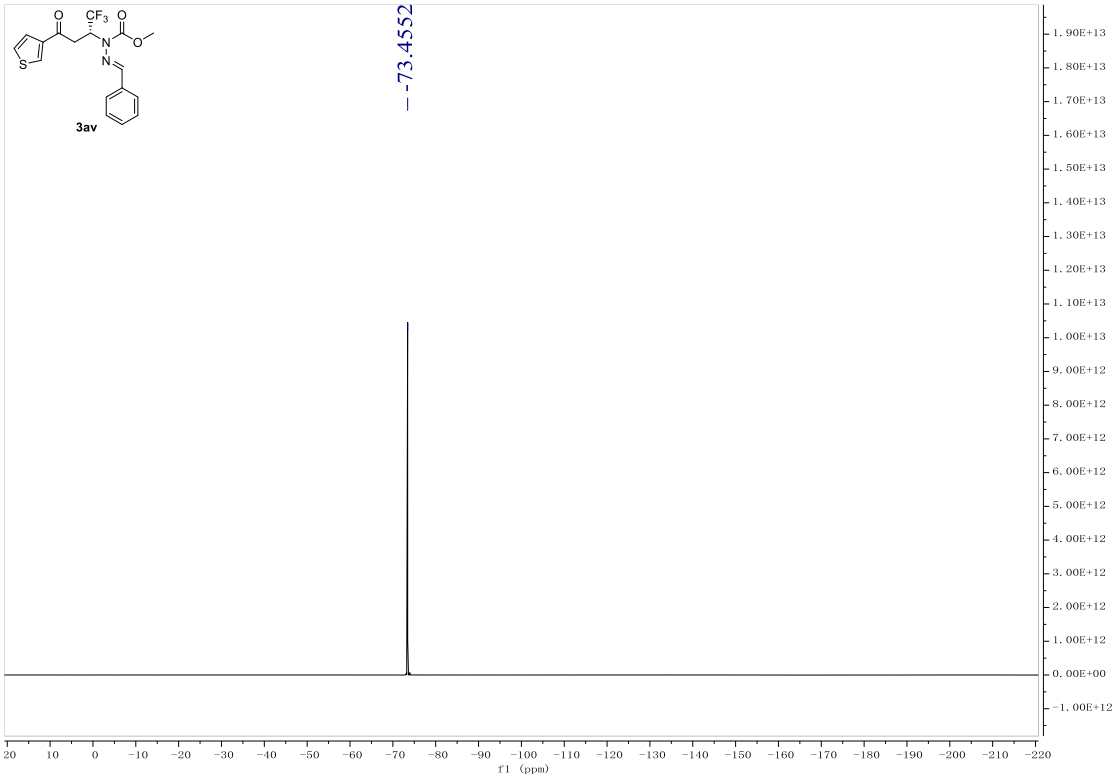
^{1}H NMR of 3av (400 MHz, $CDCl_3$)



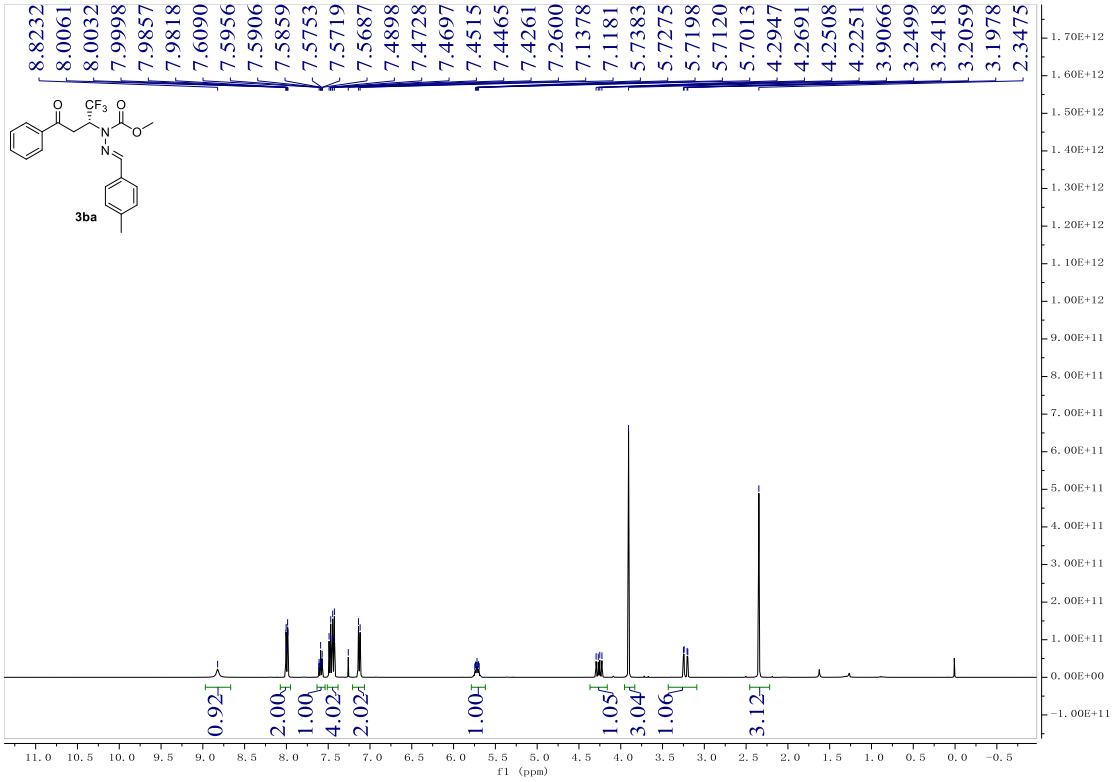
^{13}C{^{1}H} NMR of 3av (100 MHz, $CDCl_3$)



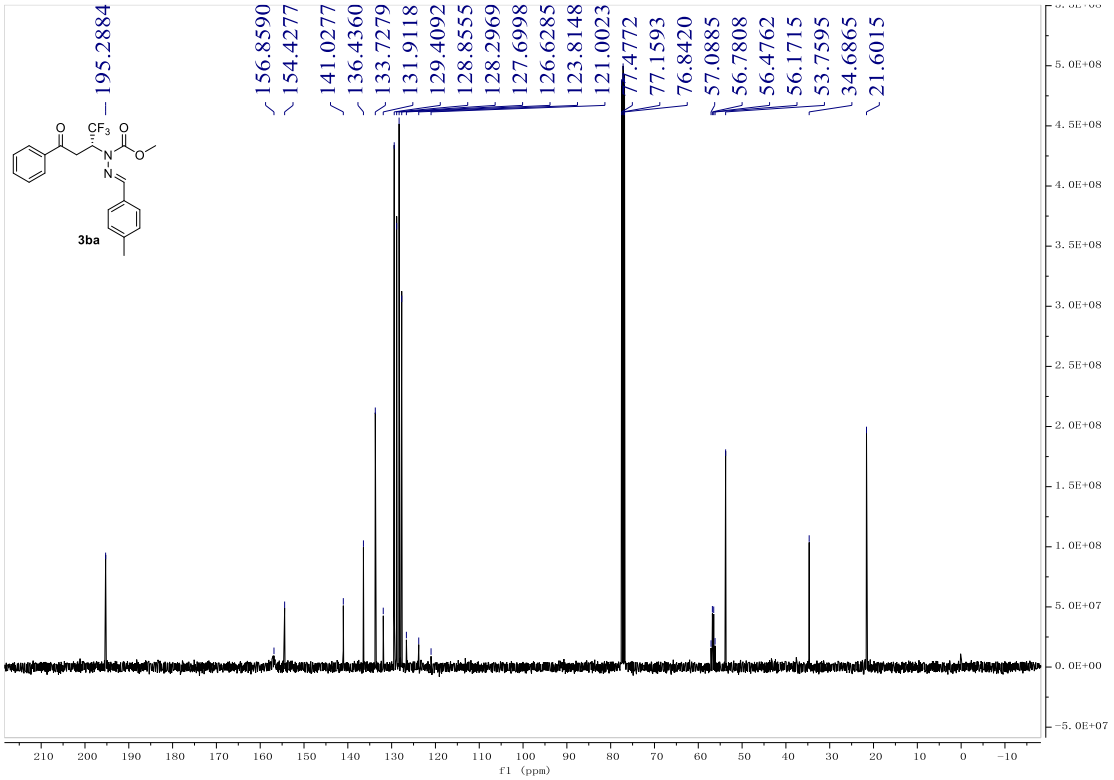
$^{19}F\{^{1}H\}$ NMR of 3av (376 MHz, $CDCl_3$)



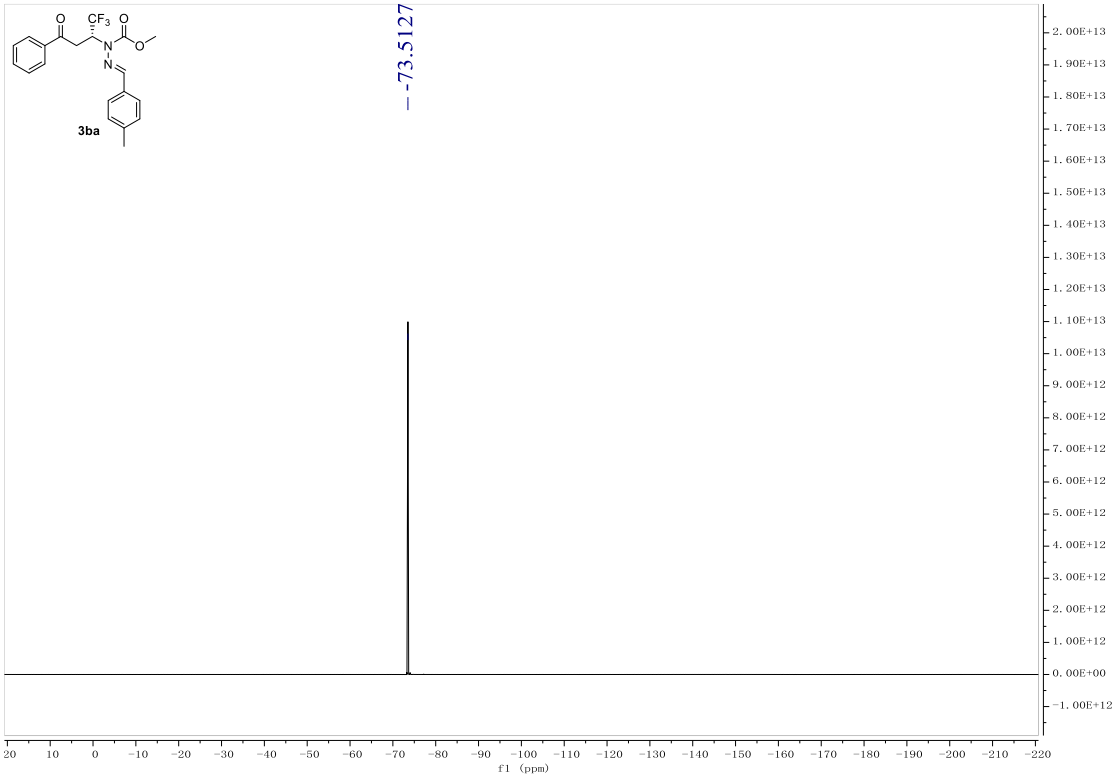
^{1}H NMR of 3ba (400 MHz, $CDCl_3$)



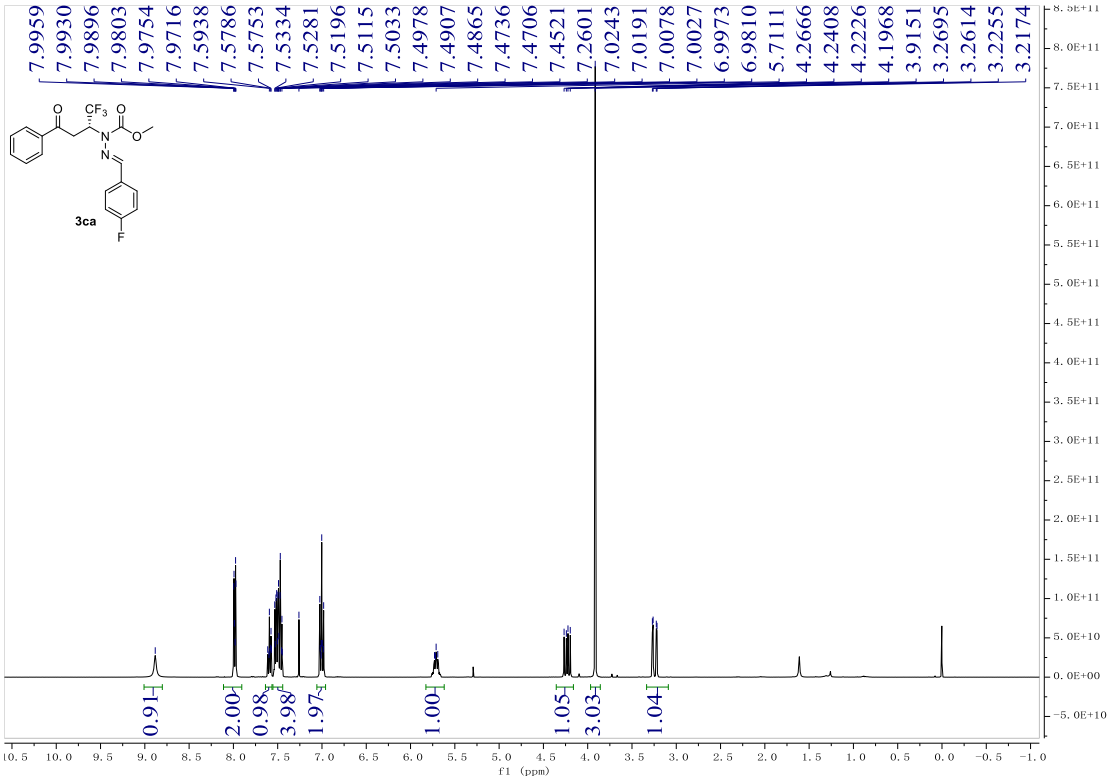
$^{13}C\{^{1}H\}$ NMR of 3ba (100 MHz, $CDCl_3$)



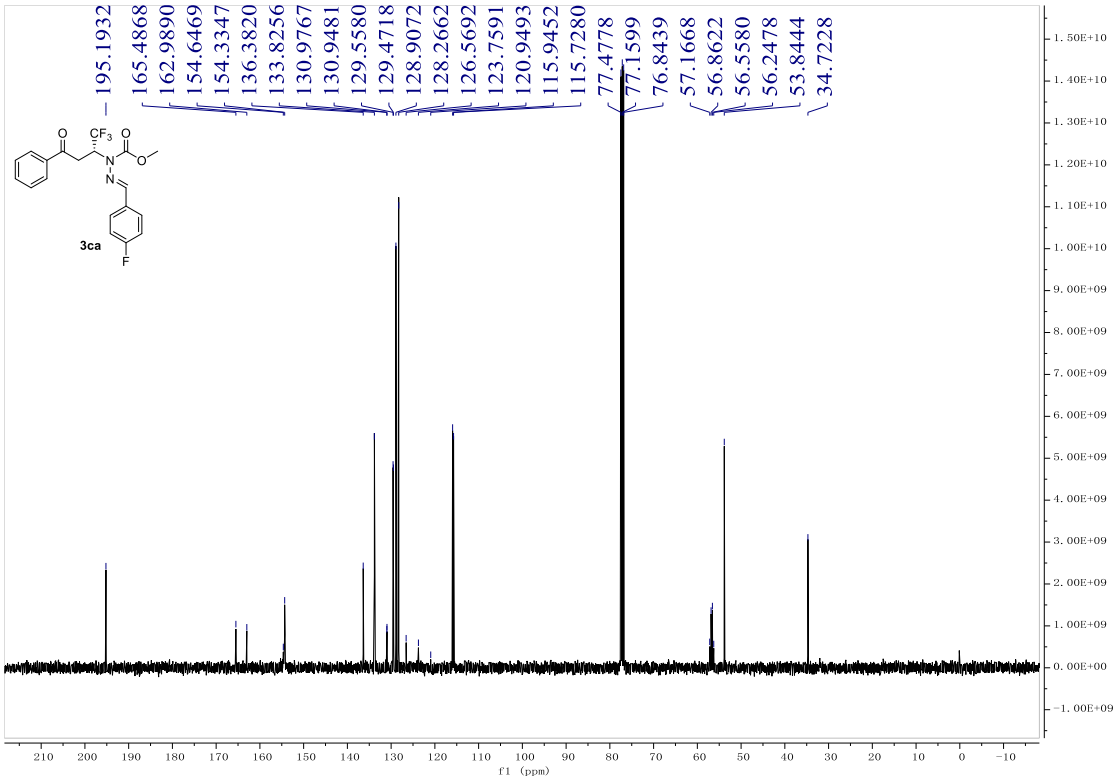
$^{19}F\{^{1}H\}$ NMR of 3ba (376 MHz, $CDCl_3$)



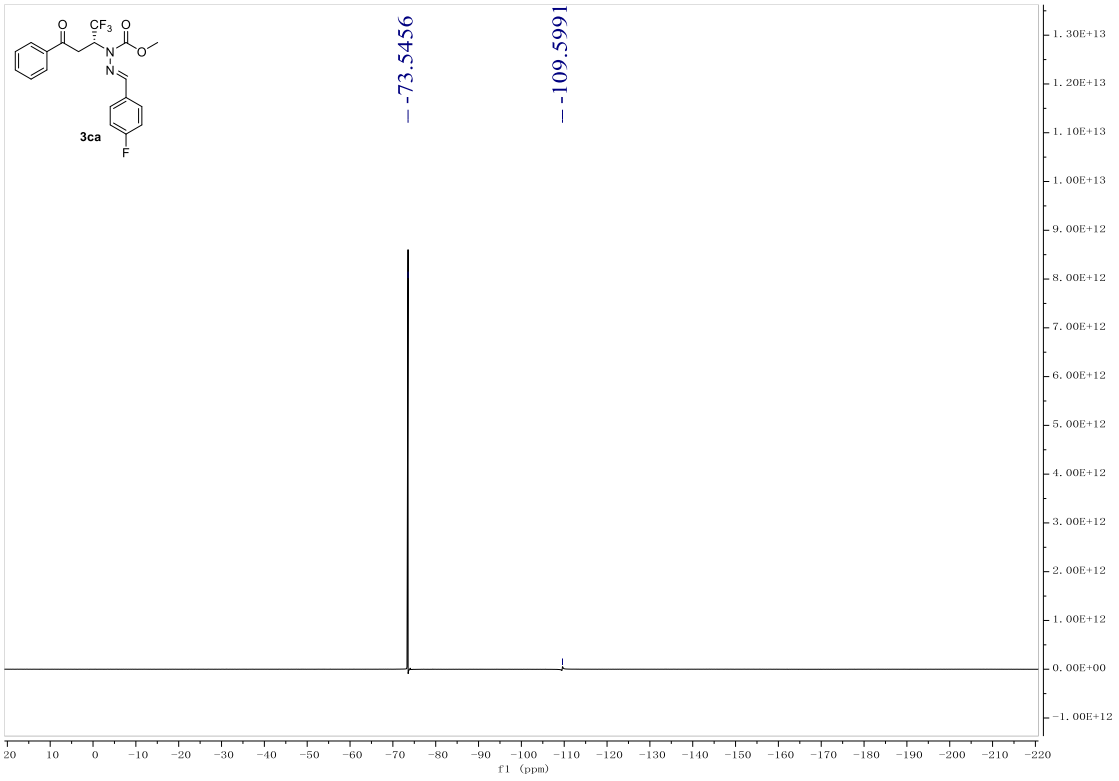
^{1}H NMR of 3ca (400 MHz, $CDCl_3$)



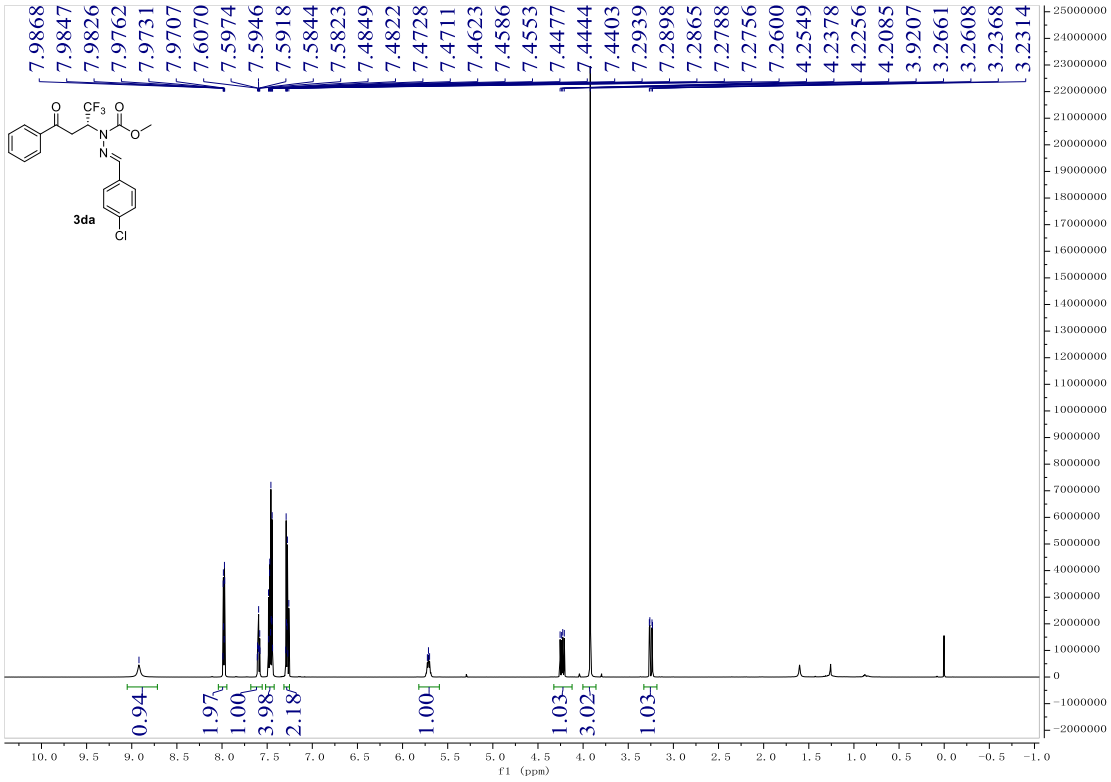
^{13}C{^{1}H} NMR of 3ca (100 MHz, $CDCl_3$)



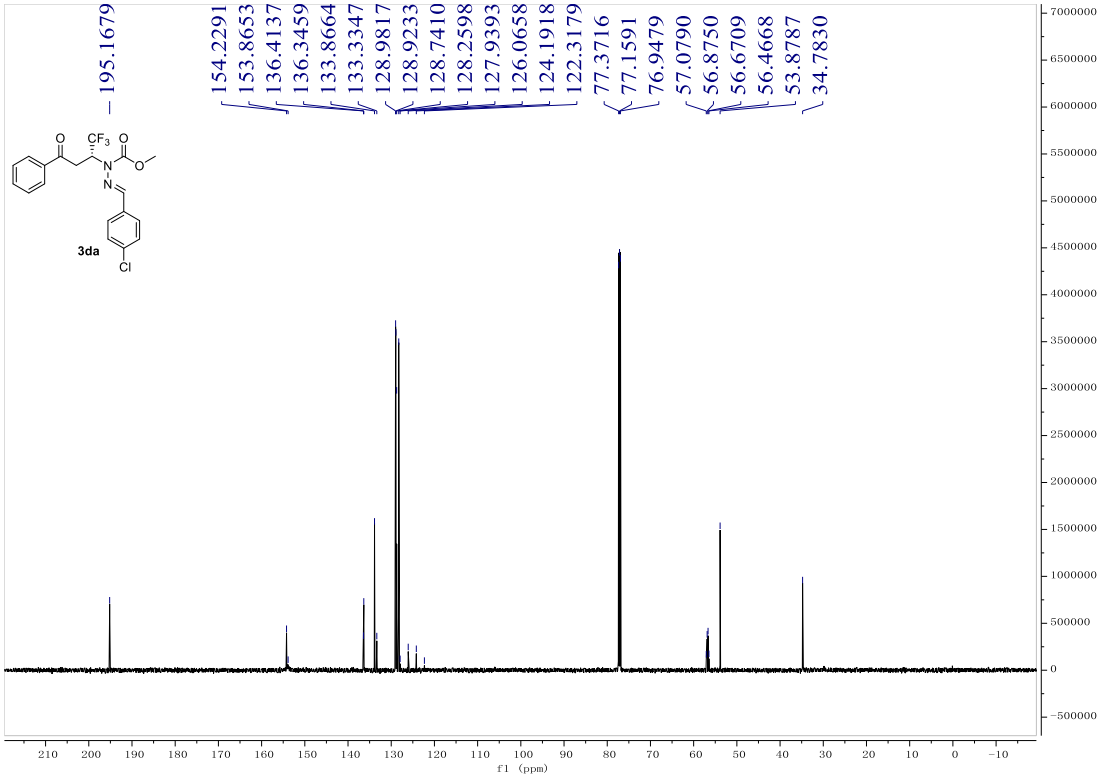
$^{19}F\{^{1}H\}$ NMR of 3ca (376 MHz, $CDCl_3$)



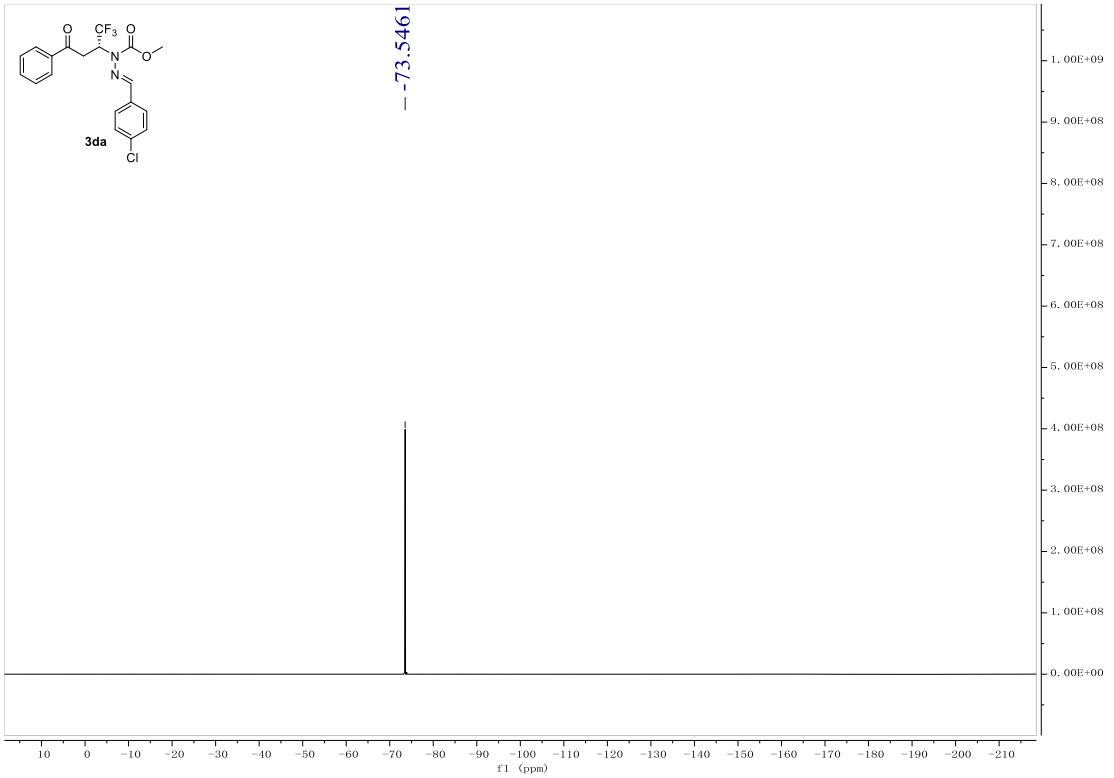
^{1}H NMR of 3da (600 MHz, $CDCl_3$)



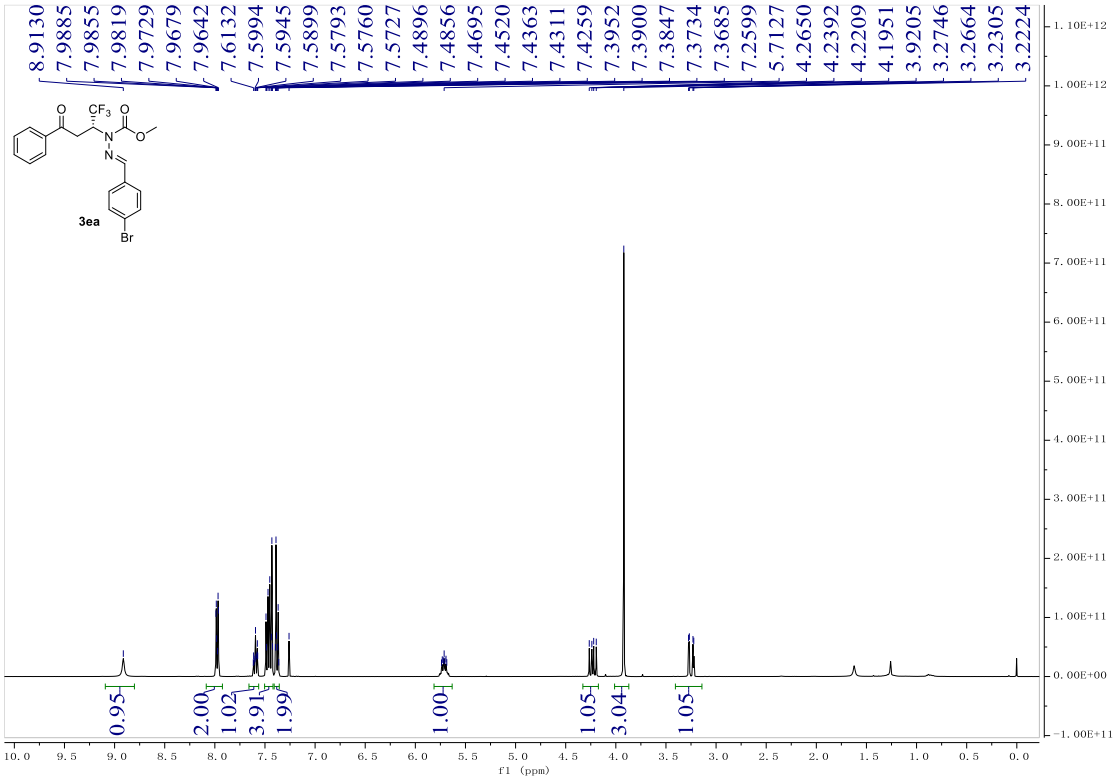
$^{13}C\{^{1}H\}$ NMR of 3da (150 MHz, $CDCl_3$)



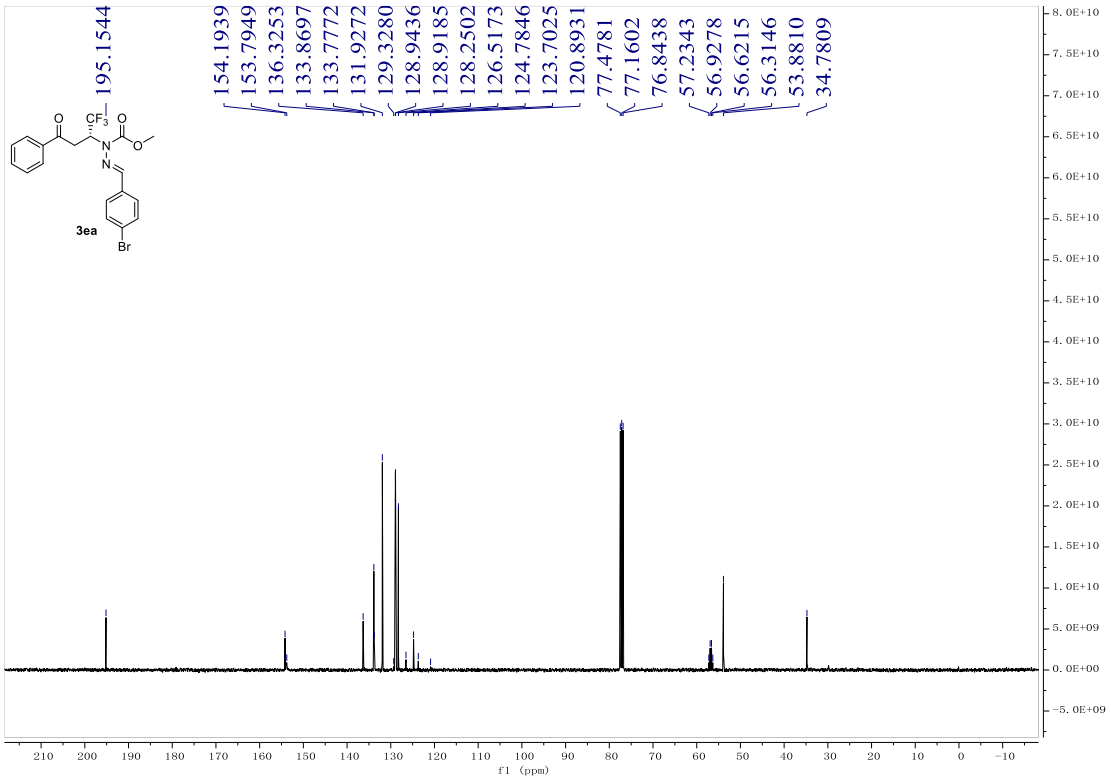
$^{19}F\{^{1}H\}$ NMR of 3da (565 MHz, $CDCl_3$)



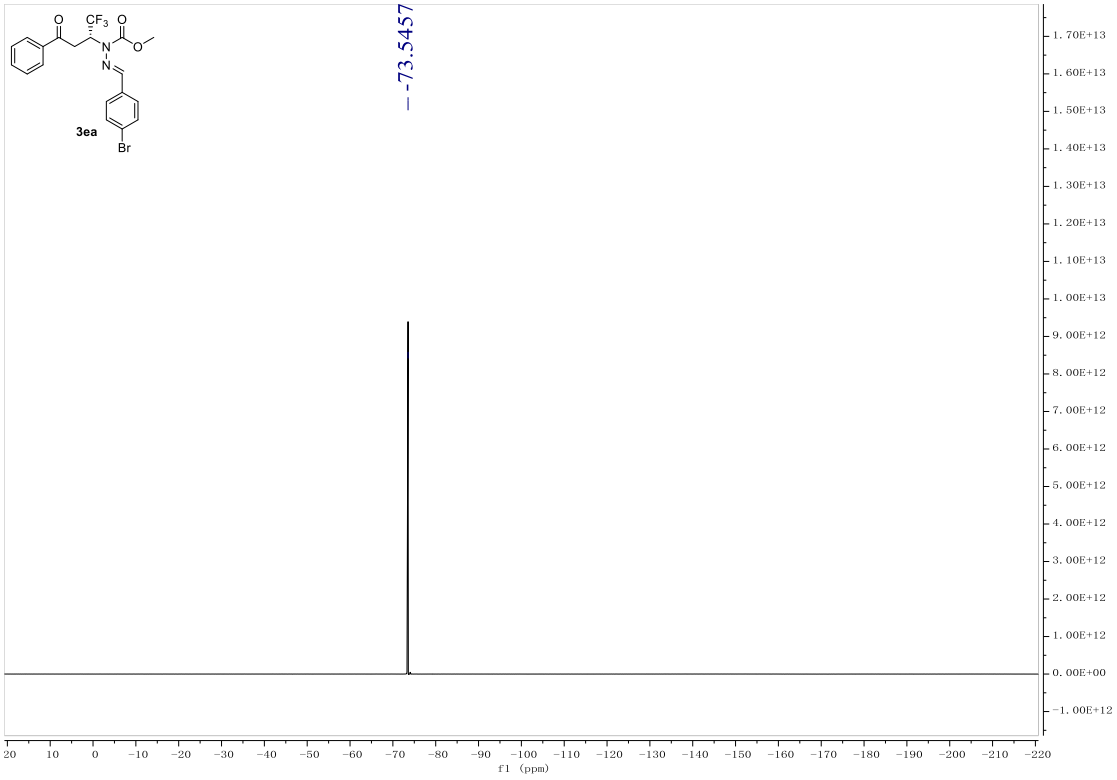
^{1}H NMR of 3ea (400 MHz, $CDCl_3$)



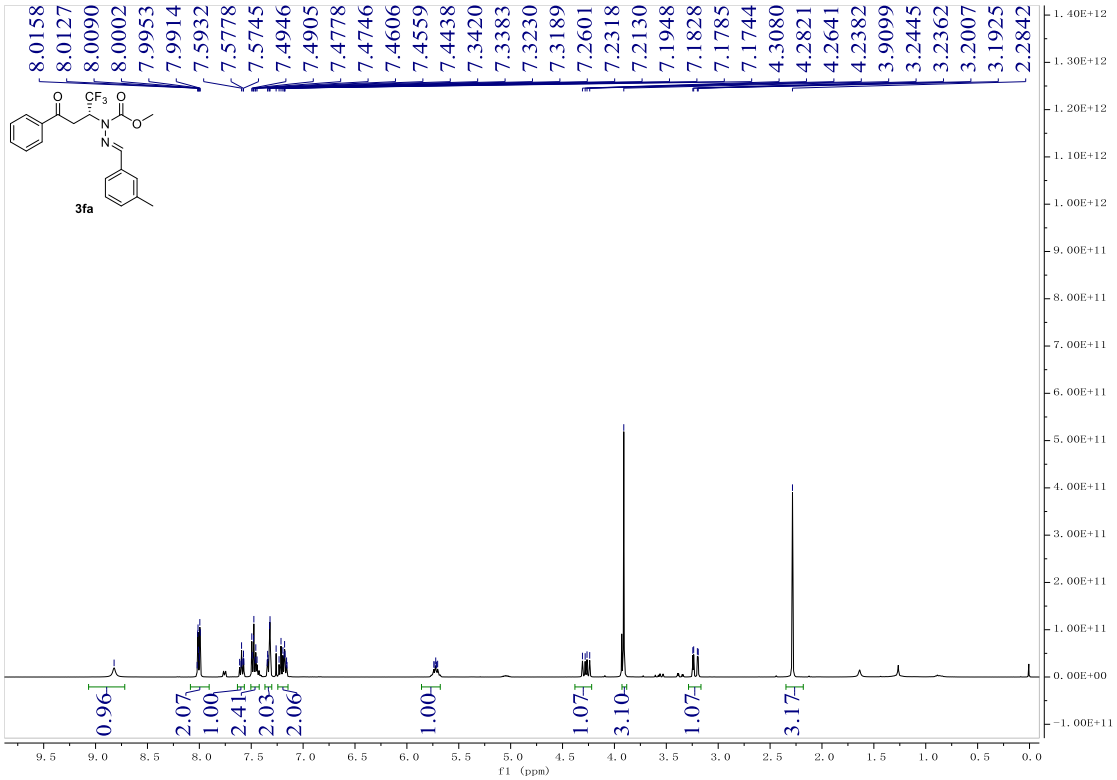
^{13}C{^{1}H} NMR of 3ea (100 MHz, $CDCl_3$)



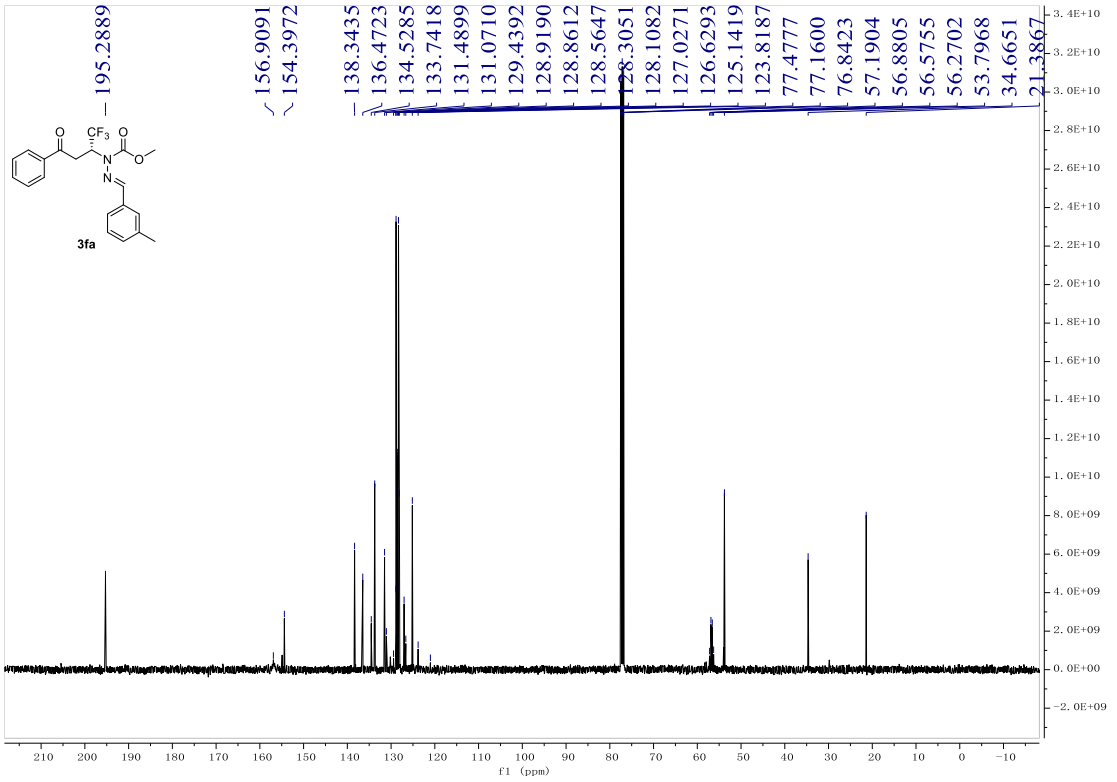
$^{19}F\{^{1}H\}$ NMR of 3ea (376 MHz, $CDCl_3$)



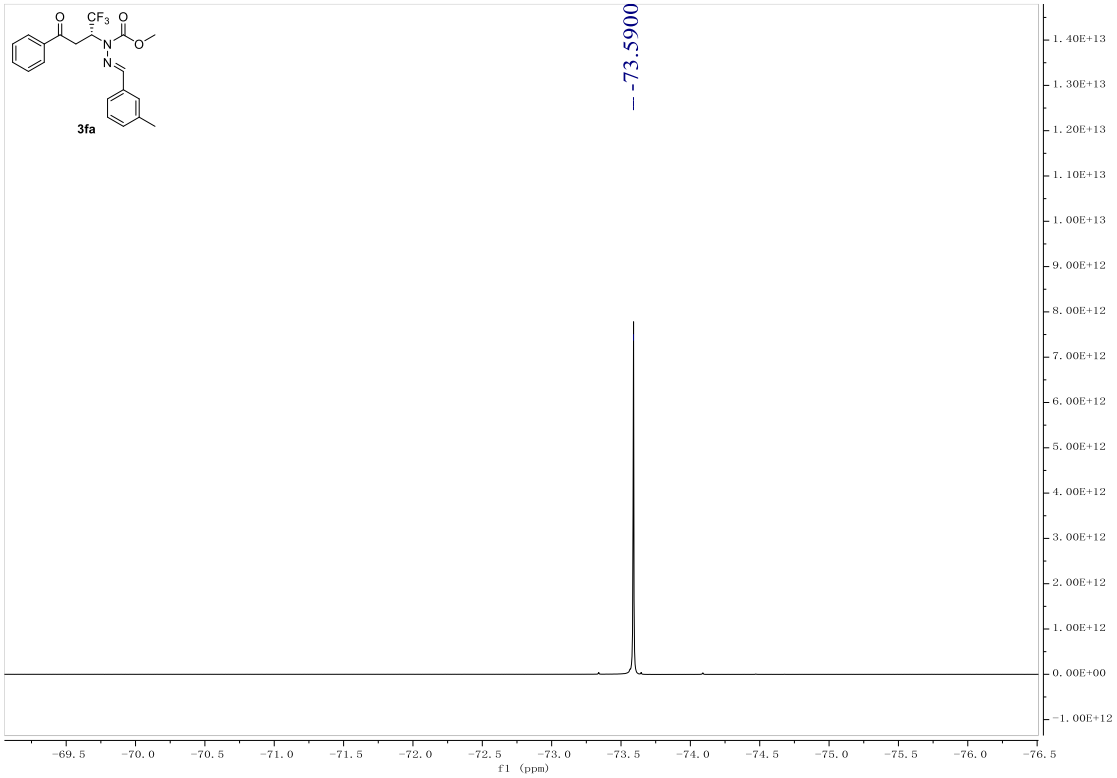
^{1}H NMR of 3fa (400 MHz, $CDCl_3$)



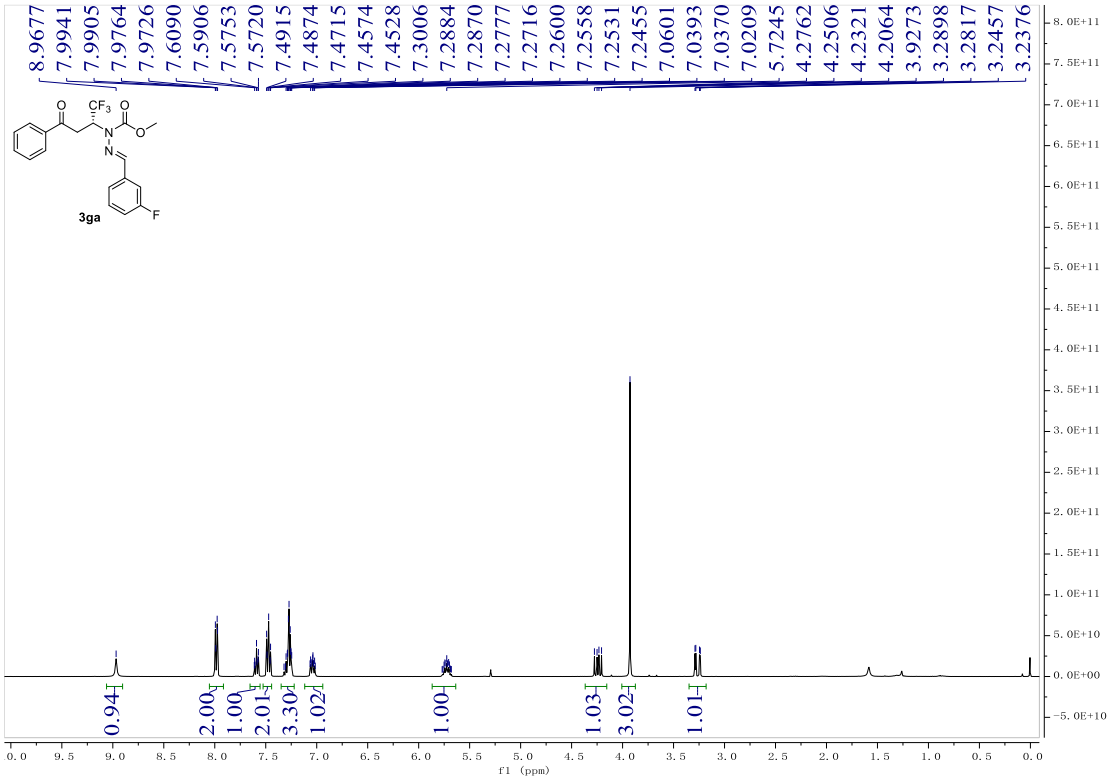
$^{13}C\{^{1}H\}$ NMR of 3fa (100 MHz, $CDCl_3$)



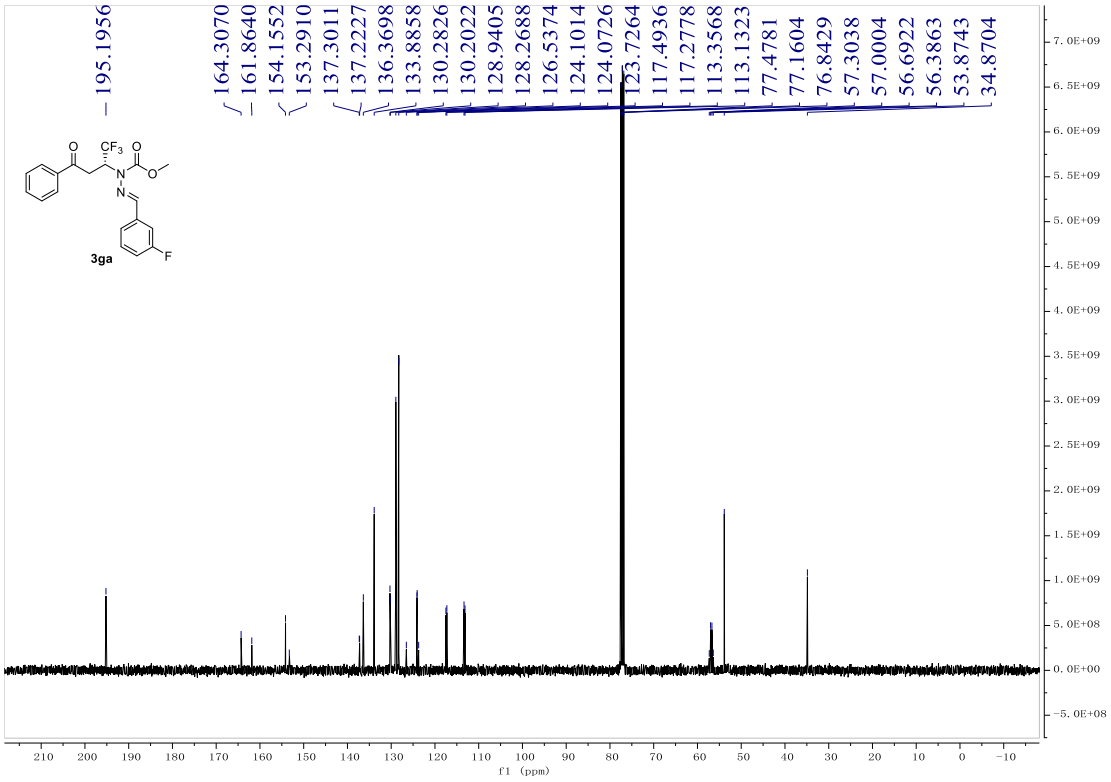
$^{19}F\{^{1}H\}$ NMR of 3fa (376 MHz, $CDCl_3$)



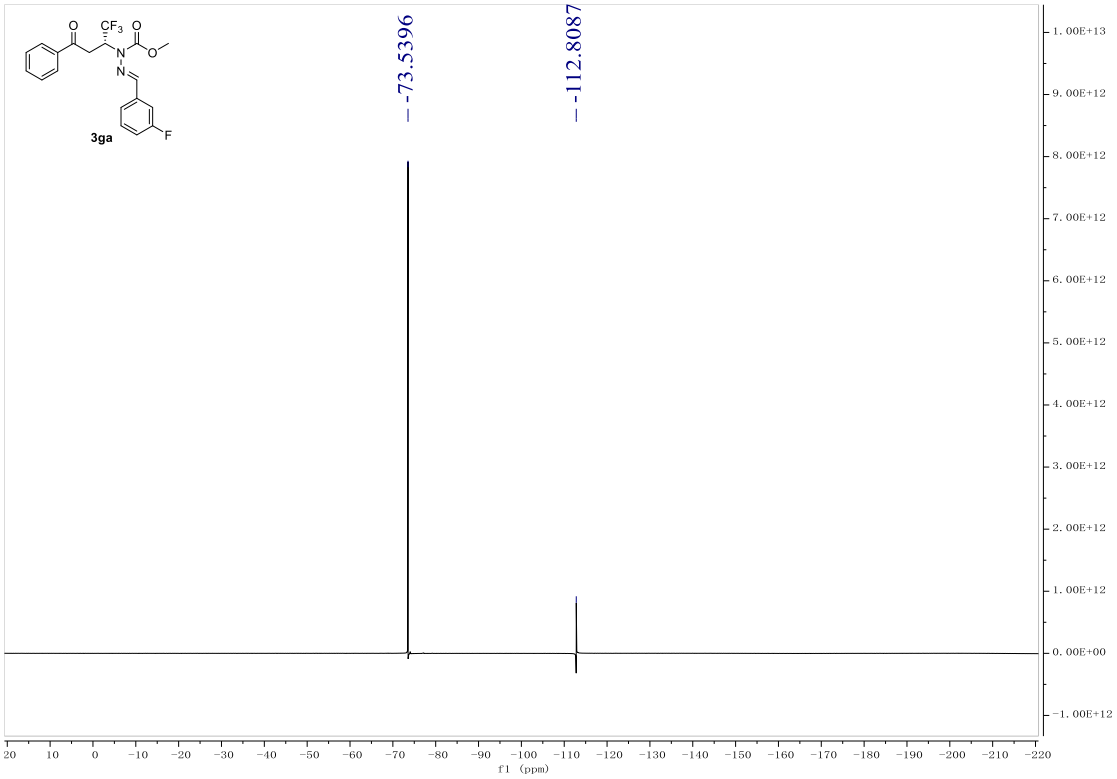
^{1}H NMR of 3ga (400 MHz, $CDCl_3$)



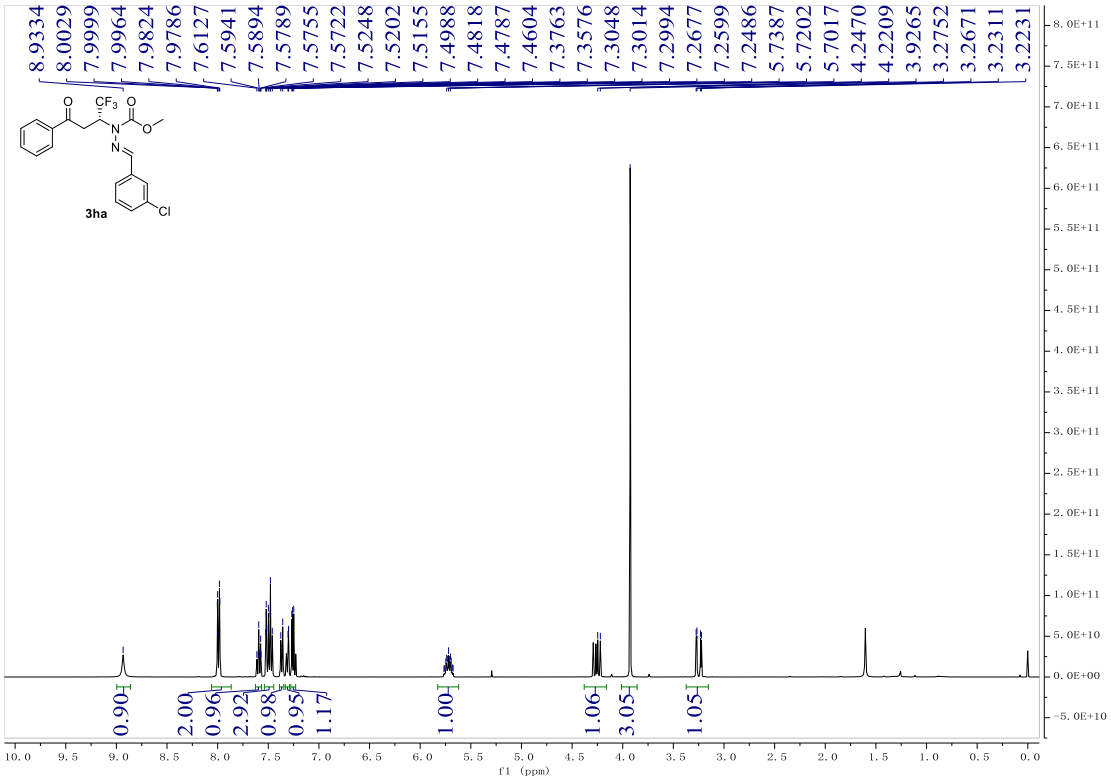
^{13}C{^{1}H} NMR of 3ga (100 MHz, $CDCl_3$)



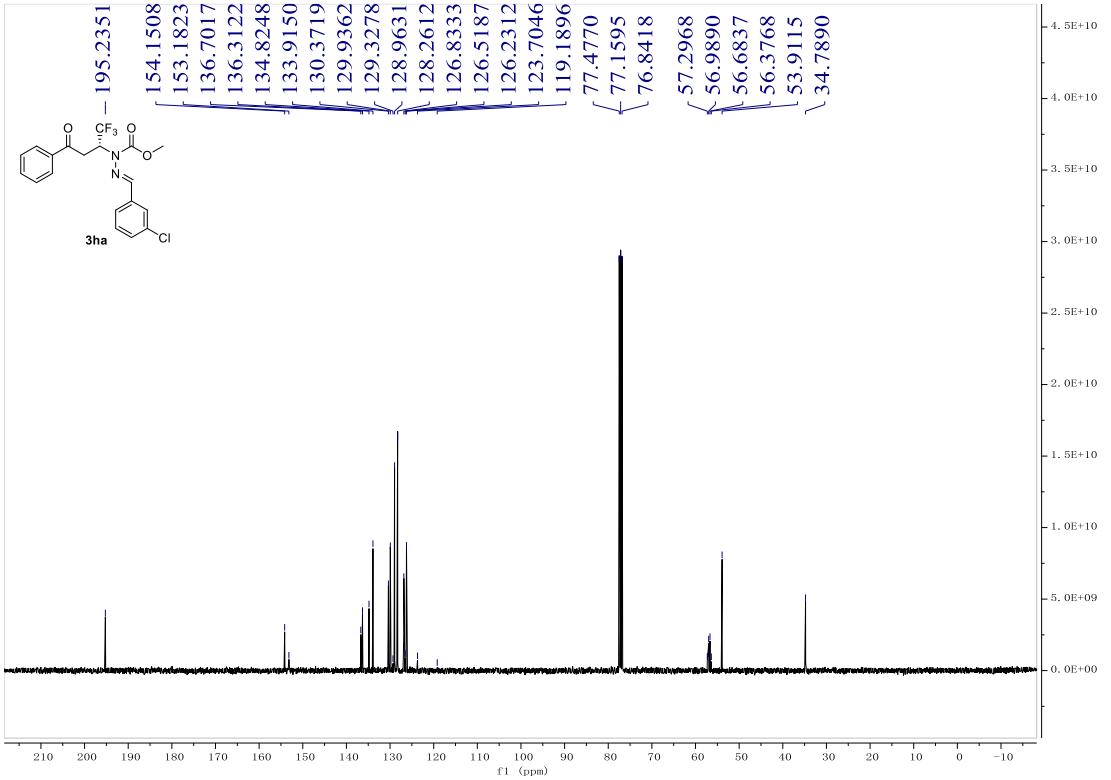
$^{19}F\{^{1}H\}$ NMR of 3ga (376 MHz, $CDCl_3$)



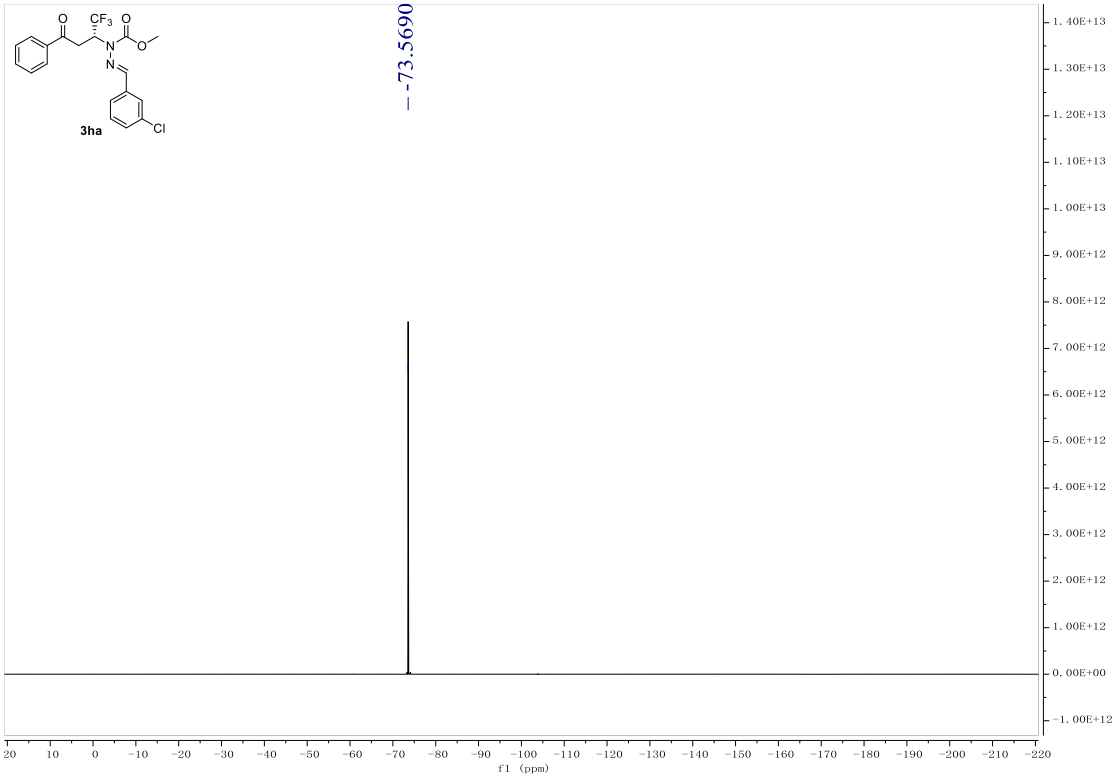
^{1}H NMR of 3ha (400 MHz, $CDCl_3$)



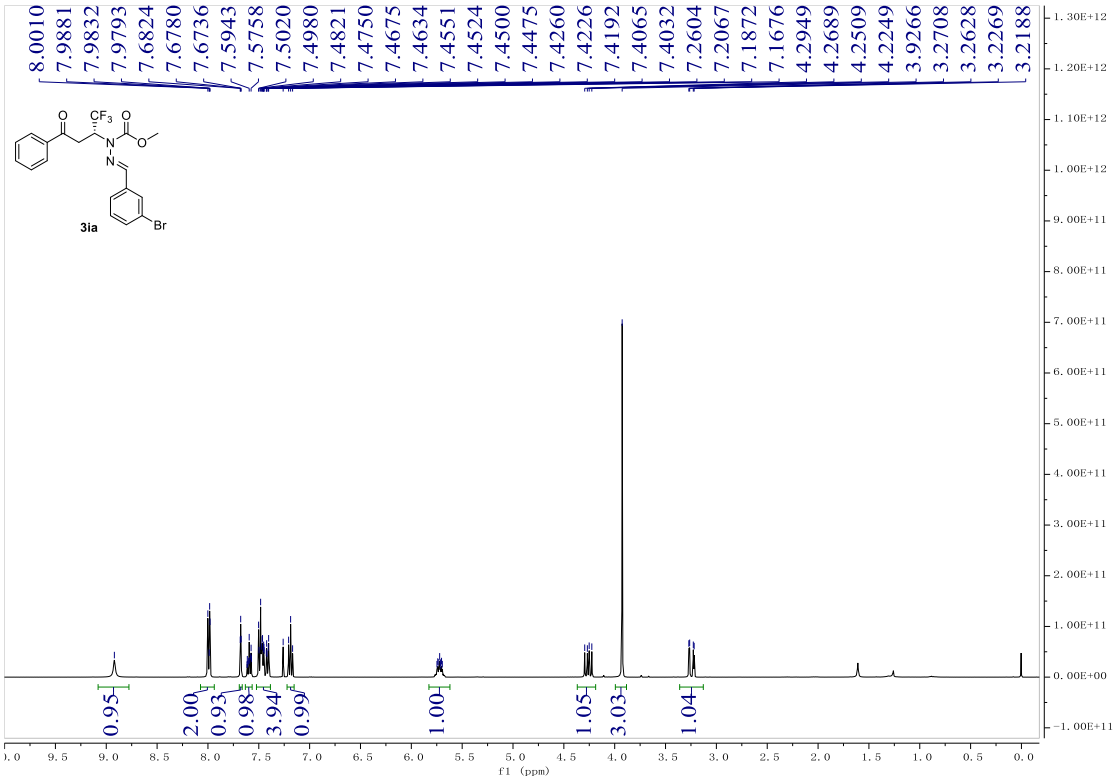
$^{13}C\{^{1}H\}$ NMR of 3ha (100 MHz, $CDCl_3$)



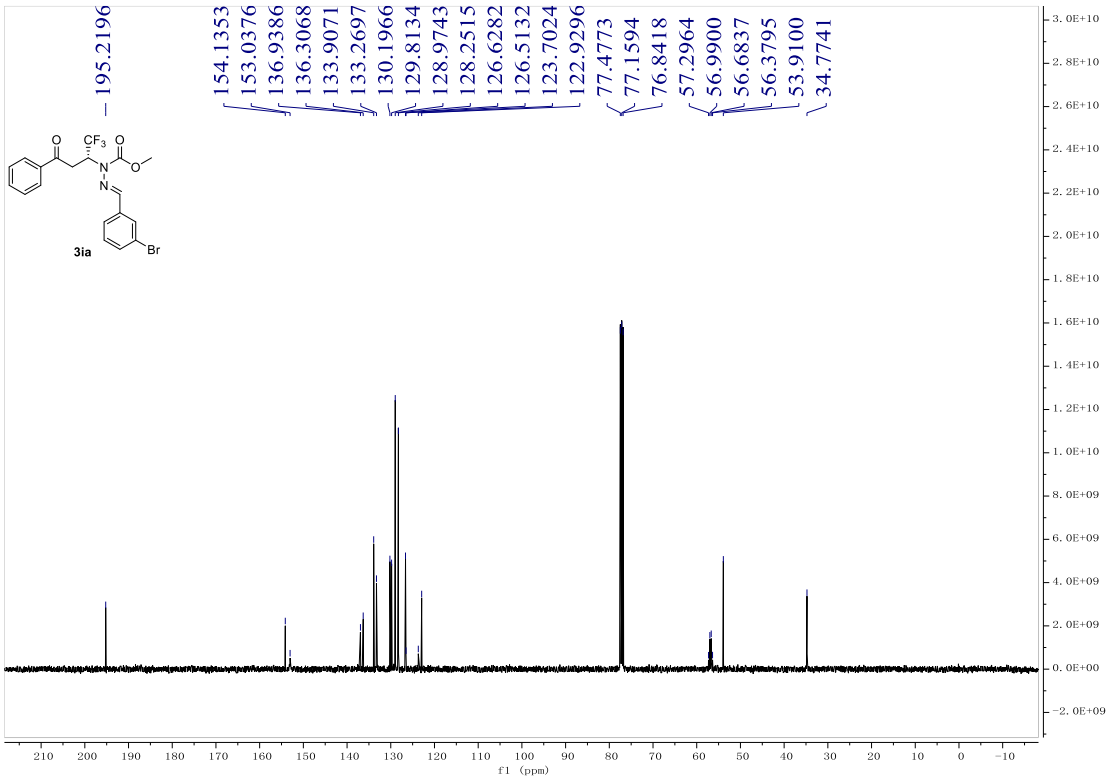
$^{19}F\{^{1}H\}$ NMR of 3ha (376 MHz, $CDCl_3$)



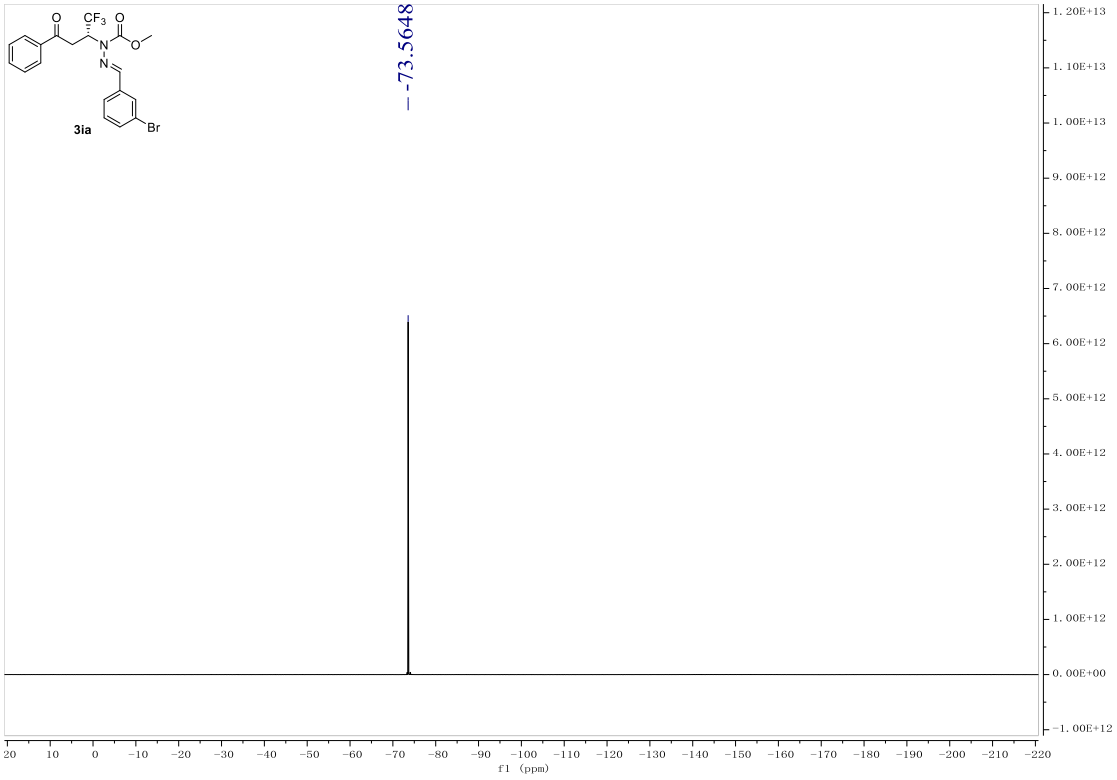
^{1}H NMR of 3ia (400 MHz, $CDCl_3$)



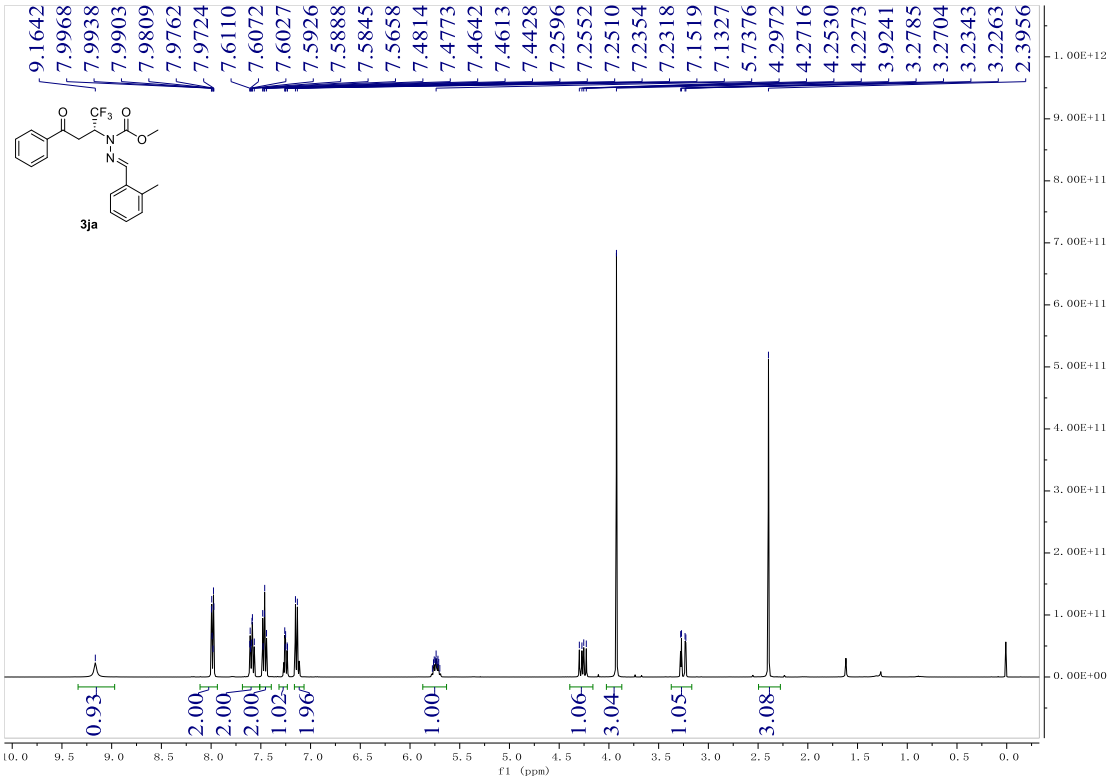
^{13}C{^{1}H} NMR of 3ia (100 MHz, $CDCl_3$)



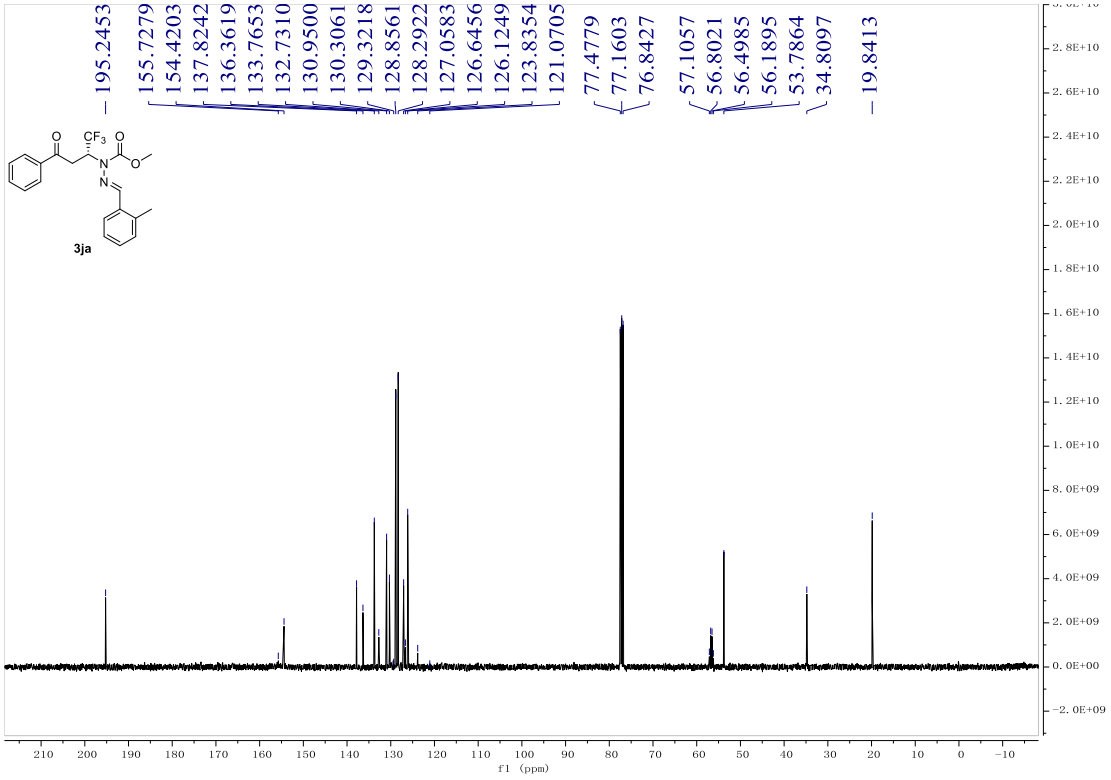
$^{19}F\{^{1}H\}$ NMR of 3ia (376 MHz, $CDCl_3$)



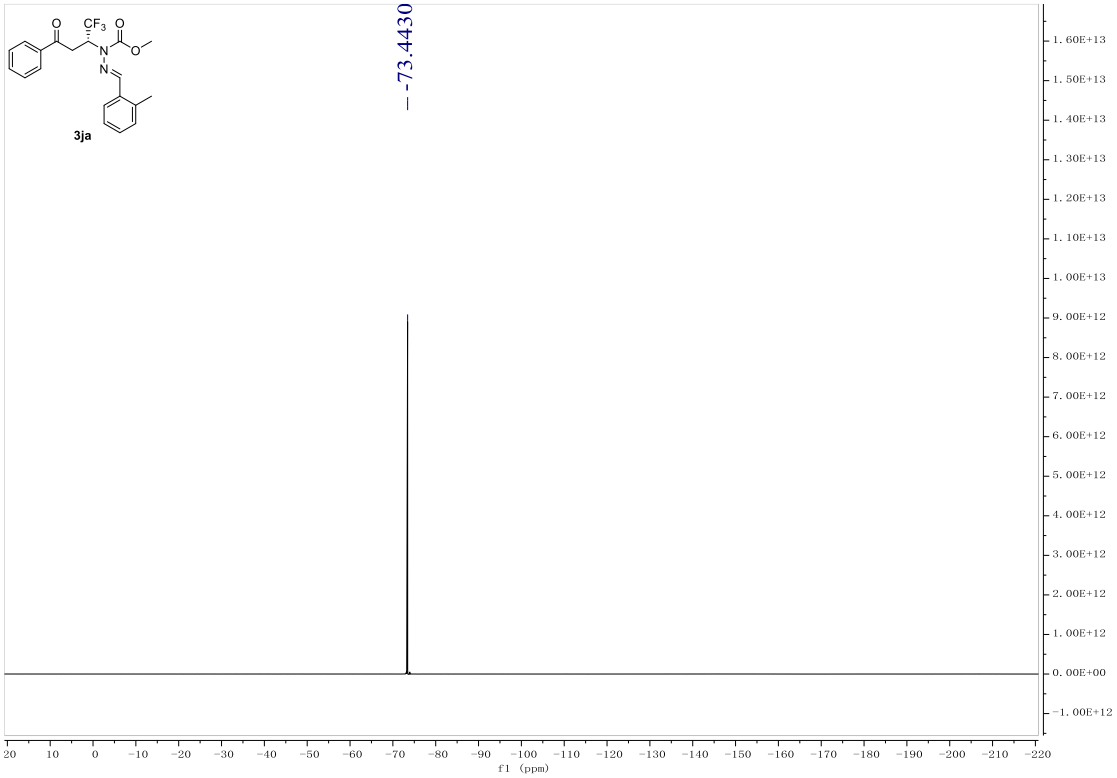
^{1}H NMR of 3ja (400 MHz, $CDCl_3$)



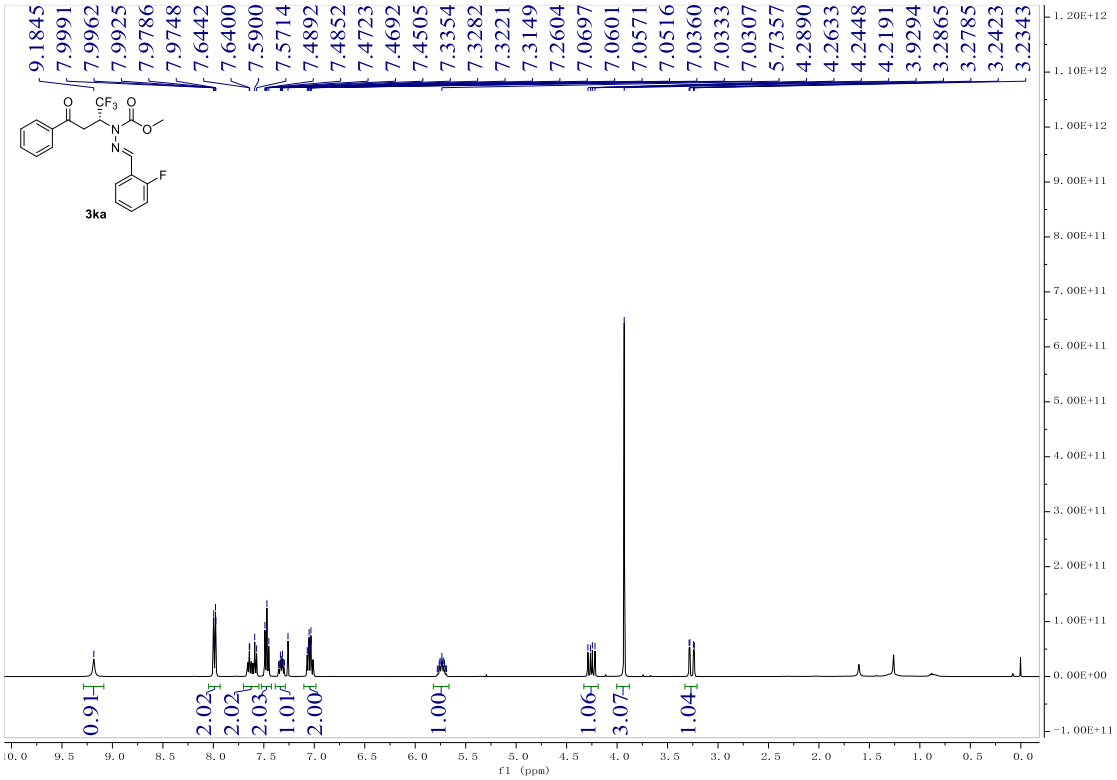
$^{13}C\{^{1}H\}$ NMR of 3ja (100 MHz, $CDCl_3$)



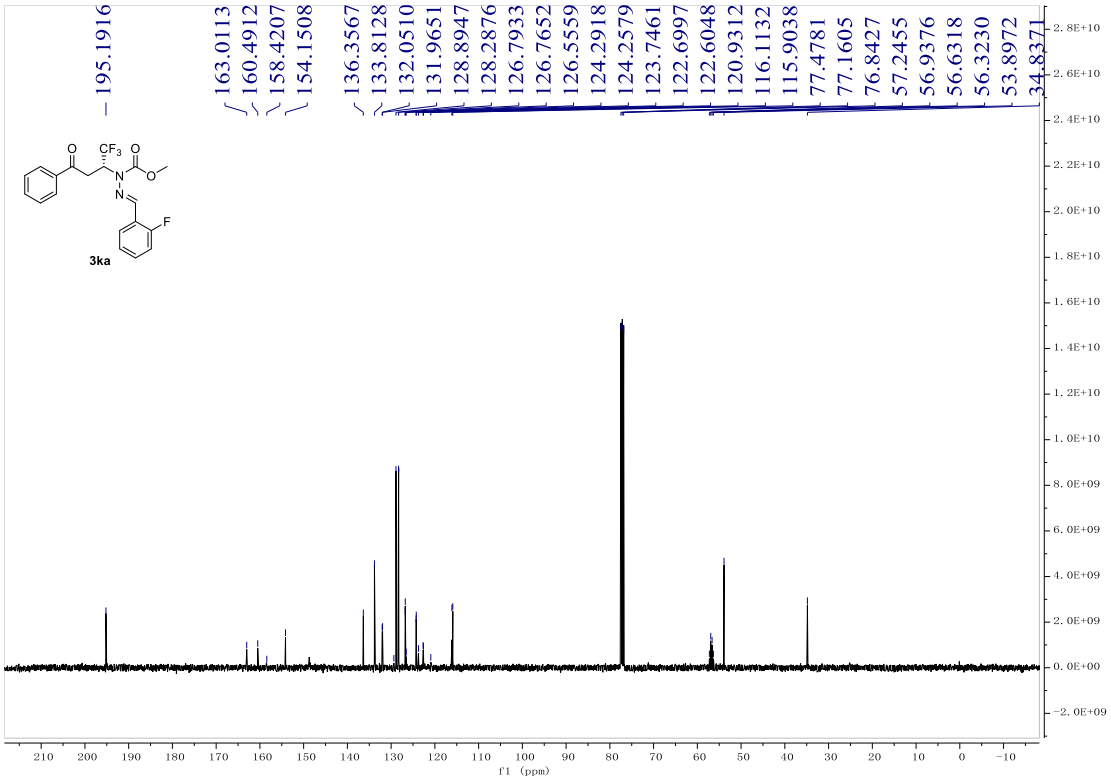
$^{19}F\{^{1}H\}$ NMR of 3ja (376 MHz, $CDCl_3$)



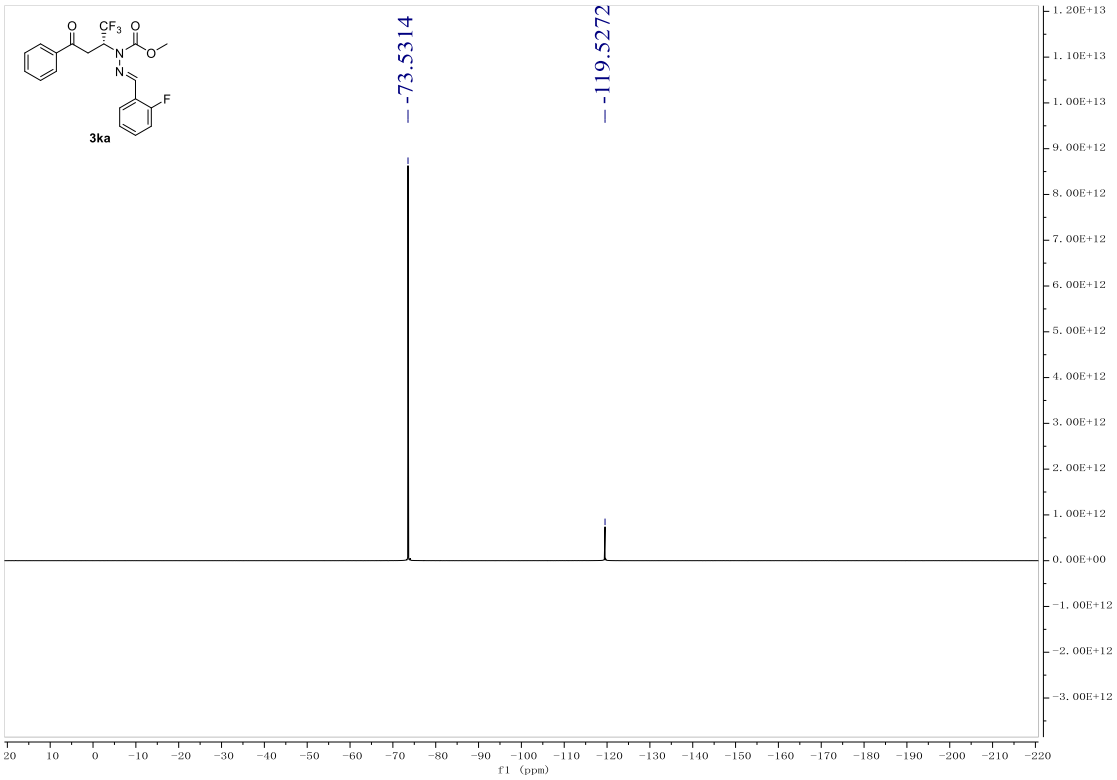
^{1}H NMR of 3ka (400 MHz, $CDCl_3$)



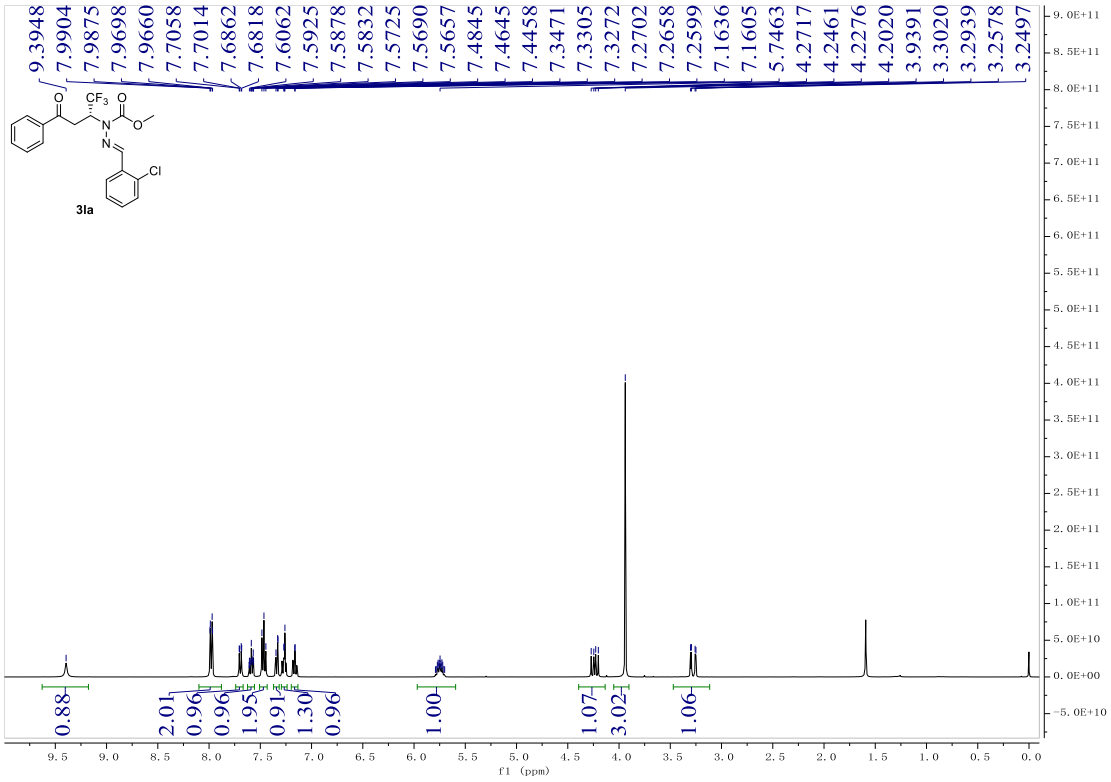
^{13}C{^{1}H} NMR of 3ka (100 MHz, $CDCl_3$)



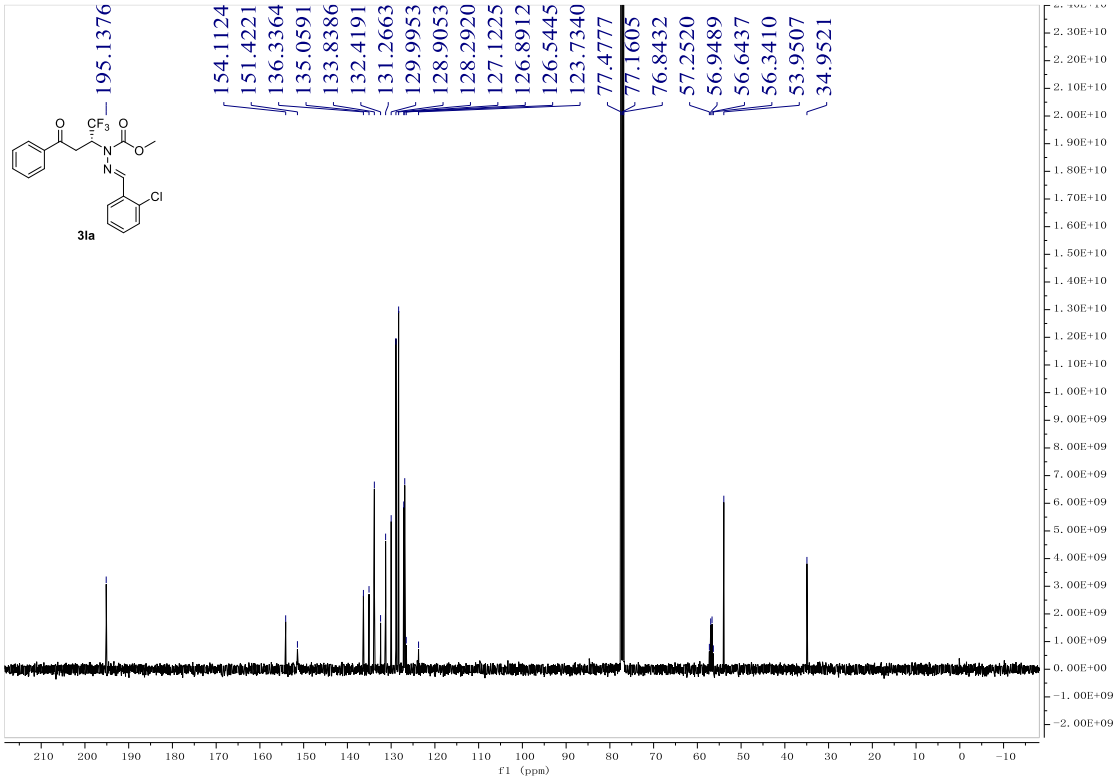
$^{19}F\{^{1}H\}$ NMR of 3ka (376 MHz, $CDCl_3$)



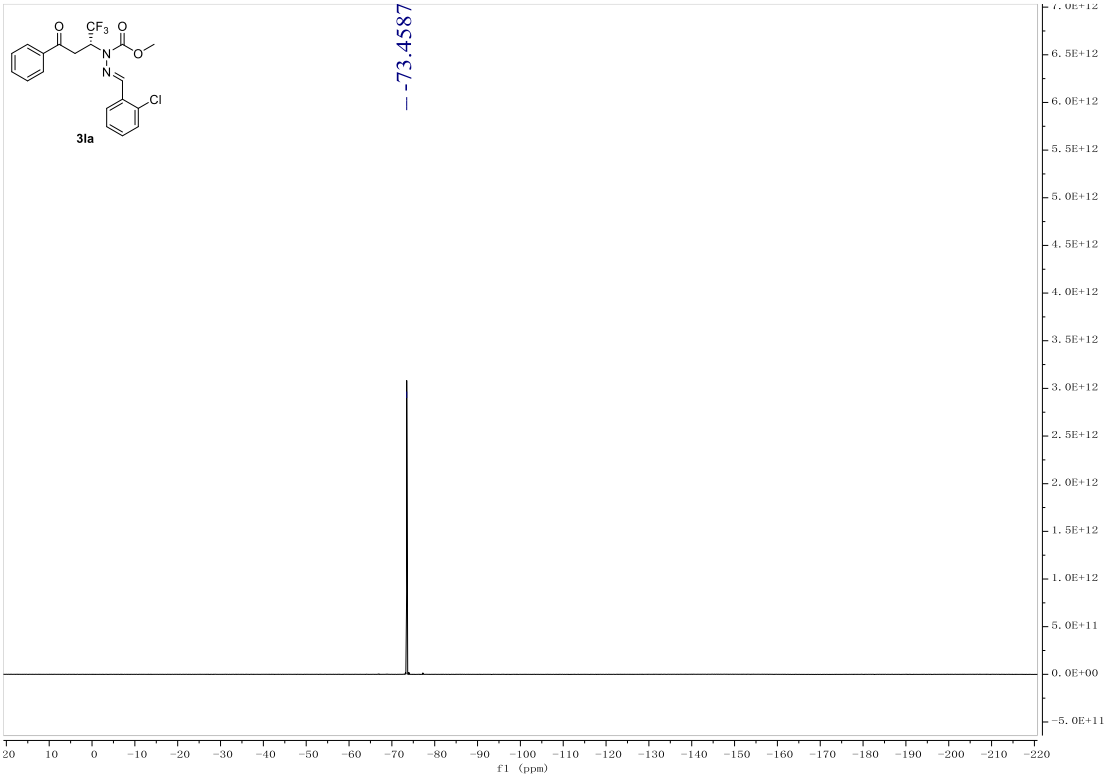
^{1}H NMR of 3la (400 MHz, $CDCl_3$)



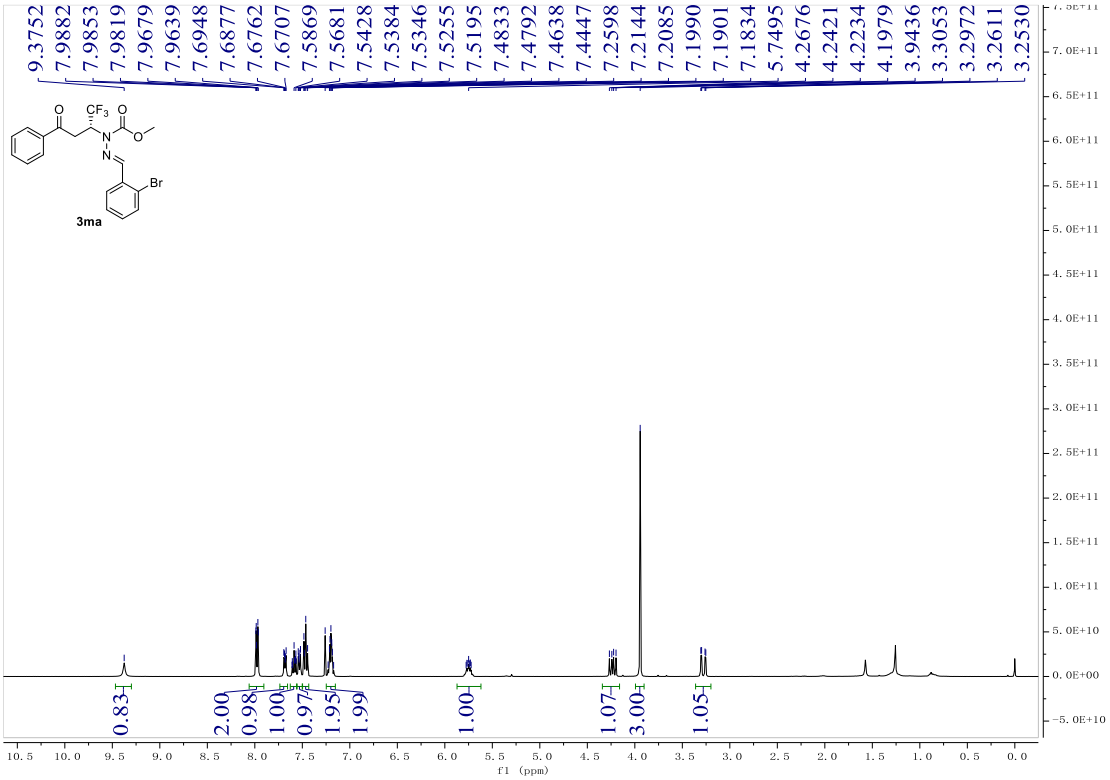
$^{13}C\{^{1}H\}$ NMR of 3la (100 MHz, $CDCl_3$)



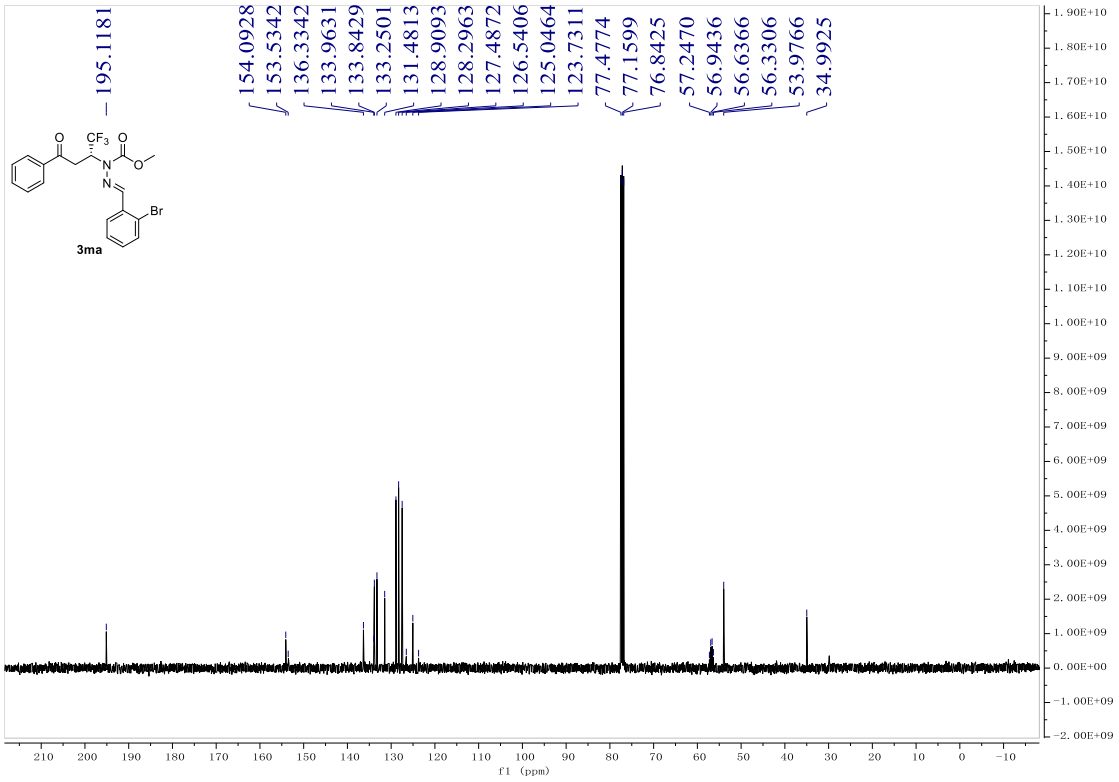
$^{19}F\{^{1}H\}$ NMR of 3la (376 MHz, $CDCl_3$)



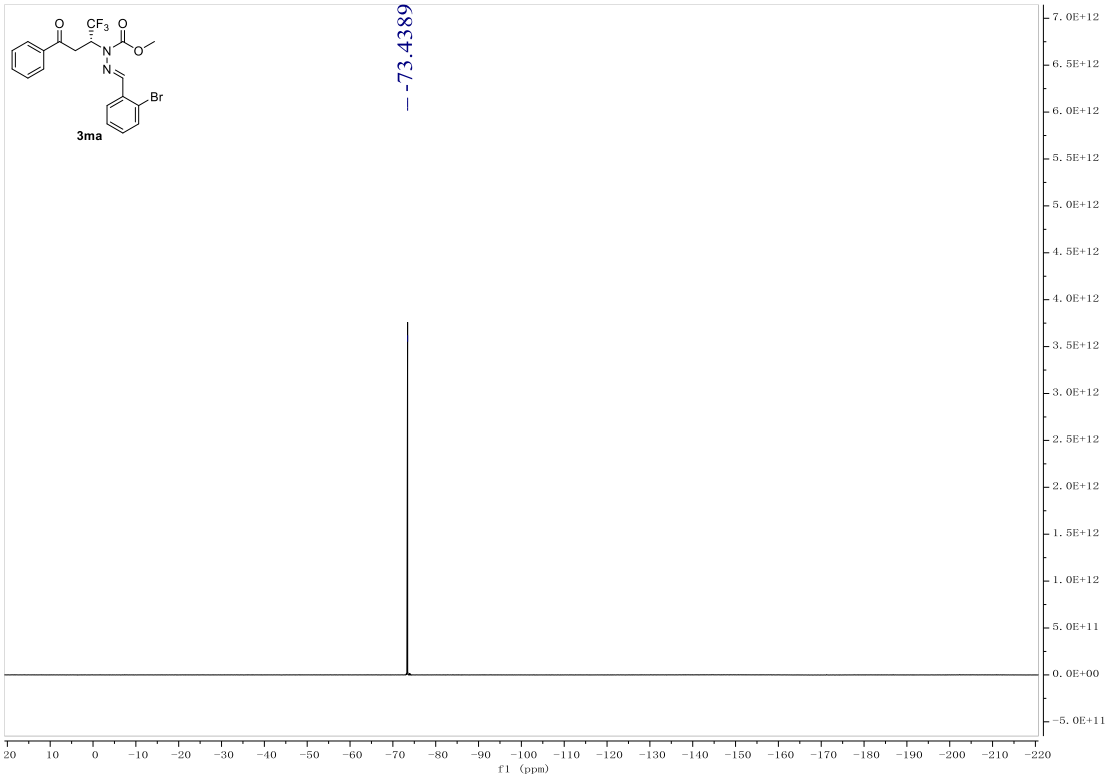
^{1}H NMR of 3ma (400 MHz, $CDCl_3$)



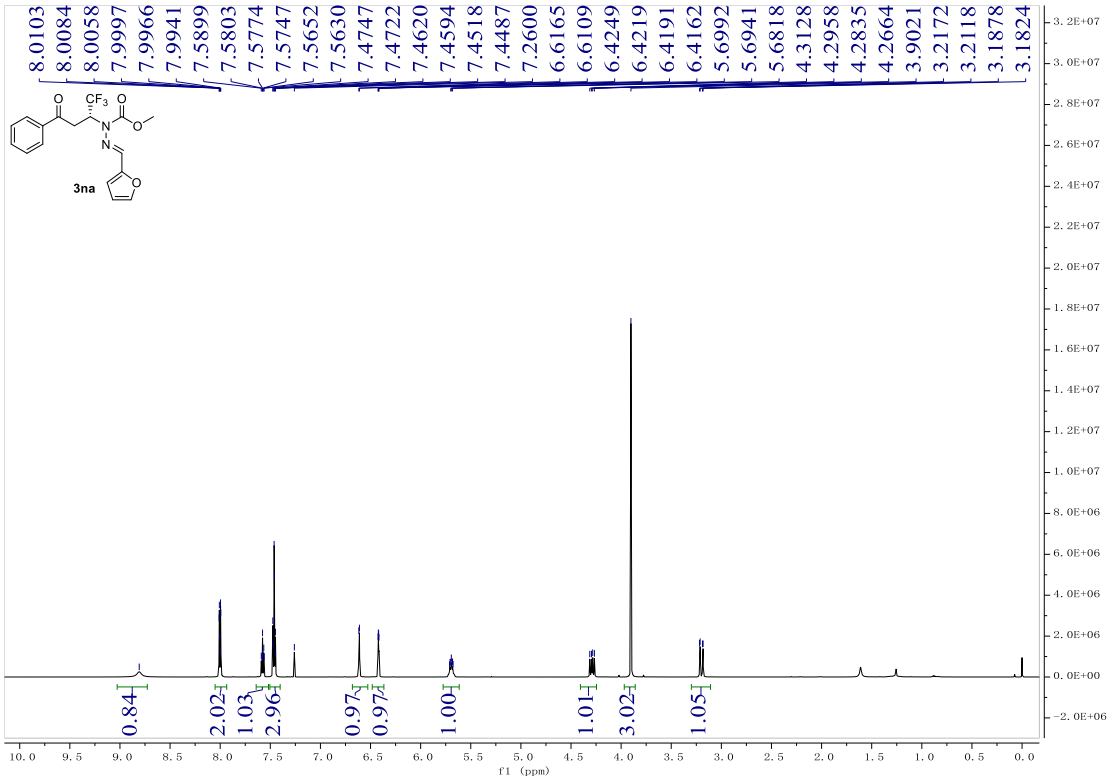
^{13}C{^{1}H} NMR of 3ma (100 MHz, $CDCl_3$)



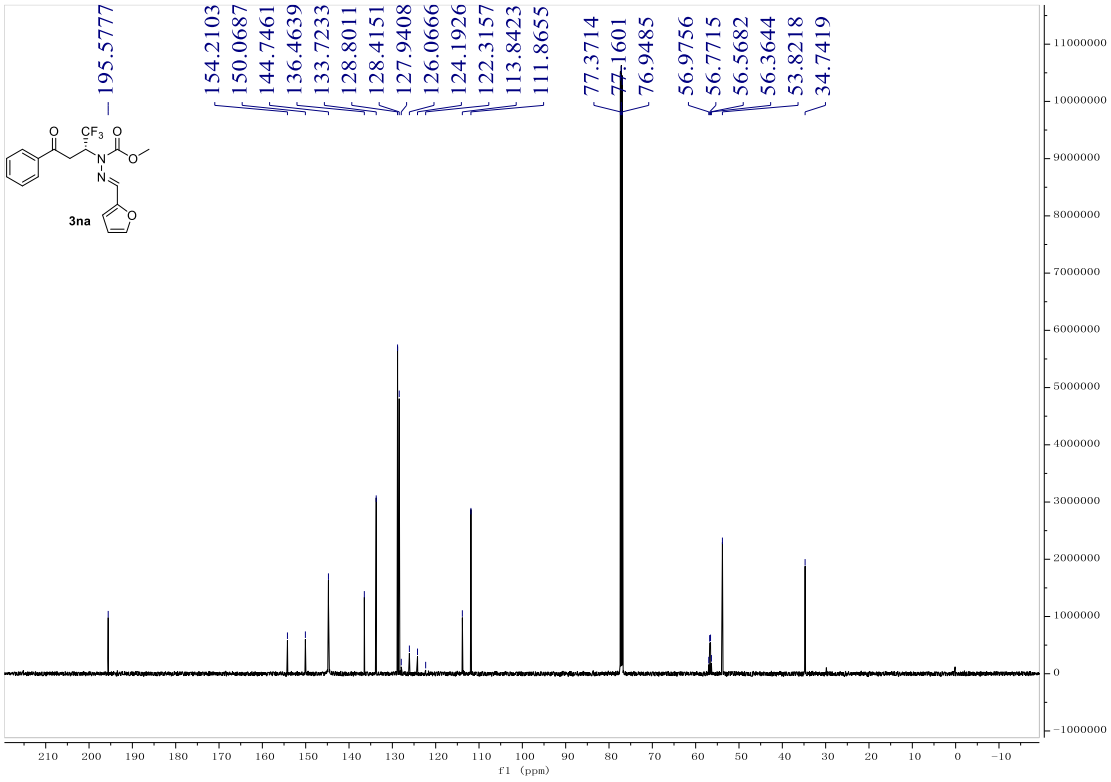
$^{19}F\{^{1}H\}$ NMR of 3ma (376 MHz, $CDCl_3$)



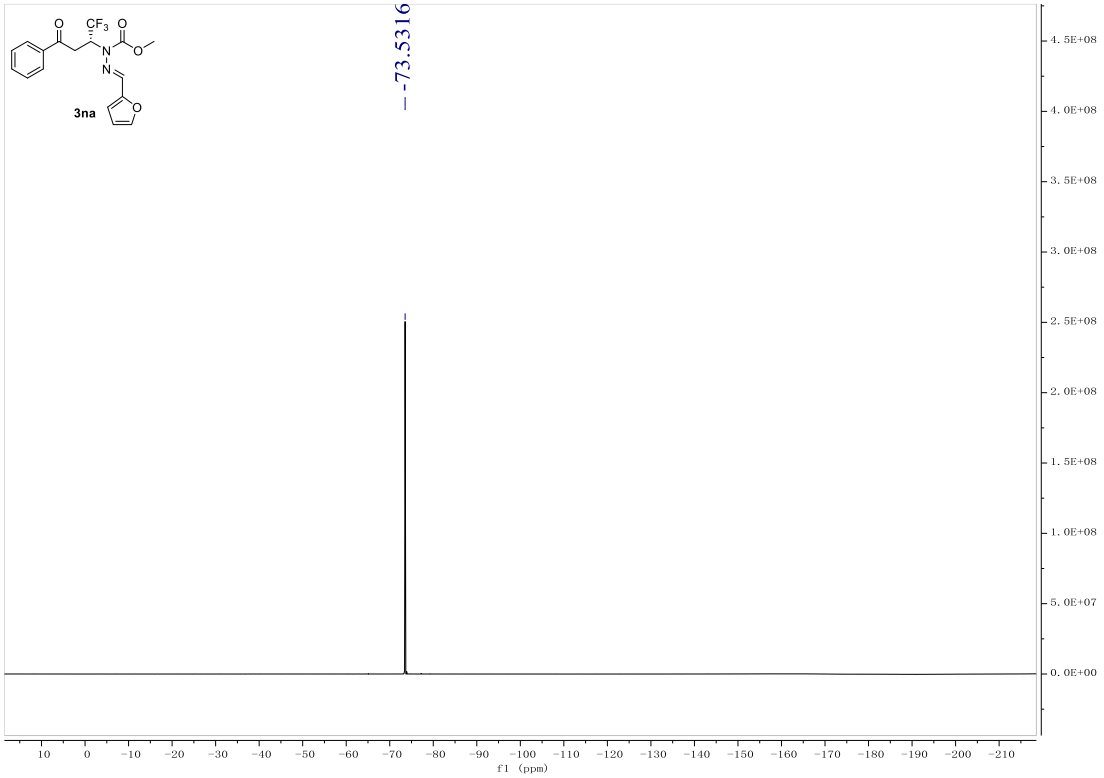
^{1}H NMR of 3na (600 MHz, $CDCl_3$)



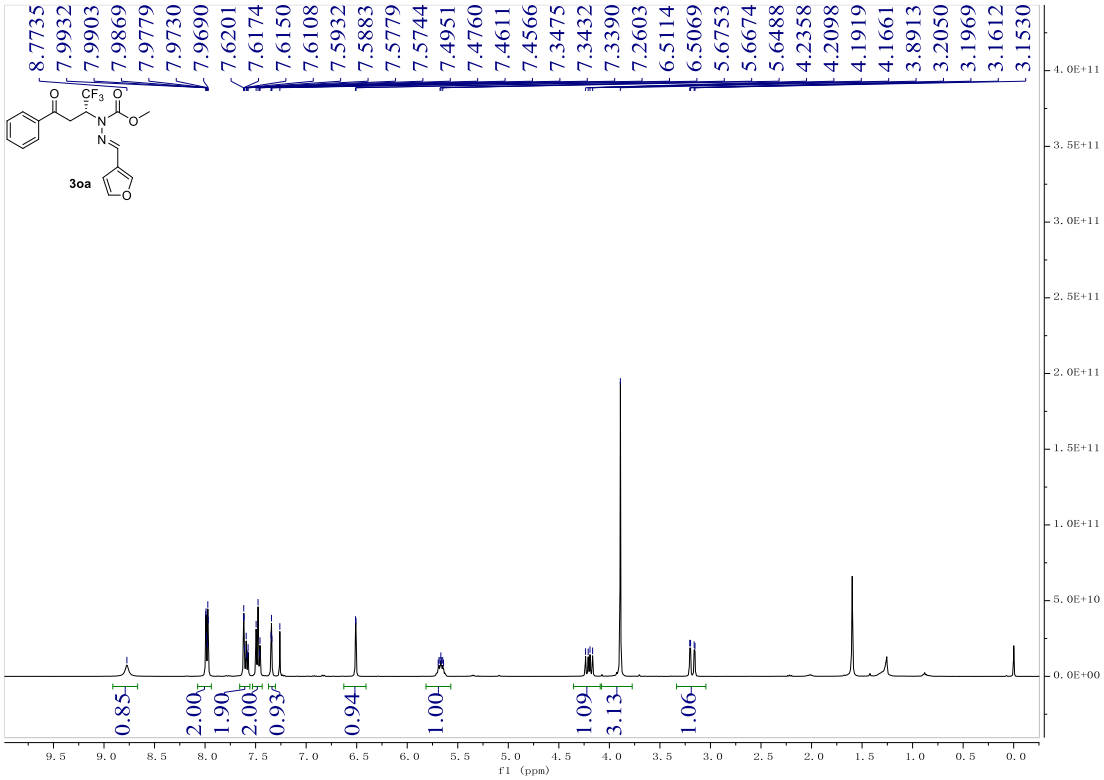
$^{13}C\{^{1}H\}$ NMR of 3na (150 MHz, $CDCl_3$)



