

Supporting Information

Construction of pyrroles and furans via intramolecular cascade desulfonylative/dehydrogenative cyclization of vinylidenecyclopropanes induced by NXS (X = I or Br)

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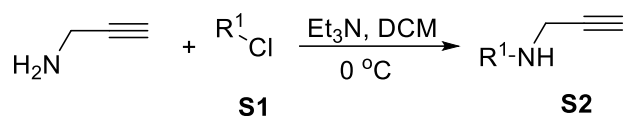
1. General remarks

^1H , ^{13}C and ^{19}F NMR spectra were recorded at 400 MHz or 600 MHz, 100 MHz or 150 MHz and 376 MHz, respectively. HRMS spectra were recorded by EI, ESI, FI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Mass spectra were recorded by EI, ESI, and HRMS was measured on an Agilent Technologies 6224 TOF LC/MS instrument and a Waters Micromass GCT Premier. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC plate analysis with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure.

2. General procedures for the synthesis of substrates 1

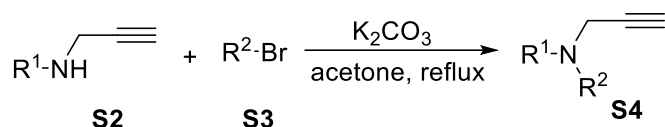
Synthesis of substrates **1a-1n**, **1q-1s**, **1r-1y**, and **1aa-1ae**^[1]

Step 1



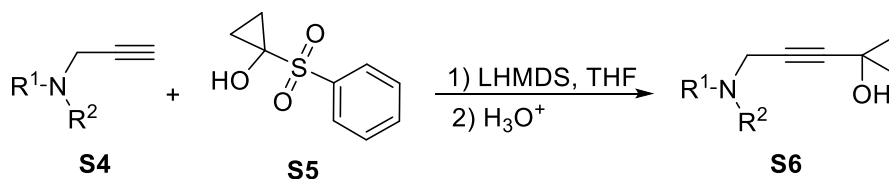
To a solution of **S1** (60 mmol) in DCM (100 mL) was added Et₃N (90 mmol) and 2-propargylamine (90 mmol) at 0 °C and the resulting solution was allowed to stir at 0 °C for 12 h. Extracted with H₂O (20 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduced pressure to dryness to give a yellow solid **S2**.

Step 2



To a solution of **S2** (50 mmol) in acetone (100 mL) was added K₂CO₃ (1.5 equiv) and **S3** (2.0 equiv). The resulting solution was allowed to stir at 70 °C for 12 h. After filtration, the organic phase was concentrated under reduced pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S4** (PE:EA = 10:1).

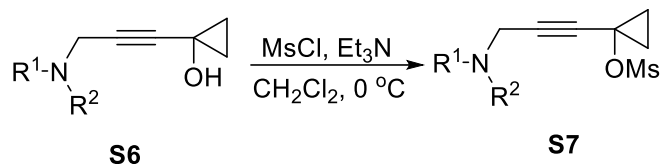
Step 3



To a solution of compounds **S4** (20 mmol) in THF (30 mL) was slowly added LHMDS (24 mmol, 1.0 M in THF) at -78 °C under the protection of argon and the resulting solution was allowed to stir at -78 °C for 30 min before a solution of **S5** (10 mmol) in THF (10 mL) was added into the above mixture. Consequently, the reaction mixture was allowed to warm up to room temperature and the mixture was left standing overnight. Then, saturated NH₄Cl solution was added to quench the reaction. Extracted with ethyl acetate, dried over anhydrous Na₂SO₄, and filtered, the organic phase

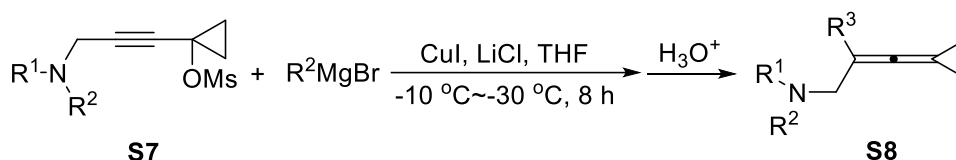
was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S6** (PE:EA = 4:1~2:1).

Step 4



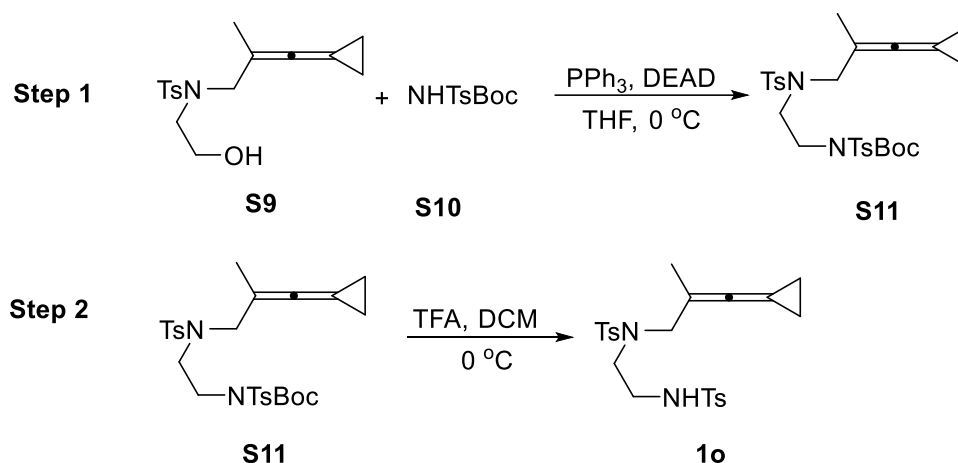
To a solution of **S6** (5.0 mmol) and anhydrous Et₃N (2.0 equiv) in CH₂Cl₂ (20 mL) was added MsCl (2.0 equiv) at 0 °C under the protection of argon and the resulting solution was allowed to stir at 0 °C for 1.0 h before some amounts of water were added to quench the reaction. Extracted with CH₂Cl₂ (20 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue purified by a flash column chromatography on silica gel to give the desired products **S7** (PE:EA = 2:1).

Step 5



To a flame dried 50 mL three-neck flask was added anhydrous CuI (8.8 mmol), LiCl (8.8 mmol) and the solvent THF (20 mL) under the protection of argon and then, the flask was cooled to -10 °C before the solution of RMgBr or RMgCl (2.0 M, 4.0 mL) was added dropwise into the flask under argon. After 5 minutes, the flask was moved into a -30~-40 °C bath and the reaction mixture was stirred for a while before a solution of **S7** (4.0 mmol) in THF (10 mL) was added dropwise into the above flask. The resulting solution was allowed to stir at -40 °C for 8 h before saturated NH₄Cl solution was added to quench the reaction. Extracted with EA (20 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S8** (PE:EA = 10:1).

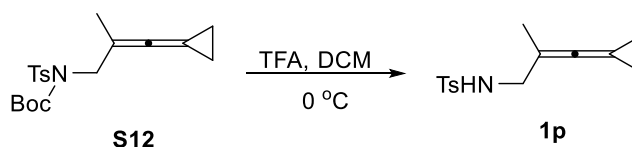
Synthesis of substrate **1o**



Step 1: To a flame dried 50 mL flask was added **S9** (2 mmol), **S10** (1.2 equiv), PPh₃ (1.2 equiv) and the solvent THF (10 mL) under the protection of argon. Then, the flask was cooled to 0 °C before the DEAD (1.2 equiv) was added dropwise into the flask under argon. The resulting solution was allowed to stir at 0 °C for 12 h before water was added to quench the reaction. Extracted with EA (20 mL × 3), dried over anhydrous Na₂SO₄, filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **S11** (PE:EA = 4:1).

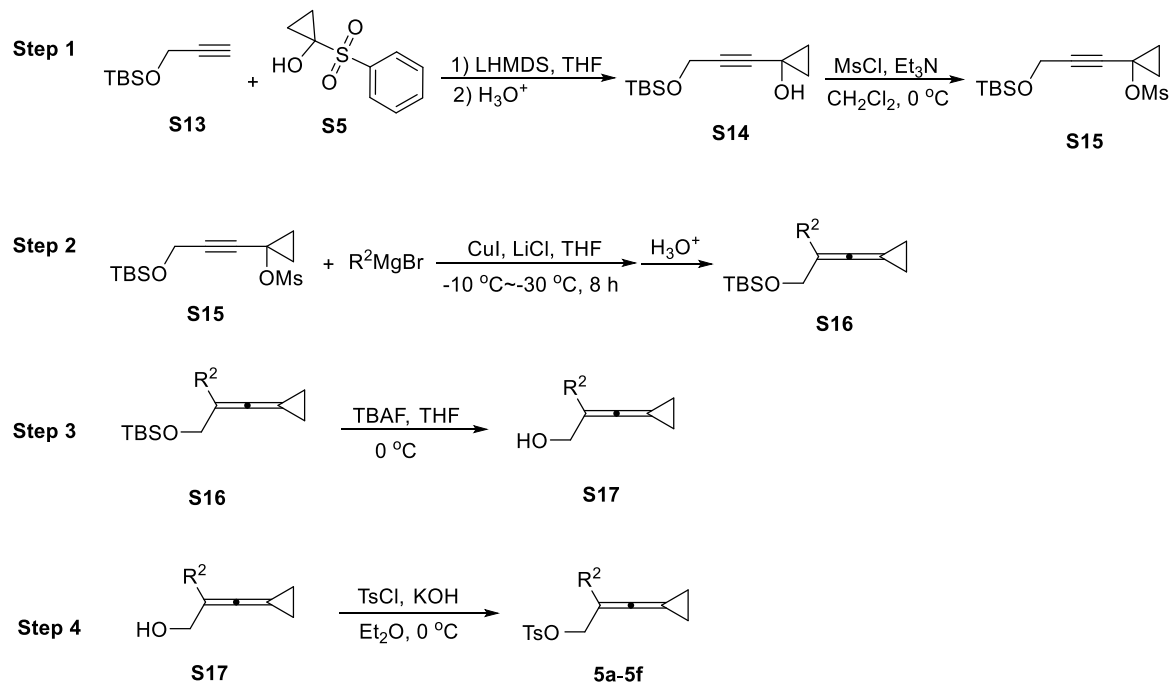
Step 2: To a solution of **S11** (1.0 mmol) in DCM (10 mL) was added TFA (2.0 mL) at 0 °C and the resulting solution was allowed to stir at 0 °C for 8 h before water was added to quench the reaction. Extracted with DCM, dried over anhydrous Na₂SO₄, filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **1o** (PE:EA = 2:1).

Synthesis of substrate **1p**.



Step 1: To a solution of **S12** (1.0 mmol) in DCM (10 mL) was added TFA (2.0 mL) at 0 °C and the resulting solution was allowed to stir at 0 °C for 8 h before water was added to quench the reaction. Extracted with DCM, dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **1p** (PE:EA = 2:1).

Synthesis of substrates **5a-5f**.

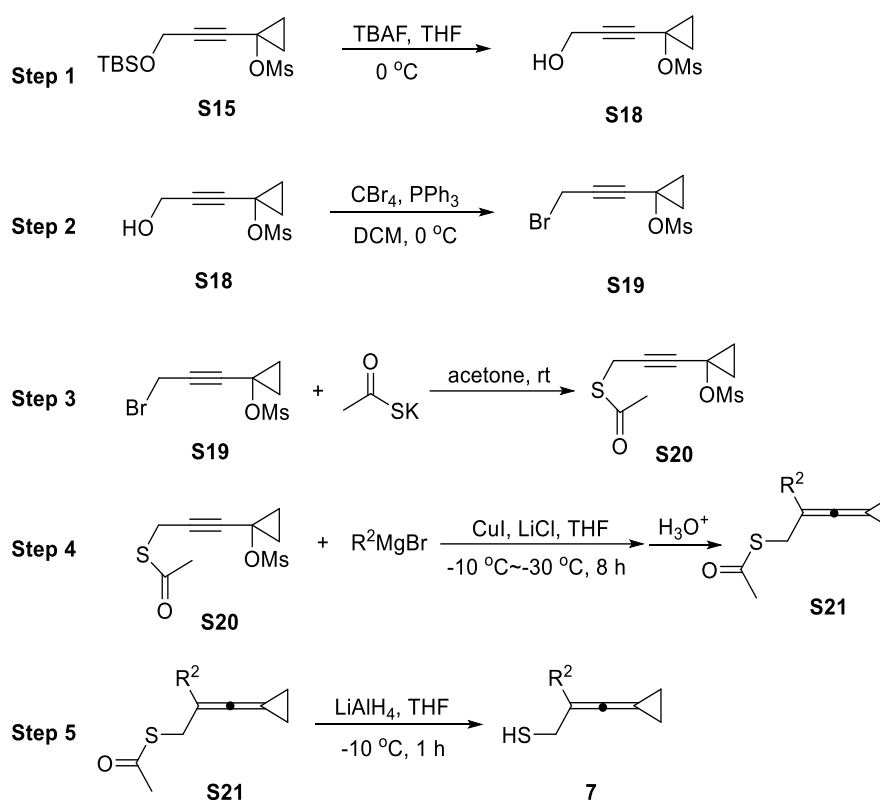


The experimental procedures of step 1 and step 2 were the same as those described above.

Step 3: To a flame dried 50 mL flask was added **S16** (2.0 mmol), and the solvent THF (10 mL) under the protection of argon and then, the flask was cooled to 0 °C before the solution of TBAF (1.0 M, 4.0 mL) was added dropwise into the flask under argon. The resulting solution was allowed to stir at 0 °C for 8.0 h before water was added to quench the reaction. Extracted with EA, dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S17** (PE:EA = 4:1).

Step 4: To a solution of **S17** (1.0 mmol) in Et₂O (10 mL) was added TsCl (1.5 equiv) and KOH (5.0 equiv) at 0 °C and the resulting solution was allowed to stir at 0 °C for 12 h before water was added to quench the reaction. Extracted with EA, dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **5a-5f** (PE:EA = 4:1).

Synthesis of substrates **7a-7h**.



Step 1: To a flame dried 50 mL flask was added **S15** (2.0 mmol), and the solvent THF (10 mL) under the protection of argon and then, the flask was cooled to 0 °C before the solution of TBAF (1.0 M, 4.0 mL) was added dropwise into the flask under argon. The resulting solution was allowed to stir at 0 °C for 8.0 h before water was added to quench the reaction. Extracted with EA, dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S18** (PE:EA = 1:1).

Step 2: To a solution of **S18** (1.0 mmol) in DCM (10 mL) was added CBr₄ (1.1 equiv) and the resulting solution was allowed to stir at 0 °C for 5 min before a solution of PPh₃ (1.2 equiv) in DCM (10 mL) was added dropwise into the above flask. The resulting solution was allowed to stir at 0 °C for 2 h before filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S19** (PE:EA = 4:1).

Step 3: To a solution of **S19** (1.0 mmol) in acetone (5 mL) was added potassium thioacetate (1.5

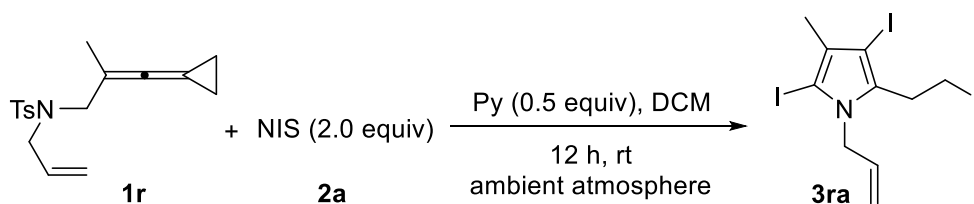
equiv) and the resulting solution was allowed to stir for 6 h before water was added to quench the reaction. Extracted with EA, dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S20** (PE:EA = 2:1).

Step 4: To a flame dried 25 mL three-neck flask was added anhydrous CuI (2.2 mmol), LiCl (2.2 mmol) and the solvent THF (10 mL) under the protection of argon and then, the flask was cooled to -10 °C before the solution of RMgBr or RMgCl (1.0 M, 2.0 mL) was added dropwise into the flask under argon. After 5 minutes, the flask was moved into a -30~-40 °C bath and the reaction mixture was stirred for a while before a solution of **S20** (1.0 mmol) in THF (10 mL) was added dropwise into the above flask. The resulting solution was allowed to stir at -40 °C for 8 h before saturated NH₄Cl solution was added to quench the reaction. Extracted with EA (10 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **S21** (PE:EA = 4:1).

Step 5: To a flame dried 25 mL flask was added LiAlH₄ (2 mmol), and the solvent THF (10 mL) under the protection of argon and then, the flask was cooled to -10 °C before the solution of **S21** (1 mmol) was added dropwise into the flask under argon. The resulting solution was allowed to stir at -10 °C for 1 h before NH₄Cl was added to quench the reaction. Extracted with EA, dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **7** (PE:EA = 10:1).

3. Optimization of reaction conditions

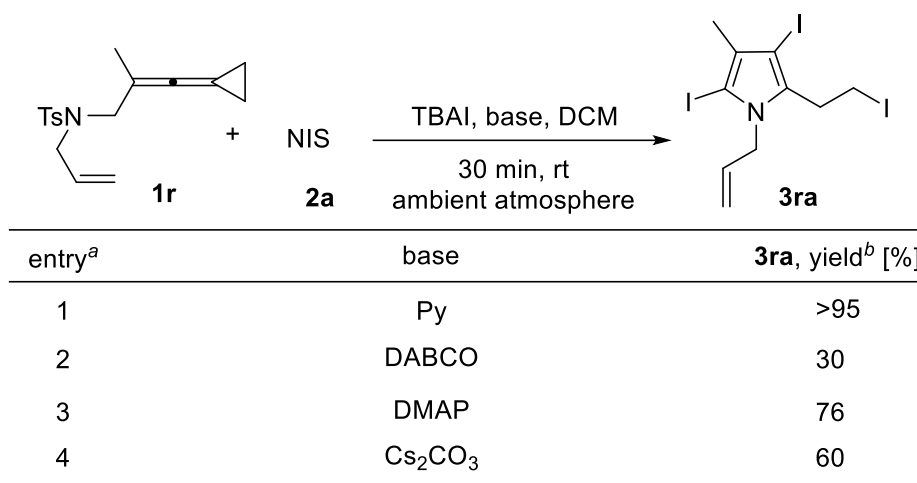
Table S1. Optimization of reaction conditions using **1r** as a template substrate (without TBAI).^a



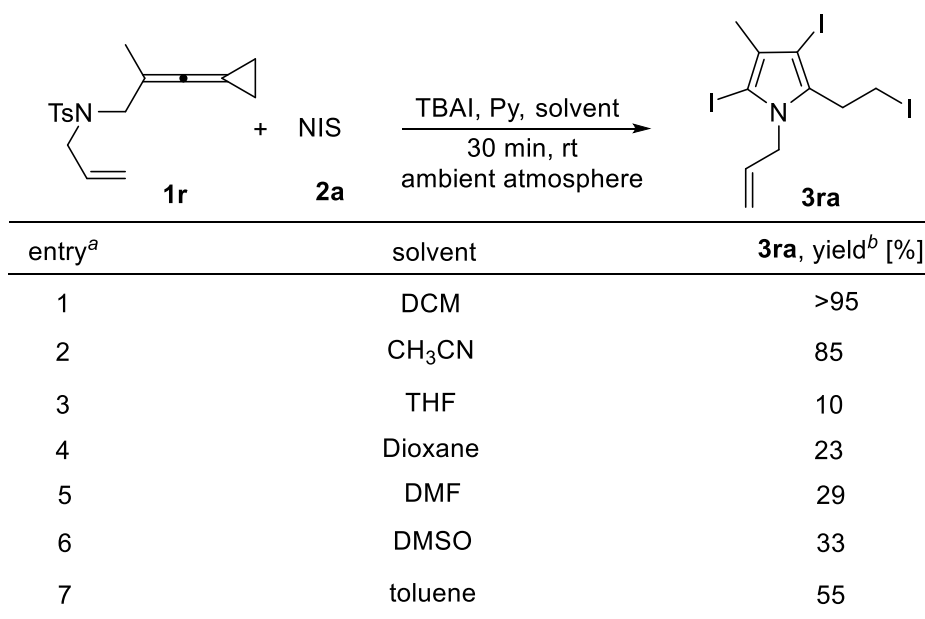
entry ^a	variation from standard condition	3ra , yield ^b [%]
1	none	60
2	Add AgNTf ₂ (0.1 equiv)	30
3	Py (2.0 equiv) instead of Py (0.5 equiv)	76
4	Add LiNTf ₂ (0.1 equiv)	60
5	Add LiNTf ₂ (0.5 equiv)	65
6	Ar instead of air	59
7	Py (0 equiv) instead of Py (0.5 equiv)	40
8	Only add IPy ₂ BF ₄	43
9	NCS instead of NIS	nd
10	NBS instead of NIS	44
11	3.0 equiv NIS instead of 2.0 equiv NIS	52
12	3.0 equiv I ₂ instead of 2.0 equiv NIS	15

^a Reaction carried out with **1r** (0.2 mmol, 1 equiv), **2a** (2.0 equiv), additive, DCM (2.0 mL).

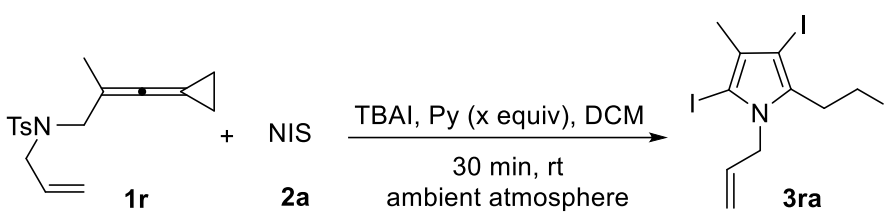
^b ¹H NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.

Table S2. Optimization of reaction conditions using **1r** as a template substrate (base).^a

^a Reaction carried out with **1r** (0.1 mmol), **2a** (3.5 equiv), base (0.5 equiv), TBAI (1.0 equiv), DCM (2.0 mL). ^b ¹H NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.

Table S3. Optimization of reaction conditions using **1r** as a template substrate (solvent).^a

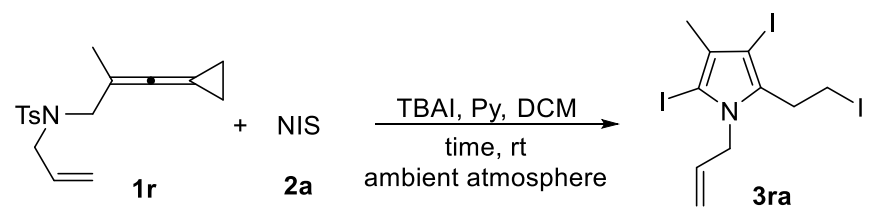
^a Reaction carried out with **1r** (0.1 mmol), **2a** (3.5 equiv), Py (0.5 equiv), TBAI (1.0 equiv), solvent (2.0 mL). ^b ¹H NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.

Table S4. Optimization of reaction conditions using **1r** as a template substrate (equiv of Py).^a

Reaction scheme showing the conversion of **1r** (a substituted allylamine derivative) and **2a** (NIS) to **3ra** (a substituted indole derivative) using TBAI, Py (x equiv), and DCM for 30 min at room temperature under ambient atmosphere.

entry ^a	X	3ra , yield ^b [%]
1	0	59
2	0.5	>95
3	1.0	68
4	2.0	55
5	3.0	50

^a Reaction carried out with **1r** (0.1 mmol), **2a** (3.5 equiv), Py (x equiv), TBAI (1.0 equiv), DCM (2.0 mL). ^b ¹H NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.

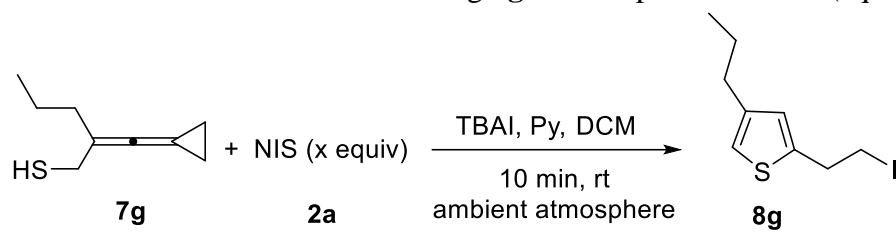
Table S5. Optimization of reaction conditions using **1r** as a template substrate (time).^a

Reaction scheme showing the conversion of **1r** (a substituted allylamine derivative) and **2a** (NIS) to **3ra** (a substituted indole derivative) using TBAI, Py, and DCM for a specified time at room temperature under ambient atmosphere.

entry ^a	Time	3ra , yield ^b [%]
1	1 h	82
2	30 min	>95
3	2 h	76
4	4 h	60
5	12 h	50

^a Reaction carried out with **1r** (0.1 mmol), **2a** (3.5 equiv), Py (0.5 equiv), TBAI (1.0 equiv), DCM (2.0 mL). ^b ¹H NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.

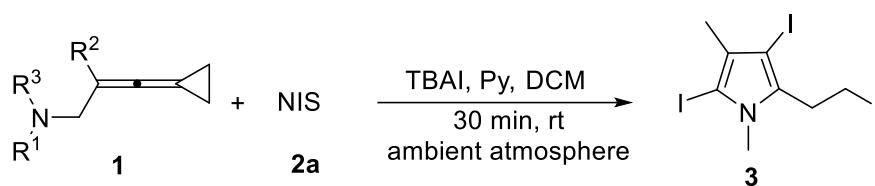
Table S6. Optimization of reaction conditions using **7g** as a template substrate (equiv of NIS).^a



entry ^a	X	yield[%] ^b
1	0	<3
2	0.1	12
3	0.5	46
4	1.0	93

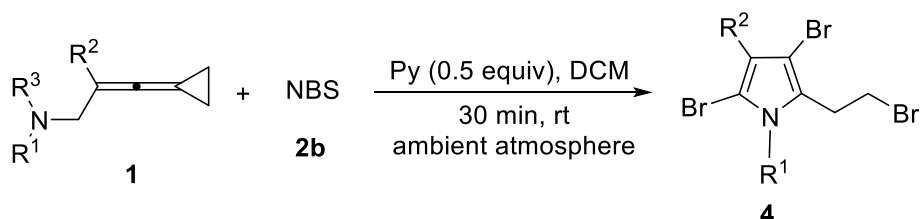
^a Reaction carried out with **7g** (0.1 mmol), **2a** (x equiv), Py (0.5 equiv), TBAI (1.0 equiv), DCM (2.0 mL). ^b ¹H NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.

4. General procedure for the synthesis of **3**, **4**, **6** and **8**



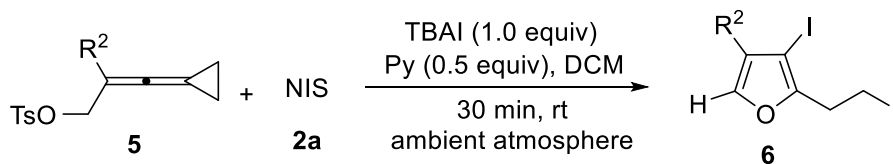
To a 4.0 mL tube were added substrate **1** (0.10 mmol, 1.0 equiv), NIS **2a** (0.35 mmol, 3.5 equiv) and TBAI (0.1 mmol, 1.0 equiv) and then DCM (2.0 mL) and pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this flask via a syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the desired products **3**.

General procedure for the synthesis of **4**



To a 4.0 mL tube were added substrate **1** (0.10 mmol, 1.0 equiv) and NBS **2b** (0.3 mmol, 3.0 equiv) and then DCM (2.0 mL) and pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this flask via a syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the desired products **4**.

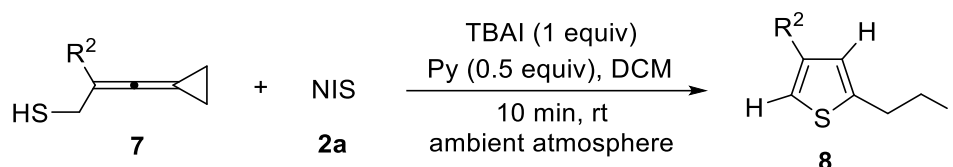
General procedure for the synthesis of **6**



To a 4.0 mL tube were added substrate **5** (0.10 mmol, 1.0 equiv) and NIS **2a** (0.2 mmol, 2.0 equiv) and then DCM (2.0 mL) and pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this flask via a

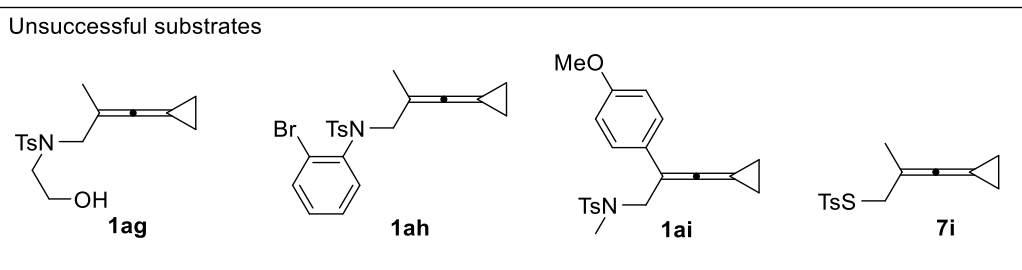
syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the desired products **6**.

General procedure for the synthesis of **8**



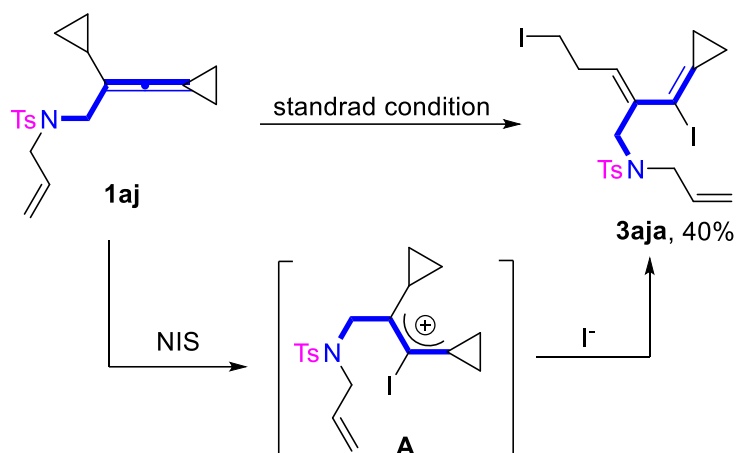
To a 4.0 mL tube were added substrate **7** (0.10 mmol, 1.0 equiv) and NIS **2a** (0.2 mmol, 1.0 equiv) and then DCM (2.0 mL) and pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this flask via a syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the desired products **8**.

Figure S1



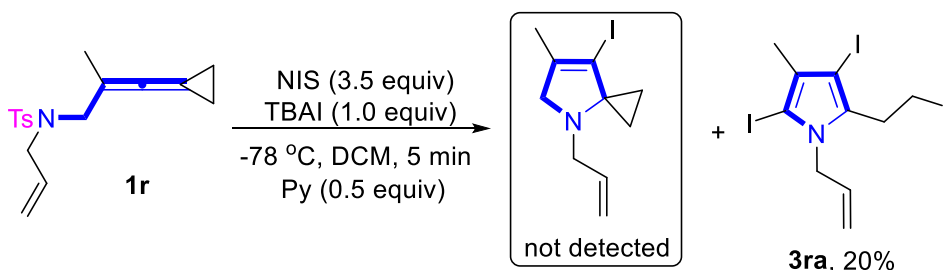
5. Control experiment

(a)



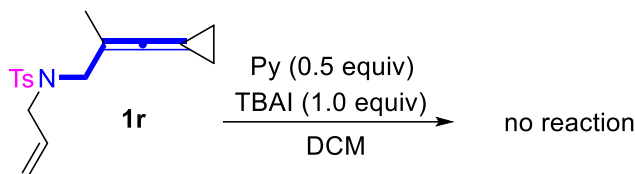
To a 4.0 mL tube were added substrate **1aj** (0.10 mmol, 1.0 equiv), **NIS** (0.35 mmol, 3.5 equiv) and TBAI (0.1 mmol, 1.0 equiv) and then DCM (2.0 mL) and pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this tube via a syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the product **3aja**.

(b)



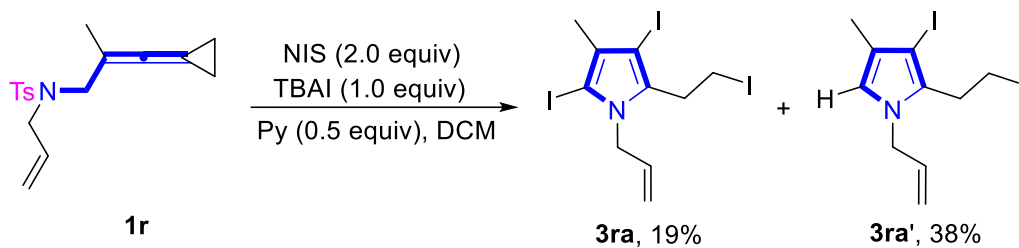
To a 4.0 mL tube were added substrate **1r** (0.10 mmol, 1.0 equiv), **NIS** (0.35 mmol, 3.5 equiv) and TBAI (0.1 mmol, 1.0 equiv) and then DCM (2.0 mL) and pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this tube via a syringe, and the flask was cooled to -78 °C. The resulting mixture was stirred for 5 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the product **3ra** in 20% yield. This result indicated that substrate **1r** did not give the expected intermediate under the standard conditions, but the corresponding product was obtained directly.

(c)



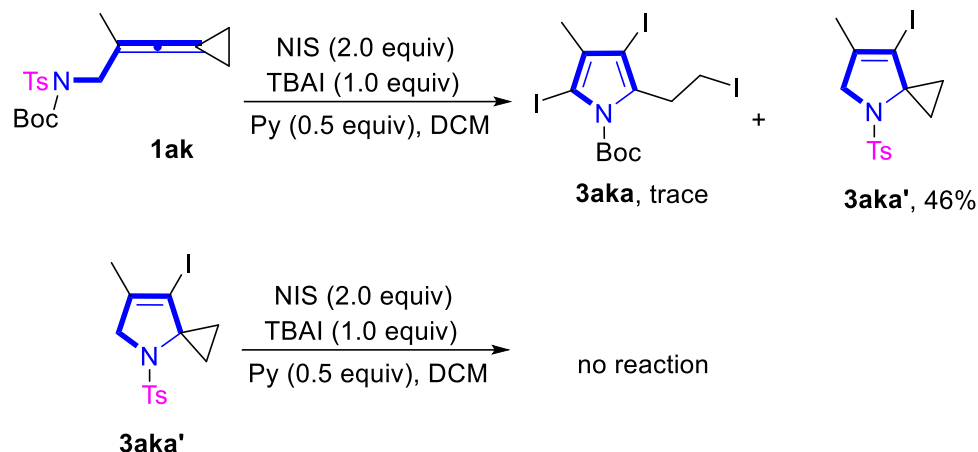
To a 4.0 mL tube were added substrate **1r** (0.10 mmol, 1.0 equiv), TBAI (0.1 mmol, 1.0 equiv) and then DCM (2.0 mL), pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this tube via a syringe. The resulting mixture was stirred for 5 min. After the removal of solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (PE / EA = 50:1). This result indicated that substrate **1r** did not react in the absence of NIS.

(d)

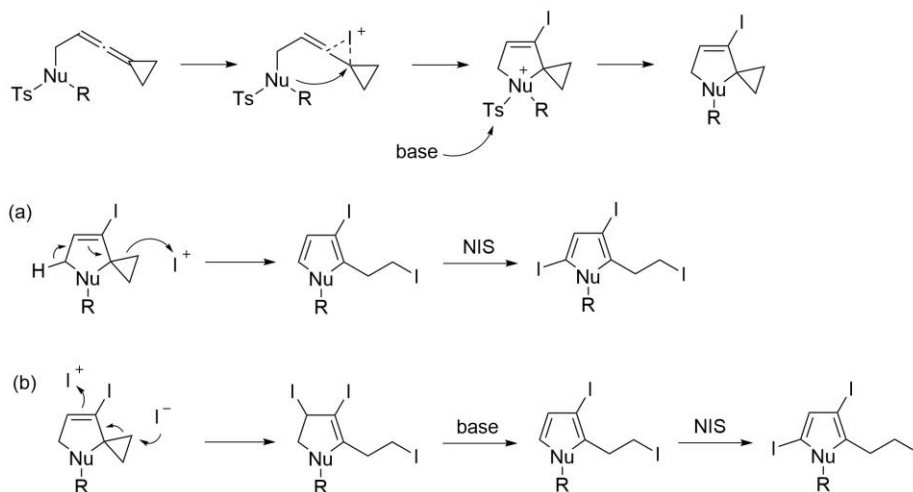


To a 4.0 mL tube were added substrate **1r** (0.10 mmol, 1.0 equiv), NIS (0.20 mmol, 2.0 equiv), TBAI (0.1 mmol, 1.0 equiv) and then DCM (2.0 mL), pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this tube via a syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the products **3ra** and **3ra'**. This result indicated that substrate **1r** produced diiodosubstituted product **3ra'** under the condition with insufficient amount of NIS, rendering that the triiodosubstituted product was afforded by the further iodination of the corresponding diiodosubstituted product.

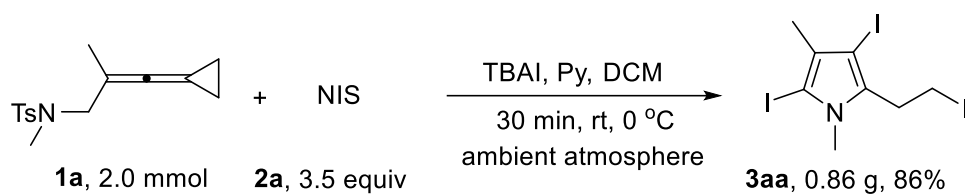
(e)



To a 4.0 mL tube were added substrate **1ak** (0.10 mmol, 1.0 equiv), NIS (0.20 mmol, 2.0 equiv), TBAI (0.1 mmol, 1.0 equiv) and then DCM (2.0 mL), pyridine (Py) (0.05 mmol, 0.5 equiv) were added to this tube via a syringe. The resulting mixture was stirred for 30 min. Then, the solvent was removed under vacuum and the residue was purified by a silica gel column chromatography (PE:EA = 50:1) to give the products **3aka'**. Then, to a 4.0 mL tube were added substrate **1ak** (0.05 mmol, 1.0 equiv), NIS (0.10 mmol, 2.0 equiv), TBAI (0.05 mmol, 1.0 equiv) and then DCM (1.0 mL), pyridine (Py) (0.025 mmol, 0.5 equiv) were added to this tube via a syringe. The resulting mixture was stirred for 30 min. No reaction occurs. These results indicated that **3aka'** was not the active intermediate for this reaction. Thus, we exclude the following reaction pathway.



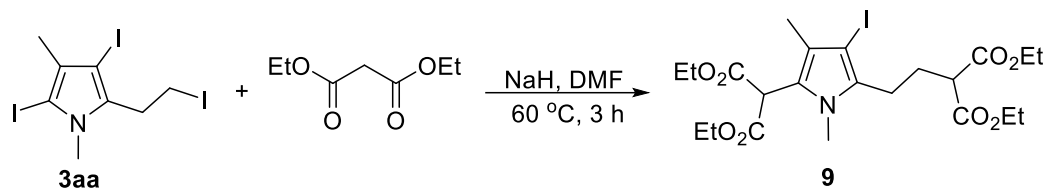
6. Gram scale reaction



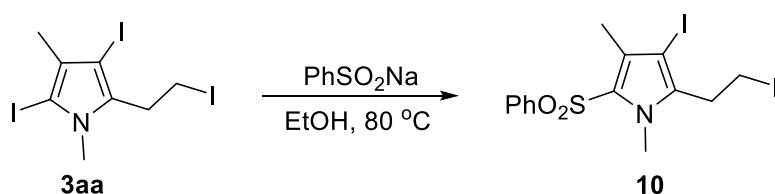
To a flame 50 mL flask was added **1a** (2.0 mmol, 0.55 g, 1.0 equiv), TBAI (2.0 mmol, 0.74 g, 1.0 equiv), pyridine (Py) (1.0 mmol, 80 uL, 0.5 equiv) and the solvent DCM (10 mL) and then, the flask was cooled to 0 °C before NIS **2a** (7.0 mmol, 1.58 g, 3.5 equiv) was added into the flask. The resulting solution was allowed to stir for 30 min before saturated water was added to quench the reaction. Extracted with EA (10 mL x 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **3aa** (PE:EA = 100:1).

7. Transformation of product 3aa

A. Substitution

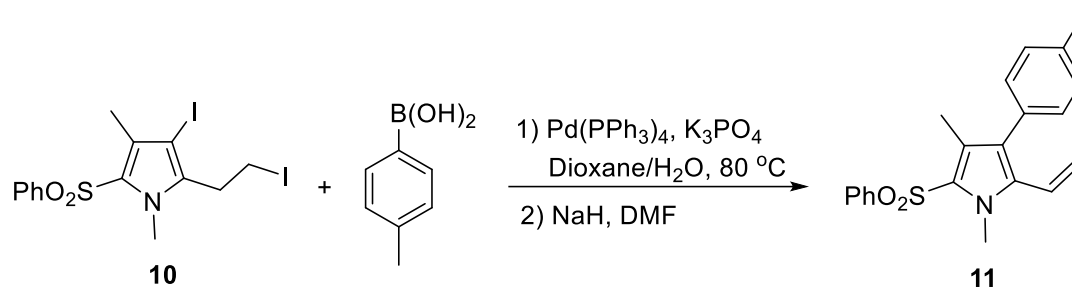


To a flame dried 50 mL flask was added NaH, diethyl malonate and the solvent DMF (20 mL) under the protection of argon and then, the flask was heated to $60\text{ }^\circ\text{C}$ before substrate **3aa** was added dropwise into the flask under argon. The resulting solution was allowed to stir for 3 h before saturated NH_4Cl solution was added to quench the reaction. Extracted with EA (20 mL \times 3), dried over anhydrous Na_2SO_4 , and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **9** (PE:EA = 2:1).^[2]



To a 50 mL flask was added **3aa**, PhSO_2Na and the solvent EtOH (20 mL) and then, the flask was heated to $80\text{ }^\circ\text{C}$. The resulting solution was allowed to stir for 12 h before the water was added to quench the reaction. Extracted with EA (20 mL \times 3), dried over anhydrous Na_2SO_4 , and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **10** (PE:EA = 4:1).^[2]

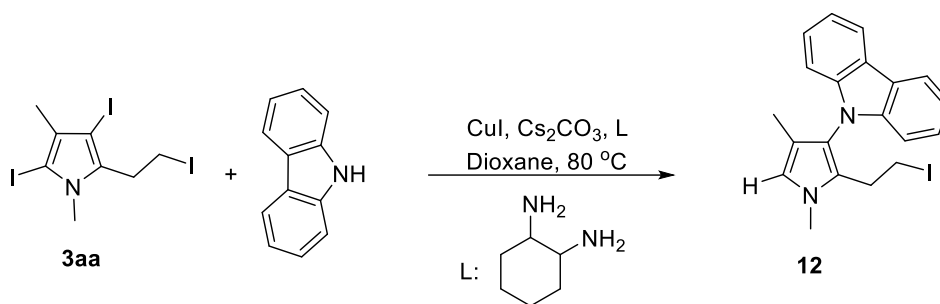
B. Suzuki Coupling



(1) To a flame dried 25 mL flask was added **10** (0.2 mmol), 4-tolylboronic acid (2.0 equiv), Pd(PPh₃)₄ (5 mol%), K₃PO₄ (2.5 equiv) and the solvent dioxane/H₂O (2.0+2.0 mL) under the protection of argon and then, the flask was heated to 80 °C. The resulting solution was allowed to stir for 12 h before saturated NH₄Cl solution was added to quench the reaction. Extracted with EA (10 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the intermediate product (PE:EA = 4:1).^[3]

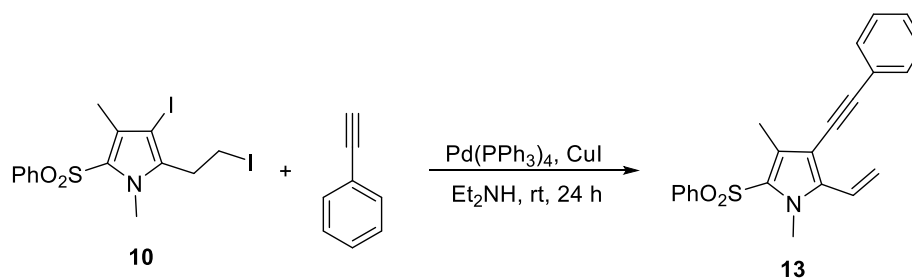
(2) To a 25 mL flask was added the intermediate product, NaH, and the solvent DMF and then, the resulting solution was allowed to stir for 12 h. Extracted with EA (10 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **11** (PE:EA = 4:1).^[4]

C. Ullmann Coupling



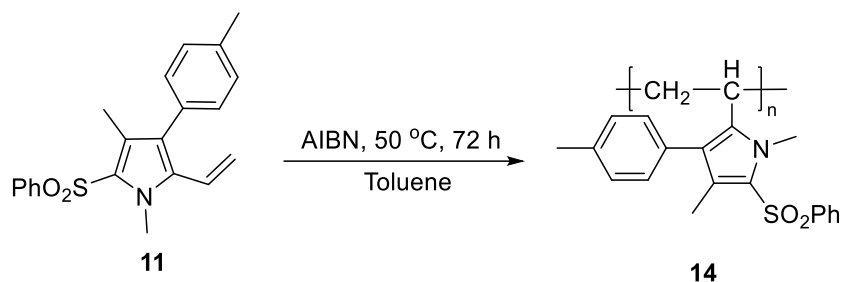
To a flame dried 25 mL flask was added **3aa** (0.2 mmol), carbazole (1.5 equiv), CuI (20 mol%), Cs₂CO₃ (2.0 equiv) and the solvent of dioxane (2.0 mL) under the protection of argon and then, the flask was heated to 80 °C. The resulting solution was allowed to stir for 12 h before water was added to quench the reaction. Extracted with EA (10 mL × 3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **12** (PE:EA = 4:1).

D. Sonogashira Coupling



To a flame dried 25 mL flask was added **10** (0.2 mmol), phenylacetylene (2.0 equiv), Pd(PPh₃)₄ (5 mol%), CuI (10 mol%) and the solvent Et₂NH (2.0 mL) under the protection of argon and then, the resulting solution was allowed to stir for 12 h before water was added to quench the reaction. Extracted with EA (10 mL×3), dried over anhydrous Na₂SO₄, and filtered, the organic phase was concentrated under reduce pressure and the residue was purified by a flash column chromatography on silica gel to give the desired product **13** (PE:EA = 4:1).^[5]

E. Polymerization



To a flame dried 10 mL flask was added **11** (150 mg), AIBN (15 mg), and the solvent of toluene (1.0 mL) under the protection of argon and then, the resulting solution was allowed to stir for 72 h. The reaction mixture was poured into n-pentane (10 mL), filtered and washed with n-pentane give 53 mg of a yellow solid **14**.^[6] The obtained polymeric product was analyzed by ¹H NMR spectroscopic data and GPC.



Figure S2. Picture of **14**

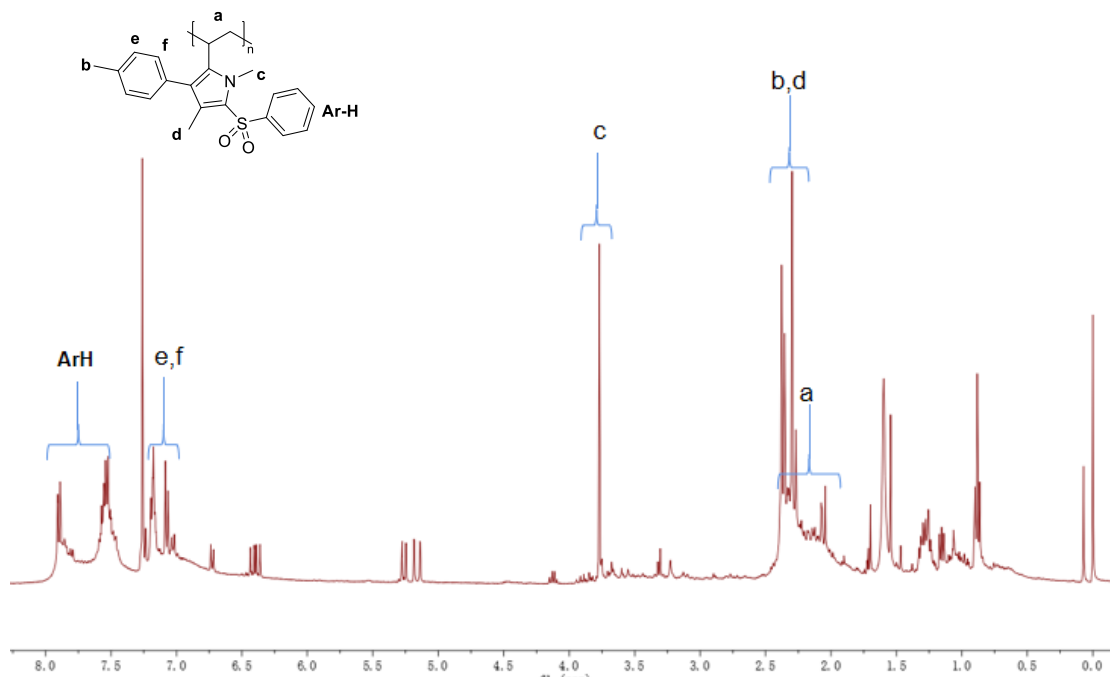


Figure S3. ¹H NMR spectra of **14**

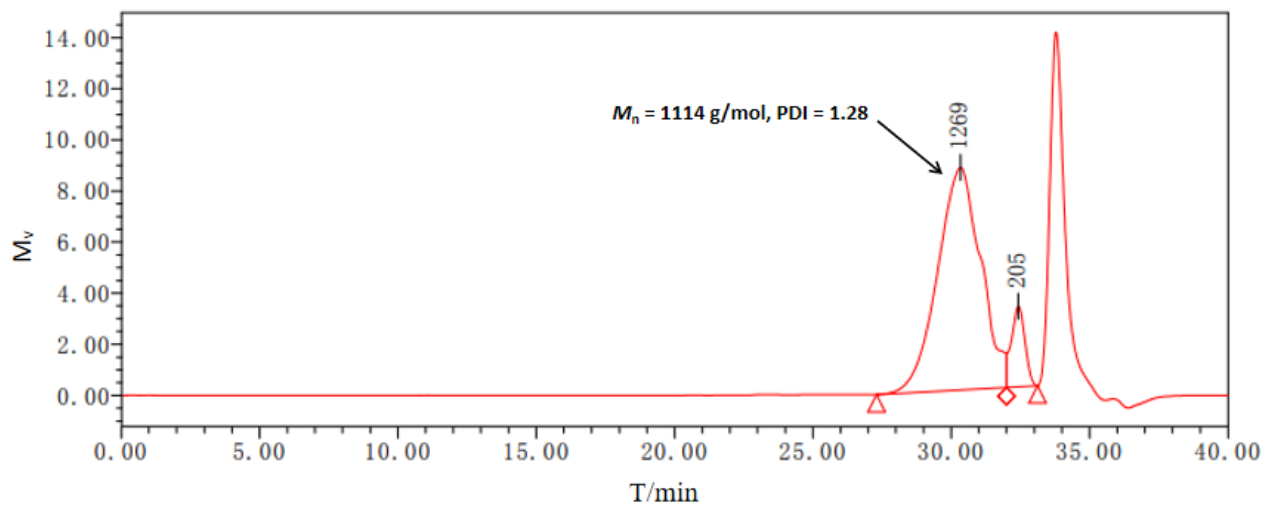
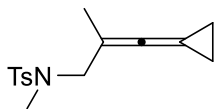


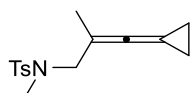
Figure S4. GPC analysis of **14**

8. Spectroscopic data of substrates 1, 5, 7

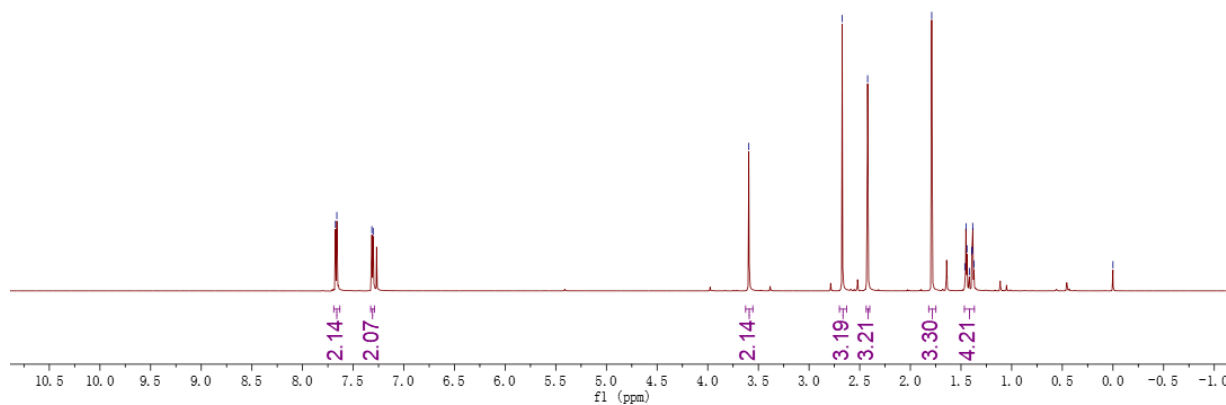


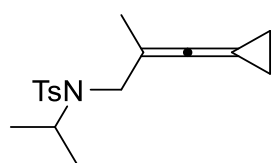
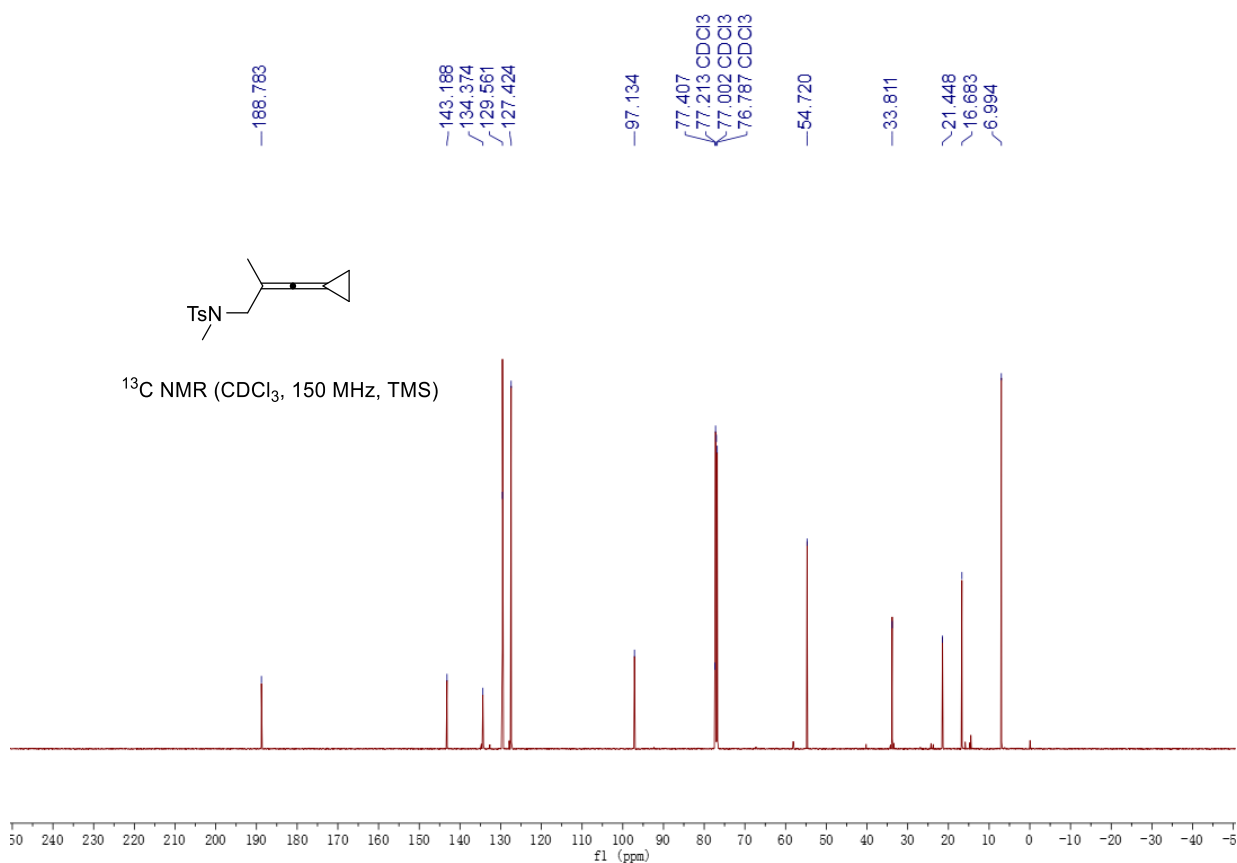
N-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-*N*,4-dimethylbenzenesulfonamide (**1a**)

A white solid, 58% yield, 178.8 mg. M.P.: 85-87 °C. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.67 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.59 (s, 2H), 2.67 (s, 3H), 2.42 (s, 3H), 1.79 (s, 3H), 1.47 - 1.37 (m, 4H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 188.8, 143.2, 134.4, 129.6, 127.4, 97.1, 77.4, 54.7, 33.8, 21.4, 16.7, 7.0. IR (neat) ν 733, 771, 894, 1045, 1089, 1155, 1339, 1443, 1605, 2019 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{SNa}$ ($\text{M}+\text{Na}$): 300.1034, Found: 300.1036.



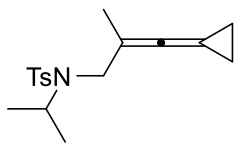
^1H NMR (CDCl_3 , 600 MHz, TMS)



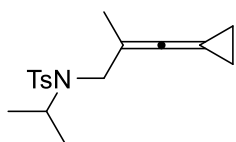
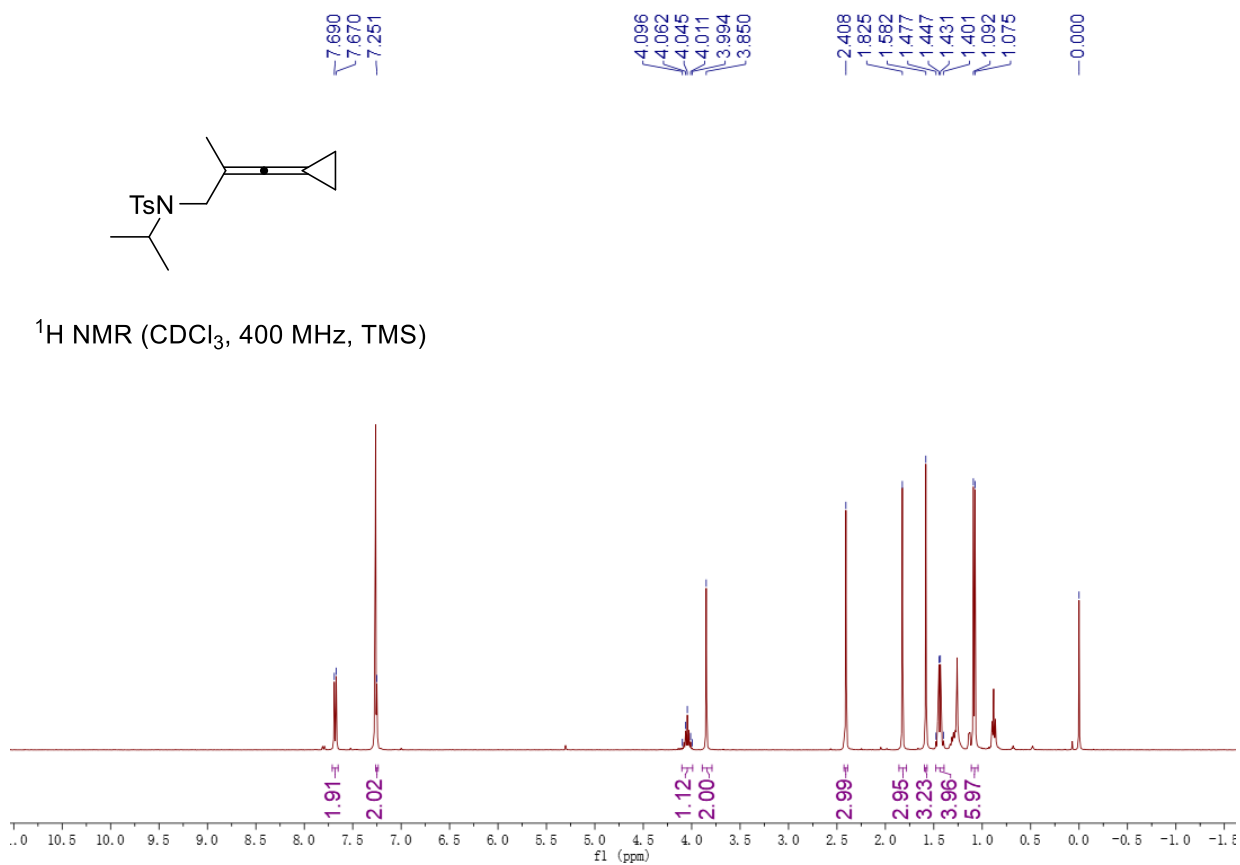


***N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-*N*-isopropyl-4-methylbenzenesulfonamide (**1b**)**

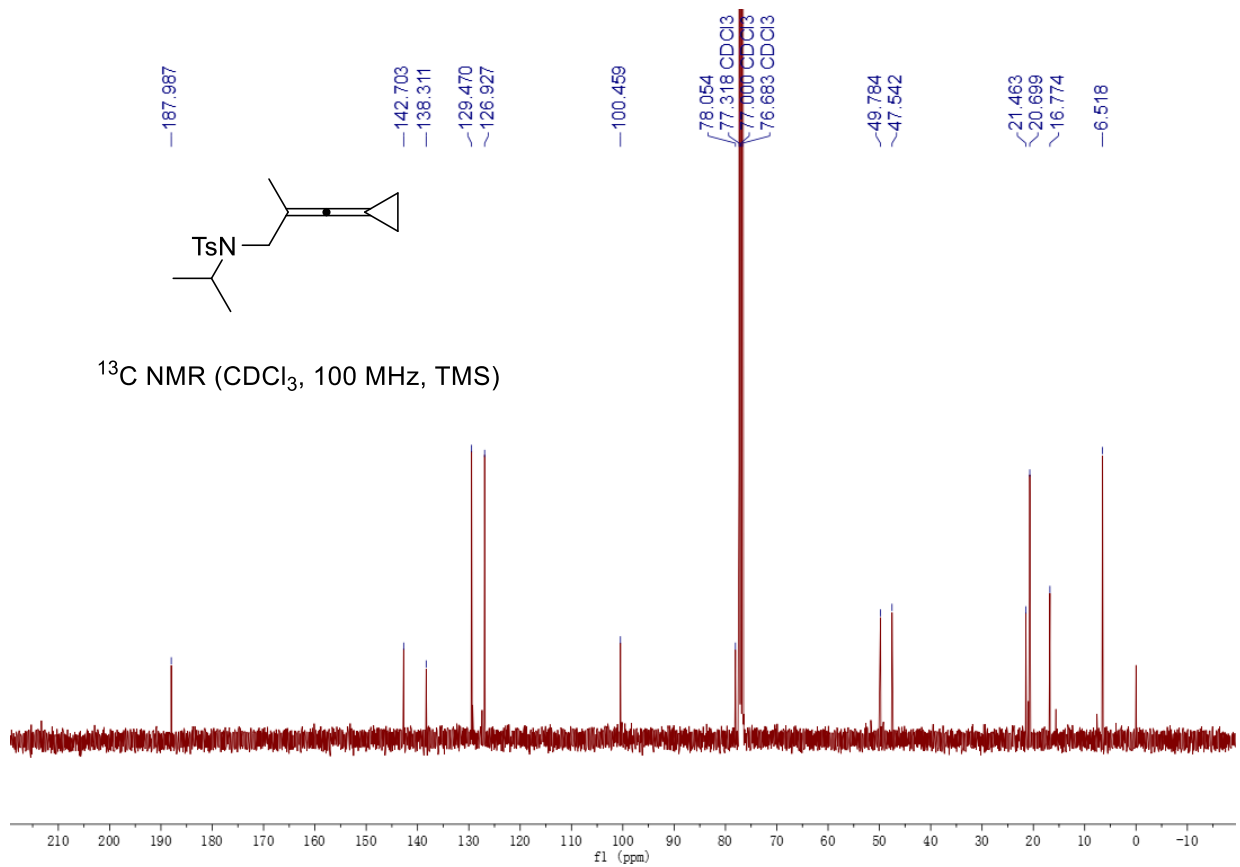
A yellow oil, 51% yield, 155.7 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.26 - 7.24 (m, 2H), 4.10 - 3.99 (m, 1H), 3.85 (s, 2H), 2.41 (s, 3H), 1.82 (s, 3H), 1.58 (s, 3H), 1.48 - 1.39 (m, 4H), 1.08 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.0, 142.7, 138.3, 129.5, 126.9, 100.5, 78.1, 49.8, 47.5, 21.5, 20.7, 16.8, 6.5. IR (neat) ν 733, 771, 894, 1045, 1089, 1155, 1339, 1443, 1605, 2019, 2917 cm⁻¹. HRMS (ESI) calcd. for C₁₇H₂₃NO₂SNa (M+Na): 328.1342, Found: 328.1343.

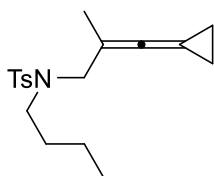


^1H NMR (CDCl_3 , 400 MHz, TMS)



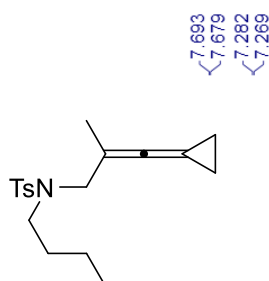
^{13}C NMR (CDCl_3 , 100 MHz, TMS)



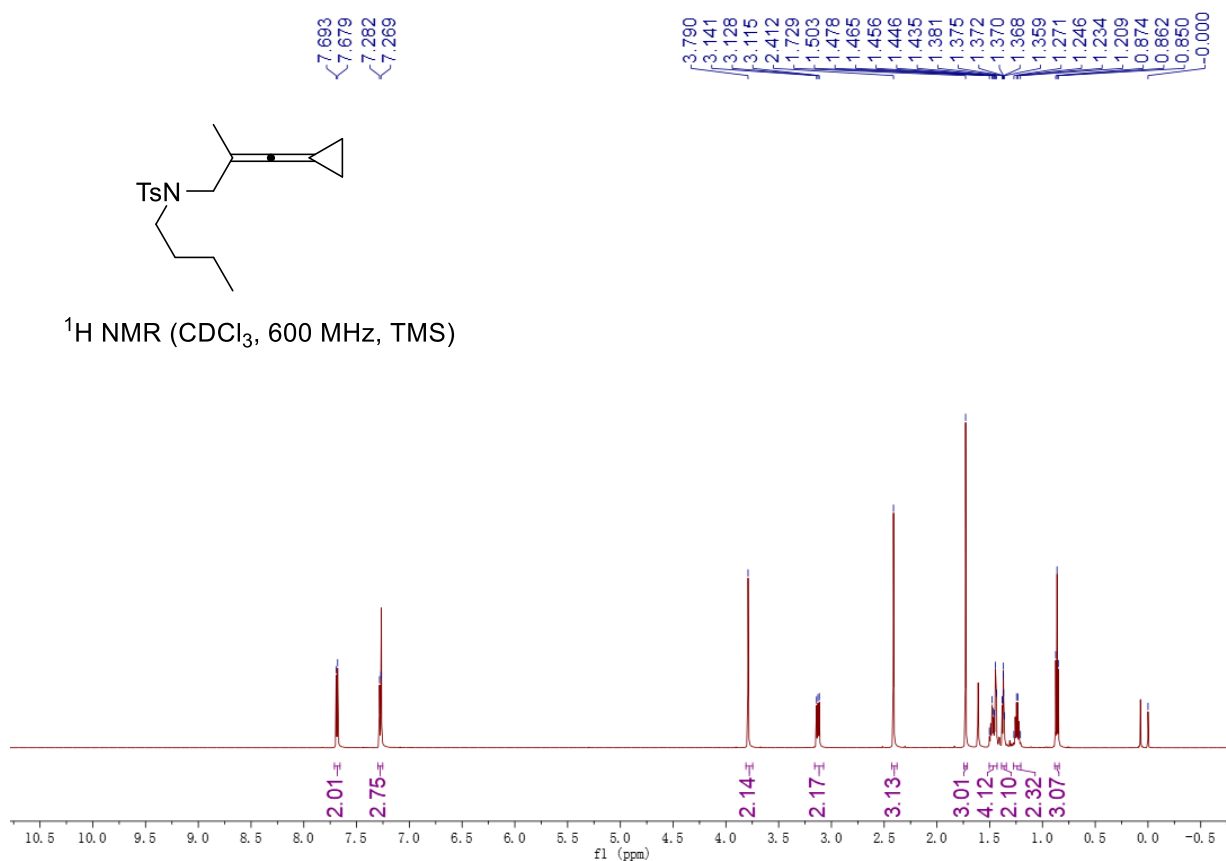


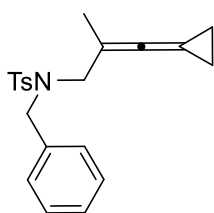
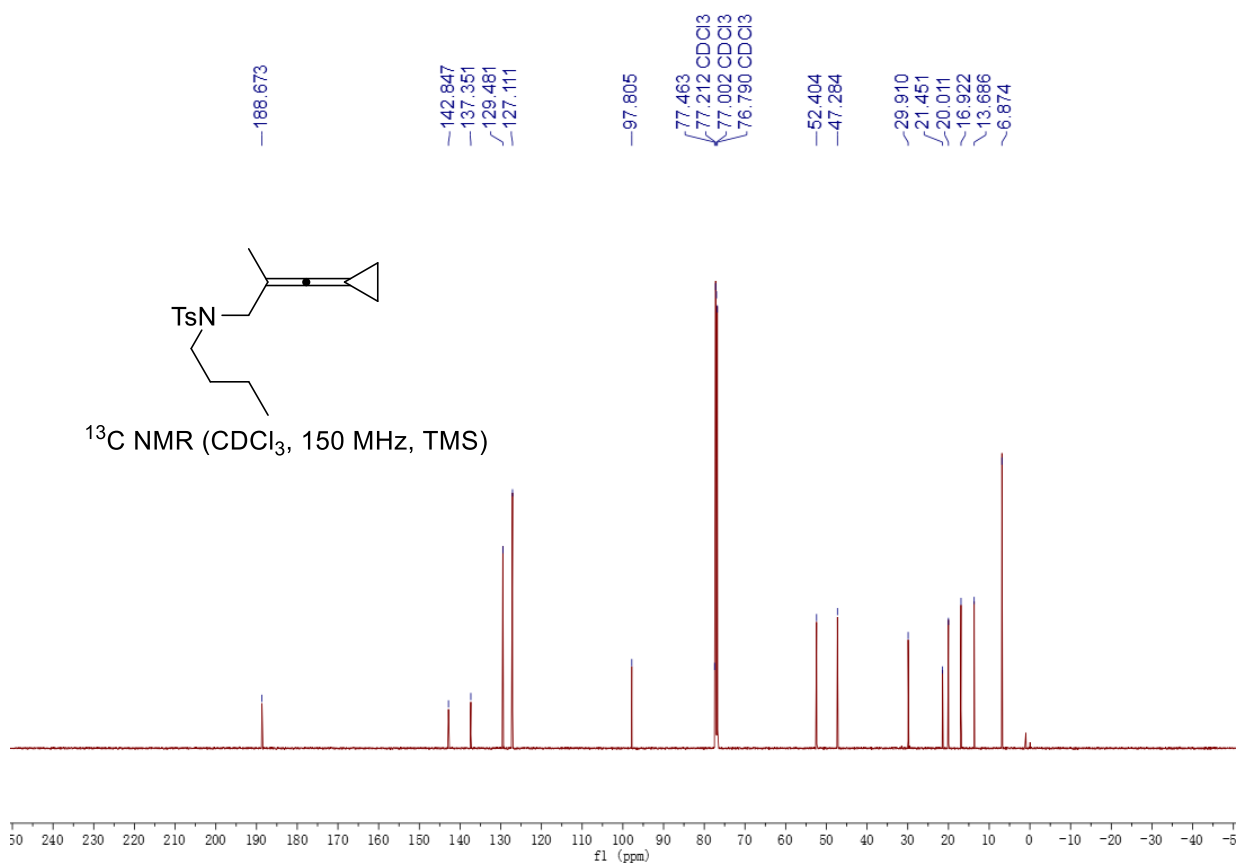
***N*-butyl-*N*-(3-cyclopropylidene-2-methyl-3 λ ⁵-allyl)-4-methylbenzenesulfonamide (1c)**

A colorless oil, 50% yield, 159.7 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.69 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 3.79 (s, 2H), 3.16 - 3.07 (m, 2H), 2.41 (s, 3H), 1.73 (s, 3H), 1.50 - 1.43 (m, 4H), 1.39 - 1.34 (m, 2H), 1.27 - 1.21 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 188.7, 142.8, 137.4, 129.5, 127.1, 97.8, 77.5, 52.4, 47.3, 29.9, 21.5, 20.0, 16.9, 13.7, 6.9. IR (neat) ν 727, 835, 921, 985, 1083, 1157, 1249, 1339, 1461, 2021, 2928 cm⁻¹. HRMS (ESI) calcd. for C₁₈H₂₅NO₂NaS (M+Na): 342.1498, Found: 342.1505.



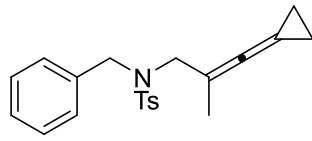
¹H NMR (CDCl₃, 600 MHz, TMS)



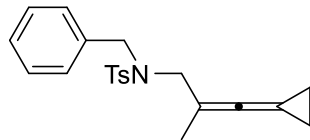
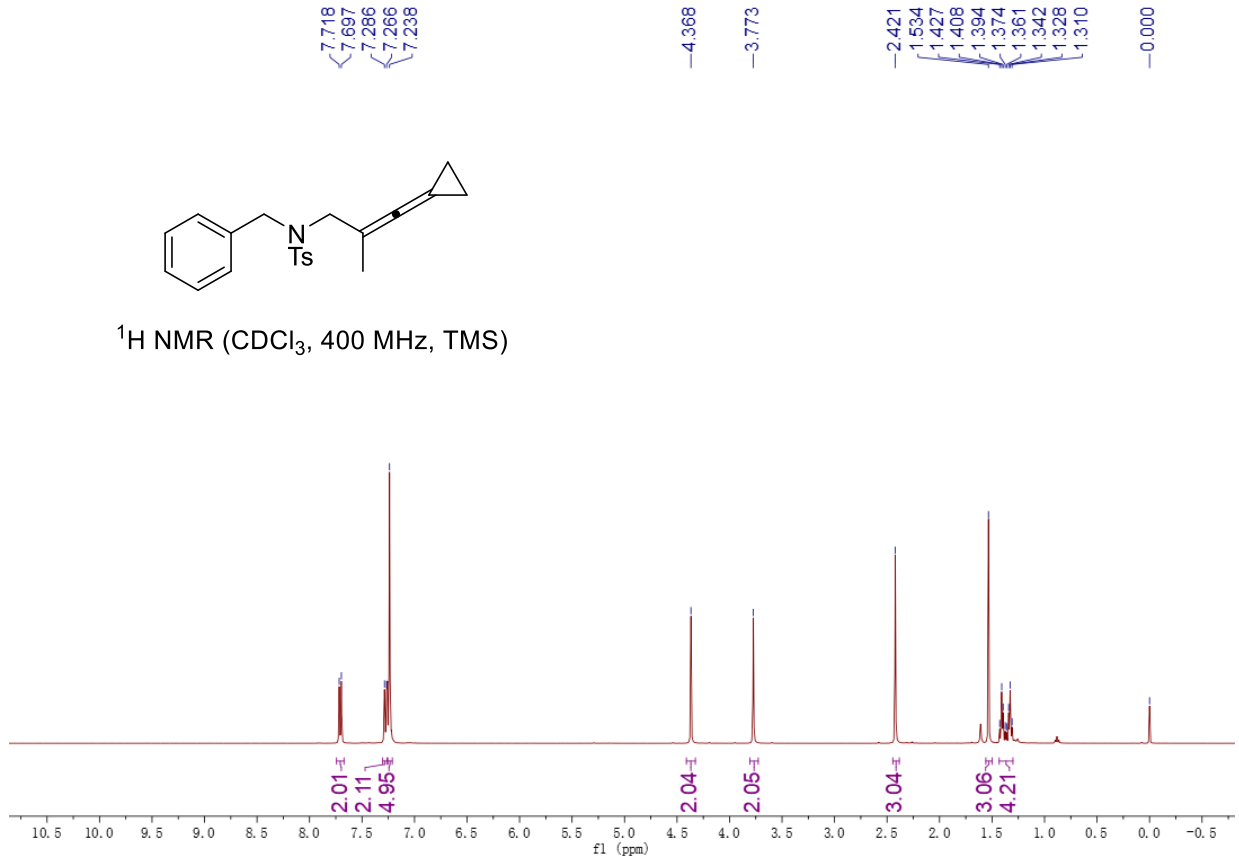


***N*-benzyl-*N*-(3-cyclopropylidene-2-methyl-3-allyl)-4-methylbenzenesulfonamide (1d)**

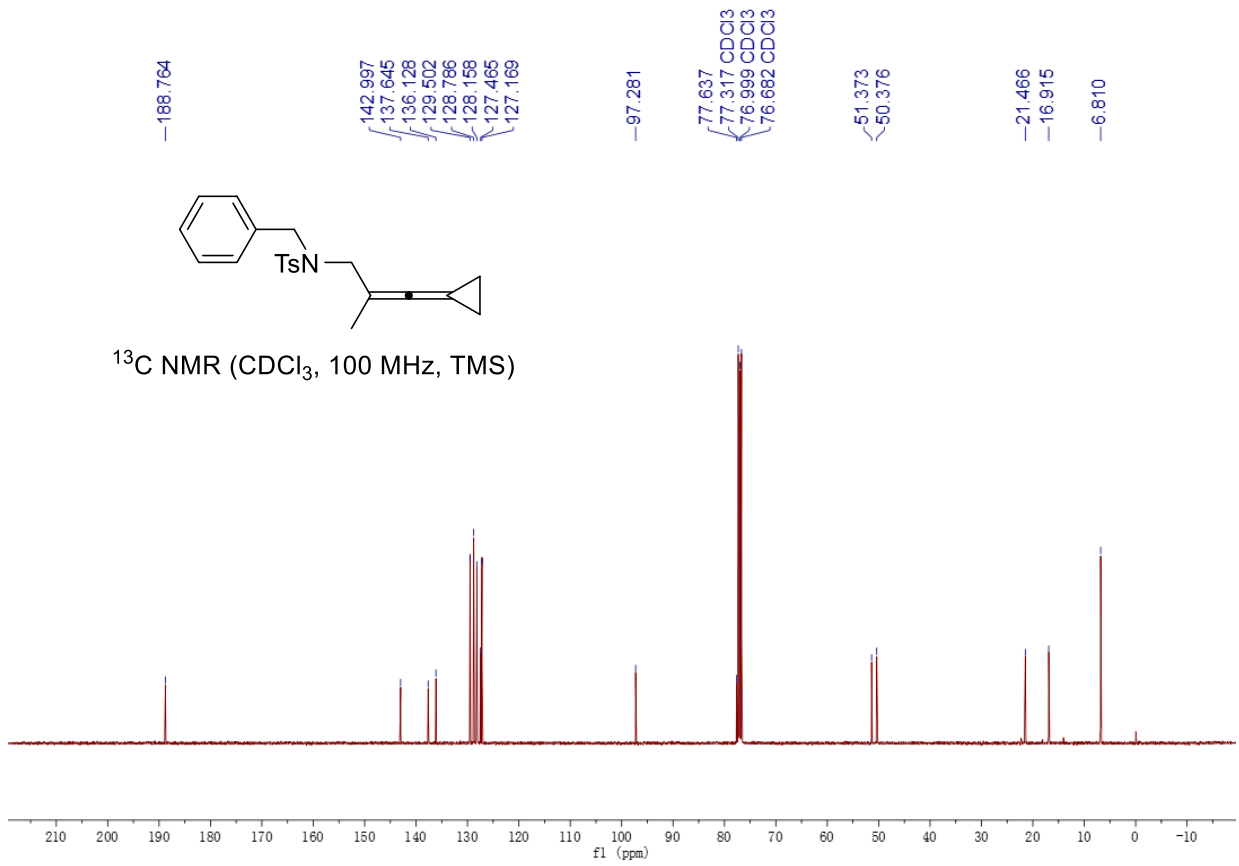
A colorless oil, 41% yield, 144.9 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24 (s, 5H), 4.37 (s, 2H), 3.77 (s, 2H), 2.42 (s, 3H), 1.53 (s, 3H), 1.43 - 1.30 (m, 4H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.8, 143.0, 137.6, 136.1, 129.5, 128.8, 128.2, 127.5, 127.2, 97.3, 77.6, 51.4, 50.4, 21.5, 16.9, 6.8. IR (neat) ν 860, 891, 1008, 1088, 1157, 1331, 2029, 2930 cm⁻¹. HRMS (ESI) calcd. for C₂₁H₂₃NO₂NaS (M+Na): 376.1342, Found: 376.1346.

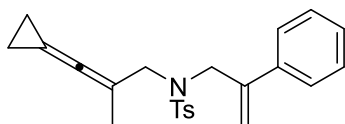


^1H NMR (CDCl_3 , 400 MHz, TMS)



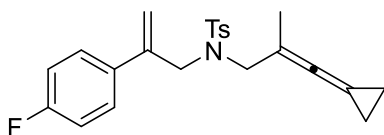
^{13}C NMR (CDCl_3 , 100 MHz, TMS)





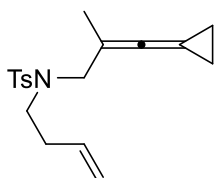
***N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1e)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[1] 46% yield, 174.6 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.22 - 7.34 (m, 7H), 5.36 (s, 1H), 5.20 (s, 1H), 4.26 (s, 2H), 3.79 (s, 2H), 2.41 (s, 3H), 1.54 (s, 3H), 1.38 - 1.42 (m, 2H), 1.29 - 1.32 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.7, 142.9, 142.8, 139.1, 137.2, 129.4, 128.2, 127.7, 127.2, 126.6, 116.1, 97.7, 77.6, 51.1, 51.6, 50.8, 21.4, 17.0, 6.6.



***N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-*N*-(2-(4-fluorophenyl)allyl)-4-methylbenzenesulfonamide (1f)**

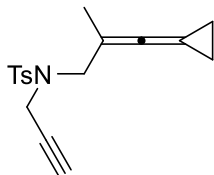
This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[1] 41% yield, 163.0 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.29 - 7.32 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 8.4 Hz, 2H), 5.31 (s, 1H), 5.19 (s, 1H), 4.22 (s, 2H), 3.77 (s, 2H), 2.42 (s, 3H), 1.52 (s, 3H), 1.39 - 1.42 (m, 2H), 1.30 - 1.33 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.7, 162.4 (d, *J* = 245.0 Hz), 143.0, 142.0, 137.1, 135.0 (d, *J* = 2.9 Hz), 129.4, 128.3 (d, *J* = 8.0 Hz), 127.2, 116.2, 115.0 (d, *J* = 20.0 Hz), 97.7, 77.5, 51.7, 51.2, 21.4, 16.9, 6.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.5 (s).



***N*-(but-3-en-1-yl)-*N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methylbenzenesulfonamide (1g)**

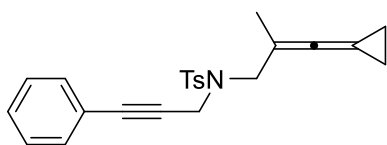
This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[7] 53% yield, 168.2 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.62 - 5.73 (m, 1H), 4.99 - 5.03 (m, 1H), 4.97 - 4.99 (m, 1H), 3.81 (m,

2H), 3.18 - 3.22 (m, 2H), 2.41 (s, 3H), 2.26 (q, $J = 8.4$ Hz, 2H), 1.73 (s, 3H), 1.43-1.47 (m, 2H), 1.36-1.41 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 188.7, 143.0, 137.2, 135.0, 129.5, 127.1, 116.7, 97.5, 77.5, 52.5, 46.9, 32.5, 21.4, 16.9, 6.9.



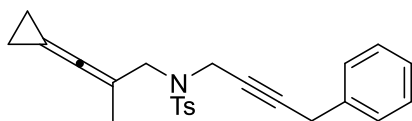
***N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1h)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[8] 49% yield, 147.7 mg. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 4.14 (s, 2H), 3.82 (s, 2H), 2.41 (s, 3H), 1.92 (t, $J = 2.4$ Hz, 1H), 1.77 (s, 3H), 1.45 - 1.48 (m, 2H), 1.39 - 1.43 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 188.9, 143.4, 136.1, 129.3, 127.7, 96.2, 77.7, 76.5, 73.4, 50.7, 35.4, 21.5, 16.7, 7.2.



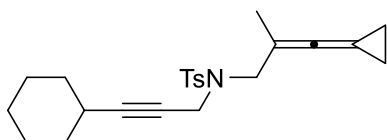
***N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1i)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[8] 43% yield, 162.3 mg. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.78 - 7.76 (m, 2H), 7.26 - 7.20 (m, 5H), 7.00 - 6.98 (m, 2H), 4.35 (s, 2H), 3.89 (s, 2H), 2.31 (s, 3H), 1.83 (s, 3H), 1.48 - 1.43 (m, 2H), 1.42 - 1.36 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 189.0, 143.3, 136.1, 131.4, 129.4, 128.2, 128.0, 127.8, 122.4, 96.4, 85.4, 81.8, 51.0, 36.4, 21.4, 16.8, 7.2.



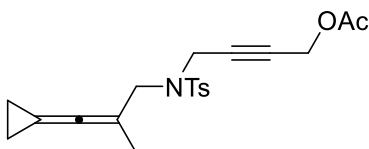
***N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-4-methyl-*N*-(4-phenylbut-2-yn-1-yl)benzenesulfonamide (1j)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[8] 48% yield, 187.9 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.16 - 7.25 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.18 (s, 2H), 3.83 (s, 2H), 3.26 (s, 2H), 2.30 (s, 3H), 1.78 (s, 3H), 1.41 - 1.44 (m, 2H), 1.30 - 1.32 (m, 2H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.9, 143.1, 136.19, 136.16, 129.2, 128.3, 127.8, 127.6, 126.5, 96.4, 83.1, 77.5, 74.6, 50.8, 35.9, 24.8, 21.4, 16.7, 7.1.



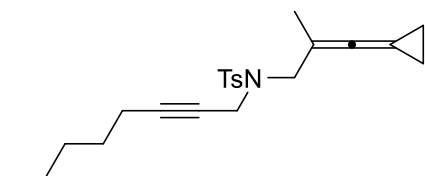
***N*-(3-cyclohexylprop-2-yn-1-yl)-*N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methylbenzenesulfonamide (1k)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[8] 40% yield, 153.4 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 4.13 (d, *J* = 2.0 Hz, 2H), 3.83 (s, 2H), 2.40 (s, 3H), 2.05 (s, 1H), 1.79 (s, 3H), 1.38 - 1.49 (m, 9H), 1.02 - 1.18 (m, 5H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.9, 143.0, 136.4, 129.3, 127.7, 96.5, 90.0, 77.4, 72.1, 50.5, 36.0, 32.1, 28.5, 25.8, 24.4, 21.4, 16.8, 7.1.



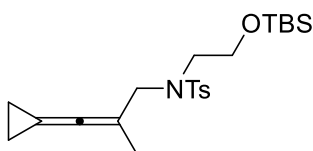
4-((*N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl acetate (1l)

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[8] 33% yield, 123.3 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 4.33 (s, 2H), 4.16 (s, 2H), 3.79 (s, 2H), 2.42 (s, 3H), 2.04 (s, 3H), 1.77 (s, 3H), 1.46 - 1.49 (m, 2H), 1.40 - 1.43 (m, 2H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.8, 169.8, 143.3, 136.0, 129.2, 127.7, 96.2, 79.4, 79.1, 77.6, 51.7, 50.9, 35.6, 21.4, 20.5, 16.7, 7.1.



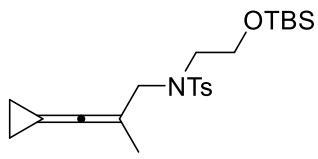
***N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-4-methyl-*N*-(oct-2-yn-1-yl)benzenesulfonamide (1m)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[8] 45% yield, 167.2 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.73 (d, J = 7.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.11 (s, 2H), 3.81 (s, 2H), 2.40 (s, 3H), 1.83 (t, J = 6.0 Hz, 2H), 1.78 (s, 3H), 1.44 - 1.48 (m, 2H), 1.38 - 1.42 (m, 2H), 1.12 - 1.22 (m, 6H), 0.84 (t, J = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.8, 143.0, 136.3, 129.1, 127.8, 96.5, 85.8, 77.4, 72.2, 50.5, 35.9, 30.7, 27.9, 22.0, 21.4, 18.3, 16.7, 13.8, 7.1.

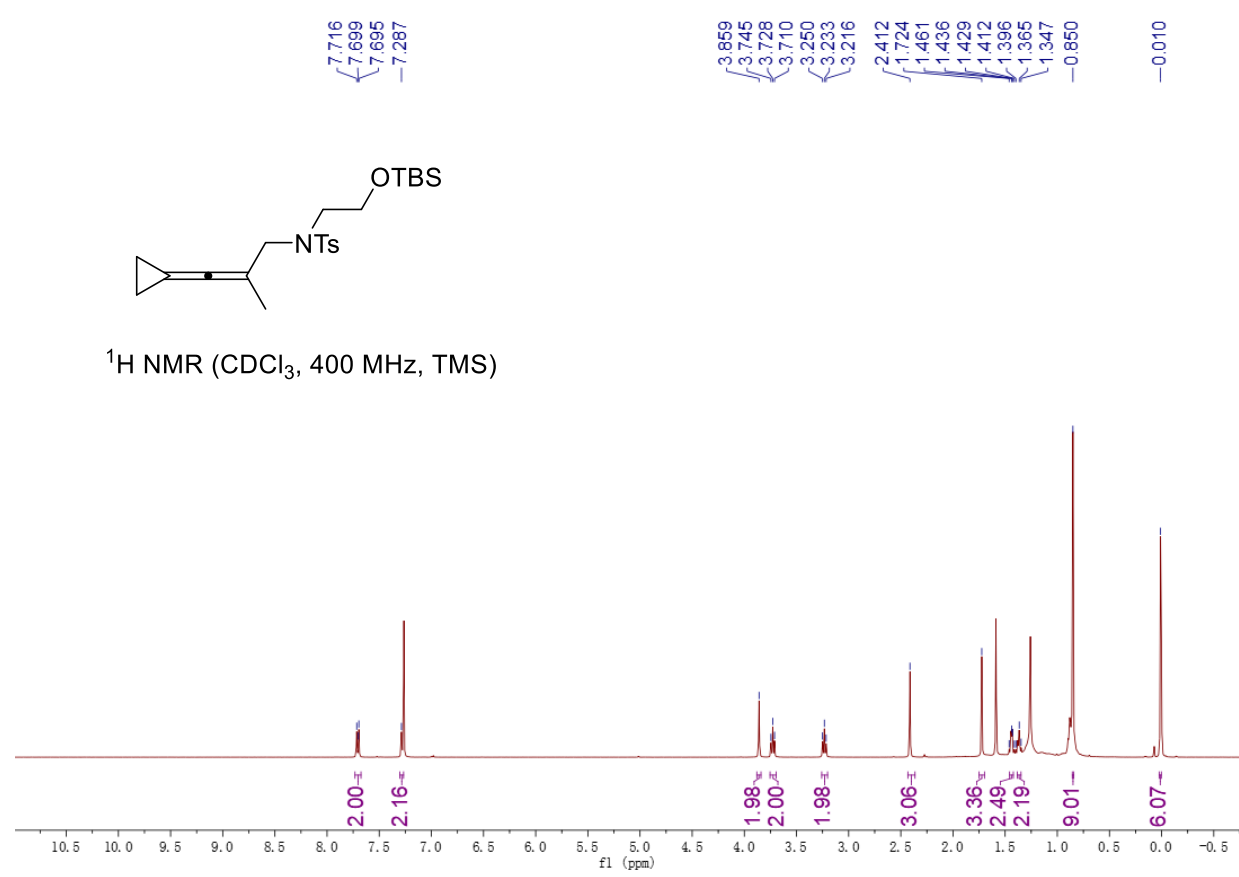


***N*-(2-((tert-butyldimethylsilyl)oxy)ethyl)-*N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-4-methylbenzenesulfonamide (1n)**

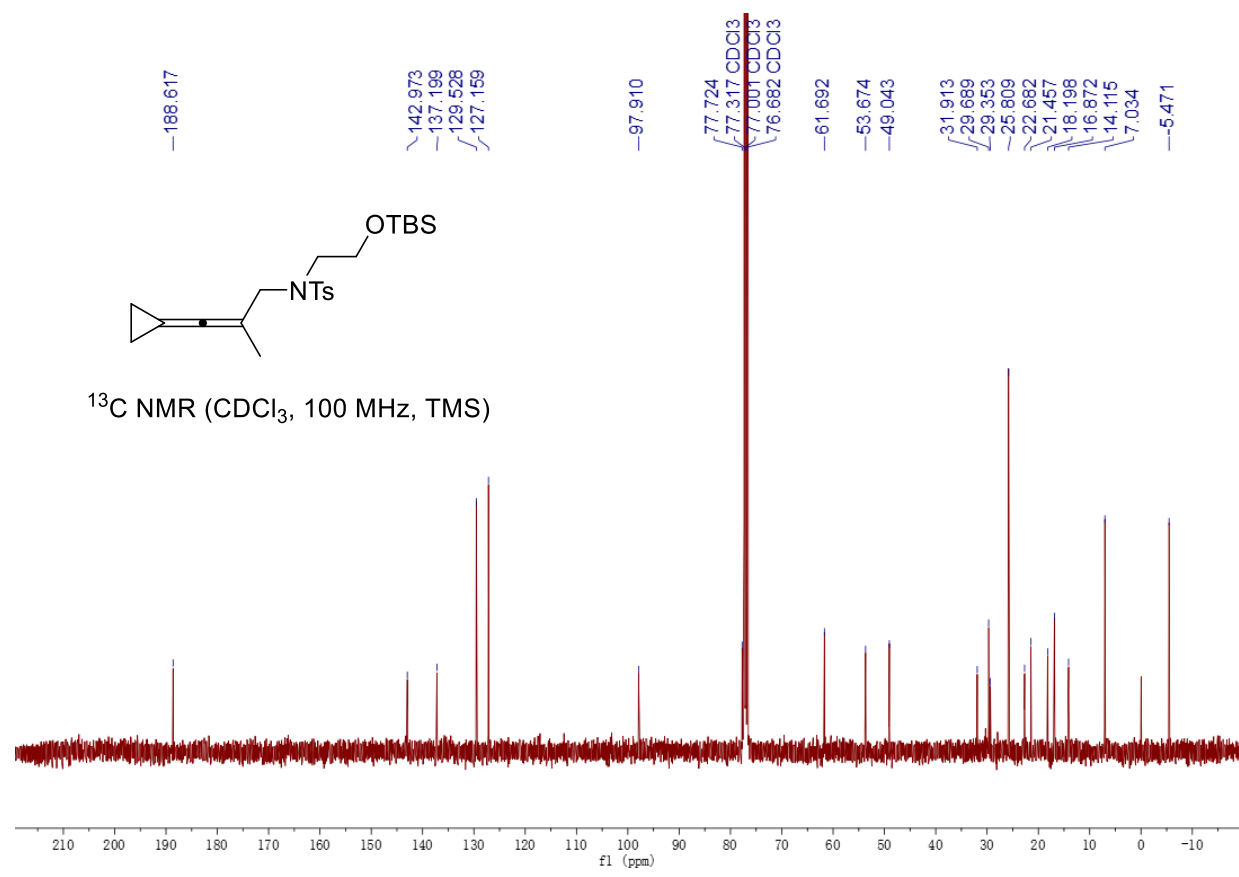
A colorless oil, 44%, 185.5 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.71 (d, J = 8.2 Hz, 2H), 7.30 - 7.27 (m, 2H), 3.86 (s, 2H), 3.73 (t, J = 6.9 Hz, 2H), 3.23 (t, J = 6.9 Hz, 2H), 2.41 (s, 3H), 1.72 (s, 3H), 1.46 - 1.42 (m, 2H), 1.38 - 1.35 (m, 2H), 0.85 (s, 9H), 0.01 (s, 6H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.6, 143.0, 137.2, 129.5, 127.2, 97.9, 77.7, 61.7, 53.7, 49.0, 31.9, 29.7, 29.4, 25.8, 22.7, 21.5, 18.2, 16.9, 14.1, 7.0, -5.5. IR (neat) ν 2921, 2851, 1710, 1609, 1586, 1431, 1317, 1061, 1024, 998, 916 cm⁻¹. HRMS (ESI) calcd. for C₂₂H₃₅NO₃NaSiS (M+Na): 444.1999, Found: 444.1996.

