Electronic Supplementary Material (ESI) for Chemical Communications.

Promoting effect of water on light and phenanthroline–diphosphine Cu(I) complex-initiated iodine atom transfer cyclisation

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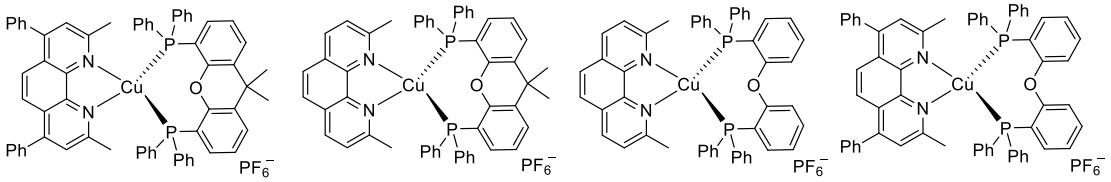
Supplementary Information

Content

1. General information

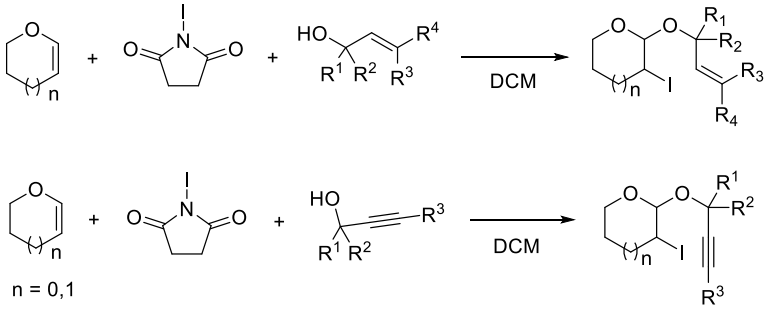
The NMR spectra were recorded on a Bruker AVANCE III-400 MHz spectrometer in $CDCl_3$. The chemical shifts of ^1H NMR spectra in $CDCl_3$ were determined based on the chemical shift of $CDCl_3$ (δ = 7.26 (ppm)); the chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.0 (ppm)). The NOE experiment was conducted on a Bruker AVANCE NEO 600 MHz spectrometer. The coupling constants (*J* value) are reported in Hz. ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet, multiplet (m) or broad (br). HR-MS analysis was performed on a Bruker APEXII FT-ICR mass instrument (ESI) instrument equipped with an ESI source. UV-vis absorption spectroscopy was measured on a TU-1901 spectrophotometer. Anhydrous acetonitrile was purchased from Energy Chemical. Distilled water was used for the reactions described herein. A set of 18 W blue LED lamps (6×3 W) (455 ± 10 nm) were provided by Shenzhen Chunda Xiguang Photoelectronics Company of China (Model GHX-4). A set of 24 W blue LED lamps (6×4 W) (410–420 nm) were provided by Wuhan Jiushang Company of China (Model GCH-4). [Cu(Xantphos)(bcp)]PF_6 (**Cat-1**), [Cu(Xantphos)(dmp)]PF_6 (**Cat-2**), [Cu(DPEphos)(dmp)PF_6] (**Cat-3)** and [Cu(DPEphos)(bcp)]PF_6 (**Cat-4**) were prepared following the reported procedure.[1]



[Cu(Xantphos)(bcp)]PF_6 (**Cat-1**) | [Cu(Xantphos)(dmp)]PF_6 (**Cat-2**) | [Cu(DPEphos)(dmp)]PF_6 (**Cat-3**) | [Cu(DPEphos)(bcp)]PF_6 (**Cat-4**)

2. Experimental procedures

General procedure for the preparation of substrates 1[2-6]

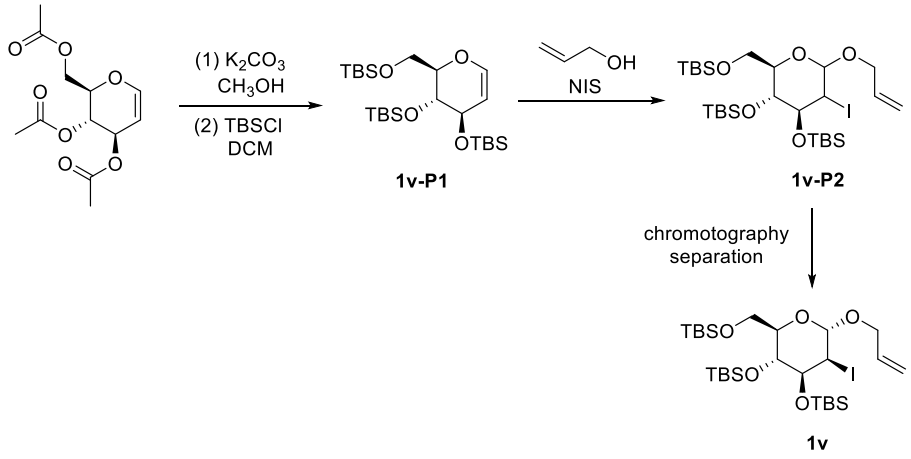


n = 0,1

Into a 100 mL round bottom flask equipped with a magnetic stirring bar were added *N*-iodosuccinimide (2.25 g, 10.0 mmol, 1.0 equiv.) and an allyl alcohol (or propargyl alcohol) (10.0 mmol) followed by 30 mL of dichloromethane (DCM). The solution was cooled to -10 ℃. 3,4-Dihydro-2*H*-pyran (0.91 mL, 10.0 mmol) (or

2,3-dihydrofuran) was then added dropwise to into the solution, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was then washed with a saturated aqueous solution of sodium thiosulfate (3×20 mL), and the combined aqueous solution was extracted with DCM (3×20 mL). The combine organic layers were washed with brine, dry over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (eluent: petroleum ether (PE) and ethyl acetate (EA)) to give the pure product.

Procedure for the preparation of compound 1v[7]

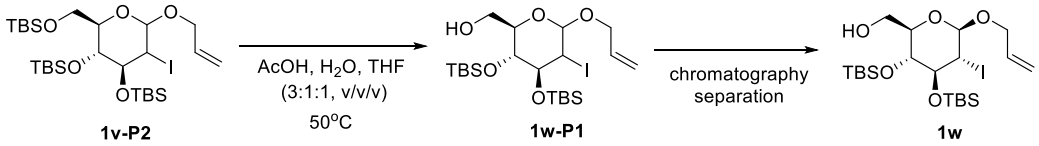


(2R,3S,4R)-2-(Acetoxymethyl)-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (5.0 g, 18.4 mmol), K_2CO_3 (0.25 g, 1.8 mmol) and 30 mL CH_3OH were added into a 100 mL round bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 4 h. The solvent was then removed under reduced pressure on a rotary evaporator, and DCM (3×40 mL) was used to further remove the remaining CH_3OH. After that, imidazole (12.3 g, 180 mmol), TBSCl (13.0 g, 86.3 mmol) and 30 mL DCM were added into the round bottom flask, and the reaction mixture was stirred at room temperature overnight. The reaction is quenched by water (40 mL), and the aqueous phase was extracted with DCM (3×20 mL). The combined organic layers were washed with brine, dry over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (eluent: PE and EA (10:1, v/v)) to give the precursor **1v-P1**.

N-iodosuccinimide (4.13 g, 18.4 mmol) and prop-2-en-1-ol (1.29 mL, 18.4 mmol) were added into a 100 mL round bottom flask equipped with a magnetic stirring bar followed by 30 mL of DCM and the prepared **1v-P1**. The reaction mixture was stirred at room temperature overnight. It was then washed with a saturated aqueous solution of sodium thiosulfate (20 mL), and the combined aqueous phases were extracted with DCM (3×20 mL). The combine organic layers were washed with brine, dry over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual

was subjected to silica gel column chromatography (eluent: PE and EA (20:1, v/v)) to give **1v-P2**. Further purification of the product with silica gel column chromatography with PE as the eluent affords 0.910 g of **1v**.

Procedure for the preparation of compound 1w[8]



2.4 g of **1v-P2** prepared in the previous step was added into a mixture of 15 mL of AcOH, 5.0 mL of H_2O and 5.0 mL of THF contained in a 100 mL round bottom flask equipped with a magnetic stirring bar. The mixture was stirred at 50 ^oC for 4 h. It was then quenched with a saturated aqueous solution $NaHCO_3$ (100 mL), and the combined aqueous phases were extracted with DCM (3×20 mL). The combine organic layers were washed with brine, dry over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (gradient elution from PE to PE and EA (100:1, v/v)) to afford the 405 mg of **1w**.

Procedure for the iodine atom transfer radical cyclisation

Protocol A

Compound **1** (0.4 mmol), [Cu(Xantphos)(bcp)]PF_6 (20 mg, 0.02 mmol, 5 mol %) and ascorbic acid (7.8 mg, 0.04 mmol, 0.1 equiv.) were added into a 20 mL glass tube equipped with a magnetic stirring bar and a rubber stopper. CH_3CN (0.5 mL) and H_2O (2.0 mL) were then added into the tube, which was evacuated and charged with argon. After that, the tube was irradiated under stirring with 18 W blue LEDs (455 nm) for 12 h. The product was extracted with DCM (4×5 mL), and the combined organic layers were concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (eluent: PE and EA) to give the pure product(s).

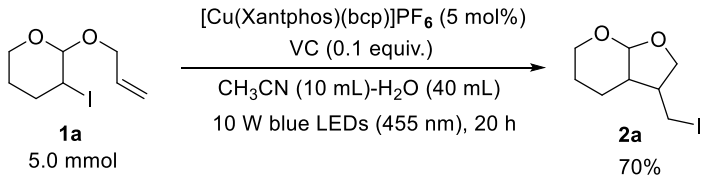
Protocol B

Compound **1** (0.4 mmol), [Cu(DPEphos)(bcp)]PF_6 (19 mg, 0.02 mmol, 5 mol %) were added into a 20 mL glass tube equipped with a magnetic stirring bar and a rubber stopper. 5.0 mL H_2O was then added into the tube, which was then evacuated and charged with argon. After that, the tube was irradiated under stirring with 18 W blue LEDs (455 nm) for 12–15 h. The product was extracted with DCM (4×5 mL) and the combined organic layers were concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (eluent: PE and EA) to give the pure product(s).

The reactions under other conditions or with other copper photocatalysts were conducted following essentially the same procedures.

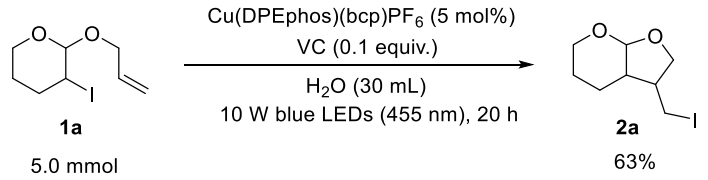
Gram scale preparation of compound 2a

Protocol A



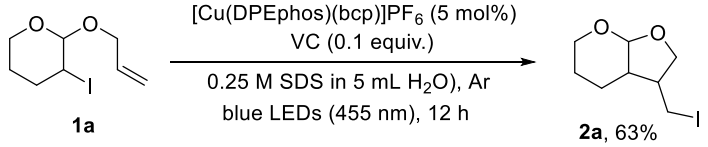
1a (1.34 g, 5.0 mmol), [Cu(Xantphos)(bcp)]PF_6 (250 mg, 0.25 mmol, 5 mol %) and ascorbic acid (88 mg, 0.5 mmol, 0.1 equiv.) were added into in a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper. 10 mL of CH_3CN and 40 mL of H_2O were then added into the flask, which was evacuated and charged with argon. The flask was irradiated under stirring with a 10 W blue LED strip (450 nm) for 20 h (a small electric fan was used to dissipate the heat emitted by the lamps). The product was extracted with DCM (4×10 mL) and the combined organic layers were concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE and EA (5:1, v/v)) to give **2a** (0.94 g, 70% yield).

Protocol B



1a (1.34 g, 5.0 mmol), [Cu(DPEphos)(bcp)]PF_6 (241 mg, 0.25 mmol, 5 mol %) and ascorbic acid (88 mg, 0.5 mmol, 0.1 equiv.) were added into in a 100 mL round bottom flask equipped with a magnetic stirring bar and a rubber stopper. 30 mL of H_2O was then added into the flask, which was evacuated and charged with argon. The flask was irradiated under stirring with a 10 W blue LED strip (450 nm) for 20 h (a small electric fan was used to dissipate the heat emitted by the lamps). The product was extracted with DCM (4×10 mL) and the combined organic layers were concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE and EA (5:1, v/v)) to give **2a** (0.84 g, 63% yield).

Procedure for the reaction of 1a in SDS micelles



1a (27.1 mg, 0.1 mmol), [Cu(DPEphos)(bcp)]PF_6 (5.0 mg, 0.005 mmol, 5 mol %) and ascorbic acid (1.8 mg, 0.01 mmol, 0.1 equiv.) and 360 mg SDS were added in 5.0

mL H_2O contained in a 20 mL glass tube equipped with a magnetic stirring bar and a rubber stopper. The mixture was sonicated until a clear yellow solution was formed. The tube was evacuated and charged with argon, and then irradiated under stirring with 18 W blue LEDs for 12 h. After the reaction finished, a small portion of NaCl was added into the tube, and the product was extracted with DCM (4×5 mL). The combined organic layers were concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE and EA (5:1, v/v)) to give 16.8 mg **2a** (63% yield).

The reaction in the absence of VC was conducted following essentially the same procedure. No product was obtained after 12 h irradiation.

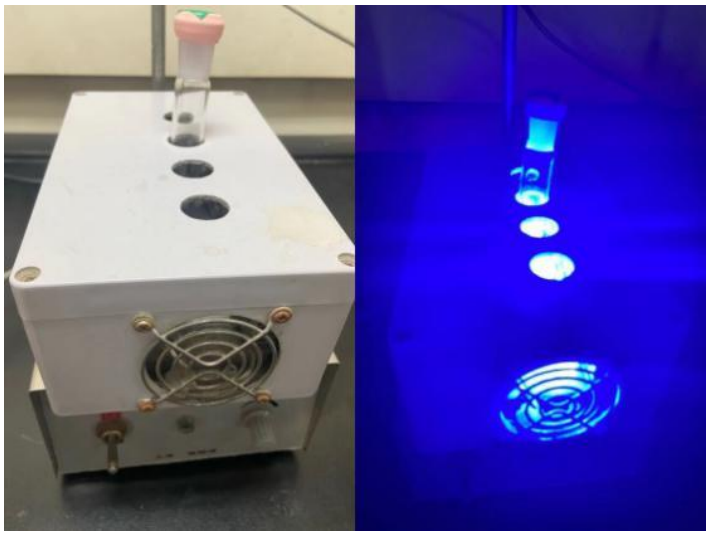
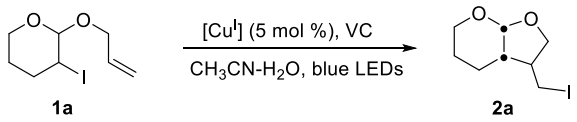


Figure S1 Experiment set up.

3. Screening of the reaction conditions

Table S1 Screening of conditions-1[a]



entry	[Cu^{I}]	VC (equiv.)	CH_3CN (mL)	H_2O (mL)	yield of **2a** (%)[b]
1	**Cat-1**	--	1.0	--	N.R.
2	**Cat-2**	--	1.0	--	N.R.
3	**Cat-3**	--	1.0	--	N.R.
4	**Cat-4**	--	1.0	--	N.R.
5	**Cat-1**	0.1	0.5	0.5	21
6	**Cat-1**	0.1	0.5	1.0	70
7	***Cat-1***	***0.1***	***0.5***	***2.0***	***77***
8	**Cat-1**	0.1	0.5	3.0	75
9	**Cat-1**	0.1	1.0	0.5	11
10	**Cat-1**	0.1	2.0	0.5	15
11	**Cat-1**	0.5	0.5	2.0	82
12	**Cat-1**	1.0	0.5	2.0	77
13	**Cat-1**	--	0.5	0.5	N.R.
14	**Cat-1**	--	0.5	1.0	N.R.
15	**Cat-1**	--	0.5	2.0	50
16	**Cat-1**	--	--	2.0	11
17	**Cat-1**	--	--	5.0	11
18	**Cat-1**	0.1	--	5.0	38
19	**Cat-1**	0.1	0.5	2.0	N.R.[c]
20	--	0.1	0.5	2.0	N.R.
21	**Cat-1**	0.1	0.5	2.0	N.R.[d]

[a] The reaction was conducted on 0.2 mmol scale under an argon atmosphere at ambient temperature (<30 ^{o}C). Reaction time: 12 h. 18 W Blue LEDs (455 ± 10 nm) were used as the light source. [b] Isolated yield. **2a** was obtained as two distereoisomers in a ratio of roughly 89/11. [c] Control experiment in the dark. [d] The reaction was conducted in the air.

Table S2 Screening of conditions-2[a]

entry	[Cu^{I}]	VC (equiv.)	CH_3CN (mL)	H_2O (mL)	yield of **2a** (%)[b]
1	**Cat-2**	--	0.5	0.5	N.R.
2	**Cat-2**	--	0.5	1.0	18
3	**Cat-2**	--	0.5	2.0	50
4	**Cat-2**	--	0.5	3.0	57
5	**Cat-2**	--	0.5	5.0	60
6	**Cat-2**	--	--	5.0	trace
7	**Cat-2**	0.1	0.5	2.0	69
8	**Cat-2**	0.1	0.5	5.0	76
9	**Cat-2**	0.1	--	5.0	38
10	**Cat-3**	--	0.5	0.5	N.R.
11	**Cat-3**	--	0.5	1.0	9
12	**Cat-3**	--	0.5	2.0	44
13	**Cat-3**	--	0.5	5.0	62
14	**Cat-3**	--	--	5.0	50
15	**Cat-3**	0.1	0.5	2.0	65
16	**Cat-3**	0.1	0.5	5.0	72
17	**Cat-3**	0.1	--	5.0	34
18	**Cat-4**	--	0.5	0.5	N.R.
19	**Cat-4**	--	0.5	1.0	9
20	**Cat-4**	--	0.5	2.0	60
21	**Cat-4**	--	0.5	3.0	67
22	**Cat-4**	--	0.5	5.0	71
23	***Cat-4***	--	--	*5.0*	*78*
24	**Cat-4**	0.1	0.5	2.0	74
25	**Cat-4**	0.1	0.5	5.0	79
26	**Cat-4**	0.1	--	5.0	81

[a] The reaction was conducted on 0.2 mmol scale under an argon atmosphere at ambient temperature (<30 °C). 18 W Blue LEDs (455 ± 10 nm) were used as the light source. Reaction time: 12 h. [b] Isolated yield.

The reaction of **1a** was also examined by using another LED light source of different wavelengths (410–420 nm, 24 W). As shown in Table S3, although the reactions took place in CH_3CN, **2a** was generated only in moderate yields. However, when the reaction medium was changed to a mixture of 0.5 mL CH_3CN and 2.0 mL H_2O, the yield was increased remarkably. The same trend was observed for all the four catalysts.

Table S3 Screening of conditions-3[a]

entry	[Cu^{I}]	VC (equiv.)	CH_3CN (mL)	H_2O (mL)	yield of **2a** (%)[b]
1	**Cat-1**	--	1.0	--	11
2	**Cat-2**	--	1.0	--	9
3	**Cat-3**	--	1.0	--	17
4	**Cat-4**	--	1.0	--	9
5	**Cat-1**	--	0.5	2.0	80
6	**Cat-2**	--	0.5	2.0	73
7	**Cat-3**	--	0.5	2.0	72
8	**Cat-4**	--	0.5	2.0	78

[a] The reaction was conducted on 0.2 mmol scale under an argon atmosphere at ambient temperature. 24 W Blue LEDs (410–420 nm) were used as the light source. Reaction time: 12 h. [b] Isolated yield.

4. UV-vis absorption measurement

(1) Compound **1a** (54 mg, 0.2 mmol) and [Cu(Xantphos)(bcp)]PF_6 (10 mg, 0.01 mmol, 5 mol %) were added into 2.5 mL CH_3CN contained in a 20 mL glass tube. After stirring for several minutes, 10 μL of the solution was transferred from the tube into a colorimetric dish with a pipette. 2.5 mL of acetonitrile was then added into the colorimetric dish. The UV-vis absorption measurement was conducted after the solution was mixed uniformly.

The remaining content in the glass tube was irradiated with 18 W blue LEDs (455 nm) for 12 h under an argon atmosphere. After that, 10 μL of the solution was taken out from the tube and transferred into a colorimetric dish, which was then diluted with acetonitrile. The UV-vis absorption measurement was conducted after solution mixed uniformly.

(2) Compound **1a** (54 mg, 0.2 mmol) and [Cu(Xantphos)(bcp)]PF_6 (10 mg, 0.01 mmol, 5 mol %) were added into a 20 mL glass tube containing 0.5 mL of CH_3CN and 2.0 mL of H_2O. After stirring the mixture for several min., 10 μL of the mixture was taken out from the tube and transferred into a colorimetric dish with a pipette. 0.5 mL of acetonitrile and 2.0 mL H_2O was then added into the colorimetric dish. The UV-vis absorption measurement was conducted after the solution mixed uniformly.

The sample for the spectrum after reaction was prepared following the above mentioned procedure.

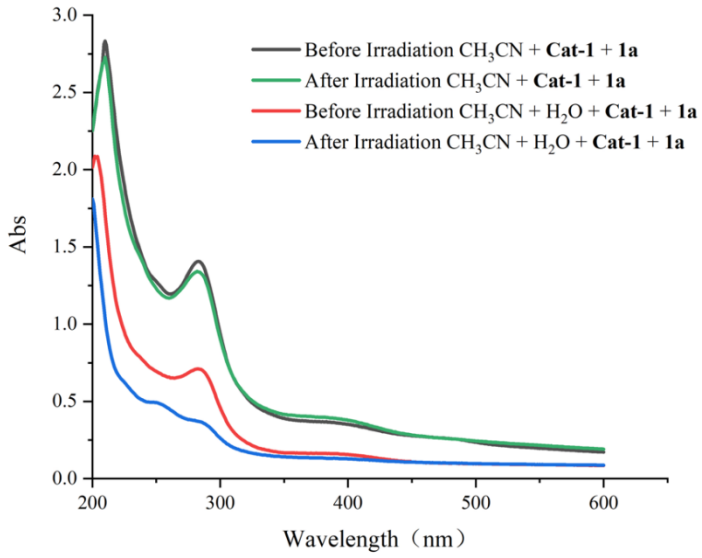
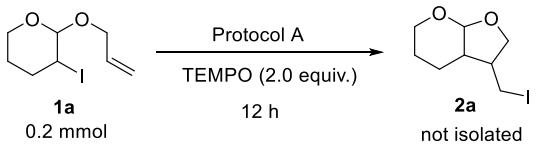


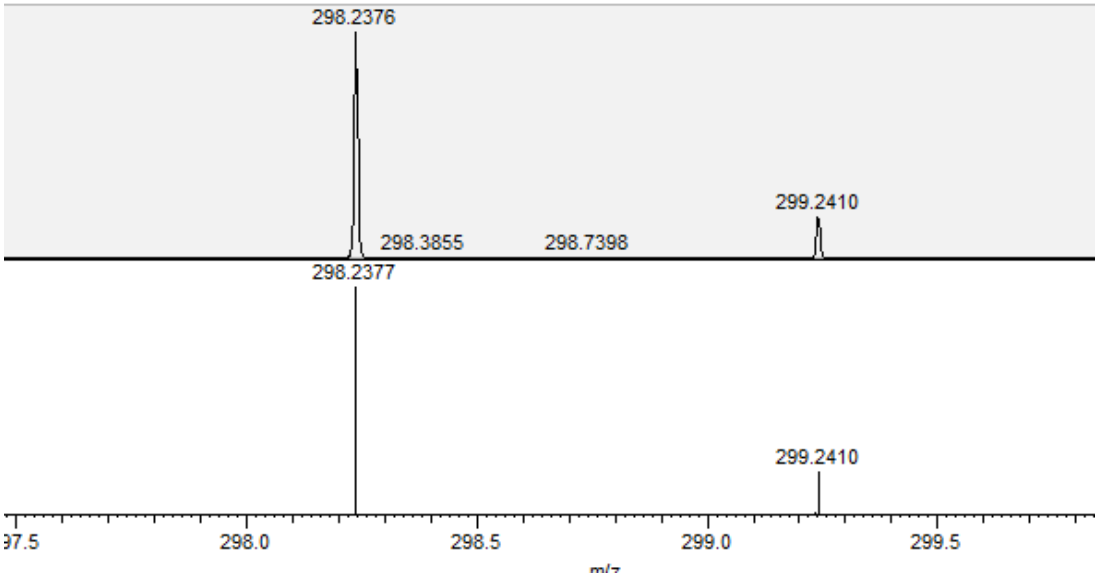
Figure S2. UV-vis absorption spectra for the mixture of **Cat-1** and **1a** in CH_3CN and CH_3CN/H_2O before and after blue LED irradiation (455 nm).

5. Mechanistic study

5.1 Inhibition experiment with TEMPO



The experiment was conducted on a 0.2 mmol scale in the presence of 0.4 mmol (2.0 equiv.) of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) with Protocol A. After 12 h irradiation, no product was detected by TLC, and most of **1a** was recovered. HRMS analysis of the crude product indicates the formation of a tiny amount of TEMPO-trapped product. The HRMS data of TEMPO-adduct is presented below. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{17}H_{32}NO_3]^+$: 298.2377, found: 298.2376.



5.2 Quantum yield measurement[9,10]

(1) Solution preparation

Potassium ferrioxalate solution (0.012 M): 148.0 mg of $K_3[Fe(C_2O_4)]$ $3H_2O$ and 70 μL of H_2SO_4 were added into a 25 mL brown volumetric flask which was then filled to the mark with ultra-pure water.

1,10-Phenanthroline solution (0.01 M): 50.0 mg of 1,10-phenantroline monohydrate was added into a 25 mL brown volumetric flask which was then filled to the mark with ultra-pure water.

NaOAc and HOAc buffer solution: 1.235 g of NaOAc and 250 μL of H_2SO_4 were added into a 25 mL volumetric flask which was then filled to the mark with ultra-pure water.

[Cu(Xantphos)(bcp)]PF_6 in MeCN and *H_2O* (v/v=1/1) *(0.001M)*: 10.0 mg of [Cu(Xantphos)(bcp)]PF_6 was added into 10 mL brown volumetric flask which was then filled to the mark with the mixture of MeCN and H_2O (v/v=1/1).

All solutions were prepared and 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 the reaction vial, and irradiated with 18 W blue LEDs for 90 second. After that, 0.1 mL of this solution was taken as an aliquot. To each aliquot, 2.0 mL of the buffer solution and 0.5 mL of 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 the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as following:

$$\text{mol of } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A}{V_2 \times l \times \varepsilon} = \frac{0.002\ \text{L} \times 0.010\ \text{L} \times 1.024}{0.0001\ \text{L} \times 1.00\ \text{cm} \times 11{,}100\ \text{L/ mol/cm}}$$

$$= 1.85 \times 10^{-5}\ \text{mol}$$

where V_1 is 0.002 L, V_2 is 0.0001 L, V_3 is 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).

$$\text{photon flux} = \frac{\text{mol of } Fe^{2+}}{\Phi \times t \times f} = \frac{1{,}85 \times 10^{-5}\ \text{mol}}{1.12 \times 90.0\ \text{s} \times 0.3933} = 4.666 \times 10^{-7}\ \text{einstein/s}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 1.12, which was reported for a 0.01 M solution at λ = 455 nm), t is the time (90.0 s), and f is the fraction of light absorbed at 455 nm (as shown in **Figure S3**). The fraction of light absorbed was determined by the following equation:

$$f = 1\text{-}10^{-A} = 1\text{-}10^{-0.217} = 0.3933$$

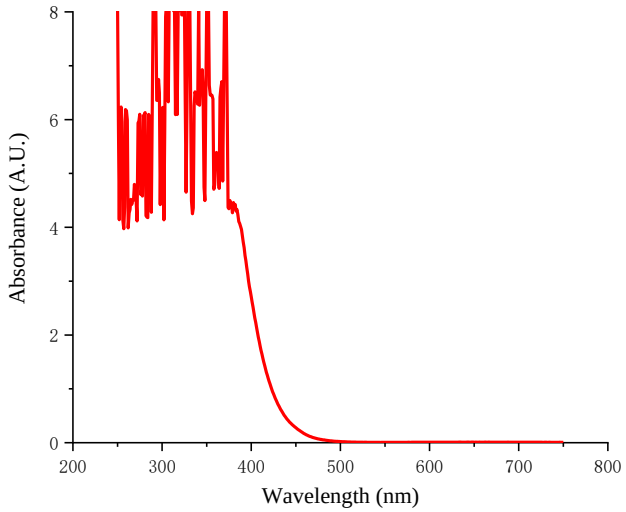
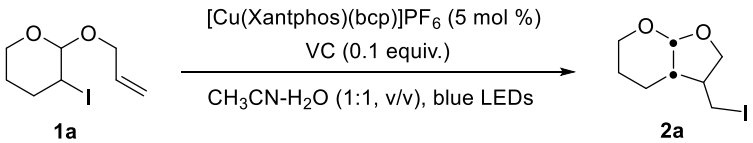


Figure S3. Absorbance of the ferrioxalate actinometer solution.

(3) Determination of quantum yield



Compound **1a** (0.04 mmol), [Cu(Xantphos)(bcp)]PF_6 (2.2 mg, 0.002 mmol, 5 mol %) and ascorbic acid (0.7 mg, 0.004 mmol, 0.1 equiv.) were added into a 20 mL glass tube equipped with a magnetic stirring bar and a rubber stopper. CH_3CN (1.0 mL) and H_2O (1.0 mL) were then added into the tube, which was evacuated and charged with argon. After that, the tube was irradiated under stirring with 18 W blue

LEDs (455 nm) for 3 h. The product was extracted with DCM (4×5 mL), and the combined organic layers were concentrated under reduced pressure on a rotary evaporator. The yield of the product **2a** was determined to be 22% (corresponding to 8.8×10^{-6} mol) by ^{1}H NMR based on a 2,4-dinitrobenzaldehyde internal standard. A 1×10^{-3} M solution of [Cu(Xantphos)(bcp)]PF_6 in acetonitrile and water (1:1, v/v) was prepared, and the absorbance of the solution at 455 nm was measured (A = 0.293). The fraction of light absorbed at 455 nm (as shown in **Figure 4**) was calculated as described above (f = 0.4907).

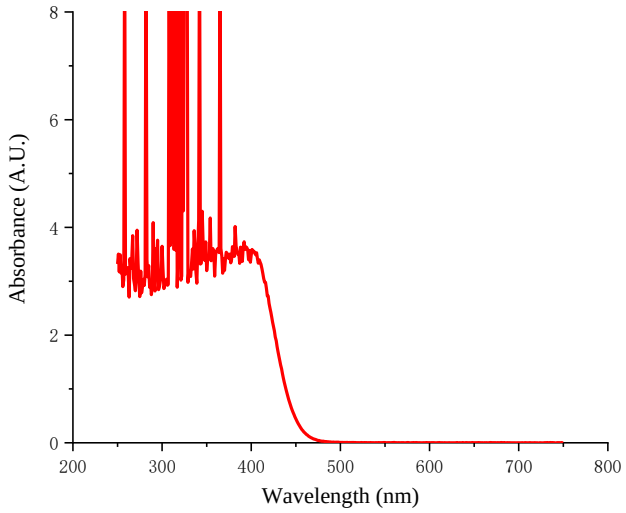


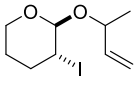
Figure S4. Absorbance of a 1.0 × 10^{-3} M solution of [Cu(Xantphos)(bcp)]PF_6 in MeCN and H_2O (1:1, v/v).

The quantum yield was calculated as follows:

$$\Phi_{\mathbf{2a}} = \frac{\text{mol of product } \mathbf{2a}}{\text{photo flux x t x f}} \quad 0.0036$$

Where mol of product **2a** was 8.8×10^{-6} mol, photo flux is determined by the ferrioxalate actinometer (4.666×10^{-7} einstein s^{-1}), t is the irradiated time (10800 s), and f is the fraction of light absorbed by [Cu(Xantphos)(bcp)]PF_6 at 455 nm (0.4907).

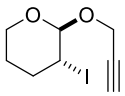
6. Characterization data



2-(But-3-en-2-yloxy)-3-iodotetrahydro-2*H*-pyran (1b)

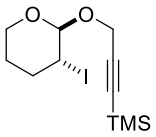
Colorless oil (1.17 g, 40% yield); R_f = 0.79 (PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93–5.84 (m, 1H), 5.77–5.68 (m, 1H), 5.24–5.21 (m, 1H), 5.19–5.16 (m, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 5.07 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.67 (d, *J* = 5.8 Hz, 1H), 4.63 (d, *J* = 5.6 Hz, 1H), 4.27–4.19 (m, 2H), 4.09–4.02 (m, 2H), 4.01–3.95 (m,

2H), 3.58–3.50 (m, 2H), 2.43–2.34 (m, 2H), 2.07–1.97 (m, 2H), 1.76–1.65 (m, 2H), 1.62–1.53 (m, 2H), 1.27 (d, *J* = 4.0 Hz, 3H), 1.26 (d, *J* = 3.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.0, 117.0, 114.7, 101.0, 99.5, 75.2, 74.1, 64.0, 63.6, 33.5, 33.1, 30.3, 29.8, 26.0, 25.9, 21.6, 19.8. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_9H_{15}IO_2Na]^+$: 305.0009, found: 305.0005.



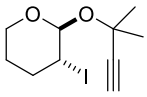
3-Iodo-2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (1f)

Colorless oil (2.22 g, 84%); R_f = 0.55 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (d, *J* = 4.6 Hz, 1H), 4.33–4.24 (m, 2H), 4.11 (*J* = 7.3, 4.4 Hz, 1H), 4.00–3.91 (m, 1H), 3.62–3.57 (m, 1H), 2.46 (t, *J* = 2.4 Hz, 1H), 2.37–2.30 (m, 1H), 2.04–1.96 (m, 1H), 1.88–1.78 (m, 1H), 1.59–1.50 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 100.2, 78.8, 74.8, 63.1, 54.6, 31.7, 28.2, 24.8. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_8H_{11}IO_2Na]^+$: 288.9696, found: 288.9700.



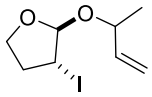
(3-((3-Iodotetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)trimethylsilane (1i)

Colorless oil (2.58 g, 76%); R_f = 0.8 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (d, *J* = 4.7 Hz, 1H), 4.30 (d, *J* = 15.9 Hz, 1H), 4.24 (d, *J* = 15.9 Hz, 1H), , 4.15–4.11 (m, 1H), 3.96–3.91 (m, 1H), 3.62–3.56 (m, 1H), 2.38–2.30 (m, 1H), 2.03–1.95 (m, 1H), 1.89–1.80 (m, 1H), 1.58–1.50 (m, 1H), 0.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 100.2, 91.9, 62.9, 55.5, 31.6, 28.4, 24.7, -0.2. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_{11}H_{19}IO_2SiNa]^+$: 361.0091, found: 361.0089.



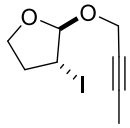
3-Iodo-2-((2-methylbut-3-yn-2-yl)oxy)tetrahydro-2*H*-pyran (1k)

Colorless oil (2.09 g, 71%); R_f = 0.69 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (d, *J* = 5.7 Hz, 1H), 4.08–3.98 (m, 2H), 3.61–3.55 (m, 1H), 2.51 (s, 1H), 2.43–2.35 (m, 1H), 2.09–2.00 (m, 1H), 1.77–1.67 (m, 1H), 1.62–1.54 (m, 1H), 1.52 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.0, 85.3, 73.3, 71.8, 63.6, 33.2, 30.4, 30.2, 29.9, 25.8. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{10}H_{16}IO_2]^+$: 295.0189, found: 295.0193.



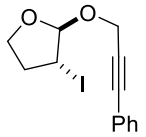
2-(But-3-en-2-yloxy)-3-iodotetrahydrofuran (1m)

Colorless oil (1.73 mg, 64%); R_f = 0.74 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87–5.78 (m, 1H), 5.71–5.62 (m, 1H), 5.45 (s, 1H), 5.37 (s, 1H), 5.23–5.14 (m, 3H), 5.08 (dt, *J* = 10.5, 1.4 Hz, 1.05H), 4.20–4.00 (m, 8H), 2.68–2.57 (m, 2H), 2.23–2.15 (m, 2H), 1.22 (d, *J* = 4.0 Hz, 3H), 1.20 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.1, 116.8, 114.6, 108.7, 107.9, 73.7, 73.4, 66.9, 66.7, 35.7, 35.5, 25.4, 25.2, 21.6, 20.2. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_8H_{14}IO_2]^+$: 269.0033, found: 269.0031.



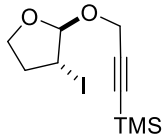
2-(But-2-yn-1-yloxy)-3-iodotetrahydrofuran (1p)

Colorless oil (1.88 g, 71%); R_f = 0.4 (PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (s, 1H), 4.22–4.16 (m, 2H), 4.14–4.07 (m, 2H), 4.01 (td, *J* = 8.4, 3.4 Hz, 1H), 2.66–2.56 (m, 1H), 2.21–2.14 (m, 1H), 1.84 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 108.7, 82.8, 74.3, 67.2, 54.6, 35.4, 24.4, 3.6. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_8H_{11}IO_2Na]^+$: 288.9696, found: 288.9691.



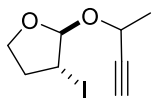
3-Iodo-2-((3-phenylprop-2-yn-1-yl)oxy)tetrahydrofuran (1q)

Yellow oil (2.30 g, 70%); R_f = 0.61 (PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.42 (m, 2H), 7.37–7.28 (m, 3H), 5.59 (s, 1H), 4.44 (d, *J* = 15.8 Hz, 1H), 4.41 (d, *J* = 15.8 Hz, 1H), 4.25 (dd, *J* = 6.4, 2.1 Hz, 1H), 4.17 (dd, *J* = 15.3, 8.4 Hz, 1H), 4.06 (td, *J* = 8.4, 3.6 Hz, 1H), 2.70–2.61 (m, 1H), 2.25–2.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.5, 128.2, 122.3, 108.9, 86.3, 84.3, 67.3, 54.7, 35.4, 24.3. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{13}H_{13}IO_2H]^+$: 329.0033, found: 329.0030.



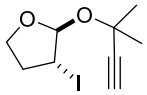
(3-((3-Iodotetrahydrofuran-2-yl)oxy)prop-1-yn-1-yl)trimethylsilane (1r)

Colorless oil (2.10 g, 65%); R_f = 0.8 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H), 4.24–4.20 (m, 2H), 4.18–4.16 (m, 1H), 4.14–4.10 (m, 1H), 4.02 (td, *J* = 8.3, 3.4 Hz, 1H), 2.67–2.57 (m, 1H), 2.22–2.16 (m, 1H), 0.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 109.0, 100.7, 91.6, 67.3, 54.8, 35.4, 24.3, -0.2. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_{10}H_{17}IO_2SiNa]^+$: 346.9935, found: 346.9933.



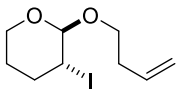
2-(But-3-yn-2-yloxy)-3-iodotetrahydrofuran (1s)

Colorless oil (1.09 g, 41%); R_f = 0.79 (PE/EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (s, 1H), 5.51 (s, 1H), 4.43 (qd, *J* = 6.7, 2.1 Hz, 1H), 4.39 (qd, *J* = 6.7, 2.1 Hz, 1H), 4.20 (dd, *J* = 6.2, 2.2 Hz, 1H), 4.17–4.09 (m, 4H), 3.99 (td, *J* = 8.4, 3.4 Hz, 1H), 2.68–2.55 (m, 2H), 2.45 (d, *J* = 2.1 Hz, 2H), 2.23–2.15 (m, 2H), 1.41 (d, *J* = 6.7 Hz, 3H), 1.38 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 108.9, 107.9, 83.9, 82.9, 73.4, 72.6, 67.3, 67.1, 62.4, 61.0, 35.4, 35.3, 24.8, 24.7, 22.0, 21.9. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_8H_{12}IO_2]^+$: 266.9876, found: 266.9872.



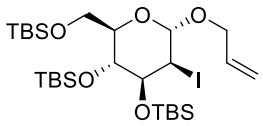
3-Iodo-2-((2-methylbut-3-yn-2-yl)oxy)tetrahydrofuran (1t)

Colorless oil (1.72 g, 62%); R_f = 0.71 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, 1H), 4.15 (dd, *J* = 6.1, 3.0 Hz, 1H), 4.09–4.06 (m, 2H), 2.61–2.52 (m, 2H), 2.20–2.14 (m, 1H), 1.50 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 107.3, 85.6, 73.0, 70.5, 67.0, 35.4, 30.3, 29.5, 26.6. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_9H_{13}IO_2Na]^+$: 302.9852, found: 302.9852.



2-(But-3-en-1-yloxy)tetrahydro-2*H*-pyran (**1u**)

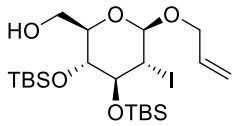
Light yellow oil (1.62 g, 58%); R_f = 0.71 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90–5.80 (m, 1H), 5.10 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.04 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.61 (d, *J* = 5.6 Hz 1H), 4.09–4.05 (m, 1H), 4.01–3.95 (m, 1H), 3.83–3.78 (m,1H), 3.60–3.49 (m, 2H), 2.40–2.34 (m, 3H), 2.06–1.97 (m, 1H), 1.77–1.68 (m, 1H), 1.62–1.52 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 116.5, 102.6, 67.9, 63.7, 33.9, 33.0, 29.4, 25.7. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_9H_{15}IO_2Na]^+$: 305.0009, found: 305.0011 .



(((2*R*,3*R*,4*R*)-6-(Allyloxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-3,4-diyl)bis(oxy))bis(*tert*-butyldimethylsilane) (1v)

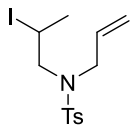
Colorless oil; R_f = 0.87 (PE/EA = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96–5.86 (m, 1H), 5.28 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.18 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.09 (d, *J* = 3.2 Hz, 1H), 4.34 (t, *J* = 3.3 Hz, 1H), 4.21 (dd, *J* = 13.0, 5.0 Hz, 1H), 3.98 (dd, *J* = 13.0, 6.1 Hz, 1H), 3.86–3.78 (m, 2H), 3.75–3.70 (m, 1H), 3.67–3.62 (m, 1H), 3.50–3.16 (m, 1H), 3.67–3.62 (m, 1H), 3.50–3.16 (m, 1H), 0.96 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.11 (s, 3H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 134.0, 117.1, 71.2, 68.2, 62.4, 26.5, 26.1, 26.0, 25.7, 25.6, 18.4, 18.3, 18.0, -3.0, -3.1, -3.2, -4.3, -4.5, -5.0, -5.3. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_{27}H_{57}IO_5SiNa]^+$: 695.2451, found: 695.2448.



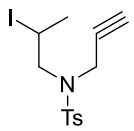
((2*R*,3*R*,4*R*)-6-(Allyloxy)-3,4-bis((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)methanol (1w)

Colorless oil; R_f = 0.63 (PE/EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 5.94–5.85 (m, 1H), 5.29 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.20 (dd, *J* = 10.4, 1.7 Hz, 1H), 5.16 (d, *J* = 2.3 Hz, 1H), 4.31 (t, *J* = 2.3 Hz, 1H), 4.17 (dd, *J* = 13.1, 5.1 Hz, 1H), 3.98 (dd, *J* = 13.1, 5.1 Hz, 1H), 3.89–3.85 (m, 1H), 3.78–3.65 (m, 3H), 3.38–3.19 (m, 1H), 1.98 (br, 1H), 0.96 (s, 9H), 0.89 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 117.3, 100.7, 74.9, 71.2, 68.5, 61.9, 26.4, 26.0, 18.3, 18.0, -3.3, -4.3, -4.7. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_{21}H_{43}IO_3Si_2Na]^+$: 581.1586, found: 581.1588.



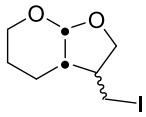
***N*-Allyl-*N*-(2-iodopropyl)-4-methylbenzenesulfonamide (1y)**

Colorless oil (1.04 g, 28%); R_f = 0.49 (PE/EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.63–5.53 (m, 1H), 5.18–5.13 (m, 2H), 4.34–4.25 (m, 1H), 3.84 (dd, *J* = 15.4, 6.6 Hz, 1H), 3.73 (dd, *J* = 15.4, 6.6 Hz, 1H), 3.76–3.70 (m, 1H), 3.47–3.37 (m, 2H), 2.42 (s, 3H), 1.91 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.1, 132.6, 129.8, 127.3, 119.8, 57.1, 52.2, 25.2, 23.9, 21.5. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{13}H_{19}INO_2S]^+$: 380.0176, found: 380.0173.

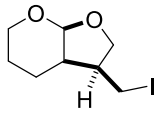


***N*-(2-Iodopropyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1aa)**

Colorless oil (1.10 g, 29%); R_f = 0.44 (PE/EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.37–4.28 (m, 1H), 4.15–4.13 (m, 2H), 3.53 (dd, *J* = 14.3, 6.5 Hz, 1H), 3.48–3.41 (m, 1H), 2.42 (s, 3H), 2.07 (t, *J* = 2.4 Hz, 1H), 1.94 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 135.1, 129.5, 127.6, 76.1, 74.3, 56.2, 37.8, 25.2, 22.8, 21.5. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{13}H_{17}INO_2S]^+$: 378.0019, found: 378.0018.

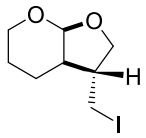


Colorless oil. **2a** (89/11), 86 mg, 77% (Protocol A).



(3aS,3aR,7aS)-3-(Iodomethyl)hexahydro-4*H*-furo[2,3-b]pyran (2a-1)[11]

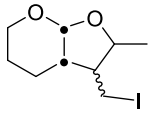
Major isomer: R_f = 0.42 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (d, *J* = 3.6 Hz, 1H), 4.00 (t, *J* = 8.2 Hz, 1H), 3.78–3.72 (m, 1H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.63–3.58 (m, 1H), 3.14 (d, *J* = 8.1 Hz, 2H), 2.86–2.76 (m, 1H), 2.11–2.04 (m, 1H), 1.80–1.73 (m, 1H), 1.6 –1.54 (m, 2H), 1.47–1.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.6, 70.1, 61.2, 44.2, 38.3, 22.7, 18.6, 2.2.



(3aR,3aR,7aS)-3-(Iodomethyl)hexahydro-4*H*-furo[2,3-b]pyran (2a-2)[11]

Minor isomer: R_f = 0.35 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (d, *J* = 3.2 Hz, 1H), 4.31 (t, *J* = 8.4 Hz, 1H), 3.92–3.87 (m, 1H), 3.67(dd. *J* = 8.8, 7.4 Hz, 1H), 3.42 (td, *J* = 11.5, 2.4 Hz, 1H), 3.33 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.11 (dd, *J* = 10. 0, 8.7 Hz, 1H), 2.63–2.54 (m, 1H), 1.87–1.82 (m, 3H), 1.70–1.64 (m, 1H), 1.43–1.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 102.5, 74.6, 64.3, 44.82, 40.6, 22.4, 20.6, 7.6.

Colorless oil. **2a** (87/13), 77 mg, 73% (Protocol B).



