Supporting Information

Iodine radical mediated cascade [3 + 2] carbocyclization of ene-vinylidenecyclopropanes with thiols and selenols via photoredox catalysis

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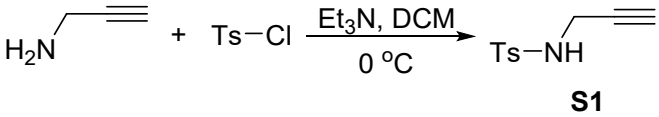
1. General remarks

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 400 MHz or 600 MHz, 100 MHz or 150 MHz and 376 MHz or 564 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 Permier. 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. Substrate **1u** is easily deteriorated in air and its ^{1}H, ^{13}C NMR spectra can not be measured.

2. General procedures for the synthesis of substrates 1, 2g, and *d*-2a

Synthesis of substrates 1a-1t[1]

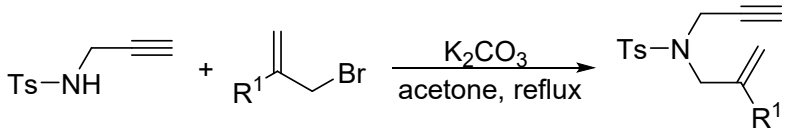
Step 1



S1

To a solution of *p*-toluenesulfonyl chloride (60 mmol) in DCM (100 mL) was added Et_3N (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 H_2O (20 mL × 3), dried over anhydrous Na_2SO_4, and filtered, the organic phase was concentrated under reduced pressure to dryness to give a yellow solid **S1**.

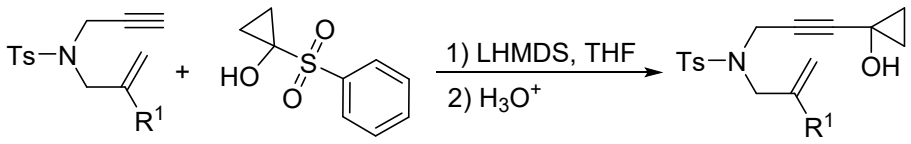
Step 2



S1 **S2** **S3**

To a solution of **S1** (50 mmol) in acetone (100 mL) was added K_2CO_3 (1.5 equiv.) and **S2** (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 **S3** (PE:EA = 10:1).

Step 3

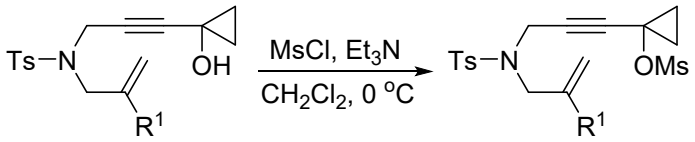


S3 **S4** **S5**

To a solution of compounds **S3** (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 **S4** (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 NH_4Cl solution was added to quench the

reaction. Extracted with ethyl acetate, 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 products **S5** (PE:EA = 4:1~2:1).

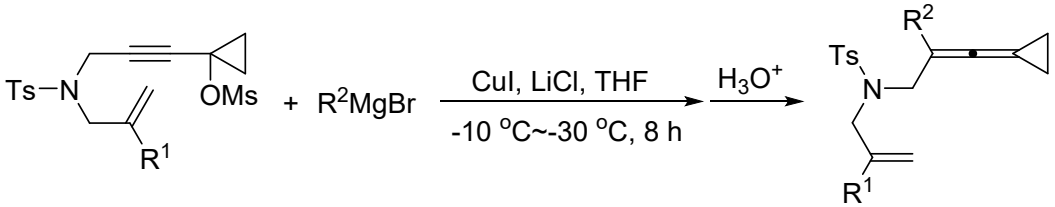
Step 4



S5 **S6**

To a solution of **S5** (5.0 mmol) and anhydrous Et_3N (2.0 equiv.) in CH_2Cl_2 (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 CH_2Cl_2 (20 mL × 3), dried over anhydrous Na_2SO_4, 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 **S6** (PE:EA = 2:1).

Step 5

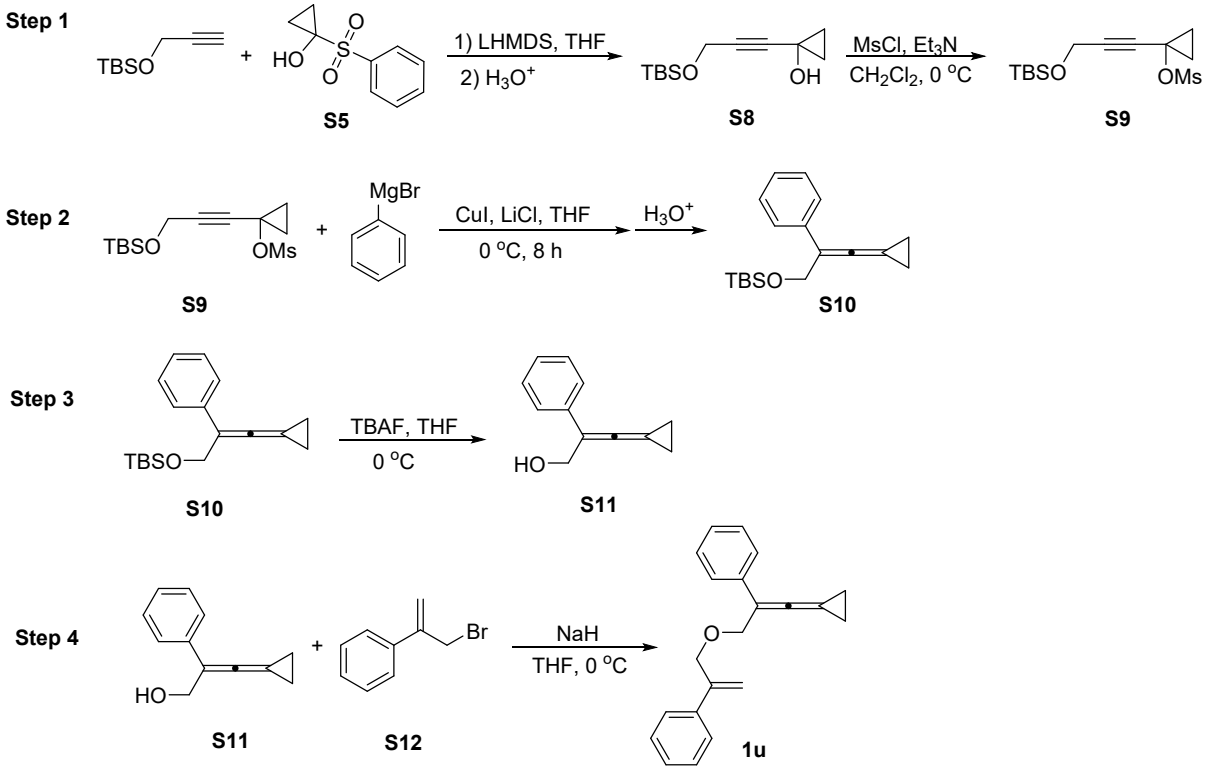


S6 **S7**

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 **S6** (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 NH_4Cl solution was added to quench the reaction. Extracted with EA (20 mL × 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 products **S7** (PE:EA = 10:1).

Synthesis of substrate 1u



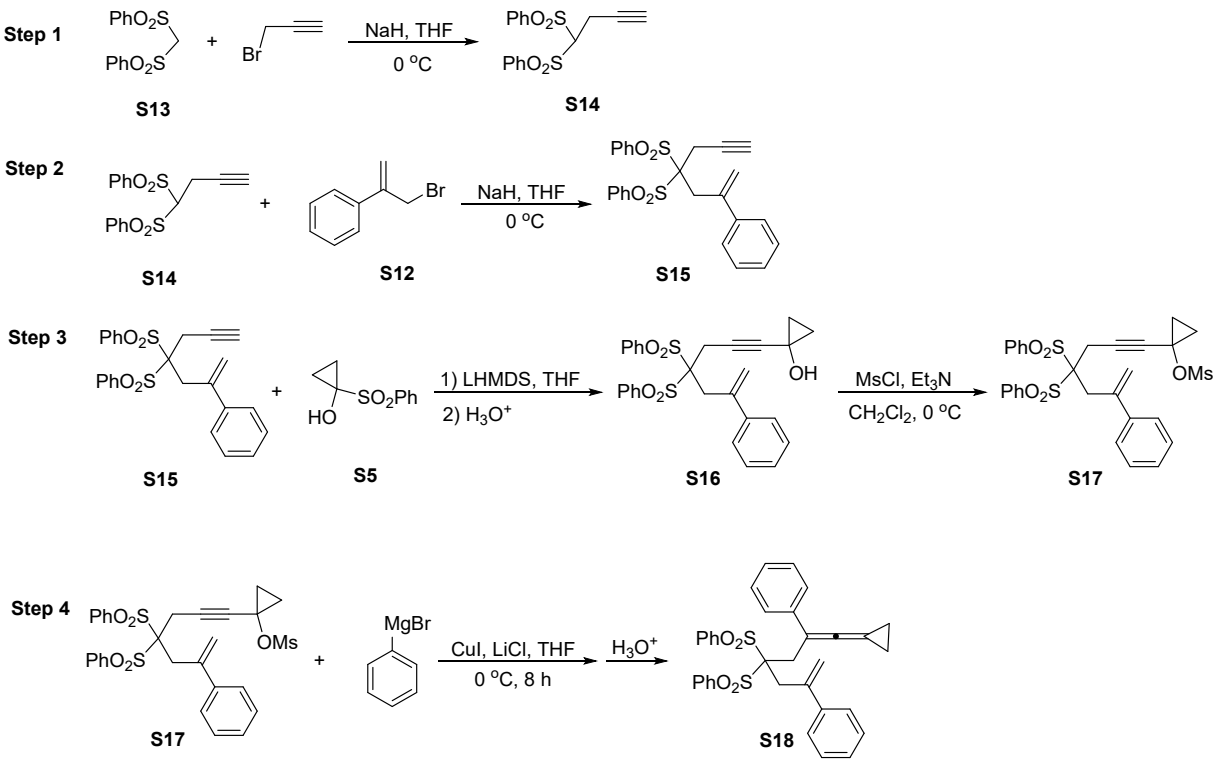
The experimental procedures of **step 1** and **step 2** were the same as those described above.

Step 3: To a flame dried 50 mL flask was added **S10** (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 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 **S11** (PE:EA = 4:1).

Step 4: To a flame dried 50 mL flask was added NaH (60% dispersion in mineral oil, 3.0 mmol, 2.0 equiv.), and the solvent THF (10 mL) under the protection of argon and then, the flask was cooled to 0 °C before the solution of **S11** (1.5 mmol) in THF was added dropwise into the flask under argon. The reaction mixture was stirred at 0 °C for 30 min. The **S12** (3.0 mmol, 2.0 equiv.) was

added slowly and the reaction mixture was warmed to room temperature overnight before water was added to quench the reaction. Extracted with EA, 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 **1u** (PE:EA = 50:1).

Synthesis of substrate 1v.[2]

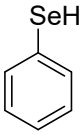


The experimental procedures of **step 3** and **step 4** were the same as those described above.

Step 1: To a flame dried 100 mL flask was added NaH (60% dispersion in mineral oil, 10.0 mmol, 2.0 equiv.), and the solvent THF (30 mL) under the protection of argon and then, the flask was cooled to 0 °C before the solution of **S13** (5.0 mmol) in THF was added dropwise into the flask under argon. The reaction mixture was stirred at 0 °C for 30 min. The propargyl bromide (10.0 mmol, 2.0 equiv.) was added slowly and the reaction mixture was warmed to room temperature overnight before water was added to quench the reaction. Extracted with EA, 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 **S14** (PE:EA = 4:1).

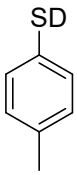
Step 2: To a flame dried 100 mL flask was added NaH (60% dispersion in mineral oil, 8.0 mmol, 2.0 equiv.), and the solvent THF (30 mL) under the protection of argon and then, the flask was cooled to 0 °C before the solution of **S14** (4.0 mmol) in THF was added dropwise into the flask under argon. The reaction mixture was stirred at 0 °C for 30 min. The propargyl bromide (8.0 mmol, 2.0 equiv.) was added slowly and the reaction mixture was warmed to room temperature overnight before water was added to quench the reaction. Extracted with EA, 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 **S15** (PE:EA = 4:1).

Synthesis of substrate 2g.[3]



Compound **2g** was synthesized according to the previously reported literature procedure.[3] Diselenide (5.0 mmol) and $NaBH_4$ (3.0 equiv.) were added in a 50 mL flask. The flask was placed under vacuum and backfilled with argon three times. Then, EtOH (10.0 mL) and was added in the flask via a syringe. Next, the mixture was allowed to stir at 0 °C. After 15 min, citric acid (5.0 equiv.) was added and the reaction mixture was stirred at 0 °C for 5 minutes before water was added to quench the reaction. Extracted with Et_2O and the organic phase was washed with saturated NH_4Cl (10 mL, aq.) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to afford the desired product **2g**, which is pure enough to be used without further purification.

Synthesis of *d*-2a[4]

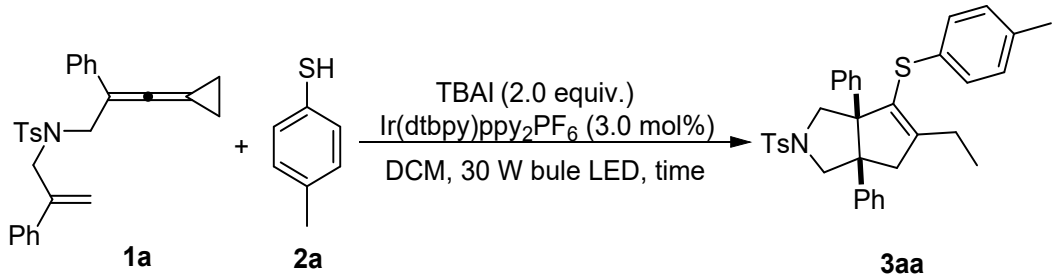


Compound *d*-**2a** was synthesized according to the previously reported literature procedure.[4] **2a** (4.0 mmol) was added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under

vacuum and backfilled with argon three times. Then, $CDCl_3$ (10.0 mL) and D_2O (10 equiv.) were added in the Schlenk tube via a syringe. Next, the resulting mixture was allowed to stir at 70 ^oC for 12 h. When the reaction is complete, the reaction mixture was allowed to cool down to room temperature and dried over anhydrous Na_2SO_4. The solvent was removed under reduce pressure to afford the desired compound *d*-**2a** as a yellow solid.

3. Optimization of reaction conditions

Table S1. Optimization of reaction conditions using **1a** as a template substrate (time).[a]

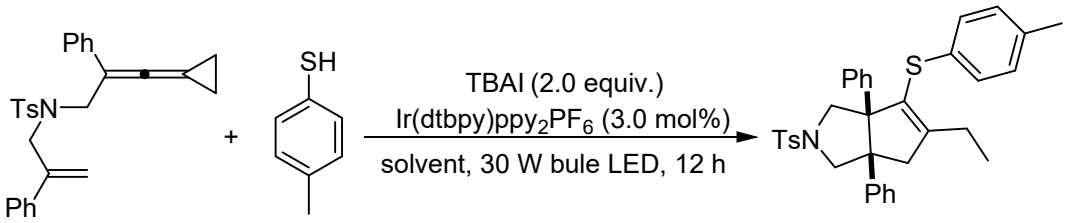


1a **2a** **3aa**

entry[a]	time	**3aa**, yield[b] [%]
1	12 h	47
2	24 h	45
3	48 h	41

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (2.0 equiv.), TBAI (2.0 equiv.), $Ir(dtbpy)ppy_2PF_6$ (3.0 mol%) in DCM (2.0 mL) at ambient temperature using 30 W blue LEDs irradiation. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard.

Table S2. Optimization of reaction conditions using **1a** as a template substrate (solvent).[a]

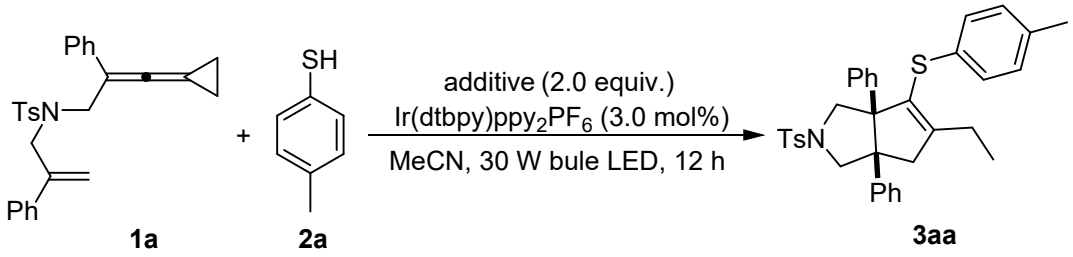


1a **2a** **3aa**

entry[a]	solvent	**3aa**, yield[b] [%]
1	DCM	47
2	CH_3CN	61
3	DMA	NR
4	DCE	39
5	DMF	NR
6	ethyl acetate	33
7	$CHCl_3$	44
8	acetone	51
9	toulene	NR

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (2.0 equiv.), TBAI (2.0 equiv.), $Ir(dtbpy)ppy_2PF_6$ (3.0 mol%) in solvent (2.0 mL) at ambient temperature using 30 W blue LEDs irradiation for 12 hours. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard.

Table S3. Optimization of reaction conditions using **1a** as a template substrate (additive).[a]

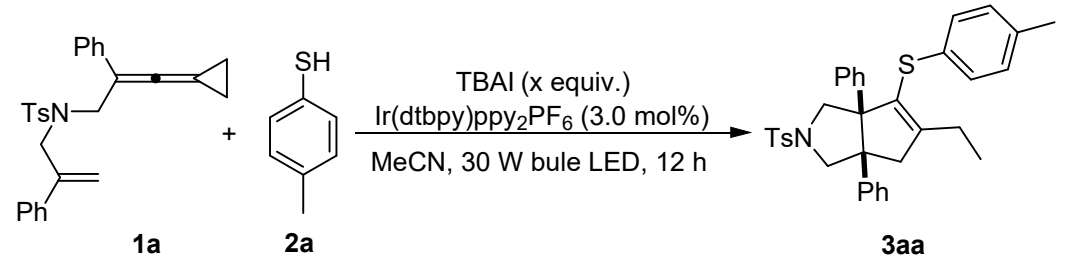


1a **2a** **3aa**

entry[a]	additive	**3aa**, yield[b] [%]
1	TBAI	61
2	KI	53
3	NaI	42
4	TBAB	58
5	$N(Me)_4I$	53
6	$N(Me)_3BnI$	59
7	$N(Et)_4I$	55
8	$S(Me)_3I$	NR

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (2.0 equiv.), additive (2.0 equiv.), $Ir(dtbpy)ppy_2PF_6$ (3.0 mol%) in MeCN (2.0 mL) at ambient temperature using 30 W blue LEDs irradiation for 12 hours. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard.

Table S4. Optimization of reaction conditions using **1a** as a template substrate (equiv. of TBAI).[a]

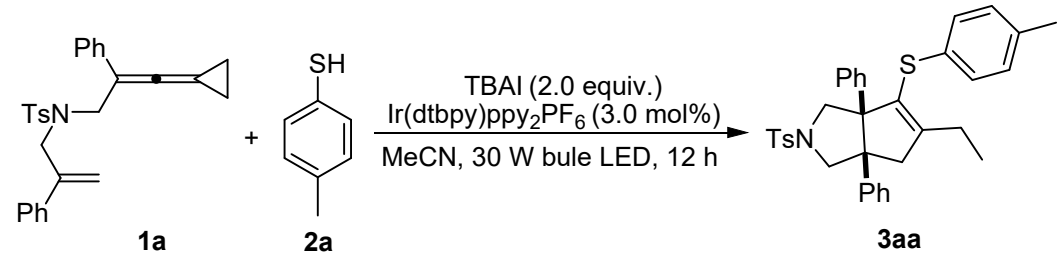


1a **2a** **3aa**

entry[a]	x	**3aa**, yield[b] [%]
1	1.0	53
2	2.0	61
3	0.5	49
4	0.2	50

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (2.0 equiv.), TBAI (x equiv.), $Ir(dtbpy)ppy_2PF_6$ (3.0 mol%) in MeCN (2.0 mL) at ambient temperature using 30 W blue LEDs irradiation for 12 hours. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard.

Table S5. Optimization of reaction conditions using **1a** as a template substrate (equiv. of **2a**).[a]

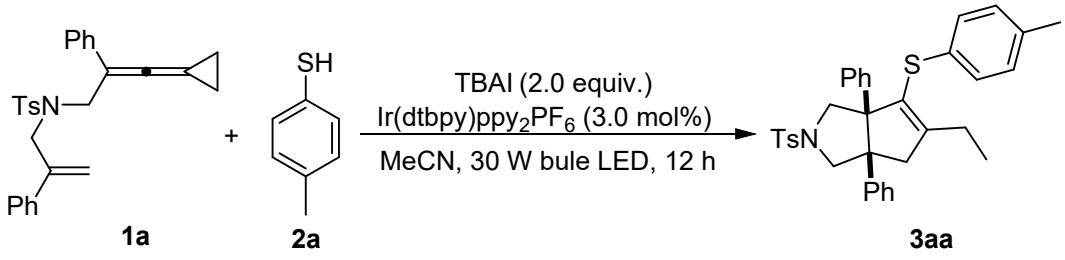


1a **2a** **3aa**

entry[a]	x	**3aa**, yield[b] [%]
1	1.0	46
2	2.0	61
3	3.0	53
4	4.0	57
5	5.0	54

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (x equiv.), TBAI (2.0 equiv.), $Ir(dtbpy)ppy_2PF_6$ (3.0 mol%) in MeCN (2.0 mL) at ambient temperature using 30 W blue LEDs irradiation for 12 hours. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard.

Table S6. Optimization of reaction conditions using **1a** as a template substrate (conc.).[a]

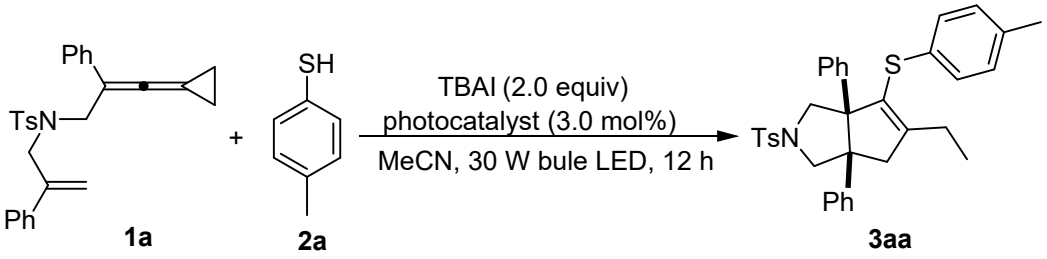


1a **2a** **3aa**

entry[a]	x	**3aa**, yield[b] [%]
1	0.5	61
2	2.0	60
3	5.0	65
4	10.0	78

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (2.0 equiv.), TBAI (2.0 equiv.), $Ir(dtbpy)ppy_2PF_6$ (3.0 mol%) in MeCN (x mL) at ambient temperature using 30 W blue LEDs irradiation for 12 hours. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard.

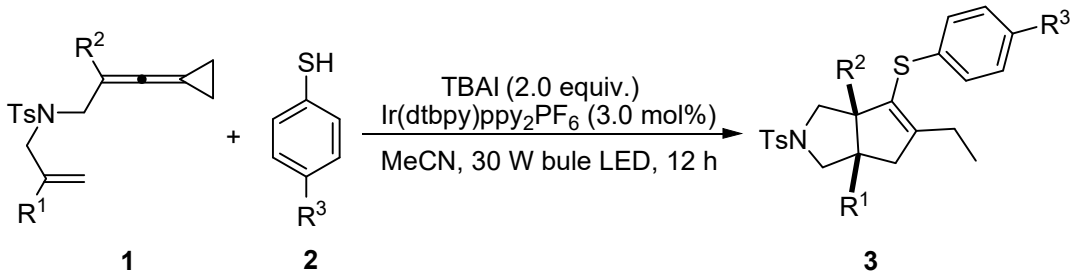
Table S7. Optimization of reaction conditions using **1a** as a template substrate (photocatalyst).[a]



entry[a]	photocatalyst	**3aa**, yield[b] [%]
1	$Ir(dtbpy)ppy_2PF_6$	78
2	$[Ir(dFCF_3ppy)_2dtbpy]PF_6$	62
3	*fac*-$Ir(ppy)_3PF_6$	55
4	4CzIPN	64
5	$[Ir(dFCF_3ppy)_2dCF_3bpy]PF_6$	66
6	$Ru(bpy)_3PF_6$	35
7	$Ir(dtbpy)ppy_2PF_6$	50[c]
8	$MesAcr^+$	NR

[a] Reaction was carried out with **1a** (0.1 mmol), **2a** (2.0 equiv.), TBAI (2.0 equiv.), photocatalyst (3.0 mol%) in MeCN (10.0 mL) at ambient temperature using 30 W blue LEDs irradiation for 12 hours. [b] ^1H NMR yield using dimethyl terephthalate as an internal standard. [c] TBAI (0.2 equiv.)

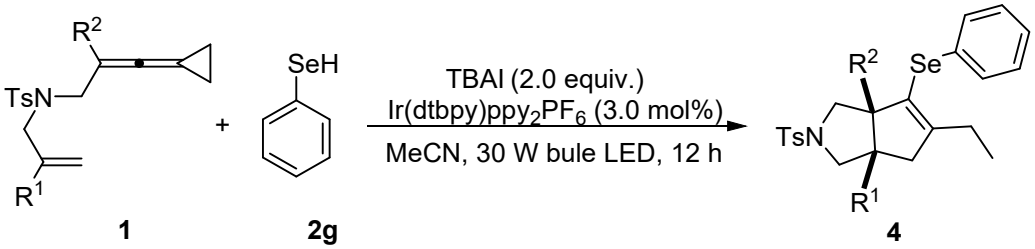
4. General procedure for the synthesis of 3, 4 and **7**



1 **2** **3**

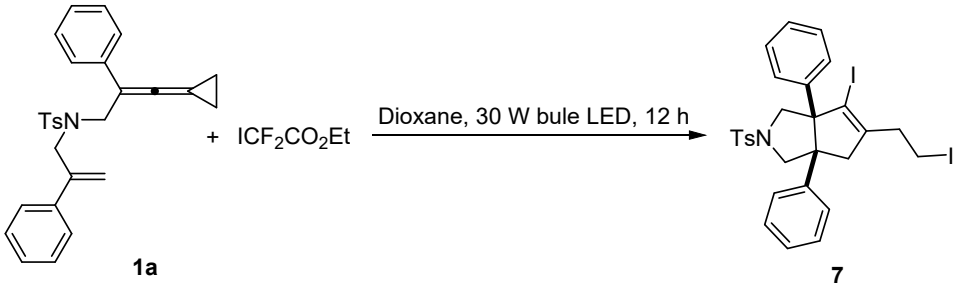
VDCPs **1** (0.1 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2** (2.0 equiv.), and Ir(dtbpy)ppy_2PF_6 (3.0 mol%) were added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (10 mL) was added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. After completion, the solvent was removed under reduced pressure. The crude product residue was purified by a column chromatography on silica gel (PE/EA = 10/1 to 4/1) to afford the purified product **3**.

General procedure for the synthesis of 4



1 **2g** **4**

VDCPs **1** (0.1 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2g** (2.0 equiv.), and Ir(dtbpy)ppy_2PF_6 (3.0 mol%) were added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (10 mL) was added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. After completion, the solvent was removed under reduced pressure. The crude product residue was purified by a column chromatography on silica gel (PE/EA = 10/1 to 4/1) to afford the purified product **4**.



VDCP **1a** (0.1 mmol, 1.0 equiv) was added in an flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, ICF_2CO_2Et (0.24 mmol, 2.4 equiv.) and dioxane (10 mL) were added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. After completion, the solvent was removed under reduced pressure. The crude product residue was purified by a column chromatography on silica gel (PE/EA = 10/1 to 4/1) to afford the purified product **7**.

5. Mechanistic studies

(a) Luminescence quenching experiments (Stern-Volmer Studies).[5]

Emission intensities were recorded using Varian Cary Eclipse spectrometer for all experiments. All Ir(dtbpy)ppy$_2$PF$_6$ solutions were excited at 365 nm and the emission intensity was collected at 580 nm. Solutions of different concentration of TBAI and **2a** were prepared and introduced to a 1.0 cm path length quartz cuvette equipped with a Teflon® septum. In a typical experiment, to a 0.1 mM solution of photocatalyst in MeCN was added the appropriate amount of TBAI in a screw-top quartz cuvette under Ar atmosphere and the emission of the sample was collected. Subsequently, to a 0.1 mM solution of photocatalyst in MeCN was added the appropriate amount of **2a** in screw-top quartz cuvette under Ar atmosphere and the emission of the sample was collected.

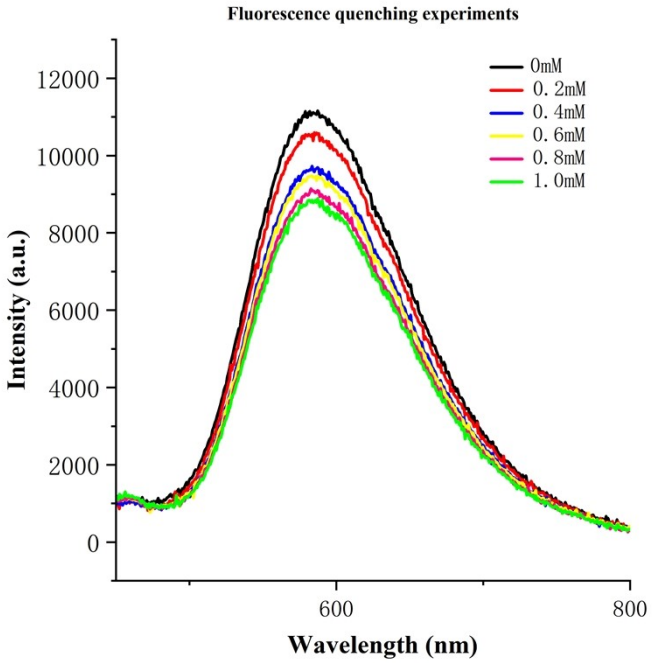


Figure S1. Quenching of the Ir(dtbpy)ppy$_2$PF$_6$ emission (0.1 mM in MeCN) in the presence of increasing amounts of TBAI.

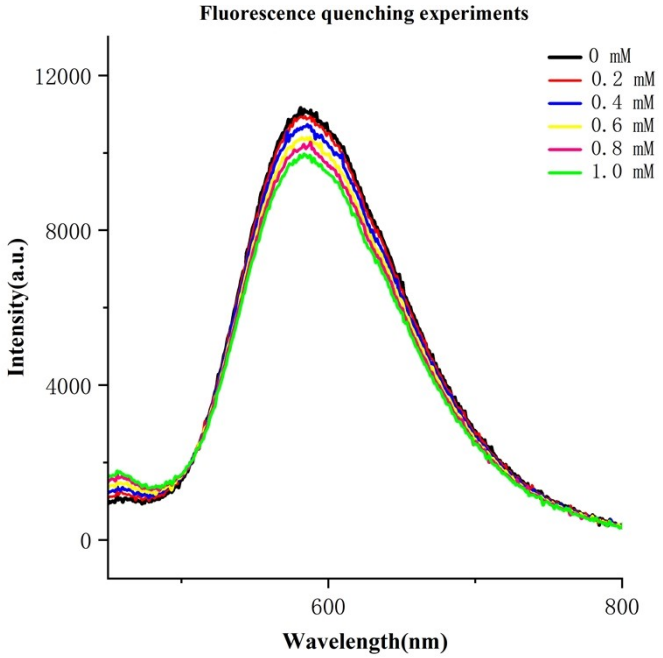


Figure S2. Quenching of the Ir(dtbpy)ppy$_2$PF$_6$ emission (0.1 mM in MeCN) in the presence of increasing amounts of **2a**.

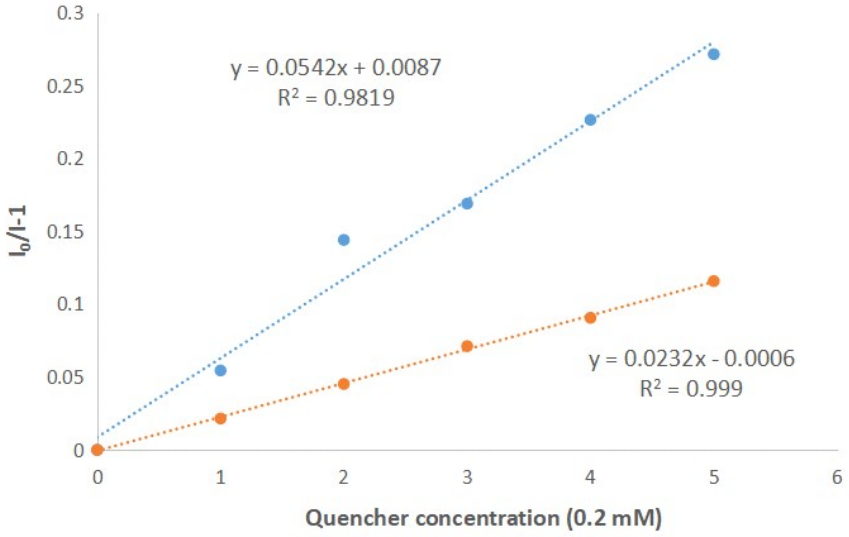
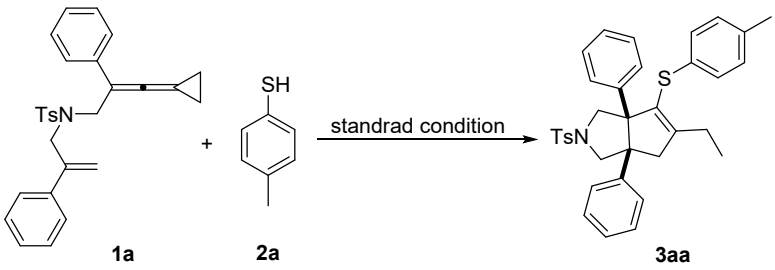


Figure S3. Stern-Volmer plot for the quenching studies above.

(b) Light on/off experiment and quantum yield.[5]

To study the necessity of continuous irradiation with visible light for the progress of the reaction, the reaction proceeding was monitored by ^{1}H NMR spectroscopy using dimethyl terephthalate as an internal standard before and after light irradiation and dark periods.

The control experiments shown below with successive intervals of irradiation and dark periods did result in interruption of the reaction progress in the absence of light, demonstrating that light is a necessary component for the reaction after triggering the reaction in the first part.



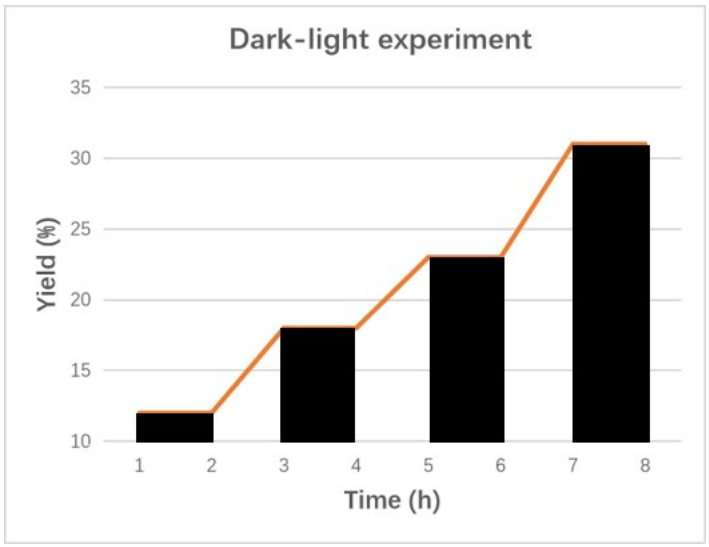


Figure S4. Light on-off experiment.

To further investigate whether the chain process is involved upon light irradiation, we measured the quantum yield of the template reaction of 1 h.

$$\phi = \frac{n_x}{n_p} = \frac{n_x}{\frac{\Delta E \times S \times t}{N_A h v}} = \frac{n_x \times N_A \times h \times c}{\Delta E \times S \times t \times \lambda}$$

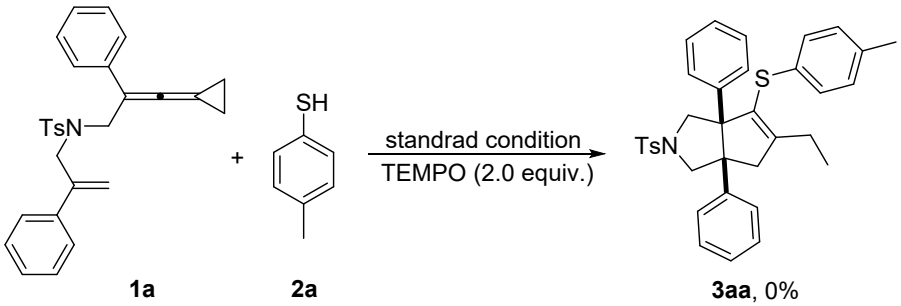
$$= \frac{0.04 \times 15\% \times 10^{-3} mol \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^{8} m \cdot s^{-1}}{(260 \times 10^{-3} W \cdot cm^{-2} \times 2cm^{2}) \times 3600 s \times 455 \times 10^{-9} m}$$

$$= 0.005$$

n_x is the amount of photochemical or photophysical events x occurred during irradiation, n_p is the number of photons absorbed by the reactant. E is the radiant power. S is the irradiated area: 2 cm^2; t is the irradiated time: 3600 s; N_A is the Avogadro constant: 6.022×10^{23}/mol; h is the Planck constant: 6.626×10^{-34} J·s; v is the frequency of incident light; c is velocity of light 2.998×10^{8} m/s). λ is the wavelength: 455 nm; n_x was analyzed by ^{1}H NMR, ΔE was measured by ILT1400 Portable Radiometer/Photometer.

VDCP **1a** (0.04 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2a** (2.0 equiv.), and Ir(dtbpy)ppy_2PF_6 (3.0 mol%) were added in a cuvette equipped with a magnetic stir bar. The reaction cuvette was placed under vacuum and backfilled with argon three times. Then, MeCN (10 mL) was added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 1.0 h. The reaction mixture was concentrated in *vacuo* and analyzed by ^{1}H NMR spectrum using dimethyl terephthalate as an internal standard. The quantum yield is calculated to be 0.005.

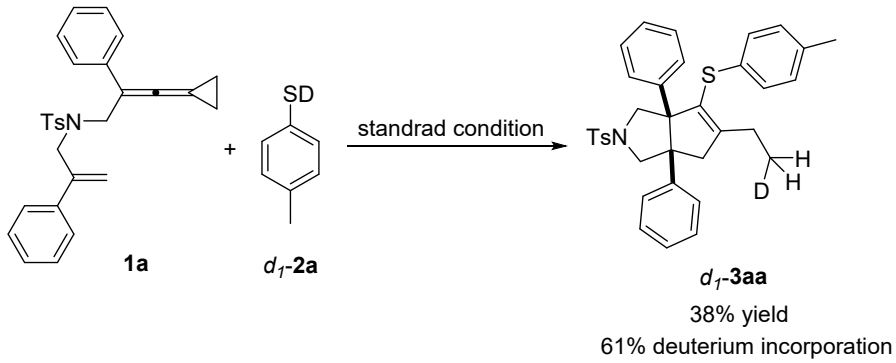
(c) Radical trapping experiments.[6]



1a **2a** **3aa**, 0%

VDCP **1a** (0.1 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2a** (2.0 equiv.), TEMPO (2.0 equiv.) and Ir(dtbpy)ppy$_2$PF$_6$ (3.0 mol%) were added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (10.0 mL) was added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. When the reaction finished up, the mixture was concentrated in vacuo. The yield of product **3aa** was determined by ^{1}H NMR spectroscopy using dimethyl terephthalate as an internal standard.

(d) Deuterium labeling experiments.[7]

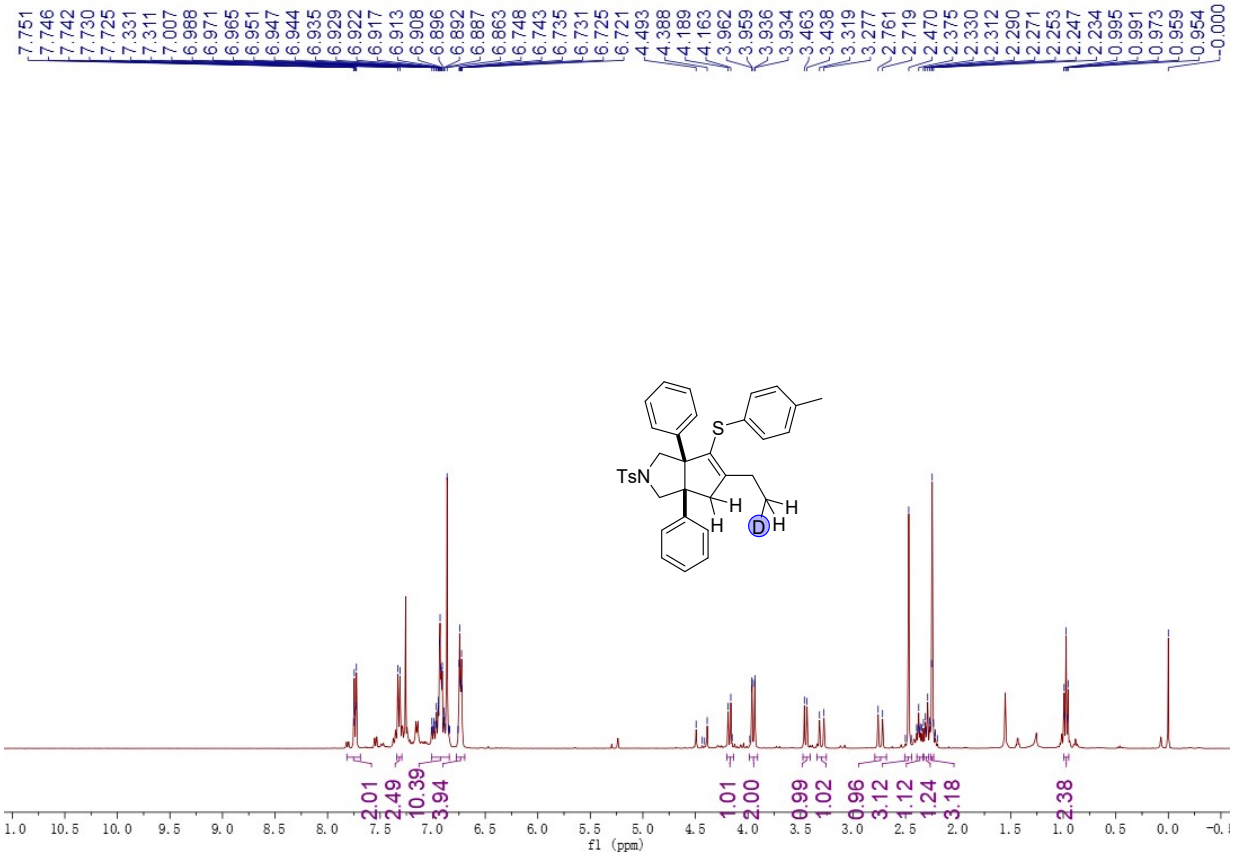


1a *d*$_1$-**2a**

d$_1$-**3aa**
38% yield
61% deuterium incorporation

VDCP **1a** (0.1 mmol, 1.0 equiv.), TBAI (2.0 equiv.), *d*$_1$-**2a** (2.0 equiv.), and Ir(dtbpy)ppy$_2$PF$_6$ (3.0 mol%) were added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (10.0 mL) was added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. When the reaction finished up, the mixture was concentrated in vacuo. The crude product was directly purified by a flash chromatography on

silica gel (petroleum ether:ethyl acetate = 10:1) to give the desired product in 38% yield with 62% deuterium incorporation.



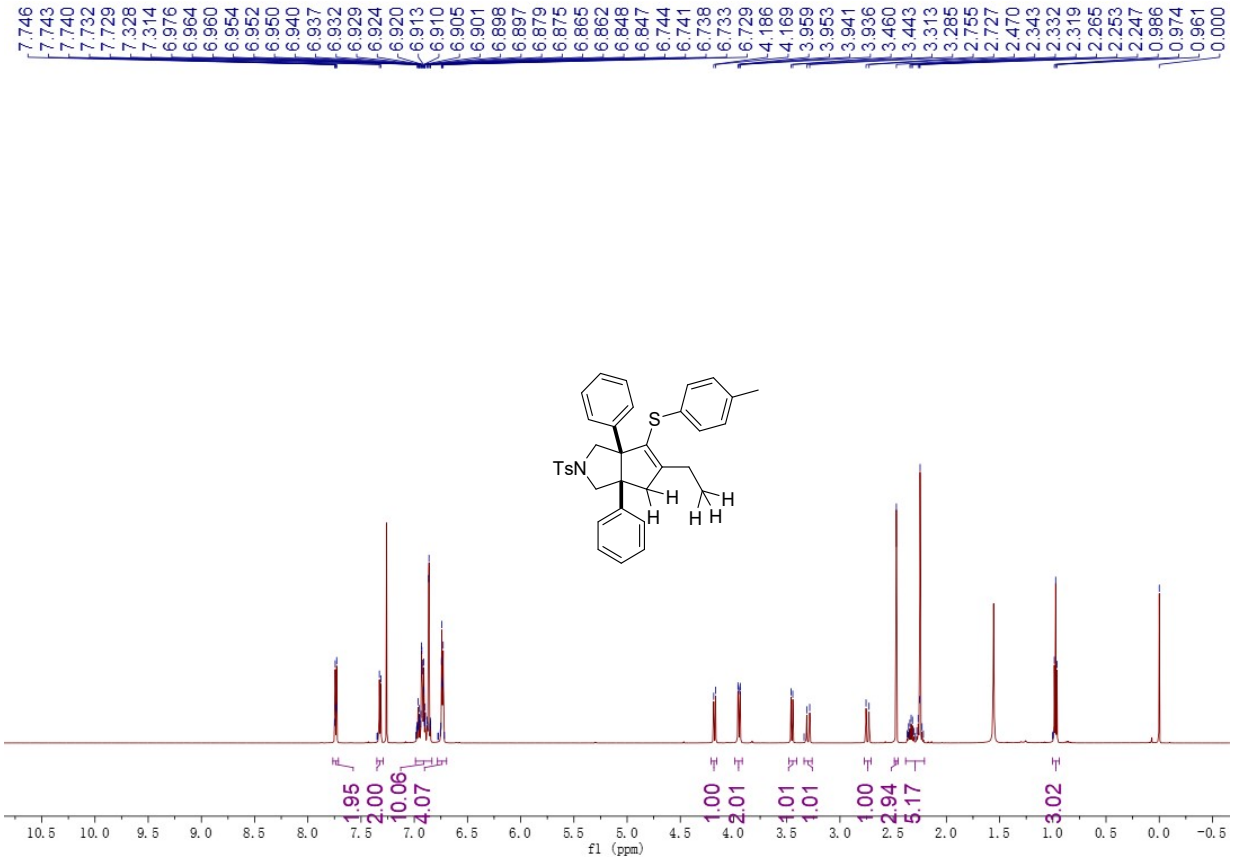
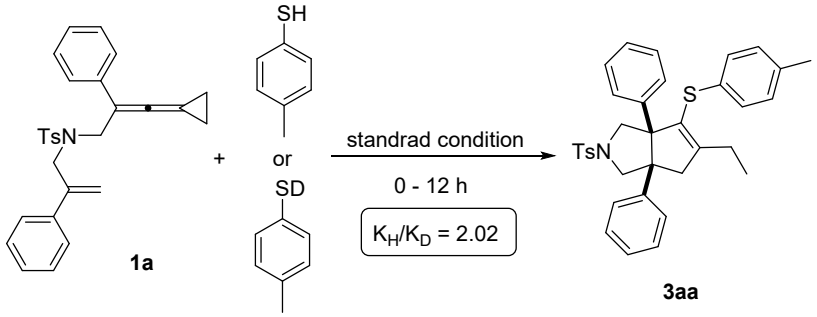


Figure S5. Deuterium labeling experiments.

(e) Kinetic isotope effect experiment.[7]



2a or *d*-**2a**, 2.0 equiv.

The reaction progress of **2a** or *d*-**2a** with **1a** was monitored in parallel at five distinct periods (0 h, 3.0 h, 6.0 h, 9.0 h, and 12 h). VDCP **1a** (0.1 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2a** or d_1-**2a** (2.0 equiv.), and Ir(dtbpy)ppy_2PF_6 (3.0 mol%) were added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (10.0 mL) was added in the Schlenk tube via a syringe. Next, the eight tubes were placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light at ambient temperature. At the end of each stage, the reaction tube was taken out. Then, the reaction mixture was concentrated in *vacuo* and analyzed by ^{1}H NMR spectrum using dimethyl terephthalate as an internal standard. The KIE of the reaction, which was calculated by dividing the rate constant of the reaction of **2a** (k_H = 6.4556) by that of *d*-**2a** (k_D = 3.1889), was determined to be 2.02

time [h]	Yield of **3aa**[%] (from **2a**)	Yield of **3aa**[%] (from d_1-**2a**)
0	0	0
3	21	11
6	37	16
9	58	28
12	78	40

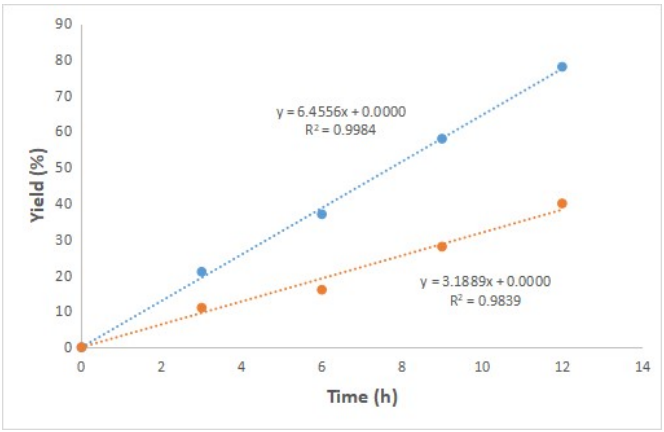
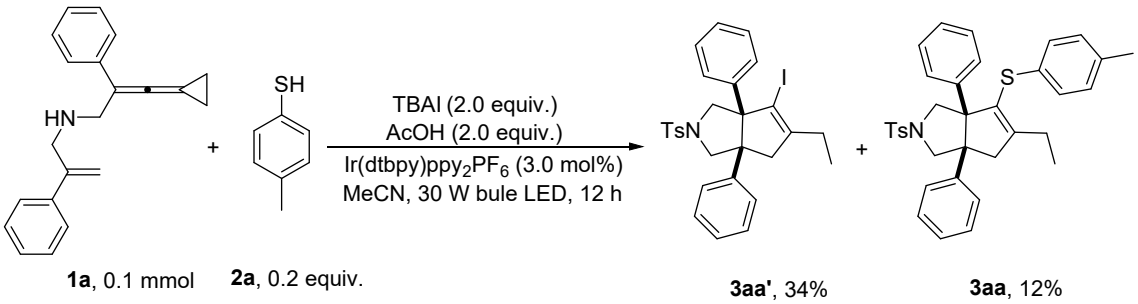
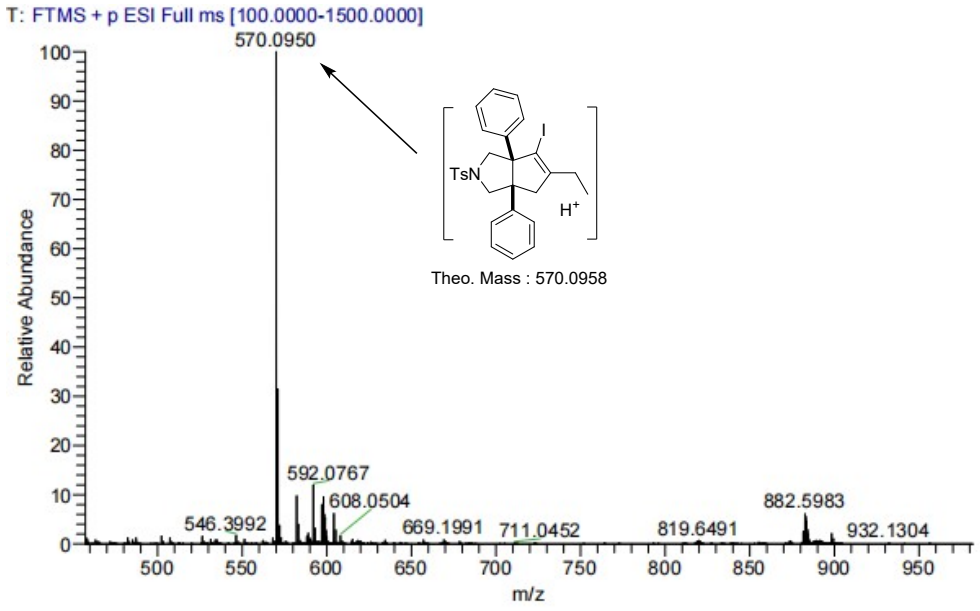


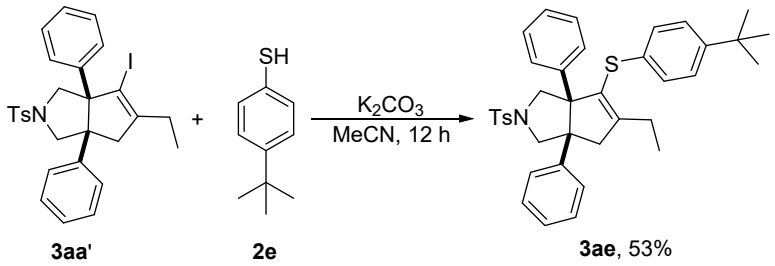
Figure S6. Kinetic isotope effect experiment

(f) Control experiment.



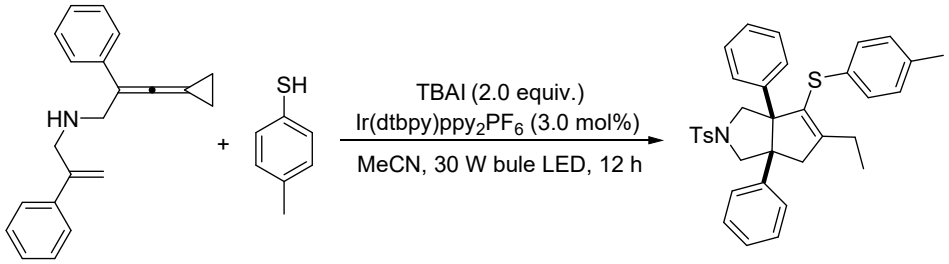
VDCP **1a** (0.1 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2a** (0.2 equiv.), AcOH (2.0 equiv.) and Ir(dtbpy)ppy_2PF_6 (3.0 mol%) were added in a flame dried 15 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (10.0 mL) was added in the Schlenk tube via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. When the reaction finished up, the reaction mixture was concentrated in vacuo. However, **3aa** and **3aa'** are similar in polarity and cannot be separated, and thus, we confirmed the presence of **3aa'** by a mass spectrometric analysis.





To a flame dried 25 mL flask was added **3aa'** (0.1 mmol), **2e** (2.0 equiv), K_2CO_3 (2.0 equiv) and the solvent MeCN (10 mL). After the reaction mixture was stirred at room temperature for 12 hours, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated. However, **3ae** and **3aa'** are similar in polarity and cannot be separated, and thus, we confirmed the presence of **3ae** by a mass spectrometric analysis.

6. Gram scale reaction

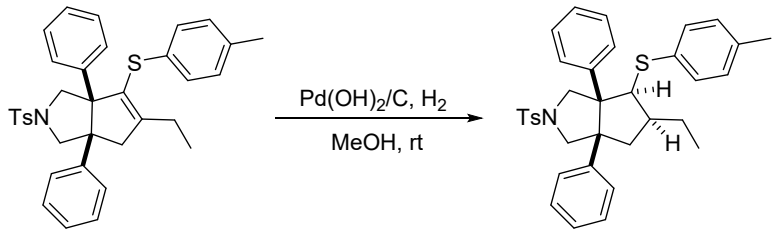


1a, 2.0 mmol, 0.88 g **2a** **3aa**, 80%, 0.90 g

VDCP **1a** (2.0 mmol, 1.0 equiv.), TBAI (2.0 equiv.), **2a** (2.0 equiv.), and Ir(dtbpy)ppy_2PF_6 (3.0 mol%) were added in a flame dried 100 mL Schlenk flask. The reaction tube was placed under vacuum and backfilled with argon three times. Then, MeCN (60 mL) was added in the Schlenk flask via a syringe. Next, the tube was placed 5.0 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. After completion, the solvent was removed under reduced pressure. The crude product residue was purified by a column chromatography on silica gel (PE/EA = 10/1) to afford the purified product **3aa** in 80% yield (0.90 g).

7. Transformation of product 3aa.[6]

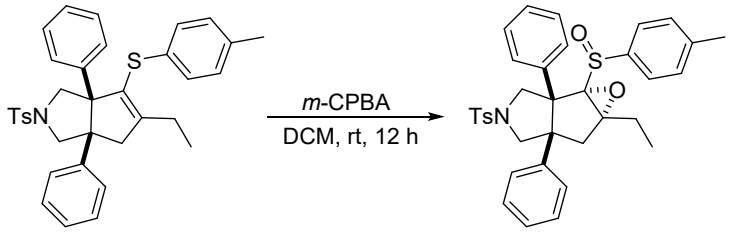
A. Hydrogenative reduction reaction



3aa **5**

To a flask was added substrate **3aa** (0.1 mmol, 1.0 equiv), $Pd(OH)_2/C$ (16 mg) and MeOH (8.0 mL). After the reaction mixture was stirred at room temperature for 12 hours under 1.0 atm H_2, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated under reduced pressure and the residue was purified with a silica gel column chromatography (PE/EA = 4/1) to give product **5** as a colorless oil (83% yield).

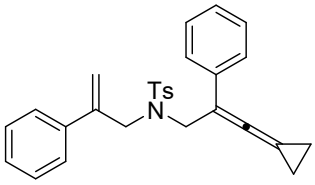
B. Oxidation reaction



3aa **6**

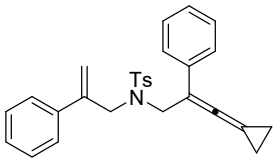
To a flask was added substrate **3aa** (0.1 mmol, 1.0 equiv.), 3-chloroperoxybenzoic acid (0.22 mmol, 2.2 equiv.), and DCM (10 mL). After the reaction mixture was stirred at room temperature for 12 hours, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated and the residue was purified with a silica gel column chromatography (PE/EA = 4/1) to give product **6** as a colorless oil (78% yield).