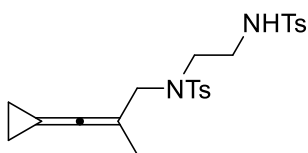


¹H NMR (CDCl₃, 400 MHz, TMS)



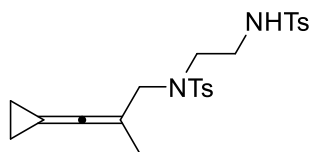
¹³C NMR (CDCl₃, 100 MHz, TMS)



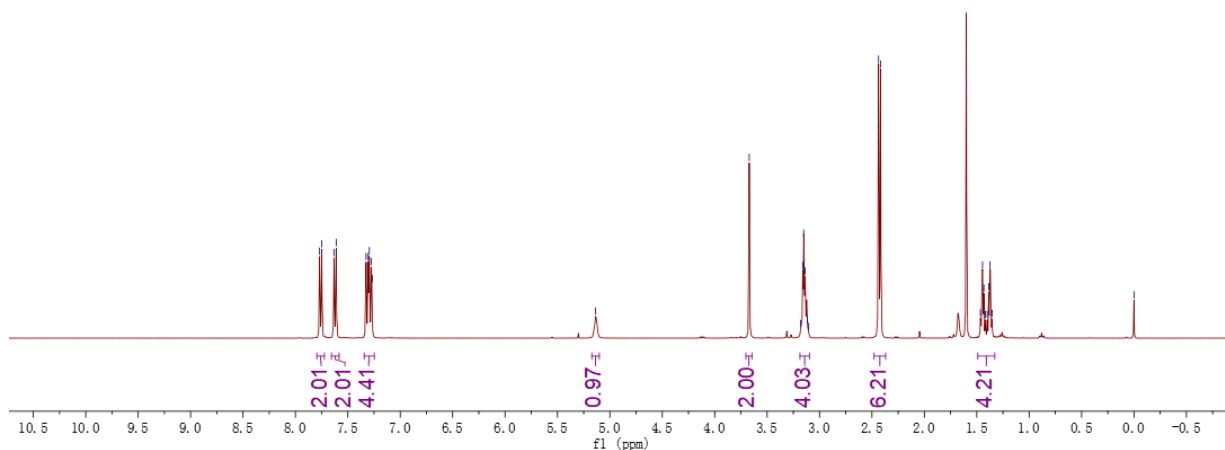


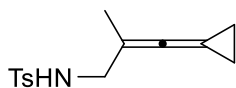
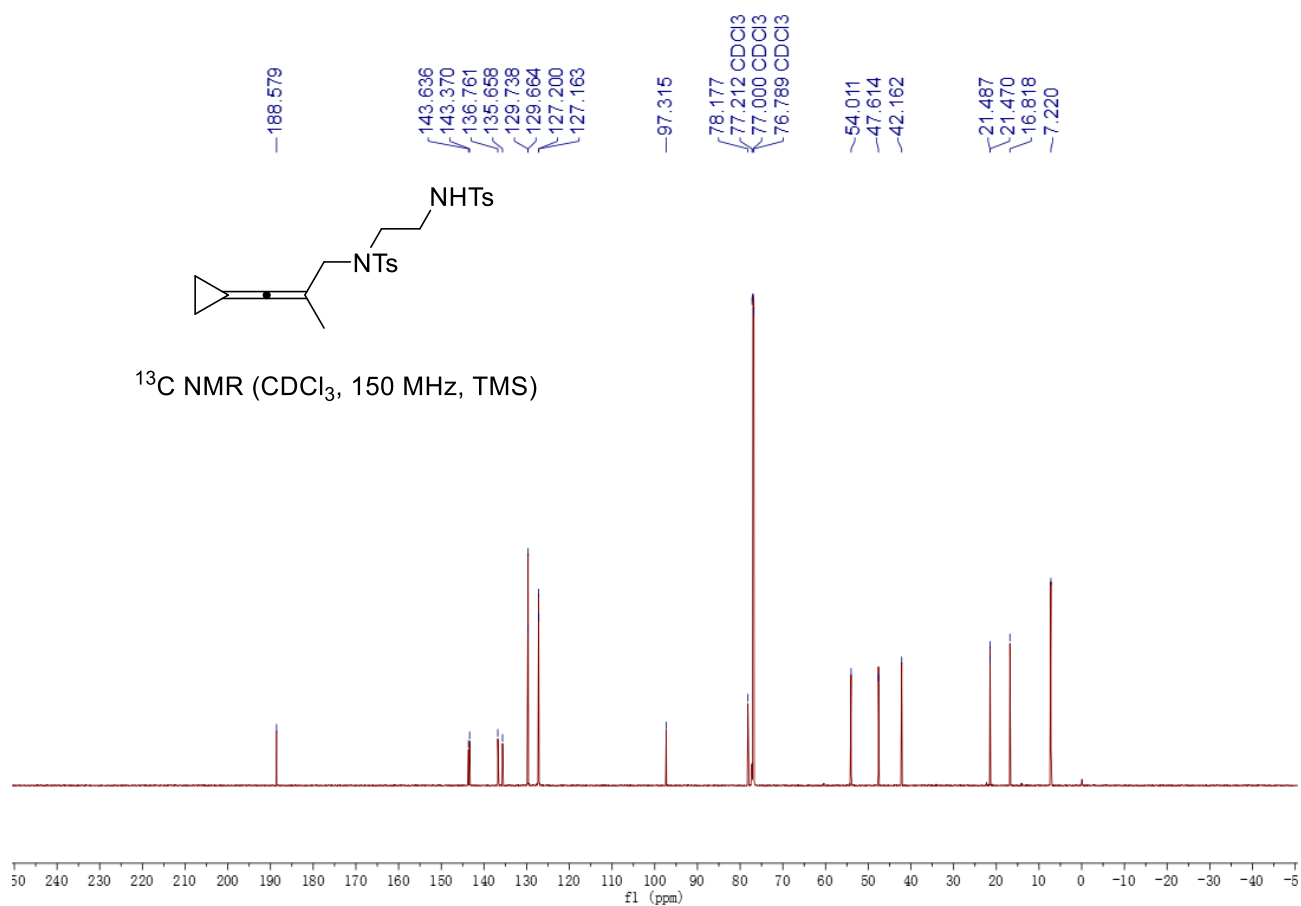
***N*-(3-cyclopropylidene-2-methyl-3-allyl)-4-methyl-*N*-(2-((4-methylphenyl)sulfonamido)ethyl)benzenesulfonamide (10)**

A colorless oil, 40% yield, 184.2 mg. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.34 - 7.25 (m, 4H), 5.14 (s, 1H), 3.67 (s, 2H), 3.19 - 3.10 (m, 4H), 2.43 (d, $J = 7.4$ Hz, 6H), 1.49 - 1.33 (m, 4H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 188.6, 143.6, 143.4, 136.8, 135.7, 129.73, 129.66, 127.20, 127.16, 97.3, 78.2, 54.0, 47.6, 42.2, 21.48, 21.47, 16.8, 7.2. IR (neat) ν 3026, 2964, 1712, 1644, 1359, 1316, 1219, 1090, 774, 698 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$): 483.1383, Found: 483.1382.



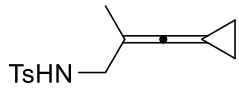
^1H NMR (CDCl_3 , 400 MHz, TMS)



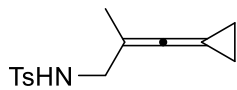
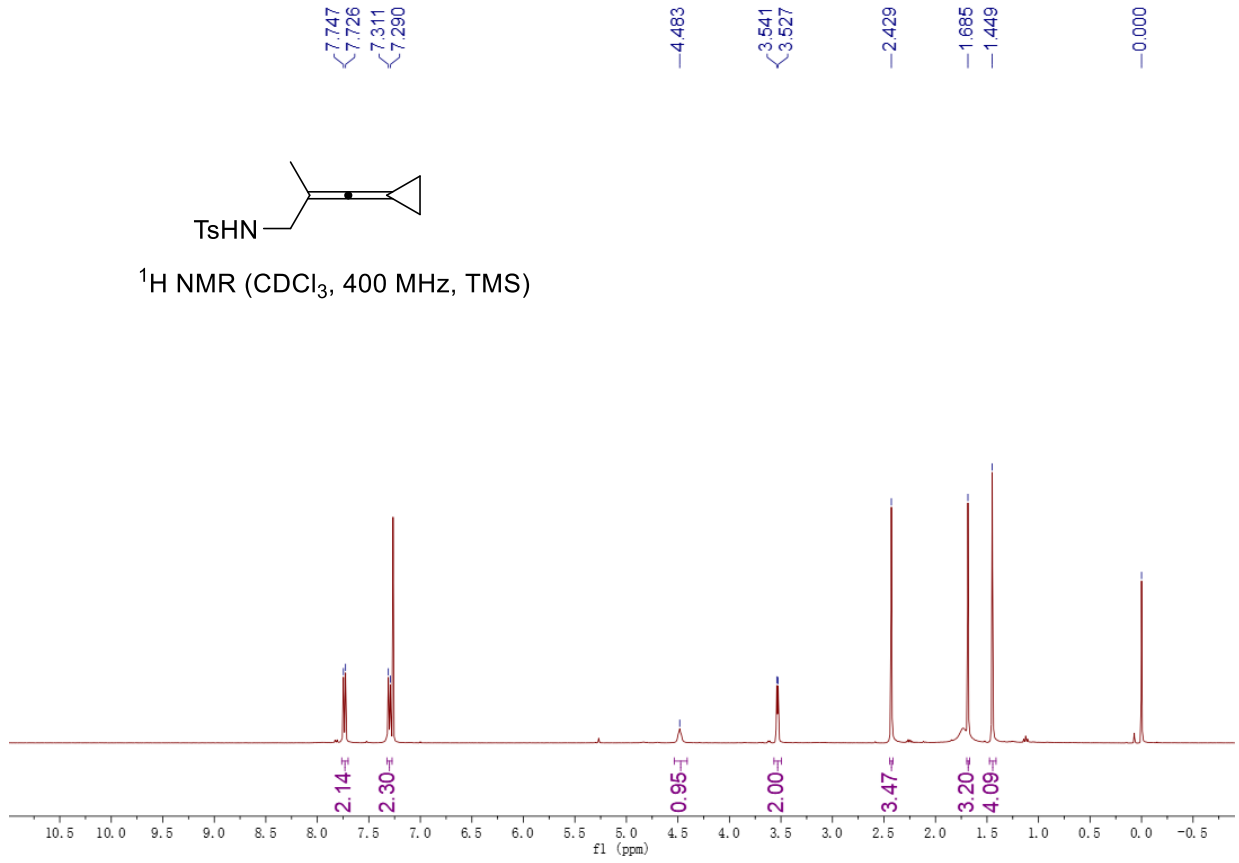


***N*-(3-cyclopropylidene-2-methyl-3-allyl)-4-methylbenzenesulfonamide (1p)**

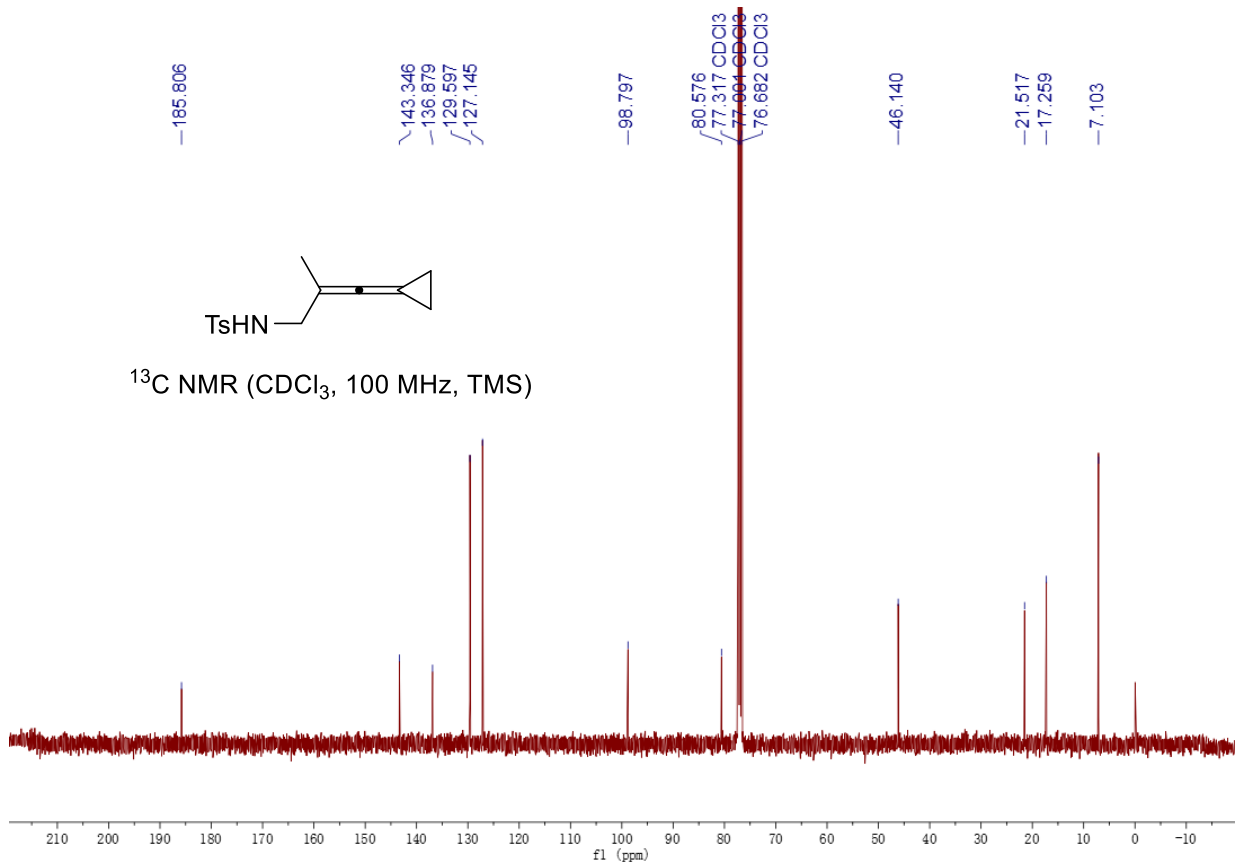
A colorless oil, 38% yield, 100.1 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.48 (s, 1H), 3.53 (d, *J* = 5.3 Hz, 2H), 2.43 (s, 3H), 1.69 (s, 3H), 1.45 (s, 4H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 185.8, 143.3, 136.9, 129.6, 127.1, 98.8, 80.6, 46.1, 21.5, 17.3, 7.1. IR (neat) ν 2917, 1694, 1511, 1477, 1464, 1396, 317, 1169, 1048, 964, 833 cm⁻¹. HRMS (ESI) calcd. for C₁₄H₁₇NO₂NaS (M+Na): 286.0872, Found: 286.0873.

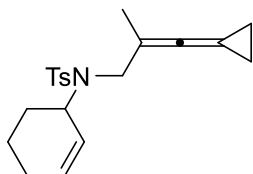


^1H NMR (CDCl_3 , 400 MHz, TMS)



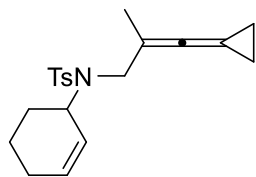
^{13}C NMR (CDCl_3 , 100 MHz, TMS)



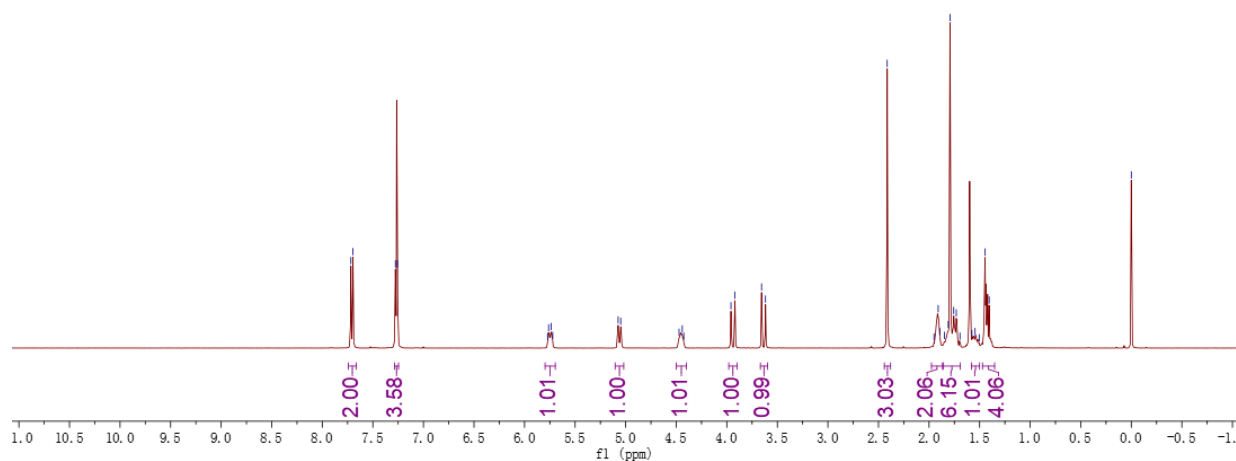


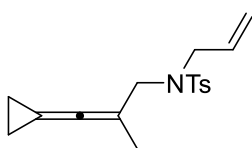
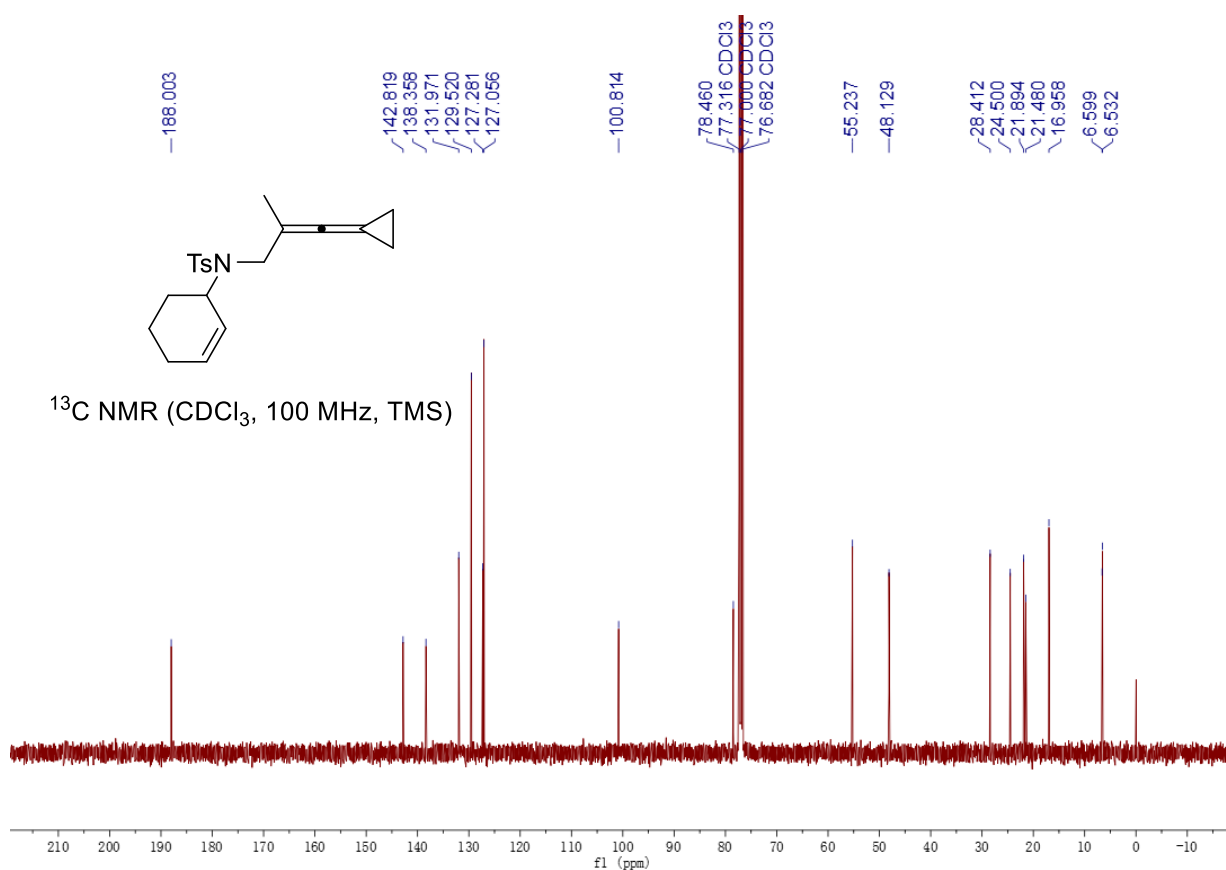
***N*-(cyclohex-2-en-1-yl)-*N*-(3-cyclopropylidene-2-methyl-3 λ ⁵-allyl)-4-methylbenzenesulfonamide (**1q**)**

A colorless oil, 22% yield, 75.6 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.71 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 5.80 - 5.70 (m, 1H), 5.06 (d, J = 10.2 Hz, 1H), 4.50 - 4.40 (m, 1H), 3.94 (d, J = 15.6 Hz, 1H), 3.64 (d, J = 15.6 Hz, 1H), 2.41 (s, 3H), 1.95 - 1.88 (m, 2H), 1.85 - 1.69 (m, 6H), 1.58 - 1.50 (m, 1H), 1.47 - 1.37 (m, 4H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.0, 142.8, 138.4, 132.0, 129.5, 127.3, 127.1, 100.8, 78.5, 55.2, 48.1, 28.4, 24.5, 21.9, 21.5, 17.0, 6.6, 6.5. IR (neat) ν 2983, 1613, 1512, 1463, 1398, 1385, 1318, 1220, 1033, 765, 713 cm⁻¹. HRMS (ESI) calcd. for C₂₀H₂₅NO₂NaS (M+Na): 366.1498, Found: 366.1493.



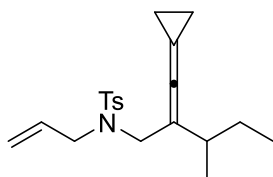
¹H NMR (CDCl₃, 400 MHz, TMS)





***N*-allyl-*N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methylbenzenesulfonamide (1r)**

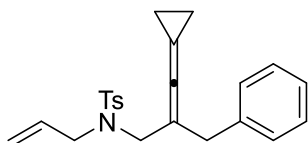
This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[7] 51%, 154.7 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 1.36-1.41 (m, 2H), 1.43-1.47 (m, 2H), 1.73 (s, 3H), 2.26 (q, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 3.18-3.22 (m, 2H), 3.81 (m, 2H), 4.97-4.99 (m, 1H), 4.99-5.03 (m, 1H), 5.62-5.73 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 6.9, 16.9, 21.4, 32.5, 46.9, 52.5, 77.5, 97.5, 116.7, 127.1, 129.5, 135.0, 137.2, 143.0, 188.7.



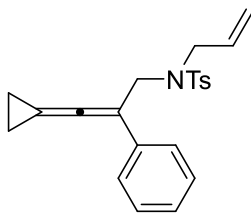
***N*-allyl-*N*-(2-(cyclopropylidene-λ⁵-methylene)-3-methylpentyl)-4-methylbenzenesulfonamide**

(1s)

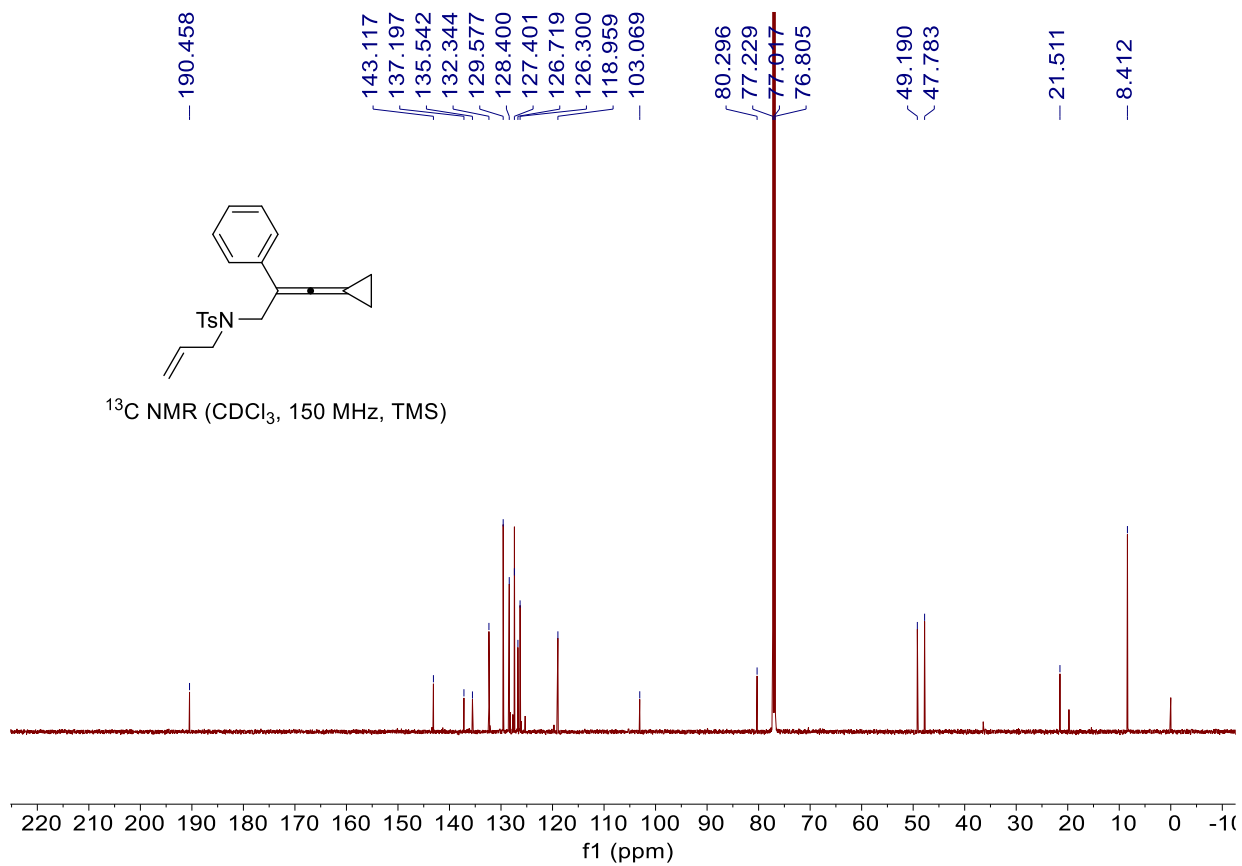
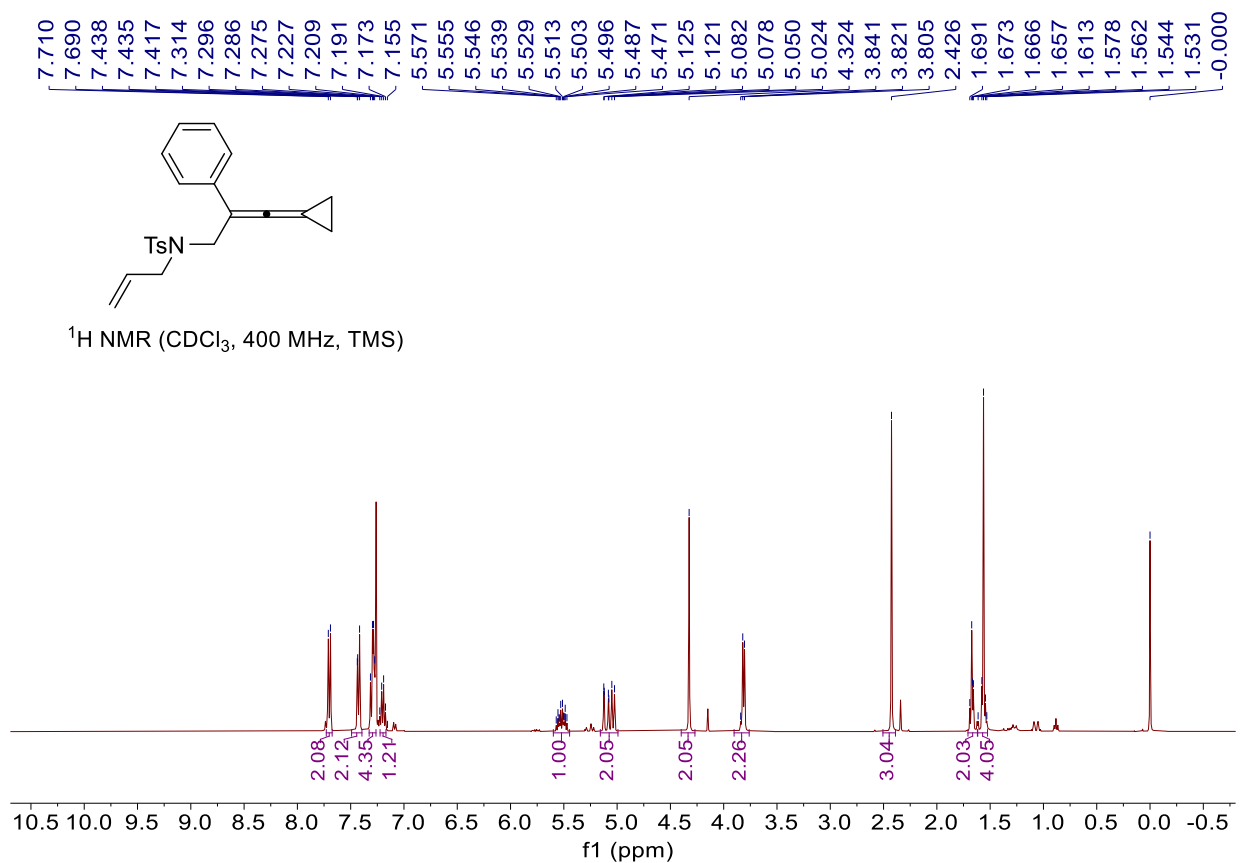
This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[9] 46% yield, 159.0 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.58 - 5.48 (m, 1H), 5.13 - 5.06 (m, 2H), 3.86 - 3.81 (m, 4H), 2.42 (s, 3H), 2.03 - 1.98 (m, 1H), 1.50 - 1.40 (m, 3H), 1.37 - 1.24 (m, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 187.9, 142.9, 137.7, 132.4, 129.5, 127.2, 119.1, 107.1, 79.6, 49.0, 48.6, 35.1, 28.2, 21.5, 19.0, 11.5, 6.9, 6.8.

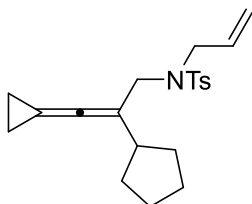
***N*-allyl-*N*-(2-benzyl-3-cyclopropylidene-3λ⁵-allyl)-4-methylbenzenesulfonamide (1t)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[7] 48% yield, 174.6 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 1.35-1.42 (m, 4H), 2.41 (s, 3H), 3.34 (s, 2H), 3.79 (s, 2H), 3.83 (d, *J* = 7.2 Hz, 2H), 5.03 (s, 1H), 5.07 (d, *J* = 8.0 Hz, 1H), 5.46-5.56 (m, 1H), 7.18-7.27 (m, 7H), 7.67 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 7.1, 21.5, 37.0, 49.1, 49.3, 78.9, 101.5, 119.2, 126.1, 127.2, 128.1, 129.0, 129.5, 132.2, 137.5, 143.0, 189.6.

***N*-allyl-*N*-(3-cyclopropylidene-2-phenyl-3λ⁵-allyl)-4-methylbenzenesulfonamide (1u)**

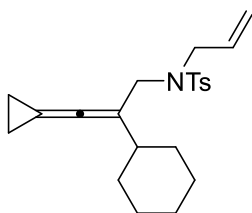
A colorless oil, 41% yield, 149.9 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 - 7.26 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 5.62 - 5.45 (m, 1H), 5.16 - 4.99 (m, 2H), 4.32 (s, 2H), 3.90 - 3.76 (m, 2H), 2.43 (s, 3H), 1.71 - 1.62 (m, 2H), 1.56 (s, 2H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 190.5, 143.1, 137.2, 135.5, 132.3, 129.6, 128.4, 127.4, 126.7, 126.3, 119.0, 103.1, 80.3, 49.2, 47.8, 21.5, 8.4. IR (neat) ν 2996, 2929, 2008, 1596, 1442, 1091, 897, 752 cm⁻¹. HRMS (ESI) calcd. for C₂₂H₂₃NO₂NaS (M+Na)⁺: 388.1341, Found: 388.1349.





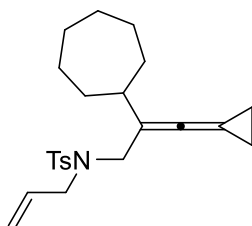
***N*-allyl-*N*-(2-cyclopentyl-3-cyclopropylidene-3λ⁵-allyl)-4-methylbenzenesulfonamide (1v)**

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[9] 51% yield, 182.3 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.54 (td, *J* = 16.8, 6.6 Hz, 1H), 5.14 - 5.06 (m, 2H), 3.86 - 3.82 (m, 4H), 2.42 (s, 3H), 2.39 - 2.33 (m, 1H), 1.85 - 1.77 (m, 2H), 1.65 - 1.59 (m, 2H), 1.53 - 1.50 (m, 2H), 1.46 - 1.43 (m, 2H), 1.39 - 1.33 (m, 4H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 187.1, 142.9, 137.6, 132.3, 129.5, 127.2, 125.2, 119.1, 106.6, 105.0, 79.6, 49.5, 49.1, 39.9, 31.8, 29.7, 24.9, 21.5, 6.9.



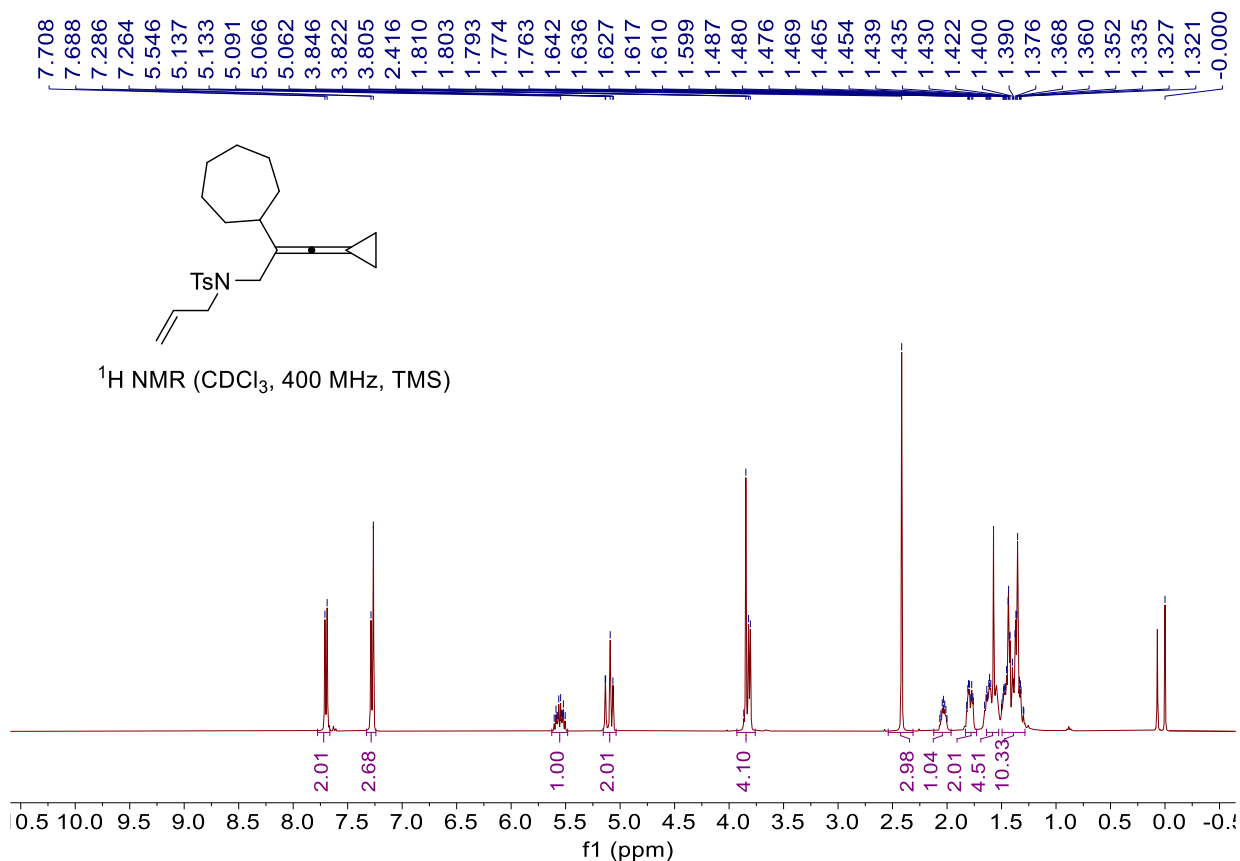
***N*-allyl-*N*-(2-cyclohexyl-3-cyclopropylidene-3λ⁵-allyl)-4-methylbenzenesulfonamide (1w)**

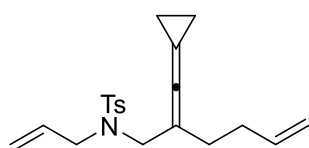
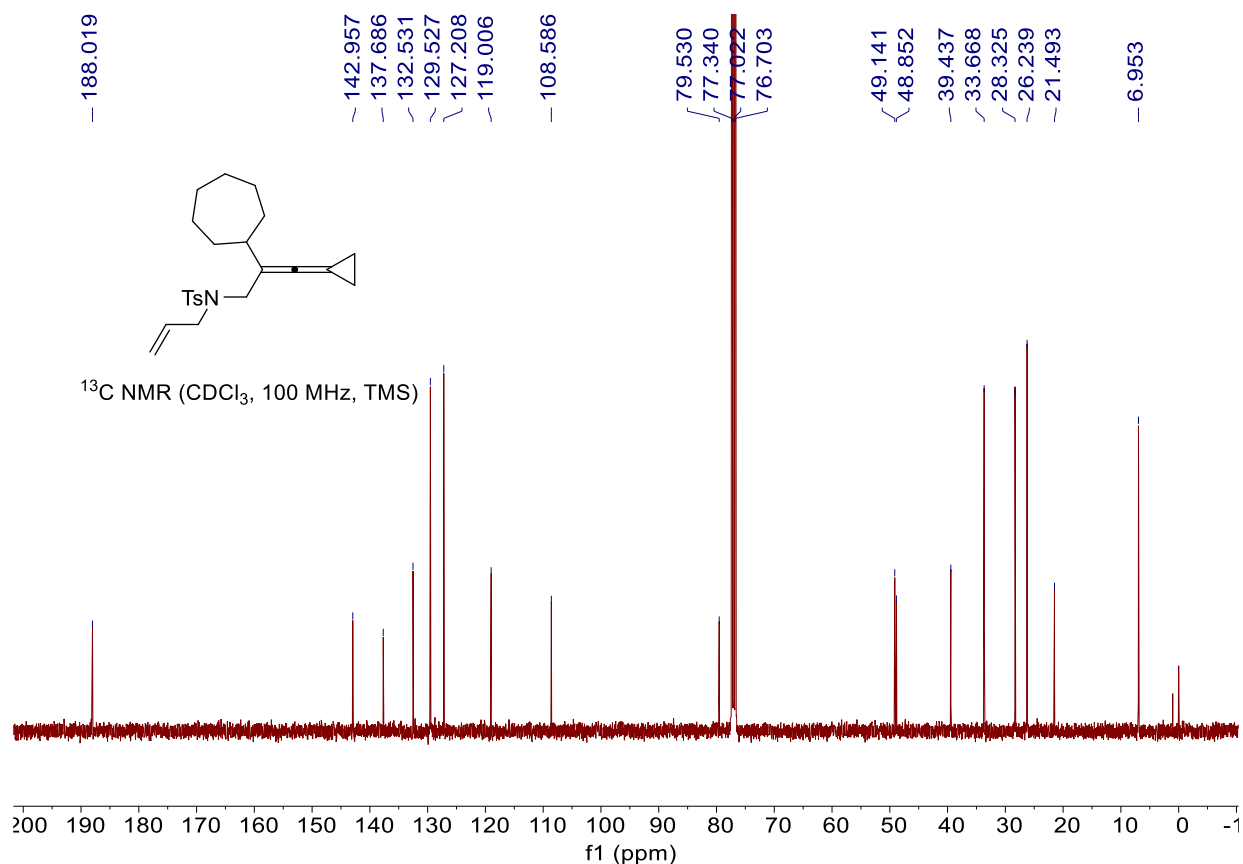
A white solid, this is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[9] 46% yield, 170.9 mg, M.P.: 87-89 °C. ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.03 - 1.25 (m, 5H), 1.33 - 1.38 (m, 2H), 1.42 - 1.46 (m, 2H), 1.61 - 1.86 (m, 6H), 2.42 (s, 3H), 3.82 (d, *J* = 6.6 Hz, 2H), 3.85 (s, 2H), 5.08 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 15.3 Hz, 1H), 5.49 - 5.62 (m, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 7.0, 21.4, 26.2, 26.3, 32.1, 37.7, 48.3, 49.0, 79.3, 107.5, 119.0, 127.2, 129.5, 132.4, 137.6, 142.9, 188.1.



***N*-allyl-*N*-(2-cycloheptyl-3-cyclopropylidene-3λ⁵-allyl)-4-methylbenzenesulfonamide (1x)**

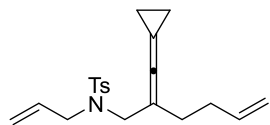
A white solid, 47% yield, 181.2 mg, M.P.: 83-86 °C. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.70 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.63 - 5.48 (m, 1H), 5.15 - 5.04 (m, 2H), 3.93 - 3.76 (m, 4H), 2.42 (s, 3H), 2.12 - 1.96 (m, 1H), 1.83 - 1.73 (m, 2H), 1.64 - 1.53 (m, 4H) 1.49 - 1.29 (m, 10H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 188.0, 143.0, 137.7, 132.5, 129.5, 127.2, 119.0, 108.6, 79.5, 49.1, 48.9, 39.4, 33.7, 28.3, 26.2, 21.5, 7.0. IR (neat) ν 2922, 2853, 2018, 1598, 1444, 1091, 905, 764 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{31}\text{NO}_2\text{NaS}$ ($\text{M}+\text{Na}$) $^+$: 408.1967, Found: 408.1972.



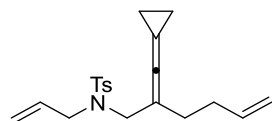
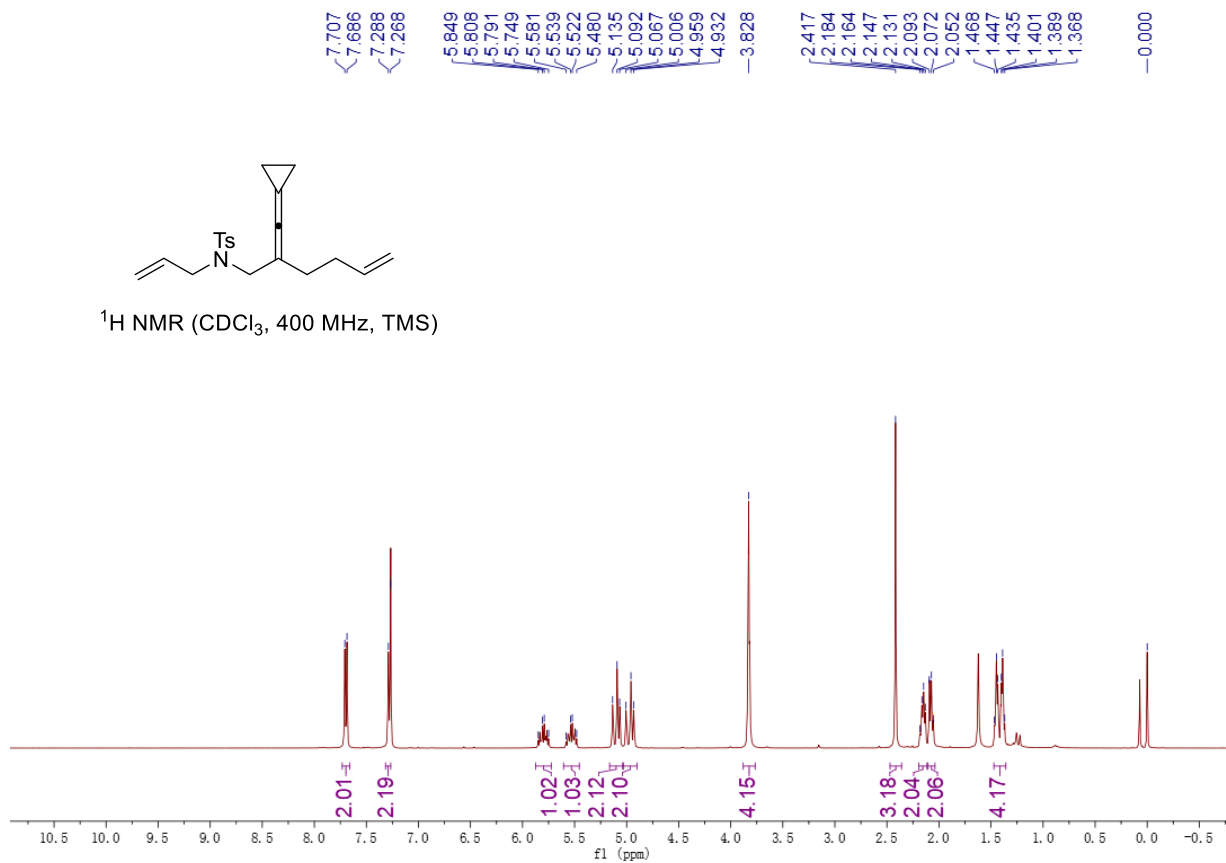


***N*-allyl-*N*-(2-(cyclopropylidene- λ^5 -methylene)hex-5-en-1-yl)-4-methylbenzenesulfonamide (1y)**

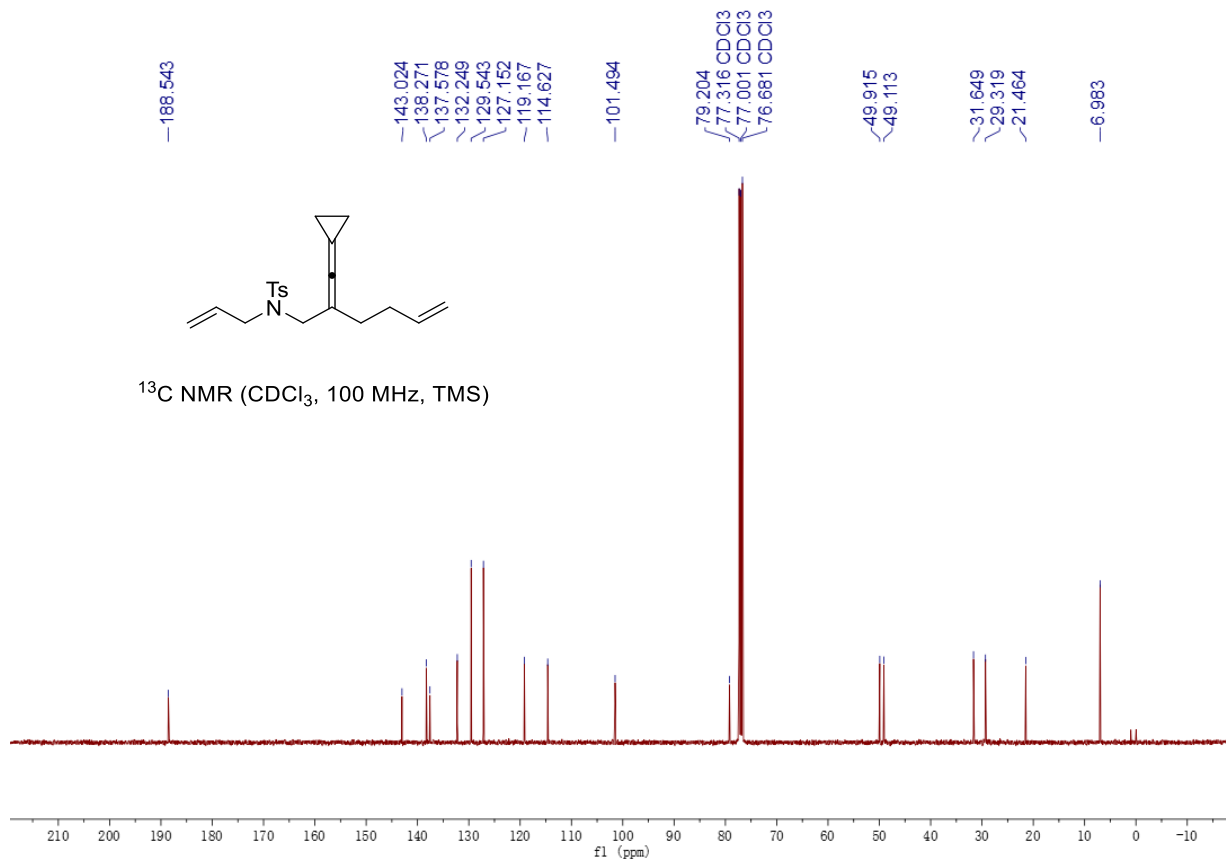
A colorless oil, 39% yield, 134.0 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.70 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.87 - 5.72 (m, 1H), 5.61 - 5.45 (m, 1H), 5.16 - 5.04 (m, 2H), 5.03 - 4.90 (m, 2H), 3.83 (s, 4H), 2.42 (s, 3H), 2.19 - 2.11 (m, 2H), 2.11 - 2.04 (m, 2H), 1.47 - 1.36 (m, 4H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.5, 143.0, 138.3, 137.6, 132.2, 129.5, 127.2, 119.2, 114.6, 101.5, 79.2, 49.9, 49.1, 31.6, 29.3, 21.5, 7.0. IR (Acetone) ν 2923, 1710, 1597, 1461, 1396, 1220, 1025, 991, 890, 803, 697 cm⁻¹. HRMS (ESI) calcd. for C₂₀H₂₅NO₂NaS (M+Na): 366.1492, Found: 366.1502.

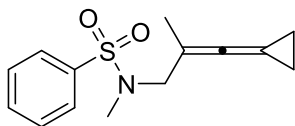


^1H NMR (CDCl_3 , 400 MHz, TMS)



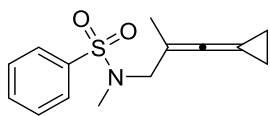
^{13}C NMR (CDCl_3 , 100 MHz, TMS)



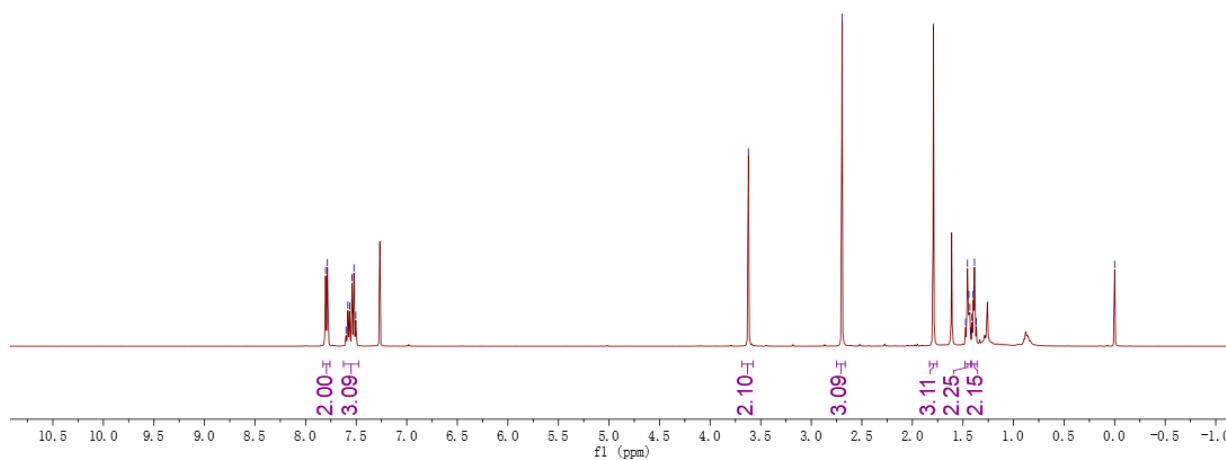


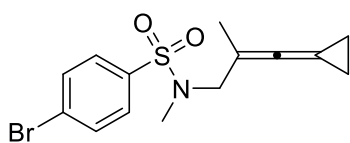
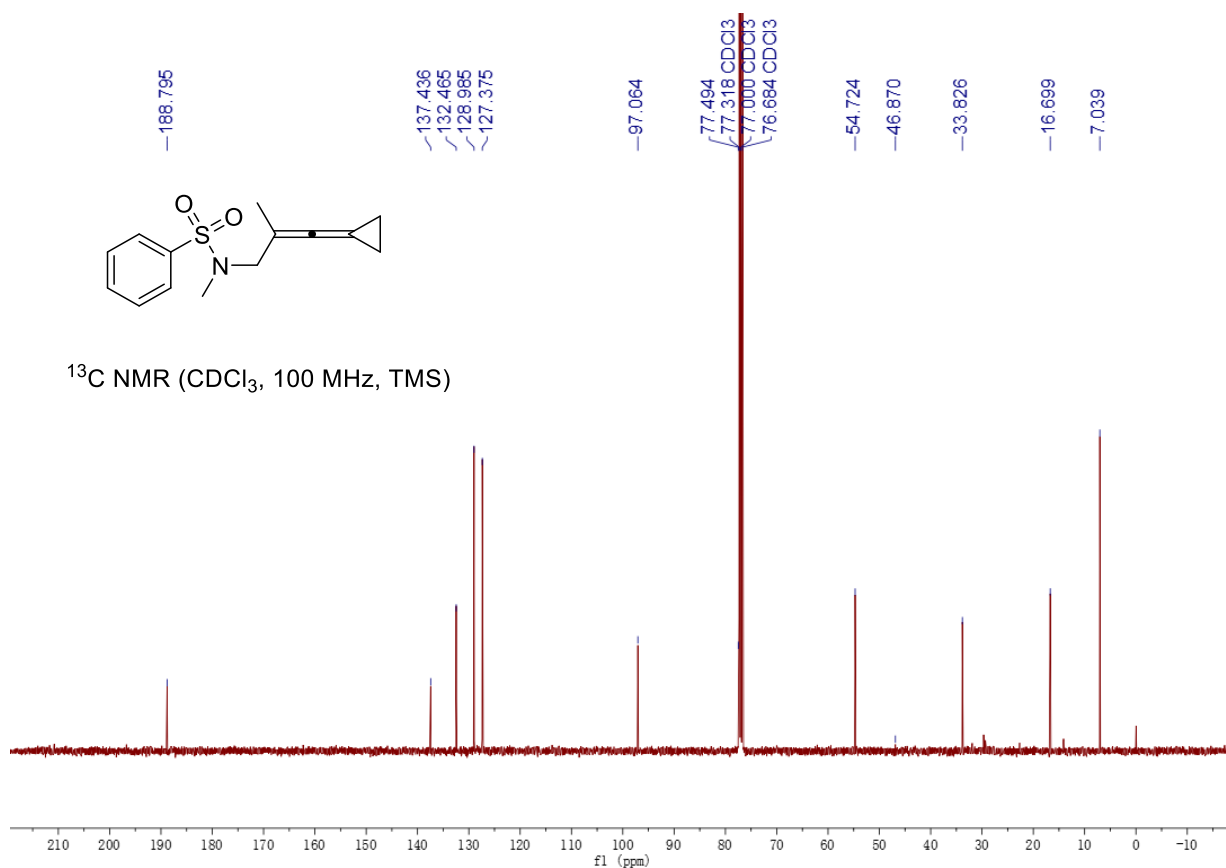
***N*-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-*N*-methylbenzenesulfonamide (1aa)**

A colorless oil, 50% yield, 131.7 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.63 - 7.48 (m, 3H), 3.62 (s, 2H), 2.70 (s, 3H), 1.79 (s, 3H), 1.48 - 1.42 (m, 2H), 1.41 - 1.36 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 188.8, 137.4, 132.5, 129.0, 127.4, 97.1, 77.5, 54.7, 46.9, 33.8, 16.7, 7.0. IR (neat) ν 2921, 2855, 1711, 1488, 1396, 1332, 1219, 1034, 991, 790, 759 cm⁻¹. HRMS (ESI) calcd. for C₁₄H₁₇NO₂NaS (M+Na): 286.0872, Found: 286.0873.



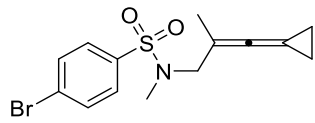
¹H NMR (CDCl₃, 400 MHz, TMS)



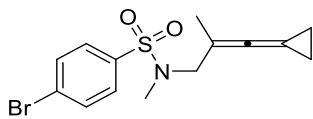
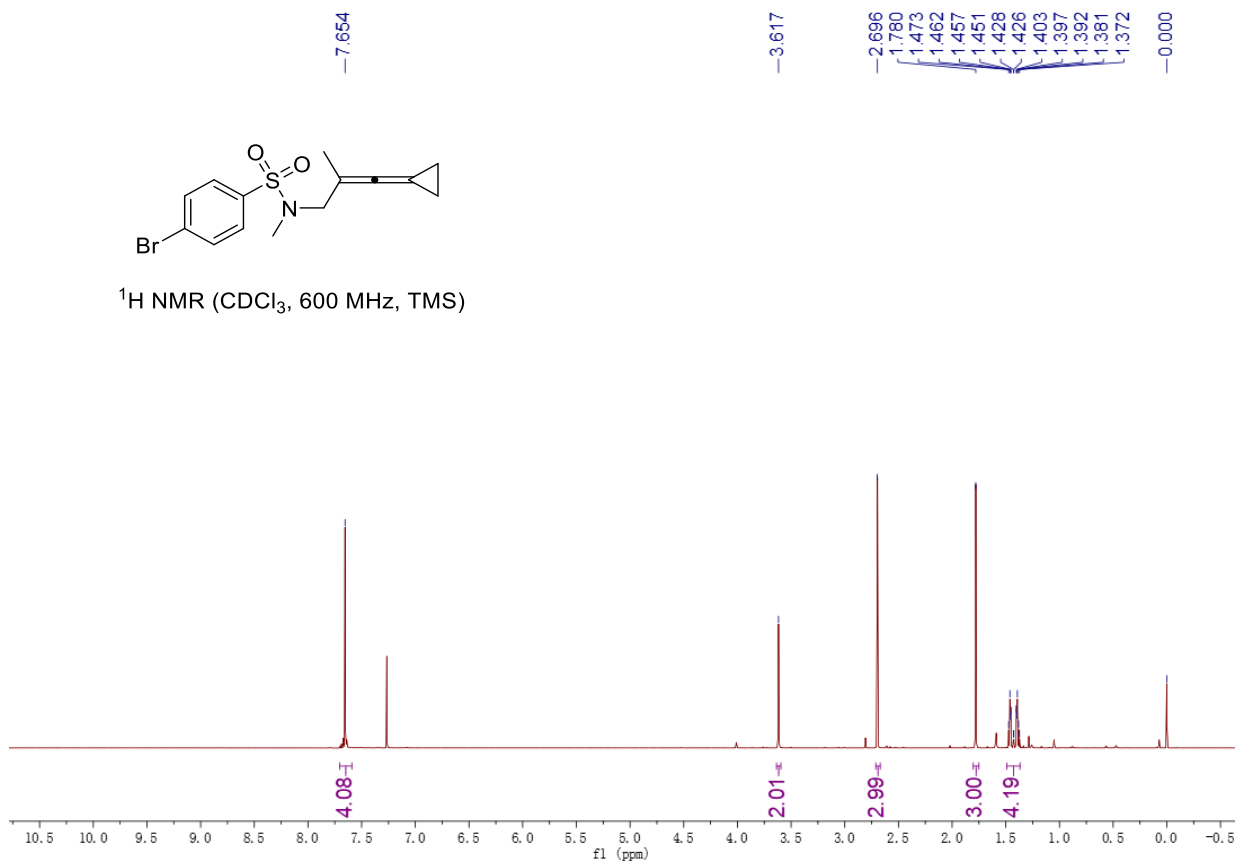


4-bromo-*N*-(3-cyclopropylidene-2-methyl-3-allyl)-*N*-methylbenzenesulfonamide (1ab)

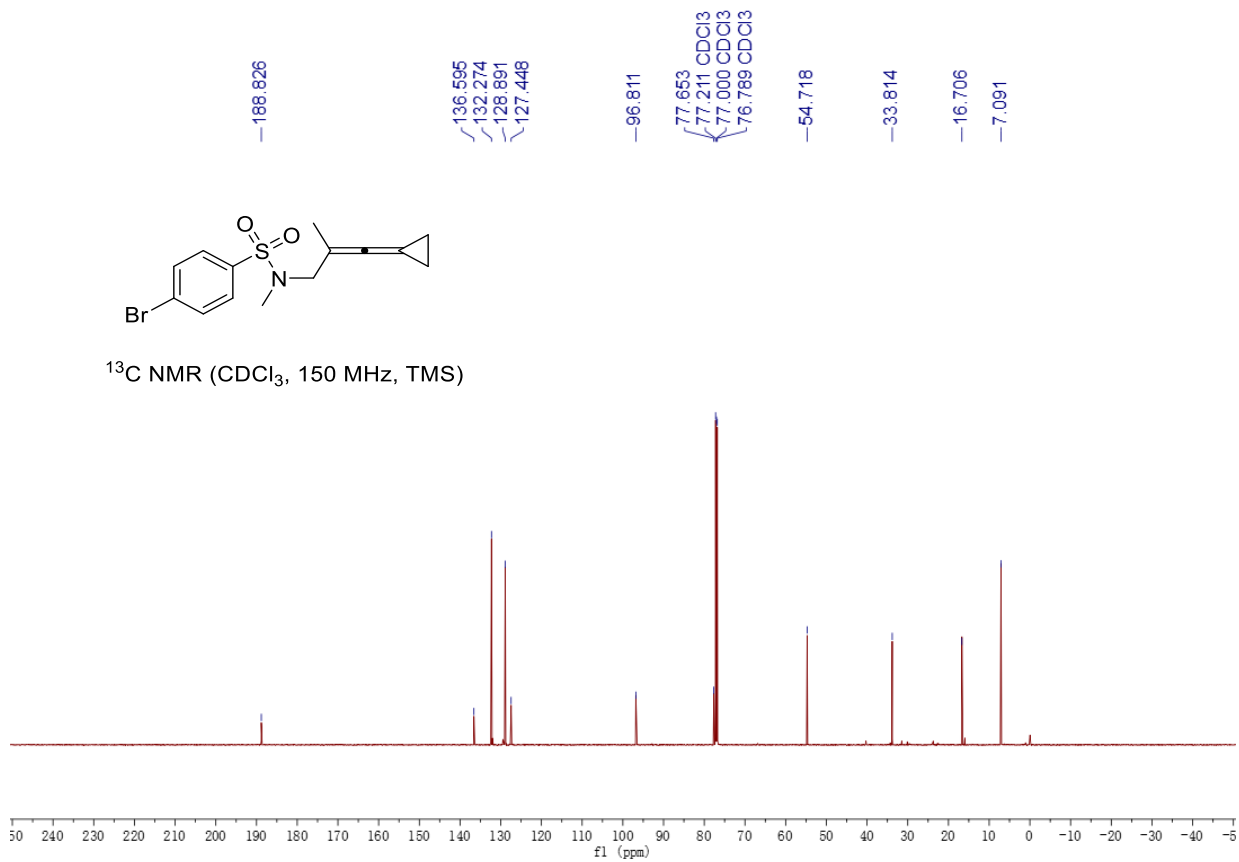
A colorless oil, 43% yield, 147.2 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.65 (s, 4H), 3.62 (s, 2H), 2.70 (s, 3H), 1.78 (s, 3H), 1.49 - 1.37 (m, 4H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 188.8, 136.6, 132.3, 128.9, 127.4, 96.8, 77.7, 54.7, 33.8, 16.7, 7.1. IR (neat) ν 2942, 1658, 1428, 1343, 1253, 1221, 1161, 992, 945, 803, 754, 699 cm⁻¹. HRMS (ESI) calcd. for C₁₄H₁₆NO₂NaSBr (M+Na): 363.9977, Found: 363.9977.

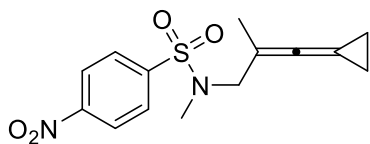


^1H NMR (CDCl_3 , 600 MHz, TMS)



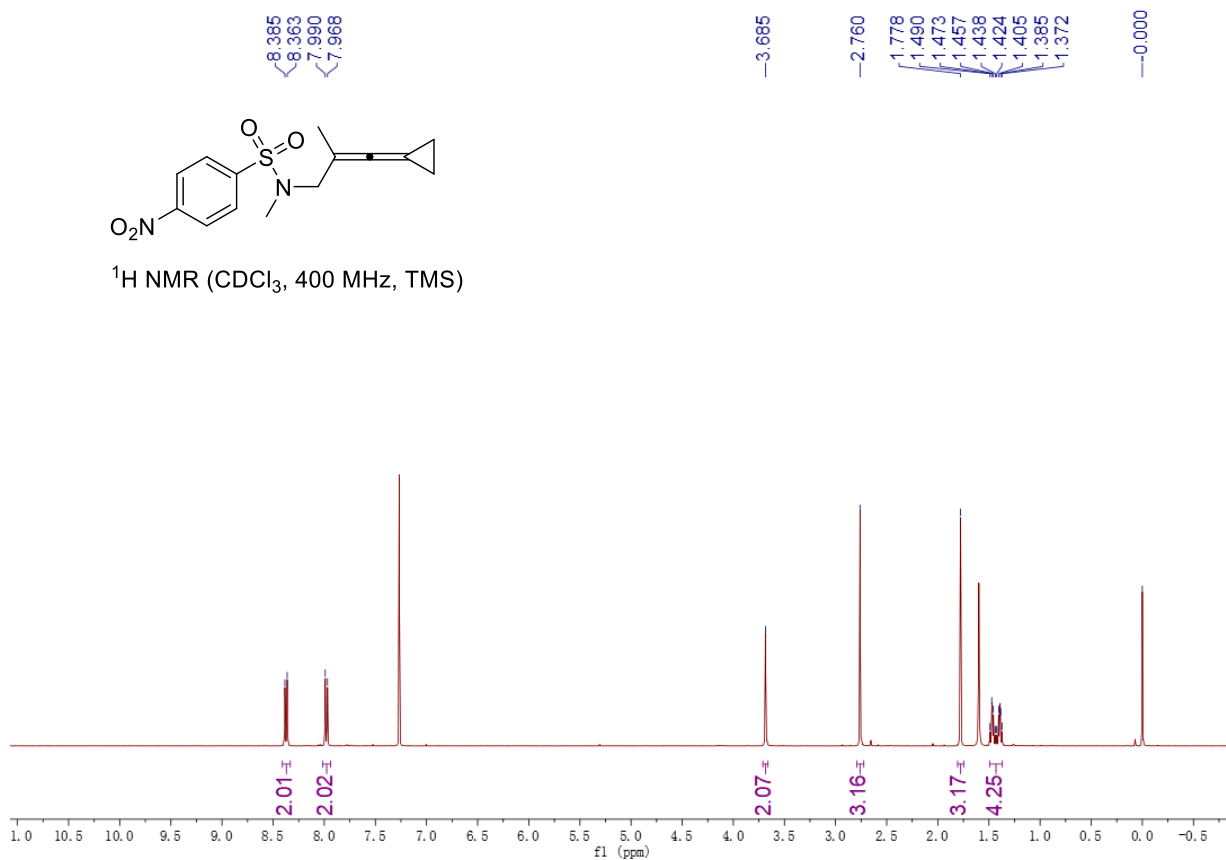
^{13}C NMR (CDCl_3 , 150 MHz, TMS)

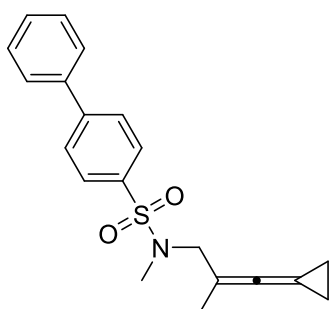
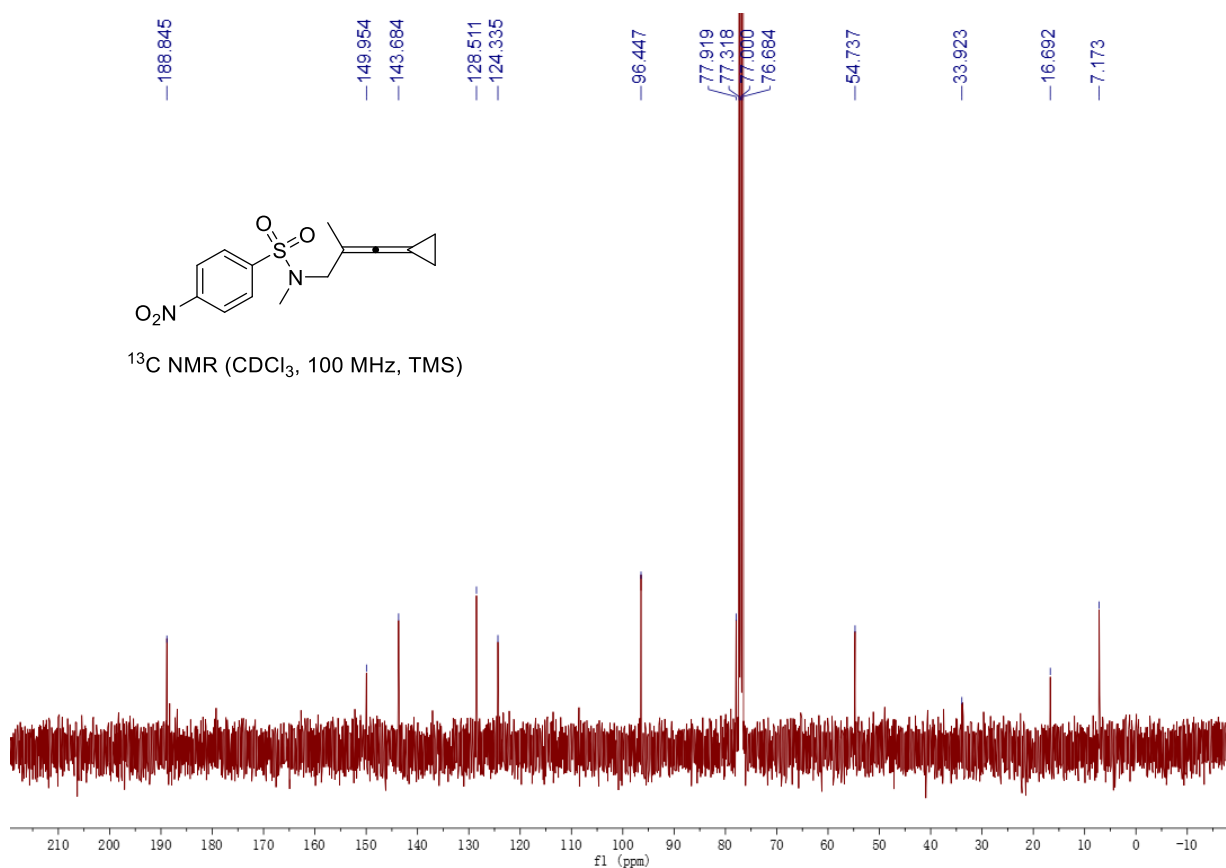




***N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-*N*-methyl-4-nitrobenzenesulfonamide (1ac)**

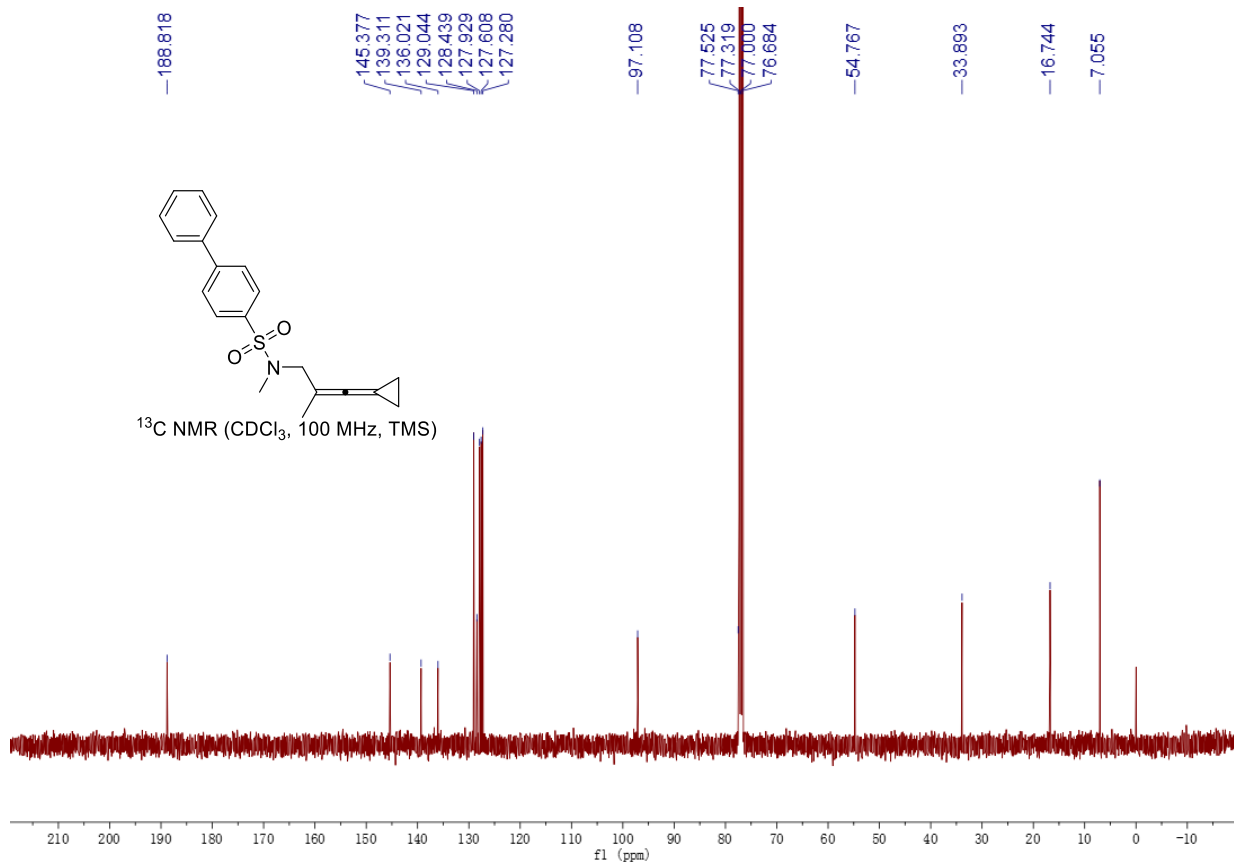
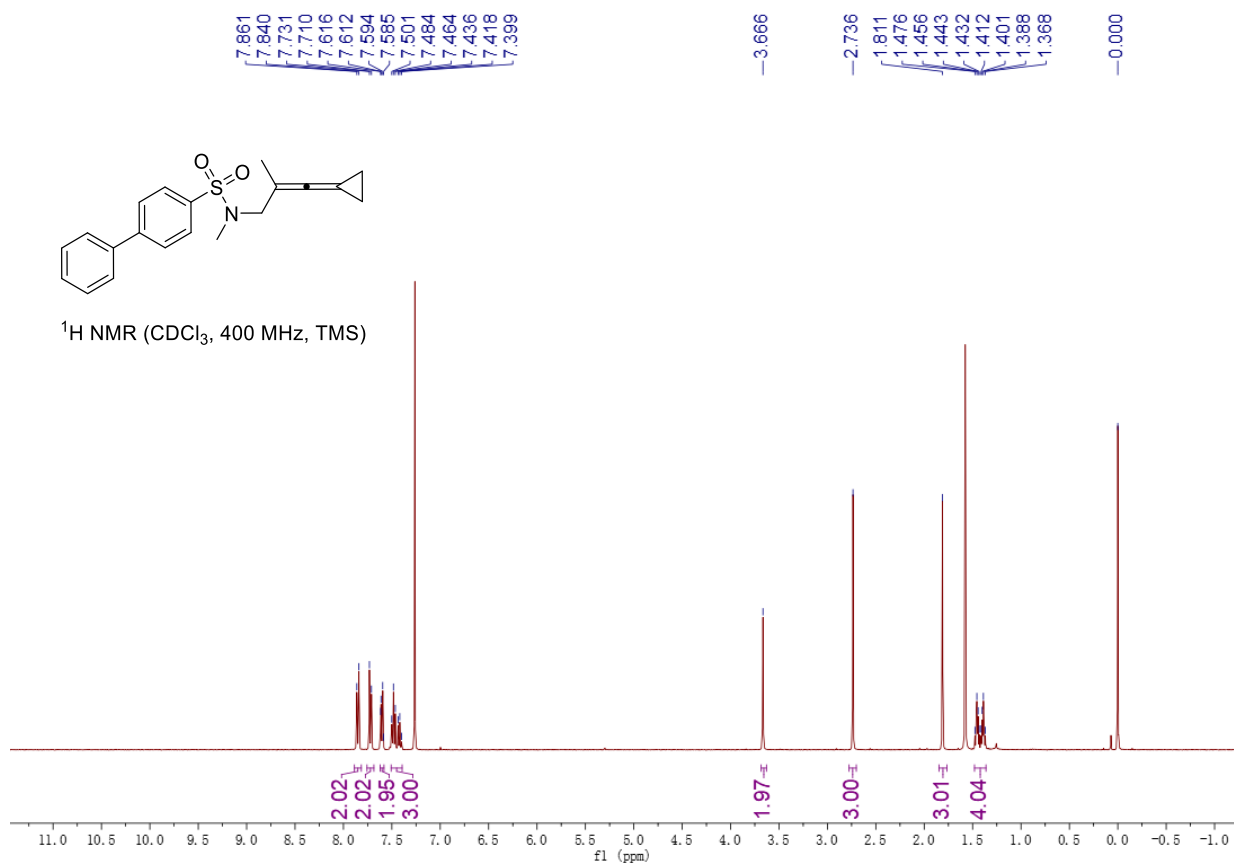
A yellow oil, 40% yield, 123.4 mg. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 8.37 (d, $J = 8.9$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 2H), 3.69 (s, 2H), 2.76 (s, 3H), 1.78 (s, 3H), 1.49 - 1.37 (m, 4H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 188.8, 150.0, 143.7, 128.5, 124.3, 96.4, 77.9, 54.7, 33.9, 16.7, 7.2. IR (neat) ν 2966, 1674, 1480, 1448, 1396, 1219, 991, 756, 738, 722, 697 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$ (M+H): 309.0905, Found: 309.0904.

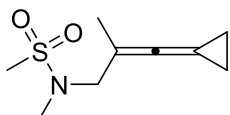




***N*-(3-cyclopropylidene-2-methyl-3 λ^5 -allyl)-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide (1ad)**

A colorless oil, 44% yield, 149.4 mg. ^1H NMR (CDCl₃, TMS, 400 MHz) δ 7.85 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.62 - 7.58 (m, 2H), 7.51 - 7.39 (m, 3H), 3.67 (s, 2H), 2.74 (s, 3H), 1.81 (s, 3H), 1.48 - 1.36 (m, 4H). ^{13}C NMR (CDCl₃, TMS, 100 MHz) δ 188.8, 145.4, 139.3, 136.0, 129.0, 128.4, 127.9, 127.6, 127.3, 97.1, 77.5, 54.8, 33.9, 16.7, 7.1. IR (neat) ν 2932, 1712, 1588, 1461, 1418, 1396, 1034, 991, 891, 747, 697 cm⁻¹. HRMS (ESI) calcd. for C₂₀H₂₂NO₂S (M+H): 340.1365, Found: 340.1366.

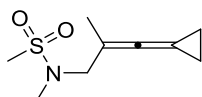




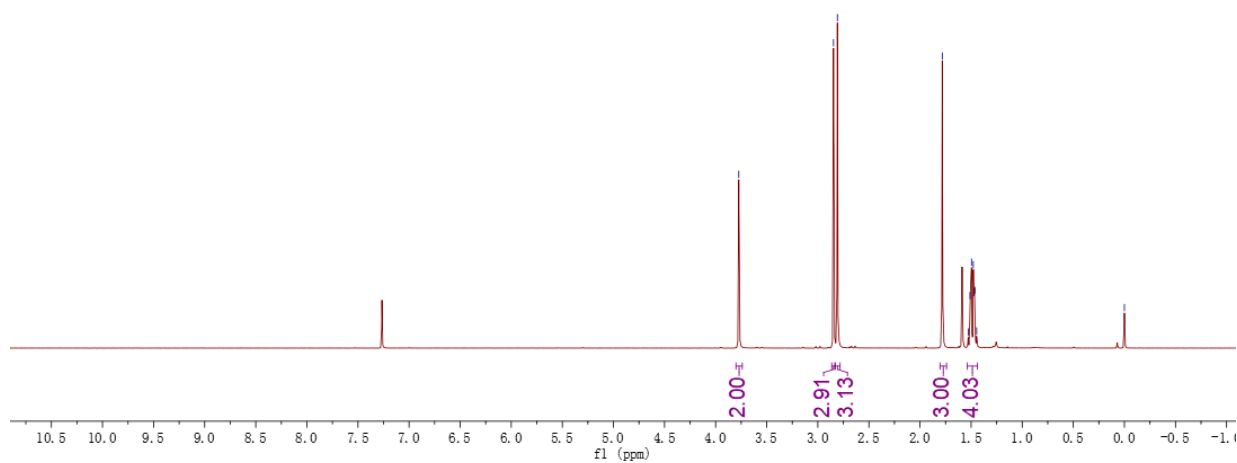
***N*-(3-cyclopropylidene-2-methyl-3-allyl)-*N*-methylmethanesulfonamide (1ae)**

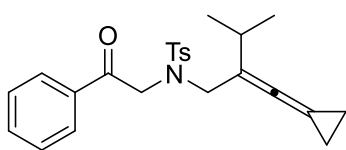
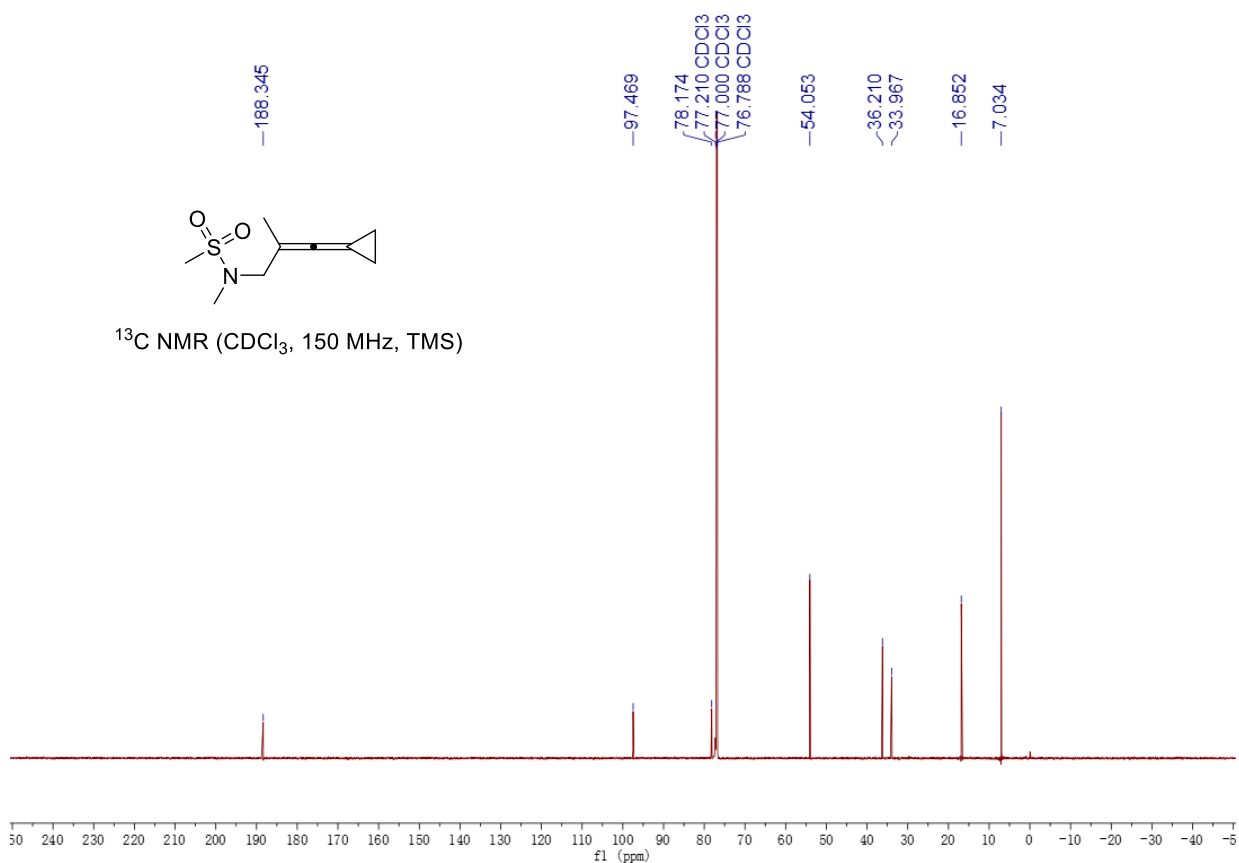
A colorless oil, 52% yield, 104.7 mg. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 3.77 (s, 2H), 2.85 (s, 3H), 2.81 (s, 3H), 1.78 (s, 3H), 1.54 - 1.44 (m, 4H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 188.3, 97.5, 78.2, 77.2, 77.0, 76.8, 54.1, 36.2, 34.0, 16.9, 7.0. IR (neat) ν 2917, 1634, 1493, 1456, 1397, 1301, 1221, 1034, 991, 746, 697 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_9\text{H}_{15}\text{NO}_2\text{NaS}$ ($\text{M}+\text{Na}$): 224.0721, Found: 224.0732.

3.773
2.847
2.809
1.782
1.528
1.510
1.496
1.478
1.464
1.446
0.000



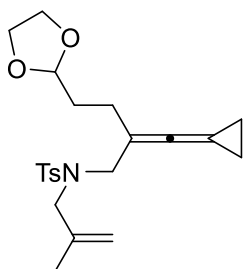
^1H NMR (CDCl_3 , 400 MHz, TMS)





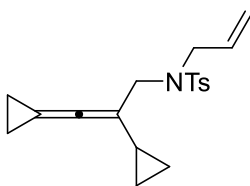
***N*-(2-(cyclopropylidene-15-methylene)-3-methylbutyl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (1z)**

A light yellow oil, this is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[10] 33% yield, 135.1 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 0.95 (d, *J* = 6.8 Hz, 6H), 1.13-1.16 (m, 2H), 1.28-1.31 (m, 2H), 2.19-2.26 (m, 1H), 2.43 (s, 3H), 4.00 (s, 2H), 4.73 (s, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J*₁ = 7.6 Hz, *J*₂ = 8.0 Hz, 2H), 7.58 (dd, *J*₁ = 7.2 Hz, *J*₂ = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 7.1, 21.49, 21.54, 28.4, 49.8, 51.8, 79.4, 108.0, 127.5, 127.9, 128.7, 129.4, 133.5, 135.3, 137.0, 143.2, 188.0, 193.9.



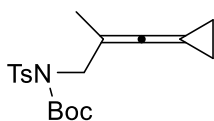
***N*-(2-(cyclopropylidene- λ^5 -methylene)-4-(1,3-dioxolan-2-yl)butyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (1af)**

A yellow oil, this is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[11] 35% yield, 141.2 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 1.32- 1.36 (m, 2H), 1.38-1.42 (m, 2H), 1.63 (s, 3H), 1.66-1.71 (m, 2H), 2.00 (t, $J = 8.0$ Hz, 3H), 2.41 (s, 3H), 3.75 (s, 2H), 3.82-3.84 (m, 4H), 3.92-3.96 (m, 2H), 4.81(t, $J = 4.8$ Hz, 1H), 4.84-4.86 (m, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 6.8, 19.9, 21.4, 23.9, 24.6, 31.8, 33.7, 50.1, 52.9, 64.7, 79.8, 101.8, 103.9, 104.4, 114.3, 127.1, 129.3, 137.5, 140.0, 142.8, 187.9



***N*-allyl-*N*-(2-cyclopropyl-3-cyclopropylidene-3-allyl)-4-methylbenzenesulfonamide (1aj)**

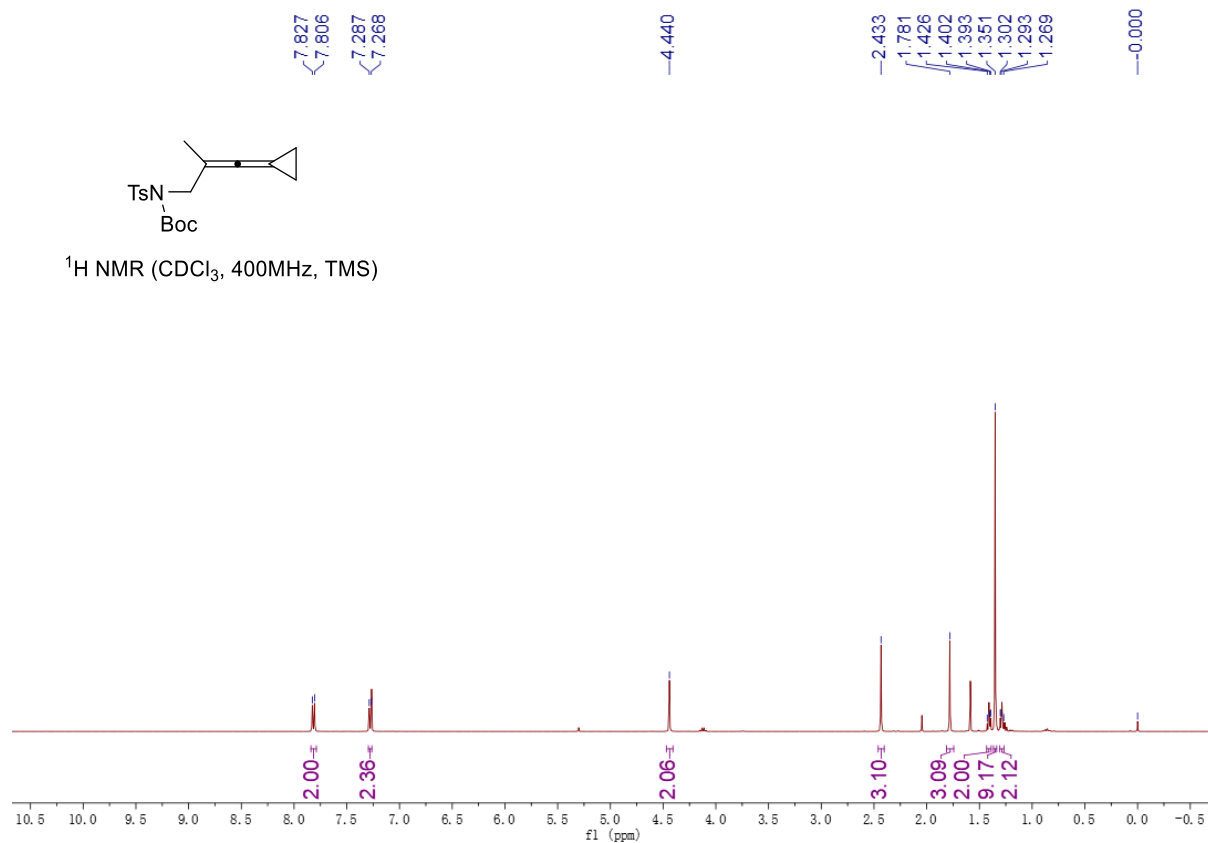
A yellow oil, this is a known compound and its spectroscopic data are consistent with those reported in the previous literature,^[11] 39% yield, 128.3 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.71 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 5.67 - 5.56 (m, 1H), 5.19 - 4.94 (m, 2H), 3.94 (s, 2H), 3.89 - 3.84 (m, 2H), 2.41 (s, 3H), 1.46 - 1.32 (m, 4H), 1.23 - 1.17 (m, 1H), 0.70 - 0.59 (m, 2H), 0.40 - 0.27 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 185.5, 141.9, 136.8, 131.4, 128.5, 126.2, 118.1, 104.6, 79.4, 48.9, 48.1, 20.5, 9.8, 6.12, 6.07.