(3aS,7aR)-3-(Iodomethyl)-2-methylhexahydro-4*H*-furo[2,3-b]pyran (2b)[11]

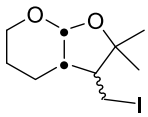
Colorless oil. 90 mg, 80% (58/42), R_f = 0.34, 0.29 (PE/EA = 5:1) (Protocol A).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (d, *J* = 3.7 Hz, 1H), 3.97–3.84 (m, 1H), 3.78–3.72 (m, 1H), 3.63–3.58 (m, 1H), 3.22–3.14 (m, 1H), 3.07 (t, *J* = 10.1 Hz, 1H), 2.35–2.27 (m, 1H), 2.19–2.12 (m, 1H), 1.87–1.77 (m, 2H), 1.63–1.54 (m, 2H), 1.27 (d, *J* = 6.1 Hz, 3H).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (d, *J* = 3.7 Hz, 1H), 3.97–3.84 (m, 2H), 3.38 (td, *J* = 11.6, 2.4 Hz,1H), 3.30 (dd, *J* = 10.4, 3.9 Hz, 1H), 3.22–3.14 (m, 1H), 1.98–1.92 (m, 1H), 1.87–1.77 (m, 2H), 1.63–1.54 (m, 1H), 1.43–1.37 (m, 2H), 1.41 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 101.2, 100.0, 82.0, 76.6, 64.3, 61.2, 52.01, 45.7, 45.4, 39.1, 22.7, 22.2, 22.1, 21.0, 20.6, 19.0, 7.5, 1.6.

Colorless oil. 69 mg, 62% (52/48) (Protocol B).



Colorless oil. **2c**, 92 mg, 80% (68/32) (Protocol A).

(3aS,7aR)-3-(Iodomethyl)-2,2-dimethylhexahydro-4*H*-furo[2,3-b]pyran (2c-1)

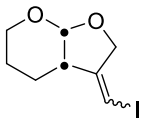
Colorless oil (61 mg, 53%); R_f = 0.29 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (d, *J* = 3.4 Hz, 1H), 3.90–3.85 (m, 1H), 3.35 (dt, *J* = 11.8, 2.3 Hz, 1H), 3.28 (dd, *J* = 10.3, 4.3 Hz, 1H), 2.97 (t, *J* = 10.4 Hz, 1H), 2.53 (ddd, *J* = 11.5, 10.2, 4.3 Hz, 1H), 1.93–1.68 (m, 4H), 1.49 (s, 3H), 1.36–1.30 (m, 1H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.8, 84.8, 64.5, 47.8, 45.6, 31.1, 23.3, 22.2, 20.2, 2.5.

HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{10}H_{18}IO_2]^+$: 297.0346, found: 297.0340.

(3aS,7aR)-3-(Iodomethyl)-2,2-dimethylhexahydro-4*H*-furo[2,3-b]pyran (2c-2)

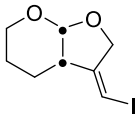
Colorless oil (31 mg, 27%); R_f = 0.42 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24–5.20 (m, 1H), 3.84–3.77 (m, 1H), 3.69–3.63 (m, 1H), 3.16 (dd, *J* = 8.6, 2 2Hz, 2H), 2.56–2.49 (m, 1H), 2.23–2.15 (m, 1H), 1.84–1.76 (m, 1H), 1.63–1.48 (m, 3H), 1.28 (dd, *J* = 11.6, 2.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 97.7, 78.9, 60.9, 53.2, 39.7, 31.0, 24.7, 23.1, 18.9, 1.0.

Colorless oil. **2c**, 94 mg, 79% (68/32) (Protocol B).

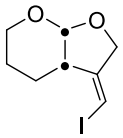


(3aS,7aR)-3-(Iodomethylene)hexahydro-4*H*-furo[2,3-b]pyran (2f)[11]

Colorless oil. 82 mg, 72% ((93/7), R_f = 0.34 (PE/EA = 5:1) (Protocol A).



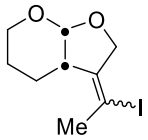
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (q, *J* = 2.6 Hz, 1H), 5.31 (d, *J* = 3.7 Hz, 1H), 4.45 (dt, *J* = 14.3, 2.5 Hz, 1H), 4.35 (ddd, *J* = 14.3, 2.7, 1.6 Hz, 1H), 3.89–3.83 (m, 1H), 3.43 (td, *J* = 11.3, 2.4 Hz, 1H), 2.70–2.66 (m, 1H), , 2.03–1.95 (m, 1H), 1.93–1.82 (m, 1H), 1.63–1.52 (m, 1H), 1.36–1.28 (m, 1H).



Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (q, *J* = 1.8 Hz, 1H), 5.24 (d, *J* = 4.0 Hz, 1H), 4.53 (dt, *J* = 13.4, 1.8 Hz, 1H), 4.26 (dd, *J* = 13.3, 1.8 Hz, 1H), 3.71–3.65 (m, 1H), 3.43 (td, *J* = 11.3, 2.4 Hz, 1H), 2.70–2.66 (m, 1H), 2.10–2.04 (m, 1H), 1.93–1.82 (m, 1H), 1.63–1.52 (m, 1H), 1.36–1.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 150.5, 102.2, 99.8, 75.4, 68.4, 67.2, 67.1, 64.3, 61.4, 44.9, 43.8, 22.6, 22.1, 21.9, 20.4.

Colorless oil. 52 mg, 50% (88/12) (Protocol B).



(3aS,7aR)-3-(1-Iodoethylidene)hexahydro-4*H*-furo[2,3-b]pyran (2g)[11]

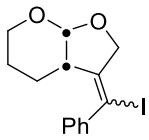
Colorless oil. 83 mg, 75% (77/23), R_f = 0.49, 0.46 (PE/EA = 5:1) (Protocol A).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (d, *J* = 4.0 Hz, 1H), 4.35–4.30 (m, 1H), 4.06–4.00 (m, 1H), 3.88–3.79 (m, 1H), 3.70–3.66 (m, 1H), 2.73–2.68 (m, 1H), 2.47 (t, *J* = 2.2 Hz, 3H), 1.89–1.82 (m, 1H), 1.65–1.33 (m, 3H).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (d, *J* =13.4 Hz, 1H), 4.35–4.30 (m, 1H), 4.06–4.00 (m, 1H), 3.88–3.79 (m, 1H), 3.70–3.66 (m, 1H), 2.56–2.50 (m, 1H), 2.29 (d, *J* = 2.6 Hz, 3H), 2.14–2.06 (m, 1H), 1.65–1.33 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 145.3, 101.1, 99.4, 87.5, 85.4, 73.8, 65.6, 61.2, 61.1, 45.9, 40.2, 29.5, 28.9, 23.7, 22.7, 22.4, 22.2.

Colorless oil. 74 mg, 66% (74/26) (Protocol B).



(3aS,7aR)-3-(Iodo(phenyl)methylene)hexahydro-4*H*-furo[2,3-b]pyran (2h)

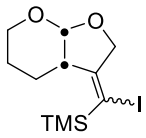
Colorless oil. 90 mg, 65% (70/30), R_f = 0.56, 0.44 (PE/EA = 5:1) (Protocol A).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 5H), 5.33–5.31 (m, 1H), 4.57 (dd, *J* = 14.3, 2.0 Hz, 1H), 4.33 (d, *J* = 14.4 Hz, 1H), 3.91–3.82 (m, 1H), 3.56–3.51 (m, 1H), 2.81–2.70 (m, 1H), 1.70–1.53 (m, 1H), 1.53–1.32 (m, 2H), 1.32–1.21 (m, 1H).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 5H), 5.33–5.31 (m, 1H), 4.56 (d, *J* = 14.1, 1.5 Hz, 1H), 4.15 (d, *J* = 14.1 Hz, 1H), 3.91–3.82 (m, 1H), 3.75–3.70 (m, 1H), 2.81–2.70 (m, 1H), 2.31–2.23 (m, 1H), 1.70–1.53 (m, 1H), 1.53–1.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.3, 142.6, 142.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 102.1, 99.2, 89.0, 88.1, 76.1, 66.5, 62.3, 61.1, 46.8, 42.2, 23.3, 22.4, 22.1, 21.9.

HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{14}H_{16}IO_2]^+$: 343.0189, found: 343.0184.



(Iodo((3aS,7aR)-tetrahydro-4*H*-furo[2,3-b]pyran-3(2*H*)-ylidene)methyl)trimethylsilane (2i)

Colorless oil. 114 mg, 84% (72/28), R_f = 0.5 (PE/EA = 10:1) (Protocol A).

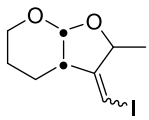
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (d, *J* = 3.6 Hz, 1H), 4.42 (dd, *J* = 15.1, 1.3 Hz, 1H), 4.10 (d, *J* = 15.2 Hz, 1H), 3.91–3.82 (m, 1H), 3.73–3.67 (m, 1H), 2.71–2.66 (m, 1H), 1.80–1.74 (m, 1H), 1.68–1.49 (m, 3H), 0.27 (s, 9H).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (d, *J* = 3.9 Hz, 1H), 4.52 (dd, *J* = 13.9, 1.5 Hz, 1H), 4.28 (d, *J* = 13.9 Hz, 1H), 3.91–3.82 (m, 1H), 3.73–3.67 (m, 1H), 2.82–2.76 (m, 1H), 2.30–2.23 (m, 1H), 1.68–1.49 (m, 2H), 1.41–1.31 (m, 1H), 0.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 159.4, 101.8, 101.4, 99.2, 98.8, 77.1, 67.1, 61.2, 60.7, 49.8, 42.5, 25.5, 23.0, 22.5, 21.8, 0.6, 0.3.

HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{11}H_{19}IO_2SiNa]^+$: 339.0272, found: 339.0268.

Colorless oil. 116 mg, 88% (74/26) (Protocol B).

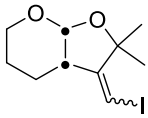


(2R,3aS,7aR)-3-(Iodomethylene)-2-methylhexahydro-4*H*-furo[2,3-b]pyran (2j)[11]

Colorless oil. 85 mg, 79% (45/29/17/9), R_f = 0.5, 0.44, 0.36 (PE/EA = 5:1) (Protocol A).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (t, *J* = 2.2 Hz, 0.66H), 5.93 (t, *J* = 2.4 Hz, 1.20H), 5.87 (t, *J* = 1.7 Hz, 0.39H), 5.30 (d, *J* = 4.3 Hz, 0.20H), 5.19 (d, *J* = 4.0 Hz, 0.39H), 5.17–5.15 (m, 1.66H), 4.78–4.73 (m, 0.20H), 4.72–4.66 (m, 1.0H), 4.48 (ddd, *J* = 14.1, 6.6, 2.6 Hz, 0.66H), 4.38 (ddd, *J* = 13.5, 6.4, 2.1 Hz, 0.39H), 3.90–3.81 (m, 2.25H), 3.74–3.69 (m, 0.39H), 3.67–3.62 (m, 0.20H), 3.56–3.50 (m, 0.66H), 3.38 (td, *J* = 11.9, 2.2 Hz, 1.0H), 2.79–2.61 (m, 2.25H), 2.24–2.16 (m, 0.39H), 2.07–1.99 (m, 1.20H), 1.93–1.72 (m, 3.00H), 1.64–1.54 (m, 3.09H), 1.61 (d, *J* = 6.6 Hz, 1.98H), 1.40 (d, *J* = 6.5 Hz, 1.17H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.31 (d, *J* = 6.4 Hz, 0.60H), 1.29–1.23 (m, 1.32H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 157.0, 155.4, 152.5, 100.7, 100.1, 98.3, 98.1, 81.0, 79.0, 75.7, 74.4, 68.8, 68.0, 67.9, 67.8, 64.7, 62.5, 61.5, 61.3, 45.6, 45.0, 44.6, 44.2, 24.6, 22.7, 22.5, 22.3, 21.9, 21.8, 21.6, 21.5, 20.4, 20.3, 19.7, 19.2.

Colorless oil. 39 mg, 35% (47/27/13/13) (Protocol B).



Colorless oil. **2k**, 85 mg, 78% (50/50) (Protocol A).

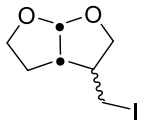
(3aS,7aR)-3-(Iodomethylene)-2,2-dimethylhexahydro-4*H*-furo[2,3-b]pyran (2k-1)

R_f = 0.49 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, *J* = 1.6 Hz, 1H), 5.31 (d, *J* = 4.1 Hz, 1H), 3.87 (td, *J* = 10.9, 3.8 Hz, 1H), 3.72–3.67 (m, 1H), 2.73–2.68 (m, 1H), 2.22–2.15 (m, 1H), 1.63–1.49 (m, 3H), 1.45 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 97.1, 81.2, 68.6, 61.2, 44.9, 30.1, 28.5, 22.7, 22.5. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{10}H_{16}IO_2]^+$: 295.0189, found: 295.0189.

(3aS,7aR)-3-(Iodomethylene)-2,2-dimethylhexahydro-4*H*-furo[2,3-b]pyran (2k-2)

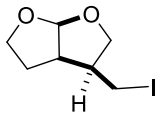
R_f = 0.37 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, *J* = 2.6 Hz, 1H), 4.99 (d, *J* = 3.8 Hz, 1H), 3.89–3.84 (m, 1H), 3.40 (td, *J* = 11.0, 2.4 Hz, 1H), 2.82–2.78 (m, 1H), 1.97–1.83 (m, 2H), 1.67 (s, 3H), 1.61–1.52 (m, 1H), 1.45 (s, 3H), 1.35–1.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 99.4, 85.5, 65.4, 64.2, 47.1, 26.7, 26.1, 23.2, 20.7. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{10}H_{16}IO_2]^+$: 295.0189, found: 295.0186.

Colorless oil, 74 mg, 63% (51/49) (Protocol B).

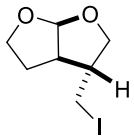


(Iodomethyl)hexahydrofuro[2,3-b]furan (2l)[12]

Colorless oil, 81 mg, 79% (96/4), R_f = 0.3 (PE/EA = 5:1) (Protocol A).



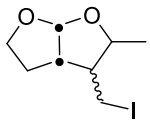
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (d, *J* = 4.9 Hz, 1H), 4.01 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.88 (dd, *J* = 7.6, 6.1 Hz, 2H), 3.43 (dd, *J* = 11.0, 8.6 Hz, 1H), 3.18–3.13 (m, 1H), 3.06 (dd, *J* = 9.9, 8.4 Hz, 1H), 2.92–2.85 (m, 1H), 2.83–2.72 (m, 1H), 1.95–1.86 (m, 1H), 1.85–1.75 (m, 1H).



Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, *J* = 5.1 Hz, 1H), 4.18 (dd, *J* = 14.1, 8.4 Hz, 1H), 3.88 (dd, *J* = 7.6, 6.1 Hz, 1H), 3.67 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.43 (dd, *J* = 11.0, 8.6 Hz, 1H), 3.18–3.13 (m, 1H), 3.06 (dd, *J* = 9.9, 8.4 Hz, 1H), 2.63–2.54 (m, 1H), 2.43–2.35 (m, 1H), 2.18–2.06 (m, 1H), 1.85–1.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 109.7, 109.0, 72.9, 72.0, 69.0, 67.7, 49.8, 48.8, 46.6, 45.3, 31.9, 24.4, 8.8, 0.3.

Colorless oil, 84 mg, 82% (98/2) (Protocol B).

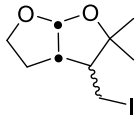


(3aS,6aR)-3-(Iodomethyl)-2-methylhexahydrofuro[2,3-b]furan (2m)

Colorless oil. 81 mg, 76% (58/21/21) (Protocol A).

R_f = 0.26 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (d, *J* = 4.8 Hz, 0.36H), 5.64 (d, *J* = 5.2 Hz, 1.35H), 5.57 (d, *J* = 5.5 Hz, 1H), 4.25 (p, *J* = 7.0 Hz, 0.36H), 4.07–4.02 (m, 0.38H), 3.98–3.78 (m, 5.43H), 3.70–3.63 (m, 1.50H), 3.61–3.56 (m, 0.96H), 3.26–3.10 (m, 4.33H), 3.00–2.92 (m, 1.56H), 2.92–2.86 (m, 2.05H), 2.56 (dd, *J* = 13.7, 8.4, Hz, 1.03H), 2.26–2.17 (m, 1.39H), 2.01–1.89 (m, 2.87H), 1.84–1.73 (m, 3.04H), 1.56–1.49 (m, 1.02H), 1.27 (d, *J* = 6.0 Hz, 3H), 1.22 (d, *J* = 6.0 Hz, 4.03H), 1.17 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 108.9, 107.5, 106.9, 79.4, 77.4, 76.8, 68.6, 67.6, 66.4, 52.6, 52.4, 51.0, 47.8, 47.2, 46.8, 32.8, 24.9, 24.8, 19.2, 19.0, 17.3, 6.7, 1.0, 0.6. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_8H_{14}IO_2]^+$: 269.0033, found: 269.0029.

Colorless oil, 88 mg, 85% (50/37/13) (Protocol B).

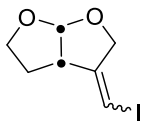


(3aS,6aR)-3-(Iodomethyl)-2,2-dimethylhexahydrofuro[2,3-b]furan (2n)

Colorless oil. 95 mg, 85% (53/47), R_f = 0.34 (PE/EA = 5:1) (Protocol A).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65–5.62 (m, 1H), 5.57–5.54 (m, 0.93H), 4.11–4.03 (m, 1H), 3.96–3.90 (m, 0.93H), 3.89–3.76 (m, 2H), 3.22–3.17 (m, 1H), 3.14–3.09 (m, 2.12H), 3.08–3.00 (m, 1.93H), 2.59–2.48 (m, 2H), 2.03–1.90 (m, 3.93H), 1.87–1.77 (m, 1.22H), 1.34–1.23 (m, 5.97H), 1.60–1.01 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 107.0, 106.1, 83.3, 82.7, 67.4, 66.0, 54.9, 53.7, 51.1, 48.3, 32.6, 30.3, 27.5, 24.8, 23.7, 21.9, 3.6, 1.2. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_9H_{16}IO_2]^+$: 283.0189, found: 283.0185.

Colorless oil, 94 mg, 85% (50/50) (Protocol B).



4-(3aS,6aR)-3-(Iodomethylene)hexahydrofuro[2,3-b]furan (2o)[11]

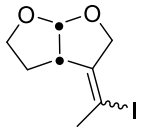
Colorless oil. 85 mg, 80% (57/43), R_f = 0.47, 0.39 (PE/EA = 5:1) (Protocol A).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (q, *J* = 2.4 Hz, 1H), 5.94 (d, *J* = 4.9 Hz, 1H), 4.45–4.33 (m, 2H), 4.00–3.92 (m, 1H), 3.82–3.75 (m, 1H), 3.33–3.29 (m, 1H), 2.25–2.09 (m, 1H), 1.93 (dd, *J* = 12.4, 5.4 Hz, 1H).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (q, *J* = 2.0 Hz, 1H), 5.81 (d, *J* = 5.0 Hz, 1H), 4.45–4.33 (m, 2H), 4.00–3.92 (m, 1H), 3.82–3.75 (m, 1H), 3.27–3.22 (m, 1H), 2.25–2.09 (m, 1H), 2.06–1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 153.3, 110.8, 108.9, 76.3, 72.3, 70.5, 69.1, 68.1, 67.4, 51.3, 49.2, 34.1, 32.2.

Colorless oil. 70 mg, 68% (58/42) (Protocol B).



(3aS,6aR)-3-(1-Iodoethylidene)hexahydrofuro[2,3-b]furan (2p)

Colorless oil. 82 mg, 77% (65/35), R_f = 0.43, 0.35 (PE/EA = 5:1). (Protocol A)

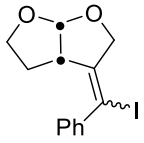
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (d, *J* = 5.0 Hz, 1H), 4.37 (td, *J* = 13.6, 2.3 Hz, 1H), 4.29 (dd, *J* = 13.6, 2.0 Hz, 1H), 3.98–3.93 (m, 1H), 3.84–3.75 (m, 1H), 3.41–3.37 (m, 1H), 2.50 (dd, *J* = 3.9, 1.7 Hz, 3H), 2.22–2.07 (m, 1H), 1.94–1.89 (m, 1H).

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (d, *J* = 5.0 Hz, 1H), 4.51 (d, *J* = 13.0 Hz, 1H), 4.43 (td, *J* = 13.0, 1.7 Hz, 1H), 3.98–3.93 (m, 1H), 3.84–3.75 (m, 1H), 3.24–3.19 (m, 1H), 2.37 (dd, *J* = 3.0, 1.6 Hz, 3H), 2.22–2.07 (m, 1H), 2.04–1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 146.3, 111.1, 108.5, 88.9, 87.1, 78.4, 69.7, 67.8, 67.6, 53.7, 46.5, 33.0, 32.7, 30.1, 29.9.

HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_8H_{11}IO_2Na]^+$: 288.9696, found: 288.9692.

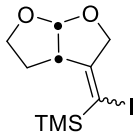
Colorless oil. 66 mg, 60% (64/36) (Protocol B).



(3aS,6aR)-3-(Iodo(phenyl)methylene)hexahydrofuro[2,3-b]furan (2q)

Colorless oil. 94 mg, 72% (56/44), R_f = 0.5, 0.4 (PE/EA = 5:1) (Protocol A).

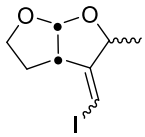
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 5.82 (d, *J* = 4.9 Hz, 1H), 4.62–4.48 (m, 2H), 3.96–3.89 (m, 1H), 3.87–3.81 (m, 1H), 3.49–3.41 (m, 1H), 2.37–2.26 (m, 1H), 1.85–1.75 (m, 1H),
Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 5.93 (d, *J* = 4.9 Hz, 1H), 4.62–4.48 (m, 1H), 4.24 (d, *J* = 13.6 Hz, 1H), 4.05 (dt, *J* = 8.8, 2.4 Hz, 1H), 3.87–3.81 (m, 1H), 3.49–3.41 (m, 1H), 2.21–2.15 (m, 1H), 1.71–1.66 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 149.0, 142.3, 142.2, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 111.0, 108.1, 92.2, 89.4, 78.9, 70.4, 68.2, 67.7, 54.7, 47.4, 33.0, 32.7.
HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $[C_{13}H_{13}IO_2Na]^+$: 350.9852, found: 350.9850.



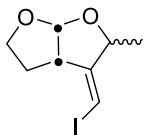
(Iodo((3aS,6aR)-tetrahydrofuro[2,3-b]furan-3(2*H*)-ylidene)methyl)trimethylsilane (2r)

Colorless oil. 97 mg, 71% (53/47), R_f = 0.67 (PE/EA = 10:1) (Protocol A).
Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, *J* = 4.9 Hz, 1H), 4.48–4.37 (m, 2H), 4.01–3.95 (m, 1H), 3.90–3.80 (m, 1H), 3.41–3.36 (m, 1H), 2.33–2.15 (m, 1H), 1.91–1.85 (m, 1H), 0.29 (d, *J* = 1.5 Hz, 9H),
Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (d, *J* = 5.0 Hz, 1H), 4.48–4.37 (m, 2H), 4.01–3.95 (m, 1H), 3.90–3.80 (m, 1H), 3.41–3.36 (m, 1H), 2.33–2.15 (m, 1H), 2.06–2.00 (m, 1H), 0.23 (d, *J* = 1.6 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.3, 111.4, 107.6, 102.4, 101.9, 81.8, 71.0, 67.9, 67.4, 57.5, 48.3, 35.4, 33.3, 0.4, 0.3.
HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{10}H_{18}IO_2Si]^+$: 339.0272, found: 339.0268.

Colorless oil. 108 mg, 83% (55/45) (Protocol B).



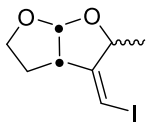
Colorless oil. **2s**, 81 mg, 78% (43/37/12/8) (Protocol A).



(**2R,3aS,6aR)-3-(Iodomethylene)-2-methylhexahydrofuro[2,3-b]furan (2s-1)**

R_f = 0.56 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (t, *J* = 2.1 Hz, 1H), 6.04 (t, *J* = 2.2 Hz, 0.84H), 5.76 (dd, *J* = 6.9, 5.0 Hz, 1.84H), 4.60–4.53 (m, 1.84H), 4.03–

3.96 (m, 1.84H), 3.92–3.86 (m, 0.84H), 3.82–3.76 (m, 1H), 3.33–3.24 (m, 1.84H), 2.29–2.14 (m, 1.84H), 2.05–1.99 (m, 1H), 1.99–1.93 (m, 0.84H), 1.33 (d, *J* = 6.5 Hz, 2.46H), 1.30 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 157.9, 107.5, 106.5, 78.4, 78.1, 71.7, 70.9, 68.2, 66.9, 52.2, 52.0, 32.6, 31.8, 21.3, 19.1.

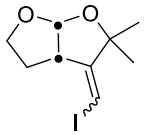


(**2R,3aS,6aR)-3-(Iodomethylene)-2-methylhexahydrofuro[2,3-b]furan (2s-2)**

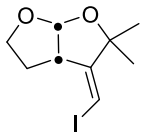
R_f = 0.49 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (t, *J* = 1.6 Hz 1H), 6.12 (t, *J* = 2.2 Hz, 0.67H), 5.95 (d, *J* = 5.6 Hz, 0.67H), 5.80 (d, *J* = 5.0 Hz, 1H), 4.78 (qt, *J* = 6.4, 2.0 Hz, 0.67H), 4.62 (qd, *J* = 6.4, 2.4 Hz, 1H), 3.99–3.90 (m, 2.67H), 3.79–3.72 (m, 0.67H), 3.41–3.33 (m, 1.67H), 2.26–2.18 (m, 1H), 2.16–2.08 (m, 0.67H), 1.95–1.87 (m, 1.67H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.34 (d, *J* = 6.5 Hz, 2.01H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 156.3, 109.6, 109.0, 82.4, 81.1, 70.1, 69.0, 66.9, 66.4, 50.6, 49.0, 33.5, 33.4, 20.0, 19.7.

HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_8H_{12}IO_2]^+$: 266.9876, found: 266.9869.

Colorless oil. **2s**, 59 mg, 57% (52/31/17) (Protocol B).

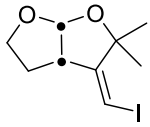


Colorless oil. **2t**, 86 mg, 77% (87/13) (Protocol A).



(3aS,6aR)-3-(Iodomethylene)-2,2-dimethylhexahydrofuro[2,3-*b*]furan (2t-1)

Major isomer: R_f = 0.44 (PE/EA = 5:1). 1H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, *J* = 2.4 Hz, 1H), 5.78 (d, *J* = 5.1 Hz, 1H), 3.96 (td, *J* = 8.6, 2.8 Hz, 1H), 3.92–3.86 (m, 1H), 3.37–3.31 (m, 1H), 2.31–2.20 (m, 1H), 2.01–1.95 (m, 1H), 1.37 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 106.3, 85.2, 71.1, 66.6, 52.2, 32.1, 29.9, 29.0.

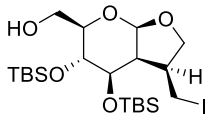


(3aS,6aR)-3-(Iodomethylene)-2,2-dimethylhexahydrofuro[2,3-b]furan (2t-2)

Minor isomer: R_f = 0.37 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (d, *J* = 2.2 Hz, 1H), 5.67 (d, *J* = 5.0 Hz, 1H), 3.93 (td, *J* = 8.3, 1.8 Hz, 1H), 3.87–3.81 (m,

1H), 3.46–3.42 (m, 1H), 2.24–2.14 (m, 1H), 1.92–1.87 (m, 1H), 1.59 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 106.5, 85.8, 67.9, 66.3, 52.4, 34.2, 26.2, 26.1.

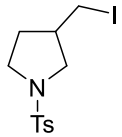
HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_9H_{14}IO_2]^+$: 281.0033, found: 281.0030.



((4*R*,5*R*,6*R*)-4,5-Bis((*tert*-butyldimethylsilyl)oxy)-3-(iodomethyl)hexahydro-4*H*-furo[2,3-b]pyran-6-yl)methanol (2w)

Colorless oil. 62 mg, 32%, R_f = 0.42 (PE/EA = 5:1) (Protocol A).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (d, *J* = 6.8 Hz, 1H), 4.04 (t *J* = 8.0 Hz, 1H), 3.97 (t, *J* = 2.0 Hz, 1H), 3.90 (dd, *J* = 10.4, 8.1 Hz, 1H), 3.80–3.72 (m, 3H), 3.68–3.62 (m, 1H), 3.34 (d, *J* = 8.1 Hz, 2H), 2.92–2.81 (m, 1H), 2.53–2.48 (m, 1H), 2.20 (t, *J* = 6.0 Hz, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.15 (s, 3H), 0.15 (s, 3H), 0.12 (s, 9H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 100.9, 75.3, 73.7, 69.2, 69.1, 63.7, 45.3, 44.4, 25.9, 25.7, 18.0, 17.8, 2.0, -0.1, -4.3, -4.4, -4.9. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{21}H_{44}IO_5Si_2]^+$: 559.1766, found: 559.1762.

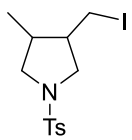


3-(Iodomethyl)-1-tosylpyrrolidine (2x)[13]

White solid. 31 mg, 22% (Protocol A).

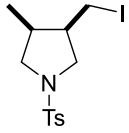
R_f = 0.21 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.45 (dd, *J* = 10.3, 7.3 Hz, 1H), 3.41–3.35 (m, 1H), 3.26–3.20 (m, 1H), 3.06–2.93 (m, 3H), 2.43 (s, 3H), 2.42–2.35 (m, 1H), 2.05–1.97 (m, 1H), 1.58–1.49 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 133.4, 129.7, 127.5, 53.6, 47.4, 41.2, 32.1, 21.5, 7.1.

White solid. 41 mg, 31% (Protocol B).

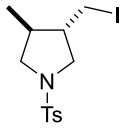


3-(Iodomethyl)-4-methyl-1-tosylpyrrolidine (2y)[14]

Colorless oil. 126 mg, 84% (78/22), R_f = 0.30 (PE/EA = 5:1) (Protocol A).

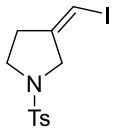


Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 3.49 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.38 (dd, *J* = 9.9, 6.4 Hz, 1H), 3.11–3.06 (m, 2H), 3.04–2.98 (m, 1H), 2.86–2.81 (m, 1H), 2.49–2.39 (m, 1H), 2.43 (s, 3H), 2.33–2.25 (m, 1H), 0.77 (*d*, *J* = 7.1 Hz, 3H).

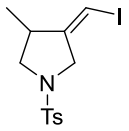


Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 3.58–3.52 (m, 2H), 3.18 (dd, *J* = 10.2, 4.0 Hz, 1H), 3.04–2.98 (m, 1H), 2.94–2.89 (m, 1H), 2.86–2.81 (m, 1H), 2.43 (s, 3H), 1.86–1.74 (m, 2H), 0.93 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.7, 133.5, 129.7, 127.5, 127.4, 55.0, 54.4, 54.3, 51.8, 47.6, 45.2, 39.2, 36.1, 21.5, 16.2, 12.4, 6.2, 2.7.

Colorless oil. 122 mg, 81% (72/28) (Protocol B).



(*Z*)-3-(Iodomethylene)-1-tosylpyrrolidine (2z)[15]
White solid. 61 mg, 42% (Protocol A).
R_f = 0.32 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.00 (quintet, *J* = 2.3 Hz, 1H), 3.72 (s, 2H), 3.40 (t, *J* = 7.0 Hz, 2H), 2.54–2.49 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 143.9, 132.4, 129.8, 127.9, 70.1, 56.5, 49.0, 33.3, 21.5.



(*Z*)-3-(Iodomethylene)-4-methyl-1-tosylpyrrolidine (2aa)
Colorless oil, 86 mg, 58% (Protocol A).
R_f = 0.32 (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.95 (q, *J* = 2.5 Hz, 1H), 3.87 (dd, *J* = 15.2, 2.4 Hz, 1H), 3.70–3.61 (m, 2H), 2.81–2.69 (m, 2H), 2.44 (s, 3H), 1.06 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 143.9, 132.4, 129.8, 127.9, 70.3, 56.9, 55.9, 39.8, 21.6,

16.2. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $[C_{13}H_{17}INO_2S]^+$: 378.0019, found: 378.0020.

Colorless oil. 25 mg, 17% (Protocol B).

7. References

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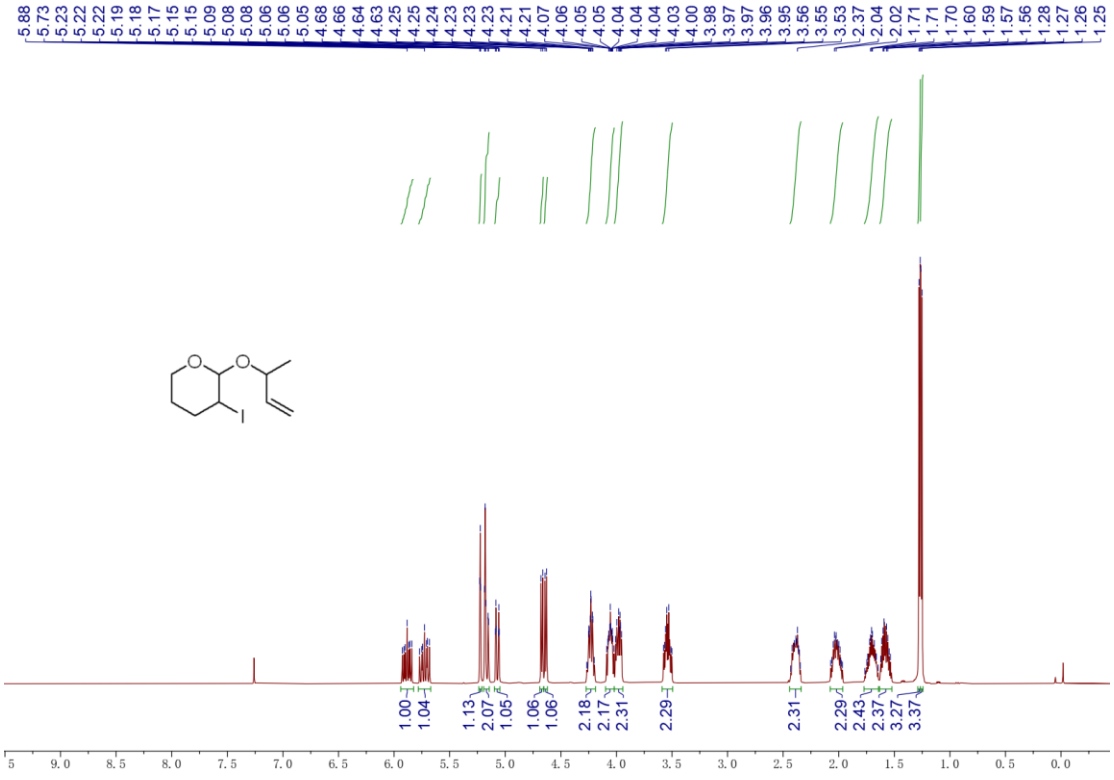
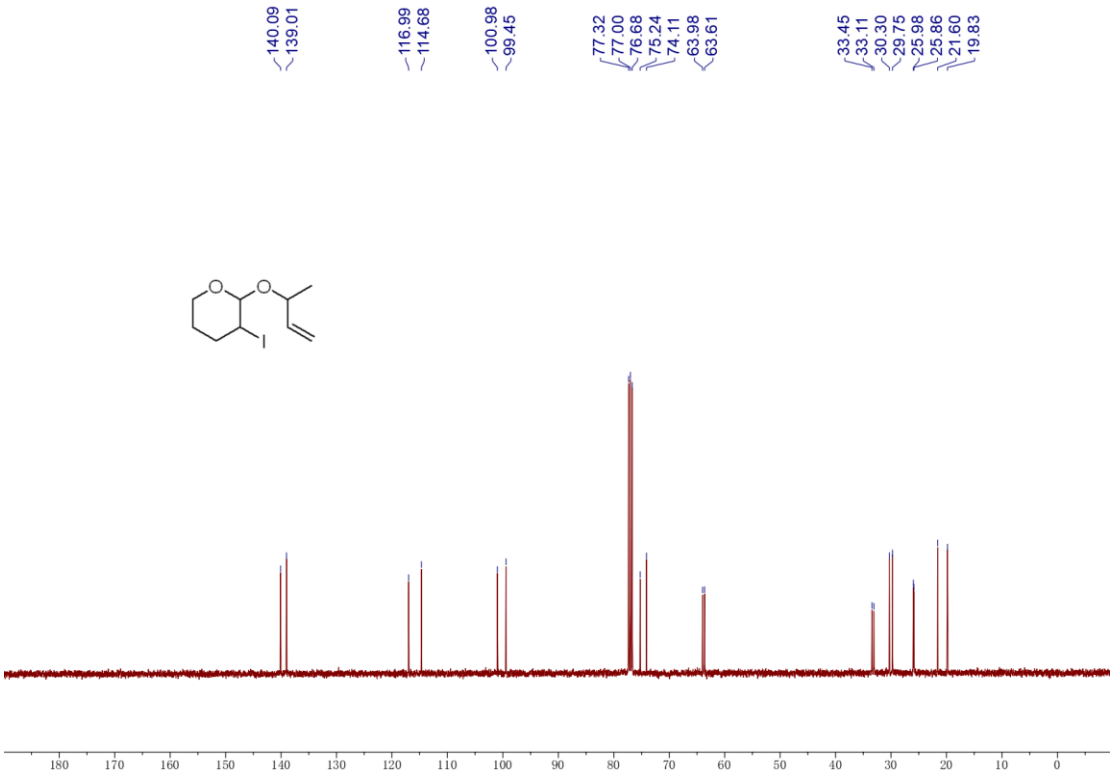
8. Copies of ^{1}H NMR and ^{13}C NMR spectra

1b

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

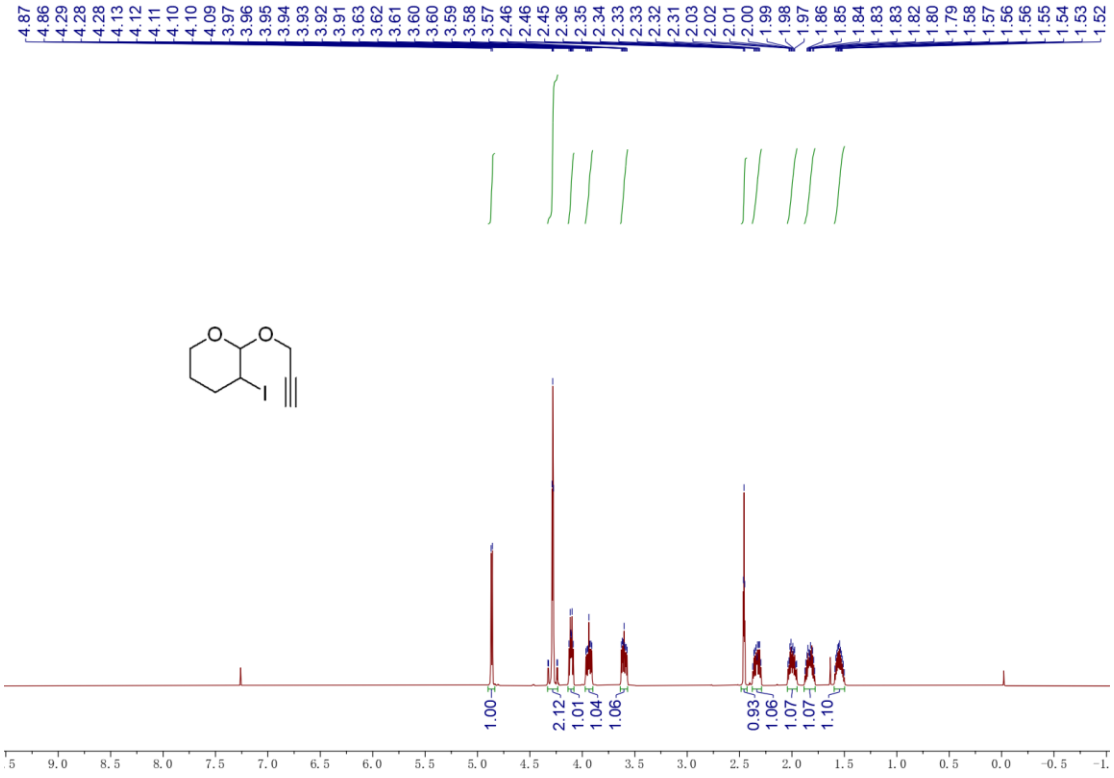


^{13}C NMR ($CDCl_3$, 101 MHz)

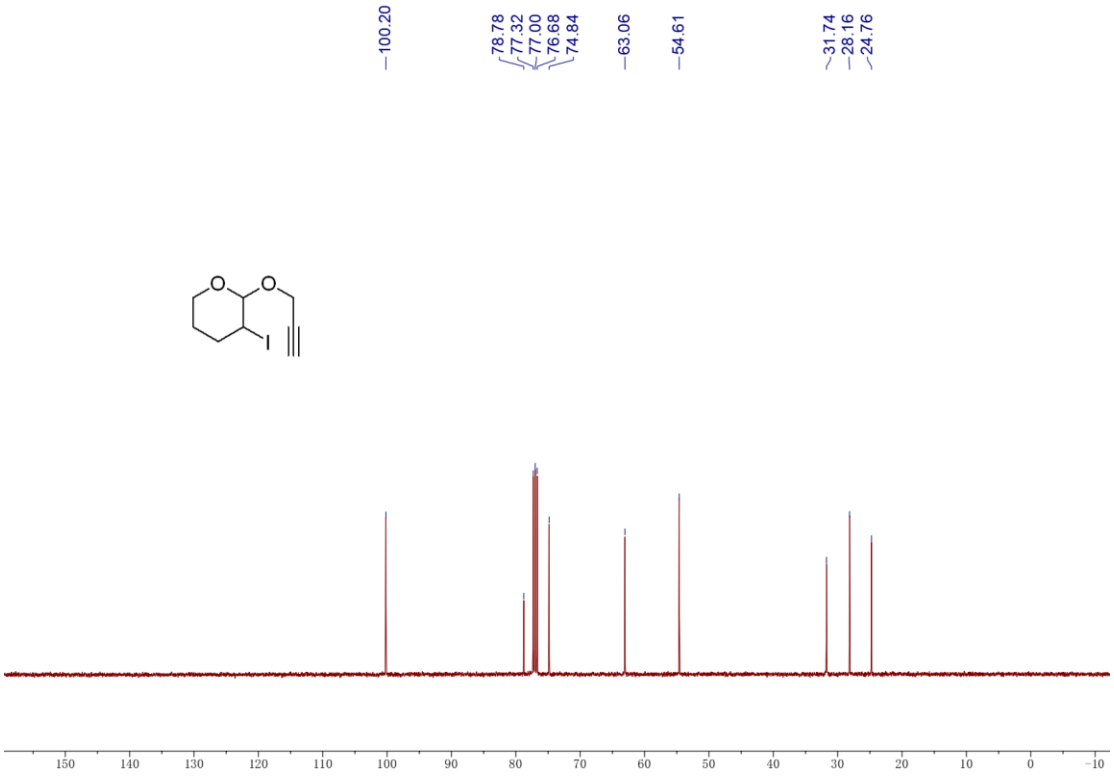


1f

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

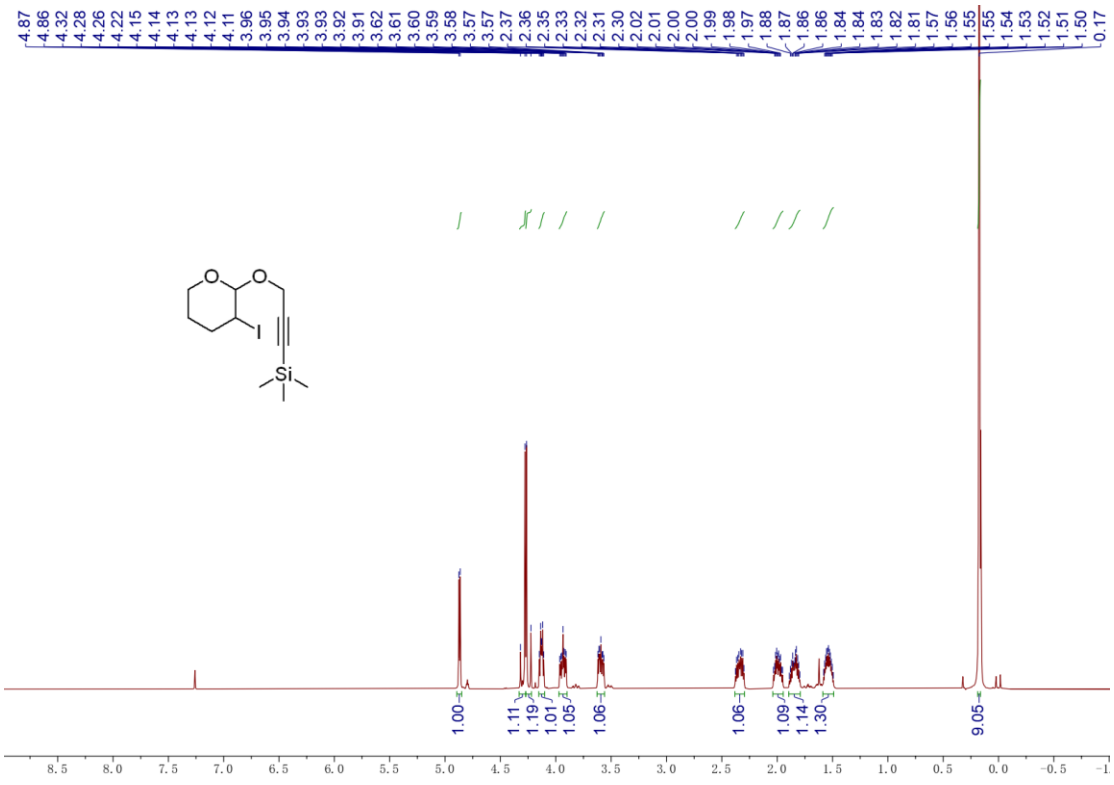


^{13}C NMR ($CDCl_3$, 101 MHz)

