Photo-induced and azide anion-facilitated atom transfer cyclization of *N*-allyl-2-bromoamides

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Supplementary Information

Content

1. General methods

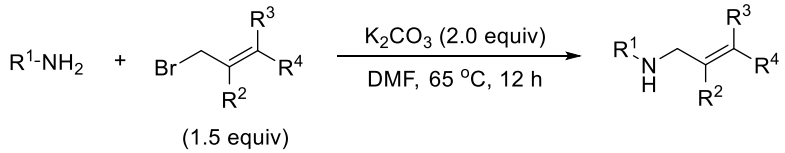
NMR spectra were measured using a Bruker Avance III-400 MHz spectrometer (400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR). NMR samples were dissolved in $CDCl_3$ unless otherwise specified. Chemical shifts in the NMR spectra were determined based on the that of residual undeuterated solvent (δ = 7.26 for ^{1}H NMR; δ = 77.0 for ^{13}C NMR). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad (br). HR-MS analysis was performed on a Bruker APEXII FT-ICR mass instrument (ESI-TOF) instrument equipped with an ESI source. UV-vis measurements were conducted on a Shimadzu RF-6000 Spectro Fluorophotometer. The Fourier transformation infrared spectra (FT-IR) were measured on a Thermo Fisher Scientific Nicolet iS50 spectrometer. The melting points (m.p.) were measured on an XT-4 melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed using silica gel plates (60 F254) visualized under short wavelength UV light (254 nm) or by immersing them into a solution of phosphomolybdic acid in ethanol (95%). Flash column chromatography was performed using silica gel of 200-300 mesh. All solvents and commercially available reagents were purchased as reagent grade and were used without further purification unless otherwise stated. The unsaturated 2-bromino amides used as the substrates were prepared following the reported methods.[1,2]

2. Experimental procedures

2.1 Preparation of the substrates

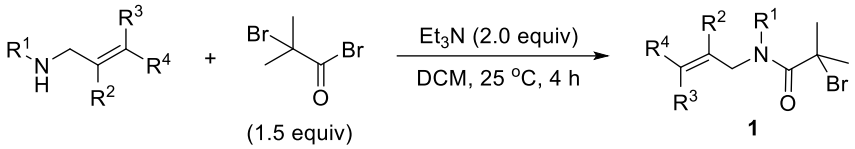
2.1.1 Method A

Step 1:



Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper was added successively K_2CO_3 (5.5 g, 40 mmol, 2.0 equiv.), DMF (60 mL) and an amine (20 mmol, 1.0 equiv.). The flask was put into an ice bath and the mixture was stirred for several min. Allyl bromide (24 mmol, 1.2 equiv.) was slowly added into the mixture, and the flask was moved into a metal bath (preheated to 65 ℃) and was heated under stirring for 12 h. After that, the flask was allowed to cool to room temperature, and ice water (30 mL) was added into it to quench the reaction. The product was extracted with methylene chloride (DCM, 3×60 mL), and the collected organic phases were washed with brine, and then dried with anhydrous Na_2SO_4. After the volatile components were removed under reduced pressure on a rotary evaporator. The residual was subjected to flash column chromatography with petroleum ether (PE) and ethyl acetate (EA) as the eluents (PE:EA = 50:1) to give the allyl amine products.

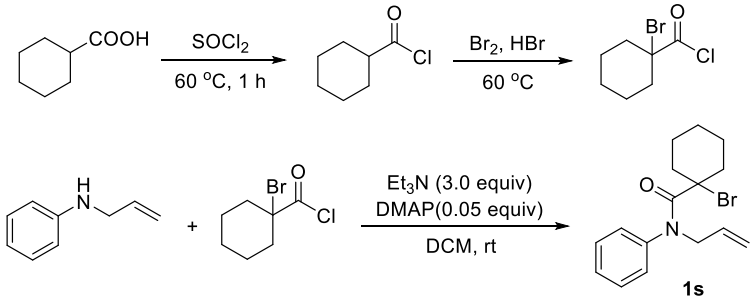
Step 2:



Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper was added successively the prepared allyl amine (14 mmol, 1.0 equiv.), DCM (28 mL, 0.5 M) and triethylamine (2.4 mL,17 mmol, 1.2 equiv.). The flask was put into in an ice bath, and 2-bromo-2-methylpropionyl bromide (17 mmol, 1.2 equiv.) was slowly dripped into the mixture under stirring (**Caution:** this process was violent and a lot of white smoke would be emitted). After the addition was finished, the ice bath was removed and the stirring was continued at room temperature for 12 h. The reaction was then quenched with water, and the aqueous phase was extracted with EA (3×60 mL). The collected organic phases were washed with brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The crude product was purified with flash column chromatography with PE and EA as eluents (PE:EA = 20:1) to afford product **1**.

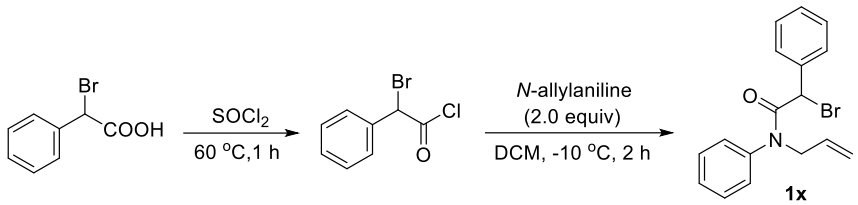
Substrates **1a**–**1s, 1u**–**1v, 1y**-**1aa** were synthesized following this procedure.

2.1.2 Method B (Synthesis of **1t)**



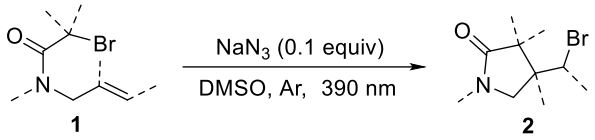
Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper was added cyclohexanecarboxylic acid (1.92 g, 15 mmol, 1.0 equiv.) and 15 mL of $SOCl_2$. The mixture was stirred at 60 ℃ for 1 h. After cooling to room temperature, Br_2 (1.02 mL, 1.1 equiv.) and a few drops of HBr (48% in water) was added into the flask, and the mixture was stirred at 60 ℃ (in a metal bath) until the red color disappeared. The excessive $SOCl_2$ was removed under reduced pressure by rotary evaporation. 30 mL of DCM was added into the flask to dissolve the crude acyl chloride product. The flask was then put into was an ice bath. Triethylamine (6.3 mL, 3.0 equiv.), DAMP (91.5 mg, 1.0 equiv), and allyl aniline (2.03 mL, 15 mmol, 1.0 equiv.) were added sequentially into the flask. The mixture was then stirred at room temperature until the reaction was complete as indicated by TLC. The mixture was poured into a separatory funnel containing ice water, and the product was extracted with DCM (3×60 mL). The collected organic layers were washed with brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was subjected to flash column chromatography with PE and EA as eluents (PE:EA = 50:1) to afford product **1t** (2.45 g. Yield: 51%).

2.1.3 Method C (Synthesis of **1x**)



Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper was added 2-bromo-2-phenylacetic acid (2.2 g, 10 mmol, 1.0 equiv.) and 15 mL of $SOCl_2$. The mixture was stirred at 60 ℃ for 1 h. The excessive $SOCl_2$ was removed under reduced pressure by rotary evaporation. After that, 10 mL of CCl_4 was added into the flask to dissolve the crude acyl chloride product. The flask was then put into an ice-salt bath (-10 ℃). 20 mL of CCl_4 containing 2.66 g of *N*-allylaniline (20 mmol) was dropped into the flask and the mixture was stirred for 2 h. The reaction was then quenched by ice water, and the product was extracted with DCM (3×60 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, and then concentrated on a rotary evaporator. The residual was subjected to flash column chromatography with PE and EA as eluents (PE:EA = 30:1) to afford product **1x** (2.03 g. Yield: 61%).

2.2 General procedure for the bromine atom transfer cyclization (Procedure A)



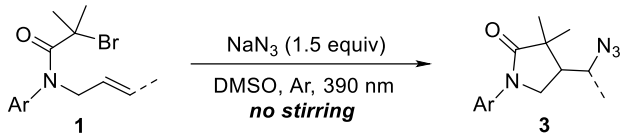
Into a 25 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was added successively *N*-allyl-2-bromoamide **1** (0.2 mmol, 1.0 equiv.), NaN_3 (1.3 mg, 0.02 mmol, 0.1 equiv.) and DMSO (2.0 mL). The tube was degassed and backfilled with argon for several times to ensure that the reaction took place in an inert atmosphere. The tube was irradiated with a 390 nm Kessil LED lamp (40 W) under stirring at 30 °C for 24 h. The reaction mixture was then poured into 10 mL of water contained in a separatory funnel, and the product was extracted with EA (3×10 mL). The combined organic phases were washed sequentially with water and brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was purified by flash column chromatography (PE and EA as eluents) to afford product **2**.

Gram scale reaction with 1a

Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper was added successively *N*-allyl-2-bromo-2-methyl-*N*-phenylpropanamide (**1a**) (1.4 g, 5 mmol, 1.0 equiv.), NaN_3 (32.5 mg, 0.5 mmol, 0.1 equiv.) and DMSO (25 mL). The flask was degassed and backfilled with argon for several times. The flask was irradiated with a 390 nm Kessil LED lamp (40 W) under stirring for 48 h. The reaction mixture was then poured into 50 mL of water contained in a separatory funnel, and the product was extracted with EA (3×50 mL). The combined organic phases were washed sequentially with water and brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was purified by flash

column chromatography (PE and EA as eluents, PE:EA = 5:1) to afford 0.58 g of **2a**. Yield: 42%.

2.3 General procedure for the cyclization/azidation (Procedure B)



Into a 100 mL glass tube equipped with a rubber stopper was added successively *N*-allyl-2-bromoamide **1** (0.2 mmol, 1.0 equiv.), NaN_3 (19.5 mg, 0.3 mmol, 1.5 equiv.) and DMSO (2.0 mL). The tube was degassed and backfilled with argon for several times. The tube was irradiated with a 390 nm Kessil LED lamp (40 W) under stirring for 24 h. The reaction mixture was then put into 10 mL water contained in a separatory funnel, and the product was extracted with EA (3×10 mL). The combined organic phases were washed sequentially with water and brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was purified by flash column chromatography (PE and EA as eluents) to afford product **3**.

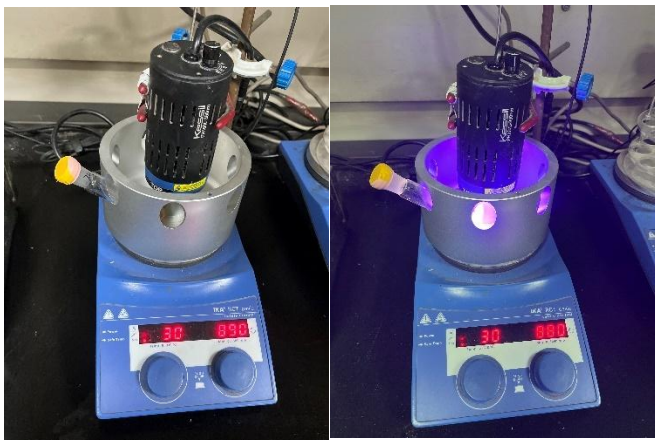
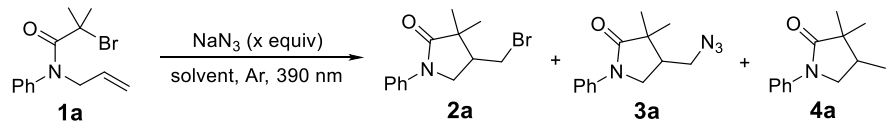


Figure S1 Experimental setup

3. Optimalization of reaction conditions

Table S1 Optimalization of reaction conditions for the bromine atom transfer cyclization of **1a**

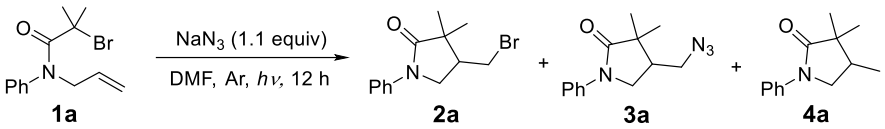


entry	solvent	x	time (h)	yield of **2a**	yield of **3a**	yield of **4a**
1	DMF	1.1	12	9%	6%	12%
2	DMF	0.2	12	30%	--[a]	54%
3	DMSO	1.1	12	30%	25%	18%
4	DMSO	0.2	12	73%	--[a]	4%
5	***DMSO***	***0.1***	***24***	***76%***	***--***[a]	***trace***
6	DMSO	0.05	48	60%	--[a]	4%

7	DMSO	0	24	-- [a]	-- [a]	-- [a]
8	CH_3CN	1.1	24	43%	-- [a]	20%
9	CH_3CN	0.1	24	34%	-- [a]	27%
10	acetone	1.1	24	40%	-- [a]	22%
11	acetone	0.1	24	30%	-- [a]	25%
12	EtOH	1.1	12	18%	trace	54%
14	THF	1.1	24	21%	-- [a]	75%
15[b]	DMSO	0.1	24	38%	-- [a]	< 1%

The reaction was conducted on 0.2 mmol scale (**1a**) in 2.0 mL of solvent under an argon atmosphere at 30 °C with a 390 nm Kessil LED lamp (40 W) as the light source. Isolated yield. [a]Not obtained. [b]$TMSN_3$ was used in place of NaN_3.

Table S2 Impact of light on the reaction



entry	Wavelength (nm)	yield of **2a**	yield of **3a**	yield of **4a**
1	420 (18 W)	4%	4%	15%
2	390 (40 W)	9%	6%	12%
3	455 (18 W)	7%	4%	10%
4	dark[a]	-- [b]	-- [b]	-- [b]

The reaction was performed on 0.2 mmol scale in 2.0 mL of DMF at 30 °C. Isolated yield. [a]Control experiment in the dark. [b]Not formed.

4. Mechanistic investigation

4.1 UV-vis Adsorption spectra

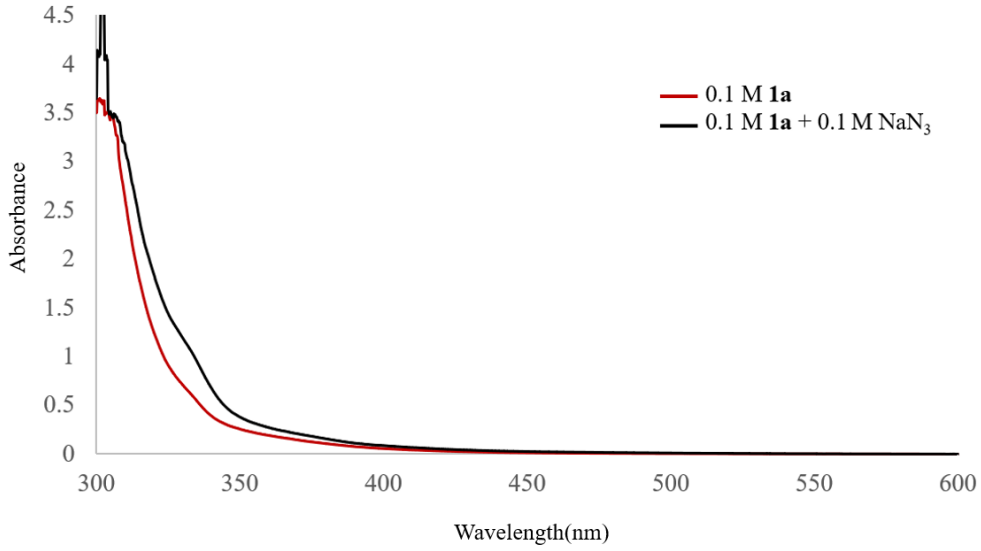
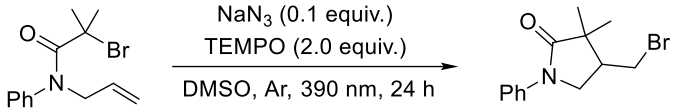


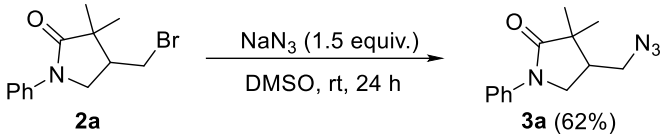
Figure S2 UV-vis spectrum of **1a** (0.1M) in the absence and presence of NaN_3 in DMSO.

4.2 Inhibition experiment



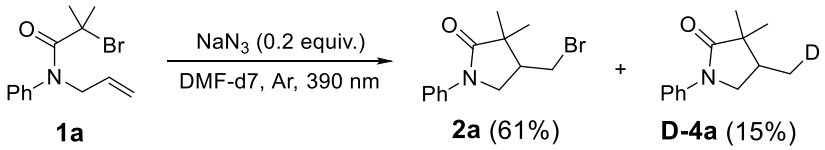
Into a 25 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was added successively **1a** (0.2 mmol, 1.0 equiv.), NaN_3 (1.3 mg, 0.02 mmol, 0.1 equiv.), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 62.5 mg, 0.4 mmol, 2.0 equiv.) and DMSO (2.0 mL). The tube was degassed and backfilled with argon for several times to ensure that the reaction took place in an inert atmosphere. The tube was irradiated with a 390 nm Kessil LED lamp (40 W) under stirring for 24 h. TLC analysis indicates that **2a** was not formed. After workup and flash chromatography, 36 mg of **1a** was recovered, along with an inseparatable mixture whose structures cannot be identified. This result confirms involvement of radical intermediates in the bromine atom transfer cyclization of **2a**.

4.3 Conversion of 2a to 3a



Into a 25 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was added successively **2a** (56.4 mg, 0.2 mmol), NaN_3 (19.5 mg, 0.3 mmol, 1.5 equiv.) and DMSO (2.0 mL). The mixture was stirred at room temperature for 24 h. After that, the mixture was poured into 10 mL of water contained in a separatory funnel, and the product was extracted with EA (3 × 10 mL). The combined organic phases were washed sequentially with water and brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was purified by flash column chromatography (PE and EA as eluents, PE:EA = 5:1) to afford product **3a** (31.2 mg. Yield: 62%).

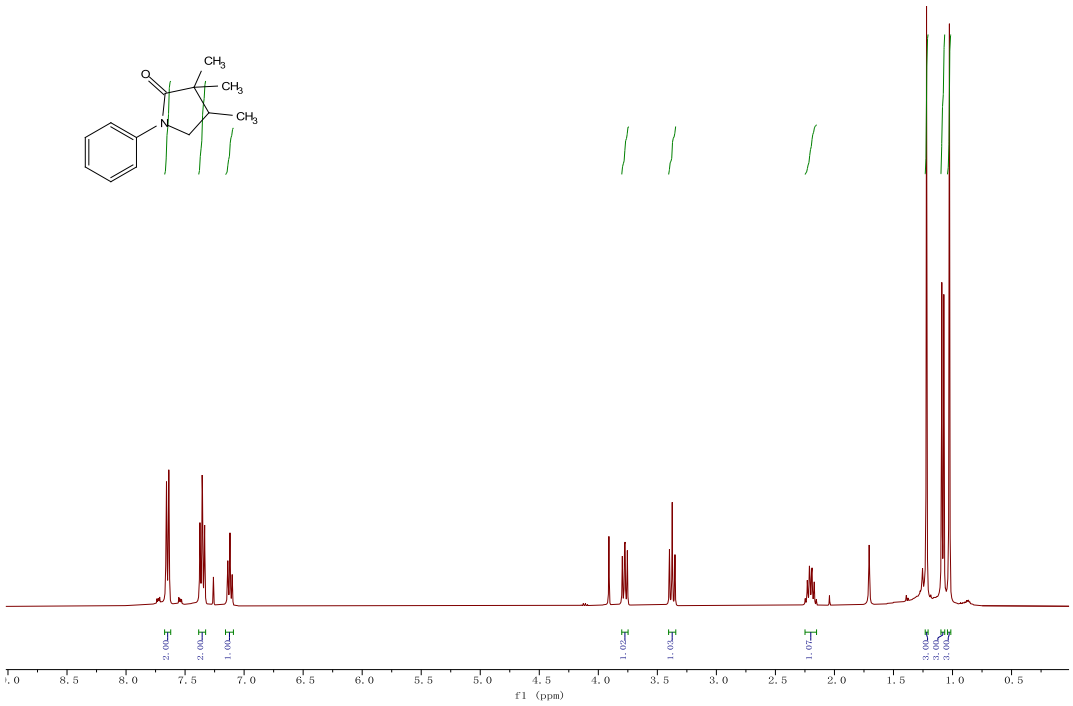
4.4 Deuterium labeling experiment



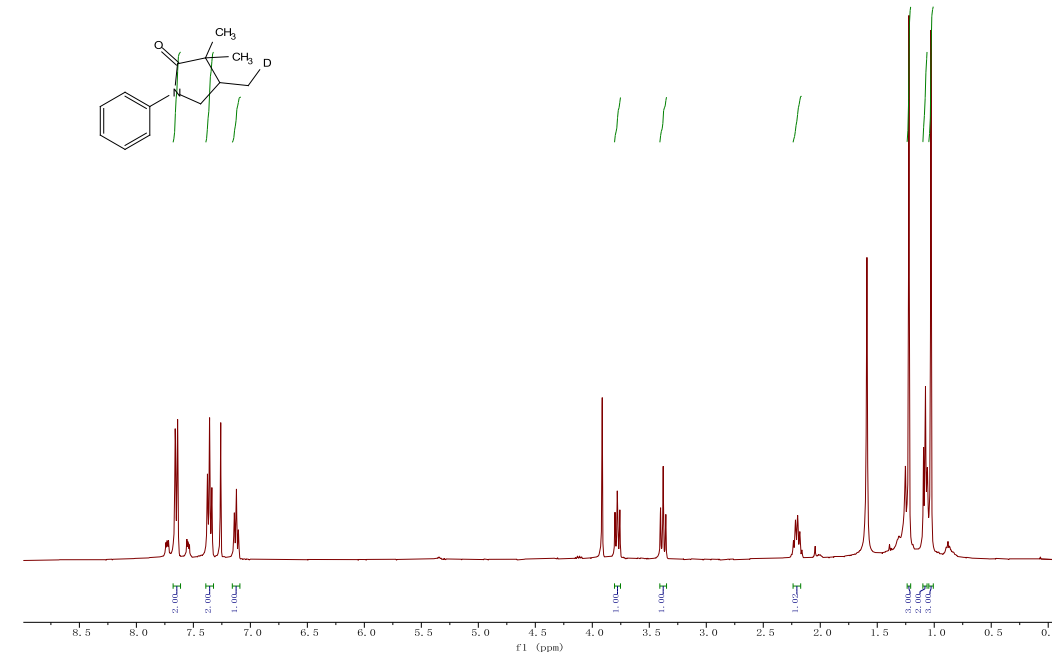
Into a 25 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was added successively **1a** (0.2 mmol, 1.0 equiv.), NaN_3 (2.6 mg, 0.04 mmol, 0.2 equiv.) and DMF-d7 (2.0 mL). The tube was degassed and backfilled with argon for several times to ensure that the reaction took place in an inert atmosphere. The tube was irradiated with a 390 nm Kessil LED lamp (40 W) under stirring for 24 h. The reaction mixture was then poured into 10 mL of water contained in a separatory funnel, and the product was extracted with EA (3×10 mL). The combined organic phases were washed sequentially with water and brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was purified by flash column chromatography (PE:EA = 5:1) to afford **2a** (34 mg. Yield: 61%) and **D-4a** (6

mg. Yield: 15%). This result confirms that the introduced hydrogen atom in **4a** comes from the solvent via HAT.

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



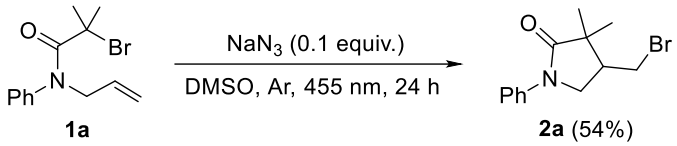
^{1}H NMR ($CDCl_3$, 400 MHz) of D-4a



4.5 Quantum yield measurement

The quantum yield measurement was performed according to the procedures described by Yoon[3] and Plaza[4]. As the Br-ATRC reaction can also be initiated by 455 nm blue

light, an apparatus of 455 nm LEDs (18 W) was used as the light source for the quantum yield measurement.



1a **2a** (54%)

(1) Solution preparation

Potassium ferrioxalate solution (0.012 M): 59.0 mg of $K_3[Fe(C_2O_4)]\cdot 3H_2O$ and 28 μL of H_2SO_4 were added into a 10 mL brown volumetric flask and filled to the mark with ultra-pure water.

1,10-Phenanthroline solution (0.01 M): 29.0 mg of 1,10-phenantroline monohydrate was added into a 10 mL brown volumetric flask and filled to the mark with ultra-pure water.

NaOAc and HOAc buffer solution: 1.24 g of NaOAc and 250 μL of H_2SO_4 were added into a 25 mL volumetric flask and filled to the mark with ultra-pure water.

All solutions were stored in the dark.

(2) Determination of the light intensity at 455 nm

2.0 mL of 0.012 M Potassium ferrioxalate solution was added into 25 mL glass tube, and was irradiated with 18 W blue LEDs for 0, 5, 10 and 20 seconds. After that, 0.1 mL of this solution was taken out as an aliquot and transferred into a tube. Into the tube containing each aliquot, 2.0 mL of the buffer solution and 0.5 mL of the 1,10-phenanthroline solution were added with a syringe, and the mixture was stirred in the dark for 1 h. The mixture was then diluted in a 10 mL brown volumetric flask with ultra-pure water. The absorbance of the resulting solution in a quartz cuvette (1×1 cm) at 510 nm was measured with a UV-vis spectrometer. A non-irradiated sample was also prepared in the same manner, and its absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as following:

5 s:

$$\text{mol of } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A}{V_2 \times l \times \varepsilon} = \frac{0.002\ \text{L} \times 0.010\ \text{L} \times 0.236}{0.0001\ \text{L} \times 1.00\ \text{cm} \times 11{,}100\ \text{L/mol/cm}} = 4.25 \times 10^{-6}\ \text{mol}$$

10 s:

$$\text{mol of } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A}{V_2 \times l \times \varepsilon} = \frac{0.002\ \text{L} \times 0.010\ \text{L} \times 0.429}{0.0001\ \text{L} \times 1.00\ \text{cm} \times 11{,}100\ \text{L/ mol/cm}} = 7.73 \times 10^{-6}\ \text{mol}$$

20 s:

$$\text{mol of } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A}{V_2 \times l \times \varepsilon} = \frac{0.002\ \text{L} \times 0.010\ \text{L} \times 0.936}{0.0001\ \text{L} \times 1.00\ \text{cm} \times 11{,}100\ \text{L/mol/cm}} = 1.69 \times 10^{-5}\ \text{mol}$$

where V_1 is the irradiated volume (0.002 L), V_2 is the aliquot of the irradiated potassium ferrioxalate solution (0.0001 L), V_3 is the final volume after complexation (0.010 L), ΔA is the difference in absorbance at 510 nm between the irradiated and non-

irradiated samples, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/mol·cm).

The photon flux of the 455 nm LEDs was determined according to the following equation:

5 s:

$$\text{photon flux} = \frac{\text{mol of } Fe^{2+}}{\Phi \times t \times f} = \frac{4.25 \times 10^{-6} \text{ mol}}{1.12 \times 5.0 \text{ s} \times 0.3690} = 2.06 \times 10^{-6} \text{ einstein/s}$$

10 s:

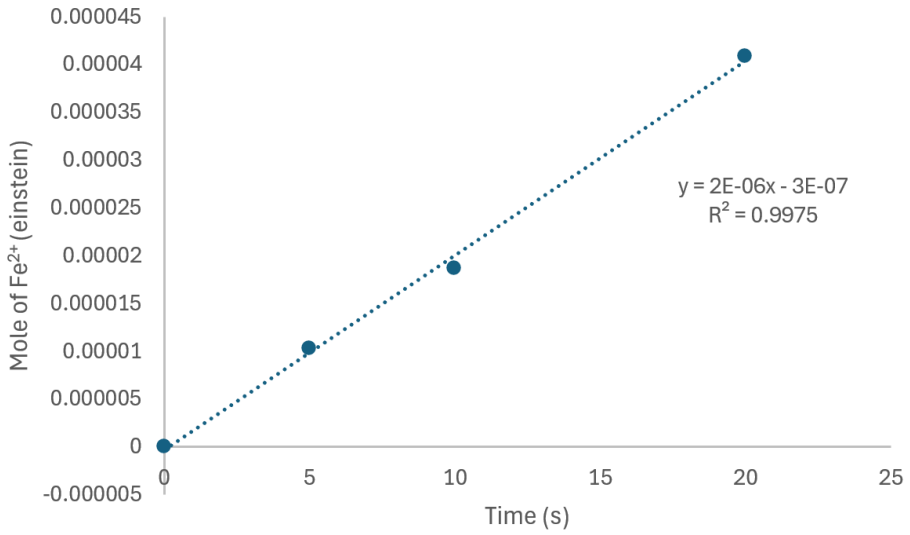
$$\text{photon flux} = \frac{\text{mol of } Fe^{2+}}{\Phi \times t \times f} = \frac{7.73 \times 10^{-6} \text{ mol}}{1.12 \times 10.0 \text{ s} \times 0.3690} = 1.87 \times 10^{-6} \text{ einstein/s}$$

20 s:

$$\text{photon flux} = \frac{\text{mol of } Fe^{2+}}{\Phi \times t \times f} = \frac{1.69 \times 10^{-5} \text{ mol}}{1.12 \times 20.0 \text{ s} \times 0.3690} = 2.04 \times 10^{-6} \text{ einstein/s}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 1.12, which was reported for a 0.01 M solution at $\lambda = 455$ nm).[5] t is the irradiation time, and f is the fraction of light absorbed at 455 nm. The absorbance of 0.012 M of ferrioxalate at 455 nm is 0.20. The fraction of light absorbed was determined by the following equation:

$$f = 1 - 10^{-A} = 1 - 10^{-0.20} = 0.3690$$



(3) Determination of quantum yield for the Br-ATRC reaction of 1a

Into a 25 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was added successively **1a** (0.2 mmol), NaN_3 (1.3 mg, 0.02 mmol, 0.1 equiv.) and 2.0 mL DMSO. The tube was degassed and backfilled with argon for several times. The tube was irradiated with 455 nm LEDs (18 W) under stirring for 15 h. The reaction mixture was then poured into 10 mL of water contained in a separatory funnel, and the product

was extracted with EA (3×10 mL). The combined organic phases were washed sequentially with water and brine, dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The yield of **2a** was determined by ^1H NMR with 2,4-dinitrobenzaldehyde as the internal standard. NMR yield for **2a** = 45%. The quantum yield for the reaction was determined according to the following equation.

$$\phi_{2a} = \frac{\text{mol of product } \mathbf{2a}}{F \times t \times f} = \frac{9.0 \times 10^{-5}}{2.0 \times 10^{-6} \times 54000 \times 0.0559} = 0.015$$

Where mol of product **2a** was 9.0×10^{-5} mol (0.2 mmol × 45%), F is the photo flux determined by the ferrioxalate actinometer (2.0×10^{-6} einstein·s^{-1}), t is the irradiated time (54000 s), and f is the fraction of light absorbed by the mixture of **2a** (0.1 M) and NaN_3 at 455 nm (0.0559). The absorbance of **2a** (0.1 M) in the presence pf NaN_3 at 455 nm is 0.02. $f = 1–10^{-0.02} = 0.0559$. The quantum yield ($\phi_{2a}$) was calculated to be 0.015.

5. Computational details

All geometric optimizations have been carried out by density functional theory using the M062X functional[6,7] with Grimme's dispersion (D3)[8] using the Gaussian 16 program. The standard 6-31G(d,p) basis set[9,10] was used for structural optimization. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies), the transition state structure has and has only one imaginary frequency, and the intrinsic reaction coordinate (IRC)[11,12] shows that the transition state is located on the correct reaction path. The def2tzvp[13] basis set was used for single point energy. The temperature used in all structural calculations is 298.15 K, and the solvent Dimethyl sulfoxide is added to calculate under the IEFPCM[14] model.

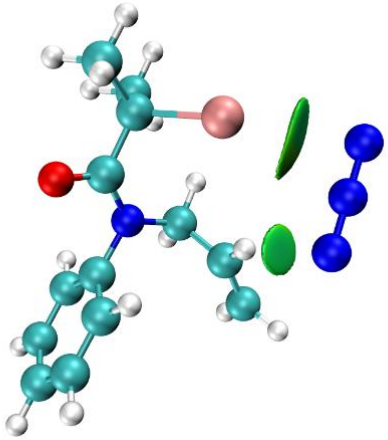
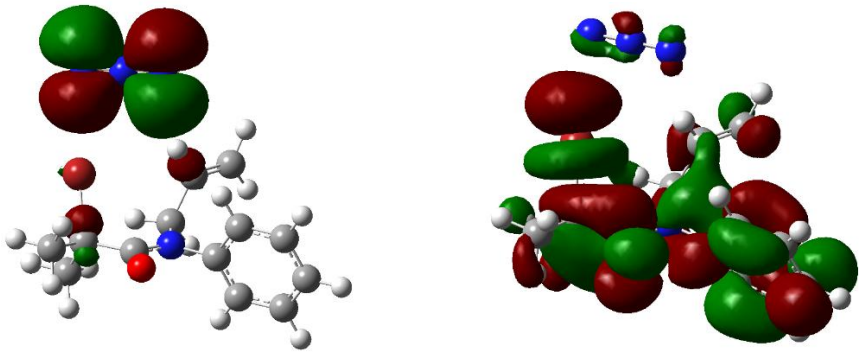


Figure S3 Halogen bonding interaction between **1a** and the azide anion

IGMH[15] analysis was performed using the Multiwfn[16] and VMD programs. The blue, green, and red regions represent strong non-covalent interactions, weak non-covalent interactions, and steric hindrance, respectively. It can be seen from the picture that there

is a blue-green isosurface between the azide anion and **1a** in the COM, indicating that there is a strong non-covalent interaction.



-0.22069 a.u. 0.02237 a.u.

Figure S4 Calculated HOMOs (left) and LUMOs (right) of halogen-bonded **1a** and the azide anion.

The BDE of C–Br bond in **1a** was calculated to be 38.5 kcal/mol. After halogen bond with the azide anion being formed, the BDE of C–Br bond was calculated to be 24.8 kcal/mol.

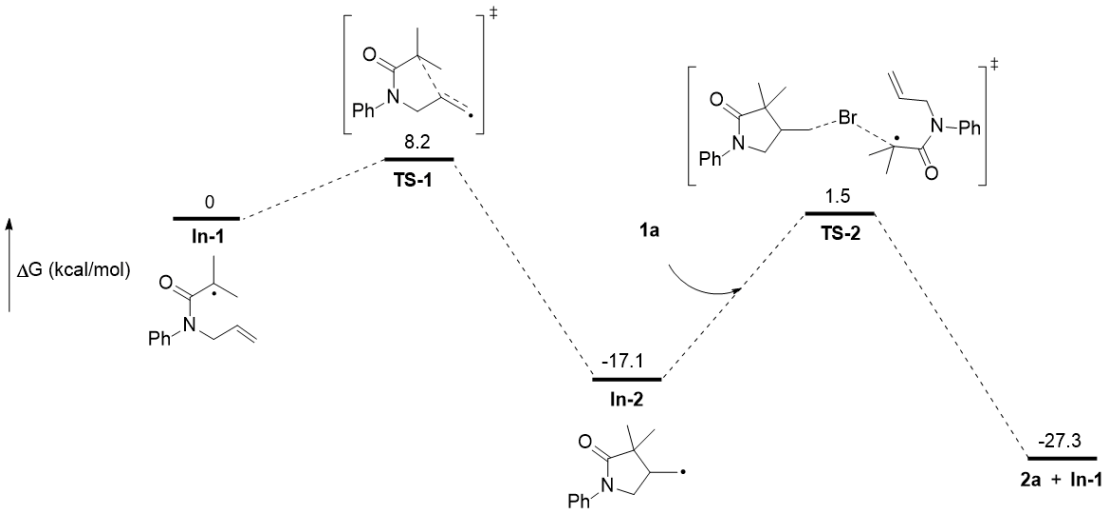


Figure S5 Computed free energy profile for the radical chain process at M062x/6-31G(d,p)//M062x/def2tzvp(IEFPCM,DMSO).

Cartesian Coordinates

1a

C	-0.16379400	1.20936100	1.02705800
C	-0.43058700	2.33817200	0.06921600
C	1.92465500	-0.97532300	0.30949400
C	0.41599700	-1.06224200	-0.01169100
H	-0.79394000	1.31053000	1.91667700
C	2.65734800	-2.11827000	-0.38043700
H	2.30428400	-3.06760500	0.02827200
H	2.46952800	-2.11278500	-1.45377900

H	3.72900900	-2.02250500	-0.19710100
C	2.21637300	-0.98499800	1.80652300
H	1.84330500	-1.92970500	2.21545900
H	3.29477600	-0.93914200	1.97049900
H	1.74444700	-0.17119800	2.35487400
N	-0.45432000	-0.09587400	0.41011800
C	-1.84577100	-0.30433200	0.11101300
C	-2.31205300	-0.16772200	-1.19495200
C	-2.72680600	-0.59215900	1.14900700
C	-3.66729900	-0.33175100	-1.46226900
H	-1.60759800	0.06385200	-1.98767100
C	-4.08521200	-0.74748900	0.87827800
H	-2.34480100	-0.69601500	2.16026900
C	-4.55572800	-0.61962200	-0.42611300
H	-4.03171600	-0.22834300	-2.47895600
H	-4.77262000	-0.97202700	1.68702000
H	-5.61302700	-0.74224400	-0.63634200
O	0.01531000	-2.05960000	-0.59640200
Br	2.65081700	0.69143600	-0.51099600
H	0.87402900	1.24049500	1.34736500
C	-1.34745800	3.27626000	0.28140700
H	-1.96658500	3.26729100	1.17514000
H	-1.50889300	4.08433600	-0.42431700
H	0.18099300	2.34342600	-0.83136100

N3-

N	0.00000000	0.00000000	-0.00004500
N	0.00000000	0.00000000	1.17783400
N	0.00000000	0.00000000	-1.17778900

COM

C	-0.43077000	0.29595700	1.54428100
C	-0.21474400	1.72695400	1.13411900
C	1.09464500	-1.94957600	0.04156200
C	-0.31748100	-1.45207600	-0.32955500
H	-1.14702800	0.23726800	2.37106600
C	1.59224100	-2.90223500	-1.03864000
H	0.94705800	-3.78323700	-1.07441400
H	1.57794600	-2.42382200	-2.01786900
H	2.61212200	-3.21196700	-0.80219400
C	1.14494700	-2.63444000	1.40501800
H	0.48519400	-3.50799400	1.37601500

H	2.16262200	-2.97765100	1.60323500
H	0.82656100	-2.00020800	2.23116700
N	-0.95748100	-0.51266100	0.43192600
C	-2.28236700	-0.14174700	0.01505100
C	-2.46287400	0.68873500	-1.08957300
C	-3.37648800	-0.57857600	0.75566900
C	-3.74786700	1.07203800	-1.46000200
H	-1.59332500	1.02497700	-1.64601200
C	-4.66201200	-0.18658100	0.38588600
H	-3.21467700	-1.22418500	1.61380000
C	-4.84859100	0.63608900	-0.72221000
H	-3.89049500	1.71627800	-2.32131200
H	-5.51560400	-0.52762200	0.96229600
H	-5.84958000	0.93958100	-1.01065600
O	-0.87638700	-1.96217200	-1.29275200
Br	2.33309800	-0.39169600	0.00116300
H	0.51087600	-0.12614900	1.88528500
C	-0.82622500	2.75233600	1.71873000
H	-1.53747000	2.60786600	2.52879300
H	-0.62905400	3.77377700	1.40822900
H	0.48951900	1.89574100	0.31870600
N	2.94440300	2.69642800	-0.68065300
N	3.93039000	2.17336500	-0.30384900
N	1.96033400	3.21898300	-1.05982800

COM*

C	0.70023400	-0.49023600	1.23371200
C	0.56932000	-1.82291800	0.54960200
C	-0.12227900	2.29405600	0.46593400
C	0.98858500	1.58899800	-0.17037500
H	1.13921900	-0.61446700	2.23134500
C	-0.89743100	3.26037700	-0.36284900
H	-0.73053700	4.29095900	-0.02203100
H	-0.61893300	3.19113600	-1.41405400
H	-1.96650200	3.04429400	-0.26211600
C	-0.44704000	2.23876000	1.92231600
H	-0.60257000	3.25523900	2.30187200
H	-1.38730900	1.69048500	2.07505700
H	0.33614500	1.76524400	2.51741400
N	1.50389600	0.44810800	0.43341700
C	2.78454700	-0.03766300	0.02482200
C	3.06783500	-0.34149100	-1.30857800
C	3.75005700	-0.26730200	1.00561500

C	4.31527400	-0.85390900	-1.65306600
H	2.30937600	-0.16455800	-2.06147100
C	4.99220400	-0.79331900	0.65849700
H	3.52189900	-0.02836400	2.04029000
C	5.27994100	-1.08388900	-0.67296700
H	4.53108800	-1.08395700	-2.69168300
H	5.73624700	-0.96869100	1.42885400
H	6.24879000	-1.48920000	-0.94593400
O	1.51389800	2.05611600	-1.18853600
Br	-2.40522100	0.01825300	-0.46756200
H	-0.30415700	-0.07784700	1.32633300
C	1.03128600	-2.96314700	1.05301000
H	1.56191900	-2.98426200	2.00226100
H	0.89457400	-3.91140000	0.54307400
H	0.02994100	-1.79443400	-0.39596500
N	-5.48532500	-1.36644900	-0.11015600
N	-5.90725500	-0.32641300	0.23367100
N	-5.06886800	-2.40922400	-0.45326200

N3$^-$+Br·

Br	-1.29244500	-0.00051200	0.00000000
N	2.15108200	0.00087200	-0.00002700
N	2.15181200	1.17496900	0.00001300
N	2.15932900	-1.17328100	0.00001300

N3·

N	0.00000000	0.00000000	-0.00002700
N	0.00000000	0.00000000	1.17506100
N	0.00000000	0.00000000	-1.17503400

1a'

C	-0.02796700	0.96773100	0.66678100
C	0.21959400	1.92400900	-0.47200700
C	1.00492900	-1.80889700	0.24308100
C	-0.17934900	-1.25207600	-0.38590600
H	-0.50135900	1.47384300	1.51430800
C	1.91732400	-2.64970300	-0.57974100
H	2.02917600	-3.64840400	-0.14120000
H	1.55175900	-2.74655300	-1.60175300
H	2.90693200	-2.17629100	-0.58964800
C	1.30623200	-1.67613900	1.69774200

H	1.50810200	-2.66736500	2.12004400
H	2.21546000	-1.07369700	1.82662300
H	0.48652500	-1.21876100	2.25460100
N	-0.84012400	-0.19399300	0.28456500
C	-2.23515100	-0.04130300	0.13385000
C	-3.05315800	-1.17656000	-0.01338900
C	-2.85244900	1.21280700	0.22712200
C	-4.43250600	-1.05039900	-0.08292500
H	-2.59947300	-2.15809200	-0.07490100
C	-4.24151300	1.32472100	0.16517500
H	-2.25744800	2.11003400	0.33034300
C	-5.04319500	0.20187900	0.00508600
H	-5.03808400	-1.94416800	-0.19761300
H	-4.69109400	2.31016400	0.23871300
H	-6.12250500	0.29492800	-0.04816700
O	-0.62720900	-1.72027100	-1.43624600
Br	3.58316000	0.61710600	-0.06314100
H	0.95409800	0.60964300	0.98533100
C	0.03408700	3.23856100	-0.40441500
H	-0.36024000	3.70693700	0.49527100
H	0.27477400	3.89375000	-1.23495800
H	0.63006600	1.46765900	-1.37178000

Br-

Br	0.00000000	0.00000000	0.00000000

I

C	0.58299300	1.59943500	0.04262900
C	-0.26126700	2.22401300	-1.03448600
C	2.79804800	-0.34006600	0.17048700
C	1.42355100	-0.75759300	-0.13398700
H	0.35861800	2.06185900	1.01121600
C	3.90483000	-1.07613900	-0.50474700
H	4.32652400	-1.83907500	0.16431100
H	3.55979300	-1.57723800	-1.40925300
H	4.72279600	-0.39150900	-0.75374900
C	3.14912900	0.54880200	1.32048800
H	3.85580100	0.02900000	1.97867700
H	3.65396600	1.46482900	0.98631200
H	2.27766600	0.83298000	1.91298400
N	0.39519100	0.14257700	0.09450100
C	-0.95768200	-0.31626100	0.14792900

C	-1.51623000	-1.07742500	-0.88054100
C	-1.74304300	0.05898800	1.23921300
C	-2.84885800	-1.47321900	-0.80161900
H	-0.90043500	-1.35820500	-1.72582000
C	-3.07863800	-0.32755900	1.30531200
H	-1.30192200	0.65089800	2.03569000
C	-3.63433700	-1.09925600	0.28706600
H	-3.27704100	-2.06886800	-1.60145400
H	-3.68194500	-0.03060300	2.15696800
H	-4.67395900	-1.40513500	0.34019600
O	1.20457700	-1.90704800	-0.52400300
H	1.63498200	1.78907300	-0.18034000
C	-1.12724200	3.20654300	-0.81136500
H	-1.28621800	3.59844500	0.19026300
H	-1.70210400	3.65359200	-1.61540200
H	-0.11700600	1.82672600	-2.03835600

TS1

C	0.64388800	1.41833400	-0.27059700
C	1.99051700	1.21879200	-0.92198100
C	2.23163800	-0.63082500	0.29445500
C	0.79628400	-0.97392900	0.09900000
H	-0.00098600	2.01140800	-0.92747900
C	3.23079200	-1.50918300	-0.38992800
H	3.42595000	-2.41264400	0.20262500
H	2.88545900	-1.82418100	-1.37747800
H	4.18022500	-0.97498200	-0.50033400
C	2.62228700	-0.08220700	1.63604900
H	2.75971600	-0.90303800	2.35206000
H	3.57102000	0.45897100	1.56027200
H	1.86771400	0.59318000	2.04819500
N	-0.01726800	0.12477100	-0.06482300
C	-1.43431300	0.07266800	-0.02966100
C	-2.14929200	-1.03534800	-0.50262100
C	-2.13479900	1.17884000	0.46724400
C	-3.54037600	-1.02794500	-0.46021200
H	-1.61466500	-1.88749500	-0.89611400
C	-3.52582300	1.17625600	0.49431800
H	-1.59348300	2.03938300	0.84523900
C	-4.23764900	0.07173800	0.03458500
H	-4.08257300	-1.89212200	-0.83082100
H	-4.05076200	2.04241300	0.88386800
H	-5.32211400	0.06903700	0.05834500

O	0.40270700	-2.13635800	0.09088300
H	0.75964000	1.97556600	0.66805000
C	3.03564500	2.04699900	-0.68210700
H	3.02942700	2.73127800	0.16130100
H	3.93103600	2.01336700	-1.29192200
H	1.98081500	0.63219500	-1.84037800

II

C	0.66143300	1.40423500	-0.25009700
C	2.08510800	0.97949700	-0.63503200
C	2.22976300	-0.40114800	0.06802200
C	0.79658700	-0.92786800	0.03904000
H	0.19762300	2.03832300	-1.00935100
C	3.17961400	-1.34644000	-0.65439900
H	3.18092500	-2.32535500	-0.16819900
H	2.88430500	-1.48132600	-1.69902300
H	4.19651700	-0.94299200	-0.63087800
C	2.62916700	-0.26268400	1.54464000
H	2.56433600	-1.23604800	2.03837000
H	3.65762800	0.10122600	1.61936200
H	1.97908600	0.43717900	2.07971100
N	-0.05853100	0.13438900	-0.13929200
C	-1.46745700	0.08777200	-0.06858800
C	-2.17700700	-1.10090900	-0.29410700
C	-2.17390400	1.26522100	0.20919400
C	-3.56633700	-1.09707400	-0.22790400
H	-1.63927200	-2.01128000	-0.51505600
C	-3.56422800	1.25190000	0.26683700
H	-1.64319100	2.19286200	0.38954900
C	-4.27043000	0.07229100	0.05152500
H	-4.10264800	-2.02395400	-0.40525500
H	-4.09303100	2.17404900	0.48505100
H	-5.35402700	0.06406500	0.09788600
O	0.47904100	-2.09578700	0.19706100
H	0.65102000	1.94492500	0.70600300
C	3.12402000	1.98908700	-0.31151900
H	3.05669200	2.57593000	0.59703200
H	4.03062500	2.05544200	-0.89807000
H	2.09282200	0.77924200	-1.71424100

TS2

C	1.13524100	-1.25806000	-0.82001300

C	0.89288300	-2.40890000	0.16236800
C	2.32600600	-2.86551700	0.53475600
C	3.09790300	-1.54493800	0.44759700
H	0.32640500	-0.52097200	-0.80332400
C	2.42247300	-3.45135000	1.93768700
H	3.46672700	-3.65323400	2.18900400
H	2.01700000	-2.75709500	2.68001100
H	1.86235600	-4.38922000	1.99656800
C	2.93107500	-3.82541600	-0.50006700
H	3.98995600	-3.98540600	-0.28035600
H	2.41932500	-4.79138900	-0.46060000
H	2.84823400	-3.43441600	-1.51912600
N	2.37665500	-0.66848100	-0.32815300
C	2.79656000	0.61891100	-0.72993000
C	3.61214800	1.40358500	0.09426100
C	2.35299300	1.12854300	-1.95522300
C	3.98321600	2.67843500	-0.32070000
H	3.94674200	1.01051700	1.04497200
C	2.72770600	2.40836200	-2.35453500
H	1.72090200	0.52587600	-2.59908000
C	3.54723100	3.18845300	-1.54239900
H	4.61340100	3.28138800	0.32503800
H	2.37663600	2.79184800	-3.30723400
H	3.83870500	4.18536400	-1.85541900
O	4.18576600	-1.33127000	0.95446800
H	1.24060000	-1.62564400	-1.85017400
C	-0.04365900	-3.45085600	-0.35772700
H	0.08932100	-3.78611800	-1.38349500
H	-0.36589600	-4.22017000	0.33830400
H	0.45847700	-1.98002000	1.07559800
C	-1.65621500	0.26452400	1.72347800
C	-0.19673200	0.43350700	2.05791800
C	-3.56881500	-0.69563700	-0.49055900
C	-2.81235300	0.62500000	-0.52816800
H	-2.27013100	0.57175500	2.57957200
C	-4.31193700	-0.93965000	-1.78414500
H	-5.13316600	-0.21951500	-1.87385300
H	-3.65829900	-0.81456600	-2.64696300
H	-4.73099300	-1.94804400	-1.78537300
C	-4.41402600	-0.98655000	0.72995700
H	-5.24496300	-0.27014500	0.75803500
H	-4.84033900	-1.98923300	0.65124900
H	-3.88035900	-0.91334200	1.67563300
N	-2.01787800	1.02718600	0.52025100

C	-1.49879200	2.36667000	0.47475700
C	-0.50908900	2.70800300	-0.44556600
C	-1.94444200	3.30079000	1.40621300
C	0.03175500	3.98957100	-0.43525900
H	-0.16845000	1.96680900	-1.16204400
C	-1.39612900	4.58197800	1.41735100
H	-2.71441500	3.02127700	2.11913700
C	-0.40940000	4.92819600	0.49752000
H	0.80764600	4.24732400	-1.14902200
H	-1.74222200	5.30804300	2.14555900
H	0.01783300	5.92547300	0.50853900
O	-2.95655400	1.34749600	-1.50870100
Br	-1.98205500	-2.22256400	-0.56575300
H	-1.84607100	-0.79094900	1.53179300
C	0.26455200	0.58669000	3.29480500
H	-0.40728400	0.64737800	4.14705800
H	1.32882400	0.65355300	3.49459600
H	0.49935700	0.39579600	1.21968600

2a

C	0.32687900	-1.08946600	-0.04669900
C	-1.02792800	-0.43021500	-0.35896100
C	-0.87425500	1.01221000	0.17363600
C	0.63819600	1.23805000	0.08338900
H	0.60292900	-1.83768800	-0.79367600
C	-1.58767200	2.07328500	-0.66337500
H	-1.28447600	3.06661100	-0.32302900
H	-1.32386900	1.97755800	-1.72101300
H	-2.67014600	1.97606400	-0.56682100
C	-1.26287000	1.14714500	1.65407100
H	-1.00072800	2.14631300	2.01055300
H	-2.34176600	1.00684000	1.77067600
H	-0.74456900	0.41526200	2.28268100
N	1.26777800	0.02672300	-0.06776000
C	2.66393400	-0.18981500	-0.06799000
C	3.56380000	0.82898500	-0.41246700
C	3.15628300	-1.46063700	0.25435500
C	4.92980900	0.56807700	-0.41716600
H	3.19040700	1.80953300	-0.66912000
C	4.52627500	-1.70527000	0.24051600
H	2.47683300	-2.26085600	0.52379100
C	5.42234300	-0.69416100	-0.09226600
H	5.61545800	1.36517300	-0.68653000

H	4.88879500	-2.69593100	0.49478200
H	6.48962900	-0.88692900	-0.10180100
O	1.17926500	2.32749000	0.17106800
H	0.32196700	-1.57365500	0.93974600
C	-2.14535500	-1.27763600	0.21689400
H	-2.10809200	-1.33755900	1.30381300
H	-1.14654400	-0.38479500	-1.44718100
H	-2.13766300	-2.28164300	-0.20516100
Br	-3.91752500	-0.55527400	-0.20255900

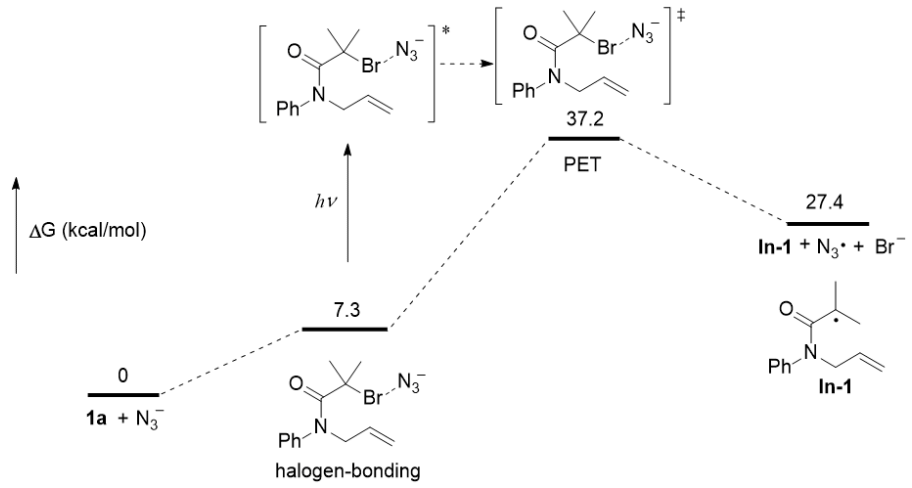


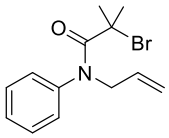
Figure S6 Computed free energy profile for SET between **1a** and the azide anion.

The energy barrier of the single-electron transfer (SET) process was calculated using Marcus theory.[18] The reorganization energy was calculated using the four-point method. The Marcus equation is as follows:

$$\triangle G_{SET} = \frac{\lambda}{4}\left(1 + \frac{\triangle G^{0\prime}}{\lambda}\right)^2$$

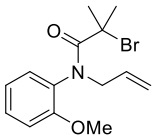
Here, $\triangle G_{SET}$ is the Marcus barrier, λ is the single-electron transfer reorganization energy, and $\triangle G^{0\prime}$ is the Gibbs free energy difference before and after the single-electron transfer.

6. Characterization data



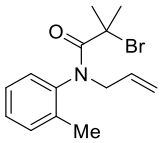
***N*-allyl-2-bromo-2-methyl-*N*-phenylpropanamide (1a)[2]**

Colorless oil, R_f = 0.51 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 – 7.24 (m, 5H), 5.89 – 5.77 (m, 1H), 5.07 – 4.97 (m, 2H), 4.20 (d, *J* = 6.4 Hz, 2H), 1.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 142.3, 142.2, 129.5, 128.7, 128.1, 58.0, 56.2, 33.1.



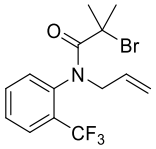
***N*-allyl-2-bromo-*N*-(2-methoxyphenyl)-2-methylpropanamide (1b)[2]**

Colorless oil, R_f = 0.54 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.21 – 7.09 (m, 3H), 5.91 (ddt, *J* = 16.7, 10.2, 6.2 Hz, 1H), 5.17 – 5.06 (m, 2H), 4.27 (d, *J* = 6.2 Hz, 2H), 2.37 (s, 3H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 142.4, 138.9, 132.5, 130.2, 128.9, 128.6, 126.6, 118.0, 58.3, 56.4, 33.3, 21.2.



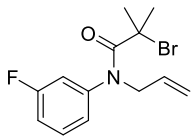
***N*-allyl-2-bromo-2-methyl-*N*-(o-tolyl)propanamide (1c)[2]**

White solid, R_f = 0.52 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 4H), 5.94 (ddt, *J* = 17.1, 11.6, 6.0 Hz, 1H), 5.12 (dd, *J* = 20.0, 13.6 Hz, 2H), 4.84 (ddt, *J* = 14.5, 5.5, 1.5 Hz, 1H), 3.43 (s, 1H), 2.27 (s, 3H), 1.90 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 141.0, 136.0, 132.0, 131.1, 130.6, 128.6, 126.1, 118.4, 58.3, 55.1, 34.1, 31.2, 18.2.



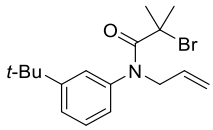
***N*-allyl-2-bromo-2-methyl-*N*-(2-(trifluoromethyl)phenyl)propenamide (1d)**

Colorless oil, R_f = 0.20 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.25 (m, 4H), 5.98 (dddd, *J* = 17.7, 10.2, 8.0, 4.9 Hz, 1H), 5.25 – 4.95 (m, 3H), 3.80 (d, *J* = 325.5 Hz, 1H), 2.08 – 1.24 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 139.9, 132.5, 132.4, 129.1, 127.7, 124.2, 122.4, 118.8, 59.2, 56.2, 34.9, 31.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{16}NOBr]^+$: 350.0362, found: 350.0356.



