Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-light Induced [1, 3]-Brook Rearrangements of α-Ketoacylsilanes and Its Subsequent Trapping in a Tandem Annulation with 1, 3, 5-Triazinanes and Azomethine Imines

Zhong Zhang, Sirui Wu, Yuqiao Zhou, Bao-Lin Li, Siyue Xiao, Xiaohu Zhao* and Zhipeng Yu*

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China.

E-mail: xhzhao@scu.edu.cn; zhipengy@scu.edu.cn

Table of Contents

1. General remarks

Reaction Materials: Unless otherwise noted, all solvents and chemicals were purchased from commercial suppliers and used directly without further purification. Anhydrous solvents (CH_2Cl_2, Toluene and THF) were purified by distillation over the standard drying agents.

NMR-Spectra: The ^{1}H, ^{13}C spectra were recorded on commercial Bruker ASCENDTM^{TM} (400 or 600 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1} H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; DMSO-d_6, 2.50 ppm for ^{1} H NMR and 39.5 ppm for ^{13}C NMR). Shifts multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs. = broad.

High-Resolution Mass Spectra (HRMS): HRMS were recorded on Thermo Q-Exactive Focus (FTMS+*c* ESI).

Photoreactor Setup: Photochemical reactions were carried out using a commercial photoreactor equipped with 10 x 10 W blue LEDs as light sources (Emission maximum: 460 nm, as seen in Figure S1) in a WP-TEC-1020 parallel reactor from WATTCAS^{TM}, China.

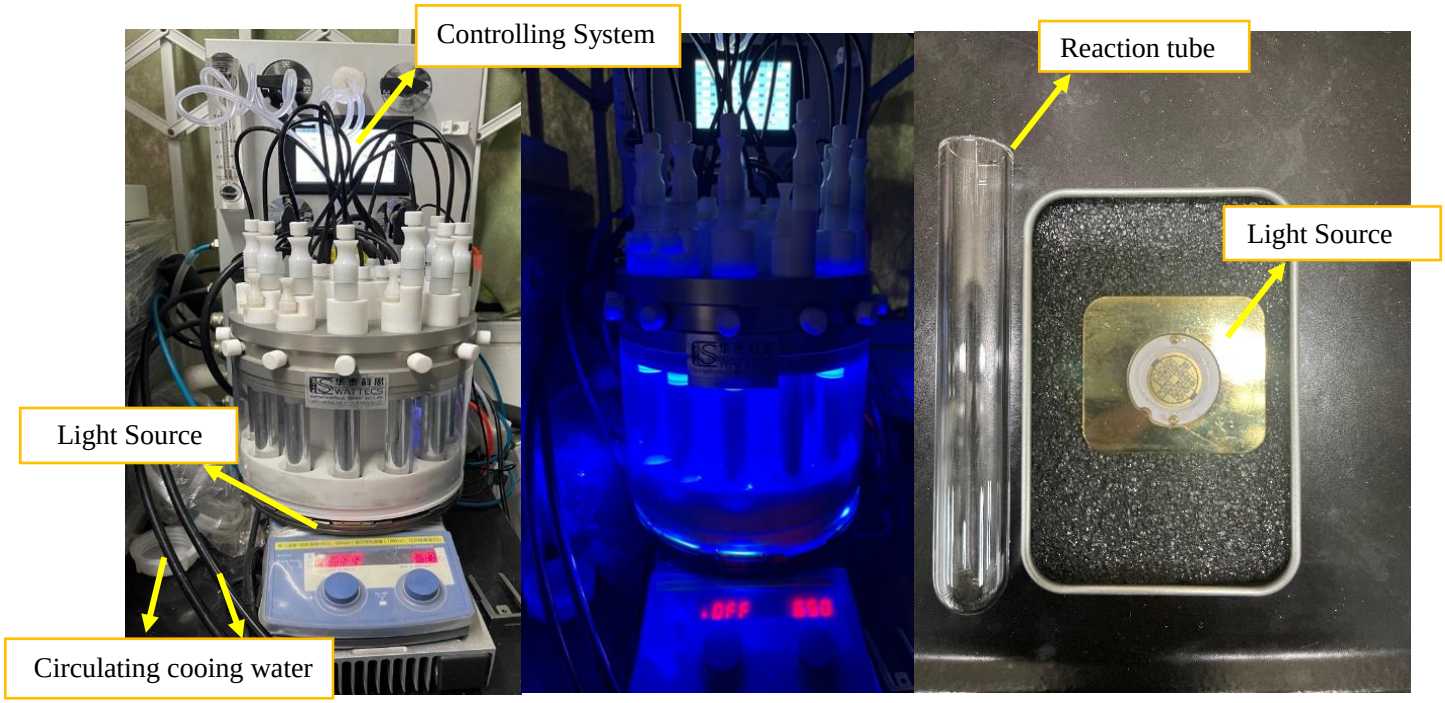


Figure S1. Setup of the photoreactor

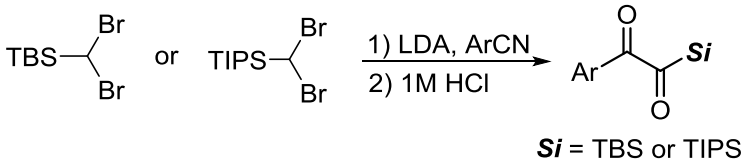
Light source: 10w blue LEDs was purchased from WATTCAS^{TM}, China.

Regular round bottom reaction tubes (15 mL) were used as reaction vessels except for bigger scales, the circulating cooling water to maintain the temperature inside the photoreactor constant. Material of the irradiation vessel: borosilicate reaction tube. Distance from the light source to the irradiation vessel: ~2.0 cm. (Not use any filters).

2. General procedure for the synthesis of substrates:

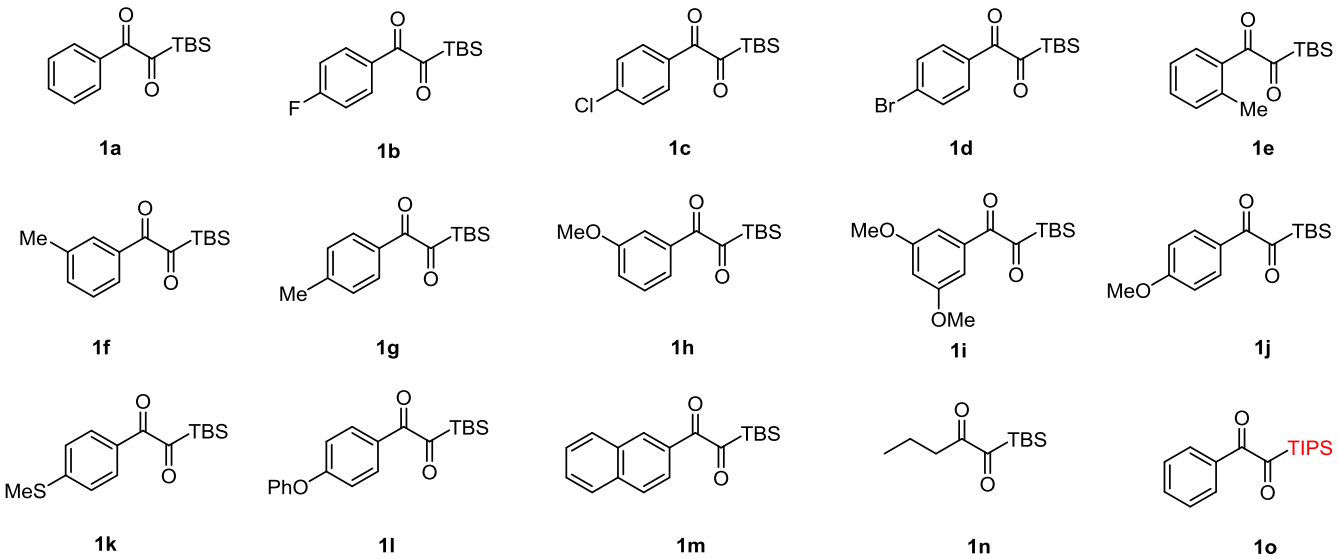
2.1 Synthesis *α*-ketoacylsilanes

The *α*-ketoacylsilane **1a-1m** and **1o** are prepared by the following procedure according to literature reports. [1-2]



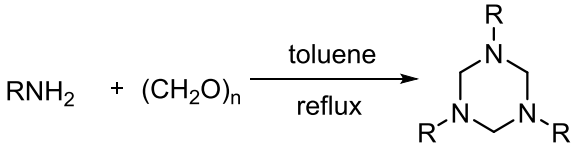
Si = TBS or TIPS

General procedure: A solution of *tert*-butyldibromomethyldimethylsilane (2.85 g, 10.0 mmol) or triisopropyldibromomethylsilane (3.27 g, 10.0 mmol) in dry THF (30 mL) was added to a solution of LDA (20.0 mmol, 2 M.) in THF (30 mL) at -78 °C. After stirred for 1 h at -78 °C, the solution turned yellow gradually. The arylnitrile (2.48 g, 24 mmol.) was added to the mixture at -78 °C. Then the mixture was stirred at same temperature for 6 h, after the reaction is completed. The reaction mixture was quenched with aqueous HCl (50 mL, 1.0 M). After stirred for 15 min at room temperature, the organic phrase turned dark red during this period. The mixture was extracted three times with hexane/ethyl acetate (10/1, 20 mL each time). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by chromatography on a silica gel column afforded the corresponding product. The alkyl α-ketoacylsilane **1n** are prepared by the reported procedure.[2]

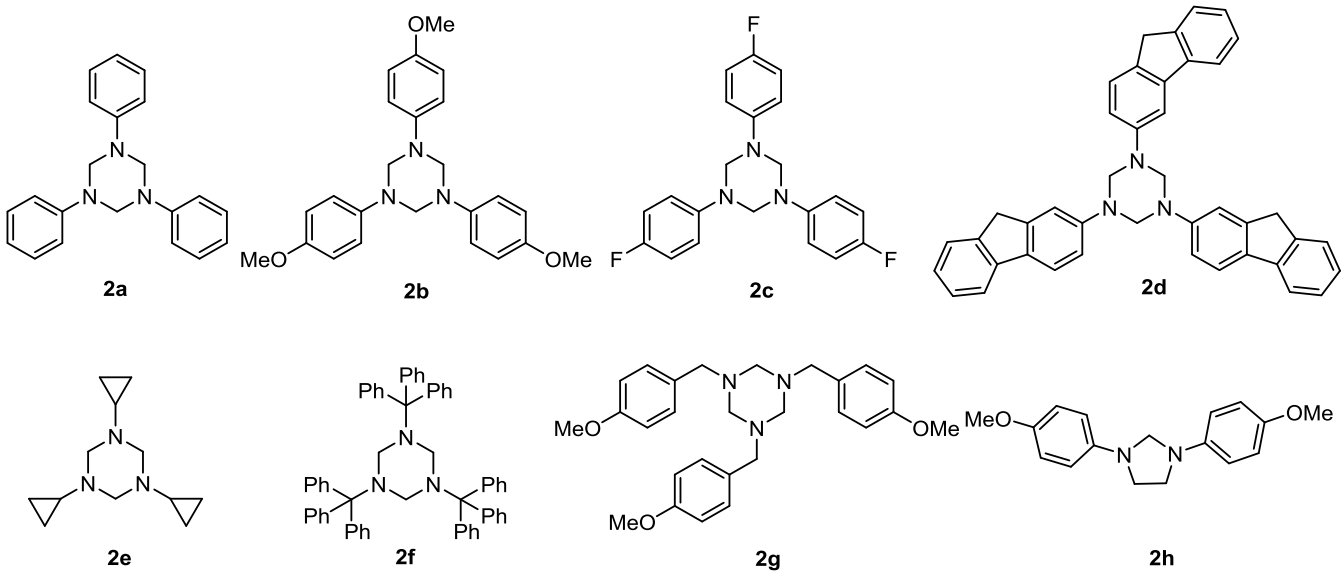


2.2 Synthesis of 1,3,5-triazinane

The 1,3,5-triazinanes **2a-2g** are prepared by the literature reports. [3-5]



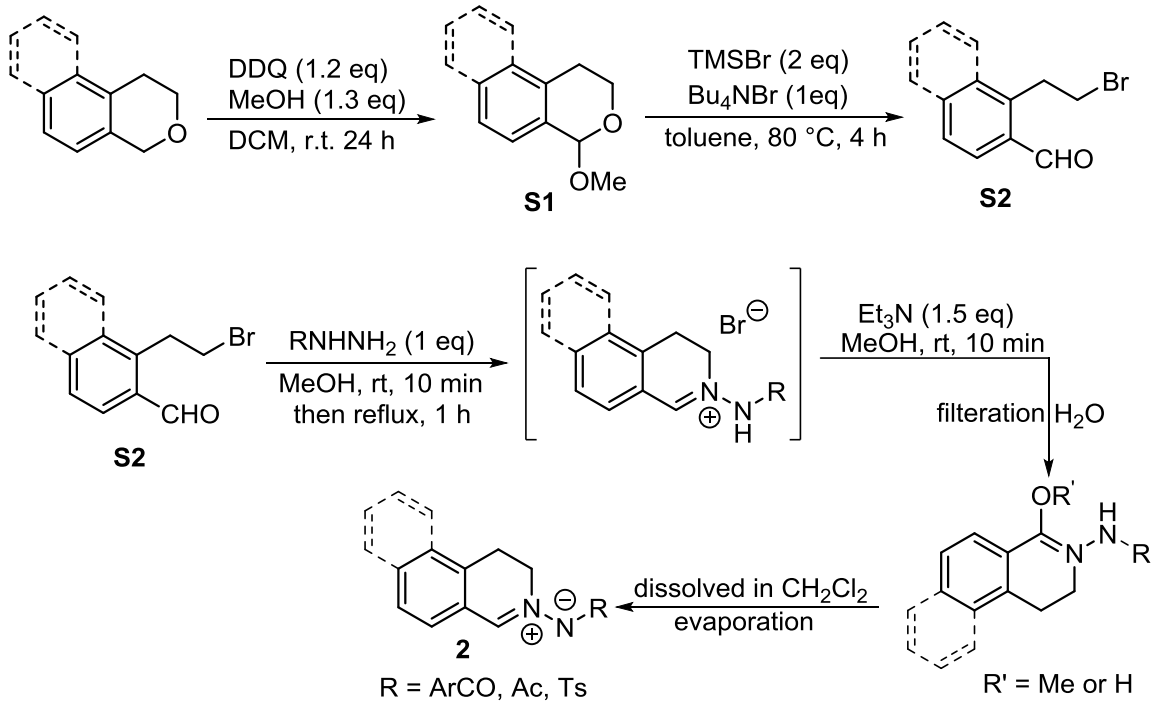
General procedure: Amines (10 mmol, 1 eq) was added to paraformaldehyde (13 mmol, 1.3 eq) in toluene (30 mL). The mixture was heated with refluxing for 2 hours, and concentrated under reduced pressure at 50 °C, until a precipitate came out from the mixture. The precipitate was collected by filtration, washed with n-hexane several times, the precipitate was dried to obtain 1,3,5-triazinanes.



The compound **2h** was synthesized via the known report[6]

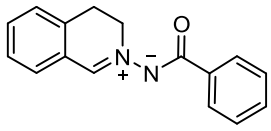
2.3 Synthesis C,N-Cyclic Azomethine Imines

The C,N-Cyclic Azomethine Imines are prepared by the literature reports. [7-9]



General procedure: MeOH (1.6 mL, 39.6 mmol) and isochroman (3.8 mL, 29.8 mmol) were added to a solution of DDQ (8.06 g, 35.8 mmol) in CH_2Cl_2 (200 mL), After stirred at room temperature for 24 h, quenched with of saturated $NaHCO_3$ (aq) and filtered through Celite. The aqueous layer was extracted with CH_2Cl_2 (2 × 60 mL), and then the combined organic layers were washed three times with brine (50 mL each time), dried by Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the yellow oil **S1**. Then 1-methoxyisochroman **S1** (1M in toluene) were added Bu_4NBr (1 eq) and TMSBr (2 eq) at room temperature. The mixture was stirred for 4 h at 80 °C. The mixture was poured into saturated $NaHCO_3$ aq and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the yellow oil **S2**.

To a 0.5 M solution of the corresponding 2-(2-bromoethyl)benzaldhyde or 1-(2- bromoethyl)-2-naphthaldehyde **S2** (1.2 eq) in MeOH was added $RNHNH_2$ (1.0 eq) at room temperature. After the immediate formation of the insoluble material, this white suspension was heated to reflux and stirred for additional 1 h to give a clear solution. Until cooling to room temperature, Et_3N (1.5 eq) was added to the mixture, after stirred for 10 minutes, poured into water and stirred for another 30 min to give a white precipitate. This solid material was washed with cold ether and then dissolved in CH_2Cl_2 to give a yellow solution. This colored solution was dried over Na_2SO_4 and evaporated *in vacuo* to give N-benzoylimino-3,4-dihydroisoquinolium as a yellow solid.



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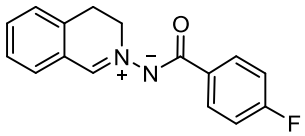

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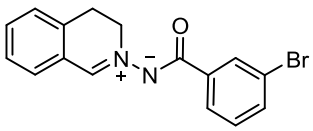

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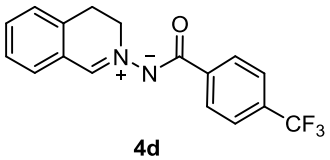

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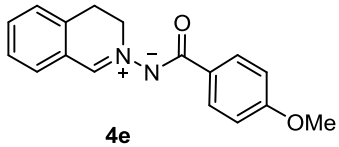

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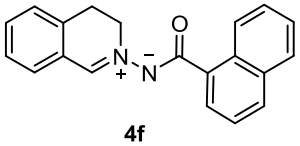

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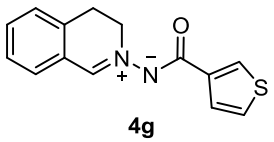
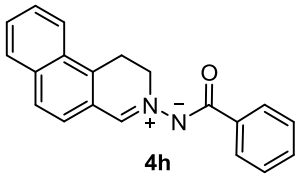
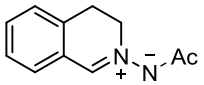


4g



4h



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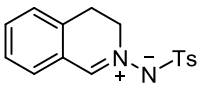
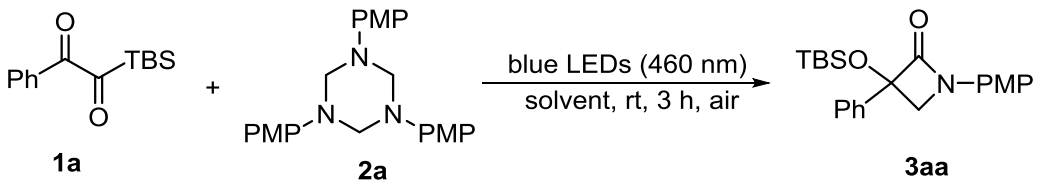


4j

3. Reaction optimization between *α*-ketoacylsilane 1a and 1,3,5- triazinane 2a.

An oven-dried reaction tube was charged with 1,3,5- triazinane **2a** (13.3 mg, 0.033 mmol), *α*-ketoacylsilane **1a** (49.6 mg, 0.2 mmol) and solvent (1.0 mL) under air. The reaction mixture was placed in parallel photoreactor and stirred under 10 W blue LEDs (λ_{max} = 460 nm) irradiation for 3.0 h at room temperature (monitored by TLC analysis), then the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with PE/EtOAc = 20:1, v/v) to afford the corresponding product.

Table S1. Optimization of reaction conditions between **1a** and **2a**



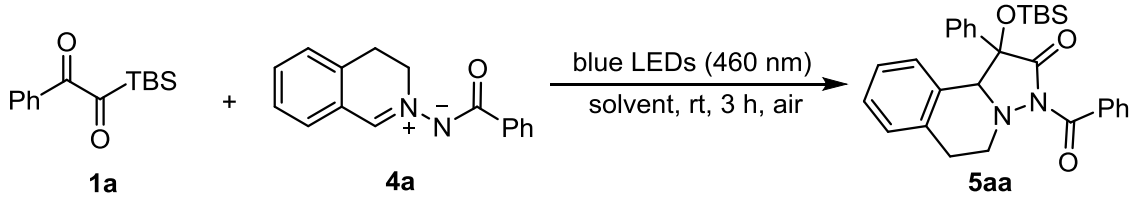
Entry[a]	Solvent	Yield of **3aa** (%)[b]
1	CH_2Cl_2	31
2	**CH_3CN**	**71**
3	THF	47
4	DCE	35
5	$CHCl_3$	29
6	Et_2O	24
7	Toluene	32
8	DMF	39
9	DMSO	49
10	n-Hexane	29
11	1,4-dioxane	27
12	EtOAc	28
13	$Cl_2CHCHCl_2$	38
14[c]	CH_3CN	74
15[d]	CH_3CN	54
16[e]	CH_3CN	N.D
17[f]	CH_3CN	N.D.
18[g]	CH_3CN	32

[a] Unless otherwise specified, the reactions were performed with **1a** (0.2 mmol), **2a** (0.033 mmol), and solvent (1.0 mL), 10 W Blue LEDs (λ_{max} = 460 nm) under air at rt (25 °C) for 3.0 h. [b] Yield of the isolated product. [c] Under N_2 condition. [d] 10 W Blue LEDs (λ_{max} = 445 nm) was used. [e] In the dark. [f] 80 °C, without light irradiation. [g] 0.1 mmol **1a** was employed.

4. Reaction optimization between *α*-ketoacylsilane 1a and C,N-cyclic azomethine imine 4a.

An oven-dried reaction tube was charged with C,N-cyclic azomethine imine **4a** (12.5 mg, 0.05 mmol), *α*-ketoacylsilane **1a** (24.8 mg, 0.1 mmol) and solvent (0.5 mL) under air. The reaction mixture was placed in parallel photoreactor and stirred under 10 W blue LEDs (λ_{max} = 460 nm) irradiation for 3.0 h at room temperature (monitored by TLC analysis), then the yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard.

Table S2. Optimization of reaction conditions between **1a** and **4a**.

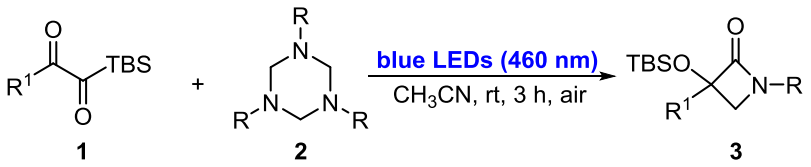


Entry[a]	Solvent	Yield (%) [b]	d.r.[c]
1	CH_2Cl_2	56	1.2:1
2	ACN	32	1.9:1
3	THF	46	1.7:1
4	DCE	53	1.4:1
5	$CHCl_3$	64	1.3:1
6	Et_2O	48	1.9:1
7	Toluene	29	1.8:1
8	DMF	30	1.8:1
9	n-Hexane	21	1.9:1
10	1,4-dioxane	45	1.9:1
11	EtOAc	25	2.0:1
12	$Cl_2CHCHCl_2$	55	1.5:1
14[d]	$CHCl_3$	48[i]	1.3:1
15[e]	$CHCl_3$	33[i]	1.3:1
16[f]	**$CHCl_3$**	**63[i]**	**1.3:1**
17[g]	$CHCl_3$	N.D.	---
18[h]	$CHCl_3$	N.D.	---

[a] The reactions conditions： **1a** (0.1 mmol), **4a** (0.05 mmol), and solvent (0.5 mL, 0.1M), 10 W Blue LEDs (λ_{max} = 460 nm) under air at rt (25 °C) for 3.0 h. [b] The yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard. [c] d.r. was determined by ^{1}H NMR. [d] **1a** (0.1 mmol) and **4a** (0.1 mmol) was used. [e] **1a** (0.1 mmol) and **4a** (0.2 mmol) was used. [f] **1a** (0.4 mmol) and **4a** (0.2 mmol) was used. [g] In the dark. [h] 80 °C, without light irradiation. [i] Isolated yield.

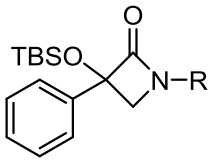
5. General procedure for two phtotochemical reactions.

General procedure for the reaction of α-ketoacylsilane 1 and 1,3,5- triazinane 2: An oven-dried reaction tube was charged with 1,3,5- triazinane **2** (0.033 mmol), *α*-ketoacylsilane **1** (0.2 mmol) and CH_3CN (1.0 mL) under air. The reaction mixture was placed in parallel photoreactor and stirred under 10 W blue LEDs (λ_{max} = 460 nm) irradiation for 3.0 h at room temperature, then the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with PE/EtOAc = 20:1, v/v) to afford the corresponding product **3**.

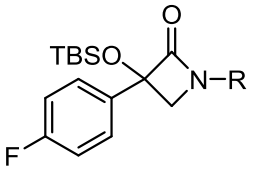


1 2 3

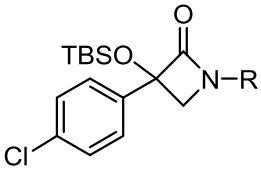
R = 4-MeOC$_6$H$_4$



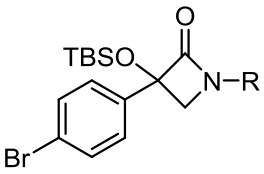
3aa, 71%



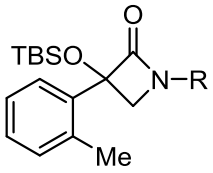
3ab, 58%



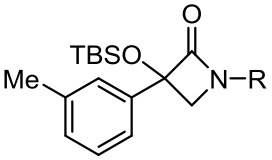
3ac, 53%



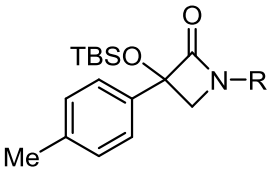
3ad, 54%



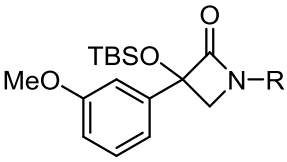
3ae, 52%



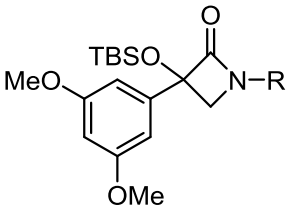
3af, 62%



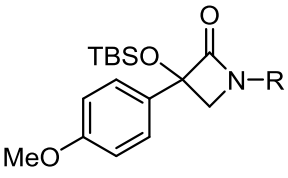
3ag, 63%



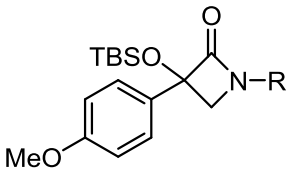
3ah, 71%



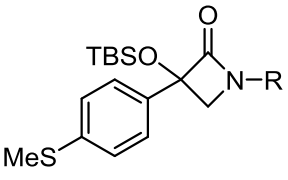
3ai, 77%



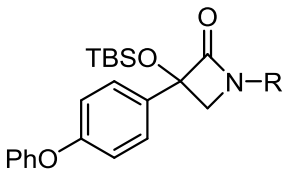
3aj, 70%



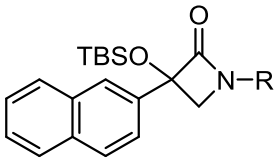
R = Triphenylmethyl
3ak, 70%



3al, 68%



3am, 65%



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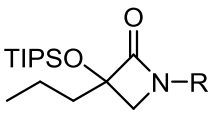

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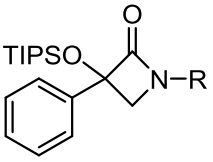

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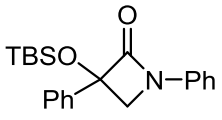
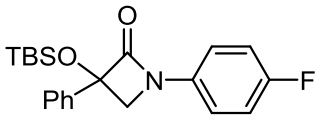
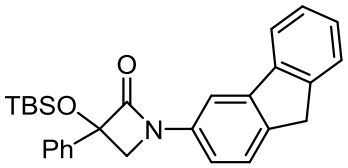


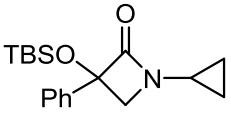
3aq, 64%



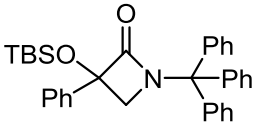
3ar, 60%



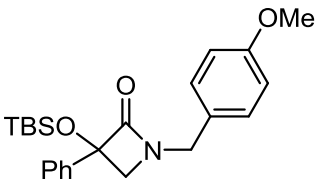
3as, 73%



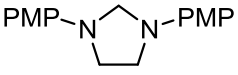
3at, 53%



3au, 75%

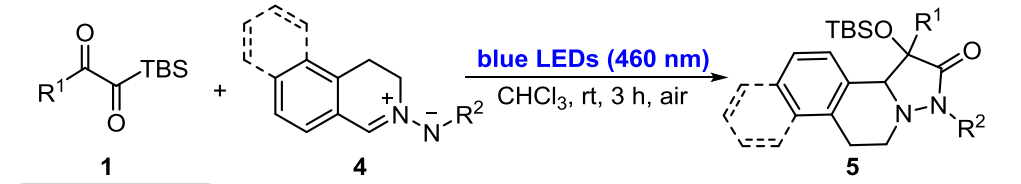


3av, 68%

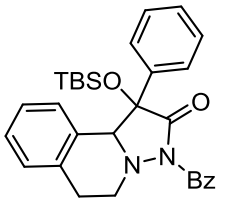


2h, N.R.

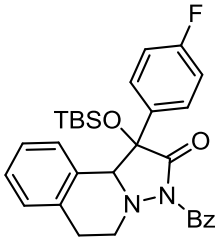
General procedure for the reaction of α-ketoacylsilane 1 and C,N-cyclic azomethine imine 4: An oven-dried reaction tube was charged with C,N-cyclic azomethine imine **4** (0.2 mmol), *α*-ketoacylsilane **1** (0.4 mmol) and $CHCl_3$ (2.0 mL) under air. The reaction mixture was placed in parallel photoreactor and stirred under 10 W blue LEDs (λ_{max} = 460 nm) irradiation for 3.0 h at room temperature (monitored by TLC analysis), then the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with PE/EtOAc = 5:1, v/v) to afford the corresponding product **5** as a diastereomeric mixtures. The d.r. of all the products were determined by ^1H NMR analysis.



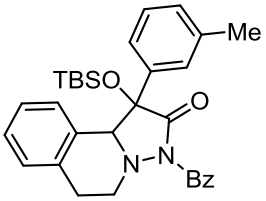
α-ketoacylsilanes



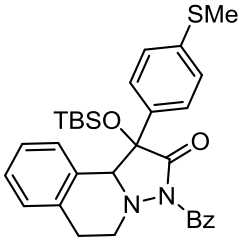
5aa, 63%, 1.3:1 d.r.



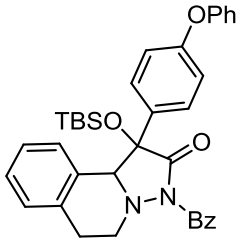
5ab, 46%, 1.9:1 d.r.



5ac, 55%, 1.3:1 d.r.

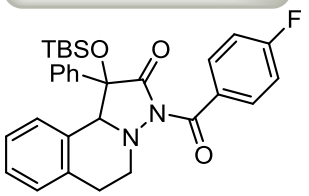


5ad, 57%, 1.4:1 d.r.

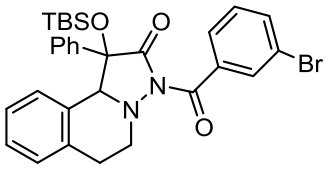


5ae, 54%, 1.3:1 d.r.

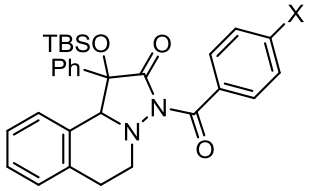
C,N-azomethine imines



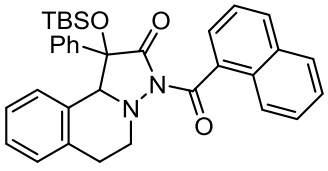
5af, 52%, 1.1:1 d.r.



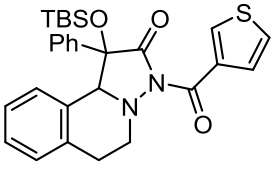
5ag, 56%, 1.3:1 d.r.



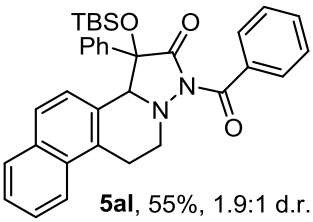
5ah, X = CF_3, 68%, 1.7:1 d.r.
5ai, X = MeO, 53%, 1.6:1 d.r.



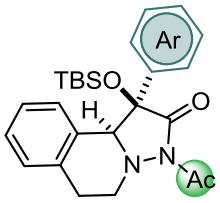
5aj, 52%, 1.1:1 d.r.



5ak, 61%, 1.4:1 d.r.

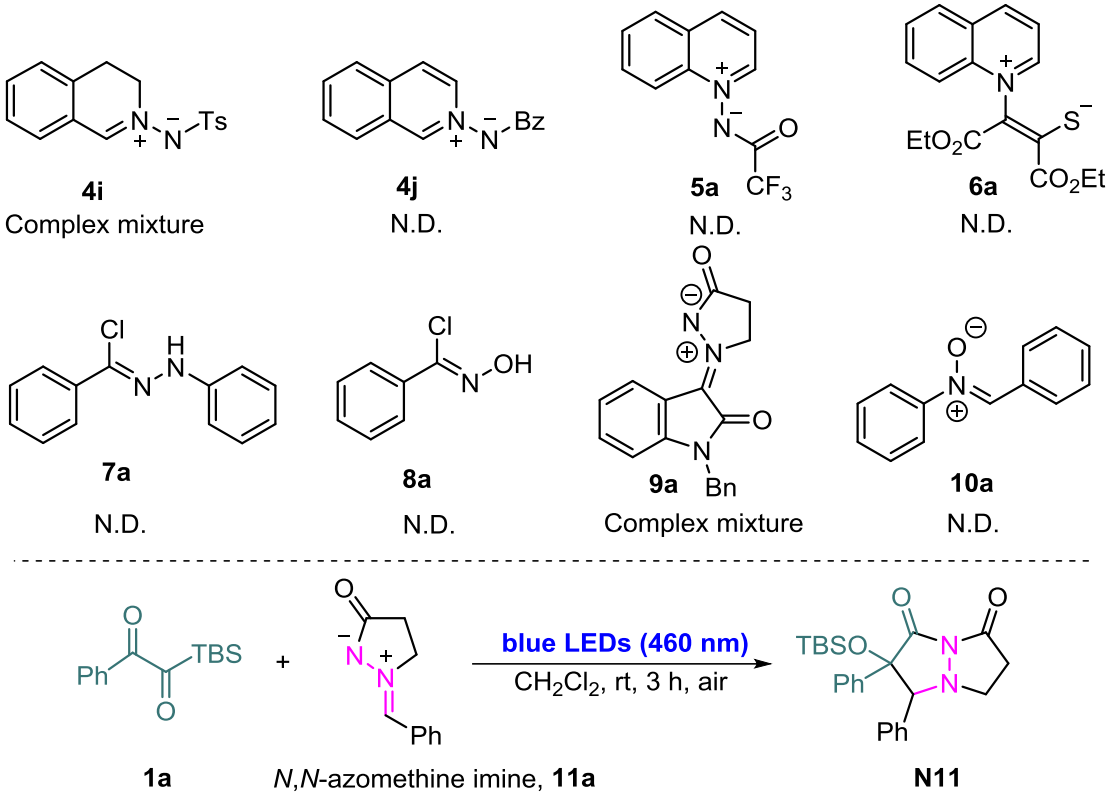


5al, 55%, 1.9:1 d.r.



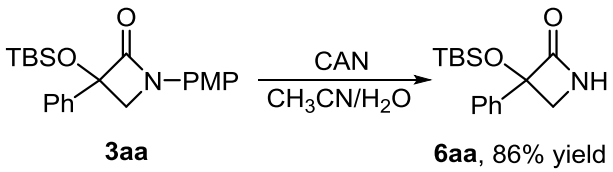
5am, Ar = Ph, 57%, 6.3:1 d.r.
5am, Ar = 4-FC_6H_4, 51%, 7.3:1 d.r.
5ao, Ar = 3-$MeOC_6H_4$, 65%, 6.1:1 d.r.
5ap, Ar = 2-Naphthyl, 57%, 6.6:1 d.r.

6. Some unsuccessful representative types of 1,3-dipoles and 1,3-dipolar precursors.

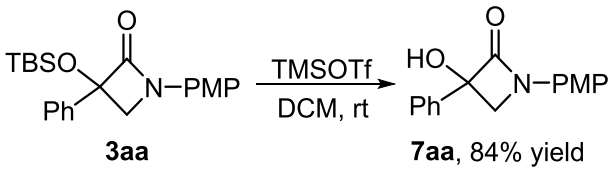


Some representative 1,n-dipoles and 1,n-dipoles precursors were evaluated, however, the desired products were not detected. When N,N-azomethine imine **11a** was employed, the corresponding product **N11** was detected, but it was difficult to purify.

7. Synthetic applications



To a yellow solid of **3aa** (114.9 mg, 0.3 mmol) was added CAN (477 mg, 0.9 mmol) in MeCN/H_2O (V/V = 4 mL / 4 mL) at 0 ºC. The reaction mixture was stirred for 1 h. After a completion, H_2O (2 mL) was added and extracted with EtOAc five times (2 mL each time). The combined organic layers were washed with 5% Na_2SO_3 and dried over Na_2SO_4. The crude product was purified by column chromatography over silica (PE/EtOAc = 5:1) gel to obtain analytically pure products **6aa** (71.5 mg, 0.26 mmol, 86% yield).



To a yellow solid of **3aa** (76.6 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) was added the solution of trimethylsilyl trifluoromethanesulfonate (0.09 mL, 0.5 mmol) under -78 °C. After the mixture cooled to room temperature, stirred at room temperature for 12 h, saturated aqueous $NaHCO_3$ (10 mL) was added to quench this reaction. The layers were separated, and the organic layer was extracted with CH_2Cl_2 three times (10 mL each time). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography over silica (PE/EtOAc = 3:1) gel to obtain analytically pure products **7aa** (42.0 mg, 0.16 mmol, 84% yield).

8. Continuous flow synthesis of two photochemical processes

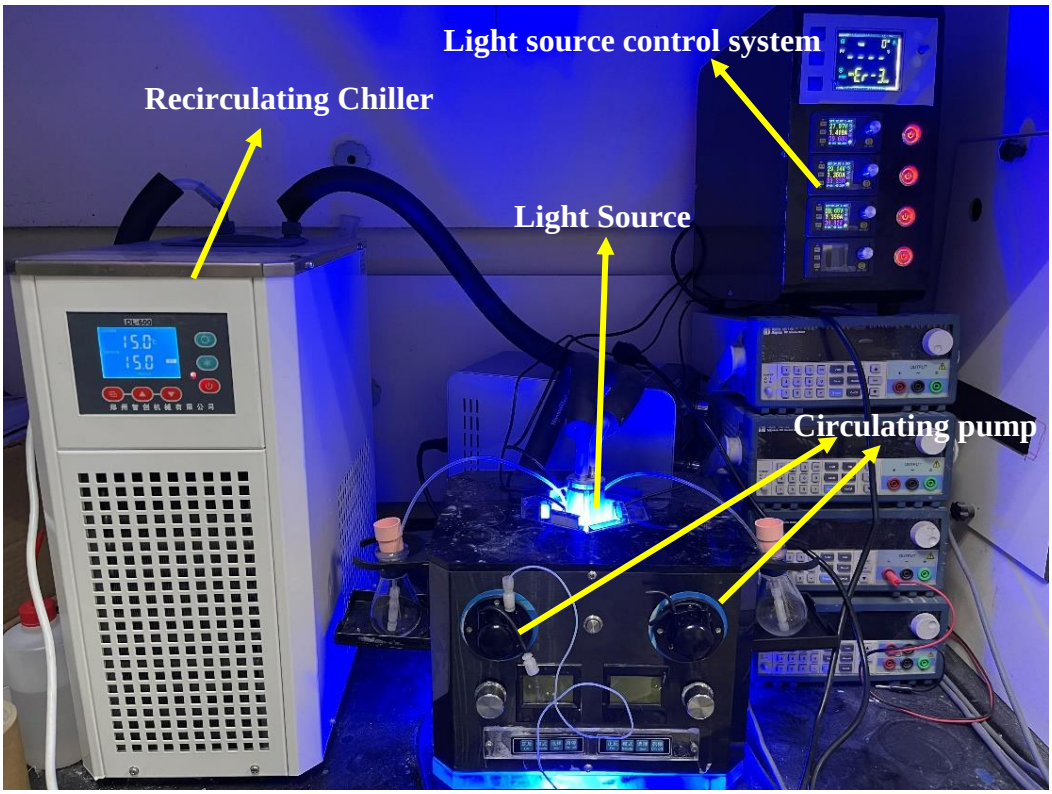
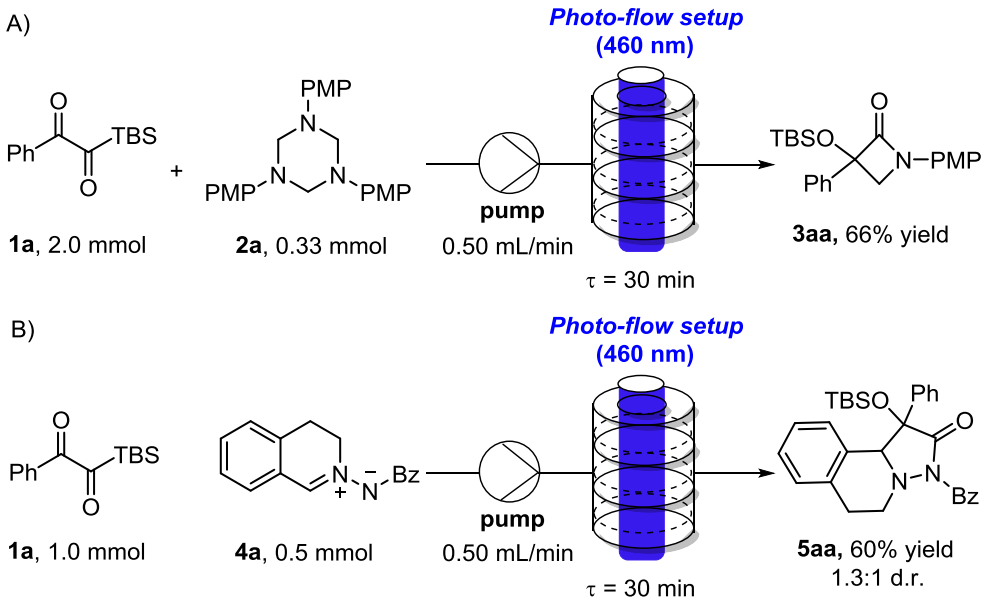


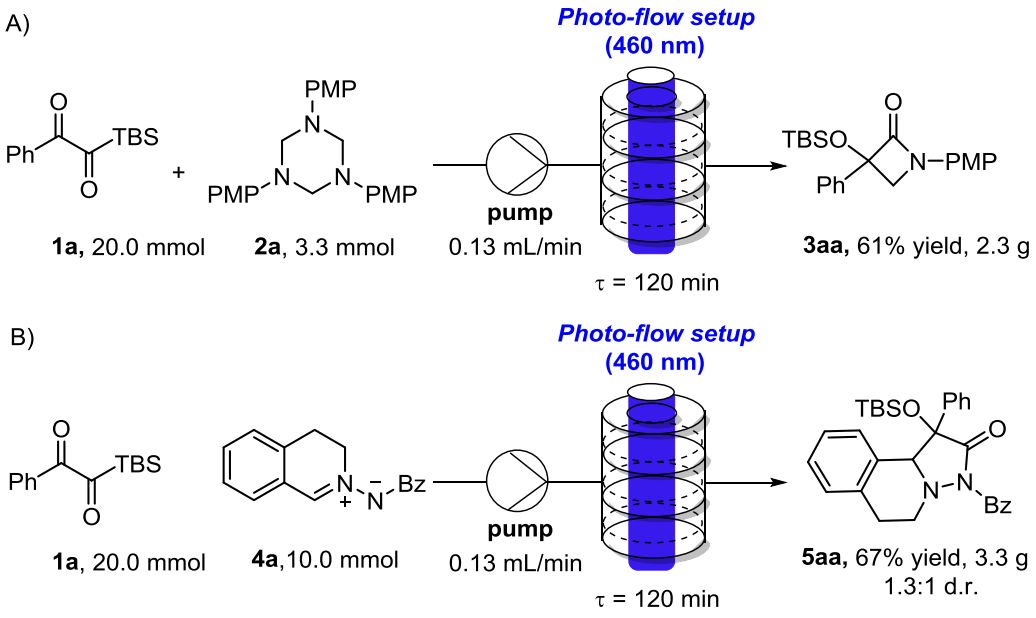
Figure S2. Photochemical flow setup



General procedure for 3aa: The flow photoreactor setup is shown in Figure S2. An oven-dried reaction flask was charged with 1,3,5- triazinane **2a** (133.6 mg, 0.33 mmol)), *α*-ketoacylsilane **1a** (446.4 mg, 2.0 mmol) and CH_3CN (10 mL) under air. The reaction mixture was placed in continuous-flow photoreactor with recirculating cooler chiller, then pumped into the photoreactor using a peristaltic pump at a flow rate of 0.50 mL/min (retention time τ = 30 min). Meanwhile, liquid inputed to the reaction system was irradiated with three 40W blue LEDs strips around the pipe. Next, the reaction mixture from the photochemical reactor output was collected in the other flask and concentrated in vacuo. The crude product was purified by column chromatography to obtain the desired product **3aa** (66% yield, 252.8 mg).

General procedure for 5aa: The flow photoreactor setup is shown in Figure S2. An oven-dried reaction flask was charged with C, N-cyclic azomethine imine **4a** (125 mg, 0.5 mmol), *α*-ketoacylsilane **1a** (248 mg, 1.0 mmol) and $CHCl_3$ (5 mL) under air. The reaction mixture was placed in continuous-flow photoreactor with recirculating cooler chiller, then pumped into the photoreactor using a peristaltic pump at a flow rate of 0.5 mL/min (retention time τ = 30 min). Meanwhile, liquid inputed to the reaction system was irradiated with three 40 W blue LEDs strips around the pipe. Next, the reaction mixture from the photochemical reactor output was collected in the other flask and concentrated in vacuo. The crude product was purified by column chromatography to obtain the product **5aa** (60% yield, 149.4 mg, 1.3:1 d.r.).

9. Continuous flow reaction for gram-scale synthesis.

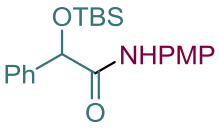


The gram-scale synthesis was carrying out by using the described flow photoreactor setup above in Figure S2: An oven-dried reaction flask was charged with 1,3,5- triazinane **2a** (1.33 g, 3.3 mmol)), *α*-ketoacylsilane **1a** (4.96 g, 20 mmol) and CH_3CN (100 mL) under air. The reaction mixture was placed in continuous-flow photoreactor with recirculating cooler chiller, then pumped into the photoreactor using a peristaltic pump at a flow rate of 0.13 mL/min (retention time τ = 120 min). Meanwhile, liquid inputed to the reaction system was irradiated with three 40 W blue LEDs

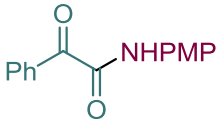
strips around the pipe. Next, the reaction mixture from the photochemical reactor output was collected in the other flask and concentrated in vacuo. The crude product was purified by column chromatography to obtain the desired product **3aa** (61% yield, 2.3 g).

The same procedure as synthesis of 3aa: An oven-dried reaction flask was charged with C, N-cyclic azomethine imine **4a** (2.5 g, 10.0 mmol), *α*-ketoacylsilane **1a** (4.96 g, 20 mmol) and $CHCl_3$ (100 mL) under air. The reaction mixture was placed in continuous-flow photoreactor with recirculating cooler chiller, then pumped into the photoreactor using a peristaltic pump at a flow rate of 0.13 mL/min (retention time τ = 120 min). Meanwhile, liquid inputed to the reaction system was irradiated with three 40 W blue LEDs strips around the pipe. Next, the reaction mixture from the photochemical reactor output was collected in the other flask and concentrated in vacuo. The crude product was purified by column chromatography to obtain the desired product **5aa** (67% yield, 3.3 g, 1.3:1 d.r.).

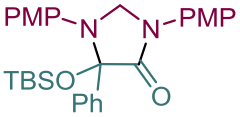
10. Mechanistic investigations.



P1

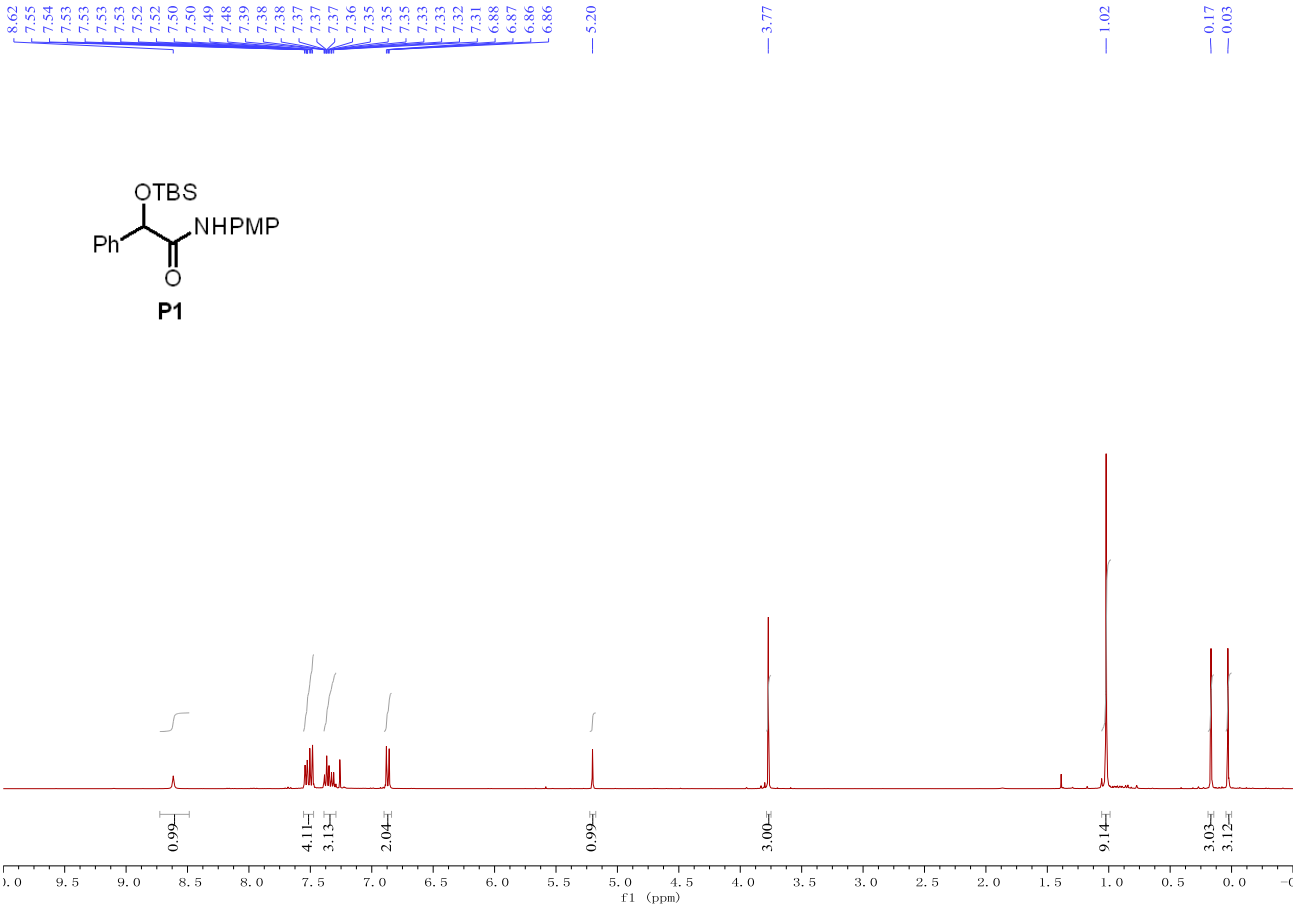


P2

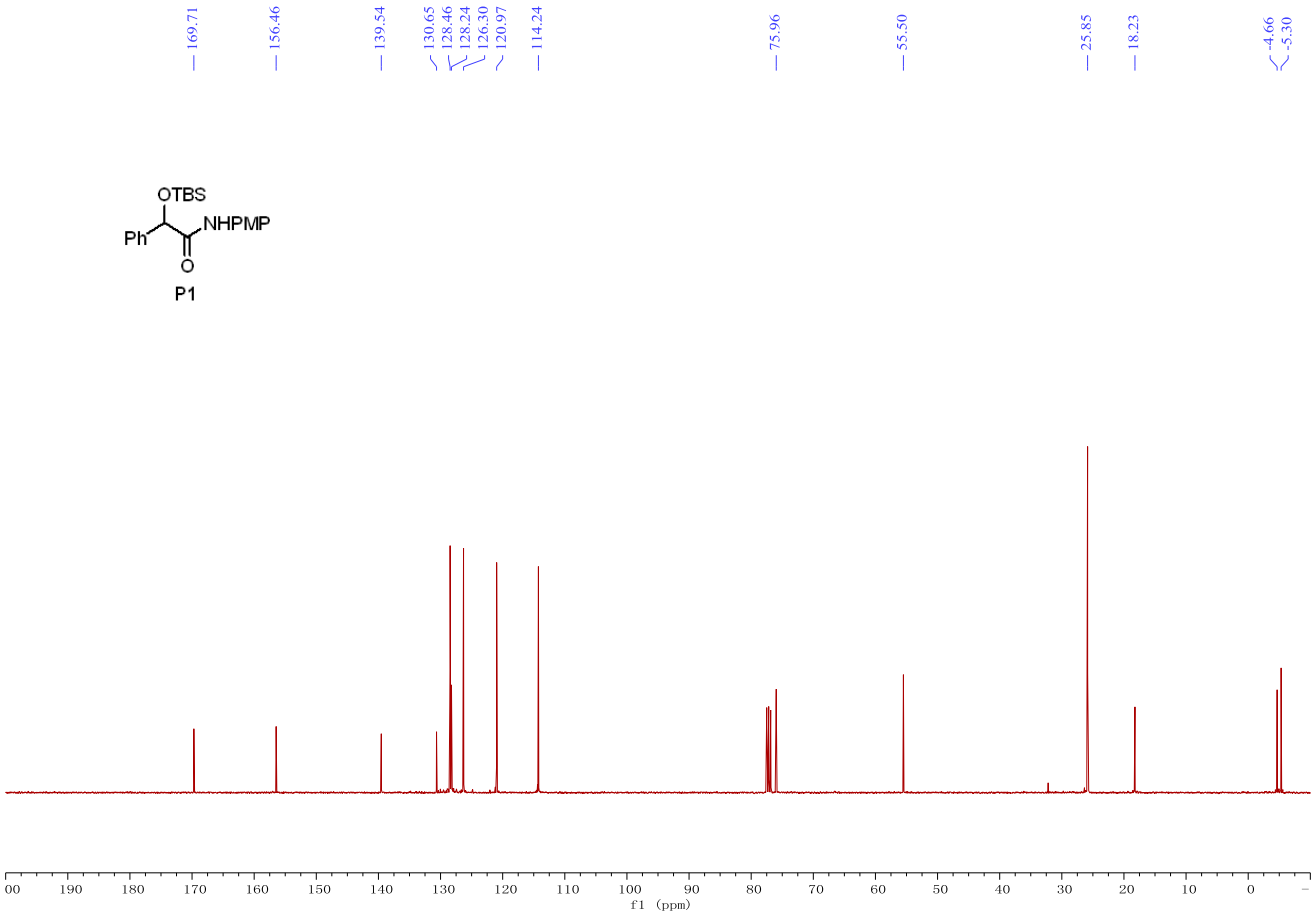


P3

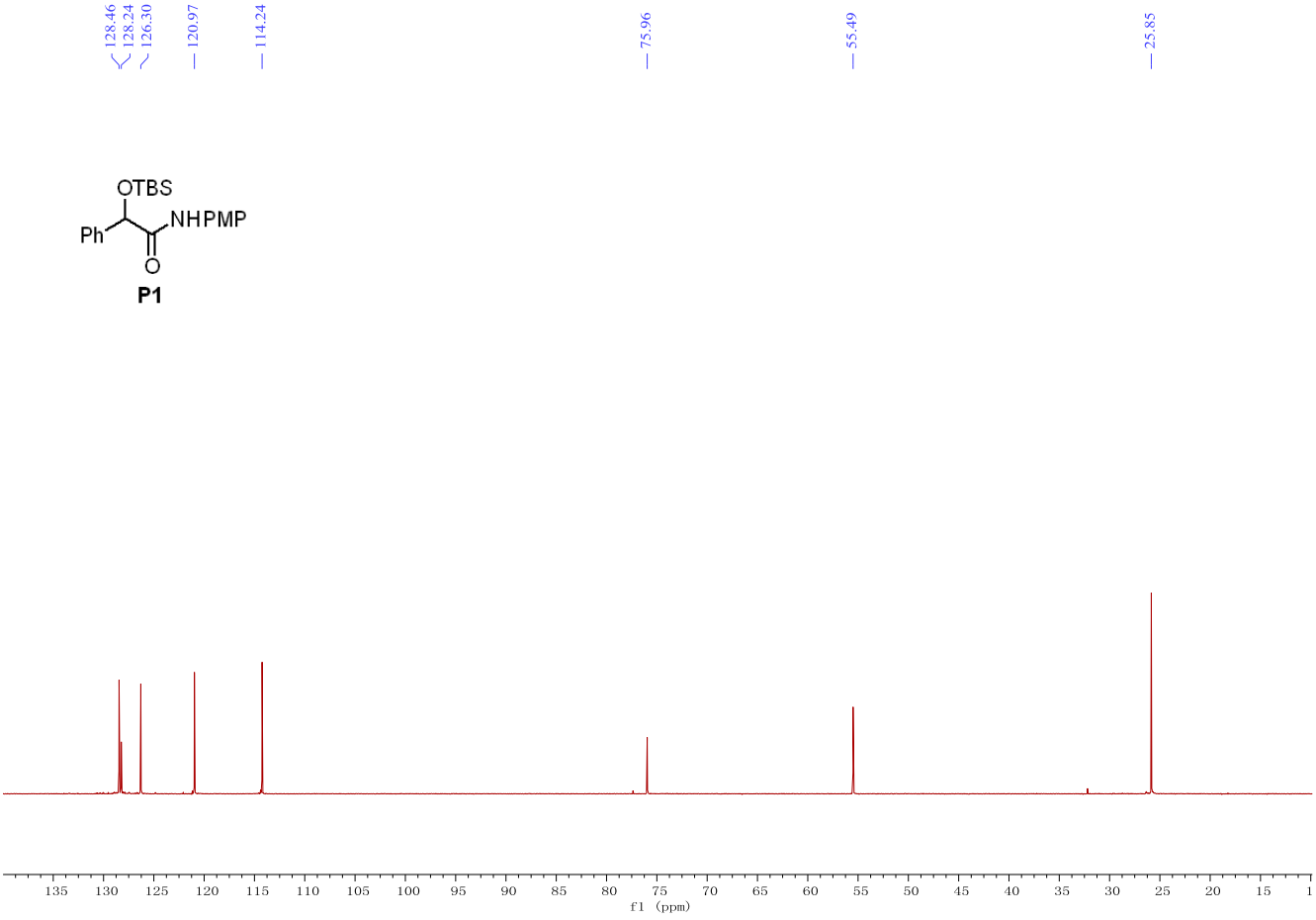
Compound **P1**, **P2** and **P3** were also detected by the analysis of LC-MS and NMR spectroscopy in this reaction, details are as follows:



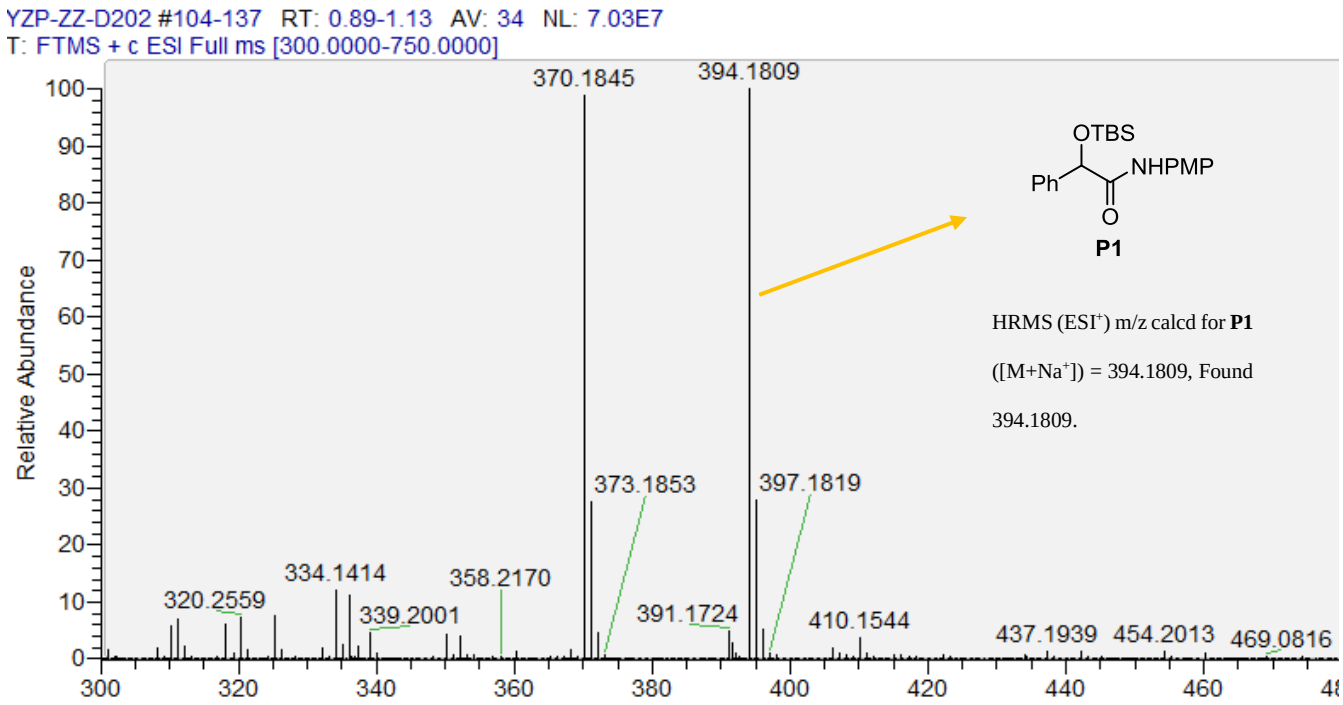
^{1}H NMR (400 MHz, $CDCl_3$) of **P1**



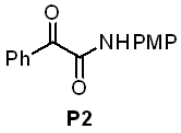
^{13}C NMR (101 MHz, $CDCl_3$) of **P1**

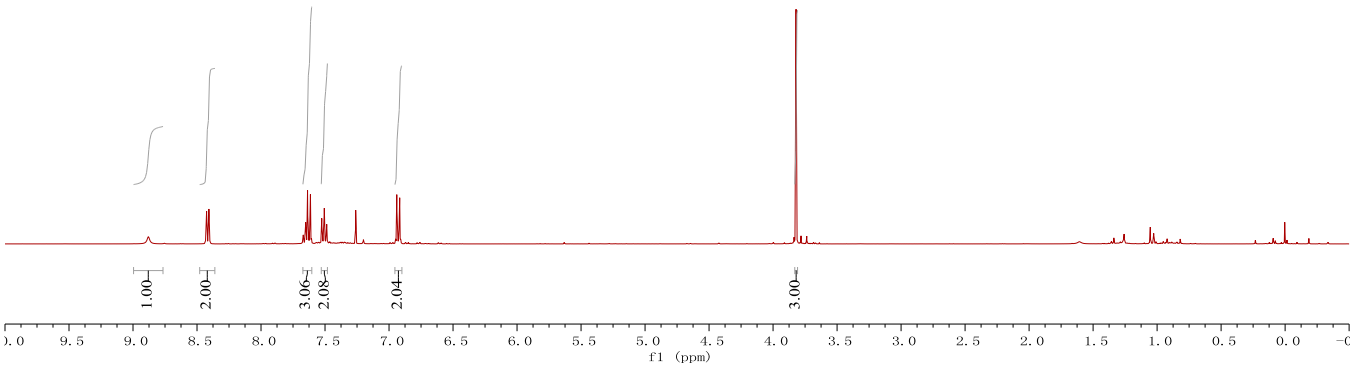


Dept135 (101 MHz, $CDCl_3$) of **P1**

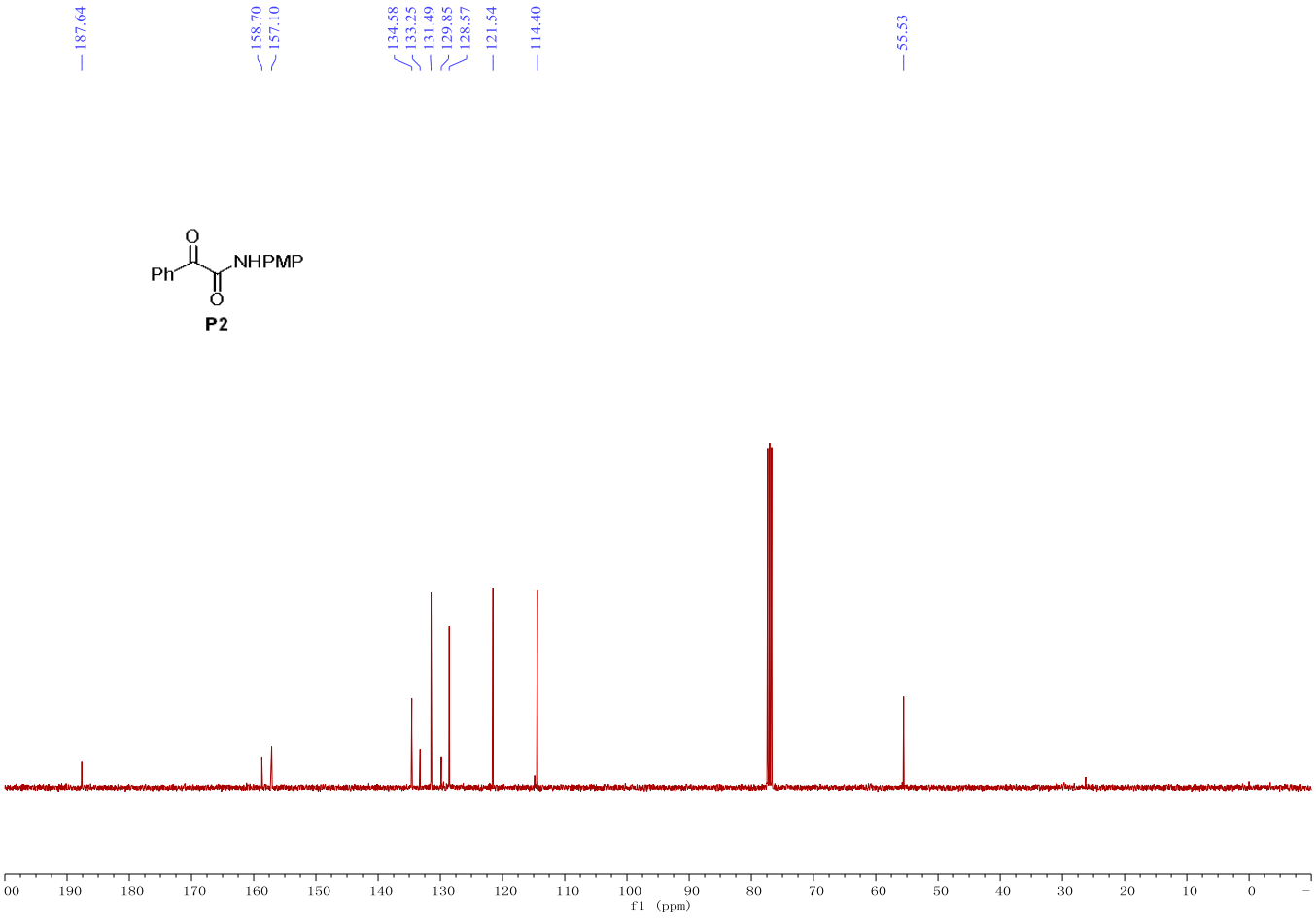


HRMS (ESI$^+$) m/z calcd for **P1** ([M+Na$^+$]) = 394.1809, Found 394.1809.