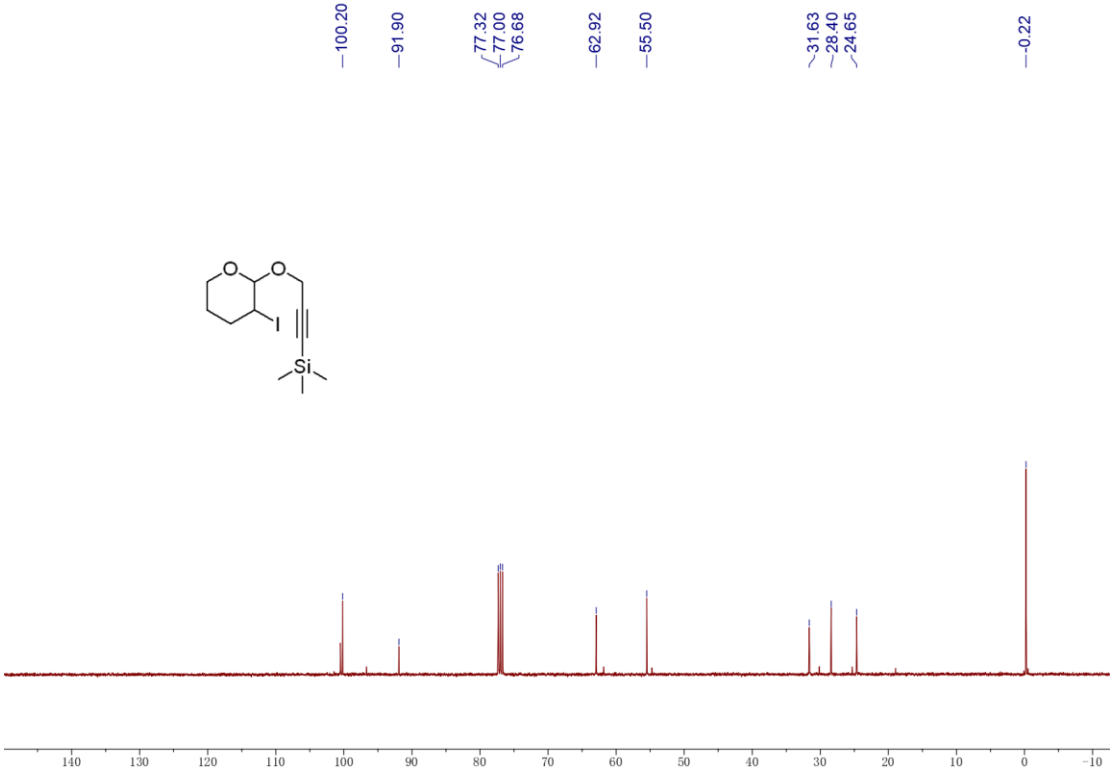


1i

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

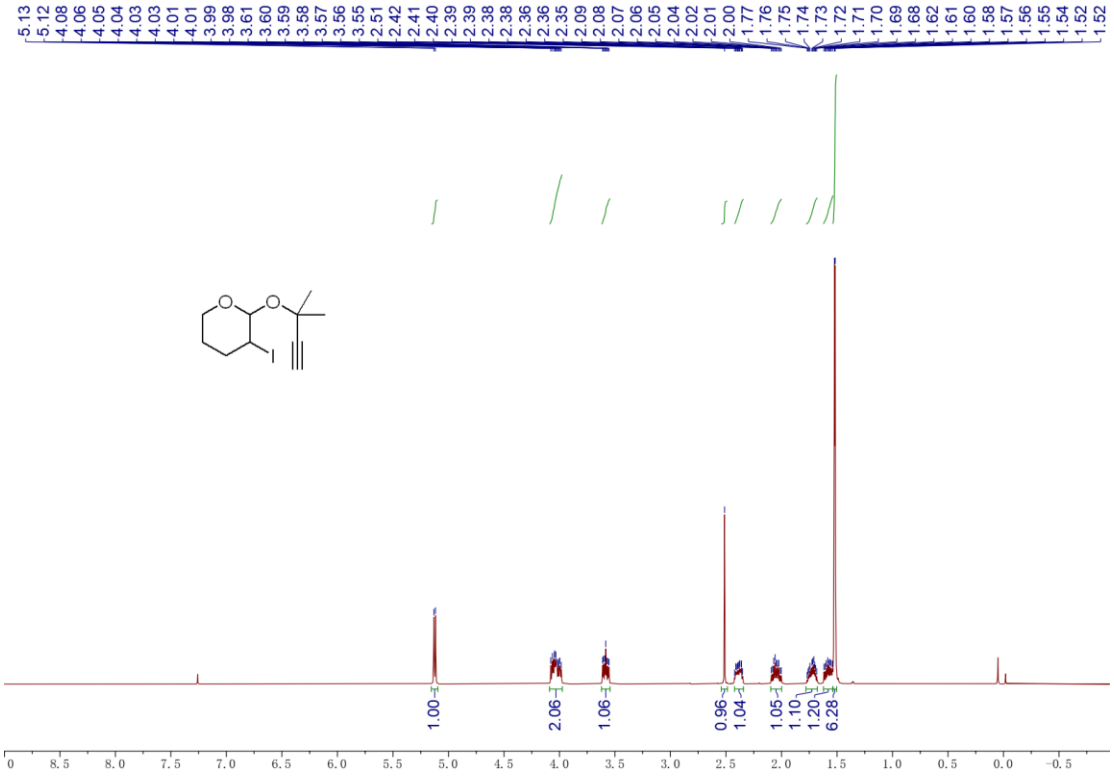


^{13}C NMR ($CDCl_3$, 101 MHz)

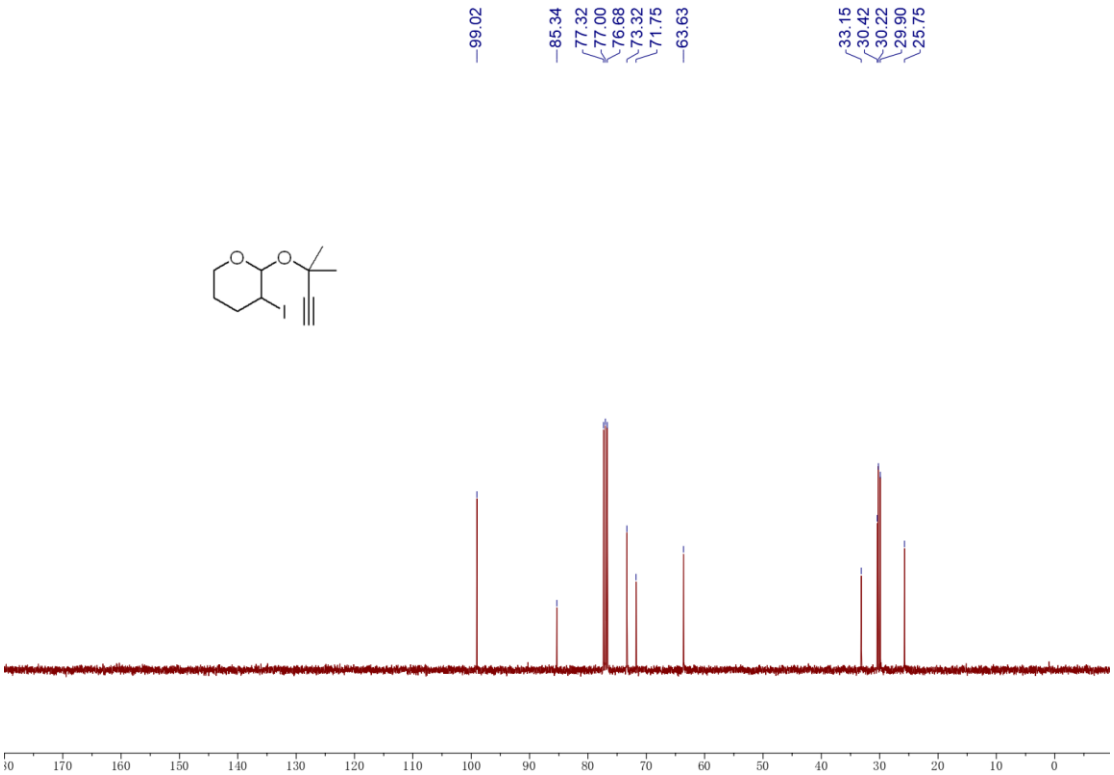


1k

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

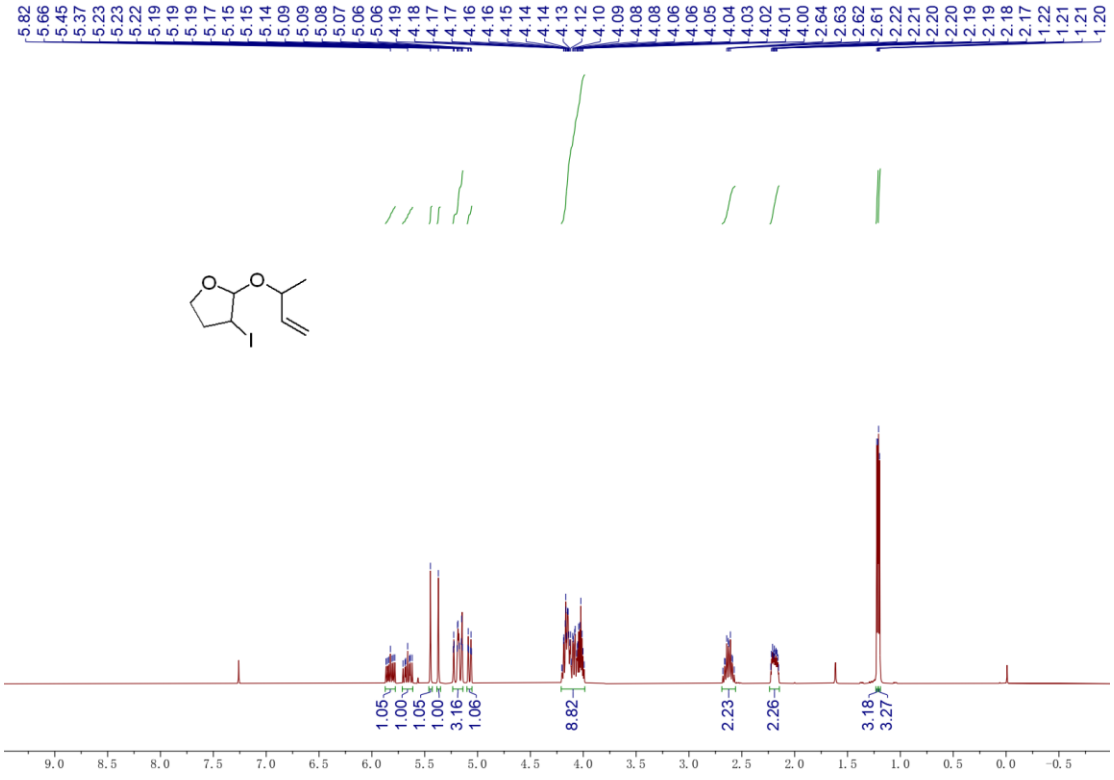


^{13}C NMR ($CDCl_3$, 101 MHz)

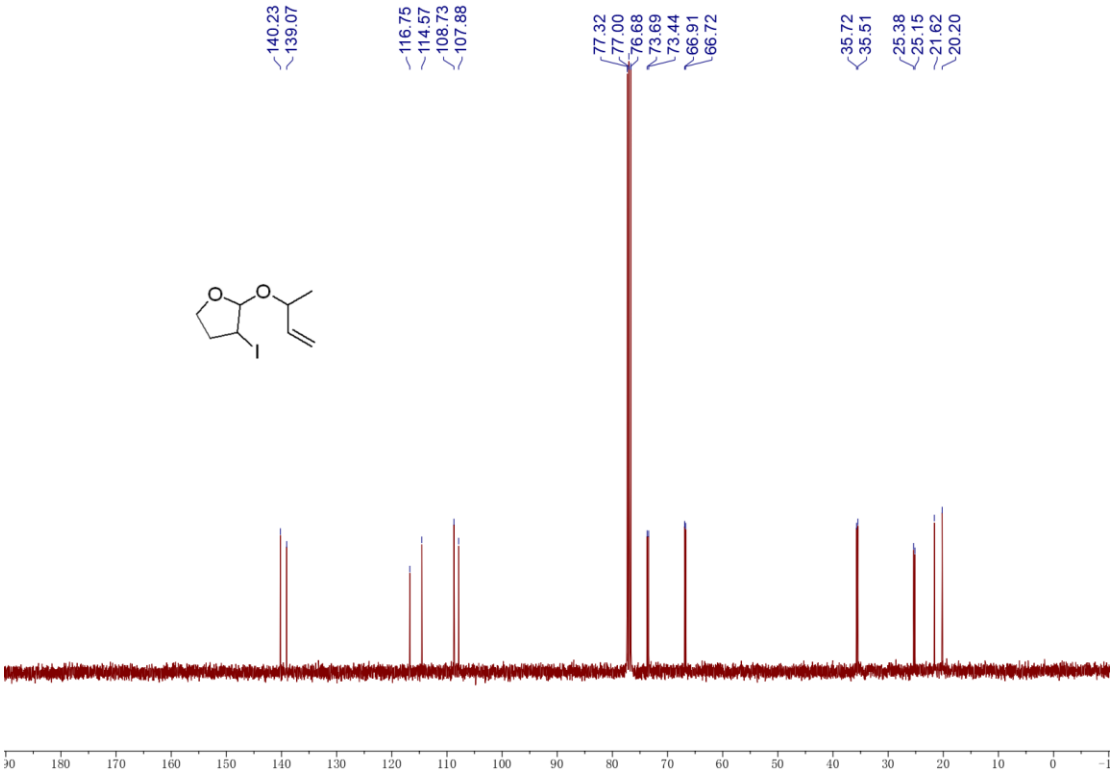


1m

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

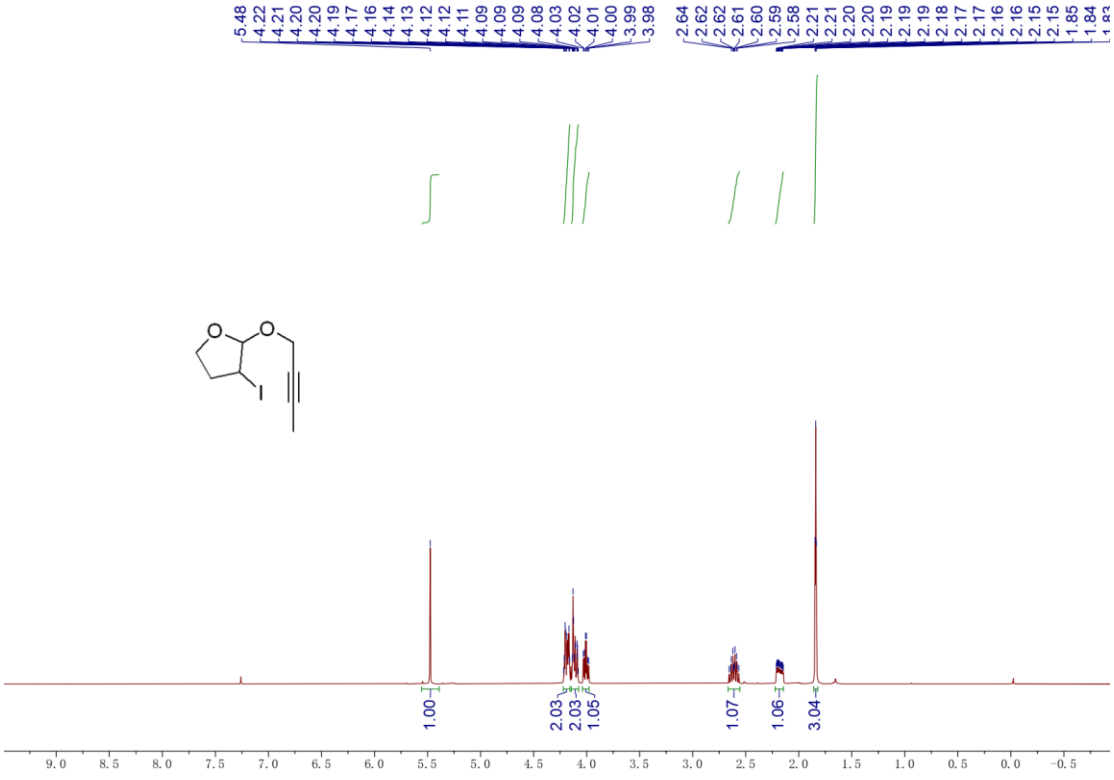


^{13}C NMR ($CDCl_3$, 101 MHz)

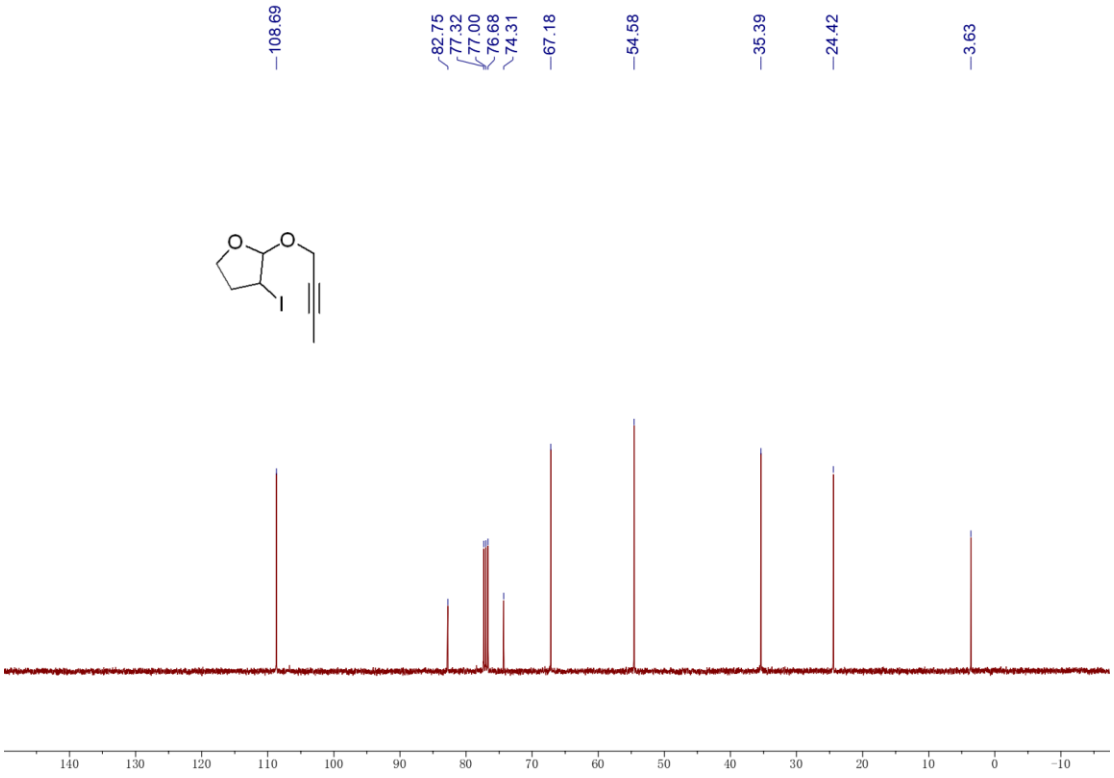


1p

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

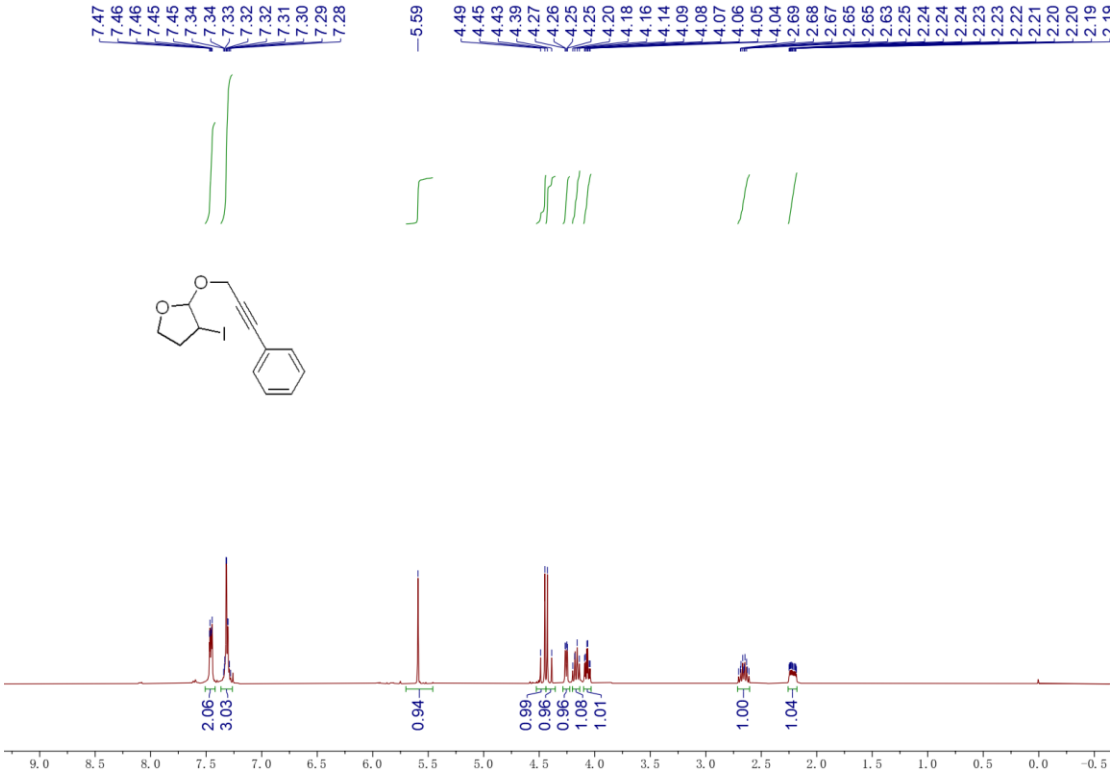


^{13}C NMR ($CDCl_3$, 101 MHz)

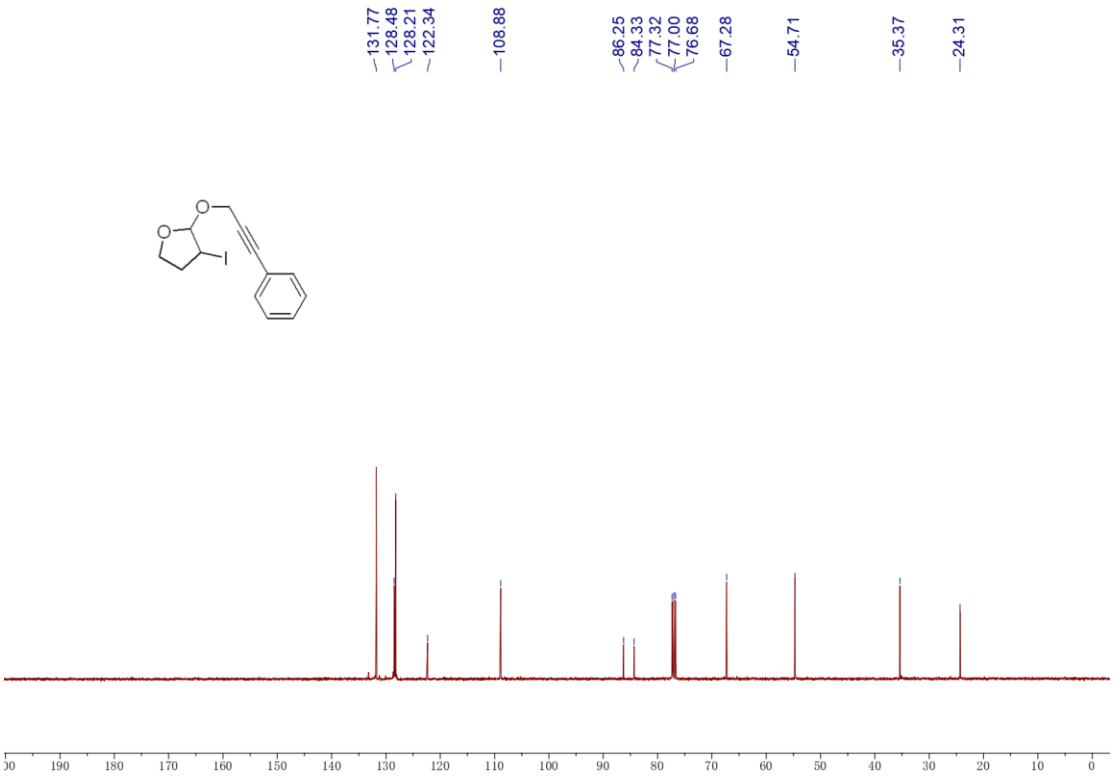


1q

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

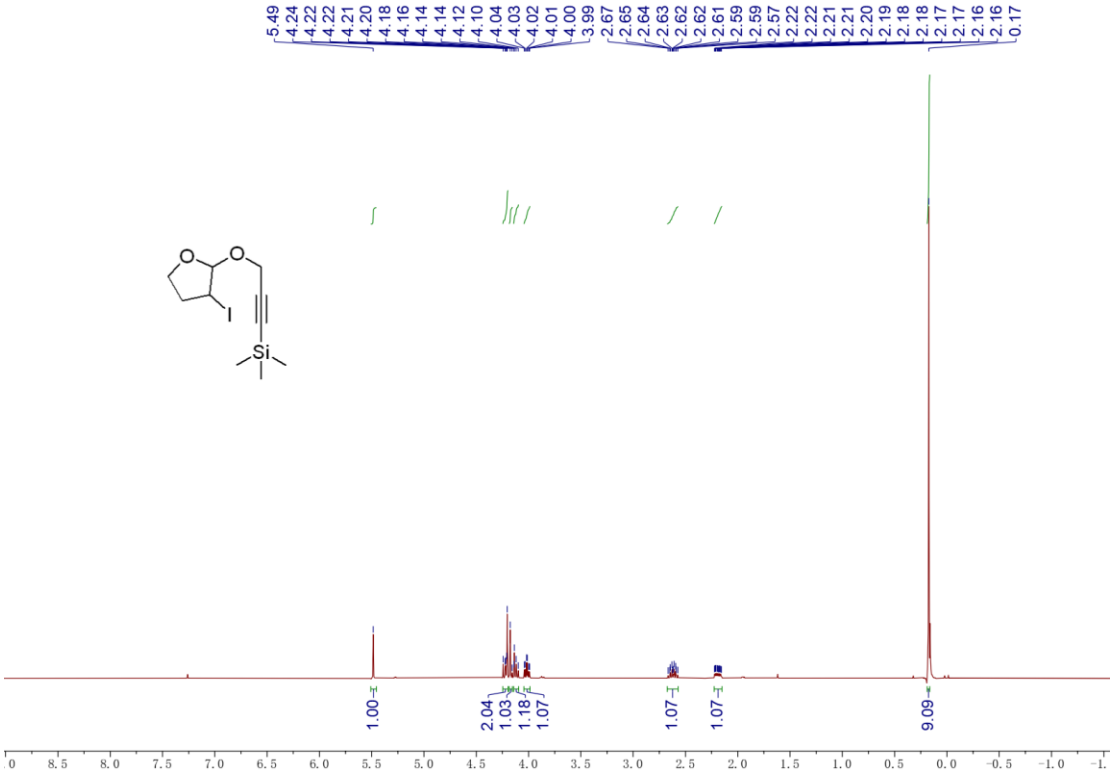


^{13}C NMR ($CDCl_3$, 101 MHz)

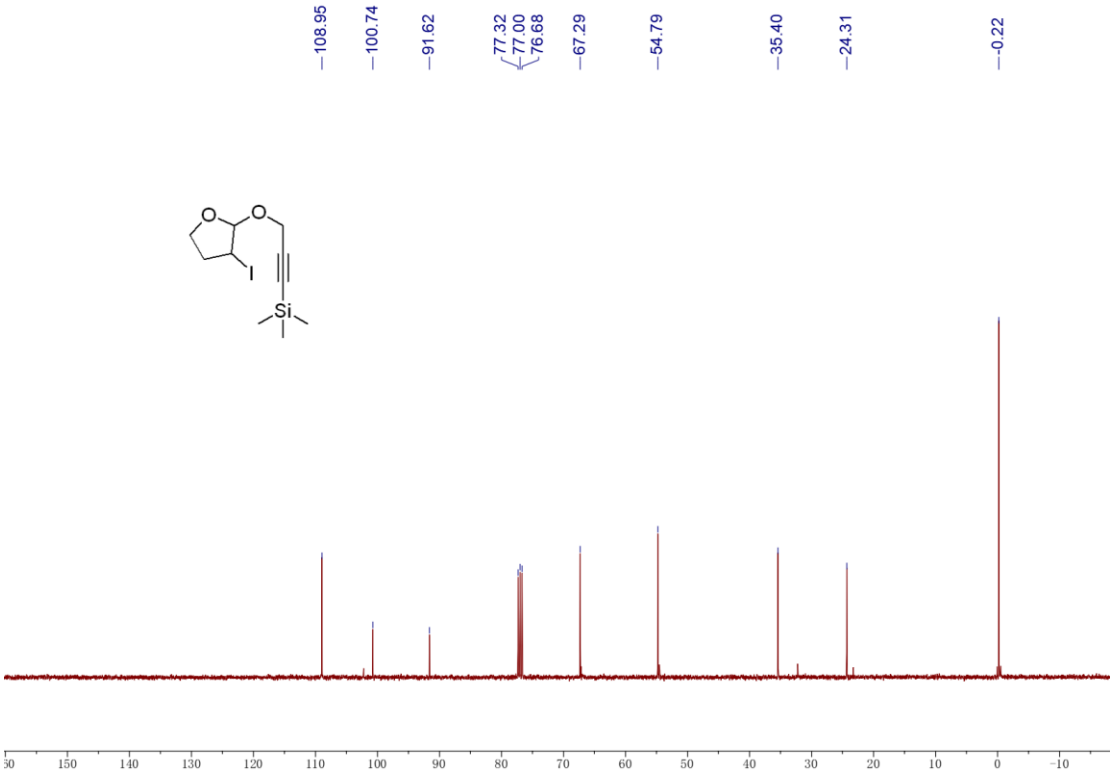


1r

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

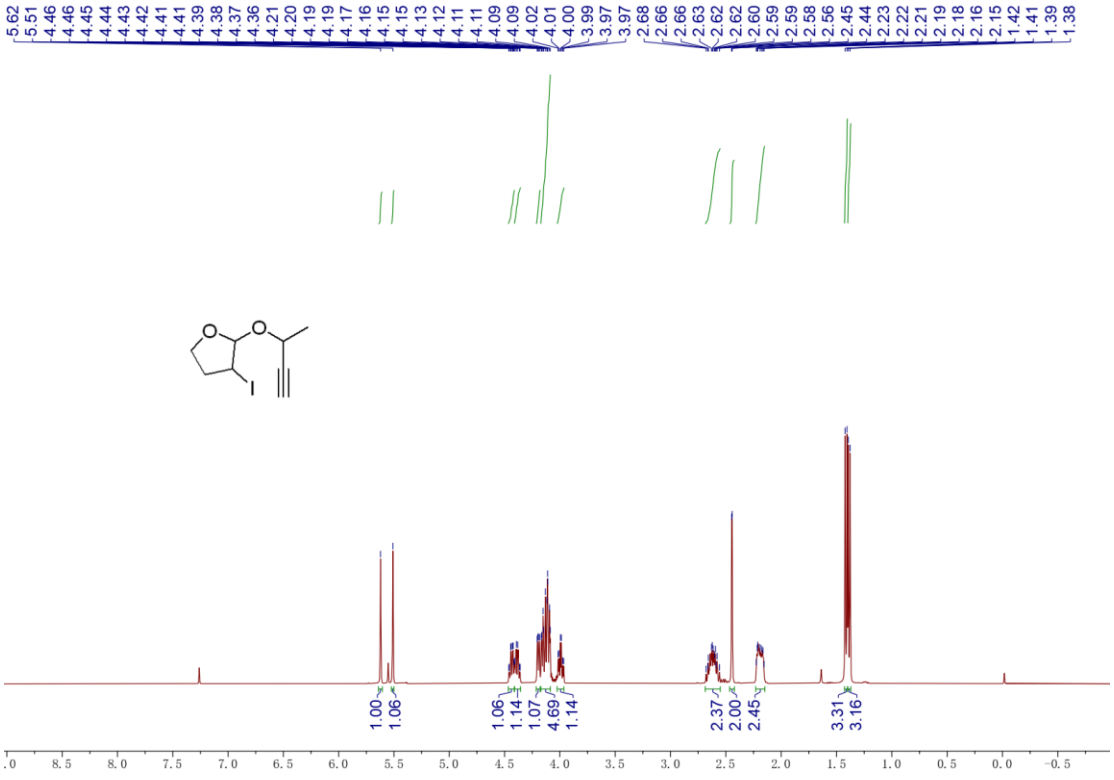


^{13}C NMR ($CDCl_3$, 101 MHz)

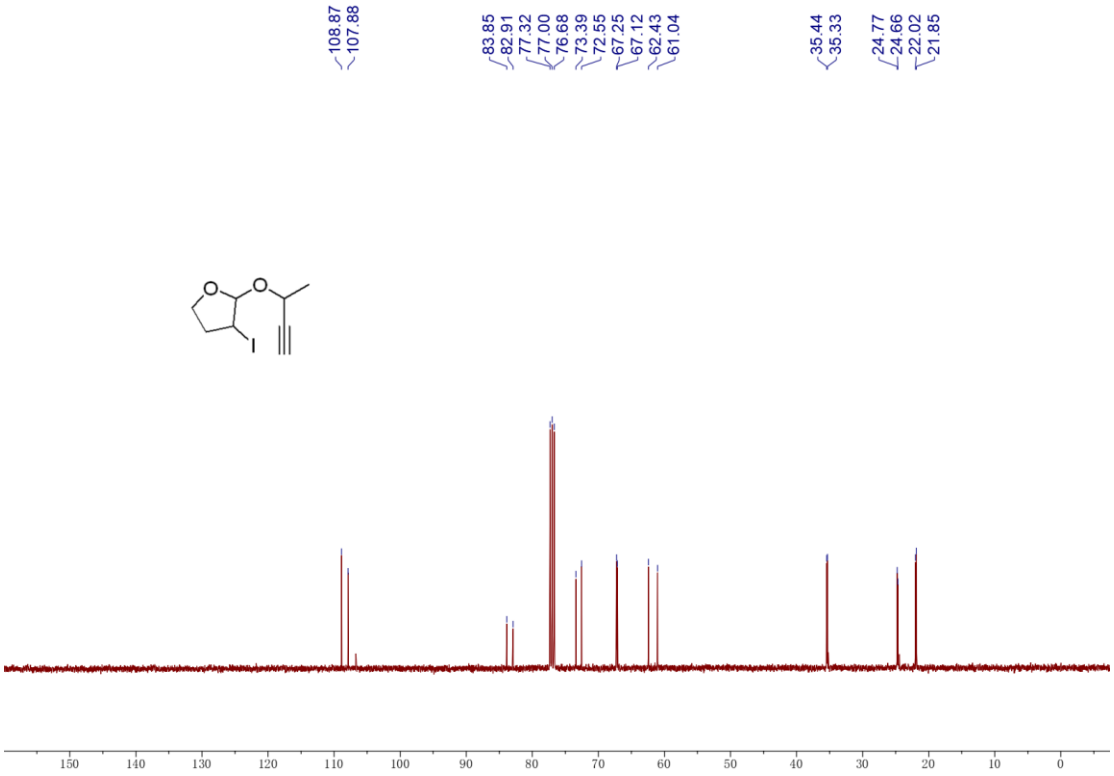


1s

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

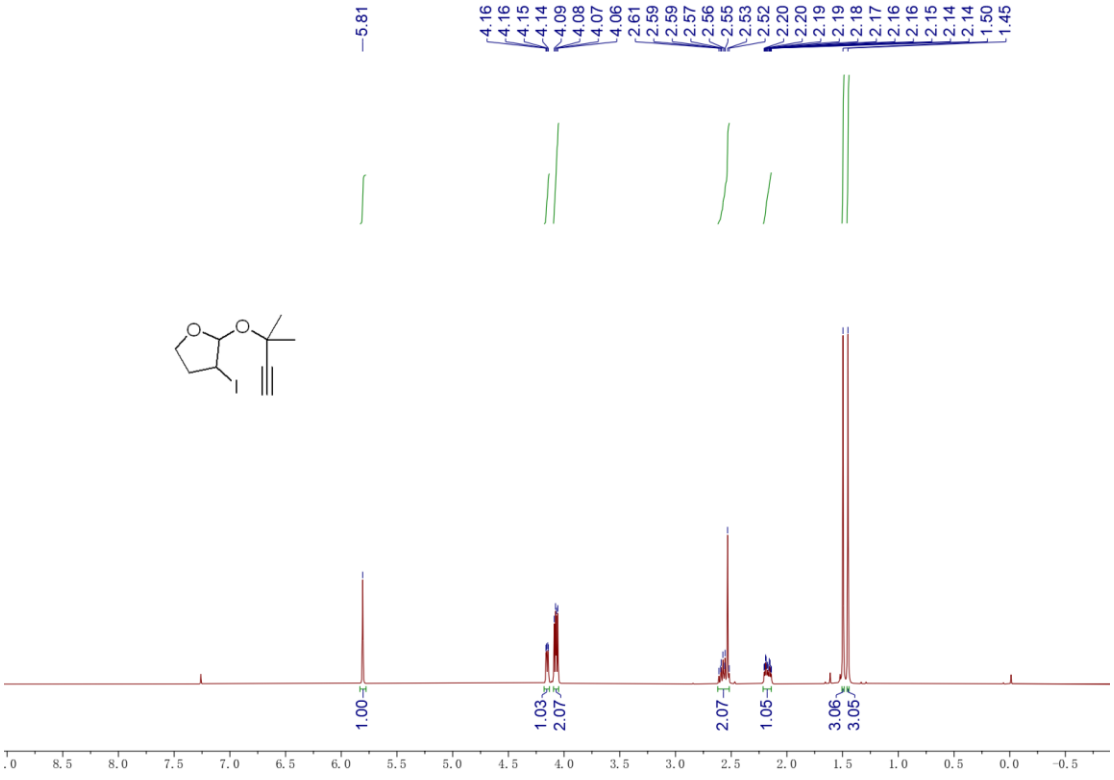


^{13}C NMR ($CDCl_3$, 101 MHz)

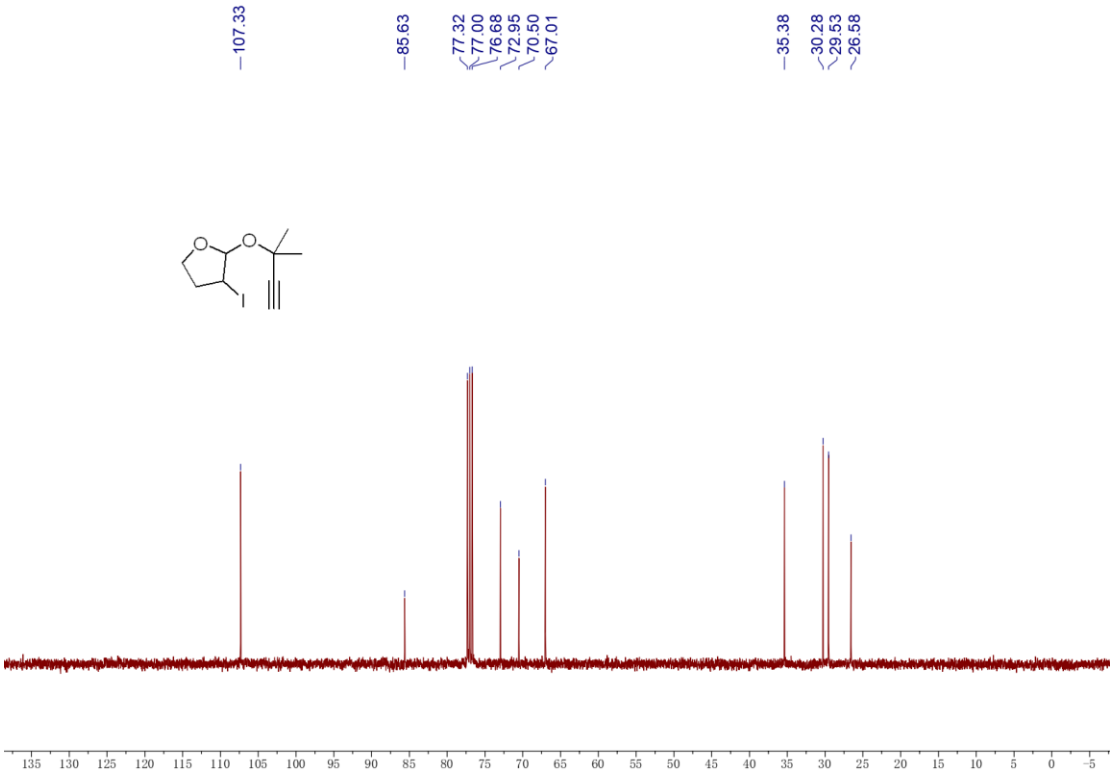


1t

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

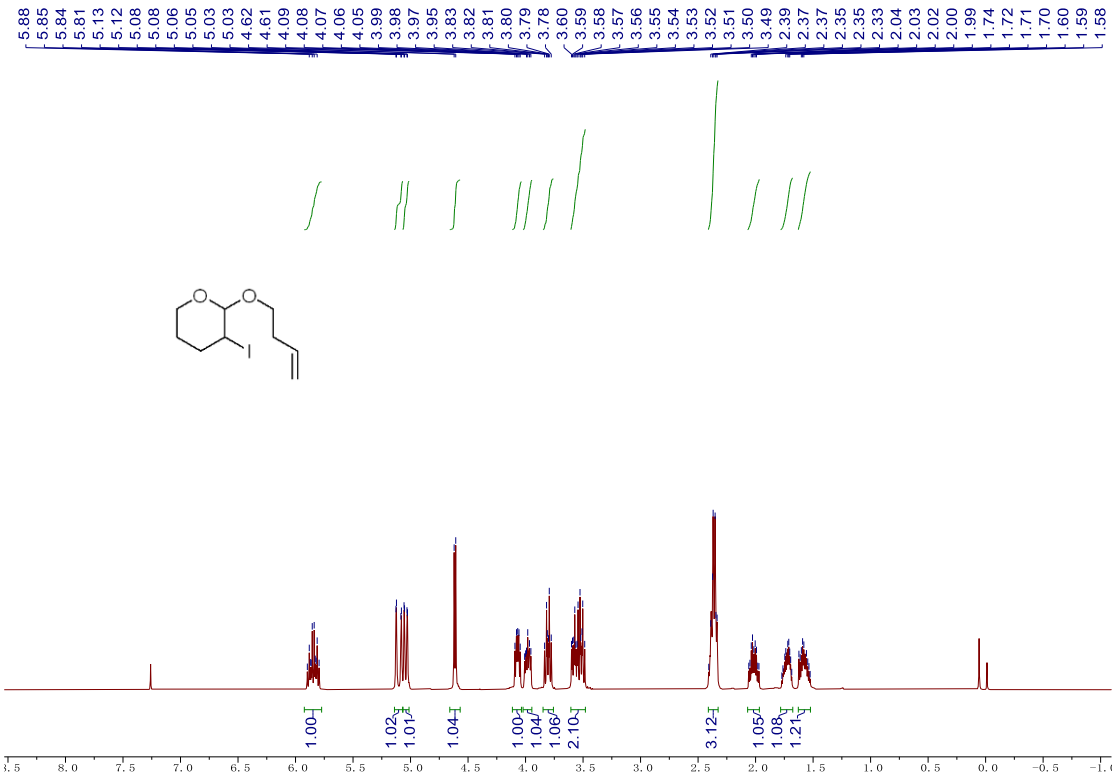


^{13}C NMR ($CDCl_3$, 101 MHz)

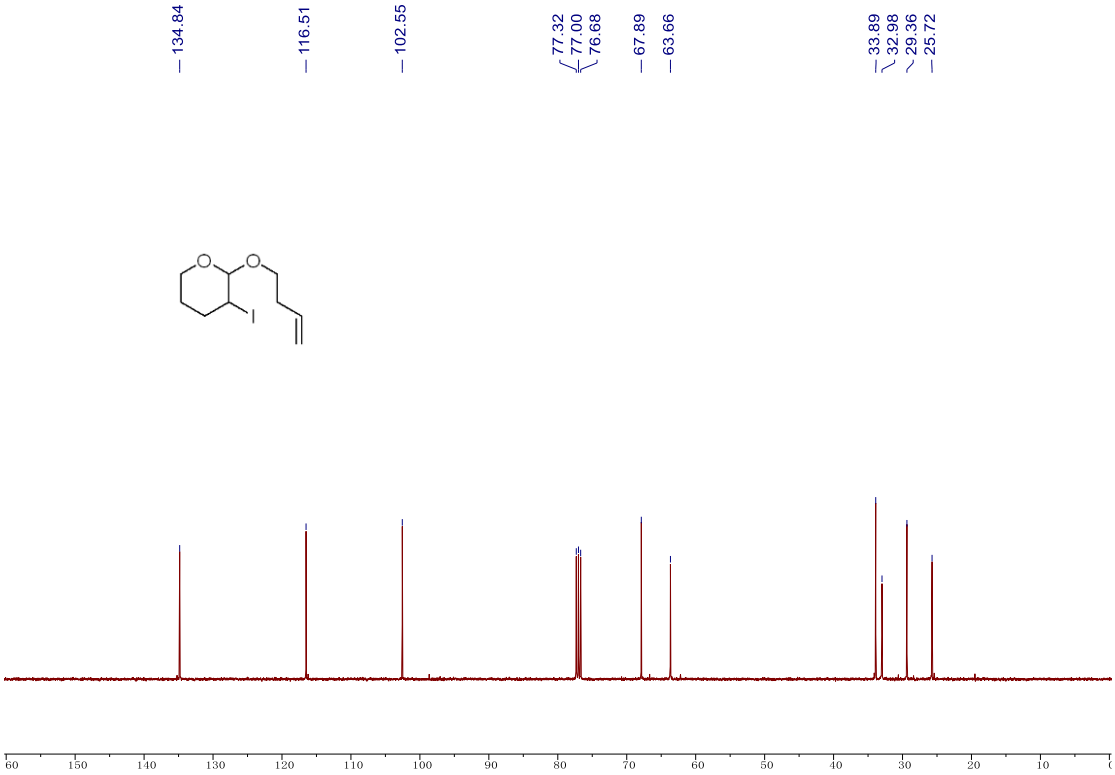


1u

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

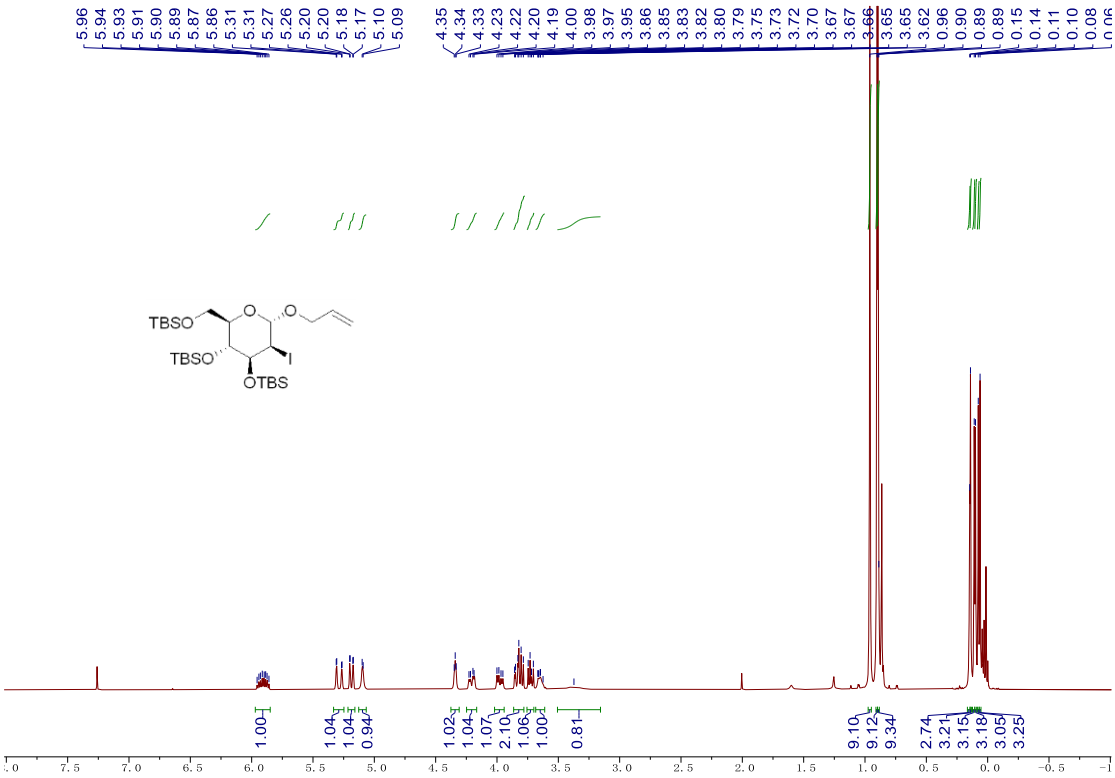


^{13}C NMR ($CDCl_3$, 101 MHz)