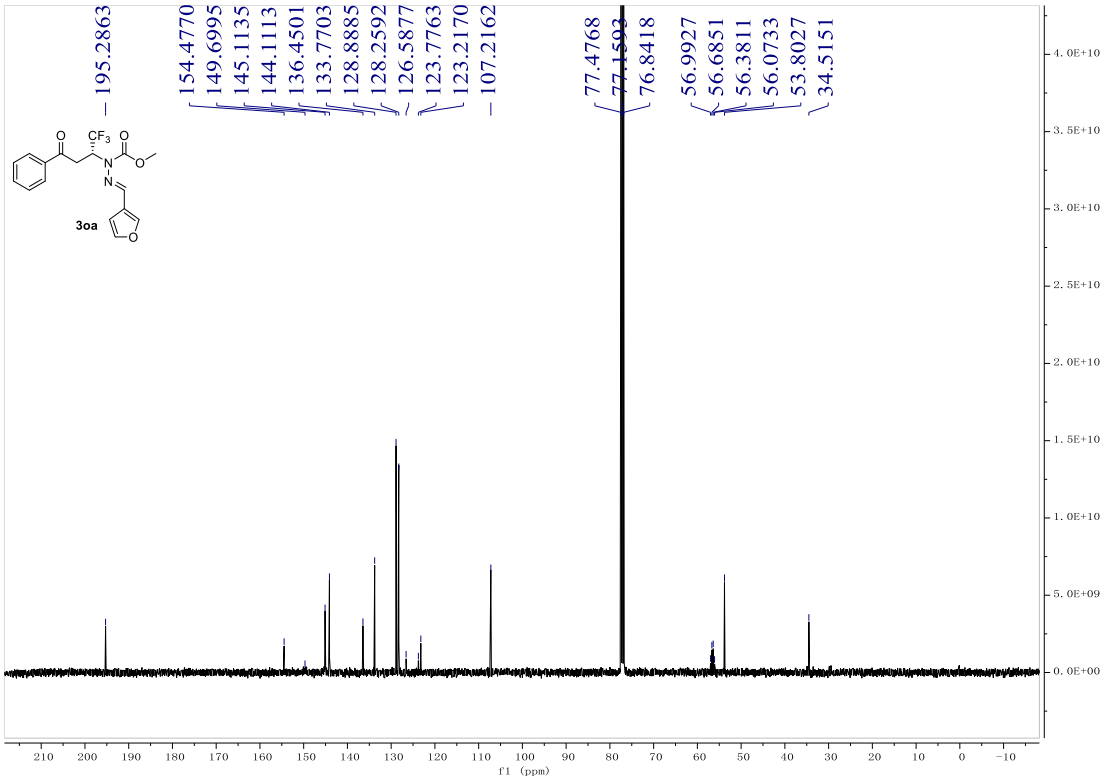
$^{19}F\{^{1}H\}$ NMR of 3na (565 MHz, $CDCl_3$)



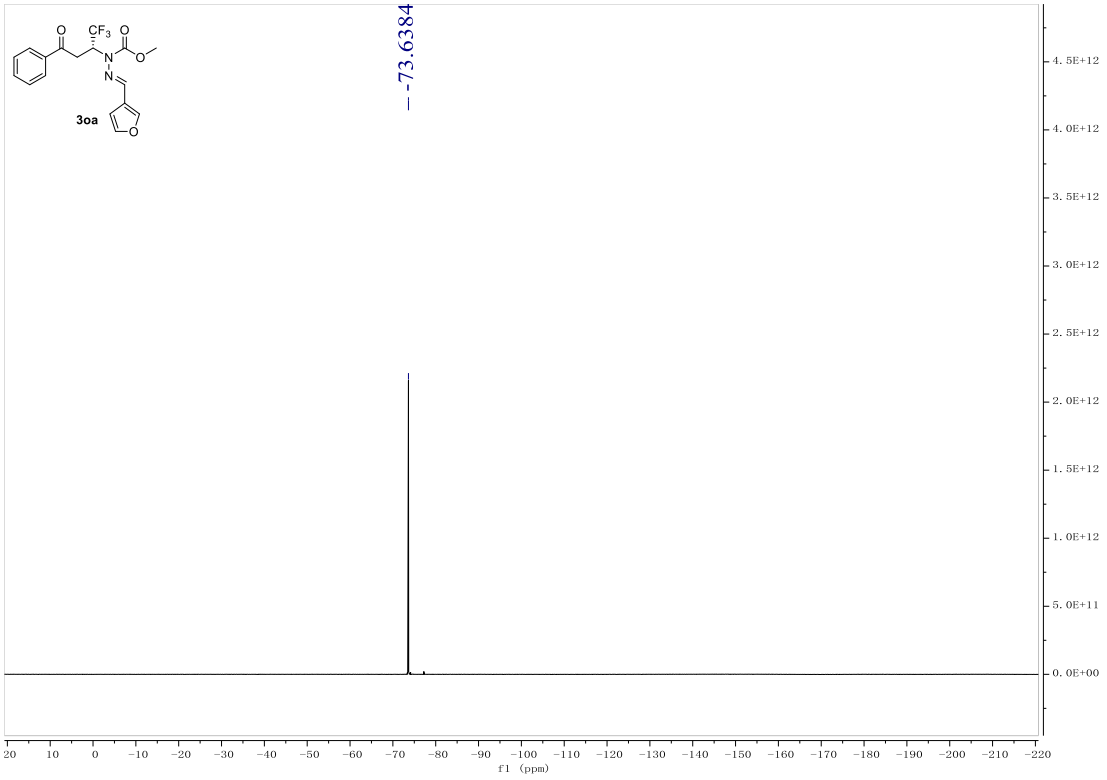
^{1}H NMR of 3oa (400 MHz, $CDCl_3$)



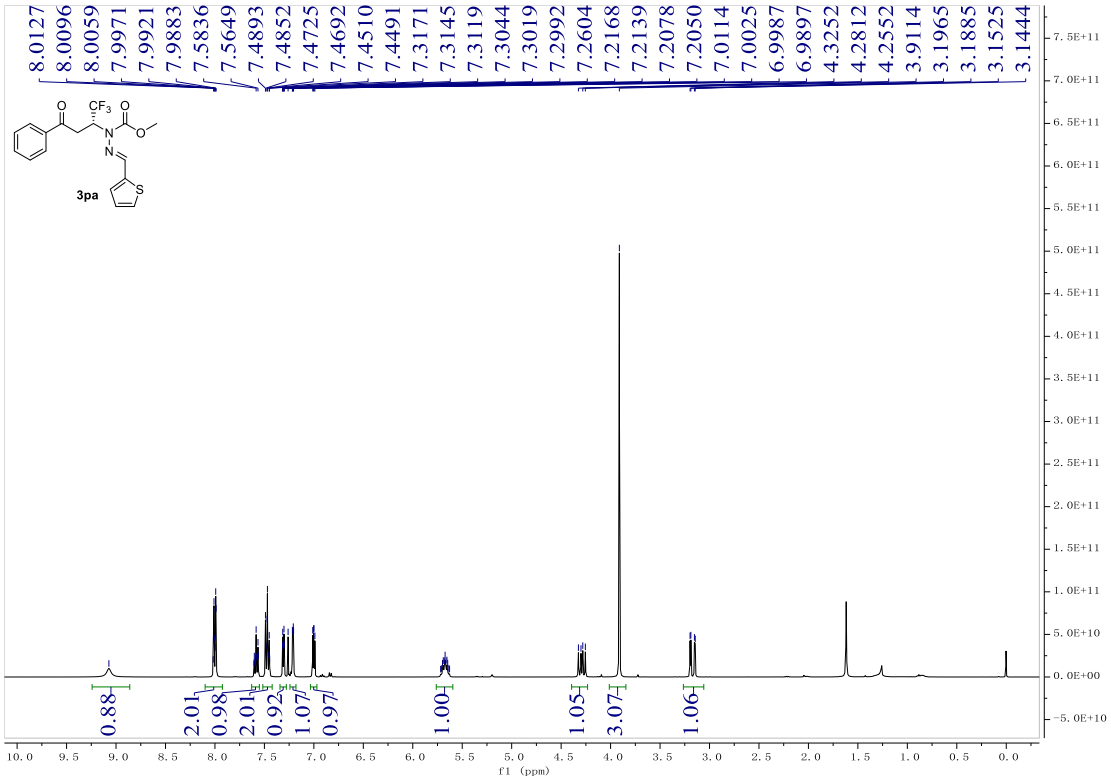
^{13}C{^{1}H} NMR of 3oa (100 MHz, $CDCl_3$)



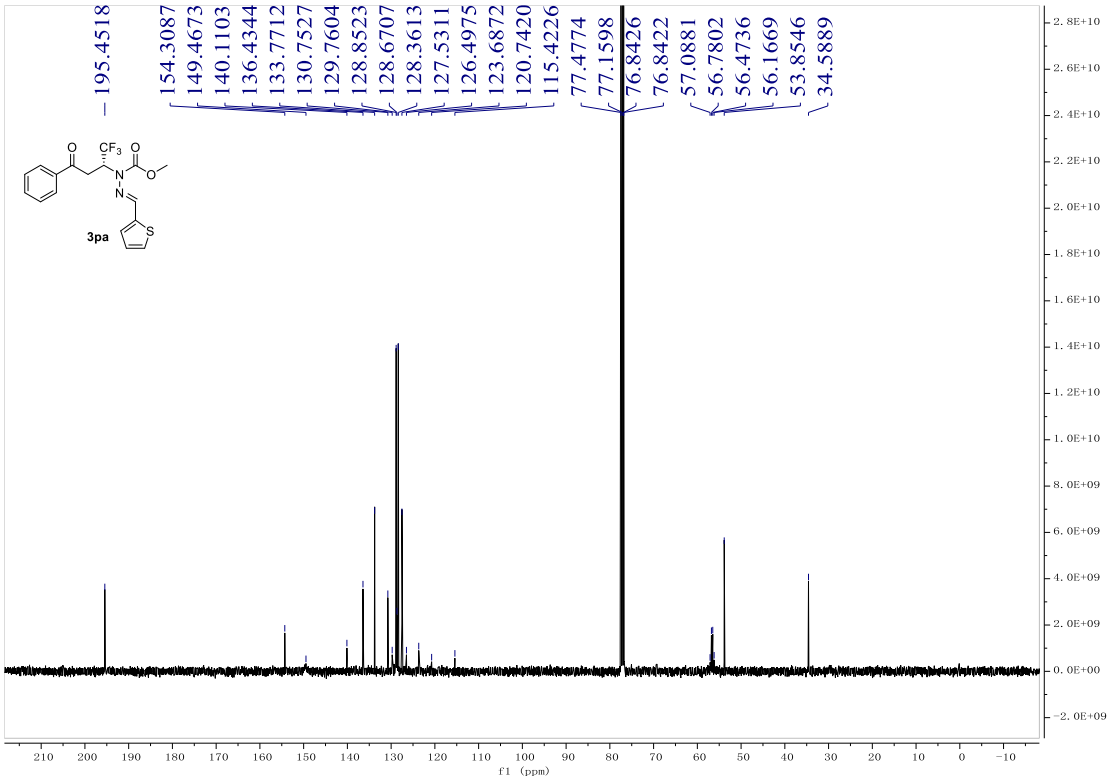
$^{19}F\{^{1}H\}$ NMR of 3oa (376 MHz, $CDCl_3$)



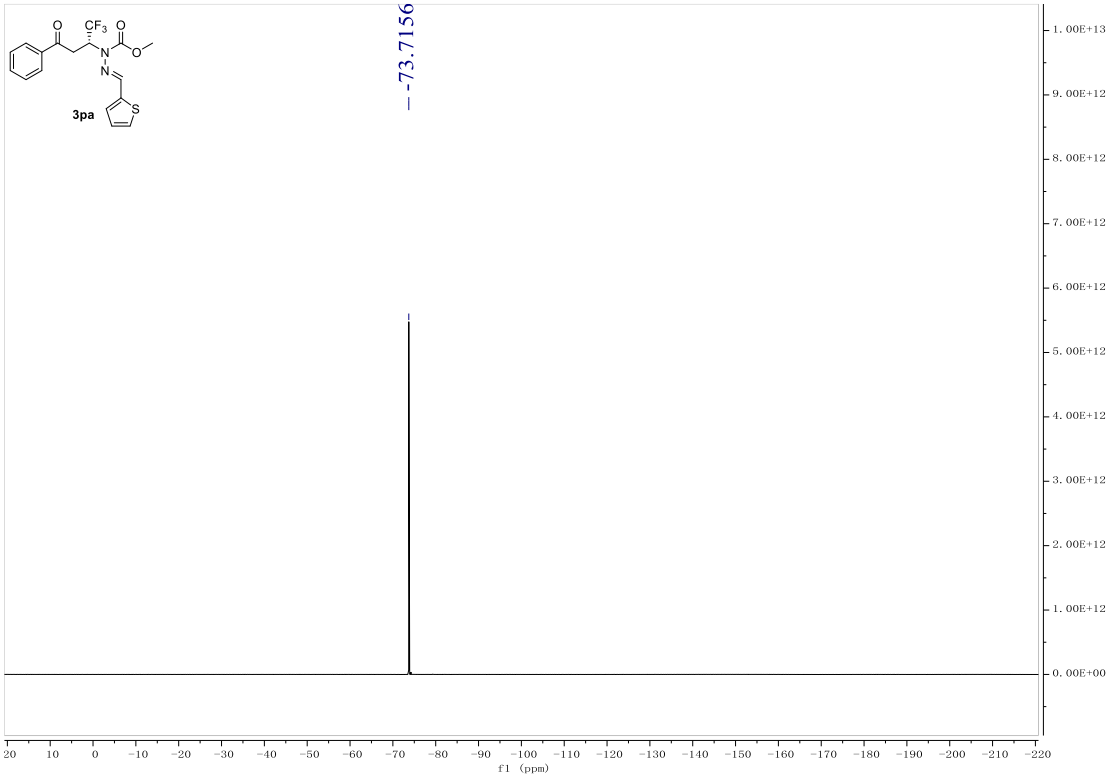
^{1}H NMR of 3pa (400 MHz, $CDCl_3$)



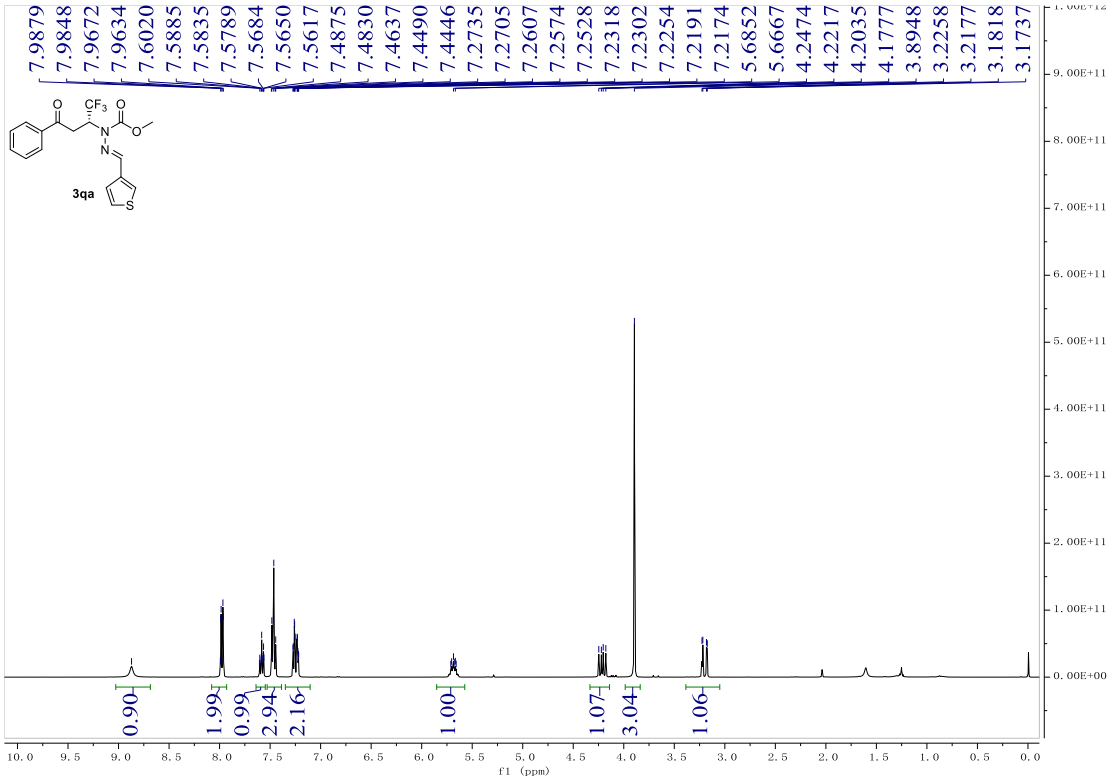
$^{13}C\{^{1}H\}$ NMR of 3pa (100 MHz, $CDCl_3$)



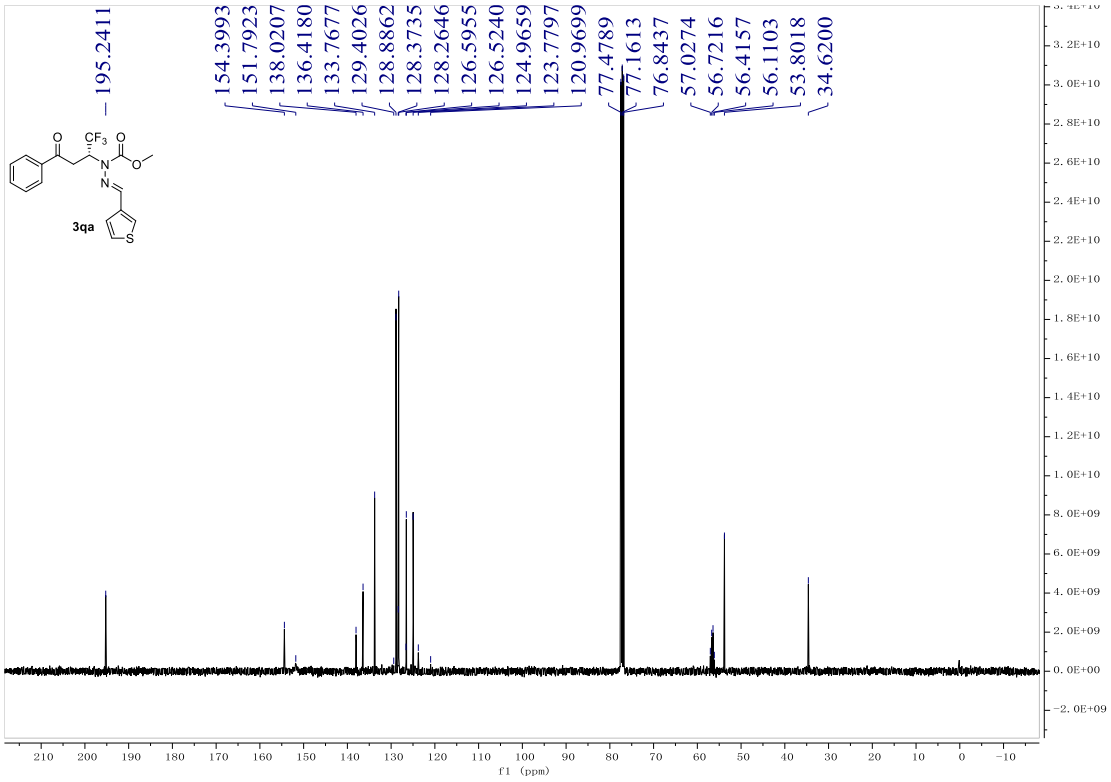
$^{19}F\{^{1}H\}$ NMR of 3pa (376 MHz, $CDCl_3$)



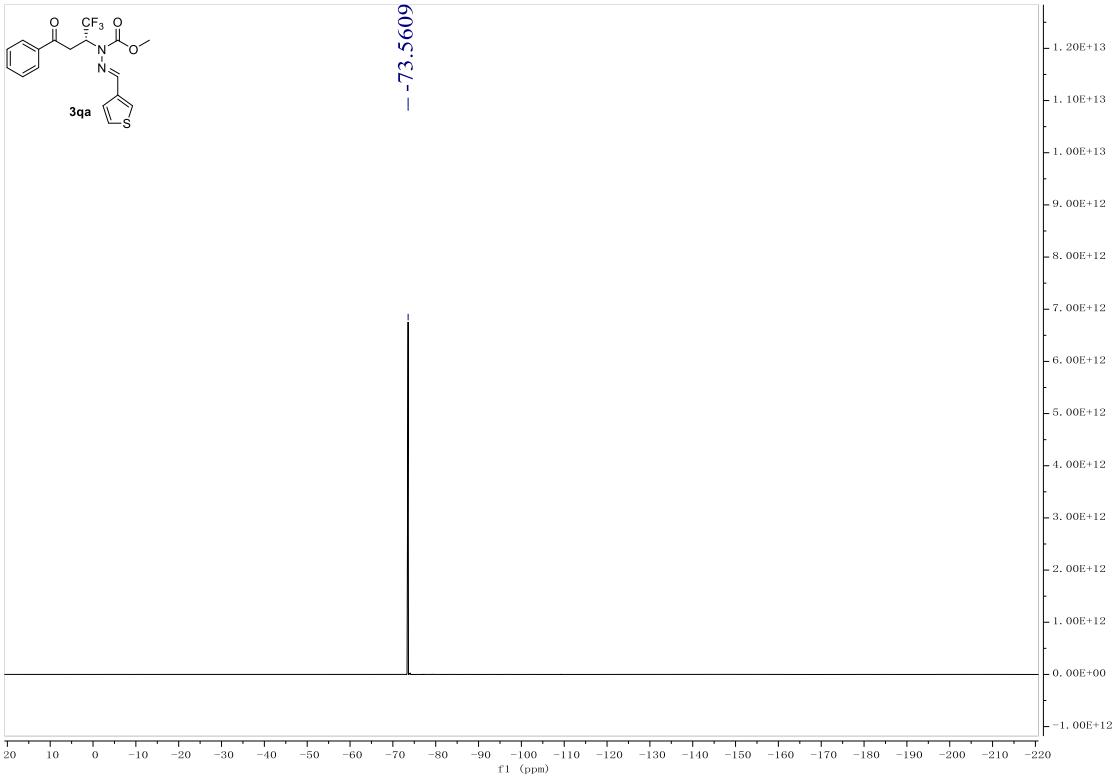
^{1}H NMR of 3qa (400 MHz, $CDCl_3$)



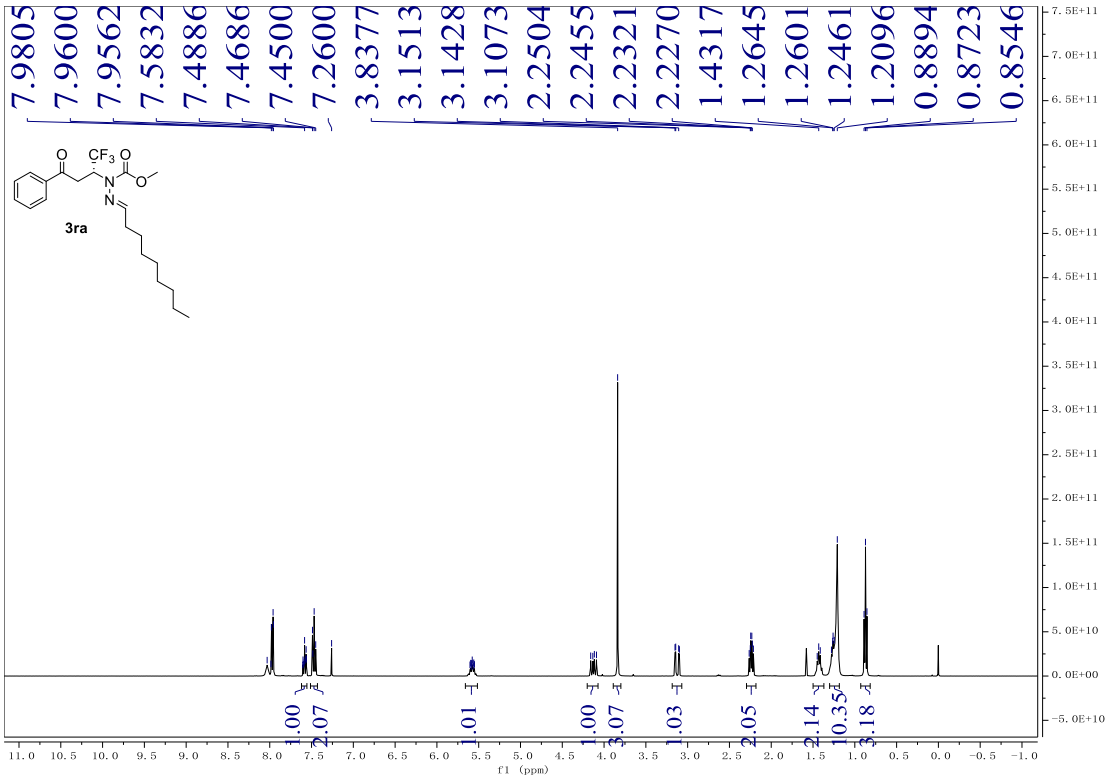
^{13}C{^{1}H} NMR of 3qa (100 MHz, $CDCl_3$)



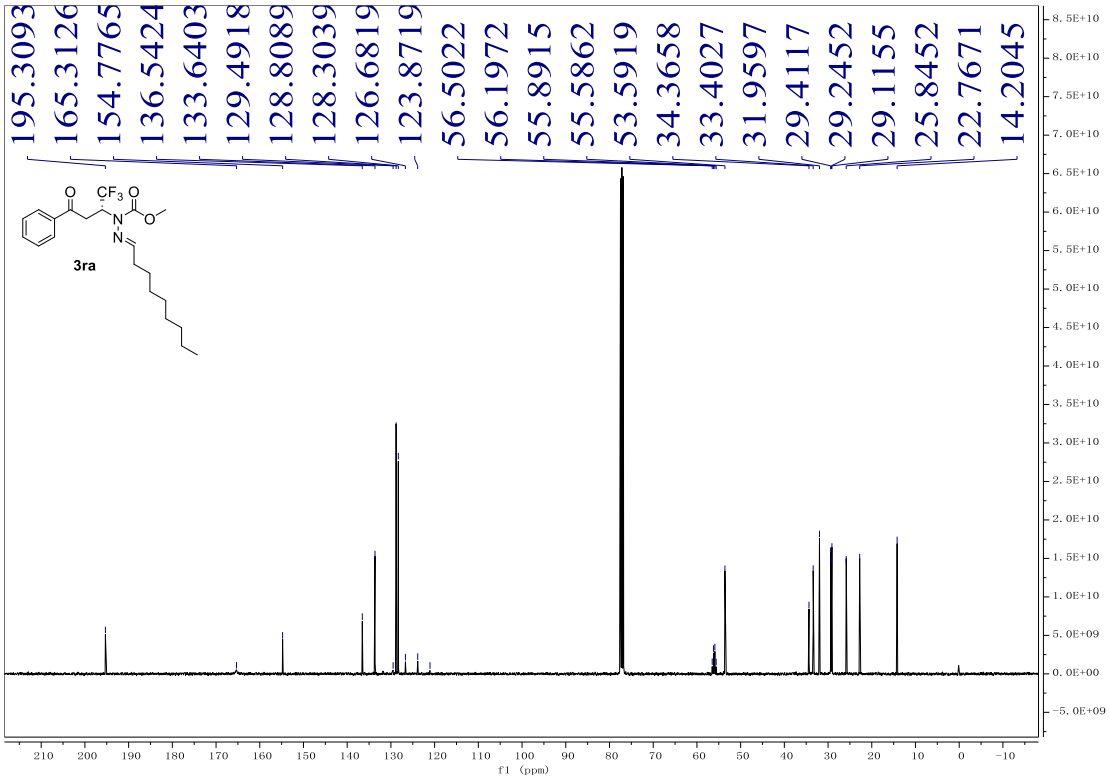
$^{19}F\{^{1}H\}$ NMR of 3qa (376 MHz, $CDCl_3$)



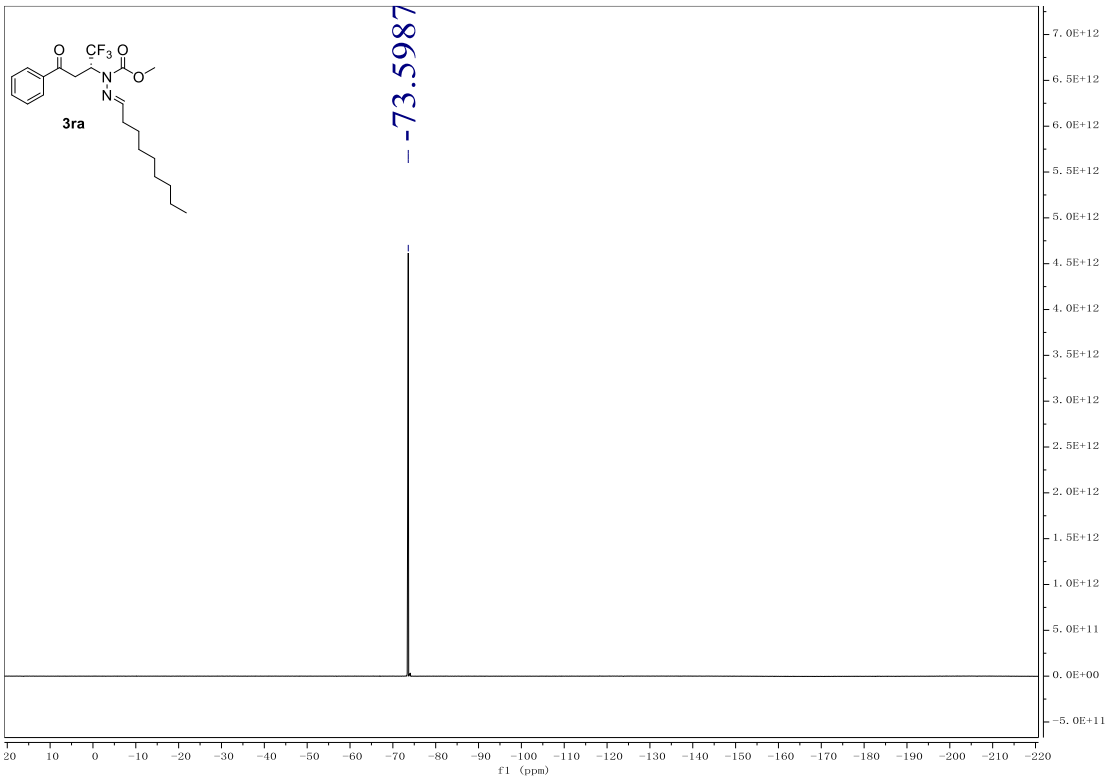
^{1}H NMR of 3ra (400 MHz, $CDCl_3$)



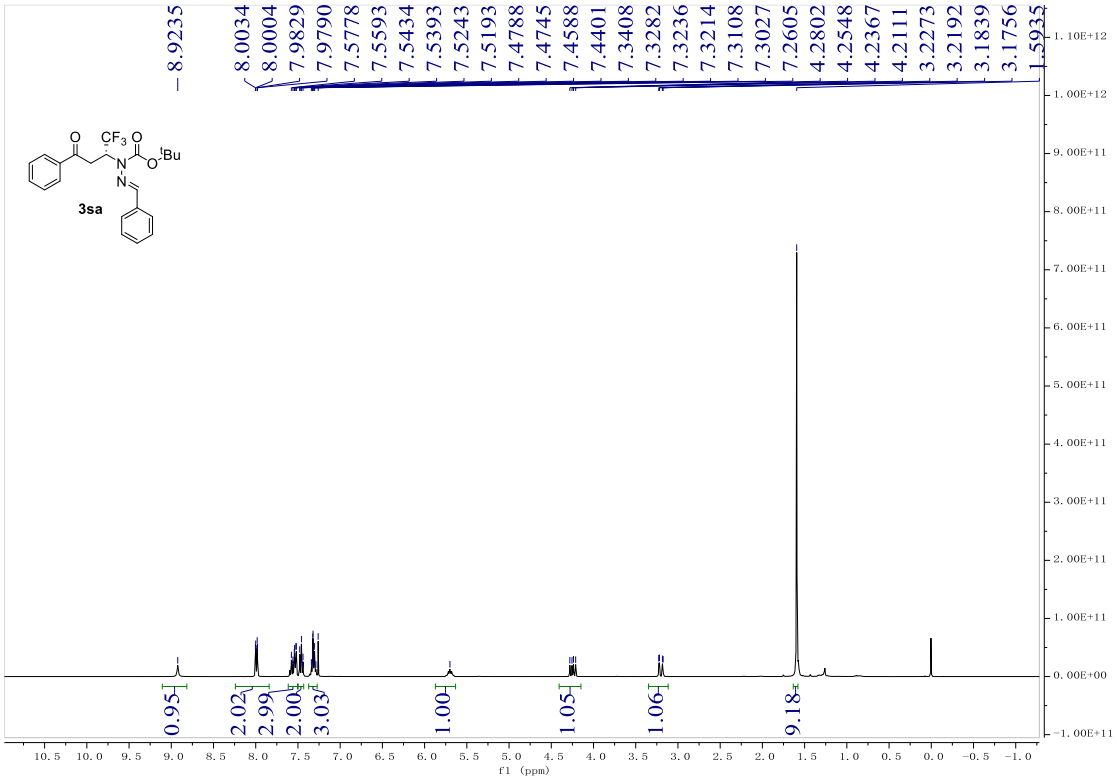
$^{13}C\{^{1}H\}$ NMR of 3ra (100 MHz, $CDCl_3$)



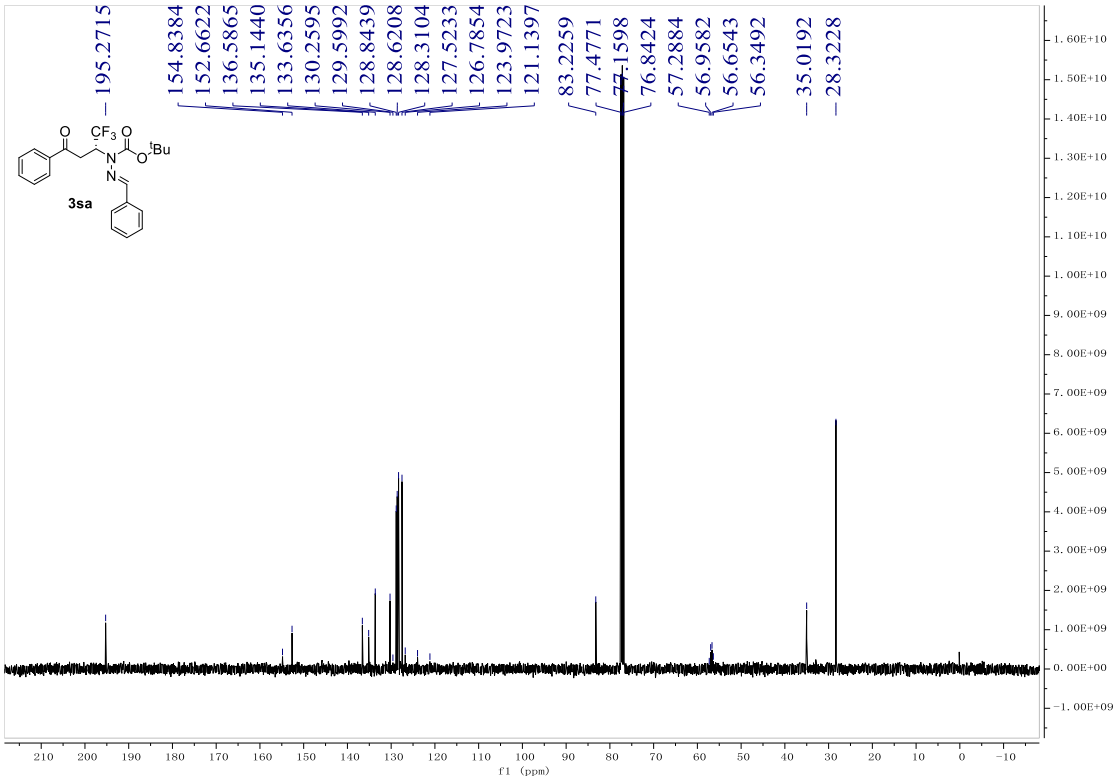
$^{19}F\{^{1}H\}$ NMR of 3ra (376 MHz, $CDCl_3$)



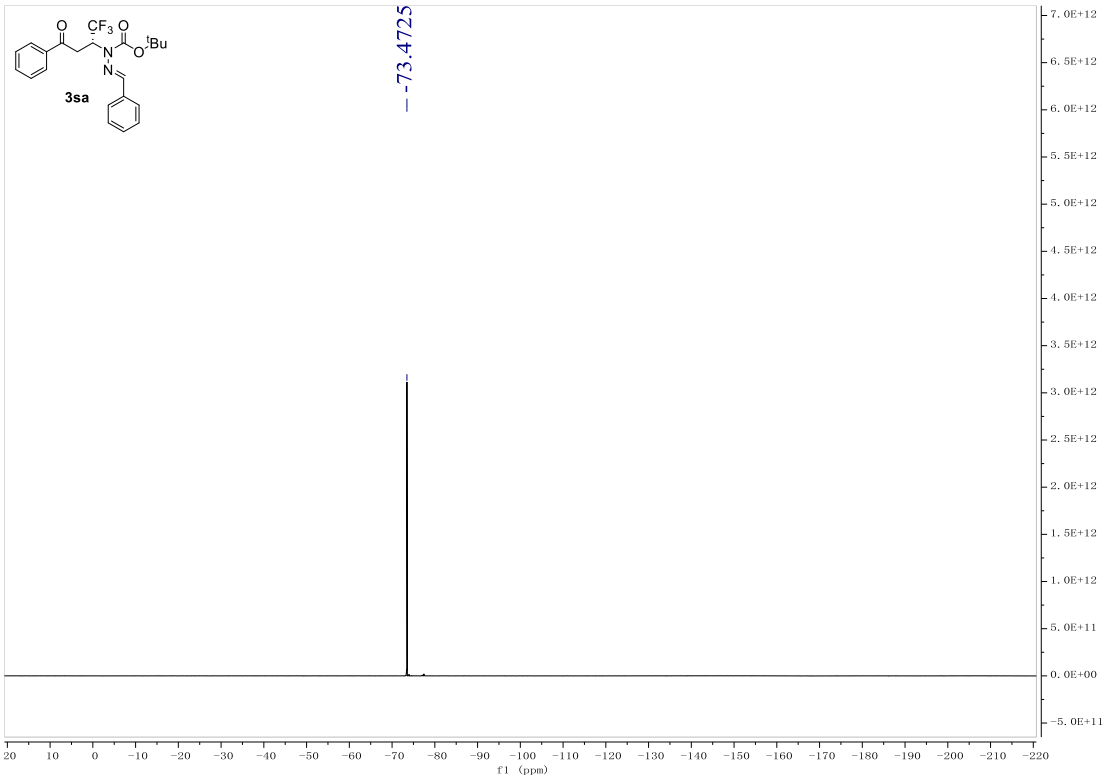
^{1}H NMR of 3sa (400 MHz, $CDCl_3$)



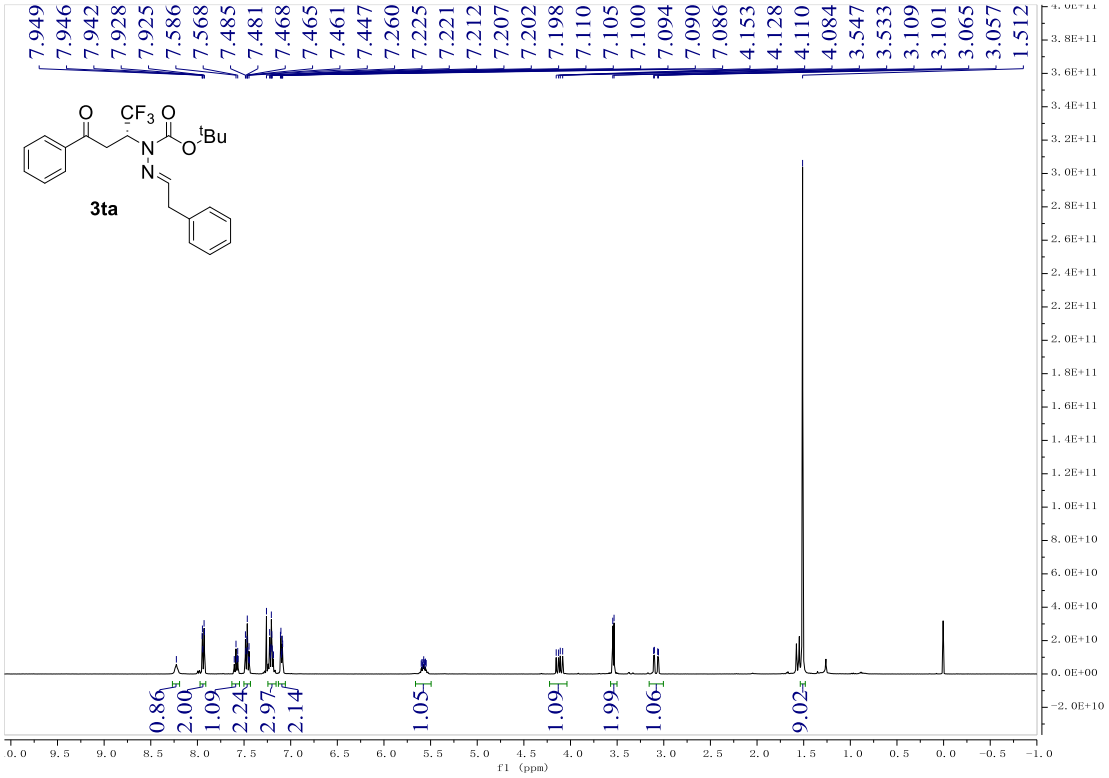
^{13}C{^{1}H} NMR of 3sa (100 MHz, $CDCl_3$)



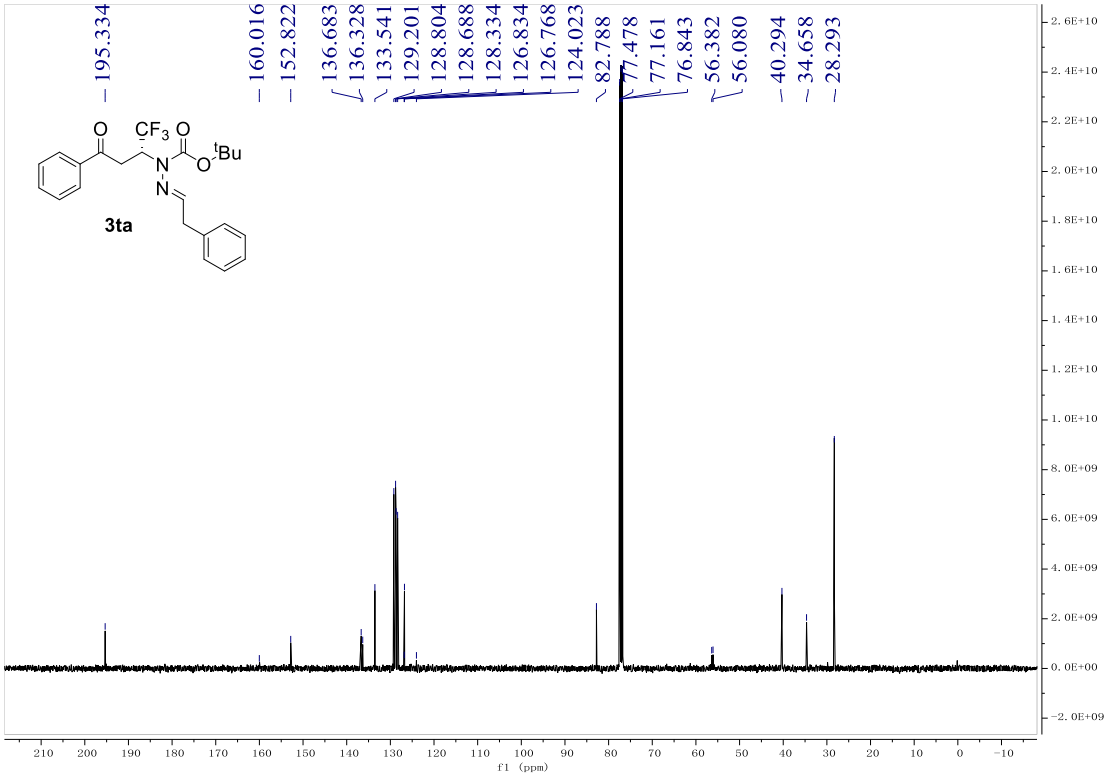
$^{19}F\{^{1}H\}$ NMR of 3sa (376 MHz, $CDCl_3$)



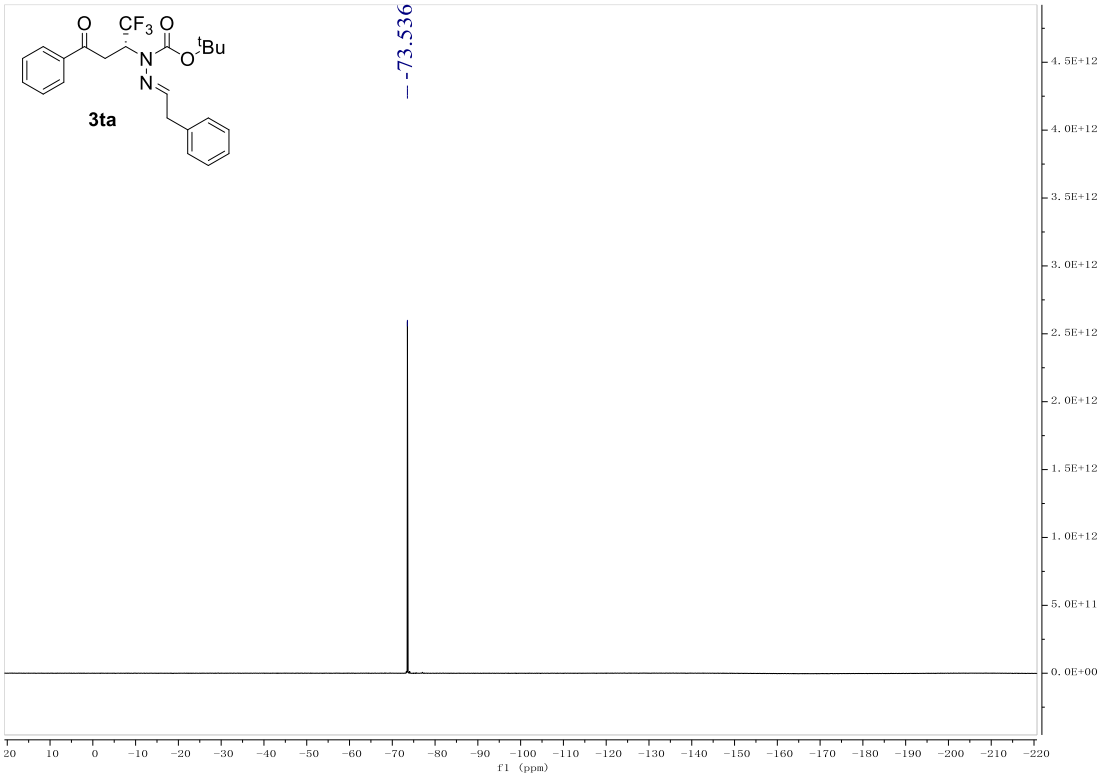
^{1}H NMR of 3ta (400 MHz, $CDCl_3$)



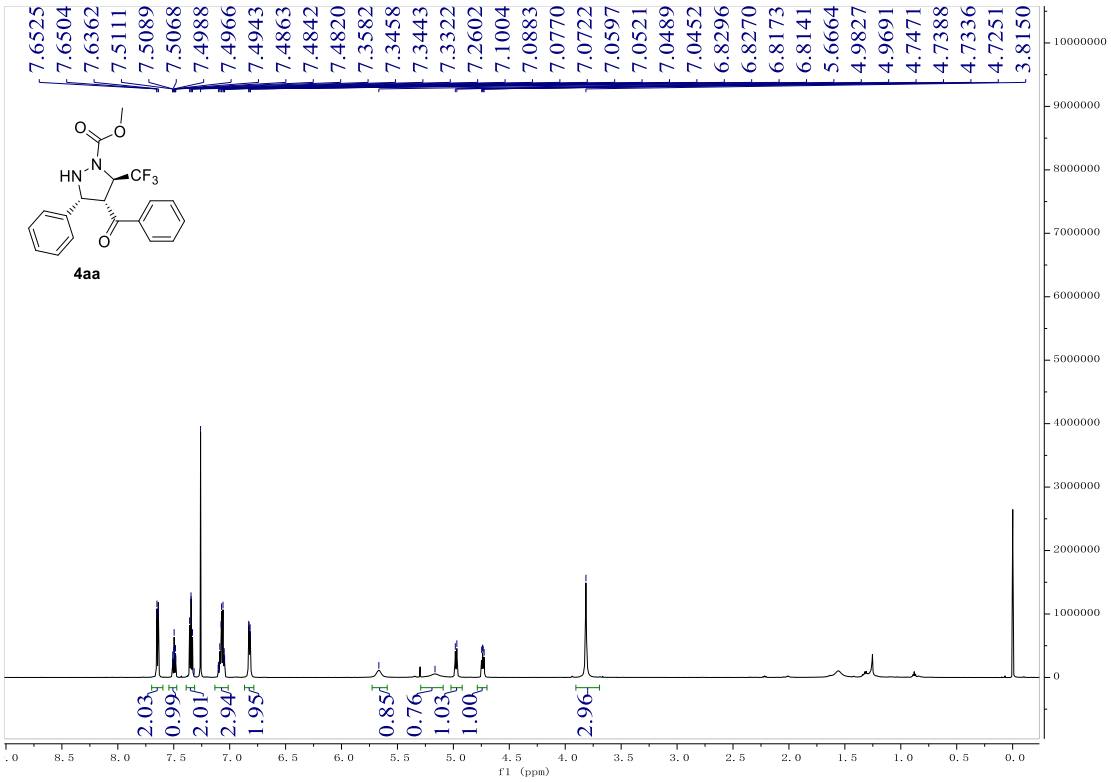
$^{13}C\{^{1}H\}$ NMR of 3ta (100 MHz, $CDCl_3$)



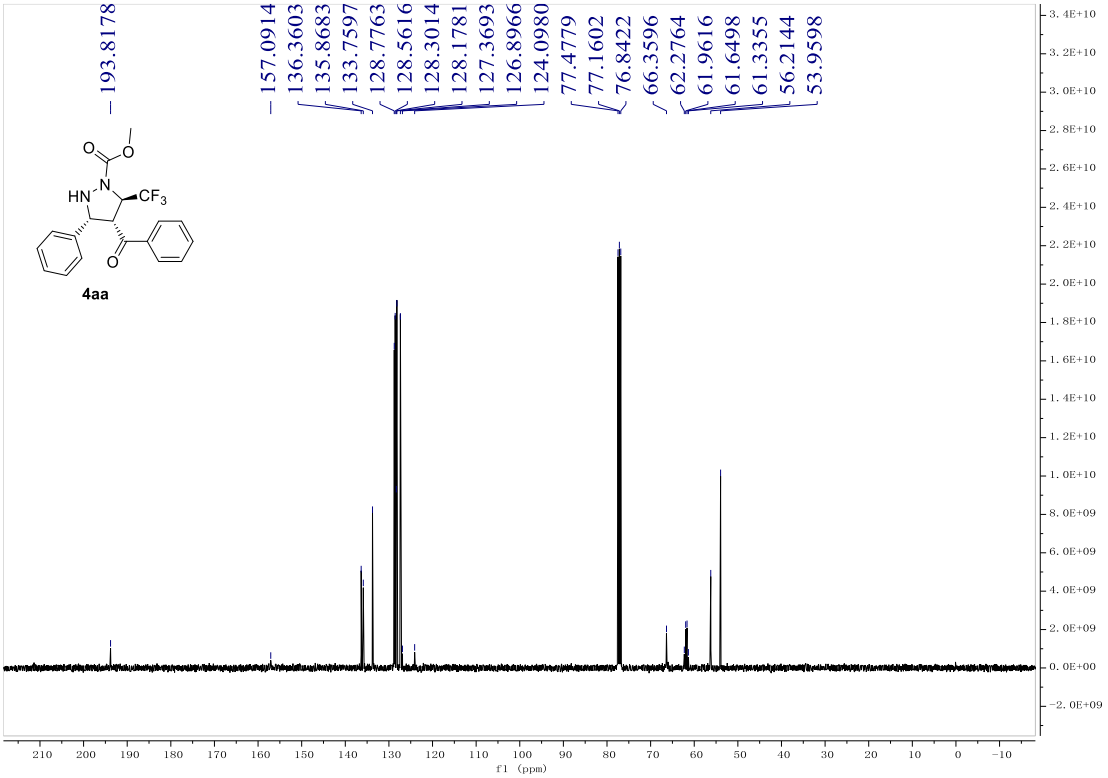
$^{19}F\{^{1}H\}$ NMR of 3ta (376 MHz, $CDCl_3$)



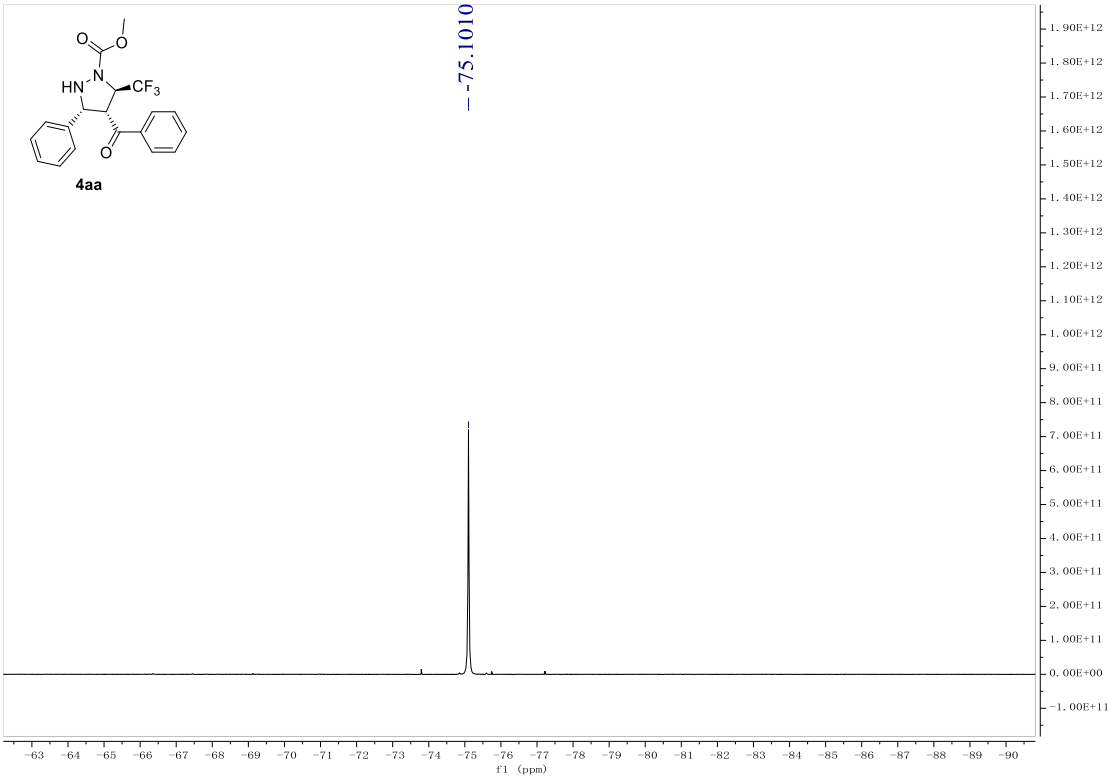
^{1}H NMR of 4aa (600 MHz, $CDCl_3$)



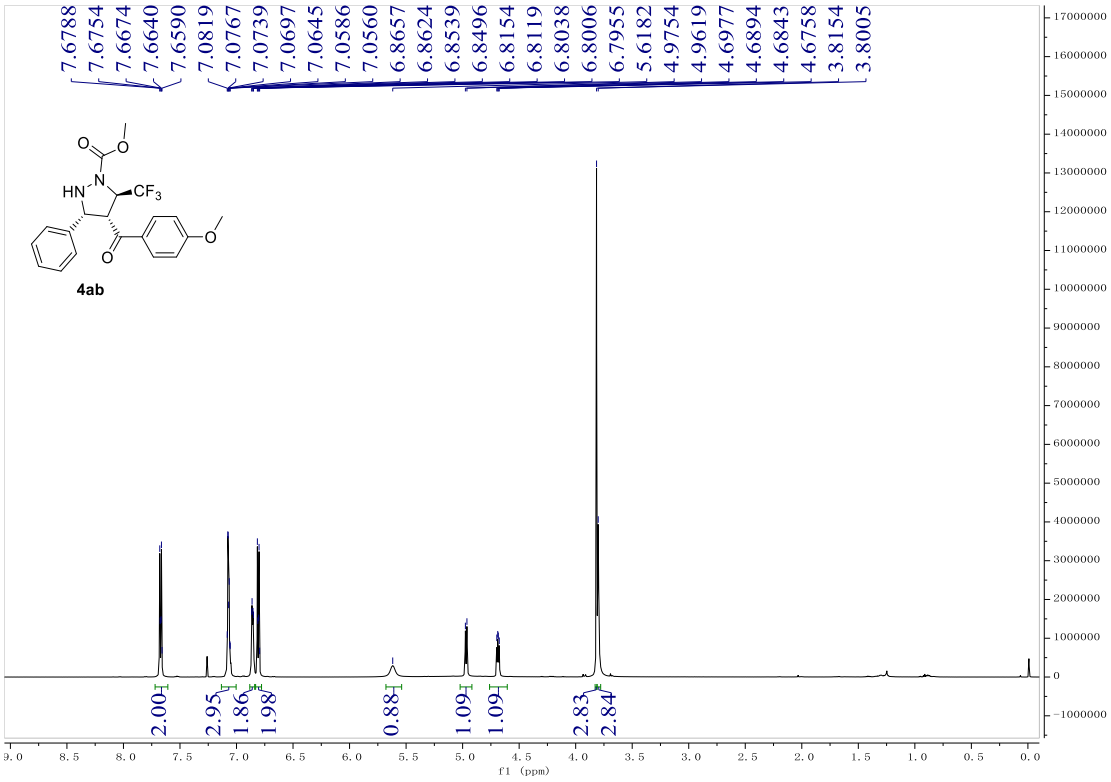
^{13}C{^{1}H} NMR of 4aa (100 MHz, $CDCl_3$)



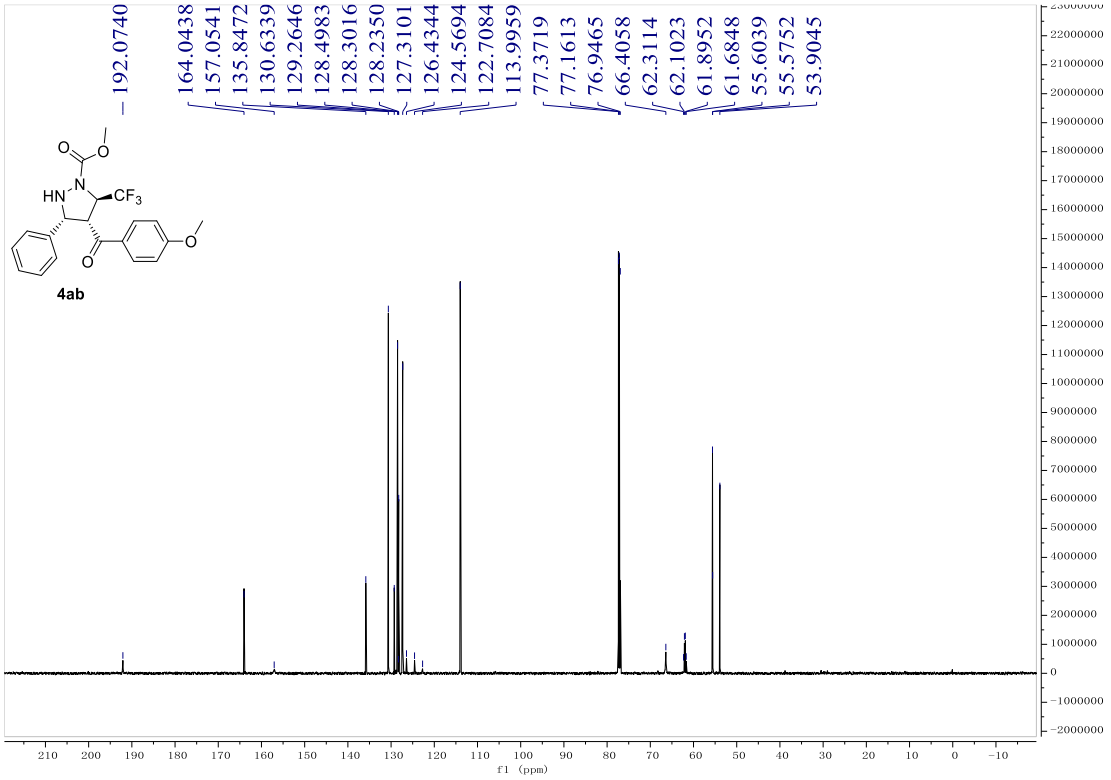
$^{19}F\{^{1}H\}$ NMR of 4aa (376 MHz, $CDCl_3$)



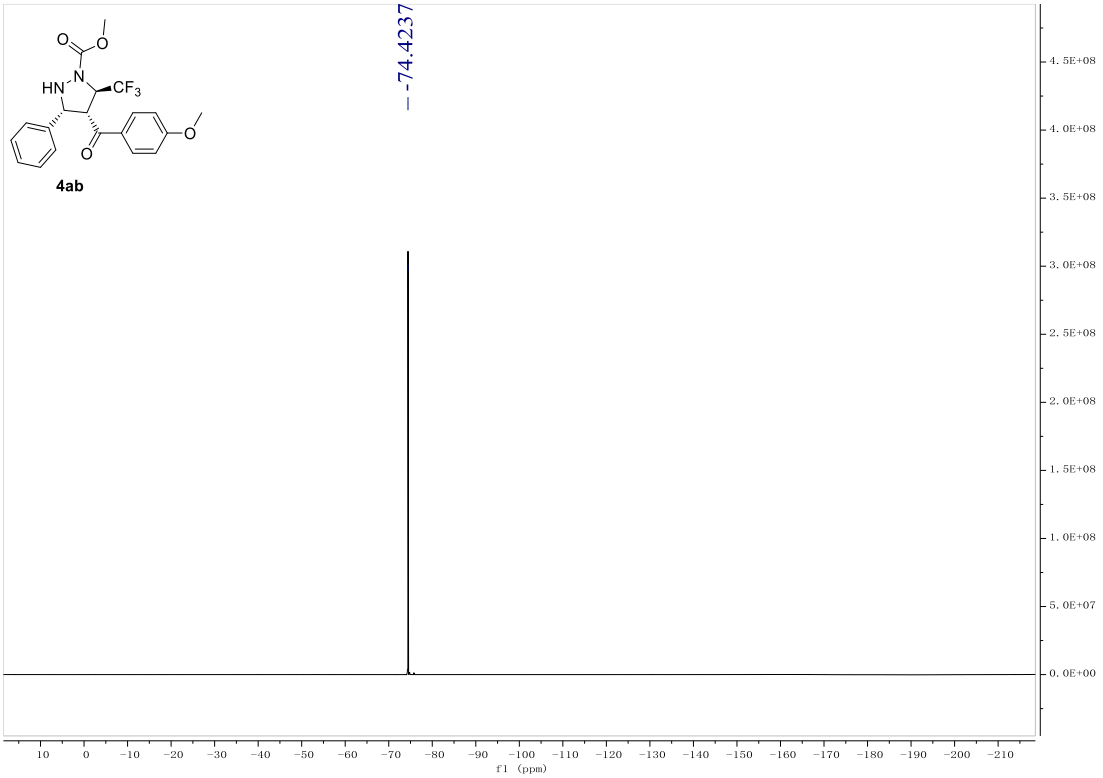
^{1}H NMR of 4ab (600 MHz, $CDCl_3$)



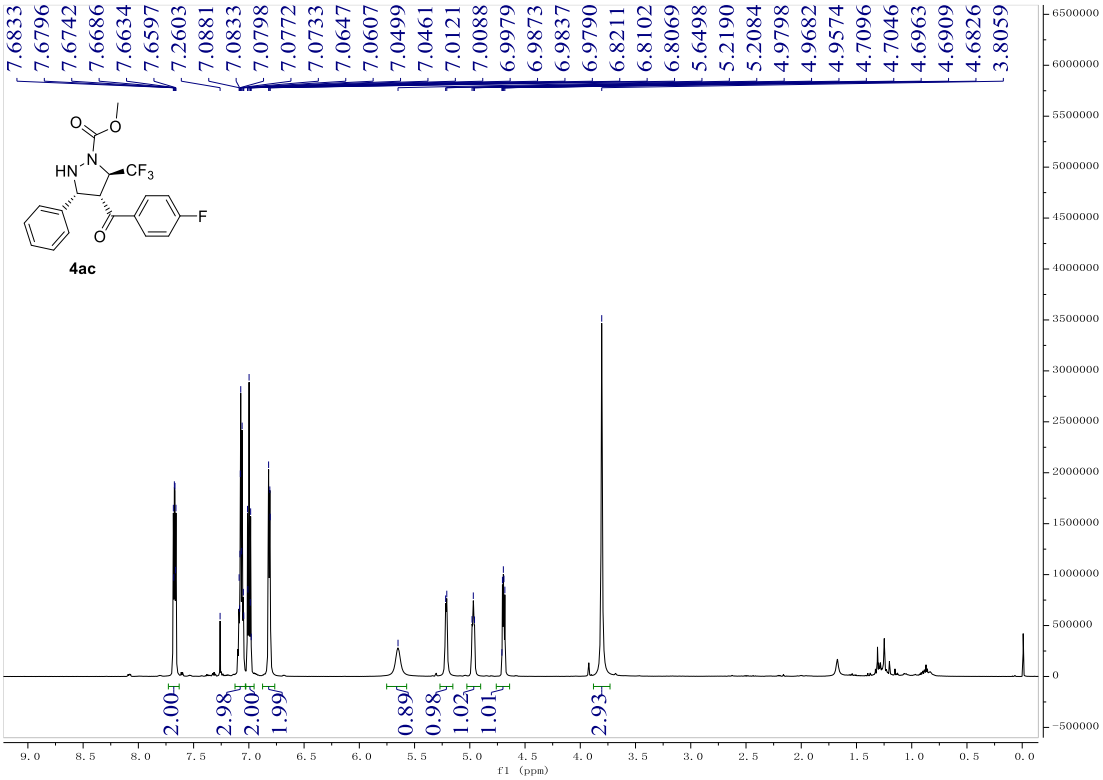
$^{13}C\{^{1}H\}$ NMR of 4ab (150 MHz, $CDCl_3$)



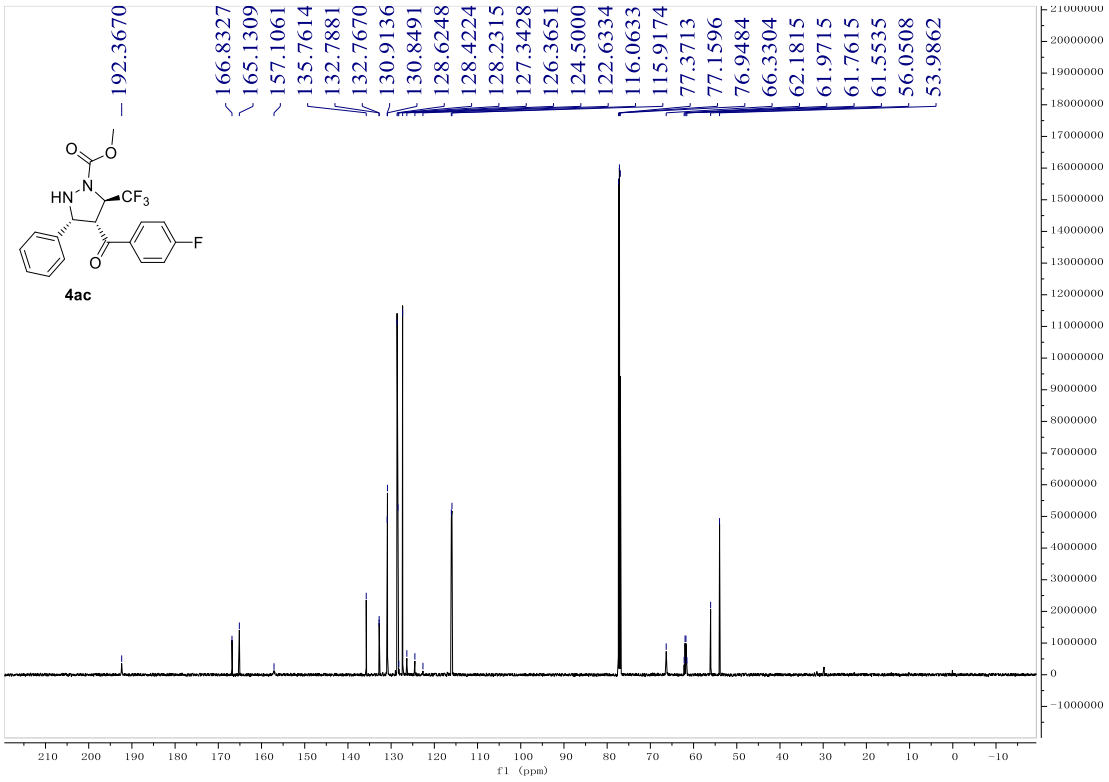
$^{19}F\{^{1}H\}$ NMR of 4ab (565 MHz, $CDCl_3$)



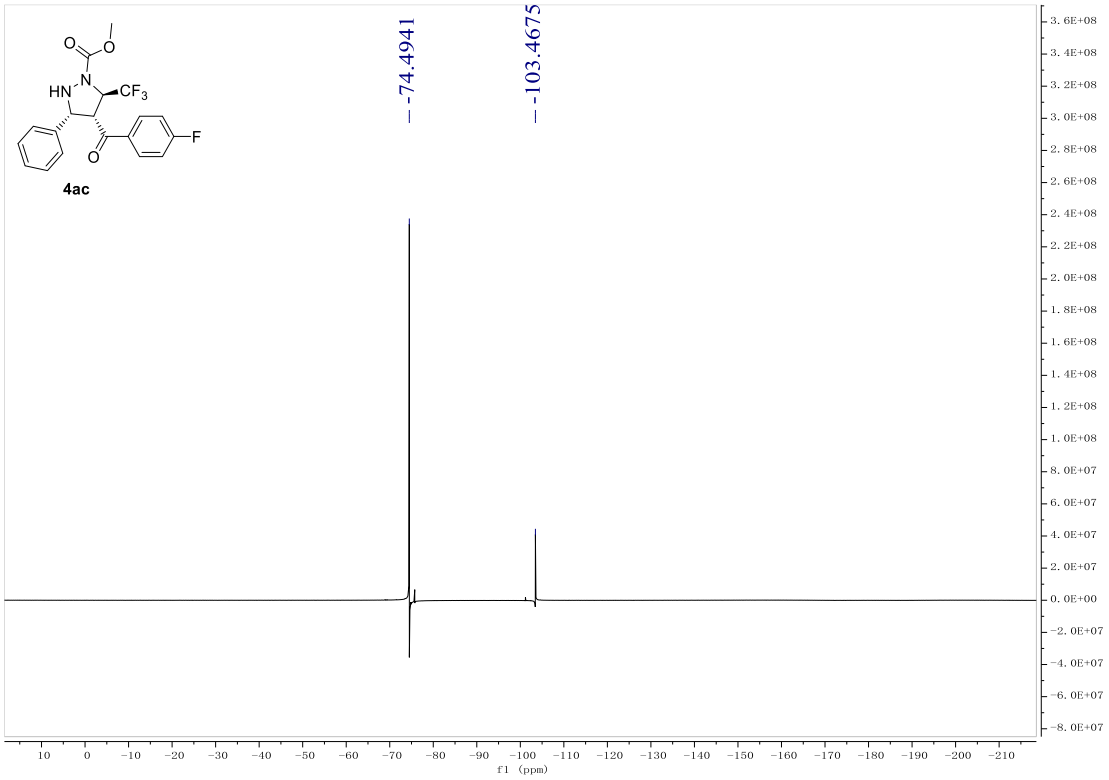
^{1}H NMR of 4ac (600 MHz, $CDCl_3$)



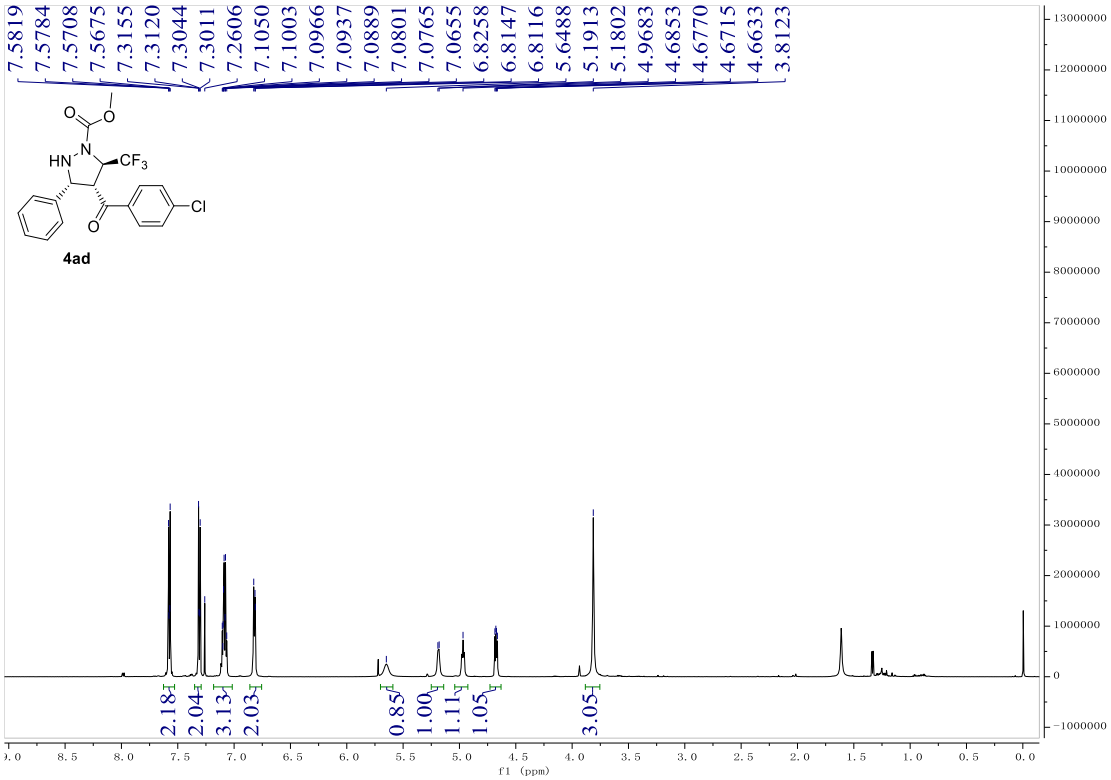
^{13}C{^{1}H} NMR of 4ac (150 MHz, $CDCl_3$)



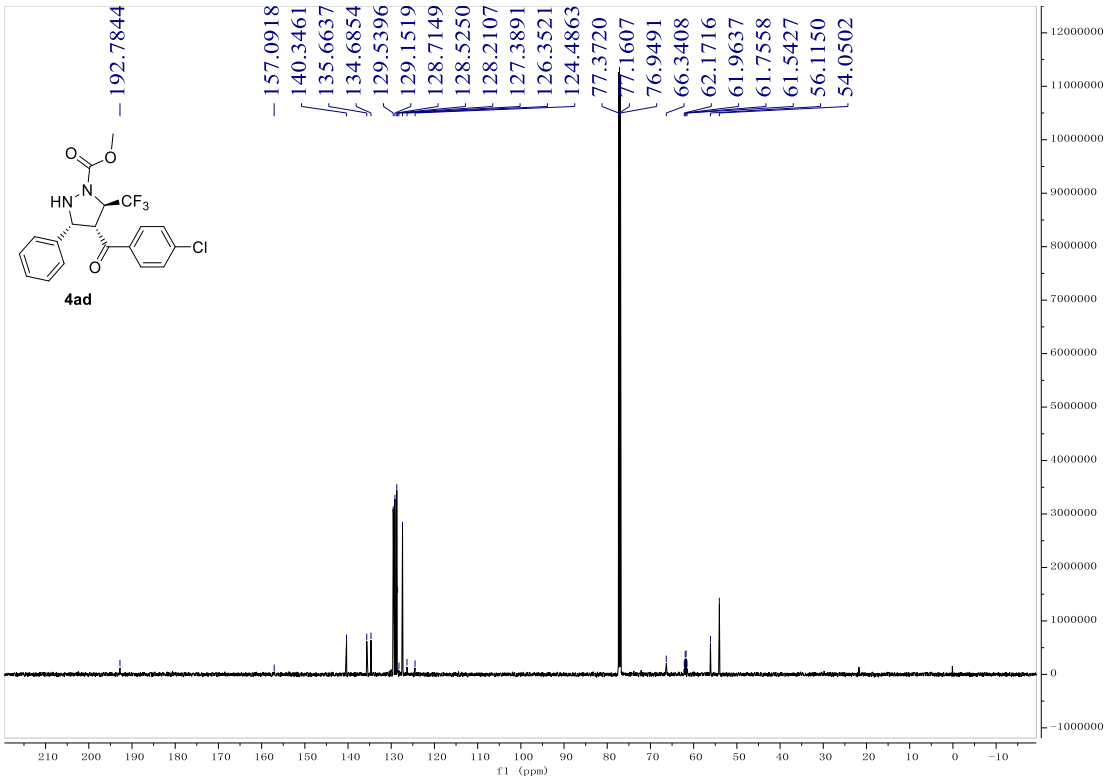
$^{19}F\{^{1}H\}$ NMR of 4ac (565 MHz, $CDCl_3$)



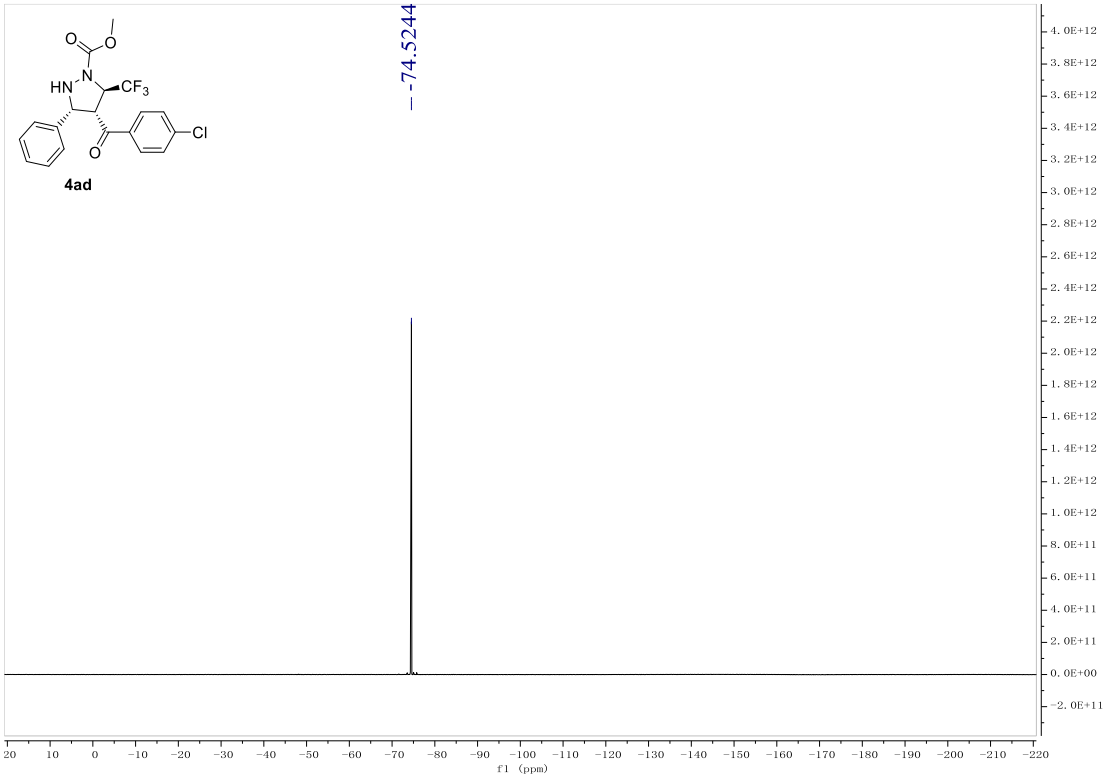
^{1}H NMR of 4ad (600 MHz, $CDCl_3$)



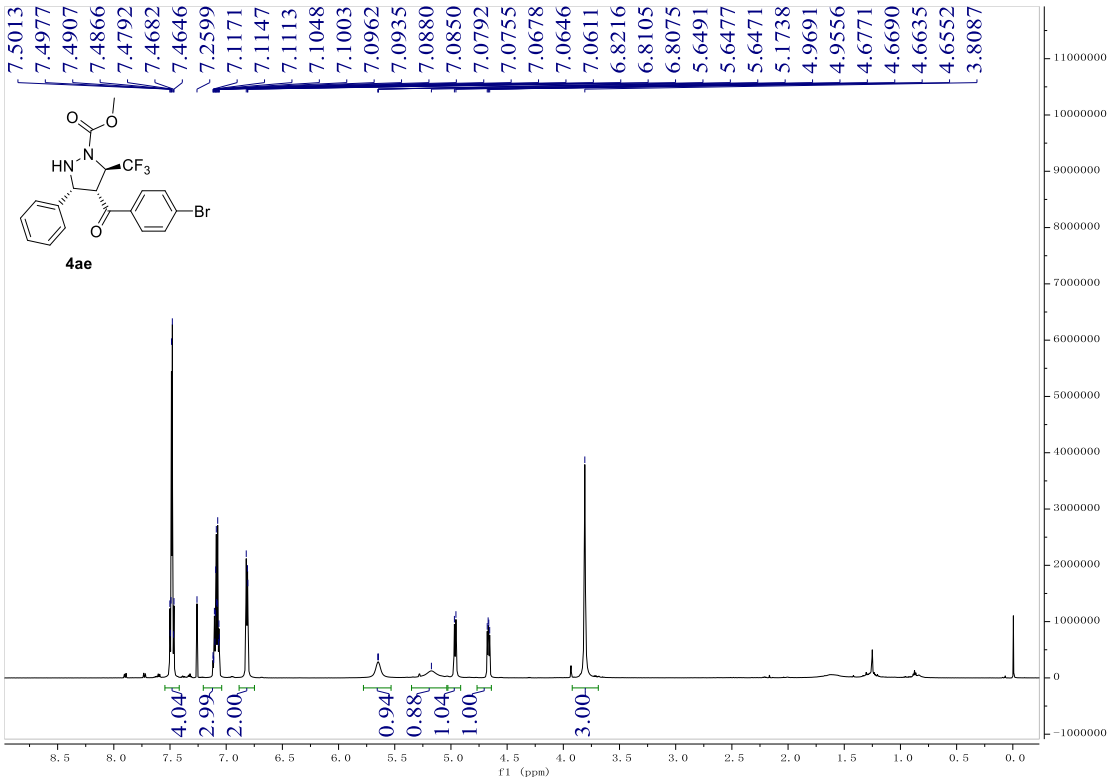
$^{13}C\{^{1}H\}$ NMR of 4ad (150 MHz, $CDCl_3$)



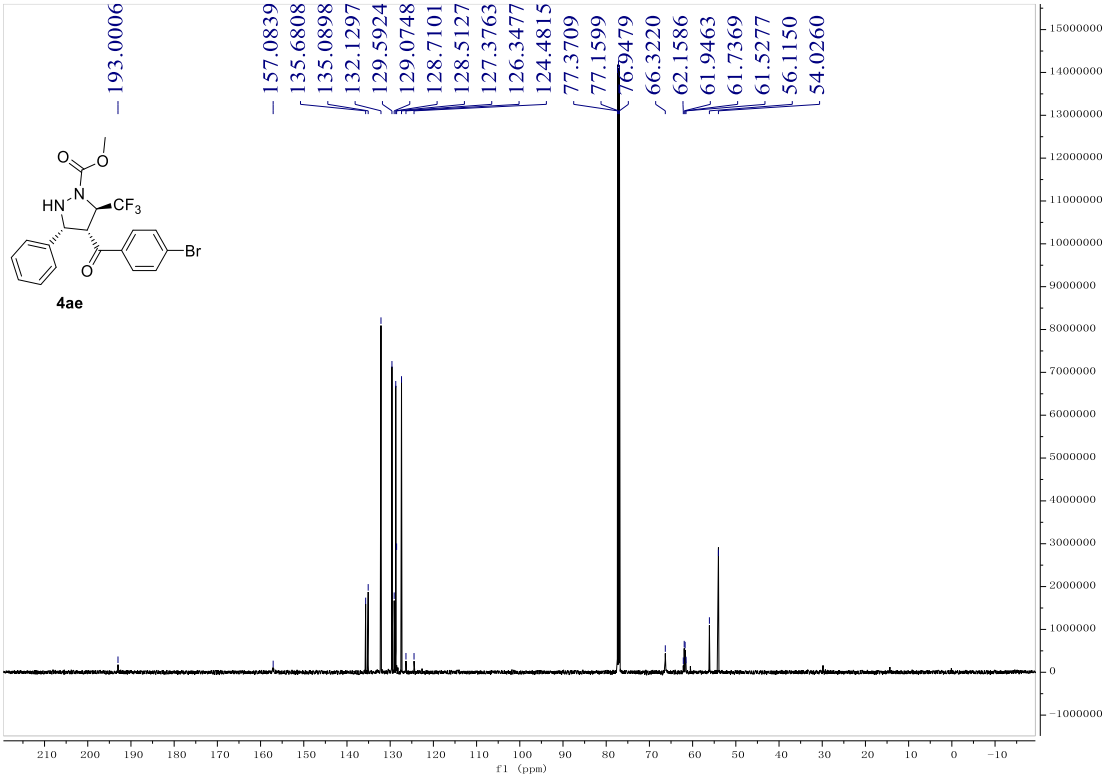
$^{19}F\{^{1}H\}$ NMR of 4ad (376 MHz, $CDCl_3$)



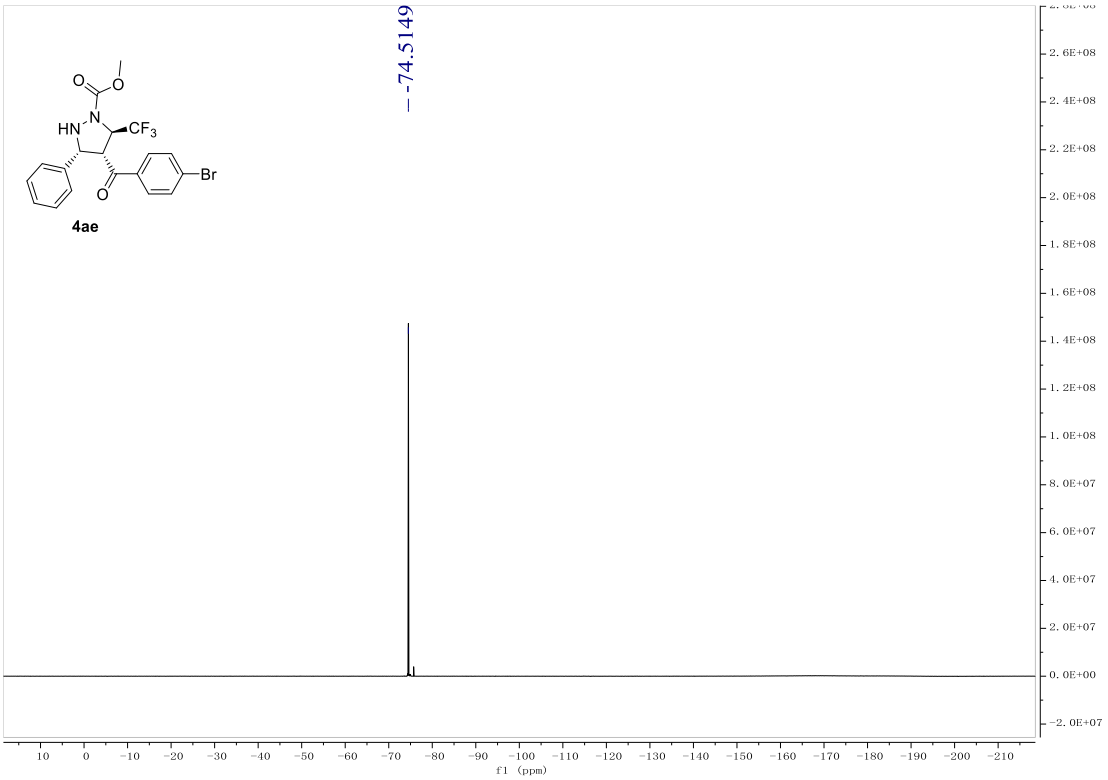
^{1}H NMR of 4ae (600 MHz, $CDCl_3$)



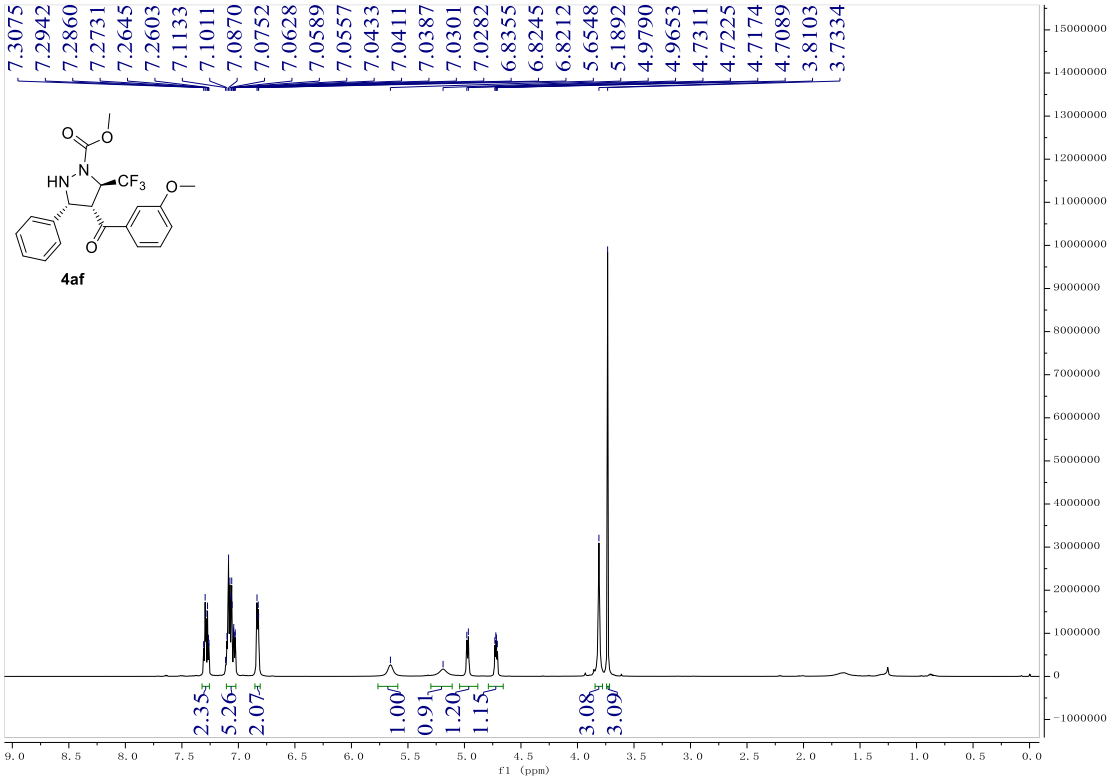
^{13}C{^{1}H} NMR of 4ae (150 MHz, $CDCl_3$)



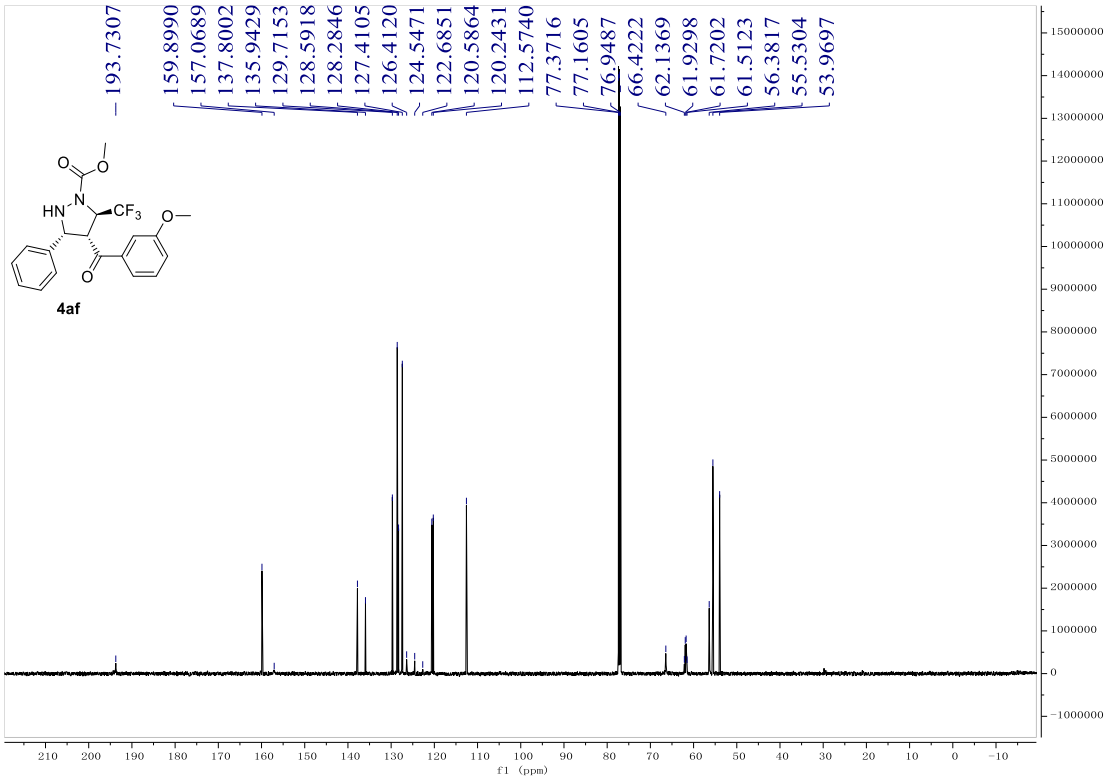
$^{19}F\{^{1}H\}$ NMR of 4ae (565 MHz, $CDCl_3$)



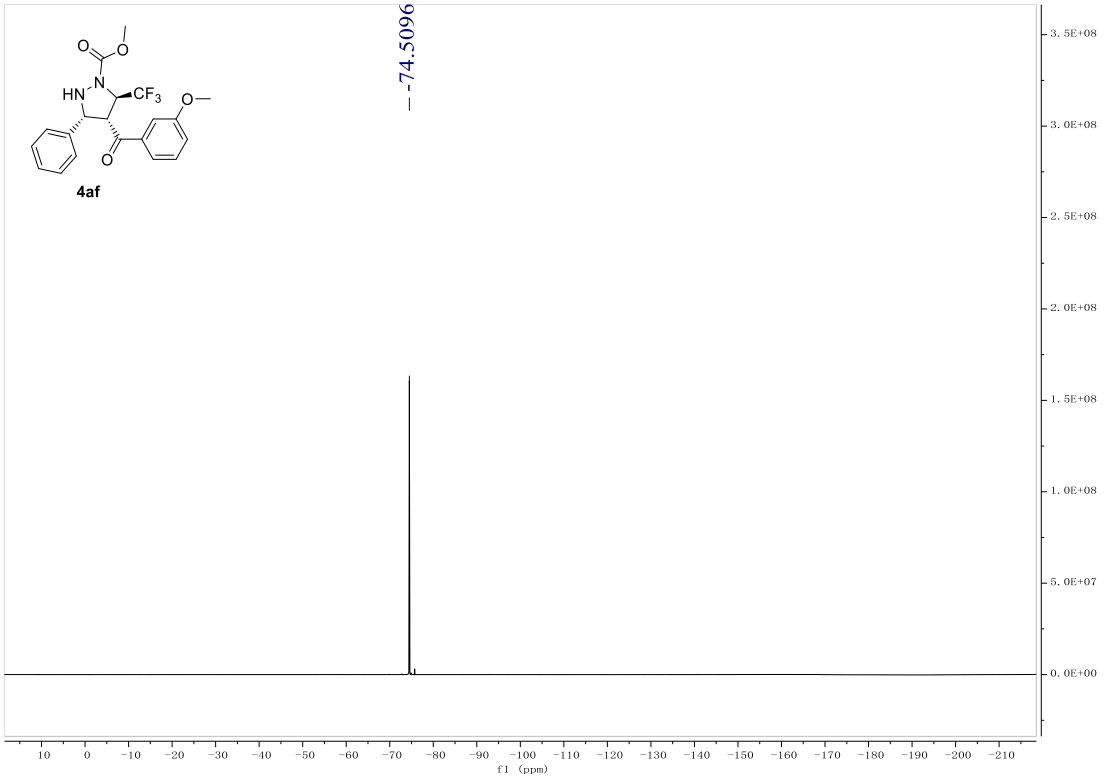
^{1}H NMR of 4af (600 MHz, $CDCl_3$)



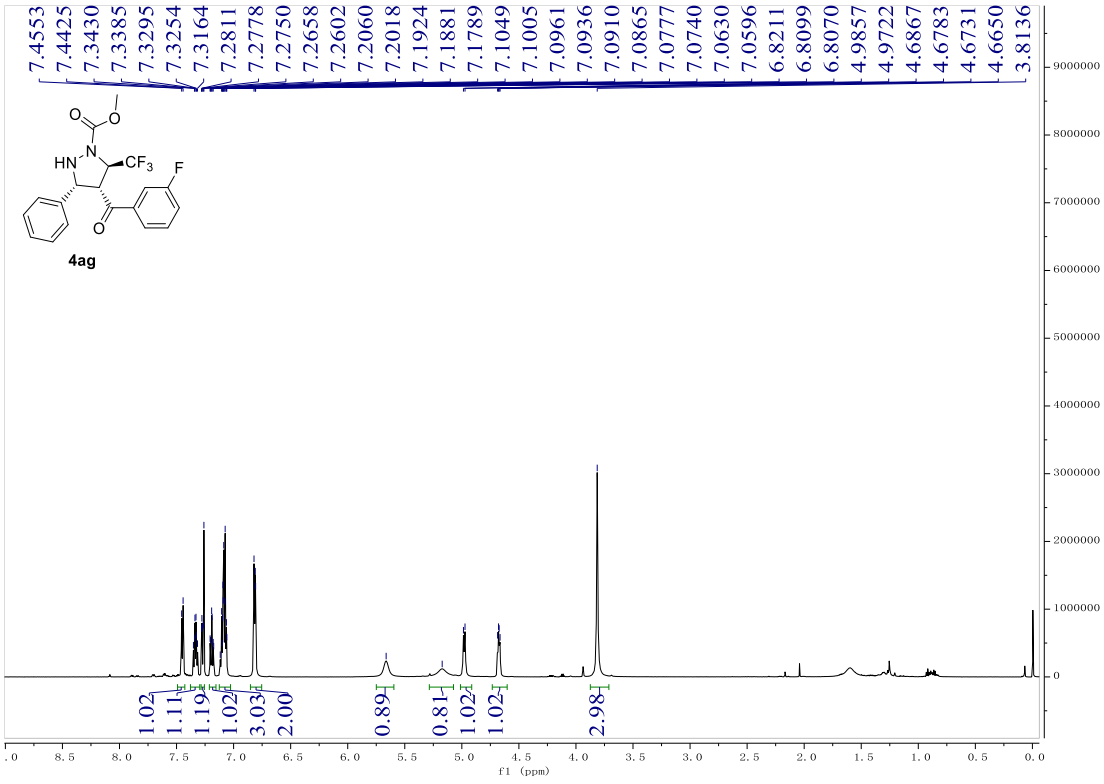
^{13}C{^{1}H} NMR of 4af (150 MHz, $CDCl_3$)



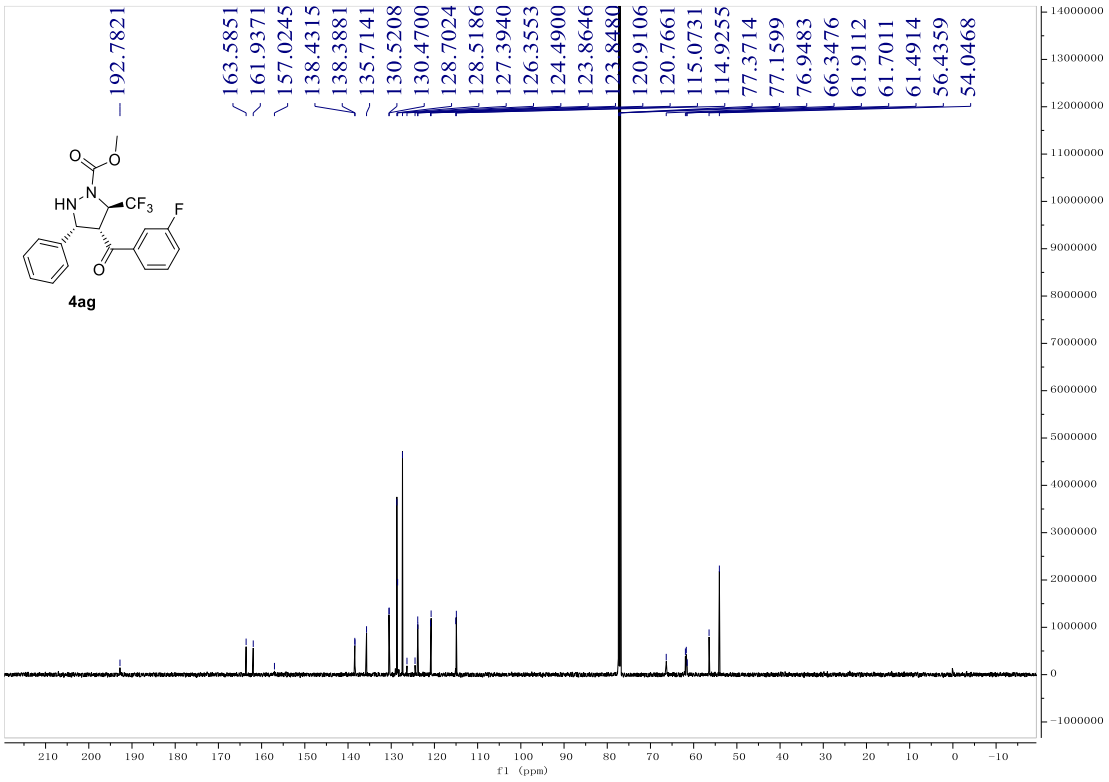
$^{19}F\{^{1}H\}$ NMR of 4af (565 MHz, $CDCl_3$)



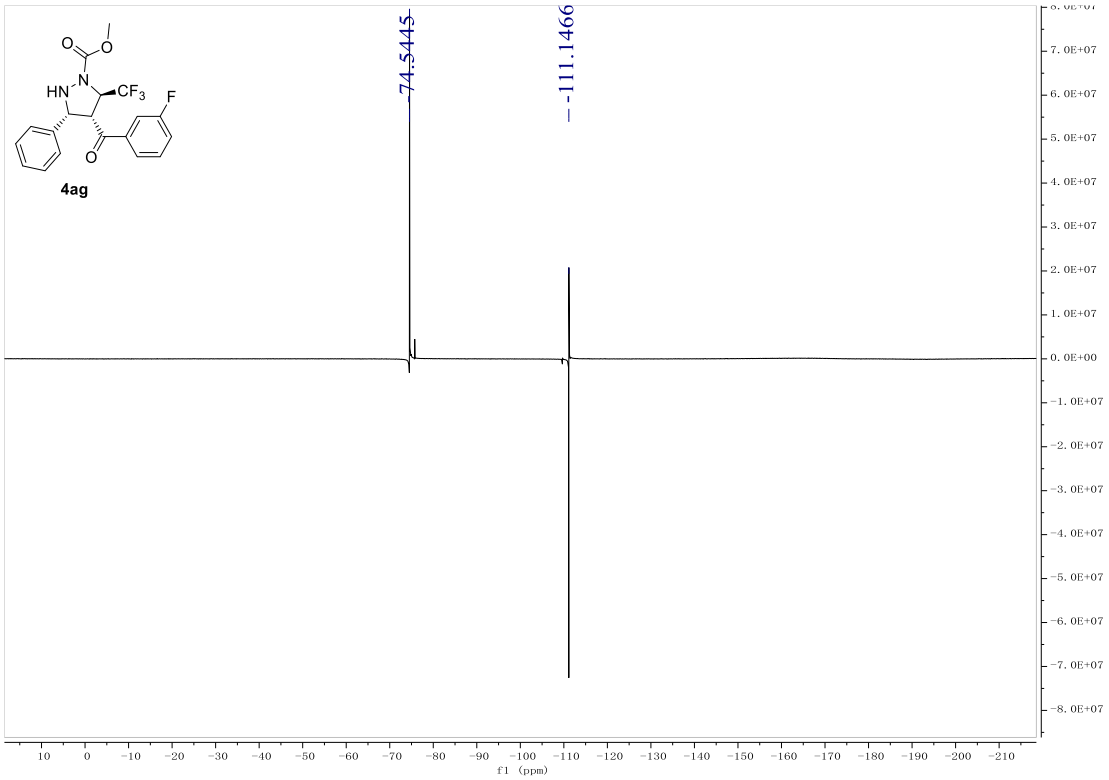
^{1}H NMR of 4ag (600 MHz, $CDCl_3$)



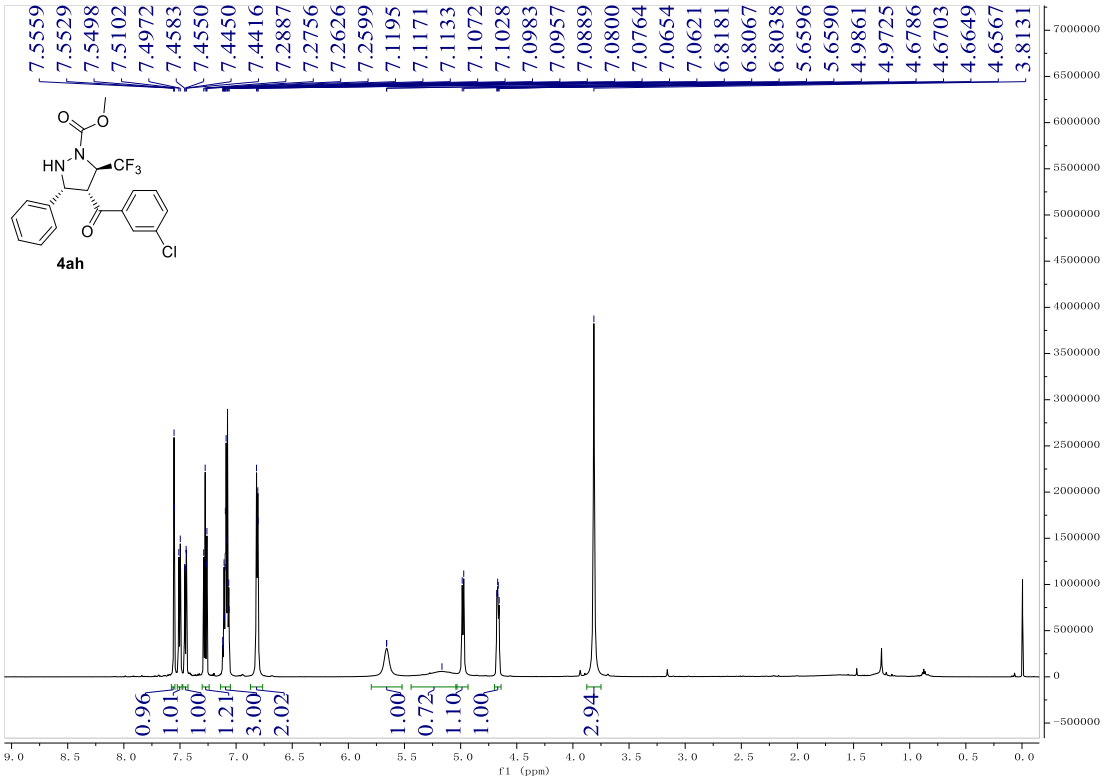
$^{13}C\{^{1}H\}$ NMR of 4af (150 MHz, $CDCl_3$)



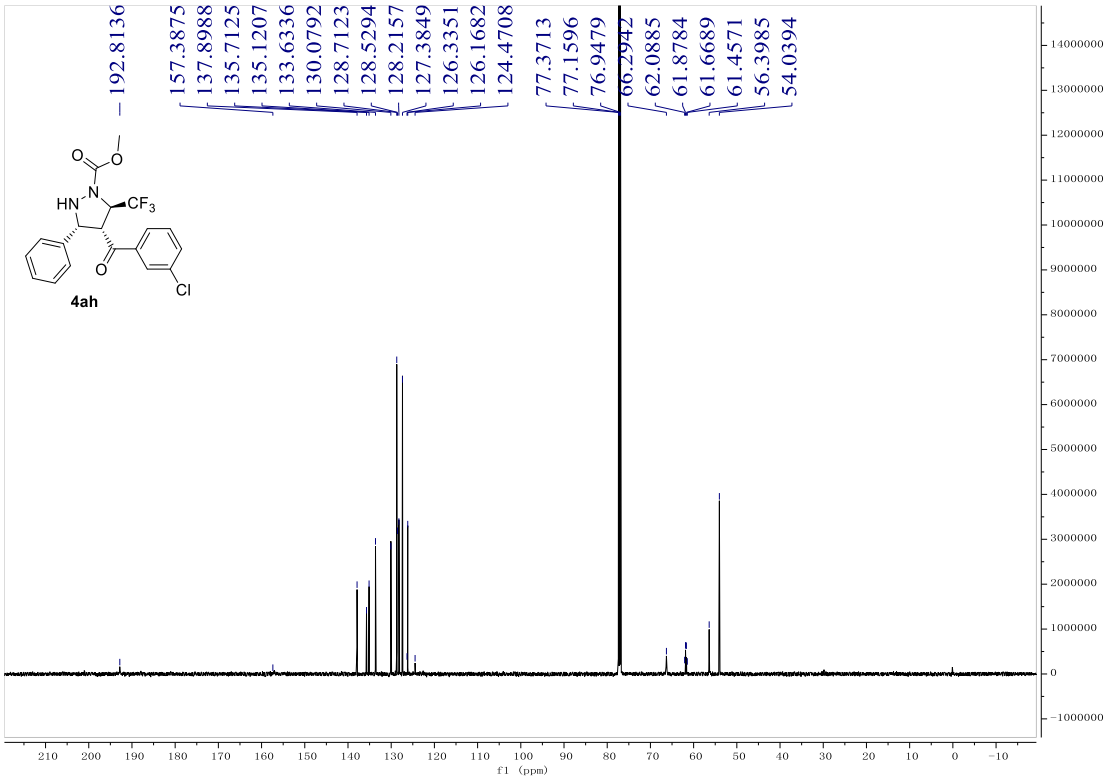
$^{19}F\{^{1}H\}$ NMR of 4ag (565 MHz, $CDCl_3$)