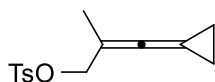
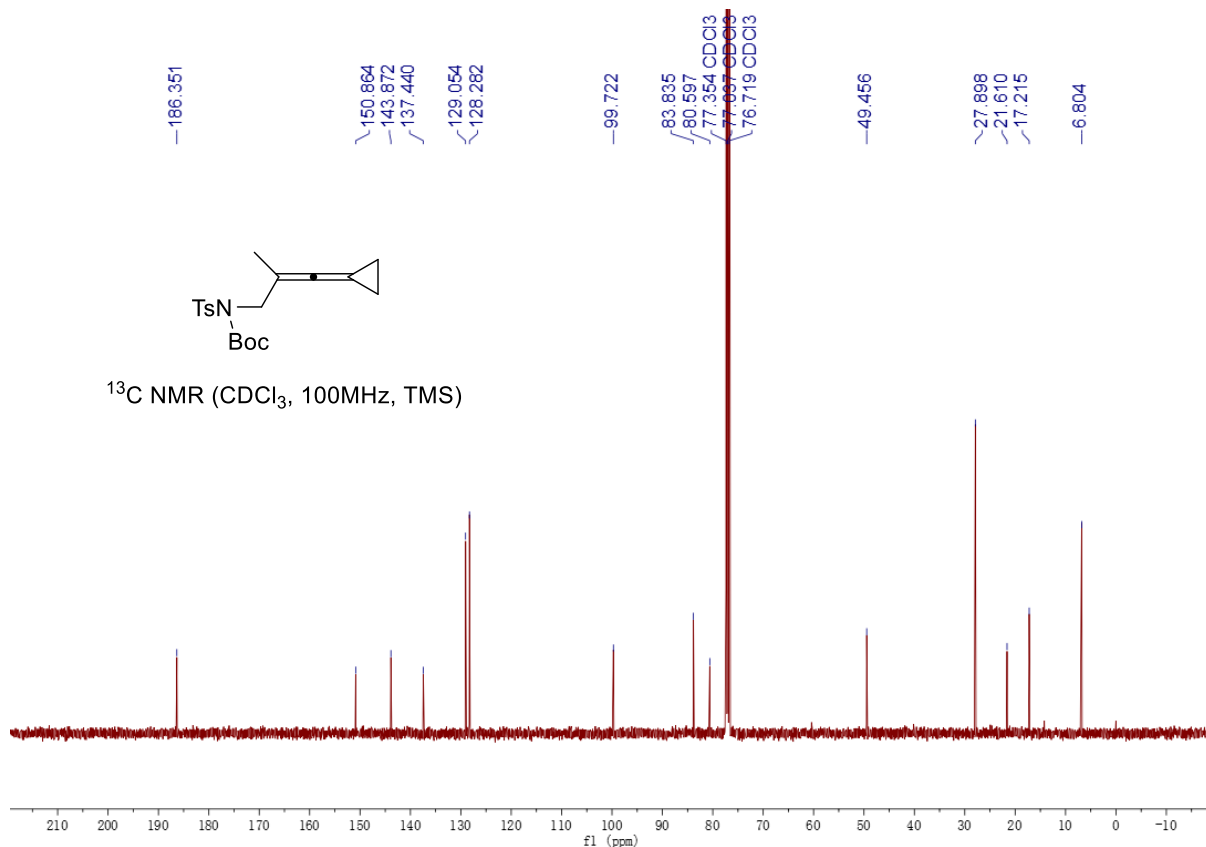


***tert*-butyl (3-cyclopropylidene-2-methyl-3 λ^5 -allyl)(tosyl)carbamate (1ak)**

A colorless oil, 60% yield, 217.8 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.82 (d, $J = 8.3$ Hz, 2H),

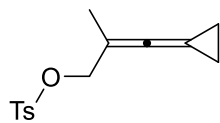
7.28 (d, $J = 7.8$ Hz, 2H), 4.44 (s, 2H), 2.43 (s, 3H), 1.78 (s, 3H), 1.43 - 1.39 (m, 2H), 1.35 (s, 9H), 1.31 - 1.27 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 186.4, 150.9, 143.9, 137.4, 129.1, 128.3, 99.7, 83.8, 80.6, 49.5, 27.9, 21.6, 17.2, 6.8. IR (neat) ν 2919, 1810, 1618, 1329, 1307, 1289, 1103, 981, 867, 709, 698 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{NS}$ ($\text{M}+\text{H}$): 364.1577, Found: 364.1563.



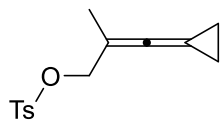
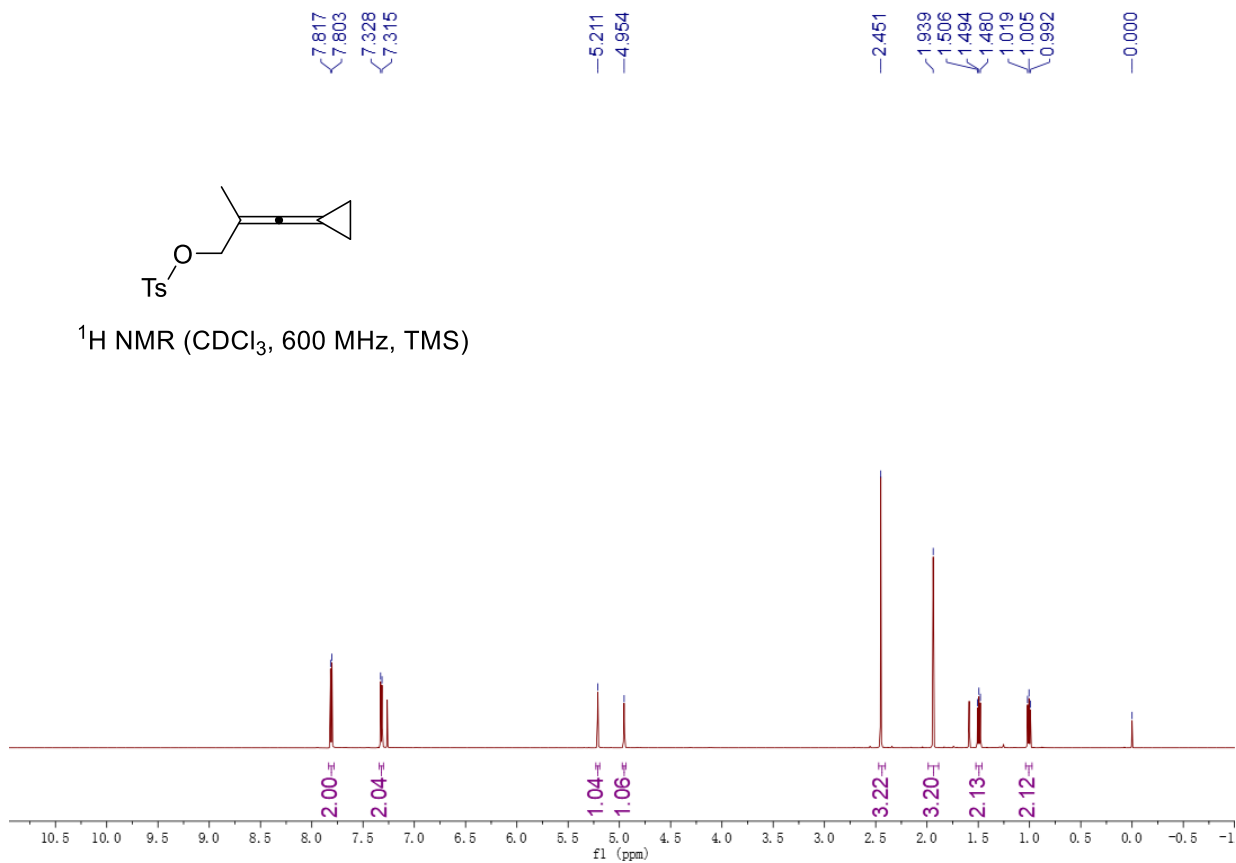


3-cyclopropylidene-2-methyl-3λ⁵-allyl 4-methylbenzenesulfonate (**5a**)

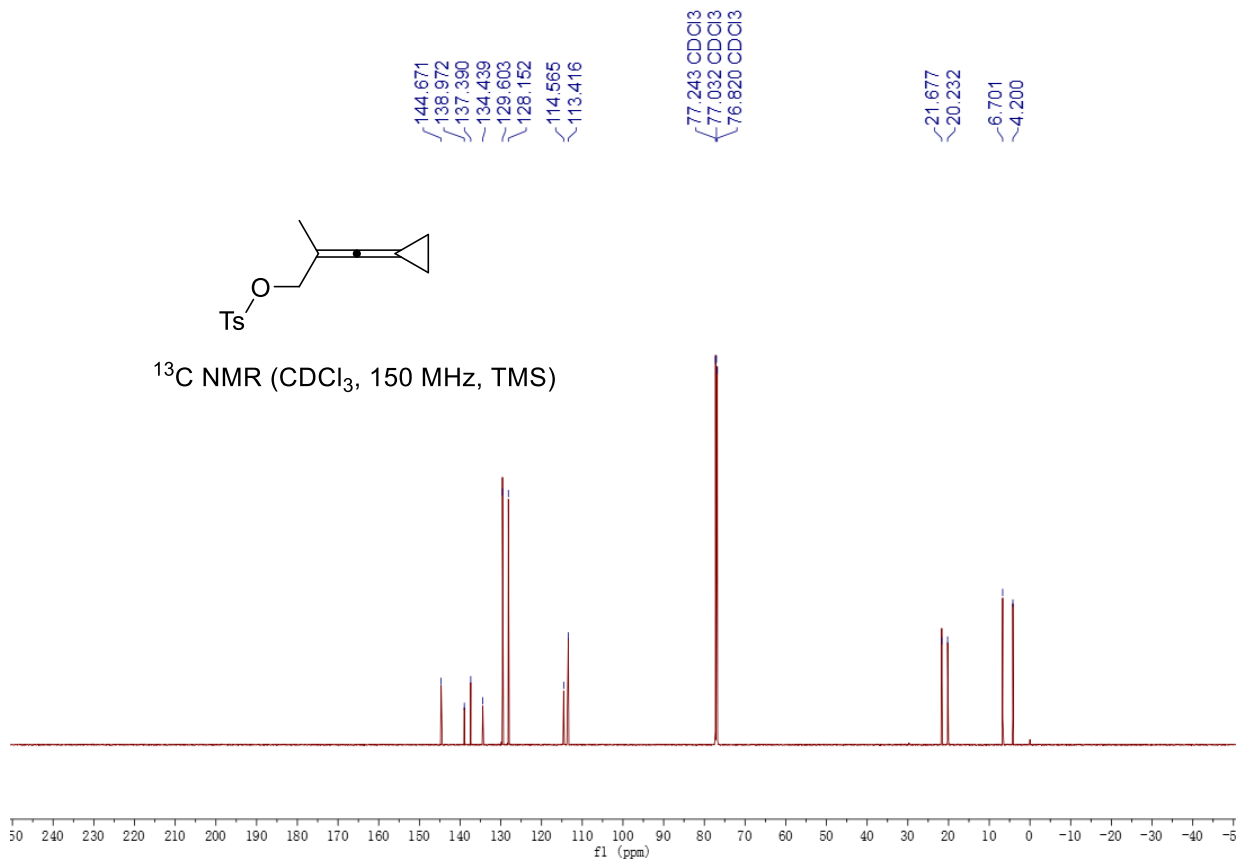
A colorless oil, 46% yield, 121.6 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.21 (s, 1H), 4.95 (s, 1H), 2.45 (s, 3H), 1.52 - 1.46 (m, 2H), 1.04 - 0.98 (m, 2H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 144.7, 139.0, 137.4, 134.4, 129.6, 128.2, 114.6, 113.4, 21.7, 20.2, 6.7, 4.2. IR (neat) ν 2925, 1710, 1508, 1437, 1397, 1358, 1335, 1219, 1025, 991, 888, 739, 697 cm⁻¹. HRMS (ESI) calcd. for C₁₄H₁₆O₃NaS (M+Na): 287.0735, Found: 287.0718.

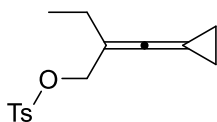


^1H NMR (CDCl_3 , 600 MHz, TMS)



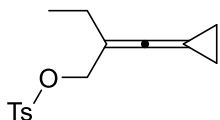
^{13}C NMR (CDCl_3 , 150 MHz, TMS)



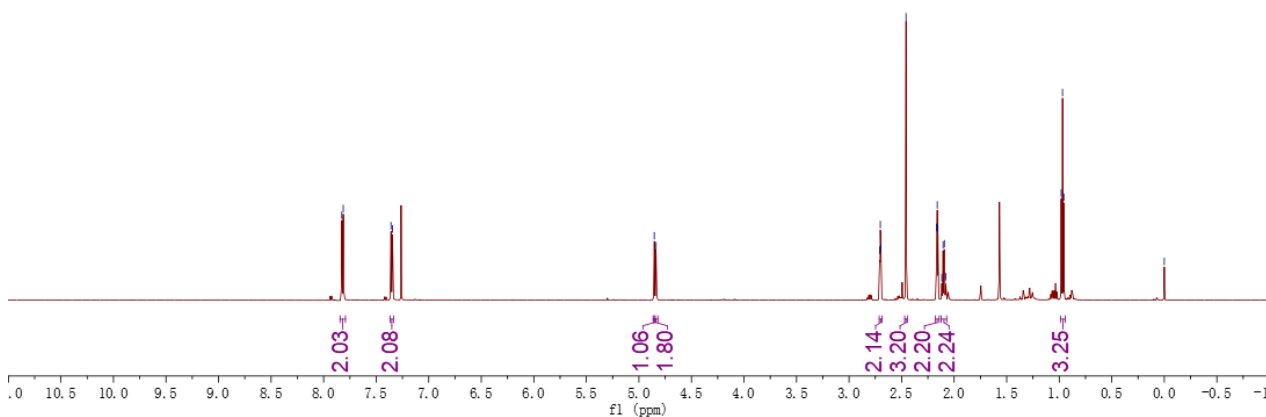


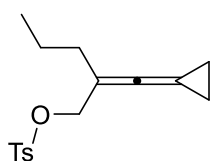
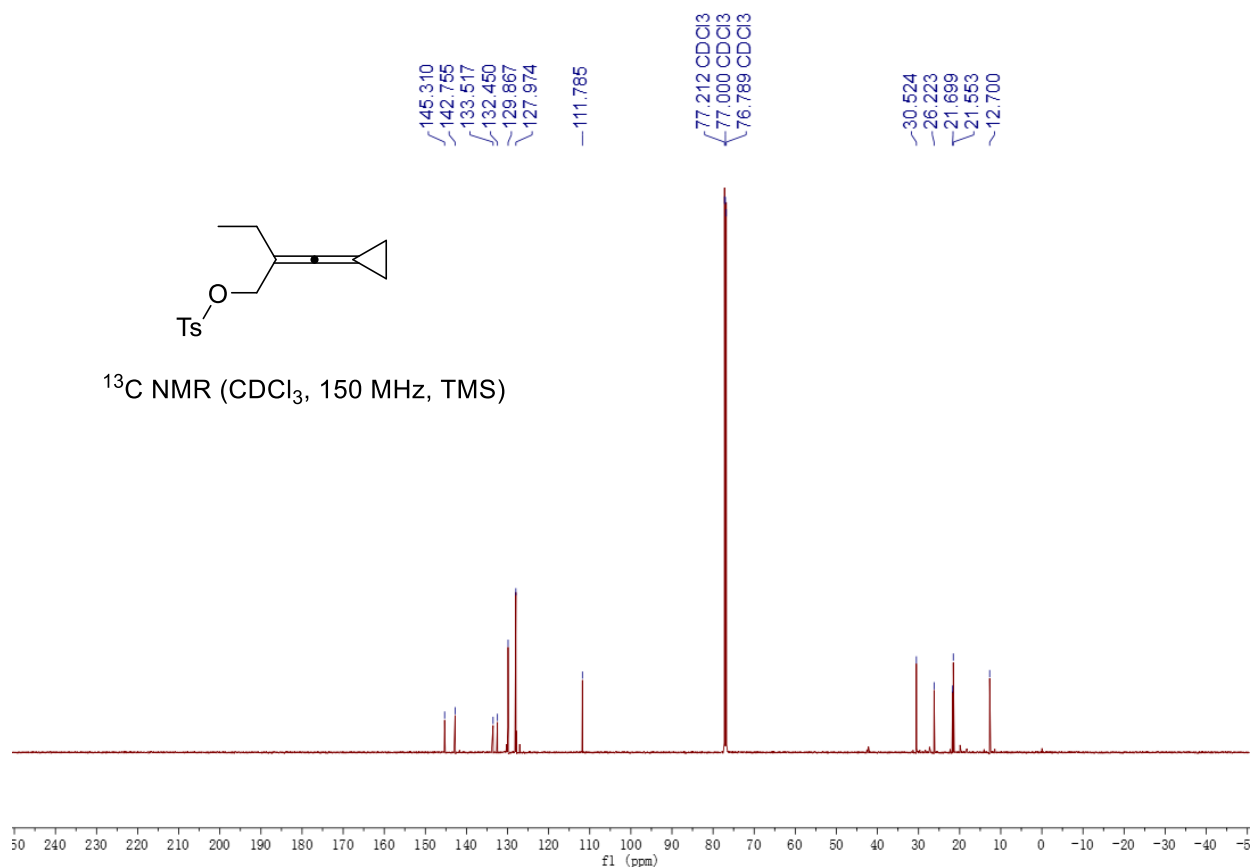
2-(cyclopropylidene- λ^5 -methylene)butyl 4-methylbenzenesulfonate (5b)

A colorless oil, 43% yield, 119.7 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 4.85 (s, 1H), 4.84 (s, 2H), 2.71 - 2.69 (m, 2H), 2.46 (s, 3H), 2.18 - 2.14 (m, 2H), 2.10 (q, $J = 7.5$ Hz, 2H), 0.97 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 145.3, 142.8, 133.5, 132.5, 129.9, 128.0, 111.8, 30.5, 26.2, 21.7, 21.6, 12.7. IR (neat) ν 2915, 1665, 1466, 1310, 1230, 1025, 991, 737, 698 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{NaS}$ ($\text{M}+\text{Na}$): 301.0887, Found: 301.0874.



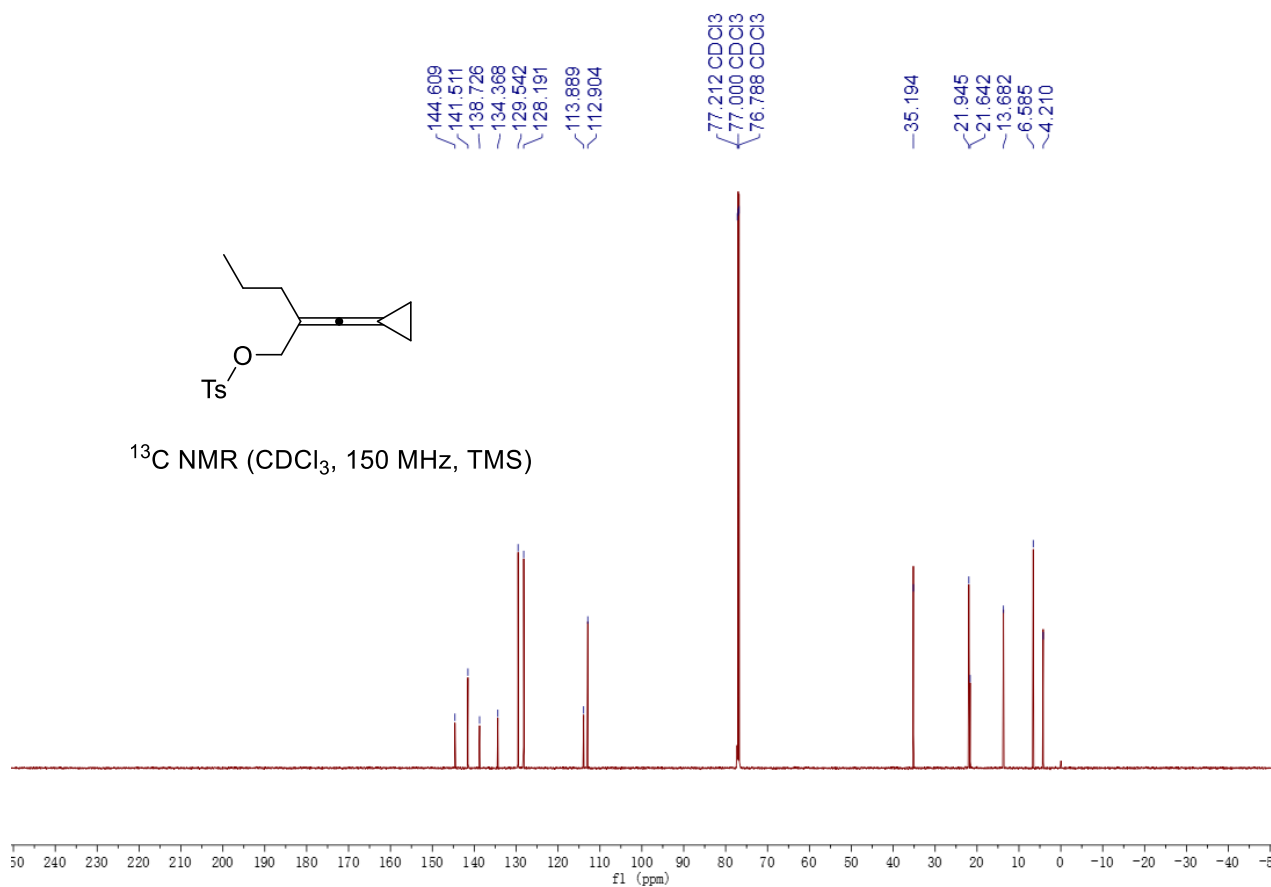
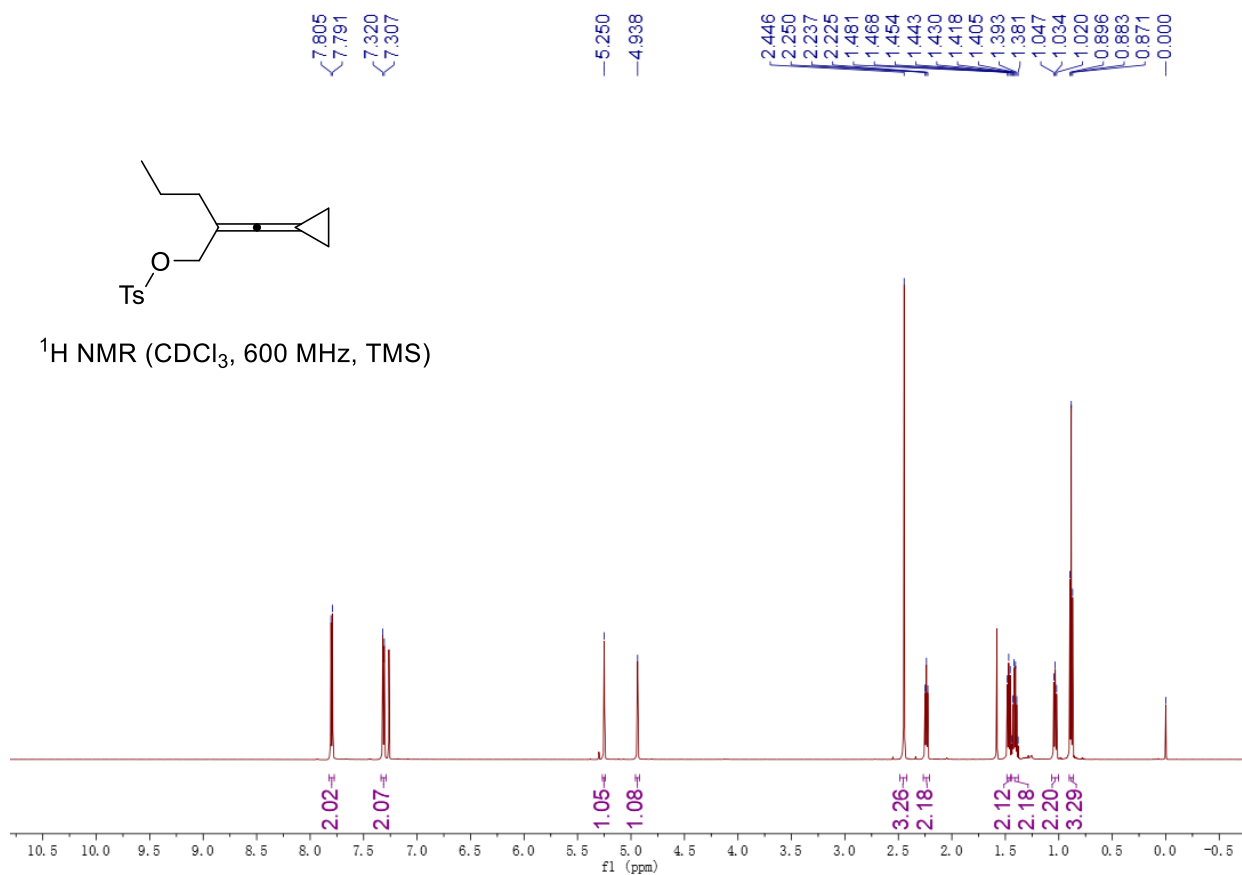
^1H NMR (CDCl_3 , 600 MHz, TMS)

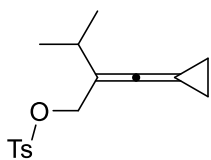




2-(cyclopropylidene- λ^5 -methylene)pentyl 4-methylbenzenesulfonate (5c)

A colorless oil, 45% yield, 131.6 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.80 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.25 (s, 1H), 4.94 (s, 1H), 2.45 (s, 3H), 2.27 - 2.21 (m, 2H), 1.49 - 1.45 (m, 2H), 1.44 - 1.38 (m, 2H), 1.07 - 1.00 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 144.6, 141.5, 138.7, 134.4, 129.5, 128.2, 113.9, 112.9, 35.2, 21.9, 21.6, 13.7, 6.6, 4.2. IR (neat) ν 3075, 2895, 2859, 1781, 1675, 1566, 1440, 1386, 1325, 1226, 1025, 981, 747, 688 cm⁻¹. HRMS (ESI) calcd. for C₁₆H₂₀O₃NaS (M+Na): 315.1048, Found: 315.1031.





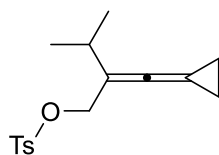
2-(cyclopropylidene- λ^5 -methylene)-3-methylbutyl 4-methylbenzenesulfonate (**5d**)

A colorless oil, 44% yield, 128.7 mg. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 5.27 (s, 1H), 4.97 (s, 1H), 2.77 - 2.66 (m, 1H), 2.44 (s, 3H), 1.51 - 1.43 (m, 2H), 1.09 - 1.05 (m, 2H), 1.02 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 148.1, 144.6, 138.8, 134.4, 129.5, 128.2, 113.4, 110.1, 29.1, 22.2, 21.6, 6.7, 4.2. IR (neat) ν 2959, 1663, 1596, 1437, 1314, 1219, 1035, 990, 783, 736, 696 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{NaS}$ ($\text{M}+\text{Na}$): 315.1058, Found: 315.1031.

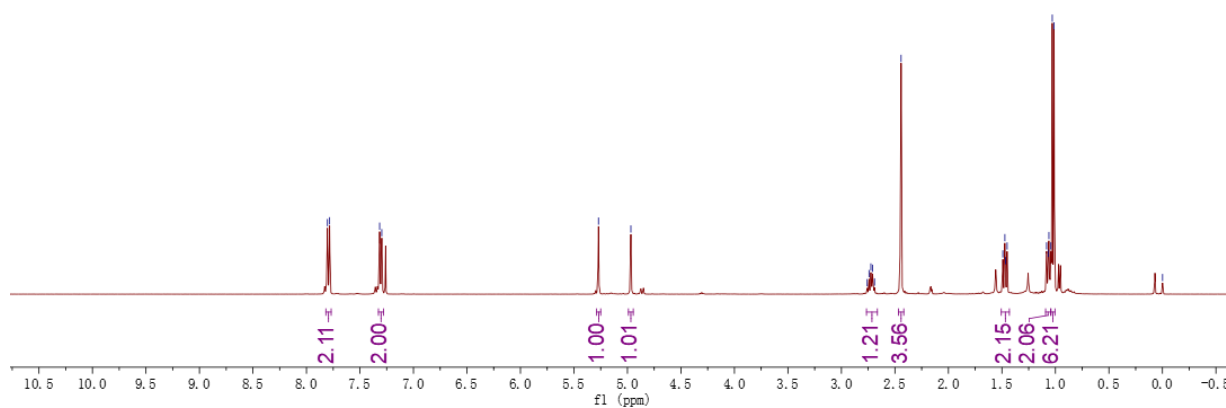
7.804
7.784
7.316
7.296

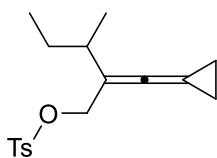
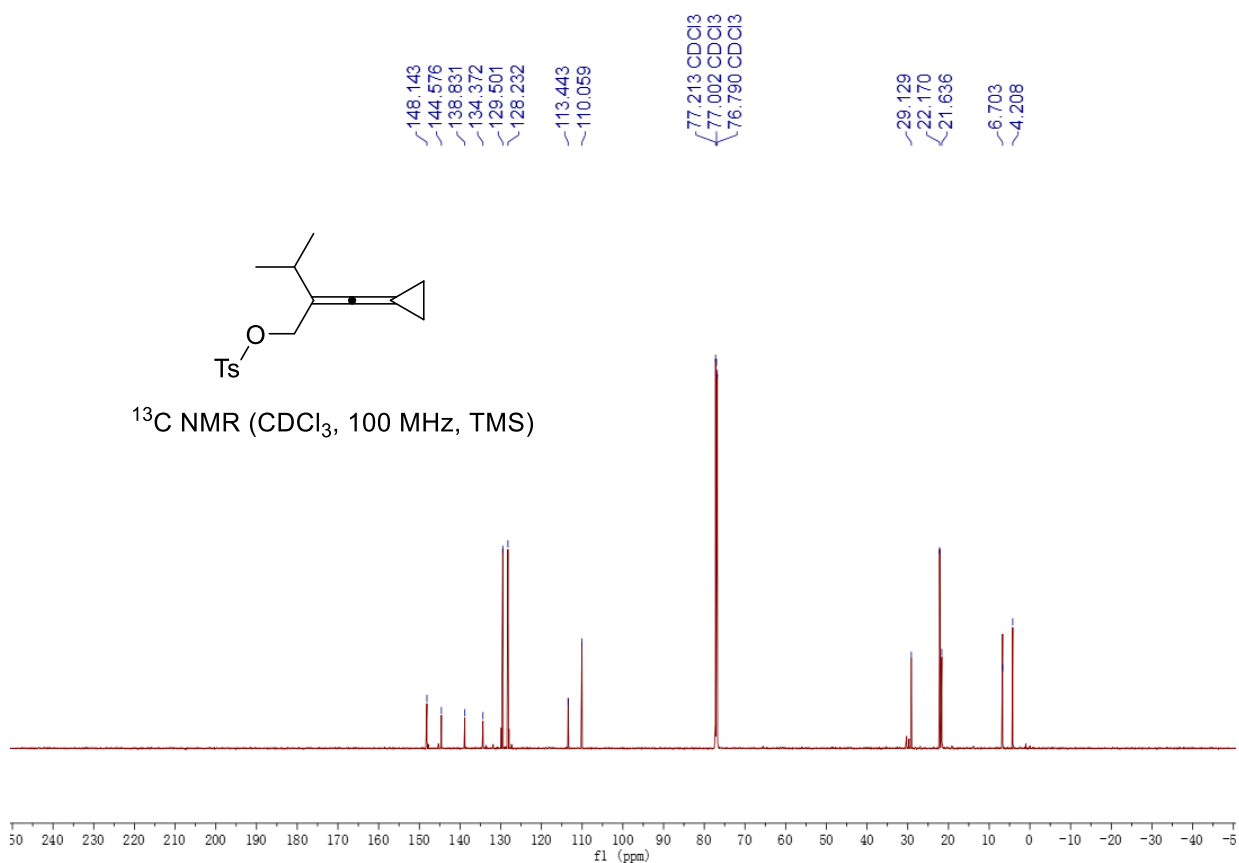
5.271
4.968

2.759
2.742
2.725
2.709
2.691
2.442
1.491
1.473
1.466
1.451
1.082
1.067
1.061
1.042
1.030
1.013
-0.001



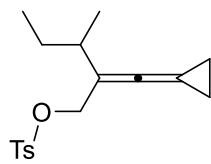
^1H NMR (CDCl_3 , 400 MHz, TMS)



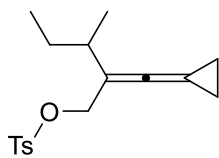
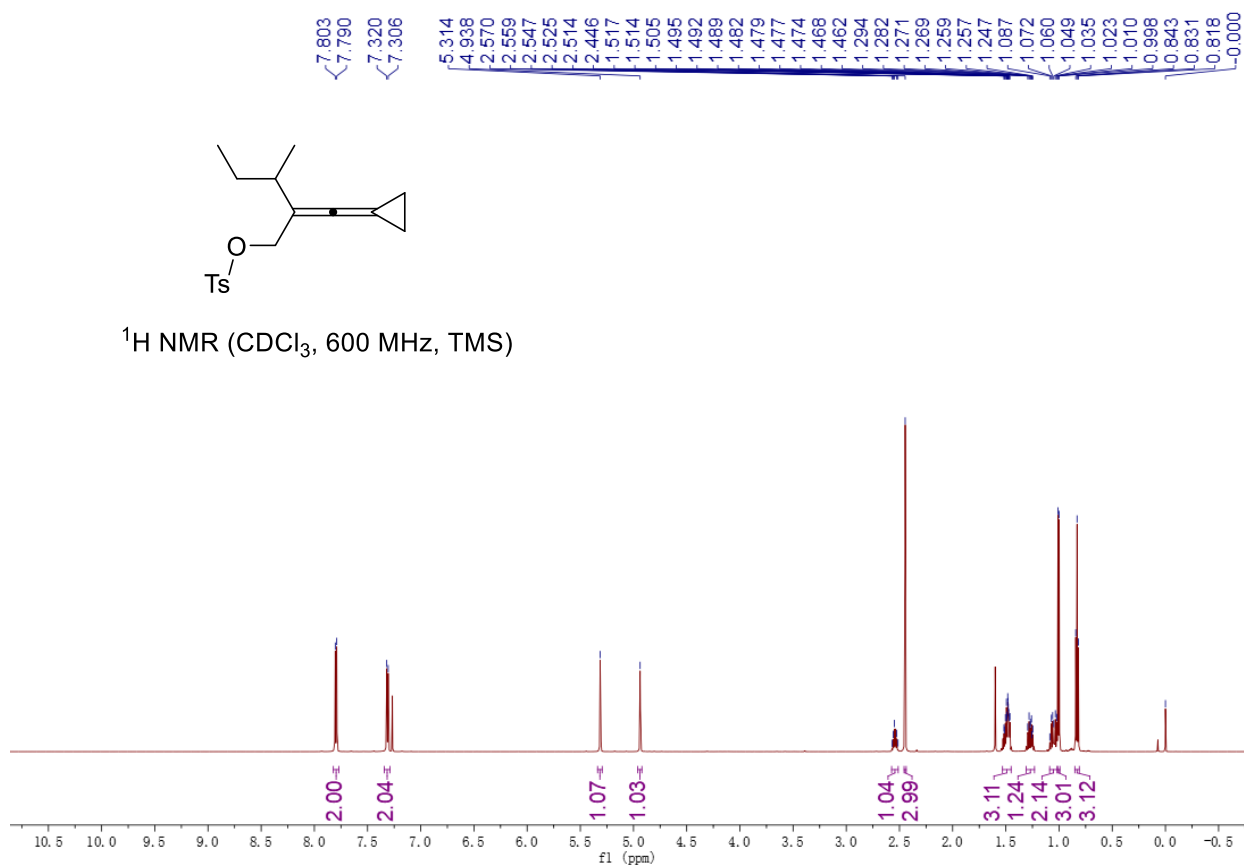


2-(cyclopropylidene- λ^5 -methylene)-3-methylpentyl 4-methylbenzenesulfonate (5e)

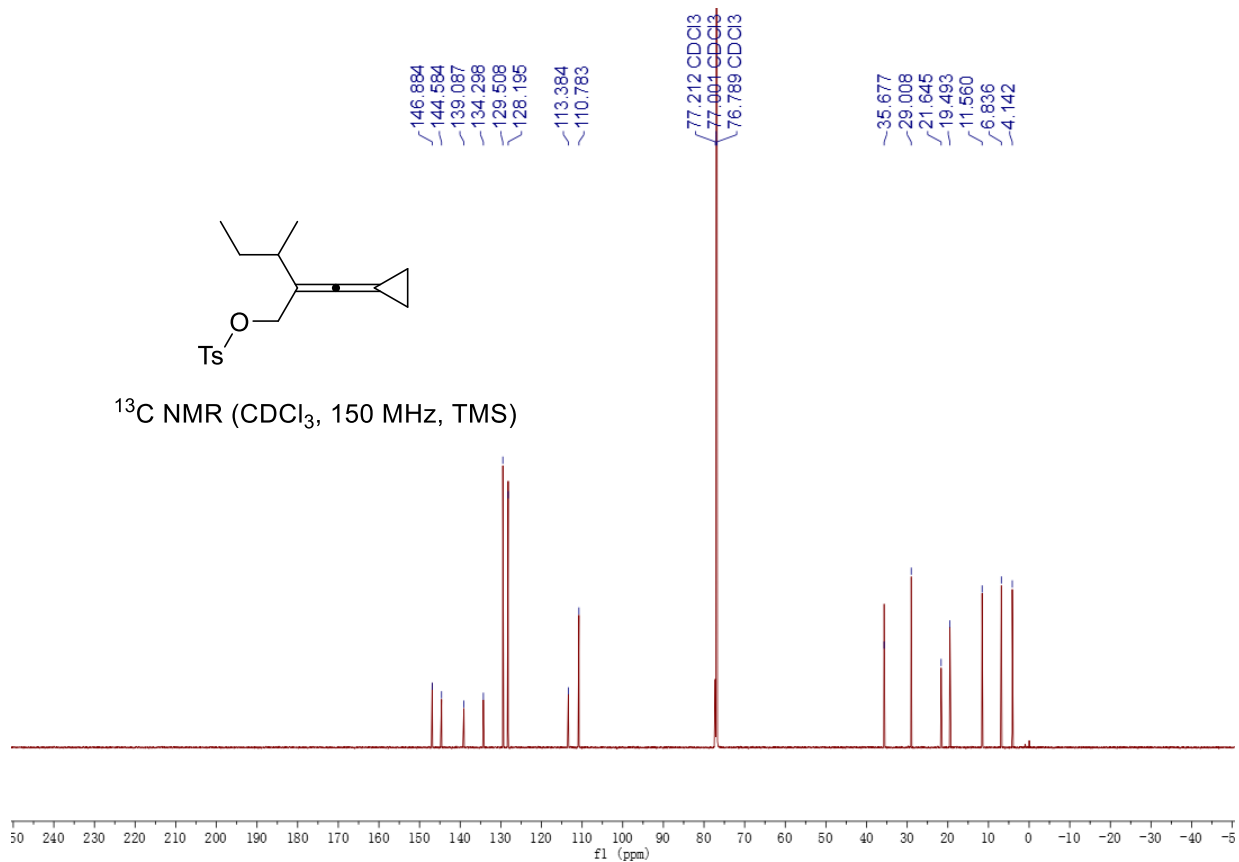
A colorless oil, 43% yield, 131.7 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.80 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.31 (s, 1H), 4.94 (s, 1H), 2.57 - 2.51 (m, 1H), 2.45 (s, 3H), 1.53 - 1.45 (m, 3H), 1.31 - 1.23 (m, 1H), 1.09 - 1.02 (m, 2H), 1.00 (d, J = 6.9 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 146.9, 144.6, 139.1, 134.3, 129.5, 128.2, 113.4, 110.8, 35.7, 29.0, 21.6, 19.5, 11.6, 6.8, 4.1. IR (neat) ν 2914, 1594, 1496, 1448, 1396, 1333, 1318, 1036, 992, 740, 709 cm⁻¹. HRMS (ESI) calcd. for C₁₇H₂₂O₃NaS (M+Na): 329.1187, Found: 329.1195.

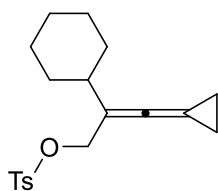


^1H NMR (CDCl_3 , 600 MHz, TMS)



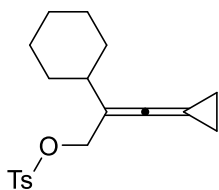
^{13}C NMR (CDCl_3 , 150 MHz, TMS)



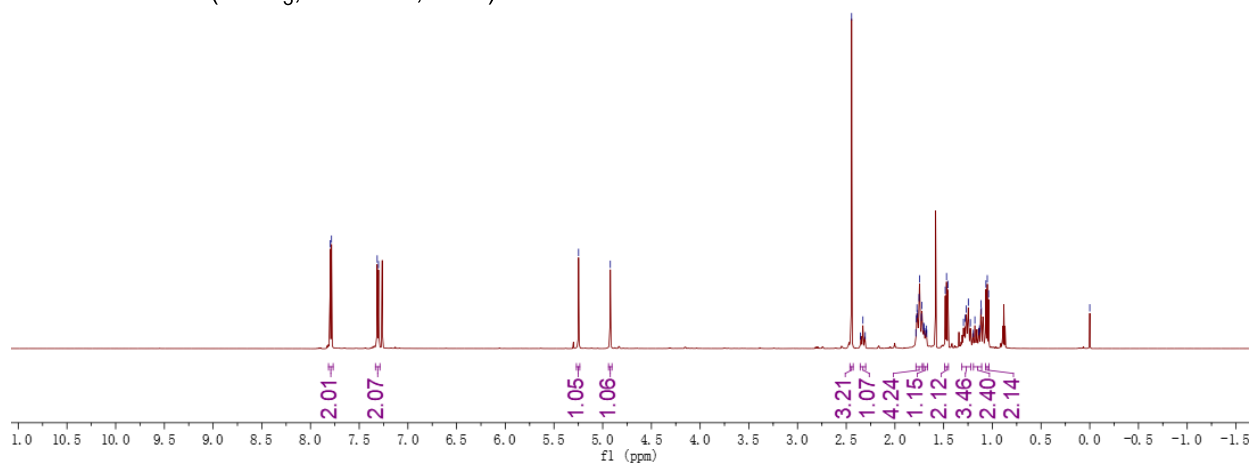


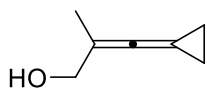
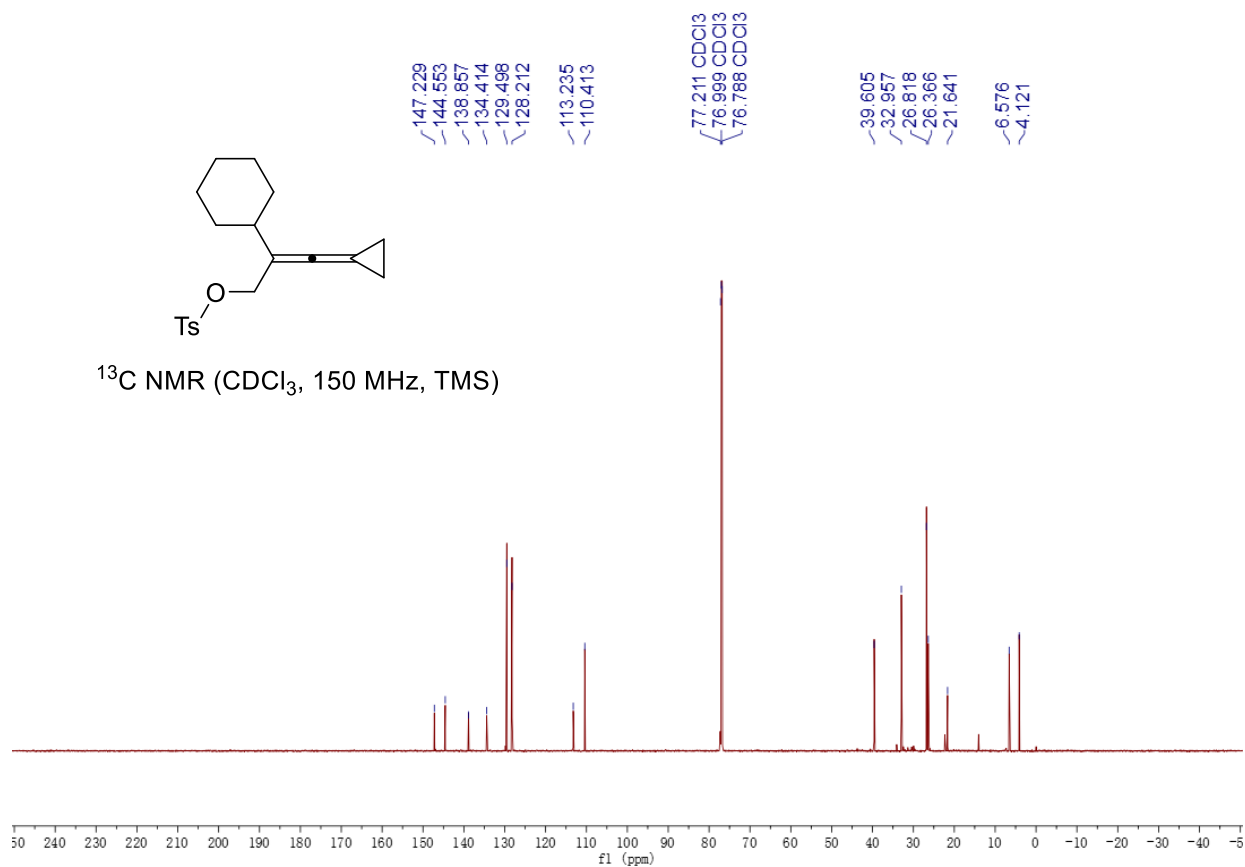
2-cyclohexyl-3-cyclopropylidene-3 λ^5 -allyl 4-methylbenzenesulfonate (5f)

A colorless oil, 45%, 149.6 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 5.25 (s, 1H), 4.92 (s, 1H), 2.45 (s, 3H), 2.36 - 2.30 (m, 1H), 1.78 - 1.72 (m, 4H), 1.71 - 1.67 (m, 1H), 1.49 - 1.45 (m, 2H), 1.31 - 1.22 (m, 3H), 1.19 - 1.11 (m, 2H), 1.07 - 1.03 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 147.2, 144.6, 138.9, 134.4, 129.5, 128.2, 113.2, 110.4, 39.6, 33.0, 26.8, 26.4, 21.6, 6.6, 4.1. IR (neat) ν 2845, 1663, 1510, 1439, 1402, 1325, 1220, 1032, 741, 703 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{NaS}$ ($\text{M}+\text{Na}$): 355.1344, Found: 355.1365.



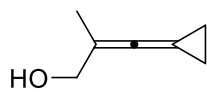
^1H NMR (CDCl_3 , 600 MHz, TMS)



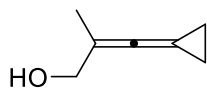
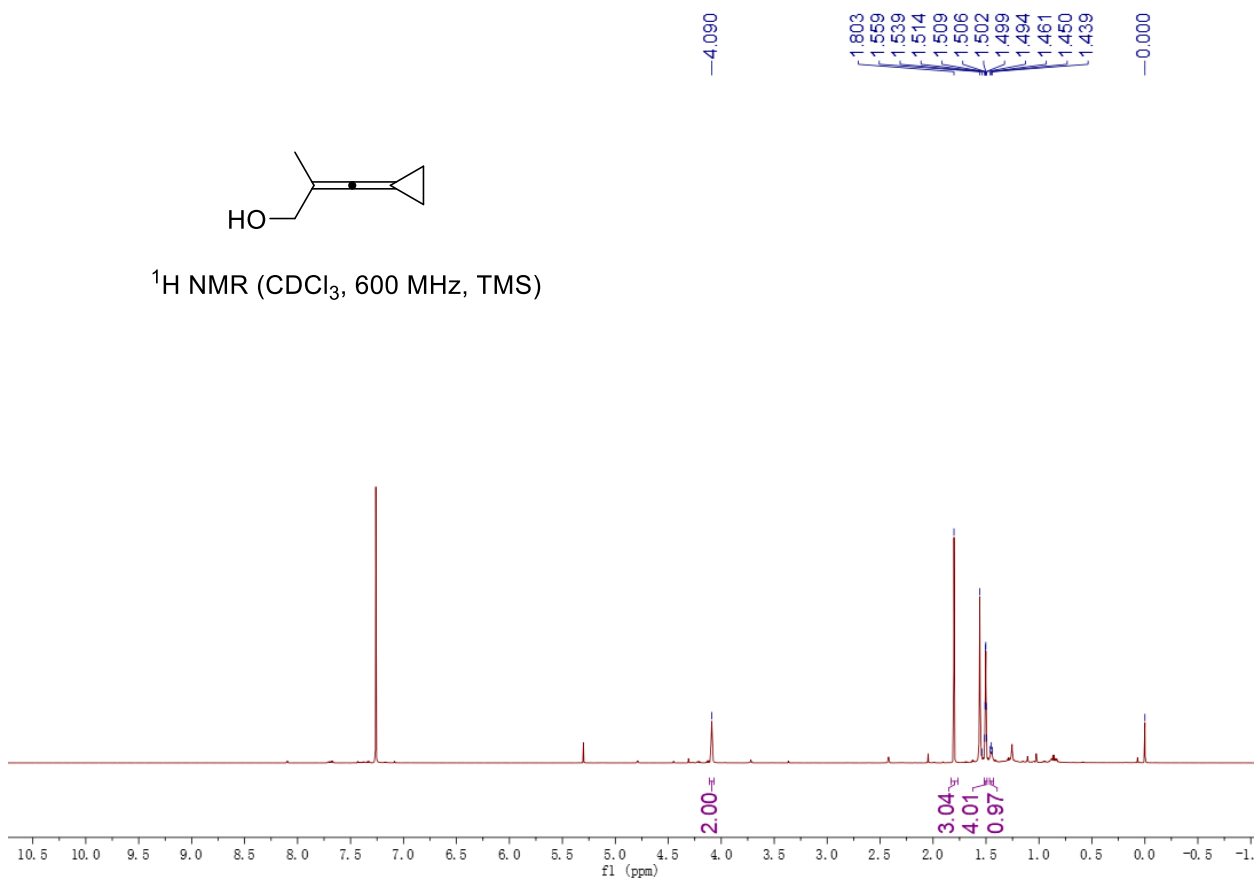


3-cyclopropylidene-2-methyl-3λ⁵-prop-2-en-1-ol (5g)

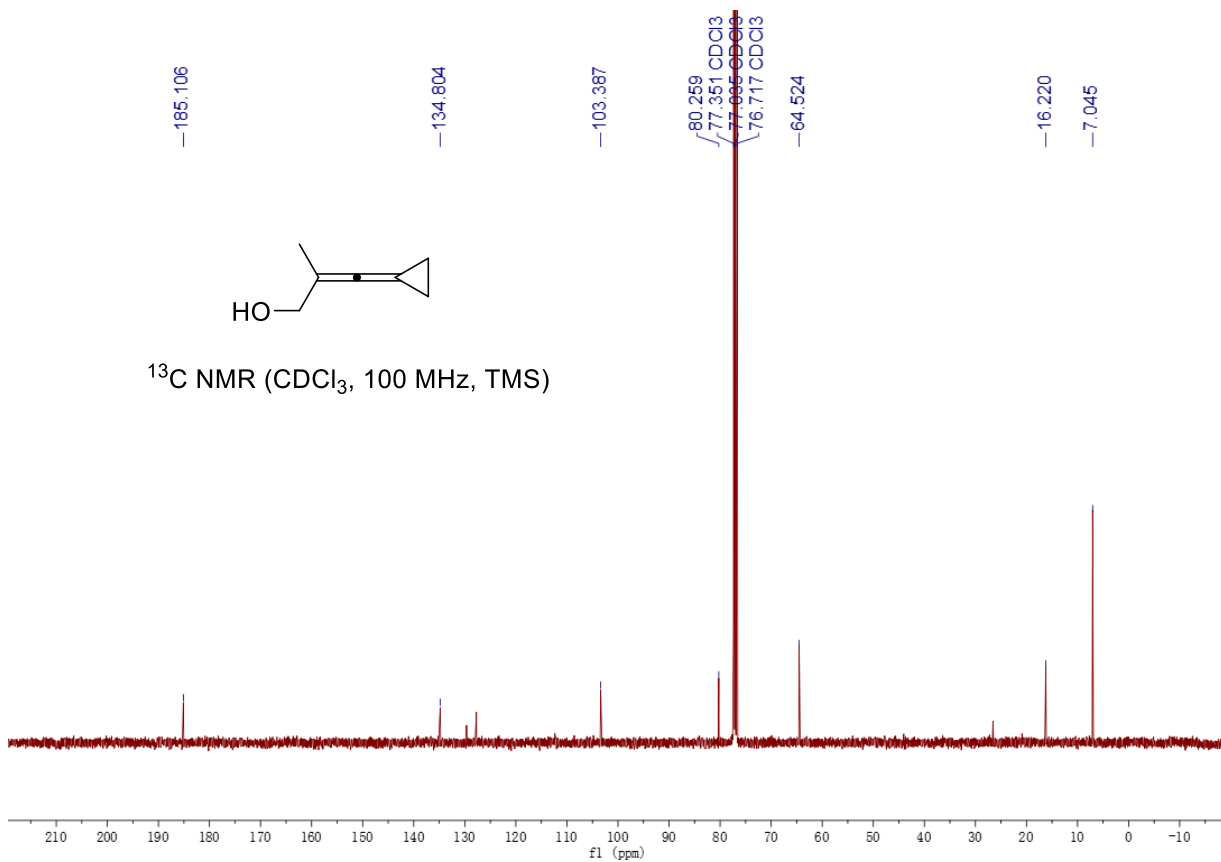
A colorless oil, 40%, 44.0 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 4.09 (s, 2H), 1.80 (s, 3H), 1.52 - 1.49 (m, 4H), 1.47 - 1.43 (m, 1H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 185.1, 134.8, 103.4, 80.3, 64.5, 16.2, 7.0. IR (neat) ν 3016, 2985, 1663, 1510, 1439, 1300, 1087, 701, 695 cm⁻¹. HRMS (EI) calcd. for C₇H₁₀O (M): 110.0726, Found: 110.0726.

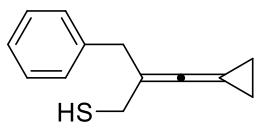


^1H NMR (CDCl_3 , 600 MHz, TMS)



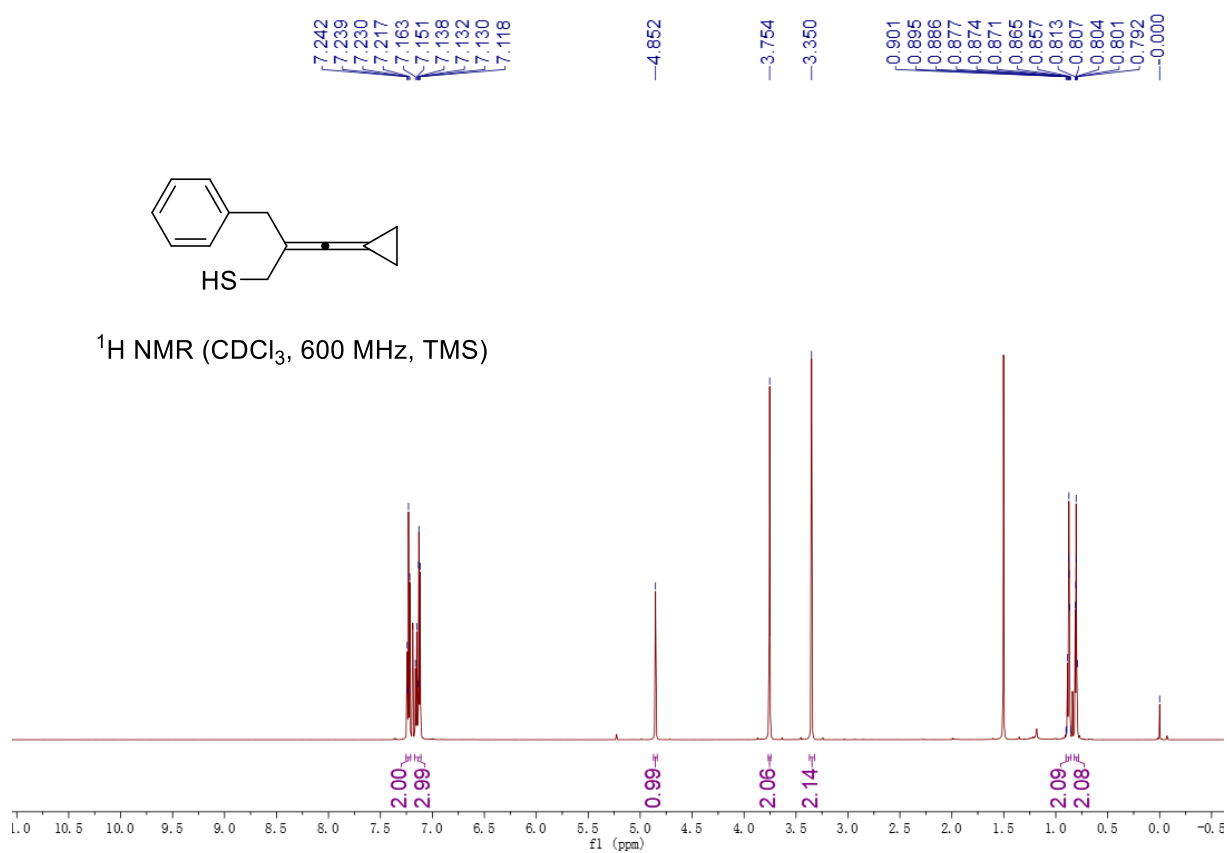
^{13}C NMR (CDCl_3 , 100 MHz, TMS)

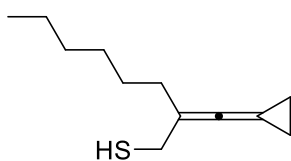
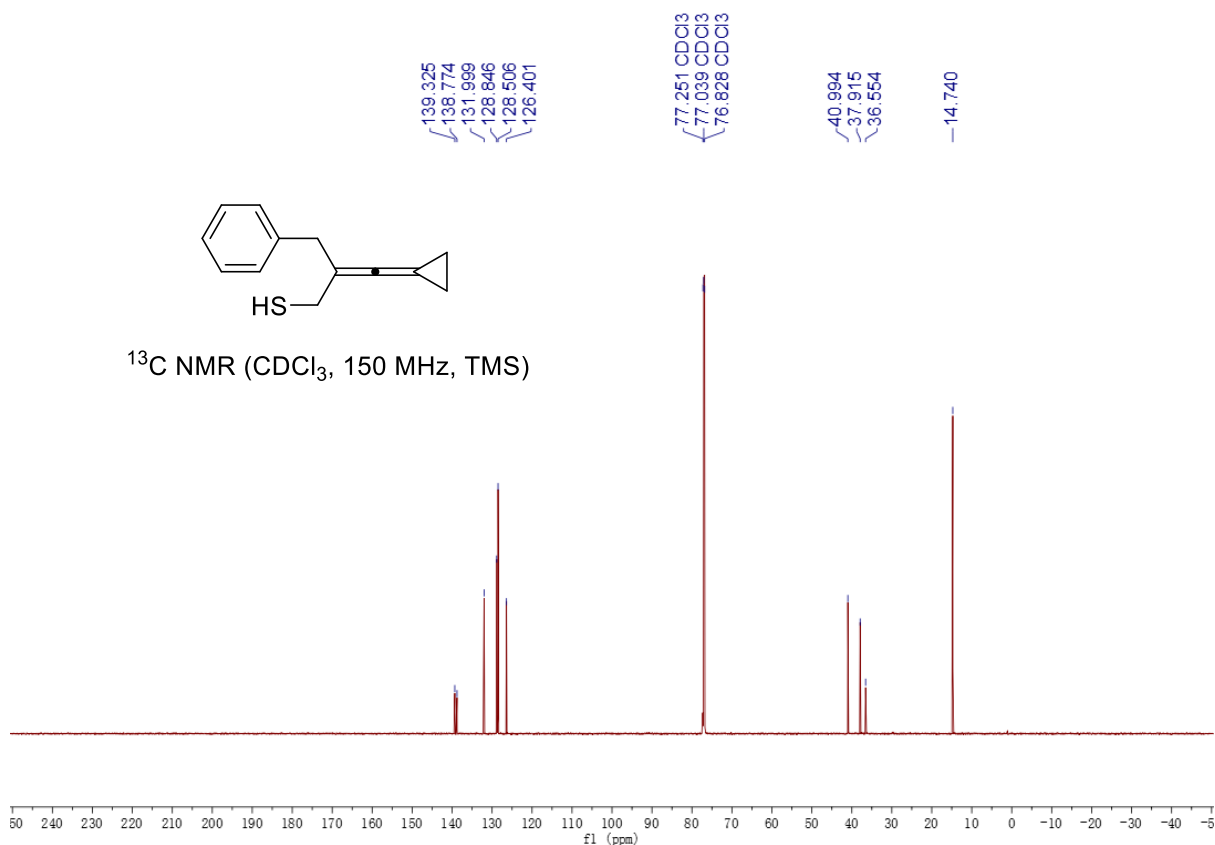




2-benzyl-3-cyclopropylidene-3 λ^5 -prop-2-ene-1-thiol (7a)

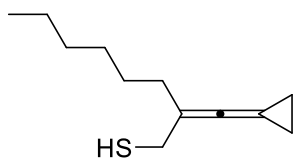
A colorless oil, 33%, 66.7 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.23 (t, $J = 7.5$ Hz, 2H), 7.17 - 7.11 (m, 3H), 4.85 (s, 1H), 3.75 (s, 2H), 3.35 (s, 2H), 0.90 - 0.85 (m, 2H), 0.82 - 0.78 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 139.3, 138.8, 132.0, 128.8, 128.5, 126.4, 41.0, 37.9, 36.6, 14.7. IR (neat) ν 733, 906, 1077, 1255, 1388, 2924, 2990 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{14}\text{S}$ (M^+): 202.0809, Found: 202.0811.



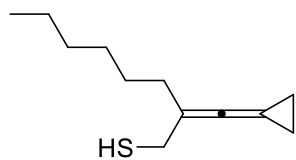
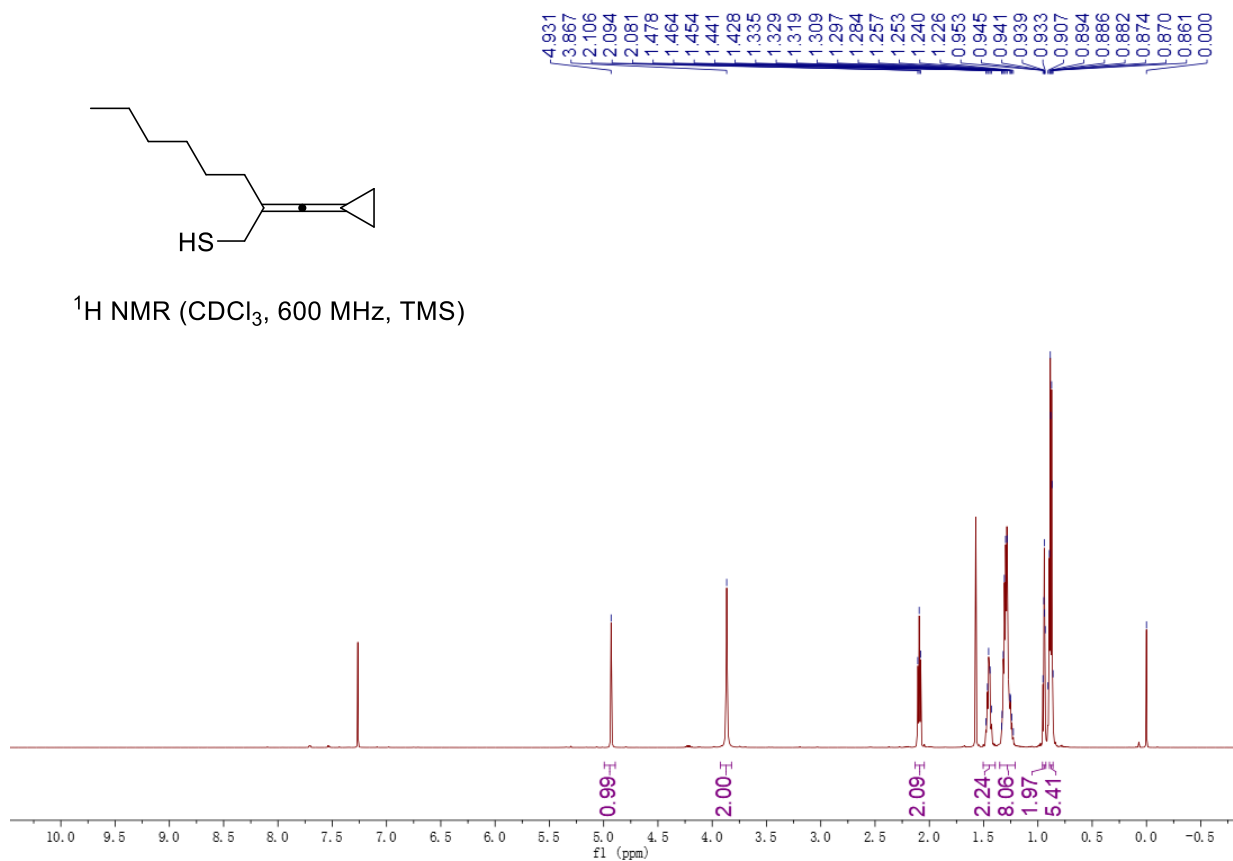


2-(cyclopropylidene- λ^5 -methylene)octane-1-thiol (7b)

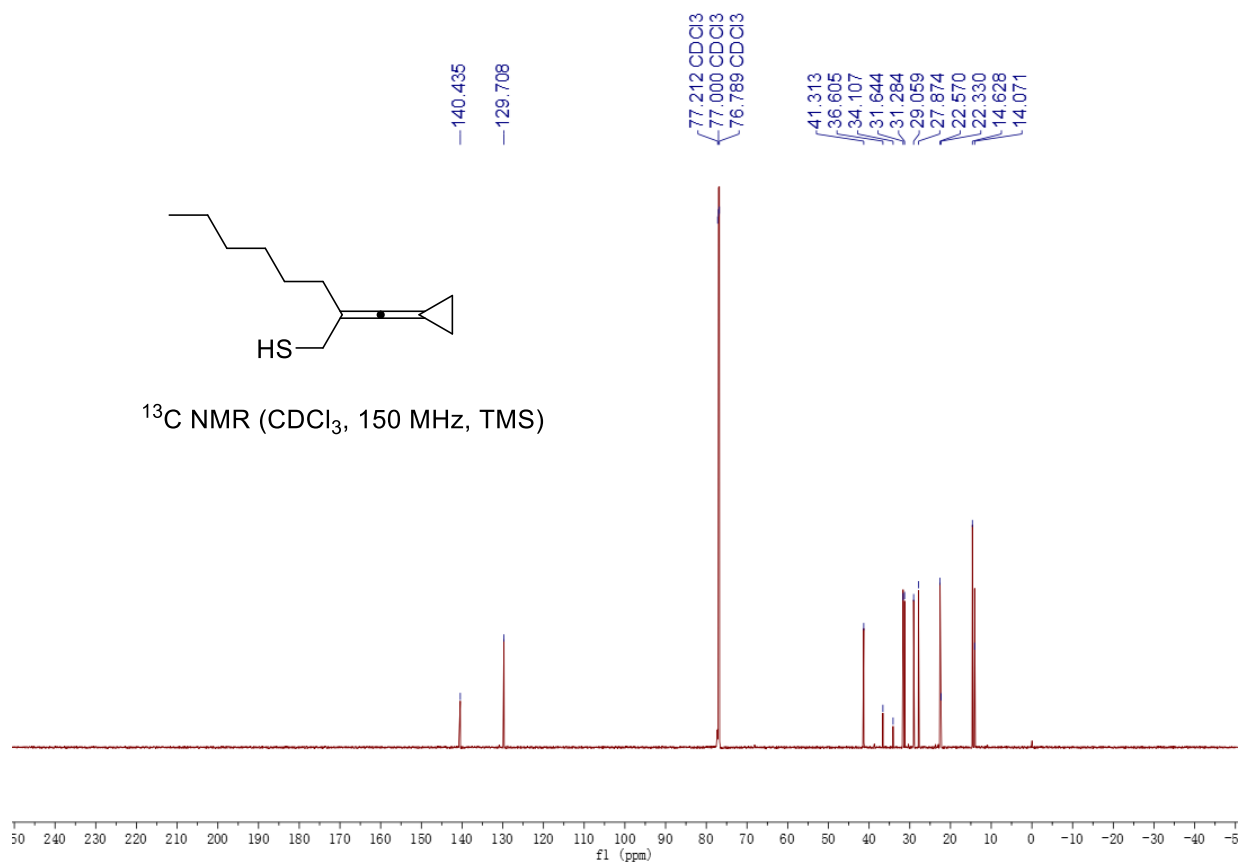
A colorless oil, 30%, 58.9 mg. ^1H NMR (CDCl₃, TMS, 600 MHz) δ 4.93 (s, 1H), 3.87 (s, 2H), 2.09 (t, $J = 7.7$ Hz, 2H), 1.50 - 1.39 (m, 2H), 1.35 - 1.21 (m, 8H), 0.96 - 0.93 (m, 2H), 0.89 - 0.86 (m, 5H). ^{13}C NMR (CDCl₃, TMS, 150 MHz) δ 140.4, 129.7, 41.3, 36.6, 34.1, 31.6, 31.3, 29.1, 27.9, 22.6, 22.3, 14.6, 14.1. IR (neat) ν 700, 928, 961, 1044, 1083, 1249, 1641, 2902 cm⁻¹. HRMS (EI) calcd. for C₁₂H₂₀S (M⁺): 196.1278, Found: 196.1280.

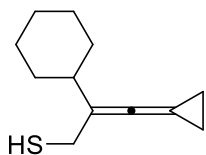


$^1\text{H NMR}$ (CDCl_3 , 600 MHz, TMS)



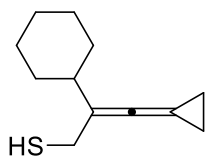
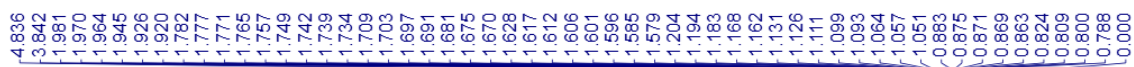
$^{13}\text{C NMR}$ (CDCl_3 , 150 MHz, TMS)



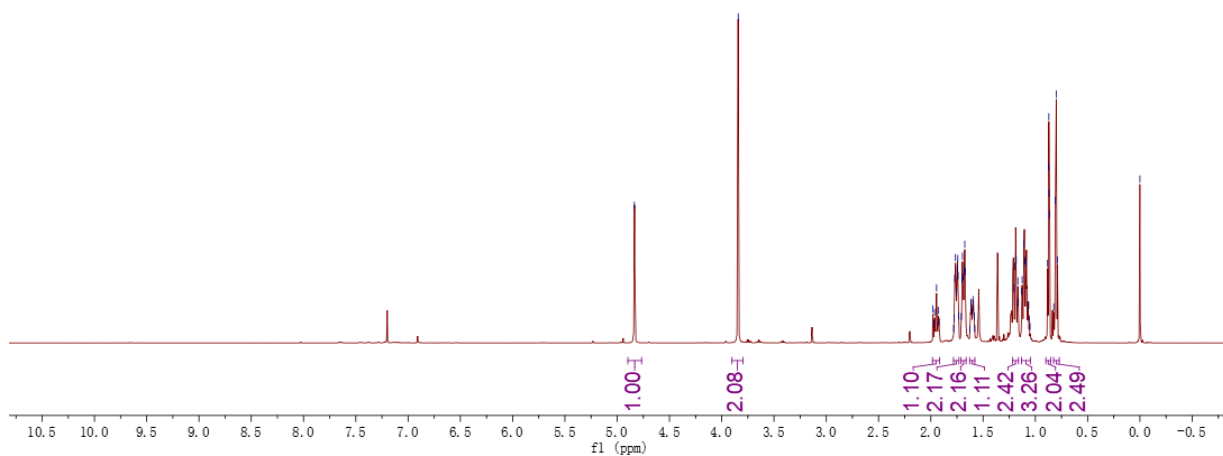


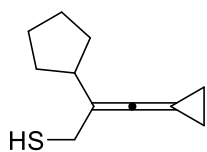
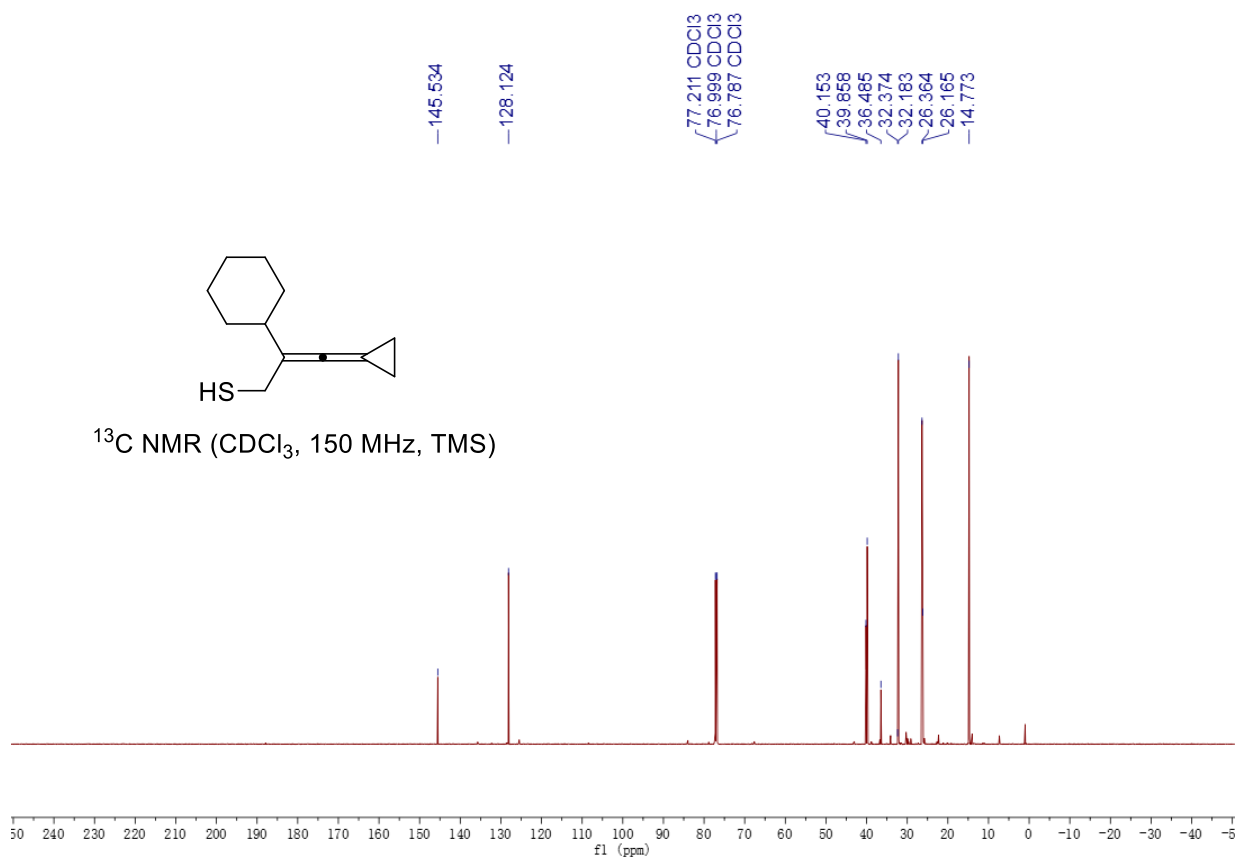
2-cyclohexyl-3-cyclopropylidene-3 λ^5 -prop-2-ene-1-thiol (7c)

A colorless oil, 35%, 68.0 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 4.84 (s, 1H), 3.84 (s, 2H), 1.98 - 1.92 (m, 1H), 1.78 - 1.73 (m, 2H), 1.69 (dt, $J = 12.9, 3.4$ Hz, 2H), 1.63 - 1.58 (m, 1H), 1.22 - 1.16 (m, 2H), 1.13 - 1.05 (m, 3H), 0.90 - 0.85 (m, 2H), 0.83 - 0.77 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 145.5, 128.1, 40.2, 39.9, 36.5, 32.4, 32.2, 26.4, 26.2, 14.8. IR (neat) ν 699, 922, 950, 1084, 1103, 1284, 1643, 2900 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{20}\text{S}$ (M^+): 194.1122, Found: 194.1124.



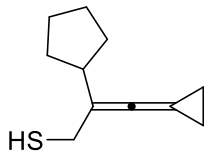
^1H NMR (CDCl_3 , 600 MHz, TMS)



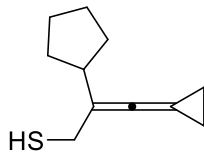
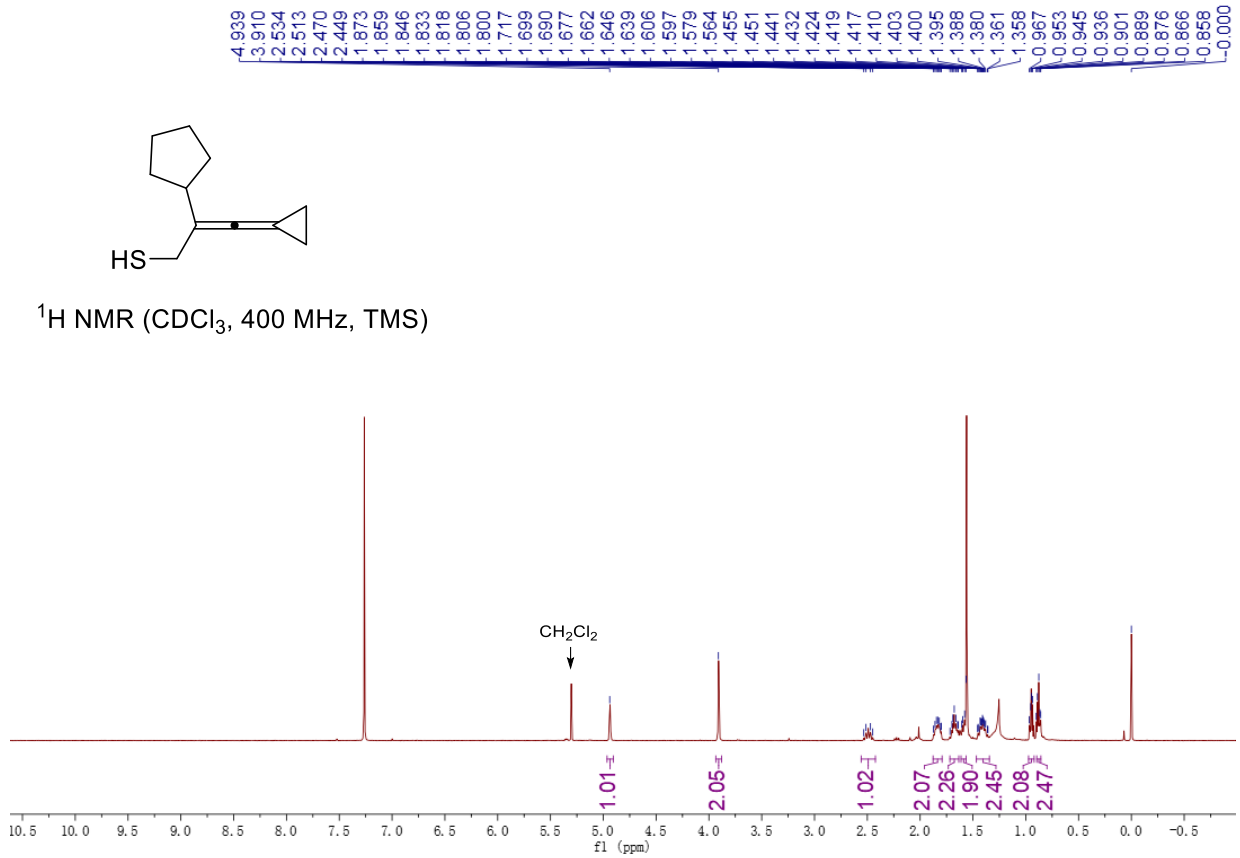


2-cyclopentyl-3-cyclopropylidene-3λ⁵-prop-2-ene-1-thiol (7d)

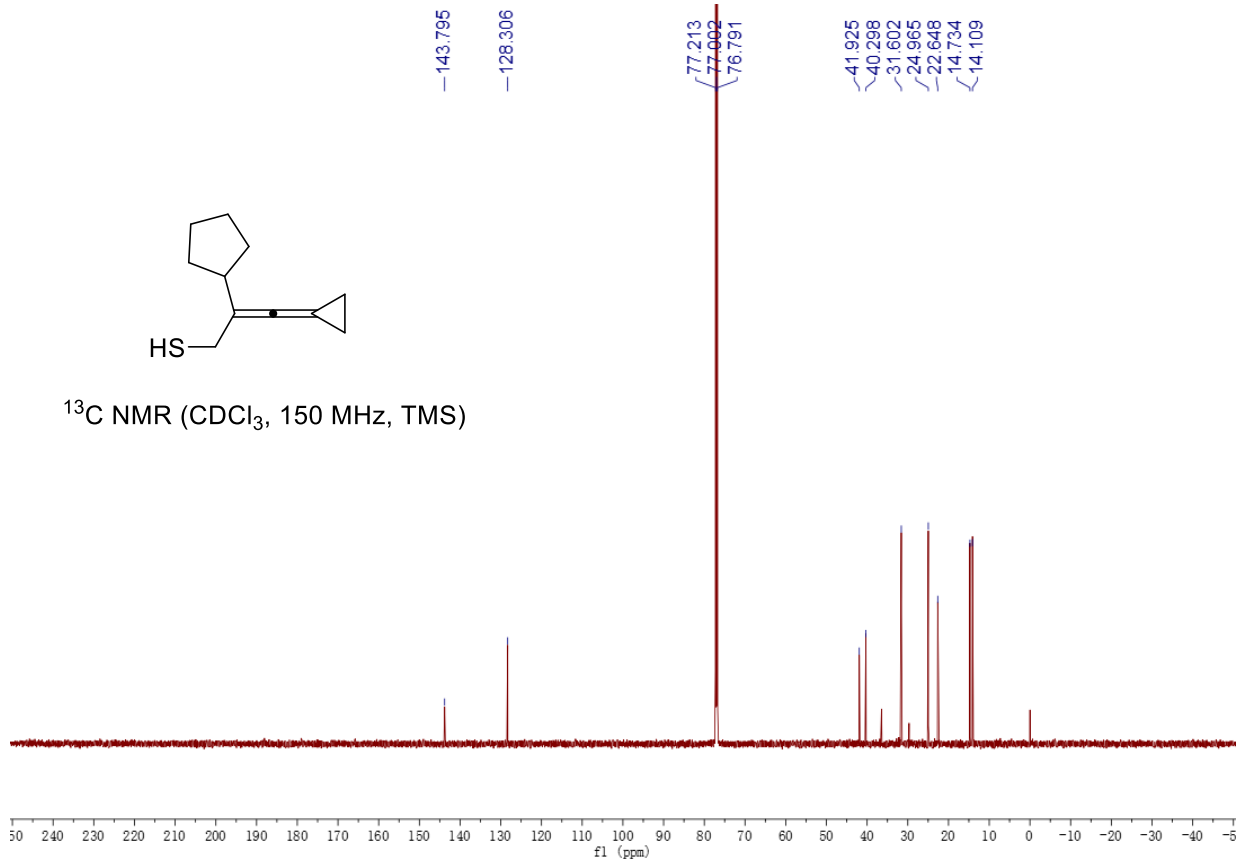
A colorless oil, 33%, 59.5 mg. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 4.94 (s, 1H), 3.91 (s, 2H), 2.56 - 2.42 (m, 1H), 1.88 - 1.79 (m, 2H), 1.72 - 1.63 (m, 2H), 1.61 - 1.56 (m, 2H), 1.47 - 1.34 (m, 2H), 0.97 - 0.92 (m, 2H), 0.90 - 0.86 (m, 2H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 143.8, 128.3, 41.9, 40.3, 31.6, 25.0, 22.6, 14.7, 14.1. IR (neat) ν 701, 902, 946, 1101, 1133, 1254, 1601, 2913 cm⁻¹. HRMS (EI) calcd. for C₁₁H₁₆S (M⁺): 180.0966, Found: 180.0967.

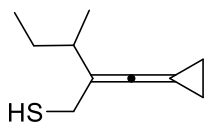


^1H NMR (CDCl_3 , 400 MHz, TMS)



^{13}C NMR (CDCl_3 , 150 MHz, TMS)

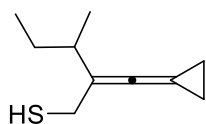




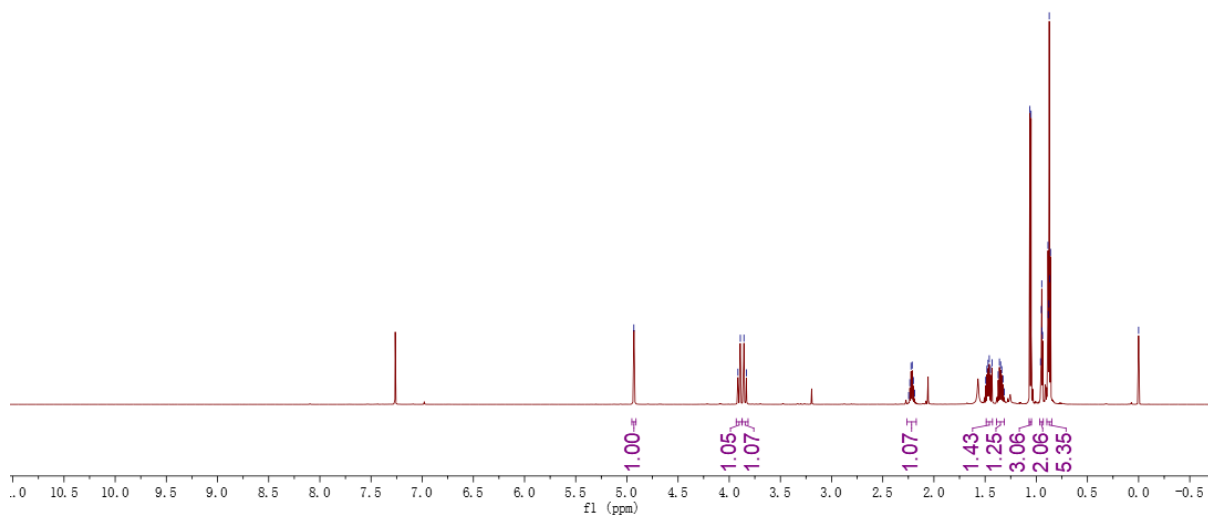
2-(cyclopropylidene- λ^5 -methylene)-3-methylpentane-1-thiol (7e)

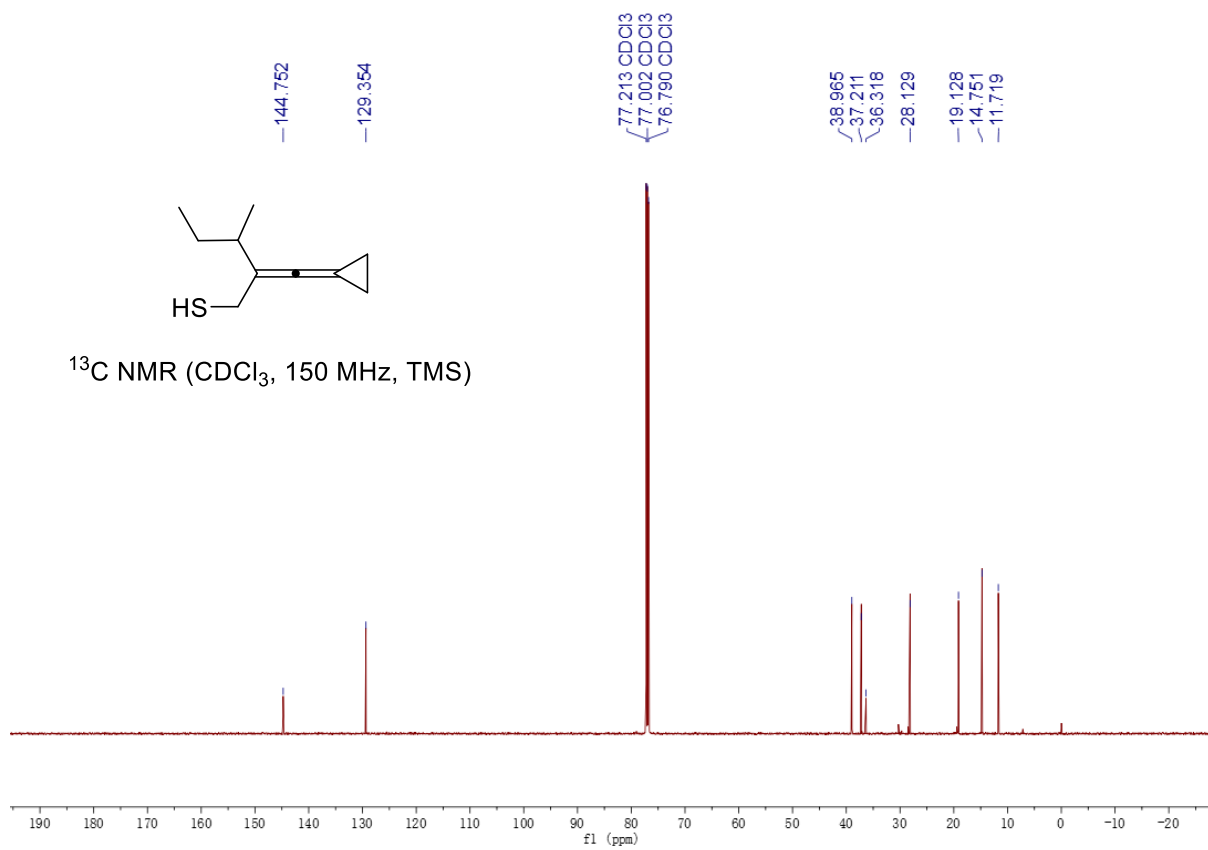
A colorless oil, 36%, 60.6 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 4.93 (s, 1H), 3.90 (d, $J = 14.2$ Hz, 1H), 3.84 (d, $J = 14.2$ Hz, 1H), 2.26 - 2.17 (m, 1H), 1.49 - 1.43 (m, 1H), 1.34 (dq, $J = 14.4$ Hz, 1H), 1.06 (d, $J = 6.9$ Hz, 3H), 0.97 - 0.93 (m, 2H), 0.90 - 0.85 (m, 5H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 144.8, 129.4, 39.0, 37.2, 36.3, 28.1, 19.1, 14.8, 11.7. IR (neat) ν 720, 902, 961, 1034, 1083, 1264, 1603, 2920 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{16}\text{S}$ (M^+): 168.0966, Found: 168.0967.

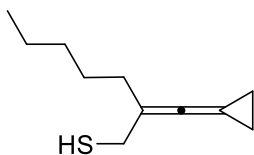
4.932
3.915
3.891
3.866
3.833
2.247
2.235
2.224
2.212
2.201
2.189
1.494
1.482
1.471
1.459
1.447
1.433
1.372
1.360
1.349
1.337
1.325
1.313
1.062
1.051
0.959
0.950
0.947
0.944
0.938
0.886
0.883
0.877
0.873
0.870
0.861
0.000



^1H NMR (CDCl_3 , 600 MHz, TMS)



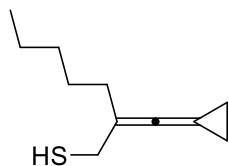




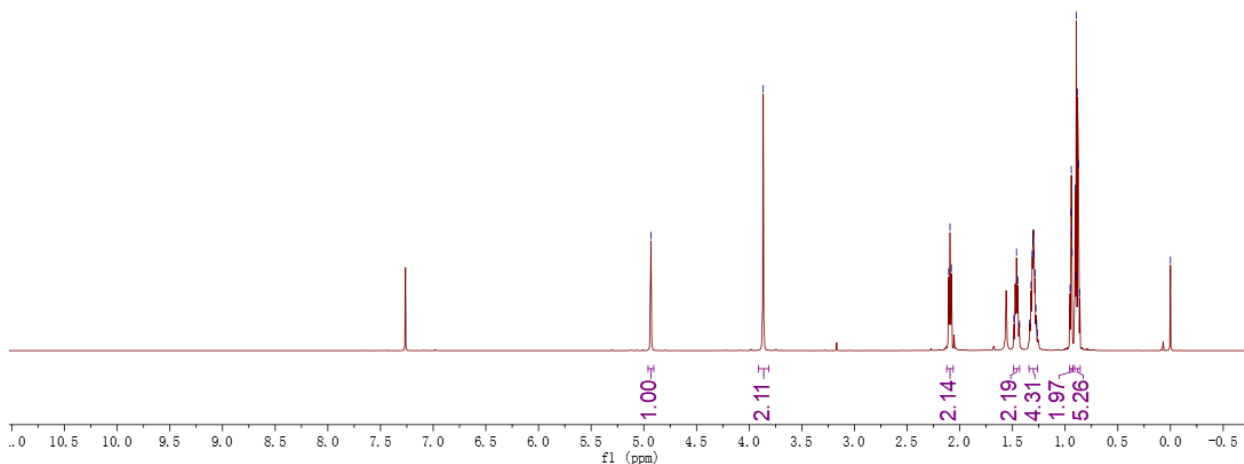
2-(cyclopropylidene- λ^5 -methylene)heptane-1-thiol (7f)

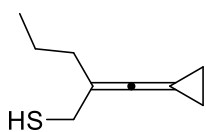
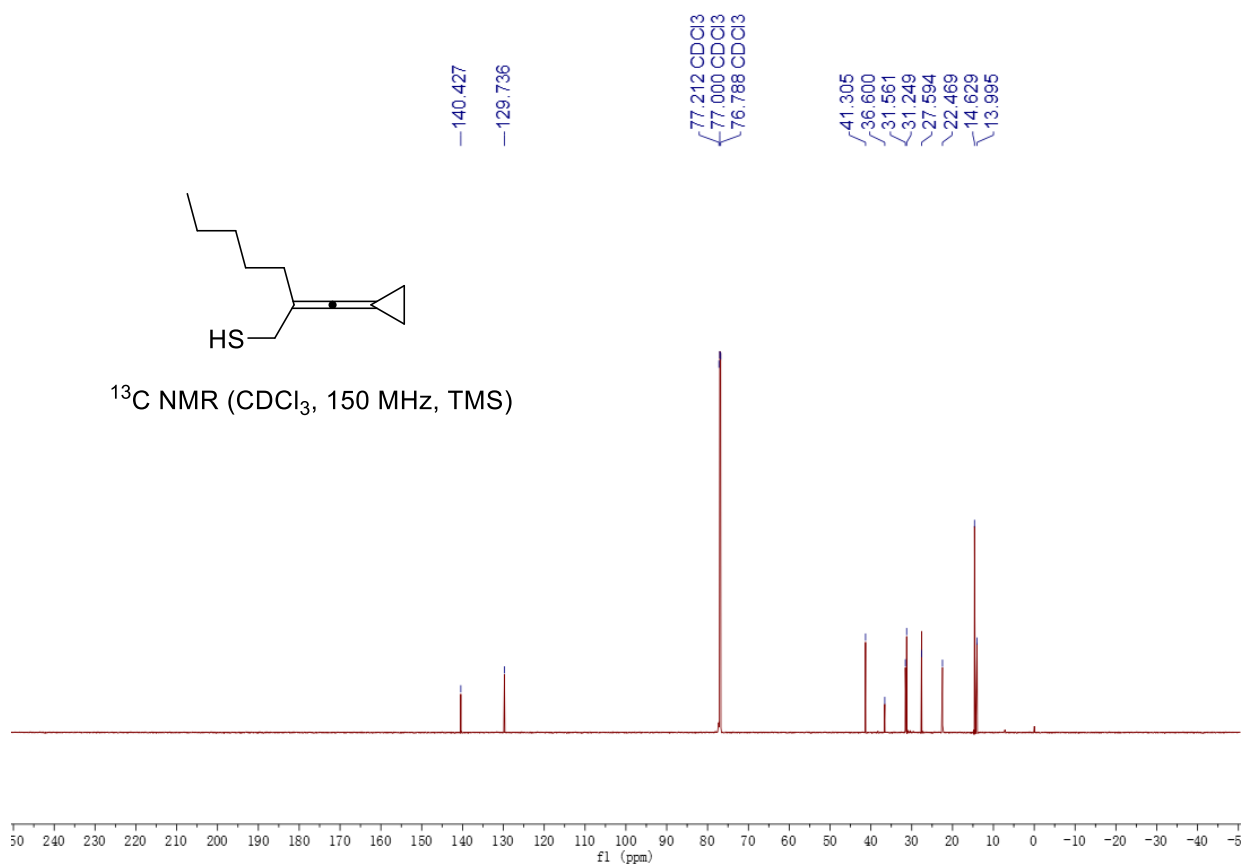
A colorless oil, 40%, 72.9 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 4.93 (s, 1H), 3.87 (s, 2H), 2.09 (t, $J = 7.7$ Hz, 2H), 1.49 - 1.43 (m, 2H), 1.34 - 1.26 (m, 4H), 0.96 - 0.93 (m, 2H), 0.91 - 0.86 (m, 5H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 140.4, 129.7, 41.3, 36.6, 31.6, 31.2, 27.6, 22.5, 14.6, 14.0. IR (neat) ν 715, 916, 931, 1064, 1093, 1224, 1613, 2933 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{18}\text{S}$ (M^+): 182.1122, Found: 182.1124.