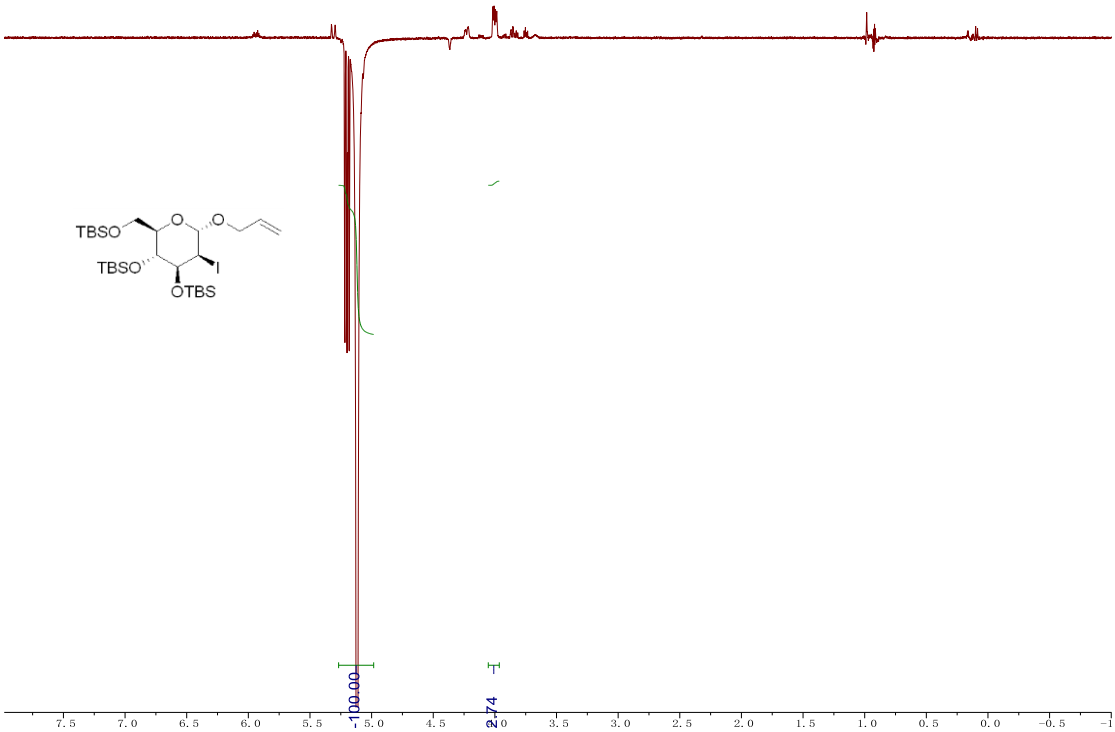


1v

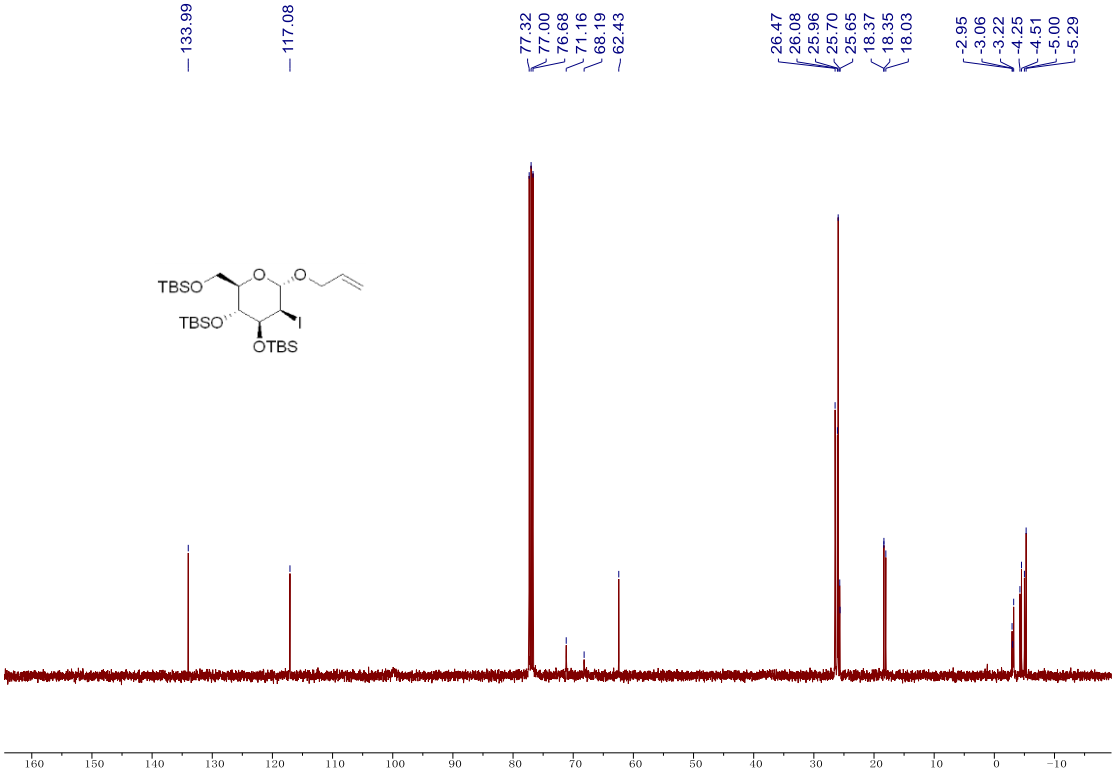
^{1}H NMR ($CDCl_3$, 400 MHz)



NOE Experiment ($CDCl_3$, 600 MHz)

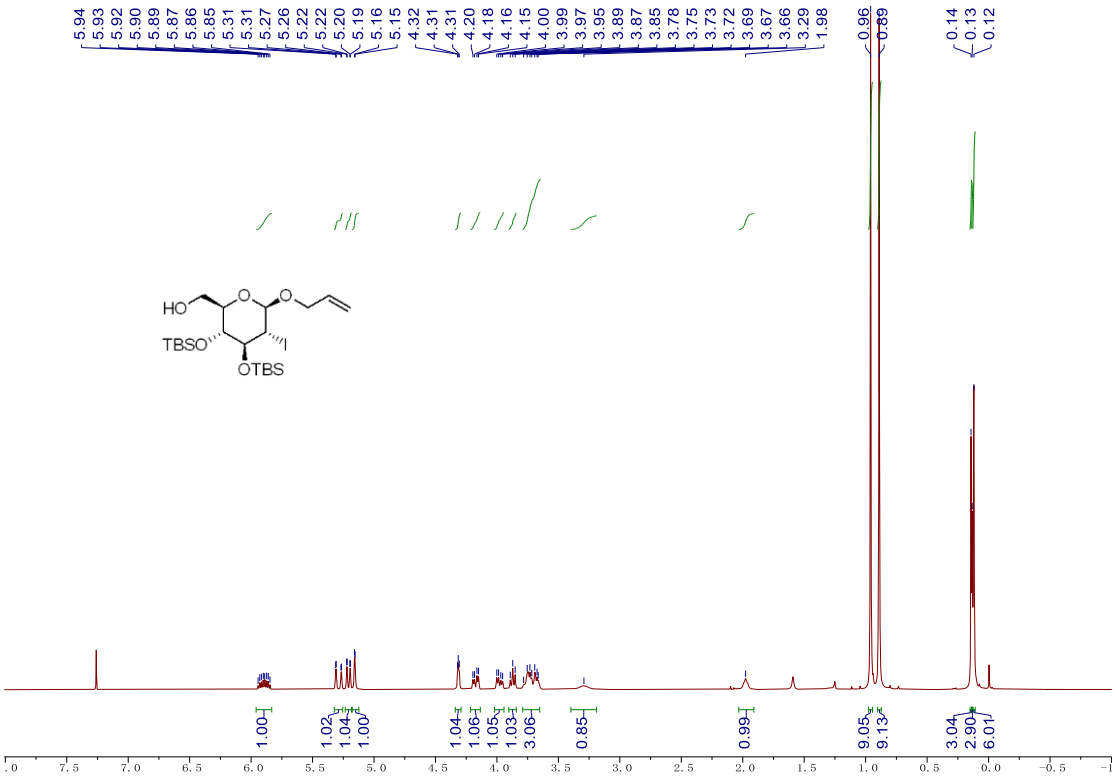


^{13}C NMR ($CDCl_3$, 101 MHz)

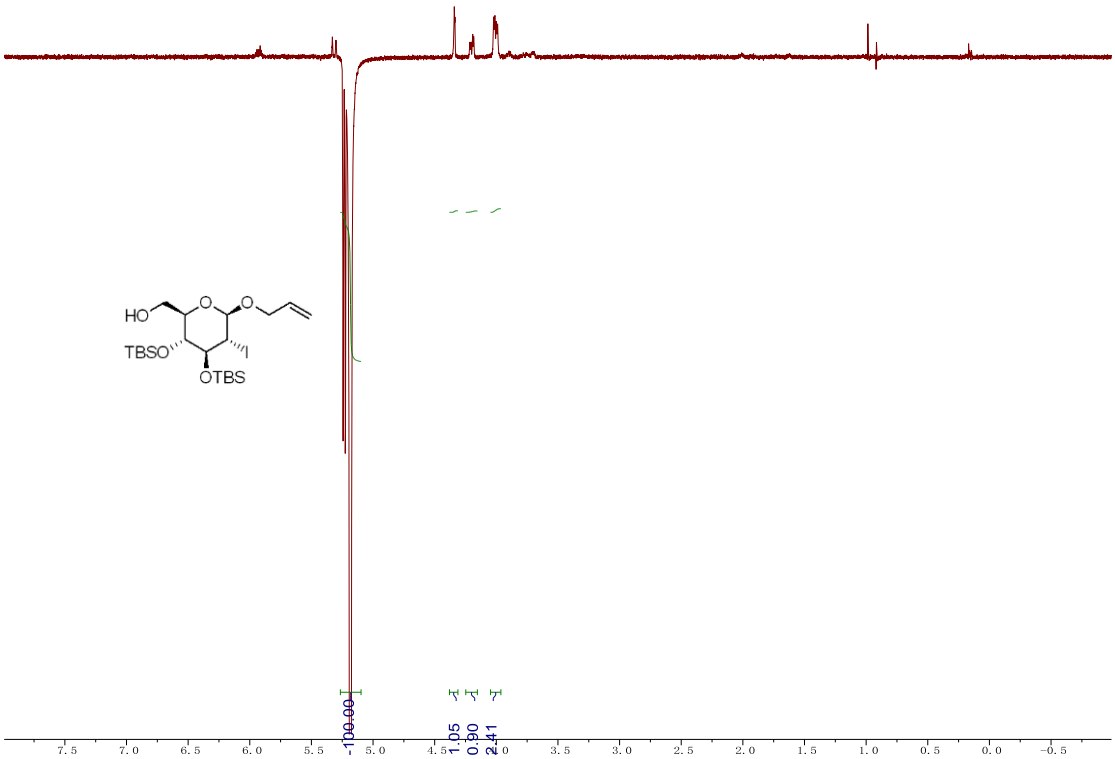


1w

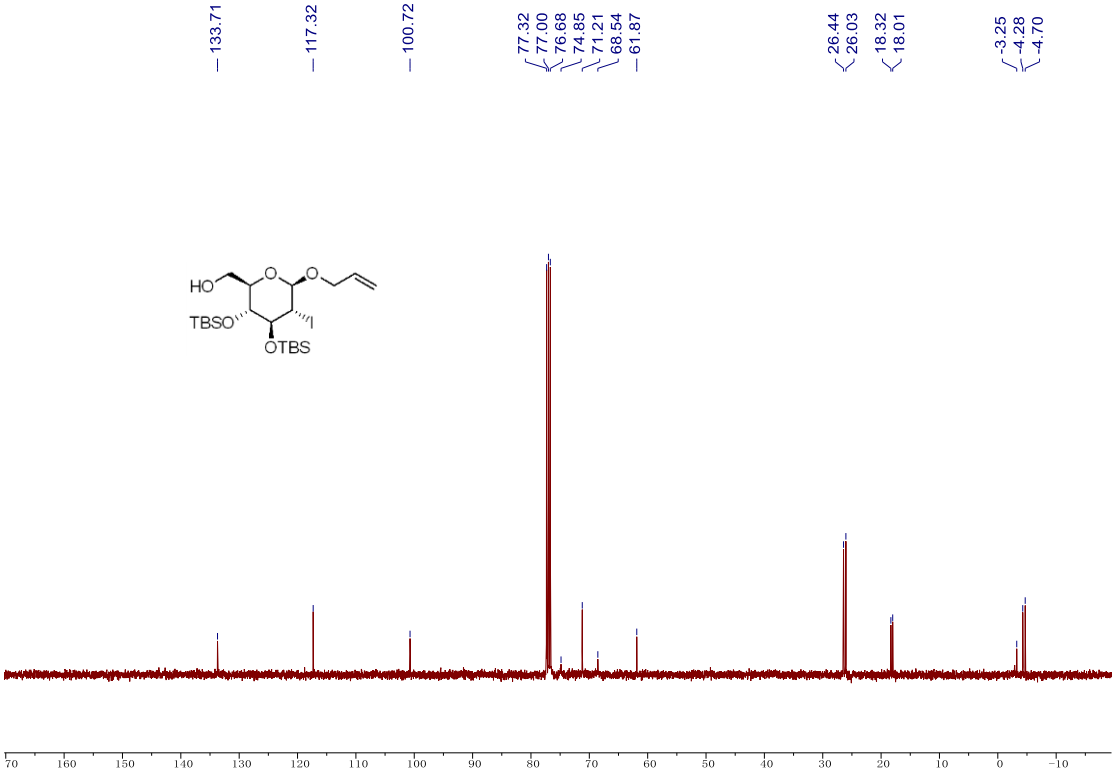
^{1}H NMR ($CDCl_3$, 400 MHz)



NOE Experiment ($CDCl_3$, 600 MHz)

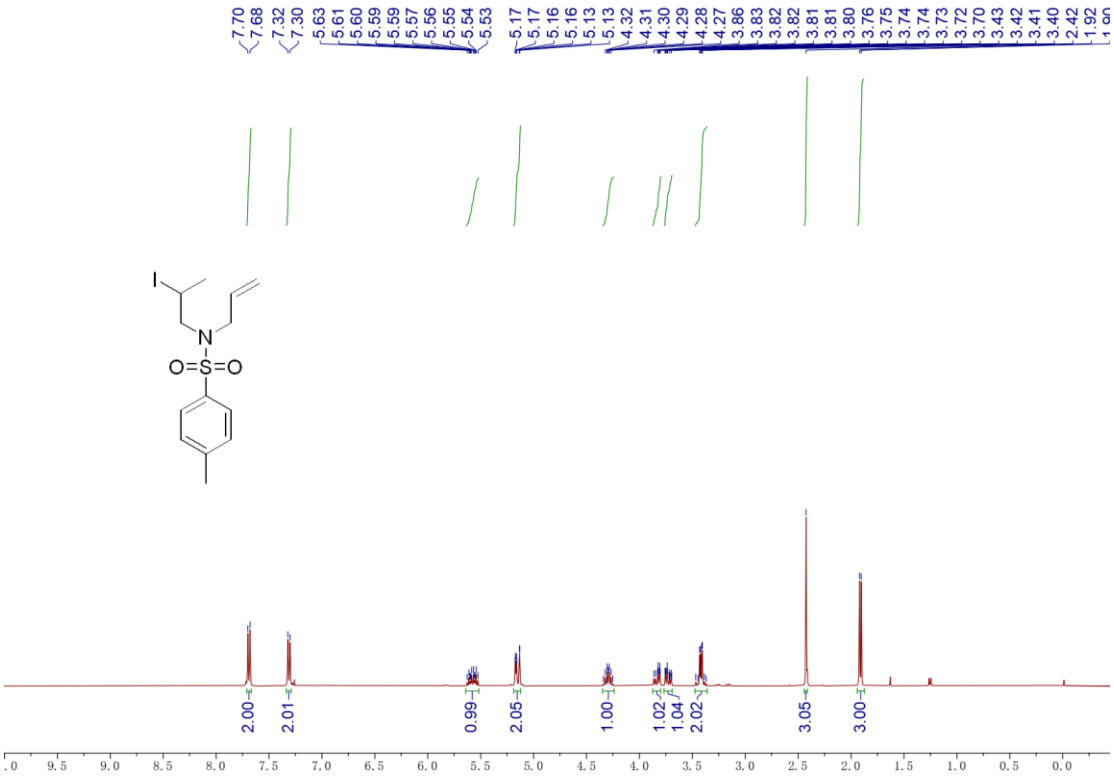


^{13}C NMR ($CDCl_3$, 101 MHz)

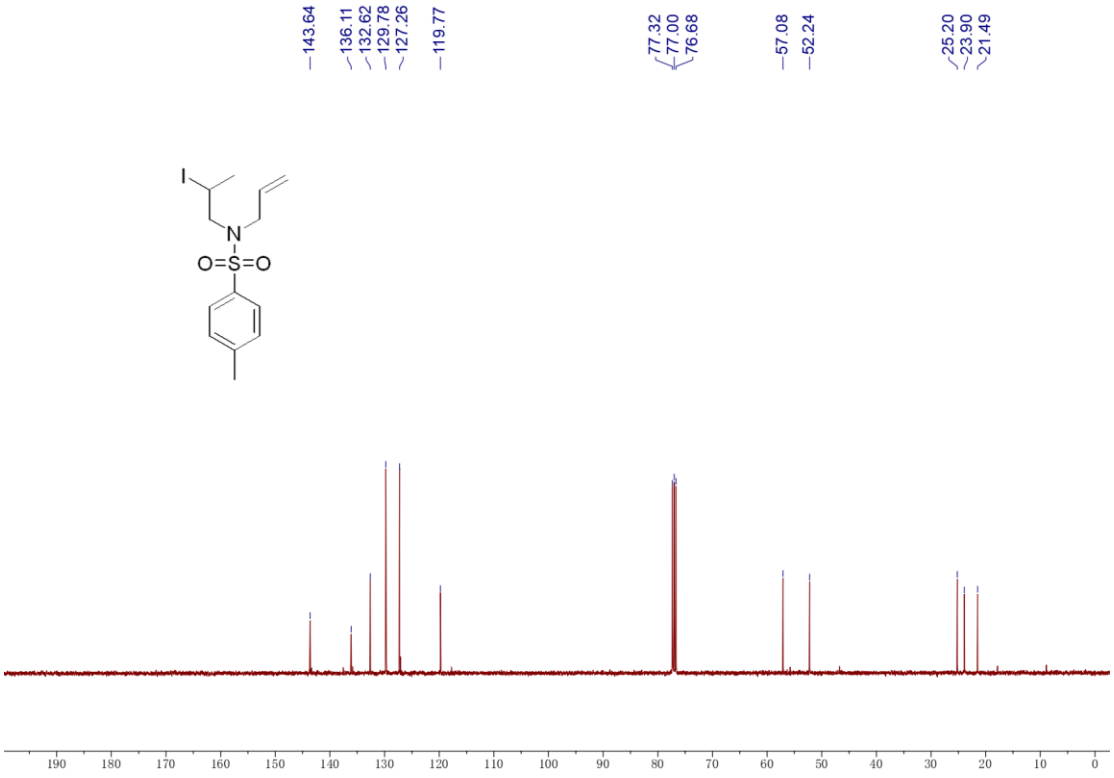


1y

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

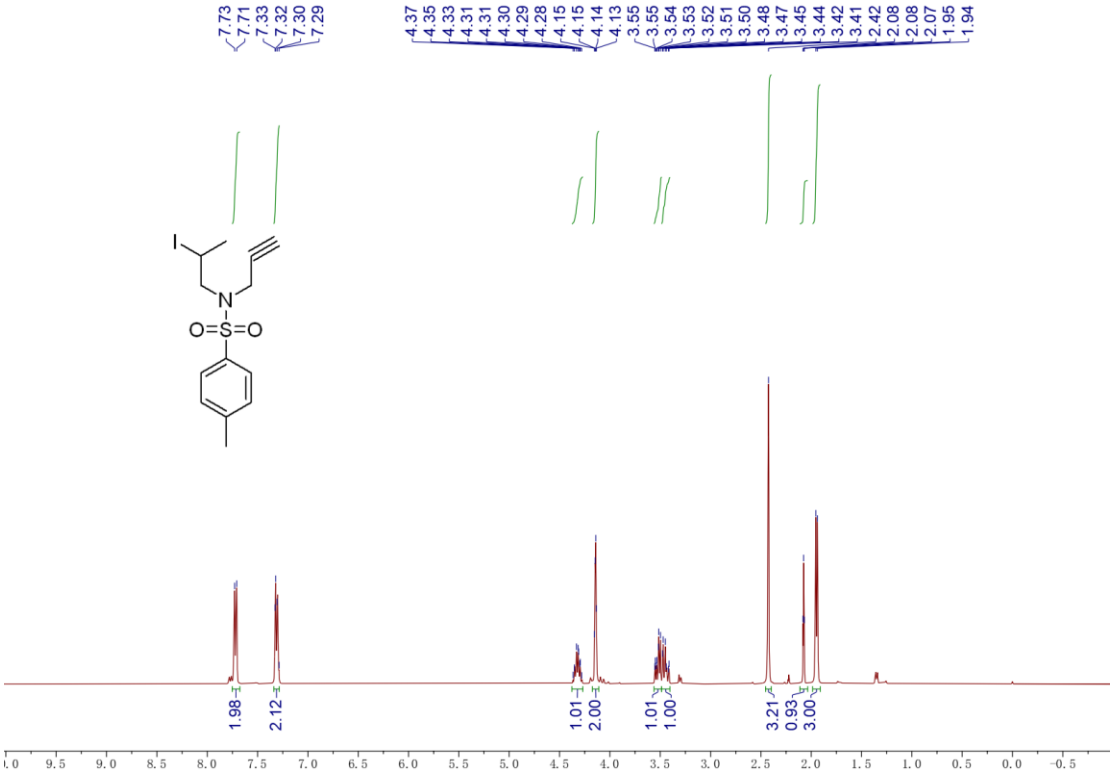


^{13}C NMR ($CDCl_3$, 101 MHz)

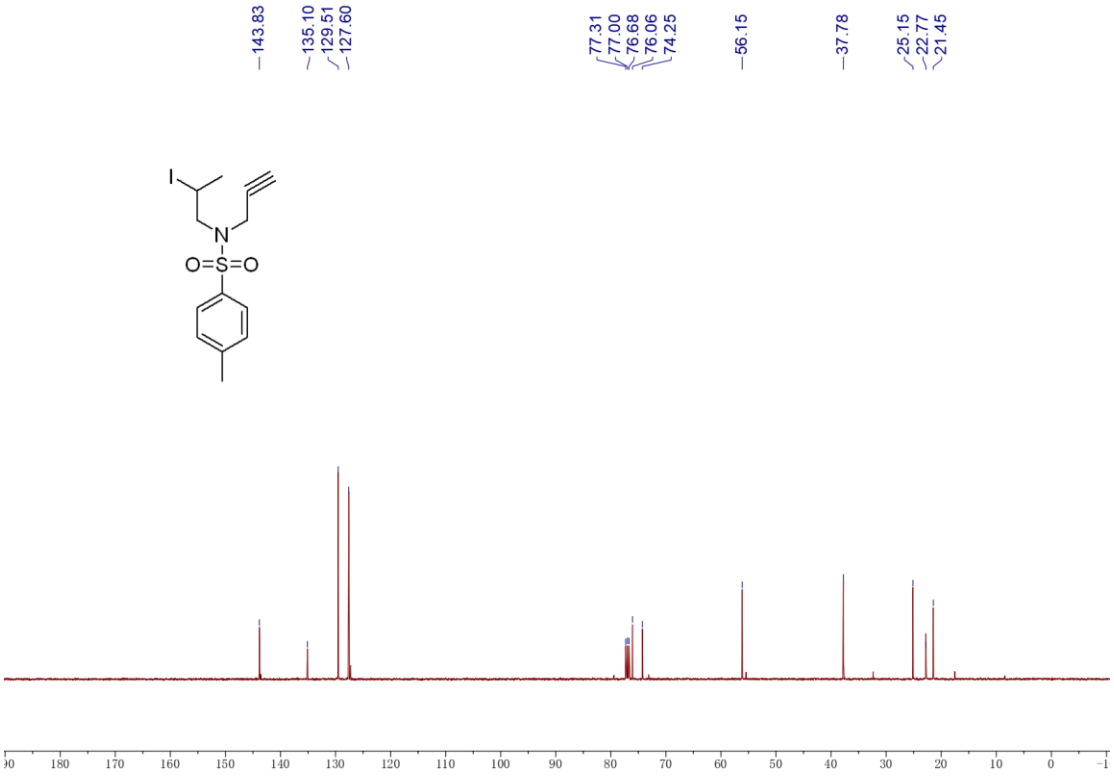


1aa

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



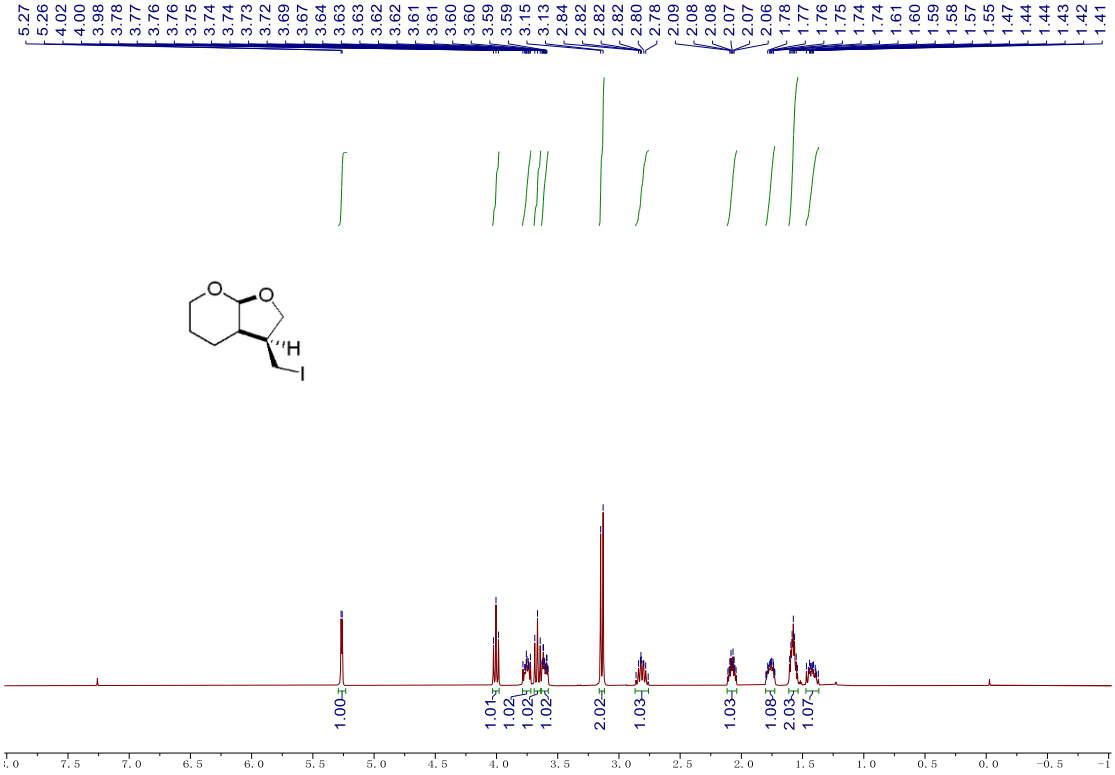
^{13}C NMR ($CDCl_3$, 101 MHz)



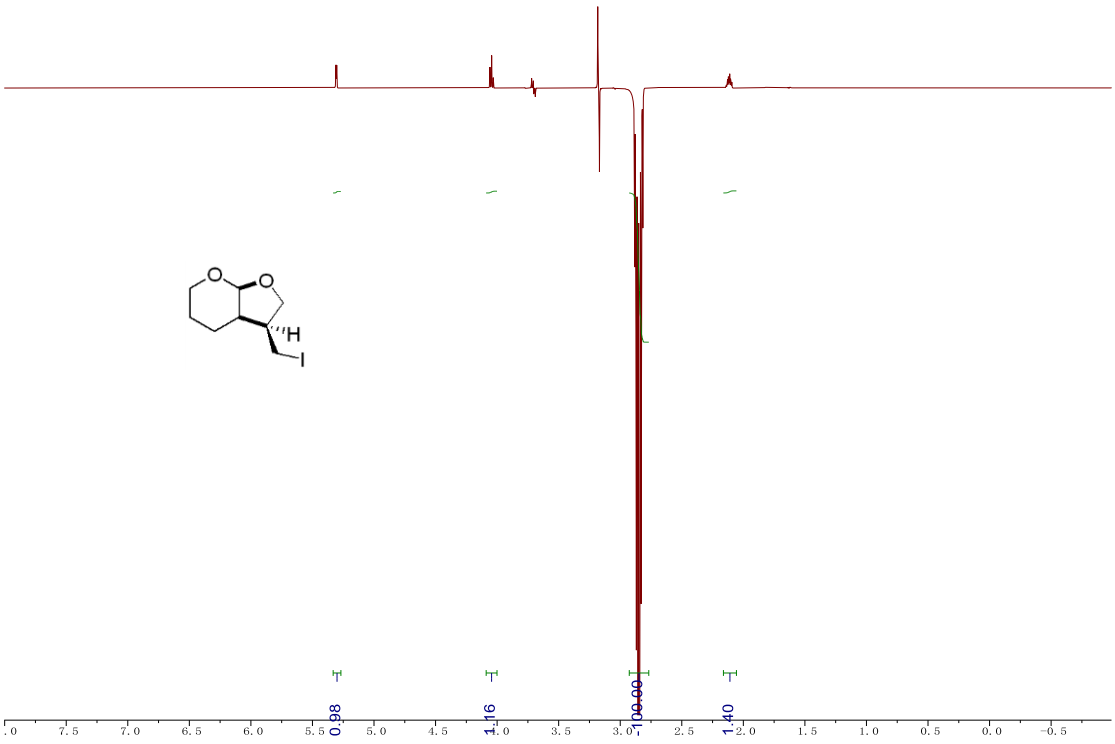
With Protocol A:

2a-1

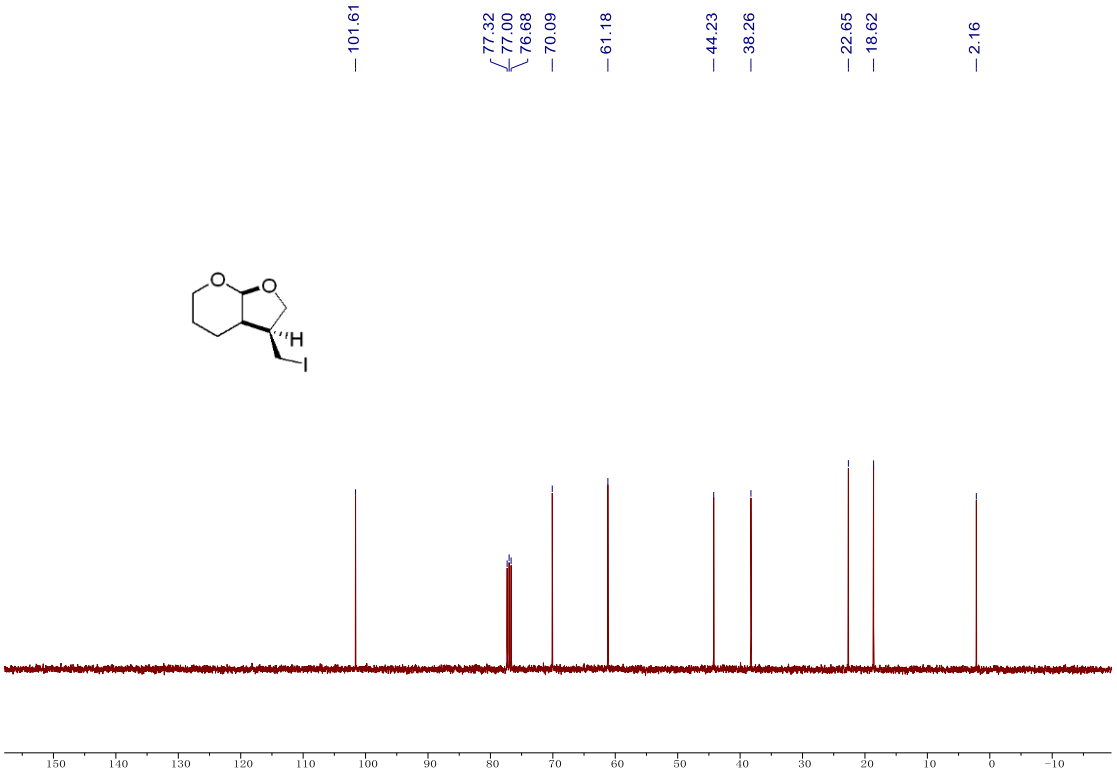
^{1}H NMR ($CDCl_3$, 400 MHz)



NOE Experiment ($CDCl_3$, 600 MHz)

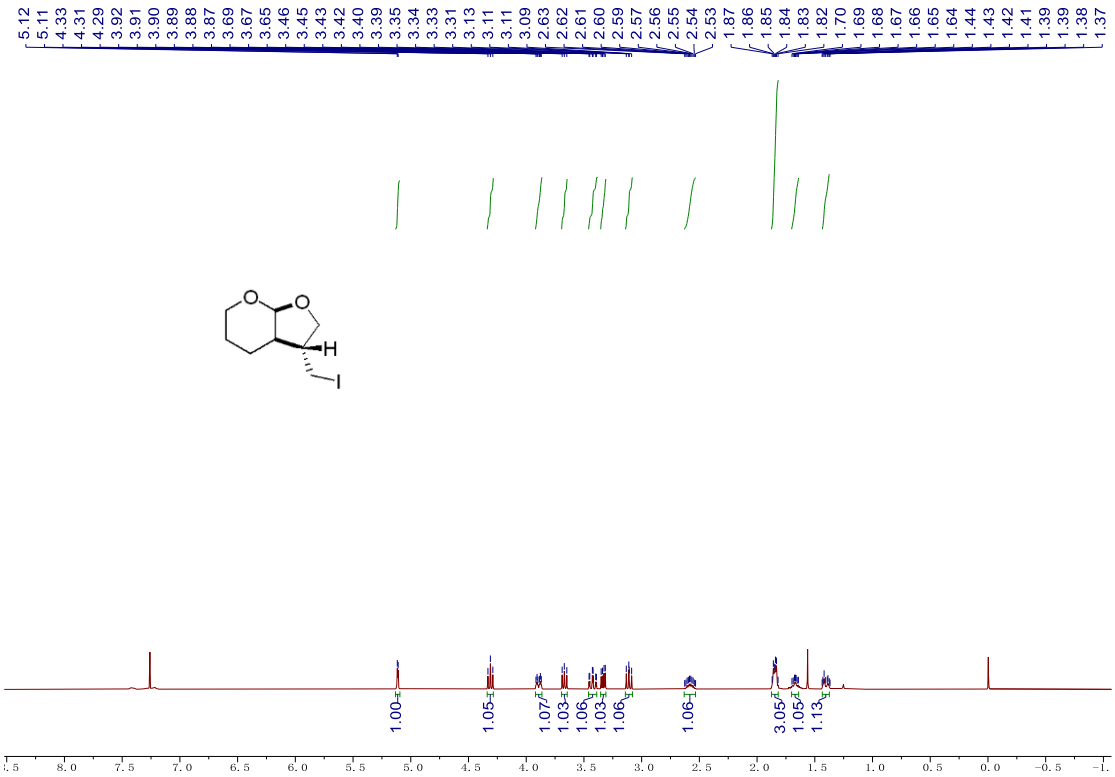


^{13}C NMR ($CDCl_3$, 101 MHz)

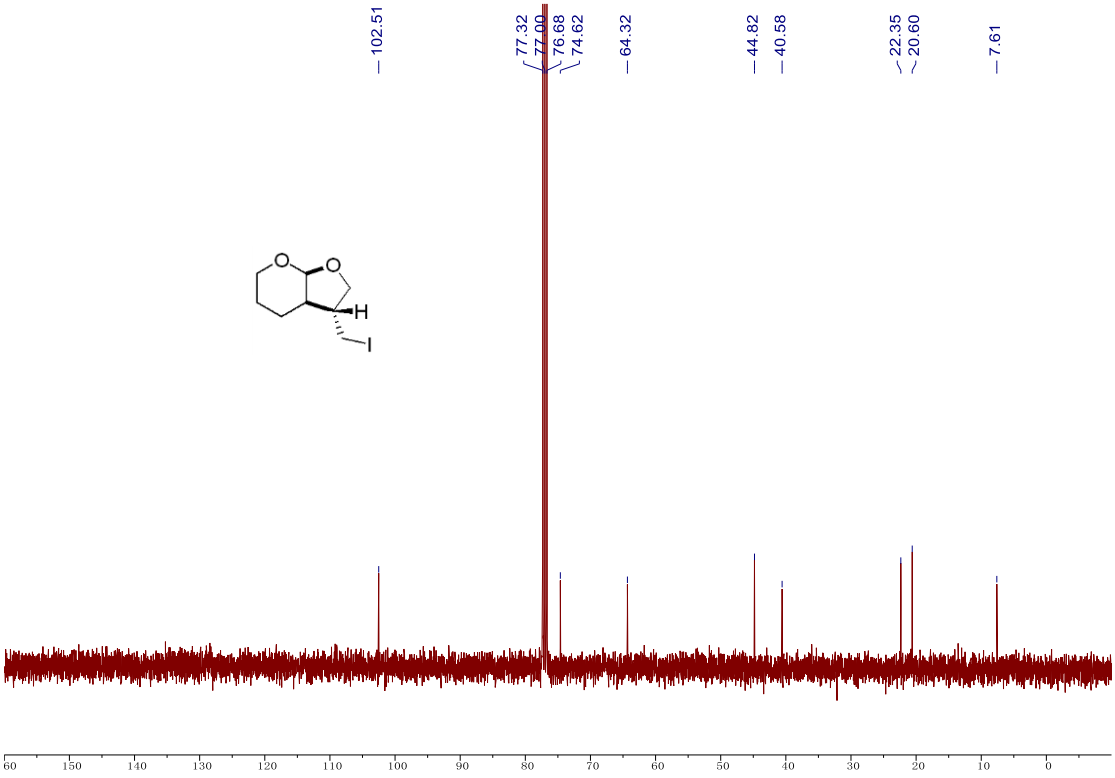


2a-2

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

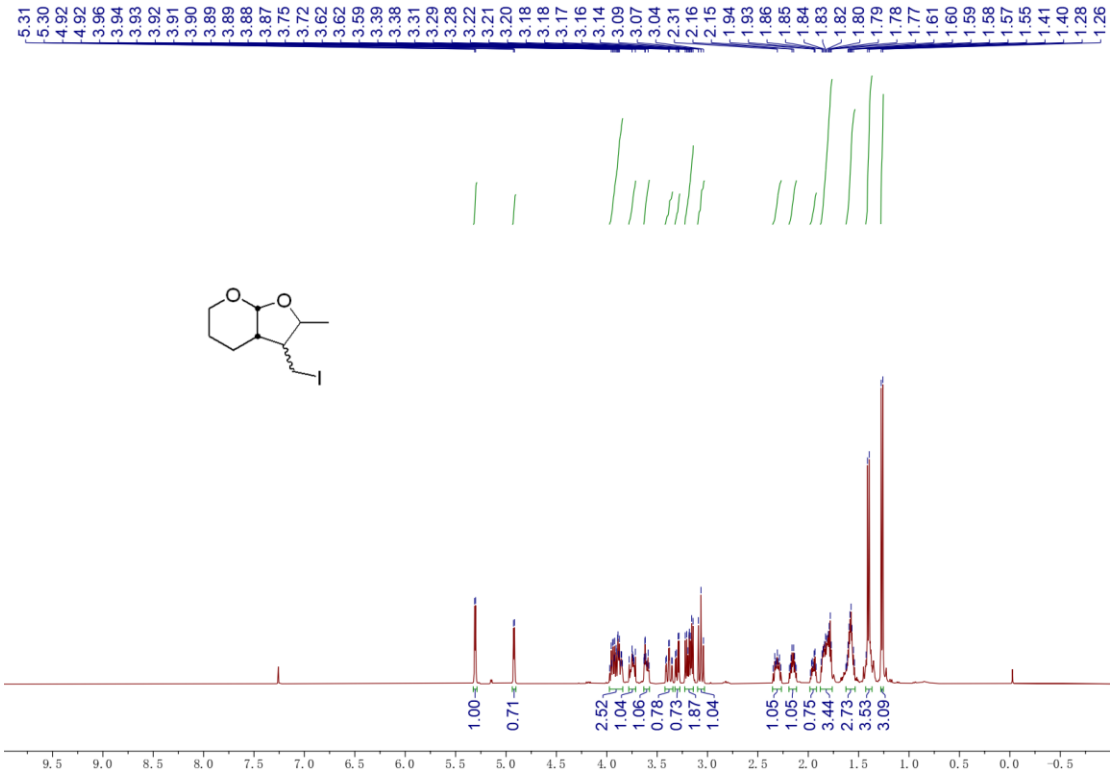


^{13}C NMR ($CDCl_3$, 101 MHz)

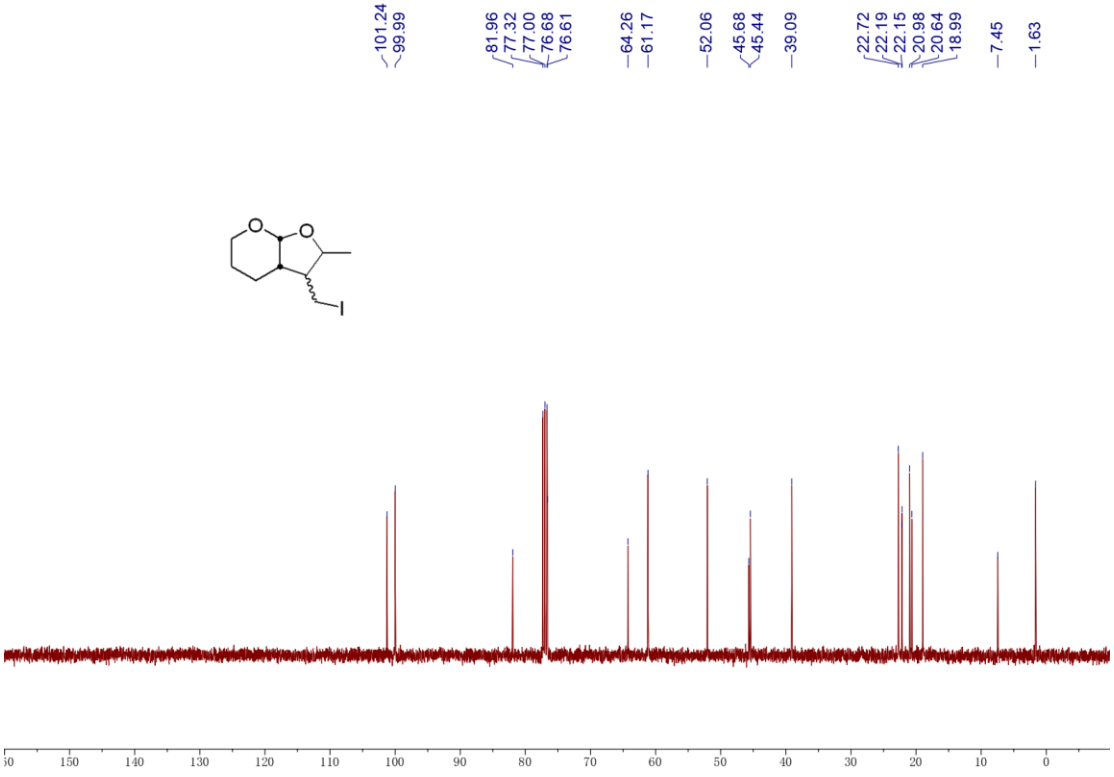


2b

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

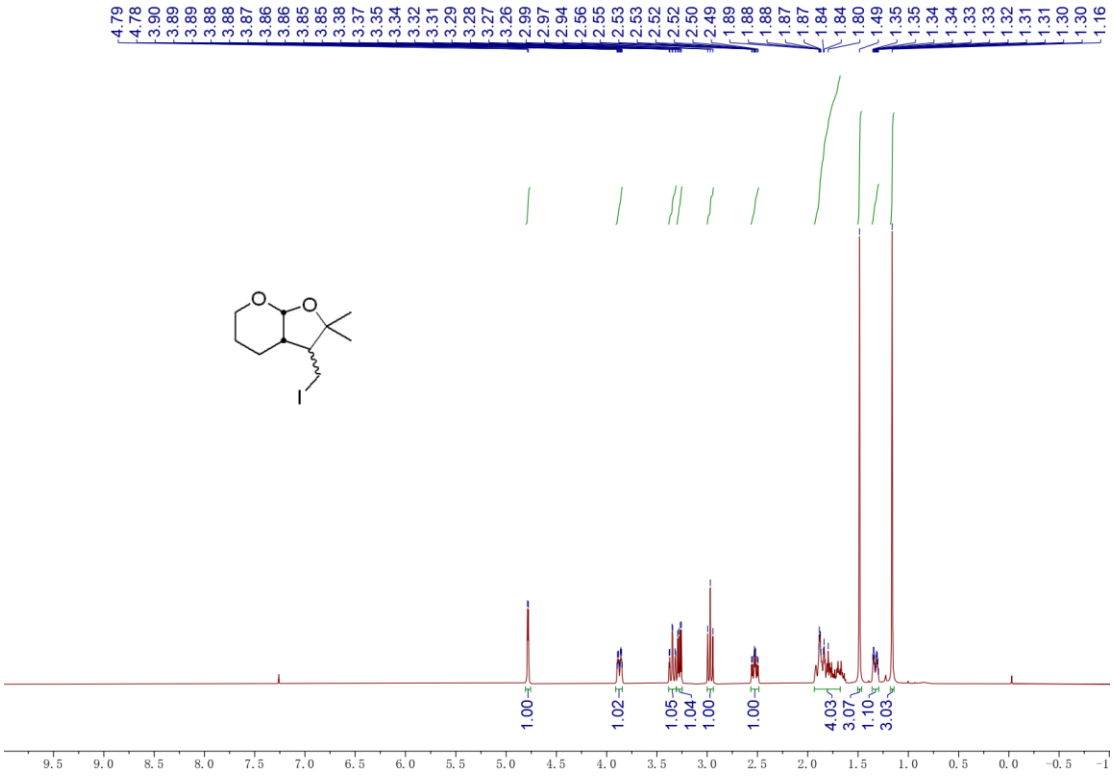


^{13}C NMR ($CDCl_3$, 101 MHz)