8. Spectroscopic data of substrates 1

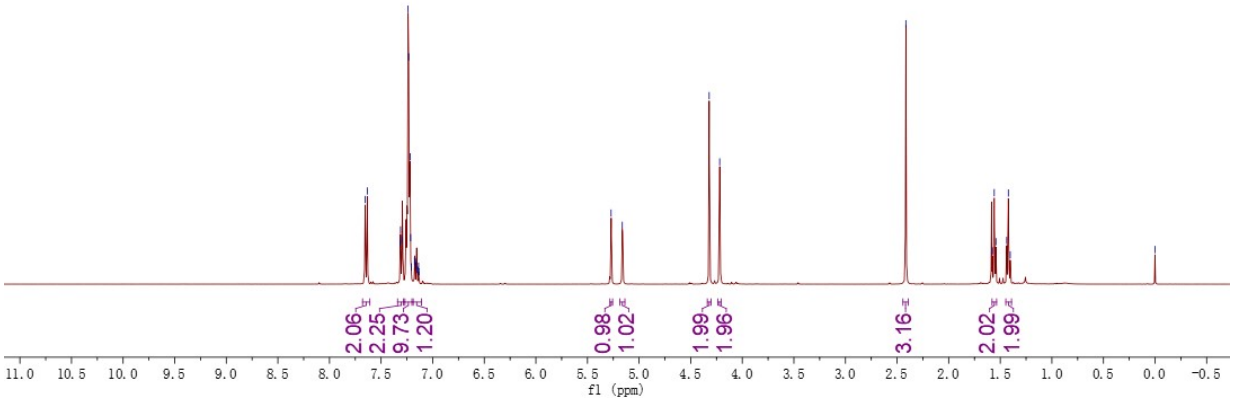


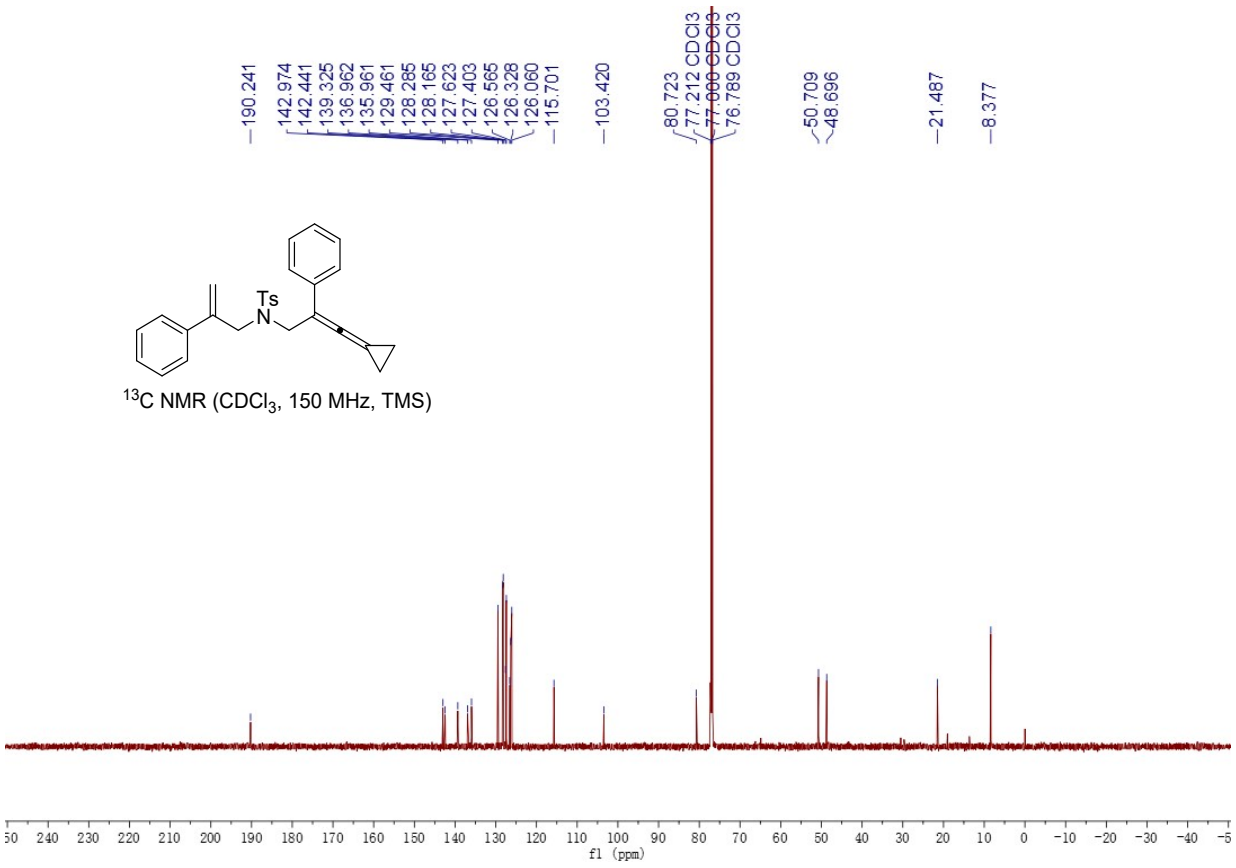
***N*-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1a)**

A colorless oil, 56% yield, 247.0 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.34 - 7.27 (m, 2H), 7.28 - 7.19 (m, 9H), 7.20 - 7.11 (m, 1H), 5.27 (s, 1H), 5.16 (s, 1H), 4.32 (s, 2H), 4.22 (s, 2H), 2.41 (s, 3H), 1.58 - 1.54 (m, 2H), 1.45 - 1.39 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.2, 143.0, 142.4, 139.3, 137.0, 136.0, 129.5, 128.3, 128.2, 127.6, 127.4, 126.6, 126.3, 126.1, 115.7, 103.4, 80.7, 50.7, 48.7, 21.5, 8.4. IR (Acetone) ν 913, 1092,1159, 1339, 1594, 1709, 2009, 2920 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{27}NO_2NaS$ (M+Na): 464.1655, Found: 464.1661.

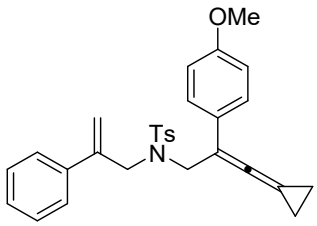


^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



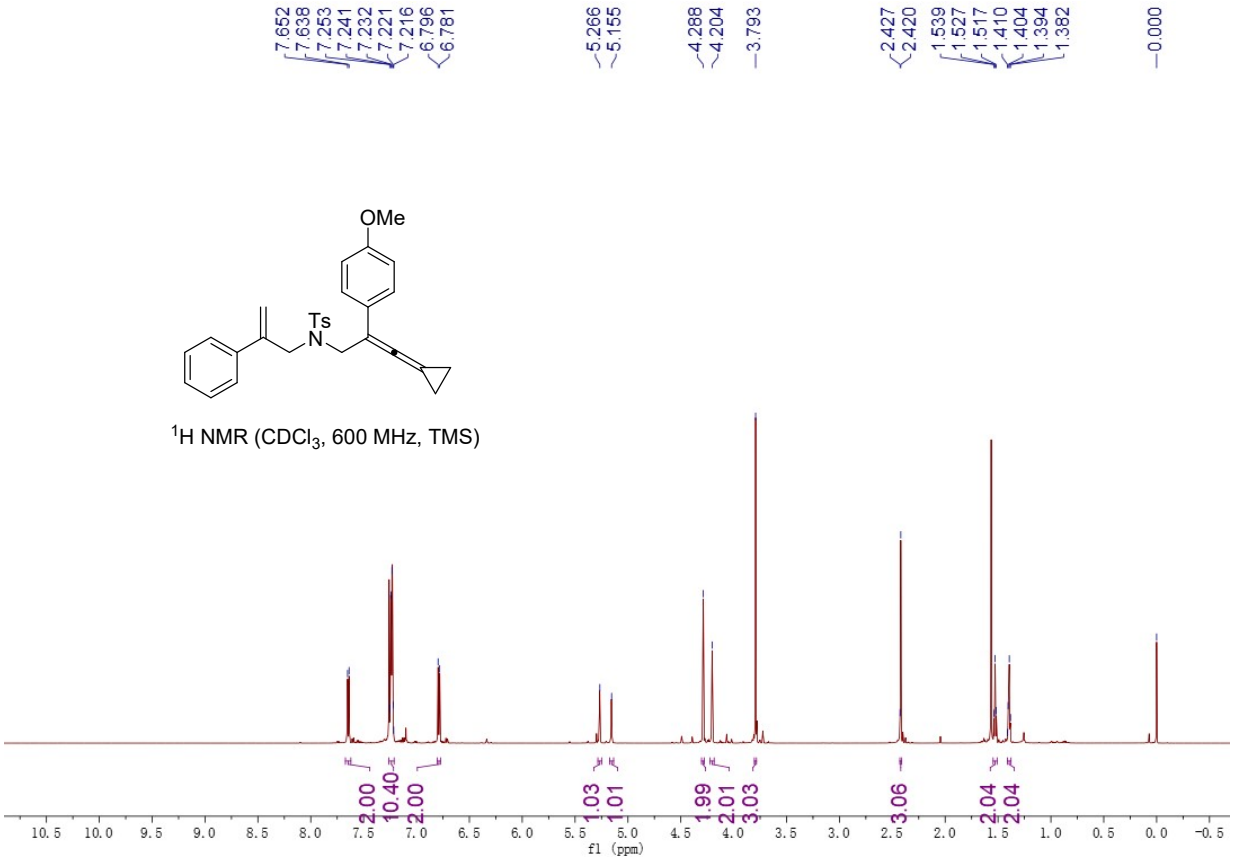


^{13}C NMR ($CDCl_3$, 150 MHz, TMS)

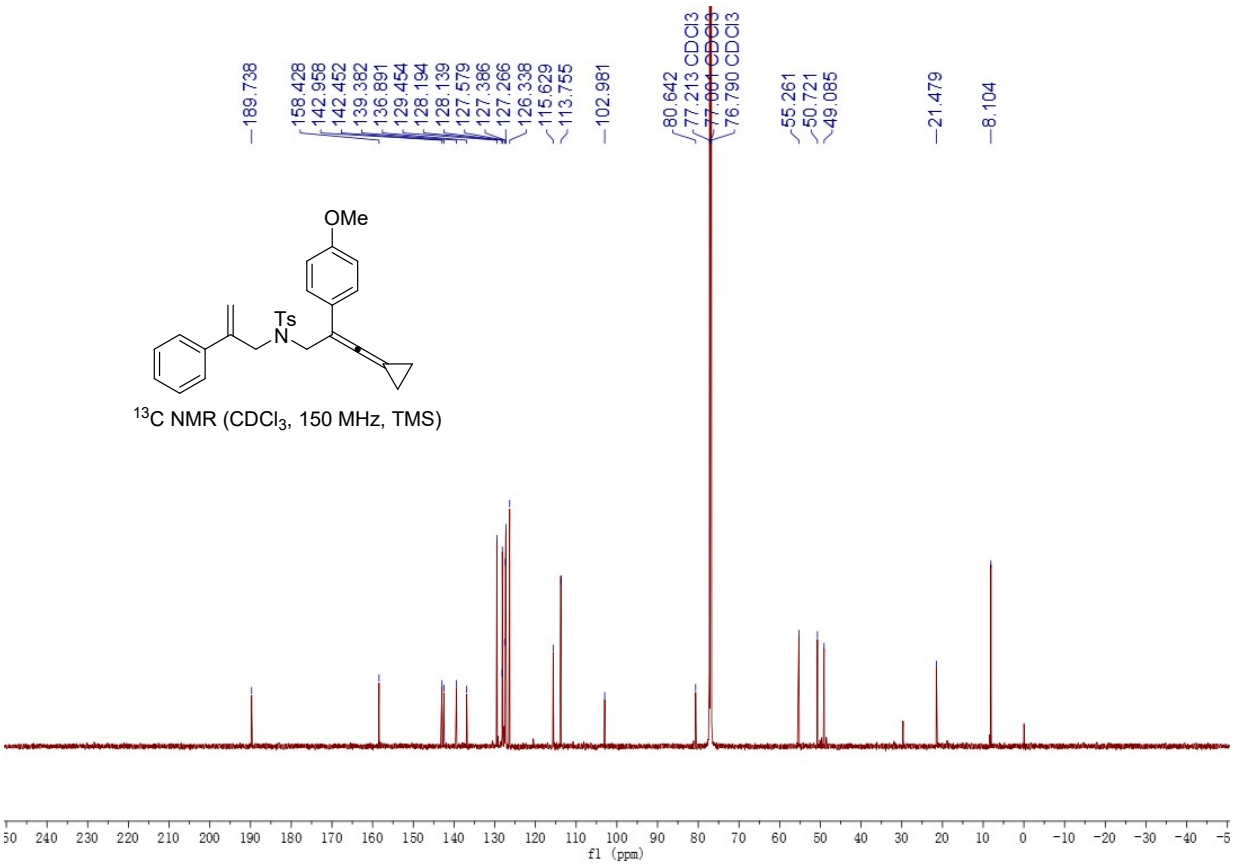


***N*-(3-cyclopropylidene-2-(4-methoxyphenyl)-3λ^5-allyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1b)**

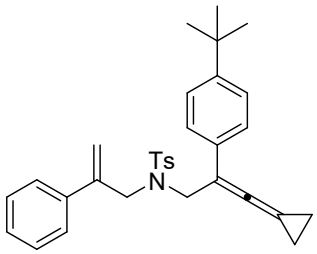
A yellow oil, 53% yield, 249.6 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.26 - 7.21 (m, 10H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.27 (s, 1H), 5.15 (s, 1H), 4.29 (s, 2H), 4.20 (s, 2H), 3.79 (s, 3H), 2.42 (s, 3H), 1.55 - 1.51 (m, 2H), 1.41 - 1.38 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 189.7, 158.4, 143.0, 142.5, 139.4, 136.9, 129.5, 128.2, 128.1, 127.6, 127.4, 127.3, 126.3, 115.6, 113.8, 103.0, 80.6, 55.3, 50.7, 49.1, 21.5, 8.1. IR (Acetone) ν 899, 1092, 1158, 1221, 1359, 1710, 3001 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{29}NO_3NaS$ (M+Na): 494.1760, Found: 494.1766.



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

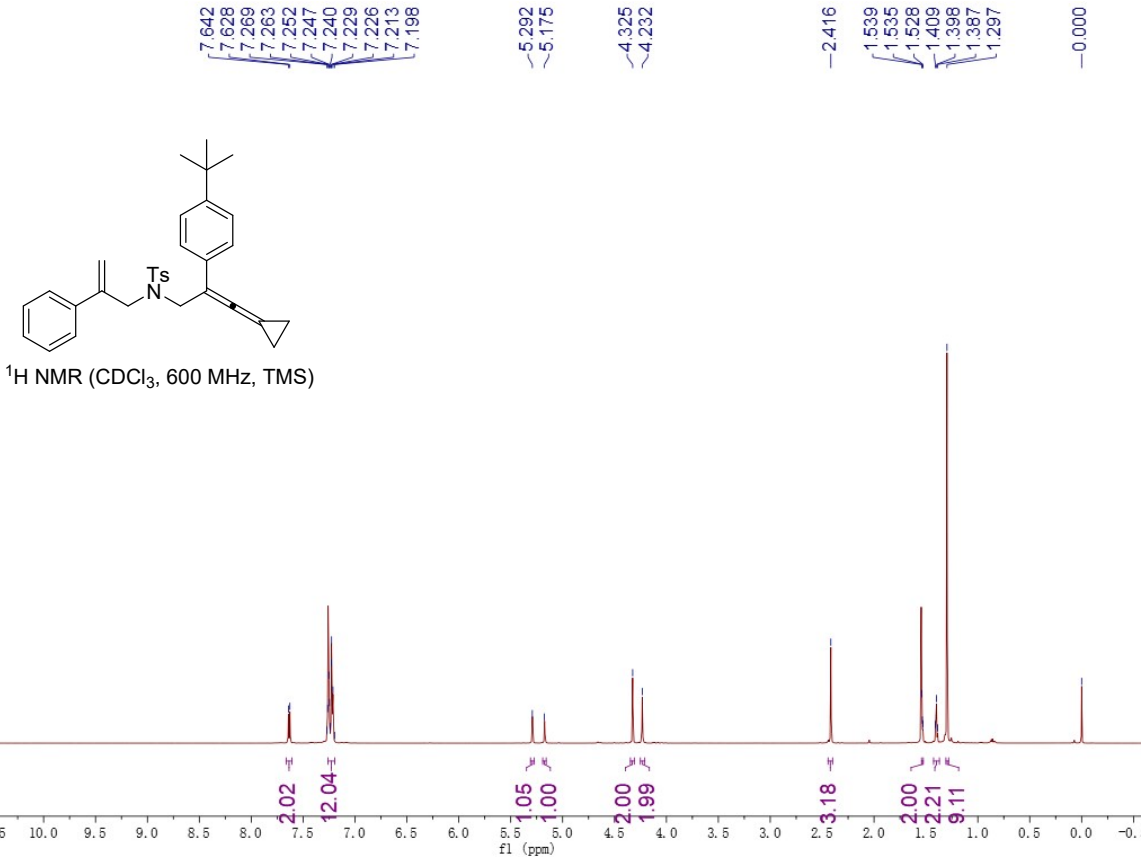


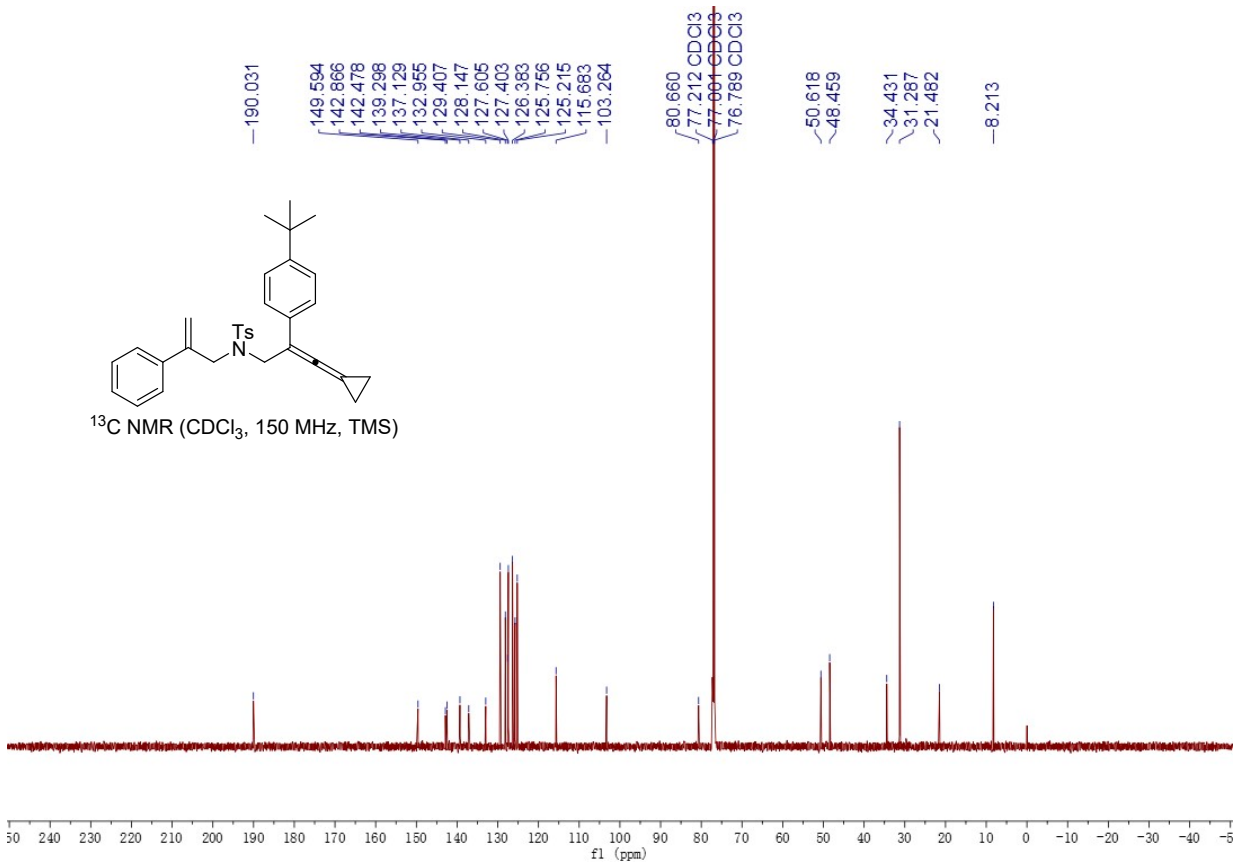
^{13}C NMR ($CDCl_3$, 150 MHz, TMS)

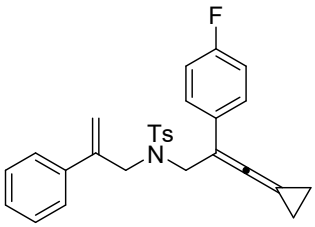


***N*-(2-(4-(tert-butyl)phenyl)-3-cyclopropylidene-3λ^5-allyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1c)**

A colorless oil, 48% yield, 239.0 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.63 (d, J = 8.4 Hz, 2H), 7.26 - 7.20 (m, 11H), 5.29 (s, 1H), 5.18 (s, 1H), 4.33 (s, 2H), 4.23 (s, 2H), 2.42 (s, 3H), 1.54 - 1.53 (m, 2H), 1.43 - 1.37 (m, 2H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.0, 149.6, 142.9, 142.5, 139.3, 137.1, 133.0, 129.4, 128.1, 127.6, 127.4, 126.4, 125.8, 125.2, 115.7, 103.3, 80.7, 50.6, 48.5, 34.4, 31.3, 21.5, 8.2. IR (Acetone) ν 1092, 1161, 1341, 1709, 2007, 2963 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{35}NO_2NaS$ (M+Na): 520.2281, Found: 520.2290.

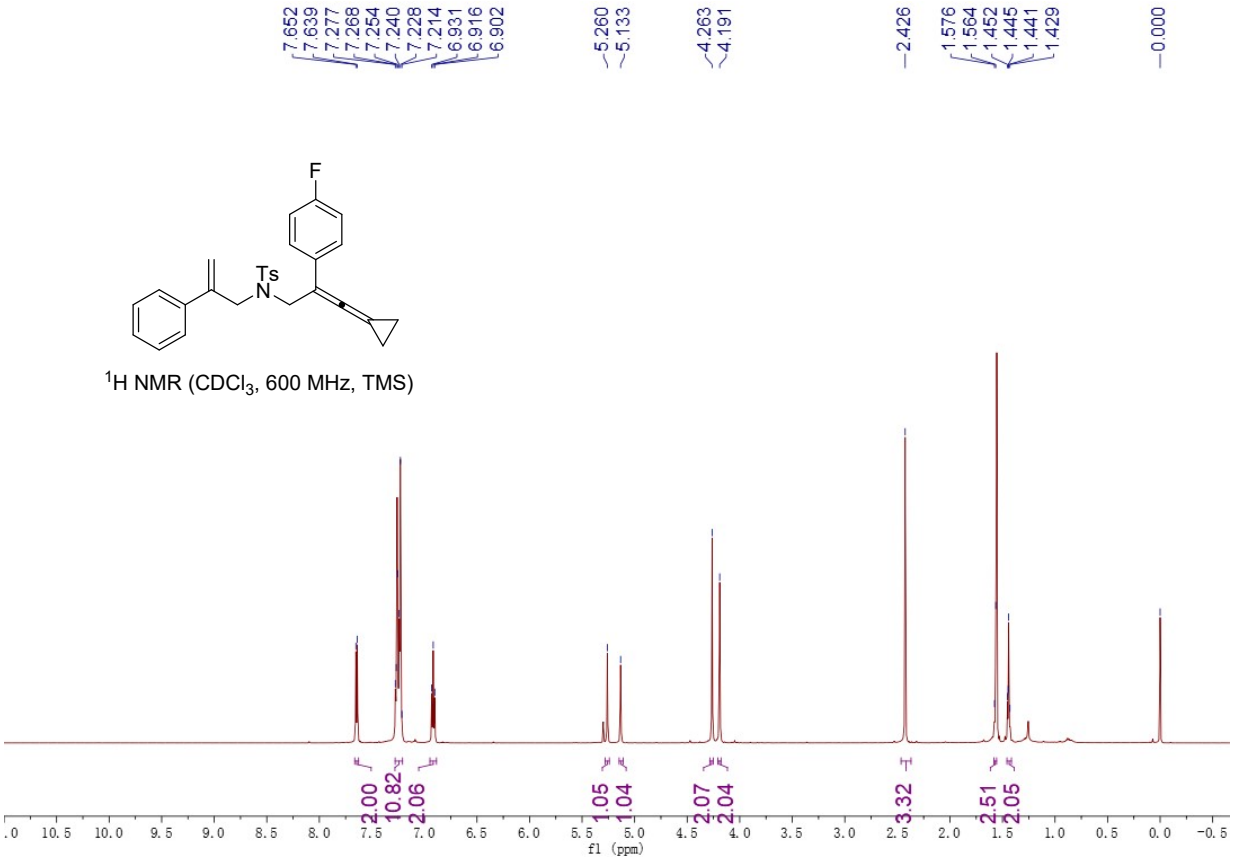




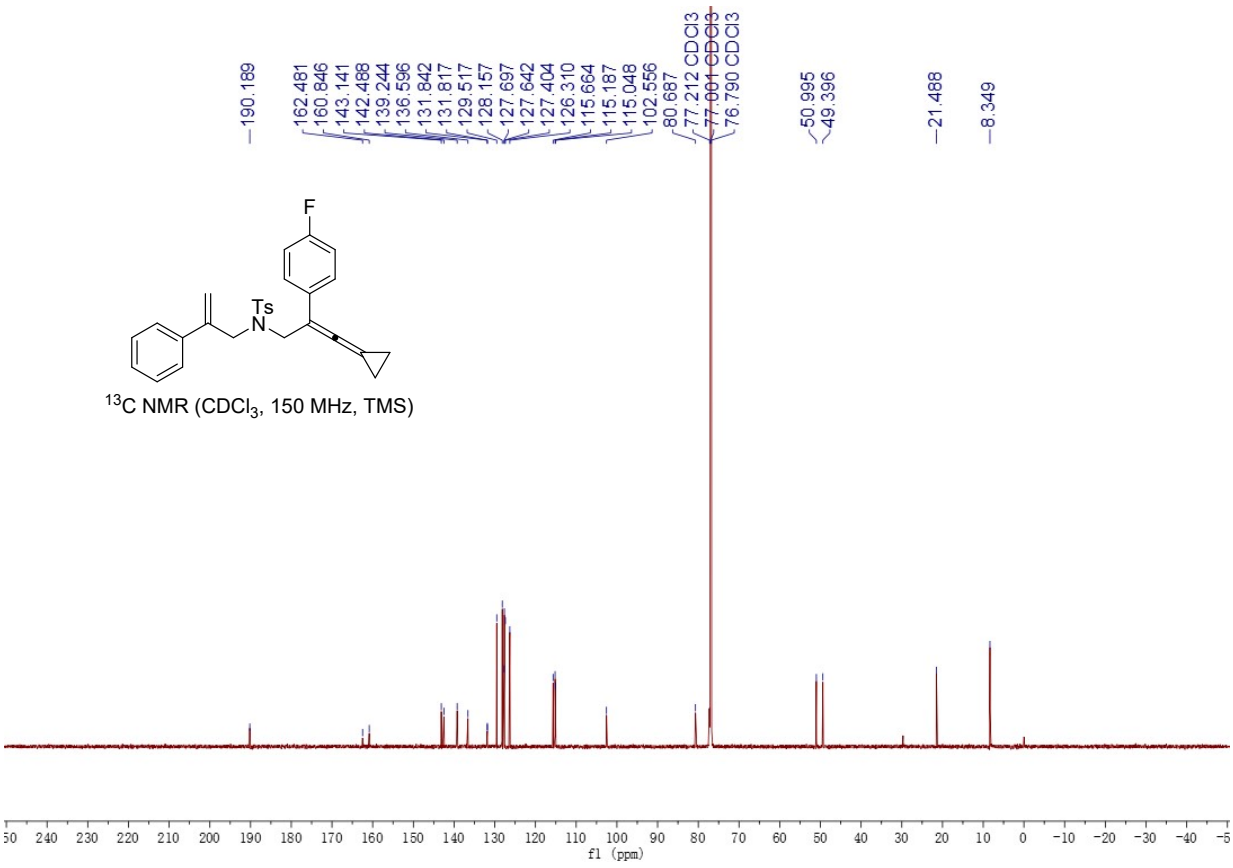


_N_-(3-cyclopropylidene-2-(4-fluorophenyl)-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1d)

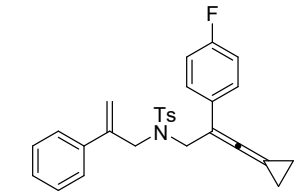
A colorless oil, 55% yield, 252.8 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.65 (d, J = 8.0 Hz, 2H), 7.28 - 7.21 (m, 9H), 6.92 (t, J = 8.7 Hz, 2H), 5.26 (s, 1H), 5.13 (s, 1H), 4.26 (s, 2H), 4.19 (s, 2H), 2.43 (s, 3H), 1.58 - 1.56 (m, 2H), 1.46 - 1.42 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.2, 161.6 (d, J = 246.9 Hz), 143.1, 142.5, 139.2, 136.6, 131.8 (d, J = 3.8 Hz), 129.5, 128.2, 127.6 (d, J = 8.3 Hz), 127.4, 126.3, 115.7, 115.1 (d, J = 21.0 Hz), 102.6, 80.7, 51.0, 49.4, 21.5, 8.3. ^{19}F NMR ($CDCl_3$, TMS, 564 MHz) δ -116.0 (s). IR (Acetone) ν 1092, 1159, 1221, 1359, 1420, 1710, 3003 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{26}NO_2FNaS$ (M+Na): 482.1561, Found: 482.1563.



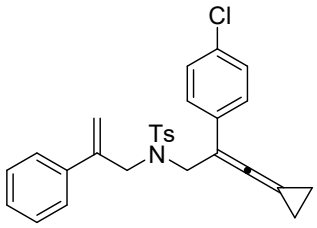
^{1}H NMR ($CDCl_3$, 600 MHz, TMS)



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

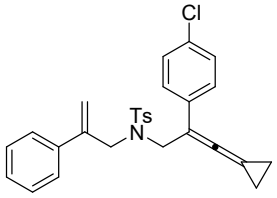


^{19}F NMR ($CDCl_3$, 564 MHz, TMS)

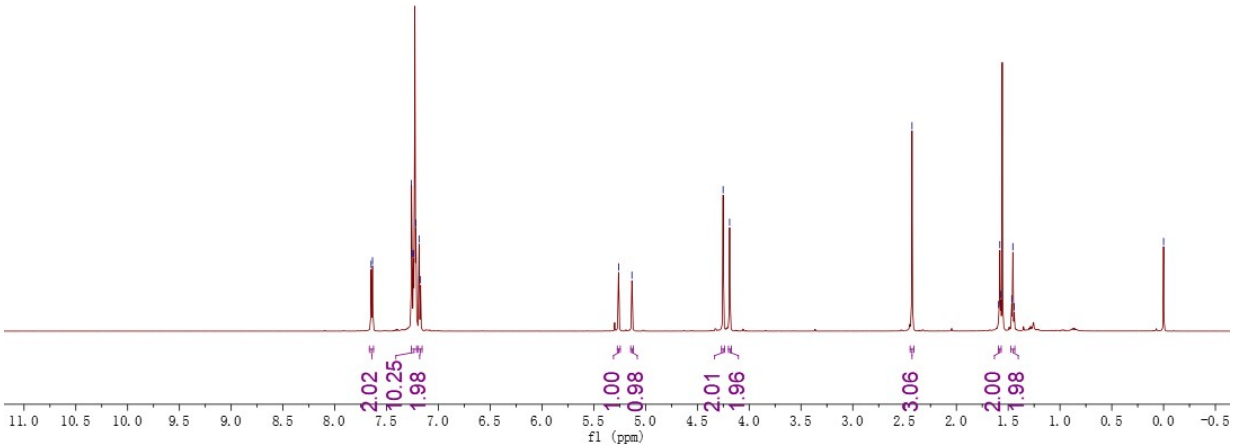


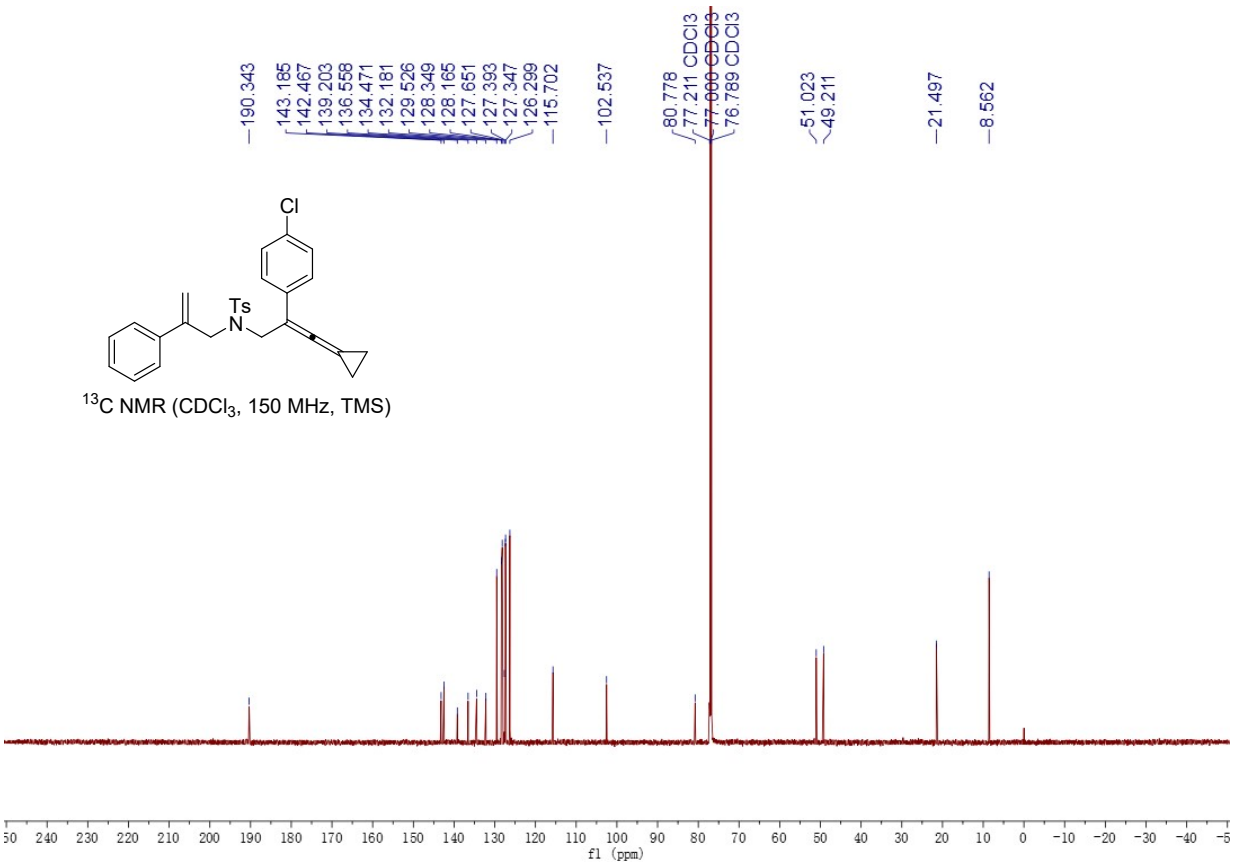
_N_-(2-(4-chlorophenyl)-3-cyclopropylidene-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1e)

A colorless oil, 60% yield, 285.6 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.64 (d, J = 8.0 Hz, 2H), 7.26 - 7.21 (m, 9H), 7.18 (d, J = 8.6 Hz, 2H), 5.26 (s, 1H), 5.13 (s, 1H), 4.25 (s, 2H), 4.19 (s, 2H), 2.43 (s, 3H), 1.59 - 1.57 (m, 2H), 1.47 - 1.44 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.3, 143.2, 142.5, 139.2, 136.6, 134.5, 132.2, 129.5, 128.3, 128.2, 127.7, 127.4, 127.3, 126.3, 115.7, 102.5, 80.8, 51.0, 49.2, 21.5, 8.6. IR (Acetone) ν 906, 1092, 1160, 1221, 1359, 1420, 1710, 3006 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{26}NO_2NaSCl$ (M+Na): 498.1265, Found: 498.1264.

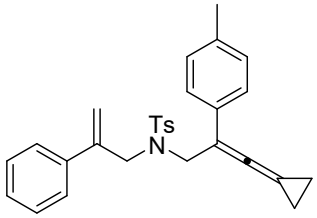


^{1}H NMR ($CDCl_3$, 600 MHz, TMS)



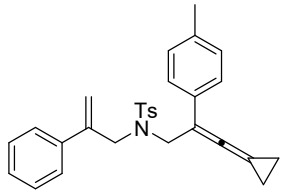


^{13}C NMR ($CDCl_3$, 150 MHz, TMS)

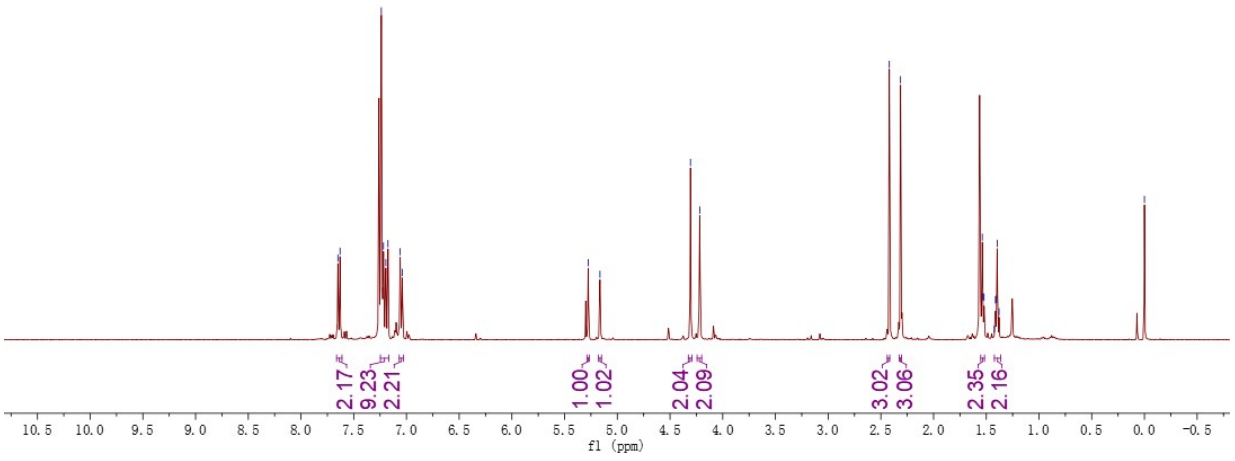


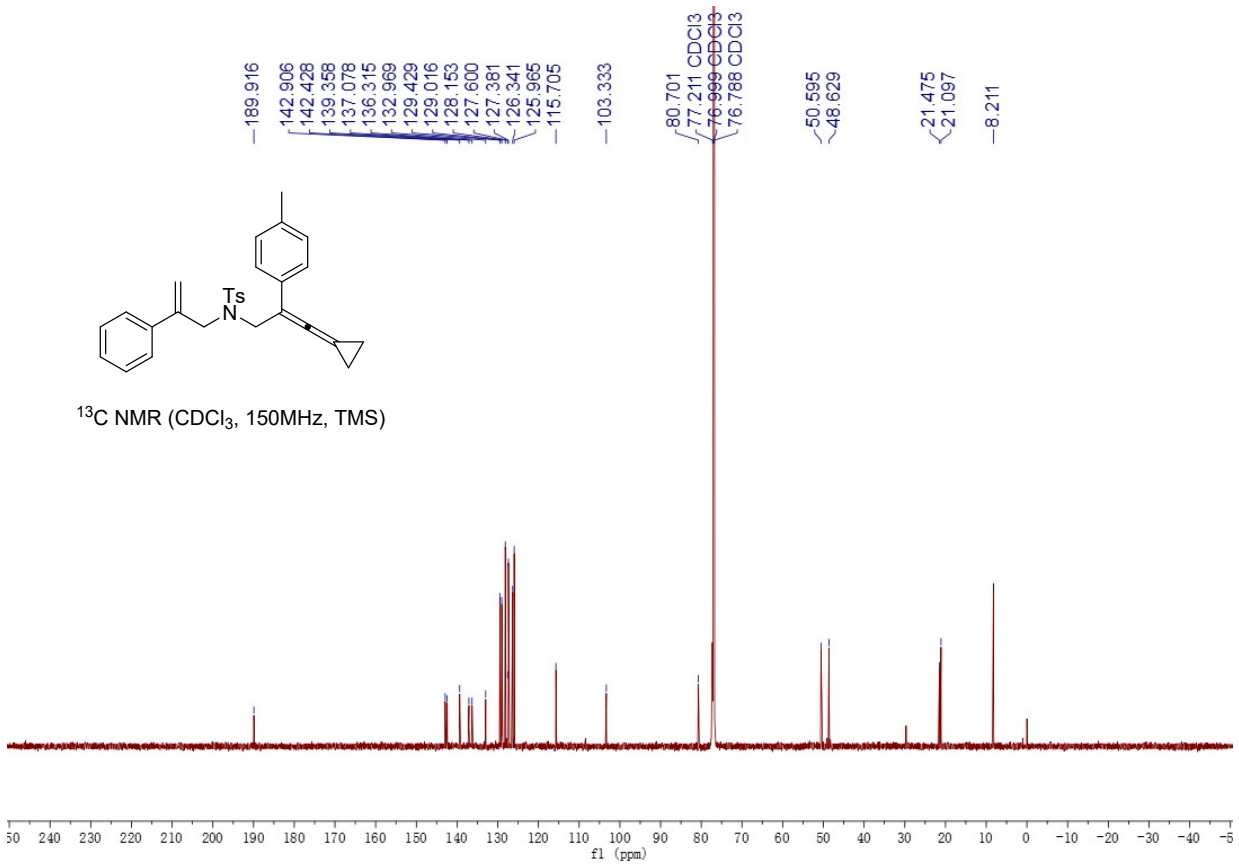
***N*-(3-cyclopropylidene-2-(p-tolyl)-3λ^5-allyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1g)**

A colorless oil, 62% yield, 282.0 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.25 - 7.17 (m, 9H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.28 (s, 1H), 5.16 (s, 1H), 4.31 (s, 2H), 4.22 (s, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 1.55 - 1.52 (m, 2H), 1.42 - 1.36 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 189.9, 142.9, 142.4, 139.4, 137.1, 136.3, 133.0, 129.4, 129.0, 128.2, 127.6, 127.4, 126.3, 126.0, 115.7, 103.3, 80.7, 50.6, 48.6, 21.5, 21.1, 8.2. IR (Acetone) ν 898, 1093, 1157, 1339, 1714, 2001, 2985 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{29}NO_2NaS$ (M+Na): 478.1811, Found: 478.1814.

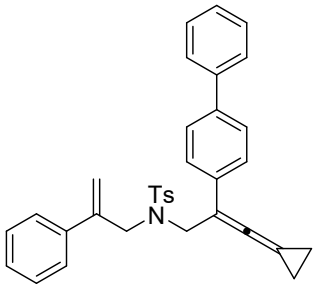


^{1}H NMR ($CDCl_3$, 400MHz, TMS)



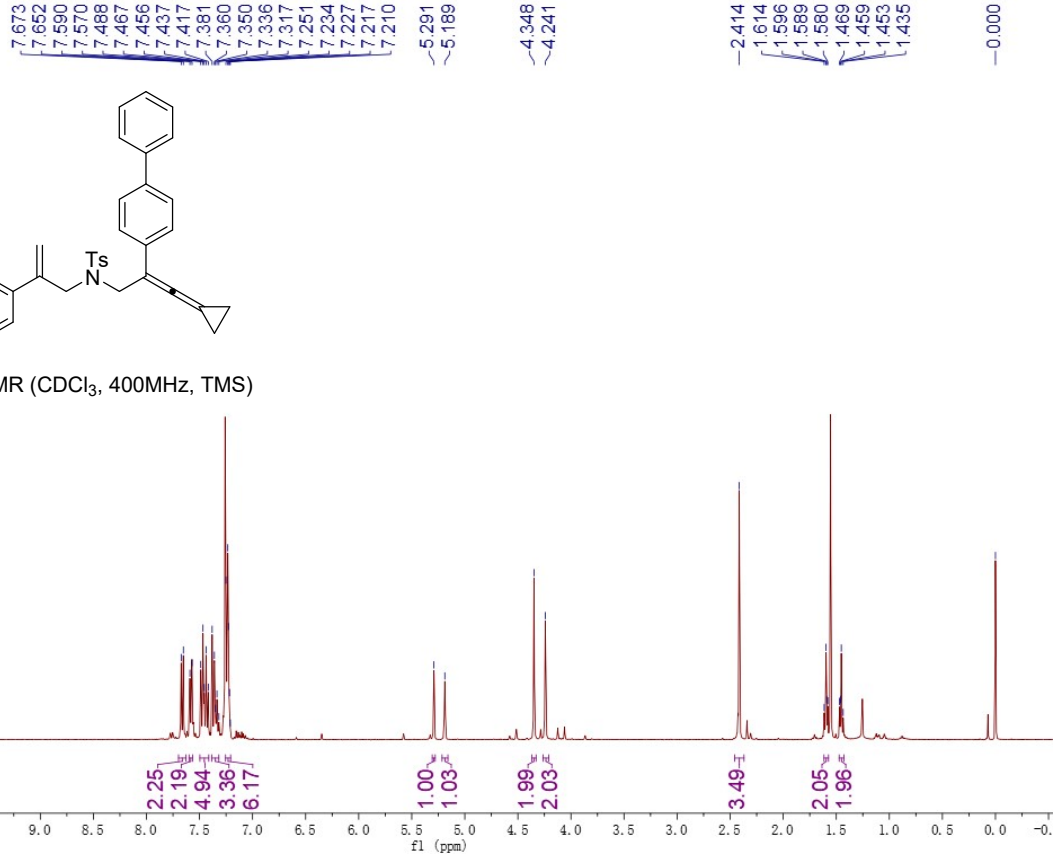


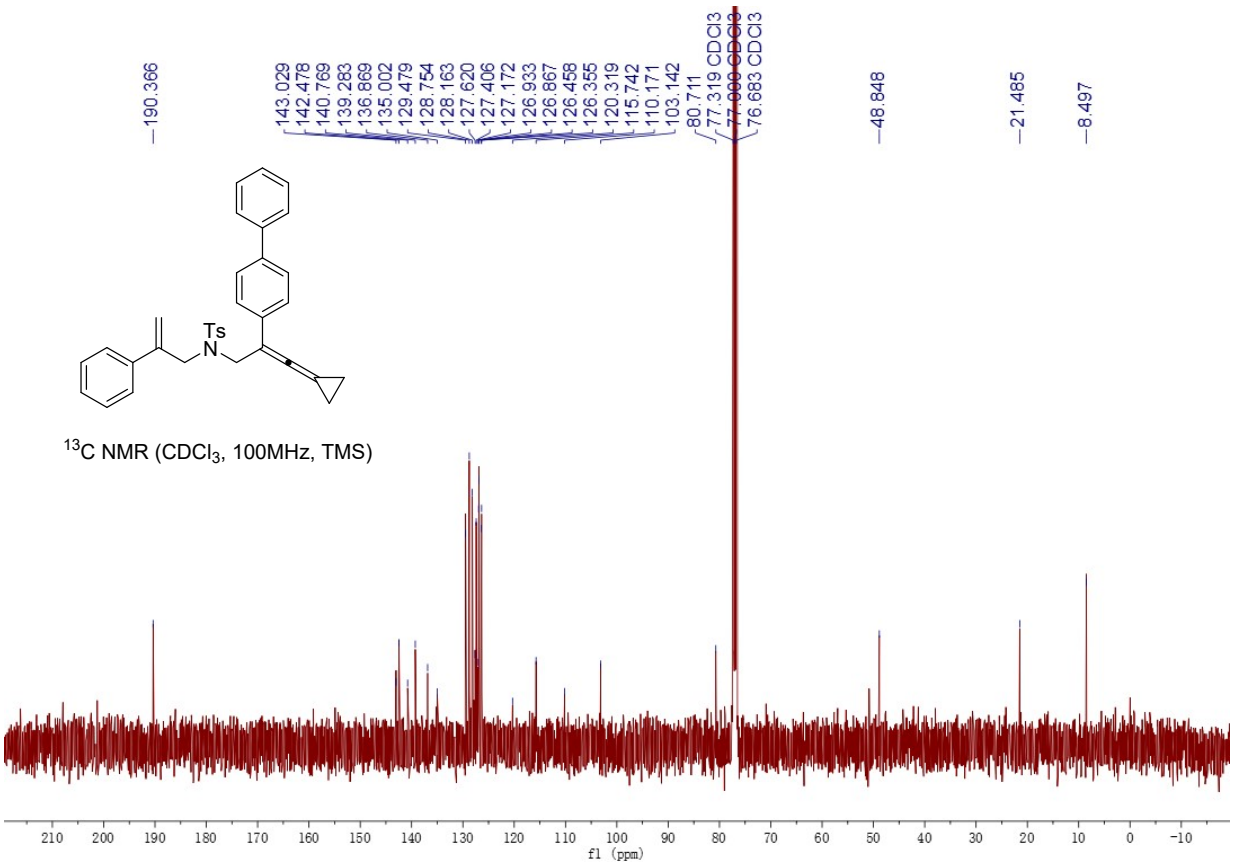
^{13}C NMR ($CDCl_3$, 150MHz, TMS)

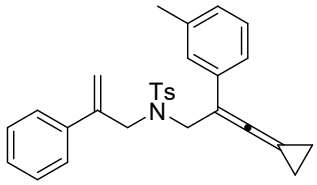


_N_-(2-([1,1'-biphenyl]-4-yl)-3-cyclopropylidene-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1h)

A colorless oil, 53% yield, 274.3 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.66 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.50 - 7.41 (m, 5H), 7.38 - 7.32 (m, 3H), 7.25 - 7.21 (m, 6H), 5.29 (s, 1H), 5.19 (s, 1H), 4.35 (s, 2H), 4.24 (s, 2H), 2.41 (s, 3H), 1.62 - 1.57 (m, 2H), 1.47 - 1.43 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 190.4, 143.0, 142.5, 140.8, 139.3, 136.9, 135.0, 129.5, 128.8, 128.2, 127.6, 127.4, 127.2, 126.93, 126.87, 126.5, 126.4, 120.3, 115.7, 110.2, 103.1, 80.7, 48.8, 21.5, 8.5. IR (Acetone) ν 1091, 1220, 1359, 1422, 1711, 2998 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{32}NO_2S$ (M+H): 518.2148, Found: 518.2117.

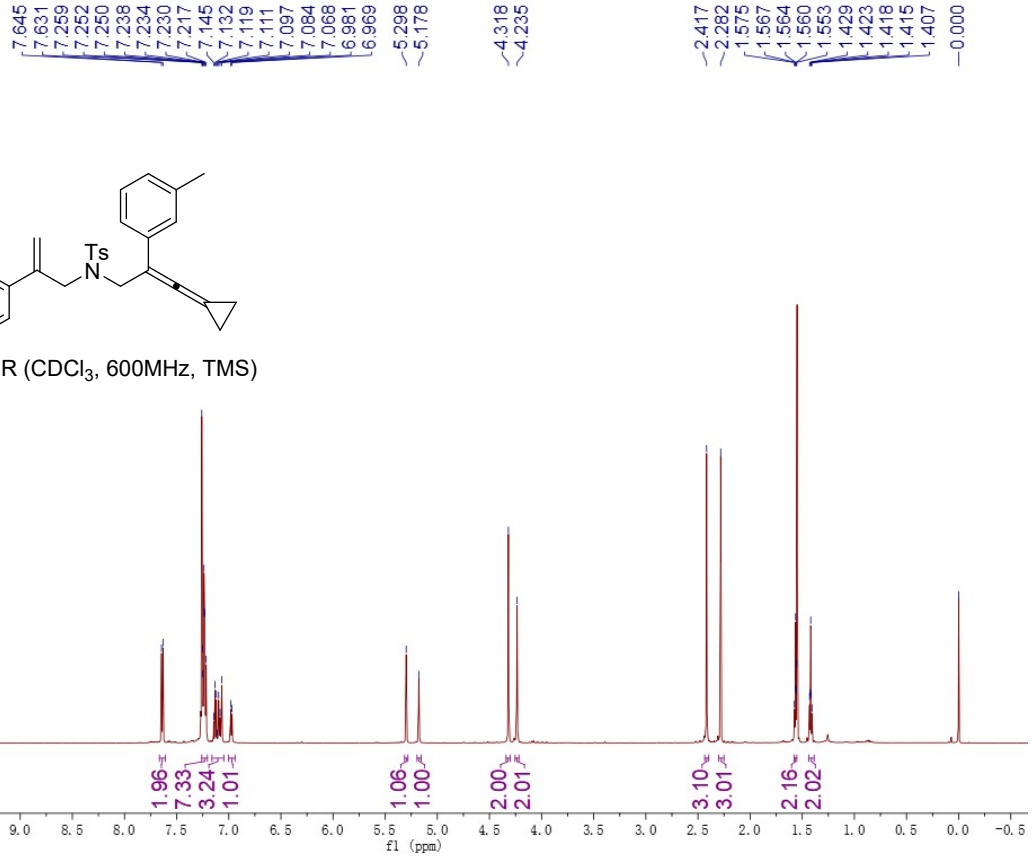


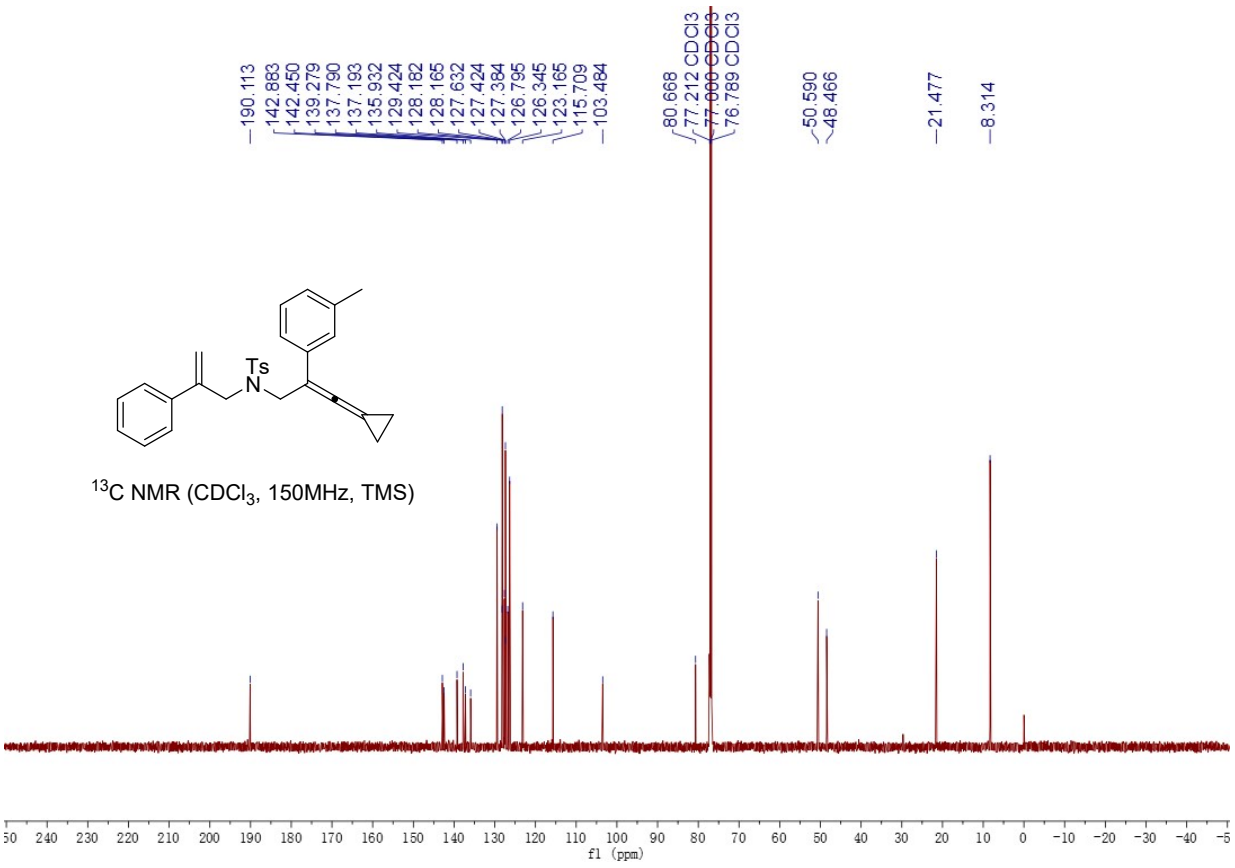

190.366
143.029
142.478
140.769
139.283
136.869
135.002
129.479
128.754
128.163
127.620
127.406
127.172
126.933
126.867
126.458
126.355
120.319
115.742
110.171
103.142
80.711
77.319 CDCl3
77.000 CDCl3
76.683 CDCl3
48.848
21.485
8.497
Ts
N
13C NMR (CDCl3, 100MHz, TMS)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



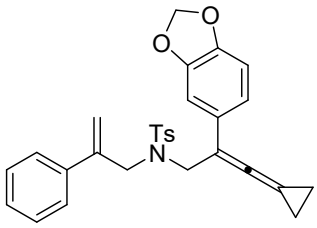
_N_-(3-cyclopropylidene-2-(m-tolyl)-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1i)

A colorless oil, 55% yield, 250.6 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.64 (d, J = 8.2 Hz, 2H), 7.26 - 7.20 (m, 7H), 7.16 - 7.05 (m, 3H), 6.98 (d, J = 7.2 Hz, 1H), 5.30 (s, 1H), 5.18 (s, 1H), 4.32 (s, 2H), 4.24 (s, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 1.58 - 1.55 (m, 2H), 1.44 - 1.39 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.1, 142.9, 142.5, 139.3, 137.8, 137.2, 135.9, 129.4, 128.18, 128.16, 127.6, 127.42, 127.38, 126.8, 126.3, 123.2, 115.7, 103.5, 80.7, 50.6, 48.5, 21.5, 8.3. IR (Acetone) ν 901, 1094, 1137, 1339, 1724, 2011, 2995 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{29}NO_2SNa$ (M+Na): 478.1811, Found: 478.1811.