4.933
3.866
2.106
2.093
2.080
1.487
1.462
1.449
1.432
1.339
1.324
1.314
1.306
1.299
1.294
1.285
1.277
1.270
1.264
0.954
0.945
0.942
0.939
0.933
0.905
0.898
0.893
0.882
0.873
0.861
0.000



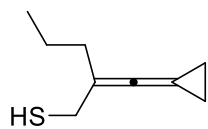
^1H NMR (CDCl_3 , 600 MHz, TMS)



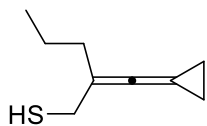
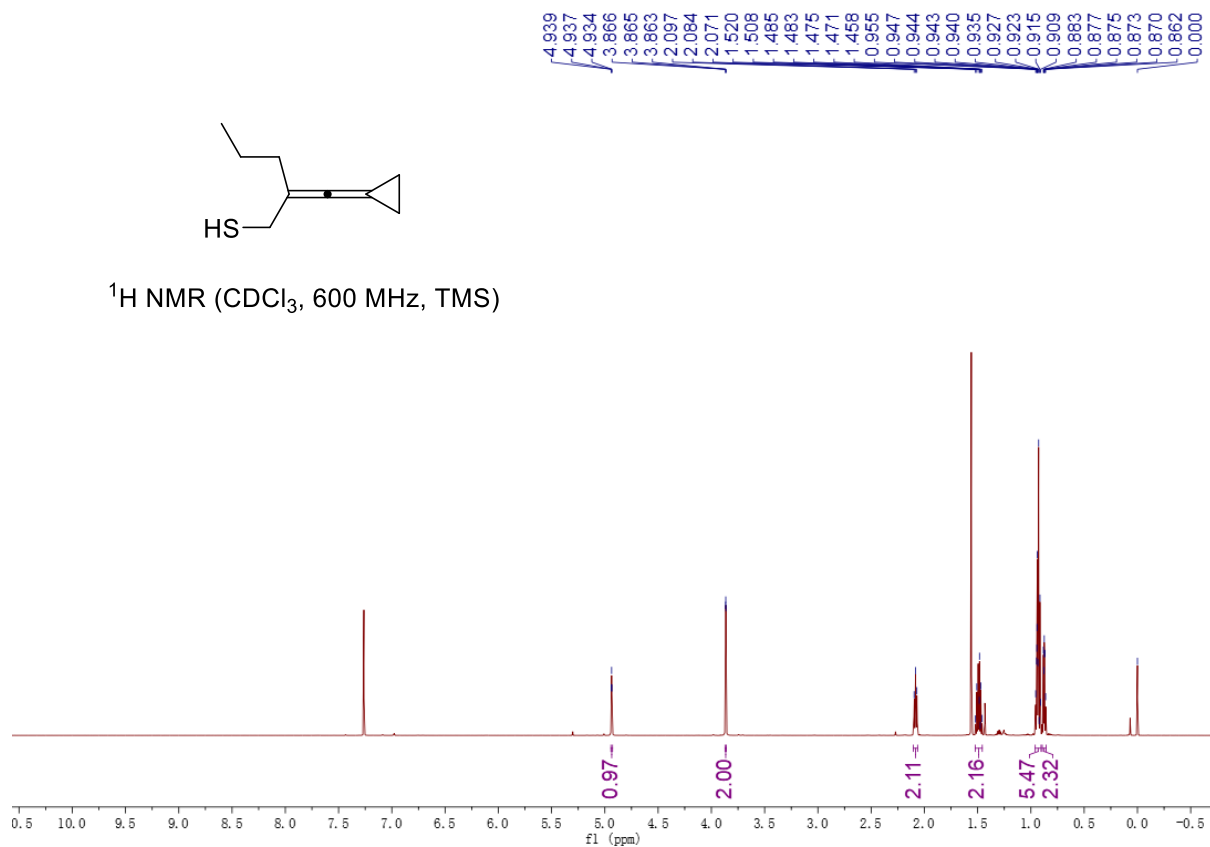


2-(cyclopropylidene- λ^5 -methylene)pentane-1-thiol (7g)

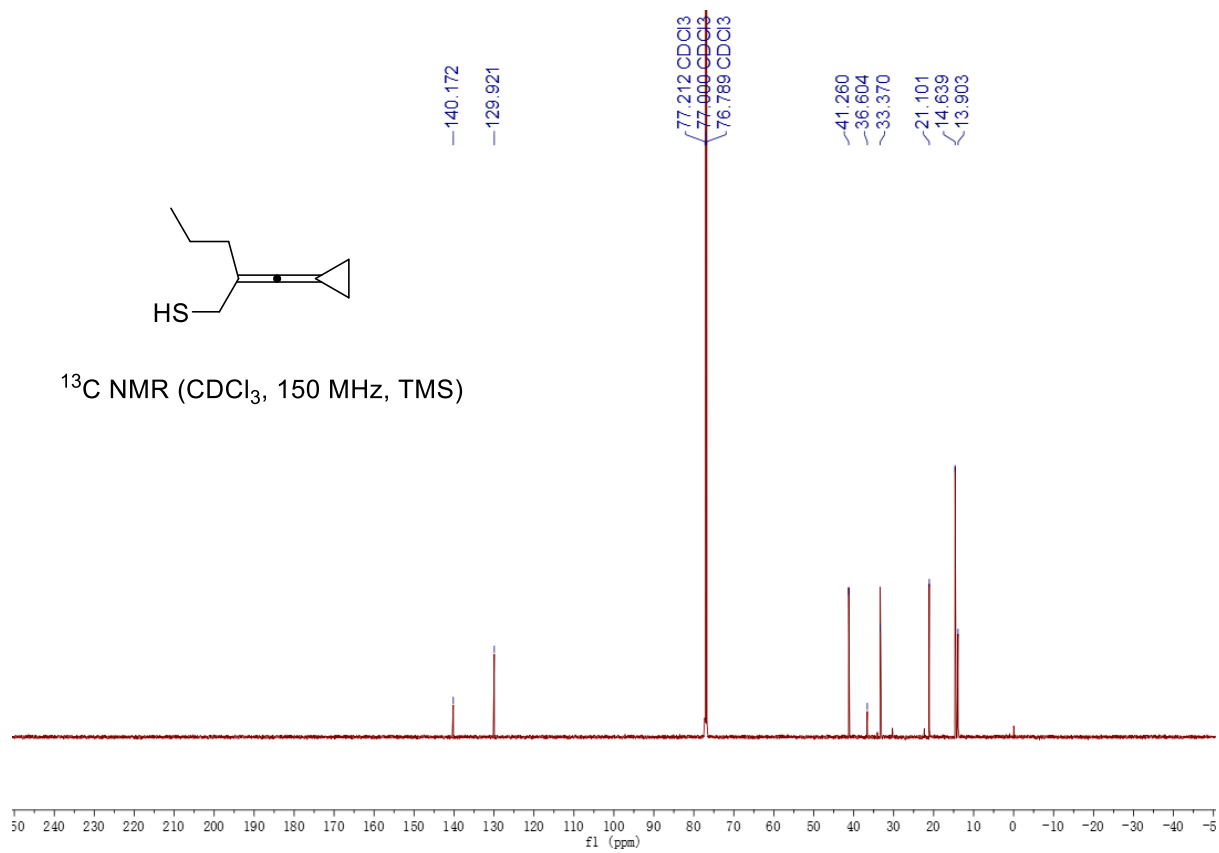
A colorless oil, 46%, 71.0 mg. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 4.94 - 4.93 (m, 1H), 3.87 - 3.86 (m, 2H), 2.10 - 2.06 (m, 2H), 1.52 - 1.46 (m, 2H), 0.96 - 0.90 (m, 5H), 0.89 - 0.86 (m, 2H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 140.2, 129.9, 41.3, 36.6, 33.4, 21.1, 14.6, 13.9. IR (neat) ν 716, 921, 965, 1033, 1088, 1270, 1611, 2914 cm⁻¹. HRMS (EI) calcd. for C₉H₁₄S (M⁺): 154.0811, Found: 154.0811.

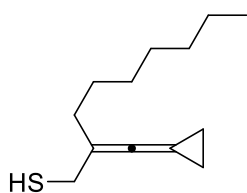


^1H NMR (CDCl_3 , 600 MHz, TMS)



^{13}C NMR (CDCl_3 , 150 MHz, TMS)

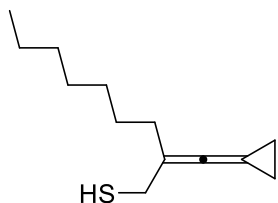




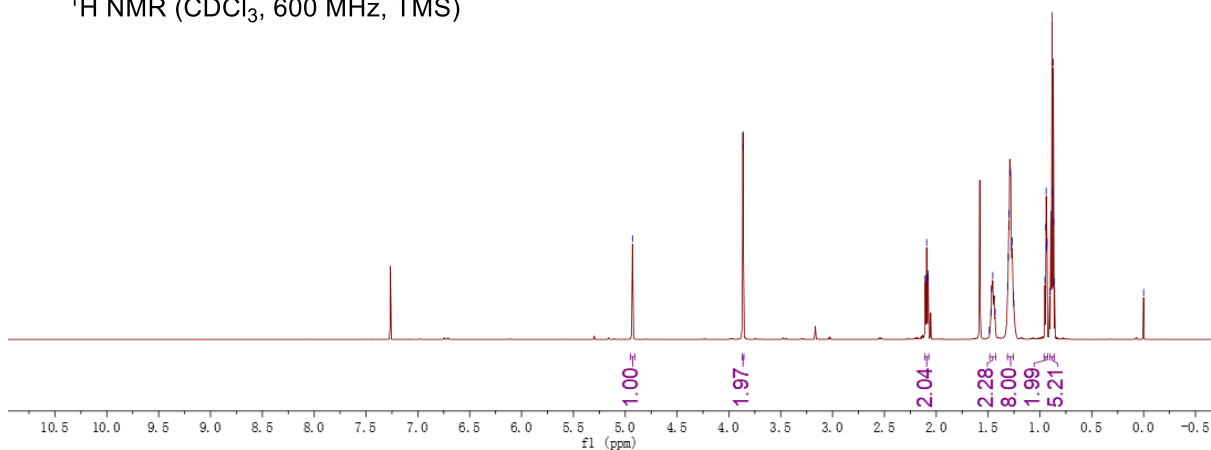
2-(cyclopropylidene- λ^5 -methylene)nonane-1-thiol (7h)

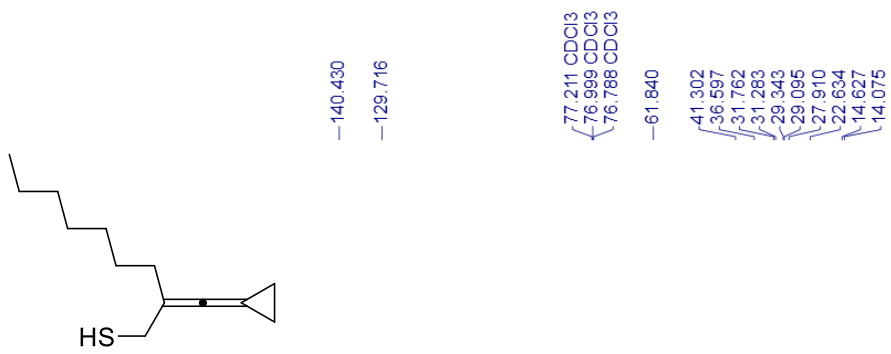
A colorless oil, 39%, 82.0 mg. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 4.93 (s, 1H), 3.86 (s, 2H), 2.11 - 2.07 (m, 2H), 1.48 - 1.43 (m, 2H), 1.31 - 1.26 (m, 8H), 0.96 - 0.93 (m, 2H), 0.90 - 0.86 (m, 5H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 140.4, 129.7, 61.8, 41.3, 36.6, 31.8, 31.3, 29.3, 29.1, 27.9, 22.6, 14.6, 14.1. IR (neat) ν 718, 900, 966, 1038, 1072, 1253, 1631, 2928 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{22}\text{S}$ (M^+): 210.1439, Found: 210.1437.

4.930
3.864
2.106
2.104
2.092
2.080
2.078
1.489
1.473
1.468
1.455
1.448
1.432
1.312
1.305
1.289
1.288
1.275
1.268
1.255
1.252
0.952
0.944
0.940
0.937
0.931
0.906
0.895
0.883
0.880
0.874
0.872
0.868
0.860
0.000

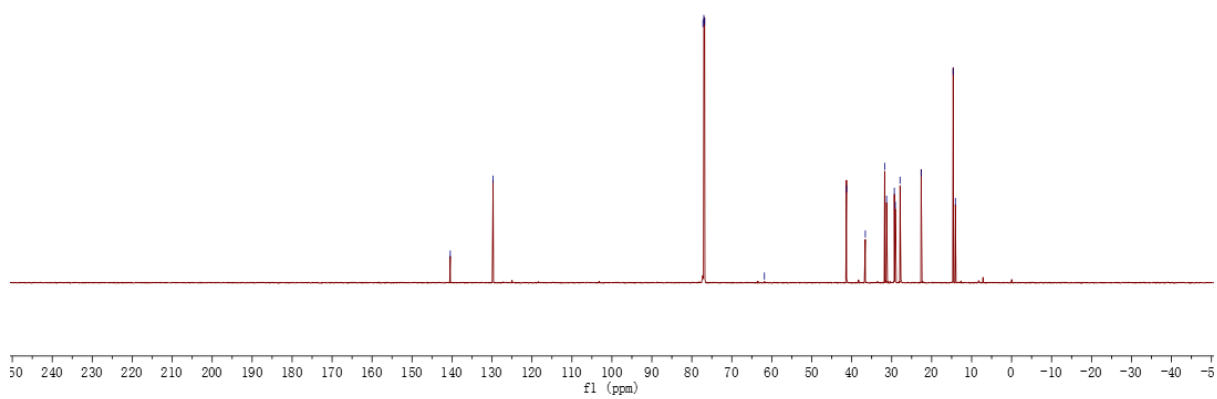


^1H NMR (CDCl_3 , 600 MHz, TMS)

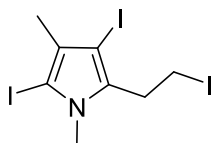




¹³C NMR (CDCl₃, 150 MHz, TMS)

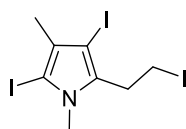


9. Spectroscopic data of products 3, 4, 6, 8, 9, 11, 12, 13.

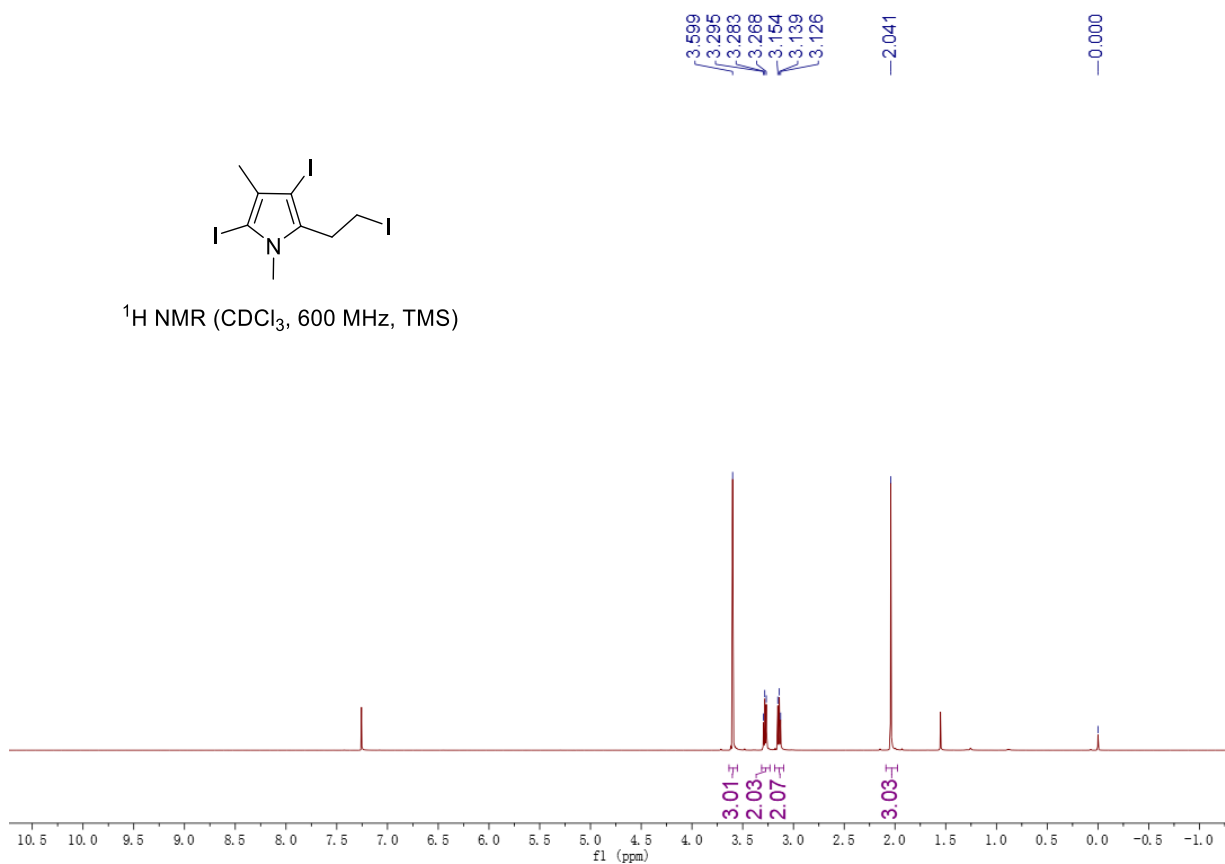


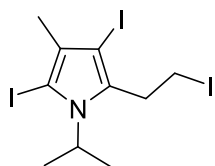
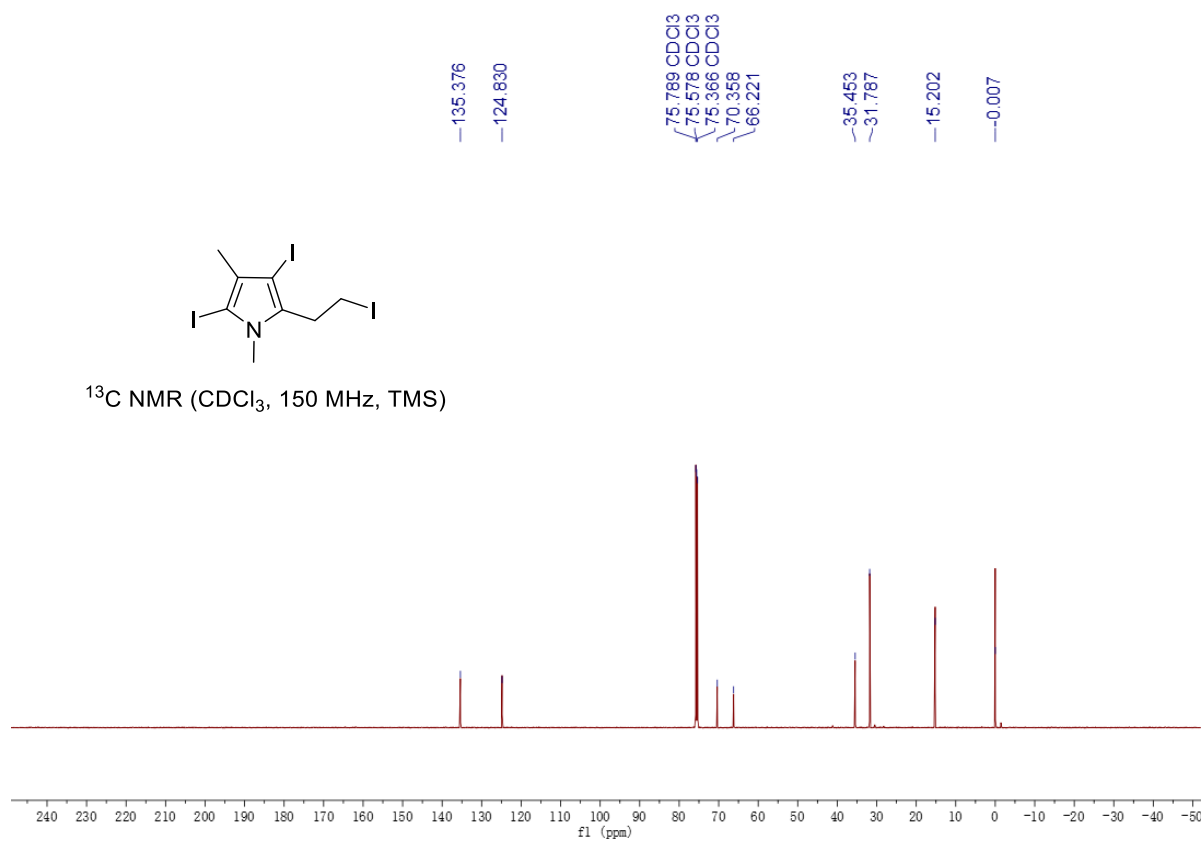
2,4-diiodo-5-(2-iodoethyl)-1,3-dimethyl-1H-pyrrole (3aa)

A colorless oil, 45.1 mg, 95% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 3.60 (s, 3H), 3.31 - 3.23 (m, 2H), 3.18 - 3.10 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 136.8, 133.2, 126.6, 117.0, 71.1, 68.5, 51.4, 33.1, 16.7, 1.9. IR (Neat) ν 722, 1007, 1051, 1168, 1332, 1387, 1431, 2843, 2920 cm^{-1} . HRMS (EI) calcd. for $\text{C}_8\text{H}_{10}\text{I}_3\text{N}$: 500.7947, Found: 500.7942.



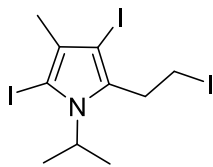
^1H NMR (CDCl_3 , 600 MHz, TMS)



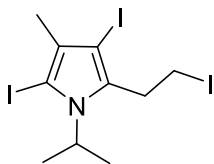
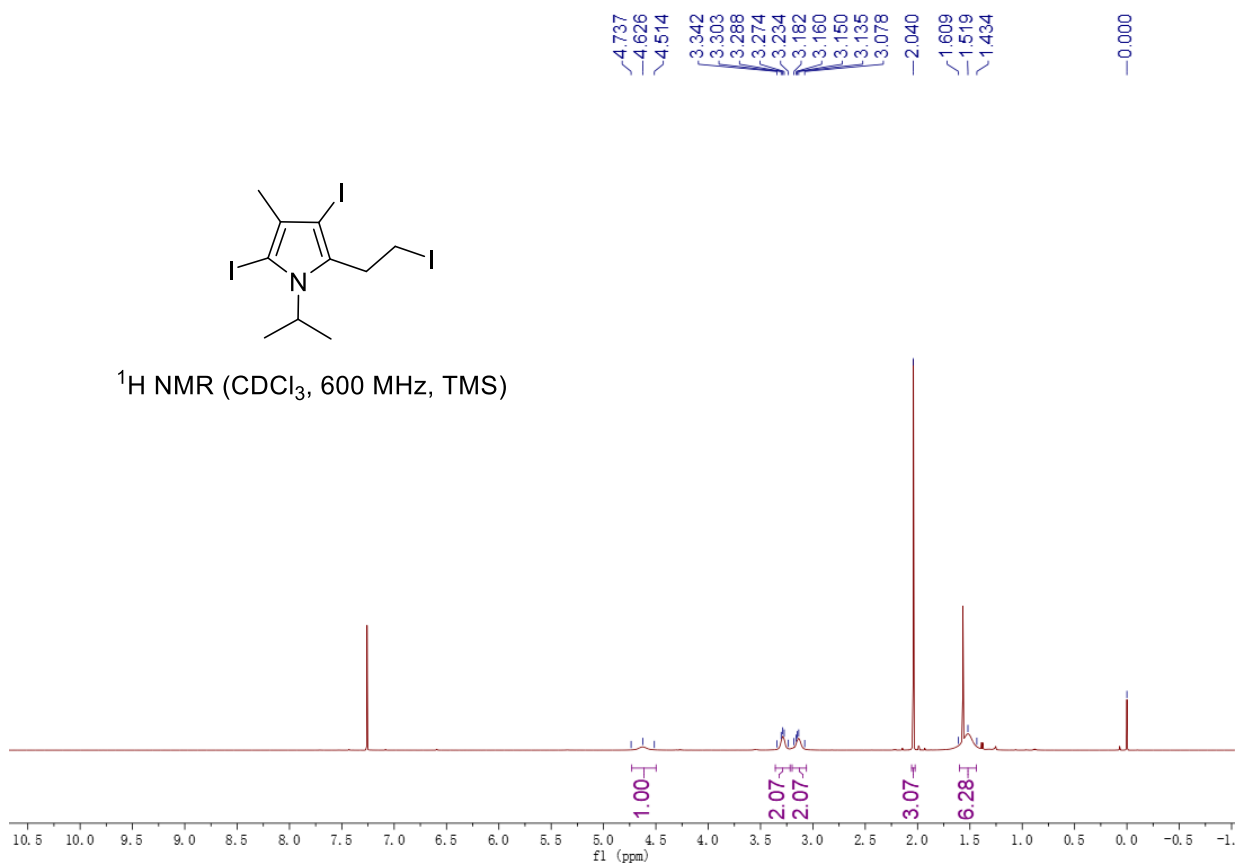


2,4-diiodo-5-(2-iodoethyl)-1-isopropyl-3-methyl-1H-pyrrole (3ba)

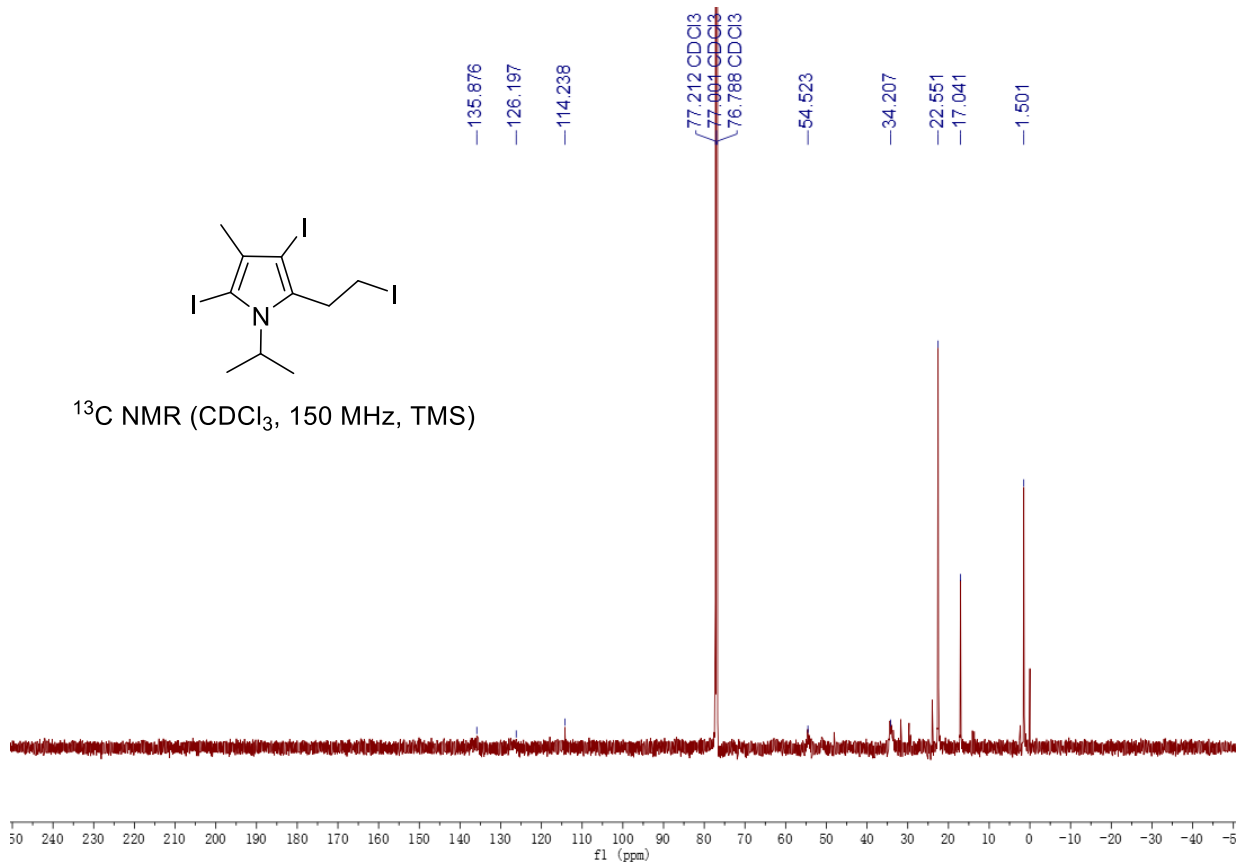
A colorless oil, 51.6 mg, 20% yield. ¹H NMR (CDCl₃, TMS, 600 MHz) 4.63 (s, 1H), 3.29 (s, 2H), 3.14 (s, 2H), 2.04 (s, 3H), 1.52 (s, 6H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 135.9, 126.2, 114.2, 54.5, 34.2, 22.6, 17.0, 1.5. IR (Neat) ν 2960, 2917, 1486, 1456, 1392, 1352, 1311, 1219, 1069, 1035, 1008, 820, 748, 735, 721 cm⁻¹. HRMS (ESI) calcd. for C₁₀H₁₅I₃N (M+H): 529.8260, Found: 529.8271.

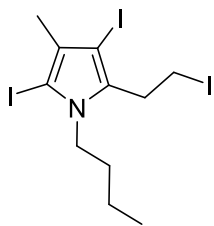


¹H NMR (CDCl₃, 600 MHz, TMS)



¹³C NMR (CDCl₃, 150 MHz, TMS)

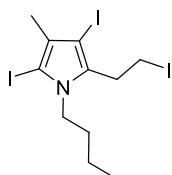




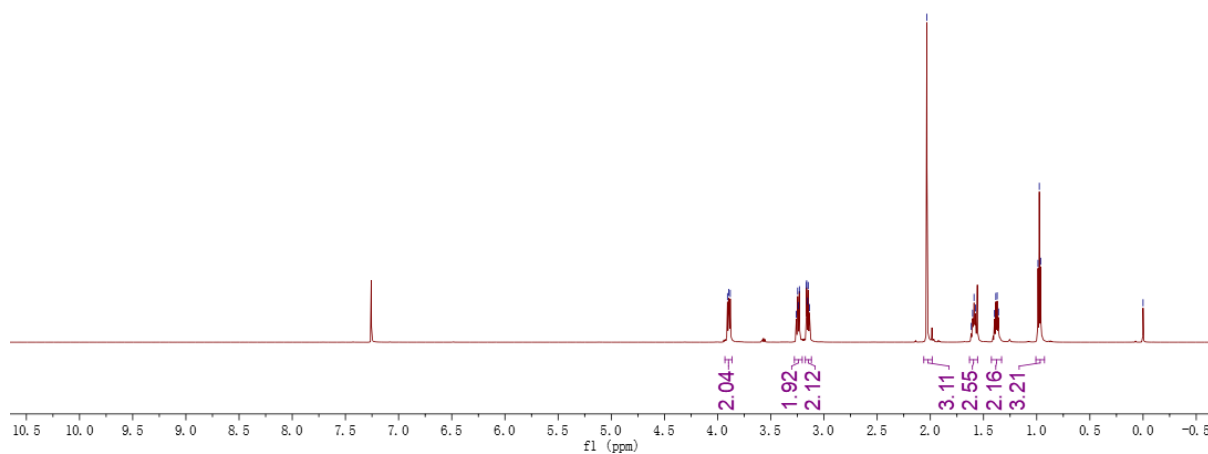
1-butyl-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3ca)

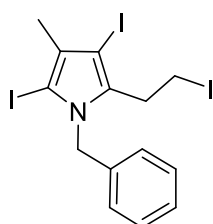
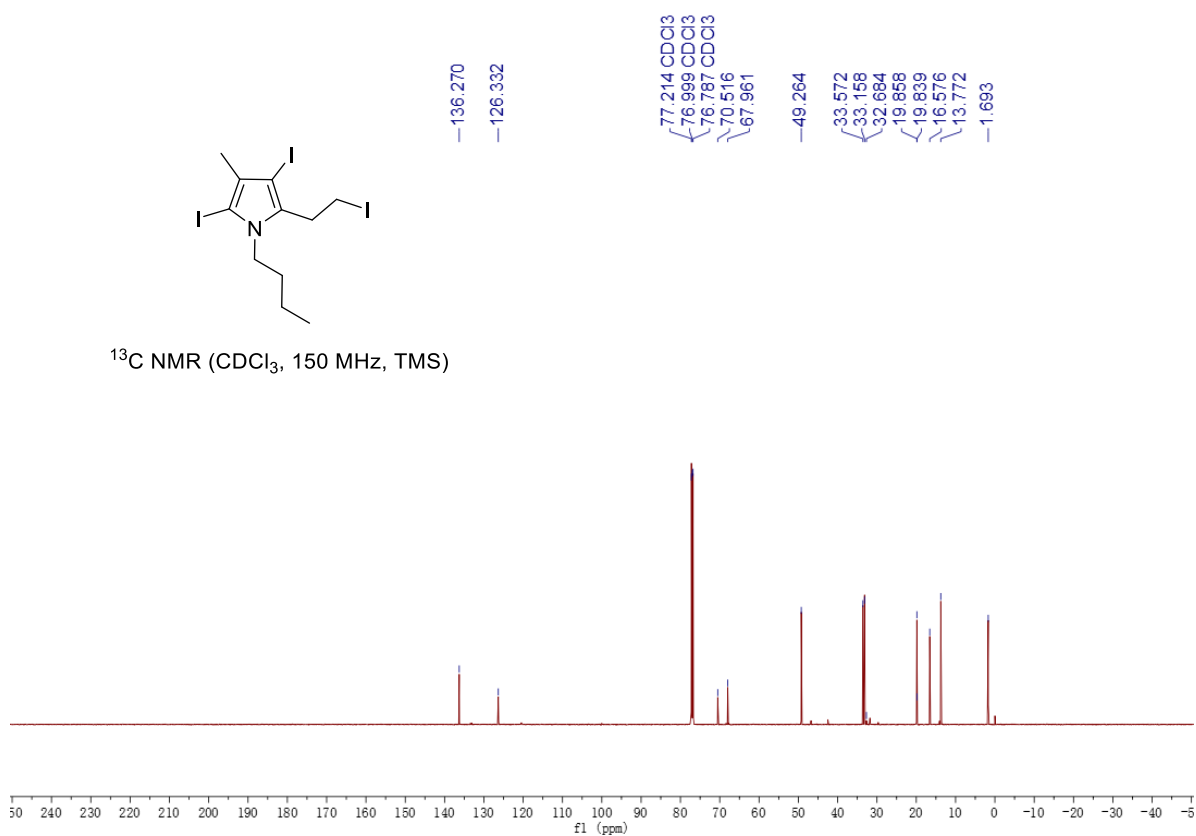
A colorless oil, 48.3 mg, 89% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 3.93 - 3.86 (m, 2H), 3.28 - 3.20 (m, 2H), 3.18 - 3.12 (m, 2H), 2.03 (s, 3H), 1.63 - 1.56 (m, 3H), 1.43 - 1.33 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 136.3, 126.3, 70.5, 68.0, 49.3, 33.6, 33.2, 32.7, 19.85, 19.83, 16.6, 13.8, 1.7. IR (Neat) ν 731, 1009, 1099, 1244, 1380, 1465, 2864, 2956 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{16}\text{I}_3\text{N}$: 542.8428, Found: 542.8411.

3.908
3.895
3.881
3.261
3.248
3.243
3.231
3.165
3.163
3.153
3.148
3.137
2.033
1.615
1.602
1.589
1.576
1.397
1.384
1.372
1.359
0.988
0.976
0.963
0.000



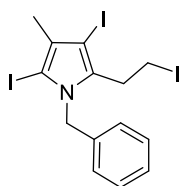
^1H NMR (CDCl_3 , 600 MHz, TMS)



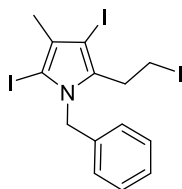
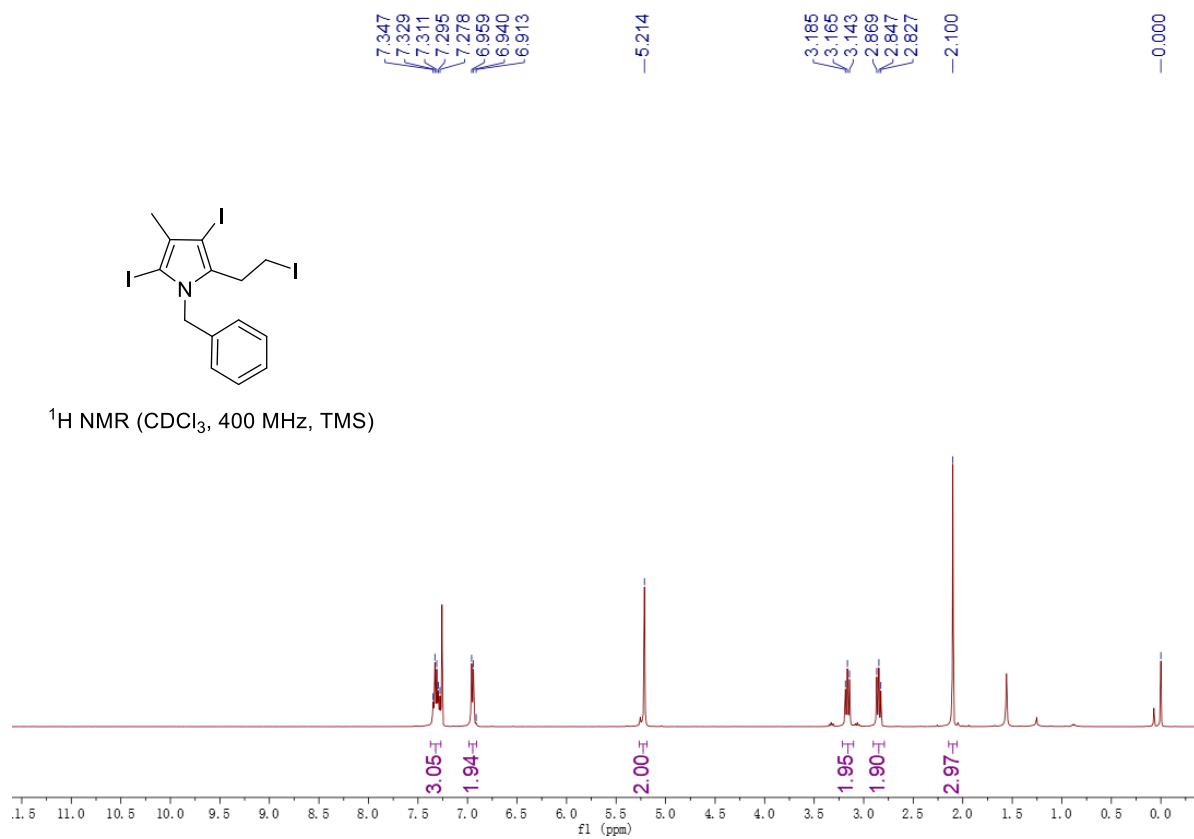


1-benzyl-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3da)

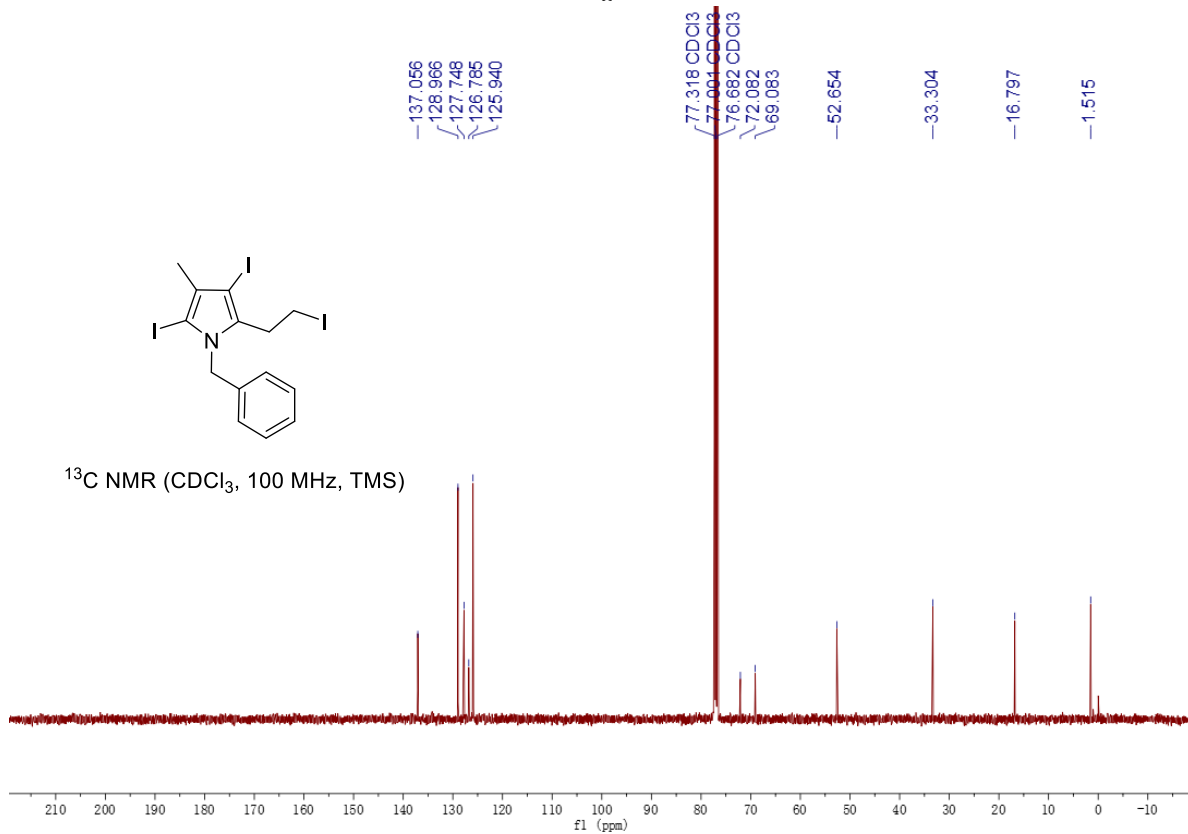
A colorless oil, 41.5 mg, 72% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.37 - 7.27 (m, 3H), 6.95 (d, *J* = 7.5 Hz, 2H), 5.21 (s, 2H), 3.21 - 3.10 (m, 2H), 2.90 - 2.79 (m, 2H), 2.10 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 137.1, 129.0, 127.7, 126.8, 125.9, 72.1, 69.1, 52.7, 33.3, 16.8, 1.5. IR (Neat) ν 693, 727, 1029, 1173, 1443, 1495, 2927 cm⁻¹. HRMS (ESI) calcd. for C₁₄H₁₅I₃N (M+H): 577.8342, Found: 577.8490.

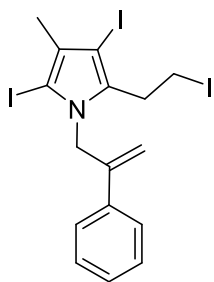


^1H NMR (CDCl_3 , 400 MHz, TMS)



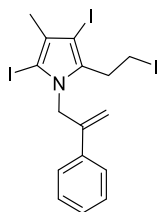
^{13}C NMR (CDCl_3 , 100 MHz, TMS)



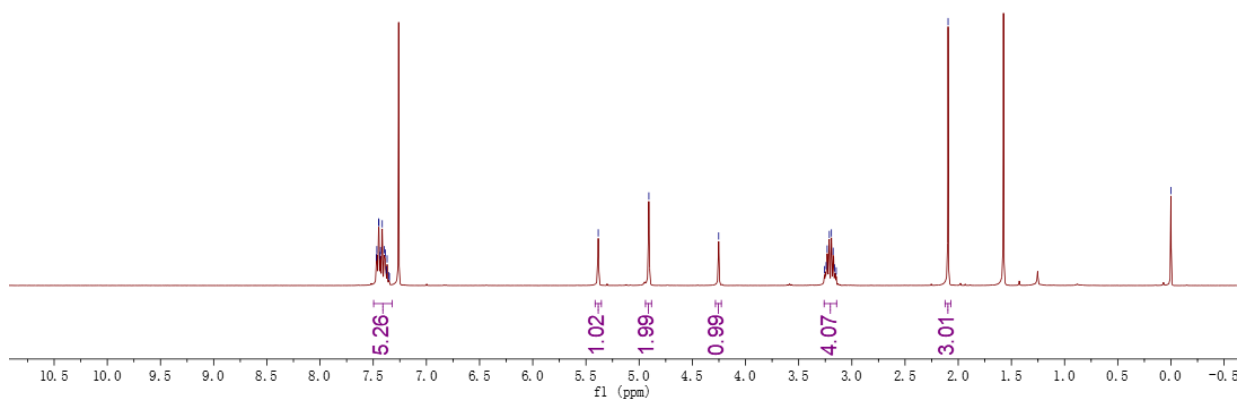


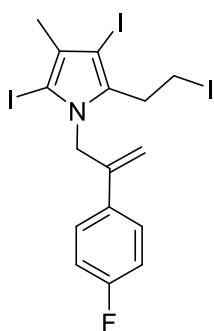
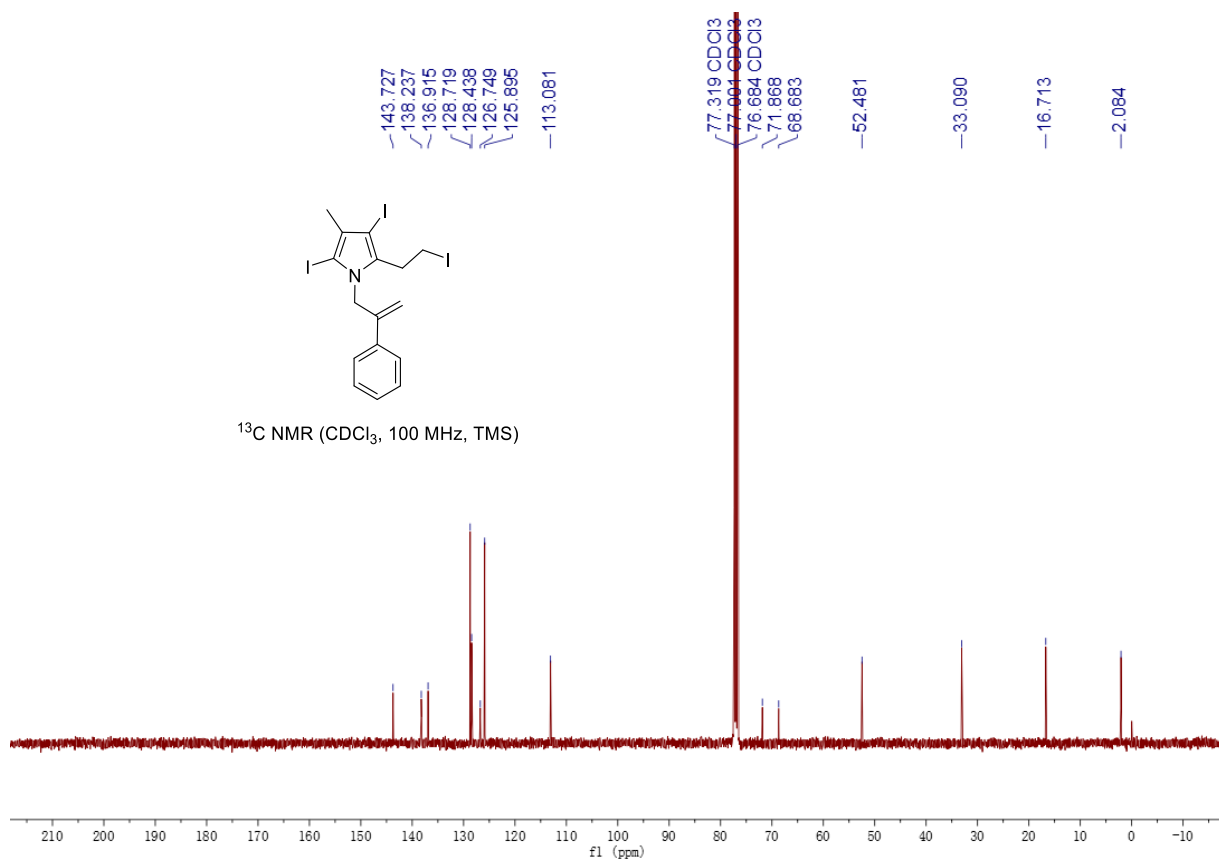
2,4-diiodo-5-(2-iodoethyl)-3-methyl-1-(2-phenylallyl)-1H-pyrrole (3ea)

A colorless oil, 40.2 mg, 82% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.50 - 7.32 (m, 5H), 5.38 (s, 1H), 4.91 (s, 2H), 4.25 (s, 1H), 3.26 - 3.14 (m, 4H), 2.10 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 143.7, 138.2, 136.9, 128.7, 128.4, 126.7, 125.9, 113.1, 71.9, 68.7, 52.5, 33.1, 16.7, 2.1. IR (Neat) ν 705, 779, 898, 1164, 1257, 1333, 1430, 2846, 2922 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{16}\text{I}_3\text{N}$: 602.8436, Found: 602.8411.



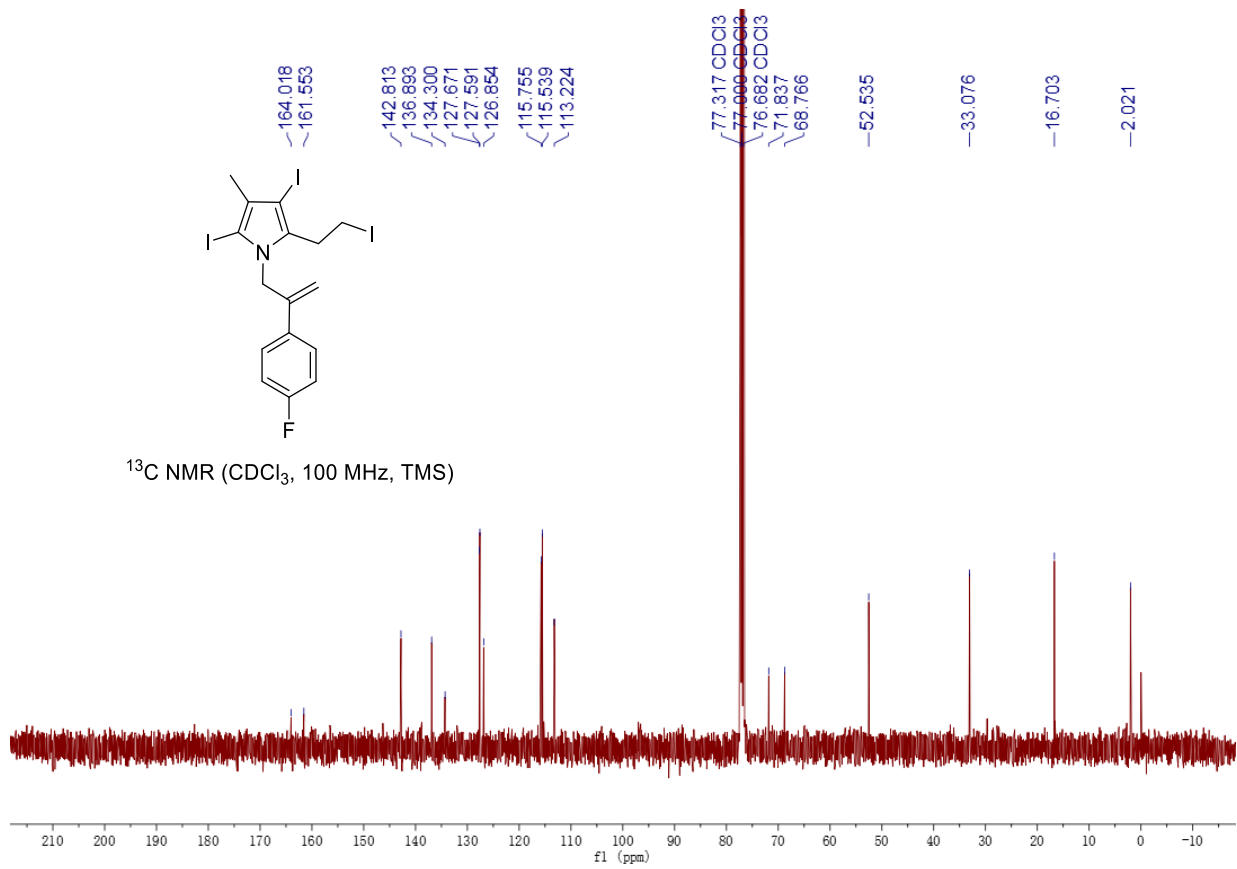
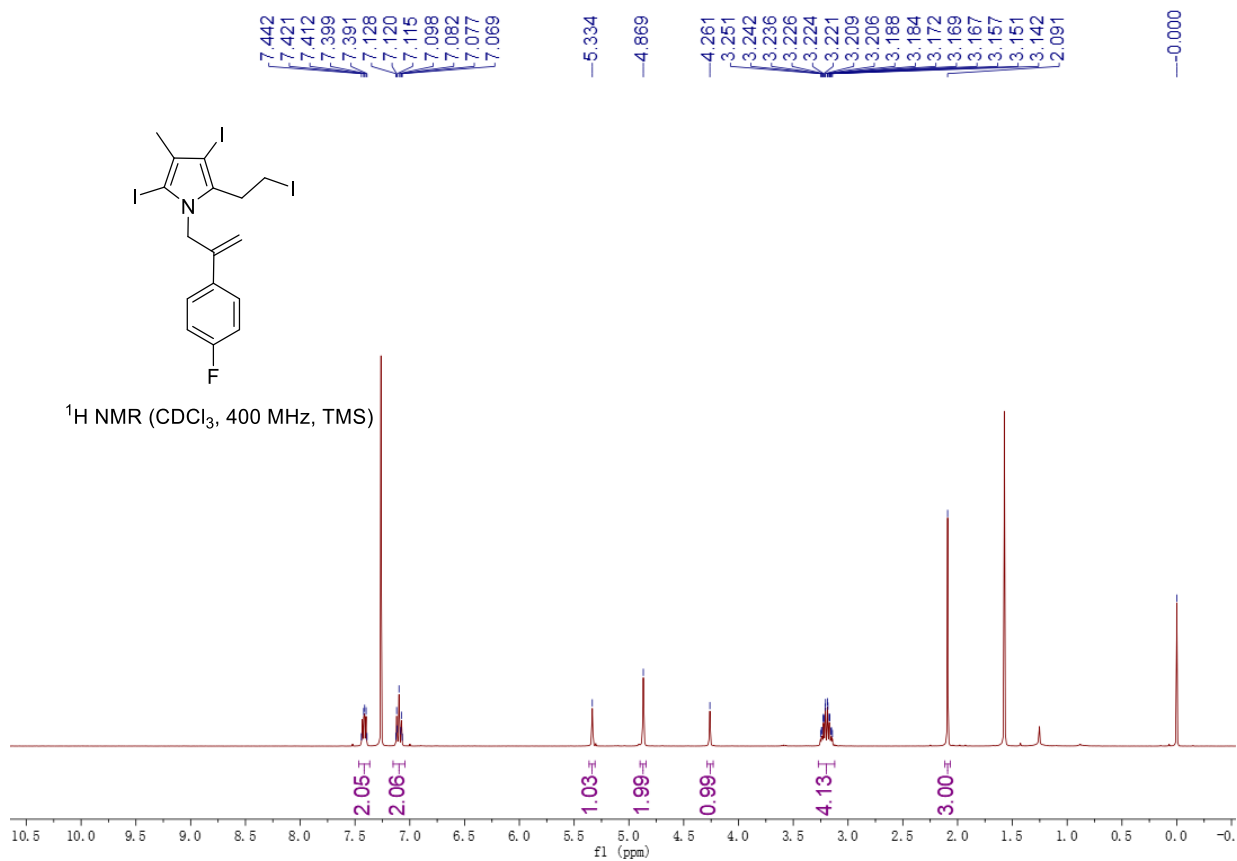
^1H NMR (CDCl_3 , 400 MHz, TMS)

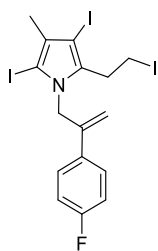




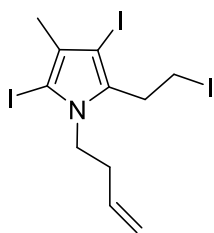
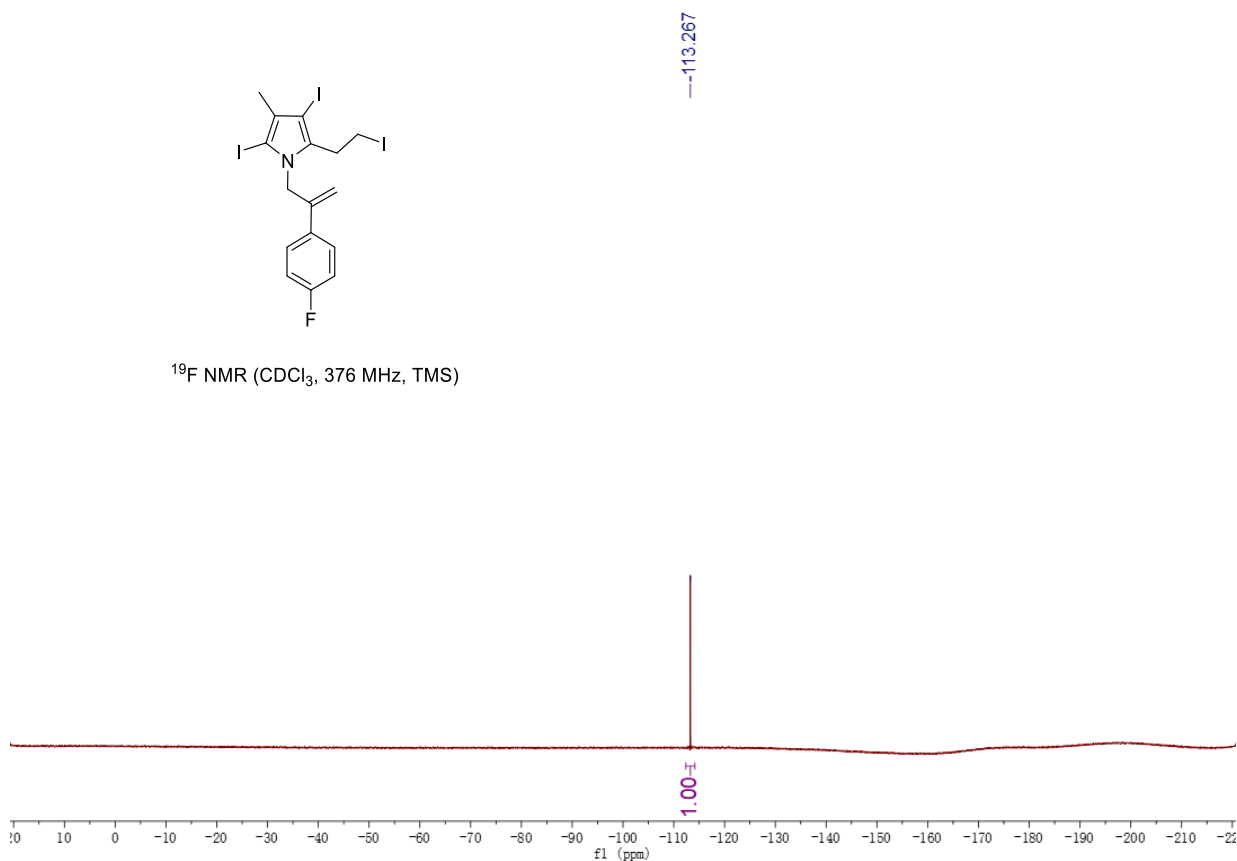
1-(2-(4-fluorophenyl)allyl)-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3fa)

A colorless oil, 48.4 mg, 78% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ δ 7.47 - 7.37 (m, 2H), 7.15 - 7.04 (m, 2H), 5.33 (s, 1H), 4.87 (s, 2H), 4.26 (s, 1H), 3.27 - 3.12 (m, 4H), 2.09 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 162.8 (d, *J* = 240.0 Hz), 142.8, 136.9, 134.3 (d, *J* = 3.6 Hz), 127.6 (d, *J* = 8.0 Hz), 126.9, 115.6 (d, *J* = 21.6 Hz), 113.2, 71.8, 68.8, 52.5, 33.1, 16.7, 2.0. ¹⁹F NMR (CDCl₃, TMS, 376 MHz) δ -113.3. IR (Neat) ν 734, 835, 906, 1161, 1233, 1331, 1399, 1508, 1602, 2919 cm⁻¹. HRMS (EI) calcd. for C₁₆H₁₅FI₃N: 620.8336, Found: 620.8317.



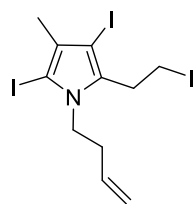


^{19}F NMR (CDCl_3 , 376 MHz, TMS)

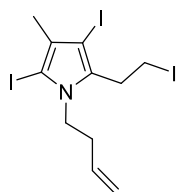
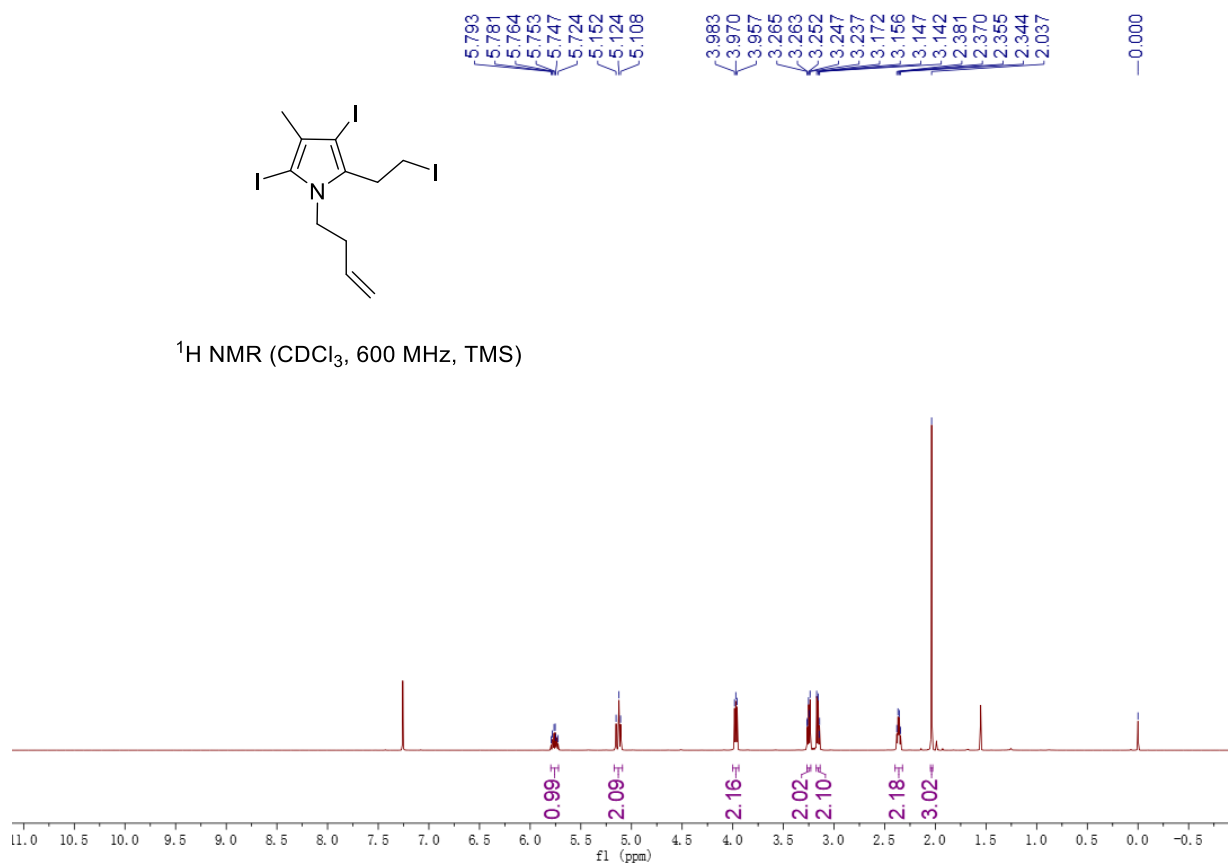


1-(but-3-en-1-yl)-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3ga)

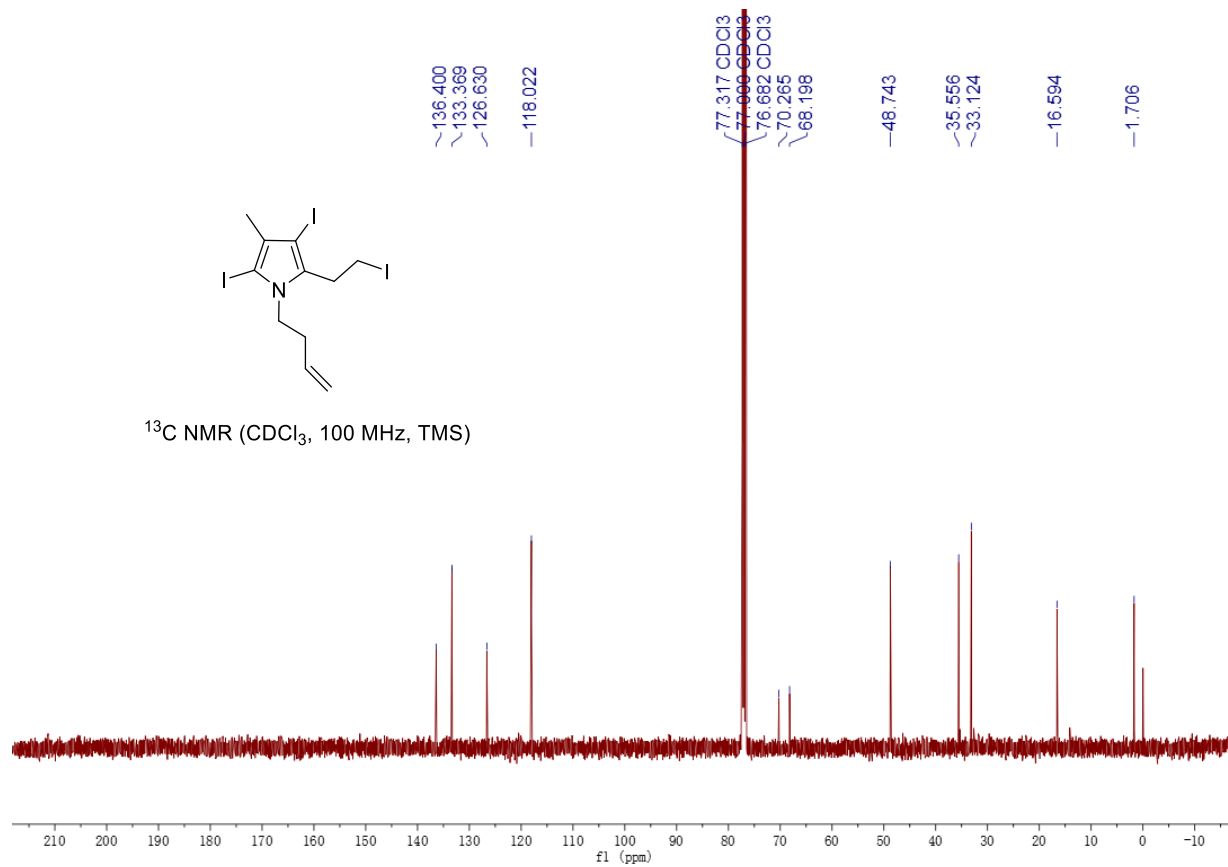
A colorless oil, 48.1 mg, 89% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 5.80 - 5.72 (m, 1H), 5.17 - 5.09 (m, 2H), 4.00 - 3.94 (m, 2H), 3.27 - 3.23 (m, 2H), 3.18 - 3.14 (m, 2H), 2.40 - 2.32 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 136.4, 133.4, 126.6, 118.0, 70.3, 68.2, 48.7, 35.6, 33.1, 16.6, 1.7. IR (Acetone) ν 927, 989, 1165, 1260, 1323, 1446, 2961 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{11}\text{H}_{15}\text{I}_3\text{N}$ (M+H): 541.8333, Found: 541.8342.

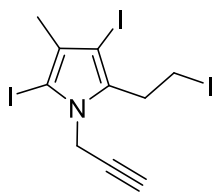


¹H NMR (CDCl₃, 600 MHz, TMS)



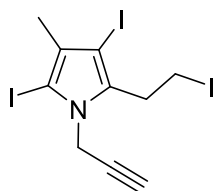
¹³C NMR (CDCl₃, 100 MHz, TMS)



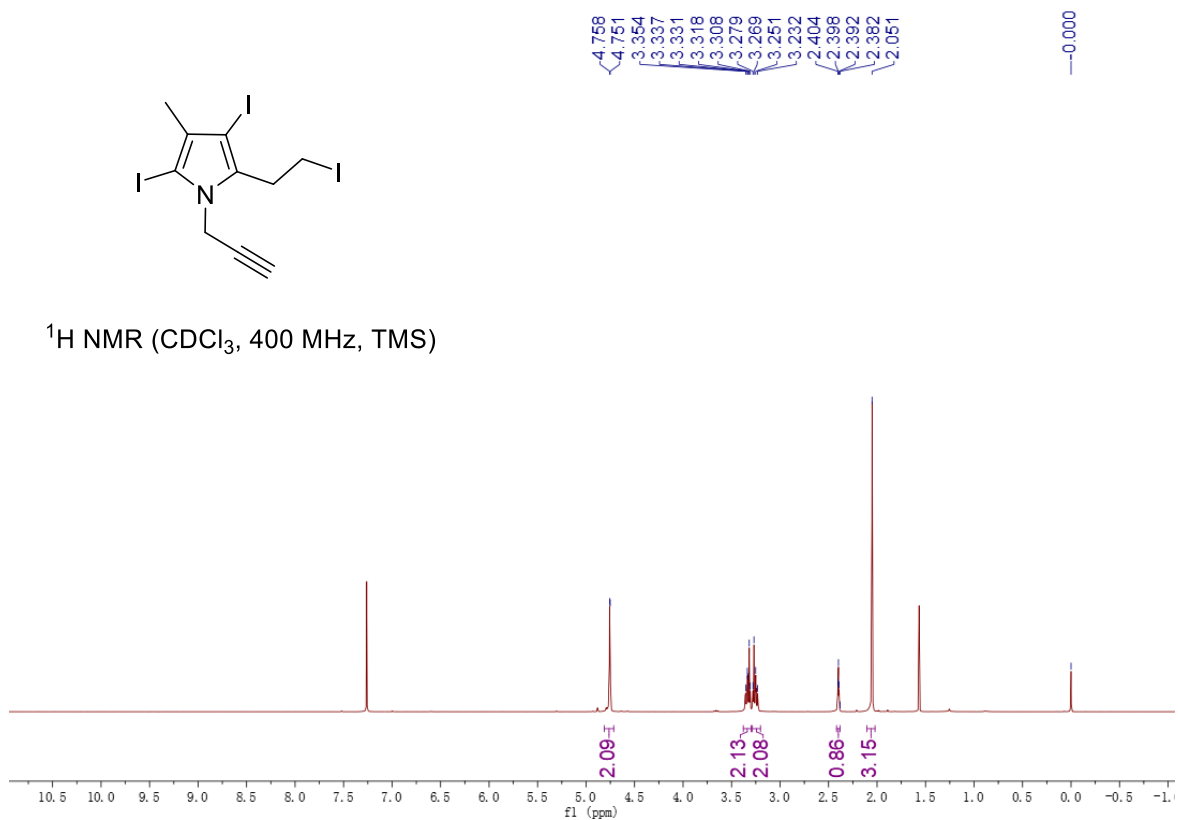


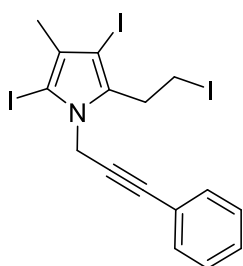
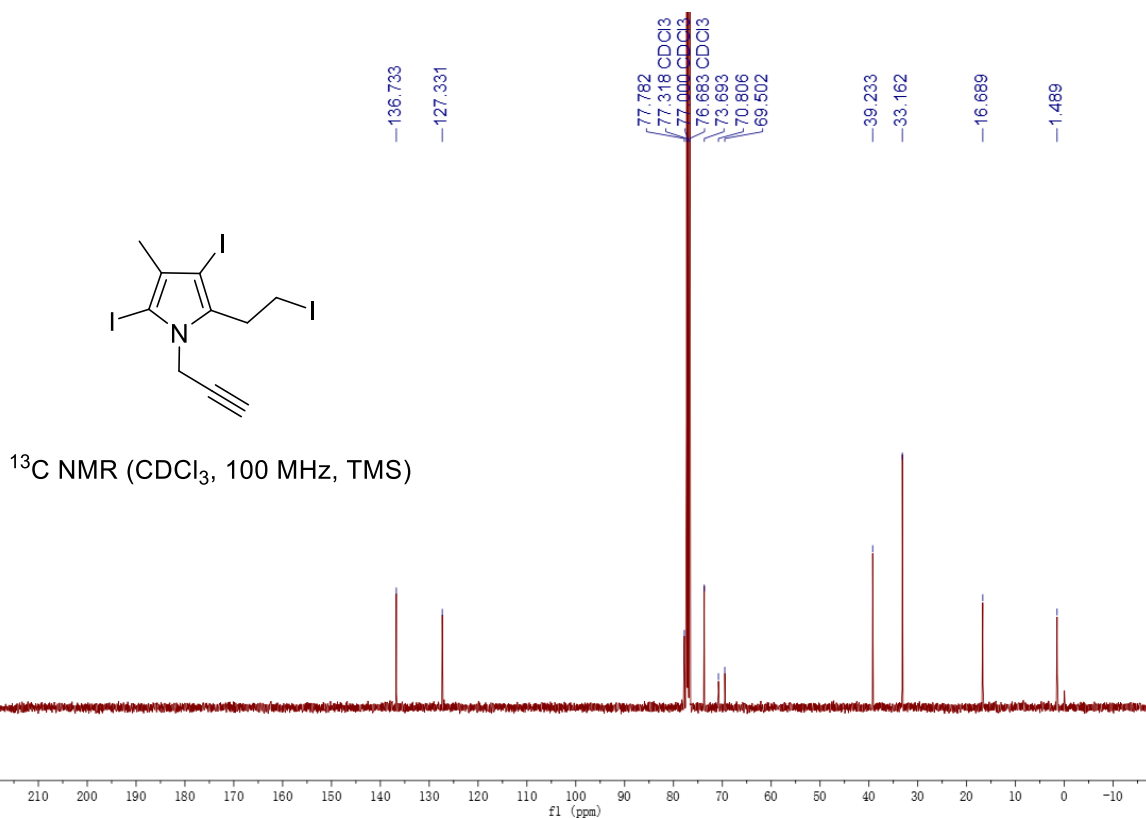
2,4-diiodo-5-(2-iodoethyl)-3-methyl-1-(prop-2-yn-1-yl)-1H-pyrrole (3ha)

A colorless oil, 44.6 mg, 85% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 4.75 (d, $J = 2.5$ Hz, 2H), 3.38 - 3.30 (m, 2H), 3.29 - 3.20 (m, 2H), 2.40 (t, $J = 2.5$ Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 136.7, 127.3, 77.8, 73.7, 70.8, 69.5, 39.2, 33.2, 16.7, 1.5. IR (Neat) ν 675, 734, 946, 1174, 1325, 1378, 1442, 2919, 3281 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{10}\text{I}_3\text{N}$: 524.7960, Found: 524.7942.



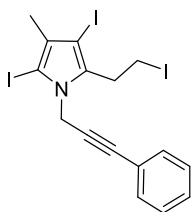
^1H NMR (CDCl_3 , 400 MHz, TMS)



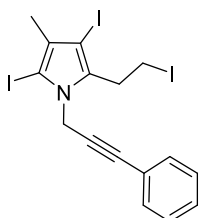
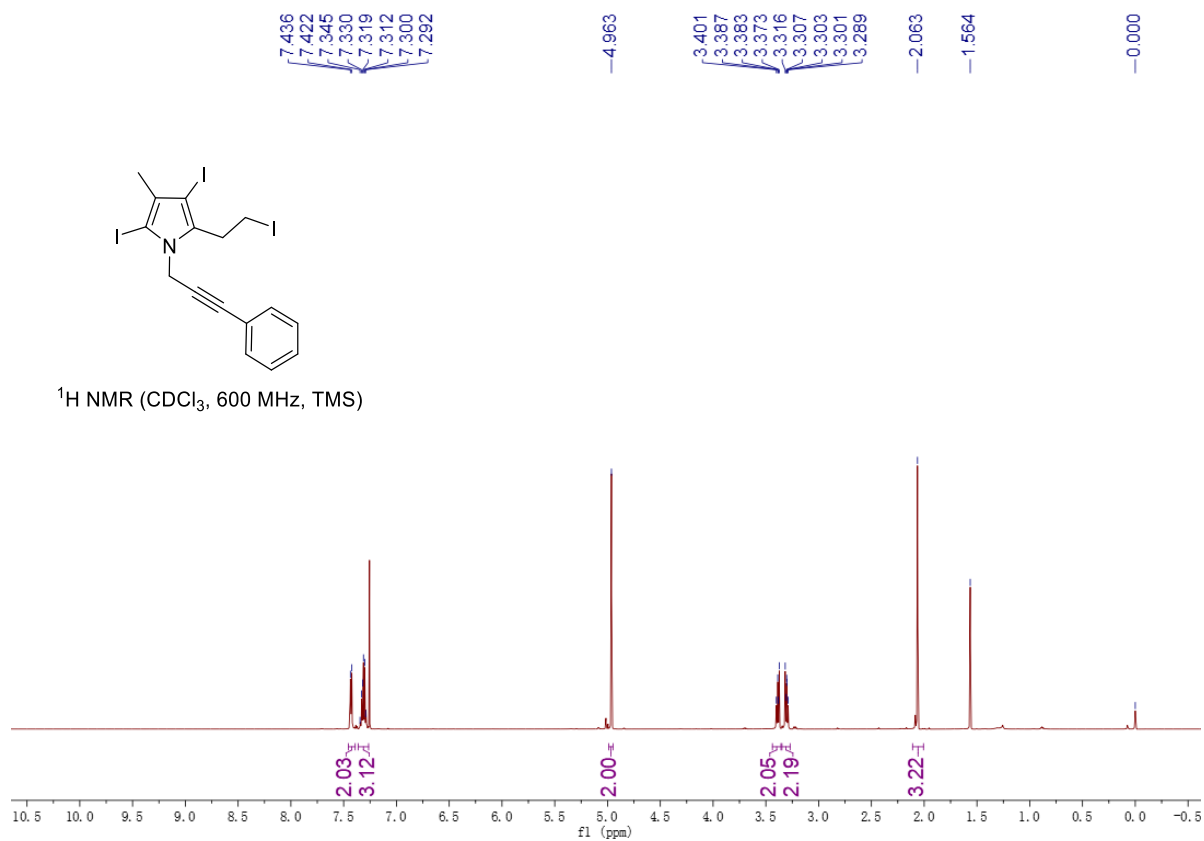


2,4-diiodo-5-(2-iodoethyl)-3-methyl-1-(3-phenylprop-2-yn-1-yl)-1H-pyrrole (3ia)

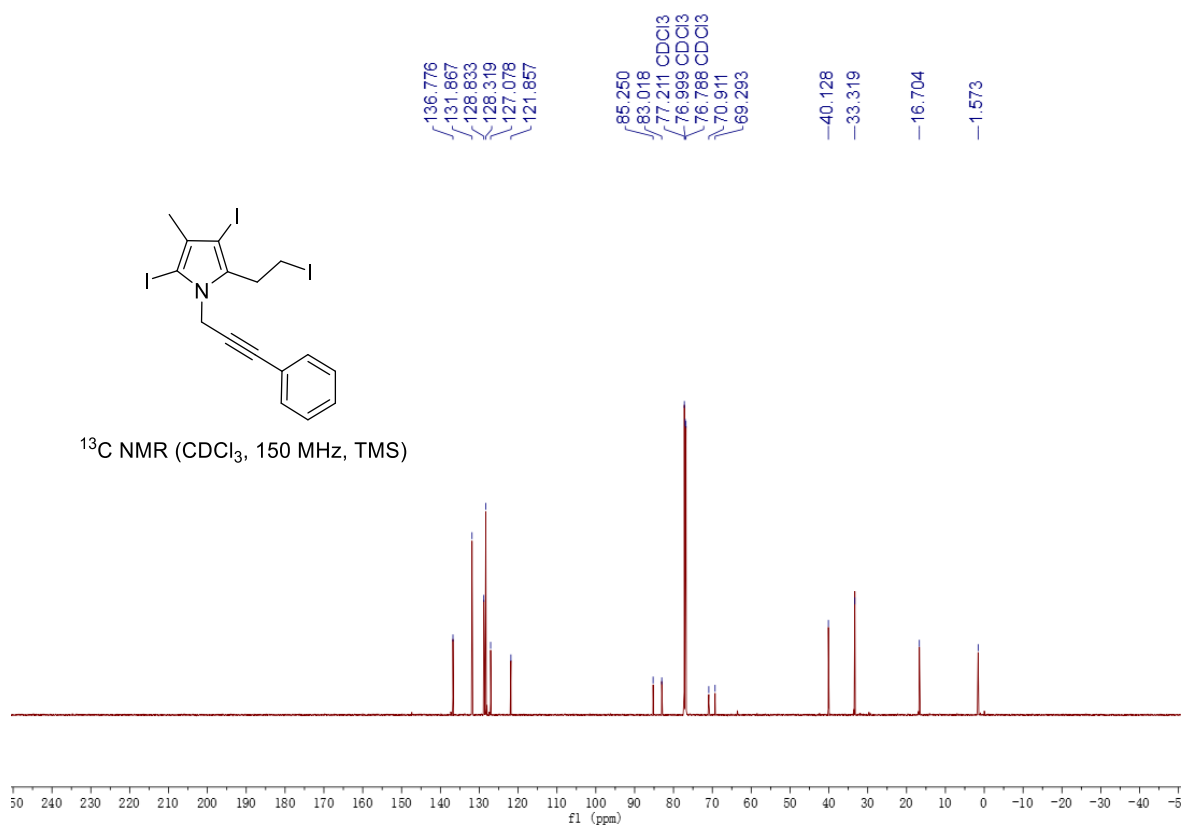
A colorless oil, 49.3 mg, 82% yield. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.36-7.26 (m, 3H), 4.96 (s, 2H), 3.44 - 3.36 (m, 2H), 3.35 - 3.27 (m, 2H), 2.06 (s, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 136.8, 131.9, 128.8, 128.3, 127.1, 121.9, 85.3, 83.0, 70.9, 69.3, 40.1, 33.3, 16.7, 1.6. IR (Neat) ν 696, 735, 792, 1028, 1172, 1261, 1327, 1380, 1490, 2922 cm⁻¹. HRMS (ESI) calcd. for C₁₆H₁₅I₃N (M+H): 601.8339, Found: 601.8547.

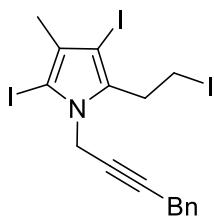


¹H NMR (CDCl₃, 600 MHz, TMS)



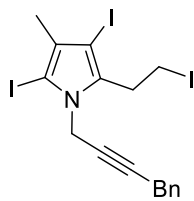
¹³C NMR (CDCl₃, 150 MHz, TMS)



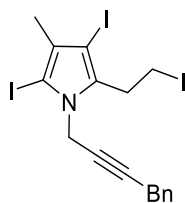
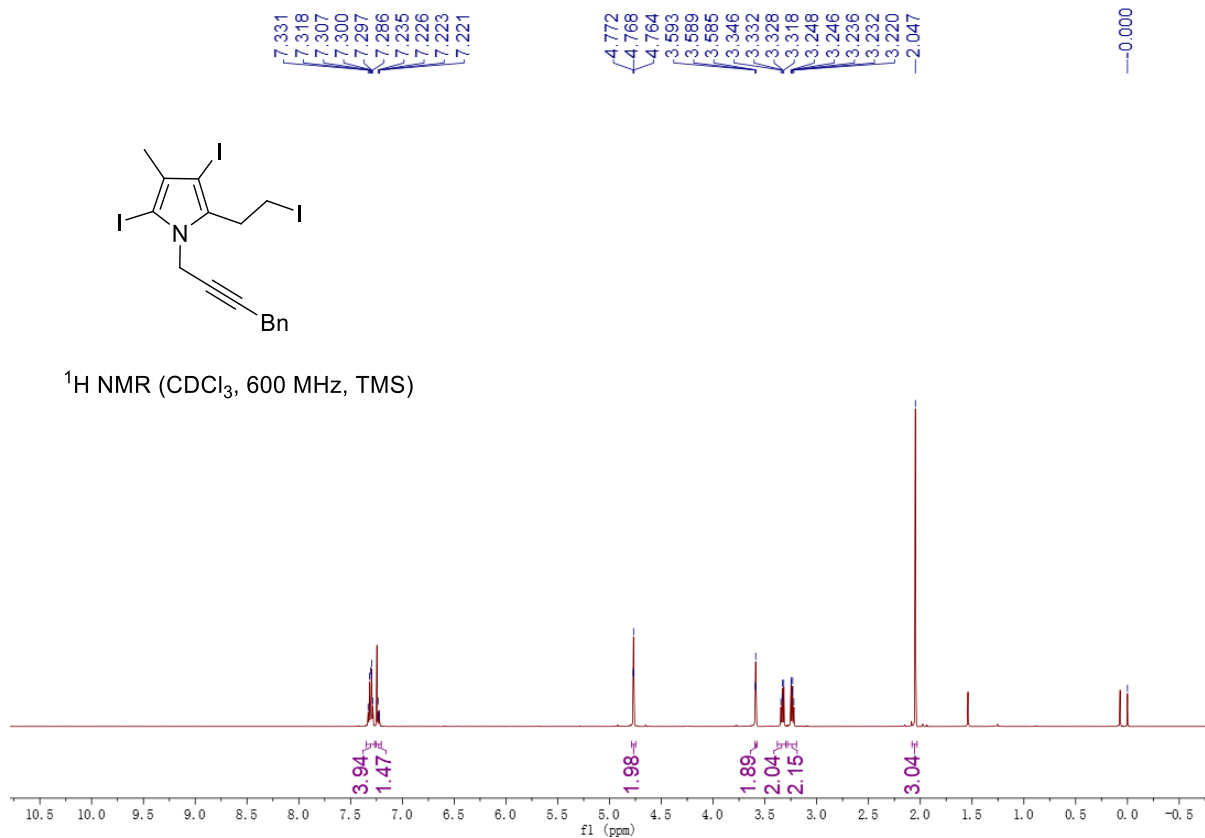


2,4-diiodo-5-(2-iodoethyl)-3-methyl-1-(4-phenylbut-2-yn-1-yl)-1H-pyrrole (3ja)

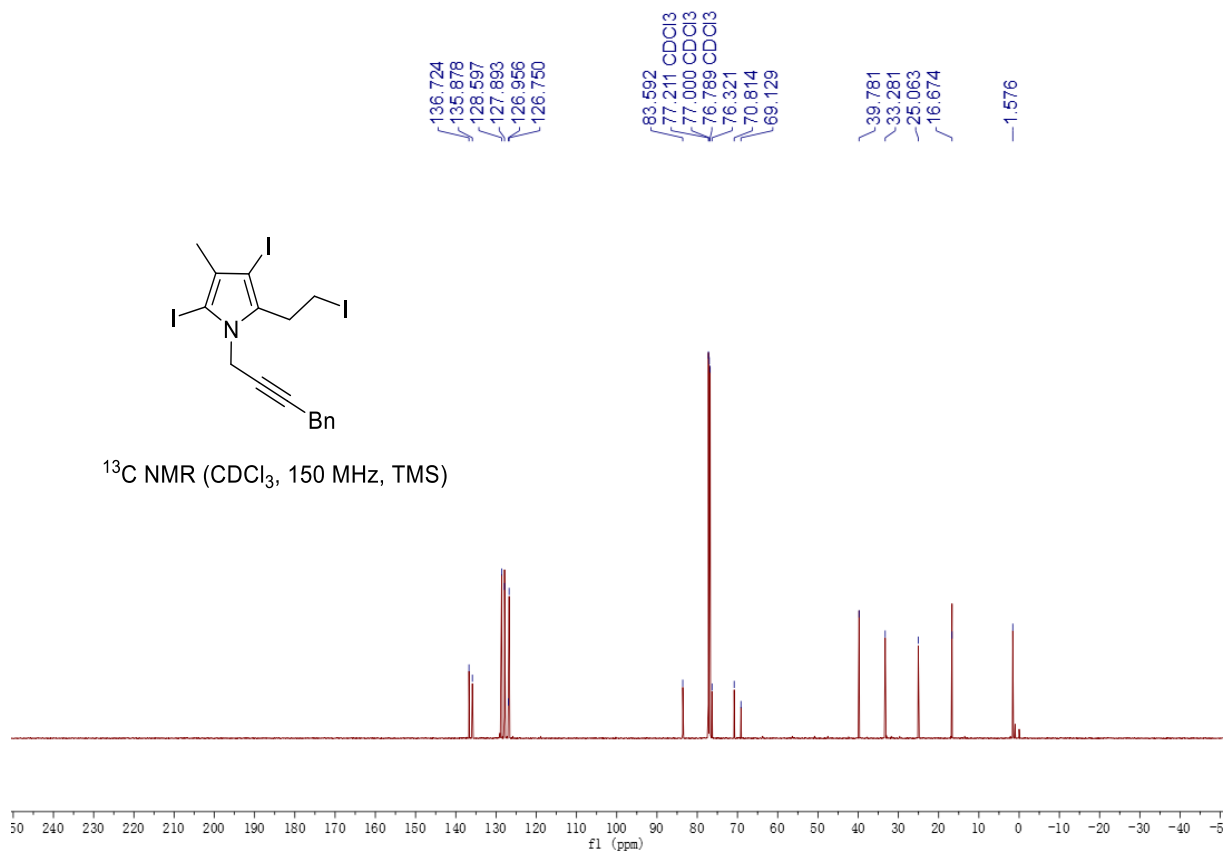
A colorless oil, 51.7 mg, 84% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.36 - 7.28 (m, 4H), 7.27 - 7.22 (m, 1H), 4.78 (t, $J = 2.3$ Hz, 2H), 3.60 - 3.58 (m, 2H), 3.39 - 3.31 (m, 2H), 3.30 - 3.21 (m, 2H), 2.06 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 136.7, 135.9, 128.6, 127.9, 127.0, 126.8, 83.6, 76.3, 70.8, 69.1, 39.8, 33.3, 25.1, 16.7, 1.6. IR (Neat) ν 703, 814, 926, 1062, 1169, 1362, 1723, 2951 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{17}\text{I}_3\text{N}$ ($\text{M}+\text{H}$): 615.8456, Found: 615.9012.