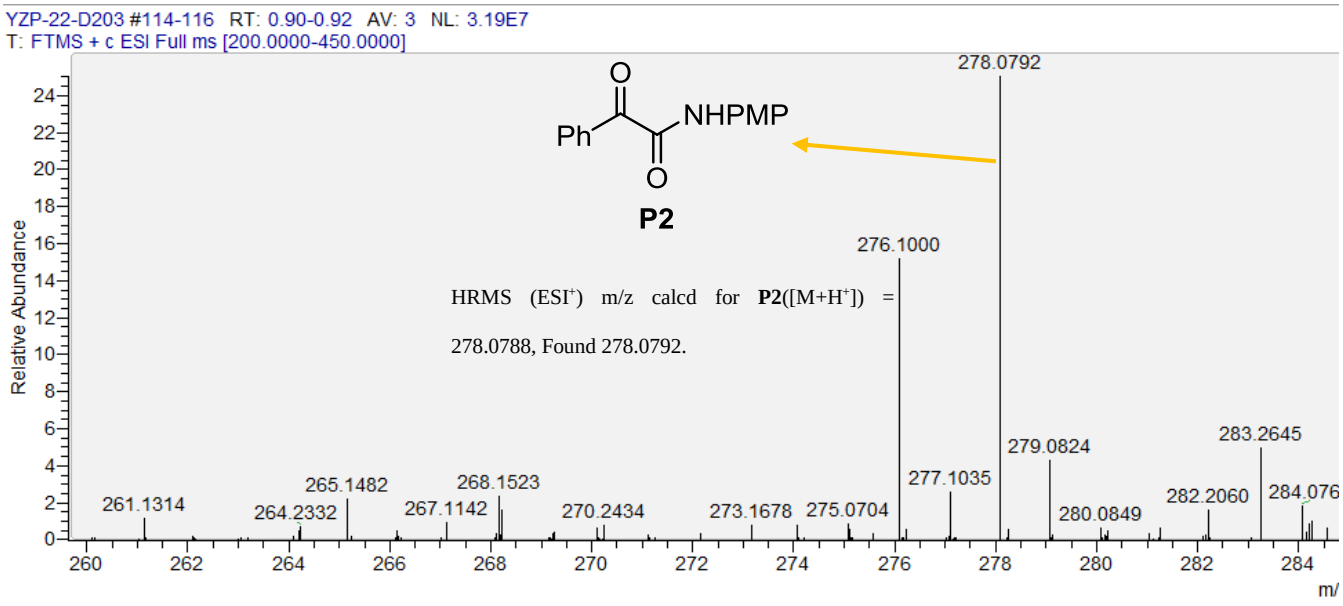


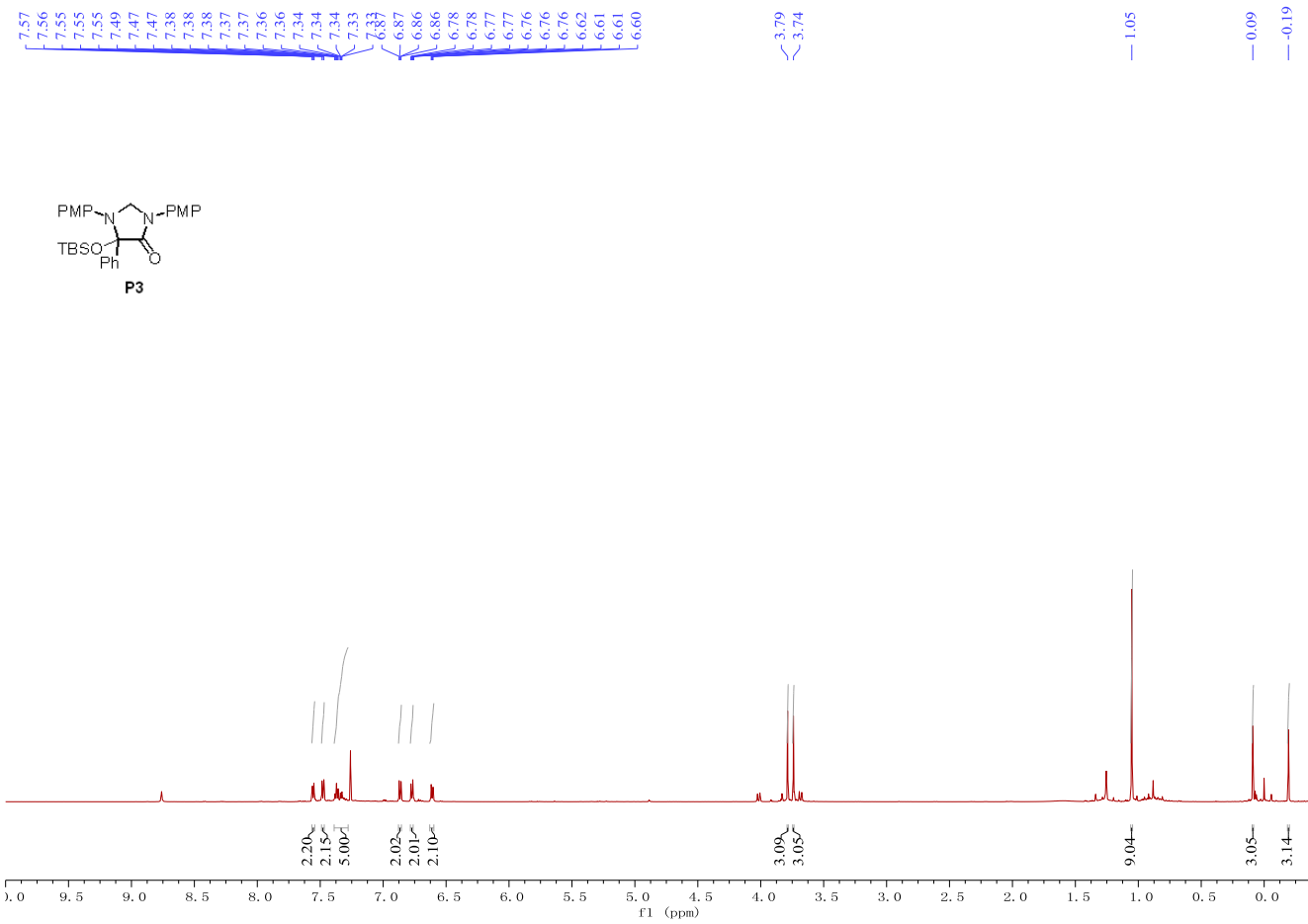


^{1}H NMR (400 MHz, $CDCl_3$) of **P2**

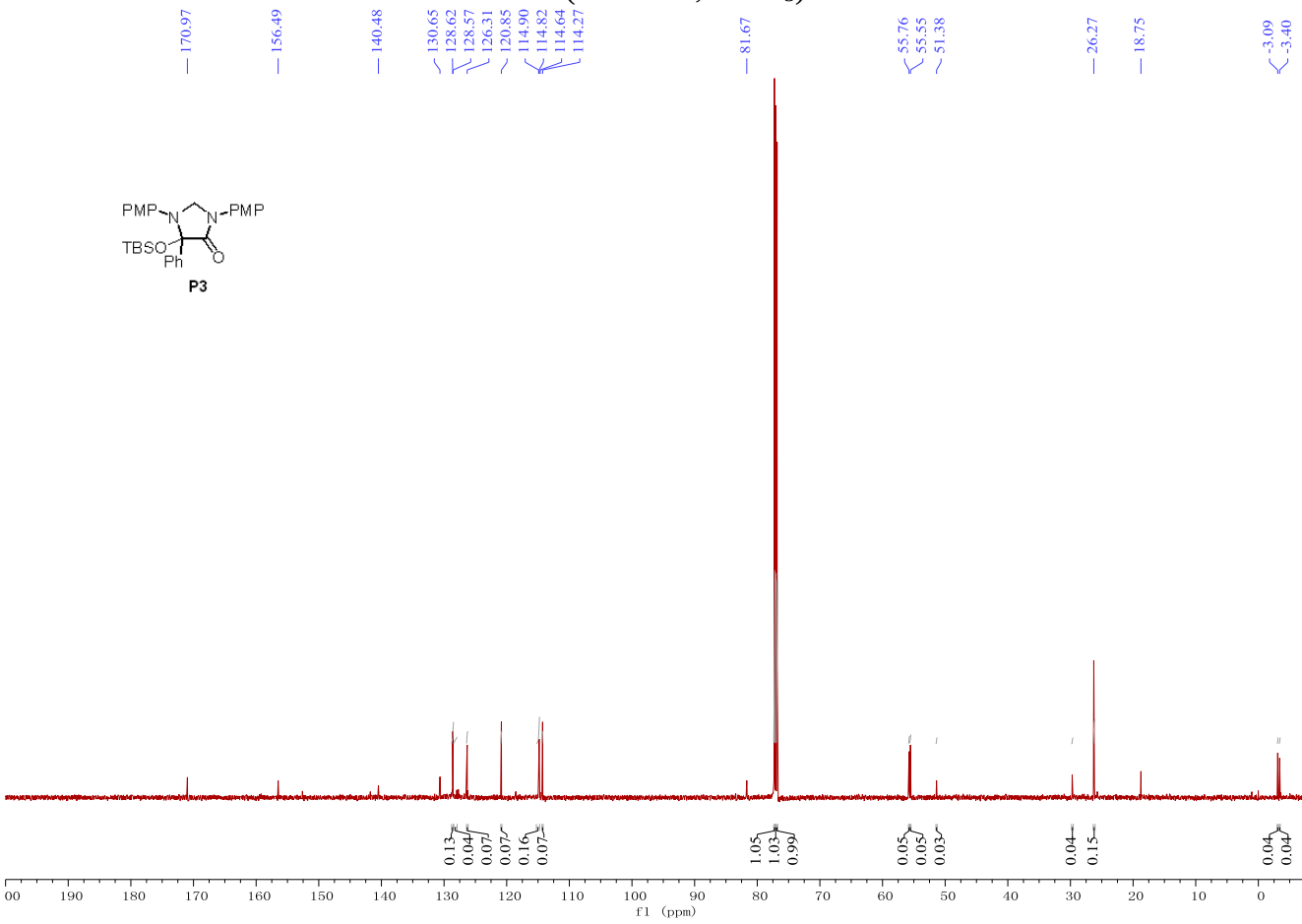


^{13}C NMR (101 MHz, $CDCl_3$) of **P2**

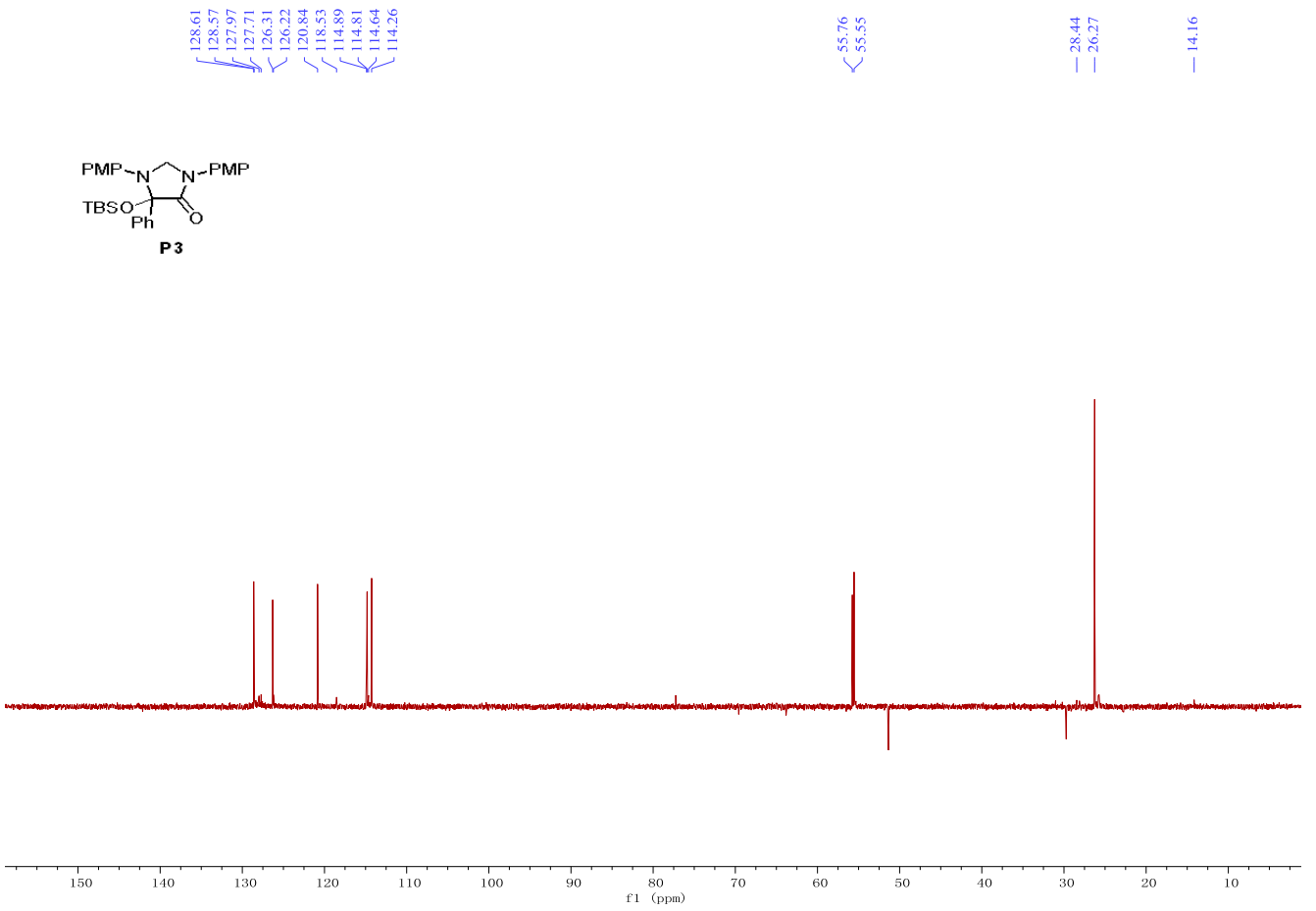




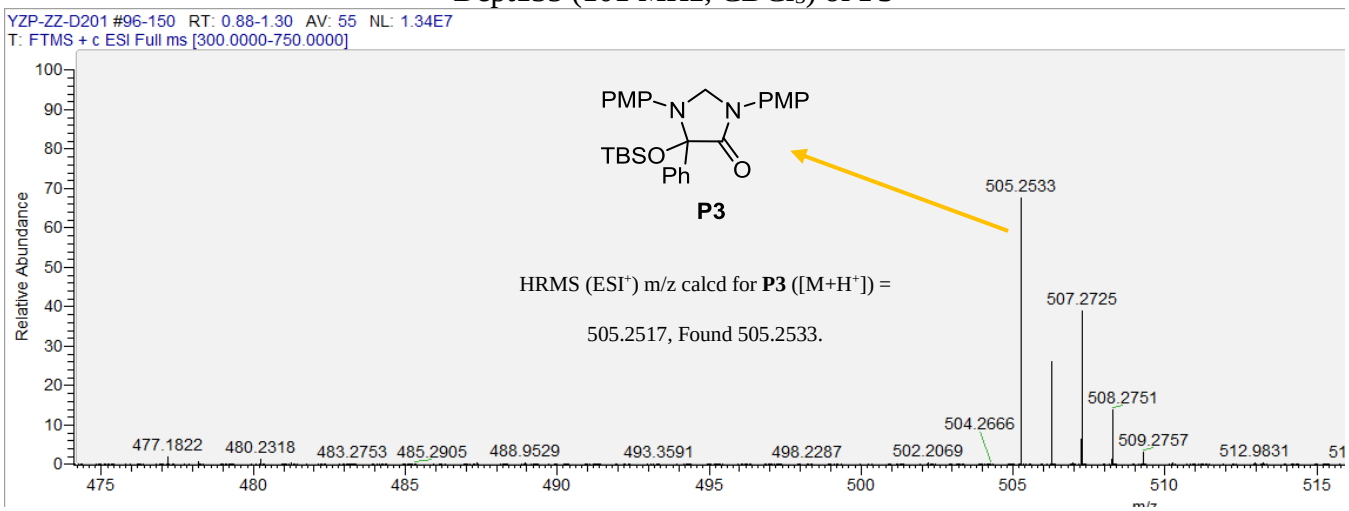
^{1}H NMR (400 MHz, $CDCl_3$) of **P3**



^{13}C NMR (101 MHz, $CDCl_3$) of **P3**



Dept135 (101 MHz, $CDCl_3$) of **P3**



The NMR spectroscopy of the compound **P3** contained a few unknown side products, they are very difficult to separated and be purified due to the same R_f value.

On the basis of above experimental results and previous reports, the plausible mechanism for two tandem annulation processes of α-ketoacylsilanes with 1,3,5-triazinanes and azomethine imines were proposed in Figure S3. Initially, the α-ketoacylsilanes were converted into siloxyketenes species via 1,3-silyl migration in the presence of blue LED as displayed in **Path A**, while the other possible pathway of formation of siloxyketenes might go through a [1,2]-sily shift, followed by a Wolff rearrangement (**Path B**), this process seems to be disfavored, because the product generated from

the reaction of the siloxycarbene with corresponding trapping agent R-NH_2 were not detected, it was also consistent with our experimental results and Glorius' work.[2] Proposed reaction mechanism for formation of **P1**, **P2** and **P3** were illustrated in Figure S3, details are as follows:

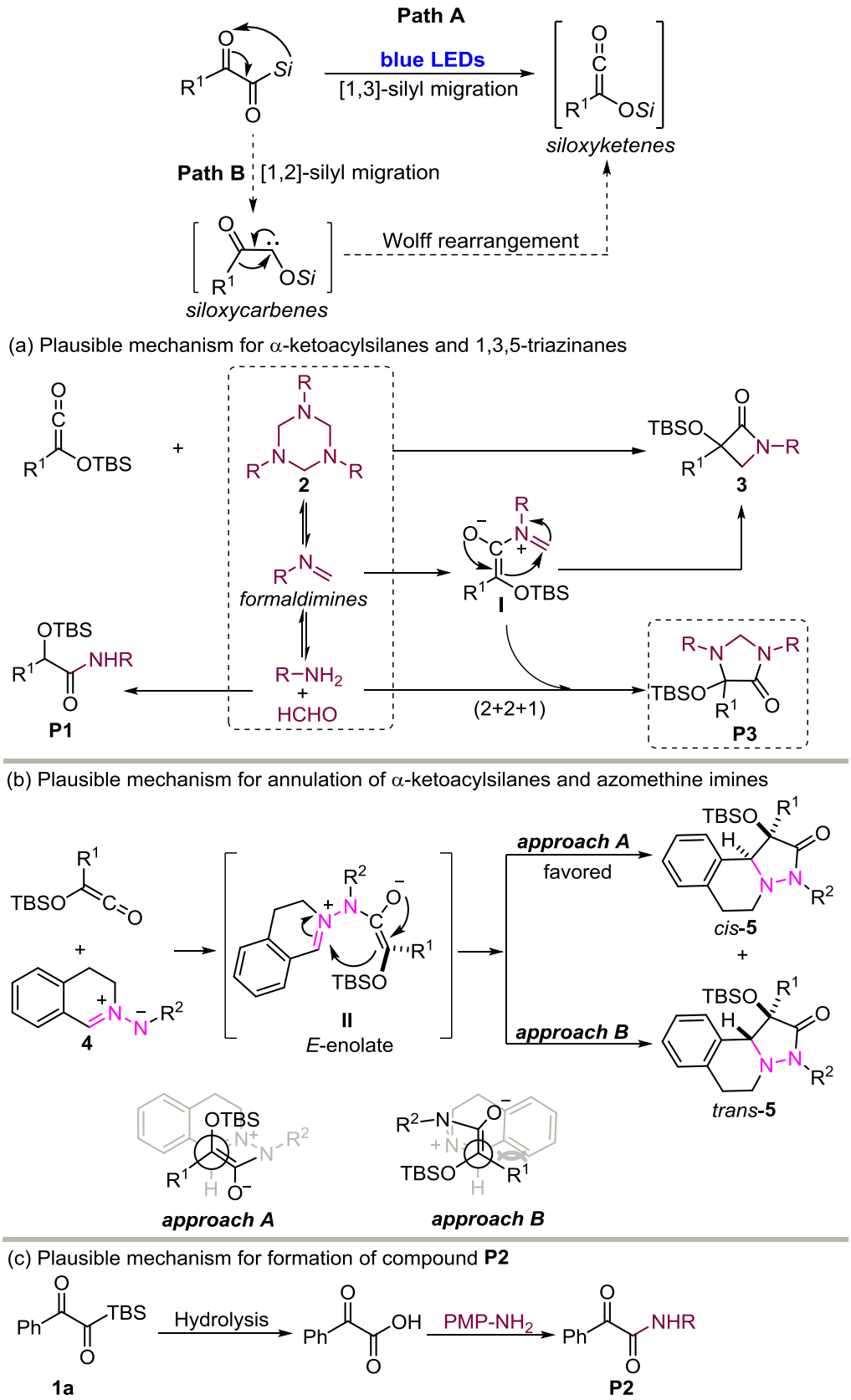
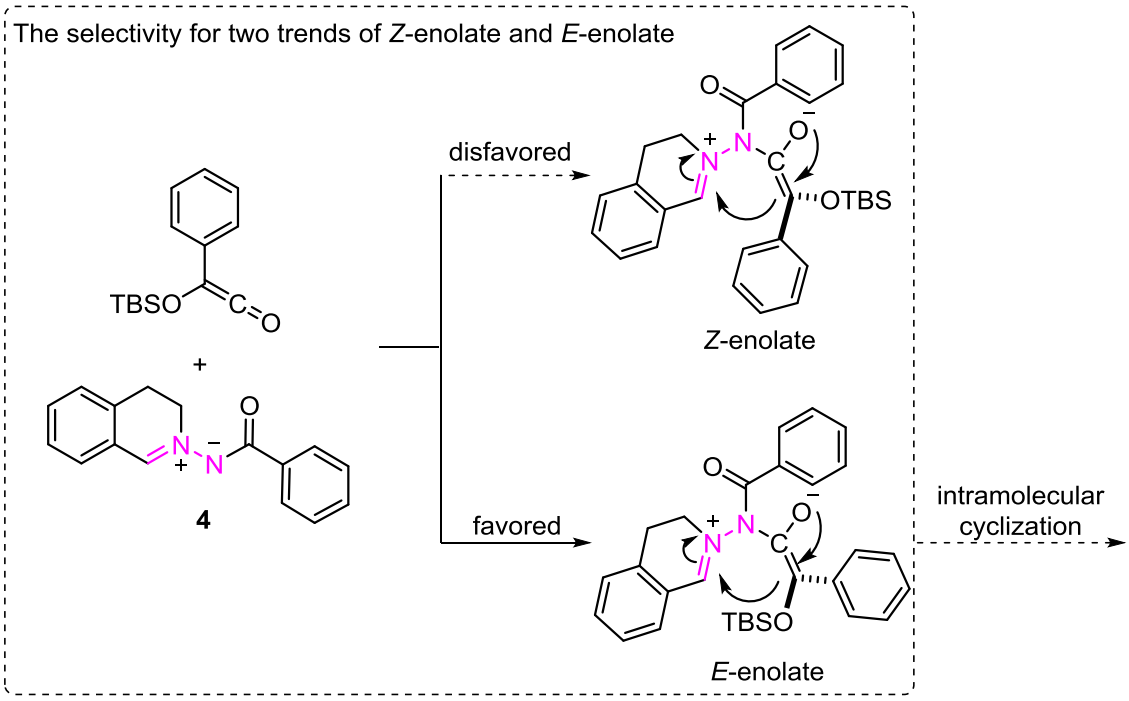


Figure S3. Proposed mechanism for cascade cyclization

The α-keto acids may be generated from the hydrolysis of α-ketoacylsilane **1a**, and then reacted with *p*-anisidine from decomposition of **2a** to give the corresponding compound **P2**, it was also in agreement with the reported structure.[10]

11. Quantum chemical calculation

The structure of azomethine imine **4** and siloxyketenes were used as the substrate for quantum chemical calculation. The energy calculations were performed at the M06-2X(D3)/6-311+G(d, p)/SMD (solvent = chloroform) level of theory; geometries optimized at the M06-2X(D3)/6-31+G(d, p)/SMD (solvent = chloroform) level of theory.



To explain clearly the selectivity of two trends of the initial nucleophilic addition of C,N-azomethine imine to the silyoxyketene (formation of *Z*-enolate or *E*-enolate). The activation barrier for formation step of *E*-enolate and *Z*-enolate was calculated by using Gaussian 09 program at the M06-2X-D3/6-311G(d,p) (SMD, Chloroform), as shown in the region of dashed frame. It was found that the formation of *E*-enolate could give a TS-*E* with a lower energy barrier ($\Delta G^{\ddagger}_{TS\text{-}E}$ = 4.8 kcal/mol) relative to *Z*-counterpart ($\Delta G^{\ddagger}_{TS\text{-}Z}$ = 9.0 kcal/mol). Therefore, the formation of *E*-enolate intermediate was proved to be favored in initial nucleophilic addition step. The calculated free energy profiles for two trend (formation of *Z*-enolate or *E*-enolate) of the initial nucleophilic addition of C,N-azomethine imine to the silyoxyketene are depicted as follows:

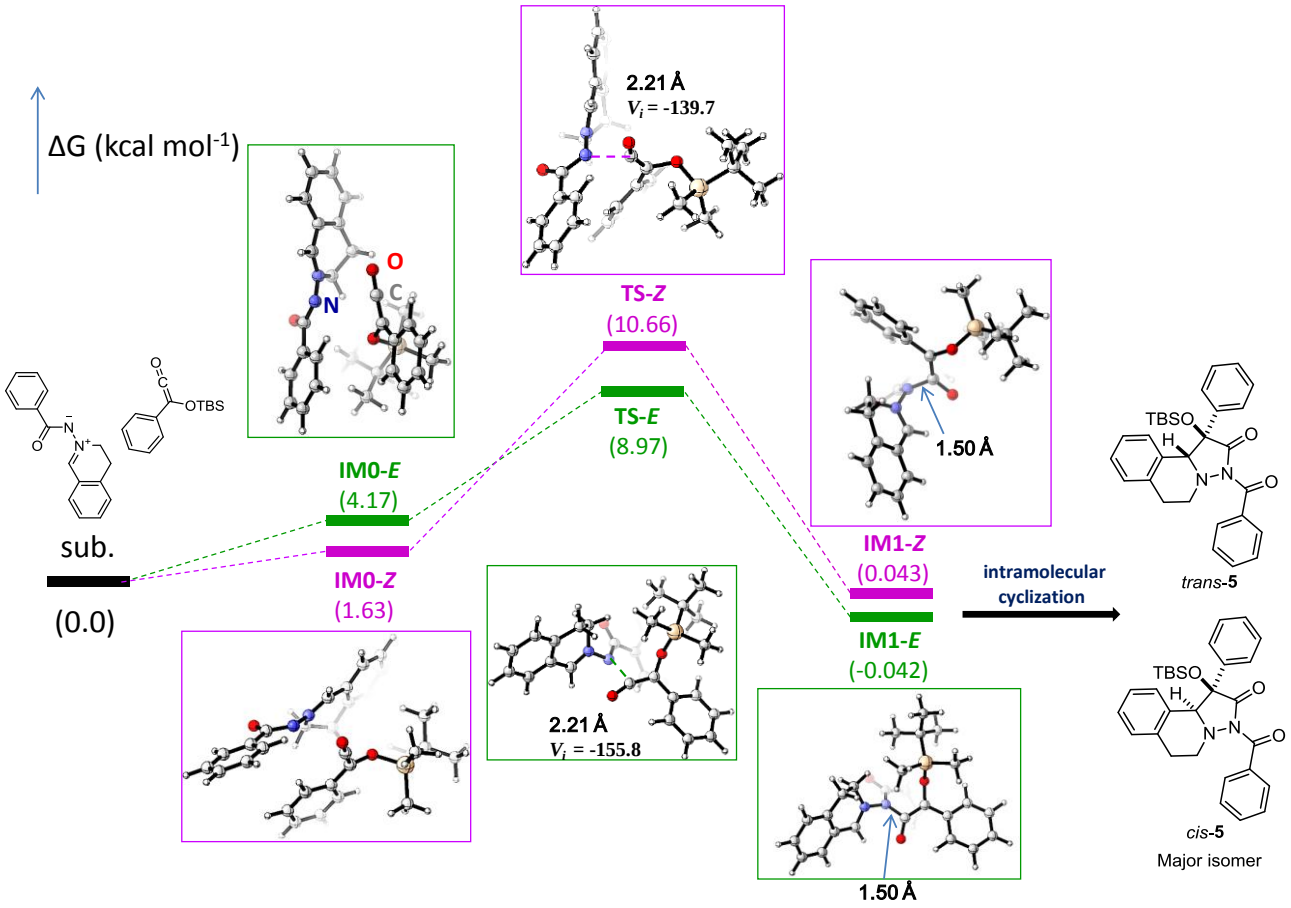
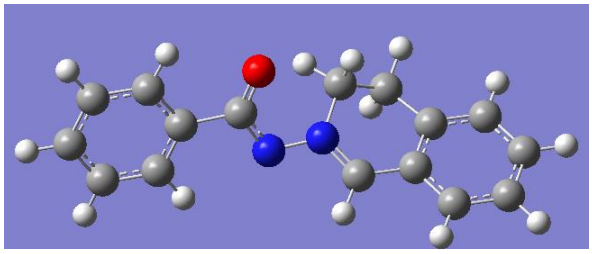


Figure S4. Gibbs free energy profiles for two trend (formation of *Z*-enolate or *E*-enolate intermediate) of the initial nucleophilic addition of C,N-azomethine imine to the silyoxyketene. The relative free energies are given in kcal·mol.

Azomethine imine



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C	2.26511300	-1.44898300	1.08293700
C	3.30294200	-0.55801600	0.45215400
C	2.84847500	0.64211200	-0.11935800
C	1.42500600	0.93349400	-0.10527200
C	4.66584700	-0.82916500	0.45543400
C	5.56433300	0.07832000	-0.10665800
C	5.10946600	1.27169800	-0.66679900
C	3.74993100	1.55978400	-0.66795100
O	-1.37199000	-1.34940200	-1.12387200
C	-3.08974000	-0.03092000	-0.12882100

C	-4.07478300	-0.76830200	-0.78797200
C	-5.42139000	-0.47395000	-0.59636200
C	-5.79274600	0.56283400	0.25772900
C	-4.81273500	1.30309200	0.91803300
C	-3.46609100	1.00876700	0.72644300
H	1.04800500	-1.82837500	-0.68665900
H	0.14987700	-1.89149700	0.83546900
H	2.60650400	-2.48664400	1.11291100
H	2.09707900	-1.12951900	2.11946300
H	1.05261600	1.93885100	-0.27620800
H	5.02724800	-1.75270100	0.89860900
H	6.62614100	-0.14674100	-0.10432000
H	5.81367800	1.97476700	-1.09853500
H	3.37919400	2.48582900	-1.09786000
H	-3.76143300	-1.57056400	-1.44783200
H	-6.18164900	-1.05209300	-1.11275300
H	-6.84285000	0.79433500	0.40858700
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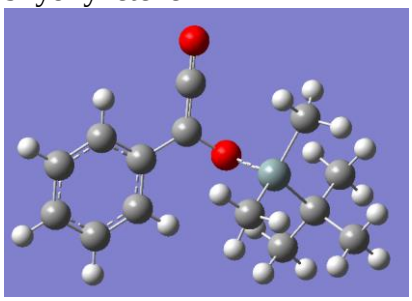
H	-2.69807600	1.58048300	1.23579300

silyoxyketene



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Si	1.45120100	0.22260000	0.48696300
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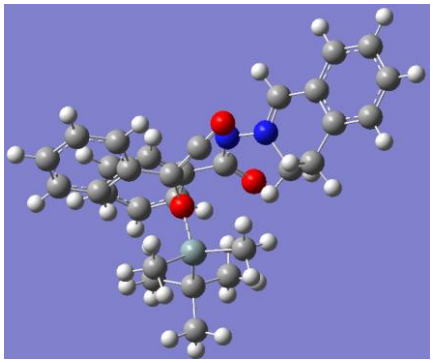

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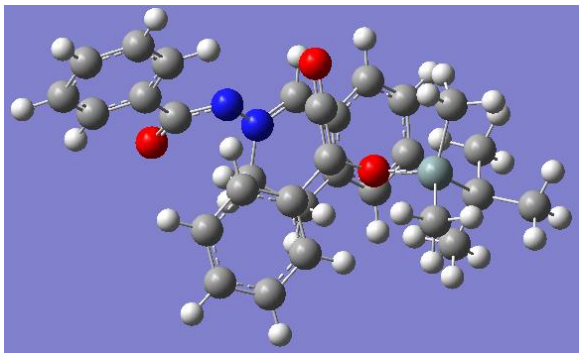

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C	0.72248500	-2.40606100	3.03142400
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H	-5.08052800	-0.31727000	1.66462100

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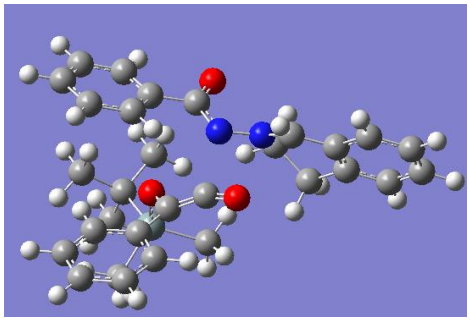
TS-*E*



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C	2.59547600	-1.40920500	0.38169600
C	3.46354600	-0.68543300	1.39602600
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C	-1.43235900	3.74967700	0.10225400
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C	-2.92695900	-2.62991900	-2.88747200
C	-3.48917000	-1.42005100	-3.28930700
C	-2.76379400	-0.23663900	-3.15124900
C	-1.48420900	-0.25919200	-2.60576600
O	-1.33269100	0.02311800	0.42371500
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C	-2.72651700	0.73927400	2.93020400
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H	3.74720500	-1.38594800	2.18574200
H	2.88964800	0.12465600	1.86595500
H	2.95657900	0.88547700	-2.07817800
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H	-3.19841400	-3.65424100	3.18558600
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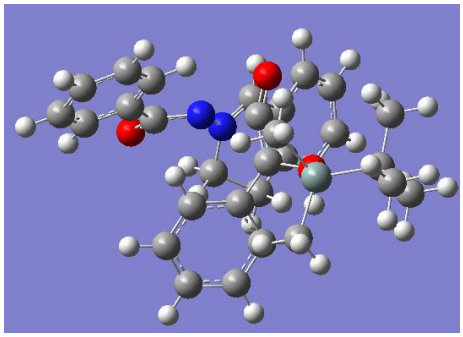
TS-Z



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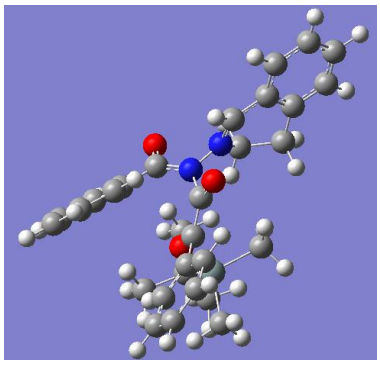
IM1-*E*



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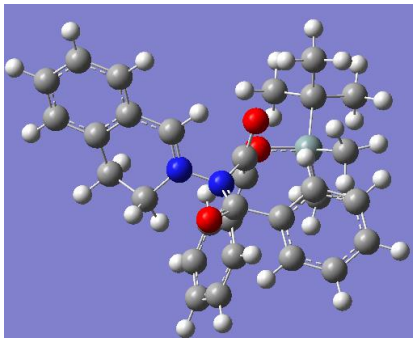
IM1-Z



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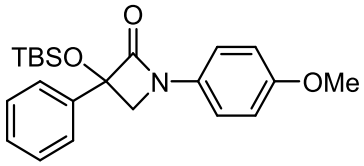
H	3.00697200	-4.14524200	-2.80526300

12. The analytical and spectral characterization data of products.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-phenylazetidin-2-one (3aa)



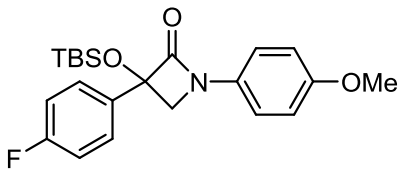
The compound **3aa** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 27.2 mg, 71% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.53 (m, 2H), 7.40 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 6.93 – 6.91 (m, 2H), 3.89 – 3.84 (q, 2H), 3.81 (s, 3H), 0.94 (s, 9H), 0.12 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.40, 156.53, 139.65, 131.57, 128.50, 128.25, 125.72, 118.10, 114.51, 86.25, 57.98, 55.54, 25.74, 18.20, -3.60, -3.73.

HRMS (ESI^{+}) m/z calcd for $C_{22}H_{29}NO_3Si$ ([M+H^{+}]) = 384.1989, Found 384.1984.

3-((tert-butyldimethylsilyl)oxy)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)azetidin-2-one (3ab)



The compound **3ab** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 23.3 mg, 58% yield.

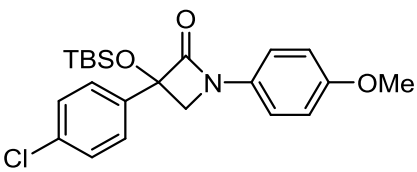
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 2H), 7.39 – 7.37 (m, 2H), 7.08 – 7.04 (m, 2H), 6.93 – 6.90 (m, 2H), 3.84 (s, 2H), 3.81 (s, 3H), 1.26 (s, 1H), 0.93 (s, 9H), 0.01 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.19, 163.87, 156.63, 131.46, 127.69, 127.61, 118.15, 115.57, 115.35, 114.56, 85.74, 57.98, 55.58, 25.72, 18.19, -3.60, -3.71.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.67.

HRMS (ESI^{+}) m/z calcd for $C_{39}H_{34}N_6$ ([M+Na^{+}]) = 424.1715, Found 424.1708.

3-((tert-butyldimethylsilyl)oxy)-3-(4-chlorophenyl)-1-(4-methoxyphenyl)azetidin-2-one (3ac)



The compound **3ac** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 22.1 mg, 53% yield.

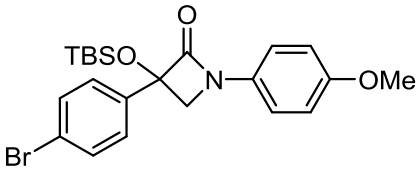
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.45 (m, 2H), 7.40 – 7.33 (m, 4H), 6.93 – 6.89 (m, 2H), 3.83 (d, 2H), 3.81 (s, 3H), 0.93 (s, 9H), 0.12(s, 3H), 0.05(s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.97, 156.67, 138.31, 134.19, 131.39, 128.76, 127.16, 118.16, 114.57, 85.79, 57.95, 55.58, 25.72, 18.20, -3.59, -3.69.

HRMS (ESI^{+}) m/z calcd for $C_{22}H_{28}Cl^{34.9689}NO_3Si$ ([M+Na^{+}]) =440.1419, Found 440.1427.

HRMS (ESI^{+}) m/z calcd for $C_{22}H_{28}Cl^{36.9659}NO_3Si$ ([M+Na^{+}]) =442.1389, Found 442.1390.

3-(4-bromophenyl)-3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)azetidin-2-one (3ad)



The compound **3ad** was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:8); light yellow solid, 24.9 mg, 54.0% yield.

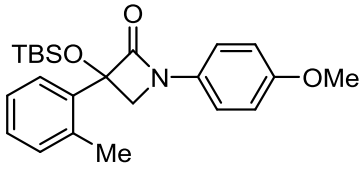
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.49 (m, 2H), 7.41 – 7.36 (m, 4H), 6.93 – 6.90 (m, 2H), 3.82 (d, *J* = 10.2 Hz, 5H), 0.93 (s, 9H), 0.12 (s, 3H), 0.05(s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.88, 156.68, 138.85, 131.71, 131.37, 127.46, 122.35, 118.17, 114.57, 85.84, 57.90, 55.58, 25.72, 18.20, -3.59, -3.68.

HRMS (ESI^{+}) m/z calcd for $C_{22}H_{28}Br^{78.9183}NO_3Si$ ([M+Na^{+}]) = 484.0914, Found 484.0923.

HRMS (ESI^{+}) m/z calcd for $C_{22}H_{28}Br^{80.9163}NO_3Si$ ([M+Na^{+}]) = 486.0894, Found 486.0895.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-(o-tolyl)azetidin-2-one (3ae)



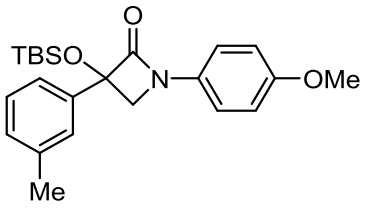
The compound **3ae** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 20.6 mg, 52% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.24 – 7.20 (m, 2H), 7.18 – 7.13 (m, 1H), 6.90-6.87 (m, 2H), 3.95-3.89 (m, 2H), 3.79 (s, 3H), 2.45 (s, 3H), 0.85 (s, 9H), 0.16 (s, 3H), -0.23 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.94, 156.40, 137.40, 137.26, 131.79, 131.38, 128.77, 127.39, 125.53, 118.04, 114.45, 86.35, 57.55, 55.55, 25.68, 19.41, 18.14, -3.42, -4.20.

HRMS (ESI^{+}) m/z calcd for $C_{23}H_{31}NO_3Si$ ([M+Na^{+}]) = 420.1965, Found 420.1965.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-(m-tolyl)azetidin-2-one (3af)



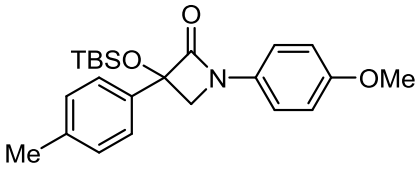
The compound **3af** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 25.04 mg, 62% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40-7.38 (m, 2H), 7.35 – 7.32 (m, 2H), 7.15 – 7.12 (m, 1H), 6.93 – 6.90 (m, 2H), 3.87 – 3.82 (m, 2H), 3.81 (s, 3H), 2.47 – 2.37 (m, 1H), 2.36 (s, 3H), 0.94 (s, 9H), 0.11 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.53, 156.51, 139.57, 138.20, 131.65, 129.01, 128.44, 126.36, 122.85, 118.13, 114.52, 86.28, 58.02, 55.58, 25.77, 21.52, 18.24, -3.56, -3.69.

HRMS (ESI^{+}) m/z calcd for $C_{23}H_{31}NO_3Si$ ([M+Na^{+}]) =420.1965, Found 420.1967.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-(p-tolyl)azetidin-2-one (3ag)



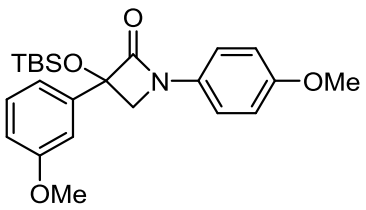
The compound **3ag** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow solid; 25.04 mg, 63% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44zz – 7.37 (m, 4H), 7.19 – 7.17 (m, 2H), 6.95 – 6.87 (m, 2H), 3.85 (q, *J* = 5.4 Hz, 2H), 3.80 (s, 3H), 2.35 (s, 3H), 0.93 (s, 9H), 0.11 (s, 3H), 0.04(s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.60, 156.49, 138.07, 136.69, 131.67, 129.20, 125.77, 118.12, 114.51, 86.16, 58.00, 55.57, 25.77, 21.18, 18.22, -3.56, -3.68.

HRMS (ESI^{+}) m/z calcd for $C_{23}H_{31}NO_3Si$ ([M+Na^{+}]) = 420.1965, Found 420.1963.

3-((tert-butyldimethylsilyl)oxy)-3-(3-methoxyphenyl)-1-(4-methoxyphenyl)azetidin-2-one (3ah)



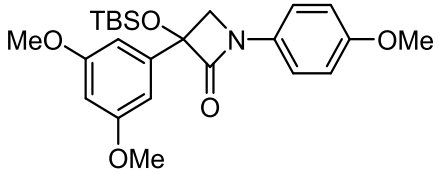
The compound **3ah** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid; 29.4 mg, 71% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.34f (m, 2H), 7.27-7.26 (m, 1H), 7.13 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.06-7.09 (m, 1H), 6.92 – 6.90 (m, 2H), 6.87 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 0.94 (s, 9H), 0.12 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.32, 159.77, 156.55, 141.27, 131.56, 129.64, 118.14, 117.81, 114.53, 113.87, 111.40, 86.18, 58.10, 55.58, 55.29, 25.77, 18.24, -3.58, -3.70.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{31}NO_4Si$ ([M+Na$^+$]) = 436.1915, Found 436.1895.

3-((tert-butyldimethylsilyl)oxy)-3-(3,5-dimethoxyphenyl)-1-(4-methoxyphenyl)azetidin-2-one (3ai)



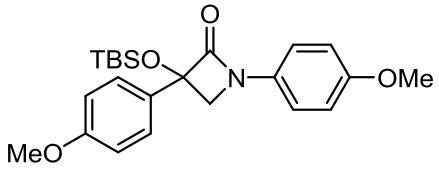
The compound **3ai** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid; 34.15 mg, 77% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.36 (m, 2H), 6.92 – 6.90f (m, 2H), 6.69 (d, *J* = 2.3 Hz, 2H), 6.41 (t, *J* = 2.3 Hz, 1H), 3.85 (d, *J* = 5.5 Hz, 1H), 3.81-3.80 (m, 4H), 3.78 (s, 6H), 0.95 (s, 9H), 0.13 (s, 3H), 0.09 (s,3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.14, 160.95, 156.55, 142.08, 131.54, 118.14, 114.52, 103.75, 100.19, 86.25, 77.25, 58.15, 55.57, 55.40, 25.77, 18.26, -3.59, -3.69.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{33}NO_5Si$ ([M+Na$^+$]) = 466.2020, Found 466.2028.

3-((tert-butyldimethylsilyl)oxy)-1,3-bis(4-methoxyphenyl)azetidin-2-one (3aj)



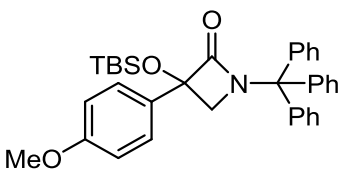
The compound **3aj** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid; 28.9 mg, 70% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.46 (m, 2H), 7.39 – 7.37 (m, 2H), 6.90 (dq, *J* = 8.3, 3.2 Hz, 4H), 3.87 – 3.83 (m, 2H), 3.80 (d, *J* = 3.4 Hz, 6H), 0.92 (s, 9H), 0.10 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.64, 159.60, 156.48, 131.75, 131.69, 127.30, 118.10, 114.51, 113.86, 85.90, 57.91, 55.56, 55.31, 25.76, 18.19, -3.56, -3.68.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{31}NO_4Si$ ([M+Na$^+$]) = 436.1915, Found 436.1905.

1,4-di(naphthalen-2-yl)-3,6-diphenyl-6a,7,12,13-tetrahydro-3*H*,6*H*-[1,2,4]triazolo[4'',3'':1',2']pyrrolo[3',2':4,5] pyridazino[3,4-b]indole (3ak)



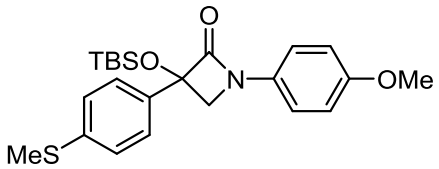
The compound **3ak** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow solid; 38.4mg, 70% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.42 (m, 2H), 7.34 – 7.30 (m, 10H), 7.25F – 7.23 (m, 6H), 6.91 – 6.89 (m, 2H), 3.83 (s, 3H), 3.66 (d, *J* = 5.2 Hz, 1H), 3.50 (d, *J* = 5.3 Hz, 1H), 0.89 (s, 9H), 0.07 (s, 3H), -0.20 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 168.68, 159.52, 142.52, 129.56, 128.24, 127.96, 127.90, 127.48, 113.70, 83.18, 73.66, 60.31, 55.28, 25.81, 18.13, -3.32, -3.75.

HRMS (ESI$^+$) m/z calcd for $C_{35}H_{39}NO_3Si$ ([M+Na$^+$]) = 572.2591, Found 572.2598.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-(4-(methylthio)phenyl)azetidin-2-one (3al)



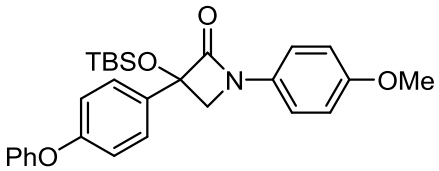
The compound **3al** as synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5) light yellow solid; 29.8mg, 68% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.46 (m, 2H), 7.41 – 7.39 (m, 2H), 7.29 – 7.26 (m, 2H), 6.94 – 6.92 (m, 2H), 3.87 – 3.84 (m, 2H), 3.83 (sf, 3H), 2.50 (s, 3H), 0.95 (s, 9H), 0.13 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.31, 156.56, 138.79, 136.45, 131.55, 126.48, 126.29, 118.13, 114.53, 85.98, 57.93, 55.58, 25.75, 18.21, 15.73, -3.57, -3.66.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{31}NO_3SSi$ ([M+Na$^+$]) = 452.1686, Found 452.1690.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-(4-phenoxyphenyl)azetidin-2-one (3am)



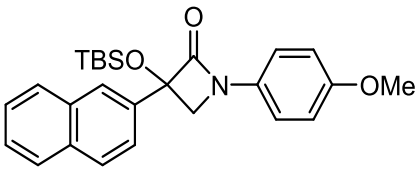
The compound **3am** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow solid; 30.91mg, 65% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.49 (m, 2H), 7.40 – 7.32 (m, 4H), 7.13 – 7.09 (m, 1H), 7.03 – 7.00 (m, 4H), 6.93 – 6.91 (m, 2H), 3.90 – 3.85 (m, 2H), 3.81 (s, 3H), 0.93 (s, 9H), 0.12 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 157.36, 156.96, 156.57, 134.39, 131.57, 129.82, 127.40, 123.51, 119.07, 118.70, 118.14, 114.54, 85.88, 57.96, 55.58, 25.75, 18.21, -3.55, -3.66.

HRMS (ESI$^+$) m/z calcd for $C_{28}H_{33}NO_4Si$ ([M+Na$^+$]) = 498.2701, Found 498.2708.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-(naphthalen-2-yl)azetidin-2-one (3an)



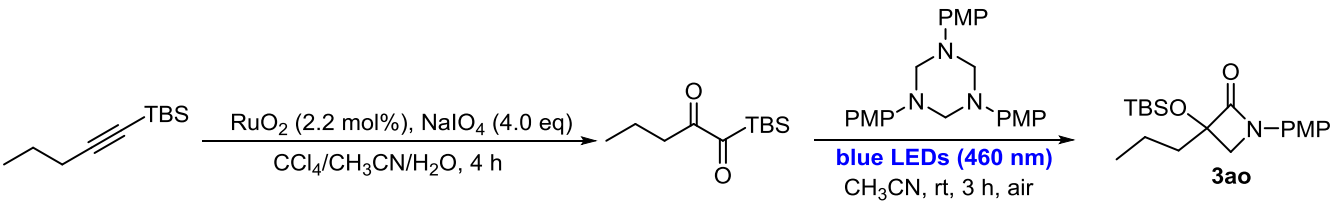
The compound **3an** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid; 36.6 mg, 60% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 1.8 Hz, 1H), 7.87-7.82 (m, 3H), 7.60 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 6.94 – 6.92 (m, 2H), 3.94 – 3.91 (m, 2H), 3.81 (s, 3H), 0.96 (s, 9H), 0.14 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.32, 156.57, 137.00, 133.08 (d, *J* = 12.3 Hz), 131.63, 128.55, 128.38, 127.65, 126.39, 124.78, 123.73, 118.17, 114.55, 86.46, 57.94, 55.59, 25.79, 18.27, -3.51, -3.66.

HRMS (ESI^{+}) m/z calcd for $C_{26}H_{31}NO_3Si$ ([M+Na^{+}]) = 456.1965, Found 456.1975.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-3-propylazetidin-2-one (3ao)



The compound **3ao** was synthesized according to the slightly modified procedure.

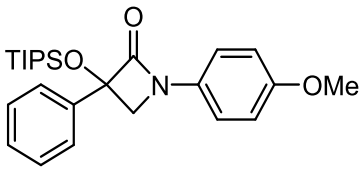
To a solution of the silyl acetylene (91 mg, 0.5 mmol) in $CCl_4/CH_3CN/H_2O$ (2.0 ml: 2.0 ml: 3.0 ml) was added $NaIO_4$ (428 mg, 2.0 mmol). Then, RuO_2 (1.5 mg, 0.011 mmol) was added. After 6 h, the organic phase was filtered through Celite. The solvent was evaporated to get the purple alkyl α-ketoacylsilane compound, which was used in the next step without further purification. Next, the compound **3ao** was synthesized according to the same procedure and purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow liquid; 14.0 mg, 40% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.30 (m, 2H), 6.89 – 6.87 (m, 2H), 3.79 (s, 3H), 3.63 (d, *J* = 5.6 Hz, 1H), 3.46 (d, *J* = 5.4 Hz, 1H), 1.86 – 1.73 (m, 2H), 1.55 – 1.41 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.89 (s, 9H), 0.20 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.06, 156.25, 131.77, 117.86, 114.41, 85.26, 55.53, 54.59, 38.45, 26.24, 25.63, 18.06, 17.19, 14.24, -3.58.