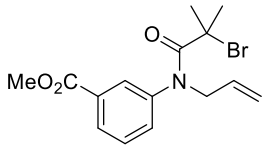
***N*-allyl-2-bromo-*N*-(3-fluorophenyl)-2-methylpropanamide (1e)**

Colorless oil, R_f = 0.60 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 1H), 7.12 – 6.97 (m, 3H), 5.89 – 5.76 (m, 1H), 5.15 – 4.95 (m, 2H), 4.22 (d, *J* = 6.4 Hz, 2H), 1.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 162.4 (d, *J* = 9.6 Hz), 143.9 (d, *J* = 9.6 Hz), 132.1, 130.0 (d, *J* = 9.2 Hz), 125.6 (d, *J* = 3.2 Hz), 118.6, 117.2 (d, *J* = 22.1 Hz), 115.4 (d, *J* = 21.0 Hz), 57.8, 56.3, 33.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -111.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}NOFBr]^+$: 300.0394, found: 300.0397.



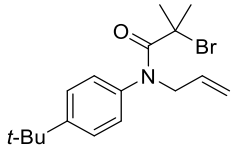
***N*-allyl-2-bromo-*N*-(3-(tert-butyl)phenyl)-2-methylpropanamide (1f)**

Yellow oil, R_f = 0.32 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 3H), 7.12 (ddd, *J* = 7.6, 2.1, 1.2 Hz, 1H), 5.93 (ddt, *J* = 16.7, 10.2, 6.3 Hz, 1H), 5.15 (dq, *J* = 10.2, 1.2 Hz, 1H), 5.09 (dq, *J* = 17.2, 1.5 Hz, 1H), 4.26 (d, *J* = 6.3 Hz, 2H), 1.68 (s, 6H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 152.2, 142.2, 132.5, 128.5, 127.4, 126.4, 124.9, 118.1, 58.4, 56.4, 34.7, 33.3, 31.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{25}NOBr]^+$: 338.1114, found: 338.1111.



methyl 3-(*N*-allyl-2-bromo-2-methylpropanamido)benzoate (1g)

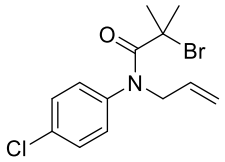
Yellow oil, R_f = 0.15 (PE/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.94 (m, 2H), 7.55 (ddd, *J* = 8.0, 2.3, 1.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 5.89 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.14 (dt, *J* = 10.3, 1.2 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.4 Hz, 1H), 4.32 (d, *J* = 6.3 Hz, 2H), 3.92 (s, 3H), 1.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 166.1, 142.6, 134.4, 132.1, 131.1, 130.9, 129.3, 129.0, 118.7, 57.7, 56.2, 52.3, 33.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{19}NO_3Br]^+$: 340.0543, found: 340.0536.



***N*-allyl-2-bromo-*N*-(4-(tert-butyl)phenyl)-2-methylpropanamide (1h)**

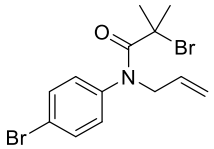
Yellow oil, R_f = 0.32 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36

(m, 2H), 7.28 – 7.24 (m, 2H), 5.92 (ddt, *J* = 16.5, 10.3, 6.1 Hz, 1H), 5.17 – 5.09 (m, 2H), 4.26 (d, *J* = 6.1 Hz, 2H), 1.71 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 151.4, 139.8, 132.5, 129.0, 125.7, 117.9, 58.4, 56.4, 34.6, 33.3, 31.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{25}NOBr]^+$: 338.1114, found: 338.1117.



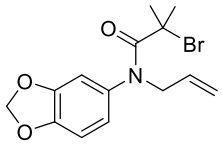
***N*-allyl-2-bromo-*N*-(4-chlorophenyl)-2-methylpropanamide (1i)**

Yellow solid, m.p. = 68–70 ℃, R_f = 0.31 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.20 (m, 2H), 5.82 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.00 (dq, *J* = 17.1, 1.5 Hz, 1H), 4.20 (dd, *J* = 6.1, 1.4 Hz, 2H), 1.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 140.9, 134.1, 132.1, 131.2, 129.1, 118.6, 57.8, 56.3, 33.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}NOClBr]^+$: 316.0098, found: 316.0094.



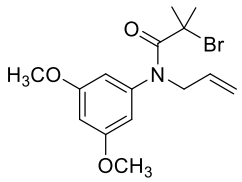
***N*-allyl-2-bromo-*N*-(4-bromophenyl)-2-methylpropanamide (1j)**

Yellow solid, m.p. = 67–70 ℃, R_f = 0.23 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.24 – 7.19 (m, 2H), 5.87 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.14 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.5 Hz, 1H), 4.26 (dt, *J* = 6.2, 1.3 Hz, 2H), 1.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 141.4, 132.1, 132.1, 131.5, 122.1, 118.7, 57.8, 56.3, 33.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}NOBr_2]^+$: 359.9586, found: 359.9588.



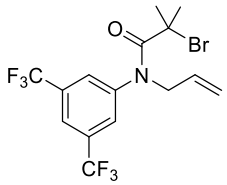
***N*-allyl-*N*-(benzo[d][1,3]dioxol-5-yl)-2-bromo-2-methylpropanamide (1k)**

Yellow solid, m.p. = 52–55 ℃, R_f = 0.14 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.74 (m, 3H), 6.01 (s, 2H), 5.88 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.14 (dt, *J* = 10.2, 1.3 Hz, 1H), 5.11 – 5.05 (m, 1H), 4.22 (d, *J* = 6.3 Hz, 2H), 1.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 147.6, 147.3, 136.1, 132.4, 123.2, 118.3, 110.4, 107.8, 101.7, 58.2, 56.5, 33.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{17}NO_3Br]^+$: 326.0386, found: 326.0379.



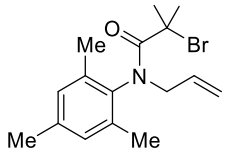
***N*-allyl-2-bromo-*N*-(3,5-dimethoxyphenyl)-2-methylpropanamide (1l)**

White solid, m.p. = 59–62 ℃, R_f = 0.48 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (d, *J* = 2.0 Hz, 2H), 6.41 (t, *J* = 2.4 Hz, 1H), 5.93–5.81 (m, 1H), 5.13 – 5.05 (m, 2H),4.21 (d, *J* = 6.4 Hz, 2H), 3.75 (s, 6H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 160.6, 144.1, 132.4, 118.0, 107.6, 100.2, 56.5, 56.2, 55.4, 33.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{21}NO_3Br]^+$: 342.0699, found: 342.0691.



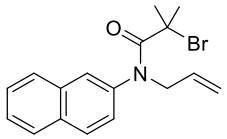
***N*-allyl-*N*-(3,5-bis(trifluoromethyl)phenyl)-2-bromo-2-methylpropanamide (1m)**

Colorless oil, R_f = 0.38 (PE/EA = 20:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (s, 2H), 5.93 – 5.84 (m, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 18.0 Hz, 1H), 4.43 (d, *J* = 6.6Hz, 1H), 1.83 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 143.7, 132.4 (q, *J* = 32.5 Hz),131.6, 130.3, 122.9 (q, *J* = 260.2 Hz,), 119.8, 56.9, 56.0, 33.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{15}NOF_6Br]^+$: 418.0236, found: 418.0238.



***N*-allyl-2-bromo-*N*-mesityl-2-methylpropanamide (1n)**

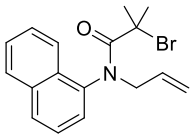
Colorless oil, R_f = 0.33 (PE/EA = 20:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.1 Hz, 2H), 6.04 – 5.82 (m, 1H), 5.12 – 5.01 (m, 2H), 4.37 (ddt, *J* = 282.3, 6.8, 1.2 Hz, 2H), 2.29 – 2.24 (m, 7H), 2.10 (d, *J* = 24.8 Hz, 4H), 1.67 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 169.1, 138.4, 138.1, 136.9, 136.7, 136.3, 135.1, 132.9, 132.0, 129.4, 129.3, 119.2, 118.5, 60.4, 57.3, 56.3, 54.4, 33.2, 32.6, 20.9, 20.9, 19.2, 17.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{16}H_{23}NOBr]^+$: 324.0958, found: 324.0951.



***N*-allyl-2-bromo-2-methyl-*N*-(naphthalen-2-yl)propenamide (1o)**

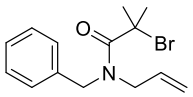
Yellow solid, m.p. = 57–59 ℃, R_f = 0.32 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 4H), 7.58 – 7.50 (m, 2H), 7.42 (dd, *J* = 8.7, 2.1 Hz, 1H), 5.98

(dd, J = 16.9, 10.4 Hz, 1H), 5.19 – 5.06 (m, 2H), 4.49 – 4.19 (m, 2H), 1.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 139.7, 133.0, 132.6, 132.4, 129.0, 128.6, 128.2, 127.7, 127.6, 126.9, 126.7, 58.2, 56.5, 33.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{19}NOBr]^+$: 332.0645, found: 332.0646.



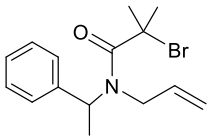
***N*-allyl-2-bromo-2-methyl-*N*-(naphthalen-1-yl)propenamide (1p)**

White solid, m.p. = 87–90 ℃, R_f = 0.30 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 3H), 7.68 – 7.44 (m, 4H), 6.02 (dddd, J = 17.3, 10.3, 7.3, 5.2 Hz, 1H), 5.15 (d, J = 10.2 Hz, 1H), 5.09 – 5.01 (m, 2H), 3.57 (s, 1H), 1.92 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 138.1, 134.4, 132.3, 130.7, 129.0, 128.6, 128.2, 127.2, 126.4, 125.0, 122.8, 118.6, 58.2, 55.5, 34.2, 31.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{19}NOBr]^+$: 332.0645, found: 332.0640.



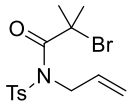
***N*-allyl-*N*-benzyl-2-bromo-2-methylpropanamide (1q)[2]**

Colorless oil, R_f = 0.58 (PE/EA = 20:1, v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 5H), 5.72 (s, 1H), 5.10 (dd, J = 29.7, 14.0 Hz, 2H), 4.63 – 3.72 (m, 3H), 1.92 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 137.0, 133.1, 132.1, 128.7, 127.4, 118.2, 57.2, 52.0, 50.9, 48.9, 32.9.



***N*-allyl-*N*-(2-bromo-2-methylpropanoyl)benzamide (1r)**

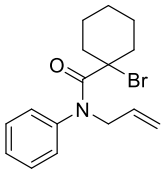
Colorless oil, R_f = 0.58 (PE/EA = 20:1, v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dq, J = 12.5, 6.4, 5.1 Hz, 5H), 5.97 (s, 1H), 5.81 (ddt, J = 17.5, 10.6, 5.4 Hz, 1H), 5.09 – 5.01 (m, 2H), 4.22 – 4.08 (m, 1H), 3.26 (dd, J = 16.1, 5.8 Hz, 1H), 2.06 (s, 3H), 1.96 (s, 3H), 1.71 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 140.2, 134.2, 128.4, 127.1, 126.4, 115.7, 57.3, 56.1, 47.6, 33.5, 32.6, 18.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{23}NOBr]^+$: 310.0801, found: 310.0803.



***N*-allyl-2-bromo-2-methyl-*N*-tosylpropanamide (1s)[2]**

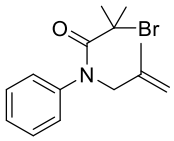
White solid, R_f = 0.52 (PE/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 5.95–5.85 (m, 1H), 5.36–5.22 (m, 2H), 4.89 –

4.85 (m, 2H), 2.32 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 144.5, 135.9, 133.4, 129.0, 128.6, 117.9, 56.0, 50.4, 31.8, 21.5.



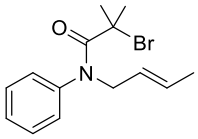
***N*-allyl-1-bromo-*N*-phenylcyclohexane-1-carboxamide (1t)**

Yellow oil, R_f = 0.35 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.42 – 7.33 (m, 2H), 7.20 – 7.11 (m, 1H), 4.00 (dd, *J* = 10.3, 6.6 Hz, 1H), 3.78 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.67 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.34 (dd, *J* = 11.5, 10.2 Hz, 1H), 2.67 (ddt, *J* = 11.5, 6.6, 3.3 Hz, 1H), 1.94 – 1.78 (m, 3H), 1.66 – 1.35 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 139.4, 128.8, 124.5, 119.8, 49.75, 5.12, 42.3, 33.4, 32.6, 27.6, 25.3, 22.4, 22.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for[$C_{16}H_{21}NOBr]^+$: 332.0801, found: 332.0794.



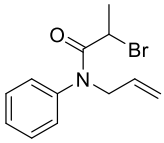
2-bromo-2-methyl-*N*-(2-methylallyl)-*N*-phenylpropanamide (1u)[2]

Black solid, m.p. = 47–49 °C, R_f = 0.58 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 5H), 4.79 (d, *J* = 31.2 Hz, 2H), 4.29 (s, 2H), 1.79 (s, 3H), 1.71 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 142.5, 140.2, 129.4, 128.7, 128.1, 113.0, 59.0, 56.2, 33.3, 20.3.



(*E*)-2-bromo-*N*-(but-2-en-1-yl)-2-methyl-N-phenylpropanamide (1v)[2]

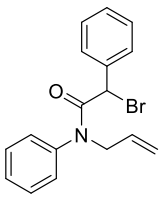
Colorless oil, R_f = 0.60 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 5.67 – 5.37 (m, 2H), 4.20 (d, *J* = 6.3 Hz, 2H), 1.71 (s, 6H), 1.65 (dd, *J* = 6.3, 1.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 142.4, 130.0, 128.9, 128.8, 128.1, 125.0, 58.4, 55.7, 33.3, 17.8.



***N*-allyl-2-bromo-*N*-phenylpropanamide (1w)**

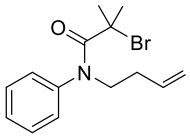
Colorless oil, R_f = 0.50 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 3H), 7.28 – 7.23 (m, 2H), 5.92 – 5.80 (m, 1H), 5.17 – 5.07 (m, 2H), 4.37 – 4.20 (m, 3H), 1.74 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 141.2, 132.1, 129.7,

128.5, 128.1, 52.8, 39.3, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{12}H_{15}NOBr]^+$: 268.0332, found: 268.0331.



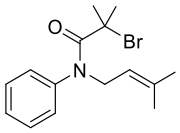
***N*-allyl-2-bromo-*N*,2-diphenylacetamide (1x)**

Yellow oil, R_f = 0.23 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.04 (m, 10H), 5.85 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.29 (s, 1H), 5.14 – 5.04 (m, 2H), 4.33 – 4.26 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 141.2, 136.6, 132.0, 129.8, 128.9, 128.8, 128.7, 128.6, 128.3, 118.6, 53.1, 46.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{17}NOBr]^+$: 330.0488, found: 330.0482.



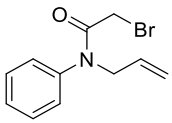
2-bromo-*N*-(but-3-en-1-yl)-2-methyl-*N*-phenylpropanamide (1y)

Colorless oil, R_f = 0.20 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 5H), 5.76 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.11 – 5.00 (m, 2H), 3.80 – 3.71 (m, 2H), 2.38 – 2.31 (m, 2H), 1.70 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 142.5, 135.9, 129.8, 129.0, 128.2, 116.8, 58.3, 52.7, 33.3, 31.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{19}NOBr]^+$: 296.0645, found: 296.0639.



2-bromo-2-methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-phenylpropanamide (1z)

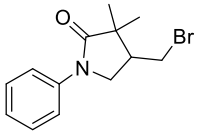
Colorless oil, R_f = 0.58 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 5.29 (t, *J* = 6.0 Hz, 1H), 4.27 (d, *J* = 4.8 Hz, 2H), 1.71 (s, 6H), 1.67 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 142.5, 136.7, 129.9, 128.8, 128.1, 118.7, 51.4, 33.4, 25.7, 17.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{21}NOBr]^+$: 310.0801, found: 310.0801.



***N*-allyl-2-bromo-*N*-phenylacetamide (1aa)**

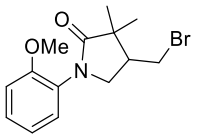
Colorless oil, R_f = 0.48 (PE/EA = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.25 (dd, *J* = 8.4, 1.7 Hz, 2H), 5.87 (ddt, *J* = 16.7, 10.3, 6.4 Hz, 1H), 5.18 – 5.08 (m, 2H), 4.31 (d, *J* = 6.3 Hz, 2H), 3.66 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 141.4, 132.1, 129.8, 128.6, 128.0, 118.6, 52.9, 27.1. HRMS (ESI-TOF) m/z:

$[M+H]^+$ calcd for $[C_{11}H_{13}NOBr]^+$: 254.0175, found: 254.0174.



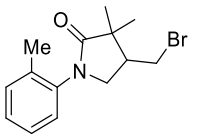
4-(bromomethyl)-3,3-dimethyl-1-phenylpyrrolidin-2-one (2a)[2]

Yield: 76% (43 mg). Yellow oil, R_f = 0.36, (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.42 – 7.28 (m, 2H), 7.19 – 7.08 (m, 1H), 4.00 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.63 – 3.51 (m, 2H), 3.40 (t, *J* = 10.5 Hz, 1H), 2.59 (dddd, *J* = 10.8, 8.6, 7.5, 4.6 Hz, 1H), 1.32 (s, 3H), 1.10 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 139.3, 128.9, 124.6, 119.8, 50.6, 45.5, 45.3, 31.2, 24.4, 18.5.



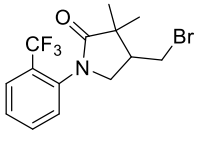
4-(bromomethyl)-1-(2-methoxyphenyl)-3,3-dimethylpyrrolidin-2-one (2b)[2]

Yield: 94% (58 mg). White solid, R_f = 0.39, (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.29 – 7.21 (m, 1H), 6.97 (ddt, *J* = 7.5, 1.7, 0.9 Hz, 1H), 3.98 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.63 – 3.50 (m, 2H), 3.39 (t, *J* = 10.5 Hz, 1H), 2.57 (dddd, *J* = 10.9, 8.7, 7.5, 4.6 Hz, 1H), 2.37 (s, 3H), 1.31 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 139.2, 138.7, 128.6, 125.4, 120.5, 116.8, 50.6, 45.4, 45.2, 31.2, 24.3, 21.6, 18.5.



4-(bromomethyl)-3,3-dimethyl-1-(o-tolyl)pyrrolidin-2-one (2c)[2]

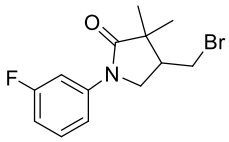
Yield: 71% (42 mg). Yellow oil, R_f = 0.15 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 3H), 7.16 – 7.08 (m, 1H), 3.82 (dd, *J* = 10.2, 7.5 Hz, 1H), 3.61 (dd, *J* = 10.1, 4.7 Hz, 1H), 3.51 – 3.35 (m, 2H), 2.67 (dddd, *J* = 10.9, 8.5, 7.5, 4.7 Hz, 1H), 2.21 (s, 3H), 1.34 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 137.1, 135.5, 131.1, 127.9, 126.8, 126.6, 52.6, 46.7, 44.2, 31.3, 24.4, 18.5, 17.8.



4-(bromomethyl)-3,3-dimethyl-1-(2-(trifluoromethyl)phenyl)pyrrolidin-2-one (2d)

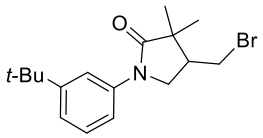
Yield: 80% (56 mg). Yellow oil, R_f = 0.42 (EA/PE = 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.63 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 –7.44 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 3.83 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.60 (dd, *J* = 10.1, 4.7 Hz, 1H), 3.43 (d, *J* = 10.5 Hz, 2H), 2.68 (dtd, *J* = 10.8, 7.9, 4.7 Hz, 1H), 1.33 (s, 3H), 1.15

(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 137.0 (d, J = 2.1 Hz), 131.9 (d, J = 289.0 Hz), 128.7 (q, J = 31.0 Hz), 127.3 (q, J = 5.1 Hz), 127.3 (q, J = 273.0 Hz), 53.8, 53.7, 47.0, 43.9, 31.1, 24.2, 18.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{16}BrF_3NO]^+$: 350.0362, found: 350.0353.



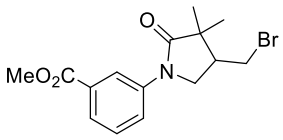
4-(bromomethyl)-1-(3-fluorophenyl)-3,3-dimethylpyrrolidin-2-one (2e)

Yield: 45% (27 mg). Yellow solid, m.p. = 103–105 ℃, R_f = 0.35 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, J = 11.4, 2.3 Hz, 1H), 7.40 – 7.27 (m, 2H), 6.85 (tdd, J = 8.2, 2.6, 1.3 Hz, 1H), 3.99 (dd, J = 9.9, 7.5 Hz, 1H), 3.63 – 3.49 (m, 2H), 3.39 (t, J = 10.5 Hz, 1H), 2.65 – 2.53 (m, 1H), 1.32 (s, 3H), 1.10 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 162.9 (d, J = 246 Hz), 140.8 (d, J = 12 Hz), 130.0 (d, J = 9.0 Hz), 114.6 (d, J = 3.0 Hz), 111.3 (d, J = 21 Hz), 107.2 (d, J = 17 Hz), 50.5, 45.4, 45.3, 31.0, 24.3, 18.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}BrFNO]^+$: 300.0394, found: 300.0390.



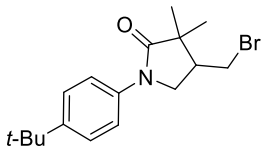
4-(bromomethyl)-1-(3-(*tert*-butyl)phenyl)-3,3-dimethylpyrrolidin-2-one (2f)

Yield: 80% (54 mg). Yellow solid, m.p. = 80–82 ℃, R_f = 0.46 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.43 – 7.36 (m, 2H), 3.98 (dd, J = 10.0, 7.5 Hz, 1H), 3.61 – 3.53 (m, 2H), 3.39 (t, J = 10.5 Hz, 1H), 2.58 (dddd, J = 10.8, 8.6, 7.5, 4.6 Hz, 1H), 1.31 (s, 12H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 147.6, 136.7, 125.7, 119.4, 50.5, 45.5, 45.2, 34.35, 31.3, 31.3, 24.4, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{25}BrNO]^+$: 338.1114, found: 338.1107.



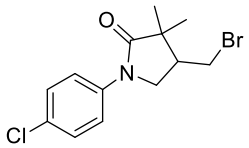
methyl 3-(4-(bromomethyl)-3,3-dimethyl-2-oxopyrrolidin-1-yl)benzoate (2g)

Yield: 83% (56 mg). Yellow oil, R_f = 0.23 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 2.0 Hz, 1H), 8.05 (ddd, J = 8.3, 2.4, 1.1 Hz, 1H), 7.82 (dt, J = 7.7, 1.3 Hz, 1H), 7.44 (s, 1H), 4.03 (dd, J = 9.9, 7.5 Hz, 1H), 3.92 (s, 3H), 3.64 – 3.55 (m, 2H), 3.40 (t, J = 10.4 Hz, 1H), 2.60 (dddd, J = 10.8, 8.7, 7.5, 4.6 Hz, 1H), 1.32 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 166.7, 139.4, 130.8, 129.0, 125.6, 124.4, 120.1, 52.3, 50.5, 45.4, 45.3, 31.0, 24.3, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{19}BrNO_3]^+$: 340.0543, found: 340.0536.



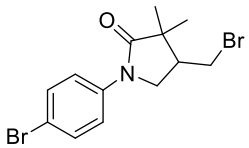
4-(bromomethyl)-1-(4-(*tert*-butyl)phenyl)-3,3-dimethylpyrrolidin-2-one (2h)

Yield: 80% (54 mg). Yellow solid, m.p. = 119–121 ℃, R_f = 0.44 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.43 – 7.35 (m, 2H), 3.98 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.63 – 3.51 (m, 2H), 3.39 (dd, *J* = 10.8, 10.1 Hz, 1H), 2.58 (dddd, *J* = 10.9, 8.5, 7.4, 4.6 Hz, 1H), 1.31 (d, *J* = 1.1 Hz, 12H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 147.6, 136.6, 131.01, 125.7, 119.4, 50.5, 45.5, 45.2, 34.4, 31.3, 31.3, 24.4, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{25}BrNO]^+$: 338.1114, found: 338.1107.



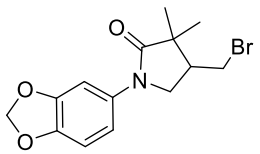
4-(bromomethyl)-1-(4-chlorophenyl)-3,3-dimethylpyrrolidin-2-one (2i)

Yield: 81% (51 mg). White solid, m.p. = 126–129 ℃, R_f = 0.40 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.37 – 7.28 (m, 2H), 3.96 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.62 – 3.48 (m, 2H), 3.38 (t, *J* = 10.5 Hz, 1H), 2.59 (dddd, *J* = 10.8, 8.7, 7.5, 4.6 Hz, 1H), 1.31 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 137.8, 129.7, 128.9, 120.8, 50.5, 45.3, 45.2, 31.0, 24.3, 18.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}BrClNO]^+$: 316.0098, found: 316.0091.



4-(bromomethyl)-1-(4-bromophenyl)-3,3-dimethylpyrrolidin-2-one (2j)

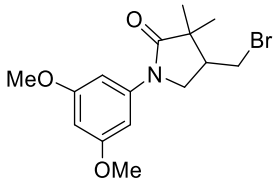
Yield: 75% (54 mg). White solid, m.p. = 129–131 ℃, R_f =0.46 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.48 (s, 2H), 3.96 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.62 – 3.47 (m, 2H), 3.38 (t, *J* = 10.5 Hz, 1H), 2.58 (dddd, *J* = 10.8, 8.7, 7.5, 4.6 Hz, 1H), 1.31 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 138.3, 131.8, 121.2, 117.4, 50.4, 45.3, 45.7, 31.0, 24.3, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}Br_2NO]^+$: 359.9593, found: 359.9586.



1-(benzo[d][1,3]dioxol-5-yl)-4-(bromomethyl)-3,3-dimethylpyrrolidin-2-one (2k)

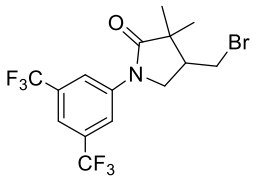
Yield: 76% (50 mg). Yellow oil, R_f = 0.20 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.78 (d, *J* = 8.4 Hz,

1H), 5.95 (s, 2H), 3.92 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.58 (dd, *J* = 10.1, 4.6 Hz, 1H), 3.50 (dd, *J* = 10.0, 8.7 Hz, 1H), 3.38 (t, *J* = 10.5 Hz, 1H), 2.57 (dddd, *J* = 10.8, 8.6, 7.5, 4.6 Hz, 1H), 1.30 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 147.8, 144.5, 133.6, 112.9, 107.9, 102.7, 101.3, 51.2, 45.4, 45.1, 31.2, 24.3, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{17}BrNO_3]^+$: 326.0386, found: 326.0378.



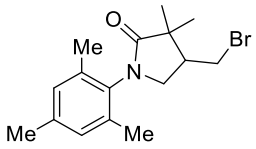
4-(bromomethyl)-1-(3,5-dimethoxyphenyl)-3,3-dimethylpyrrolidin-2-one (2l)

Yield: 79% (54 mg). Yellow oil, R_f = 0.22 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 2.2 Hz, 2H), 6.27 (t, *J* = 2.2 Hz, 1H), 3.96 (d, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 3.63 – 3.46 (m, 2H), 3.37 (t, *J* = 10.4 Hz, 1H), 2.56 (dtd, *J* = 16.0, 8.1, 4.6 Hz, 1H), 1.31 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 160.9, 141.0, 98.1, 96.9, 55.4, 50.8, 45.6, 45.2, 31.1, 29.7, 24.3, 18.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{21}BrNO_3]^+$: 342.0699, found: 342.0690.



1-(3,5-bis(trifluoromethyl)phenyl)-4-(bromomethyl)-3,3-dimethylpyrrolidin-2-one (2m)

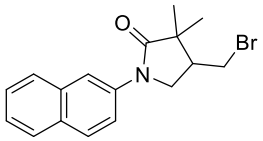
Yield: 47% (39 mg). White solid, m.p. = 99–102 ℃, R_f = 0.53 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.65 (s, 1H), 4.06 (dd, *J* = 9.8, 7.5 Hz, 1H), 3.73 – 3.52 (m, 2H), 3.41 (t, *J* = 10.5 Hz, 1H), 2.65 (dddd, *J* = 10.7, 8.7, 7.5, 4.5 Hz, 1H), 1.35 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 140.5, 132.3 (q, *J* = 33.1 Hz), 123.1 (q, *J* = 274.0 Hz), 118.9, 117.6, 117.6, 50.2, 45.4, 45.2, 30.5, 29.7, 24.2, 18.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{15}BrF_6NO]^+$: 418.0236, found: 418.0227.



4-(bromomethyl)-1-mesityl-3,3-dimethylpyrrolidin-2-one (2n)

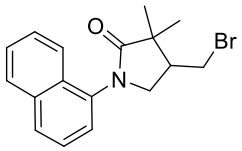
Yield: 21% (14 mg). Yellow oil, R_f = 0.16 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 6.7 Hz, 2H), 3.68 – 3.57 (m, 2H), 3.47 – 3.32 (m, 2H), 2.68 (dddd, *J* = 11.1, 8.7, 7.5, 4.8 Hz, 1H), 2.27 (s, 3H), 2.14 (d, *J* = 2.0 Hz, 6H), 1.33 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 138.0, 135.6, 135.6, 132.8, 129.4, 129.4,

50.9, 47.0, 44.1, 31.4, 24.5, 21.0, 18.6, 17.7, 17.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{16}H_{23}BrNO]^+$: 324.0958, found: 324.0951.



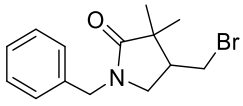
4-(bromomethyl)-3,3-dimethyl-1-(naphthalen-2-yl)pyrrolidin-2-one (2o)

Yield: 80% (53 mg). Yellow solid, m.p. = 142–145 ℃, R_f = 0.26 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.83 (dd, *J* = 15.5, 8.6 Hz, 3H), 7.45 (dddd, *J* = 19.2, 8.2, 6.8, 1.3 Hz, 2H), 4.13 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.74 – 3.59 (m, 2H), 3.45 (t, *J* = 10.5 Hz, 1H), 2.66 (dddd, *J* = 10.8, 8.6, 7.5, 4.6 Hz, 1H), 1.37 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 137.0, 133.5, 130.7, 128.6, 127.7, 127.5, 126.5, 125.3, 119.6, 116.7, 50.8, 45.5, 45.4, 31.2, 24.4, 18.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{19}BrNO]^+$: 332.0645, found: 332.0639.



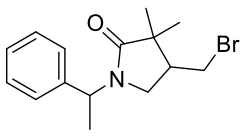
4-(bromomethyl)-3,3-dimethyl-1-(naphthalen-1-yl)pyrrolidin-2-one (2p)

Yield: 46% (31 mg). Yellow oil, R_f = 0.38 (EA/PE = 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.79 – 7.73 (m, 1H), 7.66 – 7.54 (m, 1H), 7.49 – 7.38 (m, 3H), 7.28 (dd, *J* = 7.3, 1.2 Hz, 1H), 3.91 (dd, *J* = 10.2, 7.5 Hz, 1H), 3.63 – 3.50 (m, 2H), 3.42 (t, *J* = 10.4 Hz, 1H), 2.75 (dddd, *J* = 10.7, 8.7, 7.5, 4.8 Hz, 1H), 1.36 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 135.1, 134.6, 129.7, 128.6, 128.5, 126.8, 126.4, 125.6, 124.6, 122.4, 53.8, 46.9, 44.5, 31.2, 24.5, 18.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{19}BrNO]^+$: 332.0645, found: 332.0636.



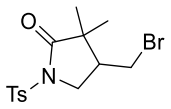
1-benzyl-4-(bromomethyl)-3,3-dimethylpyrrolidin-2-one (2q)[2]

Yield: 90% (53 mg). Yellow oil, R_f = 0.16 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 3H), 7.24 – 7.18 (m, 2H), 4.54 (d, *J* = 14.6 Hz, 1H), 4.38 (d, *J* = 14.6 Hz, 1H), 3.49 (dd, *J* = 10.0, 4.8 Hz, 1H), 3.38 (dd, *J* = 10.1, 7.6 Hz, 1H), 3.25 (t, *J* = 10.4 Hz, 1H), 2.91 (dd, *J* = 10.1, 8.6 Hz, 1H), 2.44 (dddd, *J* = 10.7, 8.5, 7.6, 4.8 Hz, 1H), 1.26 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 136.3, 128.7, 128.0, 127.6, 48.9, 46.6, 46.1, 44.0, 31.7, 24.2, 18.3.



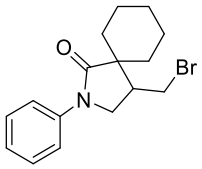
4-(bromomethyl)-3,3-dimethyl-1-(2-phenylpropyl)pyrrolidin-2-one (2r)

Yield: 40% (26 mg). Yellow oil, R_f = 0.38 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 5H), 5.47 (q, *J* = 7.1 Hz, 1H), 3.50 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.28 (t, *J* = 10.4 Hz, 1H), 3.15 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.98 (dd, *J* = 10.0, 8.4 Hz, 1H), 2.31 (dtd, *J* = 10.7, 8.0, 4.8 Hz, 1H), 1.52 (d, *J* = 7.1 Hz, 3H), 1.22 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 140.0, 128.6, 127.5, 126.9, 48.9, 45.8, 44.6, 44.3, 31.5, 24.1, 18.2, 15.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{16}H_{23}BrNO]^+$: 310.0801, found: 310.0795.



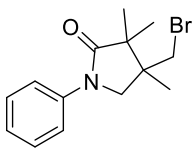
4-(bromomethyl)-3,3-dimethyl-1-tosylpyrrolidin-2-one (2s)[2]

Yield: 40% (29 mg). White solid, R_f = 0.19 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.14 (dd, *J* = 10.3, 7.4 Hz, 1H), 3.49 – 3.41 (m, 2H), 3.20 (t, *J* = 10.3 Hz, 1H), 2.44 (s, 4H), 1.16 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 145.3, 134.8, 129.7, 128.0, 48.8, 45.4, 45.0, 29.7, 23.4, 21.7, 17.8.



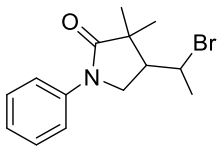
4-(bromomethyl)-2-phenyl-2-azaspiro[4.5]decan-1-one (2t)

Yield: 39% (25 mg). Yellow oil, R_f = 0.48 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.42 – 7.33 (m, 2H), 7.20 – 7.11 (m, 1H), 4.00 (dd, *J* = 10.3, 6.6 Hz, 1H), 3.78 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.67 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.34 (dd, *J* = 11.5, 10.2 Hz, 1H), 2.67 (ddt, *J* = 11.5, 6.6, 3.3 Hz, 1H), 1.94 – 1.77 (m, 3H), 1.66 – 1.35 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 139.4, 128.8, 124.5, 119.8, 49.8, 49.1, 42.3, 33.4, 32.6, 27.6, 25.3, 22.4, 22.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{16}H_{21}BrNO]^+$: 322.0801, found: 322.0794.



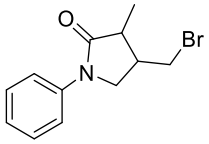
4-(bromomethyl)-3,3,4-trimethyl-1-phenylpyrrolidin-2-one (2u)[2]

Yield: 40% (24 mg). Yellow oil, R_f = 0.30 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.42 – 7.33 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 3.83 (d, *J* = 10.0 Hz, 1H), 3.58 (d, *J* = 10.3 Hz, 1H), 3.46 (dd, *J* = 14.1, 10.2 Hz, 2H), 1.25 (s, 3H), 1.20 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 139.3, 128.8, 124.5, 119.7, 55.8, 48.2, 42.2, 40.1, 20.4, 19.8 , 19.3.



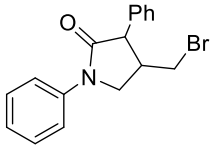
4-(1-bromoethyl)-3,3-dimethyl-1-phenylpyrrolidin-2-one (2v)[2]

Yield: 41% (27 mg). Yellow oil, R_f = 0.29 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.42 – 7.33 (m, 2H), 7.19 – 7.11 (m, 1H), 4.28 (dq, *J* = 10.0, 6.6 Hz, 1H), 3.99 (dd, *J* = 10.1, 7.7 Hz, 1H), 3.55 (t, *J* = 9.8 Hz, 1H), 2.44 (td, *J* = 9.8, 7.7 Hz, 1H), 1.90 (d, *J* = 6.7 Hz, 3H), 1.39 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 139.2, 128.8, 124.6, 119.9, 51.6, 51.4, 50.5, 45.3, 26.0, 25.6, 18.0.



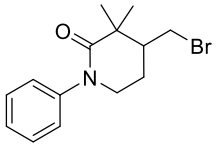
4-(bromomethyl)-3-methyl-1-phenylpyrrolidin-2-one (2w) (dr = 5:1)

Yield: 44% (24 mg). White solid, m.p. = 67–70 °C, R_f = 0.32 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2.2H), 7.37 (t, *J* = 7.9 Hz, 2.2H), 7.15 (t, *J* = 7.4 Hz, 1.1H), 4.00 – 3.88 (m, 1.2H), 3.77 – 3.71 (dd, *J* = 1.2, 1.4 Hz, 0.2H), 3.71 – 3.59 (m, 2H), 3.59 – 3.48 (dd, *J* = 1.2, 1.4 Hz, 0.2H), 3.48 (dd, *J* = 10.4, 7.8 Hz, 1H), 3.48 – 3.32 (t, *J* = 2.5 Hz, 0.2H), 2.98 – 2.81 (m, 0.4H), 2.47 (qd, *J* = 13.2, 11.3, 7.8 Hz, 2H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.24 (d, *J* = 7.1 Hz, 0.6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 139.1, 128.9, 124.6, 119.8, 119.8, 51.3, 51.2, 43.1, 42.1, 41.6, 38.2, 34.1, 31.8, 14.8, 10.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{12}H_{15}BrNO]^+$: 268.0332, found: 268.0325.



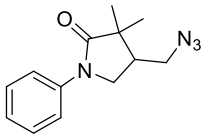
4-(bromomethyl)-1,3-diphenylpyrrolidin-2-one (2x) (dr = 10:3)

Yield: 50% (33 mg). Yellow solid, m.p. = 93–95 °C, (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2.6H), 7.39 – 7.18 (m, 10.9H), 4.13 – 4.07 (m, 0.3H), 4.07 ‒ 4.04 (m, 0.3H), 4.02 (dd, *J* = 9.8, 7.8 Hz, 1H), 3.84 – 3.79 (m, 0.3H), 3.79 (dd, *J* = 9.8, 8.4 Hz, 1H), 3.71 (d, *J* = 10.0 Hz, 1H), 3.61 (dd, *J* = 10.5, 3.9 Hz, 1H), 3.48 (dd, *J* = 10.5, 7.7 Hz, 1H), 3.19 – 3.06 (m, 0.6H), 2.99 – 2.91 (t, *J* = 8.0 Hz, 0.3H), 2.85 (dqd, *J* = 9.9, 7.9, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 172.5, 139.0, 138.9, 137.1, 134.2, 129.0, 128.9, 128.9, 128.5, 127.8, 127.7, 125.0, 124.8, 120.1, 119.8, 54.6, 53.5, 51.7, 51.0, 43.0, 39.3, 33.8, 32.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{17}BrNO]^+$: 330.0488, found: 330.0482.



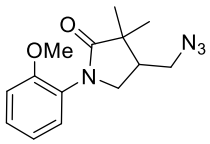
4-(bromomethyl)-3,3-dimethyl-1-phenylpiperidin-2-one (2y)

Yield: 20% (22 mg). Yellow oil, R_f = 0.49 (EA/PE = 1:5, v/v) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 2H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.81 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.11 – 4.98 (m, 2H), 3.78 (t, *J* = 7.2 Hz, 2H), 2.49 – 2.39 (m, 2H), 1.35 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.3, 141.8, 136.0, 134.5, 127.5, 122.4, 122.3, 117.4, 108.3, 44.1, 39.0, 31.9, 24.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{19}BrNO]^+$: 296.0465, found: 296.0640.



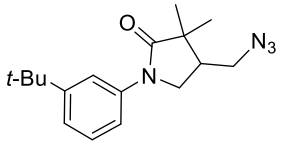
4-(azidomethyl)-3,3-dimethyl-1-phenylpyrrolidin-2-one (3a)

Yield: 51% (25 mg). Yellow oil, R_f = 0.41 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.41 – 7.33 (m, 2H), 7.19 – 7.10 (m, 1H), 3.89 (dd, *J* = 9.9, 7.6 Hz, 1H), 3.65 – 3.50 (m, 2H), 3.41 (dd, *J* = 12.2, 9.3 Hz, 1H), 2.38 (dtd, *J* = 9.3, 7.9, 5.8 Hz, 1H), 1.32 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 139.3, 128.9, 124.6, 119.7, 50.8, 49.0, 43.9, 42.4, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2099, 1695. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{17}N_4O]^+$: 245.1397, found: 245.1394.



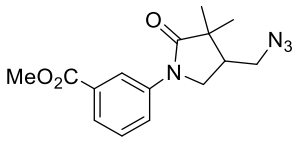
4-(azidomethyl)-1-(2-methoxyphenyl)-3,3-dimethylpyrrolidin-2-one (3b)

Yield: 30% (17 mg). Yellow oil, R_f = 0.44 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.00 – 6.94 (m, 1H), 3.88 (dd, *J* = 9.9, 7.6 Hz, 1H), 3.60 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.53 (dd, *J* = 9.9, 8.2 Hz, 1H), 3.41 (dd, *J* = 12.2, 9.3 Hz, 1H), 2.36 (s, 4H), 1.31 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 139.2, 138.8, 128.7, 125.4, 120.5, 116.7, 50.9, 49.0, 43.8, 42.4, 24.6, 21.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1700. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{19}N_4O_2]^+$: 275.1503, found: 275.1502.



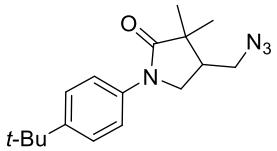
4-(azidomethyl)-1-(3-(*tert*-butyl)phenyl)-3,3-dimethylpyrrolidin-2-one (3f)

Yield: 49% (29 mg). Yellow oil, R_f = 0.47 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.42 – 7.36 (m, 2H), 3.87 (dd, *J* = 9.9, 7.6 Hz, 1H), 3.59 (dd, *J* = 12.2, 5.9 Hz, 1H), 3.53 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.40 (dd, *J* = 12.2, 9.3 Hz, 11H), 2.43 – 2.31 (m, 1H), 1.31 (s, 12H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 152.1, 139.1, 128.4, 121.8, 117.2, 116.7, 50.8, 49.1, 43.9, 42.4, 34.9, 31.3, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1699. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{25}N_4O]^+$: 301.2023, found: 301.2017.



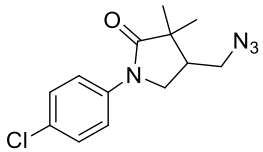
methyl 3-(4-(azidomethyl)-3,3-dimethyl-2-oxopyrrolidin-1-yl)benzoate (3g)

Yield: 45% (27 mg). Yellow oil, R_f = 0.20 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.83 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 3.92 (s, 4H), 3.66 – 3.54 (m, 2H), 3.43 (dd, *J* = 12.2, 9.1 Hz, 1H), 2.40 (dtd, *J* = 9.1, 7.9, 5.9 Hz, 1H), 1.33 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 166.7, 139.5, 130.8, 129.0, 125.6, 124.4, 120.0, 52.3, 50.7, 48.9, 43.9, 42.3, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1701. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{19}N_4O_3]^+$: 303.1452, found: 303.1444.



4-(azidomethyl)-1-(4-(*tert*-butyl)phenyl)-3,3-dimethylpyrrolidin-2-one (3h)

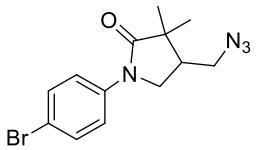
Yield: 52% (31 mg). Yellow solid, m.p. = 72–75 °C, R_f =0.36 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.42 – 7.36 (m, 2H), 3.87 (dd, *J* = 9.9, 7.6 Hz, 1H), 3.59 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.53 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.40 (dd, *J* = 12.3, 9.3 Hz, 1H), 2.37 (dtd, *J* = 9.3, 7.9, 5.8 Hz, 1H), 1.31 (s, 12H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 147.6, 136.7, 125.7, 119.4, 50.8, 48.9, 43.8, 42.4, 34.4, 31.5, 31.3, 29.7, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1698. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{25}N_4O]^+$: 301.2023, found: 301.2016



4-(azidomethyl)-1-(4-chlorophenyl)-3,3-dimethylpyrrolidin-2-one (3i)

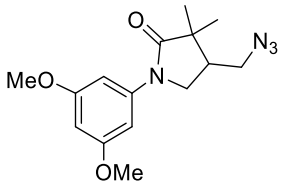
Yield: 34% (19 mg). Yellow oil, R_f = 0.32 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.0 Hz, 2H), 7.37 – 7.29 (m, 2H), 3.86 (dd, *J* = 9.8, 7.6 Hz, 1H), 3.60 (dd, *J* = 12.3, 5.8 Hz, 1H), 3.51 (dd, *J* = 9.8, 8.3 Hz, 1H), 3.41 (dd, *J* = 12.3, 9.2 Hz, 1H), 2.38 (dtd, *J* = 9.3, 7.9, 5.8 Hz, 1H), 1.31 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 177.8, 137.9, 129.7, 128.9, 120.8, 50.7, 48.9, 43.8, 42.3, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1700. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}ClN_4O]^+$: 279.1007, found: 279.1005.



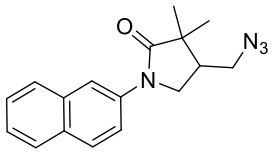
4-(azidomethyl)-1-(4-bromophenyl)-3,3-dimethylpyrrolidin-2-one (3j)

Yield: 36% (23 mg). Yellow oil, R_f = 0.36 (EA/PE = 1:5, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.50 – 7.43 (m, 2H), 3.85 (dd, *J* = 9.8, 7.6 Hz, 1H), 3.60 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.50 (dd, *J* = 9.8, 8.2 Hz, 1H), 3.40 (dd, *J* = 12.3, 9.2 Hz, 1H), 2.38 (dtd, *J* = 9.3, 7.9, 5.7 Hz, 1H), 1.31 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 138.4, 131.8, 121.1, 117.4, 50.7, 48.8, 43.8, 42.3, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1699. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{13}H_{16}BrN_4O]^+$: 323.0502, found: 323.0494.



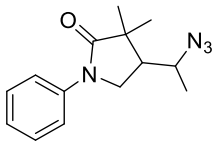
4-(azidomethyl)-1-(3,5-dimethoxyphenyl)-3,3-dimethylpyrrolidin-2-one (3l)

Yield: 42% (26 mg). Yellow oil, R_f = 0.16 (EA/PE = 1:5, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 2.2 Hz, 2H), 6.28 (t, *J* = 2.2 Hz, 1H), 3.86 (dd, *J* = 9.9, 7.7 Hz, 1H), 3.80 (s, 6H), 3.59 (dd, *J* = 12.4, 5.9 Hz, 1H), 3.49 (dd, *J* = 9.9, 8.2 Hz, 1H), 3.40 (dd, *J* = 12.3, 9.2 Hz, 1H), 2.41 – 2.31 (m, 1H), 1.31 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 160.9, 141.1, 97.9, 96.9, 55.4, 50.8, 49.1, 44.2, 42.2, 24.6, 18.8. FT-IR (KBr, cm^{-1}): 2100, 1701. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{21}N_4O_3]^+$: 305.1608, found: 305.1602.



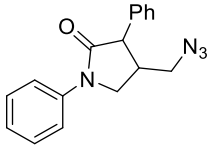
4-(azidomethyl)-3,3-dimethyl-1-(naphthalen-2-yl)pyrrolidin-2-one (3o)

Yield: 34% (20 mg). Yellow oil, R_f = 0.41 (EA/PE = 1:5, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.91 (d, *J* = 2.3 Hz, 1H), 7.82 (dd, *J* = 16.9, 8.5 Hz, 3H), 7.51 – 7.39 (m, 2H), 4.02 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.70 – 3.60 (m, 2H), 3.46 (dd, *J* = 12.3, 9.2 Hz, 1H), 2.50 – 2.39 (m, 1H), 1.36 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 137.0, 133.5, 130.7, 128.6, 127.6, 127.5, 126.5, 125.3, 119.5, 116.6, 50.8, 49.2, 43.9, 42.4, 24.6, 18.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{15}H_{21}N_4O_3]^+$: 295.1553, found: 295.1552.



4-(1-azidoethyl)-3,3-dimethyl-1-phenylpyrrolidin-2-one (3v)

Yield: 31% (16 mg). Yellow oil, R_f = 0.45 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H), 7.37 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 3.69 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.57 (dq, *J* = 10.0, 6.5 Hz, 1H), 3.39 (t, *J* = 9.7 Hz, 1H), 2.17 (td, *J* = 10.0, 8.0 Hz, 1H), 1.45 – 1.34 (m, 6H), 1.17 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 139.2, 128.9, 124.6, 119.7, 56.6, 48.0, 47.5, 44.5, 25.2, 18.6, 17.5. FT-IR (KBr, cm^{-1}): 2104, 1698. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{14}H_{19}N_4O]^+$: 259.1553, found: 259.1551.



4-(azidomethyl)-1,3-diphenylpyrrolidin-2-one (3x)

Yield: 37% (22 mg). Yellow oil, R_f = 0.21 (EA/PE = 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.43 – 7.36 (m, 4H), 7.34 – 7.29 (m, 1H), 7.26 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.20 – 7.15 (m, 1H), 4.00 (dd, *J* = 9.8, 7.9 Hz, 1H), 3.77 (dd, *J* = 9.8, 8.1 Hz, 1H), 3.70 – 3.59 (m, 2H), 3.51 (dd, *J* = 12.5, 7.3 Hz, 1H), 2.74 (dqd, *J* = 9.7, 7.8, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 139.1, 137.4, 129.0, 128.9, 128.5, 127.7, 124.8, 119.8, 53.1, 52.3, 49.8, 41.1. FT-IR (KBr, cm^{-1}): 2101, 1701. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{17}N_4O]^+$: 293.1397, found: 293.1396.