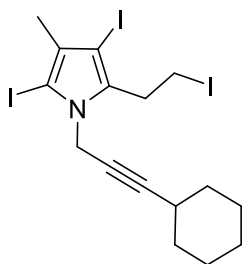


^1H NMR (CDCl_3 , 600 MHz, TMS)



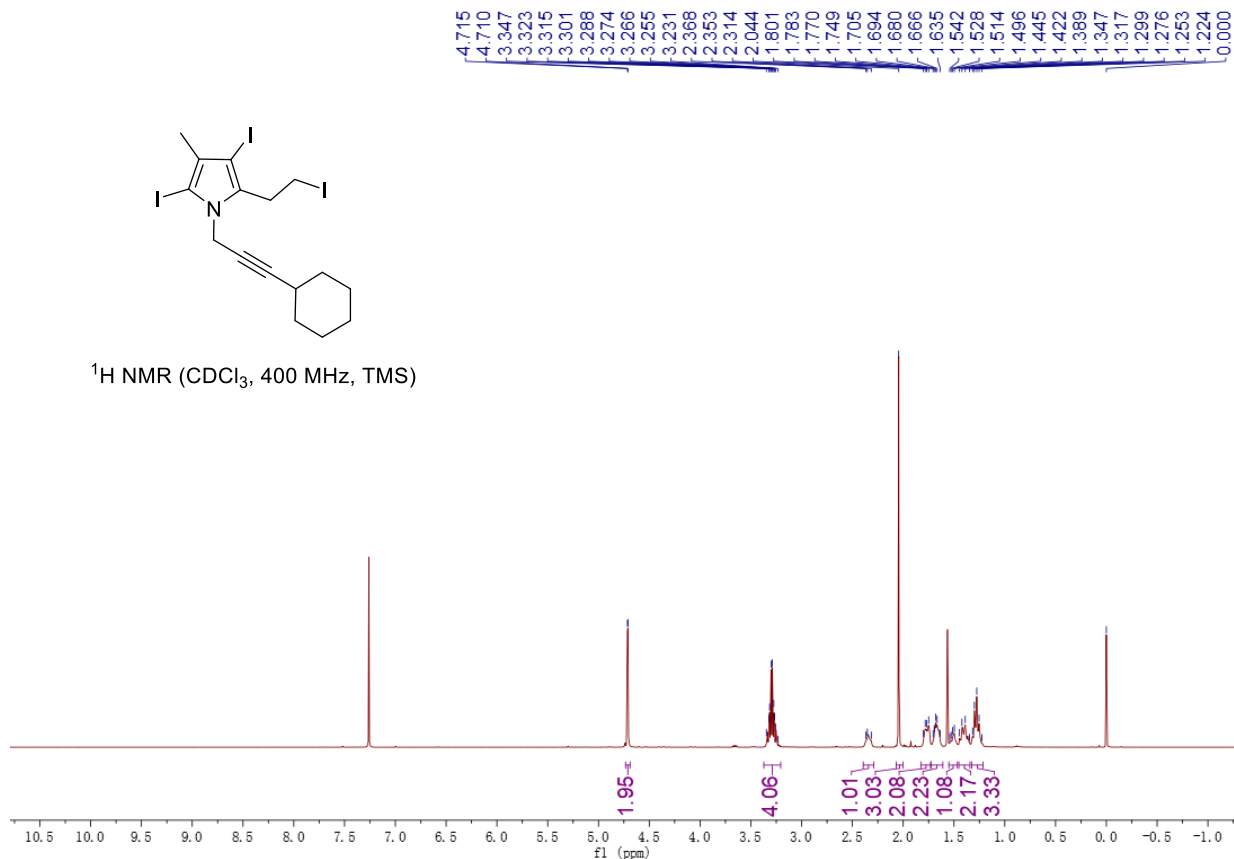
^{13}C NMR (CDCl_3 , 150 MHz, TMS)

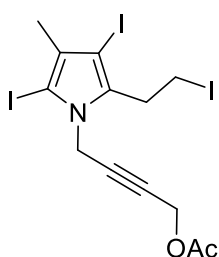
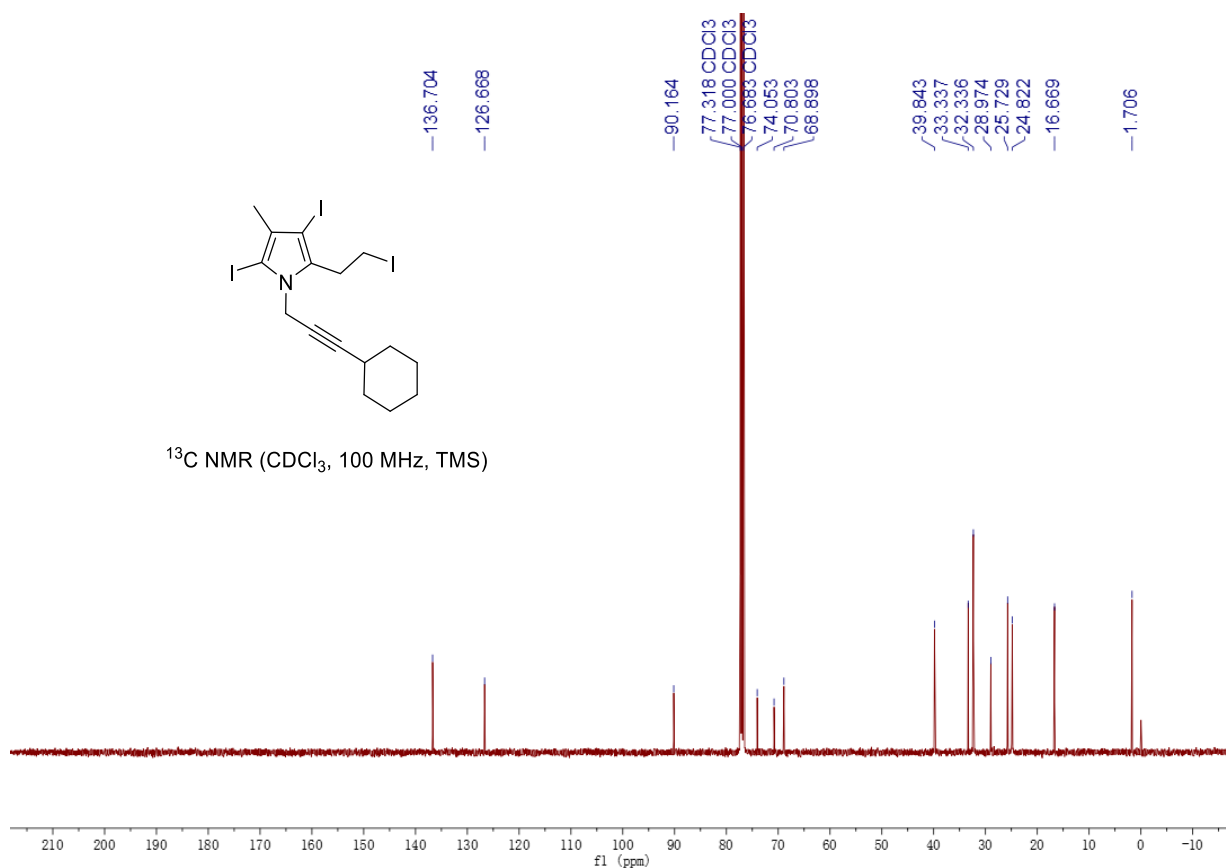




1-(3-cyclohexylprop-2-yn-1-yl)-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3ka)

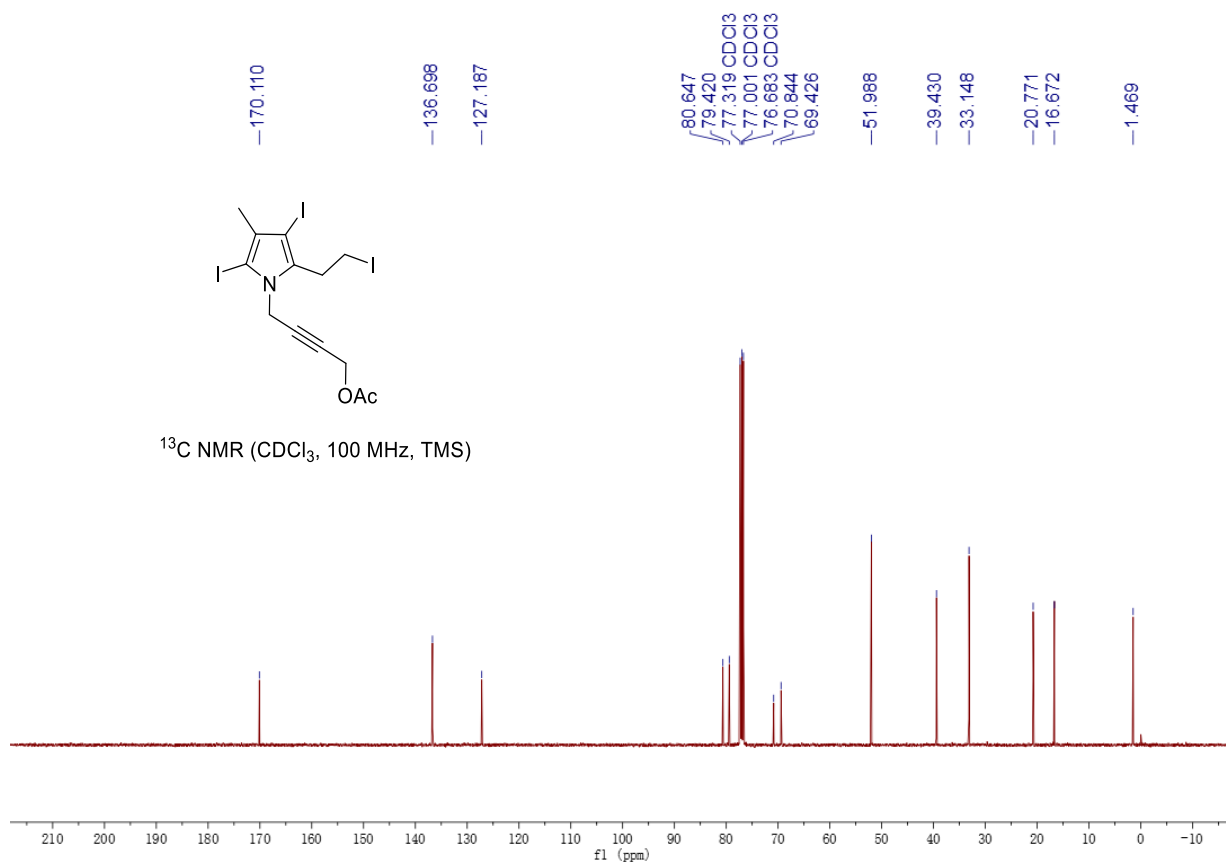
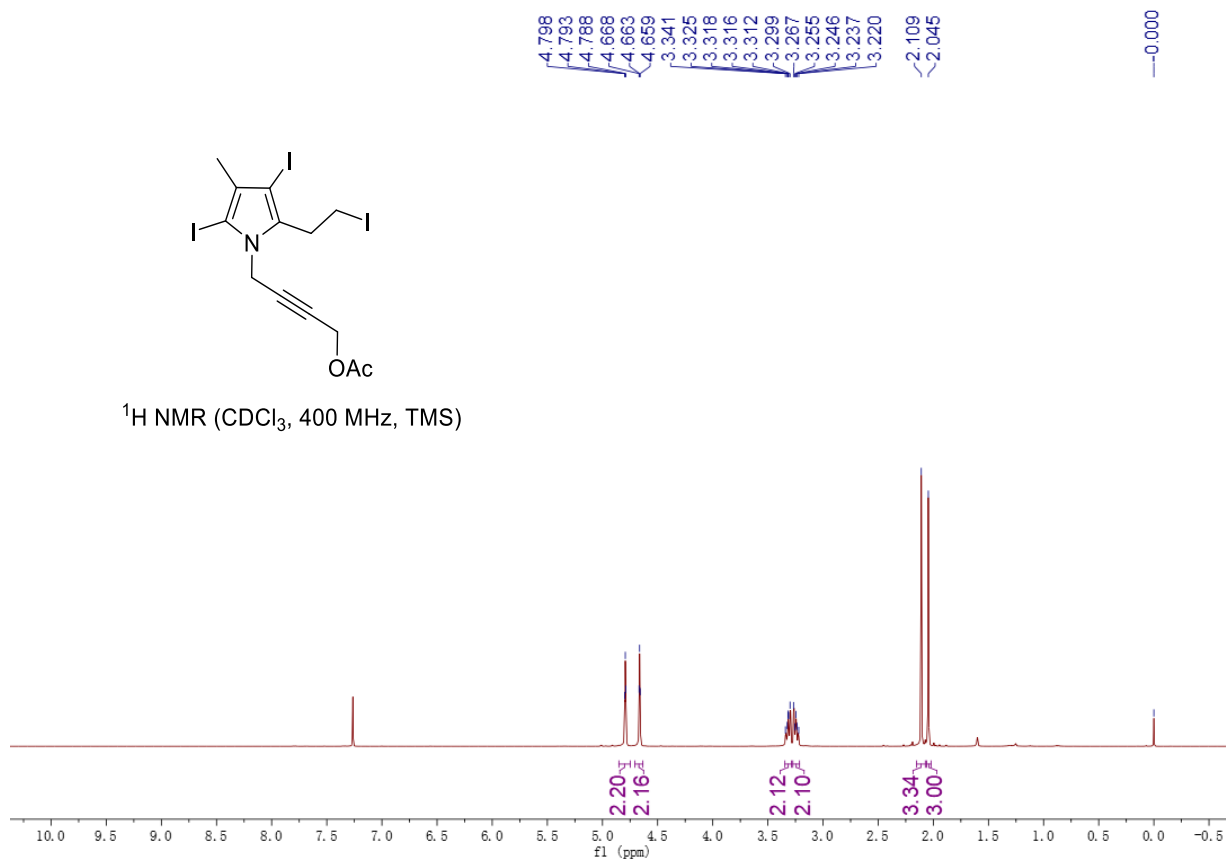
A colorless oil, 50.4 mg, 83% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 4.71 (d, $J = 2.1$ Hz, 2H), 3.37 - 3.21 (m, 4H), 2.39 - 2.29 (m, 1H), 2.04 (s, 3H), 1.83 - 1.72 (m, 2H), 1.73 - 1.61 (m, 2H), 1.55 - 1.47 (m, 1H), 1.45 - 1.34 (m, 2H), 1.33 - 1.22 (m, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 136.7, 126.7, 90.2, 74.1, 70.8, 68.9, 39.8, 33.3, 32.3, 29.0, 25.7, 24.8, 16.7, 1.7. IR (Neat) ν 721, 1173, 1326, 1442, 2213, 2849, 2919, 2934 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{20}\text{I}_3\text{N}$: 606.8750, Found: 606.8724.

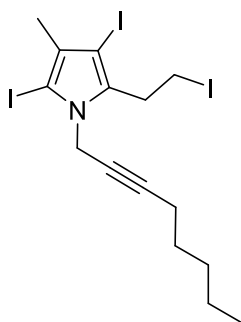




4-(2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrol-1-yl)but-2-yn-1-yl acetate (3la)

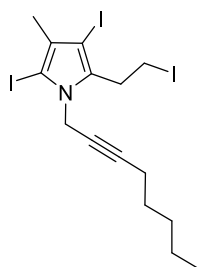
A colorless oil, 54.9 mg, 92% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 4.79 (t, *J* = 2.0 Hz, 2H), 4.66 (t, *J* = 1.9 Hz, 2H), 3.35 - 3.29 (m, 2H), 3.27 - 3.21 (m, 2H), 2.11 (s, 3H), 2.05 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 170.1, 136.7, 127.2, 80.6, 79.4, 70.8, 69.4, 52.0, 39.4, 33.1, 20.8, 16.7, 1.5. IR (Neat) ν 734, 1031, 1171, 1216, 1240, 1327, 1379, 1422, 1729 1742, 2917 cm⁻¹. HRMS (ESI) calcd. for C₁₃H₁₅NO₂I₃ (M+H): 597.8231, Found: 597.8246.



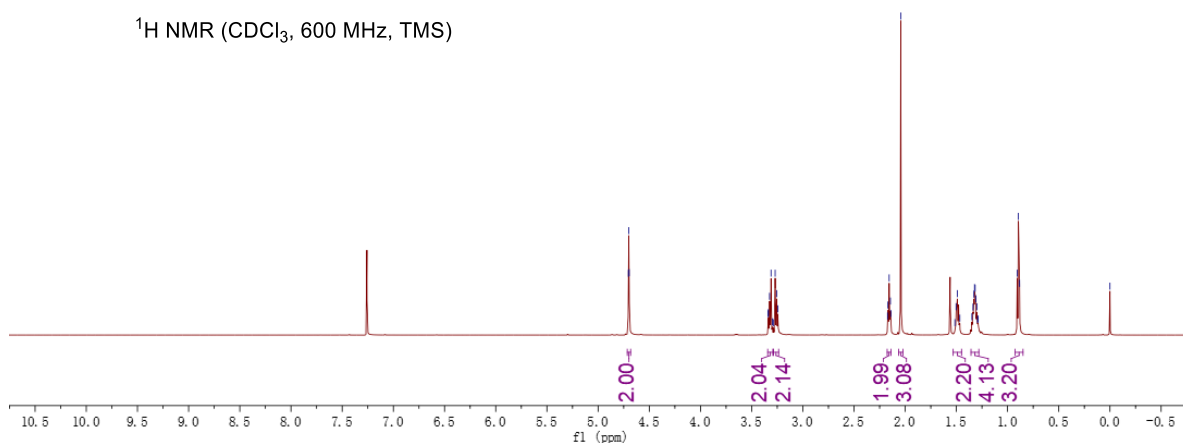


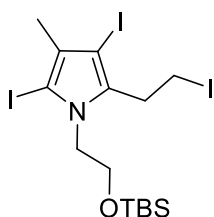
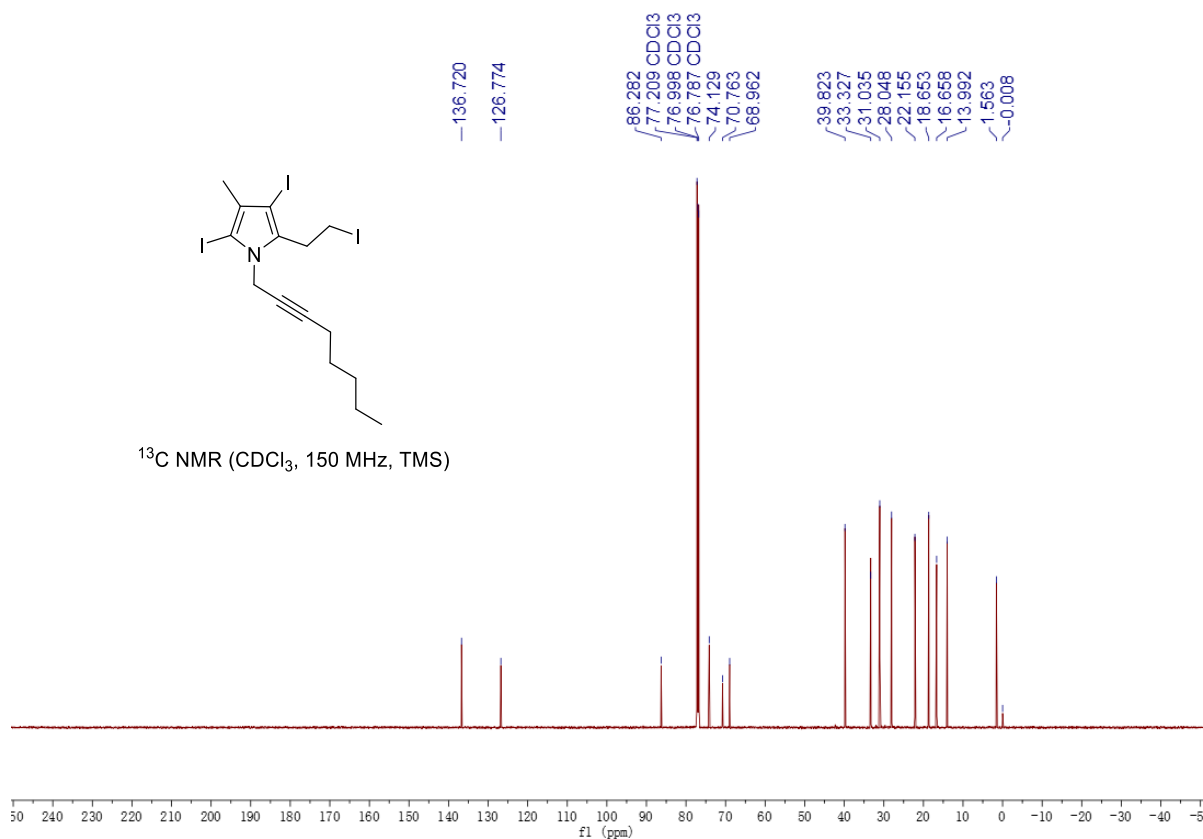
2,4-diiodo-5-(2-iodoethyl)-3-methyl-1-(oct-2-yn-1-yl)-1H-pyrrole (3ma)

A colorless oil, 50.6 mg, 85% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 4.70 (t, $J = 2.3$ Hz, 2H), 3.34 - 3.29 (m, 2H), 3.29 - 3.24 (m, 2H), 2.18 - 2.14 (m, 2H), 2.04 (s, 3H), 1.53 - 1.45 (m, 2H), 1.36 - 1.28 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 136.7, 126.8, 86.3, 74.1, 70.8, 69.0, 39.8, 33.3, 31.0, 28.0, 22.2, 18.7, 16.7, 14.0, 1.6. IR (Neat) ν 716, 896, 965, 1020, 1066, 1104, 1180, 1325, 1406, 1445, 2920 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{21}\text{I}_3\text{N}$ ($\text{M}+\text{H}$): 595.8739, Found: 595.8846.



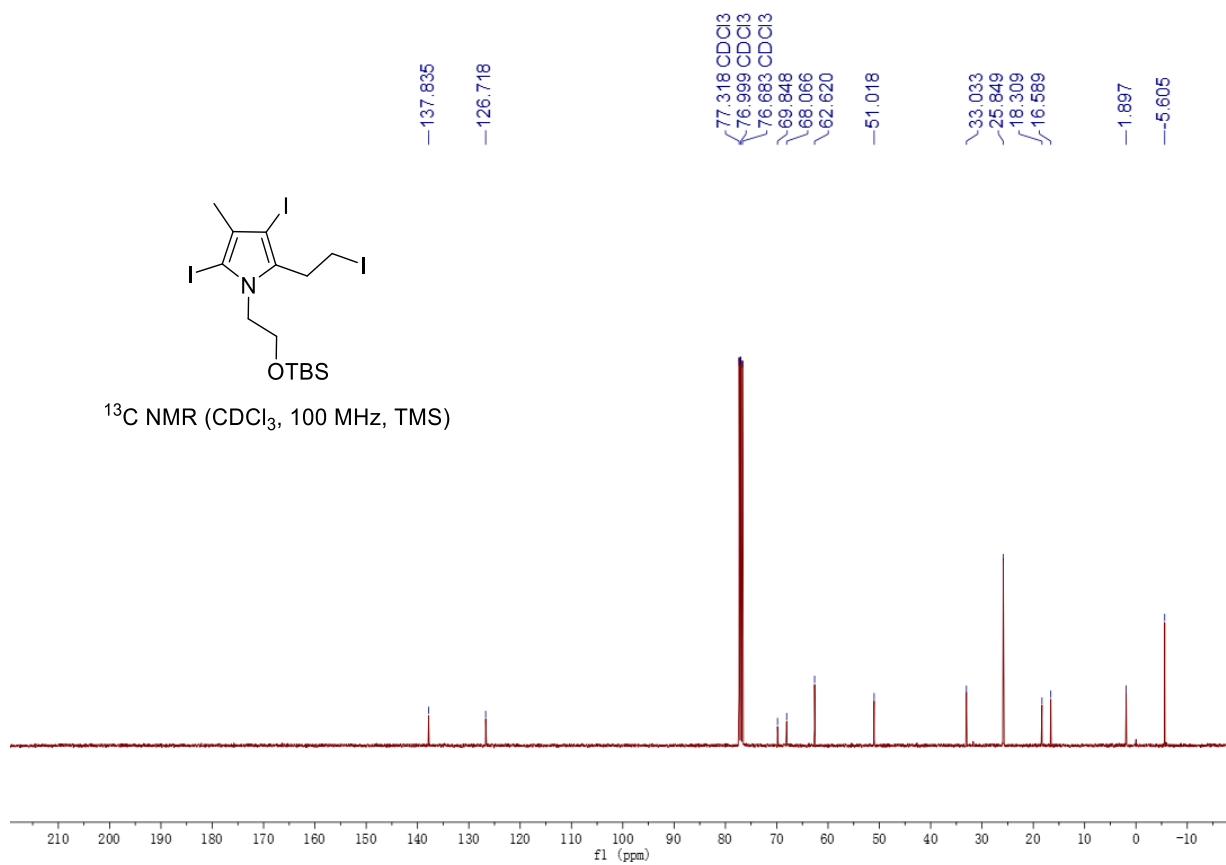
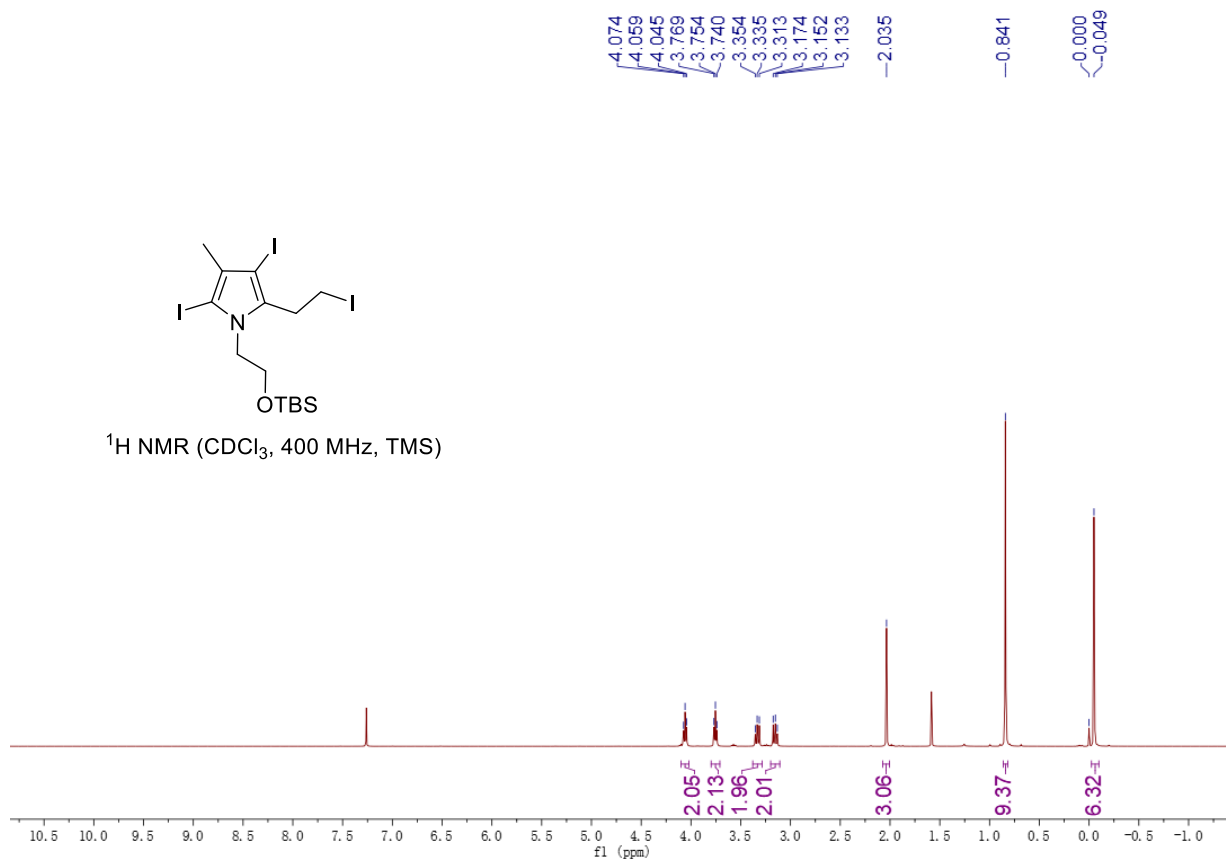
^1H NMR (CDCl_3 , 600 MHz, TMS)

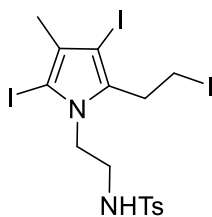




1-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3na)

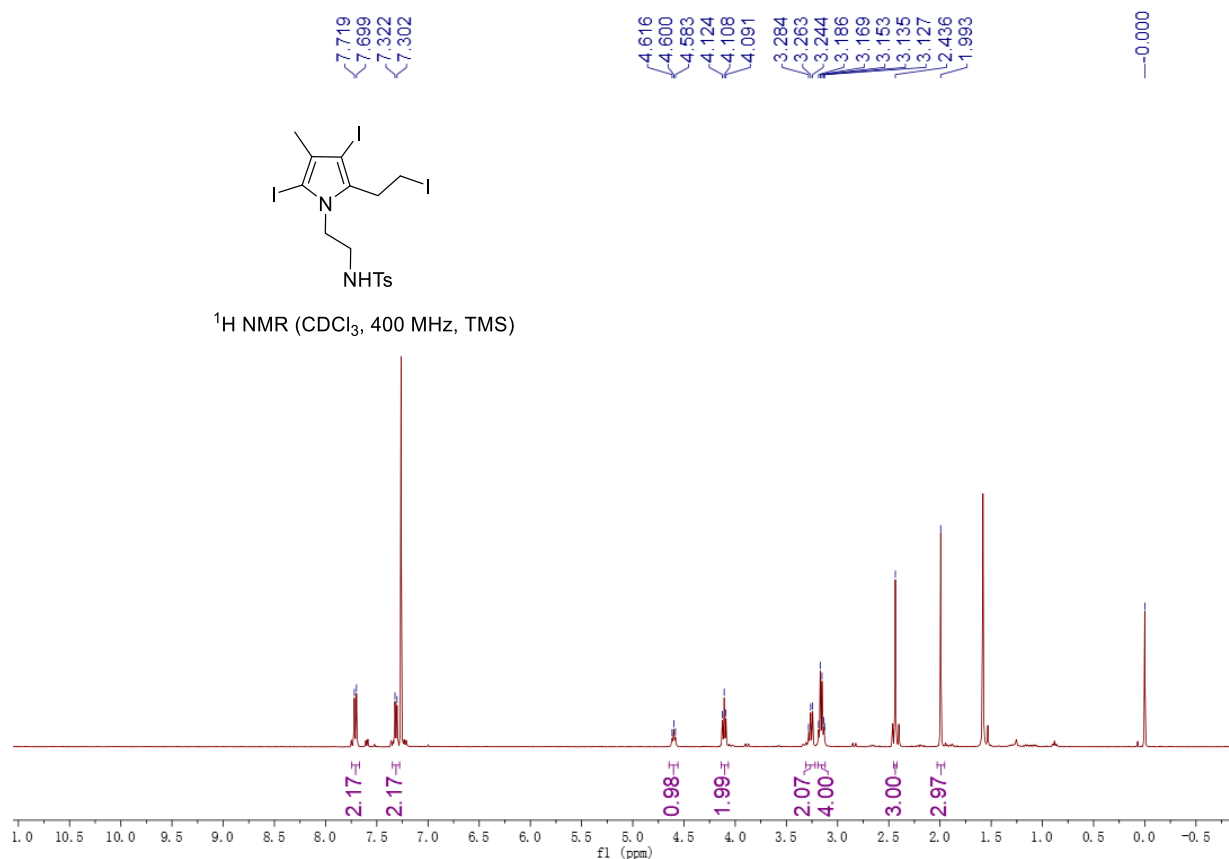
A colorless oil, 48.4 mg, 75% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 4.06 (t, *J* = 5.8 Hz, 2H), 3.75 (t, *J* = 5.8 Hz, 2H), 3.38 - 3.29 (m, 2H), 3.20 - 3.11 (m, 2H), 2.03 (s, 3H), 0.84 (s, 9H), -0.05 (s, 6H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 137.8, 126.7, 69.8, 68.1, 62.6, 51.0, 33.0, 25.8, 18.3, 16.6, 1.9, -5.6. IR (Acetone) ν 725, 1027, 1171, 1183, 1306, 1329, 1439, 1705, 2927 cm⁻¹. HRMS (ESI) calcd. for C₁₅H₂₇NOI₃Si (M+H): 645.8997, Found: 645.8996.

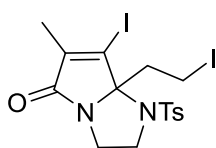
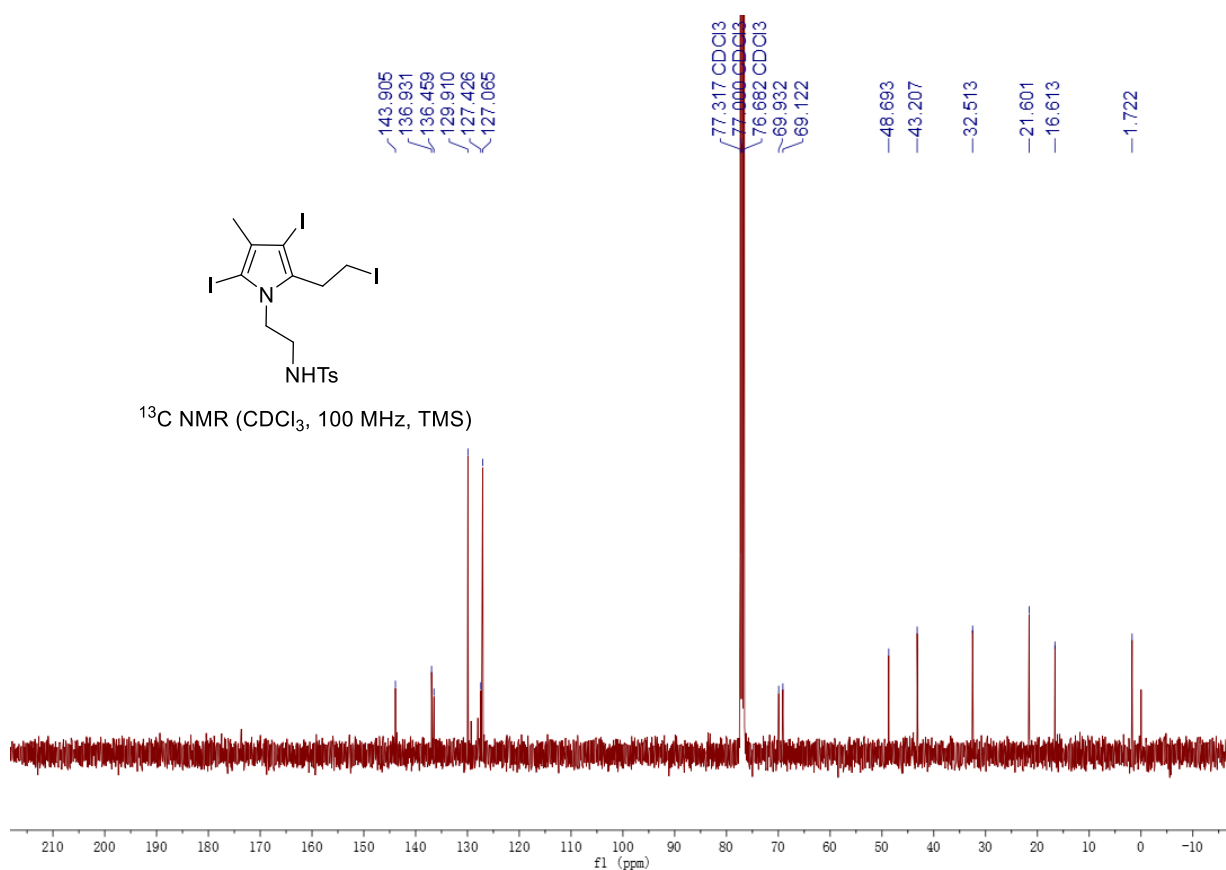




N-(2-(2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrol-1-yl)ethyl)-4-methylbenzenesulfonamide (30a)

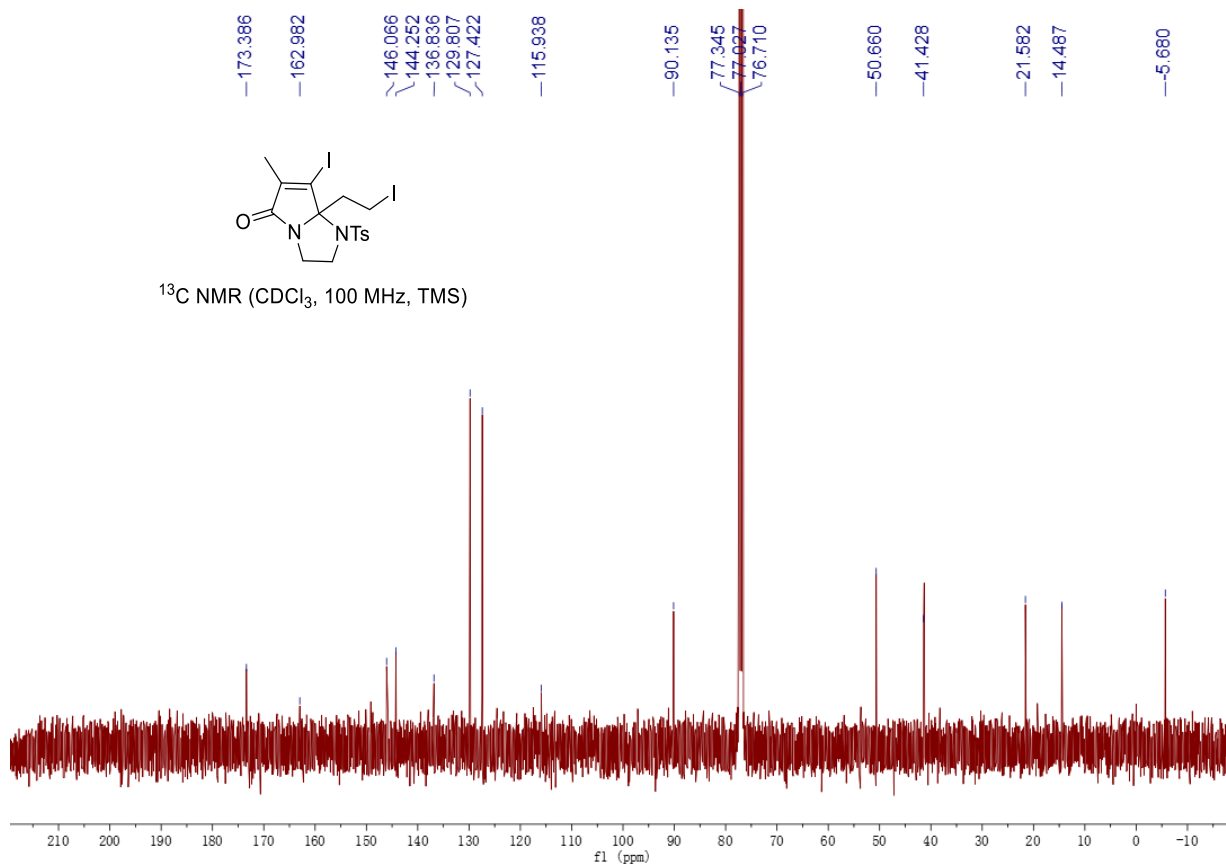
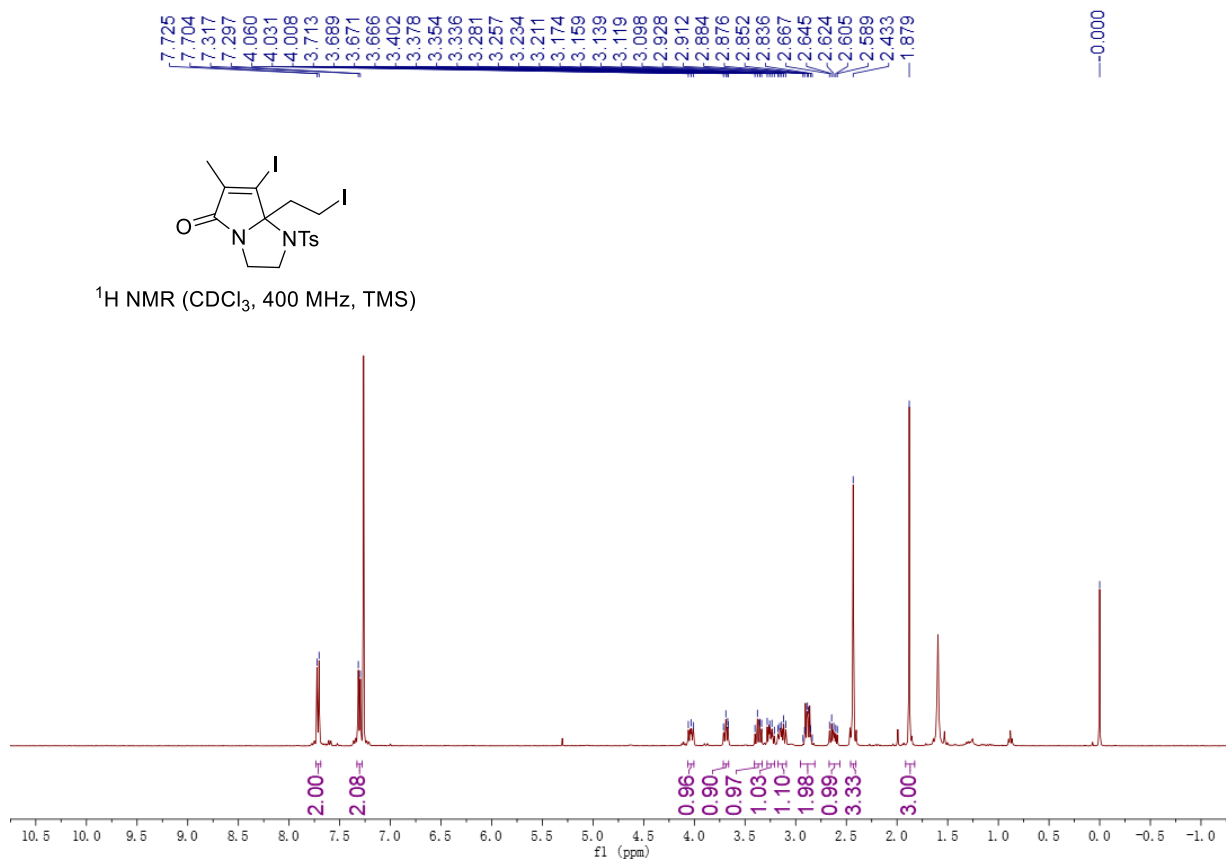
A colorless oil, 36.3 mg, 53% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 4.60 (t, $J = 6.6$ Hz, 1H), 4.11 (t, $J = 6.8$ Hz, 2H), 3.31 - 3.22 (m, 2H), 3.19 - 3.12 (m, 4H), 2.44 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 143.9, 136.9, 136.5, 129.9, 127.4, 127.1, 69.9, 69.1, 48.7, 43.2, 32.5, 21.6, 16.6, 1.7. IR (Neat) ν 758, 806, 1027, 1090, 1146, 1326, 1433, 1462, 1603, 3300 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2\text{NaSI}_3$ ($\text{M}+\text{Na}$): 706.8194, Found: 706.8189.

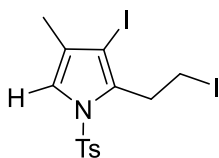




7-iodo-7a-(2-iodoethyl)-6-methyl-1-tosyl-1,2,3,7a-tetrahydro-5H-pyrrolo[1,2-a]imidazol-5-one (30a')

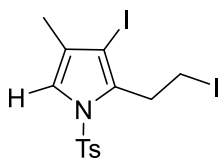
A colorless oil, 25.7 mg, 45% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.06 - 4.01 (m, 1H), 3.71 - 3.66 (m, 1H), 3.41 - 3.33 (m, 1H), 3.28 - 3.21 (m, 1H), 3.17 - 3.09 (m, 1H), 2.95 - 2.81 (m, 2H), 2.67 - 2.56 (m, 1H), 2.43 (s, 3H), 1.88 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 173.4, 163.0, 146.1, 144.3, 136.8, 129.8, 127.4, 115.9, 90.1, 77.3, 41.4, 21.6, 14.5, -5.7. IR (Neat) ν 2957, 1610, 1553, 1329, 1240, 809, 773 cm⁻¹. HRMS (ESI) calcd. for C₁₆H₁₉N₂O₃NaSI₂ (M+H): 594.9197, Found: 594.9200.



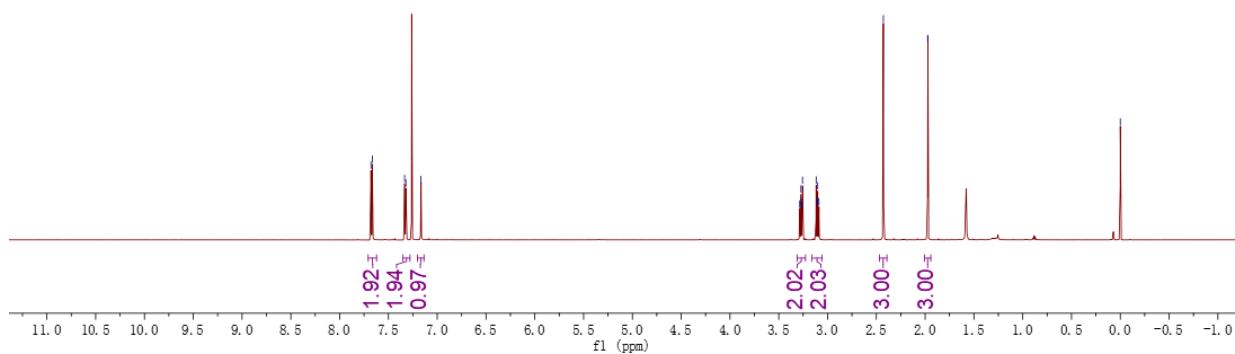


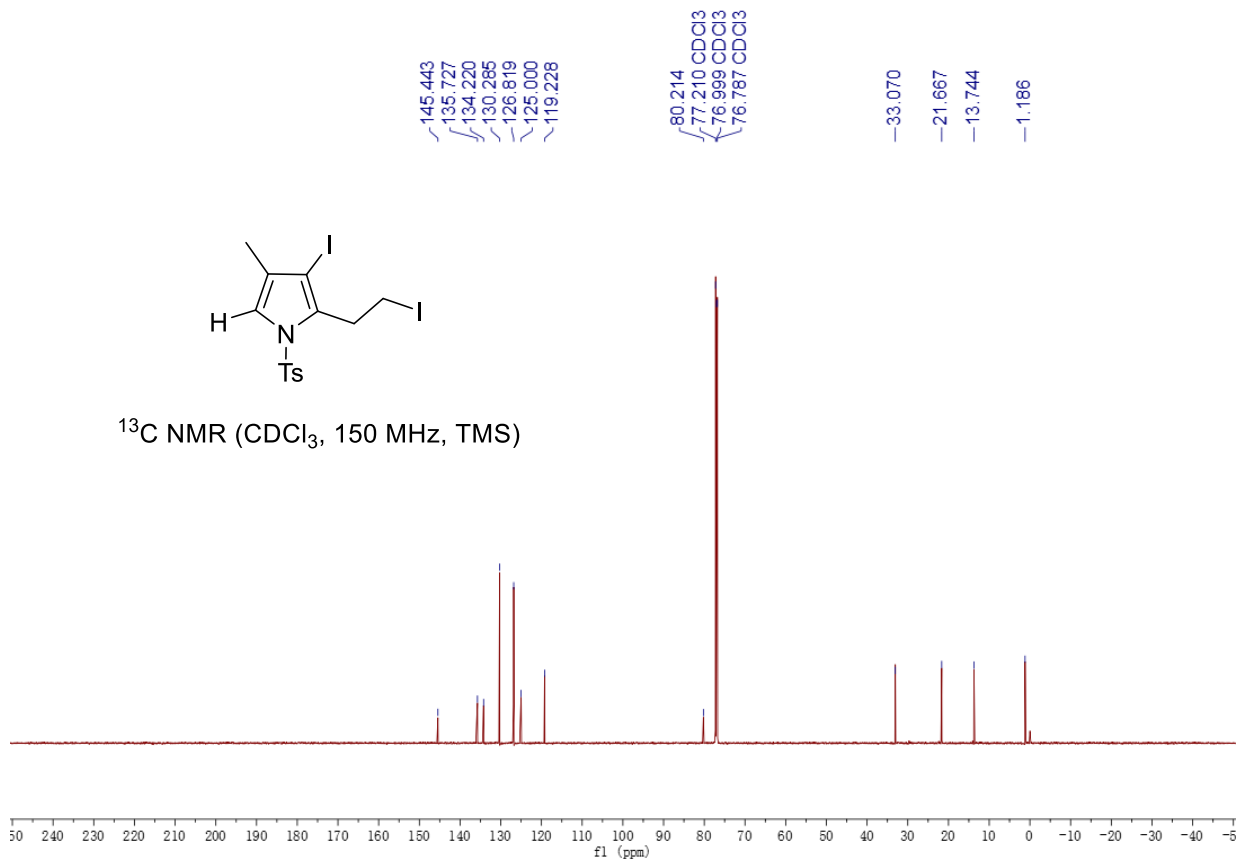
2,4-diiodo-5-(2-iodoethyl)-3-methyl-1-tosyl-1H-pyrrole (3pa)

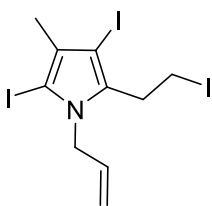
A colorless oil, 38.5 mg, 60% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.67 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.17 (s, 1H), 3.31 - 3.23 (m, 2H), 3.16 - 3.06 (m, 2H), 2.43 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 145.4, 135.7, 134.2, 130.3, 126.8, 125.0, 119.2, 80.2, 33.1, 21.7, 13.7, 1.2. IR (Acetone) ν 735, 792, 1172, 1327, 1380, 2207, 2922 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{NaSI}_2$ ($\text{M}+\text{Na}$): 537.8913, Found: 537.8903.



^1H NMR (CDCl_3 , 600 MHz, TMS)



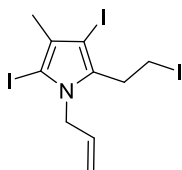




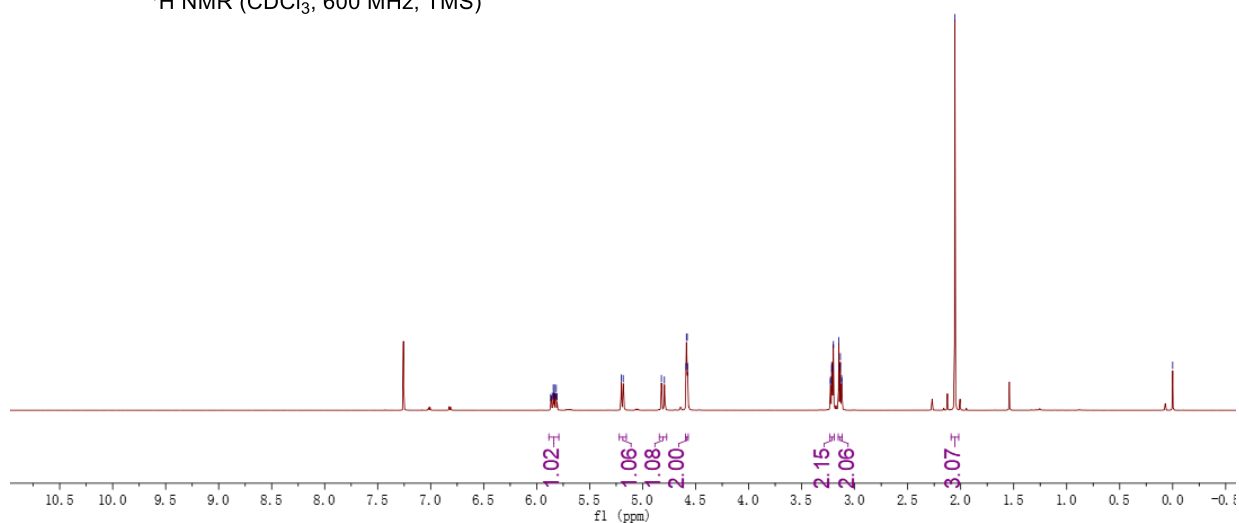
1-allyl-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3ra)

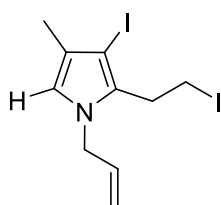
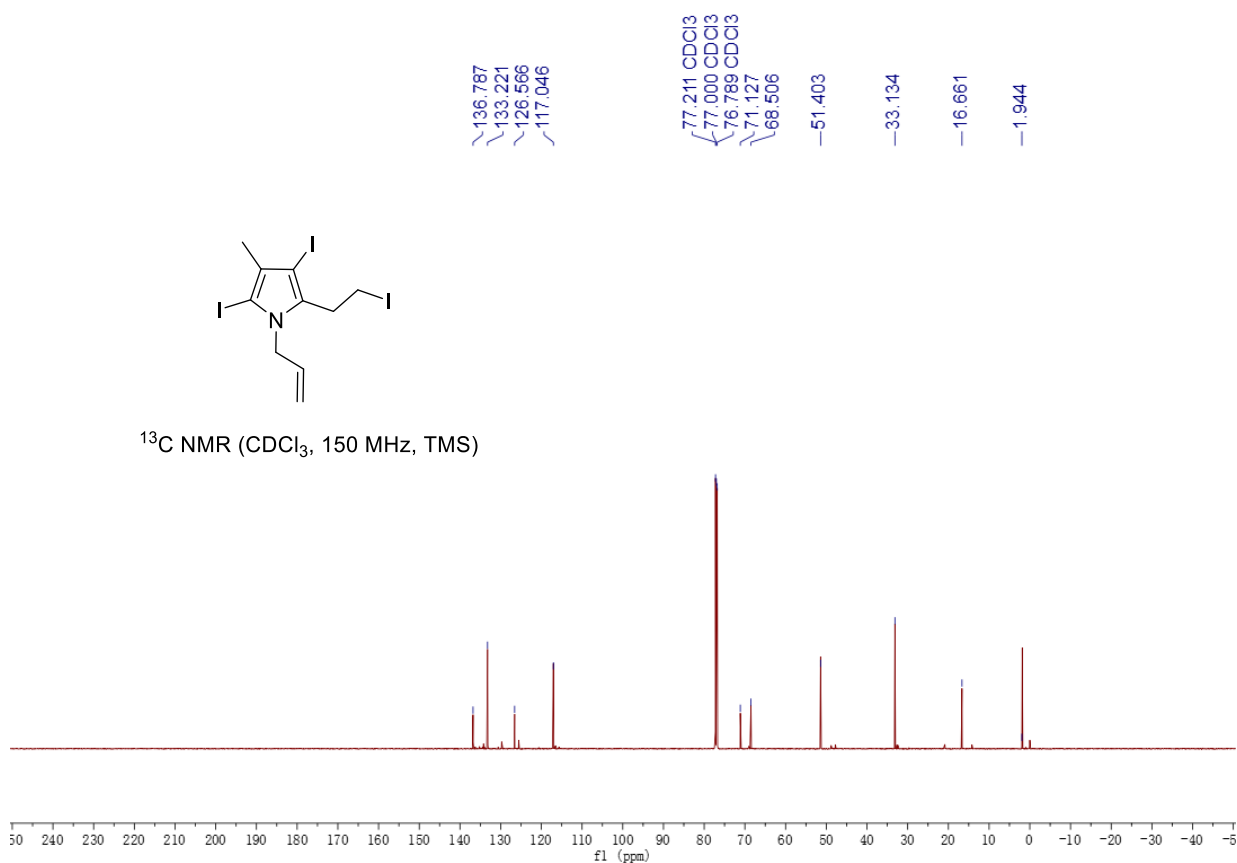
A colorless oil, 49.0 mg, 93% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 5.89 - 5.79 (m, 1H), 5.19 (d, $J = 10.5$ Hz, 1H), 4.81 (d, $J = 17.1$ Hz, 1H), 4.60 - 4.57 (m, 2H), 3.23 - 3.19 (m, 2H), 3.16 - 3.12 (m, 2H), 2.06 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 136.8, 133.2, 126.6, 117.0, 71.1, 68.5, 51.4, 33.1, 16.7, 1.9. IR (Neat) ν 927, 989, 1165, 1260, 1323, 1446, 2961 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{12}\text{NI}_3$: 526.8111, Found: 526.8098.

5.868
5.863
5.844
5.840
5.832
5.825
5.815
5.808
5.201
5.184
4.823
4.795
4.591
4.587
4.580
4.577
3.230
3.227
3.217
3.211
3.200
3.149
3.140
3.135
3.124
3.121
2.055
-0.000



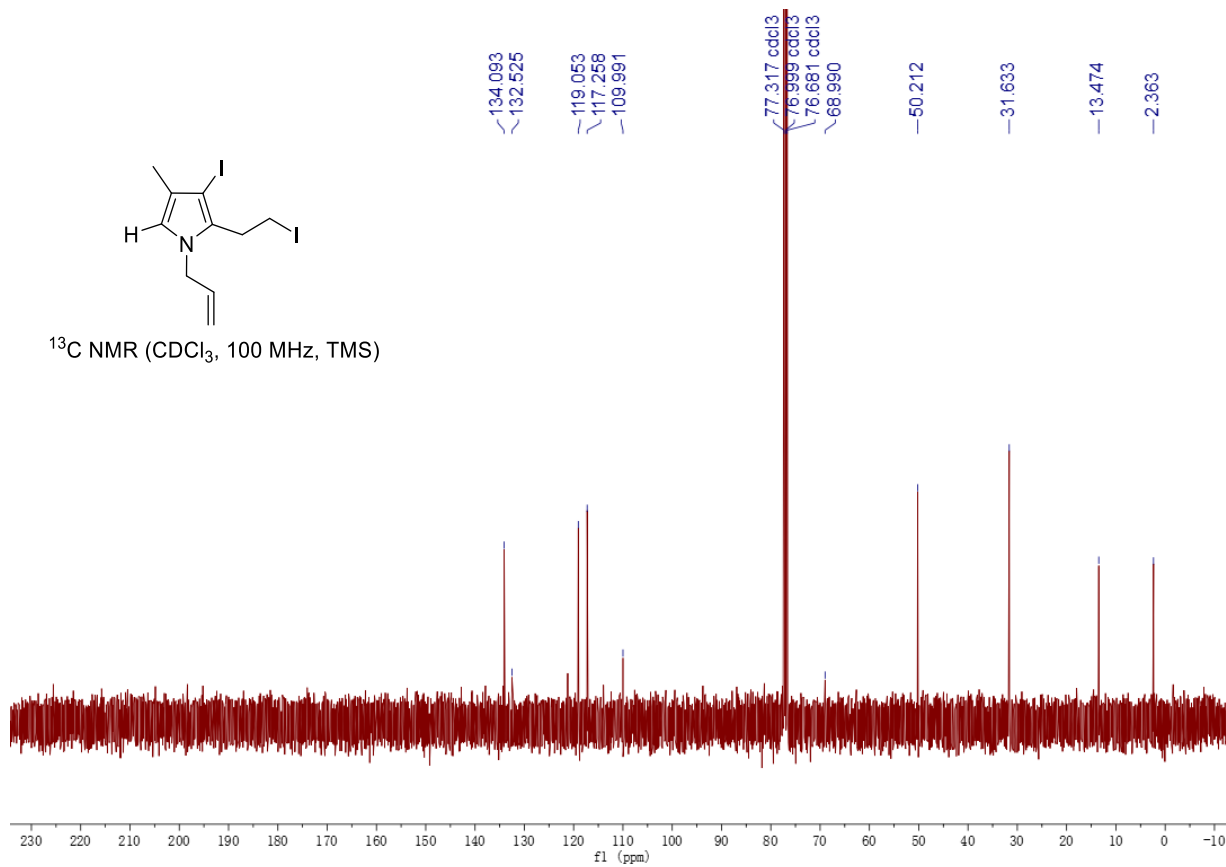
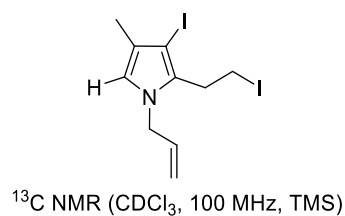
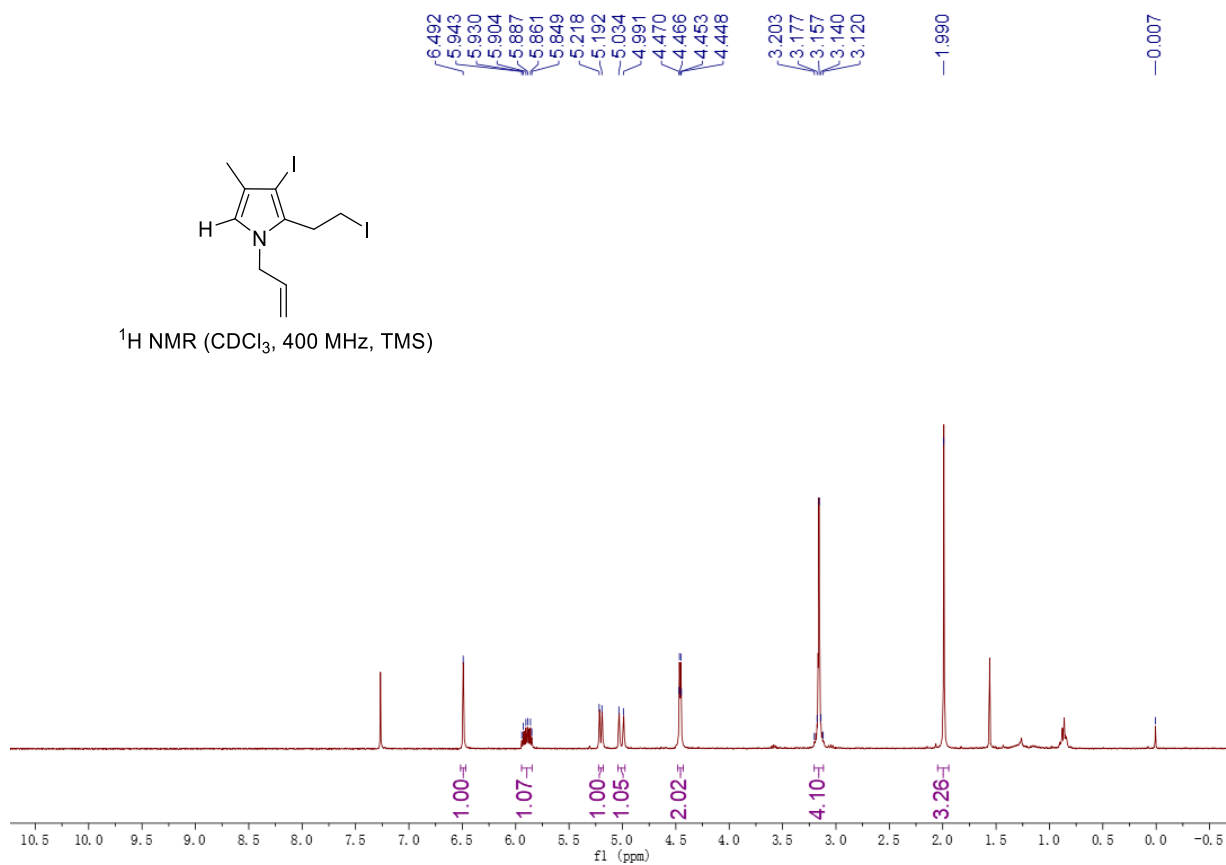
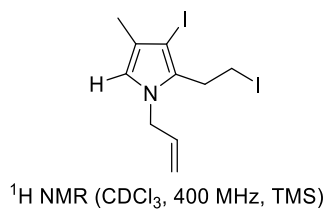
^1H NMR (CDCl_3 , 600 MHz, TMS)

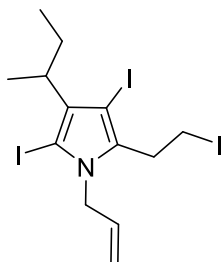




1-allyl-2,4-diiodo-5-(2-iodoethyl)-3-methyl-1H-pyrrole (3ra')

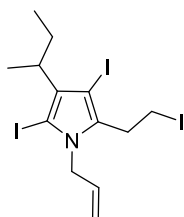
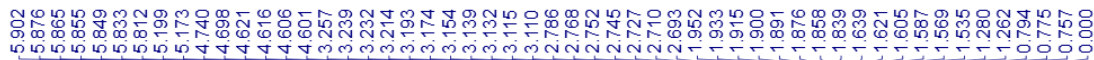
A colorless oil, 49.0 mg, 38% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 6.49 (s, 1H), 5.94 - 5.85 (m, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.48 - 4.43 (m, 2H), 3.20 - 3.12 (m, 4H), 1.99 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 134.1, 132.5, 119.1, 117.3, 110.0, 69.0, 50.2, 31.6, 13.5, 2.4. IR (Neat) ν 2966, 1450, 1337, 1168, 1089, 989 cm⁻¹. HRMS (EI) calcd. for C₁₀H₁₃NI₂: 400.9137, Found: 400.9132.



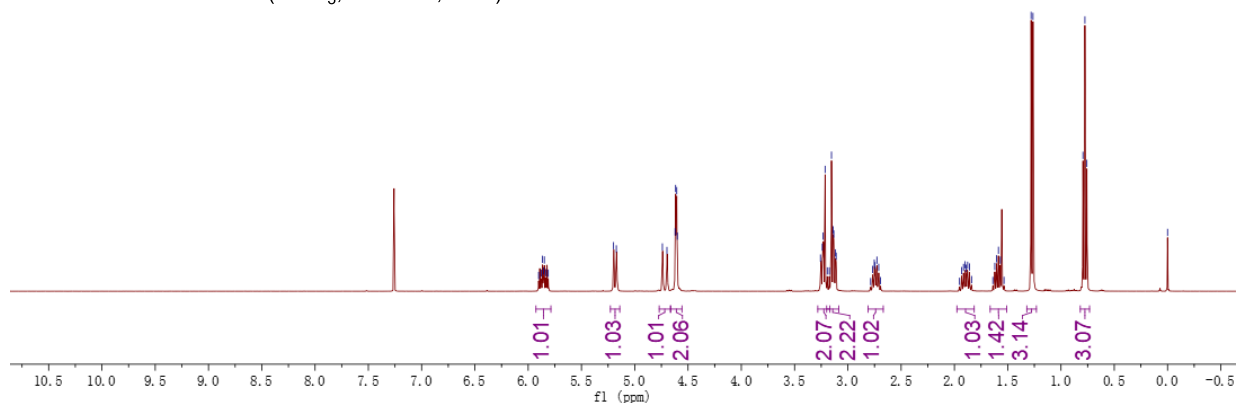


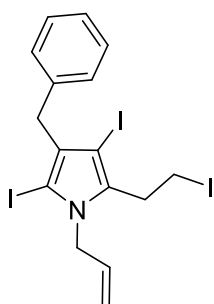
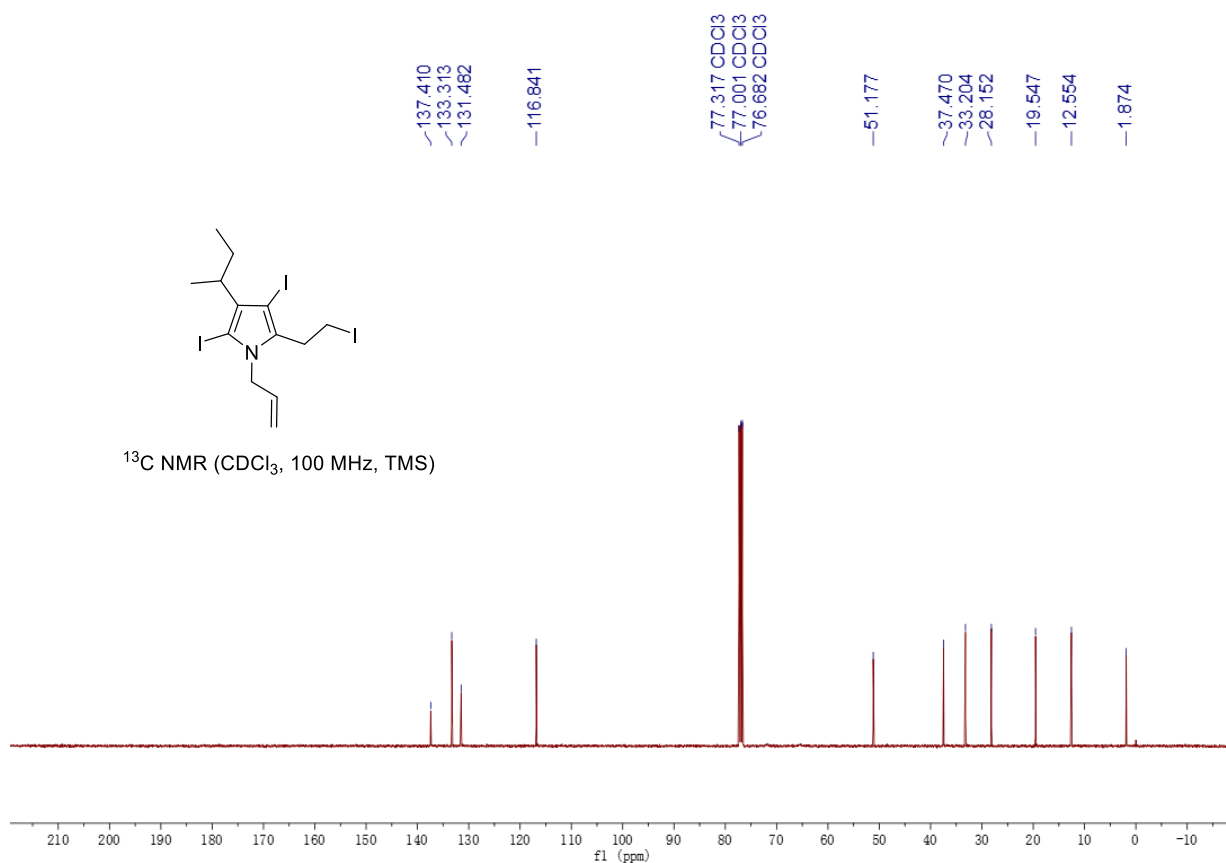
1-allyl-3-(sec-butyl)-2,4-diiodo-5-(2-iodoethyl)-1H-pyrrole (3sa)

A colorless oil, 52.3 mg, 92% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 5.93 - 5.79 (m, 1H), 5.19 (d, $J = 10.4$ Hz, 1H), 4.72 (d, $J = 17.0$ Hz, 1H), 4.66 - 4.56 (m, 2H), 3.28 - 3.17 (m, 2H), 3.20 - 3.08 (m, 2H), 2.81 - 2.67 (m, 1H), 1.98 - 1.81 (m, 1H), 1.66 - 1.51 (m, 1H), 1.27 (d, $J = 7.2$ Hz, 3H), 0.78 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 137.4, 133.3, 131.5, 116.8, 51.2, 37.5, 33.2, 28.2, 19.5, 12.6, 1.9. IR (Neat) ν 733, 923, 989, 1087, 1169, 1326, 1374, 1451, 2875, 2925, 2956 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{18}\text{NI}_3$: 568.8579, Found: 568.8568.



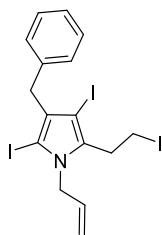
^1H NMR (CDCl_3 , 400 MHz, TMS)



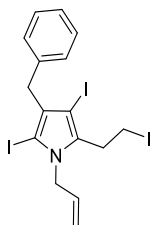
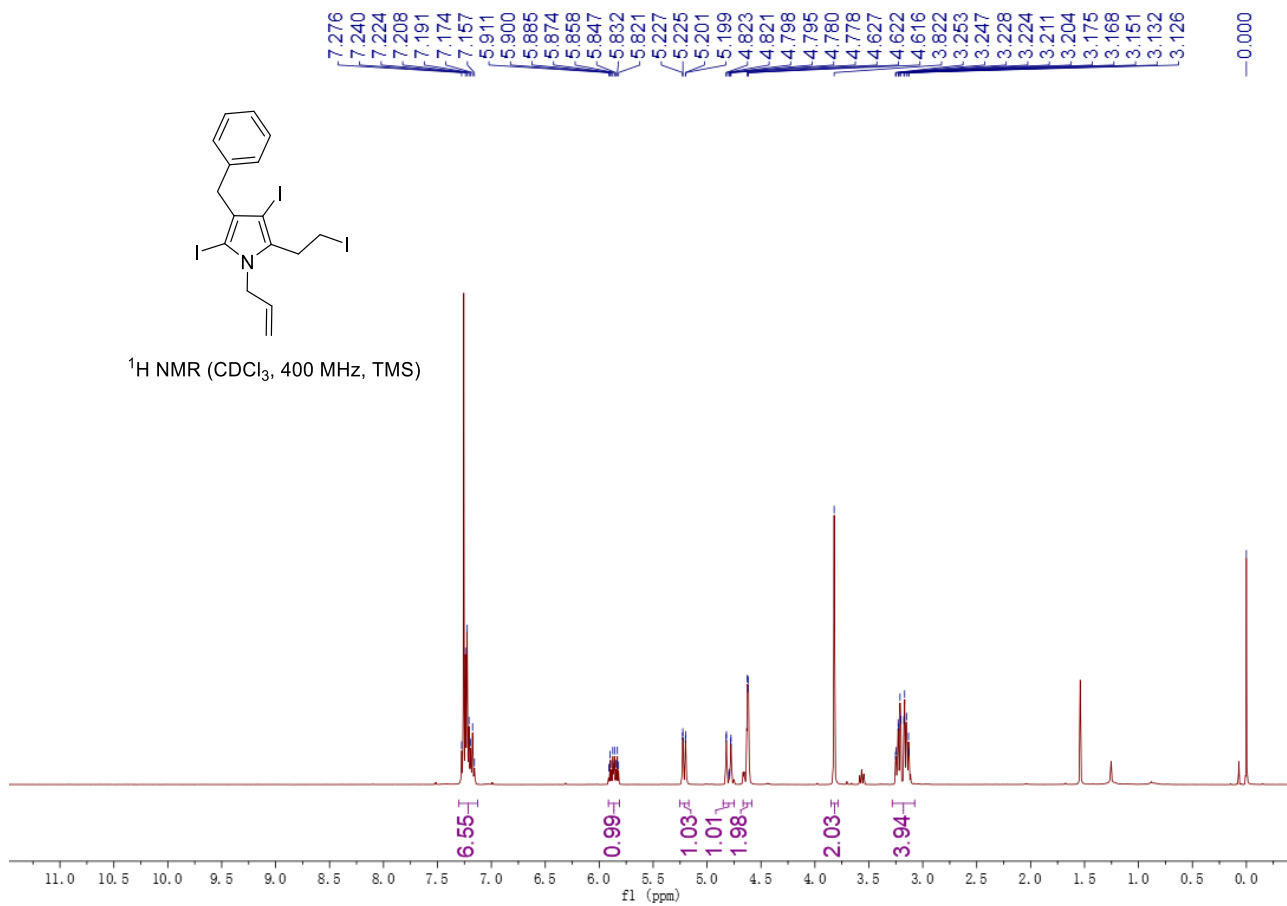


1-allyl-3-benzyl-2,4-diiodo-5-(2-iodoethyl)-1H-pyrrole (3ta)

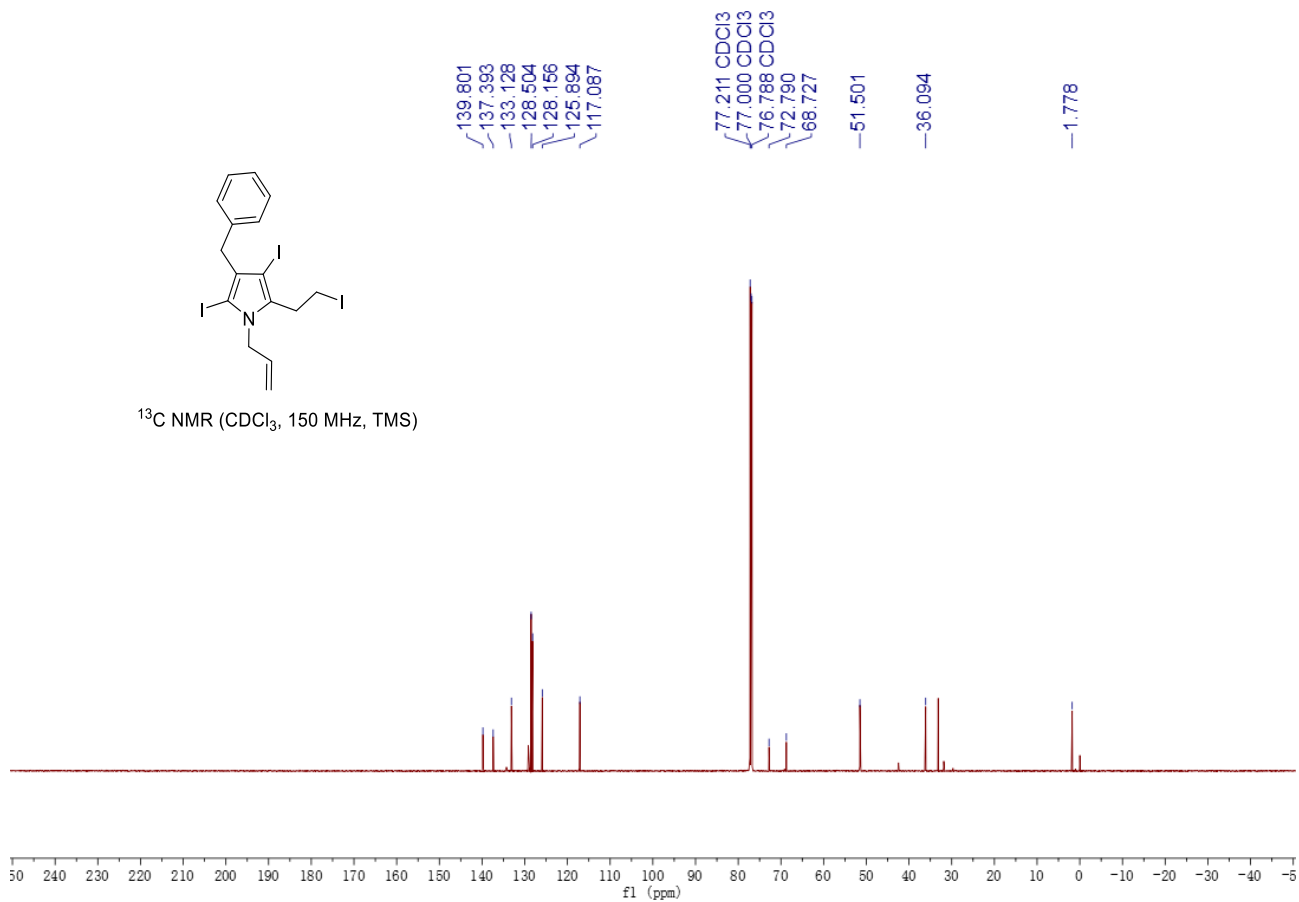
A colorless oil, 48.2 mg, 80% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.30 - 7.13 (m, 7H), 5.91 - 5.81 (m, 1H), 5.21 (d, *J* = 10.4, 0.9 Hz, 1H), 4.80 (d, *J* = 17.0, 0.9 Hz, 1H), 4.67 - 4.59 (m, 2H), 3.82 (s, 2H), 3.28 - 3.08 (m, 4H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 139.8, 137.4, 133.1, 128.5, 128.2, 125.9, 117.1, 72.8, 68.7, 51.5, 36.1, 1.8. IR (Neat) ν 728, 925, 990, 1053, 1171, 1348, 1493, 2917, 3021 cm⁻¹. HRMS (EI) calcd. for C₁₆H₁₆I₃N: 602.8433, Found: 602.8411.

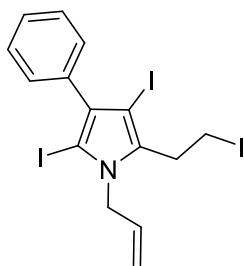


¹H NMR (CDCl₃, 400 MHz, TMS)



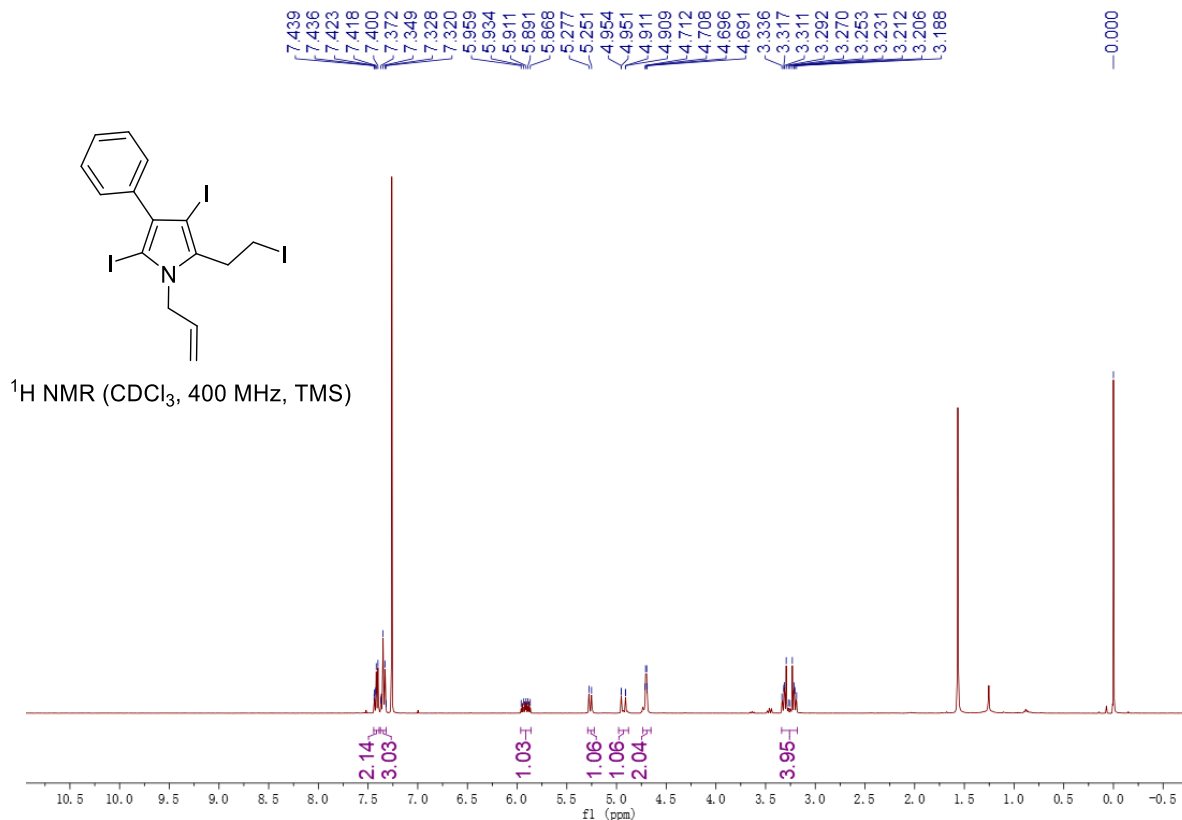
¹³C NMR (CDCl₃, 150 MHz, TMS)

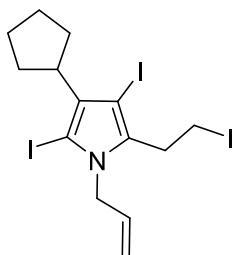
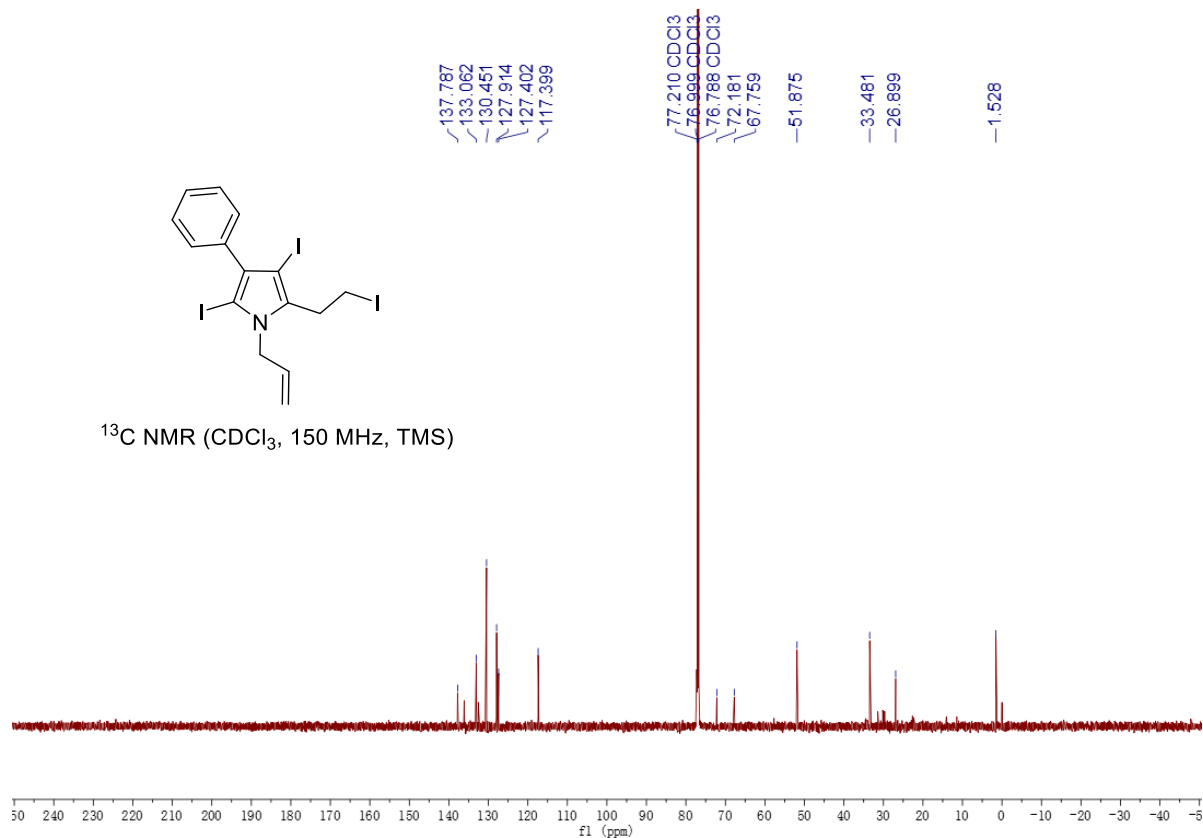




1-allyl-2,4-diiodo-5-(2-iodoethyl)-3-phenyl-1H-pyrrole (3ua)

A colorless oil, 5.89 mg, 10% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.44 - 7.39 (m, 2H), 7.38 - 7.32 (m, 3H), 5.96 - 5.86 (m, 1H), 5.26 (d, $J = 10.3$ Hz, 1H), 4.98 - 4.88 (m, 1H), 4.74 - 4.65 (m, 2H), 3.34 - 3.18 (m, 4H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 137.8, 133.1, 130.5, 127.9, 127.4, 117.4, 72.2, 67.8, 51.9, 33.5, 26.9, 1.5. IR (Acetone) ν 3059, 2969, 2928, 1603, 1492, 1461, 1445, 1359, 1339, 1302, 1219, 1062, 1046, 1028, 905, 810, 759, 738, 700 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{14}\text{I}_3\text{NNa}$ ($\text{M}+\text{Na}$): 611.8758, Found: 611.9030.

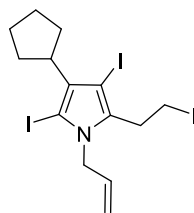




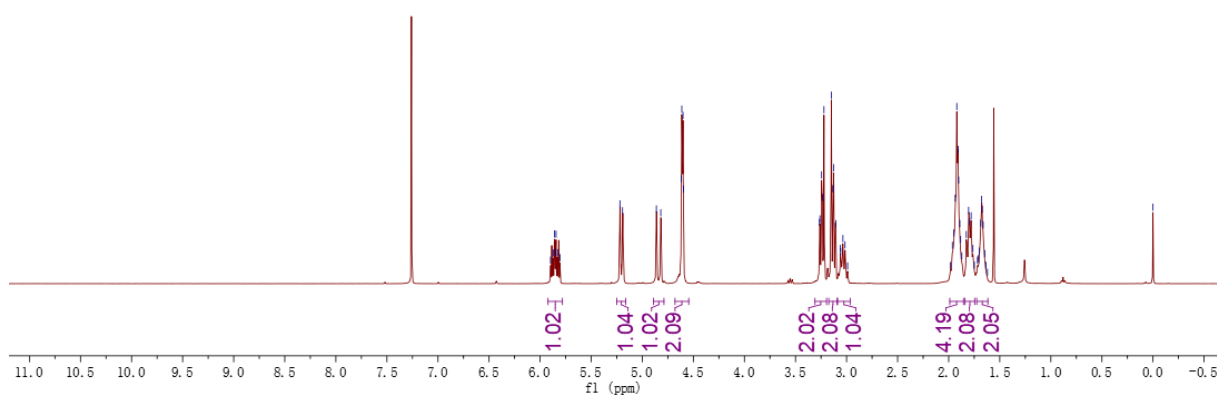
1-allyl-3-cyclopentyl-2,4-diiodo-5-(2-iodoethyl)-1H-pyrrole (3va)

A colorless oil, 50.5 mg, 87% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 5.92 - 5.78 (m, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.84 (d, *J* = 17.2 Hz, 1H), 4.68 - 4.55 (m, 2H), 3.31 - 3.20 (m, 2H), 3.17 - 3.09 (m, 2H), 3.09 - 2.96 (m, 1H), 1.99 - 1.86 (m, 4H), 1.84 - 1.75 (m, 2H), 1.73 - 1.62 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 137.5, 133.3, 130.0, 117.2, 71.7, 65.6, 51.4, 41.2, 33.3, 31.4, 26.4, 1.7. IR (Neat) ν 731, 906, 1169, 1341, 1398, 1448, 1647, 2859, 2949 cm⁻¹. HRMS (EI) calcd. for C₁₄H₁₈I₃N: 580.8584, Found: 580.8568.

5.888
5.872
5.860
5.849
5.844
5.829
5.806
5.219
5.193
4.862
4.819
4.618
4.602
4.597
4.597
3.265
3.261
3.244
3.236
3.221
3.149
3.134
3.126
3.105
3.061
3.058
3.036
3.015
2.990
1.965
1.964
1.950
1.935
1.921
1.908
1.903
1.891
1.883
1.872
1.828
1.805
1.795
1.780
1.763
1.749
1.718
1.709
1.700
1.686
1.679
1.671
1.663
1.648
1.634
1.621
-0.000



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



-137.526
-133.282
-129.950

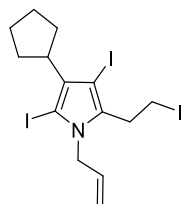
-117.183

77.318 CDCl_3
77.206
77.001 CDCl_3
76.683 CDCl_3
71.721
65.562

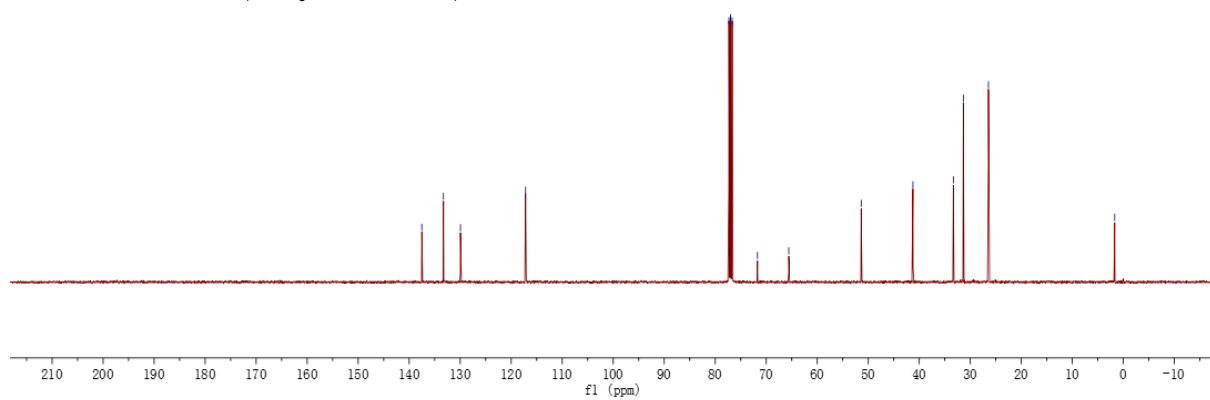
-51.384

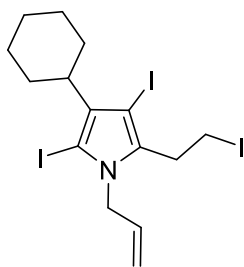
41.246
33.325
31.368
26.443

-1.691



$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS)

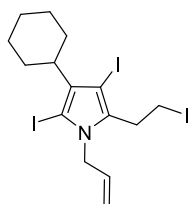




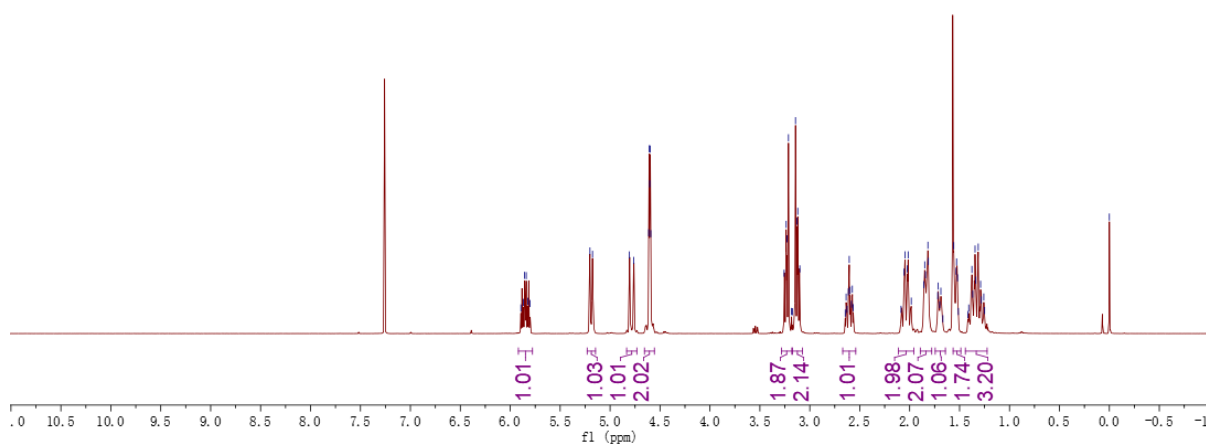
1-allyl-3-cyclohexyl-2,4-diiodo-5-(2-iodoethyl)-1H-pyrrole (3wa)

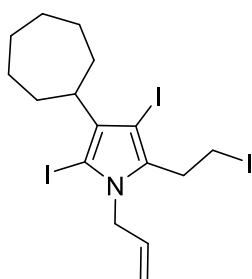
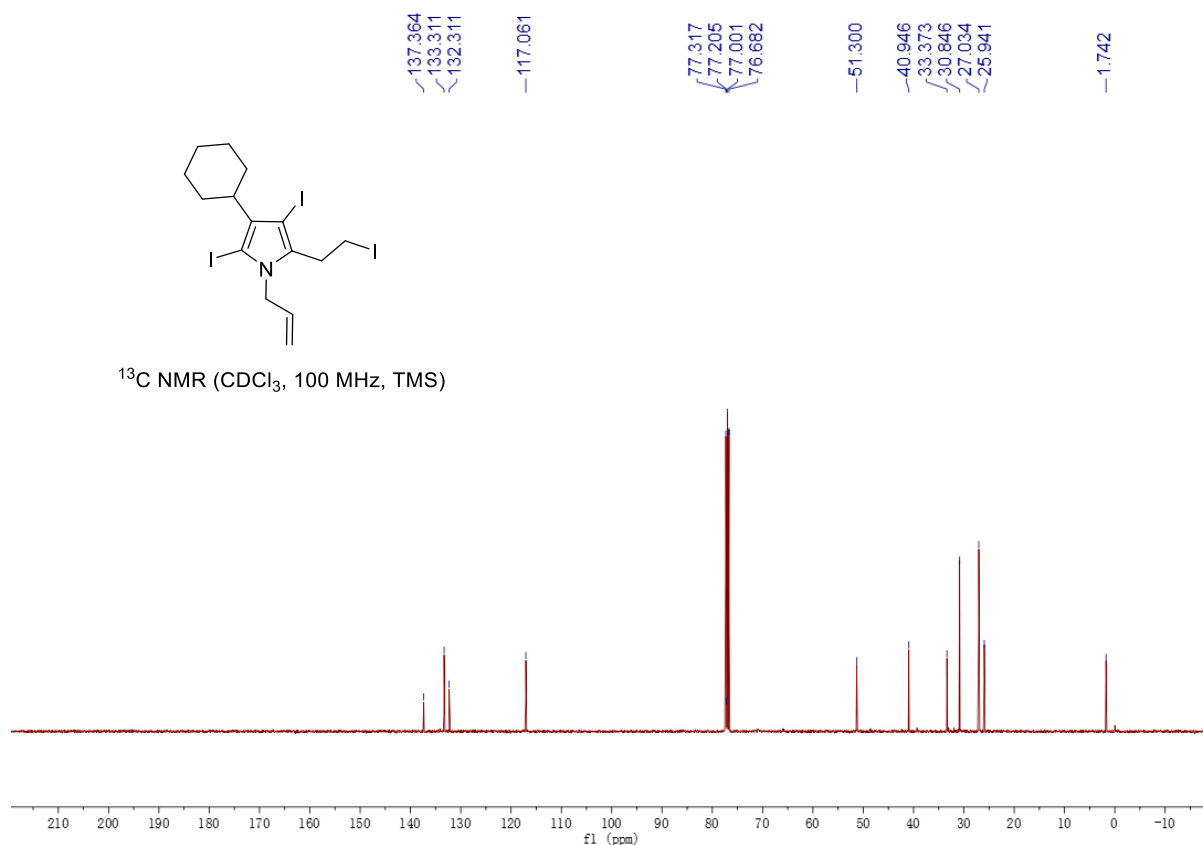
A colorless oil, 48.7 mg, 82% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 5.92 - 5.78 (m, 1H), 5.19 (d, $J = 10.4$ Hz, 1H), 4.79 (d, $J = 17.1$ Hz, 1H), 4.66 - 4.56 (m, 2H), 3.28 - 3.18 (m, 2H), 3.17 - 3.07 (m, 2H), 2.67 - 2.54 (m, 1H), 2.11 - 1.96 (m, 2H), 1.89 - 1.78 (m, 2H), 1.74 - 1.64 (m, 1H), 1.58 - 1.49 (m, 2H), 1.44 - 1.22 (m, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 137.4, 133.3, 132.3, 117.1, 76.7, 51.3, 40.9, 33.4, 30.8, 27.0, 25.9, 1.7. IR (Acetone) ν 717, 921, 1172, 1337, 1402, 1431, 1645, 2847, 2925 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{20}\text{I}_3\text{N}$: 594.8753, Found: 594.8724.