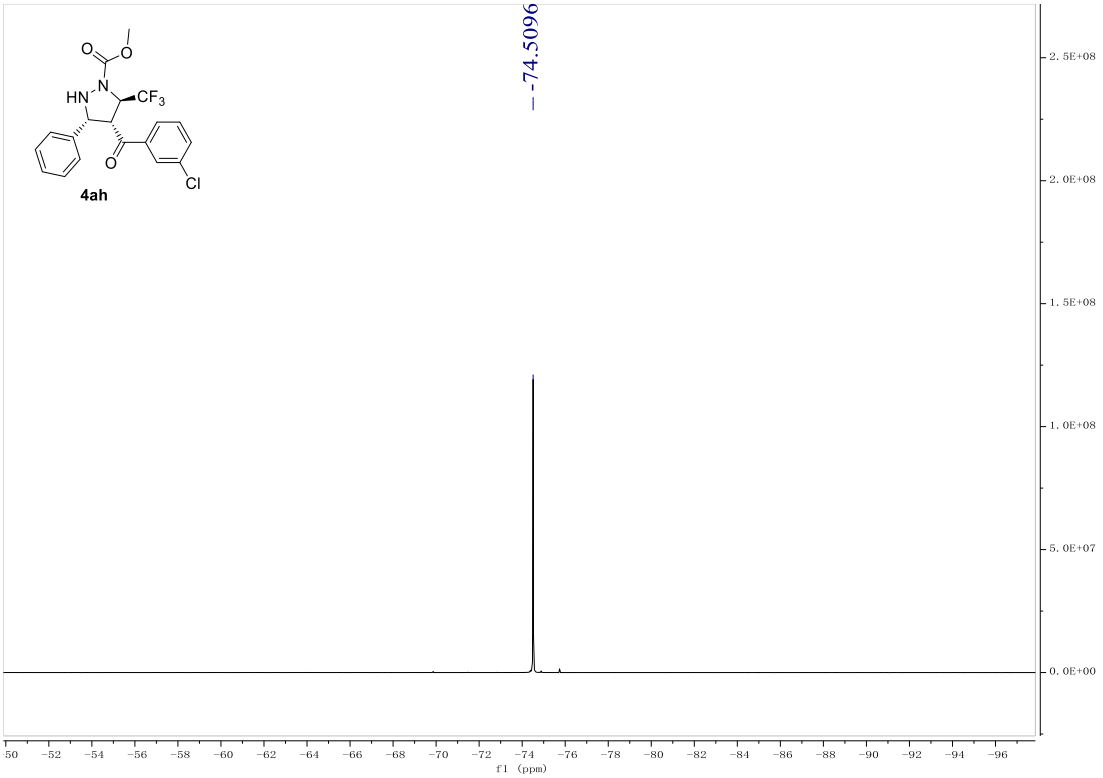
^{1}H NMR of 4ah (600 MHz, $CDCl_3$)



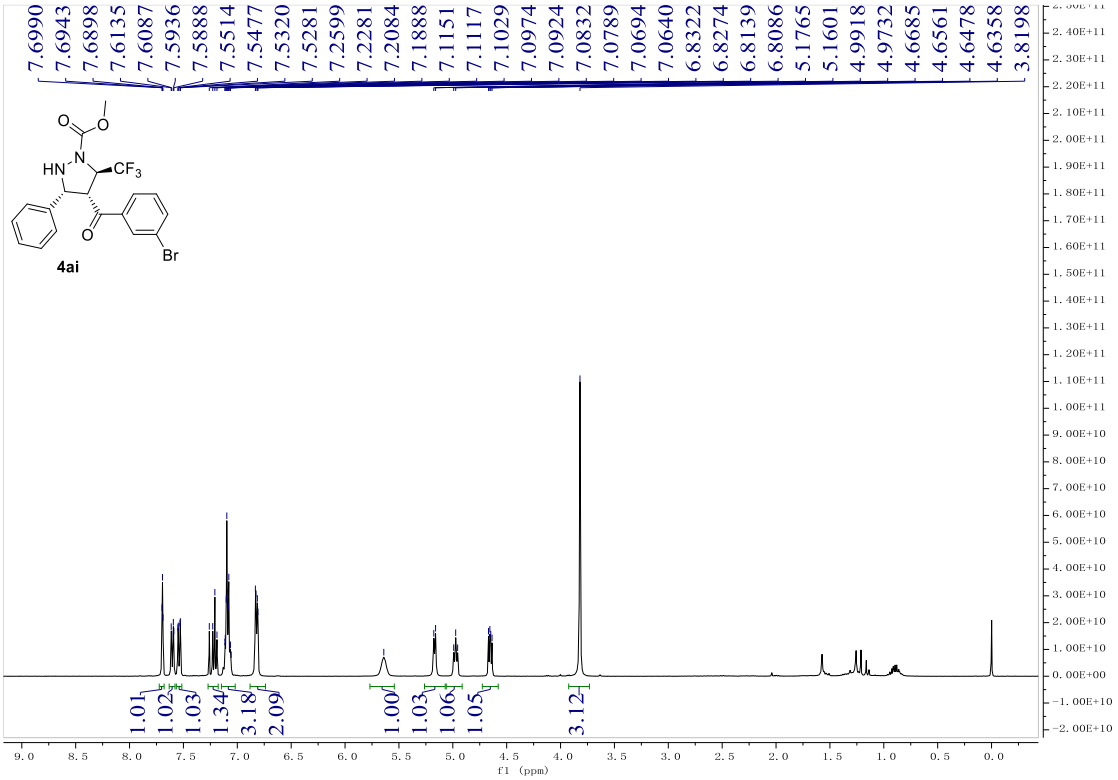
$^{13}C\{^{1}H\}$ NMR of 4ah (150 MHz, $CDCl_3$)



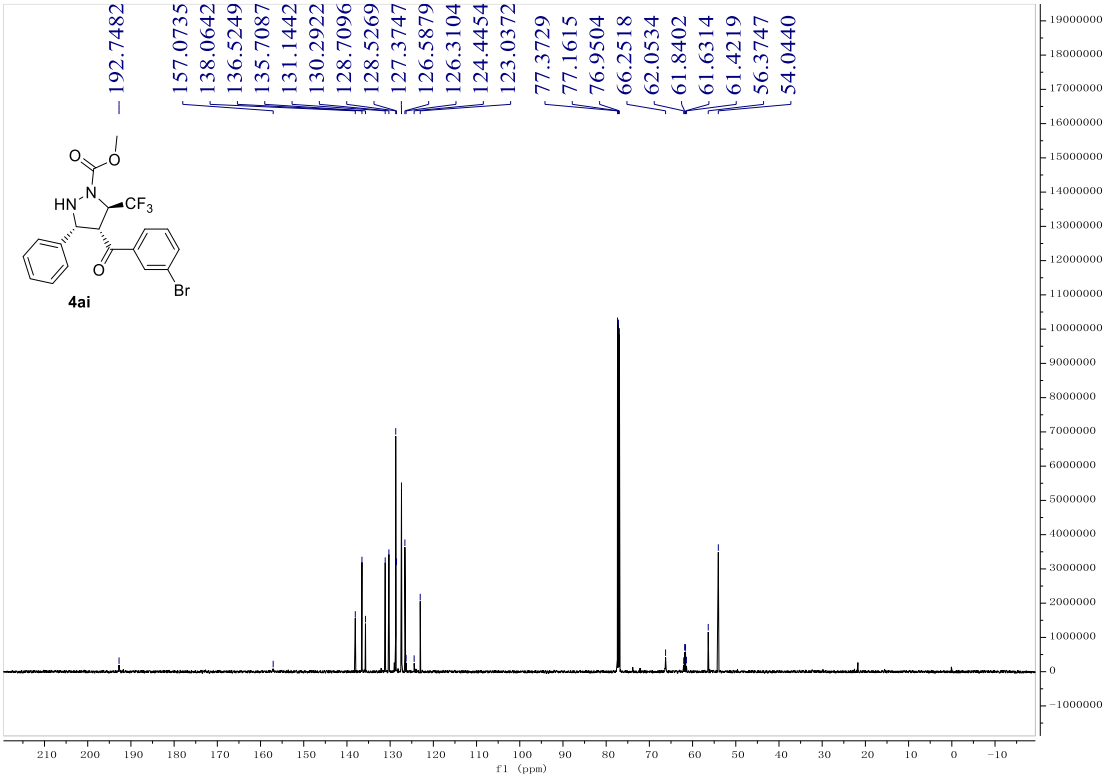
$^{19}F\{^{1}H\}$ NMR of 4ah (565 MHz, $CDCl_3$)



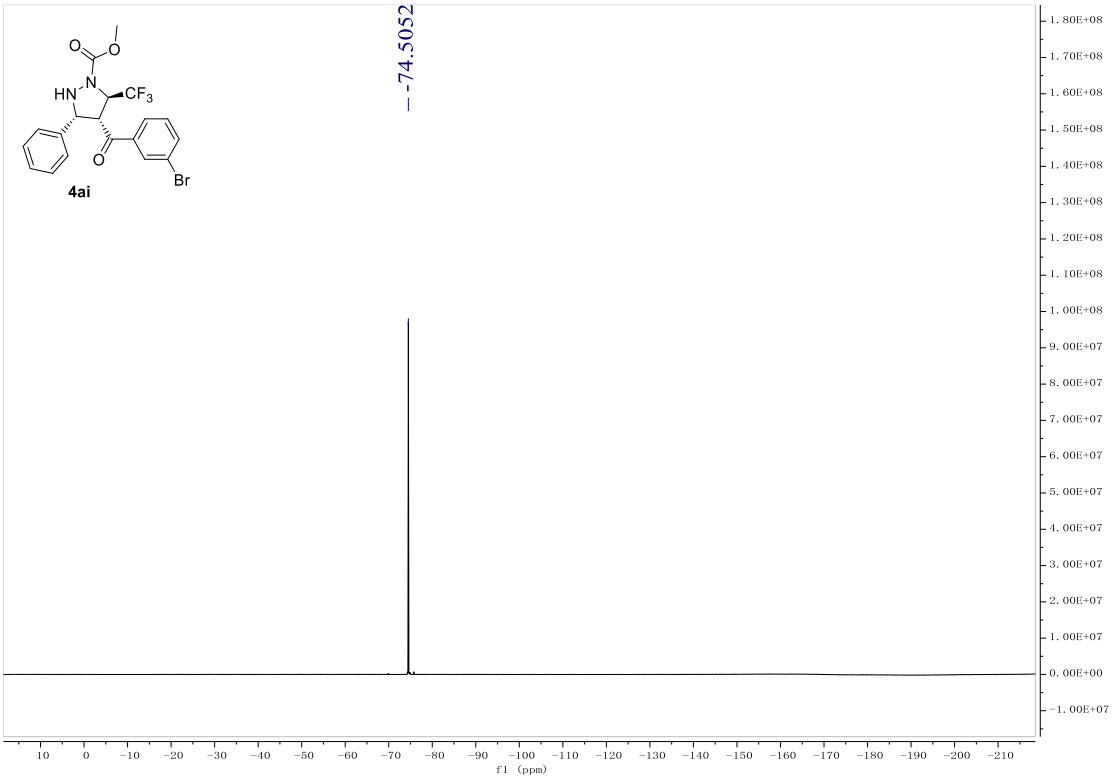
^{1}H NMR of 4ai (400 MHz, $CDCl_3$)



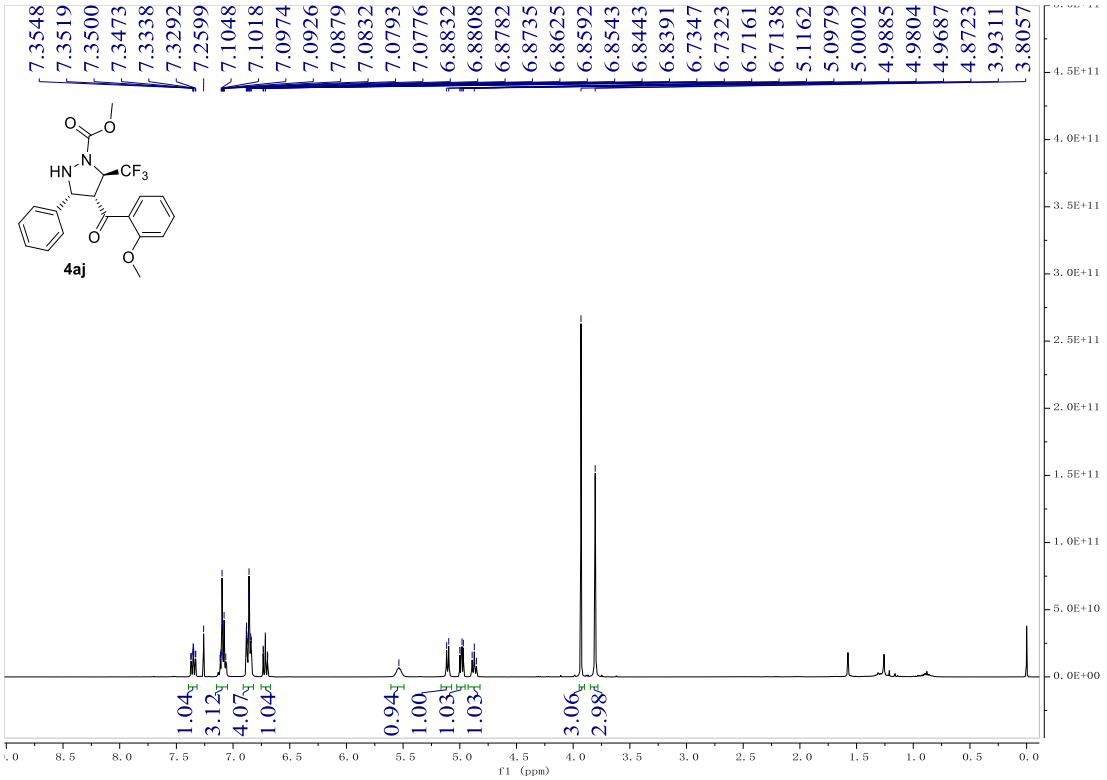
^{13}C{^{1}H} NMR of 4ai (150 MHz, $CDCl_3$)



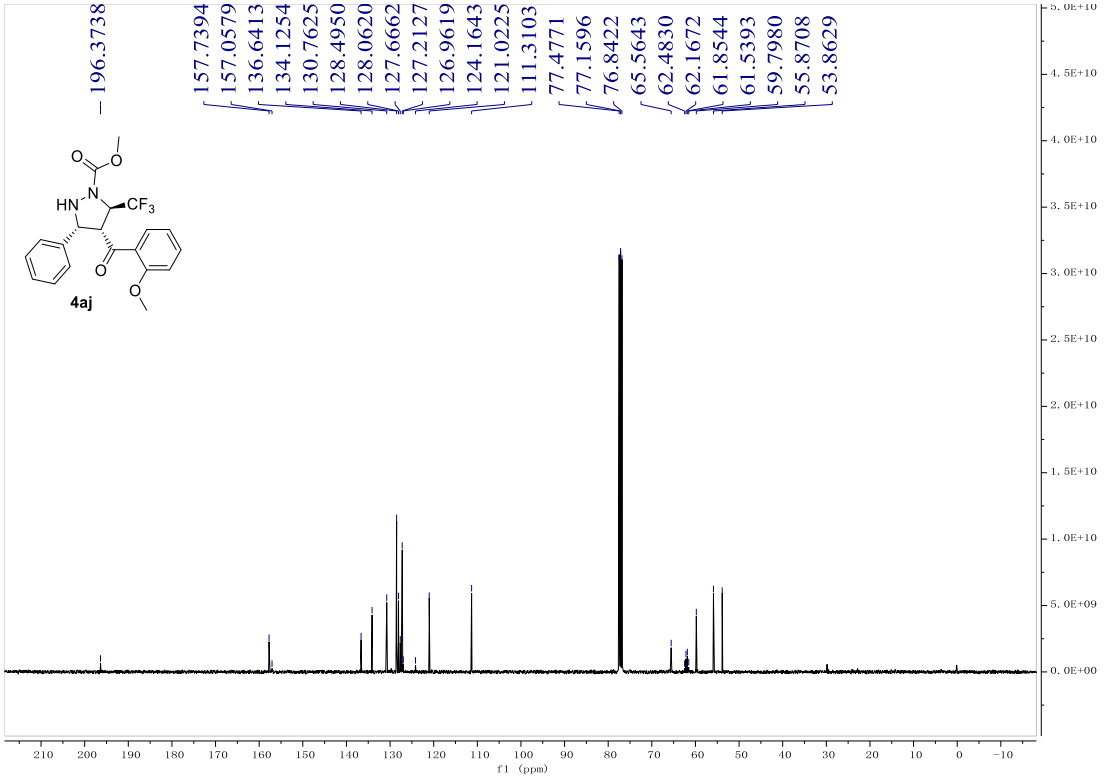
$^{19}F\{^{1}H\}$ NMR of 4ai (565 MHz, $CDCl_3$)



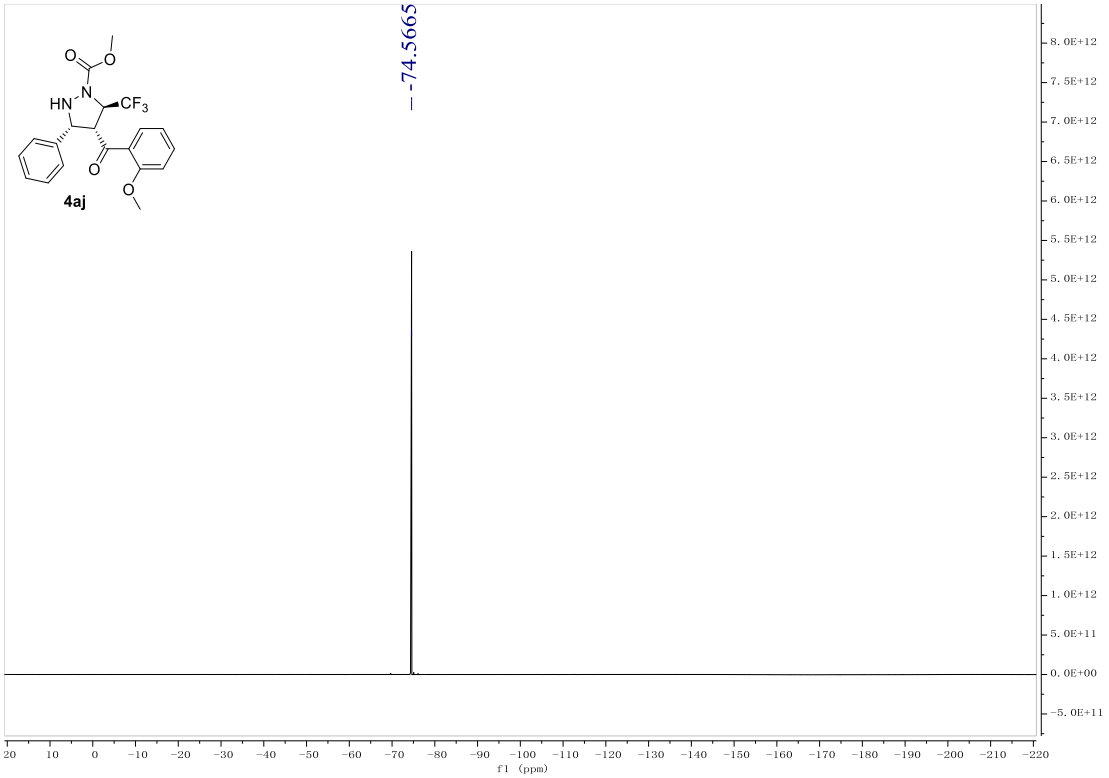
^{1}H NMR of 4aj (400 MHz, $CDCl_3$)



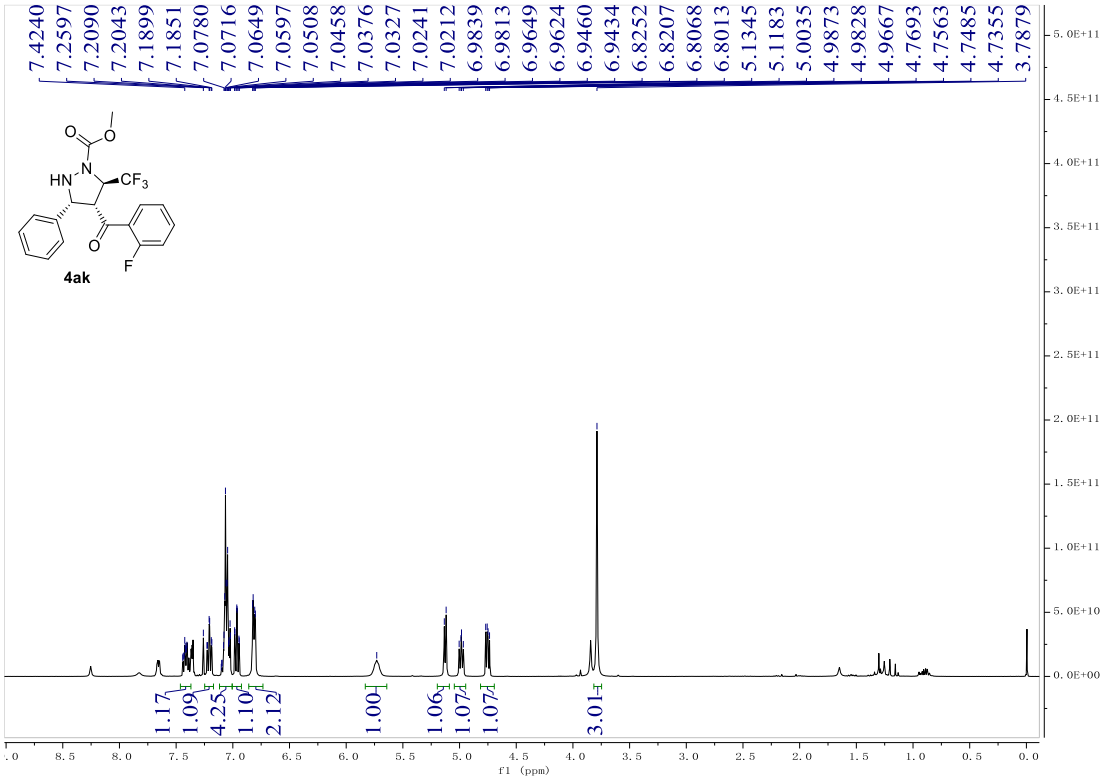
$^{13}C\{^{1}H\}$ NMR of 4aj (100 MHz, $CDCl_3$)



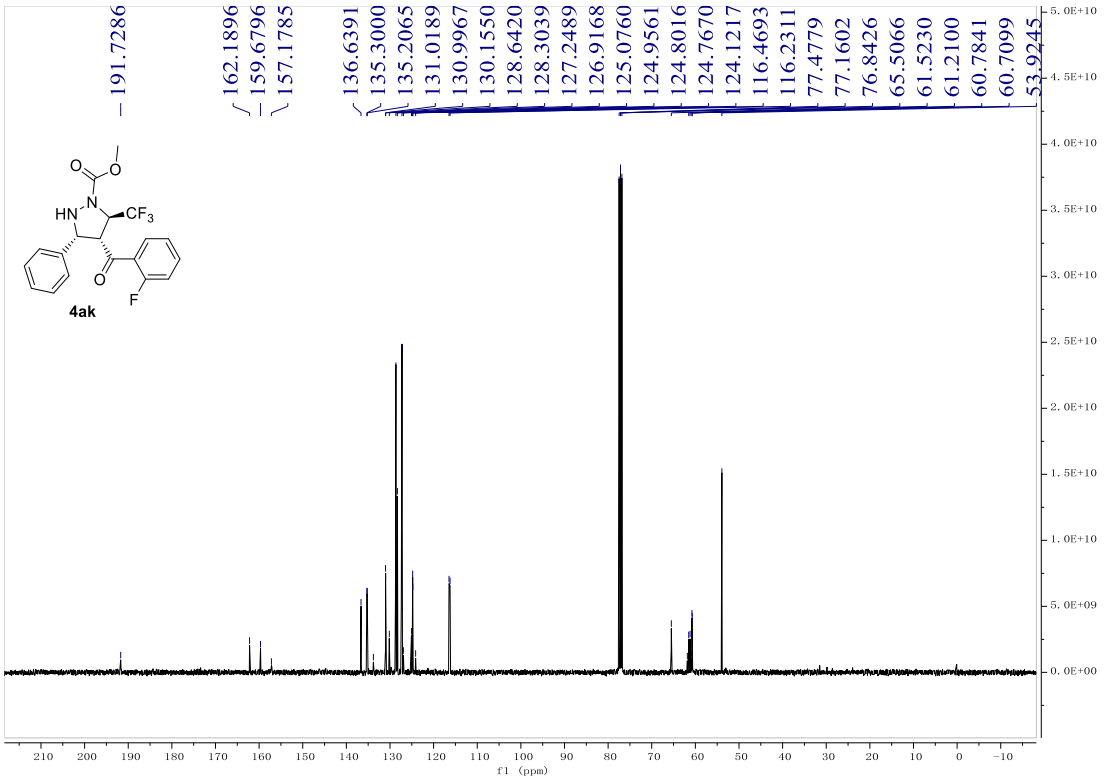
$^{19}F\{^{1}H\}$ NMR of 4aj(376 MHz, $CDCl_3$)



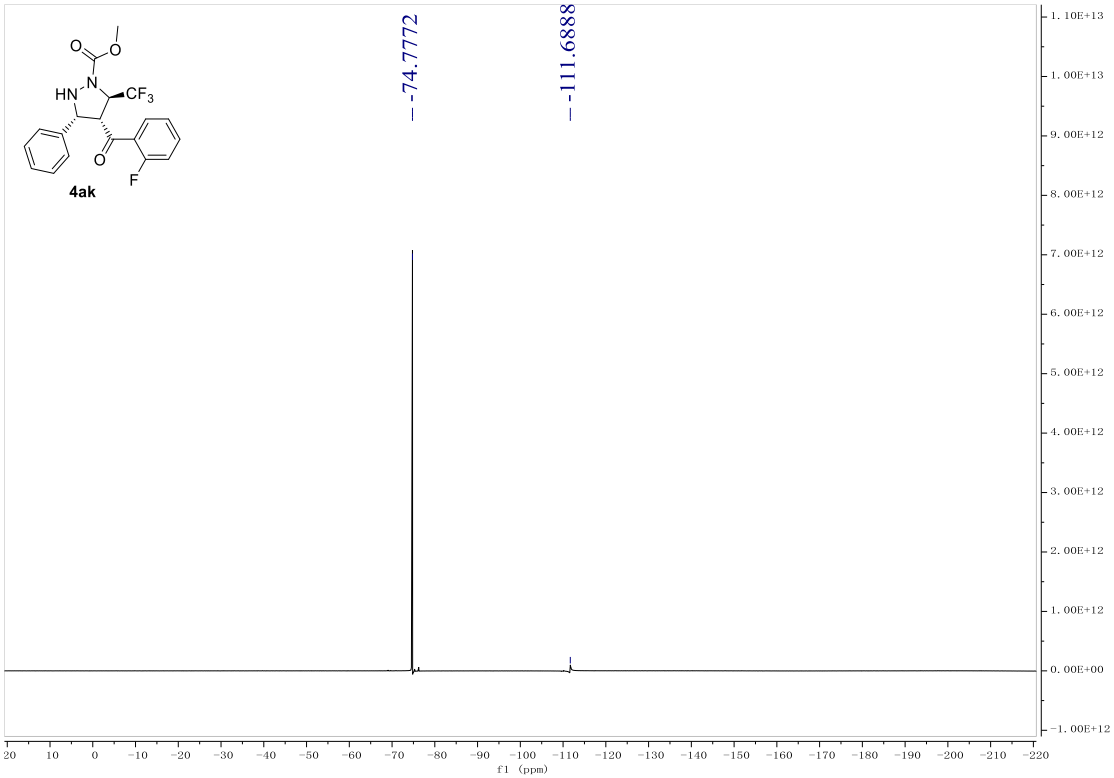
^{1}H NMR of 4ak (400 MHz, $CDCl_3$)



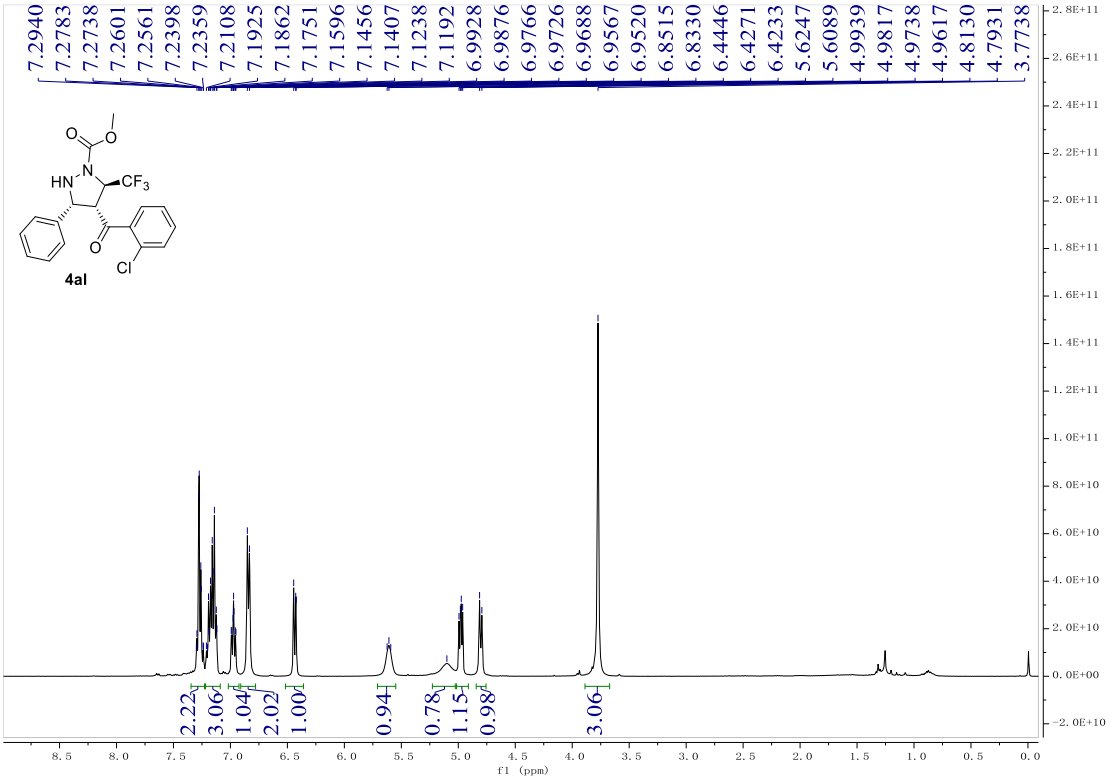
^{13}C{^{1}H} NMR of 4ak (100 MHz, $CDCl_3$)



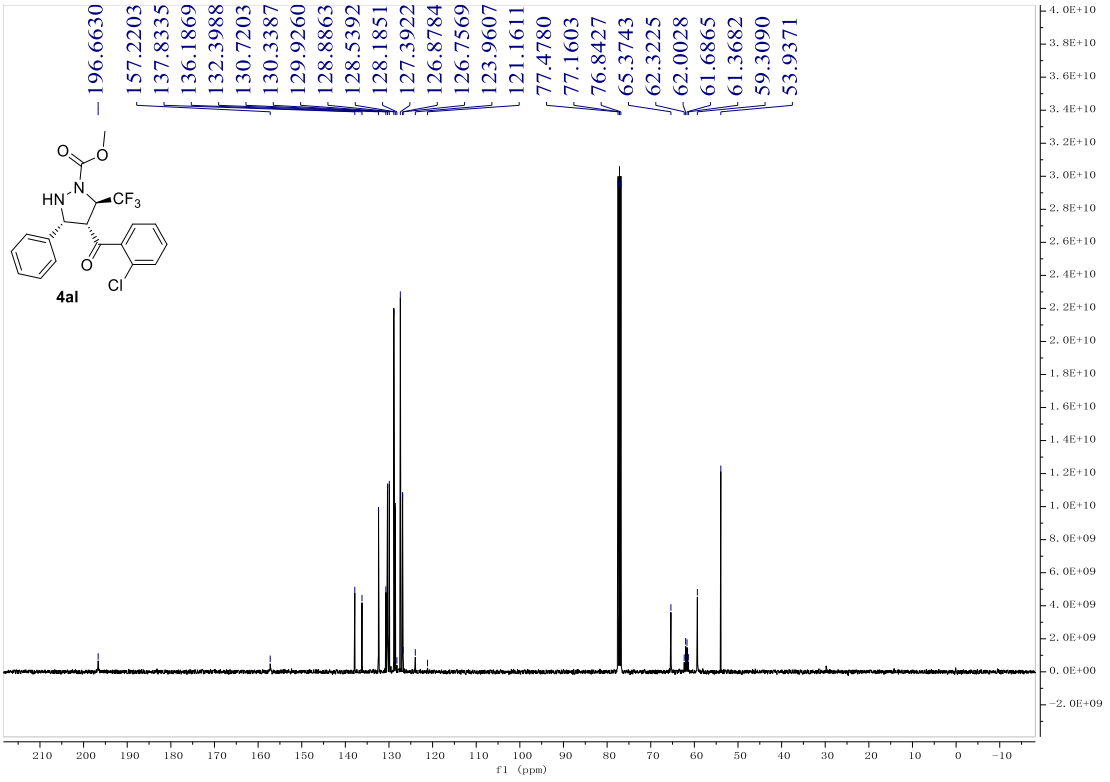
$^{19}F\{^{1}H\}$ NMR of 4ak (376 MHz, $CDCl_3$)



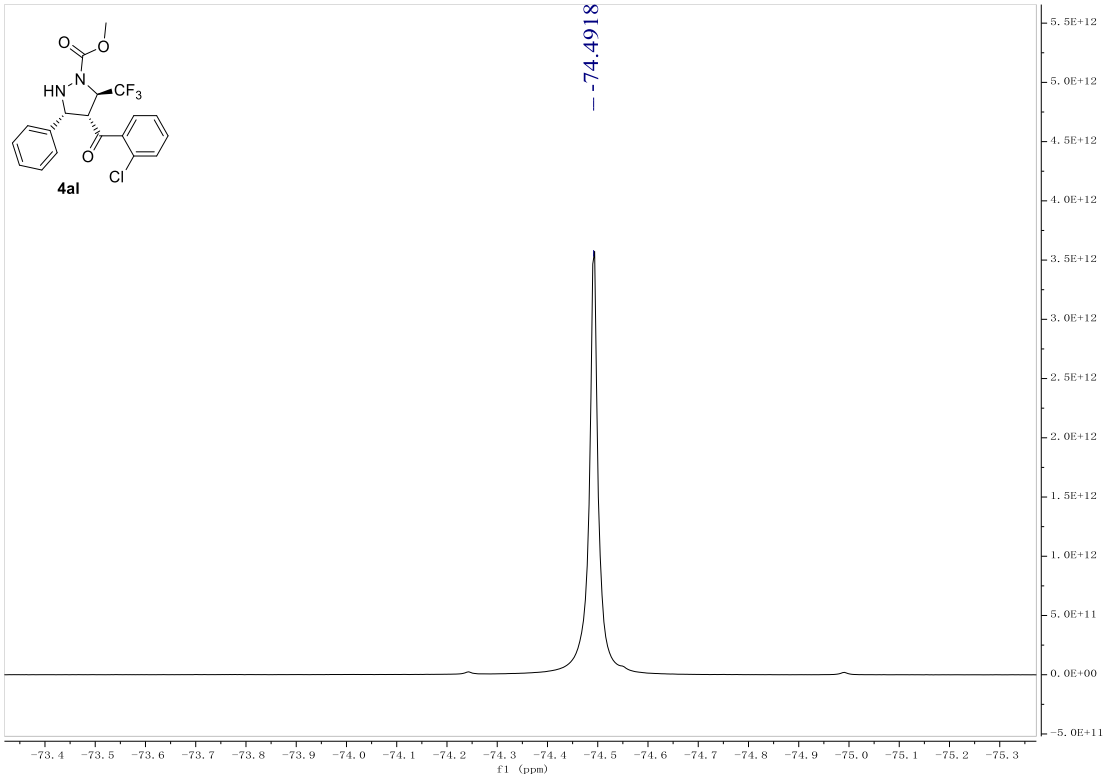
^{1}H NMR of 4al (400 MHz, $CDCl_3$)



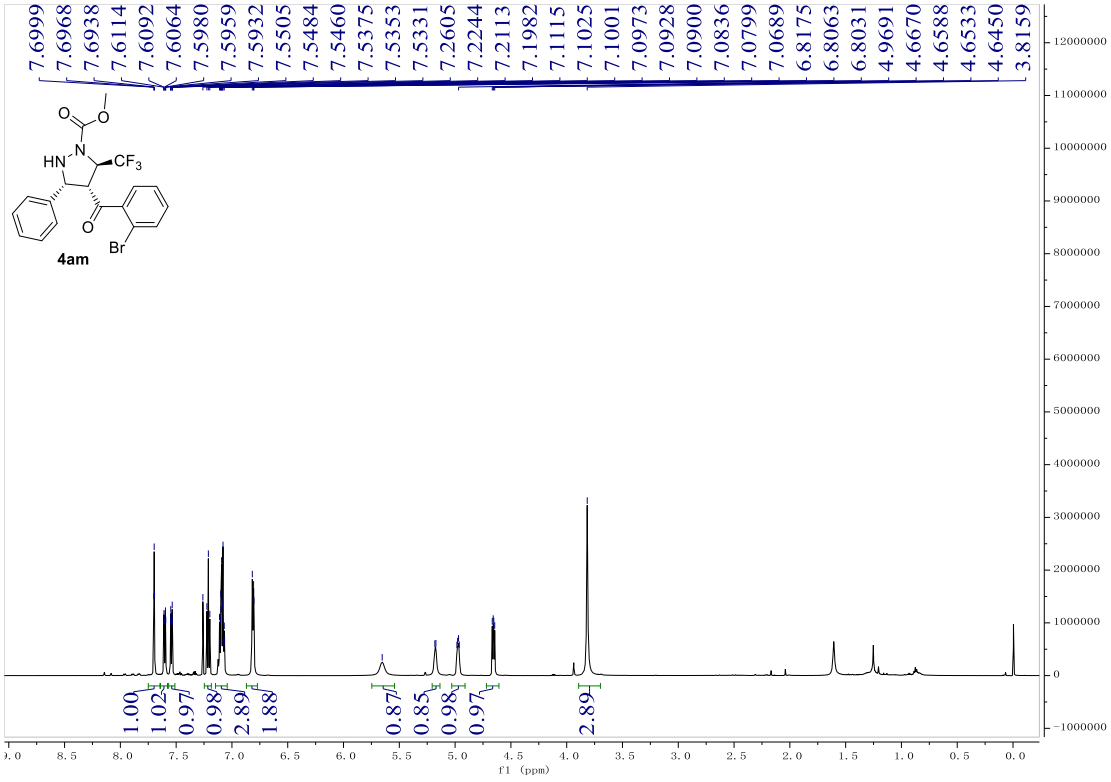
^{13}C{^{1}H} NMR of 4al (100 MHz, $CDCl_3$)



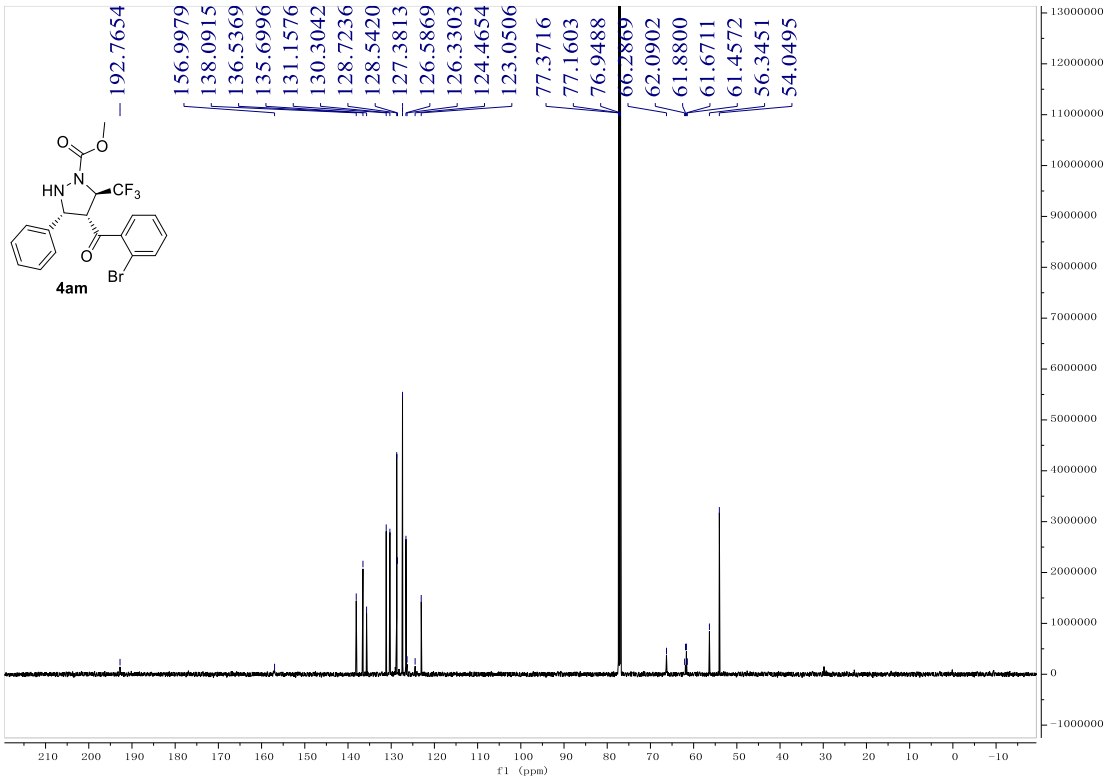
$^{19}F\{^{1}H\}$ NMR of 4al (376 MHz, $CDCl_3$)



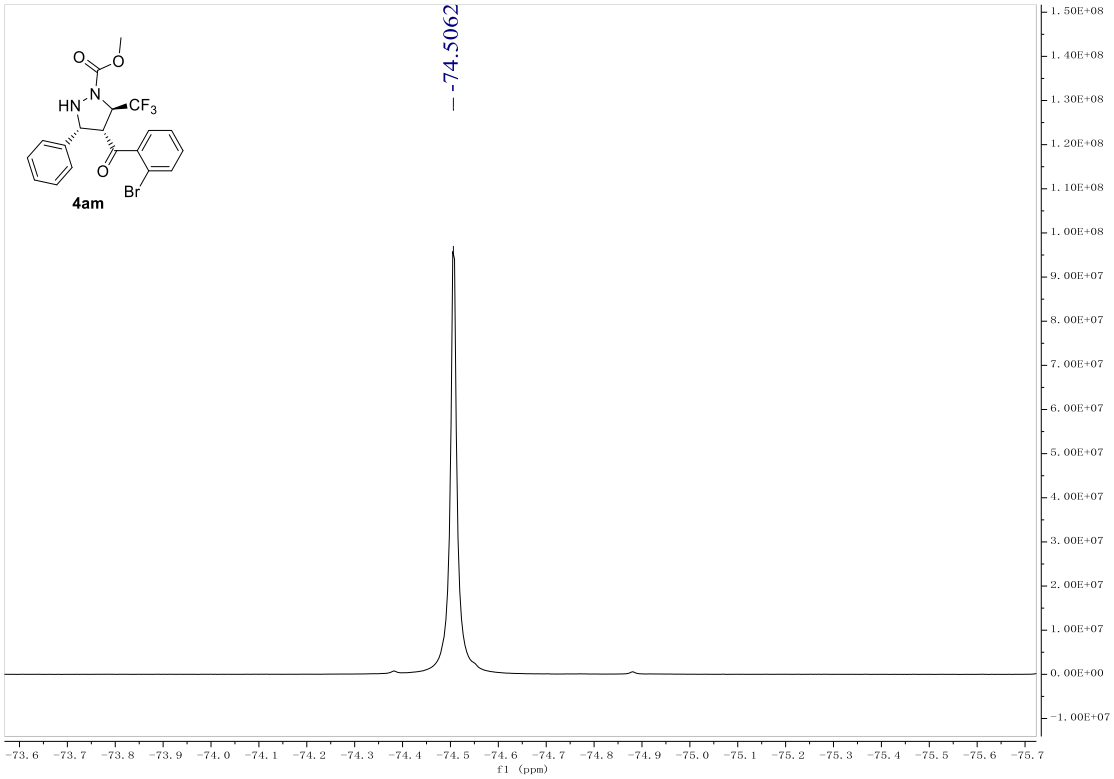
^{1}H NMR of 4am (600 MHz, $CDCl_3$)



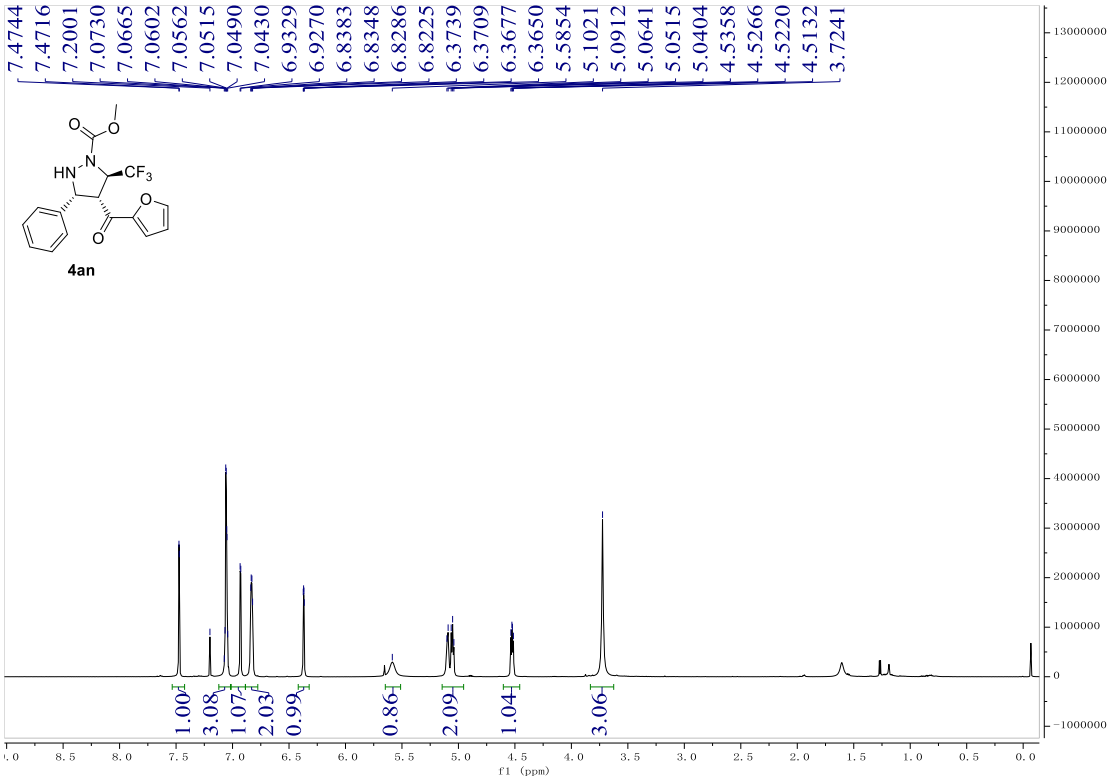
$^{13}C\{^{1}H\}$ NMR of 4am (150 MHz, $CDCl_3$)



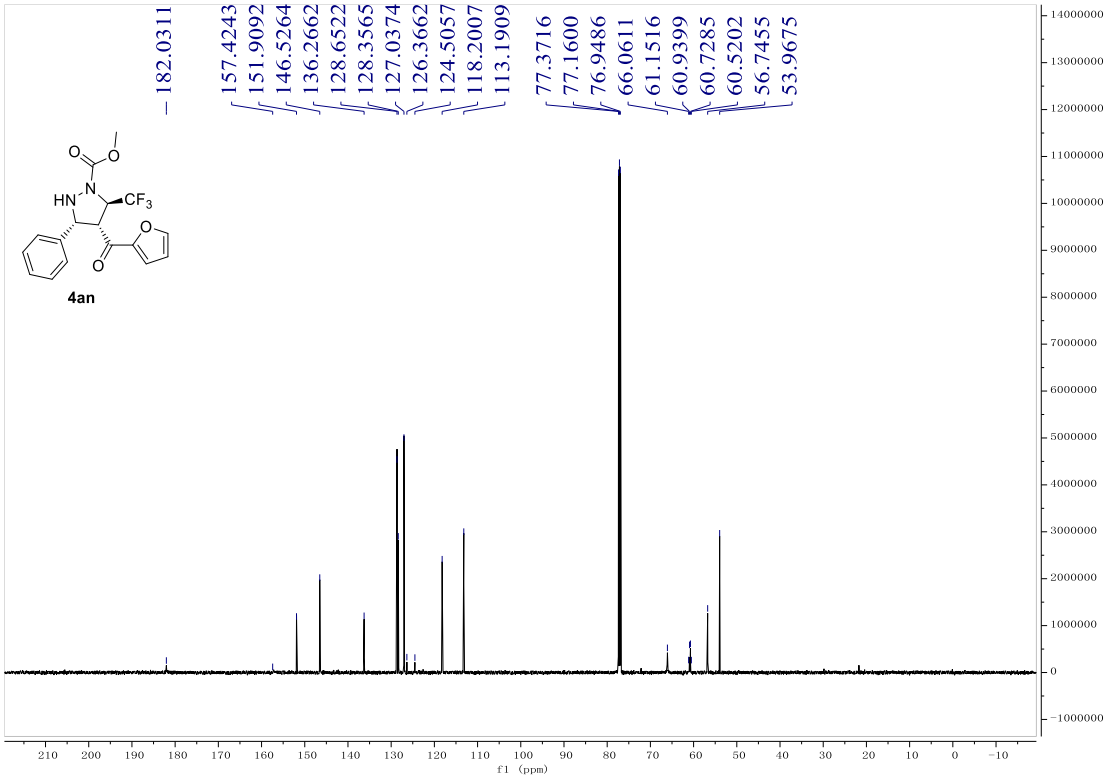
$^{19}F\{^{1}H\}$ NMR of 4am (565 MHz, $CDCl_3$)



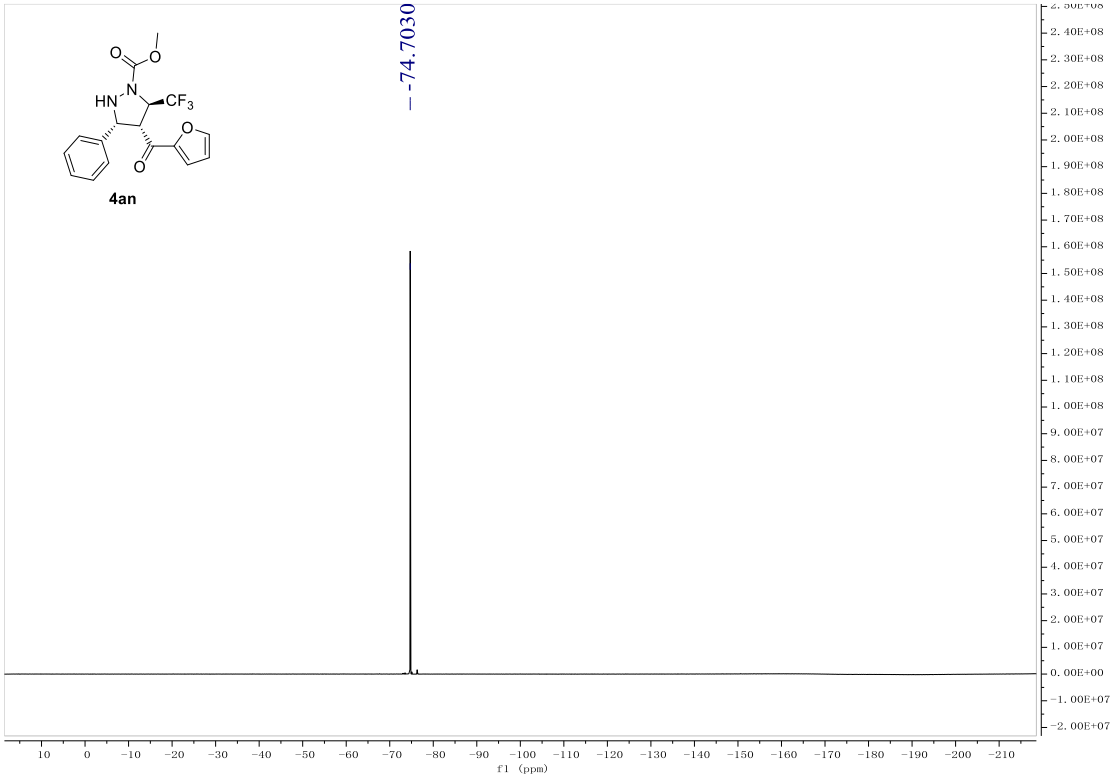
^{1}H NMR of 4an (600 MHz, $CDCl_3$)



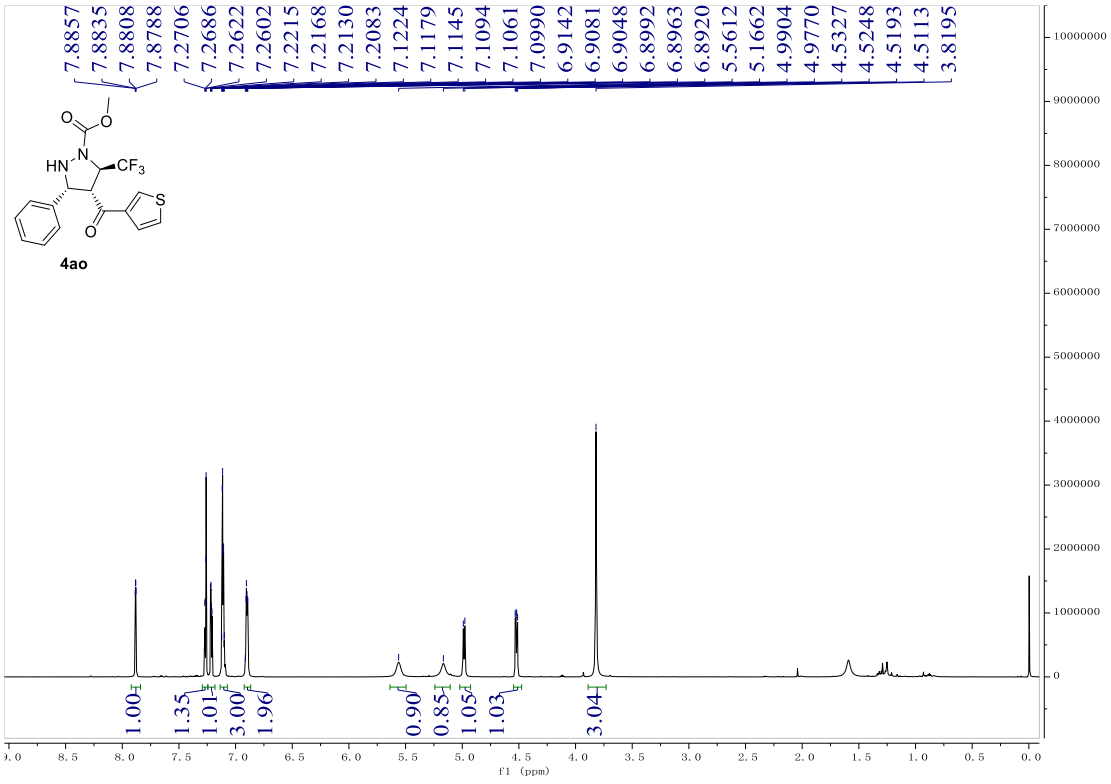
$^{13}C\{^{1}H\}$ NMR of 4an (150 MHz, $CDCl_3$)



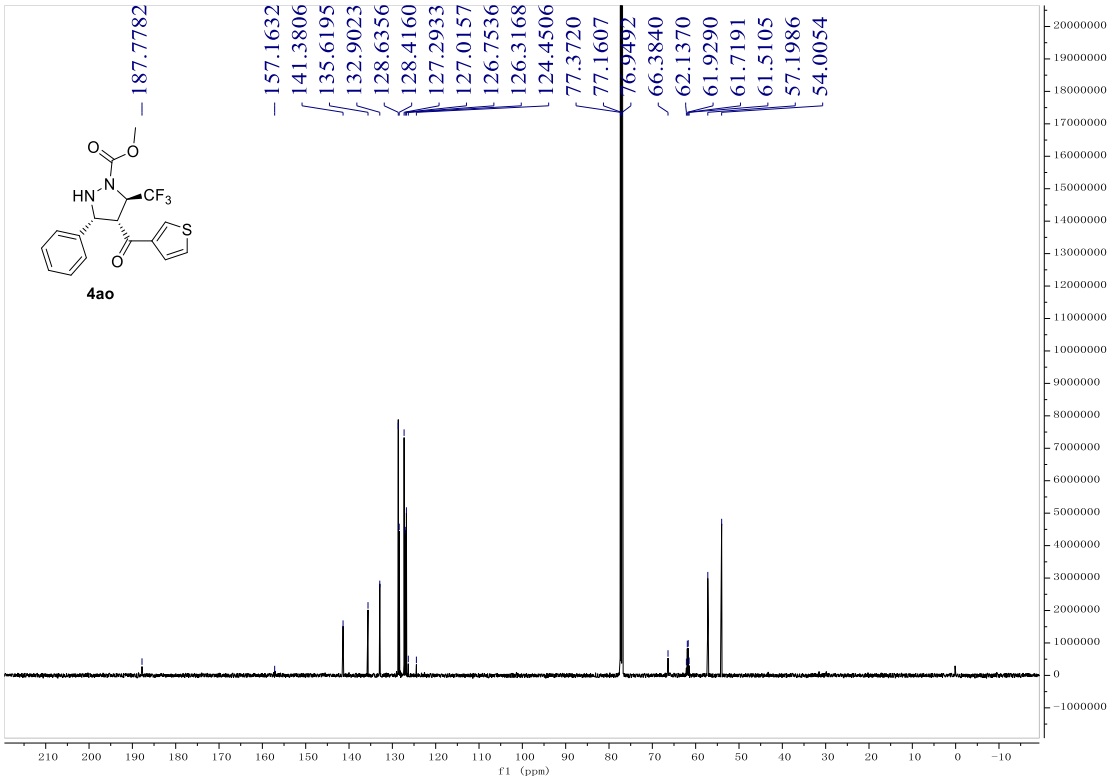
$^{19}F\{^{1}H\}$ NMR of 4an (565 MHz, $CDCl_3$)



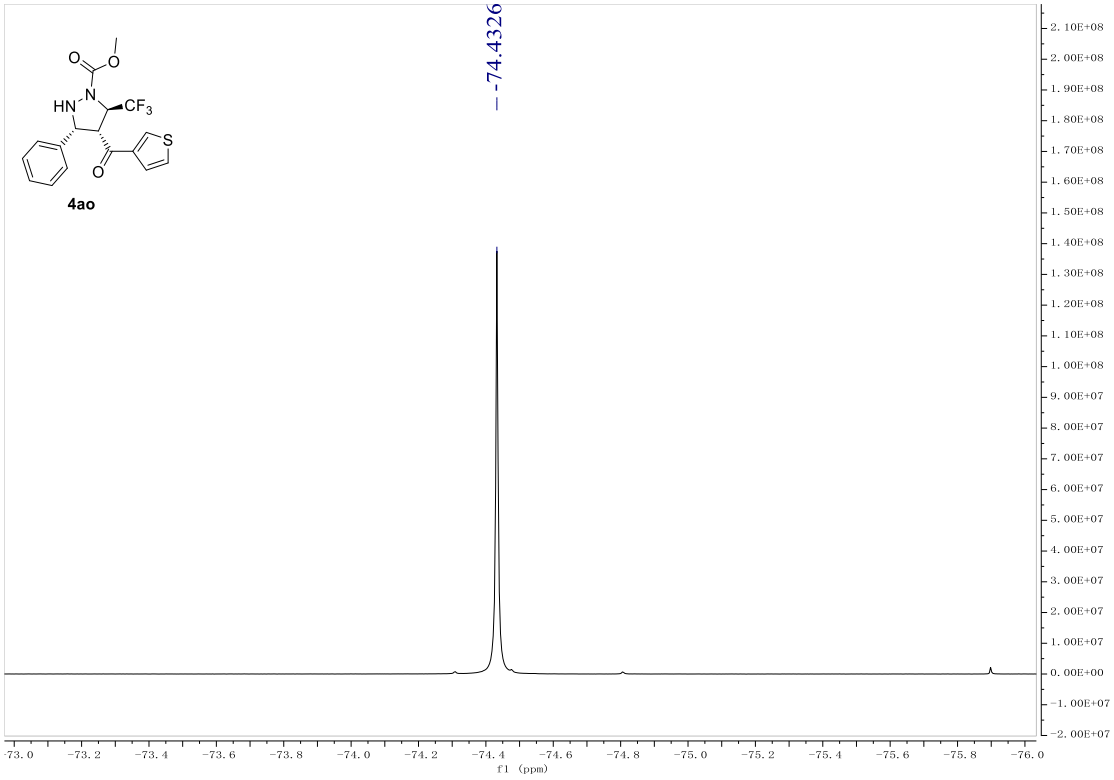
^{1}H NMR of 4ao (600 MHz, $CDCl_3$)



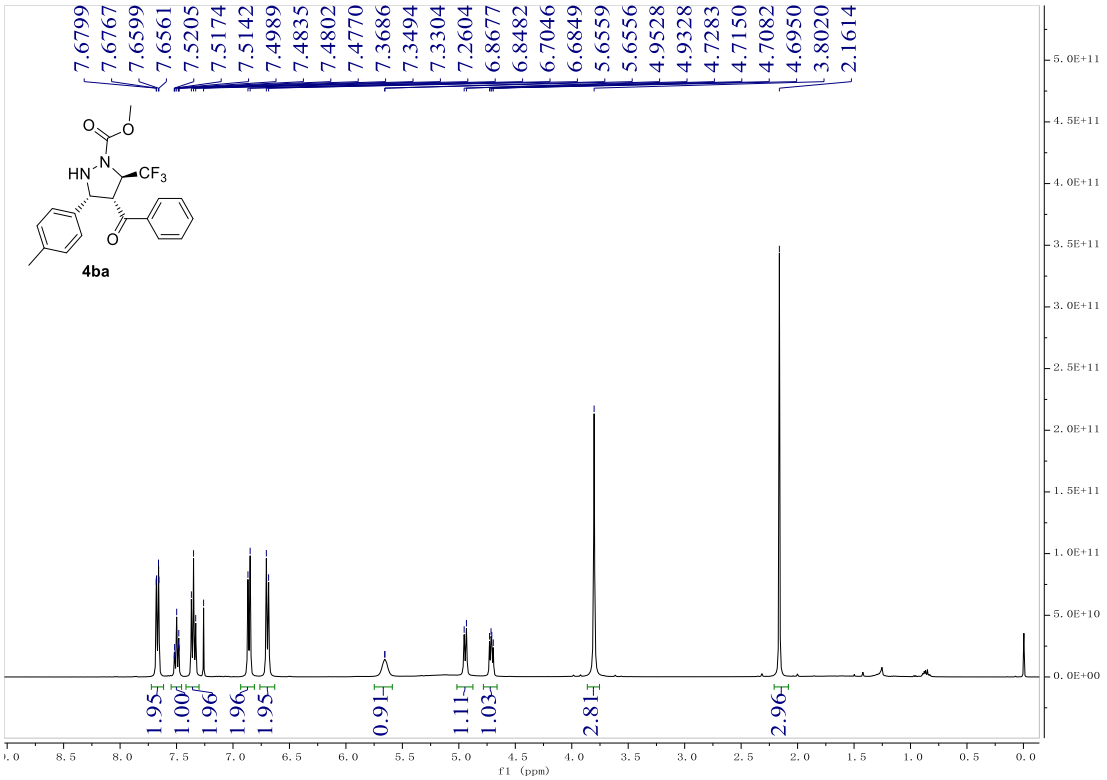
^{13}C{^{1}H} NMR of 4ao (150 MHz, $CDCl_3$)



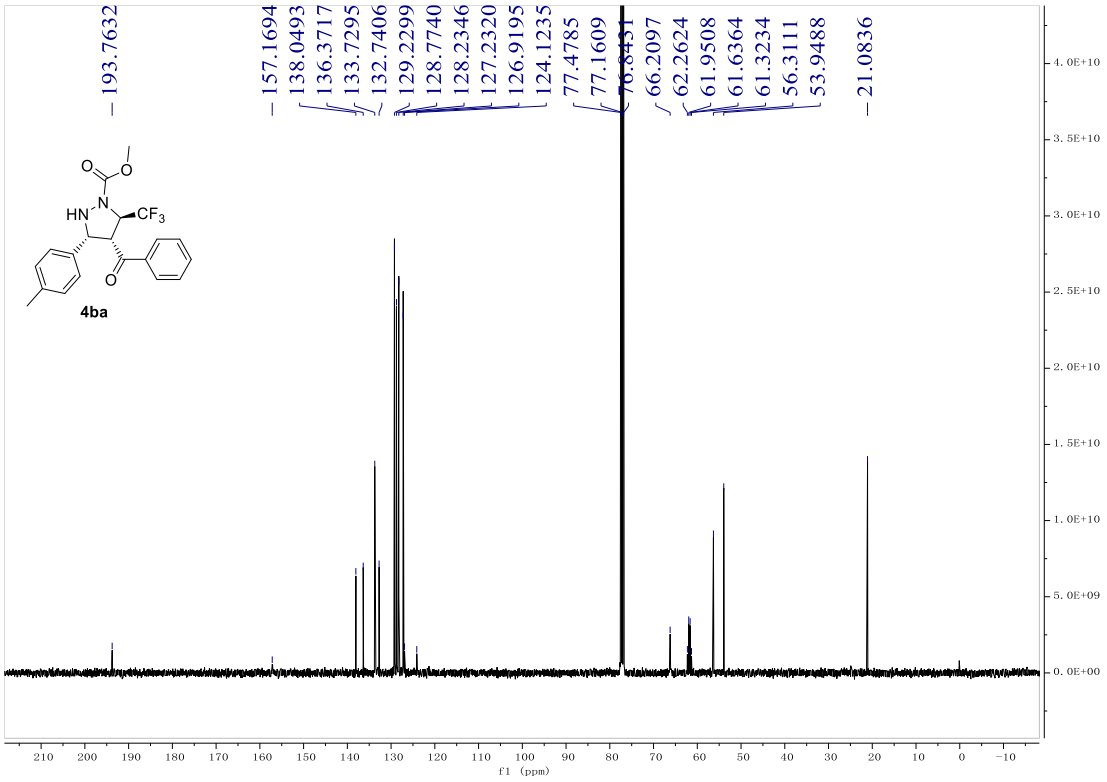
$^{19}F\{^{1}H\}$ NMR of 4ao (565 MHz, $CDCl_3$)



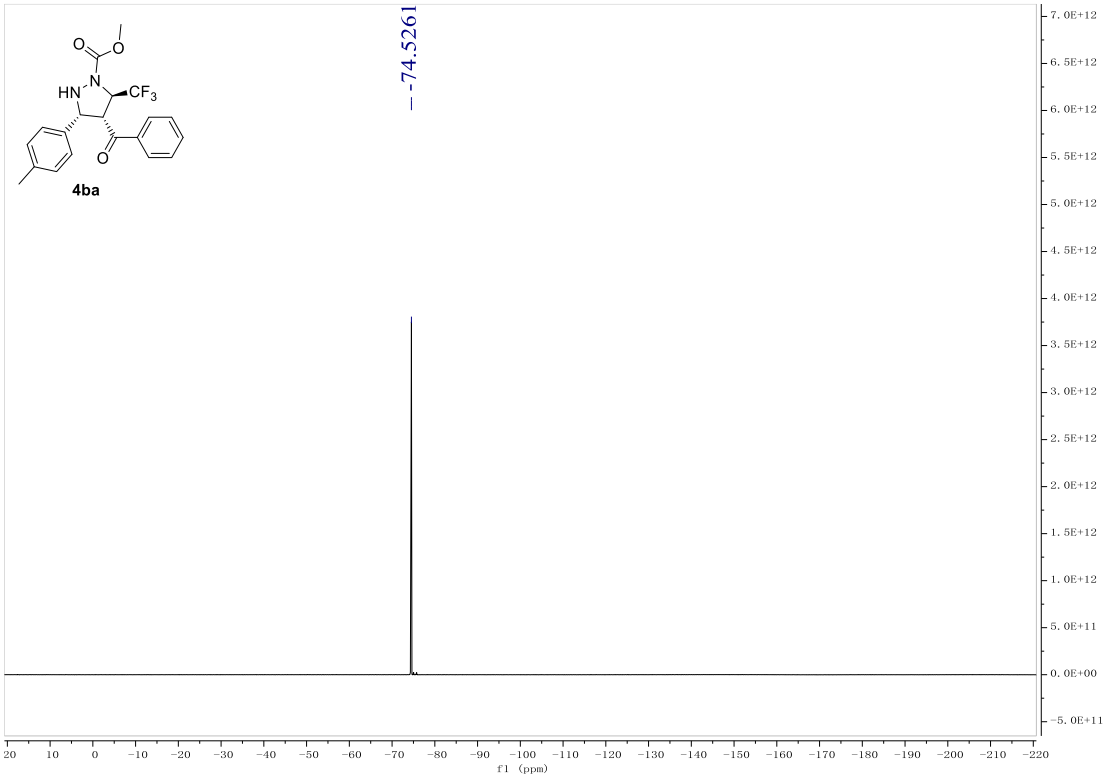
^{1}H NMR of 4ba (400 MHz, $CDCl_3$)



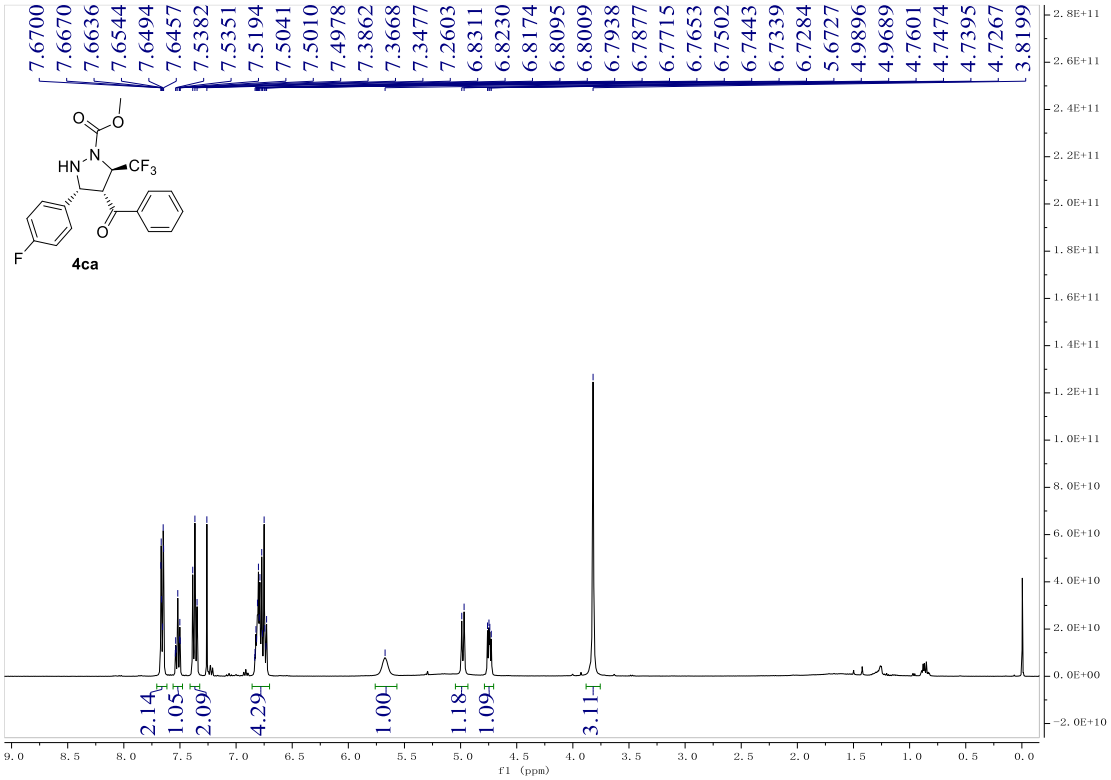
$^{13}C\{^{1}H\}$ NMR of 4ba (100 MHz, $CDCl_3$)



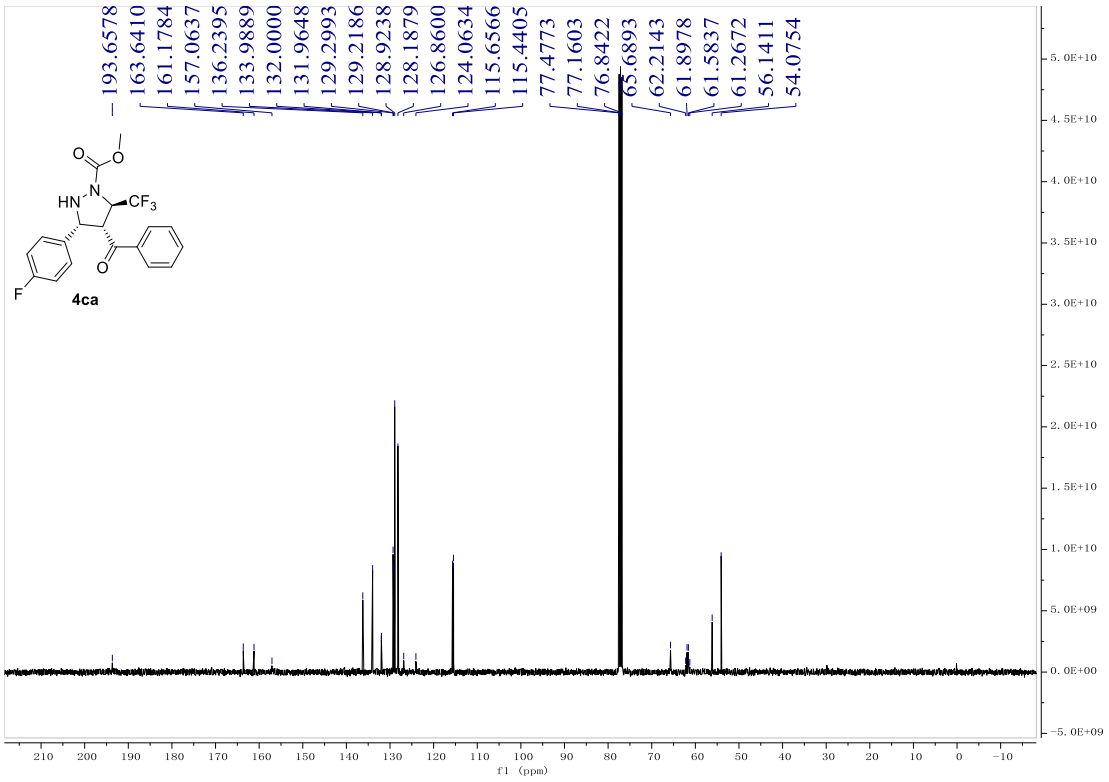
$^{19}F\{^{1}H\}$ NMR of 4ba (376 MHz, $CDCl_3$)



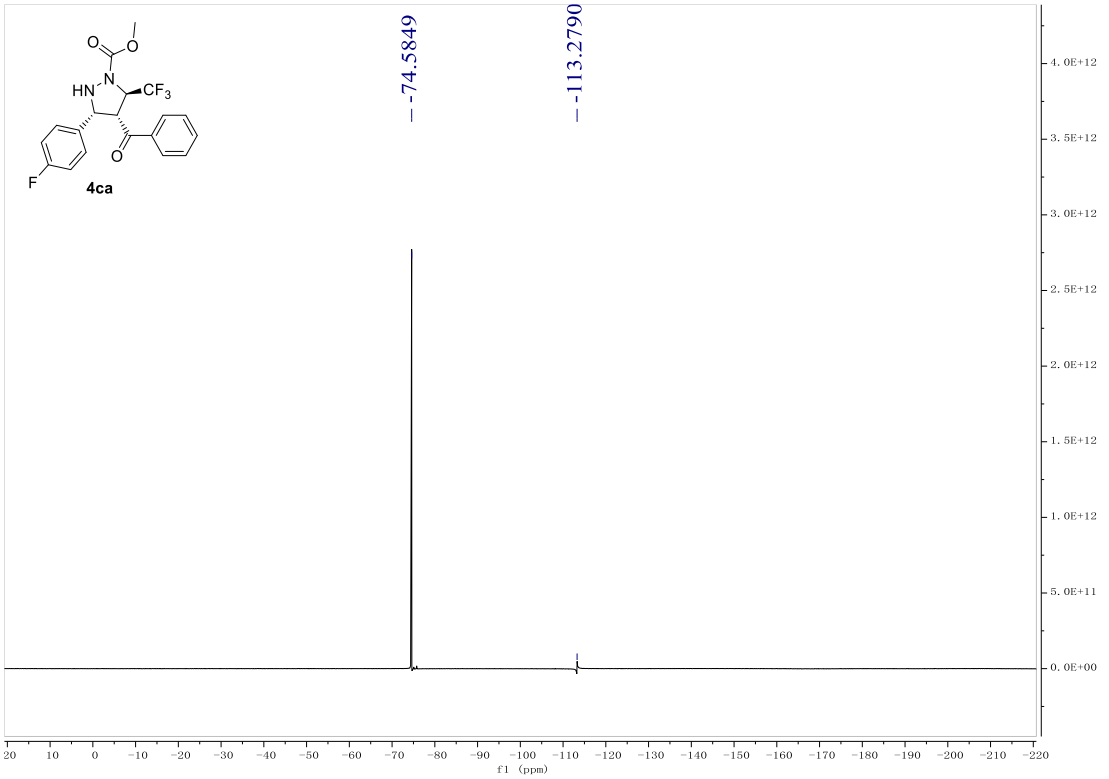
^{1}H NMR of 4ca (400 MHz, $CDCl_3$)



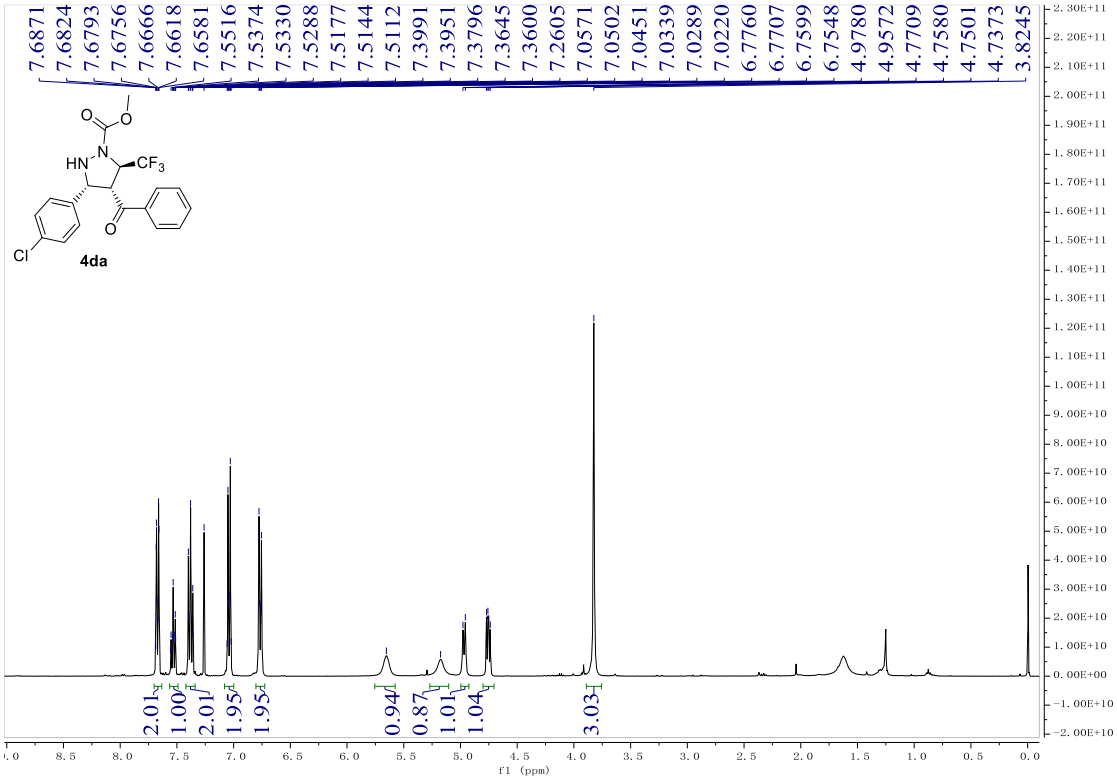
^{13}C{^{1}H} NMR of 4ca (100 MHz, $CDCl_3$)



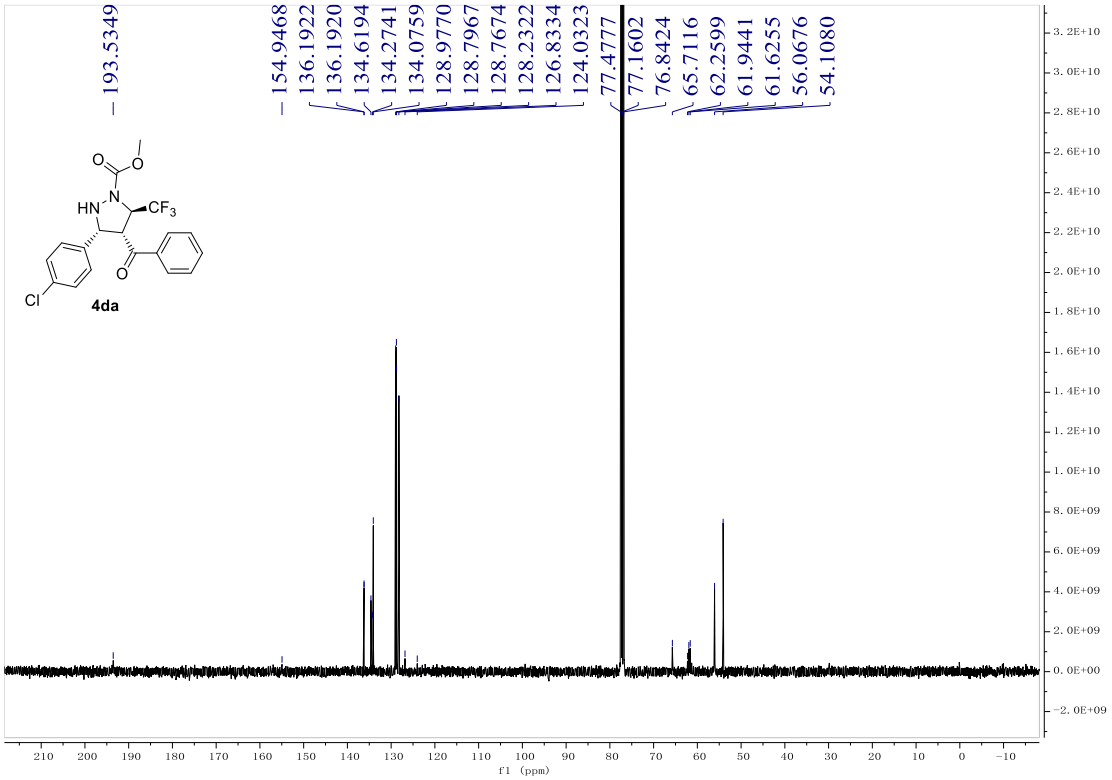
$^{19}F\{^{1}H\}$ NMR of 4ca (376 MHz, $CDCl_3$)



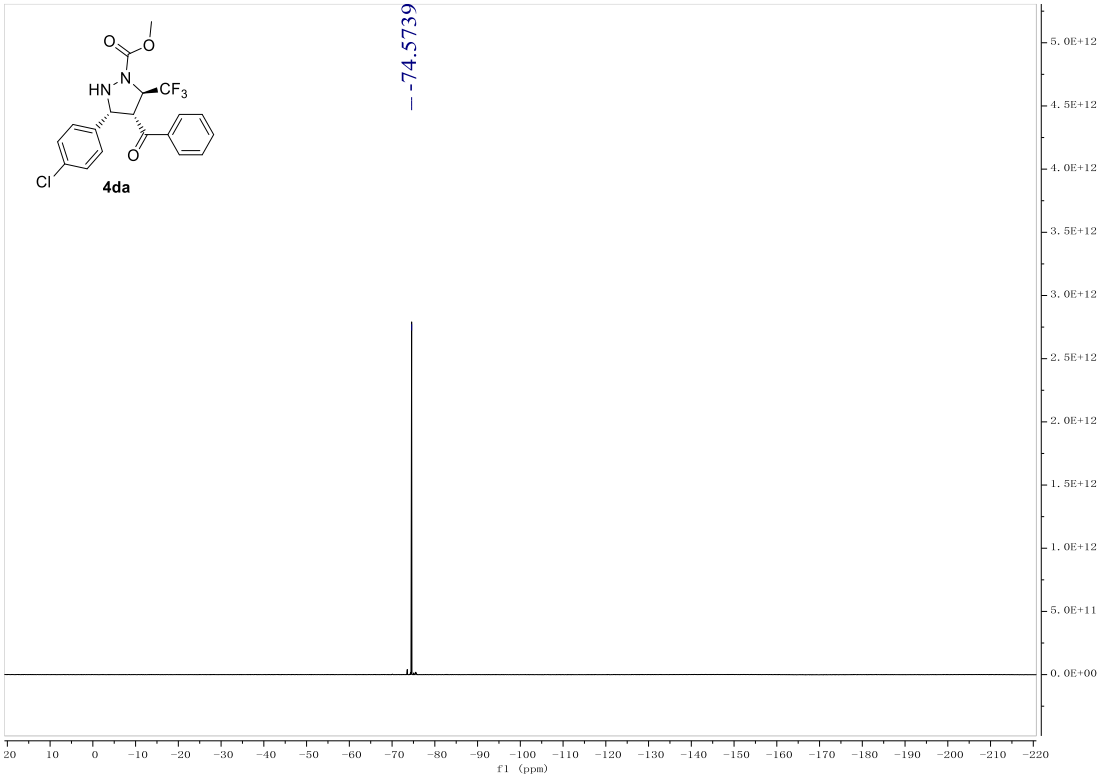
^{1}H NMR of 4da (400 MHz, $CDCl_3$)



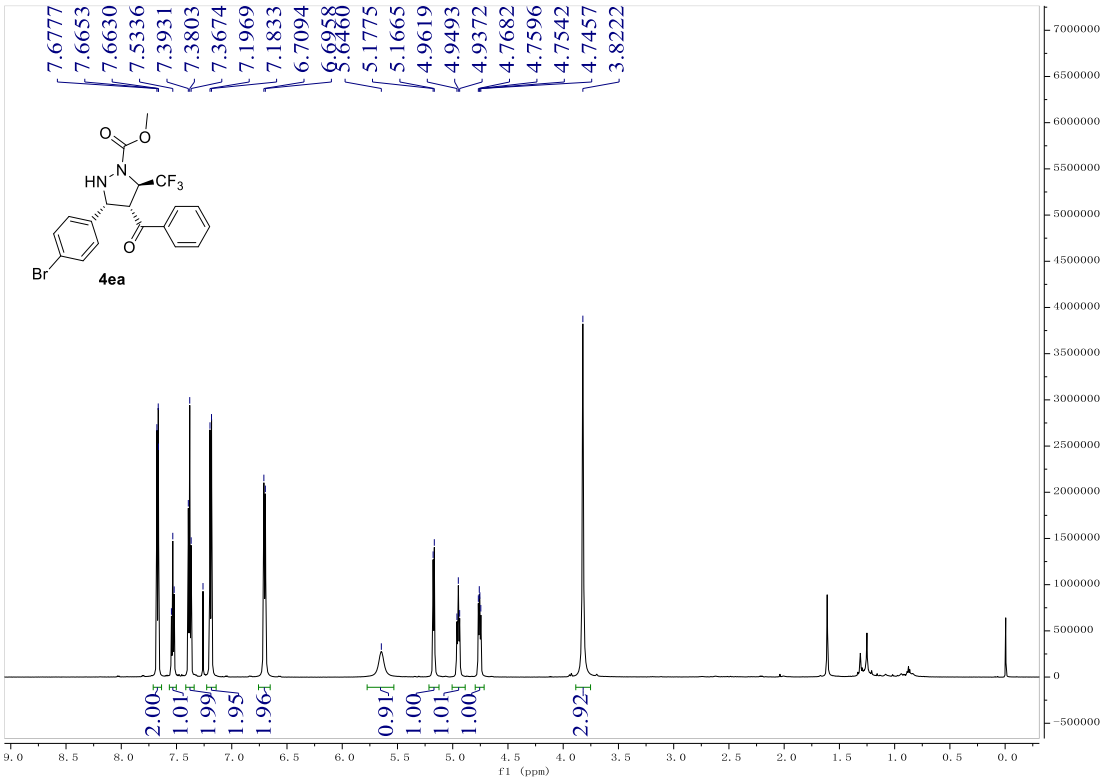
^{13}C{^{1}H} NMR of 4da (100 MHz, $CDCl_3$)



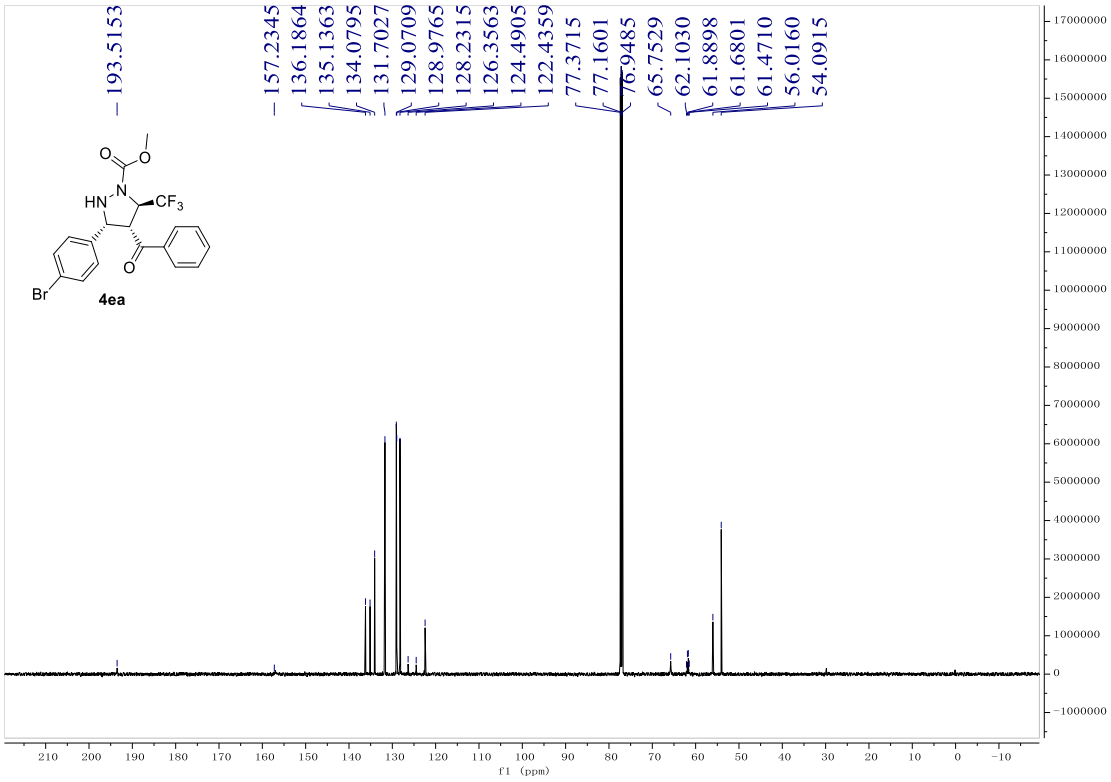
^{19}F{^{1}H} NMR of 4da (376 MHz, $CDCl_3$)



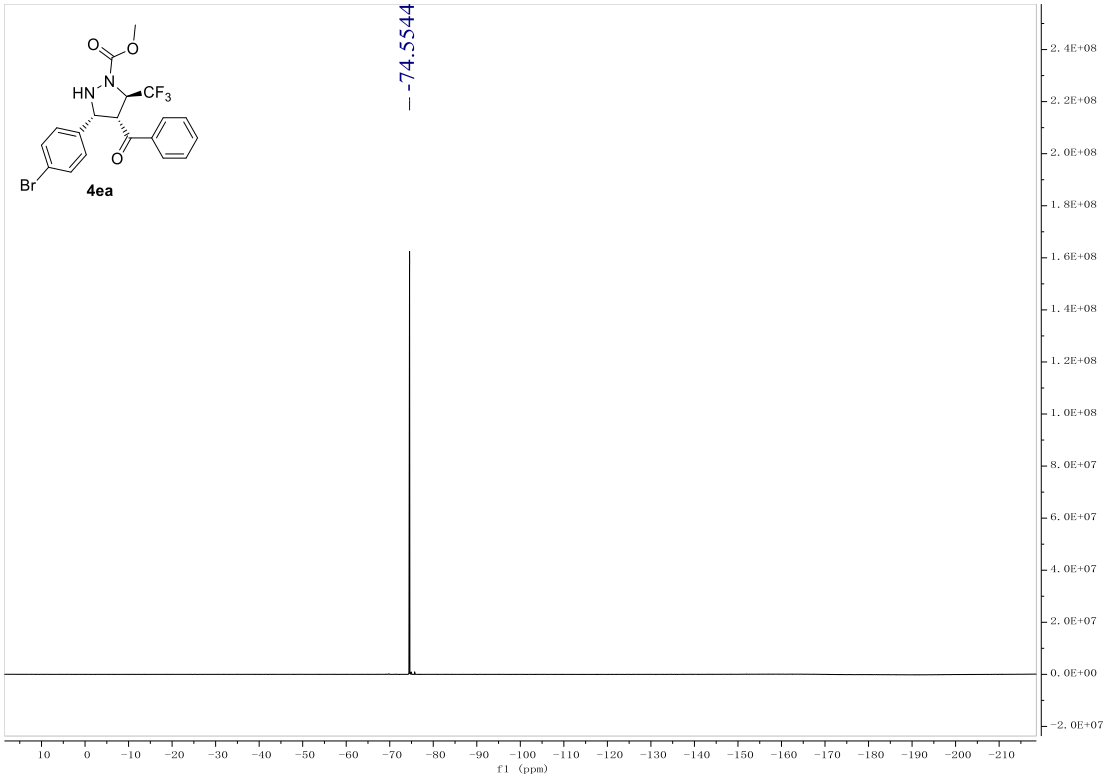
^{1}H NMR of 4ea (600 MHz, $CDCl_3$)



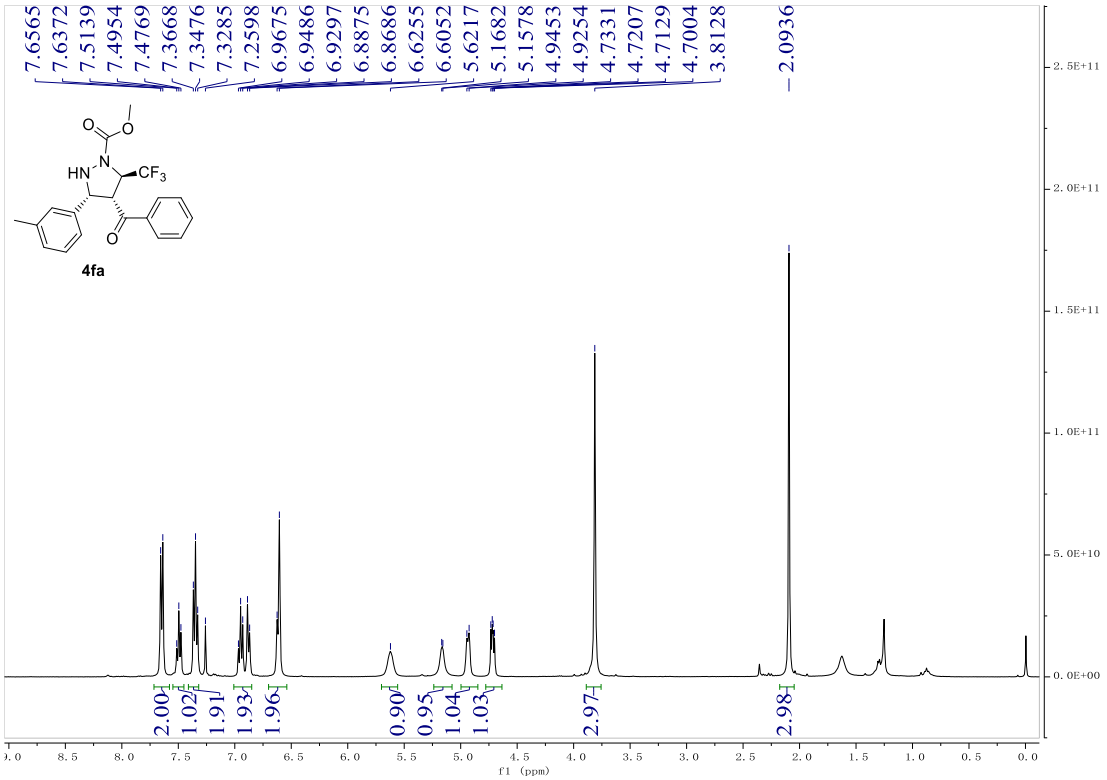
^{13}C{^{1}H} NMR of 4ea (150 MHz, $CDCl_3$)



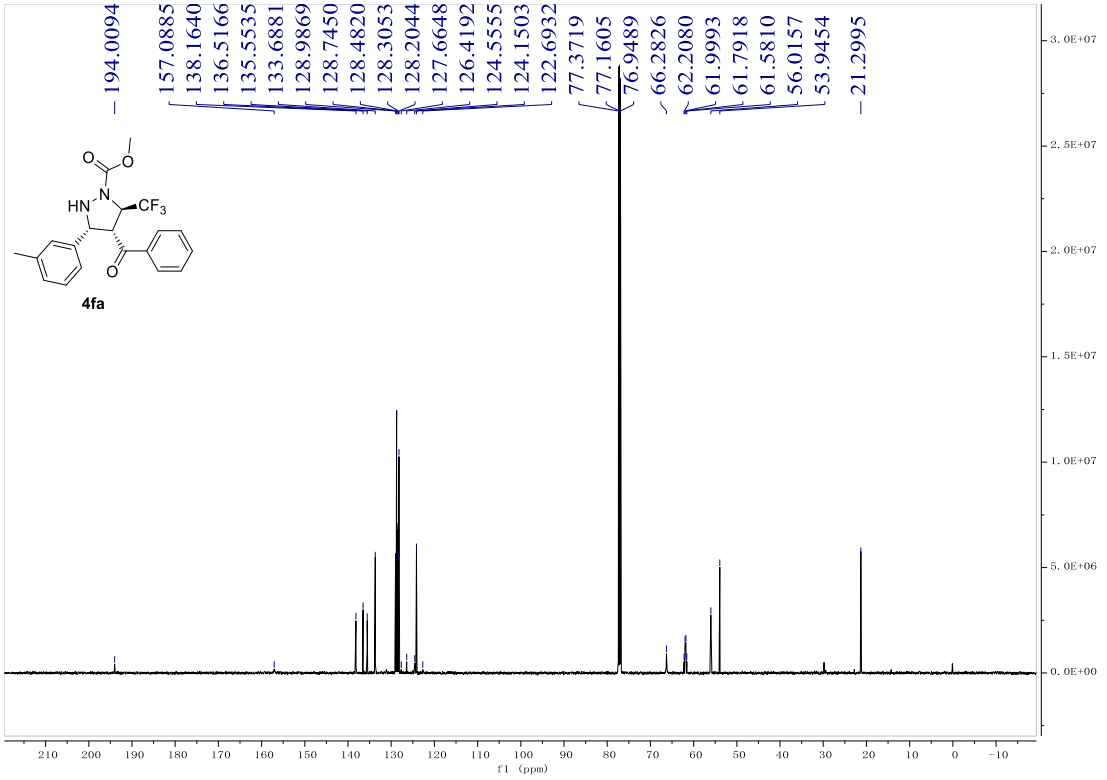
$^{19}F\{^{1}H\}$ NMR of 4ea (565 MHz, $CDCl_3$)



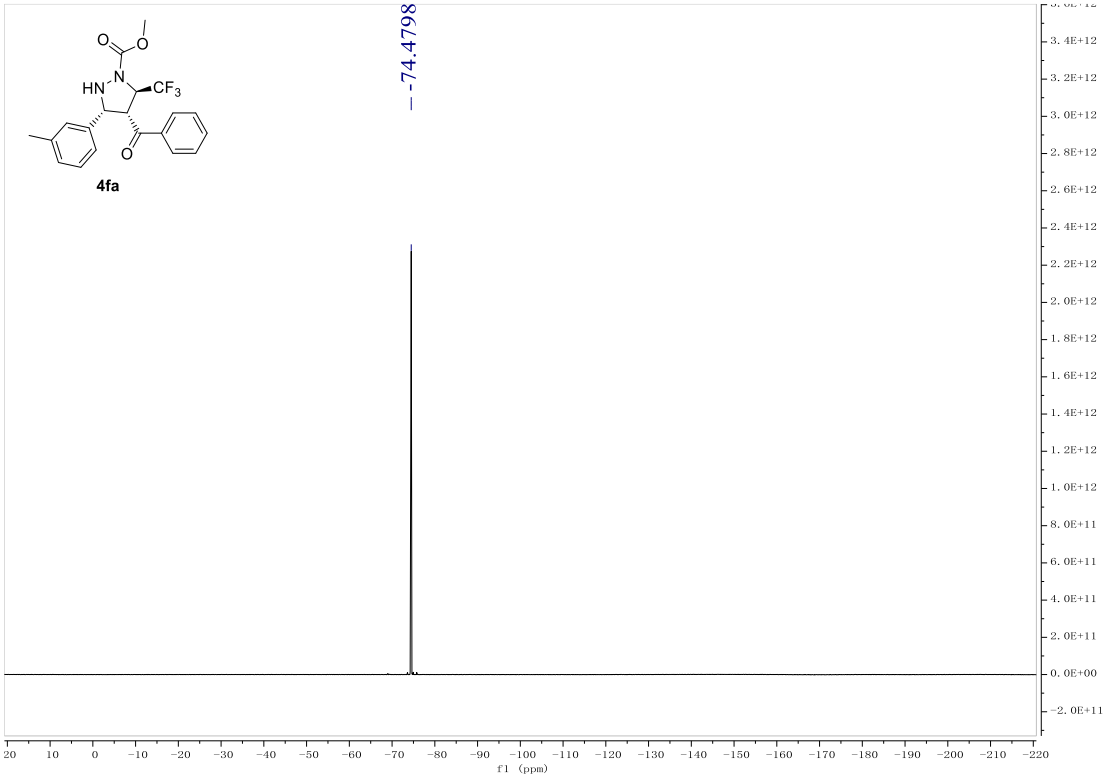
^{1}H NMR of 4fa (400 MHz, $CDCl_3$)



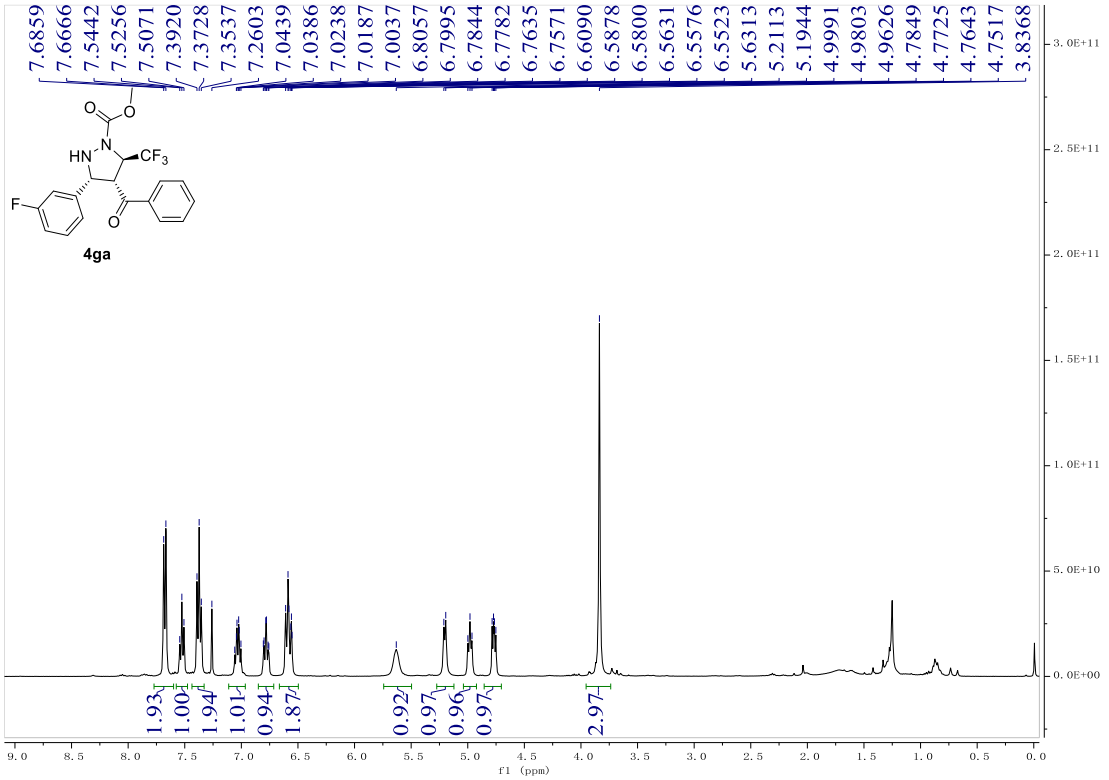
$^{13}C\{^{1}H\}$ NMR of 4fa (150 MHz, $CDCl_3$)



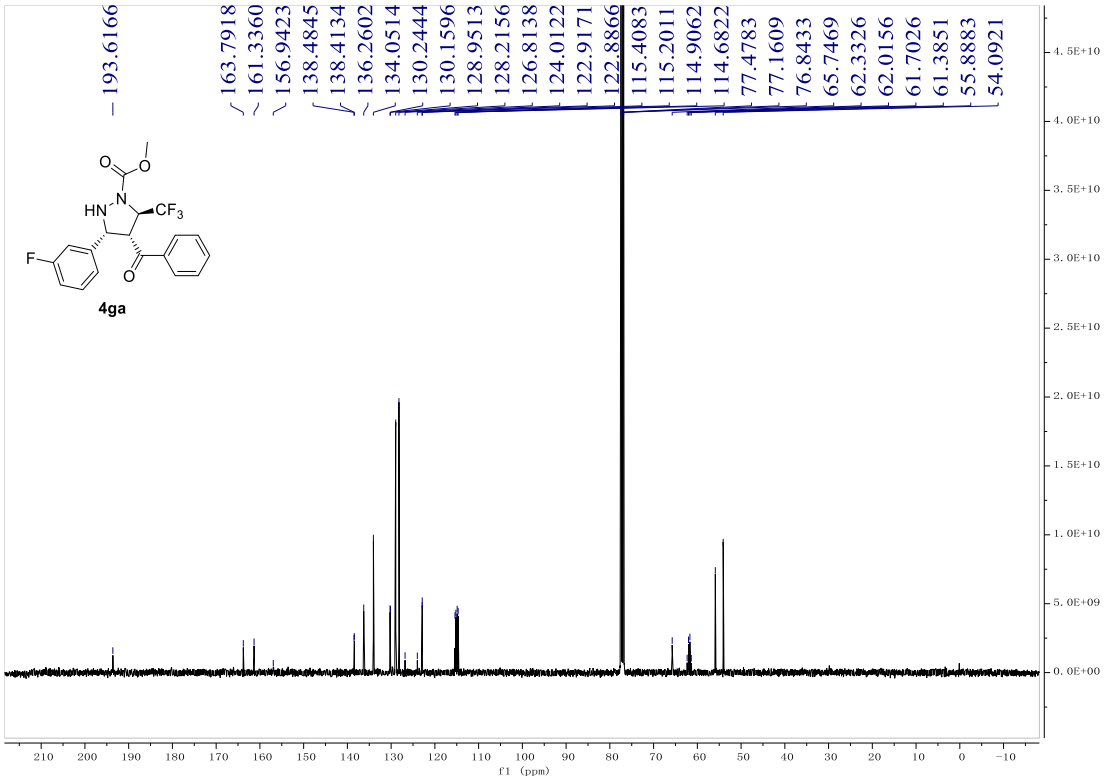
$^{19}F\{^{1}H\}$ NMR of 4fa (376 MHz, $CDCl_3$)



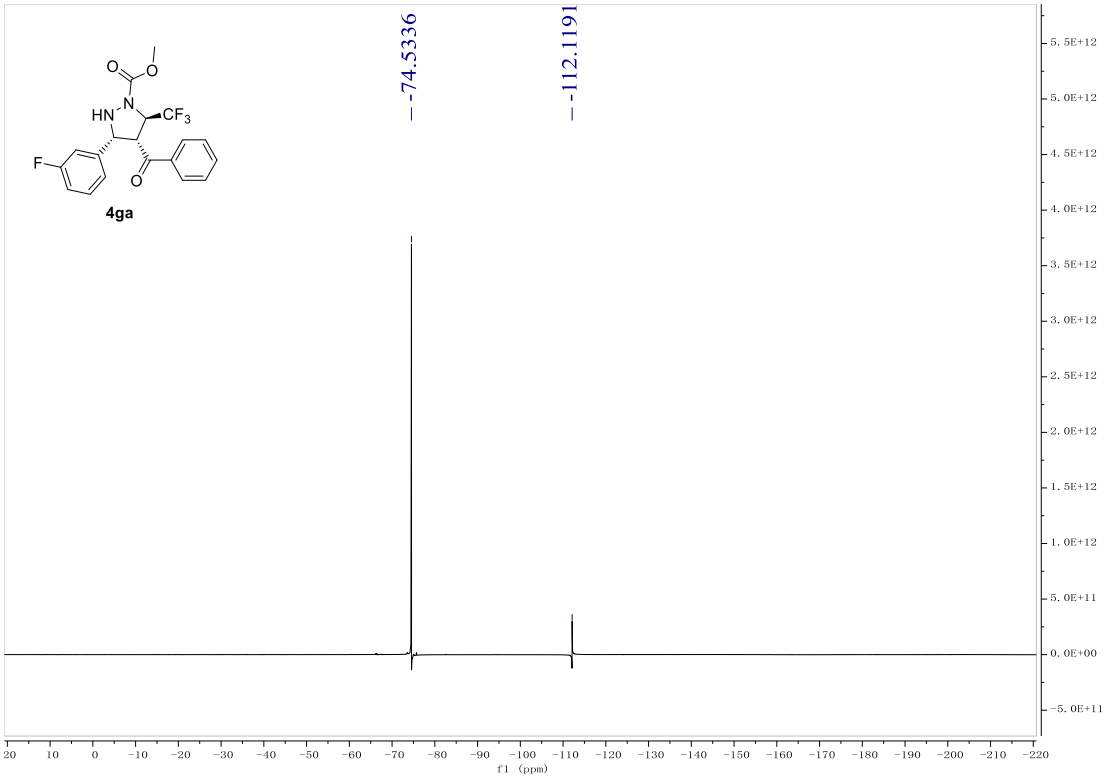
^{1}H NMR of 4ga (400 MHz, $CDCl_3$)



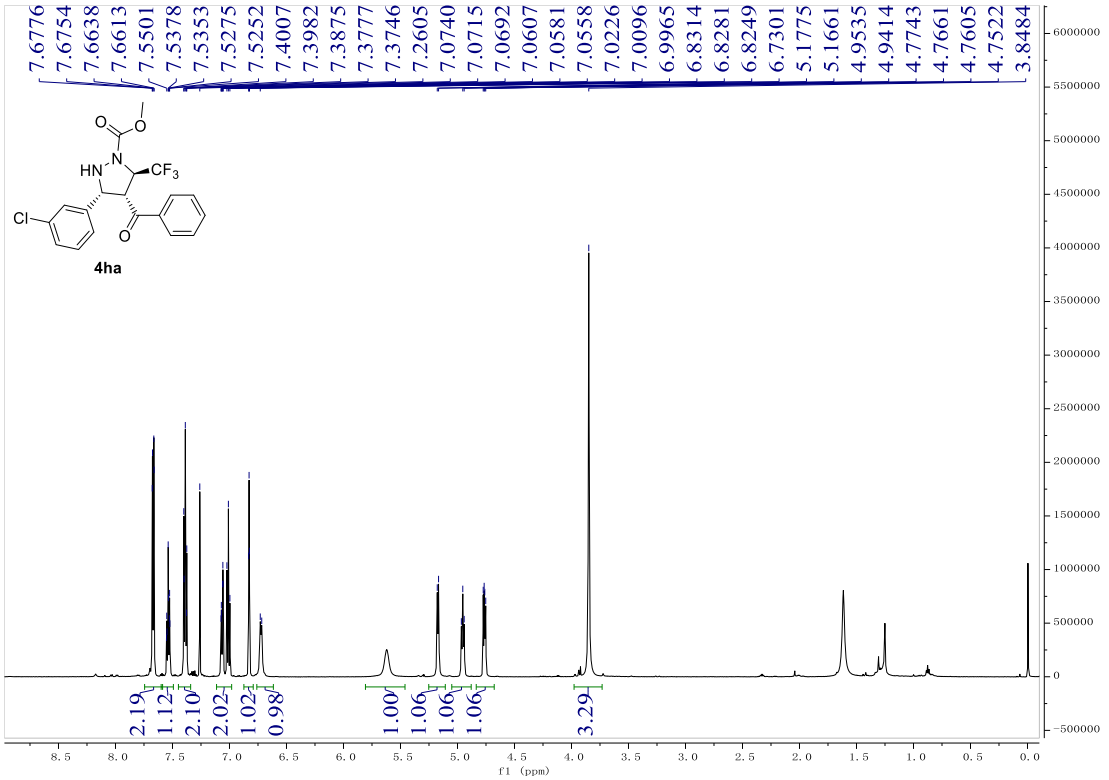
^{13}C{^{1}H} NMR of 4ga (100 MHz, $CDCl_3$)