HRMS (ESI+) m/z calcd for $C_{19}H_{31}NNaO_3Si$ ([M+Na+]) = 372.1965, Found 372.1966.

1-(4-methoxyphenyl)-3-phenyl-3-((triisopropylsilyl)oxy)azetidin-2-one (3ap)



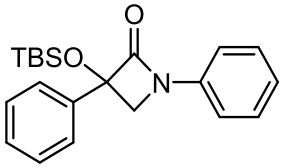
The compound **3ap** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 24.2 mg, 57% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.44 (m, 1H), 7.29 – 7.25 (m, 3H), 7.24 – 7.18 (m, 2H), 6.81 – 6.77 (m, 2H), 3.79 – 3.73 (m, 2H), 3.69 (s, 3H), 1.10-0.89 (m, 3H), 0.91 (dd, *J*=7.4Hz, 9H), 0.90 (dd, *J*=7.4Hz, 9H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.48, 156.55, 140.18, 131.47, 128.50, 128.24, 125.66, 118.17, 114.53, 86.29, 58.41, 55.55, 18.10, 18.06, 17.98, 12.95.

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{35}NO_3Si$ ([M+Na$^+$]) = 448.2278 Found 448.2272.

3-((tert-butyldimethylsilyl)oxy)-1,3-diphenylazetidin-2-one (3aq)



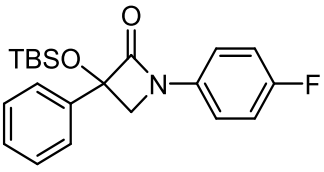
The compound **3aq** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); light yellow solid; 22.5 mg, 64% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.56– 7.53 (m, 2H), 7.46 – 7.43 (m, 2H), 7.40 – 7.37 (m, 3H), 7.36 – 7.33 (m, 2H), 7.17-7.13 (m, 1H), 3.93 – 3.88 (q, 2H), 0.94 (s, 9H), 0.12 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 166.03, 139.51, 137.93, 129.25, 128.53, 128.32, 125.76, 124.44, 116.87, 86.18, 57.82, 25.72, 18.19, -3.59, -3.74.

HRMS (ESI$^+$) m/z calcd for $C_{21}H_{27}NO_2Si$ ([M+Na$^+$]) = 376.1703, Found 376.1696.

3-((tert-butyldimethylsilyl)oxy)-1-(4-fluorophenyl)-3-phenylazetidin-2-one (3ar)



The compound **3ar** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); yellow solid; 22.26 mg, 60% yield.

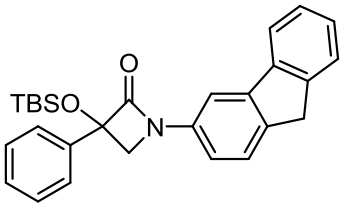
^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.53 (m, 2H), 7.44 – 7.39 (m, 3H), 7.38 – 7.32 (m, 2H), 7.10 – 7.05 (m, 2H), 3.92 – 3.87 (q, 2H), 0.94 (s, 9H), 0.12 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.79, 139.39, 134.24, 128.62, 128.47, 125.82, 118.32, 118.24, 116.21, 115.99, 86.48, 58.04, 25.75, 18.22, -3.56, -3.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -117.25.

HRMS (ESI^+) m/z calcd for $C_{21}H_{26}FNO_2Si$ ($[M+H^+]$) = 372.1790, Found 372.1797.

3-((tert-butyldimethylsilyl)oxy)-1-(9H-fluoren-3-yl)-3-phenylazetidin-2-one (3as)



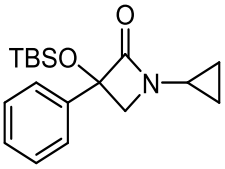
The compound **3as** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow solid; 32.19 mg, 73% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.75 (m, 3H), 7.62 – 7.50 (m, 2H), 7.56 – 7.54 (m, 1H), 7.44 – 7.36 (m, 5H), 7.33 – 7.29 (m, 1H), 4.01-3.92 (q, 2H), 3.92 (s, 2H), 0.99 (s, 9H), 1.02 – 0.85 (m, 3H), 0.18 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 166.04, 144.64, 143.10, 139.62, 136.87, 128.63, 128.42, 126.94, 126.56, 125.85, 125.07, 120.46, 119.66, 115.44, 114.17, 86.18, 58.22, 37.04, 25.82, 18.29, -3.47, -3.63.

HRMS (ESI^+) m/z calcd for $C_{28}H_{31}NO_2Si$ ($[M+Na^+]$) = 464.2016, Found 464.1999.

3-((tert-butyldimethylsilyl)oxy)-1-cyclopropyl-3-phenylazetidin-2-one (3at)



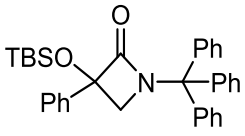
The compound **3at** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); yellow solid; 16.8 mg, 53% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.46 – 7.43 (m, 2H), 7.37-7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 3.45 – 3.42 (m, 2H), 2.70-2.64 (m, 1H), 0.92 (s, 9H), 0.89 – 0.82 (m, 2H), 0.81 – 0.75 (m, 2H), 0.10 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 169.20, 139.88, 128.44, 128.02, 125.54, 86.15, 59.08, 25.76, 24.04, 18.19, 5.20, 5.13, -3.58, -3.72.

HRMS (ESI^+) m/z calcd for $C_{18}H_{27}NO_2Si$ ($[M+Na^+]$) = 340.1703 Found 340.1695.

3-((tert-butyldimethylsilyl)oxy)-3-phenyl-1-tritylazetidin-2-one (3au)



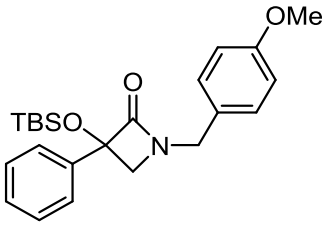
The compound **3au** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); yellow solid; 38.9 mg, 75% yield.

^1H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.54 (m, 2H), 7.40 – 7.38 (m, 3H), 7.37 – 7.34 (m, 9H), 7.31 – 7.29 (m, 6H), 3.72 (d, *J* = 5.4 Hz, 1H), 3.57 (d, *J* = 5.4 Hz, 1H), 0.95 (s, 9H), 0.13 (s, 3H), -0.15 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 168.57, 142.58, 140.20, 129.62, 128.51, 128.36, 128.00, 127.58, 126.83, 83.72, 73.85, 60.31, 25.92, 18.24, -3.21, -3.71.

HRMS (ESI$^+$) m/z calcd for $C_{34}H_{37}NO_2Si$ ([M+Na$^+$]) = 542.2486, Found 542.2496.

3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxybenzyl)-3-phenylazetidin-2-one (3av)



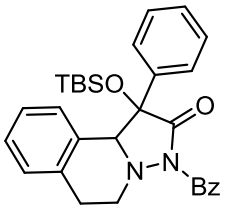
The compound **3av** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10); yellow solid; 23.4 mg, 57% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.44 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.22 – 7.18 (m, 2H), 6.90 – 6.86 (m, 2H), 4.48-4.37 (m, 2H), 3.81 (s, 3H), 3.37 (s, 2H), 0.90 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H).

^{13} C NMR (101 MHz, Chloroform-d) δ 168.70, 159.31, 139.84, 129.74, 128.43, 128.07, 127.17, 125.71, 114.25, 87.23, 57.86, 55.32, 45.20, 25.76, 18.19, -3.55, -3.72.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{31}NO_3Si$ ([M+Na$^+$]) = 420.1965, Found 420.1967.

3-benzoyl-1-((tert-butyldimethylsilyl)oxy)-1-phenyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5aa)



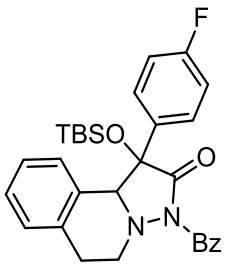
The compound **5aa** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow liquid (62.8 mg, 63% yield, 1.3:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.79 (m, 4H), 7.75 – 7.70 (m, 1H), 7.60 – 7.53 (m, 2H), 7.51 – 7.42 (m, 5H), 7.33 – 7.28 (m, 4H), 7.32 – 7.28 (m, 1H), 7.24 – 7.14 (m, 4H), 7.12 – 7.11 (m, 2H), 7.03-6.99 (s, 2H), 6.45 (dd, *J* = 6.45, 9.07 Hz, 1H), 5.19 (s, 1H), 4.77 (s, 1H), 3.81-3.74 (m, 1H), 3.66-3.62 (m, 1H), 3.21 – 3.16 (m, 1H), 3.15 – 3.13 (m, 1H), 3.05-2.98 (m, 1H), 2.97-2.90 (m, 1H), 2.85-2.79 (m, 1H), 1.62 (s, 3H), 1.26 (s, 3H), 0.94 (s, 7H), 0.64 (s, 9H), 0.13 (s, 3H), 0.05 (s, 2H), -0.16 (s, 3H), -0.34 (s,2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.29, 173.63, 166.67, 166.51, 140.06, 139.81, 134.25, 133.70, 133.67, 133.52, 132.42, 132.21, 130.58, z129.15, 129.13, 128.81, 128.63, 128.54, 128.52, 128.21, 128.16, 128.07, 127.99, 127.90, 127.82, 127.46, 127.03, 125.87, 125.29, 84.23, 83.51, 70.57, 69.93, 49.76, 47.18, 28.68, 28.40, 26.19, 25.48, 18.73, 18.46, -2.92, -3.05, -3.11, -3.71.

HRMS(ESI$^+$) m/z calcd for $C_{30}H_{34}N_2O_3Si$ ([M+Na$^+$]) = 521.2231, Found 521.2240.

3-benzoyl-1-((tert-butyldimethylsilyl)oxy)-1-(4-fluorophenyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ab)



The compound **5ab** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow liquid (47.4 mg, 46% yield, 1.9:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

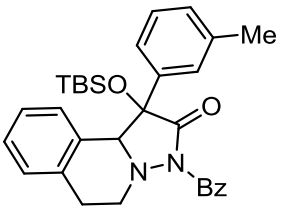
^{1}H NMR (400 MHz, Chloroform-d) δ 7.83-7.80 (m, 3H), 7.71 – 7.68 (m, 1H), 7.59 – 7.53 (m, 2H), 7.48-7.44 (m, 3H), 7.34 – 7.28 (m, 3H), 7.25 – 7.17 (m, 3H), 7.16 – 7.07 (m, 4H), 7.04 – 7.00 (m, 2H), 5.17 (s, 1H), 4.70 (s, 1H), 4.15-4.09 (m, 1H), 3.81-3.75 (m, 1H), 3.63 – 3.59 (m, 1H), 3.19 – 3.11 (m, 2H), 3.03-2.91 (m, 1H), 2.84-2.79 (m, 1H), 2.50-2.45 (m, 1H), 2.04 (s, 1H), 1.27-1.24 (m, 2H), 0.95 (s, 4H), 0.91 (s, 4H), 0.63 (s, 9H), 0.14 (s, 3H), 0.09 (s, 2H), 0.08 (s, 2H), -0.17 (s, 3H), -0.31 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.09, 173.37, 166.62, 166.42, 163.75, 135.78, 134.29, 133.59, 132.53, 132.31, 130.47, 130.40, 129.19, 128.95, 128.87, 128.85, 128.68, 128.28, 128.08, 128.06, 127.74, 127.61, 126.86, 125.99, 125.33, 115.12, 115.01, 114.90, 114.80, 83.80, 77.29, 70.45, 69.91, 49.76, 47.36, 28.63, 28.37, 26.15, 25.68, 25.45, 18.70, 18.43, -2.92, -3.11, -3.15, -3.56, -3.63.

^{19}F NMR (376 MHz, Chloroform-d) δ -112.56, -113.64.

HRMS (ESI$^+$) m/z calcd for $C_{30}H_{33}FN_2O_3Si$ ([M+Na$^+$]) = 539.2137, Found 539.2137.

3-benzoyl-1-((tert-butyldimethylsilyl)oxy)-1-(m-tolyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ac)

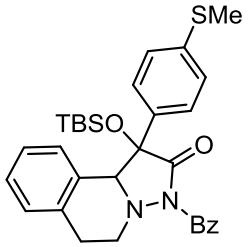


The compound **5ac** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow liquid (56.3 mg, 55% yield, 1.3:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.84-7.81 (m, 3H), 7.75-7.72 (m, 1H), 7.59 – 7.53 (m, 2H), 7.49-7.44 (m, 4H), 7.34 – 7.28 (m, 2H), 7.25 – 7.11 (m, 6H), 7.03 – 6.95 (m, 3H), 6.92 – 6.85 (m, 2H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 4.77 (s, 1H), 3.80-3.74 (m, 1H), 3.64-3.60 (m, 1H), 3.20 – 3.12 (m, 2H), 3.05 – 2.90 (m, 2H), 2.84-2.78 (m, 1H), 2.40 (s, 3H), 2.10 (s, 2H), 1.62 (s, 1H), 1.26 (s,1H), 0.95 (s, 7H), 0.64 (s, 9H), 0.13 (s, 3H), 0.04 (s2H), -0.15 (s, 3H), -0.35 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 137.53, 134.24, 133.73, 132.37, 132.20, 130.71, 129.65, 129.21, 129.14, 128.90, 128.87, 128.48, 128.12, 128.05, 127.98, 127.86, 127.83, 127.71, 127.60, 127.42, 127.12, 125.74, 125.62, 125.21, 124.15, 84.16, 77.26, 70.52, 69.93, 49.79, 47.15, 28.69, 28.42, 26.18, 25.49, 21.61, 21.27, 18.71, 18.48, -2.90, -3.01, -3.08, -3.70.HRMS (ESI$^+$) m/z calcd for $C_{31}H_{36}N_2O_3Si$ ([M+Na$^+$]) = 535.2387, Found 535.2397.

3-benzoyl-1-((tert-butyldimethylsilyl)oxy)-1-(4-(methylthio)phenyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ad)



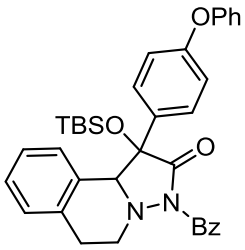
The compound **5ad** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow liquid (62.1 mg, 57% yield, 1.4:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 – 7.79 (m, 4H), 7.72 – 7.69 (m, 1H), 7.59 – 7.53 (m, 2H), 7.49-7.43 (m, 4H), 7.31 – 7.30 (m, 1H), 7.29 – 7.28 (m, 2H), 7.27 (s, 1H), 7.25– 7.24 (m, 1H), 7.22-7.14 (m, 3H), 7.04-6.97 (m, 4H), 6.95-6.92 (m, 2H), 6.51-6.48 (m, 1H), 5.17 (s, 1H), 4.72 (s, 1H), 3.79-3.73 (m, 1H), 3.63-3.59 (m, 1H), 3.20-3.11 (m, 2H), 3.04-2.90 (m, 2H), 2.84-2.78 (m, 1H), 2.53 (s, 3H), 2.39 (s, 3H), 1.62 (s, 2H), 1.27 (s, 1H), 1.26 (s.2H), 0.94 (s, 1H), 0.62 (s, 1H), 0.12 (s, 3H), 0.06 (s, 3H), -0.15 (s, 3H), -0.31 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 173.50, 136.71, 134.25, 133.64, 132.44, 132.24, 129.16, 129.07, 128.96, 128.84, 128.66, 128.19, 128.07, 127.93, 127.82, 127.50, 126.99, 125.89, 125.63, 125.32, 124.99, 83.99, 77.26, 70.50, 69.85, 49.76, 47.23, 28.66, 28.42, 26.17, 25.46, 18.71, 18.44, 15.48, 14.96, -2.88, -3.02, -3.12, -3.53.

HRMS (ESI$^+$) m/z calcd for $C_{31}H_{36}N_2O_3SS$ ([M+Na$^+$]) = 567.2108, Found 567.2115.

3-benzoyl-1-((tert-butyldimethylsilyl)oxy)-1-(4-phenoxyphenyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ae)



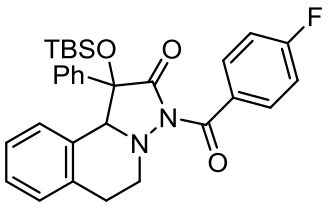
The compound **5ae** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (63.7 mg, 54% yield, 1.3:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.78 (m, 4H), 7.71 – 7.69 (m, 1H), 7.59 – 7.53 (m, 2H), 7.49 – 7.43 (m, 4H), 7.40 – 7.36 (m, 3H), 7.34 – 7.29 (m, 4H), 7.24 – 7.12 (m, 5H), 7.11 – 7.02 (m, 9H), 6.94 – 6.92 (m, 2H), 6.73 – 6.71 (m, 2H), 6.54 – 6.52 (m, 1H), 5.17 (s, 1H), 4.74 (s, 1H), 3.80 – 3.74 (m, 1H), 3.67 – 3.63 (m, 1H), 3.22 – 3.13 (m, 2H), 3.09 – 2.94 (m, 2H), 2.85 – 2.80 (m, 1H), 2.54 – 2.49 (m, 1H), 1.60 (s, 2H), 1.26 (s, 2H), 0.95 (s, 7H), 0.62 (s, 9H), 0.13 (s, 3H), 0.08 (s, 2H), -0.14 (s, 3H), -0.28 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 156.64, 156.27, 134.51, 134.29, 133.70, 132.43, 132.21, 130.14, 129.91, 129.84, 129.14, 128.76, 128.62, 128.52, 128.22, 128.08, 127.96, 127.80, 127.52, 126.96, 125.92, 125.33, 123.81, 123.79, 119.47, 119.34, 117.78, 117.50, 83.94, 83.04, 77.25, 70.50, 69.83, 49.73, 47.24, 28.68, 28.44, 26.17, 25.45, 18.72, 18.44, -2.88, -3.04, -3.13, -3.58.

HRMS (ESI$^+$) m/z calcd for $C_{36}H_{38}N_2O_4Si$ ([M+Na$^+$]) = 613.2493, Found 613.2512.

1-((tert-butyldimethylsilyl)oxy)-3-(4-fluorobenzoyl)-1-phenyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5af)



The compound **5af** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow liquid (53.7 mg, 52% yield, 1.1:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 – 7.86 (m, 4H), 7.73 – 7.71 (m, 1H), 7.48 – 7.37 (m, 3H), 7.37 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 7.20 – 7.11 (m, 8H), 7.10 – 7.09 (m, 4H), 7.03 – 6.99 (m, 2H), 6.44 (d, *J* = 7.5 Hz, 1H), 5.29 (s, 1H), 5.18 (s, 1H), 3.81 – 3.75 (m, 1H), 3.60 – 3.56 (m, 1H), 3.19 – 3.08 (m, 2H), 3.05 – 2.90 (m, 2H), 2.85 – 2.79 (m,

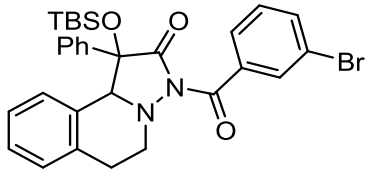
1H), 2.48 – 2.42 (m, 1H), 1.60 (s, 3H), 1.29 (s, 1H), 1.26 (s, 2H), 0.95 (s, 9H), 0.64 (s, 9H), 0.13 (s, 3H), 0.05 (s, 3H), -0.15 (s, 3H), -0.33 (s, 3H).

^{z13}C NMR (101 MHz, Chloroform-d) δ 139.96, 139.72, 134.15, 133.44, 132.03, 131.93, 131.78, 131.69, 130.48, 129.02, 128.58, 128.27, 128.18, 128.03, 127.96, 127.89, 127.87, 127.53, 127.04, 127.00, 125.93, 125.35, 115.43, 115.20, 84.18, 83.47, 70.56, 69.93, 49.87, 47.28, 28.66, 28.39, 26.18, 25.47, 18.73, 18.46, -2.90, -3.04, -3.07, -3.69.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.80, -105.57.

HRMS (ESI$^+$) m/z calcd for $C_{30}H_{33}FN_2O_3Si$ ([M+Na$^+$]) = 539.2317, Found 539.2317.

3-(3-bromobenzoyl)-1-((tert-butyldimethylsilyl)oxy)-1-phenyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ag)



The compound **5ag** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (64.6 mg, 56% yield, 1.3:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

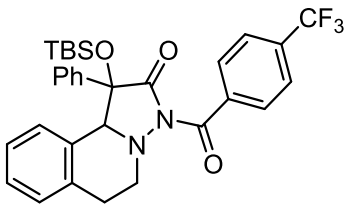
^{1}H NMR (400 MHz, Chloroform-d) δ 7.95 – 7.94 (m, 2H), 7.75 – 7.66 (m, 5H), 7.45 – 7.38 (m, 3H), 7.37 – 7.29 (m, 5H), 7.24 – 7.15 (m, 4H), 7.12 – 6.99 (m, 6H), 5.18 (s, 1H), 4.75 (s, 1H), 3.22 – 3.13 (m, 2H), 3.03 – 2.91 (m, 2H), 2.86 – 2.80 (m, 1H), 2.47 – 2.43 (m, 1H), 1.60 (s, 1H), 1.29 (s, 1H), 1.26 (s, 2H), 0.95 (s, 7H), 0.64 (s, 9H), 0.13 (s, 1H), 0.05 (s, 2H), -0.16 (s, 3H), -0.34 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 173.70, 135.57, 135.24, 135.06, 133.43, 131.95, 131.70, 129.64, 128.94, 128.63, 128.57, 128.31, 128.19, 128.03, 127.98, 127.89, 127.57, 127.55, 127.25, 127.04, 127.02, 125.93, 125.35, 122.10, 84.09, 77.25, 70.56, 69.95, 49.80, 47.20, 28.65, 28.36, 26.17, 25.46, 18.72, 18.46, -2.89, -3.04, -3.70.^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.43.

HRMS (ESI$^+$) m/z calcd for $C_{30}H_{33}Br^{78.9183}N_2O_3Si$ ([M+Na$^+$]) = 599.1336, Found 599.1344.

HRMS (ESI$^+$) m/z calcd for $C_{30}H_{33}Br^{80.9163}N_2O_3Si$ ([M+Na$^+$]) = 601.1316, Found 601.1315.

1-((tert-butyldimethylsilyl)oxy)-1-phenyl-3-(4-(trifluoromethyl)benzoyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ah)



The compound **5ah** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (76.9 mg, 68% yield, 1.7:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

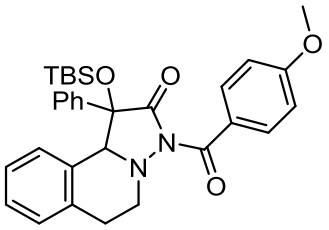
^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 – 7.86 (m, 6H), 7.75 – 7.71 (m, 7H), 7.46 – 7.38 (m, 4H), 7.34 – 7.29 (m, 4H), 7.25 – 7.16 (m, 5H), 7.12 – 7.01 (m, 11H), 6.45 – 6.42 (m, 1H), 5.19 (s, 2H), 4.77 (s, 1H), 3.82 – 3.76 (m, 1H), 3.68 – 3.63 (m, 1H), 3.23 – 3.11 (m, 3H), 3.04 – 2.92 (m, 4H), 2.87 – 2.82 (m, 1H), 2.50 – 2.43 (m, 2H), 1.60 (s, 3H), 1.29 (s, 1H), 1.26 (s, 2H), 0.94 (s, 13H), 0.64 (s, 9H), 0.11 (s, 3H), 0.03 (s, 5H), -0.17 (s, 3H), -0.34 (s, 5H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.51, 165.28, 139.66, 139.47, 137.22, 133.38, 130.30, 129.26, 128.87, 128.70, 128.59, 128.53, 128.37, 128.20, 128.08, 128.04, 127.93, 127.88, 127.59, 127.01, 126.94, 125.97, 125.37, 125.22, 125.18, 125.14, 84.11, 83.42, 70.60, 69.93, 49.64, 47.11, 28.62, 28.35, 26.14, 25.44, 18.71, -2.93, -3.05, -3.10, -3.69.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.04, -63.01.

HRMS (ESI$^+$) m/z calcd for $C_{31}H_{33}F_3N_2O_3Si$ ([M+Na$^+$]) = 589.2105, Found 589.2113.

1-((tert-butyldimethylsilyl)oxy)-3-(4-methoxybenzoyl)-1-phenyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ai)



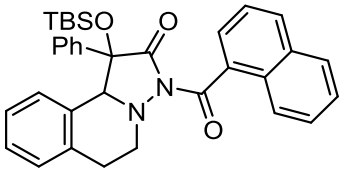
The compound **5ai** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); yellow liquid (55.9 mg, 53% yield, 1.6:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 – 7.88 (m, 3H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.35 (m, 6H), 7.23 – 7.07 (m, 6H), 7.02 – 6.99 (m, 2H), 6.96 – 6.93 (m, 4H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.19 (s, 1H), 4.77 (s, 1H), 3.88 (d, *J* = 4.6 Hz, 5H), 3.80 – 3.74 (m, 1H), 3.19 – 2.90 (m, 3H), 2.83 – 2.78 (m, 1H), 2.47 – 2.42 (m, 1H), 1.58 (s, 2H), 1.25 (s, 5H), 0.95 (s, 7H), 0.63 (s, 9H), 0.15 (s, 3H), 0.15 (s, 3H), 0.08 (s, 2H), -0.14 (s, 3H), -0.33 (s, 2H)..

^{13}C NMR (101 MHz, Chloroform-d) δ 163.11, 140.25, 134.23, 131.99, 131.81, 129.25, 128.60, 128.49, 128.41, 128.11, 127.93, 127.86, 127.80, 127.76, 127.39, 127.02, 125.82, 125.25, 113.35, 113.30, 84.24, 77.22, 70.56, 69.94, 55.43, 50.00, 47.38, 28.70, 28.43, 26.18, 25.47, 18.44, -2.89, -3.06, -3.73.

HRMS (ESI$^+$) m/z calcd for $C_{31}H_{36}N_2O_4Si$ ([M+Na$^+$]) = 551.2337, Found 551.2347.

3-(1-naphthoyl)-1-((tert-butyldimethylsilyl)oxy)-1-phenyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5aj)



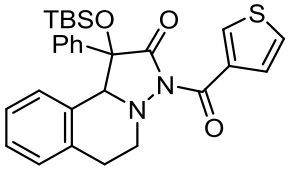
The compound **5aj** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (57.1 mg, 52% yield, 1.1:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 – 7.97 (m, 4H), 7.95 – 7.91 (m, 2H), 7.73 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.65 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.62 – 7.53 (m, 7H), 7.38 – 7.29 (m, 4H), 7.25 – 7.19 (m, 4H), 7.18 – 7.14 (m, 1H), 7.09 – 6.99 (m, 16H), 6.44 (d, *J* = 7.6 Hz, 1H), 5.21 (s, 1H), 4.80 (s, 1H), 3.49 – 3.46 (m, 1H), 3.55 – 3.27 (m, 1H), 3.10 – 3.00 (m, 2H), 2.94 – 2.88 (m, 1H), 2.53 – 2.45 (m, 1H), 1.63 (s, 2H), 1.27 (s, 2H), 0.90 (s, 9H), 0.63 (s, 9H), 0.01 (s, 3H), -0.16 (s, 3H), -0.30 (s, 3H), -0.45 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 166.19, 139.80, 133.56, 133.42, 132.67, 130.96, 130.66, 129.85, 129.01, 128.81, 128.73, 128.62, 128.58, 128.55, 128.21, 127.95, 127.81, 127.49, 127.35, 127.30, 127.03, 126.92, 126.49, 126.45, 125.86, 125.51, 125.26, 124.86, 124.81, 124.61, 124.21, 124.13, 84.21, 83.55, 77.28, 70.61, 69.93, 49.22, 46.71, 28.68, 28.40, 26.14, 25.46, 18.67, 18.45, -3.18, -3.31, -3.77.

HRMS (ESI$^+$) m/z calcd for $C_{34}H_{36}N_2O_3Si$ ([M+Na$^+$]) = 571.2387, Found 571.2394.

1-((tert-butyldimethylsilyl)oxy)-1-phenyl-3-(thiophene-3-carbonyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ak)



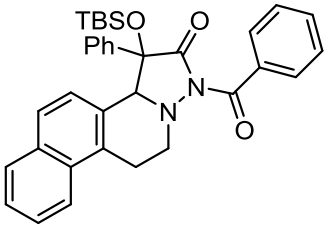
The compound **5ak** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow liquid (61.6 mg, 61% yield, 1.4:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.50 (ddd, *J* = 12.1, 3.0, 1.2 Hz, 1H), 7.47 (ddd, *J* = 7.3, 5.1, 1.2 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.45 – 7.39 (m, 3H), 7.38 – 7.35 (m, 3H), 7.33 – 7.27 (m, 3H), 7.24 – 7.14 (m, 3H), 7.12 – 7.07 (m, 3H), 7.06 – 7.00 (m, 2H), 6.46 – 6.44 (m, 1H), 5.20 (s, 1H), 4.75 (s, 1H), 3.85 – 3.78 (m, 1H), 3.51 – 3.47 (m, 1H), 3.21 – 3.13 (m, 1H), 3.03 – 2.89 (m, 2H), 2.86 – 2.80 (m, 1H), 2.46 – 2.41 (m, 1H), 1.61 (s, 3H), 0.95 (s, 7H), 0.64 (s, 9H), 0.15 (s, 3H), 0.10 (s, 2H), -0.10 (s, 3H), -0.32 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.29, 173.56, 140.20, 134.09, 133.99, 129.33, 128.71, 128.59, 128.52, 128.20, 128.18, 128.00, 127.98, 127.82, 127.53, 127.08, 126.01, 125.42, 125.05, 125.01, 83.83, 83.12, 70.65, 69.86, 50.39, 47.57, 28.72, 28.43, 26.22, 25.50, 18.76, 18.45, -2.82, -3.09, -3.71.

HRMS (ESI$^+$) m/z calcd for $C_{28}H_{32}N_2O_3SSi$ ([M+Na$^+$]) = 527.1798, Found 527.1804.

3-benzoyl-1-((tert-butyldimethylsilyl)oxy)-1-phenyl-1,5,6,12c-tetrahydrobenzo[h]pyrazolo[5,1-a]isoquinolin-2(3H)-one (5al)



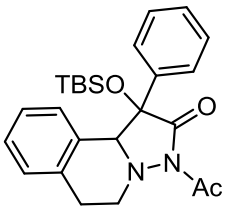
The compound **5al** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow solid (57.3 mg, 55% yield, 1.9:1 d.r.) as an inseparable diastereomer mixtures, it was not separated; the d.r. was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 – 7.96 (m, 4H), 7.89 – 7.79 (m, 16H), 7.61 – 7.42 (m, 23H), 7.20 – 7.17 (m, 4H), 7.13 – 7.02 (m, 7H), 6.53 (d, *J* = 8.6 Hz, 1H), 5.31 (s, 2H), 4.90 (s, 1H), 3.46 – 3.27 (m, 5H), 3.18 – 3.09 (m, 4H), 3.04 – 2.96 (m, 2H), 1.61 (s, 2H), 1.27 (s, 3H), 0.99 (s, 19H), 0.52 (s, 9H), 0.14 (s, 3H), 0.09 (s, 7H), -0.13 (s, 3H), -0.31 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.28, 166.72, 139.88, 133.70, 132.94, 132.45, 132.25, 129.58, 129.20, 128.85, 128.65, 128.60, 128.52, 128.29, 128.11, 127.98, 127.04, 126.57, 126.39, 126.25, 125.99, 125.79, 125.70, 124.85, 123.20, 123.04, 83.89, 77.26, 71.20, 70.46, 49.57, 47.04, 26.25, 25.32, 25.22, 25.15, 18.79, 18.42, -2.90, -3.02, -3.69.

HRMS (ESI$^+$) m/z calcd for $C_{34}H_{36}N_2O_3Si$ ([M+Na$^+$]) = 571.2387, Found 571.2379.

3-acetyl-1-((tert-butyldimethylsilyl)oxy)-1-phenyl-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5am)



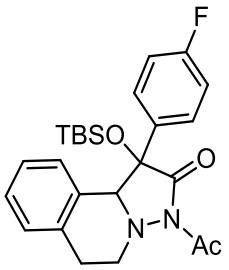
The compound **5am** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (49.7 mg, 57% yield, 6.3:1 d.r.) as a diastereomer mixture, and major diastereomer could be separated.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.36 (m, 3H), 7.31 – 7.28 (m, 2H), 7.17 – 7.15 (m, 2H), 6.99 – 6.94 (m, 1H), 6.36 (dt, *J* = 7.6, 1.0 Hz, 1H), 4.64 (s, 1H), 3.74-3.69 (m, 1H), 3.62-3.55 (m, 1H), 3.30 – 3.21 (m, 1H), 2.85-2.79 (m, 1H), 2.67 (s, 3H), 1.25 (s, 1H), 0.64 (s, 9H), 0.06 (s, 3H), -0.11 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.46, 166.94, 139.81, 134.36, 128.96, 128.25, 128.11, 127.37, 126.97, 126.86, 125.20, 84.50, 70.11, 48.49, 28.57, 25.44, 25.26, 18.45, -3.03, -3.46.

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{32}N_2O_3Si$ ([M+Na$^+$]) = 459.2074, Found 459.2078.

3-acetyl-1-((tert-butyldimethylsilyl)oxy)-1-(4-fluorophenyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5an)



The compound **5an** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (46.3 mg, 51% yield, 7.3:1) as a diastereomer mixture, and major diastereomer could be separated.

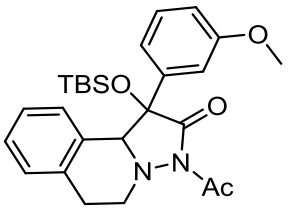
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.23 (m, 2H), 7.23 – 7.14 (m, 2H), 7.18 – 7.06 (m, 2H), 7.04 – 6.94 (m, 1H), 6.38 – 6.31 (m, 1H), 4.57 (s, 1H), 3.71 (ddd, *J* = 9.3, 5.7, 2.0 Hz, 1H), 3.58 (ddd, *J* = 12.8, 9.3, 3.6 Hz, 1H), 3.26 (ddd, *J* = 17.5, 12.5, 5.6 Hz, 1H), 2.83 (ddd, *J* = 16.5, 3.7, 2.0 Hz, 1H), 2.66 (s, 3H), 1.25 (d, *J* = 1.4 Hz, 1H), 0.92 – 0.80 (m, 1H), 0.63 (d, *J* = 6.0 Hz, 1H), 0.63 (s, 8H), 0.06 (d, *J* = 6.7 Hz, 1H), 0.06 (s, 3H), -0.13 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d6) δ 124.11, 124.03, 123.48, 122.77, 121.92, 120.49, 110.42, 110.20, 72.60, 72.49, 72.28, 71.97, 65.26, 43.70, 23.77, 20.65, 20.52, -7.85, -8.29.

^{19}F NMR (376 MHz, DMSO-d_6) δ -118.34.

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{31}FN_2O_3Si$ ([M+Na$^+$]) = 477.1980, Found 477.1973.

3-acetyl-1-((tert-butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ao)



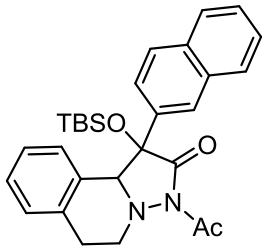
The compound **5ao** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:6); light yellow liquid (60.7 mg, 65% yield, 6.1:1) as a diastereomer mixture, and major diastereomer could be separated.

^{1}1H NMR (400 MHz, Chloroform-d) δ 7.91 (t, *J* = 7.3 Hz, 2H), 7.88 – 7.80 (m, 2H), 7.59 – 7.50 (m, 2H), 7.38 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.20 – 7.12 (m, 2H), 6.95 – 6.87 (m, 1H), 6.33 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.76 (s, 1H), 3.75 (ddd, *J* = 9.3, 5.6, 2.0 Hz, 1H), 3.64 (ddd, *J* = 12.8, 9.3, 3.5 Hz, 1H), 3.29 (ddd, *J* = 17.6, 12.5, 5.6 Hz, 1H), 2.85 (ddd, *J* = 16.5, 3.7, 1.9 Hz, 1H), 2.71 (s, 3H), 1.27 (s, 1H), 1.26 (s, 1H), 0.71 (s, 9H), 0.71 (d, *J* = 6.1 Hz, 0H), 0.09 (s, 3H), -0.10 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.35, 166.99, 137.14, 134.40, 132.57, 128.97, 128.27, 128.13, 127.95, 127.76, 127.40, 126.90, 126.74, 126.63, 126.55, 125.23, 124.35, 84.63, 77.24, 69.85, 48.58, 28.60, 25.50, 25.33, 18.55, -3.00, -3.42.

HRMS (ESI^{+}) m/z calcd for $C_{26}H_{34}N_2O_4Si$ ([M+Na^{+}]) = 489.2180, Found 489.2183.

3-acetyl-1-((tert-butyldimethylsilyl)oxy)-1-(naphthalen-2-yl)-1,5,6,10b-tetrahydropyrazolo[5,1-a]isoquinolin-2(3H)-one (5ap)



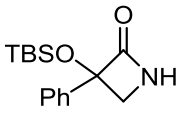
The compound **5ap** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:5); light yellow liquid (55.5 mg, 57% yield, 6.6:1) as a diastereomer mixture, and major diastereomer could be separated.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 (t, *J* = 7.9 Hz, 1H), 7.20 – 7.00 (m, 2H), 6.96 – 6.87 (m, 1H), 6.86 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 6.83 – 6.75 (m, 2H), 6.38 – 6.32 (m, 1H), 4.59 (s, 1H), 3.74 (s, 3H), 3.65 (ddd, *J* = 9.3, 5.6, 2.0 Hz, 1H), 3.50 (ddd, *J* = 12.7, 9.3, 3.6 Hz, 1H), 3.19 (ddd, *J* = 17.5, 12.4, 5.5 Hz, 1H), 2.76 (ddd, *J* = 16.5, 3.6, 2.0 Hz, 1H), 2.60 (s, 3H), 1.20 (s, 1H), 1.19 (s, 0H), 0.97 – 0.79 (m, 1H), 0.58 (s, 8H), -0.12 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.28, 166.93, 159.19, 141.51, 134.36, 129.24, 128.97, 128.09, 127.39, 127.01, 125.15, 119.16, 113.90, 112.89, 84.44, 77.26, 70.08, 55.35, 48.49, 28.57, 25.42, 25.25, 18.45, -2.94, -3.47.

HRMS (ESI^{+}) m/z calcd for $C_{29}H_{34}N_2O_3Si$ ([M+Na^{+}]) = 509.2231, Found 509.2238.

3-((tert-butyldimethylsilyl)oxy)-3-phenylazetidin-2-one (6aa)



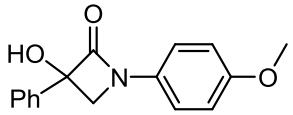
The compound **6aa** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:3); light yellow solid; 71.5 mg, 84% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.51 (m, 1H), 7.39 – 7.29 (m, 3H), 6.63 (s, 1H), 3.59 – 3.54 (m, 2H), 0.93 (s, 1H), 0.13 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 170.35, 139.55, 128.45, 128.15, 125.56, 88.95, 55.06, 25.74, 18.22, -3.61, -3.72.

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{23}NO_2Si$ ([M+Na$^+$]) = 300.1390, Found 300.1392.

3-hydroxy-1-(4-methoxyphenyl)-3-phenylazetidin-2-one (7aa)



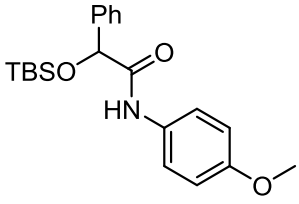
The compound **7aa** was synthesized according to the general procedure, purified by flash column chromatography (ethyl acetate/petroleum ether, 1:3); light yellow solid; 55.5 mg, 84% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.53 (m, 2H), 7.40 – 7.31 (m, 5H), 6.90 – 6.86 (m, 2H), 6.92 – 6.81 (m, 4H), 4.14 (s, 1H), 3.96 (d, *J* = 5.6 Hz, 2H), 3.90 (d, *J* = 5.6 Hz, 2H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 166.09, 156.66, 138.33, 131.27, 128.84, 128.72, 125.62, 118.29, 114.47, 84.51, 77.25, 56.58, 55.55.

HRMS (ESI$^+$) m/z calcd for $C_{16}H_{15}NO_3$ ([M+Na$^+$]) = 292.0944, Found 292.0944.

2-((tert-butyldimethylsilyl)oxy)-N-(4-methoxyphenyl)-2-phenylacetamide (P1)



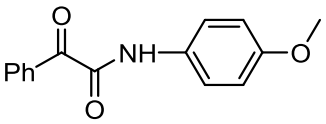
A thimbleful of compound **P1** was detected in this reaction, however, it was very difficult to separate completely to evaluate accurately the isolated yield of **P1** due to very low content and complex system.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.62 (s, 1H), 7.55 – 7.48 (m, 4H), 7.39 – 7.31 (m, 3H), 6.88 – 6.86 (m, 2H), 5.20 (s, 1H), 3.77 (s, 3H), 1.02 (s, 9H), 0.17 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 169.71, 156.46, 139.54, 130.65, 128.46, 128.24, 126.30, 120.97, 114.24, 75.96, 55.50, 25.85, 18.23, -4.66, -5.30.

HRMS (ESI$^+$) m/z calcd for $C_{21}H_{29}NO_3Si$ ([M+Na$^+$]) = 394.1809, Found 394.1809.

N-(4-methoxyphenyl)-2-oxo-2-phenylacetamide (P2)



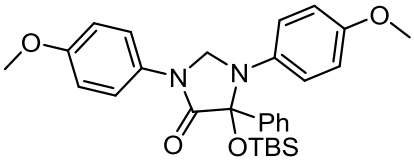
A thimbleful of compound **P2** was detected in this reaction, however, it was very difficult to separate completely to evaluate accurately the isolated yield of **P2** due to very low content and complex system.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.88 (s, 1H), 8.43 – 8.40 (m, 2H), 7.67 – 7.61 (m, 3H), 7.53 – 7.48 (m, 2H), 6.94 – 6.92 (m, 2H), 3.82 (s, 3H).

^{13}13C NMR (101 MHz, Chloroform-d) δ 187.64, 158.70, 157.10, 134.58, 133.25, 131.49, 129.85, 128.57, 121.54, 114.40, 55.53.

HRMS (ESI^{+}) m/z calcd for $C_{15}H_{13}NO_3$ ([M+H^{+}]) = 278.0788, Found 278.0792.

5-((tert-butyldimethylsilyl)oxy)-1,3-bis(4-methoxyphenyl)-5-phenylimidazolidin-4-one (P3)



A thimbleful of compound **P3** was likely formed in this reaction, however, it was very difficult to separate and be purified to evaluate accurately the isolated yield of **P3** due to very low content and complex system.

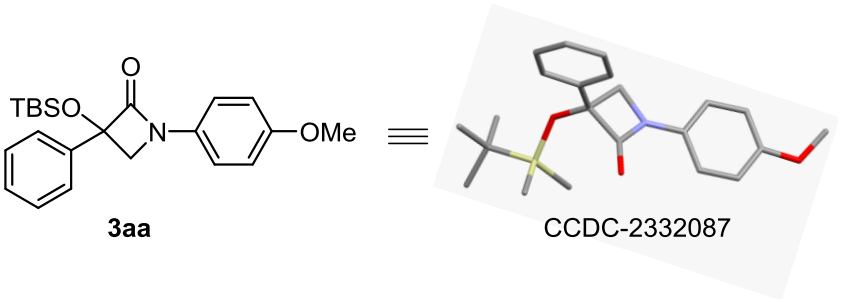
^{1}H NMR (600 MHz, Chloroform-d) δ 8.76 (s, 1H), 7.57 – 7.55 (m, 2H), 7.49 – 7.47 (m, 2H), 7.39 – 7.29 (m, 5H), 6.87 – 6.86 (m, 2H), 6.78 – 6.77 (m, 2H), 6.62 – 6.60 (m, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 1.05 (s, 9H), 0.09 (s, 3H), -0.19 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 170.96 , 156.47 , 140.47 , 130.64 , 128.61 , 128.56 , 126.30 , 120.84 , 114.88 , 114.81 , 114.26 , 81.66 , 55.76 , 55.54 , 51.37 , 26.27 , 26.16 , 18.75 , -3.09 , -3.40 .

HRMS (ESI^{+}) m/z calcd for $C_{29}H_{36}N_2O_4Si$ ([M+H^{+}]) = 505.2517, Found 505.2533.

13. The X-ray data.

The X-ray data for 3aa: The **3aa** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at rt. CCDC-2332087 (**3aa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.



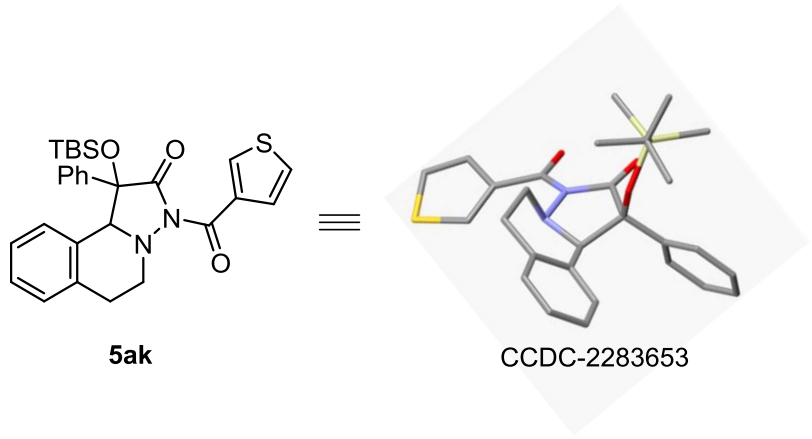
Crystallographic Data for **3aa**.

Formula	$C_{22}H_{29}NO_3Si$
Formula mass (amu)	383.55
Space group	P 1 21/c 1
a (Å)	14.9654(7)
b (Å)	14.3064(9)
c (Å)	10.3877(4)
α (deg)	90
β (deg)	90.521(4)
γ (deg)	90
V (Å^3)	2223.92(19)
Z	4
λ (Å)	0.71073
T (K)	293
ρ_{calcd} (g cm^{-3})	1.146
μ (mm^{-1})	0.126
Transmission factors	0.691, 1.000
θ_{max} (deg)	26.367
No. of unique data, including $F_o^2 < 0$	4508
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2770
No. of variables	255
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0714
$R_w(F_o^2)$ [b]	0.1998
Goodness of fit	1.021

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

The X-ray data for 5ak: The **5ak** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at rt. CCDC-2283653 (**5ak**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.



Crystallographic Data for **5ak**.

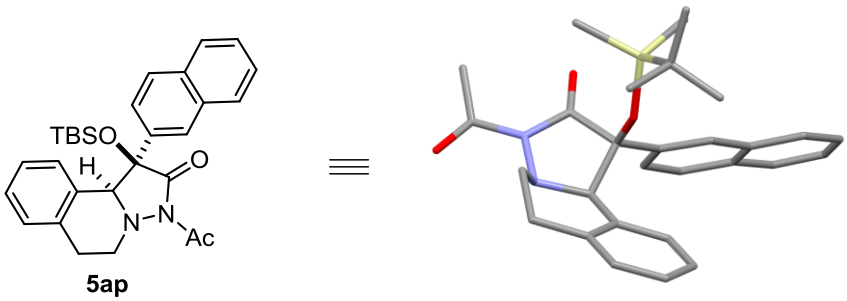
Formula	$C_{28}H_{32}N_2O_3SSi$
Formula mass (amu)	504.70
Space group	P-1
a (Å)	9.7024(2)
b (Å)	12.0009(3)
c (Å)	12.1350(3)
α (deg)	105.321(1)
β (deg)	100.939(1)
γ (deg)	92.931(1)
V (Å3)	1330.32(5)
Z	2
λ (Å)	1.54178
T (K)	173
ρcalcd (g cm-3)	1.260
μ (mm-1)	1.764
Transmission factors	0.852, 1.000
θ max (deg)	68.376
No. of unique data, including Fo2 < 0	4870
No. of unique data, with Fo2 > 2σ(Fo2)	4537

No. of variables	321
R(F) for Fo2 > 2σ(Fo2) a	0.0328
Rw(Fo2) b	0.0859
Goodness of fit	1.041

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

The X-ray data for 5ap: The **5ap** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at rt. CCDC-2344771 (**5ap**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.



5ap

Crystallographic Data for **5ap**.

Formula	$C_{29}H_{34}N_2O_3Si$
Formula mass (amu)	486.67
Space group	P 21/c
a (Å)	9.3844(3)
b (Å)	31.1691(8)
c (Å)	8.9688(2)
α (deg)	90
β (deg)	95.664(1)
γ (deg)	90
V (Å^3)	2610.60(12)
Z	4
λ (Å)	1.54178
T (K)	173K
ρ_{calcd} (g cm^{-3})	1.238

μ (mm^{-1})	1.051
Transmission factors	0.568, 1.000
θ_{max} (deg)	68.556
No. of unique data, including $F_o^2 < 0$	4794
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4415
No. of variables	251
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0877
$R_w(F_o^2)$ [b]	0.2261
Goodness of fit	1.040

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

14. References

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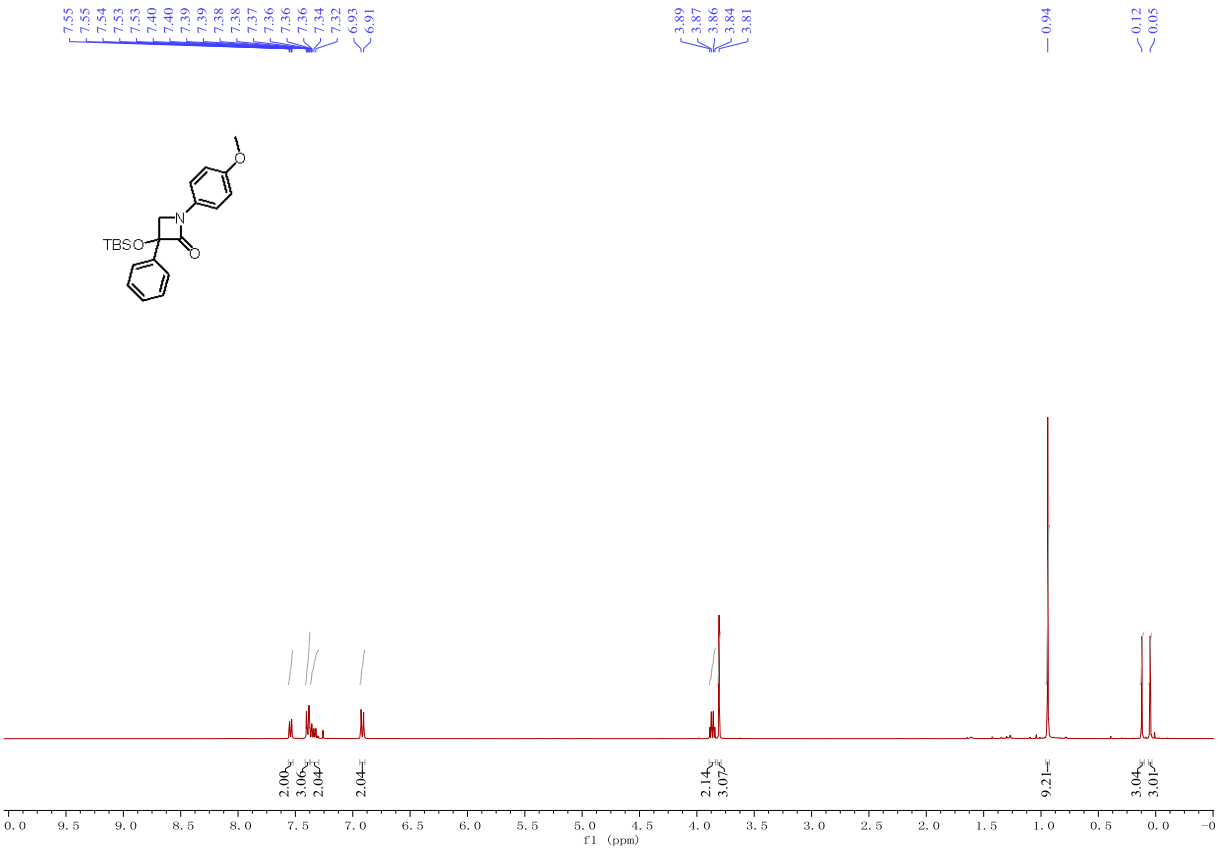
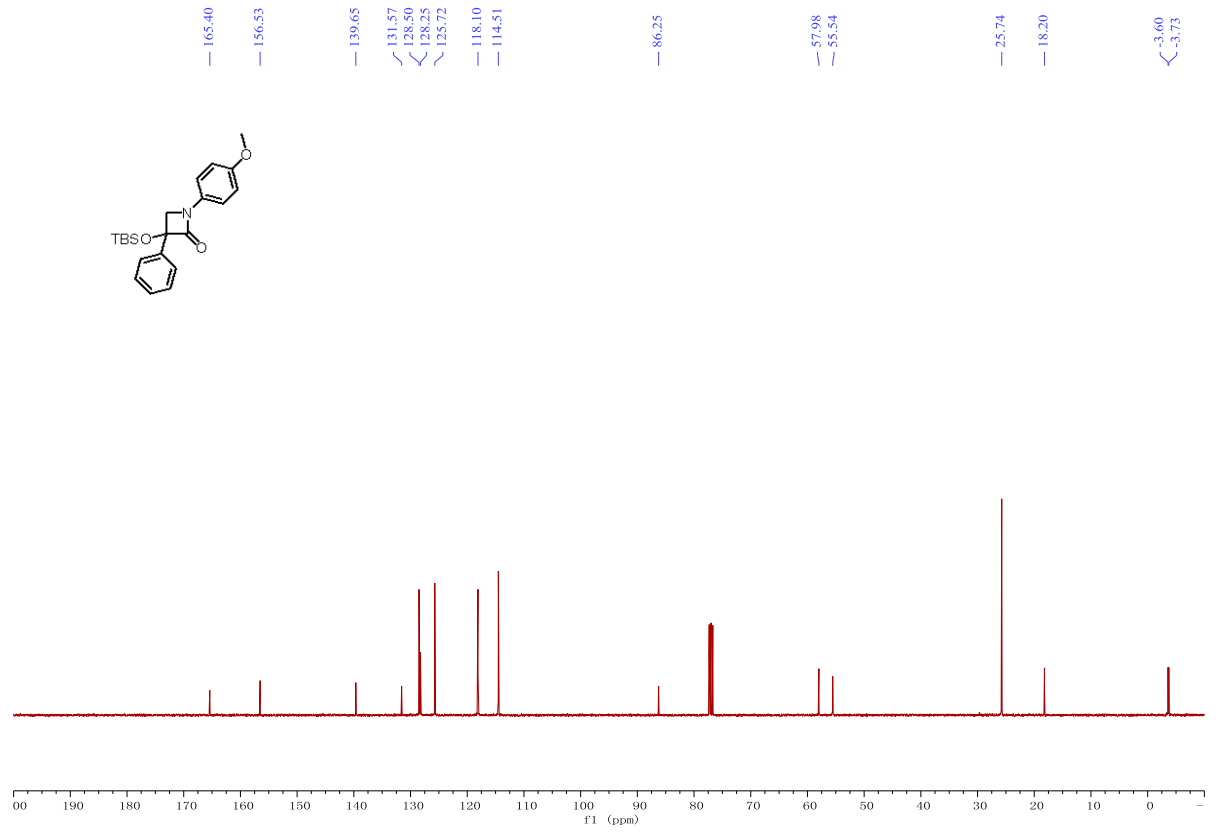
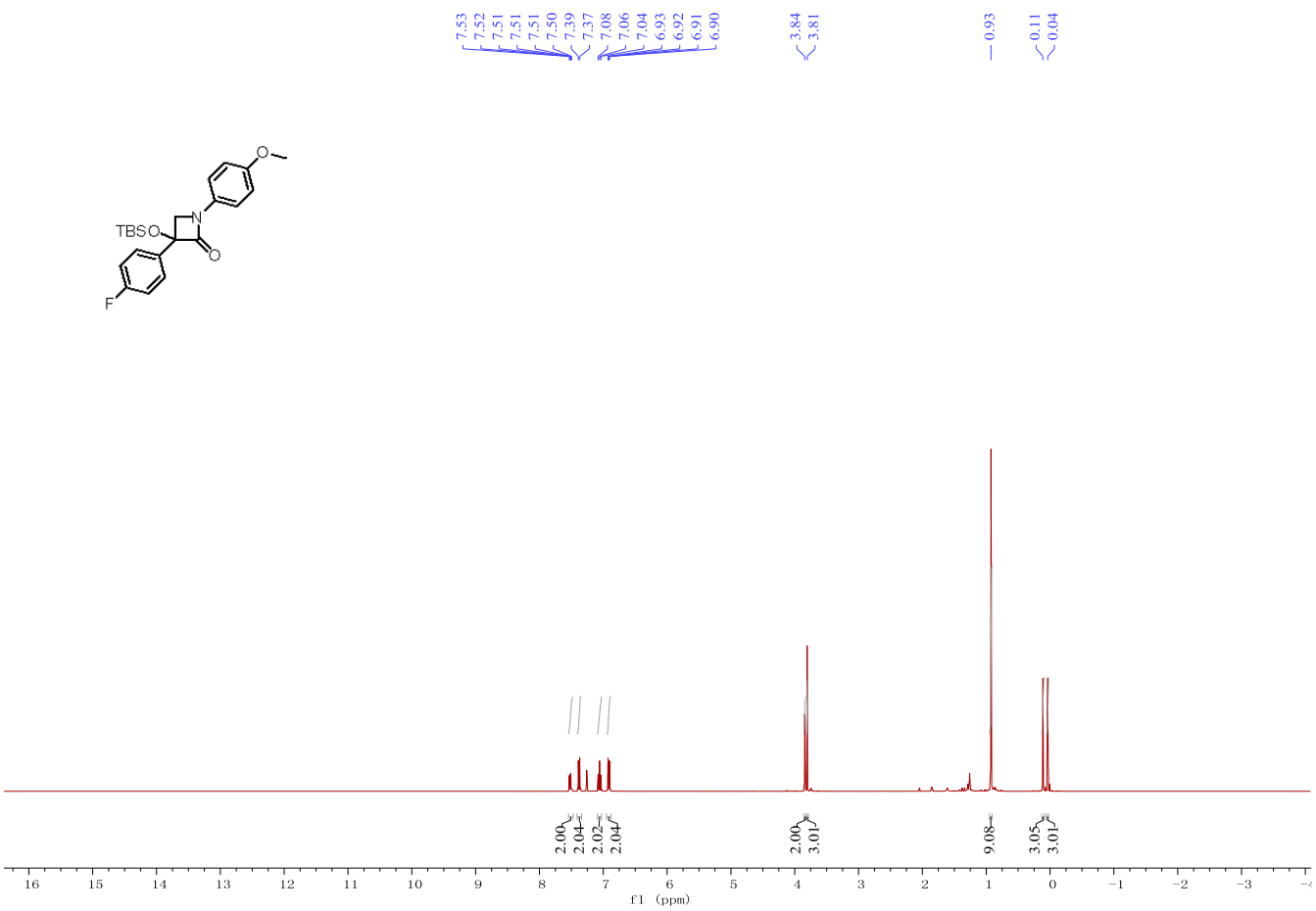
15. Copies of NMR spectra for the reaction products