5.893
5.867
5.856
5.840
5.825
5.802
5.202
5.176
4.806
4.764
4.614
4.609
4.603
4.597
4.593
3.257
3.237
3.228
3.214
3.143
3.129
3.121
3.100
2.636
2.627
2.614
2.605
2.596
2.583
2.574
2.565
2.055
2.047
2.024
2.015
1.984
1.858
1.849
1.842
1.817
1.812
1.719
1.714
1.689
1.667
1.558
1.535
1.530
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1.345
1.338
1.313
1.289
1.282
1.258
0.000



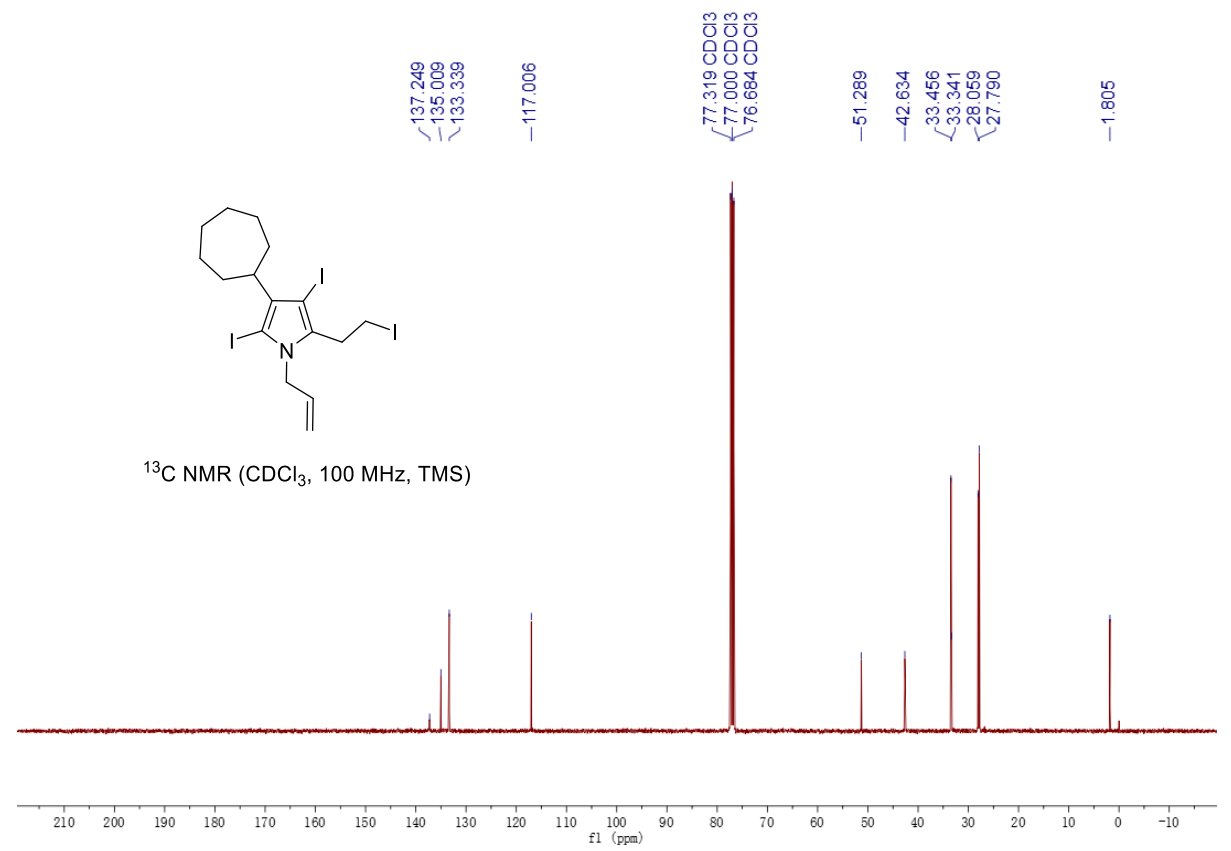
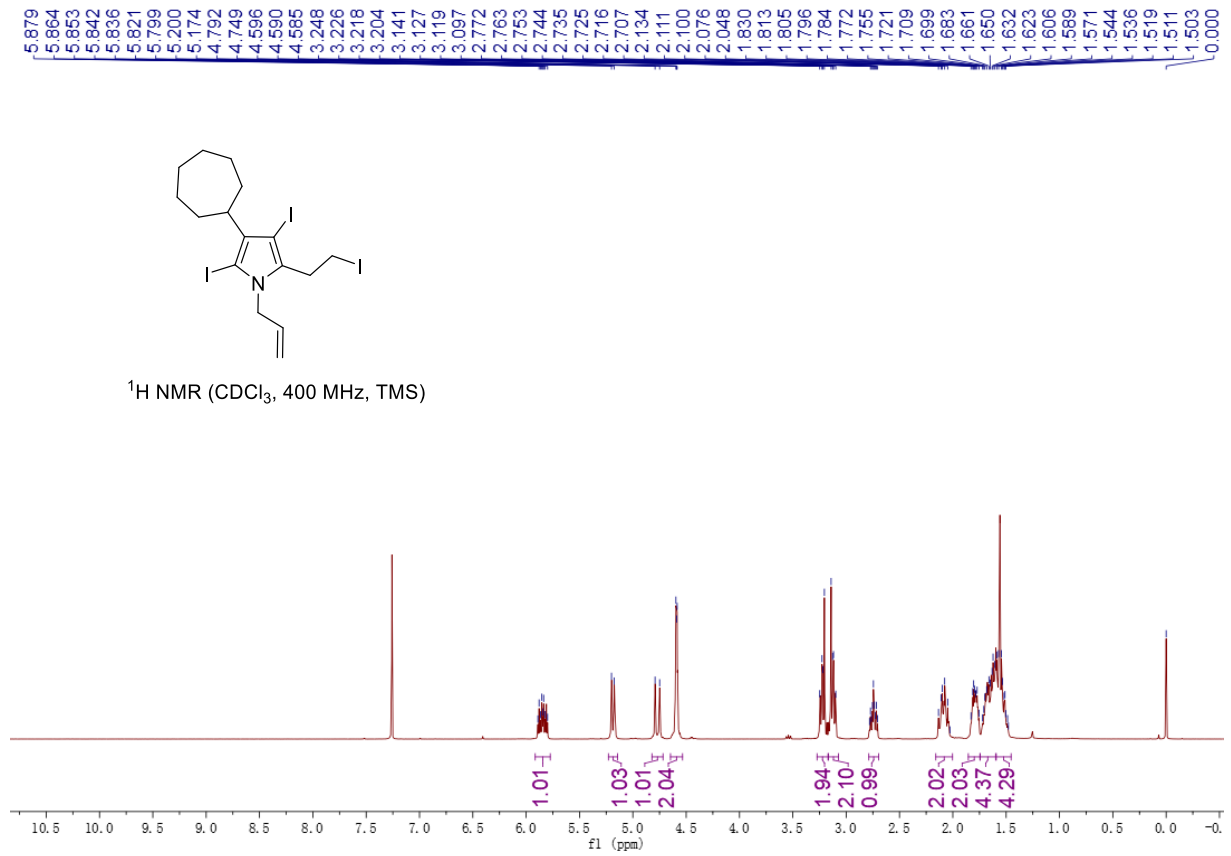
^1H NMR (CDCl_3 , 400 MHz, TMS)

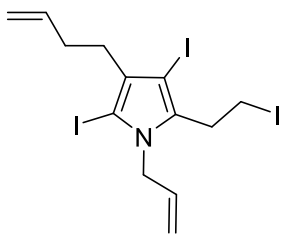




1-allyl-3-cycloheptyl-2,4-diiodo-5-(2-iodoethyl)-1H-pyrrole (3xa)

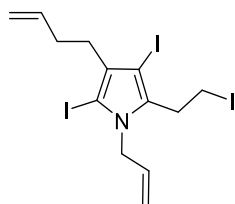
A colorless oil, 49.3 mg, 81% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 5.92 - 5.77 (m, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.77 (d, *J* = 17.2 Hz, 1H), 4.65 - 4.53 (m, 2H), 3.27 - 3.17 (m, 2H), 3.17 - 3.07 (m, 2H), 2.74 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.16 - 2.00 (m, 2H), 1.85 - 1.74 (m, 2H), 1.75 - 1.60 (m, 4H), 1.59 - 1.45 (m, 4H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 137.3, 135.0, 133.3, 117.0, 76.7, 51.3, 42.6, 33.5, 33.3, 28.1, 27.8, 1.8. IR (Neat) ν 731, 921, 1170, 1327, 1401, 1444, 2235, 2848 cm⁻¹. HRMS (EI) calcd. for C₁₆H₂₂I₃N: 608.8910, Found: 608.8881.



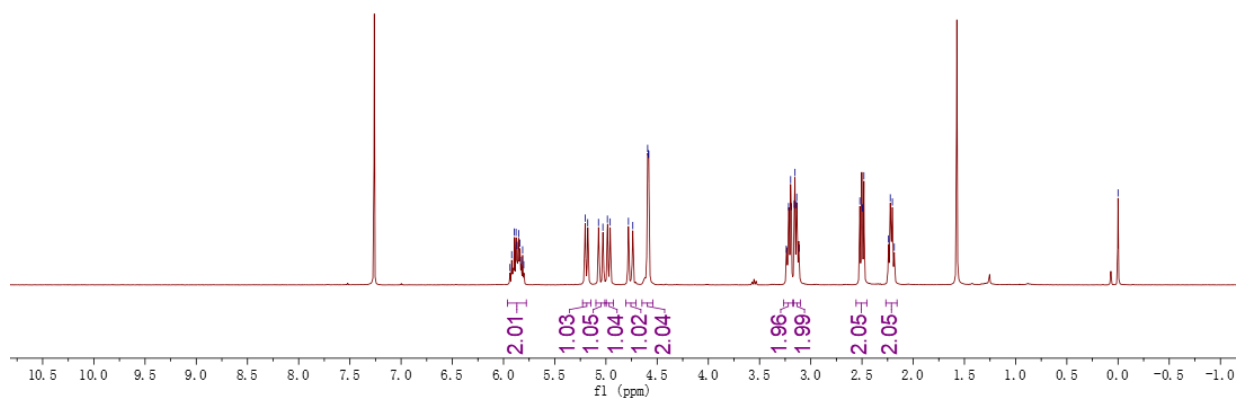


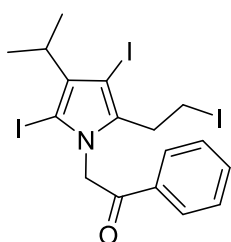
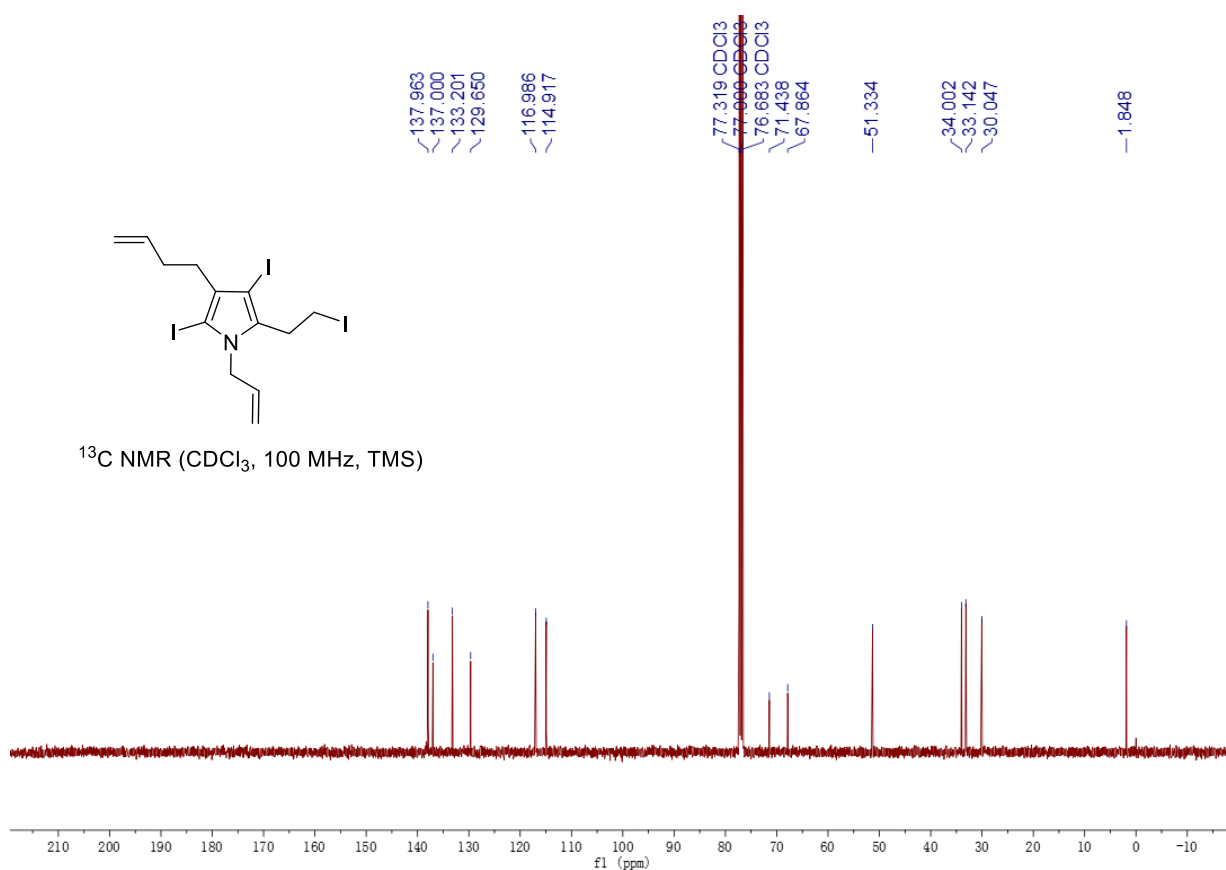
1-allyl-3-(but-3-en-1-yl)-2,4-diiodo-5-(2-iodoethyl)-1H-pyrrole (3ya)

A colorless oil, 41.4 mg, 73% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 5.96 - 5.78 (m, 2H), 5.19 (d, $J = 10.1$ Hz, 1H), 5.05 (d, $J = 17.1$ Hz, 1H), 4.97 (d, $J = 10.9$ Hz, 1H), 4.76 (d, $J = 17.1$ Hz, 1H), 4.65 - 4.54 (m, 2H), 3.26 - 3.18 (m, 2H), 3.17 - 3.10 (m, 2H), 2.56 - 2.45 (m, 2H), 2.21 (q, $J = 7.1$ Hz, 2H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 138.0, 137.0, 133.2, 129.7, 117.0, 114.9, 71.4, 67.9, 51.3, 34.0, 33.1, 30.0, 1.8. IR (Neat) ν 729, 906, 1050, 1169, 1300 1332, 1453, 2248, 2966 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{17}\text{I}_3\text{N}$ ($\text{M}+\text{H}$): 567.8432, Found: 567.8661.



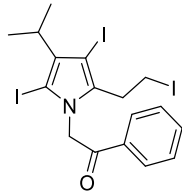
^1H NMR (CDCl_3 , 400 MHz, TMS)



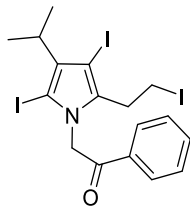
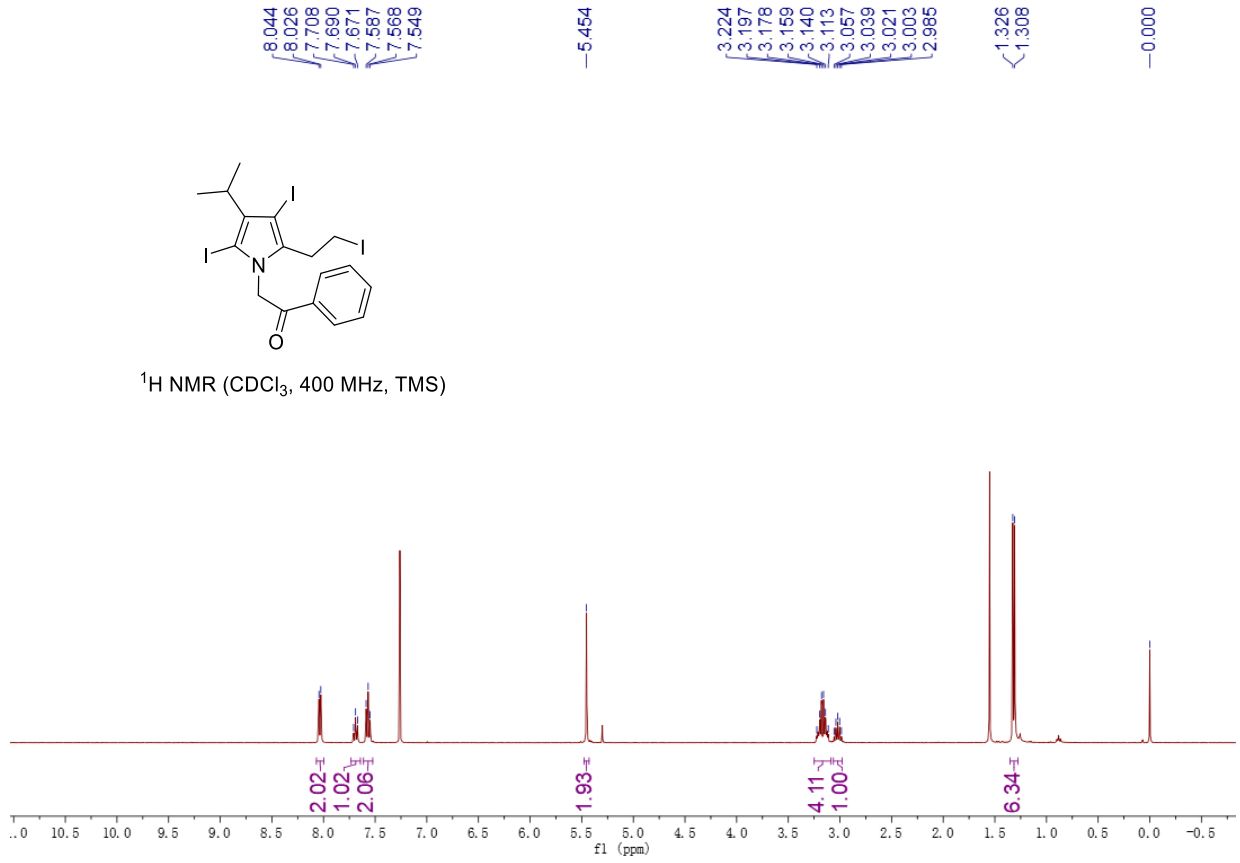


2-(2,4-diiodo-5-(2-iodoethyl)-3-isopropyl-1H-pyrrol-1-yl)-1-phenylethan-1-one (3za)

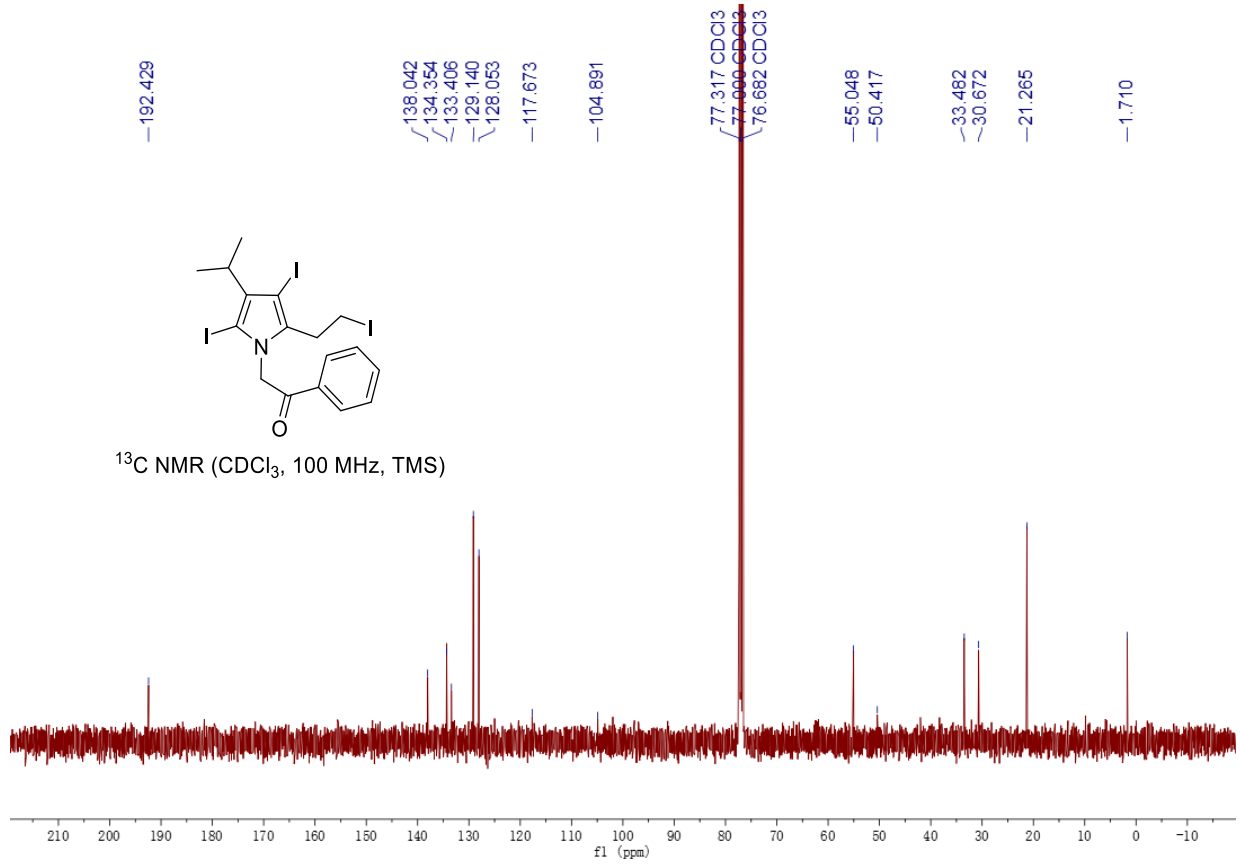
A colorless oil, 27.2 mg, 43% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 8.03 (d, *J* = 7.0 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 5.45 (s, 2H), 3.25 - 3.09 (m, 4H), 3.02 (p, *J* = 7.1 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 192.4, 138.0, 134.4, 133.4, 129.1, 128.1, 117.7, 104.9, 55.0, 50.4, 33.5, 30.7, 21.3, 1.7. IR (Acetone) ν 733, 925, 995, 1210.60, 1271, 1313, 1353, 1449, 1715, 2950 cm⁻¹. HRMS (ESI) calcd. for C₁₇H₁₈I₃NONa (M+Na): 655.8420, Found: 655.8408.

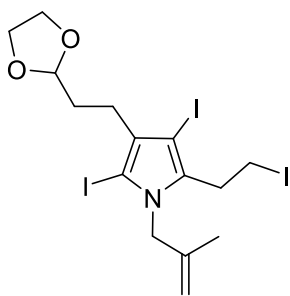


$^1\text{H NMR}$ (CDCl_3 , 400 MHz, TMS)



$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS)

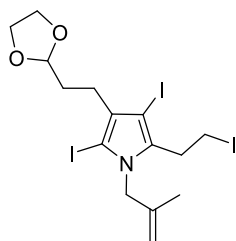




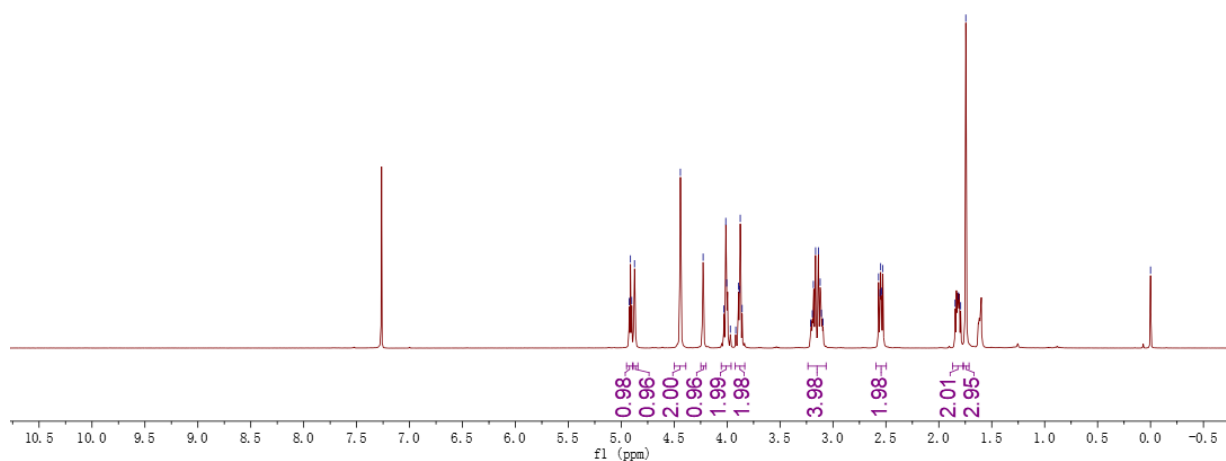
3-(2-(1,3-dioxolan-2-yl)ethyl)-2,4-diiodo-5-(2-iodoethyl)-1-(2-methylallyl)-1H-pyrrole (3afa)

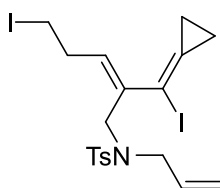
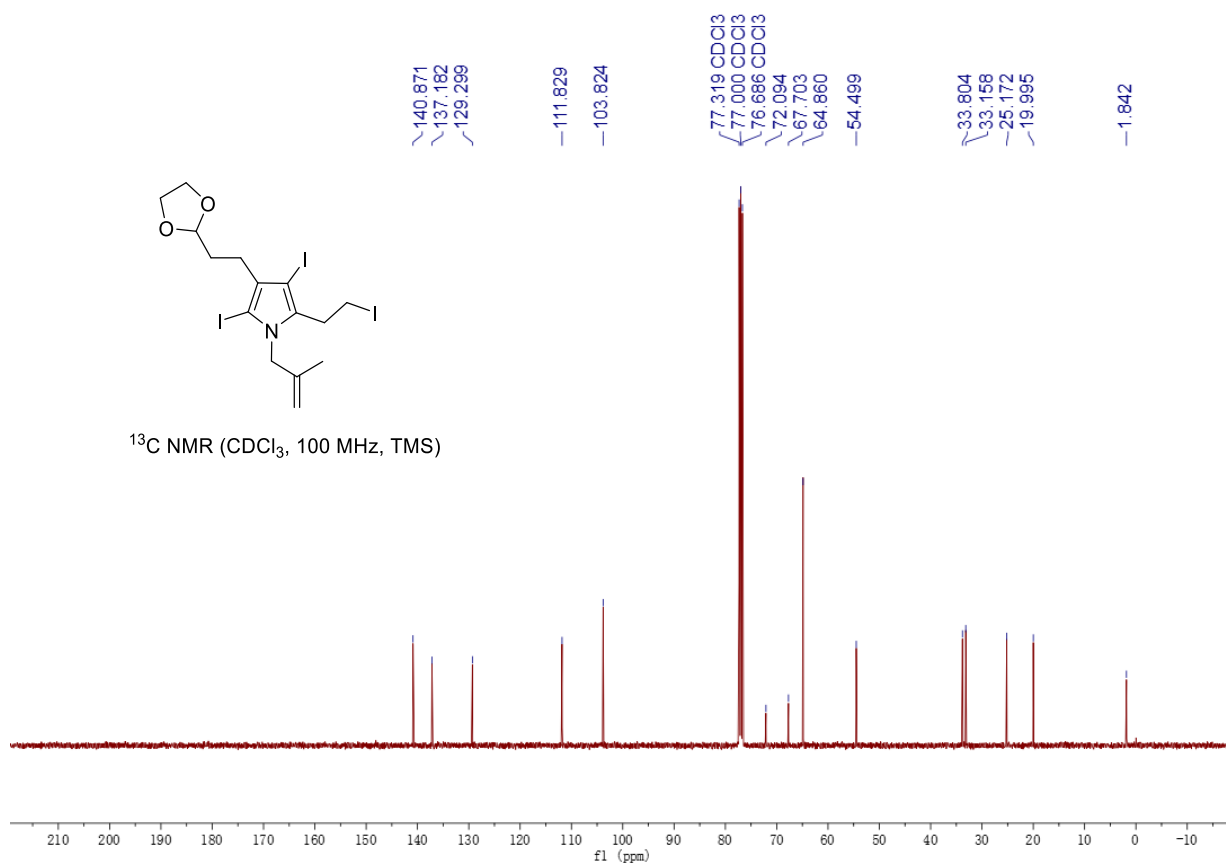
A colorless oil, 50.8 mg, 81% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 4.91 (t, $J = 4.7$ Hz, 1H), 4.87 (s, 1H), 4.44 (s, 2H), 4.23 (s, 1H), 4.06 - 3.96 (m, 2H), 3.92 - 3.83 (m, 2H), 3.24 - 3.06 (m, 4H), 2.59 - 2.50 (m, 2H), 1.87 - 1.77 (m, 2H), 1.75 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 140.9, 137.2, 129.3, 111.8, 103.8, 72.1, 67.7, 64.9, 54.5, 33.8, 33.2, 25.2, 20.0, 1.8. IR (Acetone) ν 716, 896, 965, 1066, 1180, 1325, 1445, 2920 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{20}\text{NO}_2\text{NaI}_3$ ($\text{M}+\text{Na}$): 649.8520, Found: 649.8517.

4.924
4.913
4.901
4.875
4.441
4.227
4.030
4.013
4.004
3.969
3.918
3.893
3.884
3.876
3.858
3.211
3.195
3.185
3.164
3.137
3.121
3.110
3.094
2.569
2.555
2.549
2.542
2.529
1.846
1.814
1.794
1.745
-0.000



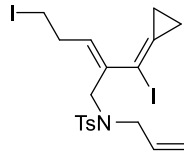
^1H NMR (CDCl_3 , 400 MHz, TMS)



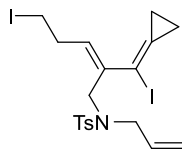
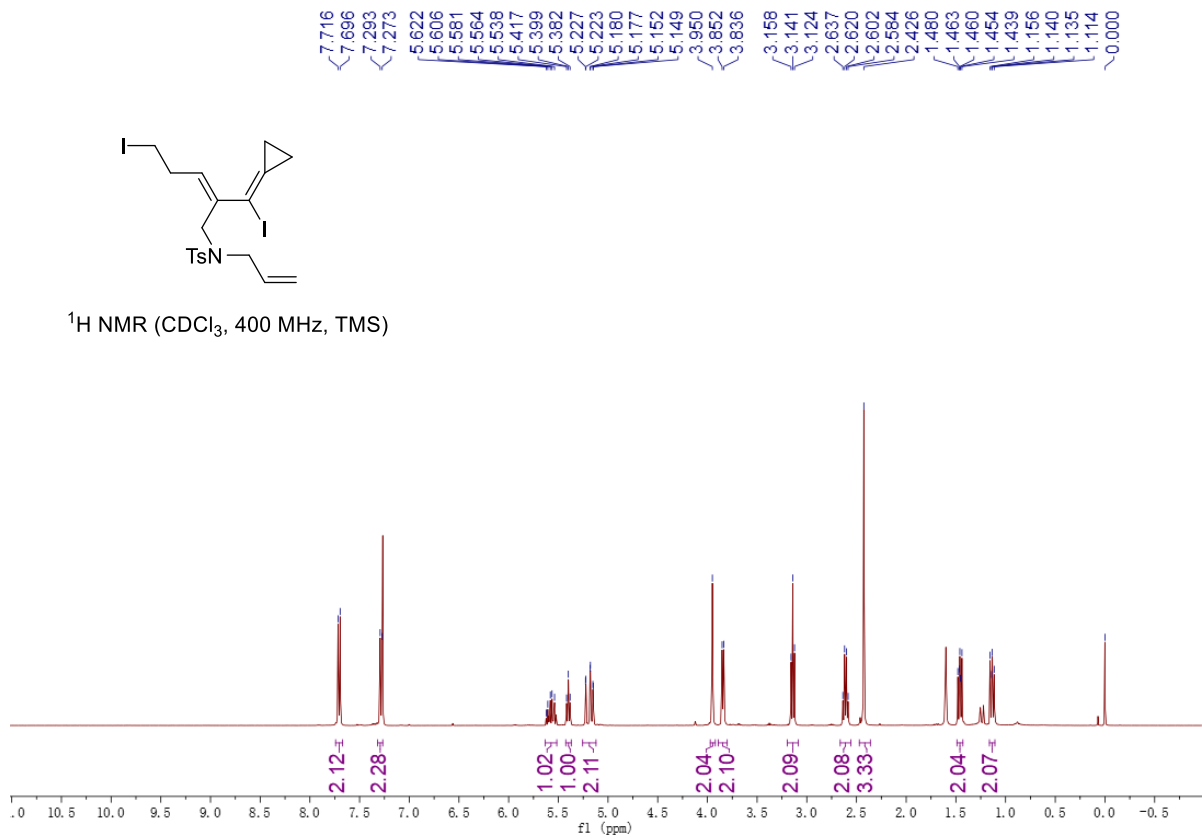


(*E*)-*N*-allyl-*N*-(2-(cyclopropylideneiodomethyl)-5-iodopent-2-en-1-yl)-4-methylbenzenesulfonamide (3aja)

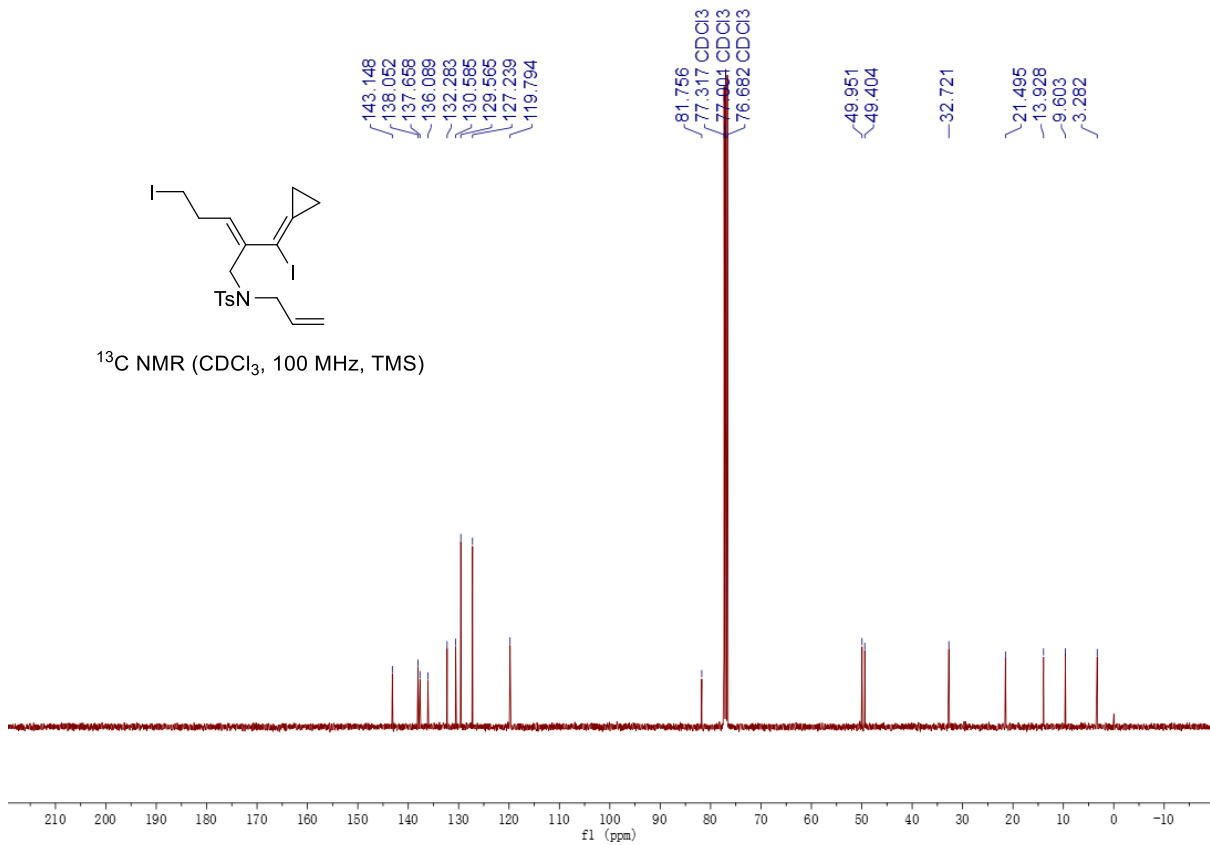
A colorless oil, 50.8 mg, 40% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.63 - 5.52 (m, 1H), 5.40 (t, *J* = 7.0 Hz, 1H), 5.26 - 5.12 (m, 2H), 3.95 (s, 2H), 3.84 (d, *J* = 6.5 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.61 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.49 - 1.43 (m, 2H), 1.16 - 1.11 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 143.1, 138.1, 137.7, 136.1, 132.3, 130.6, 129.6, 127.2, 119.8, 81.8, 50.0, 49.4, 32.7, 21.5, 13.9, 9.6, 3.3. IR (Acetone) ν 719, 890, 993, 1036, 1200, 1325, 1455, 2930 cm⁻¹. HRMS (ESI) calcd. for C₁₉H₂₃NO₂NaSI₂ (M+Na): 605.9431, Found: 605.9442

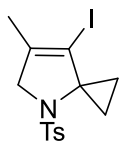


$^1\text{H NMR}$ (CDCl_3 , 400 MHz, TMS)



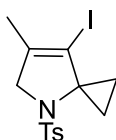
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS)



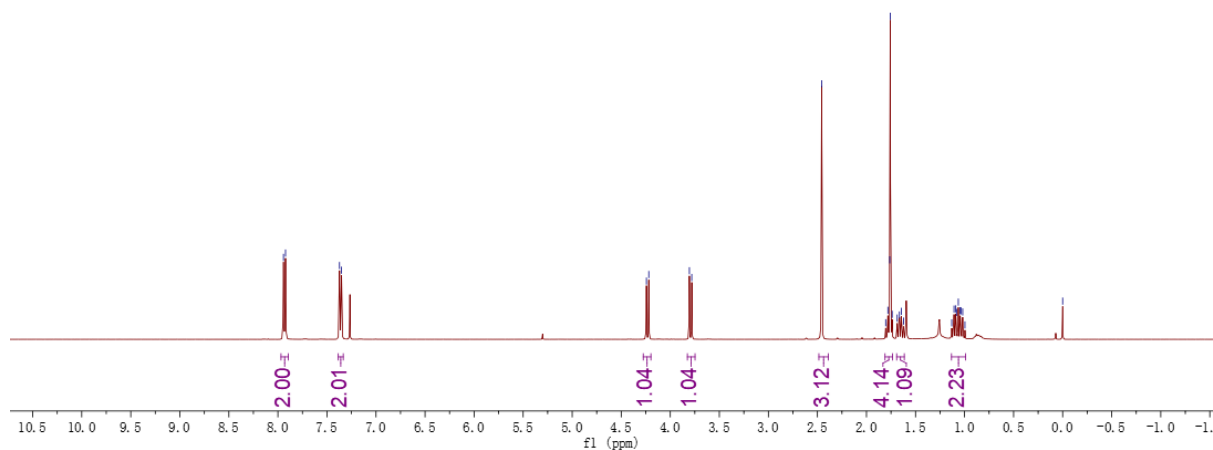


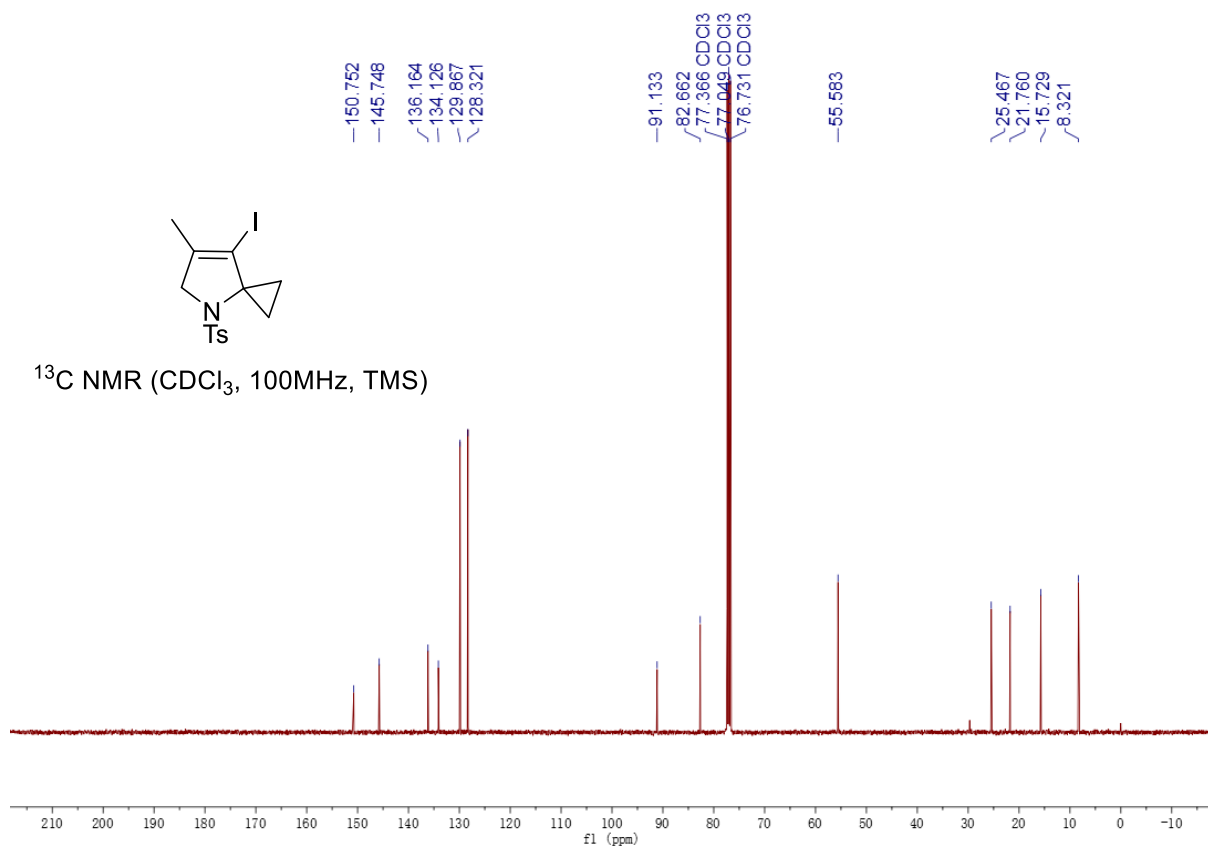
7-iodo-6-methyl-4-tosyl-4-azaspiro[2.4]hept-6-ene (3aka')

A colorless oil, 35.8 mg, 46% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.93 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 4.23 (d, $J = 9.7$ Hz, 1H), 3.79 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 1.76 (s, 4H), 1.69 - 1.61 (m, 1H), 1.13 - 0.99 (m, 2H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 150.8, 145.7, 136.2, 134.1, 129.9, 128.3, 91.1, 82.7, 55.6, 25.5, 21.8, 15.7, 8.3. IR (Acetone) ν 694, 778, 901, 957, 1123, 1210, 1335, 1445, 2960 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{SI}$ ($\text{M}+\text{H}$): 390.0019, Found: 390.0001

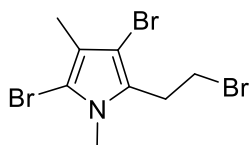


^1H NMR (CDCl_3 , 400MHz, TMS)



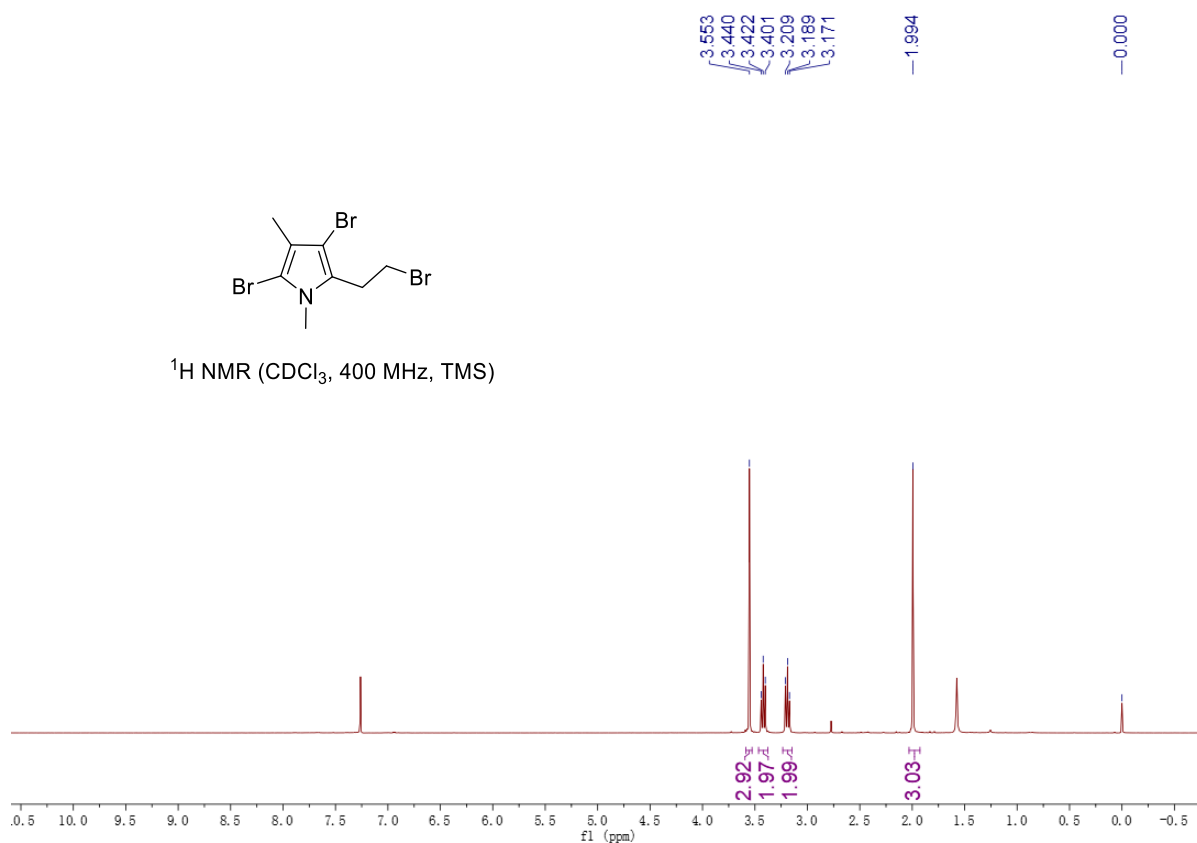


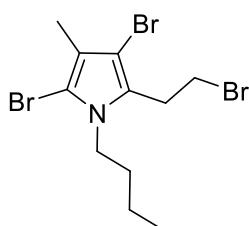
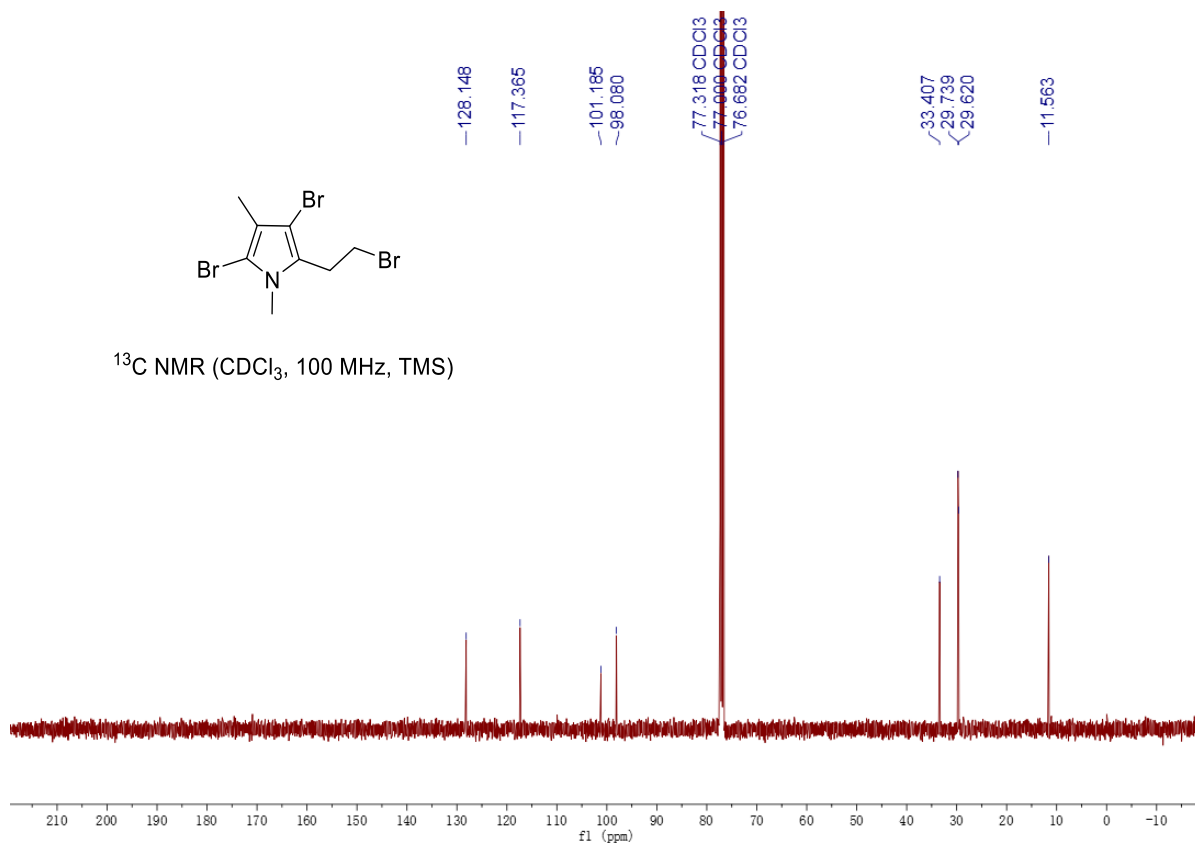
9. Spectroscopic data of products 4.



2,4-dibromo-5-(2-bromoethyl)-1,3-dimethyl-1H-pyrrole (4a)

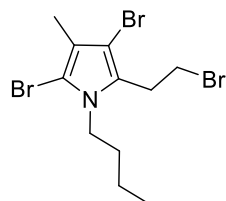
A colorless oil, 21.6 mg, 60% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 3.55 (s, 3H), 3.42 (t, $J = 7.8$ Hz, 2H), 3.19 (t, $J = 7.8$ Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 128.1, 117.4, 101.2, 98.1, 33.4, 29.7, 29.6, 11.6. IR (Neat) ν 731, 757, 909, 943, 1165, 1348, 1530, 2922 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_8\text{H}_{11}\text{NBr}_3$ ($\text{M}+\text{H}$): 360.8240, Found: 360.8343.



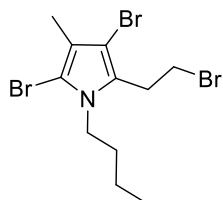
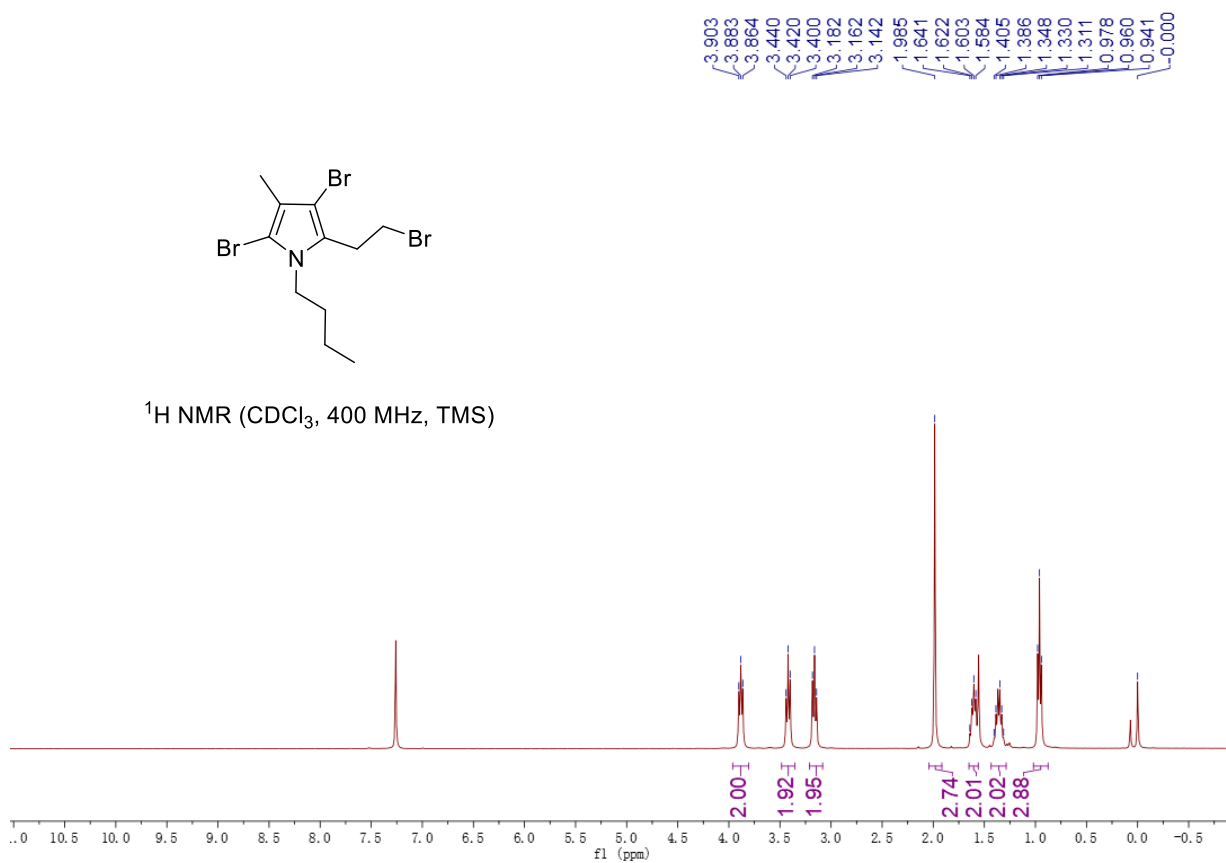


2,4-dibromo-5-(2-bromoethyl)-1-butyl-3-methyl-1H-pyrrole (4b)

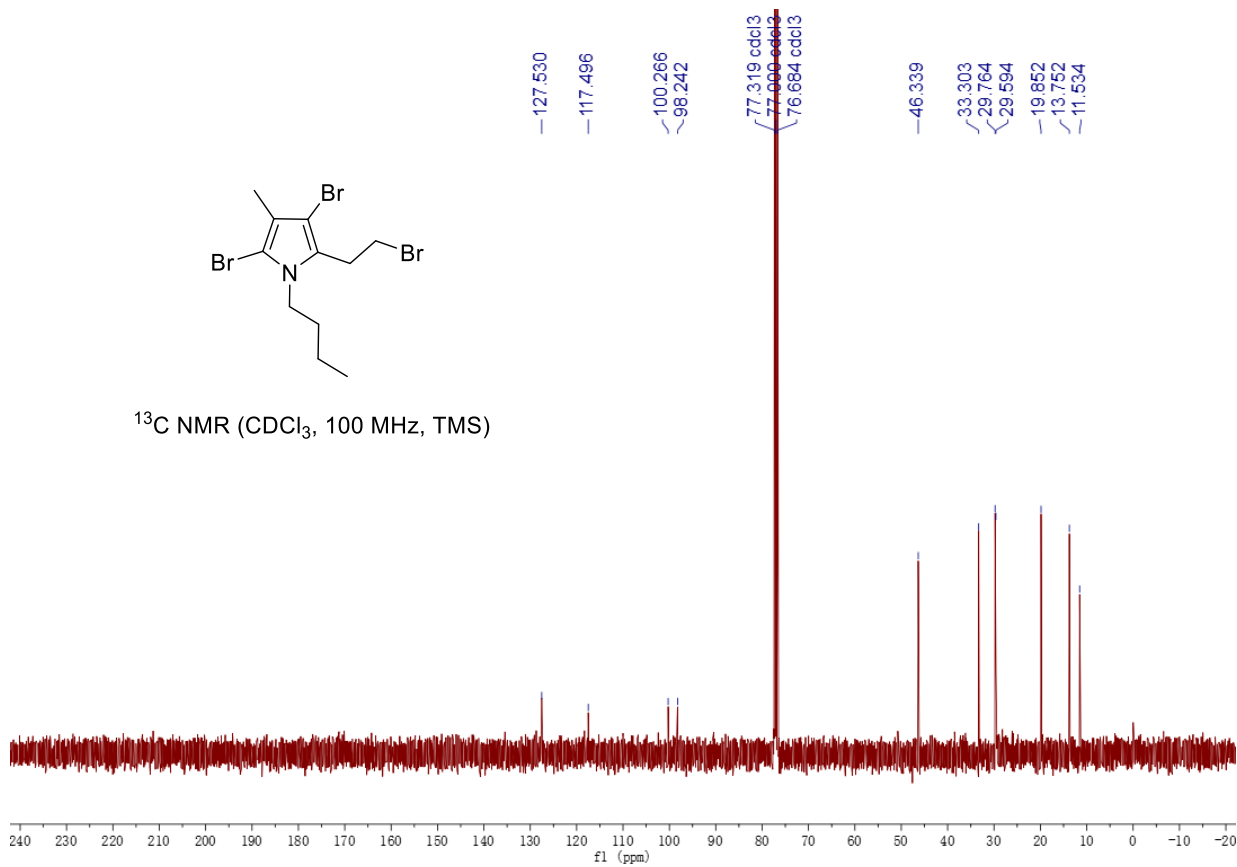
A colorless oil, 28.1 mg, 70% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 3.88 (t, *J* = 7.8 Hz, 2H), 3.42 (t, *J* = 8.0 Hz, 2H), 3.16 (t, *J* = 8.0 Hz, 2H), 1.99 (s, 3H), 1.65 - 1.56 (m, 2H), 1.43 - 1.29 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ¹³C NMR CDCl₃, TMS, 100 MHz) δ 127.5, 117.5, 100.3, 98.2, 46.3, 33.3, 29.8, 29.6, 19.9, 13.8, 11.5. IR (Neat) ν 762, 878, 1165, 1352, 1453, 1524, 2959 cm⁻¹. HRMS (ESI) calcd. for C₁₁H₁₇NBr₃ (M+H): 403.8870, Found: 403.9716.

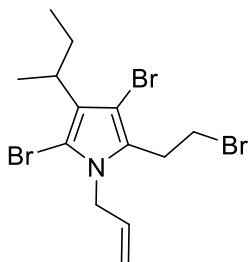


$^1\text{H NMR}$ (CDCl_3 , 400 MHz, TMS)



$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS)

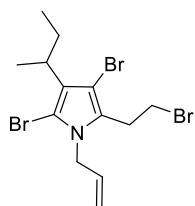




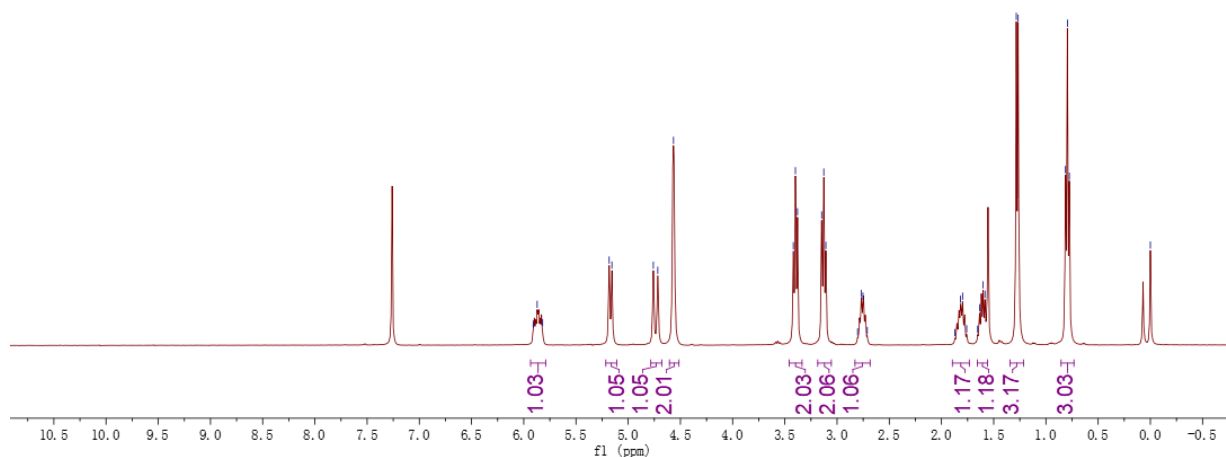
1-allyl-2,4-dibromo-5-(2-bromoethyl)-3-(sec-butyl)-1H-pyrrole (4c)

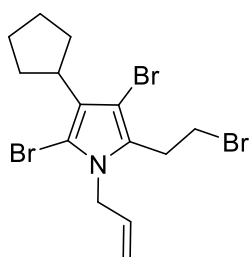
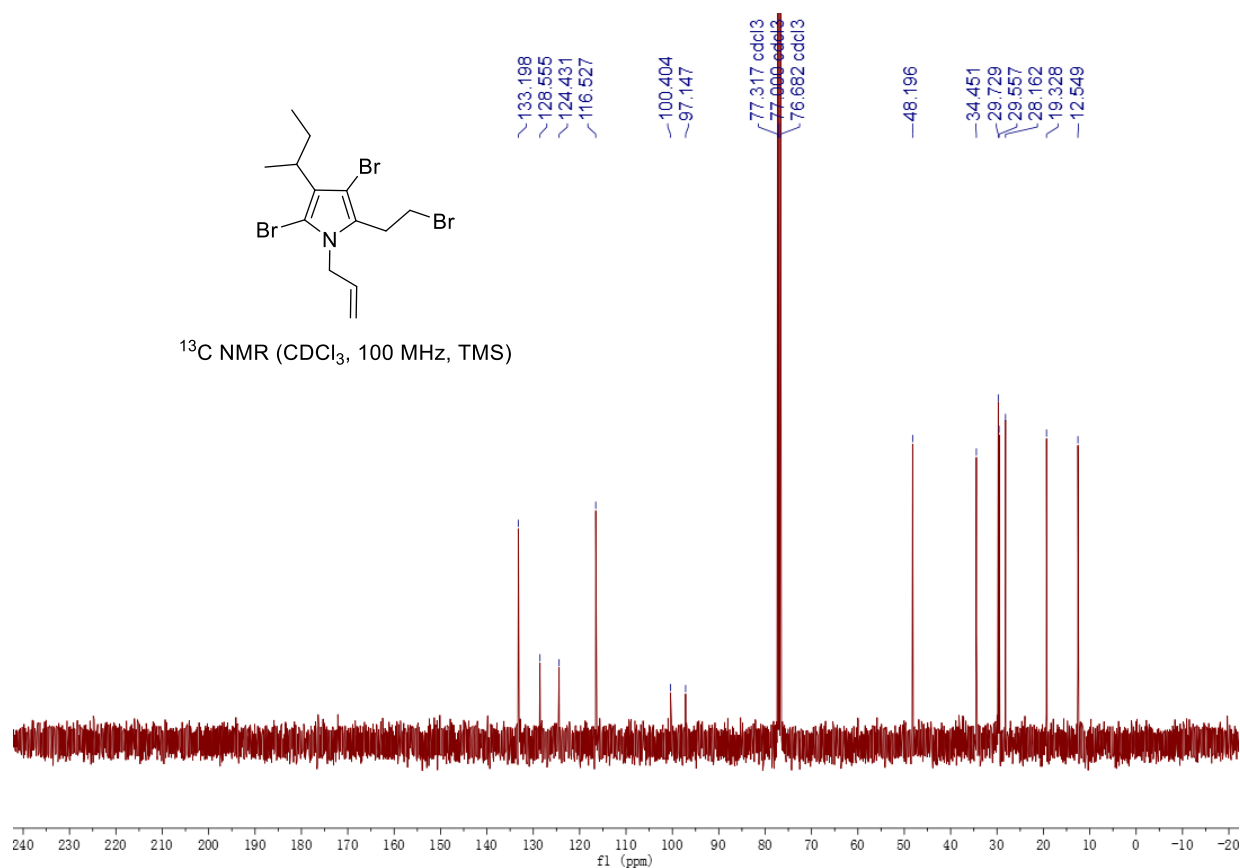
A colorless oil, 29.1 mg, 68% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 5.93 - 5.79 (m, 1H), 5.17 (d, $J = 10.4$ Hz, 1H), 4.74 (d, $J = 17.1$ Hz, 1H), 4.57 (s, 2H), 3.40 (t, $J = 8.1$ Hz, 2H), 3.13 (t, $J = 8.1$ Hz, 2H), 2.83 - 2.68 (m, 1H), 1.90 - 1.73 (m, 1H), 1.66 - 1.56 (m, 1H), 1.27 (d, $J = 7.2$ Hz, 3H), 0.79 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 133.2, 128.6, 124.4, 116.5, 100.4, 97.1, 48.2, 34.5, 29.7, 29.6, 28.2, 19.3, 12.5. IR (Neat) ν 728, 905, 1147, 1376, 2918, 2950 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{19}\text{Br}_3\text{N}$ ($\text{M}+\text{H}$): 429.9026, Found: 429.9027.

5.910
5.871
5.819
5.182
5.156
4.759
4.717
4.566
3.419
3.399
3.379
3.148
3.127
3.107
2.803
2.769
2.752
2.711
1.871
1.818
1.798
1.759
1.654
1.636
1.601
1.584
1.284
1.266
0.813
0.794
0.776
-0.000



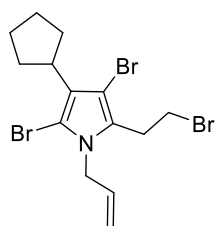
^1H NMR (CDCl_3 , 400 MHz, TMS)



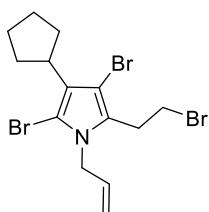
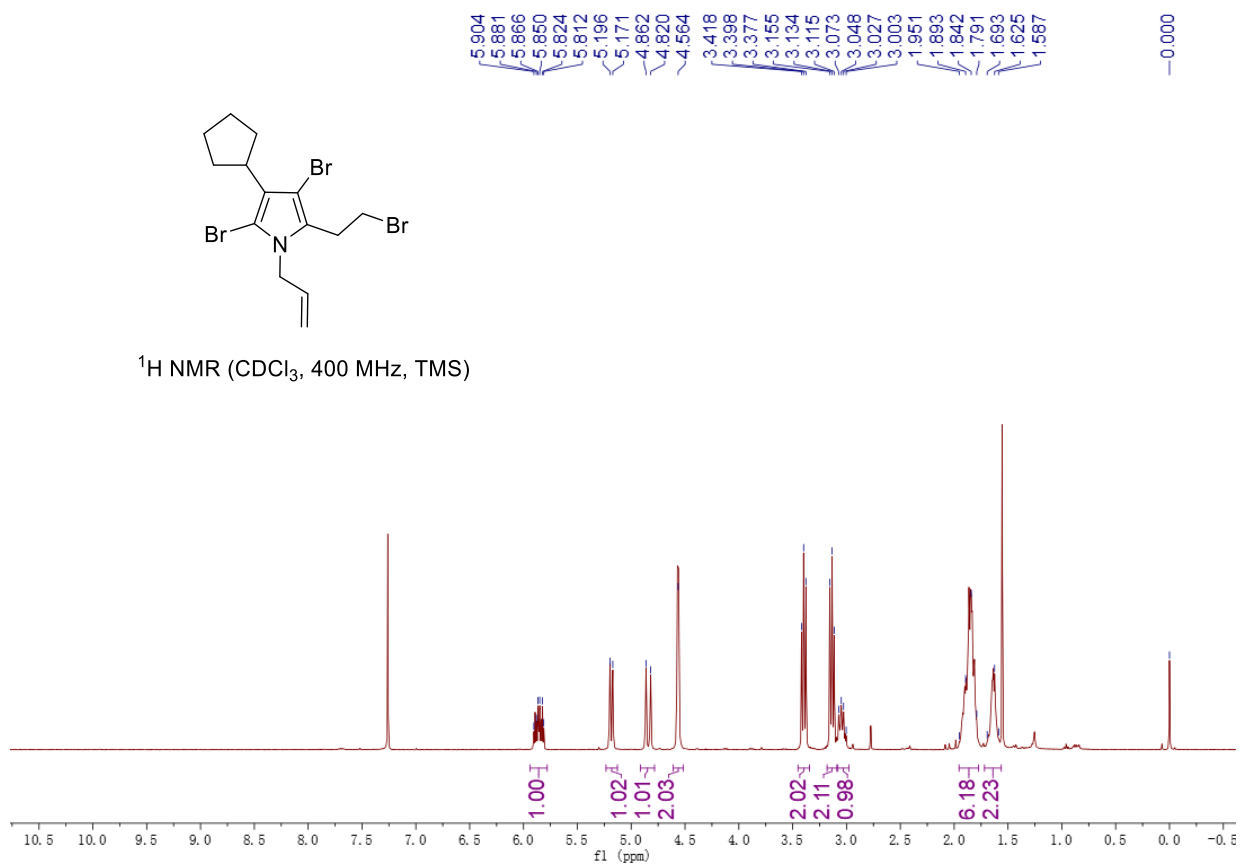


1-allyl-2,4-dibromo-5-(2-bromoethyl)-3-cyclopentyl-1H-pyrrole (4d)

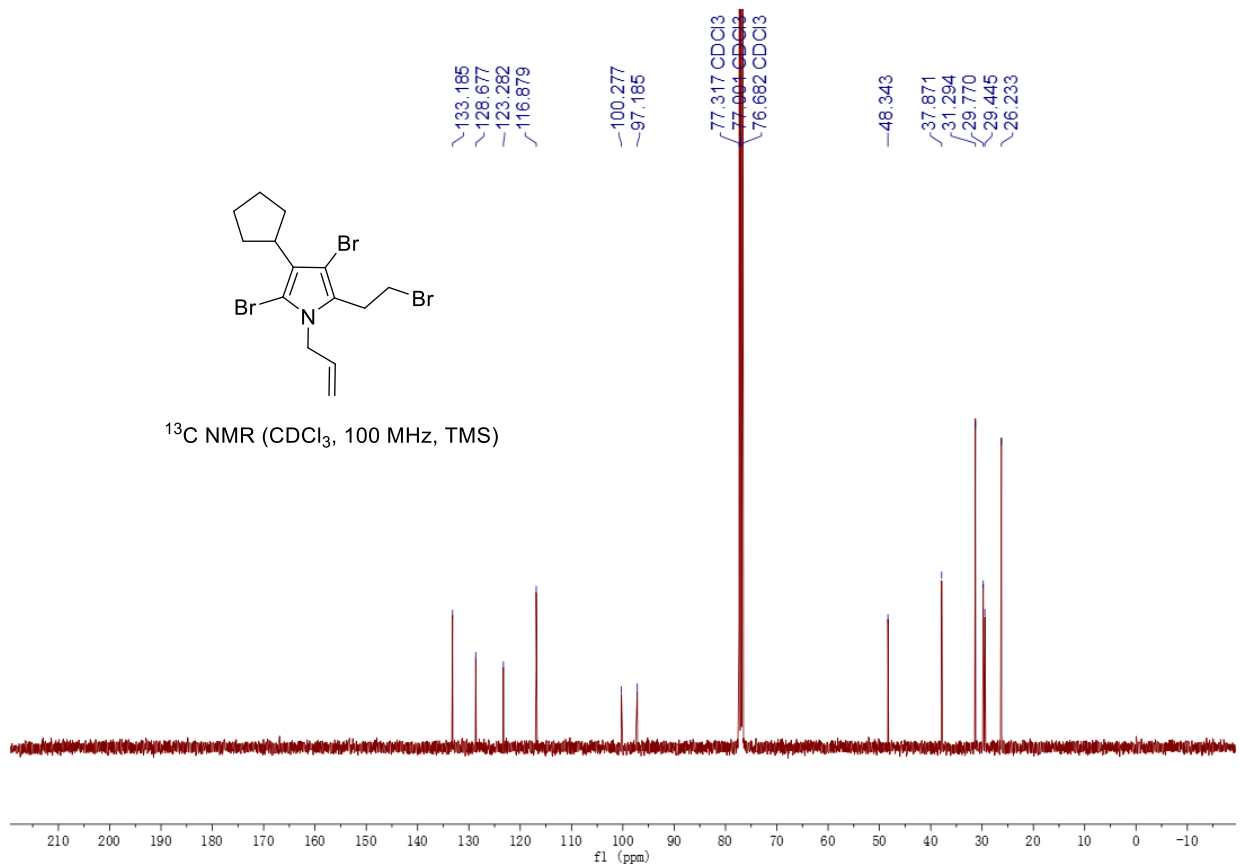
A colorless oil, 28.6 mg, 65% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 5.94 - 5.78 (m, 1H), 5.18 (d, *J* = 10.1 Hz, 1H), 4.84 (d, *J* = 17.1 Hz, 1H), 4.56 (s, 2H), 3.45 - 3.34 (m, 2H), 3.18 - 3.09 (m, 2H), 3.08 - 2.98 (m, 1H), 1.95 - 1.77 (m, 6H), 1.72 - 1.56 (m, 2H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 133.2, 128.7, 123.3, 116.9, 100.3, 97.2, 48.3, 37.9, 31.3, 29.8, 29.4, 26.2. IR (Acetone) ν 759, 1023, 1120, 1433, 2921, 2930 cm⁻¹. HRMS (ESI) calcd. for C₁₄H₁₉NBr₃ (M+H): 441.9023, Found: 441.9027.

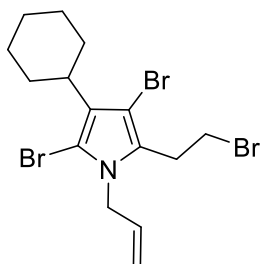


¹H NMR (CDCl₃, 400 MHz, TMS)



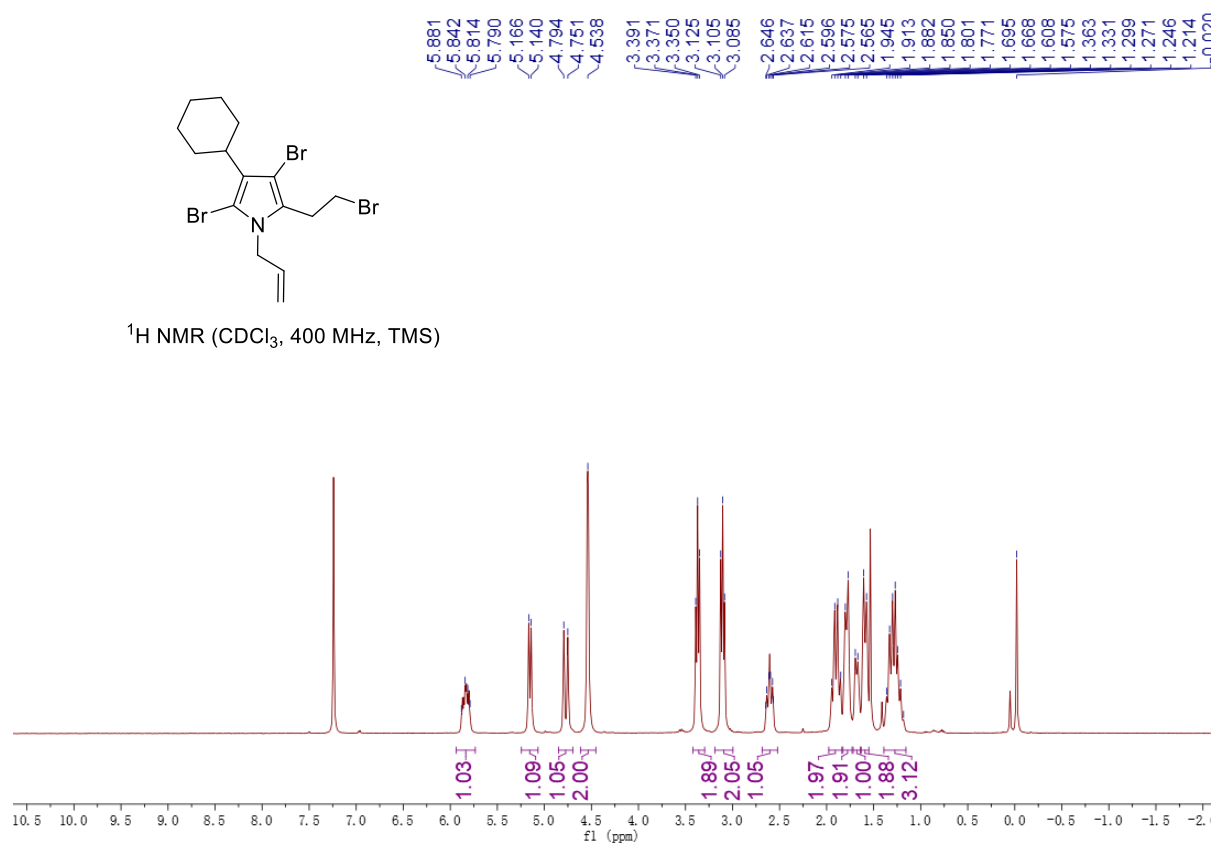
¹³C NMR (CDCl₃, 100 MHz, TMS)

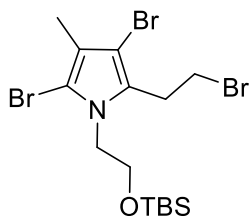
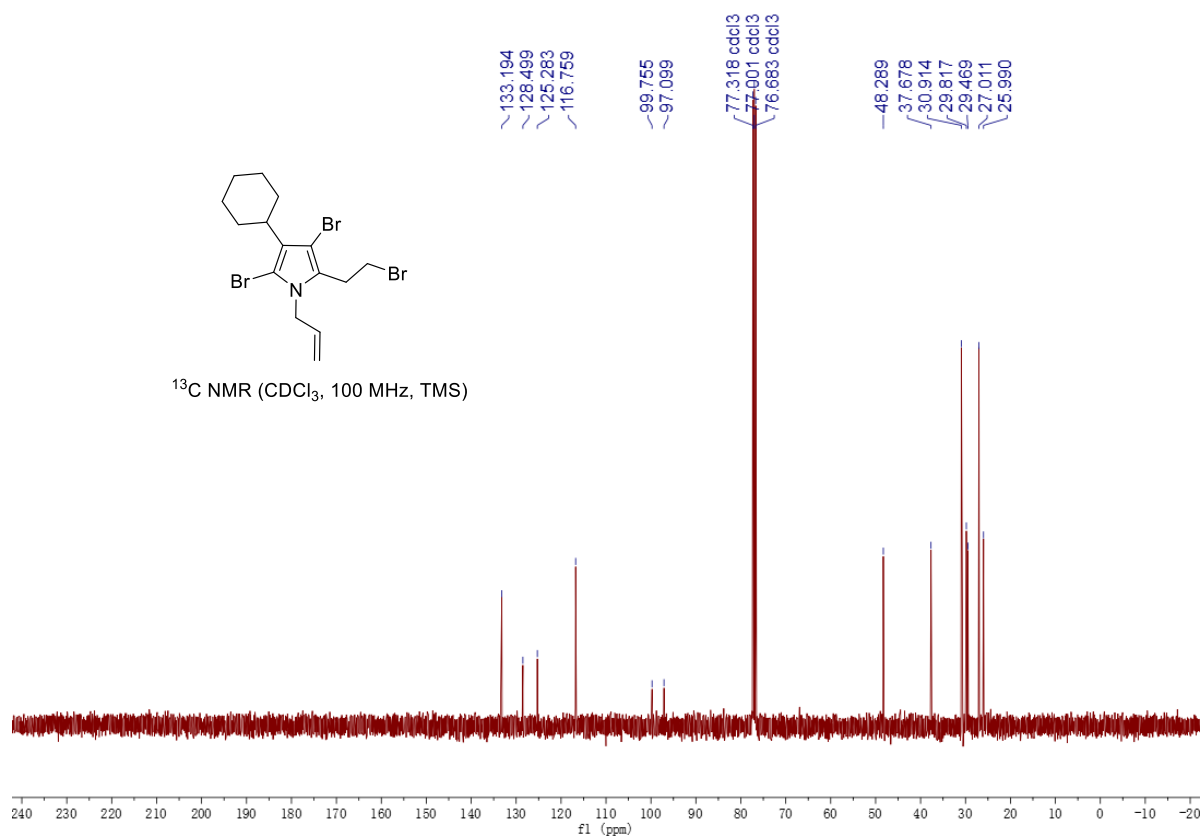




1-allyl-2,4-dibromo-5-(2-bromoethyl)-3-cyclohexyl-1H-pyrrole (4e)

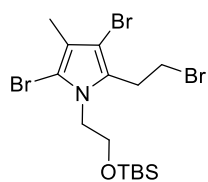
A colorless oil, 26.3 mg, 58% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 5.94 - 5.73 (m, 1H), 5.15 (d, $J = 10.3$ Hz, 1H), 4.77 (d, $J = 17.1$ Hz, 1H), 4.54 (s, 2H), 3.37 (t, $J = 8.1$ Hz, 2H), 3.11 (t, $J = 8.1$ Hz, 2H), 2.69 - 2.52 (m, 1H), 1.98 - 1.84 (m, 2H), 1.83 - 1.73 (m, 2H), 1.72 - 1.64 (m, 1H), 1.63 - 1.55 (m, 2H), 1.39 - 1.16 (m, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 133.2, 128.5, 125.3, 116.8, 99.8, 97.1, 48.3, 37.7, 30.9, 29.8, 29.5, 27.0, 26.0. IR (Neat) ν 699, 1021, 1129, 1448, 2931, 2950, 2977 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{22}\text{NBr}_3$ ($\text{M}+\text{H}$): 453.9204, Found: 453.9184.



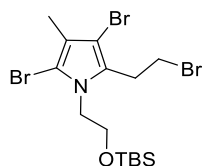
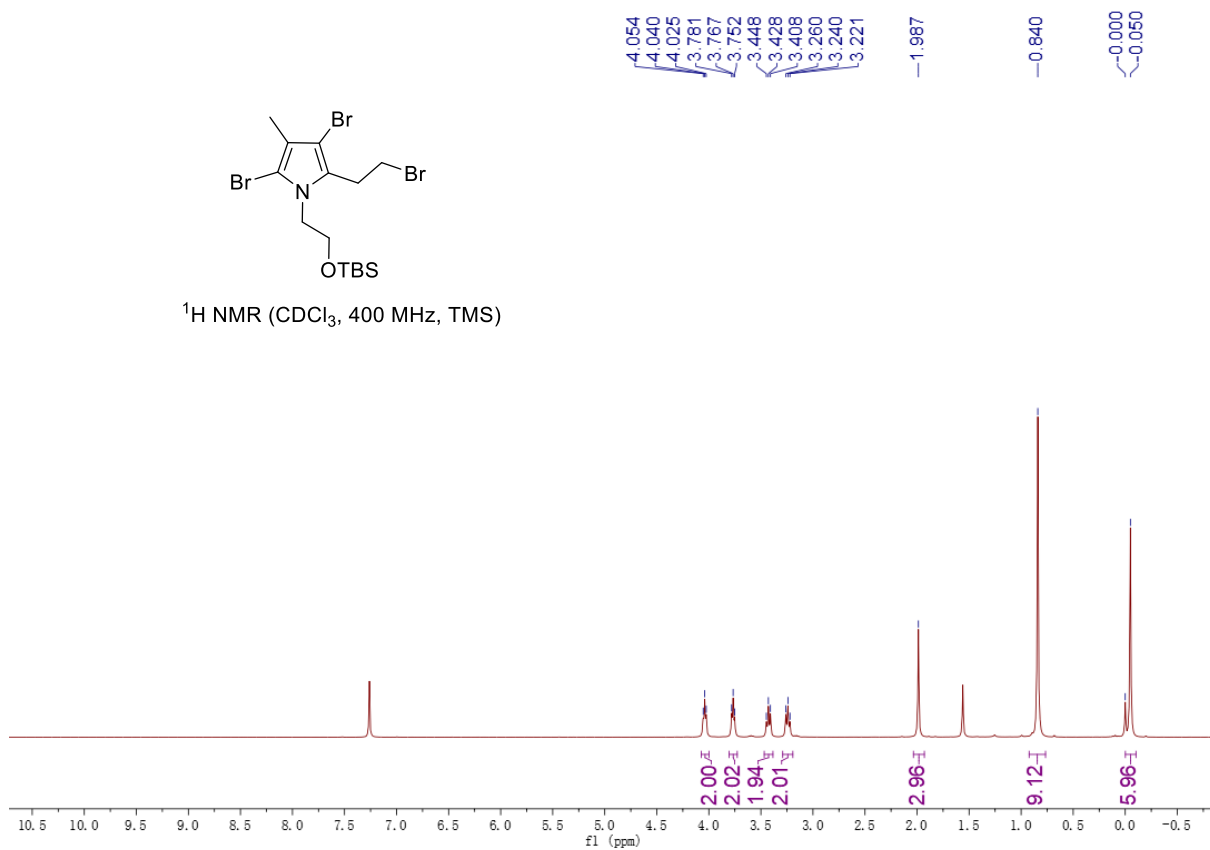


2,4-dibromo-5-(2-bromoethyl)-1-(2-((tert-butyldimethylsilyloxy)ethyl)-3-methyl-1H-pyrrole (4f)

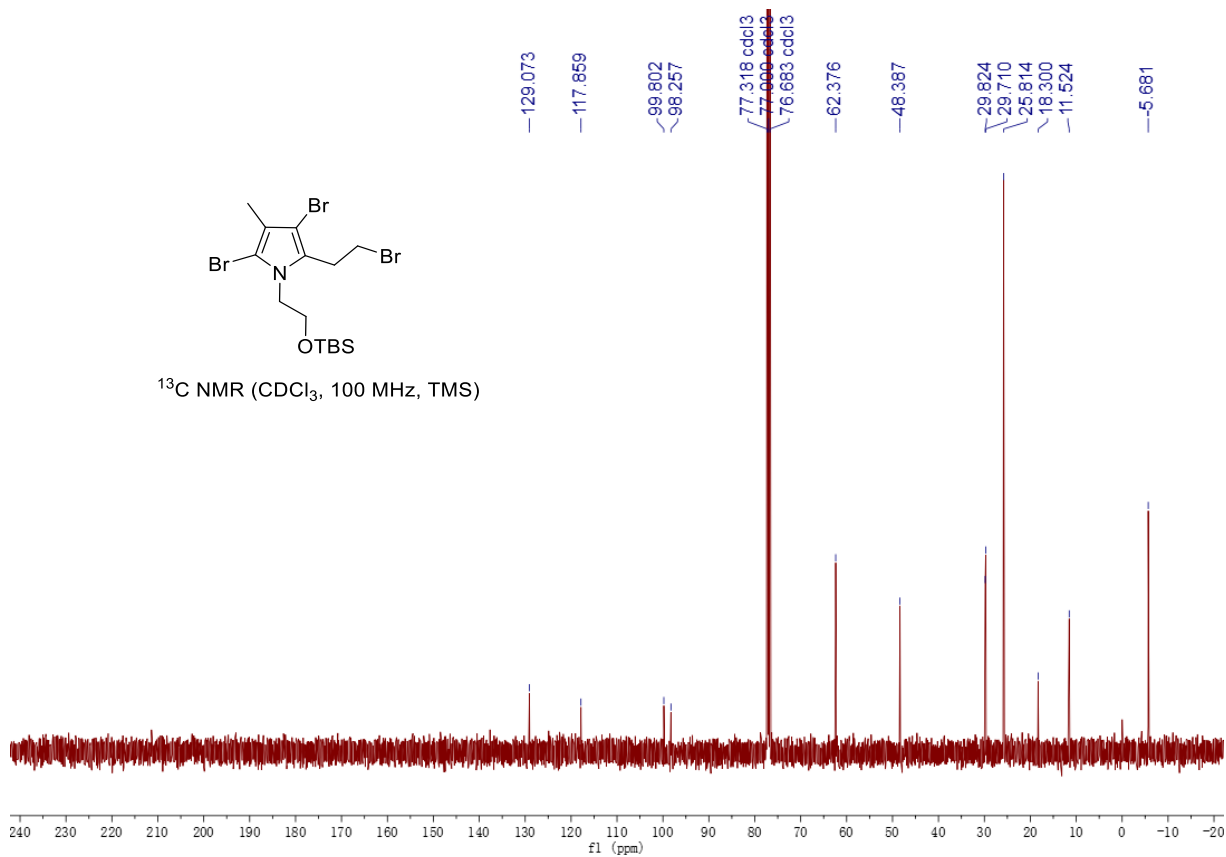
A colorless oil, 36.8 mg, 73% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 4.04 (t, *J* = 5.7 Hz, 2H), 3.77 (t, *J* = 5.8 Hz, 2H), 3.43 (t, *J* = 7.8 Hz, 2H), 3.24 (t, *J* = 7.9 Hz, 2H), 1.99 (s, 3H), 0.84 (s, 9H), -0.05 (s, 6H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 129.1, 117.9, 99.8, 98.3, 62.4, 48.4, 29.8, 29.7, 25.8, 18.3, 11.5, -5.7. IR (Neat) ν 732, 1025, 1146, 1188, 1308, 1345, 1705, 2956 cm⁻¹. HRMS (ESI) calcd. for C₁₅H₂₇NOSiBr₃ (M+H): 503.9392, Found: 503.9392.