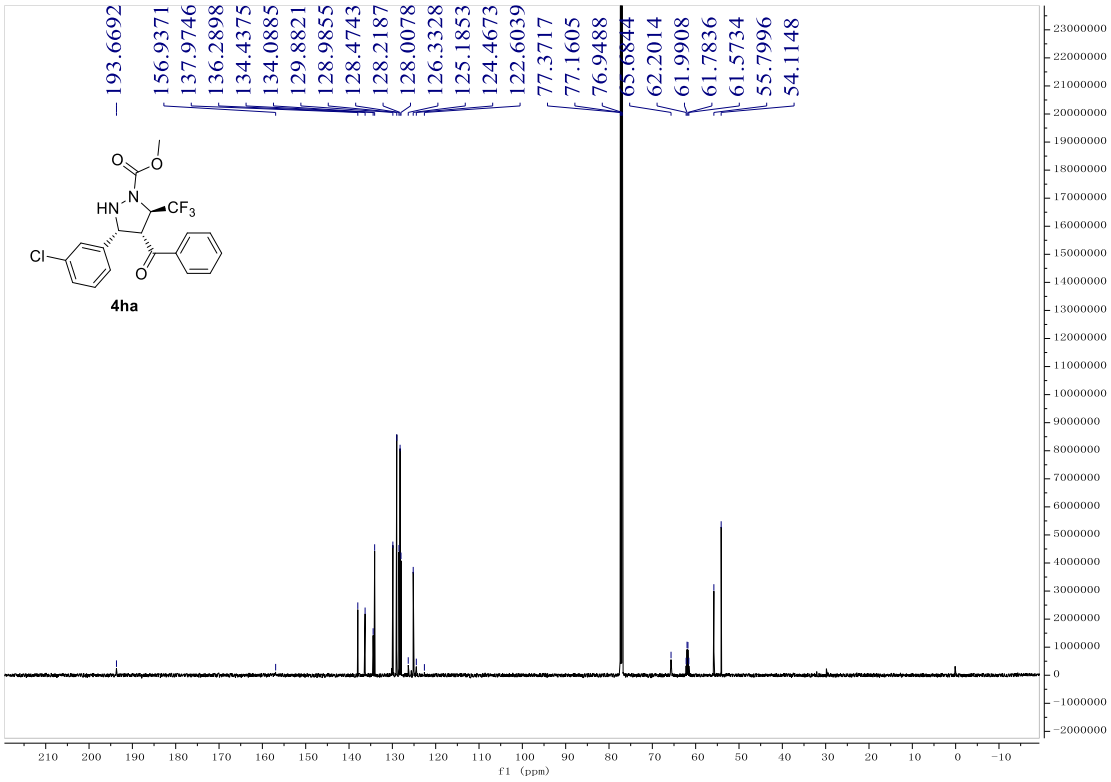
$^{19}F\{^{1}H\}$ NMR of 4ga (376 MHz, $CDCl_3$)



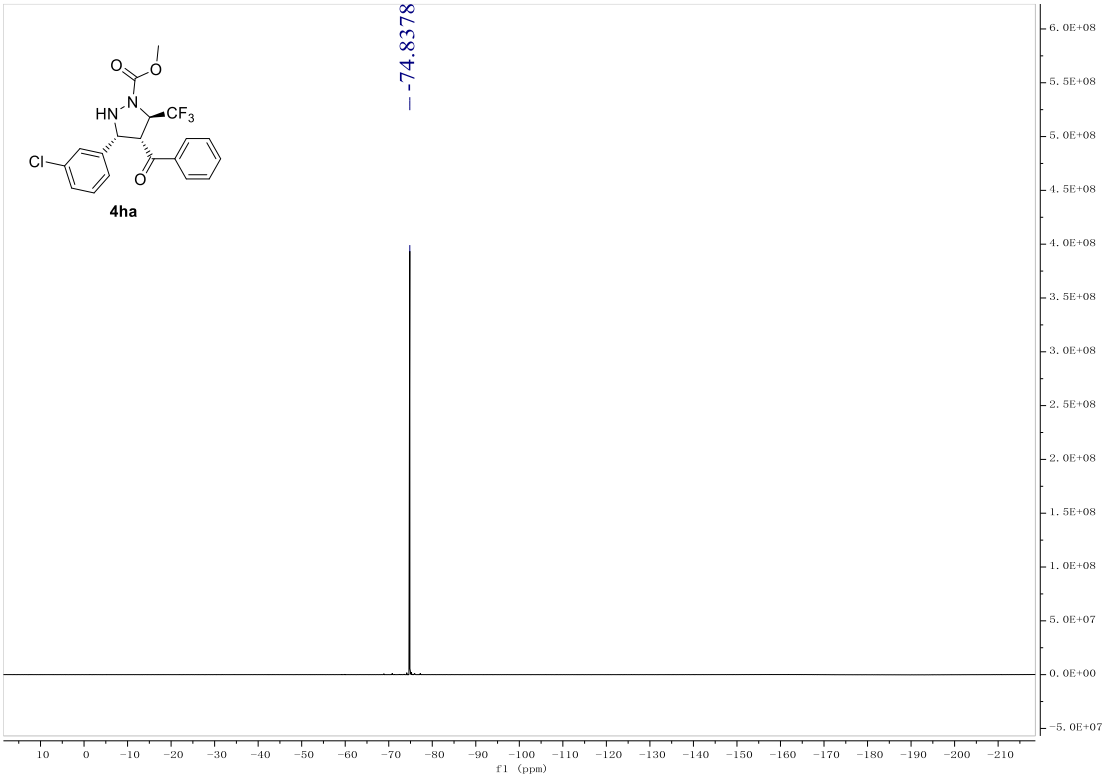
^{1}H NMR of 4ha (600 MHz, $CDCl_3$)



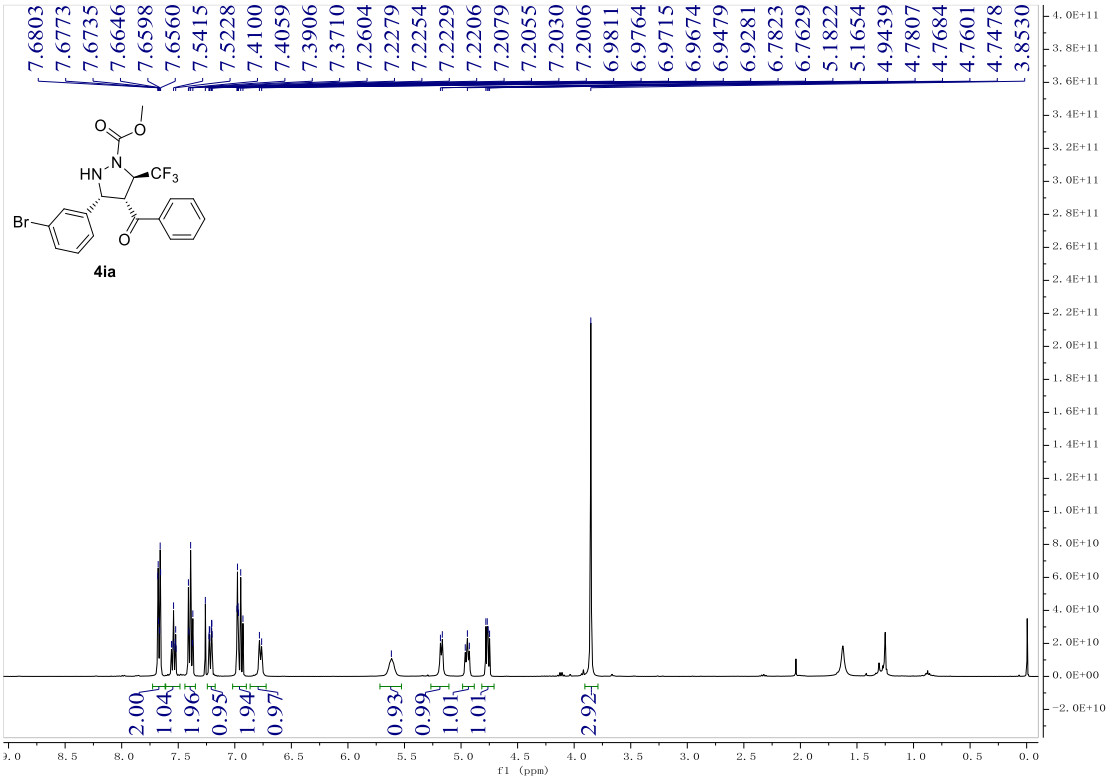
$^{13}C\{^{1}H\}$ NMR of 4ha (150 MHz, $CDCl_3$)



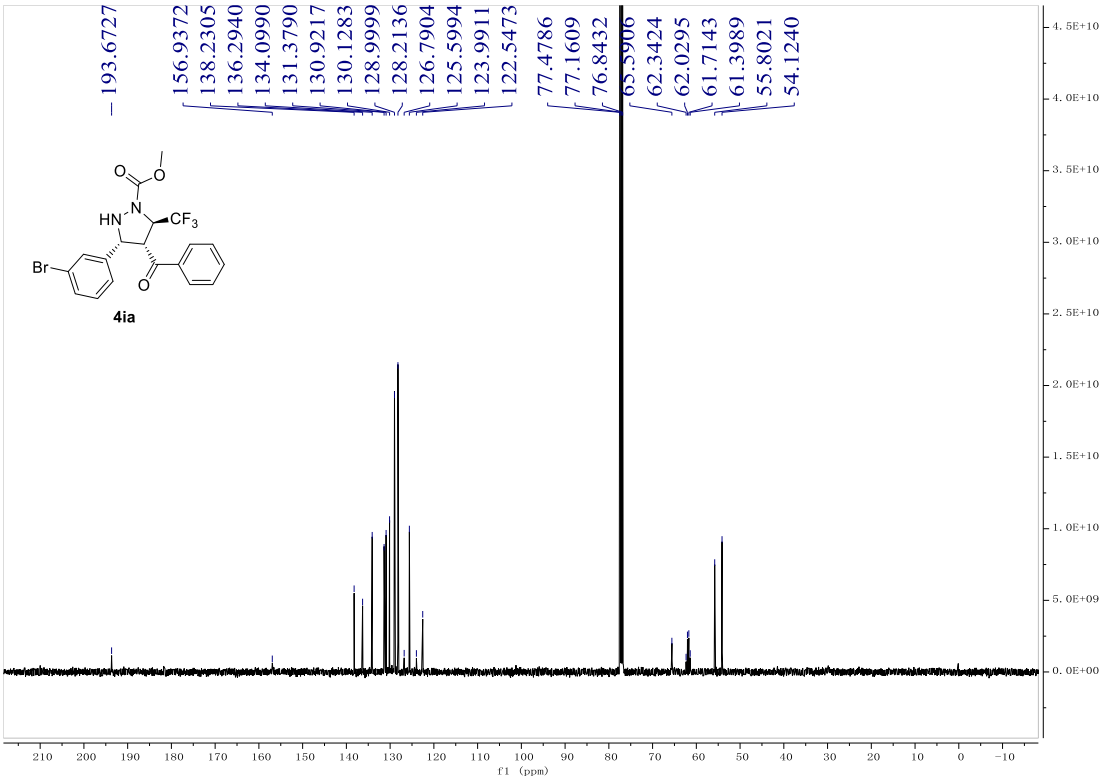
$^{19}F\{^{1}H\}$ NMR of 4ha (565 MHz, $CDCl_3$)



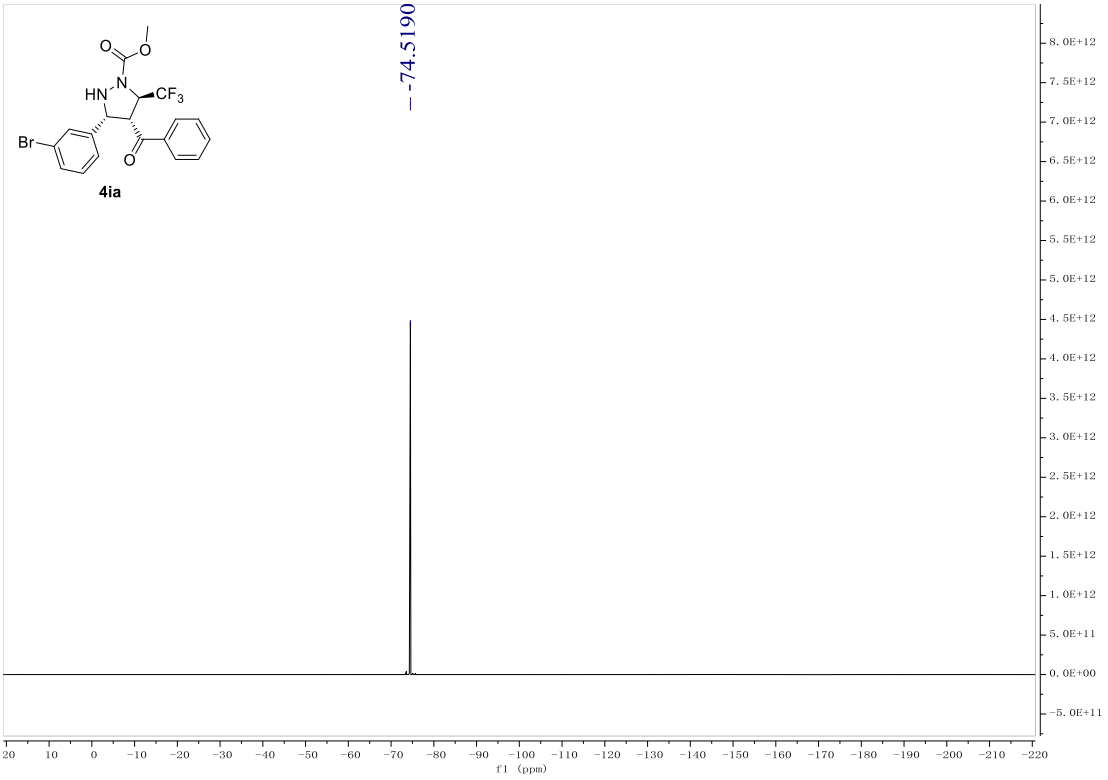
^{1}H NMR of 4ia (400 MHz, $CDCl_3$)



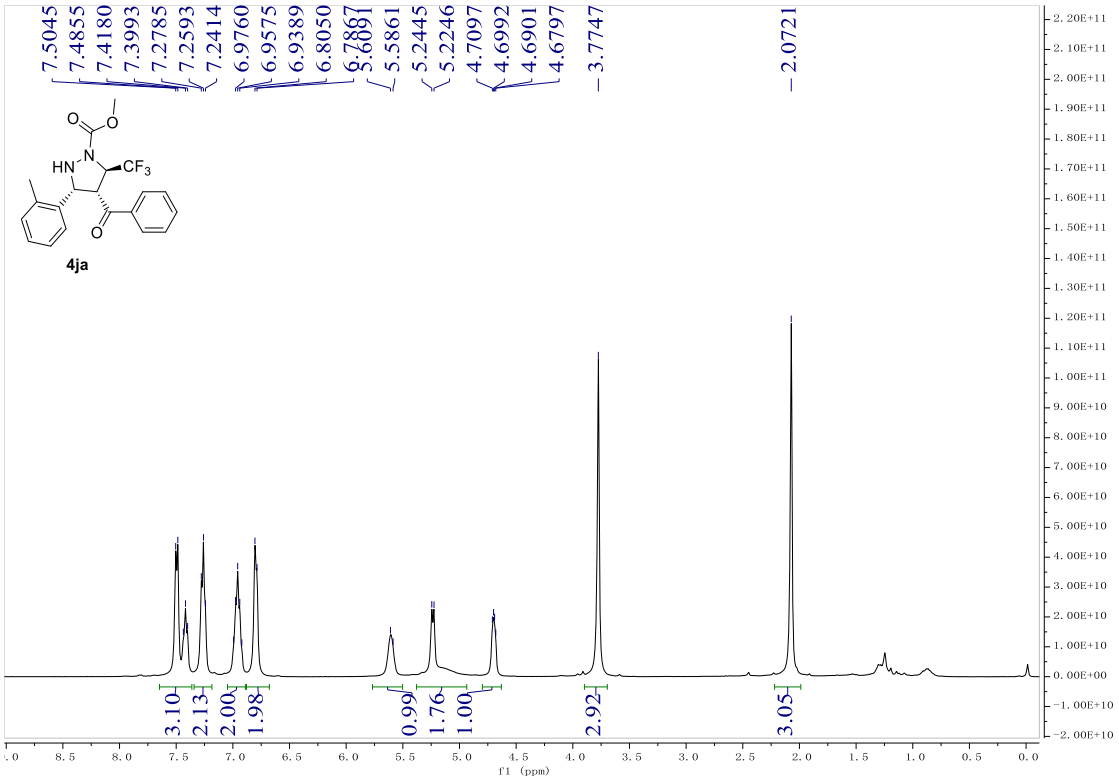
^{13}C{^{1}H} NMR of 4ia (100 MHz, $CDCl_3$)



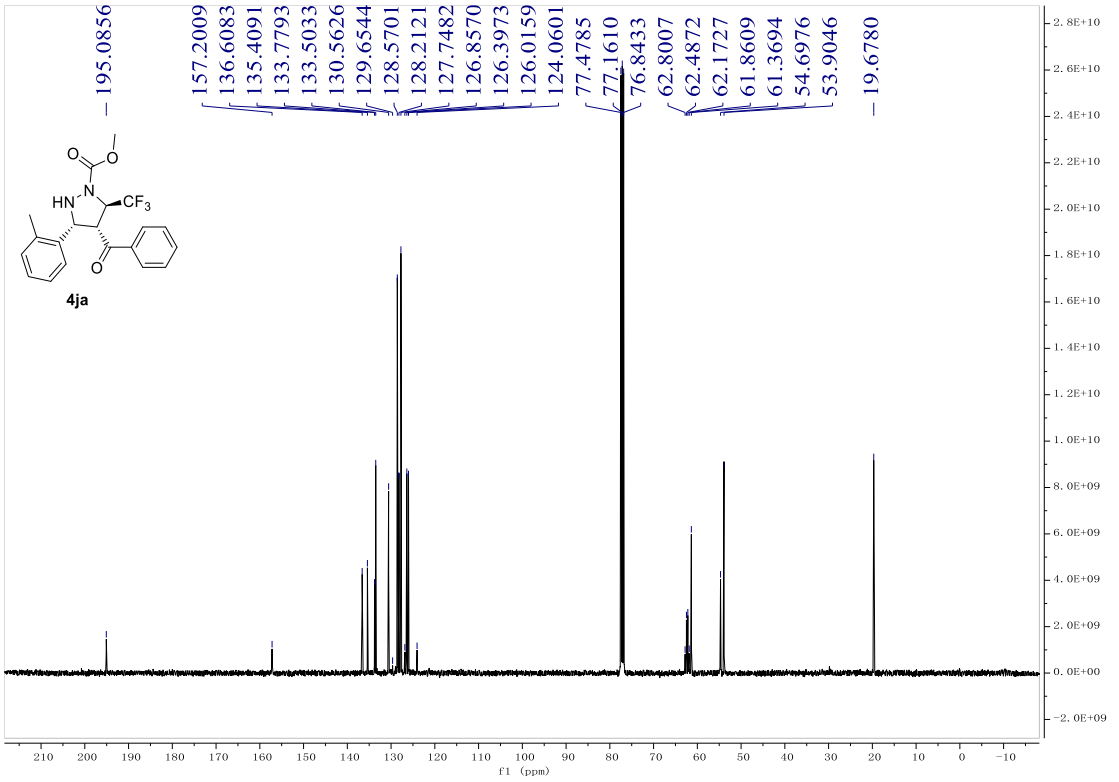
$^{19}F\{^{1}H\}$ NMR of 4ia (376 MHz, $CDCl_3$)



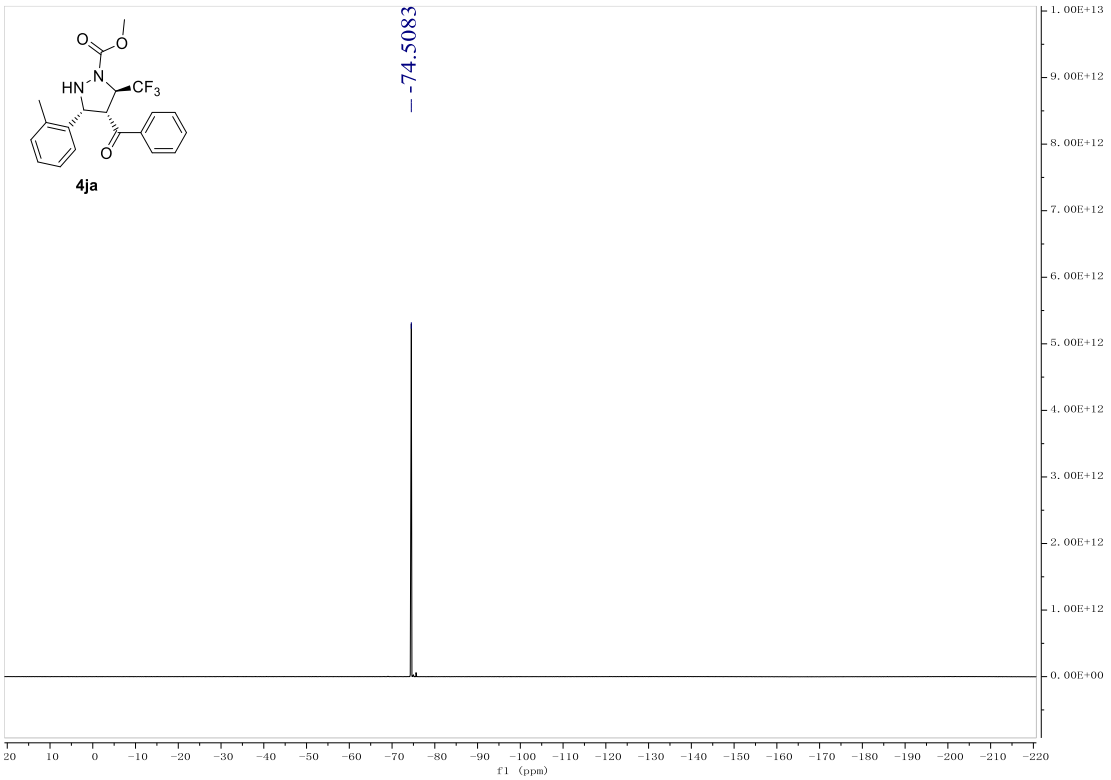
^{1}H NMR of 4ja (600 MHz, $CDCl_3$)



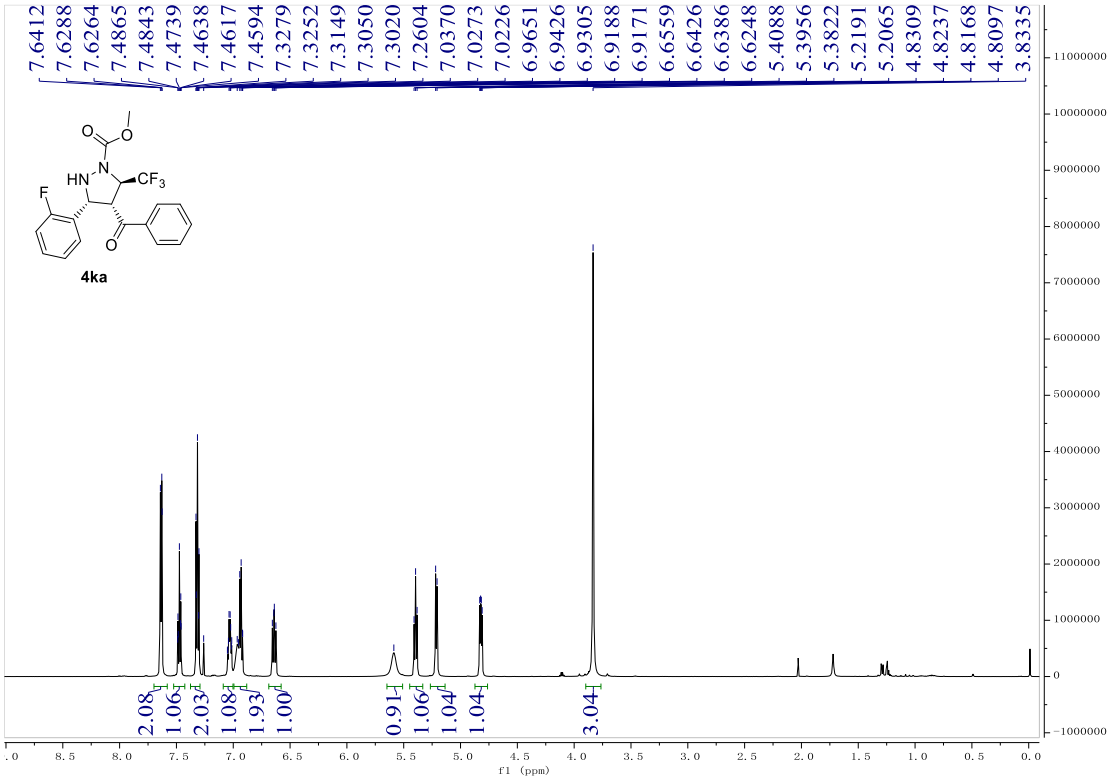
$^{13}C\{^{1}H\}$ NMR of 4ja (100 MHz, $CDCl_3$)



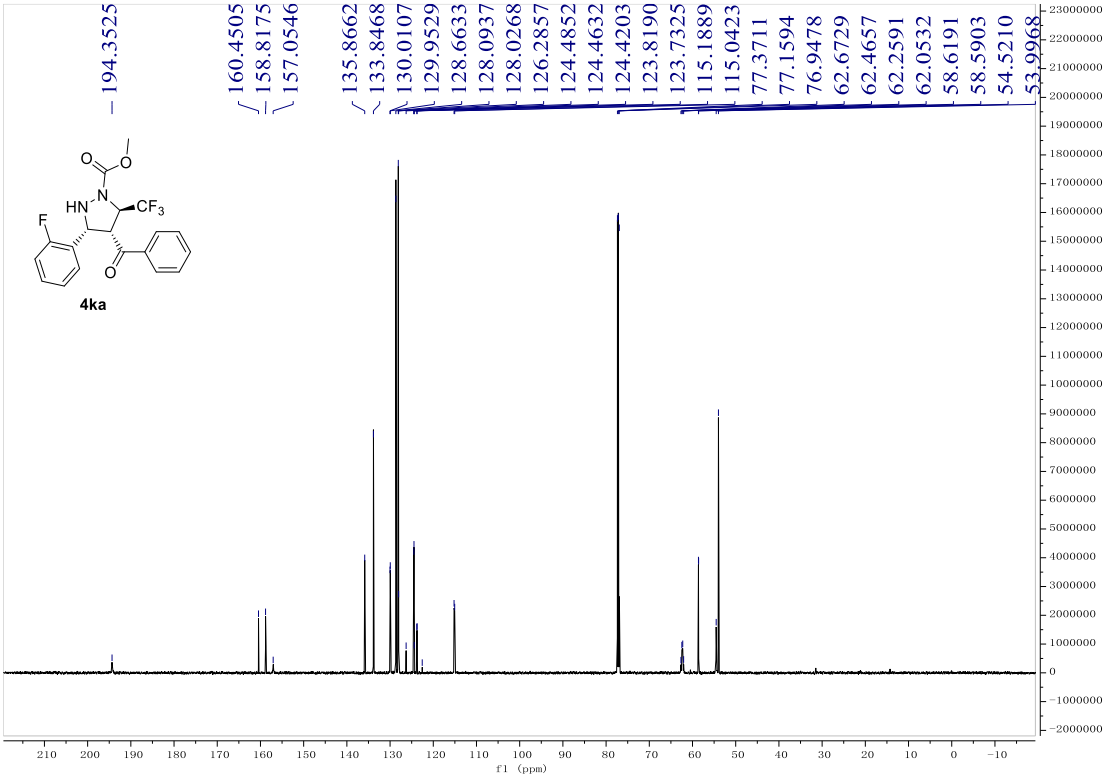
$^{19}F\{^{1}H\}$ NMR of 4ja (376 MHz, $CDCl_3$)



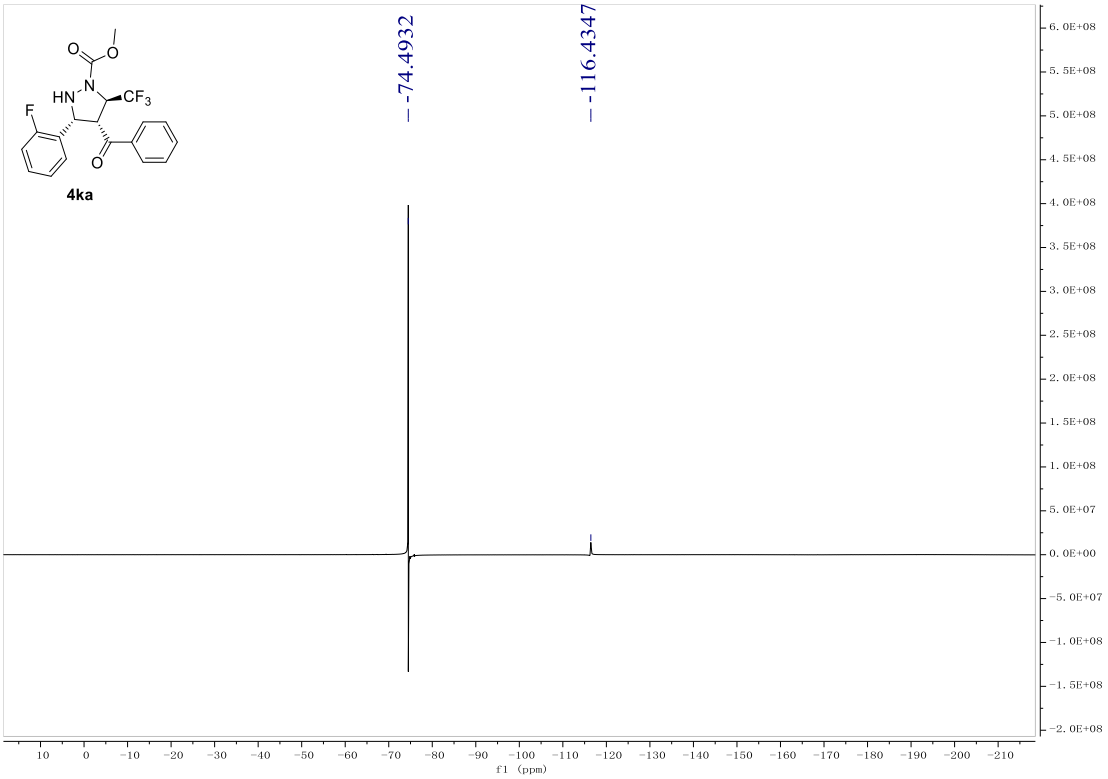
^{1}H NMR of 4ka (600 MHz, $CDCl_3$)



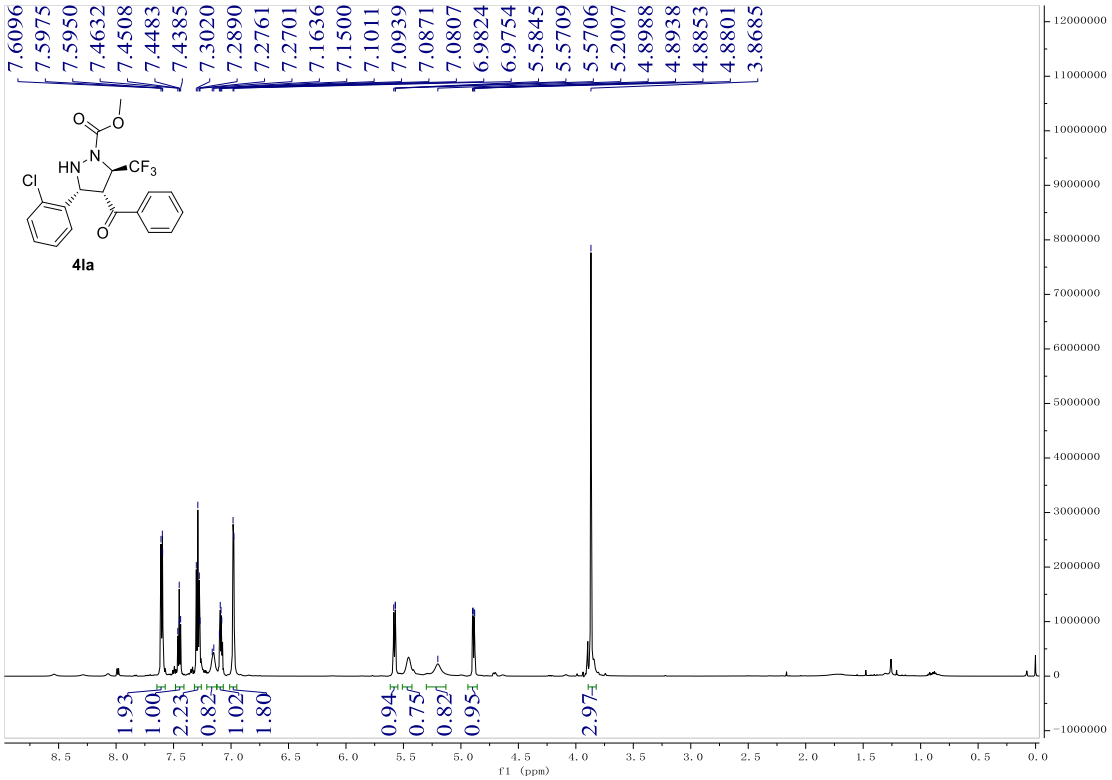
^{13}C{^{1}H} NMR of 4ka (150 MHz, $CDCl_3$)



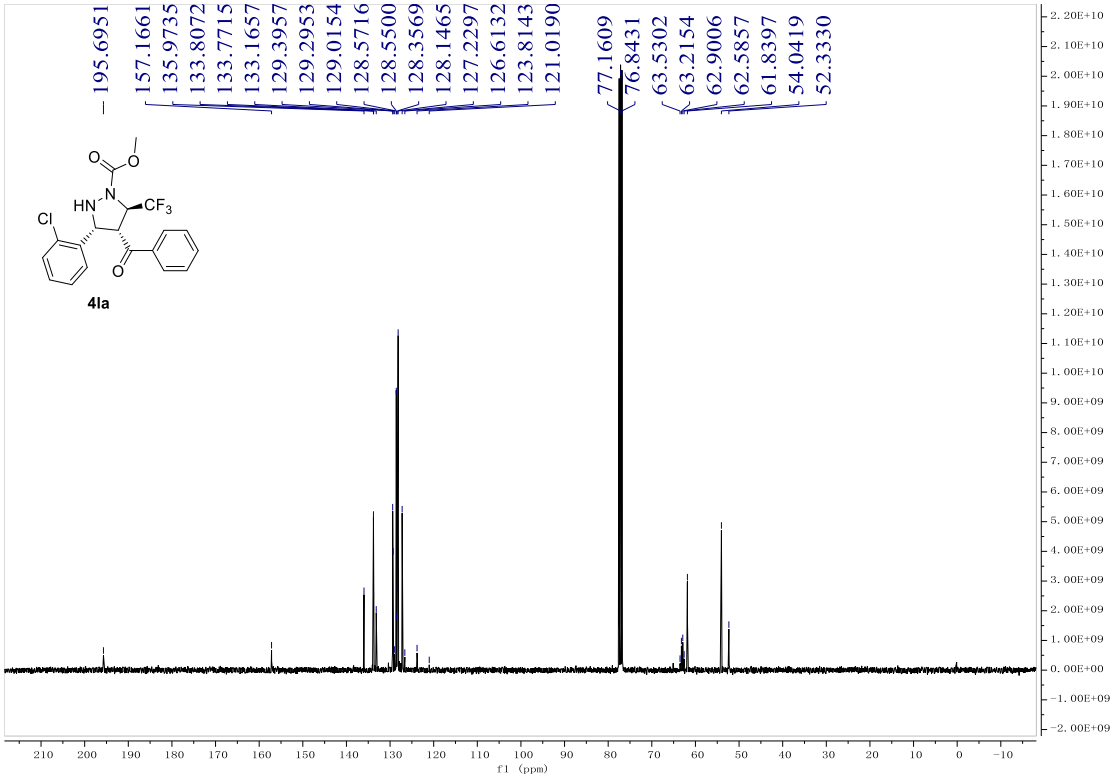
$^{19}F\{^{1}H\}$ NMR of 4ka (565 MHz, $CDCl_3$)



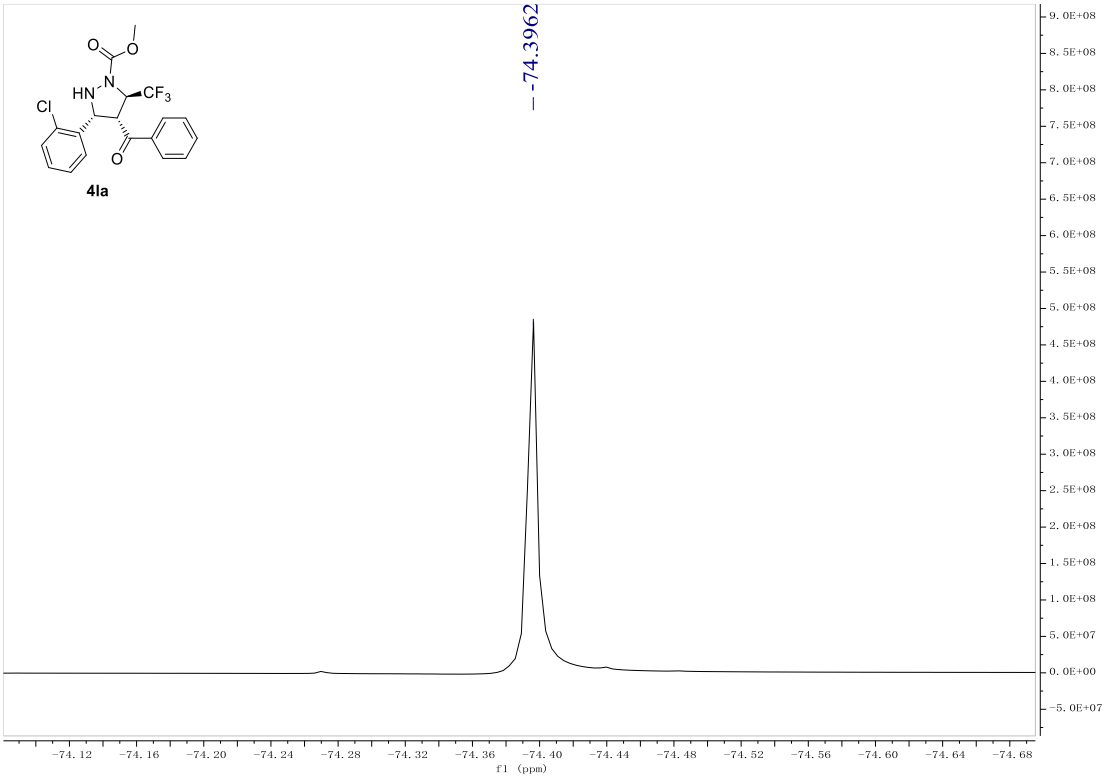
^{1}H NMR of 4la (600 MHz, $CDCl_3$)



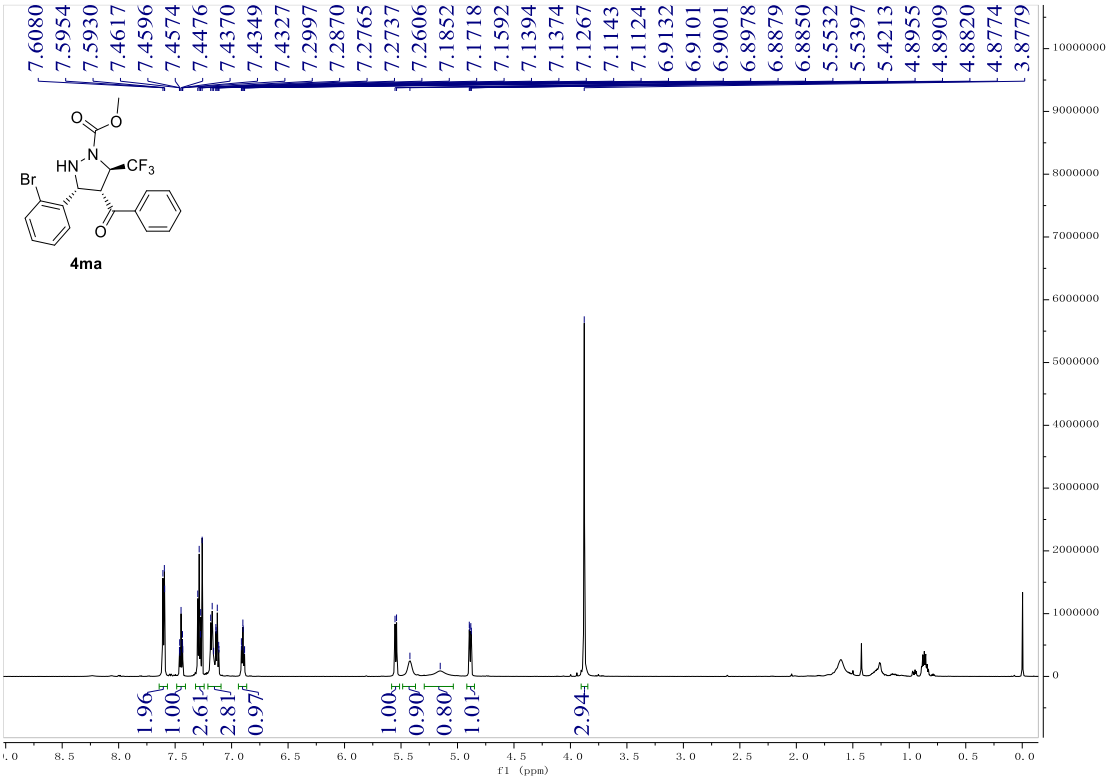
$^{13}C\{^{1}H\}$ NMR of 4la (150 MHz, $CDCl_3$)



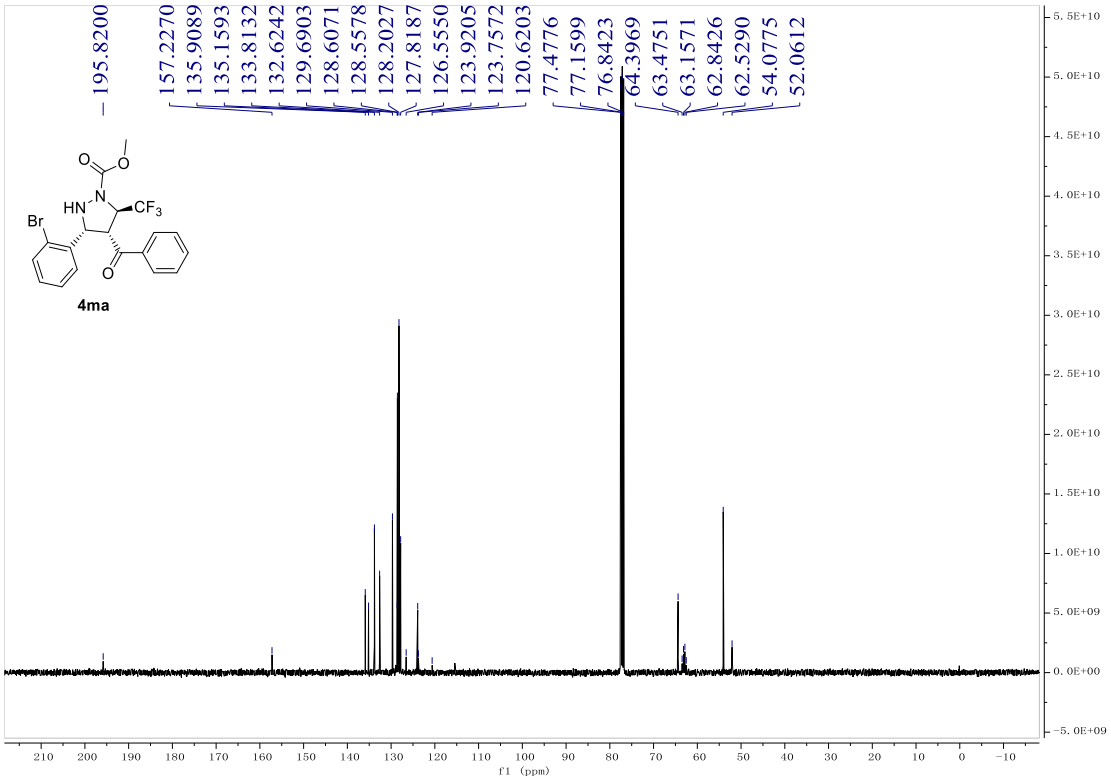
$^{19}F\{^{1}H\}$ NMR of 4la (565 MHz, $CDCl_3$)



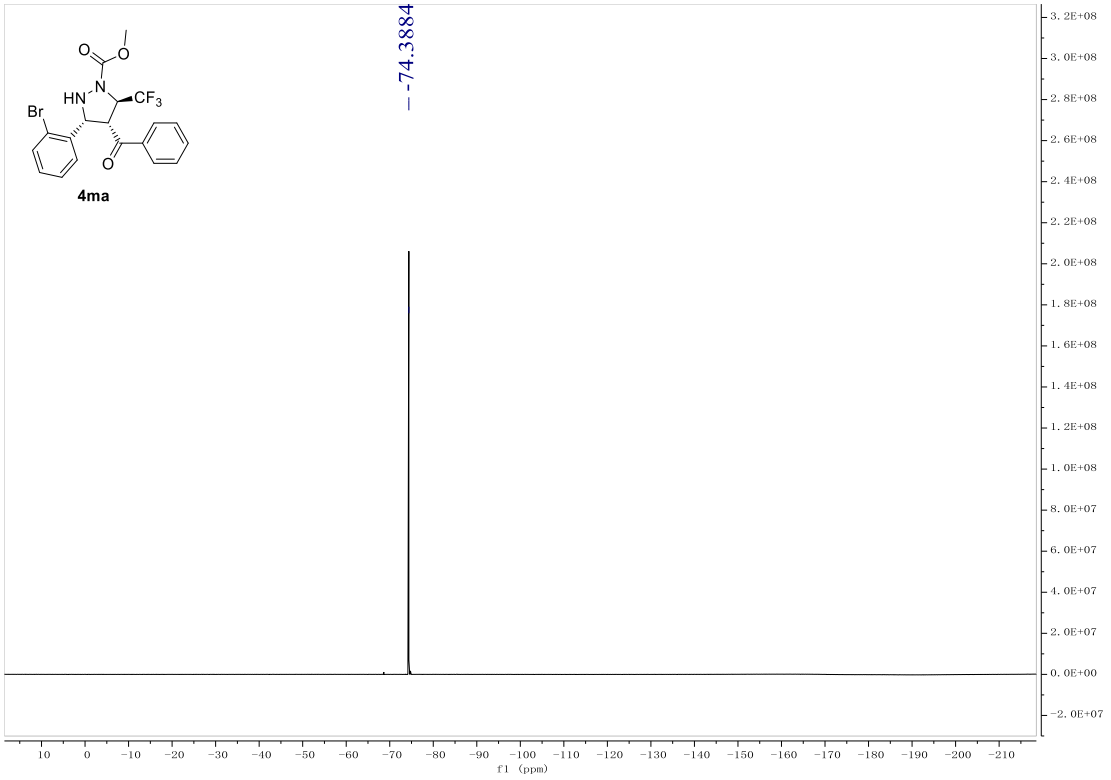
^{1}H NMR of 4ma (600 MHz, $CDCl_3$)



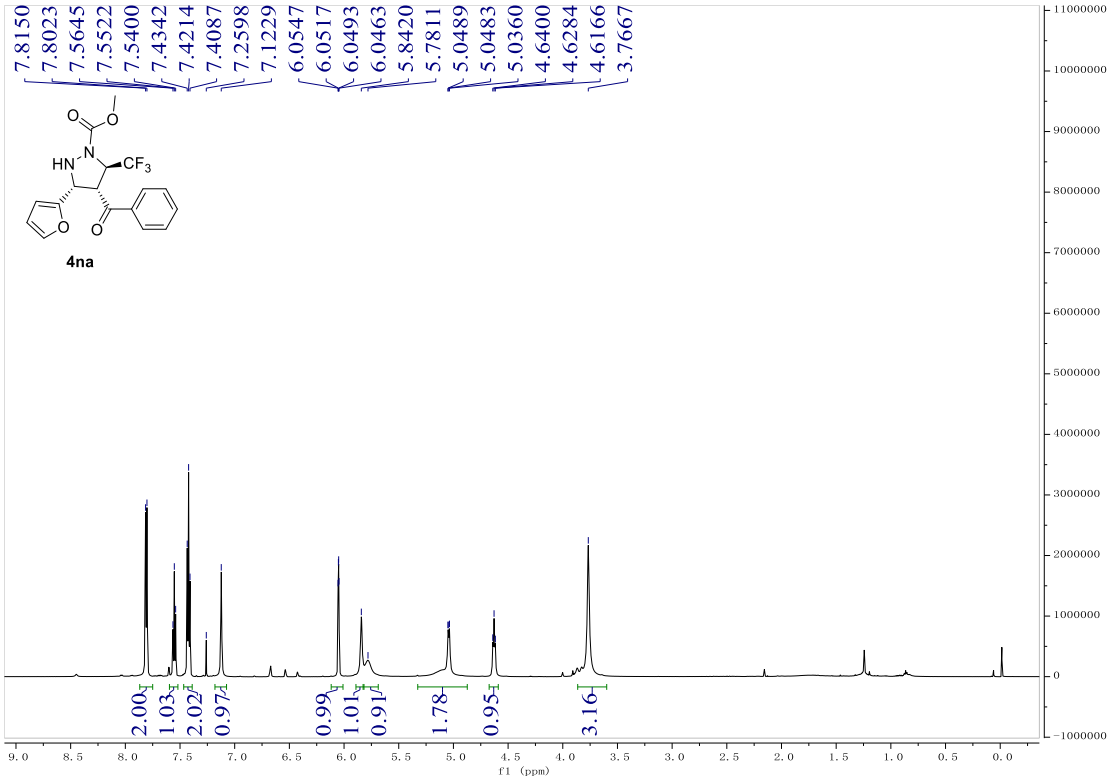
^{13}C{^{1}H} NMR of 4ma (100 MHz, $CDCl_3$)



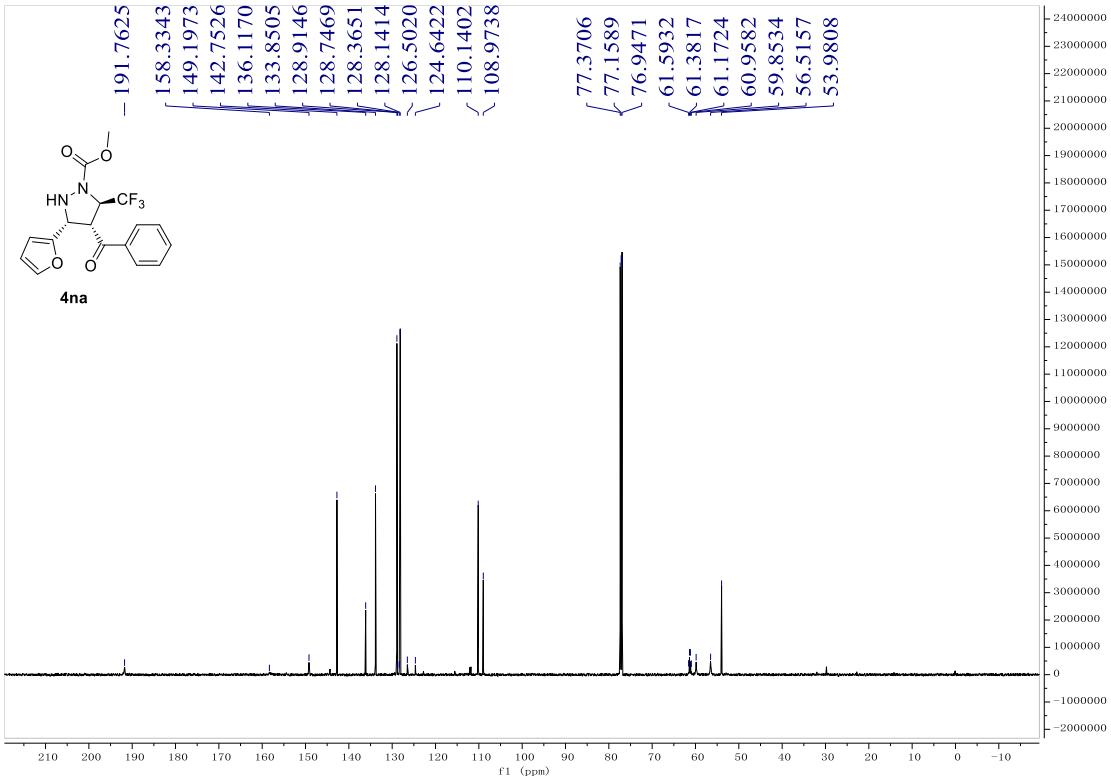
$^{19}F\{^{1}H\}$ NMR of 4ma (565 MHz, $CDCl_3$)



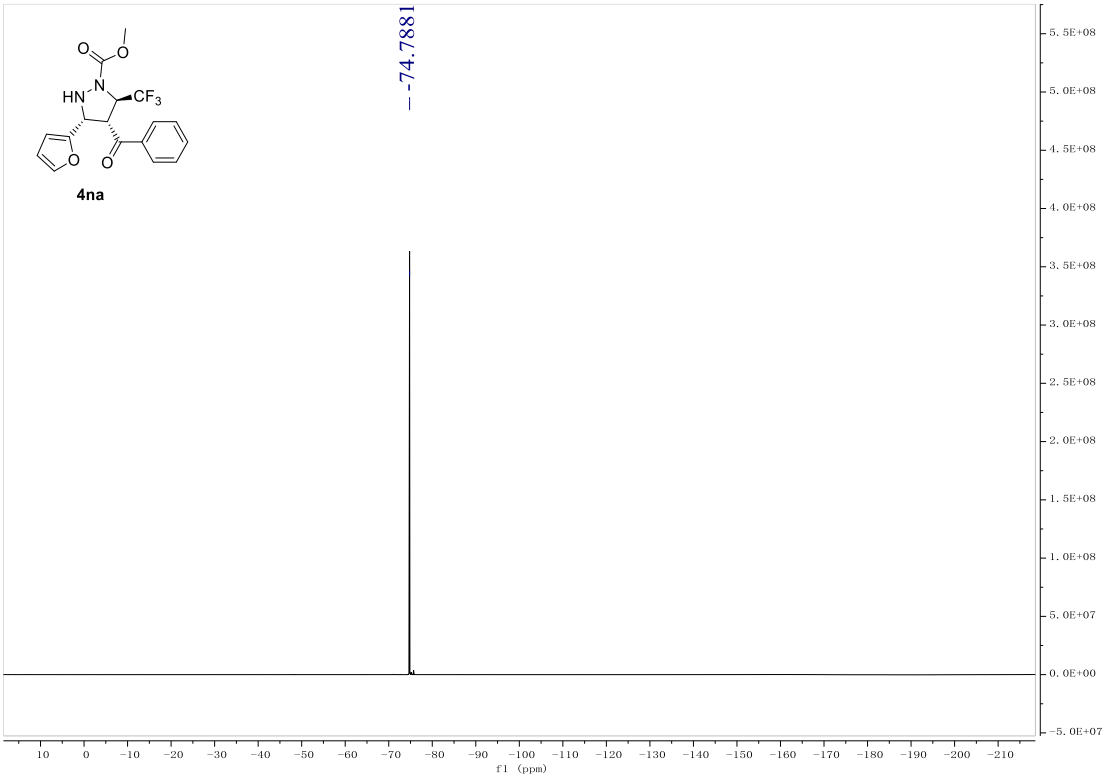
^{1}H NMR of 4na (600 MHz, $CDCl_3$)



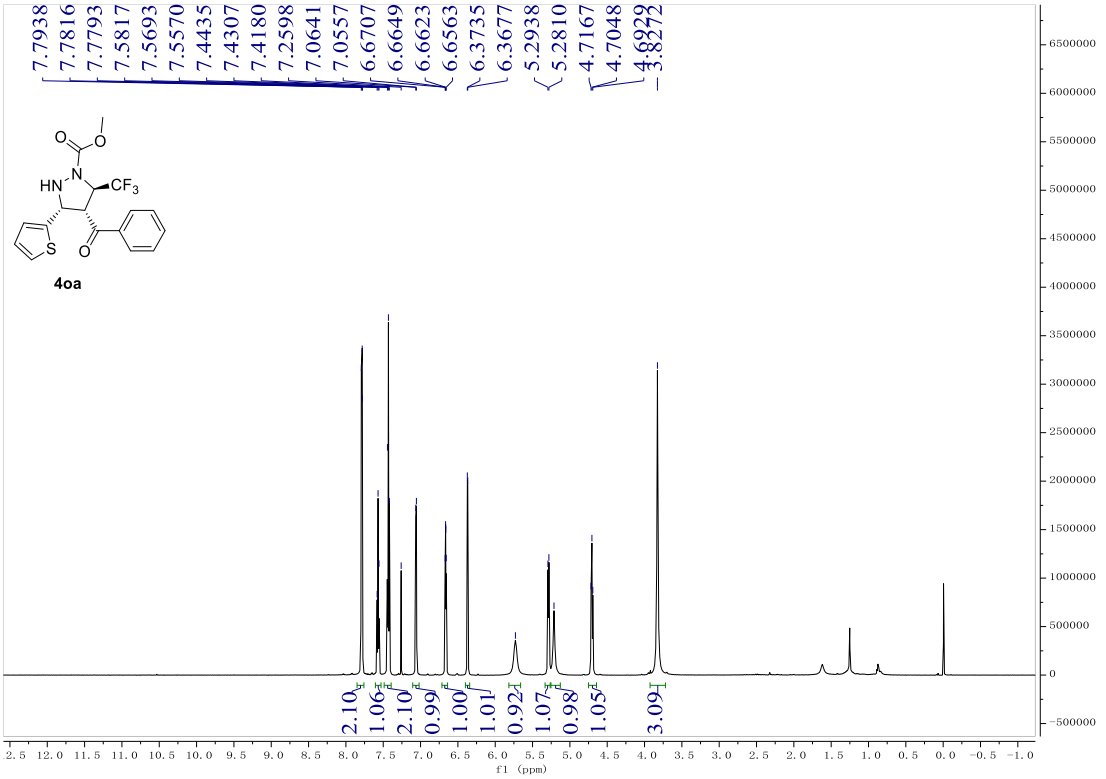
$^{13}C\{^{1}H\}$ NMR of 4na (150 MHz, $CDCl_3$)



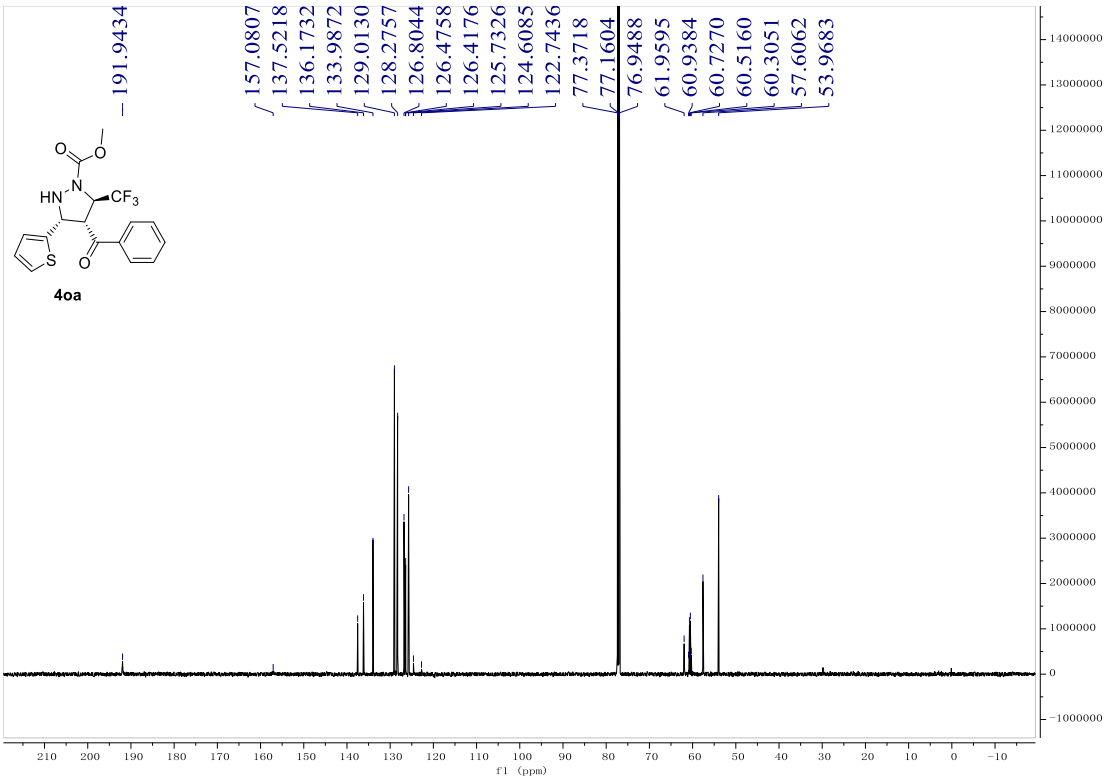
$^{19}F\{^{1}H\}$ NMR of 4na (565 MHz, $CDCl_3$)



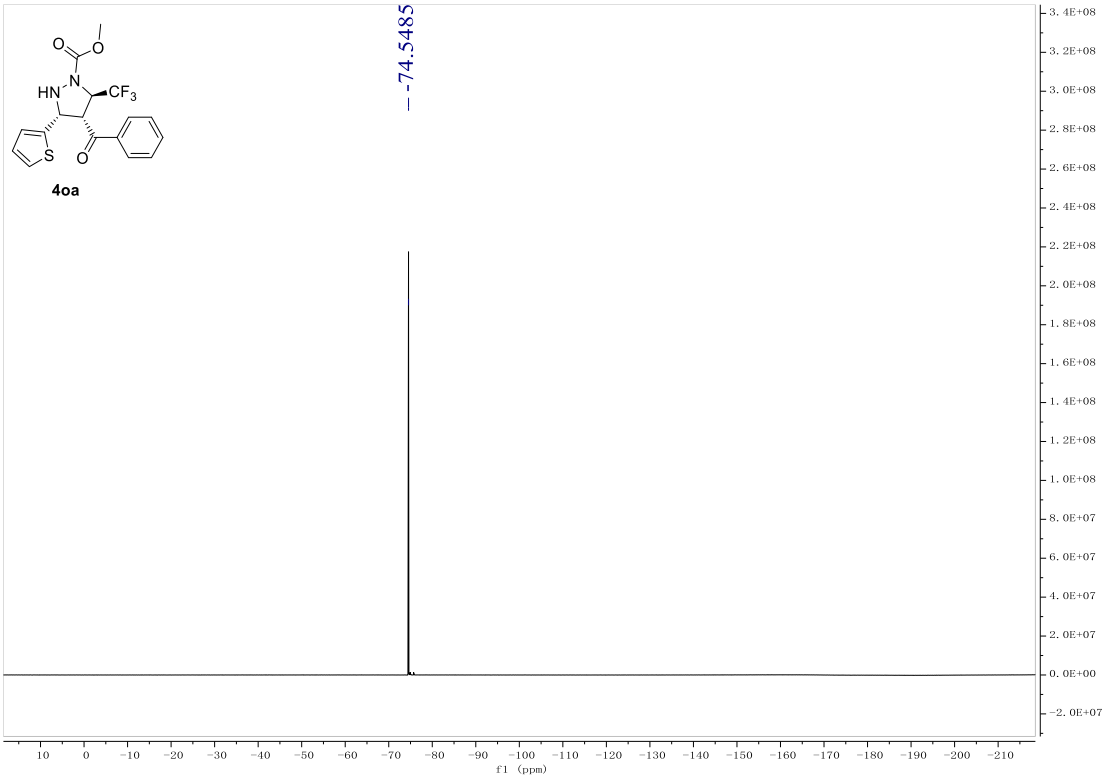
^{1}H NMR of 4oa (600 MHz, $CDCl_3$)



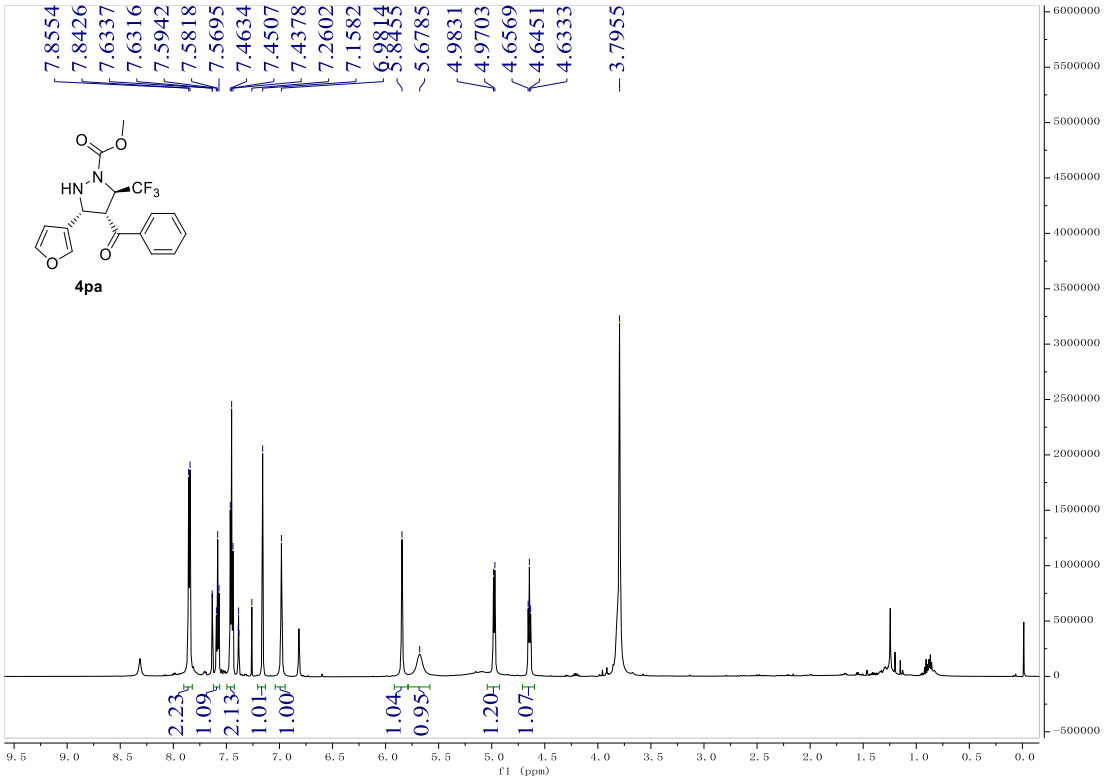
^{13}C{^{1}H} NMR of 4oa (150 MHz, $CDCl_3$)



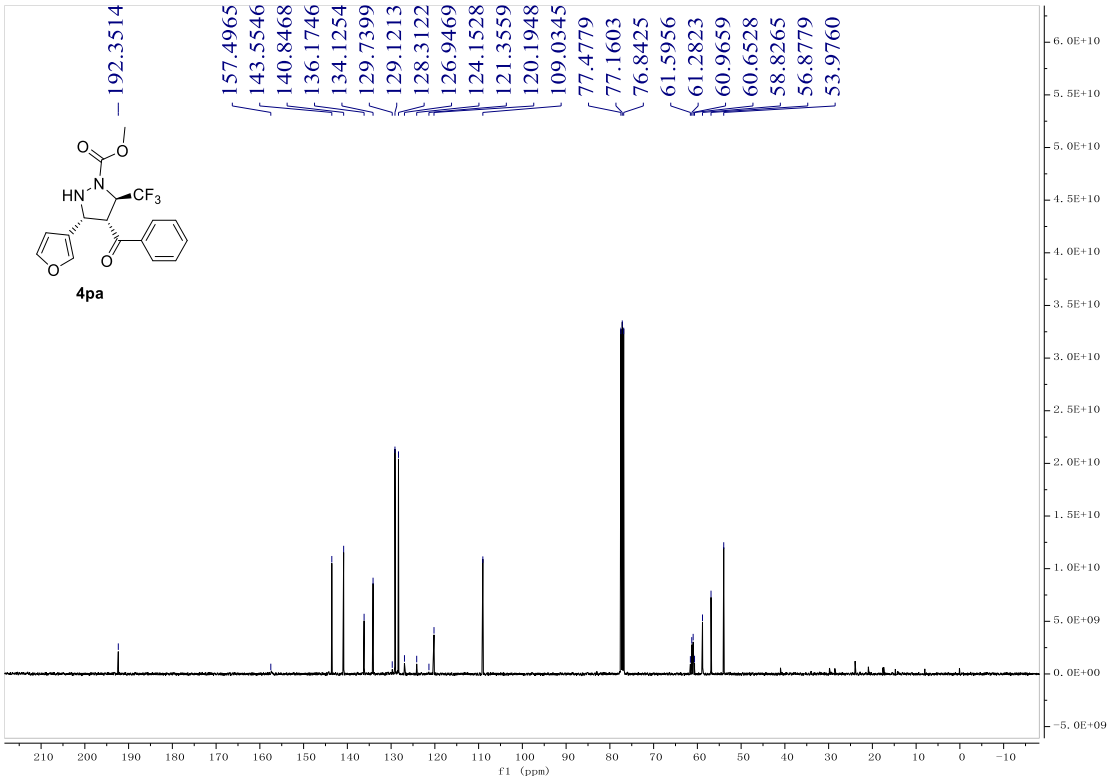
$^{19}F\{^{1}H\}$ NMR of 4oa (565 MHz, $CDCl_3$)



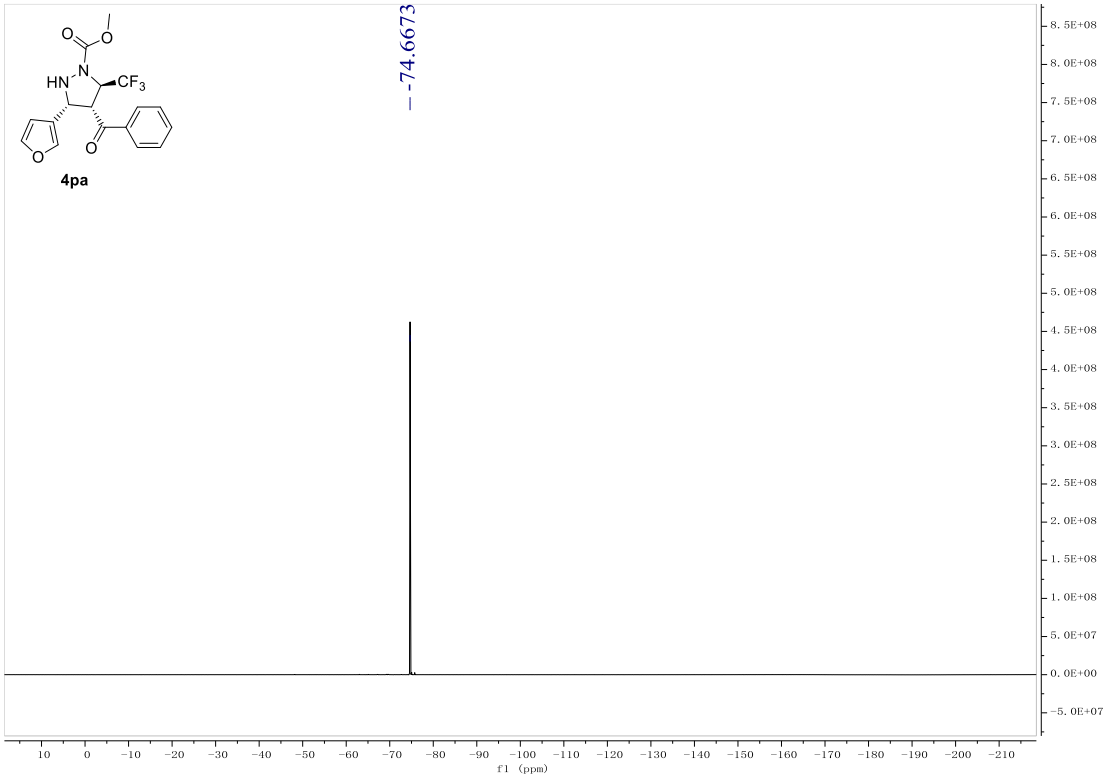
^{1}H NMR of 4pa (600 MHz, $CDCl_3$)



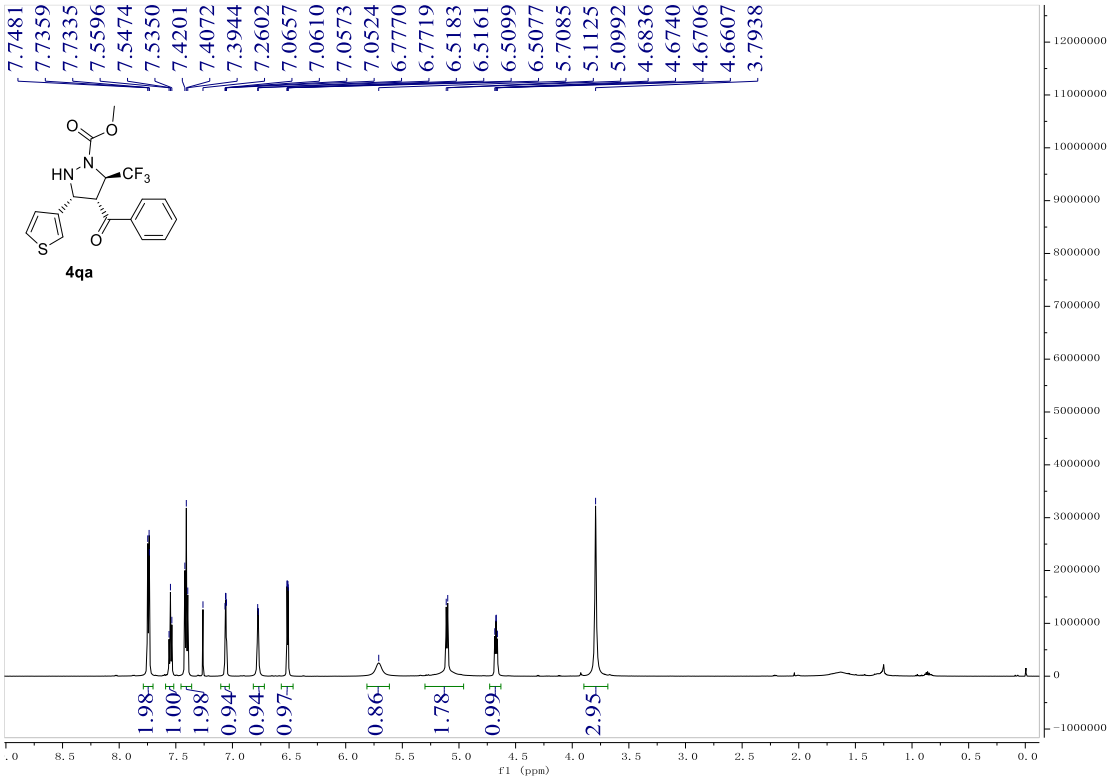
$^{13}C\{^{1}H\}$ NMR of 4pa (100 MHz, $CDCl_3$)



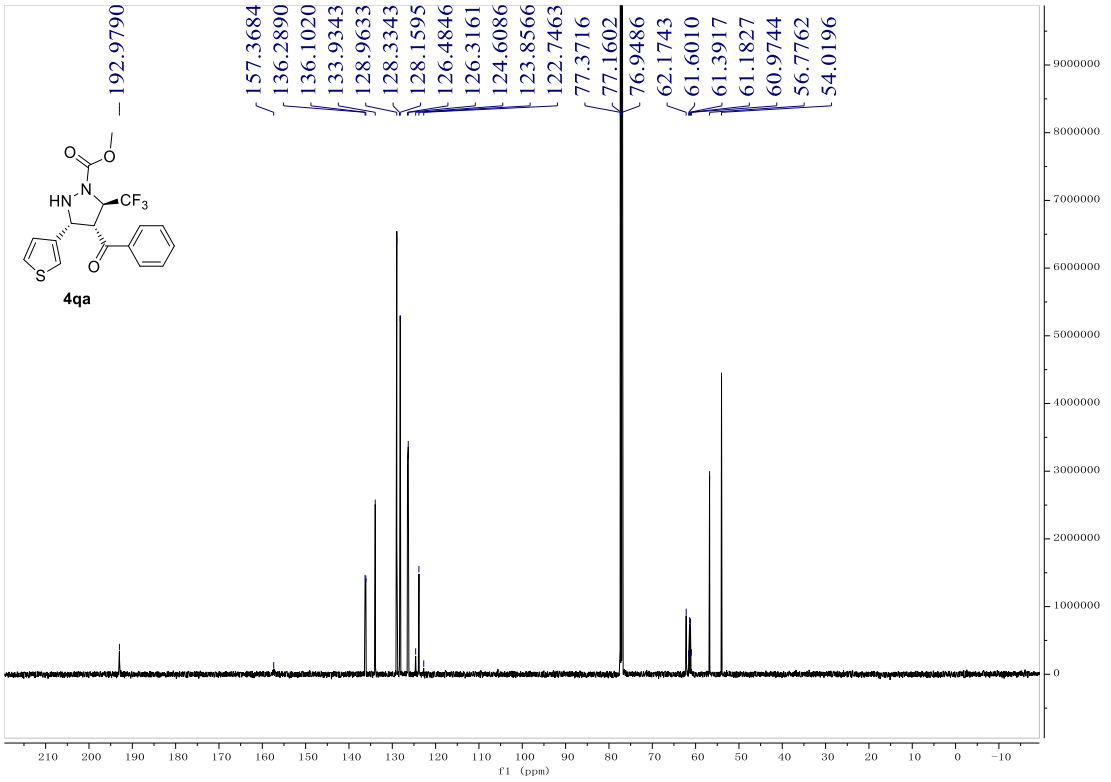
$^{19}F\{^{1}H\}$ NMR of 4pa (565 MHz, $CDCl_3$)



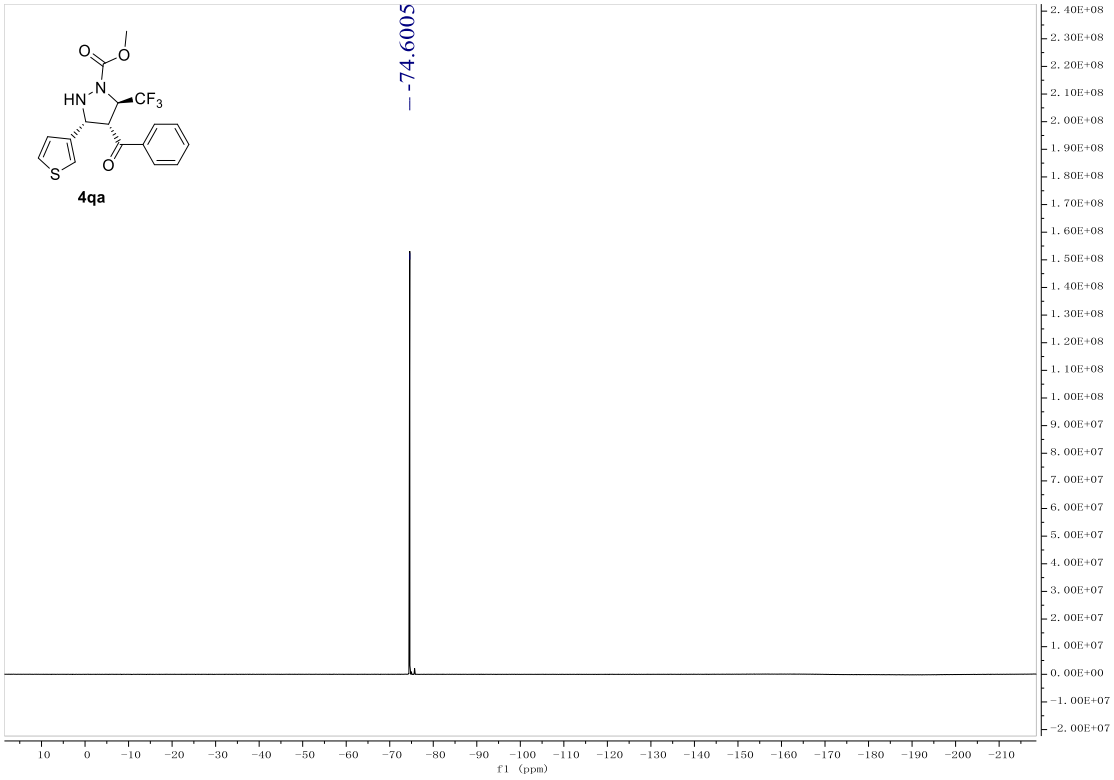
^{1}H NMR of 4qa (600 MHz, $CDCl_3$)



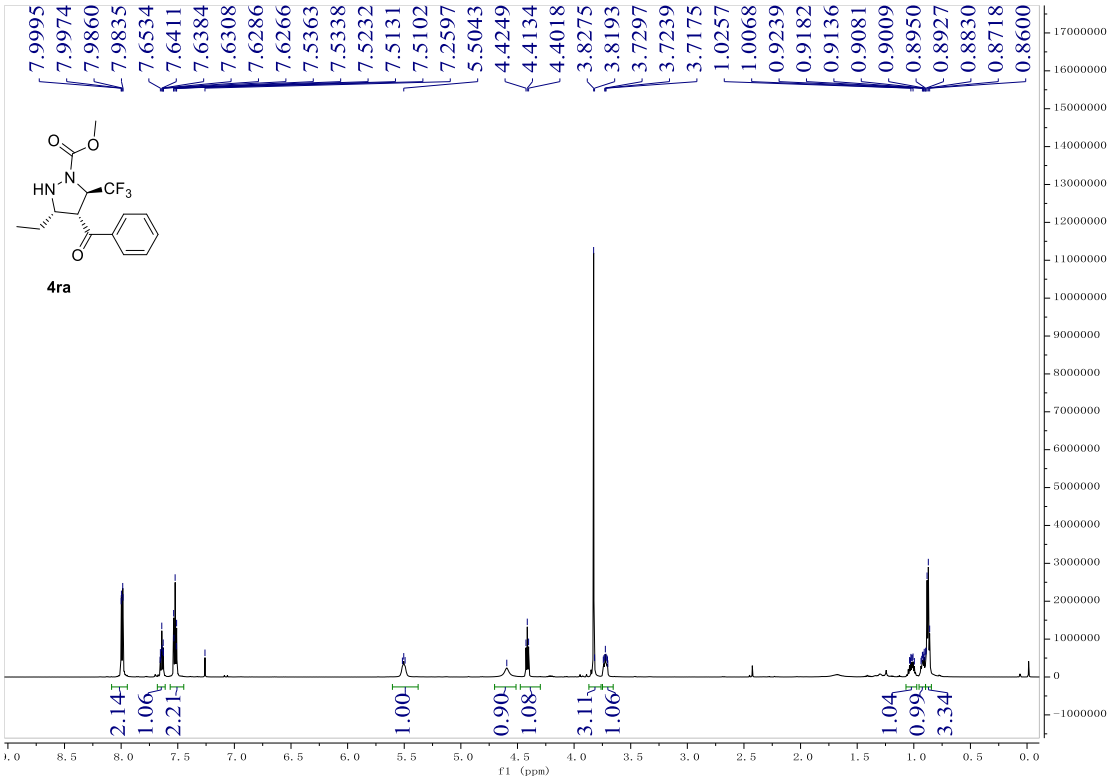
^{13}C{^{1}H} NMR of 4qa (150 MHz, $CDCl_3$)



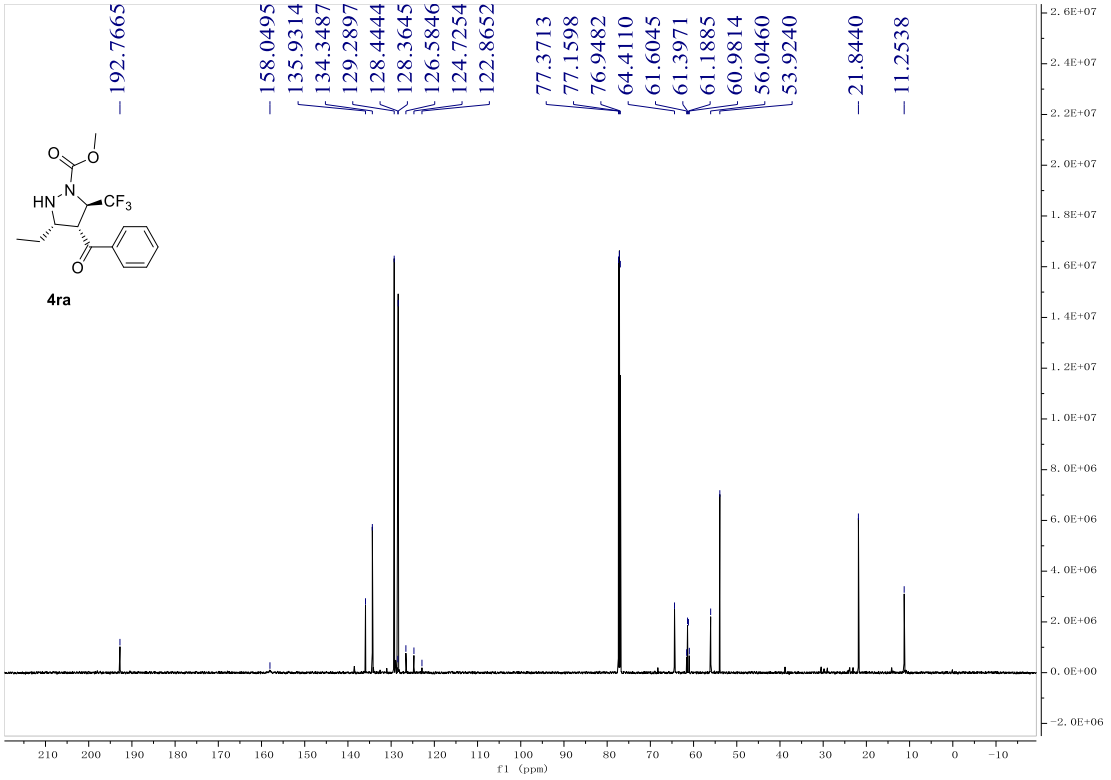
$^{19}F\{^{1}H\}$ NMR of 4qa (565 MHz, $CDCl_3$)



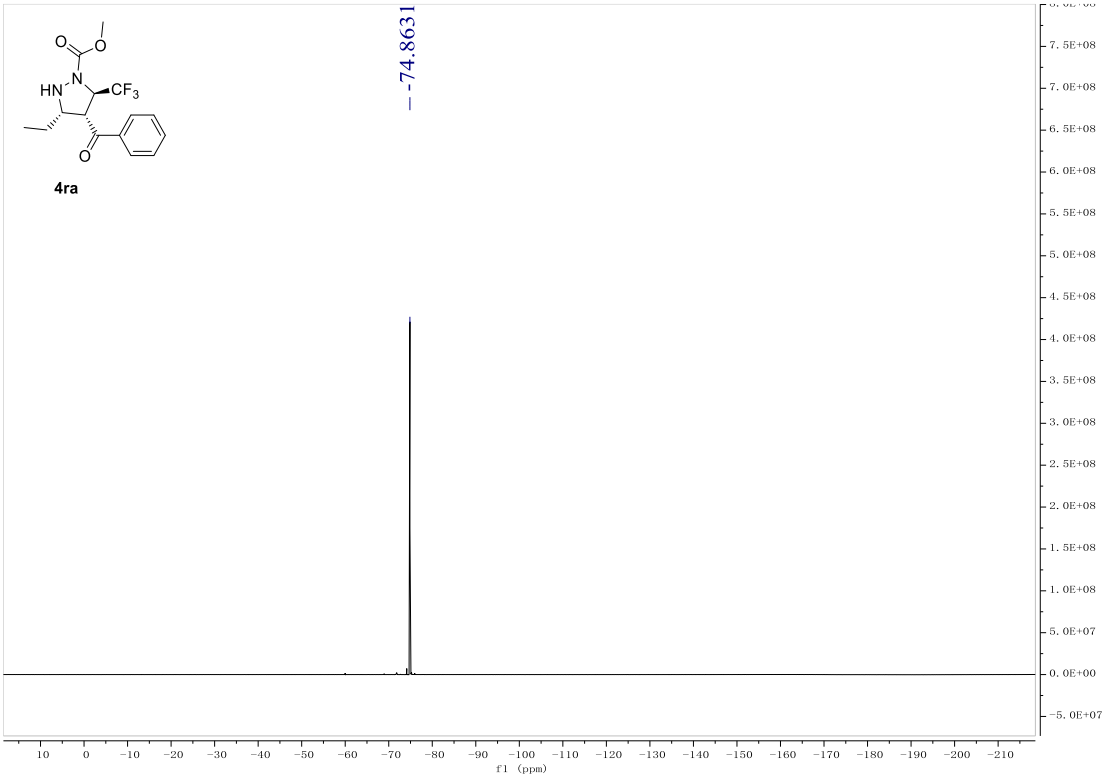
^{1}H NMR of 4ra (600 MHz, $CDCl_3$)



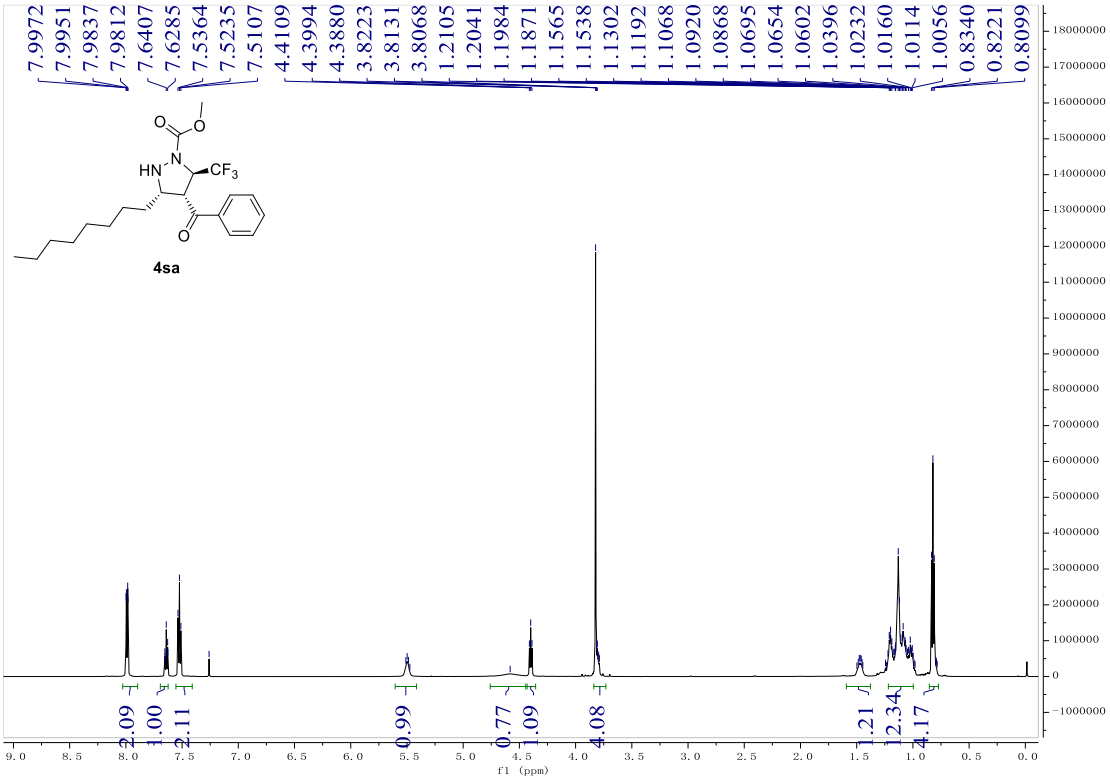
$^{13}C\{^{1}H\}$ NMR of 4ra (150 MHz, $CDCl_3$)



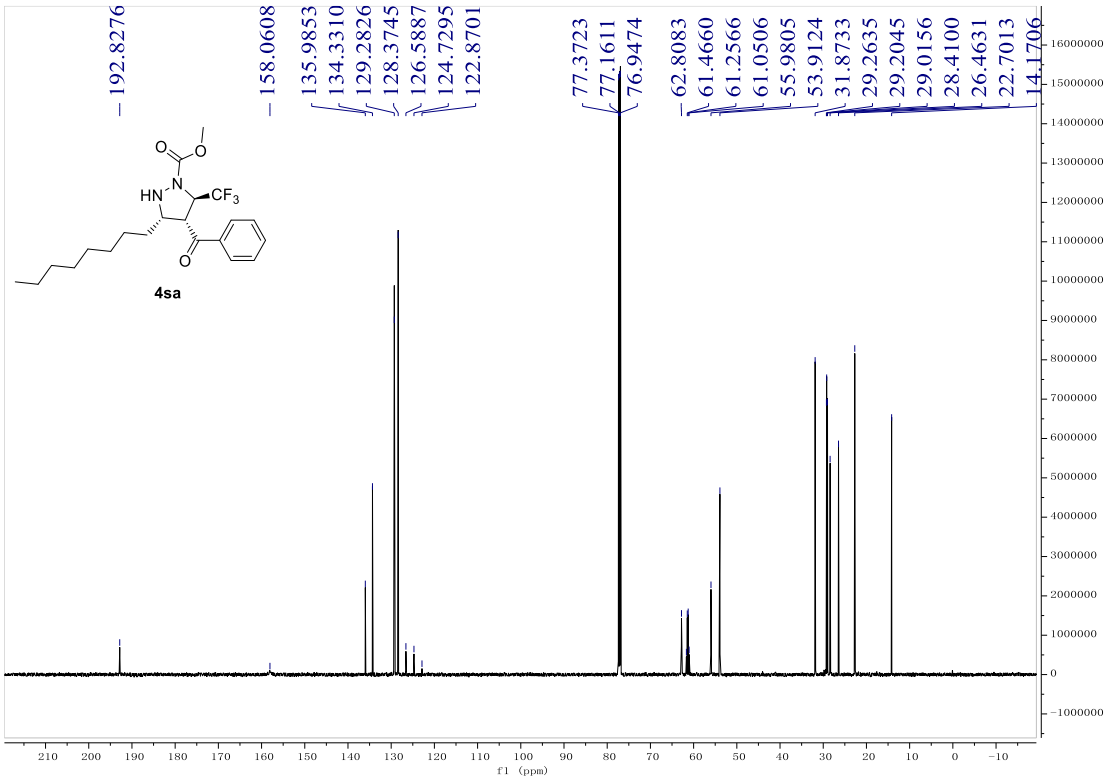
$^{19}F\{^{1}H\}$ NMR of 4ra (565 MHz, $CDCl_3$)



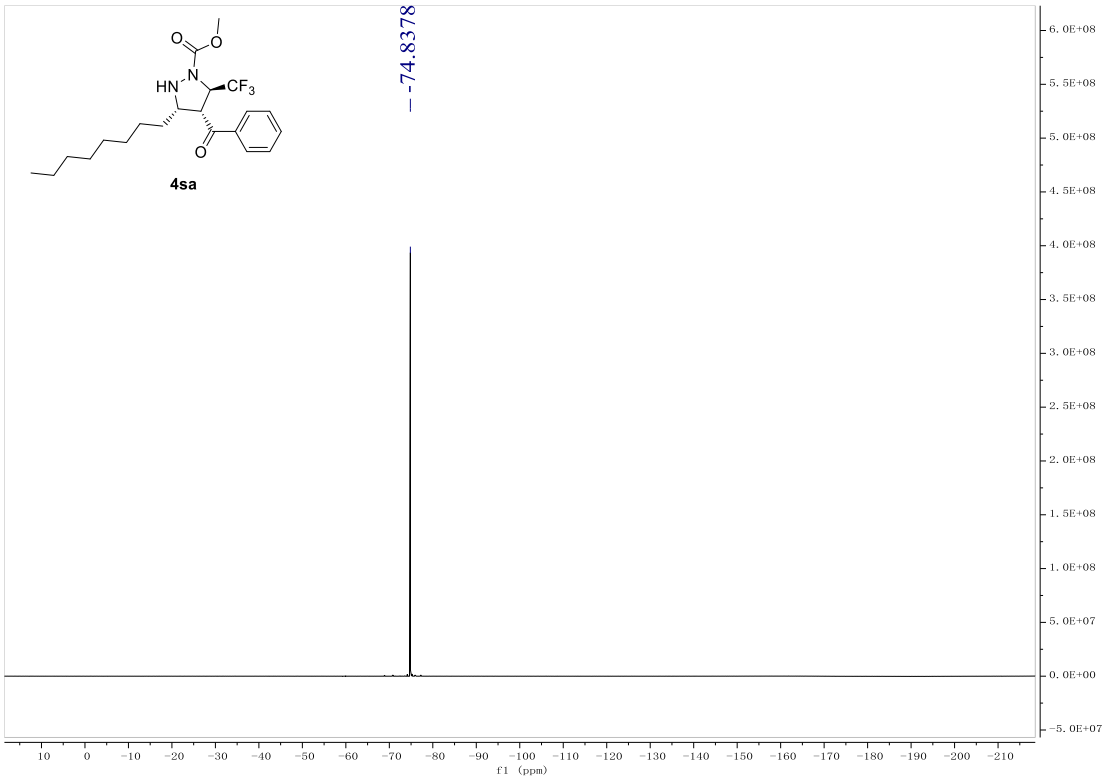
^{1}H NMR of 4sa (600 MHz, $CDCl_3$)



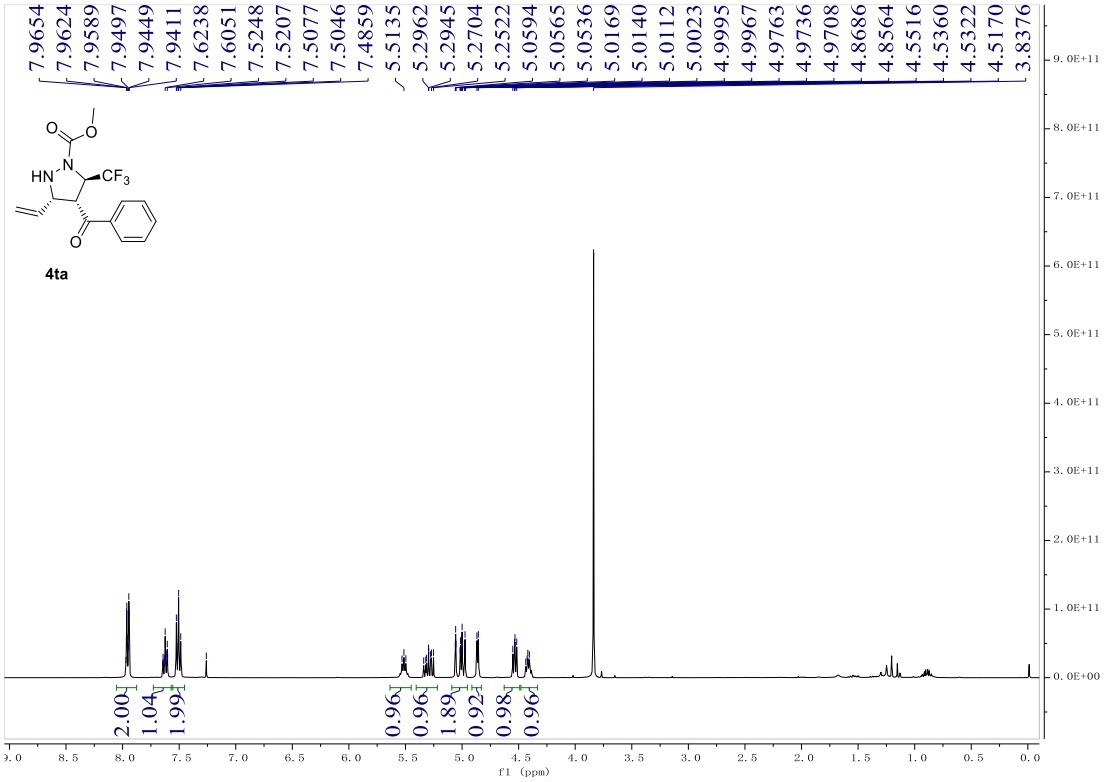
^{13}C{^{1}H} NMR of 4sa (150 MHz, $CDCl_3$)



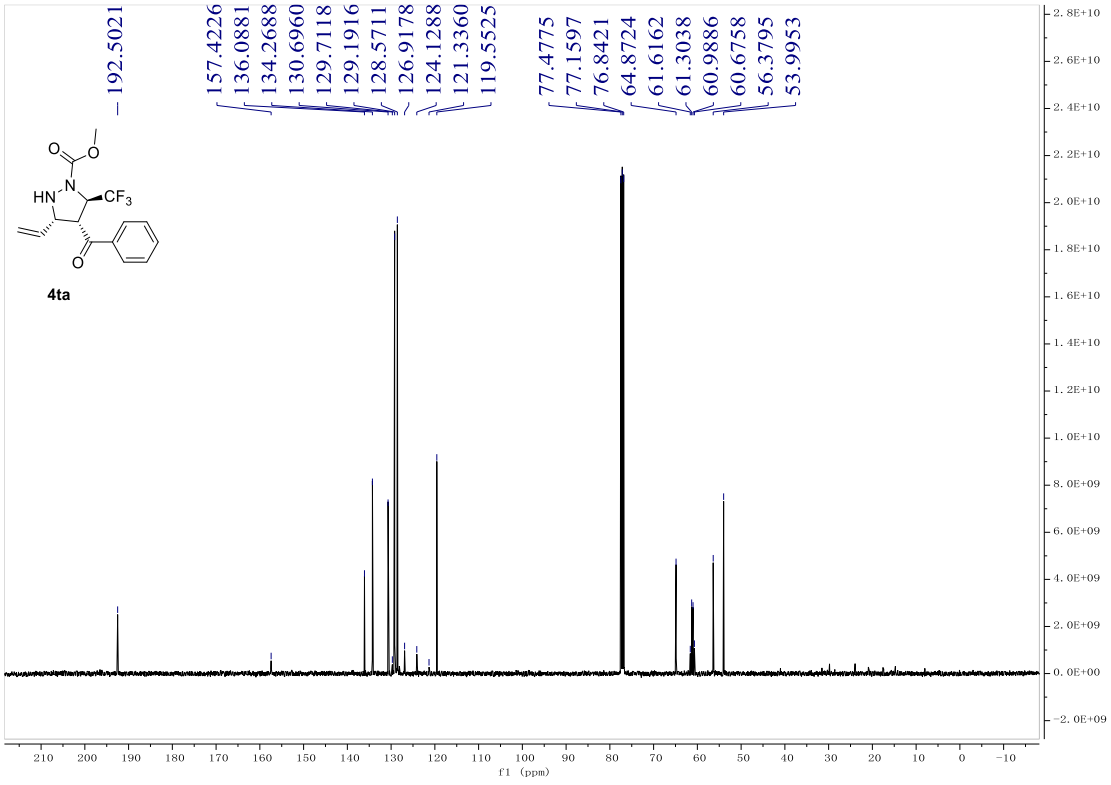
$^{19}F\{^{1}H\}$ NMR of 4sa (565 MHz, $CDCl_3$)



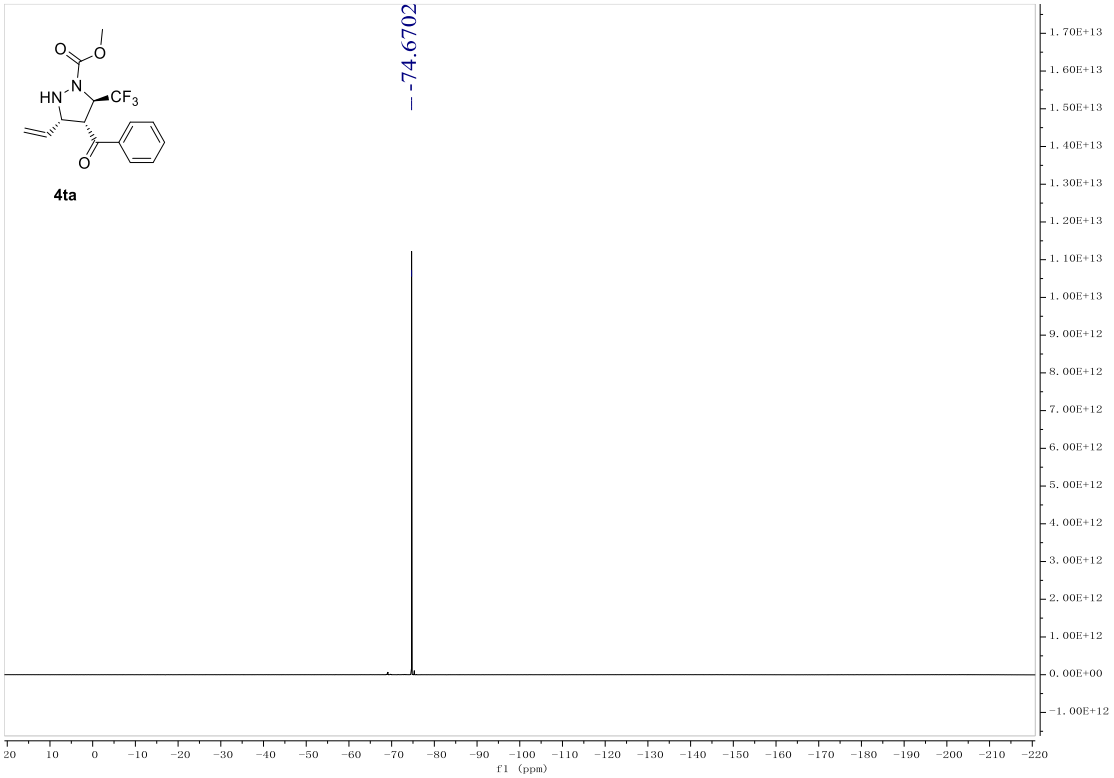
^{1}H NMR of 4ta (400 MHz, $CDCl_3$)



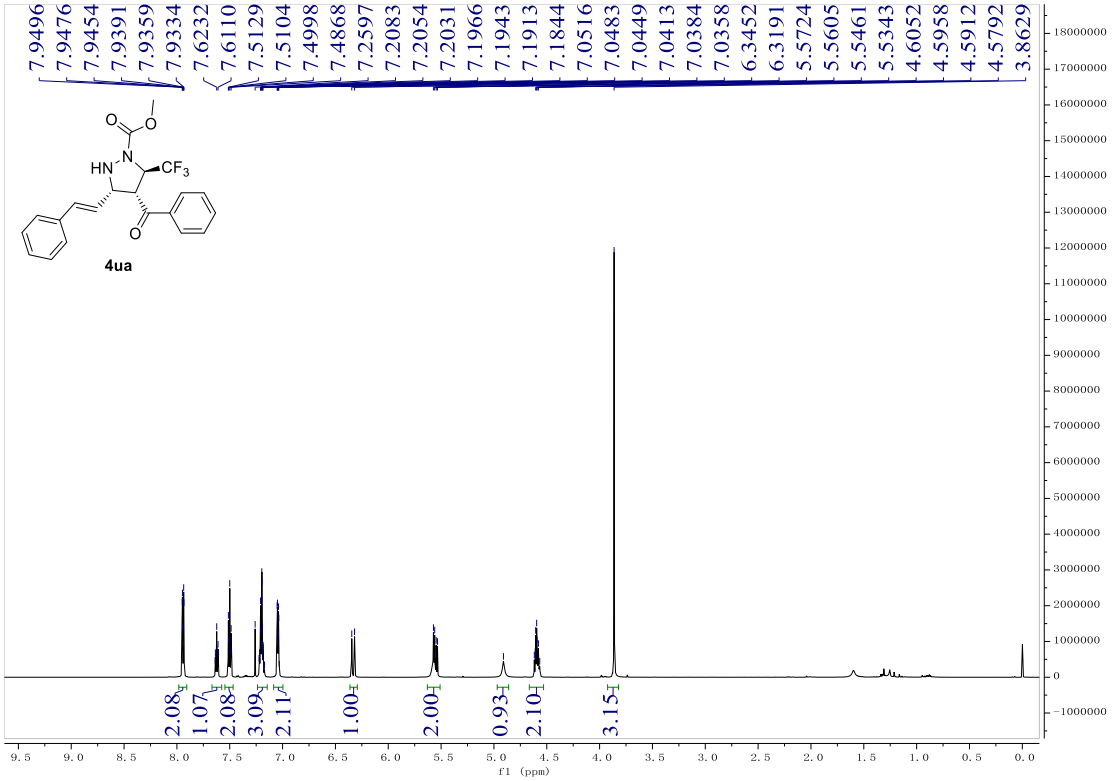
$^{13}C\{^{1}H\}$ NMR of 4ta (100 MHz, $CDCl_3$)



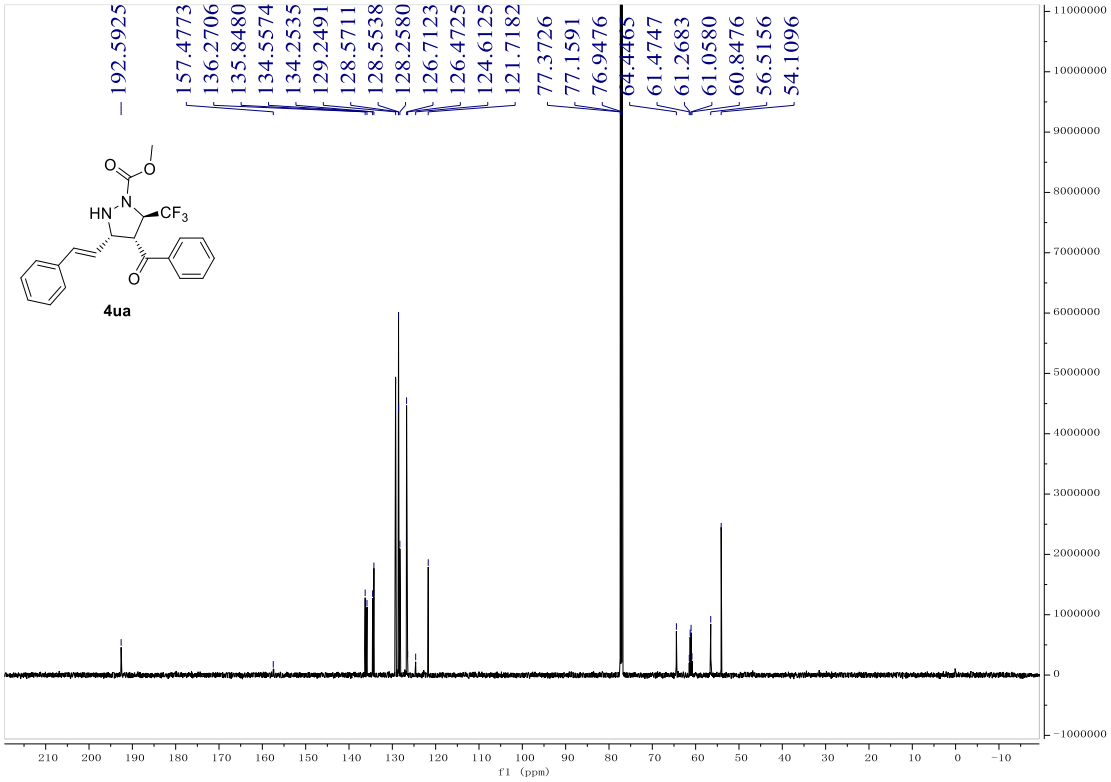
$^{19}F\{^{1}H\}$ NMR of 4ta (376 MHz, $CDCl_3$)