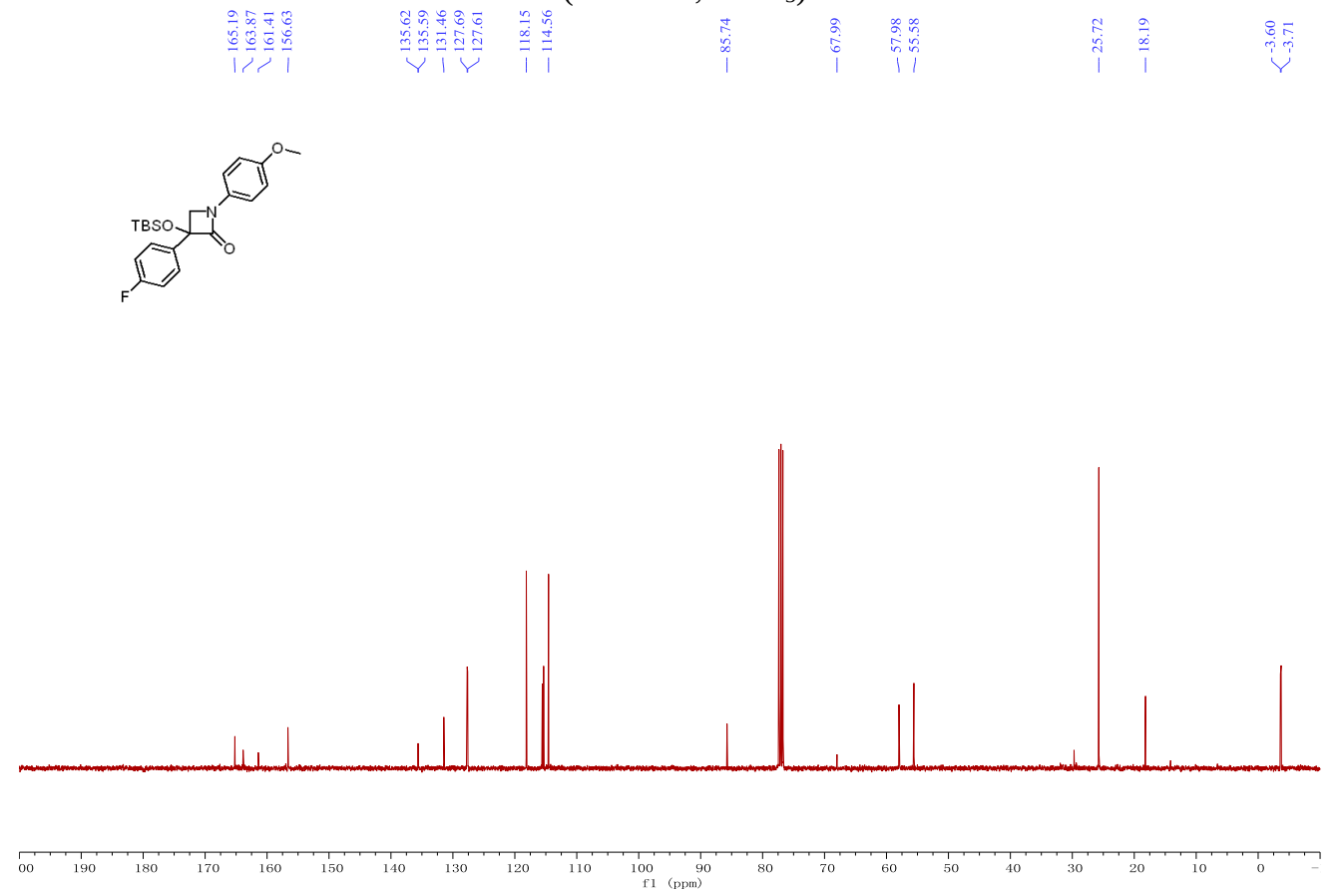
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



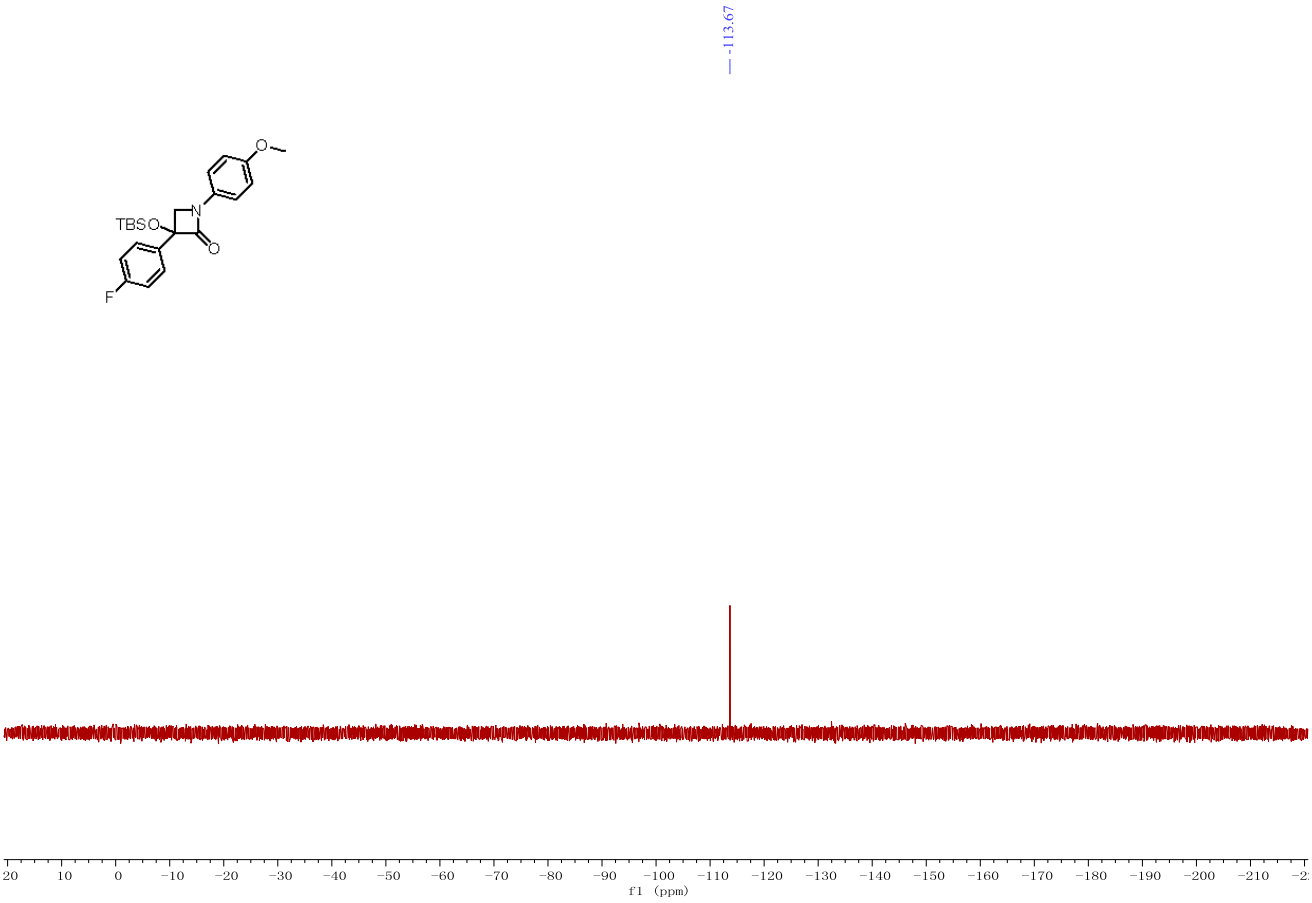
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



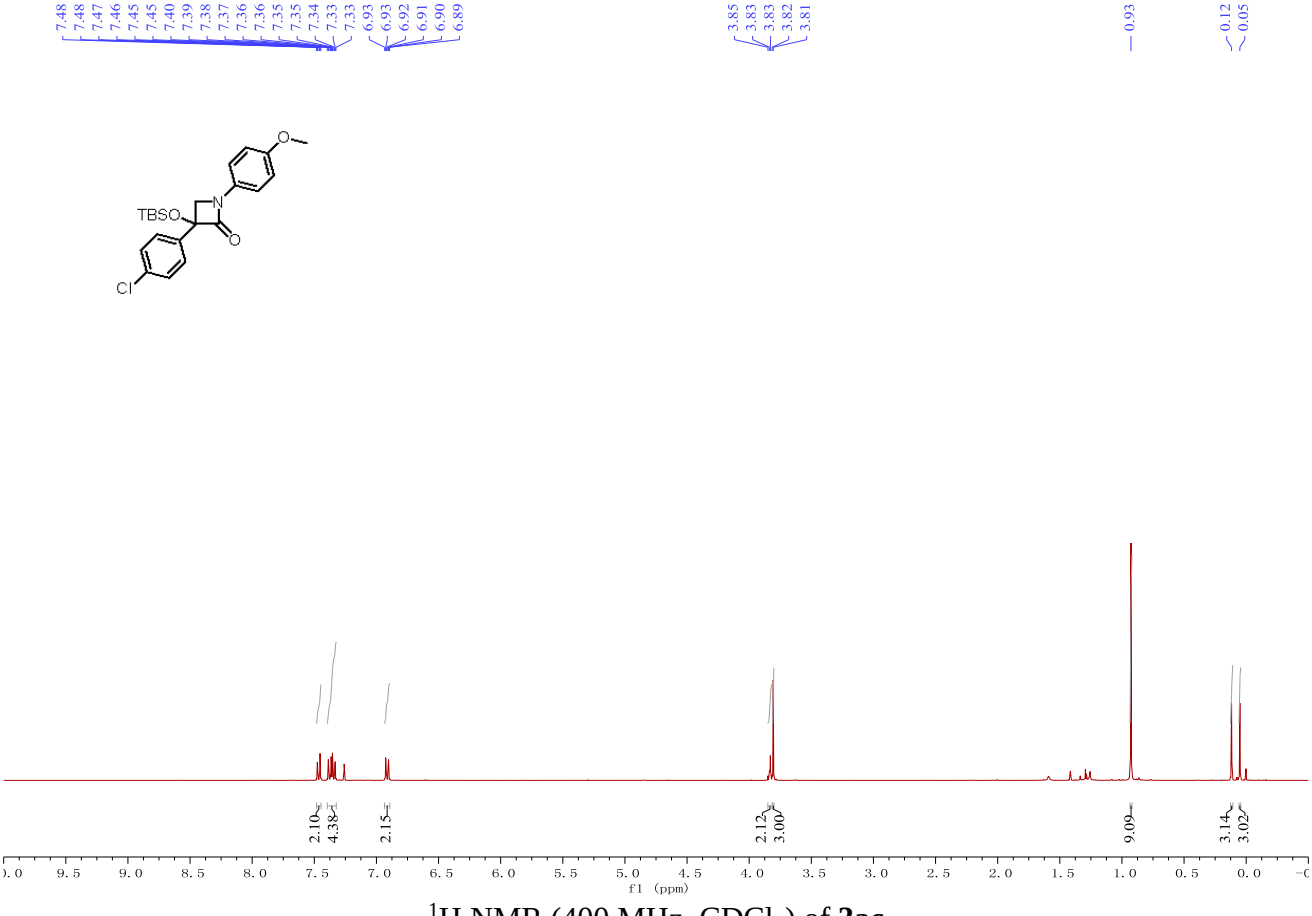
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



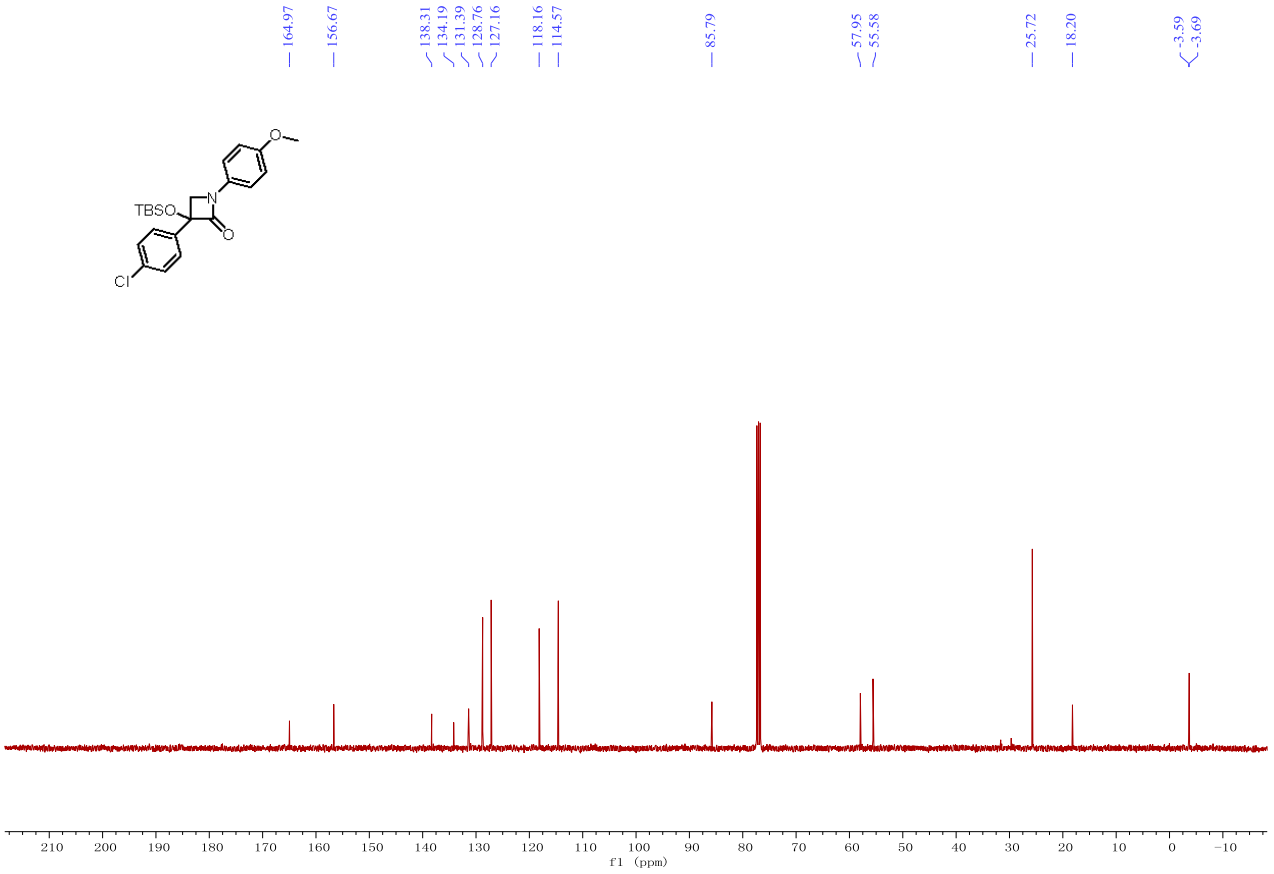
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



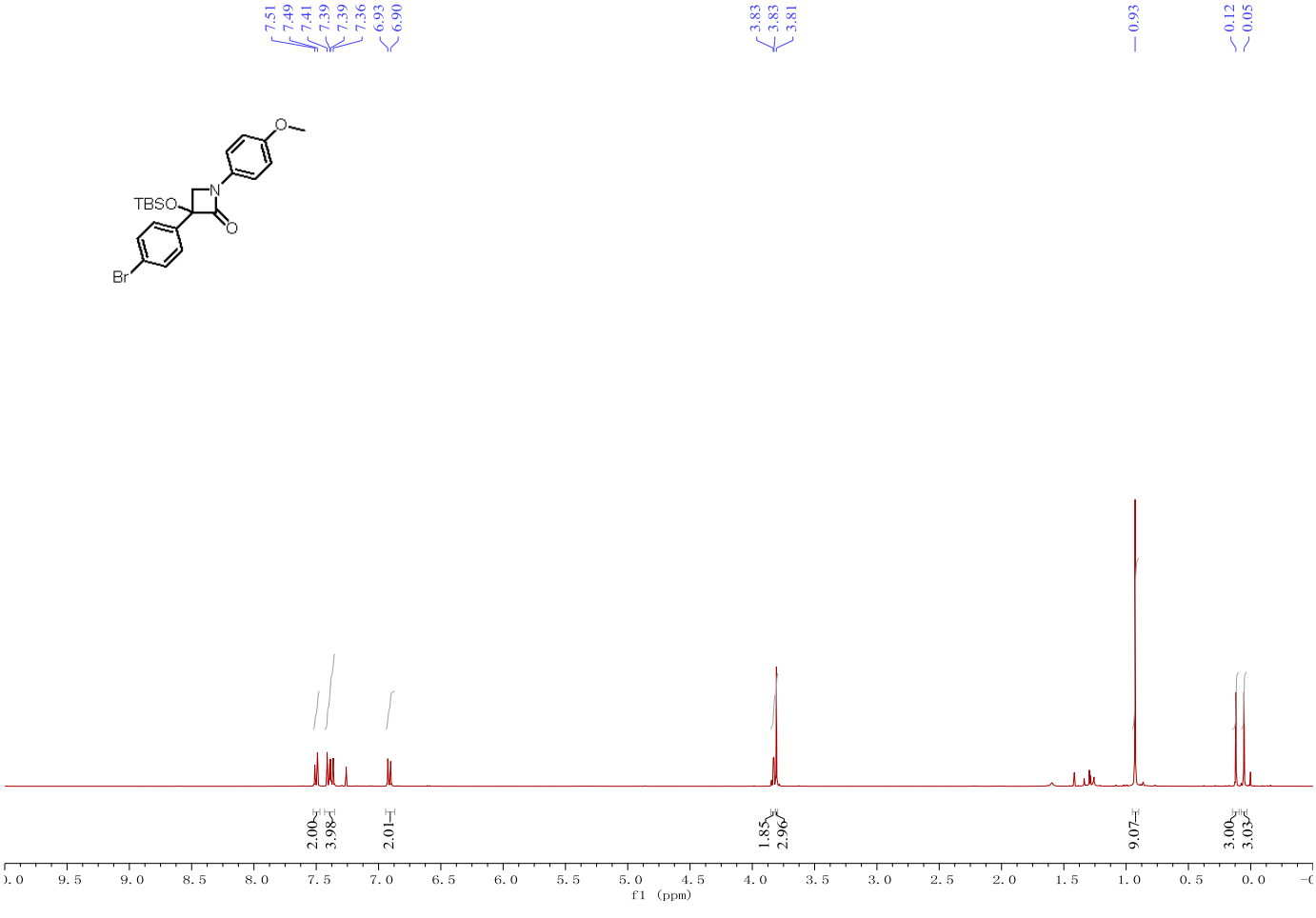
^{19}F NMR (376 MHz, $CDCl_3$) of **3ab**



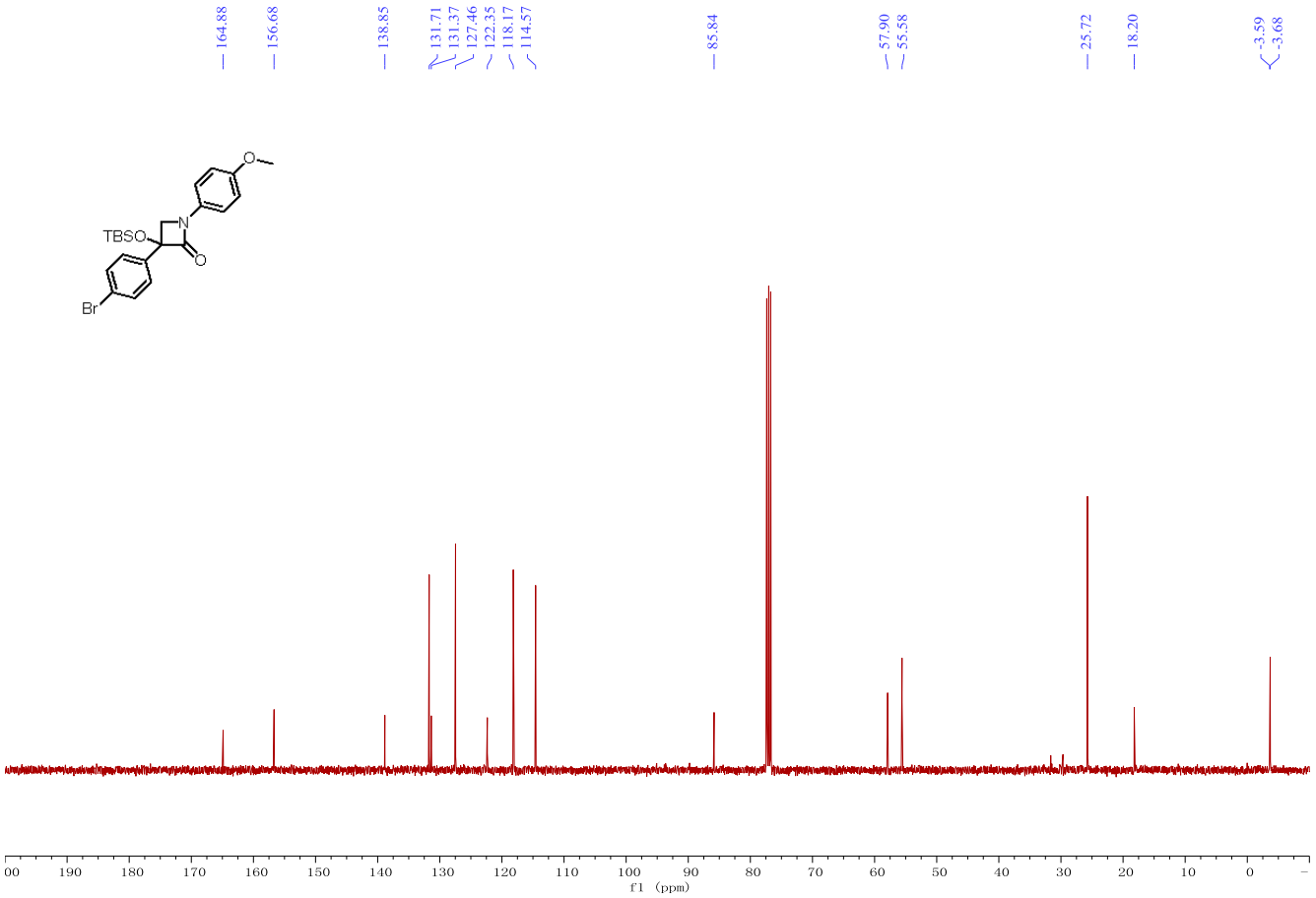
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



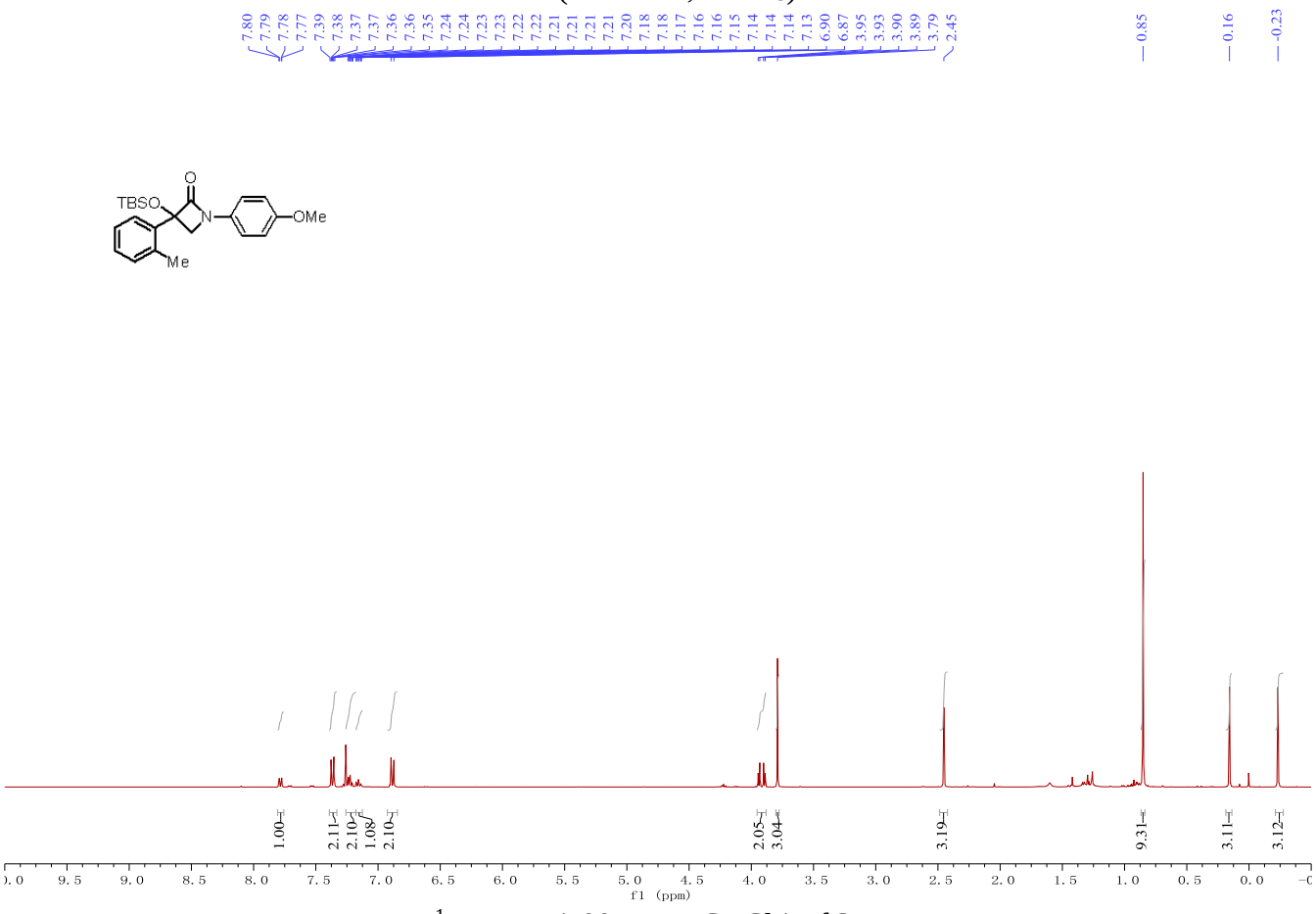
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



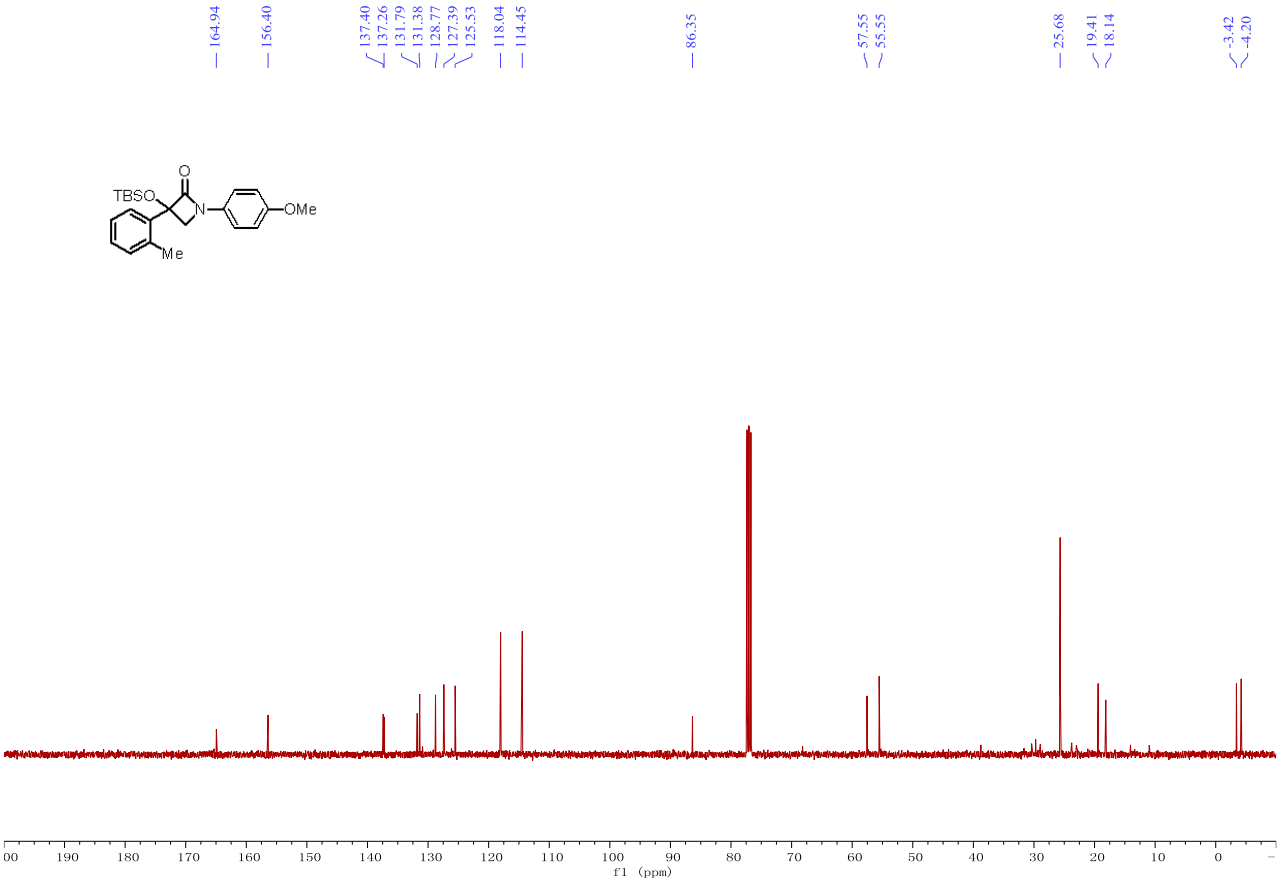
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



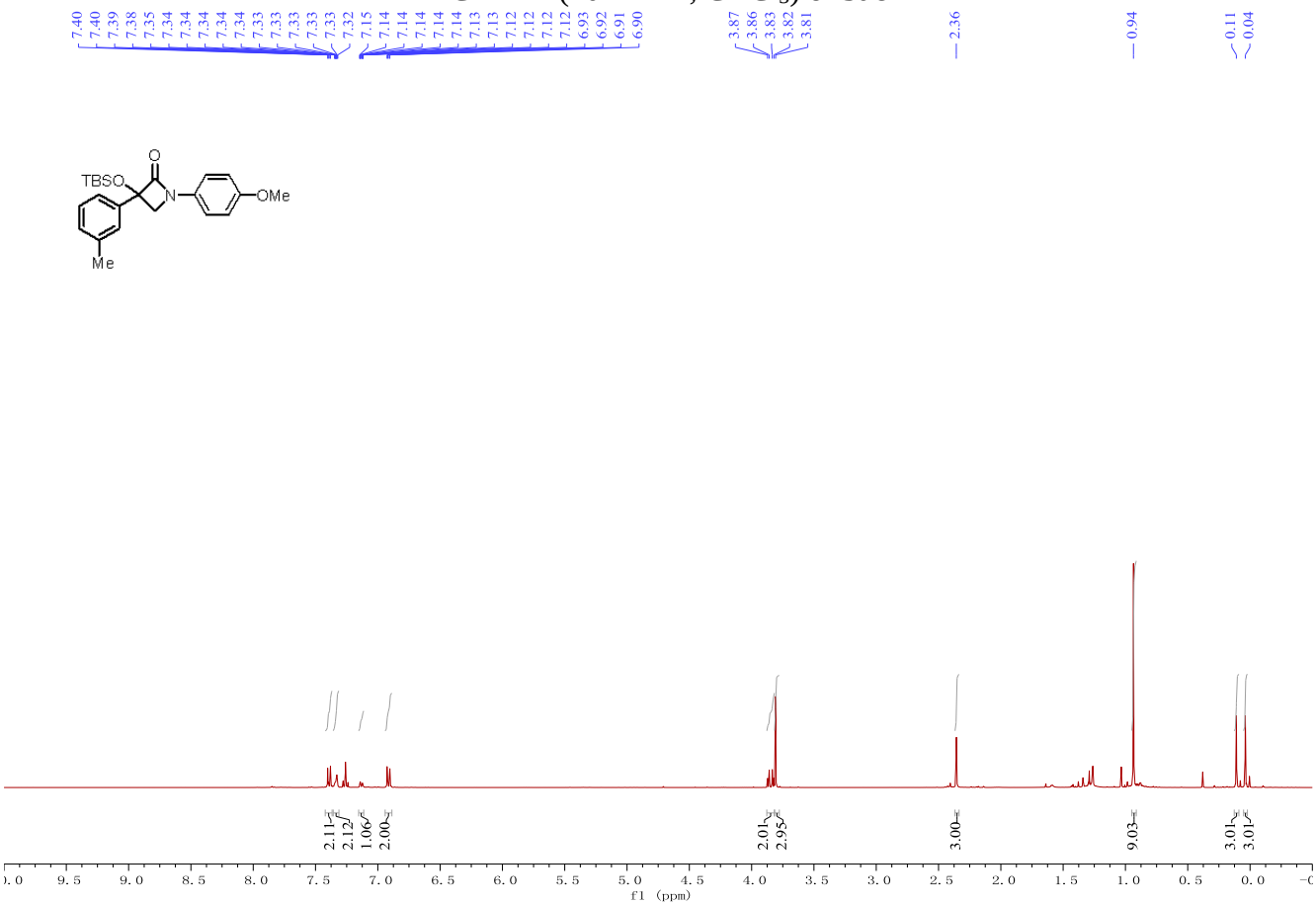
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



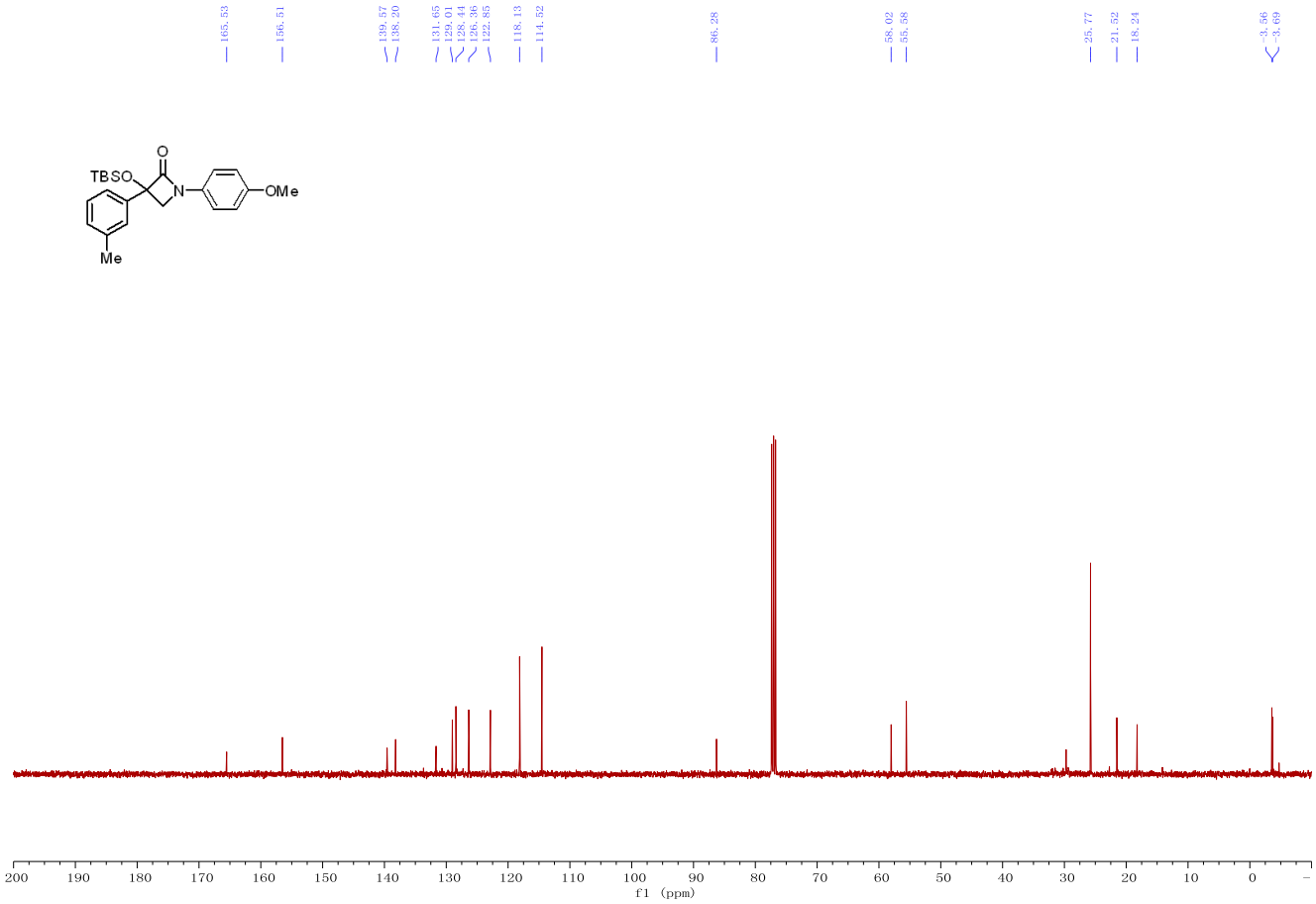
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



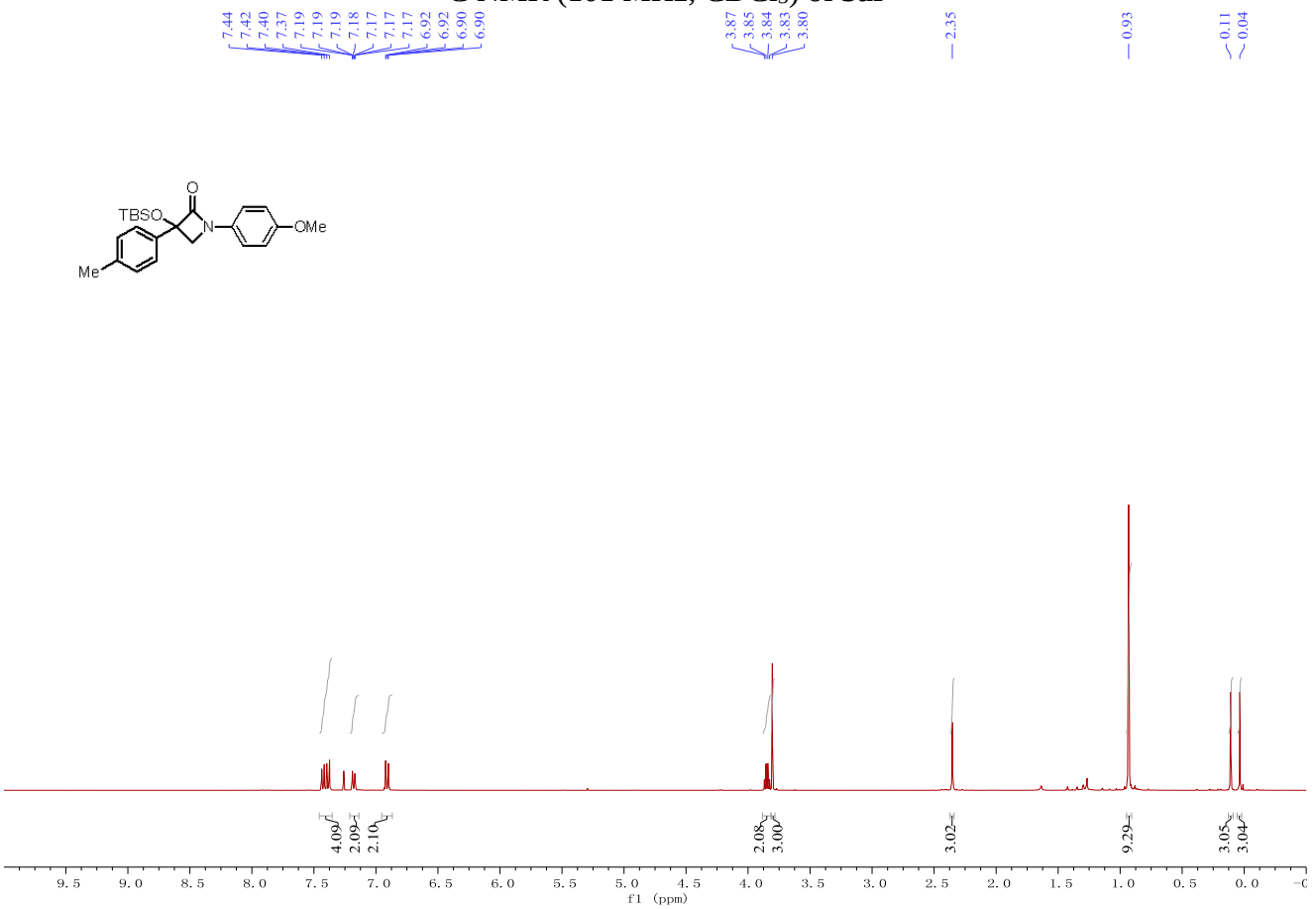
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



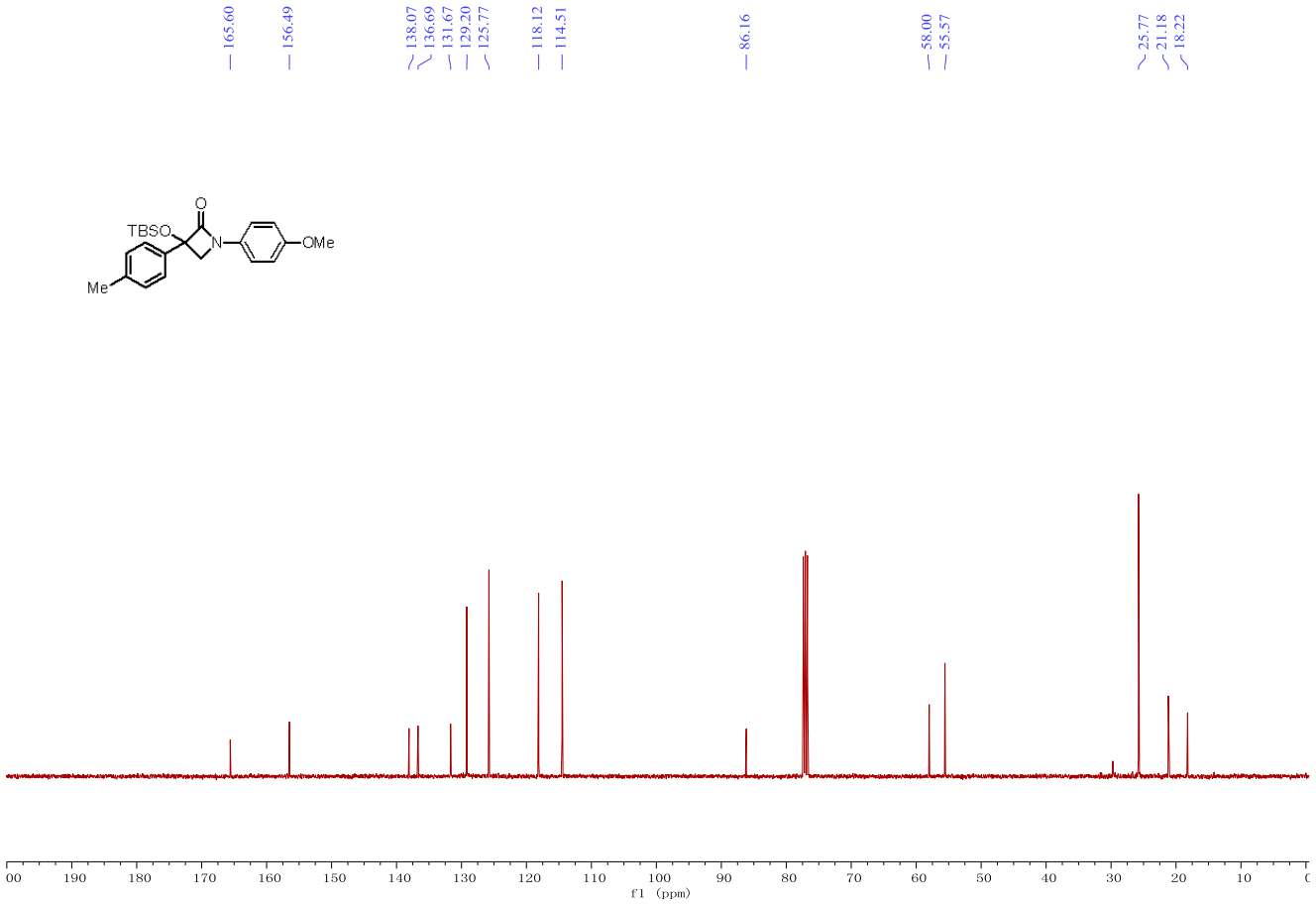
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



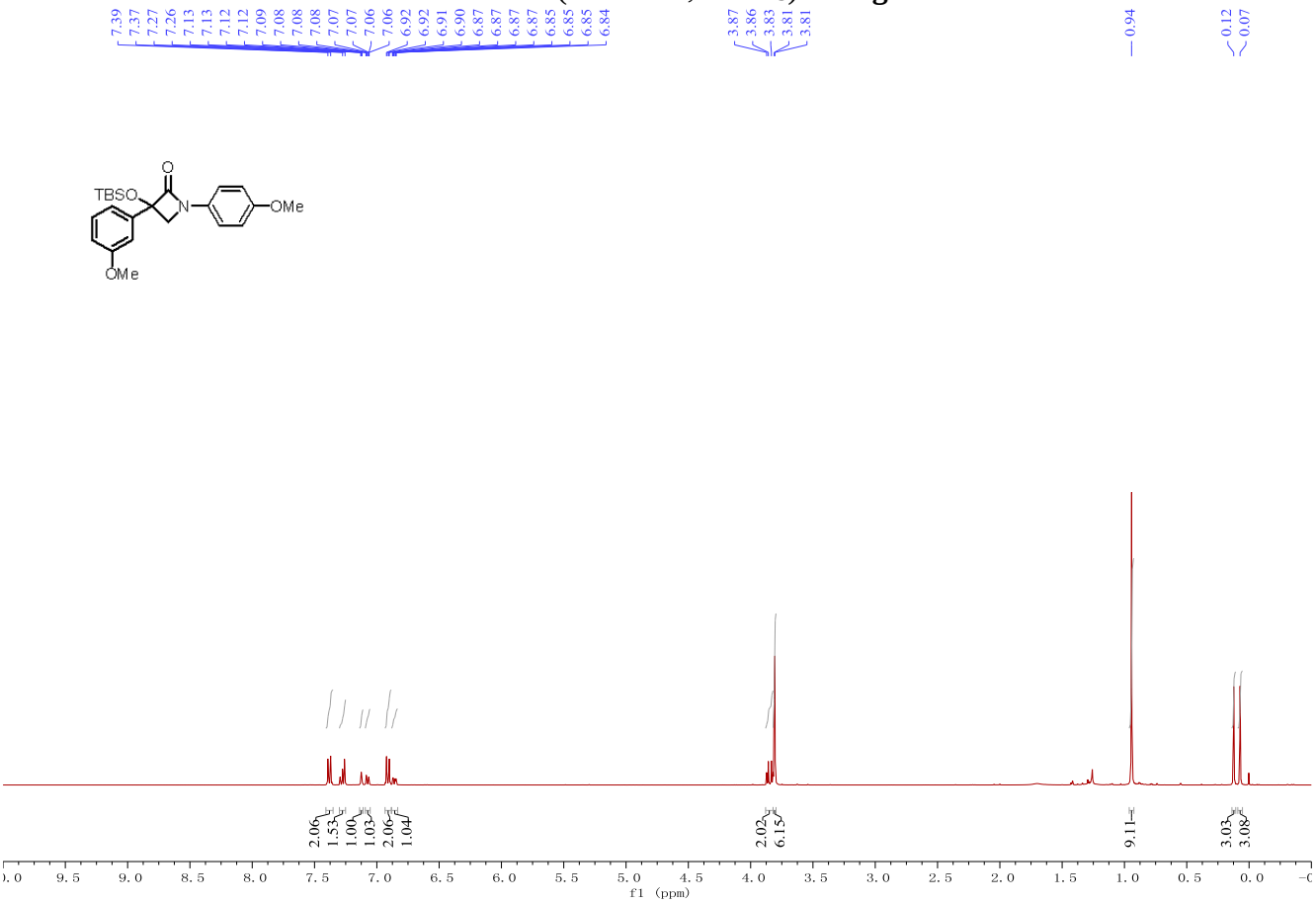
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



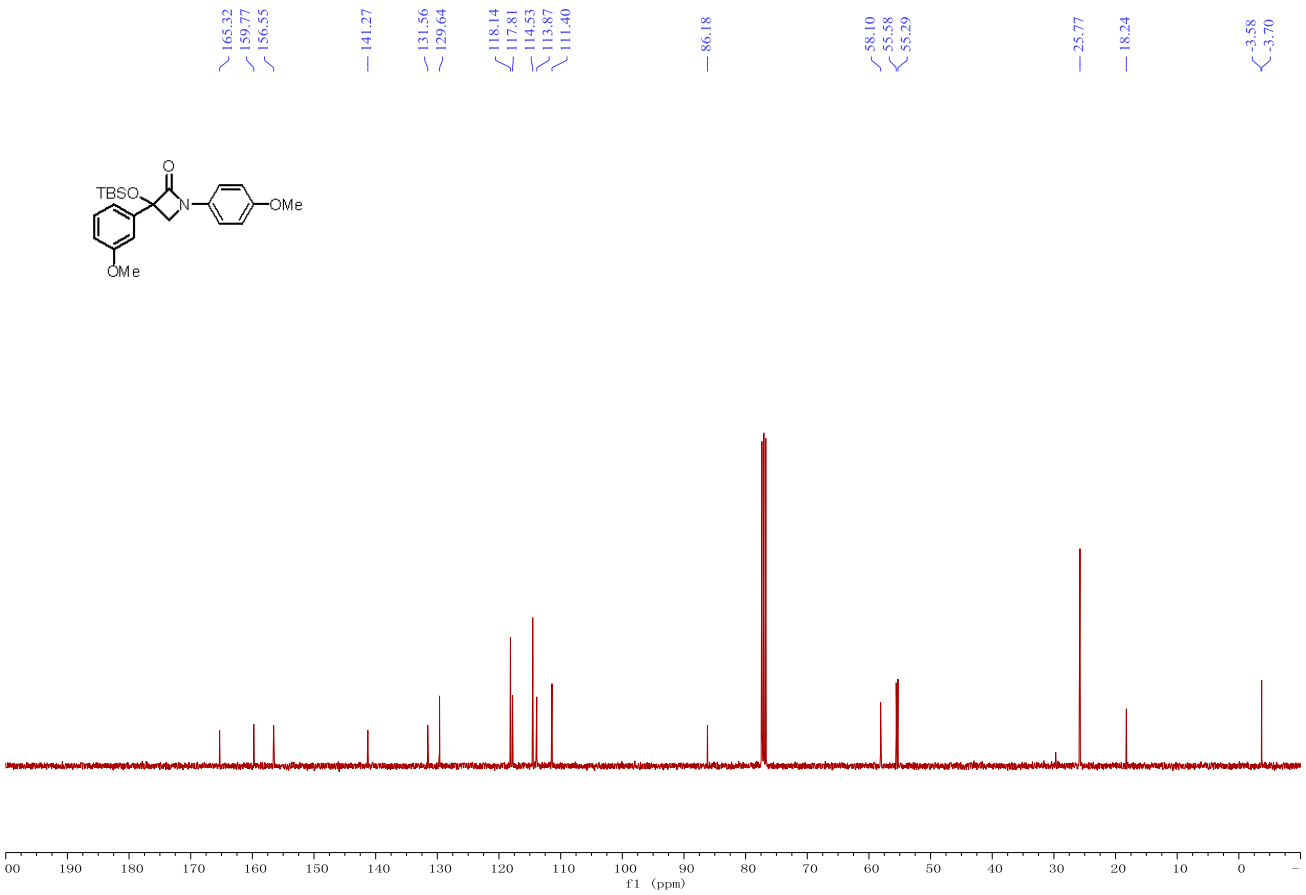
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



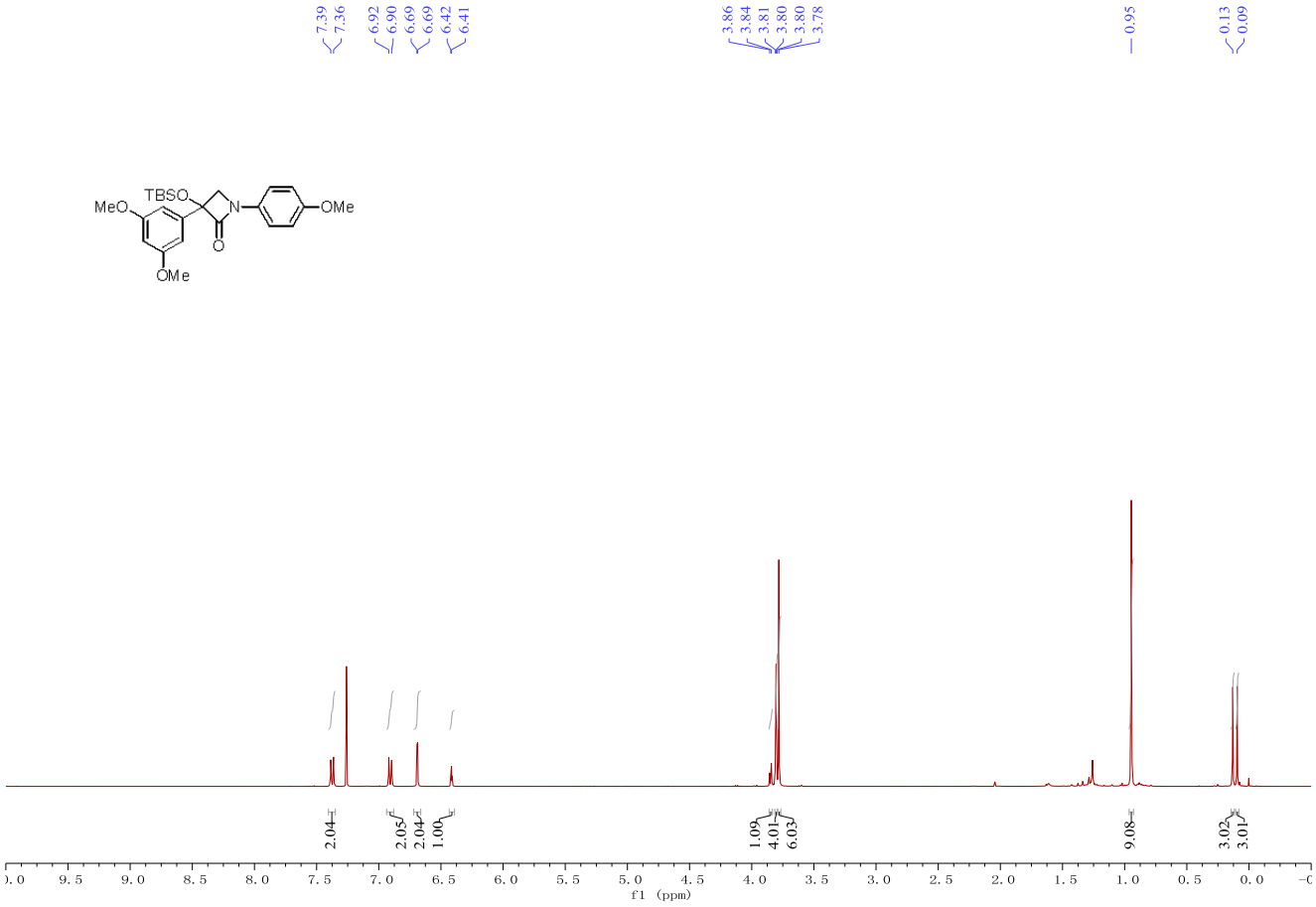
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



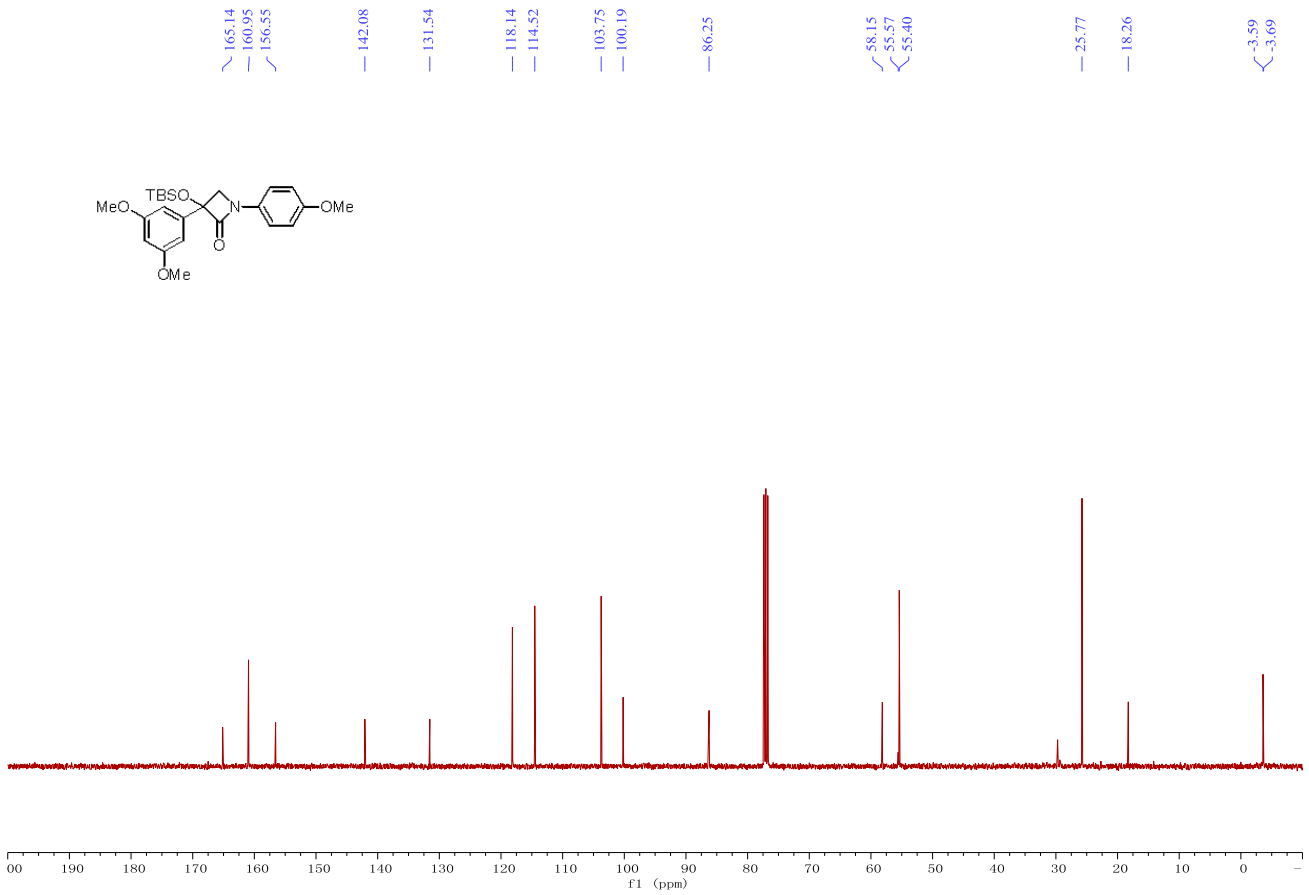
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



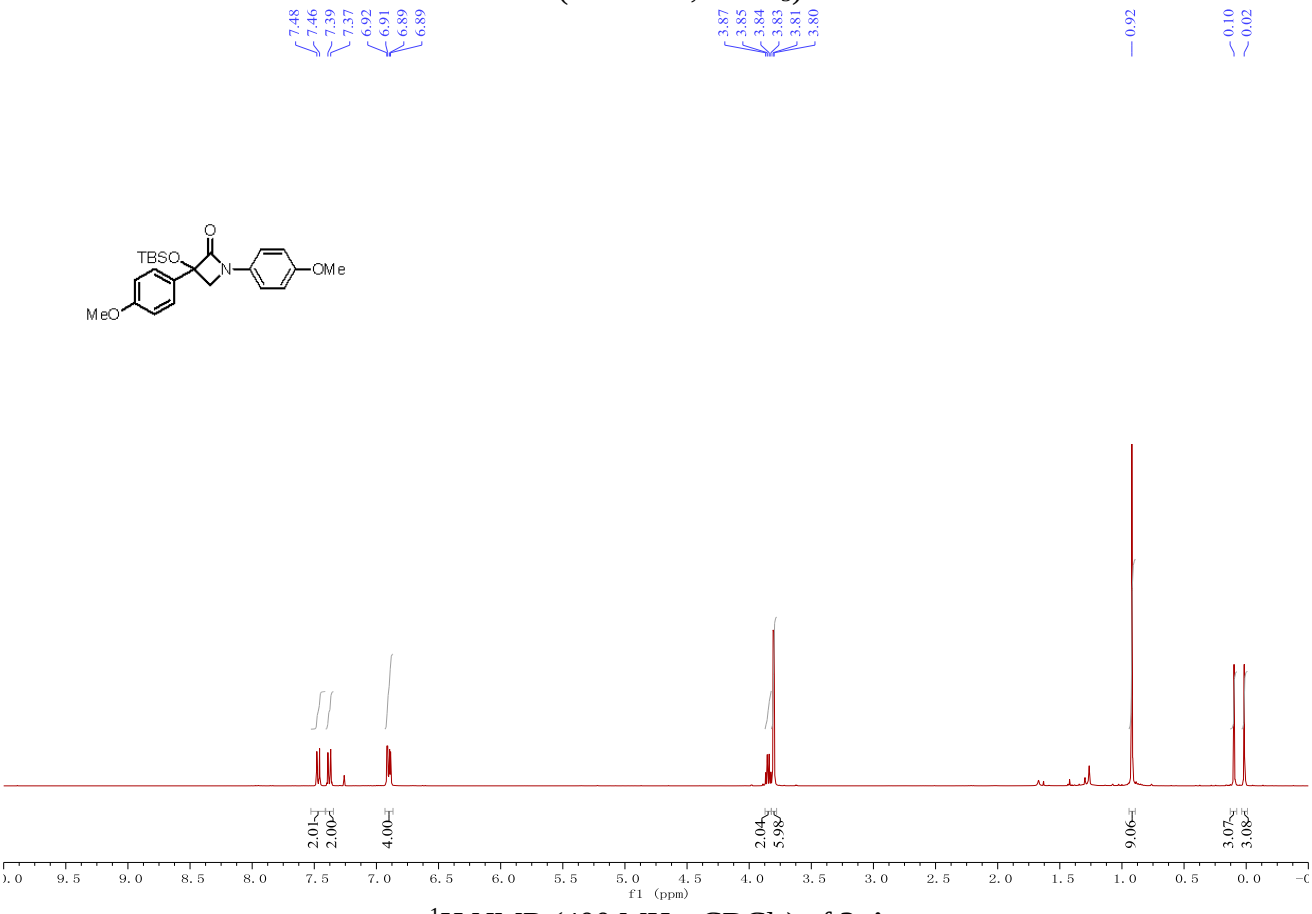
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**