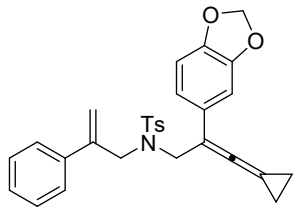


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

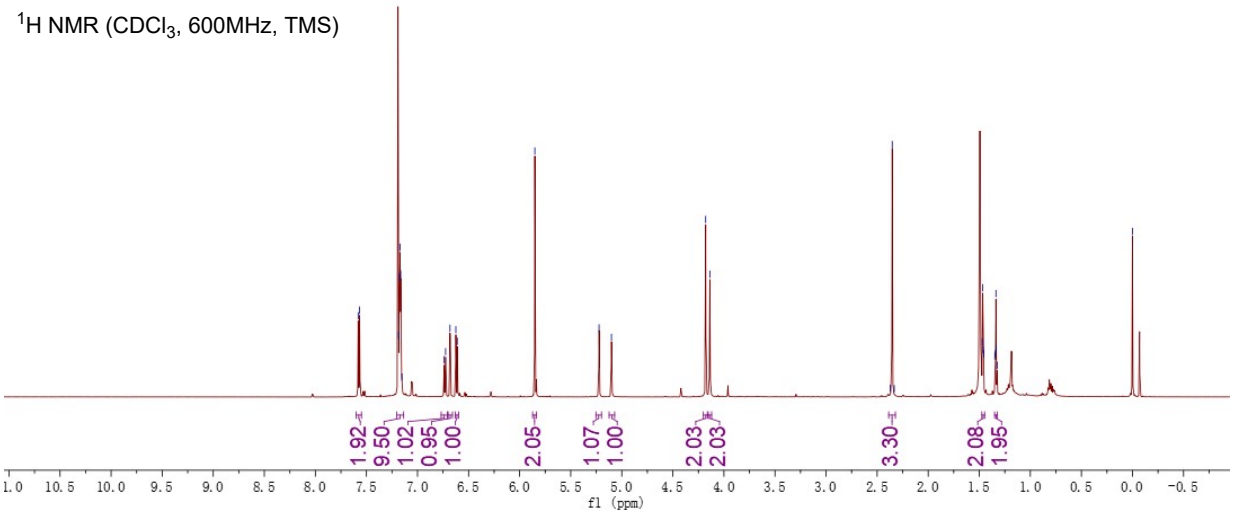


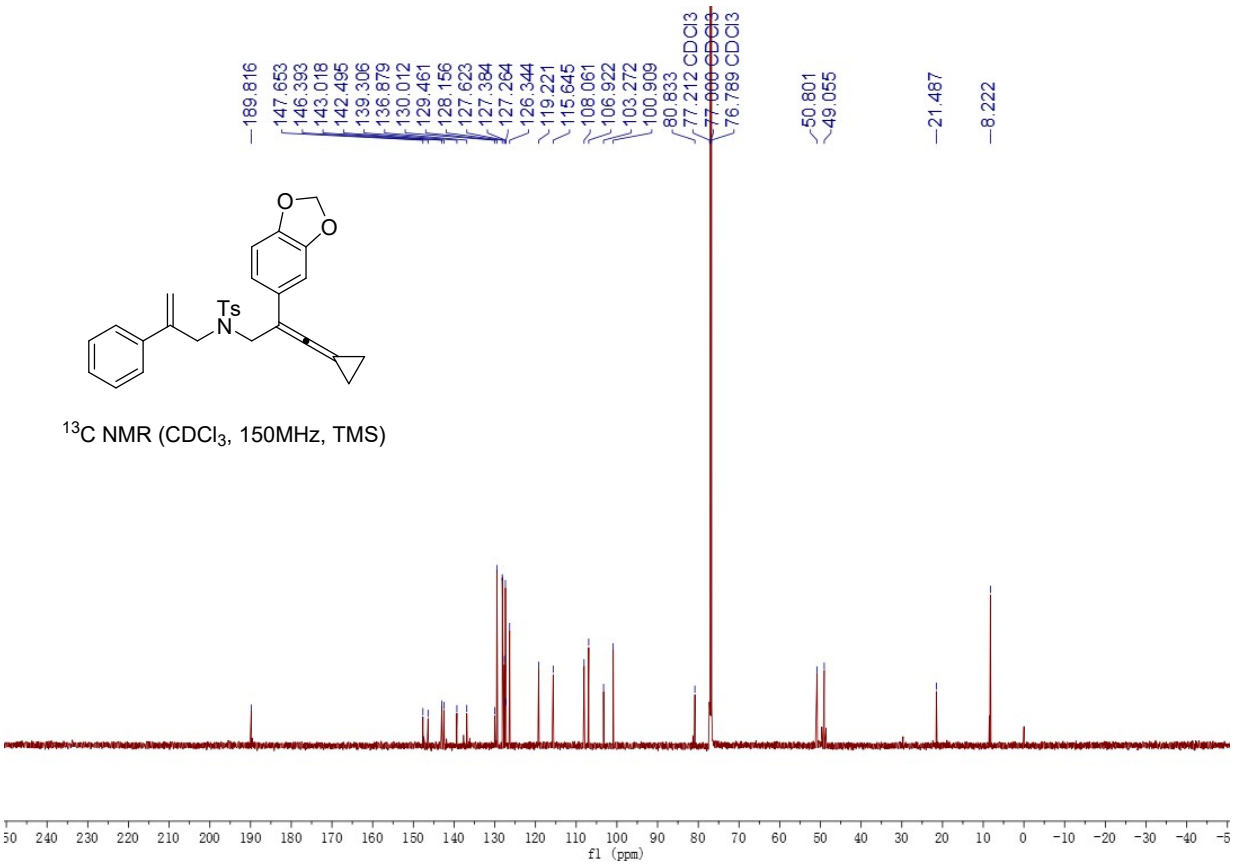
***N*-(2-(benzo[*d*][1,3]dioxol-5-yl)-3-cyclopropylidene-3λ^5-allyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1j)**

A colorless oil, 42% yield, 203.9 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.20 - 7.15 (m, 7H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.68 (s, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 5.85 (s, 2H), 5.22 (s, 1H), 5.10 (s, 1H), 4.18 (s, 2H), 4.14 (s, 2H), 2.35 (s, 3H), 1.47 - 1.45 (m, 2H), 1.35 - 1.32 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 189.8, 147.7, 146.4, 143.0, 142.5, 139.3, 136.9, 130.0, 129.5, 128.2, 127.6, 127.4, 127.3, 126.3, 119.2, 115.6, 108.1, 106.9, 103.3, 100.9, 80.8, 50.8, 49.1, 21.5, 8.2. IR (Acetone) ν 900, 1092, 1221, 1359, 1421, 1709, 3001 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{27}NO_4SNa$ (M+Na): 508.1553, Found: 508.1548.

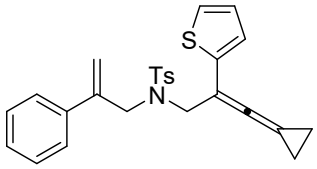


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



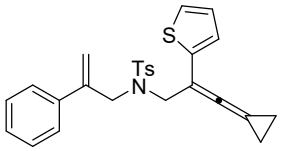


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

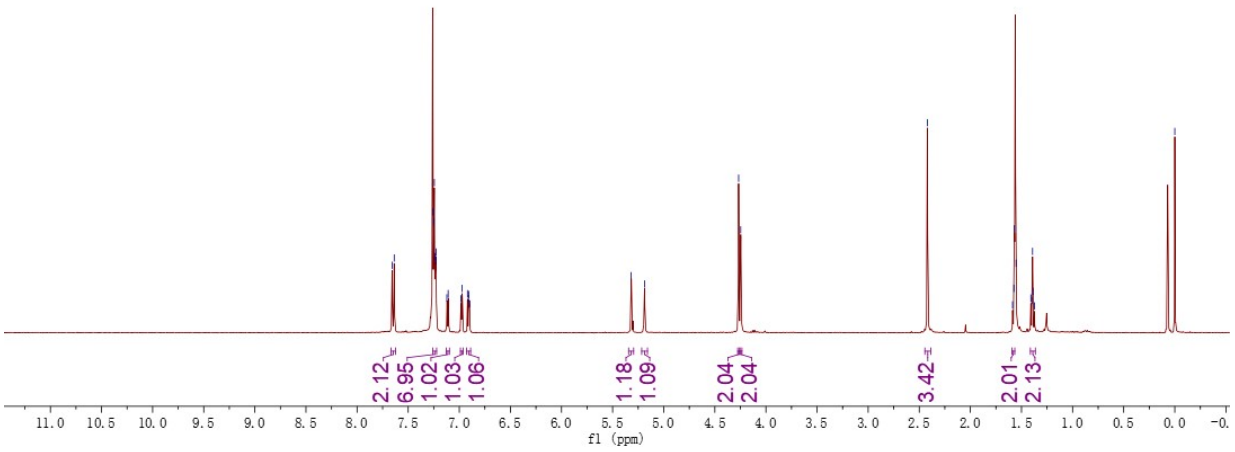


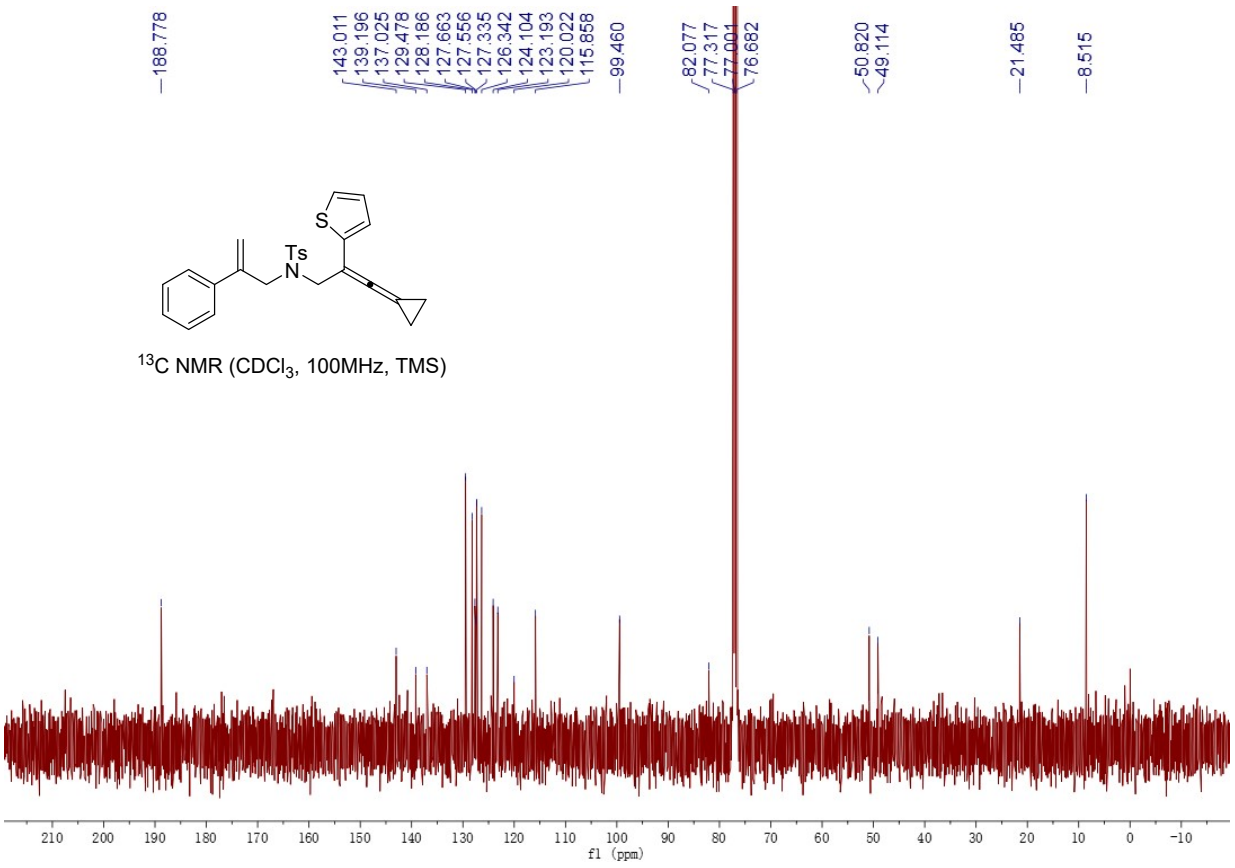
_N_-(3-cyclopropylidene-2-(thiophen-2-yl)-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1k)

A colorless oil, 48% yield, 214.8 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.26 - 7.22 (m, 7H), 7.12 (d, *J* = 5.1 Hz, 1H), 6.98 (d, *J* = 3.7 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.32 (s, 1H), 5.19 (s, 1H), 4.27 (s, 2H), 4.25 (s, 2H), 2.42 (s, 3H), 1.59 - 1.57 (m, 2H), 1.41 - 1.36 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 188.8, 143.0, 139.2, 137.0, 129.5, 128.2, 127.7, 127.6, 127.3, 126.3, 124.1, 123.2, 120.0, 115.9, 99.5, 82.1, 50.8, 49.1, 21.5, 8.5. IR (Acetone) ν 1092, 1220, 1359, 1420, 1711, 3009 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{25}NO_2S_2Na$ (M+Na): 470.1219, Found: 470.1221.

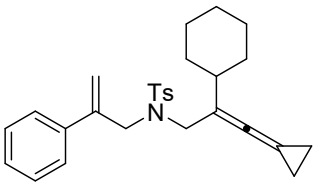


^{1}H NMR ($CDCl_3$, 400MHz, TMS)



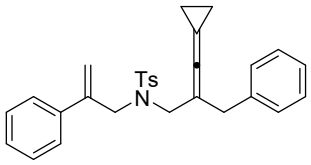


^{13}C NMR ($CDCl_3$, 100MHz, TMS)



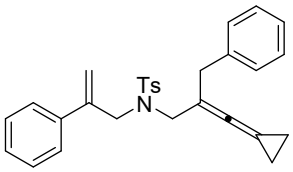
_N_-(2-cyclohexyl-3-cyclopropylidene-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1m)

This is a known compound and its spectroscopic data are consistent with those reported in the previous literature,[8] 63% yield, 282.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.27 - 7.26 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H), 5.39 (s, 1H), 5.24 (s, 1H), 4.25 (s, 2H), 3.84 (s, 2H), 2.41 (s, 3H), 1.67 - 1.58 (m, 5H), 1.39 - 1.36 (m, 2H), 1.28 - 1.24 (m, 2H), 1.15 - 0.88 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 142.8, 142.7, 139.2, 137.4, 129.4, 128.2, 127.7, 127.3, 126.5, 115.8, 108.0, 79.7, 50.6, 48.8, 38.2, 32.1, 26.3, 26.2, 21.4, 6.9.

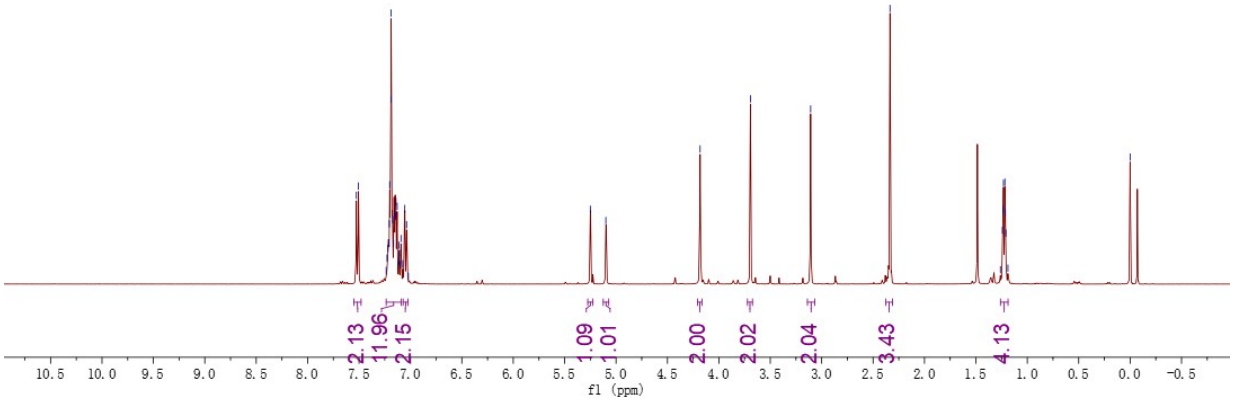


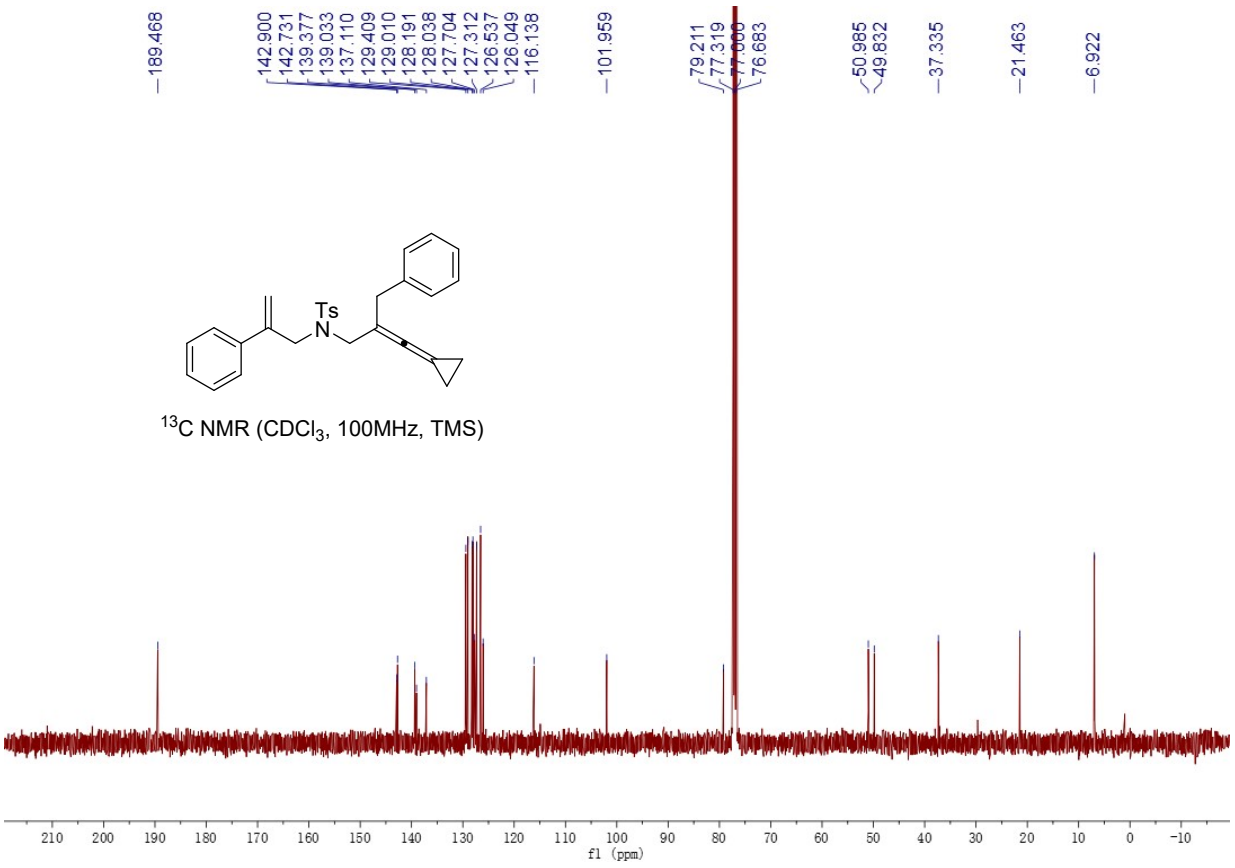
_N_-(2-benzyl-3-cyclopropylidene-3λ^5-allyl)-4-methyl-_N_-(2-phenylallyl)benzenesulfonamide (1n)

A colorless oil, 62% yield, 282.5 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.52 (d, J = 8.3 Hz, 2H), 7.24 - 7.09 (m, 10H), 7.07 - 7.02 (m, 2H), 5.25 (s, 1H), 5.10 (s, 1H), 4.18 (s, 2H), 3.69 (s, 2H), 3.11 (s, 2H), 2.34 (s, 3H), 1.26 - 1.19 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 189.5, 142.9, 142.7, 139.4, 139.0, 137.1, 129.4, 129.0, 128.2, 128.0, 127.7, 127.3, 126.5, 126.0, 116.1, 102.0, 79.2, 51.0, 49.8, 37.3, 21.5, 6.9. IR (Acetone) ν 1093, 1157, 1337, 1498, 2022, 2917 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{30}NO_2S$ (M+H): 456.1992, Found: 456.1959.

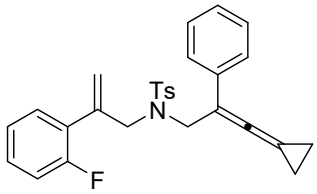


^{1}H NMR ($CDCl_3$, 400MHz, TMS)



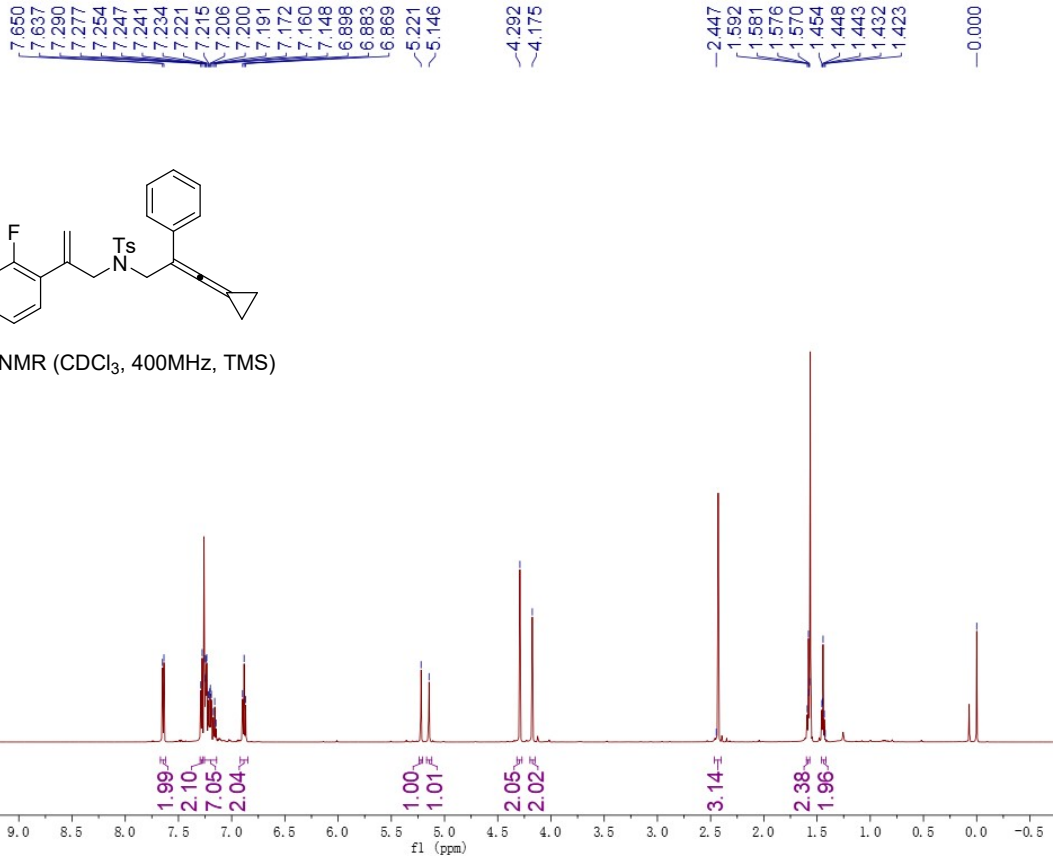


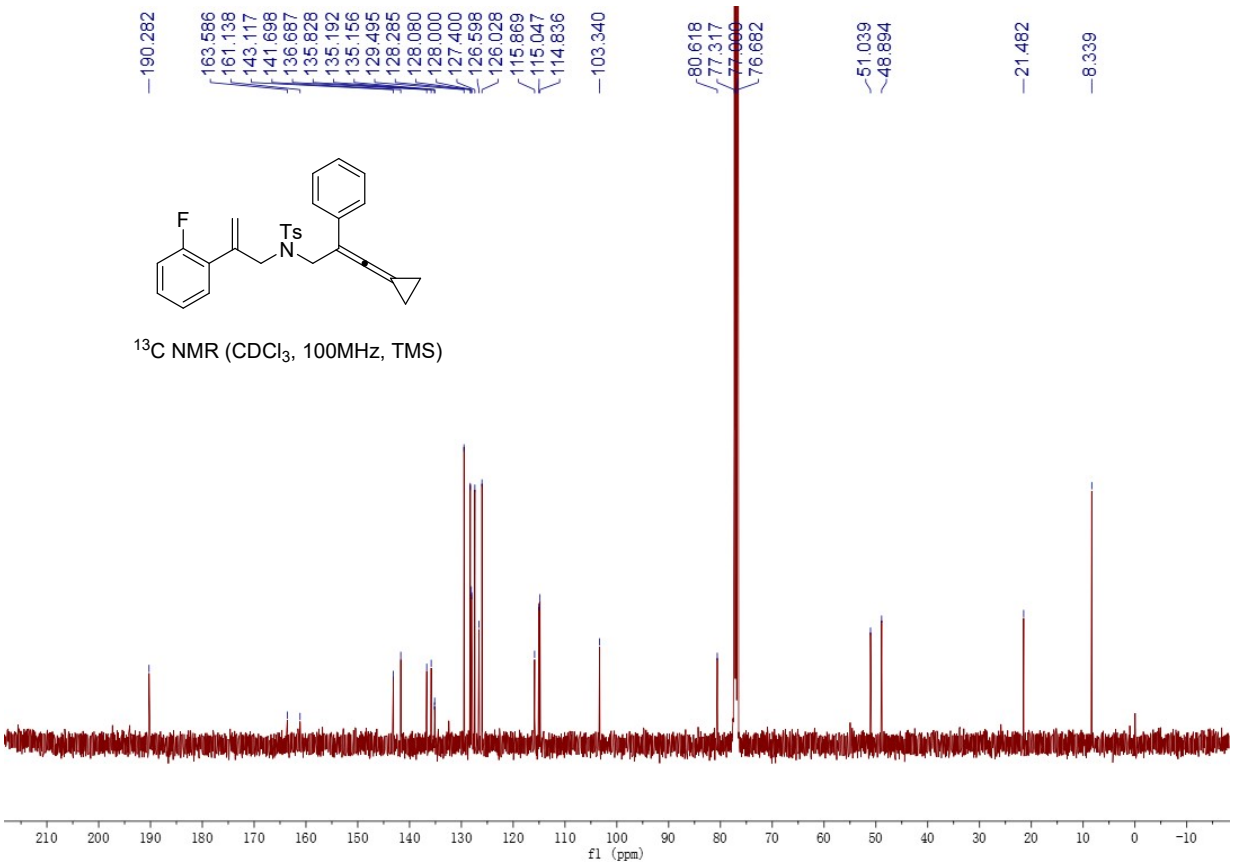
^{13}C NMR ($CDCl_3$, 100MHz, TMS)



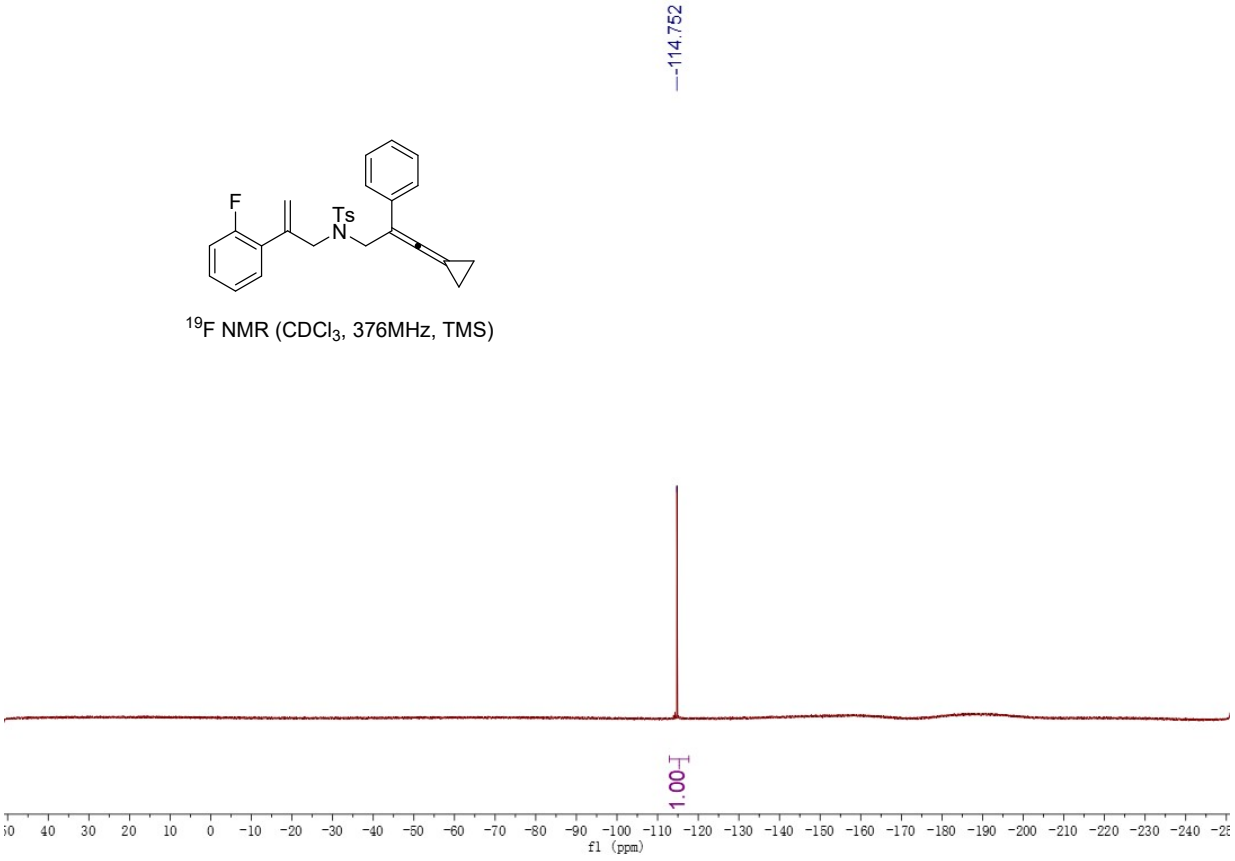
N-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-*N*-(2-(2-fluorophenyl)allyl)-4-methylbenzenesulfonamide (1o)

A colorless oil, 55%, 252.8 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.22 - 7.19 (m, 1H), 7.18 - 7.07 (m, 5H), 7.03 - 6.97 (m, 1H), 6.94 - 6.89 (m, 1H), 6.88 - 6.80 (m, 1H), 5.27 (s, 1H), 5.11 (s, 1H), 4.25 (s, 2H), 4.08 (s, 2H), 2.34 (s, 3H), 1.50 - 1.47 (m, 2H), 1.39 - 1.33 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 190.3, 159.8 (d, *J* = 245.5 Hz), 142.9, 139.2, 136.7, 135.9, 130.2 (d, *J* = 4.5 Hz), 129.5, 129.1 (d, *J* = 8.1 Hz), 128.3, 127.8 (d, *J* = 14.5 Hz), 127.3, 126.5, 126.1, 123.9 (d, *J* = 3.3 Hz), 118.9, 115.5 (d, *J* = 22.3 Hz), 103.2, 80.6, 51.2, 49.2, 21.5, 8.4. ^{19}F NMR ($CDCl_3$, TMS, 376 MHz) δ -114.3 (s) IR (Acetone) ν 1159, 1339, 1488, 1709, 2009, 2985 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{27}NO_2SF$ (M+H): 460.1741, Found: 460.1709.

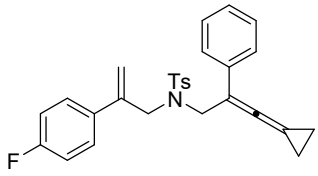




^{13}C NMR ($CDCl_3$, 100MHz, TMS)

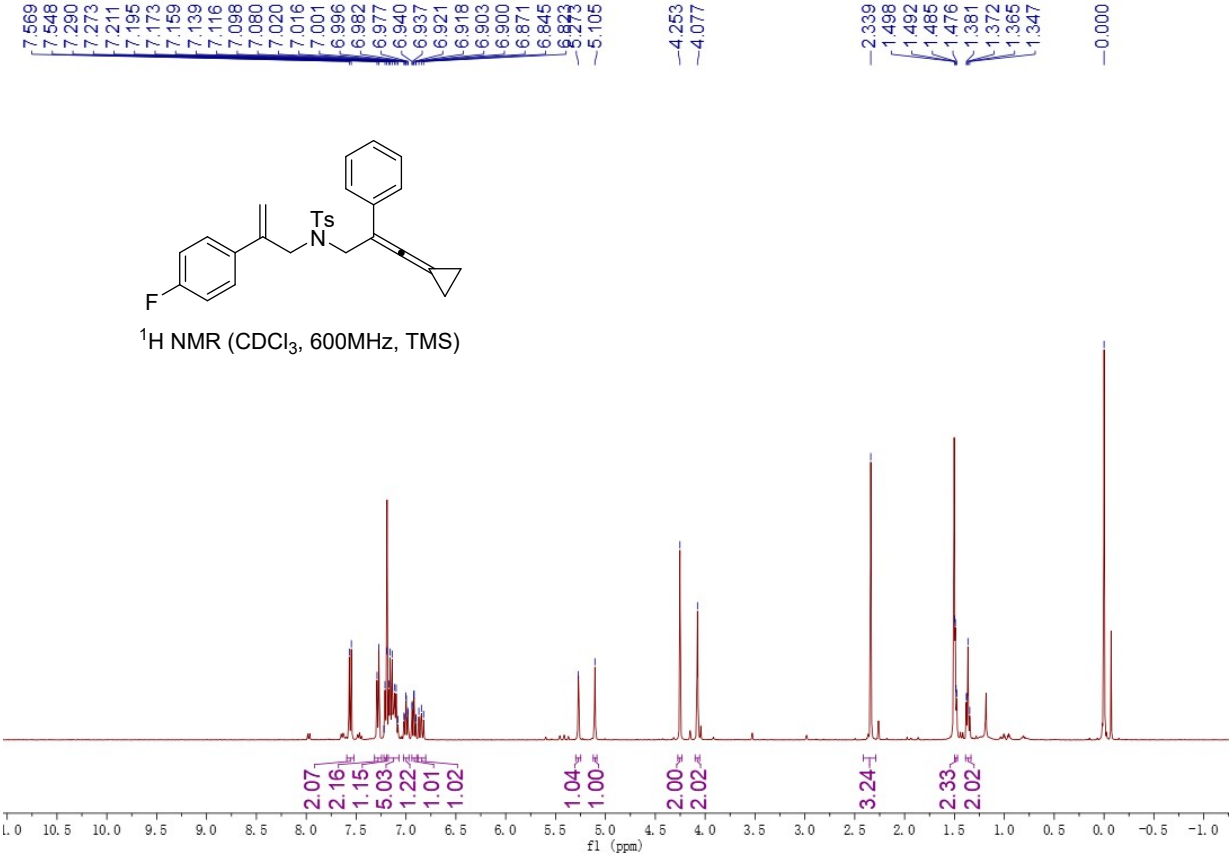


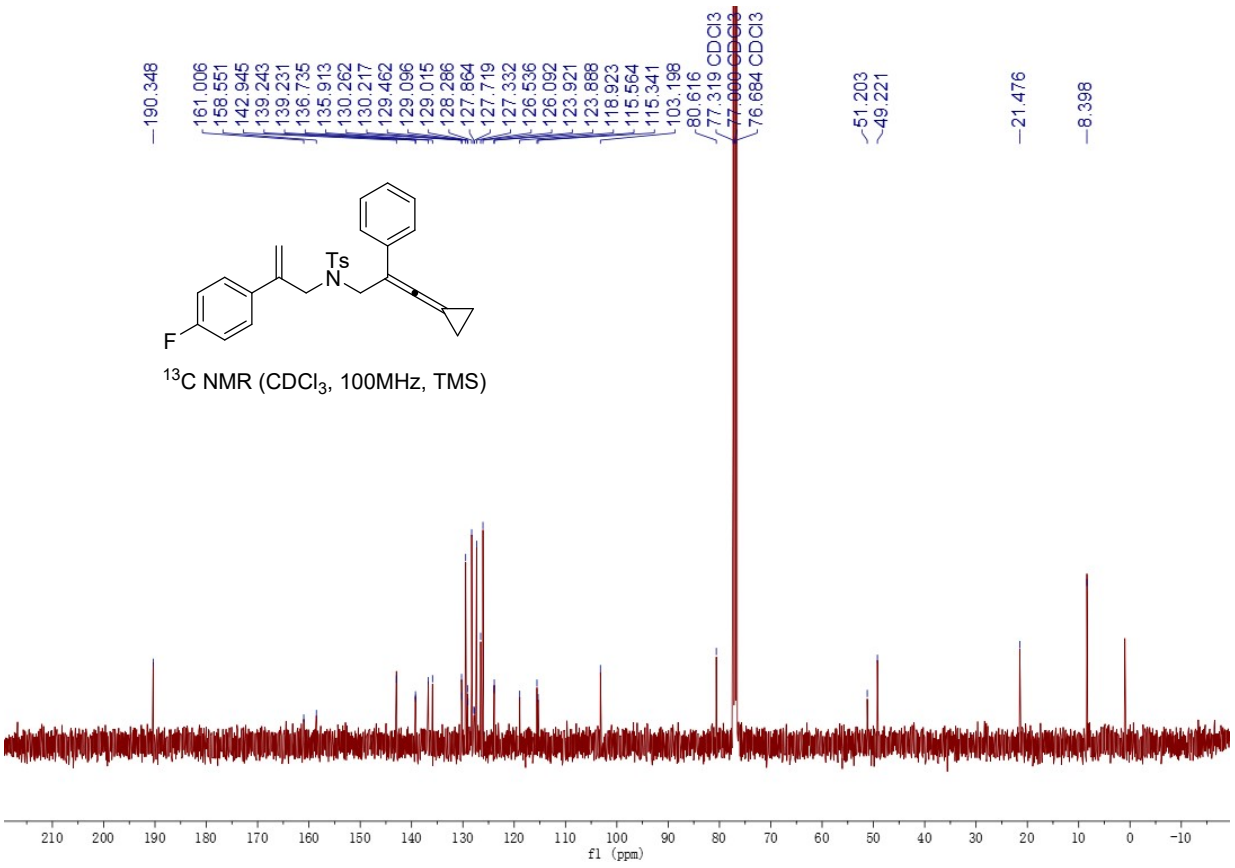
^{19}F NMR ($CDCl_3$, 376MHz, TMS)



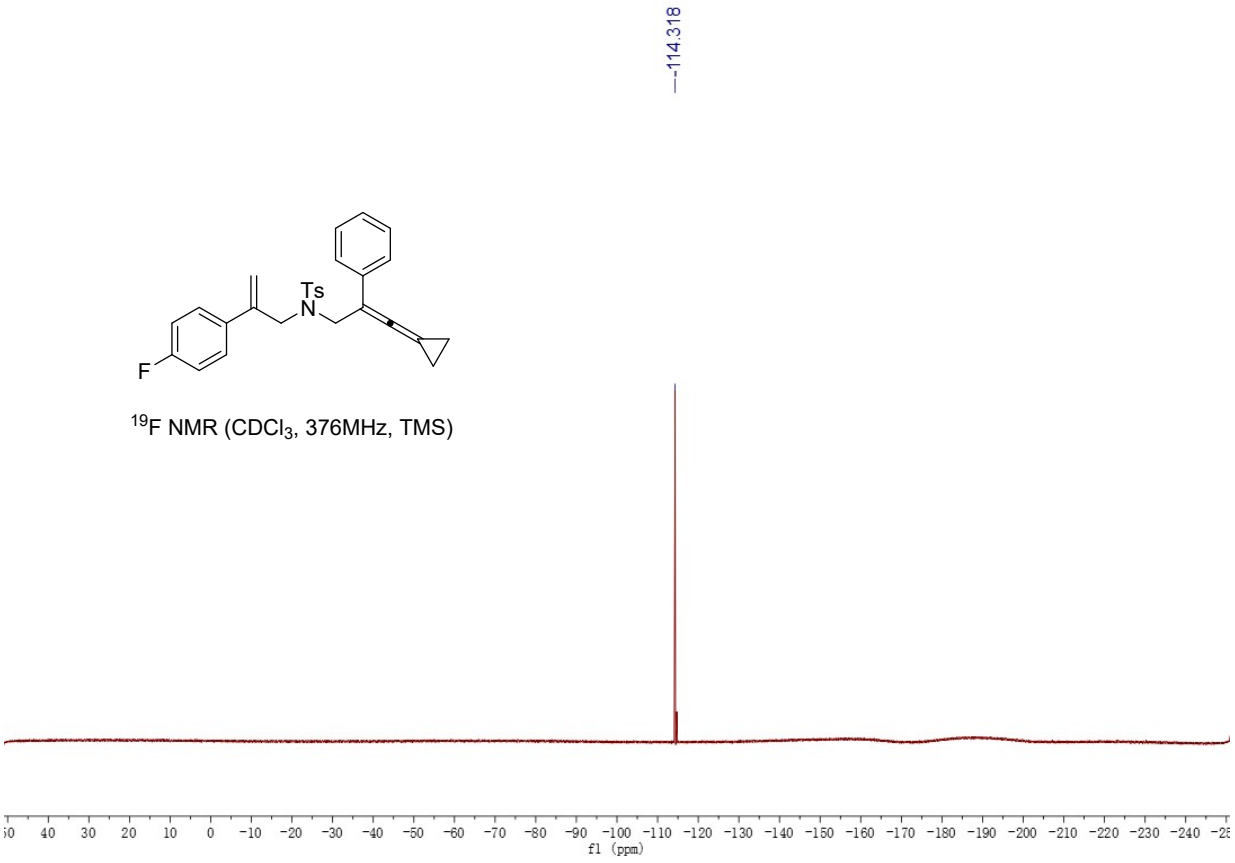
_N_-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-_N_-(2-(4-fluorophenyl)allyl)-4-methylbenzenesulfonamide (1p)

A colorless oil, 59%, 271.1 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.64 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.26 - 7.14 (m, 7H), 6.88 (t, J = 8.6 Hz, 2H), 5.22 (s, 1H), 5.15 (s, 1H), 4.29 (s, 2H), 4.18 (s, 2H), 2.45 (s, 3H), 1.60 - 1.57 (m, 2H), 1.46 - 1.42 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 190.3, 162.3 (d, J = 244.8 Hz), 143.1, 141.7, 136.7, 135.8, 135.2 (d, J = 3.6 Hz), 129.5, 128.3, 128.0 (d, J = 8.0 Hz), 127.4, 126.6, 126.0, 115.9, 114.9 (d, J = 21.1 Hz), 103.3, 80.6, 51.0, 48.9, 21.5, 8.3. ^{19}F NMR ($CDCl_3$, TMS, 377 MHz) δ -114.8 (s). IR (Acetone) ν 1092, 1220, 1359, 1420, 1711, 3009 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{27}NO_2FS$ (M+H): 460.1741, Found: 460.1712.

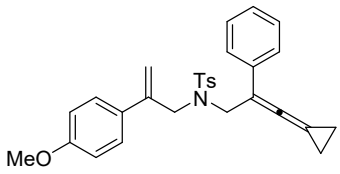




^{13}C NMR ($CDCl_3$, 100MHz, TMS)

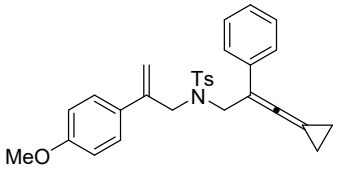


^{19}F NMR ($CDCl_3$, 376MHz, TMS)

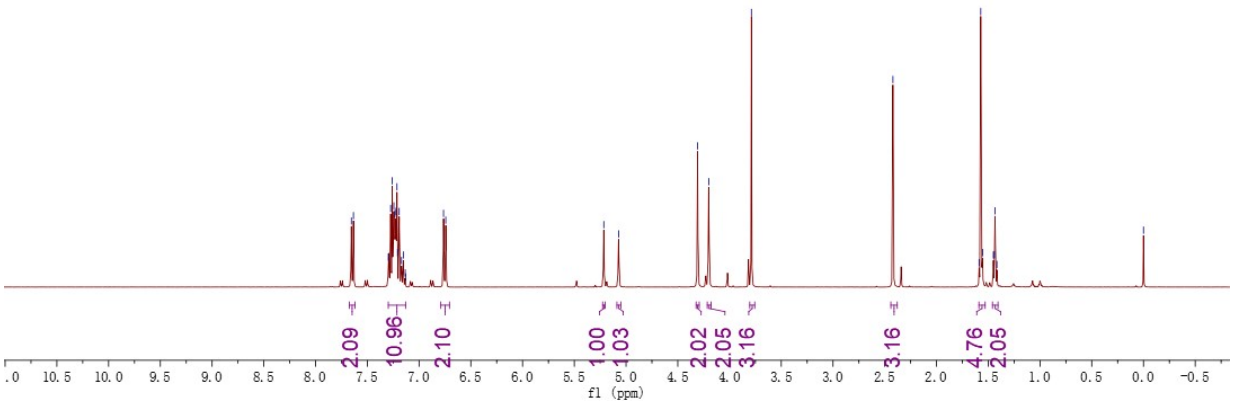


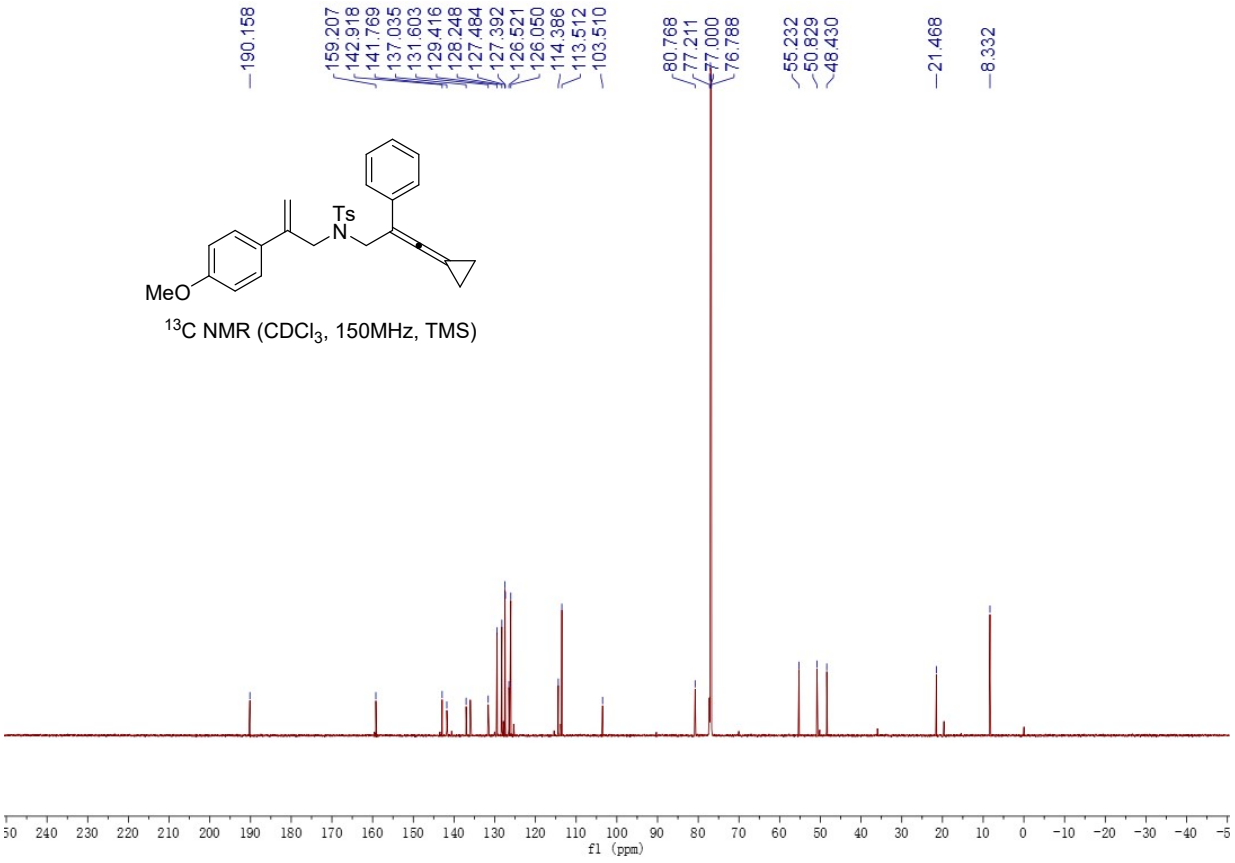
_N_-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-_N_-(2-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (1q)

A colorless oil, 60% yield, 283.0 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.64 (d, J = 8.1 Hz, 2H), 7.30 - 7.13 (m, 9H), 6.75 (d, J = 8.7 Hz, 2H), 5.22 (s, 1H), 5.07 (s, 1H), 4.31 (s, 2H), 4.20 (s, 2H), 3.79 (s, 3H), 2.42 (s, 3H), 1.59 - 1.53 (m, 2H), 1.46 - 1.41 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.2, 159.2, 142.9, 141.8, 137.0, 131.6, 129.4, 128.2, 127.5, 127.4, 126.5, 126.1, 114.4, 113.5, 103.5, 80.8, 55.2, 50.8, 48.4, 21.5, 8.3. IR (Acetone) ν 1031, 1157, 1248, 1513, 1605, 2001, 2938 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{30}NO_3S$ (M+H): 472.1941, Found: 472.1907.

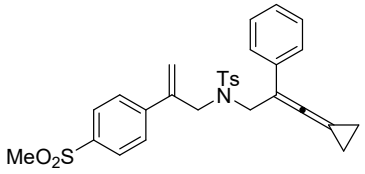


^{1}H NMR ($CDCl_3$, 400MHz, TMS)



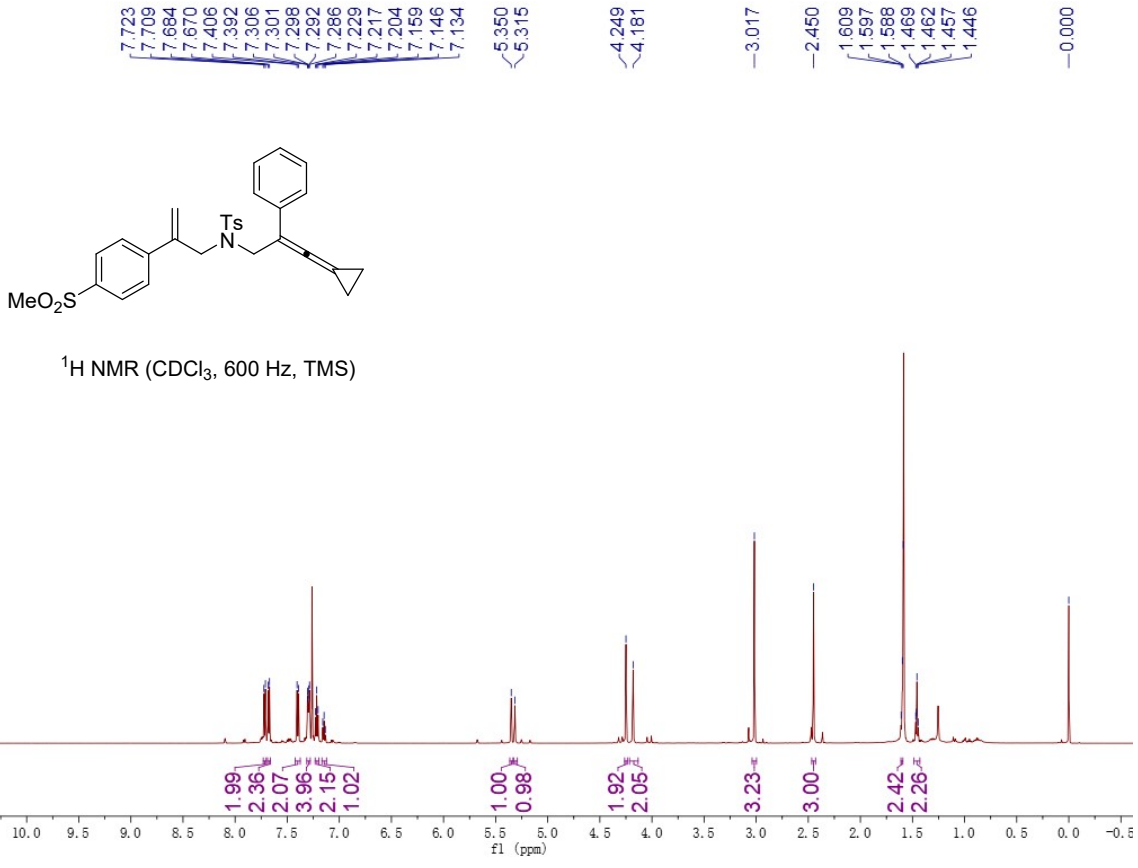


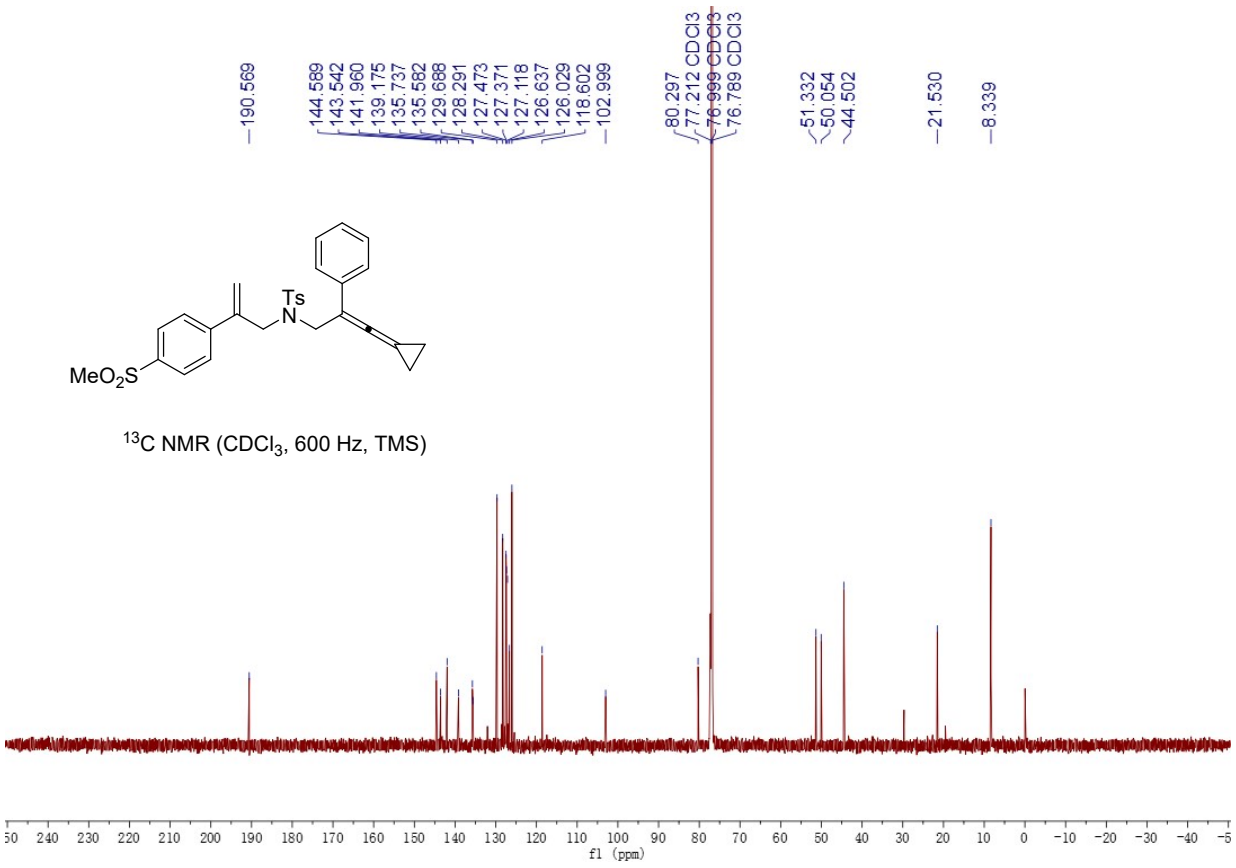
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



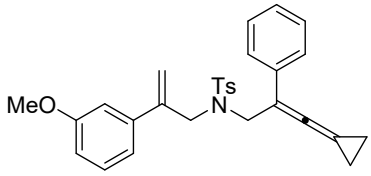
_N_-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-4-methyl-_N_-(2-(4-(methylsulfonyl)phenyl)allyl)benzenesulfonamide (1r)

A colorless oil, 38% yield, 197.2 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.31 - 7.28 (m, 4H), 7.23 - 7.20 (m, 2H), 7.17 - 7.12 (m, 1H), 5.35 (s, 1H), 5.32 (s, 1H), 4.25 (s, 2H), 4.18 (s, 2H), 3.02 (s, 3H), 2.45 (s, 3H), 1.61 - 1.59 (m, 2H), 1.49 - 1.43 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 190.6, 144.6, 143.5, 142.0, 139.2, 135.7, 135.6, 129.7, 128.3, 127.5, 127.4, 127.1, 126.6, 126.0, 118.6, 103.0, 80.3, 51.3, 50.1, 44.5, 21.5, 8.3 cm^{-1}. IR (Acetone) ν 1026, 1139, 1234, 1553, 1670, 2013, 2905 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{30}NO_4S_2$ (M+H): 520.1611, Found: 520.1580.



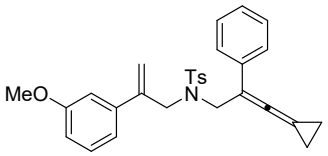


^{13}C NMR ($CDCl_3$, 600 Hz, TMS)

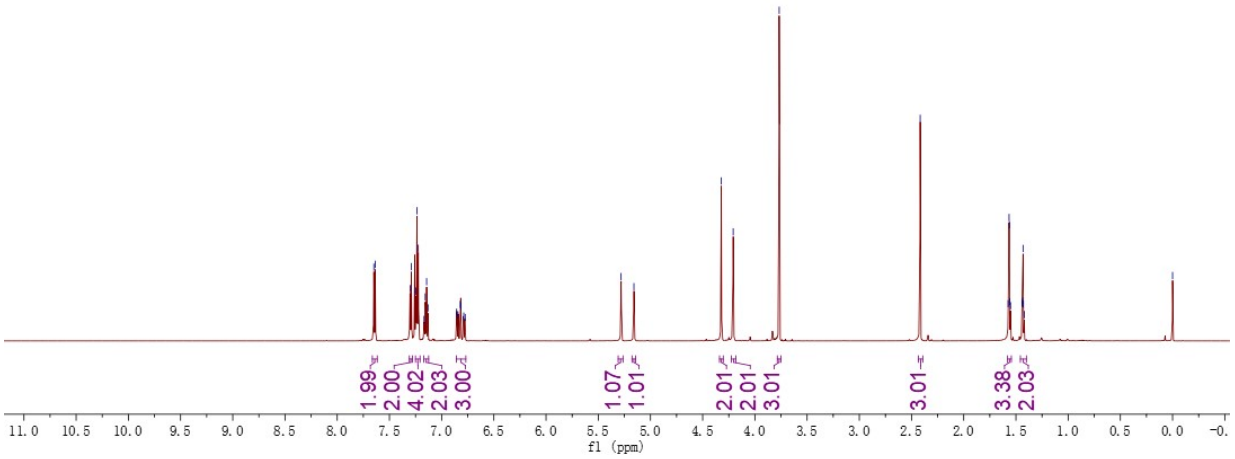


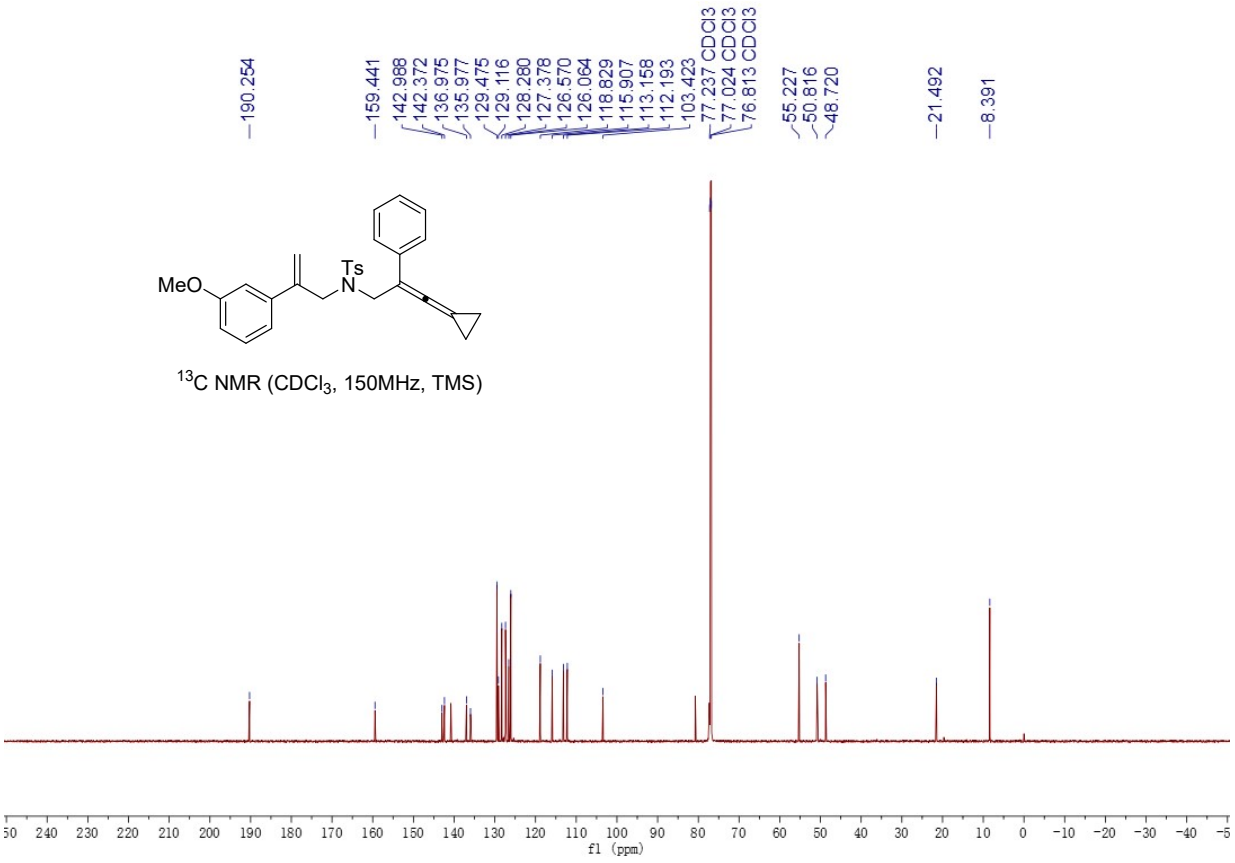
_N_-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-_N_-(2-(3-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (1s)

A colorless oil, 41% yield, 193.4 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.64 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 7.1 Hz, 2H), 7.25 - 7.21 (m, 4H), 7.17 - 7.12 (m, 2H), 6.86 - 6.77 (m, 3H), 5.28 (s, 1H), 5.16 (s, 1H), 4.32 (s, 2H), 4.21 (s, 2H), 3.77 (s, 3H), 2.42 (s, 3H), 1.58 - 1.54 (m, 2H), 1.46 - 1.40 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.3, 159.4, 143.0, 142.4, 137.0, 136.0, 129.5, 129.1, 128.3, 127.4, 126.6, 126.1, 118.8, 115.9, 113.2, 112.2, 103.4, 55.2, 50.8, 48.7, 21.5, 8.4. IR (Acetone) ν 1035, 1161, 1254, 1523, 1612, 2031, 2935 cm^{-1}. HRMS (ESI) calcd. for $C_{29}H_{30}NO_3S$ (M+H): 472.1941, Found: 472.1911.