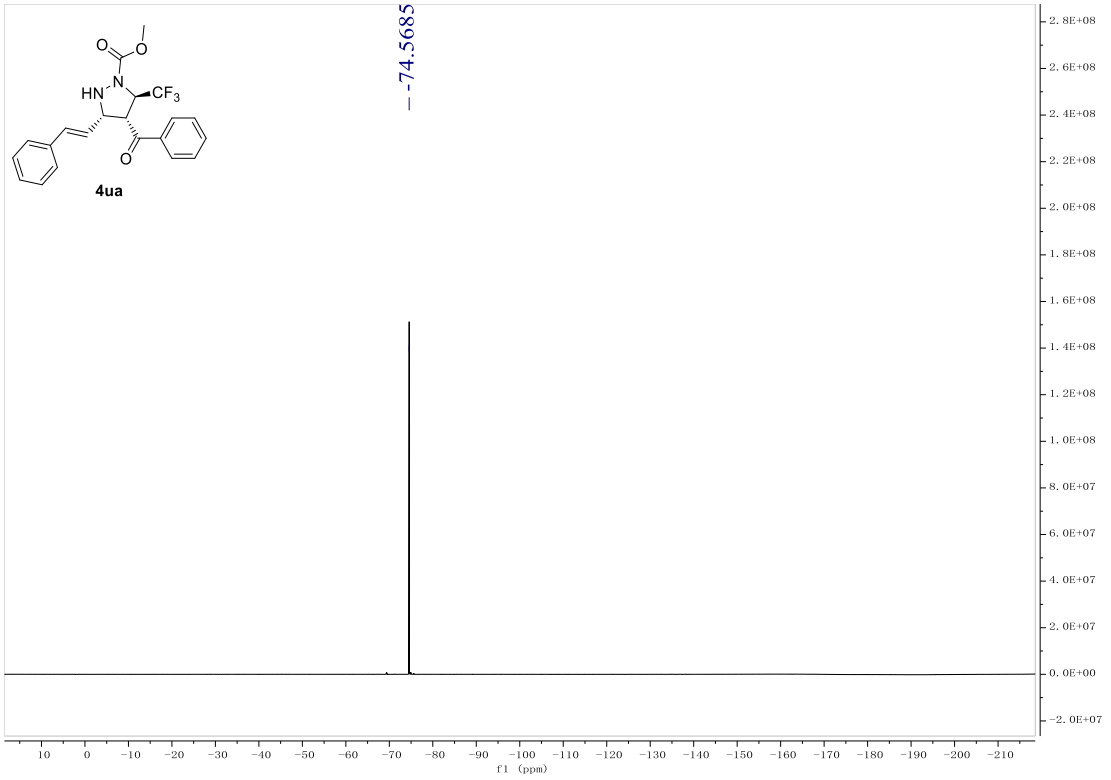
^{1}H NMR of 4ua (600 MHz, $CDCl_3$)



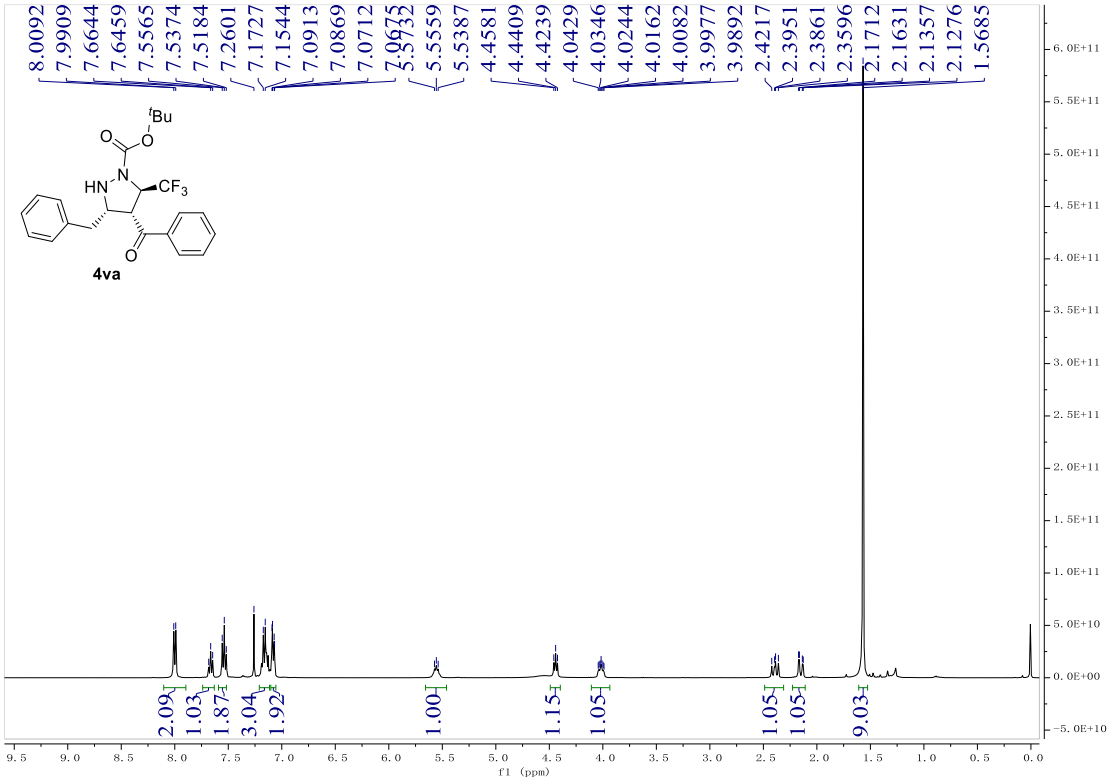
^{13}C{^{1}H} NMR of 4ua (150 MHz, $CDCl_3$)



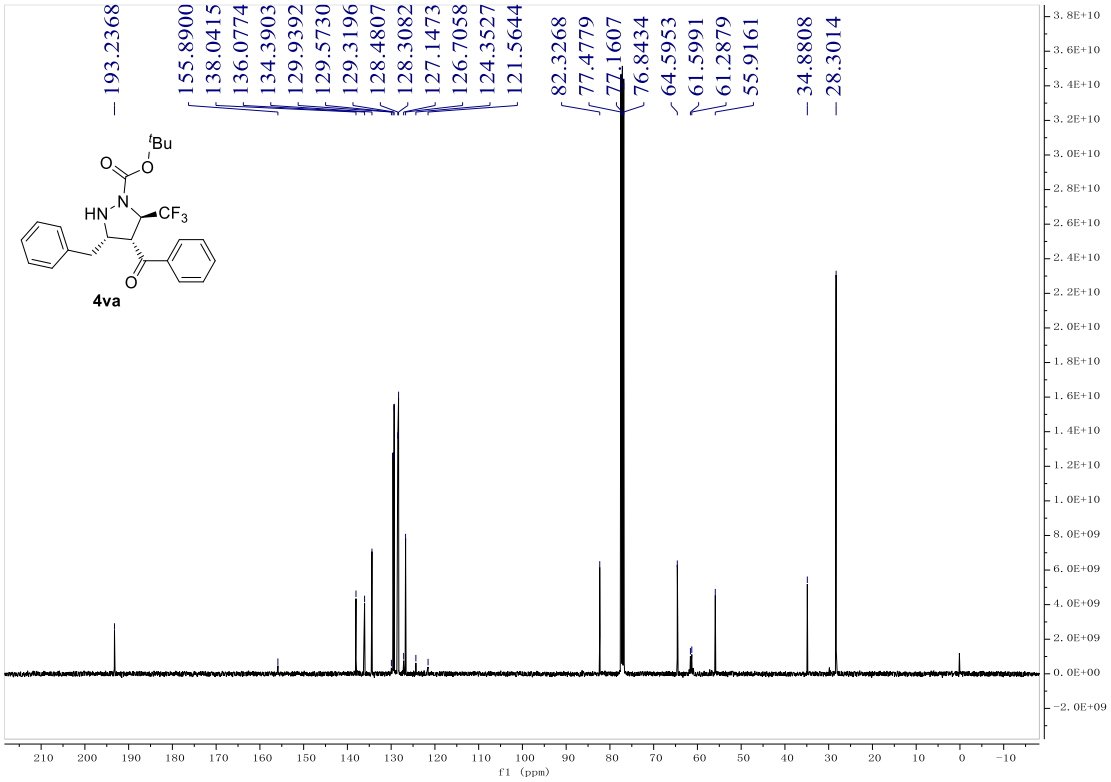
$^{19}F\{^{1}H\}$ NMR of 4ua (565 MHz, $CDCl_3$)



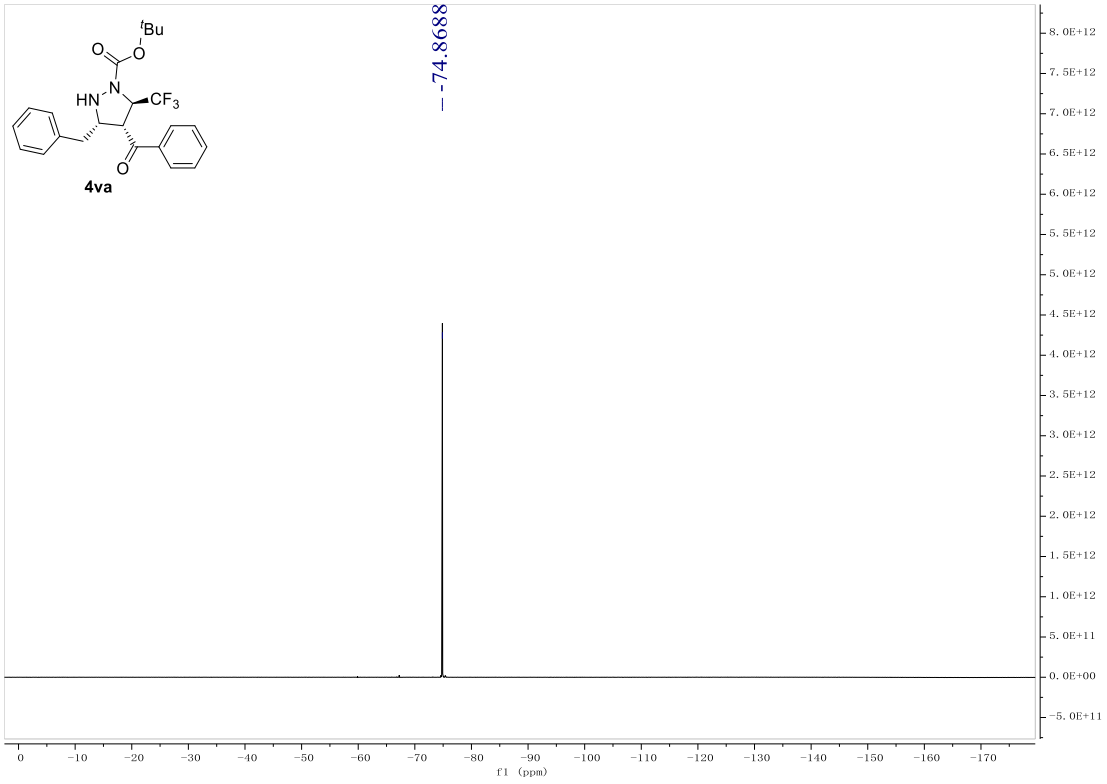
^{1}H NMR of 4va (400 MHz, $CDCl_3$)



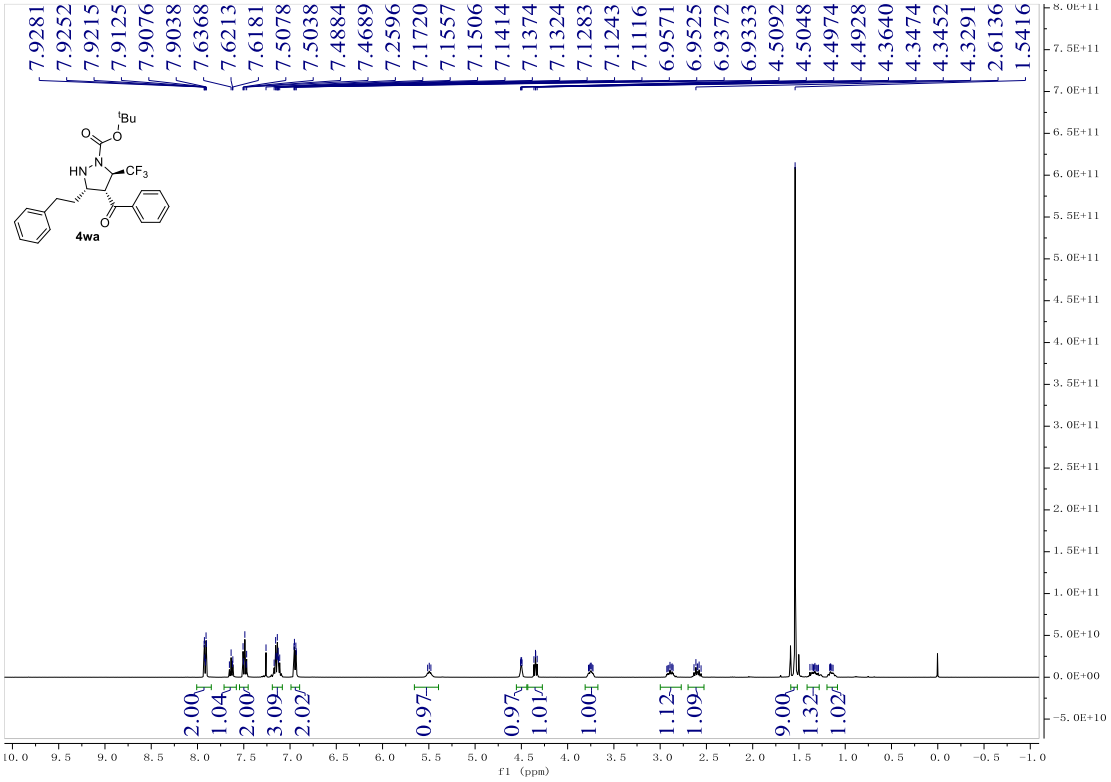
$^{13}C\{^{1}H\}$ NMR of 4va (100 MHz, $CDCl_3$)



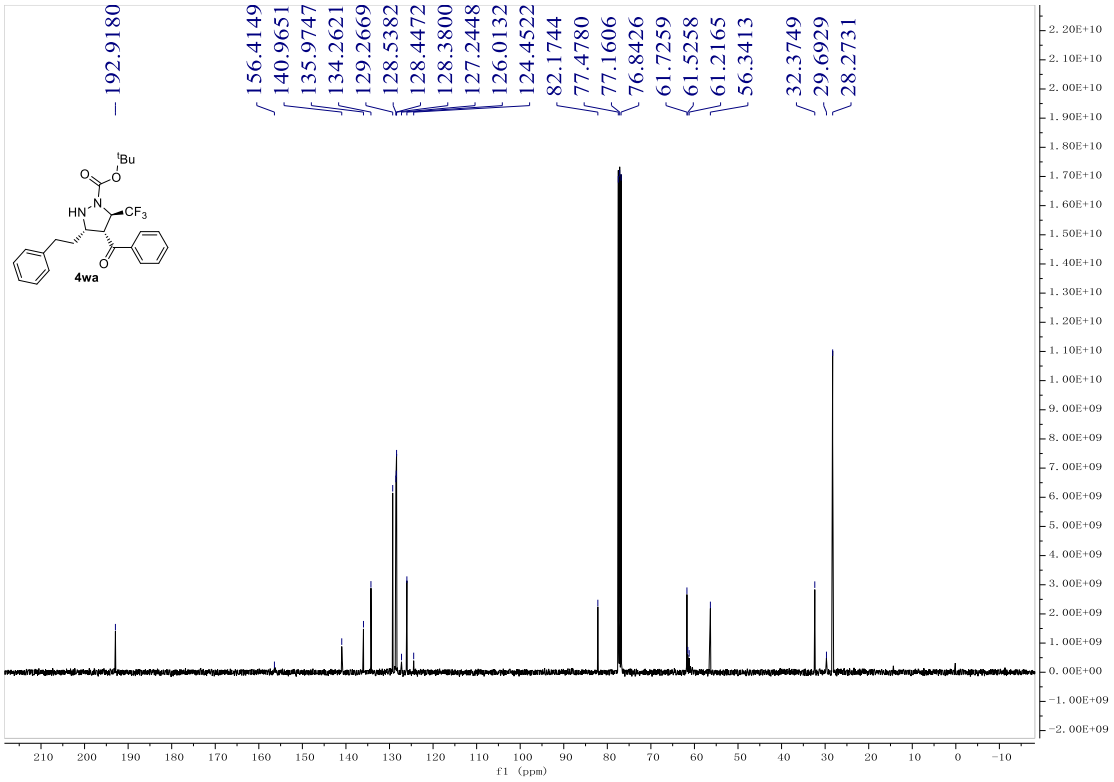
$^{19}F\{^{1}H\}$ NMR of 4va (376 MHz, $CDCl_3$)



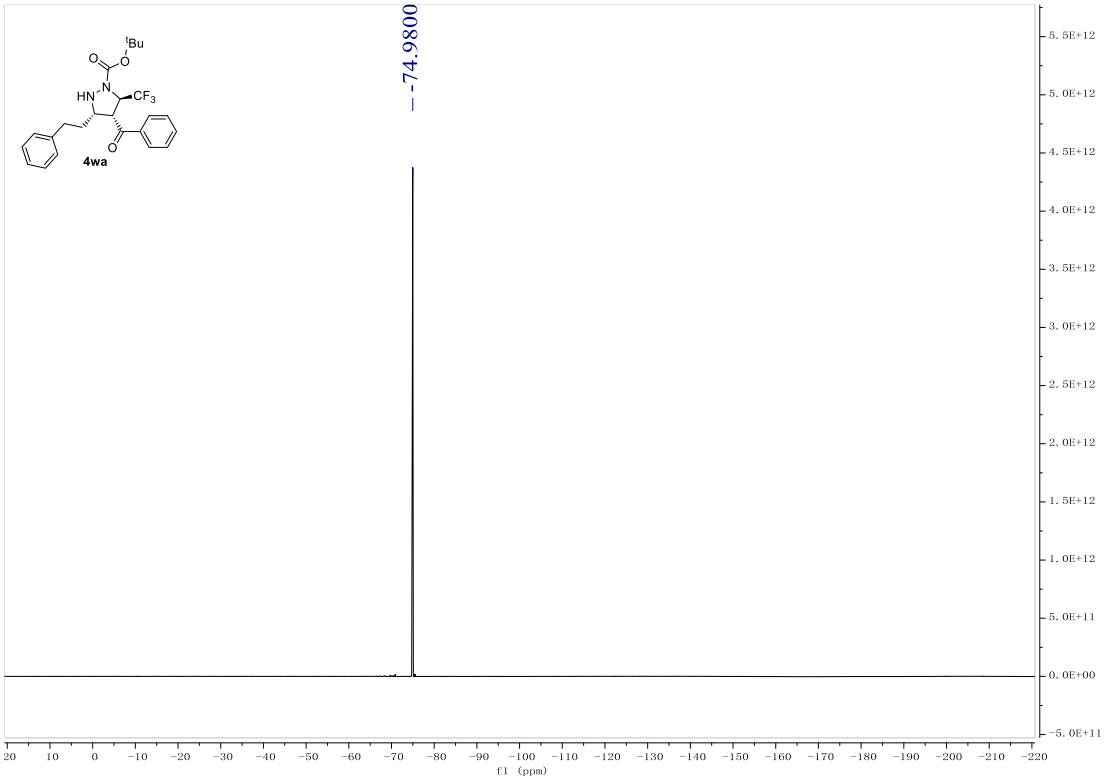
^{1}H NMR of 4wa (400 MHz, $CDCl_3$)



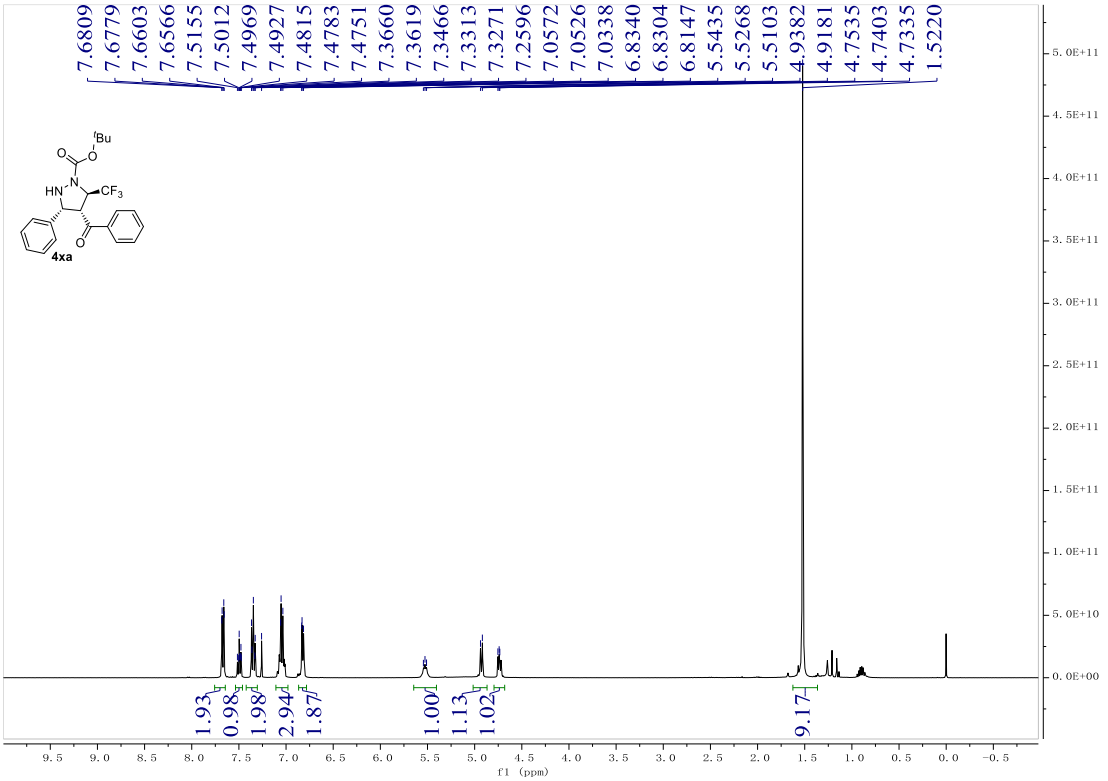
^{13}C{^{1}H} NMR of 4wa (100 MHz, $CDCl_3$)



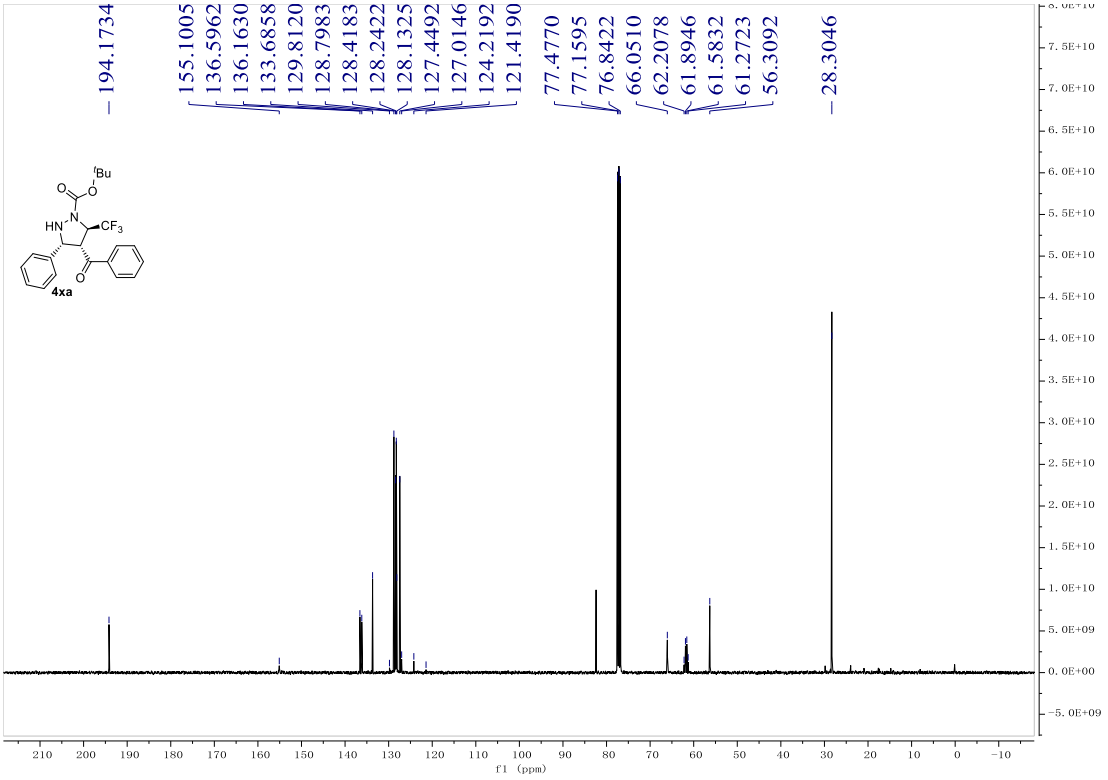
$^{19}F\{^{1}H\}$ NMR of 4wa (376 MHz, $CDCl_3$)



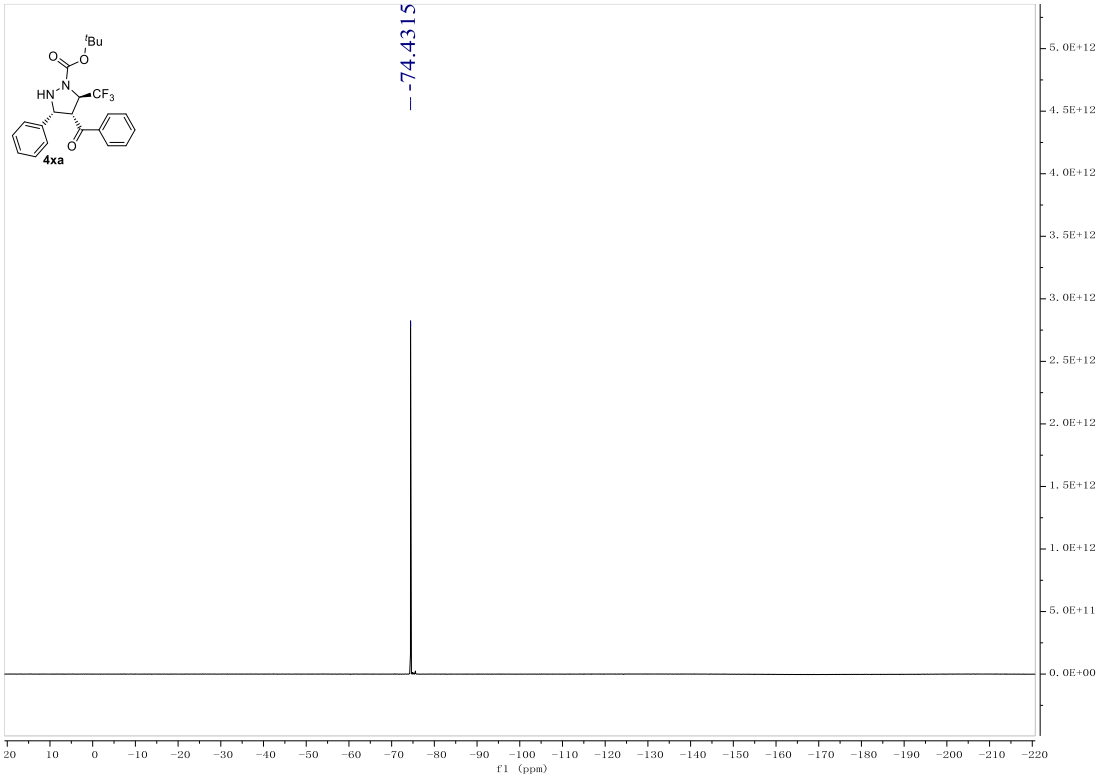
^{1}H NMR of 4xa (400 MHz, $CDCl_3$)



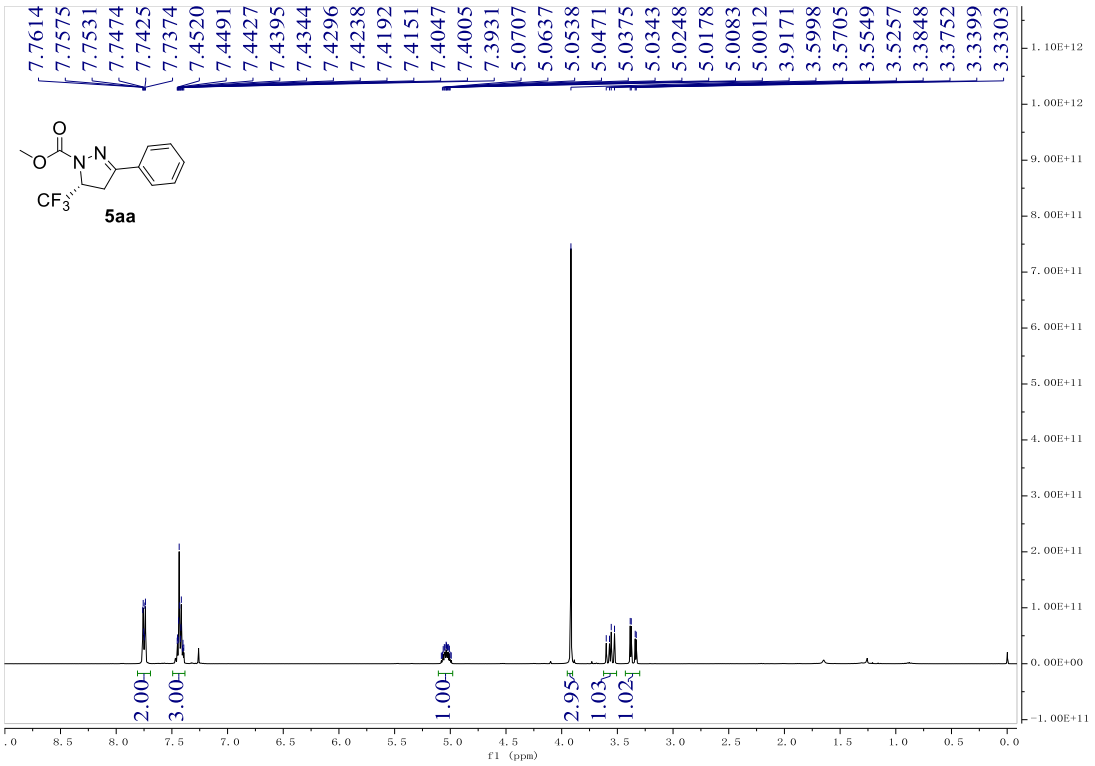
$^{13}C\{^{1}H\}$ NMR of 4xa (100 MHz, $CDCl_3$)



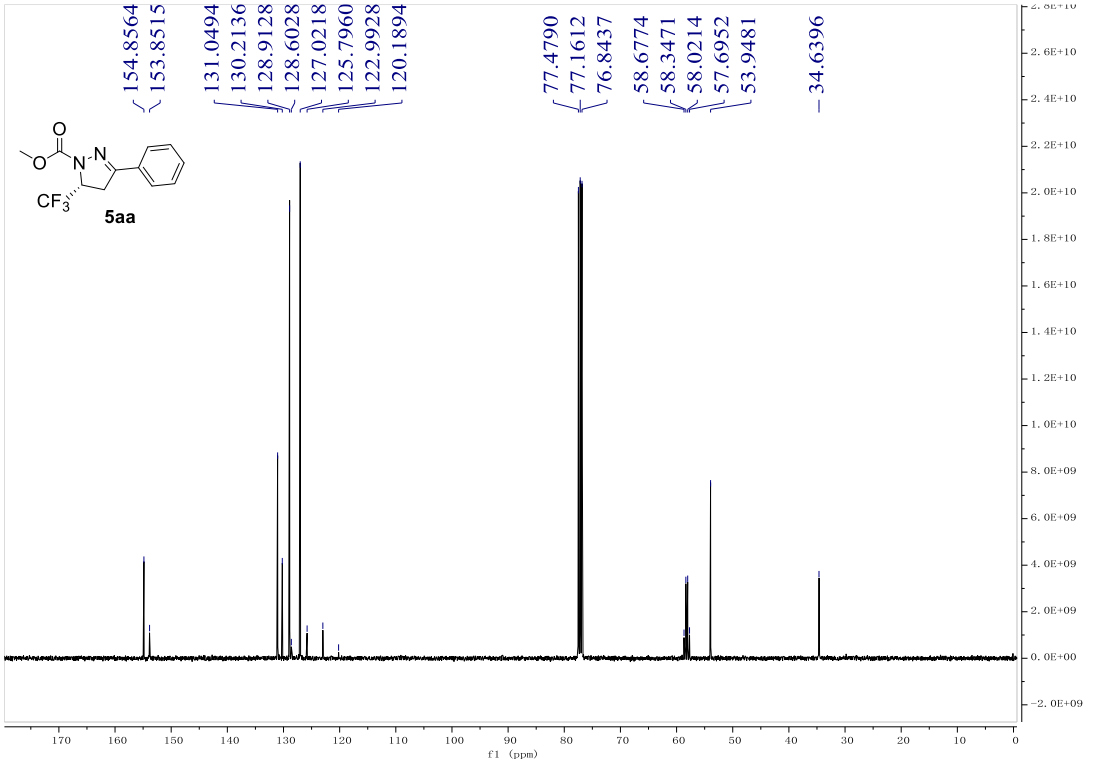
$^{19}F\{^{1}H\}$ NMR of 4xa (376 MHz, $CDCl_3$)



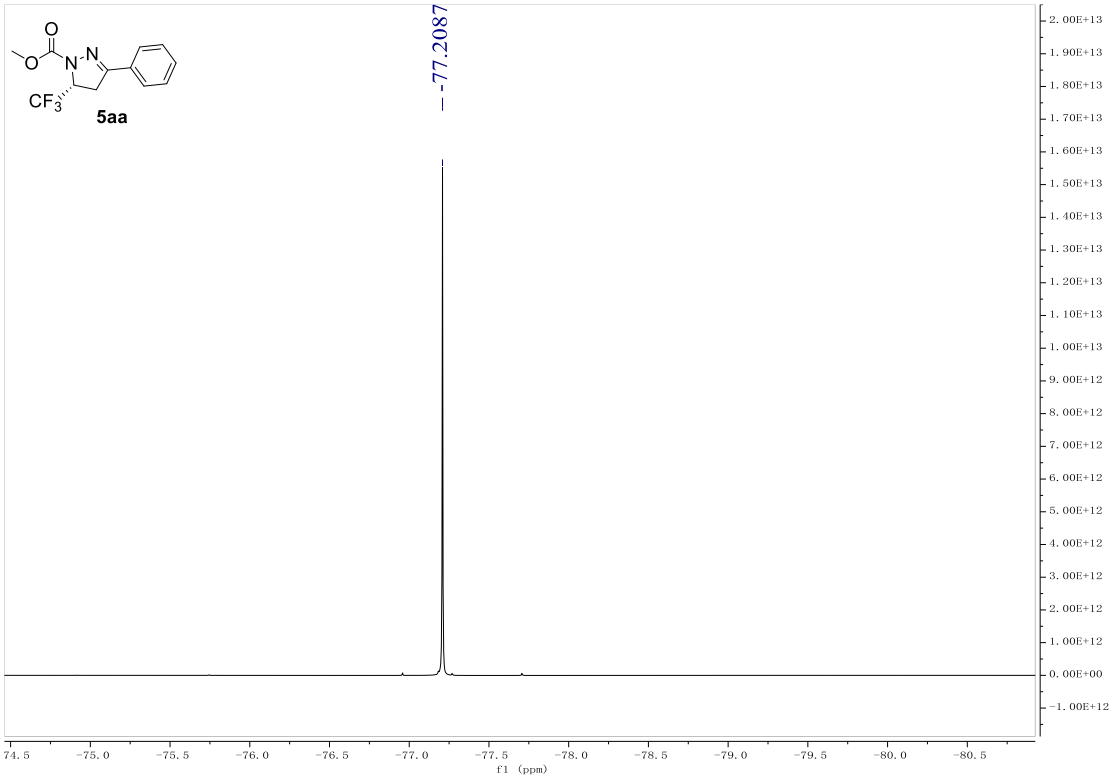
^{1}H NMR of 5aa (400 MHz, $CDCl_3$)



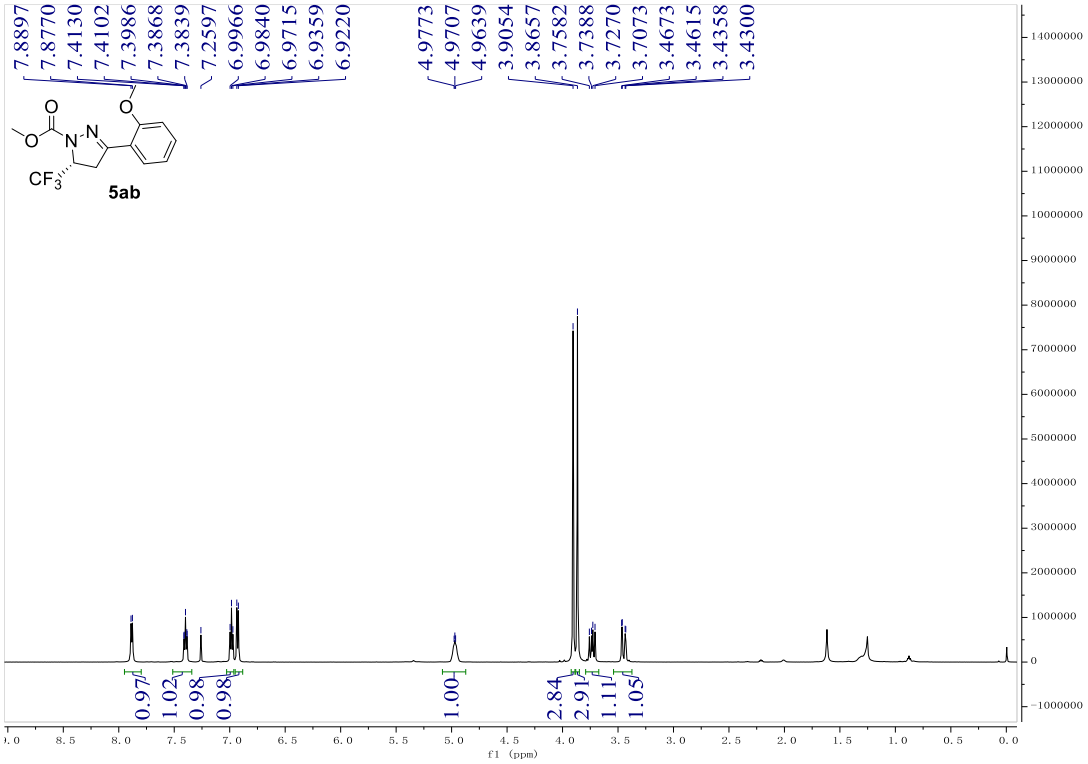
^{13}C{^{1}H} NMR of 5aa (100 MHz, $CDCl_3$)



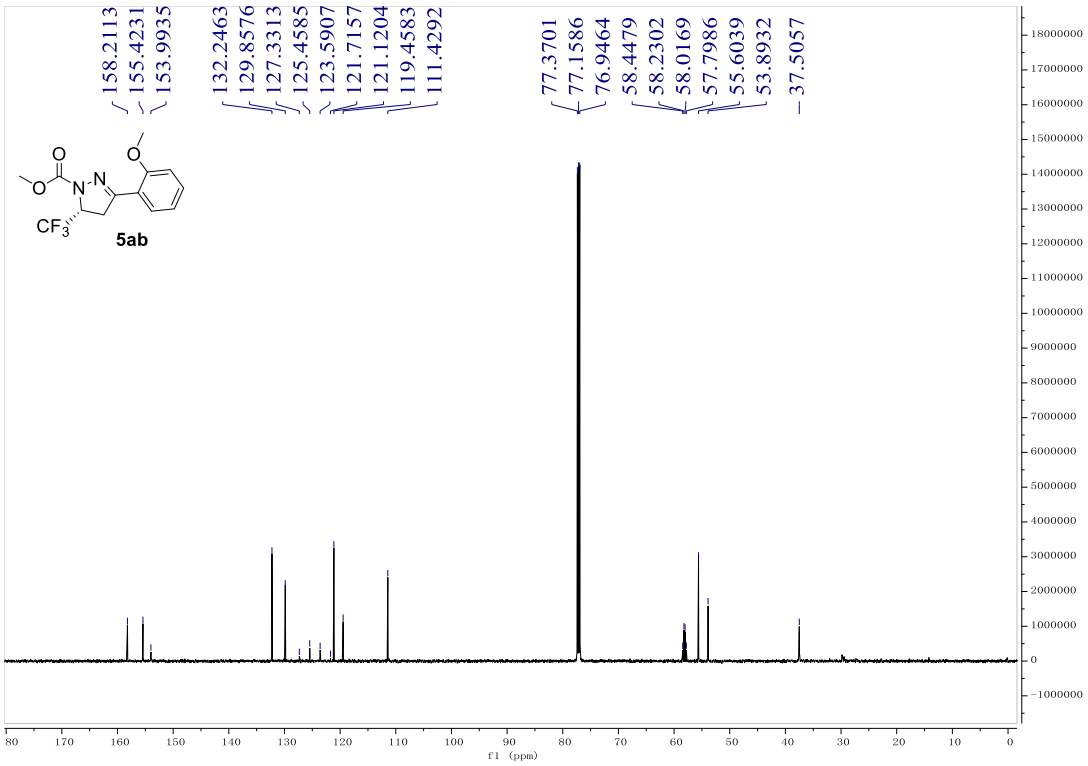
$^{19}F\{^{1}H\}$ NMR of 5aa (376 MHz, $CDCl_3$)



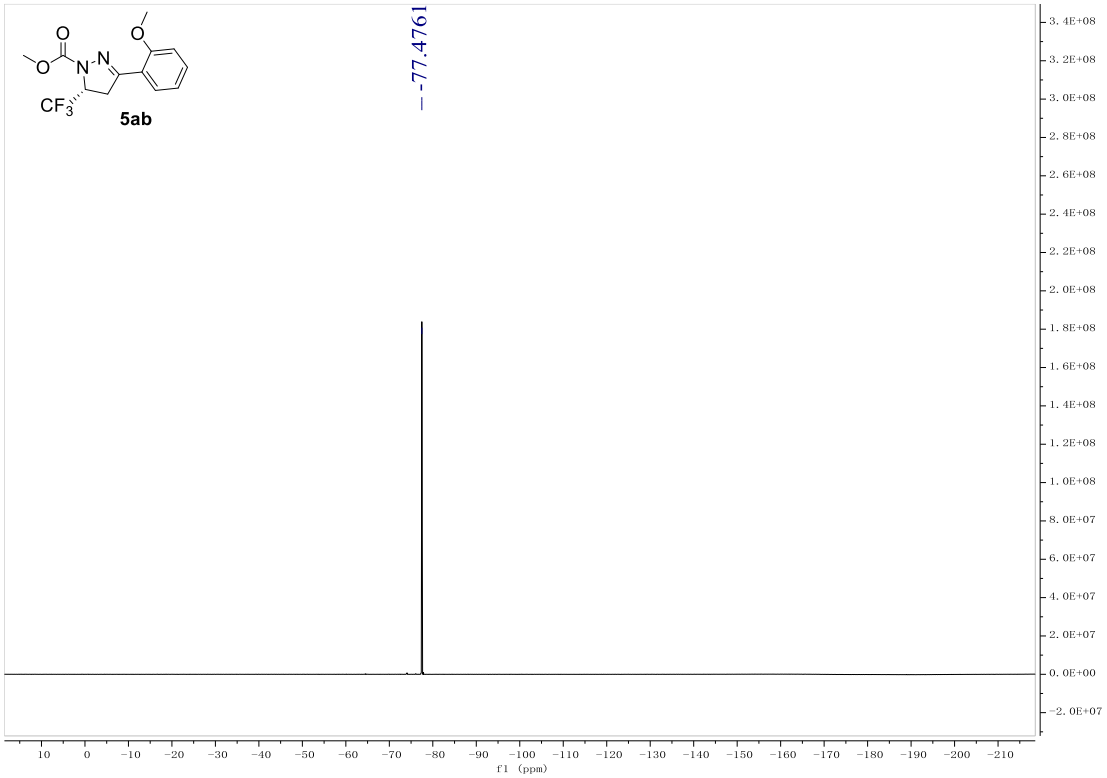
^{1}H NMR of 5ab (600 MHz, $CDCl_3$)



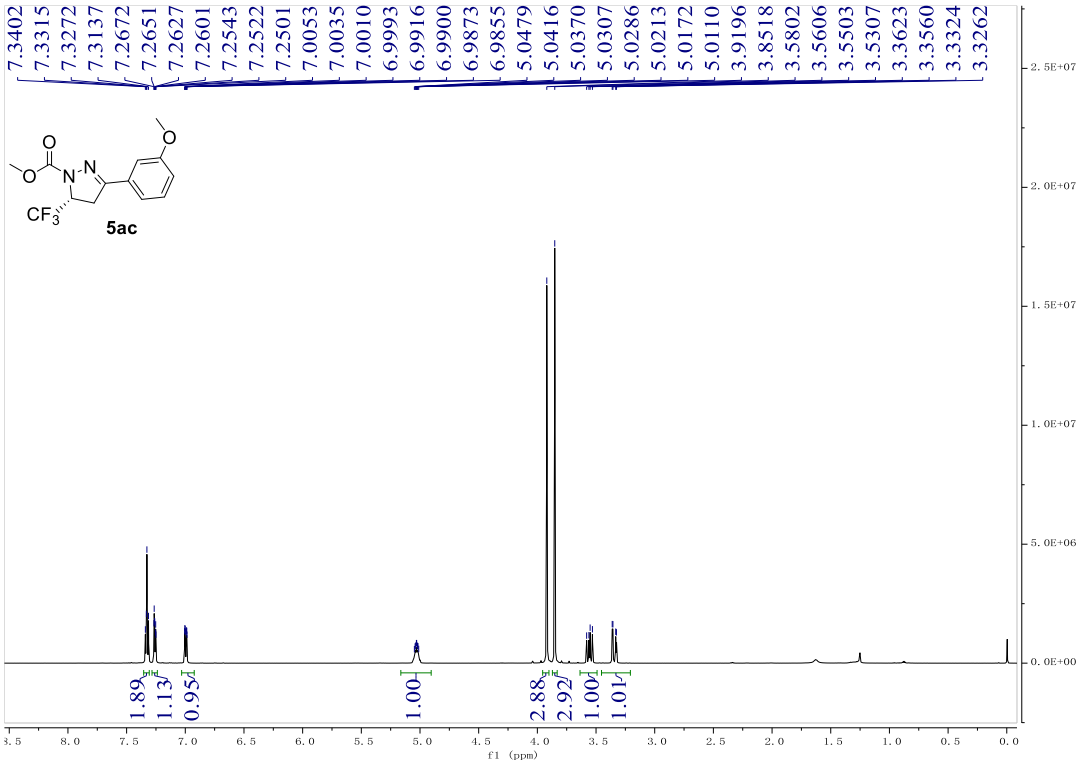
$^{13}C\{^{1}H\}$ NMR of 5ab (150 MHz, $CDCl_3$)



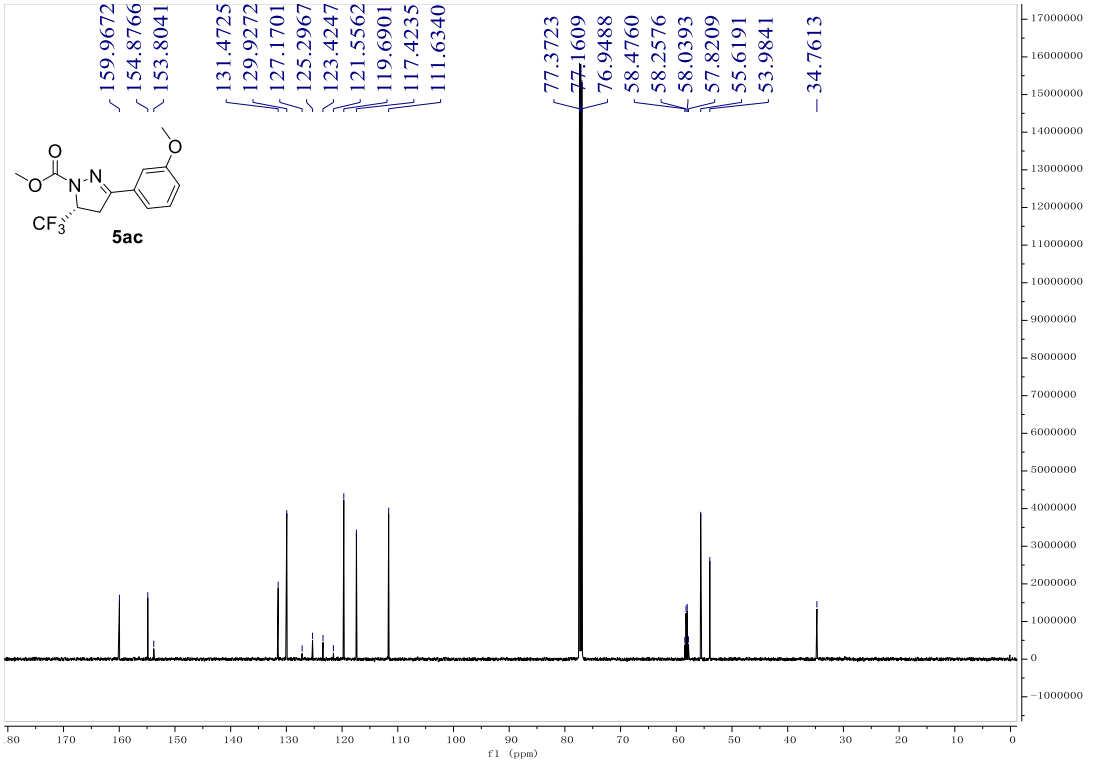
$^{19}F\{^{1}H\}$ NMR of 5ab(565 MHz, $CDCl_3$)



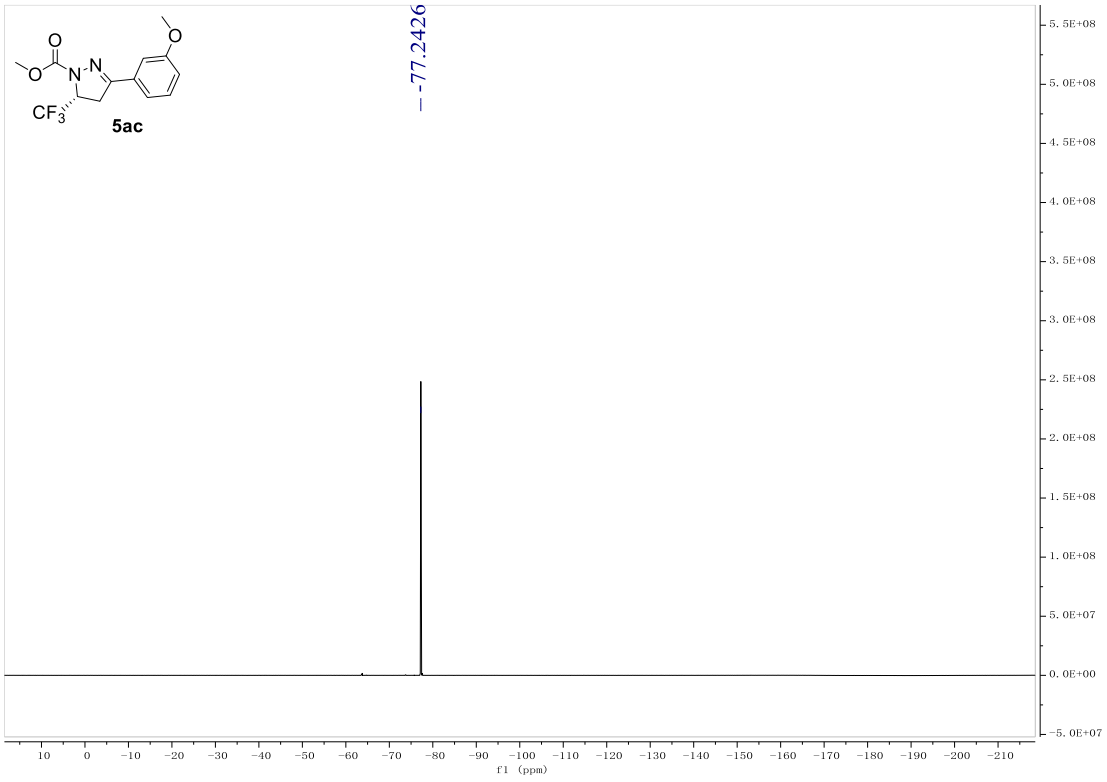
^{1}H NMR of 5ac (600 MHz, $CDCl_3$)



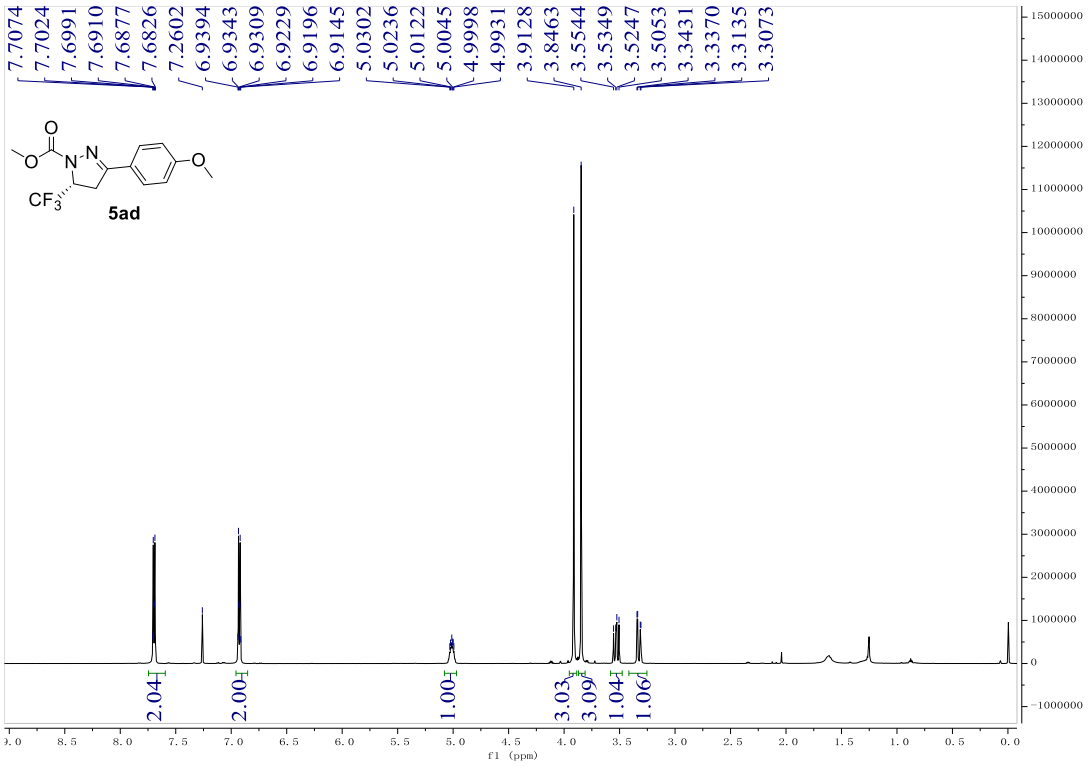
$^{13}C\{^{1}H\}$ NMR of 5ac (150 MHz, $CDCl_3$)



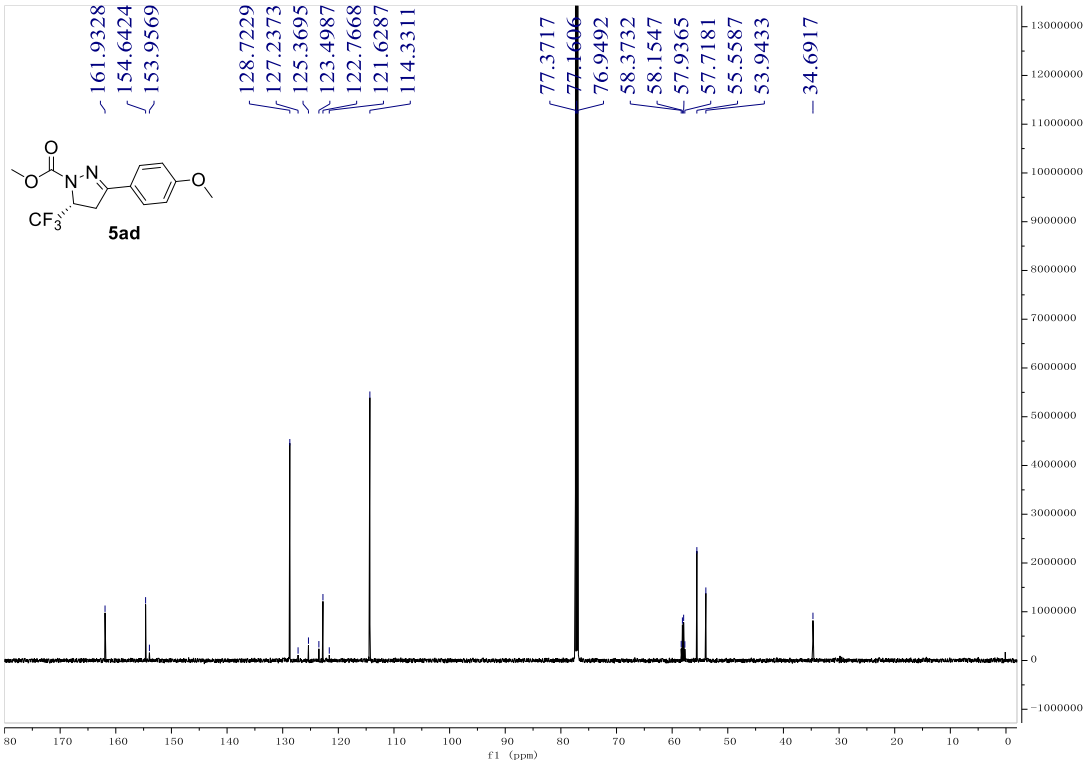
$^{19}F\{^{1}H\}$ NMR of 5ac (565 MHz, $CDCl_3$)



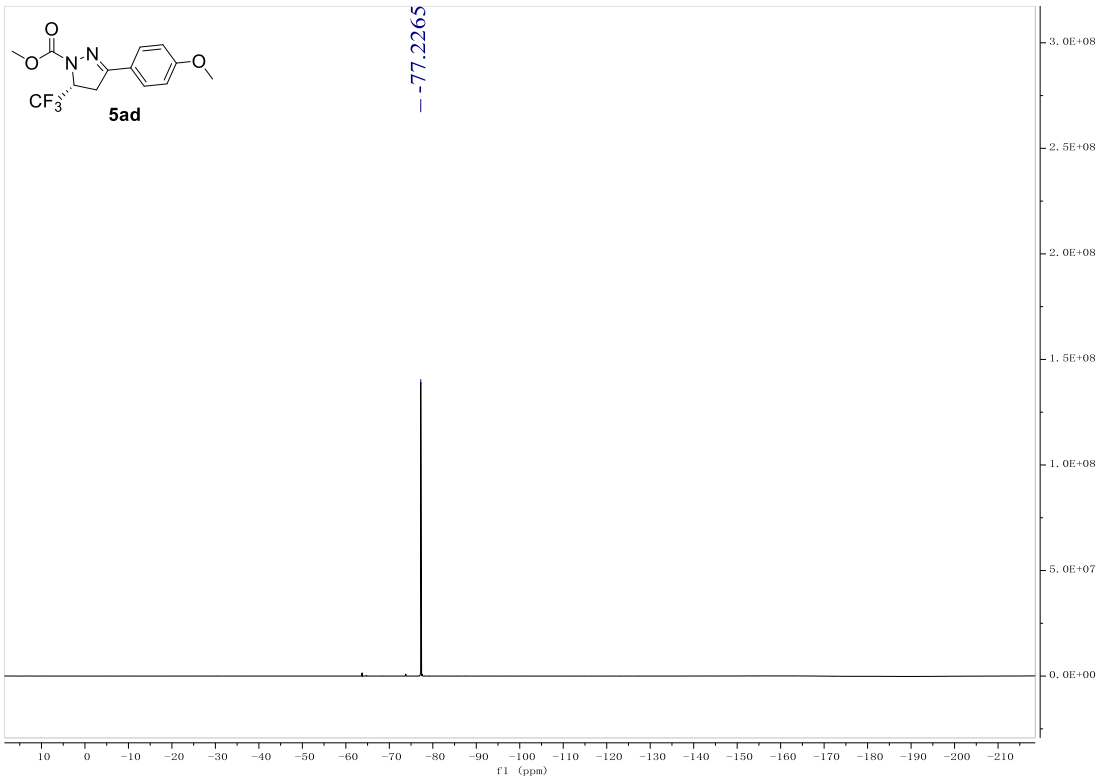
^{1}H NMR of 5ad (600 MHz, $CDCl_3$)



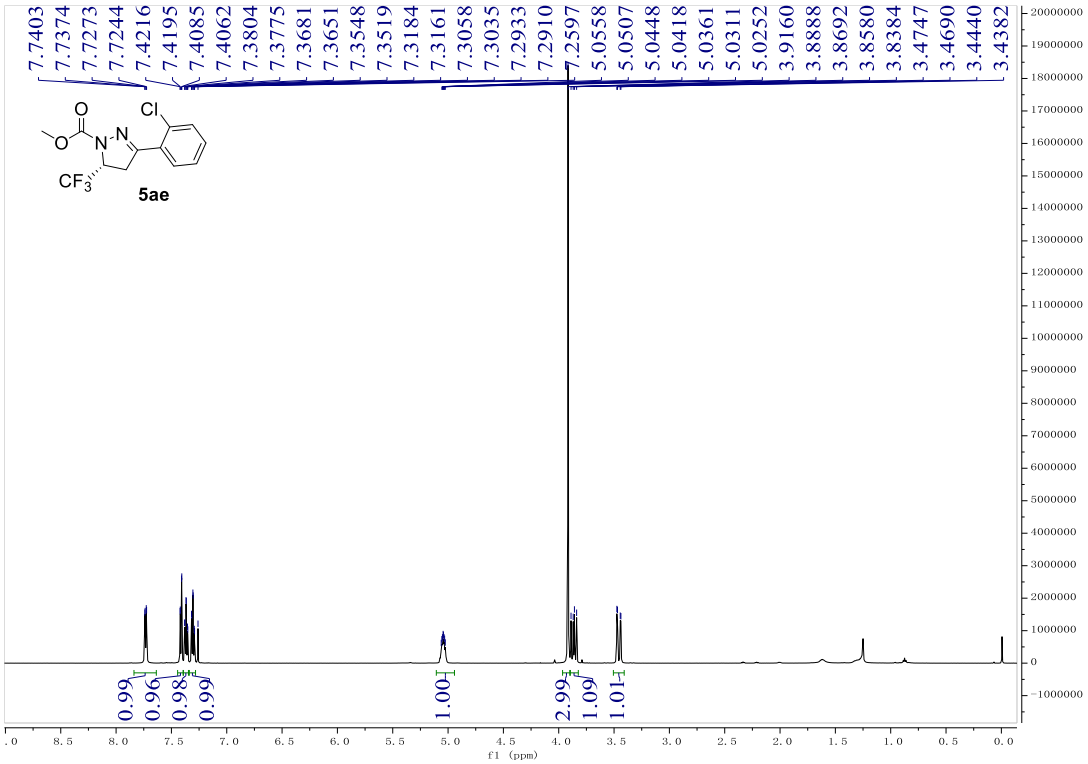
^{13}C{^{1}H} NMR of 5ad (150 MHz, $CDCl_3$)



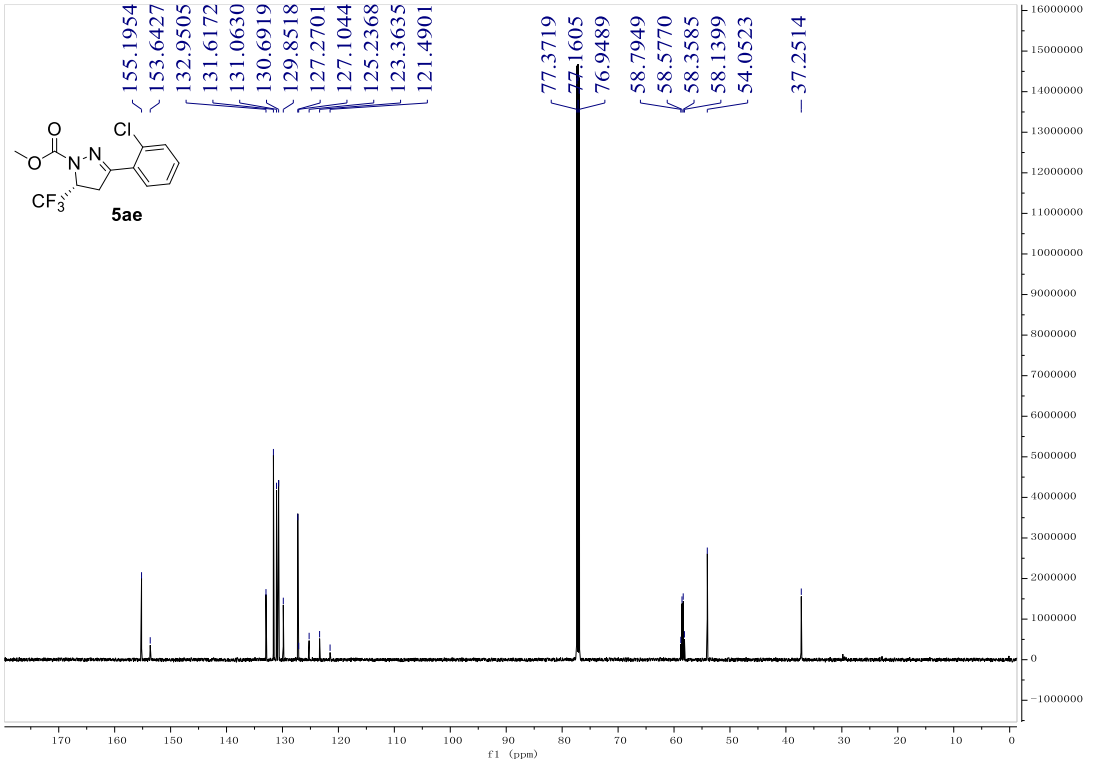
^{19}F{^{1}H} NMR of 5ad (565 MHz, $CDCl_3$)



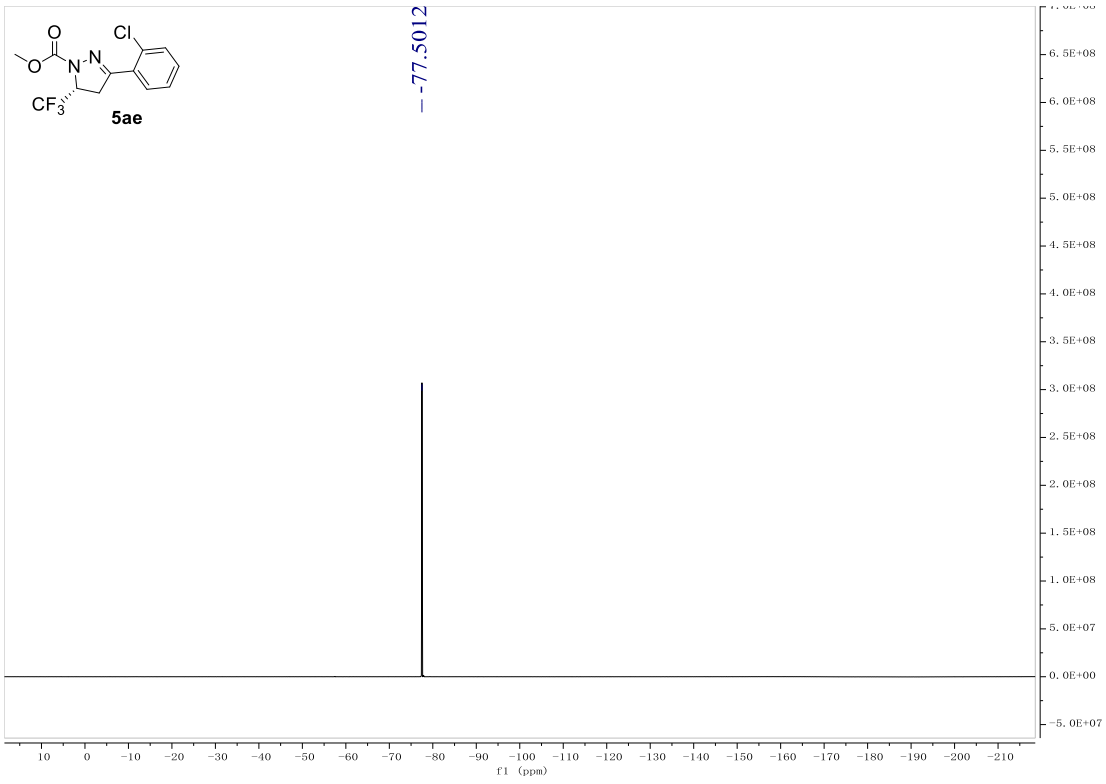
^{1}H NMR of 5ae (600 MHz, $CDCl_3$)



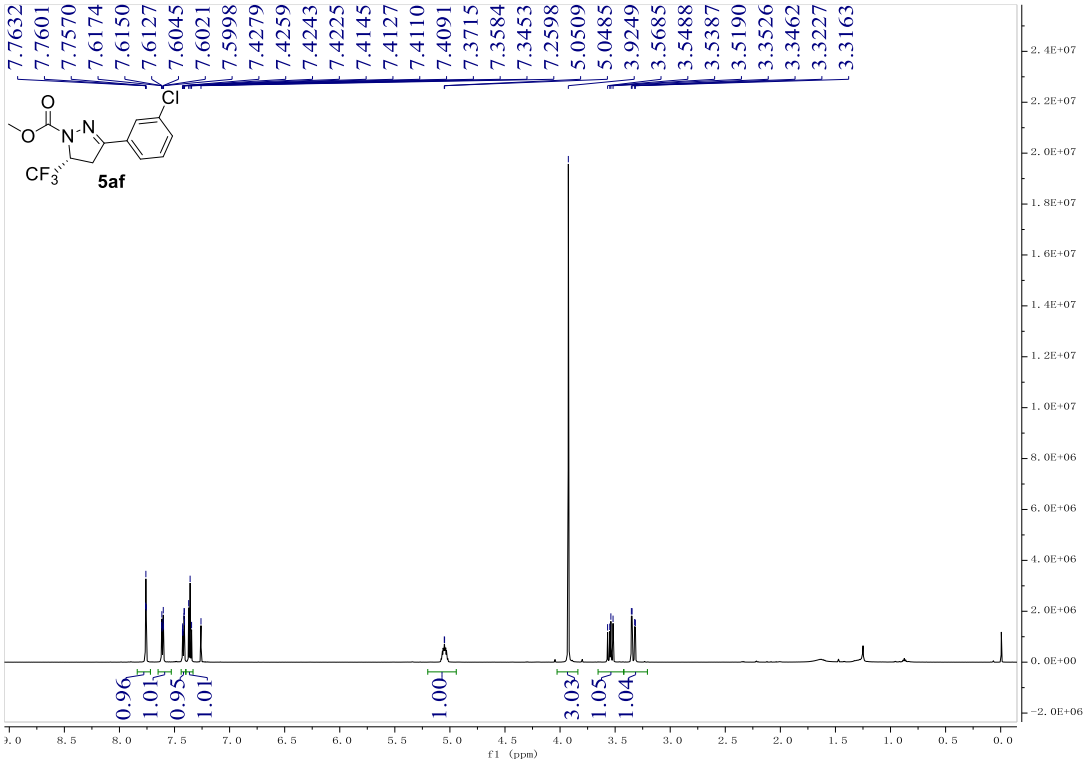
^{13}C{^{1}H} NMR of 5ae (150 MHz, $CDCl_3$)



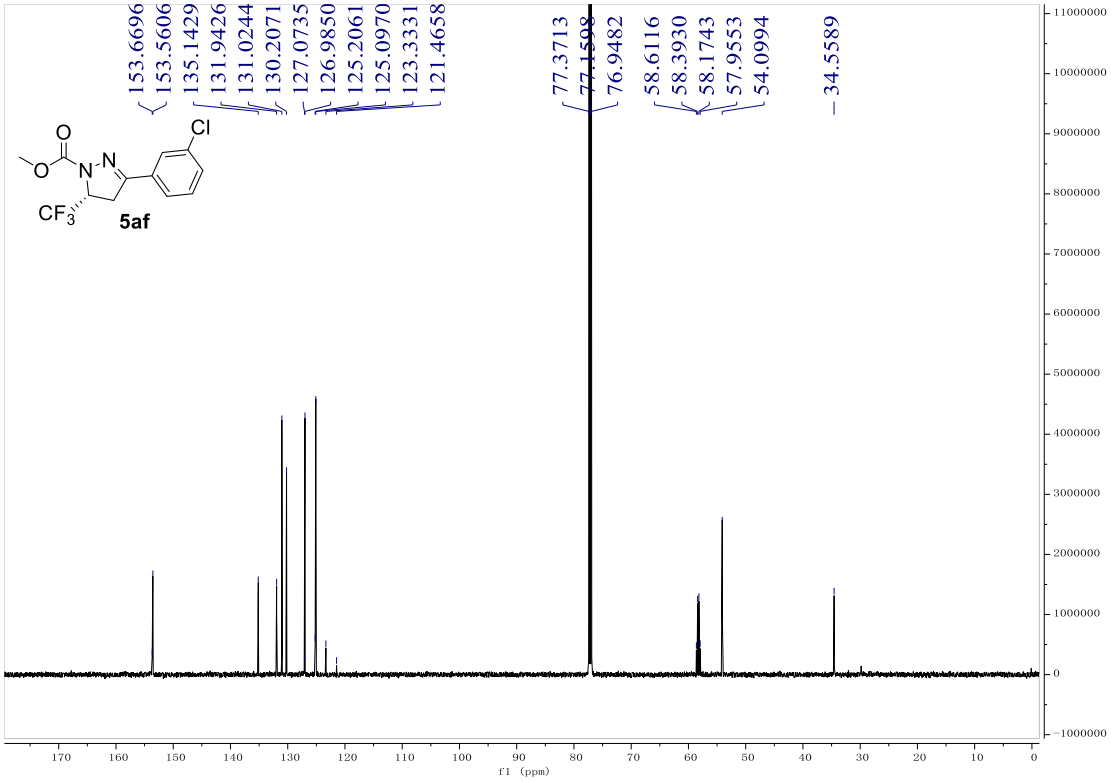
$^{19}F\{^{1}H\}$ NMR of 5ae (565 MHz, $CDCl_3$)



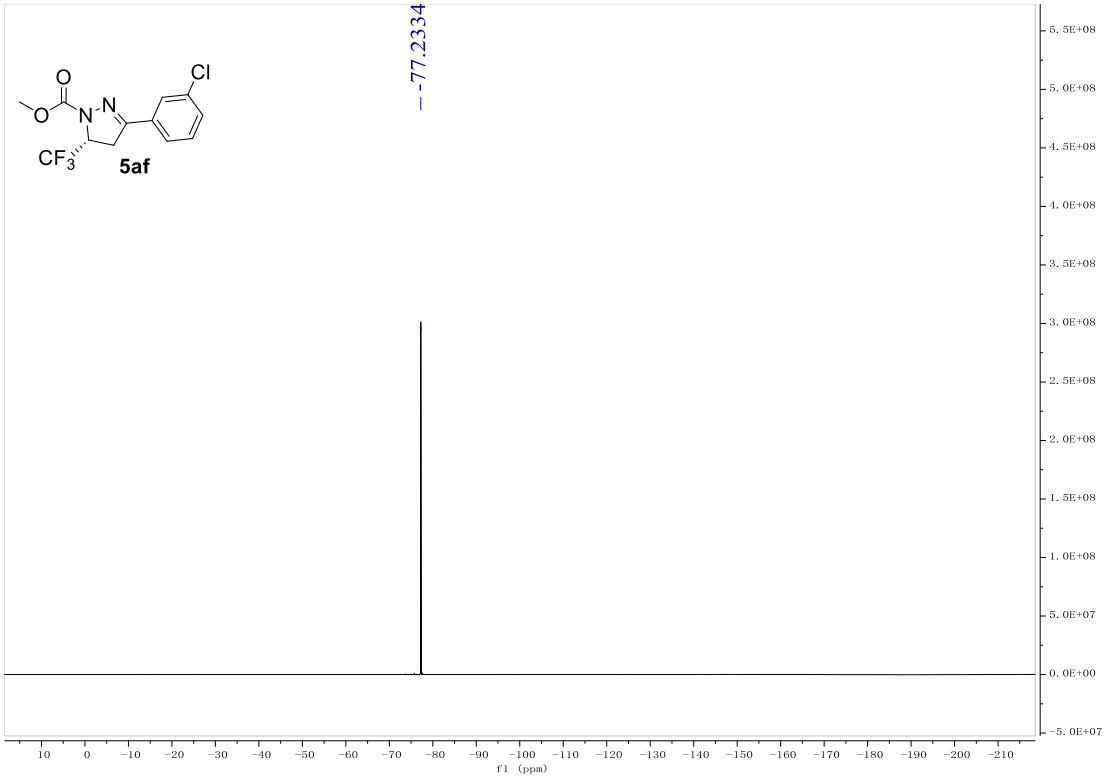
^{1}H NMR of 5af (600 MHz, $CDCl_3$)



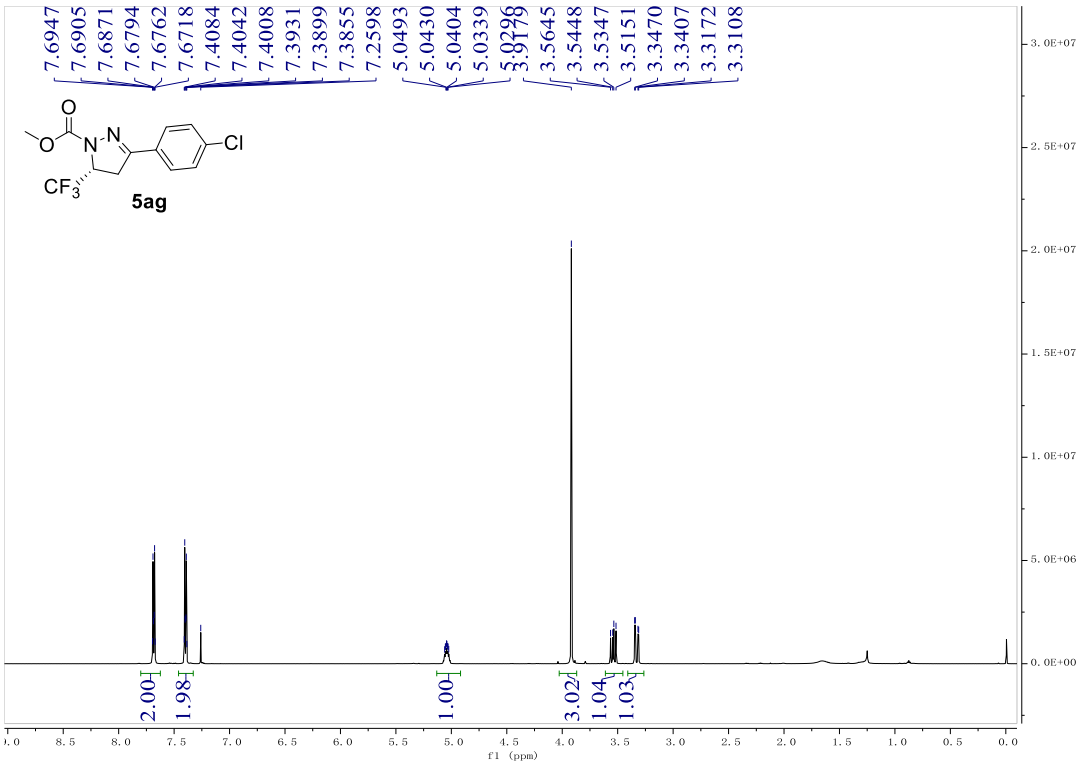
$^{13}C\{^{1}H\}$ NMR of 5af (150 MHz, $CDCl_3$)



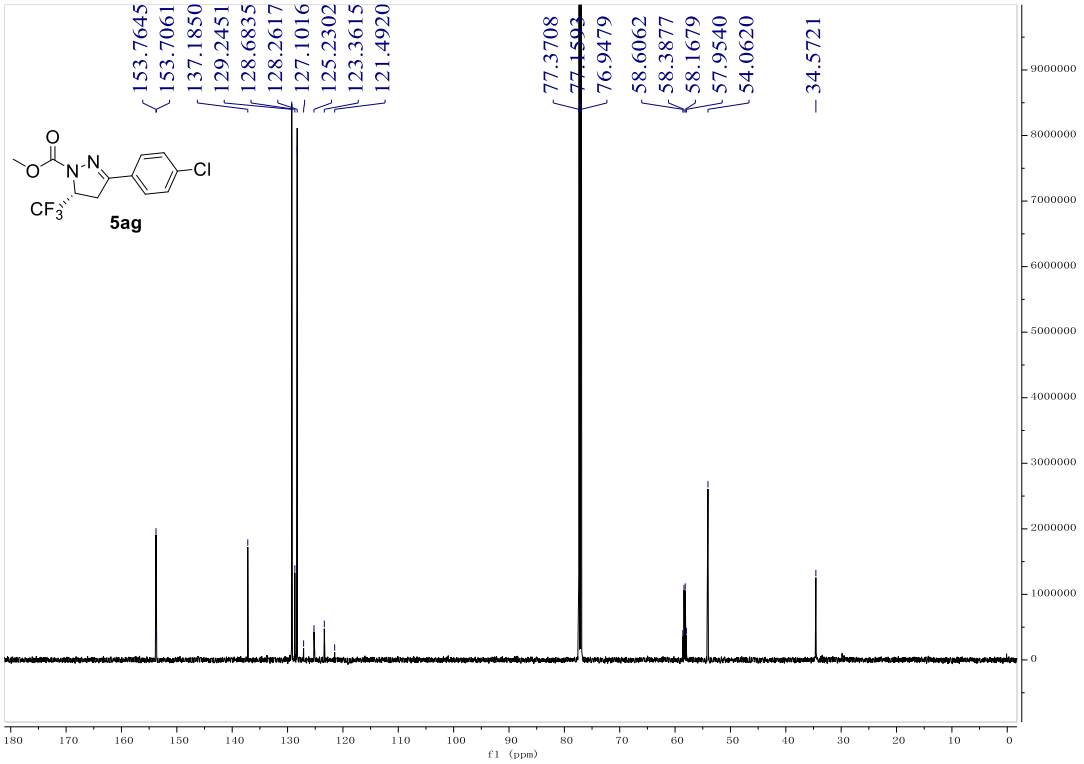
$^{19}F\{^{1}H\}$ NMR of 5af (565 MHz, $CDCl_3$)



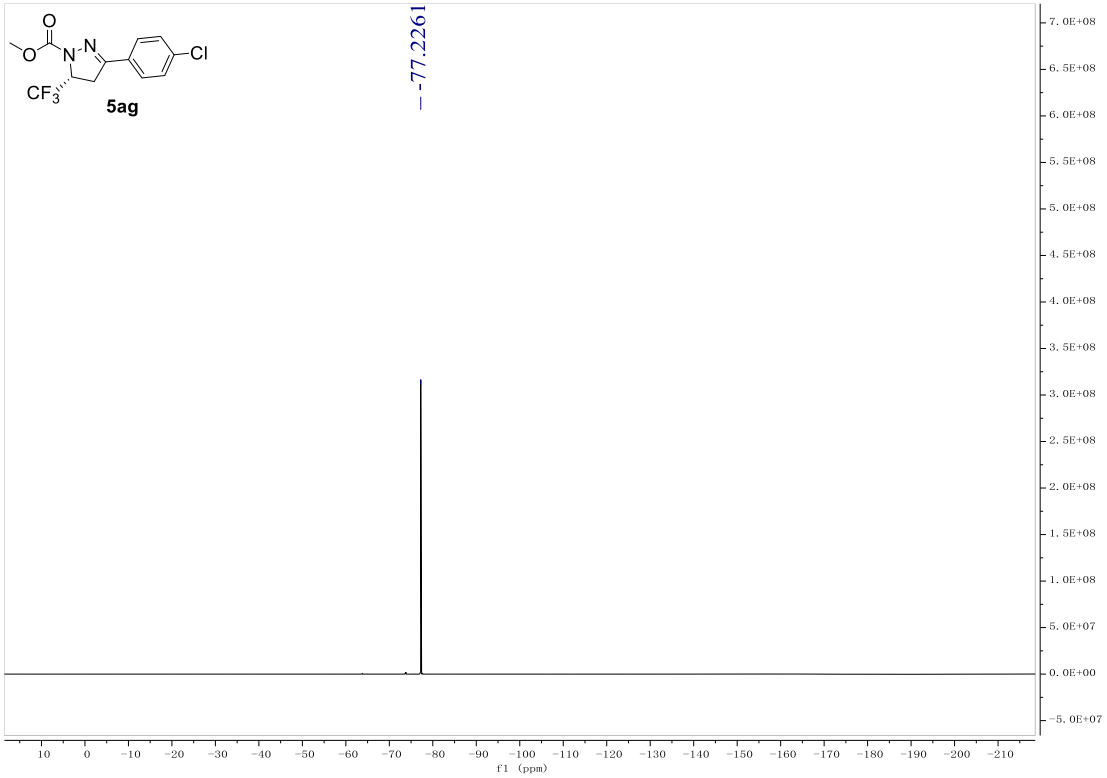
^{1}H NMR of 5ag (600 MHz, $CDCl_3$)



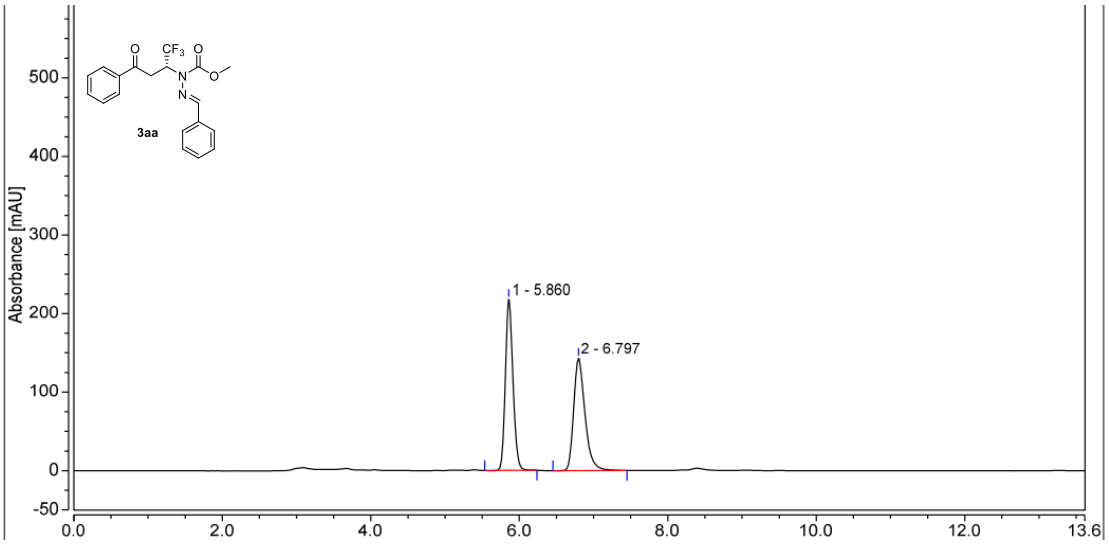
^{13}C{^{1}H} NMR of 5ag (150 MHz, $CDCl_3$)



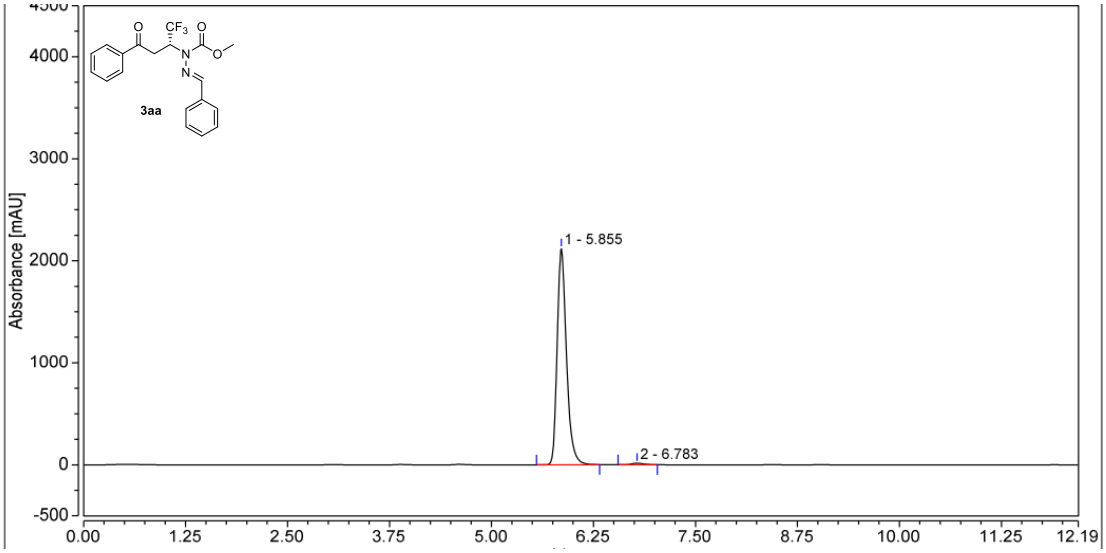
$^{19}F\{^{1}H\}$ NMR of 5ag (565 MHz, $CDCl_3$)



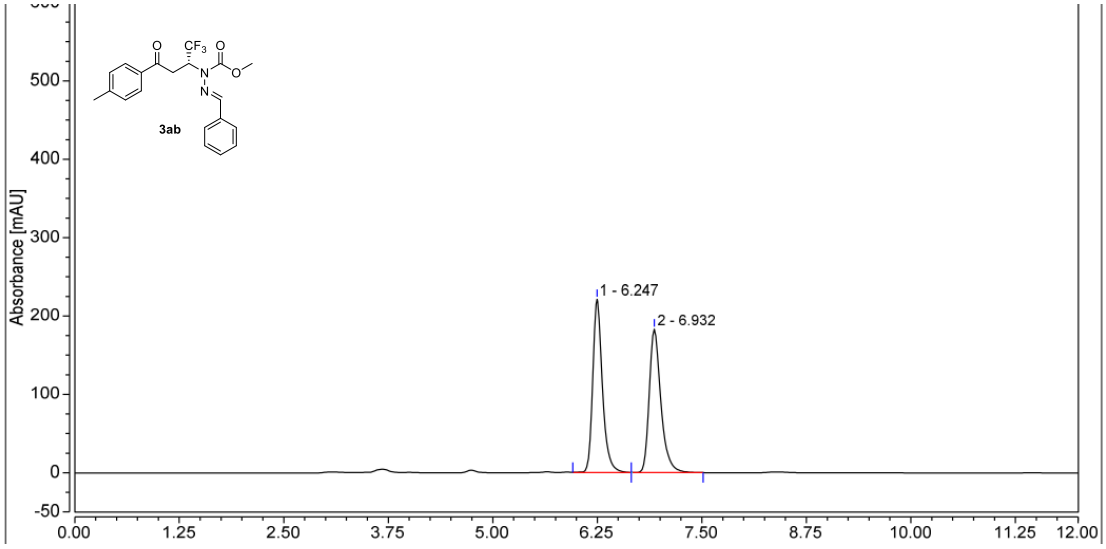
11. Copies of HPLC spectra for racemic and chiral adducts



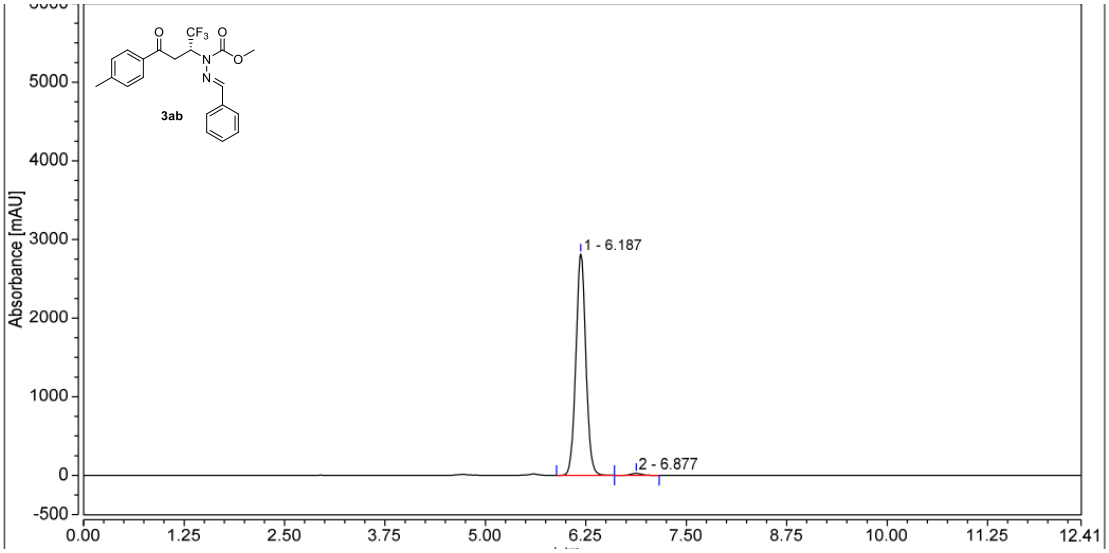
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.860	25.810	217.863	50.61	60.33	n.a.
2		6.797	25.184	143.236	49.39	39.67	n.a.
Total:			**50.994**	**361.099**	**100.00**	**100.00**	



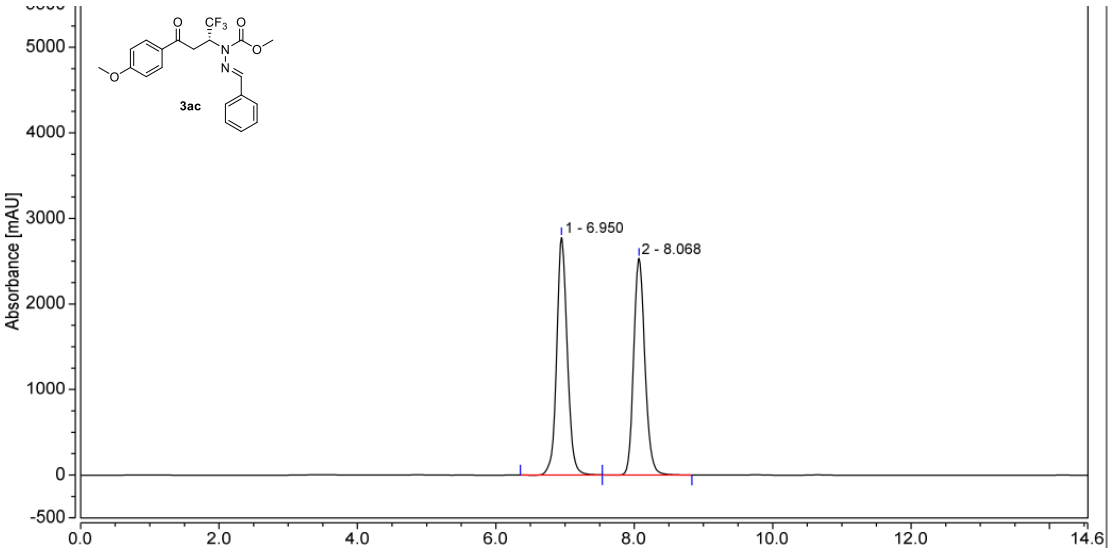
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.855	278.479	2116.709	99.15	99.33	n.a.
2		6.783	2.388	14.356	0.85	0.67	n.a.
Total:			**280.868**	**2131.065**	**100.00**	**100.00**	



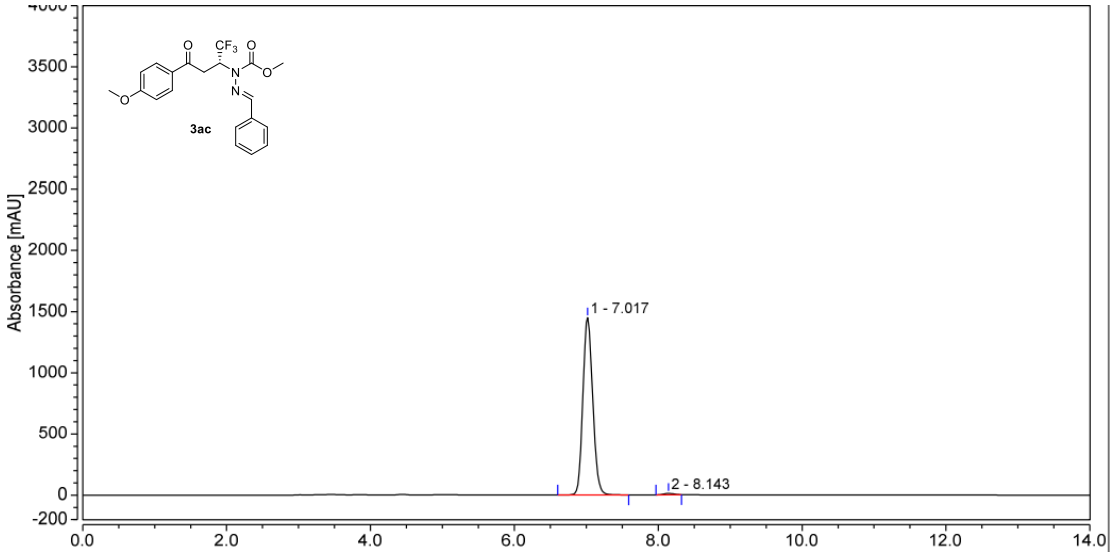
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.247	29.897	220.780	50.11	54.70	n.a.
2		6.932	29.768	182.831	49.89	45.30	n.a.
Total:			**59.665**	**403.611**	**100.00**	**100.00**	



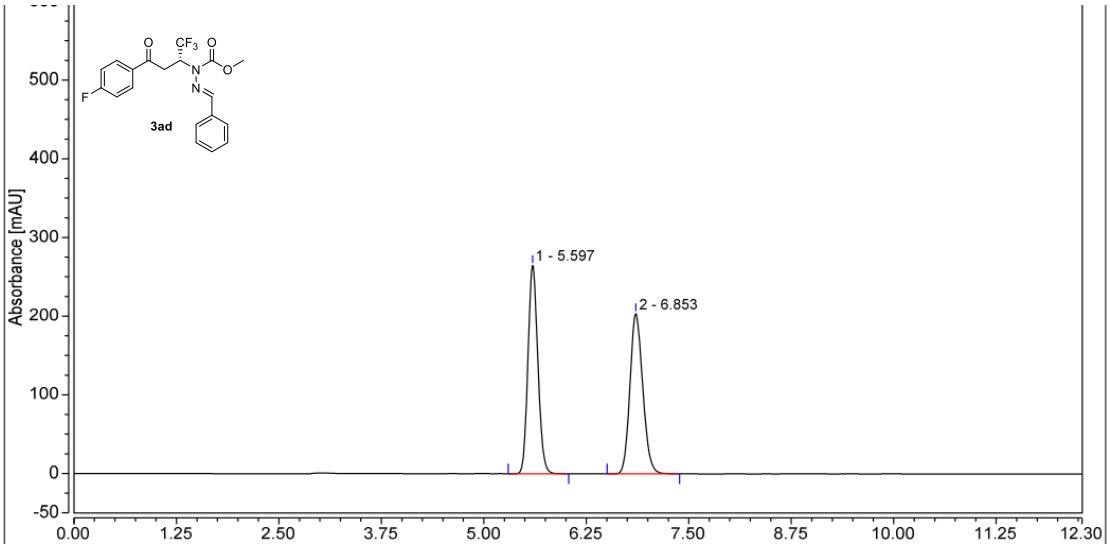
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.187	405.859	2814.143	98.93	99.08	n.a.
2		6.877	4.375	26.250	1.07	0.92	n.a.
Total:			**410.234**	**2840.393**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.950	493.182	2776.114	50.87	52.29	n.a.
2		8.068	476.342	2533.274	49.13	47.71	n.a.
Total:			**969.524**	**5309.388**	**100.00**	**100.00**	

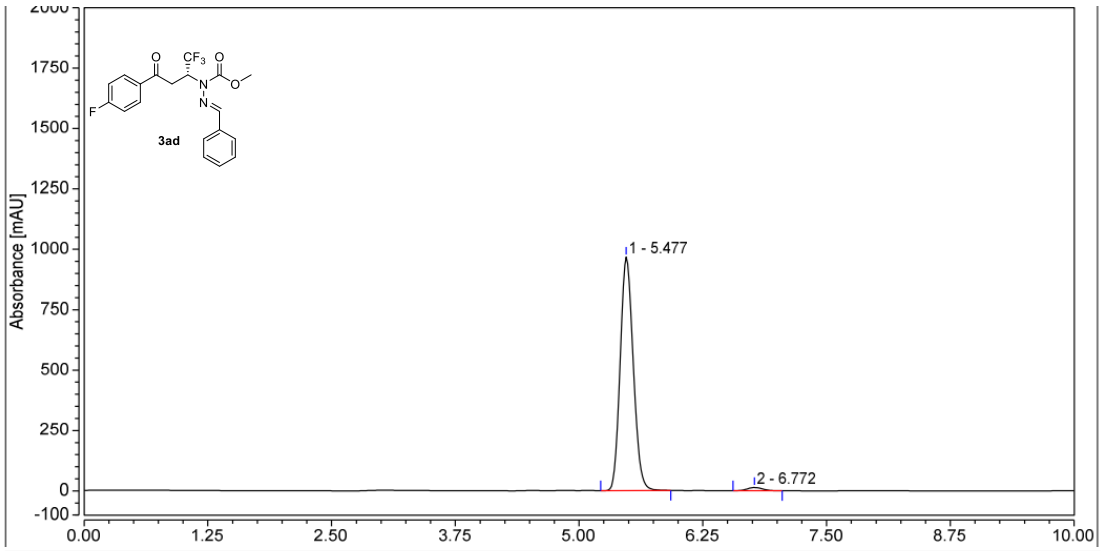


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.017	229.346	1448.037	99.18	99.19	n.a.
2		8.143	1.895	11.855	0.82	0.81	n.a.
Total:			**231.240**	**1459.892**	**100.00**	**100.00**	



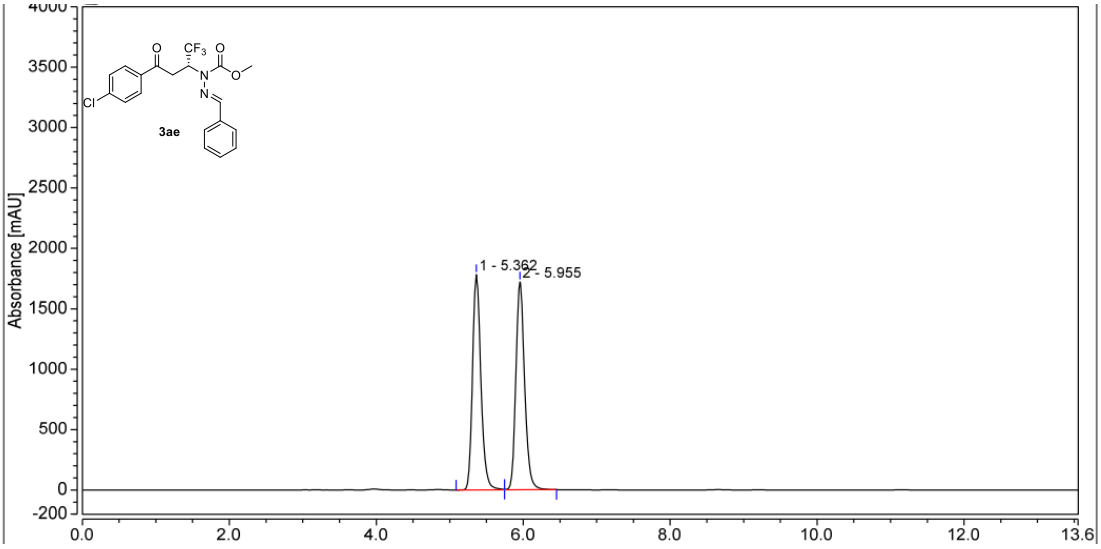
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.597	37.082	264.786	50.06	56.55	n.a.
2		6.853	36.990	203.486	49.94	43.45	n.a.
Total:			**74.072**	**468.271**	**100.00**	**100.00**	



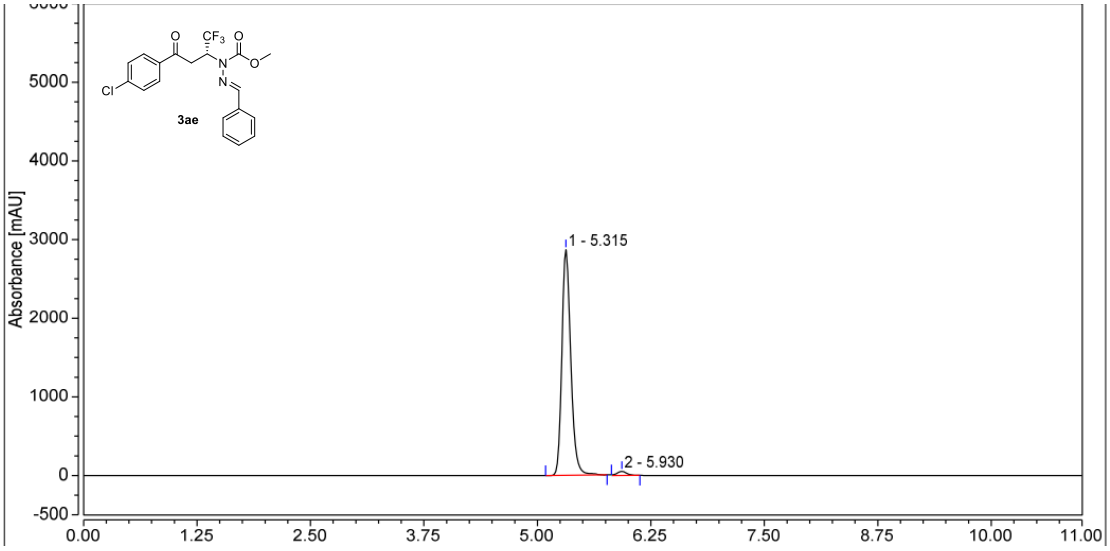
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.477	148.288	966.485	98.36	98.62	n.a.
2		6.772	2.478	13.494	1.64	1.38	n.a.
Total:			**150.766**	**979.979**	**100.00**	**100.00**	



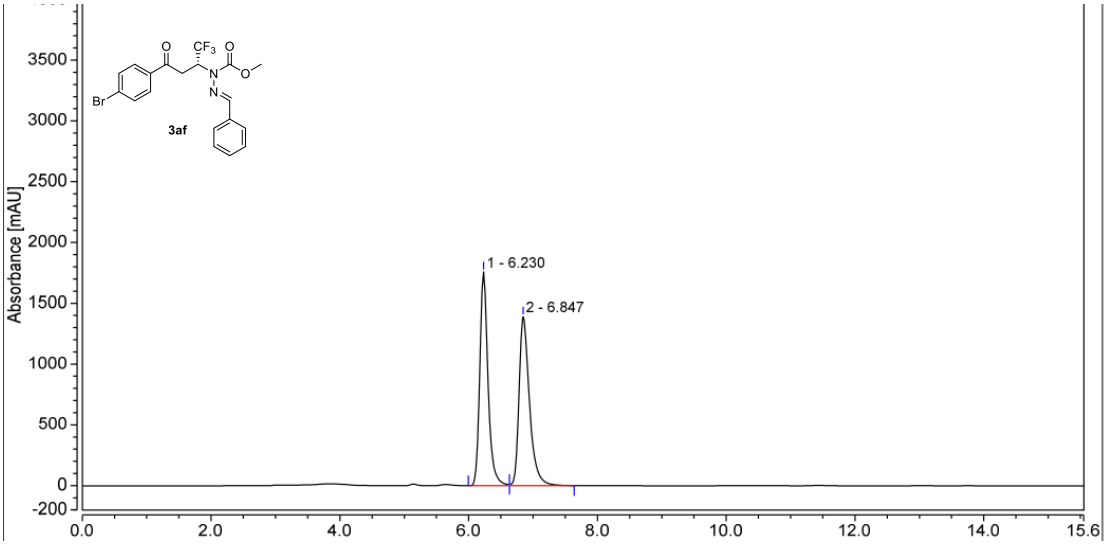
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.362	237.192	1783.109	50.00	50.88	n.a.
2		5.955	237.236	1721.317	50.00	49.12	n.a.
Total:			**474.427**	**3504.425**	**100.00**	**100.00**	

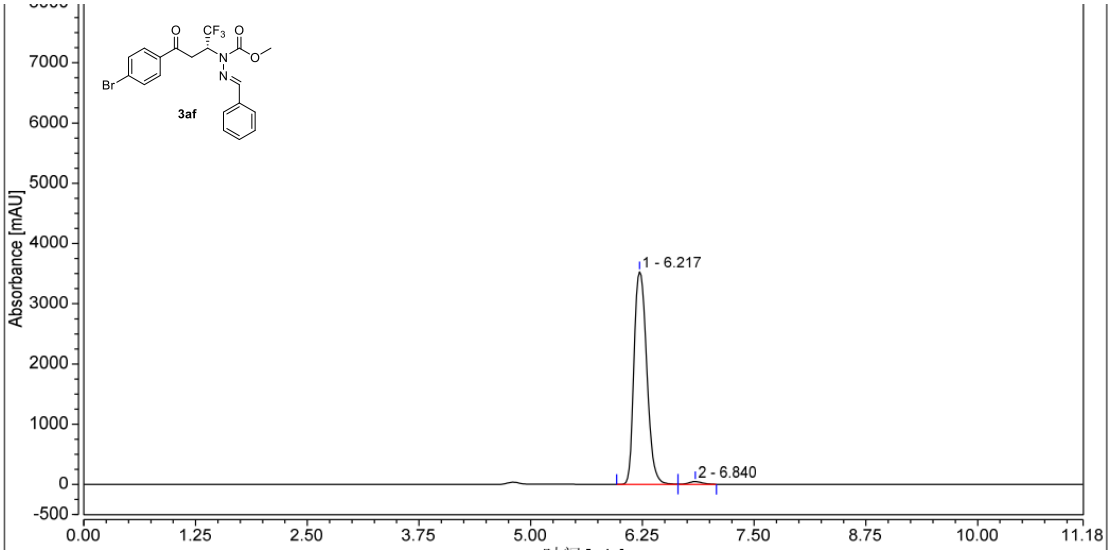


Integration Results

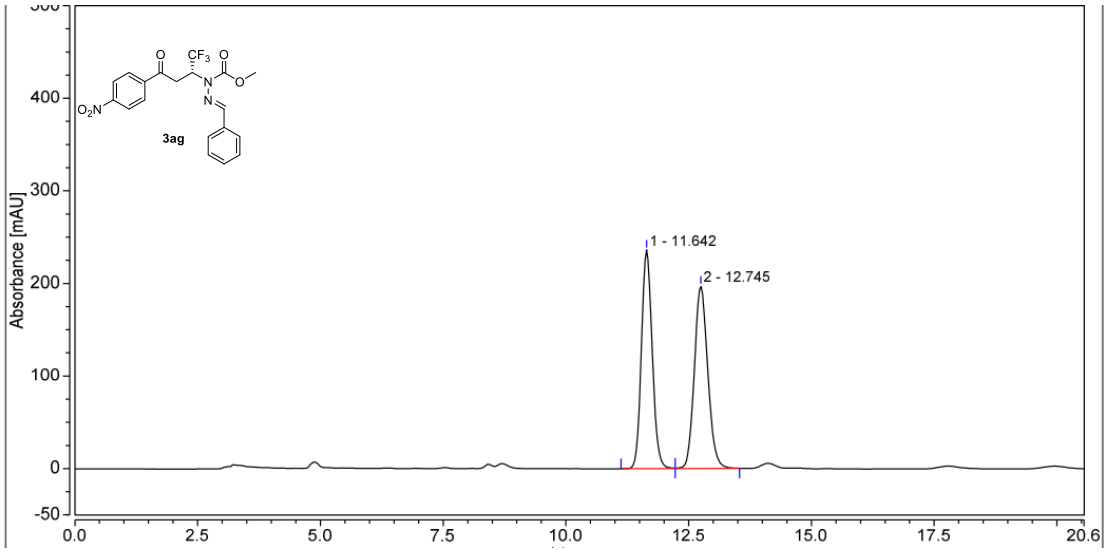
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.315	329.253	2867.530	98.08	98.26	n.a.
2		5.930	6.434	50.635	1.92	1.74	n.a.
Total:			**335.686**	**2918.164**	**100.00**	**100.00**	