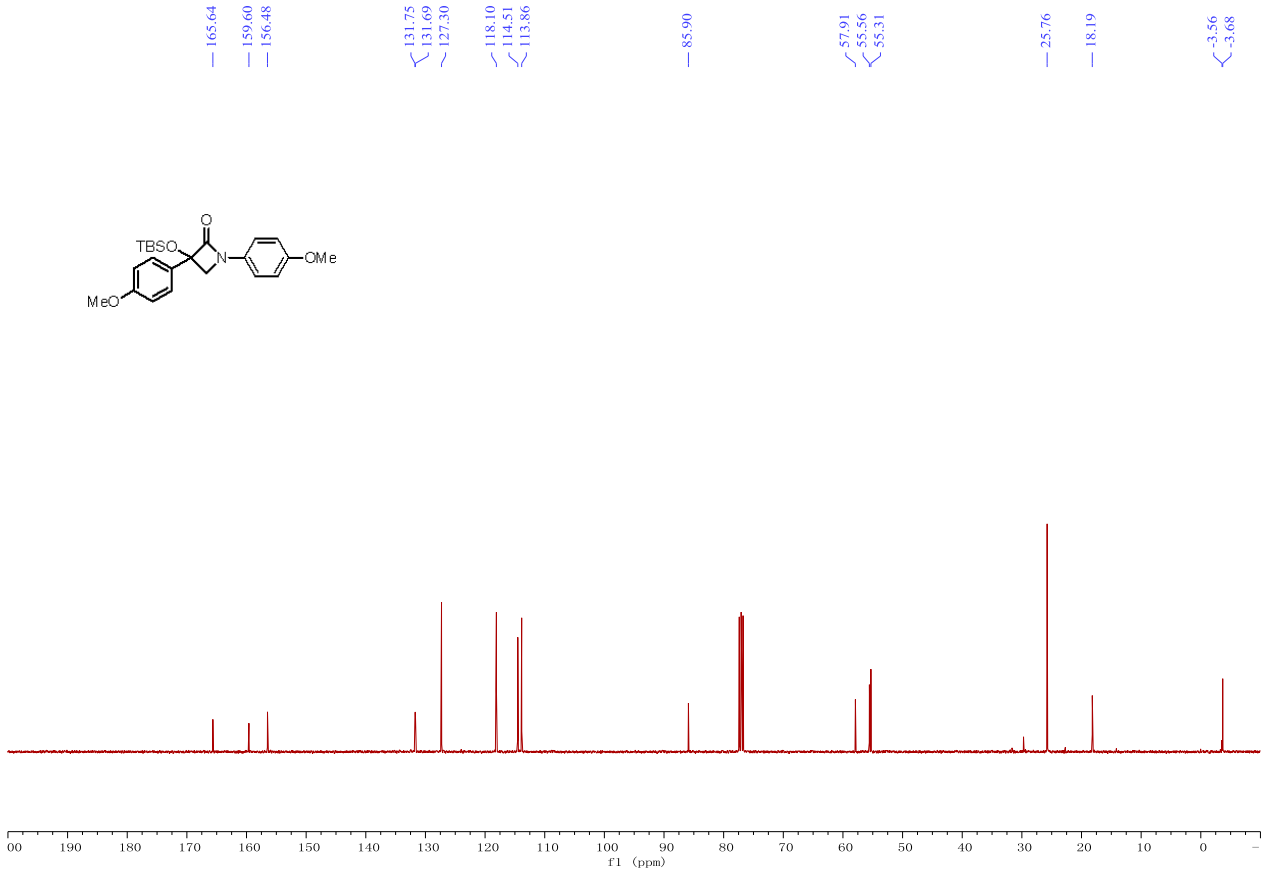
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



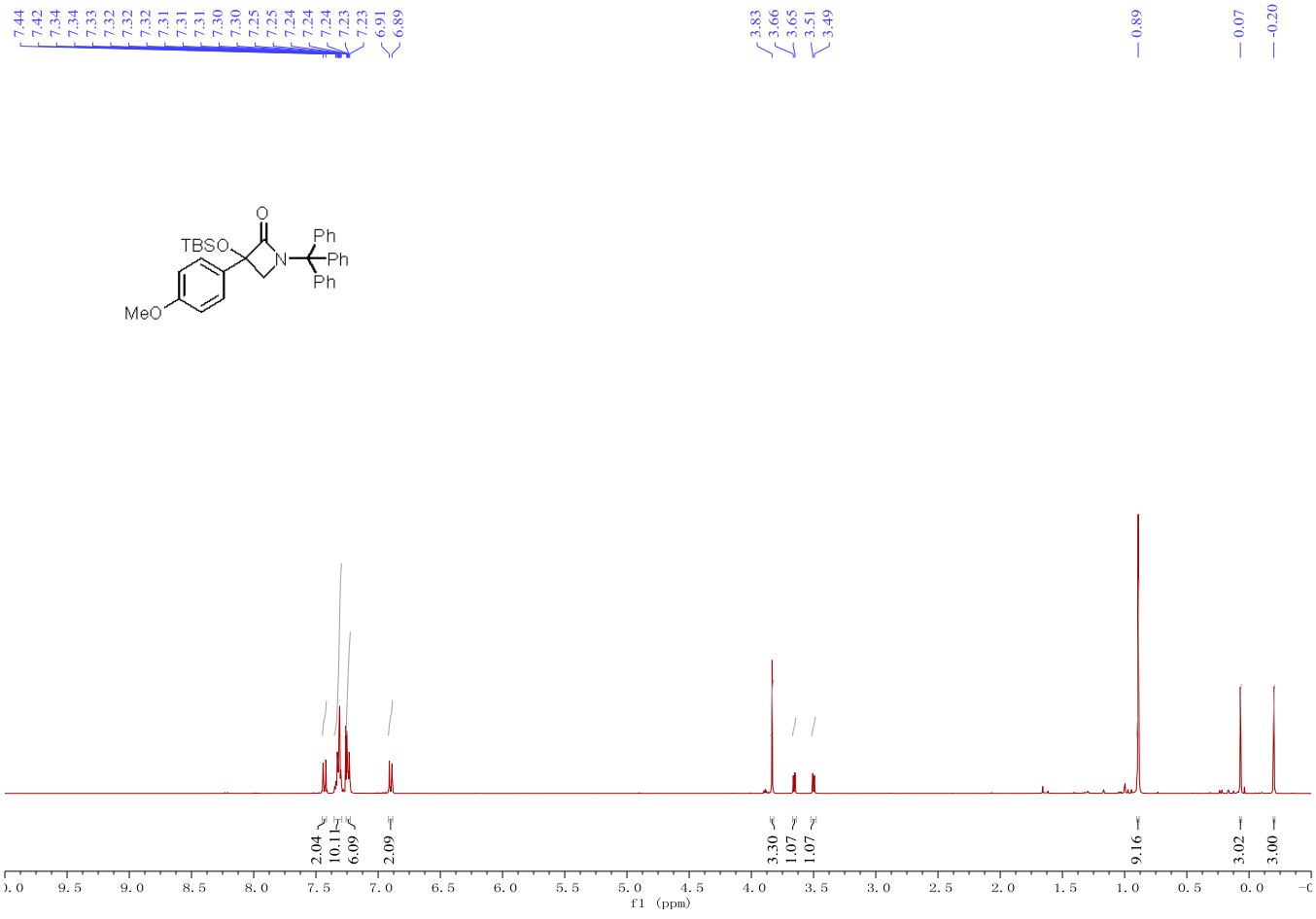
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



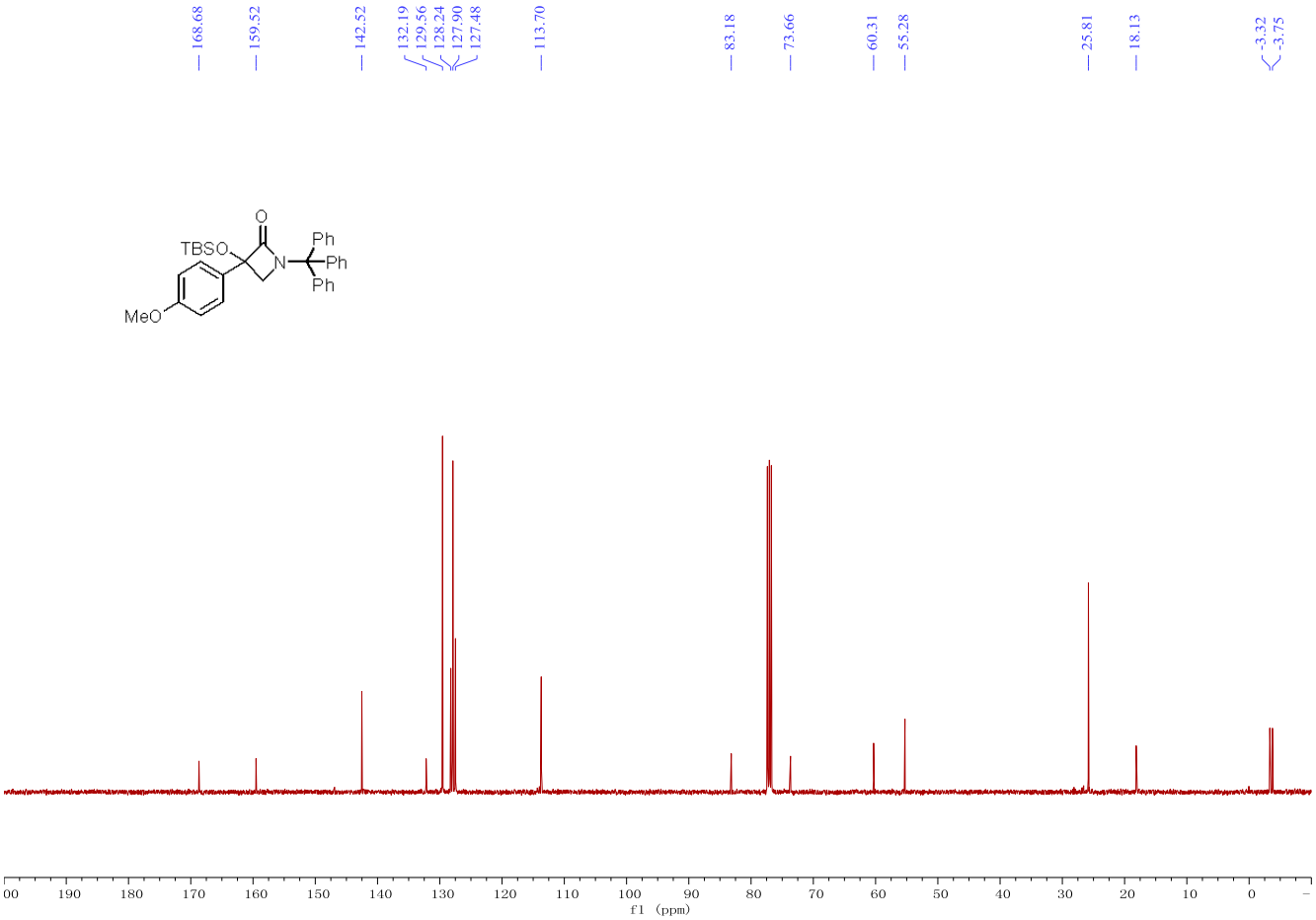
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



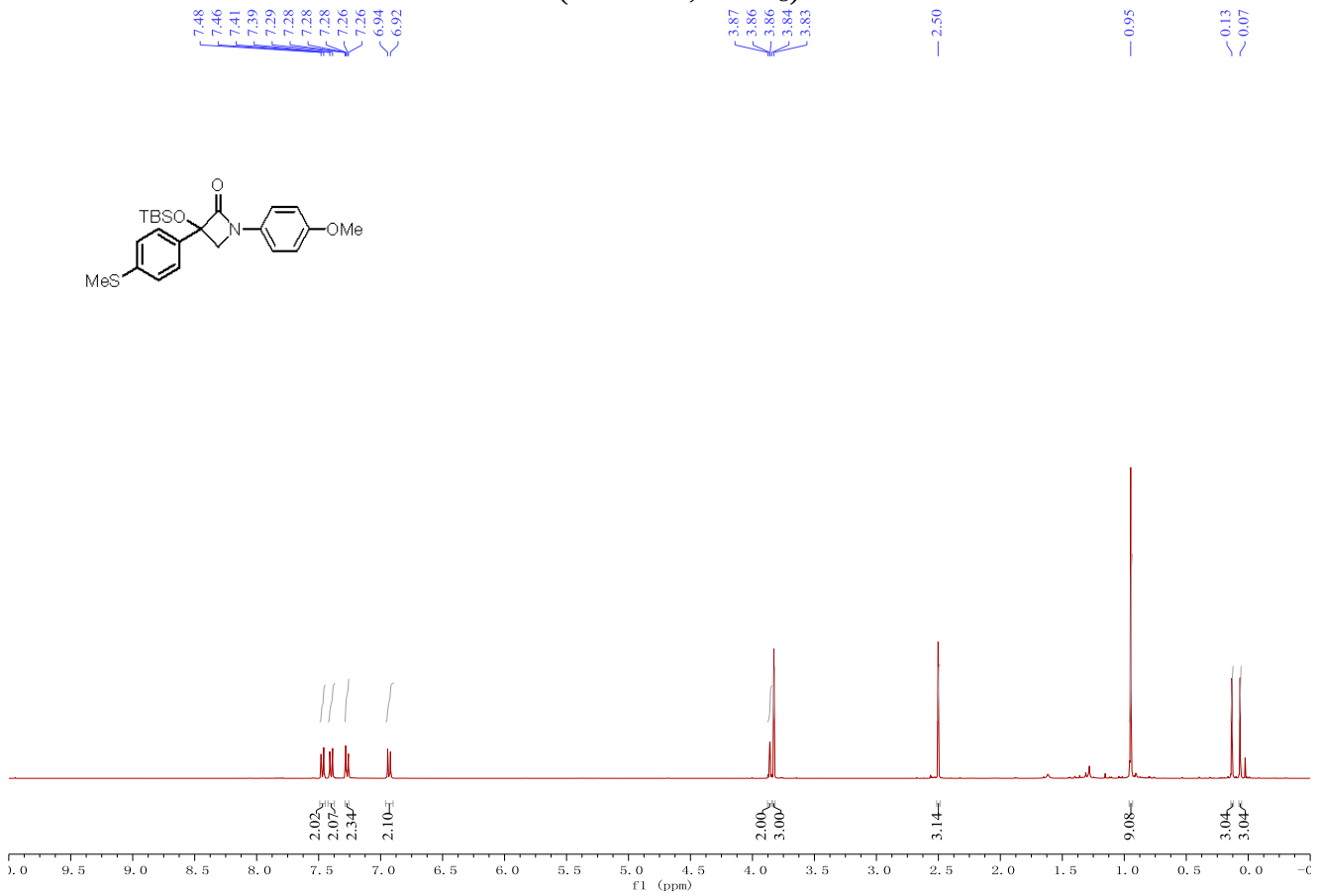
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



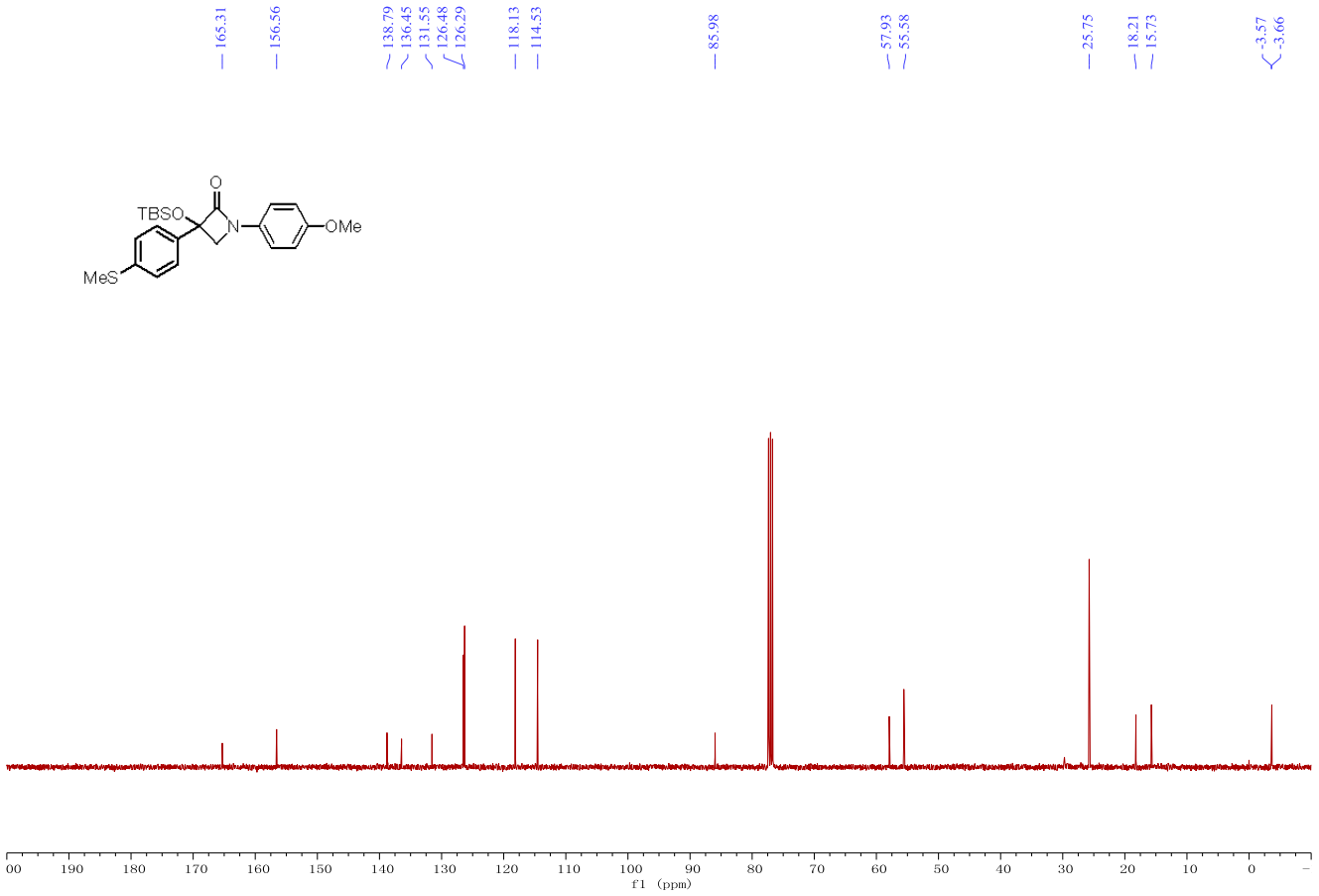
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



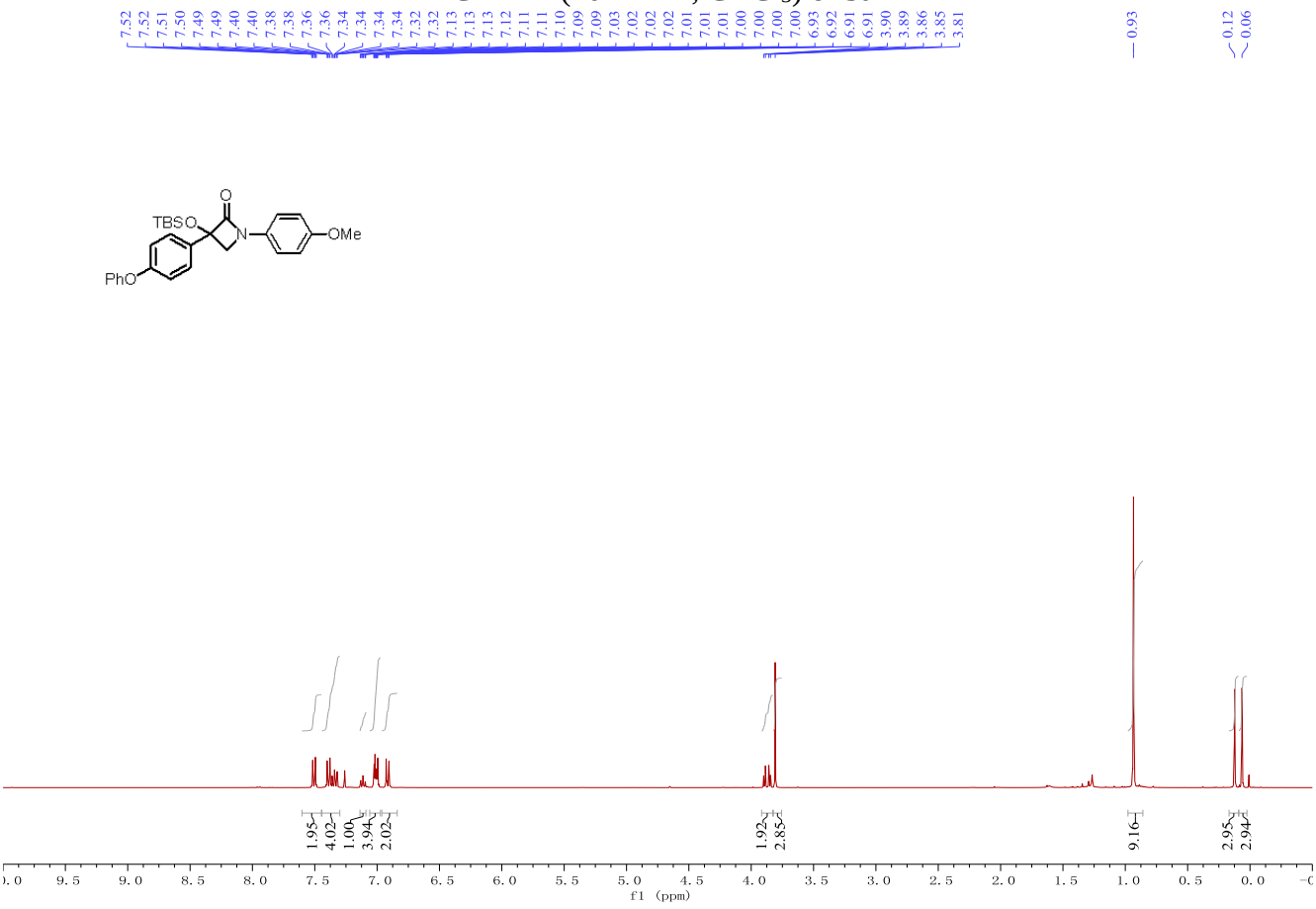
^{13}C NMR (101 MHz, $CDCl_3$) of **3ak**



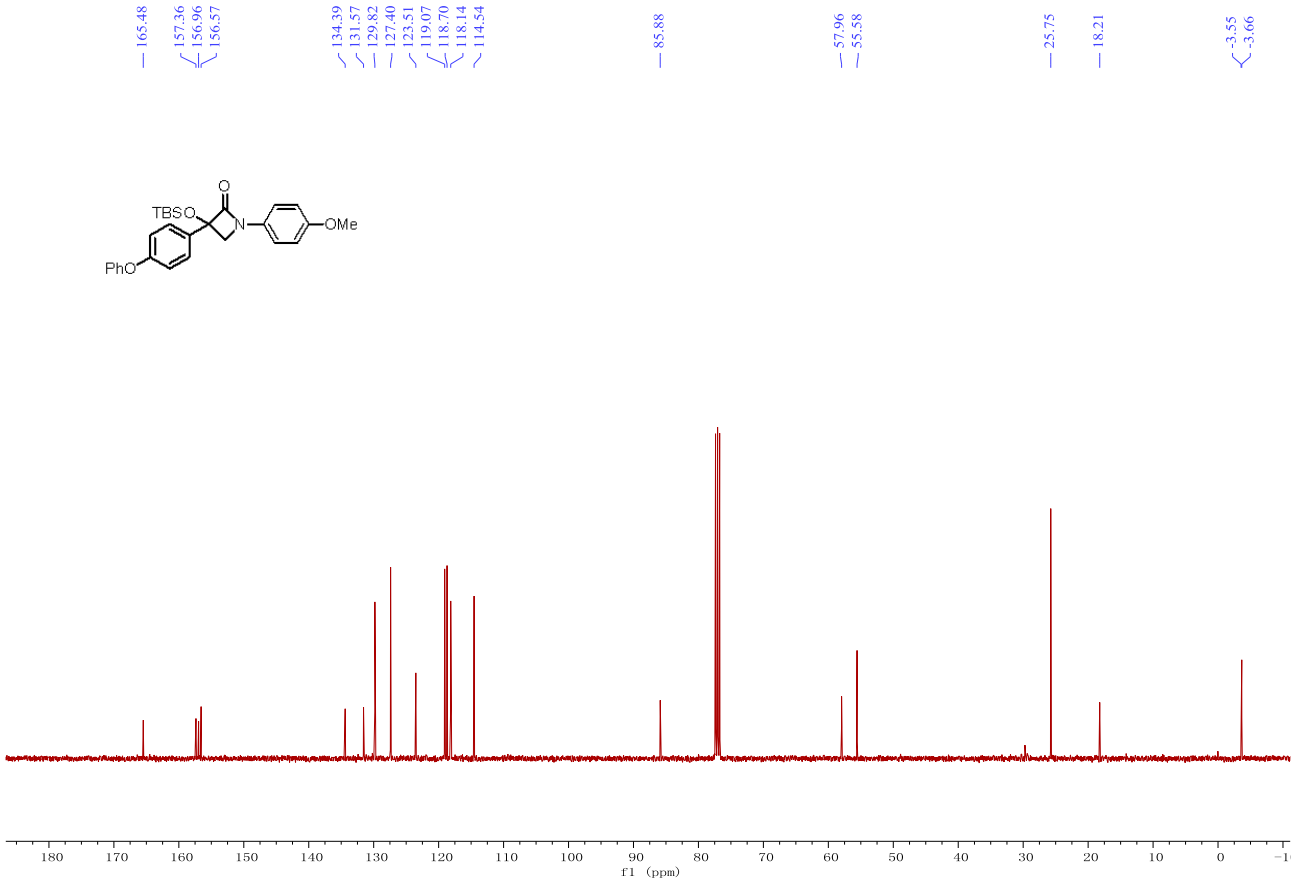
^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



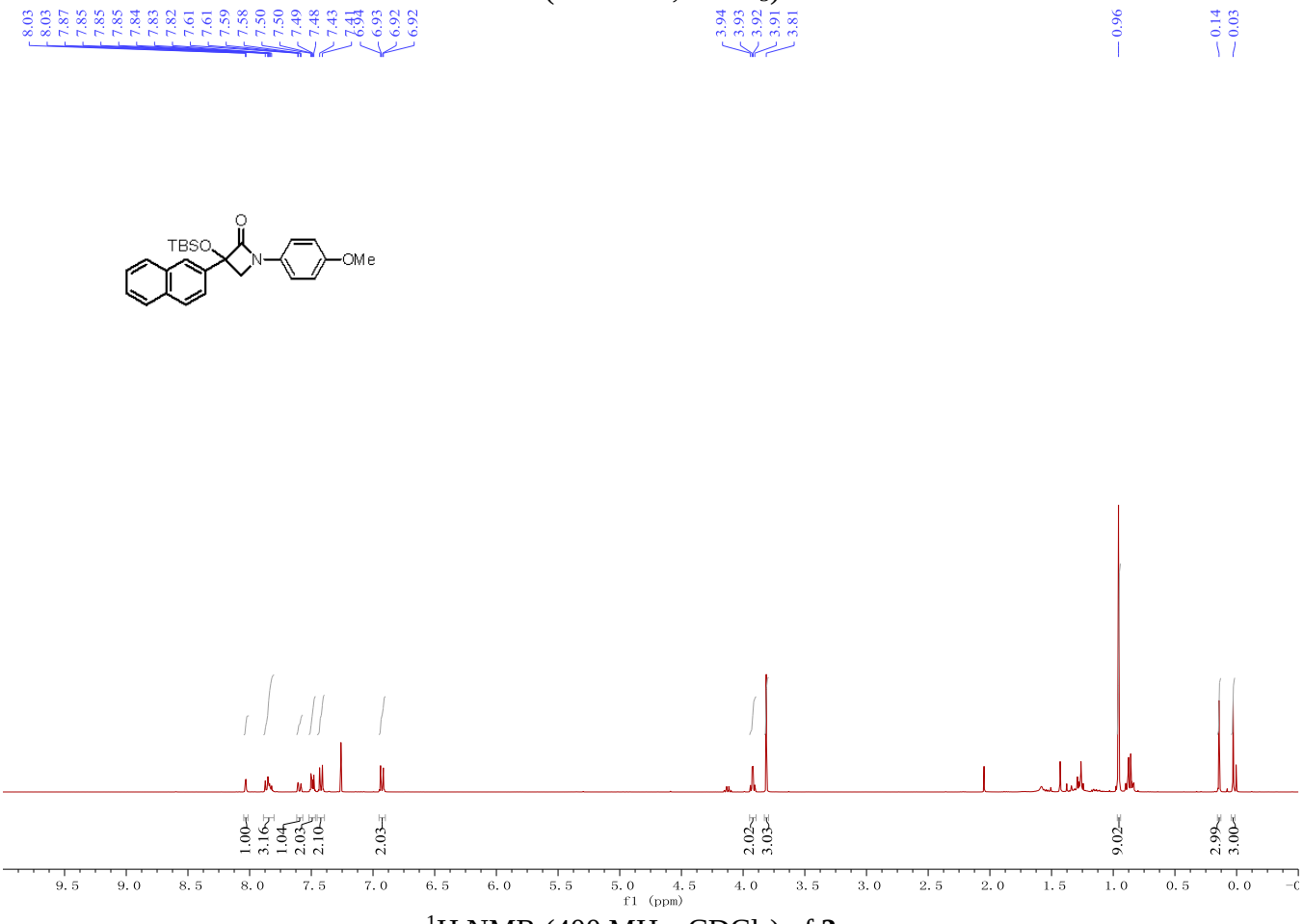
^{13}C NMR (101 MHz, $CDCl_3$) of **3al**



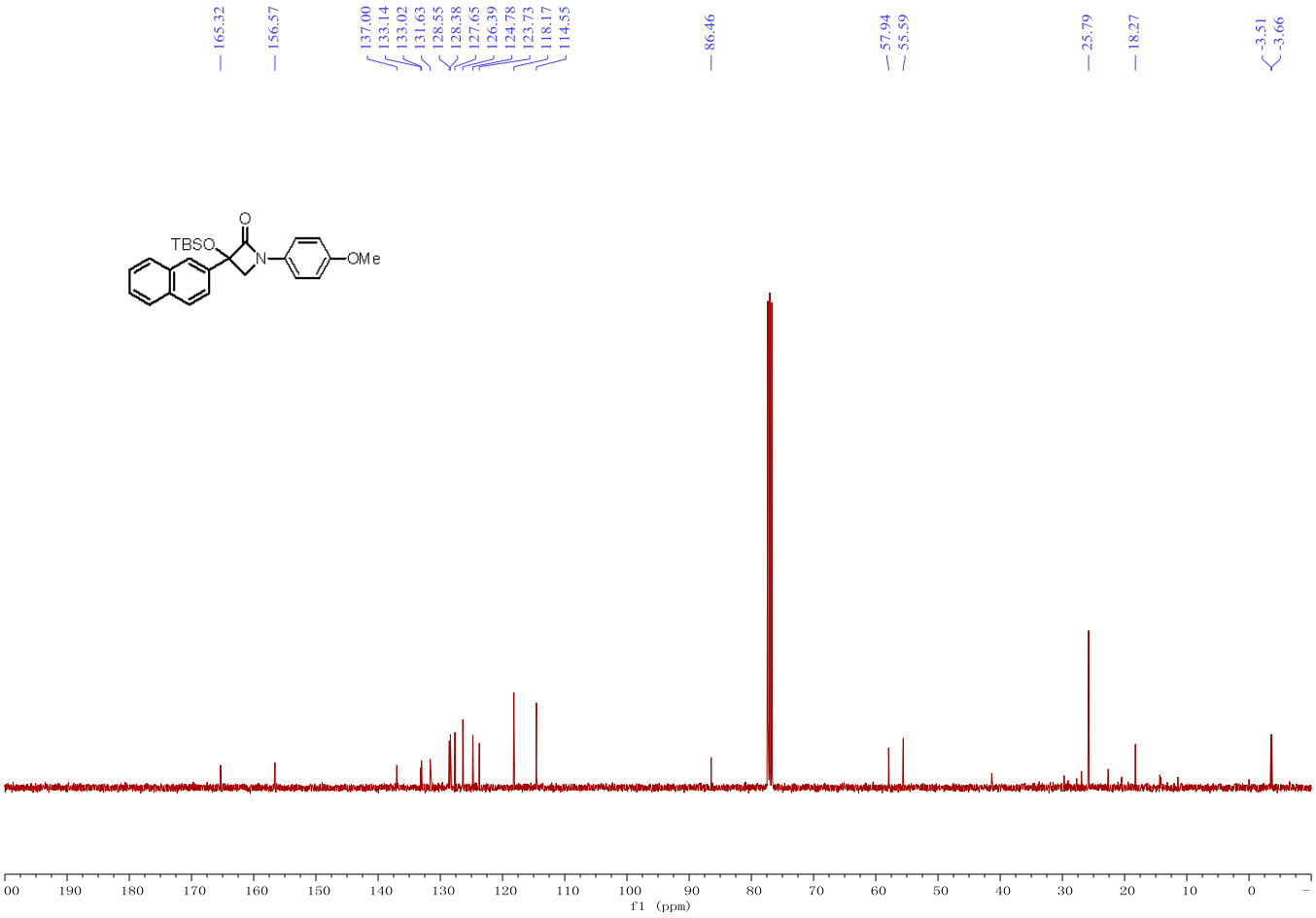
^{1}H NMR (400 MHz, $CDCl_3$) of **3am**



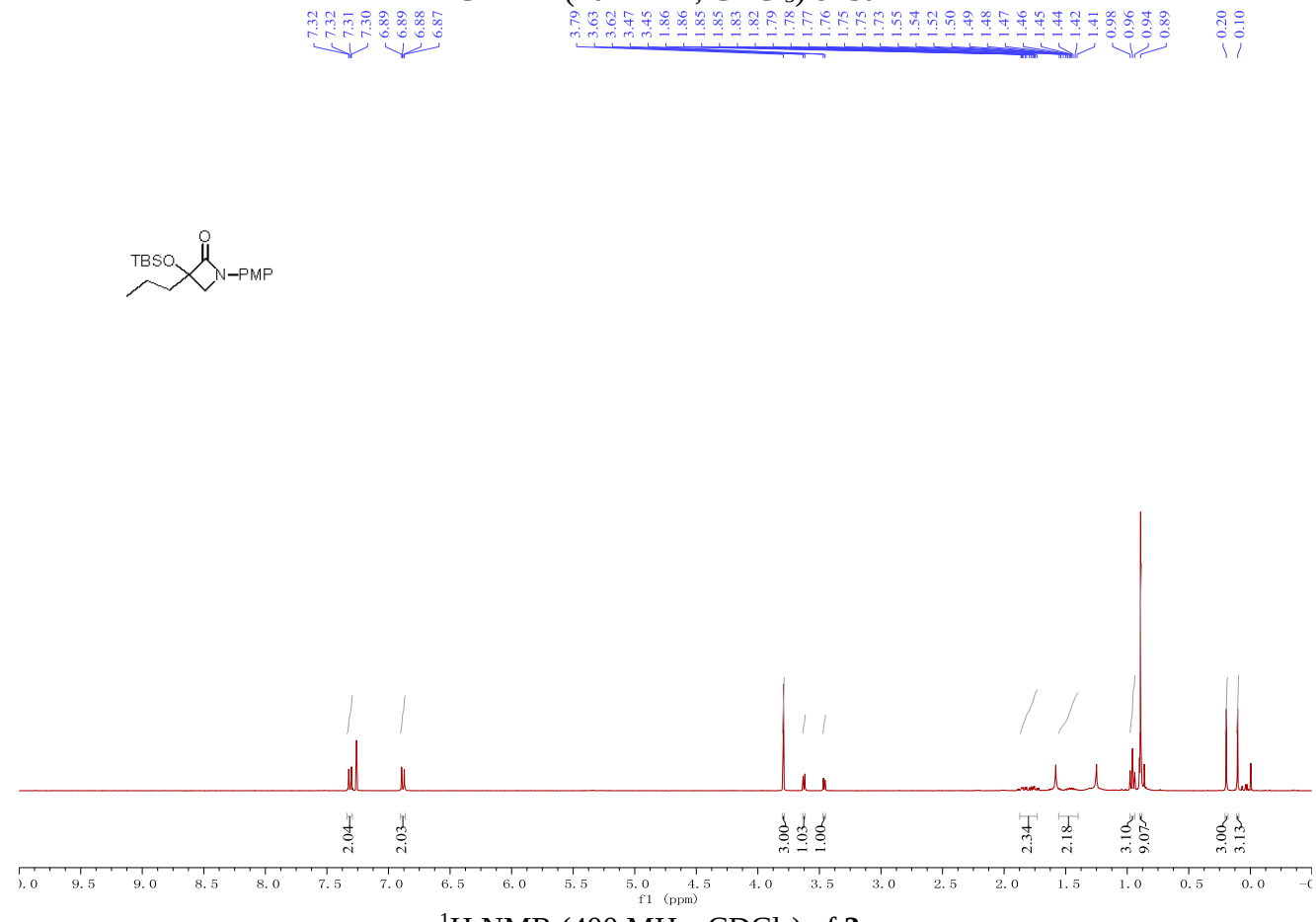
^{13}C NMR (101 MHz, $CDCl_3$) of **3am**



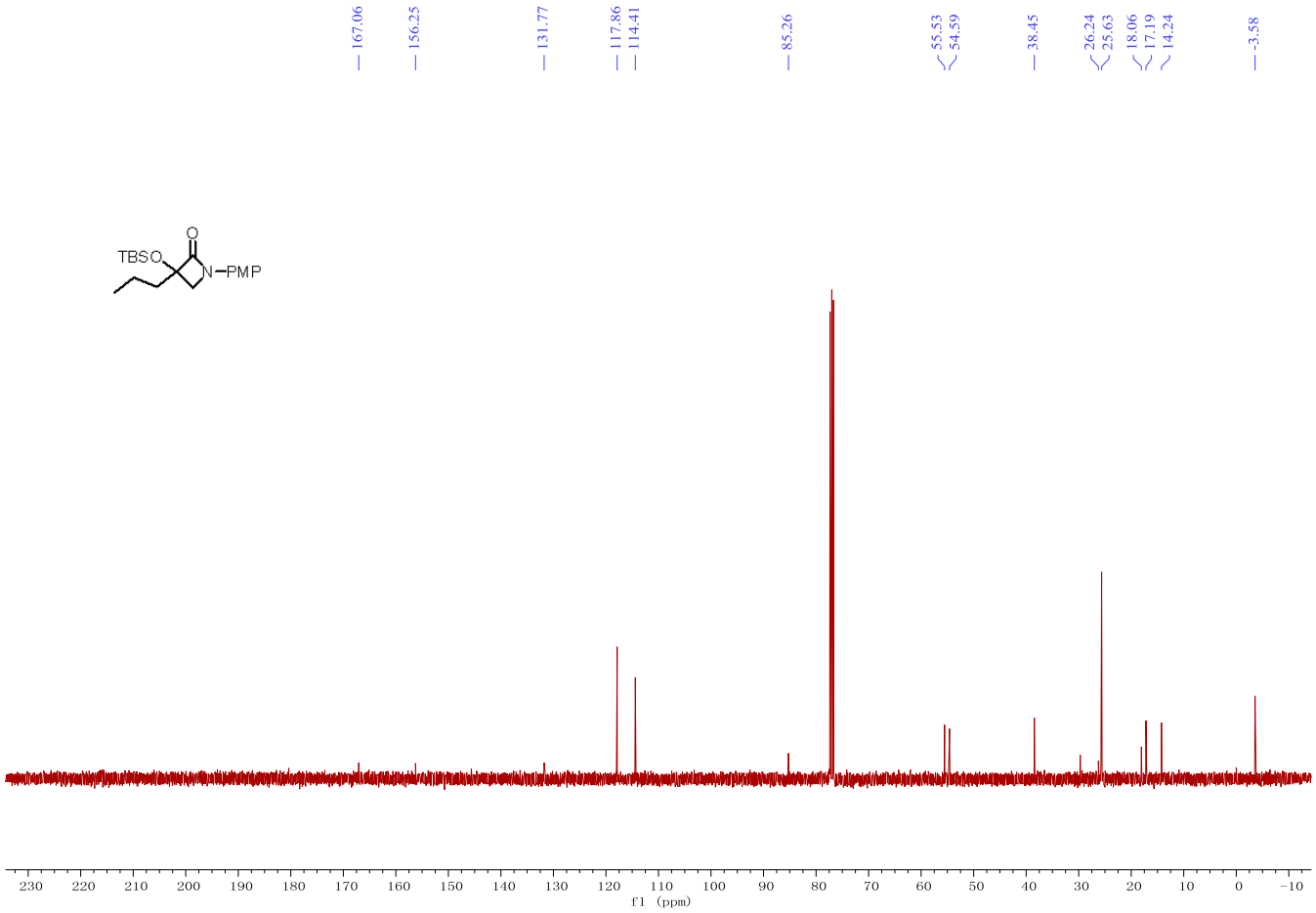
^{1}H NMR (400 MHz, $CDCl_3$) of **3an**



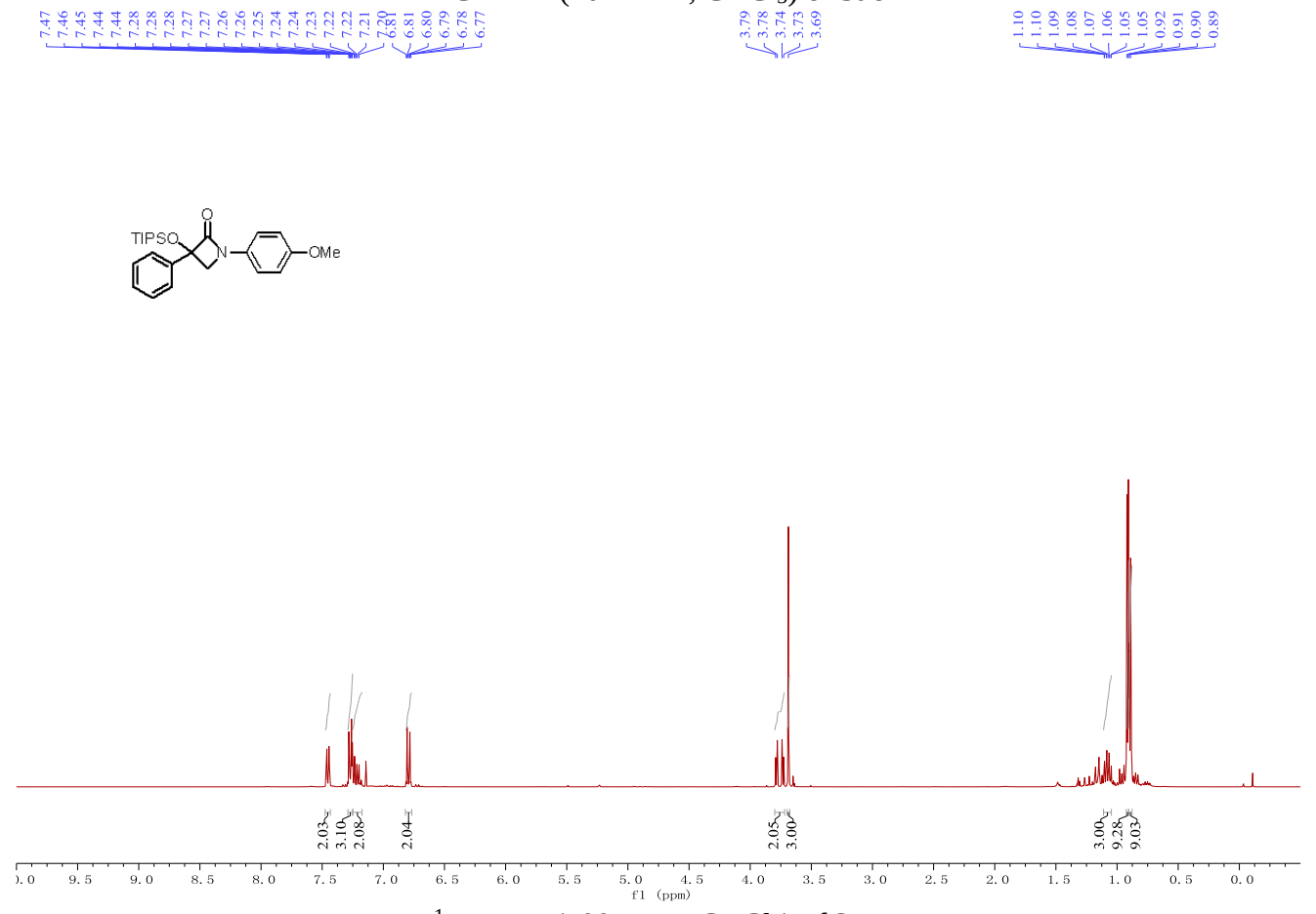
^{13}C NMR (101 MHz, $CDCl_3$) of **3an**



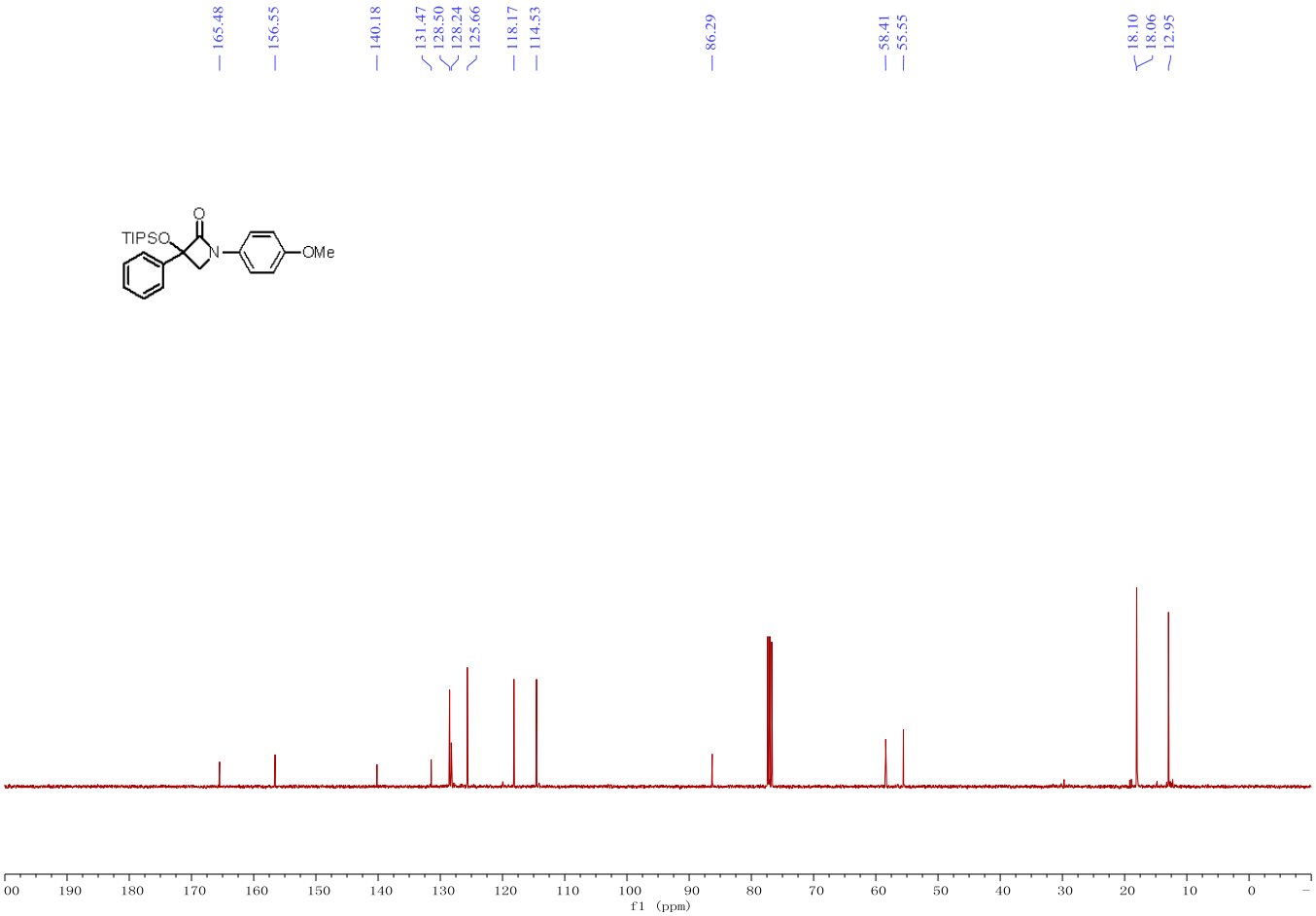
^{1}H NMR (400 MHz, $CDCl_3$) of **3ao**



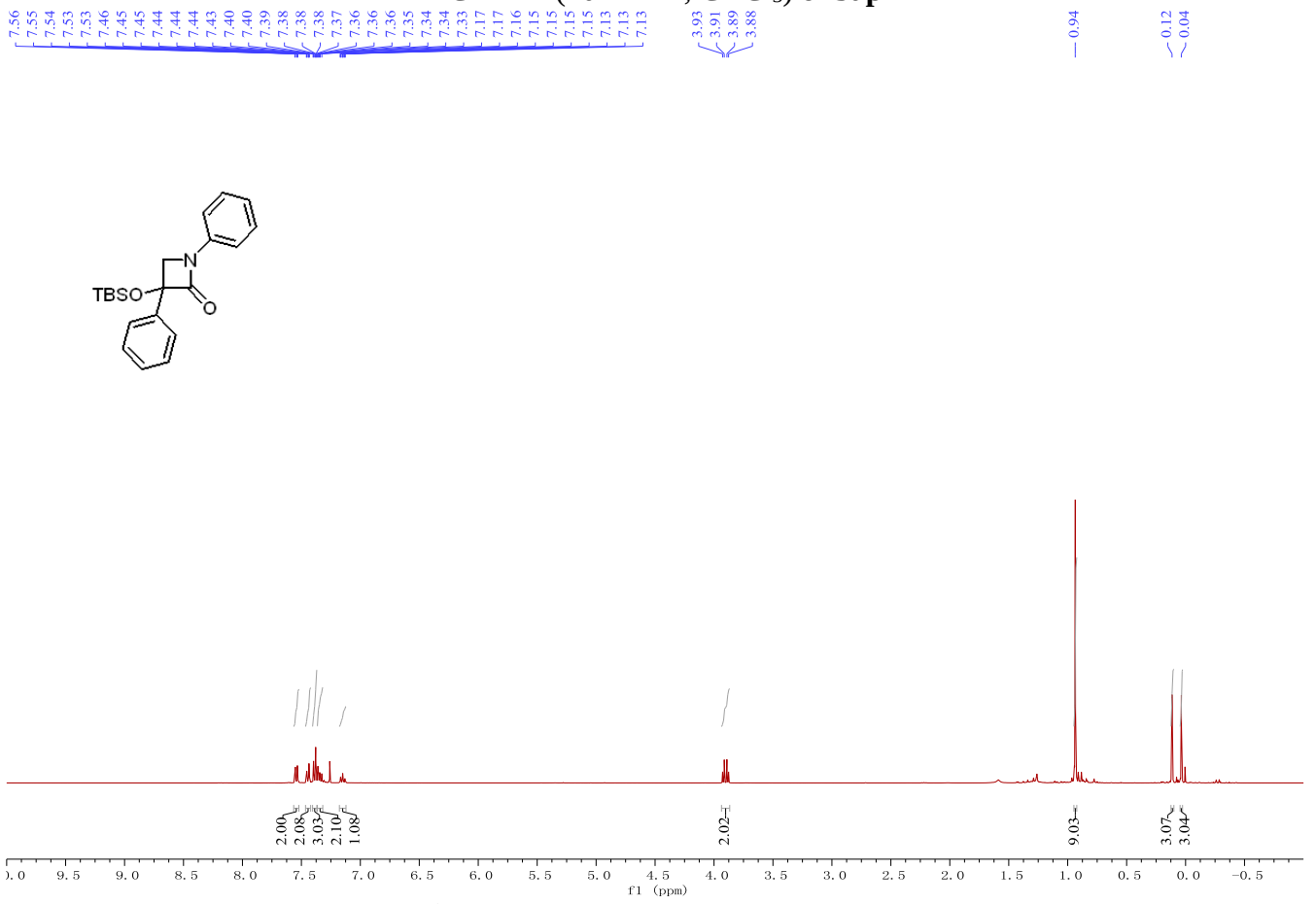
^{13}C NMR (101 MHz, $CDCl_3$) of **3ao**



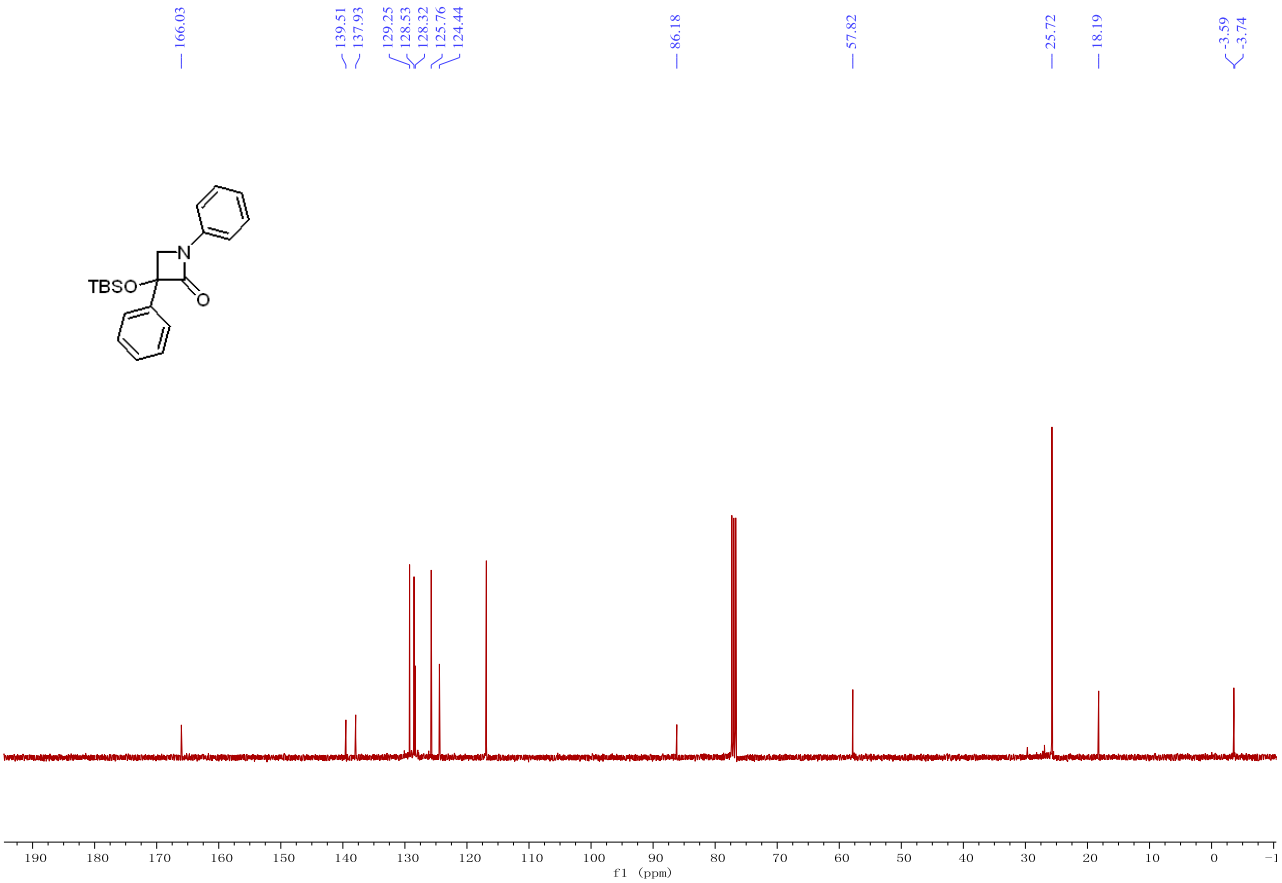
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap**



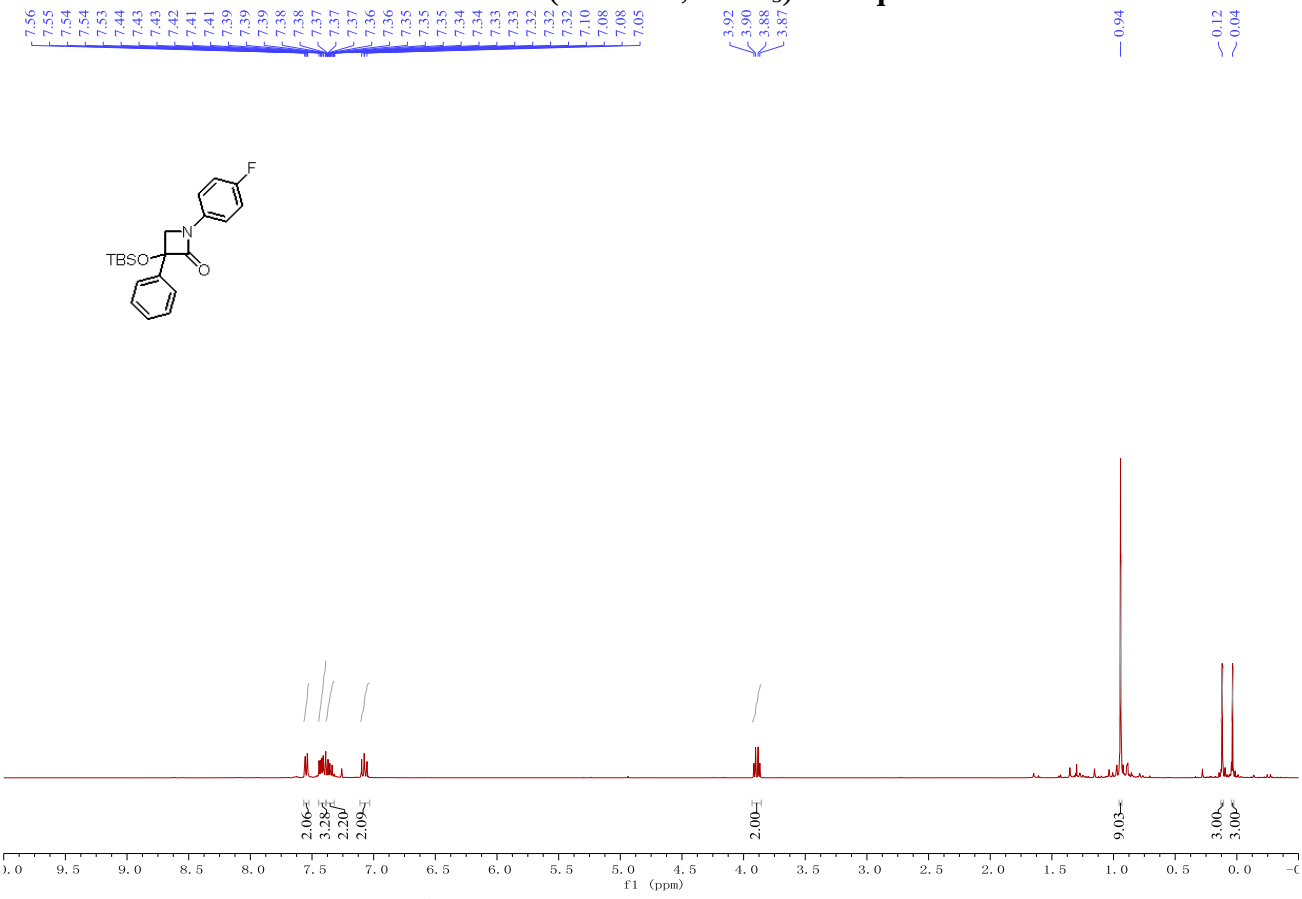
^{13}C NMR (101 MHz, $CDCl_3$) of **3ap**