7. References

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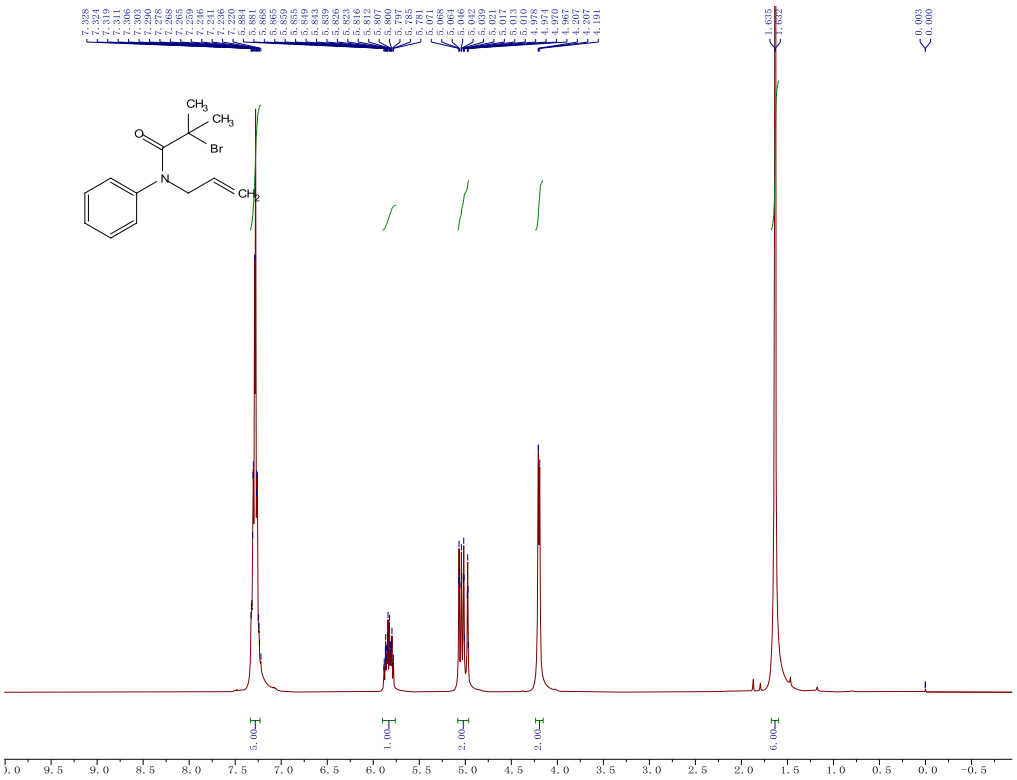
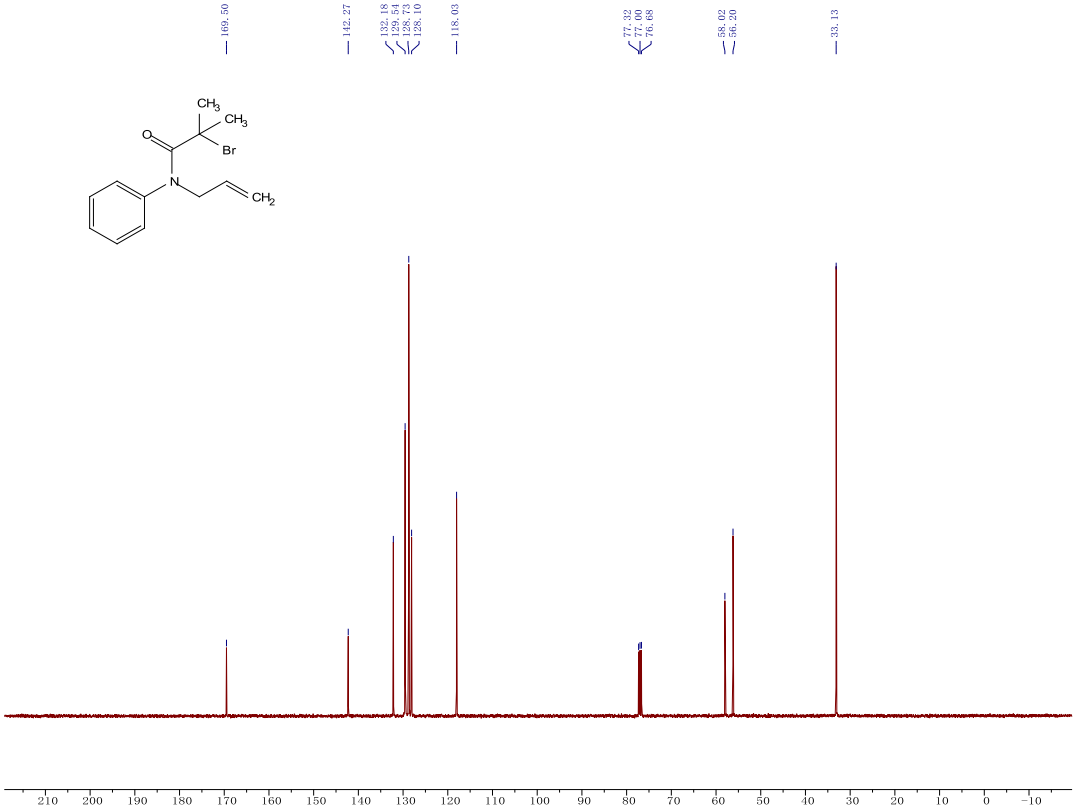
8. Copies of ^{1}H NMR and ^{13}C NMR Spectra

(1a)

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

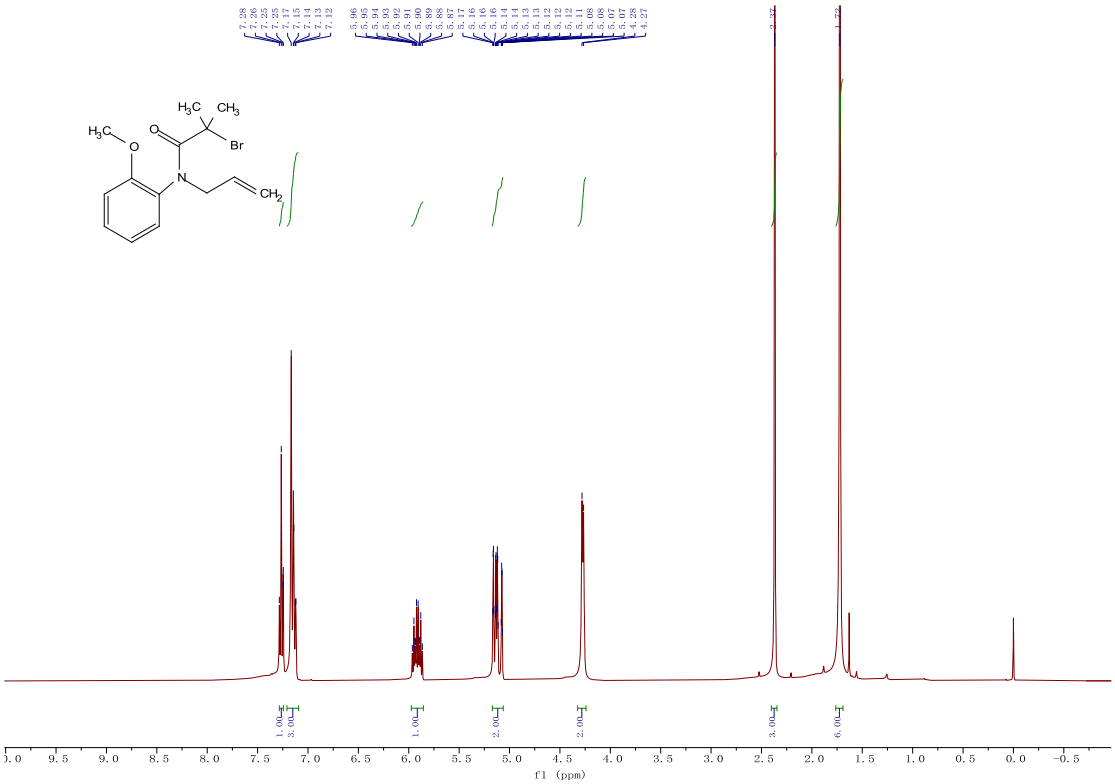


^{13}C NMR ($CDCl_3$, 101 MHz)

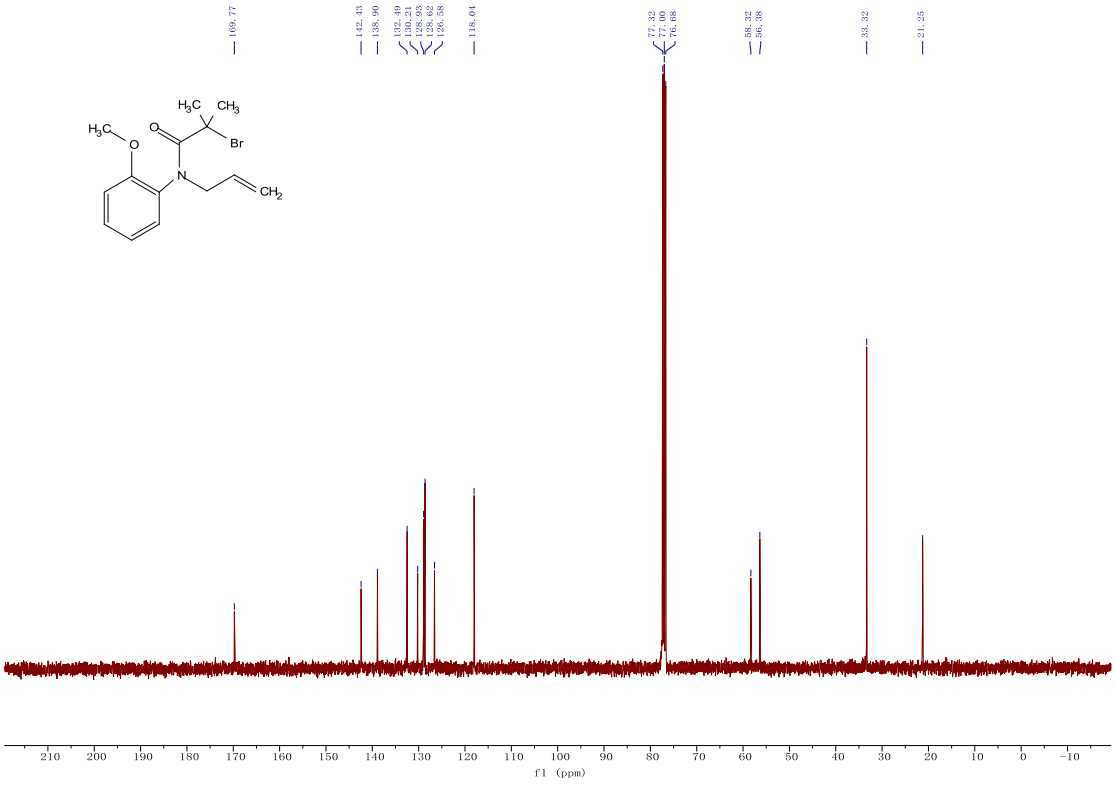


(1b)

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

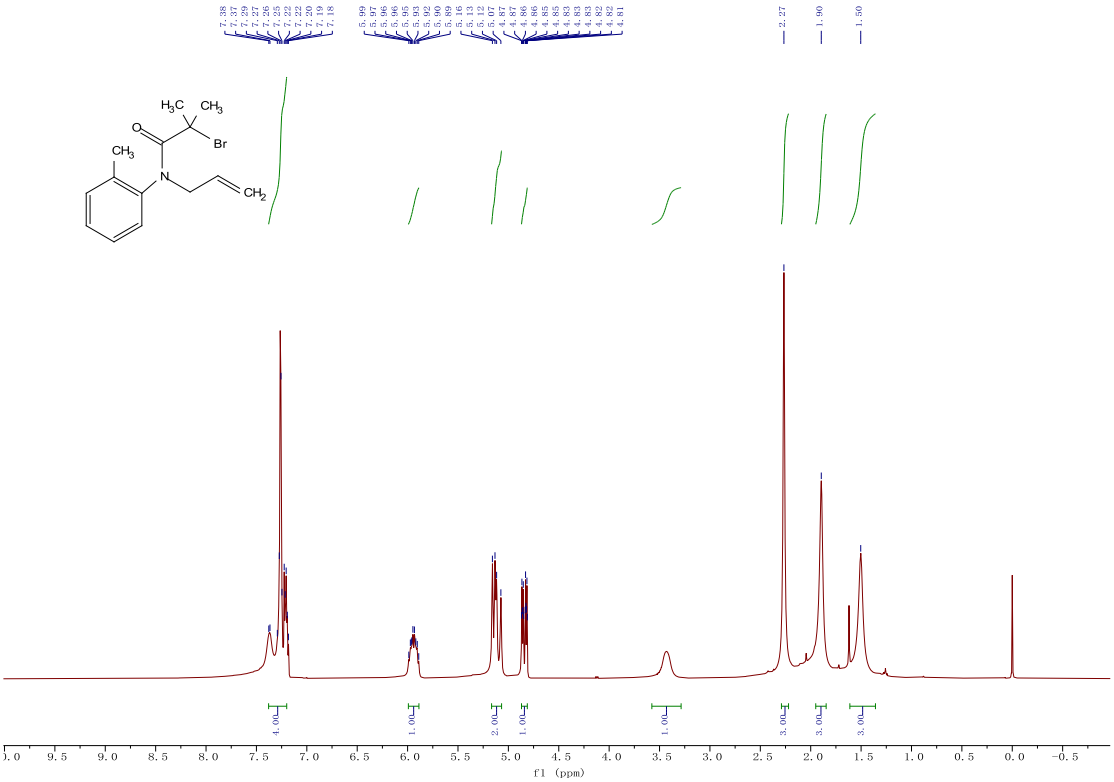


^{13}C NMR ($CDCl_3$, 101 MHz)

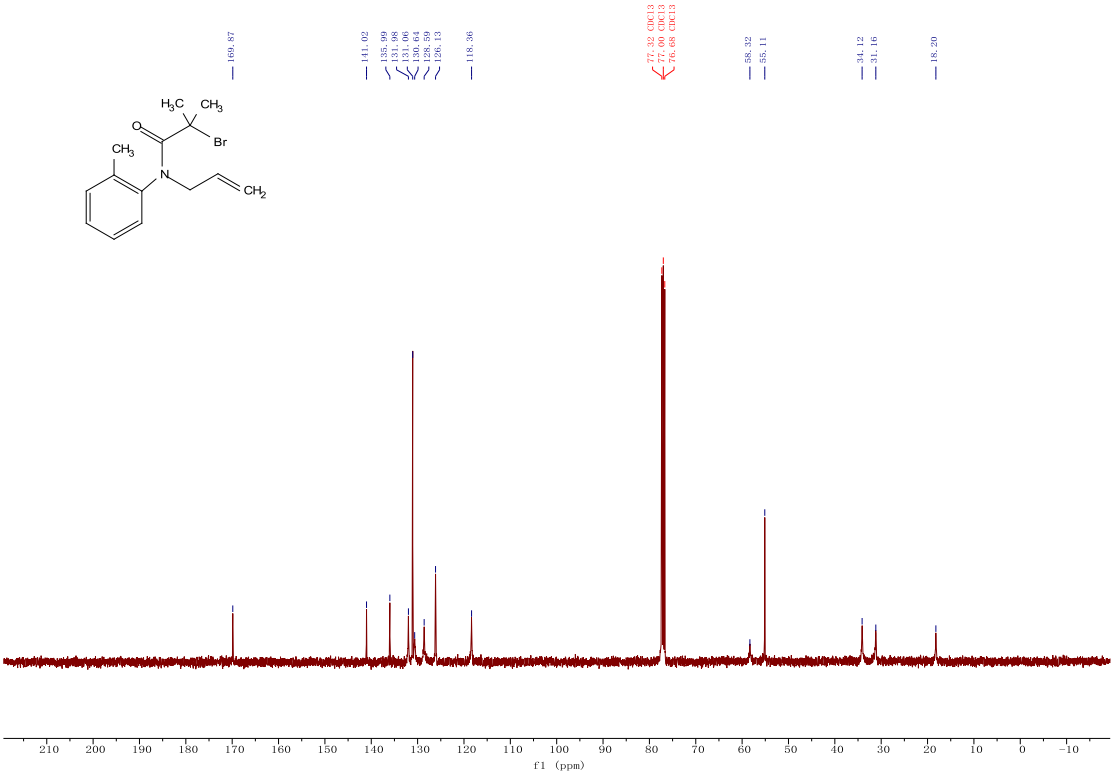


(1c)

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

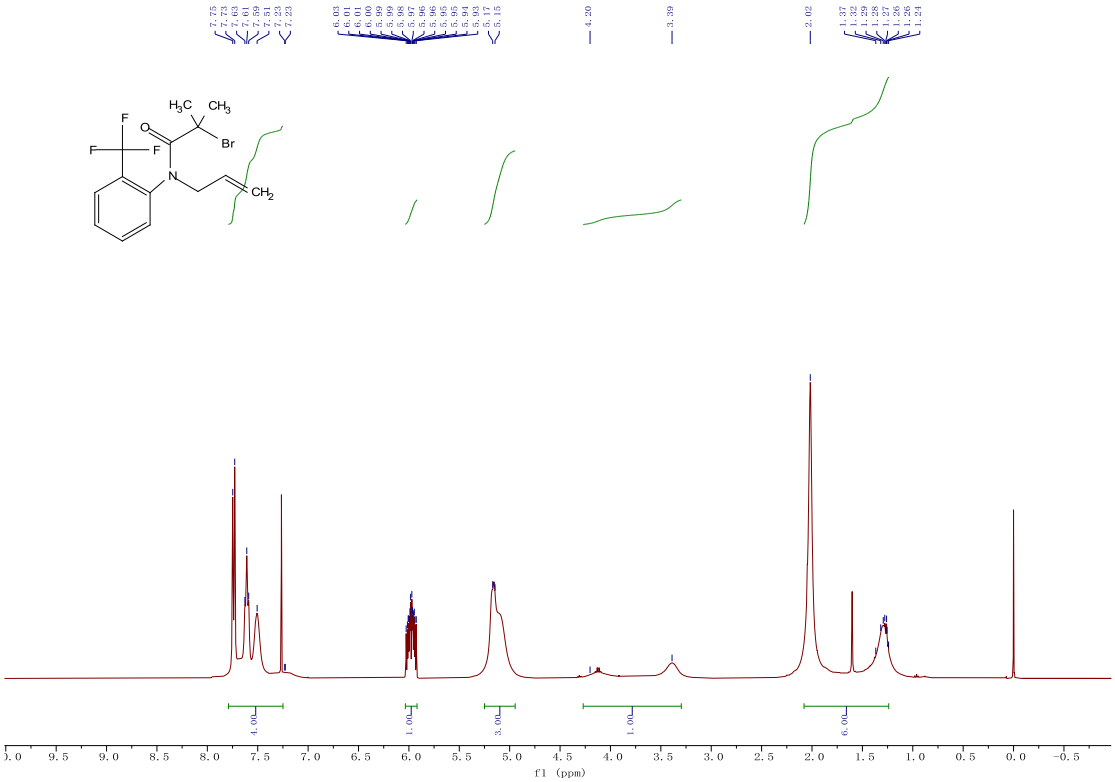


^{13}C NMR ($CDCl_3$, 101 MHz)

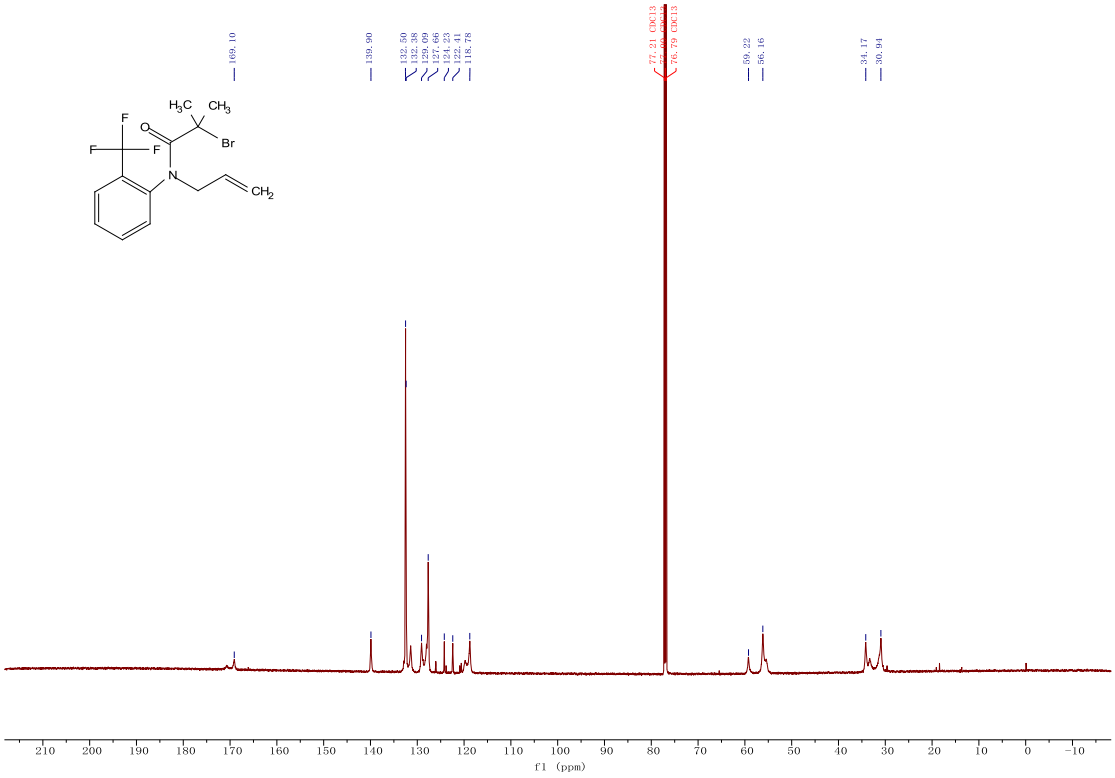


(1d)

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

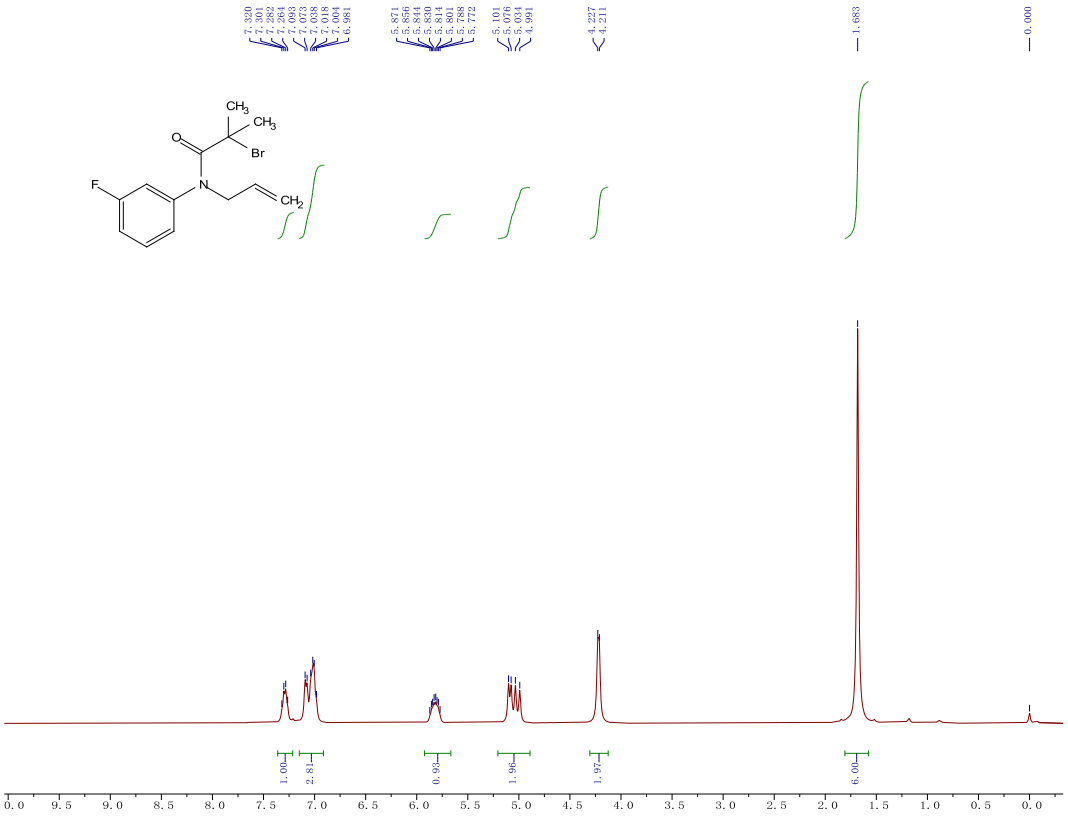


^{13}C NMR ($CDCl_3$, 151 MHz)

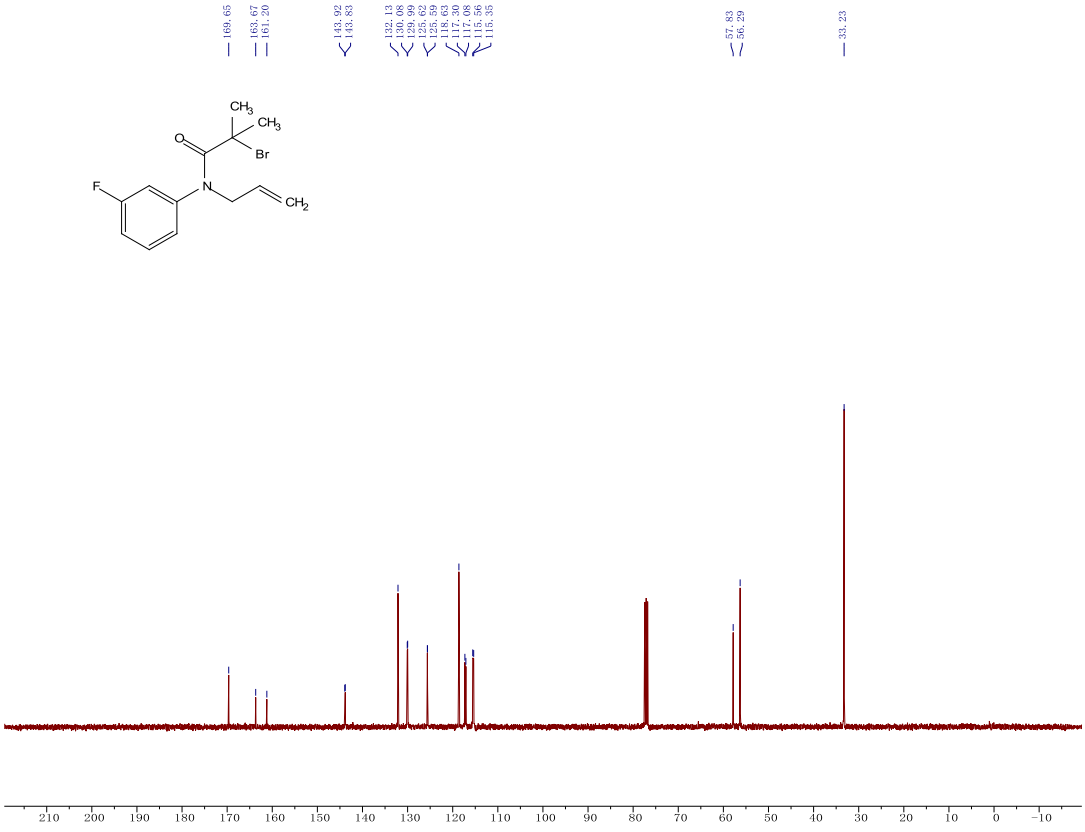


(1e)

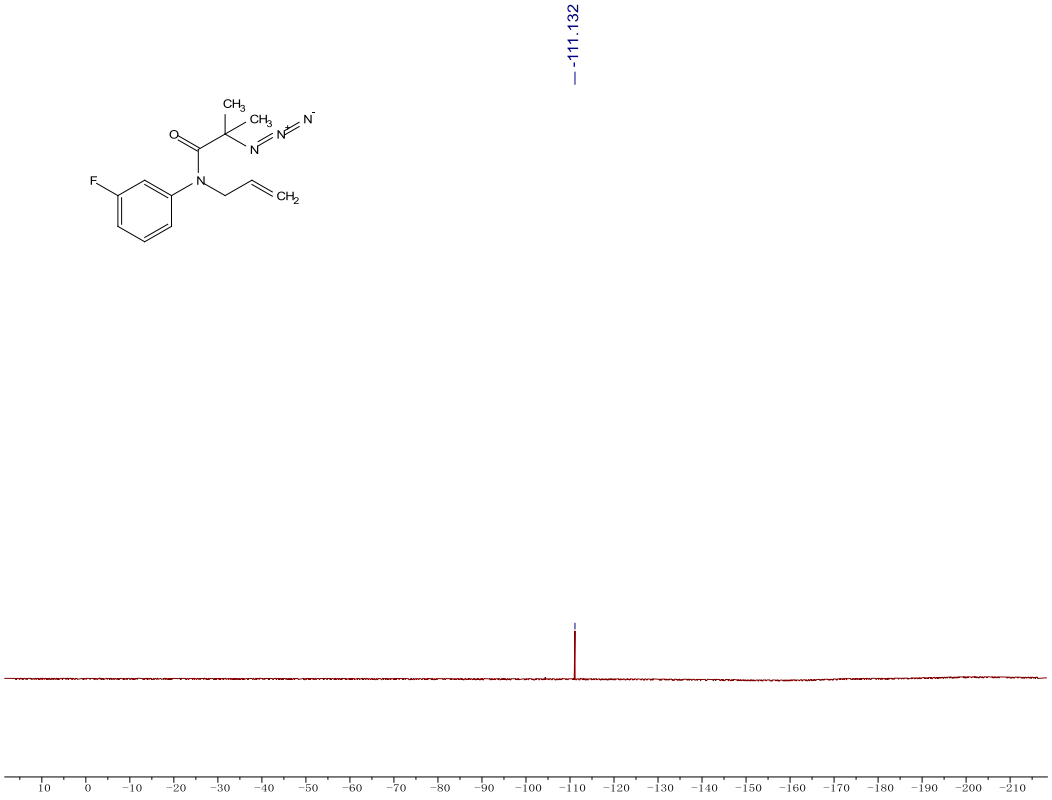
^{1}H NMR ($CDCl_3$, 400 MHz)



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

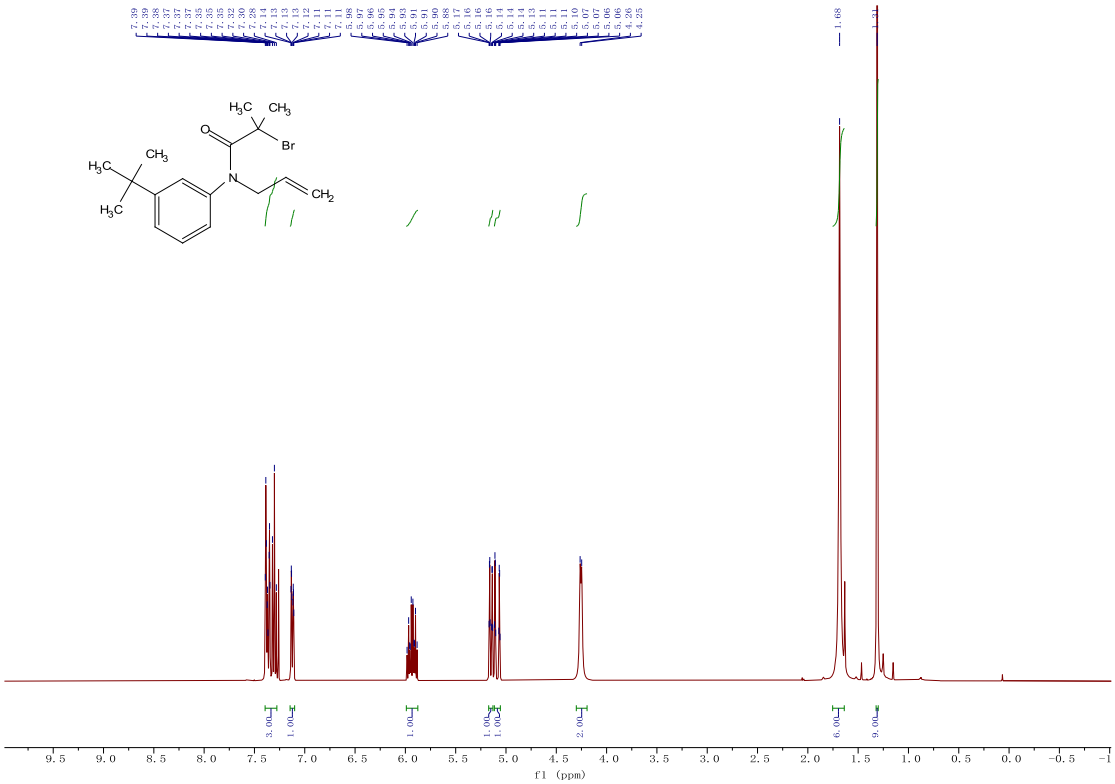


^{19}F NMR ($CDCl_3$, 376 MHz)

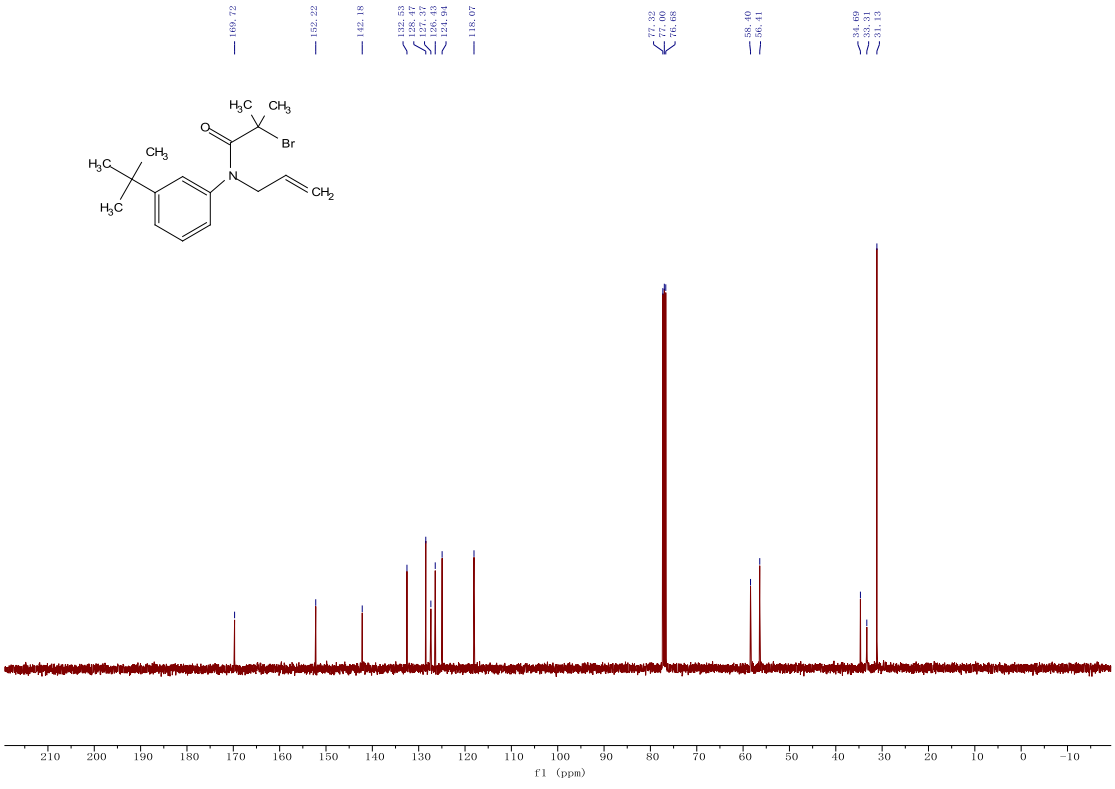


(1f)

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

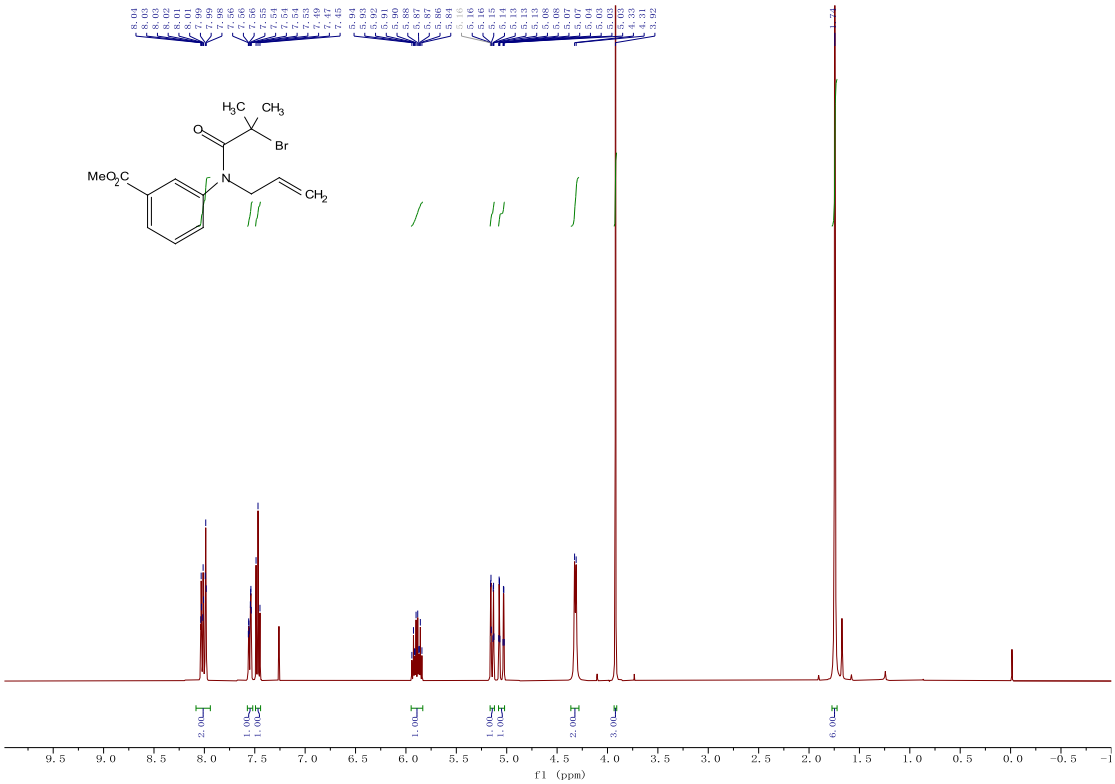


^{13}C NMR ($CDCl_3$, 101 MHz)

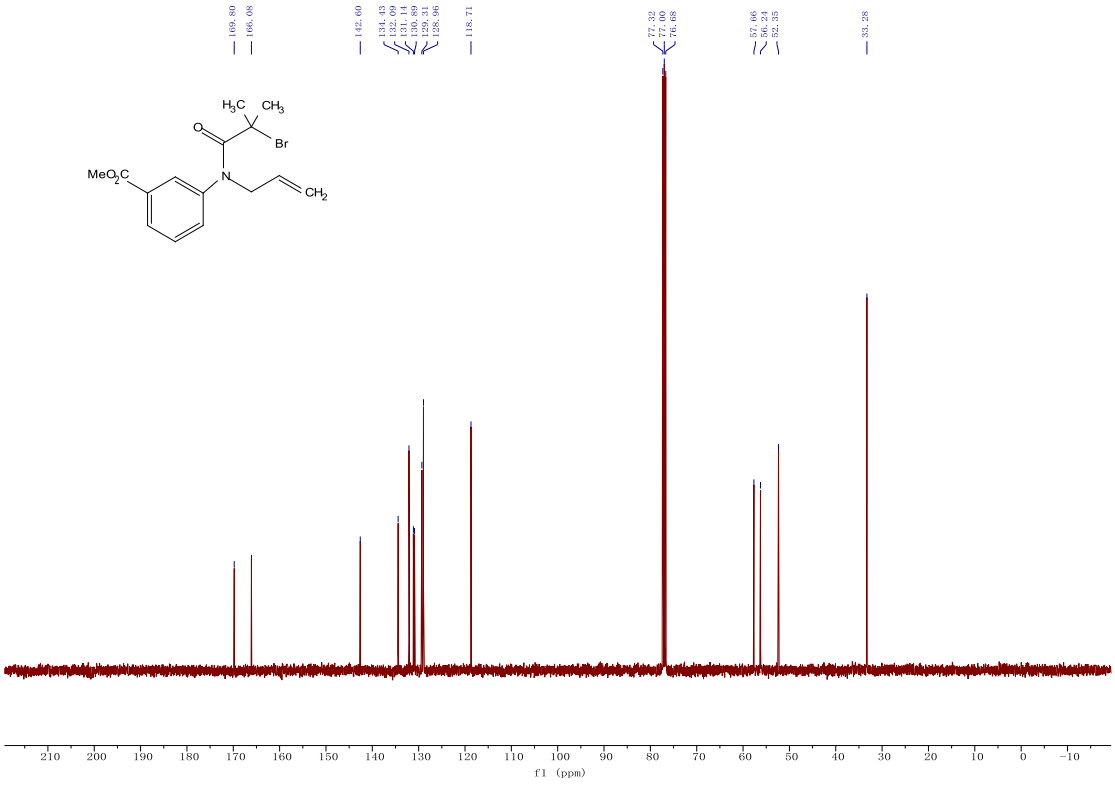


(1g)

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

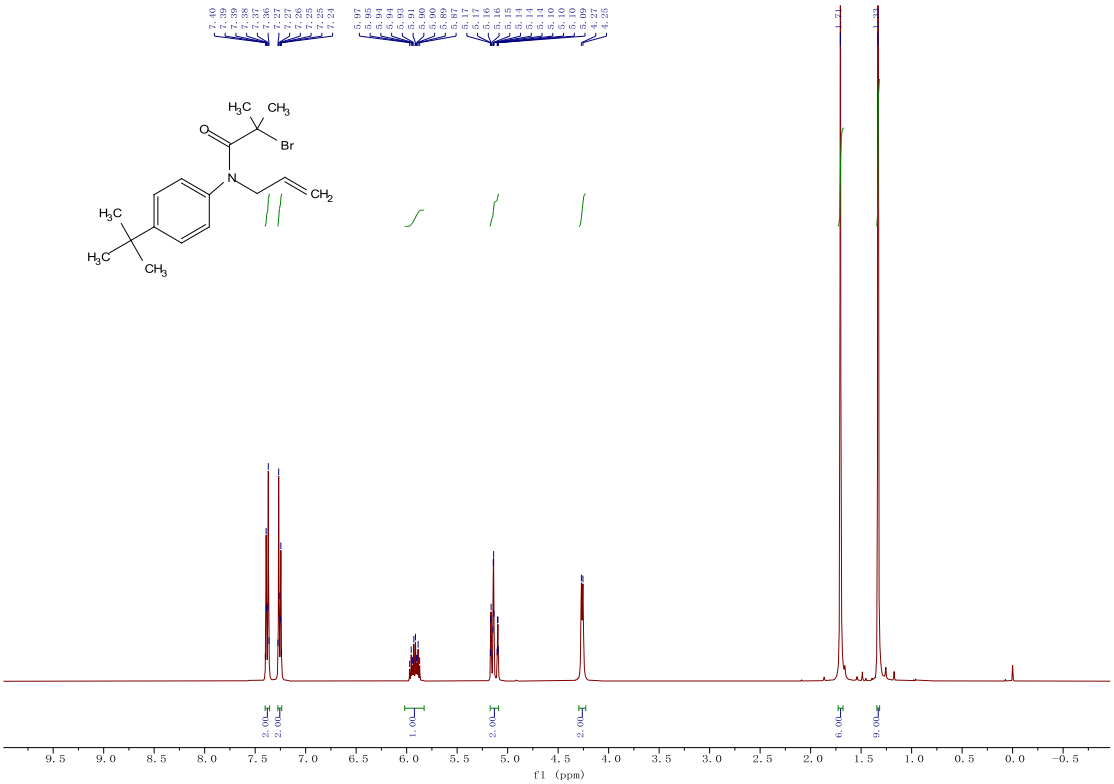


^{13}C NMR ($CDCl_3$, 101 MHz)

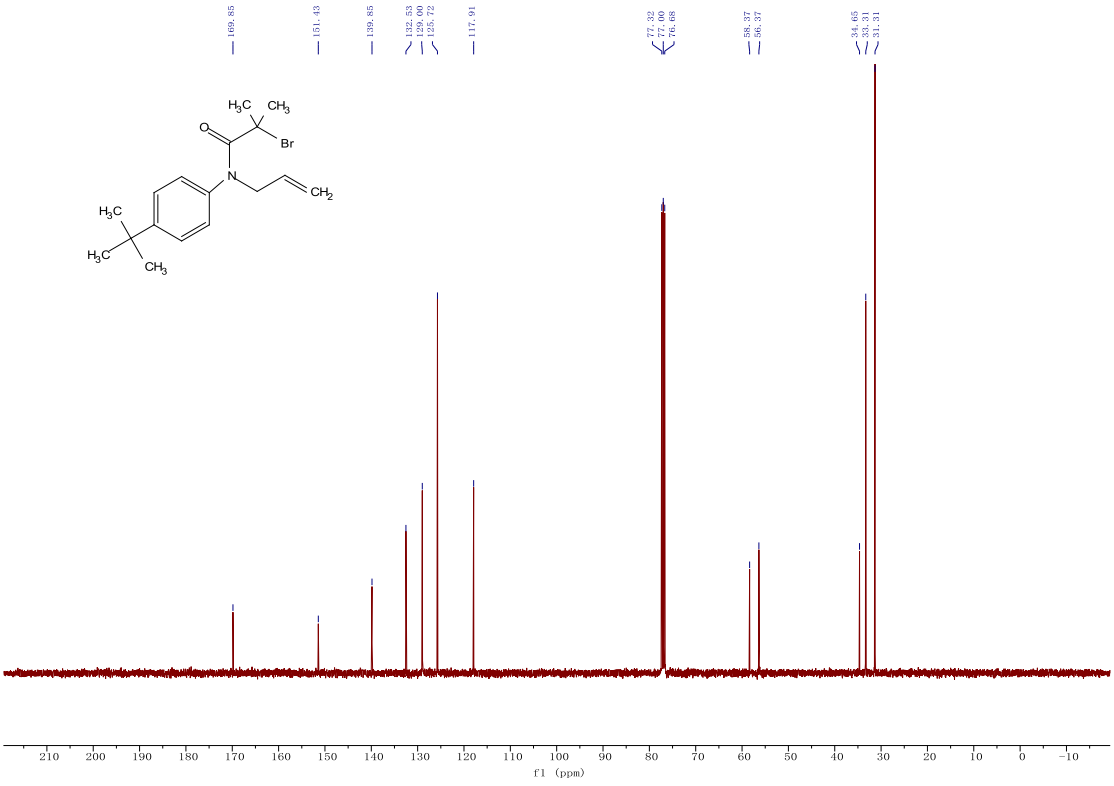


(1h)

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

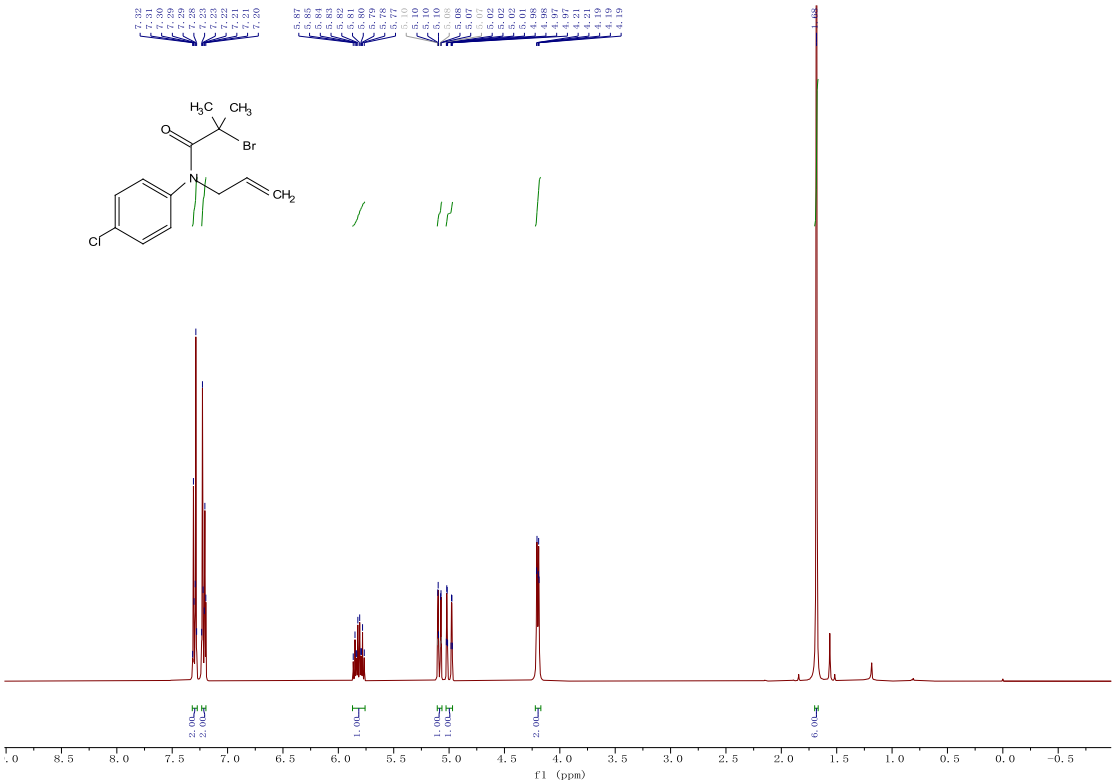


^{13}C NMR ($CDCl_3$, 101 MHz)

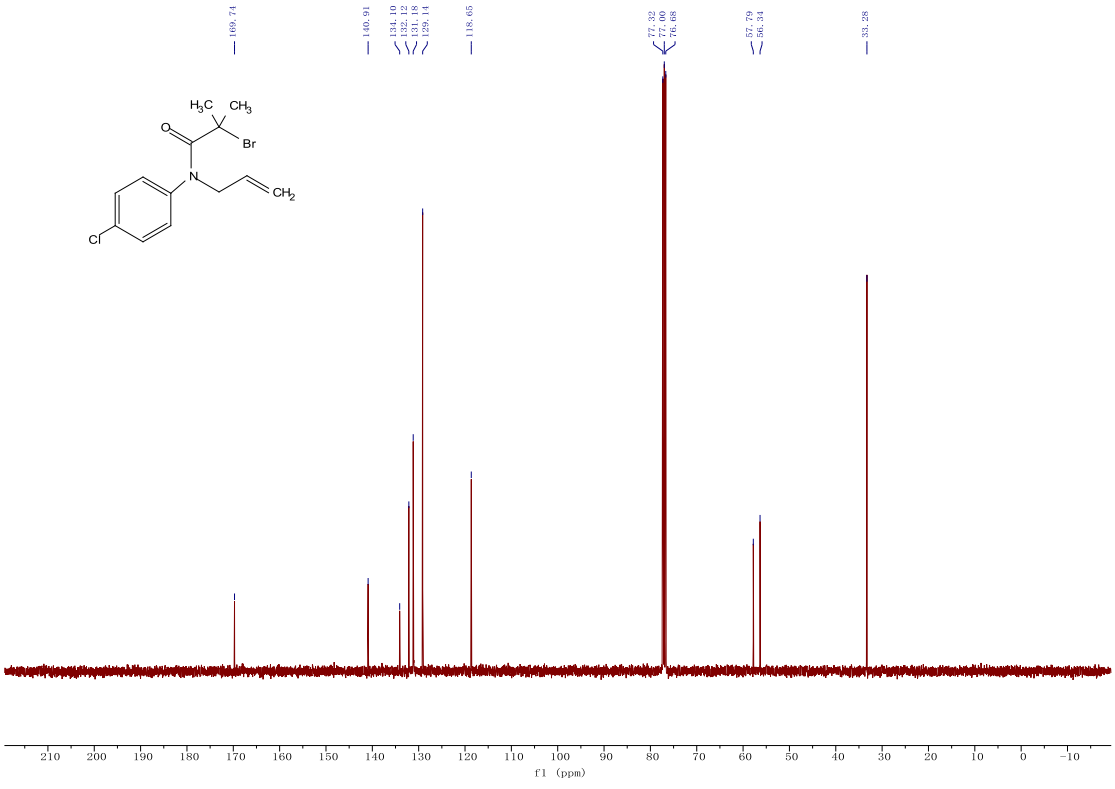


(1i)

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

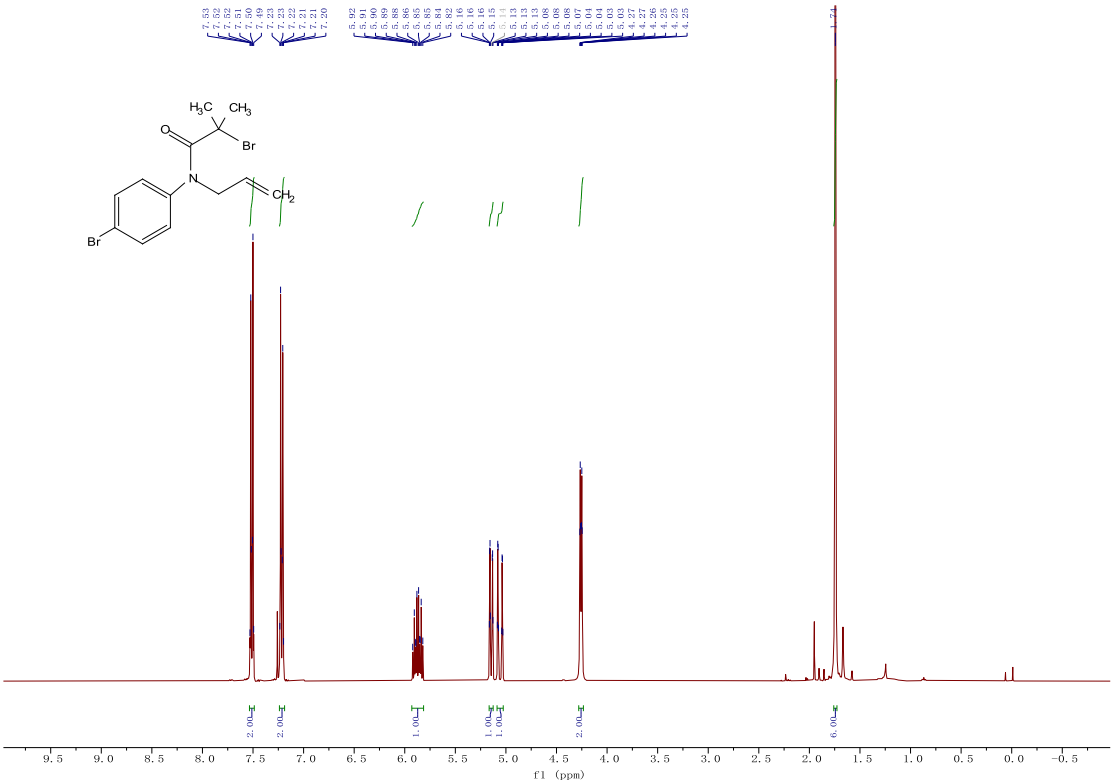


^{13}C NMR ($CDCl_3$, 101 MHz)

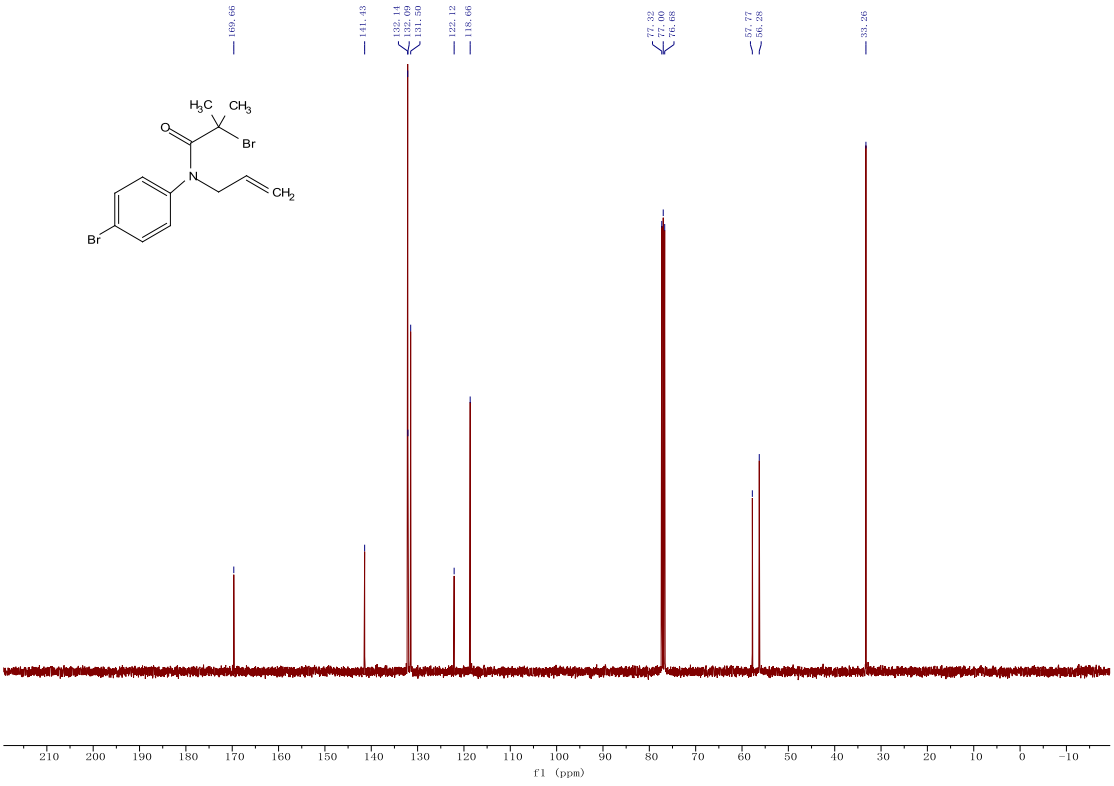


(1j)

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

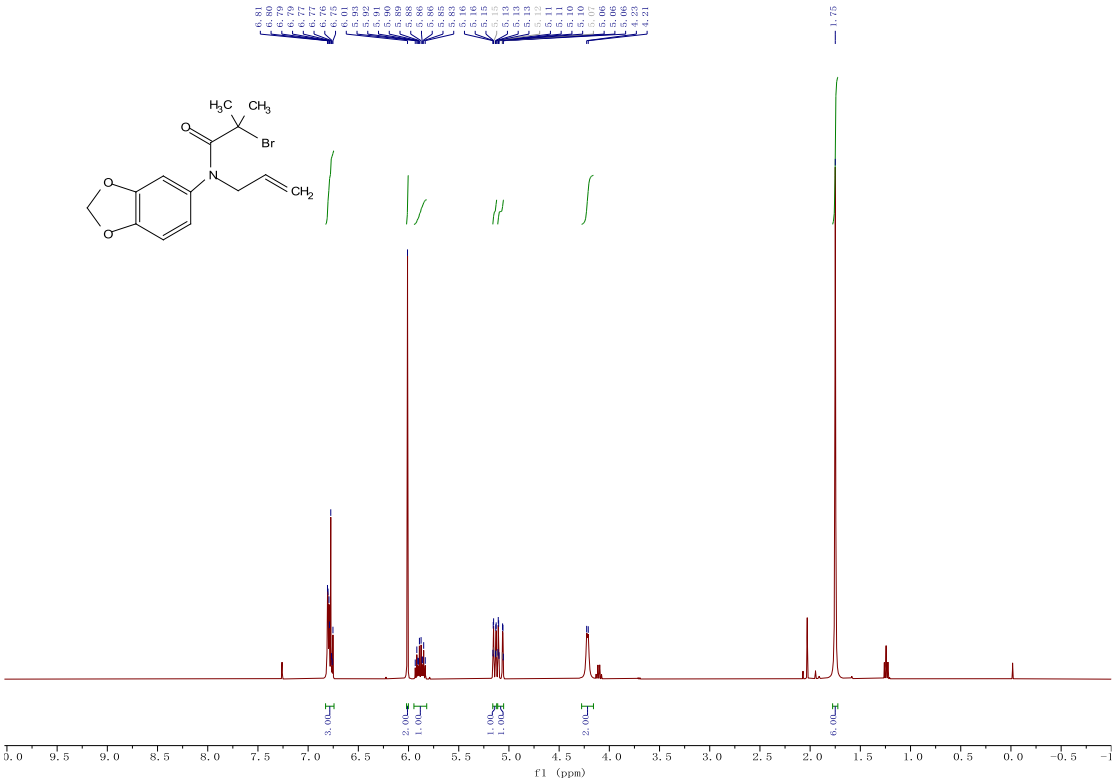


^{13}C NMR ($CDCl_3$, 101 MHz)

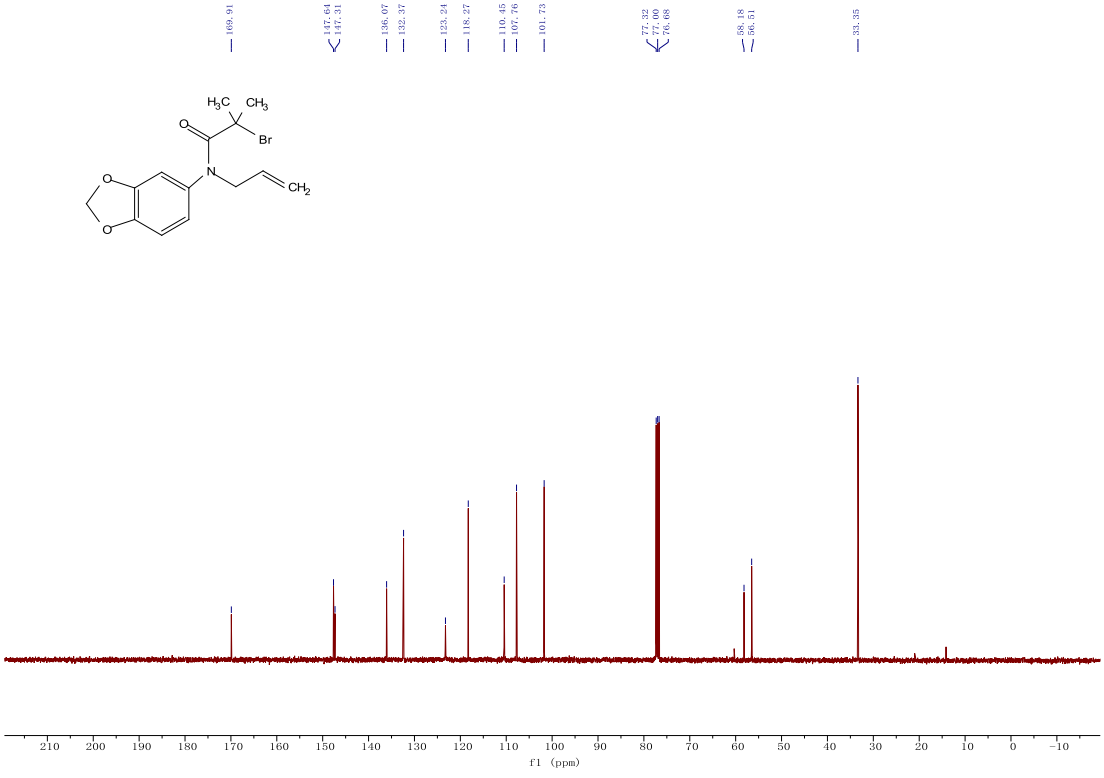


(1k)

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

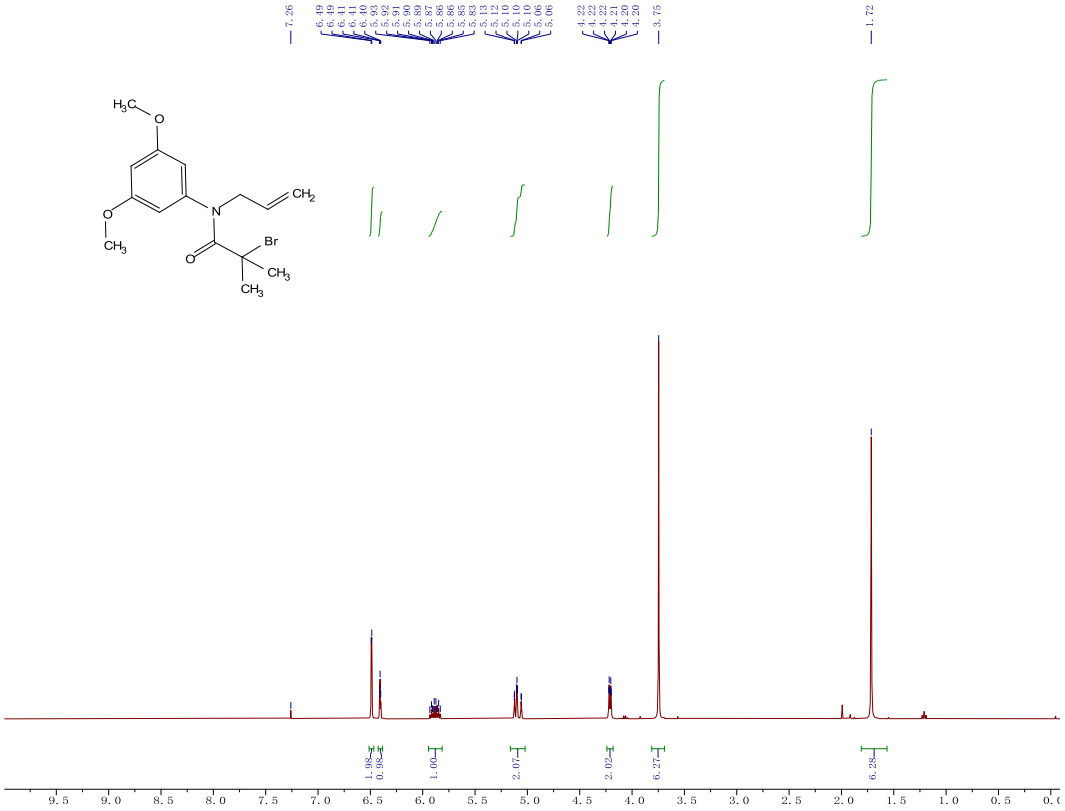


^{13}C NMR ($CDCl_3$, 101 MHz)