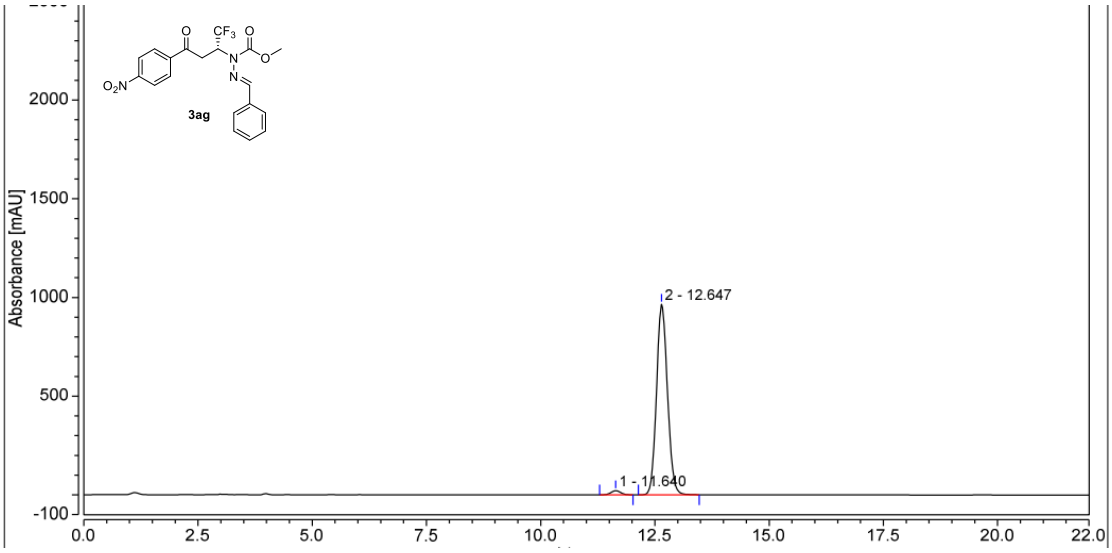
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.230	258.368	1759.377	49.89	55.89	n.a.
2		6.847	259.460	1388.346	50.11	44.11	n.a.
Total:			**517.828**	**3147.723**	**100.00**	**100.00**	



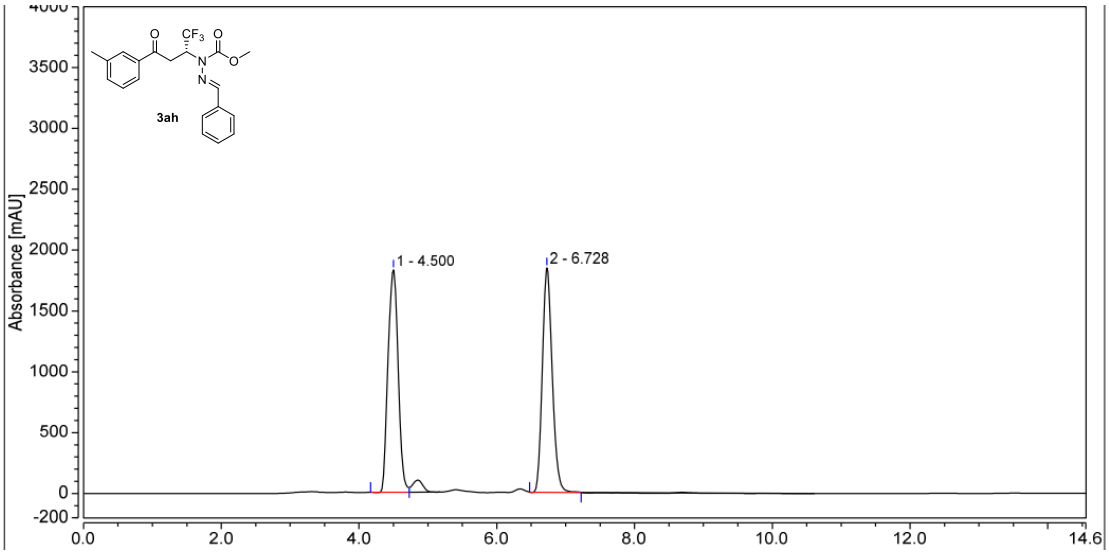
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.217	583.192	3527.505	98.64	98.71	n.a.
2		6.840	8.031	46.247	1.36	1.29	n.a.
Total:			**591.223**	**3573.752**	**100.00**	**100.00**	



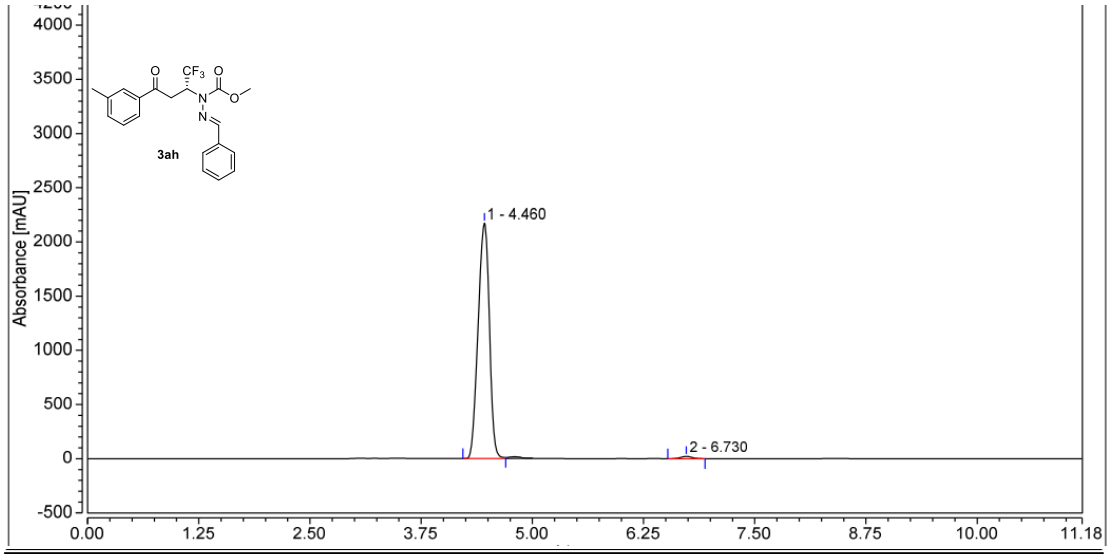
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.642	60.413	236.186	49.15	54.55	n.a.
2		12.745	62.498	196.747	50.85	45.45	n.a.
Total:			**122.910**	**432.933**	**100.00**	**100.00**	



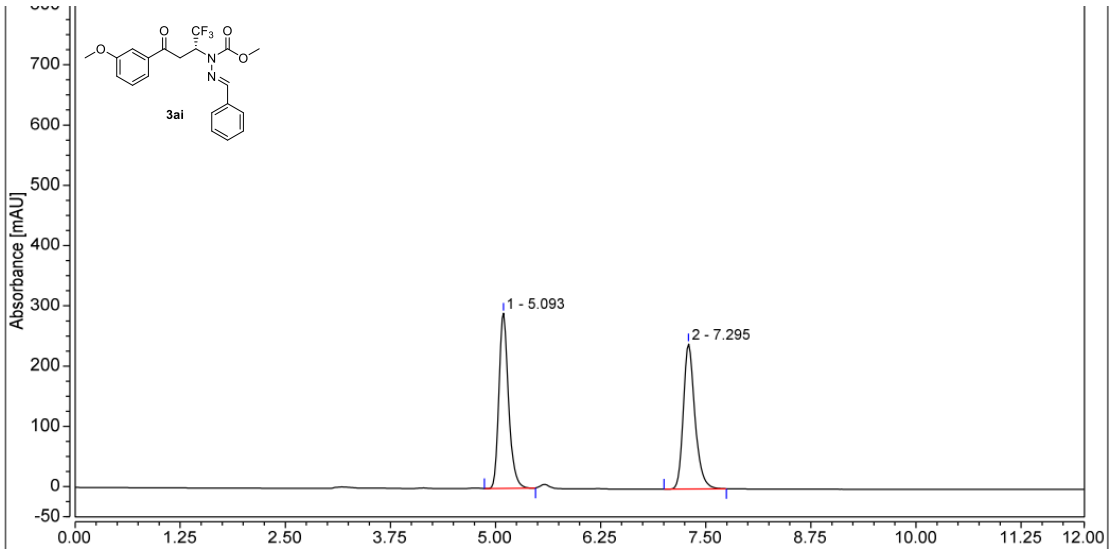
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.640	5.151	21.024	1.88	2.13	n.a.
2		12.647	268.837	965.289	98.12	97.87	n.a.
Total:			**273.988**	**986.313**	**100.00**	**100.00**	



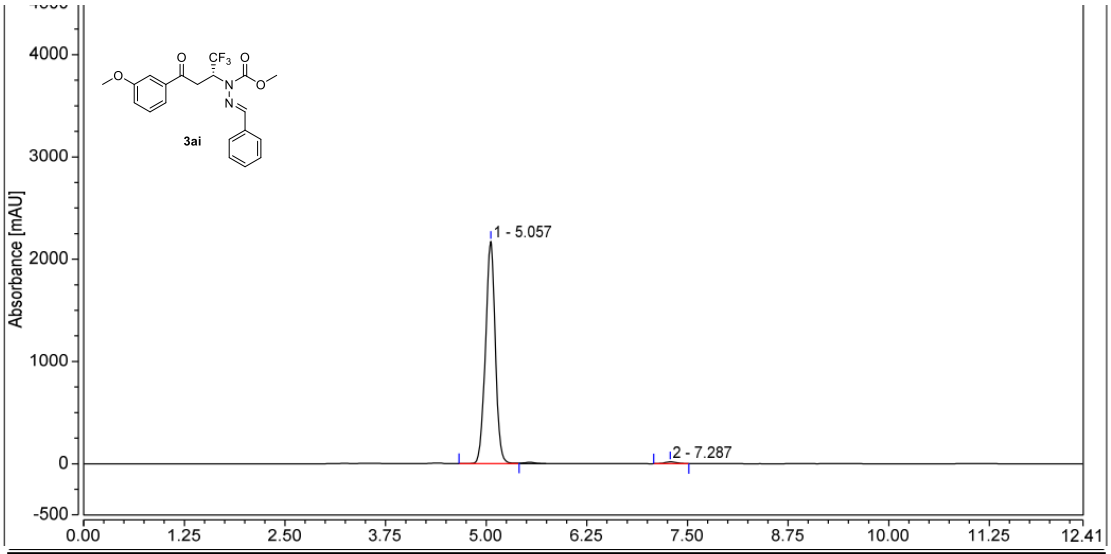
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.500	312.557	1826.391	50.43	49.75	n.a.
2		6.728	307.250	1844.409	49.57	50.25	n.a.
Total:			**619.807**	**3670.800**	**100.00**	**100.00**	



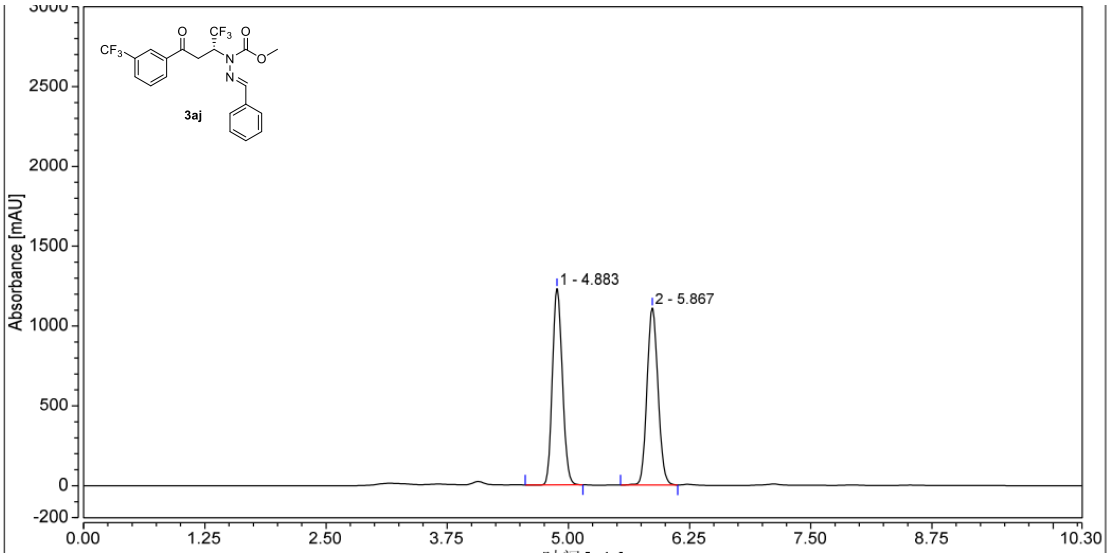
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.460	318.720	2171.171	99.05	99.03	n.a.
2		6.730	3.055	21.314	0.95	0.97	n.a.
Total:			**321.775**	**2192.485**	**100.00**	**100.00**	



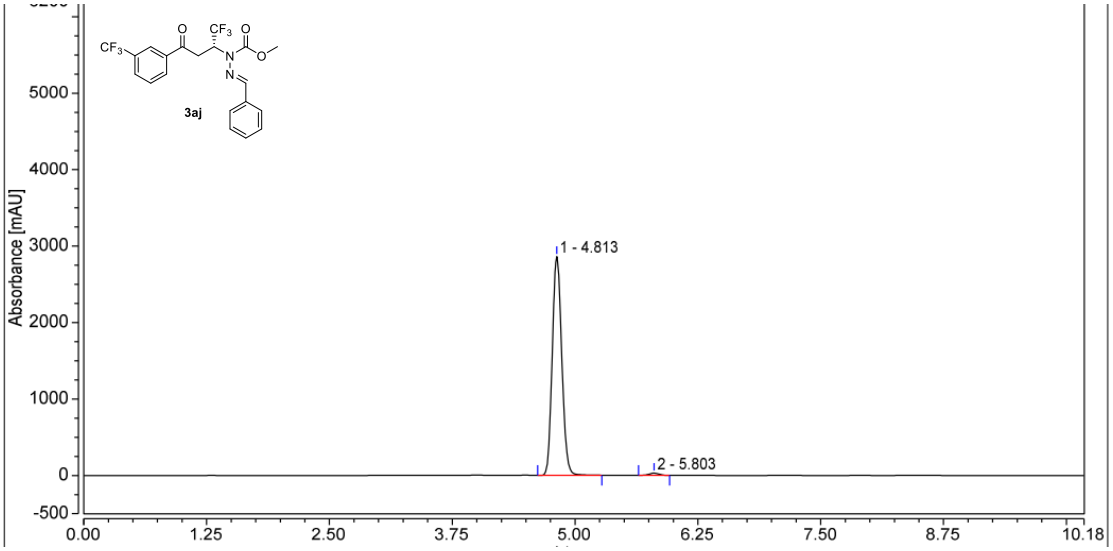
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.093	38.631	291.008	49.93	54.71	n.a.
2		7.295	38.741	240.866	50.07	45.29	n.a.
Total:			**77.372**	**531.873**	**100.00**	**100.00**	



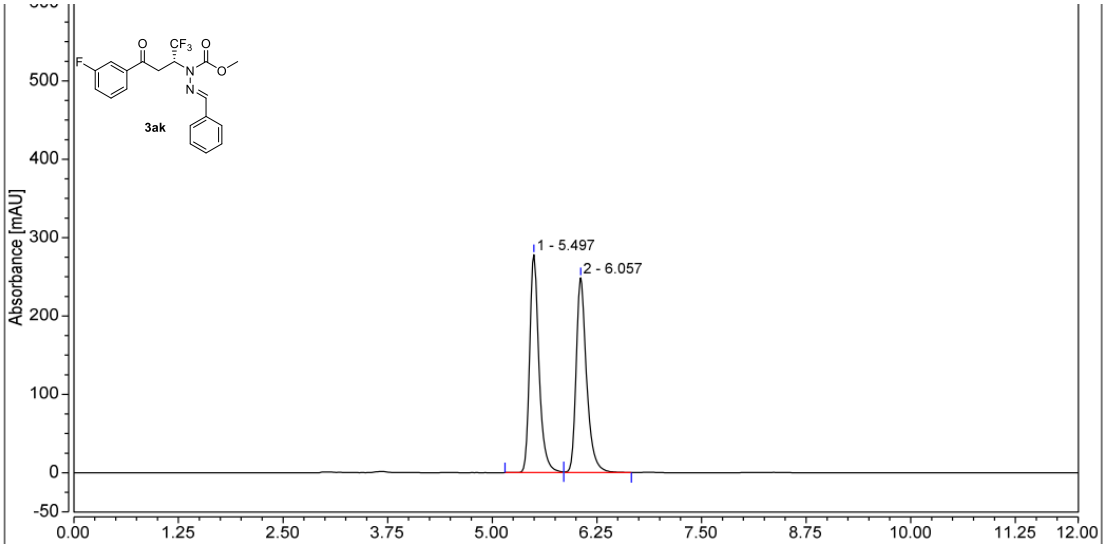
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.057	304.916	2173.489	99.03	99.15	n.a.
2		7.287	2.997	18.713	0.97	0.85	n.a.
Total:			**307.913**	**2192.202**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.883	145.607	1228.608	50.03	52.57	n.a.
2		5.867	145.416	1108.465	49.97	47.43	n.a.
Total:			**291.024**	**2337.073**	**100.00**	**100.00**	

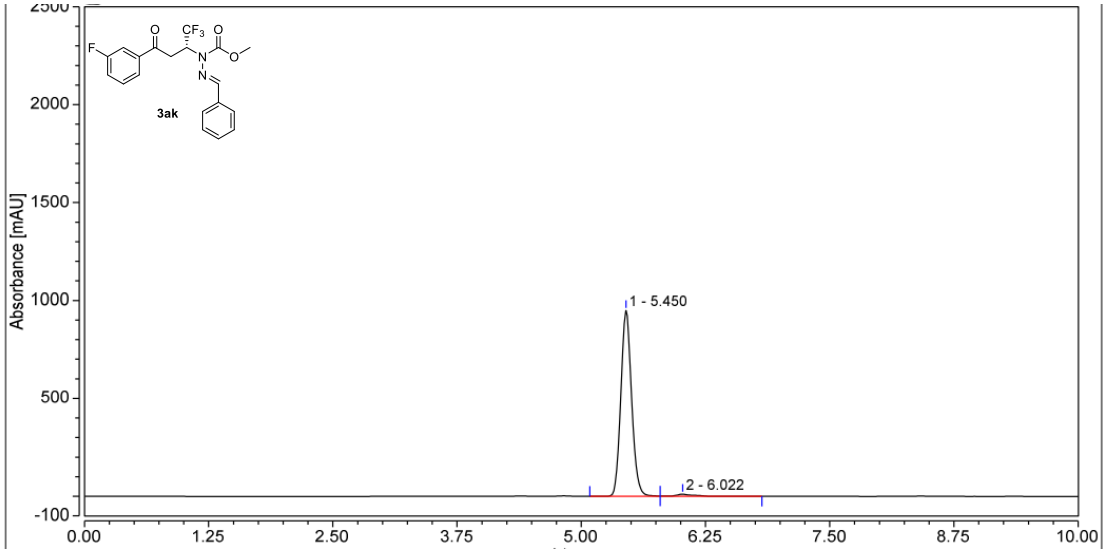


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.813	321.251	2862.039	98.89	98.98	n.a.
2		5.803	3.619	29.452	1.11	1.02	n.a.
Total:			**324.869**	**2891.491**	**100.00**	**100.00**	



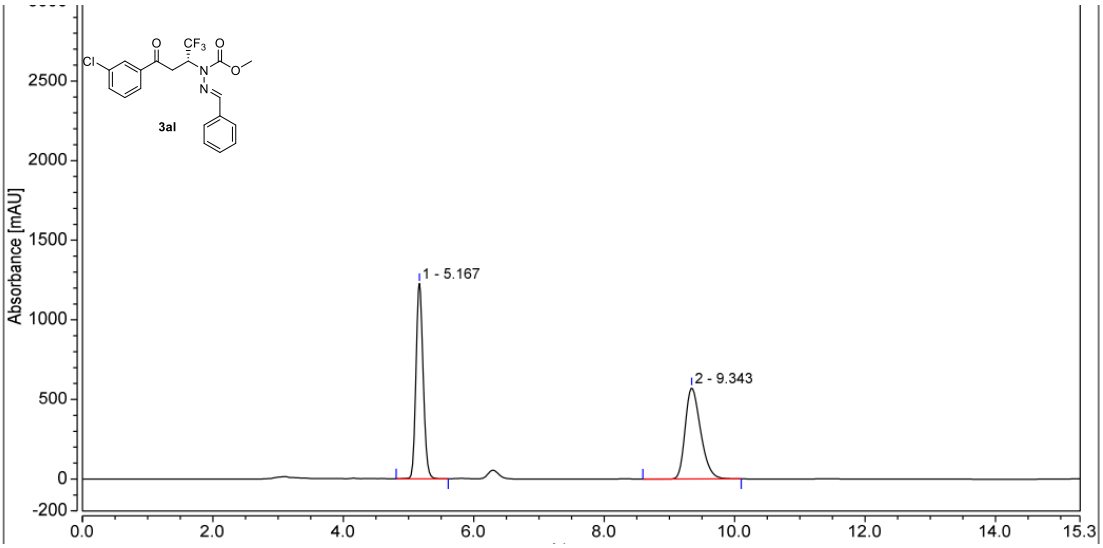
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.497	35.692	277.988	49.83	52.78	n.a.
2		6.057	35.929	248.714	50.17	47.22	n.a.
Total:			**71.621**	**526.701**	**100.00**	**100.00**	



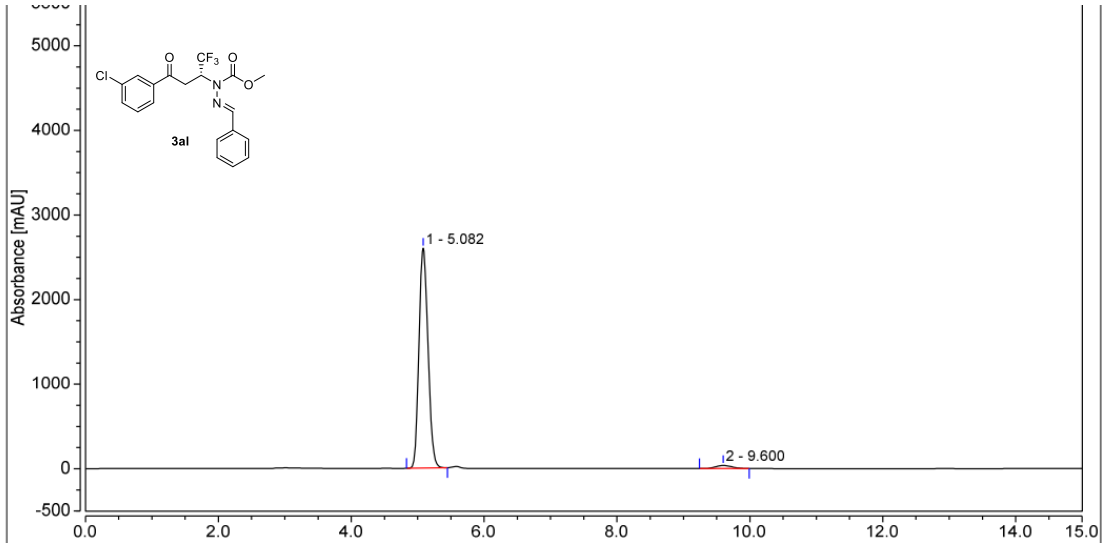
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.450	119.503	948.851	98.18	98.86	n.a.
2		6.022	2.210	10.963	1.82	1.14	n.a.
Total:			**121.713**	**959.814**	**100.00**	**100.00**	



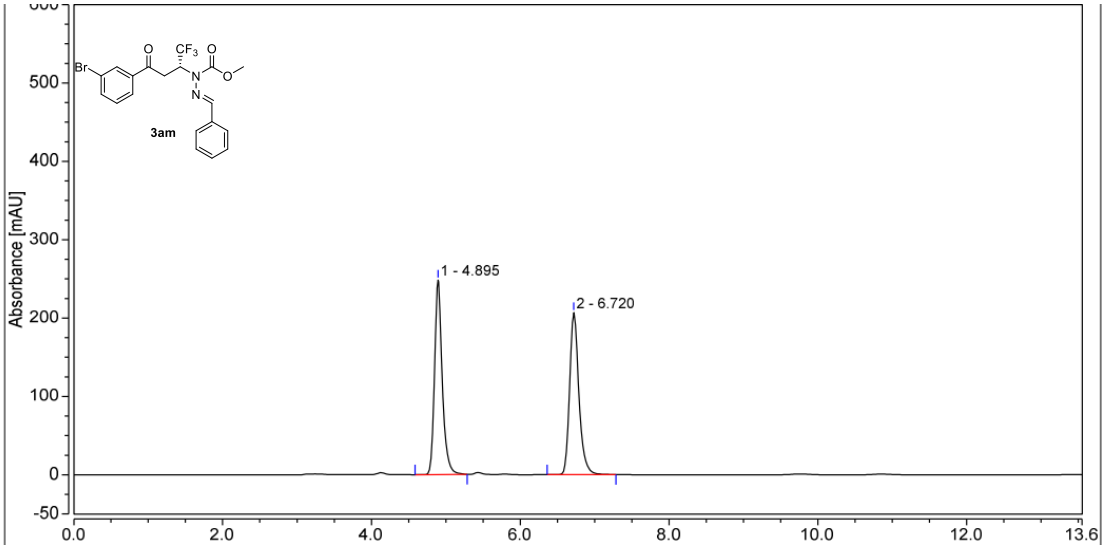
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.167	156.123	1226.987	49.83	68.19	n.a.
2		9.343	157.189	572.502	50.17	31.81	n.a.
Total:			**313.312**	**1799.489**	**100.00**	**100.00**	



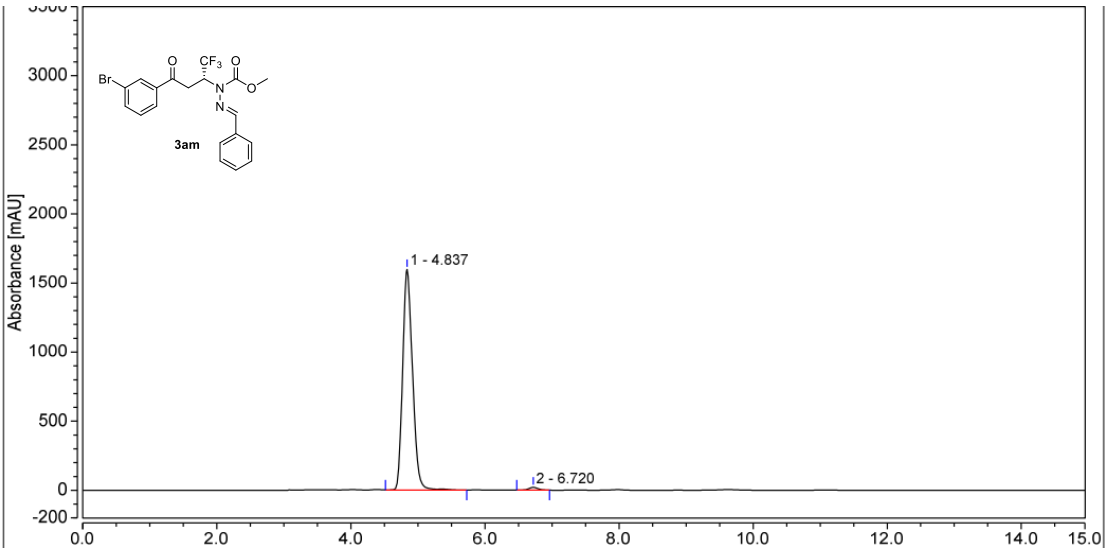
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.082	411.680	2599.764	97.52	98.60	n.a.
2		9.600	10.448	36.850	2.48	1.40	n.a.
Total:			**422.128**	**2636.613**	**100.00**	**100.00**	



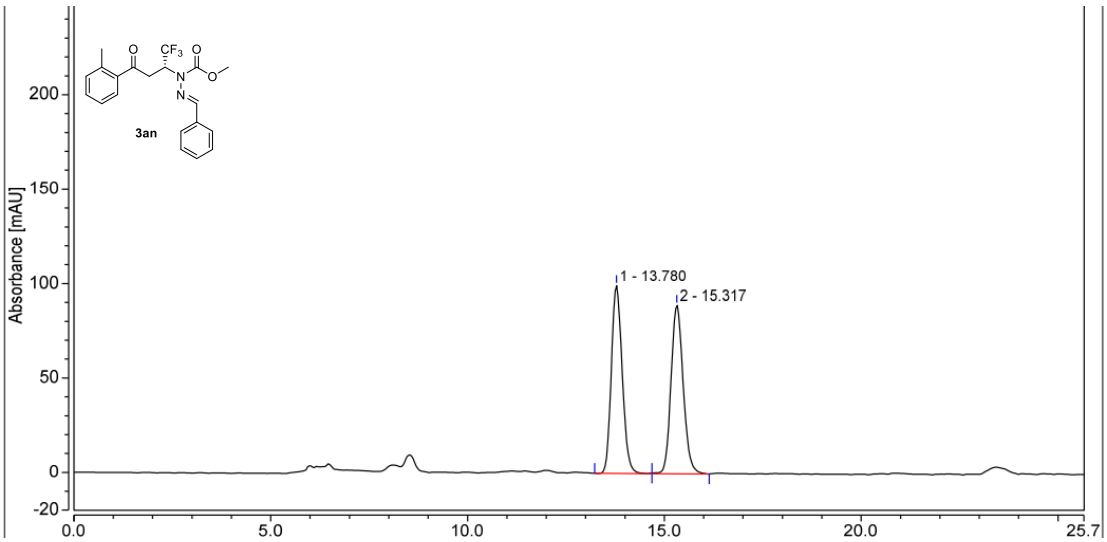
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.895	29.854	248.147	49.96	54.51	n.a.
2		6.720	29.906	207.054	50.04	45.49	n.a.
Total:			**59.760**	**455.201**	**100.00**	**100.00**	

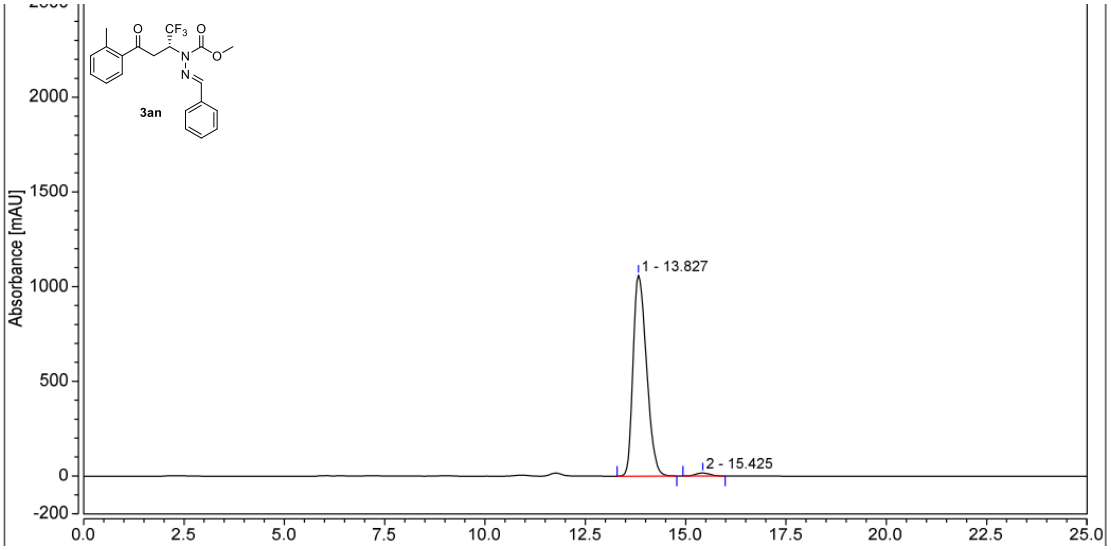


Integration Results

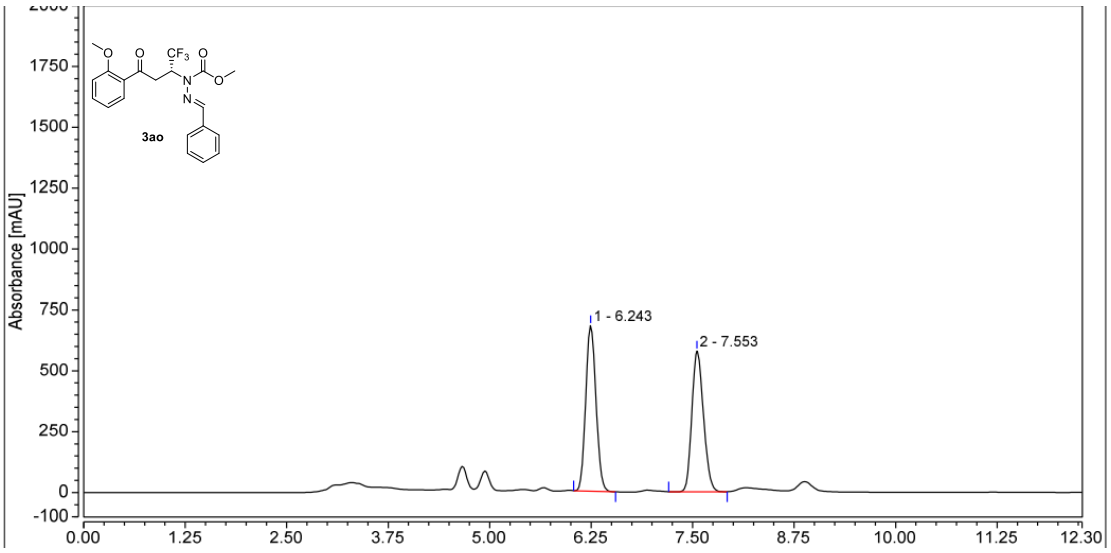
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.837	273.111	1595.772	98.80	98.73	n.a.
2		6.720	3.322	20.511	1.20	1.27	n.a.
Total:			**276.433**	**1616.284**	**100.00**	**100.00**	



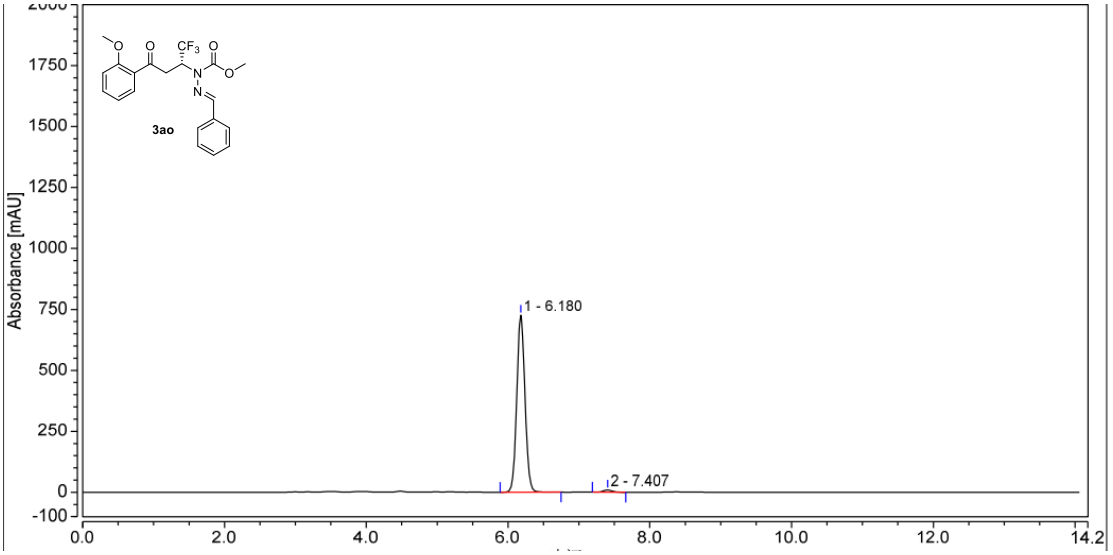
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.780	31.808	99.586	49.77	52.71	n.a.
2		15.317	32.103	89.356	50.23	47.29	n.a.
Total:			**63.911**	**188.941**	**100.00**	**100.00**	



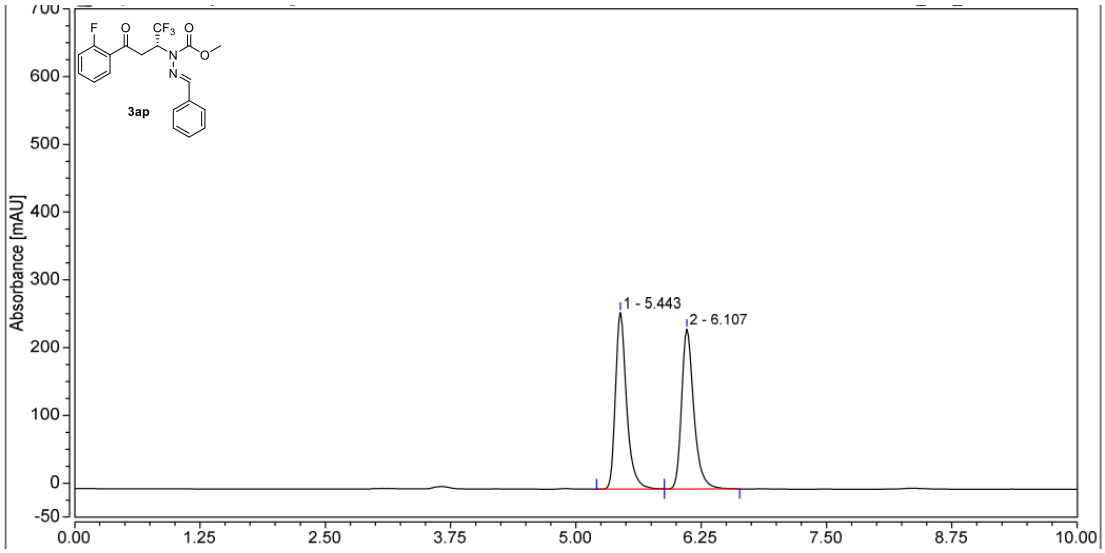
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.827	413.776	1060.541	98.44	98.50	n.a.
2		15.425	6.551	16.128	1.56	1.50	n.a.
Total:			**420.328**	**1076.668**	**100.00**	**100.00**	



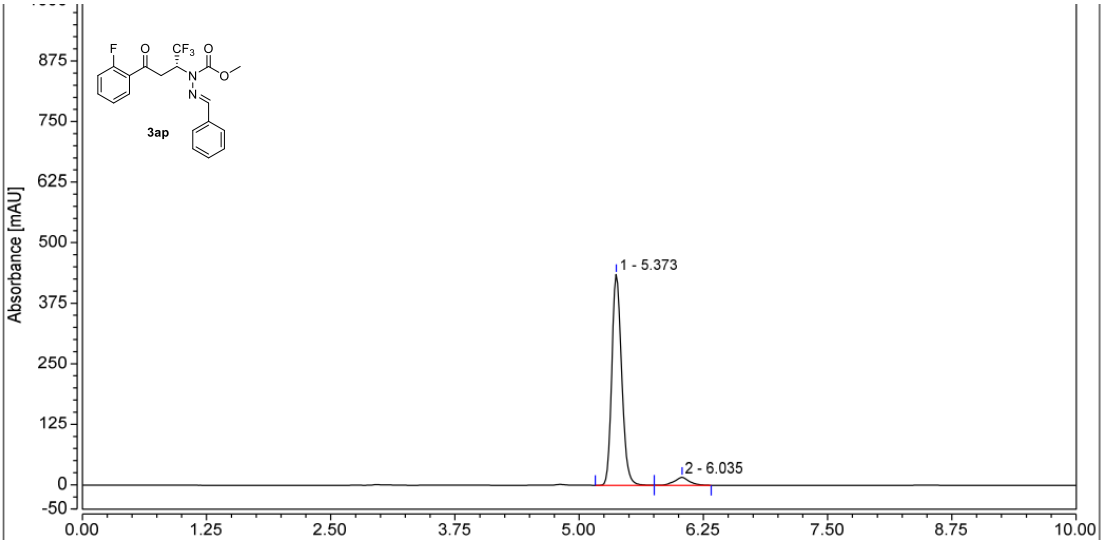
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.243	99.863	680.453	50.97	54.07	n.a.
2		7.553	96.071	578.040	49.03	45.93	n.a.
Total:			**195.934**	**1258.493**	**100.00**	**100.00**	



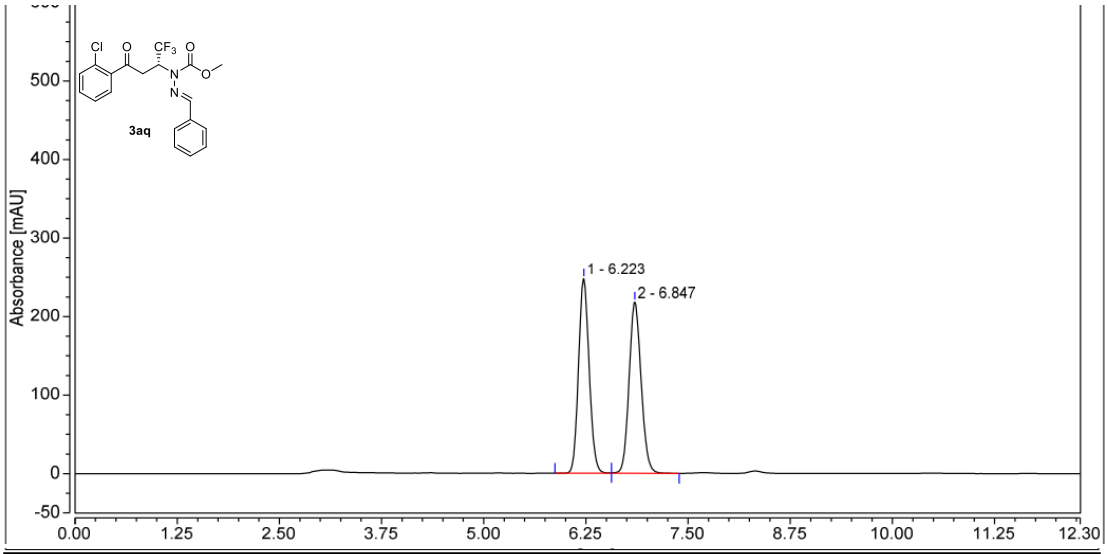
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.180	96.905	725.746	98.68	98.79	n.a.
2		7.407	1.294	8.853	1.32	1.21	n.a.
Total:			**98.199**	**734.599**	**100.00**	**100.00**	



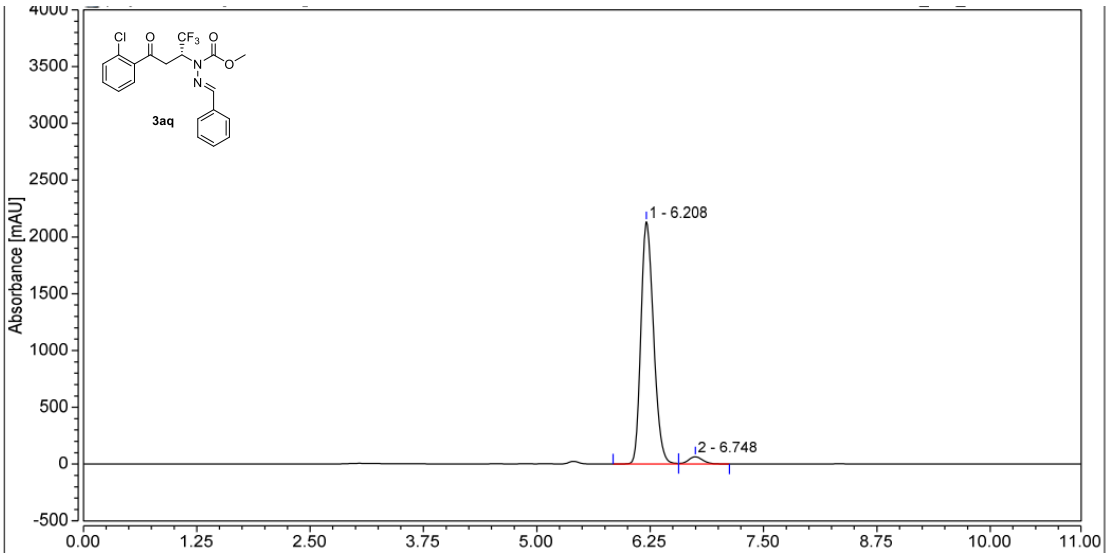
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.443	33.470	260.575	50.13	52.48	n.a.
2		6.107	33.301	235.932	49.87	47.52	n.a.
Total:			**66.771**	**496.507**	**100.00**	**100.00**	



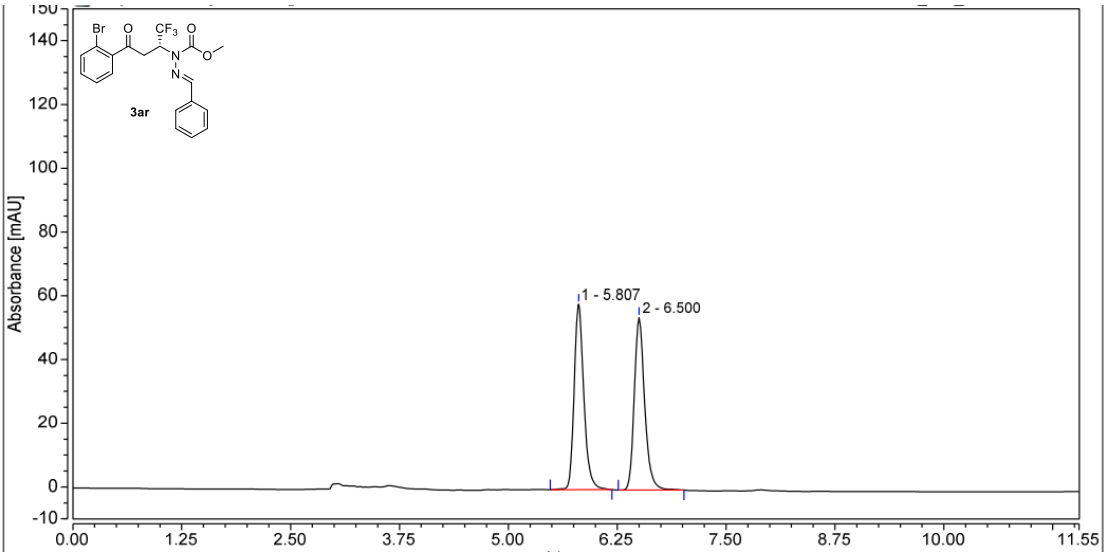
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.373	50.140	435.424	94.60	96.39	n.a.
2		6.035	2.863	16.325	5.40	3.61	n.a.
Total:			**53.003**	**451.749**	**100.00**	**100.00**	



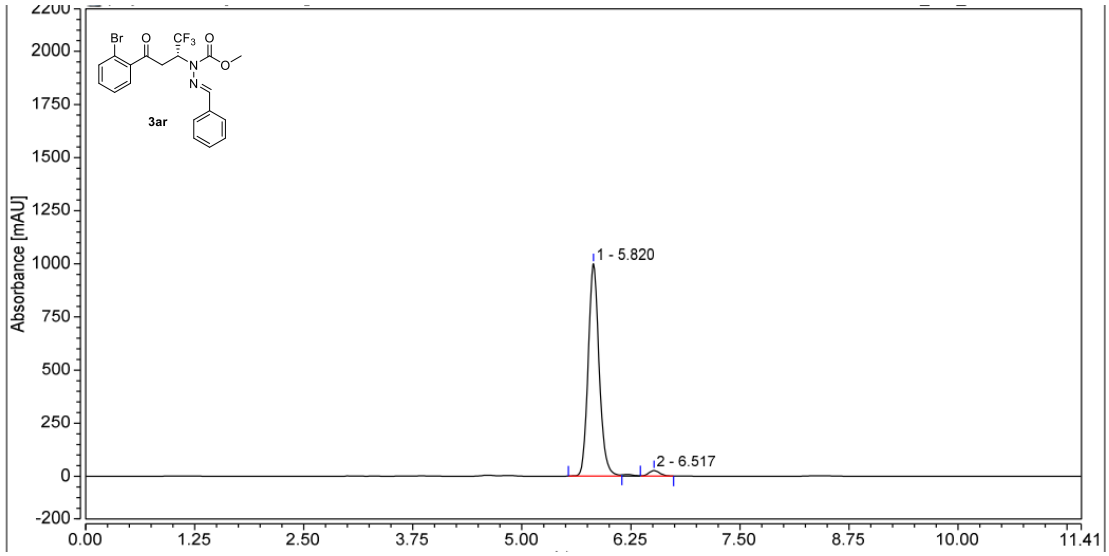
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.223	37.319	247.621	49.94	53.17	n.a.
2		6.847	37.415	218.055	50.06	46.83	n.a.
Total:			**74.734**	**465.676**	**100.00**	**100.00**	



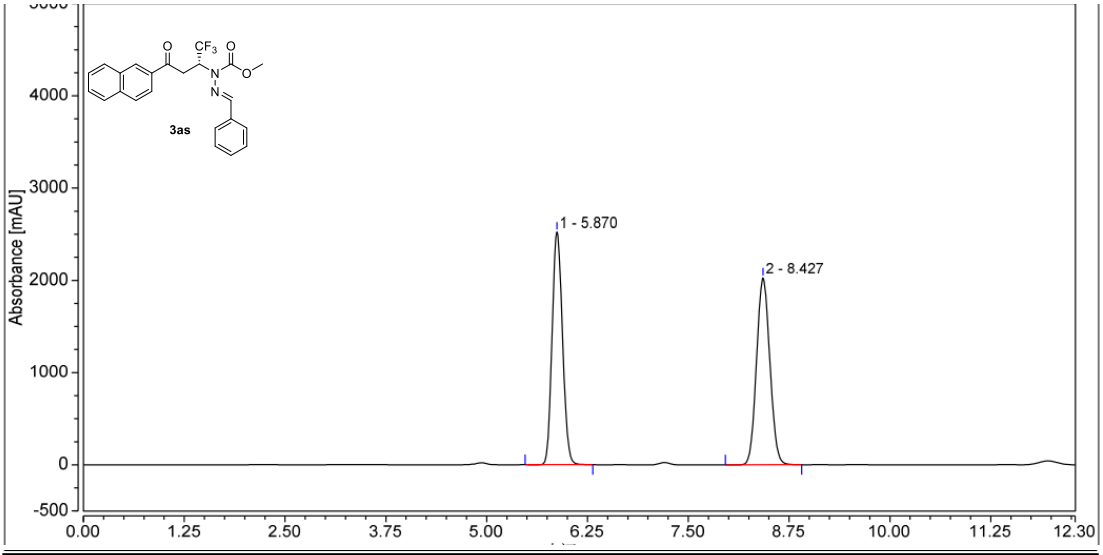
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.208	344.479	2132.262	96.79	97.13	n.a.
2		6.748	11.406	63.026	3.21	2.87	n.a.
Total:			**355.886**	**2195.288**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.807	7.531	58.193	49.97	51.78	n.a.
2		6.500	7.538	54.190	50.03	48.22	n.a.
Total:			**15.069**	**112.383**	**100.00**	**100.00**	

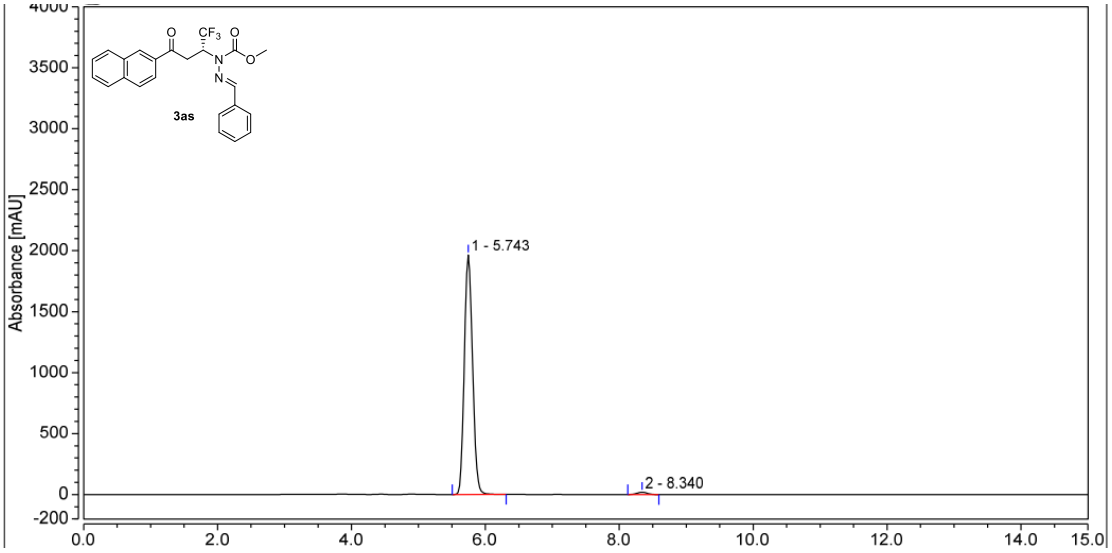


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.820	145.891	998.810	97.42	97.46	n.a.
2		6.517	3.867	26.055	2.58	2.54	n.a.
Total:			**149.758**	**1024.865**	**100.00**	**100.00**	



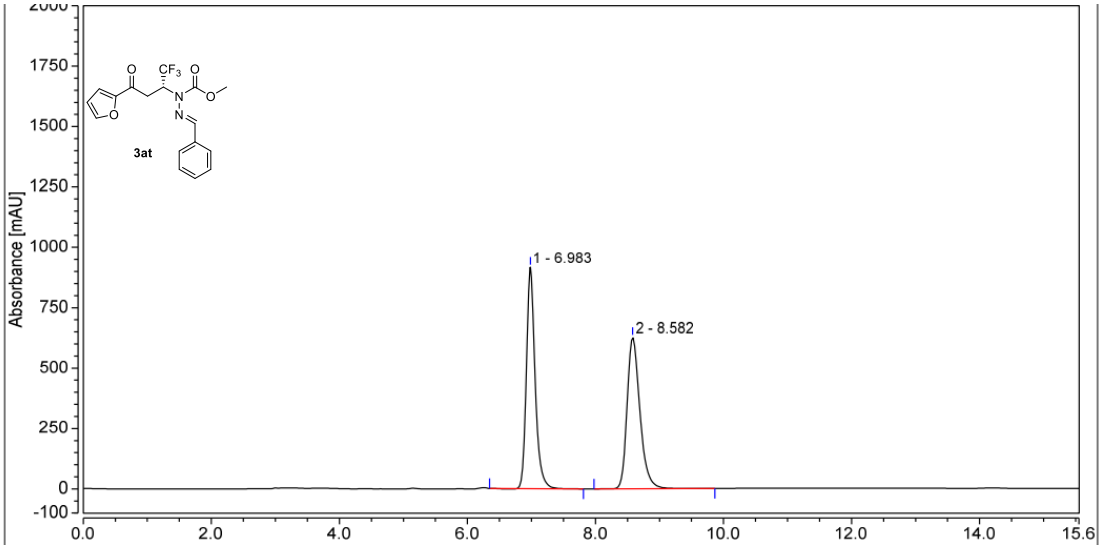
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.870	376.340	2521.603	49.23	55.45	n.a.
2		8.427	388.144	2025.979	50.77	44.55	n.a.
Total:			**764.484**	**4547.582**	**100.00**	**100.00**	



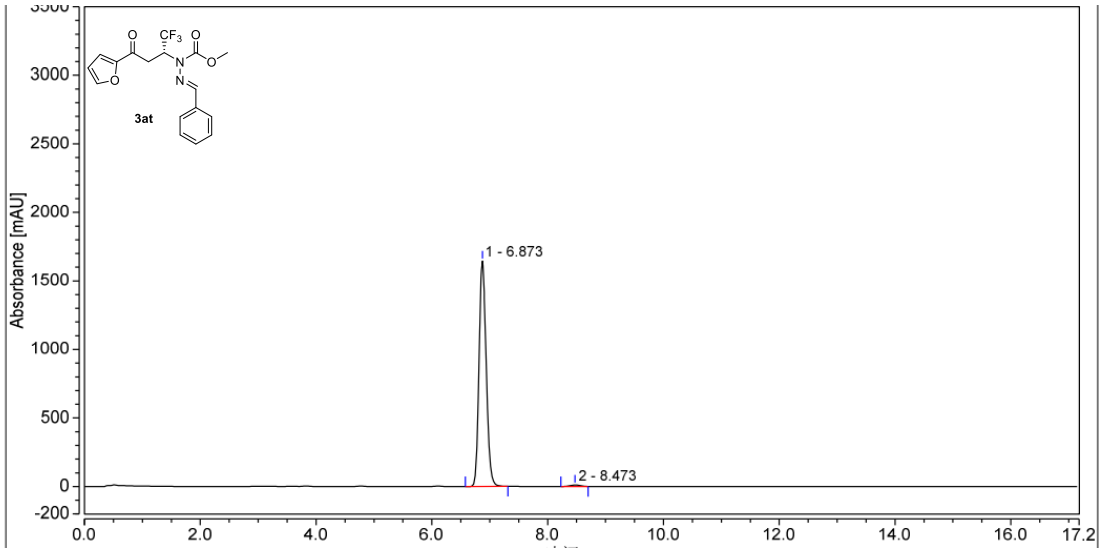
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.743	280.648	1964.751	98.79	99.02	n.a.
2		8.340	3.425	19.421	1.21	0.98	n.a.
Total:			**284.073**	**1984.173**	**100.00**	**100.00**	



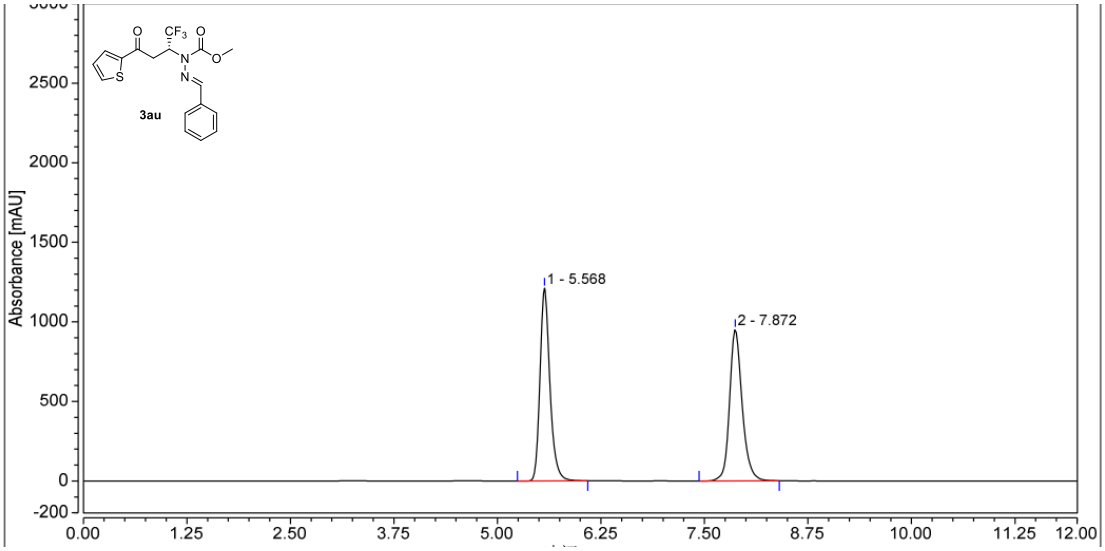
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.983	145.762	916.815	50.12	59.40	n.a.
2		8.582	145.048	626.570	49.88	40.60	n.a.
Total:			**290.810**	**1543.385**	**100.00**	**100.00**	



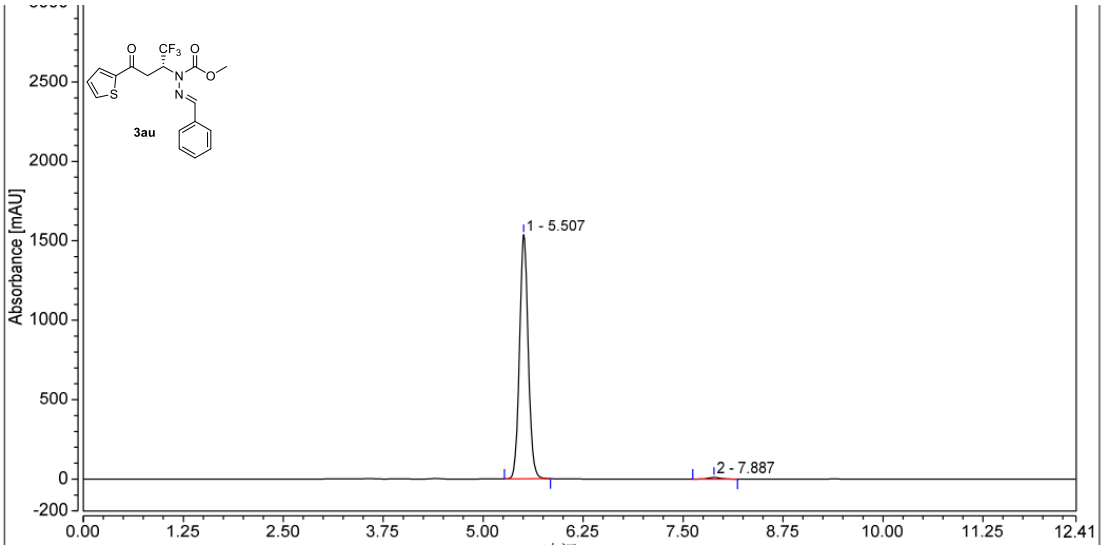
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.873	234.404	1644.048	99.05	99.31	n.a.
2		8.473	2.241	11.481	0.95	0.69	n.a.
Total:			**236.645**	**1655.529**	**100.00**	**100.00**	



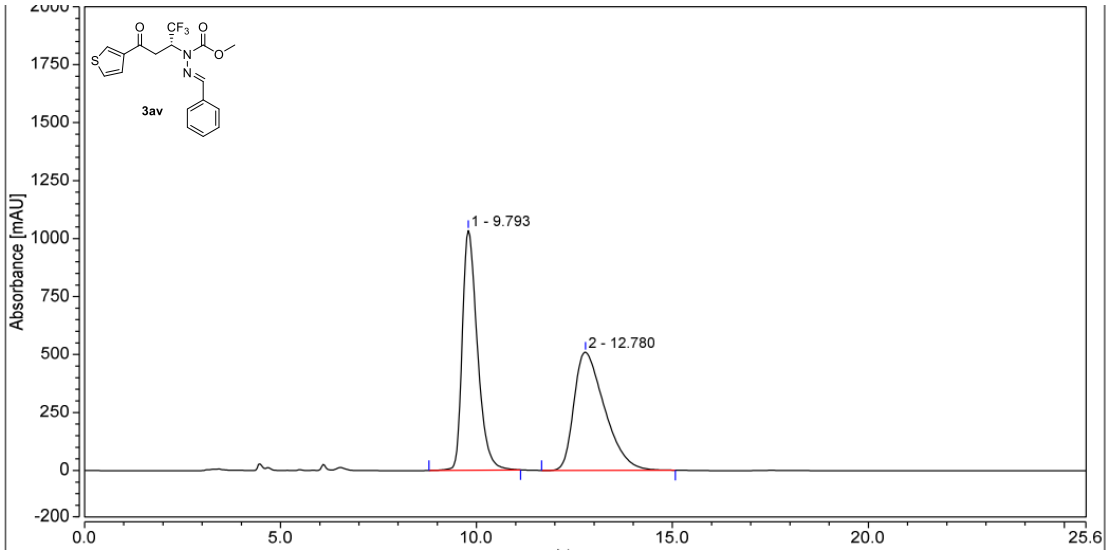
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.568	168.141	1211.268	50.02	56.01	n.a.
2		7.872	168.022	951.480	49.98	43.99	n.a.
Total:			**336.163**	**2162.748**	**100.00**	**100.00**	

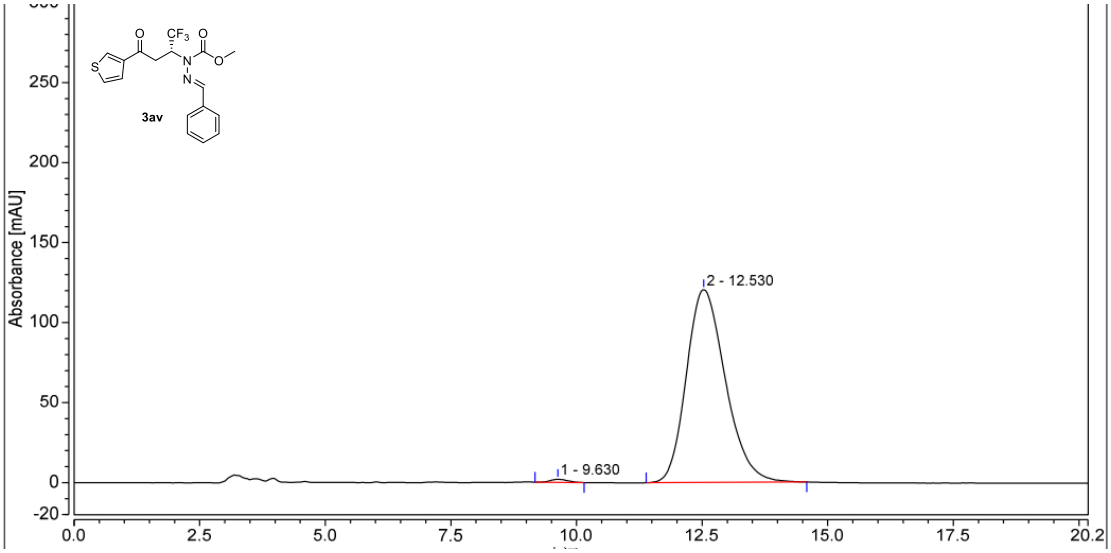


Integration Results

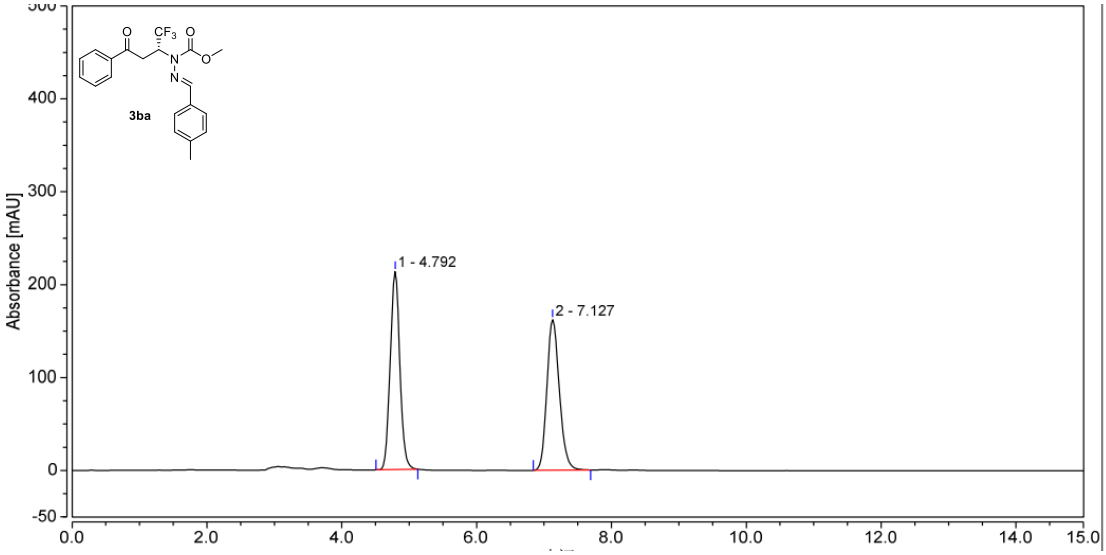
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.507	193.354	1536.690	99.01	99.30	n.a.
2		7.887	1.935	10.778	0.99	0.70	n.a.
Total:			**195.289**	**1547.468**	**100.00**	**100.00**	



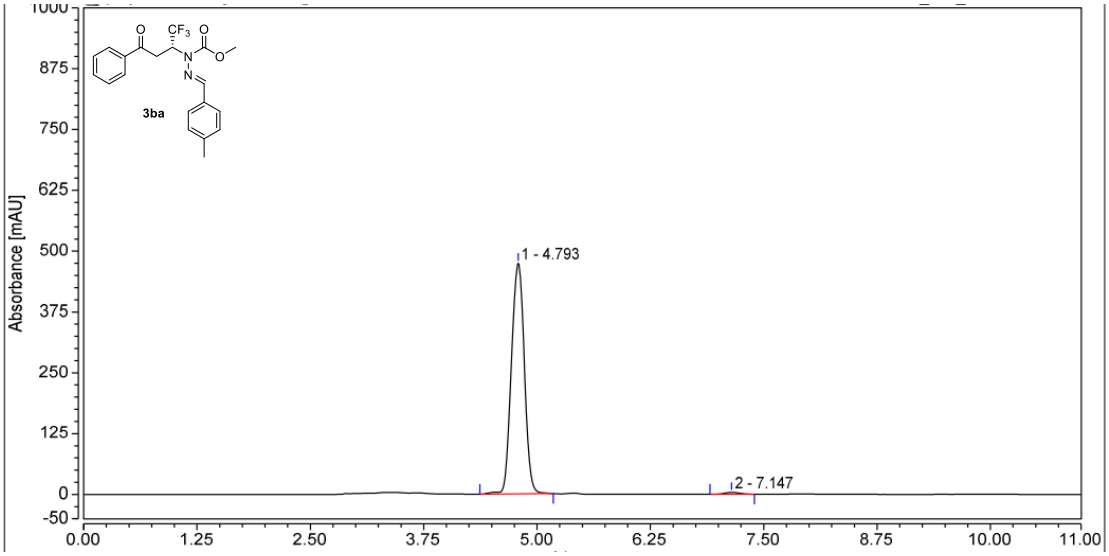
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.793	461.241	1033.374	50.05	66.96	n.a.
2		12.780	460.394	509.937	49.95	33.04	n.a.
Total:			**921.635**	**1543.311**	**100.00**	**100.00**	



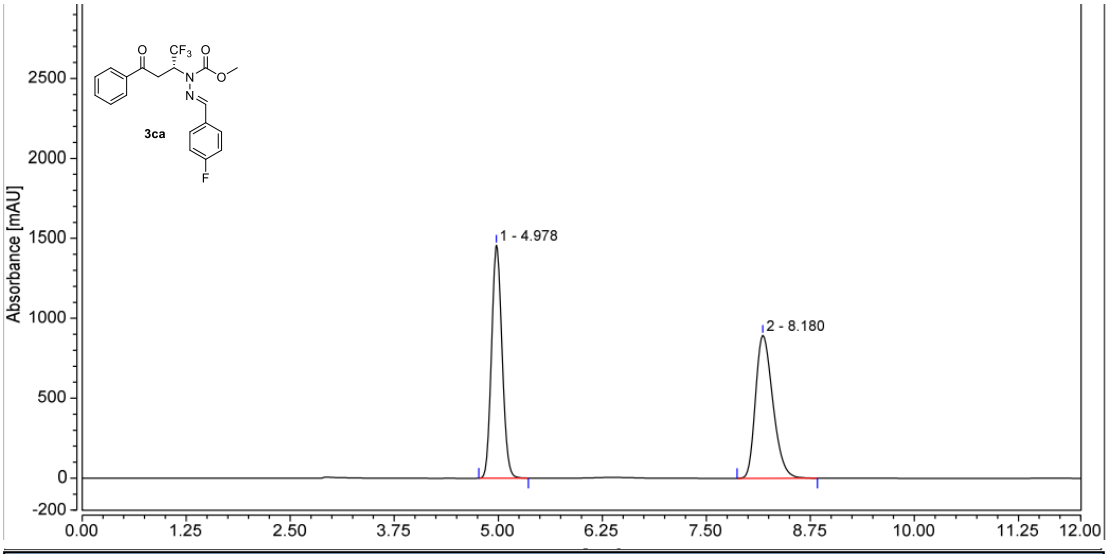
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.630	0.748	1.879	0.68	1.54	n.a.
2		12.530	108.625	120.427	99.32	98.46	n.a.
Total:			**109.373**	**122.306**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.792	35.249	213.114	50.44	56.81	n.a.
2		7.127	34.637	161.997	49.56	43.19	n.a.
Total:			**69.886**	**375.111**	**100.00**	**100.00**	

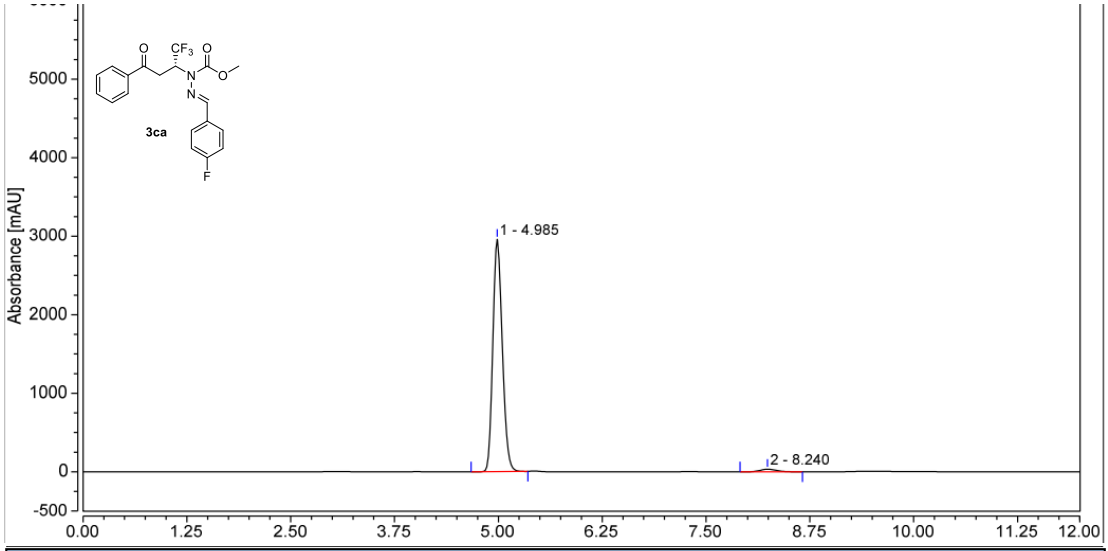


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.793	78.667	473.796	99.02	99.18	n.a.
2		7.147	0.780	3.929	0.98	0.82	n.a.
Total:			**79.447**	**477.724**	**100.00**	**100.00**	



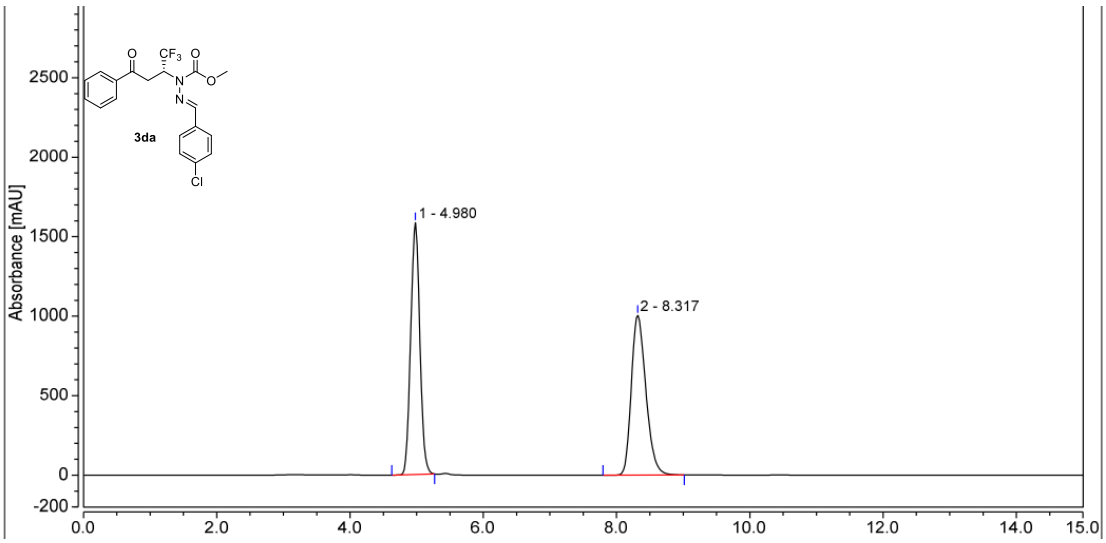
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.978	213.499	1458.010	49.64	61.97	n.a.
2		8.180	216.561	894.790	50.36	38.03	n.a.
Total:			**430.060**	**2352.800**	**100.00**	**100.00**	



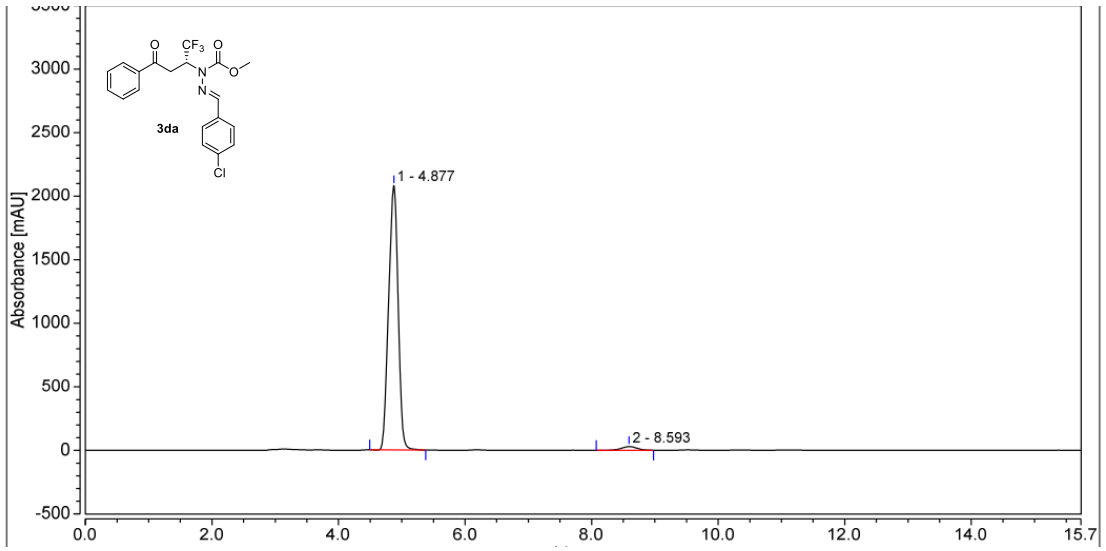
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.985	390.805	2957.487	98.11	98.92	n.a.
2		8.240	7.509	32.177	1.89	1.08	n.a.
Total:			**398.314**	**2989.663**	**100.00**	**100.00**	



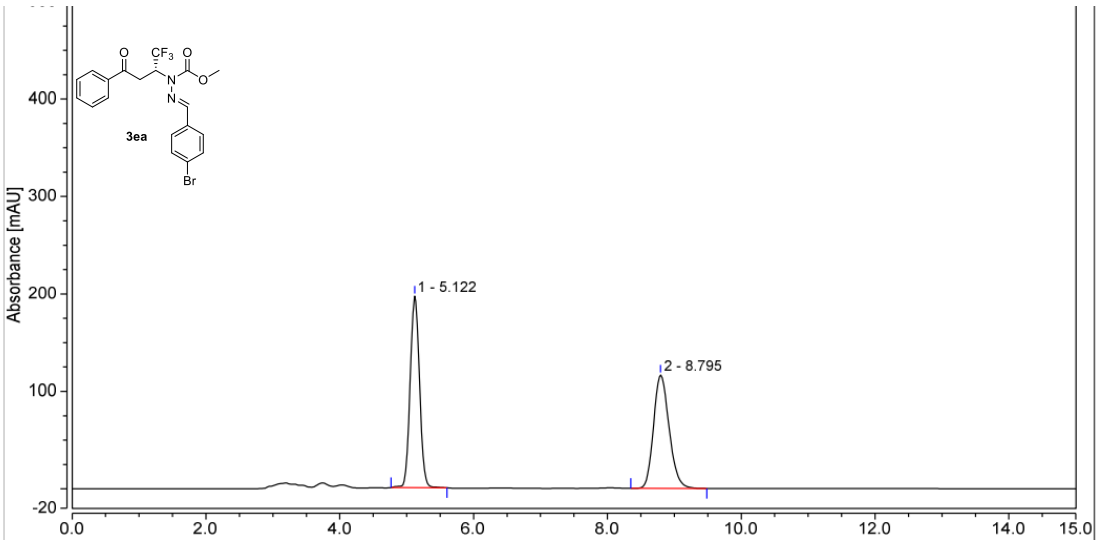
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.980	251.357	1583.268	49.69	61.17	n.a.
2		8.317	254.464	1004.882	50.31	38.83	n.a.
Total:			**505.821**	**2588.150**	**100.00**	**100.00**	

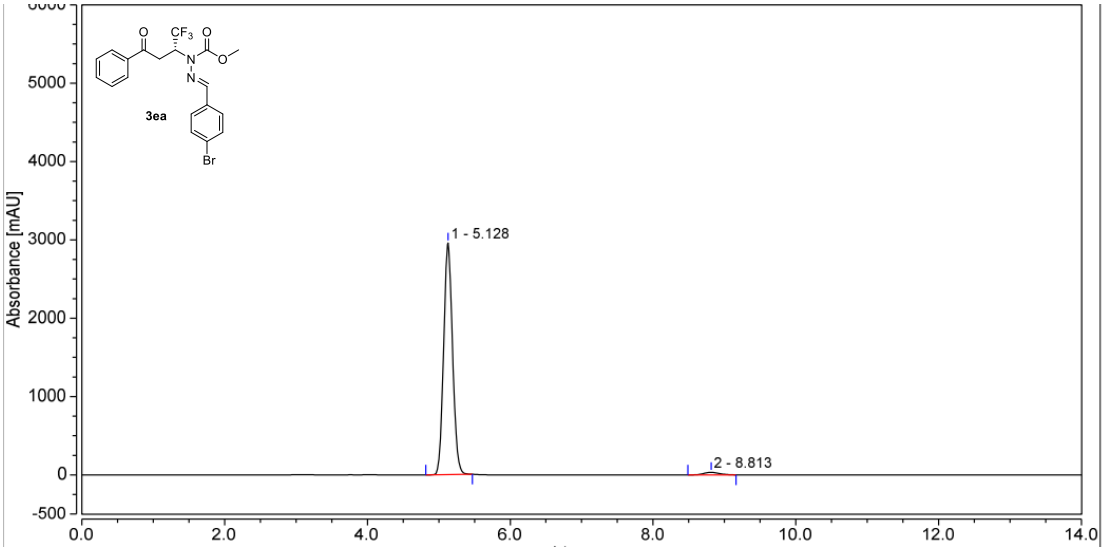


Integration Results

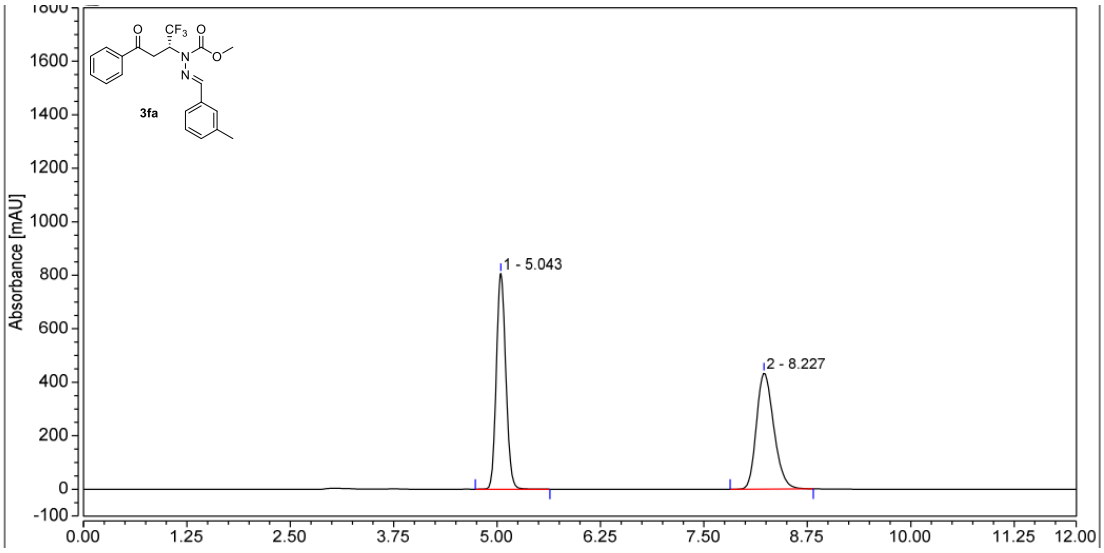
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.877	360.112	2081.281	97.78	98.64	n.a.
2		8.593	8.185	28.662	2.22	1.36	n.a.
Total:			**368.297**	**2109.943**	**100.00**	**100.00**	



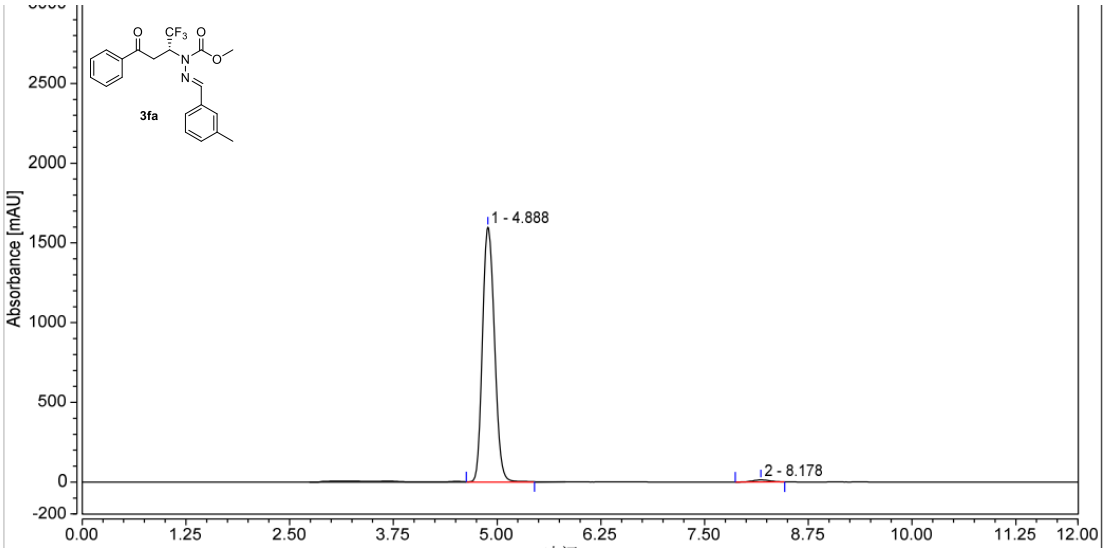
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.122	31.943	196.552	50.42	62.80	n.a.
2		8.795	31.407	116.423	49.58	37.20	n.a.
Total:			**63.350**	**312.975**	**100.00**	**100.00**	



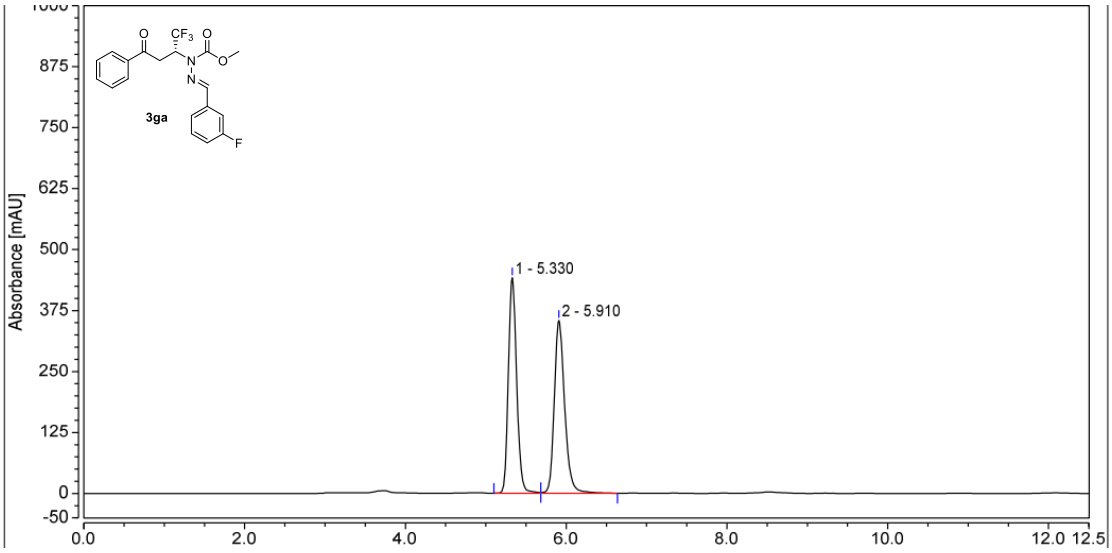
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.128	426.667	2956.789	98.08	98.92	n.a.
2		8.813	8.333	32.155	1.92	1.08	n.a.
Total:			**435.000**	**2988.944**	**100.00**	**100.00**	



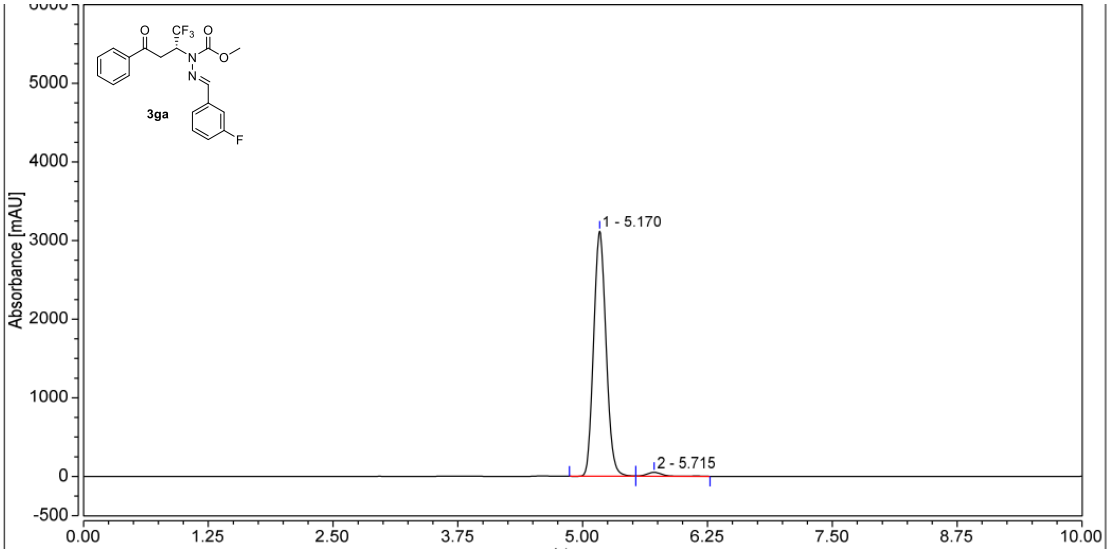
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.043	106.415	806.498	50.17	65.01	n.a.
2		8.227	105.715	434.042	49.83	34.99	n.a.
Total:			**212.130**	**1240.540**	**100.00**	**100.00**	



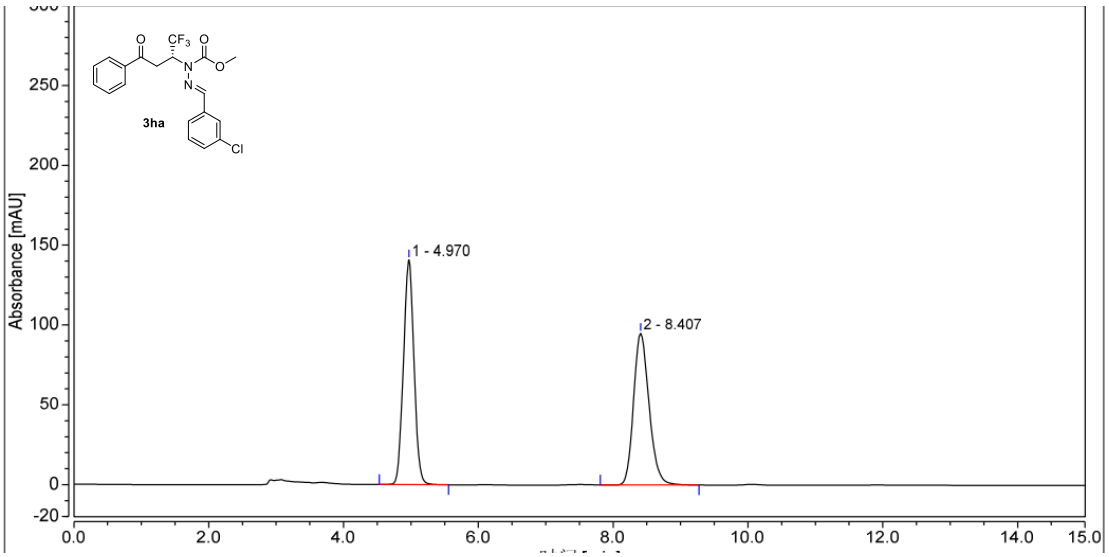
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.888	269.692	1599.618	98.88	99.20	n.a.
2		8.178	3.045	12.853	1.12	0.80	n.a.
Total:			**272.737**	**1612.471**	**100.00**	**100.00**	



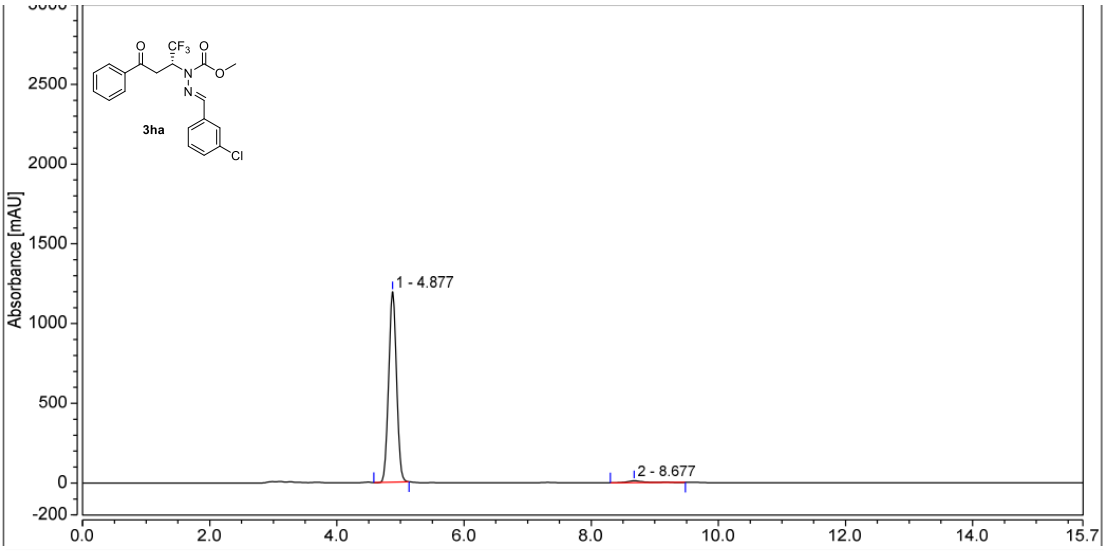
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.330	52.752	441.583	49.81	55.47	n.a.
2		5.910	53.153	354.465	50.19	44.53	n.a.
Total:			**105.905**	**796.048**	**100.00**	**100.00**	



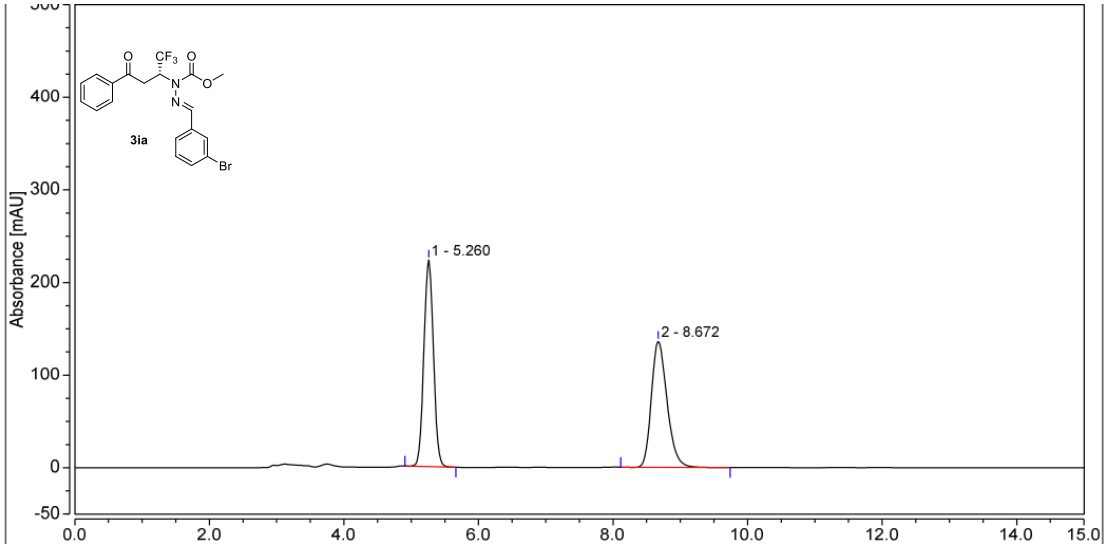
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.170	449.767	3118.352	97.99	98.40	n.a.
2		5.715	9.246	50.769	2.01	1.60	n.a.
Total:			**459.013**	**3169.121**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.970	25.546	140.704	50.23	59.71	n.a.
2		8.407	25.316	94.948	49.77	40.29	n.a.
Total:			**50.862**	**235.652**	**100.00**	**100.00**	

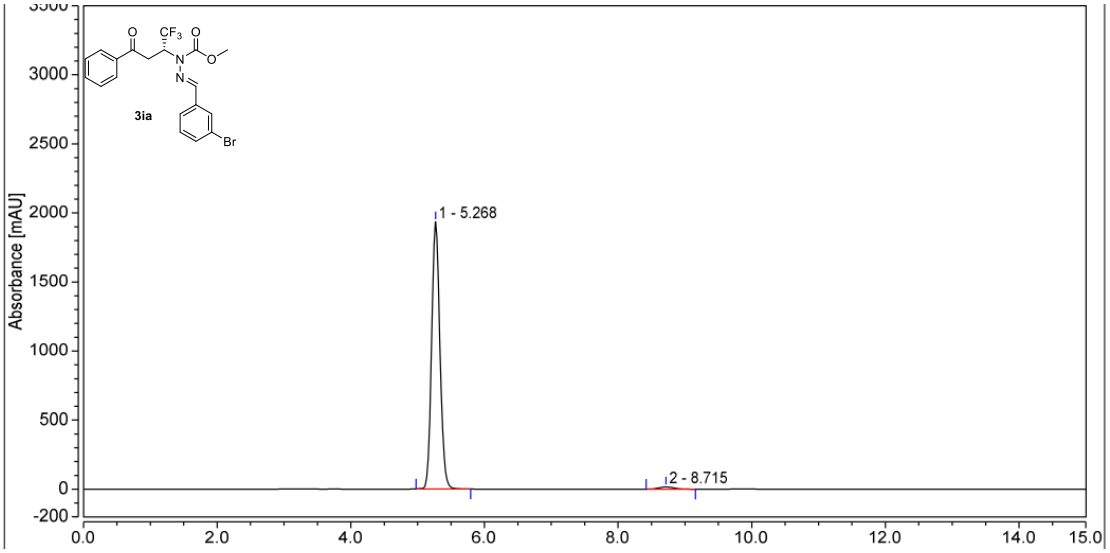


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.877	170.926	1194.219	98.07	99.05	n.a.
2		8.677	3.359	11.472	1.93	0.95	n.a.
Total:			**174.285**	**1205.691**	**100.00**	**100.00**	



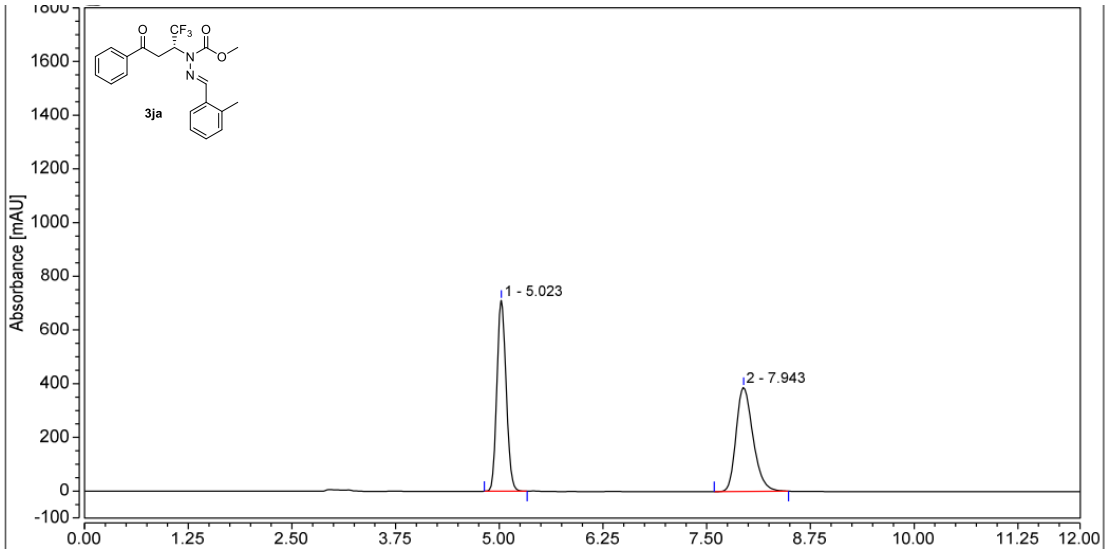
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.260	36.736	222.889	50.02	62.09	n.a.
2		8.672	36.708	136.073	49.98	37.91	n.a.
Total:			**73.444**	**358.962**	**100.00**	**100.00**	

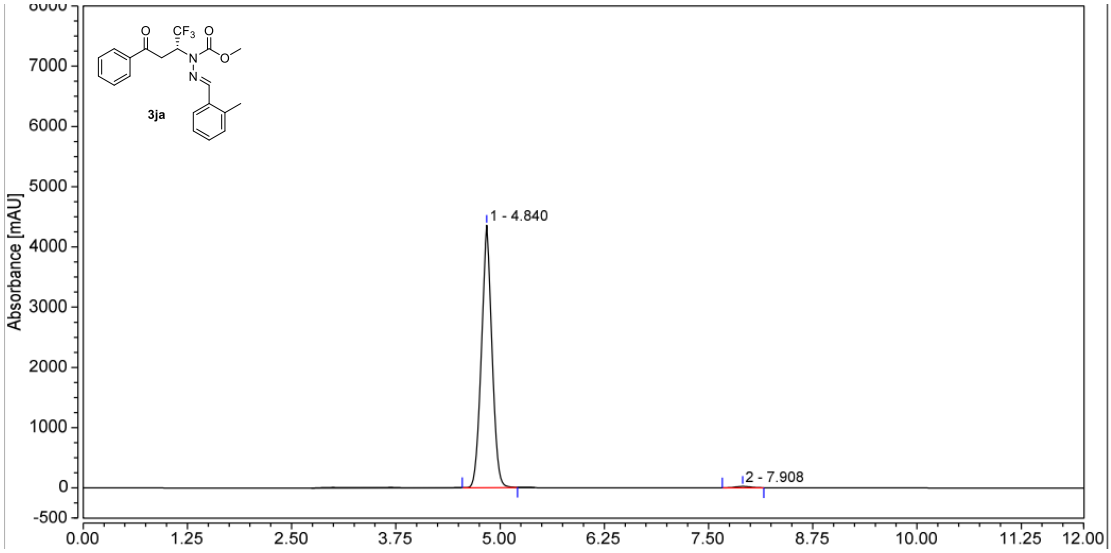


Integration Results

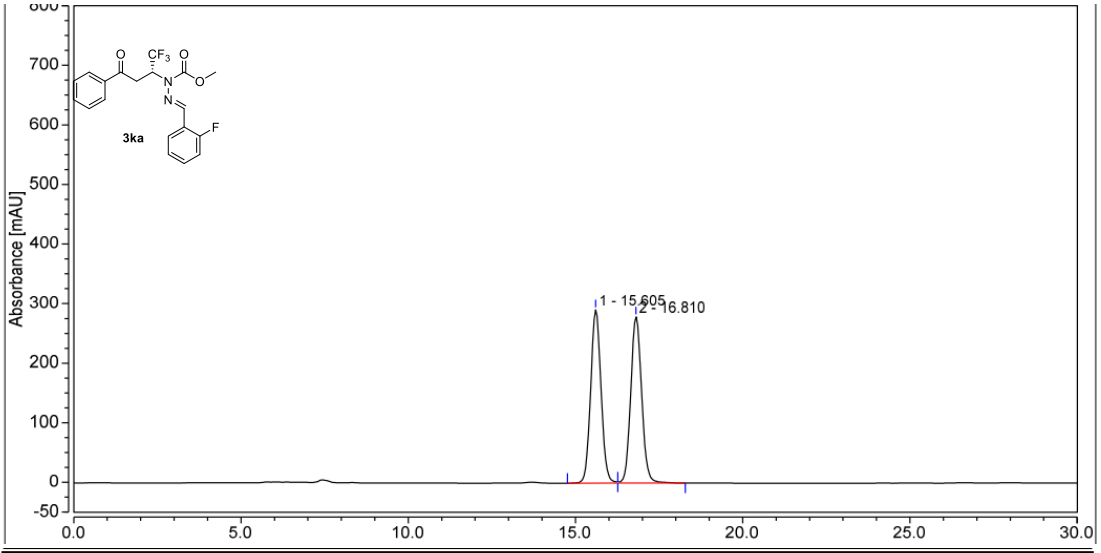
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.268	278.883	1933.491	98.55	99.20	n.a.
2		8.715	4.101	15.506	1.45	0.80	n.a.
Total:			**282.984**	**1948.996**	**100.00**	**100.00**	



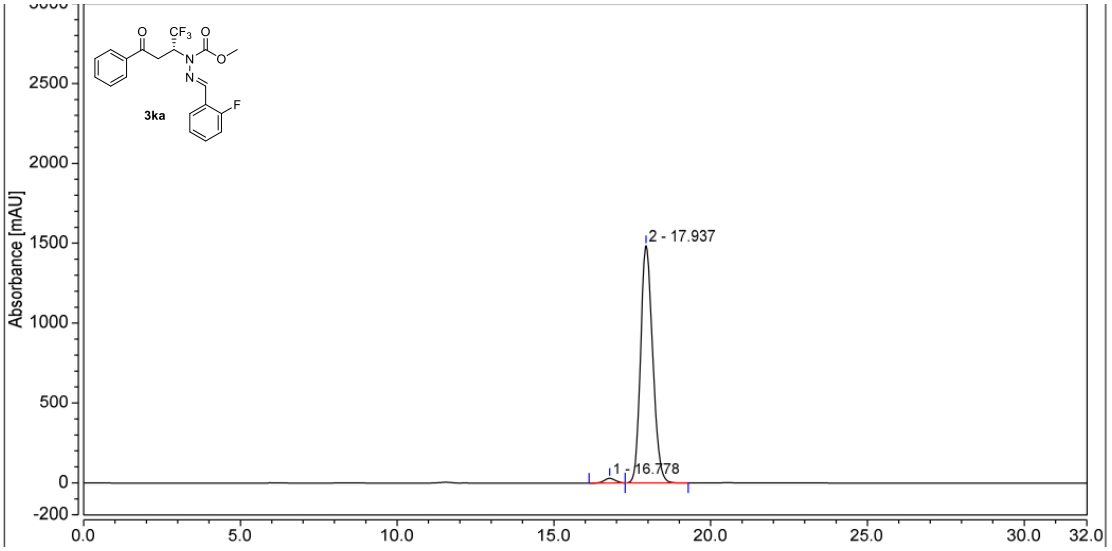
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.023	91.567	710.554	50.02	64.73	n.a.
2		7.943	91.478	387.190	49.98	35.27	n.a.
Total:			**183.045**	**1097.744**	**100.00**	**100.00**	



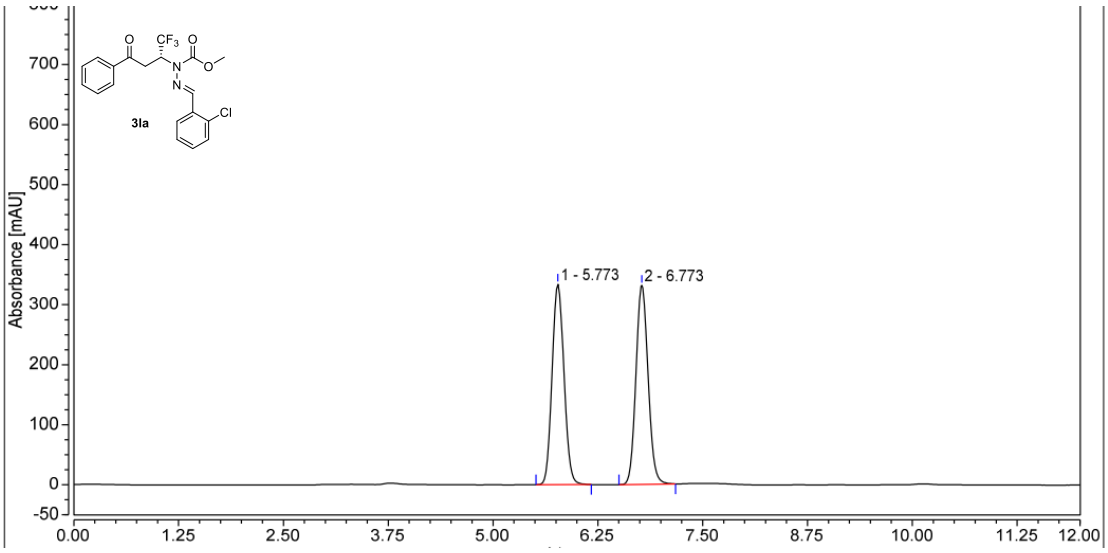
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.840	634.168	4356.731	99.21	99.47	n.a.
2		7.908	5.051	23.380	0.79	0.53	n.a.
Total:			**639.218**	**4380.111**	**100.00**	**100.00**	



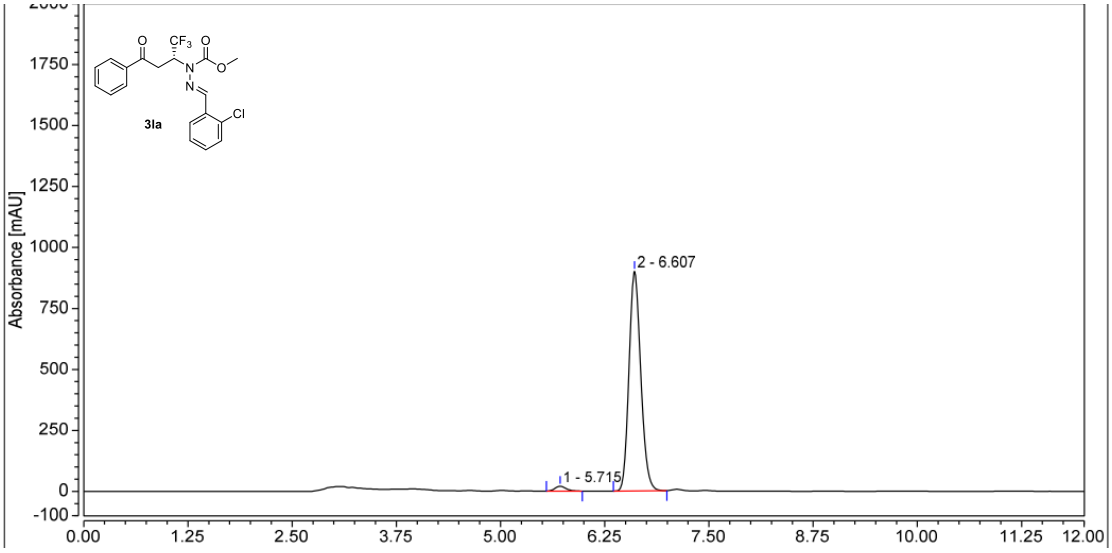
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.605	104.864	291.091	49.73	51.04	n.a.
2		16.810	106.016	279.229	50.27	48.96	n.a.
Total:			**210.880**	**570.320**	**100.00**	**100.00**	