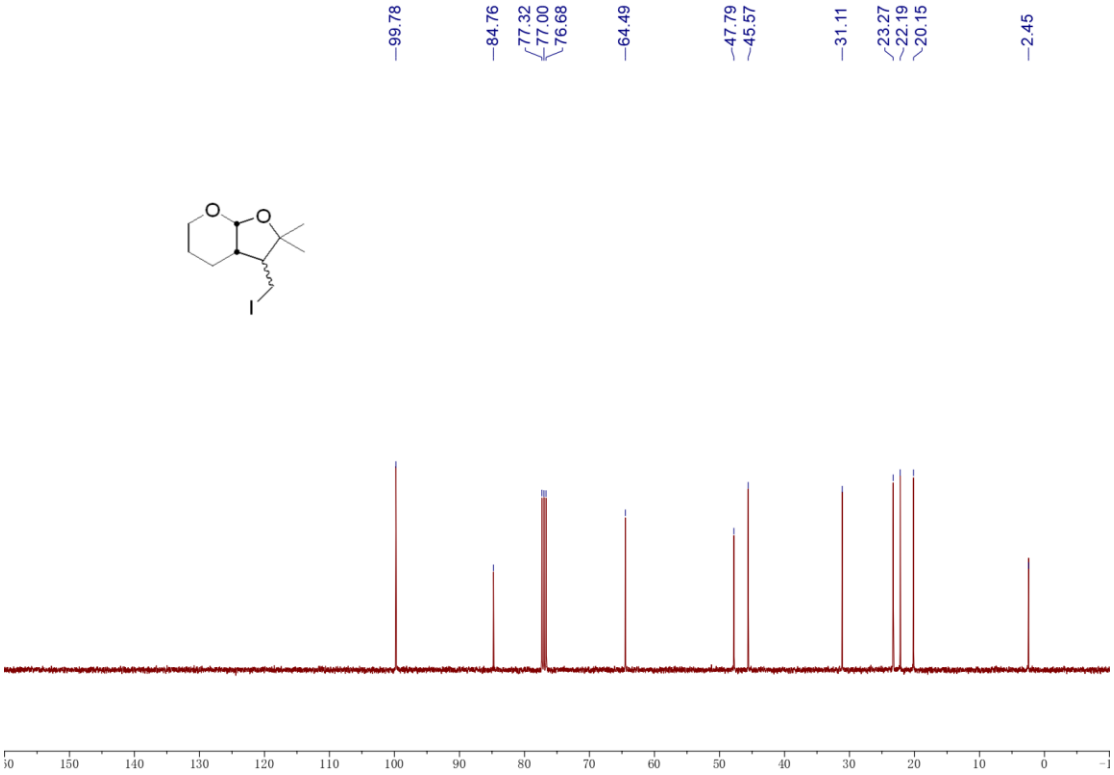


2c-1

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

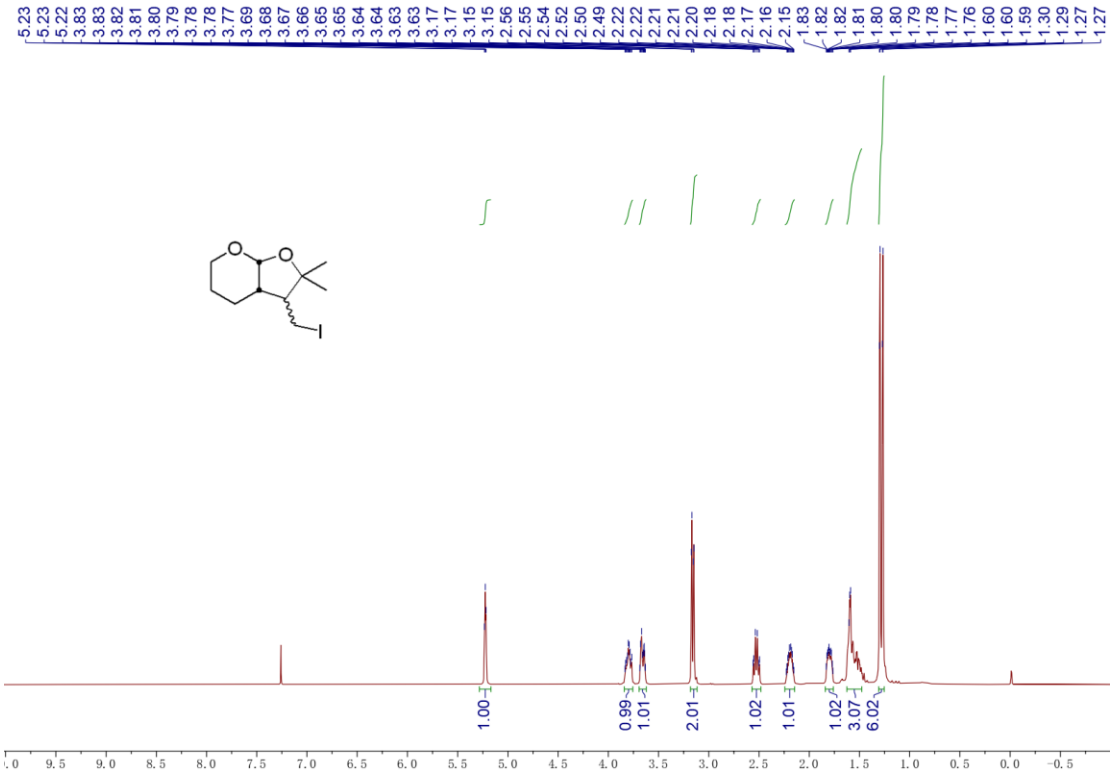


^{13}C NMR ($CDCl_3$, 101 MHz)

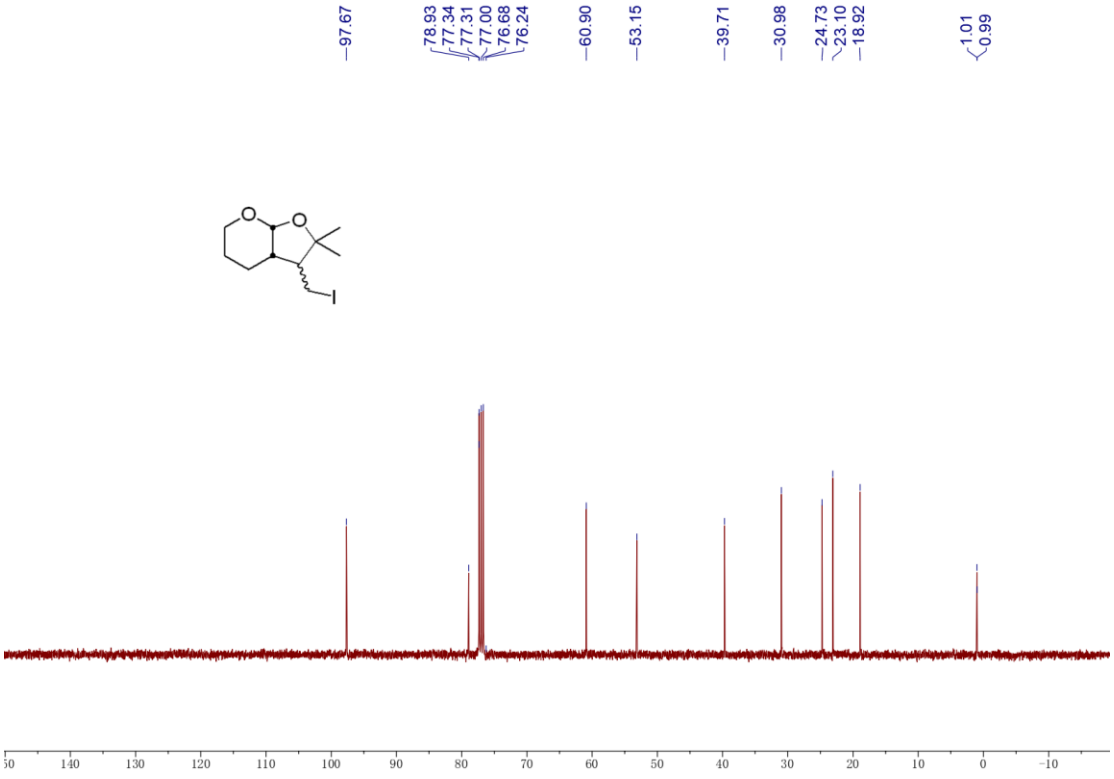


2c-2

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

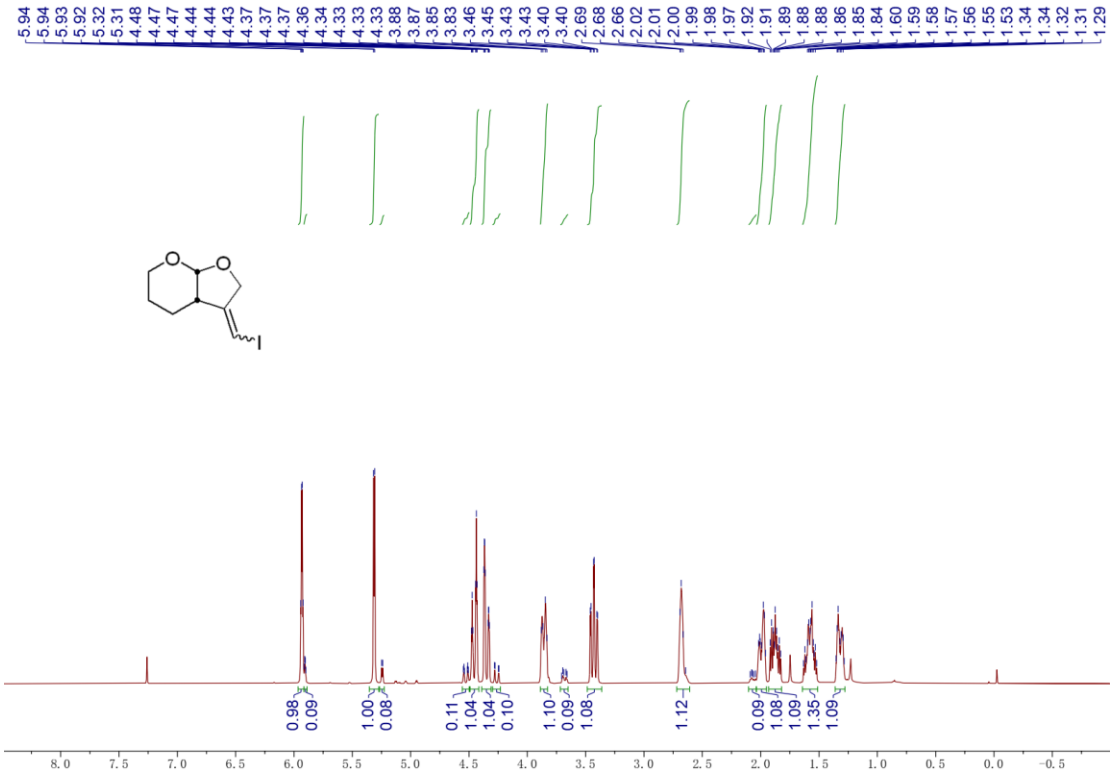


^{13}C NMR ($CDCl_3$, 101 MHz)

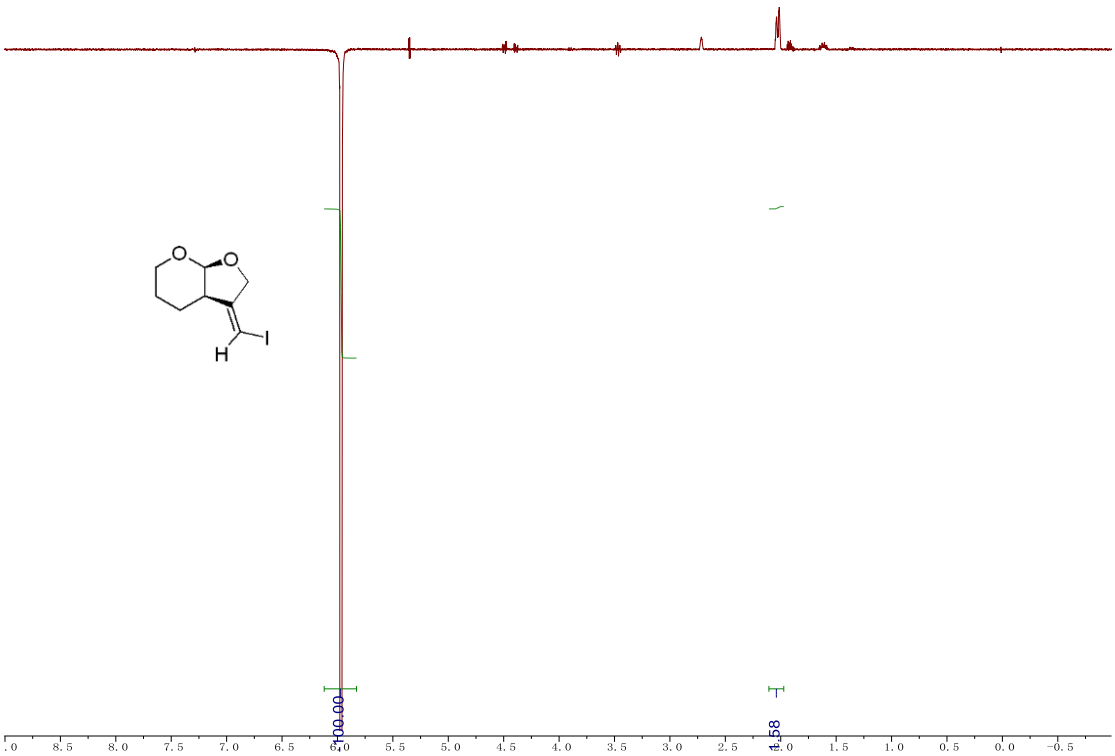


2f

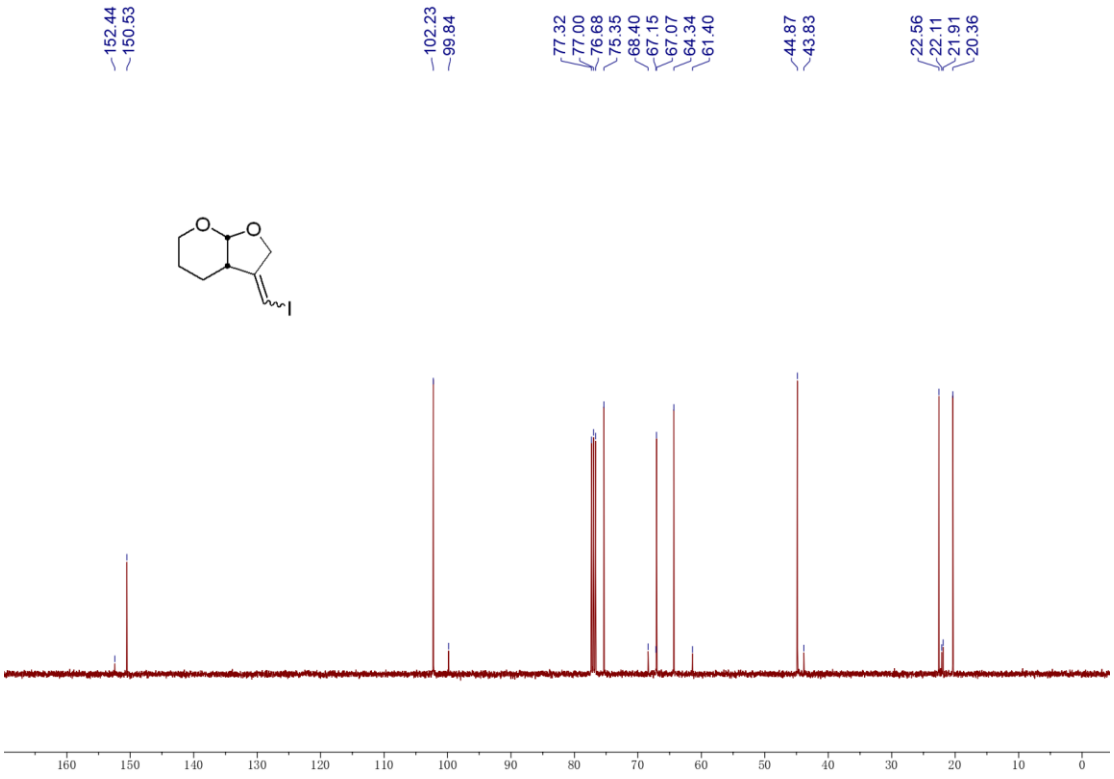
^{1}H NMR ($CDCl_3$, 400 MHz)



NOE Experiment ($CDCl_3$, 600 MHz)

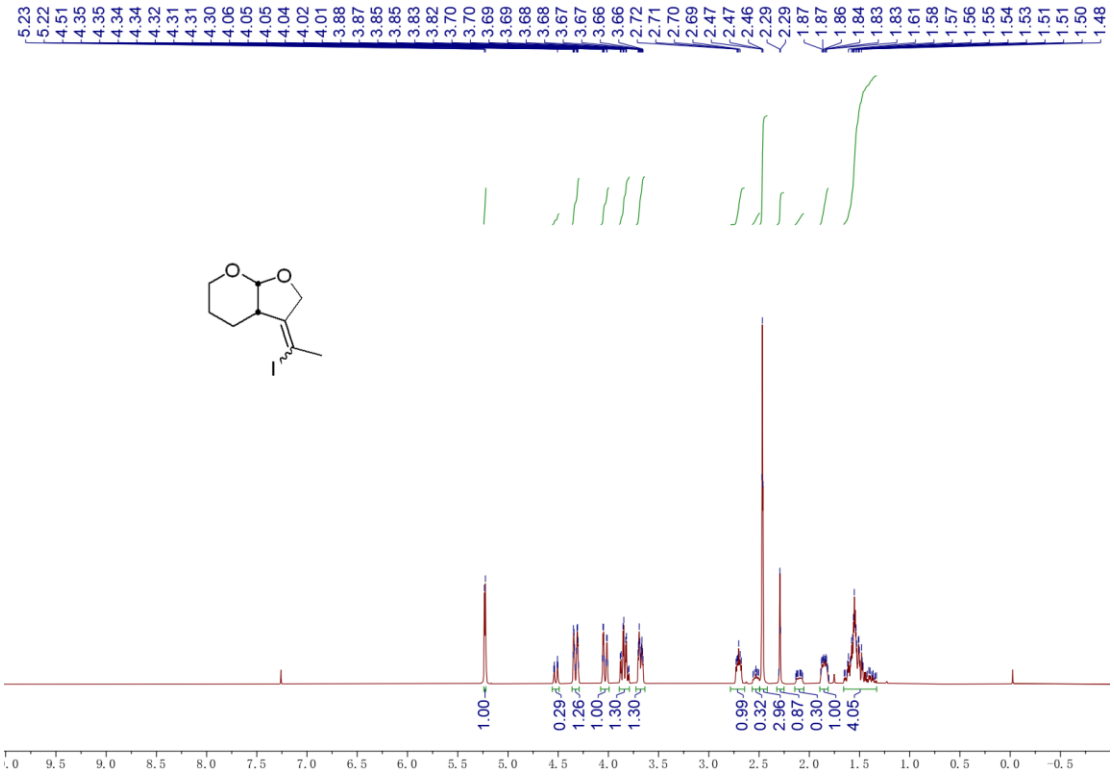


^{13}C NMR ($CDCl_3$, 101 MHz)

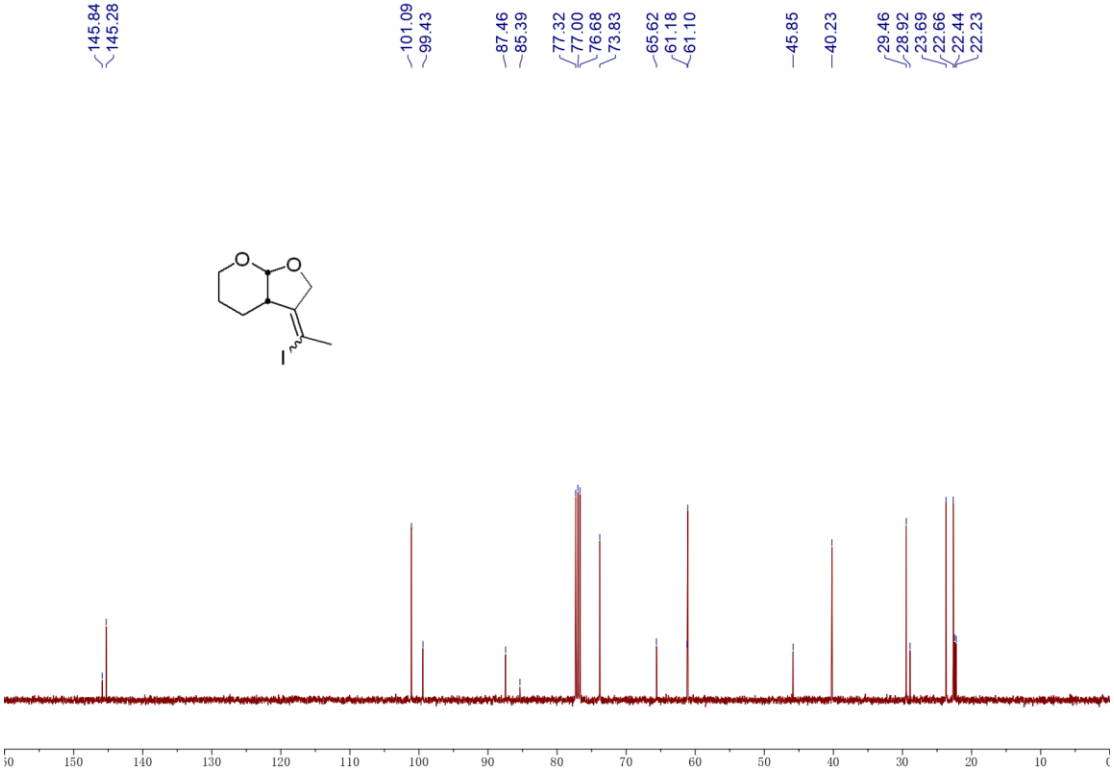


2g

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

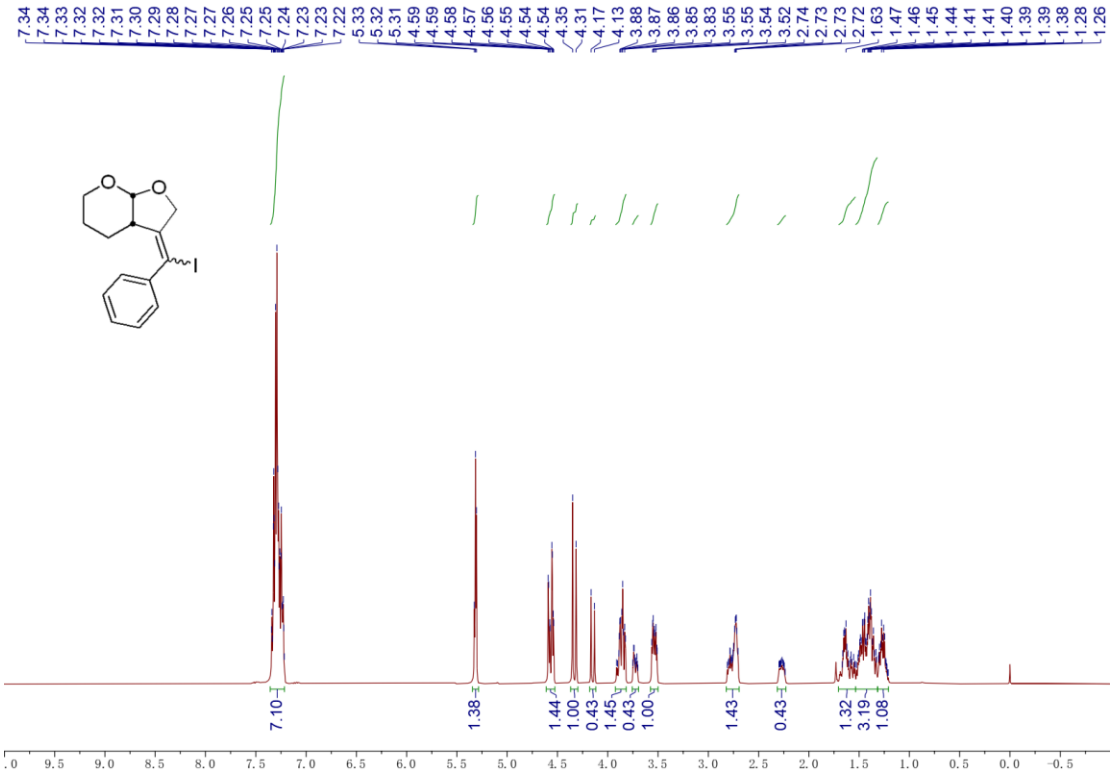


^{13}C NMR ($CDCl_3$, 101 MHz)

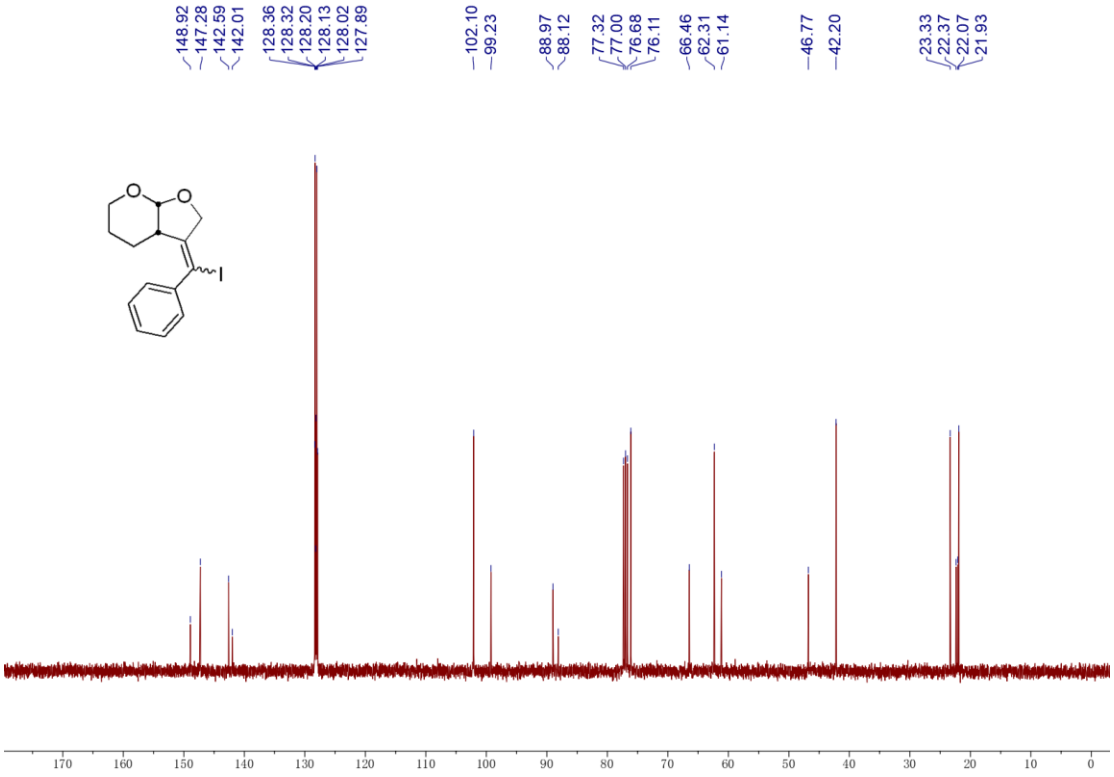


2h

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

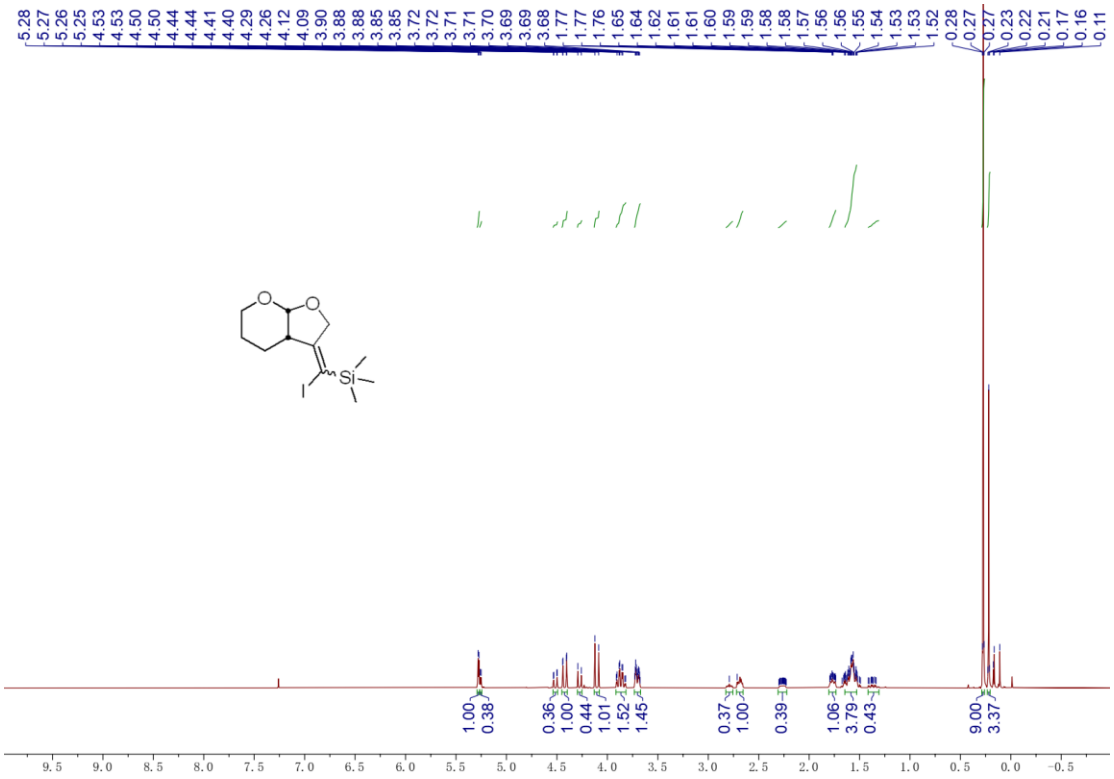


^{13}C NMR ($CDCl_3$, 101 MHz)

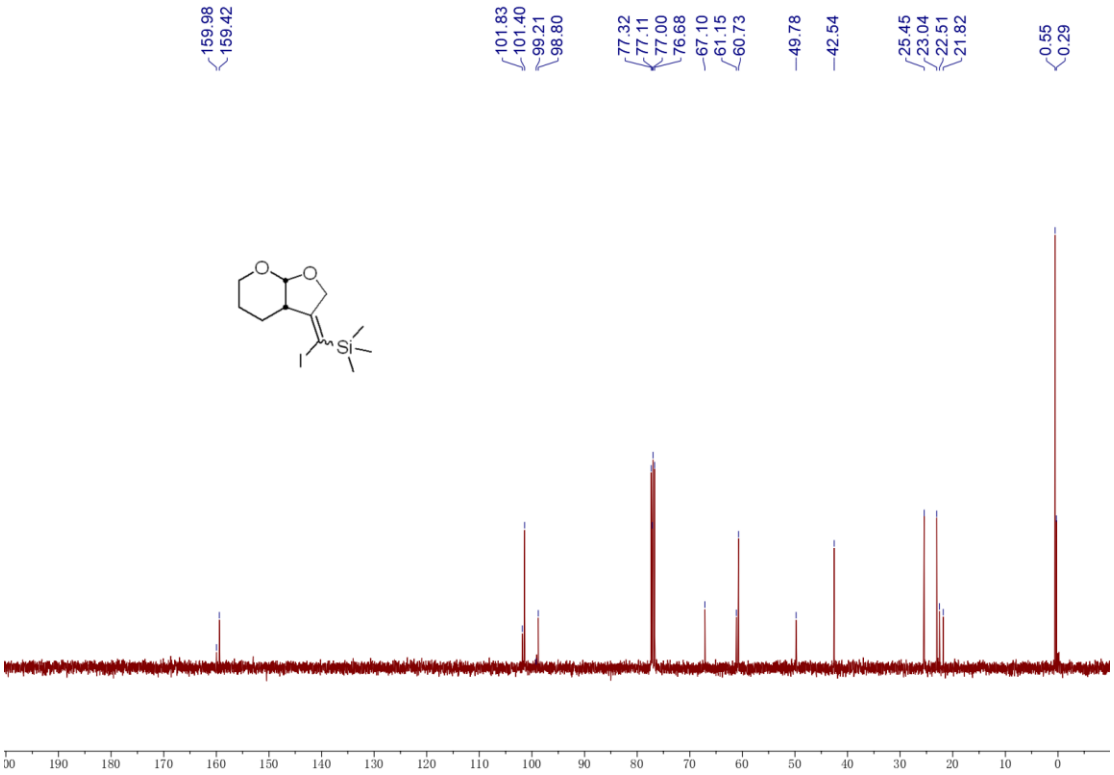


2i

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

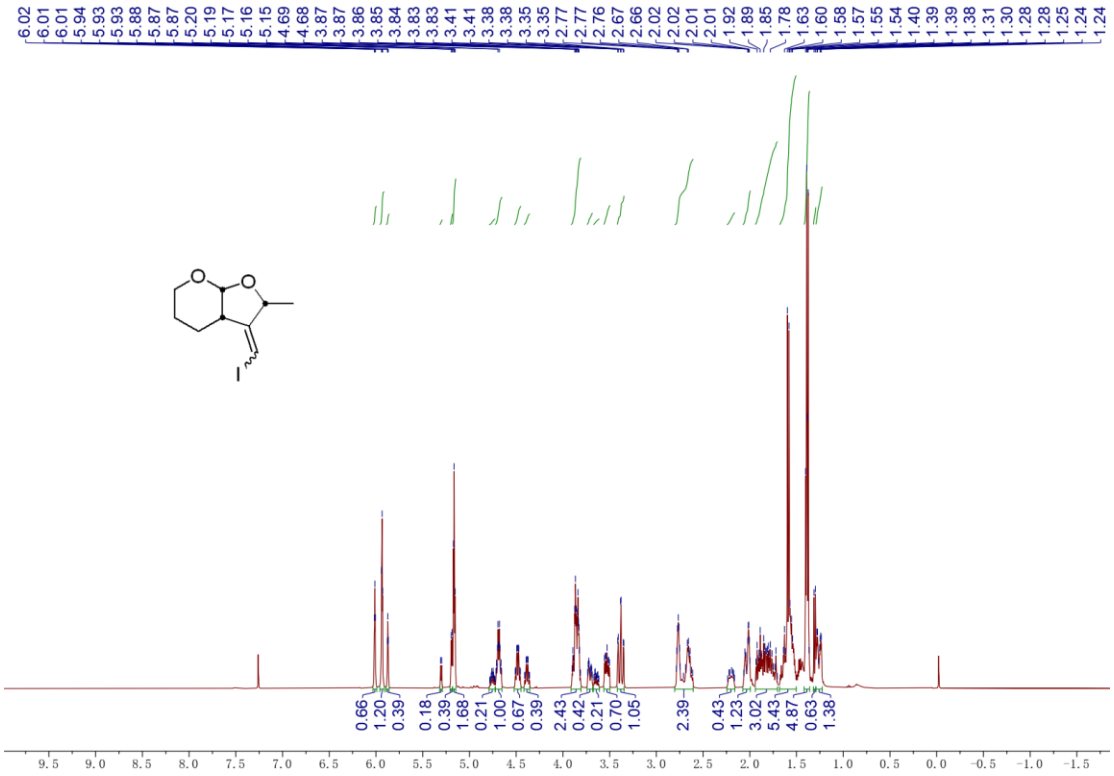


^{13}C NMR ($CDCl_3$, 101 MHz)

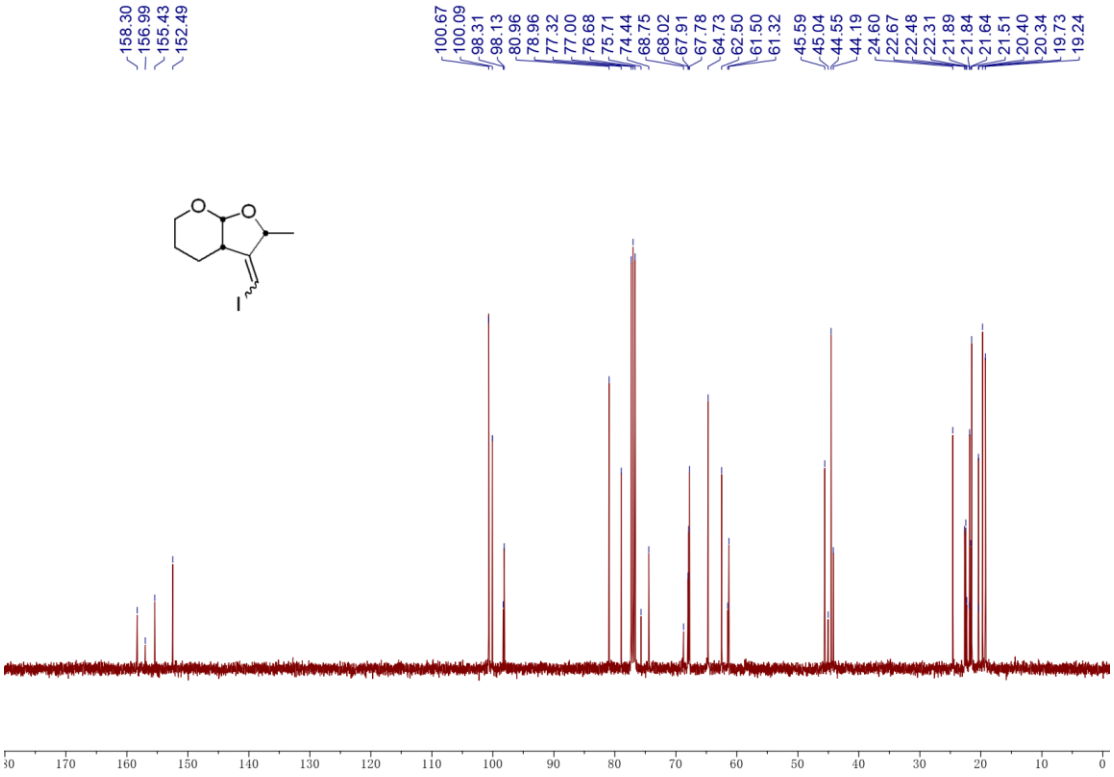


2j

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

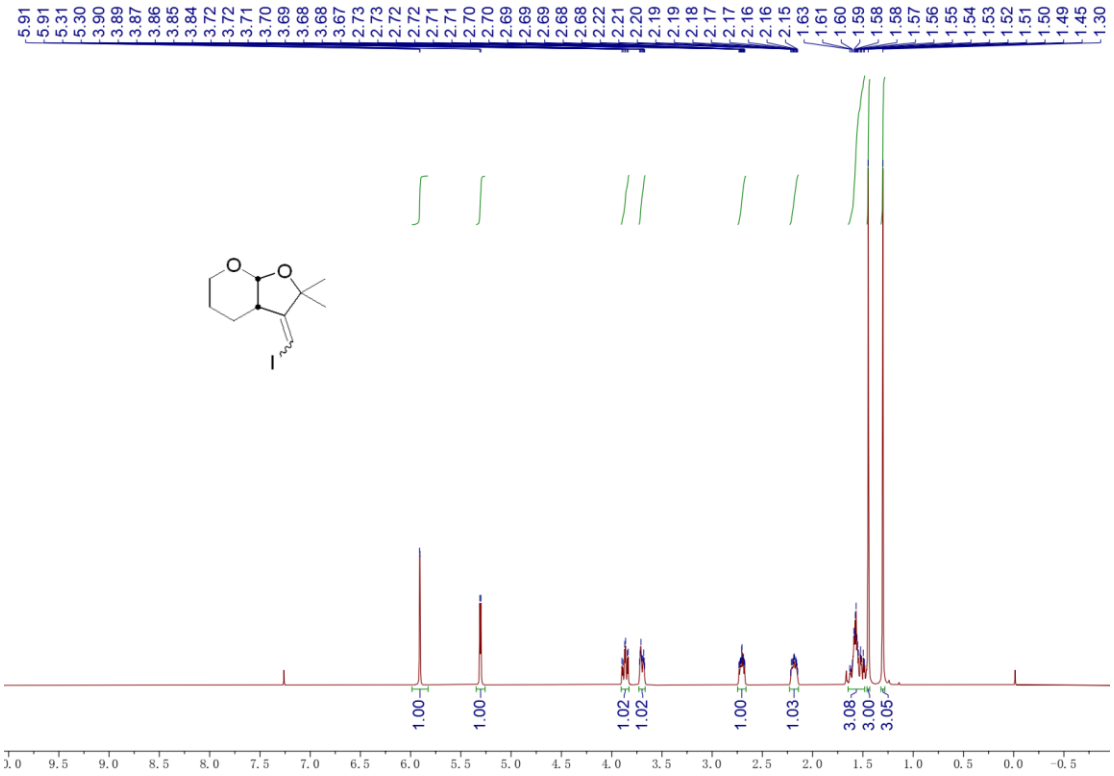


^{13}C NMR ($CDCl_3$, 101 MHz)

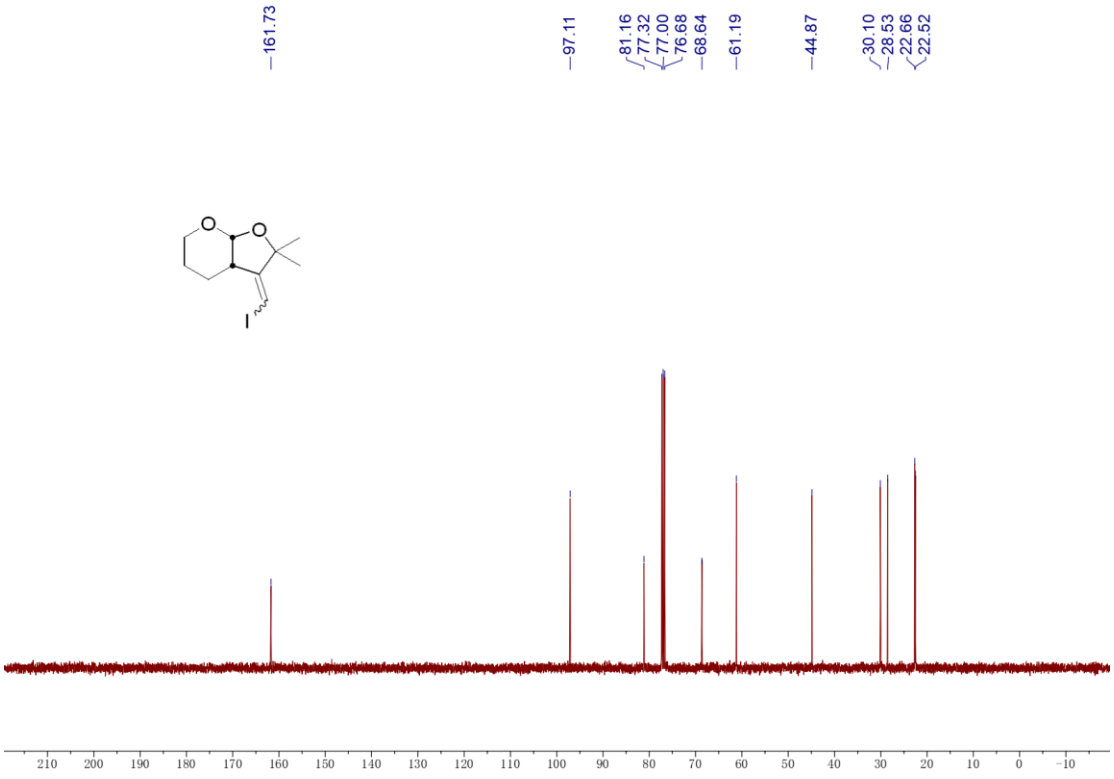


2k-1

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

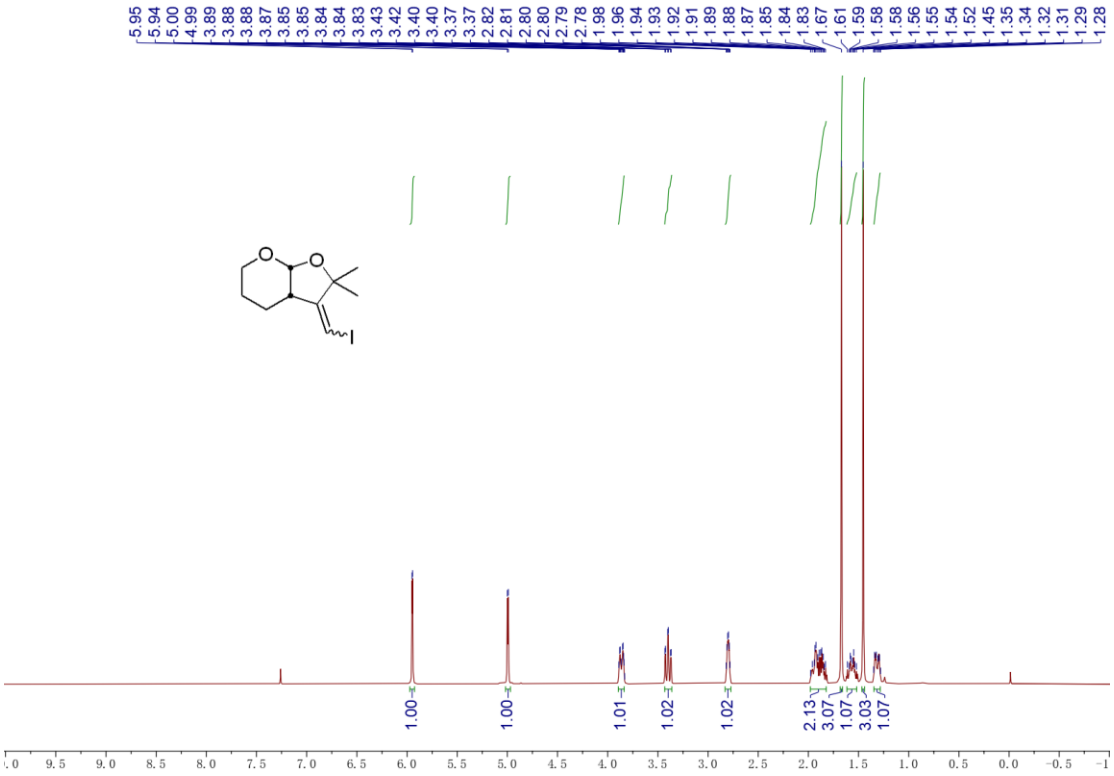


^{13}C NMR ($CDCl_3$, 101 MHz)