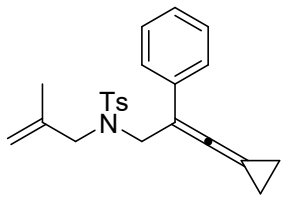


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



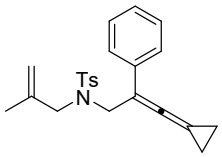


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

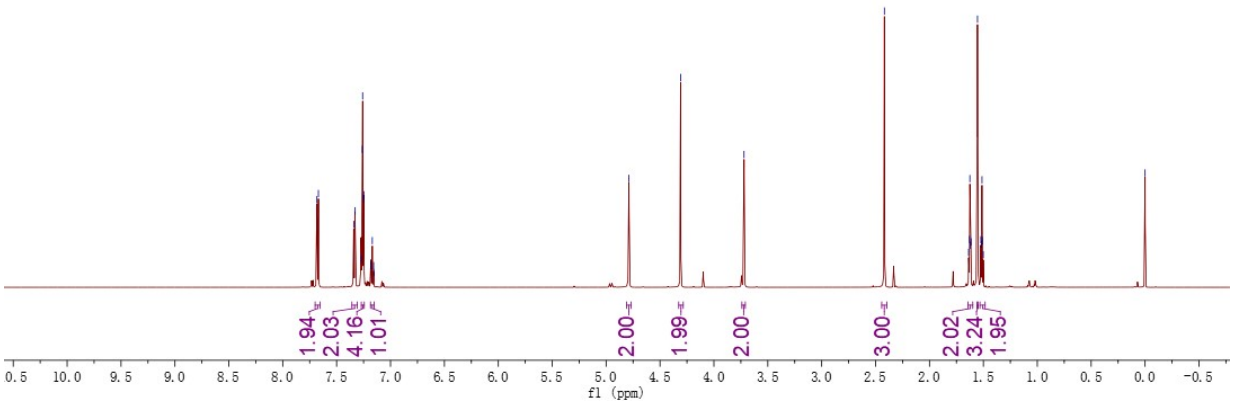


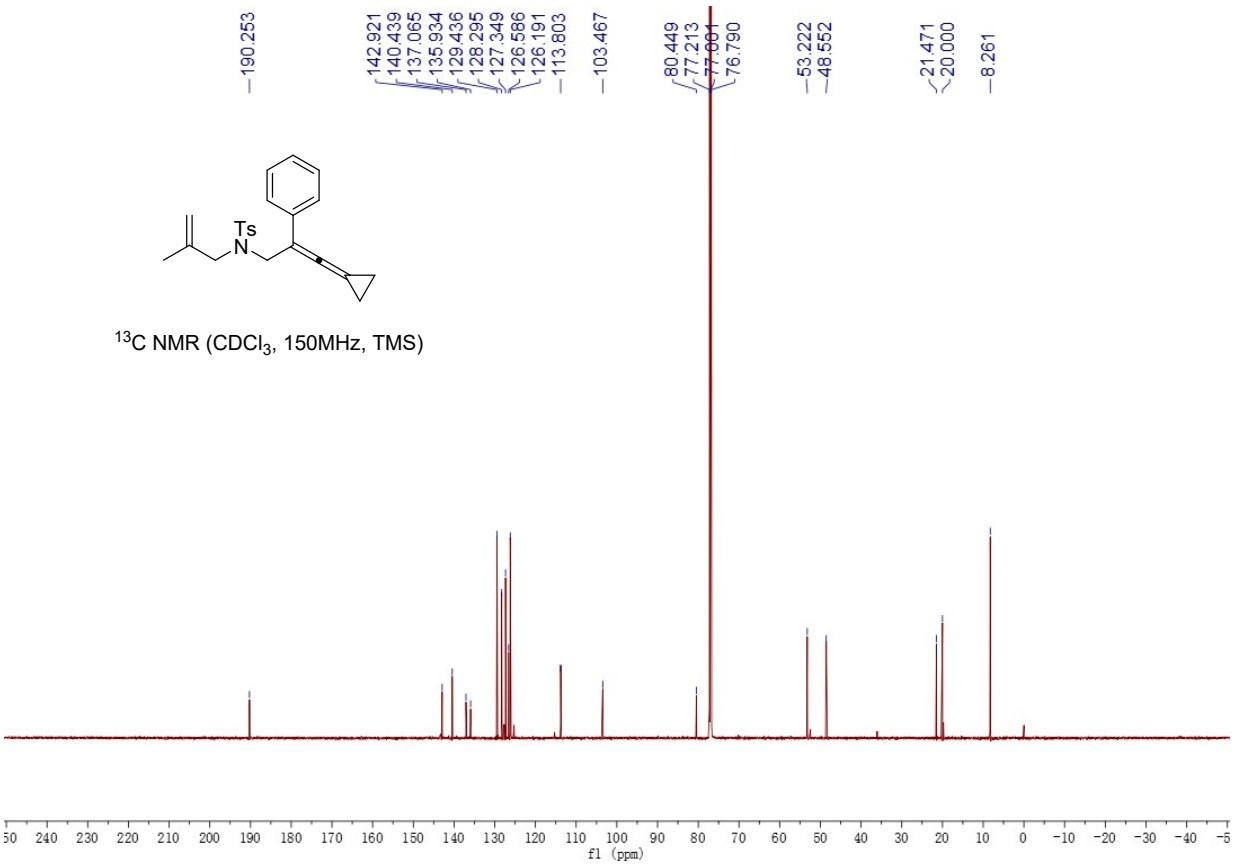
_N_-(3-cyclopropylidene-2-phenyl-3λ^5-allyl)-4-methyl-_N_-(2-methylallyl)benzenesulfonamide (1t)

A colorless oil, 65% yield, 246.7 mg. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.68 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.27 - 7.24 (m, 4H), 7.19 - 7.15 (m, 1H), 4.79 (s, 2H), 4.31 (s, 2H), 3.72 (s, 2H), 2.42 (s, 3H), 1.64 - 1.60 (m, 2H), 1.55 (s, 3H), 1.53 - 1.48 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 190.3, 142.9, 140.4, 137.1, 135.9, 129.4, 128.3, 127.3, 126.6, 126.2, 113.8, 103.5, 80.4, 53.2, 48.6, 21.5, 20.0, 8.3. IR (Acetone) ν 1159, 1221, 1359, 1710, 2009, 3001 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{26}NO_2S$ (M+H): 380.1679, Found: 380.1653.

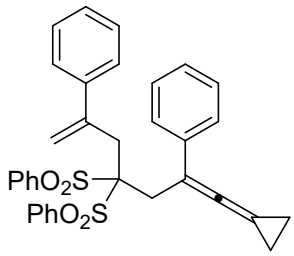


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



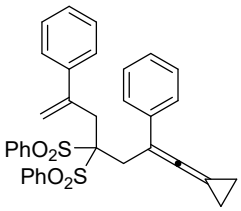


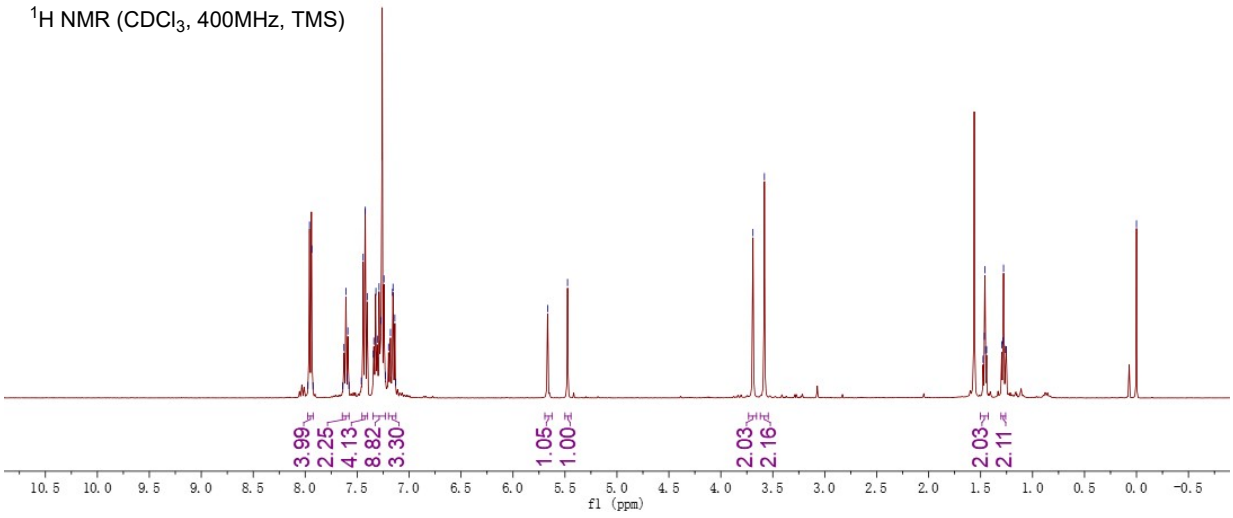
^{13}C NMR ($CDCl_3$, 150MHz, TMS)

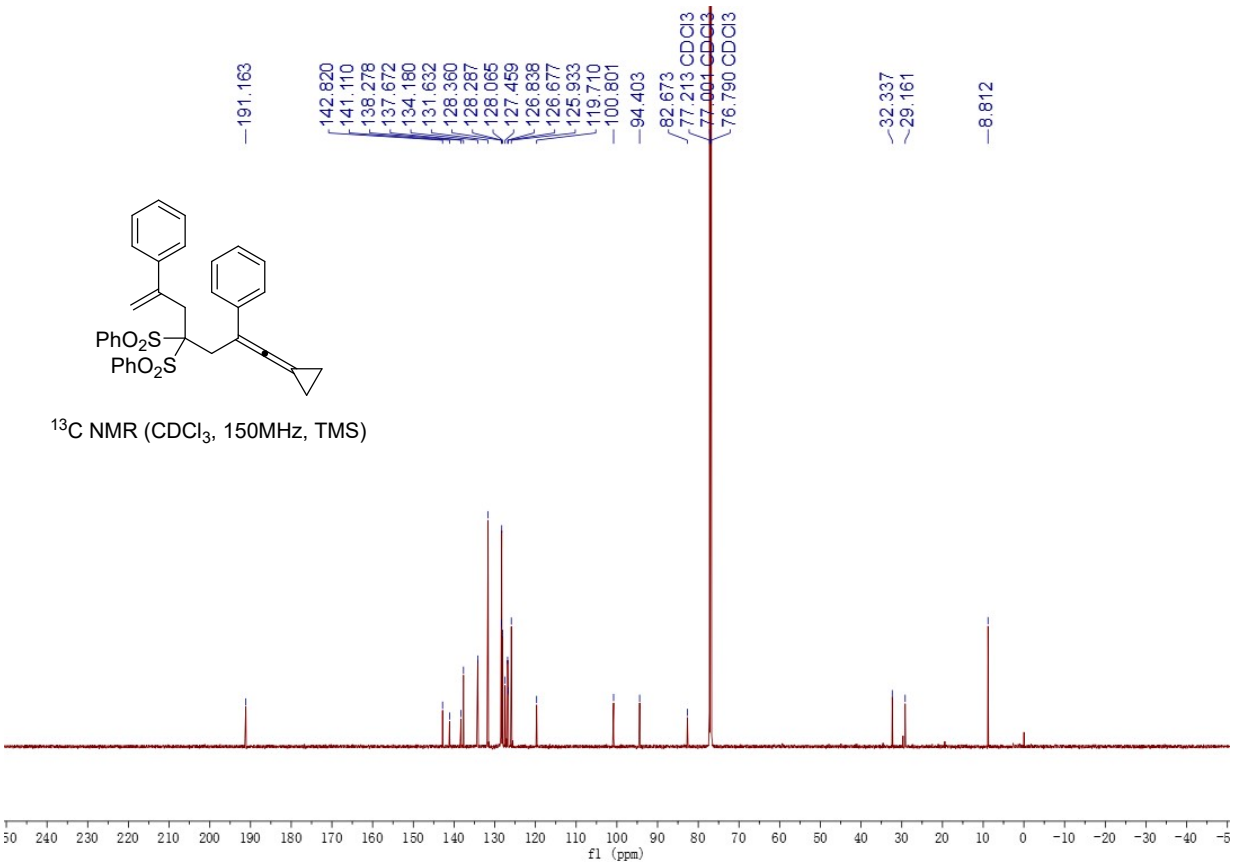


(1-cyclopropylidene-2,6-diphenyl-1λ^5-hepta-1,6-diene-4,4-diyldisulfonyl)dibenzene (1v)

A colorless oil, 41% yield, 149.9 mg. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.98 - 7.92 (m, 4H), 7.64 - 7.58 (m, 2H), 7.45 - 7.40 (m, 4H), 7.35 - 7.23 (m, 7H), 7.20 - 7.13 (m, 3H), 5.67 (s, 1H), 5.48 (s, 1H), 3.69 (s, 2H), 3.58 (s, 2H), 1.50 - 1.43 (m, 2H), 1.30 - 1.26 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 191.2, 142.8, 141.1, 138.3, 137.7, 134.2, 131.6, 128.4, 128.3, 128.1, 127.5, 126.8, 126.7, 125.9, 119.7, 100.8, 94.4, 82.7, 32.3, 29.2, 8.8. IR (Acetone) ν 909, 1073, 1145, 1328, 1446, 1493, 2915 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{31}O_4S_2$ (M+H): 567.1658, Found: 567.1625.

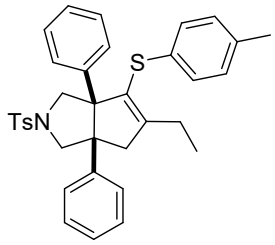






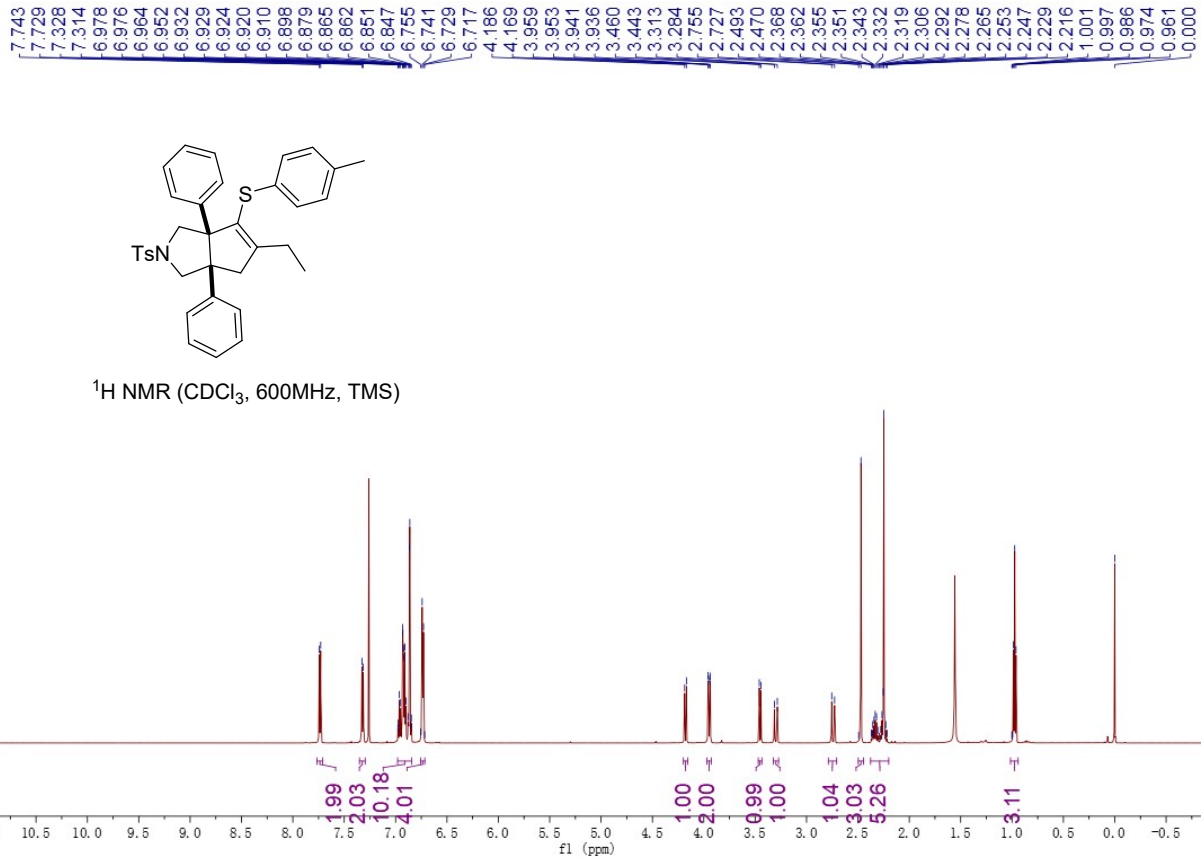
^{13}C NMR ($CDCl_3$, 150MHz, TMS)

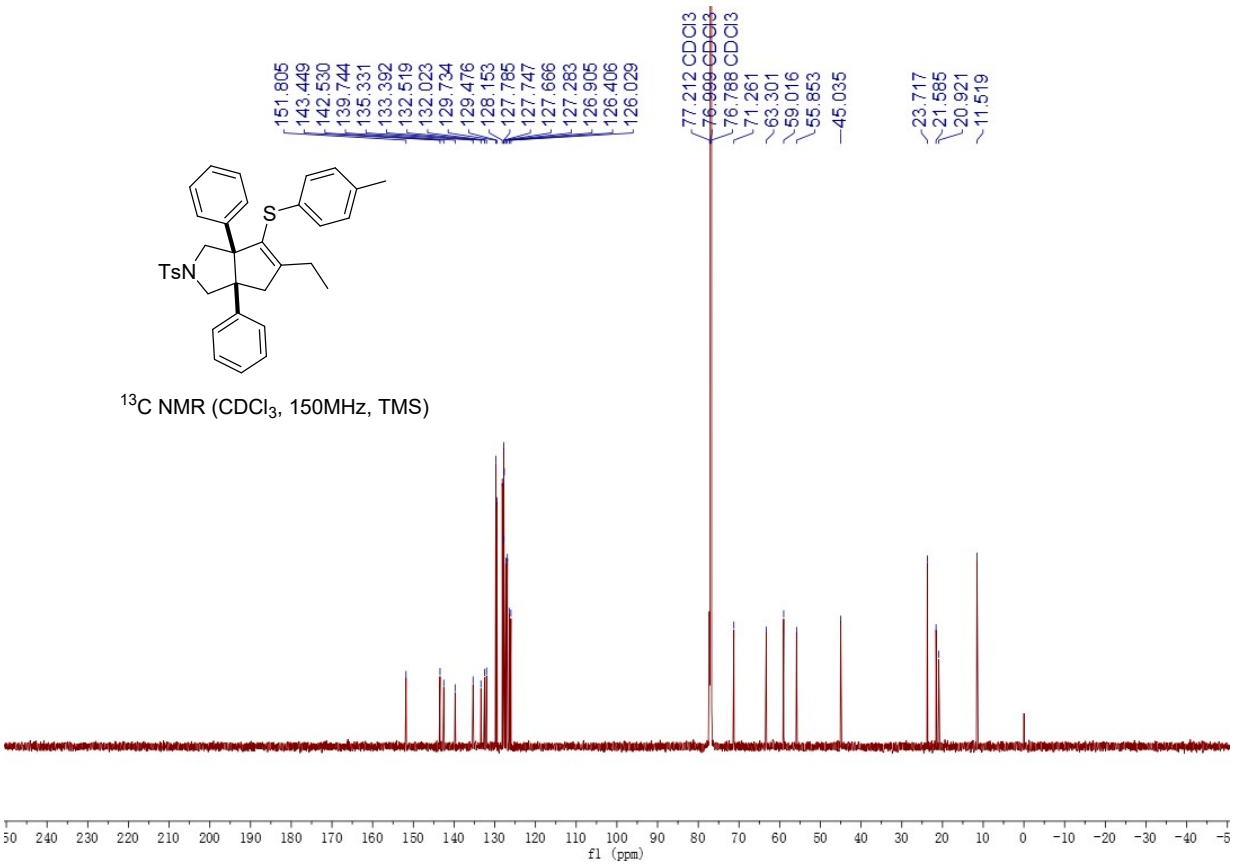
9. Spectroscopic data of products 3, 4, 5, and 6



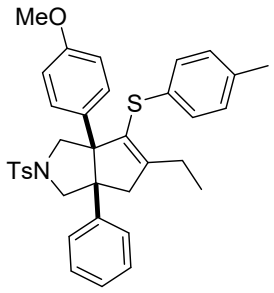
5-ethyl-3a,6a-diphenyl-6-(phenylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3aa)

A colorless oil, 44.1 mg, 73% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.98 - 6.84 (m, 10H), 6.76 - 6.72 (m, 4H), 4.18 (d, *J* = 10.2 Hz, 1H), 3.95 (dd, *J* = 10.1, 3.3 Hz, 2H), 3.45 (d, *J* = 9.9 Hz, 1H), 3.30 (d, *J* = 16.9 Hz, 1H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.47 (s, 3H), 2.38 - 2.20 (m, 5H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 151.8, 143.4, 142.5, 139.7, 135.3, 133.4, 132.5, 132.0, 129.7, 129.5, 128.2, 127.8, 127.74, 127.67, 127.3, 126.9, 126.4, 126.0, 71.3, 63.3, 59.0, 55.9, 45.0, 23.7, 21.6, 20.9, 11.5. IR (Acetone) ν 1030, 1100, 1159, 1255, 1335, 1511, 2954 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{35}NO_2S_2Na$ (M+Na): 588.2001, Found: 588.1999.



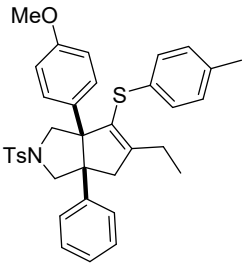


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

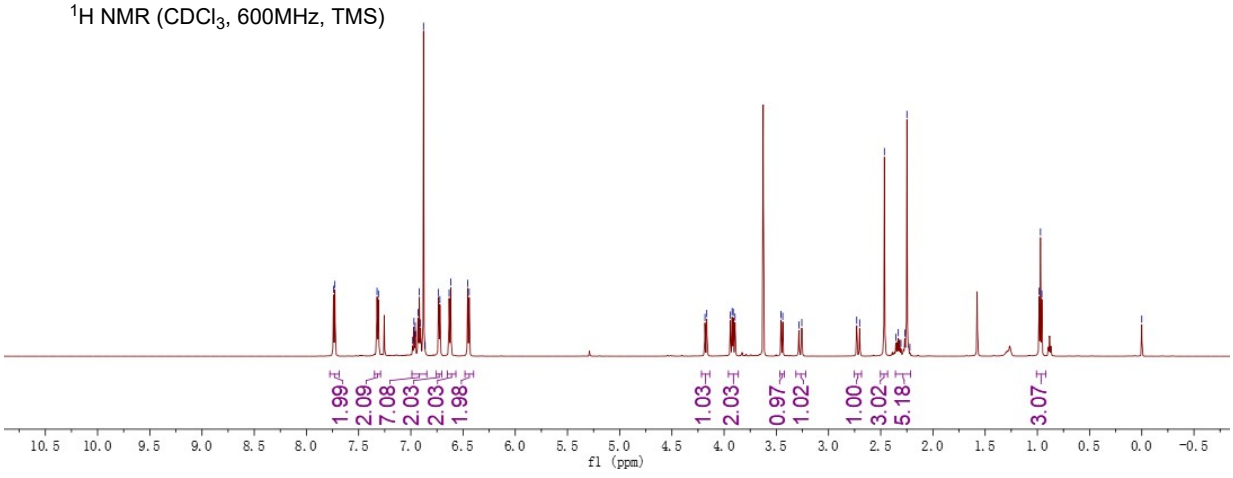


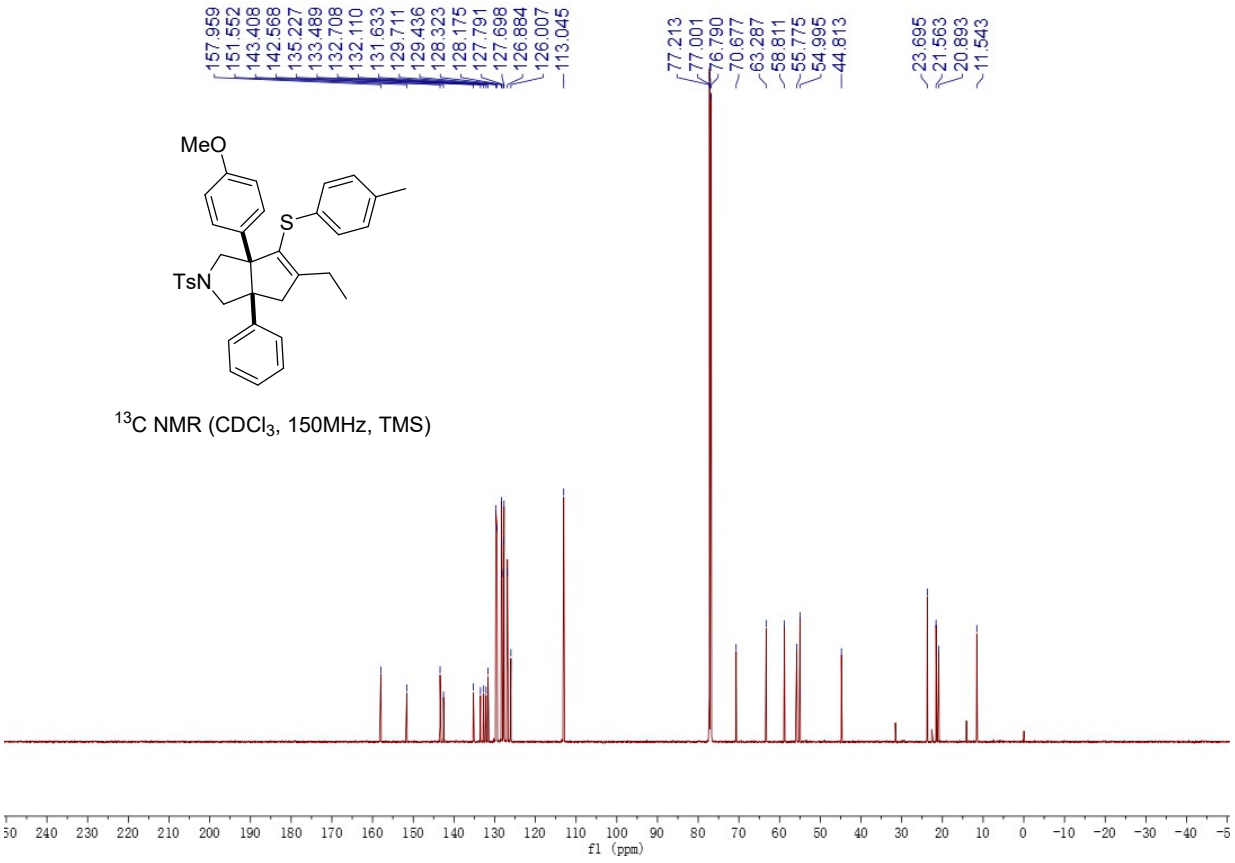
5-ethyl-6a-(4-methoxyphenyl)-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ba)

A colorless oil, 41.7 mg, 70% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.99 - 6.85 (m, 7H), 6.73 (d, *J* = 7.7 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 4.17 (d, *J* = 10.3 Hz, 1H), 3.92 (dd, *J* = 16.6, 10.1 Hz, 2H), 3.63 (s, 3H), 3.45 (d, *J* = 10.0 Hz, 1H), 3.27 (d, *J* = 16.8 Hz, 1H), 2.72 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 2.36 - 2.22 (m, 5H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 158.0, 151.6, 143.4, 142.6, 135.2, 133.5, 132.7, 132.1, 131.6, 129.7, 129.4, 128.3, 128.2, 127.8, 127.7, 126.9, 126.0, 113.0, 70.7, 63.3, 58.8, 55.8, 55.0, 44.8, 23.7, 21.6, 20.9, 11.5. IR (Acetone) ν 1043, 1120, 1139, 1245, 1331, 1501, 2974 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{37}O_3NS_2Na$ (M+Na): 618.2107, Found: 618.2103.

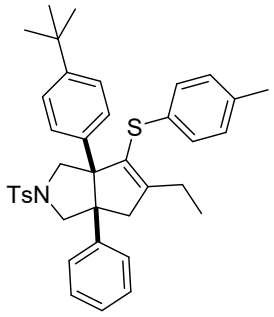


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



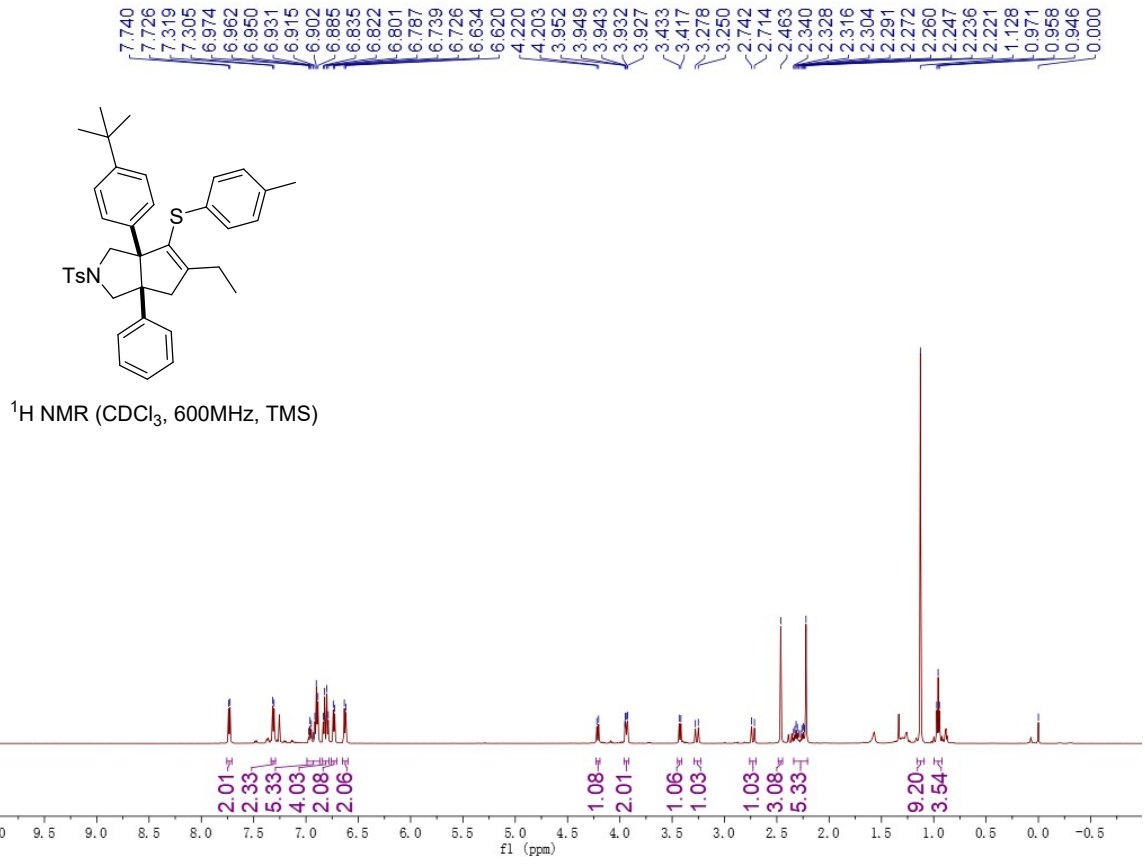


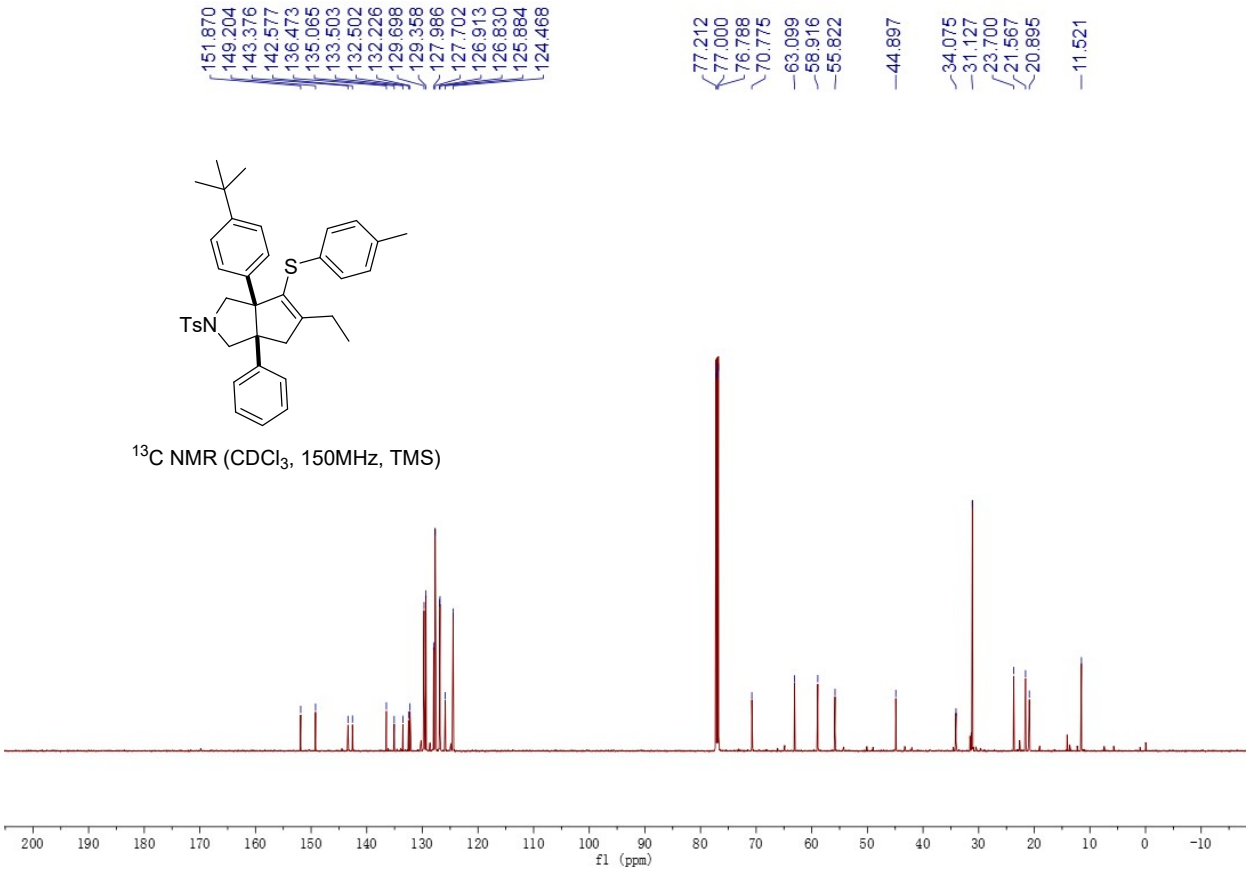
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



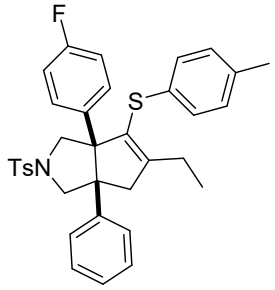
6a-(4-(*tert*-butyl)phenyl)-5-ethyl-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ca)

A colorless oil, 37.3 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.99 - 6.87 (m, 5H), 6.84 - 6.78 (m, 4H), 6.73 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 4.21 (d, *J* = 10.3 Hz, 1H), 3.96 - 3.92 (m, 2H), 3.42 (d, *J* = 9.8 Hz, 1H), 3.26 (d, *J* = 16.8 Hz, 1H), 2.73 (d, *J* = 16.7 Hz, 1H), 2.46 (s, 3H), 2.34 - 2.21 (m, 5H), 1.13 (s, 9H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 151.9, 149.2, 143.4, 142.6, 136.5, 135.1, 133.5, 132.5, 132.2, 129.7, 129.4, 128.0, 127.7, 126.9, 126.8, 125.9, 124.5, 70.8, 63.1, 58.9, 55.8, 44.9, 34.1, 31.1, 23.7, 21.6, 20.9, 11.5. IR (Acetone) ν 1033, 1100, 1145, 1231, 1301, 1555, 2994 cm^{-1}. HRMS (ESI) calcd. for $C_{39}H_{43}O_2NS_2Na$ (M+Na): 644.2627, Found: 644.2627.



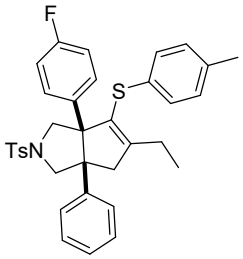


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

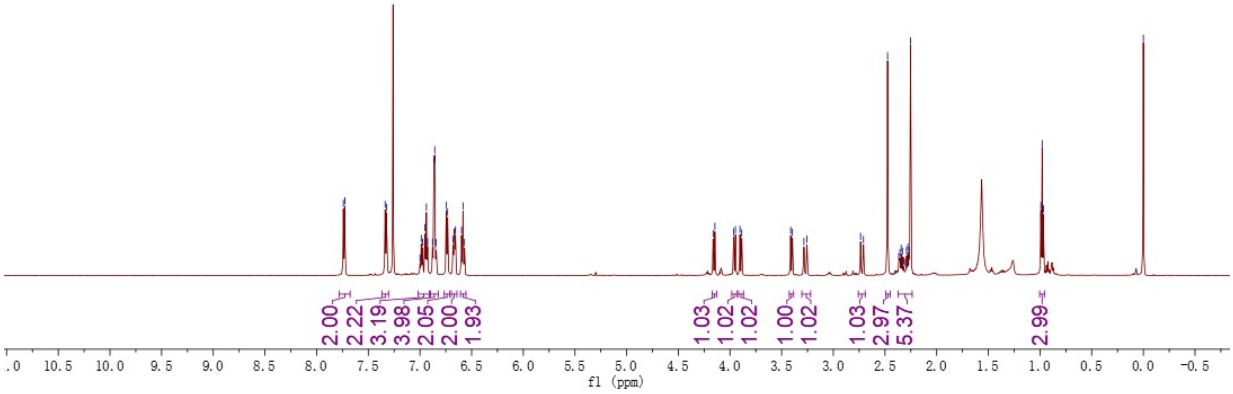


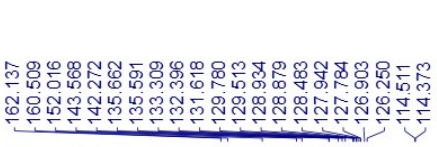
5-ethyl-6a-(4-fluorophenyl)-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3da)

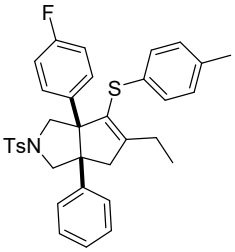
A colorless oil, 41.4 mg, 71% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.02 - 6.91 (m, 3H), 6.90 - 6.82 (m, 4H), 6.74 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 14.1 Hz, 2H), 6.58 (t, *J* = 8.7 Hz, 2H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.96 (d, *J* = 10.0 Hz, 1H), 3.90 (d, *J* = 10.3 Hz, 1H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.27 (d, *J* = 16.9 Hz, 1H), 2.72 (d, *J* = 16.9 Hz, 1H), 2.48 (s, 3H), 2.37 - 2.24 (m, 5H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 161.3 (d, *J* = 245.8 Hz), 152.0, 143.6, 142.3, 135.7, 135.6 (d, *J* = 3.3 Hz), 133.3, 132.4, 131.6, 129.8, 129.5, 128.9 (d, *J* = 8.3 Hz), 128.5, 127.9, 127.8, 126.9, 126.2, 114.4 (d, *J* = 20.8 Hz), 70.8, 63.2, 59.1, 56.0, 44.8, 23.7, 21.6, 20.9, 11.6. ^{19}F NMR ($CDCl_3$, TMS, 564 MHz) δ -116.3 (s). IR (Acetone) ν 1093, 1220, 1359, 1420, 1711, 3006 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{34}O_2NFS_2Na$ (M+Na): 606.1907, Found: 606.1911.



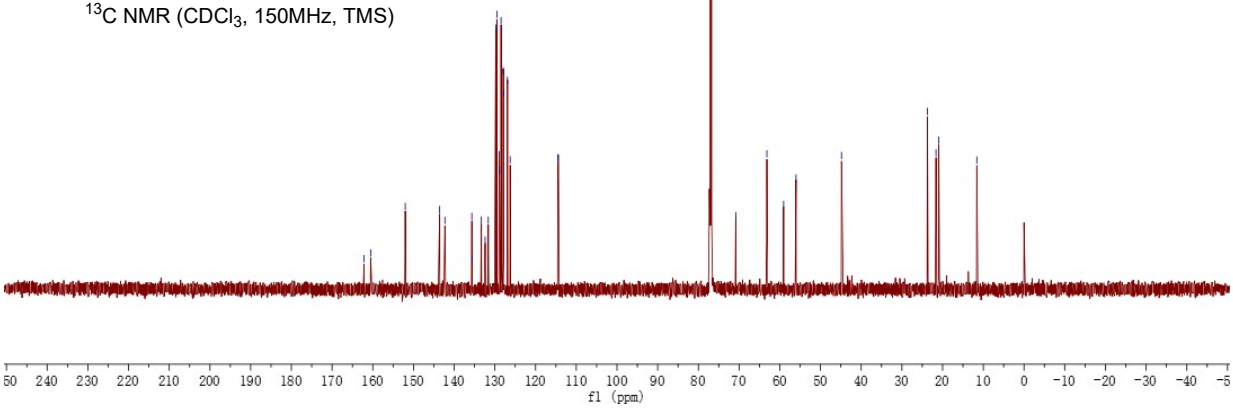
^{1}H NMR ($CDCl_3$, 600MHz, TMS)

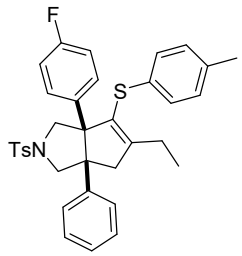




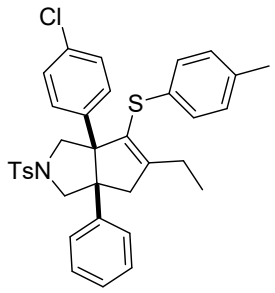


^{13}C NMR ($CDCl_3$, 150MHz, TMS)



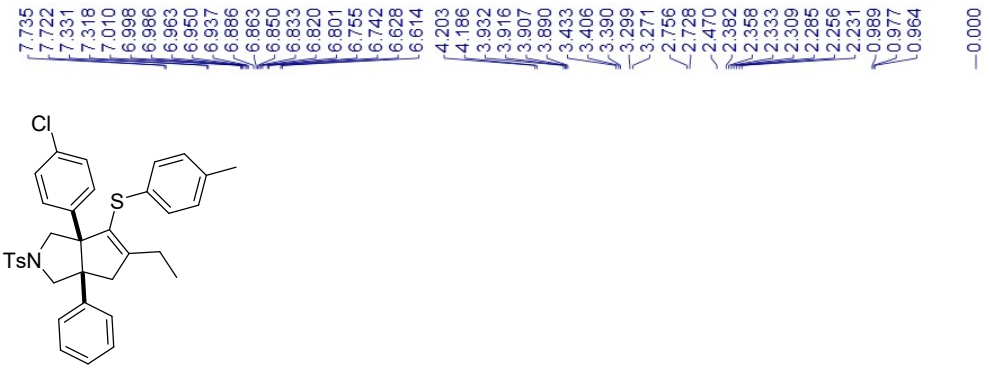


^{19}F NMR ($CDCl_3$, 565MHz, TMS)

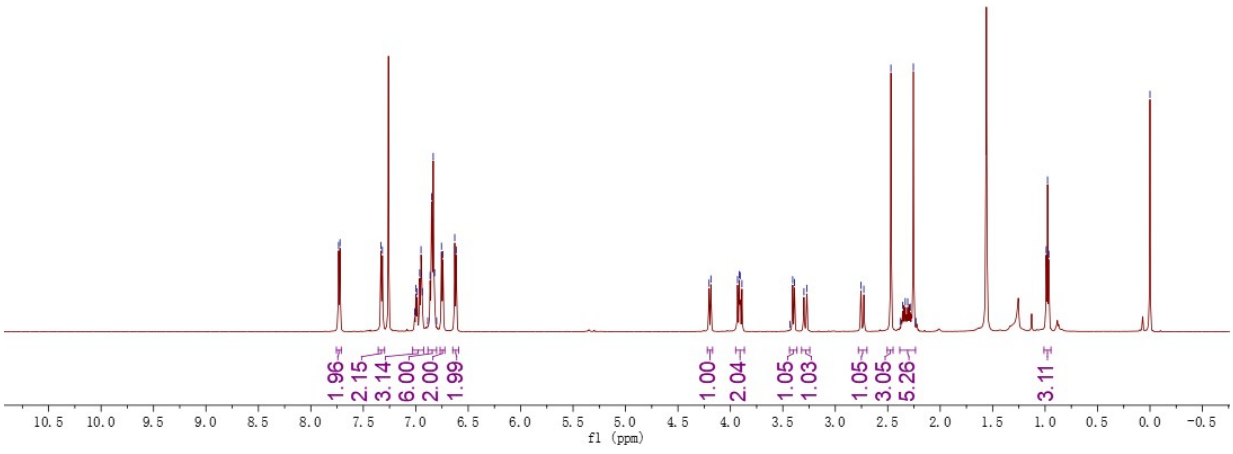


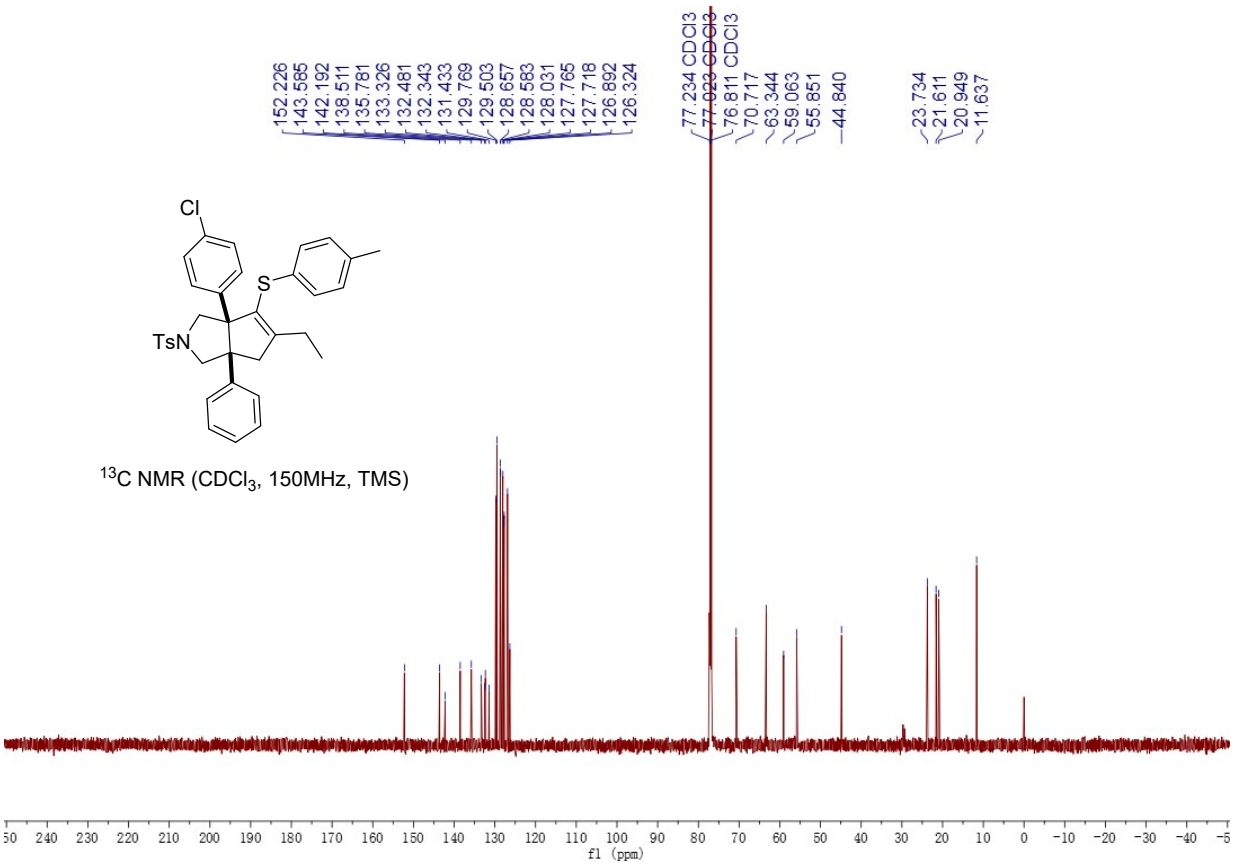
6a-(4-chlorophenyl)-5-ethyl-3a-phenyl-6-(p-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ea)

A colorless oil, 48.0 mg, 80% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.03 - 6.93 (m, 3H), 6.88 - 6.80 (m, 6H), 6.75 (d, *J* = 7.7 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.19 (d, *J* = 10.3 Hz, 1H), 3.91 (dd, *J* = 15.2, 10.1 Hz, 2H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.28 (d, *J* = 16.9 Hz, 1H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.47 (s, 3H), 2.39 - 2.24 (m, 5H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 152.2, 143.6, 142.2, 138.5, 135.8, 133.3, 132.5, 132.3, 131.4, 129.8, 129.5, 128.7, 128.6, 128.0, 127.8, 127.7, 126.9, 126.3, 70.7, 63.3, 59.1, 55.9, 44.8, 23.7, 21.6, 20.9, 11.6. IR (Acetone) ν 1009, 1092, 1168, 1344, 1491, 2870 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{34}O_2NClS_2Na$ (M+Na): 622.1612, Found: 622.1620.

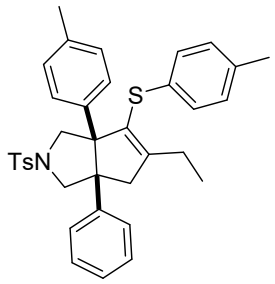


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



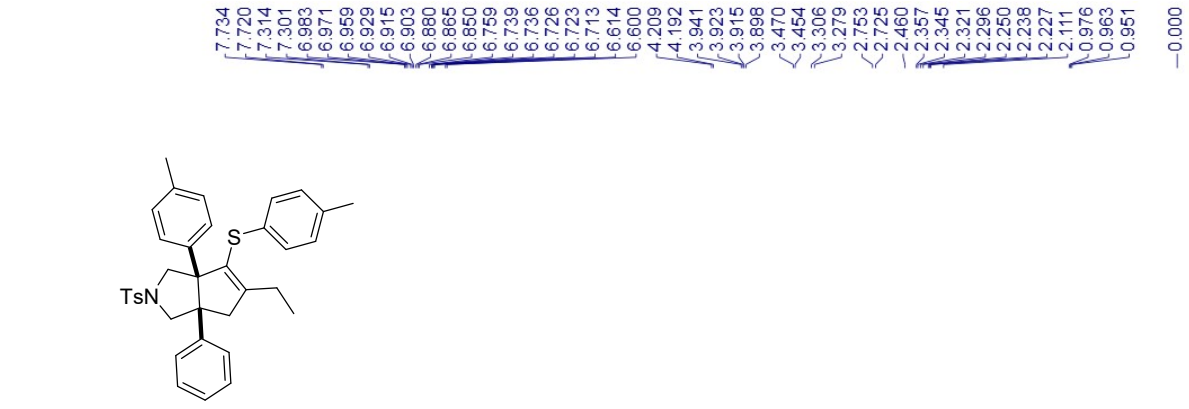


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

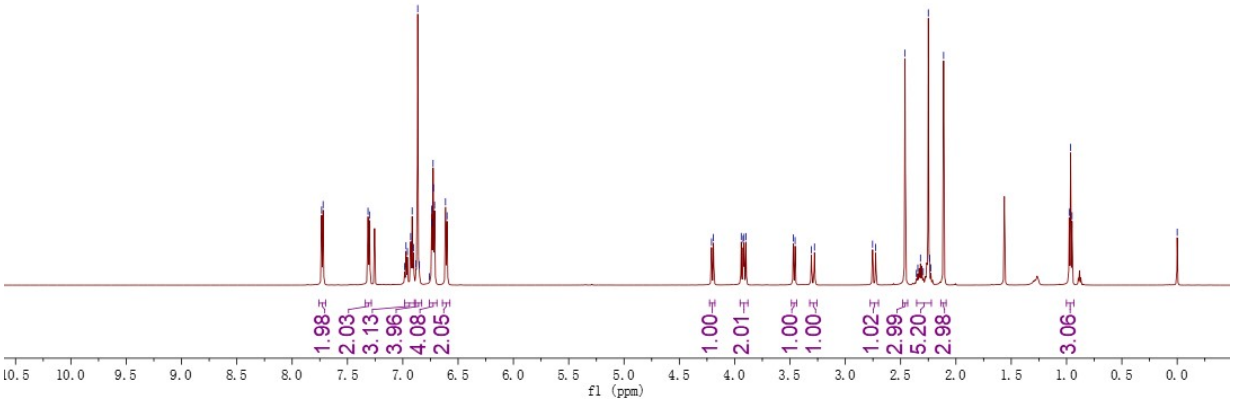


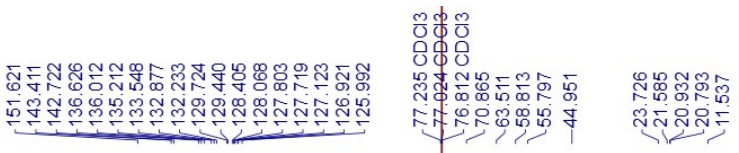
5-ethyl-3a-phenyl-6a-(*p*-tolyl)-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ga)

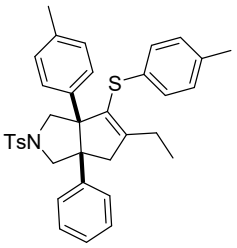
A colorless oil, 36.5 mg, 63% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.98 - 6.90 (m, 3H), 6.89 - 6.83 (m, 4H), 6.79 - 6.69 (m, 4H), 6.61 (d, *J* = 8.2 Hz, 2H), 4.20 (d, *J* = 10.2 Hz, 1H), 3.92 (dd, *J* = 15.3, 10.1 Hz, 2H), 3.46 (d, *J* = 9.9 Hz, 1H), 3.29 (d, *J* = 16.7 Hz, 1H), 2.74 (d, *J* = 16.7 Hz, 1H), 2.46 (s, 3H), 2.35 - 2.22 (m, 5H), 2.11 (s, 3H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 151.6, 143.4, 142.7, 136.6, 136.0, 135.2, 133.5, 132.9, 132.2, 129.7, 129.4, 128.4, 128.1, 127.8, 127.7, 127.1, 126.9, 126.0, 70.9, 63.5, 58.8, 55.8, 45.0, 23.7, 21.6, 20.9, 20.8, 11.5. IR (Acetone) ν 1116, 1158 1165, 1346, 1487, 2923 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{37}O_2NS_2Na$ (M+Na): 602.2158, Found: 602.2148.