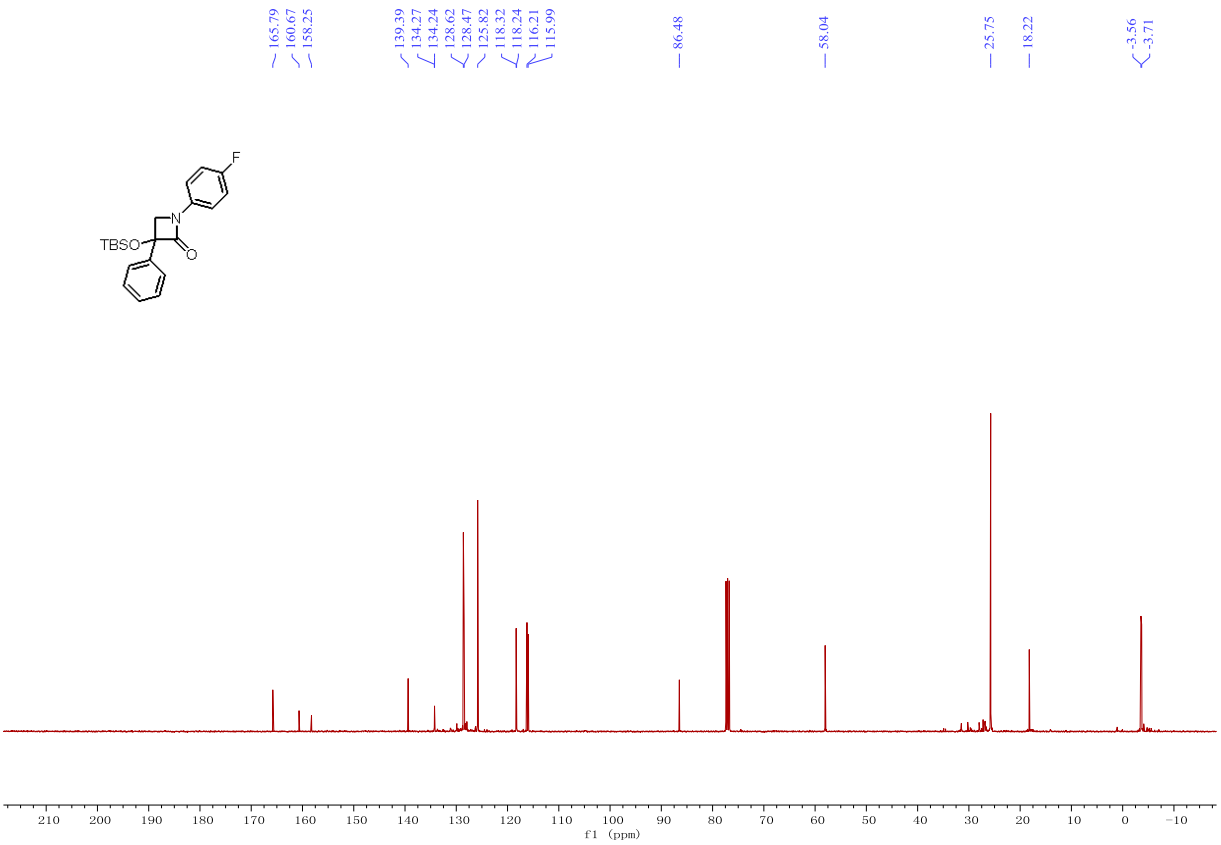
^{1}H NMR (400 MHz, $CDCl_3$) of **3aq**



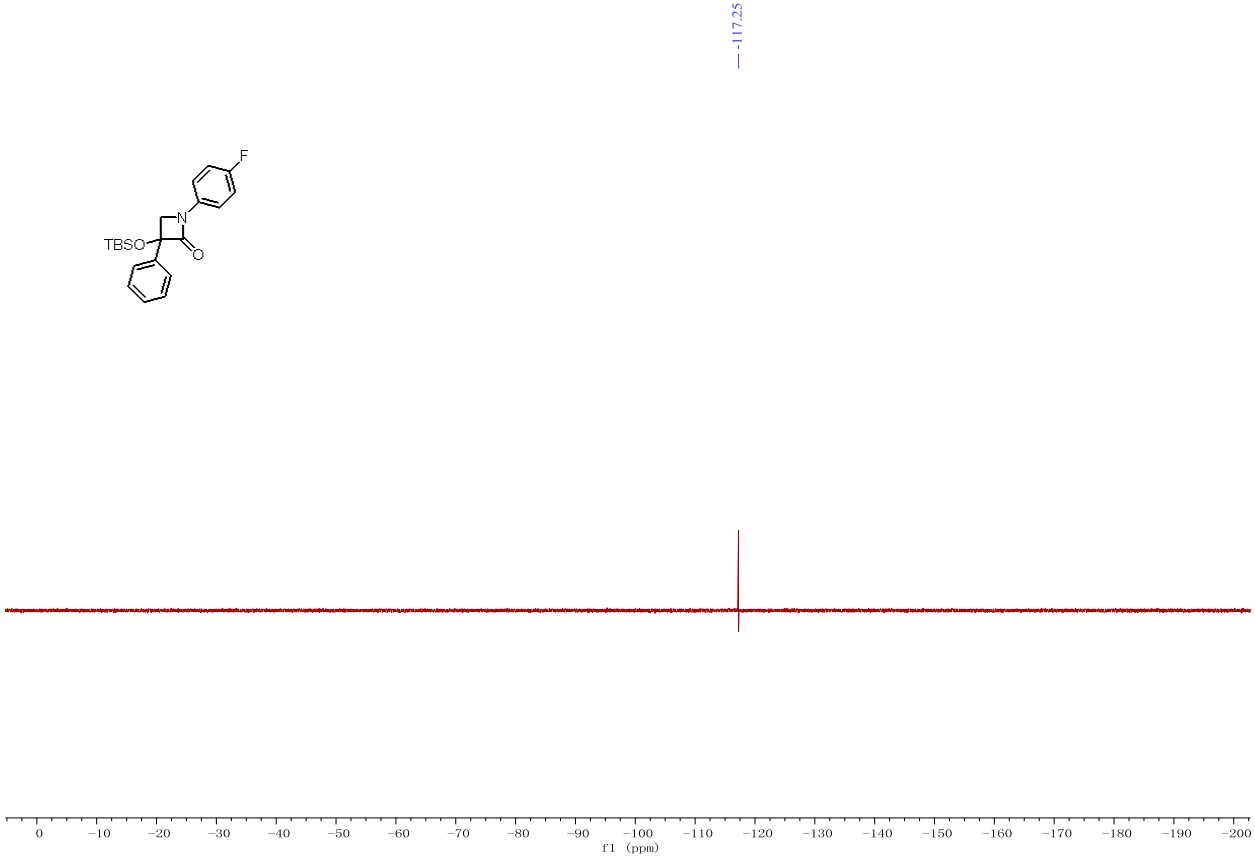
^{13}C NMR (101 MHz, $CDCl_3$) of **3aq**



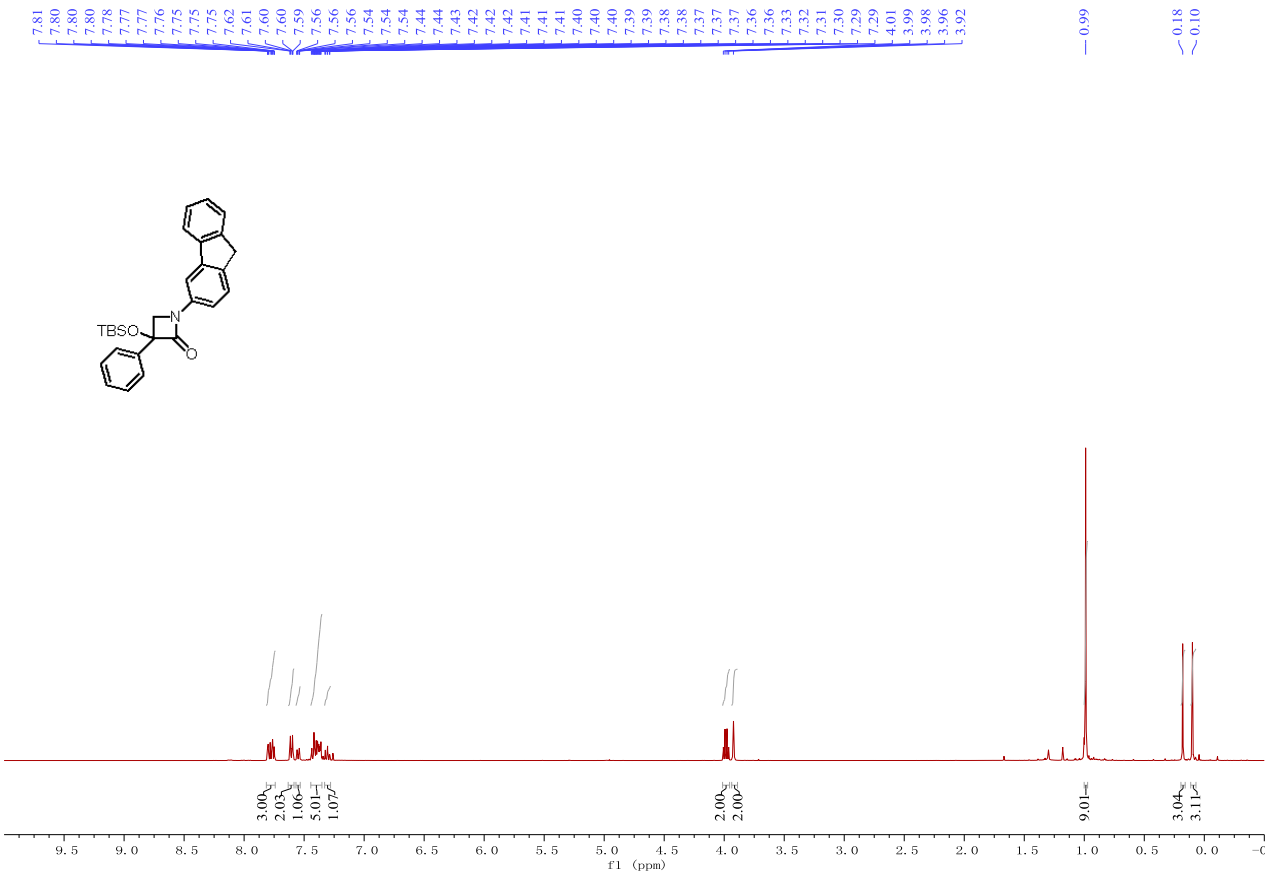
^{1}H NMR (400 MHz, $CDCl_3$) of **3ar**



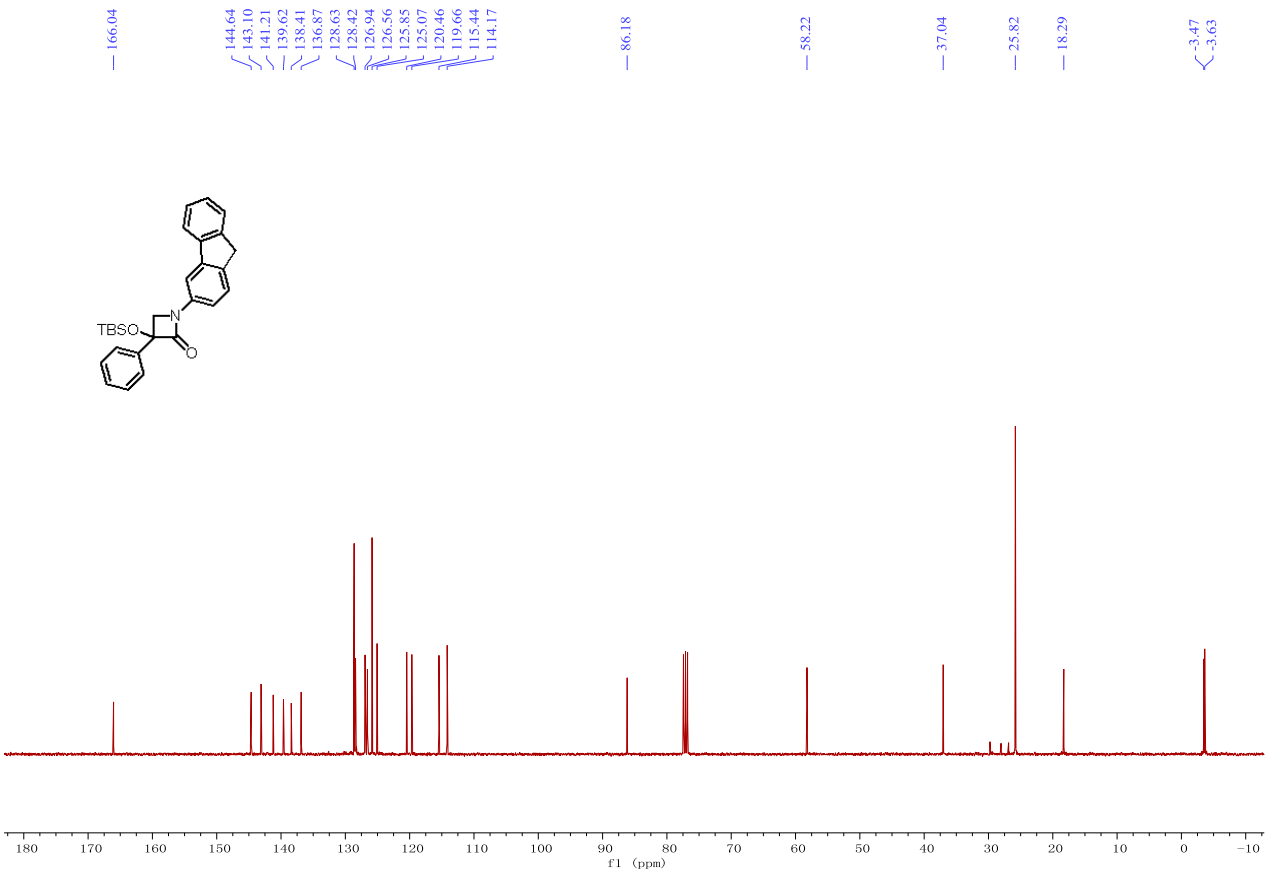
^{13}C NMR (101 MHz, $CDCl_3$) of **3ar**



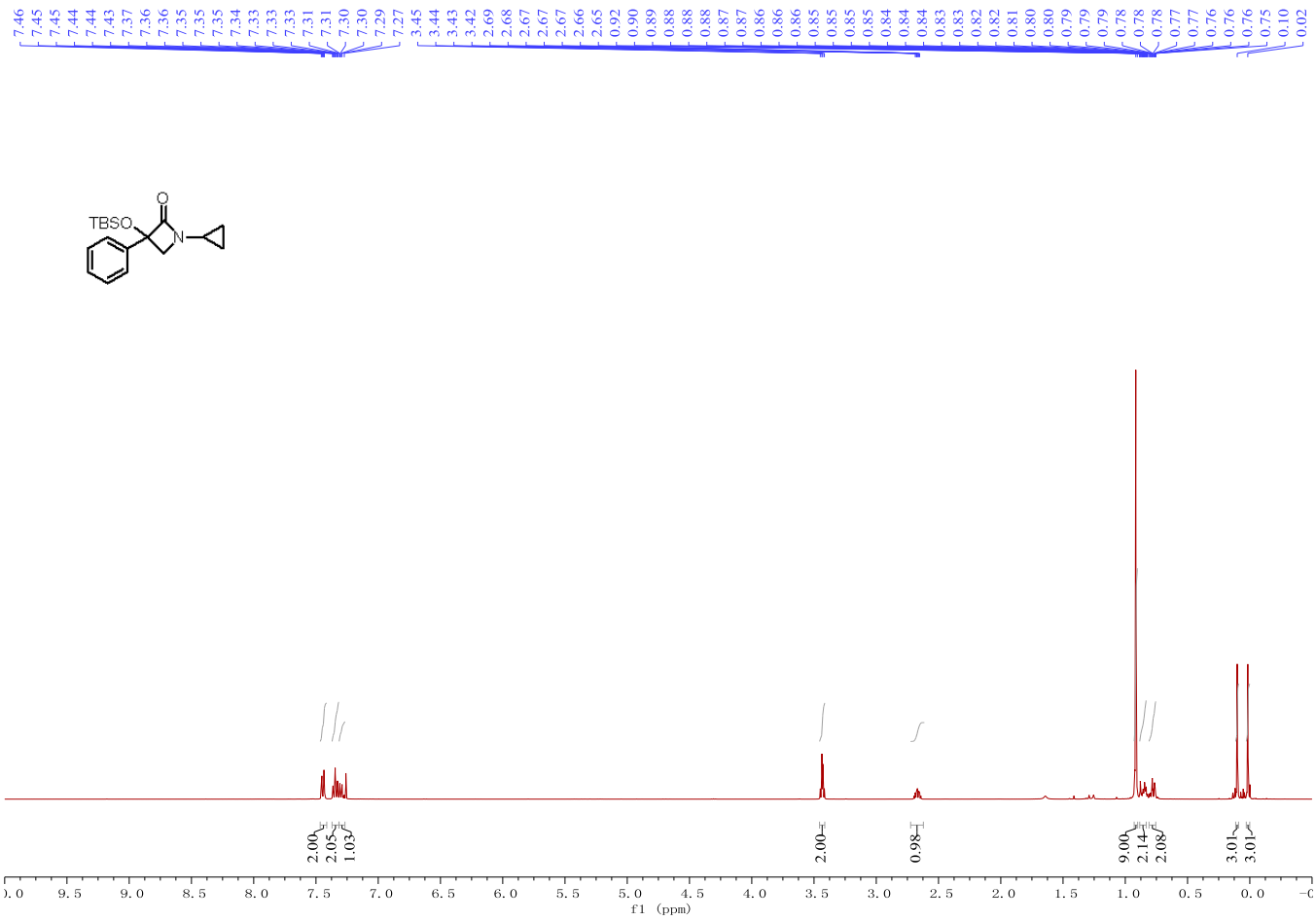
^{19}F NMR (376 MHz, $CDCl_3$) of **3ar**



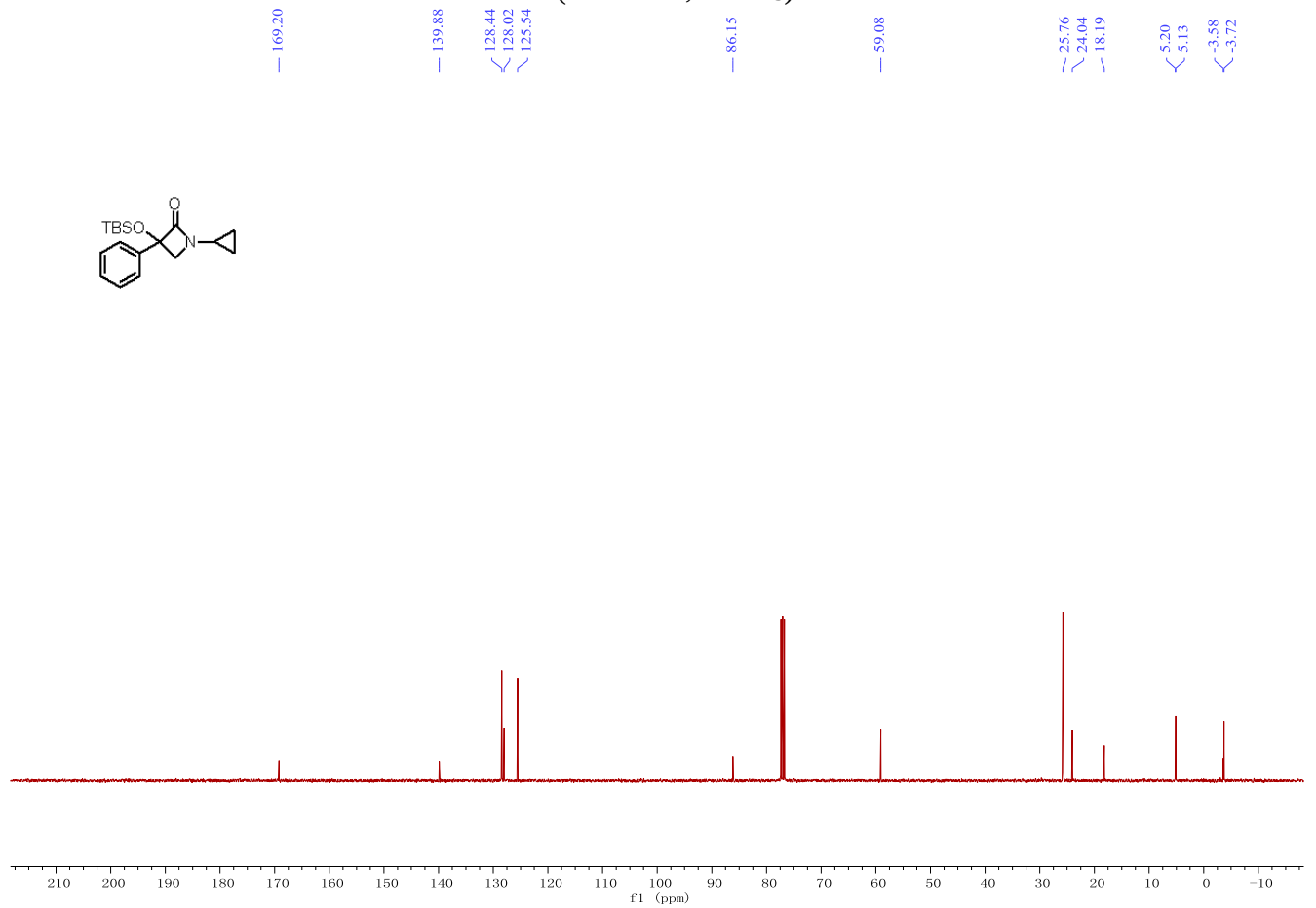
^{1}H NMR (400 MHz, $CDCl_3$) of **3as**



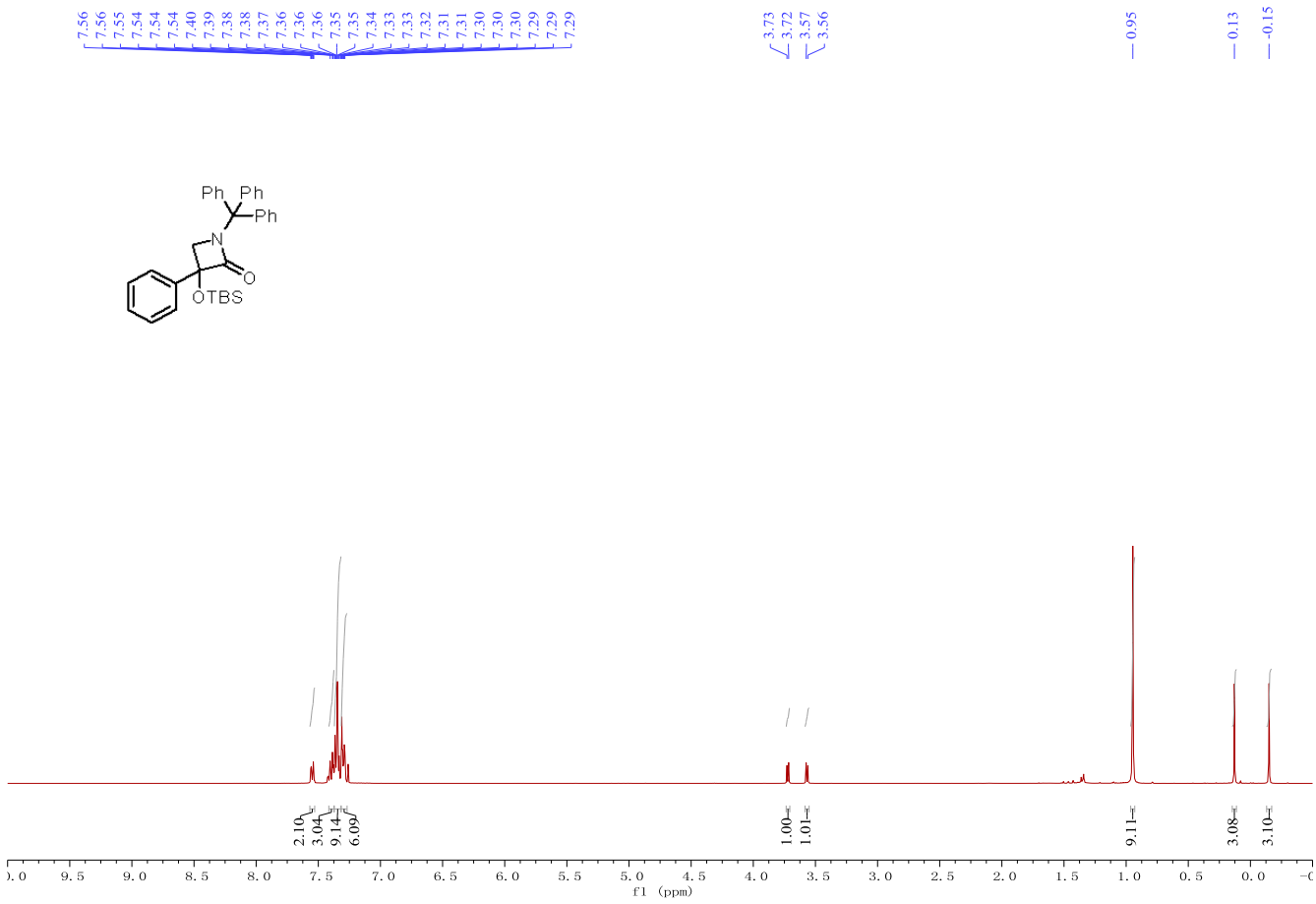
^{13}C NMR (101 MHz, $CDCl_3$) of **3as**



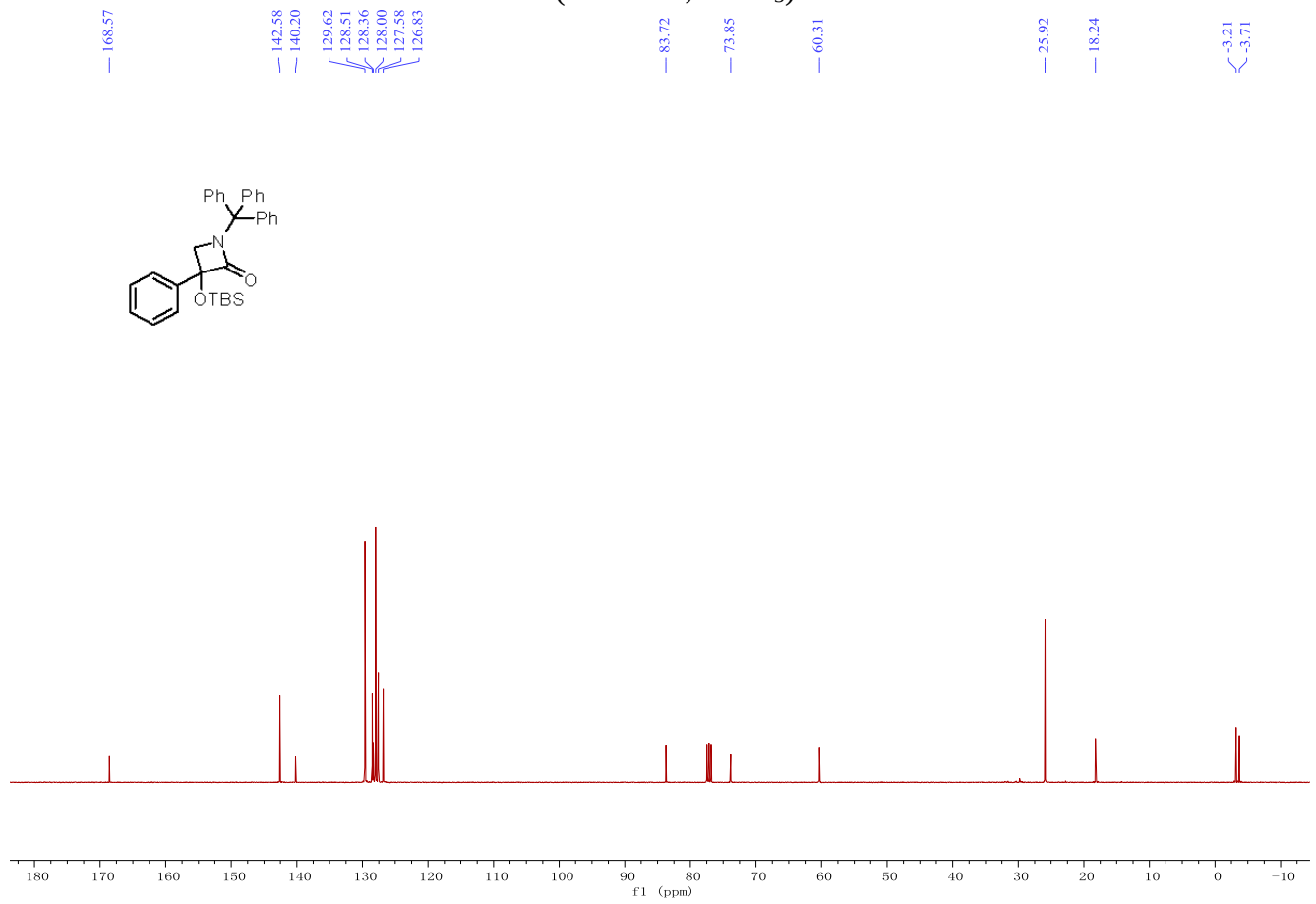
^{1}H NMR (400 MHz, $CDCl_3$) of **3at**



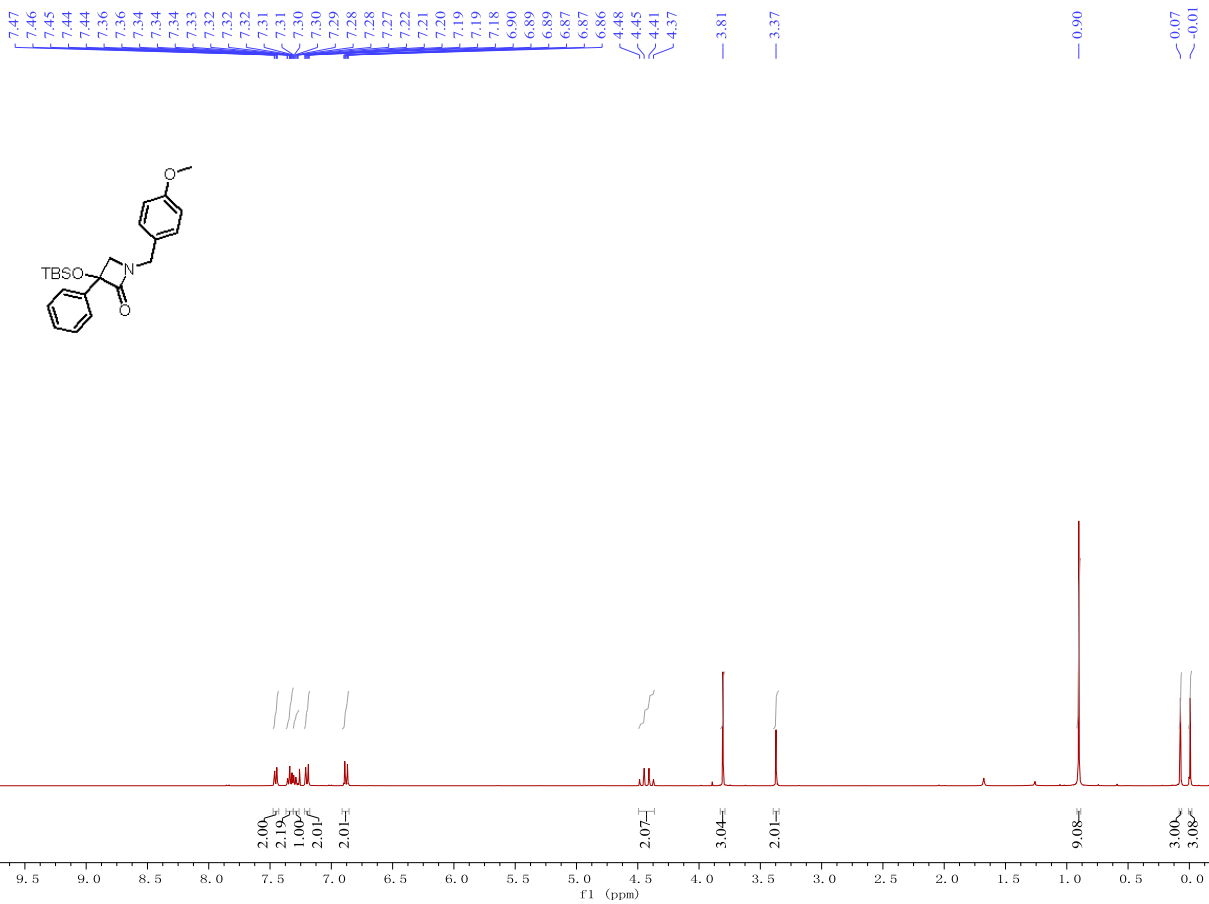
^{13}C NMR (101 MHz, $CDCl_3$) of **3at**



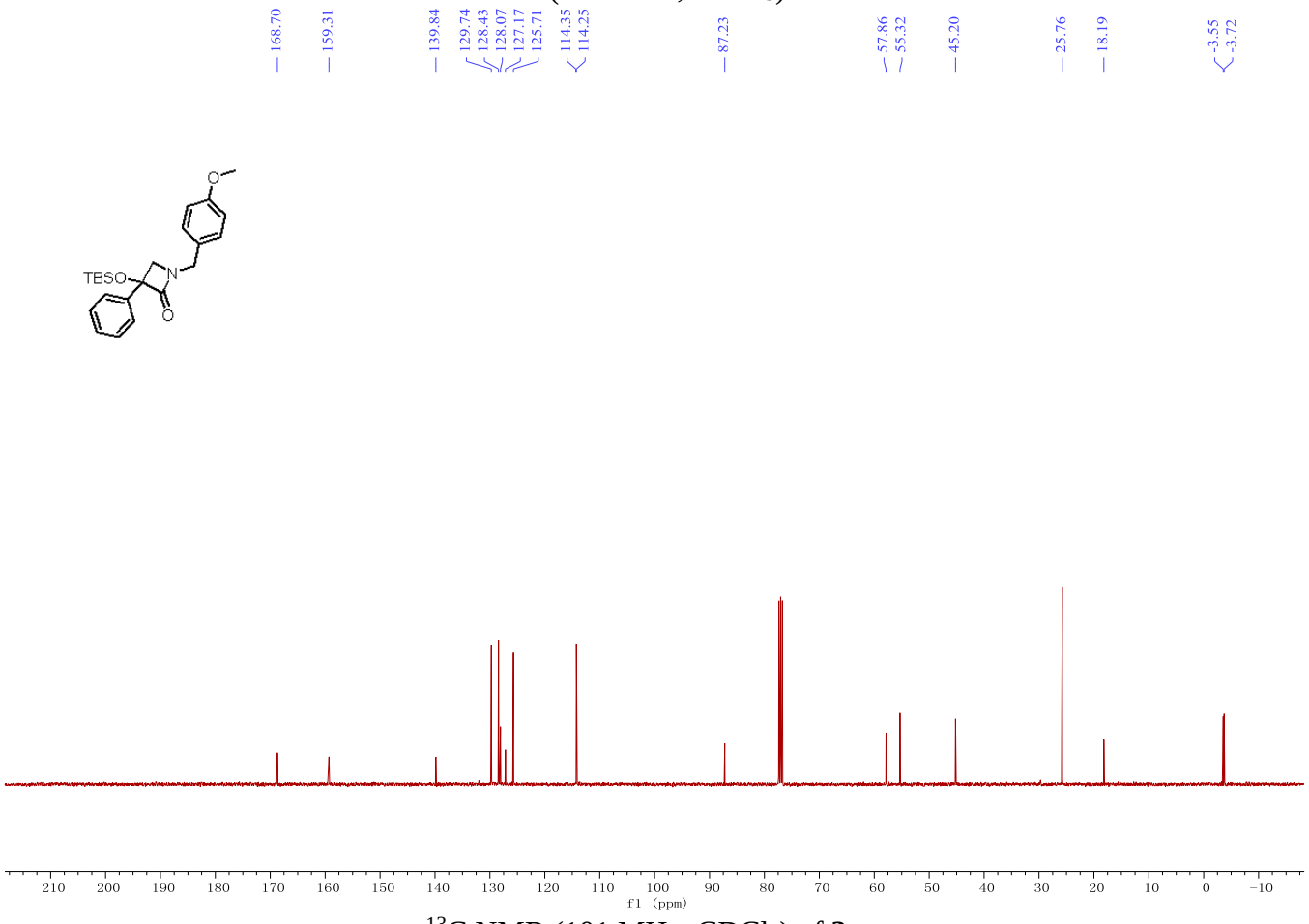
^{1}H NMR (400 MHz, $CDCl_3$) of **3au**



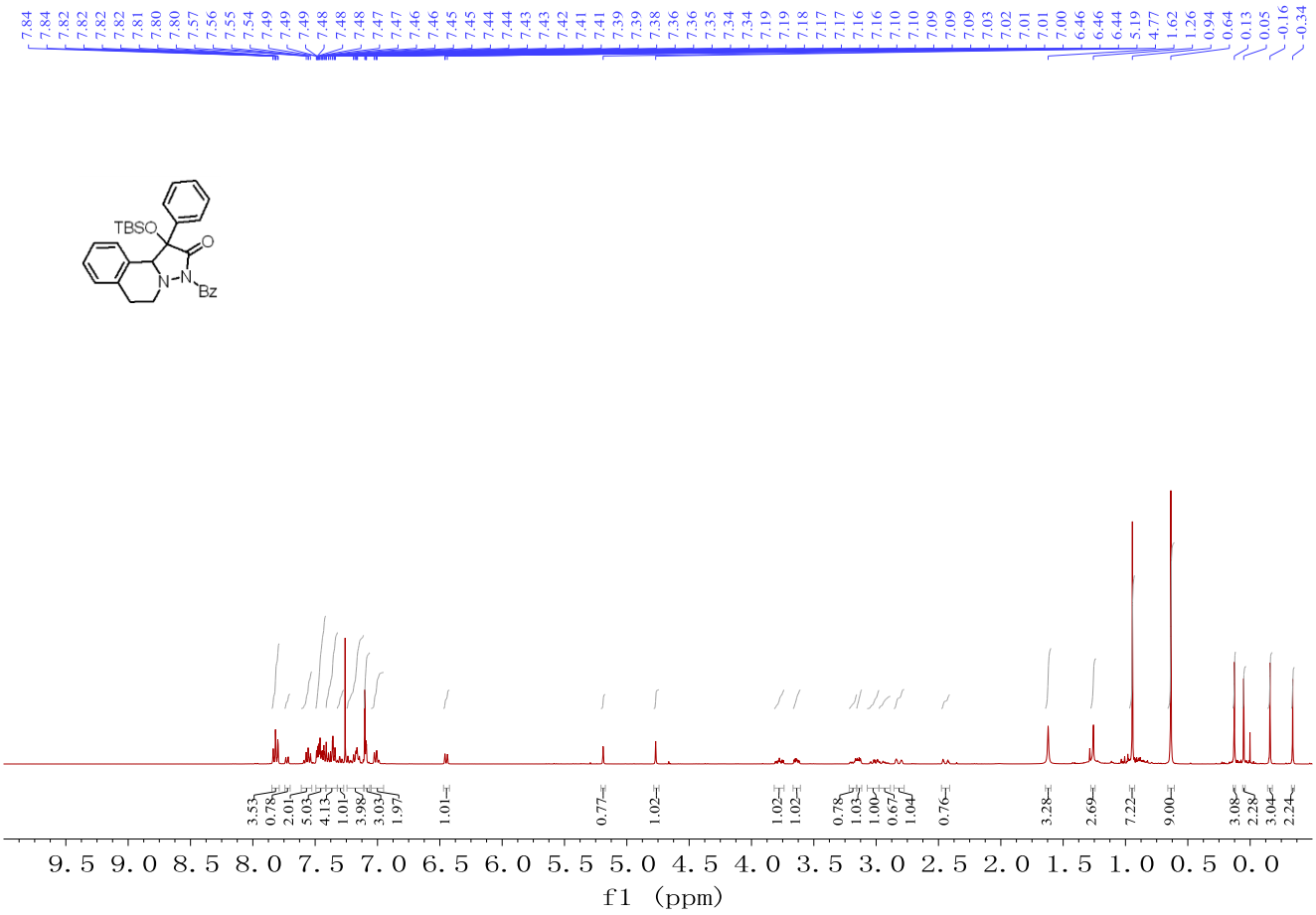
^{13}C NMR (101 MHz, $CDCl_3$) of **3au**



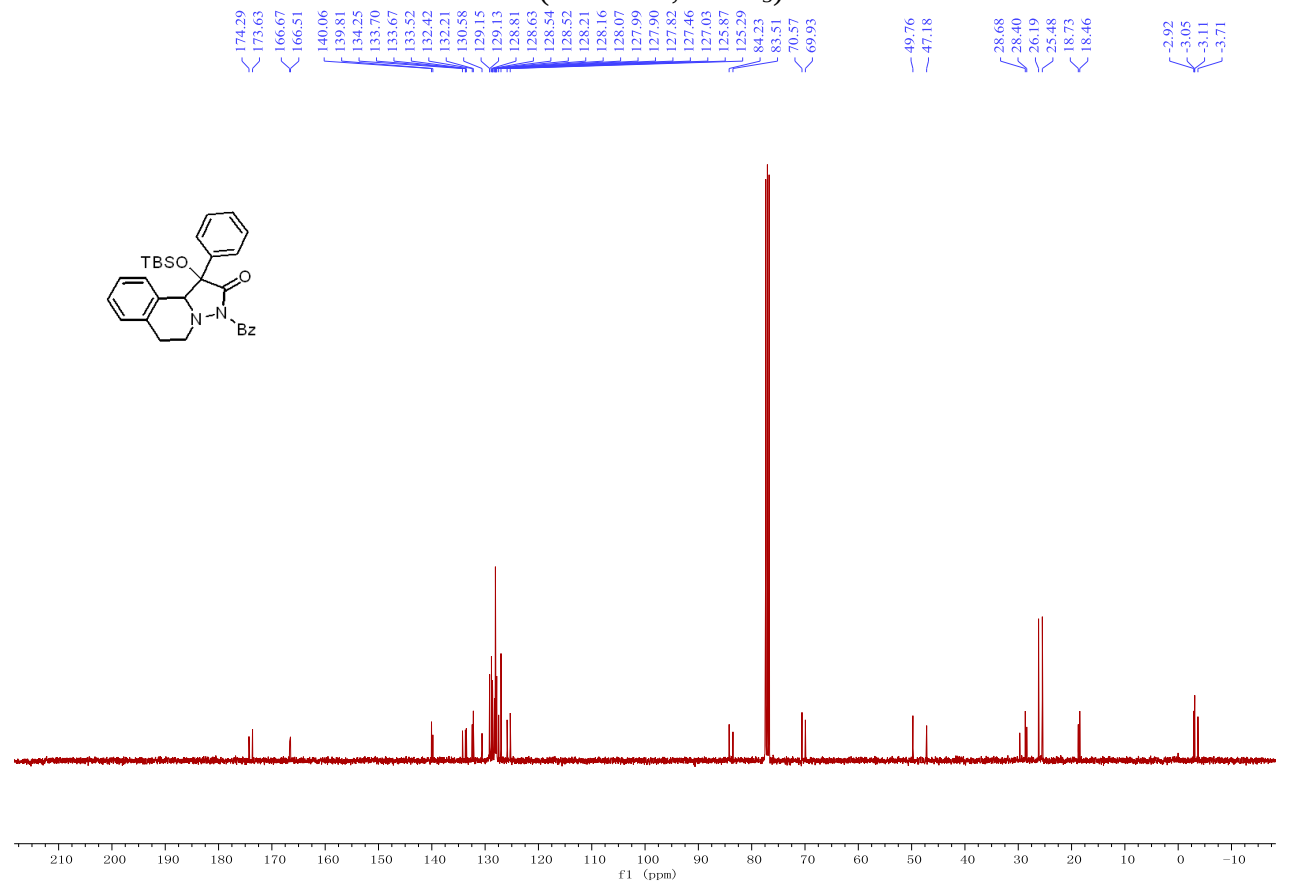
^{1}H NMR (400 MHz, $CDCl_3$) of **3av**



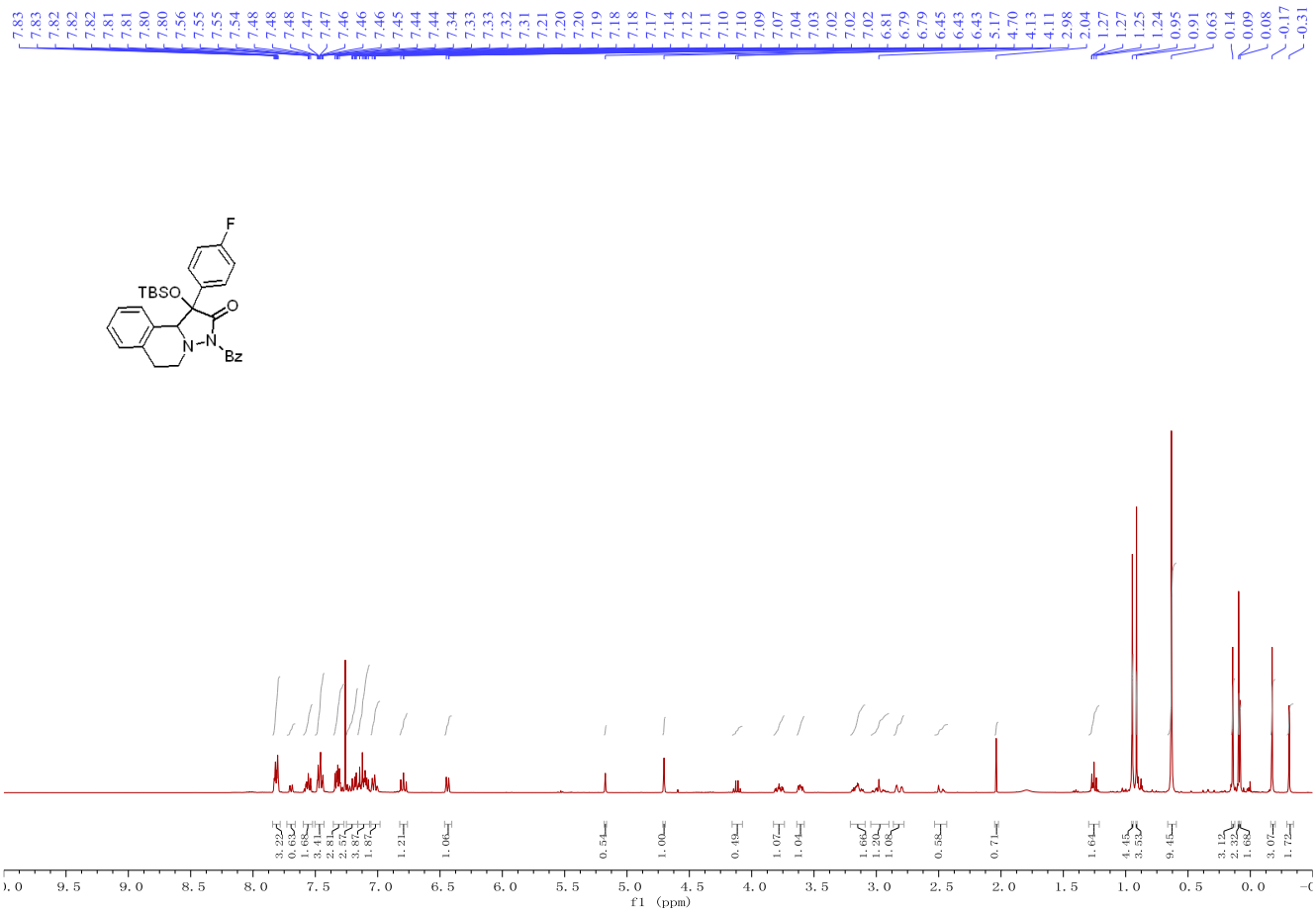
^{13}C NMR (101 MHz, $CDCl_3$) of **3av**



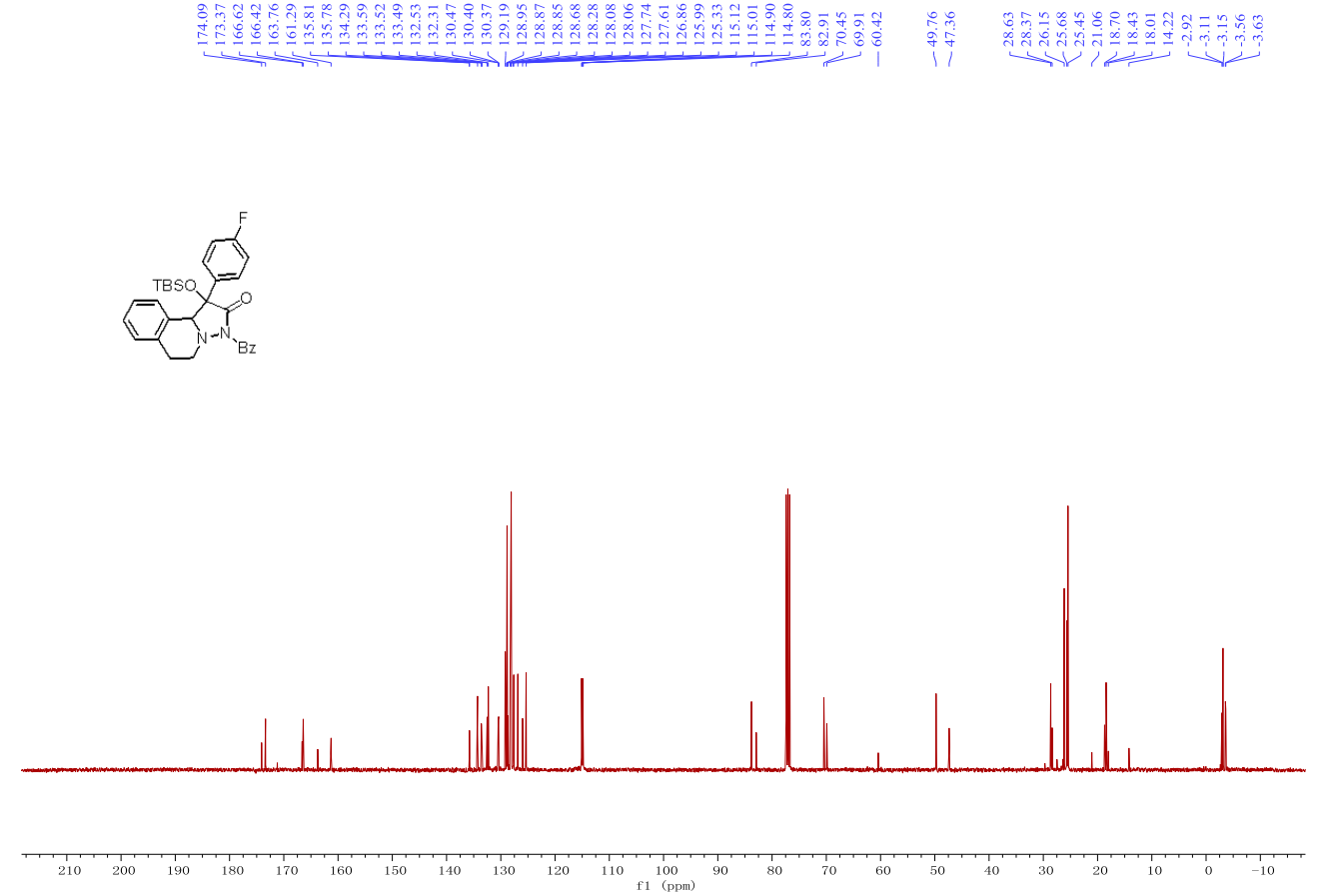
^{1}H NMR (400 MHz, $CDCl_3$) of **5aa**



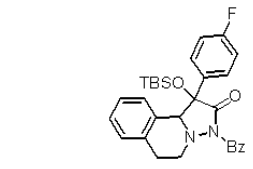
^{13}C NMR (101 MHz, $CDCl_3$) of **5aa**



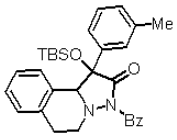
^{1}H NMR (400 MHz, $CDCl_3$) of **5ab**

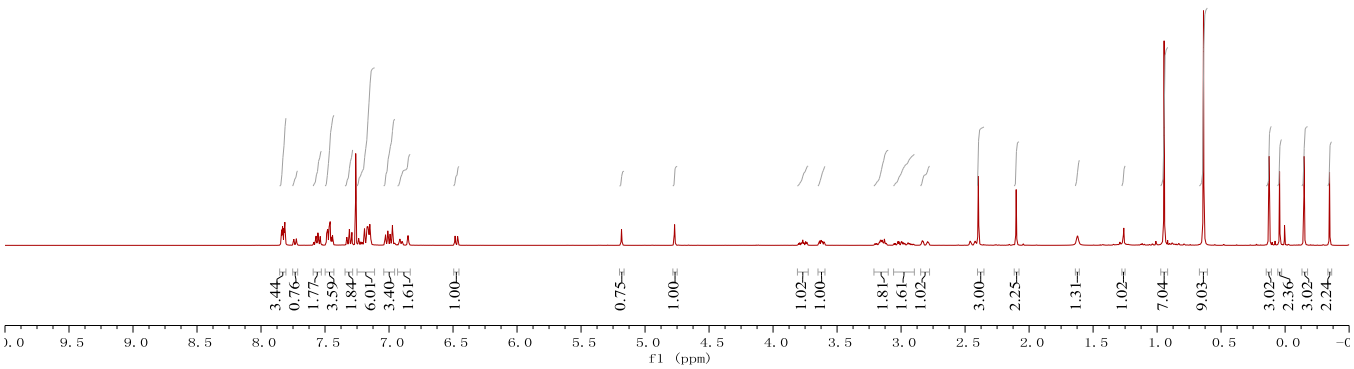


^{13}C NMR (101 MHz, $CDCl_3$) of **5ab**

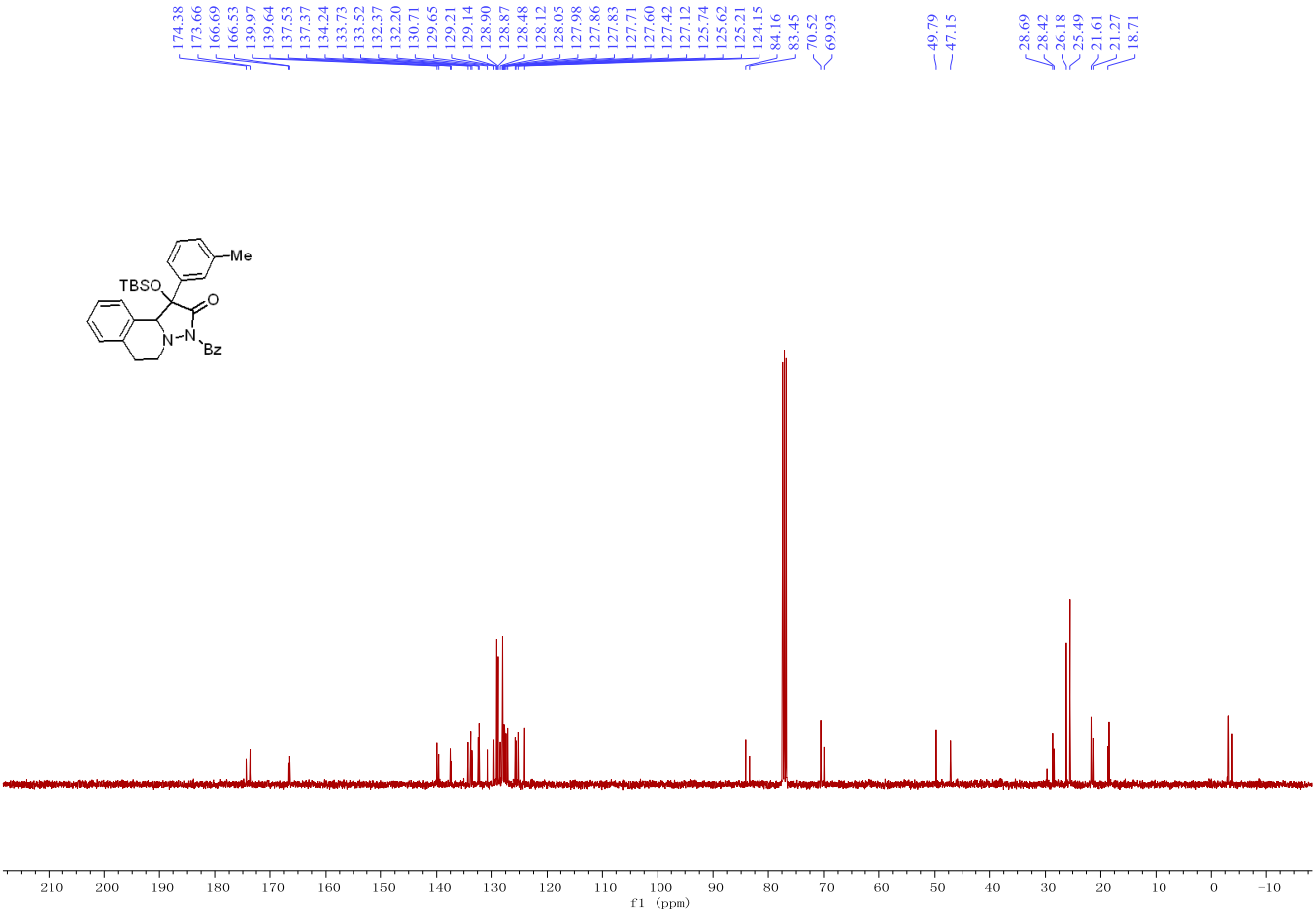


^{19}F NMR (376 MHz, $CDCl_3$) of **5ab**

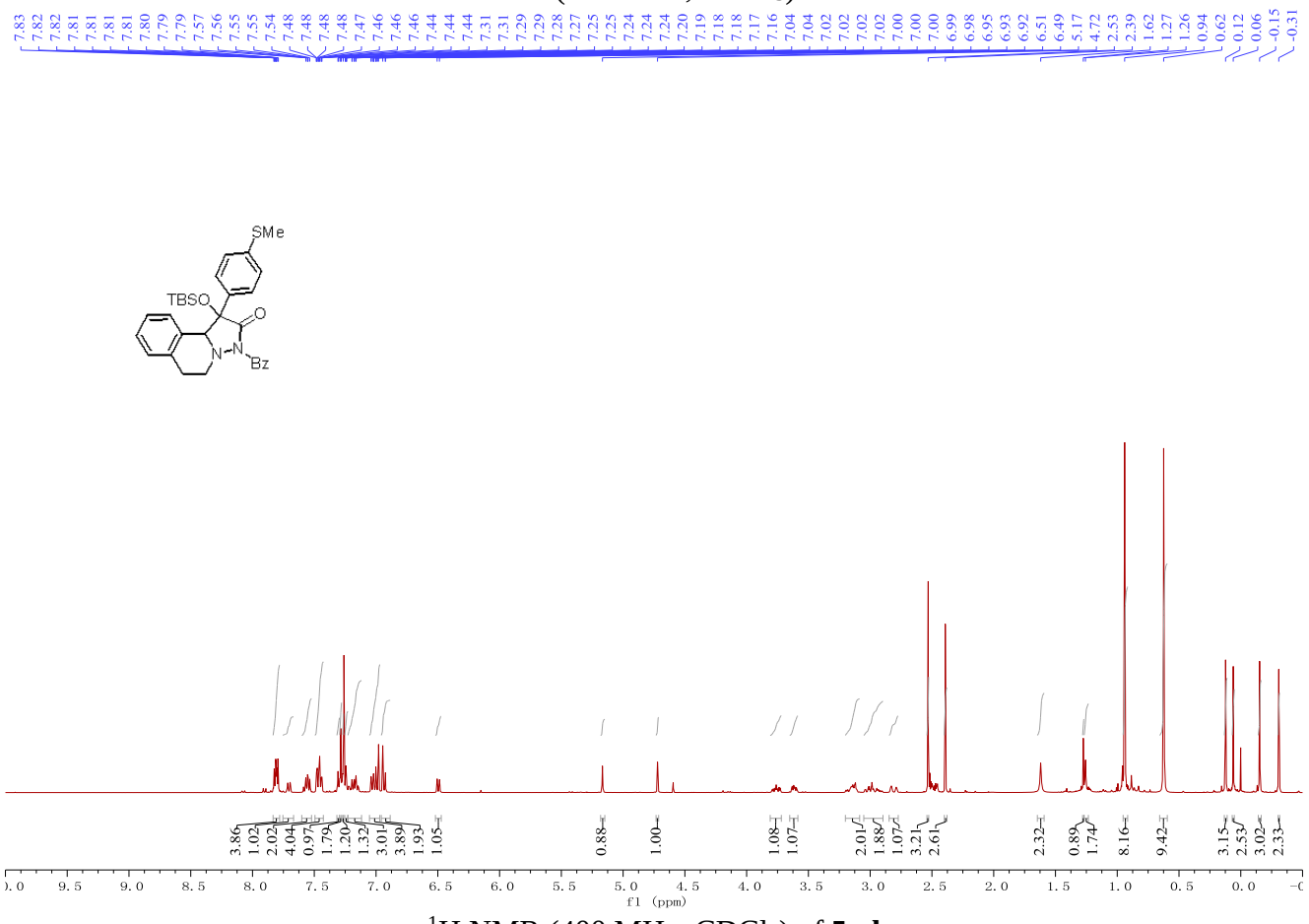




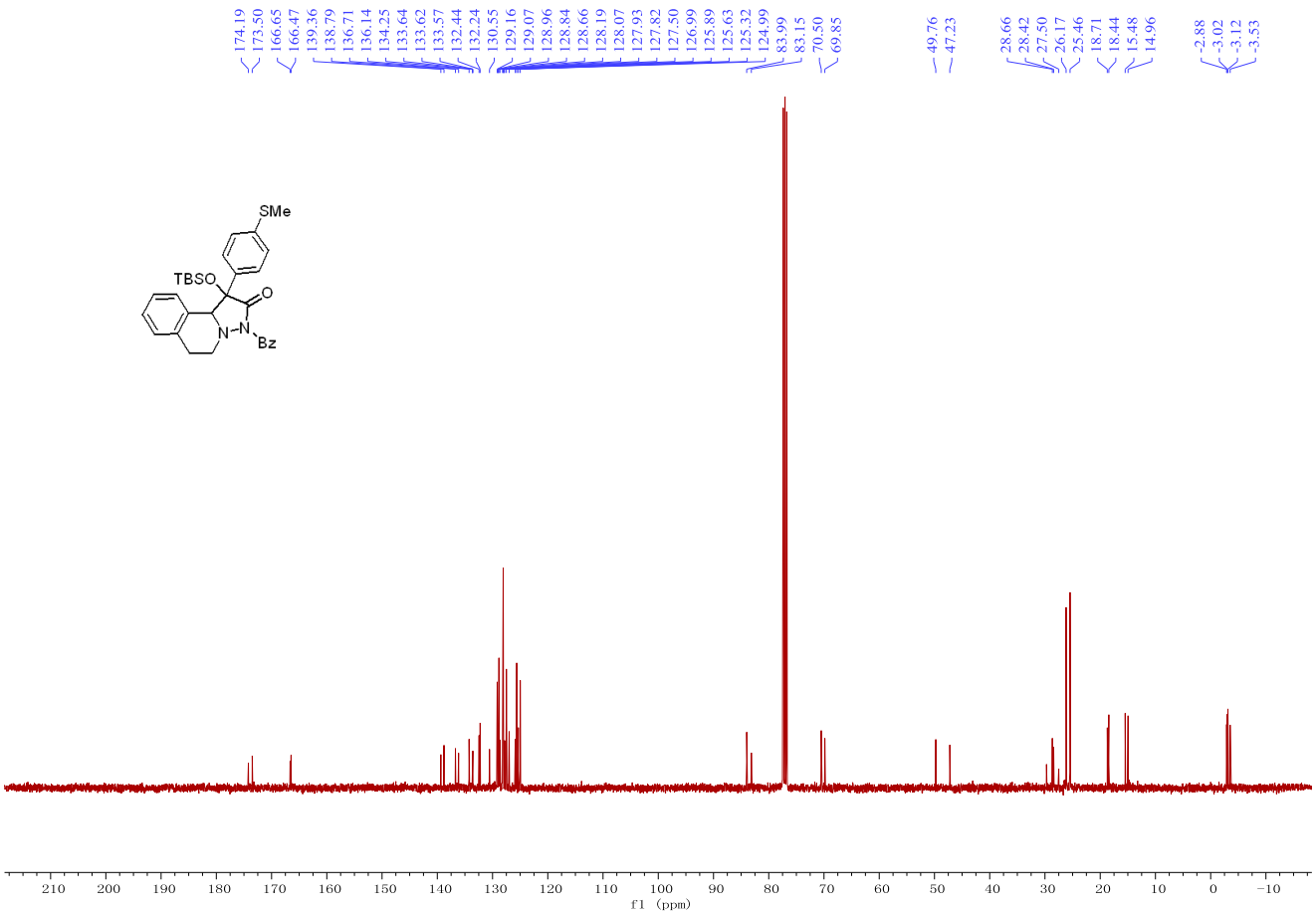
^{1}H NMR (400 MHz, $CDCl_3$) of **5ac**