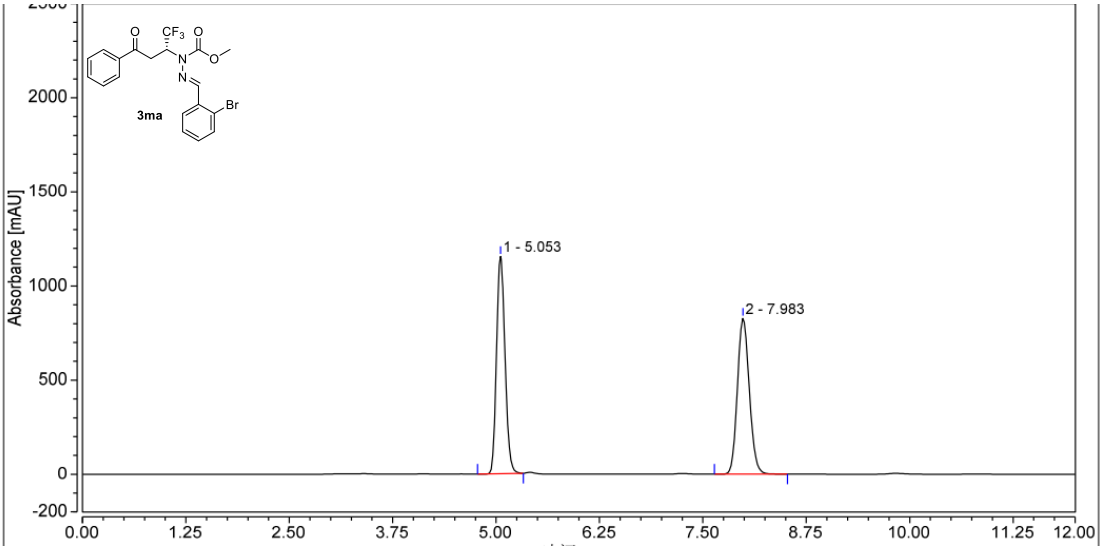
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.778	12.113	29.355	1.80	1.94	n.a.
2		17.937	662.532	1485.587	98.20	98.06	n.a.
Total:			**674.645**	**1514.943**	**100.00**	**100.00**	



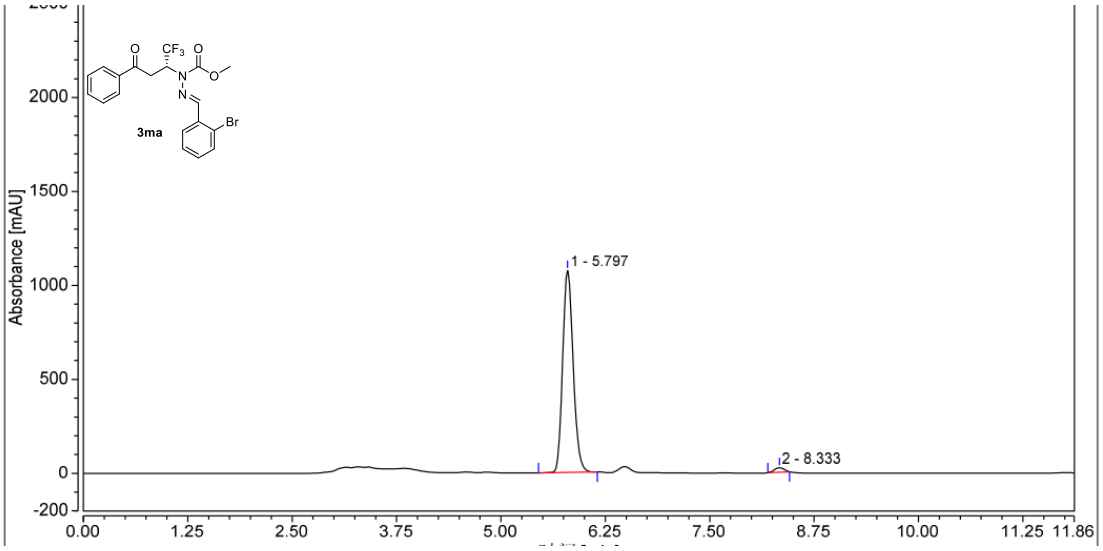
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.773	54.873	334.295	49.80	50.20	n.a.
2		6.773	55.321	331.691	50.20	49.80	n.a.
Total:			**110.194**	**665.986**	**100.00**	**100.00**	



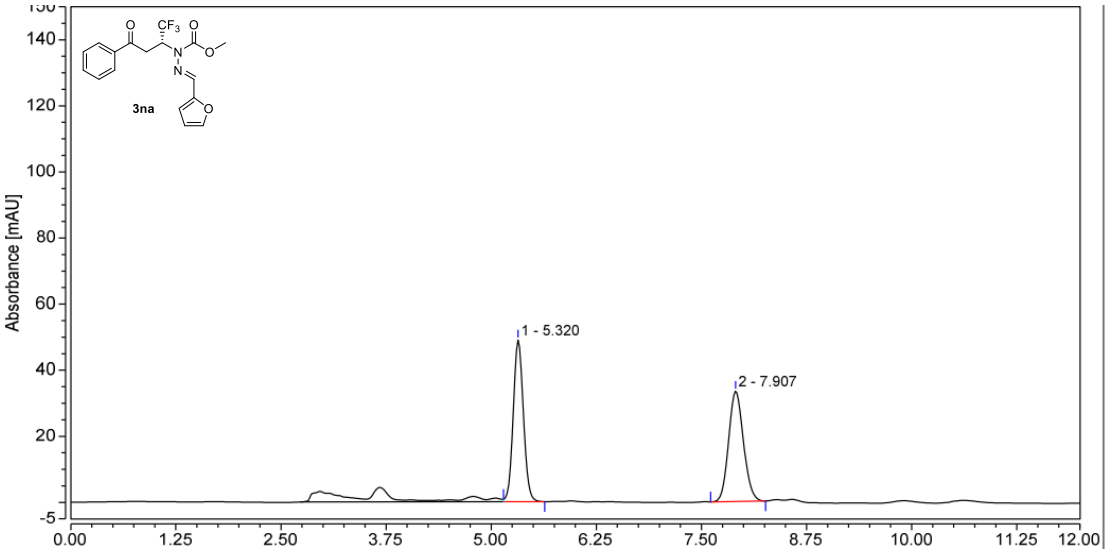
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.715	3.098	20.016	2.06	2.17	n.a.
2		6.607	147.429	900.520	97.94	97.83	n.a.
Total:			**150.527**	**920.536**	**100.00**	**100.00**	



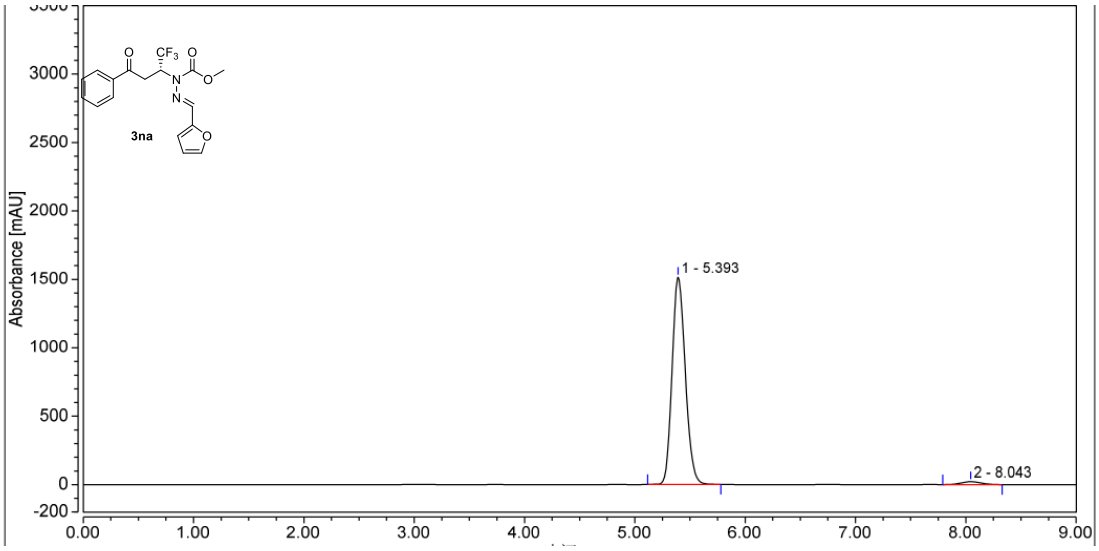
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.053	136.262	1154.533	49.69	58.22	n.a.
2		7.983	137.973	828.489	50.31	41.78	n.a.
Total:			**274.236**	**1983.022**	**100.00**	**100.00**	



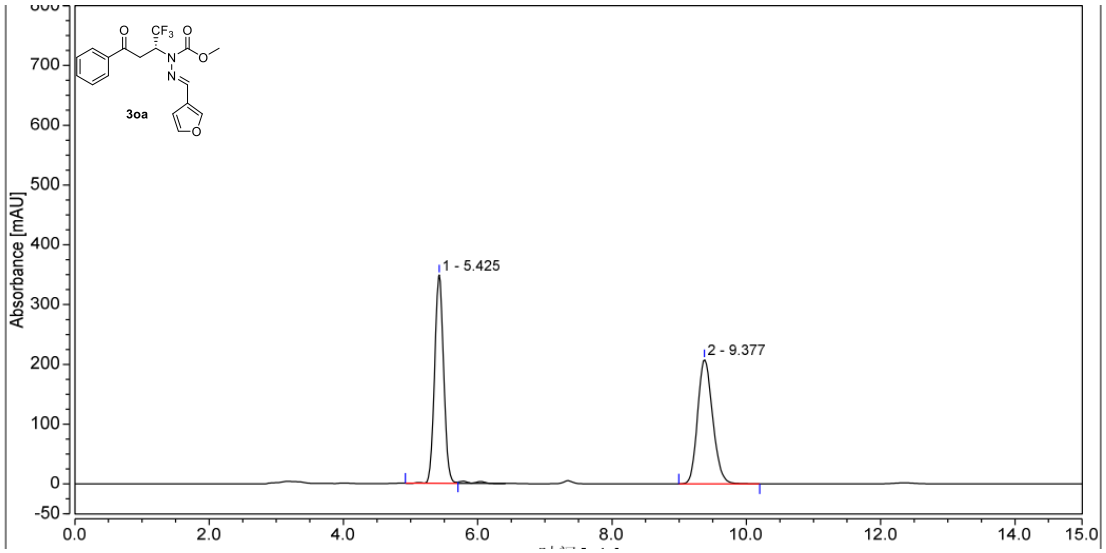
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.797	157.219	1073.540	98.00	97.82	n.a.
2		8.333	3.216	23.879	2.00	2.18	n.a.
Total:			**160.436**	**1097.418**	**100.00**	**100.00**	



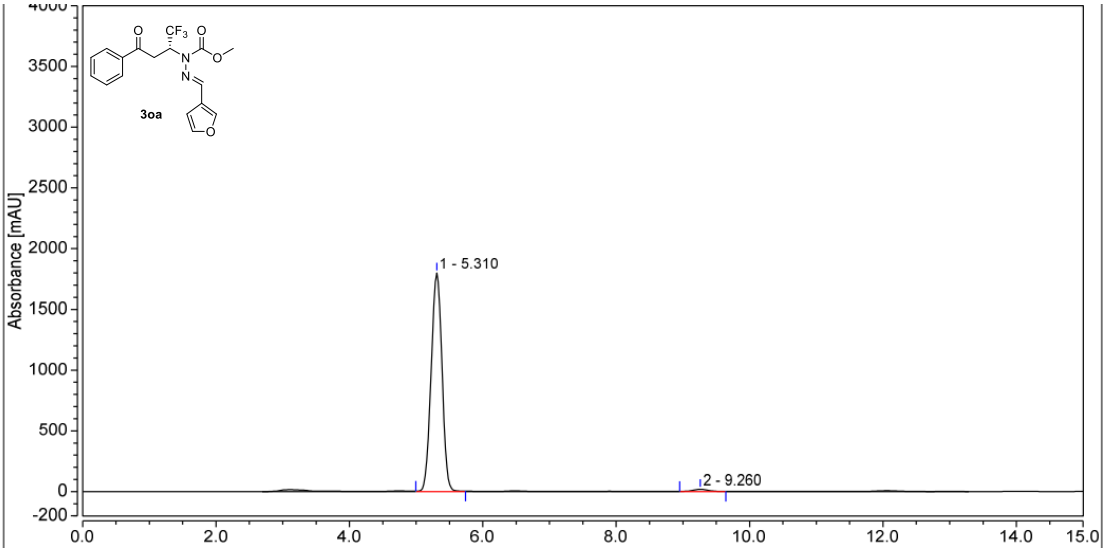
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.320	6.937	48.951	50.31	59.46	n.a.
2		7.907	6.851	33.371	49.69	40.54	n.a.
Total:			**13.788**	**82.322**	**100.00**	**100.00**	



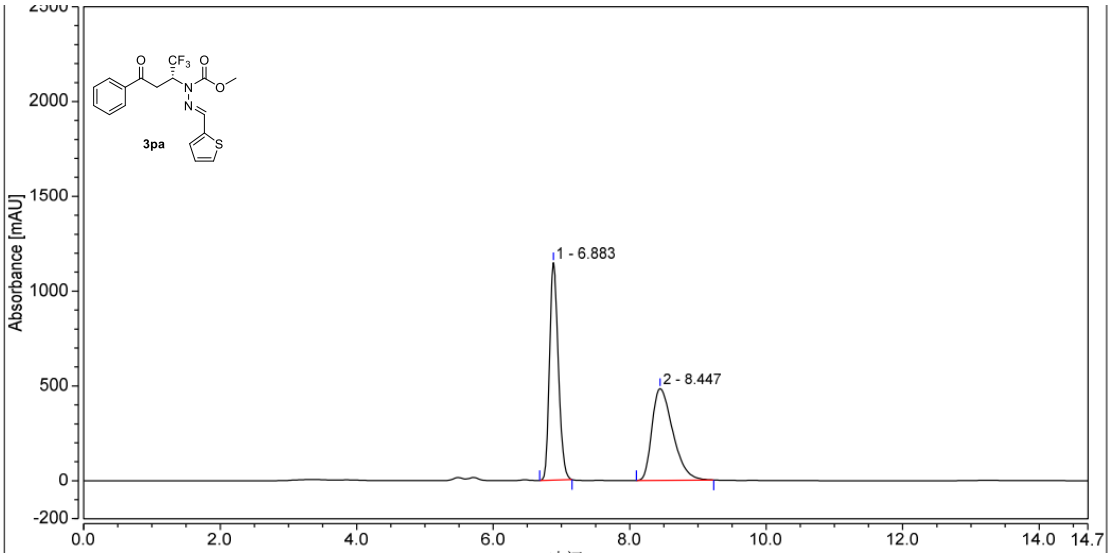
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.393	210.293	1514.539	97.96	98.61	n.a.
2		8.043	4.383	21.416	2.04	1.39	n.a.
Total:			**214.676**	**1535.955**	**100.00**	**100.00**	



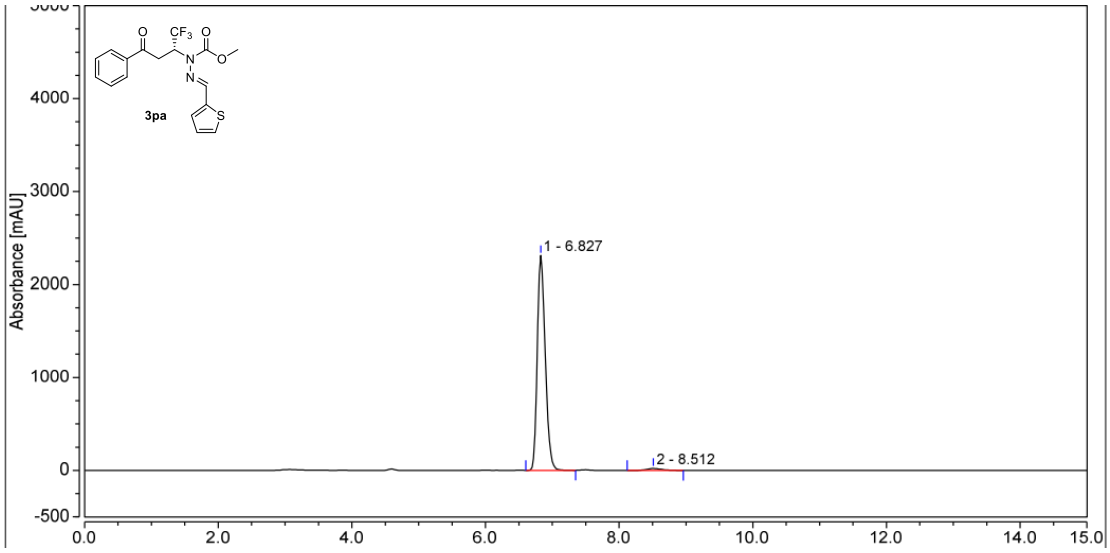
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.425	54.109	348.470	49.99	62.63	n.a.
2		9.377	54.121	207.884	50.01	37.37	n.a.
Total:			**108.230**	**556.354**	**100.00**	**100.00**	



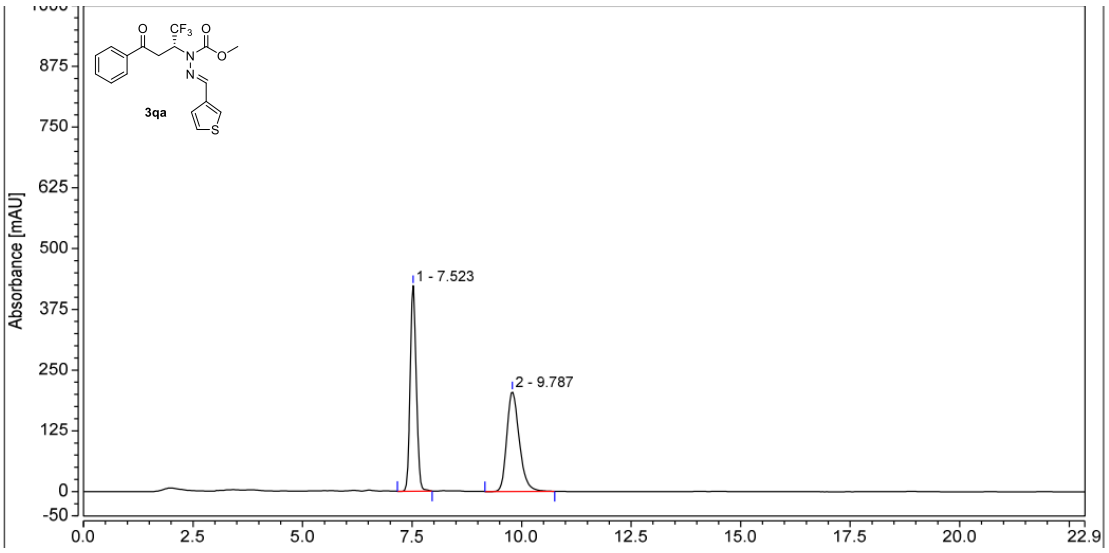
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.310	338.807	1799.607	98.52	99.00	n.a.
2		9.260	5.101	18.253	1.48	1.00	n.a.
Total:			**343.908**	**1817.860**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.883	170.554	1147.145	49.87	70.29	n.a.
2		8.447	171.413	484.958	50.13	29.71	n.a.
Total:			**341.967**	**1632.102**	**100.00**	**100.00**	

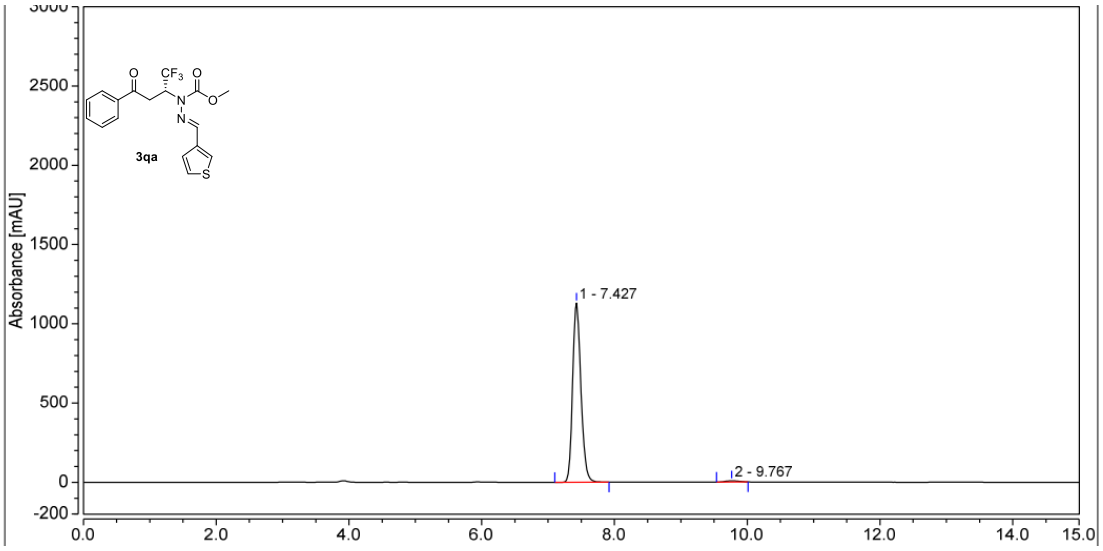


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.827	319.541	2311.499	98.32	99.12	n.a.
2		8.512	5.466	20.448	1.68	0.88	n.a.
Total:			**325.007**	**2331.947**	**100.00**	**100.00**	



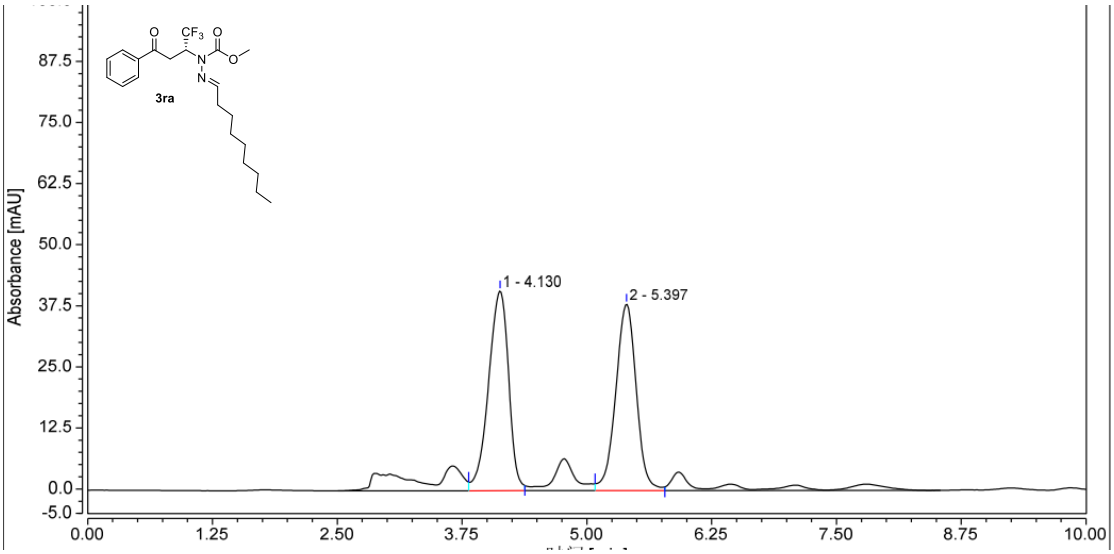
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.523	68.223	423.136	50.20	67.33	n.a.
2		9.787	67.673	205.283	49.80	32.67	n.a.
Total:			**135.896**	**628.419**	**100.00**	**100.00**	

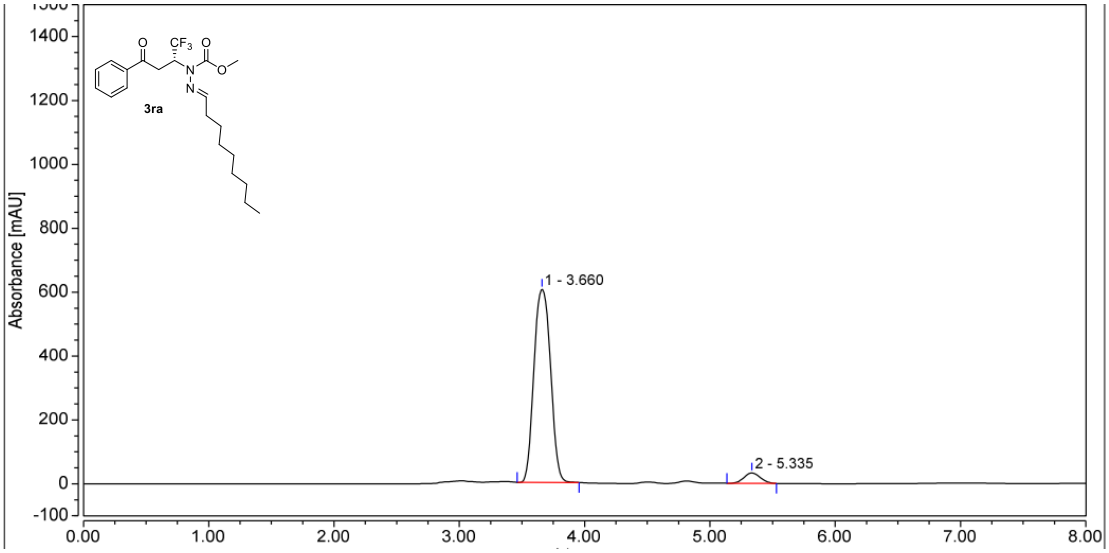


Integration Results

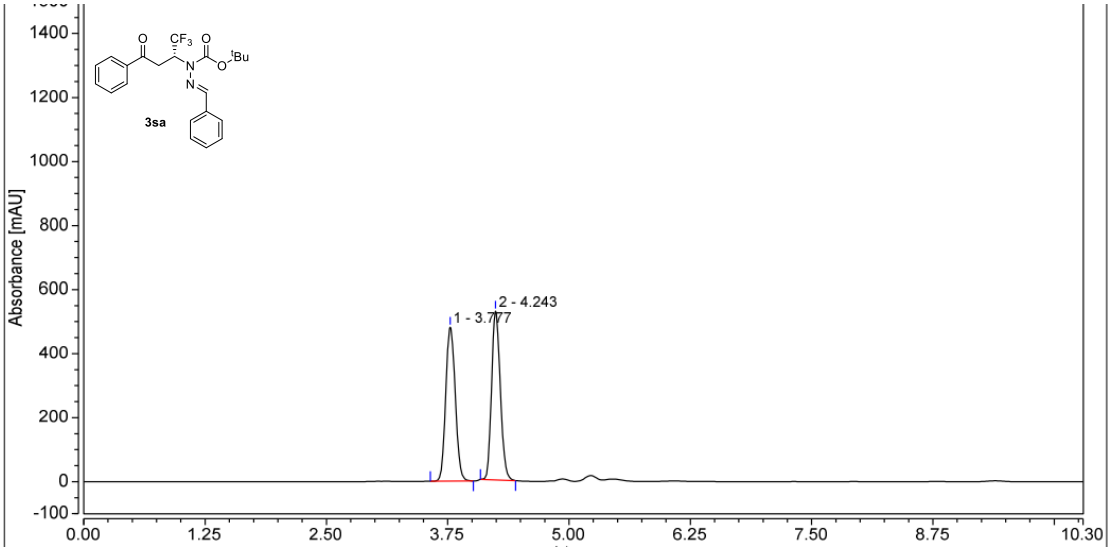
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.427	164.256	1131.054	98.90	99.33	n.a.
2		9.767	1.822	7.681	1.10	0.67	n.a.
Total:			**166.077**	**1138.735**	**100.00**	**100.00**	



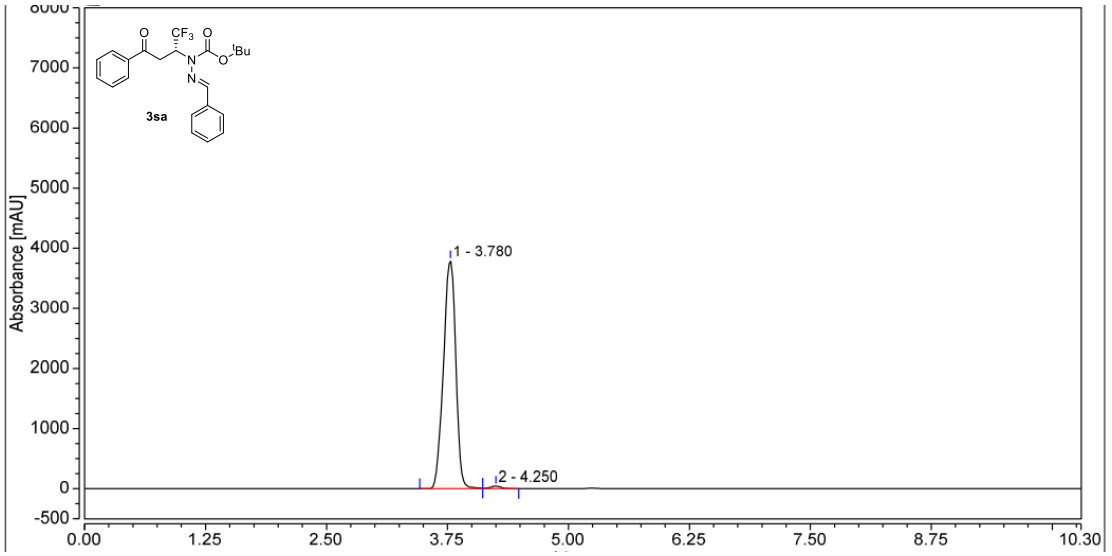
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.130	9.531	40.892	51.10	51.72	n.a.
2		5.397	9.119	38.173	48.90	48.28	n.a.
Total:			**18.650**	**79.065**	**100.00**	**100.00**	



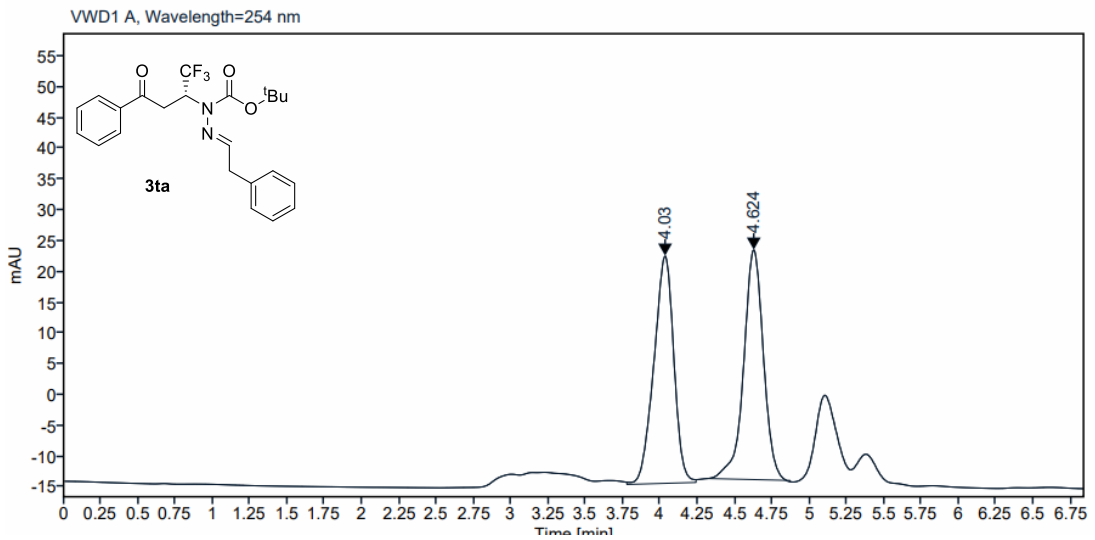
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.660	93.161	605.274	95.01	94.90	n.a.
2		5.335	4.894	32.529	4.99	5.10	n.a.
Total:			**98.055**	**637.804**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.777	54.995	481.340	50.13	47.72	n.a.
2		4.243	54.717	527.415	49.87	52.28	n.a.
Total:			**109.713**	**1008.755**	**100.00**	**100.00**	

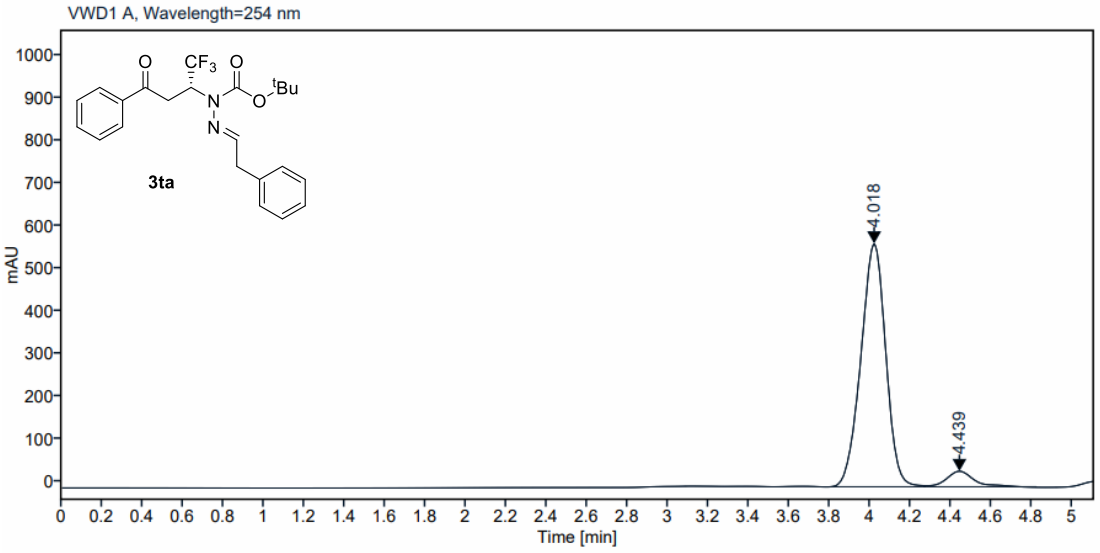


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.780	562.036	3790.156	99.04	98.90	n.a.
2		4.250	5.422	42.059	0.96	1.10	n.a.
Total:			**567.458**	**3832.214**	**100.00**	**100.00**	



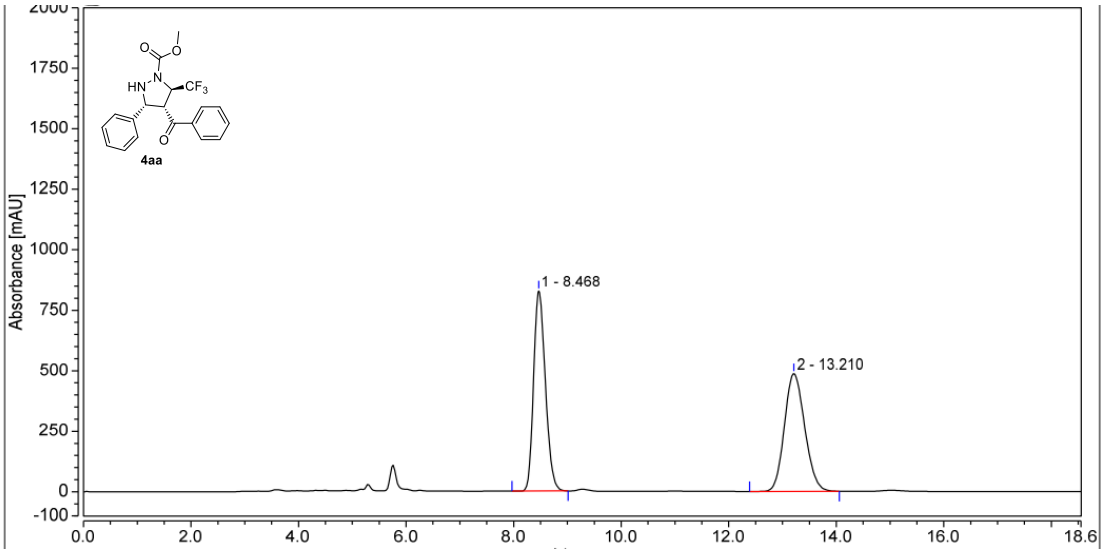
Signal: VWD1 A, Wavelength=254 nm

RT [min]	Area	Height	Area%
4.030	343.2620	36.9901	49.9094
4.624	344.5086	37.3554	50.0906
Sum	687.7706		

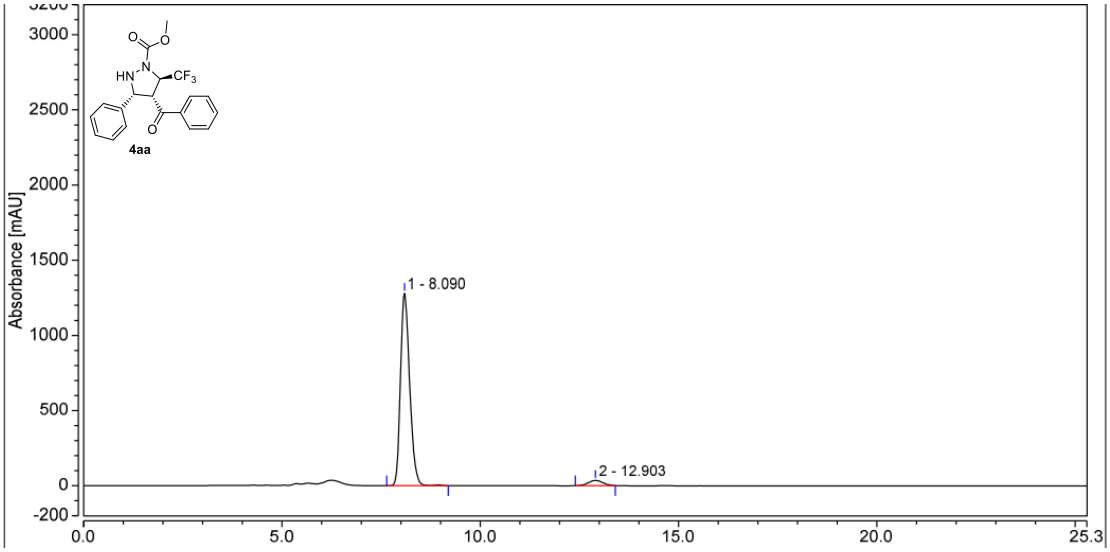


Signal: VWD1 A, Wavelength=254 nm

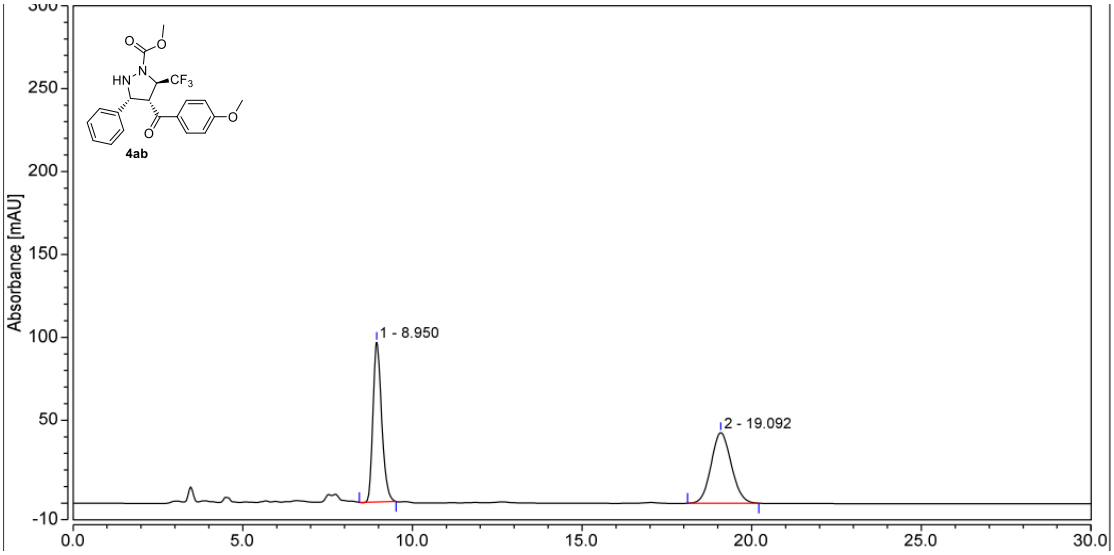
RT [min]	Area	Height	Area%
4.018	4886.3584	571.9642	93.4804
4.439	340.7892	36.3758	6.5196
Sum	5227.1476		



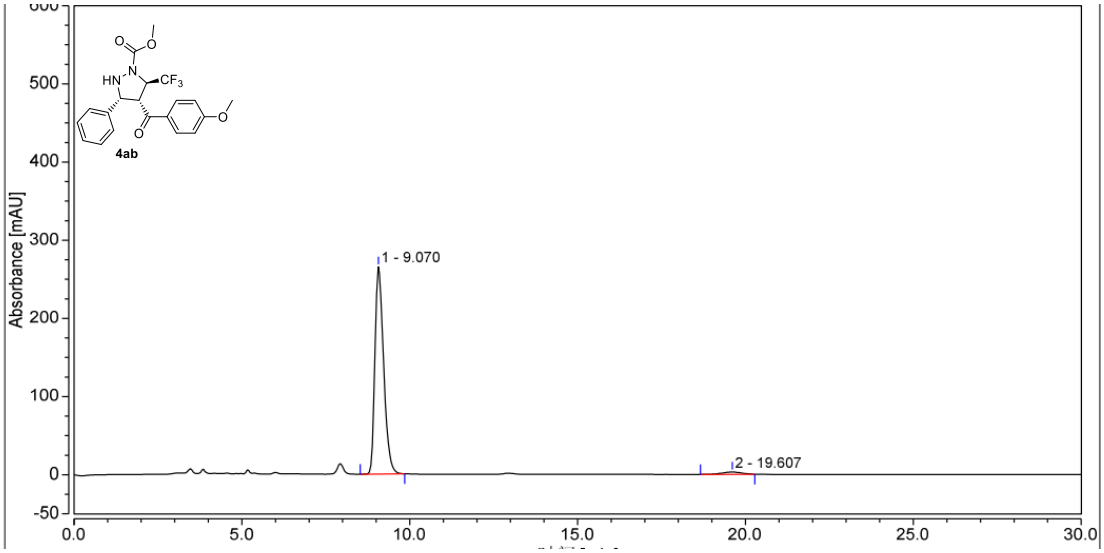
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.468	209.935	827.023	49.62	62.94	n.a.
2		13.210	213.139	486.875	50.38	37.06	n.a.
Total:			**423.074**	**1313.898**	**100.00**	**100.00**	



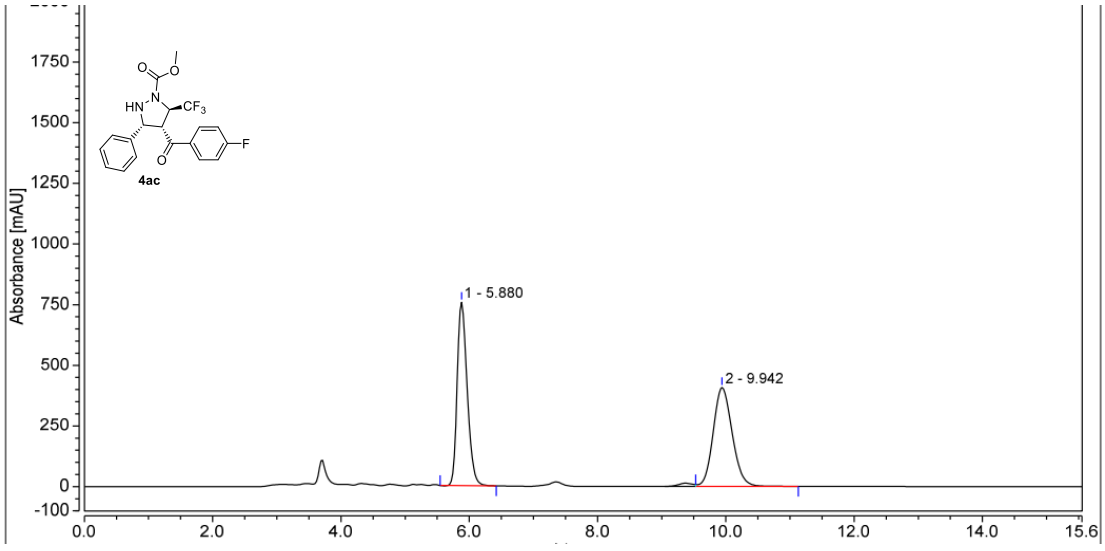
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.090	345.079	1280.025	95.82	97.34	n.a.
2		12.903	15.035	34.972	4.18	2.66	n.a.
Total:			**360.114**	**1314.996**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.950	28.585	96.259	49.33	69.32	n.a.
2		19.092	29.360	42.610	50.67	30.68	n.a.
Total:			**57.944**	**138.869**	**100.00**	**100.00**	

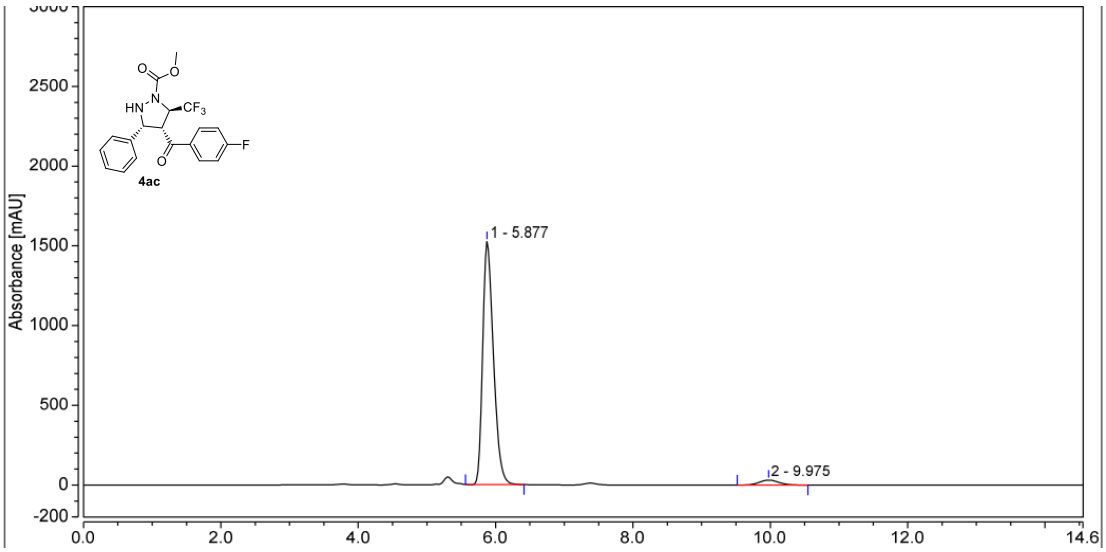


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.070	79.893	265.126	97.63	98.92	n.a.
2		19.607	1.937	2.888	2.37	1.08	n.a.
Total:			**81.830**	**268.014**	**100.00**	**100.00**	



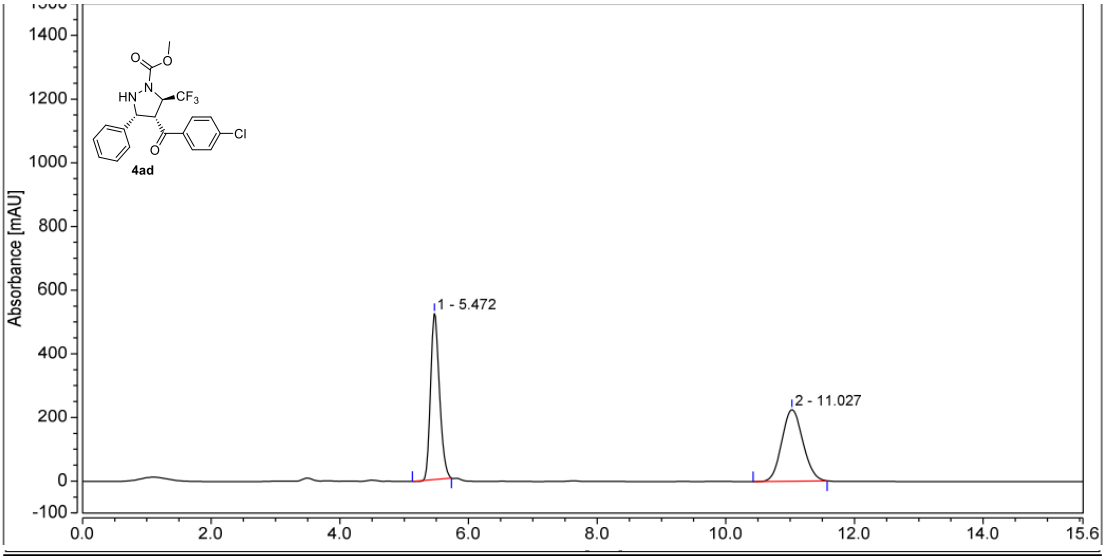
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.880	136.381	756.255	49.41	64.96	n.a.
2		9.942	139.628	407.855	50.59	35.04	n.a.
Total:			**276.010**	**1164.109**	**100.00**	**100.00**	

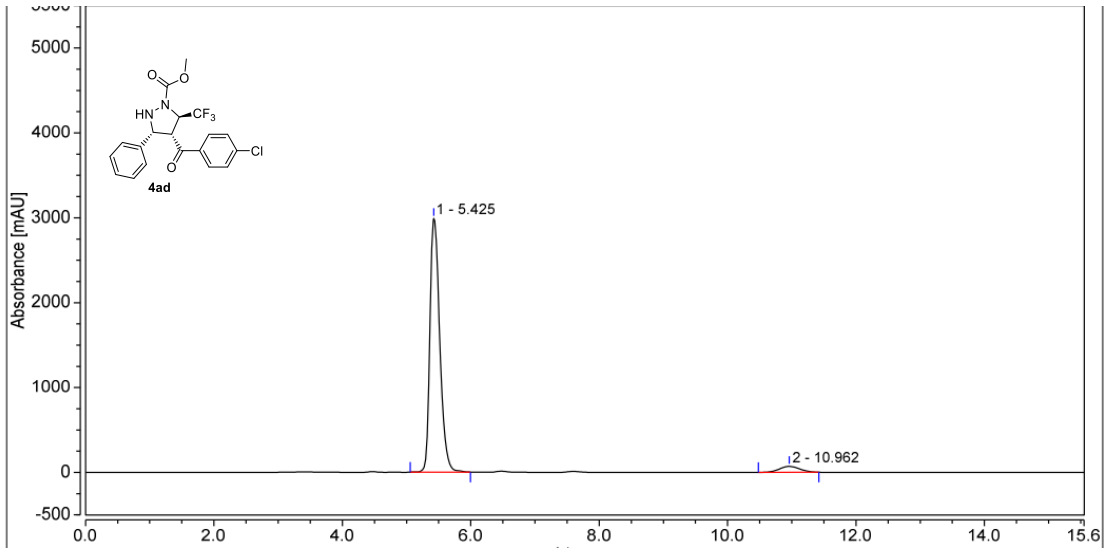


Integration Results

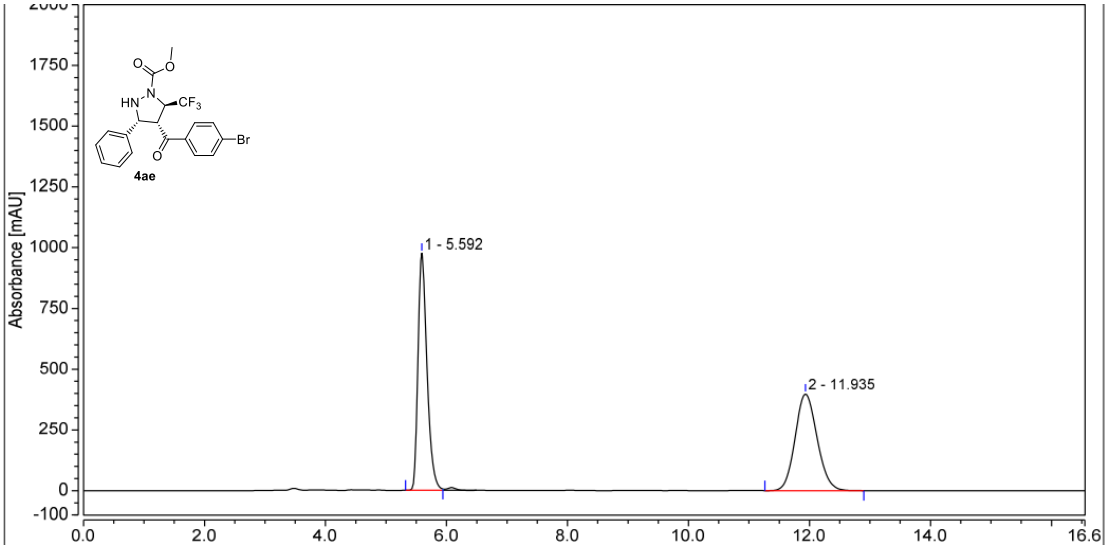
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.877	277.294	1523.207	96.42	98.03	n.a.
2		9.975	10.307	30.677	3.58	1.97	n.a.
Total:			**287.601**	**1553.884**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.472	84.311	521.224	49.71	69.89	n.a.
2		11.027	85.294	224.562	50.29	30.11	n.a.
Total:			**169.605**	**745.787**	**100.00**	**100.00**	

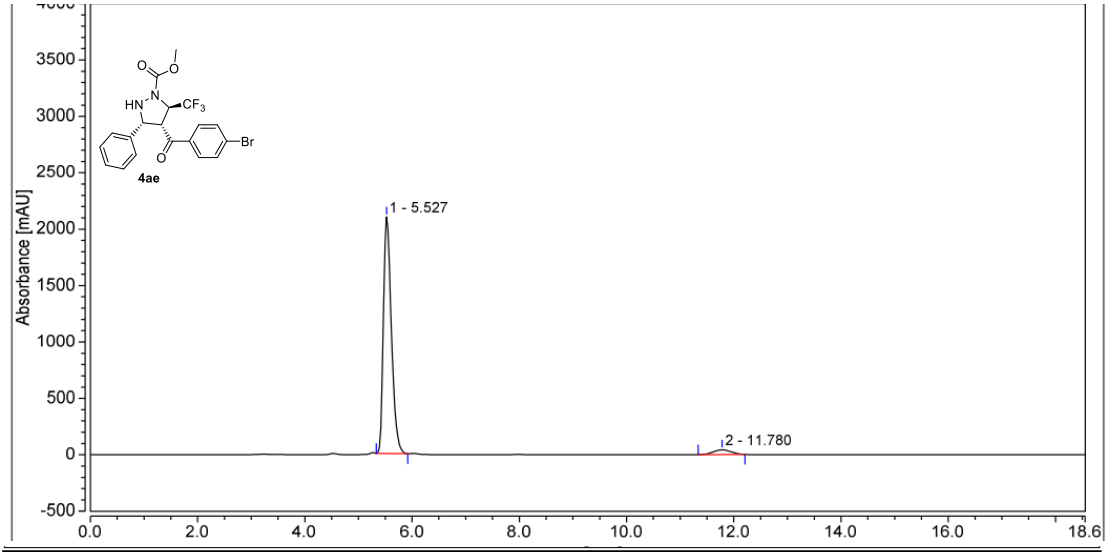


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.425	532.530	2990.806	95.34	97.72	n.a.
2		10.962	26.045	69.892	4.66	2.28	n.a.
Total:			**558.575**	**3060.698**	**100.00**	**100.00**	



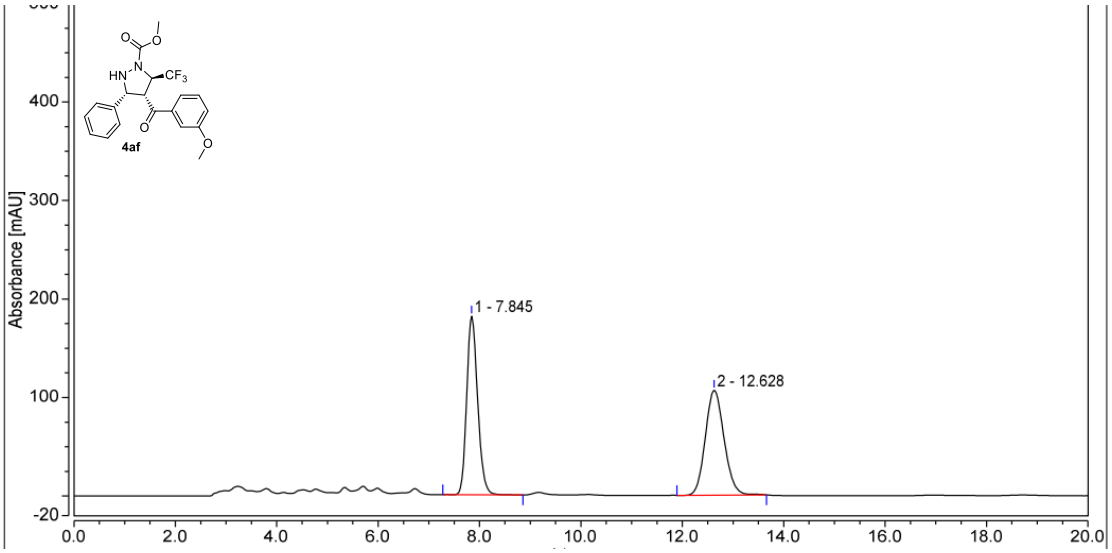
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.592	167.566	975.304	50.00	71.05	n.a.
2		11.935	167.548	397.370	50.00	28.95	n.a.
Total:			**335.114**	**1372.674**	**100.00**	**100.00**	

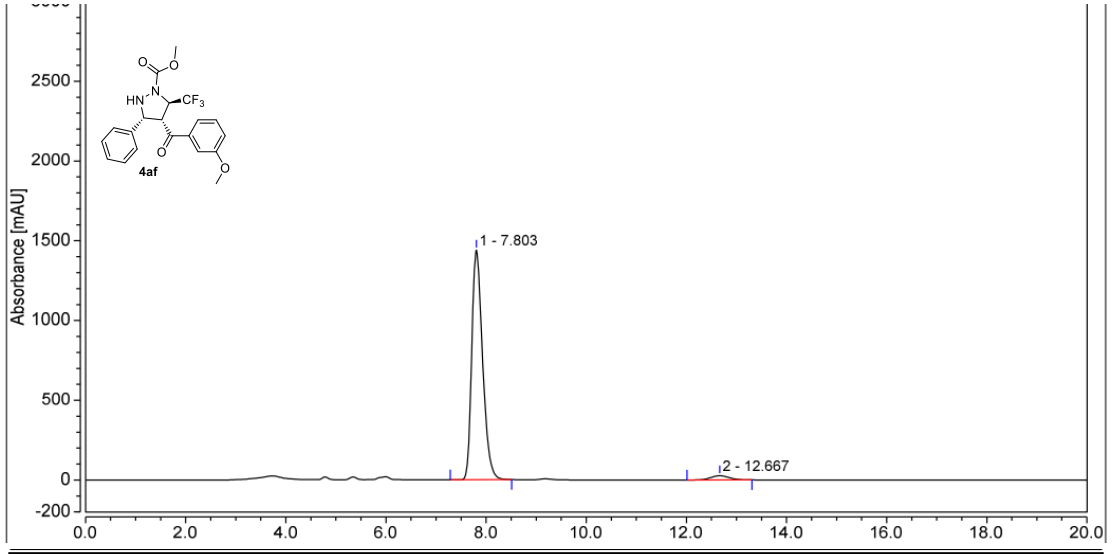


Integration Results

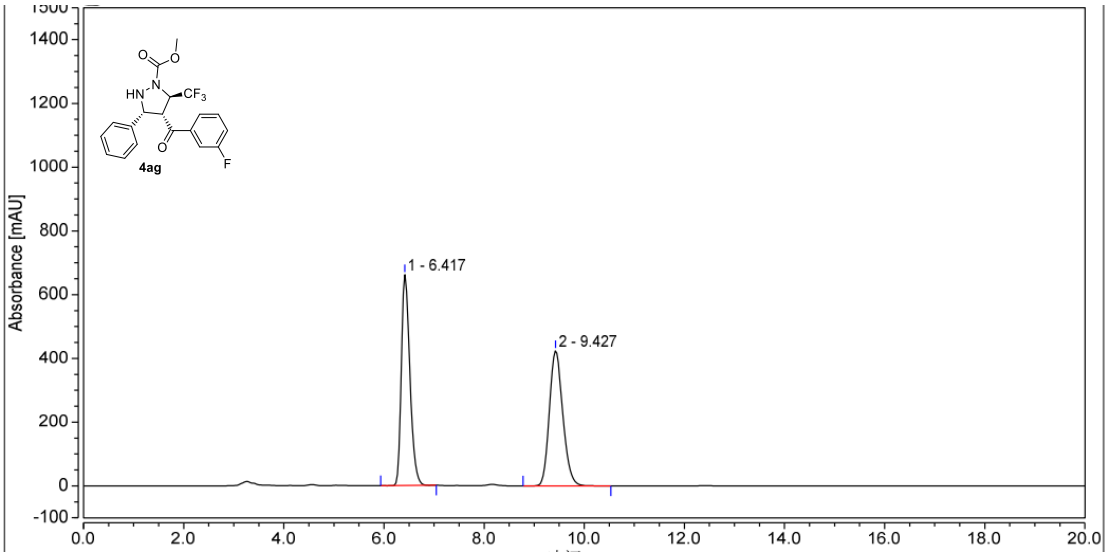
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.527	362.198	2098.538	95.68	98.05	n.a.
2		11.780	16.354	41.774	4.32	1.95	n.a.
Total:			**378.552**	**2140.313**	**100.00**	**100.00**	



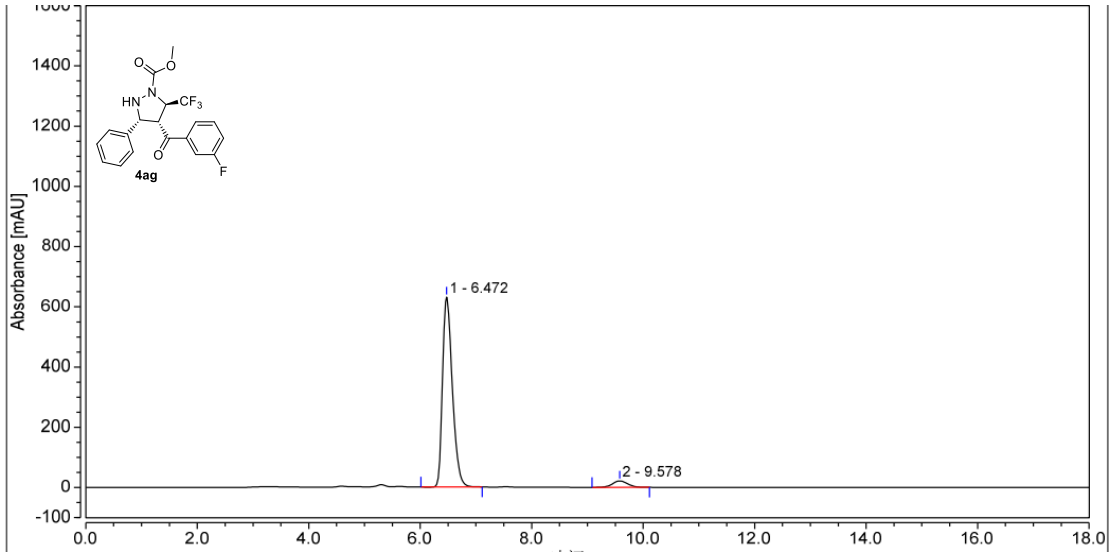
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.845	45.513	181.698	49.90	63.03	n.a.
2		12.628	45.692	106.577	50.10	36.97	n.a.
Total:			**91.205**	**288.275**	**100.00**	**100.00**	



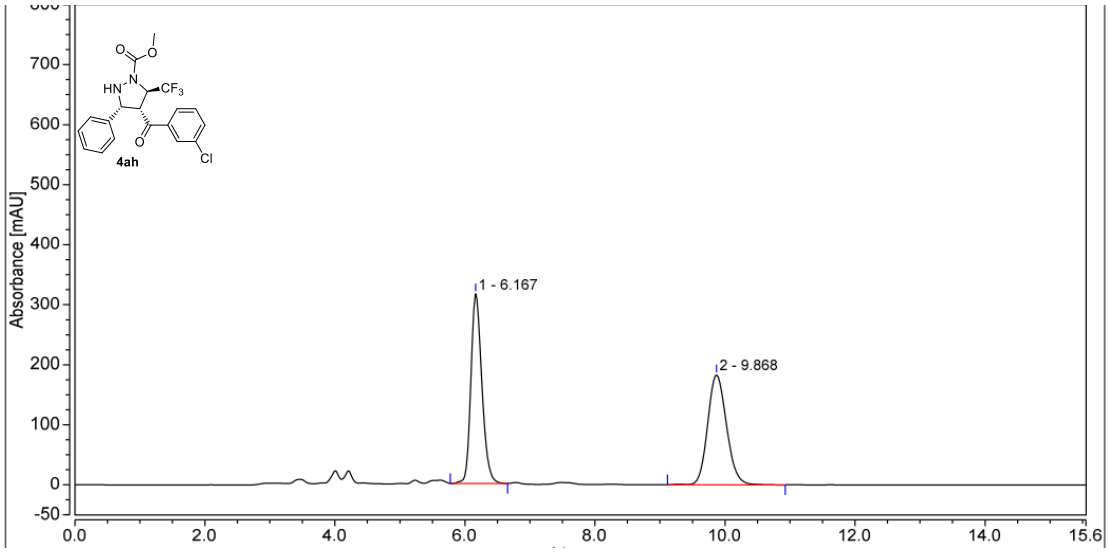
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.803	361.171	1439.709	96.95	98.17	n.a.
2		12.667	11.350	26.809	3.05	1.83	n.a.
Total:			**372.522**	**1466.518**	**100.00**	**100.00**	



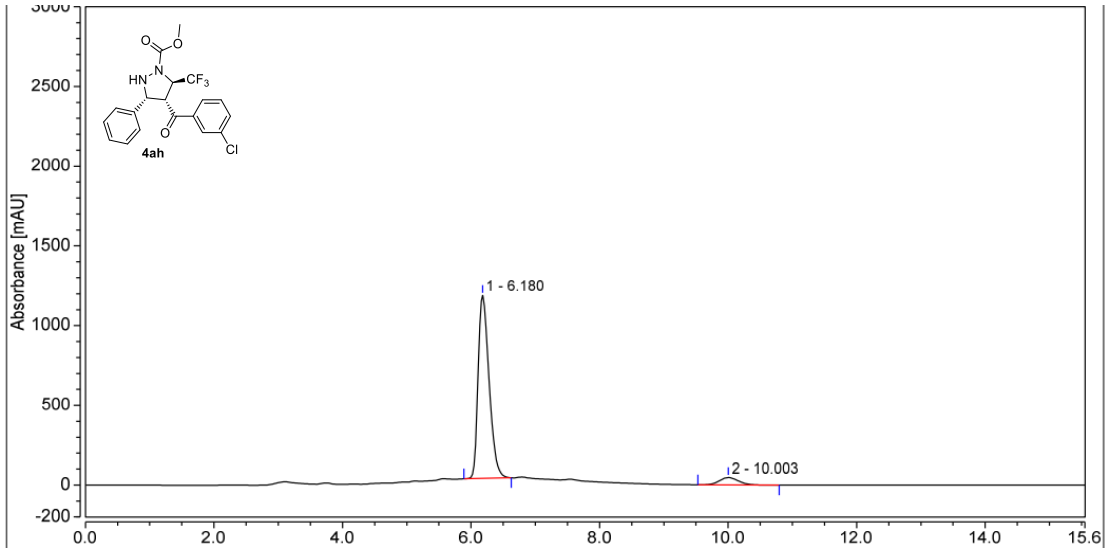
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.417	130.692	661.449	49.78	60.93	n.a.
2		9.427	131.835	424.090	50.22	39.07	n.a.
Total:			**262.527**	**1085.539**	**100.00**	**100.00**	



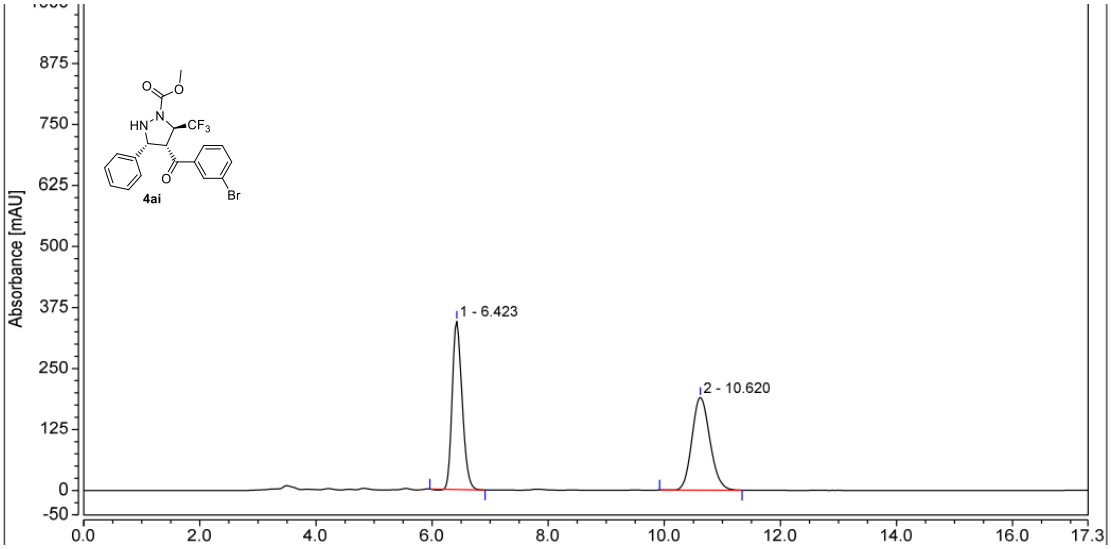
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.472	128.766	630.644	95.02	96.75	n.a.
2		9.578	6.752	21.153	4.98	3.25	n.a.
Total:			**135.518**	**651.797**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.167	61.756	316.107	50.05	63.31	n.a.
2		9.868	61.622	183.197	49.95	36.69	n.a.
Total:			**123.378**	**499.304**	**100.00**	**100.00**	

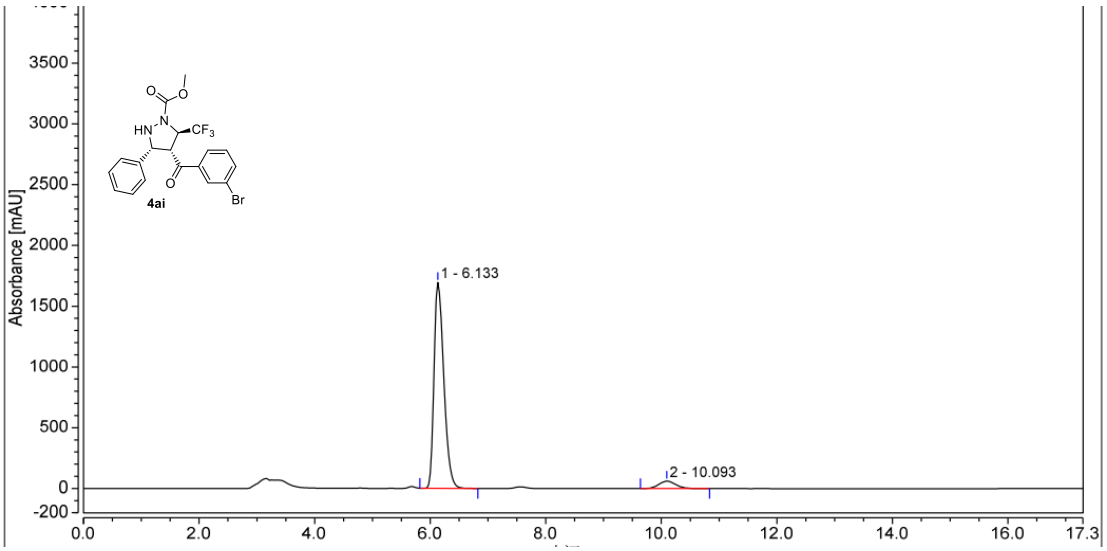


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.180	225.989	1147.912	93.48	96.13	n.a.
2		10.003	15.759	46.174	6.52	3.87	n.a.
Total:			**241.748**	**1194.086**	**100.00**	**100.00**	



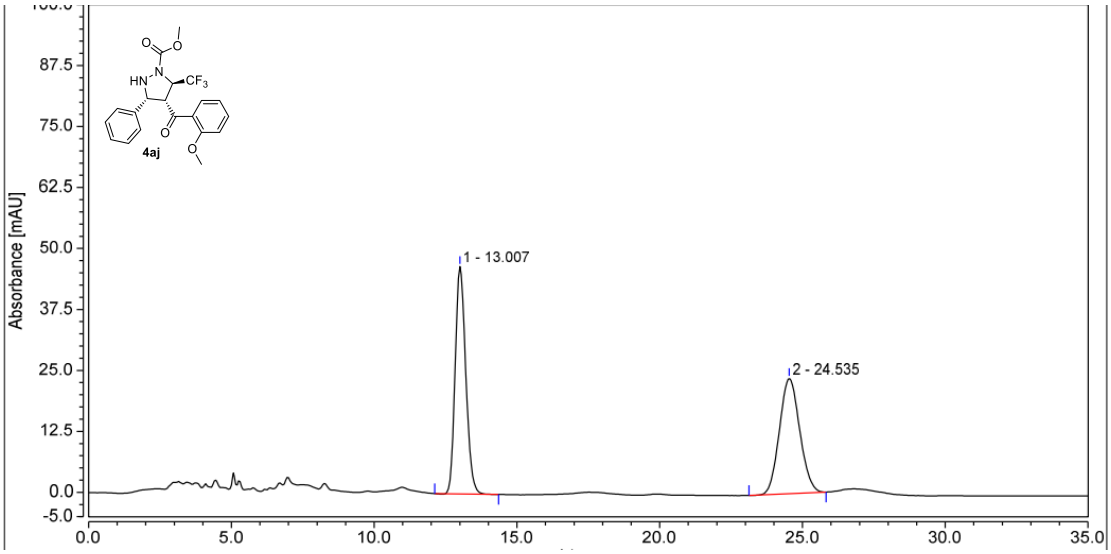
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.423	68.023	345.242	49.93	64.50	n.a.
2		10.620	68.212	189.989	50.07	35.50	n.a.
Total:			**136.234**	**535.231**	**100.00**	**100.00**	

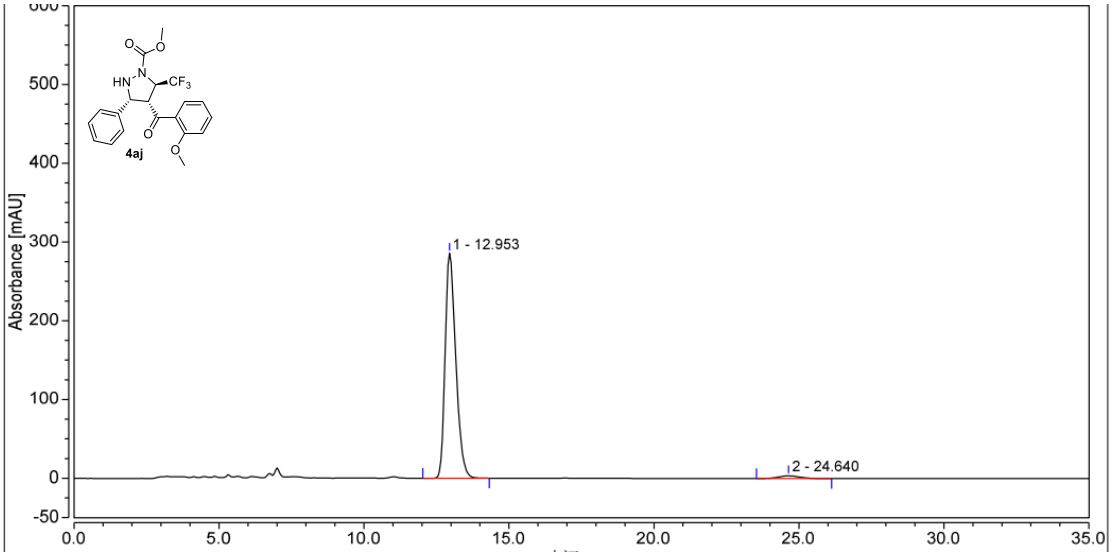


Integration Results

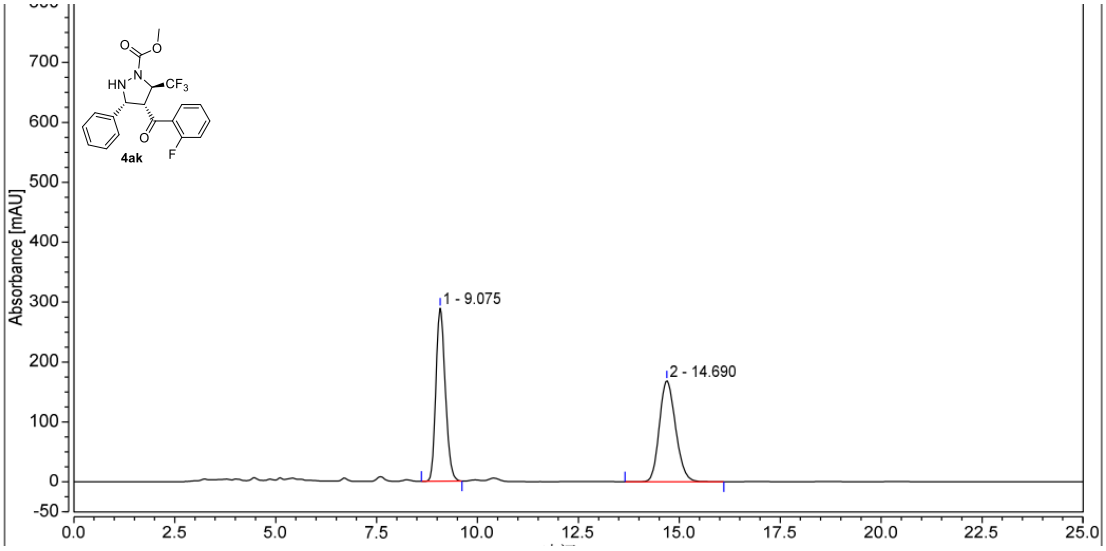
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.133	330.491	1693.540	94.05	96.53	n.a.
2		10.093	20.894	60.844	5.95	3.47	n.a.
Total:			**351.385**	**1754.384**	**100.00**	**100.00**	



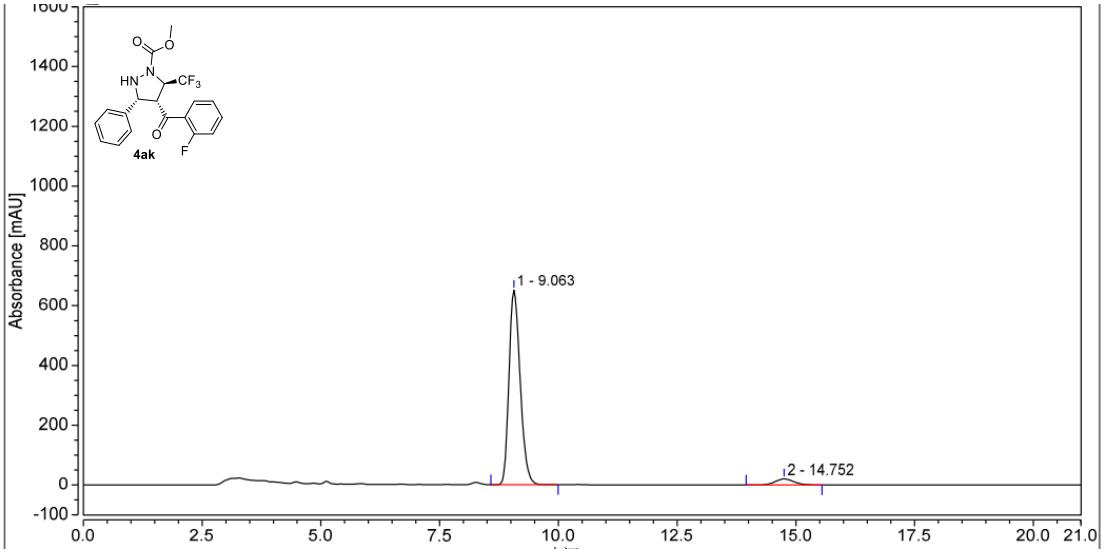
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.007	20.011	46.634	50.75	66.38	n.a.
2		24.535	19.420	23.623	49.25	33.62	n.a.
Total:			**39.431**	**70.257**	**100.00**	**100.00**	



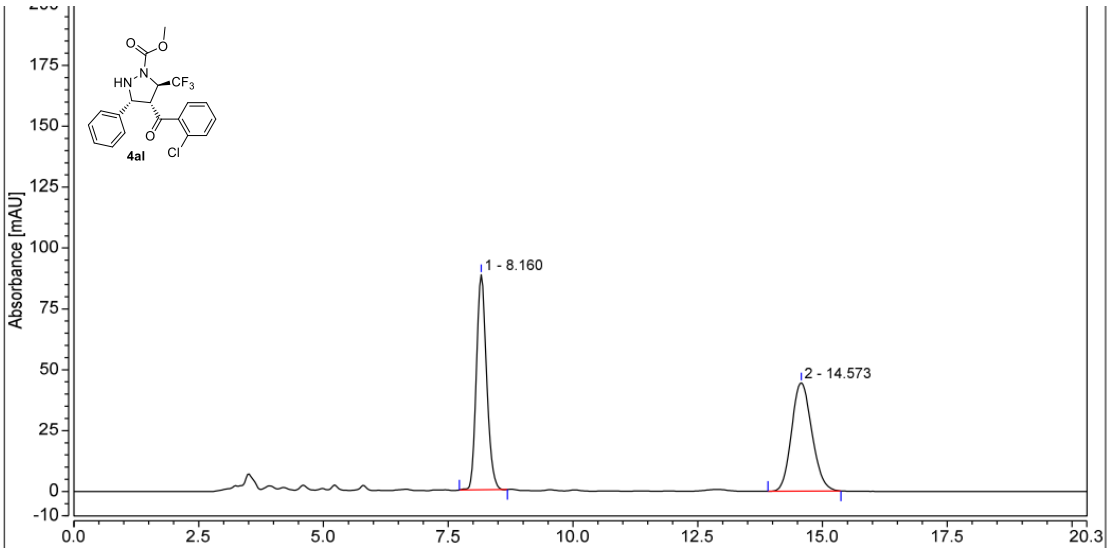
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.953	121.598	285.624	97.66	98.82	n.a.
2		24.640	2.918	3.425	2.34	1.18	n.a.
Total:			**124.516**	**289.049**	**100.00**	**100.00**	



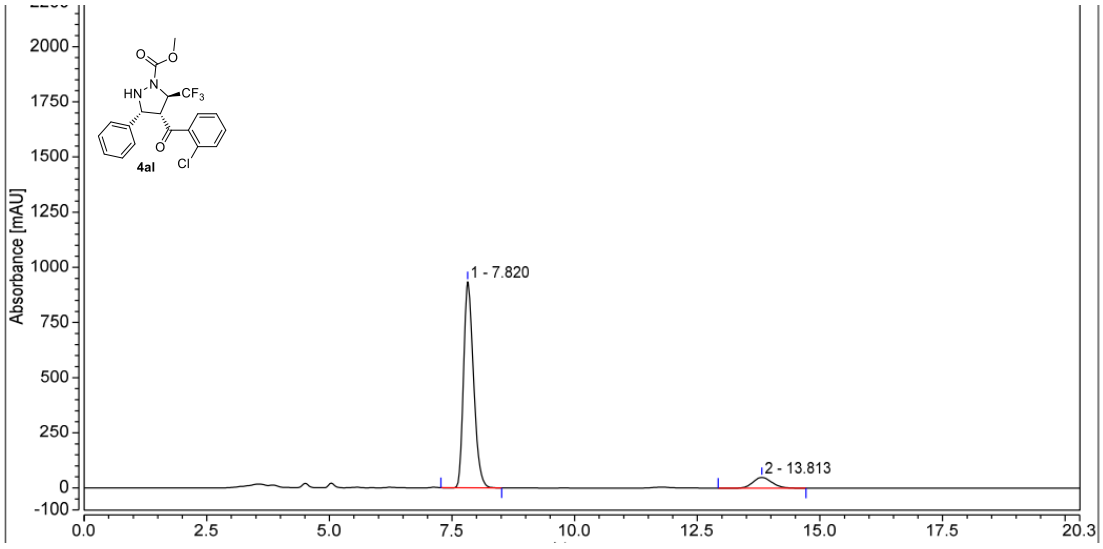
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.075	77.712	289.029	49.74	63.17	n.a.
2		14.690	78.509	168.527	50.26	36.83	n.a.
Total:			**156.221**	**457.557**	**100.00**	**100.00**	



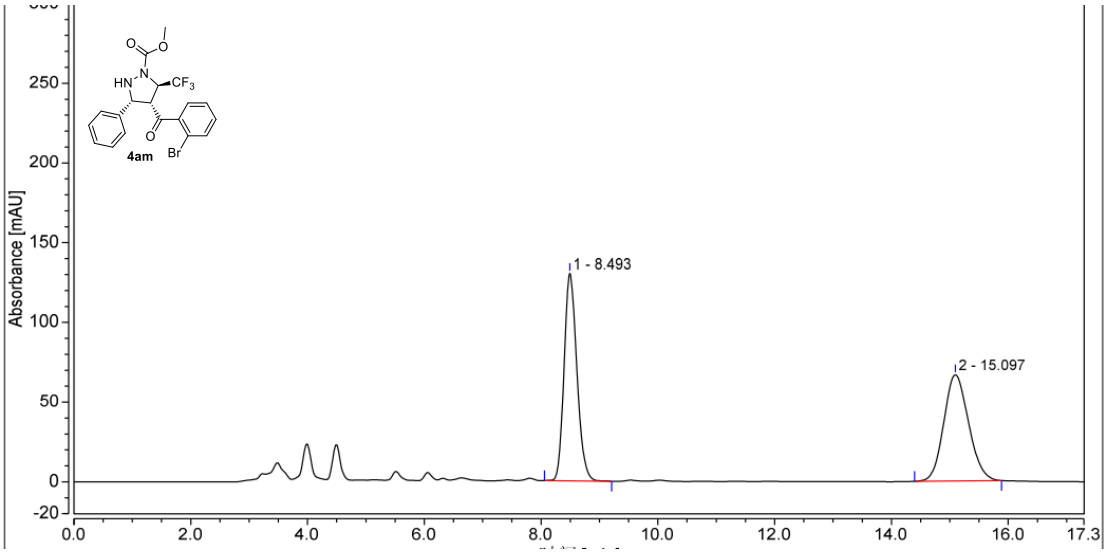
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.063	177.485	651.014	95.01	96.98	n.a.
2		14.752	9.317	20.266	4.99	3.02	n.a.
Total:			**186.802**	**671.280**	**100.00**	**100.00**	



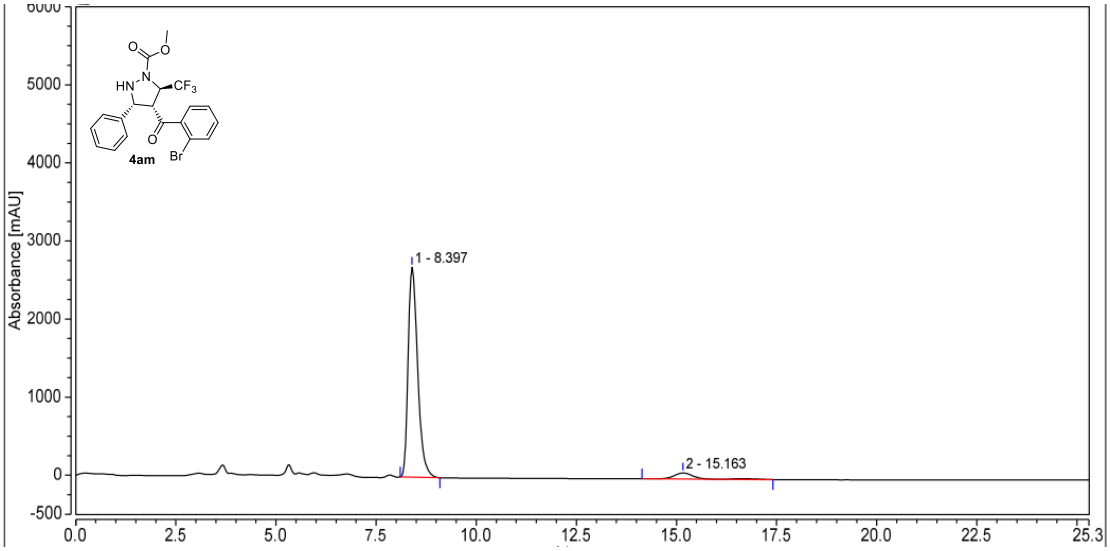
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.160	20.968	88.327	49.92	66.51	n.a.
2		14.573	21.036	44.479	50.08	33.49	n.a.
Total:			**42.004**	**132.806**	**100.00**	**100.00**	



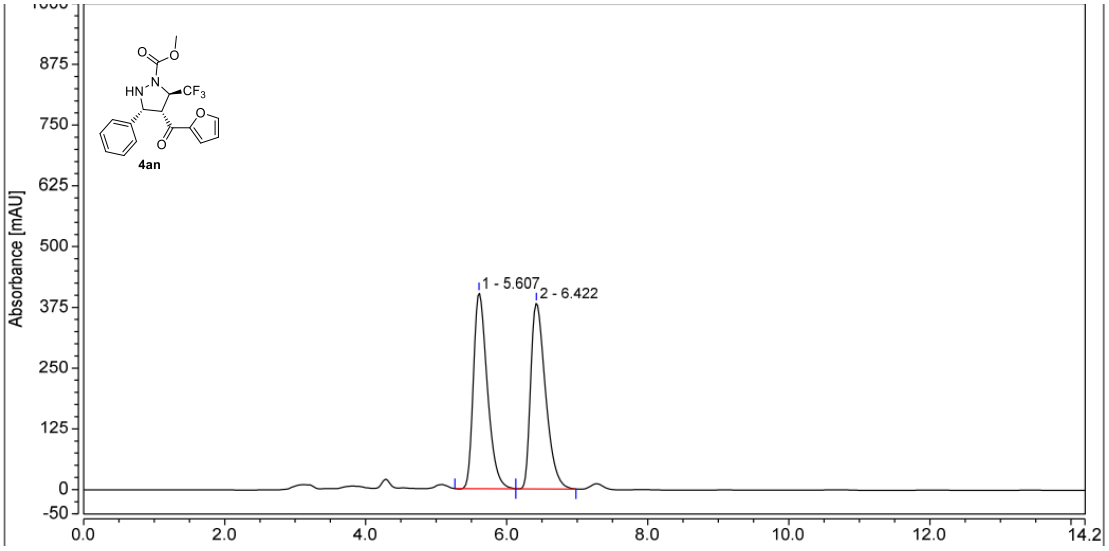
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.820	219.602	934.028	91.02	95.06	n.a.
2		13.813	21.667	48.547	8.98	4.94	n.a.
Total:			**241.270**	**982.575**	**100.00**	**100.00**	



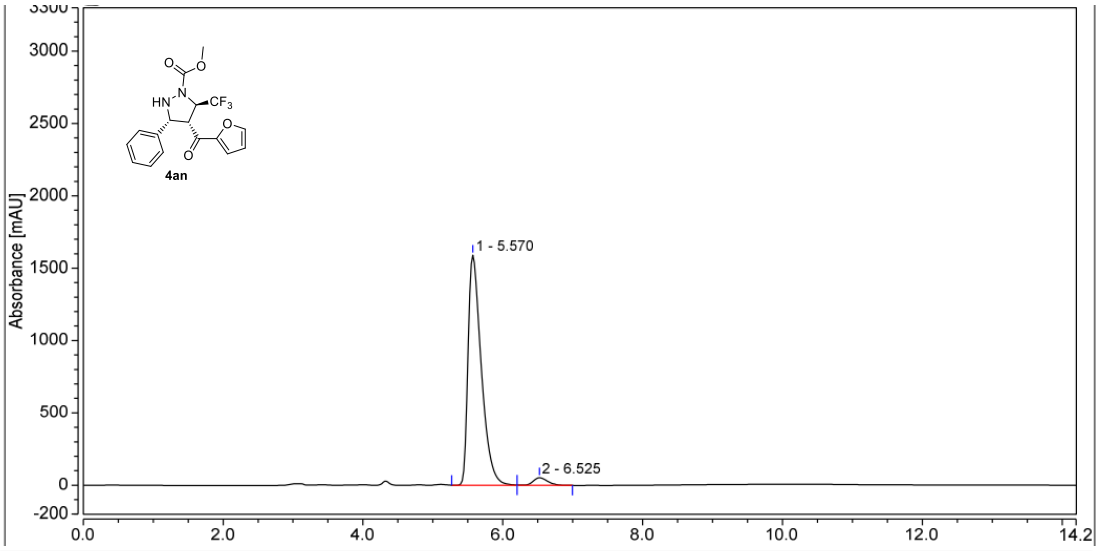
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.493	33.073	130.109	50.21	66.12	n.a.
2		15.097	32.800	66.678	49.79	33.88	n.a.
Total:			**65.873**	**196.787**	**100.00**	**100.00**	



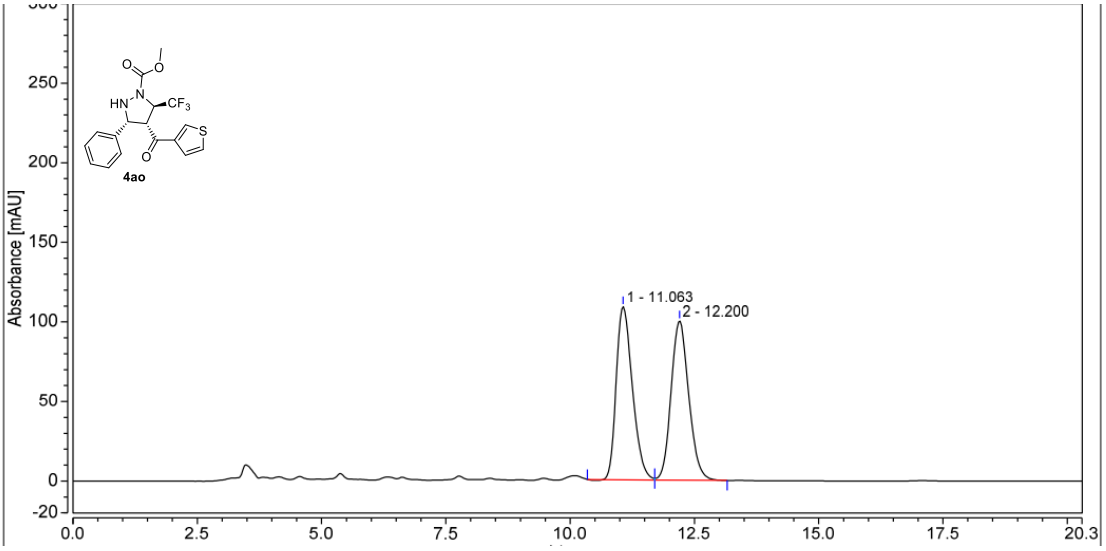
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.397	741.747	2689.607	93.89	97.18	n.a.
2		15.163	48.277	77.959	6.11	2.82	n.a.
Total:			**790.024**	**2767.566**	**100.00**	**100.00**	



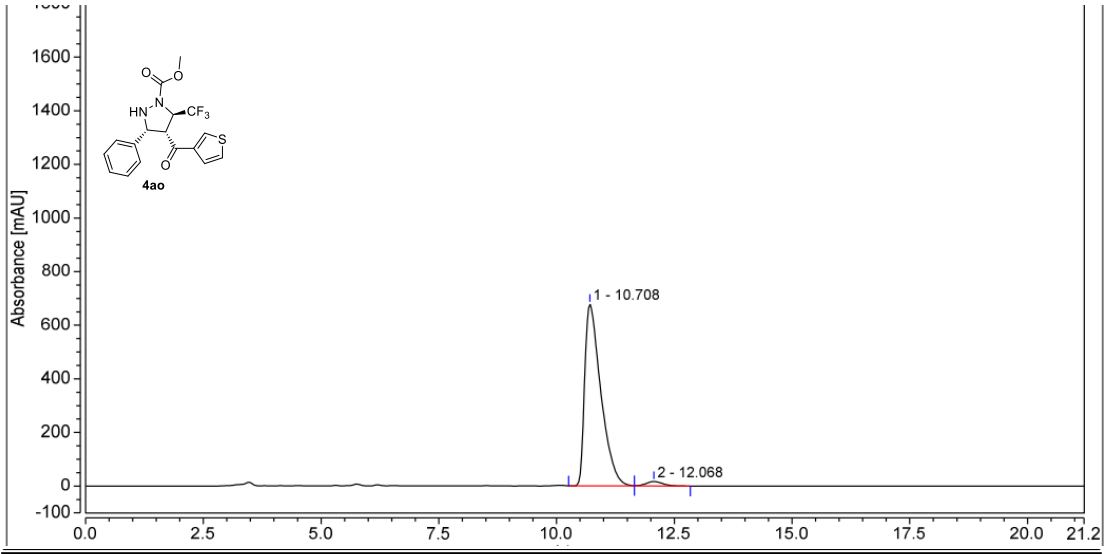
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.607	92.614	403.390	50.02	51.31	n.a.
2		6.422	92.540	382.809	49.98	48.69	n.a.
Total:			**185.154**	**786.198**	**100.00**	**100.00**	



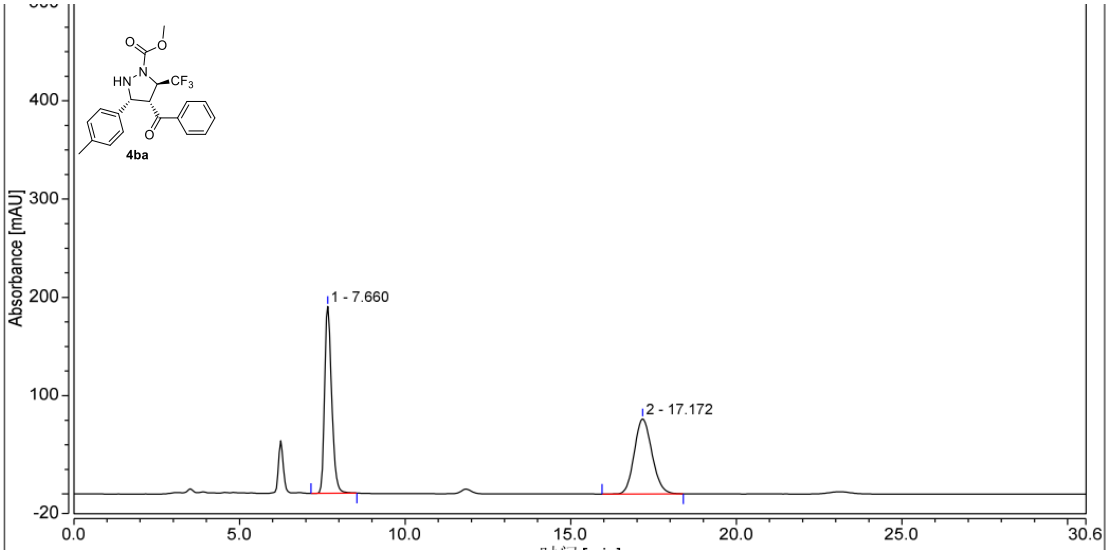
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.570	349.679	1590.698	96.51	96.81	n.a.
2		6.525	12.652	52.500	3.49	3.19	n.a.
Total:			**362.331**	**1643.197**	**100.00**	**100.00**	



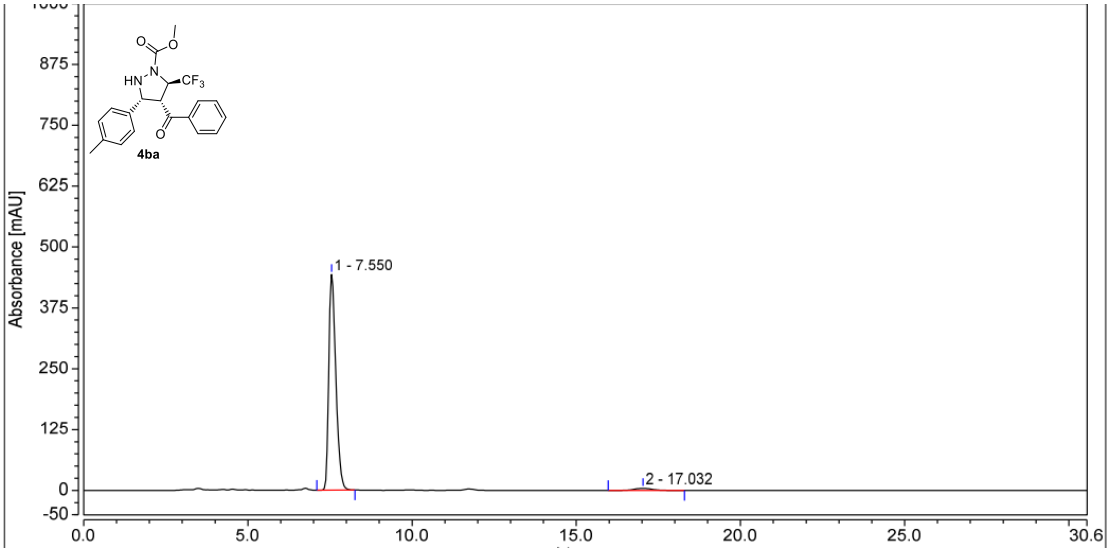
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.063	40.936	108.781	49.81	52.08	n.a.
2		12.200	41.245	100.102	50.19	47.92	n.a.
Total:			**82.181**	**208.883**	**100.00**	**100.00**	



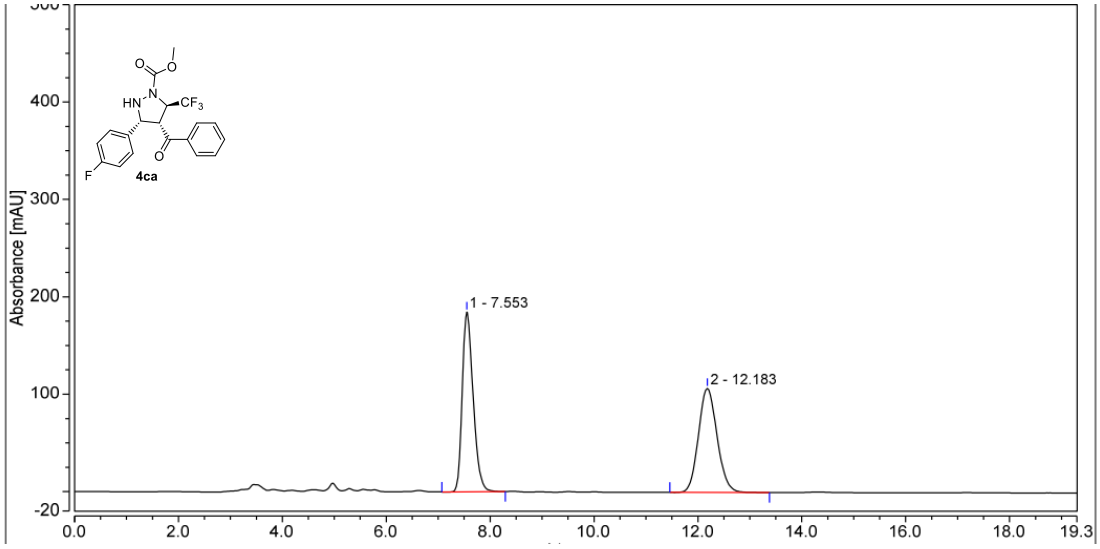
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.708	269.486	677.375	97.49	97.60	n.a.
2		12.068	6.936	16.641	2.51	2.40	n.a.
Total:			**276.422**	**694.016**	**100.00**	**100.00**	



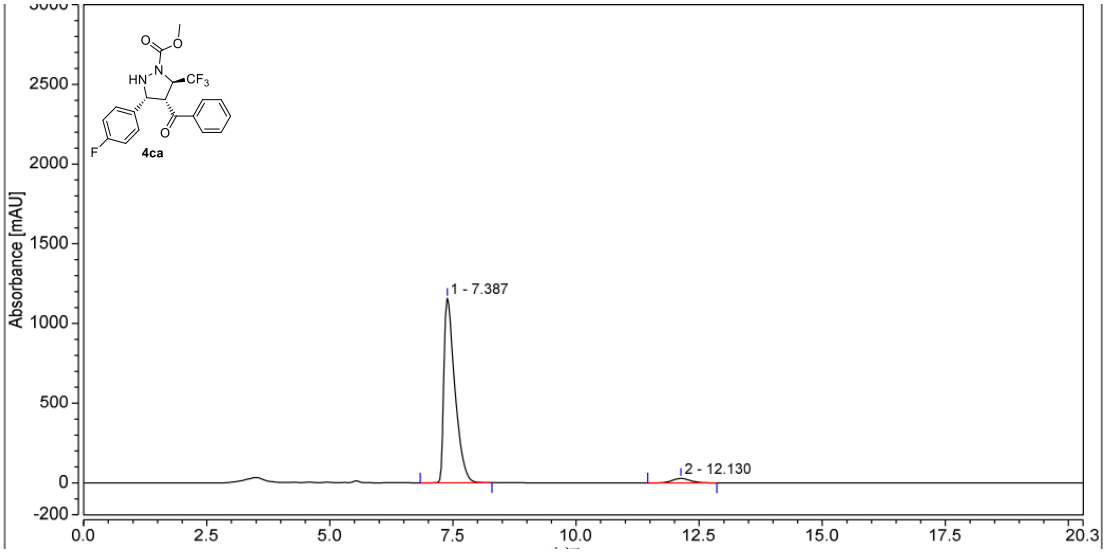
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.660	47.032	190.259	49.84	71.35	n.a.
2		17.172	47.341	76.401	50.16	28.65	n.a.
Total:			**94.373**	**266.660**	**100.00**	**100.00**	



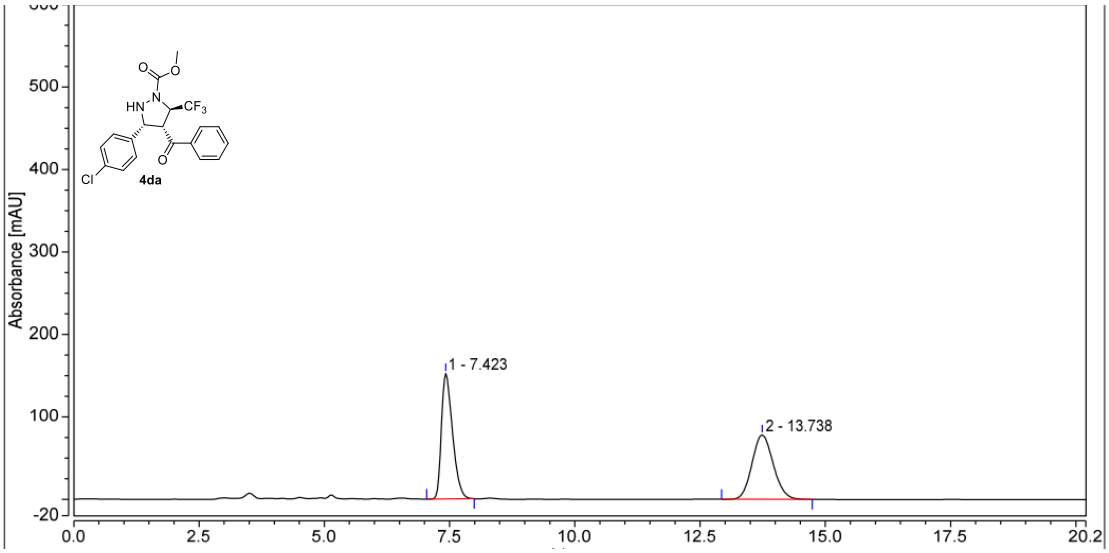
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.550	110.140	442.909	97.72	99.05	n.a.
2		17.032	2.567	4.245	2.28	0.95	n.a.
Total:			**112.707**	**447.154**	**100.00**	**100.00**	



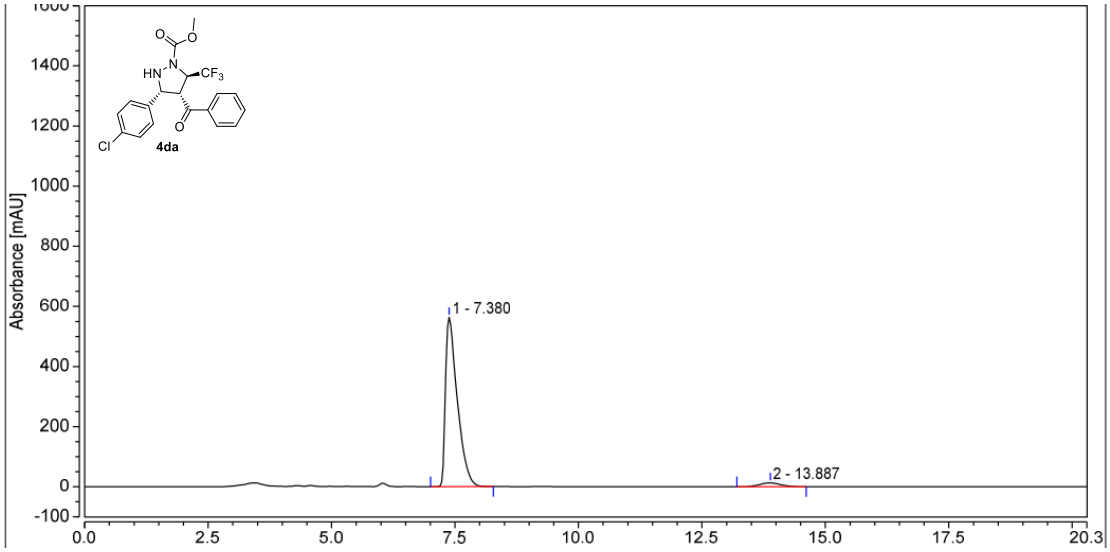
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.553	44.745	184.540	50.16	63.33	n.a.
2		12.183	44.457	106.870	49.84	36.67	n.a.
Total:			**89.202**	**291.410**	**100.00**	**100.00**	



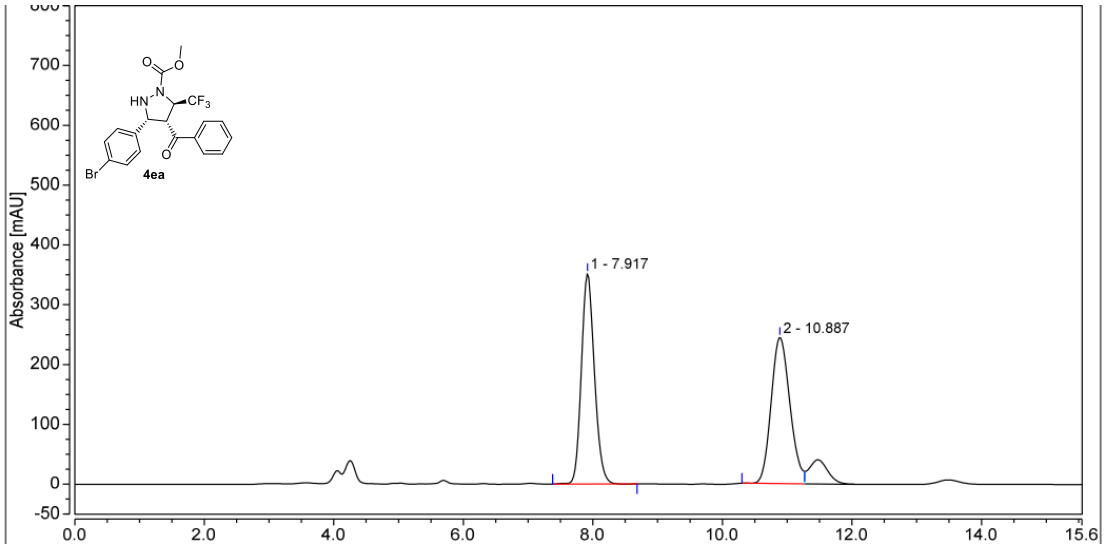
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.387	298.990	1157.045	96.23	97.64	n.a.
2		12.130	11.710	27.997	3.77	2.36	n.a.
Total:			**310.699**	**1185.042**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.423	39.020	152.043	50.40	66.10	n.a.
2		13.738	38.407	77.984	49.60	33.90	n.a.
Total:			**77.427**	**230.028**	**100.00**	**100.00**	