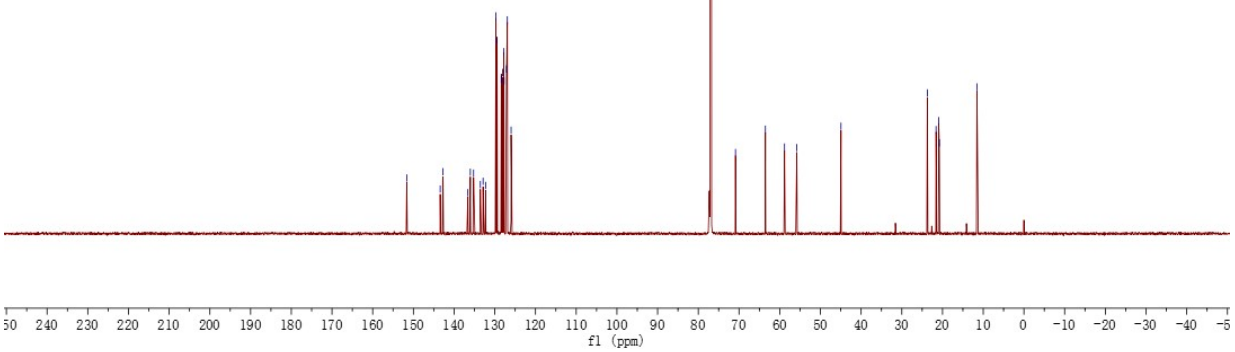
^{1}H NMR ($CDCl_3$, 600MHz, TMS)

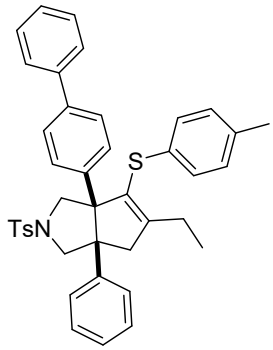






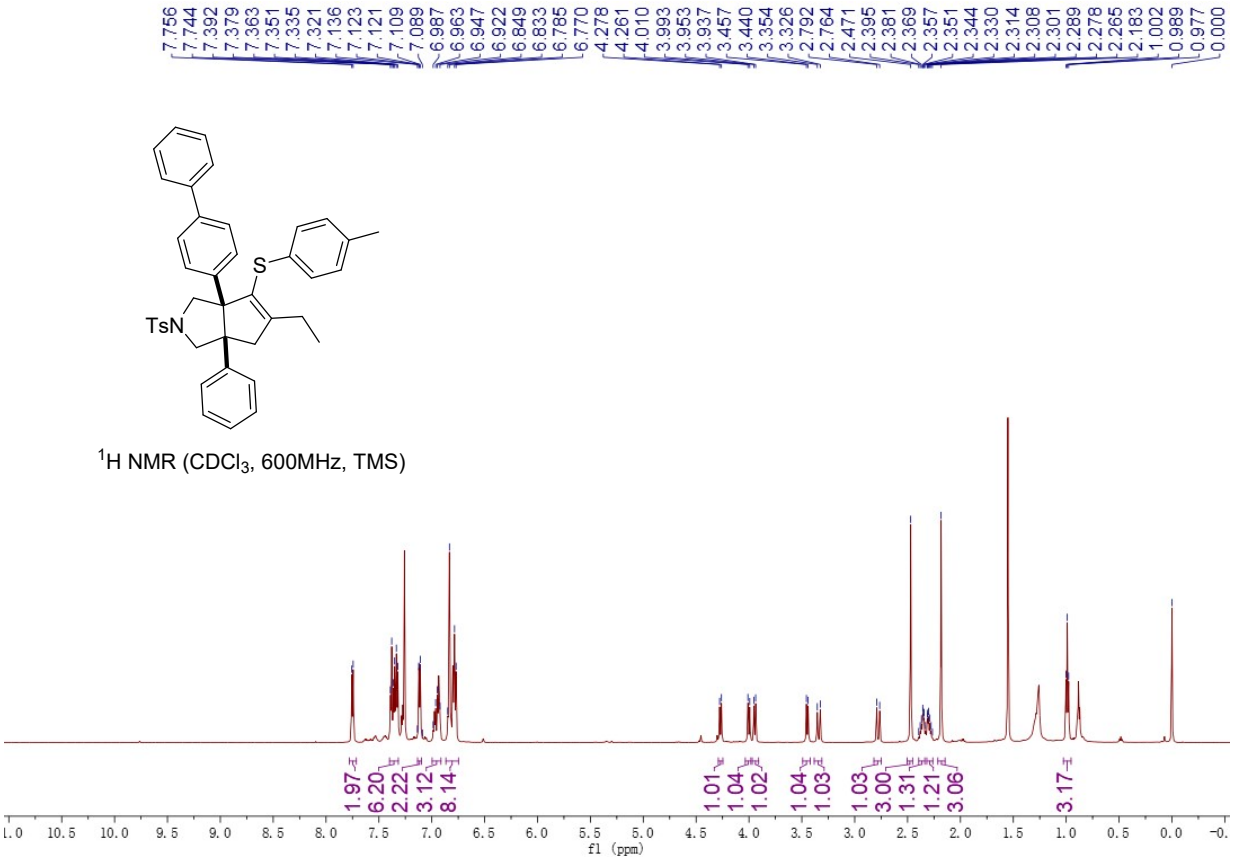
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



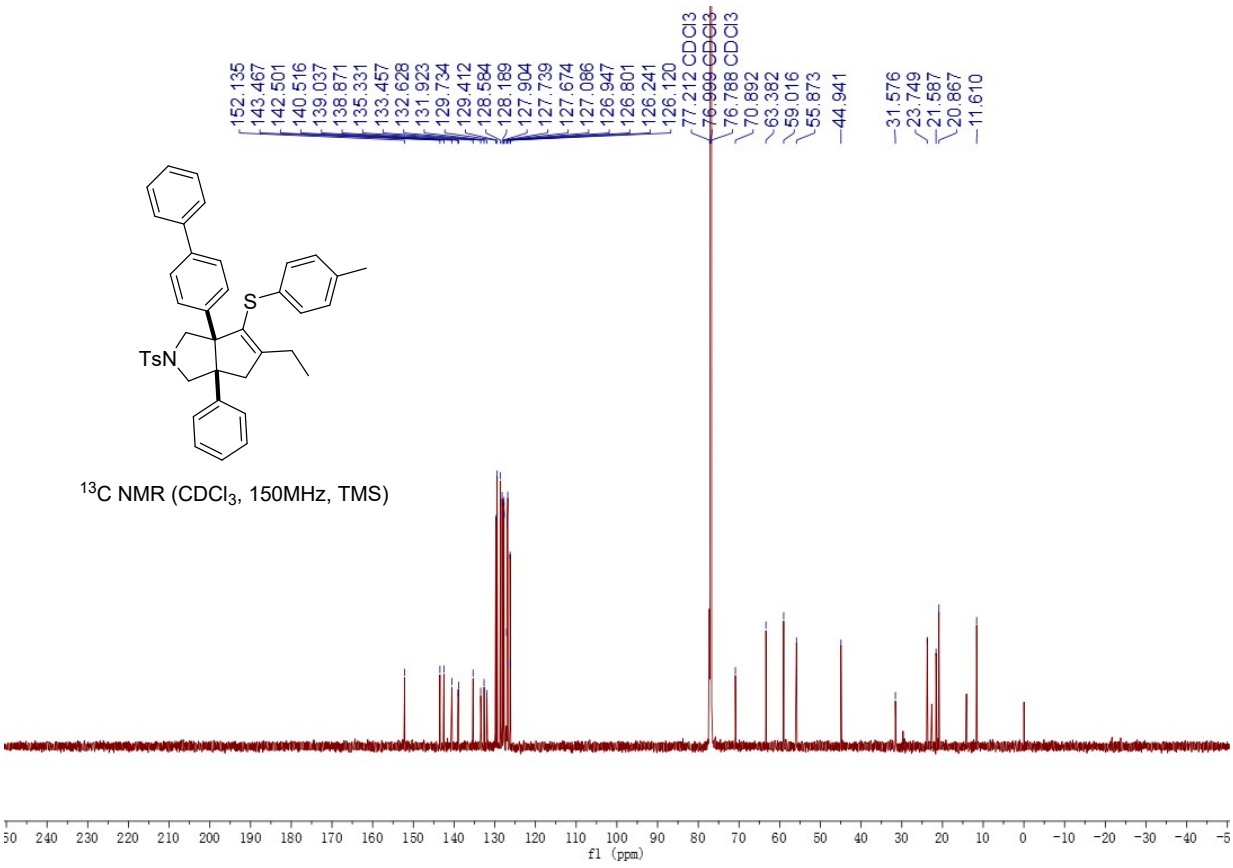


6a-([1,1'-biphenyl]-4-yl)-5-ethyl-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ha)

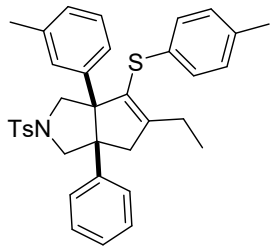
A colorless oil, 36.6 mg, 57% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.40 - 7.27 (m, 7H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.00 - 6.91 (m, 3H), 6.87 - 6.75 (m, 8H), 4.27 (d, *J* = 10.3 Hz, 1H), 4.00 (d, *J* = 10.3 Hz, 1H), 3.95 (d, *J* = 9.9 Hz, 1H), 3.45 (d, *J* = 9.9 Hz, 1H), 3.34 (d, *J* = 16.9 Hz, 1H), 2.78 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 2.39 - 2.34 (m, 1H), 2.32 - 2.26 (m, 1H), 2.18 (s, 3H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 152.1, 143.5, 142.5, 140.5, 139.0, 138.9, 135.3, 133.5, 132.6, 131.9, 129.7, 129.4, 128.6, 128.2, 127.9, 127.73, 127.67, 127.1, 126.9, 126.8, 126.2, 126.1, 70.9, 63.4, 59.0, 55.9, 44.9, 31.6, 23.7, 21.6, 20.9, 11.6. IR (Acetone) ν 1126, 1148 1175, 1326, 1483, 2921 cm^{-1}. HRMS (ESI) calcd. for $C_{41}H_{39}O_2NS_2Na$ (M+Na): 664.2314, Found: 664.2316.



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

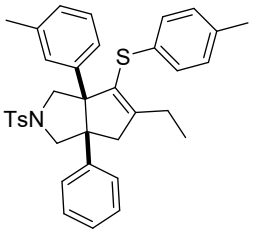


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

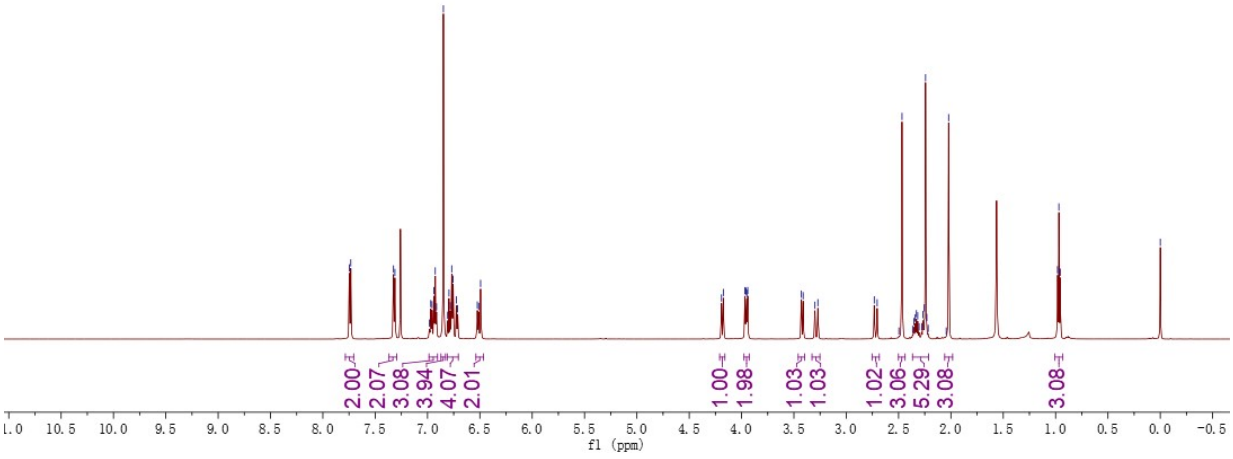


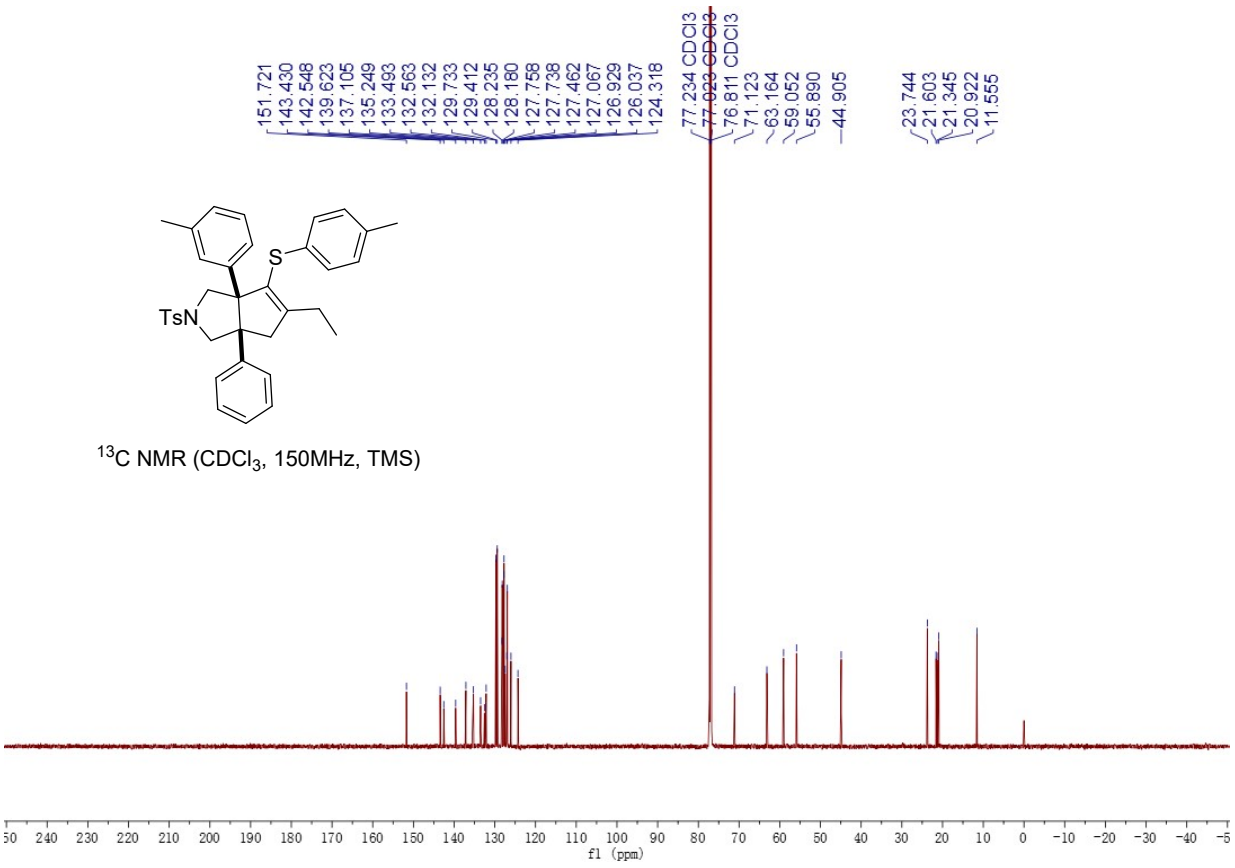
5-ethyl-3a-phenyl-6a-(*m*-tolyl)-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ia)

A colorless oil, 35.3 mg, 61% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.99 - 6.90 (m, 3H), 6.85 (s, 4H), 6.81 - 6.71 (m, 4H), 6.54 - 6.46 (m, 2H), 4.18 (d, *J* = 10.3 Hz, 1H), 3.95 (dd, *J* = 10.1, 5.4 Hz, 2H), 3.42 (d, *J* = 9.9 Hz, 1H), 3.29 (d, *J* = 16.8 Hz, 1H), 2.72 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 2.37 - 2.21 (m, 5H), 2.02 (s, 3H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 151.7, 143.4, 142.5, 139.6, 137.1, 135.2, 133.5, 132.6, 132.1, 129.7, 129.4, 128.23, 128.18, 127.8, 127.7, 127.5, 127.1, 126.9, 126.0, 124.3, 71.1, 63.2, 59.1, 55.9, 44.9, 23.7, 21.6, 21.3, 20.9, 11.6. IR (Acetone) ν 1116, 1158, 1165, 1346, 1487, 2922 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{37}O_2NNaS_2$ (M+Na): 602.2158, Found: 602.2159.

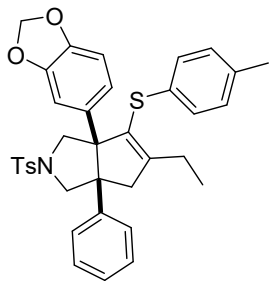


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



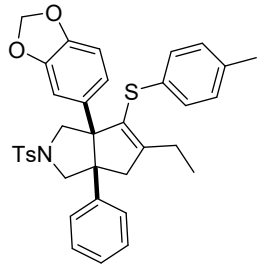


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

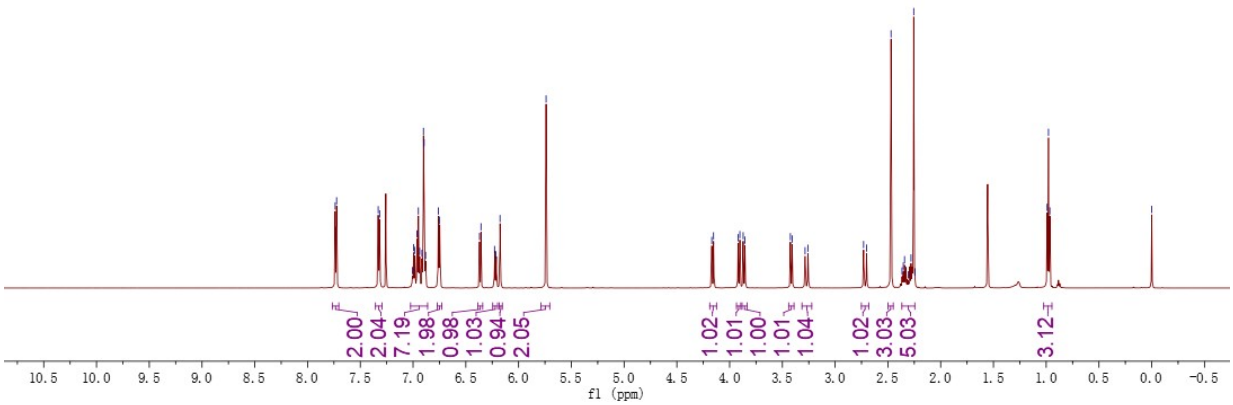


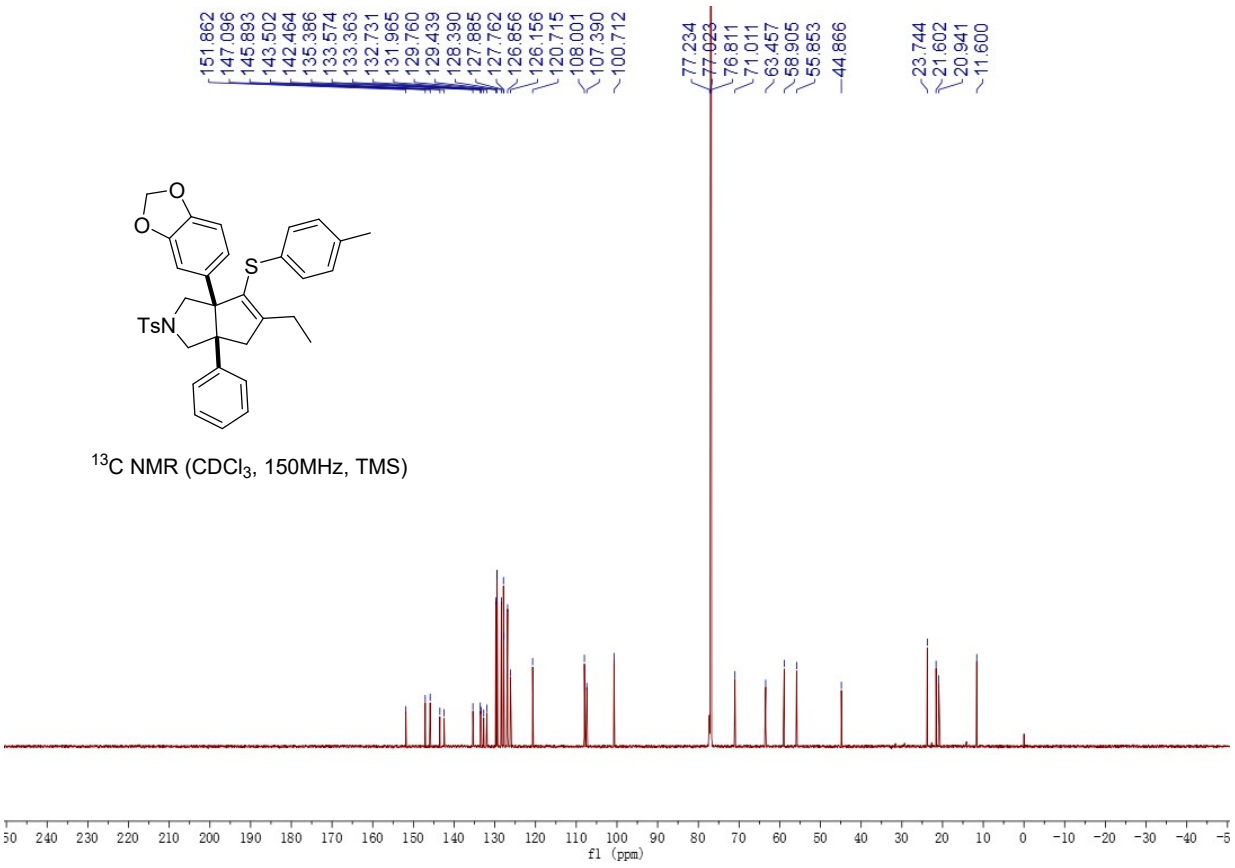
6a-(benzo[*d*][1,3]dioxol-5-yl)-5-ethyl-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ja)

A colorless oil, 36.6 mg, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.02 - 6.86 (m, 7H), 6.75 (d, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 8.2 Hz, 1H), 6.22 (d, *J* = 8.2 Hz, 1H), 6.18 (s, 1H), 5.74 (s, 2H), 4.16 (d, *J* = 10.2 Hz, 1H), 3.91 (d, *J* = 10.0 Hz, 1H), 3.86 (d, *J* = 10.3 Hz, 1H), 3.42 (d, *J* = 10.0 Hz, 1H), 3.27 (d, *J* = 16.9 Hz, 1H), 2.72 (d, *J* = 16.9 Hz, 1H), 2.47 (s, 3H), 2.37 - 2.25 (m, 5H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 151.9, 147.1, 145.9, 143.5, 142.5, 135.4, 133.6, 133.4, 132.7, 132.0, 129.8, 129.4, 128.4, 127.9, 127.8, 126.9, 126.2, 120.7, 108.0, 107.4, 100.7, 71.0, 63.5, 58.9, 55.9, 44.9, 23.7, 21.6, 20.9, 11.6. IR (Acetone) ν 1170, 1246, 1346, 1485, 1594, 2878 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{35}O_4NS_2Na$ (M+Na): 632.1900, Found: 632.1900.

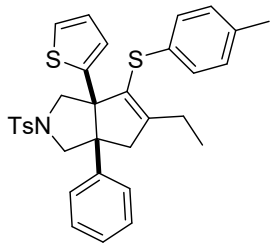


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



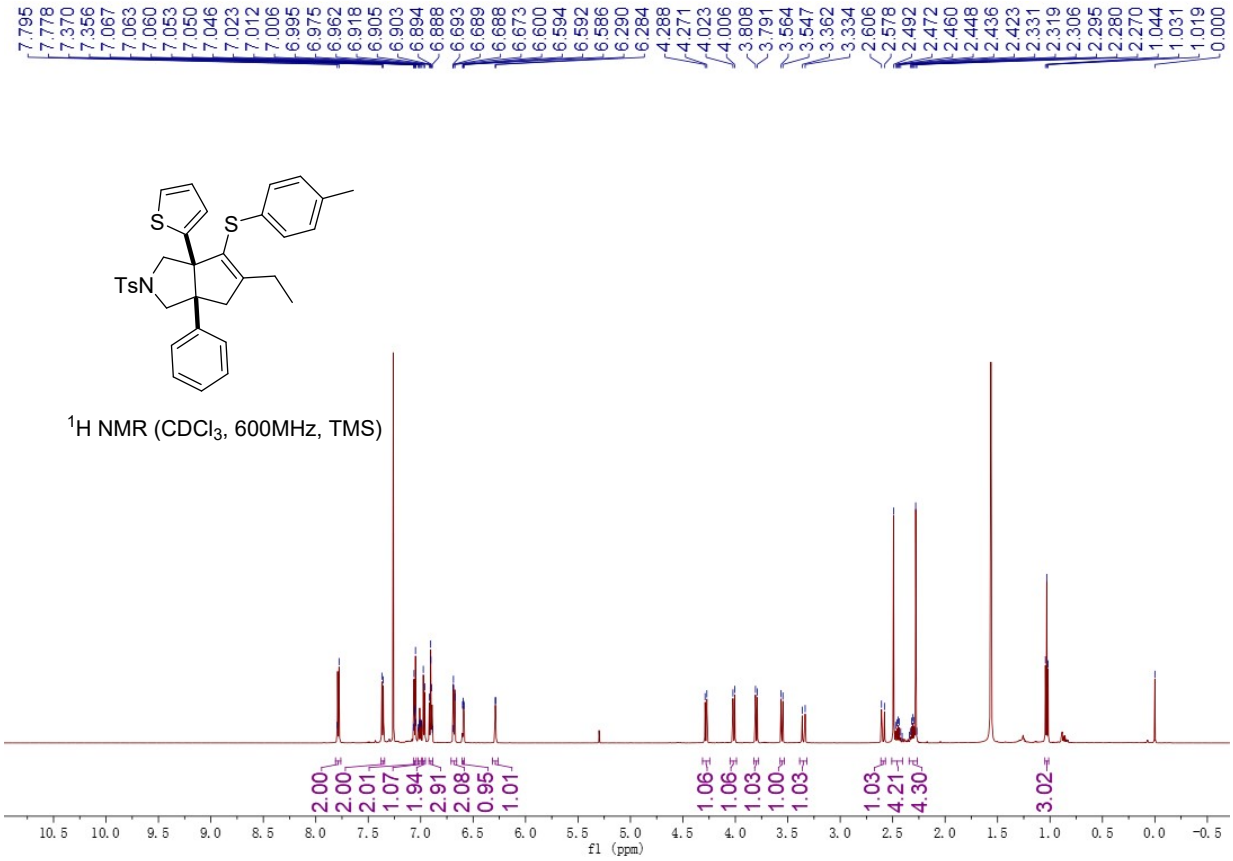


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

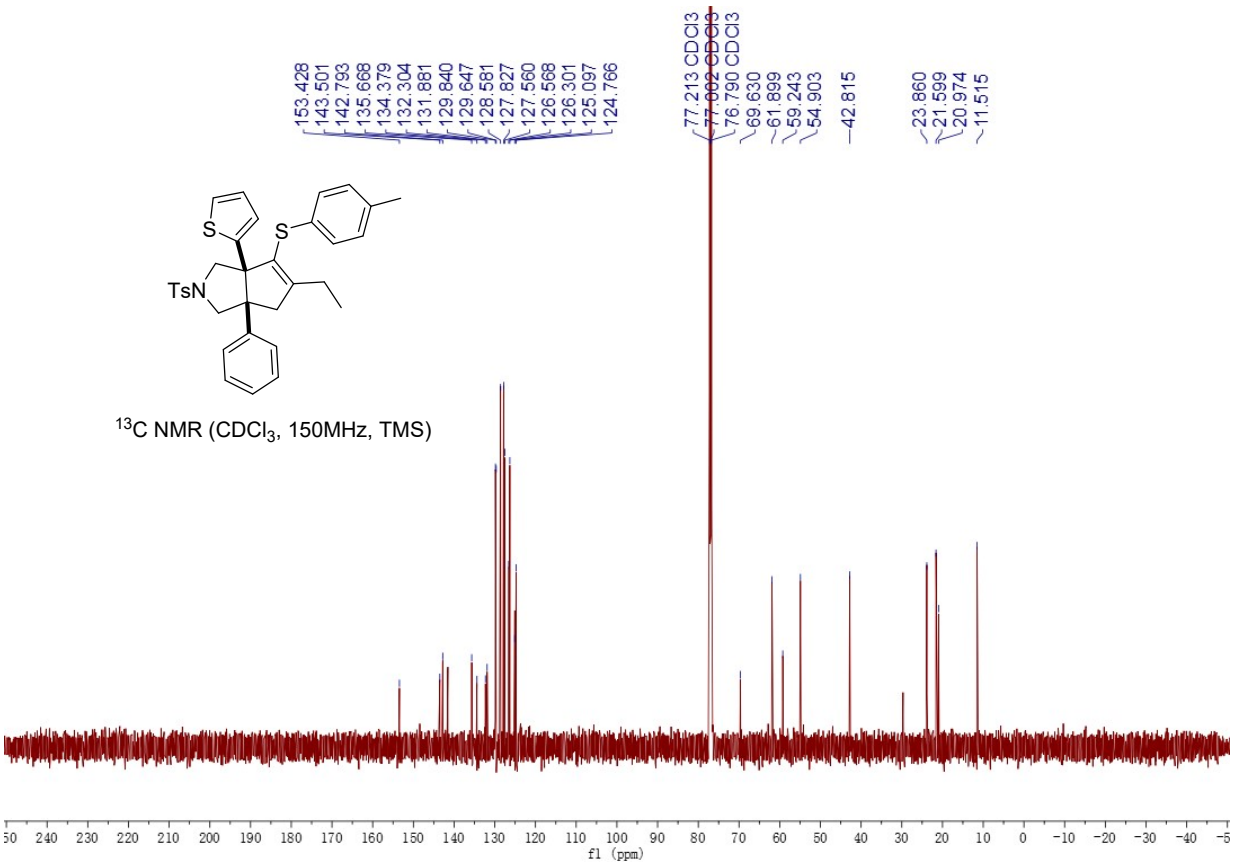


5-ethyl-3a-phenyl-6a-(thiophen-2-yl)-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ka)

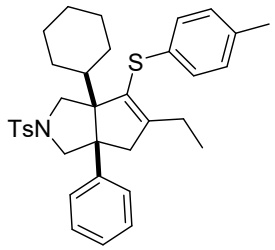
A colorless oil, 26.3 mg, 46% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.81 - 7.76 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.07 - 7.04 (m, 2H), 7.03 - 6.99 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.92 - 6.88 (m, 3H), 6.71 - 6.66 (m, 2H), 6.59 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.29 (d, *J* = 3.6 Hz, 1H), 4.28 (d, *J* = 10.2 Hz, 1H), 4.01 (d, *J* = 10.2 Hz, 1H), 3.80 (d, *J* = 10.2 Hz, 1H), 3.56 (d, *J* = 10.2 Hz, 1H), 3.35 (d, *J* = 16.8 Hz, 1H), 2.59 (d, *J* = 16.8 Hz, 1H), 2.51 - 2.41 (m, 4H), 2.34 - 2.27 (m, 4H), 1.03 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 153.4, 143.5, 142.8, 135.7, 134.4, 132.3, 131.9, 129.8, 129.6, 128.6, 127.8, 127.6, 126.6, 126.3, 125.1, 124.8, 69.6, 61.9, 59.2, 54.9, 42.8, 23.9, 21.6, 21.0, 11.5. IR (Acetone) ν 1089, 1163, 1346, 1493, 1594, 2915 cm^{-1}. HRMS (ESI) calcd. for $C_{33}H_{33}S_3NO_2Na$ (M+Na): 594.1566, Found: 594.1568.



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

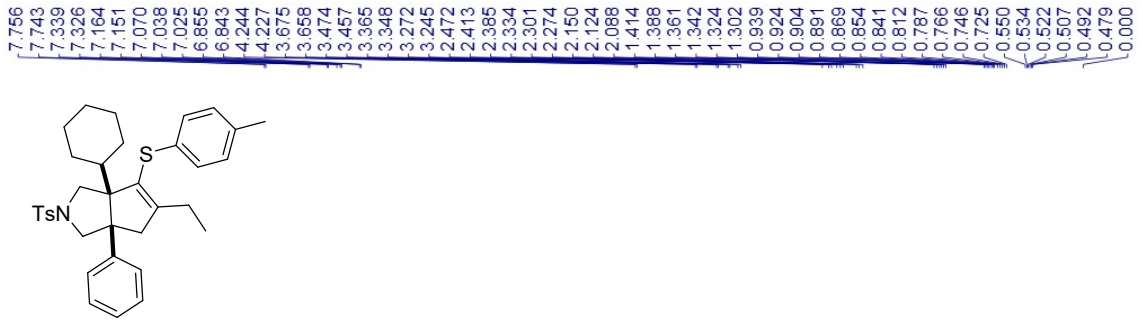


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

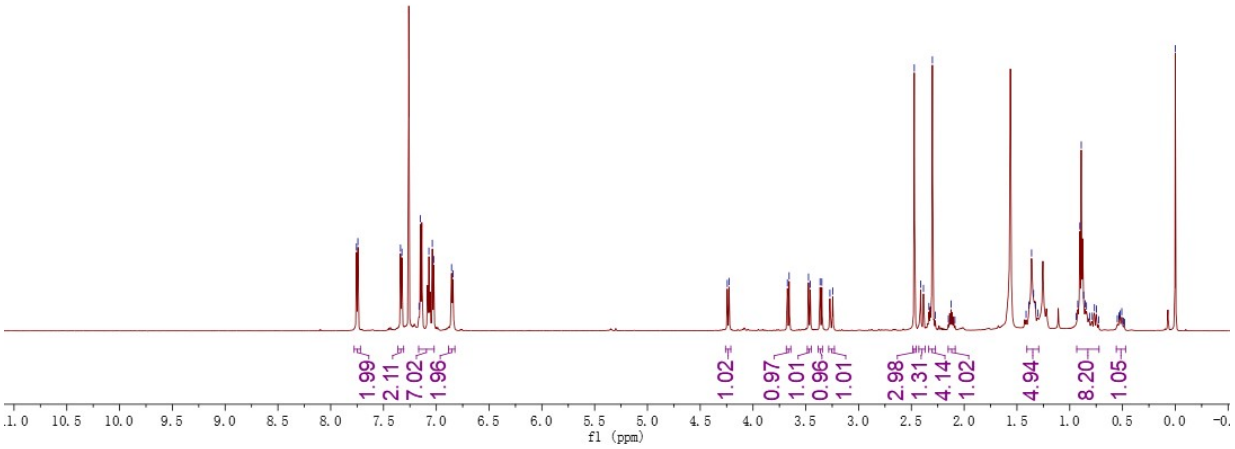


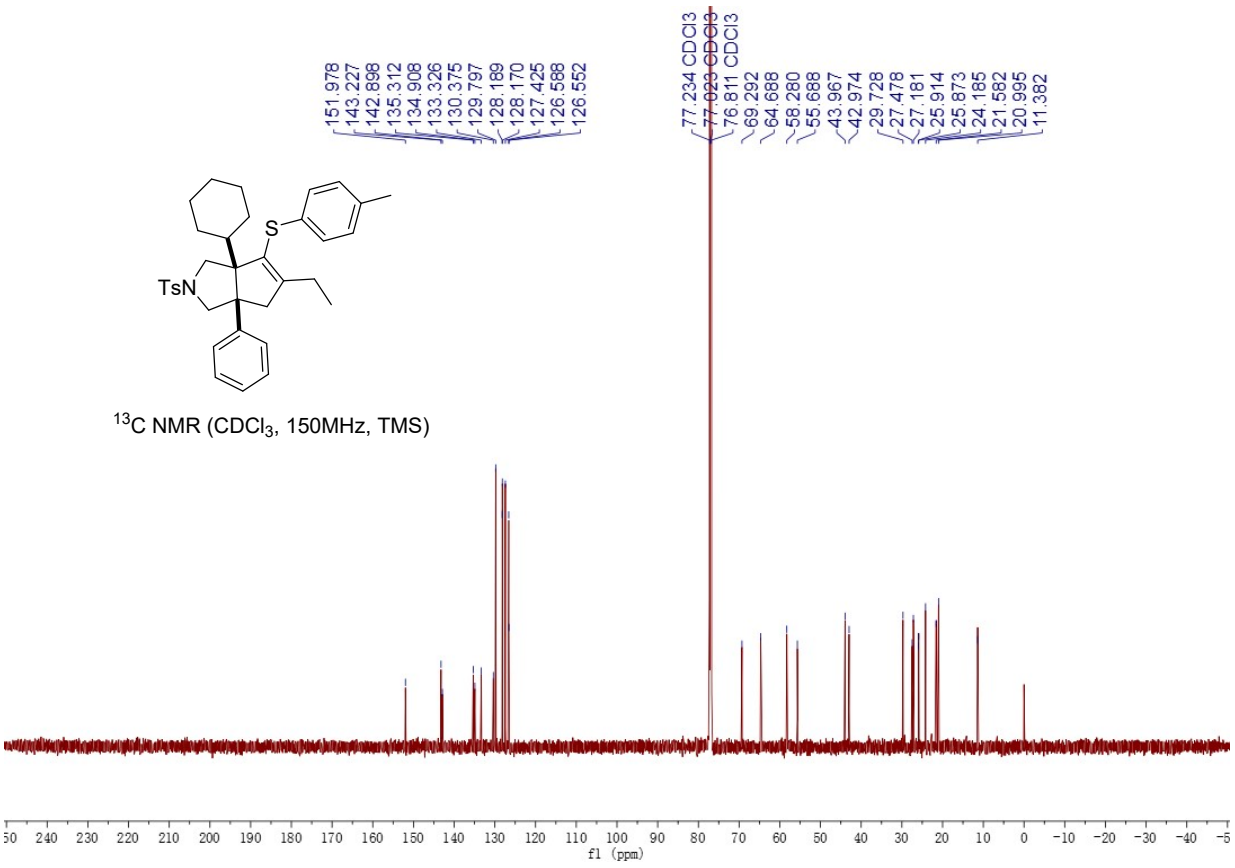
6a-cyclohexyl-5-ethyl-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ma)

A colorless oil, 30.3 mg, 53% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.17 - 7.02 (m, 7H), 6.85 (d, *J* = 7.7 Hz, 2H), 4.24 (d, *J* = 10.0 Hz, 1H), 3.67 (d, *J* = 10.1 Hz, 1H), 3.47 (d, *J* = 10.1 Hz, 1H), 3.36 (d, *J* = 10.1 Hz, 1H), 3.26 (d, *J* = 16.2 Hz, 1H), 2.47 (s, 3H), 2.40 (d, *J* = 16.3 Hz, 1H), 2.34 - 2.27 (m, 4H), 2.15 - 2.08 (m, 1H), 1.41 - 1.29 (m, 5H), 0.93 - 0.72 (m, 8H), 0.56 - 0.47 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 152.0, 143.2, 142.9, 135.3, 134.9, 133.3, 130.4, 129.8, 128.19, 128.17, 127.4, 126.59, 126.55, 69.3, 64.7, 58.3, 55.7, 44.0, 43.0, 29.7, 27.5, 27.2, 25.91, 25.87, 24.2, 21.6, 21.0, 11.4. IR (Acetone) ν 1015, 1105, 1166, 1342, 1490, 2920 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{41}NNaO_2S_2$ (M+Na): 594.2471, Found: 594.2467.

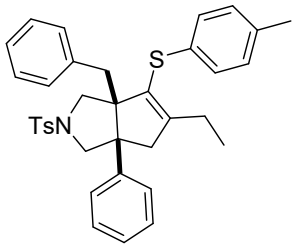


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



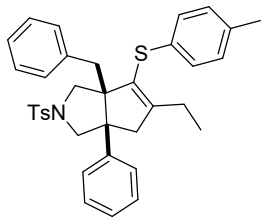


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

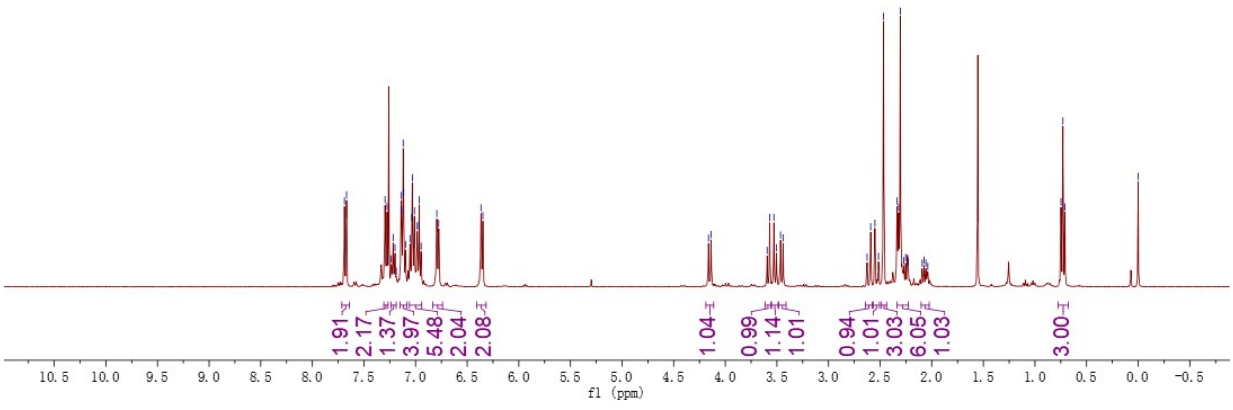


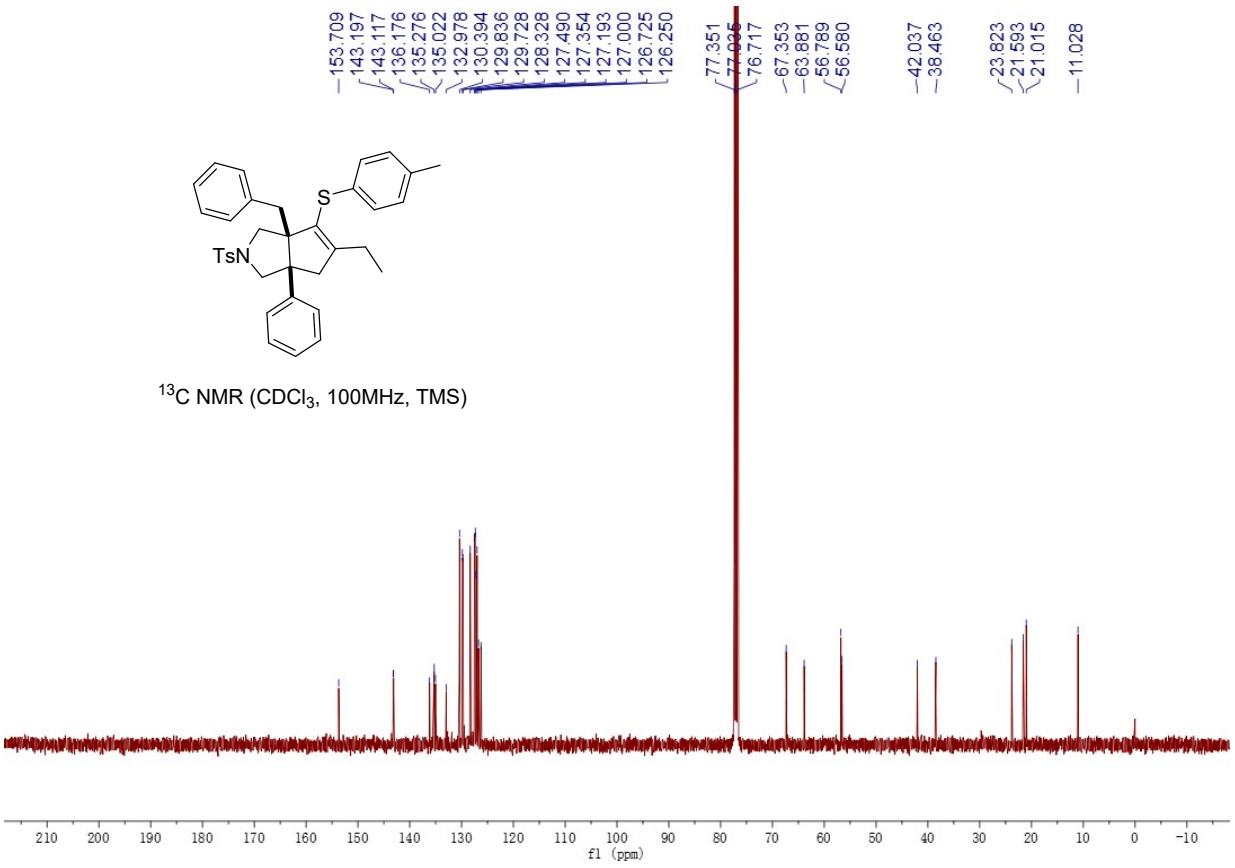
6a-benzyl-5-ethyl-3a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3na)

A colorless oil, 24.9 mg, 43% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 - 7.19 (m, 1H), 7.15 - 7.09 (m, 4H), 7.06 - 6.94 (m, 5H), 6.79 (d, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 7.4 Hz, 2H), 4.15 (d, *J* = 10.0 Hz, 1H), 3.58 (d, *J* = 10.0 Hz, 1H), 3.52 (d, *J* = 10.0 Hz, 1H), 3.45 (d, *J* = 10.0 Hz, 1H), 2.61 (d, *J* = 13.9 Hz, 1H), 2.53 (d, *J* = 13.9 Hz, 1H), 2.47 (s, 3H), 2.34 - 2.23 (m, 6H), 2.10 - 2.03 (m, 1H), 0.73 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 153.7, 143.2, 143.1, 136.2, 135.3, 135.0, 133.0, 130.4, 129.8, 129.7, 128.3, 127.5, 127.4, 127.2, 127.0, 126.7, 126.3, 67.4, 63.9, 56.8, 56.6, 42.0, 38.5, 23.8, 21.6, 21.0, 11.0. IR (Acetone) ν 1039, 1161, 1343, 1490, 2972 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{38}O_2NS_2$ (M+H): 580.2338, Found: 580.2303.

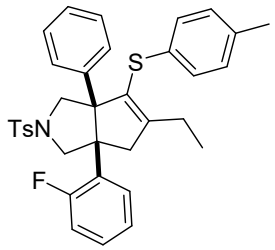


^{1}H NMR ($CDCl_3$, 400MHz, TMS)



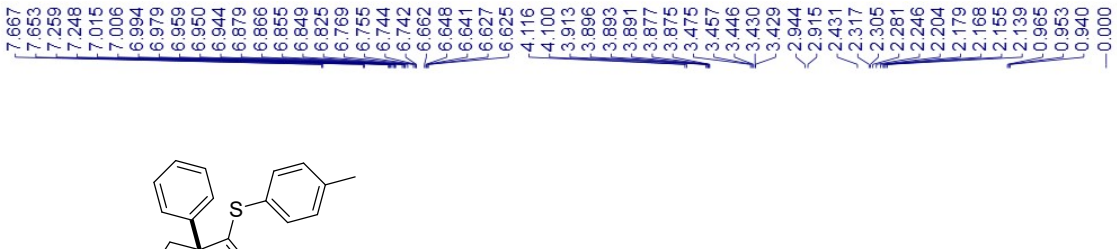


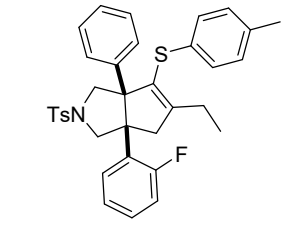
^{13}C NMR ($CDCl_3$, 100MHz, TMS)



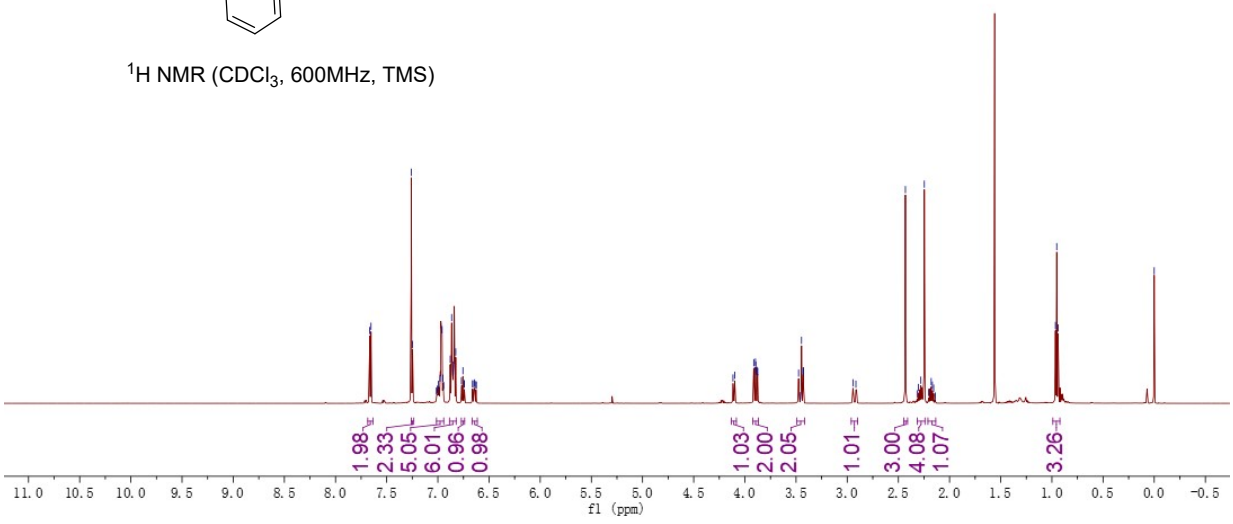
5-ethyl-3a-(2-fluorophenyl)-6a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3oa)

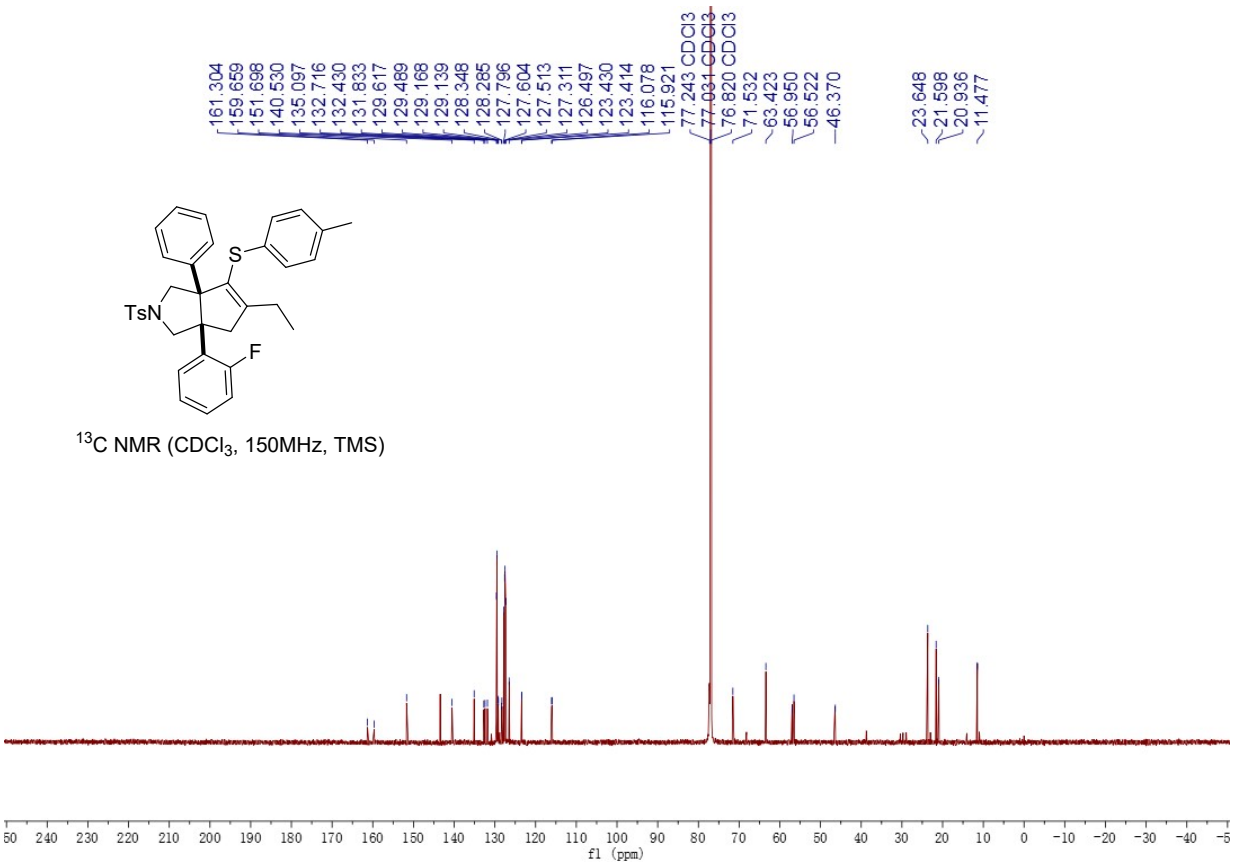
A colorless oil, 35.6 mg, 61% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.01 - 6.94 (m, 5H), 6.89 - 6.82 (m, 6H), 6.77 - 6.74 (m, 1H), 6.67 - 6.61 (m, 1H), 4.11 (d, *J* = 10.0 Hz, 1H), 3.92 - 3.87 (m, 2H), 3.49 - 3.42 (m, 2H), 2.93 (d, *J* = 17.3 Hz, 1H), 2.43 (s, 3H), 2.32 - 2.24 (m, 4H), 2.21 - 2.13 (m, 1H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 160.5 (d, *J* = 246.8 Hz), 151.7, 140.5, 135.1, 132.6 (d, *J* = 42.9 Hz), 131.8, 129.6, 129.5, 129.2 (d, *J* = 4.4 Hz), 128.3 (d, *J* = 9.2 Hz), 127.8, 127.6, 127.5, 127.3, 126.5, 123.4 (d, *J* = 2.4 Hz), 116.0 (d, *J* = 23.6 Hz), 71.5, 63.4, 57.0, 56.5, 46.4, 23.6, 21.6, 20.9, 11.5. ^{19}F NMR ($CDCl_3$, TMS, 376 MHz) δ -116.0 (s). IR (Acetone) ν 1029, 1170, 1325, 1422, 2981 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{35}NO_2S_2F$ (M+H): 584.2088, Found: 584.2050.



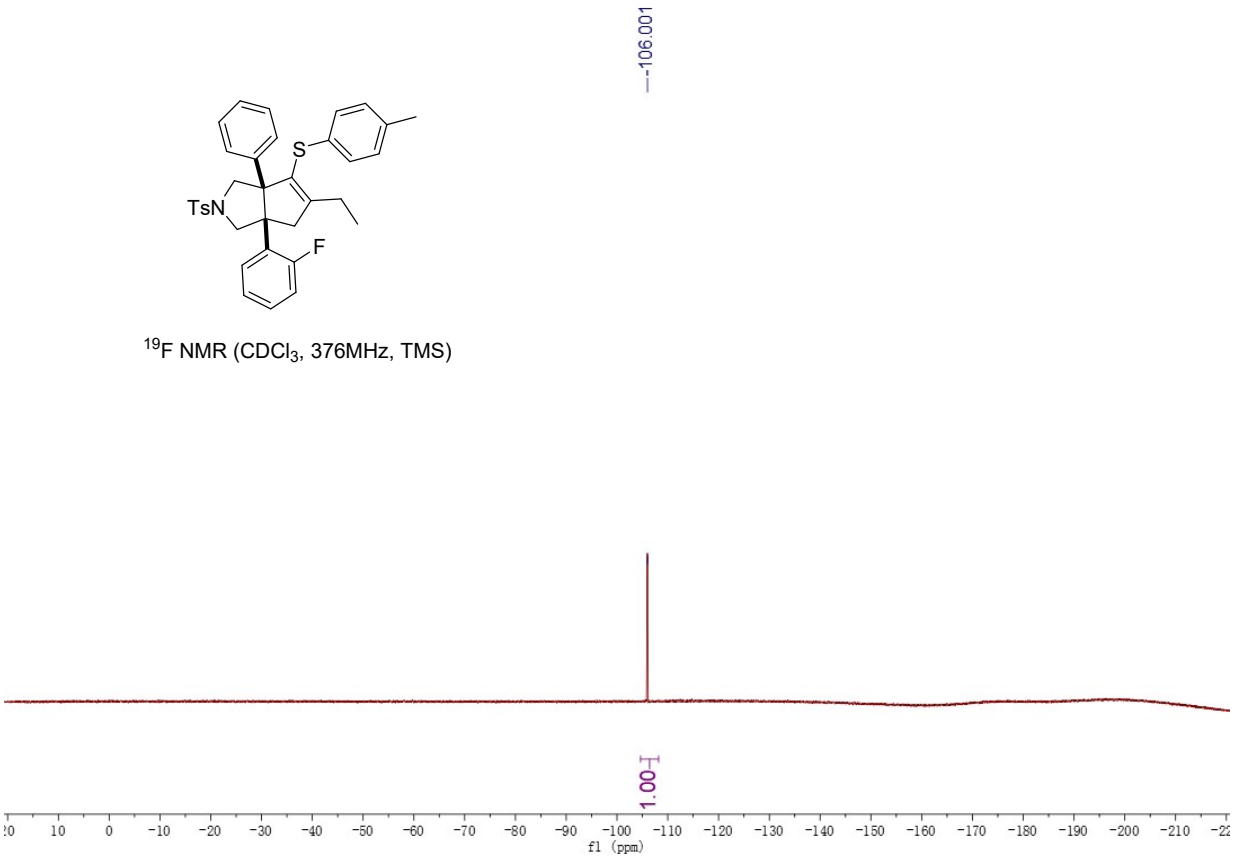


^{1}H NMR ($CDCl_3$, 600MHz, TMS)

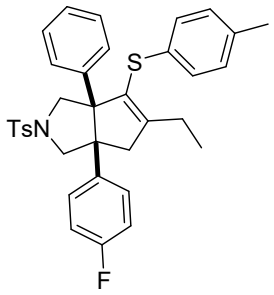




^{13}C NMR ($CDCl_3$, 150MHz, TMS)

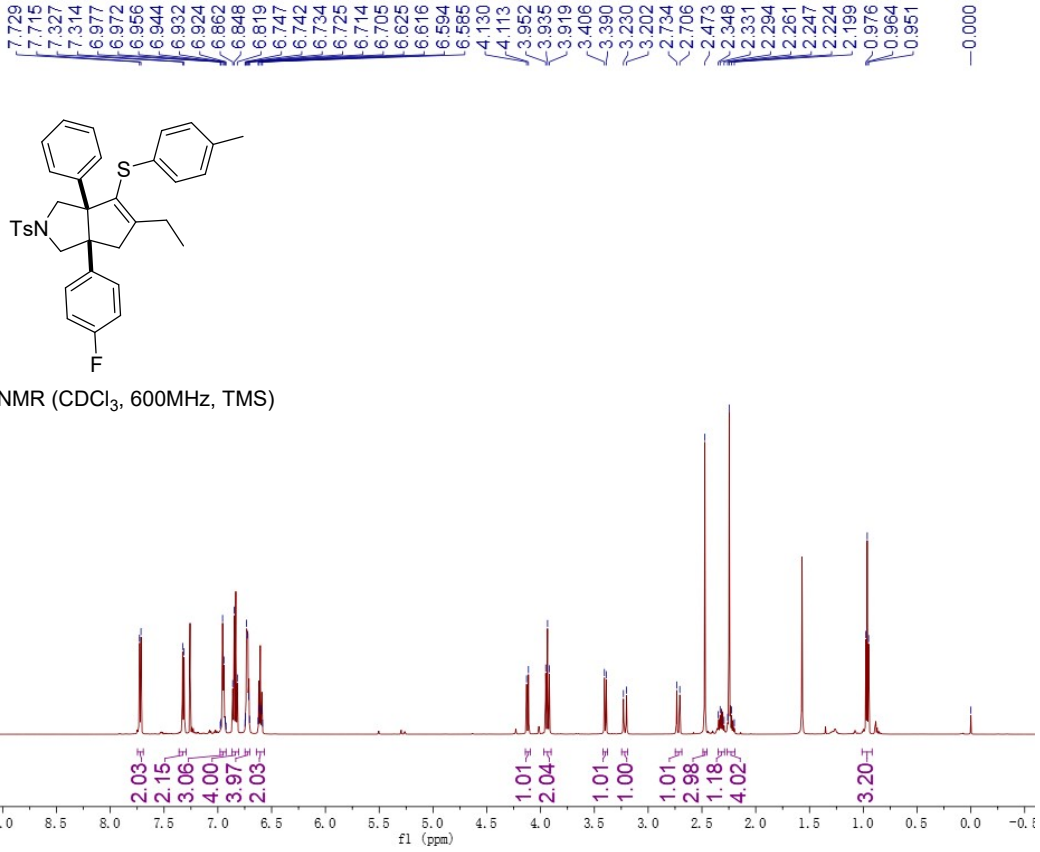


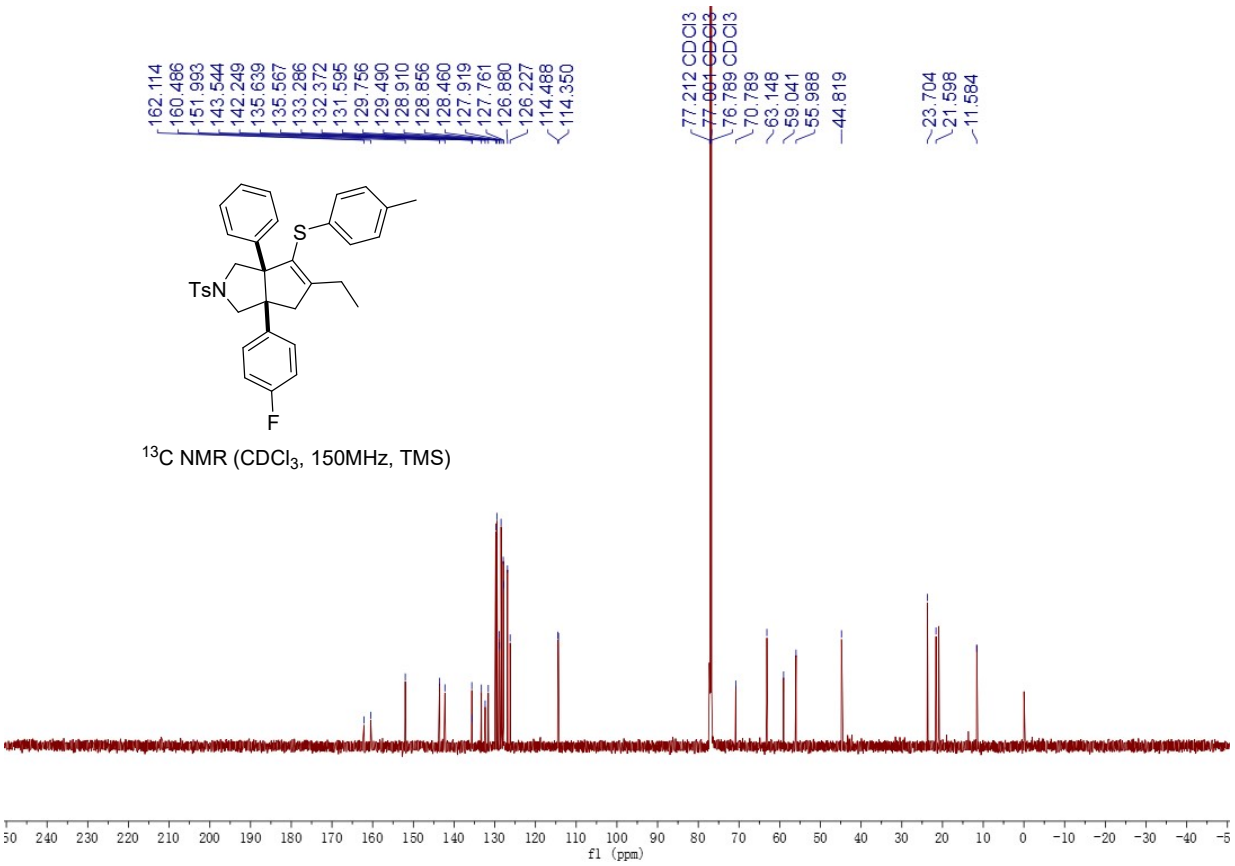
^{19}F NMR ($CDCl_3$, 376MHz, TMS)



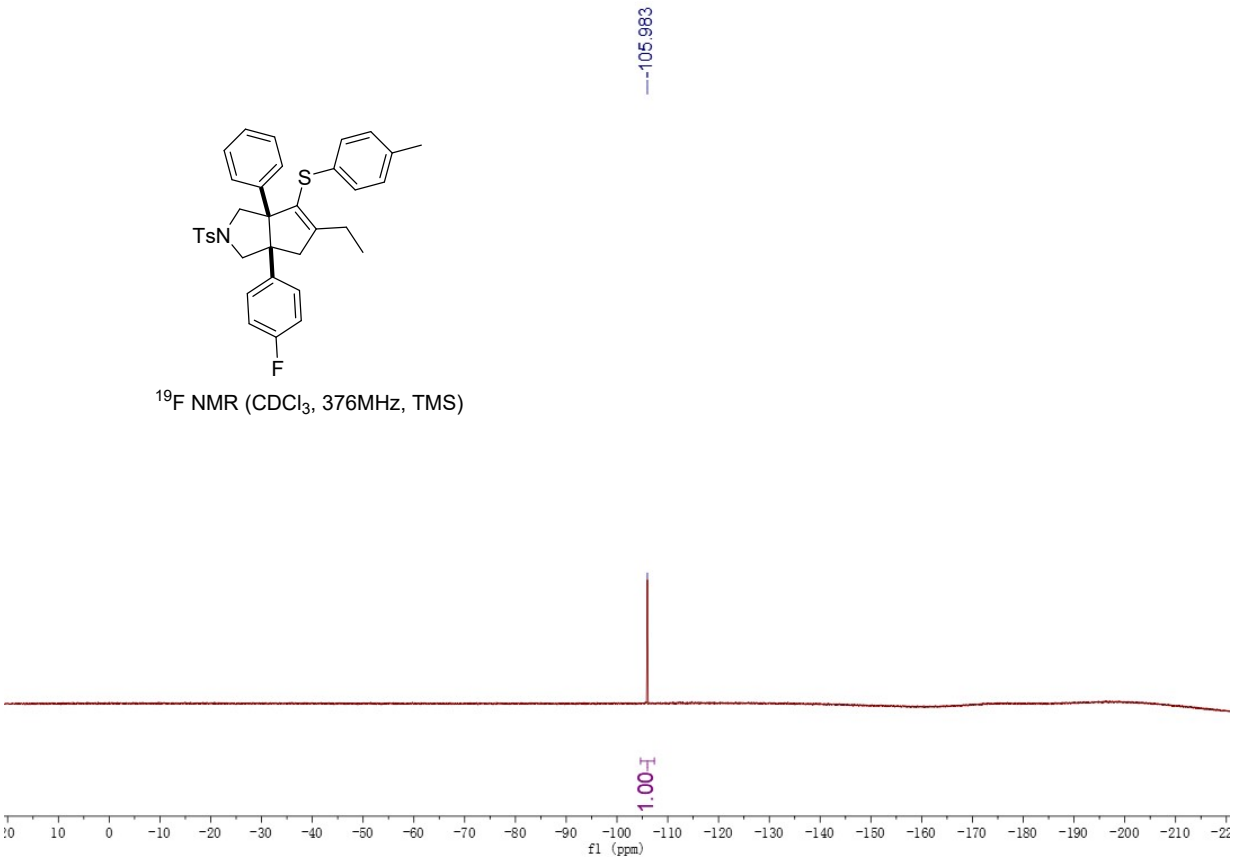
5-ethyl-3a-(4-fluorophenyl)-6a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3pa)

A colorless oil, 42.6 mg, 73% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.98 - 6.92 (m, 3H), 6.87 - 6.81 (m, 4H), 6.75 - 6.70 (m, 4H), 6.64 - 6.57 (m, 2H), 4.12 (d, *J* = 10.4 Hz, 1H), 3.94 (t, *J* = 10.1 Hz, 2H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.22 (d, *J* = 16.9 Hz, 1H), 2.72 (d, *J* = 16.9 Hz, 1H), 2.47 (s, 3H), 2.35 - 2.29 (m, 1H), 2.26 - 2.19 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 161.3 (d, *J* = 244.2 Hz), 152.0, 143.5, 142.2, 135.6 (d, *J* = 3.5 Hz), 133.3, 132.4, 131.6, 129.8, 129.5, 128.9 (d, *J* = 8.1 Hz), 128.5, 127.9, 127.8, 126.9, 126.2, 114.4 (d, *J* = 20.7 Hz), 70.8, 63.1, 59.0, 56.0, 44.8, 23.7, 21.6, 11.6. ^{19}F NMR ($CDCl_3$, TMS, 376 MHz) δ -106.0 (s). IR (Acetone) ν 1220, 1356, 1418, 1721, 3013 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{34}NFO_2NaS_2$ (M+Na): 606.1907, Found: 606.1907.