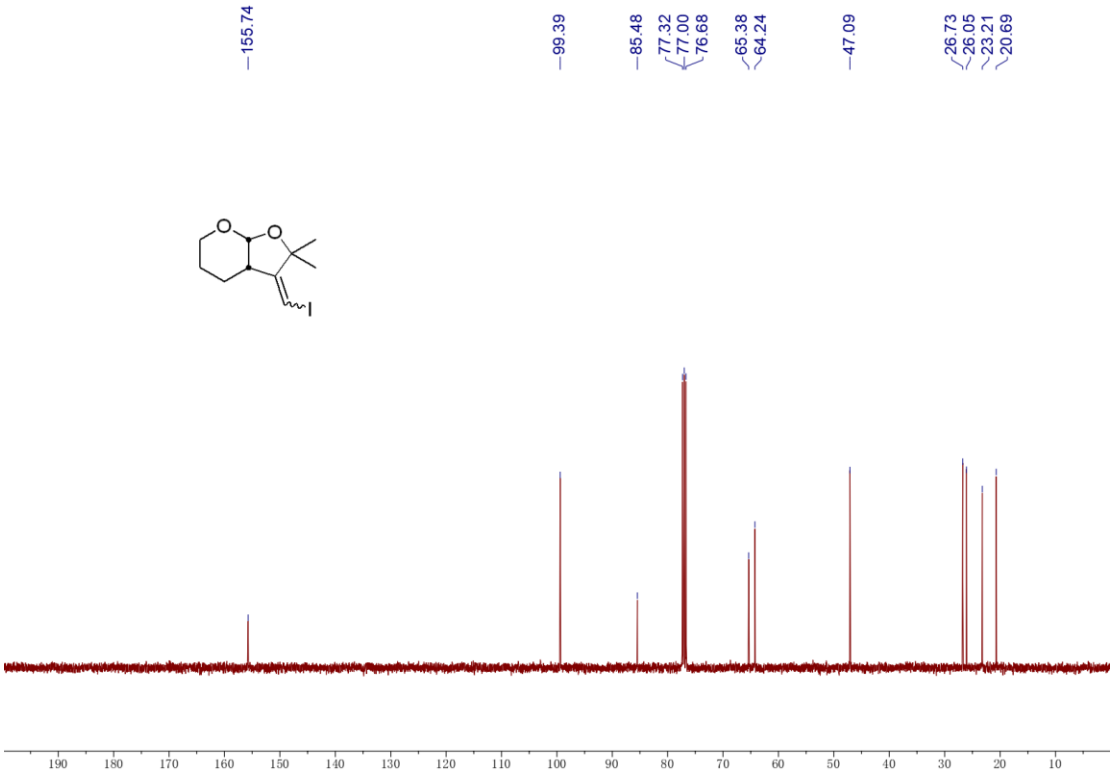


2k-2

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

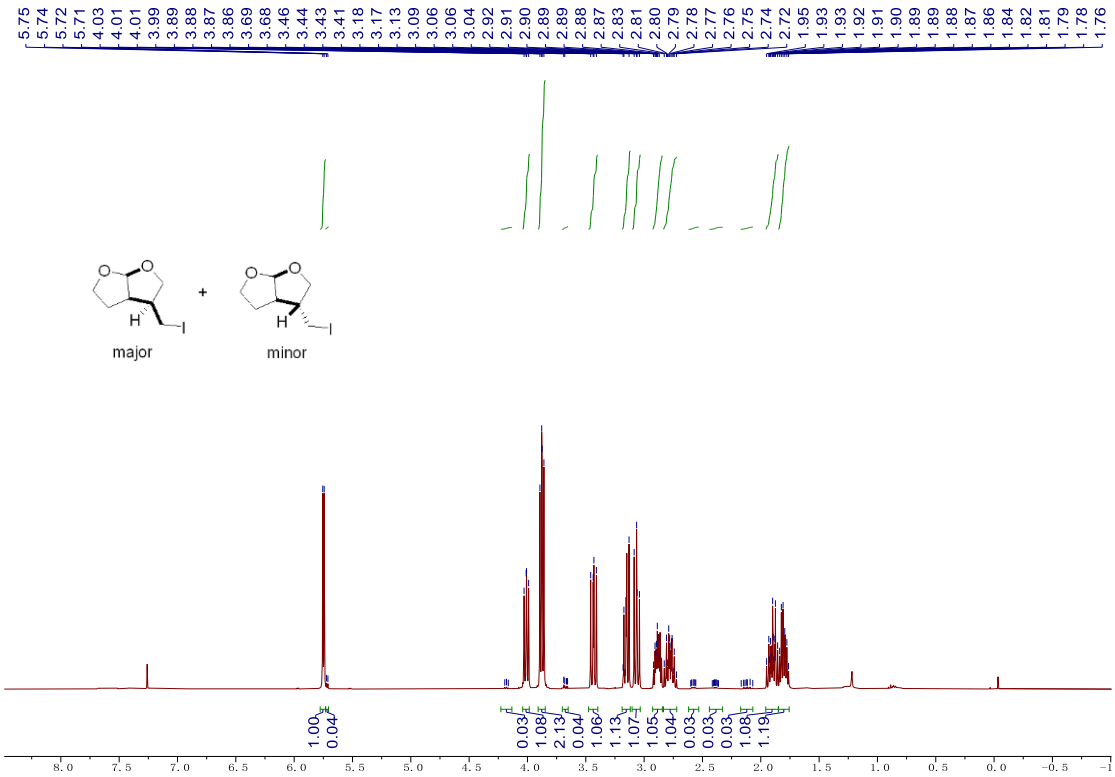


^{13}C NMR ($CDCl_3$, 101 MHz)

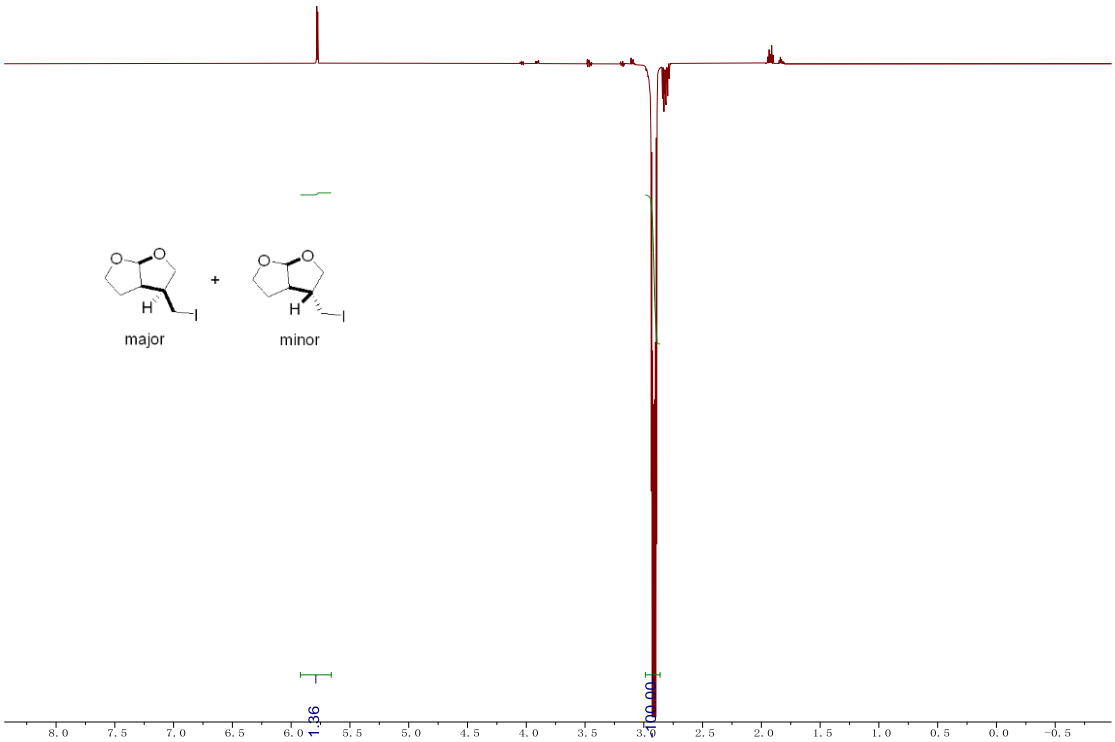


2l

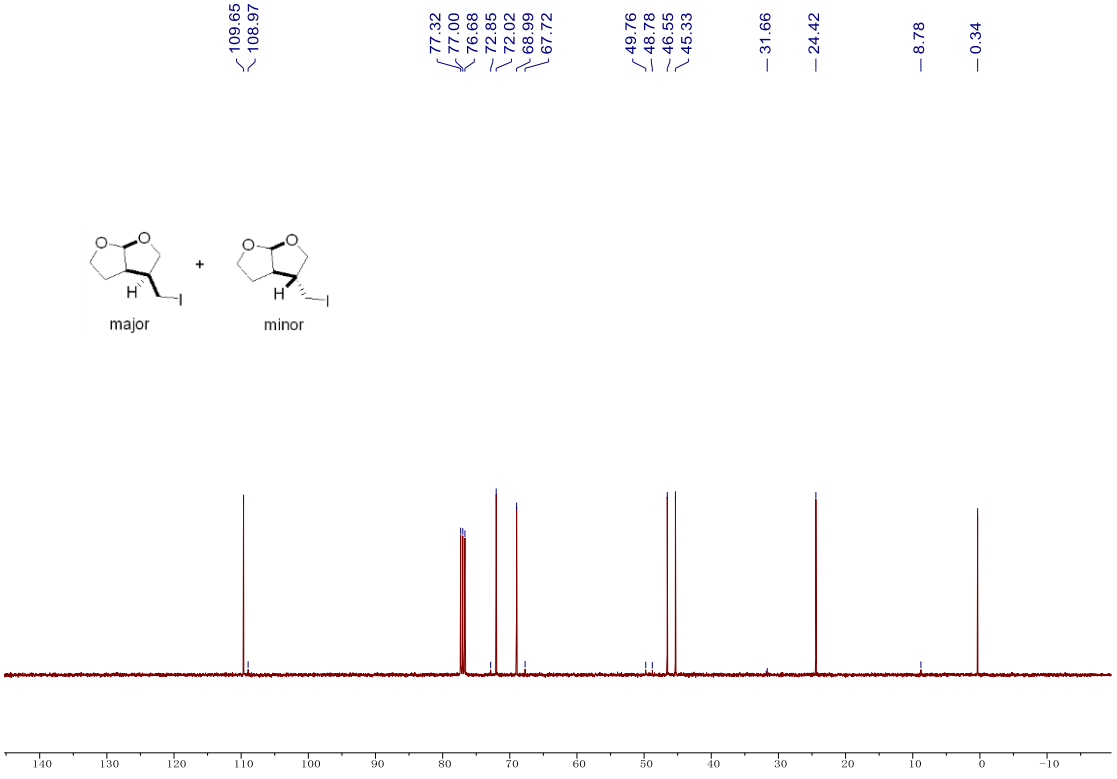
^{1}H NMR ($CDCl_3$, 400 MHz)



NOE Experiment ($CDCl_3$, 600 MHz)

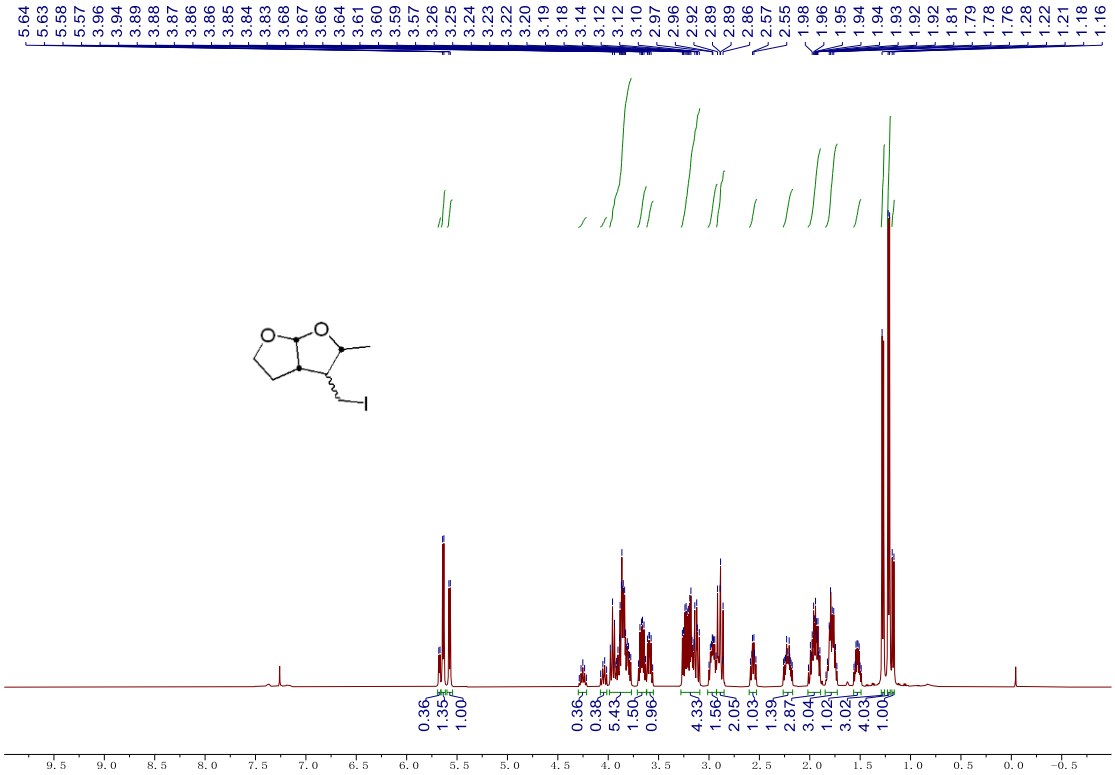


^{13}C NMR ($CDCl_3$, 101 MHz)

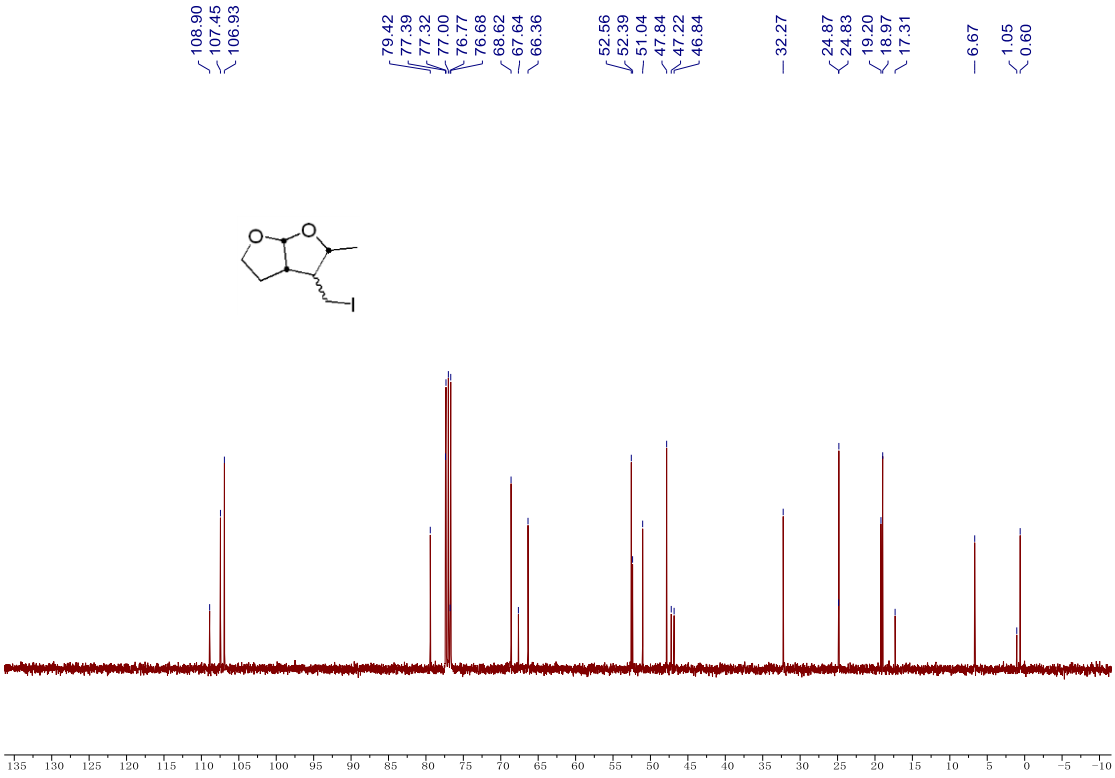


2m

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

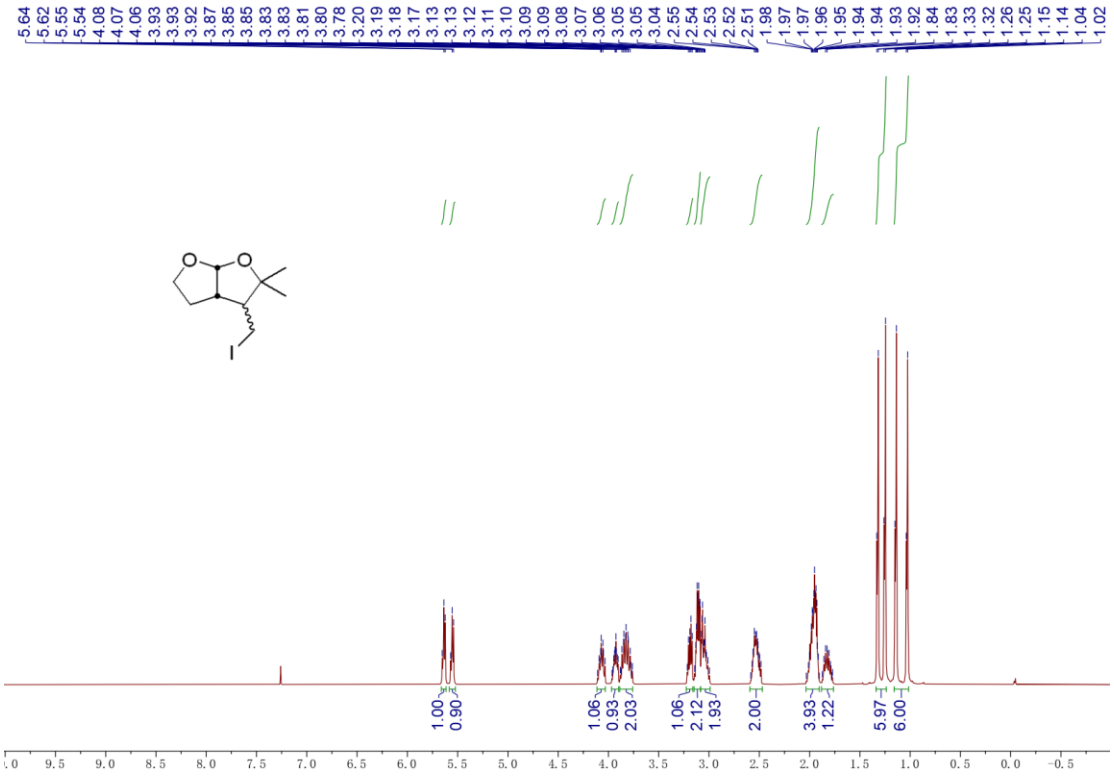


^{13}C NMR ($CDCl_3$, 101 MHz)

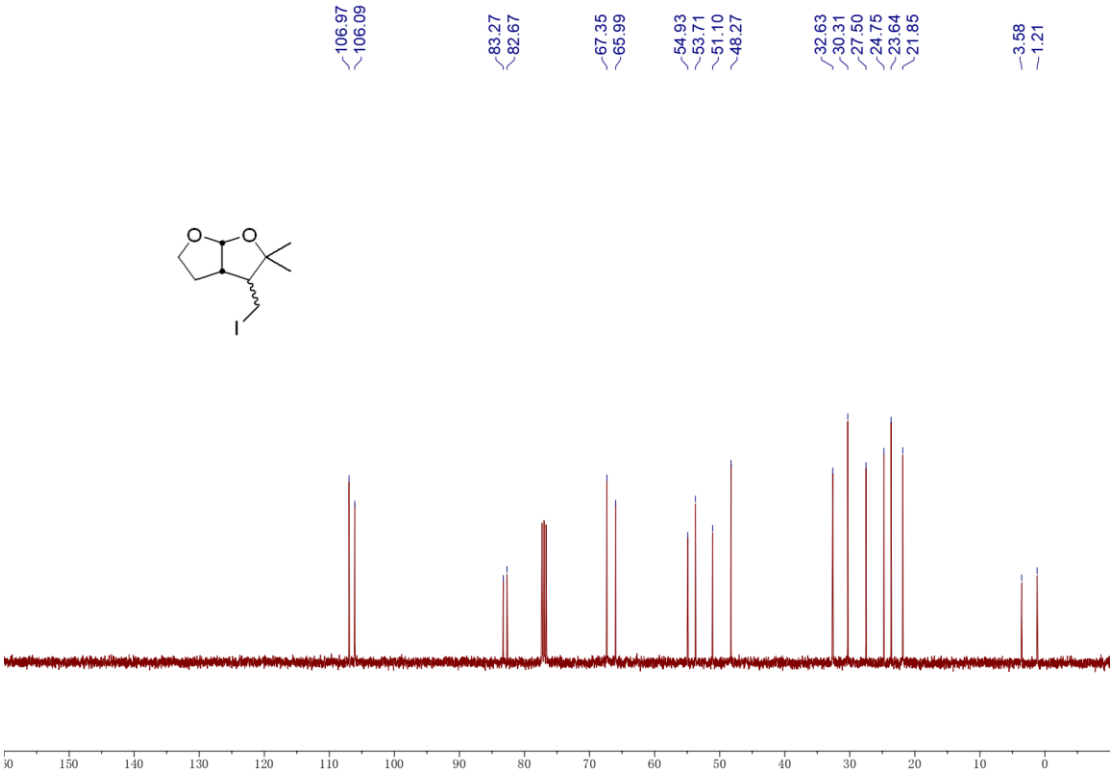


2n

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

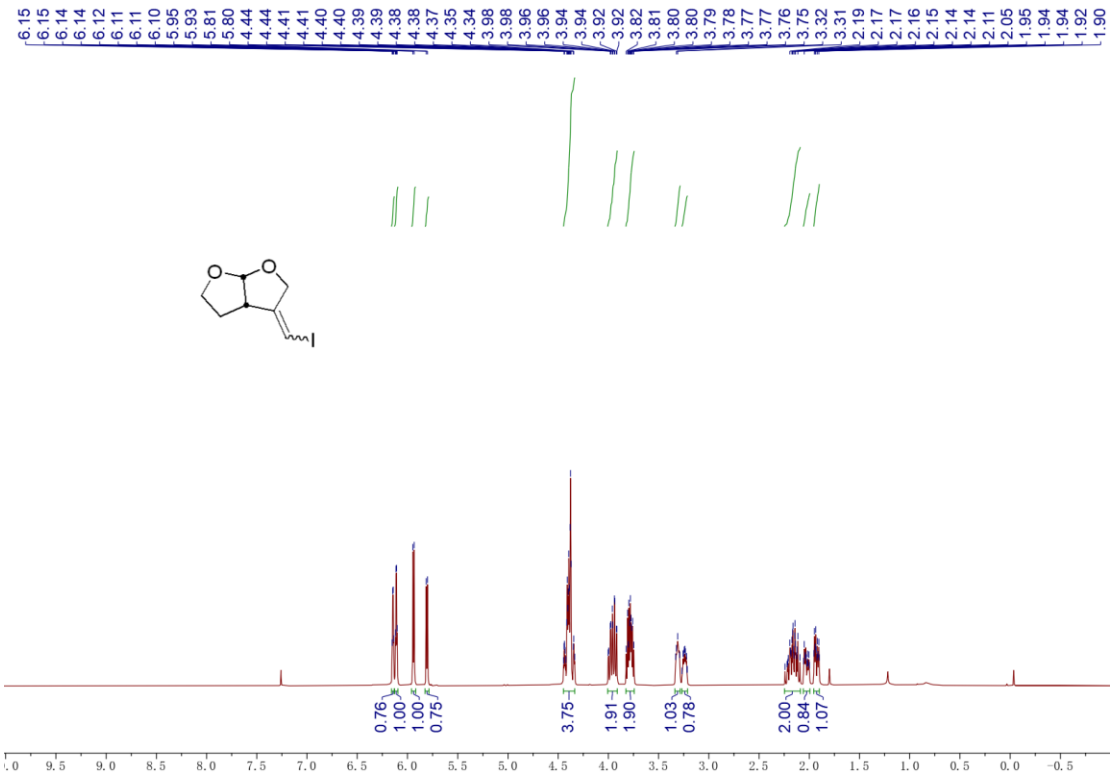


^{13}C NMR ($CDCl_3$, 101 MHz)

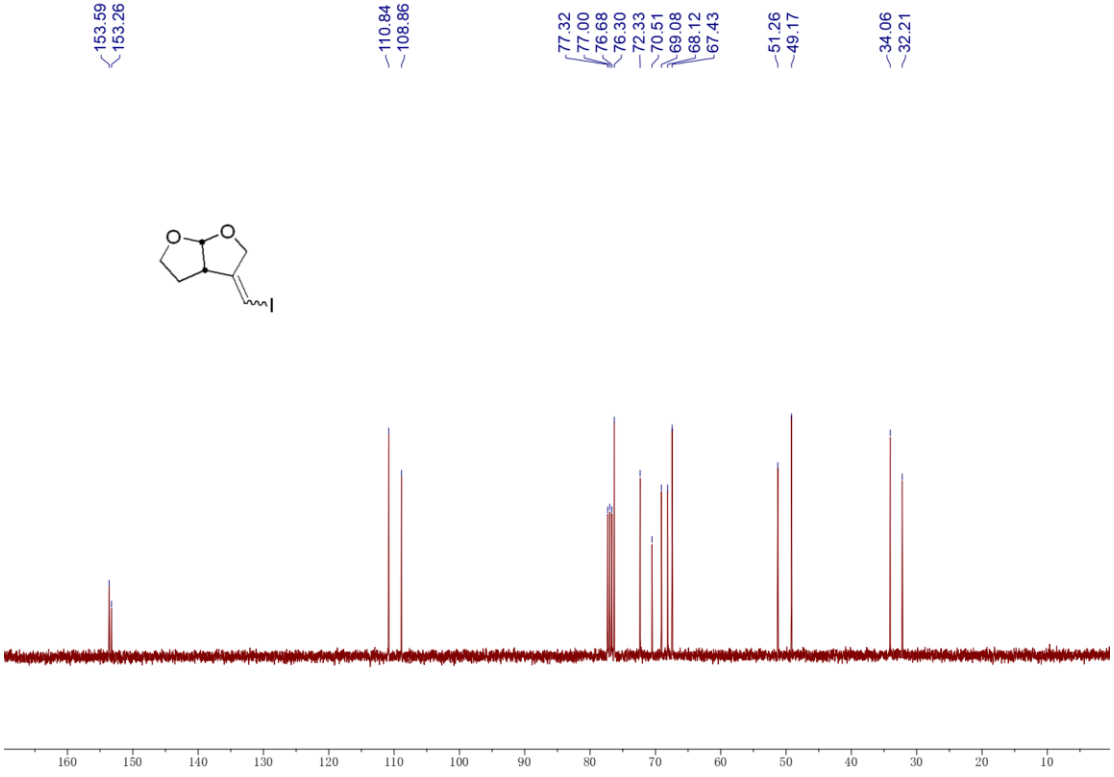


2o

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

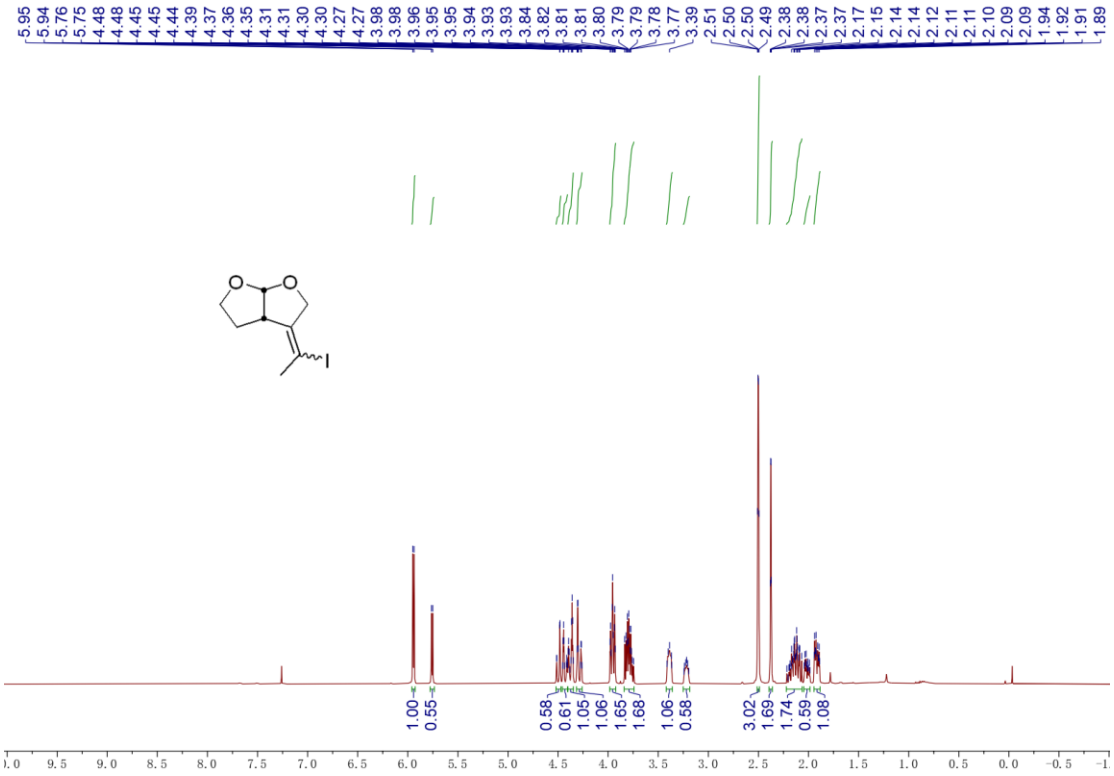


^{13}C NMR ($CDCl_3$, 101 MHz)

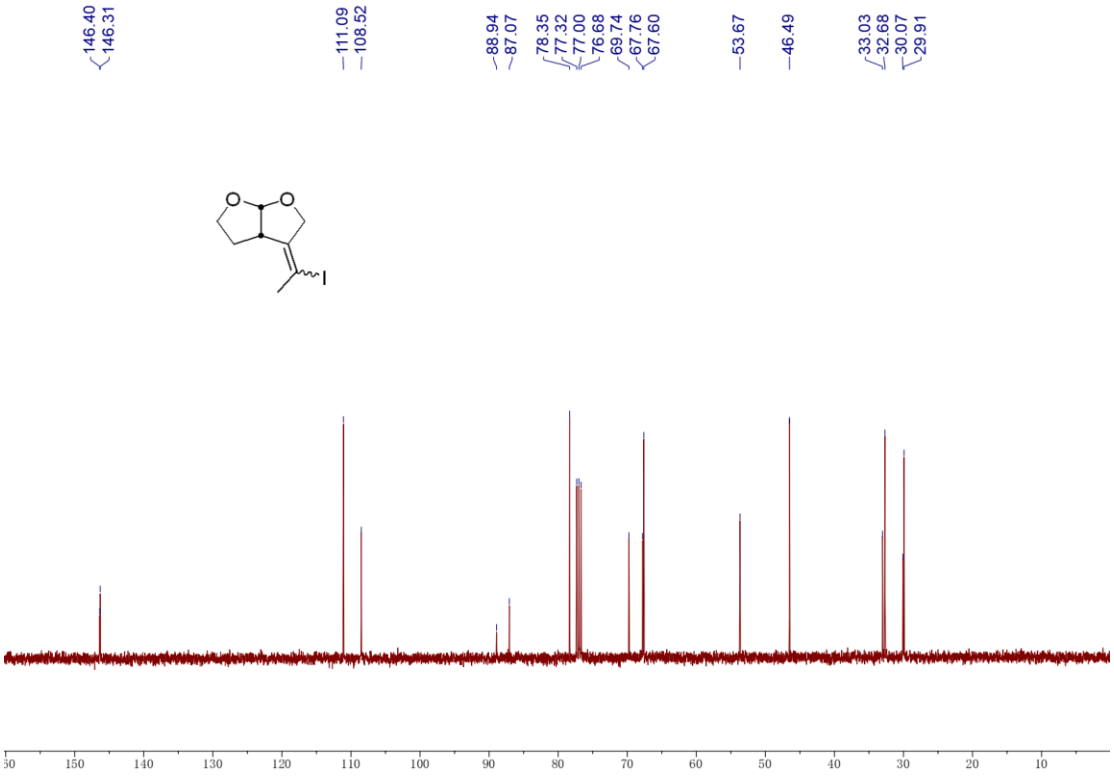


2p

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

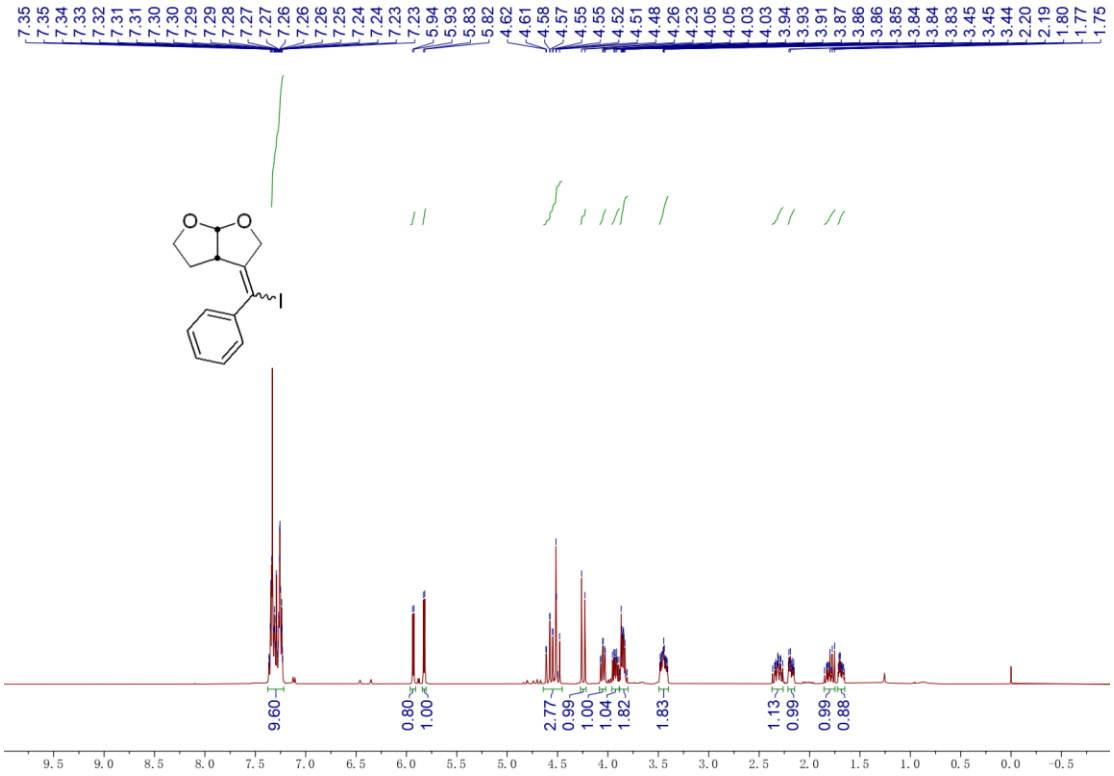


^{13}C NMR ($CDCl_3$, 101 MHz)

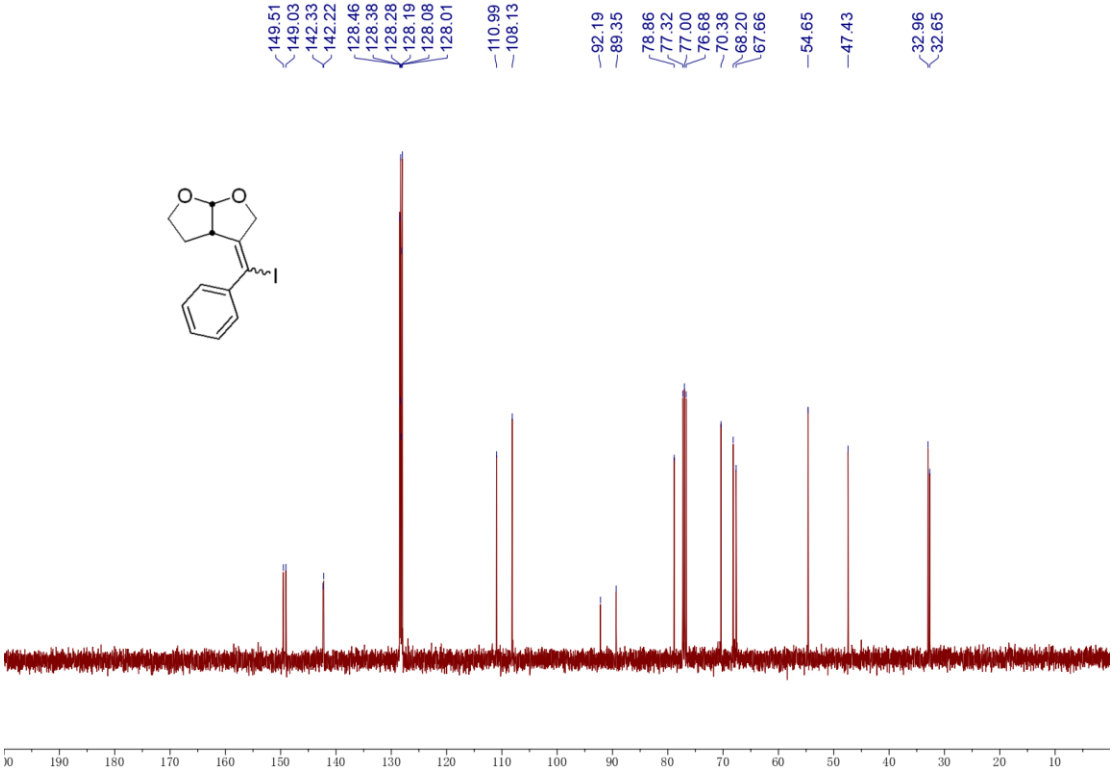


2q

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

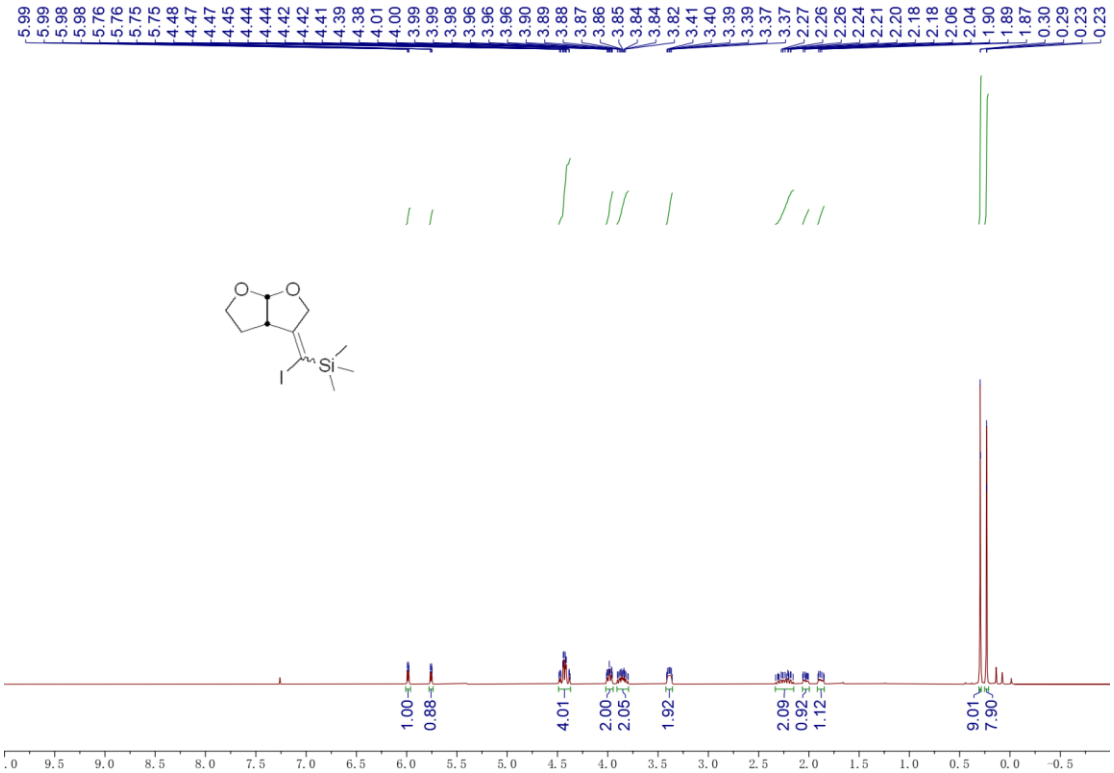


^{13}C NMR ($CDCl_3$, 101 MHz)

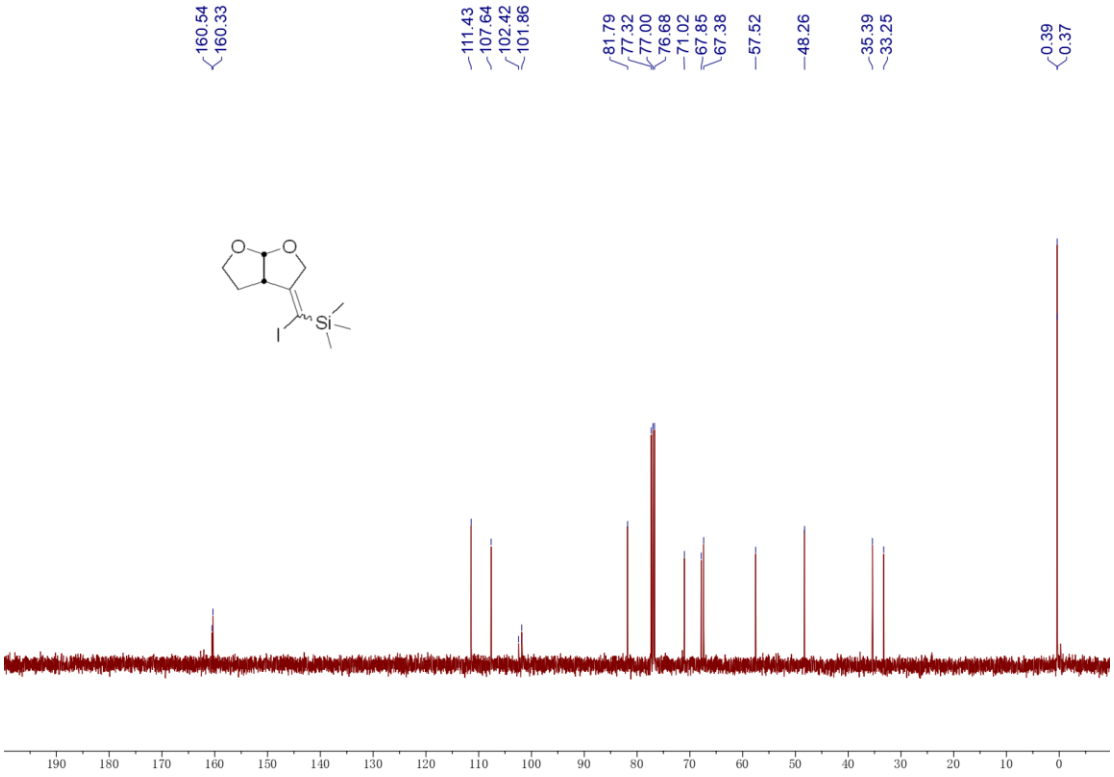


2r

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

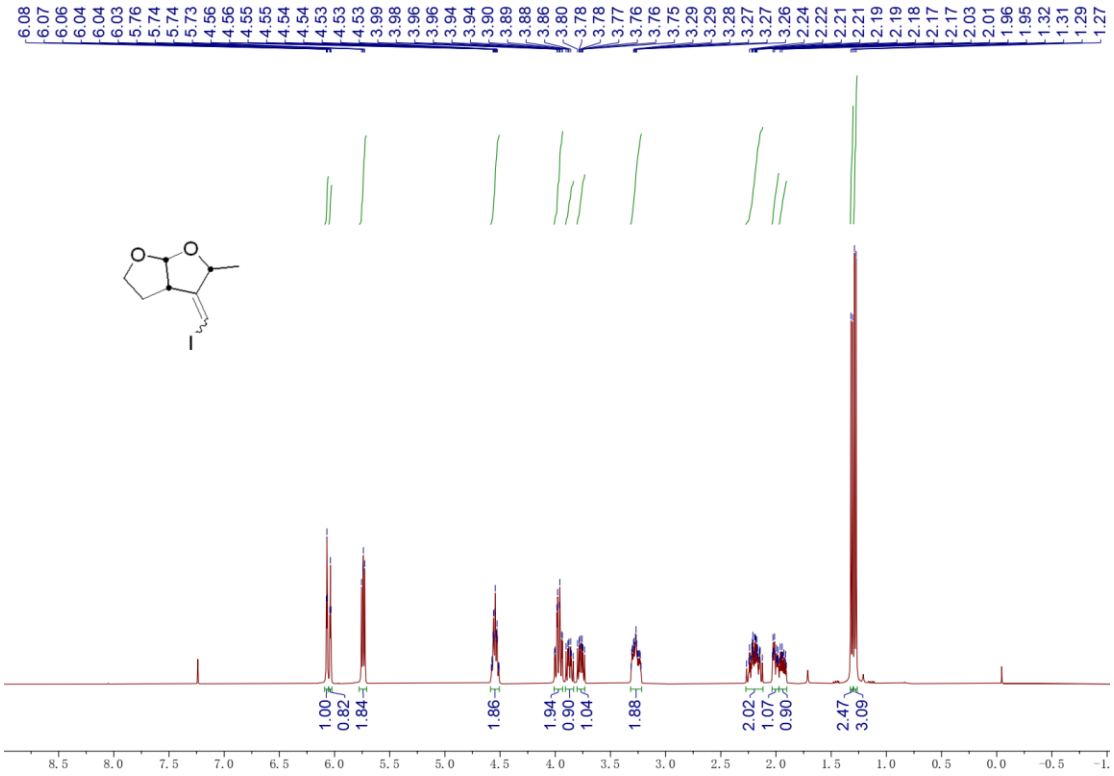


^{13}C NMR ($CDCl_3$, 101 MHz)

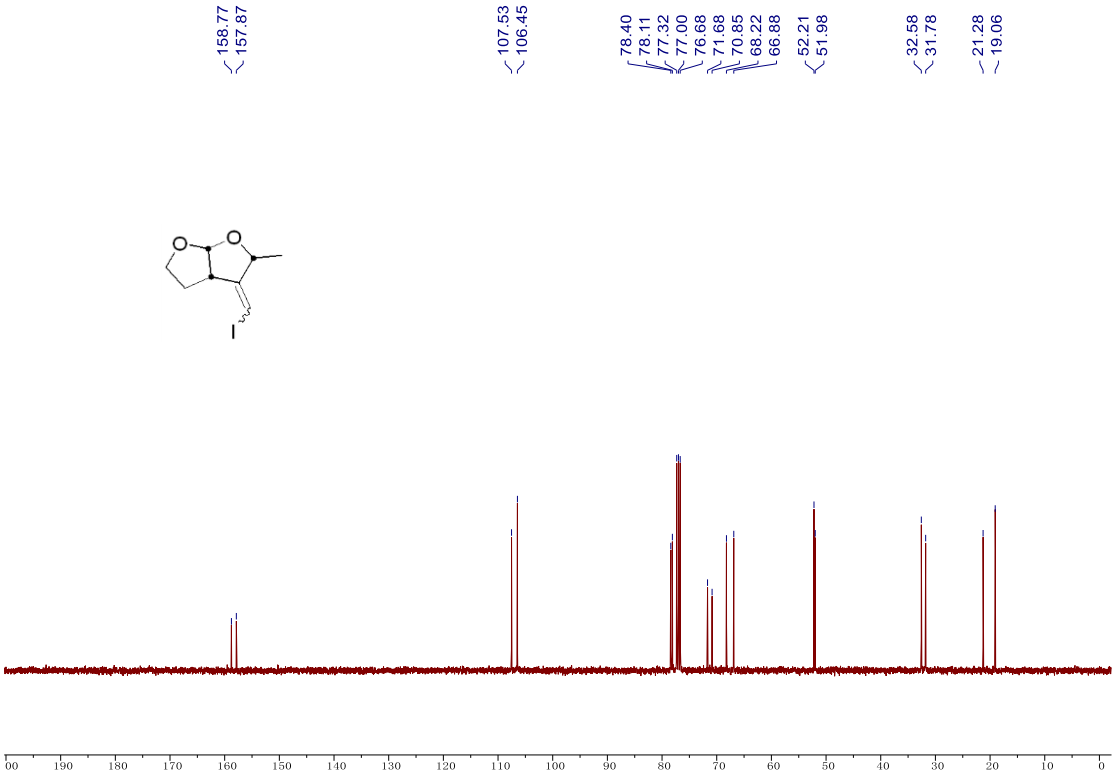


2s-1

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

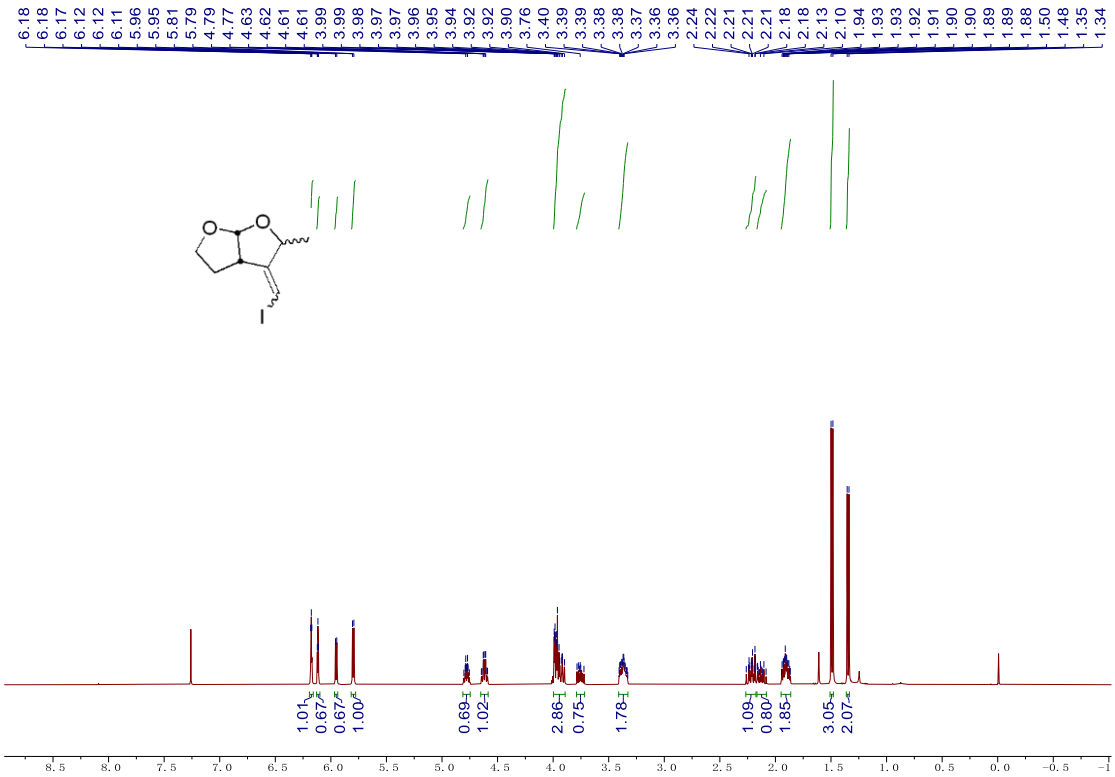


^{13}C NMR ($CDCl_3$, 101 MHz)