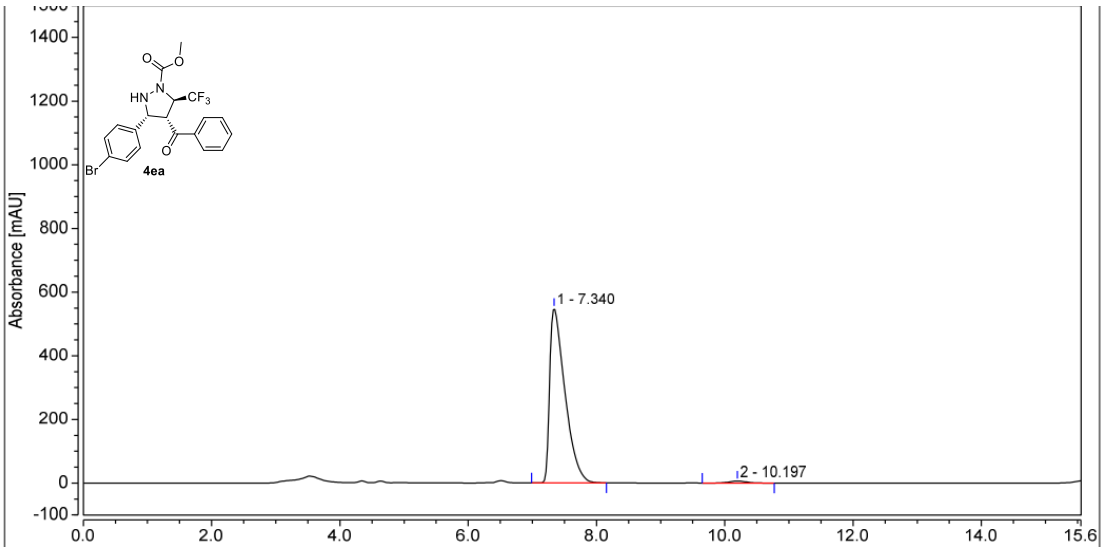


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.380	155.840	562.915	96.03	97.77	n.a.
2		13.887	6.447	12.847	3.97	2.23	n.a.
Total:			**162.287**	**575.762**	**100.00**	**100.00**	



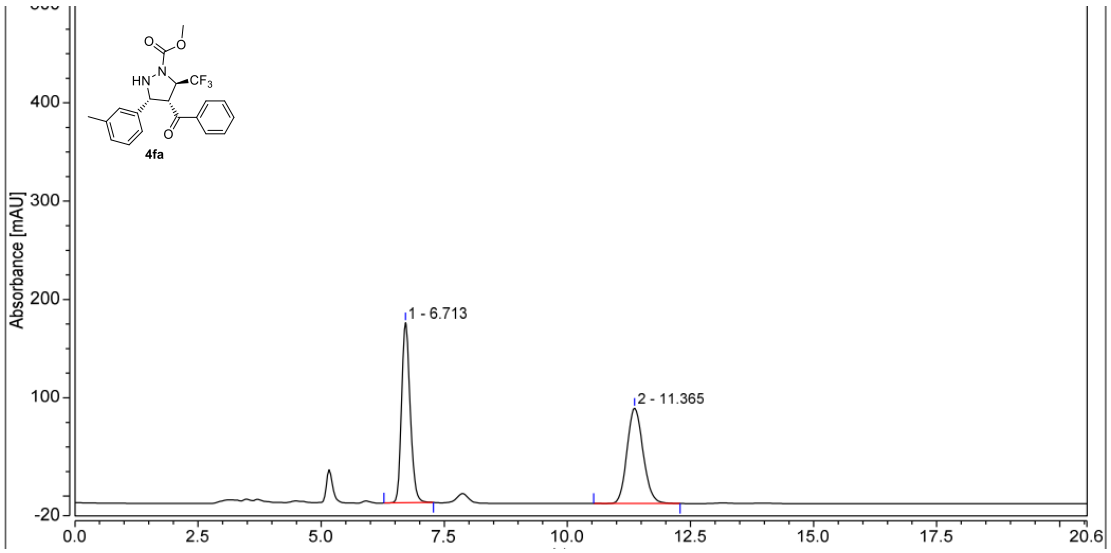
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.917	83.013	352.095	50.35	59.00	n.a.
2		10.887	81.856	244.657	49.65	41.00	n.a.
Total:			**164.869**	**596.752**	**100.00**	**100.00**	

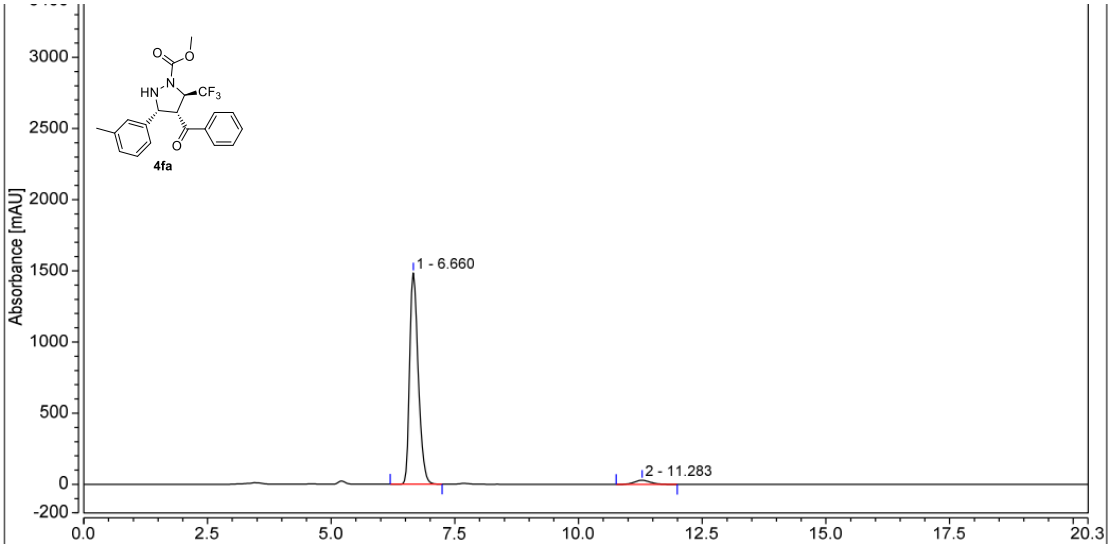


Integration Results

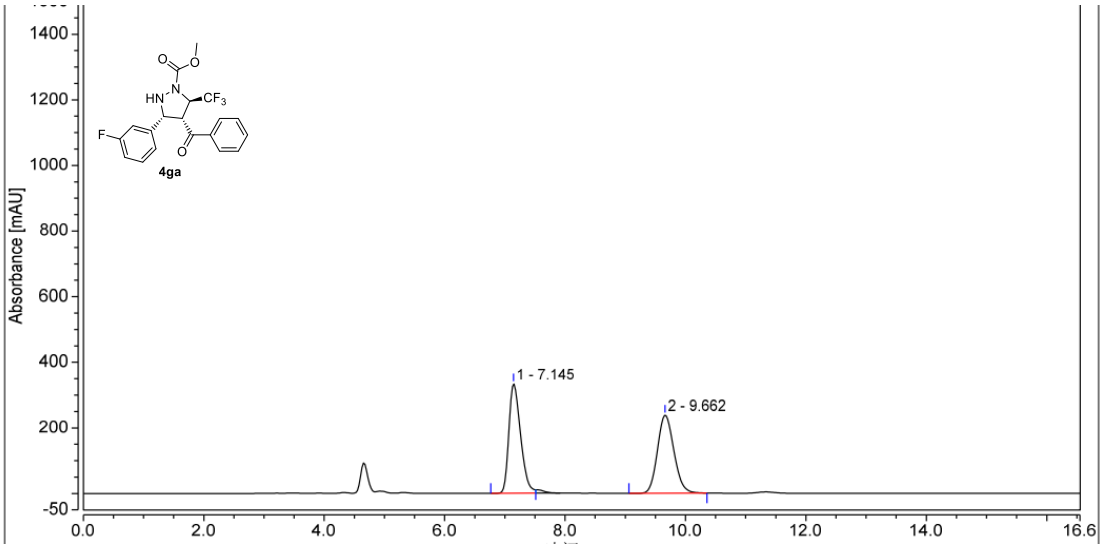
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.340	150.872	548.024	98.74	98.87	n.a.
2		10.197	1.927	6.266	1.26	1.13	n.a.
Total:			**152.799**	**554.290**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.713	37.155	183.050	50.27	65.36	n.a.
2		11.365	36.754	97.025	49.73	34.64	n.a.
Total:			**73.908**	**280.075**	**100.00**	**100.00**	

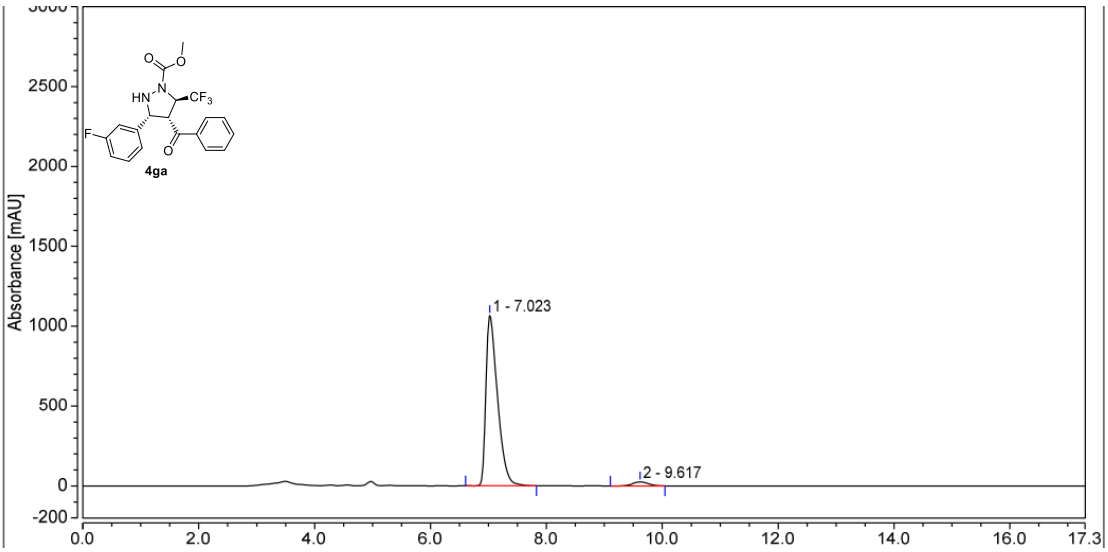


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.660	298.829	1484.752	96.56	98.10	n.a.
2		11.283	10.653	28.826	3.44	1.90	n.a.
Total:			**309.483**	**1513.577**	**100.00**	**100.00**	



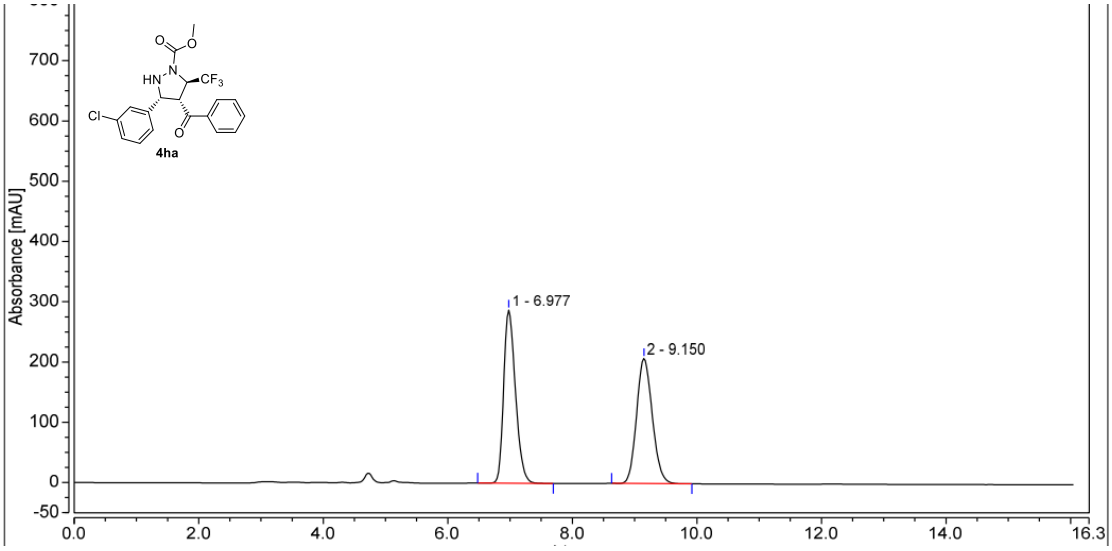
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.145	74.977	333.801	50.03	58.35	n.a.
2		9.662	74.897	238.307	49.97	41.65	n.a.
Total:			**149.874**	**572.109**	**100.00**	**100.00**	

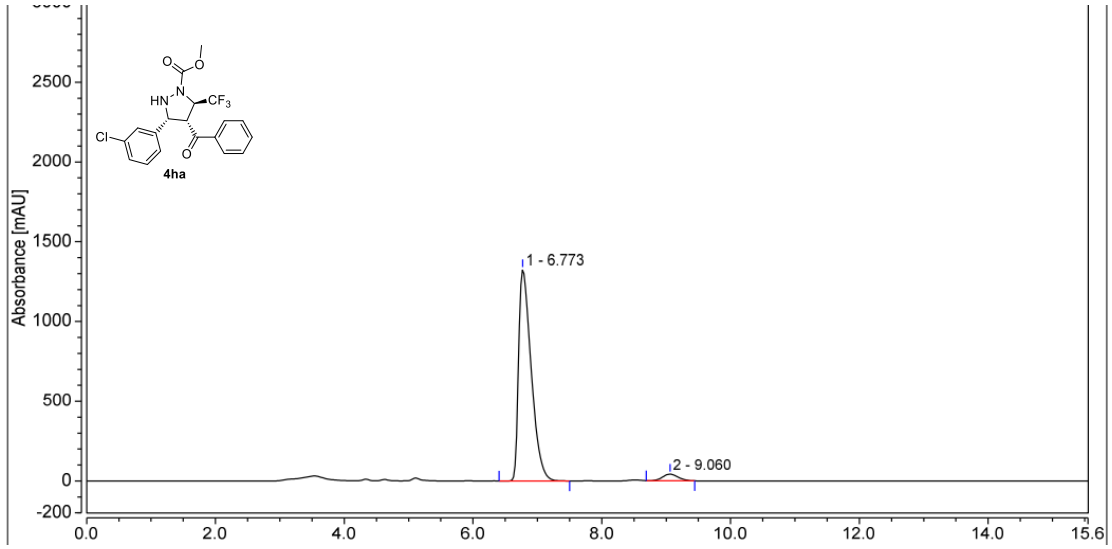


Integration Results

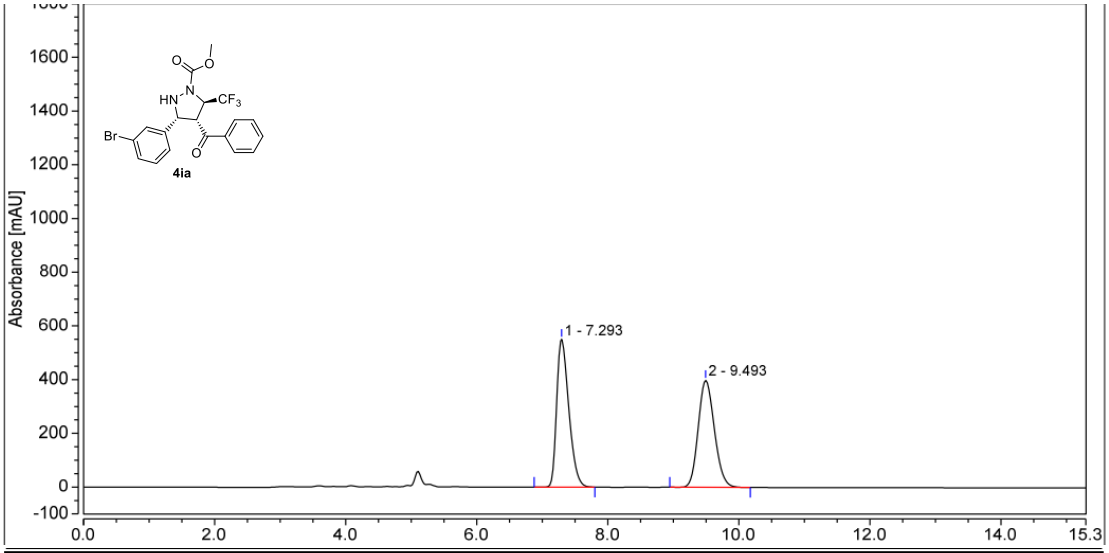
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.023	247.366	1066.172	96.89	97.66	n.a.
2		9.617	7.951	25.541	3.11	2.34	n.a.
Total:			**255.317**	**1091.713**	**100.00**	**100.00**	



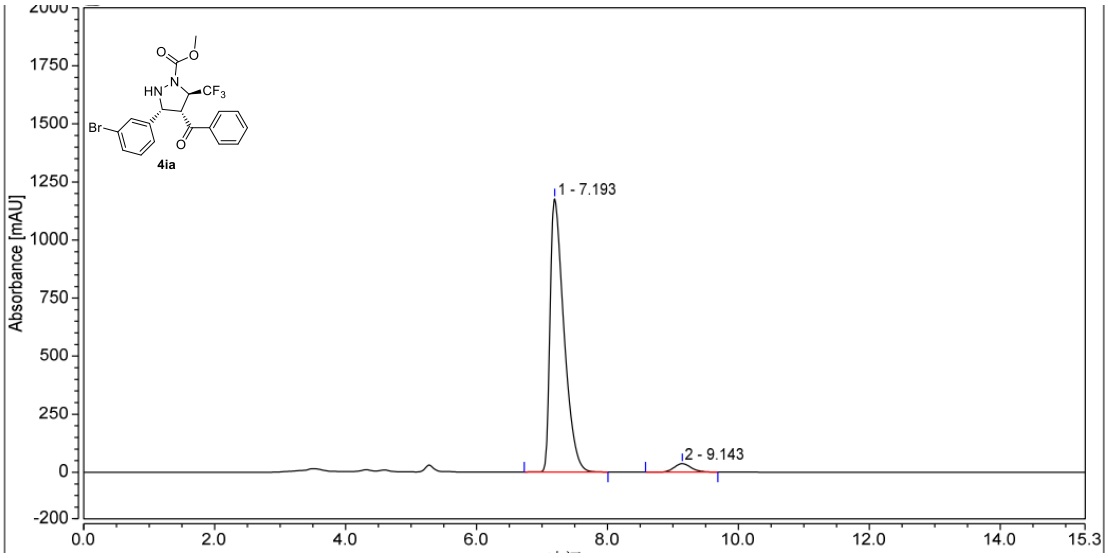
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.977	62.910	287.144	50.88	58.08	n.a.
2		9.150	60.722	207.252	49.12	41.92	n.a.
Total:			**123.632**	**494.395**	**100.00**	**100.00**	



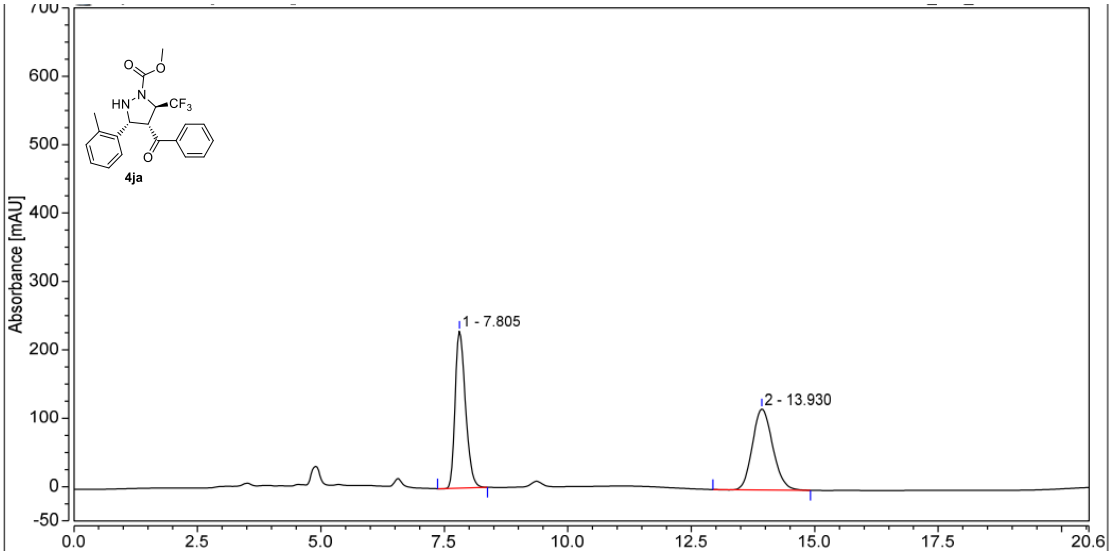
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.773	299.584	1325.657	96.28	96.94	n.a.
2		9.060	11.566	41.890	3.72	3.06	n.a.
Total:			**311.150**	**1367.547**	**100.00**	**100.00**	



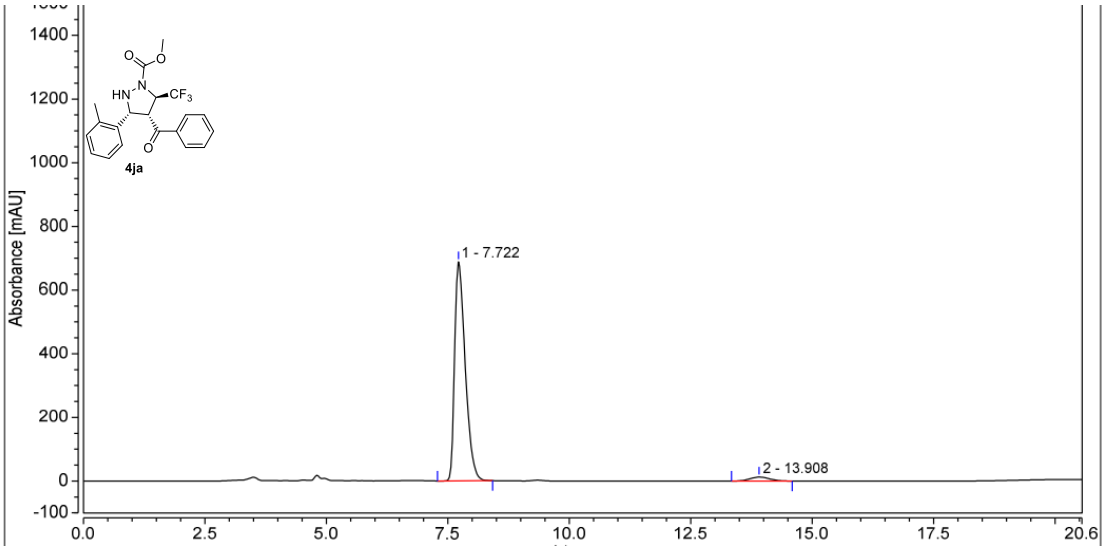
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.293	118.423	550.228	50.92	58.03	n.a.
2		9.493	114.140	397.967	49.08	41.97	n.a.
Total:			**232.563**	**948.195**	**100.00**	**100.00**	



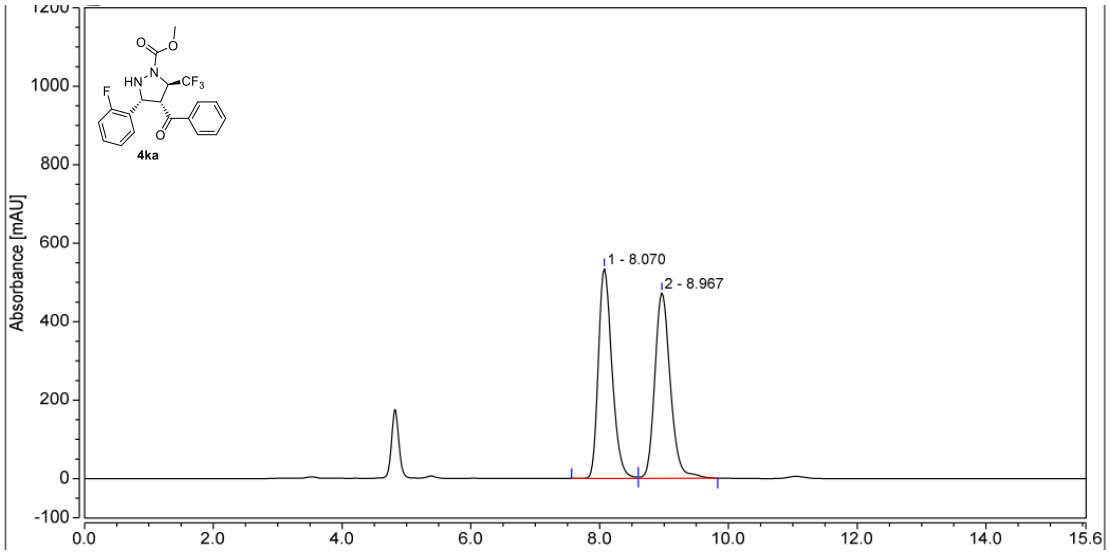
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.193	289.705	1176.226	96.31	96.97	n.a.
2		9.143	11.093	36.791	3.69	3.03	n.a.
Total:			**300.798**	**1213.017**	**100.00**	**100.00**	



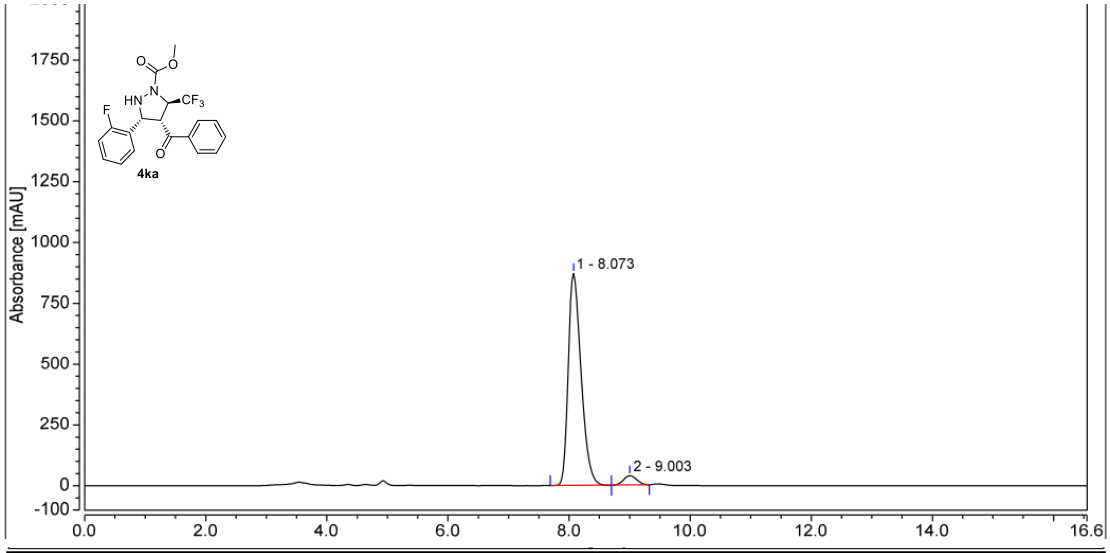
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.805	55.731	229.521	49.73	65.96	n.a.
2		13.930	56.344	118.443	50.27	34.04	n.a.
Total:			**112.075**	**347.963**	**100.00**	**100.00**	



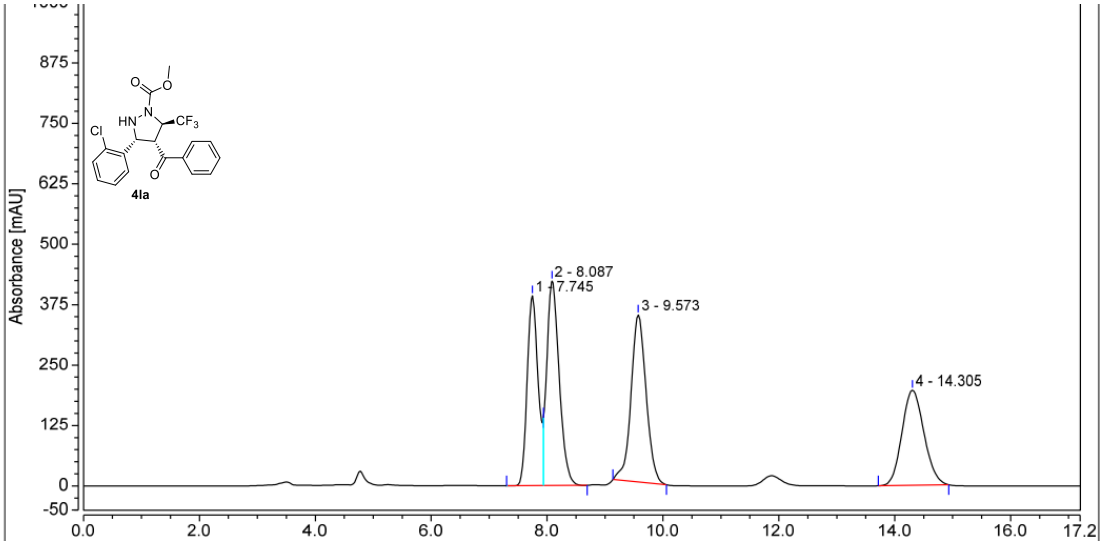
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.722	174.584	688.534	96.73	98.22	n.a.
2		13.908	5.900	12.507	3.27	1.78	n.a.
Total:			**180.484**	**701.041**	**100.00**	**100.00**	



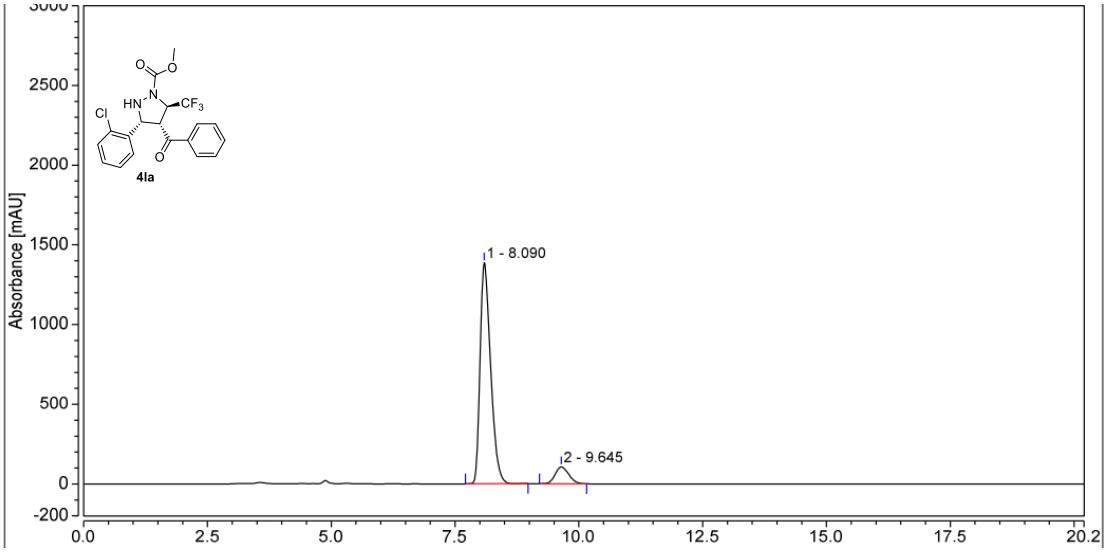
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.070	131.073	534.381	49.80	53.07	n.a.
2		8.967	132.114	472.588	50.20	46.93	n.a.
Total:			**263.187**	**1006.969**	**100.00**	**100.00**	



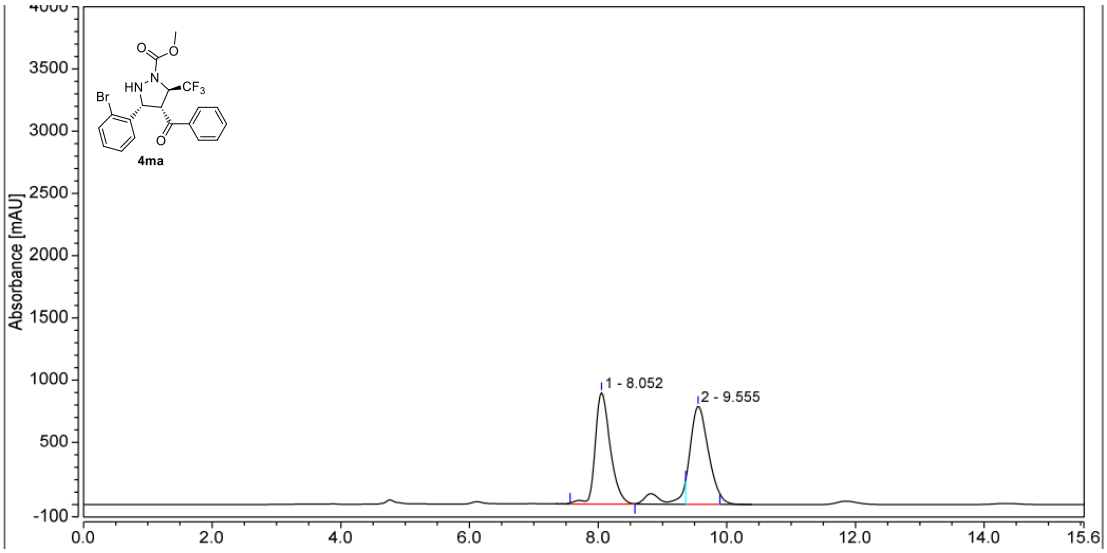
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.073	215.295	871.805	95.89	95.86	n.a.
2		9.003	9.230	37.640	4.11	4.14	n.a.
Total:			**224.525**	**909.445**	**100.00**	**100.00**	



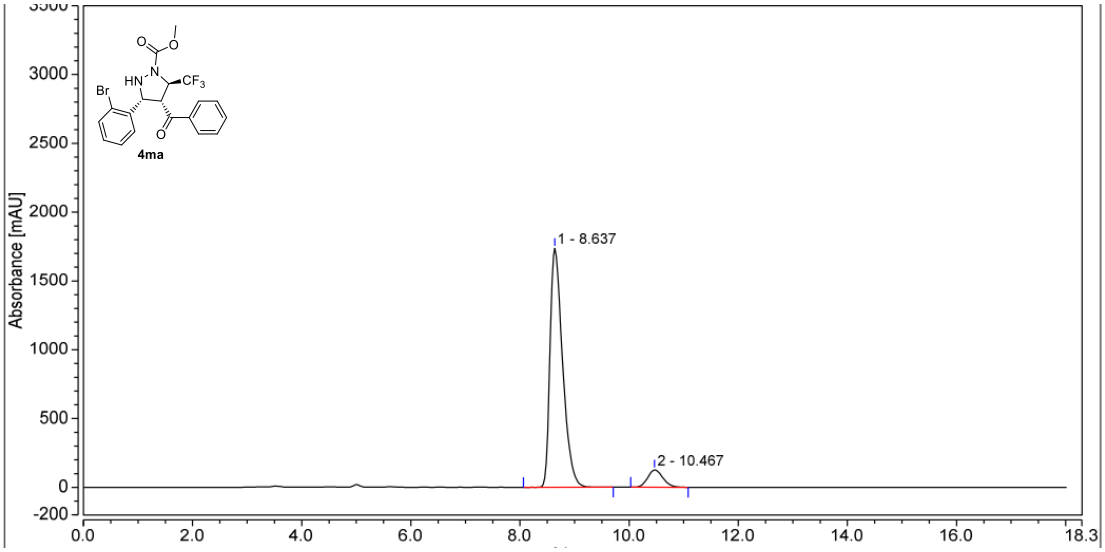
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.745	86.797	392.736	22.71	28.92	n.a.
2		8.087	104.436	422.984	27.32	31.15	n.a.
3		9.573	104.430	345.720	27.32	25.46	n.a.
4		14.305	86.539	196.646	22.64	14.48	n.a.
Total:			**382.202**	**1358.085**	**100.00**	**100.00**	



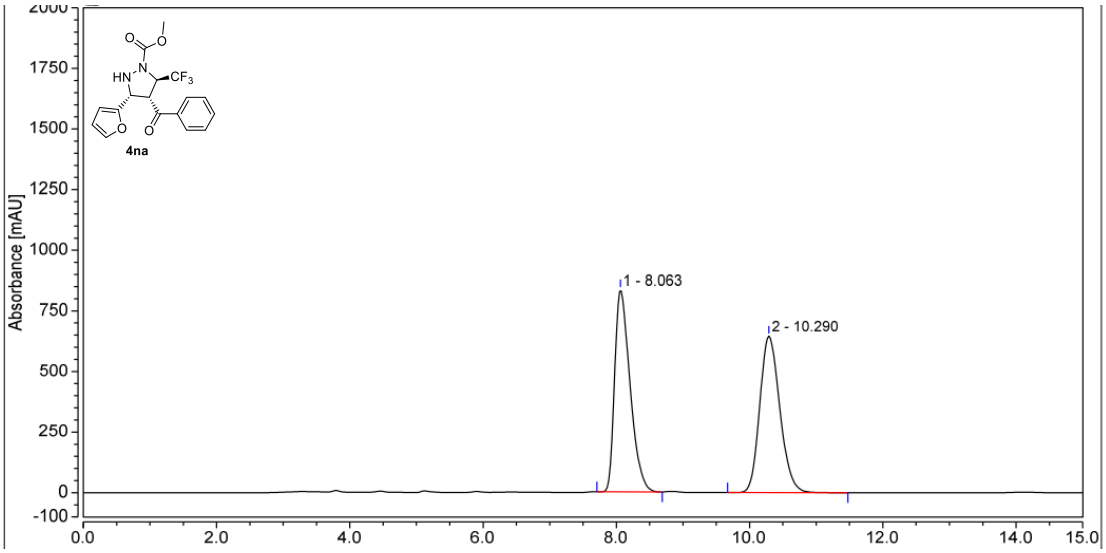
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.090	342.046	1386.789	90.96	92.88	n.a.
2		9.645	34.009	106.305	9.04	7.12	n.a.
Total:			**376.054**	**1493.094**	**100.00**	**100.00**	



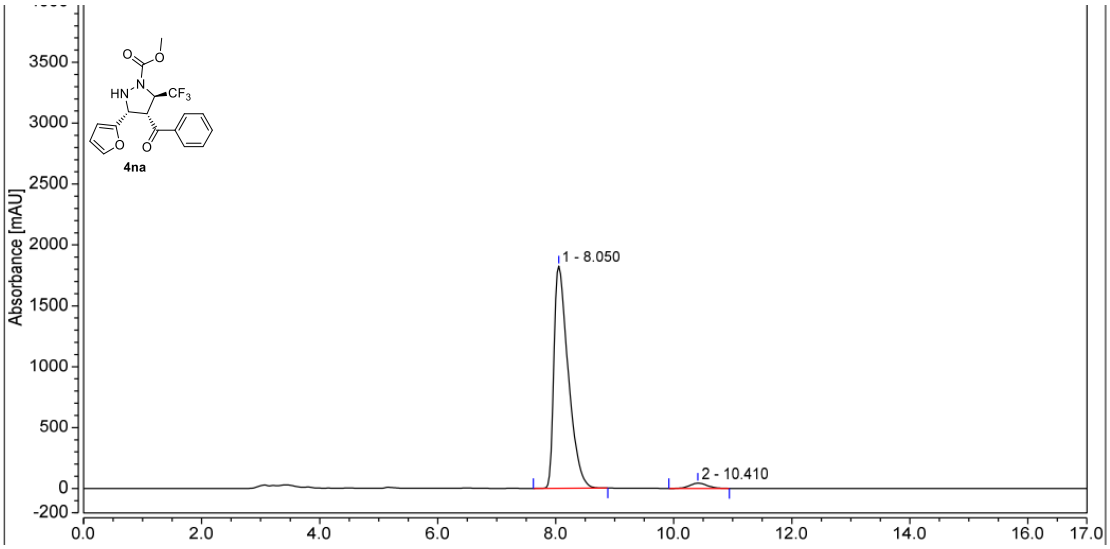
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.052	242.617	895.631	49.52	53.19	n.a.
2		9.555	247.329	788.193	50.48	46.81	n.a.
Total:			**489.946**	**1683.823**	**100.00**	**100.00**	



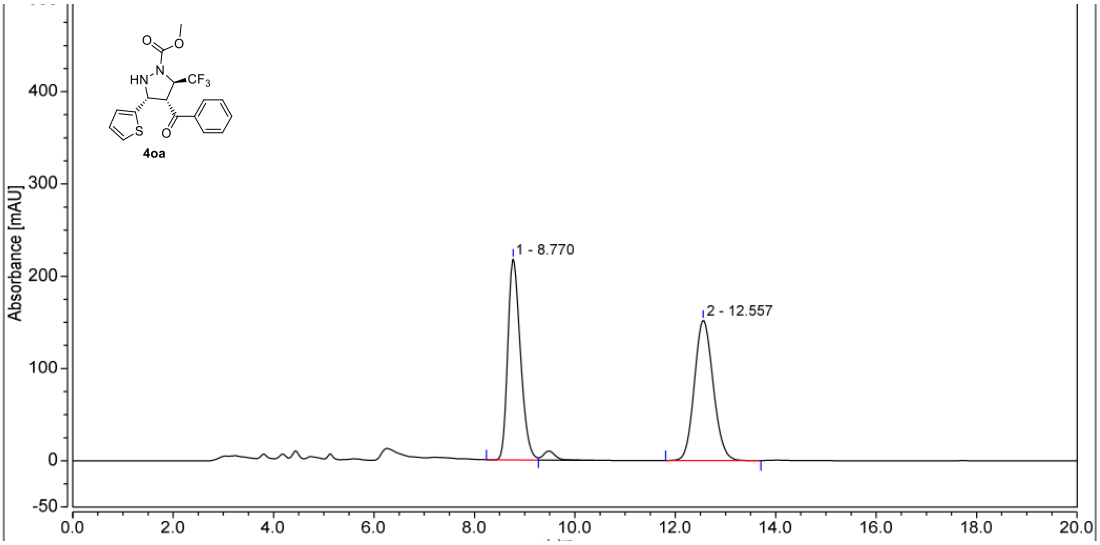
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.637	463.999	1736.595	91.91	93.25	n.a.
2		10.467	40.834	125.761	8.09	6.75	n.a.
Total:			**504.834**	**1862.356**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.063	222.750	833.192	49.69	56.33	n.a.
2		10.290	225.559	645.973	50.31	43.67	n.a.
Total:			**448.309**	**1479.165**	**100.00**	**100.00**	

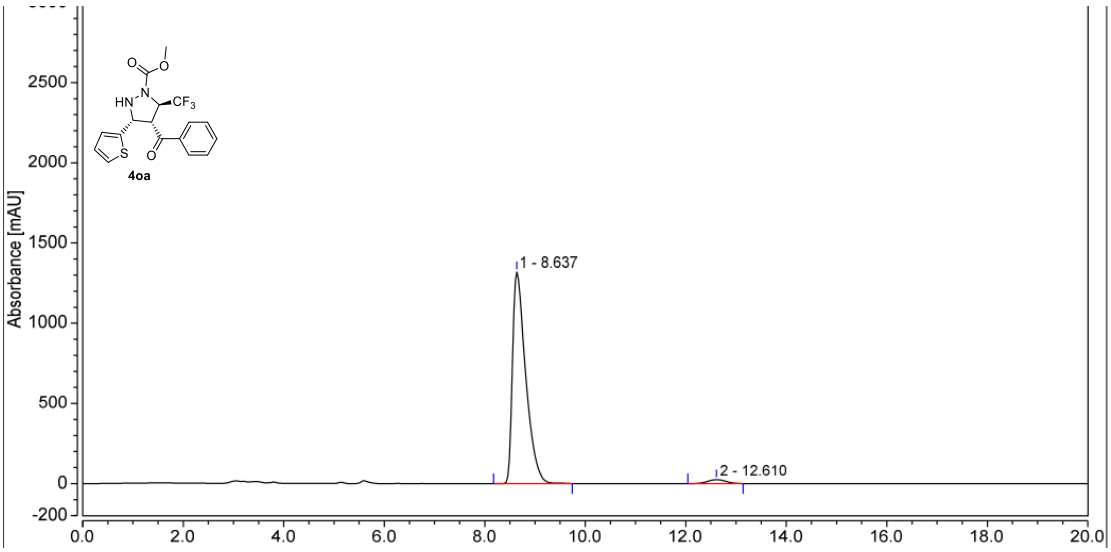


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.050	513.193	1826.240	97.20	97.70	n.a.
2		10.410	14.790	43.045	2.80	2.30	n.a.
Total:			**527.983**	**1869.285**	**100.00**	**100.00**	



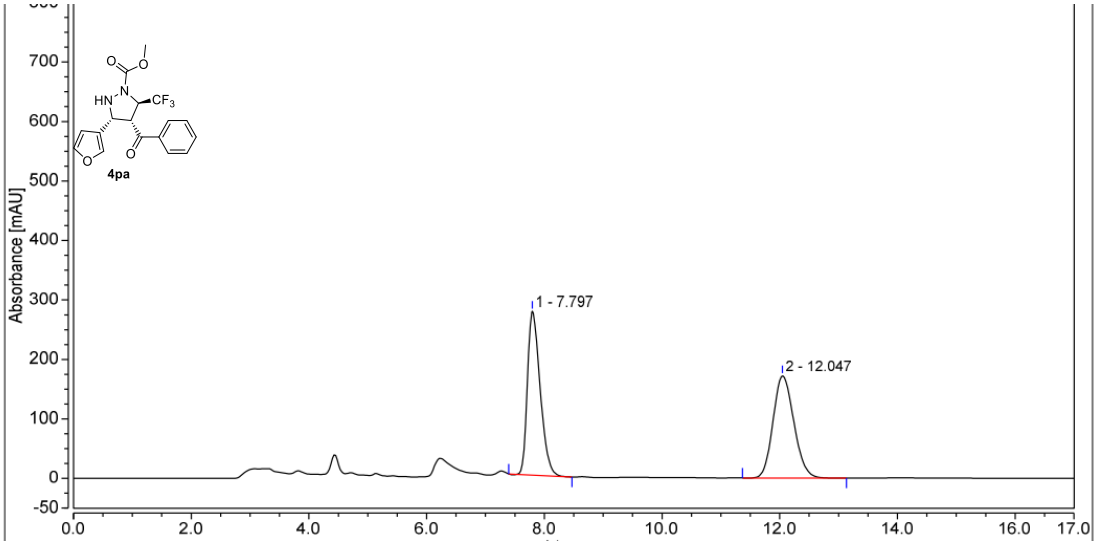
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.770	63.220	217.516	49.00	58.87	n.a.
2		12.557	65.803	151.939	51.00	41.13	n.a.
Total:			**129.023**	**369.455**	**100.00**	**100.00**	



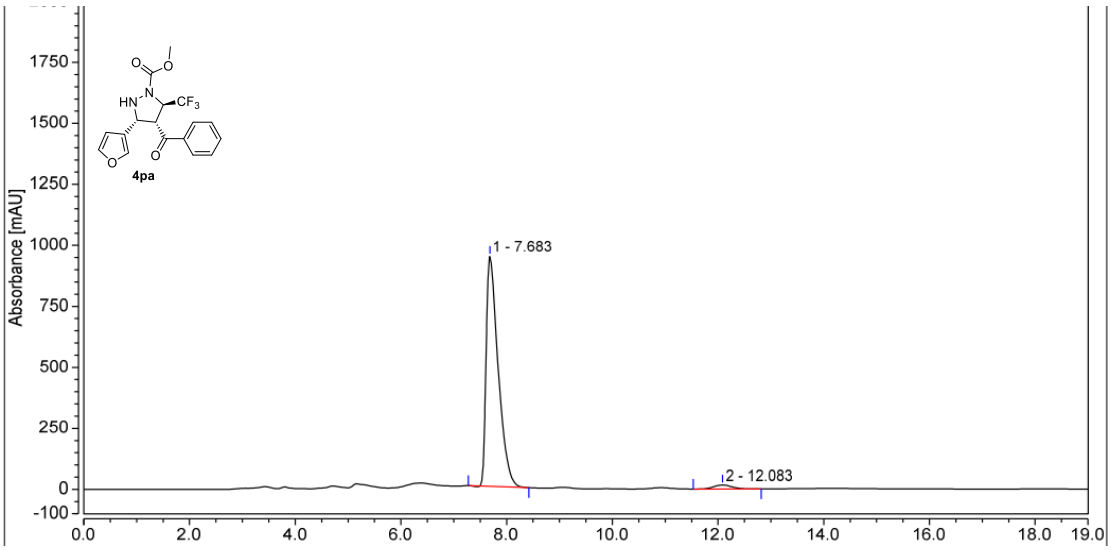
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.637	401.531	1320.163	97.48	98.17	n.a.
2		12.610	10.367	24.555	2.52	1.83	n.a.
Total:			**411.898**	**1344.718**	**100.00**	**100.00**	



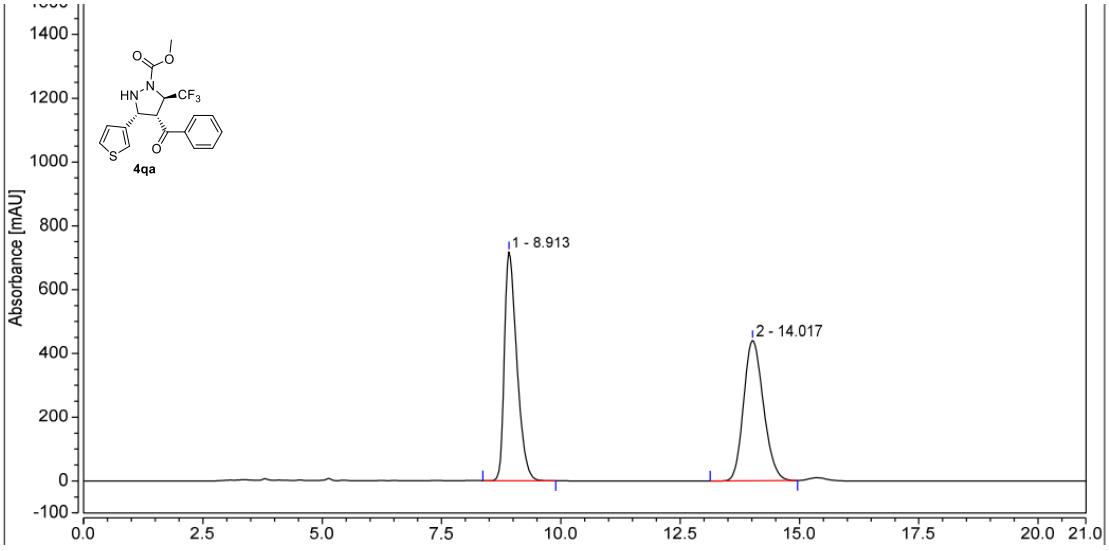
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.797	68.889	275.801	49.41	61.58	n.a.
2		12.047	70.531	172.055	50.59	38.42	n.a.
Total:			**139.420**	**447.855**	**100.00**	**100.00**	

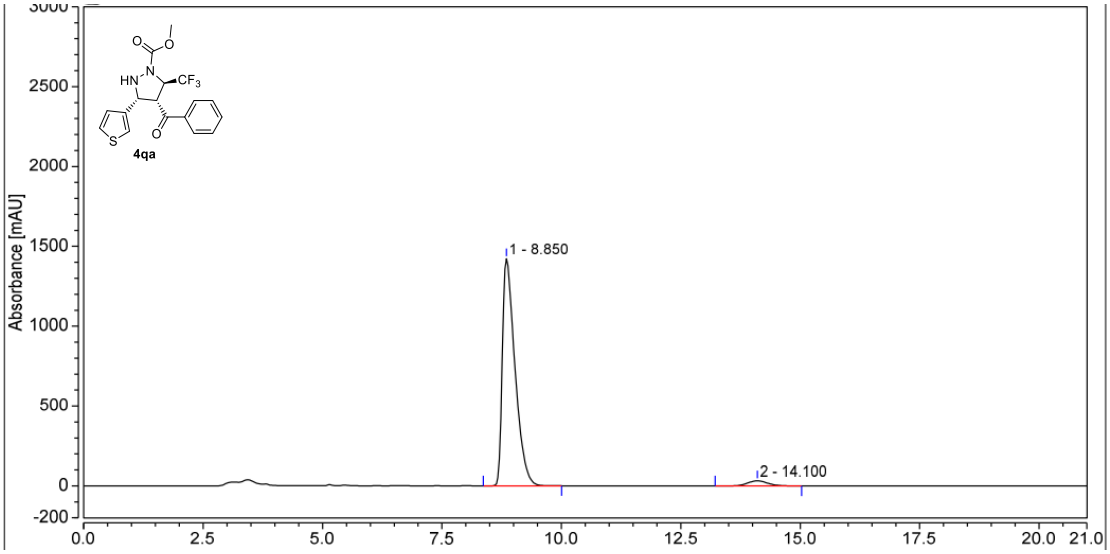


Integration Results

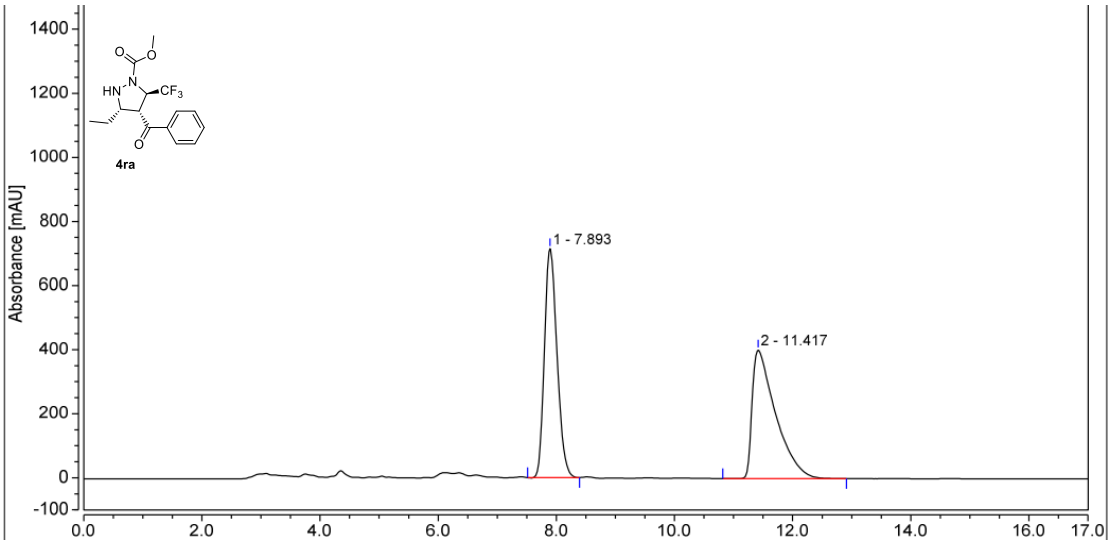
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.683	246.482	943.520	97.40	98.31	n.a.
2		12.083	6.580	16.185	2.60	1.69	n.a.
Total:			**253.062**	**959.705**	**100.00**	**100.00**	



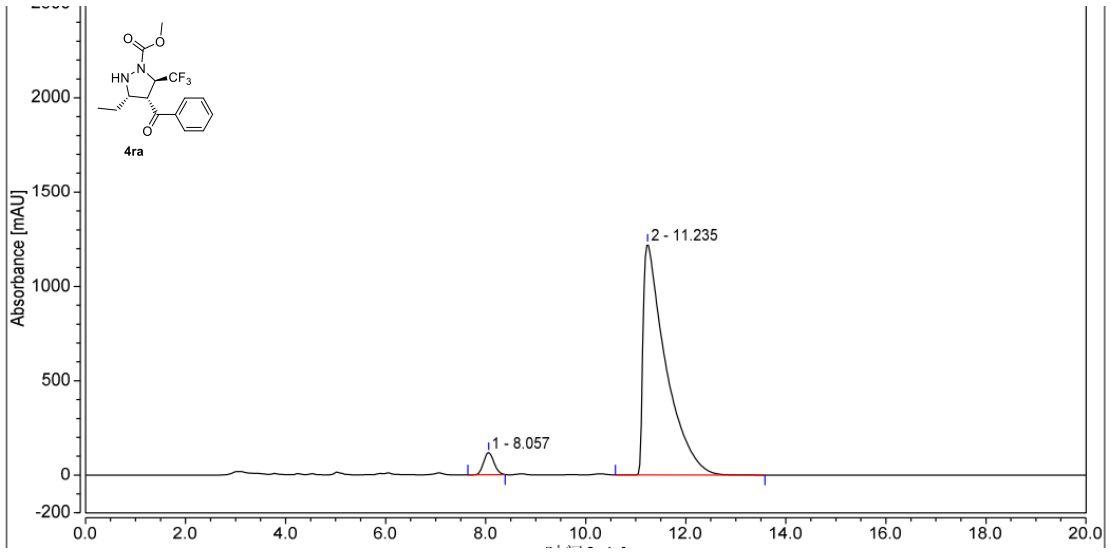
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.913	216.370	717.730	50.50	61.99	n.a.
2		14.017	212.120	440.178	49.50	38.01	n.a.
Total:			**428.489**	**1157.908**	**100.00**	**100.00**	



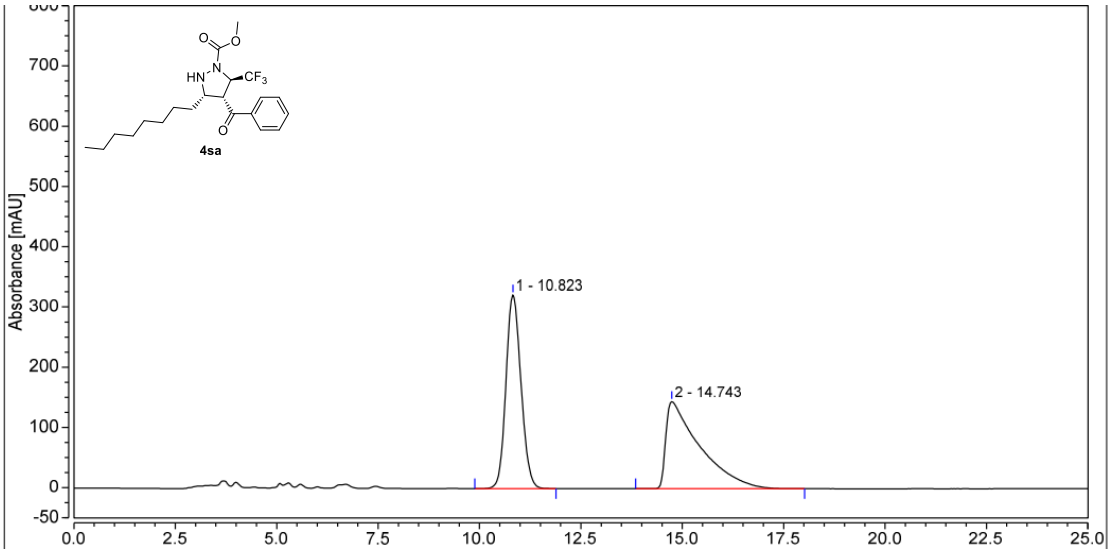
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.850	437.129	1421.702	96.61	97.81	n.a.
2		14.100	15.326	31.809	3.39	2.19	n.a.
Total:			**452.455**	**1453.511**	**100.00**	**100.00**	



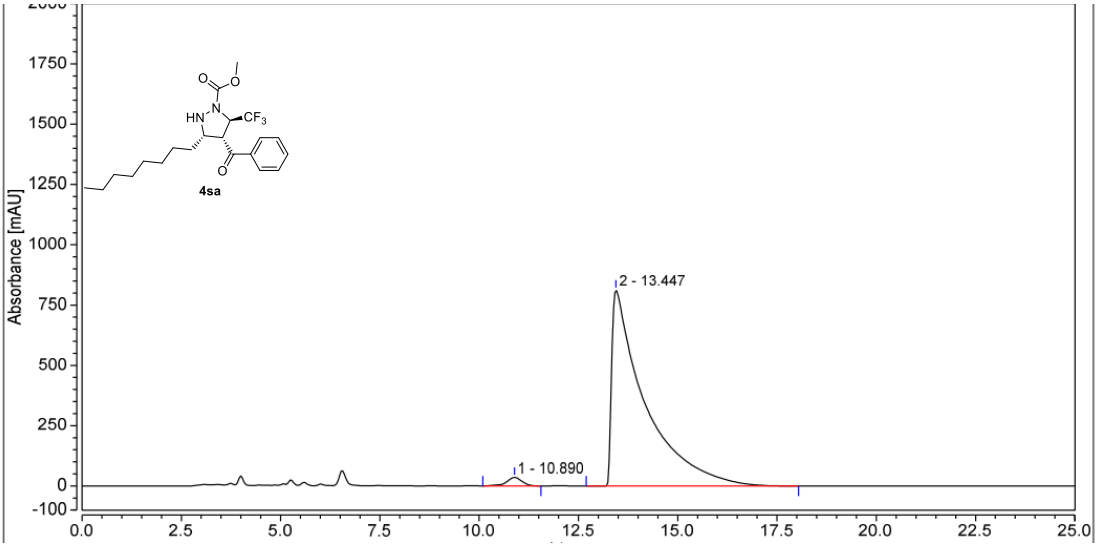
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.893	176.323	714.424	48.86	64.02	n.a.
2		11.417	184.533	401.461	51.14	35.98	n.a.
Total:			**360.857**	**1115.886**	**100.00**	**100.00**	



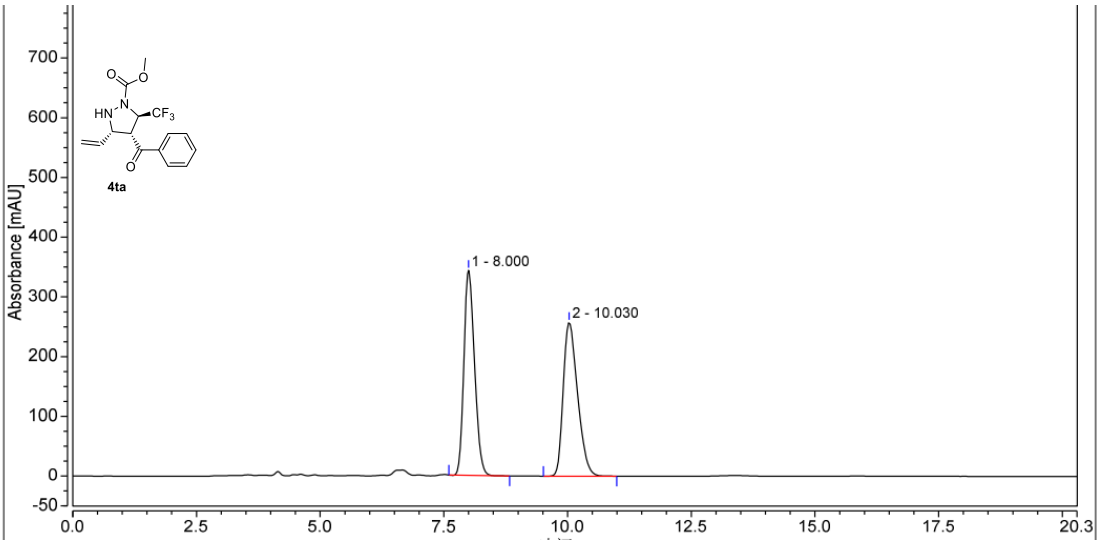
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.057	28.099	117.466	4.21	8.76	n.a.
2		11.235	639.291	1223.268	95.79	91.24	n.a.
Total:			**667.390**	**1340.735**	**100.00**	**100.00**	



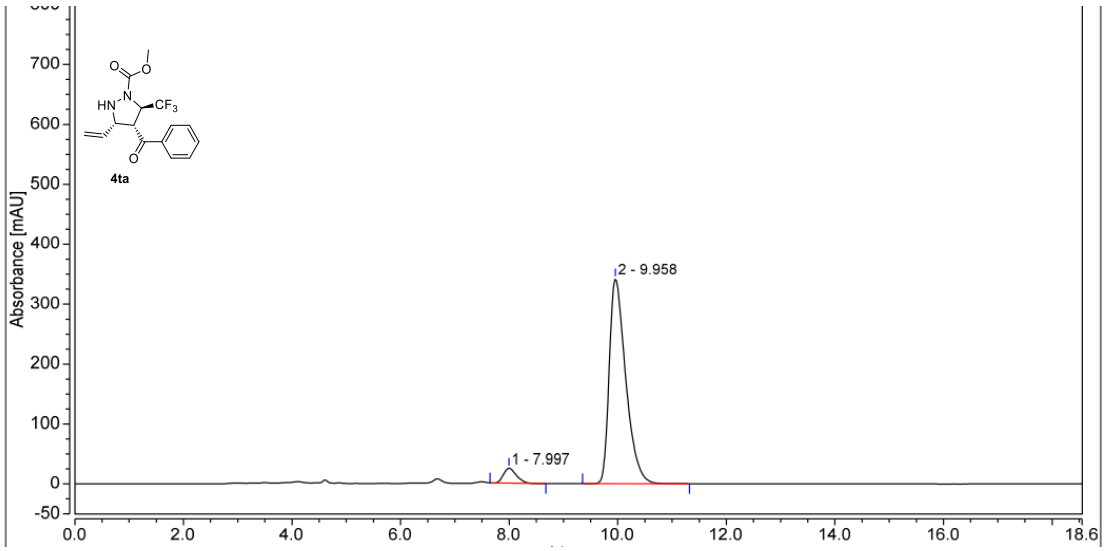
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.823	138.110	321.588	49.68	68.96	n.a.
2		14.743	139.904	144.731	50.32	31.04	n.a.
Total:			**278.014**	**466.319**	**100.00**	**100.00**	



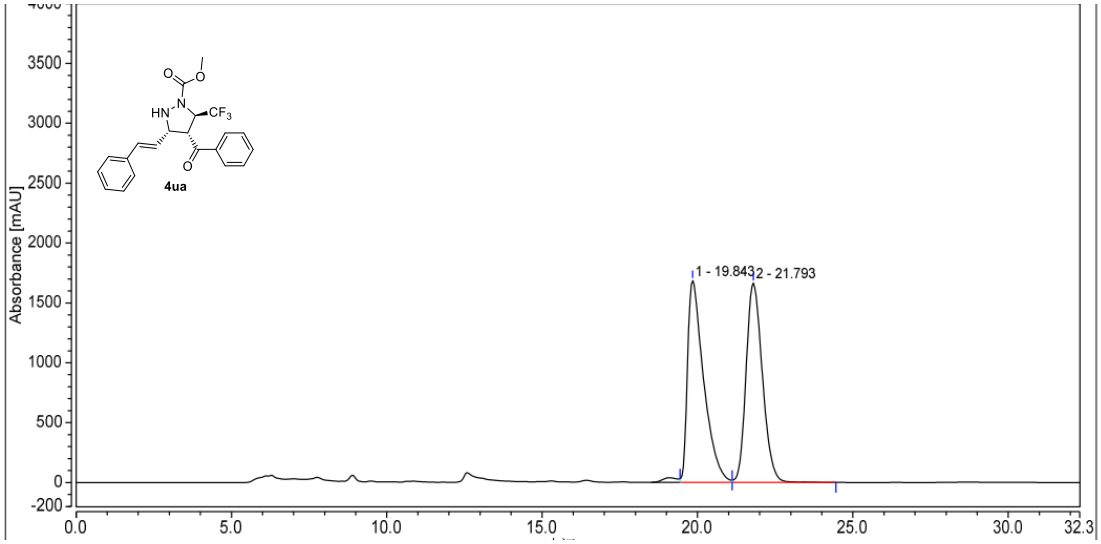
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.890	15.713	34.954	1.97	4.13	n.a.
2		13.447	781.597	811.956	98.03	95.87	n.a.
Total:			**797.310**	**846.910**	**100.00**	**100.00**	



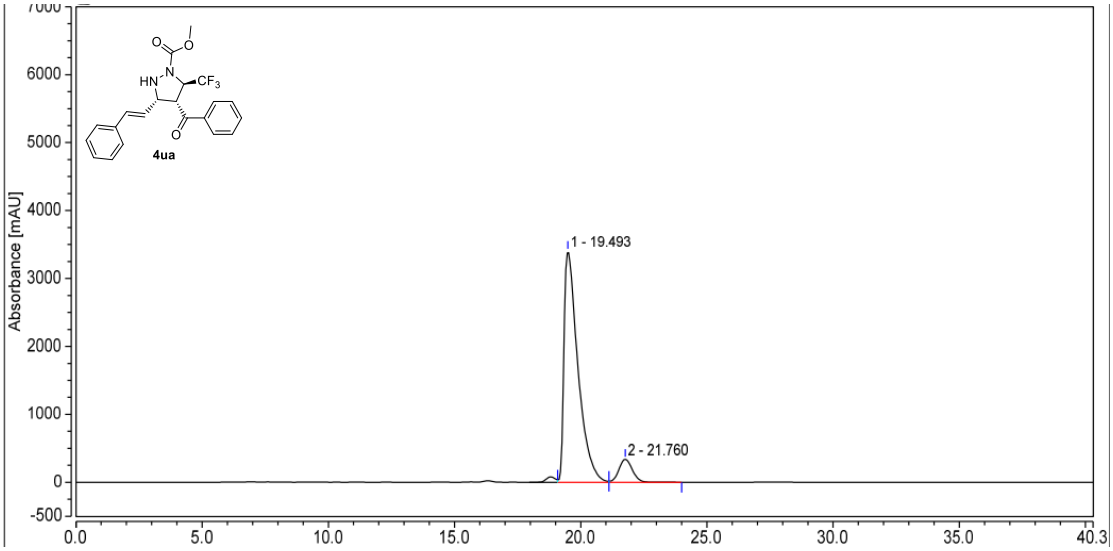
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.000	85.631	343.187	49.78	57.13	n.a.
2		10.030	86.396	257.524	50.22	42.87	n.a.
Total:			**172.026**	**600.711**	**100.00**	**100.00**	



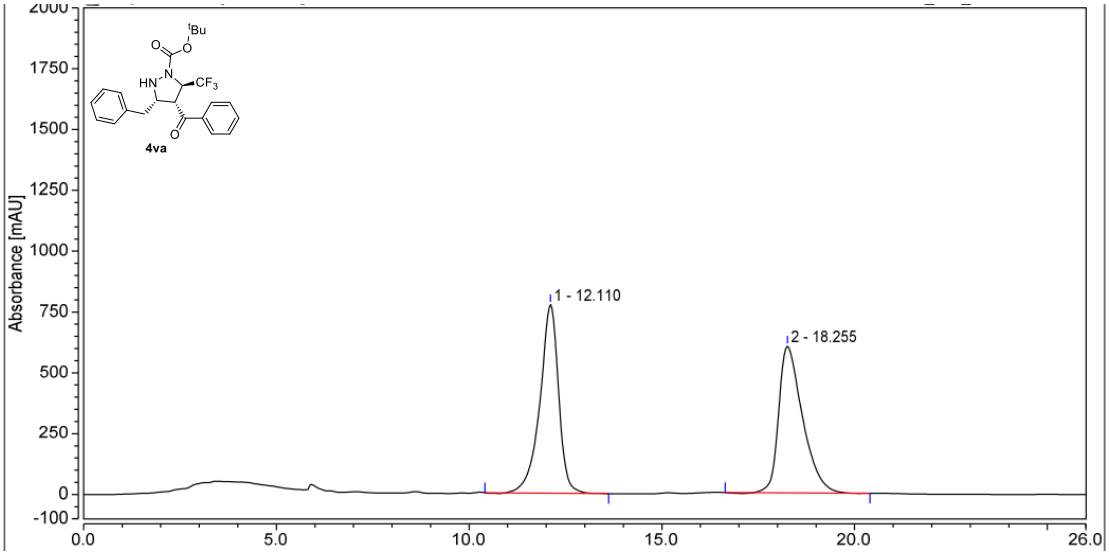
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.997	6.856	25.008	5.39	6.81	n.a.
2		9.958	120.323	341.949	94.61	93.19	n.a.
Total:			**127.179**	**366.957**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.843	1013.327	1685.344	50.04	50.32	n.a.
2		21.793	1011.797	1663.623	49.96	49.68	n.a.
Total:			**2025.124**	**3348.967**	**100.00**	**100.00**	

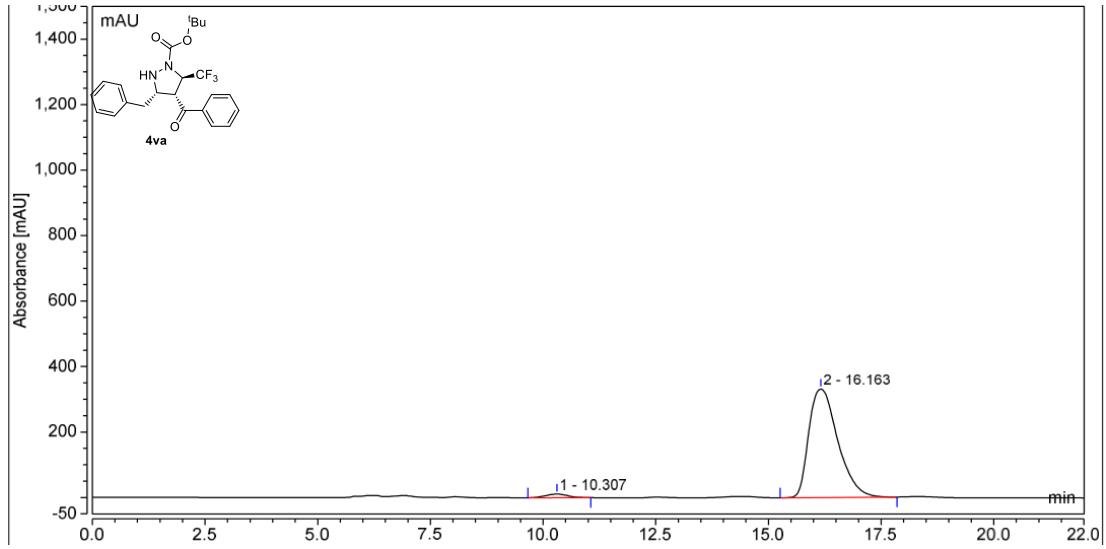


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.493	2171.594	3397.164	91.16	90.95	n.a.
2		21.760	210.521	338.028	8.84	9.05	n.a.
Total:			**2382.115**	**3735.192**	**100.00**	**100.00**	



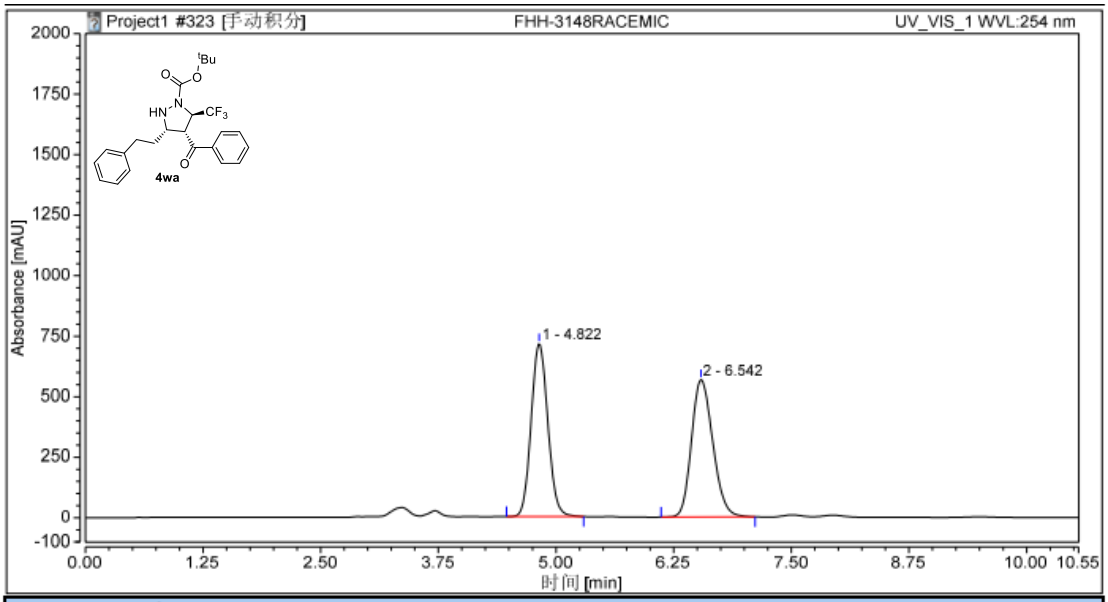
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.110	436.011	775.523	50.24	56.24	n.a.
2		18.255	431.778	603.376	49.76	43.76	n.a.
Total:			**867.788**	**1378.899**	**100.00**	**100.00**	



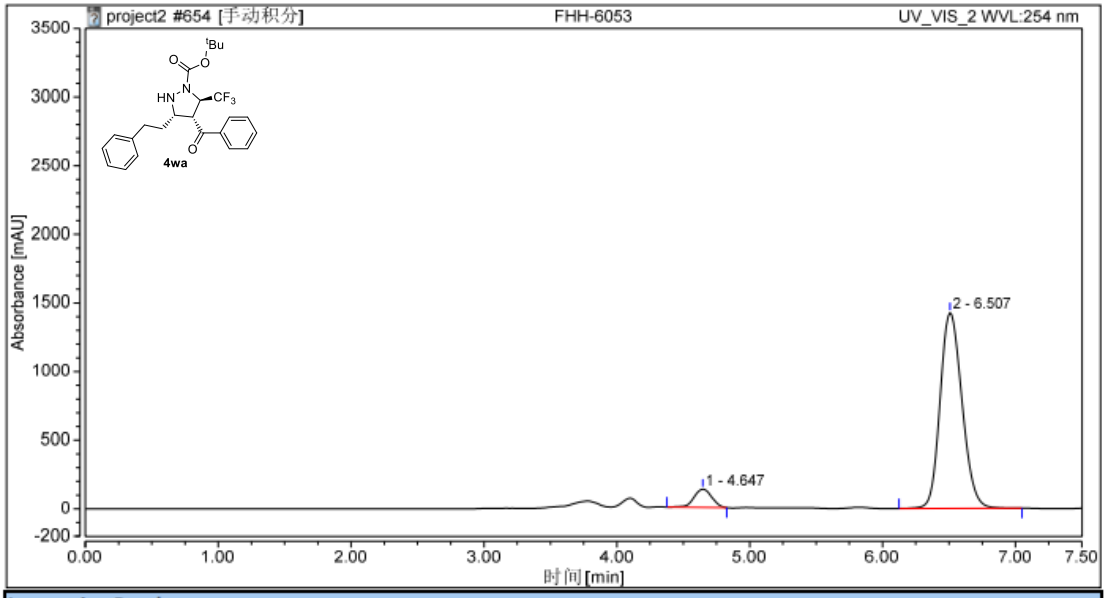
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.307	6.235	11.077	2.46	3.24	n.a.
2		16.163	247.464	331.312	97.54	96.76	n.a.
Total:			**253.700**	**342.389**	**100.00**	**100.00**	



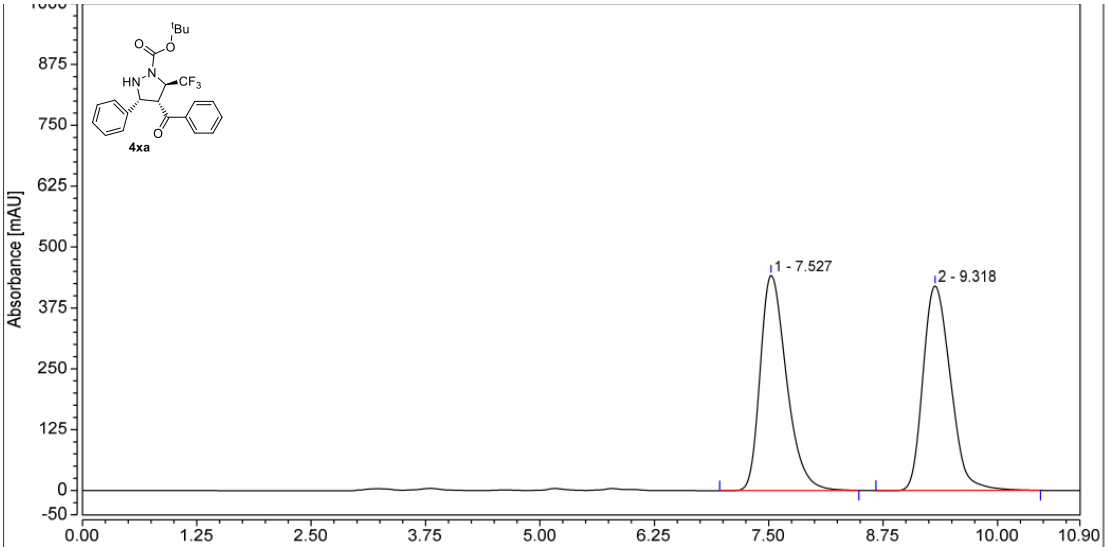
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.822	147.014	714.181	49.67	55.71	n.a.
2		6.542	148.986	567.877	50.33	44.29	n.a.
Total:			**296.000**	**1282.058**	**100.00**	**100.00**	

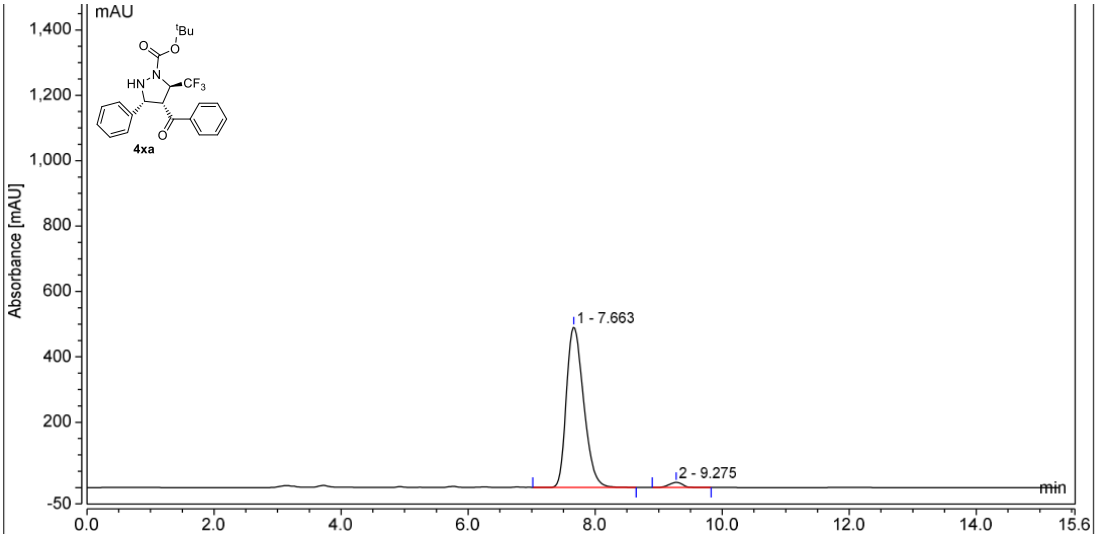


Integration Results

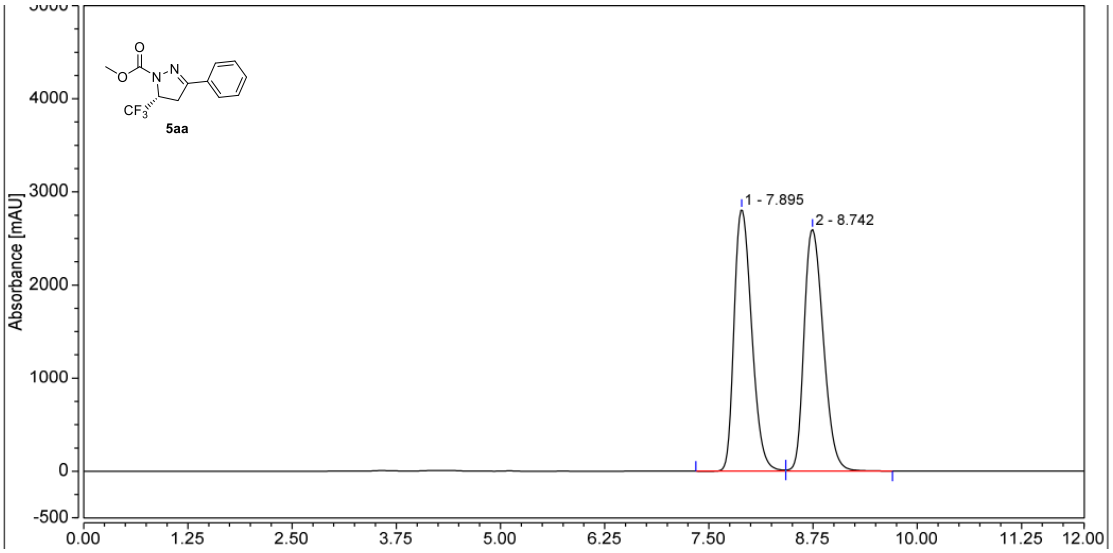
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.647	20.714	133.587	7.11	8.56	n.a.
2		6.507	270.475	1426.269	92.89	91.44	n.a.
Total:			**291.189**	**1559.855**	**100.00**	**100.00**	



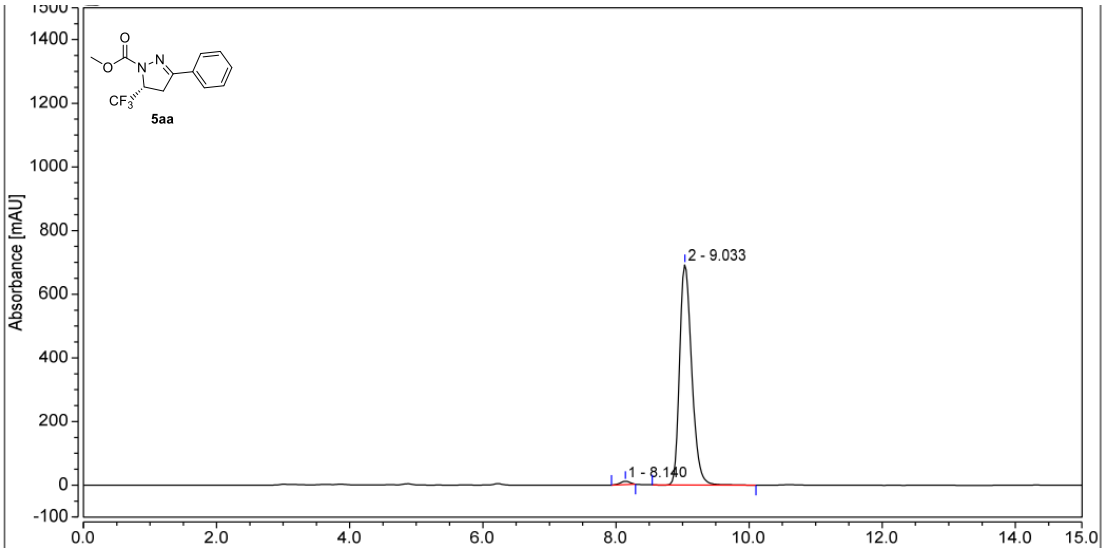
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.527	146.452	442.241	50.01	51.26	n.a.
2		9.318	146.375	420.491	49.99	48.74	n.a.
Total:			**292.827**	**862.732**	**100.00**	**100.00**	



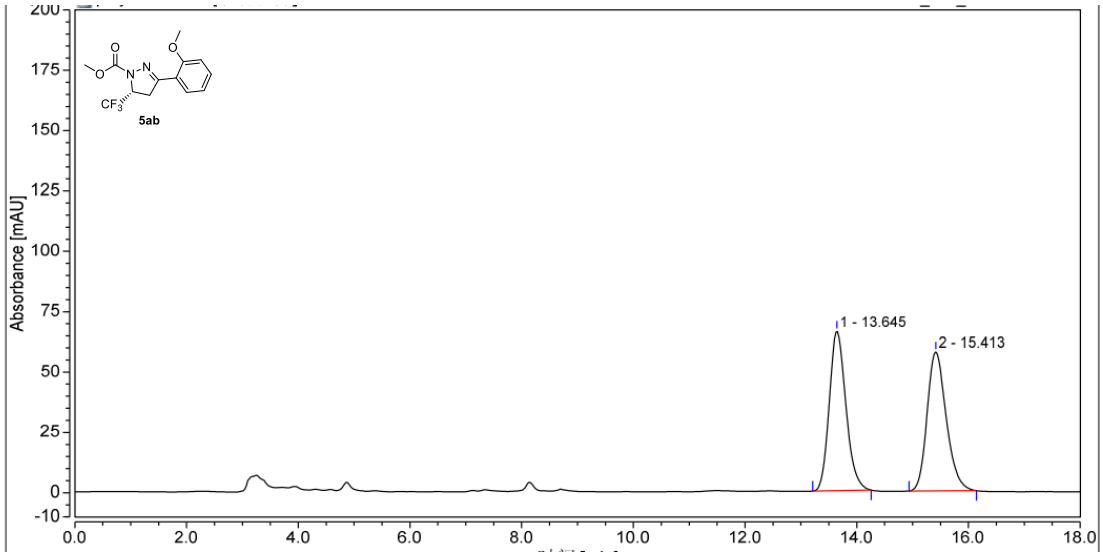
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.663	154.417	490.769	97.50	96.92	n.a.
2		9.275	3.960	15.584	2.50	3.08	n.a.
Total:			**158.377**	**506.353**	**100.00**	**100.00**	



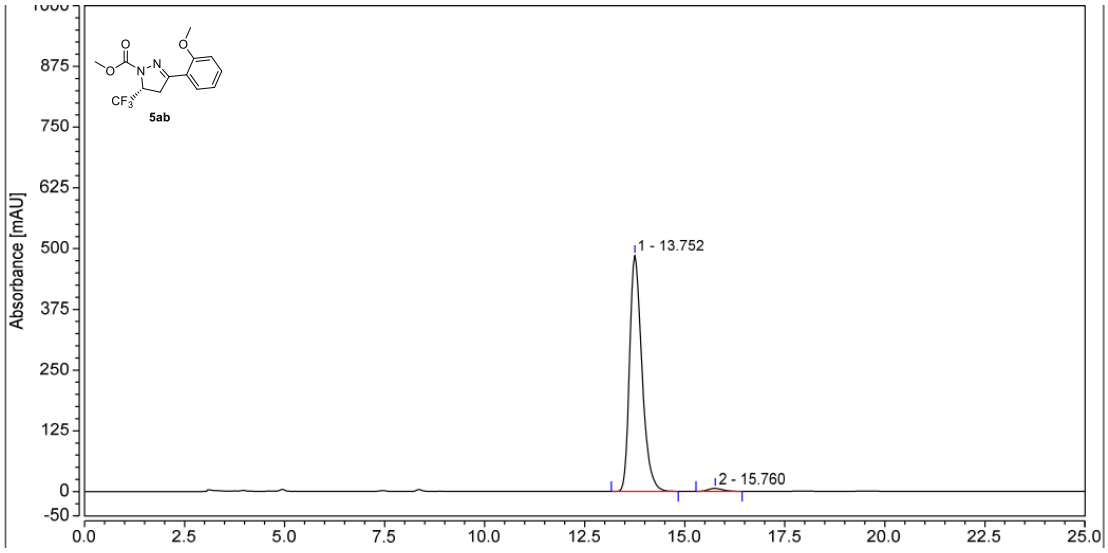
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.895	688.247	2810.642	49.72	51.97	n.a.
2		8.742	695.957	2597.203	50.28	48.03	n.a.
Total:			**1384.204**	**5407.845**	**100.00**	**100.00**	



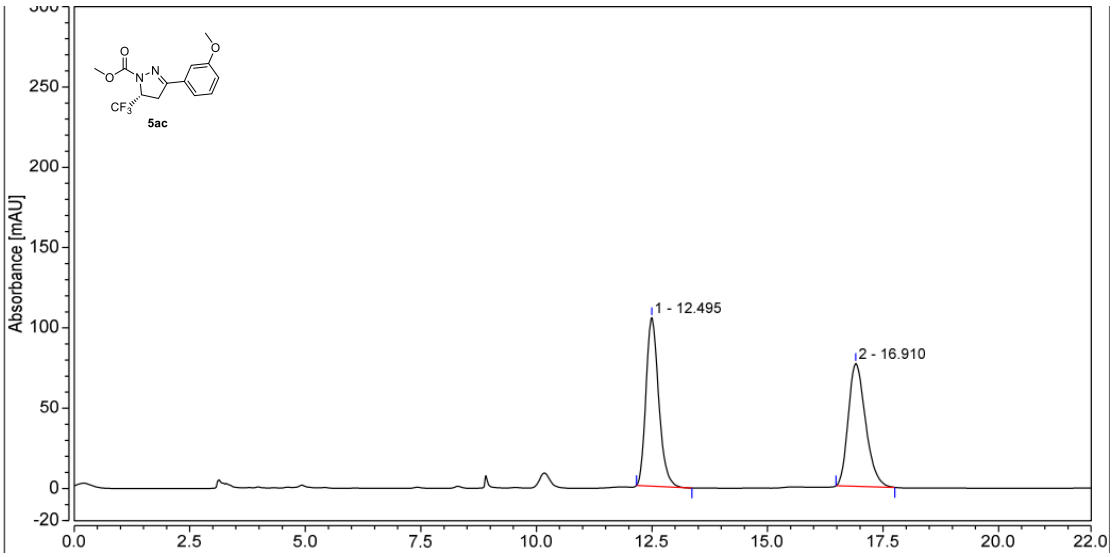
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.140	1.714	10.252	1.16	1.46	n.a.
2		9.033	145.662	692.290	98.84	98.54	n.a.
Total:			**147.375**	**702.542**	**100.00**	**100.00**	



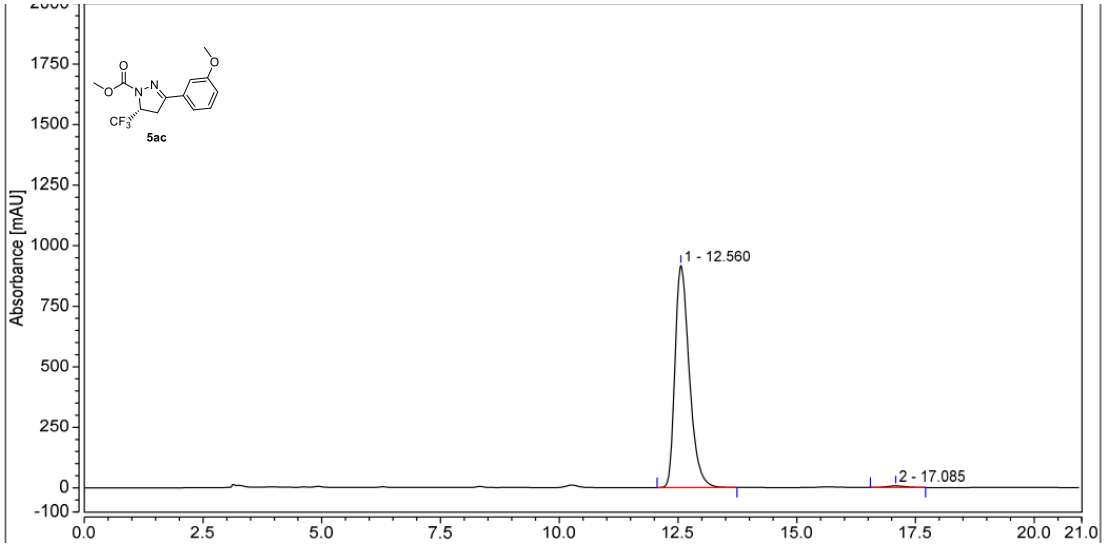
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.645	22.890	66.115	50.07	53.45	n.a.
2		15.413	22.825	57.571	49.93	46.55	n.a.
Total:			**45.714**	**123.686**	**100.00**	**100.00**	



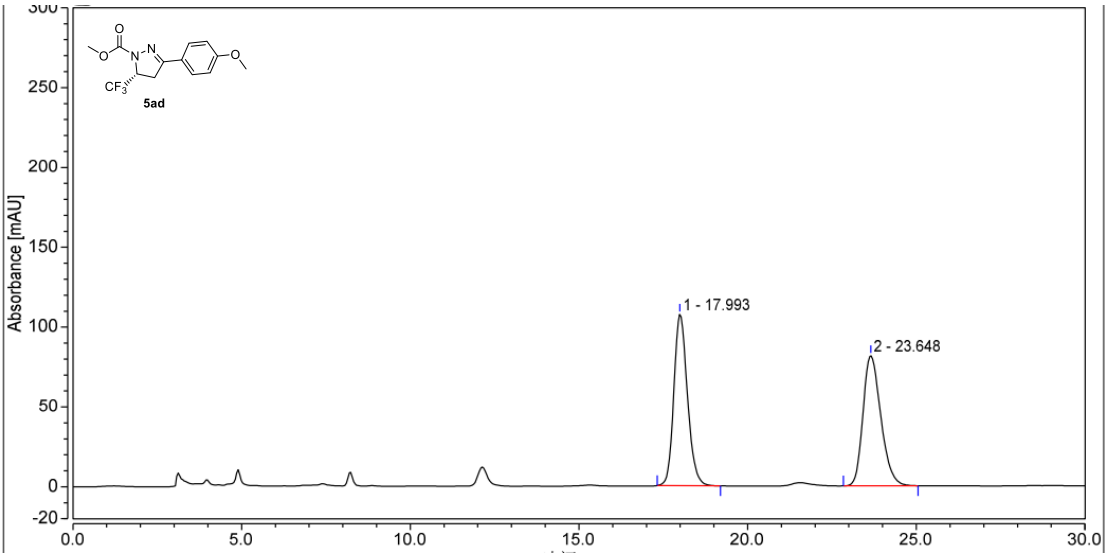
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.752	173.918	485.946	98.54	98.74	n.a.
2		15.760	2.568	6.211	1.46	1.26	n.a.
Total:			**176.487**	**492.157**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.495	33.517	104.985	50.19	57.84	n.a.
2		16.910	33.266	76.536	49.81	42.16	n.a.
Total:			**66.783**	**181.521**	**100.00**	**100.00**	

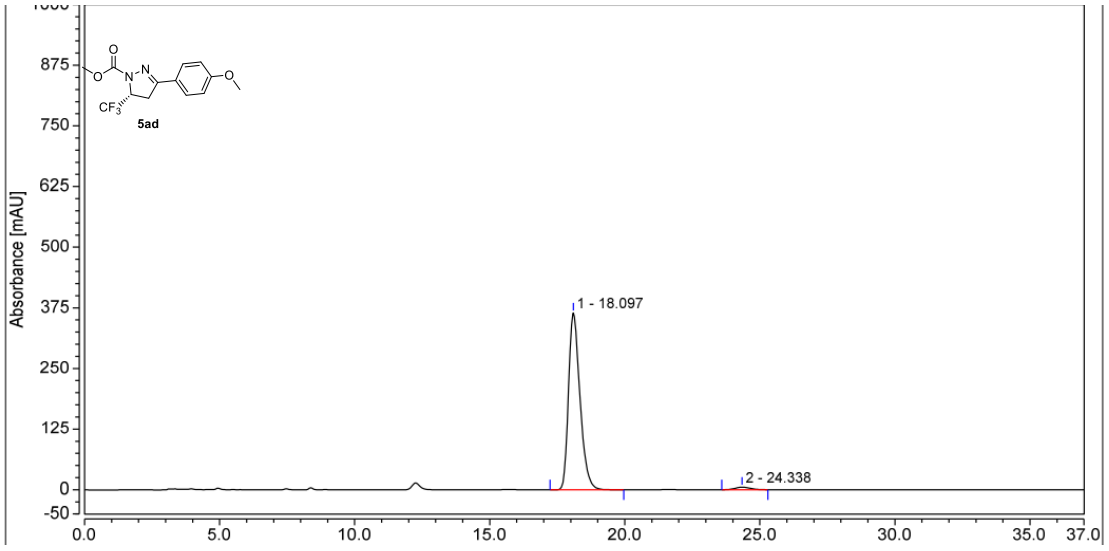


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.560	320.533	917.082	99.08	99.26	n.a.
2		17.085	2.982	6.804	0.92	0.74	n.a.
Total:			**323.515**	**923.886**	**100.00**	**100.00**	



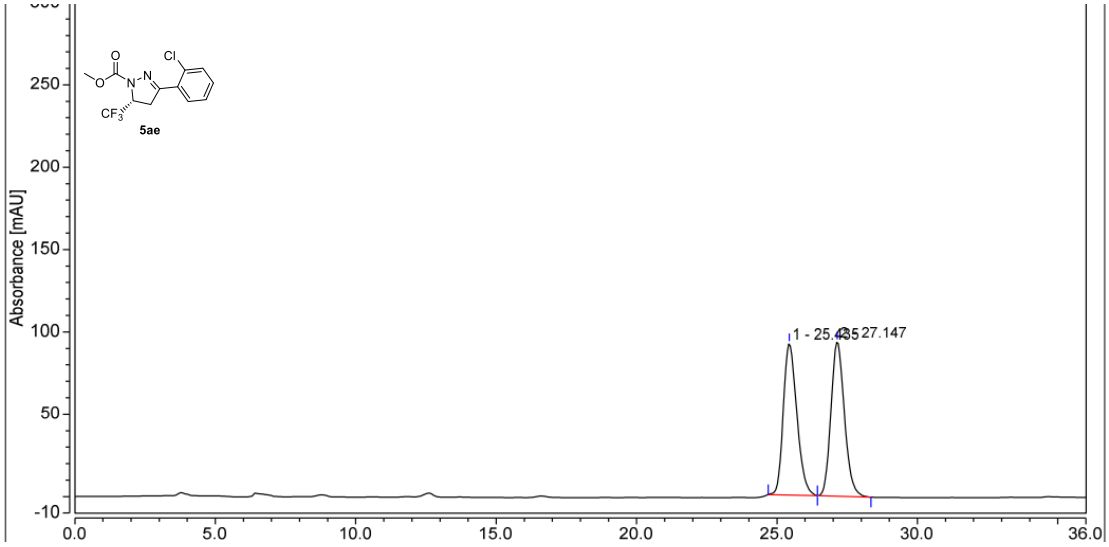
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.993	50.195	107.509	50.10	56.86	n.a.
2		23.648	49.992	81.581	49.90	43.14	n.a.
Total:			**100.187**	**189.090**	**100.00**	**100.00**	

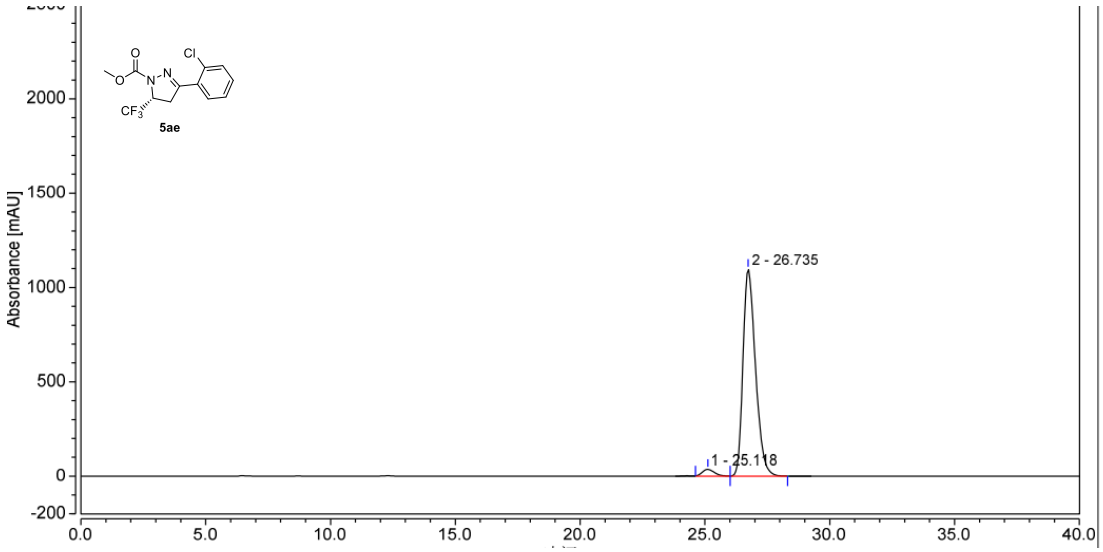


Integration Results

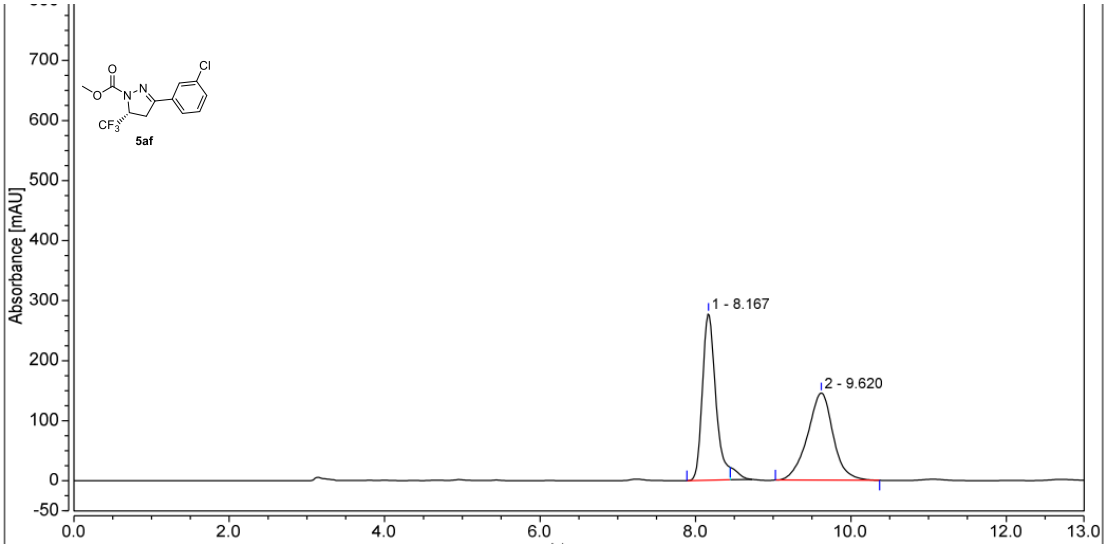
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.097	179.621	364.531	98.12	98.60	n.a.
2		24.338	3.439	5.184	1.88	1.40	n.a.
Total:			**183.060**	**369.716**	**100.00**	**100.00**	



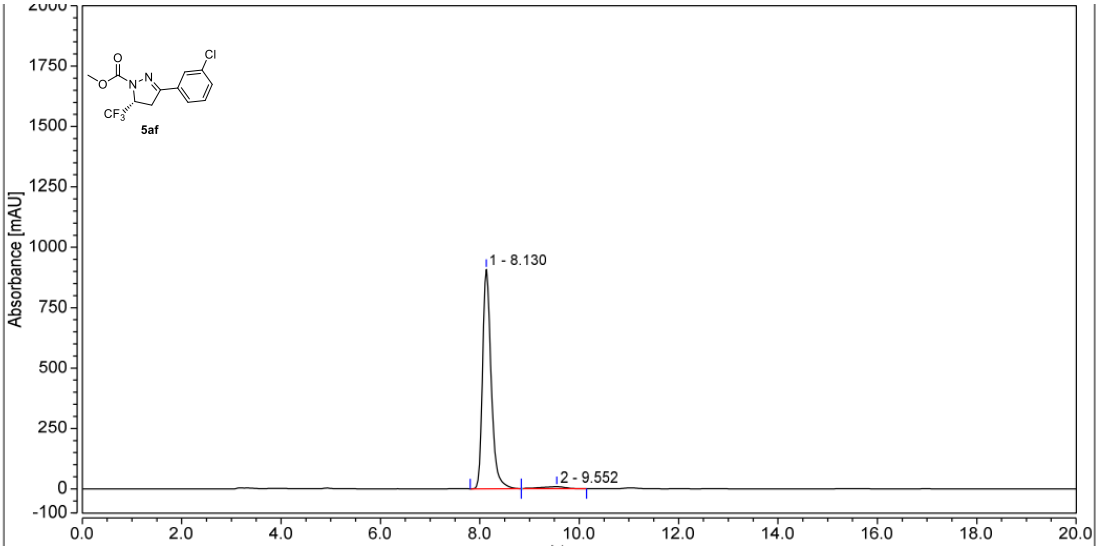
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25.435	51.494	91.962	49.64	49.52	n.a.
2		27.147	52.231	93.736	50.36	50.48	n.a.
Total:			**103.724**	**185.699**	**100.00**	**100.00**	



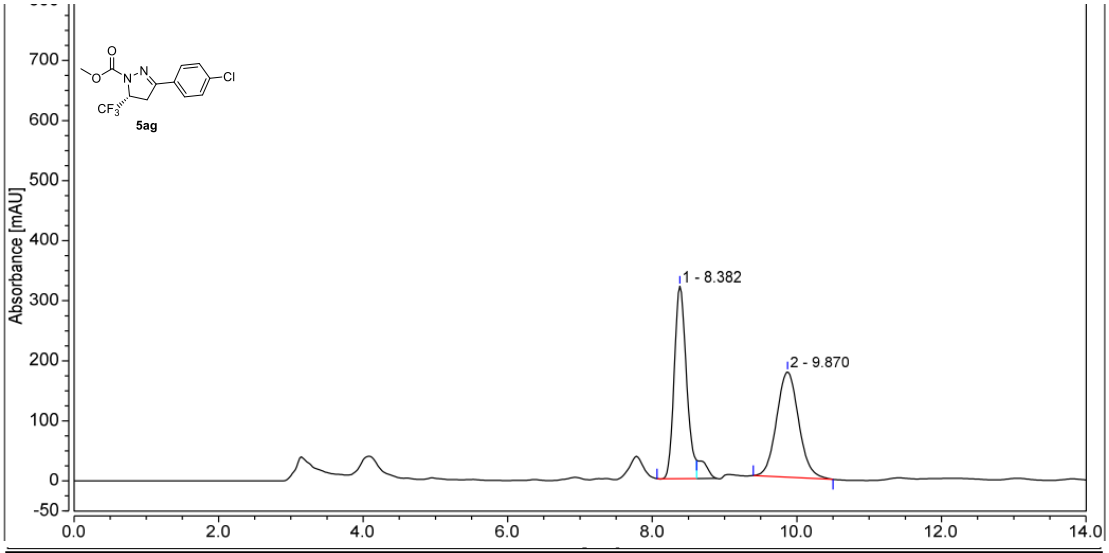
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25.118	20.970	36.274	3.19	3.20	n.a.
2		26.735	636.923	1097.510	96.81	96.80	n.a.
Total:			**657.893**	**1133.784**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.167	55.011	278.026	49.77	65.67	n.a.
2		9.620	55.518	145.336	50.23	34.33	n.a.
Total:			**110.529**	**423.363**	**100.00**	**100.00**	

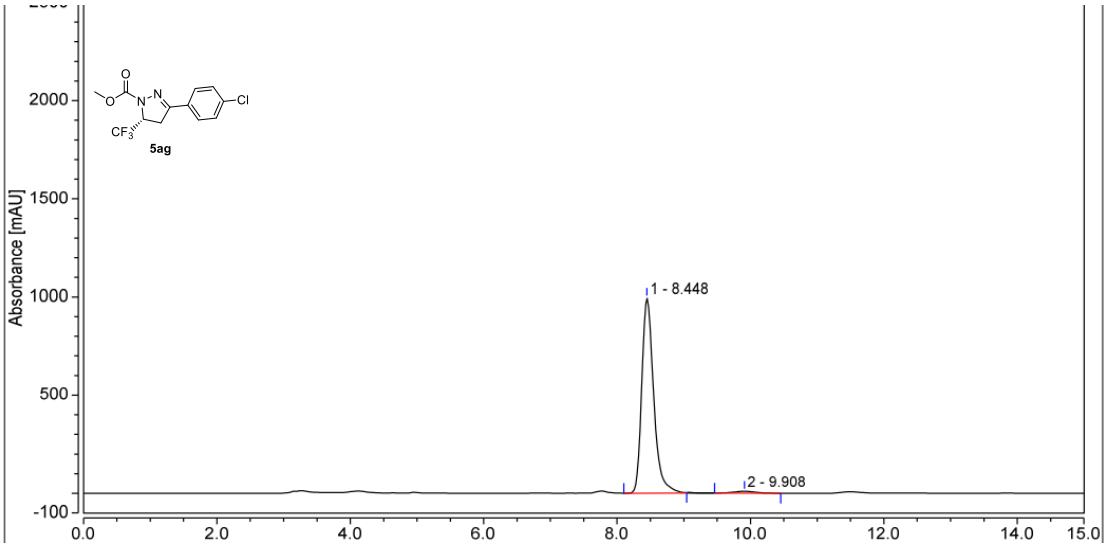


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.130	182.736	908.092	97.27	99.07	n.a.
2		9.552	5.128	8.549	2.73	0.93	n.a.
Total:			**187.864**	**916.640**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.382	62.880	320.365	50.38	64.64	n.a.
2		9.870	61.928	175.261	49.62	35.36	n.a.
Total:			**124.808**	**495.626**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.448	206.147	993.950	98.29	99.04	n.a.
2		9.908	3.587	9.609	1.71	0.96	n.a.
Total:			**209.734**	**1003.559**	**100.00**	**100.00**	