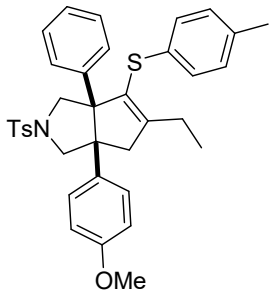




^{13}C NMR ($CDCl_3$, 150MHz, TMS)

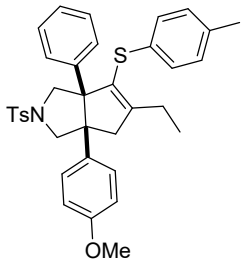


^{19}F NMR ($CDCl_3$, 376MHz, TMS)

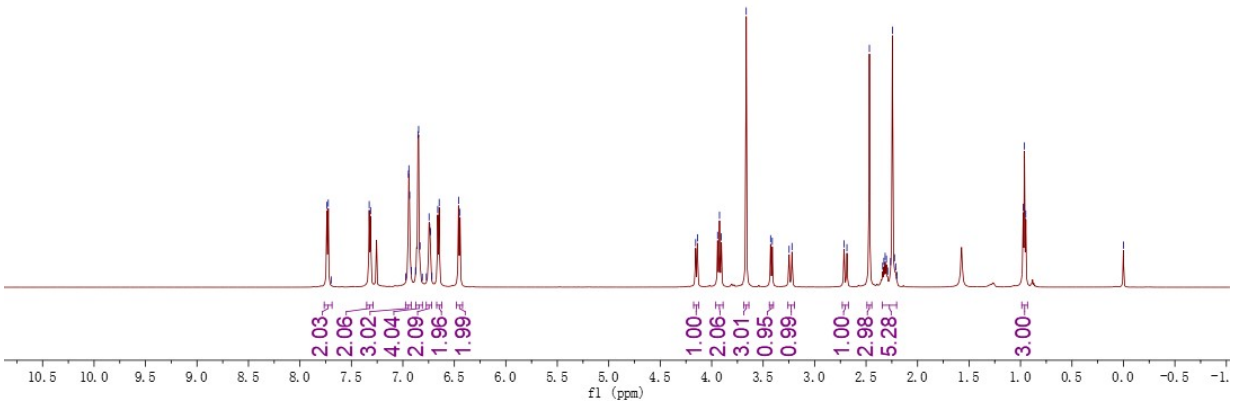


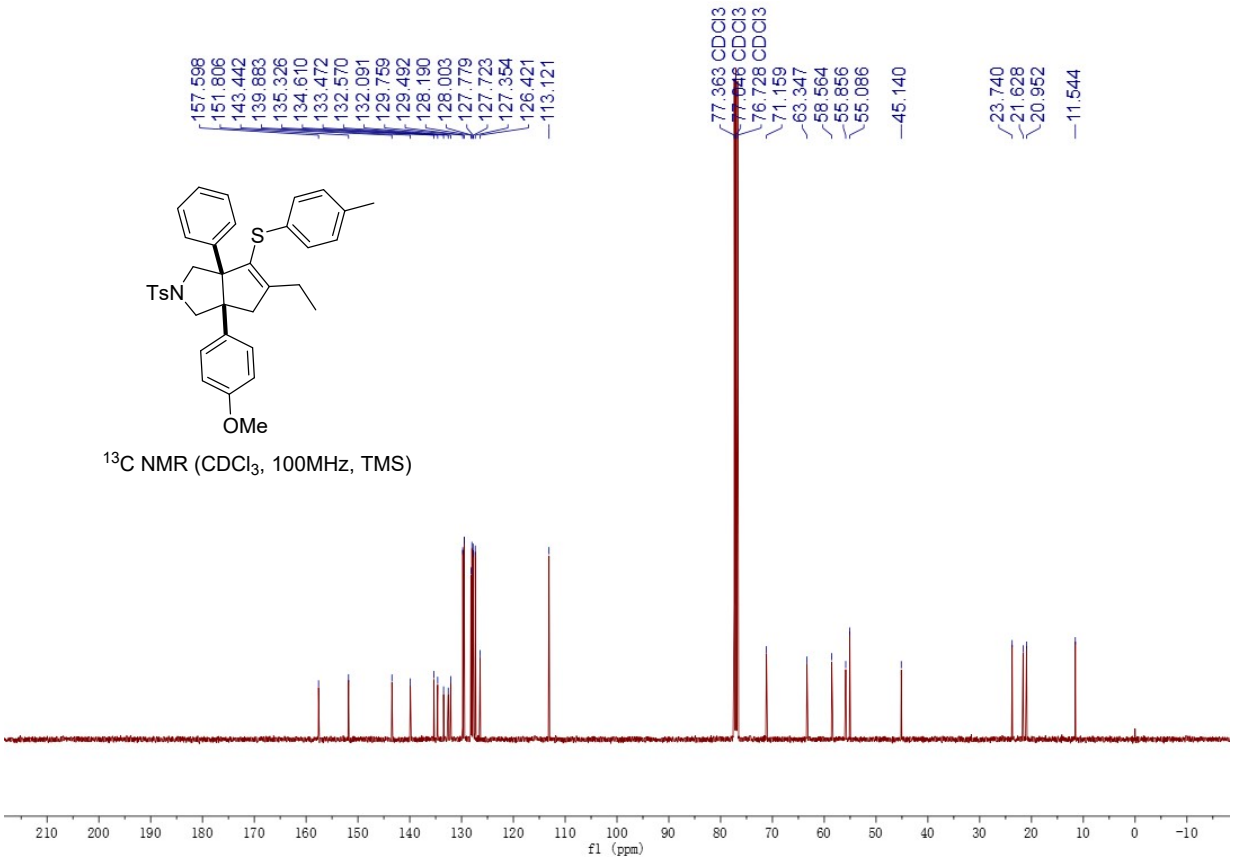
5-ethyl-3a-(4-methoxyphenyl)-6a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3qa)

A colorless oil, 51.8 mg, 87% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.97 - 6.92 (m, 3H), 6.88 - 6.81 (m, 4H), 6.74 (d, *J* = 7.5Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.92 (t, *J* = 10.9 Hz, 2H), 3.66 (s, 3H), 3.42 (d, *J* = 9.9 Hz, 1H), 3.23 (d, *J* = 16.8 Hz, 1H), 2.70 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 2.34 - 2.20 (m, 5H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 157.6, 151.8, 143.4, 139.9, 135.3, 134.6, 133.5, 132.6, 132.1, 129.8, 129.5, 128.2, 128.0, 127.8, 127.7, 127.4, 126.4, 113.1, 71.2, 63.3, 58.6, 55.9, 55.1, 45.1, 23.7, 21.6, 21.0, 11.5. IR (Acetone) ν 1034, 1164, 1355, 1514, 2923 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{38}NO_3S_2$ (M+H): 596.2288, Found: 596.2250.

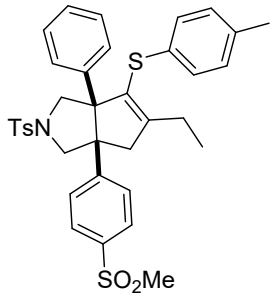


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



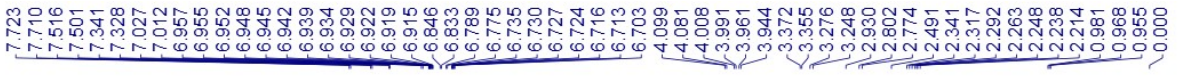


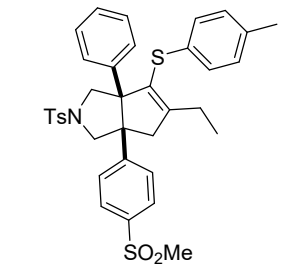
^{13}C NMR ($CDCl_3$, 100MHz, TMS)



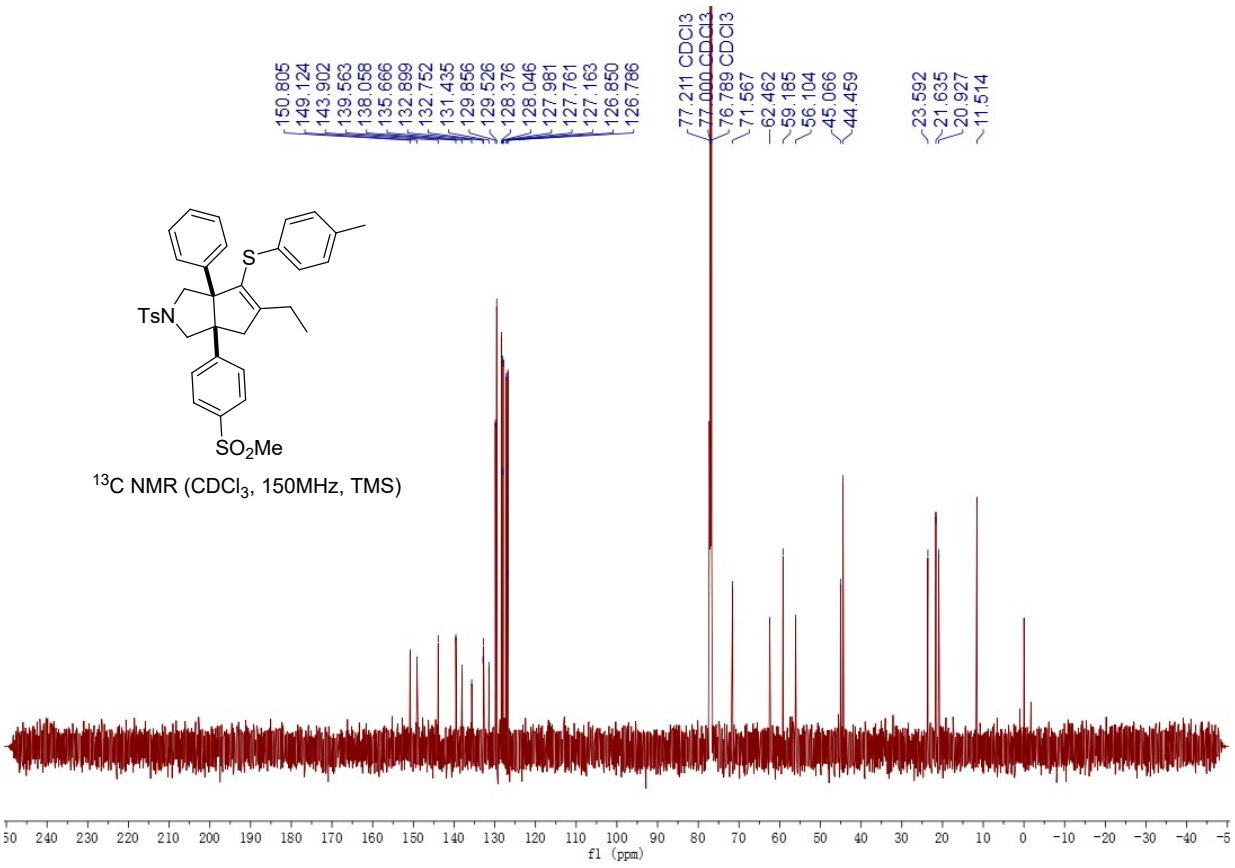
5-ethyl-3a-(4-(methylsulfonyl)phenyl)-6a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ra)

A colorless oil, 53.4 mg, 83% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.96 - 6.90 (m, 3H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.74 - 6.70 (m, 2H), 4.09 (d, *J* = 10.6 Hz, 1H), 4.00 (d, *J* = 10.6 Hz, 1H), 3.95 (d, *J* = 10.0 Hz, 1H), 3.36 (d, *J* = 10.0 Hz, 1H), 3.26 (d, *J* = 16.9 Hz, 1H), 2.93 (s, 3H), 2.79 (d, *J* = 17.0 Hz, 1H), 2.49 (s, 3H), 2.35 - 2.29 (m, 1H), 2.28 - 2.20 (m, 4H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 150.8, 149.1, 143.9, 139.6, 138.1, 135.7, 132.9, 132.8, 131.4, 129.9, 129.5, 128.4, 128.05, 127.98, 127.8, 127.2, 126.9, 126.8, 71.6, 62.5, 59.2, 56.1, 45.1, 44.5, 23.6, 21.6, 20.9, 11.5. IR (Acetone) ν 1020, 1184, 1298, 1431, 2950 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{38}NO_4S_3$ (M+H): 644.1957, Found: 644.1918.

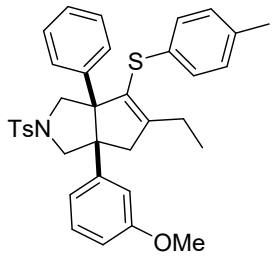




^{1}H NMR ($CDCl_3$, 600MHz, TMS)

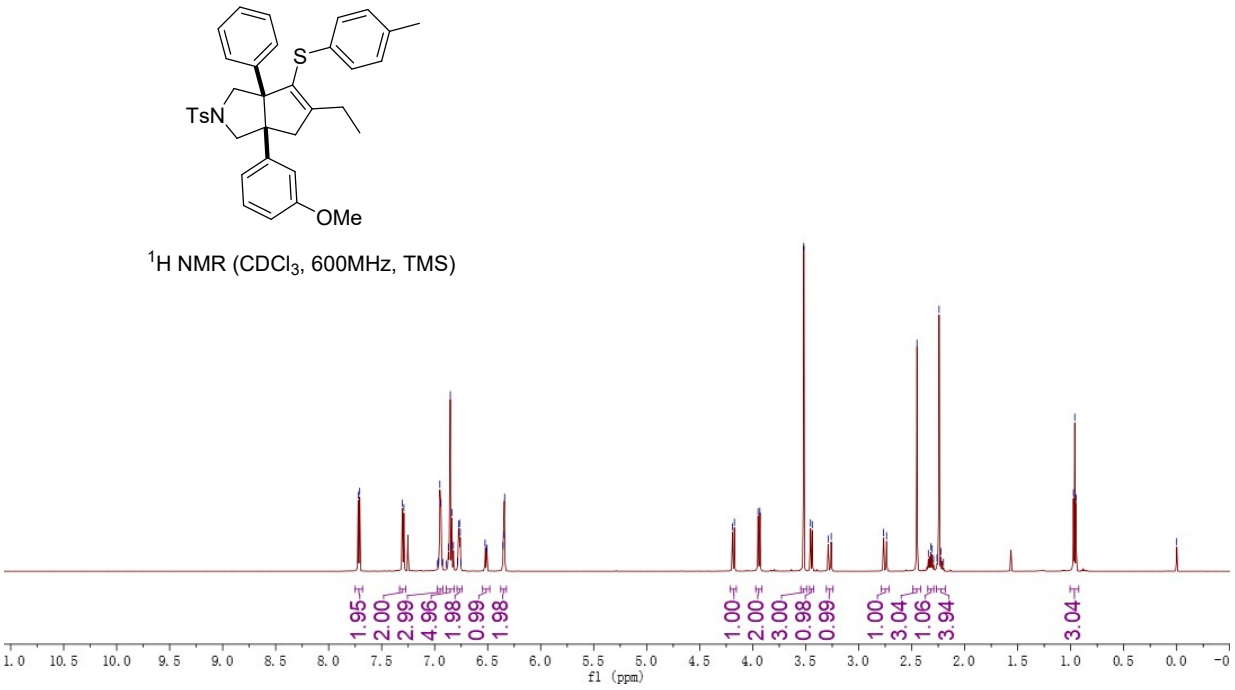


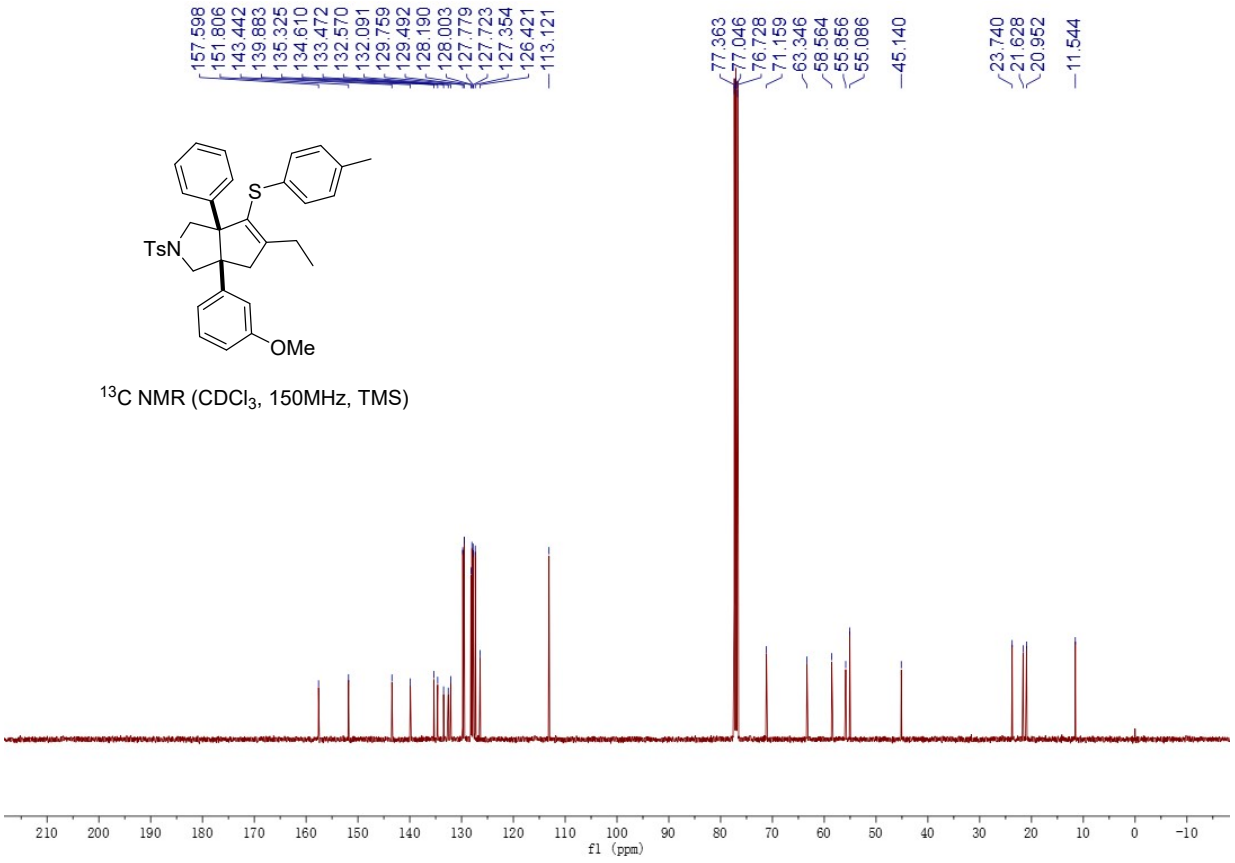
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



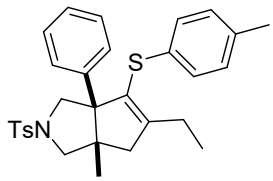
5-ethyl-3a-(3-methoxyphenyl)-6a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3sa)

A colorless oil, 48.9 mg, 82% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.97 - 6.92 (m, 3H), 6.89 - 6.82 (m, 5H), 6.79 - 6.74 (m, 2H), 6.55 - 6.48 (m, 1H), 6.38 - 6.32 (m, 2H), 4.18 (d, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 10.3 Hz, 2H), 3.52 (s, 3H), 3.45 (d, *J* = 9.9 Hz, 1H), 3.27 (d, *J* = 16.9 Hz, 1H), 2.75 (d, *J* = 16.9 Hz, 1H), 2.45 (s, 3H), 2.35 - 2.29 (m, 1H), 2.27 - 2.18 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 157.6, 151.8, 143.4, 139.9, 135.3, 134.6, 133.5, 132.6, 132.1, 129.8, 129.5, 128.2, 128.0, 127.8, 127.7, 127.4, 126.4, 113.1, 71.2, 63.3, 58.6, 55.9, 55.1, 45.1, 23.7, 21.6, 21.0, 11.5. IR (Acetone) ν 1018, 1179, 1338, 1521, 3000 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{38}NO_3S_2$ (M+H): 596.2288, Found: 596.2250.



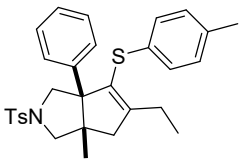


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

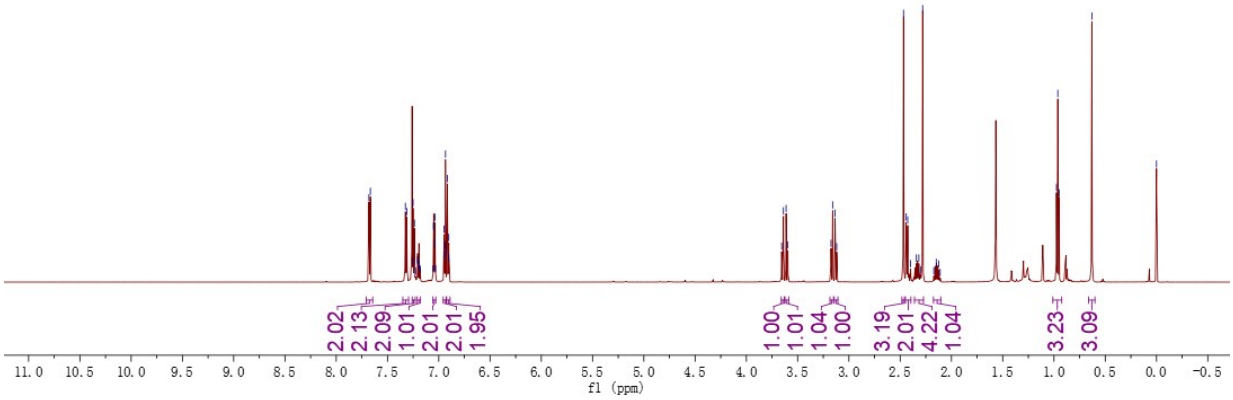


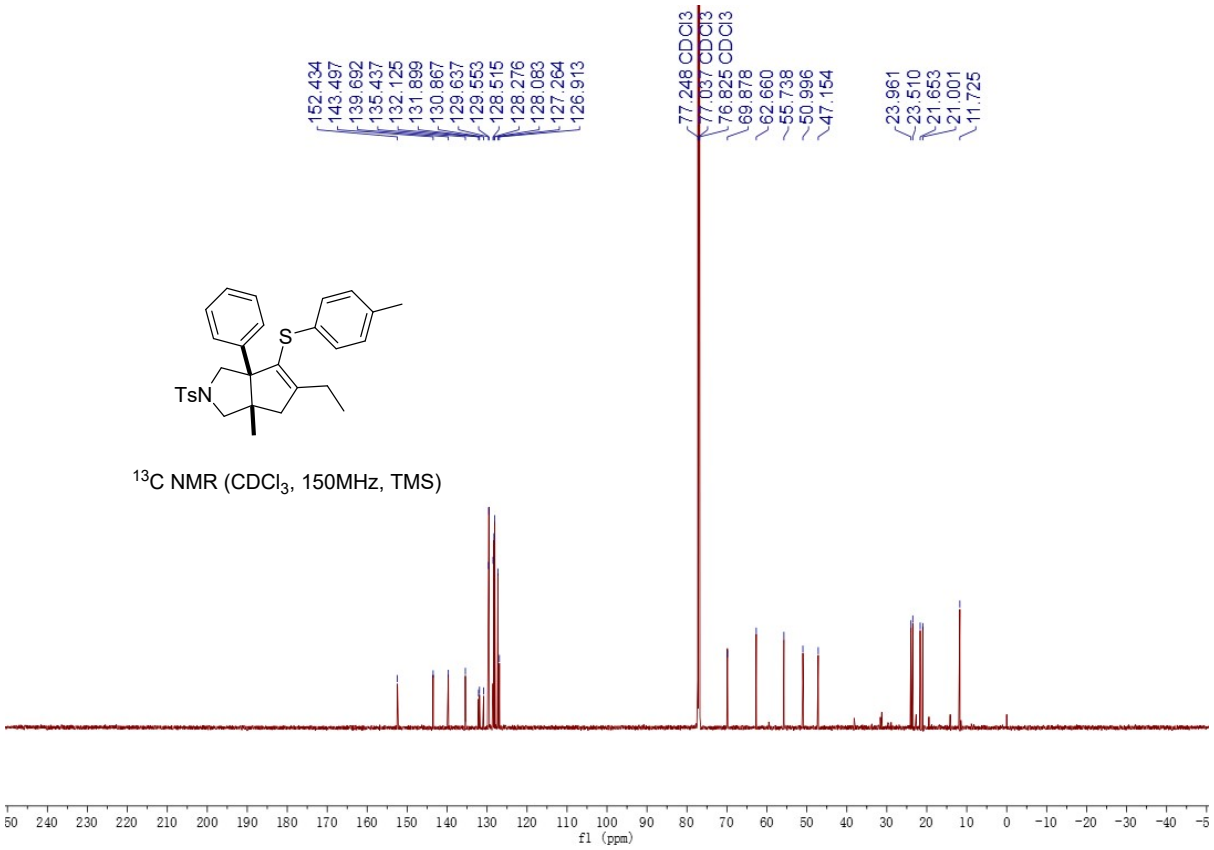
5-ethyl-3a-methyl-6a-phenyl-6-(*p*-tolylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ta)

A colorless oil, 20.7 mg, 41% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 - 7.23 (m, 2H), 7.21 - 7.18 (m, 1H), 7.06 - 7.03 (m, 2H), 6.96 - 6.93 (m, 2H), 6.92 - 6.89 (m, 2H), 3.65 (d, *J* = 10.3 Hz, 1H), 3.60 (d, *J* = 10.3 Hz, 1H), 3.17 (d, *J* = 9.3 Hz, 1H), 3.13 (d, *J* = 9.3 Hz, 1H), 2.47 (s, 3H), 2.45 - 2.40 (m, 2H), 2.36 - 2.27 (m, 4H), 2.18 - 2.10 (m, 1H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.63 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 152.4, 143.5, 139.7, 135.4, 132.1, 131.9, 130.9, 129.64, 129.55, 128.5, 128.3, 128.1, 127.3, 126.9, 69.9, 62.7, 55.7, 51.0, 47.2, 24.0, 23.5, 21.7, 21.0, 11.7. IR (Acetone) ν 1018, 1163, 1305, 1412, 2993 cm^{-1}. HRMS (ESI) calcd. for $C_{30}H_{34}NO_2S_2$ (M+H): 504.2025, Found: 504.1979.

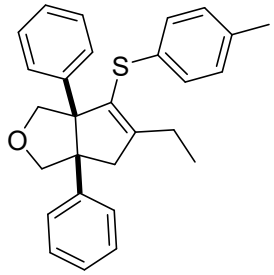


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



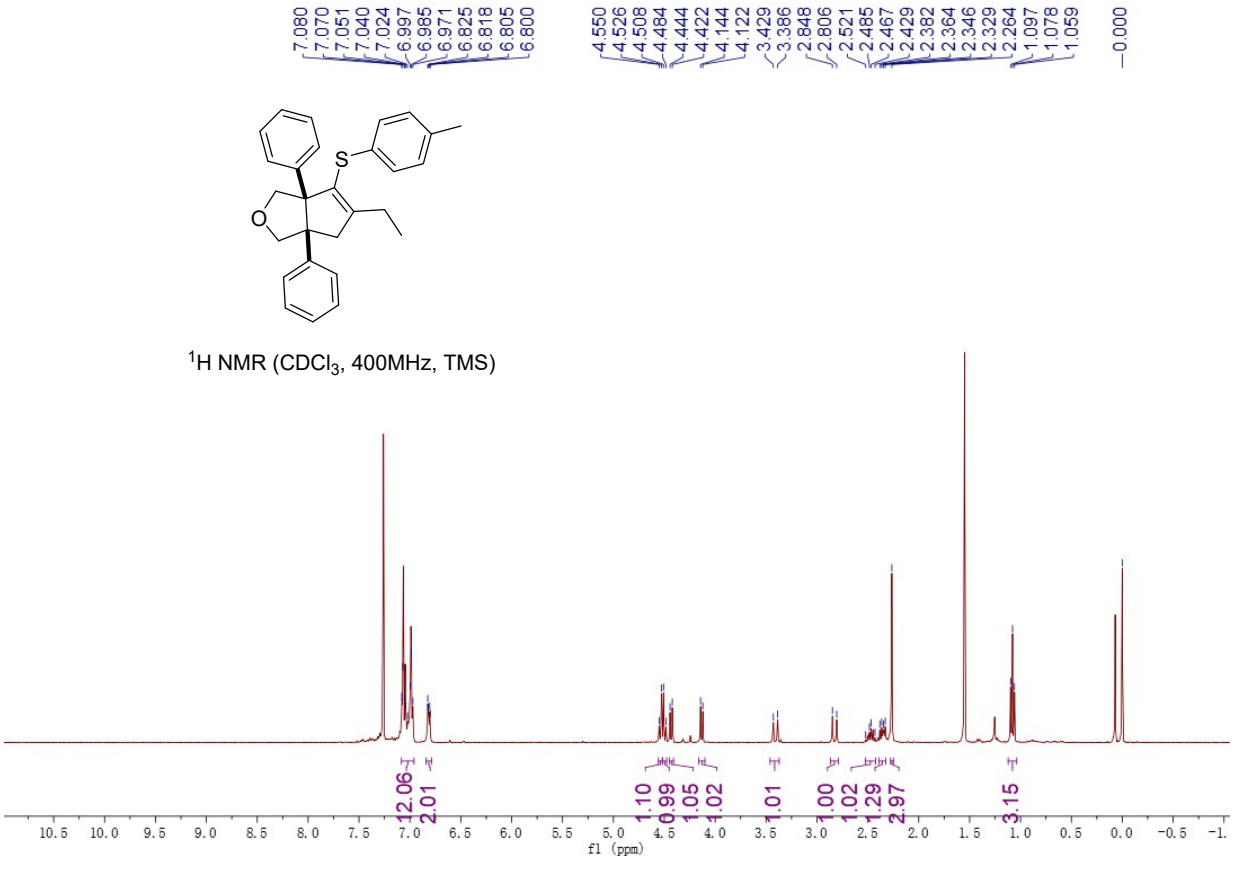


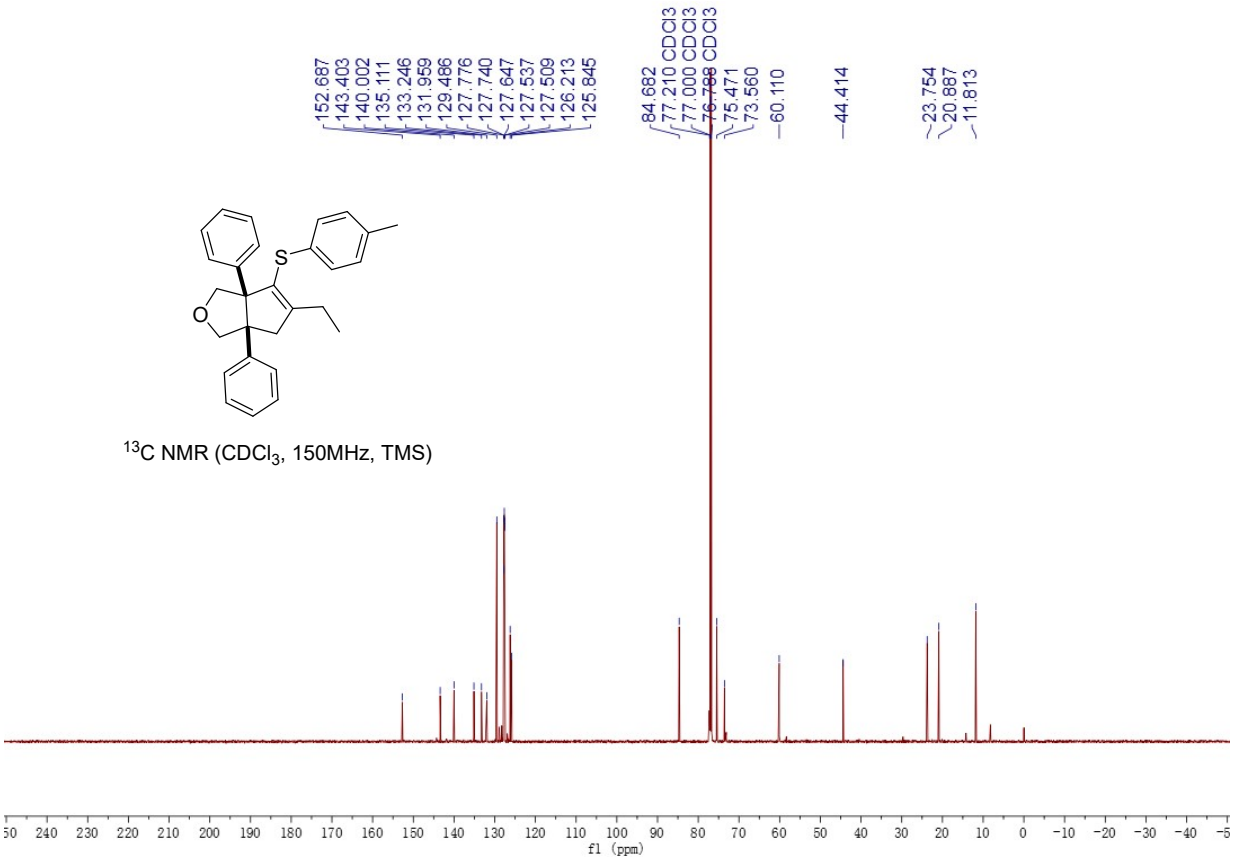
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



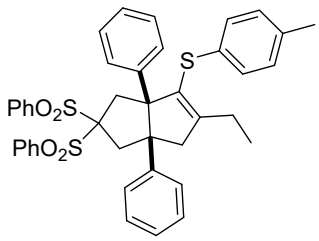
5-ethyl-3a,6a-diphenyl-6-(*p*-tolylthio)-3,3a,4,6a-tetrahydro-1*H*-cyclopenta[*c*]furan (3ua)

A colorless oil, 16.9 mg, 43% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.08 - 6.96 (m, 12H), 6.84 - 6.79 (m, 2H), 4.54 (d, *J* = 9.5 Hz, 1H), 4.50 (d, *J* = 9.4 Hz, 1H), 4.43 (d, *J* = 8.8 Hz, 1H), 4.13 (d, *J* = 8.8 Hz, 1H), 3.41 (d, *J* = 17.0 Hz, 1H), 2.83 (d, *J* = 17.0 Hz, 1H), 2.52 - 2.42 (m, 1H), 2.39 - 2.33 (m, 1H), 2.26 (s, 3H), 1.08 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 152.7, 143.4, 140.0, 135.1, 133.2, 132.0, 129.5, 127.8, 127.7, 127.6, 127.5, 126.2, 125.8, 84.7, 75.5, 73.6, 60.1, 44.4, 23.8, 20.9, 11.8. IR (Acetone) ν 1167, 1221, 1359, 1420, 1709, 3011 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{29}OS$ (M+H): 413.1934, Found: 413.1902.



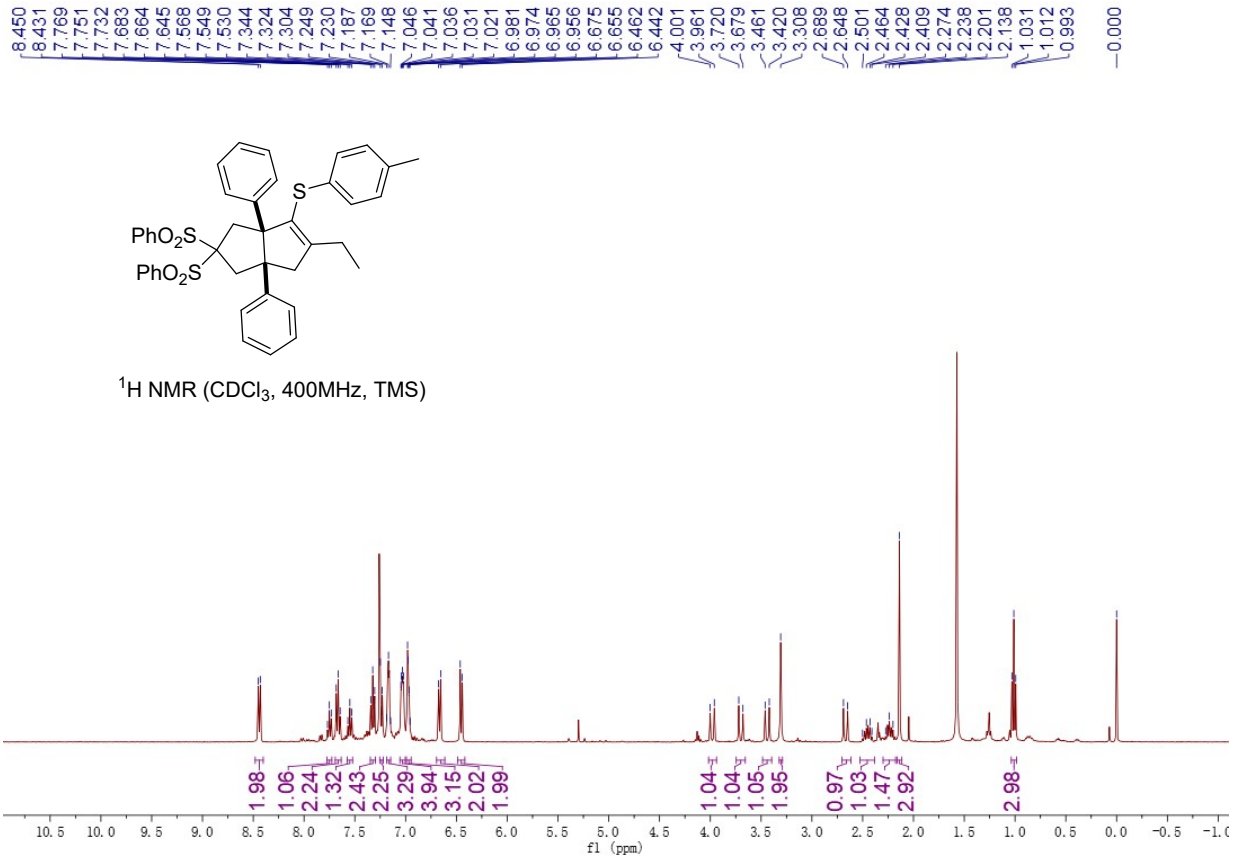


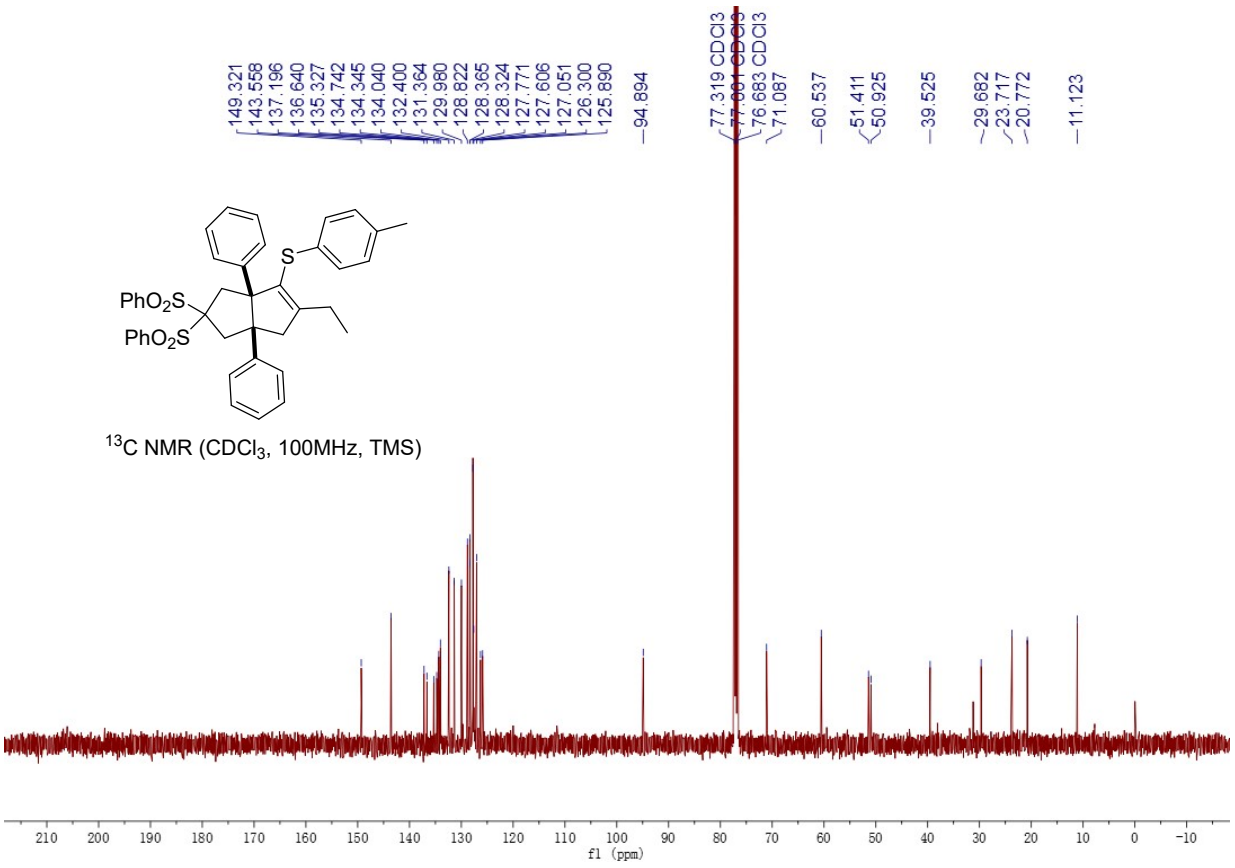
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



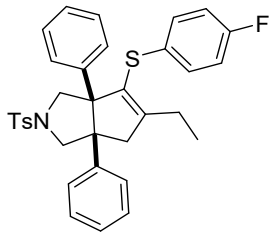
(2-ethyl-3a,6a-diphenyl-5,5-bis(phenylsulfonyl)-3,3a,4,5,6,6a-hexahydropentalen-1-yl)(*p*-tolyl)sulfane (3va)

A colorless oil, 36.6 mg, 45% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 8.44 (d, *J* = 7.8 Hz, 2H), 7.77 - 7.73 (m, 1H), 7.69 - 7.63 (m, 2H), 7.58 - 7.52 (m, 1H), 7.35 - 7.30 (m, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.19 - 7.15 (m, 3H), 7.06 - 7.00 (m, 4H), 6.99 - 6.95 (m, 3H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 8.2 Hz, 2H), 3.98 (d, *J* = 16.3 Hz, 1H), 3.70 (d, *J* = 16.3 Hz, 1H), 3.44 (d, *J* = 16.3 Hz, 1H), 3.31 (s, 2H), 2.67 (d, *J* = 16.3 Hz, 1H), 2.53 - 2.38 (m, 1H), 2.30 - 2.18 (m, 1H), 2.14 (s, 3H), 1.01 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 149.3, 143.6, 137.2, 136.6, 135.3, 134.7, 134.3, 134.0, 132.4, 131.4, 130.0, 128.8, 128.4, 128.3, 127.8, 127.6, 127.1, 126.3, 125.9, 94.9, 71.1, 60.5, 51.4, 50.9, 39.5, 29.7, 23.7, 20.8, 11.1. IR (Acetone) ν 1073, 1145, 1328, 1446, 1492.67, 2915 cm^{-1}. HRMS (ESI) calcd. for $C_{41}H_{39}S_3O_4$ (M+H): 691.2005, Found: 691.1938.



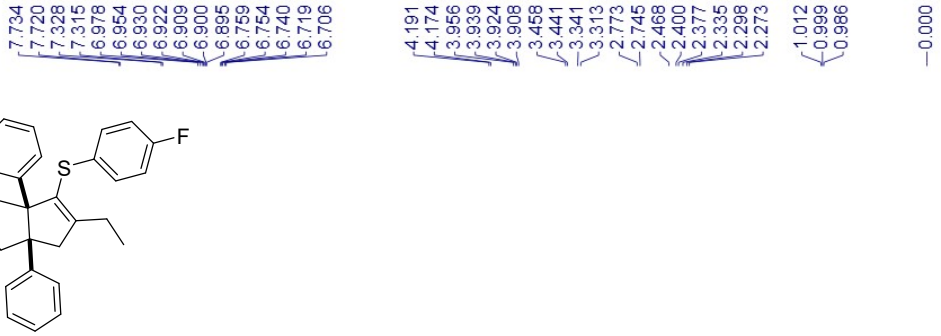


^{13}C NMR ($CDCl_3$, 100MHz, TMS)

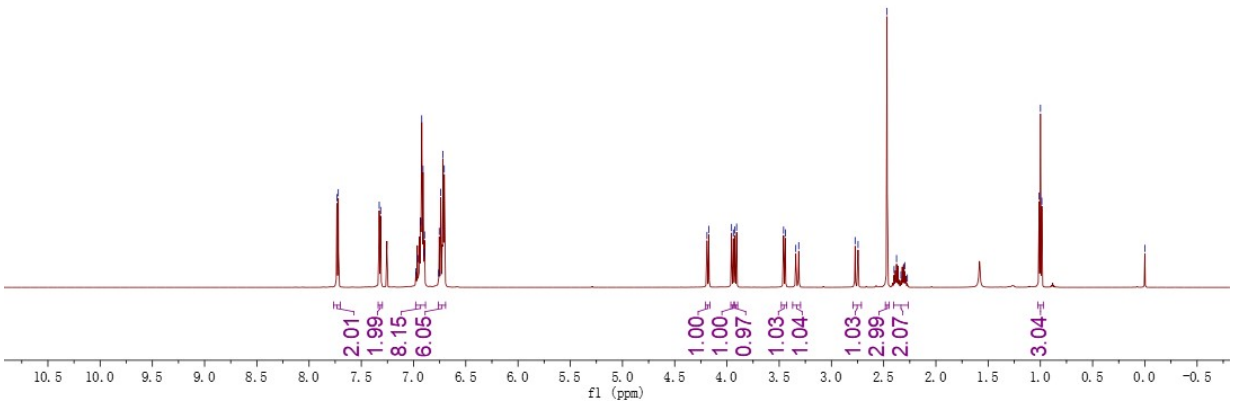


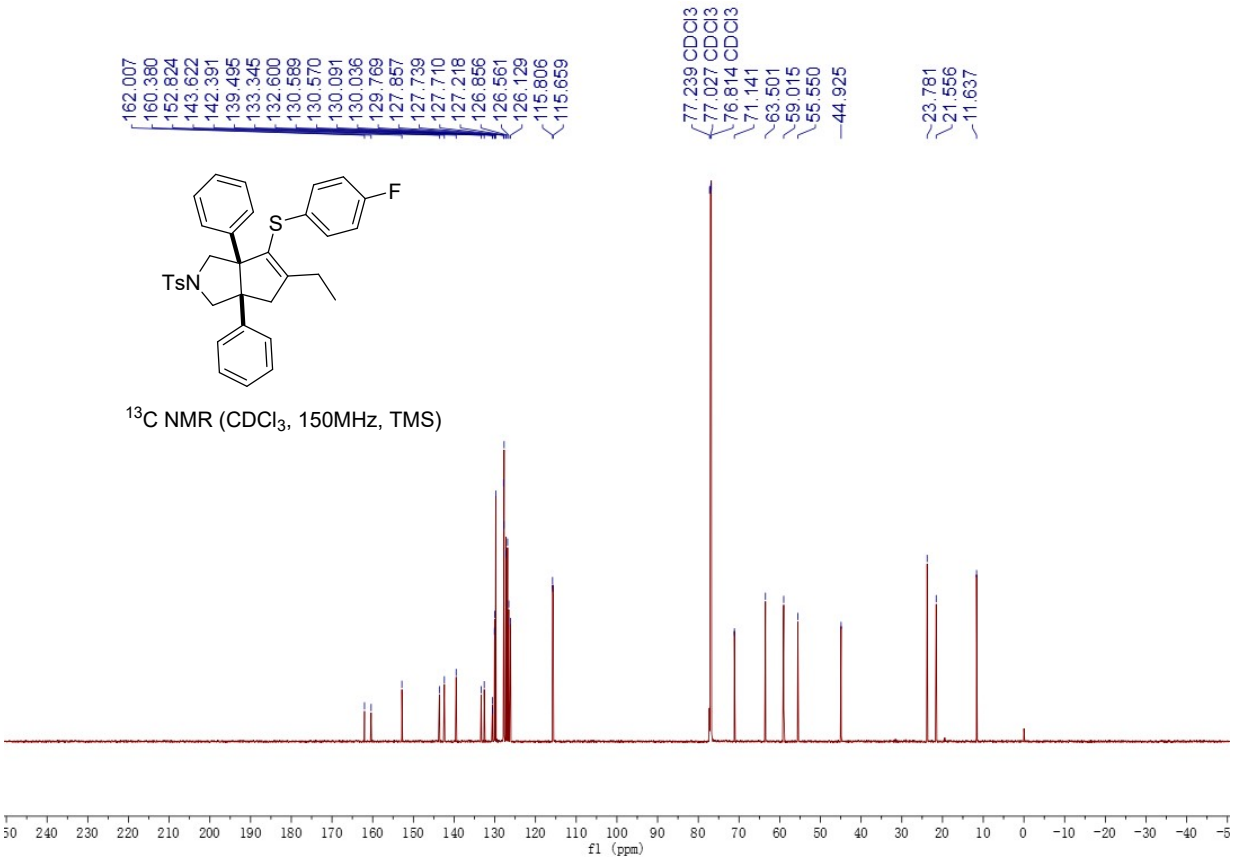
5-ethyl-6-((4-fluorophenyl)thio)-3a,6a-diphenyl-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ab)

A colorless oil, 44.4 mg, 78% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.98 - 6.89 (m, 8H), 6.76 - 6.69 (m, 6H), 4.18 (d, *J* = 10.3 Hz, 1H), 3.95 (d, *J* = 10.3 Hz, 1H), 3.92 (d, *J* = 10.0 Hz, 1H), 3.45 (d, *J* = 10.0 Hz, 1H), 3.33 (d, *J* = 16.9 Hz, 1H), 2.76 (d, *J* = 16.9 Hz, 1H), 2.47 (s, 3H), 2.40 - 2.27 (m, 2H), 1.00 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 161.2 (d, *J* = 244.1 Hz), 152.8, 143.6, 142.4, 139.5, 133.3, 132.6, 130.6 (d, *J* = 2.9 Hz), 130.1 (d, *J* = 8.5 Hz), 129.8, 127.9, 127.74, 127.71, 127.2, 126.9, 126.6, 126.1, 115.8 (d, *J* = 22.1 Hz), 71.1, 63.5, 59.0, 55.5, 44.9, 23.8, 21.6, 11.6. ^{19}F NMR ($CDCl_3$, TMS, 564 MHz) δ -116.6 (s). IR (Acetone) ν 1097, 1161, 1222, 1342, 1489, 2849 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{33}O_2NFS_2$ (M+H): 570.1931, Found: 570.1896.