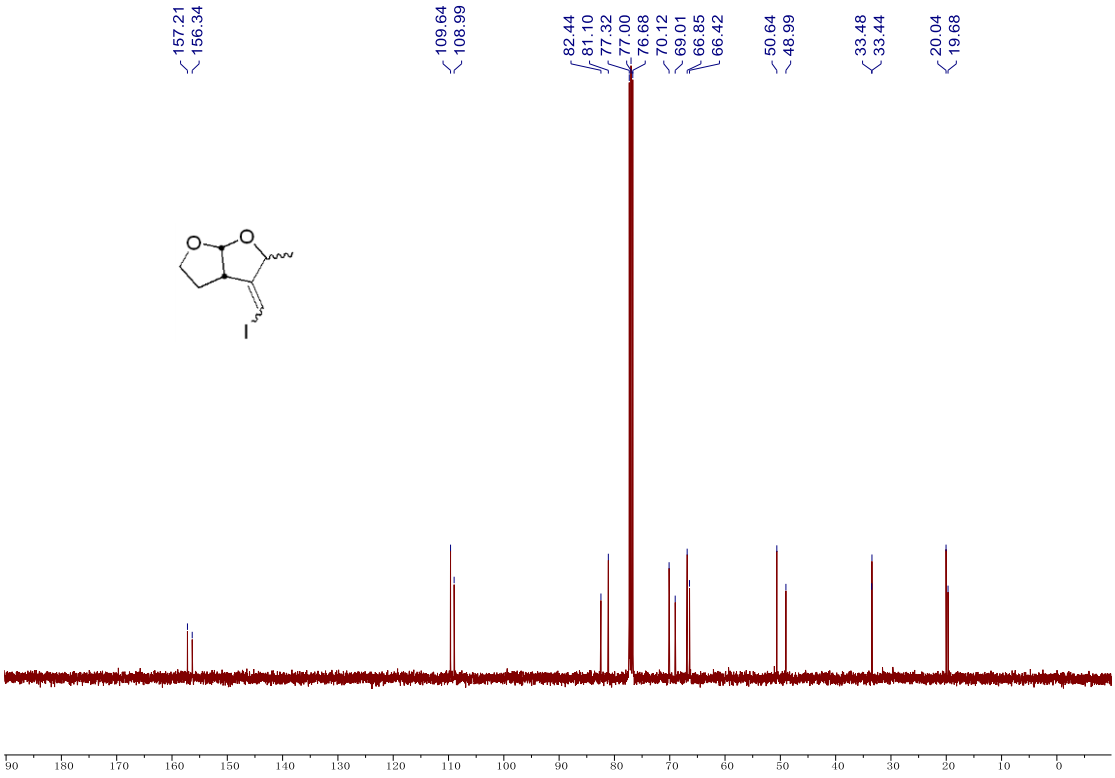


2s-2

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

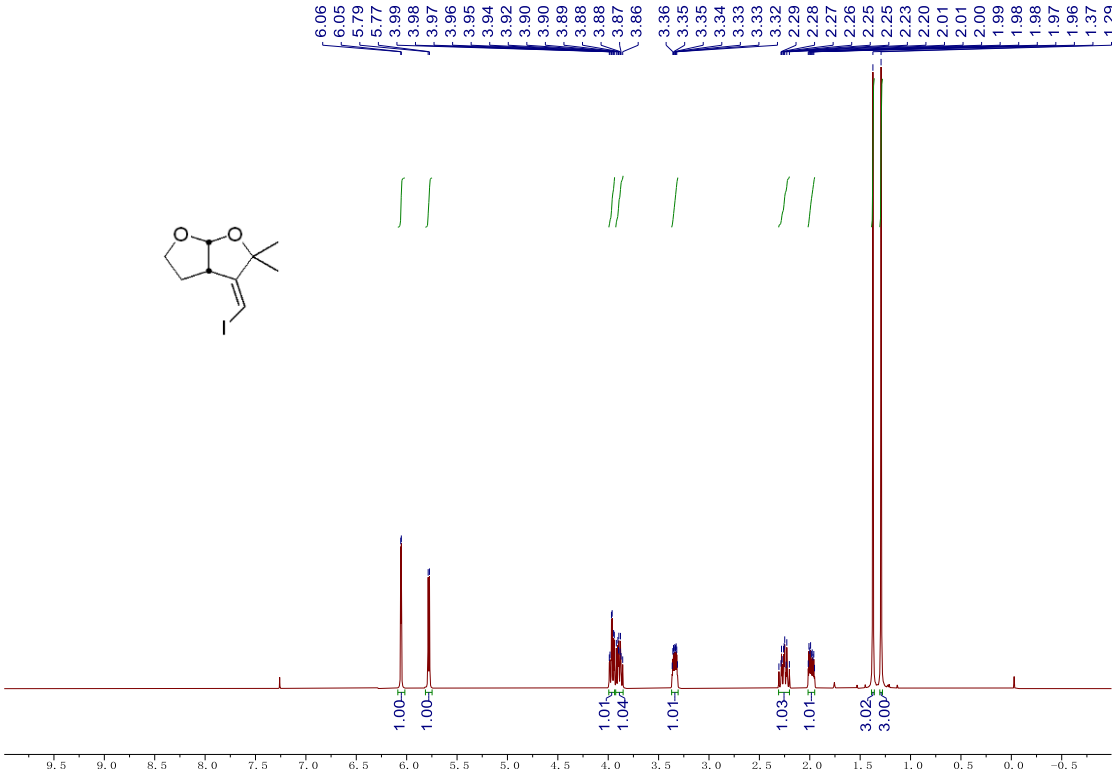


^{13}C NMR ($CDCl_3$, 101 MHz)

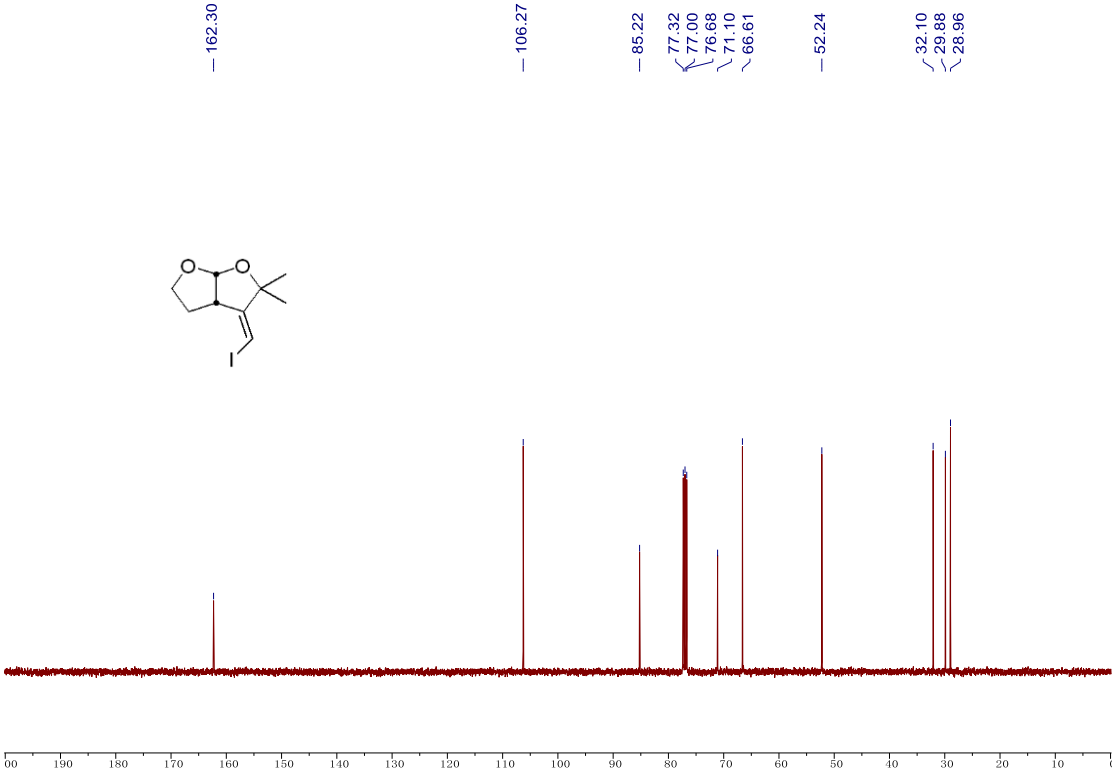


2t-1

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

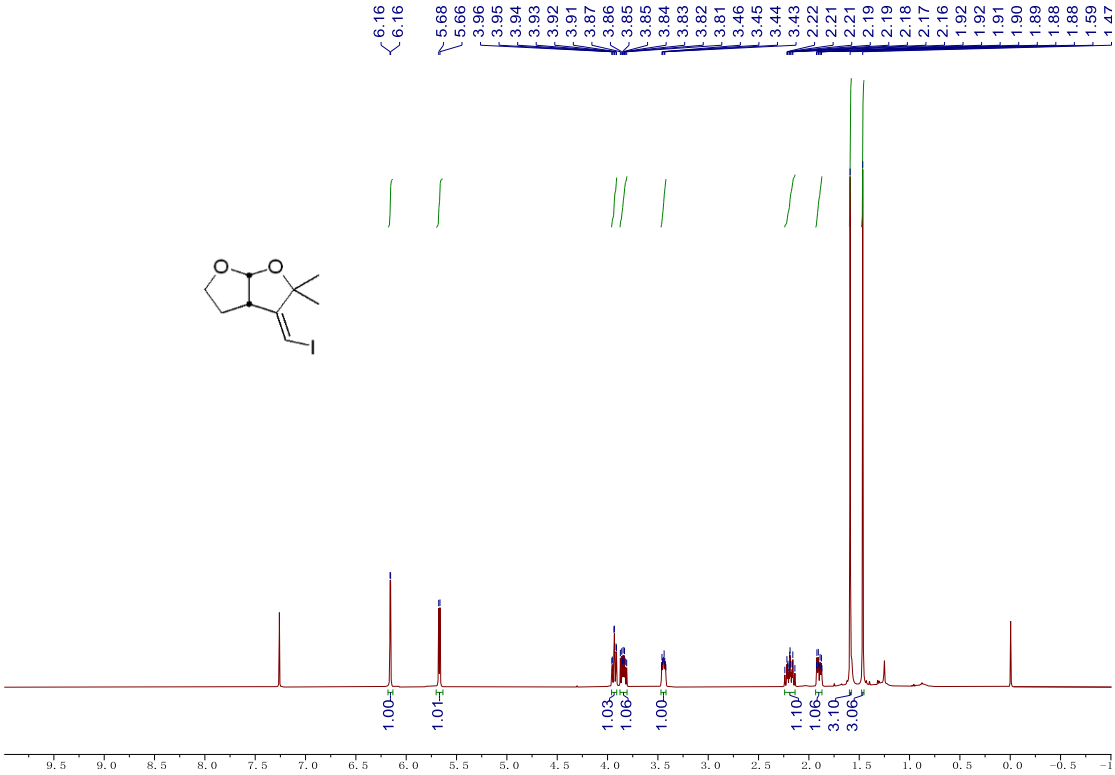


^{13}C NMR ($CDCl_3$, 101 MHz)

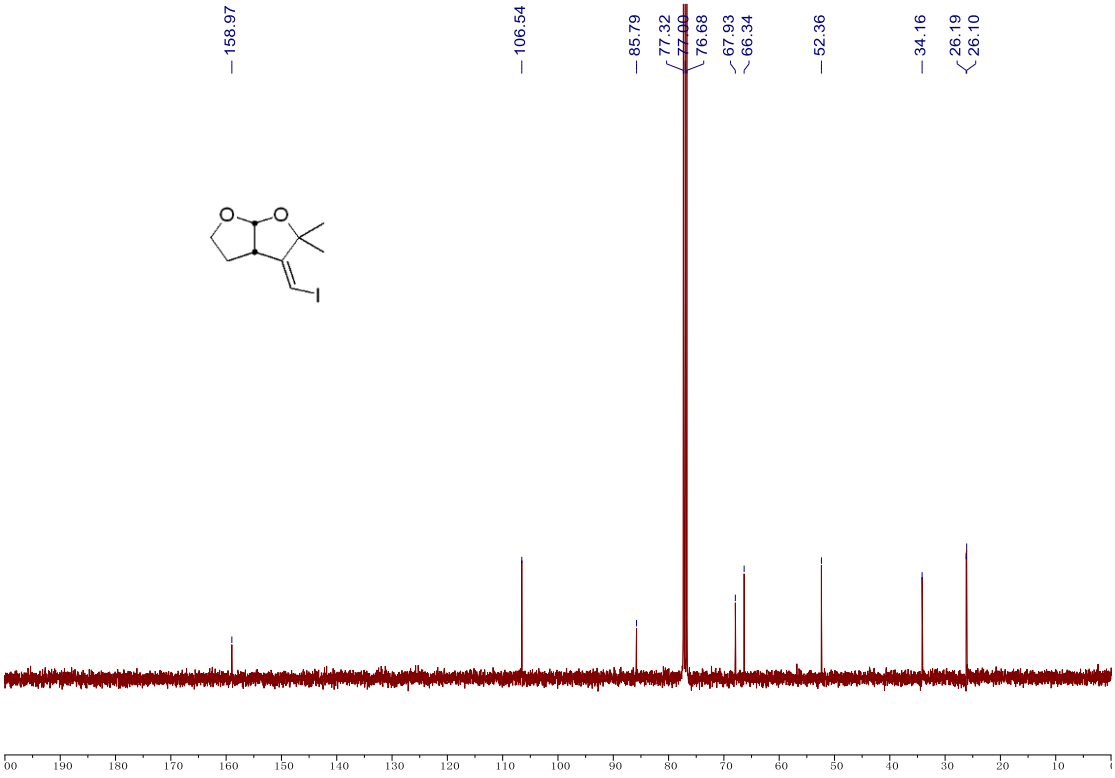


2t-2

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

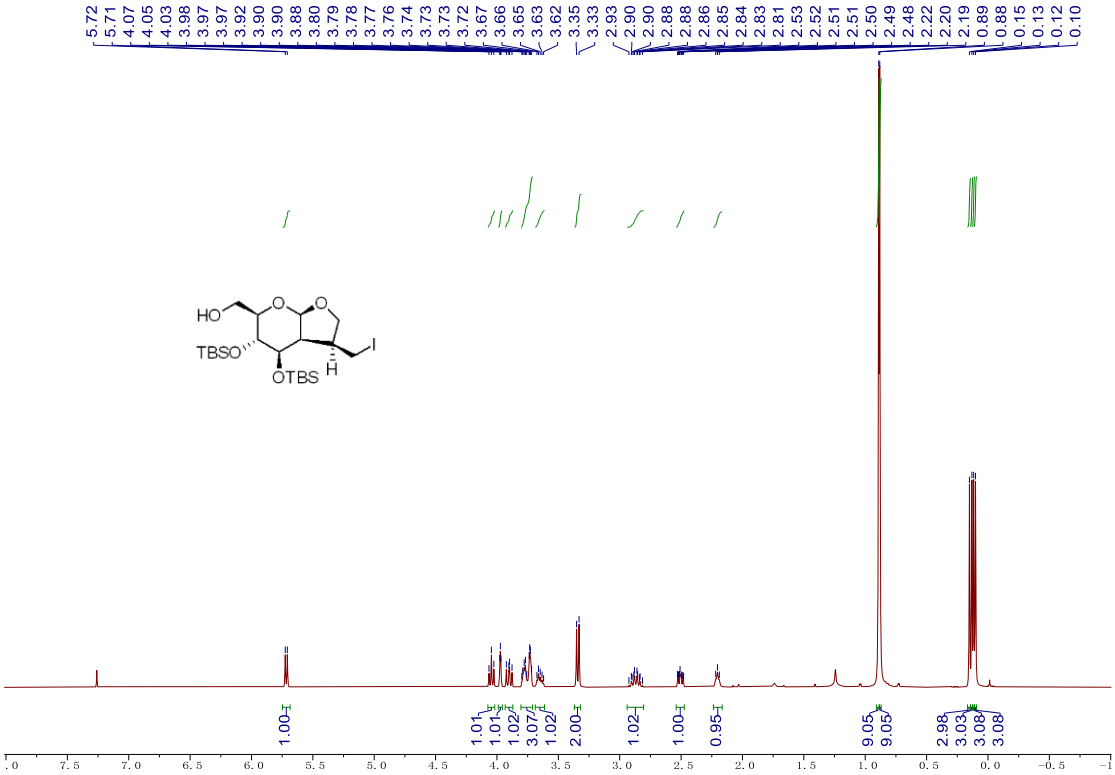


^{13}C NMR ($CDCl_3$, 101 MHz)

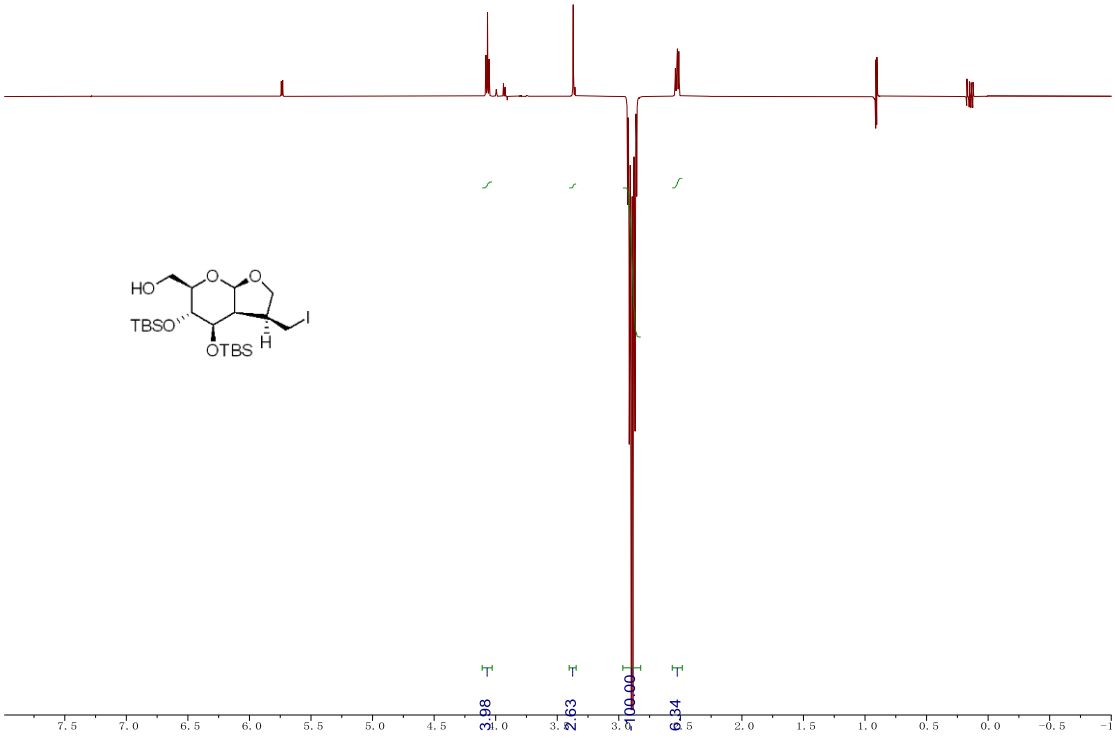


2w

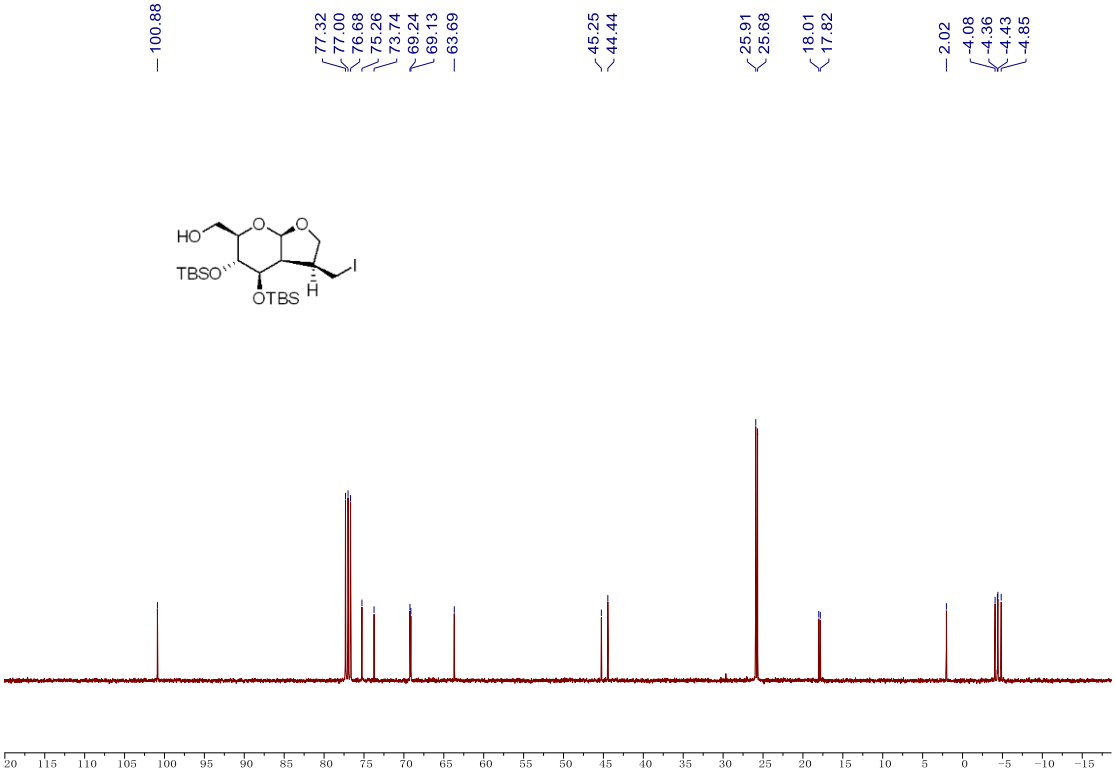
^{1}H NMR ($CDCl_3$, 400 MHz)



NOE Experiment ($CDCl_3$, 600 MHz)

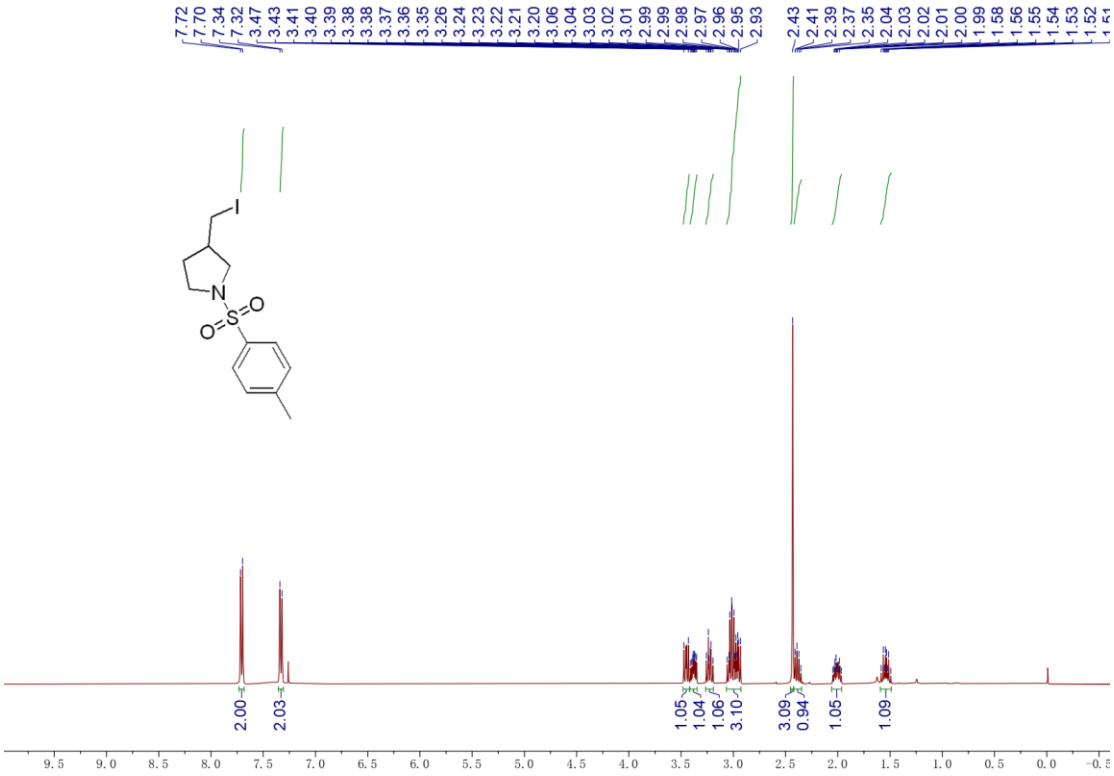


^{13}C NMR ($CDCl_3$, 101 MHz)

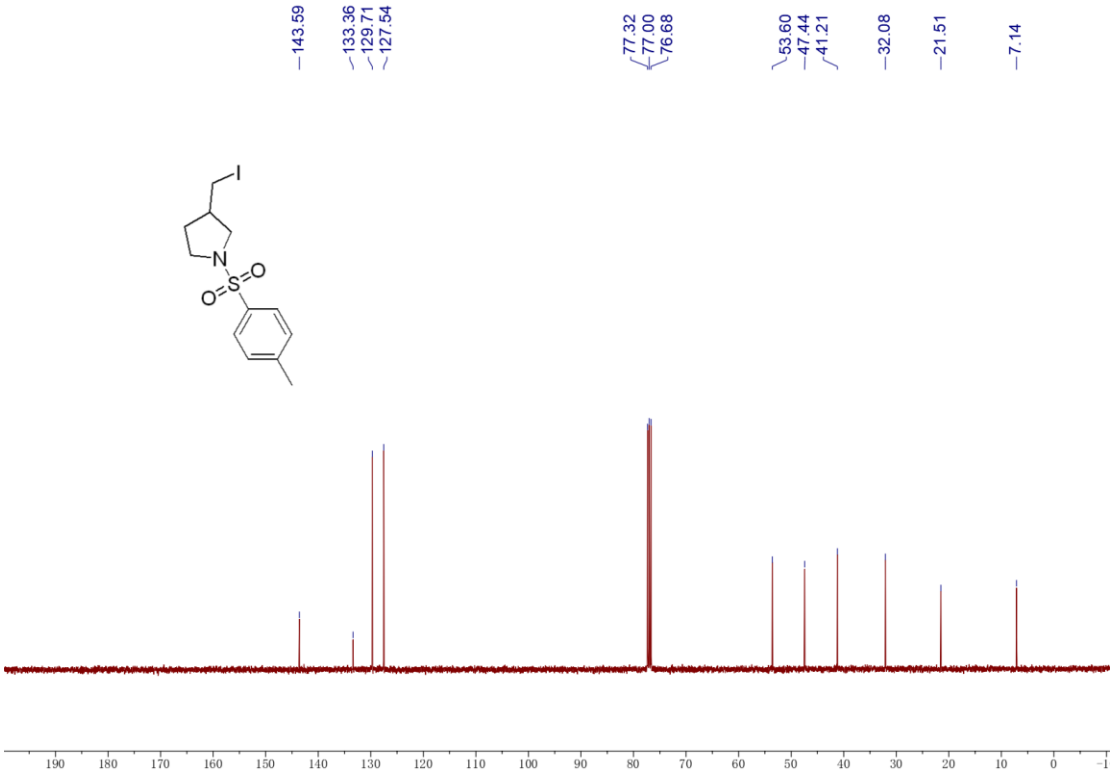


2x

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

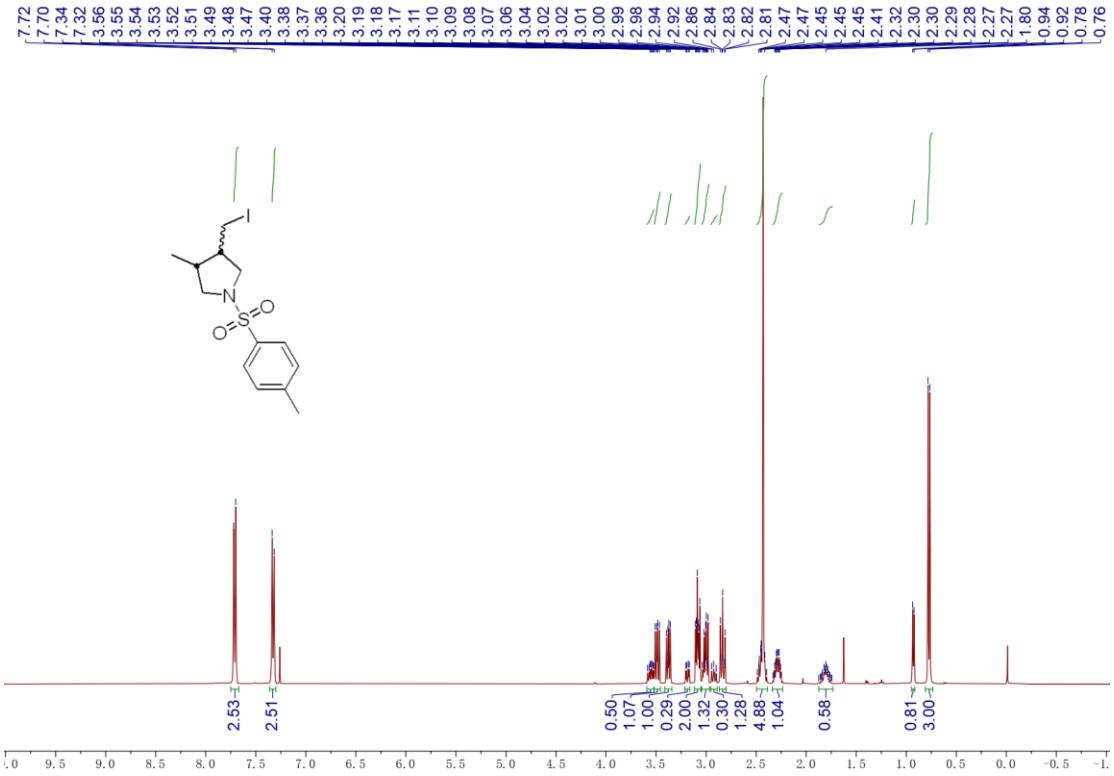


^{13}C NMR ($CDCl_3$, 101 MHz)

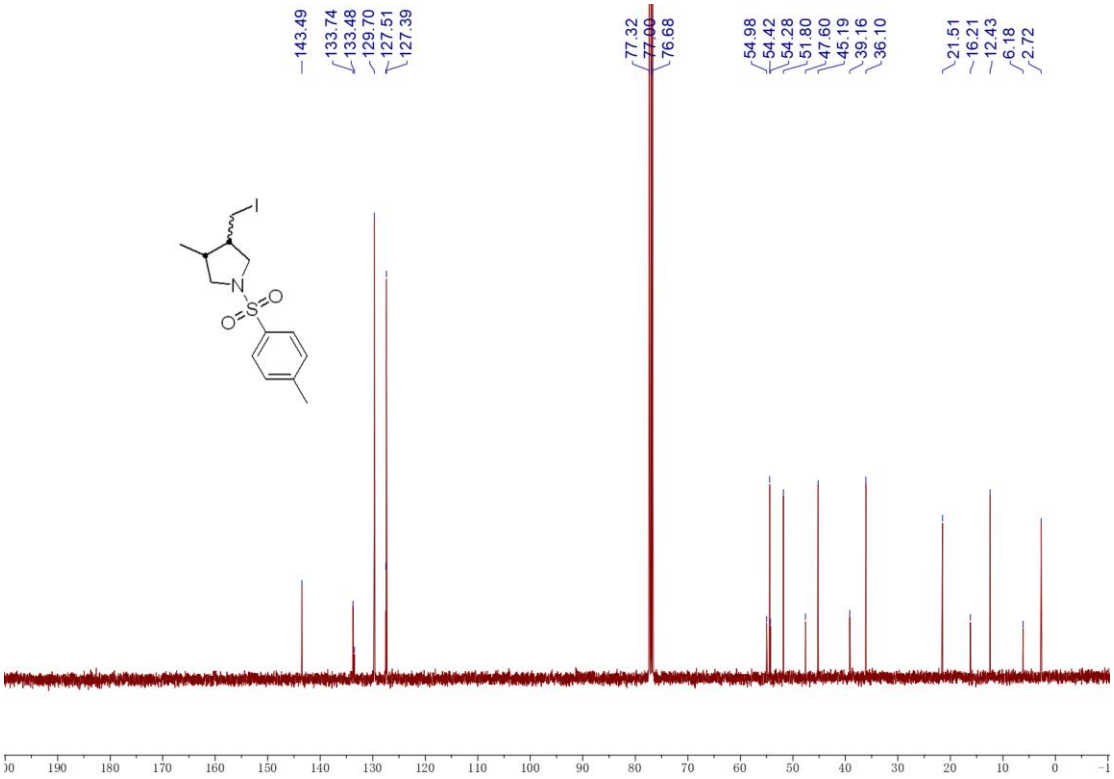


2y

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

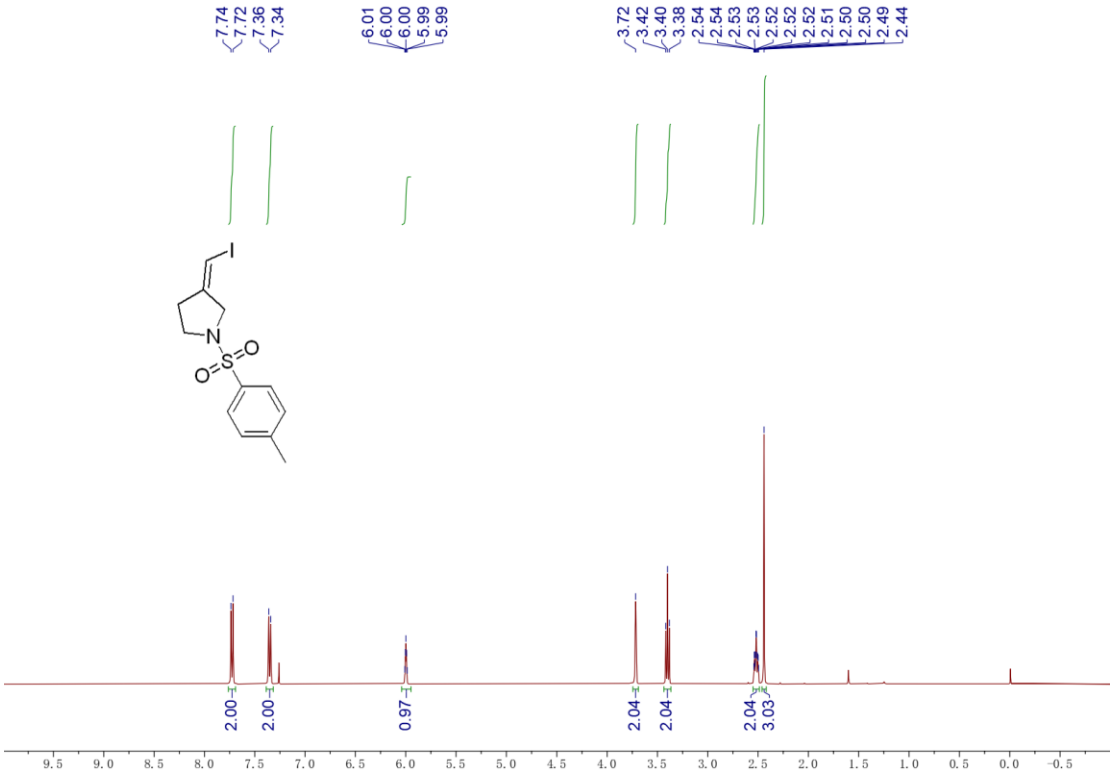


^{13}C NMR ($CDCl_3$, 101 MHz)

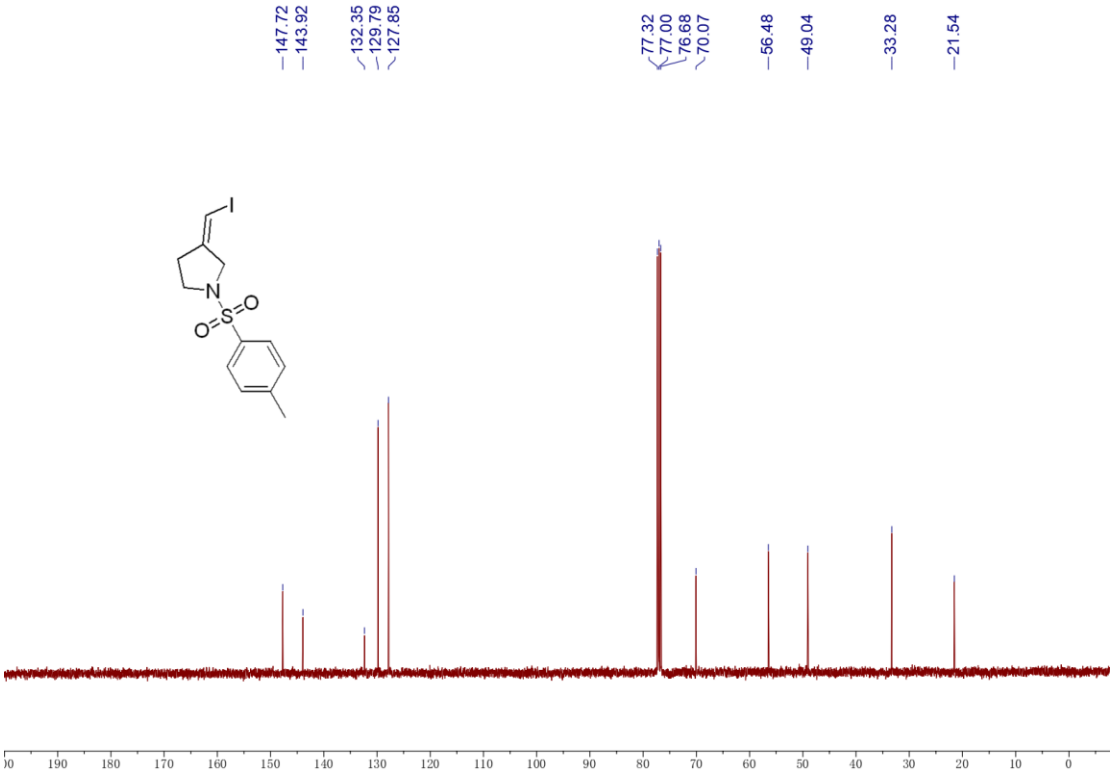


2z

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

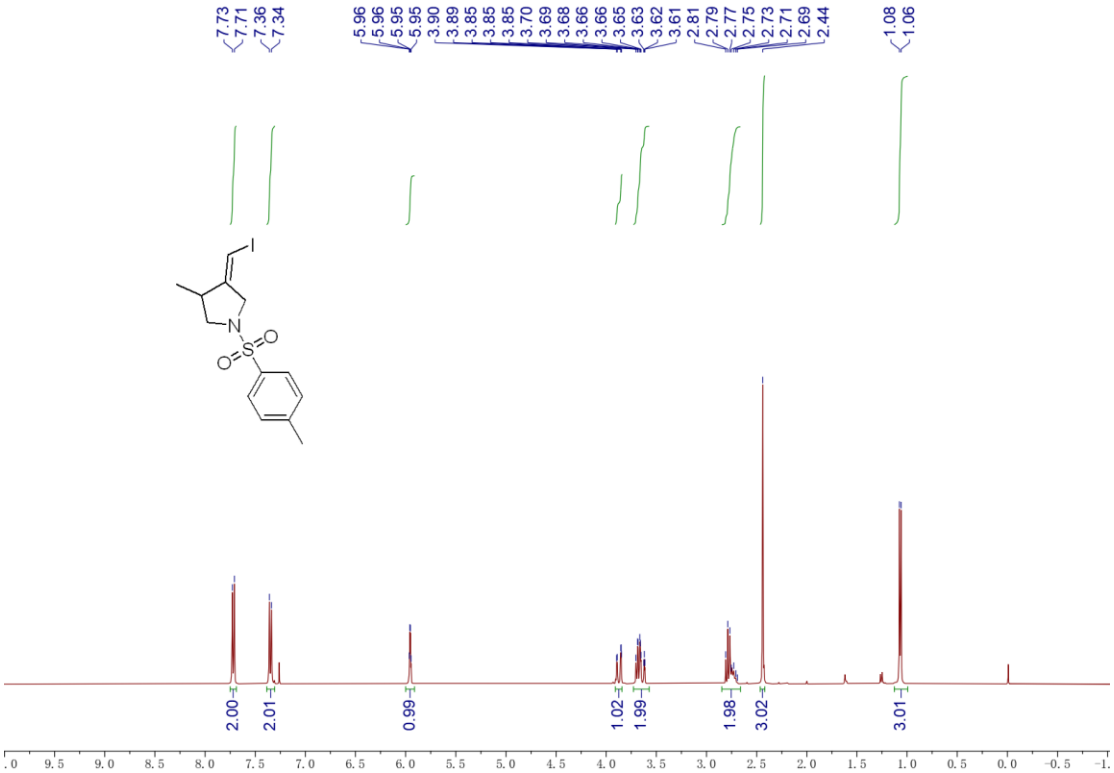


^{13}C NMR ($CDCl_3$, 101 MHz)

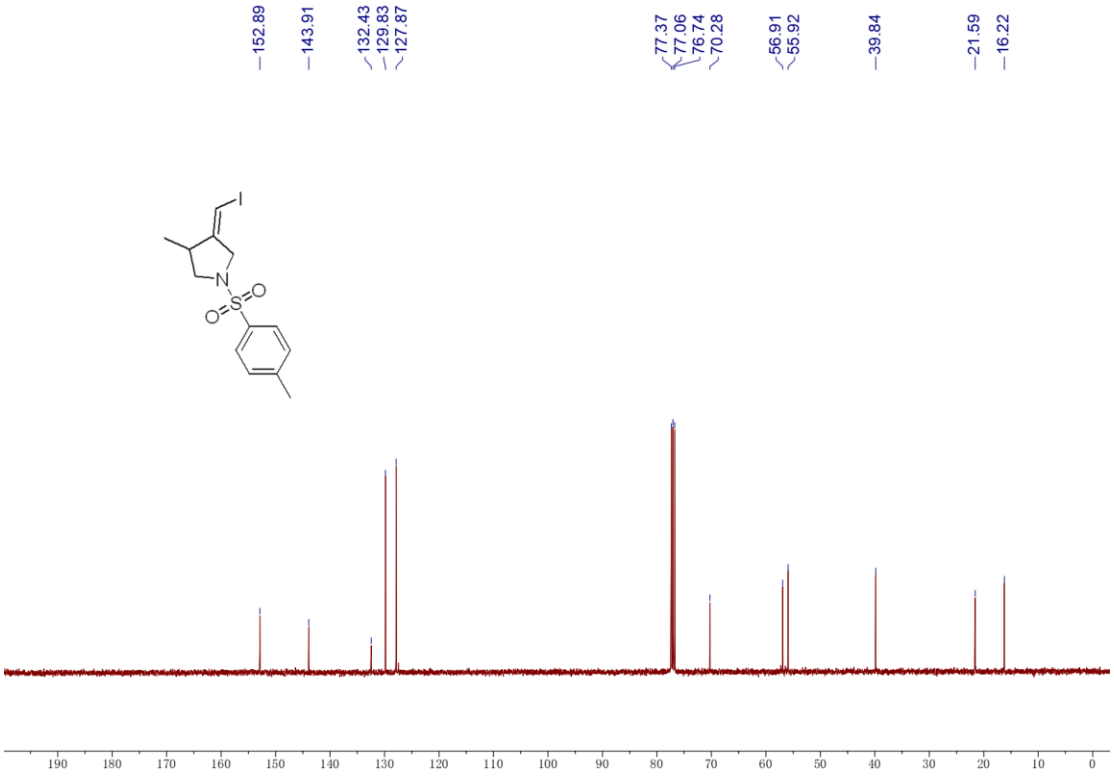


2aa

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



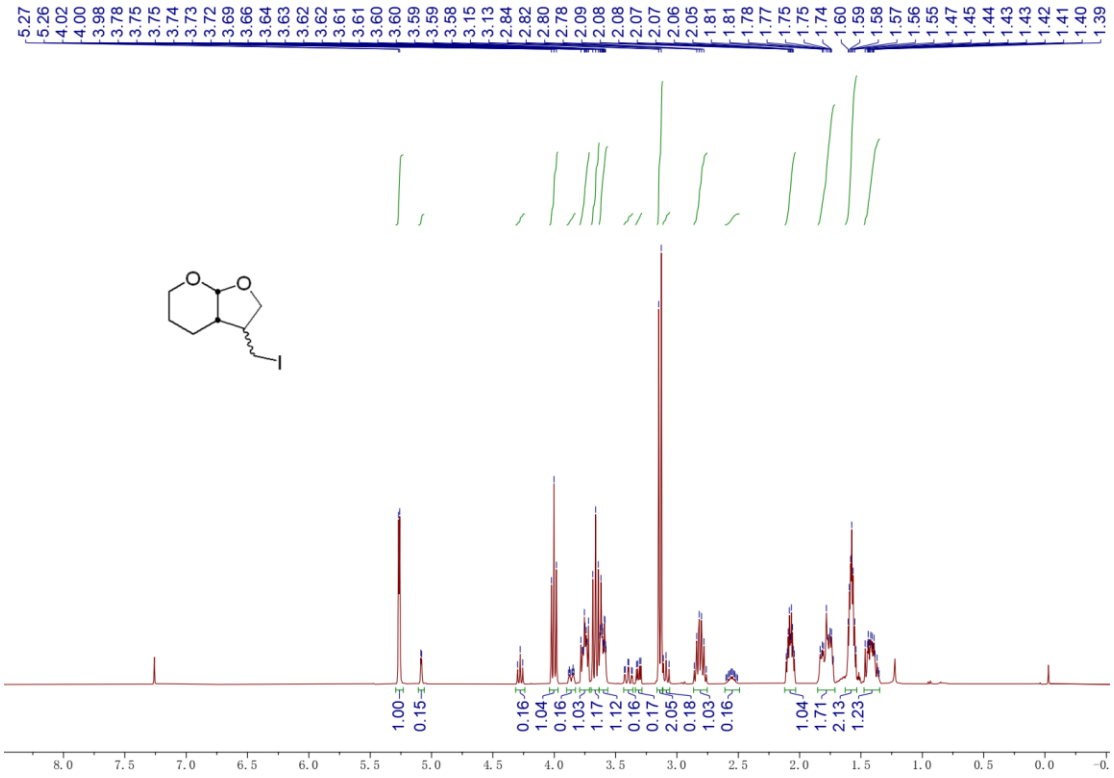
^{13}C NMR ($CDCl_3$, 101 MHz)