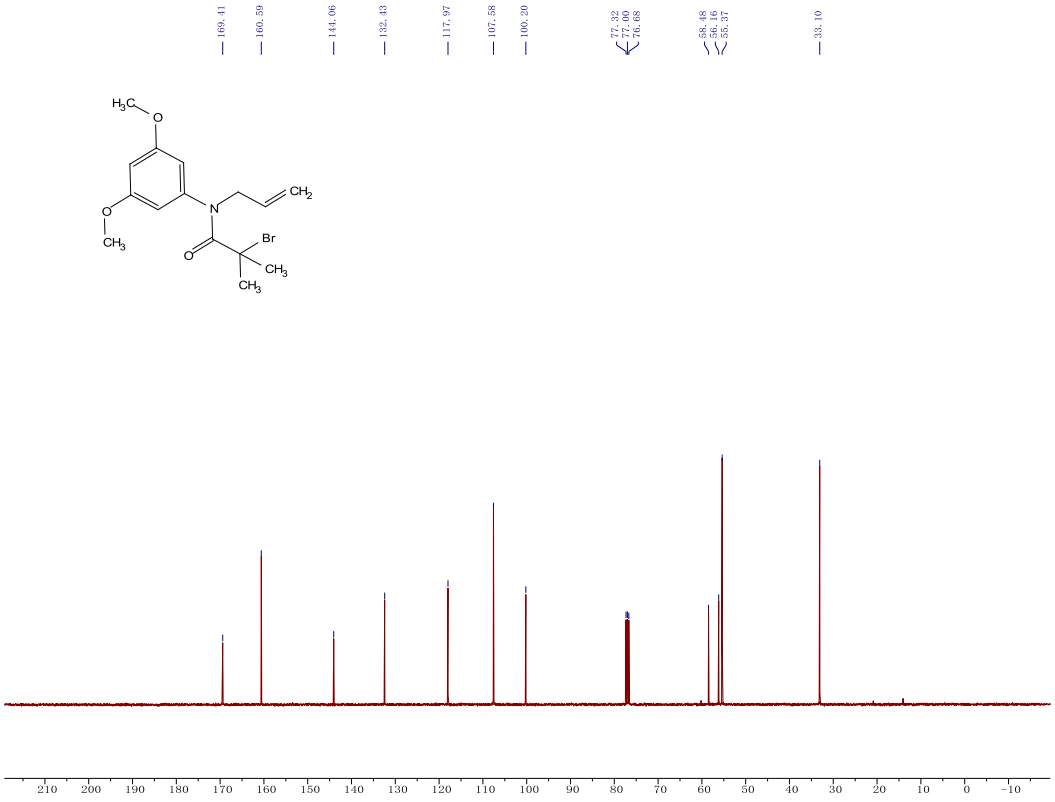


(1l)

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

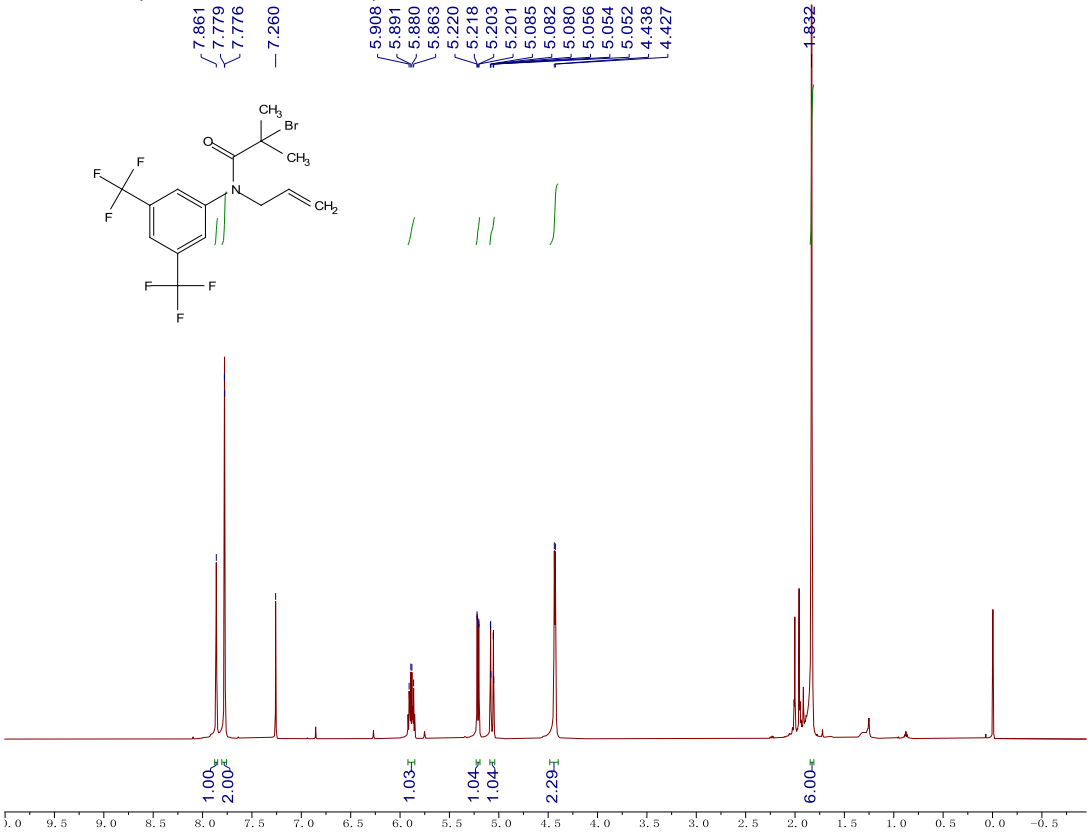


^{13}C NMR ($CDCl_3$, 101 MHz)

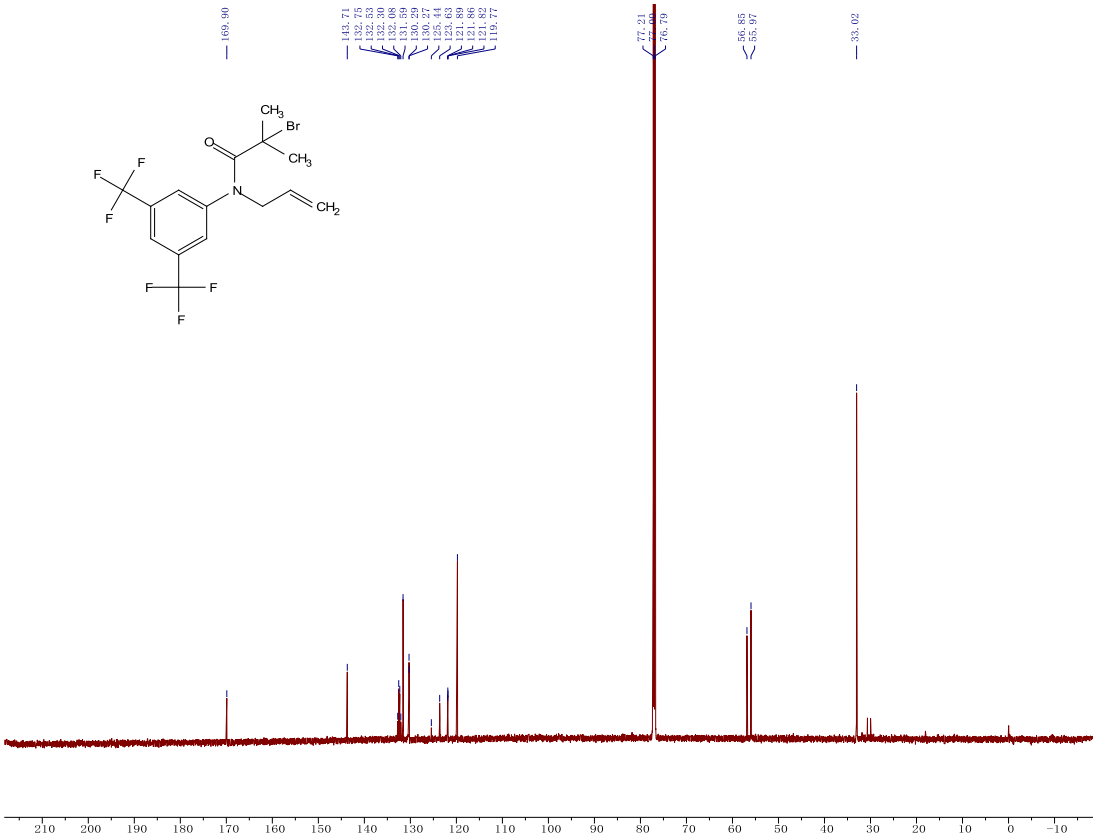


(1m)

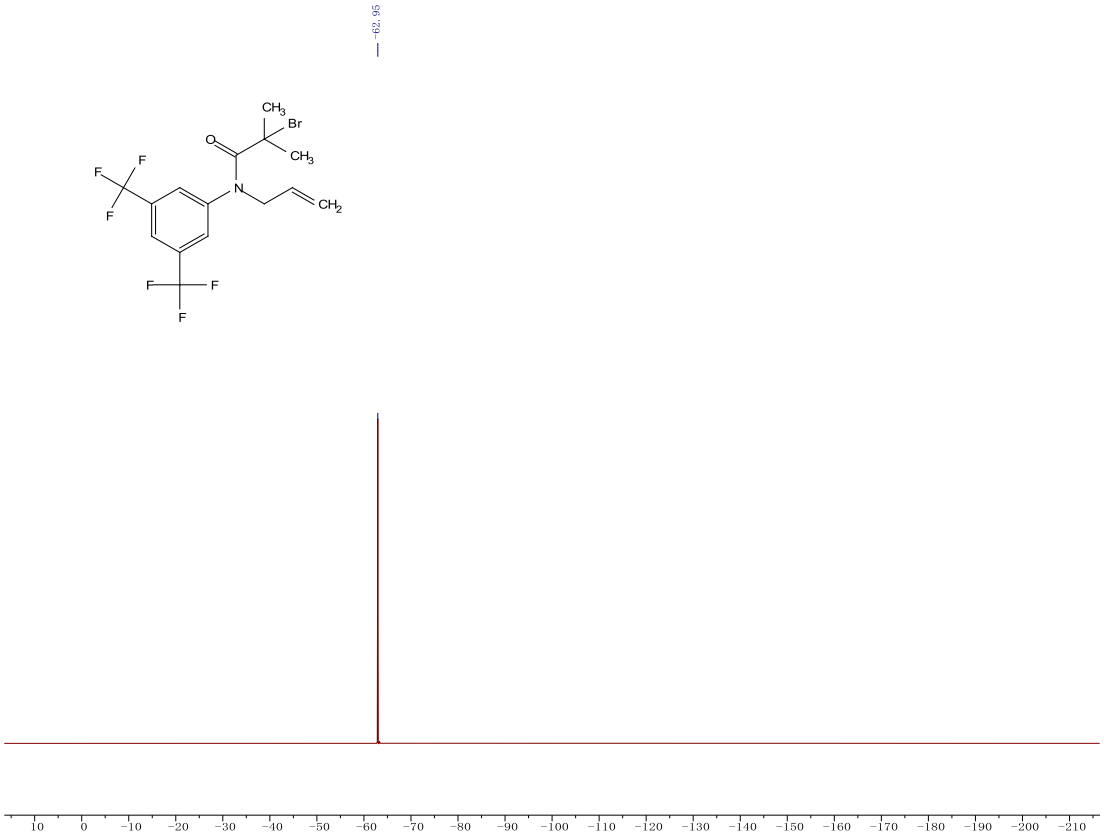
^{1}H NMR ($CDCl_3$, 400 MHz)



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

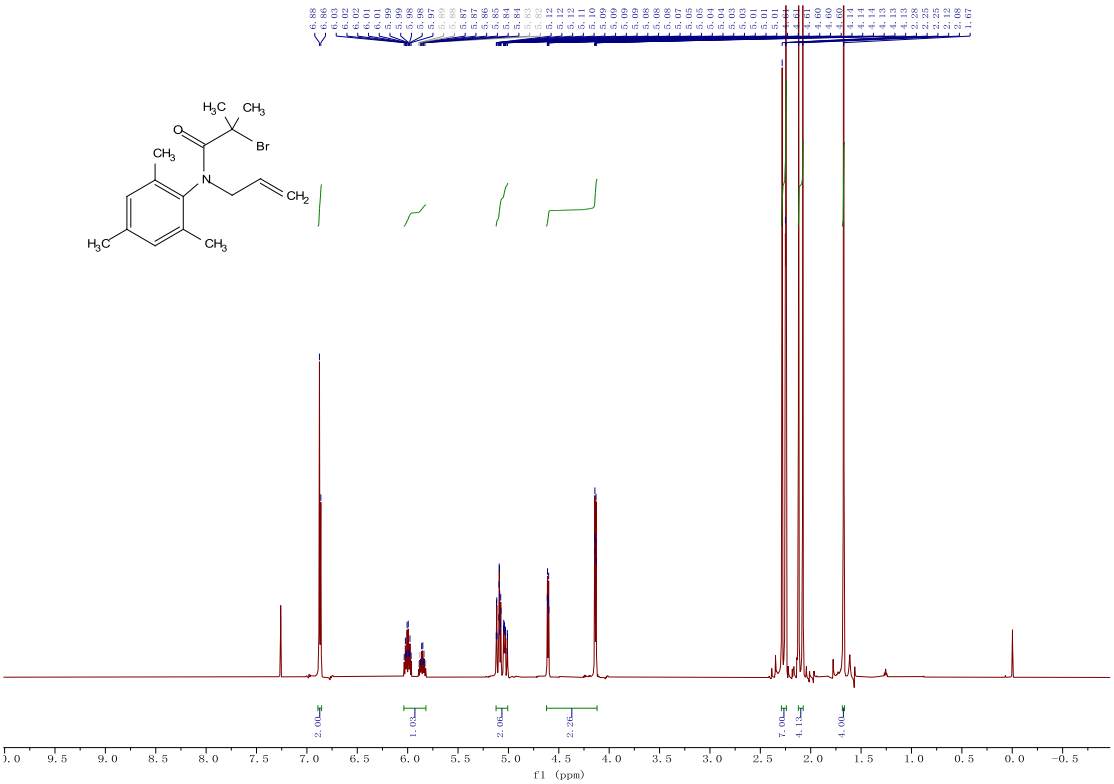


^{19}F NMR ($CDCl_3$, 565 MHz)

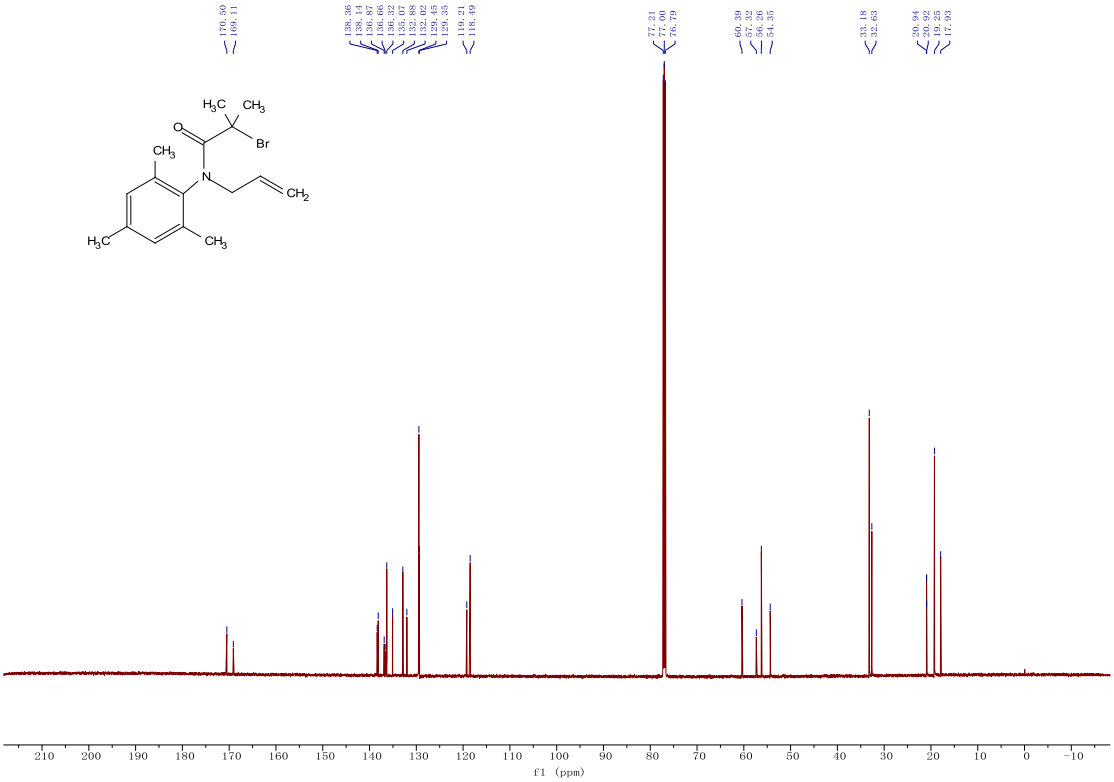


(1n)

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

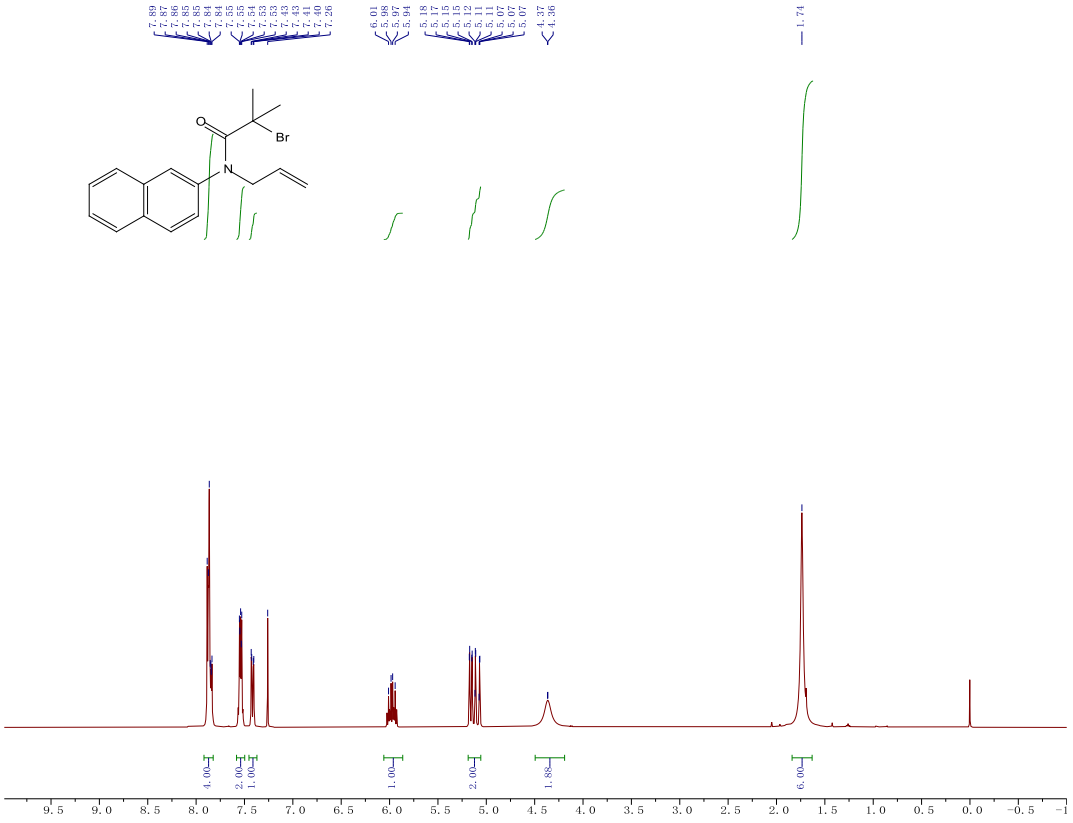


^{13}C NMR ($CDCl_3$, 151 MHz)

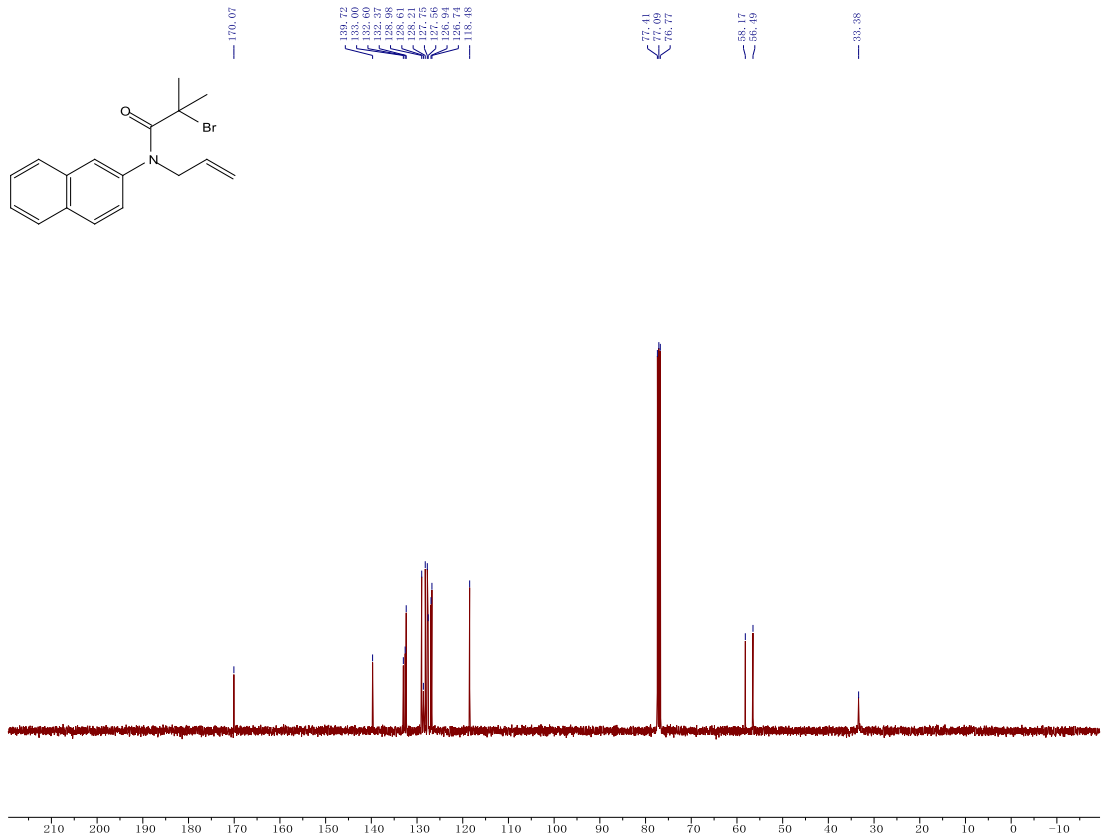


(1o)

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

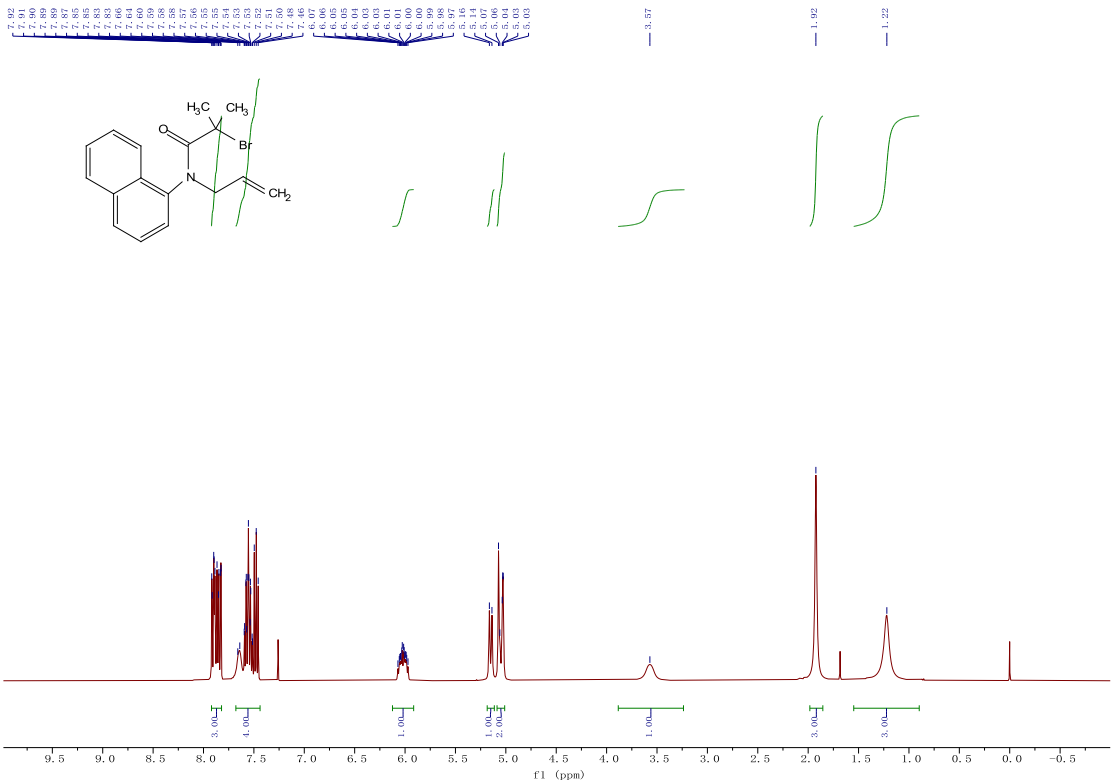


^{13}C NMR ($CDCl_3$, 101 MHz)

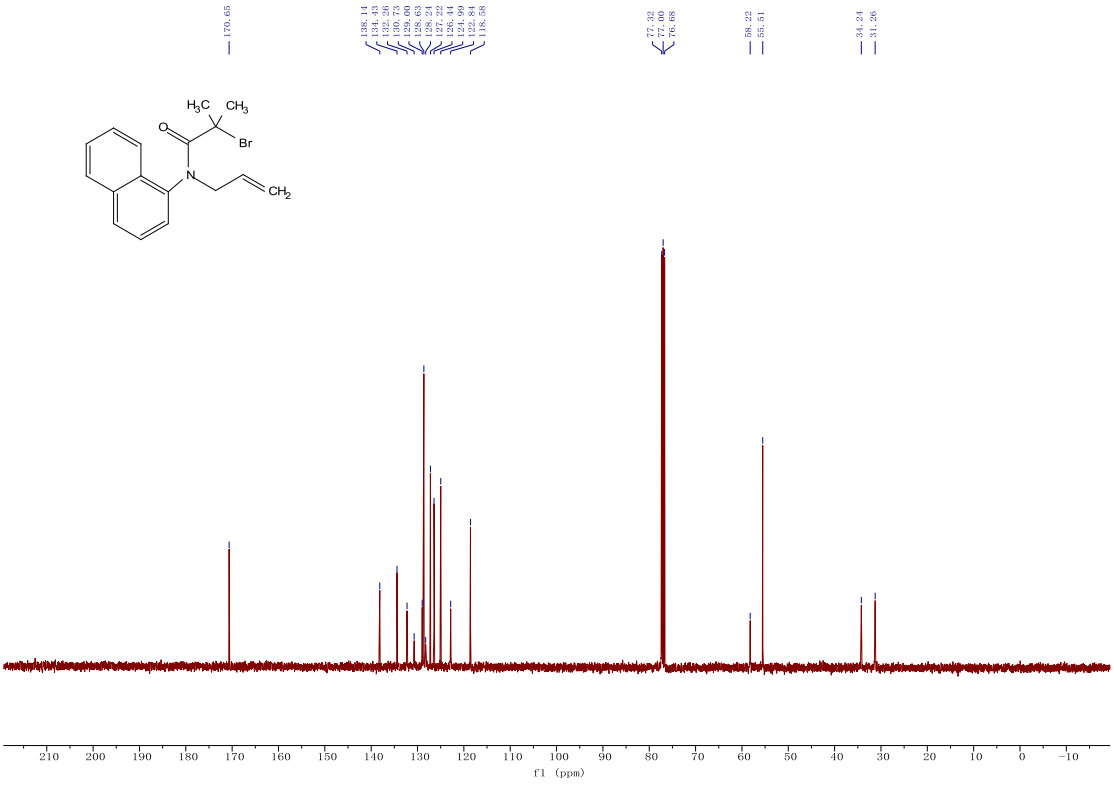


(1p)

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

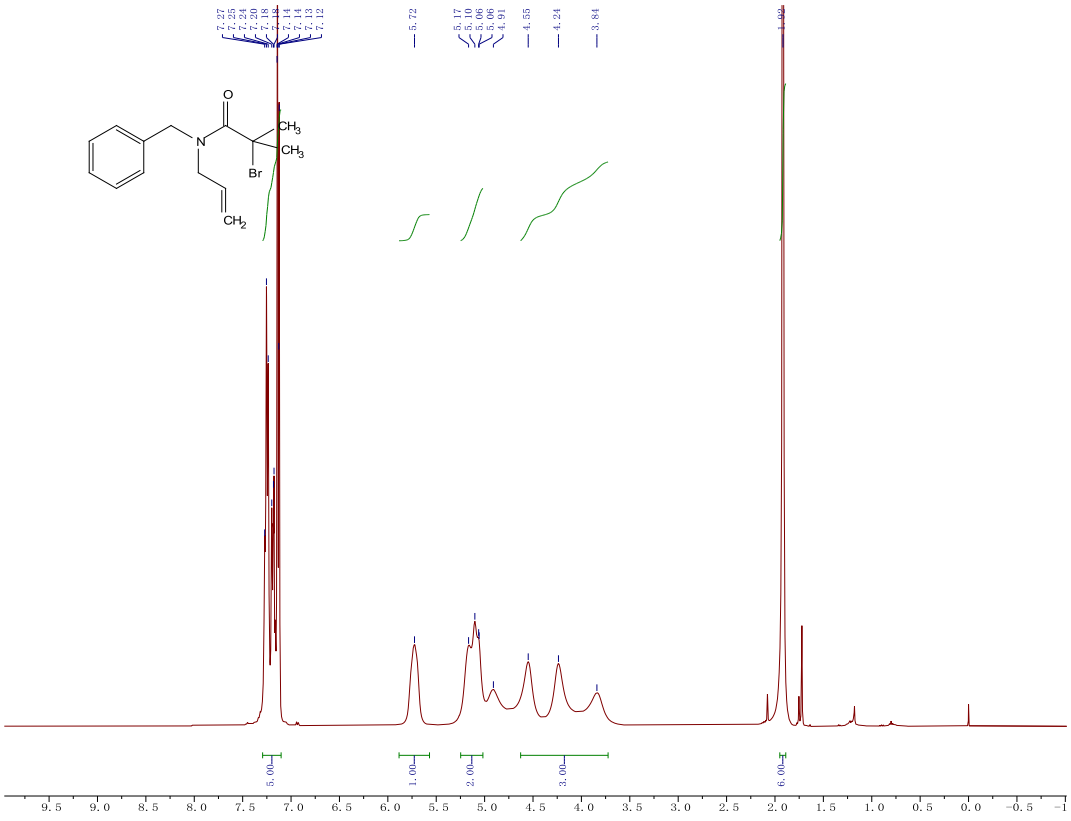


^{13}C NMR ($CDCl_3$, 101 MHz)

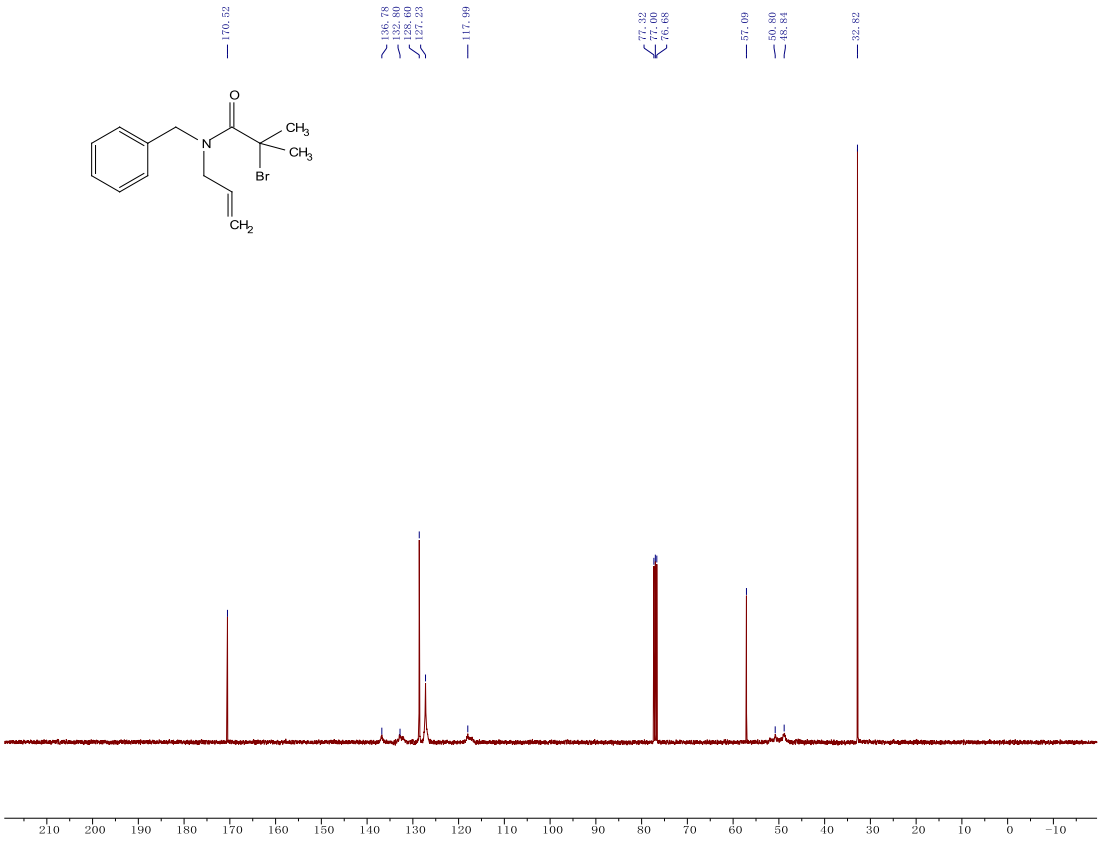


(1q)

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

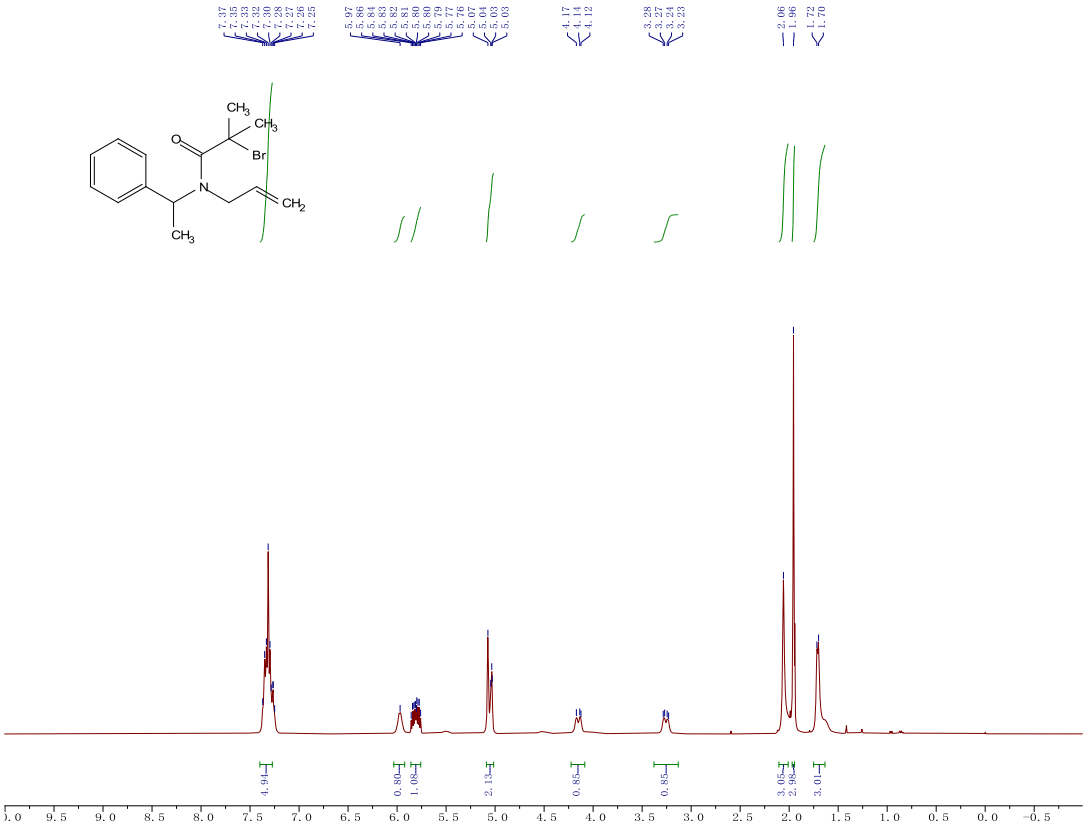


^{13}C NMR ($CDCl_3$, 101 MHz)

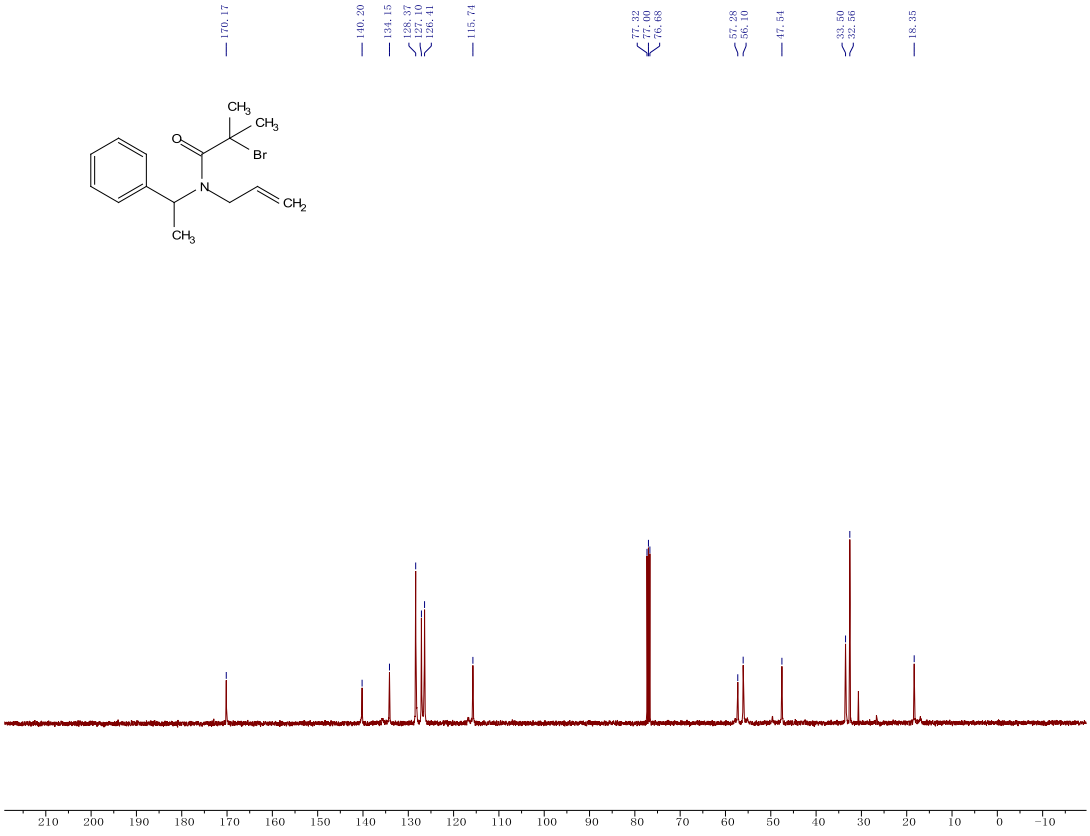


(1r)

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

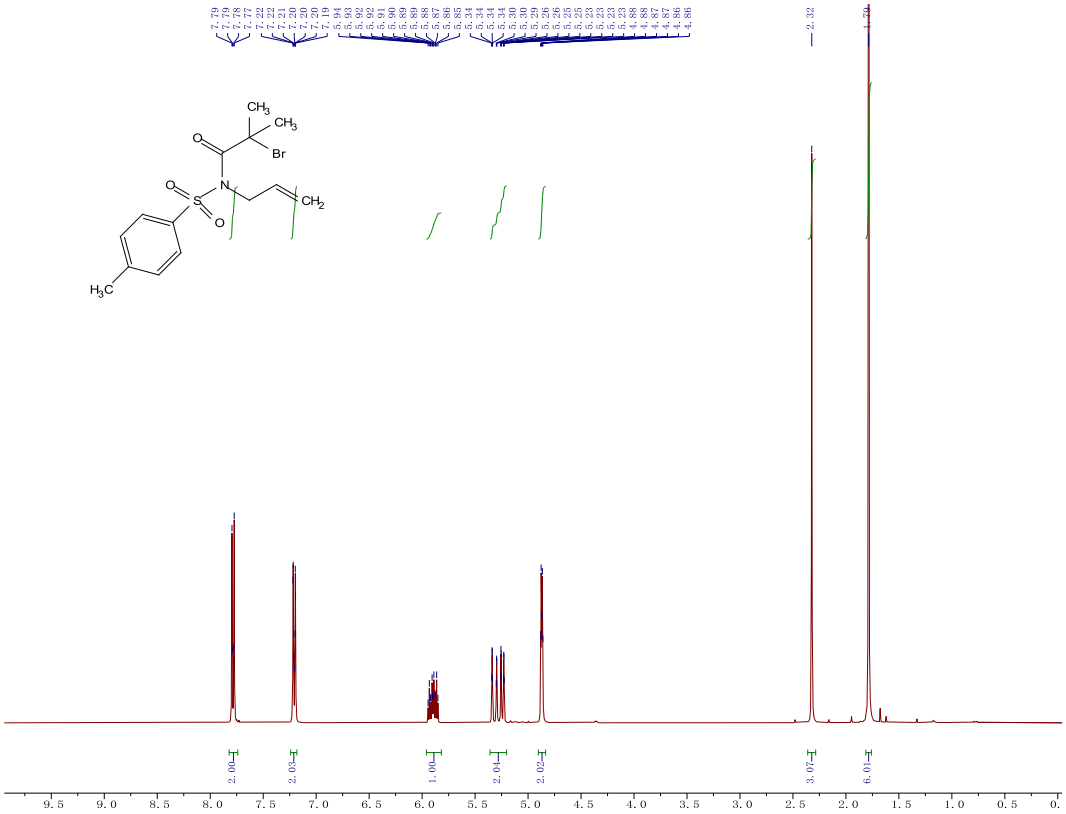


^{13}C NMR ($CDCl_3$, 101 MHz)

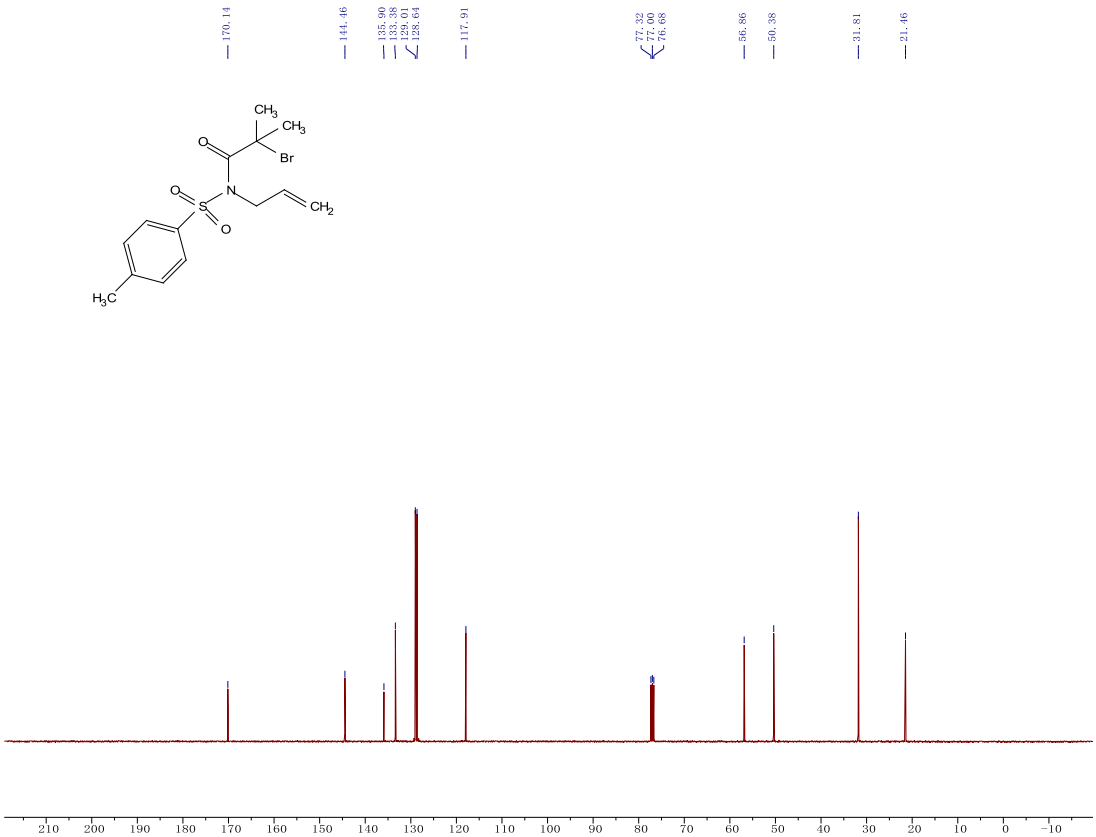


(1s)

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

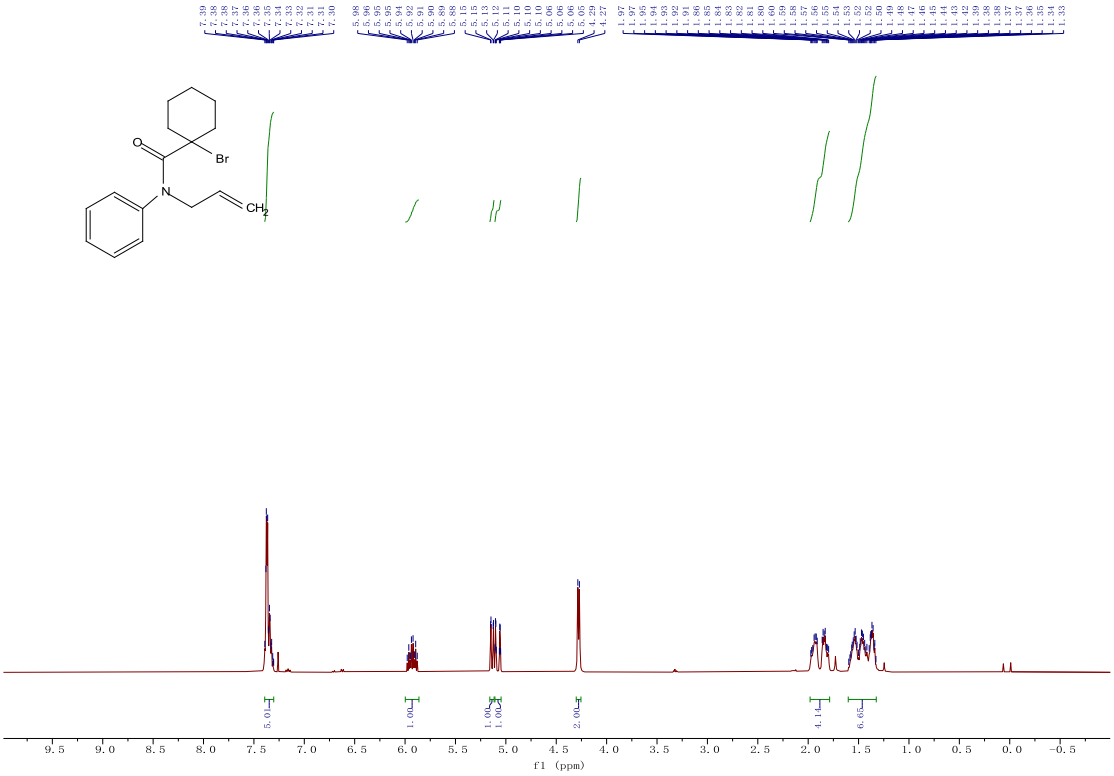


^{13}C NMR ($CDCl_3$, 101 MHz)

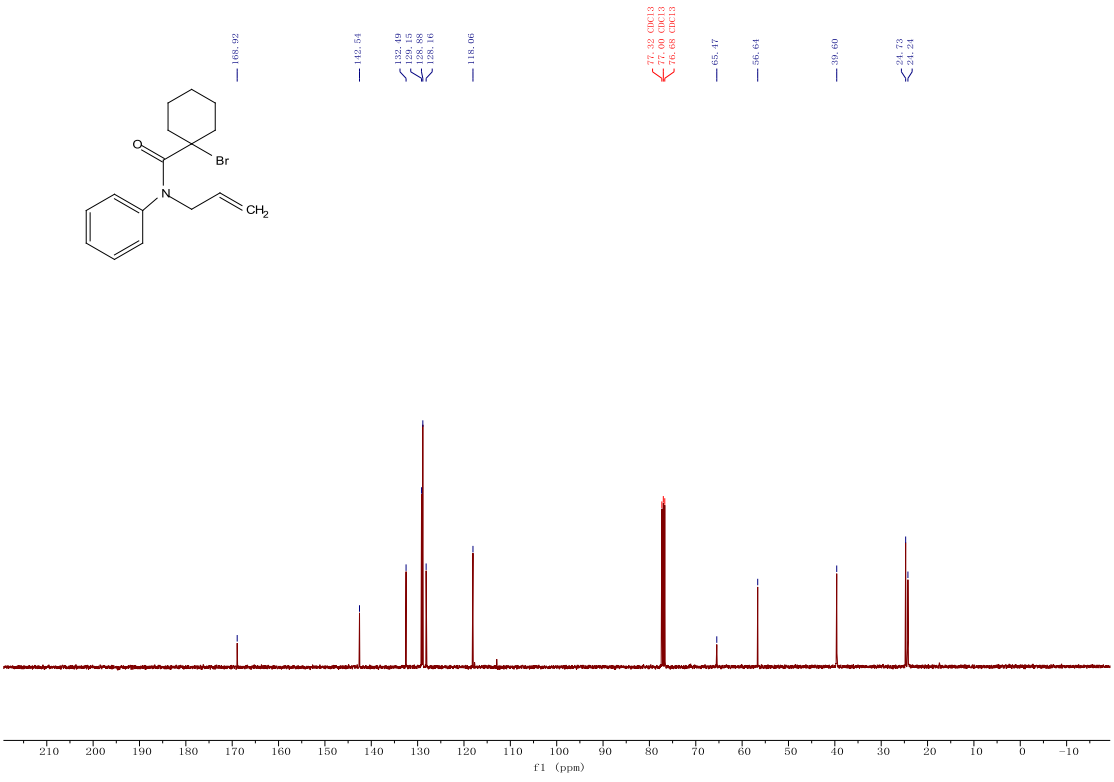


(1t)

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

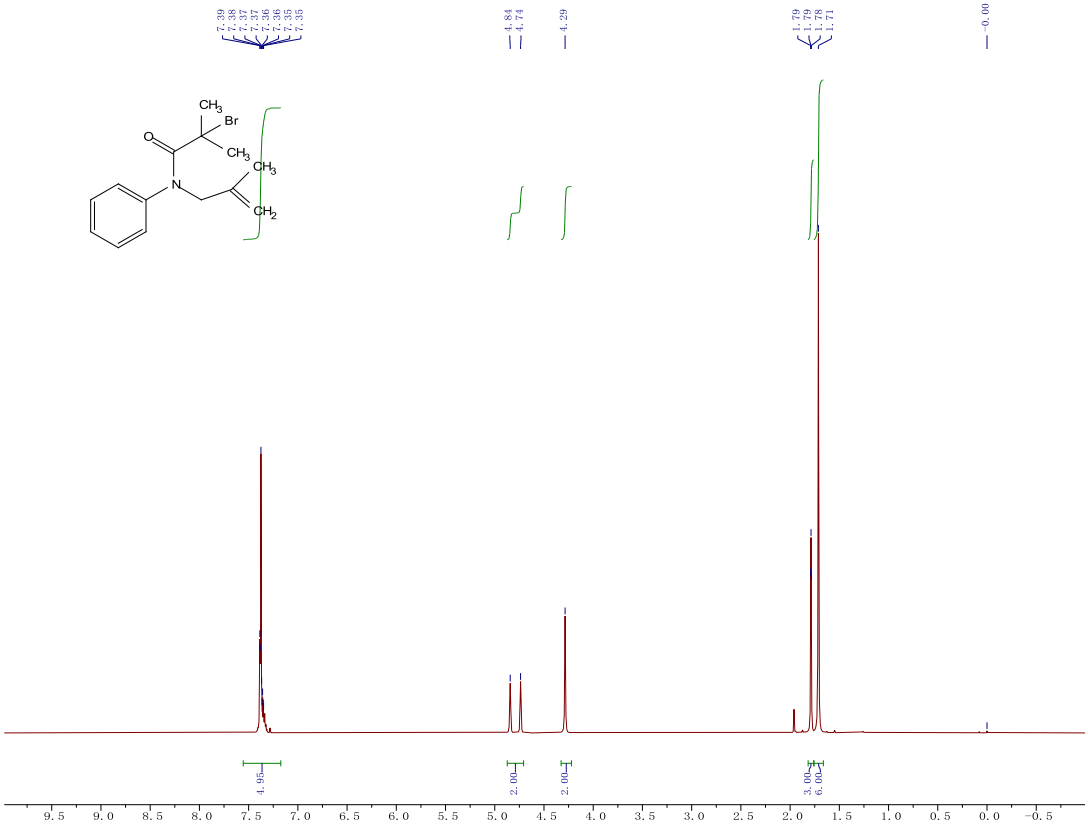


^{13}C NMR ($CDCl_3$, 101 MHz)

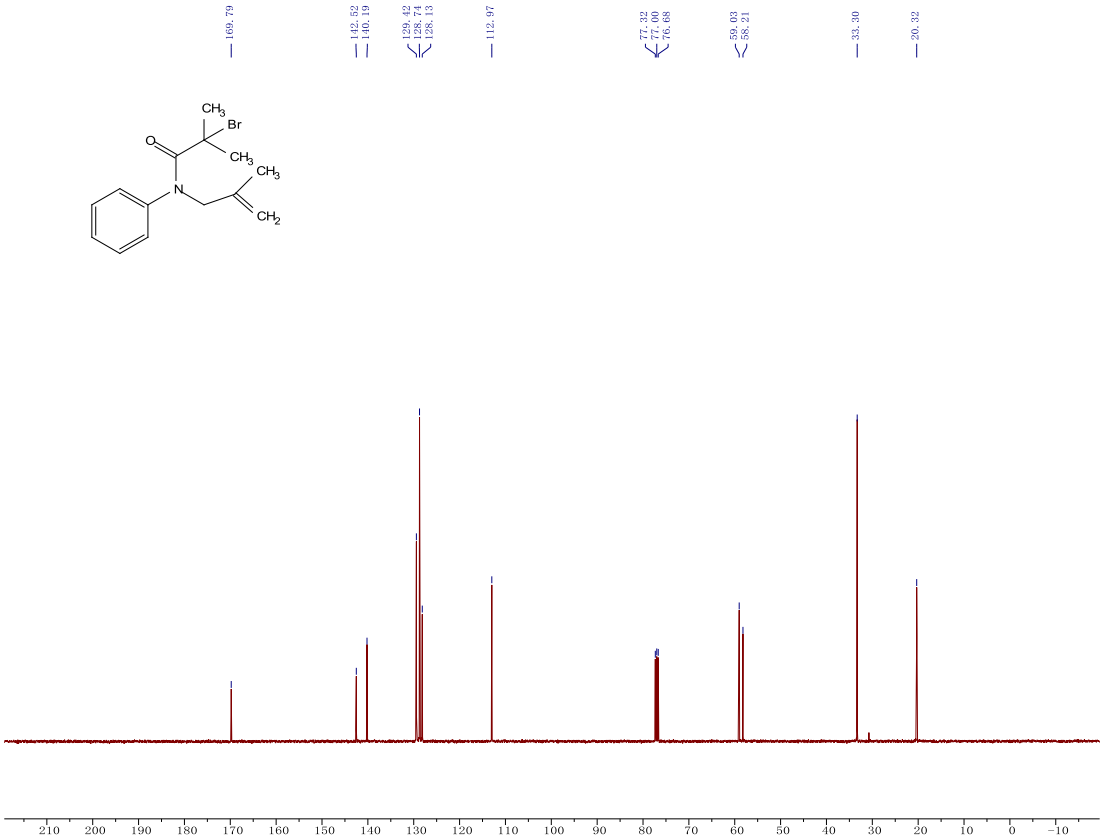


(1u)

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

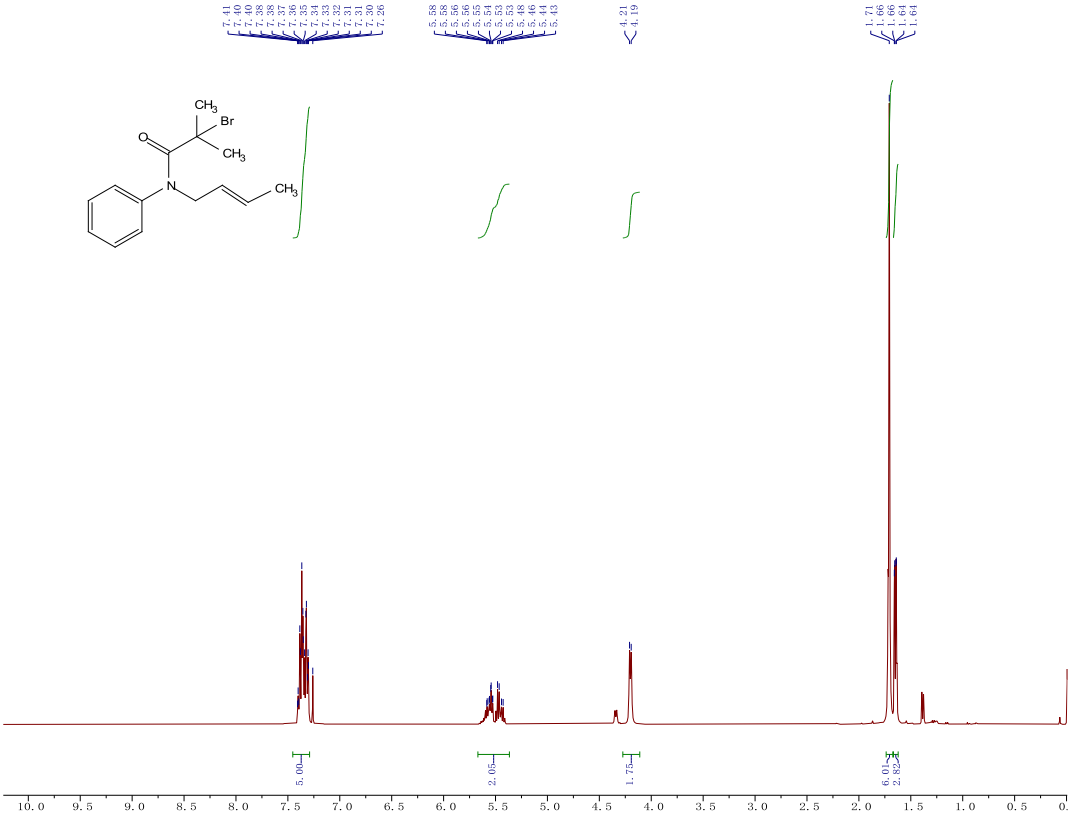


^{13}C NMR ($CDCl_3$, 101 MHz)