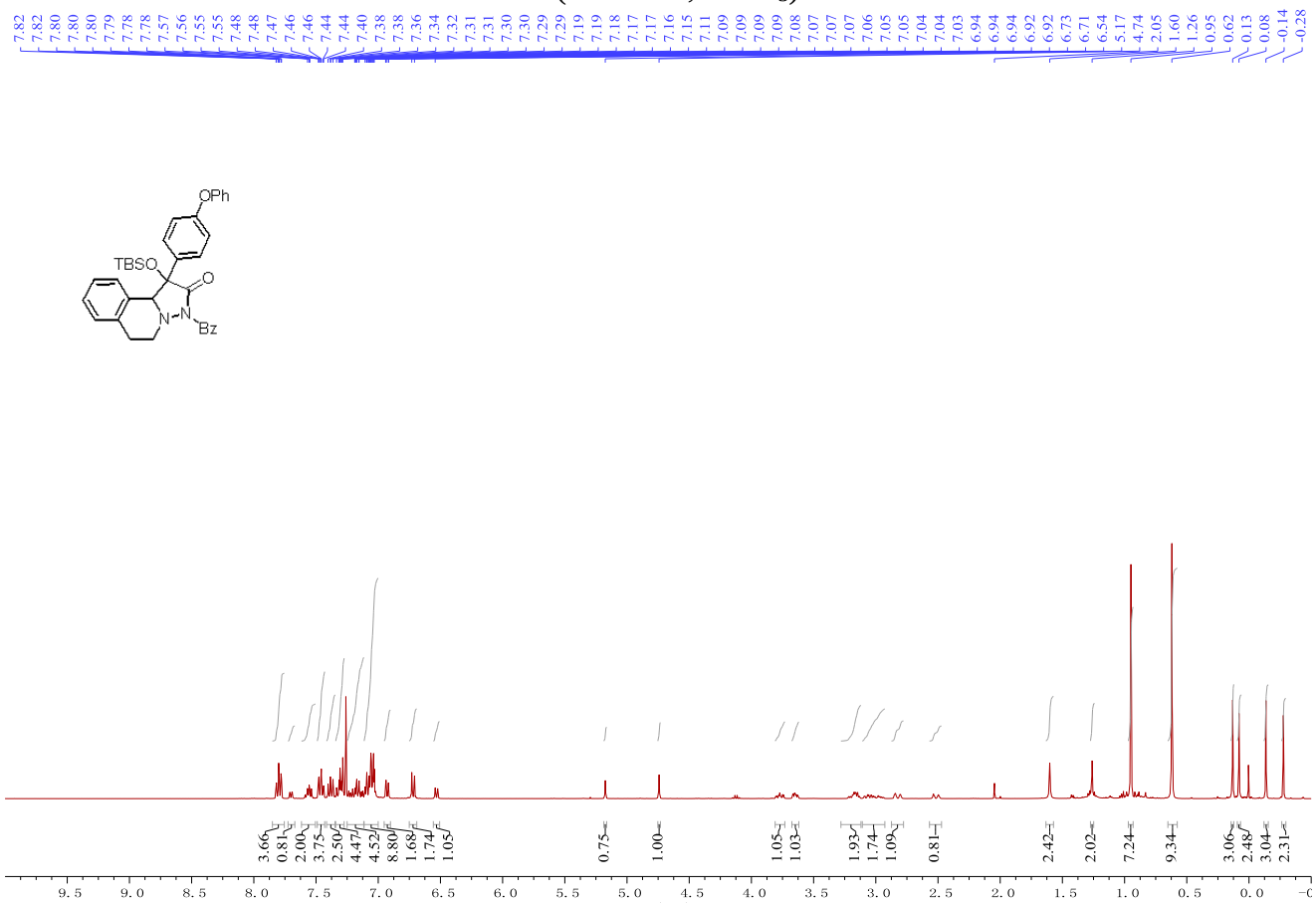
^{13}C NMR (101 MHz, $CDCl_3$) of **5ac**



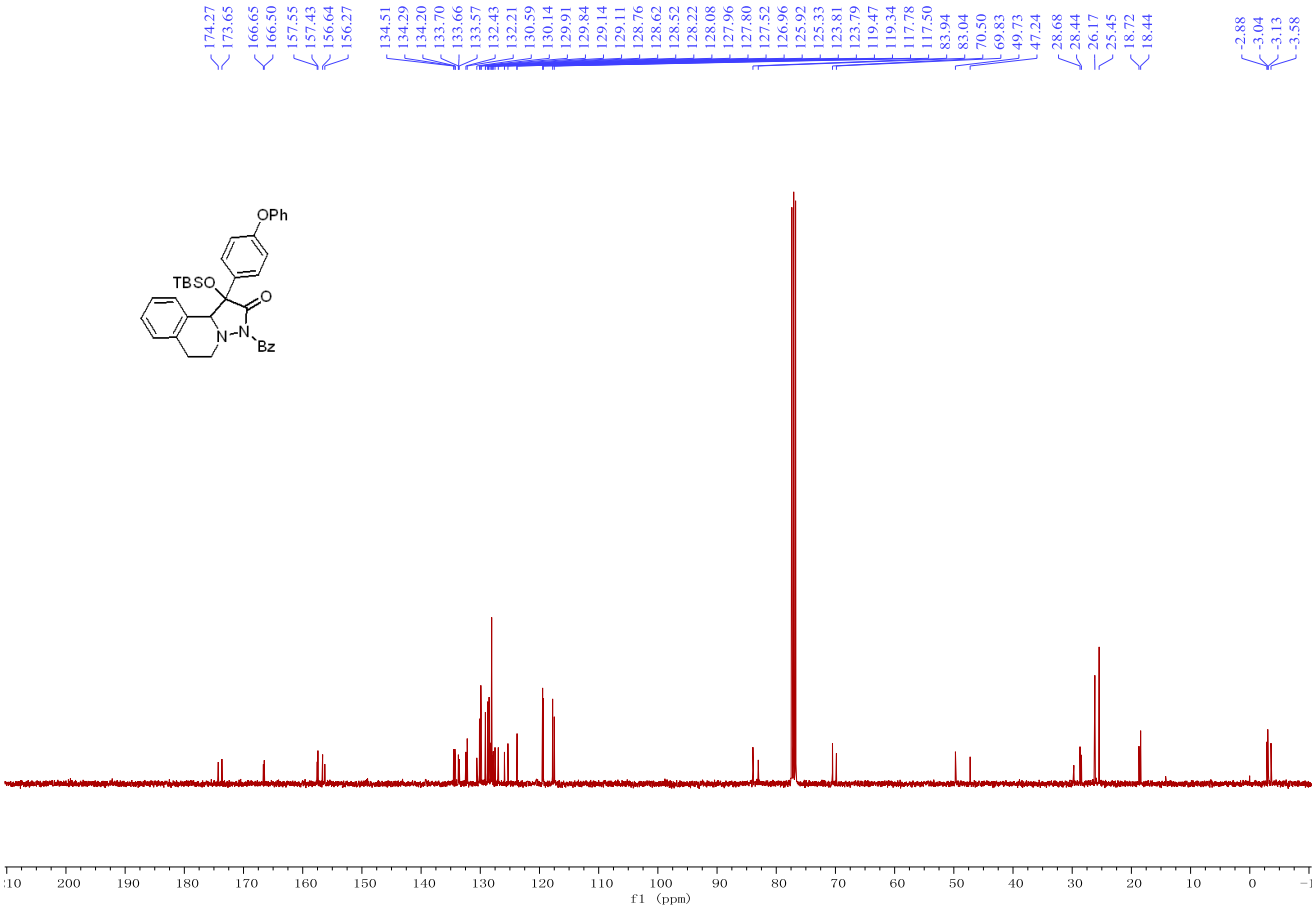
^{1}H NMR (400 MHz, $CDCl_3$) of **5ad**



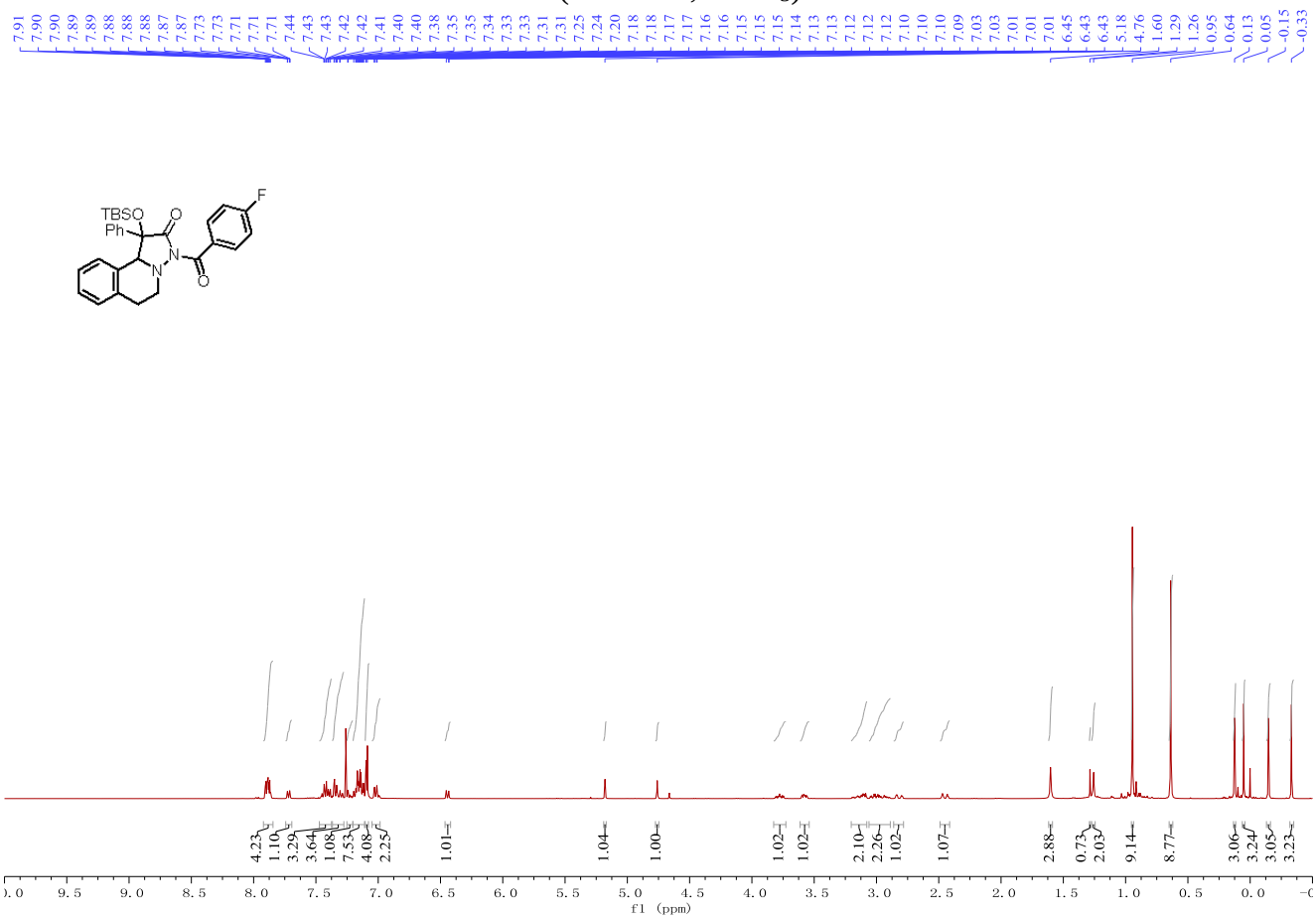
^{13}C NMR (101 MHz, $CDCl_3$) of **5ad**



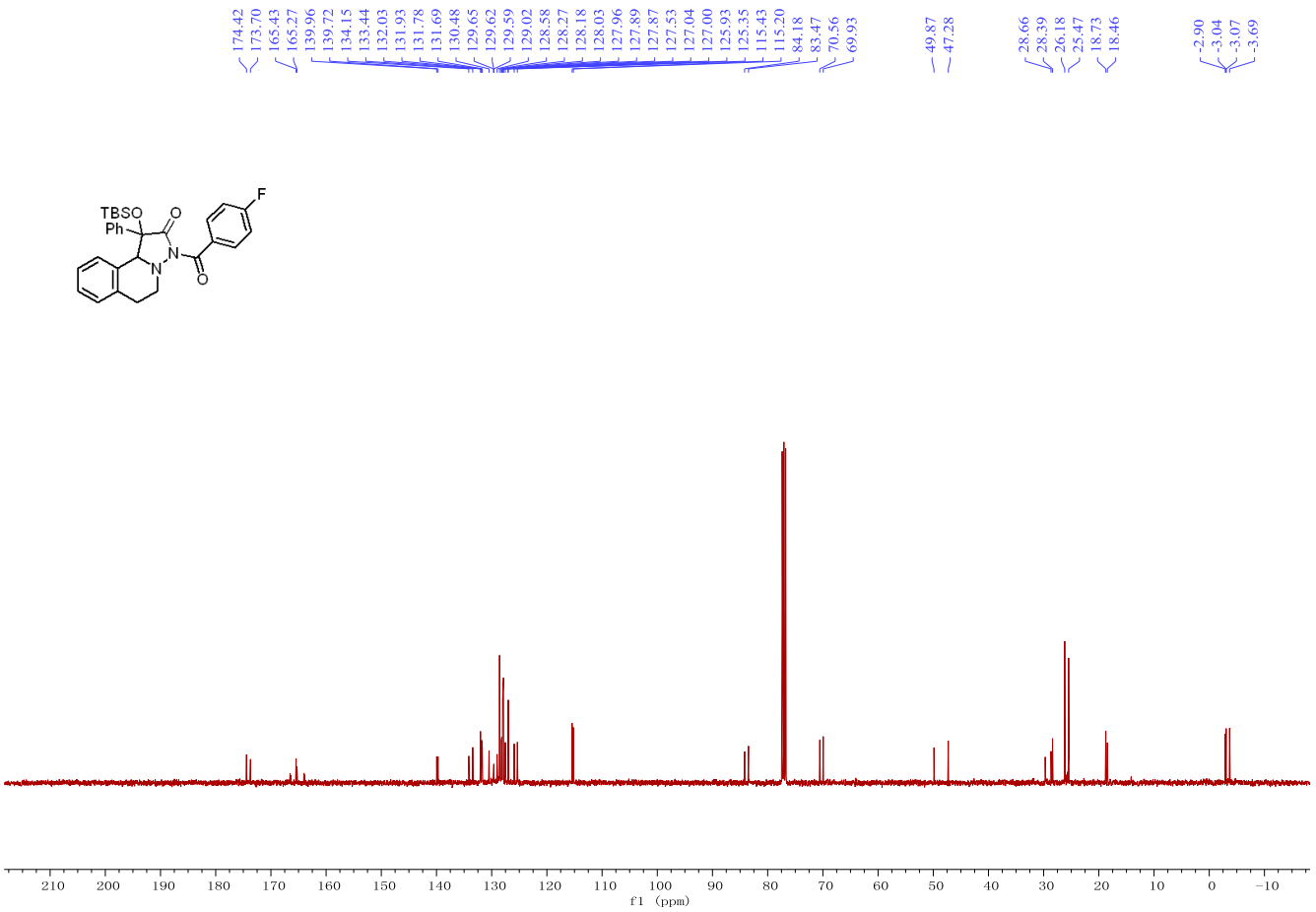
^{1}H NMR (400 MHz, $CDCl_3$) of **5ae**



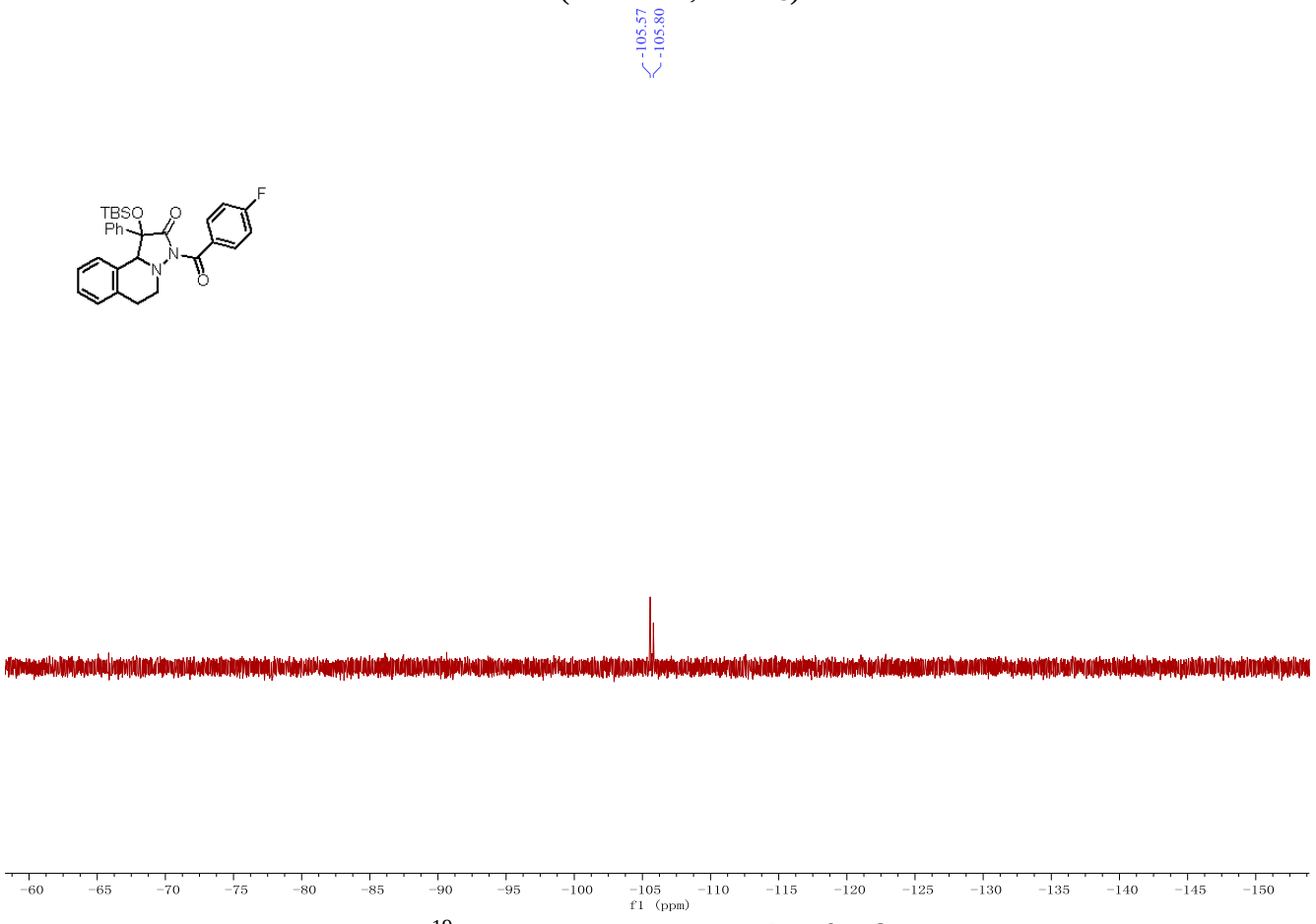
^{13}C NMR (101 MHz, $CDCl_3$) of **5ae**



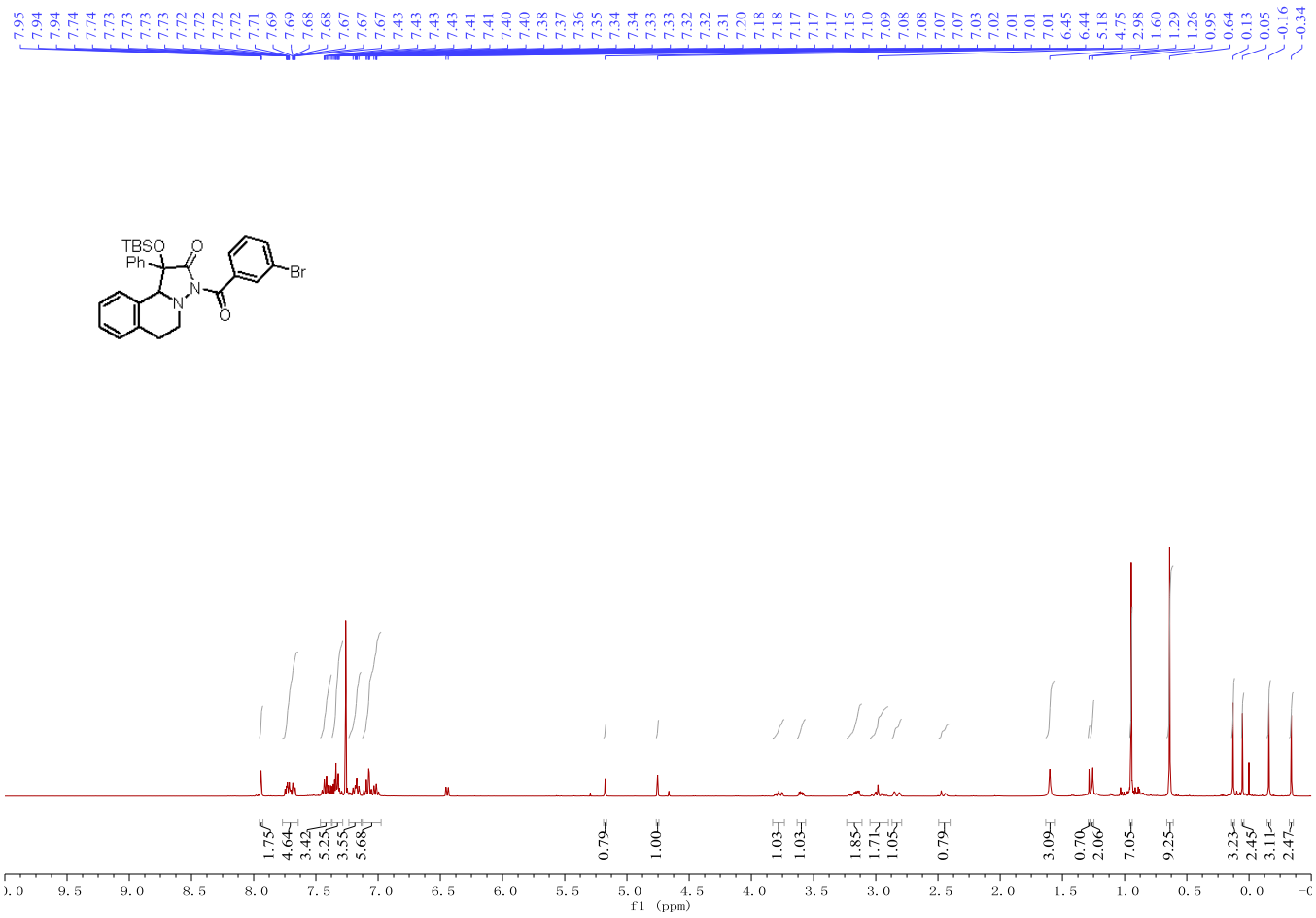
^{1}H NMR (400 MHz, $CDCl_3$) of **5af**



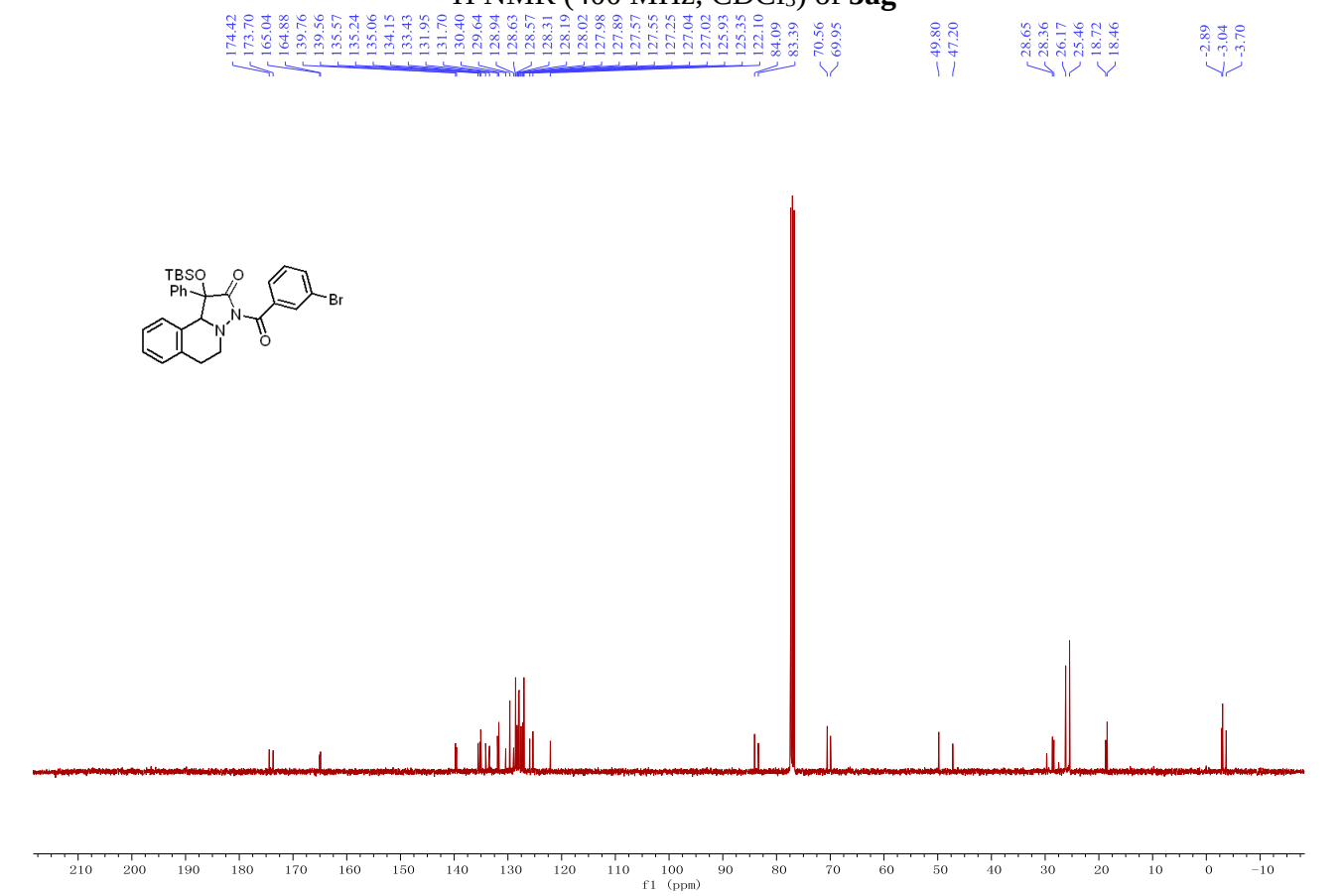
^{13}C NMR (101 MHz, $CDCl_3$) of **5af**



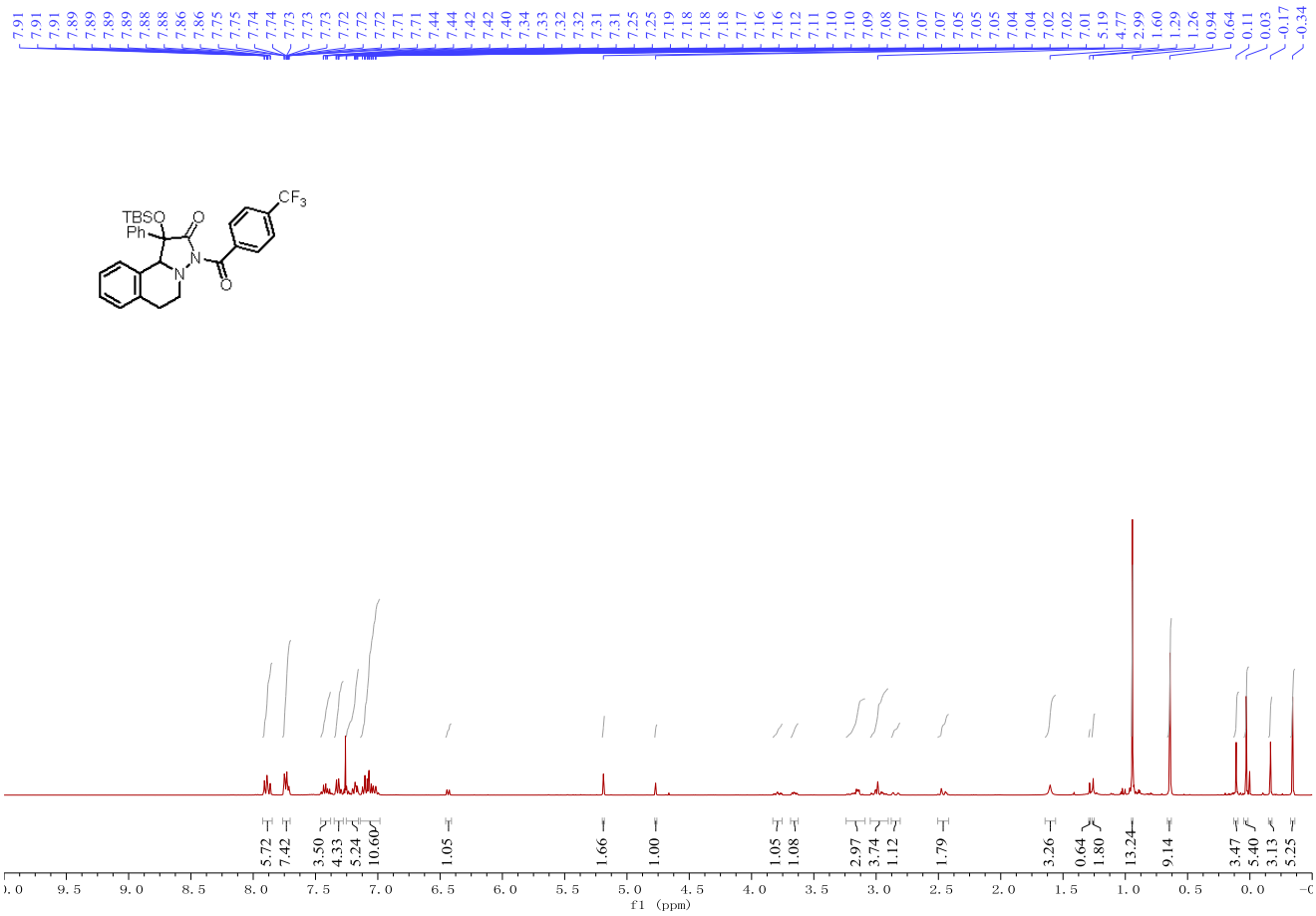
^{19}F NMR (376 MHz, $CDCl_3$) of **5af**



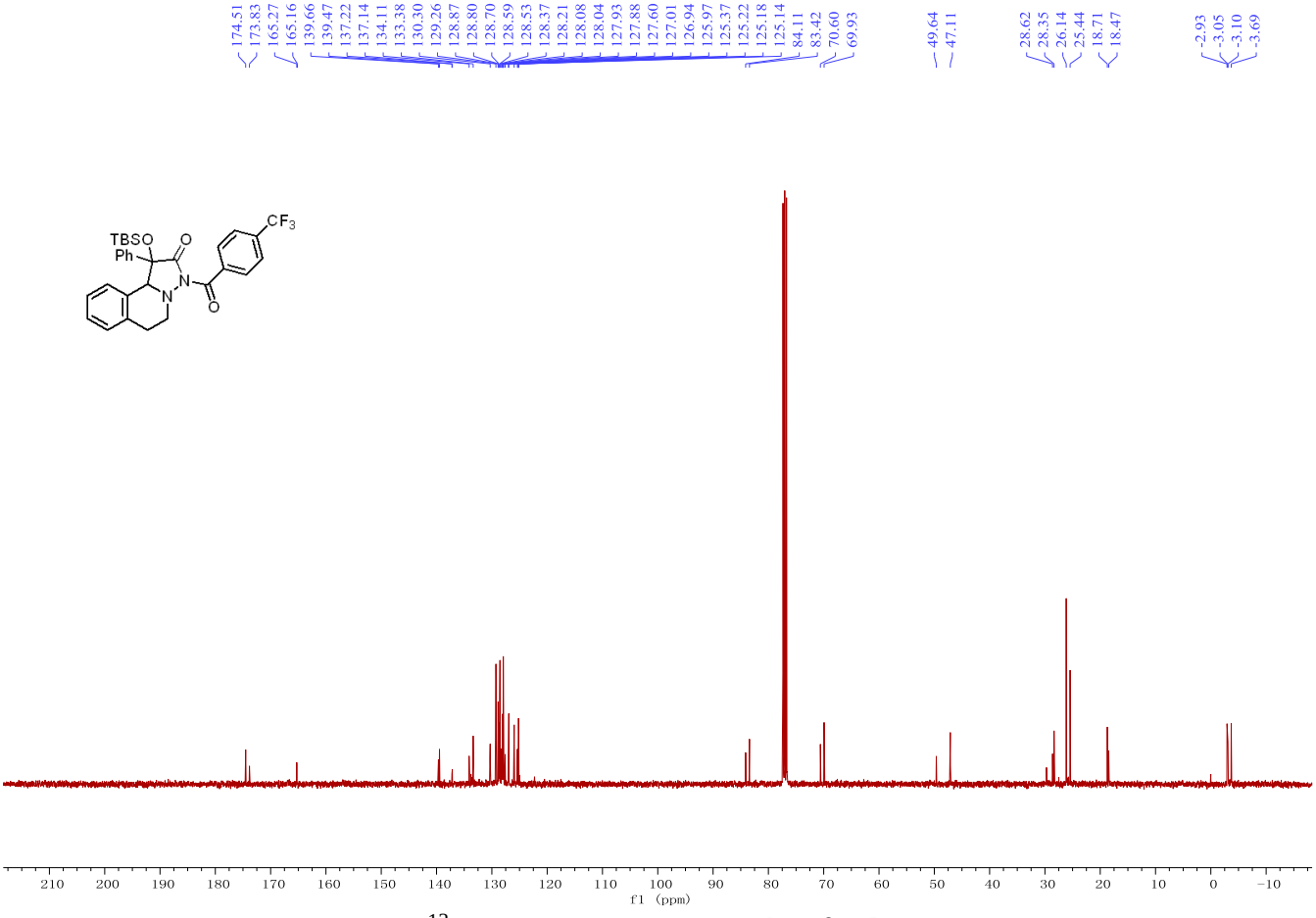
^{1}H NMR (400 MHz, $CDCl_3$) of **5ag**



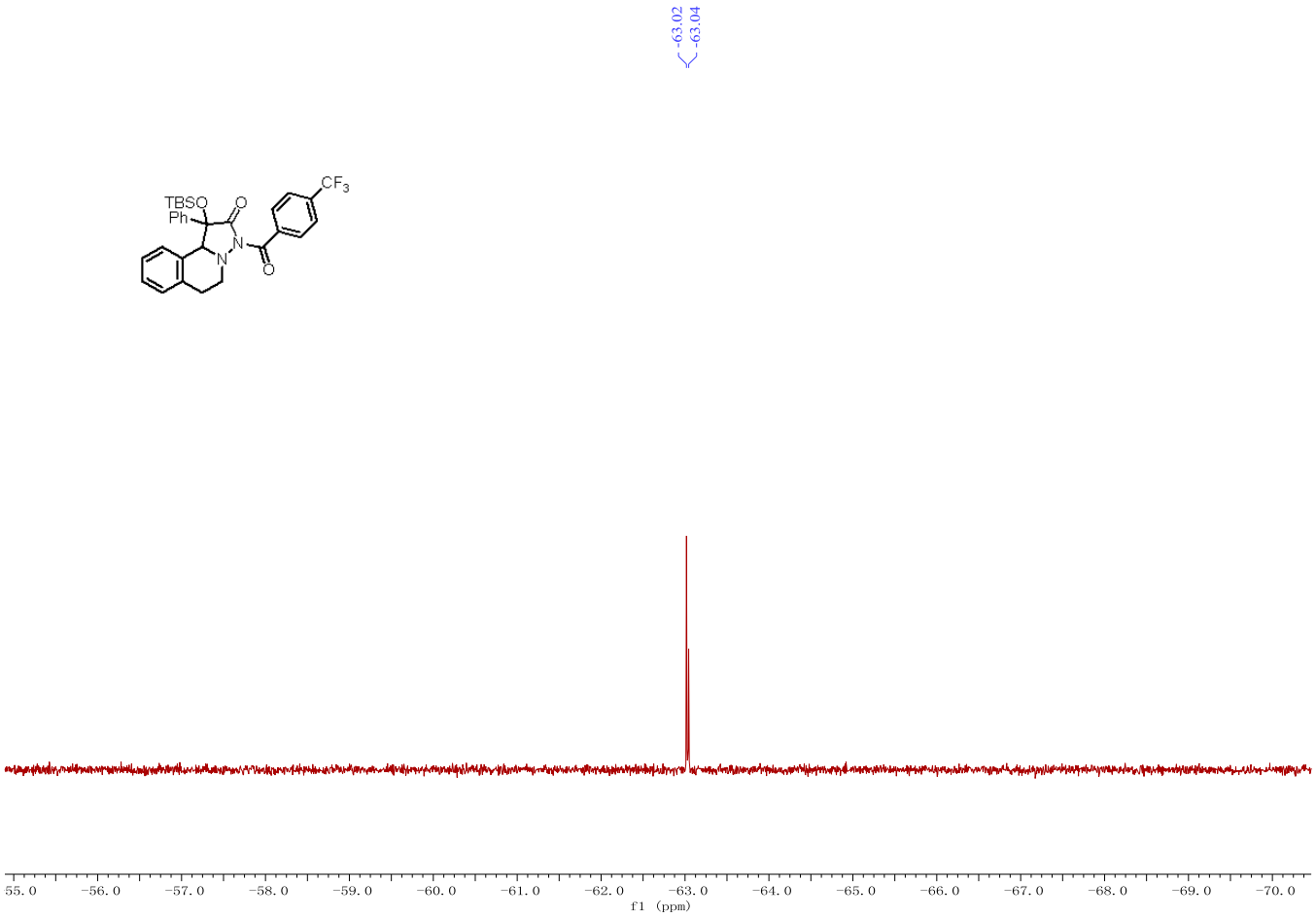
^{13}C NMR (101 MHz, $CDCl_3$) of **5ag**



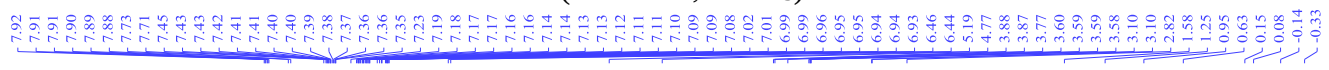
^{1}H NMR (400 MHz, $CDCl_3$) of **5ah**

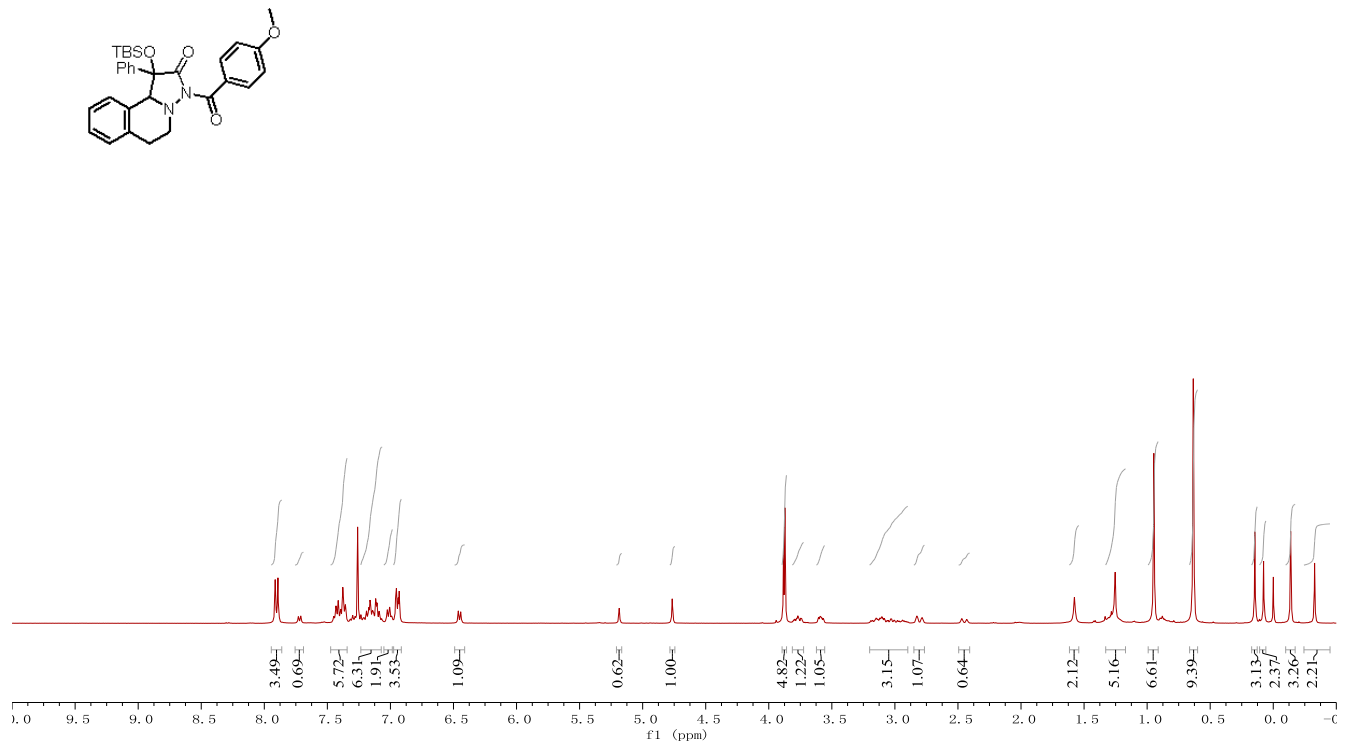


^{13}C NMR (101 MHz, $CDCl_3$) of **5ah**

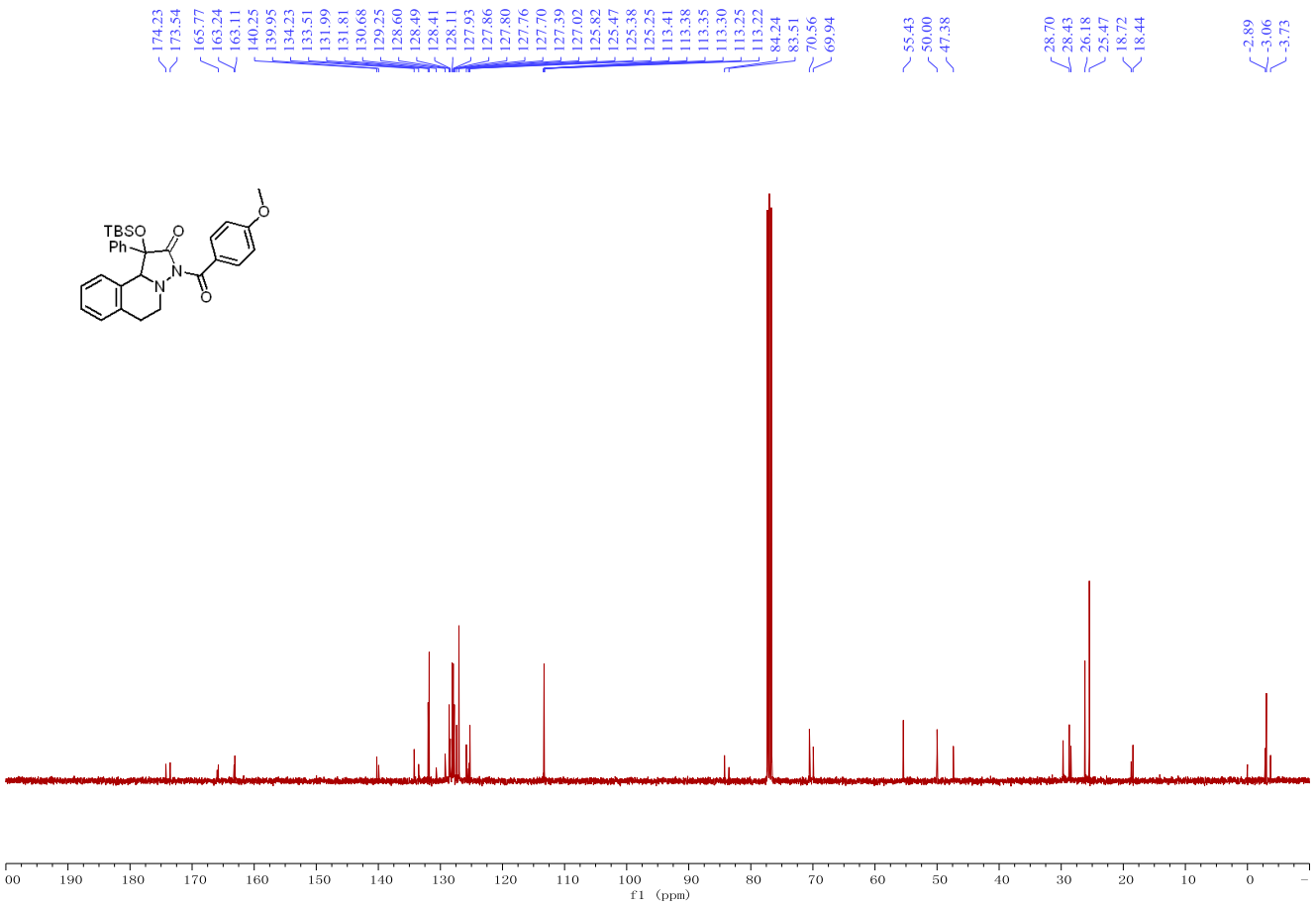


^{19}F NMR (376 MHz, $CDCl_3$) of **5ah**

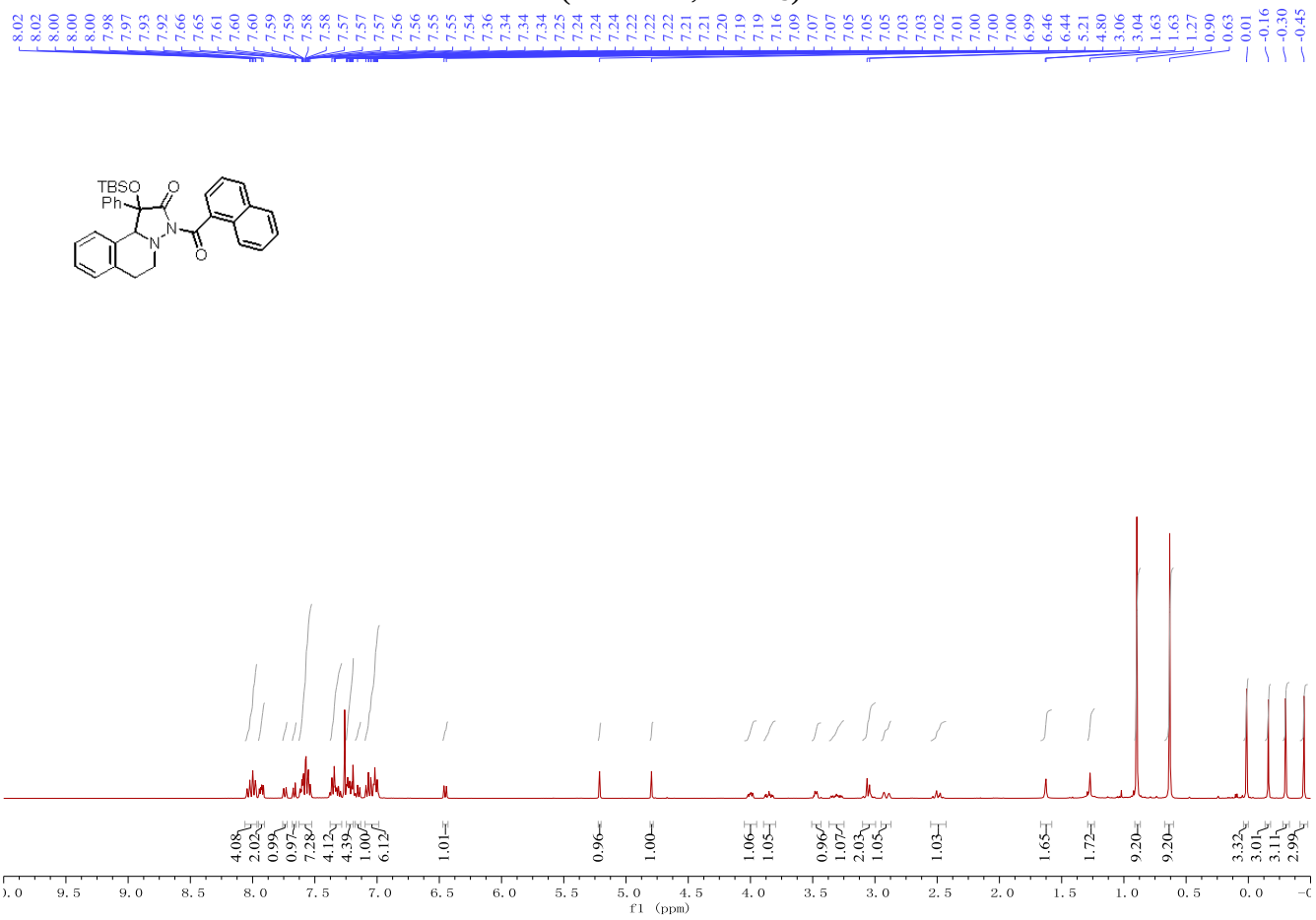




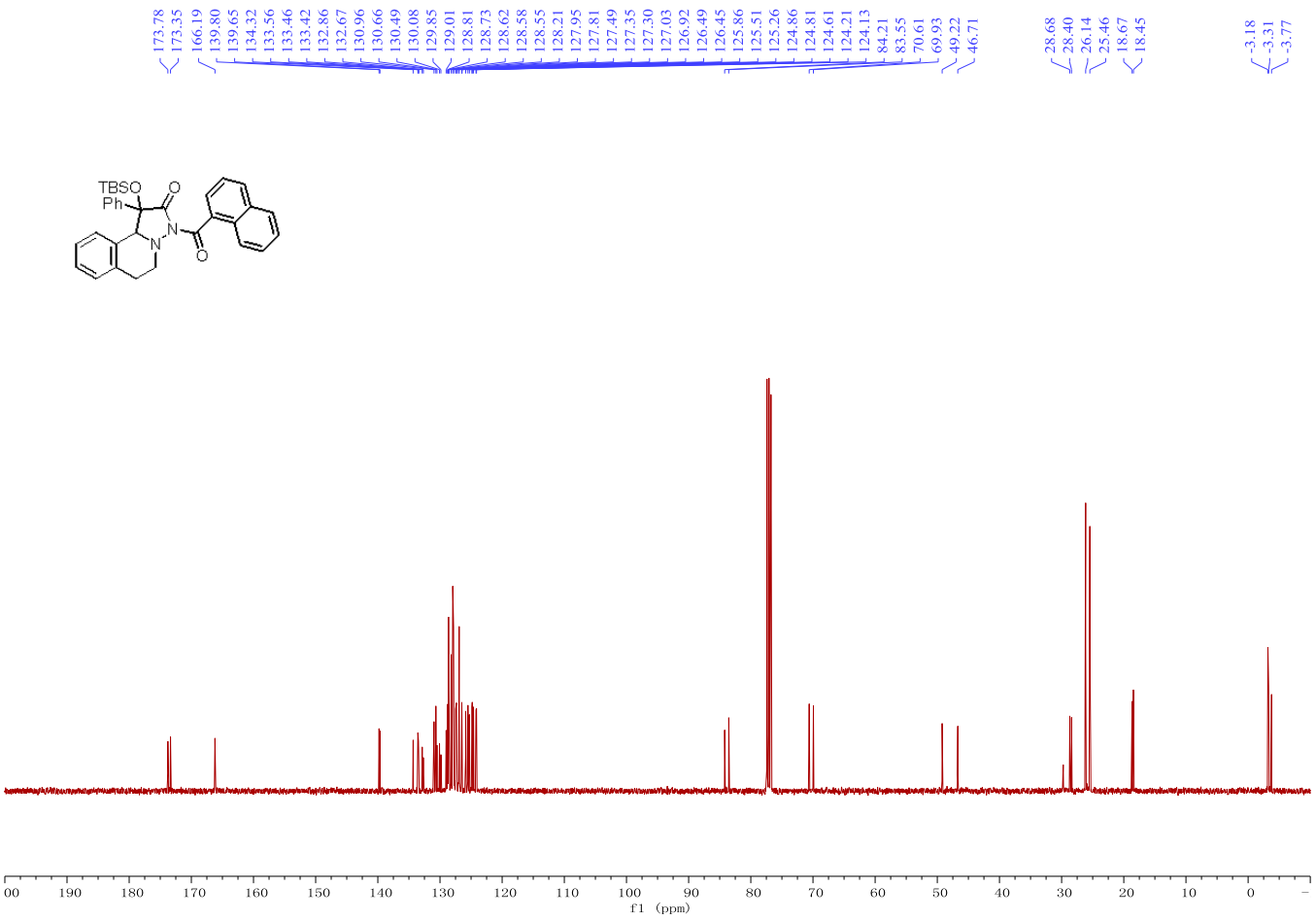
^{1}H NMR (400 MHz, $CDCl_3$) of **5ai**



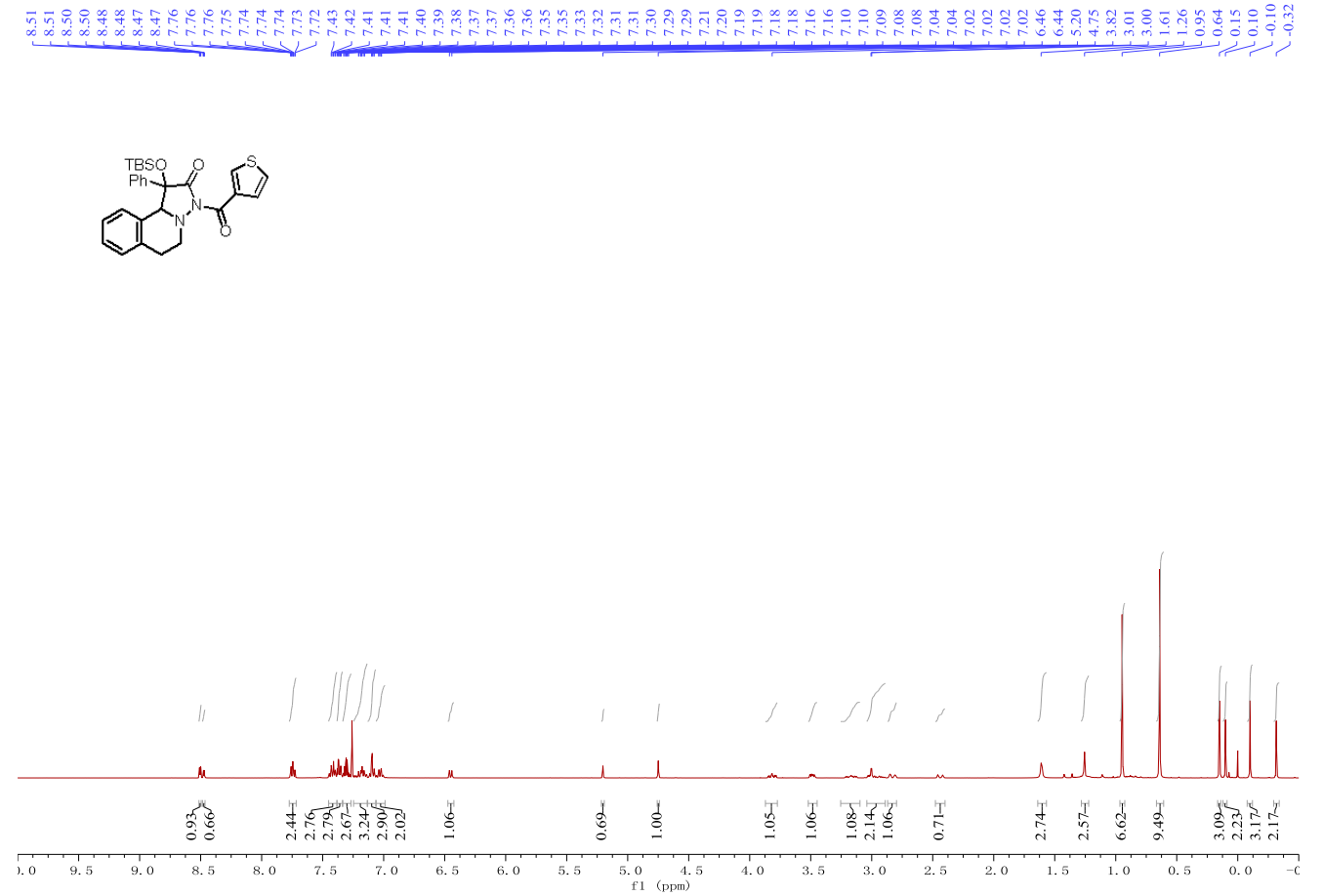
^{13}C NMR (101 MHz, $CDCl_3$) of **5ai**