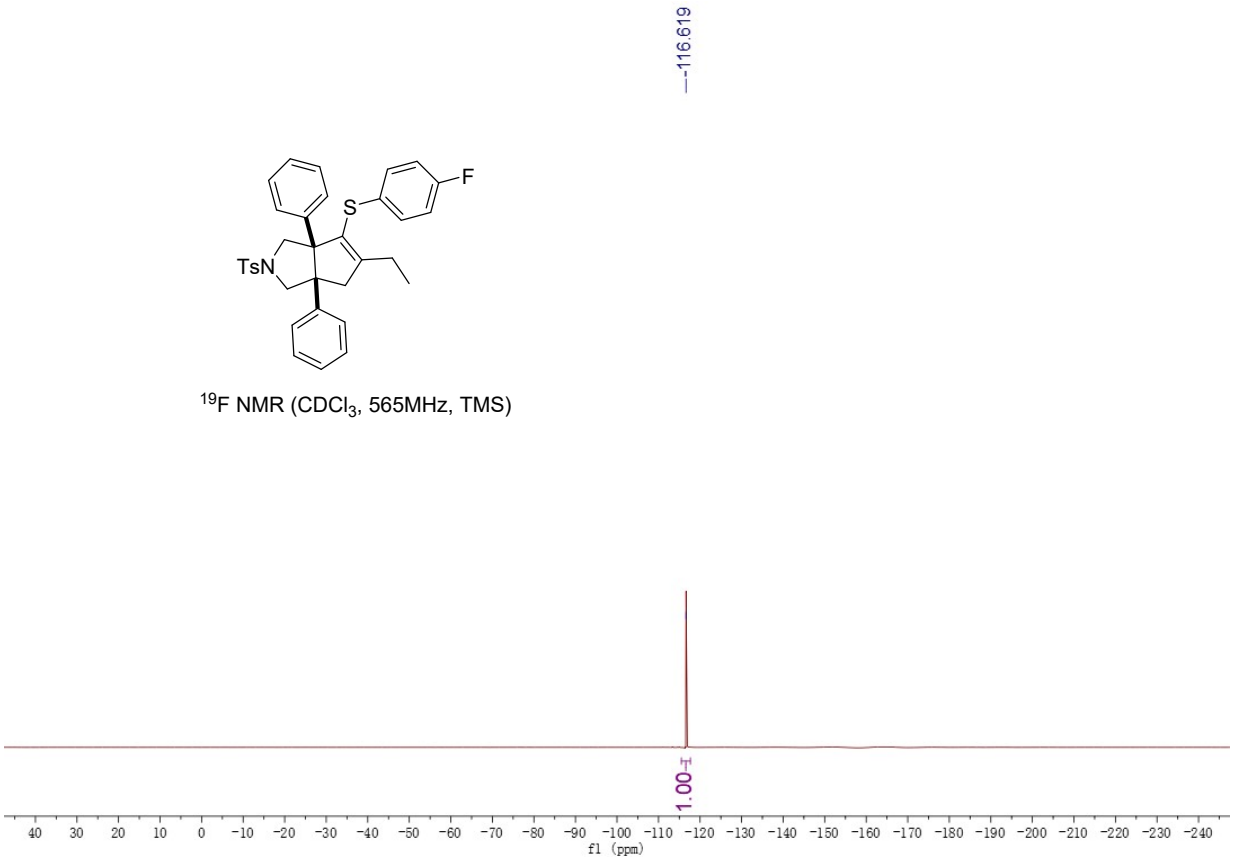


^{1}H NMR ($CDCl_3$, 600MHz, TMS)

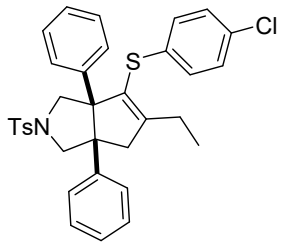




^{13}C NMR ($CDCl_3$, 150MHz, TMS)

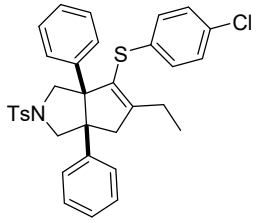


^{19}F NMR ($CDCl_3$, 565MHz, TMS)

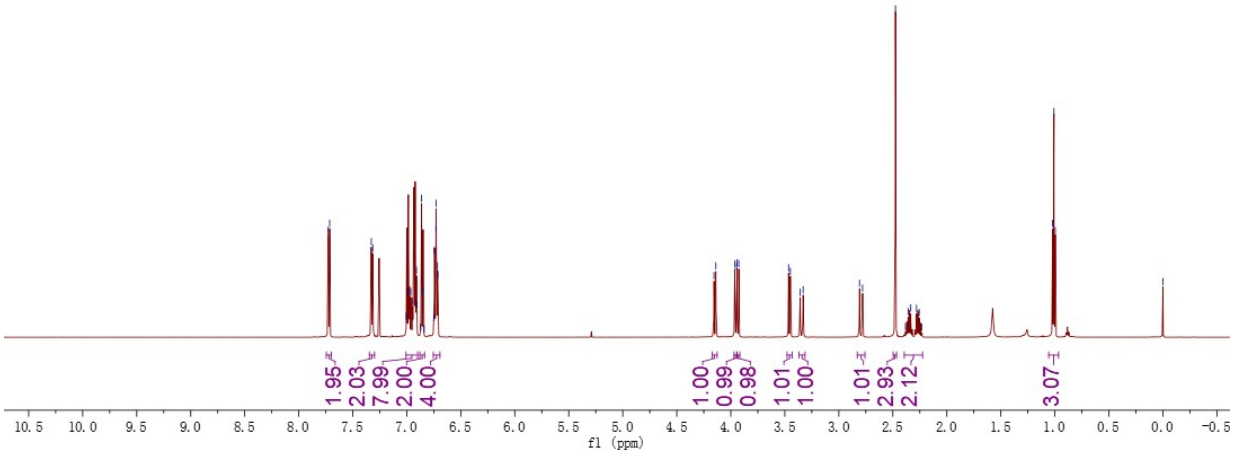


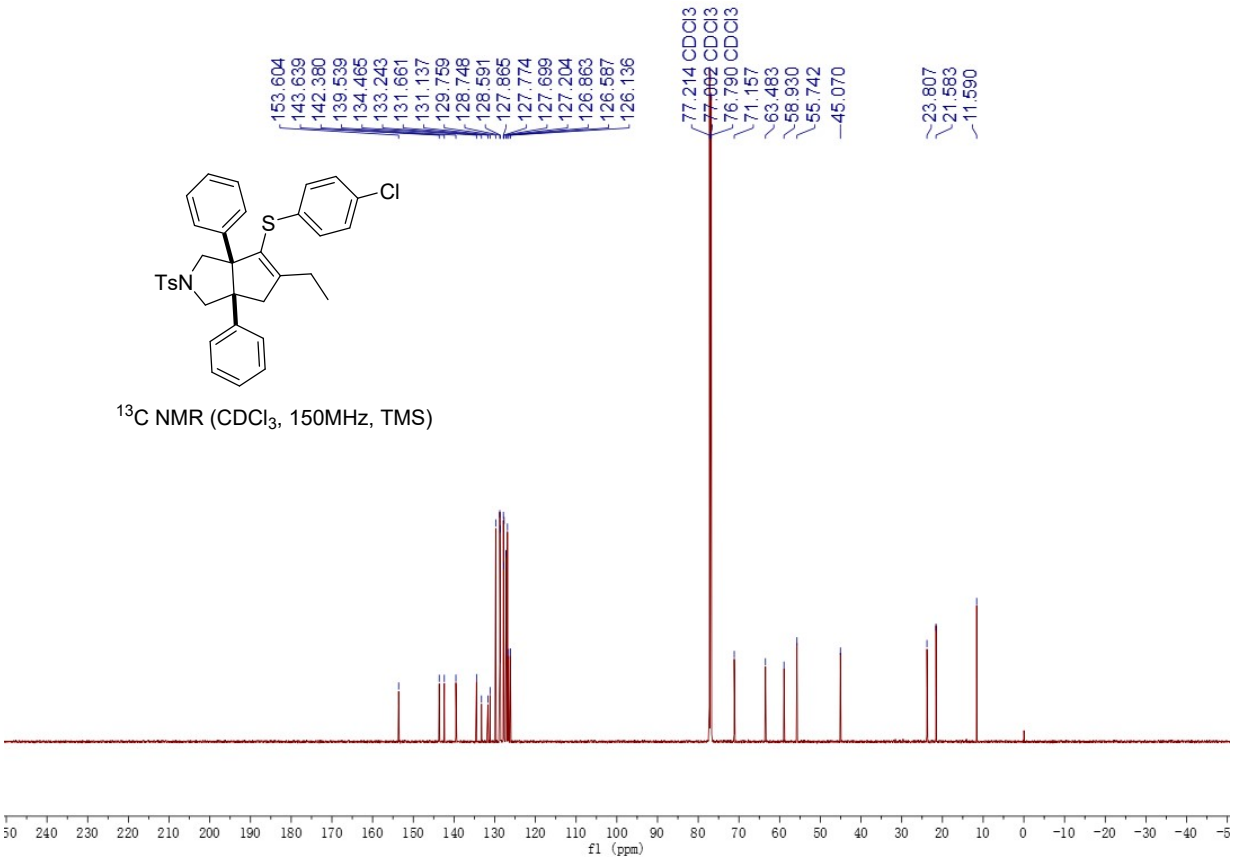
6-((4-chlorophenyl)thio)-5-ethyl-3a,6a-diphenyl-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ac)

A colorless oil, 47.4 mg, 81% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.01 - 6.90 (m, 8H), 6.88 - 6.83 (m, 2H), 6.75 - 6.69 (m, 4H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.96 (d, *J* = 10.4 Hz, 1H), 3.93 (d, *J* = 10.0 Hz, 1H), 3.46 (d, *J* = 10.0 Hz, 1H), 3.34 (d, *J* = 16.9 Hz, 1H), 2.79 (d, *J* = 17.0 Hz, 1H), 2.48 (s, 3H), 2.39 - 2.22 (m, 2H), 1.01 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 153.6, 143.6, 142.4, 139.5, 134.5, 133.2, 131.7, 131.1, 129.8, 128.7, 128.6, 127.9, 127.8, 127.7, 127.2, 126.9, 126.6, 126.1, 71.2, 63.5, 58.9, 55.7, 45.1, 23.8, 21.6, 11.6. IR (Acetone) ν 1090, 1165, 1345, 1472, 2967 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{33}O_2NS_2Cl$ (M+H): 586.1636, Found: 586.1601.

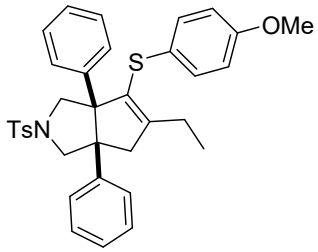


^{1}H NMR ($CDCl_3$, 600MHz, TMS)





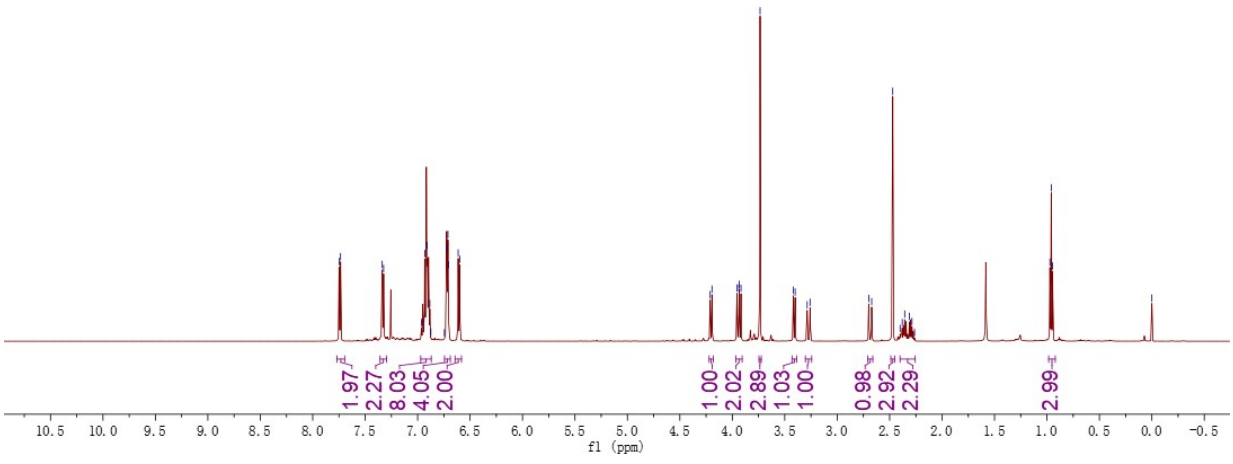
^{13}C NMR ($CDCl_3$, 150MHz, TMS)

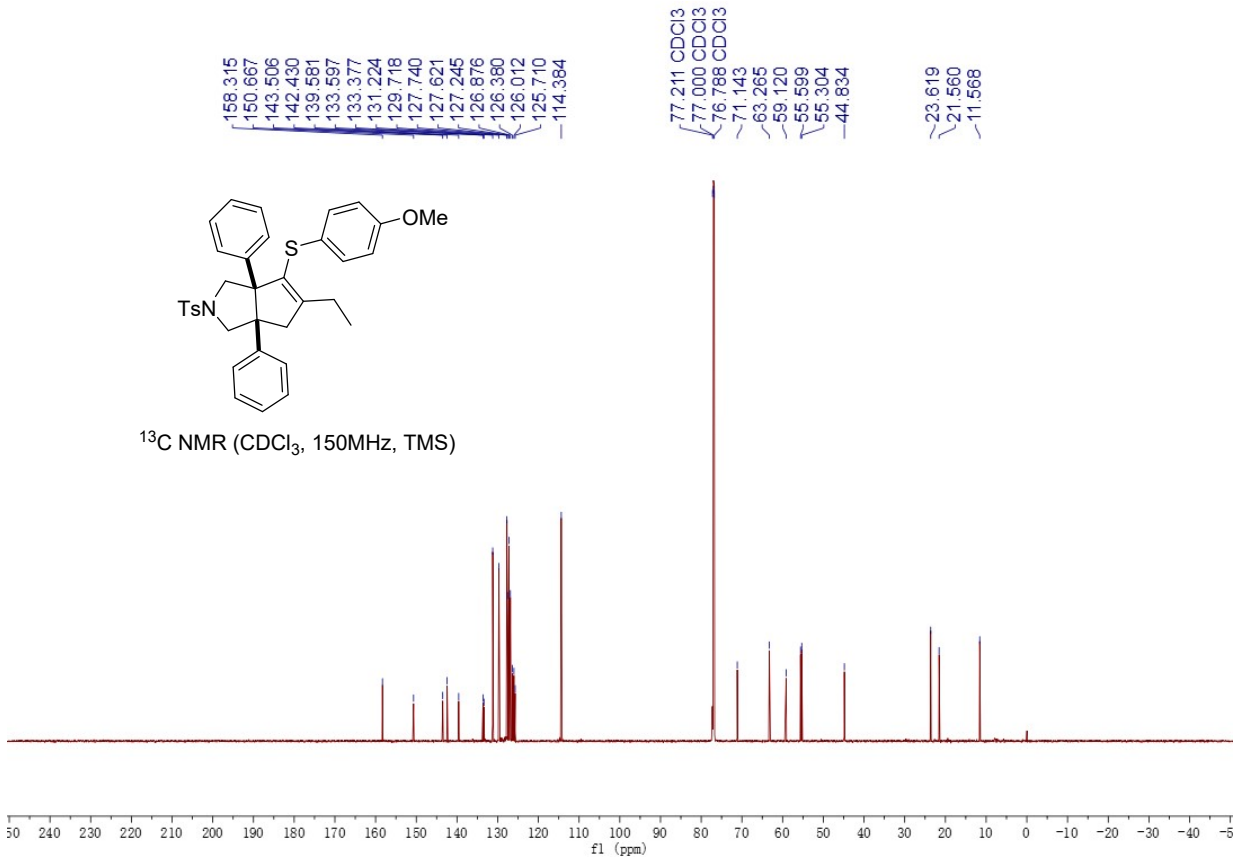


5-ethyl-6-((4-methoxyphenyl)thio)-3a,6a-diphenyl-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ad)

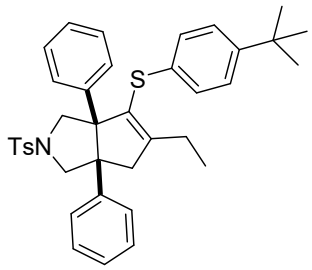
A colorless oil, 37.8 mg, 65% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.97 - 6.87 (m, 8H), 6.74 - 6.69 (m, 4H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.20 (d, *J* = 10.3 Hz, 1H), 3.94 (dd, *J* = 12.6, 10.1 Hz, 2H), 3.74 (s, 3H), 3.41 (d, *J* = 10.0 Hz, 1H), 3.27 (d, *J* = 16.7 Hz, 1H), 2.69 (d, *J* = 16.7 Hz, 1H), 2.47 (s, 3H), 2.40 - 2.26 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 158.3, 150.7, 143.5, 142.4, 139.6, 133.6, 133.4, 131.2, 129.7, 127.7, 127.6, 127.2, 126.9, 126.4, 126.0, 125.7, 114.4, 71.1, 63.3, 59.1, 55.6, 55.3, 44.8, 23.6, 21.6, 11.6. IR (Acetone) ν 1166 1175, 1243, 1344, 1492, 1597, 2969 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{36}O_3NS_2$ (M+H): 582.2131, Found: 582.2098.

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



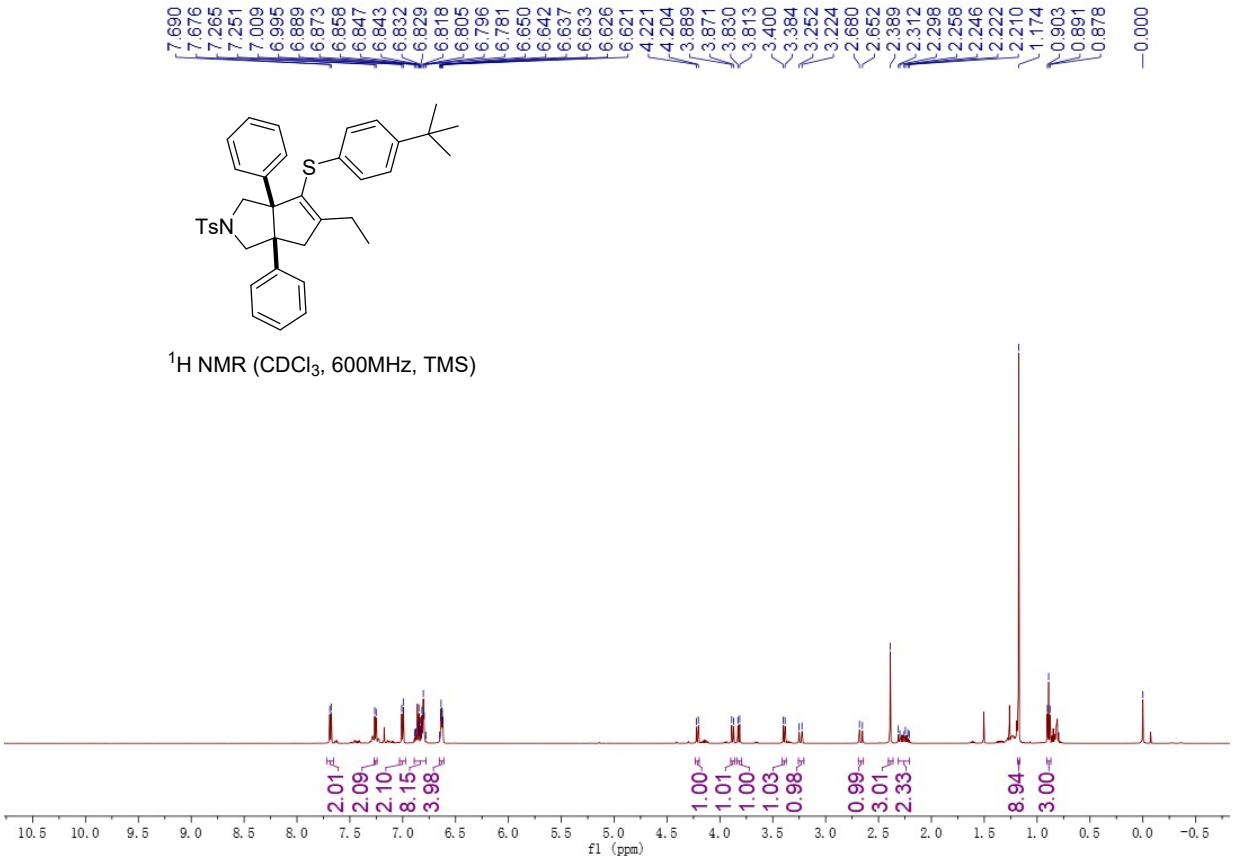


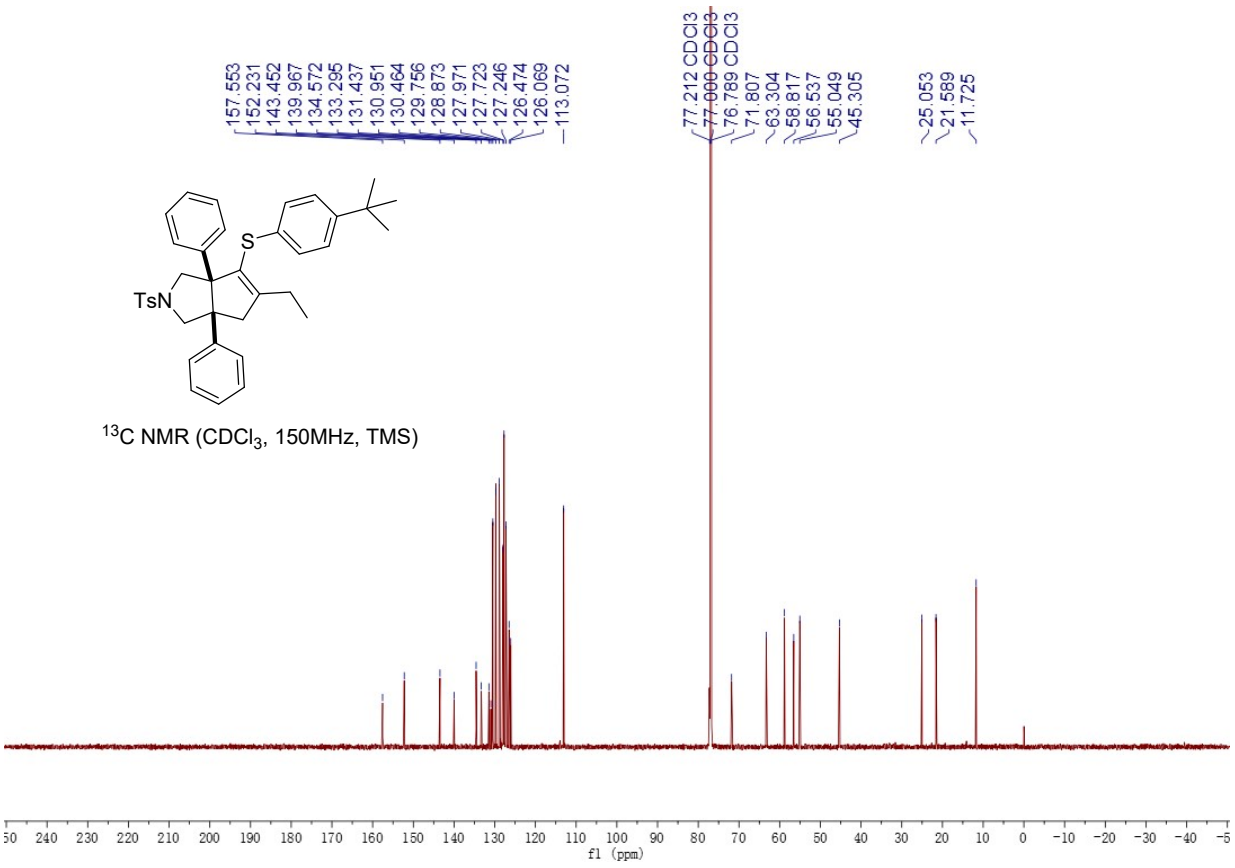
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



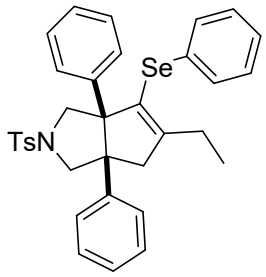
6-((4-(*tert*-butyl)phenyl)thio)-5-ethyl-3a,6a-diphenyl-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (3ae)

A colorless oil, 37.1 mg, 61% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.89 - 6.78 (m, 8H), 6.65 - 6.61 (m, 4H), 4.21 (d, *J* = 10.3 Hz, 1H), 3.88 (d, *J* = 10.3 Hz, 1H), 3.82 (d, *J* = 9.9 Hz, 1H), 3.39 (d, *J* = 9.9 Hz, 1H), 3.24 (d, *J* = 16.7 Hz, 1H), 2.67 (d, *J* = 16.8 Hz, 1H), 2.39 (s, 3H), 2.31 - 2.21 (m, 2H), 1.17 (s, 9H), 0.89 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 157.6, 152.2, 143.5, 140.0, 134.6, 133.3, 131.4, 131.0, 130.5, 129.8, 128.9, 128.0, 127.7, 127.2, 126.5, 126.1, 113.1, 71.8, 63.3, 58.8, 56.5, 55.0, 45.3, 25.1, 21.6, 11.7. IR (Acetone) ν 1163, 1347, 14802, 1592, 2909 cm^{-1}. HRMS (ESI) calcd. for $C_{38}H_{42}O_2NS_2$ (M+H): 607.2612, Found: 607.2617.



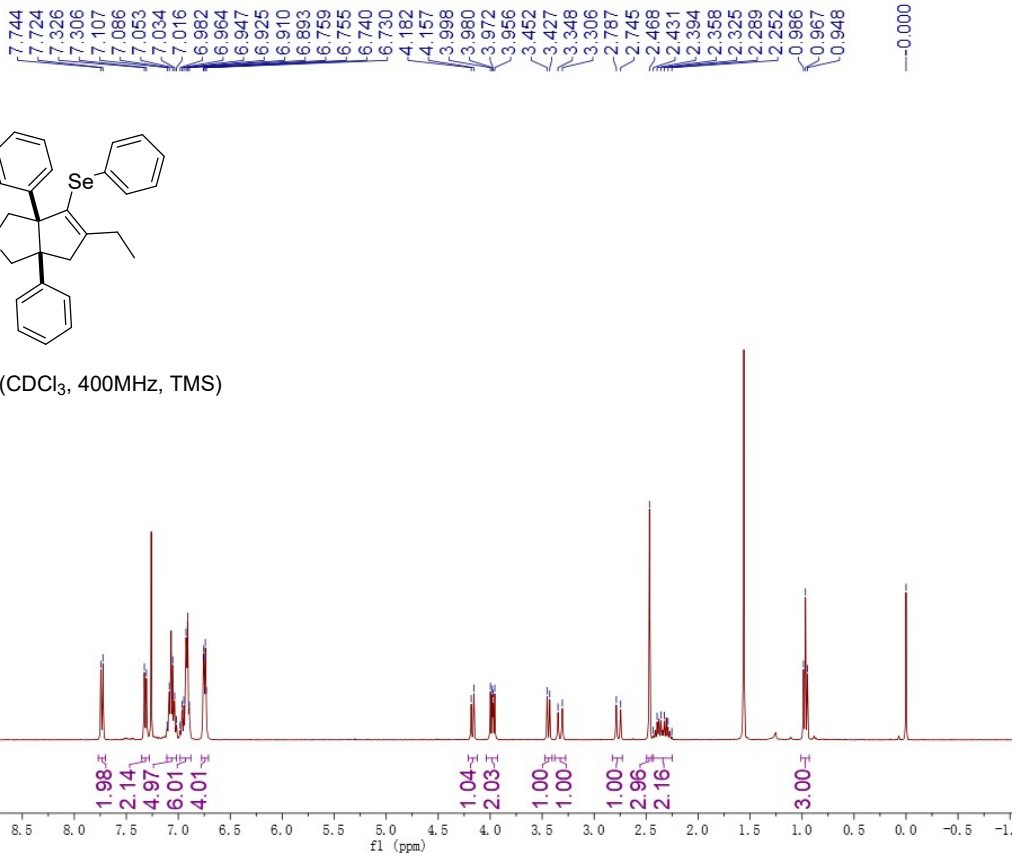


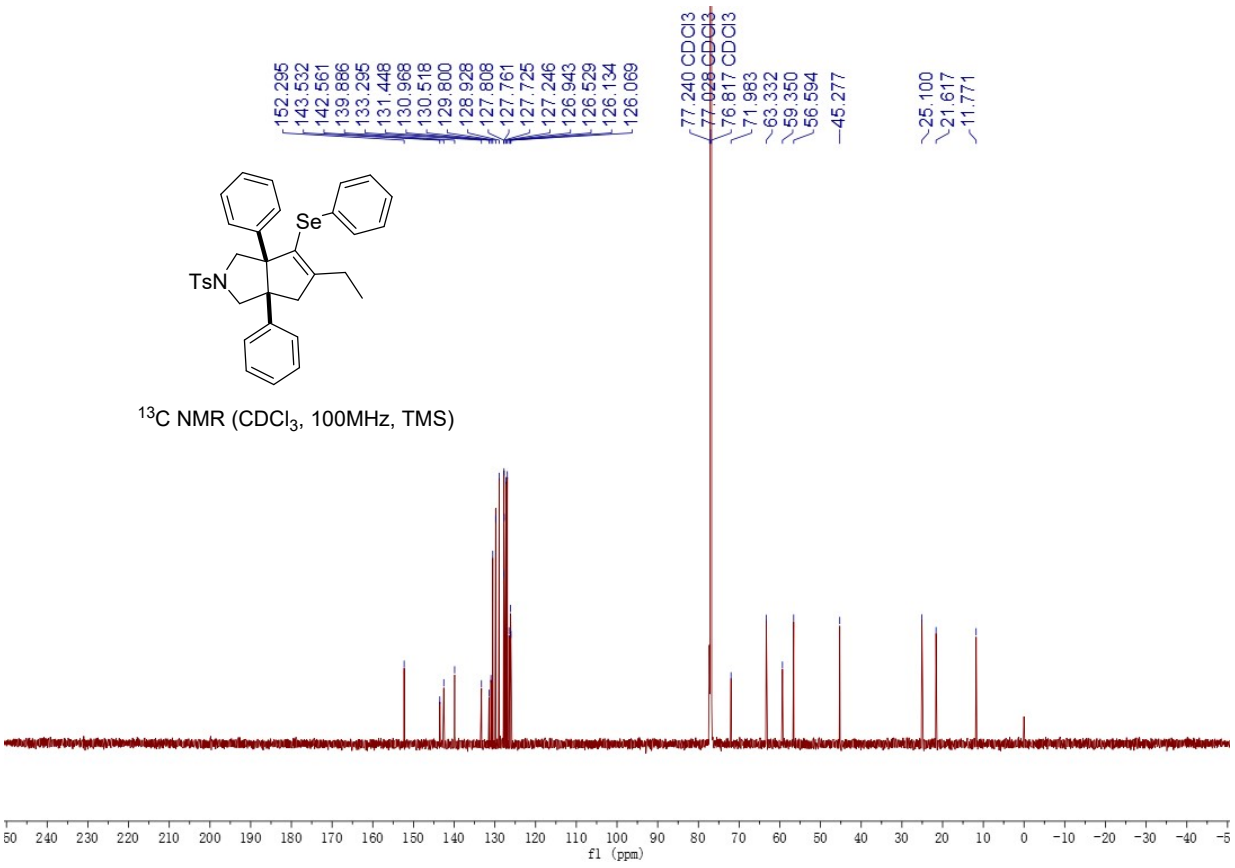
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



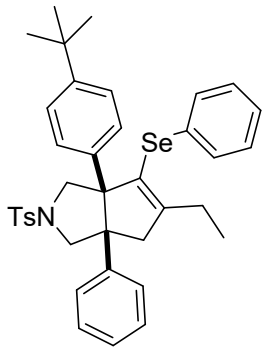
5-ethyl-3a,6a-diphenyl-6-(phenylselanyl)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (4a)

A colorless oil, 41.4 mg, 47% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 - 7.02 (m, 5H), 6.98 - 6.88 (m, 6H), 6.78 - 6.71 (m, 4H), 4.17 (d, *J* = 10.3 Hz, 1H), 3.98 (dd, *J* = 10.1, 6.9 Hz, 2H), 3.44 (d, *J* = 9.9 Hz, 1H), 3.33 (d, *J* = 16.7 Hz, 1H), 2.77 (d, *J* = 16.7 Hz, 1H), 2.47 (s, 3H), 2.43 - 2.25 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 152.3, 143.5, 142.6, 139.9, 133.3, 131.4, 131.0, 130.5, 129.8, 128.9, 127.81, 127.76, 127.7, 127.2, 126.9, 126.5, 126.13, 126.07, 72.0, 63.3, 59.4, 56.6, 45.3, 25.1, 21.6, 11.8. IR (Acetone) ν 1163, 1347, 1480, 1592 ,2909 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{34}O_2NSSe$ (M+H): 600.1470, Found: 600.1432.



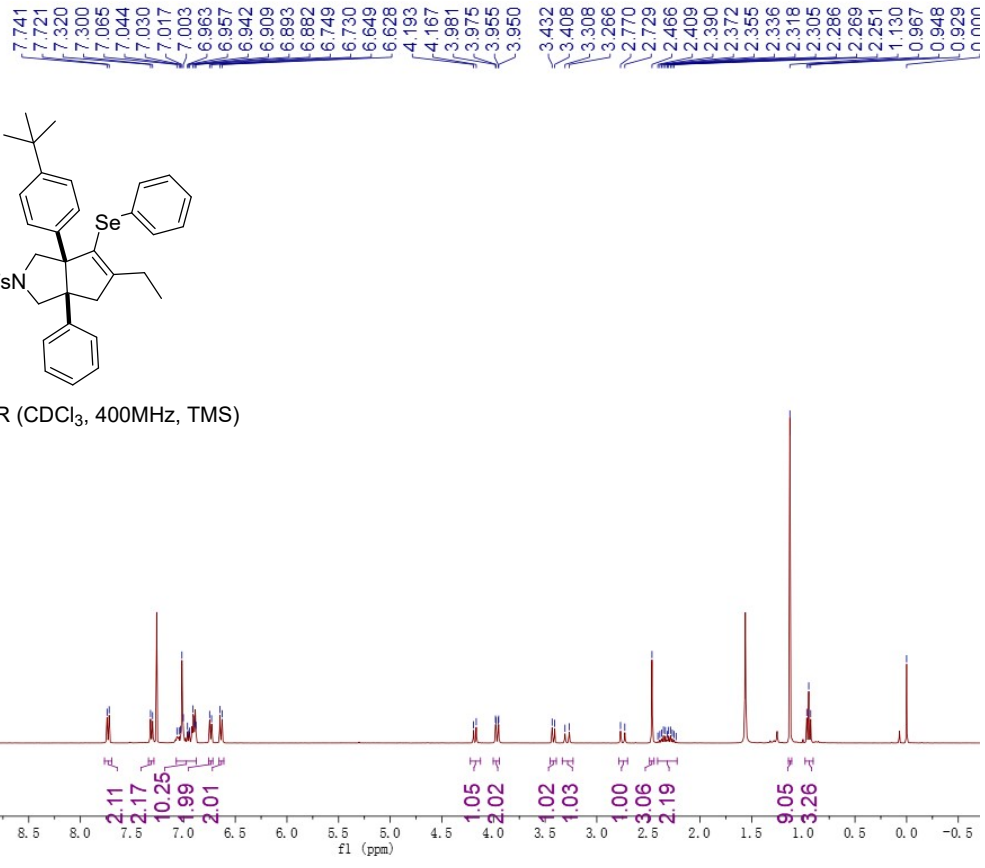


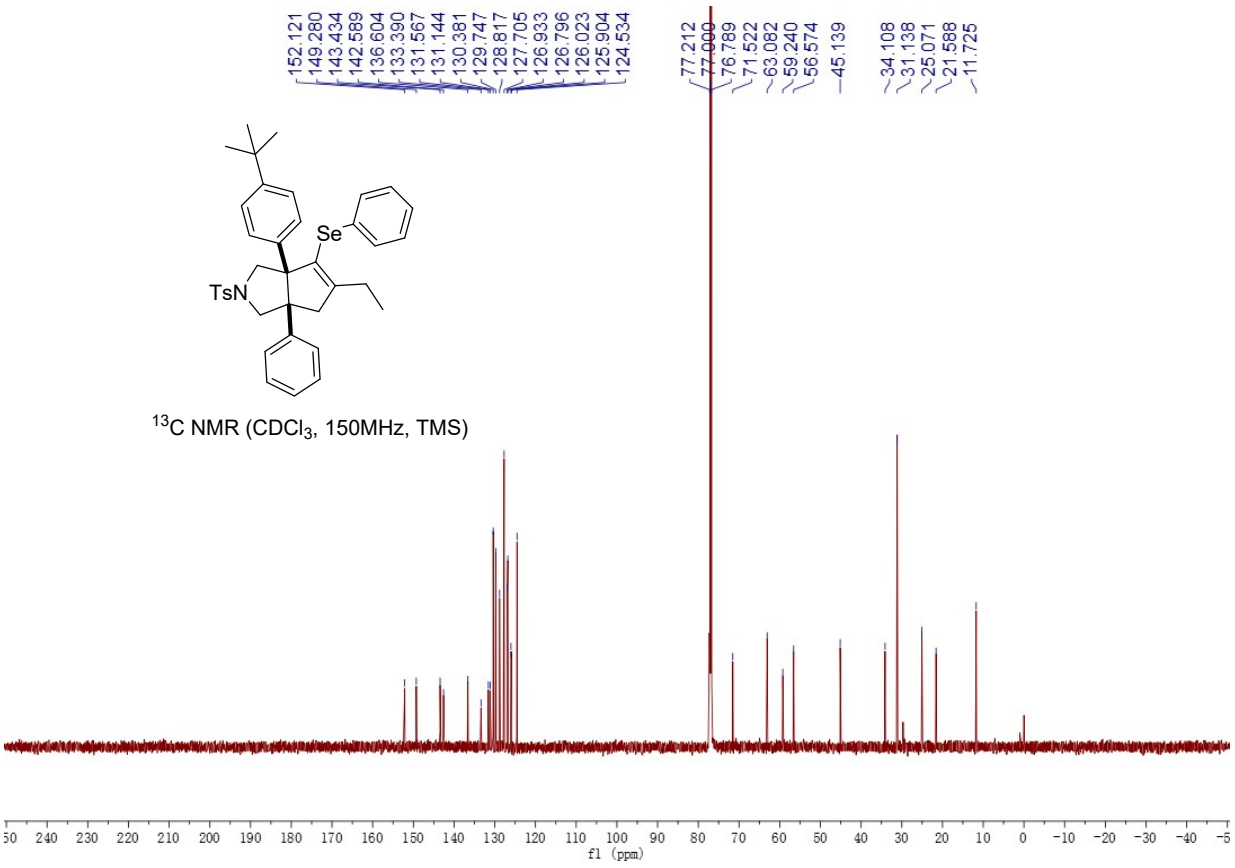
^{13}C NMR ($CDCl_3$, 100MHz, TMS)



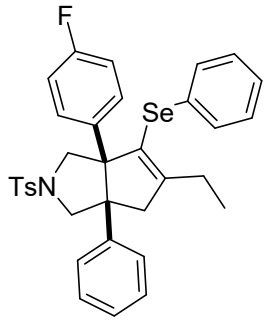
6a-(4-(tert-butyl)phenyl)-5-ethyl-3a-phenyl-6-(phenylselanyl)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (4b)

A colorless oil, 22.9 mg, 35% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.07 - 6.88 (m, 10H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.18 (d, *J* = 10.3 Hz, 1H), 3.97 (dd, *J* = 10.1, 2.1 Hz, 2H), 3.42 (d, *J* = 9.9 Hz, 1H), 3.29 (d, *J* = 16.6 Hz, 1H), 2.75 (d, *J* = 16.6 Hz, 1H), 2.47 (s, 3H), 2.41 - 2.22 (m, 2H), 1.13 (s, 9H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 152.1, 149.3, 143.4, 142.6, 136.6, 133.4, 131.6, 131.1, 130.4, 129.7, 128.8, 127.7, 126.9, 126.8, 126.0, 125.9, 124.5, 71.5, 63.1, 59.2, 56.6, 45.1, 34.1, 31.1, 25.1, 21.6, 11.7. IR (Acetone) ν 1163, 1250, 1341, 1516, 2917 cm^{-1}. HRMS (ESI) calcd. for $C_{38}H_{42}O_2NSSe$ (M+H): 656.2096, Found: 656.2060.



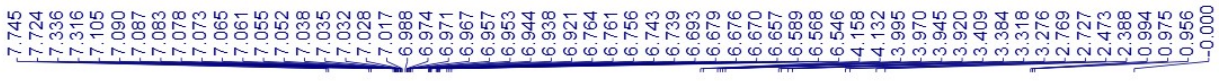


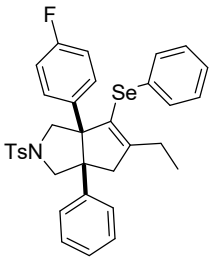
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



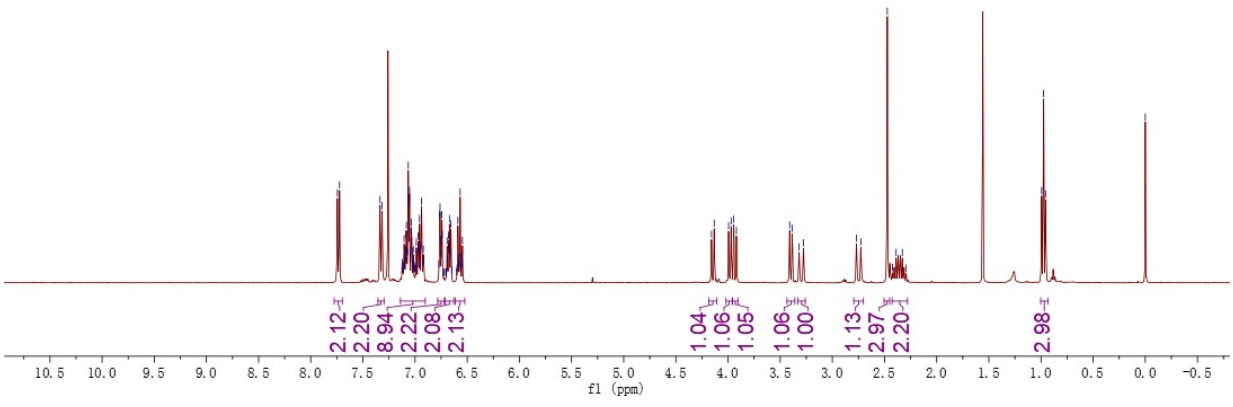
5-ethyl-6a-(4-fluorophenyl)-3a-phenyl-6-(phenylselanyl)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (4c)

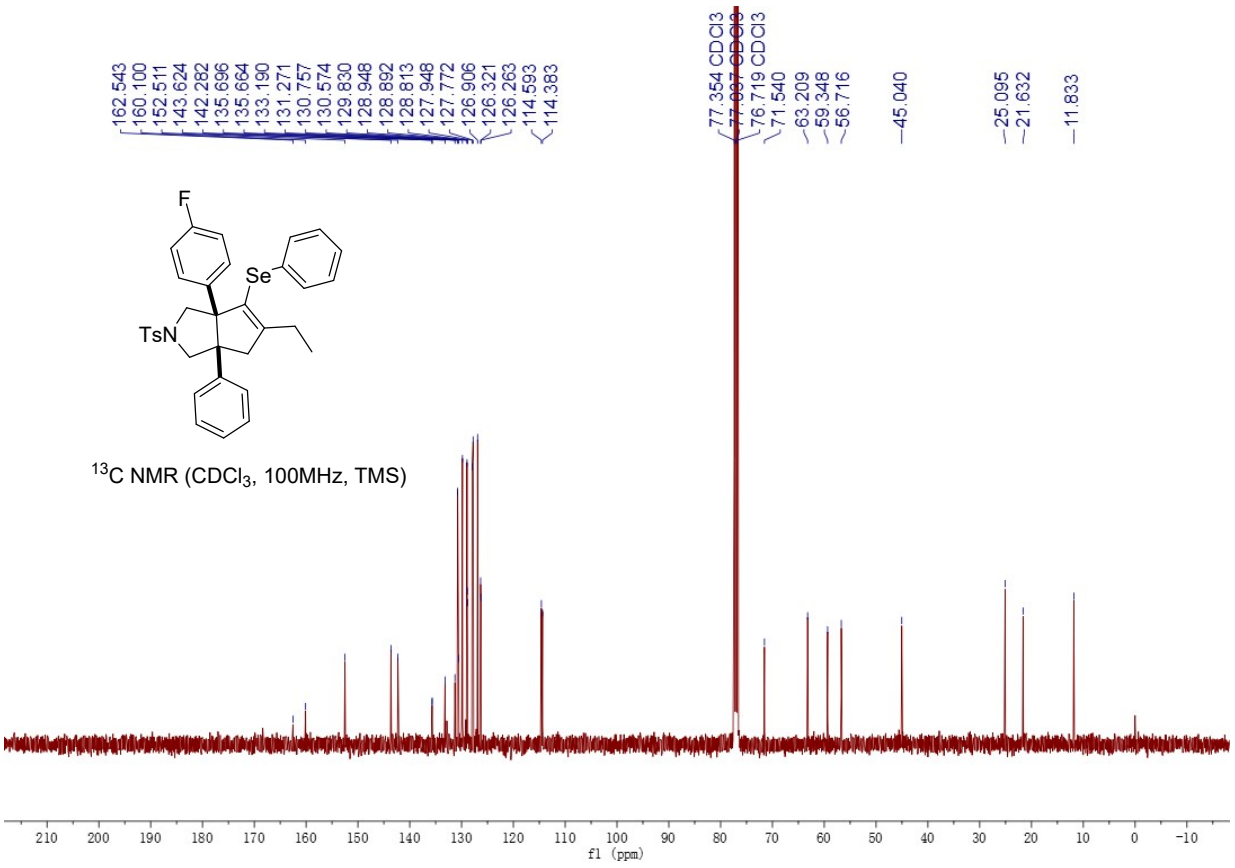
A colorless oil, 35.8 mg, 58% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.73 (d, *J* = 8.2 Hz), 7.33 (d, *J* = 8.0 Hz), 7.14 - 6.90 (m, 9H), 6.78 - 6.72 (m, 2H), 6.71 - 6.63 (m, 2H), 6.61 - 6.52 (m, 2H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.98 (d, *J* = 9.9 Hz, 1H), 3.93 (d, *J* = 10.3 Hz, 1H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 16.7 Hz, 1H), 2.75 (d, *J* = 16.7 Hz, 1H), 2.47 (s, 3H), 2.43 - 2.28 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 162.5 (d, *J* = 244.3 Hz), 160.1, 152.5, 143.6, 142.3, 135.7 (d, *J* = 3.2 Hz), 133.2, 131.3, 130.8, 130.6, 129.8, 128.9 (d, *J* = 7.9 Hz), 128.8, 127.9, 127.8, 126.9, 126.3 (d, *J* = 5.8 Hz), 114.5 (d, *J* = 21.0 Hz), 71.5, 63.2, 59.3, 56.7, 45.0, 25.1, 21.6, 11.8. ^{19}F NMR ($CDCl_3$, TMS, 376 MHz) δ -116.2 (s). IR (Acetone) ν 1046, 1160, 1346, 1506, 1597, 2873 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{33}NO_2FSSe$ (M+H): 618.1376, Found: 618.1338.



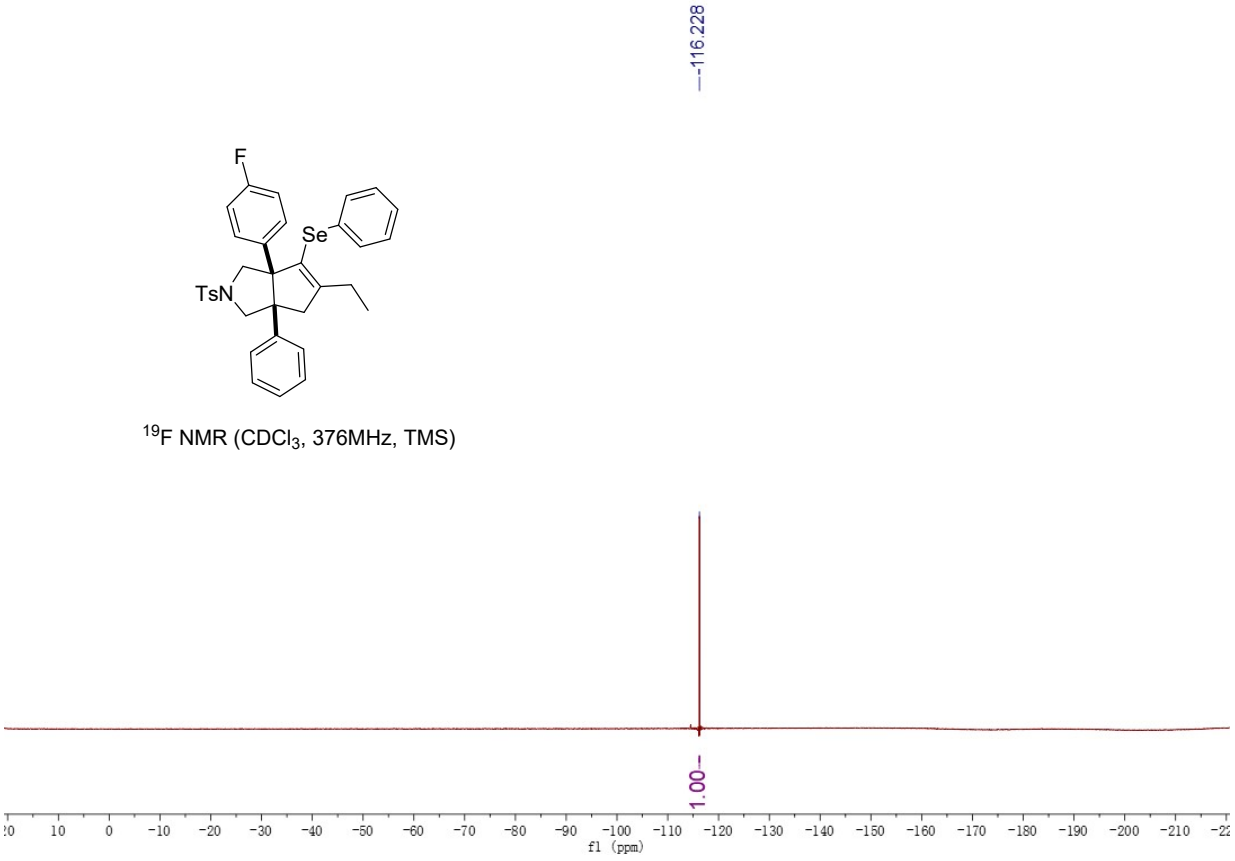


^{1}H NMR ($CDCl_3$, 400MHz, TMS)

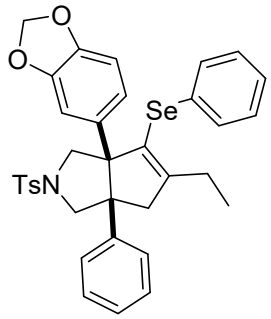




^{13}C NMR ($CDCl_3$, 100MHz, TMS)

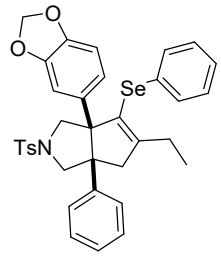


^{19}F NMR ($CDCl_3$, 376MHz, TMS)

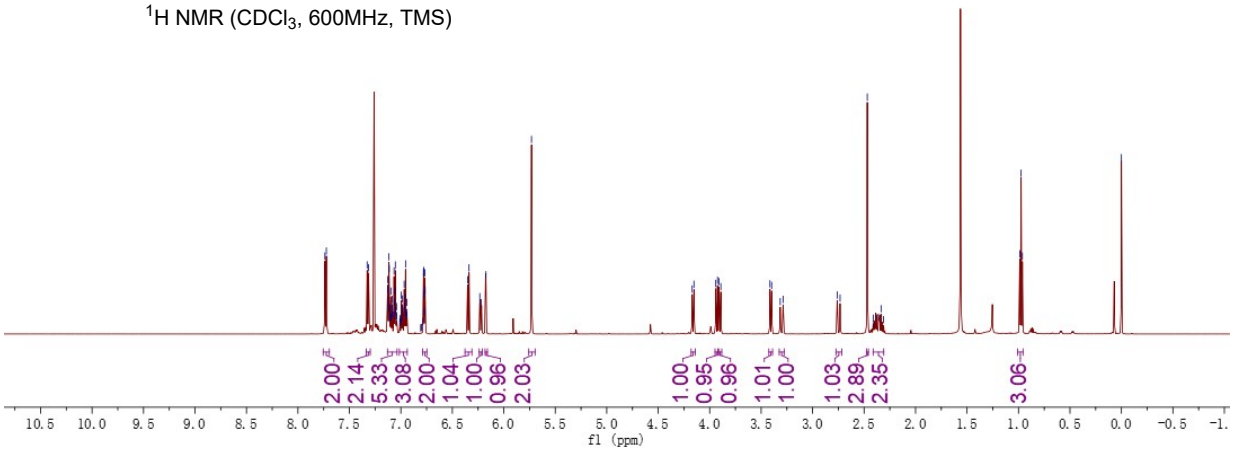


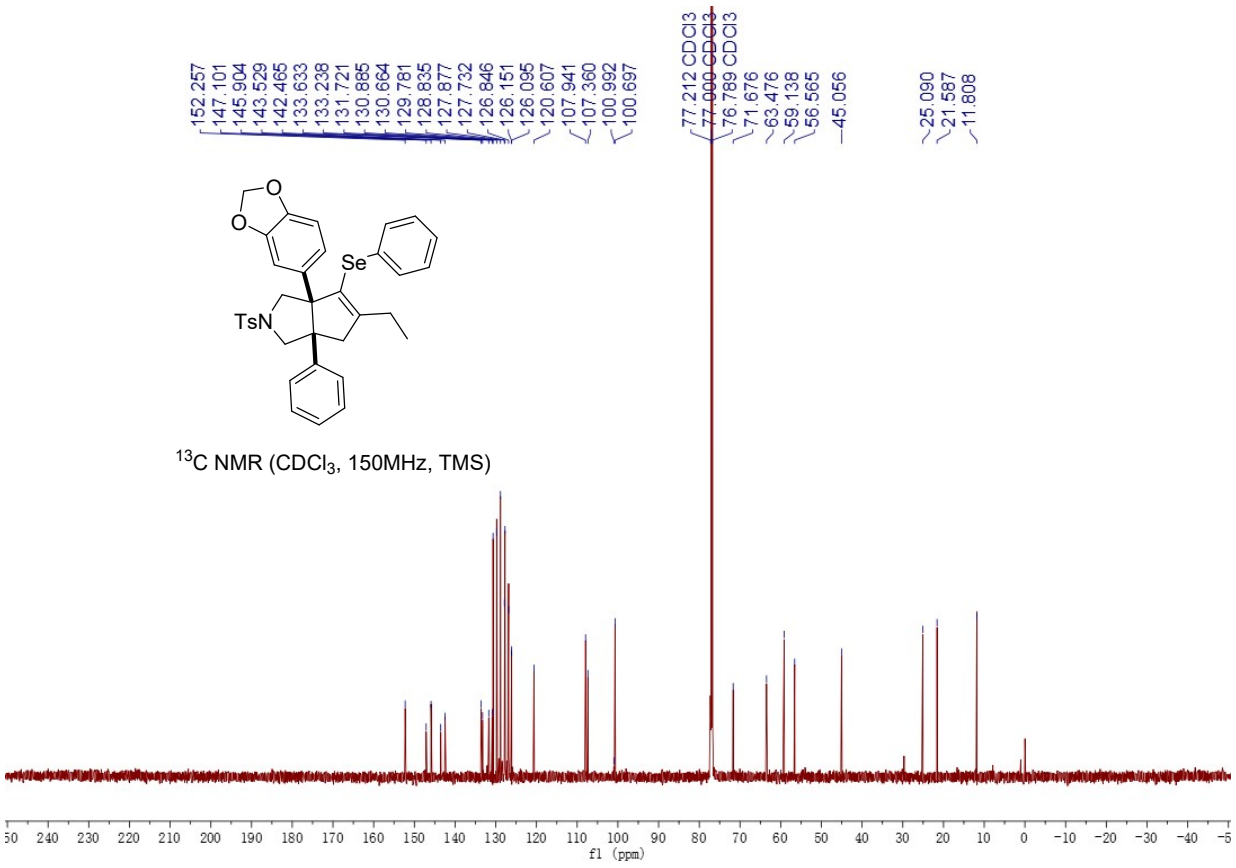
6a-(benzo[*d*][1,3]dioxol-5-yl)-5-ethyl-3a-phenyl-6-(phenylselanyl)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (4d)

A colorless oil, 32.1 mg, 50% yield. ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 - 7.04 (m, 5H), 7.01 - 6.94 (m, 3H), 6.79 - 6.75 (m, 2H), 6.34 (d, *J* = 8.2 Hz, 1H), 6.23 (d, *J* = 8.2 Hz, 1H), 6.17 (s, 1H), 5.73 (s, 1H), 4.16 (d, *J* = 10.3 Hz, 1H), 3.93 (d, *J* = 9.9 Hz, 1H), 3.90 (d, *J* = 10.3 Hz, 1H), 3.41 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 16.7 Hz, 1H), 2.75 (d, *J* = 16.7 Hz, 1H), 2.47 (s, 3H), 2.41 - 2.31 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 152.3, 147.1, 145.9, 143.5, 142.5, 133.6, 133.2, 131.7, 130.9, 130.7, 129.8, 128.8, 127.9, 127.7, 126.8, 126.2, 126.1, 120.6, 107.9, 107.4, 101.0, 100.7, 71.7, 63.5, 59.1, 56.6, 45.1, 25.1, 21.6, 11.8. IR (Acetone) ν 1166, 1346, 1490, 1720, 2964 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{34}NO_4SSe$ (M+H): 644.1368, Found: 644.1315.

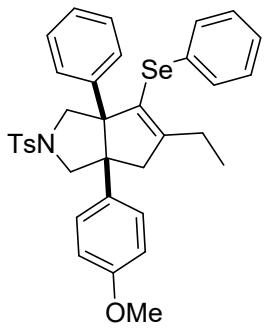


^{1}H NMR ($CDCl_3$, 600MHz, TMS)



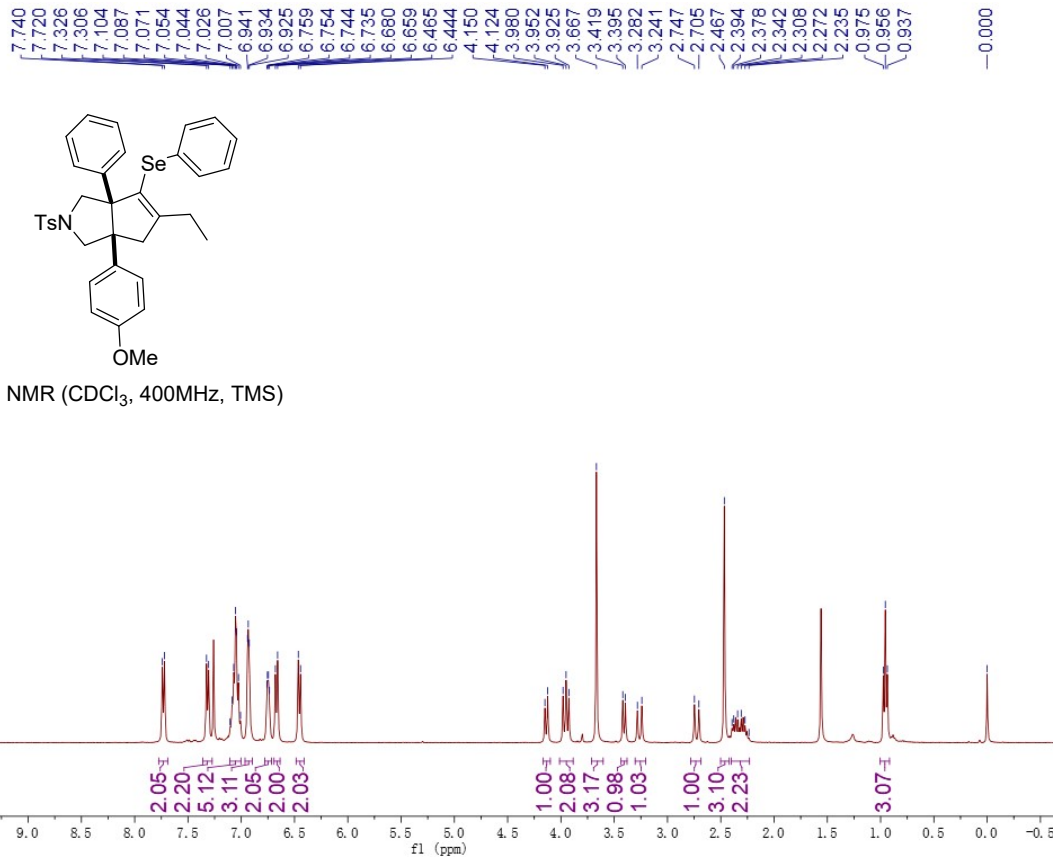


^{13}C NMR ($CDCl_3$, 150MHz, TMS)

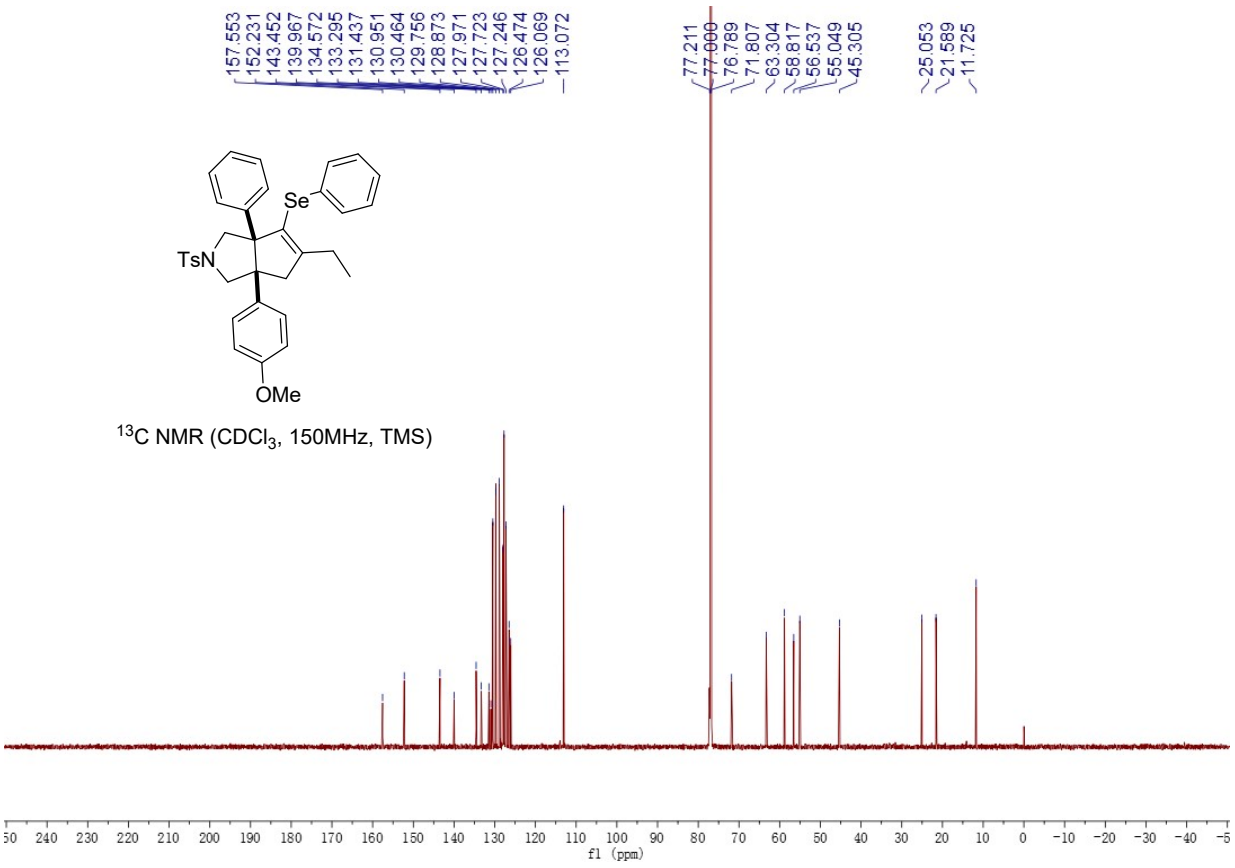


5-ethyl-3a-(4-methoxyphenyl)-6a-phenyl-6-(phenylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (4e)

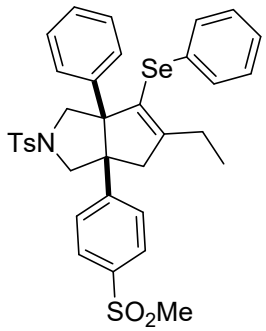
A colorless oil, 32.7 mg, 52% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.11 - 7.00 (m, 5H), 6.96 - 6.90 (m, 3H), 6.78 - 6.71 (m, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 4.14 (d, *J* = 10.3 Hz, 1H), 4.01 - 3.89 (m, 2H), 3.67 (s, 3H), 3.41 (d, *J* = 9.8 Hz, 1H), 3.26 (d, *J* = 16.7 Hz, 1H), 2.73 (d, *J* = 16.7 Hz, 1H), 2.47 (s, 3H), 2.40 - 2.23 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 150 MHz) δ 157.6, 152.2, 143.5, 140.0, 134.6, 133.3, 131.4, 131.0, 130.5, 129.8, 128.9, 128.0, 127.7, 127.2, 126.5, 126.1, 113.1, 71.8, 63.3, 58.8, 56.5, 55.0, 45.3, 25.1, 21.6, 11.7. IR (Acetone) ν 1160, 1332, 1487, 1723, 2964 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{36}NO_3SSe$ (M+H): 630.1581, Found: 630.1538.