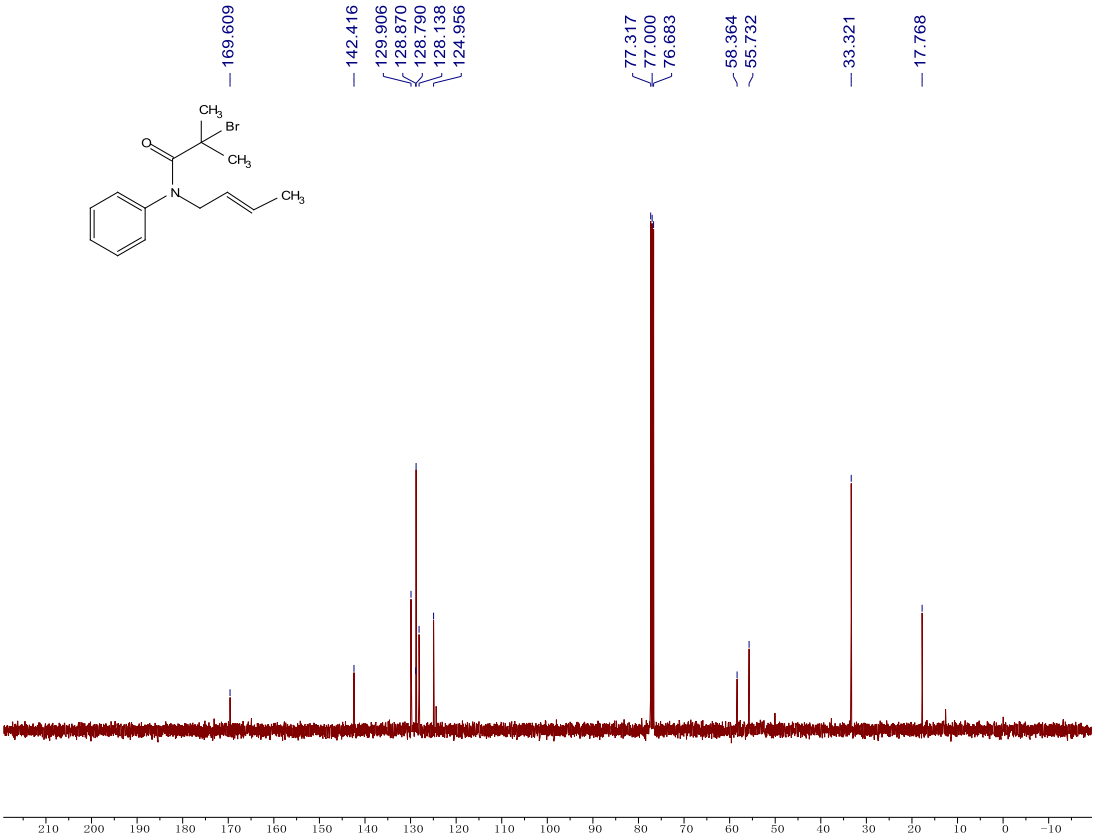


(1v)

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

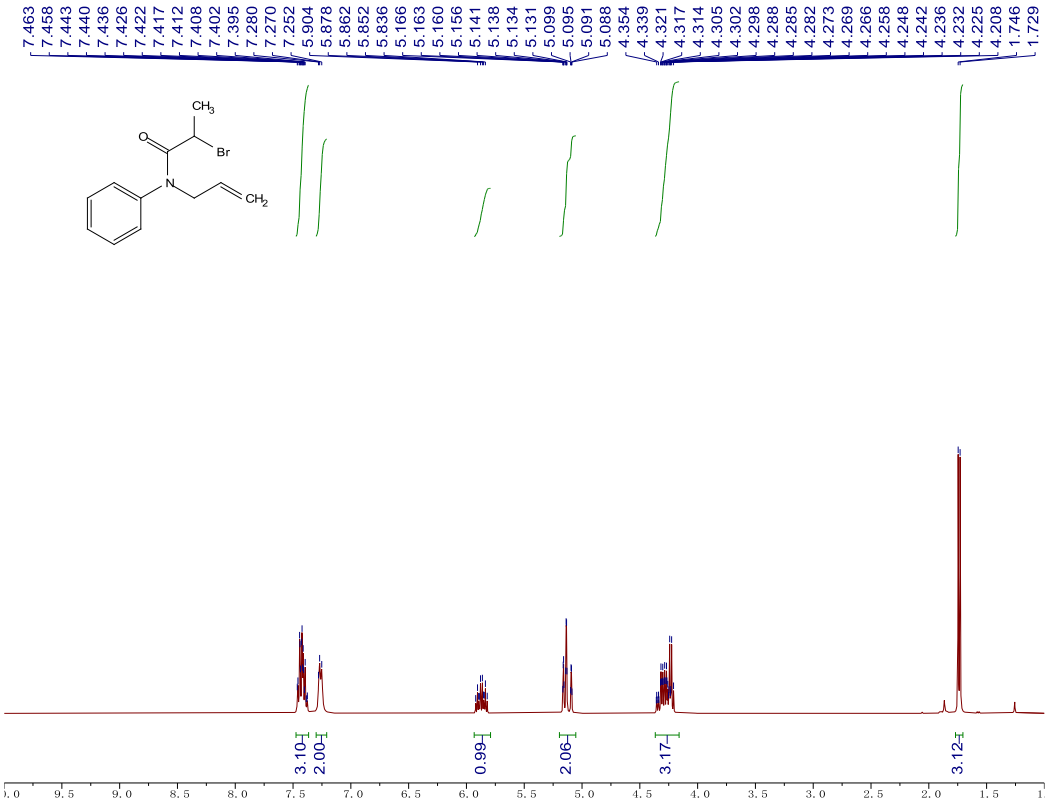


^{13}C NMR ($CDCl_3$, 101 MHz)

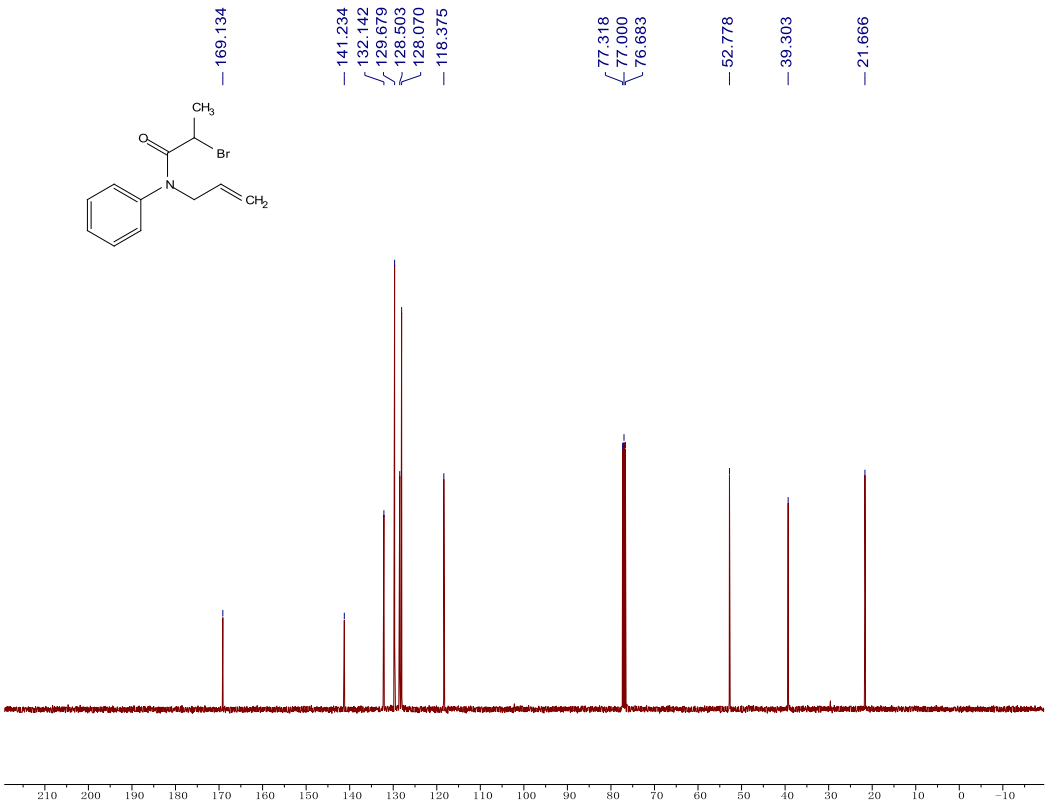


(1w)

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

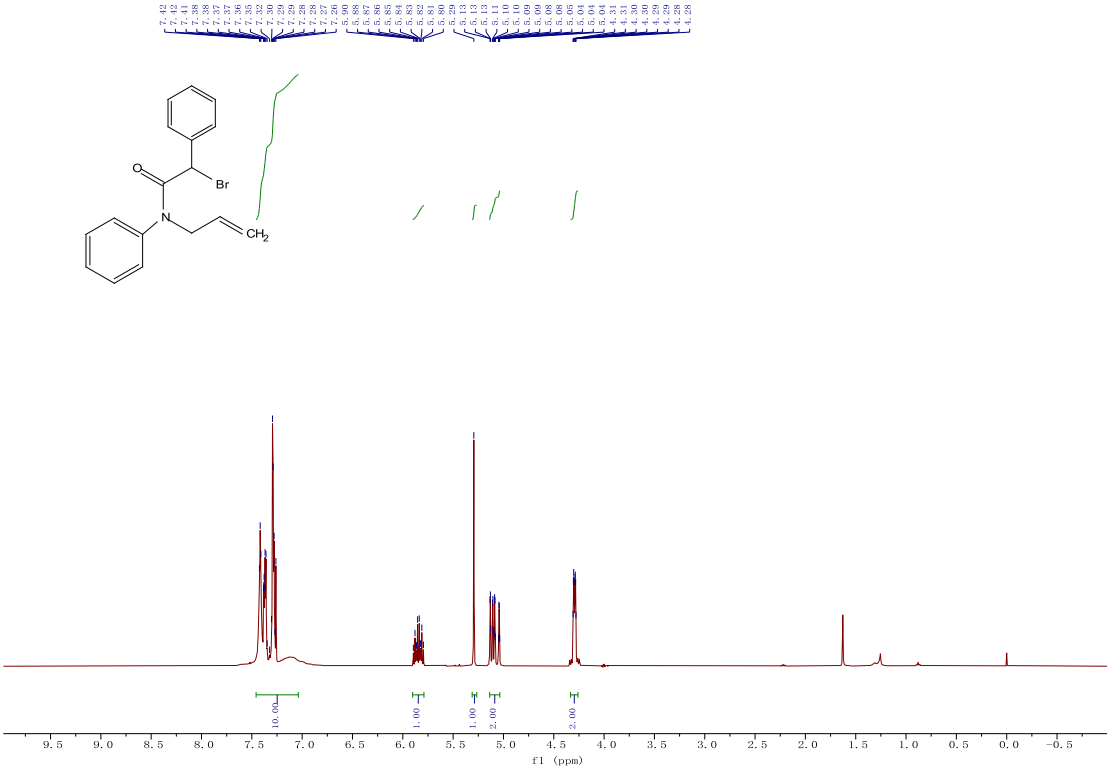


^{13}C NMR ($CDCl_3$, 101 MHz)

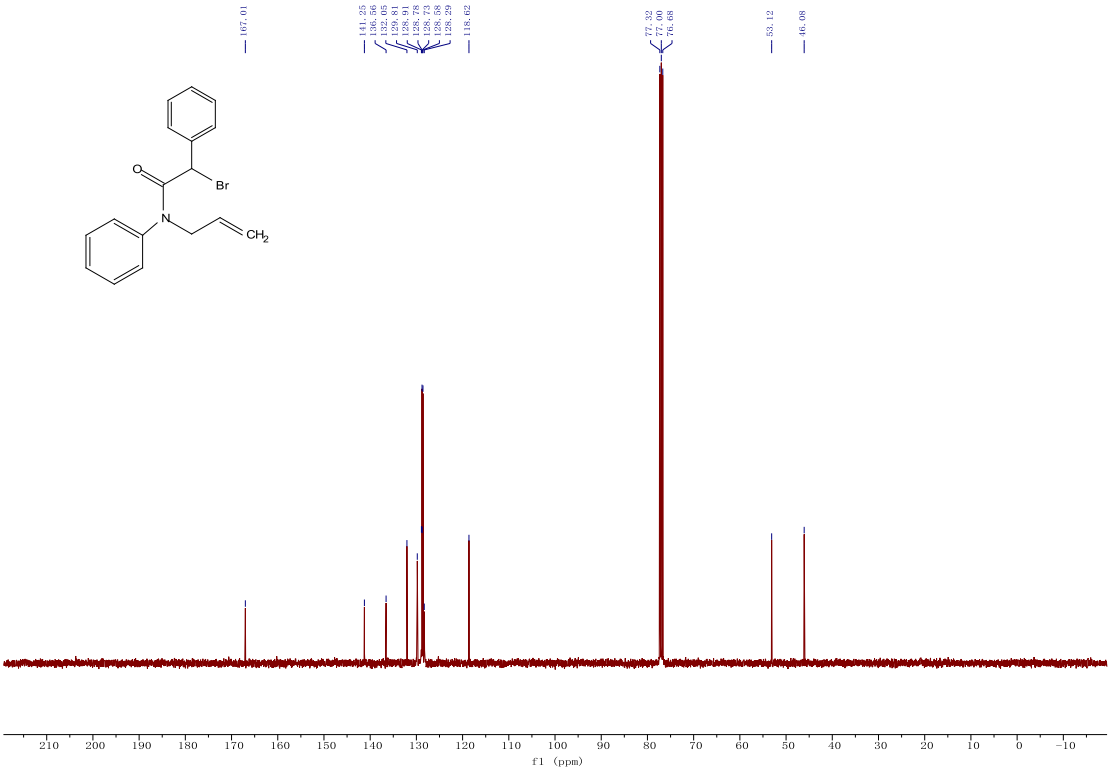


(1x)

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

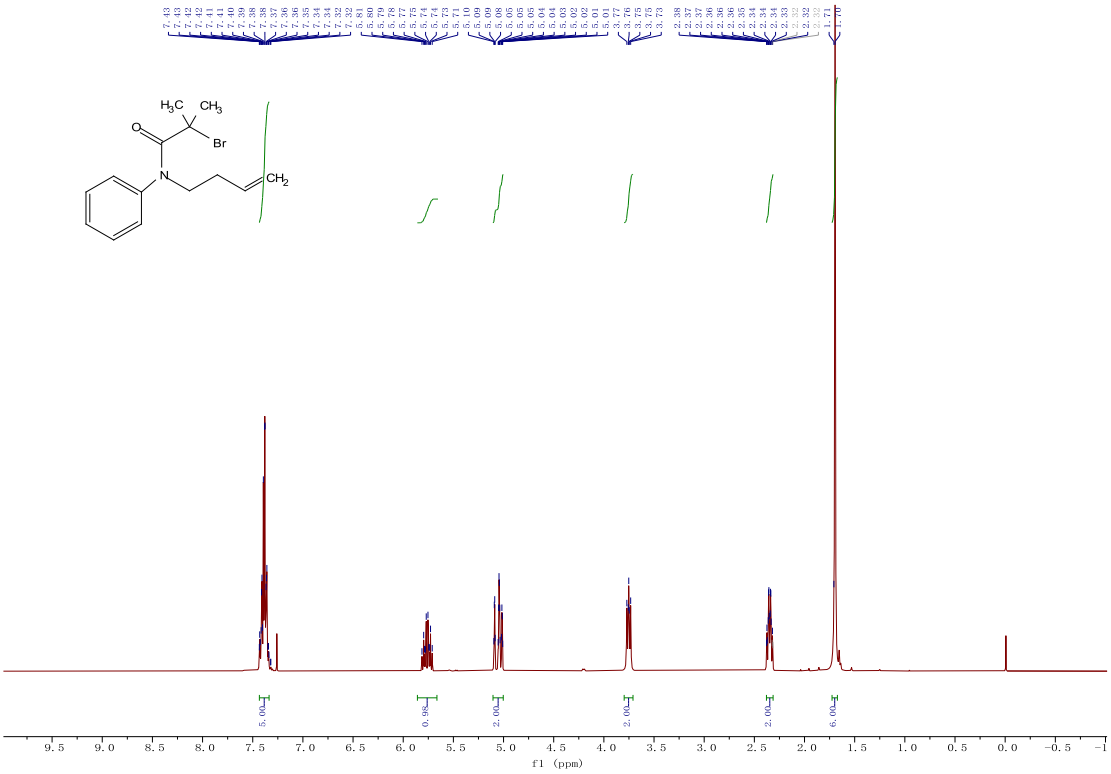


^{13}C NMR ($CDCl_3$, 101 MHz)

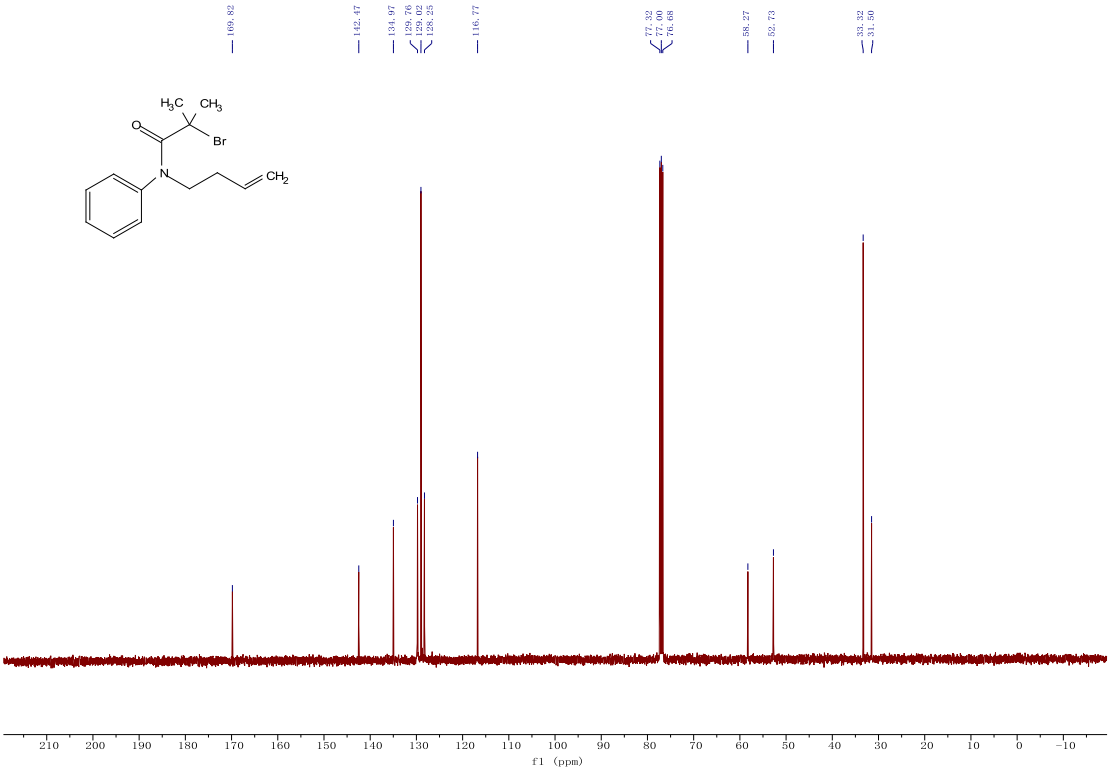


(1y)

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

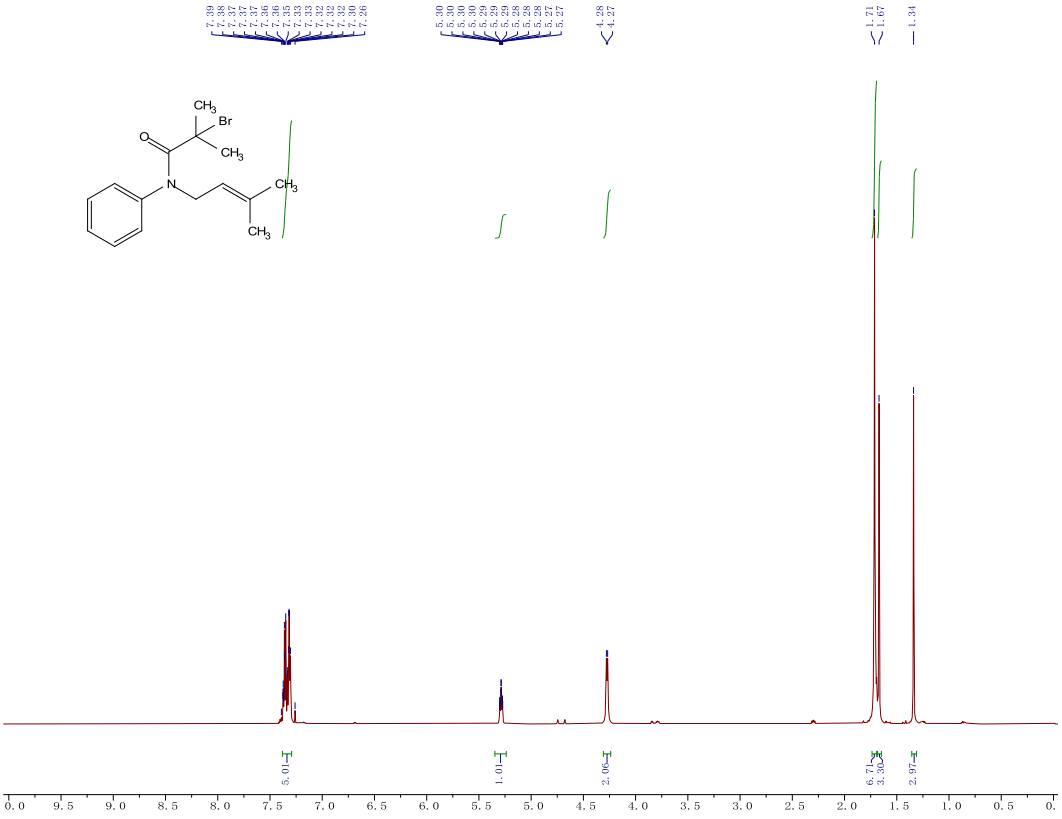


^{13}C NMR ($CDCl_3$, 101 MHz)

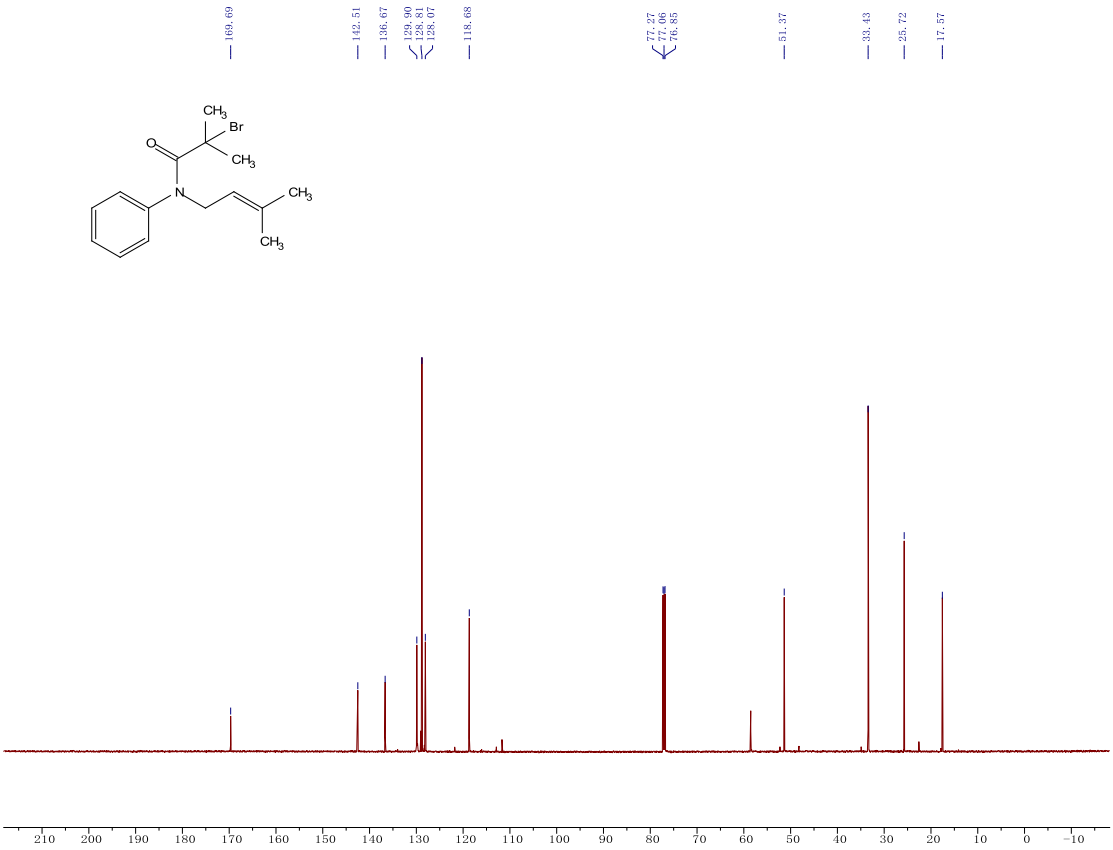


(1z)

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

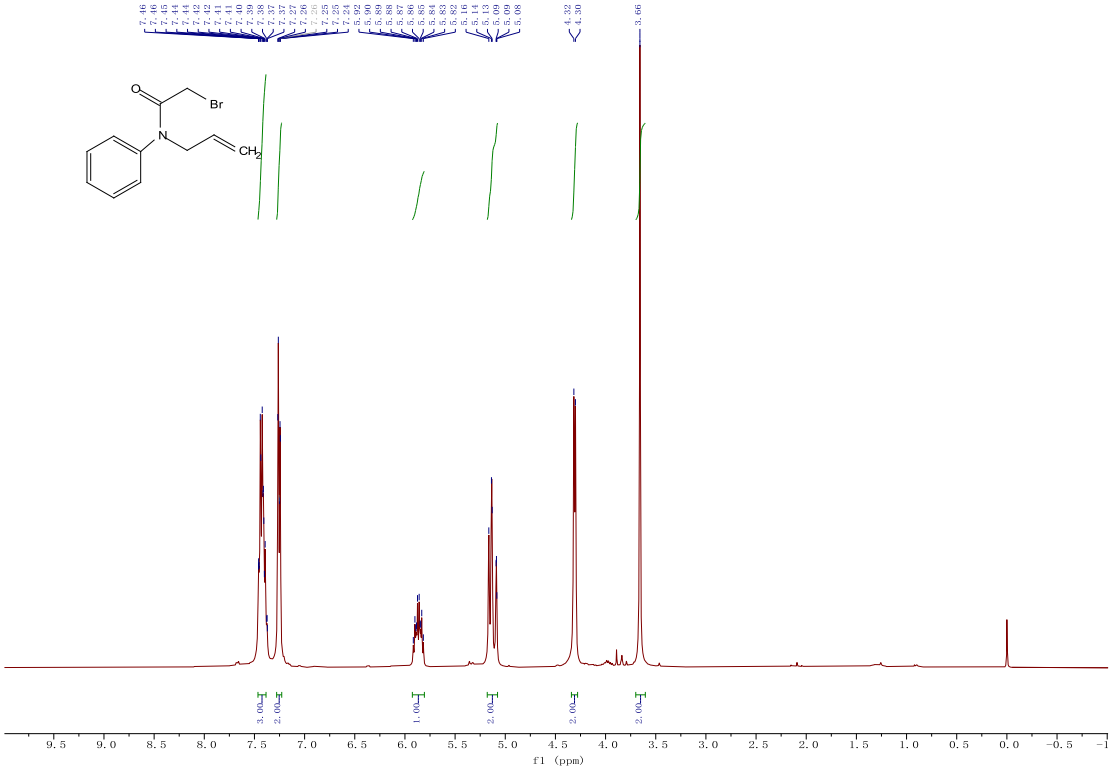


^{13}C NMR ($CDCl_3$, 101 MHz)

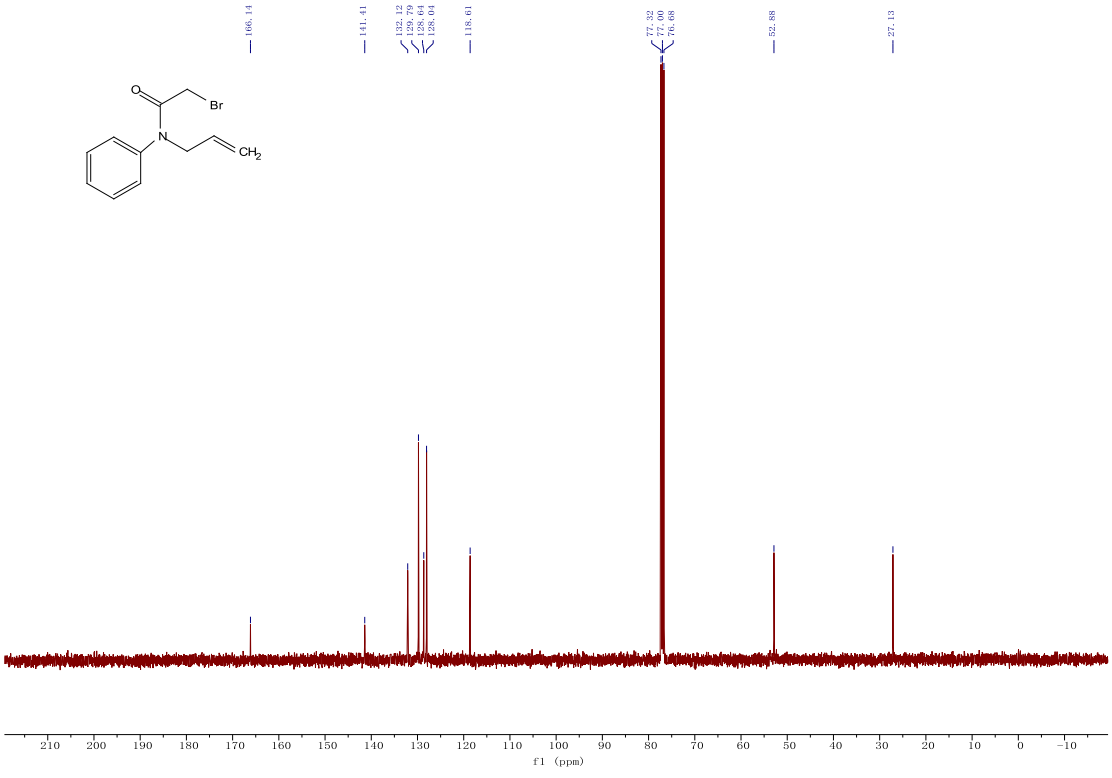


(1aa)

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

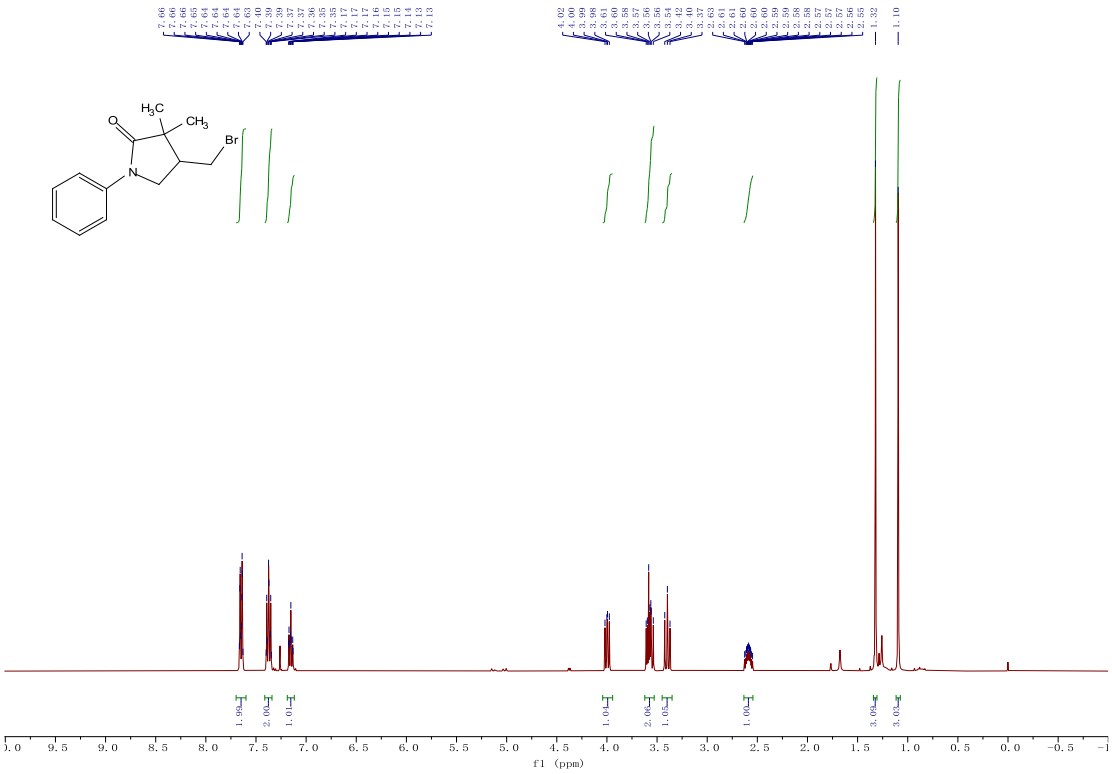


^{13}C NMR ($CDCl_3$, 101 MHz)

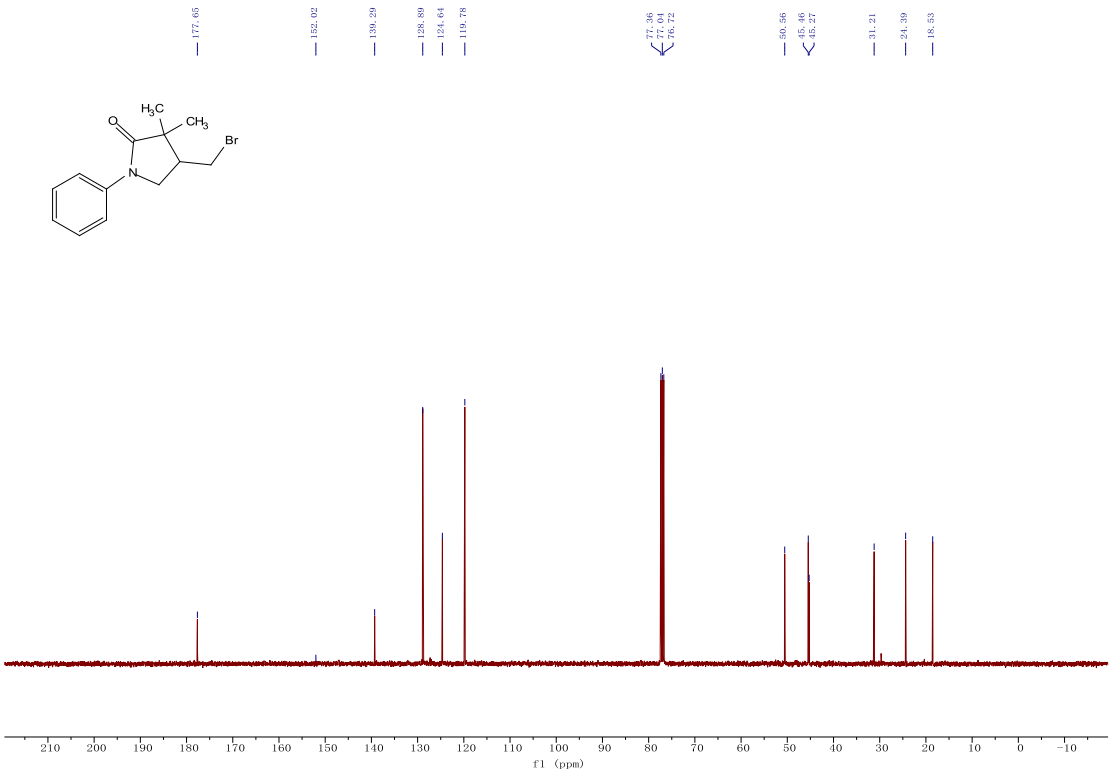


(2a)

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

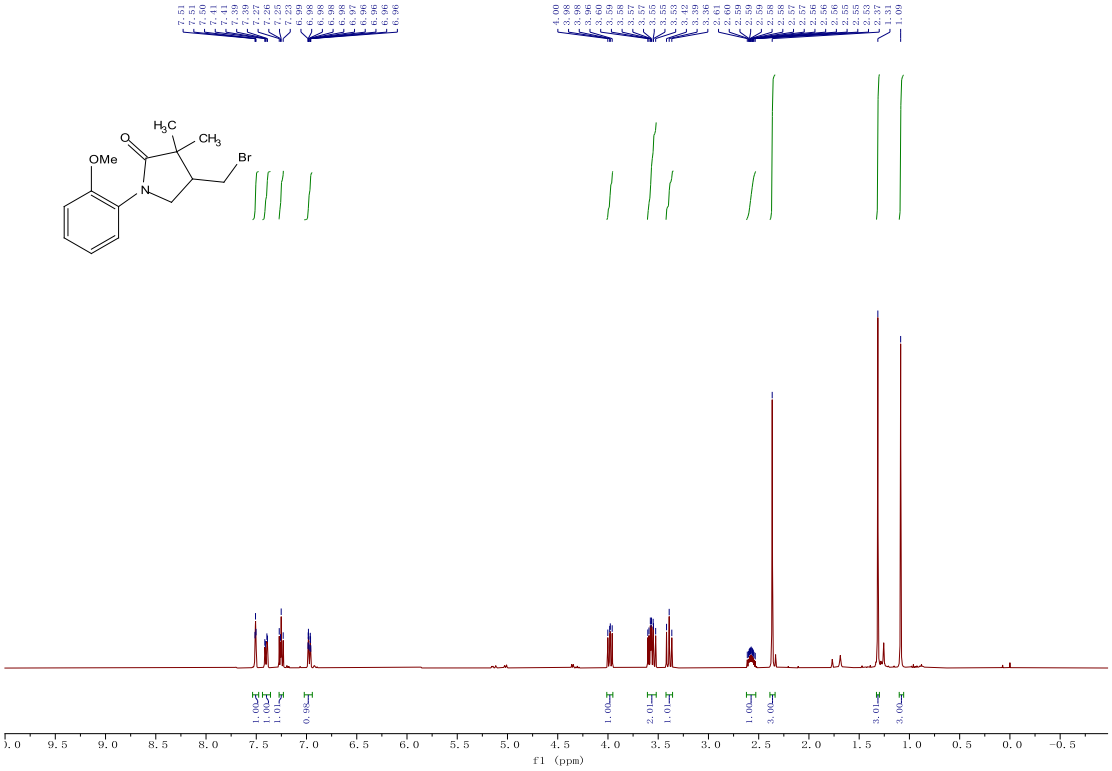


^{13}C NMR ($CDCl_3$, 101 MHz)

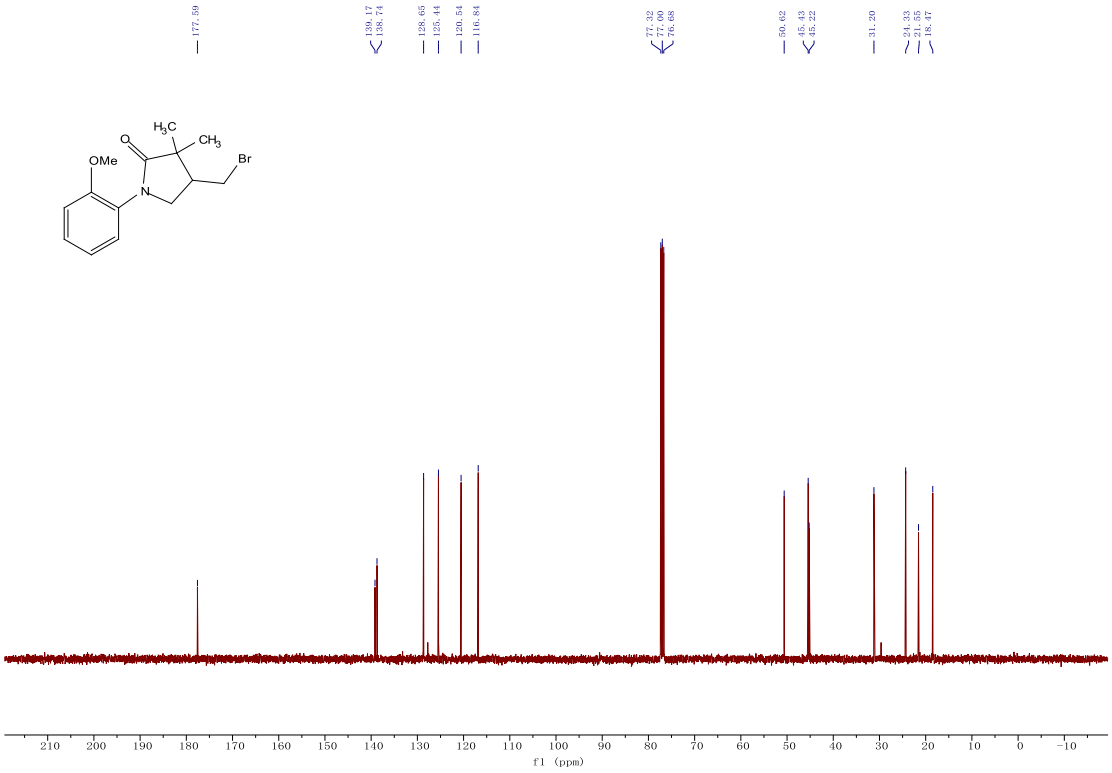


(2b)

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

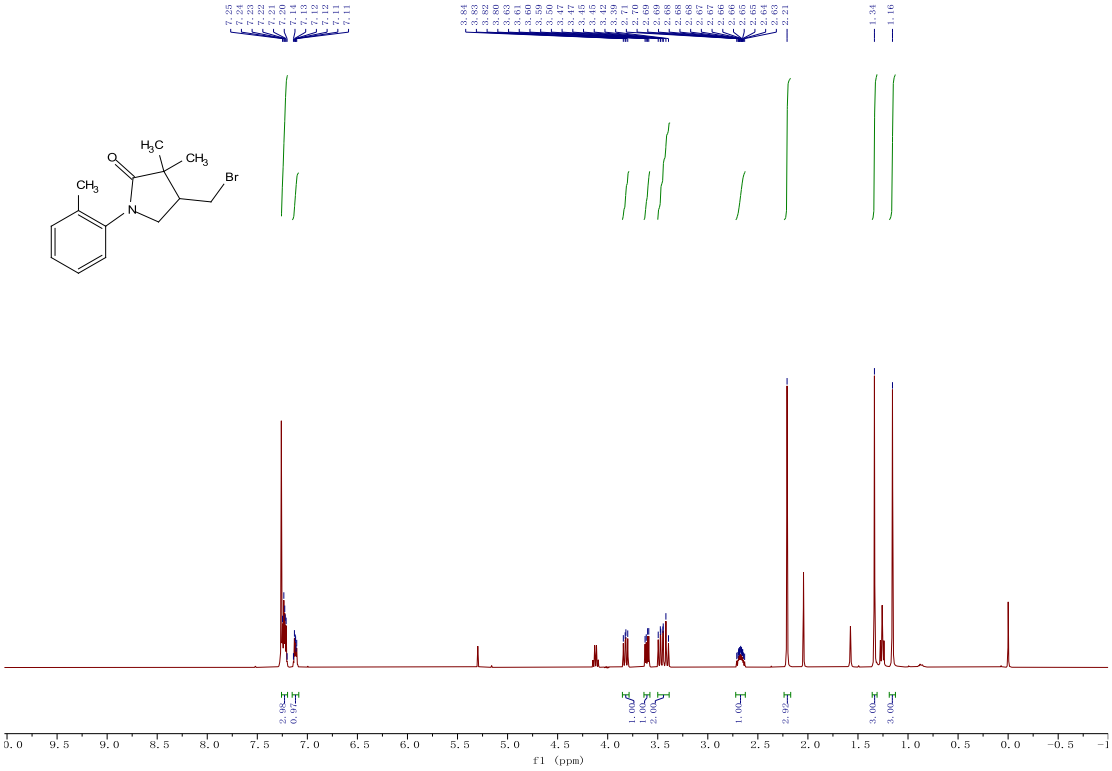


^{13}C NMR ($CDCl_3$, 101 MHz)

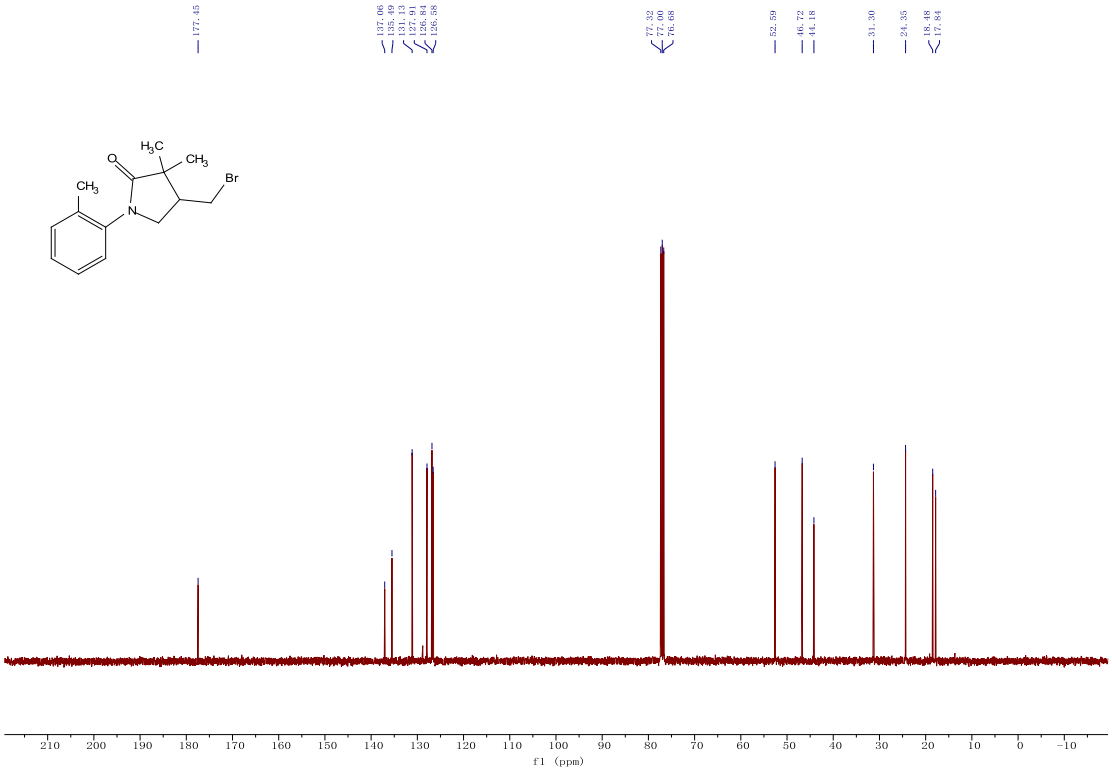


(2c)

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

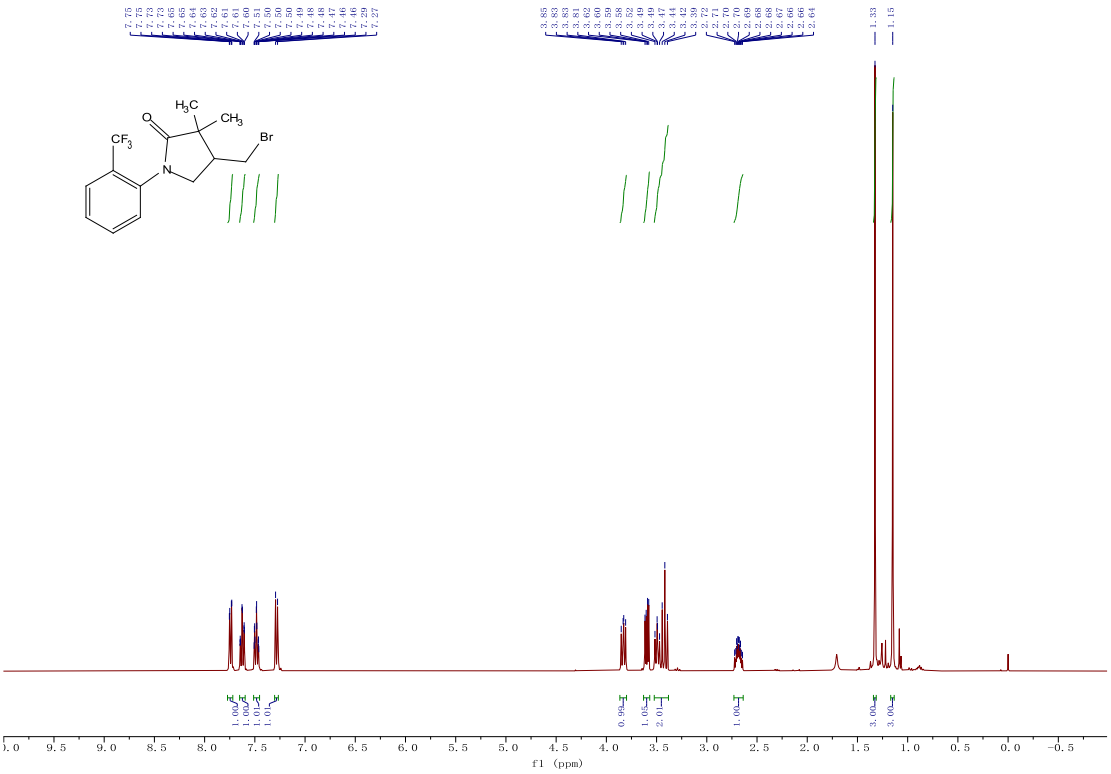


^{13}C NMR ($CDCl_3$, 101 MHz)

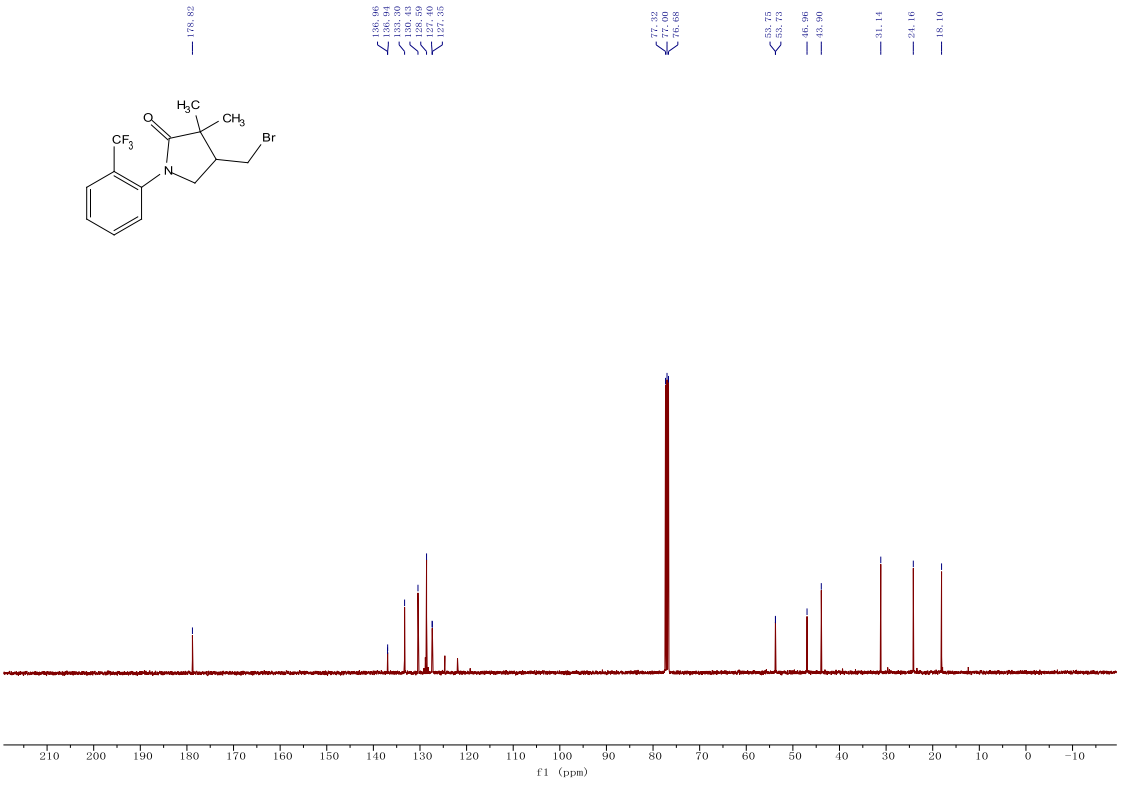


(2d)

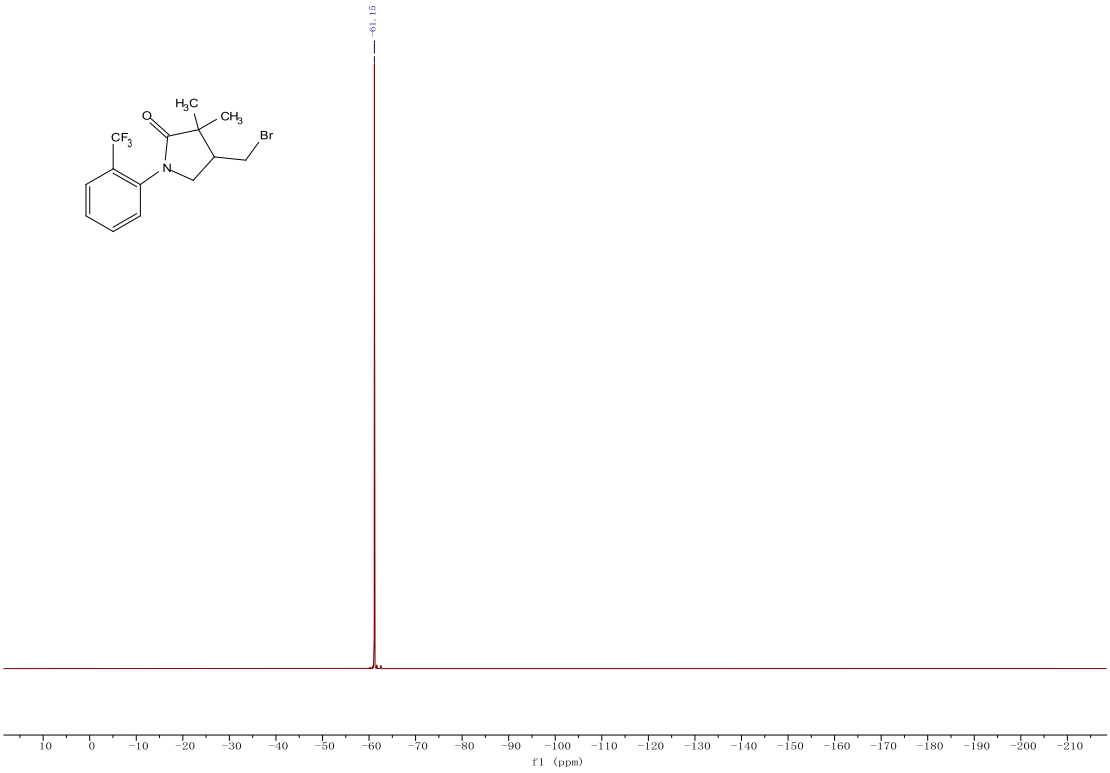
^{1}H NMR ($CDCl_3$, 400 MHz)



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

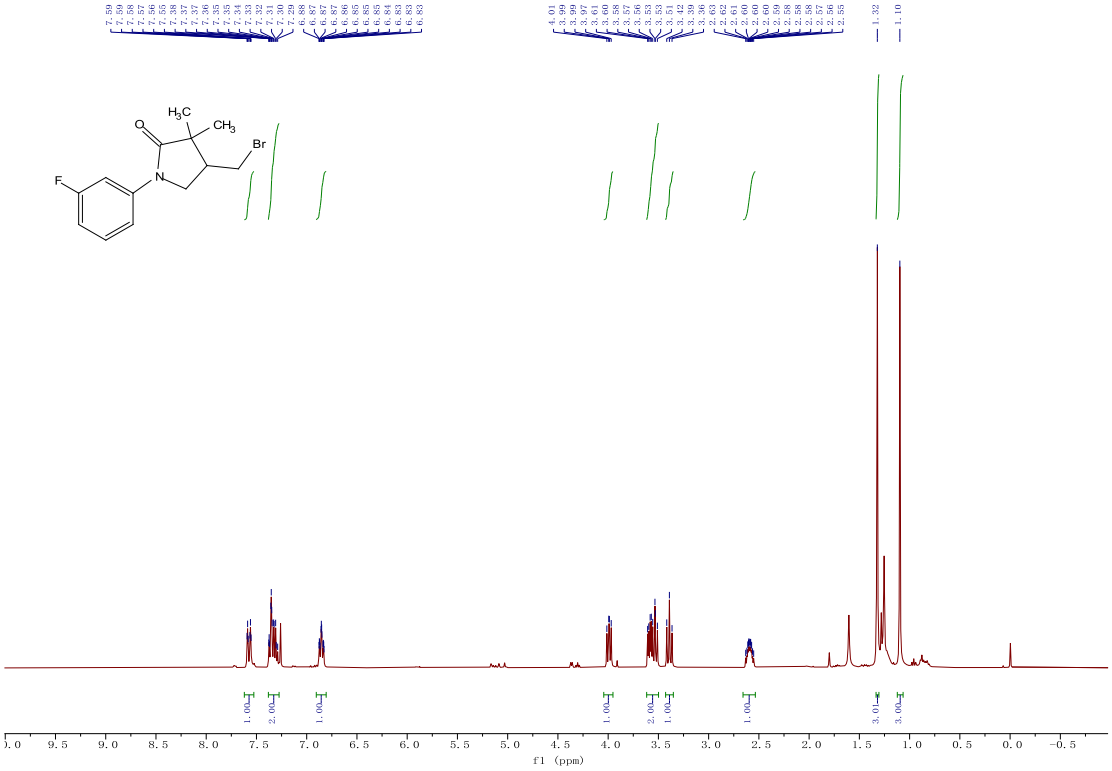


^{19}F NMR ($CDCl_3$, 376 MHz)