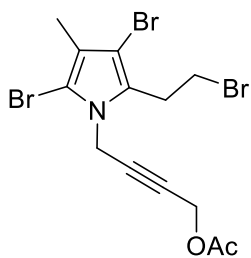


¹H NMR (CDCl₃, 400 MHz, TMS)



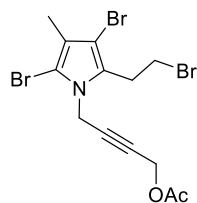
¹³C NMR (CDCl₃, 100 MHz, TMS)



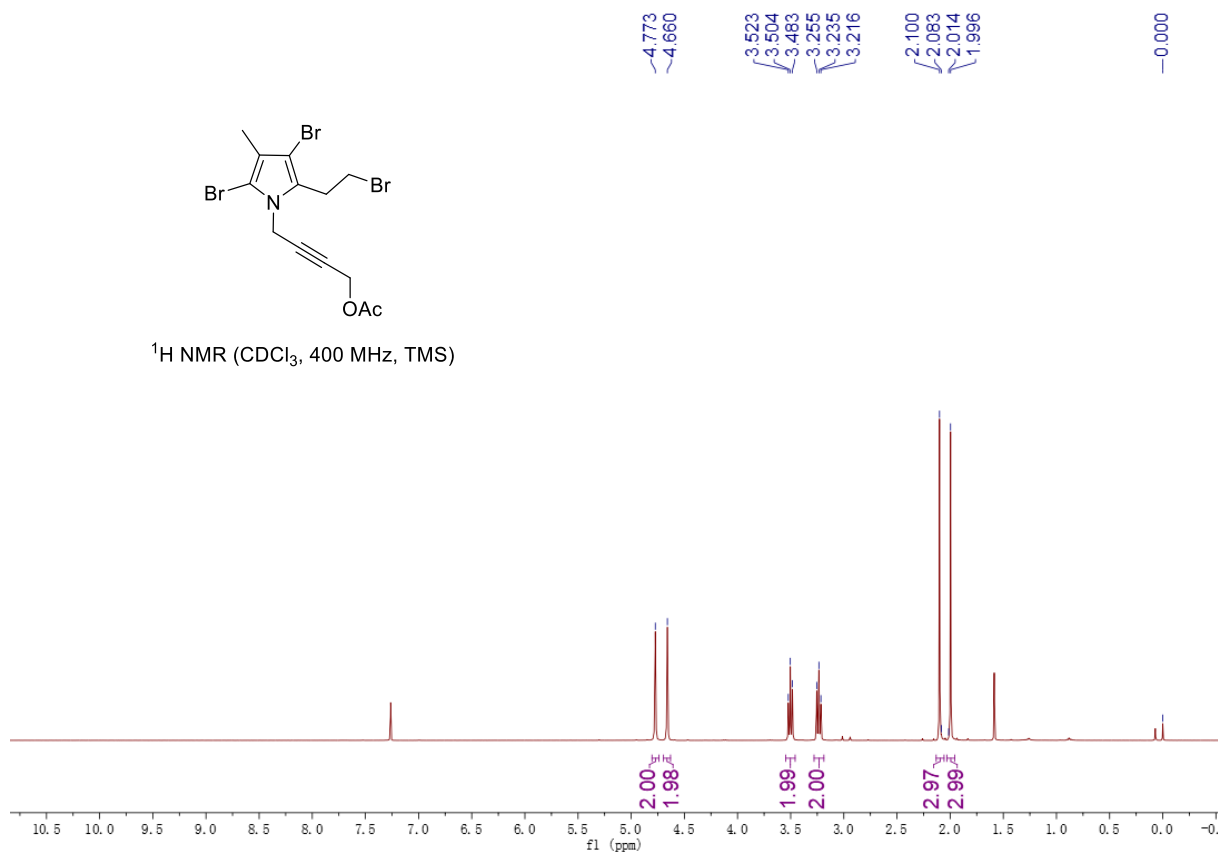


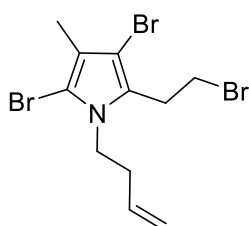
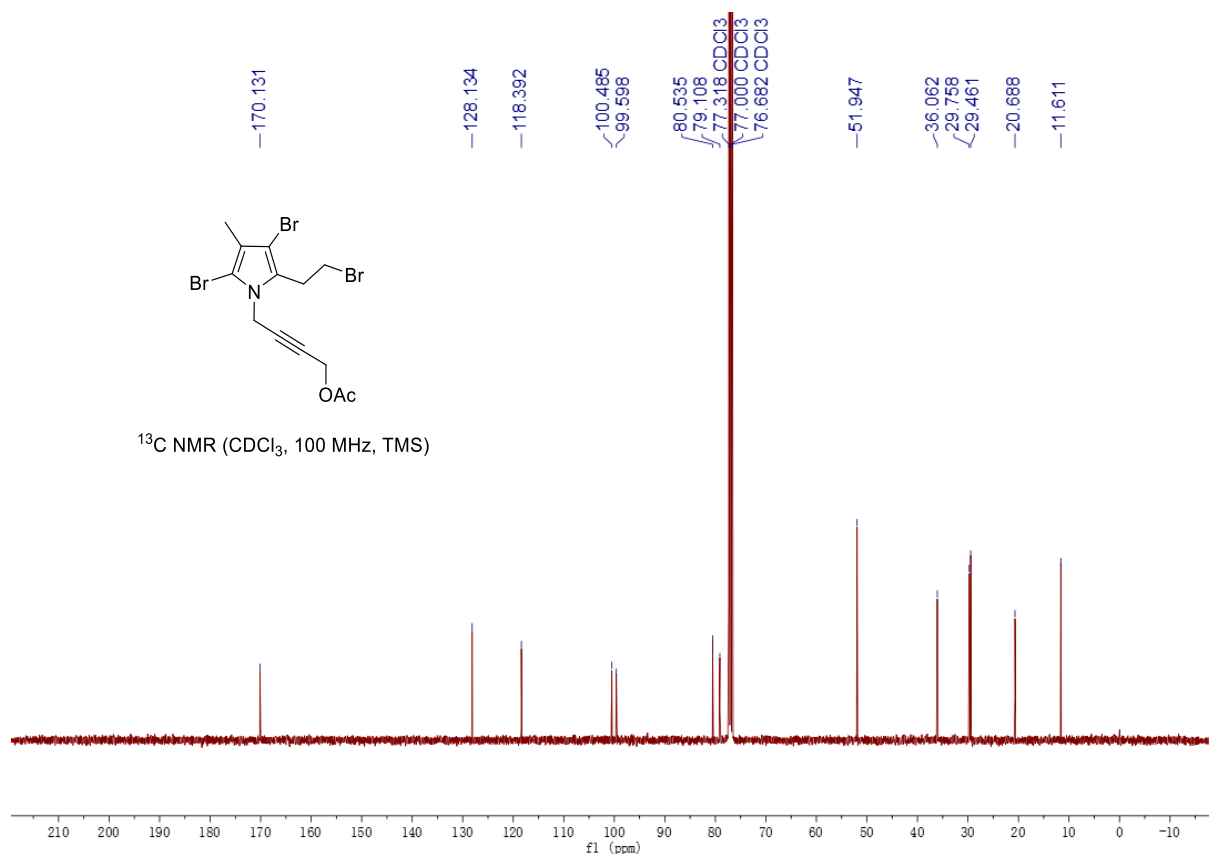
4-(2,4-dibromo-5-(2-bromoethyl)-3-methyl-1H-pyrrol-1-yl)but-2-yn-1-yl acetate (4g)

A colorless oil, 36.5 mg, 80% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 4.77 (s, 2H), 4.66 (s, 2H), 3.50 (t, $J = 7.9$ Hz, 2H), 3.24 (t, $J = 7.9$ Hz, 2H), 2.10 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 170.1, 128.1, 118.4, 100.5, 99.6, 80.5, 79.1, 51.9, 36.1, 29.8, 29.5, 20.7, 11.6. IR (Acetone) ν 730, 1047, 1165, 1203, 1444, 1760 1799, 2963 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_2\text{Br}_3$ ($\text{M}+\text{H}$): 455.8632, Found: 455.8626.



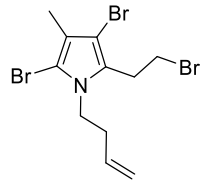
^1H NMR (CDCl_3 , 400 MHz, TMS)



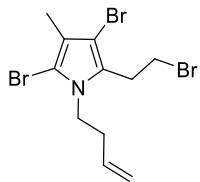
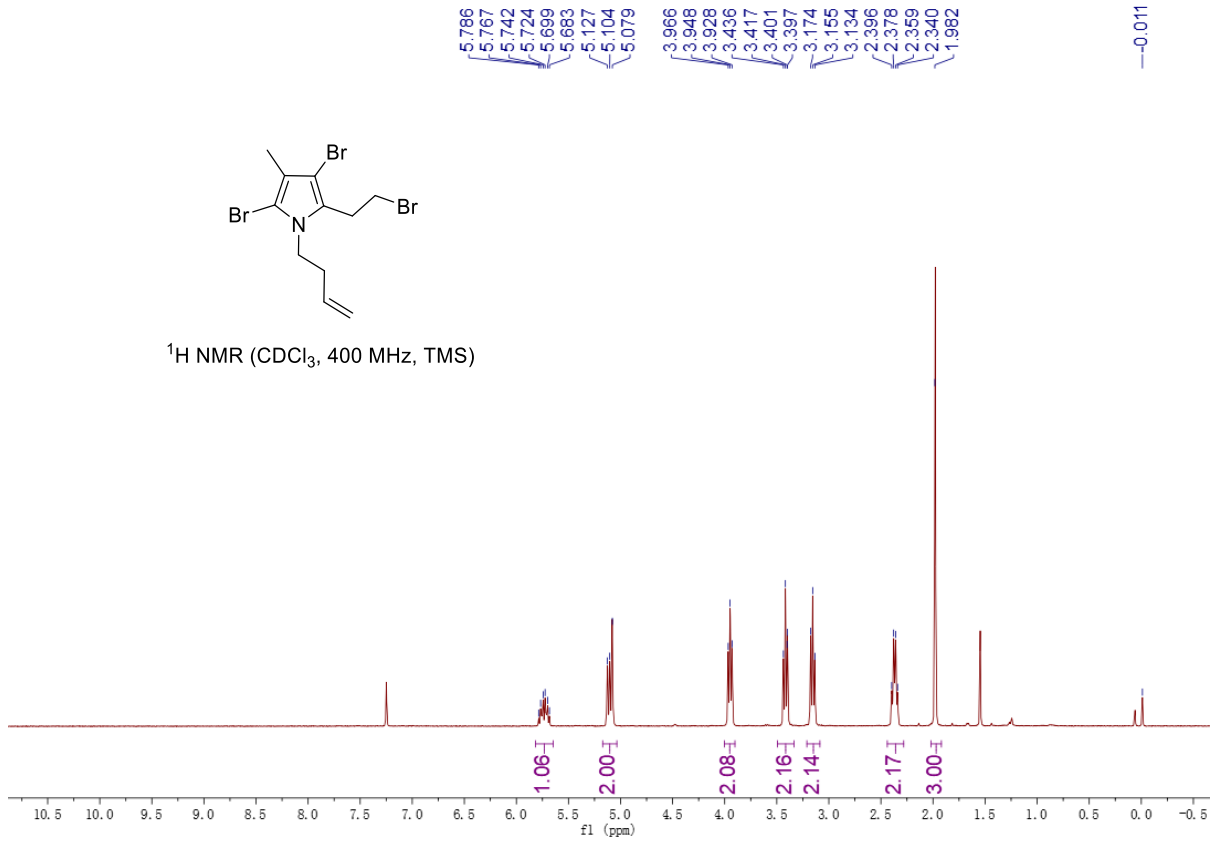


2,4-dibromo-5-(2-bromoethyl)-1-(but-3-en-1-yl)-3-methyl-1H-pyrrole (4h)

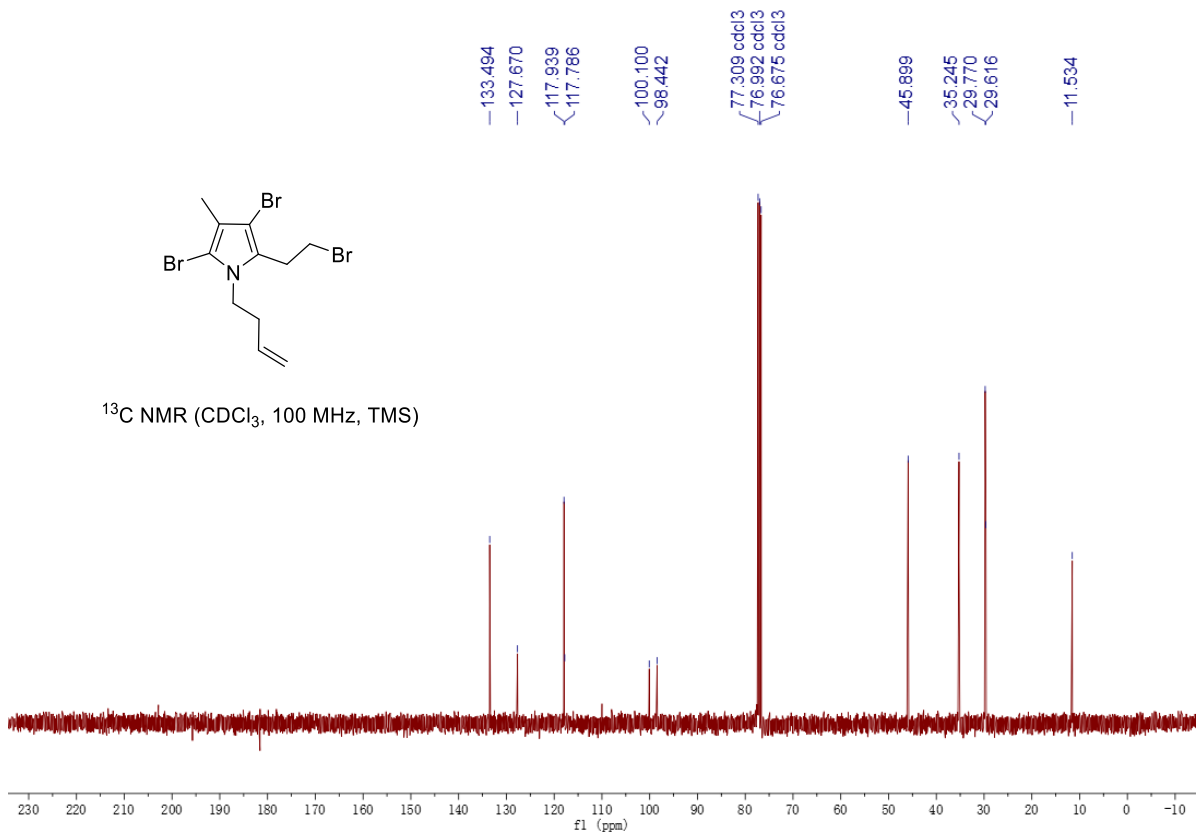
A colorless oil, 31.2 mg, 78% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 5.82 - 5.65 (m, 1H), 5.17 - 5.04 (m, 2H), 3.95 (t, *J* = 7.7 Hz, 2H), 3.42 (t, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.37 (q, *J* = 7.7 Hz, 2H), 1.98 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 133.5, 127.7, 117.9, 117.8, 100.1, 98.4, 45.9, 35.2, 29.8, 29.6, 11.5. IR (Acetone) ν 2936, 2924, 2853, 1611, 1589, 1497, 1457, 1356, 1310, 1272, 1250, 1230, 1214, 1150, 1058, 1029, 959, 823, 788, 744, 700 cm⁻¹. HRMS (ESI) calcd. for C₁₃H₂₁Br₃N (M+H): 427.9224, Found: 427.9231.



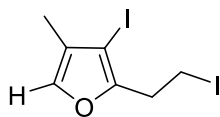
¹H NMR (CDCl₃, 400 MHz, TMS)



¹³C NMR (CDCl₃, 100 MHz, TMS)

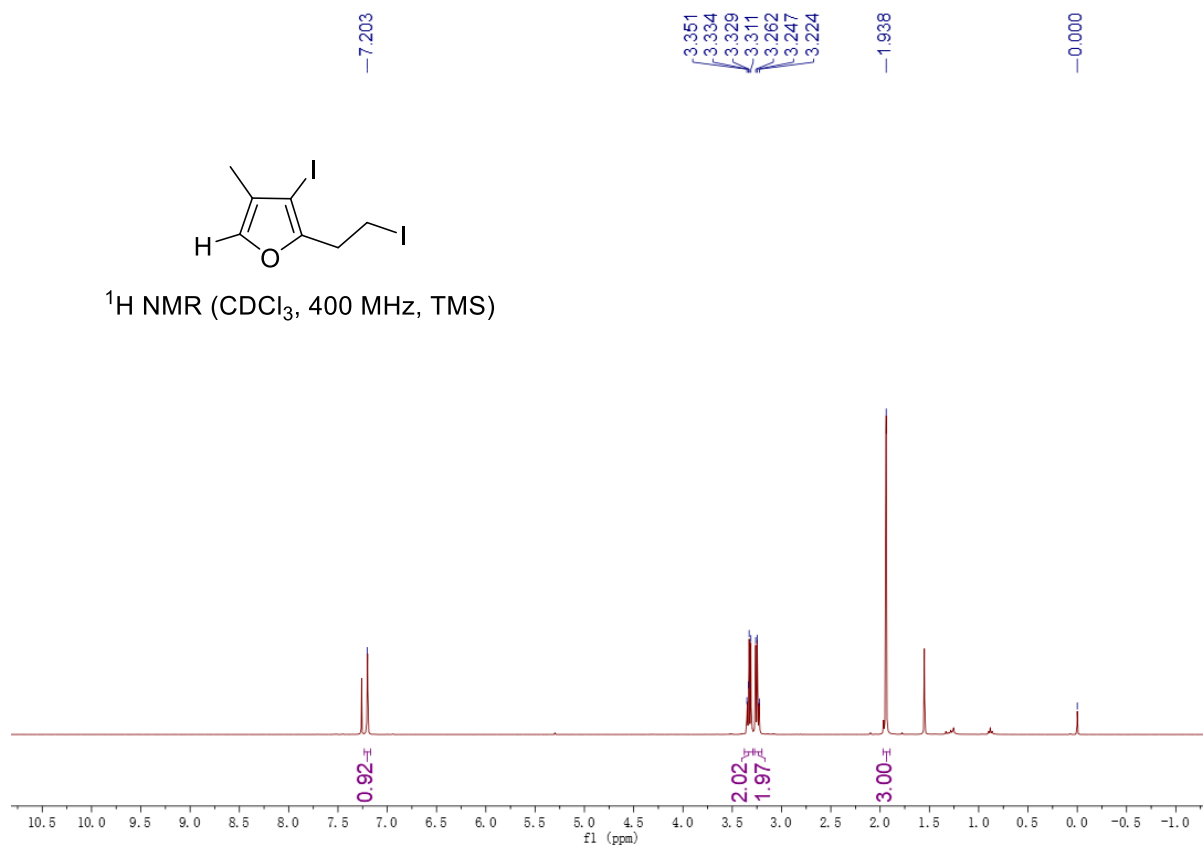


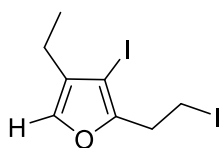
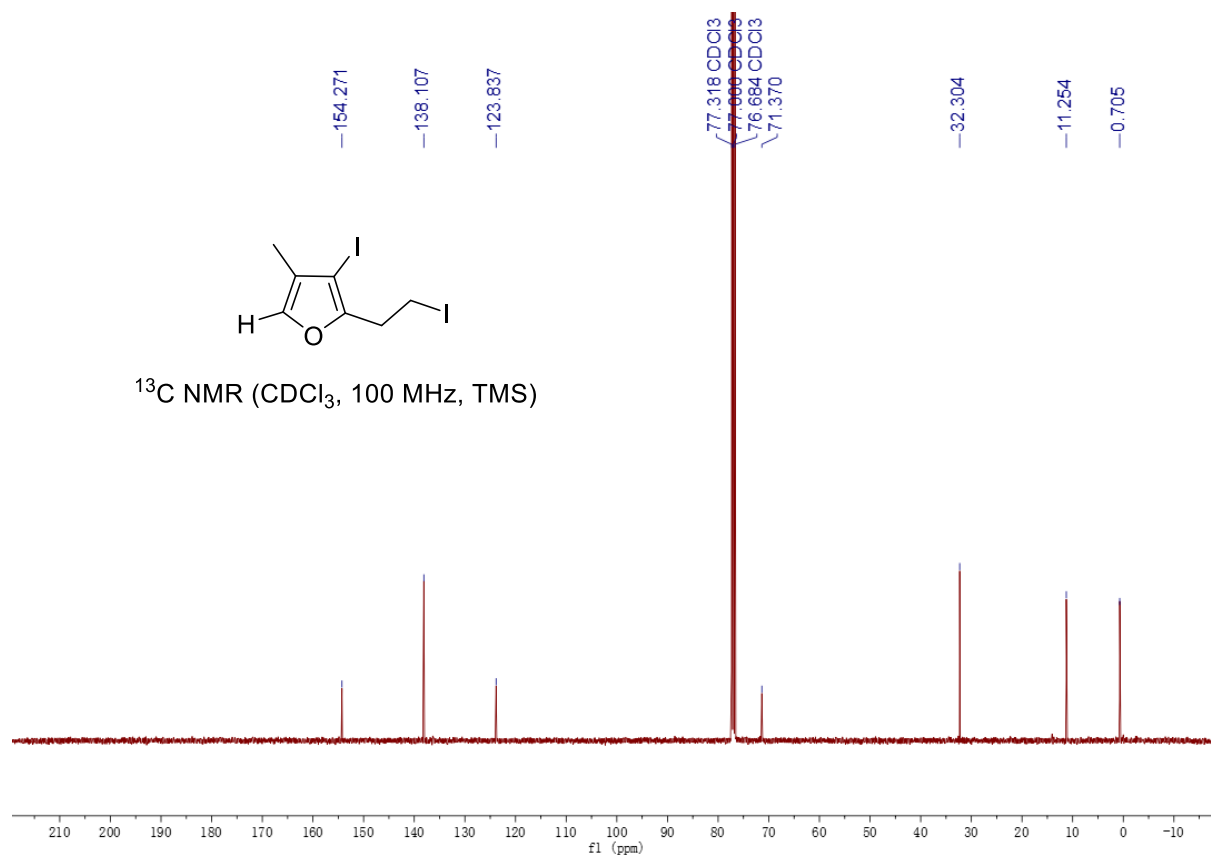
9. Spectroscopic data of products 6.



3-iodo-2-(2-iodoethyl)-4-methylfuran (6a)

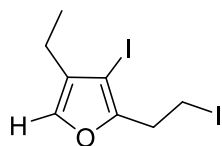
A colorless oil, 27.5 mg, 76% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 7.20 (s, 1H), 3.38 - 3.29 (m, 2H), 3.27 - 3.20 (m, 2H), 1.94 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 154.3, 138.1, 123.8, 71.4, 32.3, 11.3, 0.7. IR (Acetone) ν 2936, 2924, 2853, 1611, 1589, 1497, 1457, 1356, 1310, 1272, 1250, 1230, 1214, 1150, 1058, 1029, 959, 823, 788, 744, 700 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_7\text{H}_8\text{I}_2\text{ONa}$ ($\text{M}+\text{Na}$): 384.8562, Found: 384.8673.



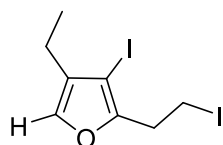
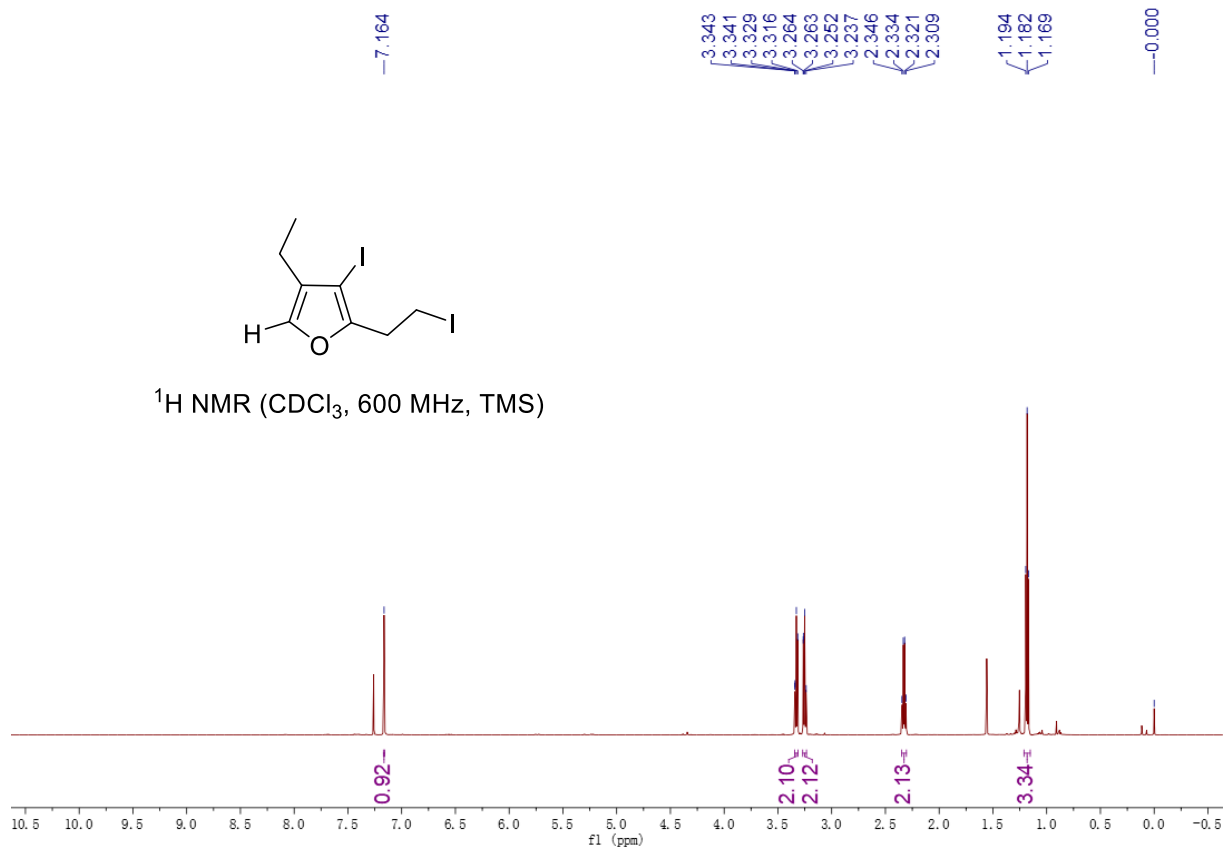


4-ethyl-3-iodo-2-(2-iodoethyl)furan (6b)

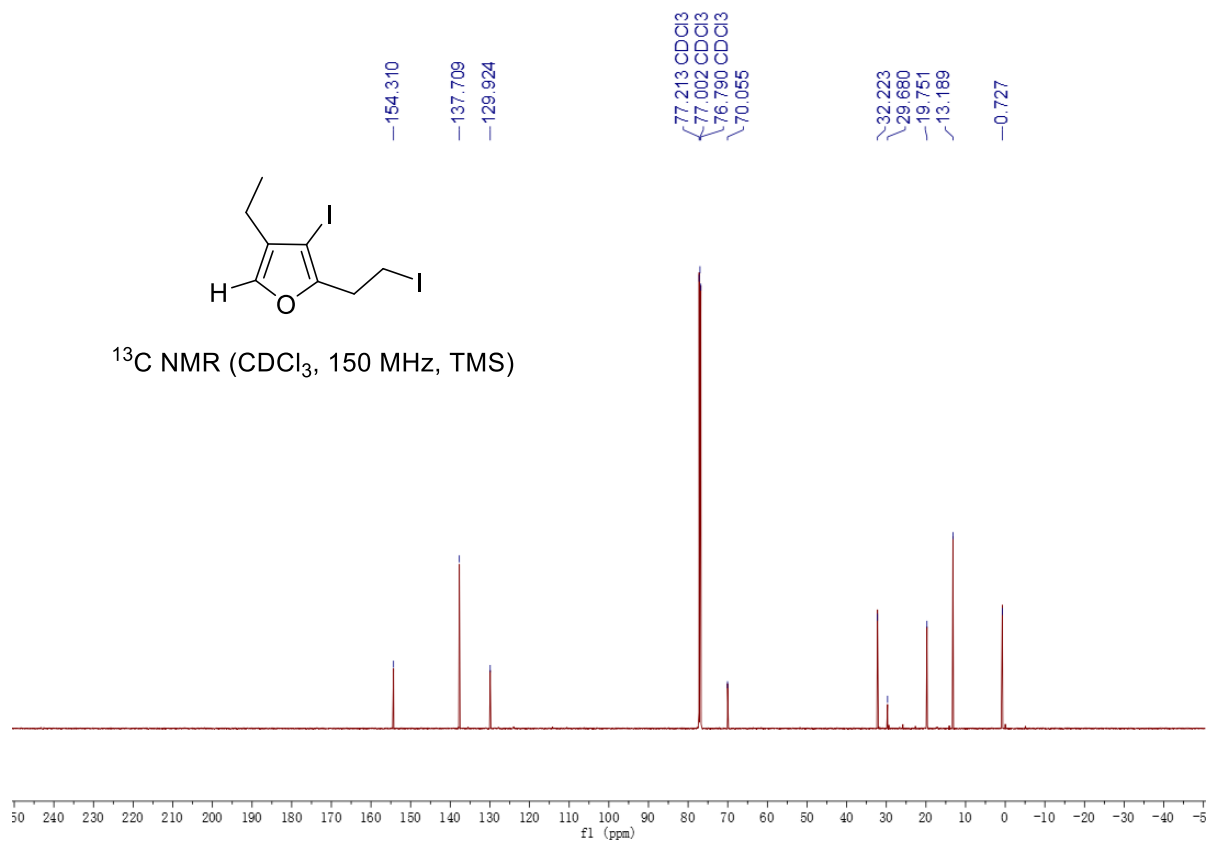
A colorless oil, 27.1 mg, 72% yield. ^1H NMR (CDCl₃, TMS, 600 MHz) δ 7.16 (s, 1H), 3.35 - 3.31 (m, 2H), 3.27 - 3.23 (m, 2H), 2.33 (q, $J = 7.5$ Hz, 2H), 1.18 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (CDCl₃, TMS, 150 MHz) δ 154.3, 137.7, 129.9, 70.1, 32.2, 29.7, 19.8, 13.2, 0.7. IR (Acetone) ν 2972, 2929, 2892, 1735, 1484, 1247, 1086, 1044, 879 cm^{-1} . HRMS (ESI) calcd. for C₈H₁₁I₂O (M+H): 376.8899, Found: 376.8912.

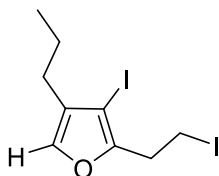


¹H NMR (CDCl₃, 600 MHz, TMS)



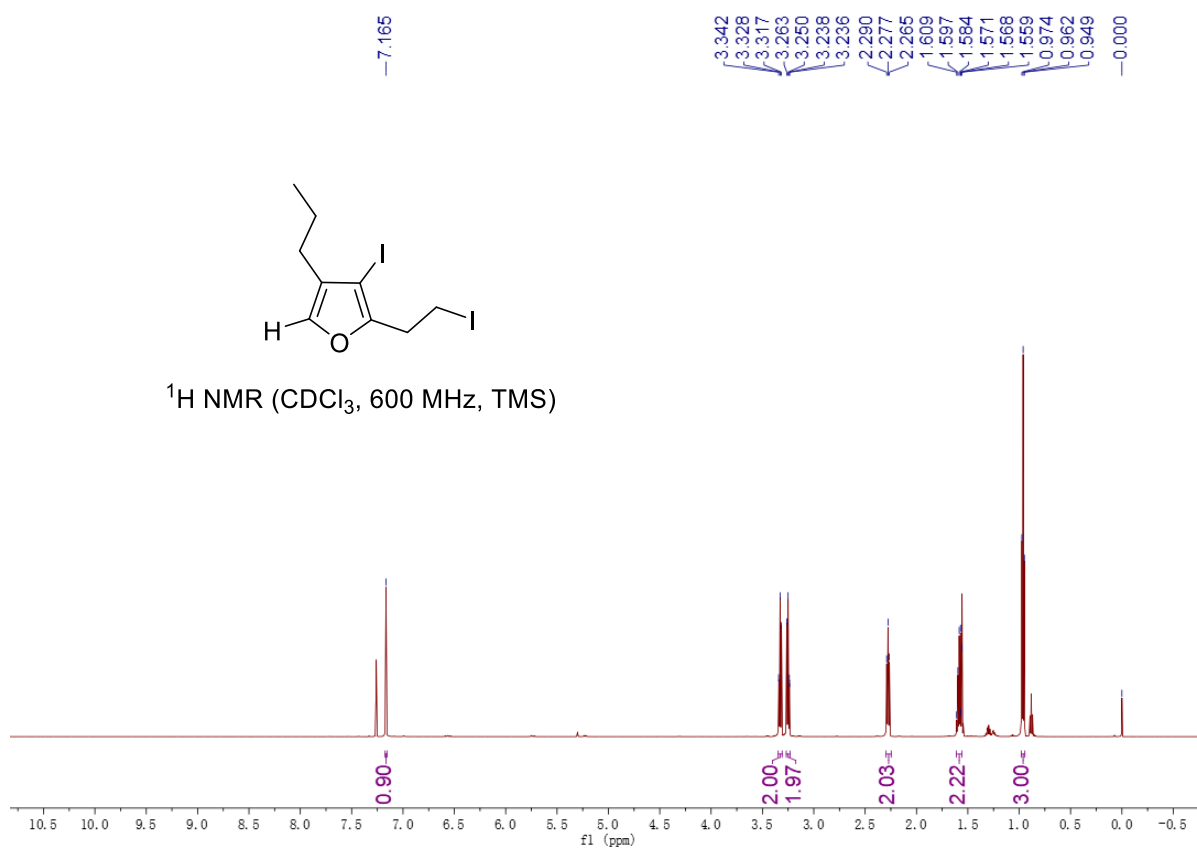
¹³C NMR (CDCl₃, 150 MHz, TMS)

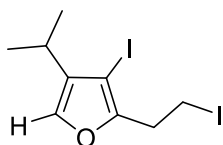
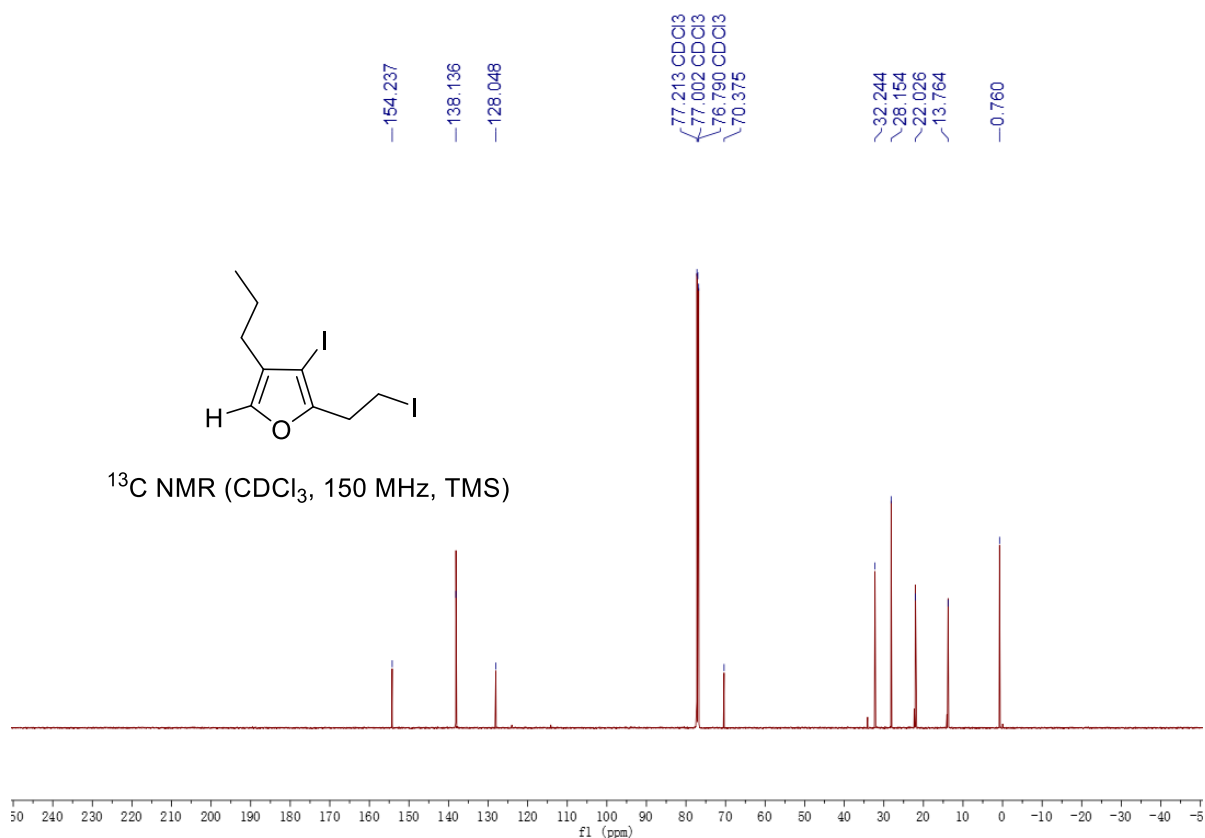




3-iodo-2-(2-iodoethyl)-4-propylfuran (6c)

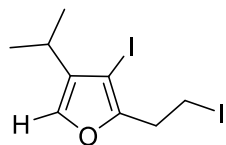
A colorless oil, 27.3 mg, 70% yield ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.16 (s, 1H), 3.35 - 3.31 (m, 2H), 3.27 - 3.23 (m, 2H), 2.28 (t, $J = 7.6$ Hz, 2H), 1.61 - 1.56 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 154.2, 138.1, 128.0, 70.4, 32.2, 28.2, 22.0, 13.8, 0.8. IR (Acetone) ν 2958, 2890, 1735, 1462, 1445, 1362, 1342, 1243, 1035, 904, 811 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_9\text{H}_{12}\text{I}_2\text{ONa}$ ($\text{M}+\text{Na}$): 412.8875, Found: 412.8903.



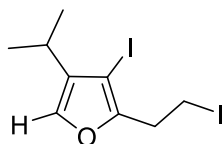
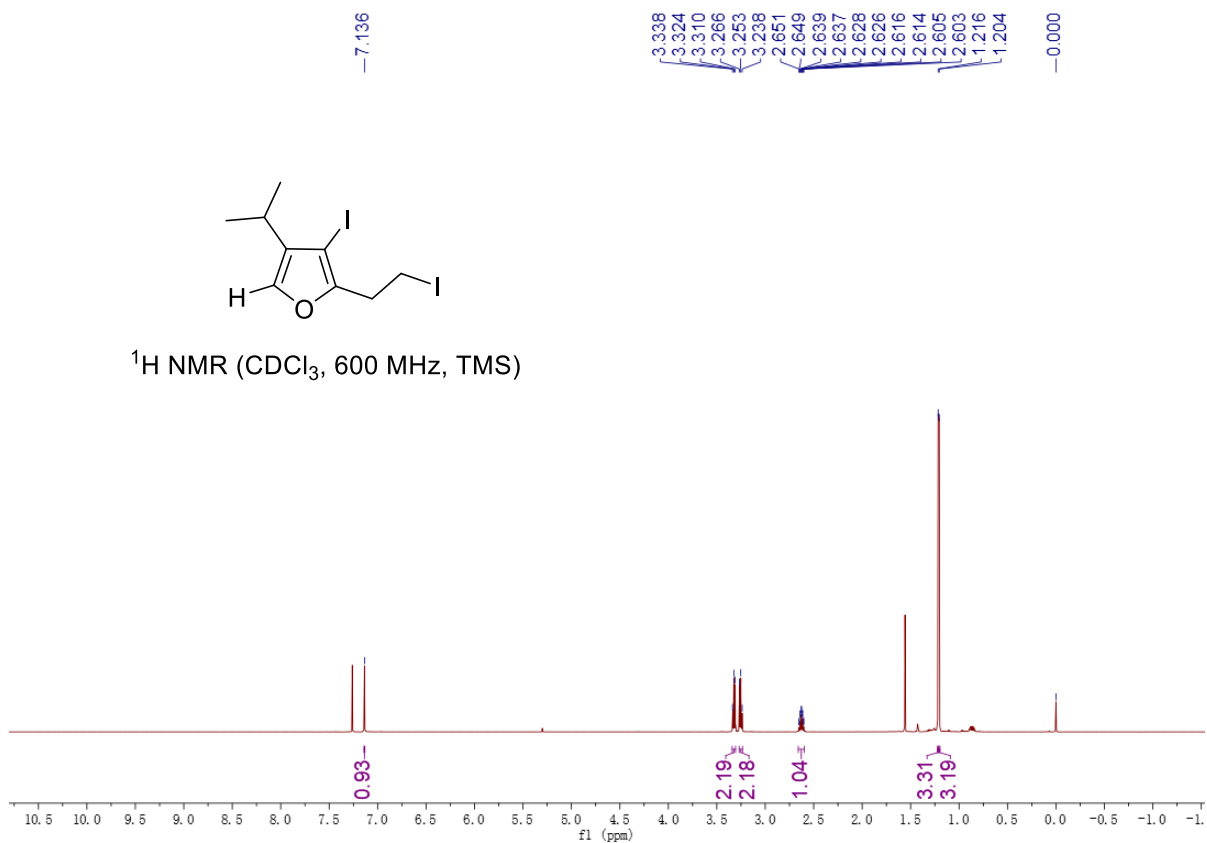


3-iodo-2-(2-iodoethyl)-4-isopropylfuran (6d)

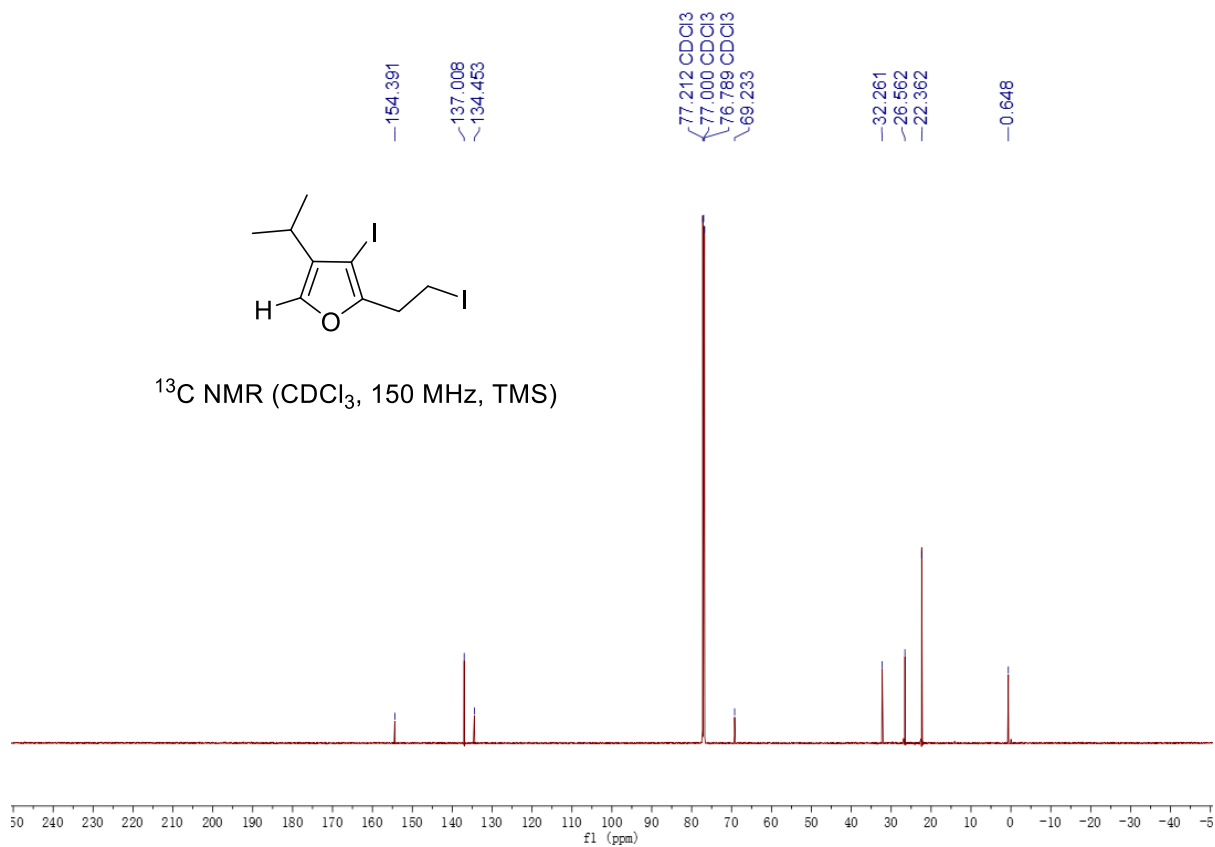
A colorless oil, 25.7 mg, 66% yield. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.14 (s, 1H), 3.34 - 3.31 (m, 2H), 3.27 - 3.23 (m, 2H), 2.66 - 2.60 (m, 1H), 1.22 (s, 3H), 1.20 (s, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 154.4, 137.0, 134.5, 69.2, 32.3, 26.6, 22.4, 0.6. IR (Acetone) ν 2969, 2890, 1734, 1458, 1341, 1240, 1035, 896, 809 764, 736 cm⁻¹. HRMS (ESI) calcd. for C₉H₁₃I₂O (M+H): 390.9065, Found: 390.9143.

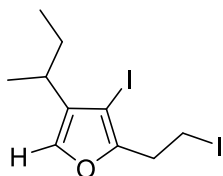


¹H NMR (CDCl₃, 600 MHz, TMS)



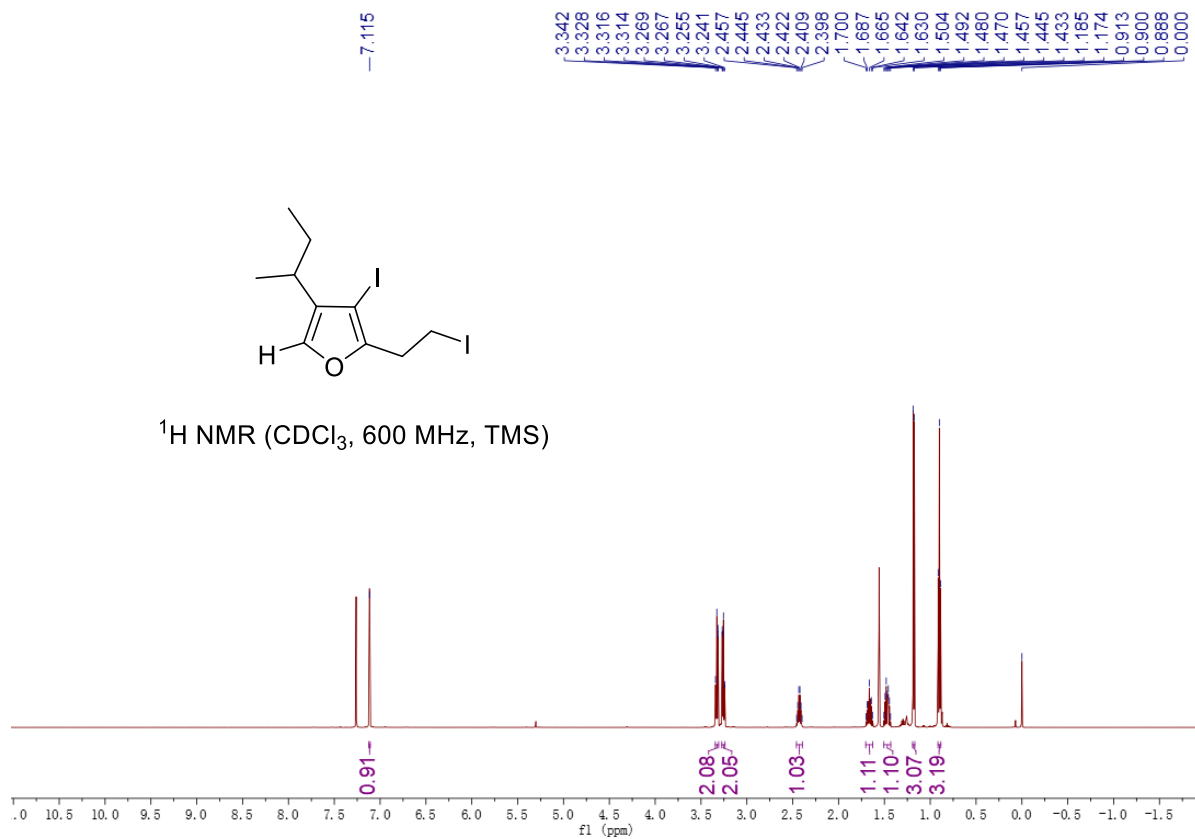
¹³C NMR (CDCl₃, 150 MHz, TMS)

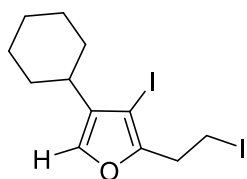
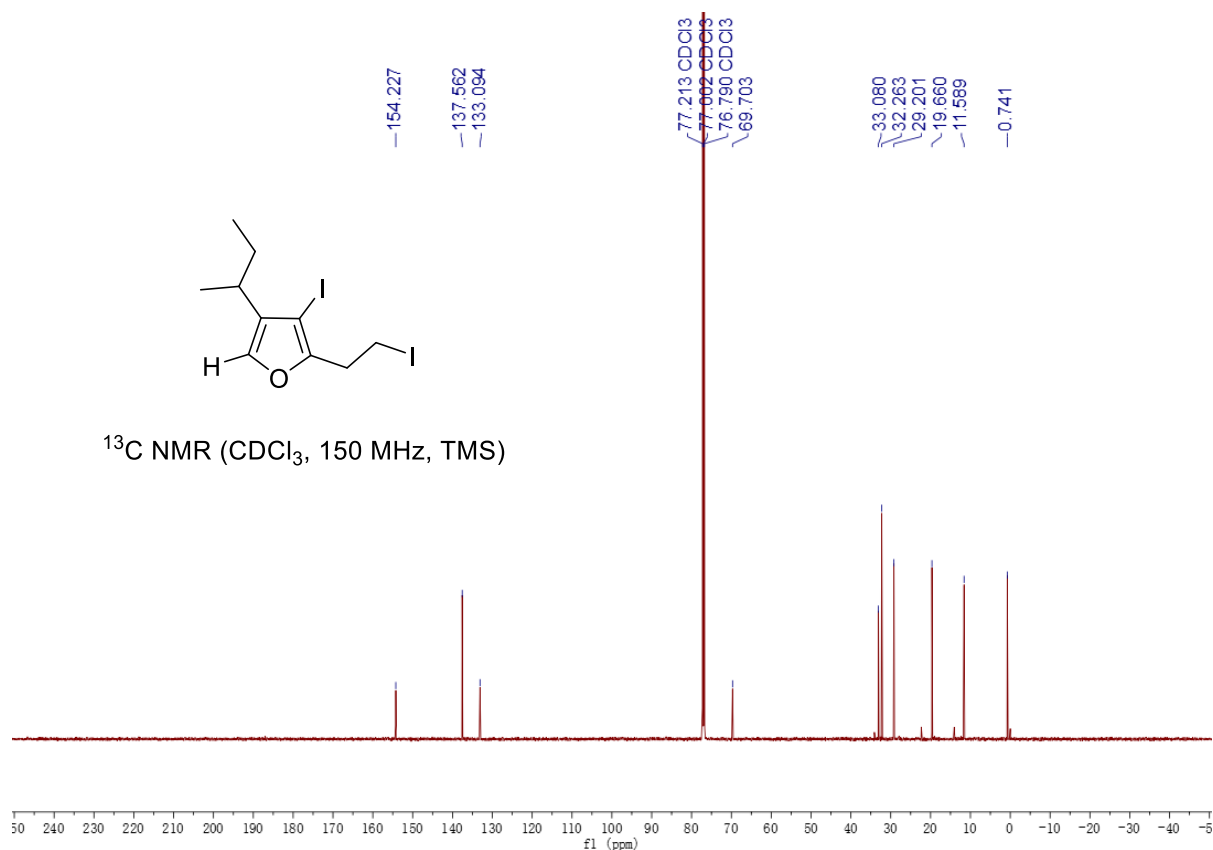




4-(sec-butyl)-3-iodo-2-(2-iodoethyl)furan (6e)

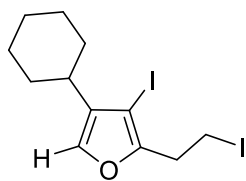
A colorless oil, 27.5 mg, 68% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.11 (s, 1H), 3.34 - 3.31 (m, 2H), 3.27 - 3.24 (m, 2H), 2.46 - 2.39 (m, 1H), 1.70 - 1.63 (m, 1H), 1.51 - 1.43 (m, 1H), 1.18 (d, $J = 6.9$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 154.2, 137.6, 133.1, 69.7, 33.1, 32.3, 29.2, 19.7, 11.6, 0.7. IR (Acetone) ν 3021, 2960, 2919, 1735, 1456, 1445, 1361, 1342, 1243, 1035, 807, 770 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{15}\text{I}_2\text{O}$ ($\text{M}+\text{H}$): 404.9212, Found: 404.9352.



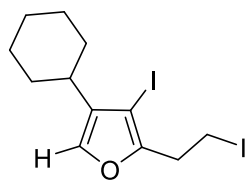
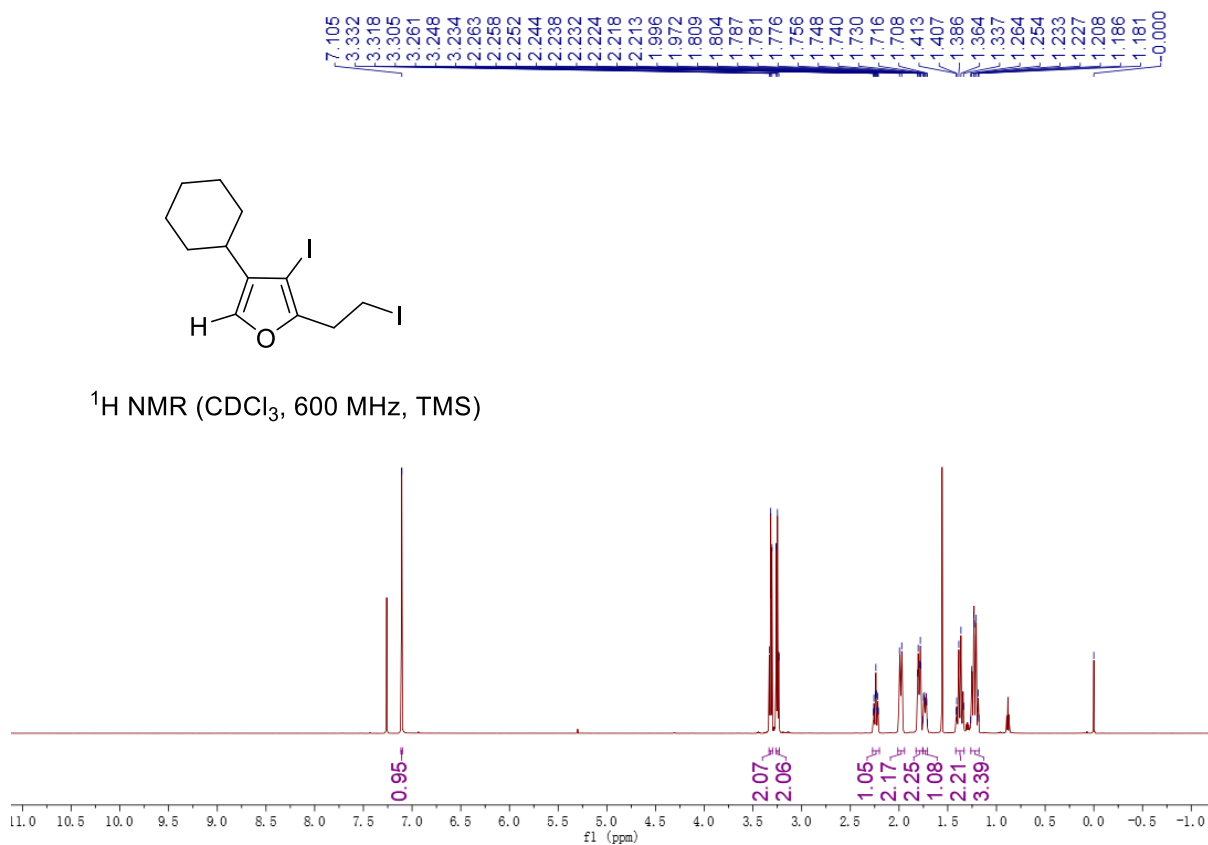


4-cyclohexyl-3-iodo-2-(2-iodoethyl)furan (**6f**)

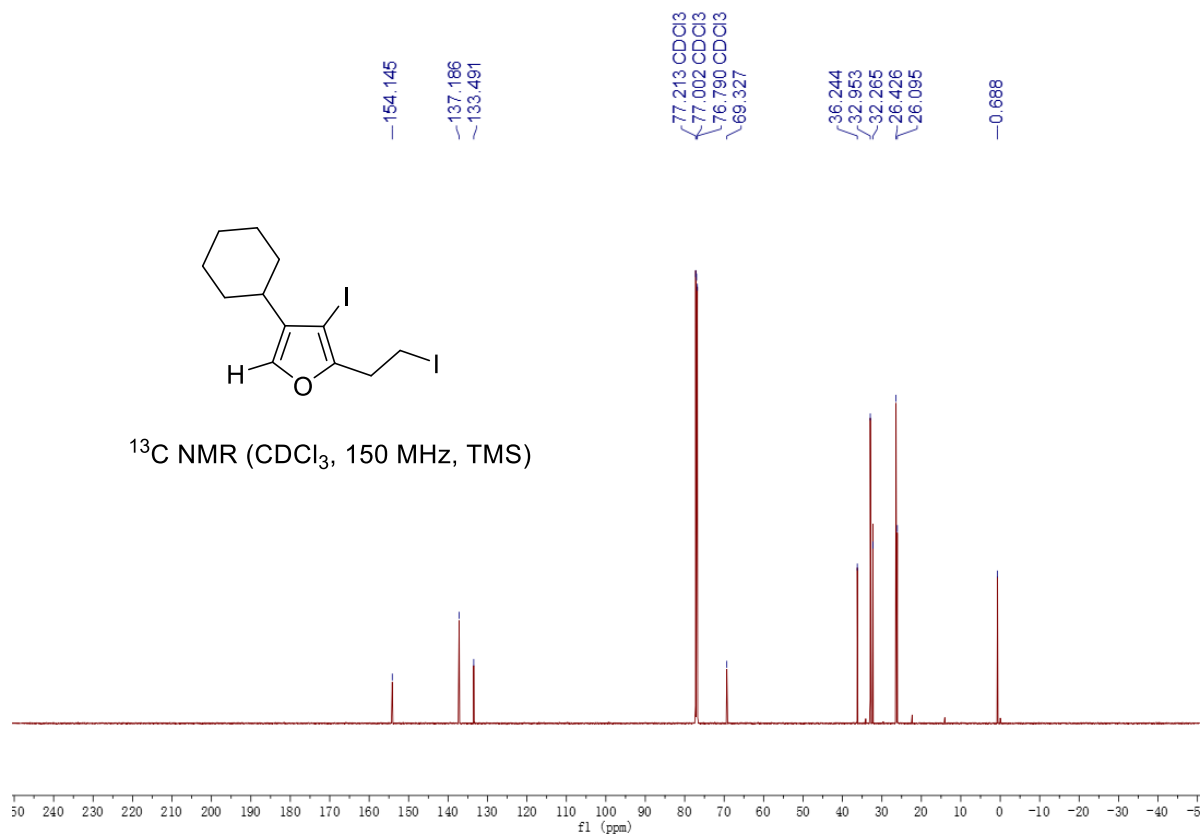
A colorless oil, 71.1 mg, 65% yield. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 7.11 (s, 1H), 3.33 - 3.30 (m, 2H), 3.27 - 3.23 (m, 2H), 2.24 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.01-1.94 (m, 2H), 1.83 - 1.75 (m, 2H), 1.76 - 1.71 (m, 1H), 1.42 - 1.33 (m, 2H), 1.26 - 1.18 (m, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 154.1, 137.2, 133.5, 69.3, 36.2, 33.0, 32.3, 26.4, 26.1, 0.7. IR (Acetone) ν 2936, 2924, 2853, 1611, 1589, 1497, 1457, 1356, 1250, 1230, 1214, 1029, 959, 823, 788, 744, 700 cm⁻¹. HRMS (ESI) calcd. for C₁₂H₁₆I₂ONa (M+Na): 452.9188, Found: 452.9236.



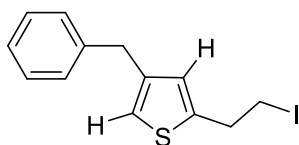
¹H NMR (CDCl₃, 600 MHz, TMS)



¹³C NMR (CDCl₃, 150 MHz, TMS)

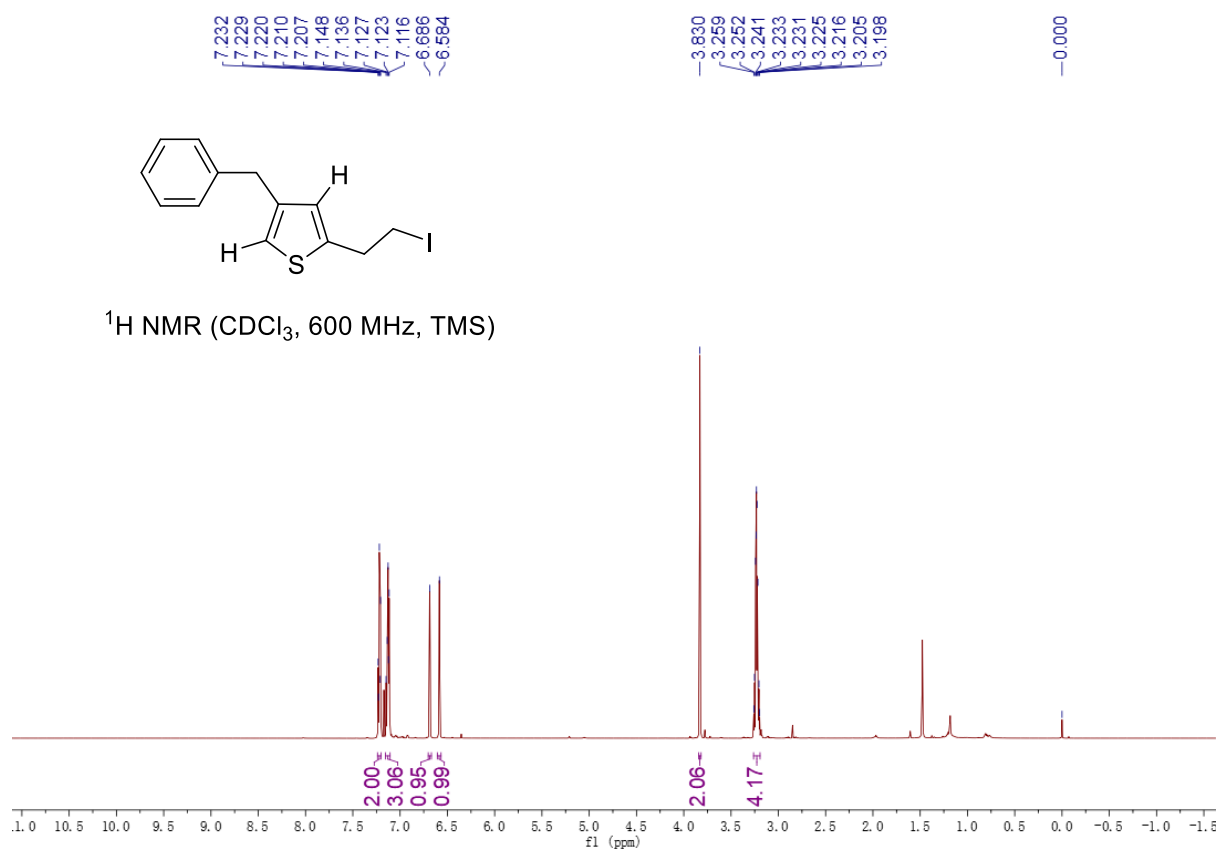


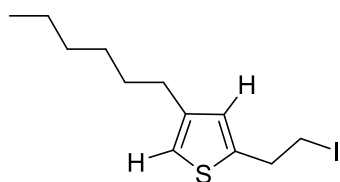
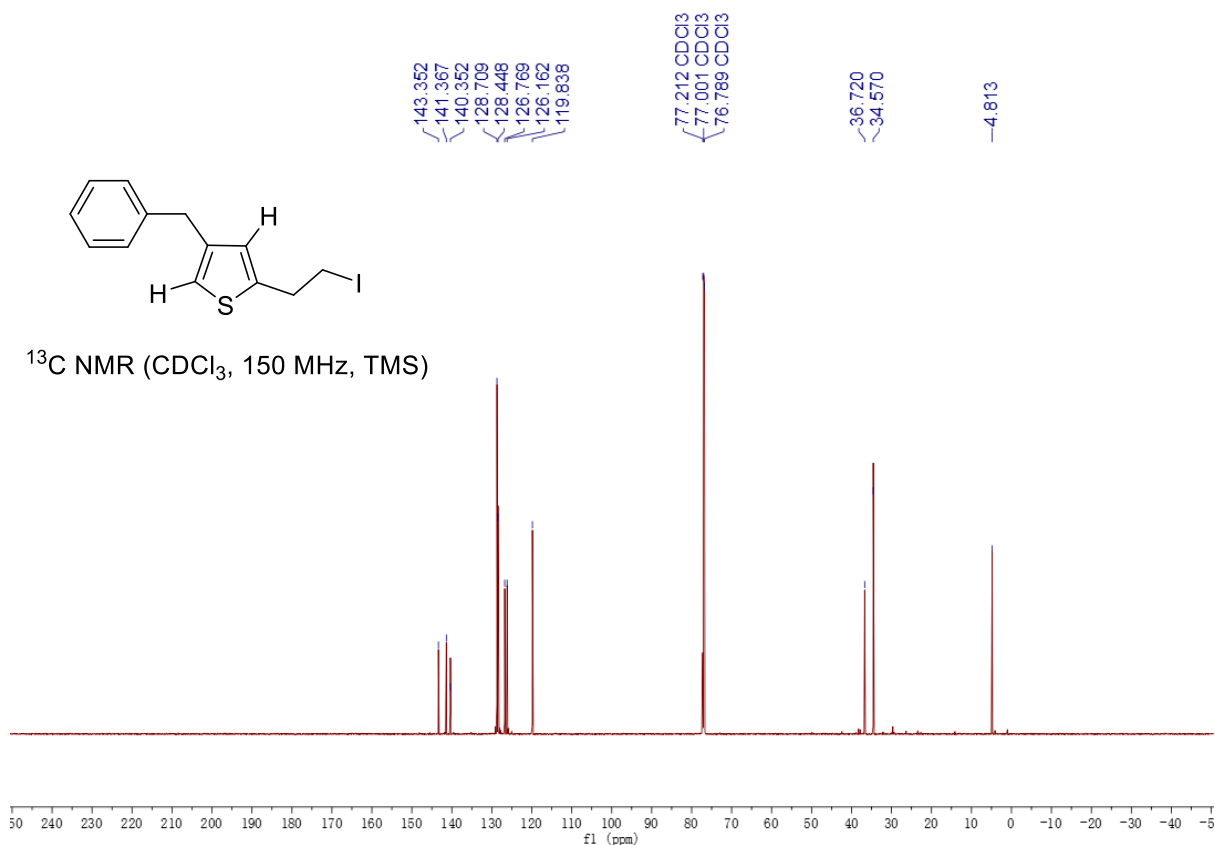
9. Spectroscopic data of products 8.



4-benzyl-2-(2-iodoethyl)thiophene (8a)

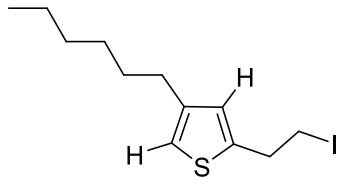
A colorless oil, 27.9 mg, 85% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.22 (t, $J = 7.5$ Hz, 2H), 7.13 (dd, $J = 12.5, 7.2$ Hz, 3H), 6.69 (s, 1H), 6.58 (s, 1H), 3.83 (s, 2H), 3.26 - 3.19 (m, 4H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 143.4, 141.4, 140.3, 128.7, 128.4, 126.8, 126.2, 119.8, 36.7, 34.6, 4.8. IR (Acetone) ν 927, 961, 1245, 1730, 1978, 2027, 2174, 2920 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{13}\text{IS}$ (M^+): 327.9785, Found: 327.9777.



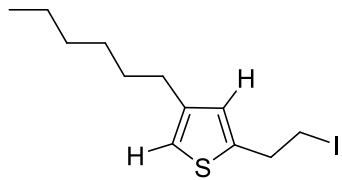
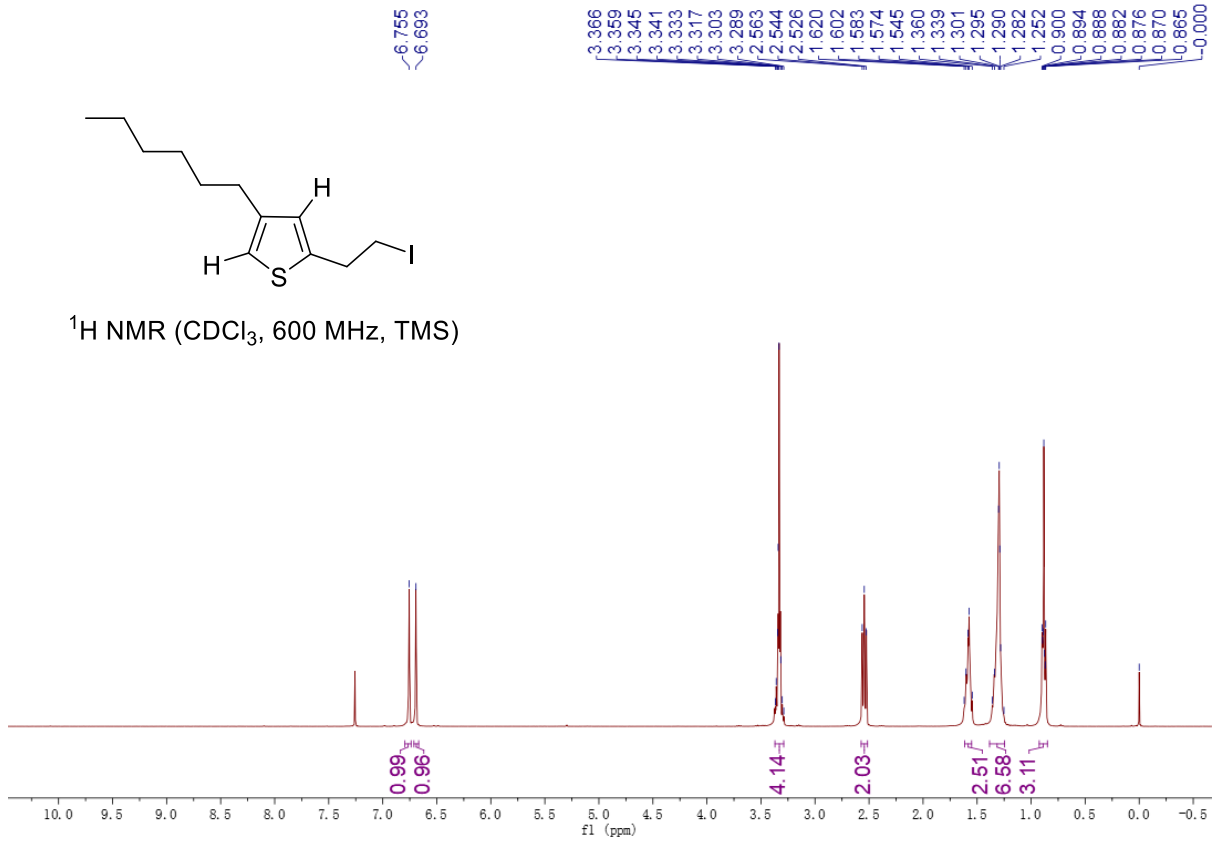


4-hexyl-2-(2-iodoethyl)thiophene (8b)

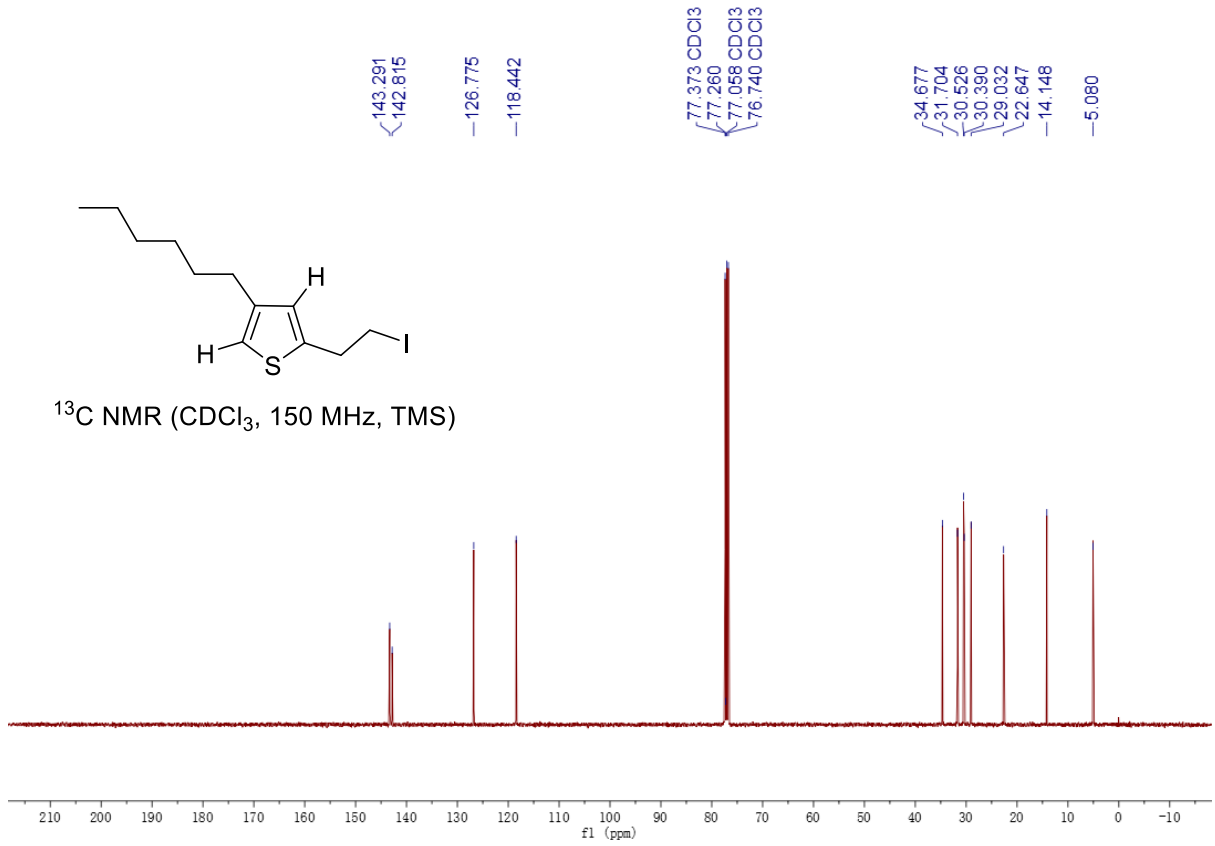
A colorless oil, 28.7 mg, 89% yield. ¹H NMR (CDCl₃, TMS, 600 MHz) δ 6.75 (s, 1H), 6.69 (s, 1H), 3.37 - 3.29 (m, 4H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.61 - 1.55 (m, 3H), 1.38 - 1.25 (m, 7H), 0.92 - 0.85 (m, 3H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 143.2, 142.8, 126.7, 118.4, 34.6, 31.6, 30.5, 30.3, 29.0, 22.6, 14.1, 5.0. IR (Acetone) ν 927, 961, 1245, 1730, 1978, 2027, 2174, 2920 cm⁻¹. HRMS (EI) calcd. for C₁₂H₁₉IS (M⁺): 322.0255, Found: 322.0247.

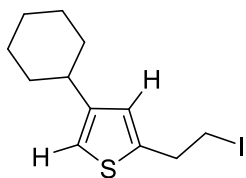


$^1\text{H NMR}$ (CDCl_3 , 600 MHz, TMS)



$^{13}\text{C NMR}$ (CDCl_3 , 150 MHz, TMS)

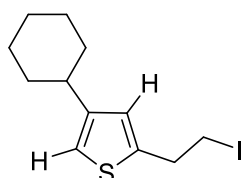




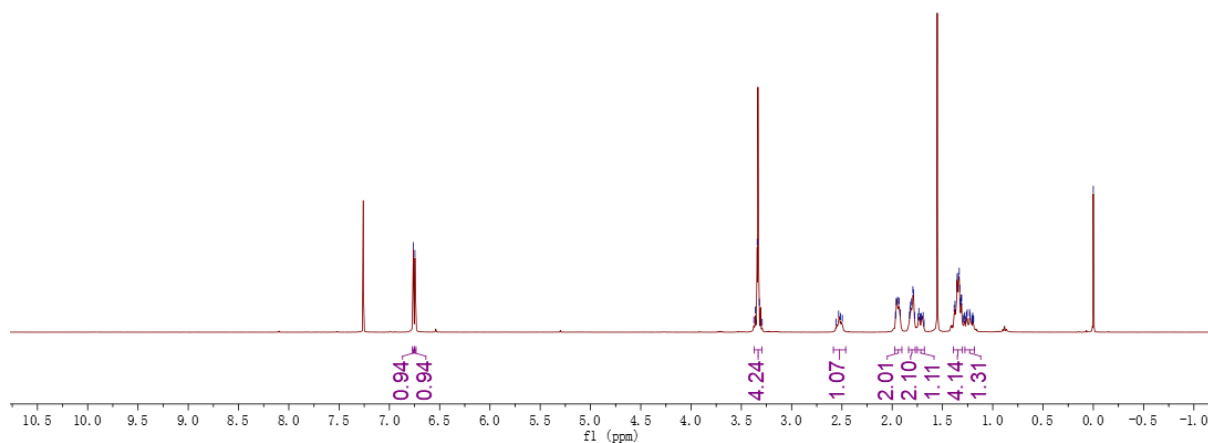
4-cyclohexyl-2-(2-iodoethyl)thiophene (8c)

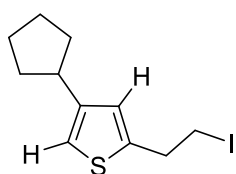
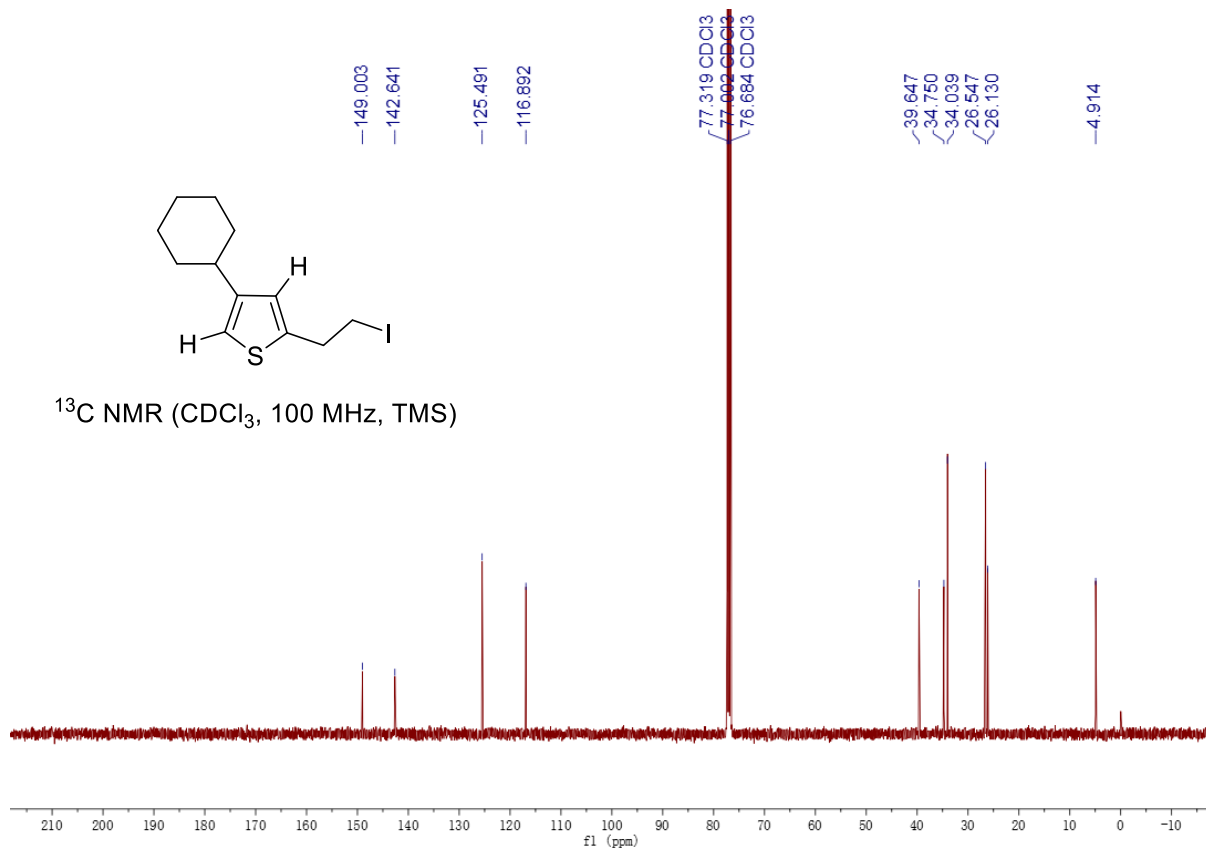
A colorless oil, 25.6 mg, 80% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 6.76 (s, 1H), 6.75 (s, 1H), 3.37 - 3.29 (m, 4H), 2.58 - 2.46 (m, 1H), 1.94 (d, $J = 5.7$ Hz, 2H), 1.84 - 1.77 (m, 2H), 1.75 - 1.68 (m, 1H), 1.39 - 1.30 (m, 4H), 1.28 - 1.18 (m, 1H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 149.0, 142.6, 125.5, 116.9, 39.6, 34.8, 34.0, 26.5, 26.1, 4.9. IR (neat) ν 700, 732, 906, 1074, 1167, 1443, 1602, 2915 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{17}\text{IS}$ (M^+): 320.0098, Found: 320.0090.

6.762
6.746
3.375
3.360
3.342
3.321
3.293
2.560
2.533
2.514
2.496
1.968
1.960
1.946
1.931
1.919
1.828
1.823
1.818
1.807
1.794
1.786
1.776
1.742
1.735
1.723
1.720
1.712
1.692
1.683
1.384
1.375
1.354
1.342
1.333
1.329
1.323
1.317
1.314
1.309
1.294
1.284
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1.227
1.208
1.203
1.199
1.196
1.191
0.000



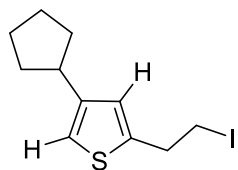
^1H NMR (CDCl_3 , 400 MHz, TMS)



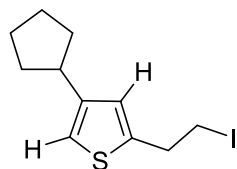
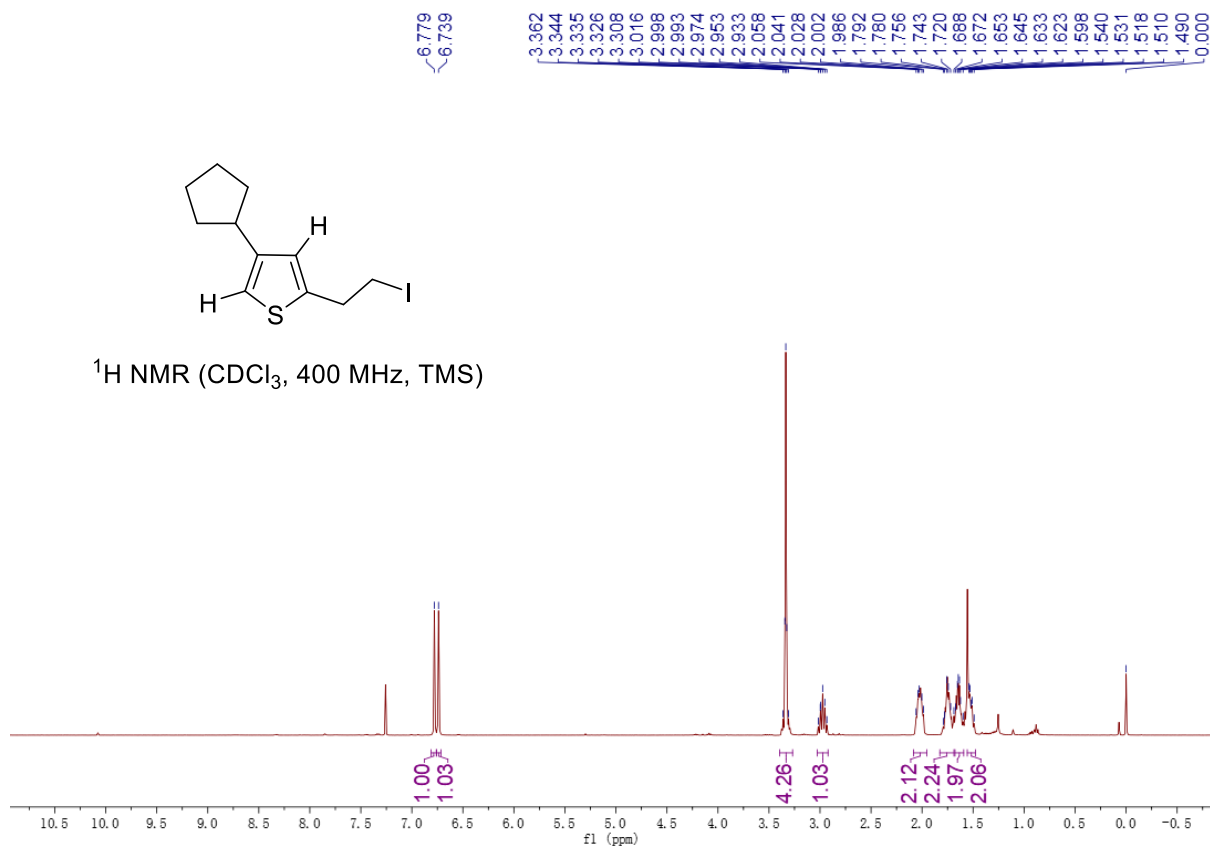


4-cyclopentyl-2-(2-iodoethyl)thiophene (8d)

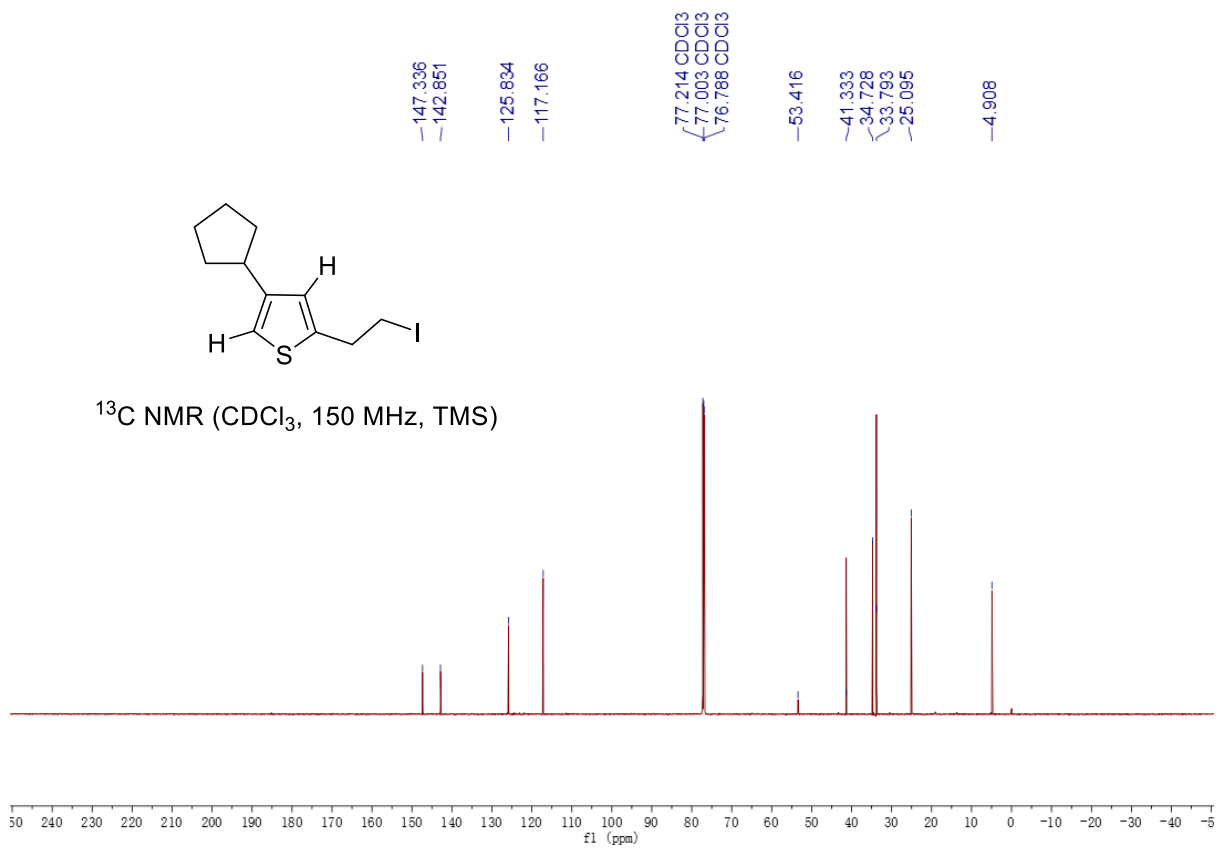
A colorless oil, 25.1 mg, 82% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 6.78 (s, 1H), 6.74 (s, 1H), 3.40 - 3.27 (m, 4H), 3.03 - 2.92 (m, 1H), 2.08 - 1.95 (m, 2H), 1.83 - 1.69 (m, 2H), 1.68 - 1.59 (m, 2H), 1.56 - 1.48 (m, 2H). ¹³C NMR (CDCl₃, TMS, 150 MHz) δ 147.3, 142.9, 125.8, 117.2, 53.4, 41.3, 34.7, 33.8, 25.1, 4.9. IR (Acetone) ν 930, 965, 1233, 1720, 2013, 2177, 2900 cm⁻¹.

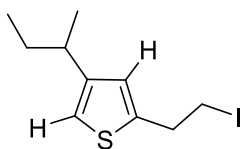


¹H NMR (CDCl₃, 400 MHz, TMS)



¹³C NMR (CDCl₃, 150 MHz, TMS)



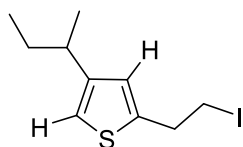


4-(sec-butyl)-2-(2-iodoethyl)thiophene (8e)

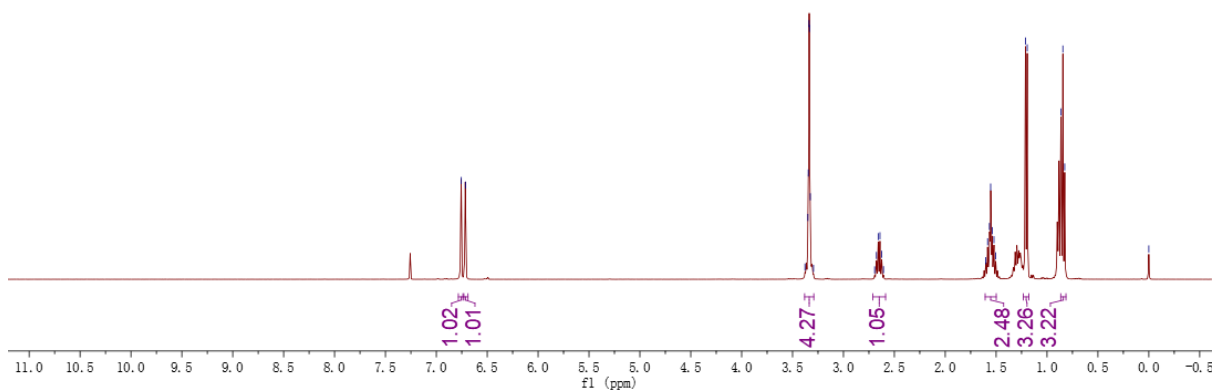
A colorless oil, 25.1 mg, 88% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 6.75 (s, 1H), 6.71 (s, 1H), 3.38 - 3.29 (m, 4H), 2.71 - 2.59 (m, 1H), 1.61 - 1.50 (m, 2H), 1.20 (d, $J = 6.9$ Hz, 3H), 0.84 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 148.5, 142.7, 125.3, 117.5, 36.9, 34.7, 34.1, 30.7, 22.3, 21.0, 14.1, 11.9, 5.1. IR (Acetone) ν 937, 980, 1223, 1713, 2003, 2167, 2912 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{15}\text{IS}$ (M^+): 293.9941, Found: 293.9934.