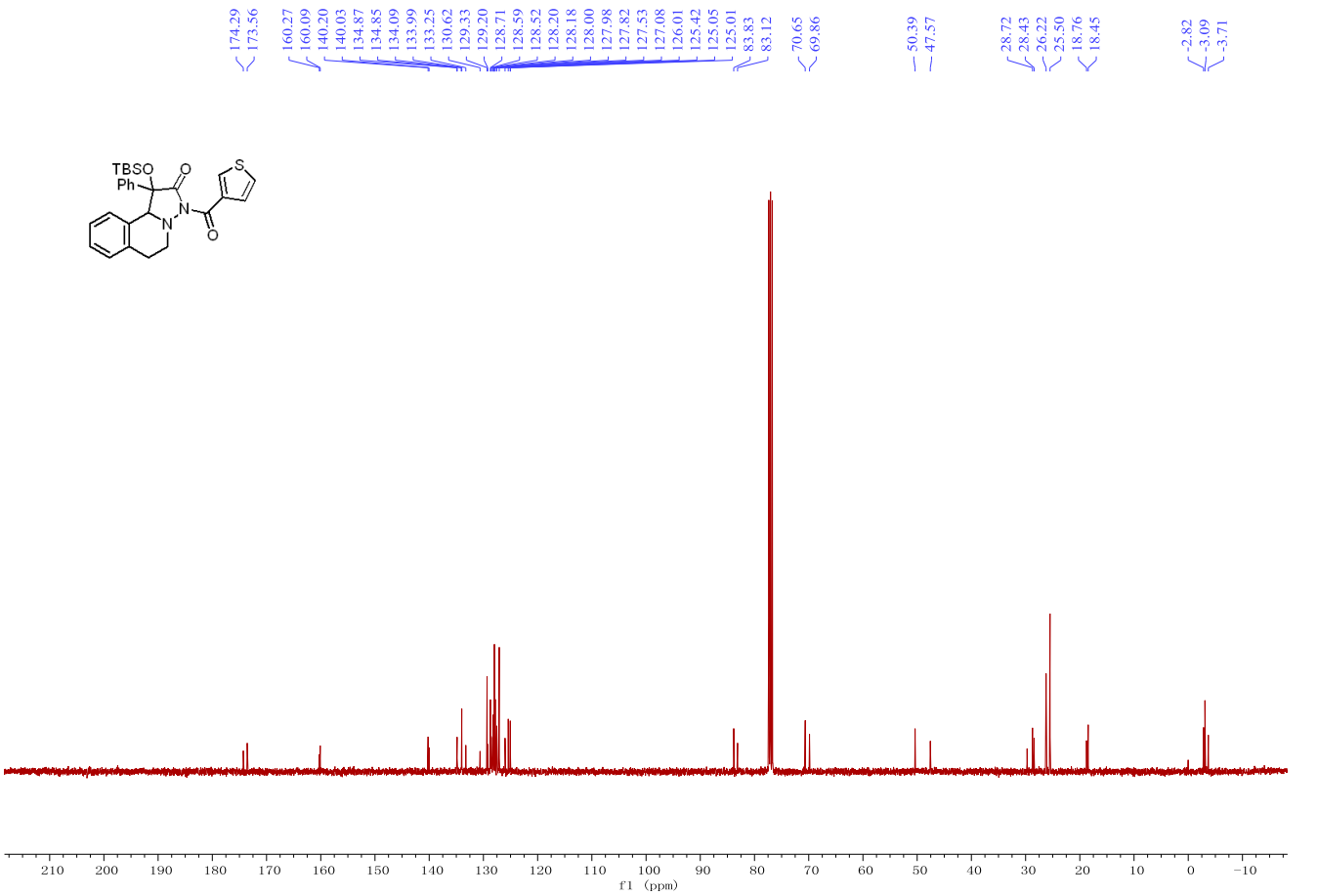
^{1}H NMR (400 MHz, $CDCl_3$) of **5aj**



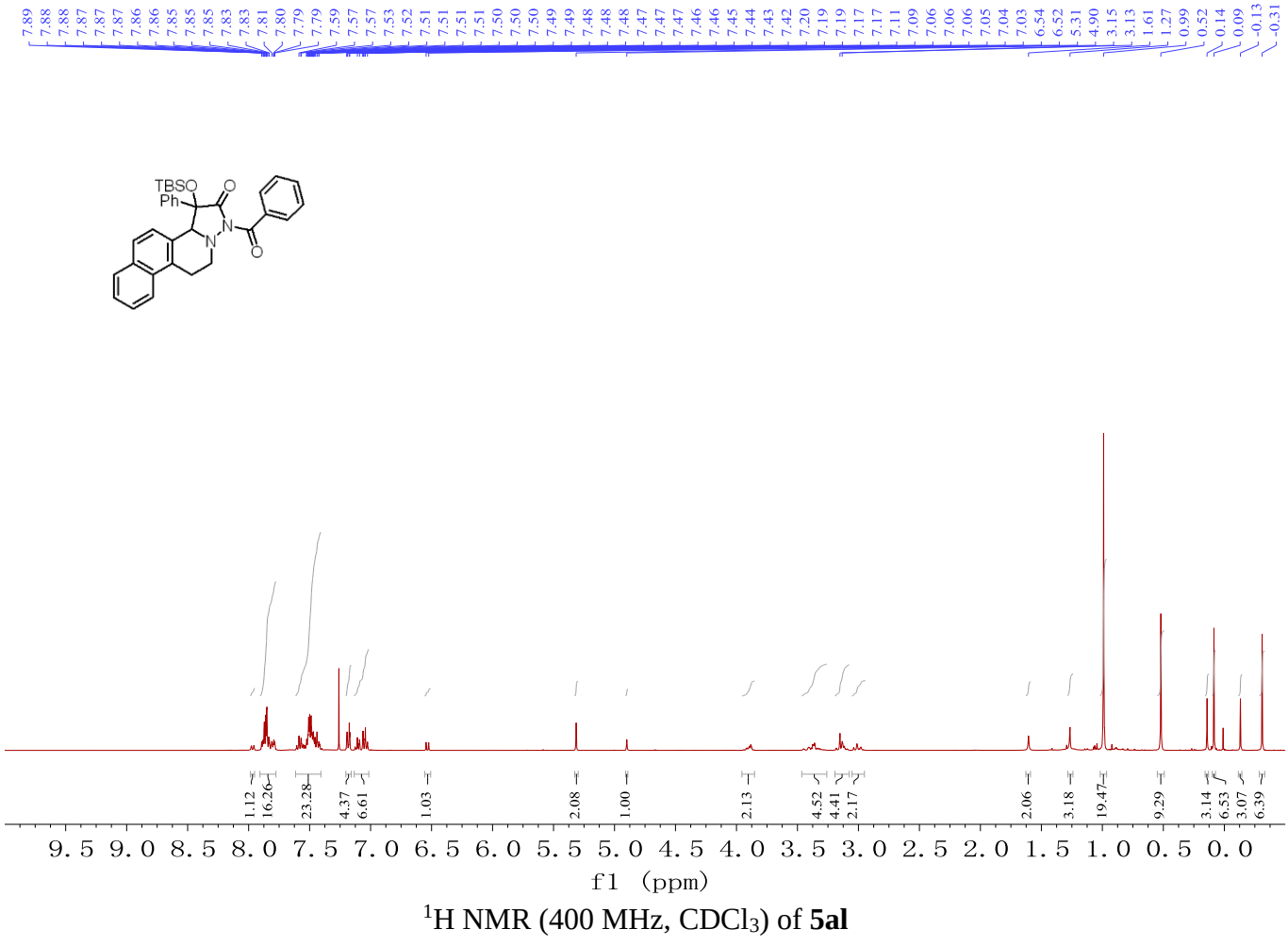
^{13}C NMR (101 MHz, $CDCl_3$) of **5aj**



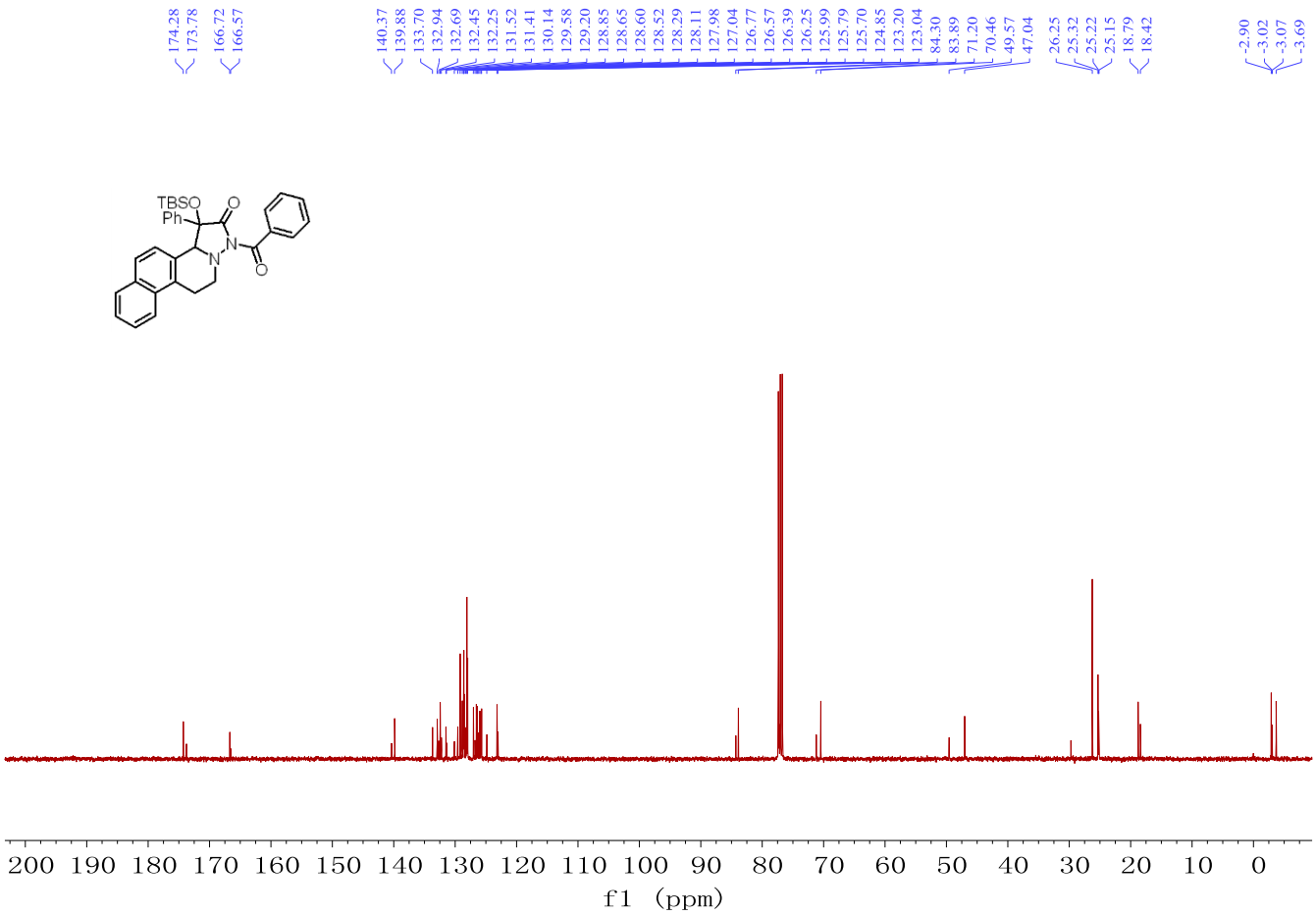
^{1}H NMR (400 MHz, $CDCl_3$) of **5ak**



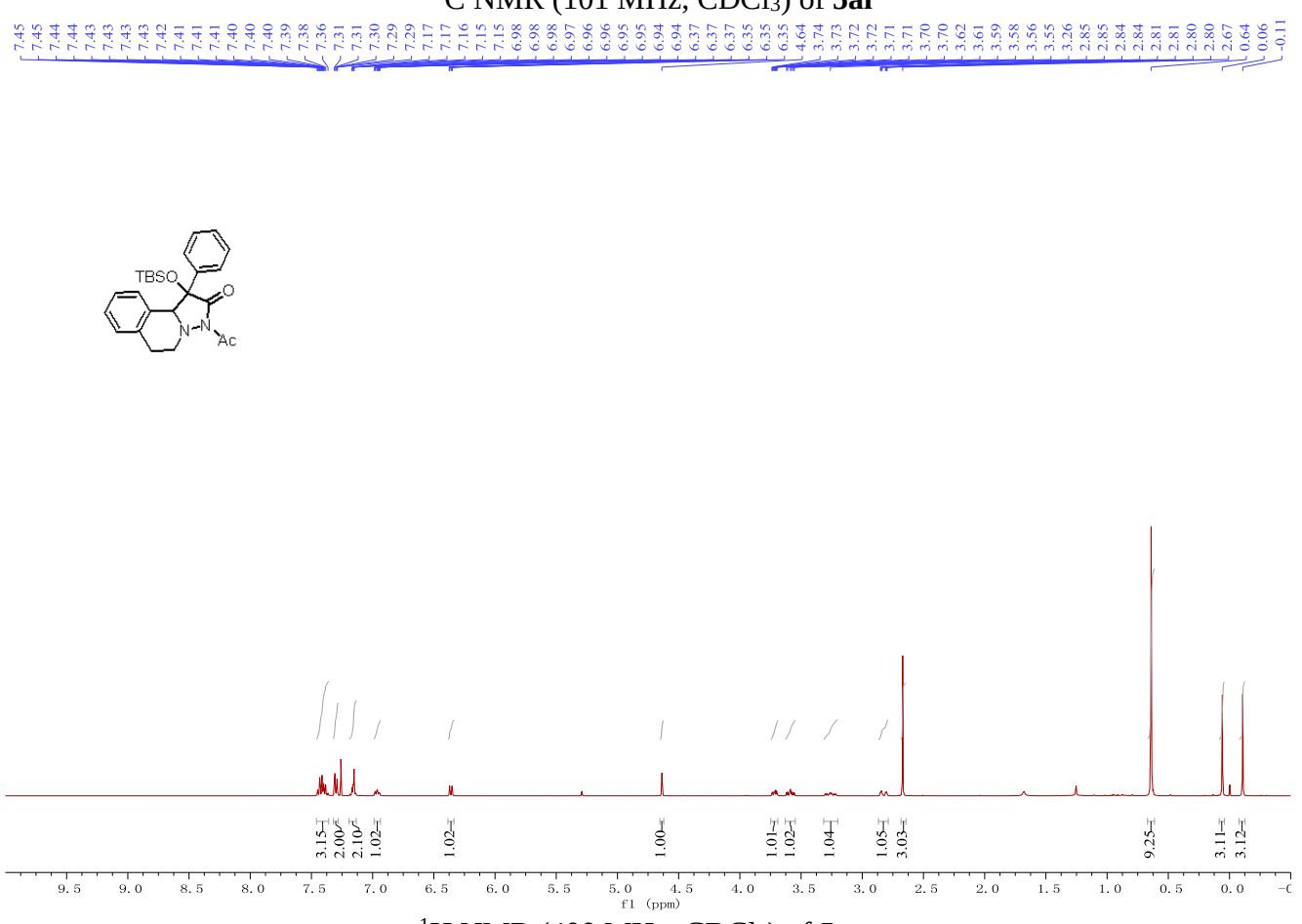
^{13}C NMR (101 MHz, $CDCl_3$) of **5ak**



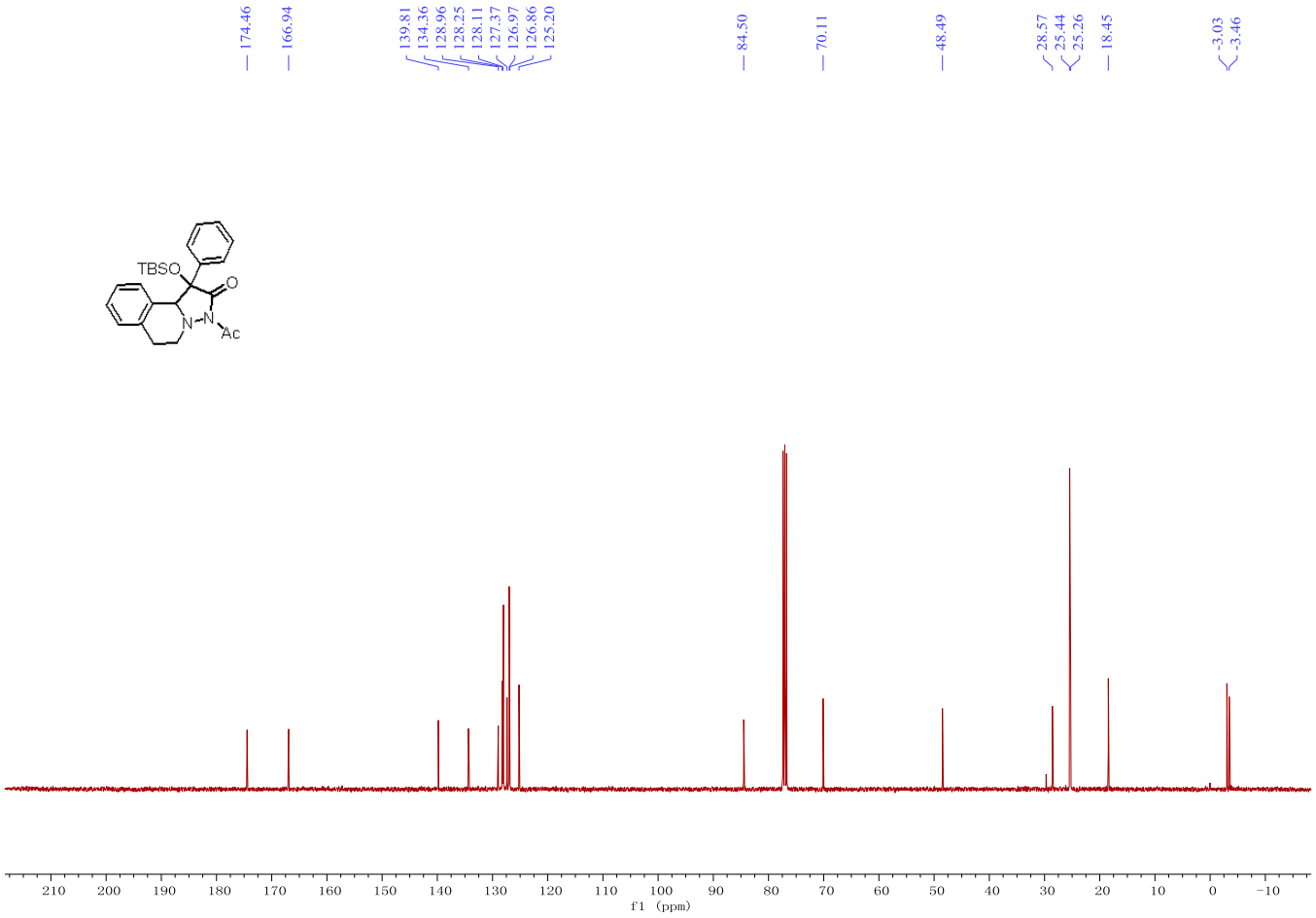
^{1}H NMR (400 MHz, $CDCl_3$) of **5al**



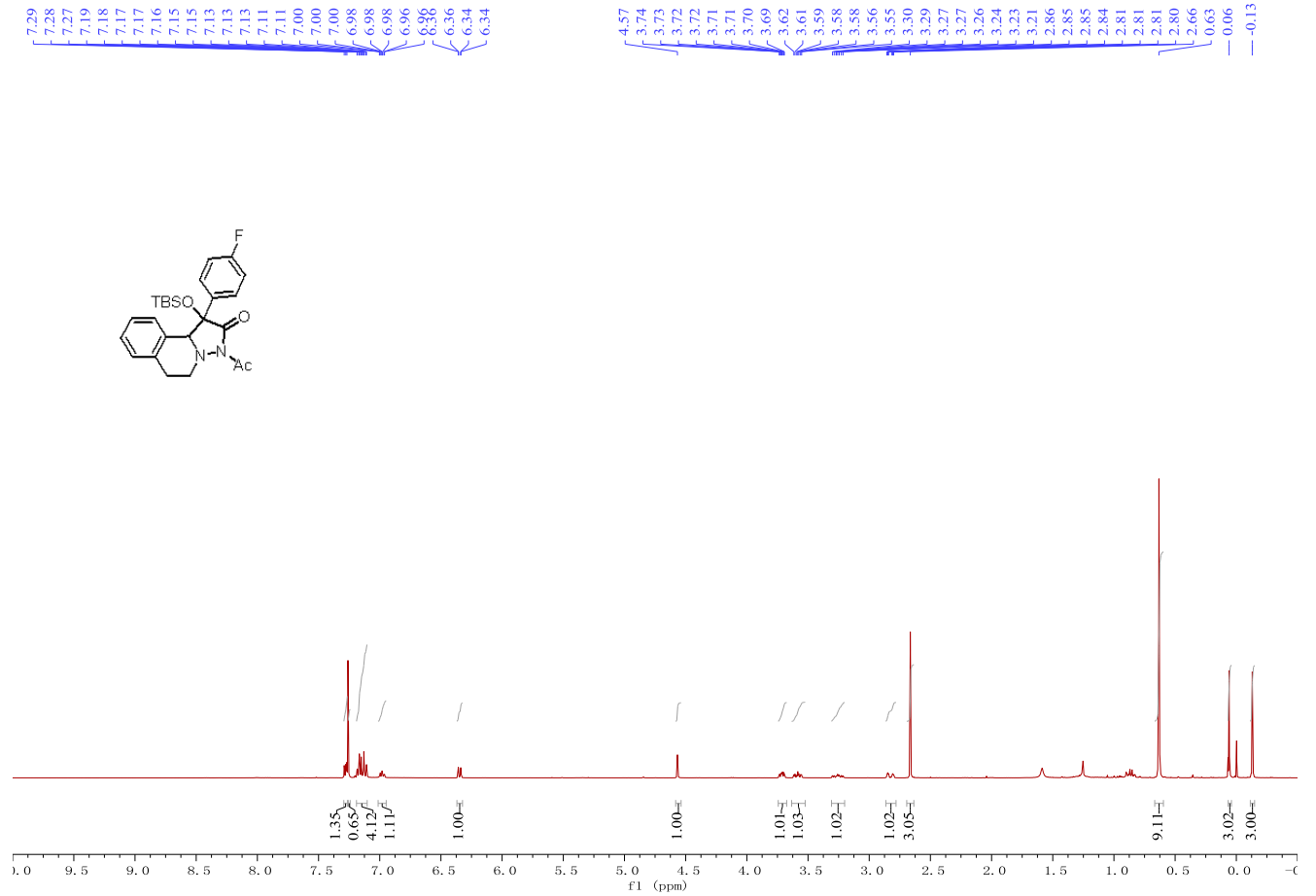
^{13}C NMR (101 MHz, $CDCl_3$) of **5al**



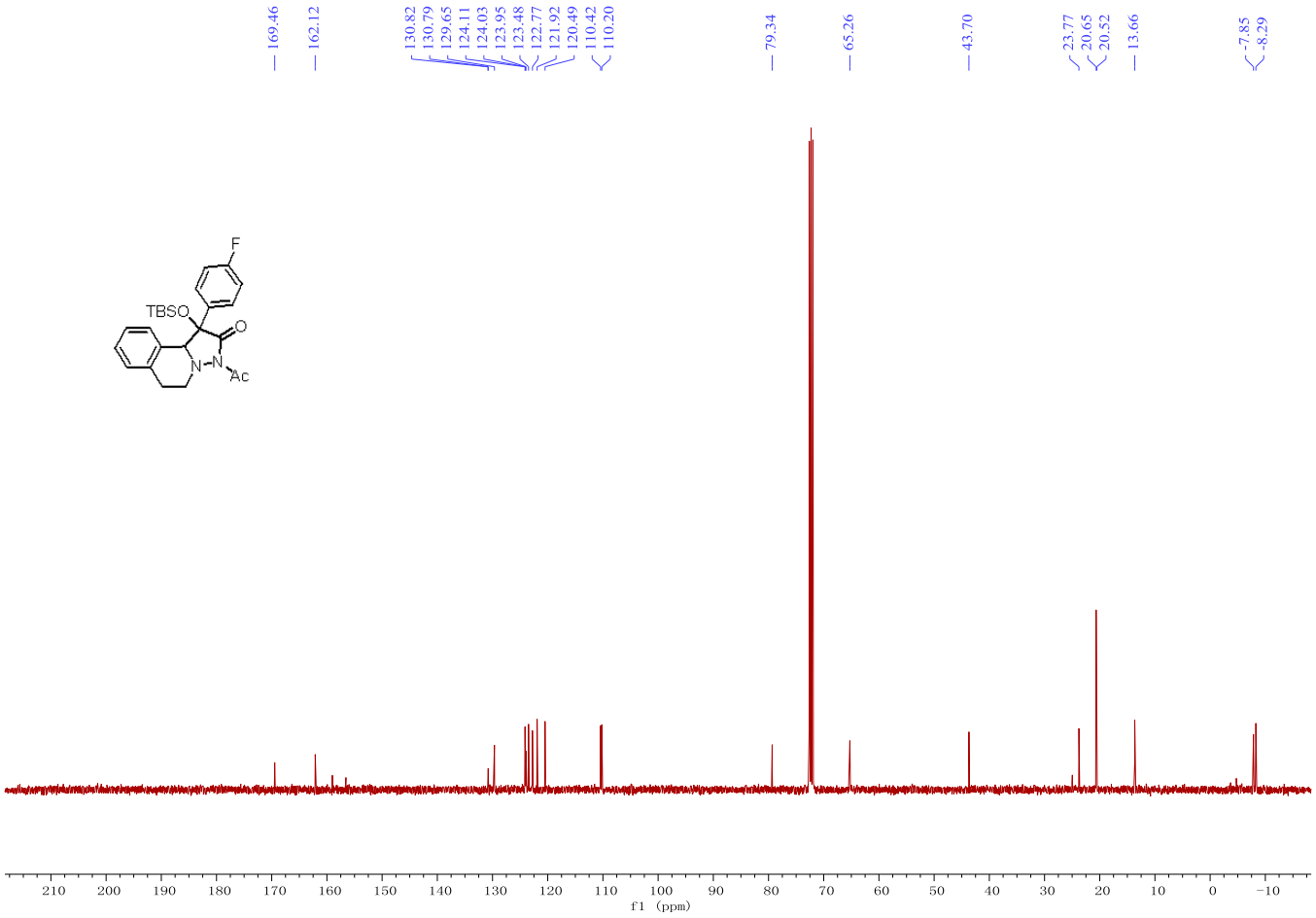
^{1}H NMR (400 MHz, $CDCl_3$) of **5am**



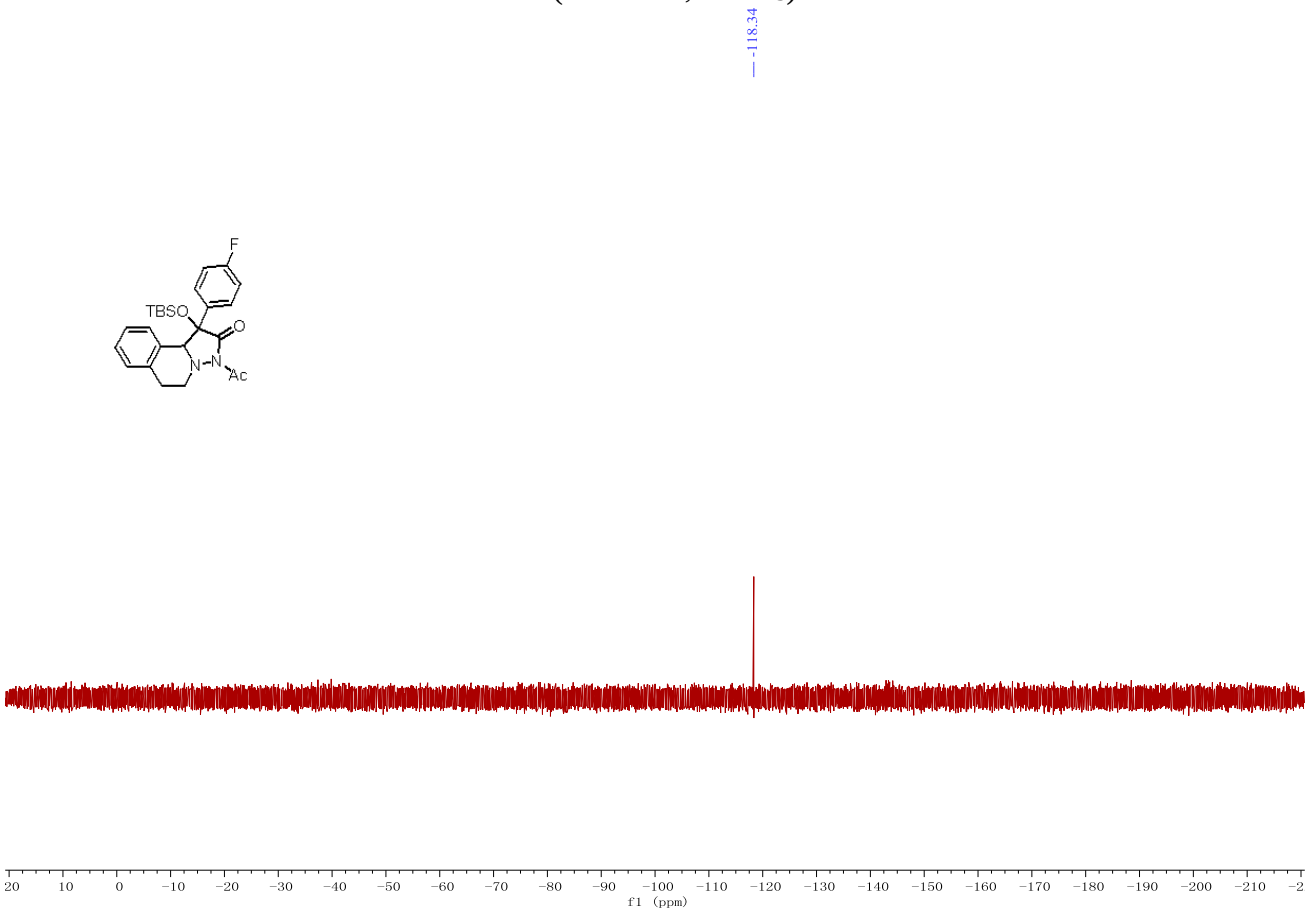
^{13}C NMR (101 MHz, $CDCl_3$) of **5am**



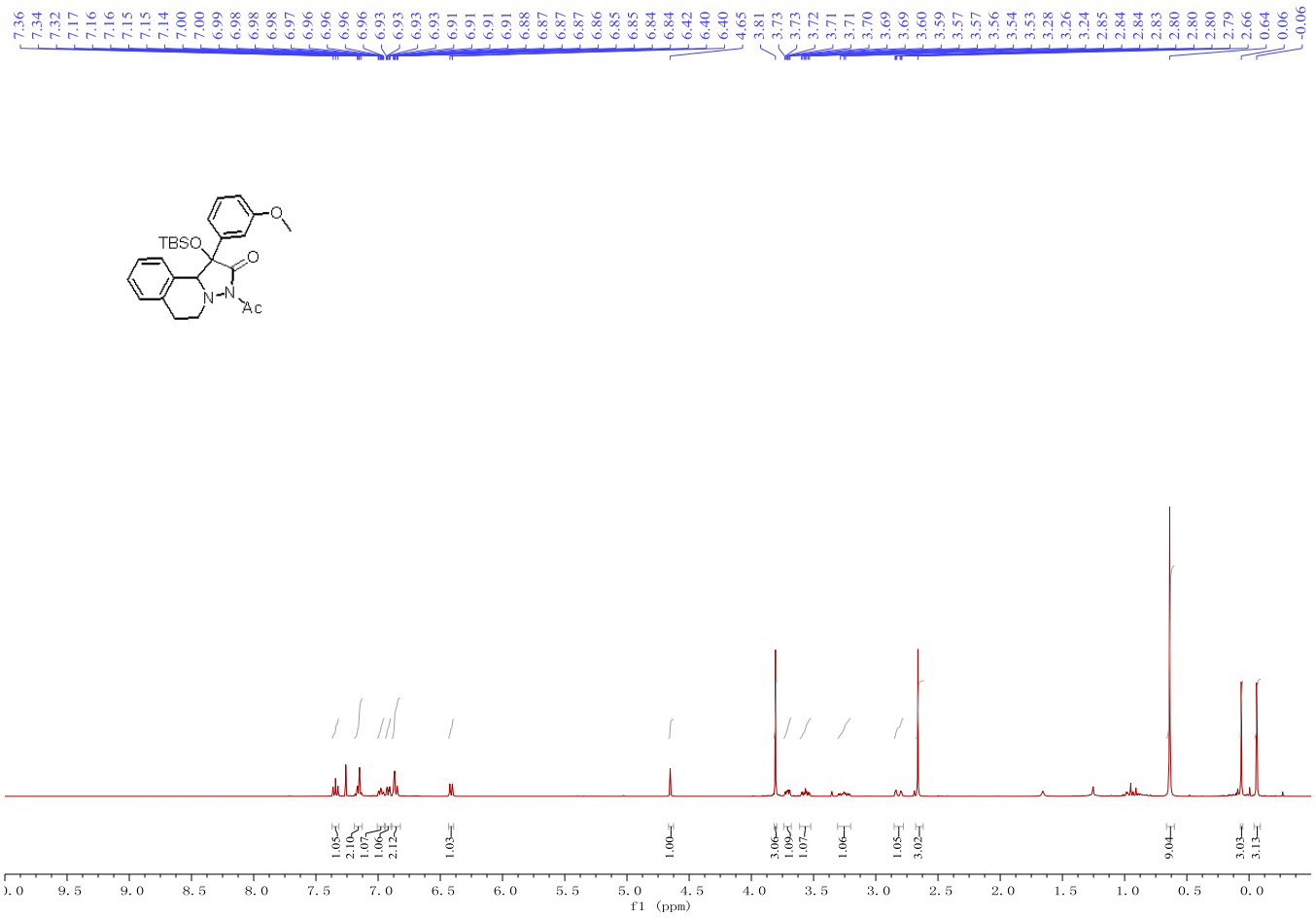
^{1}H NMR (400 MHz, $CDCl_3$) of **5an**



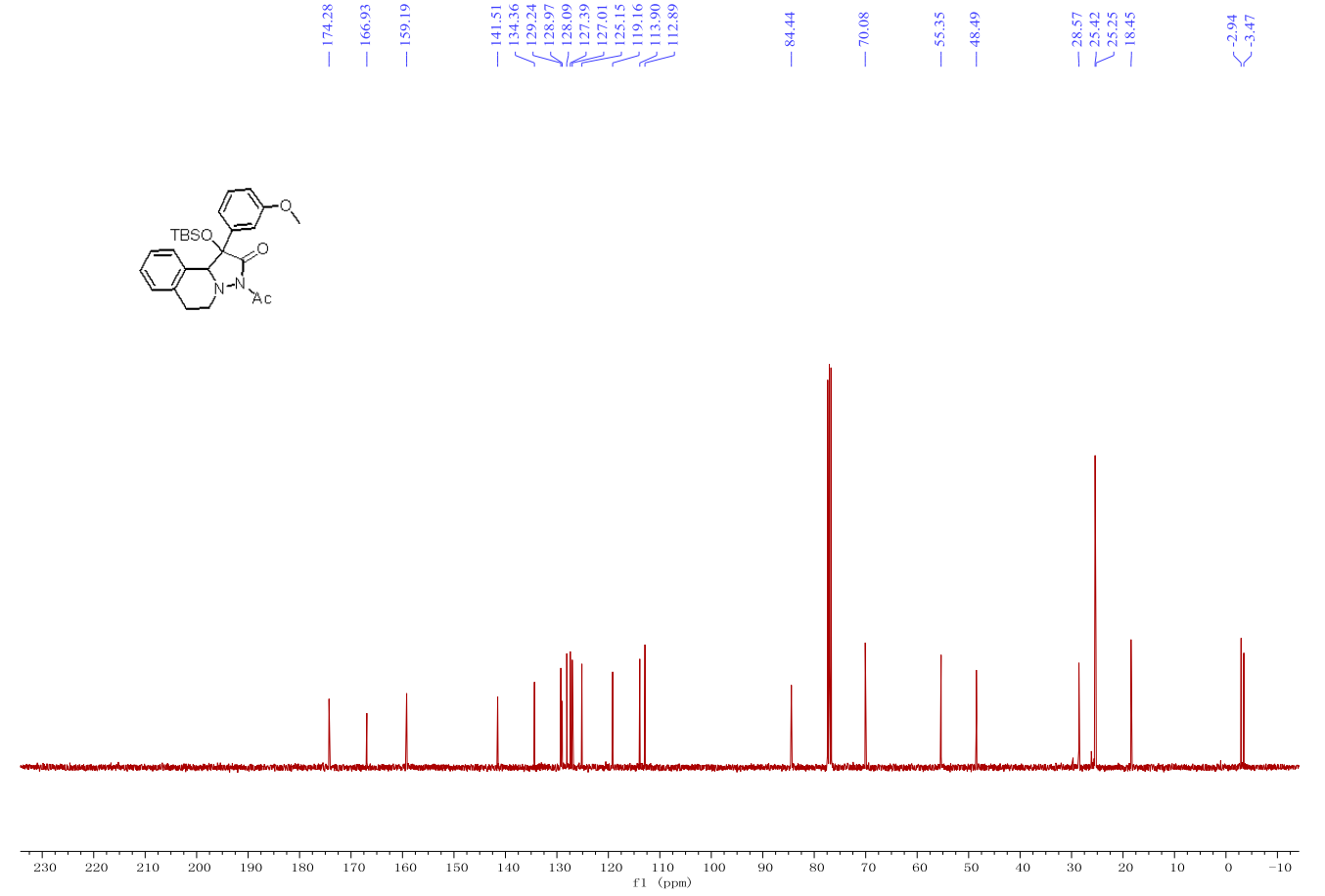
^{13}C NMR (101 MHz, $CDCl_3$) of **5an**



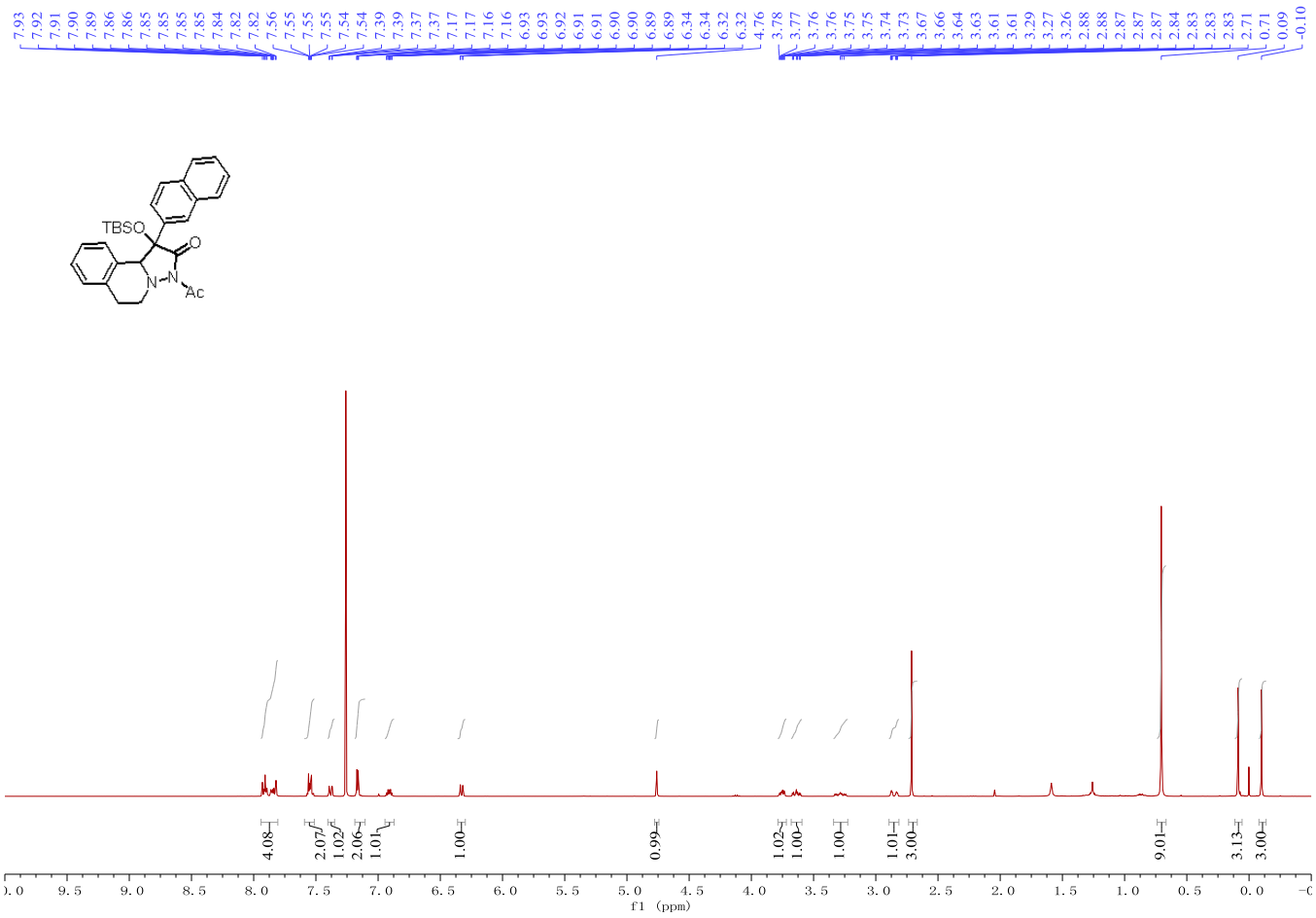
^{19}F NMR (376 MHz, $CDCl_3$) of **5an**



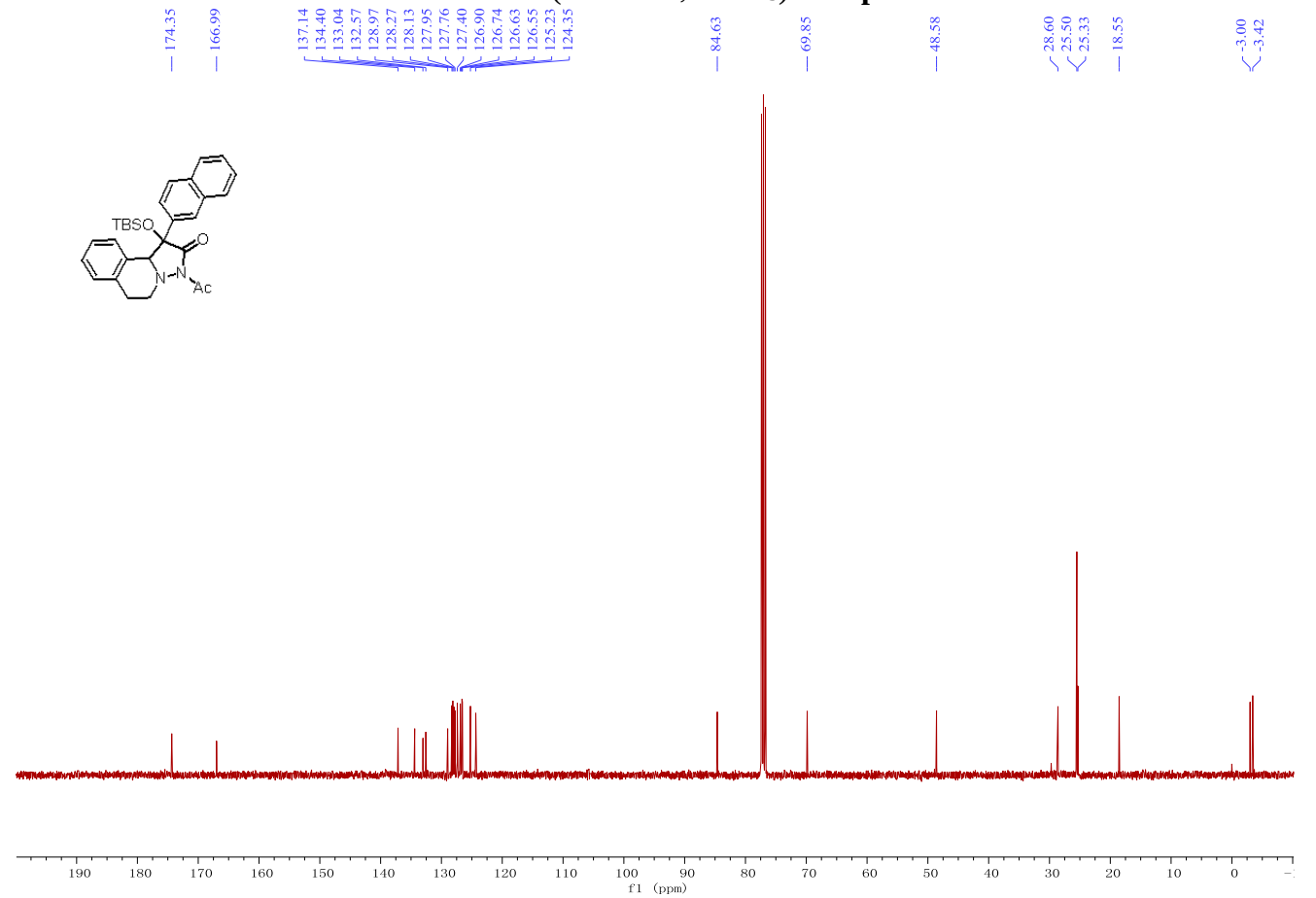
^{1}H NMR (400 MHz, $CDCl_3$) of **5ao**



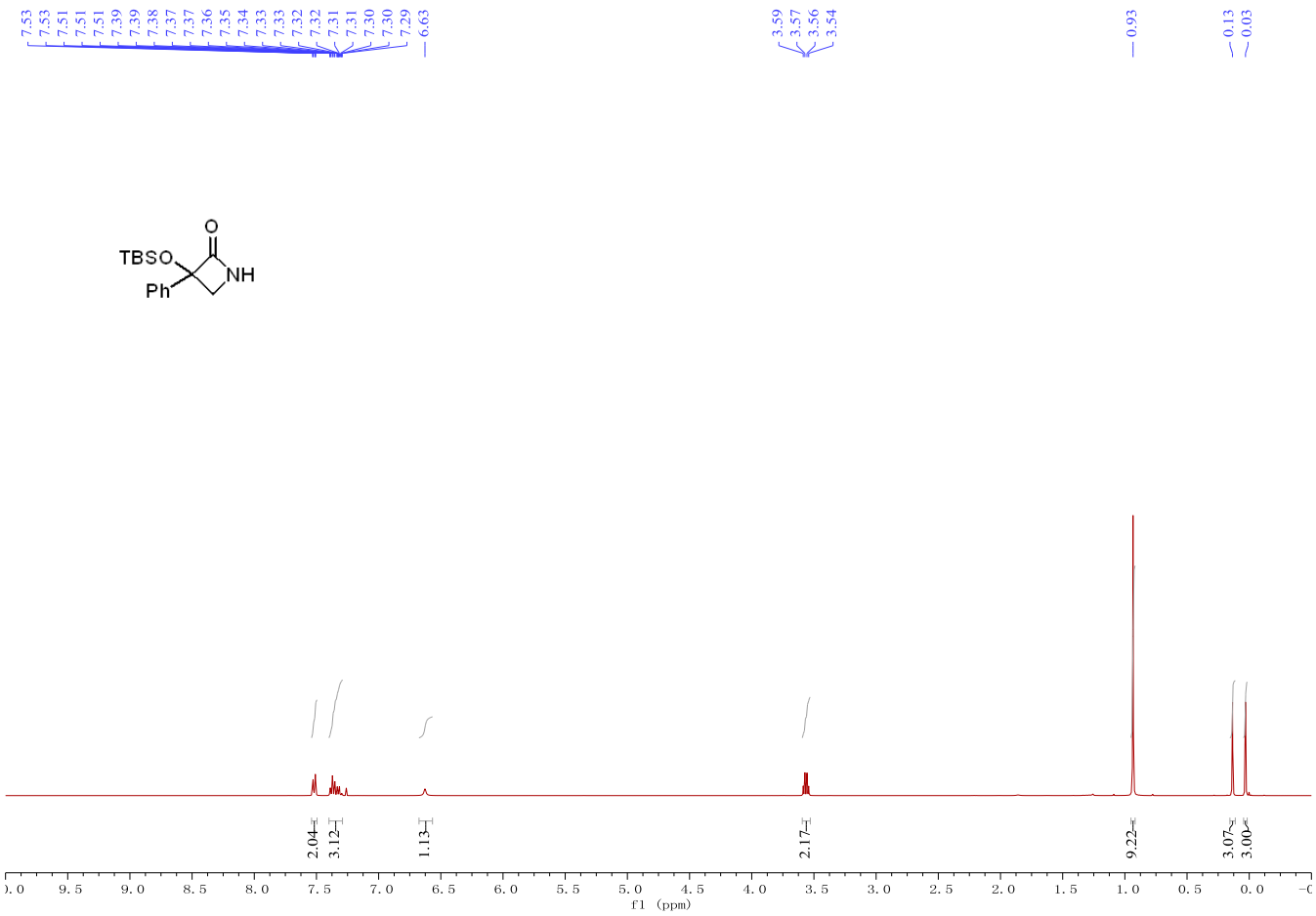
^{13}C NMR (101 MHz, $CDCl_3$) of **5ao**



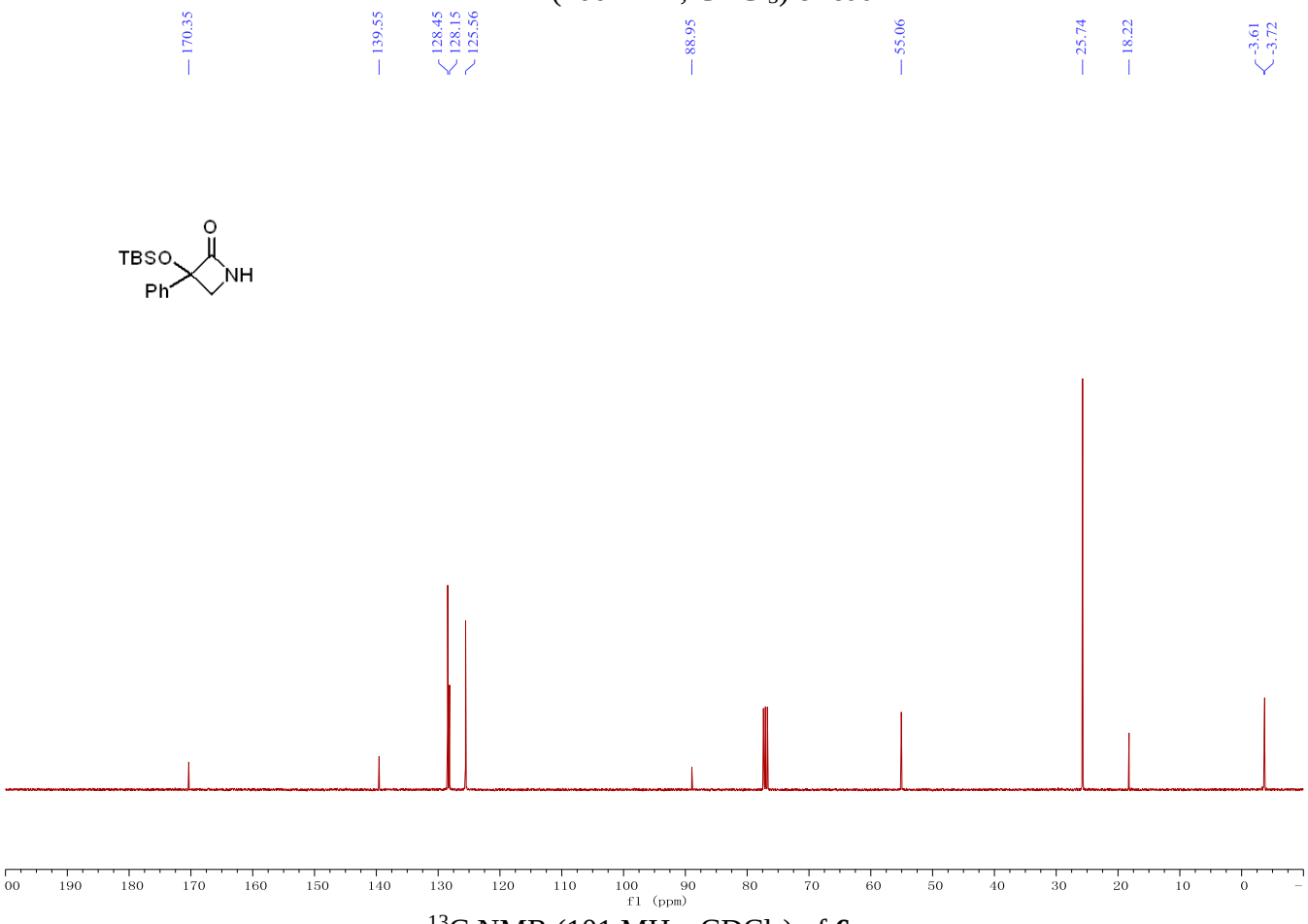
^{1}H NMR (400 MHz, $CDCl_3$) of **5ap**



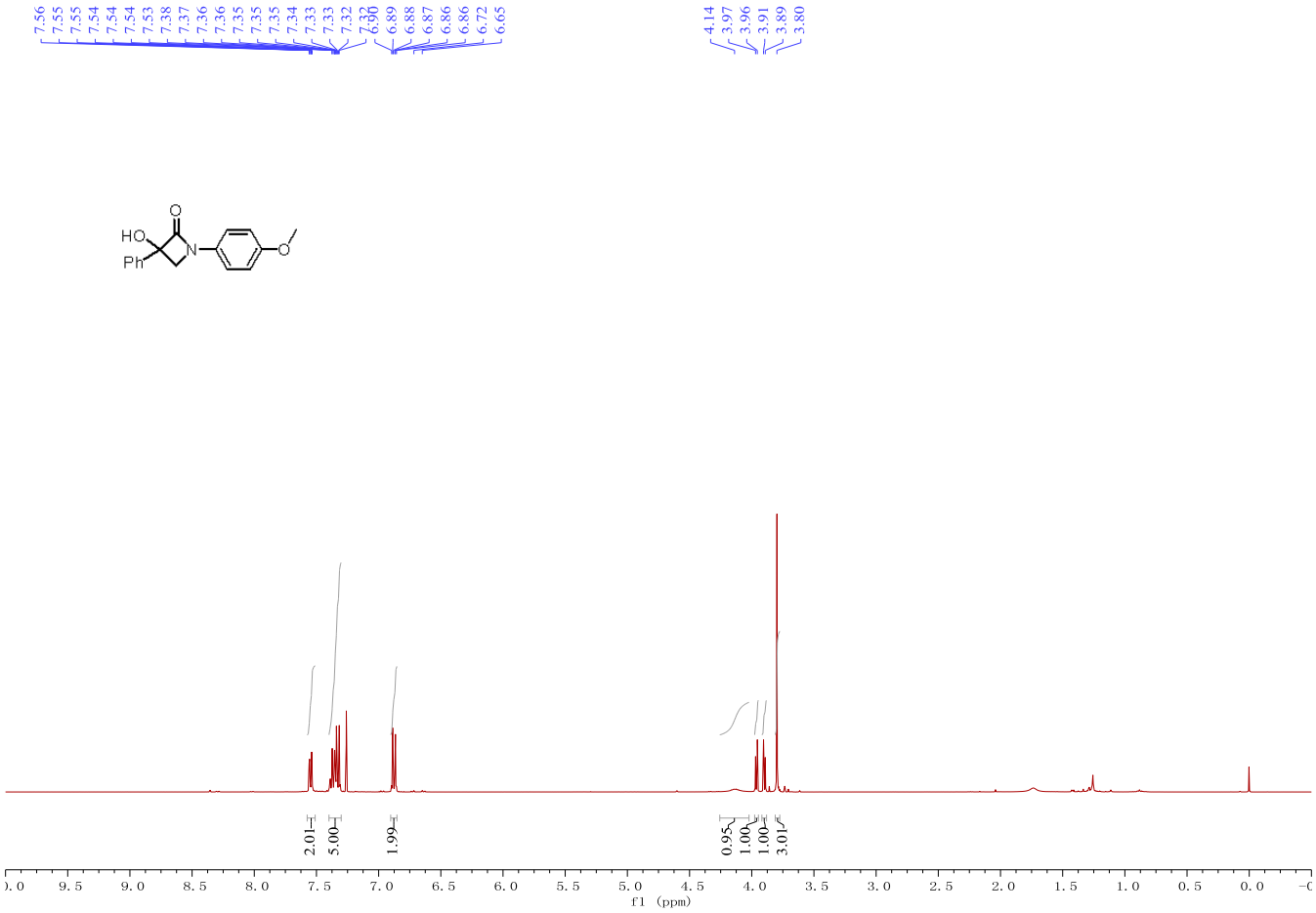
^{13}C NMR (101 MHz, $CDCl_3$) of **5ap**



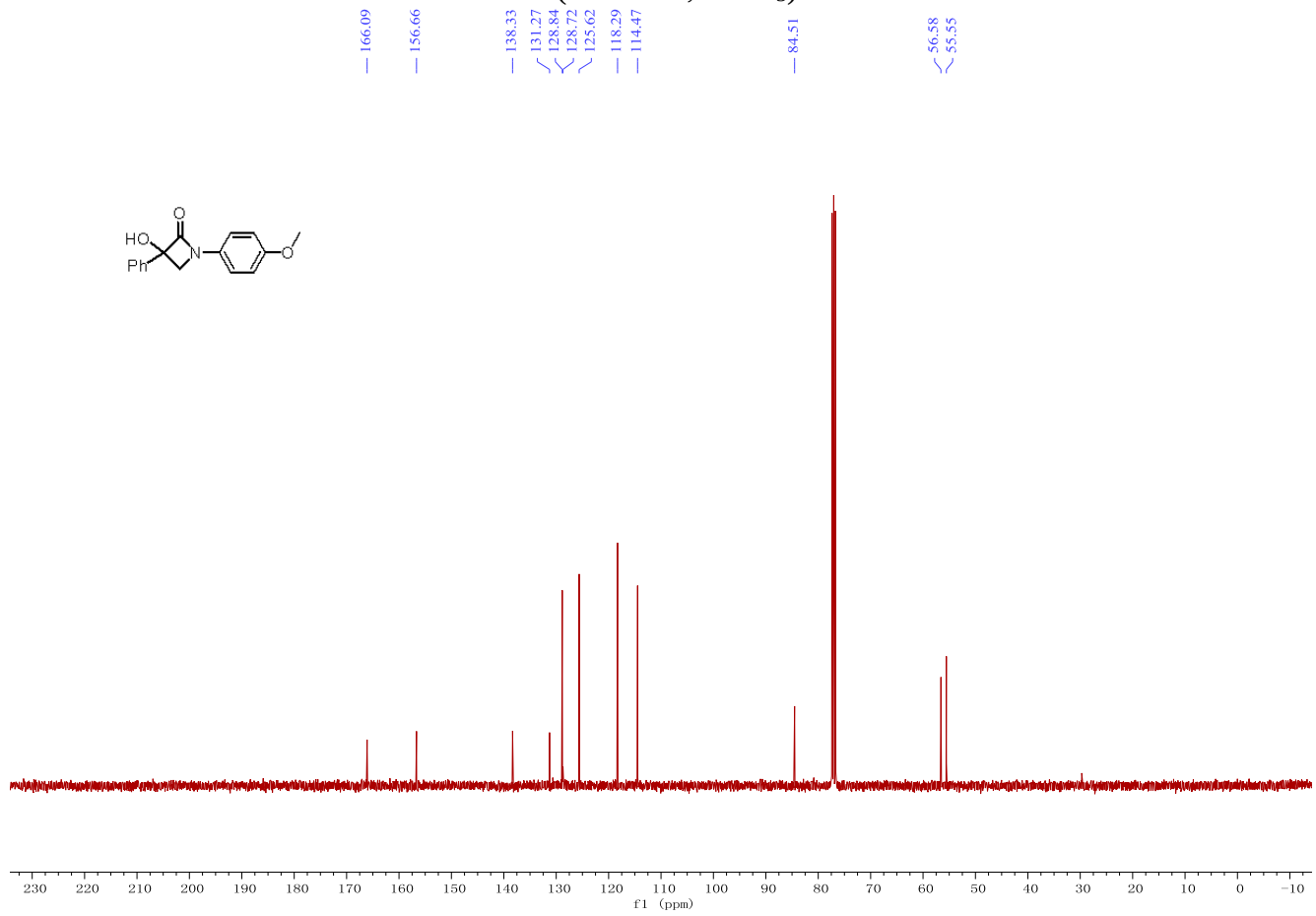
^{1}H NMR (400 MHz, $CDCl_3$) of **6aa**



^{13}C NMR (101 MHz, $CDCl_3$) of **6aa**



^{1}H NMR (400 MHz, $CDCl_3$) of **7aa**



^{13}C NMR (101 MHz, $CDCl_3$) of **7aa**