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

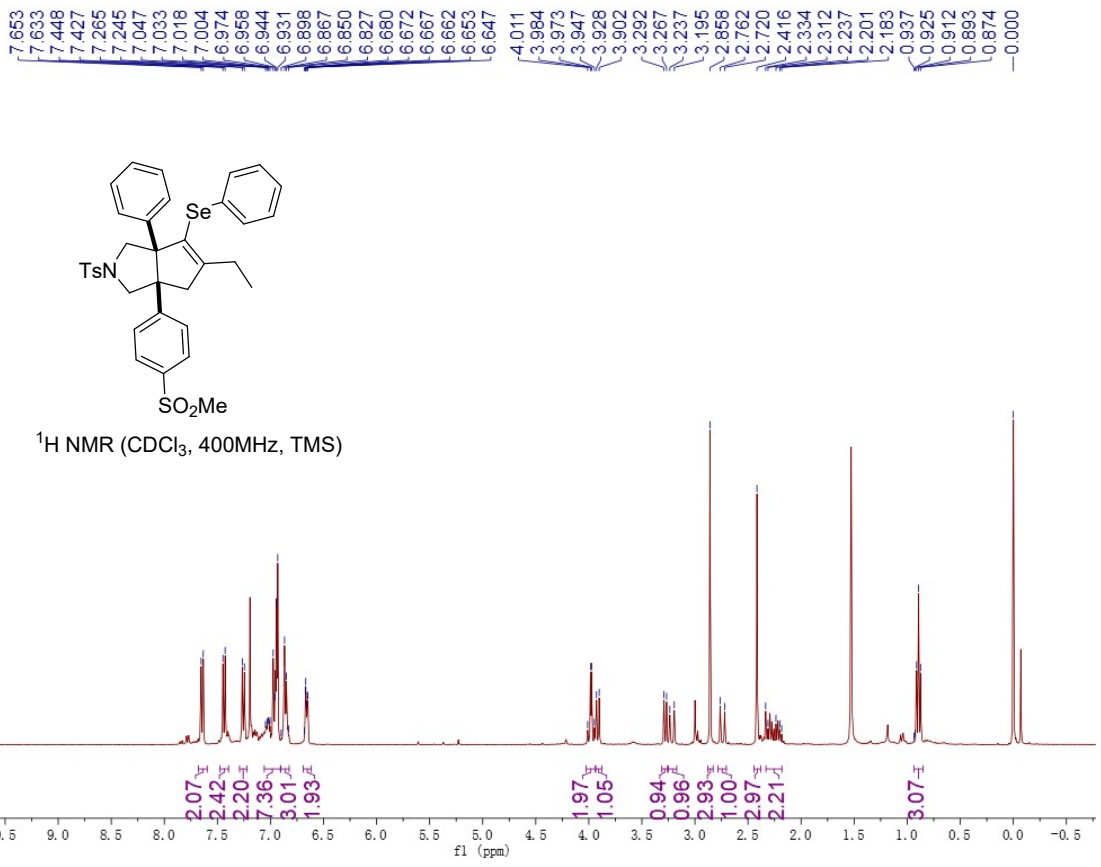


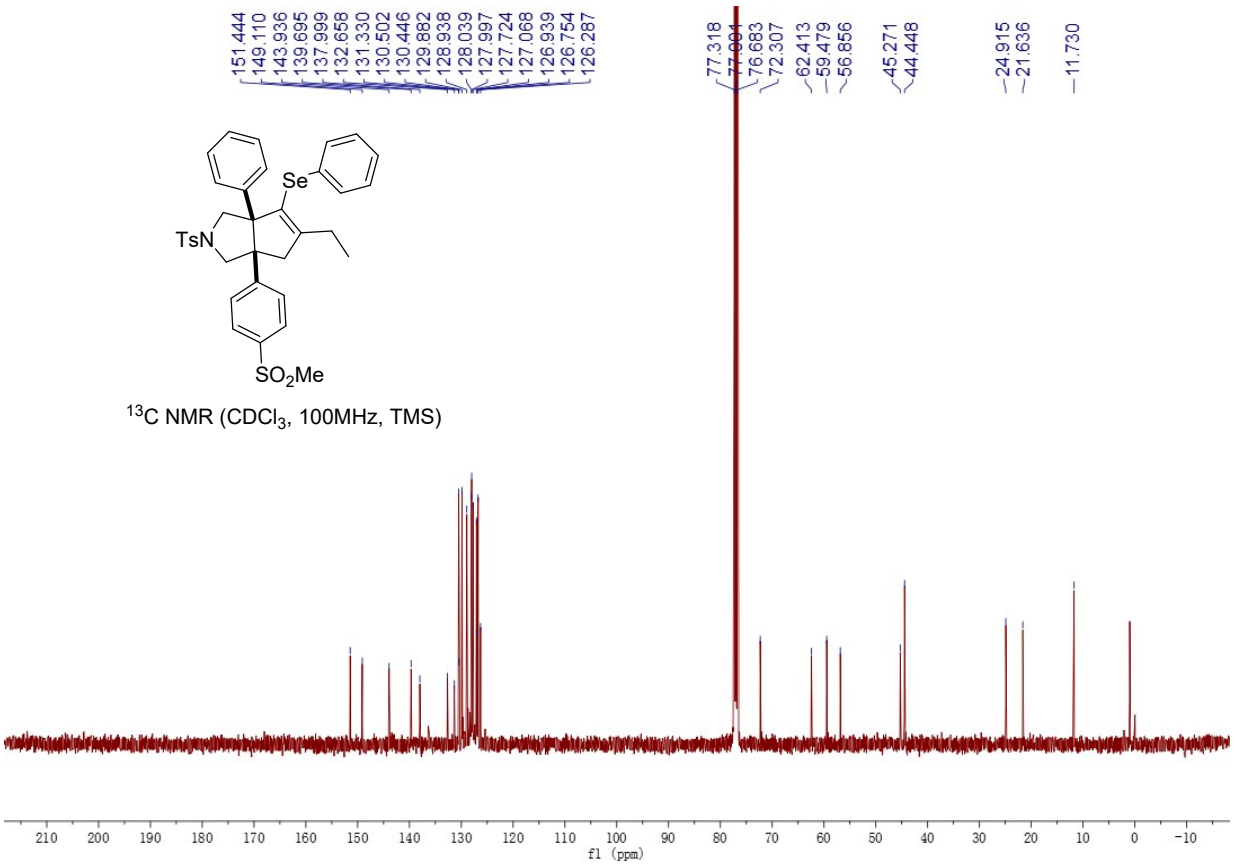
^{13}C NMR ($CDCl_3$, 150MHz, TMS)



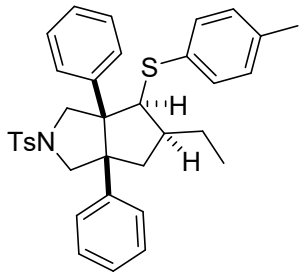
5-ethyl-3a-(4-(methylsulfonyl)phenyl)-6a-phenyl-6-(phenylthio)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (4f)

A colorless oil, 45.3 mg, 67% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.06 - 6.91 (m, 7H), 6.90 - 6.82 (m, 3H), 6.69 - 6.61 (m, 2H), 4.03 - 3.94 (m, 2H), 3.91 (d, *J* = 10.1 Hz, 1H), 3.28 (d, *J* = 10.0 Hz, 1H), 3.22 (d, *J* = 16.8 Hz, 1H), 2.86 (s, 3H), 2.74 (d, *J* = 16.8 Hz, 1H), 2.42 (s, 3H), 2.33 - 2.18 (m, 2H), 0.89 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR $CDCl_3$, TMS, 100 MHz) δ 151.4, 149.1, 143.9, 139.7, 138.0, 132.7, 131.3, 130.5, 130.4, 129.9, 128.9, 128.04, 128.00, 127.7, 127.1, 126.9, 126.8, 126.3, 72.3, 62.4, 59.5, 56.9, 45.3, 44.4, 24.9, 21.6, 11.7. IR (Acetone) ν 1093, 1151, 1306, 1346, 1597, 2928 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{36}NO_4S_2Se$ (M+H): 678.1245, Found: 678.1200.





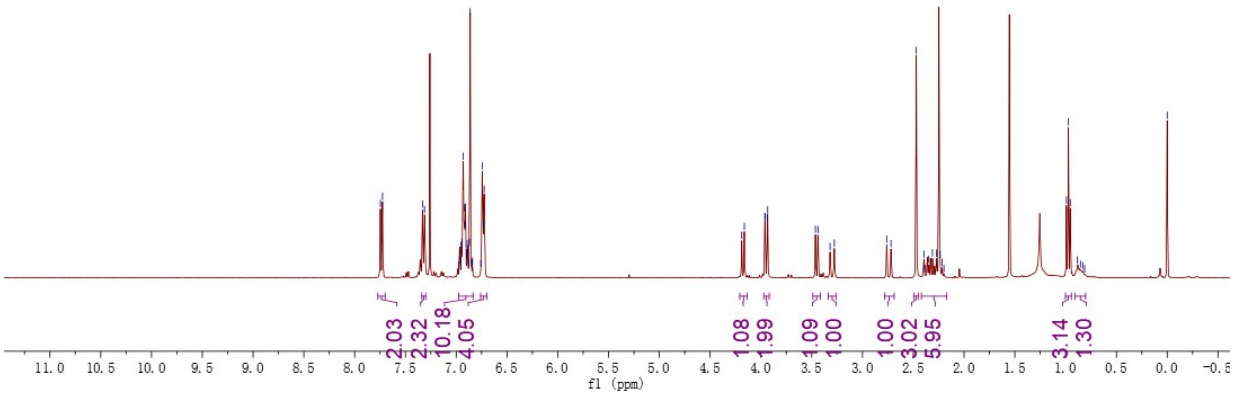
^{13}C NMR ($CDCl_3$, 100MHz, TMS)

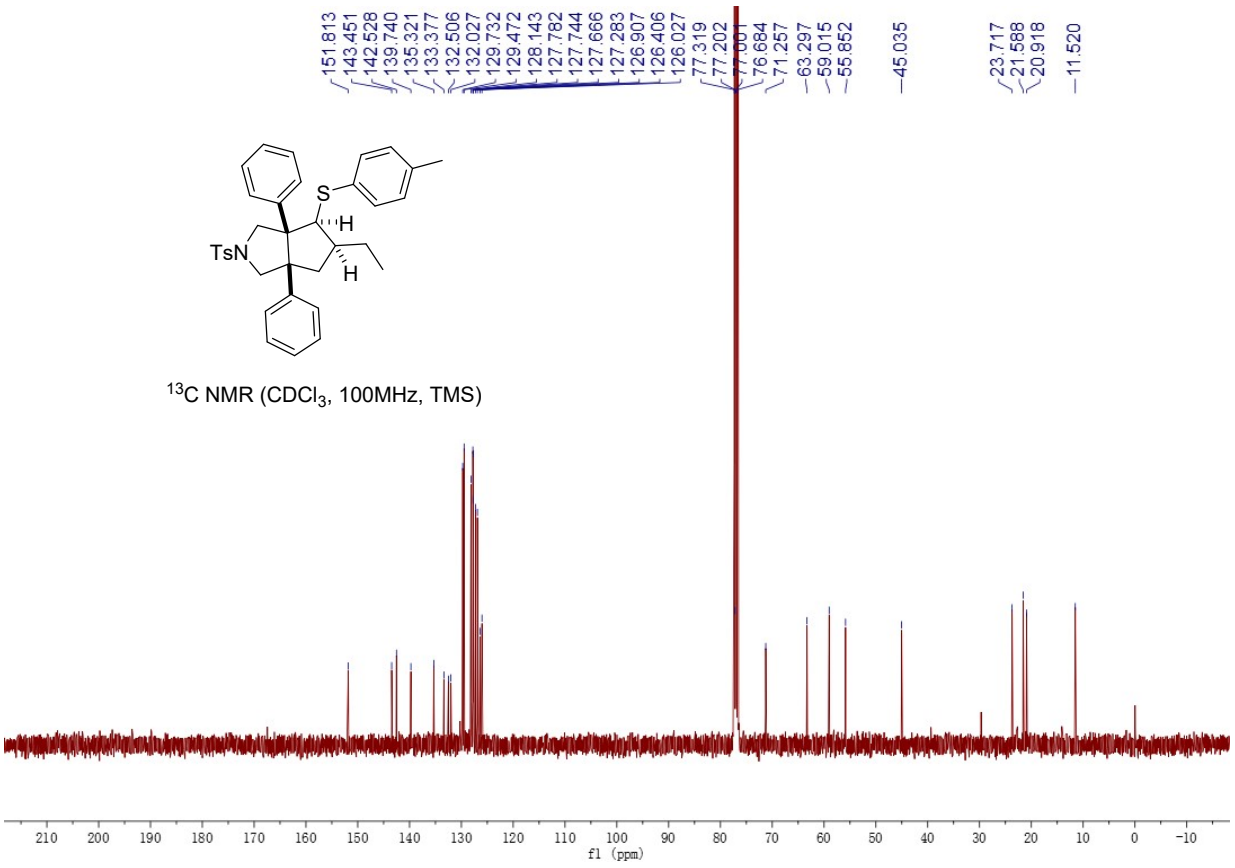


5-ethyl-3a,6a-diphenyl-4-(p-tolylthio)-2-tosyloctahydrocyclopenta[*c*]pyrrole (5)

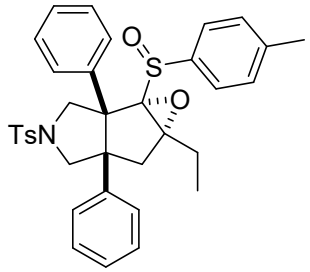
A colorless oil, 48.2 mg, 85% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.98 - 6.83 (m, 10H), 6.76 - 6.70 (m, 4H), 4.18 (d, *J* = 10.2 Hz, 1H), 3.97 - 3.92 (m, 2H), 3.45 (d, *J* = 9.9 Hz, 1H), 3.30 (d, *J* = 16.9 Hz, 1H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.47 (s, 3H), 2.42 - 2.17 (m, 6H), 0.97 (t, *J* = 7.6 Hz, 3H), 0.91 - 0.80 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 151.8, 143.5, 142.5, 139.7, 135.3, 133.4, 132.5, 132.0, 129.7, 129.5, 128.1, 127.78, 127.74, 127.3, 126.9, 126.4, 126.0, 71.3, 63.3, 59.0, 55.9, 45.0, 23.7, 21.6, 20.9, 11.5. IR (Acetone) ν 759, 1023, 1120, 1433, 2921, 2930 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{36}NO_2S_2$ (M-H): 566.2182, Found: 566.2142.

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



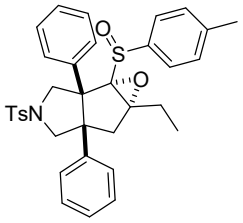


^{13}C NMR ($CDCl_3$, 100MHz, TMS)

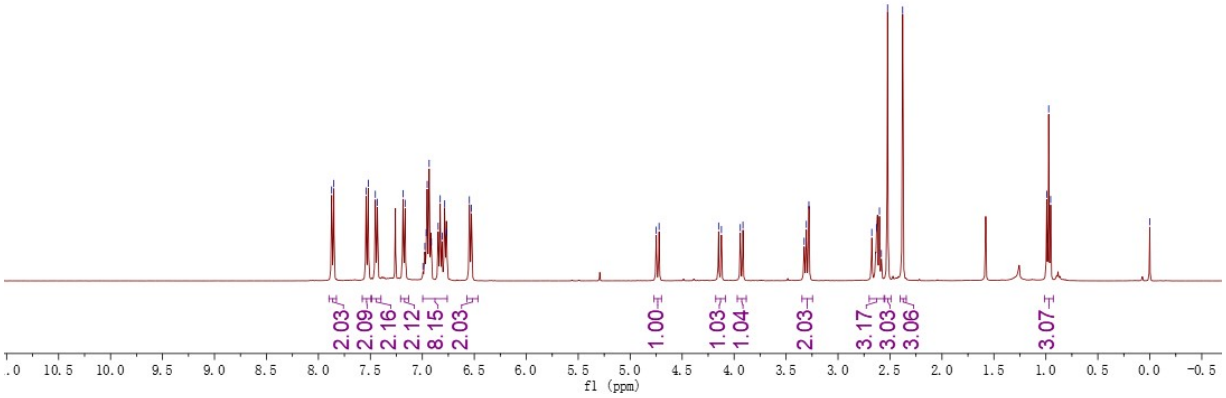


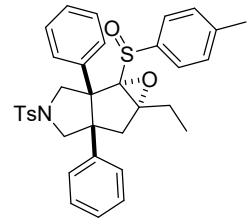
5a-ethyl-1b,4a-diphenyl-1a-(*p*-tolylsulfinyl)-3-tosyloctahydrooxireno[2',3':3,4]cyclopenta[1,2-*c*]pyrrole (6)

A colorless oil, 46.6 mg, 78% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.00 - 6.76 (m, 8H), 6.54 (d, *J* = 7.9 Hz, 2H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.14 (d, *J* = 10.9 Hz, 1H), 3.93 (d, *J* = 10.2 Hz, 1H), 3.35 - 3.25 (m, 2H), 2.70 - 2.56 (m, 3H), 2.52 (s, 3H), 2.38 (s, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 159.4, 143.9, 143.8, 140.55, 140.51, 139.5, 137.5, 133.0, 130.0, 129.4, 127.91, 127.86, 127.7, 127.5, 127.1, 126.9, 126.7, 126.4, 70.6, 62.3, 59.4, 54.6, 45.6, 23.5, 21.6, 21.5, 11.5. IR (Acetone) ν 1165, 1345, 1446, 1597, 2954 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{36}O_4NS_2$ (M+H): 598.2086, Found: 598.2042.

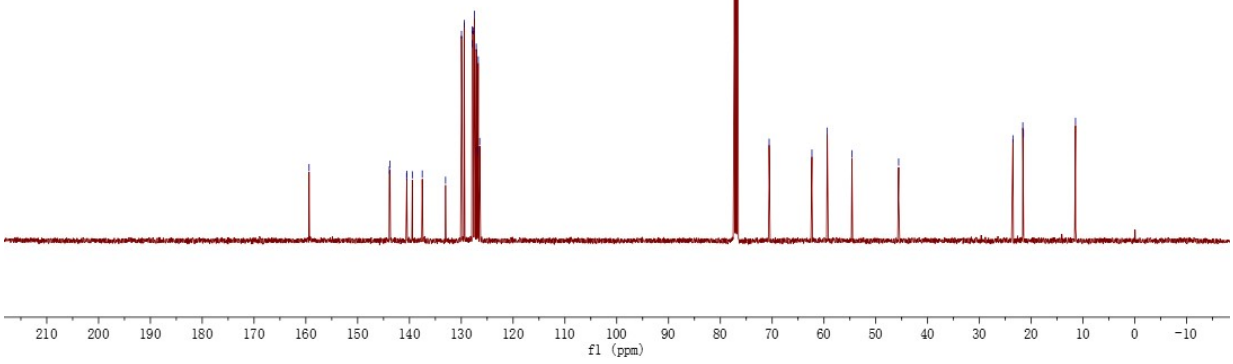


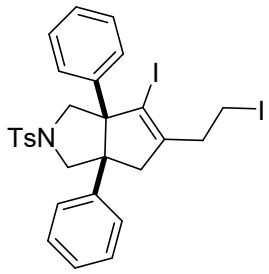
^{1}H NMR ($CDCl_3$, 400MHz, TMS)





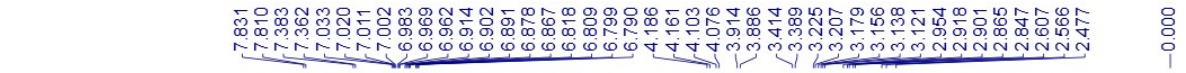
^{13}C NMR ($CDCl_3$, 100MHz, TMS)

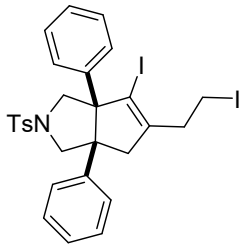




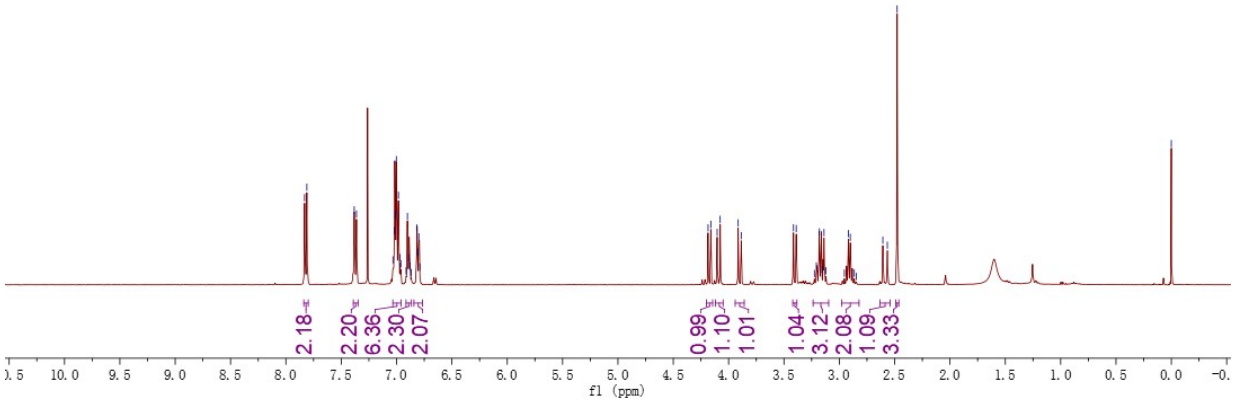
6-iodo-5-(2-iodoethyl)-3a,6a-diphenyl-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole (7)

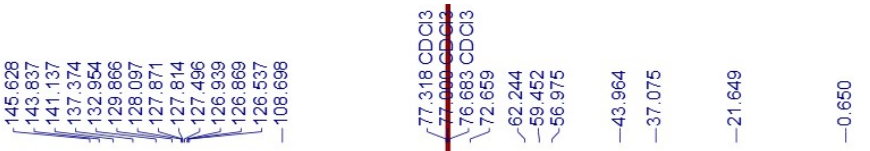
A colorless oil, 27.8 mg, 20% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.03 - 6.96 (m, 6H), 6.91 - 6.87 (m, 2H), 6.84 - 6.77 (m, 2H), 4.17 (d, *J* = 9.9 Hz, 1H), 4.09 (d, *J* = 10.9 Hz, 1H), 3.90 (d, *J* = 10.9 Hz, 1H), 3.40 (d, *J* = 9.8 Hz, 1H), 3.24 - 3.10 (m, 3H), 2.98 - 2.82 (m, 2H), 2.59 (d, *J* = 16.2 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 145.6, 143.8, 141.1, 137.4, 133.0, 129.9, 128.1, 127.9, 127.8, 127.5, 126.9, 126.9, 126.5, 108.7, 72.7, 62.2, 59.5, 57.0, 44.0, 37.1, 21.6, 0.6. IR (Acetone) ν 1159, 1215, 1371, 1466, 1627, 3014 cm^{-1}. HRMS (ESI) calcd. for $C_{28}H_{28}O_2NSI_2$ (M+H): 695.9925, Found: 695.9955.

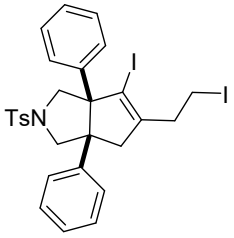




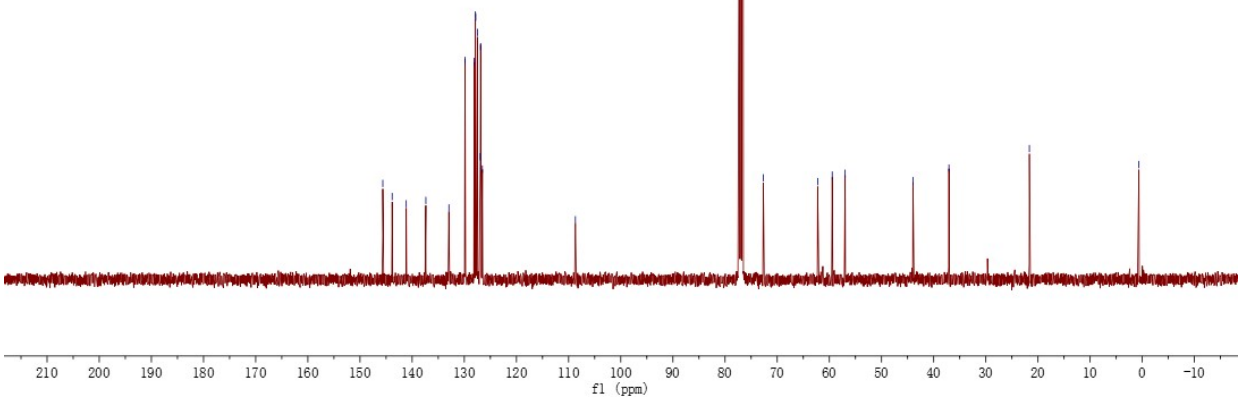
^{1}H NMR ($CDCl_3$ 400MHz TMS)







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



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)/Lanl2dz 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(acetonitrile)/B3LYP/6-311+G(d,p)/Lanl2dz//B3LYP/6-31G(d)/Lanl2dz 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 salvation model in acetonitrile (ε = 35.69).

Table S8. The total energies, enthalpies and free energies of all species in acetonitrile shown in Schemes 4G.

	E_{tot}	H_{298}	G_{298}
INT1	-1698.628114	-1698.114835	-1698.217212
TS1	-1698.607399	-1698.095176	-1698.194483
INT2	-1698.654056	-1698.138691	-1698.236583
TS2	-1698.633381	-1698.119466	-1698.214798
INT3	-1698.663246	-1698.147348	-1698.244799
TS3	-1698.645026	-1698.131453	-1698.229087
INT4	-1698.66523	-1698.151246	-1698.250505
TS4	-2329.285471	-2328.664736	-2328.783492
INT5	-2329.333307	-2328.70495	-2328.828984
TS1'	-1698.584723	-1698.07365	-1698.172735
INT2'	-1698.594569	-1698.082314	-1698.181342
PhSH	-630.512729	-630.406911	-630.443293

Archive entries

INT1

```
Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.792629a.u.
Zero-point correction = 0.480591Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.381727a.u.
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 C -1.05873200,1.81809000,0.08570000
 C -1.97718900,1.64777000,-0.87701200
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TS1

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.769348a.u.
Zero-point correction = 0.480608Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.356432a.u.
Imaginary Frequency is -409.44 cm^{-1}

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INT2

Opt @ B3LYP/6-31G(d)/Lanl2dz
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Zero-point correction = 0.484231Hartree/Particle
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TS2

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.793043a.u.
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Imaginary Frequency is -409.44 cm^{-1}

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C 0.36741900,1.55738000,-3.13804900
C -0.46230900,0.14297400,1.66835000

C -0.32215400,1.45779400,0.91409200
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C 1.23486800,-0.21792100,-1.34958900
C -0.55335600,-1.55294200,-0.29297300
I 3.33486000,0.24977500,-1.79699900
N -1.10838200,-0.95891600,0.95368700
C -3.84348700,-0.71912200,0.44675500
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C 2.80605500,-1.57284000,1.14547000
C 3.66001900,-2.40498500,1.86849100
C 3.61054200,-3.78893000,1.69246100
C 2.69349600,-4.33594600,0.79311800
C 1.83045700,-3.50498200,0.08014000
H -0.52814800,-0.42583800,-3.72118300
H -1.71805300,0.72748700,-2.95208200
H 0.01064700,2.58208100,-3.03972000
H 1.21440300,1.45094700,-3.81480200
H -1.03216000,0.28314000,2.59219100
H 0.53205500,-0.19466000,1.98537300
H -0.97060700,2.62791300,-0.75150300
H -1.76060600,0.97957500,-0.57001700
H -0.67620600,-2.63425200,-0.20771500
H -1.13454000,-1.21526900,-1.15553900
H -3.82480700,-2.25011600,-1.06726100
H -5.47536400,-1.07683900,-2.50578500
H -5.76230900,2.07699900,0.39953400
H -4.09935900,0.91395100,1.82779000
H -6.70795300,0.96993700,-3.05799400
H -7.78609900,1.04313200,-1.66023200
H -6.66390200,2.36963600,-1.96971700

H 0.99978800,3.47689200,-0.37356300
H 2.48912600,5.16444300,0.60804700
H 3.00829900,5.12263700,3.04422700
H 1.99681200,3.35686000,4.48015400
H 0.48726800,1.68593400,3.51612900
H 2.85323600,-0.49825500,1.29054400
H 4.36402500,-1.96878100,2.57204800
H 4.27768100,-4.43642800,2.25491700
H 2.64602000,-5.41168000,0.64729000
H 1.12402700,-3.94457000,-0.61894900

INT3

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.826285a.u.
Zero-point correction = 0.485245Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.407838a.u.

C -0.84588300,0.05837800,0.18337700
C -0.83870600,1.39650700,-1.90273600
C -0.12838000,2.51702900,-2.64935000
C -1.59333700,2.31072200,-2.87468400
C 0.03213700,-2.03500200,-0.73994000
C -1.00115000,-0.94767000,-1.06685400
C -0.52916600,-0.06494400,-2.26773800
C -1.12918100,1.39604100,-0.45368500
C 0.69266400,-0.05210800,0.50111100
I -1.03352900,3.19329200,0.70068500
N 1.17005000,-1.26450300,-0.20296900
C 3.84246100,-1.12031300,0.17811600
C 4.41629300 ,-0.38423600,1.21348800
C 5.53330100,0.40856800,0.94418900
C 6.08705400,0.46857500,-0.34042600
C 5.49147200,-0.28993900,-1.36249600
C 4.37723300,-1.08436000,-1.11342500
C 7.31137800,1.30670000,-0.62248800
S 2.41689800,-2.15355900,0.50633800
O 2.51655100,-3.38603500,-0.28251700
O 2.25042000,-2.21883300,1.96828100
C -2.40825500,-1.49856400,-1.31017100
C -3.44385000,-0.64333600,-1.72929600
C -4.72483500,-1.12581500,-1.99157100
C -5.00936900,-2.48537600,-1.85216900
C -3.99439600,-3.35005500,-1.44926500

C -2.71251500,-2.86208800,-1.18178700
C -1.72210400,-0.32630100,1.37571200
C -3.01333100,0.20575100,1.51222500
C -3.84388500,-0.17511600,2.56511800
C -3.40485400,-1.10752200,3.50618200
C -2.12754900,-1.65208700,3.38022000
C -1.29371900,-1.26491100,2.32858100
H 0.18812700,3.38728700,-2.08180800
H 0.56302400,2.20810900,-3.43035500
H -1.92353300,1.86662400,-3.81055500
H -2.28174900,3.03349400,-2.44479100
H 0.34441700,-2.60626600,-1.61729200
H -0.36277500,-2.73305200,0.00630000
H -1.01543000,-0.37217000,-3.19844200
H 0.55201000,-0.18514400,-2.39675800
H 0.86734700,-0.10674500,1.57785000
H 1.23242200,0.81784700,0.11618700
H 3.99688700,-0.44225300,2.21206600
H 5.98257100,0.98577700,1.74835500
H 5.91138700,-0.25889000,-2.36509300
H 3.92931400,-1.67870900,-1.90305000
H 7.49392600,2.03205900,0.17628200
H 8.20700200,0.67765800,-0.70887900
H 7.21158600,1.85630000,-1.56525200
H -3.25089200,0.41676300,-1.85019500
H -5.50179100,-0.43471200,-2.30848400
H -6.00675700,-2.86392500,-2.05873700
H -4.19201800,-4.41327000,-1.34120900
H -1.95219200,-3.57300900,-0.87915400
H -3.37098500,0.92851500,0.78744600
H -4.83648100,0.25984400,2.64807200
H -4.05068100,-1.40471700,4.32816200
H -1.76806100,-2.37950600,4.10315500
H -0.30331000,-1.70614600,2.27171800

TS3

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.808273a.u.
Zero-point correction = 0.482870Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.392334a.u.
Imaginary Frequency is -630.03 cm^{-1}

C -0.86141200,0.04746500,0.17605700

C -0.61046500,1.32635100,-1.87498000
C 0.95321700,2.26787900,-2.48478300
C -0.47121500,2.43955200,-2.85820600
C -0.09422900,-2.09645900,-0.74090300
C -1.08031900,-0.96765500,-1.06767900
C -0.59519800,-0.13860500,-2.30424100
C -0.94453500,1.38954900,-0.52378000
C 0.63016400,-0.22278800,0.59661700
I -0.90016600,3.22563800,0.57375900
N 1.08453500,-1.36271800,-0.23884000
C 3.74295800,-1.27224800,0.23627900
C 4.28498900,-0.65382800,1.36170200
C 5.40935500,0.16007300,1.21290100
C 6.00092000,0.35680900,-0.04085400
C 5.43653500,-0.28534200,-1.15617000
C 4.31594300,-1.09925300,-1.02740800
C 7.23233200,1.21758900,-0.19478300
S 2.31234900,-2.33465900,0.40973400
O 2.43857500,-3.47393500,-0.50543900
O 2.09786300,-2.56215600,1.84923200
C -2.52044800,-1.44298300,-1.27626300
C -3.48213100,-0.55789700,-1.79722400
C -4.79694400,-0.96022800,-2.02225000
C -5.19017400,-2.27004600,-1.74091800
C -4.25080800,-3.16359300,-1.23158800
C -2.93474600,-2.75396400,-1.00051300
C -1.85016700,-0.20219300,1.31534100
C -3.07656000,0.47834700,1.36107500
C -4.01282300,0.21786300,2.36070700
C -3.75089100,-0.74269600,3.33829900
C -2.54479100,-1.44084700,3.29870200
C -1.60546900,-1.17342100,2.30036100
H 1.38770100,2.87820100,-1.70366000
H 1.60075800,1.60239100,-3.04187100
H -0.73874100,2.17276100,-3.88286000
H -0.92820600,3.38325000,-2.55772200
H 0.17904900,-2.69596300,-1.61171100
H -0.50197800,-2.76359300,0.02747000
H -1.24634600,-0.30679400,-3.16909400
H 0.41421100,-0.44931200,-2.58807600
H 0.71475300,-0.44329400,1.66278100
H 1.25679100,0.64533900,0.37958800
H 3.83556300,-0.81790600,2.33514500
H 5.83442600,0.64582700,2.08755100
H 5.88665100,-0.14770200,-2.13647600

H 3.89186900,-1.60491000,-1.88864500
H 7.40001700,1.84006300,0.68943000
H 8.12825500,0.59983100,-0.33936000
H 7.15255100,1.87792200,-1.06573700
H -3.20232800,0.46677200,-2.02216600
H -5.51429400,-0.24761700,-2.42122200
H -6.21355700,-2.58852800,-1.91979000
H -4.53495000,-4.18921200,-1.01134000
H -2.23662200,-3.48452500,-0.60825800
H -3.30312000,1.22111900,0.60499500
H -4.94989000,0.76837700,2.37206600
H -4.47877400,-0.94568000,4.11932100
H -2.32460200,-2.19718000,4.04741800
H -0.67976000,-1.74074900,2.30578300

INT4

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.828213a.u.
Zero-point correction = 0.482235Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.413488a.u.

C -0.98459400,0.08648000, 0.24910000
C -0.37077800,0.91498900,-1.94894600
C 1.54438600,1.23013000,-3.52336000
C 0.20672500,1.73516300,-3.07236700
C -0.52926500,-2.25796200,-0.40612000
C -1.38572800,-1.05843000,-0.85458100
C -0.83469800,-0.49640500,-2.20852900
C -0.48102000,1.20726900,-0.65036000
C 0.24299900,-0.54199200, 0.98496400
I 0.30197500,3.02478200, 0.20932900
N 0.70098300,-1.59557300, 0.06045600
C 3.36749900,-1.58397000, 0.45561400
C 3.96891000,-1.03915100, 1.58811700
C 5.10453500,-0.24079900, 1.43520800
C 5.64514200,0.01542100, 0.16997300
C 5.02341800,-0.55758900,-0.95335500
C 3.89188100,-1.35514500,-0.82090000
C 6.86655300,0.88797500, 0.00419200
S 1.92425200,-2.62740700, 0.63342900
O 1.99785900,-3.72507300,-0.33672300
O 1.74436500,-2.91103800, 2.06589900
C -2.87607500,-1.36905200,-0.97927900

C -3.74455900,-0.39427200,-1.50231000
C -5.10377700,-0.64581000,-1.67047500
C -5.63594400,-1.89112800,-1.32800400
C -4.79002600,-2.87286200,-0.81776000
C -3.42712100,-2.61335200,-0.64399900
C -2.11982400,0.46520900, 1.20309600
C -2.89476400,1.61424800, 0.98697400
C -3.95854200,1.94317000, 1.82744100
C -4.28441100,1.12045100, 2.90509600
C -3.53972800,-0.03857400, 3.12307000
C -2.47344000,-0.36055400, 2.28274600
H 2.27854200,0.90568900,-2.79269900
H 1.85711000,1.33760100,-4.55672600
H -0.49348100,1.72564800,-3.92020700
H 0.28263500,2.78717400,-2.75158900
H -0.30782200,-2.95752600,-1.21368400
H -1.00597200,-2.80819200, 0.41691900
H -1.59170700,-0.53431400,-3.00097000
H 0.01776600,-1.09192900,-2.56023700
H -0.03198300,-0.96784200,1.95475200
H 1.03550500,0.19130600, 1.15016600
H 3.55800900,-1.24945700,2.56972400
H 5.57815600, 0.18533400, 2.31585700
H 5.43890800,-0.38061200,-1.94263300
H 3.42398200,-1.80819300,-1.68863400
H 7.30377000, 1.15407400, 0.97114800
H 7.63843600, 0.38373300,-0.58919500
H 6.61746500, 1.82068200,-0.51771600
H -3.35043500, 0.57958000,-1.77785600
H -5.74804900, 0.13238000,-2.07129900
H -6.69538900,-2.09212900,-1.46168700
H -5.18386200,-3.85077900,-0.55358700
H -2.80204000,-3.40902000,-0.25394600
H -2.66585900, 2.26592500, 0.15128000
H -4.53187200, 2.84631000, 1.63529900
H -5.11061500, 1.37557900, 3.56318700
H -3.78585700,-0.69969200, 3.94975200
H -1.92921700,-1.27909000, 2.47719600

TS4

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -2328.254373a.u.
Zero-point correction = 0.582209Hartree/Particle
Sum of electronic and thermal Free Energies = -2327.752394a.u.

Imaginary Frequency is -261.84 cm^{-1}

C -0.26972300,1.30324900,-0.03445700
C 0.53015300,-0.77146200, 0.94512600
C 1.74040000,-1.70738200, 2.97481500
C 0.73527300,-1.93818300, 1.88001500
C -0.28644400, 0.31291600,-2.30487800
C 0.68983700, 0.55562300,-1.13720700
C 1.05576100,-0.81242600,-0.46734900
C -0.15556600, 0.35548400, 1.15101400
C -1.69818000, 1.15771900,-0.64630000
I -1.29929400, 0.70482900, 2.94523100
N -1.55521400, 0.04277600,-1.60236300
C -4.03147900,-1.03406900,-1.49878900
C -5.14172400,-0.32997400,-1.03487900
C -6.03921200,-0.96831600,-0.17760900
C -5.84293900,-2.29729300, 0.21788900
C -4.72204400,-2.98519600,-0.27657700
C -3.81636100,-2.36561200,-1.13144800
C -6.80306600,-2.97717200, 1.16480500
S -2.88810500,-0.24072400,-2.62364300
O -2.42270200,-1.21895100,-3.61246300
O -3.49095300, 1.02840300,-3.06191200
C 1.95735000, 1.31287200,-1.53457000
C 3.01289700, 1.42574700,-0.61192500
C 4.19979500, 2.07786600,-0.93918700
C 4.36954600, 2.63472300,-2.20896200
C 3.33785700, 2.52823700,-3.13866100
C 2.14658100, 1.87733700,-2.80405300
C 0.11384800, 2.75632600, 0.25449700
C 0.89844000, 3.08589200, 1.36965700
C 1.29036000, 4.40076500, 1.62098200
C 0.91439500, 5.42488600, 0.75243500
C 0.15292800, 5.11378800,-0.37387900
C -0.23989900, 3.79746700,-0.61894900
H 1.76909000,-0.73240500, 3.45574300
H 1.98440700,-2.55395800, 3.61448700
H -0.23119700,-2.19046100, 2.35233300
H 1.02220200,-2.82492300, 1.29978200
H -0.00544600,-0.53402600,-2.93283300
H -0.38714200, 1.20386600,-2.93890900
H 2.13196000,-1.01201900,-0.49933100
H 0.57023400,-1.64261700,-0.99871400
H -2.02005200, 2.06910200,-1.15941400

H -2.44387600, 0.91557200, 0.11421300
H -5.30174000, 0.69405200,-1.35480000
H -6.90825800,-0.42479300, 0.18425800
H -4.56311000,-4.02242100, 0.00857600
H -2.96069600,-2.90479500,-1.52398600
H -6.38720400,-3.02313900, 2.17994100
H -7.75567100,-2.44177700, 1.22342700
H -7.00980300,-4.00720800, 0.85372200
H 2.91448500, 0.99262500, 0.37845800
H 4.99234200, 2.14540500,-0.19888700
H 5.29531900, 3.14094800,-2.46883000
H 3.45304100, 2.94832600,-4.13445800
H 1.37532000, 1.80918100,-3.56298200
H 1.20977200, 2.30551900, 2.05500600
H 1.89204900, 4.62073700, 2.49891800
H 1.21550800, 6.45068800, 0.94691000
H -0.13889800, 5.89569600,-1.06995700
H -0.81678700, 3.59542200,-1.51551400
S 4.69063000,-1.48228400, 1.80509100
H 3.35553200,-1.59086500, 2.29922700
C 4.54524600,-2.67110700, 0.47031200
C 4.77558400,-2.25606400,-0.84936700
C 4.25075200,-4.01893100, 0.72757000
C 4.71191300,-3.17952600,-1.89562100
H 4.99417900,-1.21194600,-1.05149700
C 4.16659100,-4.93122100,-0.32461600
H 4.10023400,-4.34955800, 1.75116900
C 4.40124300,-4.51572900,-1.63818700
H 4.89507100,-2.84821800,-2.91430100
H 3.93180200,-5.97181800,-0.11593300
H 4.34459900,-5.23047500,-2.45455800

INT5

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -2328.306384a.u.
Zero-point correction = 0.588822Hartree/Particle
Sum of electronic and thermal Free Energies = -2327.802061a.u.

C -0.63781700, 1.17434900,-0.36495800
C -0.09167700, 0.06033500, 1.72721100
C 1.08550800, 0.11188900, 3.97368500
C -0.10321900,-0.42139600, 3.15002700
C 0.15648400,-0.74232600,-1.71545600

C 0.66742800, 0.21865900,-0.62550900
C 0.84965700,-0.55895000, 0.72168500
C -0.85650700, 0.97902100, 1.12949600
C -1.78033500, 0.44017800,-1.13740300
I -2.52406300, 1.93420000, 2.11120900
N -1.25437500,-0.92572700,-1.32936100
C -3.54232800,-2.35815000,-1.31386400
C -4.79887000,-1.82058000,-1.58743900
C -5.87884700,-2.17630700,-0.77768700
C -5.71883100,-3.06026000, 0.29623300
C -4.44232900,-3.59494800, 0.54019400
C -3.35456000,-3.25280900,-0.25583200
C -6.88405000,-3.42689100, 1.18423200
S -2.15416200,-1.93692200,-2.36090800
O -1.32078100,-3.12614500,-2.56807500
O -2.66947800,-1.18367800,-3.51580200
C 1.95693400, 0.94999000,-0.99582300
C 2.60486400, 1.74193300,-0.02973400
C 3.79551000, 2.40778600,-0.31254100
C 4.38272700, 2.29386200,-1.57574100
C 3.76180800, 1.50537100,-2.54245700
C 2.56386000, 0.84290500,-2.25480600
C -0.45116200, 2.62500500,-0.81884600
C -0.10332500, 3.63011300, 0.09591200
C 0.11118200, 4.94590400,-0.31510000
C -0.00575600, 5.29088400,-1.66114400
C -0.32859800, 4.30097300,-2.58913000
C -0.54696600, 2.98724800,-2.17250200
H 1.05839300, 1.20565200, 4.03236300
H 1.04563500,-0.28207900, 4.99516100
H -1.04157700,-0.13395100, 3.63419300
H -0.06856100,-1.51976400, 3.14603900
H 0.67949000,-1.70005200,-1.72701400
H 0.22359000,-0.29113300,-2.71508700
H 1.88999500,-0.54735300, 1.06538400
H 0.57694500,-1.61538500, 0.59405600
H -1.99524500, 0.91207400,-2.10097000
H -2.70673500, 0.41315400,-0.55950700
H -4.92412600,-1.14613000,-2.42765400
H -6.86143500,-1.76178400,-0.98807200
H -4.30322700,-4.29229600, 1.36282900
H -2.37349600,-3.67793200,-0.07216900
H -6.80131200,-2.93761200, 2.16345000
H -7.83733300,-3.12215000, 0.74181200
H -6.92333900,-4.50695900, 1.36603700

H 2.16707700, 1.84334300, 0.95859900
H 4.26427200, 3.01765000, 0.45518600
H 5.30948200, 2.81495400,-1.80044300
H 4.20271600, 1.40252300,-3.53077600
H 2.11928900, 0.23345800,-3.03353200
H -0.00005200, 3.38532600, 1.14696500
H 0.36992500, 5.70069900, 0.42291700
H 0.15712500, 6.31569900,-1.98375600
H -0.41244100, 4.54669000,-3.64448100
H -0.78102700, 2.24432100,-2.92810700
S 4.52425500,-2.11014200, 2.61234500
H 2.04575500,-0.18514600, 3.53833800
C 5.54356900,-2.19994800, 1.22211100
C 5.44401700,-1.24029000, 0.17809500
C 6.50294500,-3.24198200, 1.09486000
C 6.26461600,-1.32588600,-0.93858400
H 4.71849100,-0.43846900, 0.26738300
C 7.31829900,-3.31832600,-0.02540200
H 6.58122200,-3.97502900, 1.89139500
C 7.20184500,-2.36248400,-1.04512000
H 6.17261400,-0.58622300,-1.72832700
H 8.04683500,-4.11951500,-0.11326600
H 7.84118700,-2.42673100,-1.92145300

TS1'

Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.74973a.u.
Zero-point correction = 0.479165Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.337742a.u.
Imaginary Frequency is -449.06 cm^{-1}

C -0.78485600,-0.24125100, 0.00392400
C -1.23772600,-1.85402100, 1.99906200
C -1.38660800,-2.99504600, 2.91144000
C -1.35405700,-1.56774300, 3.44884500
C 0.04984900, 2.20283900, 0.14539900
C -0.86082700, 1.49081700, 1.14947100
C -0.24434000, 1.22009800, 2.39788500
C -1.05573100,-1.50042100, 0.74415200
C 0.71657300,-0.12684100,-0.30579300
I -0.90639800,-3.31113000,-0.62480400
N 1.15234200, 1.27754600,-0.13422900
C 3.83716900, 1.03620300,-0.37496700

C 4.40196500,-0.07625200,-0.99716100
C 5.51399800,-0.68728100,-0.41525700
C 6.07260800,-0.19727800, 0.77155900
C 5.48672000, 0.93010000, 1.37166800
C 4.37669200, 1.55079700, 0.80803300
C 7.29278200,-0.84409900, 1.38295100
S 2.41196200, 1.83746200,-1.10718400
O 2.49183400, 3.28114700,-0.86038400
O 2.27832300, 1.32060600,-2.47876400
C -2.28204500, 1.98329800, 1.21886900
C -3.24082100, 1.29930500, 1.98560600
C -4.54494100, 1.77355600, 2.10741200
C -4.92708200, 2.95359400, 1.46563000
C -3.98877400, 3.64683800, 0.70272000
C -2.68328600, 3.16708400, 0.57892800
C -1.72950600, 0.03293900,-1.12324800
C -3.09317900,-0.29575800,-0.99026800
C -4.00087500,-0.03898800,-2.01258500
C -3.57217400, 0.55303200,-3.20347400
C -2.22475300, 0.87888700,-3.35701600
C -1.31230100, 0.62285200,-2.33241800
H -2.33959300,-3.52279200, 2.91769600
H -0.52156500,-3.63533600, 3.07904200
H -0.46247100,-1.23495600, 3.97633700
H -2.27885400,-1.14551100, 3.83859600
H 0.45817900, 3.12373300, 0.56638100
H -0.50766000, 2.45841200,-0.76148500
H -0.82821800, 1.09967000, 3.30069700
H 0.83098900, 1.08850100, 2.46268700
H 0.92439000,-0.47788200,-1.32155100
H 1.28106100,-0.75829600, 0.38631000
H 3.98099200,-0.44689800,-1.92550500
H 5.95566800,-1.55634900,-0.89619900
H 5.91101800, 1.32773600, 2.29056100
H 3.93732500, 2.43035700, 1.26716100
H 7.45782600,-1.84882700, 0.98192200
H 8.19532800,-0.25388000, 1.17697100
H 7.20086800,-0.92281700, 2.47201900
H -2.96380700, 0.37207300, 2.47281200
H -5.26532500, 1.21768200, 2.70216100
H -5.94339000, 3.32629600, 1.55943100
H -4.26749300, 4.56890100, 0.19970900
H -1.97691300, 3.74102000,-0.01076400
H -3.43801400,-0.76544900,-0.07546900
H -5.04596300,-0.30629500,-1.88087700

H -4.27990000, 0.75114100,-4.00393100
H -1.87204300, 1.32790300,-4.28160300
H -0.26923200, 0.87194000,-2.49894500

INT2'

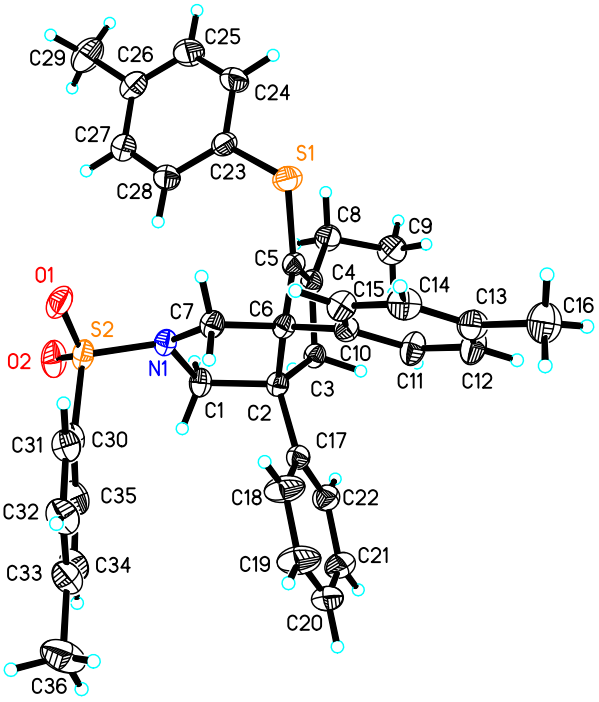
Opt @ B3LYP/6-31G(d)/Lanl2dz
SCF Done: E(B3LYP) = -1697.759348a.u.
Zero-point correction = 0.480077Hartree/Particle
Sum of electronic and thermal Free Energies = -1697.346121a.u.

C 0.83237000, 0.12088400, 0.07080100
C 1.43987000, 1.74743900, 2.03877500
C 1.67823100, 2.87241800, 2.95499200
C 1.61882200, 1.44058400, 3.47662100
C -0.10739700,-2.12613300, 0.12805900
C 0.87119600,-1.26014200, 0.97299700
C 0.25224800,-1.07899900, 2.32523700
C 1.17841300, 1.42348300, 0.78728500
C -0.69040200, 0.19490100,-0.28213300
I 1.00916400, 3.19682400,-0.53878000
N -1.19273000,-1.18591100,-0.17255300
C -3.87937700,-0.92774800,-0.37215600
C -4.44977300, 0.21236500,-0.93641900
C -5.55527800, 0.79644400,-0.31554500
C -6.10185400, 0.25288300, 0.85338500
C -5.51028100,-0.90071200, 1.39519500
C -4.40664200,-1.49516000, 0.79207900
C -7.31520500, 0.87116300, 1.50657300
S -2.45924900,-1.69260200,-1.15254600
O -2.53505700,-3.14618200,-0.97218500
O -2.33924300,-1.10839200,-2.49787700
C 2.24362600,-1.92801900, 1.12384400
C 3.29673500,-1.26399300, 1.77356700
C 4.53002700,-1.88007400, 1.98008500
C 4.74315800,-3.19039300, 1.54860900
C 3.70697100,-3.86948600, 0.91117700
C 2.47377500,-3.24619500, 0.70311700
C 1.71667300,-0.07167500,-1.17722400
C 3.08209000, 0.25131400,-1.12289300
C 3.91614200, 0.06003400,-2.22189000
C 3.40402000,-0.46188700,-3.41111600
C 2.04986400,-0.78156300,-3.48464800
C 1.21379500,-0.58695600,-2.38174700
H 2.64919900, 3.36528800, 2.91818300

H 0.84741100, 3.54205500, 3.17371600
H 0.74173100, 1.13154900, 4.04114600
H 2.54250700, 0.97190200, 3.81167400
H -0.48926300,-2.97828600, 0.69230300
H 0.38115500,-2.49456000,-0.78066900
H 0.81092600,-1.30395200, 3.22432500
H -0.79695400,-0.81629600, 2.41366200
H -0.84769000, 0.61138000,-1.27901000
H -1.21299600, 0.83206200, 0.43843300
H -4.03811700, 0.62469300,-1.85126900
H -6.00161300, 1.68655500,-0.75170400
H -5.92491600,-1.33977300, 2.29954900
H -3.96264300,-2.39437600, 1.20651500
H -7.48651000, 1.89164400, 1.15039900
H -8.21959300, 0.28862700, 1.28723600
H -7.20983200, 0.90414600, 2.59680000
H 3.15338500,-0.24483000, 2.10902500
H 5.32581400,-1.33304100, 2.47943600
H 5.70262100,-3.67440600, 1.70937500
H 3.85053900,-4.89188700, 0.57181200
H 1.69205900,-3.81461100, 0.21199600
H 3.49583300, 0.67267100,-0.21355300
H 4.96753500, 0.32523800,-2.14839000
H 4.05218800,-0.61040200,-4.27065400
H 1.62895600,-1.17912200,-4.40421600
H 0.16313800,-0.83302500,-2.49142400

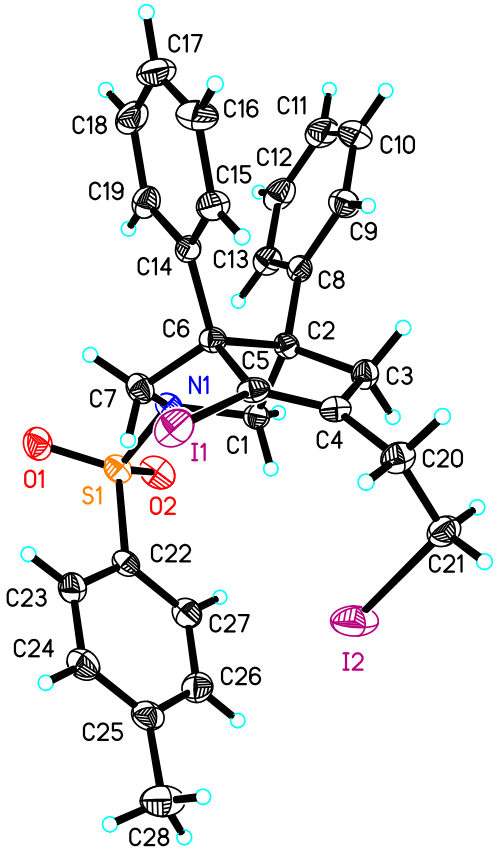
11. X-Ray structures

Compound 3ga



The crystal data of **3ga** have been deposited in CCDC with number 2244043. Empirical Formula: $C_{36}H_{37}NO_2S_2$; Formula Weight: 579.78; Crystal Color, Habit: colorless, Crystal Dimensions: 0.160 x 0.130 x 0.080 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 9.2165(12) Å, b = 12.9551(18) Å, c = 14.964(2) Å, α = 65.519(4)°, β = 84.823(4)°, γ = 71.049(4)°, V = 1535.9(4) $Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.254 g/cm^3; F_{000} = 616; Final R indices [I>2sigma(I)] R1 = 0.0519, wR2 = 0.1300.

Compound 7



The crystal data of **7** have been deposited in CCDC with number 2073868. Empirical Formula: $C_{28}H_{27}I_2NO_2S$; Formula Weight: 695.36; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.110 x 0.080 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 13.1688(3) Å, alpha = 90 deg. b = 18.3576(4) Å, beta = 107.0810(10) deg. c = 11.5032(3) Å, gamma = 90 deg; V = 2658.21(11) $Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.738 g/cm^3; F_{000} = 1360; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0331, 0.0714.

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