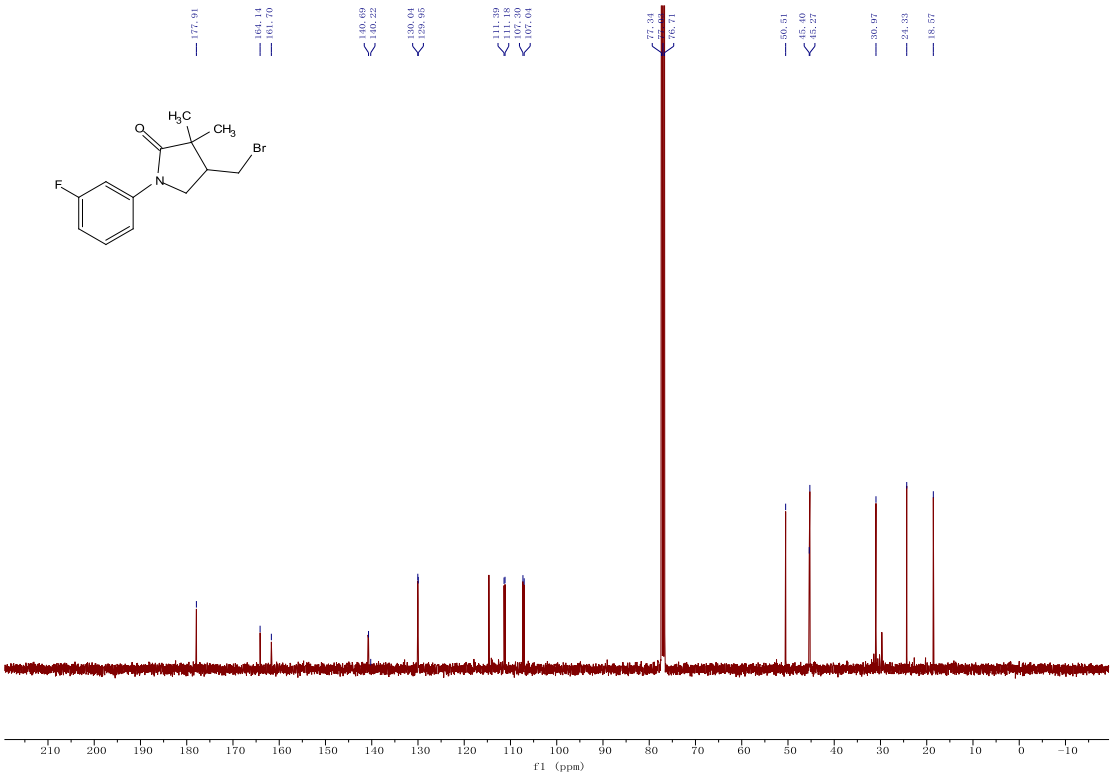


(2e)

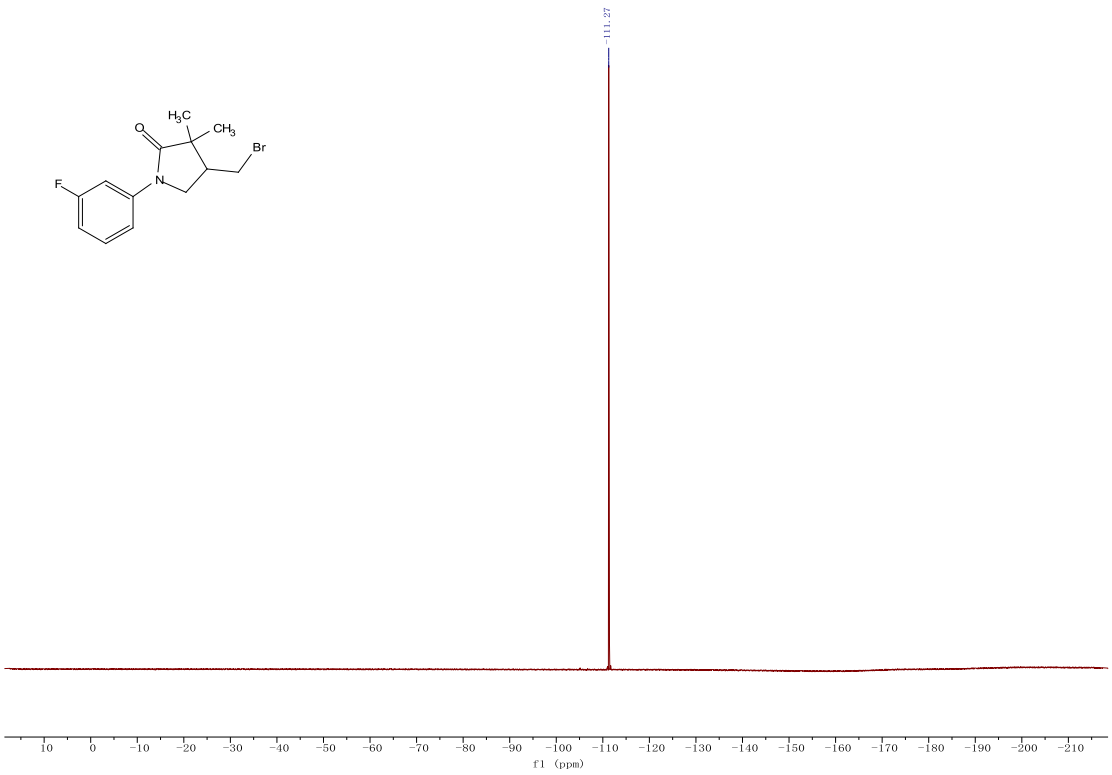
^{1}H NMR ($CDCl_3$, 400 MHz)



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

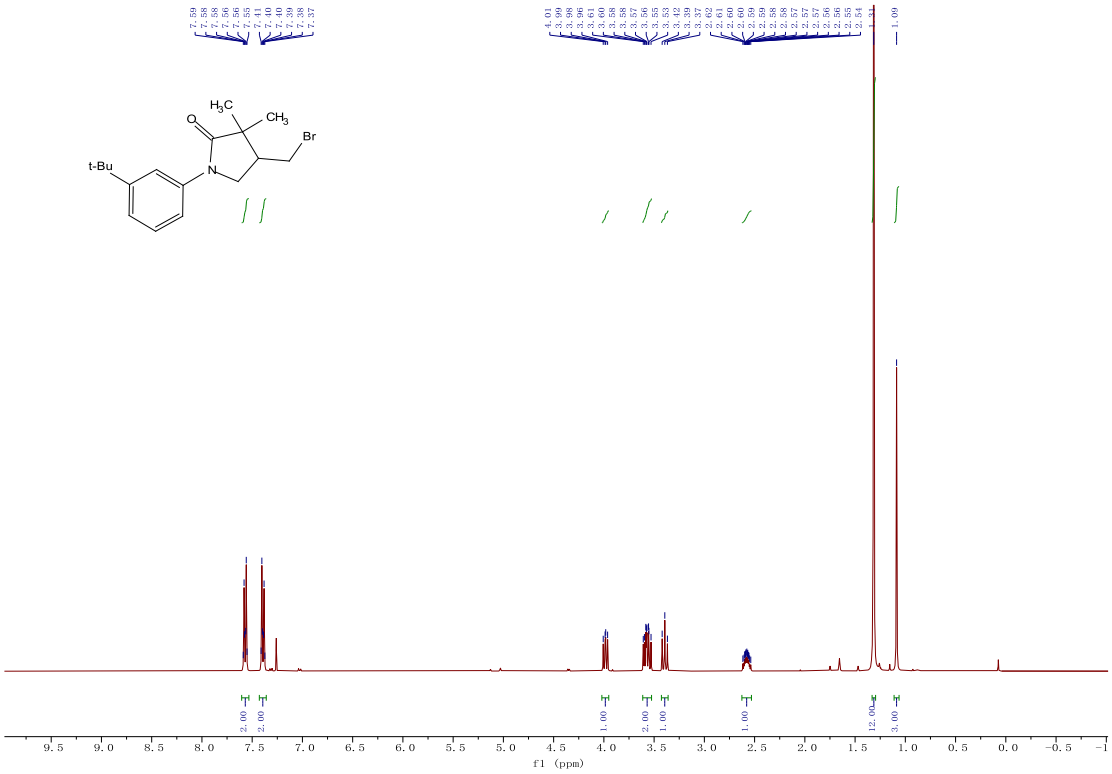


^{19}F NMR ($CDCl_3$, 376 MHz)

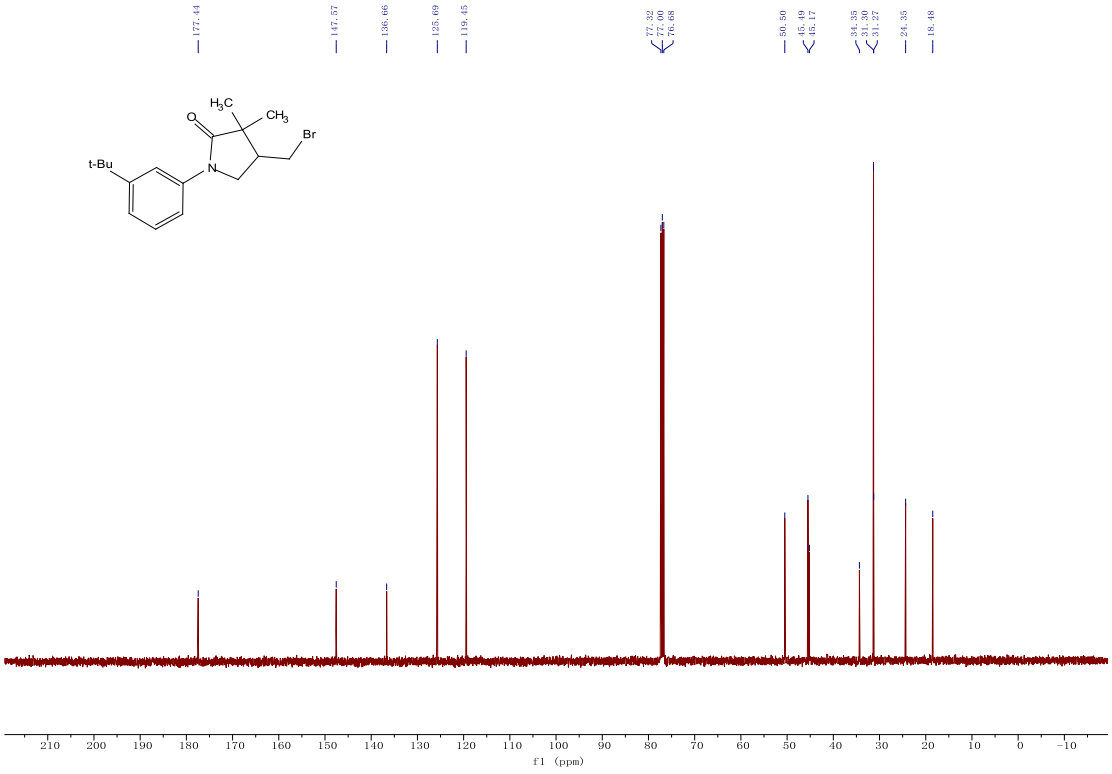


(2f)

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

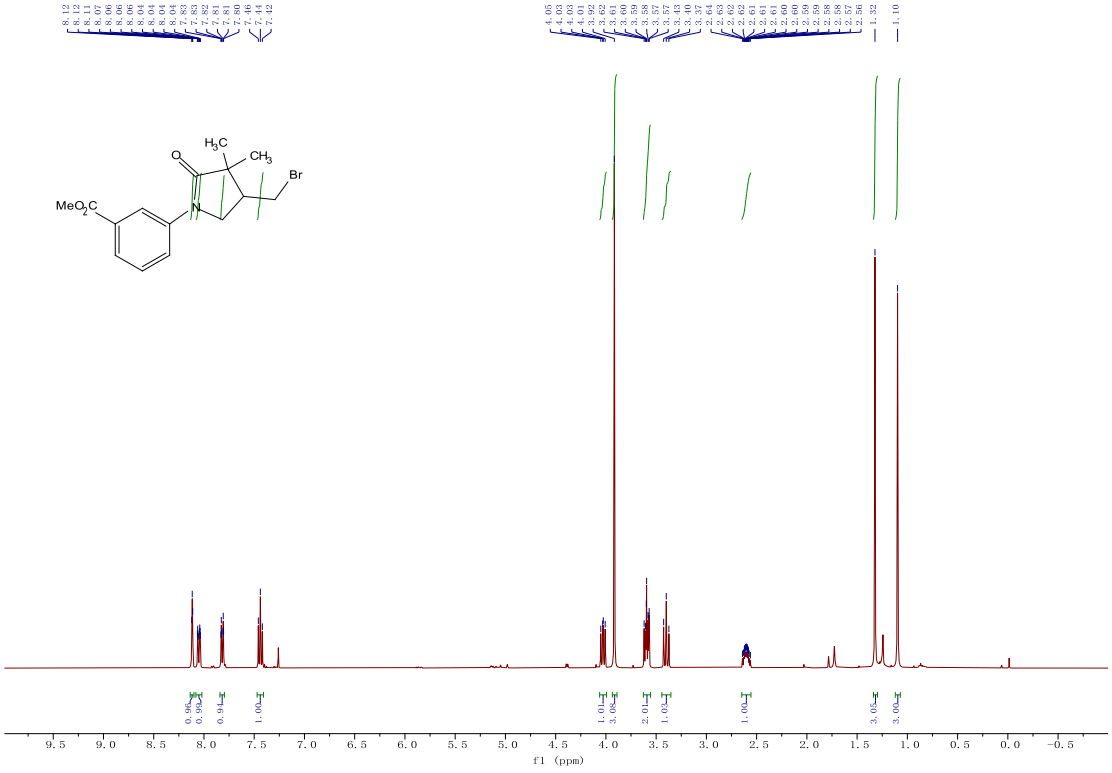


^{13}C NMR ($CDCl_3$, 101 MHz)

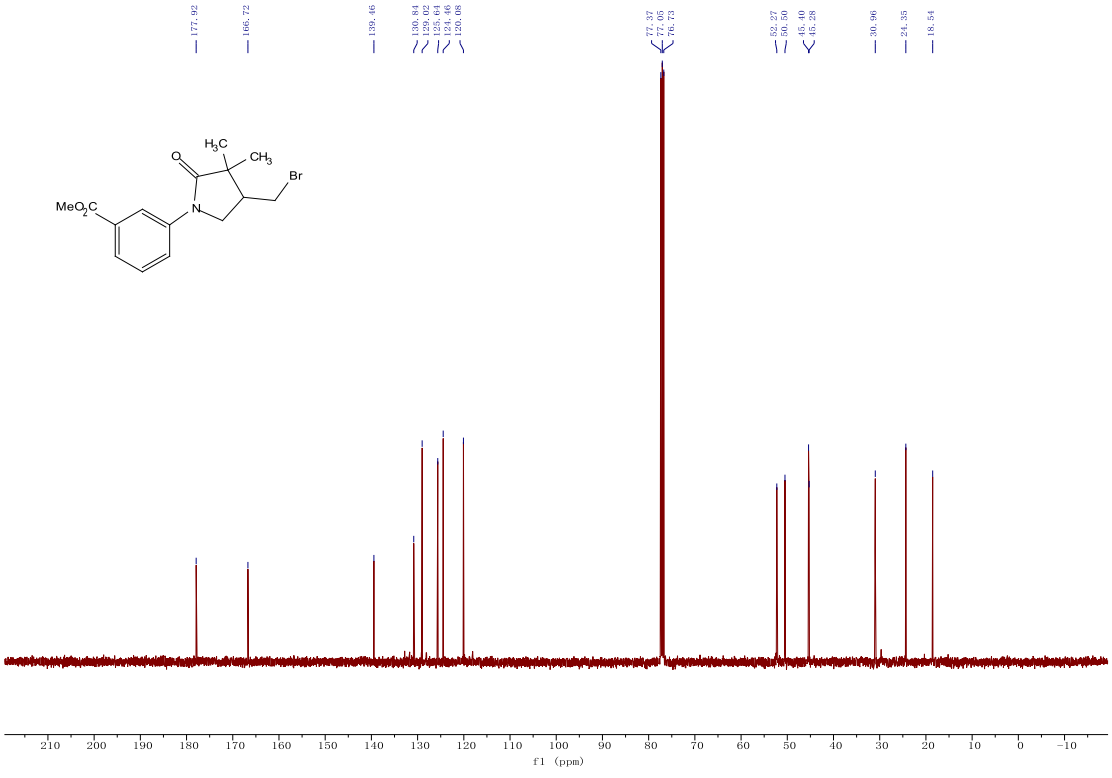


(2g)

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

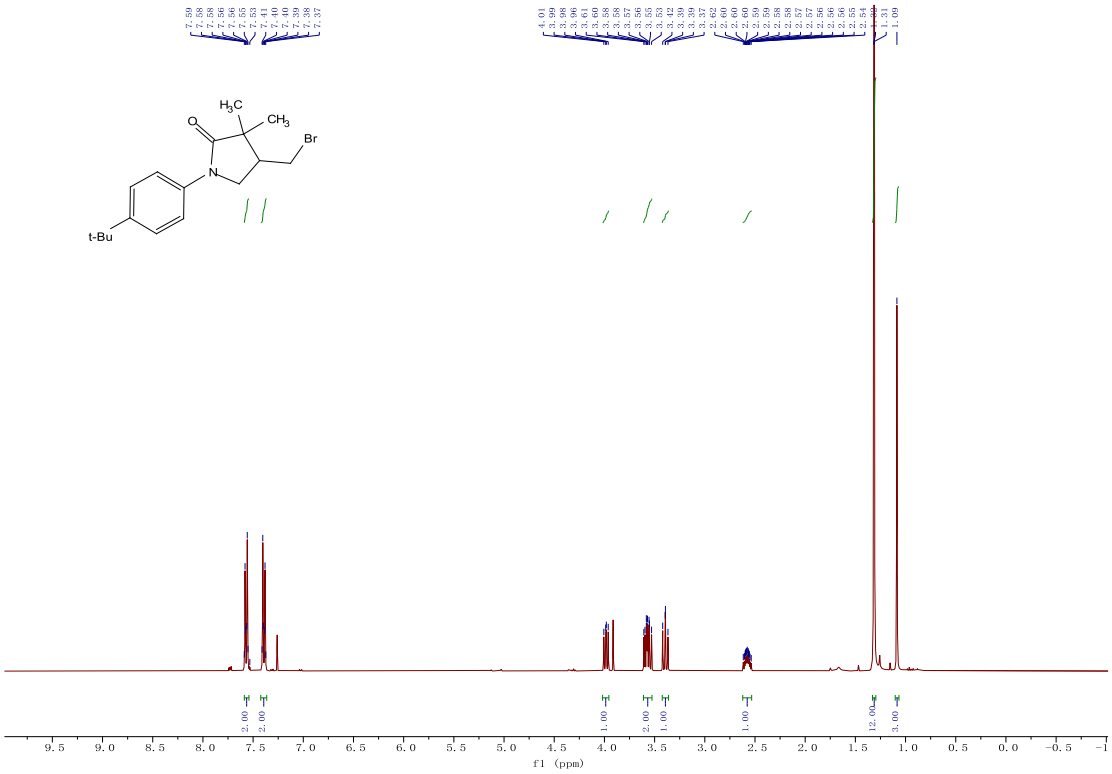


^{13}C NMR ($CDCl_3$, 101 MHz)

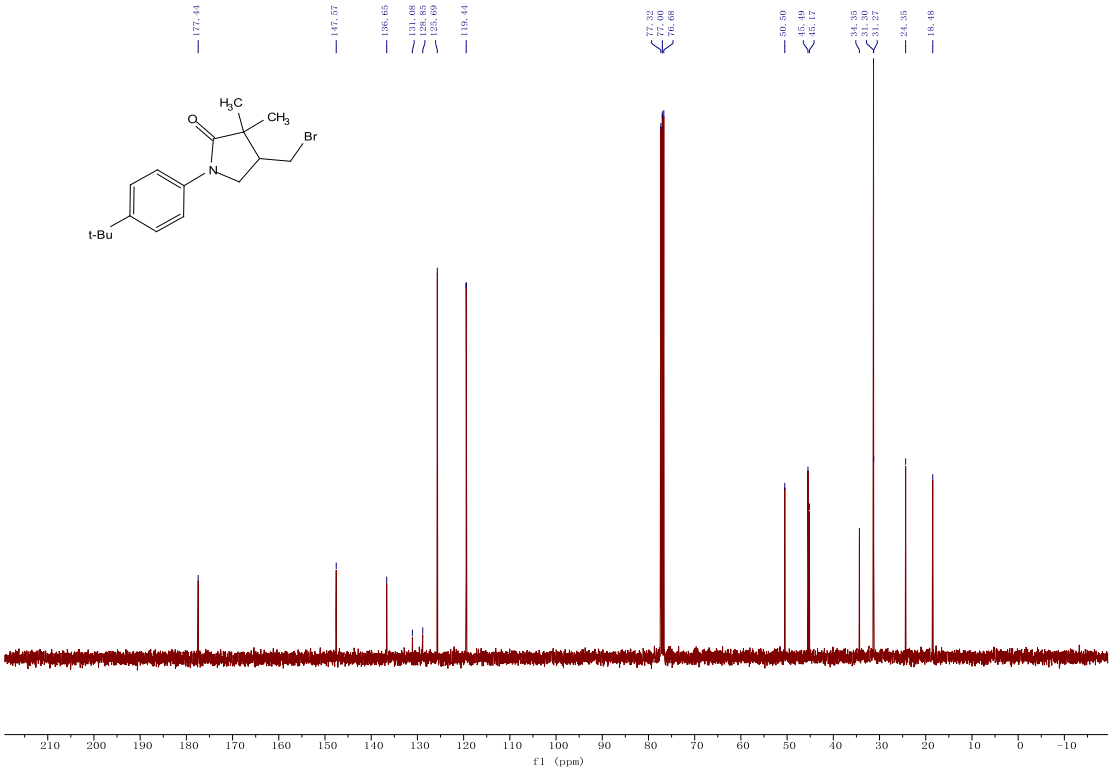


(2h)

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

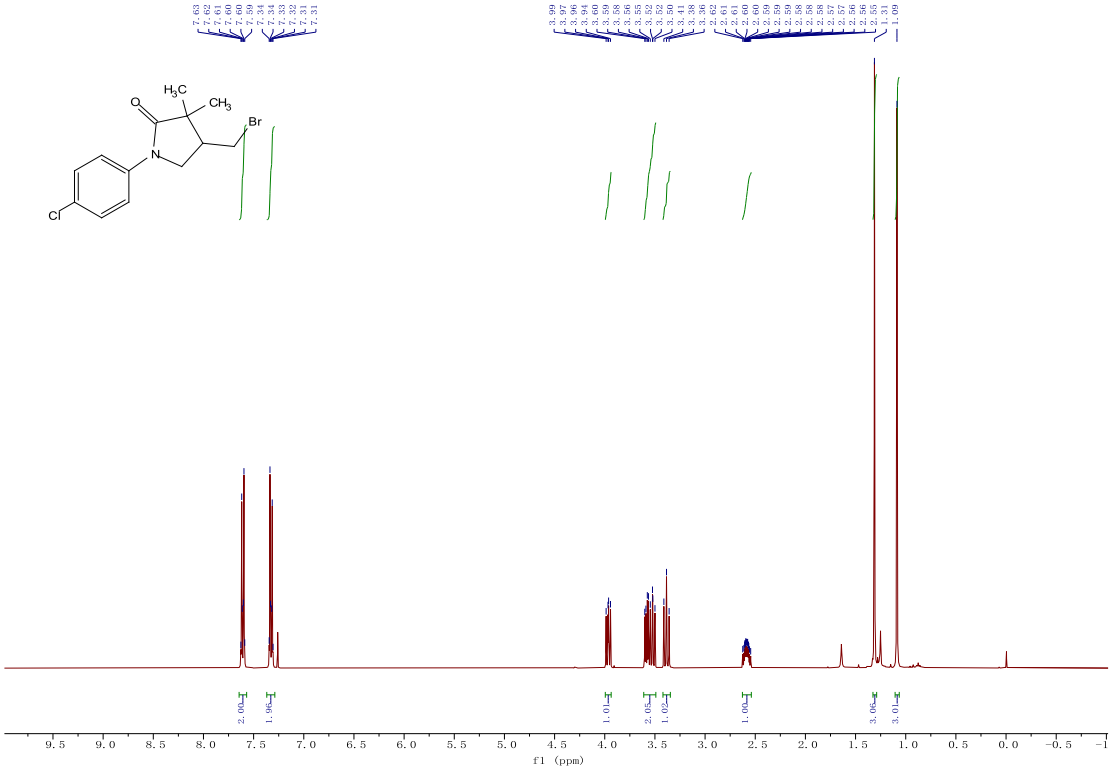


^{13}C NMR ($CDCl_3$, 101 MHz)

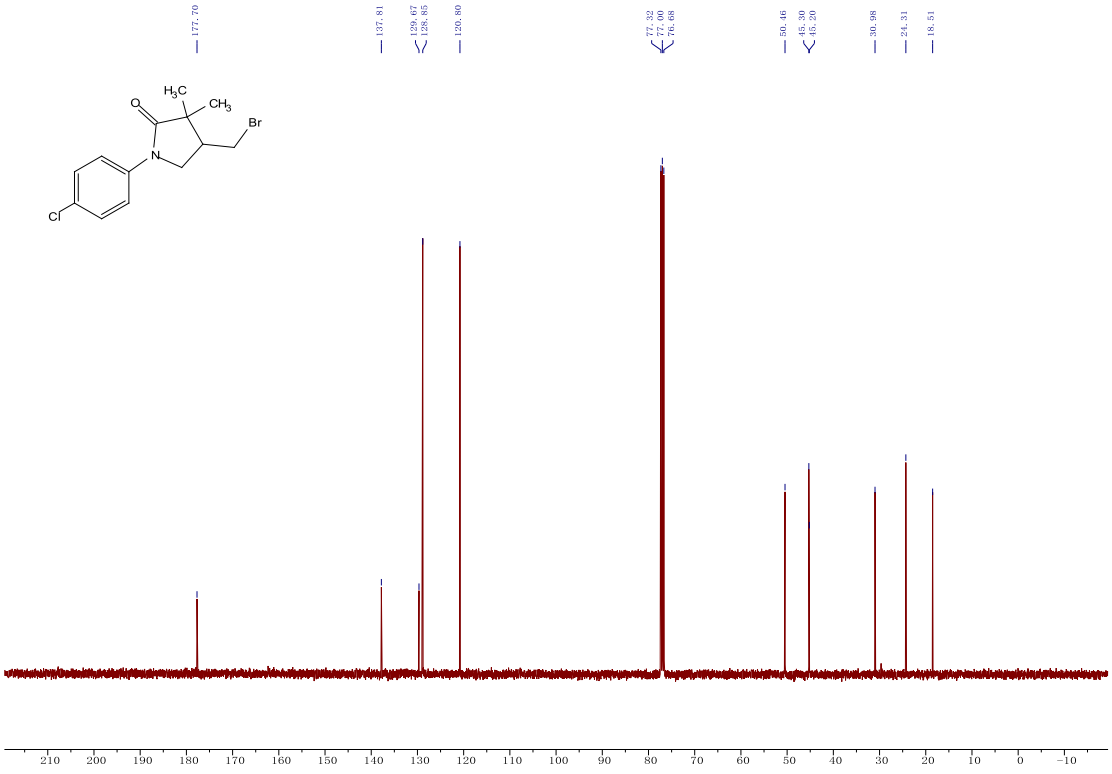


(2i)

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

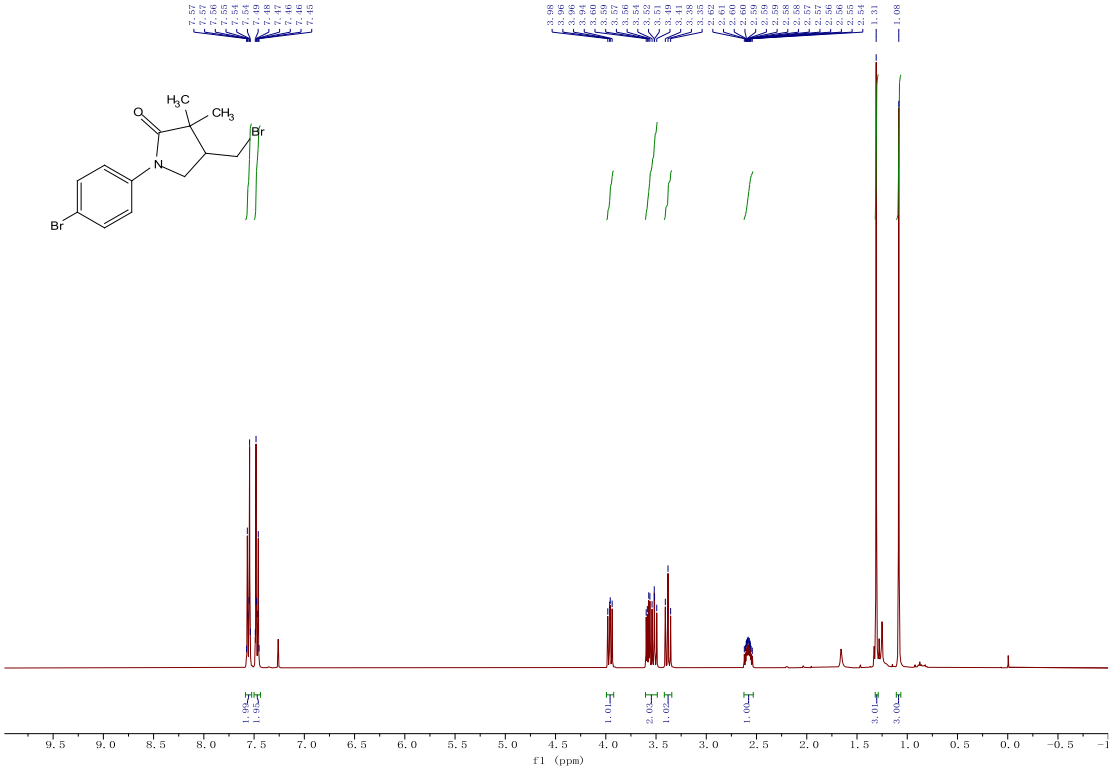


^{13}C NMR ($CDCl_3$, 101 MHz)

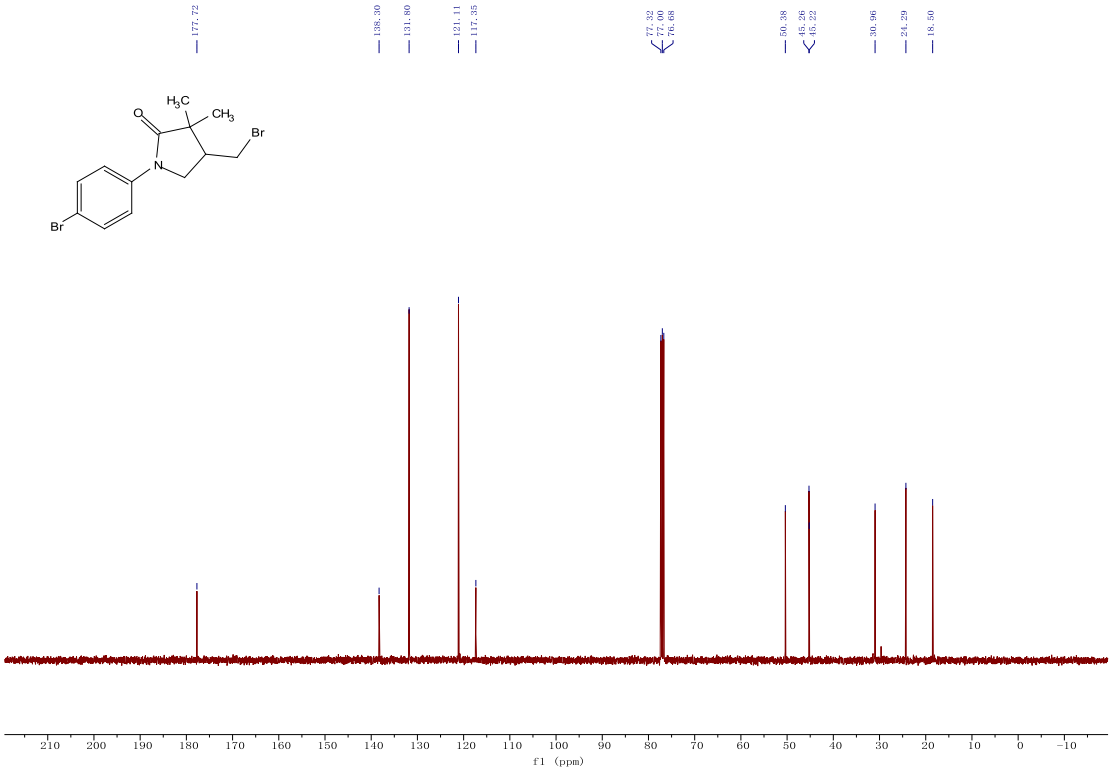


(2j)

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

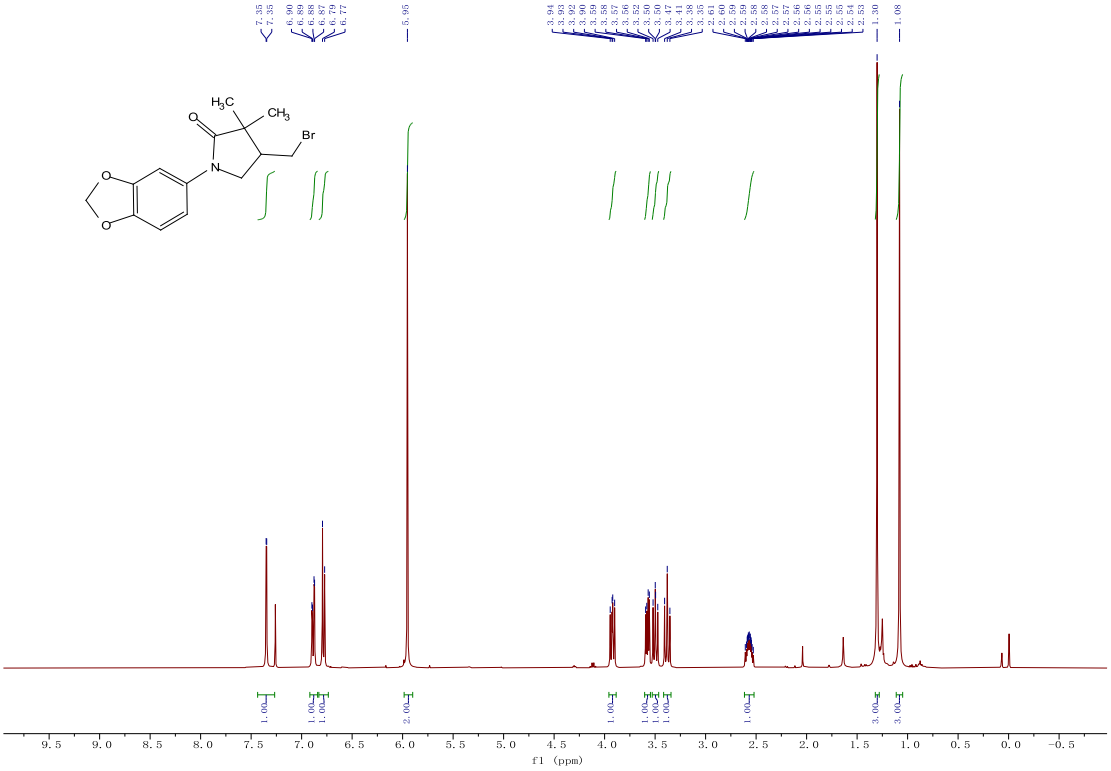


^{13}C NMR ($CDCl_3$, 101 MHz)

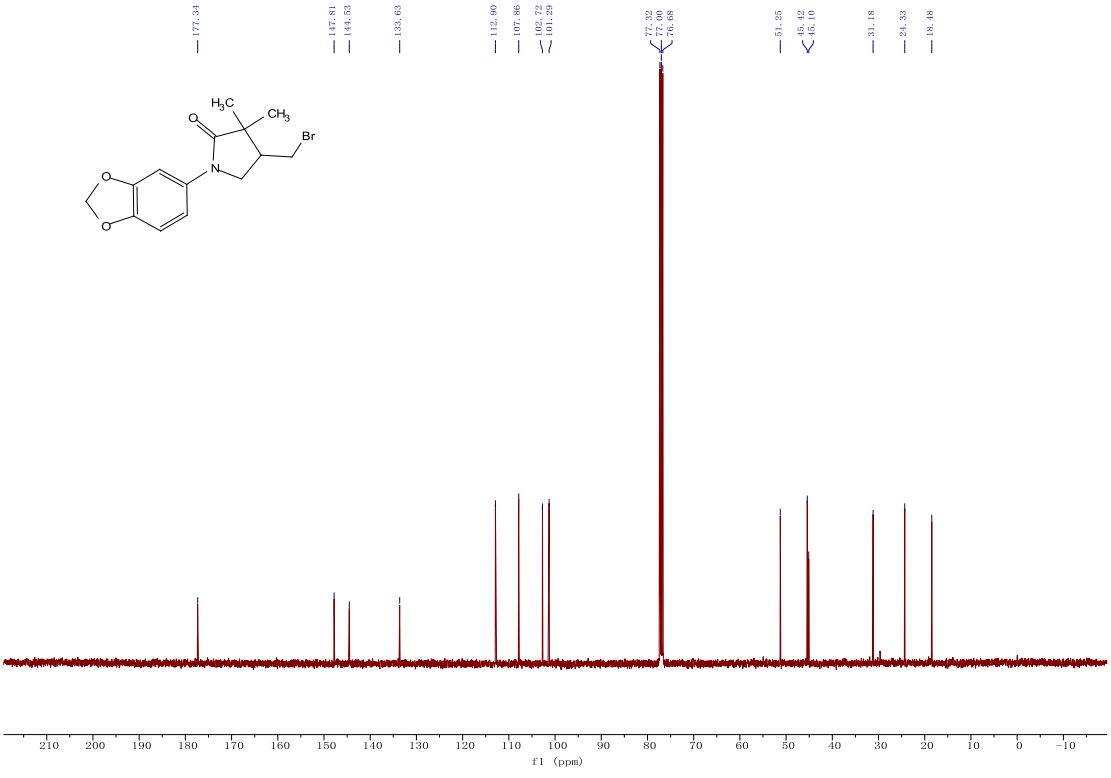


(2k)

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

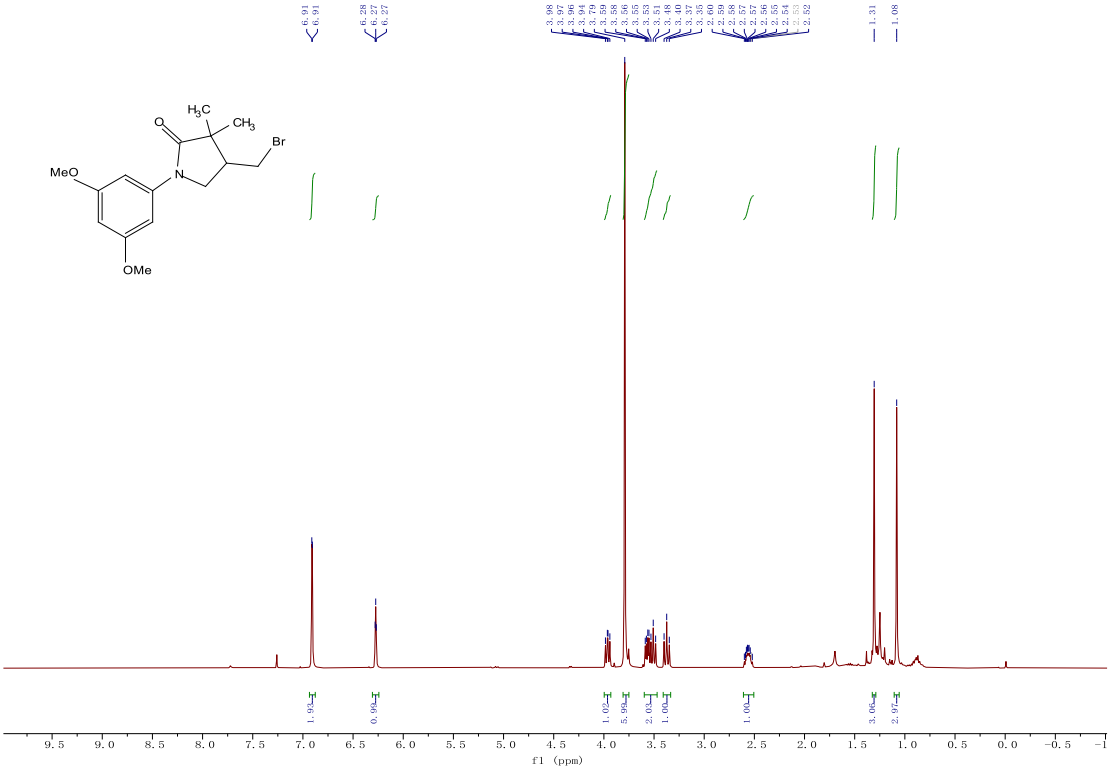


^{13}C NMR ($CDCl_3$, 101 MHz)

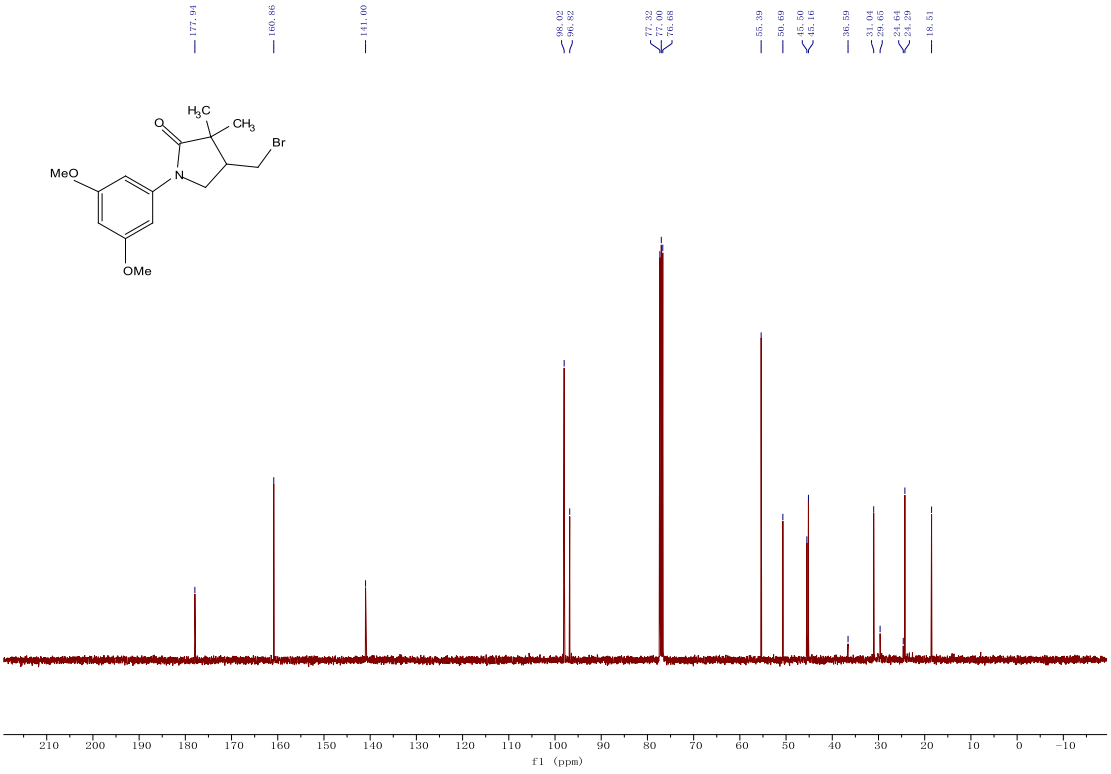


(2l)

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

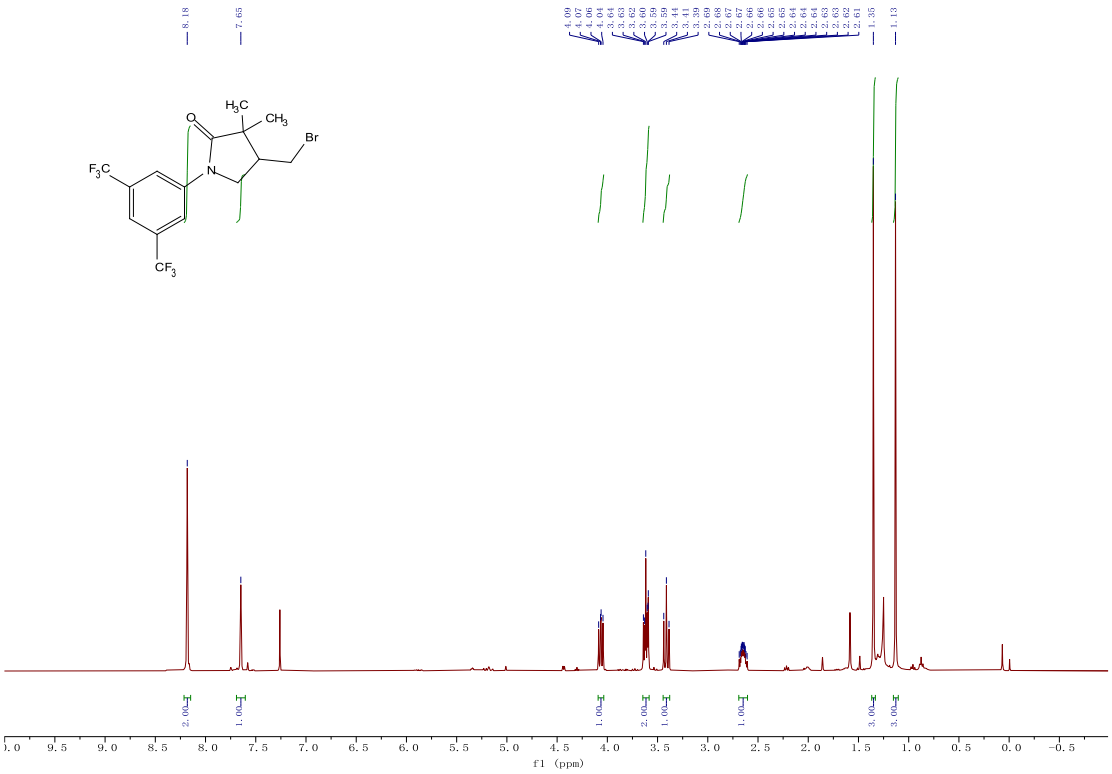


^{13}C NMR ($CDCl_3$, 101 MHz)

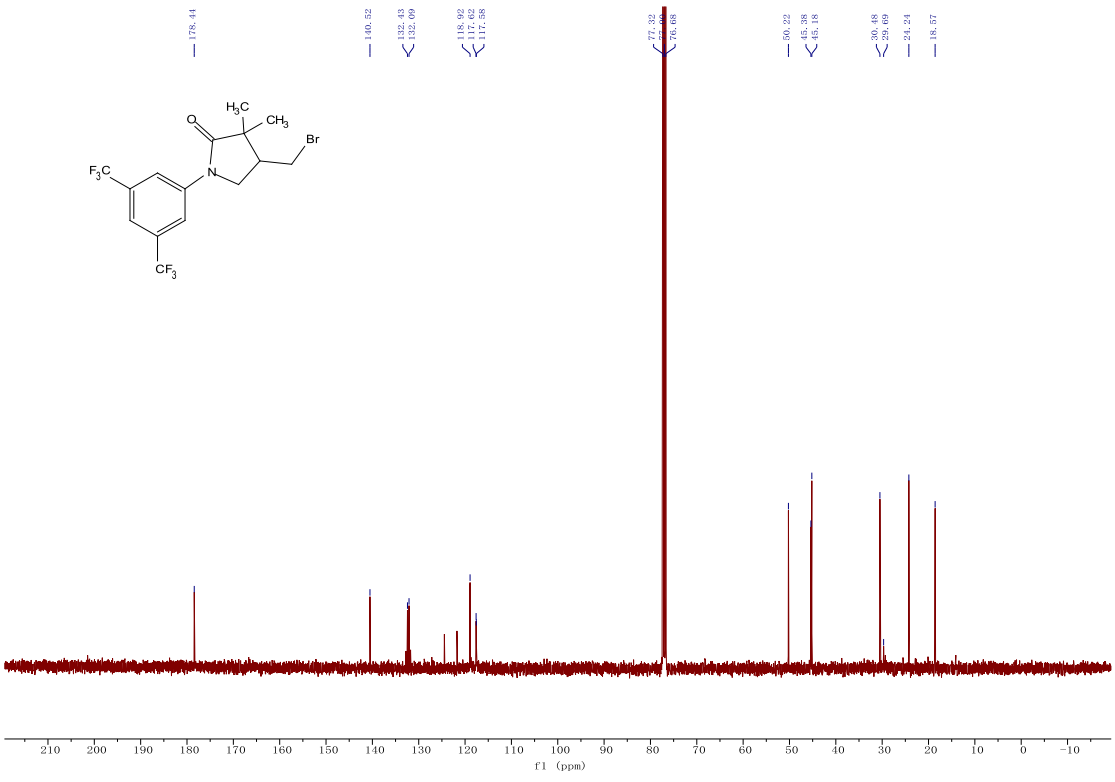


(2m)

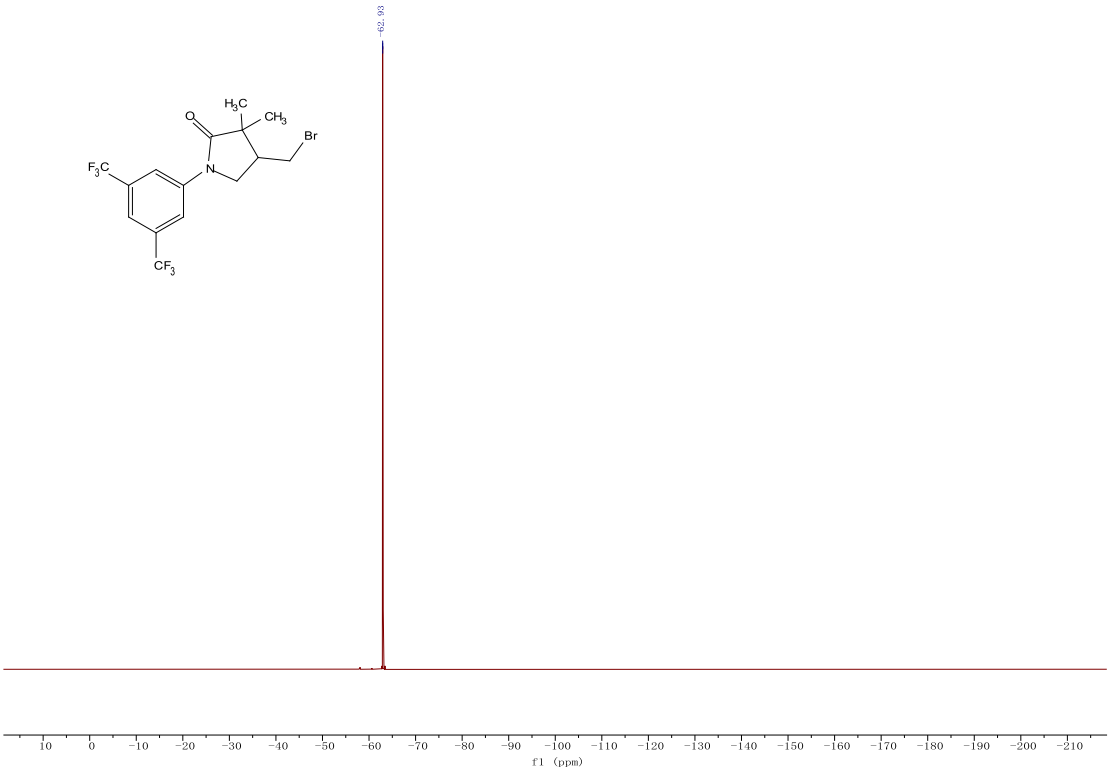
^{1}H NMR ($CDCl_3$, 400 MHz)



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

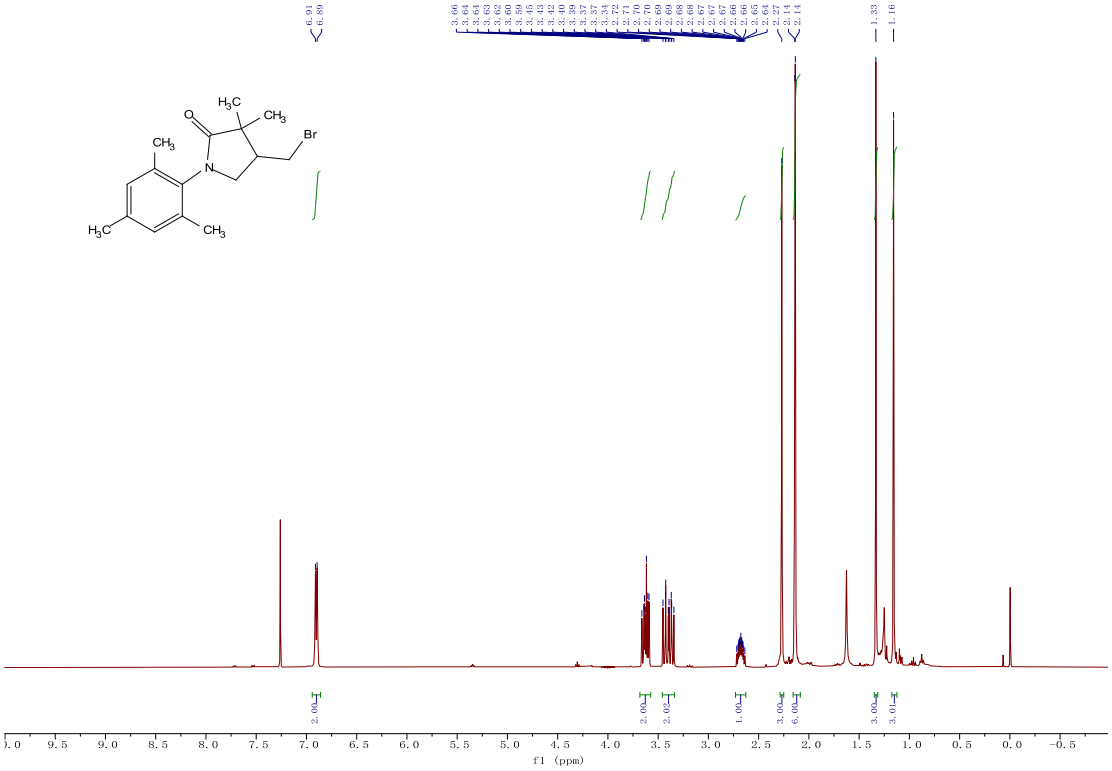


^{19}F NMR ($CDCl_3$, 376 MHz)

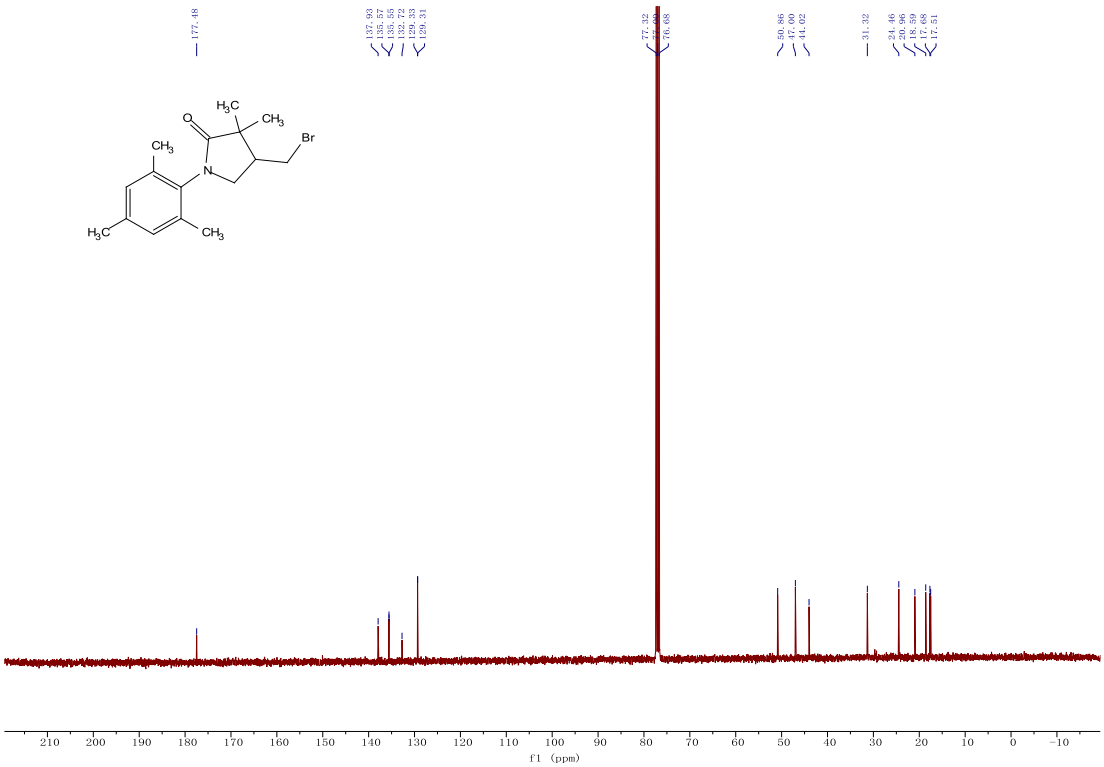


(2n)