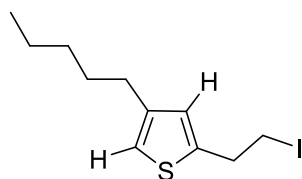
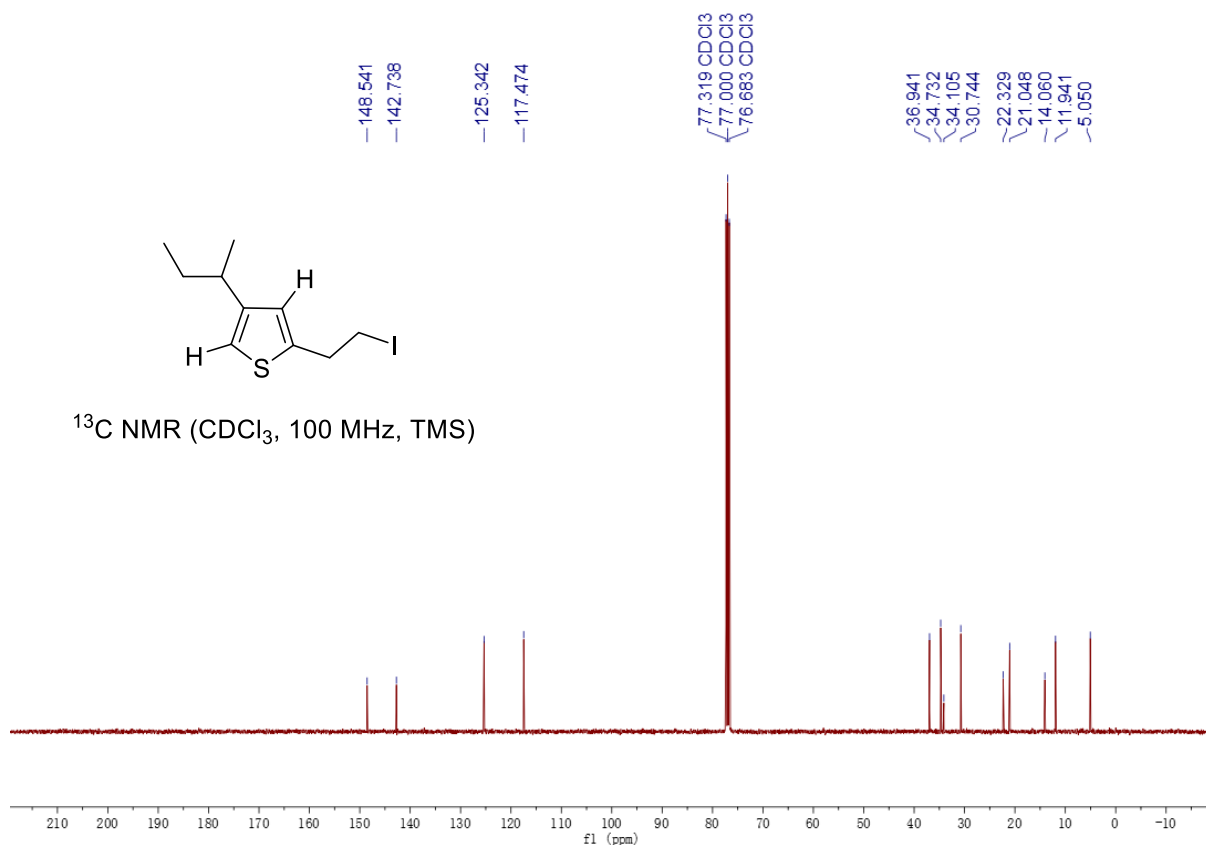
6.755
6.714

3.378
3.350
3.346
3.338
3.334
3.326
3.294
2.693
2.676
2.659
2.641
2.624
2.607
1.603
1.584
1.566
1.554
1.539
1.521
1.504
1.212
1.194
0.863
0.844
0.826
0.000



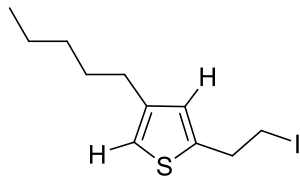
^1H NMR (CDCl_3 , 400 MHz, TMS)



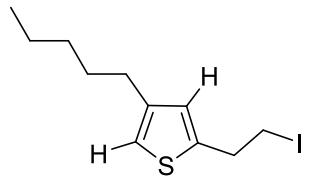
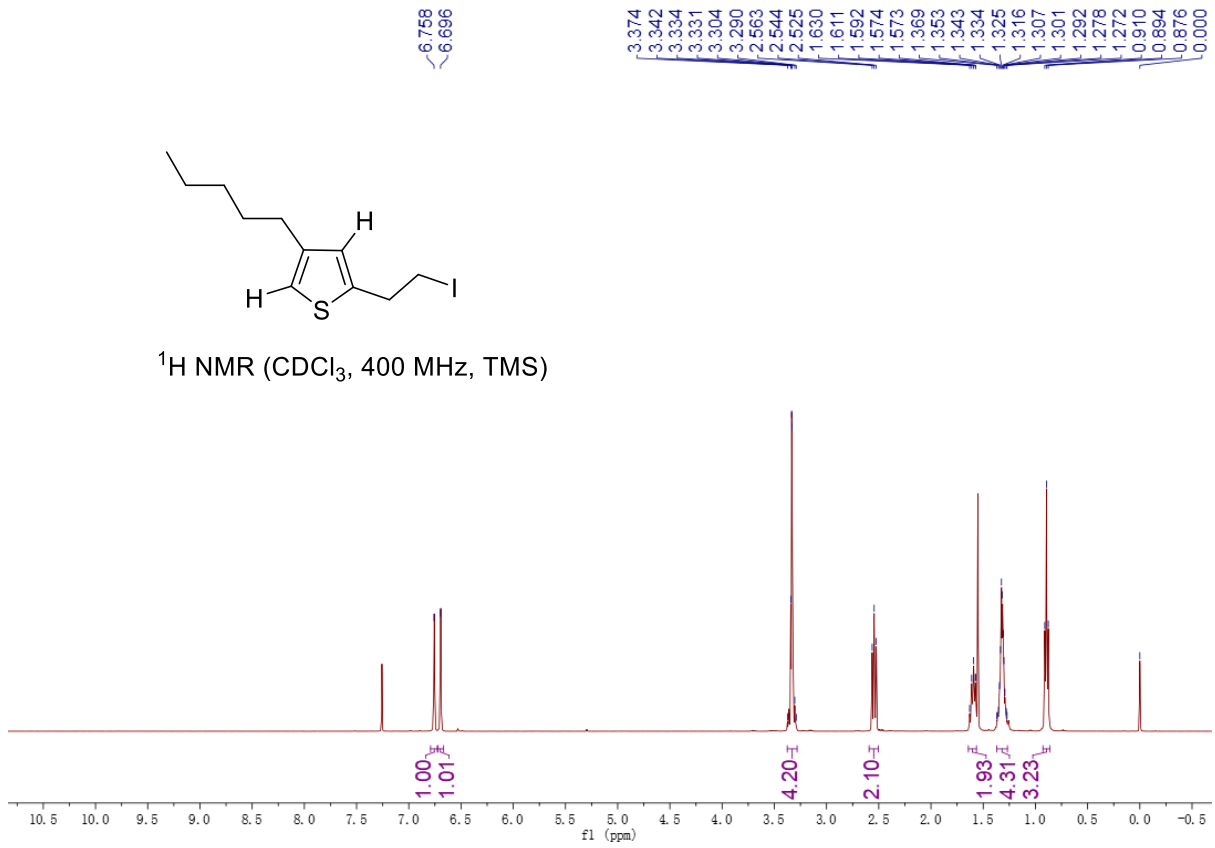


2-(2-iodoethyl)-4-pentylthiophene (8f)

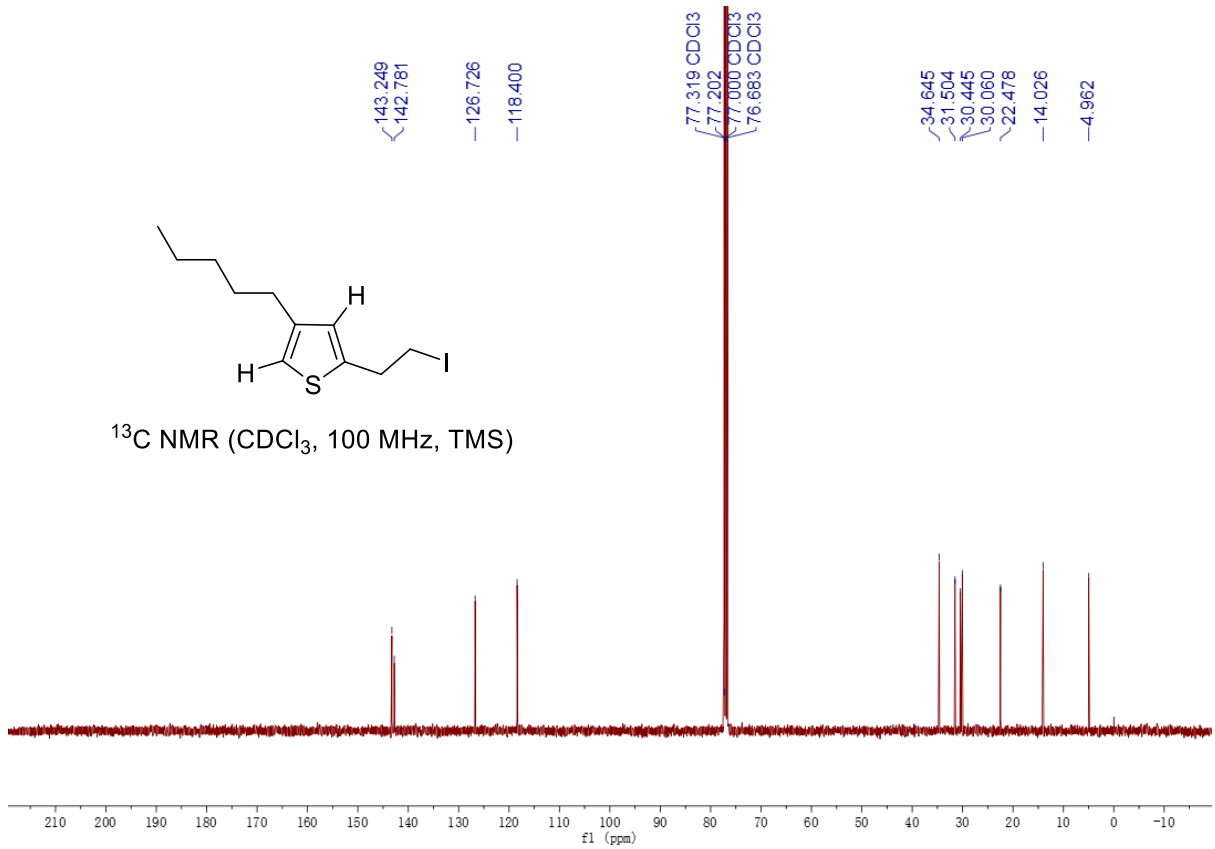
A colorless oil, 25.6 mg, 83% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 6.76 (s, 1H), 6.70 (s, 1H), 3.38 - 3.28 (m, 4H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.64 - 1.56 (m, 2H), 1.37 - 1.27 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 143.2, 142.8, 126.7, 118.4, 76.7, 34.6, 31.5, 30.4, 30.1, 22.5, 14.0, 5.0. IR (Acetone) ν 927, 960, 1263, 1733, 2022, 2155, 2908 cm⁻¹. HRMS (EI) calcd. for C₁₁H₁₇IS (M⁺): 308.0095, Found: 308.0090.

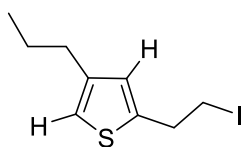


^1H NMR (CDCl_3 , 400 MHz, TMS)



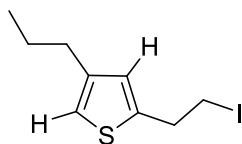
^{13}C NMR (CDCl_3 , 100 MHz, TMS)



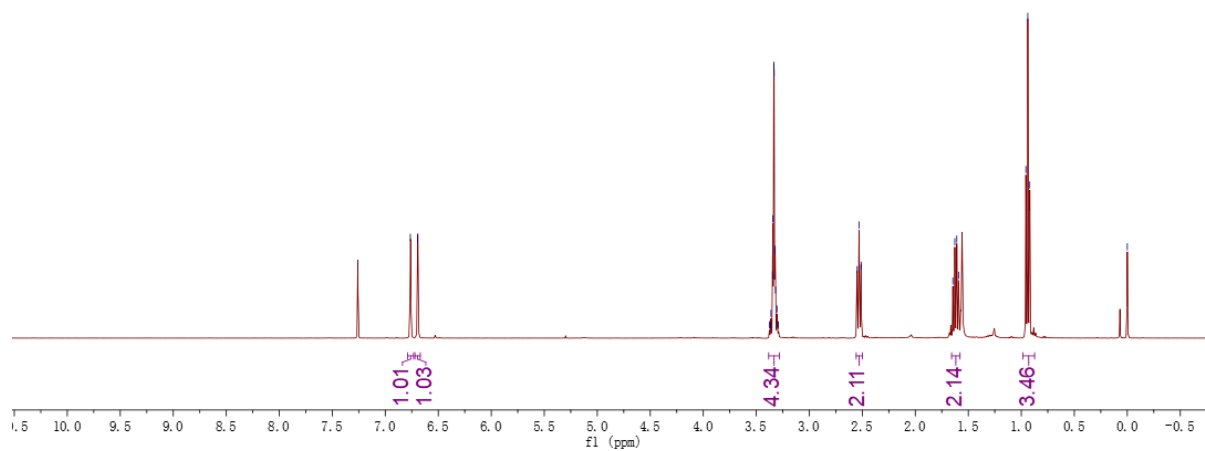


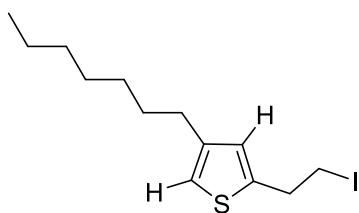
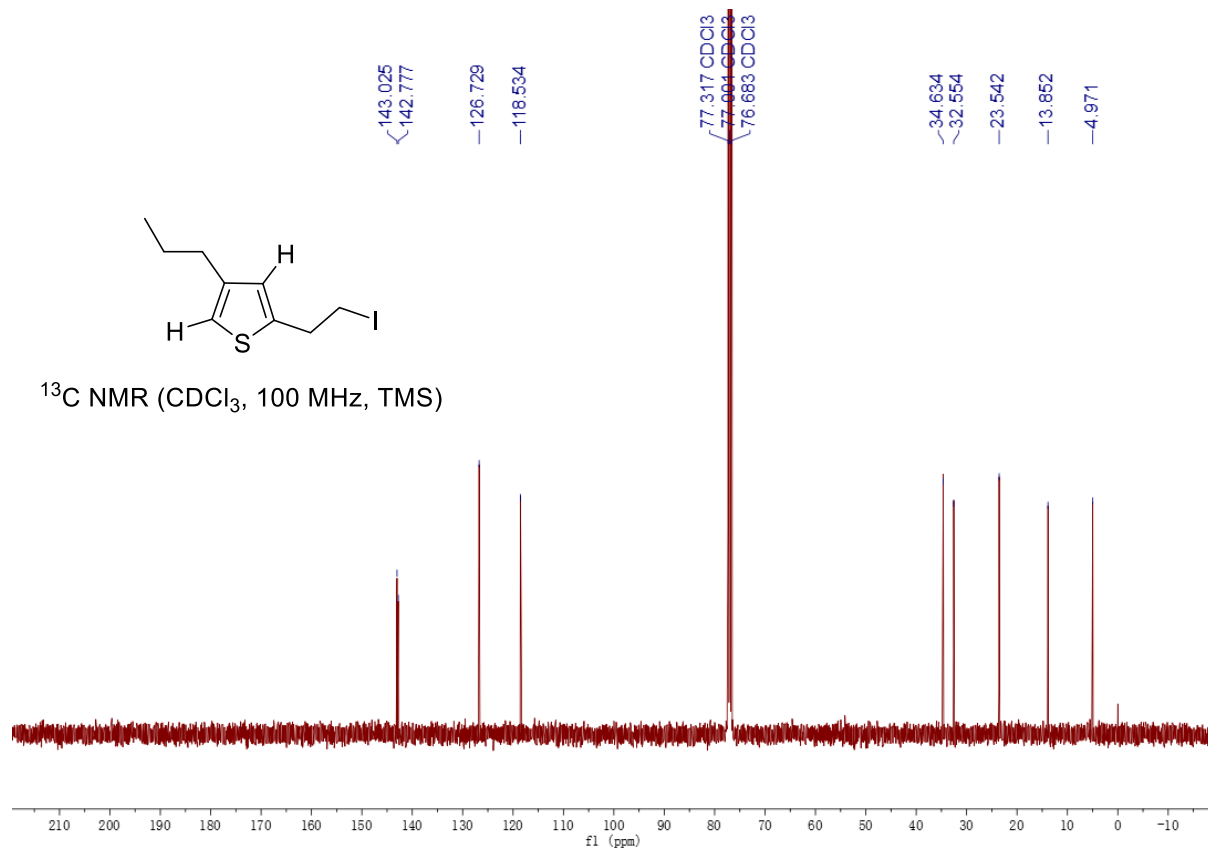
2-(2-iodoethyl)-4-propylthiophene (8g)

A colorless oil, 26.1 mg, 93% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 6.76 (s, 1H), 6.70 (s, 1H), 3.38 - 3.28 (m, 4H), 2.53 (t, $J = 7.6$ Hz, 2H), 1.66 - 1.58 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , TMS, 100 MHz) δ 143.0, 142.8, 126.7, 118.5, 34.6, 32.6, 23.5, 13.9, 5.0. IR (neat) ν 937, 954, 1241, 1761, 2035, 2124, 2911 cm^{-1} . HRMS (EI) calcd. for $\text{C}_9\text{H}_{13}\text{IS}$ (M^+): 279.9780, Found: 279.9777.



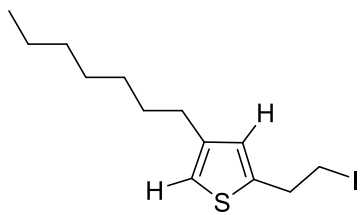
^1H NMR (CDCl_3 , 400 MHz, TMS)



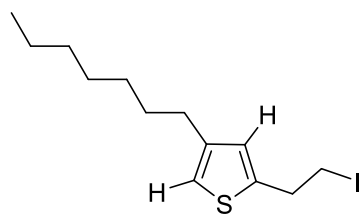
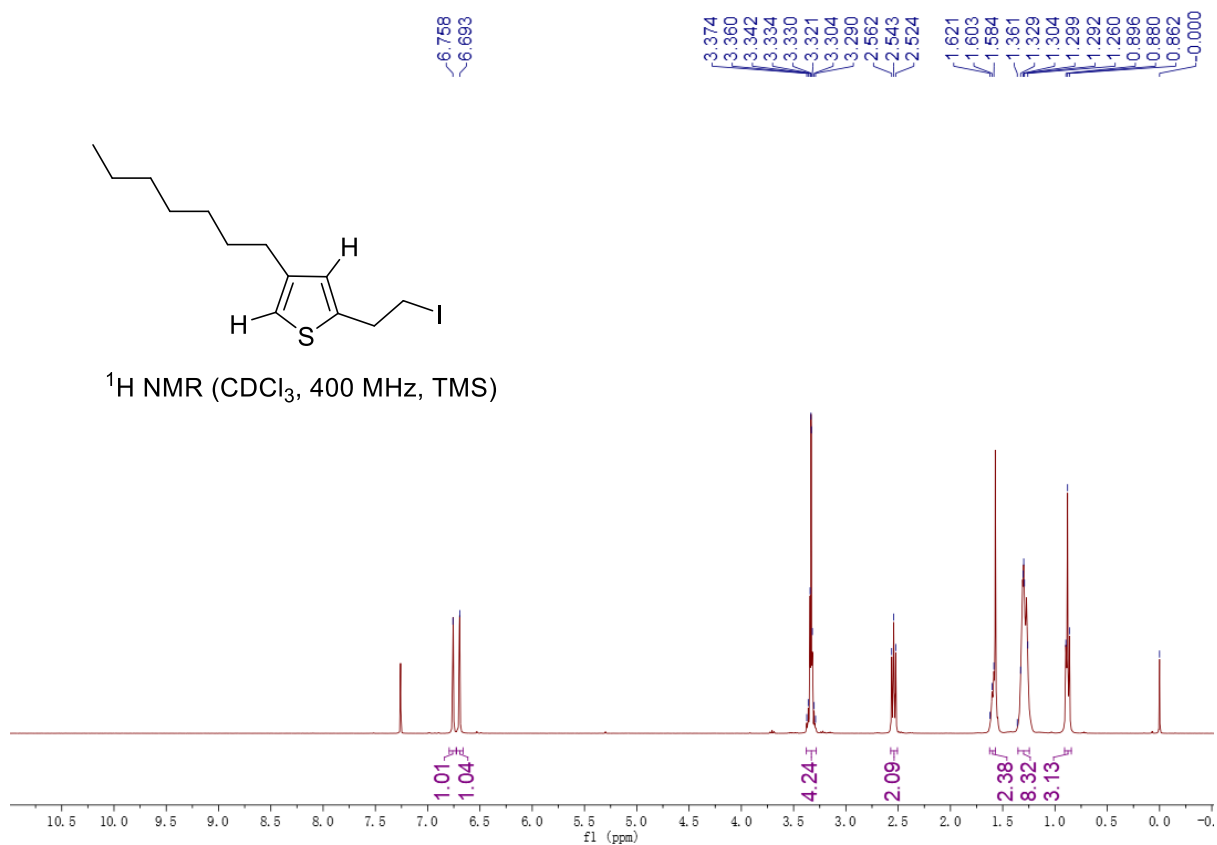


4-heptyl-2-(2-iodoethyl)thiophene (8h)

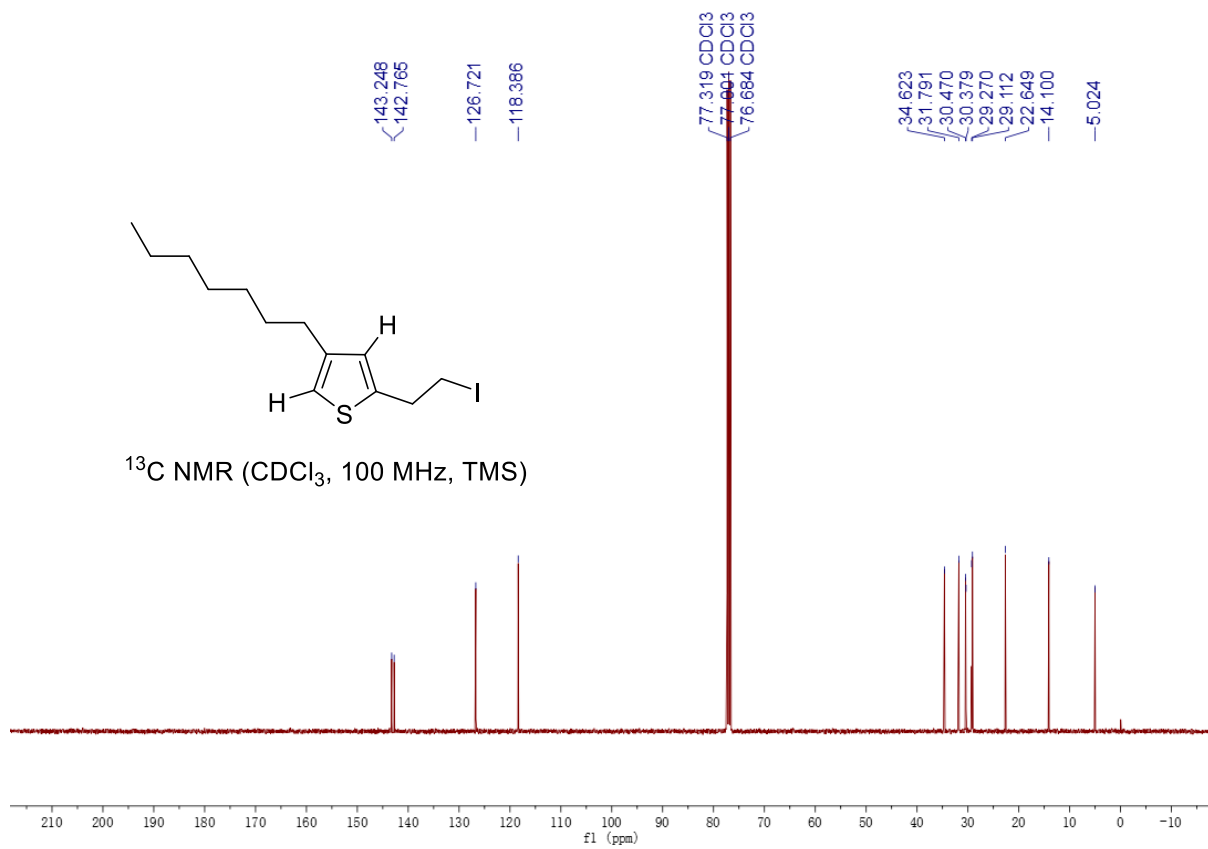
A colorless oil, 27.2 mg, 81% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 6.76 (s, 1H), 6.69 (s, 1H), 3.38 - 3.28 (m, 4H), 2.57 - 2.51 (m, 2H), 1.63 - 1.57 (m, 2H), 1.35 - 1.25 (m, 8H), 0.91 - 0.84 (m, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 143.2, 142.8, 126.7, 118.4, 34.6, 31.8, 30.5, 30.4, 29.3, 29.1, 22.6, 14.1, 5.0. IR (neat) ν 927, 934, 1221, 1781, 2015, 2144, 2931 cm⁻¹. HRMS (EI) calcd. for C₁₃H₂₁IS (M⁺): 336.0414, Found: 336.0403.

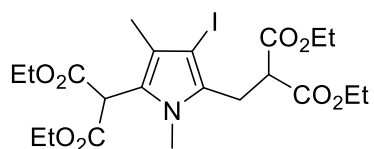


$^1\text{H NMR}$ (CDCl_3 , 400 MHz, TMS)



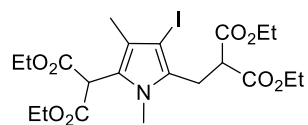
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS)



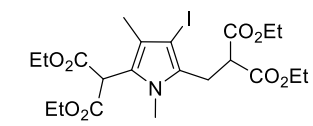
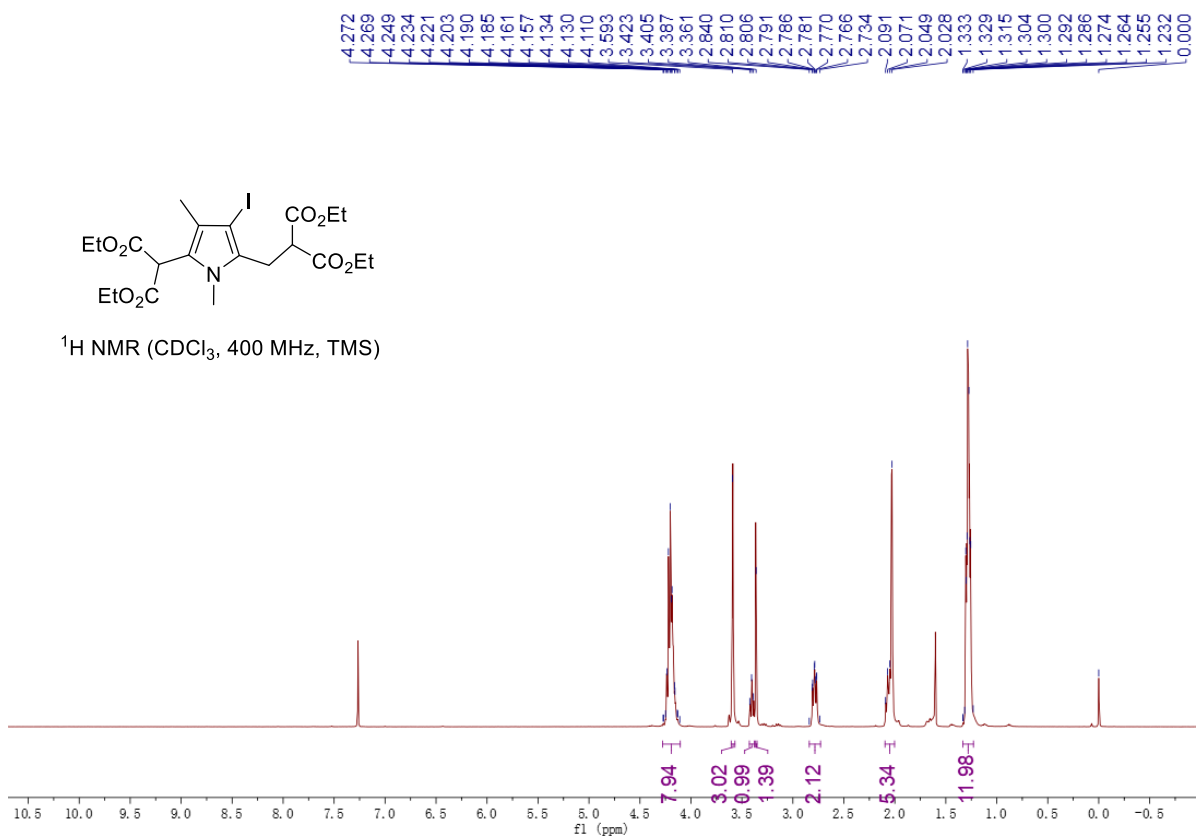


diethyl 2-((5-(1,3-diethoxy-1,3-dioxopropan-2-yl)-3-iodo-1,4-dimethyl-1H-pyrrol-2-yl)methyl)malonate (9)

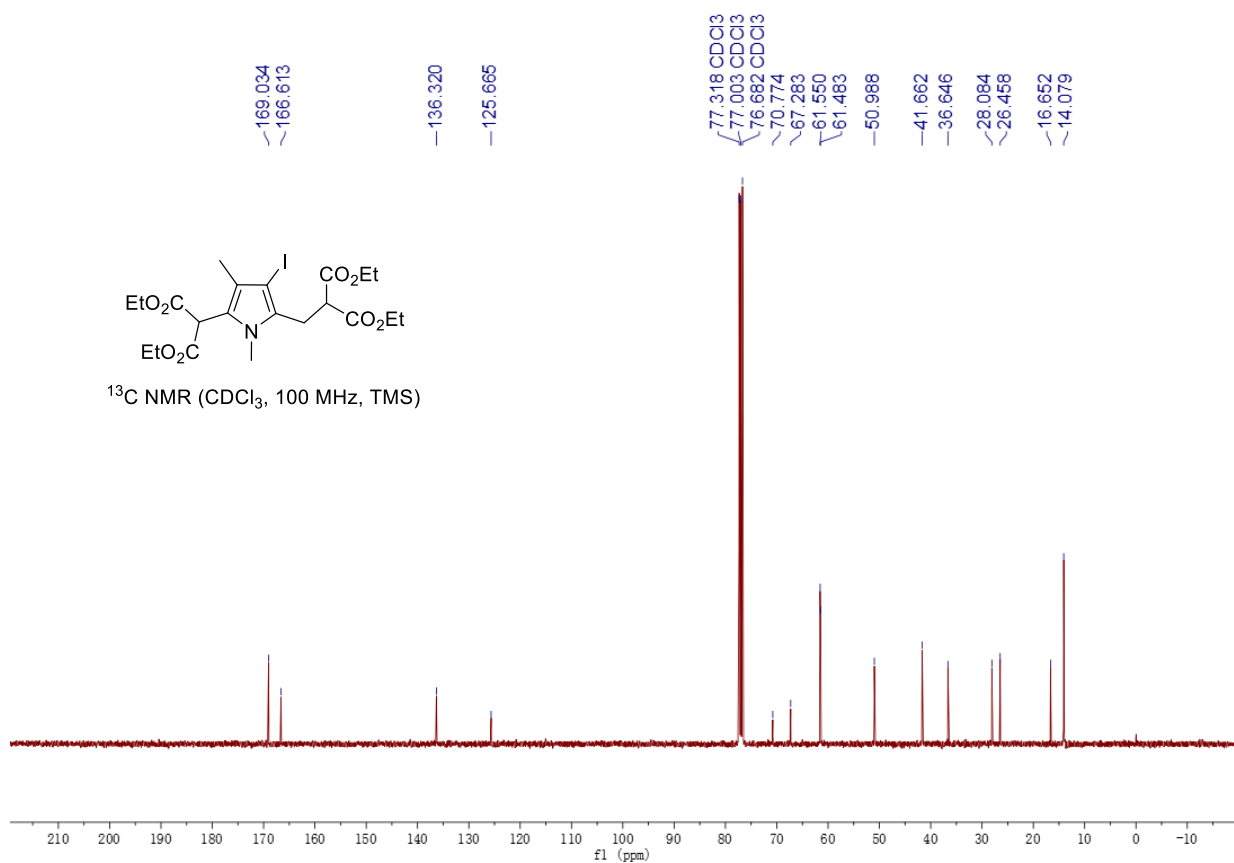
A yellow oil, 37.5 mg, 68% yield. ^1H NMR (CDCl_3 , TMS, 400 MHz) δ 4.27 - 4.10 (m, 8H), 3.59 (s, 3H), 3.40 (t, $J = 7.1$ Hz, 1H), 3.36 (s, 1H), 2.84 - 2.73 (m, 2H), 2.09-2.01 (m, 5H), 1.33 - 1.23 (m, 12H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 169.0, 166.6, 136.3, 125.7, 70.8, 67.3, 61.6, 51.0, 41.7, 36.7, 28.1, 26.4, 16.7, 14.1. IR (neat) ν 615, 803, 933, 1179, 1316, 1758, 2901, 2988 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{30}\text{INO}_8\text{Na}$ ($\text{M}+\text{Na}$): 574.0914, Found: 574.0918.

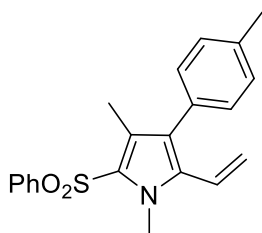


$^1\text{H NMR}$ (CDCl_3 , 400 MHz, TMS)



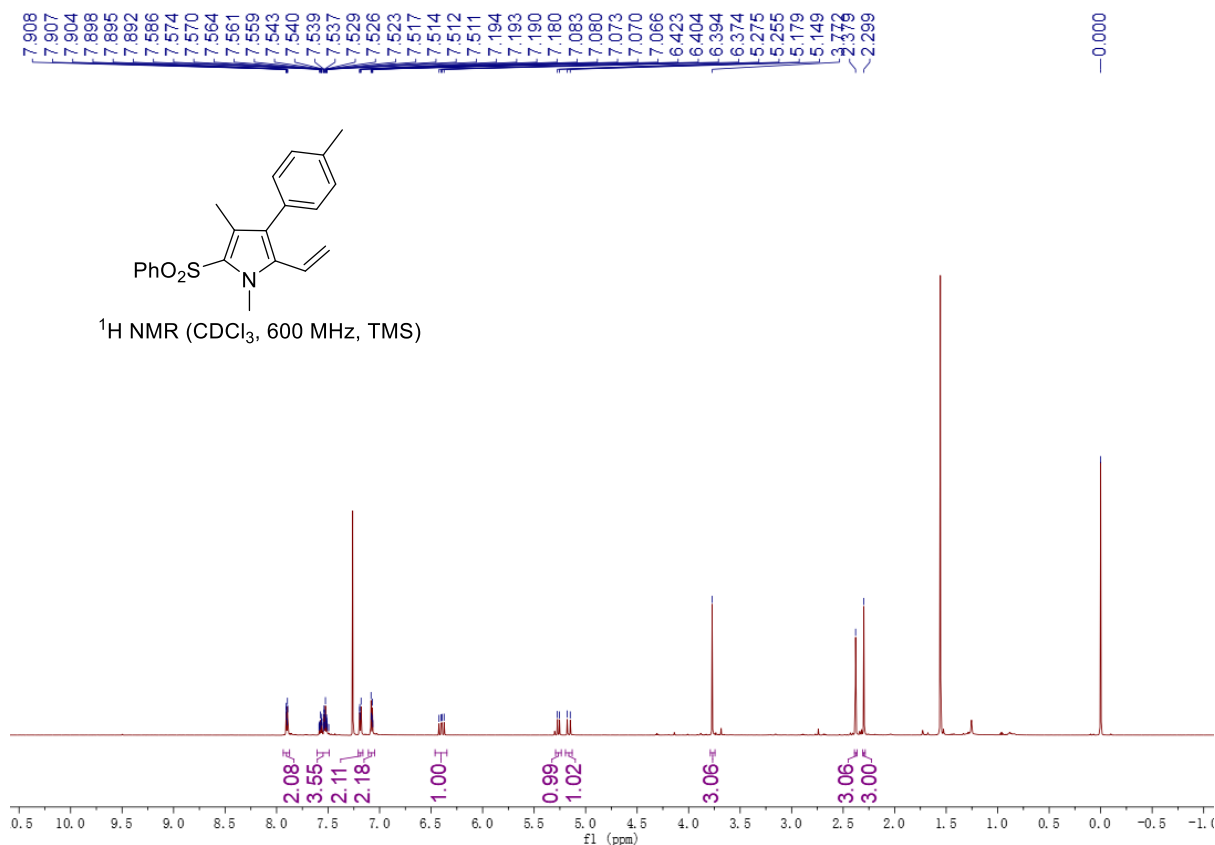
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, TMS)

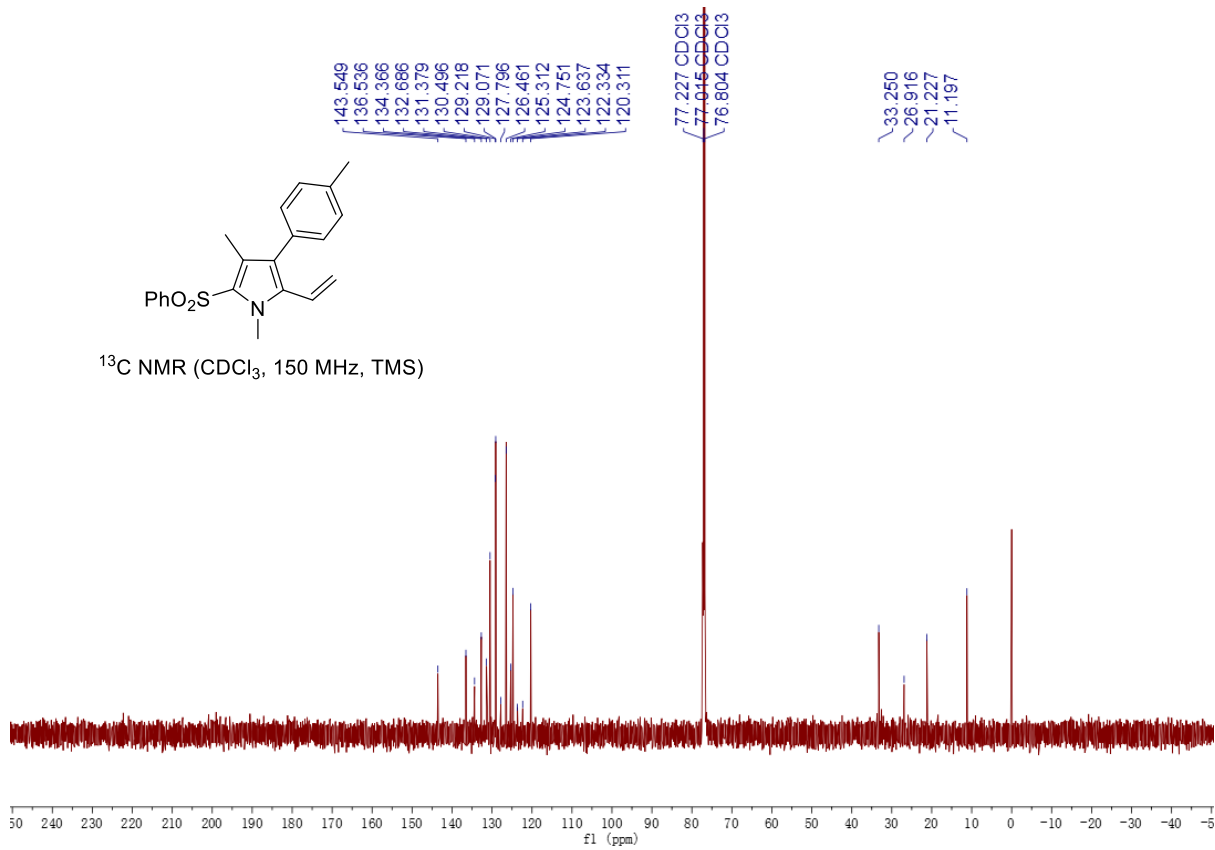


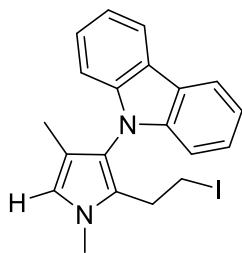


1,3-dimethyl-2-(phenylsulfonyl)-4-(p-tolyl)-5-vinyl-1H-pyrrole (11)

A yellow oil, 16.9 mg, 68% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 7.91 - 7.89 (m, 2H), 7.59 - 7.56 (m, 1H), 7.54 - 7.50 (m, 2H), 7.20 - 7.17 (m, 2H), 7.09 - 7.06 (m, 2H), 6.40 (dd, $J = 17.9, 11.9$ Hz, 1H), 5.27 (d, $J = 11.8$ Hz, 1H), 5.16 (d, $J = 17.8$ Hz, 1H), 3.77 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 143.5, 136.5, 134.4, 132.7, 131.4, 130.5, 129.2, 129.1, 127.8, 126.4, 125.3, 124.7, 123.6, 122.3, 120.3, 33.2, 26.9, 21.2, 11.2. IR (neat) ν 603, 815, 957, 1179, 1316, 2921, 2978 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{S}$ ($\text{M}+\text{H}$): 352.1371, Found: 352.1399.

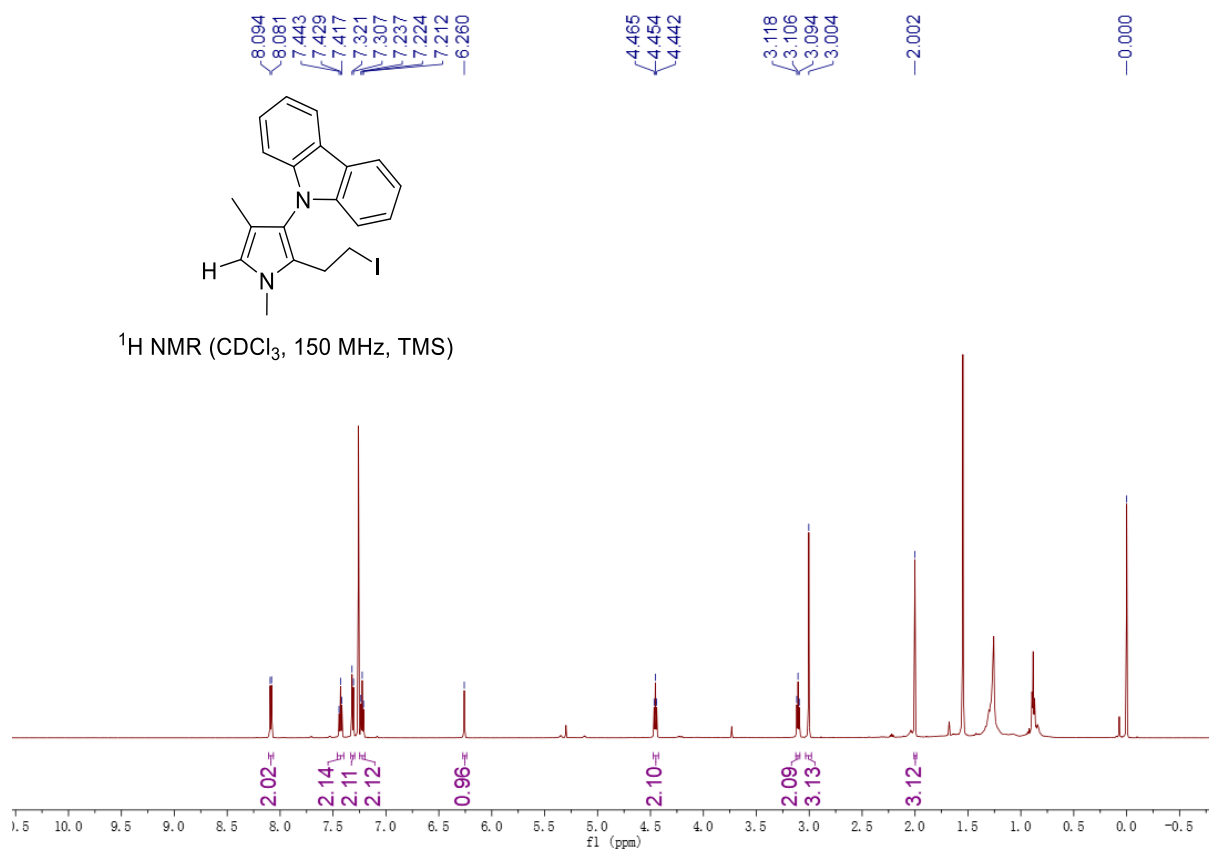


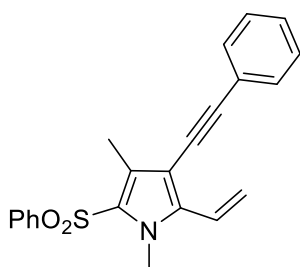
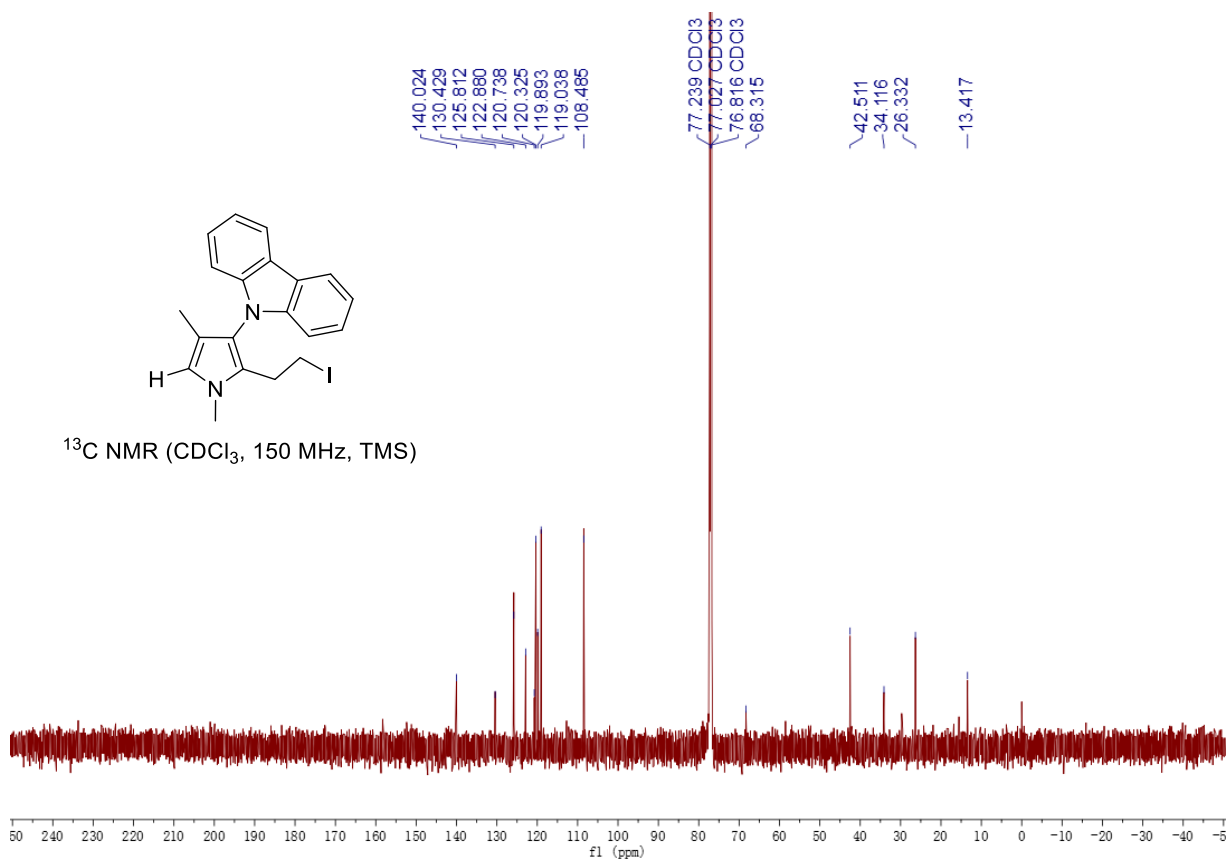




9-(2-(2-iodoethyl)-1,4-dimethyl-1H-pyrrol-3-yl)-9H-carbazole (12)

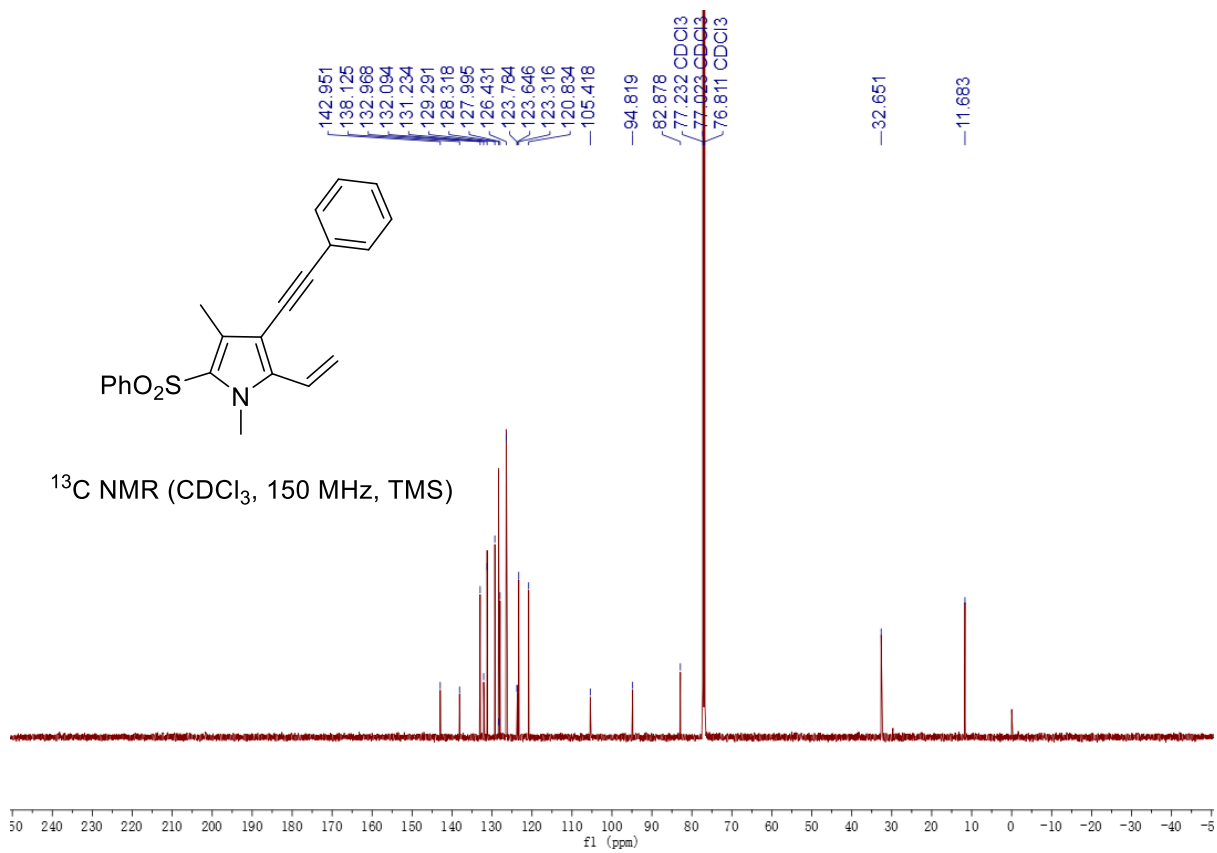
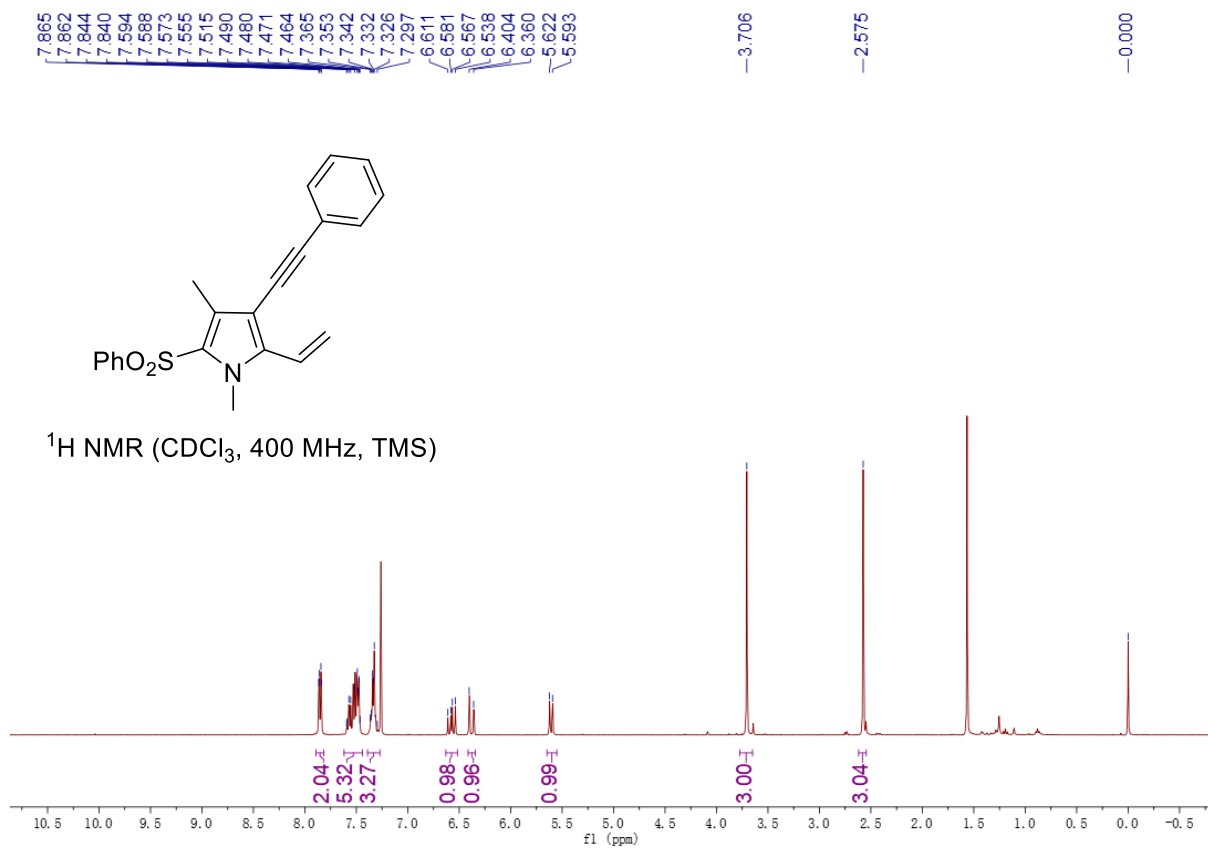
A yellow oil, 14.5 mg, 35% yield. ^1H NMR (CDCl_3 , TMS, 600 MHz) δ 8.09 (d, $J = 7.7$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.22 (t, $J = 7.4$ Hz, 2H), 6.26 (s, 1H), 4.45 (t, $J = 7.1$ Hz, 2H), 3.11 (t, $J = 7.1$ Hz, 2H), 3.00 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (CDCl_3 , TMS, 150 MHz) δ 140.0, 130.4, 125.8, 122.9, 120.7, 120.3, 119.9, 119.0, 108.5, 68.3, 42.5, 34.1, 26.3, 13.4. IR (neat) ν 927, 934, 1221, 1781, 2015, 2144, 2931 cm^{-1} . HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{I}$ (M^+): 414.0593, Found: 414.0593.





1,3-dimethyl-4-(phenylethynyl)-2-(phenylsulfonyl)-5-vinyl-1H-pyrrole (13)

A yellow oil, 23.1 mg, 64% yield. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.60 - 7.46 (m, 5H), 7.37 - 7.30 (m, 3H), 6.57 (dd, *J* = 17.5, 11.6 Hz, 1H), 6.38 (d, *J* = 17.5 Hz, 1H), 5.61 (d, *J* = 11.6 Hz, 1H), 3.71 (s, 3H), 2.57 (s, 3H). ¹³C NMR (CDCl₃, TMS, 100 MHz) δ 143.0, 138.1, 133.0, 132.1, 131.2, 129.3, 128.4, 128.0, 126.4, 123.8, 123.6, 123.3, 120.8, 105.4, 94.8, 82.9, 32.7, 11.7. IR (neat) ν 754, 913, 1079, 1326, 2901, 2988 cm⁻¹. HRMS (EI) calcd. for C₂₂H₁₉NO₂SNa (M+Na): 384.1034, Found: 384.1022.



10. Computational studies

All quantum mechanical calculations have been performed with Gaussian 16. The geometries of all species have been optimized at B3LYP/6-31G(d) level. The subsequent frequency calculations on the stationary points were carried out at the same level of theory to ascertain the nature of the stationary points as minima on the respective potential energy surfaces. The conformational space of flexible systems has first been searched manually and checked by xtb 6.0 program. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The thermochemical corrections have been combined with single-point energies calculated at the SMD/B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level to yield free energy G_{298} at 298.15 K. The solvent effect was estimated by the IEFPCM method with radii and nonelectrostatic terms for SMD solvation model in dichloromethane ($\epsilon = 8.93$).

Table S7. The total energies, enthalpies and free energies of all species in dichloromethane shown in Schemes 7a, 7c.

	E_{tot}	H_{298}	G_{298}
1a+NIS	-1558.078019	-1557.652874	-1557.755107
TS1	-1558.055398	-1557.63175	-1557.726428
INT1	-1558.076812	-1557.650978	-1557.740193
TS2	-1558.051763	-1557.632819	-1557.731027
TsH	-820.2882496	-820.139865	-820.1866468
INT2	-737.825833	-737.551705	-737.623488
I⁻	-11.563306	-11.560946	-11.580154
INT3	-749.396661	-749.12022	-749.201193
TS3	-749.3817925	-749.1067992	-749.1861772
INT4	-749.405308	-749.128639	-749.209718
INT1'	-1273.629836	-1273.294532	-1273.385194
TS1'	-1273.618541	-1273.284287	-1273.365089
INT2'	-1273.682114	-1273.343481	-1273.429288
TS2'	-1273.650194	-1273.313635	-1273.390803
INT3'	-1273.731928	-1273.390522	-1273.466922
TS3'	-1273.706467	-1273.372462	-1273.450496
INT4'	-1273.755657	-1273.415319	-1273.499759

Archive entries

1a+NIS

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1558.078019a.u.

Zero-point correction = 0.393975Hartree/Particle

Sum of electronic and thermal Free Energies = -1557.755107a.u.

N 1.56217,1.362111,-0.046872
C 2.705964,2.201257,-0.418152
C 2.318108,3.638975,-0.742306
S 1.8037,0.222429,1.170006
O 2.646675,0.858896,2.184742
O 0.468696,-0.293113,1.506987
C 2.736396,-1.138038,0.460066
C 4.133319,-1.102539,0.512313
C 4.86347,-2.133077,-0.075795
C 4.221957,-3.204073,-0.715396
C 2.820439,-3.216667,-0.749224
C 2.070018,-2.195473,-0.167203
C 5.020665,-4.333934,-1.320895
C 3.388104,4.439291,-1.455200
C 1.163493,4.15861,-0.389059
C 0.027586,4.673324,-0.055968
C -1.389944,4.951193,-0.386216
C -0.796536,5.371849,0.956405
I -3.520698,-0.811767,-1.385803
H 3.408205,2.209325,0.421191
H 3.236635,1.76916,-1.284933
H 4.63504,-0.290768,1.028161
H 5.949661,-2.109055,-0.030966
H 2.302169,-4.041182,-1.232416
H 0.985981,-2.240413,-0.184135
H 6.00462,-3.993591,-1.659984
H 5.187276,-5.133917,-0.587247
H 4.50017,-4.779938,-2.174702
H 3.068029,5.471641,-1.615594
H 4.320449,4.457056,-0.873075
H 3.629035,3.996135,-2.431651
H -1.607233,5.728803,-1.117173
H -2.089061,4.116529,-0.398599
H -1.093083,4.818293,1.845588
H -0.614595,6.431855,1.127373

C 0.693918,0.953504,-1.156112
H -0.200481,0.472097,-0.762026
H 0.39534,1.856272,-1.692789
H 1.202203,0.271822,-1.855607
C -2.391798,-1.026737,2.815701
C -1.70839,-2.297121,2.285301
H -1.654095,-0.268685,3.097268
H -3.060656,-1.18723,3.665314
H -0.64162,-2.343316,2.507414
H -2.179659,-3.216216,2.652415
N -2.814844,-1.226639,0.51498
C -1.896075,-2.253647,0.773091
O -1.387921,-2.967394,-0.062769
C -3.187321,-0.466969,1.641063
O -3.969710,0.452043,1.637592

TS1

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1558.055398a.u.

Zero-point correction = 0.394176Hartree/Particle

Sum of electronic and thermal Free Energies = -1557.726428a.u.

C -1.775465,1.150147,0.207488
C -0.269438,1.41033,0.153173
I 2.86208,0.200859,0.012134
C -2.168754,-0.34,-1.715454
C 0.187566,2.836778,0.225166
C 0.46724,0.29817,0.100992
C -0.195221,-0.952746,0.089408
C -0.044289,-2.153823,0.957849
C 0.083229,-2.26544,-0.555325
N 5.16087,0.158109,-0.102746
C 5.948883,1.290206,-0.029584
C 7.426398,0.869848,-0.13969
C 7.384325,-0.655071,-0.291285
C 5.88564,-1.006872,-0.256882
O 5.429789,-2.134098,-0.352072
O 5.556527,2.437025,0.099687
N -1.99824,-0.253182,-0.243328
C -4.812228,-0.311077,0.218971
C -5.263206,0.755891,1.003926
C -6.462303,1.377239,0.66748
C -7.222007,0.948034,-0.432759
C -6.748925,-0.132095,-1.193089
C -5.551758,-0.769819,-0.875794

C -8.535876,1.611245,-0.765447
S -3.283504,-1.124225,0.646169
O -2.992921,-0.891198,2.057009
O -3.268758,-2.459209,0.048137
H -2.145676,1.250572,1.232776
H -2.343579,1.833401,-0.436152
H -3.064753,0.203627,-2.031931
H -2.238343,-1.384096,-2.015746
H -1.284895,0.11471,-2.166226
H -0.205574,3.427375,-0.614845
H -0.165443,3.32198,1.146649
H 1.277744,2.897244,0.207273
H -0.923671,-2.610144,1.399283
H 0.843635,-2.164539,1.584312
H 1.059809,-2.374425,-1.020006
H -0.729281,-2.793613,-1.045352
H 7.877181,1.386651,-0.993511
H 7.956806,1.21015,0.755958
H 7.89116,-1.193616,0.516459
H 7.810022,-1.017563,-1.232973
H -4.696412,1.074652,1.871926
H -6.819744,2.204714,1.274563
H -7.329839,-0.485045,-2.040924
H -5.20561,-1.622455,-1.449859
H -9.351219,1.173,-0.175086
H -8.512059,2.682477,-0.541085
H -8.792838,1.486699,-1.821749

INT1

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1558.076812a.u.

Zero-point correction = 0.396900Hartree/Particle

Sum of electronic and thermal Free Energies = -1557.740193a.u.

N -3.199615,-1.160023,-0.011127
C -3.11547,-1.097837,1.495715
C -1.634882,-0.972132,1.77072
C -0.920743,-1.275981,0.675584
C -1.836775,-1.664391,-0.438164
C -4.389726,-1.914521,-0.489923
C -1.463441,-1.756973,-1.897235
C -1.69645,-3.020242,-1.119494
C -1.164245,-0.556581,3.129138
I 1.243356,-1.017502,0.353173

N 3.64598,-0.358098,-0.173803
C 4.75565,-1.15877,0.002138
C 6.03153,-0.391727,-0.411092
C 5.509091,0.978026,-0.848983
C 3.982404,0.868081,-0.655957
O 3.208958,1.79828,-0.920357
O 4.752526,-2.307378,0.420335
C -2.135903,1.698942,-0.347784
C -2.156212,2.490253,0.811585
C -1.032801,3.253717,1.101707
C 0.110948,3.216647,0.28333
C 0.09479,2.415544,-0.873068
C -1.025704,1.666299,-1.205177
C 1.345429,4.006391,0.622731
S -3.540893,0.717098,-0.71337
O -4.683361,1.094225,0.11946
O -3.67079,0.45069,-2.143124
H -3.550627,-2.02745,1.890615
H -3.73569,-0.269352,1.853372
H -5.286441,-1.411372,-0.123993
H -4.346093,-2.92917,-0.090676
H -4.400403,-1.933216,-1.579582
H -0.443019,-1.476824,-2.141273
H -2.206021,-1.47943,-2.637673
H -2.581004,-3.604338,-1.352664
H -0.839462,-3.603714,-0.796838
H -1.523097,0.45048,3.385538
H -1.537306,-1.236122,3.908241
H -0.073072,-0.552202,3.175305
H 6.541056,-0.946832,-1.206273
H 6.718485,-0.354049,0.441326
H 5.887032,1.811663,-0.246184
H 5.720936,1.222798,-1.89589
H -3.033575,2.516181,1.447801
H -1.033952,3.880002,1.989689
H 1.002139,2.330268,-1.463057
H -1.034864,1.0532,-2.098114
H 1.367843,4.943339,0.049025
H 1.376475,4.268056,1.685116
H 2.238922,3.433969,0.351303

TS2

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1558.051763a.u.

Zero-point correction = 0.388545Hartree/Particle

Sum of electronic and thermal Free Energies = -1557.731027a.u.

N -1.160879,-3.678937,0.294615
C -1.669682,-2.938223,1.401466
C -0.778616,-1.794314,1.597353
C 0.177122,-1.780599,0.574926
C -0.095647,-2.924372,-0.269937
C -2.02071,-4.57738,-0.456091
C 0.138839,-2.85006,-1.822618
C 1.063344,-3.663762,-1.035835
C -0.883832,-0.863637,2.760824
I 1.892046,-0.361037,0.34998
S -2.551461,-0.559878,-0.438058
O -3.606507,-1.438431,0.27084
H -2.68035,-2.399248,1.052922
C -3.312901,1.082352,-0.391415
O -2.263707,-0.89481,-1.869285
C -4.172991,1.437339,0.647795
C -4.675658,2.736808,0.686401
C -4.319695,3.685675,-0.283688
C -3.449193,3.294818,-1.311232
C -2.932705,2.001452,-1.369385
C -4.84006,5.101286,-0.209119
H -1.979992,-3.543691,2.262963
H -2.61098,-5.169436,0.248768
H -2.705868,-4.030188,-1.117592
H -1.415618,-5.267116,-1.051828
H 0.445278,-1.867019,-2.162389
H -0.638226,-3.324229,-2.412114
H 0.958865,-4.744932,-1.038975
H 2.052473,-3.278314,-0.807226
H -1.928727,-0.700195,3.046486
H -0.369995,-1.291746,3.632844
H -0.413543,0.097488,2.540792
H -4.465283,0.70356,1.390611
H -5.361826,3.016811,1.481999
H -3.168975,4.012268,-2.078412
H -2.264317,1.701694,-2.169346
H -4.143183,5.745864,0.34278
H -4.963563,5.536009,-1.206447
H -5.805201,5.14777,0.305589
N 3.69488,1.182674,0.035046
C 3.802603,2.390021,0.690085
C 5.080105,3.115068,0.220748

C 5.694466,2.166836,-0.814216
C 4.724804,0.969024,-0.854553
O 4.863831,-0.0124,-1.570975
O 3.018665,2.832486,1.517333
H 5.722706,3.299099,1.08852
H 4.804048,4.094687,-0.184095
H 5.769711,2.596525,-1.818993
H 6.693671,1.80646,-0.546834

TsH

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -820.2882496a.u.

Zero-point correction = 0.138006Hartree/Particle

Sum of electronic and thermal Free Energies = -820.1866468a.u.

S -2.141367,0.197988 ,0.500172
O -2.612191,-1.187909,0.208215
O -2.488909,1.229288,-0.788787
C -0.339472,0.149202,0.252693
C 0.290668,-1.085068,0.113768
C 1.678149,-1.129676,-0.029054
C 2.445678,0.042082,-0.019263
C 1.785443,1.272830,0.128408
C 0.401716,1.3343790,0.268831
C 3.950229,-0.012591,-0.139602
H -0.310356,-1.989456,0.107040
H 2.172735,-2.090810,-0.148324
H 2.364784,2.193303,0.130143
H -0.099076,2.293521,0.369627
H 4.283326,-0.958310,-0.578307
H 4.332825,0.804350,-0.761210
H 4.428078,0.079359,0.844678
H -2.143793,0.824268,-1.610045

INT2

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -737.825833a.u.

Zero-point correction = 0.254550Hartree/Particle

Sum of electronic and thermal Free Energies = -737.623488a.u.

N -4.135332,-0.182618,0.000134
C -3.999965,1.14504,-0.000487

C -2.647203,1.546584,-0.000726
C -1.876441,0.389026,-0.000142
C -2.80193,-0.742607,0.000389
C -5.38651,-0.92106,0.000765
C -2.504512,-2.059586,-0.738274
C -2.504526,-2.058858,0.740367
C -2.166338,2.9698,-0.001723
I 0.345355,0.201429,-0.000118
H -4.882103,1.778292,-0.000671
H -6.215794,-0.211283,0.000272
H -5.466494,-1.552404,-0.890349
H -5.46641,-1.551076,0.892827
H -3.339159,-2.515676,-1.26273
H -1.554093,-2.077606,-1.26242
H -1.554125,-2.076346,1.264559
H -3.339184,-2.514409,1.265274
H -3.002945,3.676309,0.004288
H -1.540559,3.172,0.874079
H -1.551275,3.174614,-0.884556
N 2.737905,-0.067521,-0.000103
C 3.644596,0.968465,0.001132
C 5.077885,0.39683,0.001011
C 4.877551,-1.121743,-0.000582
C 3.345471,-1.301059,-0.001061
O 2.77698,-2.385607,-0.00214
O 3.37695,2.161687,0.002185
H 5.610442,0.772706,0.881426
H 5.611058,0.774501,-0.87826
H 5.294591,-1.623081,-0.880878
H 5.294303,-1.624937,0.878788

I

Opt @ B3LYP/6-31G(d)
SCF Done: E(B3LYP) = -11.563306a.u.
Zero-point correction = 0.000000Hartree/Particle
Sum of electronic and thermal Free Energies = -11.580154a.u.

I 0.000000,0.000000,0.000000

INT3

Opt @ B3LYP/6-31G(d)
SCF Done: E(B3LYP) = -749.396661a.u.
Zero-point correction = 0.254538Hartree/Particle
Sum of electronic and thermal Free Energies = -749.201193a.u.

N 2.161431,-1.783219,-0.674182
C 1.56355,-2.896618,-0.27006
C 0.1967,-2.689989,0.037672
C -0.067183,-1.351583,-0.203494
C 1.181153,-0.727822,-0.633229
C 3.544648,-1.665926,-1.125315
C 1.267621,0.475638,-1.587829
C 1.589788,0.700511,-0.168782
C -0.750148,-3.750171,0.522162
I -2.005923,-0.372404,-0.034588
H 2.125367,-3.823346,-0.213595
H 4.039878,-2.624889,-0.958136
H 3.569122,-1.432418,-2.195284
H 4.084694,-0.878611,-0.57336
H 2.091481,0.455778,-2.295795
H 0.310041,0.801837,-1.983294
H 0.847164,1.172942,0.466465
H 2.635507,0.83319,0.122112
H -0.251661,-4.722689,0.60108
H -1.158837,-3.495539,1.506355
H -1.604308,-3.857176,-0.155809
N -4.30726,0.712573,0.104976
C -5.353642,0.208402,0.833052
C -6.595878,1.120773,0.684244
C -6.123553,2.234379,-0.25082
C -4.651528,1.863801,-0.555759
O -3.929805,2.529809,-1.290539
O -5.348643,-0.812305,1.51381
H -6.900504,1.471929,1.676934

H -7.428506,0.528315,0.287571
H -6.679889,2.291062,-1.193597
H -6.153555,3.23462,0.196404
I 5.494852,1.17752,0.472685

TS3

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -749.396661a.u.

Zero-point correction = 0.253259Hartree/Particle

Sum of electronic and thermal Free Energies = -749.201046a.u.

N -2.147824,2.685058,0.45645
C -1.36345,3.680128,-0.01917
C -0.072775,3.214108,-0.273661
C -0.051439,1.849743,0.076451
C -1.361281,1.509917,0.521312
C -3.517148,2.824838,0.920965
C -2.168696,0.089272,-0.233726
C -1.868858,0.25436,1.183314
C 1.060802,4.031709,-0.821029
I 1.695908,0.555248,0.028847
H -1.771132,4.674106,-0.163085
H -3.911641,3.780229,0.56733
H -4.147128,2.020975,0.527743
H -3.569115,2.804663,2.016345
H -3.095072,0.440019,-0.659238
H -1.483567,-0.445281,-0.879321
H -1.079929,-0.373422,1.591703
H -2.713941,0.380624,1.856282
H 0.751521,5.06773,-1.00093
H 1.910931,4.044633,-0.129135
H 1.431336,3.616502,-1.765287
N 3.831963,-0.905576,0.02875
C 4.726268,-0.964894,-1.00718
C 5.882059,-1.939074,-0.665071
C 5.536938,-2.436444,0.73809
C 4.214849,-1.701986,1.076037
O 3.629158,-1.841981,2.145373
O 4.664211,-0.352093,-2.069151
H 6.834341,-1.39912,-0.725962
H 5.916646,-2.730427,-1.422962
H 5.36861,-3.517966,0.799045
H 6.287865,-2.188445,1.497424
I -4.544385,-1.942958,-0.313642\

INT4

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -749.405308a.u.

Zero-point correction = 0.254642Hartree/Particle

Sum of electronic and thermal Free Energies = -749.209718a.u.

N -2.519047, 2.741229, 0.299388
C -1.751681, 3.838537, -0.02659
C -0.432671, 3.45261, -0.149418
C -0.389929, 2.050428, 0.12599
C -1.680832, 1.635602, 0.413945
C -3.928458, 2.78889, 0.624378
C -2.568055, -0.4336, -0.577651
C -2.209638, 0.268786, 0.729846
C 0.721708, 4.339947, -0.510163
I 1.374892, 0.811054, 0.092023
H -2.210148, 4.812763, -0.142622
H -4.325977, 3.761443, 0.322091
H -4.487722, 2.012434, 0.08999
H -4.108639, 2.661999, 1.70061
H -3.278394, 0.124816, -1.186527
H -1.686936, -0.691811, -1.16253
H -1.441456, -0.307214, 1.25354
H -3.086412, 0.318564, 1.385919
H 0.389256, 5.371384, -0.680117
H 1.480795, 4.355063, 0.281905
H 1.229064, 3.992025, -1.418404
N 3.655202, -0.761854, 0.048723
C 4.58825, -0.745118, -0.949889
C 5.740419, -1.744026, -0.648525
C 5.343243, -2.354195, 0.692674
C 4.000665, -1.647778, 1.030882
O 3.376372, -1.894242, 2.061842
O 4.573405, -0.05658, -1.969561
H 6.691695, -1.198176, -0.628908
H 5.808553, -2.469549, -1.468405
H 5.179176, -3.438261, 0.661169
H 6.060505, -2.165757, 1.500925
I -3.608152, -2.397644, -0.247052

INT1'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.629836a.u.

Zero-point correction = 0.310225Hartree/Particle
Sum of electronic and thermal Free Energies = -1273.385194a.u.

S 4.058511,2.891923,1.357998
C 3.748336,1.073729,1.33139
C 2.683948,0.685956,0.324034
C 1.59868,2.373319,-1.342697
C 0.528565,3.35288,-1.64772
C 1.618167,3.035157,-2.667569
C 2.297368,-0.79117,0.322113
C 2.140166,1.541714,-0.516067
H 5.024257,2.836171,2.301252
H 4.68237,0.552054,1.094899
H 3.436056,0.748254,2.3317
H -0.476603,2.971634,-1.818622
H 0.571623,4.317758,-1.144282
H 2.386931,3.783418,-2.852443
H 1.347133,2.442496,-3.539794
H 1.932768,-1.072167,1.320883
H 1.459505,-0.928911,-0.371367
N -3.075612,0.076923,0.539203
C -2.326196,1.142278,0.019886
C -1.423266,1.637063,1.146653
C -1.760226,0.761507,2.36541
C -2.820044,-0.22952,1.887577
I -4.455894,-0.968522,-0.593475
O -3.349694,-1.108527,2.522374
O -2.40038,1.565701,-1.110935
H -0.381781,1.547867,0.821305
H -1.619143,2.701773,1.306039
H -2.173293,1.326538,3.206902
H -0.904123,0.196924,2.747065
C 3.438197,-1.724943,-0.059451
C 3.844037,-2.754269,0.797946
C 4.097213,-1.577876,-1.288858
C 4.878552,-3.621916,0.438006
H 3.342647,-2.881939,1.75513
C 5.130331,-2.441311,-1.651428
H 3.798438,-0.776292,-1.959946
C 5.524928,-3.467718,-0.7885
H 5.177926,-4.41582,1.117379
H 5.628688,-2.313574,-2.608928
H 6.330155,-4.140439,-1.071266

TS1'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.618541a.u.

Zero-point correction = 0.311345Hartree/Particle

Sum of electronic and thermal Free Energies = -1273.365089a.u.

C -3.338183,1.4052,-0.799831
C -2.026389,0.610891,-0.742219
C -2.130917,-0.818635,-1.229001
C -0.942627,1.254811,-0.305355
C -1.035658,2.622449,0.108419
C -0.317625,3.380886,1.189236
C -0.163048,3.793564,-0.256996
I 1.265814,0.304408,-0.163423
H -4.17321,0.891765,-0.313157
H -3.644084,1.644748,-1.826036
H -1.125016,-1.249369,-1.247706
H -2.499307,-0.828848,-2.265176
H -0.888187,4.037046,1.842392
H 0.497481,2.850586,1.67372
H 0.759734,3.550449,-0.775254
H -0.63778,4.718608,-0.572306
C 5.138102,-2.193718,-0.208159
C 5.655338,-0.924681,0.479814
H 5.217357,-3.094625,0.409278
H 5.634387,-2.413653,-1.159226
H 6.030425,-1.094133,1.494663
H 6.451092,-0.415076,-0.073672
N 3.351011,-0.642678,-0.016111
C 3.649733,-1.909386,-0.480916
O 2.875268,-2.68186,-1.017839
C 4.429982,0.004084,0.553388
O 4.426495,1.12349,1.037449
S -3.073874,3.010893,0.041087
H -3.29954,2.585819,1.30305
C -3.053671,-1.670233,-0.367774
C -4.26587,-2.161692,-0.867702
C -2.70454,-1.968125,0.958322
C -5.111482,-2.934933,-0.067034
H -4.545201,-1.949667,-1.898015
C -3.544748,-2.741392,1.758826
H -1.762598,-1.598352,1.355971
C -4.753109,-3.226046,1.249274
H -6.0454,-3.312489,-0.475382

H -3.253387,-2.972237,2.78022
H -5.405822,-3.831058,1.872826

INT2'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.682114a.u.

Zero-point correction = 0.315190Hartree/Particle

Sum of electronic and thermal Free Energies = -1273.429288a.u.

S -4.157832,-2.553241,0.669711
C -3.655532,-0.861476,1.214307
C -2.455525,-0.478478,0.37643
C -1.778297,0.850268,0.621741
C -2.095552,-1.367021,-0.558912
C -2.90108,-2.607006,-0.666705
C -3.233232,-3.212782,-2.015488
C -2.286416,-3.92663,-1.082188
H -3.414899,-0.877598,2.284925
H -4.483024,-0.15619,1.074449
H -1.426784,0.895882,1.66283
H -0.886971,0.910392,-0.015198
H -1.251525,-1.210167,-1.227424
H -2.827886,-2.727943,-2.900857
H -4.230489,-3.624282,-2.146321
H -2.639604,-4.824888,-0.582132
H -1.225723,-3.938346,-1.325059
N 3.053622,-0.51174,0.214698
C 1.839398,-0.99116,-0.290277
C 1.476167,-2.227446,0.528268
C 2.582864,-2.365827,1.587005
C 3.576001,-1.240946,1.299703
I 4.003997,1.15362,-0.562931
O 4.607137,-0.999508,1.876823
O 1.214307,-0.501848,-1.204764
H 0.47375,-2.086736,0.943823
H 1.422032,-3.083575,-0.152082
H 3.115498,-3.320506,1.545101
H 2.217629,-2.246024,2.611929
C -2.67664,2.054151,0.365731
C -2.92607,2.995352,1.371214
C -3.263778,2.248186,-0.892957
C -3.736916,4.107088,1.128667
H -2.478166,2.859477,2.353472
C -4.073712,3.356292,-1.139407

H -3.085592,1.520293,-1.680819
C -4.313402,4.290956,-0.128311
H -3.917588,4.826822,1.92298
H -4.518752,3.491012,-2.121948
H -4.944991,5.154285,-0.320013

TS2'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.33181495a.u.

Zero-point correction = 0.314033Hartree/Particle

Sum of electronic and thermal Free Energies = -1273.072436a.u.

S -3.7821313398,-3.1321385918,0.2007489455
C -2.6549494554,-1.6839463302,0.1403372394
C -2.6278061279,-1.2337504719,-1.2895786011
C -1.7574325946,-0.0721223616,-1.6860181621
C -3.3228525619,-2.0290669942,-2.1380812123
C -3.9280838278,-3.183030819,-1.5298553792
C -4.6696715269,-4.2317417268,-2.2342616703
C -3.3584204707,-4.9791560192,-2.4569034321
H -1.640536306,-1.9676169208,0.4522965536
H -3.0320005551,-0.9108249647,0.817049265
H -0.7278900588,-0.4569581879,-1.6655761491
H -1.9822477186,0.2083929004,-2.7215983932
H -3.3656963596,-1.8798896228,-3.2124330752
H -5.1439444151,-3.876548856,-3.152606985
H -5.3983562034,-4.7649462356,-1.6195595145
H -3.3072769145,-5.9018536416,-1.8852308909
H -3.0999380194,-5.0836486786,-3.5073936937
N 1.1997546174,-3.8504218482,-1.142380932
C 1.451601399,-2.6986064284,-0.4481272778
C 2.956129827,-2.598919593,-0.1628674018
C 3.5504791593,-3.8671991516,-0.7876198661
C 2.3442034598,-4.6018457392,-1.3961516348
I -0.911950104,-4.4221863548,-1.8000636364
O 2.3860170729,-5.655762881,-1.996173186
O 0.6241001686,-1.8584846053,-0.0959910234
H 3.3379319852,-1.6703397899,-0.6003854692
H 3.1055650122,-2.5268582738,0.9195625674
H 4.0364271371,-4.5281333749,-0.0627514329
H 4.2793877395,-3.668700196,-1.5798209107
C -1.8483736426,1.1351847785,-0.7668281697
C -0.8934584582,1.3291984693,0.2407757653
C -2.8910743517,2.0613905667,-0.9028266609
C -0.982858415,2.4312472032,1.0944949002

H -0.0849789325,0.6101058165,0.3513436547
C -2.9790084102,3.1633167597,-0.0510076828
H -3.6354999512,1.9215387282,-1.6841334982
C -2.0238317174,3.3505534424,0.9510629937
H -0.2345515348,2.572696451,1.8699717676
H -3.7902671548,3.8765391052,-0.1716051047
H -2.0896716601,4.2096212474,1.6133797339

INT3'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.42187615 a.u.

Zero-point correction = 0.319756 Hartree/Particle

Sum of electronic and thermal Free Energies = -1273.156870 a.u.

S -2.6154103326,-2.5804373944,0.8156167995
C -2.0152010275,-0.9493176506,1.4254627454
C -1.0867360424,-0.3557801379,0.3412308507
C -0.9931546241,1.2005199028,0.4339785933
C -1.6624129271,-0.8891336799,-0.9620420642
C -2.3878976509,-2.0109042225,-0.8603203565
C -3.0081551882,-2.7790178778,-1.9924064637
C -2.6173819064,-4.2524312965,-2.0800006131
H -1.5339792232,-1.0597442256,2.3929892679
H -2.8878412406,-0.2984792227,1.509301256
H -0.5512092934,1.4393010989,1.4086971767
H -0.2782876731,1.5166649814,-0.3329971114
H -1.4135878286,-0.4373370867,-1.9124638027
H -2.7877934641,-2.2735556869,-2.9381539946
H -4.1034265783,-2.7688772929,-1.8688866487
H -2.728419817,-4.7775751644,-1.1314835644
H -3.1798910652,-4.7697670402,-2.8561513235
N 0.3281726142,-0.8685355179,0.481300708
C 1.2232176773,-0.8429040645,-0.6033374955
C 2.5273165441,-1.5007626837,-0.1733230643
C 2.3802615383,-1.7104651468,1.335578352
C 0.9780247928,-1.2135687313,1.6760483721
I -0.5033564397,-4.5816306466,-2.6470730006
O 0.526408154,-1.1166957831,2.8004043718
O 0.9927160926,-0.3527889035,-1.689398387
H 2.6356230306,-2.4365720776,-0.731579492
H 3.3634855861,-0.8553409981,-0.4562466643
H 3.1023134173,-1.1436525225,1.9309718467
H 2.4597418918,-2.7574129769,1.6448045921
C -2.290155363,1.9627407723,0.2606014298
C -3.0322646496,2.3836532972,1.373702653

C -2.7696424369,2.286463746,-1.017348523
C -4.2256590224,3.0916127537,1.2174834506
H -2.6658707913,2.1627600194,2.3739455682
C -3.9613252281,2.993839104,-1.1784430974
H -2.197611816,1.9914184019,-1.8933198129
C -4.6957939747,3.3963762212,-0.0607313831
H -4.7826879673,3.409917524,2.094752361
H -4.3127461337,3.2371060513,-2.1777844987
H -5.6223392034,3.9502681574,-0.1854426229

TS3'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.39066515 a.u.

Zero-point correction = 0.311719 Hartree/Particle

Sum of electronic and thermal Free Energies = -1273.134694 a.u.

S,0,1.0998705263,0.8744672144,2.9769269029
C -0.3331268693,1.6935007589,2.3737369128
C -1.2070443256,0.7804285833,1.7512683642
C -2.5540090419,1.2178732795,1.2170691232
C -0.6060712108,-0.4888976898,1.5951114379
C 0.6446471407,-0.5876919475,2.1788635331
C 1.6282429699,-1.7194818384,2.0691674523
C 2.5611767439,-1.6068461264,0.8544488819
H -0.6413209111,2.622762866,2.8433835774
H -3.1931982182,1.4625852471,2.0778379922
H -2.3993974158,2.1558497111,0.6662872228
H -1.0597799828,-1.2986031348,1.0371843083
H 1.0971520019,-2.6768755515,2.0596811647
H 2.2756106231,-1.7274051668,2.9574882712
H 2.8966030081,-0.5845898007,0.6743175651
H 3.4076563501,-2.2866100566,0.9449896039
N 0.7430292249,2.5678476693,-0.1741953343
C -0.039633498,3.1714927198,-1.1277847968
C 0.8261773611,3.4648350737,-2.3618544306
C 2.2040973726,2.88365134,-2.0090046156
C 2.0279470957,2.3078150016,-0.5955719694
I 1.6063411688,-2.2101556997,-1.0482163741
O 2.8833055508,1.7085676085,0.0407476101
O -1.233071642,3.4240415341,-1.0163088821
H 0.3640569054,3.0025008777,-3.2397981947
H 0.8367916182,4.5456548056,-2.5380294001
H 3.0059636822,3.6291206071,-1.9932400901
H 2.5262578497,2.0803143877,-2.679004432
C -3.2542353717,0.2162452755,0.3209508602

C -3.9851921469,-0.8506527072,0.861720484
C -3.1796539267,0.3471856952,-1.072224743
C -4.6218294971,-1.7732102548,0.029834009
H -4.0613507429,-0.9564014851,1.9422273626
C -3.8178951369,-0.5737275867,-1.9054436903
H -2.6294480397,1.1834802474,-1.4962228344
C -4.5381390326,-1.6370917296,-1.3576989346
H -5.1874717058,-2.5931903257,0.4647577507
H -3.7554997474,-0.4568560741,-2.9841992828
H -5.0361677328,-2.3522809262,-2.0069533383
H 0.2087390026,2.1723305978,1.0785849528

INT4'

Opt @ B3LYP/6-31G(d)

SCF Done: E(B3LYP) = -1273.43625870 a.u.

Zero-point correction = 0.317087 Hartree/Particle

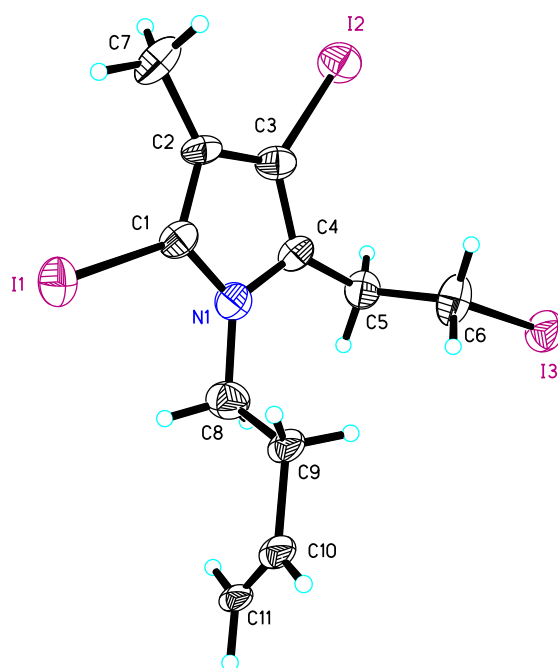
Sum of electronic and thermal Free Energies = -1273.180361 a.u.

S -0.2581231778,-1.5056150896,-1.3421239879
C 0.979854784,-0.3449139768,-0.9627634331
C 1.1517793816,-0.1915832778,0.3903406121
C 2.2040990278,0.6988728041,1.0232786583
C 0.2506673313,-1.0254400486,1.1335257106
C -0.5710123732,-1.7936928536,0.3547272932
C -1.6225483764,-2.7668396965,0.805560693
C -3.0504164005,-2.4722488034,0.3473783145
H 1.5248048866,0.1248021386,-1.7716720506
H 3.070827166,0.0807077509,1.2951556458
H 2.5668355039,1.4075063442,0.267409486
H 0.210329325,-1.0330764161,2.2177291185
H -1.5887870287,-2.835954465,1.8978876886
H -1.3880272523,-3.7737536795,0.4234152932
H -3.1222690857,-2.3186990169,-0.7292984893
H -3.7395846561,-3.2588547112,0.6540139961
N -0.6310559268,2.3861128309,-1.9434681164
C -1.1747945337,3.5984340083,-1.5362244071
C -1.5921631233,4.3510463698,-2.8016094869
C -1.1792340142,3.439449622,-3.9717176721
C -0.5594388249,2.2016326384,-3.3196775584
I -3.8977009382,-0.6279862386,1.2226164485
O -0.0797359275,1.2333344721,-3.8716765285
O -1.2780688296,3.9690722867,-0.3859223489
H -2.6695417965,4.5390212173,-2.7569123188
H -1.0975507283,5.3270492719,-2.8111304518
H -0.4399559571,3.8936745934,-4.6387411698

H -2.0205776866, 3.1229077985, -4.596060236
C 1.7396262871, 1.4513715645, 2.260211852
C 2.3028117453, 1.1720062325, 3.5115932558
C 0.7449065865, 2.43727554, 2.1777327593
C 1.8883628105, 1.8584055838, 4.6559137448
H 3.0775452802, 0.4119915197, 3.5910228807
C 0.3301029094, 3.1245371396, 3.3182213008
H 0.2823591294, 2.6793429966, 1.2241214033
C 0.8996850005, 2.8379504578, 4.5617925921
H 2.3397998424, 1.6269001166, 5.6173360344
H -0.4406923357, 3.885390334, 3.2303477369
H 0.5748669361, 3.3747142595, 5.4492849453
H -0.2967551304, 1.6801910319, -1.2902140585

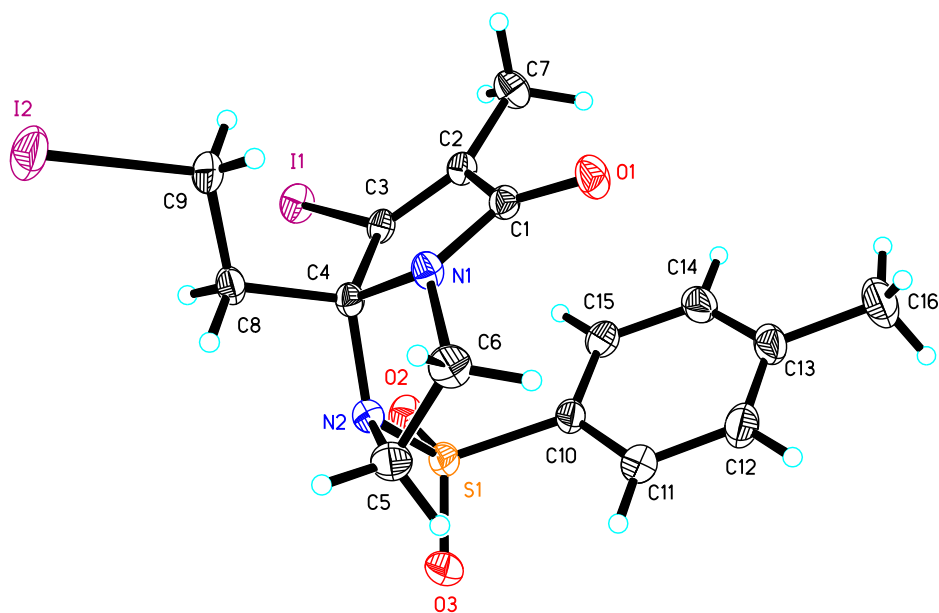
11. X-Ray structures

(a) **3ga**



The crystal data of **3ga** have been deposited in CCDC with number 2083431. Empirical Formula: $C_{11}H_{14}I_3N$; Formula Weight: 540.93; Crystal Color, Habit: colorless, Crystal Dimensions: 0.170 x 0.140 x 0.060 mm³; Crystal System: Triclinic; Lattice Parameters: $a = 8.6649(8) \text{ \AA}$, $b = 8.8569(8) \text{ \AA}$, $c = 9.8661(9) \text{ \AA}$, $\alpha = 84.893(3)^\circ$, $\beta = 88.222(3)^\circ$, $\gamma = 84.477(3)^\circ$, $V = 750.47(12) \text{ \AA}^3$; Space group: P $\bar{1}$; $Z = 2$; $D_{calc} = 2.394 \text{ g/cm}^3$; $F_{000} = 492$; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0798$, $wR2 = 0.2460$.

(b) **3oa'**



The crystal data of **3oa'** have been deposited in CCDC with number 2142800. Empirical Formula: $C_{16}H_{18}I_2N_2O_3S$; Formula Weight: 572.18; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.150 x 0.120 mm³; Crystal System: Monoclinic; Lattice Parameters: $a = 11.5550(4)$ Å, $b = 8.3352(2)$ Å, $c = 20.4748(6)$ Å, $\alpha = 90^\circ$, $\beta = 105.3480(10)^\circ$, $\gamma = 90^\circ$, $V = 1901.66(10)$ Å³; Space group: P 21/c; Z = 4; D_{calc} = 1.999 g/cm³; F₀₀₀ = 1096; Final R indices [$I > 2\sigma(I)$] R1 = 0.0245, wR2 = 0.0571.

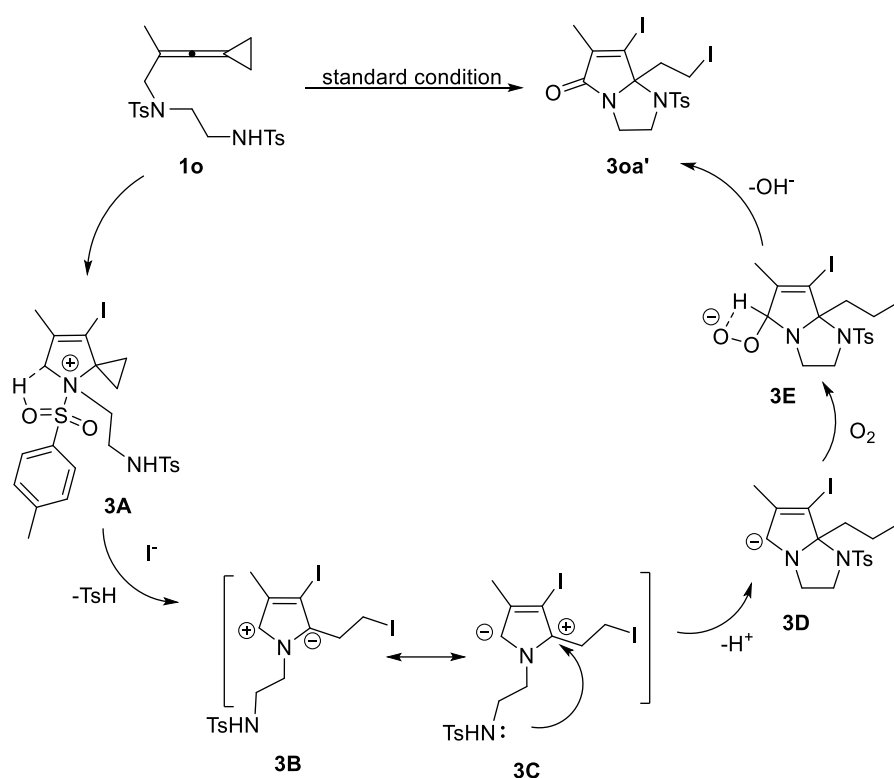


Figure S5. Proposed reaction mechanism of **3oa'**

According to Scheme 7a in the main text, intermediate **3A** is firstly generated through the cyclization reaction. The Ts moiety in intermediate **3A** promotes subsequent dehydrogenation to afford intermediate **3B**. The NHTs moiety in intermediate **3C**, which is the resonance structure of intermediate **3B** undergoes the intramolecular nucleophilic attack to give the cyclized intermediate **3D**. Intermediate **3D** reacts with molecular oxygen under ambient atmosphere to obtain intermediate **3E**. Finally the hydroxide anion in intermediate **3E** is released to deliver the corresponding product **3oa'**. This result indicates that the zwitterionic intermediate **1D** shown in Scheme 7b might be indeed involved in the reaction system.

12. References

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