With Protocol B:

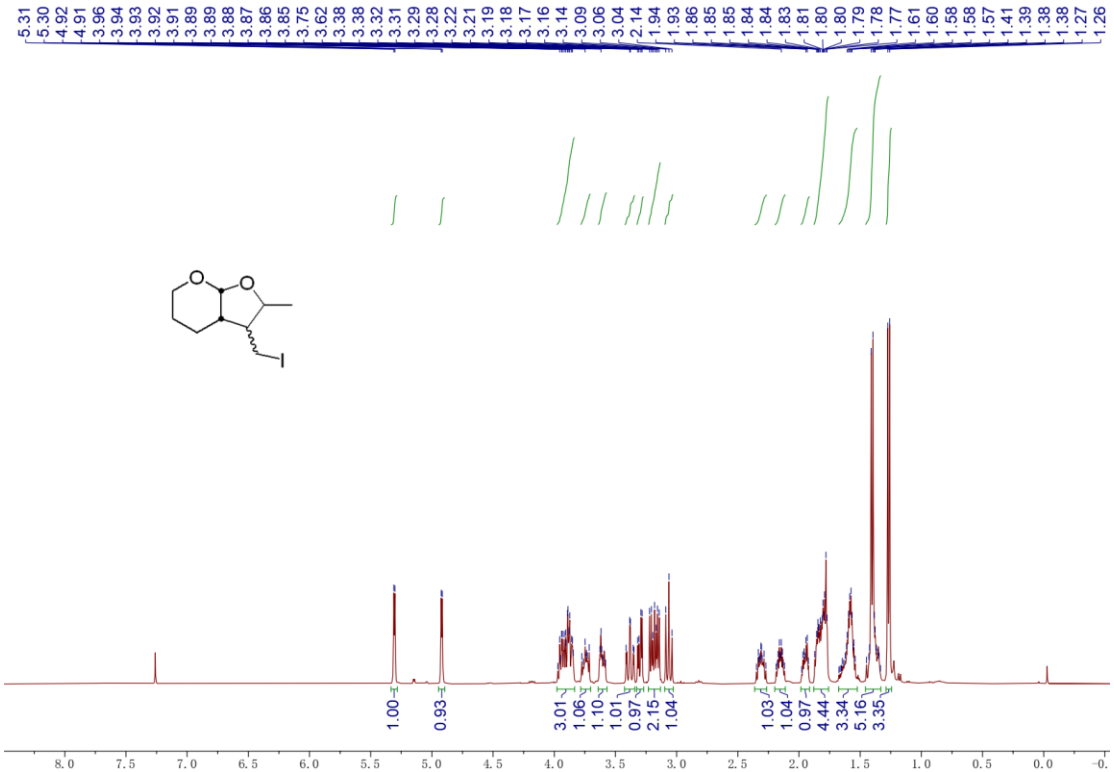
2a

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



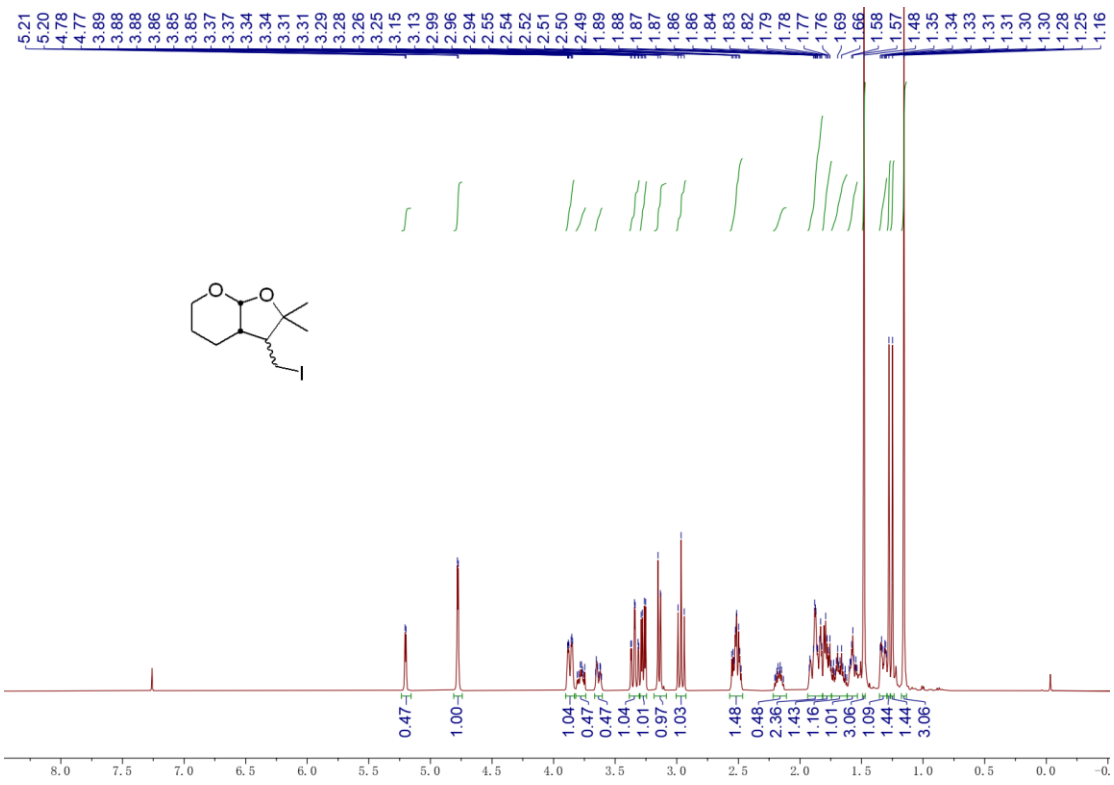
2b

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



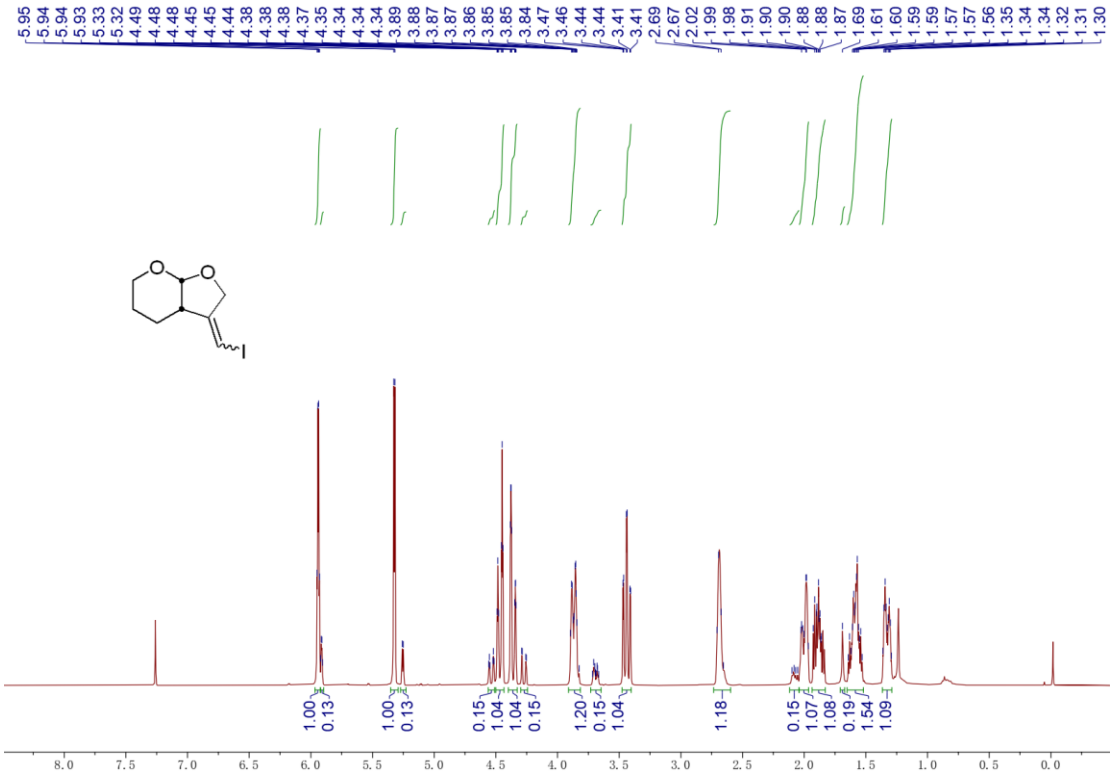
2c

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



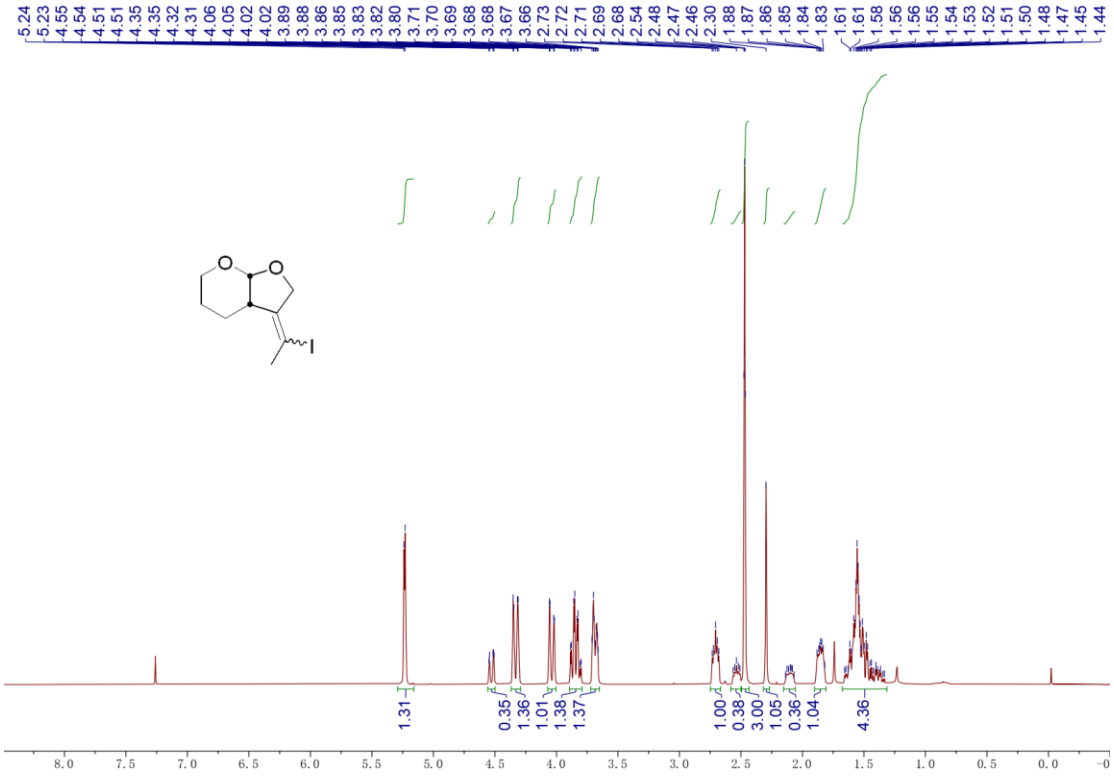
2f

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



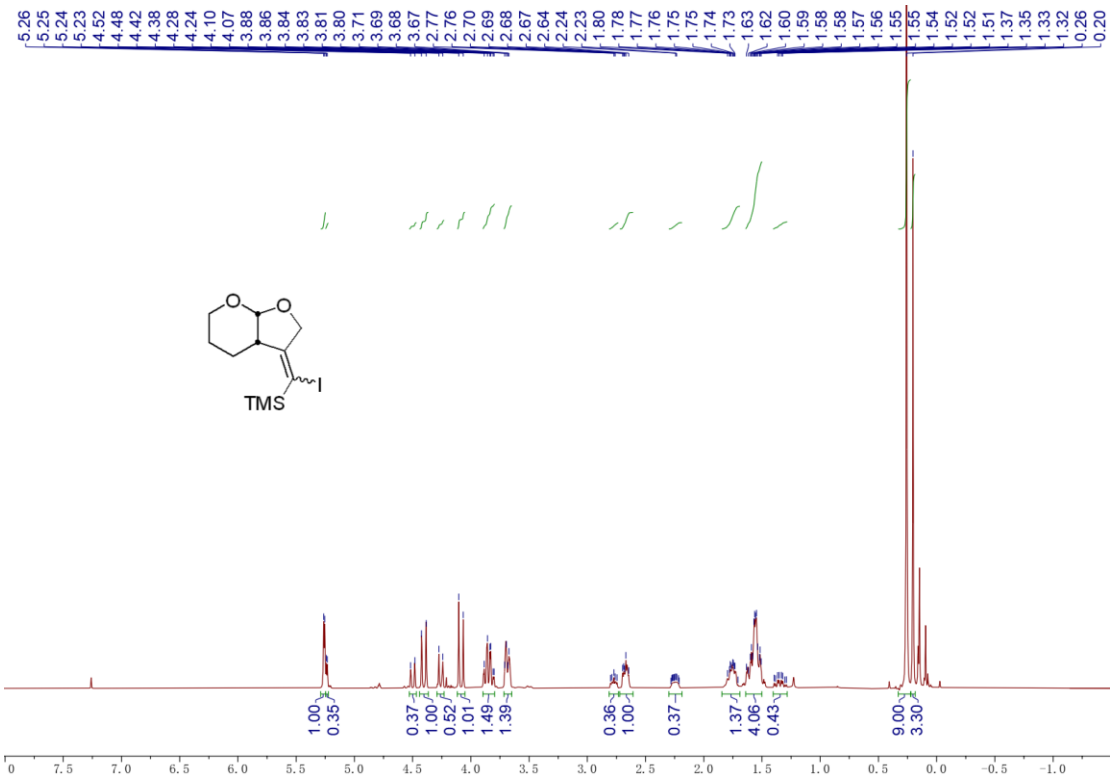
2g

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



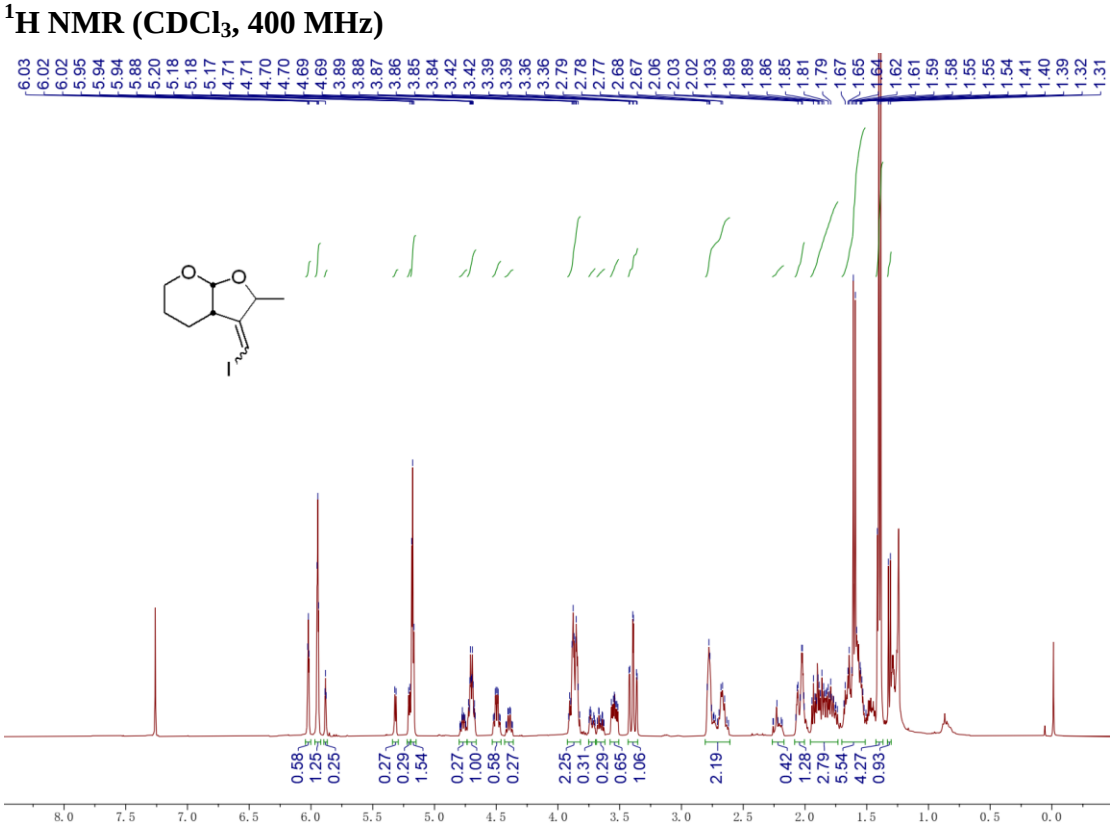
2i

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



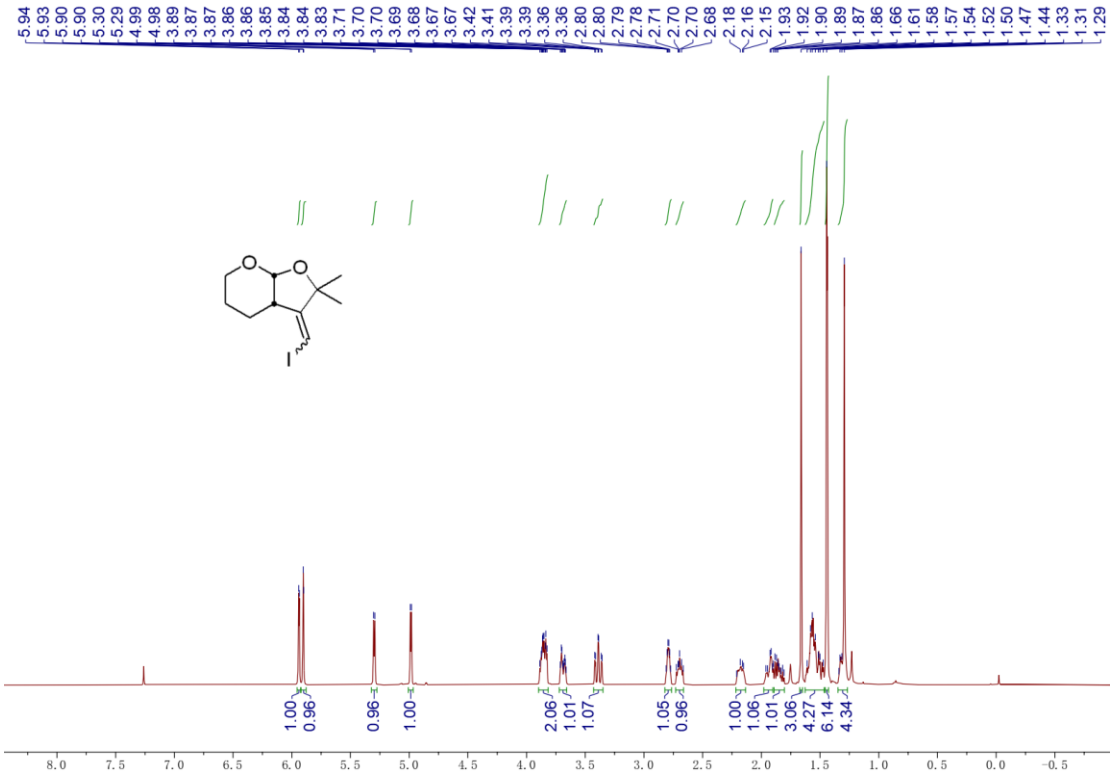
2j

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



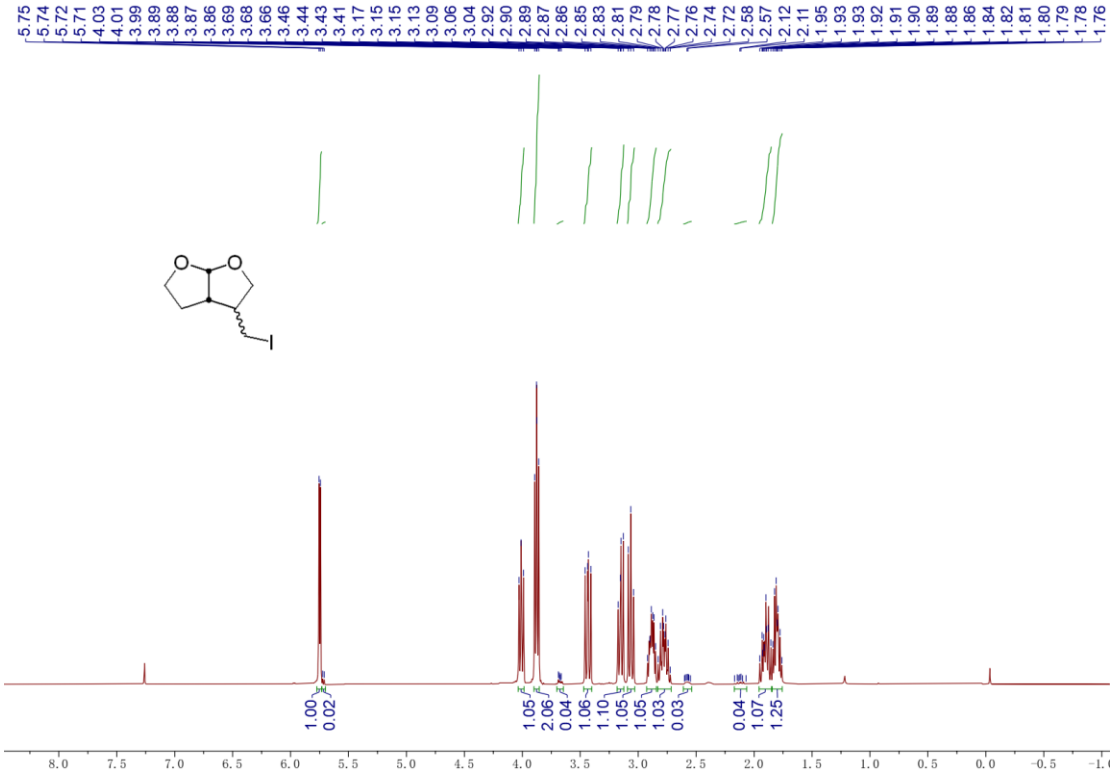
2k

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



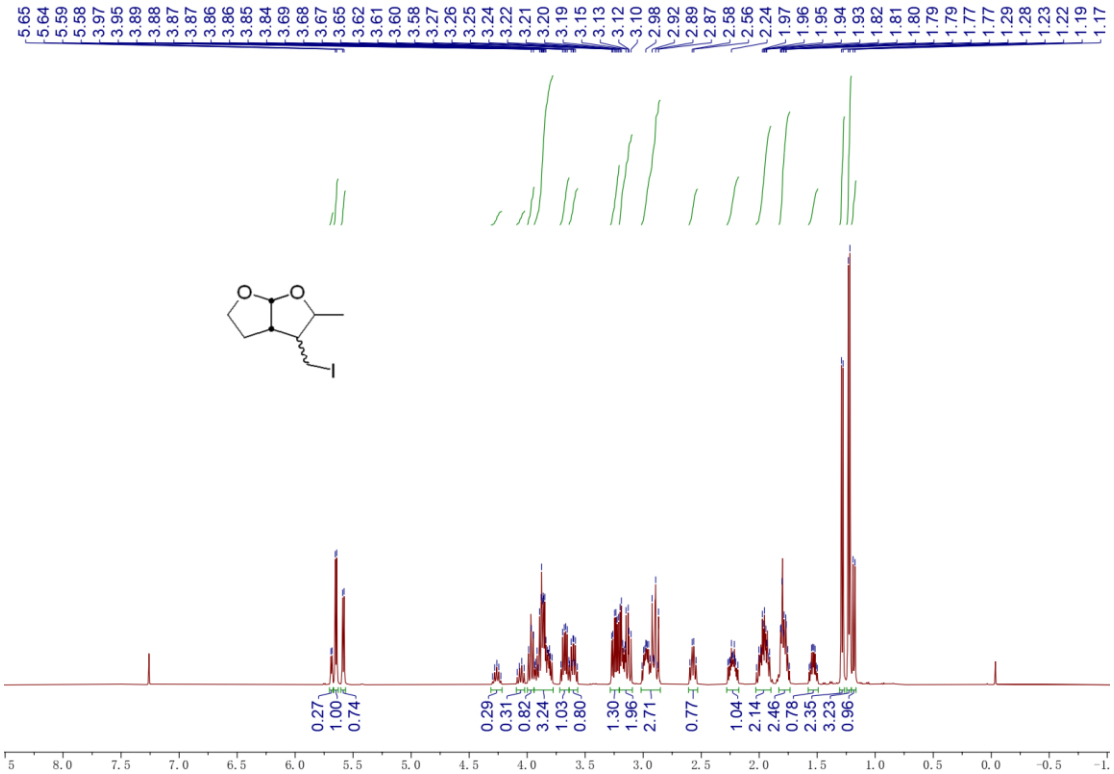
2l

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



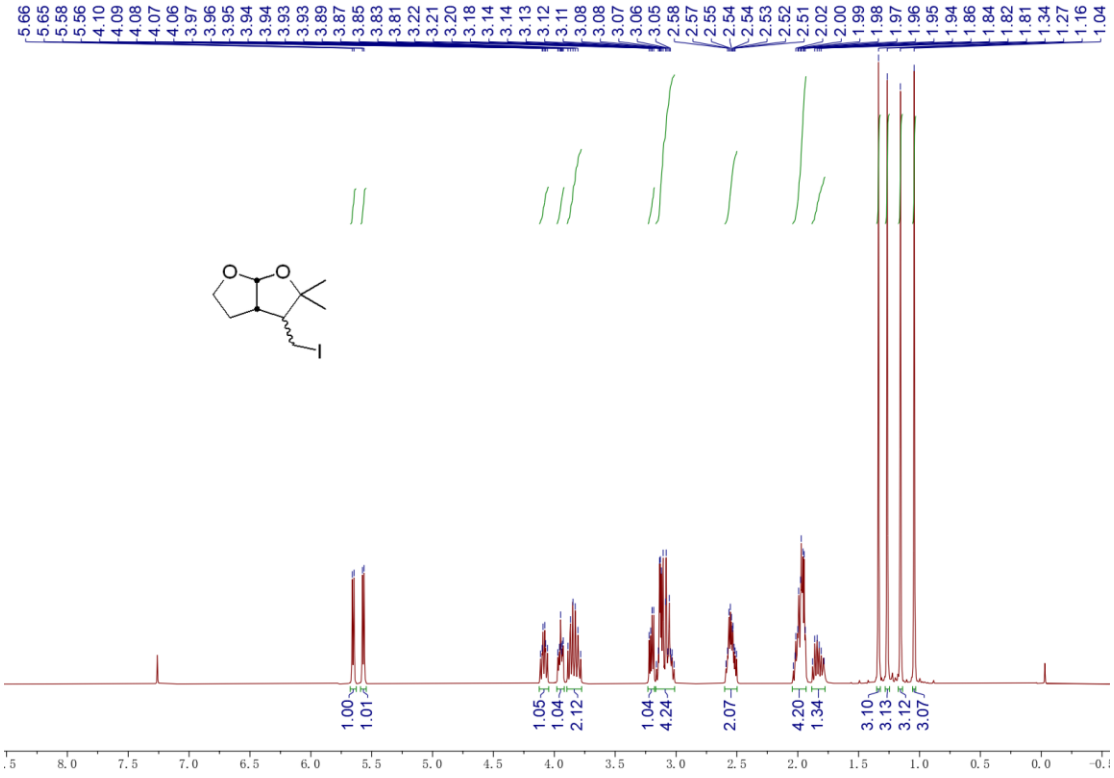
2m

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



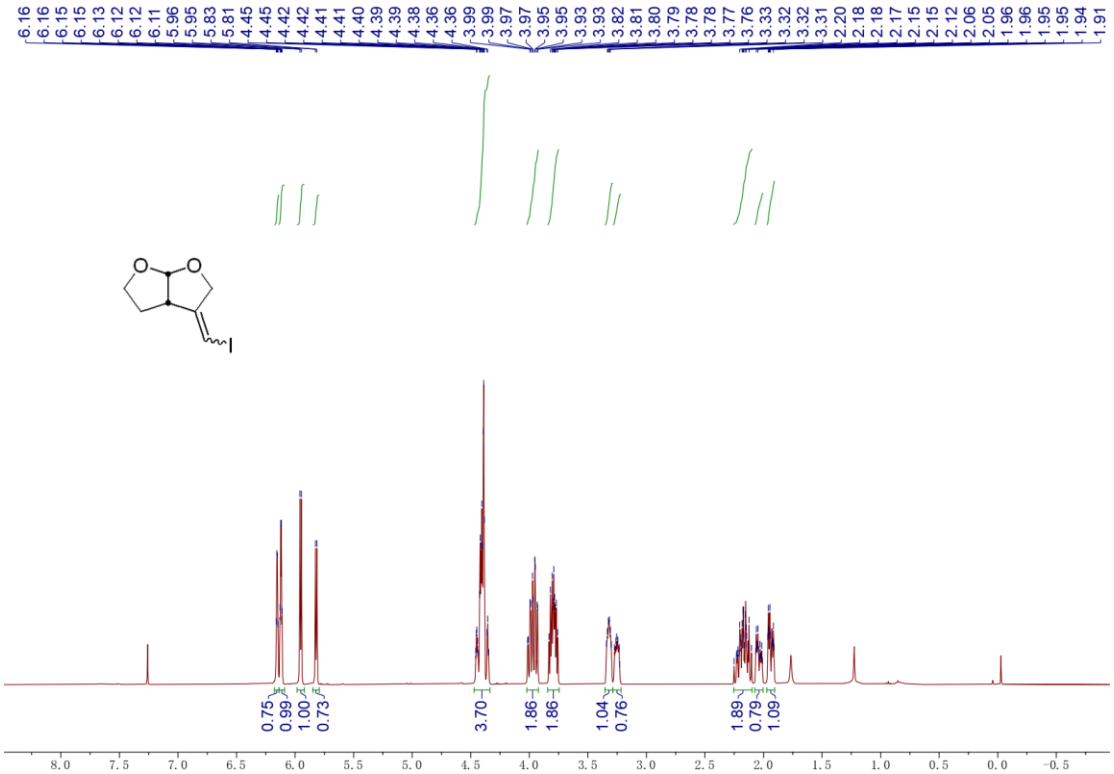
2n

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



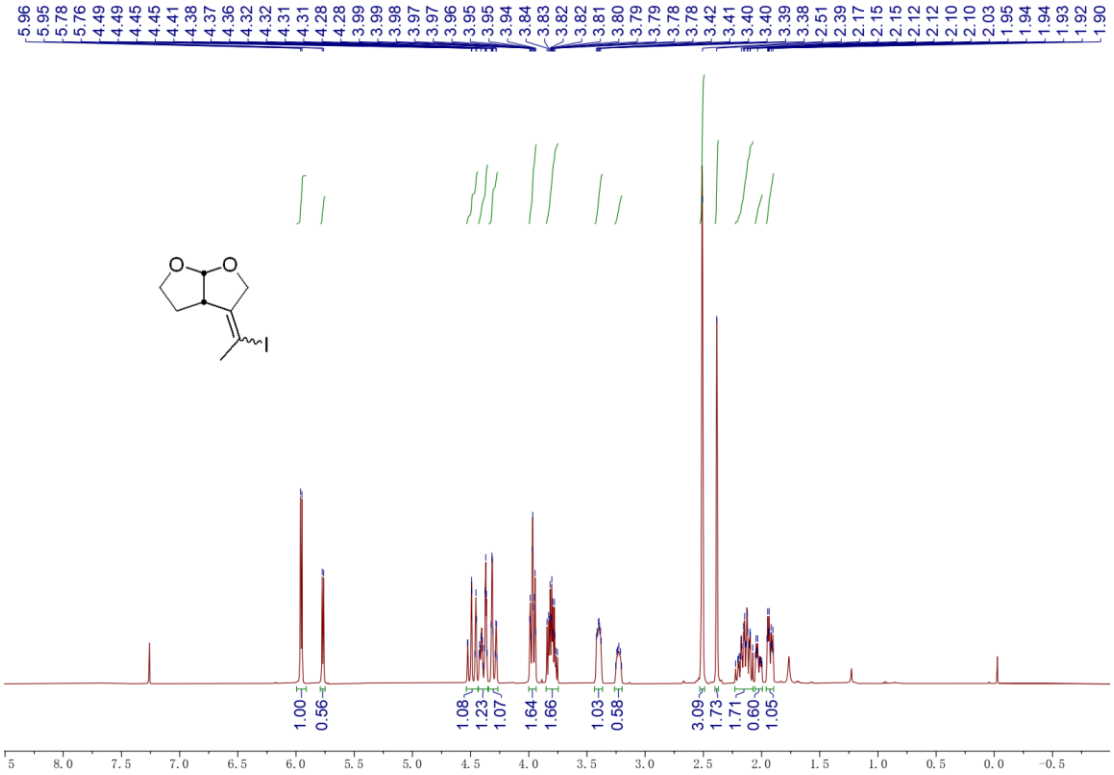
2o

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



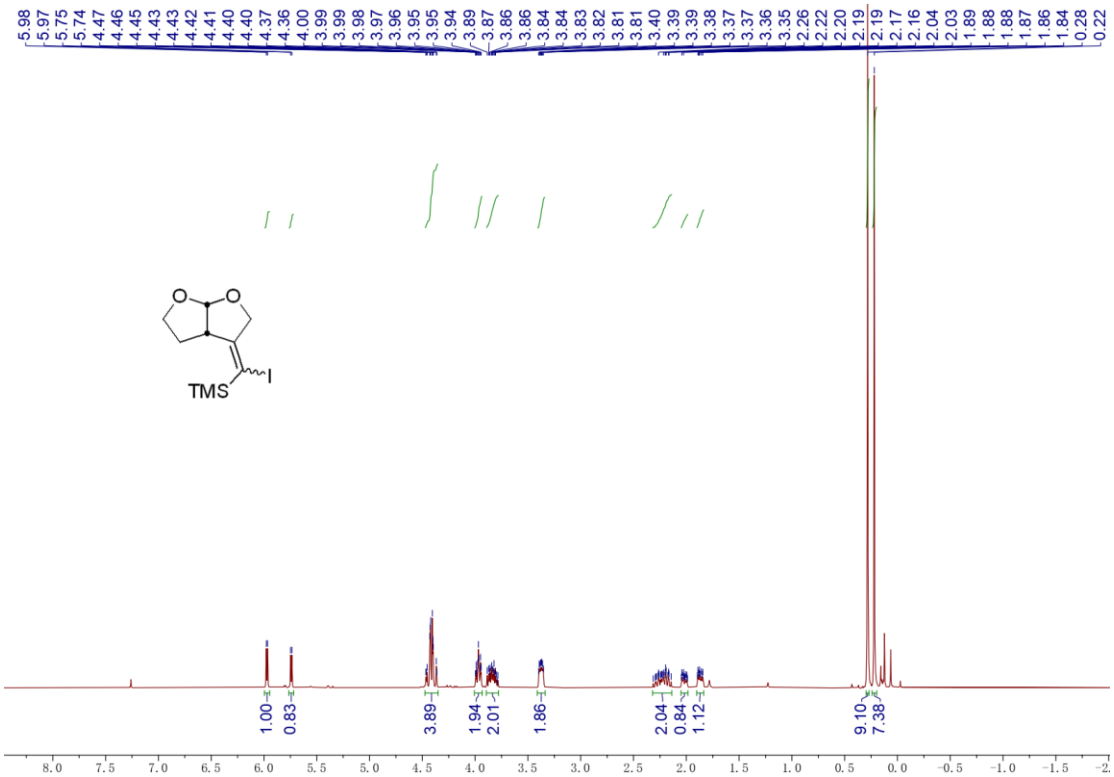
2p

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



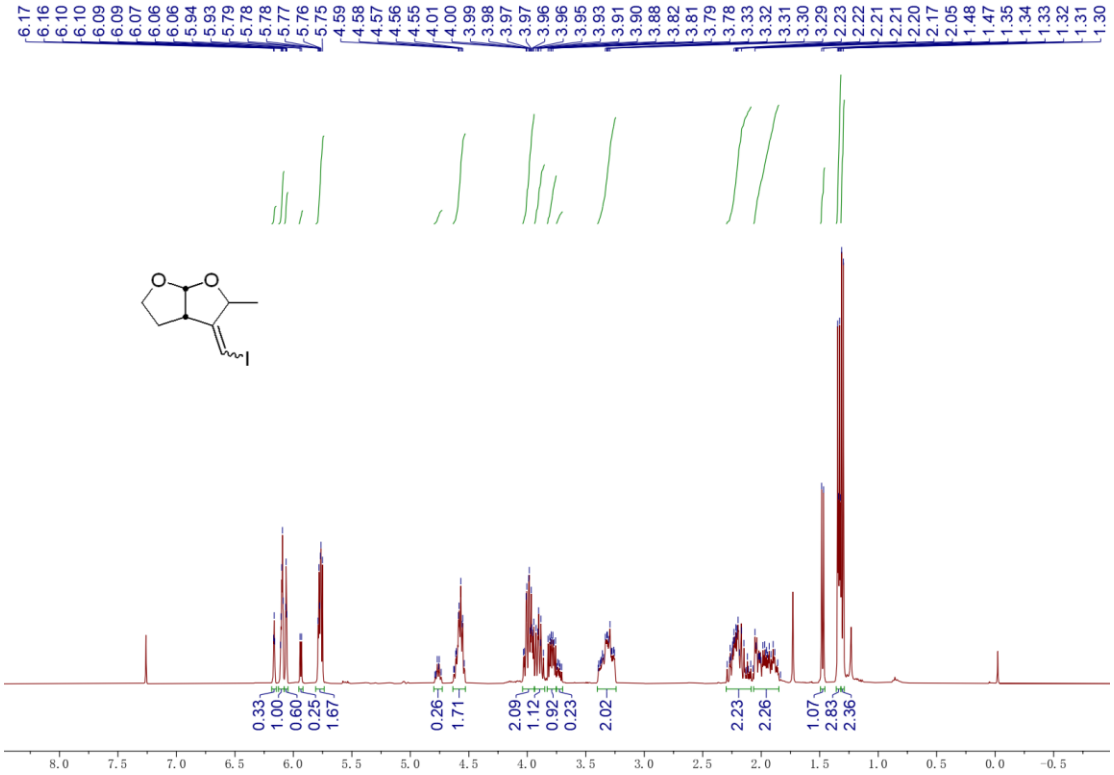
2r

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



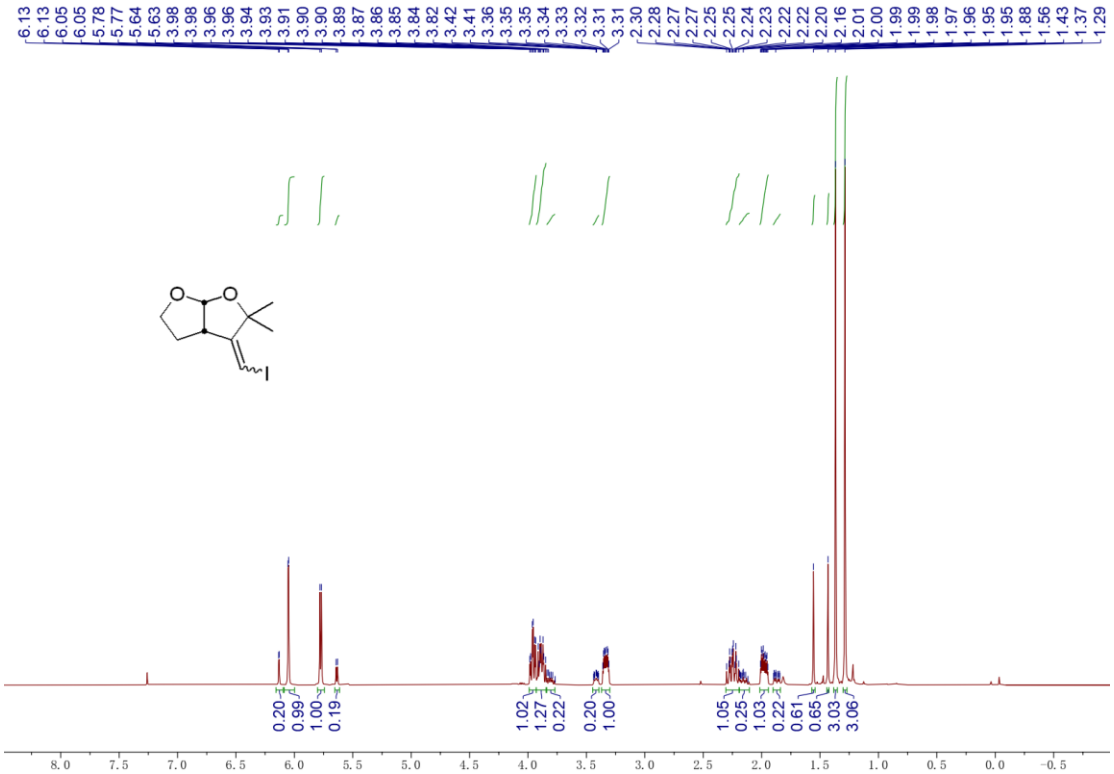
2s

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



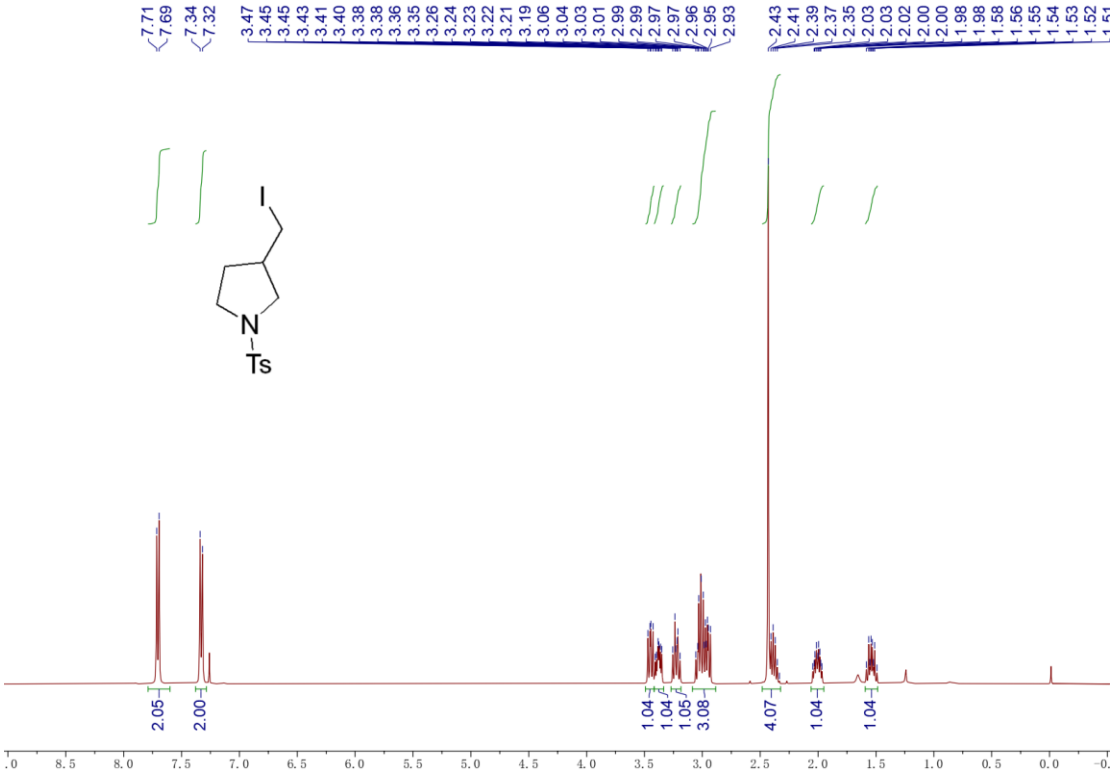
2t

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



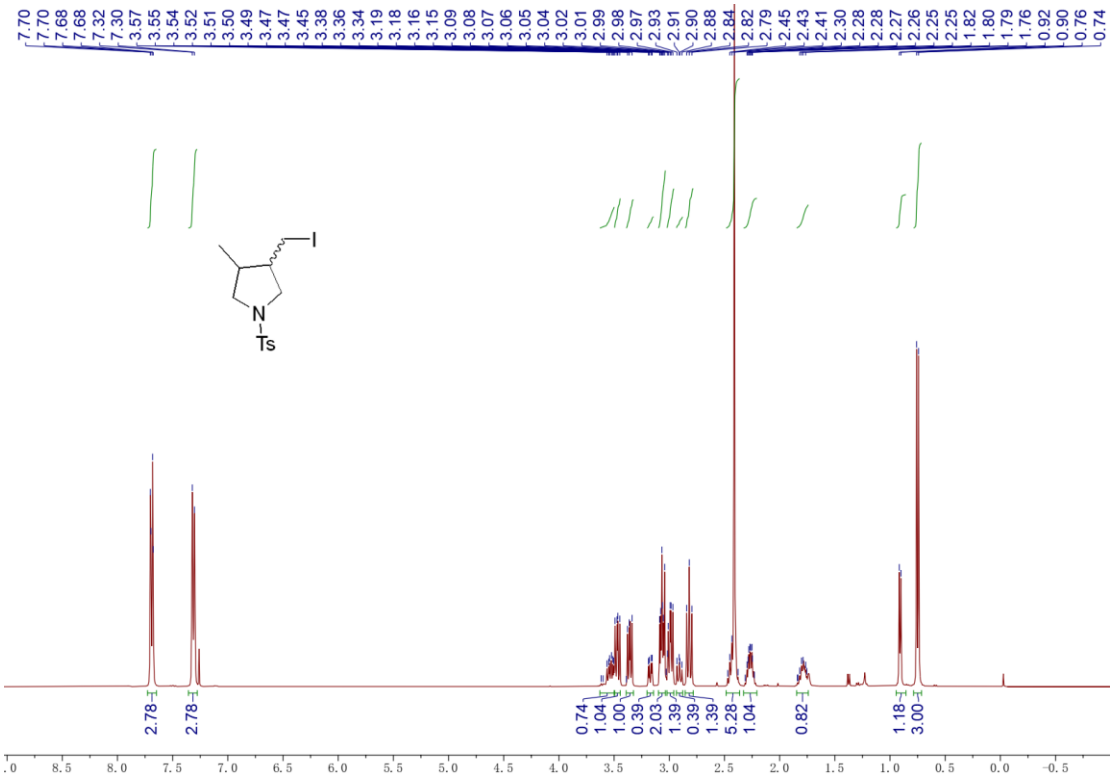
2x

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



2y

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



2aa

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