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

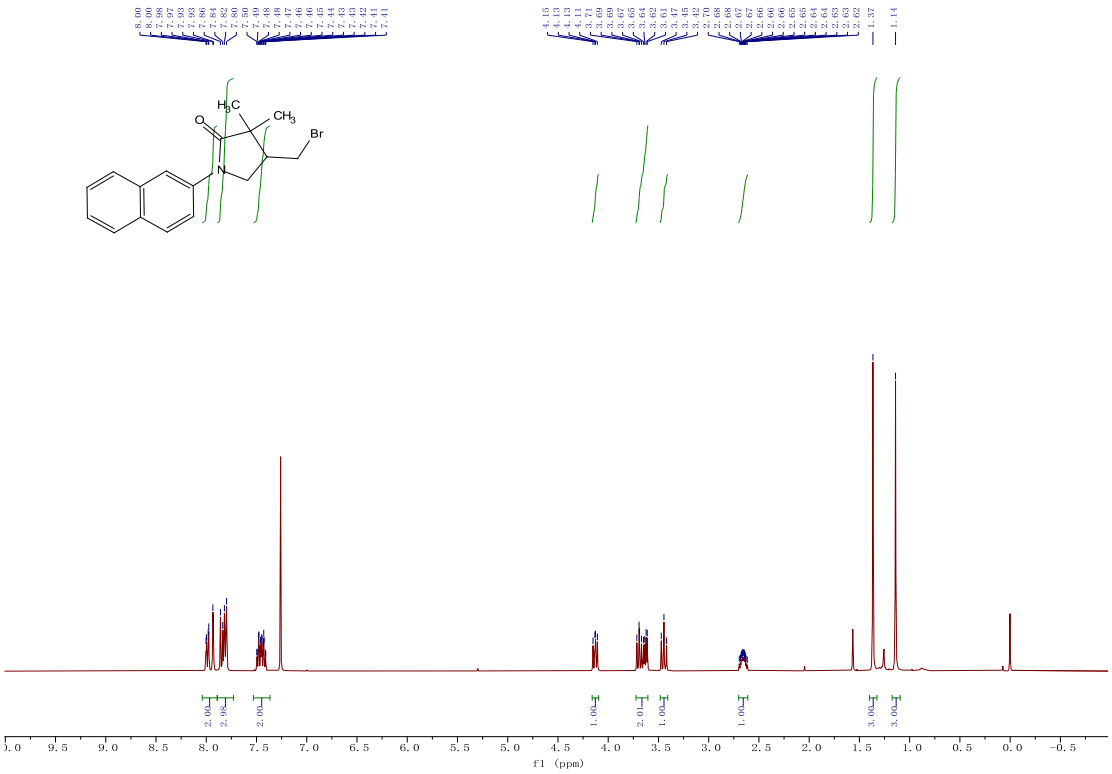


^{13}C NMR ($CDCl_3$, 101 MHz)

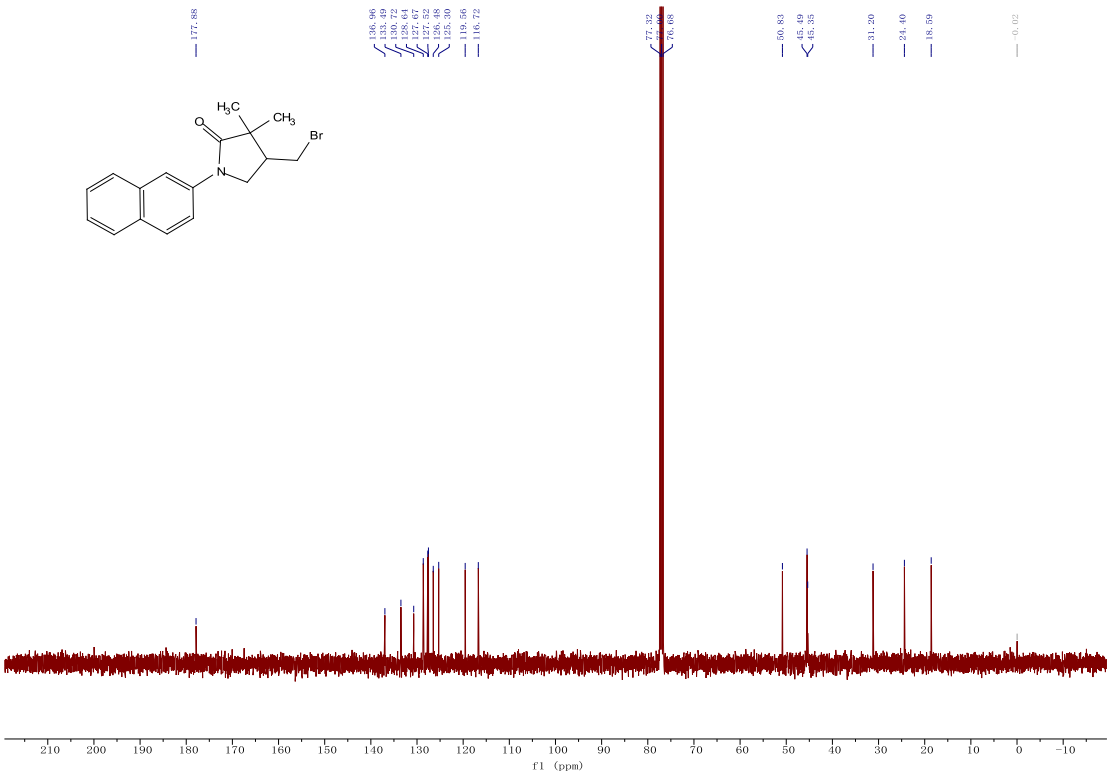


(2o)

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

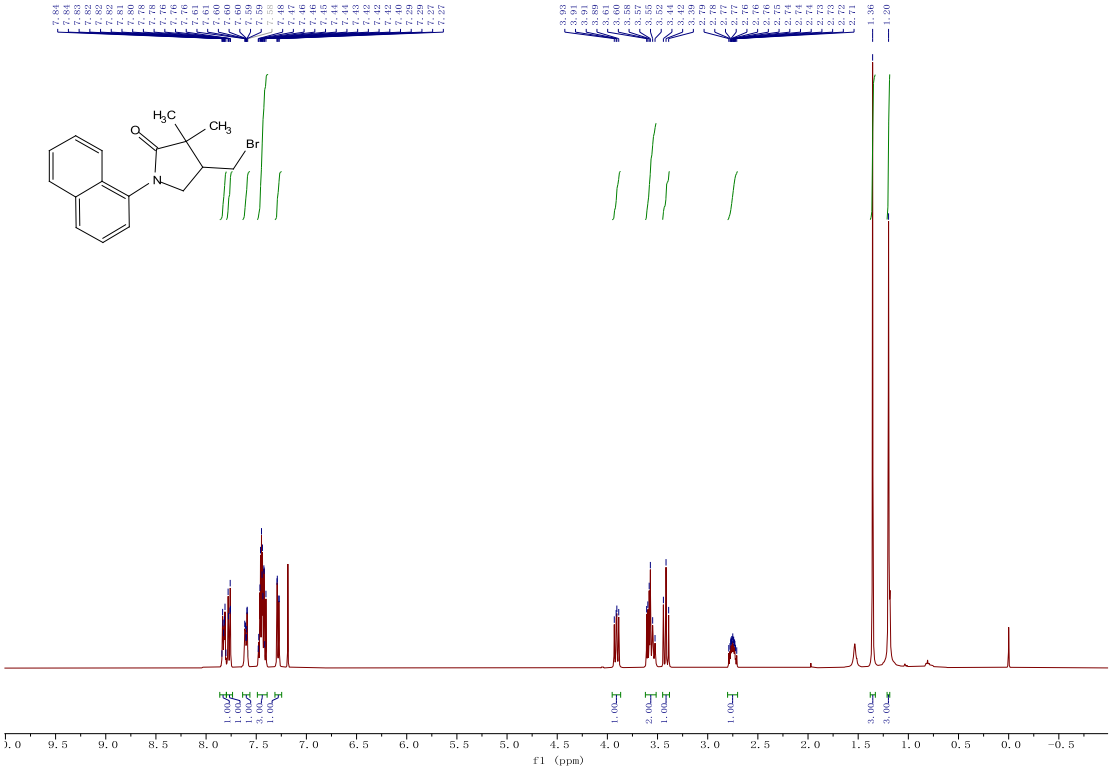


^{13}C NMR ($CDCl_3$, 101 MHz)

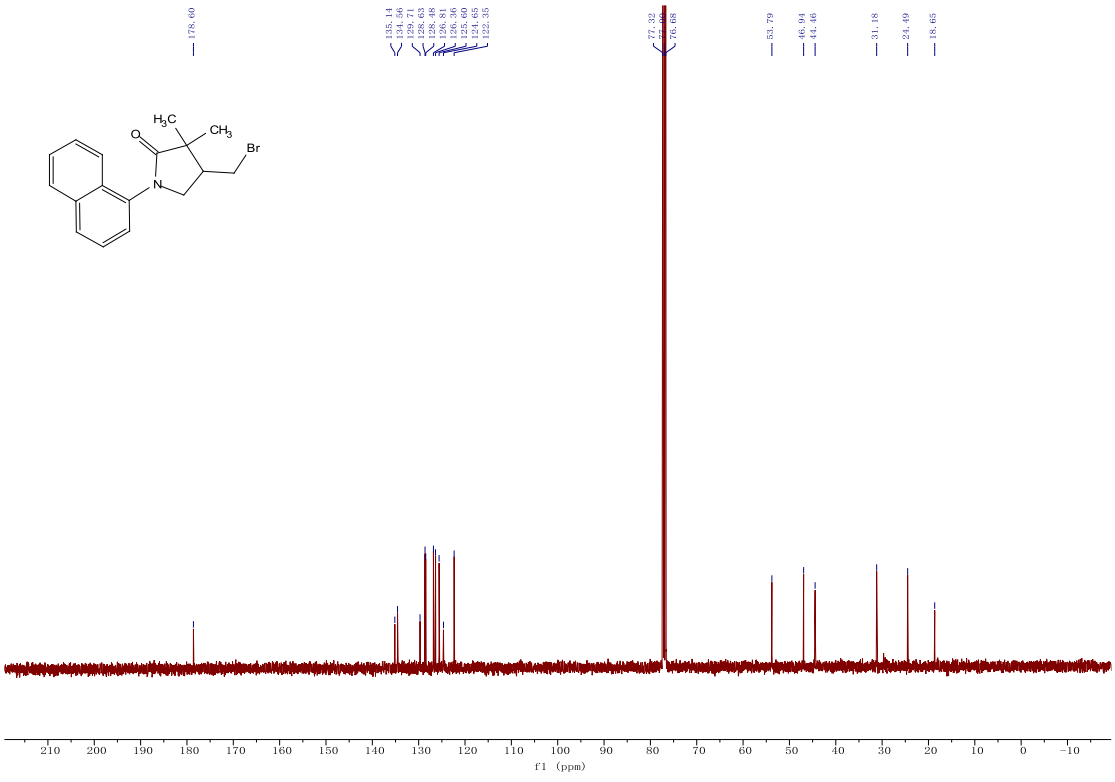


(2p)

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

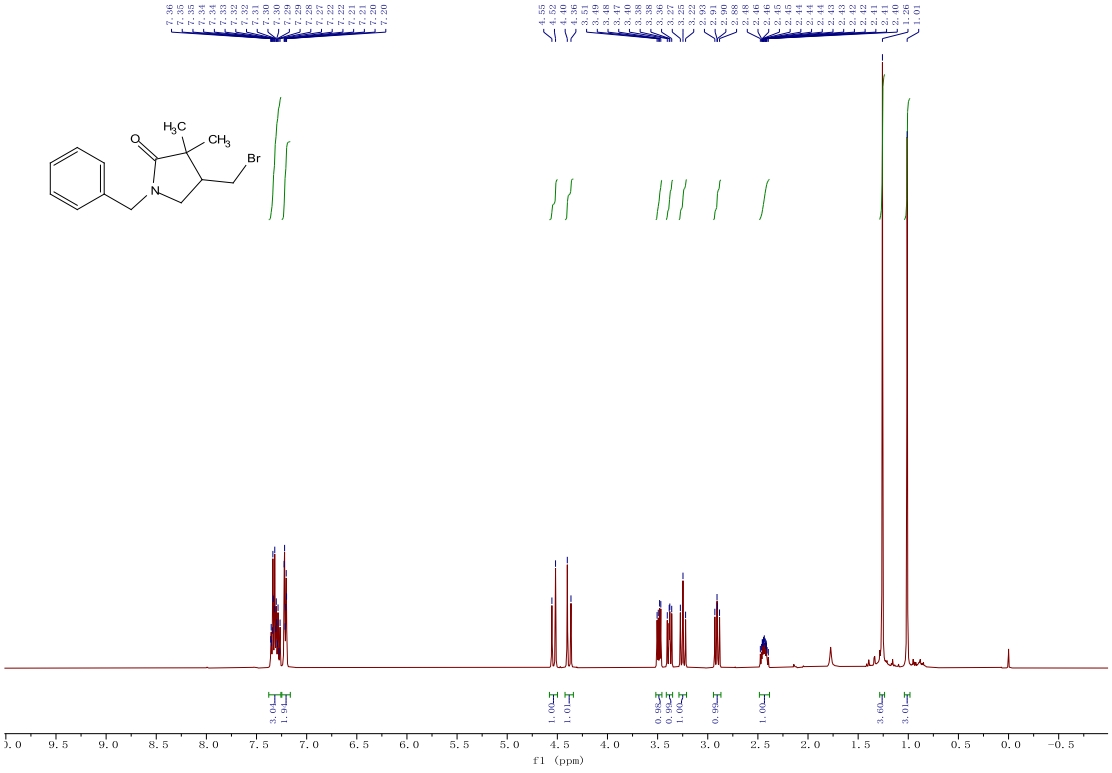


^{13}C NMR ($CDCl_3$, 101 MHz)

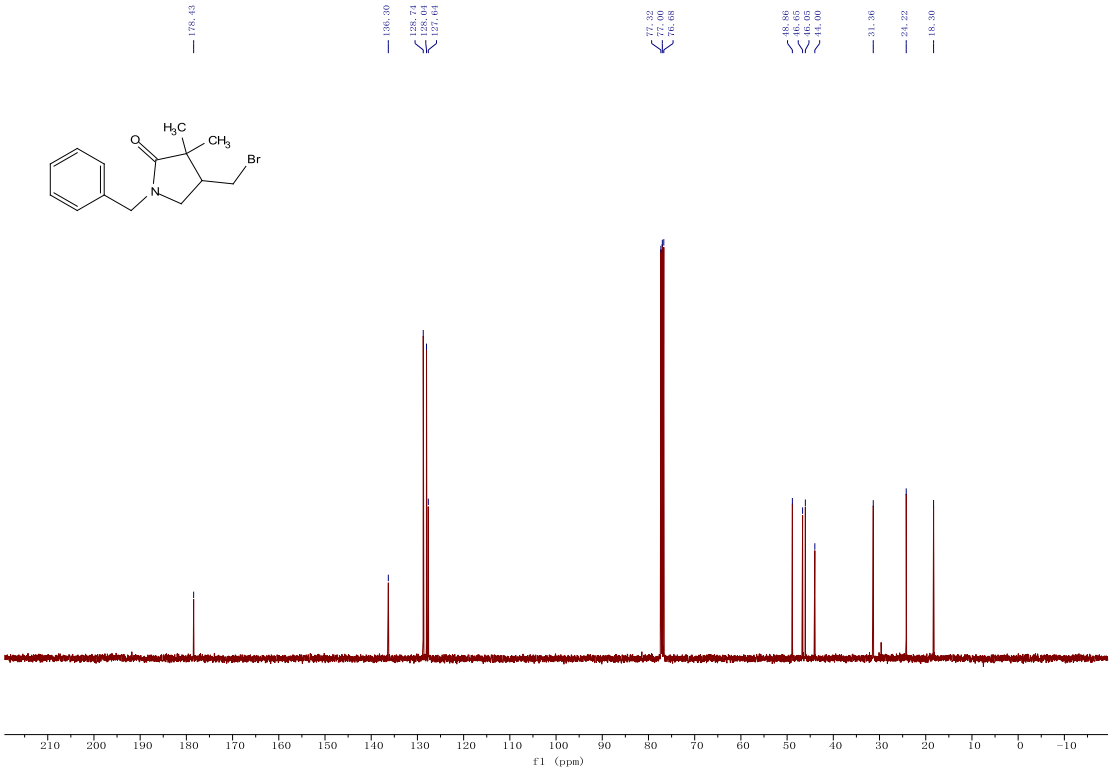


(2q)

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

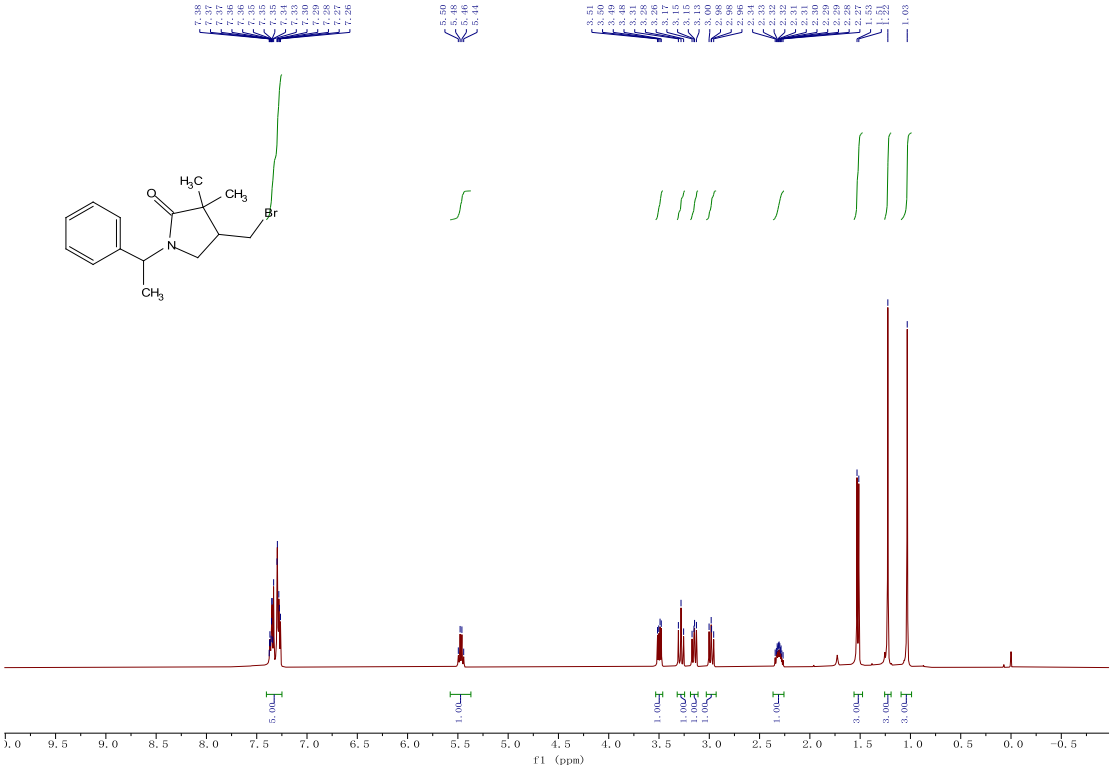


^{13}C NMR ($CDCl_3$, 101 MHz)

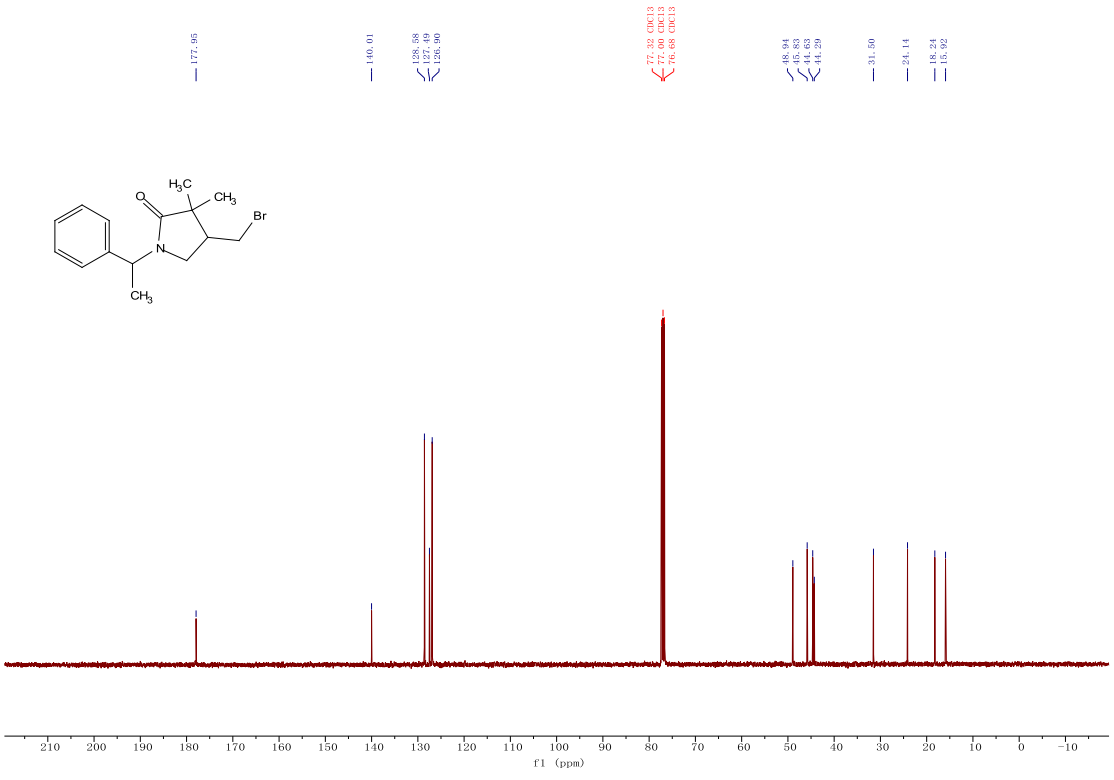


(2r)

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

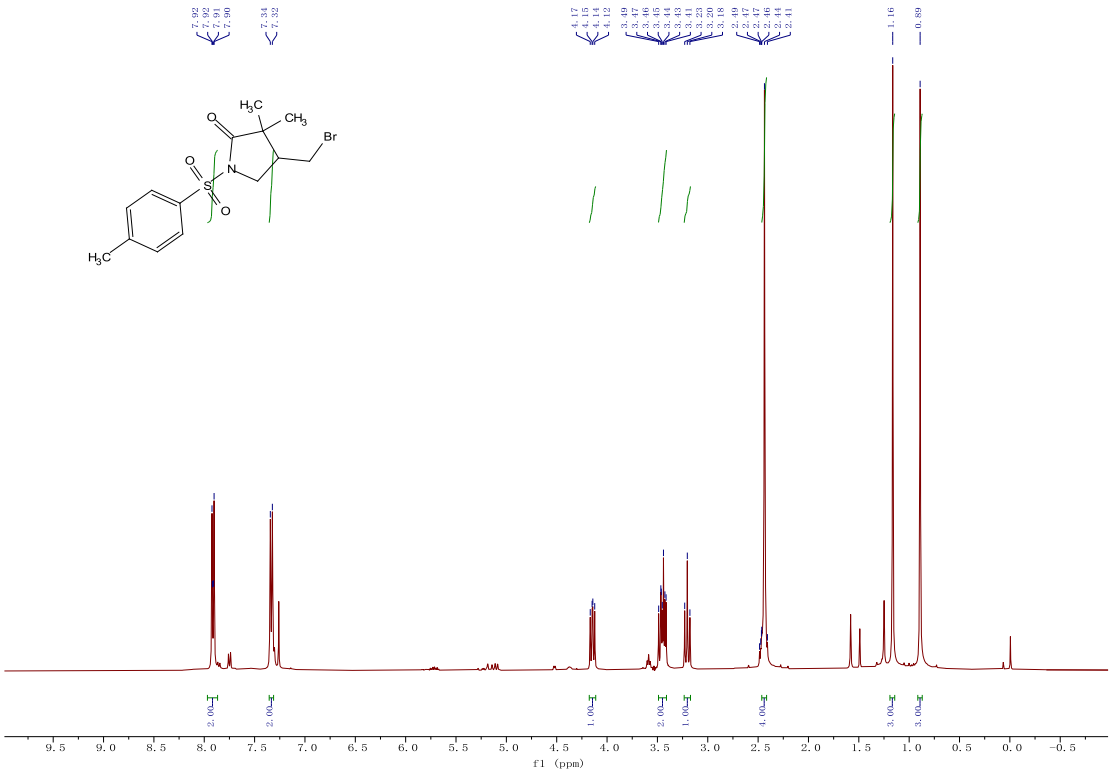


^{13}C NMR ($CDCl_3$, 101 MHz)

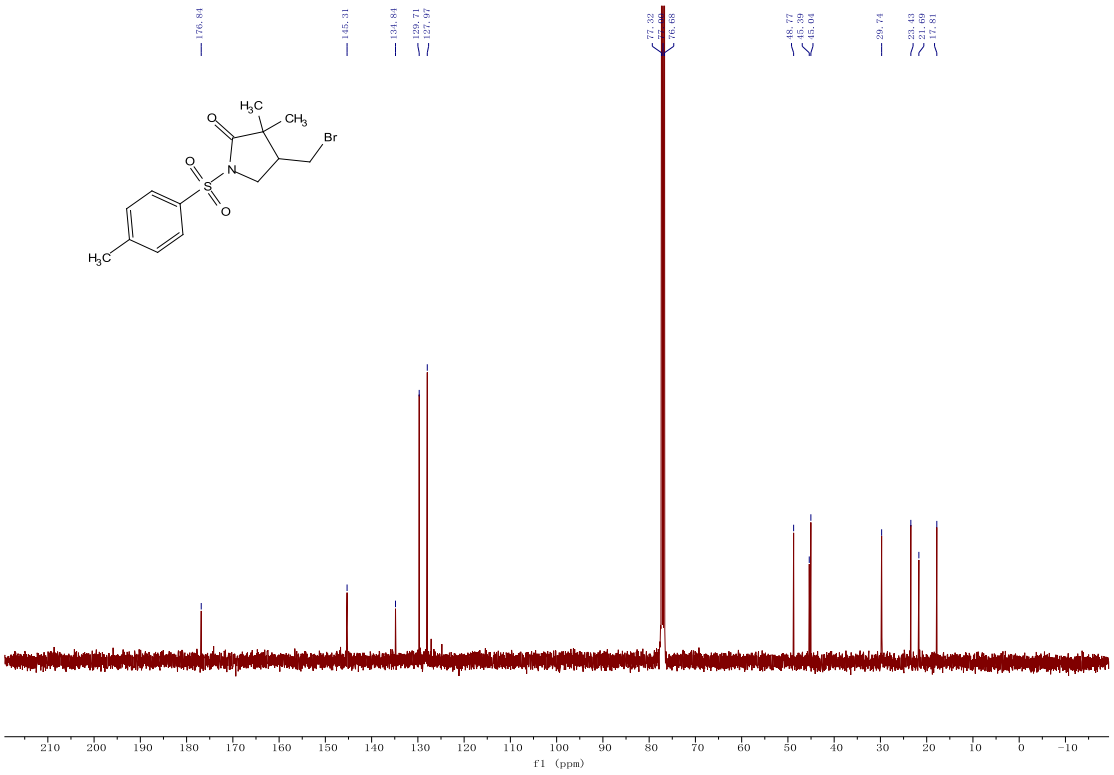


(2s)

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

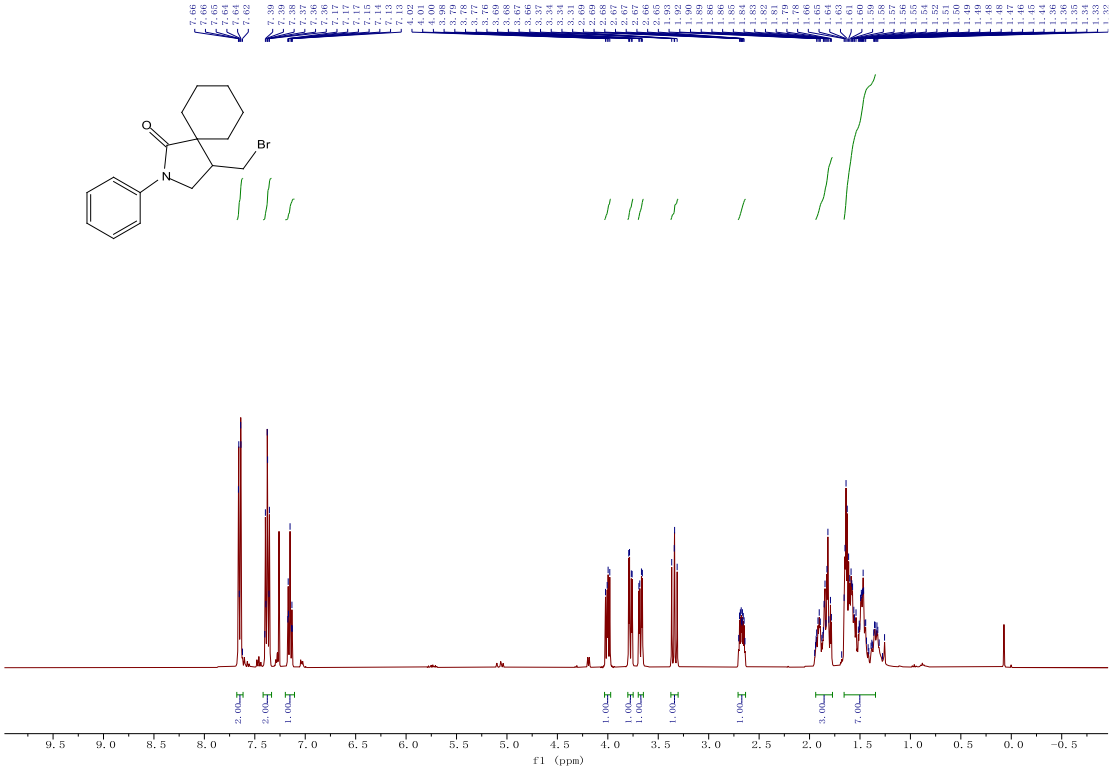


^{13}C NMR ($CDCl_3$, 101 MHz)

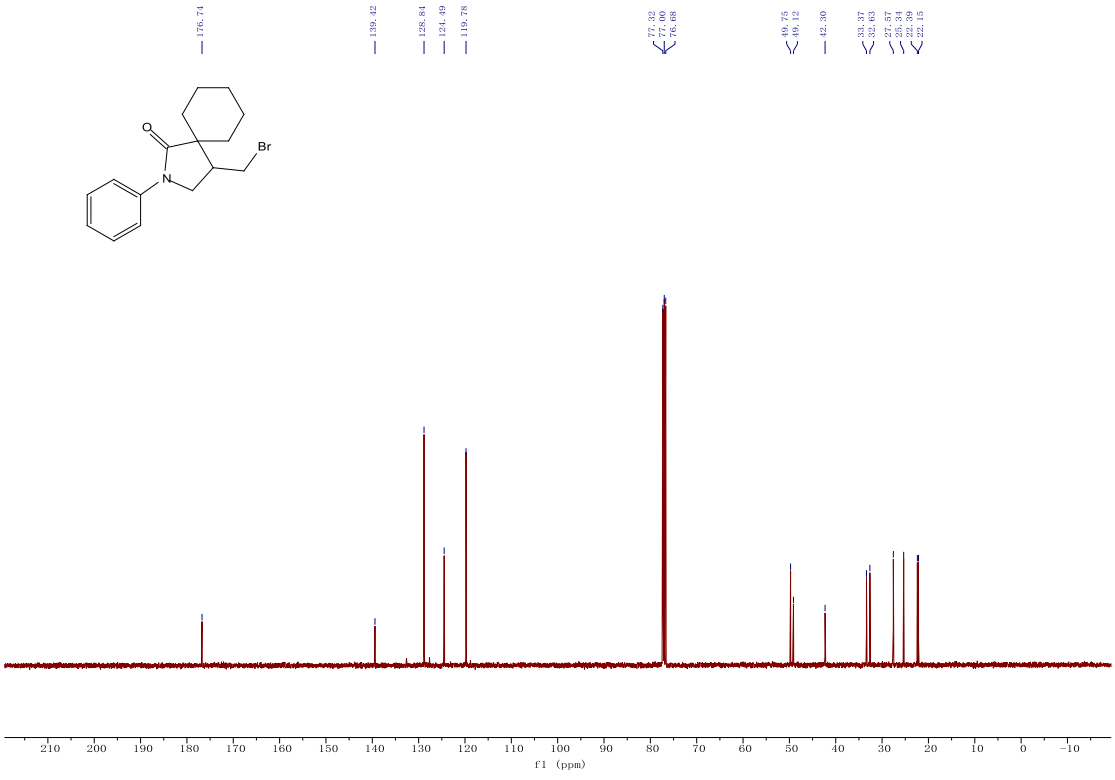


(2t)

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

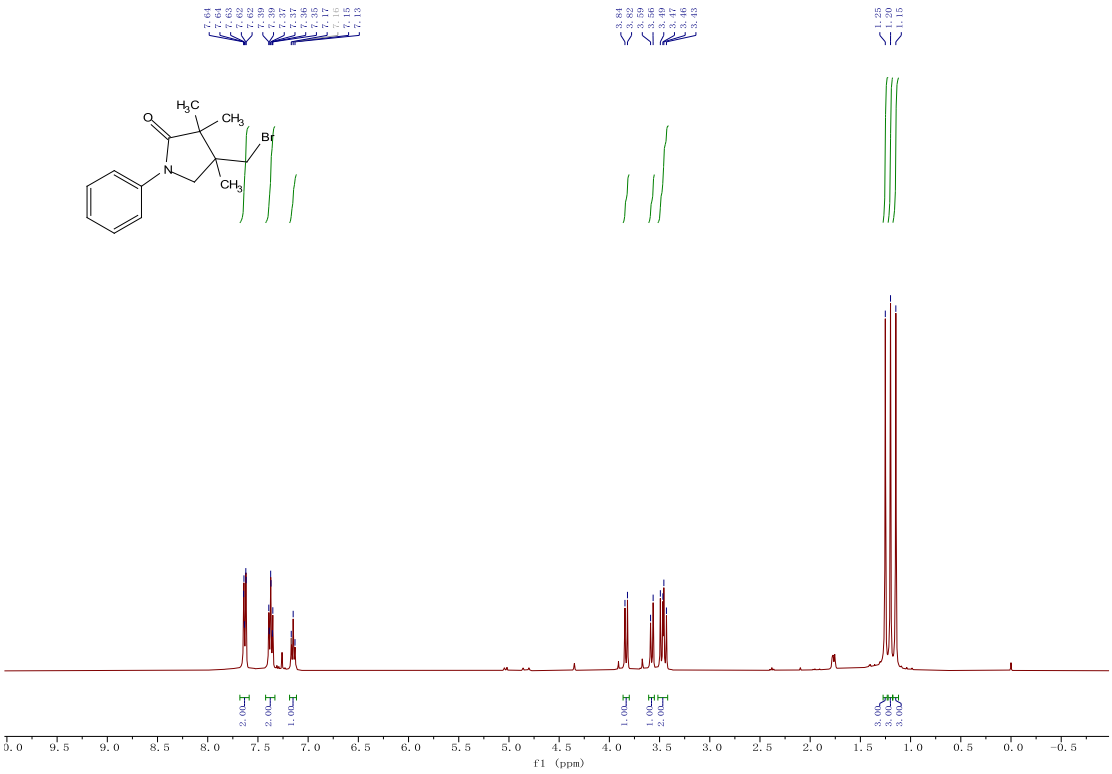


^{13}C NMR ($CDCl_3$, 101 MHz)

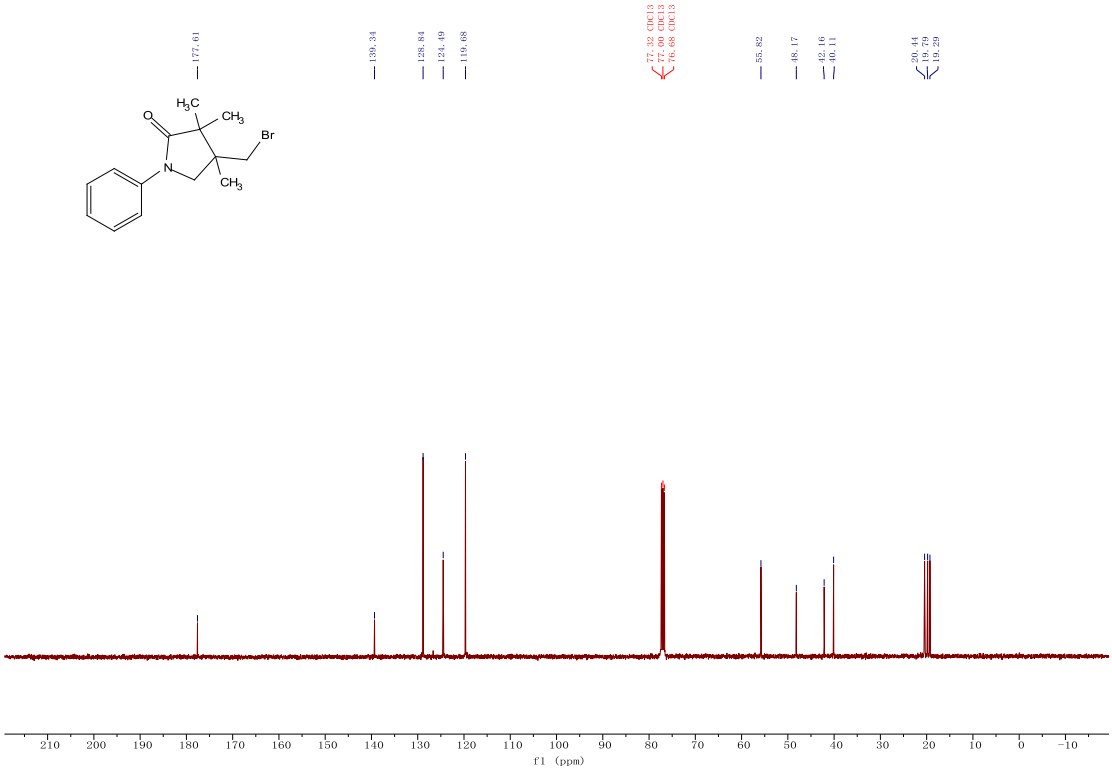


(2u)

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

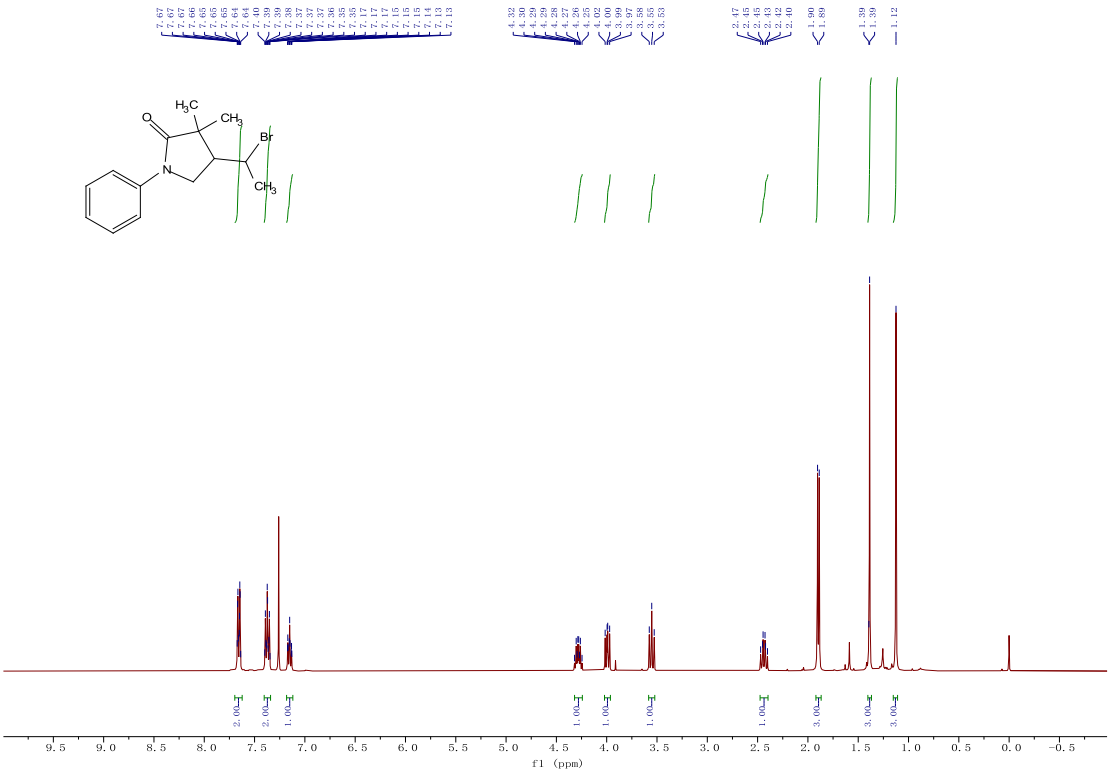


^{13}C NMR ($CDCl_3$, 101 MHz)

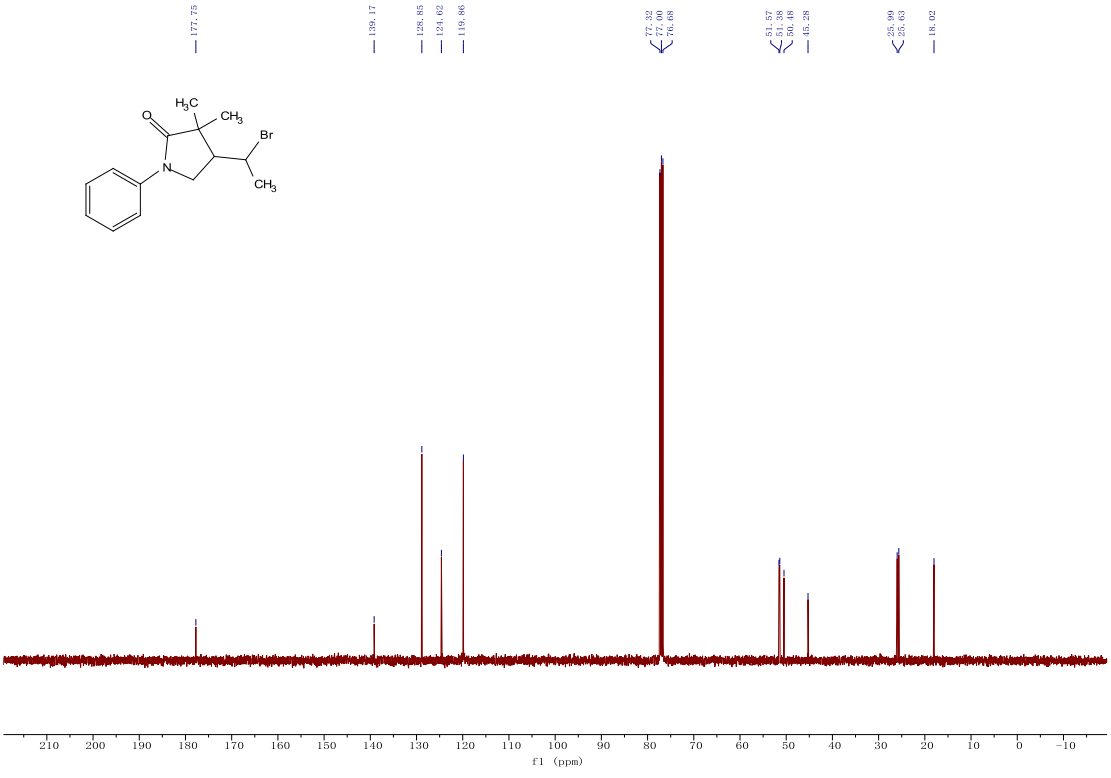


(2v)

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

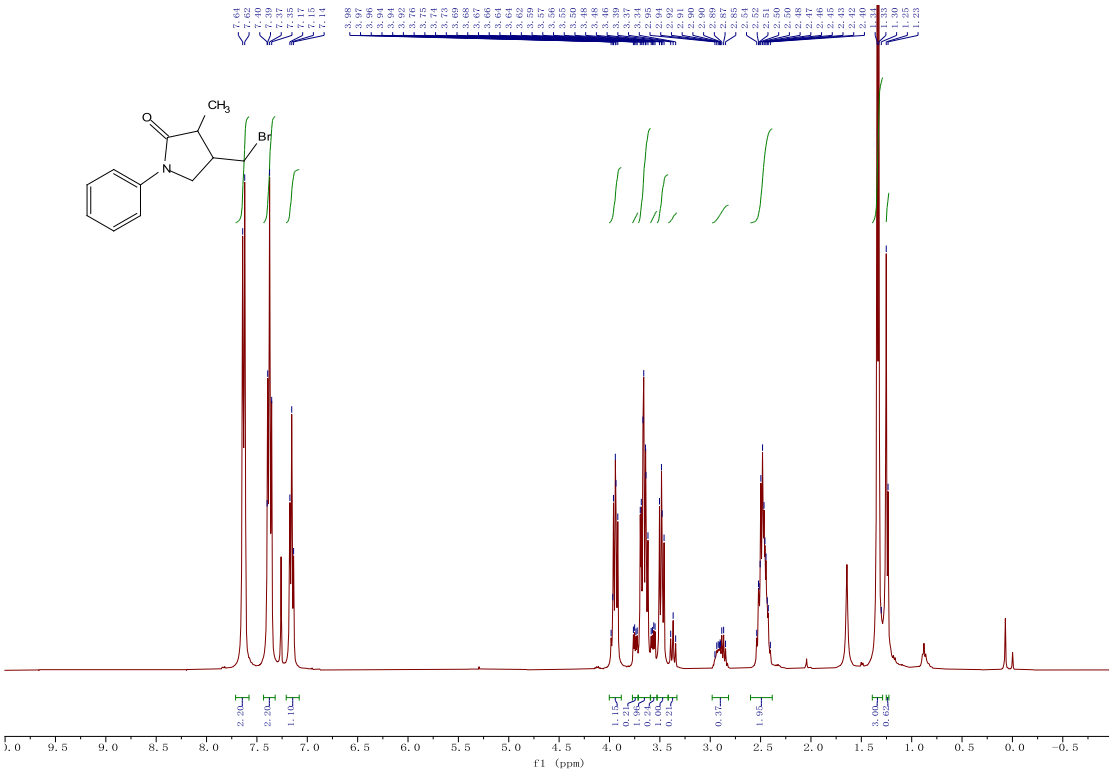


^{13}C NMR ($CDCl_3$, 101 MHz)

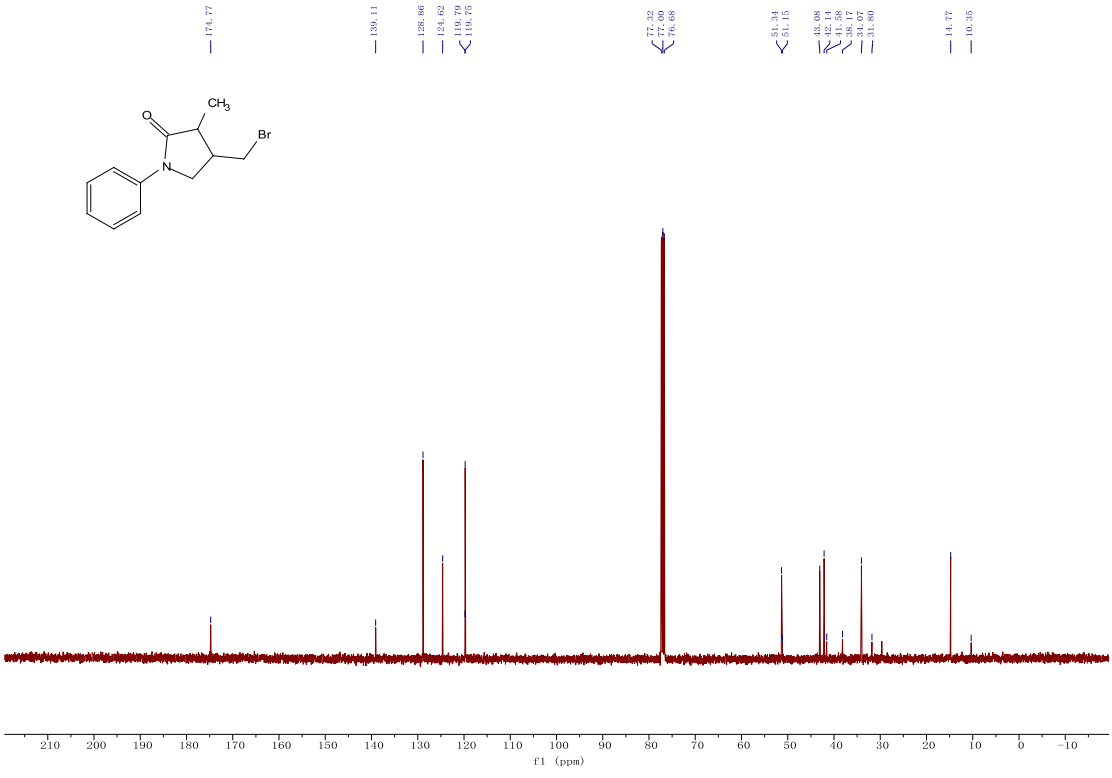


(2w)

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

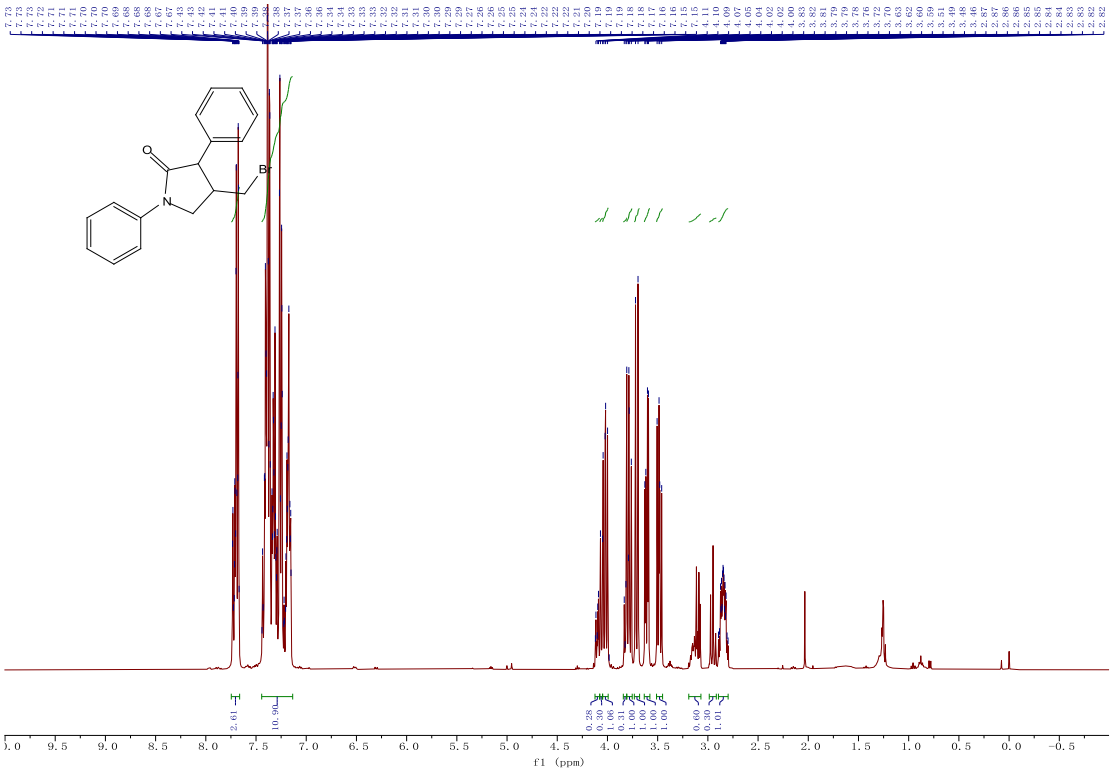


^{13}C NMR ($CDCl_3$, 101 MHz)

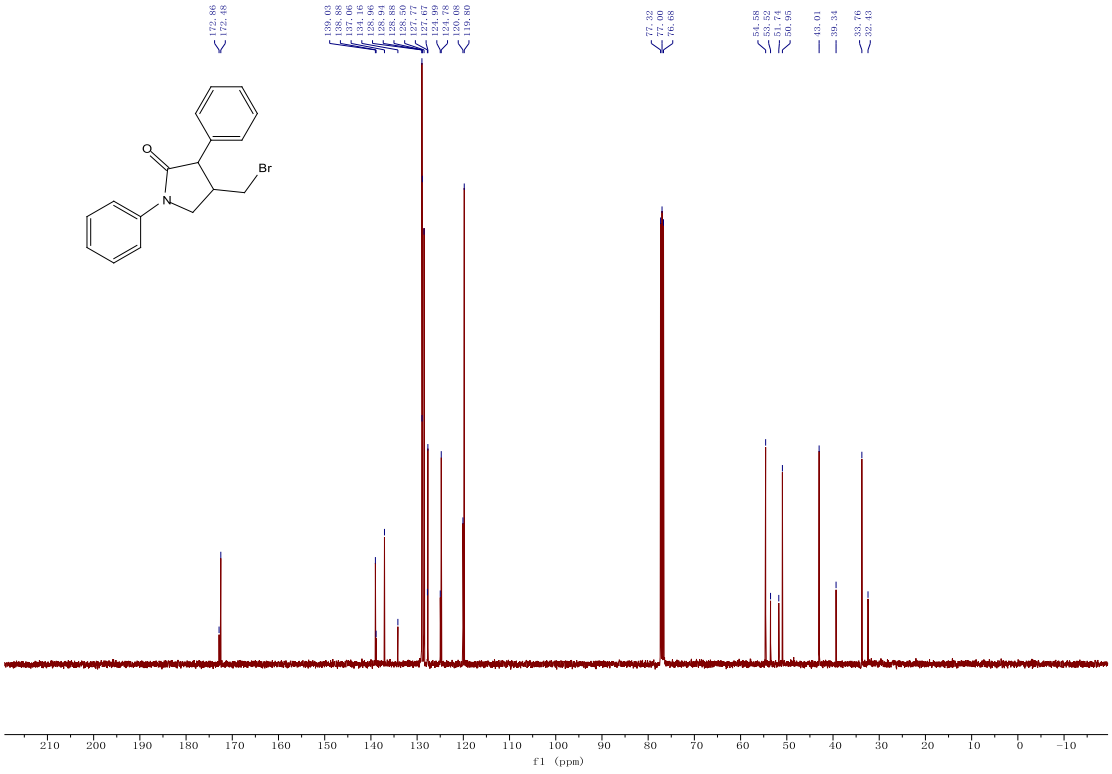


(2x)

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

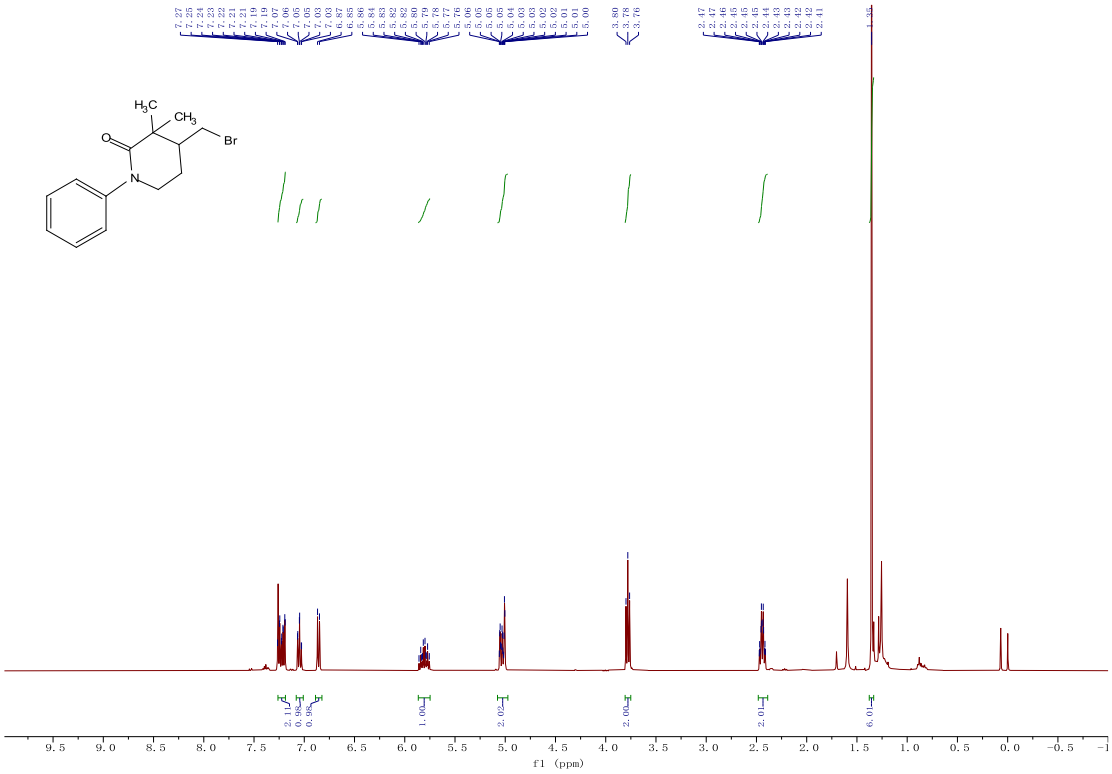


^{13}C NMR ($CDCl_3$, 101 MHz)

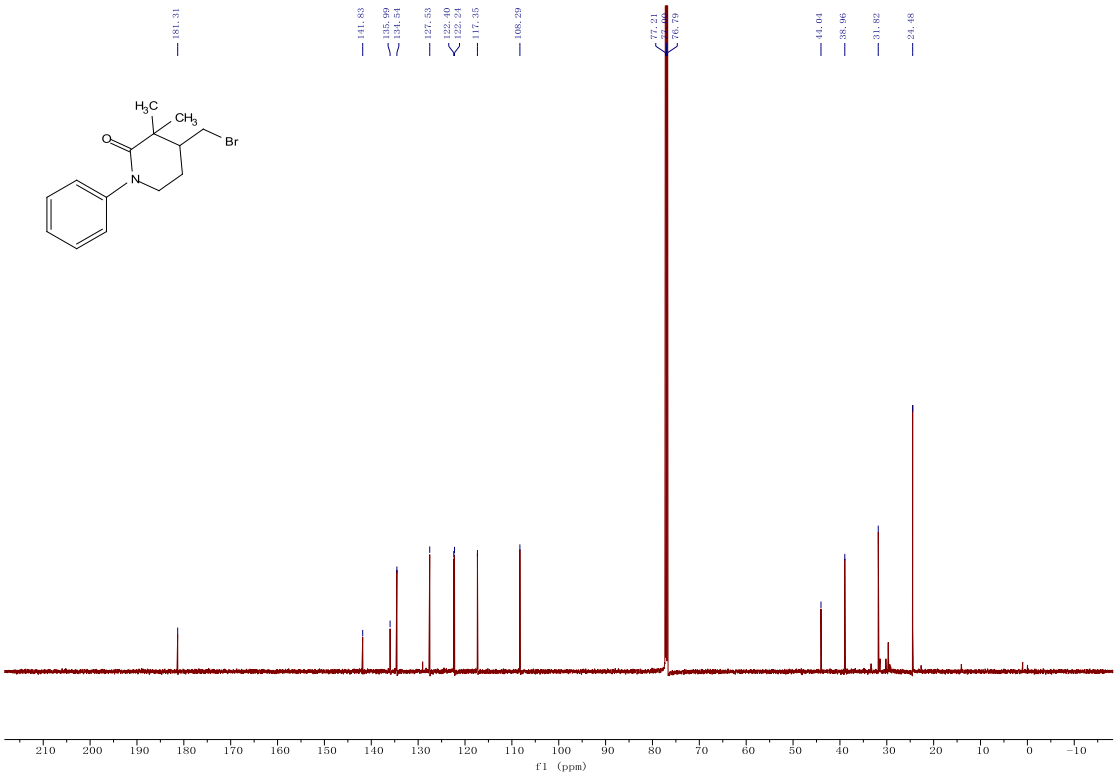


(2y)

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

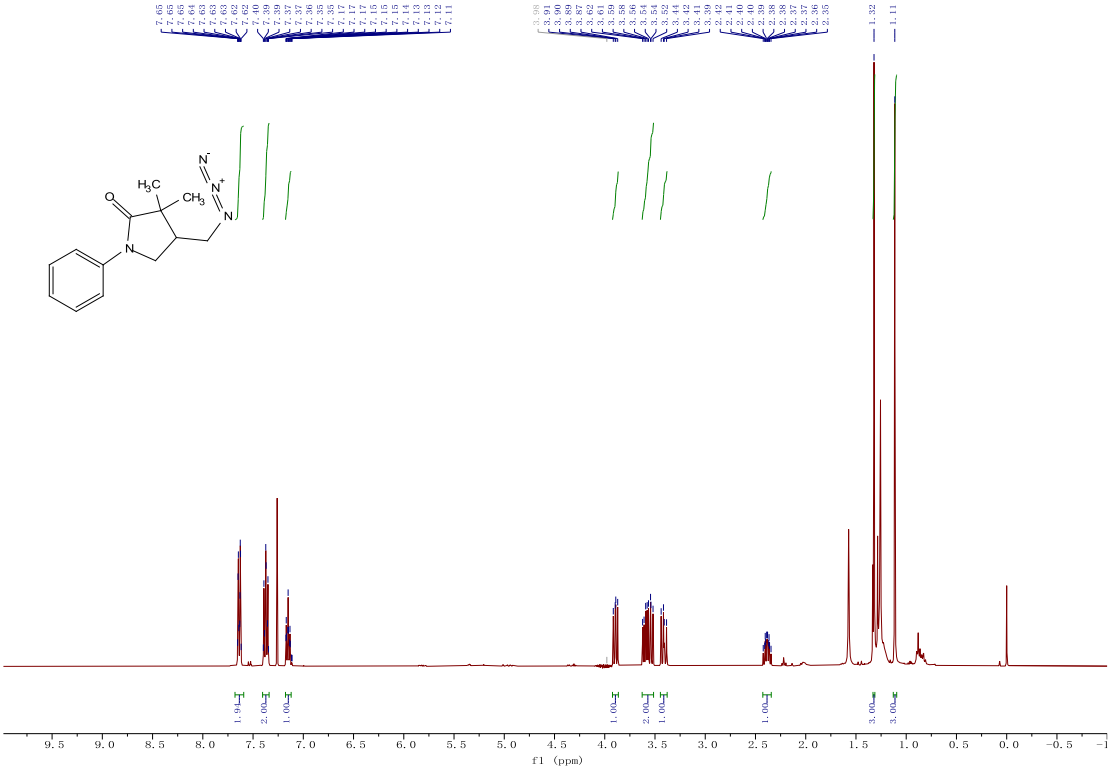


^{13}C NMR ($CDCl_3$, 101 MHz)

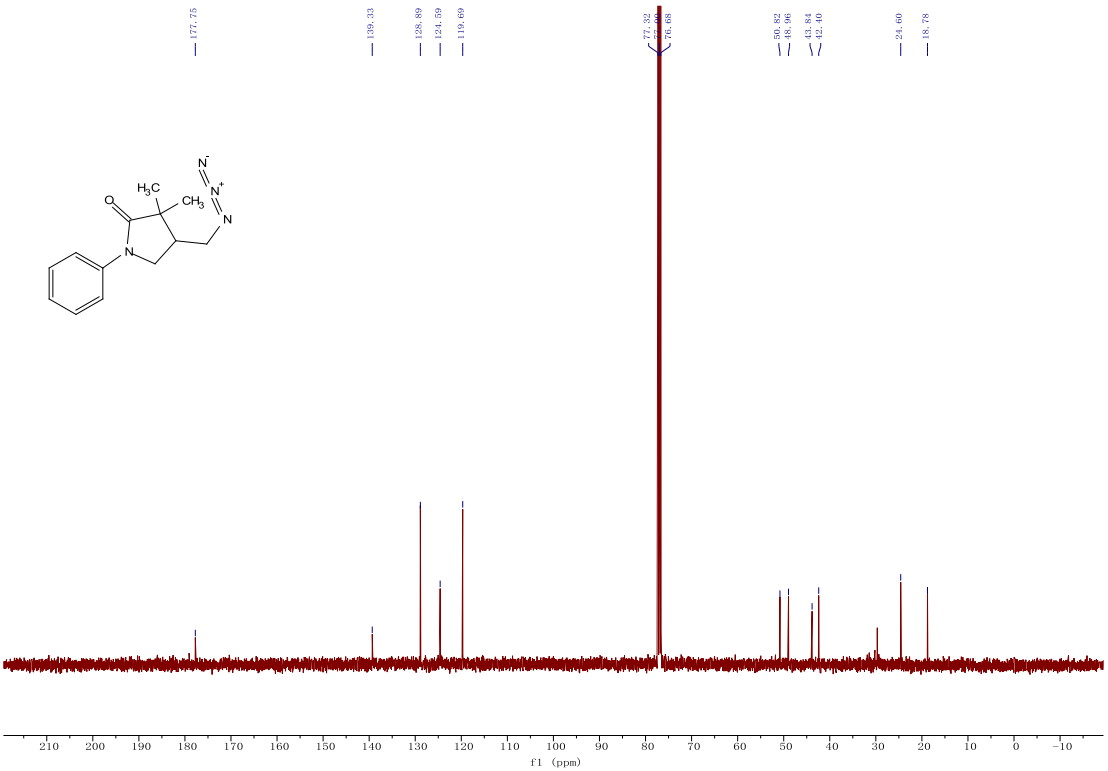


(3a)

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

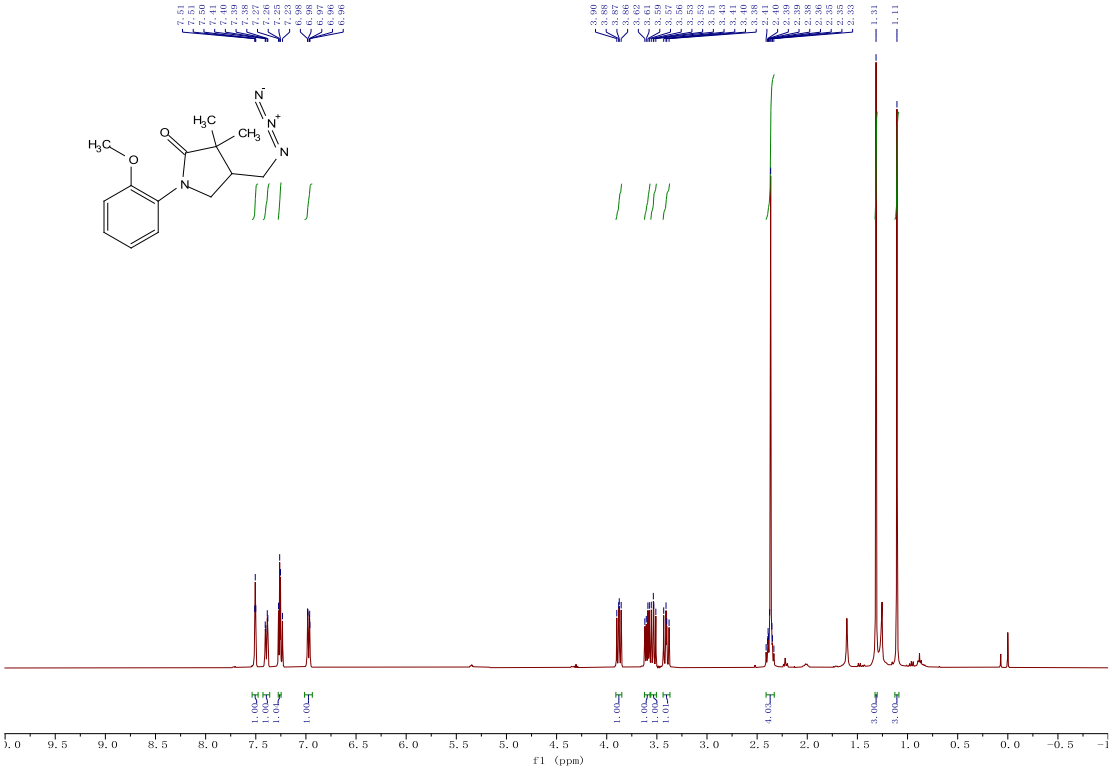


^{13}C NMR ($CDCl_3$, 101 MHz)

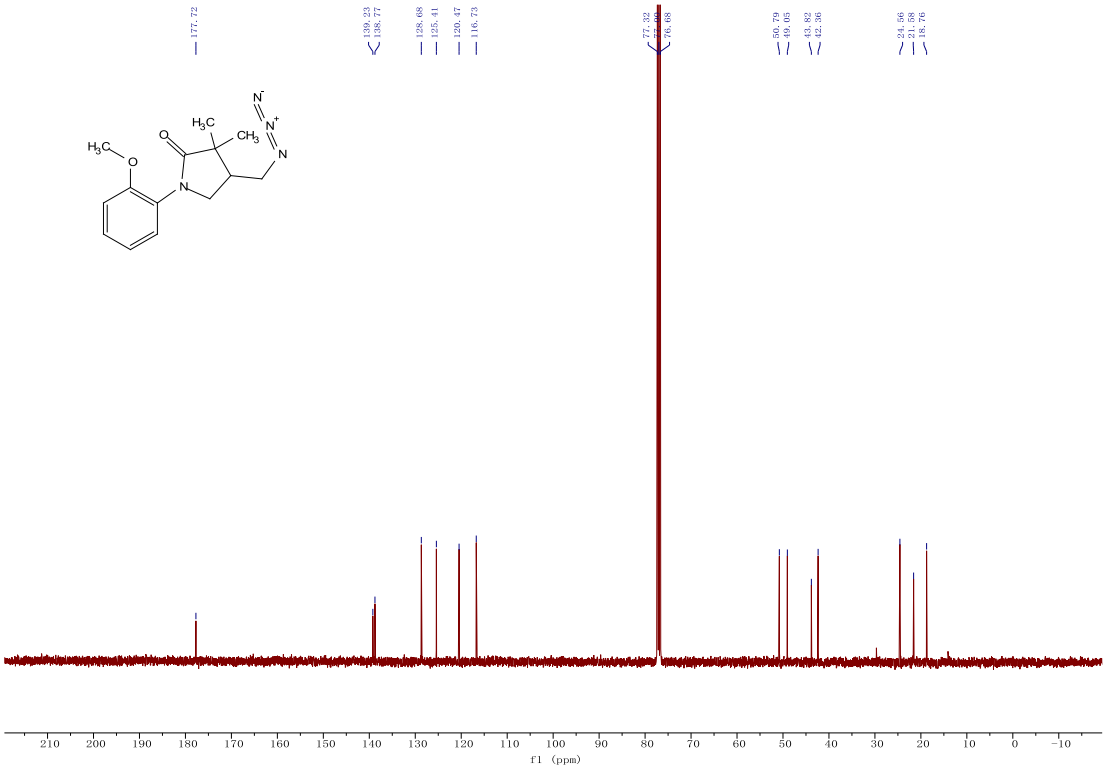


(3b)

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

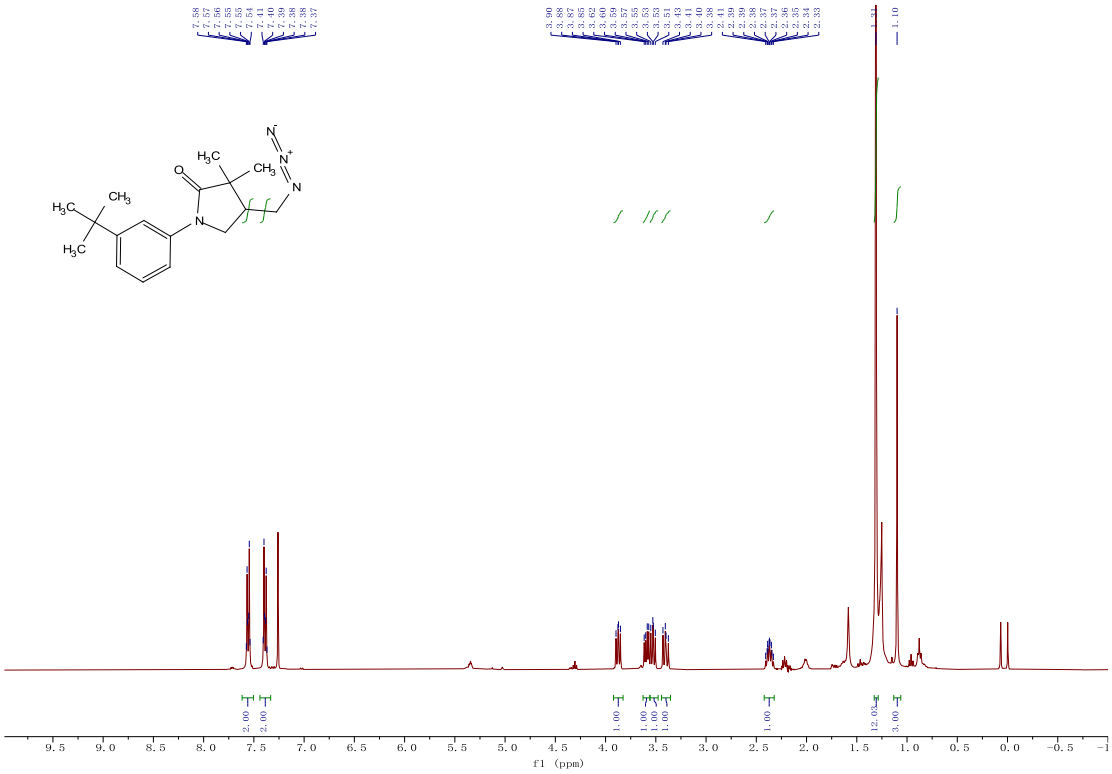


^{13}C NMR ($CDCl_3$, 101 MHz)

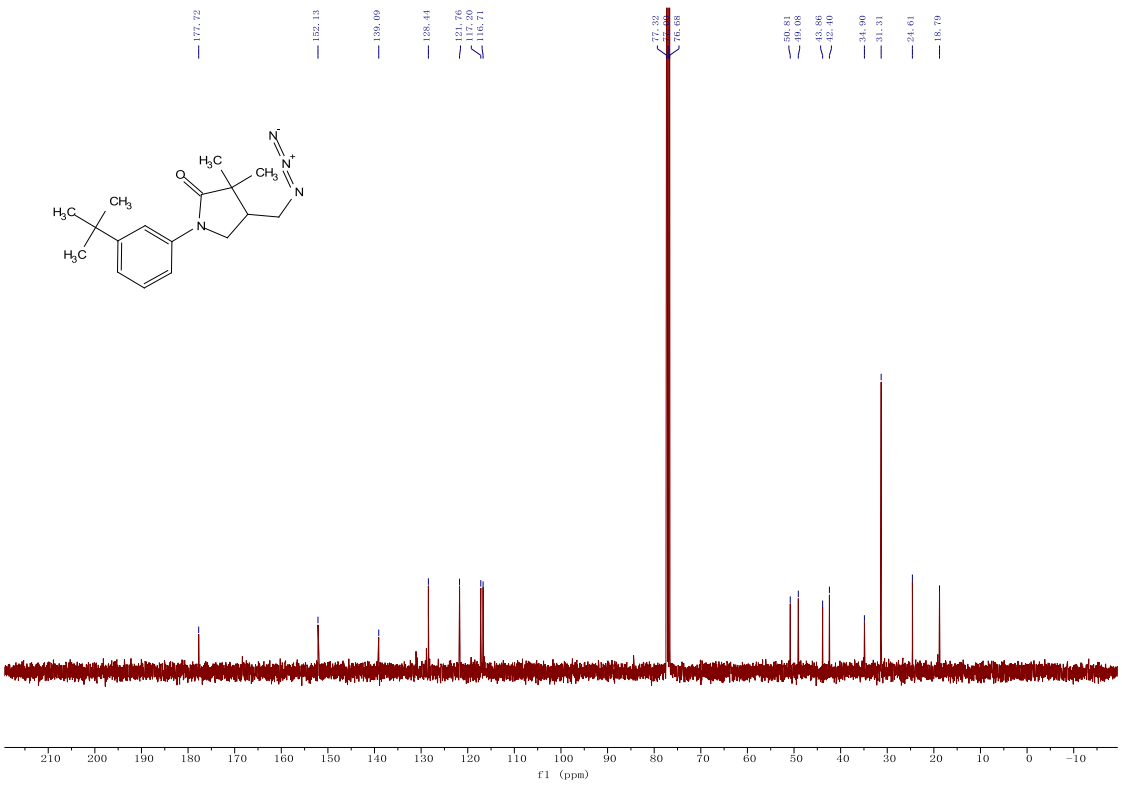


(3f)

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

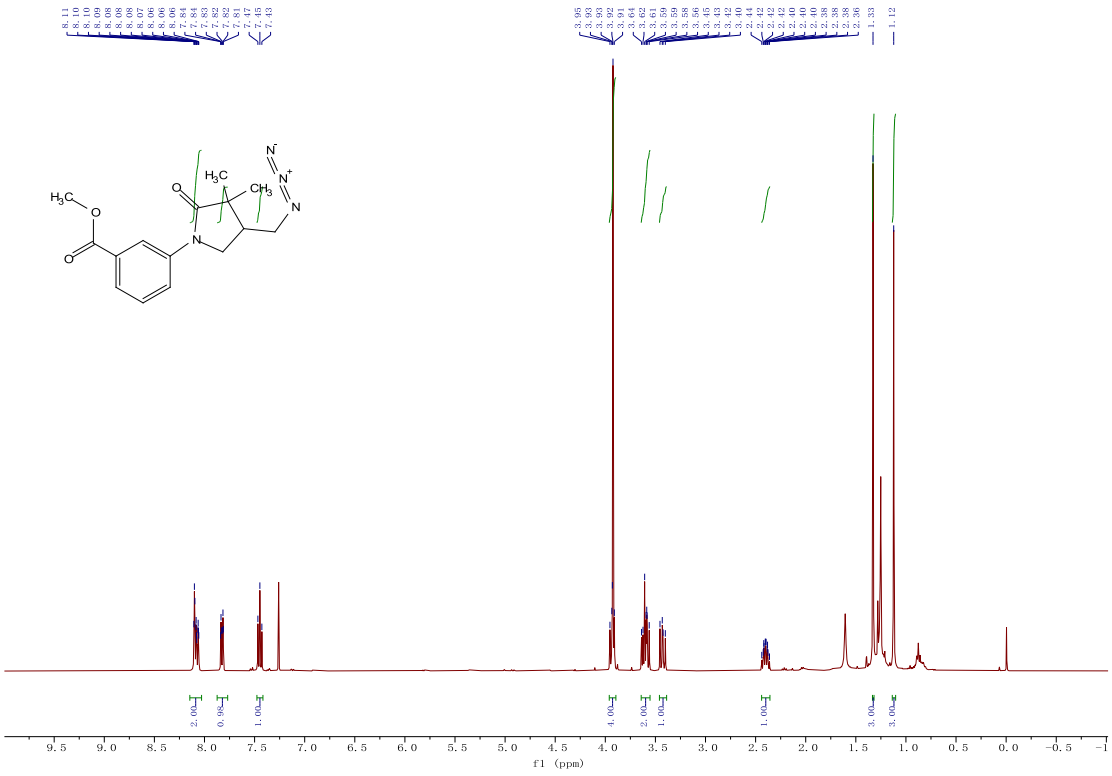


^{13}C NMR ($CDCl_3$, 101 MHz)

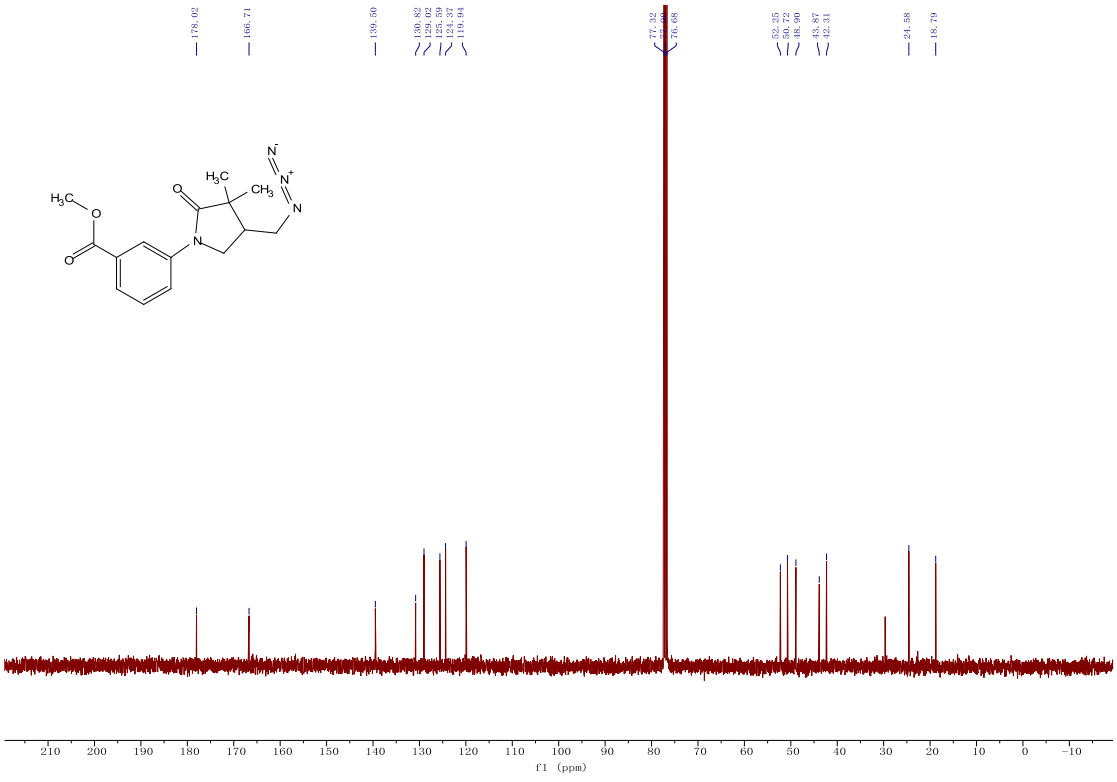


(3g)

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

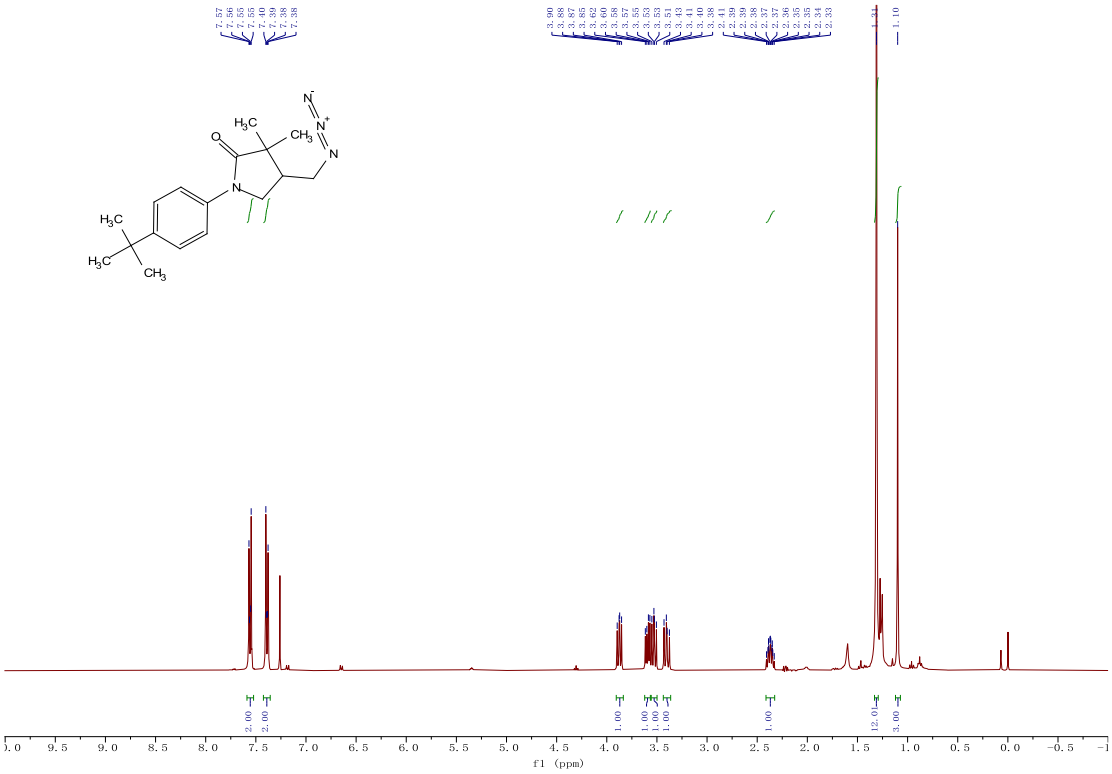


^{13}C NMR ($CDCl_3$, 101 MHz)

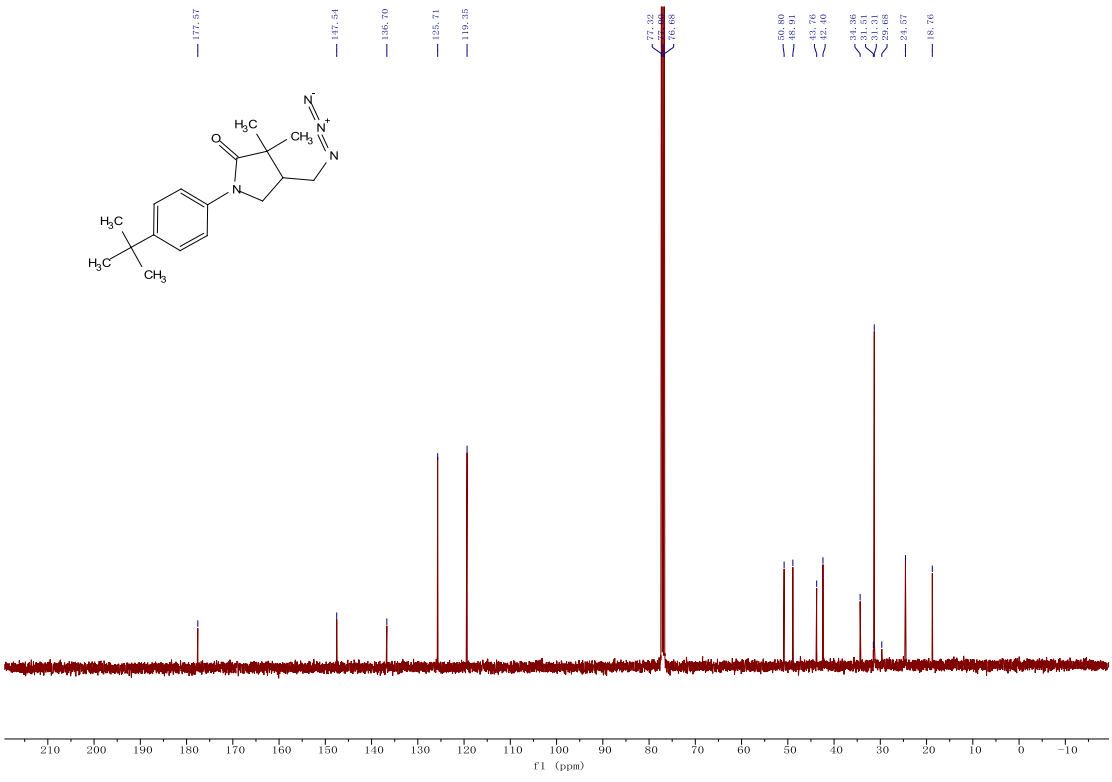


(3h)

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

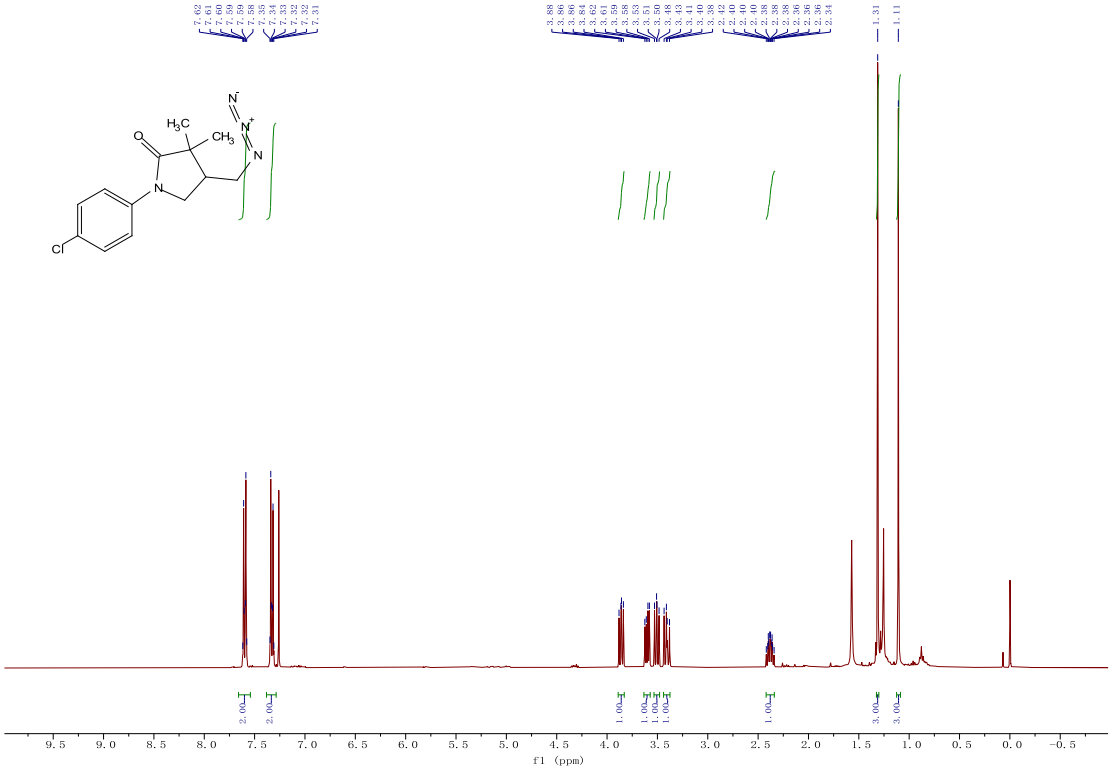


^{13}C NMR ($CDCl_3$, 101 MHz)

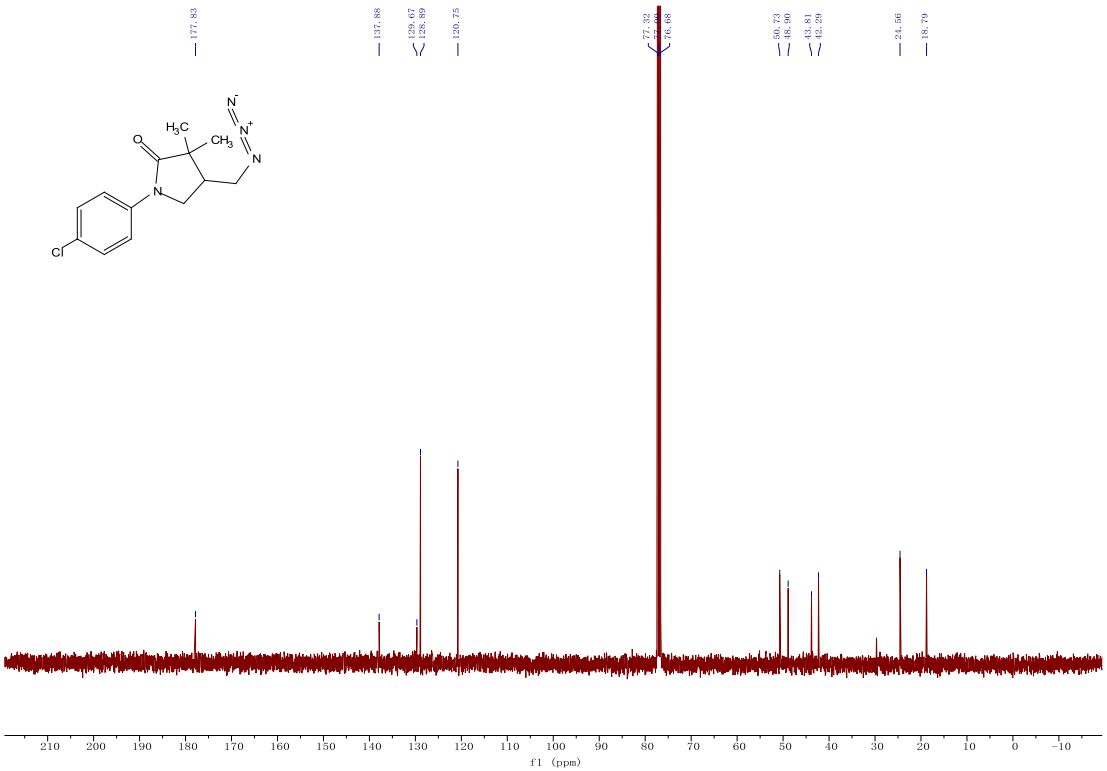


(3i)

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

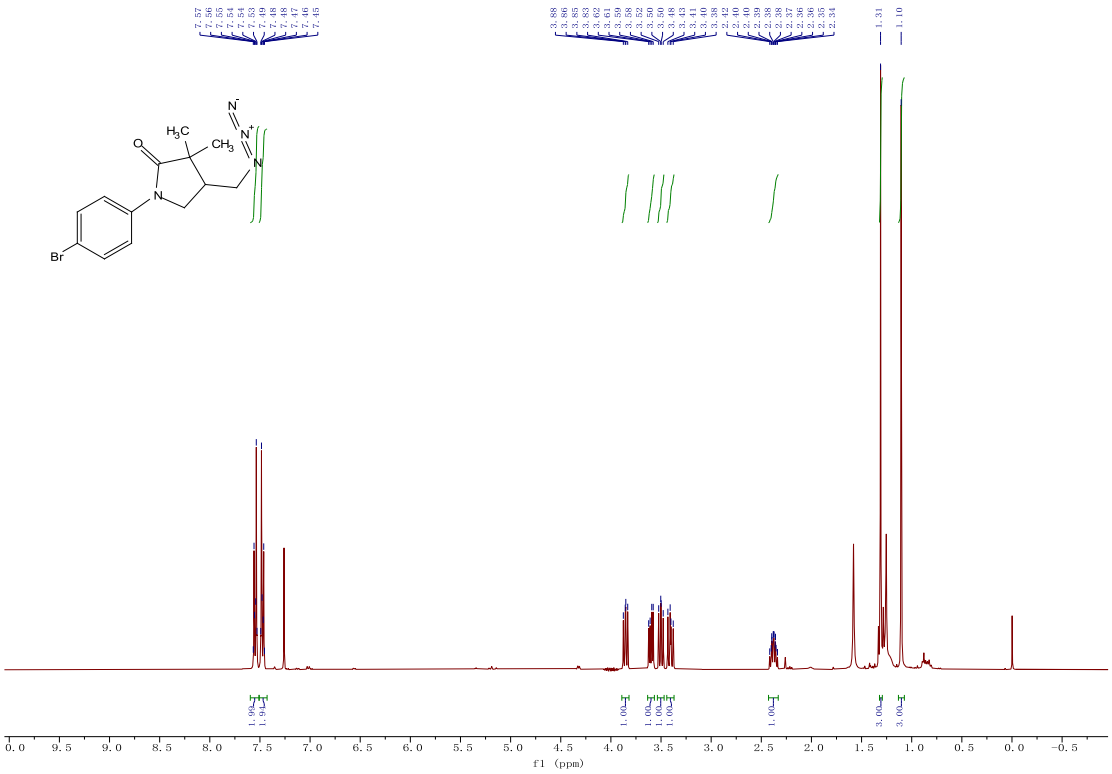


^{13}C NMR ($CDCl_3$, 101 MHz)

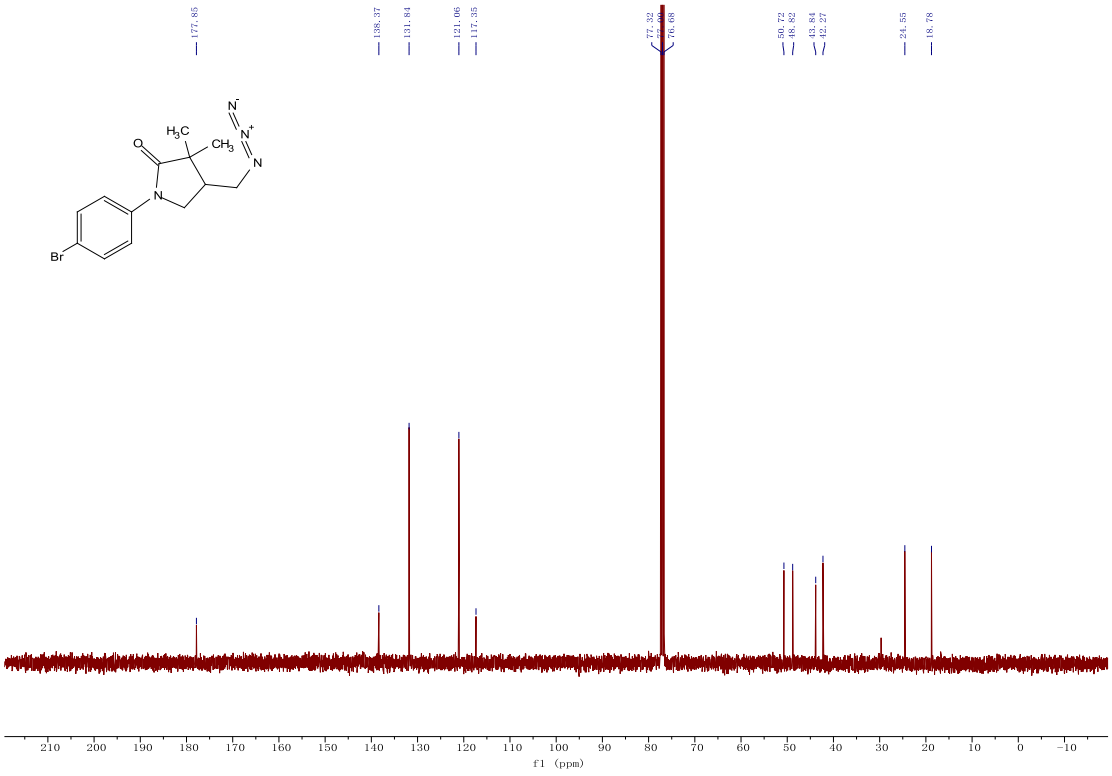


(3j)

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

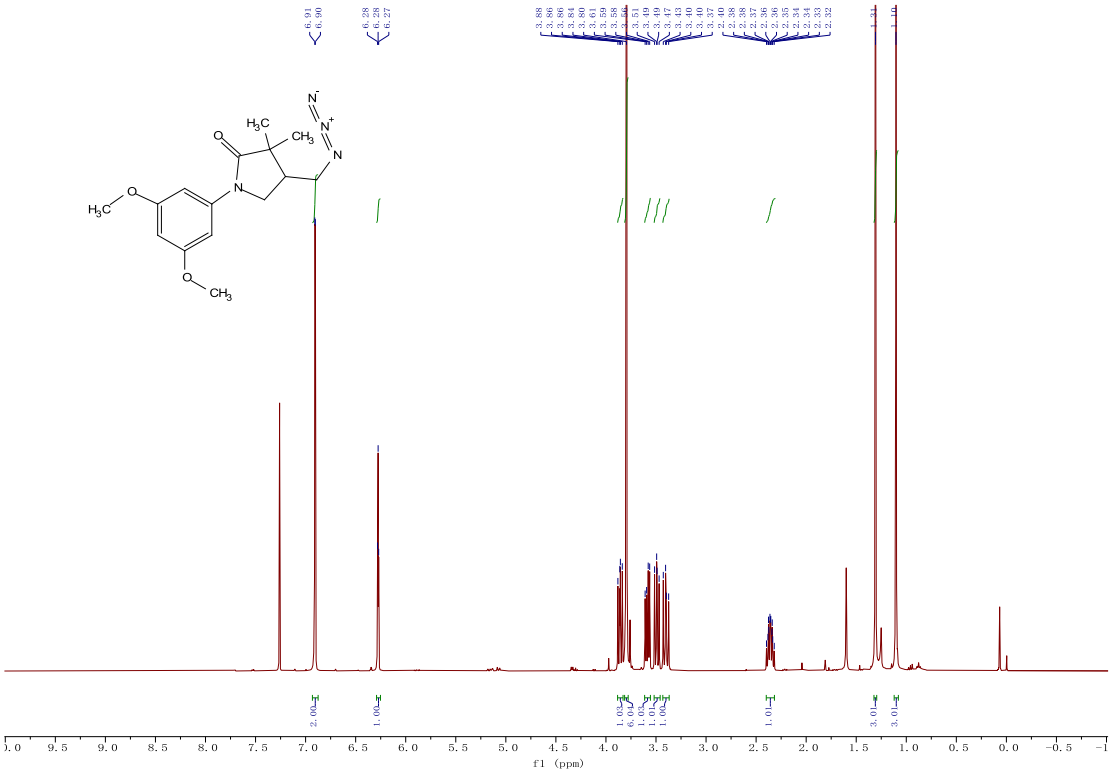


^{13}C NMR ($CDCl_3$, 101 MHz)

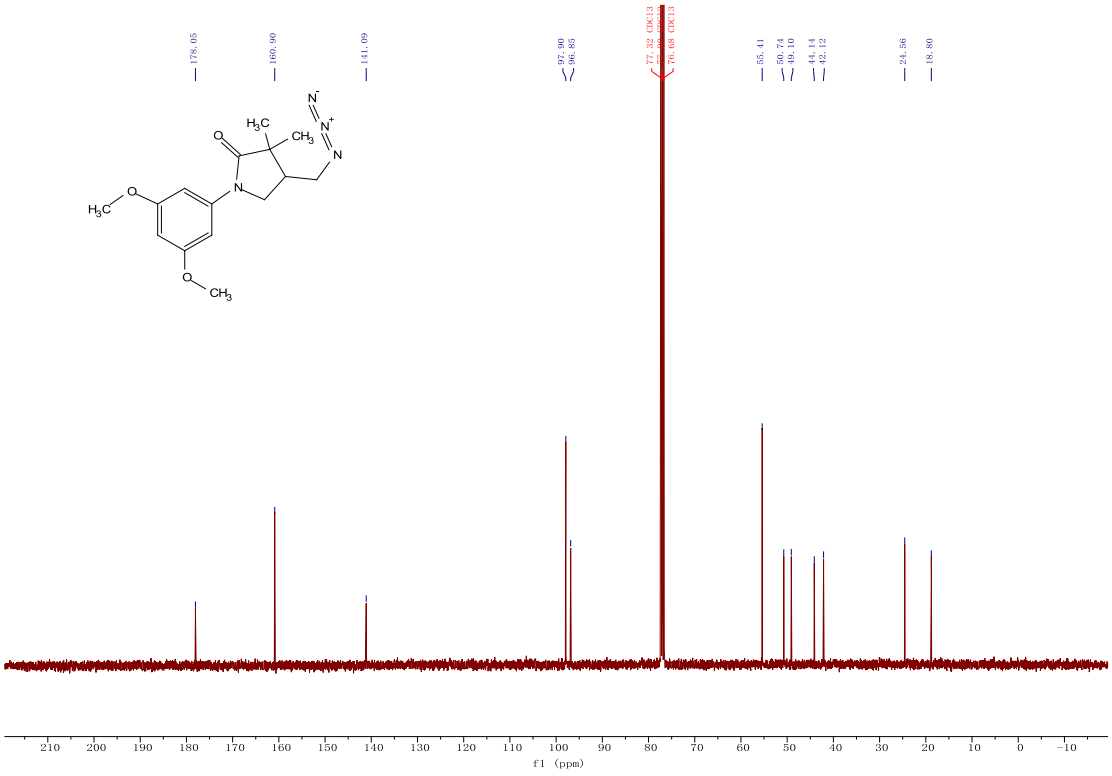


(3l)

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

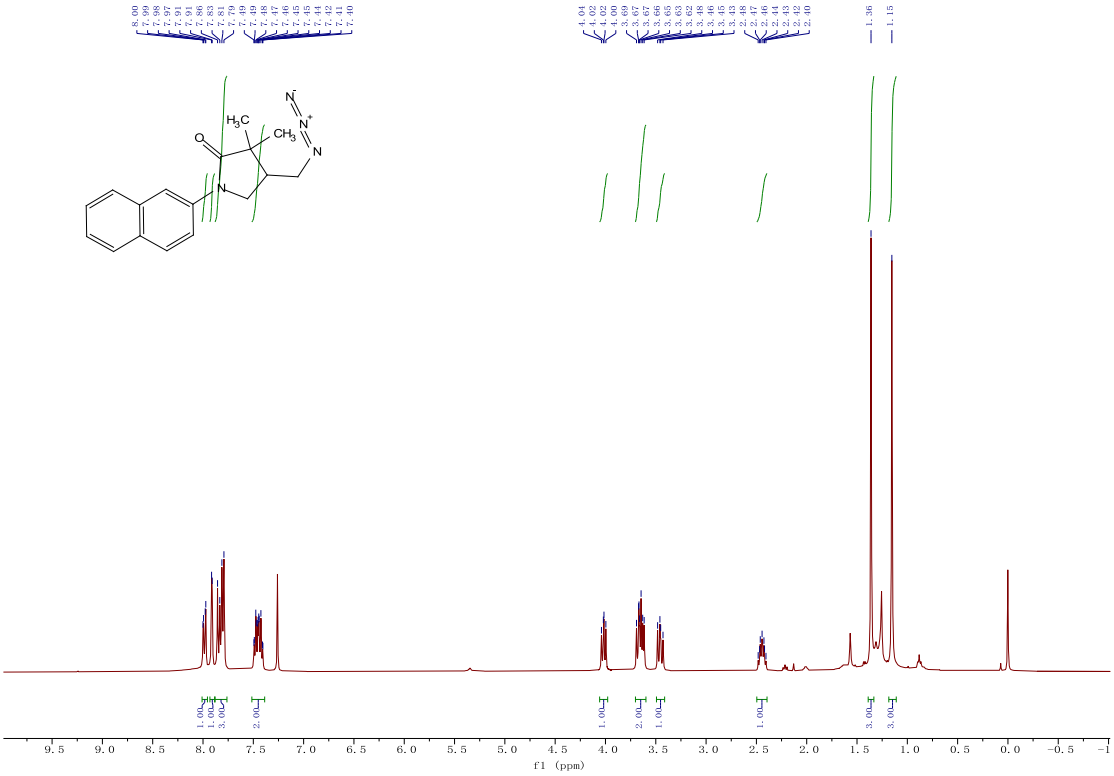


^{13}C NMR ($CDCl_3$, 101 MHz)

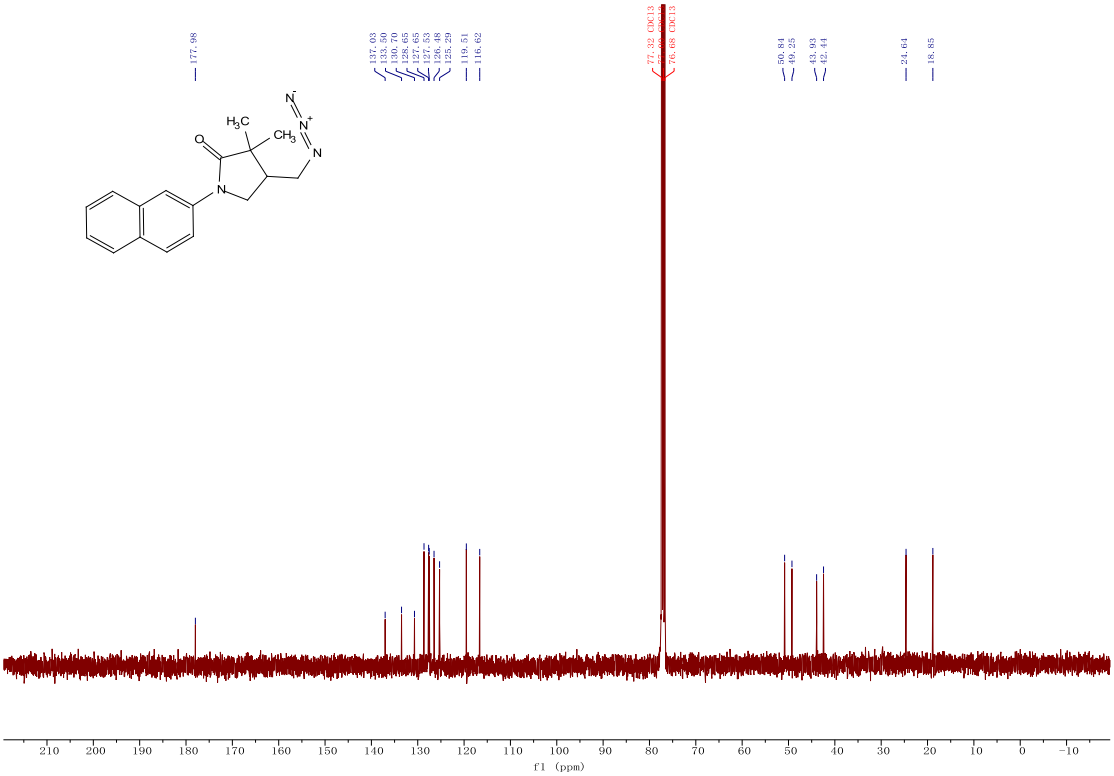


(3o)

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

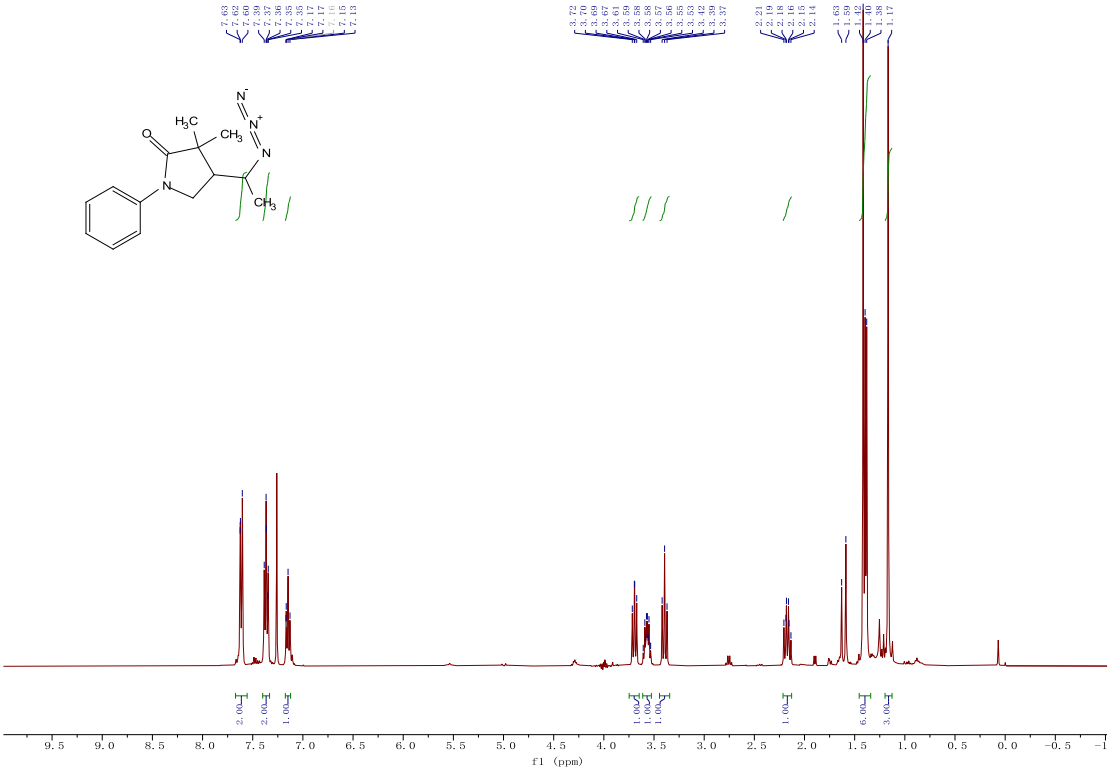


^{13}C NMR ($CDCl_3$, 101 MHz)

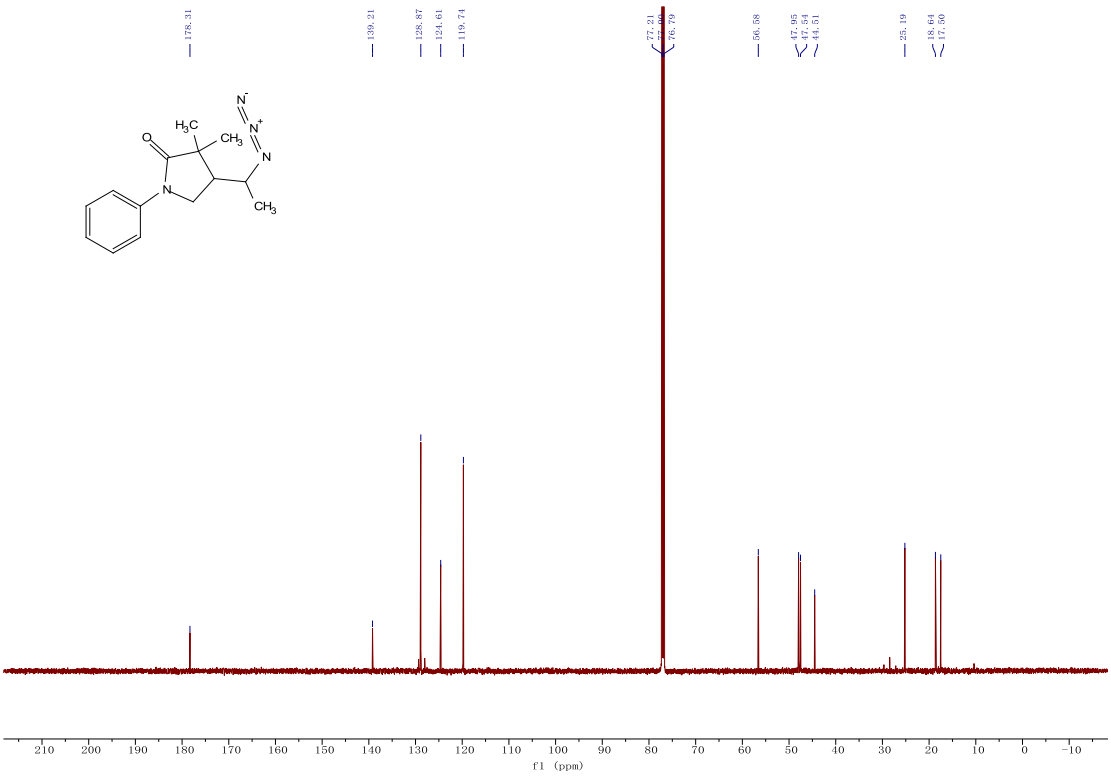


(3v)

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

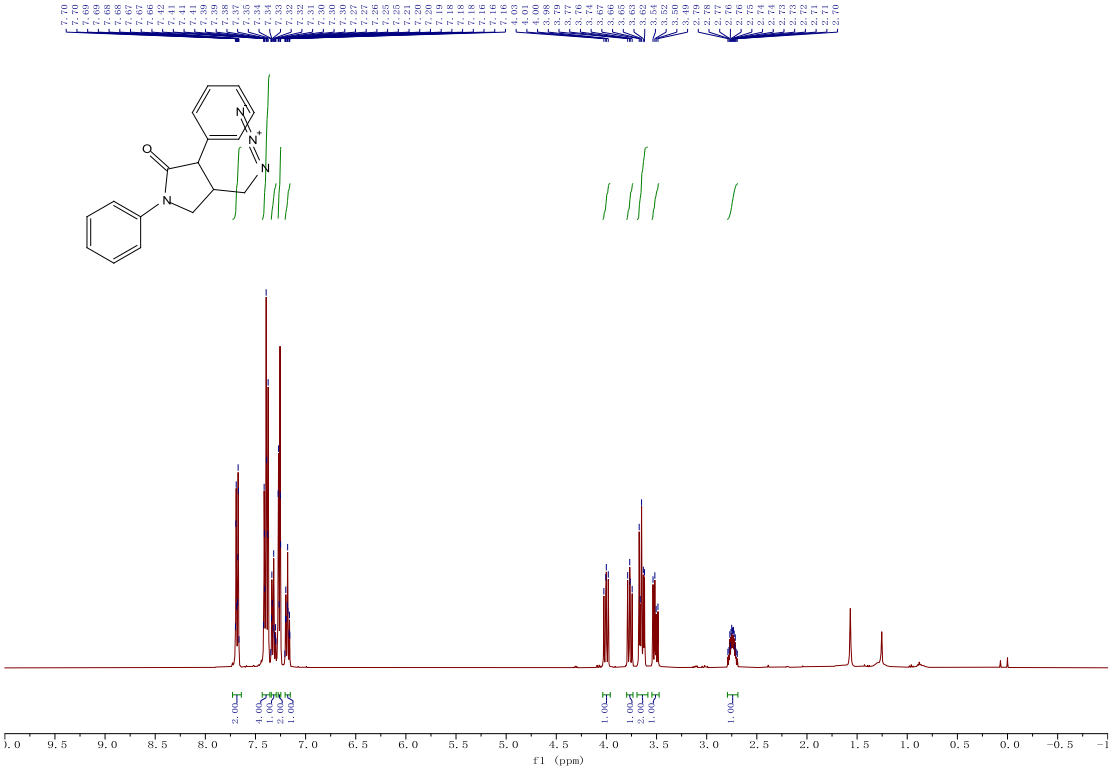


^{13}C NMR ($CDCl_3$, 101 MHz)



(3x)

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



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